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Supporting Information

Central-to-Axial Chirality Conversion Approach Designed on Organocatalytic Enantioselective Povarov Cycloadditions: First Access to Configurationally Stable Indole–Quinoline Atropisomers

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General methods and materials

General Methods. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova 300, Mercury 400 or Inova 600 spectrometer. Chemical shifts (δ) are reported in ppm relative to residual solvents signals[1] for ^{1}H and ^{13}C NMR. ^{13}C NMR were acquired with 1 H broad-band decoupled mode. Chromatographic purifications were performed using 70-230 mesh silica. Mass spectra were recorded on a Waters Xevo Q-TOF spectrometer. Optical rotations were measured on a Perkin Elmer 241 Polarimeter provided with a sodium lamp and are reported as follows: $[\alpha]_{\lambda}^{T(^{\circ}C)}$ (c = g/100 mL, solvent). The enantiomeric excess of the products (*ee*) were determined by chiral stationary phase HPLC (Daicel Chiralpak AD-H or Chiralcel OD-H columns), using an UV detector operating at 254 nm. Products **3**, **4**, **5bc, 6lc** and **7bc** were found to be sensitive to traces of DCl in $CDCl_3$ darkening immediately upon contact and showing slow decomposition upon prolonged standing. In order to conveniently record the spectra in $CDCl_3$ the solvent had to be filtered over basic alumina prior to use. Products **3** were all obtained as single all-*trans* isomers.

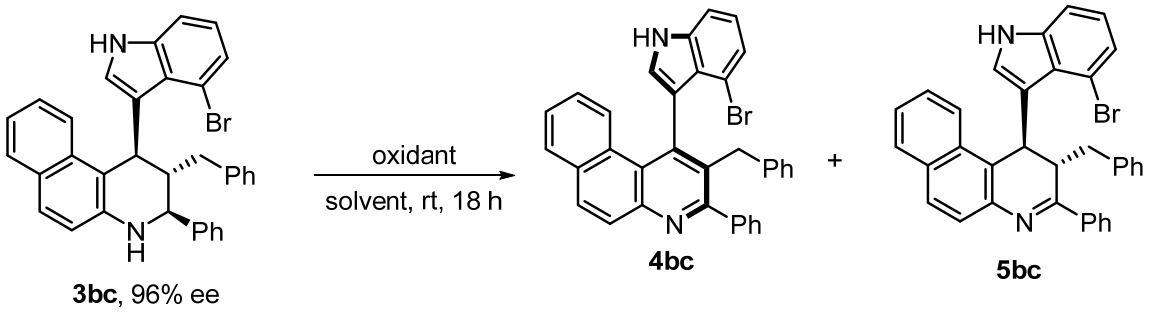
Materials. Analytical grade solvents and commercially available reagents were used as received, unless otherwise stated. **(*R*)-TRIP** and **Catalyst A** were synthesized following literature procedures.[2] Imine **1b** was purchased from TCI-chemicals. Imines **1a**, **1c**, **1d**, **1e** and **1f** are known compounds and were synthesized following the general procedure reported for imines **1g-l**. For imines **1g-l**, 6-bromo-2-naphthylamine was employed instead of simple 2-naphthylamine, which use is discouraged by the Italian law. 3-alkenyndoles **2a** and **2b** were synthetized following a literature procedure.[3] Racemic products **3** were prepared using diphenyl phosphate (10 mol%) instead of **(*R*)-TRIP** as catalyst. Racemic **4** and **5** were prepared from racemic **3**, racemic **6lc** was prepared from racemic **4lc** and racemic **7bc** from racemic **4bc** following the same procedures reported for the enantioenriched products.

[1] H. E. Gottlieb, V. Kottlyar, A. Nudelman, *J. Org. Chem.* **1997**, *62*, 7512.
[2] a) S. Hoffmann, A. Majeed, B. List, *Angew. Chem. Int. Ed.* **2005**, *44*, 7424; b) S. Müller, M. J. Webber, B. List, *J. Am. Chem. Soc.* **2011**, *133*, 18534; c) C.-H. Xing, Y.-X. Liao, J. Ng, Q.-S. Hu, *J. Org. Chem.* **2011**, *76*, 4125; d) L. Caruana, M. Fochi, S. Ranieri, A. Mazzanti, L. Bernardi, *Chem. Commun.* **2013**, *49,* 880.
[3] S. Sahu, A. Banerjee, M. S. Maji, *Org. Lett.* **2017**, *19*, 464.

Additional reactivity studies

Screening of Oxidants

Table S1. Additional oxidants screening



3bc, 96% ee

4bc

5bc

Entry[a]	Oxidant	Solvent	*ee* of **4bc** [%][b]	**4bc**/**5bc** ratio[c]
1	DDQ	CH_2Cl_2	67-90[d]	73:27
2	MnO_2	Toluene	-	>2:98
3	Dess Martin	CH_2Cl_2	-	-
4	PCC	CH_2Cl_2	63	30:70
5	CAN	THF/H_2O 4:3	-	-
6	TEMPO	CH_2Cl_2	-	-
7	TEMPO-BAIB	CH_2Cl_2	-	>2:98
8	*m*-CPBA	CH_2Cl_2	-	-
9	*o*-chloranil	CH_2Cl_2	37	33:51[e]
10	*p*-chloranil	CH_2Cl_2	-	-
11	*p*-fluoranil	CH_2Cl_2	-	-

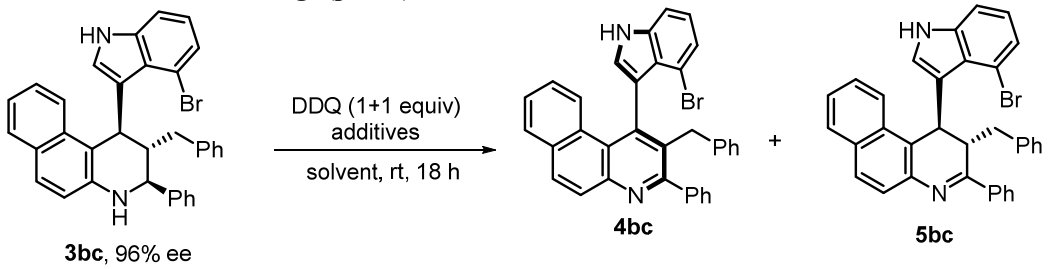
[a] General method: **3bc** 0.03 mmol, oxidant 0.06 mmol, solvent 300 µL, rt. [b] Determined by chiral HPLC analysis after chromatographic column. [c] Determined on the crude reaction mixture by ^{1}H NMR analysis after reductive work-up (full consumption of **3bc** was observed in all cases, unless otherwise stated). [d] Different results obtained by running the same reaction multiple times. [e] 16% Of product **3bc** was detected along with **4bc** and **5bc**.

Different oxidants have been tested and the results are shown in Table S1. Different solvents were employed case by case for optimal compatibility with the different oxidizing systems. Very dissimilar behaviors were registered during this screening. For example, Dess-Martin periodinane provided a complex mixture (entry 3), while oxidants such as CAN (cerium ammonium nitrate, entry 5), TEMPO ((2,2,6,6-Tetramethylpiperidin-1-yl)oxyl, entry 6), *m*-CPBA (*m*-chloroperoxybenzoic acid, entry 8) *p*-chloranil (2,3,5,6-tetrachlorocyclohexa-2,5-diene-1,4-dione, entry 10) and *p*-fluoranil (2,3,5,6-tetrafluorocyclohexa-2,5-diene-1,4-dione, entry 11) did not show any reactivity and, after appropriate quenching only product **3bc** was recovered from the reaction mixture. Oxidizing agents such as manganese dioxide (entry 2) and the TEMPO-BAIB system (bis(acetoxy)iodobenzene, entry 7) gave selectively product **5bc**. Only PCC (pyridinium chlorochromate, entry 4), *o*-chloranil (3,4,5,6-tetrachlorocyclohexa-3,5-diene-1,2-dione, entry 9) and DDQ led to the formation of the desired product **4bc**,

unfortunately along with intermediate **5bc**. In particular, the best result in terms of both reactivity and stereoselectivity were obtained with DDQ as oxidizing agent, that was chosen as optimal for further screenings.

Screening of Concentration and Additives

Table S2. Miscellaneous screenings (part 1)



3bc, 96% ee **4bc** **5bc**

Entry[a]	solvent	concentration [M]	additives	atmosphere	*ee* of **4bc** [%][b]	**4bc**/**5bc** ratio[c]
1	CH_2Cl_2	0.3	none	air	87	71:29
2	CH_2Cl_2	0.1	none	air	67-90[d]	73:27
3	CH_2Cl_2	0.03	none	air	86	84:16
4	CH_2Cl_2	0.03	Na_2CO_3[e]	air	87	83:17
5	CH_2Cl_2	0.03	PhCOOH[e]	air	87	78:22
6	CH_2Cl_2	0.03	none	N_2	84	32:78
7	CH_2Cl_2	0.03	H_2O[f]	air	55	60:40
8	CH_2Cl_2	0.03	4 Å MS[g]	N_2	85	75:25
9	CH_3CN	0.03	none[h]	air	65	93:7
10	CH_3CN	0.03	4 Å MS[g]	N_2	66	94:6
11	CH_2Cl_2	CH_2Cl_2	TEMPO	air	85	82:18

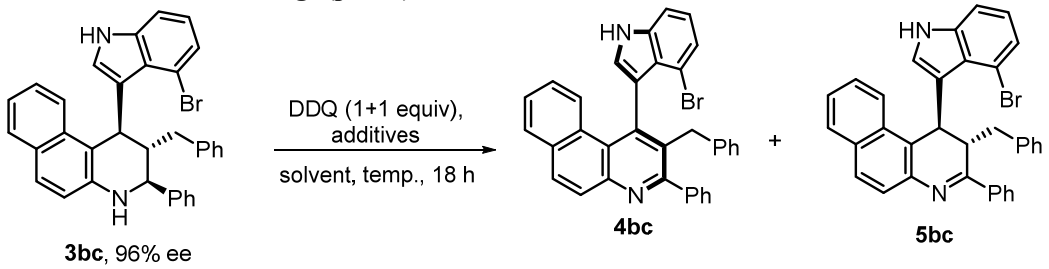
[a] General method: **3bc** 0.03 mmol, DDQ 0.06 mmol (added in 2 portions: 0.03 mmol at the beginning and 0.03 mmol after 2 h), solvent 100, 300 or 900 µL, rt. [b] Determined by chiral HPLC analysis after chromatographic column. [c] Determined on the crude reaction mixture by ^{1}H NMR analysis after reductive work-up (full consumption of **3bc** was observed in all cases). [d] Different results obtained by running the same reaction multiple times. [e] 0.06 mmol added. [f] Solvent previously saturated by vigorously shaking it with water in a separatory funnel (approximately 0.011 mmol of H_2O in 900 µL, 33 mol%). [g] Powdered 4 Å molecular sieves (30 mg), thermally activated *in vacuo* for 5 min. [h] Acetonitrile HPLC grade, Sigma Aldrich (0.02% H_2O from specification data sheet), used as such (0.01 mmol of H_2O in 900 µL, 33 mol%).

In order to understand which parameter influences the reproducibility of the reaction, we started to investigate the influence of the concentration of the medium (Table S2, entries 1-3). Even though the retention of the enantiomeric excess was not correlated to the concentration, some improvement in terms of reactivity was found under diluted conditions (entry 3). This is probably due to a smaller degree of precipitation of some activated species or intermediates. Other parameters studied were the presence of acids, bases, atmospheric oxygen and water. Regarding acid and base additives, no changes were observed in terms of both stereoselectivity and reactivity (entries 4 and 5). However, it was found that atmospheric oxygen might take a role in the oxidation of **3bc** into **4bc**, but with irrelevant consequences for the enantioselection

of the reaction (compare entry 6 with entry 3). A crucial role was played by the presence of water, at least in CH_2Cl_2 (entries 7 and 8). Although the **4bc/5bc** ratio was similar, an important lowering of the enantiomeric excess was observed when the reaction solvent was saturated with water (entry 7) in comparison with the anhydrous solvent (entry 8). It was thus hypothesized that the presence of water might be the parameter influencing the reproducibility of the reactions in CH_2Cl_2. However, acetonitrile was found to be much less sensitive to this aspect (entries 9 and 10). It is important to stress that non-anhydrified acetonitrile contains about the same quantity of water compared to saturated CH_2Cl_2. As such, acetonitrile was chosen as a more practical solvent, for which inert atmosphere and rigorous removal of water are not necessary. Finally, TEMPO ((2,2,6,6-Tetramethylpiperidin-1-yl)oxyl, entry 11) was added as an additive, to check if some radical species is involved in the oxidation mechanism (note that TEMPO alone does not promote any oxidation of **3bc**, Table S2, entry 6). Since the results were comparable with the ones obtained with DDQ alone, we discarded a radical oxidation pathway.

Screening of anhydrifyng agents and equivalents of DDQ

Table S3. Miscellaneous screenings (part 2)

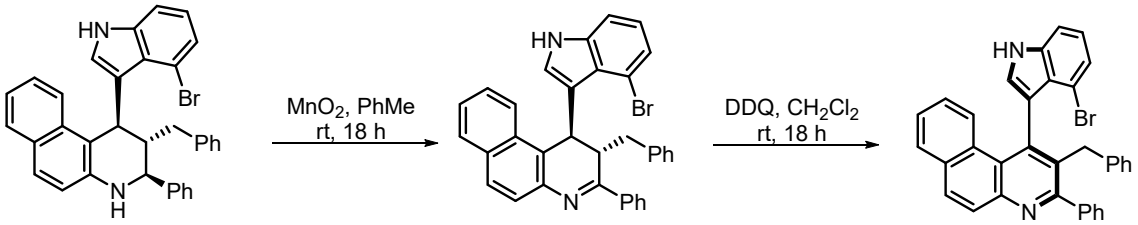


Entry[a]	solvent	equiv	additives	Temperature [°C]	*ee* of **4bc** [%][b]	**4bc**/**5bc** ratio[c]
1	CH_2Cl_2	1+1[d]	4 Å MS[e]	25	85	70:30
2	CH_2Cl_2	2	4 Å MS[e]	25	85	75:25
3	CH_2Cl_2	3	4 Å MS[e]	25	90	78:22
4	CH_2Cl_2	2	4 Å MS[e]	0	86	40:60
5	CH_2Cl_2	3	4 Å MS[e]	0	91	50:50
6	CH_3CN	1+1	none	25	65	>98:2
7	CH_3CN	2	none	25	40	>98:2
8	CH_3CN	3	none	25	88	>98:2
9	CH_3CN	1+1	none	0	78	93:7
10	CH_3CN	2	none	0	89	95:5
11	CH_3CN	3	none	0	94	90:10
12	CH_3CN	4	none	0	94	91:9
13[f]	CH_3CN	3	none	-30	-	-
14[g]	CH_3CN	3	none	0	94	>98:2

[a] General method: **3bc** 0.03 mmol, DDQ 0.06 mmol or 0.09 mmol (added in one portion or portion-wise as specified case by case), solvent 900 μL, temp. [b] Determined by chiral HPLC analysis after chromatographic column. [c] Determined on the crude reaction mixture by ^{1}H NMR analysis after reductive work-up (full consumption of **3bc** was observed in all cases unless otherwise noted). [d] DDQ 0.06 mmol (added in 2 portions: 0.03 mmol at the beginning and 0.03 mmol after 2 h). [e] Powdered 4 Å molecular sieves (30 mg), thermally activated *in vacuo* for 5 min. Reaction run under N_2 atmosphere. [f] No conversion was observed and **3bc** was isolated after reductive work-up. [g] Reaction time: 48 h.

Taking into account the good enantiomeric excess observed in anhydrous CH_2Cl_2 and the excellent reactivity detected in acetonitrile (Table S3), we moved to examine the effects of the amount of DDQ added in both solvents either at room temperature or at 0 °C (Table S3). In anhydrous CH_2Cl_2 the number of equivalents did not influence either the retention of the enantiomeric excess or the **4bc**/**5bc** ratio (entries 1-3) and a decrease in the temperature caused the reactivity to drop significantly with no substantial improvement of the enantiomeric excess (entries 4 and 5). On the other hand, in CH_3CN at room temperature the amount of DDQ influenced the enantiomeric excess greatly (entries 6-8). Although difficult to rationalize, the results presented arise from multiple reactions run under the same conditions, rendering every time analogous data. Thus, an excess of DDQ might be the key factor to achieve high enantiomeric retentions under these conditions and an inaccurate measurement of the oxidant added the parameter responsible for the irreproducibility. Pleasingly, a similarly good reactivity was observed in CH_3CN at 0 °C with some improvement of the retention of the enantiomeric excess, with a less significant (but linear) dependence upon the equivalents of oxidant, resulting in more robust reaction conditions (entries 9-11). Further increase in the equivalents of DDQ did not improve the enantiomeric retention (entry 12) and running the reaction at -30 °C caused the oxidation to stop completely (entry 13). Thus, to overcome the small decrease in reactivity observed at 0 °C, the reaction time has to be prolonged to 48 h, to achieve full conversion of **5bc** in **4bc** (entry 14).

Preparation, characterization and reactivity of (1*R*,2*S*)-2-benzyl-1-(4-bromo-1*H*-indol-3-yl)-3-phenyl-1,2-dihydrobenzo[*f*]quinoline, intermediate 5bc.



3bc, 96% ee **5bc**, 96% *ee* **4bc**, 63% *ee*

In a small vial equipped with a magnetic stirring bar, tetrahydroquinoline **3bc** (0.15 mmol, 78.8 mg, 96% *ee*), toluene (8 mL) and MnO_2 (378 mg, 4.5 mmol, 30 equiv) were added. MnO_2 was activated prior to use by standing in a 120 °C oven and then under *vacuum* for 30 min. The resulting solution was stirred for 18 h at room temperature and then filtered over a short plug of Celite®, eluted multiple times with CH_2Cl_2, obtaining an analytically pure product as a yellow powder in quantitative yield. This compound was found to be identical to **5bc**, isolated by column chromatography (*n*-hexane/Et_2O = 3:1) from mixtures containing **4bc**, obtained using DDQ as the oxidant.

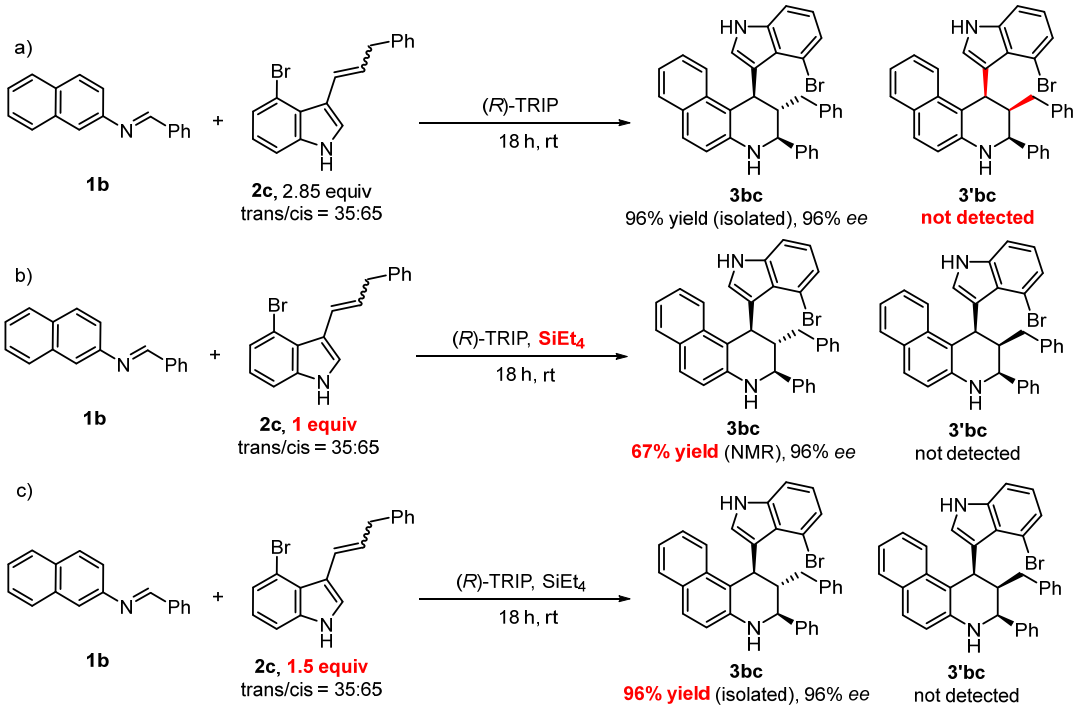
$[\alpha]_D^{25}$ = +131 (c = 0.2 in $CHCl_3$) for 96% ee.**^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.12 (d, *J* = 2.7 Hz, 1H), 7.91 (dd, *J* = 7.4, 2.1 Hz, 1H), 7.83 – 7.77 (m, 1H), 7.73 – 7.63 (m, 4H), 7.41 – 7.32 (m, 2H), 7.22 – 7.10 (m, 4H), 7.10 – 7.00 (m, 3H), 6.98 – 6.91 (m, 3H), 6.82 (t, *J* = 7.9 Hz, 1H), 6.00 (d, *J* = 2.7 Hz, 1H), 5.67 (s, 1H), 4.00 (ddd, *J* = 9.3, 5.9, 1.3 Hz, 1H), 2.79 (dd, *J* = 13.3, 6.0 Hz, 1H), 2.64 (dd, *J* = 13.3, 9.3 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 167.4, 138.3, 135.7, 135.1, 130.9, 128.7, 127.9, 127.5 (2C), 126.0, 125.8 (2C), 125.7, 125.6 (2C), 125.4, 124.7 (2C), 124.2, 123.9, 123.4, 123.0, 122.9, 121.8, 121.6, 121.3, 121.1, 119.9, 112.2, 110.9, 108.0, 42.3, 34.0, 28.7. **ESI-MS**: 540 [M(^{79}Br) + H^+], 542 [M(^{81}Br) + H^+] **HPLC**: OD-H (*n*-hexane/iPrOH 90:10, flow-rate 0.75 mL/min; t_{minor} = 10.6; t_{major} = 11.5 min).

Compound **5bc** was proved as a reactive intermediate as follows. In a small vial equipped with a magnetic stirring bar, **5bc** (0.05 mmol, 26.2 mg, 96% *ee*) was dissolved in CH_2Cl_2 (300 μL) and treated with DDQ (0.15 mmol, 3 equiv, 34.1 mg) for 18 h. The crude mixture was then poured into a solution of Na_2SO_3 (1 M) and extracted with DCM (3 x 30 mL). The combined organic phases were dried over $MgSO_4$, filtered and evaporated under reduced pressure. The crude residue was then purified by column chromatography on silica gel (*n*-hexane/Et_2O = 3:1) to obtain **4bc** in 90% yield (63% *ee*).

Furthermore, chemical intuition points towards the effective intermediacy of **5bc** in the oxidation of **3bc** to **4bc**, as DDQ is in fact a two-electron oxidant and the loss of the two couples of protons should proceed stepwise. The CH-NH bond is also reported to be the more reactive in the oxidation of similar tetrahydroquinolines to quinolines.[4] Moreover, NMR analysis performed at different times on the same reaction mixture of the oxidation of **3bc** to **4bc** revealed an increase of the **4bc**/**5bc** ratio over time, indicating a transformation of **5bc** into **4bc** (**3bc** being already consumed).

[4] a) J. Xiao, W. Zhou, P. Taboonpong, A. Aboo, L. Zhang, J. Jiang, *Synlett*, **2016**, *27*, 1806; b) X. Chen, H. Zhao, C. Chen, H. Jiang, M. Zhang, *Org. Lett.* **2018**, *20*, 1171.

Cis/*trans*-isomerization studies in compounds 2



Scheme S1 *Cis*/*trans*-isomerization studies in compound **2c**

Since 3-vinylindoles **2** could not be obtained as exclusively *trans* isomers, we investigated if the *cis*/*trans* mixture was equally exploitable in the Povarov cycloaddition. First of all, we examined if the *cis* isomer could participate in the reaction. We thus set up an experiment by reacting imine **1b** with 2.85 equivalents of 3-vinylindole **2c** as a *cis*/*trans* mixture (65:35 *cis*/*trans*, equal to 1 equivalent of *trans* isomer added, Scheme S1, equation a). Cycloadduct **3bc** was isolated after chromatographic purification in 96% yield and 96% *ee* as a single diastereoisomer. This indicates that ***cis*-2c** does not take part to the Povarov reaction, as it would have rendered isomer **3'bc** that was not detected into the crude mixture. Moreover, no trace of *trans* **2c** was found after the cycloaddition, whereas the *cis* form was found unreacted in the crude mixture. However, electron-rich *cis* dienophiles are reported to isomerize to the *trans* forms under acidic conditions and similar cases were observed in Povarov cycloadditions with vinylcarbamates.[5] We thus subjected 1 equivalent of *cis*/*trans* **2c** (equal to 0.35 equivalents of *trans* **2c**, equation b) to the reaction with **1b**, in the presence of $SiEt_4$ as internal standard. Since product **3bc** was formed in 67% NMR yield (again as a single diastereoisomer in 96% *ee*), we verified that *cis*/*trans* isomerization occurs in our case as well, turning the unreactive *cis* isomer into the productive *trans* one. We also propose that *cis* **2c** acts a stable reservoir of the highly reactive and unstable *trans* dienophile, rendering a controlled addition by syringe-pump (usually needed in Povarov cycloadditions with 3-vinylindoles) unnecessary.(ref. 15a, main text) Finally, employing 1.5 equivalents of **2c** (*cis*/*trans* mixture) we could obtain product **3bc** in quantitative NMR yield (95% isolated) and 96% *ee* (equation c).

[5] G. Dagousset, J. Zhu, G. Masson, *J. Am. Chem. Soc.* **2011**, *133*, 14804.

X-RAY data

X-ray crystallographic data were obtained on single crystals of the Povarov intermediate **3ic** and of the atropisomeric compound **4gc** (Figure S1).

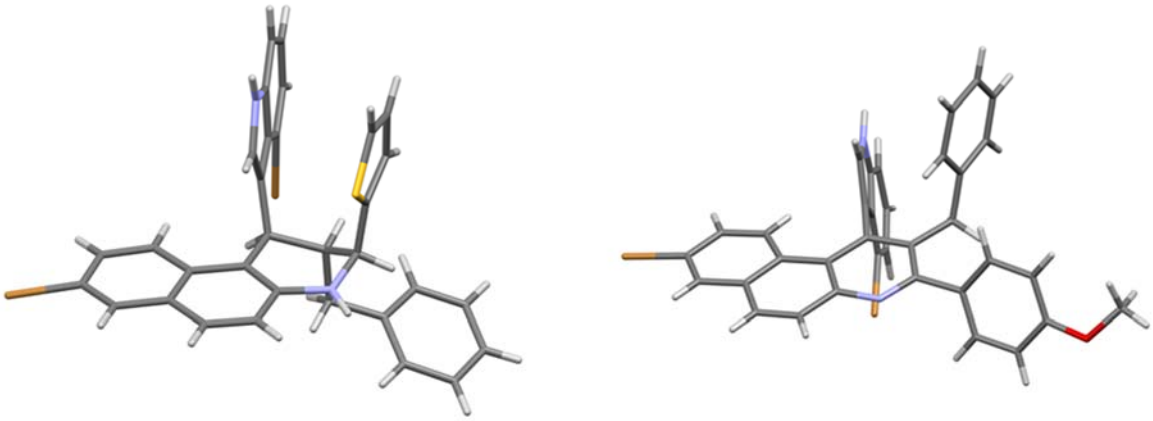
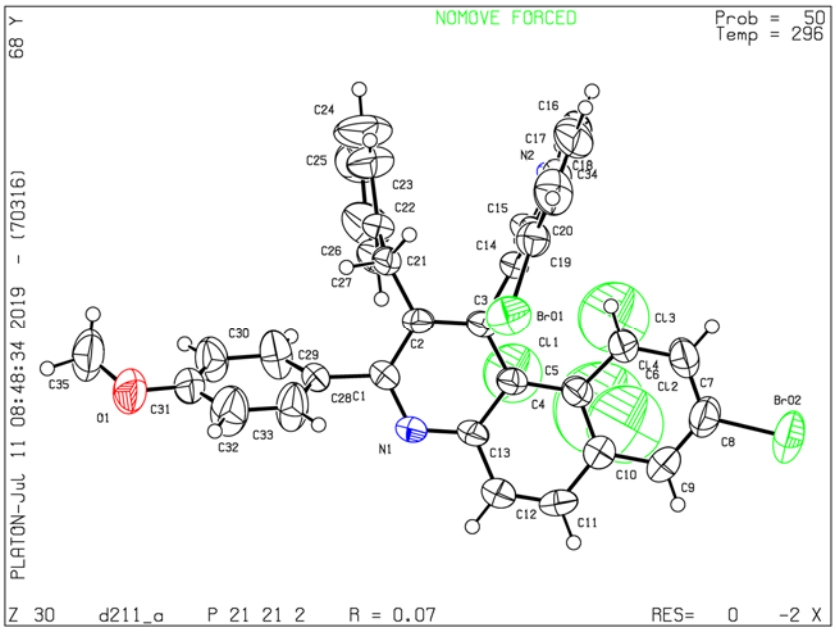


Figure S1. X-ray structures of **3ic** and **4gc**. In the case of **4gc** a disordered molecule of chloroform was removed for clarity.

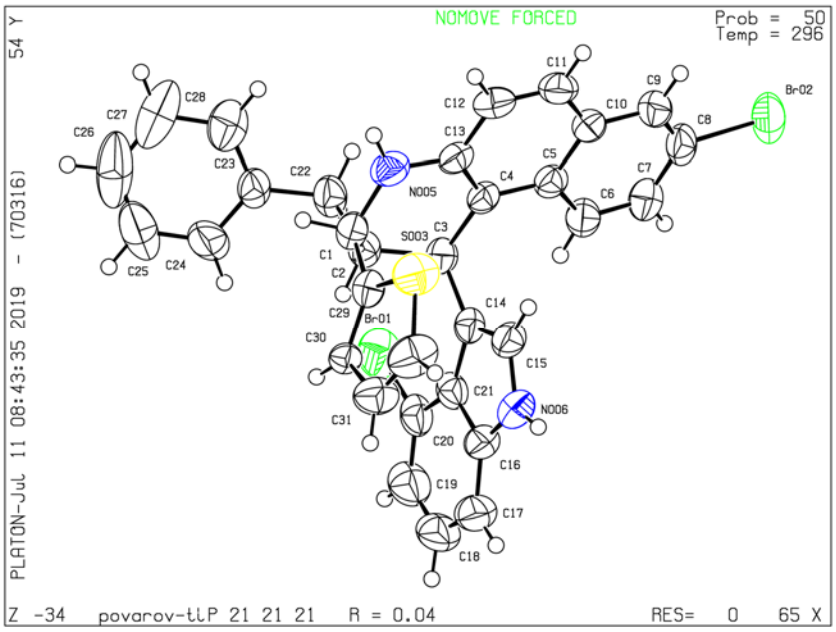
As known in the literature, the Povarov intermediate has the three substituents on the tetrahydroquinoline ring in *anti* disposition, being 2*S*,3*R*,4*S* its absolute configuration. The atropisomeric compound **4gc** has *aS* absolute configuration at the stereogenic axis, and derives from the conformation of the Povarov adduct by removal of the H4 hydrogen. CCDC-1940645 and CCDC-1940646 contain the crystallographic data.

Crystal structure of compound 4gc.



A specimen of $C_{35}H_{24}Br_2Cl_3N_2O$, approximate dimensions 0.150 mm x 0.150 mm x 0.300 mm, was used for the X-ray crystallographic analysis. The total exposure time was 20.00 hours (2400 frames). The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 43568 reflections to a maximum θ angle of 25.00° (0.84 Å resolution), of which 5890 were independent (average redundancy 7.397, completeness = 99.4%, R_{int} = 4.10%, R_{sig} = 3.18%) and 5276 (89.58%) were greater than $2\sigma(F^2)$. The final cell constants of a = 16.9575(8) Å, b = 18.0819(9) Å, c = 10.9785(5) Å, volume = 3366.3(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 9913 reflections above 20 σ(I) with 4.804° < 2θ < 52.83°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.724. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.5010 and 0.6900. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 21 21 2, with Z = 4 for the formula unit, $C_{35}H_{24}Br_2Cl_3N_2O$. The final anisotropic full-matrix least-squares refinement on F^2 with 382 variables converged at R1 = 6.82%, for the observed data and wR2 = 21.06% for all data. The goodness-of-fit was 1.041. The largest peak in the final difference electron density synthesis was 1.391 $e^-/Å^3$ and the largest hole was -0.705 $e^-/Å^3$ with an RMS deviation of 0.104 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.489 g/cm^3 and F(000), 1508 e^-. Flack parameter was 0.037(5). The cell contains a disordered molecule of Chloroform. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1940645.

Crystal structure of compound 3ic.



A specimen of $C_{32}H_{24}Br_2N_2S_1$, approximate dimensions 0.150 mm x 0.250 mm x 0.300 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The total exposure time was 20.00 hours (2400 frames). The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 36009 reflections to a maximum θ angle of 26.00° (0.81 Å resolution), of which 5255 were independent (average redundancy 6.852, completeness = 99.7%, R_{int} = 5.07%, R_{sig} = 3.65%) and 4642 (88.33%) were greater than $2\sigma(F^2)$. The final cell constants of a = 8.864(2) Å, b = 10.659(2) Å, c = 28.558(6) Å, α = 90.00(3)°, β = 90.00(3)°, γ = 90.00(3)°, volume = 2698.2(10) Å^3, are based upon the refinement of the XYZ-centroids of 9968 reflections above 20 σ(I) with 4.814° < 2θ < 52.01°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.751. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.4560 and 0.6530. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 21 21 21, with Z = 4 for the formula unit, $C_{32}H_{24}Br_2N_2S_1$. The final anisotropic full-matrix least-squares refinement on F^2 with 342 variables converged at R1 = 4.26%, for the observed data and wR2 = 11.26% for all data. The goodness-of-fit was 1.041. The largest peak in the final difference electron density synthesis was 0.652 e^-/Å^3 and the largest hole was -0.411 e^-/Å^3 with an RMS deviation of 0.062 e^-/Å^3. On the basis of the final model, the calculated density was 1.547 g/cm^3 and F(000), 1264 e^-. Flack parameter= 0.042(5). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1940646.

Computational details.

All the calculations were performed with the Gaussian 16 suite of programs,[6] using DFT and two different computational levels (B3LYP/6-31G(d) and M06-2x/6-31G(d). All the ground and transition states (GS and TS, respectively) were validated by frequency analysis showing no imaginary frequencies for the GS and a single negative frequency for the TS. The normal mode corresponding to the negative frequency was visualized with Gausswiew[7] to check whether it corresponded to the correct reaction pathway. The key stationary points for the reaction pathway were further optimized including the solvent with the SMD formalism at the M06-2x/6-31G(d) level. The rotational barriers for atropisomers racemization were evaluated with B3LYP functional, that is known to reproduce well the rotational barriers in biphenyls,[8] and using a mixed basis set (6-31G(d) was used for all the atoms, except for bromine, where the 6-311++G(d,p) was used). In all the manuscript the reported energies are ZPE-corrected enthalpies in standard conditions (298 K and 1 atm), because the $\Delta G°$ and $\Delta\Delta G^{\neq}$ evaluation is hampered by the presence of many low-frequency vibrations.[9]

Evaluation of the indole rotational barriers

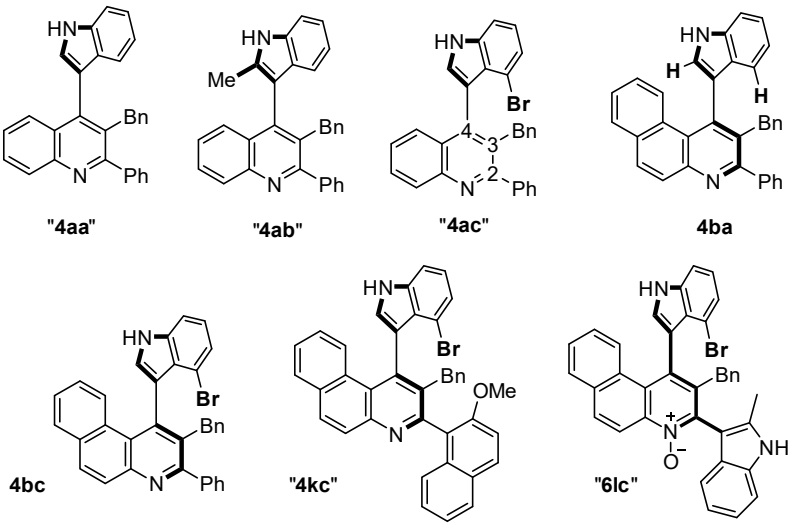
The rotational barriers for the *aS*/*aR* interconversion of compounds **4ac**, **4ab**, **4ba**, **4bc**, **4kc** and **6lc** (Scheme S2) were evaluated by DFT calculations using B3LYP and the mixed basis set. In some cases the calculations were run on model compounds where the OMe (**4ac** and **4ab**), the bromine of the benzoquinoline ring (**4kc** and **6lc**) and tosyl (**6lc**) were substituted by hydrogen to reduce the computational times, without interfere with the rotational barriers.

[6] Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[7] Gausswiew 6.0.16.

[8] L. Lunazzi, M. Mancinelli, A. Mazzanti, S. Lepri, R. Ruzziconi, M. Schlosser , *Org. Biomol. Chem.* **2012**, *10*, 1847. E. Masson *Org. Biomol. Chem.* **2013**, *11*, 2859.

[9] a) R. F. Ribeiro, A. V. Marenich, C. J. Cramer, and D. G. Truhlar, *J. Phys. Chem. B* **2011**, *115*, 14556; b) S. Grimme, *Chemistry-Eur. J.* **2012**, *18*, 9955.



Scheme S2: model compounds for the evaluation of the rotational barriers for racemization and diastereomerization

Taking the model of **4ac** as example, there are two available transition state geometries (TS) for racemization *via* the indole rotation. In the first one, the bromine moves towards the benzyl group in position 3 (TS-0), in the second one, the bromine moves towards the aromatic ring (TS-180, Figure S2). Between the two, the lower energy one represents the threshold TS to be considered for racemization.

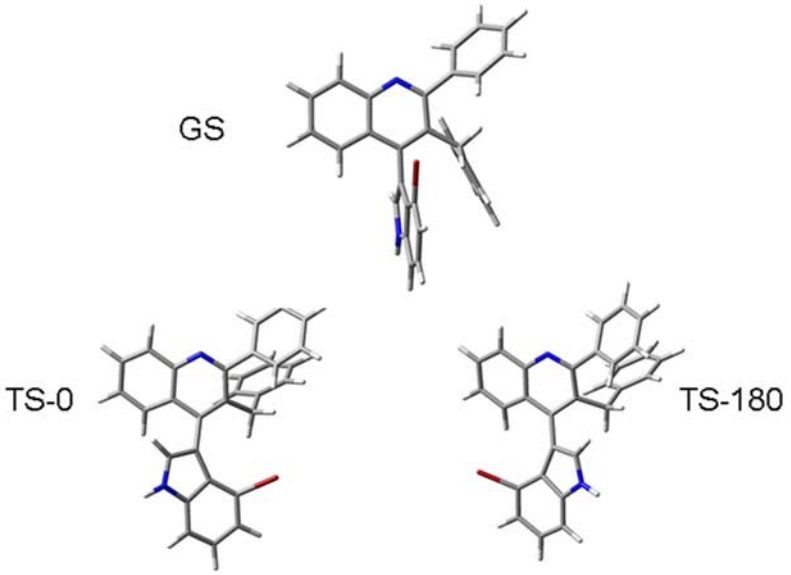


Figure S2. Ground state and the two transition states for racemization of the model of **4ac**

Each TS was validated by frequency analysis, showing that the displacement vectors related to the single negative frequency were related to the rotation of the indole. Table S4 reports the results for all the compounds. In the case of compounds with two stereogenic axes, there are two threshold TS that account for diastereomerization (the lower energy one) and racemization (the higher one). In all the compounds the threshold TS for racemization corresponds to the rotation of indole towards the benzyl group in position 3.

Table S4. Calculated racemization barriers. Calculations with B3LYP and 6-31G(d) basis set for C, H, N, O atoms, 6-311++G(d,p) basis set for Br.

Compd.	GS (a.u.)	TS-0 (a.u.)	TS-180 (a.u.)	$\Delta H^{\neq}$ (kcal/mol)[a]
4aa (model)	-1265.508114	**-1265.475536**	-1265.473966	20.4
4ac (model)	-3839.035351	**-3838.973403**	-3838.973326	38.9
4ab (model)	-1304.799957	**-1304.753008**	-1304.752626	29.5
4ba	-1419.095564	**-1419.063274**	-1419.058757	20.3
4bc	-3992.620308	**-3992.559200**	-3992.546895	38.3
4kc (model)	-4260.691961 (*anti*) -4260.692080 (*syn*)	**-4260.629761** **-4260.649702**	-4260.619289 -4260.633085	39.1 (rac) 26.6 (diast)
6lc (model)	-4238.601705 (*anti*) -4238.603962 (*syn*)	**-4238.545778** -4238.561737	-4238.531926 **-4238.564454**	36.5 (rac) 24.8 (diast)
Compd.	GS (a.u.)	TS-0 (a.u.)	TS-180 (a.u.)	$\Delta G^{\neq}$ (kcal/mol)[a]
4aa (model)	-1265.590641	**-1265.553227**	-1265.551526	23.5
4ac (model)	-3839.122903	-3839.055668	**-3839.055985**	42.0
4ab (model)	-1304.886050	**-1304.833248**	-1304.832759	33.1
4ba	-1419.183711	**-1419.146778**	-1419.143110	23.2
4bc	-3992.712300	**-3992.647538**	-3992.634566	40.6
4kc (model)	-4260.795373 (*anti*) -4260.796218 (*syn*)	**-4260.729474** -4260.734851	-4260.720301 **-4260.748928**	41.9 (rac) 29.7 (diast)
6lc (model)	-4238.704290 (*anti*) -4238.705926 (*syn*)	**-4238.643524** **-4238.661774**	-4238.630163 -4238.659013	39.2 (rac) 27.7 (diast)

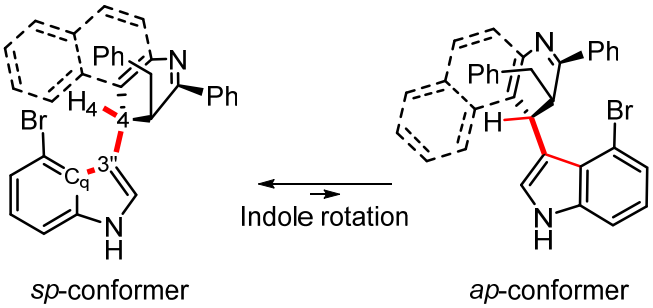
[a] Threshold transition state energy value.

Computational study of the oxidation reaction

A computational study based on DFT calculations was performed to investigate the oxidation pathway that converts the Povarov adducts **3** to the final atropisomeric compounds **4**. The pathway to the final compound is divided into two main steps: the first oxidation of the Povarov adduct **3** to yield the ketimine (**5**), and subsequent oxidation to the final compound **4**. Compound **3bc** was selected for the computational analysis. As a matter of fact, the first oxidation of the Povarov adduct is not the limiting TS of the reaction. Imine **5bc** can be obtained from **3bc** by MnO_2 oxidation and further oxidized to the final compound with DDQ. When the reaction with two or more equivalents of DDQ is stopped at an early stage imine **5bc** is the main reaction product. It is therefore clear that the limiting (and atropo-selective) stage of the reaction has to be found in the second oxidation step. Preliminary calculations were performed on the starting reagent imine **5bc** and of a possible intermediate (enamine).

Conformational analysis of imine

The two GS conformations linked by the rotation of 4-bromoindole have the CH in position 4 of the tetrahydroquinoline ring pointing towards the bromine in position 4 of the indole, or towards the H-2 of indole. They can be conveniently named as *syn*-periplanar (*sp*) and *anti*-periplanar (*ap*) using the nomenclature based on the dihedral angle.[10] For the sake of clarity the most convenient dihedral to be monitored for these compounds is the H-4–C4–C3''–Cq(indole), (see Scheme S3, red bonds) because in the following discussion the steric relationship on H-4 with the rest of the molecule will be of primary importance.



Scheme S3. *sp* and *ap* conformations of imine.

The two ground states were optimized with M06-2x/6-31G(d). The *sp* conformer was calculated as much more stable than the *ap* (Figure S3), the difference being 10.1 kcal/mol. The huge difference in the GS energies is due to the steric clash of the dihydrobenzoquinoline ring with the bromine atom on the indole in the *ap* conformation, and it implies a very unbiased population at ambient temperature, the minor conformation having a negligible population.

[10] B. Testa, *Studies in Organic Chemistry*, vol. 6: Principles of Organic Stereochemistry" page 87. Marcel Dekker, New York, 1979.

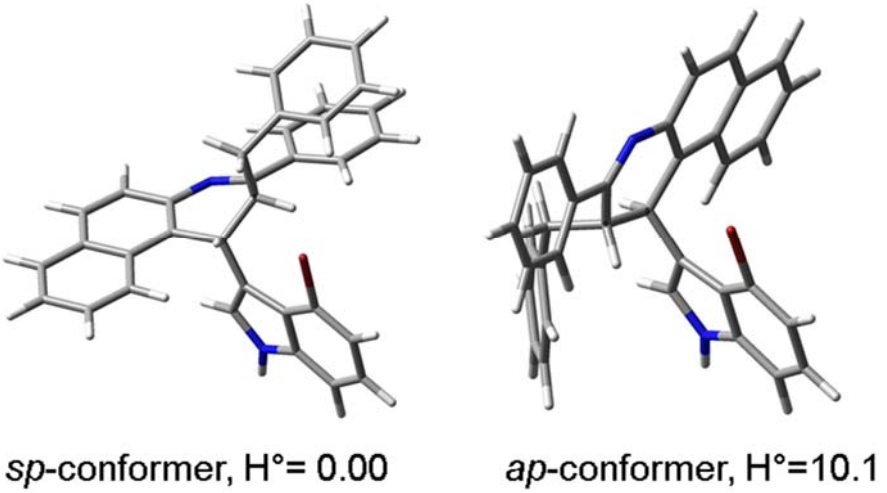


Figure S3. Optimized geometries of the two conformations of imine **5bc**. Relative energies in kcal/mol at the M06-2x/6-31G(d) level.

Unfortunately, the strongly unbiased equilibrium did not allow the experimental determination of the rotational barrier of 4-bromoindole because only a conformation is populated, and dynamic NMR analysis[11] would be insensitive to rotation. For this reason, the rotational barrier was evaluated by DFT calculations. There are two different TS geometries in which the bromine atom rotates towards the planar part of the dihydrobenzoquinoline ring, or towards the CH in position 3 of the dihydroquinoline ring (Figure S4). The former TS was found to be the threshold one with a calculated rotational barrier of 17.5 kcal/mol (17.0 at the B3LYP/6-31G(d) level).

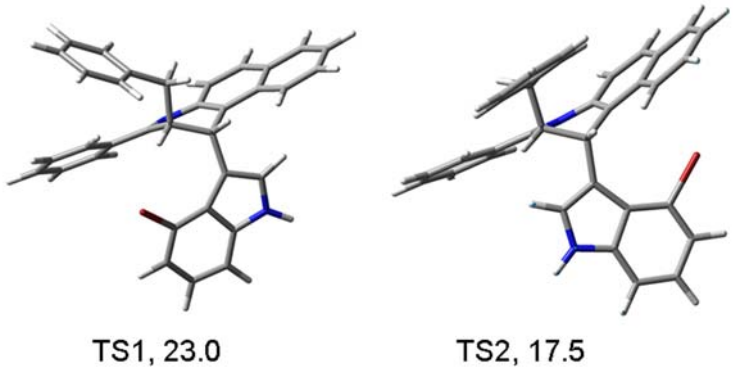


Figure S4. The two transition states for rotation of the 4-bromoindole ring in **5bc**. Energies at the M06-2x/6-31G(d) level, relative to the more stable *sp* GS.

Conformational analysis of enamine

It is well known that enamines are key intermediates in DDQ-mediated oxidations.[12] In the present case, the absence of any EWG group does not allow observation of the enamine, but the participation of the enamine to the reaction mechanism cannot be excluded *a priori*. DFT calculations were performed on the two enamines derived by the *sp*/*ap* conformations of imine

[11] D. Casarini, L. Lunazzi, A. Mazzanti *Eur. J. Org. Chem.* **2010**, 2035-2056

[12] a) O. Quinonero, M. Jean, N. Vanthuyne, C. Roussel, D. Bonne, T. Constantieux, C. Bressy, X. Bugaut, J. Rodriguez. *Angew. Chem., Int. Ed.* **2016**, *55*, 1401. b) A. I. Meyers, D. G. Wettlaufer, *J. Am. Chem. Soc.* **1984**, *106*, 1135. c) X. Chen, H. Zhao, C. Chen, H. Jiang, M. Zhang. *Org. Lett.* **2018**, *20*, 1171.

5bc. When optimized at the M06-2x/6-31G(d) level, the *sp* conformation was found again to be more stable than the *ap*. The energy gap is largely reduced, but it is still 3.1 kcal/mol (Figure S7). The smaller energy difference is mainly due to the sp^2 hybridization of C3 that reduces the steric hindrance exerted by the dihydro-benzoquinoline ring in the *ap* conformation. However, due to the absence of a stabilizing EWG moiety, the energies of *sp* conformer of the enamine is higher than the corresponding imine by 6.3 kcal/mol, while the *ap*-enamine is more stable than the corresponding ketimine by 0.7 kcal/mol (see Table S5 for a summary), albeit the difference with the most stable *sp* imine is still very large. The tautomerization to enamine also changes the steric interaction in the rotational transition state of the indole ring. Calculations suggest that the threshold transition state for the rotation of 4-bromoindole in the enamine is the crossing of the bromine over C3, with an estimated barrier of 15.1 kcal/mol.

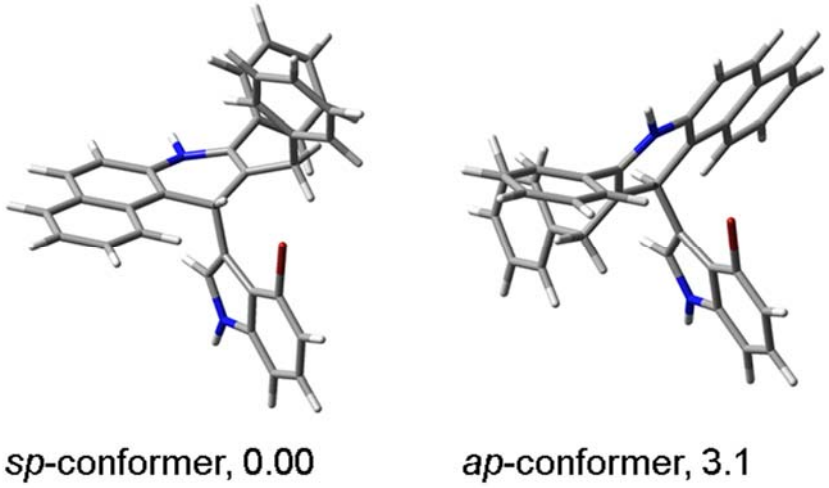


Figure S5. Optimized geometries of the two conformations of the enamine of **5bc**. Relative energies in kcal/mol.

Table S5. GS and TS for imine and enamine of 5bc. Calculations at the M06-2x/6-31G(d) level, relative energies in kcal/mol.

Compd. **4bc**	*sp* conformer (a.u.)	*sp* conformer (a.u.)	$\Delta H^{[a]}$	$\Delta H^{[a]}$
Imine	-3990.886664	-3990.870556	0.00	10.1
Imine TS rotation	-3990.854396 (TS1)	-3990.861582 (TS2)	20.2	15.7[b]
Enamine	-3990.876542	-3990.871680	6.35	9.40
Enamine TS rot.	-3990.862554 (TS1)	-3990.851476 (TS2)	15.1[b]	22.1

[a] ΔH° for ground states and $\Delta H^{\neq}$ for the rotational TS. [b] Threshold TS for rotation

Complexation with DDQ

As evident from the experimental outcomes, a deep colored solution is formed as soon as DDQ is added to a solution of the imine **5bc** (also at temperatures as low as -78°C). This behavior strongly suggests the formation of a complex between the imine and DDQ. The same complex can also be formed (or conserved during tautomerization) on the enamine. Calculations have been run to investigate the nature of this complex, and to evaluate its energetic stabilization with respect to the reagents. Due to the electron-poor character of DDQ, the most reasonable starting point for the formation of the complex was to place the DDQ close to the electron rich aromatic part of the dihydrobenzoquinoline. Full optimization found the four structures shown in Figure S6 (two conformers of the ketimine and two conformers of the enamine). A second

conceivable geometry of the complex would be to place DDQ on the other side of the dihydroquinoline ring, but the steric interaction with the indole (instead of the H4) makes this geometry very high in energy, especially in the case of the *ap* conformer.

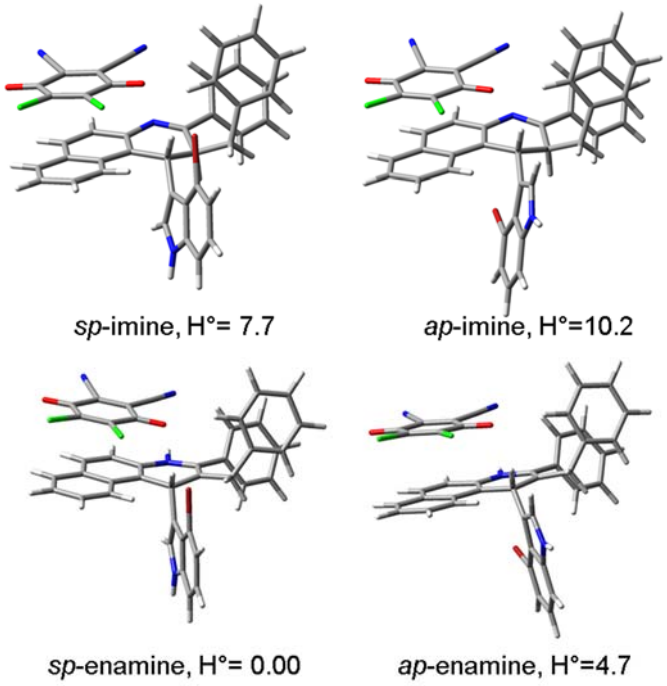


Figure S6. DDQ-complex optimized structures for imine and enamine. Relative energies in kcal/mol, at the M06-2x/6-31G(d) level.

Table S6. Relative energies of the DDQ complexes with imine and enamine, at the M06-2X/6-31G(d) level. Relative energies in kcal/mol.

Compd. **4bc**	*sp* conformer (a.u.)	*ap* conformer (a.u.)	ΔH°	ΔH°
Imine-DDQ (complexation energy)	-5475.655279 (-16.9 kcal/mol)	-5475.651181 (-18.2 kcal/mol)	7.7	10.2
Enamine-DDQ (complexation energy)	-5475.667518 (-21.5 kcal/mol)	-5475.660074 (-21.4 kcal/mol)	0.00	4.7

In both complexes, the *sp* conformation is again the more stable, but the energies of the two enamine-DDQ complexes were found to be lower in energy with respect to the DDQ-complexes of the imines. This inversion can be related to the larger electronic density on the aromatic ring of the enamine with respect to the imine. In the case of the most stable enamine (*sp*), the distance between DDQ and the heteroaryl ring is ≈ 3.2 Å. MO analysis showed that the HOMO is mainly localized on the dihydrobenzoquinoline ring, while the LUMO is entirely localized on the DDQ (Figure S7). TD-DFT calculations with CAM-B3LYP/6-311++G(2d,p) of the UV spectrum of the *sp*-enamine complex suggested that the lowest energy UV/vis band is due to a charge-transfer HOMO-LUMO transition, calculated at 992 nm. The LUMO is also involved in the remaining six transitions found in the visible range (605, 515, 514, 455, 463, 397 nm, respectively).

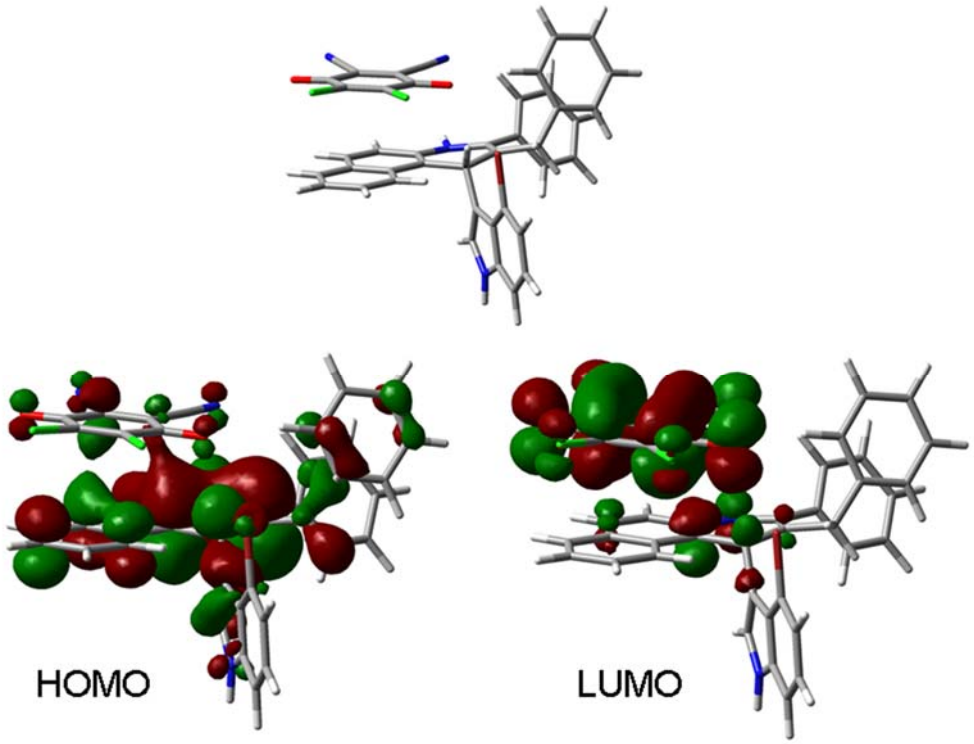


Figure S7. HOMO and LUMO MOs of the *sp*-enamine of **5bc**.

To account for the errors due to the BSSE effect, the complexation energies were estimated using the counterpoise method,[13] yielding a corrected stabilization of 21.5 kcal/mol for both *sp* and *ap* conformers of enamines (Table S6). The rotational barrier of the 4-bromoindole within the DDQ-complexes was estimated to be 19.2 kcal/mol for the enamine complex and 19.5 kcal/mol for the imine complex. The higher barrier in the complex with respect to the free enamine (or imine) is due to the less conformational freedom of the benzyl group in position 3, that cannot be displaced away from the indole because of the presence of DDQ. The same calculations on the imine complex yielded higher energies for the DDQ-complexes, most probably because of the less effective interaction between DDQ and the electron-poor aryl ring (complexation energies were and 16.9 and 18.2 kcal/mol for the *sp* and *ap* conformers of imine). This energy difference implies that the imine-enamine tautomerism should be biased towards the enamine, albeit there was no experimental evidence for the formation of the enamine. However, this is in agreement with the following proposed reaction pathway.

HTO pathway on enamine

Once the DDQ-complex with the enamine is formed, a single transition state drives the reaction to the formation of a pyridinum salt that rapidly evolves to the final compound by an acid-base reaction with the $DDQH^-$ anion. As underlined many times in the literature,[14] the first step of oxidation by DDQ takes places by hydride extraction from the carbon of the reductant to the oxygen of DDQ (HTO pathway) to yield $DDQH^-$ and a carbocation. In this case the benzylic carbocation on C4 is tertiary and strongly stabilized by the benzoquinoline ring (being perpendicular, the indole ring does not provide any additional stabilization by conjugation). The

[13] S. F. Boys, F. Bernardi, *Mol. Phys.* **1970**, *19,* 553.
[14] a) A. E. Wendlandt, S. S. Stahl *Angew. Chem. Int. Ed.* **2015**, *54*, 14638; b) B. Li, A. E. Wendlandt, A. A. Stahl, *Org. Lett.* **2019**, *21*,1176

two TSs for the HTO reaction were pinpointed on the two conformers of enamine by a scan on the C-H bond length starting from the DDQ-complex geometry, and then fully optimized at the M06-2x/6-31G(d) level. The single negative frequency indeed corresponded to the H4 moving from the carbon to the oxygen of DDQ, with very large absolute values for the negative frequency.

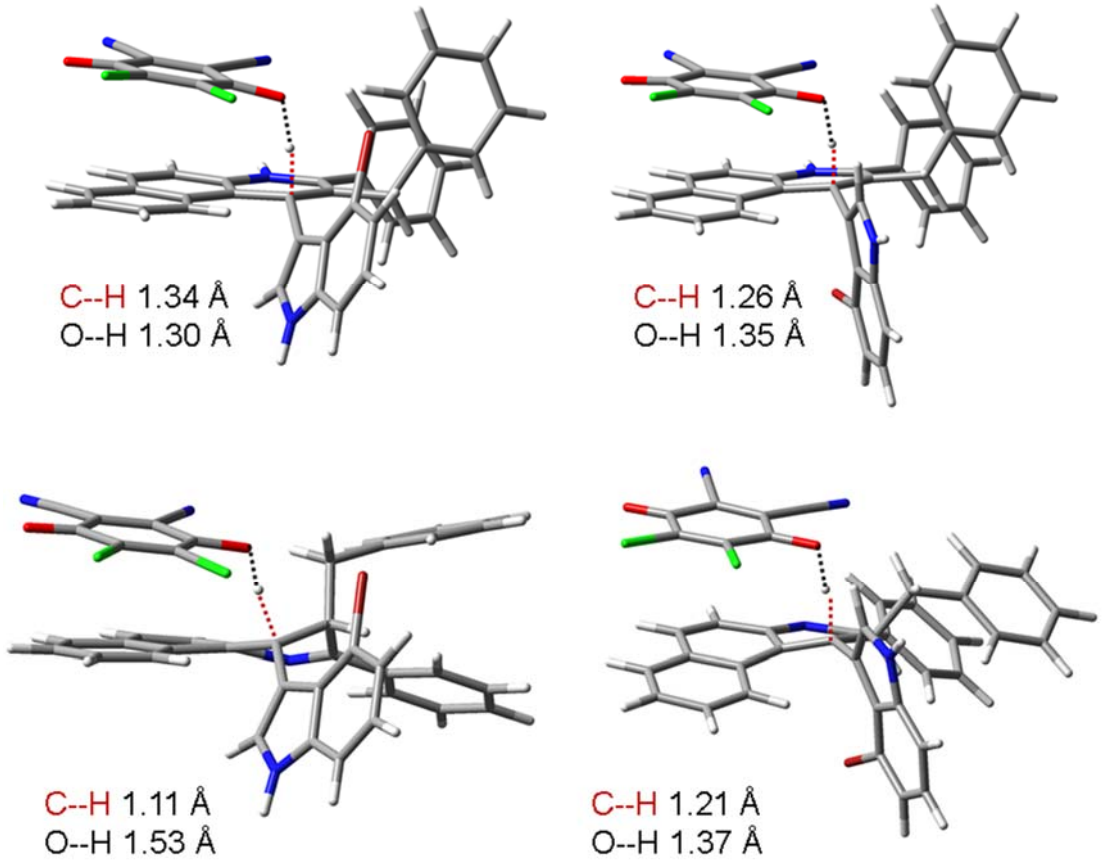


Figure S8. TS geometries for the HTO process on the two conformers of enamine (top) and imine (bottom); *sp* conformers on the left, *ap* on the right.

The TS for the hydride removal from the less stable *ap* conformer of the enamine was found to be lower in energy by 4.5 kcal/mol with respect to the analogue TS of the *sp* conformer, in apparent contradiction with the experimental outcome where the main enantiomer derives from the HTO pathway on the more stable *sp* conformation. However, it has to be considered that *both* these TSs have smaller energies than the rotational barrier for the *sp*/*ap* interconversion by indole rotation, which is calculated to be 19.2 kcal/mol. When the enamine is formed, the HTO pathway leading to the observed compound is the only available because the alternative pathway is forbidden by the higher energy required for the *sp*/*ap* rearrangement. For the same reason, the HTO pathway starting from imines is disfavored because the two HTO transition states are much higher in energy (25.6 and 37.0 kcal/mol for the *ap*-imine and *sp*-imine, respectively). Table S7 and Figure S9 summarize the energy values and the reaction scheme.

Table S7. Relative energies of the GS and TS for rotation and for HTO TS in the DDQ complexes of imine and enamine of 5bc. Calculations at the M06-2X/6-31G(d) level.

Compd. **4bc**	*sp* conformer (a.u.)	*ap* conformer (a.u.)	$\Delta H^{[a]}$	$\Delta H^{[a]}$
Imine-DDQ	-5475.655279	-5475.651181	7.7	10.2
Imine DDQ HTO TS imaginary freq. value	-5475.611244 -1144 cm^{-1}	-5475.624732 -1334 cm^{-1}	35.3	26.8
Imine-DDQ *sp*/*ap* rotation imaginary freq. value	-5475.632330 -39 cm^{-1}	-5475.636473 -23 cm^{-1}	22.1	19.5[b]
Enamine-DDQ	-5475.667518	-5475.660074	**0.0**	4.7
Enamine-DDQ HTO TS imaginary freq. value	-5475.643462 -1542 cm^{-1}	-5475.650705 -1214 cm^{-1}	15.1	10.6
Enamine-DDQ sp/ap rot imaginary freq. value	-5475.636911 -40 cm^{-1}	-5475.632360 -23 cm^{-1}	19.2[b]	22.1
Pyridinium-salt-DDQ	-5475.686488	-5475.690466	-11.9	-14.1

[a] ΔH° for ground states and $\Delta H^{\neq}$ for the TS (given in kcal/mol). [b] Threshold TS for rotation.

As a summary, we suggest that the oxidation proceeds by fast formation of the DDQ-complex of the imine, that evolves by tautomerism to the more reactive (and more stable) enamine complex. Once the enamine is formed, it is quickly oxidized by DDQ with HTO mechanism to the benzoquinolinium cation (this is in agreement with the impossibility to observe the enamine during reaction). Since the HTO mechanism has activation energy lower (or similar) to the rotation of the bromoindole, the reaction takes place on the more stable *sp* conformer, despite the HTO TS calculated for the *ap* conformation has a lower barrier. This interpretation is also in agreement with a better enantioselectivity at 0°C (the conformer lifetime is extended) and with a better enantioselectivity when excess DDQ is used (i.e. the bimolecular HTO reaction is faster while rotation rate does not change).

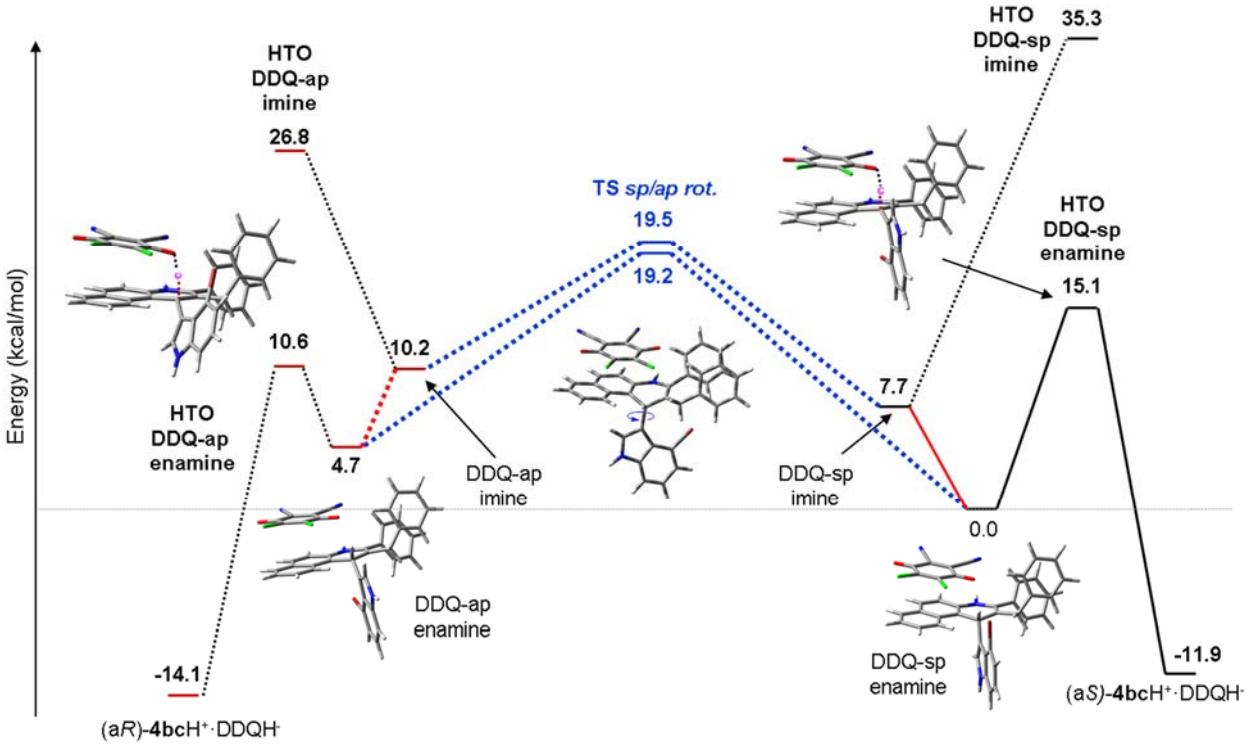


Figure S9. Proposed reaction pathway. Blue lines indicate the 4-bromoindole rotation, red lines indicate tautomerism. The filled line indicates the enantioselective pathway. a*S*-4bcH$^+$·DDQH$^-$ and a*R*-4bcH$^+$·DDQH$^-$ are not enantiomers due to the complexation with DDQH$^-$. Energy values in kcal/mol, as ZPE-corrected entalpies.

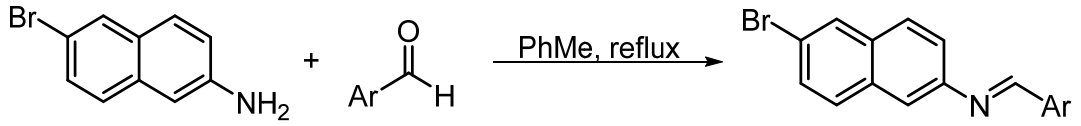
Table S8. Relative free energies of the GS and TS for rotation and for HTO TS in the DDQ complexes of imine and enamine of 5bc. Calculations at the M06-2X/6-31G(d) level.

Compd. **4bc**	*sp* conformer (a.u.)	*ap* conformer (a.u.)	$\Delta G^{[a]}$	$\Delta G^{[a]}$
Imine-DDQ	-5475.774147	-5475.770920	8.1	9.5
Imine DDQ HTO TS imaginary freq. value	-5475.729699 -1144 cm^{-1}	-5475.741636 -1334 cm^{-1}	36.0	28.5
Imine-DDQ *sp*/*ap* rotation imaginary freq. value	-5475.750569 -39 cm^{-1}	-5475.757369 -23 cm^{-1}	22.9	18.6[b]
Enamine-DDQ	-5475.787000	-5475.780189	**0.0**	4.3
Enamine-DDQ HTO TS imaginary freq. value	-5475.758692 -1542 cm^{-1}	-5475.767456 -1214 cm^{-1}	17.8	12.3
Enamine-DDQ sp/ap rot imaginary freq. value	-5475.752226 -40 cm^{-1}	-5475.750834 -23 cm^{-1}	21.8[b]	22.7
Pyridinium-salt-DDQ	-5475.805322	-5475.810420	-11.5	-14.7

[a] ΔG° for ground states and $\Delta G^{\neq}$ for the TS (given in kcal/mol). [b] Threshold TS for rotation.

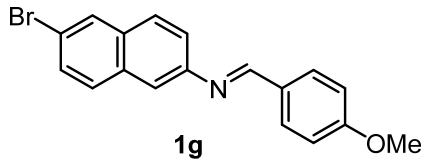
Preparation of Starting Materials

Synthesis of *N*-arylimines 1g-l



To a stirred suspension of 6-bromonaphthalen-2-amine (1.11 g, 5 mmol) in toluene (5 mL), the aldehyde (5 mmol) was added. The resulting suspension was stirred at 110 °C in a Dean-Stark apparatus for 18 h, before it was cooled to room temperature and precipitated with 10 mL of Et_2O. The resulting solid was dried under reduced pressure and used without further purification.

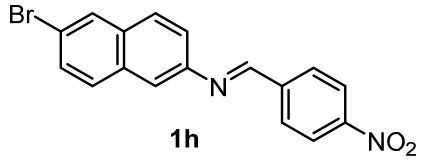
(*E*)-*N*-(6-bromonaphthalen-2-yl)-1-(4-methoxyphenyl)methanimine 1g



1g

Following the model procedure using 4-methoxybenzaldehyde compound **1g** was obtained as a white solid in 90% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.47 (s, 1H), 7.96 (d, *J* = 1.9 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.70 (dd, *J* = 16.3, 8.7 Hz, 2H), 7.59 – 7.47 (m, 2H), 7.43 (dd, *J* = 8.7, 2.0 Hz, 1H), 6.98 (d, *J* = 8.6 Hz, 2H), 3.86 (s, 3H).

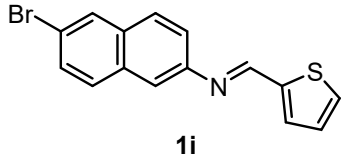
(*E*)-*N*-(6-bromonaphthalen-2-yl)-1-(4-nitrophenyl)methanimine 1h



1h

Following the model procedure using 4-nitrobenzaldehyde compound **1h** was obtained as a yellow solid in 77% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.63 (s, 1H), 8.30 (d, *J* = 8.8 Hz, 2H), 8.07 (d, *J* = 8.8 Hz, 2H), 7.97 (d, *J* = 1.9 Hz, 1H), 7.72 (dd, *J* = 19.8, 8.8 Hz, 2H), 7.58 (d, *J* = 2.1 Hz, 1H), 7.53 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.44 (dd, *J* = 8.7, 2.1 Hz, 1H).

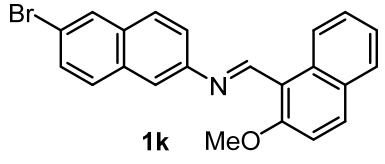
(*E*)-*N*-(6-bromonaphthalen-2-yl)-1-(thiophen-2-yl)methanimine 1i



1i

Following the model procedure using thiophene-2-carbaldehyde compound **1i** was obtained as a yellow solid in 98% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.70 (s, 1H), 7.98 (s, 1H), 7.83 – 7.42 (m, 7H), 7.17 (t, *J* = 4.4 Hz, 1H).

(*E*)-*N*-(6-bromonaphthalen-2-yl)-1-(2-methoxynaphthalen-1-yl)methanimine 1k

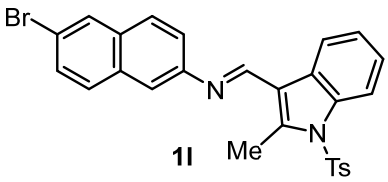


1k

Following the model procedure using 2-methoxy-1-naphthaldehyde compound **1j** was obtained as an orange solid in 80% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 9.56 (d, *J* = 8.7

Hz, 1H), 9.38 (s, 1H), 8.03 – 7.96 (m, 2H), 7.86 – 7.72 (m, 3H), 7.68 – 7.52 (m, 4H), 7.42 (m, 1H), 7.32 (d, *J* = 8.8 Hz, 1H), 4.05 (s, 3H).

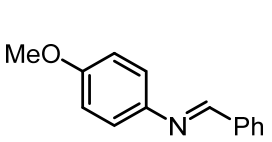
(*E*)-*N*-(6-bromonaphthalen-2-yl)-1-(2-methyl-1-tosyl-1H-indol-3-yl)methanimine 1l



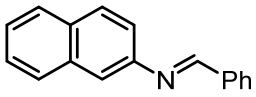
1l

Following the model procedure using 2-methyl-1-tosyl-1*H*-indole-3-carbaldehyde compound **1l** was obtained as a brown solid in 69% yield. **^{1}H NMR** (300 MHz, DMSO-d_6) δ = 8.92 (s, 1H), 8.54 – 8.48 (m, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 8.11 – 8.05 (m, 1H), 7.91 – 7.84 (m, 1H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.74 (d, *J* = 2.1 Hz, 1H), 7.58 (t, *J* = 6.1 Hz, 1H), 7.55 (t, *J* = 7.1 Hz, 1H), 7.38 – 7.29 (m, 5H), 3.25 (s, 3H), 2.86 (s, 3H).

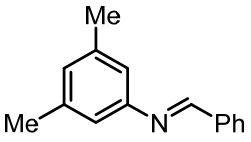
Imines **1a**-**1f**, reported below, are known compounds and were synthesized following literature procedures. Imine **1b** is commercially available.



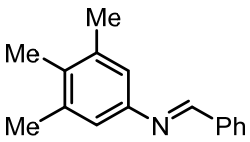
1a



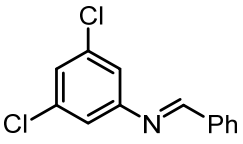
1b



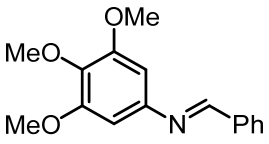
1c



1d

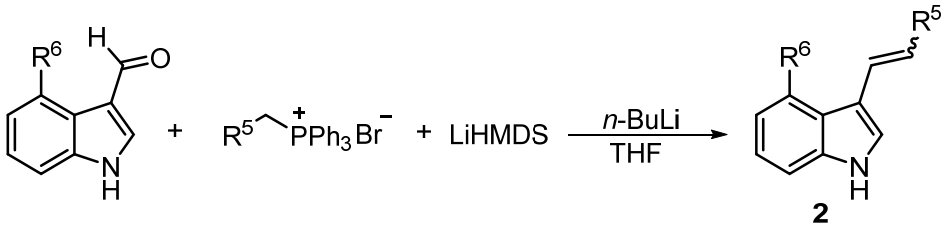


1e



1f

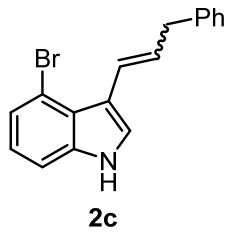
Synthesis of 3-alkenylindoles 2



The following procedure, serving for the synthesis of compound **2c** can be used as the model for the preparation of all the analogous substrates, obtained upon variation of indole-3-carbaldehydes or phosphonium salts, accordingly.

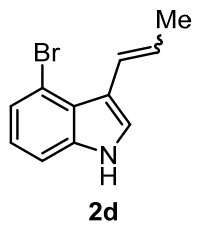
To a stirred suspension of phenethyltripenylphosphonium bromide (3.22 g, 7.2 mmol) in anhydrous THF (16 mL), *n*-BuLi (1.6 M solution in hexanes, 4.5 mL, 8.64 mmol) was added dropwise at -50 °C. The resulting red solution, containing the phosphonium ylide, was stirred and warmed to 0 °C for approximately 45 minutes. In a different flask, a solution of HMDS (1,1,1,3,3,3-hexamethyldisilazane, 1.25 mL, 5 mmol) in anhydrous THF (9 mL) was lithiated by slow addition of a solution of *n*-BuLi at 0 °C (1.6 M solution in hexanes, 3.9 mL, 6.19 mmol). This freshly prepared solution of LiHMDS was added, *via* syringe, to a pre-cooled solution of indole-3-carboxaldehyde (0.897 g, 5 mmol) in anhydrous THF (8 mL) at 0 °C. The resulting solution of lithiated aldehyde was added dropwise to the previously prepared solution of phosphonium ylide cooled back to -30 °C. The resulting mixture was stirred at room temperature for 1 h and then it was poured into H_2O and extracted with EtOAc (2 x 100 mL). The combined organic phases were dried over $MgSO_4$, filtered and evaporated under reduced pressure. The crude residue was then purified by a short and fast column chromatography on silica gel (*n*-hexane/EtOAc = 1:1).

4-bromo-3-(3-phenylprop-1-en-1-yl)-1*H*-indole 2c



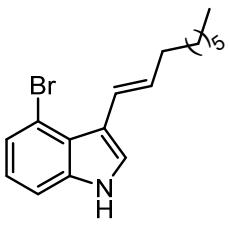
Following the model procedure, compound **2c** was obtained in 75% yield (35:65 trans/cis ratio), as an orange oil. **^{1}H NMR** (300 MHz, DMSO-d_6) δ = 11.54 (bs, 1H cis), 11.48 (bs, 1H trans), 7.62 (s, 1H trans), 7.44 (s, 1H cis), 7.41 (dd, *J* = 8.1, 0.9 Hz, 1H cis), 7.35 (dd, *J* = 8.1, 0.9 Hz, 1H trans), 7.33 – 7.14 (m, 7H cis + 7H trans), 7.00 (t, *J* = 7.80 Hz, 1H cis), 6.94 (t, *J* = 7.80 Hz, 1H trans), 6.06 (dt, *J* = 15.7, 6.9 Hz, 1H trans), 5.72 (dt, *J* = 11.4, 7.1 Hz, 1H cis), 3.62 (dd, *J* = 7.2, 1.9 Hz, 2H cis), 3.49 (dd, *J* = 7.0, 1.5 Hz, 2H trans).

4-bromo-3-(prop-1-en-1-yl)-1*H*-indole 2d



Following the model procedure, from 4-bromoindole-3-carboxaldehyde and ethyltripenylphosphonium bromide, compound **2d** was obtained in 72% yield (76:24 trans/cis ratio), as a pale yellow oil. **^{1}H NMR** (300 MHz, DMSO-d_6) δ = 11.54 (bs, 1H cis), 11.43 (bs, 1H trans), 7.57 (d, *J* = 2.5 Hz, 1H trans), 7.45 (d, *J* = 2.4 Hz, 1H cis), 7.41 (dd, *J* = 8.1, 0.9 Hz, 1H cis), 7.37 (dd, *J* = 8.1, 0.8 Hz, 1H trans), 7.27 – 7.07 (m, 2H cis + 2H trans), 6.99 (t, *J* =8.24 Hz, 1H cis), 6.95 (t, *J* =7.54 Hz, 1H trans), 5.92 (dq, *J* = 15.6, 6.6 Hz, 1H trans), 5.66 (dq, *J* = 11.4, 7.0 Hz, 1H cis), 1.86 – 1.78 (m, 3H cis + 3H trans).

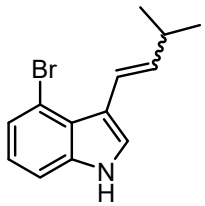
4-bromo-3-(oct-1-en-1-yl)-1*H*-indole 2e



2e

Following the model procedure, from 4-bromoindole-3-carboxaldehyde and octyltripenylphosphonium bromide, compound **2e** was obtained in 66% yield (57:43 trans/cis ratio), as a green oil. **^{1}H NMR** (300 MHz, DMSO-d_6) δ = 11.49 (bs, 1H cis), 11.43 (bs, 1H trans), 7.57 (d, *J* = 2.2 Hz, 1H trans), 7.39 (dd, *J* = 8.1, 0.9 Hz, 1H cis), 7.36 (dd, *J* = 2.7, 0.6 Hz, 1H trans), 7.36 (dd, *J* = 8.1, 0.9 Hz, 1H trans), 7.19 (dd, J = 4.7, 0.9 Hz, 1H cis), 7.18 – 7.09 (m, 1H cis + 1H trans), 7.06 (m, 1H cis), 7.01 – 6.91 (m, 1H cis + 1H trans), 5.91 (dt, *J* = 15.7, 6.9 Hz, 1H trans), 5.54 (dt, *J* = 11.5, 7.0 Hz, 1H cis), 2.34 – 2.07 (m, 2H cis + 2H trans), 1.49 – 1.10 (m, 10H cis + 10H trans), 0.94 – 0.73 (m, 3H cis + 3H trans).

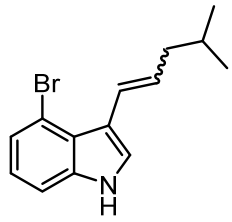
4-bromo-3-(3-methylbut-1-en-1-yl)-1*H*-indole 2f



2f

Following the model procedure, from 4-bromoindole-3-carboxaldehyde and isobutyltripenylphosphoniumbromide, compound **2f** was obtained in 76% yield (67:33 trans/cis ratio), as a green oil. **^{1}H NMR** (400 MHz, DMSO-d_6) δ = 11.46 (bs, 1H cis), 11.42 (bs, 1H trans), 7.57 (d, *J* = 2.6 Hz, 1H trans), 7.41 – 7.37 (m, 1H cis + 1H trans), 7.35 (dd, *J* = 8.1, 0.8 Hz, 1H cis), 7.32 (d, *J* = 2.6 Hz, 1H cis), 7.26 – 7.19 (m, 1H trans), 7.19 – 7.08 (m, 1H cis + 1H trans), 6.94 (m, 1H cis + 1H trans), 5.92 (dd, *J* = 15.9, 6.4 Hz, 1H trans), 5.38 (dd, *J* = 11.4, 9.8 Hz, 1H cis), 2.88 – 2.72 (m, 1H cis), 2.46 – 2.34 (m, 1H trans), 1.06 (d, *J* = 6.7 Hz, 3H trans), 1.00 (d, *J* = 6.6 Hz, 3H cis).

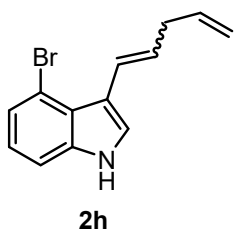
4-bromo-3-(4-methylpent-1-en-1-yl)-1*H*-indole 2g



2g

Following the model procedure, from 4-chloroindole-3-carboxaldehyde and isopentyltripenylphosphonium bromide, compound **2g** was obtained in 75% yield (77:23 trans/cis ratio), as a green oil. **^{1}H NMR** (300 MHz, DMSO-d_6) δ = 11.48 (bs, 1H cis), 11.44 (bs, 1H trans), 7.59 (d, *J* = 2.5 Hz, 1H trans), 7.40 (dd, *J* = 8.3, 0.9 Hz, 1H cis), 7.36 (dd, *J* = 7.9, 0.9 Hz, 1H trans), 7.36 (d, *J* = 2.84 Hz, 1H cis), 7.16 (m, 2H cis + 2H trans), 6.96 (m, 1H cis + 1H trans), 5.90 (dt, *J* = 15.6, 7.3 Hz, 1H trans), 5.58 (dt, *J* = 11.6, 7.0 Hz, 1H cis), 2.16 (td, *J* = 6.9, 1.9 Hz, 2H cis), 2.04 (td, *J* = 7.1, 1.3 Hz, 2H trans), 1.69 (m, 1H cis + 1H trans), 0.91 (m, 6H cis + 6H trans).

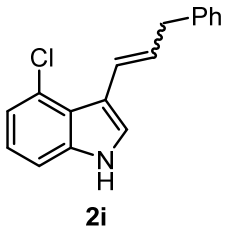
4-bromo-3-(penta-1,4-dien-1-yl)-1*H*-indole 2h



2h

Following the model procedure, from 4-bromoindole-3-carboxaldehyde and homoallyltriphenylphosphonium bromide, compound **2h** was obtained in 83% yield (60:40 trans/cis ratio), as a green oil. **^{1}H NMR** (300 MHz, DMSO-d_6) δ = 11.50 (bs, 1H trans), 11.43 (bs, 1H cis), 7.59 (d, *J* = 2.5 Hz, 1H cis), 7.40 – 7.29 (m, 1H cis + 2H trans), 7.20 – 7.07 (m, 2H cis + 2H trans), 7.00 – 6.87 (m, 1H cis + 1H trans), 5.98 – 5.79 (m, 2H cis + 1H trans), 5.54 (ddd, *J* = 11.4, 8.3, 6.6 Hz, 1H trans), 5.07 (dd, *J* = 17.4, 1.8 Hz, 1H cis + 1H trans), 4.99 (dd, *J* = 10.2, 2.0 Hz, 1H cis + 1H trans), 2.98 (td, *J* = 7.4, 6.9, 2.0 Hz, 2H trans), 2.94 – 2.82 (m, 2H cis).

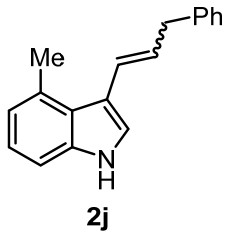
4-chloro-3-(3-phenylprop-1-en-1-yl)-1*H*-indole 2i



2i

Following the model procedure, from 4-chloroindole-3-carboxaldehyde and phenethyltripenylphosphonium bromide, compound **2i** was obtained in 77% yield (46:54 trans/cis ratio), as a dark yellow oil. **^{1}H NMR** (300 MHz, DMSO-d_6) δ = 11.58 (bs, 1H cis), 11.49 (bs, 1H trans), 7.65 (s, 1H cis), 7.46 (s, 1H trans), 7.42 – 6.97 (m, 9H cis + 9H trans), 6.11 (dt, *J* = 15.6, 6.9 Hz, 1H trans), 5.72 (dt, *J* = 11.4, 7.1 Hz, 1H cis), 3.66 (dd, *J* = 7.0, 1.9 Hz, 2H cis), 3.51 (d, *J* = 7.0 Hz, 2H trans).

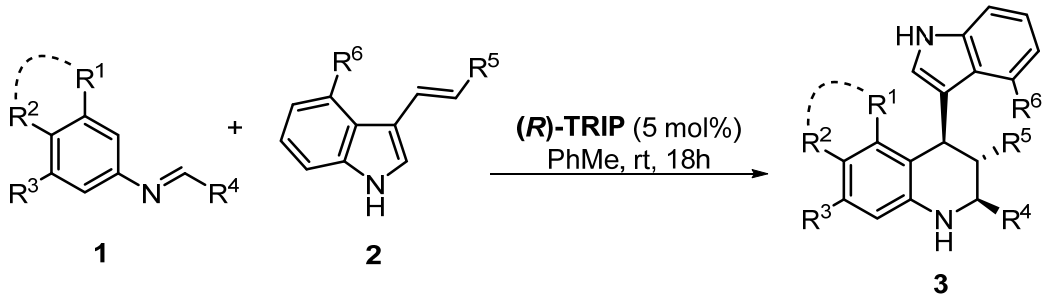
4-methyl-3-(3-phenylprop-1-en-1-yl)-1*H*-indole 2j



2j

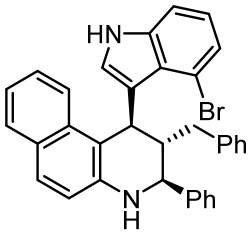
Following the model procedure, from 4-methylindole-3-carboxaldehyde and phenethyltripenylphosphonium bromide, compound **2j** was obtained in 66% yield (33:66 trans/cis ratio), as an intense orange oil. **^{1}H NMR** (300 MHz, DMSO-d_6) δ = 11.16 (bs, 1H cis), 11.08 (bs, 1H trans), 7.44 (s, 1H trans), 7.37 – 7.09 (m, 7H cis + 6H trans), 7.02 – 6.85 (m, 2H cis + 2H trans), 6.80 – 6.69 (m, 1H cis + 1H trans), 6.02 (dt, *J* = 15.5, 6.9 Hz, 1H trans), 5.70 (dt, *J* = 11.2, 7.1 Hz, 1H cis), 3.64 (dd, *J* = 7.1, 1.8 Hz, 2H cis), 3.51 (dd, *J* = 6.9, 1.5 Hz, 2H trans), 2.63 (s, 3H cis), 2.59 (s, 3H trans).

General procedure for the synthesis of products 3.



In a small vial equipped with a magnetic stirring bar, 3-vinylindole **2** (1.5 equiv, 0.45 mmol, *E*/*Z* mixture), *N*-arylimine **1** (1.0 equiv, 0.3 mmol), toluene (2 mL) and catalyst **(*R*)-TRIP** (11 mg, 0.015 mmol, 5 mol%) were added in this order. The resulting solution was stirred for 18 h at room temperature and then directly purified by column chromatography on silica gel to afford the desired compounds **3** as solids. Products **3** were found to be sensitive to traces of DCl in $CDCl_3$ darkening immediately upon contact and showing slow decomposition upon prolonged standing. In order to conveniently record the spectra in $CDCl_3$ the solvent had to be filtered over basic alumina prior to use. Products **3** were all obtained as single all-*trans* isomers.

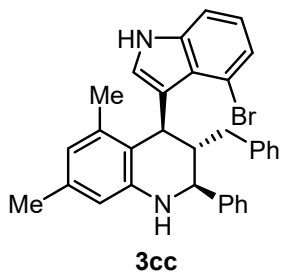
(1*R*,2*S*,3*S*)-2-benzyl-1-(4-bromo-1*H*-indol-3-yl)-3-phenyl-1,2,3,4-tetrahydrobenzo [*f*]quinoline 3bc



3bc

Following the general procedure from *N*-arylimine **1b** and 3-vinylindole **2c**, product **3bc** was obtained as a white solid in 95% yield after column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 2:1). $[\alpha]_D^{25}$ = +107 (c = 0.2 in $CHCl_3$) for 96% *ee*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.79 – 7.67 (m, 2H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.49 (t, *J* = 8.3 Hz, 2H), 7.35 (dt, *J* = 13.3, 4.6 Hz, 3H), 7.25 – 7.11 (m, 4H), 7.09 (bs, 1H), 6.99 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.90 (t, *J* = 7.90 Hz, 1H), 6.89 – 6.83 (m, 2H), 6.81 – 6.66 (m, 3H), 5.62 (d, *J* = 1.9 Hz, 1H), 5.27 (s, 1H), 4.67 (bs, 1H), 4.29 (s, 1H), 3.62 – 3.45 (m, 1H), 3.33 (dd, *J* = 13.6, 4.0 Hz, 1H), 2.80 (dd, *J* = 13.5, 12.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 144.6, 141.2, 140.1, 137.7, 133.9, 129.5 (2C), 128.5, 128.4 (2C), 128.3, 128.0, 127.7, 127.2 (2C), 126.4, 126.1, 125.10 (2C), 125.05, 124.5, 123.7, 122.9, 122.0, 121.3, 118.6, 117.7, 113.6, 110.7, 110.1, 52.1, 44.4, 40.3, 34.9. **ESI-MS**: 565 [M(^{79}Br) + Na^+], 567 [M(^{81}Br) + Na^+]. **HPLC**: AD-H (*n*-hexane/iPrOH 80:20, flow-rate 0.75 mL/min; t_{major} = 20.9 min; t_{minor} = 42.8 min).

(2*S*,3*S*,4*R*)-3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-5,7-dimethyl-2-phenyl-1,2,3,4-tetrahydroquinoline 3cc

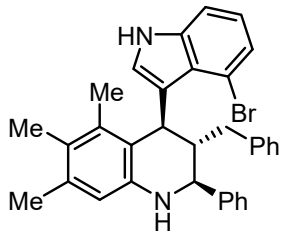


3cc

Following the general procedure from *N*-arylimine **1c** and 3-vinylindole **2c**, product **3cc** was obtained as a white solid in 83% yield after column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 2:1). $[\alpha]_D^{25}$ = +100 (c = 0.2 in $CHCl_3$) for 99% *ee*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.44 (d, *J* = 7.1 Hz, 2H), 7.35 – 7.29 (m, 2H), 7.27 (dd, *J* = 7.5, 0.9 Hz, 1H), 7.23 – 7.16 (m, 2H), 6.99 (dd, *J* = 8.1, 0.9 Hz, 1H), 6.89 (t, *J* = 7.8 Hz, 1H), 6.86 – 6.80 (m, 2H), 6.78 – 6.68 (m, 3H), 6.55 (s, 1H), 6.44 (s, 1H), 5.80 (dd, *J* = 2.5, 0.8 Hz, 1H), 4.77 (s, 1H), 4.38 (s, 1H), 4.20 (s, 1H), 3.40 (ddt, *J* = 11.6, 3.9, 1.8 Hz, 1H), 3.22 (dd, *J*

= 13.5, 4.1 Hz, 1H), 2.78 (dd, *J* = 13.4, 11.7 Hz, 1H), 2.35 (s, 3H), 2.04 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 145.0, 143.0, 141.3, 138.7, 137.8, 136.7, 129.5 (2C), 128.4 (2C), 127.0 (2C), 126.7, 126.0, 125.1 (2C), 124.8, 124.6, 123.6, 121.9, 120.2, 118.7, 116.8, 113.6, 112.0, 110.0, 52.3, 45.0, 40.4, 35.6, 21.3, 19.0. **ESI-MS**: 543 [M(^{79}Br) + Na^+], 545 [M(^{81}Br) + Na^+]. **HPLC**: AD-H (*n*-hexane/iPrOH 80:20, flow-rate 0.75 mL/min; t_{major} = 7.0 min; t_{minor} = 8.0 min).

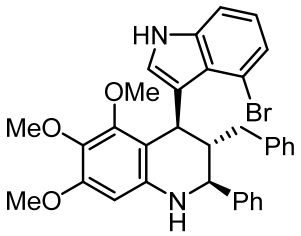
(2*S*,3*S*,4*R*)-3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-5,6,7-trimethyl-2-phenyl-1,2,3,4-tetrahydroquinoline 3dc



3dc

Following the general procedure from *N*-arylimine **1d** and 3-vinylindole **2c**, product **3dc** was obtained as a white solid in 79% yield after column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 2:1). $[\alpha]_D^{25}$ = +39 (c = 0.2 in $CHCl_3$) for 94% *ee*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.45 (d, *J* = 7.3 Hz, 2H), 7.31 (dd, *J* = 15.1, 7.5 Hz, 3H), 7.19 (dd, *J* = 13.9, 6.4 Hz, 2H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.89 (dd, *J* = 15.0, 7.2 Hz, 1H), 6.83 (d, *J* = 6.7 Hz, 2H), 6.78 – 6.67 (m, 3H), 6.60 (s, 1H), 5.78 (d, *J* = 2.0 Hz, 1H), 4.84 (s, 1H), 4.28 (s, 1H), 4.17 (s, 1H), 3.45 – 3.34 (m, 1H), 3.24 (dd, *J* = 13.4, 3.8 Hz, 1H), 2.80 (dd, *J* = 13.4, 11.7 Hz, 1H), 2.36 (s, 3H), 2.14 (s, 3H), 2.00 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 145.3, 141.4, 140.6, 137.8, 136.9, 135.4, 129.5 (2C), 128.4 (2C), 127.2, 127.0 (2C), 126.0, 125.1 (2C), 124.7, 124.5, 123.8, 123.6, 121.9, 119.1, 117.5, 113.6, 113.0, 110.0, 51.9, 45.0, 40.5, 36.3, 21.1, 15.7, 15.3. **ESI-MS**: 557 [M(^{79}Br) + Na^+], 559 [M(^{81}Br) + Na^+]. **HPLC**: AD-H (*n*-hexane/iPrOH 80:20, flow-rate 0.75 mL/min; t_{major} = 6.0 min; t_{minor} = 8.1 min).

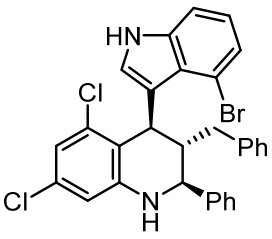
(2*S*,3*S*,4*R*)-3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-5,6,7-trimethoxy-2-phenyl-1,2,3,4-tetrahydroquinoline 3ec



3ec

Following the general procedure from *N*-arylimine **1e** and 3-vinylindole **2c**, product **3ec** was obtained as a white solid in 97% yield after column chromatography on silica gel (CH_2Cl_2/Et_2O = 50:1). $[\alpha]_D^{25}$ = +82 (c = 0.2 in $CHCl_3$) for 98% *ee*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.40 (d, *J* = 7.3 Hz, 2H), 7.33 – 7.22 (m, 4H), 7.17 (t, *J* = 7.3 Hz, 1H), 6.97 (dd, *J* = 8.1, 0.8 Hz, 1H), 6.86 (dd, *J* = 13.5, 5.7 Hz, 1H), 6.82 (d, *J* = 6.8 Hz, 2H), 6.78 – 6.70 (m, 3H), 6.17 (s, 1H), 5.90 (d, *J* = 2.0 Hz, 1H), 4.93 (s, 1H), 4.28 (s, 1H), 4.17 (bs, 1H), 3.93 (s, 3H), 3.79 (s, 3H), 3.60 (s, 3H), 3.34 (ddt, *J* = 11.7, 4.0, 2.1 Hz, 1H), 3.24 (dd, *J* = 13.5, 3.7 Hz, 1H), 2.71 (dd, *J* = 13.3, 11.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 153.1, 153.0, 144.8, 141.3, 139.5, 137.8, 133.8, 129.4 (2C), 128.3 (2C), 127.1 (2C), 126.1, 126.0, 125.1 (2C), 124.9, 124.6, 123.6, 121.9, 120.3, 113.7, 110.1, 107.4, 92.7, 61.0, 60.8, 55.8, 52.8, 44.9, 40.1, 33.1. **ESI-MS**: 605 [M(^{79}Br) + Na^+], 607 [M(^{81}Br) + Na^+]. **HPLC**: OD-H (*n*-hexane/iPrOH 80:20, flow-rate 0.75 mL/min; t_{major} = 11.3 min; t_{minor} = 13.4 min).

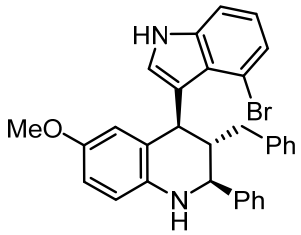
(2*S*,3*S*,4*R*)-3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-5,7-dichloro-2-phenyl-1,2,3,4-tetrahydroquinoline 3fc



3fc

Following the general procedure from *N*-arylimine **1f** and 3-vinylindole **2c**, product **3fc** was obtained as a white solid in 45% yield after column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 2:1). $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = +67 (c = 0.2 in $CHCl_3$) for 87% *ee*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.44 (d, *J* = 7.2 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.19 (m, 3H), 7.00 (dd, *J* = 8.0, 0.7 Hz, 1H), 6.91 (t, *J* = 7.8 Hz, 1H), 6.85 – 6.71 (m, 7H), 5.81 (d, *J* = 1.8 Hz, 1H), 5.01 (s, 1H), 4.66 (s, 1H), 4.27 (s, 1H), 3.57 – 3.44 (m, 1H), 3.26 (dd, *J* = 13.6, 4.1 Hz, 1H), 2.65 (dd, *J* = 13.4, 12.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 145.3, 143.6, 140.5, 137.8, 137.1, 133.0, 129.4 (2C), 128.5 (2C), 127.1 (2C), 126.3, 125.9, 125.1, 124.7 (2C), 124.4, 123.8, 122.2, 117.6, 117.5, 117.3, 113.5, 111.6, 110.1, 52.4, 44.4, 40.1, 36.2. **ESI-MS**: 583 [M(^{79}Br,^{35}Cl,^{35}Cl) + Na^+], 585 [M(^{79}Br,^{37}Cl,^{35}Cl) and M(^{81}Br,^{35}Cl,^{35}Cl) + Na^+], 587 [M(^{81}Br,^{37}Cl,^{35}Cl) and M(^{79}Br,^{37}Cl,^{37}Cl) + Na^+], 589 [M(^{81}Br,^{37}Cl,^{37}Cl) + Na^+]. **HPLC**: AD-H (*n*-hexane/iPrOH 80:20, flow-rate 0.75 mL/min; t_{major} = 7.9 min; t_{minor} = 10.6 min).

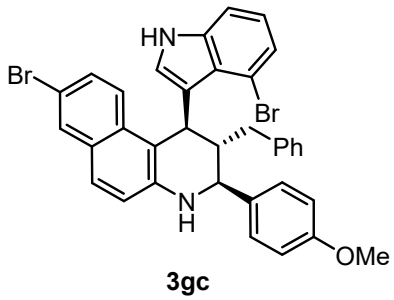
(2*S*,3*S*,4*R*)-3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-6-methoxy-2-phenyl-1,2,3,4-tetrahydroquinoline 3ac



3ac

Following the general procedure from *N*-arylimine **1a** and 3-vinylindole **2c**, product **3ac** was obtained as a white solid in 90% yield after column chromatography on silica gel (*n*-hexane/CH_2Cl_2/Et_2O = 10:1:1). $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = +39 (c = 0.37 in $CHCl_3$) for 86% *ee*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.76 (bs, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.19 – 7.10 (m, 3H), 7.08 – 6.91 (m, 7H), 6.85 (d, *J* = 7.0 Hz, 2H), 6.70 (dd, *J* = 8.7, 2.8 Hz, 1H), 6.66 – 6.56 (m, 2H), 6.38 (bs, 1H), 5.14 (d, *J* = 6.6 Hz, 1H), 4.27 (d, *J* = 6.6 Hz, 1H), 4.03 (bs, 1H), 3.63 (s, 3H), 3.07 (s, 1H), 2.95 (dd, *J* = 13.8, 4.2 Hz, 1H), 2.71 (dd, *J* = 13.9, 8.3 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 151.8, 143.5, 141.0, 137.9, 137.2, 128.9 (2C), 127.85 (2C), 127.70 (2C), 127.0 (2C), 126.5, 125.9, 125.7, 125.5, 125.3, 124.4, 122.3, 120.2, 116.4, 114.5, 113.8, 113.5, 110.4, 58.5, 55.8, 47.2, 39.3, 38.7. **ESI-MS**: 545 [M(^{79}Br) + Na^+], 547 [M(^{81}Br) + Na^+]. **HPLC**: AD-H (*n*-hexane/iPrOH 80:20, flow-rate 0.75 mL/min; t_{major} = 11.2 min; t_{minor} = 12.3 min).

(1*R*,2*S*,3*S*)-2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(4-methoxyphenyl)-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3gc

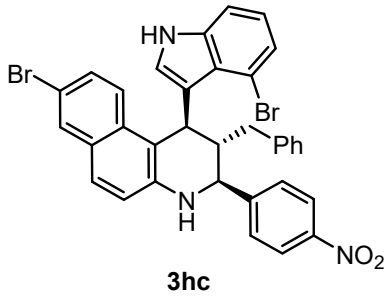


3gc

Following the general procedure from *N*-arylimine **1g** and 3-vinylindole **2c**, product **3gc** was obtained as a white solid in 77% yield after column chromatography on silica gel (from *n*-hexane/CH_2Cl_2/Et_2O = 10:1:1 to *n*-hexane/CH_2Cl_2/Et_2O = 8:1:1). $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = +84 (c = 0.2 in $CHCl_3$) for 97% *ee*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.83 (d, *J* = 2.1 Hz, 1H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.47 – 7.38 (m, 2H), 7.36 – 7.29 (m, 4H), 7.39 – 7.31 (m, 3H), 7.11 (d, *J* = 8.8 Hz, 1H), 7.01 (dd, *J* = 8.1, 1.0 Hz, 1H), 6.94 (t, *J* = 7.7 Hz, 1H), 6.78 – 6.72 (m, 2H), 6.32 – 6.27 (m, 2H), 5.58 (dd, *J* = 2.6, 1.0 Hz, 1H), 5.18 (s, 1H), 4.69 (bs, 1H), 4.24 (bs, 1H), 3.57 (s, 3H), 3.52 – 3.43 (m, 1H), 3.27 (dd, *J* = 13.6, 4.1 Hz, 1H), 2.73 (dd, *J* = 13.6, 11.8 Hz, 1H). **^{13}C**

NMR (101 MHz, $CDCl_3$) δ = 157.0, 141.0, 140.5, 137.7, 136.4, 132.4, 130.1, 129.55 (2C), 129.43, 129.2, 128.4 (2C), 127.5, 127.4, 126.1, 125.9 (2C), 124.8, 124.4, 123.8, 122.1, 118.65, 118.61, 114.7, 113.6, 112.7 (2C), 110.9, 110.1, 55.2, 51.6, 44.4, 40.2, 34.8. **ESI-MS**: 651 [M(^{79}Br, ^{79}Br) + H^+], 653 [M(^{81}Br, ^{79}Br) + H^+], 655 [M(^{81}Br,^{81}Br) + H^+]. **HPLC**: AD-H (*n*-hexane/iPrOH 80:20, flow-rate 0.75 mL/min; t_{major} = 11.9 min; t_{minor} = 23.5 min).

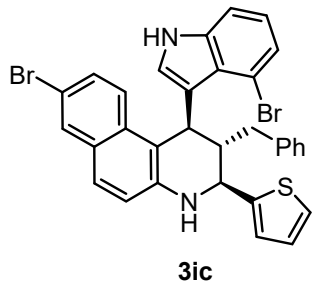
(1*R*,2*S*,3*S*)-2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(4-nitrophenyl)-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3hc



3hc

Following the general procedure from *N*-arylimine **1h** and 3-vinylindole **2c**, product **3hc** was obtained as a white solid in 95% yield after column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 1.5:1). $[\alpha]_D^{25}$ = +237 (c = 0.2 in $CHCl_3$) for 98% *ee*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.86 (d, *J* = 2.1 Hz, 1H), 7.69 – 7.62 (m, 1H), 7.57 – 7.50 (m, 2H), 7.49 – 7.41 (m, 4H), 7.39 – 7.31 (m, 3H), 7.31 – 7.23 (m, 2H), 7.14 (d, *J* = 8.8 Hz, 1H), 7.01 – 6.95 (m, 2H), 6.95 – 6.89 (m, 2H), 5.59 (dd, *J* = 2.6, 1.0 Hz, 1H), 5.22 – 5.15 (m, 1H), 4.70 (dd, *J* = 5.1, 1.4 Hz, 1H), 4.30 (d, *J* = 4.9 Hz, 1H), 3.63 (ddd, *J* = 11.8, 4.4, 1.9 Hz, 1H), 3.26 (dd, *J* = 13.6, 4.2 Hz, 1H), 2.70 (dd, *J* = 13.7, 11.7 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 153.0, 145.2, 140.4, 139.7, 137.9, 132.2, 130.2, 129.7, 129.4 (2C), 128.7 (2C), 127.9, 127.1, 126.5, 125.7 (2C), 124.5, 124.3, 124.1 (2C), 122.8, 122.1, 118.4 (2C), 118.0, 115.2, 113.4, 110.8, 110.4, 52.5, 44.9, 39.9, 34.7. **ESI-MS**: 666 [M(^{79}Br, ^{79}Br) + H^+], 668 [M(^{81}Br, ^{79}Br) + H^+], 670 [M(^{81}Br,^{81}Br) + H^+]. **HPLC**: AD-H (*n*-hexane/iPrOH 80:20, flow-rate 0.75 mL/min; t_{major} = 16.8 min; t_{minor} = 33.2 min).

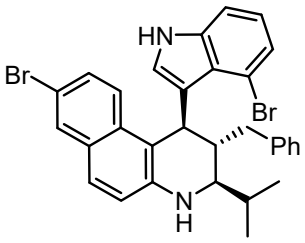
(1*R*,2*S*,3*S*)-2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(thiophen-2-yl)-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3ic



3ic

Following the general procedure from *N*-arylimine **1i** and 3-vinylindole **2c**, product **3ic** was obtained as a white solid in 95% yield after column chromatography on silica gel (*n*-hexane/ CH_2Cl_2 = 1.5:1). $[\alpha]_D^{25}$ = +8 (c = 0.2 in $CHCl_3$) for 97% ee. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.83 (d, *J* = 2.1 Hz, 1H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.48 – 7.37 (m, 4H), 7.36 – 7.27 (m, 3H), 7.24 – 7.16 (m, 2H), 7.13 – 7.04 (m, 2H), 7.00 (t, *J* = 7.8 Hz, 1H), 6.69 (dt, *J* = 5.0, 0.9 Hz, 1H), 6.39 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.18 (dt, *J* = 3.6, 1.4 Hz, 1H), 5.72 (dd, *J* = 2.6, 0.9 Hz, 1H), 5.32 – 5.29 (m, 1H), 4.83 (bs, 1H), 4.48 (s, 1H), 3.45 (ddd, *J* = 11.8, 4.2, 2.0 Hz, 1H), 3.29 (dd, *J* = 13.7, 4.1 Hz, 1H), 2.70 (dd, *J* = 13.7, 11.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 151.5, 140.5, 139.7, 137.5, 132.3, 130.1, 129.58, 129.51, 129.3 (2C), 128.5 (2C), 127.6, 126.8, 126.6, 126.3, 124.9, 124.4, 123.9, 122.39, 122.34, 120.9, 119.1, 118.7, 115.0, 113.6, 110.9, 110.3, 49.9, 44.8, 39.9, 34.6. **ESI-MS**: 627 [M(^{79}Br, ^{79}Br) + H^+], 629 [M(^{81}Br, ^{79}Br) + H^+], 631 [M(^{81}Br,^{81}Br) + H^+]. **HPLC**: AD-H (*n*-hexane/iPrOH 80:20, flow-rate 0.75 mL/min; t_{major} = 9.7 min; t_{minor} = 13.5 min).

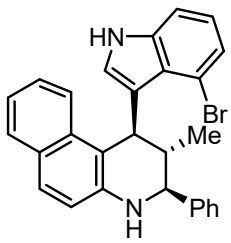
(1*R*,2*S*,3*R*)-2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-isopropyl-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3jc



3jc

Compound **3jc** was prepared following a three-component procedure. In a small vial equipped with a magnetic stirring bar, 6-bromo-2-naphthylamine (73 mg, 1 equiv, 0.3 mmol) and isobutyraldehyde (27.4 μL, 2 equiv, 0.6 mmol) were mixed in toluene (2 mL) until a clear solution was obtained (30 min). Then, 3-vinylindole **2c** (140 mg, 1.5 equiv, 0.45 mmol, *E*/*Z* mixture), and catalyst **(*R*)-TRIP** (11 mg, 0.015 mmol, 5 mol%) were added in this order, and the resulting mixture was stirred for 18 h at room temperature. Product **3jc** was obtained as a white solid in 50% yield after column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 2:1). $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = -29 (c = 0.2 in $CHCl_3$) for 66% *ee*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.86 (bs, 1H), 7.81 (bs, 1H), 7.52 (bd, *J* = 8.8 Hz, 1H), 7.41 (dd, *J* = 7.6, 0.9 Hz, 1H) overlapped with 7.60 – 7.35 (very broad s, 1H), 7.34 – 7.23 (m, 6H), 7.22 – 7.15 (m, 1H), 7.04 (t, *J* = 7.9 Hz, 1H), 6.89 (bs, 1H), 6.25 (dd, *J* = 2.6, 1.0 Hz, 1H), 5.20 (bs, 1H), 4.51 (bs, 1H), 3.32 (bd, *J* = 10.7 Hz, 1H), 3.11 (dd, *J* = 13.6, 4.4 Hz, 1H), 2.55 (dd, *J* = 13.6, 11.3 Hz, 1H), 2.45 (bs, 1H), 1.45 – 1.36 (m, 1H), 0.70 (d, *J* = 6.5 Hz, 3H), 0.07 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 140.9, 140.7, 138.0, 132.3, 130.1, 129.5 (2C), 129.3, 128.2 (2C), 127.2, 125.9, 125.8, 125.4, 124.3 (2C), 122.7, 119.7, 118.7, 114.2, 113.7, 110.7, 109.7, 58.4, 41.1, 38.8, 34.7, 31.8, 21.2, 18.5. **ESI-MS**: 587 [M(^{79}Br, ^{79}Br) + H^+], 589 [M(^{81}Br, ^{79}Br) + H^+], 591 [M(^{81}Br,^{81}Br) + H^+]. **HPLC**: AD-H (*n*-hexane/iPrOH 80:20, flow-rate 0.75 mL/min; t_{minor} = 6.4 min; t_{major} = 7.3 min).

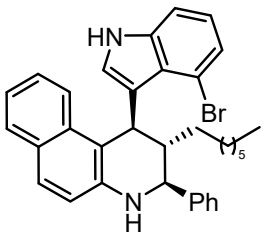
(1*R*,2*S*,3*S*)-1-(4-bromo-1*H*-indol-3-yl)-2-methyl-3-phenyl-1,2,3,4-tetrahydrobenzo [*f*]quinoline 3bd



3bd

Following the general procedure from *N*-arylimine **1b** and 3-vinylindole **2d**, product **3bd** was obtained as a white solid in 96% yield after column chromatography on silica gel (from *n*-hexane/CH_2Cl_2 = 3:2 to *n*-hexane/CH_2Cl_2 = 1:1). $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = -110 (c = 0.2 in $CHCl_3$) for 98% *ee*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.68 – 7.55 (m, 3H), 7.39 (bs, 1H), 7.34 (dd, *J* = 7.6, 0.7 Hz, 1H), 7.20 (d, *J* = 7.2 Hz, 2H), 7.16 – 6.98 (m, 7H), 6.95 (t, *J* = 7.8 Hz, 1H), 6.01 (d, *J* = 2.4 Hz, 1H), 5.28 (d, *J* = 4.5 Hz, 1H), 4.49 (bs, 1H), 4.30 (d, *J* = 5.1 Hz, 1H), 3.08 – 2.88 (m, 1H), 1.23 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 143.7, 141.4, 137.2, 133.7, 128.4, 128.2, 128.1, 127.8 (2C), 126.22 (2C), 126.20 (2C), 126.1, 124.9, 124.1, 123.5, 122.0, 121.4, 121.2, 117.8, 113.9, 113.7, 110.3, 60.0, 42.2, 36.3, 19.8. **ESI-MS**: 467 [M(^{79}Br) + H^+], 469 [M(^{81}Br) + H^+]. **HRMS**: calculated for [$C_{28}H_{23}BrN_2$ - H^+]: 465.0972 [M(^{79}Br) - H^+], 467.0951 [M(^{81}Br) - H^+]; found 465.0966 [M(^{79}Br) - H^+], 467.0950 [M(^{81}Br) - H^+]. **HPLC**: AD-H (*n*-hexane/iPrOH 80:20, flow-rate 0.75 mL/min; t_{major} = 14.9 min; t_{minor} = 20.8 min).

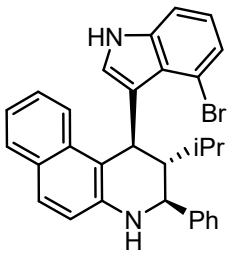
(1*R*,2*S*,3*S*)-1-(4-bromo-1*H*-indol-3-yl)-3-phenyl-2-heptyl-1,2,3,4-tetrahydrobenzo [*f*]quinoline 3be



3be

Following the general procedure from *N*-arylimine **1b** and 3-vinylindole **2e**, product **3be** was obtained as a white solid in 76% yield after column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 2:1). $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = -15 (c = 0.2 in $CHCl_3$) for 98% *ee*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.70 – 7.63 (m, 2H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.29 (dt, *J* = 7.1, 3.5 Hz, 1H), 7.21 – 7.14 (m, 1H), 7.15 – 7.01 (m, 5H), 7.00 – 6.95 (m, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.89 – 6.76 (m, 3H), 5.67 (s, 1H), 5.12 (s, 1H), 4.59 (s, 2H), 3.15 (d, *J* = 6.7 Hz, 1H), 1.84 – 1.48 (m, 4H), 1.40 – 1.30 (m, 8H), 0.89 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 144.8, 140.3, 137.6, 133.8, 128.2, 128.0, 127.33, 127.25 (3C), 126.2, 125.4 (2C), 125.1, 124.6, 123.7, 122.9, 121.9, 121.2, 119.3, 117.6, 113.7, 111.8, 110.0, 53.8, 43.2, 35.8, 34.1, 31.9, 29.8, 29.4, 27.9, 22.7, 14.2. **ESI-MS**: 551 [M(^{79}Br) + H^+], 553 [M(^{81}Br) + H^+]. **HPLC**: AD-H (*n*-hexane/iPrOH 80:20, flow-rate 0.75 mL/min; t_{minor} = 7.6 min; t_{major} = 9.3 min).

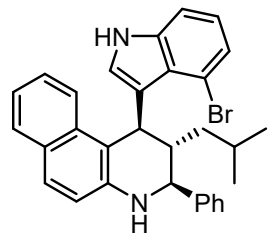
(1*R*,2*S*,3*S*)-1-(4-bromo-1*H*-indol-3-yl)-2-isopropyl-3-phenyl-1,2,3,4-tetrahydrobenzo [*f*]quinoline 3bf



3bf

Following the general procedure from *N*-arylimine **1b** and 3-vinylindole **2f**, product **3bf** was obtained as a white solid in 92% yield after column chromatography on silica gel (*n*-hexane/Et_2O/CH_2Cl_2 = 10:1:1). $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = -88 (c = 0.2 in $CHCl_3$) for 99% *ee*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.75 – 7.68 (m, 2H), 7.66 (d, *J* = 8.7 Hz, 1H), 7.25 (ddd, *J* = 8.5, 6.8, 1.3 Hz, 2H), 7.20 (bs, 1H), 7.15 (t, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 8.2, 1.1 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 1H), 6.92 – 6.79 (m, 4H), 6.77 – 6.71 (m, 1H), 5.86 (dd, *J* = 2.6, 1.0 Hz, 1H), 5.39 (s, 1H), 4.64 (s, 1H), 4.44 (bs, 1H), 3.12 (dt, *J* = 7.2, 2.3 Hz, 1H), 2.01 (sept, *J* = 6.9 Hz, 1H), 1.15 (d, *J* = 6.7 Hz, 3H), 1.09 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 145.5, 141.3, 138.0, 133.1, 128.3, 128.0, 127.8, 127.4, 126.9 (2C), 126.5, 125.2 (2C), 124.9, 124.7, 123.6, 122.0, 121.8, 121.2, 118.9, 117.2, 113.6, 112.2, 110.0, 54.3, 49.0, 32.3, 31.3, 21.4, 21.0. **ESI-MS**: 495 [M(^{79}Br) + H^+], 497 [M(^{81}Br) + H^+]. **HPLC**: OD-H (*n*-hexane/iPrOH 80:20, flow-rate 0.75 mL/min; t_{major} = 16.6 min; t_{minor} = 20.4 min).

(1*R*,2*S*,3*S*)-1-(4-bromo-1*H*-indol-3-yl)-2-isobutyl-3-phenyl-1,2,3,4-tetrahydrobenzo [*f*]quinoline 3bg

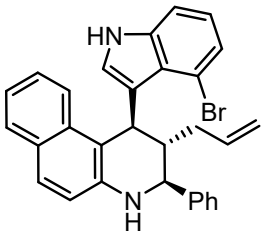


3bg

Following the general procedure from *N*-arylimine **1b** and 3-vinylindole **2g**, product **3bg** was obtained as a white solid in 94% yield after column chromatography on silica gel (*n*-hexane/CH_2Cl_2 =2:1). $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = -7 (c = 0.2 in $CHCl_3$) for 98% *ee*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.67 (d, *J* = 8.9 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 1H), 7.29 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.20 – 7.02 (m, 6H), 6.97 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.89 – 6.75 (m, 3H), 5.62 (d, *J* = 2.1 Hz, 1H), 5.04 (s, 1H), 4.61 (s, 2H), 3.28 (d, *J* = 11.3 Hz, 1H), 1.95 – 1.80 (m, 1H), 1.71 (ddd, *J* = 15.3, 11.5, 3.8 Hz, 1H), 1.52 (ddd, *J* = 13.9, 10.7, 3.3 Hz, 1H), 1.13 (d, *J* = 6.5 Hz, 3H), 0.96 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 144.9, 140.1, 137.6, 133.8, 128.25, 128.22, 128.0, 127.6, 127.3 (2C), 126.2, 125.2 (2C), 125.1, 124.6, 123.6, 122.9, 121.9, 121.2, 119.0, 117.6, 113.6, 111.7, 110.0, 53.1, 42.8, 40.0, 35.7, 25.5, 24.4, 21.6. **ESI-MS**: 509

[M(^{79}Br) + H$^+$], 511 [M(^{81}Br) + H$^+$]. **HPLC**: AD-H (*n*-hexane/iPrOH 80:20, flow-rate 0.75 mL/min; t_{major} = 13.7 min; t_{minor} = 15.3 min).

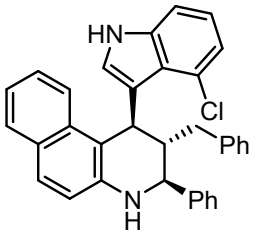
(1*R*,2*S*,3*S*)-2-allyl-1-(4-bromo-1*H*-indol-3-yl)-3-phenyl-1,2,3,4-tetrahydrobenzo [*f*]quinoline 3bh



3bh

Following the general procedure from *N*-arylimine **1b** and 3-vinylindole **2h**, product **3bh** was obtained as a white solid in 88% yield after column chromatography on silica gel (*n*-hexane/Et_2O/CH_2Cl_2 = 10:1:1). $[\alpha]_D^{25}$ = +40 (c = 0.2 in $CHCl_3$) for 97% *ee*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.70 – 7.64 (m, 2H), 7.54 (d, *J* = 8.7 Hz, 1H), 7.30 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.22 – 6.97 (m, 7H), 6.90 (t, *J* = 7.63 Hz, 1H), 6.90 (t, *J* = 7.8 Hz, 1H), 6.88 – 6.76 (m, 3H), 6.09 (dddd, *J* = 17.0, 10.1, 8.7, 5.5 Hz, 1H), 5.69 (bs, 1H), 5.17 – 5.08 (m, 3H), 4.58 (d, *J* = 2.4 Hz, 1H), 3.32 – 3.21 (m, 1H), 2.58 (d, *J* = 13.9 Hz, 1H), 2.36 (ddd, *J* = 14.0, 10.3, 8.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 144.6, 140.2, 137.74, 137.68, 133.8, 128.3, 128.2, 128.0, 127.4, 127.3 (2C), 126.3, 125.3 (2C), 125.1, 124.5, 123.7, 122.9, 122.0, 121.3, 118.9, 117.6, 116.8, 113.6, 111.0, 110.0, 53.1, 42.6, 38.7, 35.1. **ESI-MS**: 493 [M(^{79}Br) + H$^+$], 495 [M(^{81}Br) + H$^+$]. **HPLC**: AD-H (*n*-hexane/i-PrOH 80:20, flow-rate 0.75 mL/min; t_{minor} = 9.0 min; t_{major} = 9.6 min).

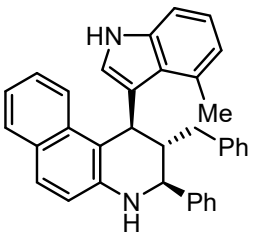
(1*R*,2*S*,3*S*)-2-benzyl-1-(4-chloro-1*H*-indol-3-yl)-3-phenyl-1,2,3,4-tetrahydrobenzo [*f*]quinoline 3bi



3bi

Following the general procedure from *N*-arylimine **1b** and 3-vinylindole **2i**, product **3bi** was obtained as a white solid in 96% yield after column chromatography on silica gel (*n*-hexane/Et_2O = 1:1). $[\alpha]_D^{25}$ = +129 (c = 0.2 in $CHCl_3$) for 99% *ee*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.77 – 7.68 (m, 2H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.45 (d, *J* = 7.0 Hz, 2H), 7.38 – 7.30 (m, 2H), 7.25 – 7.07 (m, 6H), 7.00 (t, J = 8.03 Hz, 1H), 6.94 (dd, *J* = 8.1, 1.1 Hz, 1H), 6.91 – 6.84 (m, 2H), 6.80 – 6.69 (m, 3H), 5.59 (dd, *J* = 2.5, 0.8 Hz, 1H), 5.18 (s, 1H), 4.67 (bs, 1H), 4.30 (s, 1H), 3.52 (ddd, *J* = 5.9, 4.3, 2.3 Hz, 1H), 3.24 (dd, *J* = 13.5, 4.1 Hz, 1H), 2.82 (dd, *J* = 13.4, 11.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 144.5, 141.2, 140.1, 137.8, 133.9, 129.5 (2C), 128.5, 128.4 (2C), 128.3, 128.0, 127.2 (2C), 127.1, 126.3, 126.1, 125.6, 125.1 (3C), 123.1, 122.9, 121.7, 121.3, 120.2, 118.4, 117.7, 110.8, 109.5, 52.3, 44.6, 40.7, 35.4. **ESI-MS**: 521 [M(^{35}Cl) + Na$^+$], 523 [M(^{37}Cl) + Na$^+$]. **HRMS** calculated for [$C_{34}H_{27}ClN_2$ - H$^+$]: 497.1790 [M(^{35}Cl) - H$^+$], 499.1761 [M(^{37}Cl) - H$^+$]; found 497.1785 [M(^{35}Cl) - H$^+$], 499.1772 [M(^{37}Cl) - H$^+$] **HPLC**: AD-H (*n*-hexane/iPrOH 80:20, flow-rate 0.75 mL/min; t_{major} = 9.4 min; t_{minor} = 16.7 min).

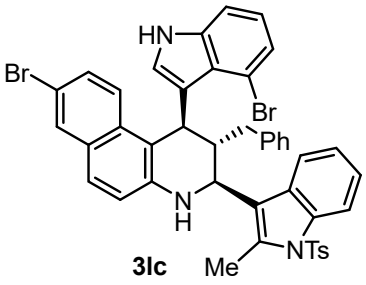
(1*R*,2*S*,3*S*)-2-benzyl-1-(4-methyl-1*H*-indol-3-yl)-3-phenyl-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3bj



3bj

Following the general procedure from *N*-arylimine **1b** and 3-vinylindole **2j**, product **3bj** was obtained as a white solid in 95% yield after column chromatography on silica gel (*n*-hexane/Et_2O = 4:1). $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = +75 (c = 0.2 in $CHCl_3$) for 98% *ee*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.78 – 7.67 (m, 2H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.43 – 7.30 (m, 4H), 7.24 – 7.08 (m, 4H), 7.00 (dd, *J* = 9.2, 5.9 Hz, 2H), 6.96 – 6.85 (m, 4H), 6.85 – 6.75 (m, 3H), 5.54 (s, 1H), 4.99 (s, 1H), 4.67 (bs, 1H), 4.34 (s, 1H), 3.37 – 3.23 (m, 1H), 3.14 (dd, *J* = 13.7, 4.6 Hz, 1H), 3.00 (s, 3H), 2.91 (dd, *J* = 13.6, 11.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 144.1, 140.7, 139.9, 136.6, 133.8, 129.6, 129.3 (2C), 128.5 (2C), 128.4, 128.2, 128.1, 127.2 (2C), 126.34, 126.32, 126.2, 125.1, 125.0 (2C), 124.7, 123.0, 121.3, 121.0, 120.8, 118.8, 117.6, 111.4, 108.7, 52.6, 44.6, 40.9, 36.2, 20.9. **ESI-MS**: 501 [M + Na^+]. **HPLC**: AD-H (*n*-hexane/iPrOH 80:20, flow-rate 0.75 mL/min; t_{major} = 9.0 min; t_{minor} = 11.6 min).

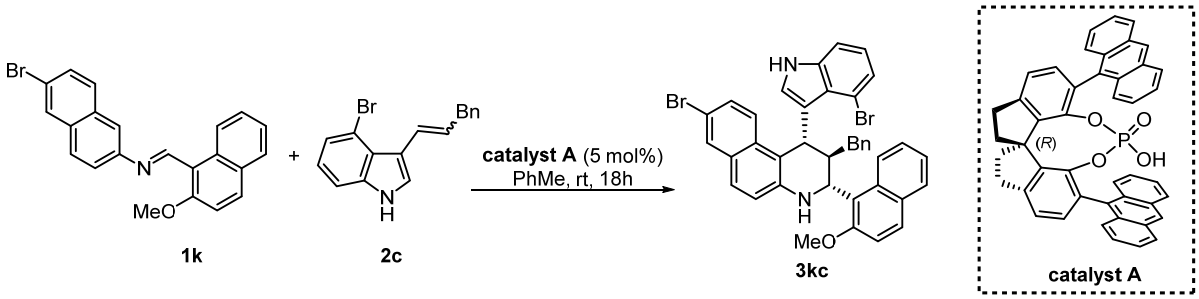
(1*R*,2*S*,3*S*)-2-benzyl-8-bromo-3-(2-methyl-1-tosyl-1*H*-indol-3-yl)-1-(4-bromo-1*H*-indol-3-yl)-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3lc



3lc

Following the general procedure from *N*-arylimine **1l** and 3-vinylindole **2c**, product **3lc** was obtained as a white solid in 85% yield after column chromatography on silica gel (*n*-hexane/Et_2O = 3:1). $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = +90 (c = 0.2 in $CHCl_3$) for 97% *ee*. **^{1}H NMR** (400 MHz, Acetone-d_6) δ = 9.54 (bs, 1H), 8.00 (s, 1H), 7.89 (d, *J* = 2.2 Hz, 1H), 7.86 (dt, *J* = 8.4, 0.9 Hz, 1H), 7.71 (d, *J* = 8.8 Hz, 1H), 7.56 – 7.47 (m, 4H), 7.28 (d, *J* = 8.8 Hz, 1H), 7.26 – 7.19 (m, 4H), 7.17 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.14 – 7.06 (m, 3H), 7.06 – 7.00 (m, 2H), 6.97 – 6.87 (m, 2H), 6.18 (dd, *J* = 2.7, 0.8 Hz, 1H), 6.12 (d, *J* = 3.5 Hz, 1H), 5.36 (d, *J* = 3.9 Hz, 1H), 4.63 (t, *J* = 3.9 Hz, 1H), 3.52 – 3.43 (m, 1H), 3.23 (dd, *J* = 13.5, 3.5 Hz, 1H), 2.71 (dd, *J* = 13.6, 10.7 Hz, 1H), 2.32 (s, 3H), 2.16 (s, 3H). **^{13}C NMR** (101 MHz, Acetone-d_6) δ = 144.8, 142.9, 140.8, 138.0, 136.6, 135.7, 132.7, 131.6, 130.1, 130.0, 129.9 (2C), 129.5, 129.3, 129.2 (2C), 128.6, 127.8 (2C), 127.5, 126.1 (2C), 125.9, 125.8, 124.9, 123.4, 122.9, 122.2, 121.8, 121.2, 120.5, 119.2, 118.7, 113.7, 113.6, 112.7, 111.9, 111.1, 49.5, 47.5, 39.4, 36.1, 20.5, 12.6. **ESI-MS**: 828 [M(^{79}Br, ^{79}Br) + H^+], 830 [M(^{81}Br, ^{79}Br) + H^+], 832 [M(^{81}Br,^{81}Br) + H^+]. **HPLC**: AD-H (*n*-hexane/iPrOH 80:20, flow-rate 0.75 mL/min; t_{minor} = 16.3 min; t_{major} = 29.5 min).

(1*S*,2*R*,3*R*)-2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(2-methoxynaphthalen-1-yl)-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3kc

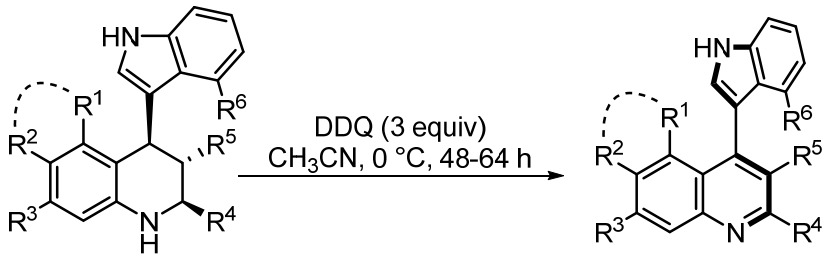


In a small vial equipped with a magnetic stirring bar, 3-vinylindole **2c** (1.5 equiv, 0.45 mmol, *E*/*Z* mixture), *N*-arylimine **1k** (1.0 equiv, 0.3 mmol), toluene (2 mL) and **catalyst A** (10 mg, 0.015 mmol, 5 mol%) were added in this order. The resulting solution was stirred for 18 h at room temperature and then directly purified by column chromatography on silica gel to afford compound **3kc** as a white solid in 92% yield after column chromatography on silica gel (*n*-hexane/CH_2Cl_2/Et_2O = 10:1:1). $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = +122 (c = 0.2 in $CHCl_3$) for 90% ee **^{1}HNMR** (400 MHz, $CDCl_3$) δ = 8.42 (d, *J* = 8.7 Hz, 1H), 7.80 (d, *J* = 2.2 Hz, 1H), 7.76 – 7.66 (m, 2H), 7.57 – 7.46 (m, 3H), 7.31 (d, *J* = 7.5 Hz, 2H), 7.27 – 7.14 (m, 2H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.00 – 6.87 (m, 3H), 6.72 – 6.60 (m, 4H), 6.42 – 6.31 (m, 2H), 5.65 (d, *J* = 7.7 Hz, 1H), 5.40 (d, *J* = 8.3 Hz, 1H), 4.39 (bs, 1H), 3.74 (s, 3H), 3.57 (td, *J* = 8.1, 5.5 Hz, 1H), 3.28 (dd, *J* = 14.2, 2.8 Hz, 1H), 2.69 (dd, *J* = 14.3, 9.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 155.2, 144.1, 140.9, 136.9, 133.0, 132.4, 130.04, 130.02, 129.5, 129.3, 128.9, 128.3, 128.2 (2C), 126.9, 126.8 (2C), 125.9, 125.6, 125.3, 124.82, 124.78, 124.7, 124.5, 122.81, 122.77, 122.3, 121.1, 119.5, 117.1, 114.9, 113.8, 112.6, 110.7, 56.1, 54.1, 51.2, 38.3, 38.0. **ESI-MS**: 701 [M(^{79}Br, ^{79}Br) + H^+], 703 [M(^{81}Br, ^{79}Br) + H^+], 705 [M(^{81}Br,^{81}Br) + H^+]. **HPLC**: AD-H (*n*-hexane/iPrOH 80:20, flow-rate 0.75 mL/min; t_{major} = 11.5 min; t_{minor} = 17.1 min).

The same reaction, performed in the presence of **(*R*)-TRIP** as catalyst afforded product ***ent*-3kc** in 70% *ee* (opposite configuration of the major enantiomer detected by chiral stationary phase HPLC). **(*R*)-TRIP** should give the same absolute configuration of the three chiral centers independently from the substituents on these centers. Thus ***ent*-3kc** has the same configuration of all other products **3** showed above and **3kc** has the opposite one. Moreover, it is not uncommon that BINOL and SPINOL phosphoric acid derivatives, having the same configuration, impart opposite chirality to the product they form.[15]

[15] L. Zhang, S.-H Xiang, J. (J.) Wang, J. Xiao, J.-Q. Wang, B. Tan *Nat. Commun.* **2019**, *10*, 566.

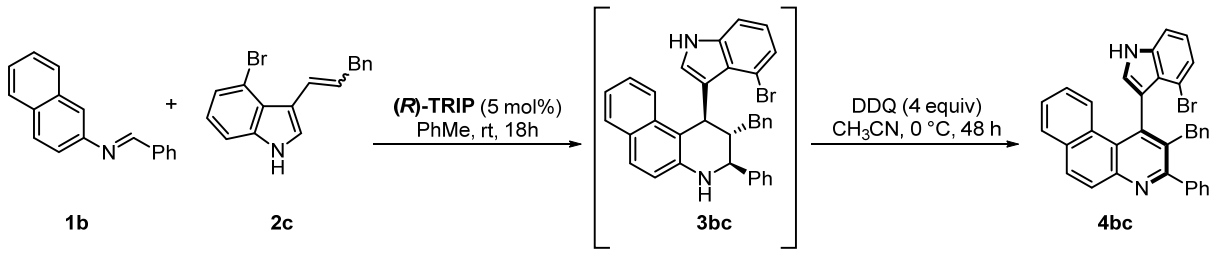
General procedure for the synthesis of products 4.



3 **4**

In a test tube equipped with a magnetic stirring bar, tetrahydroquinoline **3** (0.1 mmol) and CH_3CN (3 mL) were added. In the case of poorly soluble substrates, a small amount of DCM (300 µL) could be added in order to ensure complete dissolution (*vide infra*). The resulting mixture was cooled to 0°C and DDQ (68.4 mg, 0.03 mmol, 3 equiv.) was added in one portion. The resulting solution was stirred for 48-64 h at 0°C and then poured into a solution of Na_2SO_3 (1 M, 10 mL) and extracted with DCM (3 x 30 mL). The combined organic phases were dried over $MgSO_4$, filtered and evaporated under reduced pressure. The crude residue was then purified by column chromatography on silica gel.

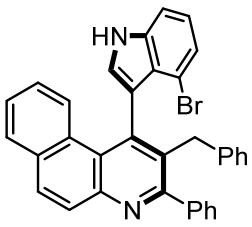
One-pot procedure for the synthesis of product 4bc



1b **2c** **3bc** **4bc**

In a round bottom flask equipped with a magnetic stirring bar, 3-vinylindole **2c** (70.2 mg, 1.5 equiv, 0.225 mmol, *E*/*Z* mixture), *N*-arylimine **1b** (34.8 mg, 1.0 equiv, 0.15 mmol), toluene (1 mL) and catalyst **(*R*)-TRIP** (5.7 mg, 0.0075 mmol, 5 mol%) were added in this order. The resulting solution was stirred for 18 h at room temperature and then the solvent was removed *in vacuo*. Subsequently, the residue was dissolved in acetonitrile (4.5 mL), the solution was cooled to 0 °C and DDQ (136.2 mg, 4.0 equiv, 0.6 mmol) was added in one portion. The resulting solution was stirred for 48 h at 0°C and then poured into a solution of Na_2SO_3 (1 M, 15 mL) and extracted with DCM (3 x 30 mL). The combined organic phases were dried over $MgSO_4$, filtered and evaporated under reduced pressure. The crude residue was then purified by column chromatography on silica gel (*n*-hexane/Et_2O = 1:1) to afford **4bc** as a white solid in 76% yield (90% *ee*).

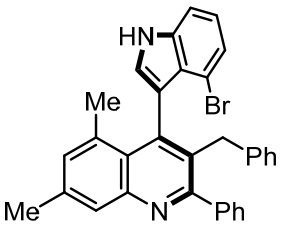
(*aS*)-2-benzyl-1-(4-bromo-1*H*-indol-3-yl)-3-phenylbenzo[*f*]quinoline 4bc



4bc

Following the general procedure (48 h) from tetrahydroquinoline **3bc**, product **4bc** was obtained as a white solid in 97% yield after column chromatography on silica gel (*n*-hexane/Et_2O = 1:1). $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = +154 (c = 0.2 in $CHCl_3$) for 94% *ee*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.88 (d, *J* = 1.9 Hz, 1H), 8.08 (d, *J* = 9.0 Hz, 1H), 7.95 (d, *J* = 8.9 Hz, 1H), 7.86 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.70 (dd, *J* = 8.4, 0.5 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.42 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 7.39 – 7.27 (m, 5H), 7.13 (t, *J* = 7.9 Hz, 1H), 7.02 (ddd, *J* = 8.6, 7.0, 1.5 Hz, 1H), 6.97 – 6.90 (m, 3H), 6.48 – 6.41 (m, 2H), 6.38 (d, *J* = 2.5 Hz, 1H), 4.25 (d, *J* = 15.9 Hz, 1H), 3.91 (d, *J* = 15.9 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 159.5, 147.1, 142.5, 141.4, 141.3, 137.0, 134.5, 133.2, 131.1, 130.8, 129.1 (2C), 128.6, 128.5, 128.2 (2C), 128.0, 127.9 (2C), 127.6 (2C), 127. 4, 126.22, 126.21, 125.7, 125.2, 124.8, 124.6, 124.0, 123.6, 116.1, 114.6, 111.1, 36.7. **ESI-MS**: 539 [M(^{79}Br) + H^+], 541 [M(^{81}Br) + H^+]. **HRMS** calculated for [$C_{34}H_{23}BrN_2$ + H^+]: 539.1117 [M(^{79}Br) + H^+], 541.1097 [M(^{81}Br) + H^+]; found 539.1123 [M(^{79}Br) + H^+], 541.1106 [M(^{81}Br) + H^+]. **HPLC**: OD-H (*n*-hexane/iPrOH 90:10, flow-rate 0.75 mL/min; t_{major} = 13.1 min; t_{minor} = 40.3 min).

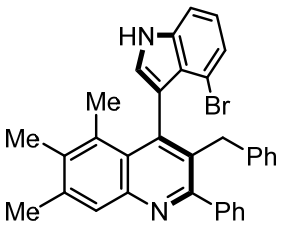
(*aS*)-3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-5,7-dimethyl-2-phenylquinoline 4cc



4cc

Following the general procedure (64 h, CH_2Cl_2 added) from tetrahydroquinoline **3cc**, product **4cc** was obtained as a white solid in 50% yield after column chromatography on silica gel (*n*-hexane/Et_2O = 1:1). $[\alpha]_D^{25}$ = +162 (c = 0.2 in $CHCl_3$) for 92% *ee*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.37 (bs, 1H), 7.88 (s, 1H), 7.49 – 7.39 (m, 2H), 7.35 (dd, *J* = 8.1, 0.8 Hz, 1H), 7.33 – 7.27 (m, 4H), 7.11 – 7.04 (m, 2H), 6.99 – 6.92 (m, 3H), 6.55 (d, *J* = 2.5 Hz, 1H), 6.53 – 6.44 (m, 2H), 4.08 (d, *J* = 15.9 Hz, 1H), 3.75 (d, *J* = 16.0 Hz, 1H), 2.48 (s, 3H), 1.91 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 160.1, 147.9, 141.8, 141.6, 138.3, 136.3, 135.8, 132.9, 132.2, 128.8 (2C), 128.3, 128.03 (2C), 127.95 (2C), 127.74, 127.68, 127.6 (2C), 126.8, 125.9, 125.1, 125.0, 124.4, 123.4, 115.8, 114.7, 110.7, 36.6, 23.4, 21.3. **ESI-MS**: 517 [M(^{79}Br) + H^+], 519 [M(^{81}Br) + H^+]. **HPLC**: OD-H (*n*-hexane/iPrOH 90:10, flow-rate 0.75 mL/min; t_{major} = 11.6; t_{minor} = 28.5 min).

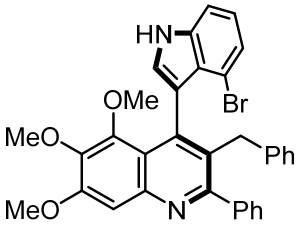
(*aS*)-3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-5,6,7-trimethyl-2-phenylquinoline 4dc



4dc

Following the general procedure (48 h) from tetrahydroquinoline **3dc**, product **4dc** was obtained as a white solid in 44% yield after column chromatography on silica gel (*n*-hexane/Et_2O = 1:1). $[\alpha]_D^{25}$ = +102 (c = 0.1 in $CHCl_3$) for 92% *ee*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.25 (bs, 1H), 7.89 (s, 1H), 7.48 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.38 (dd, *J* = 3.0, 0.8 Hz, 1H), 7.36 (dd, *J* = 2.6, 0.8 Hz, 1H), 7.34 – 7.30 (m, 3H), 7.12 (t, *J* = 7.9 Hz, 1H), 6.95 – 6.82 (m, 3H), 6.45 (d, *J* = 2.5 Hz, 1H), 6.34 (dd, *J* = 7.8, 1.6 Hz, 2H), 4.13 (d, *J* = 15.9 Hz, 1H), 3.79 (d, *J* = 15.9 Hz, 1H), 2.49 (s, 3H), 2.27 (s, 3H), 1.90 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 159.3, 145.9, 141.6, 141.1, 138.5, 136.5, 135.6, 133.1, 133.0, 130.0, 128.9 (2C), 128.2, 128.1 (2C), 127.82, 127.76 (2C), 127.6, 127.5 (2C), 126.9, 125.4, 125.0, 124.5, 123.5, 117.0, 114.9, 110.7, 36.6, 21.6, 19.2, 16.7. **ESI-MS**: 531 [M(^{79}Br) + H^+], 533 [M(^{81}Br) + H^+]. **HRMS**: calculated for [$C_{33}H_{27}BrN_2$ + H^+]: 531.1430 [M(^{79}Br) + H^+], 533.1410 [M(^{81}Br) + H^+]; found 531.1436 [M(^{79}Br) + H^+], 533.1421 [M(^{81}Br) + H^+]. **HPLC**: OD-H (*n*-hexane/i-PrOH 90:10, flow-rate 0.75 mL/min; t_{major} = 11.3; t_{minor} = 25.3 min).

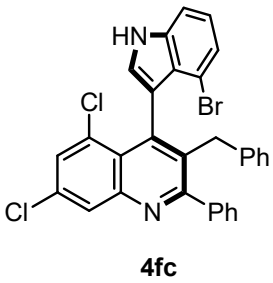
(*aS*)-3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-5,6,7-trimethoxy-2-phenylquinoline 4ec



4ec

Following the general procedure (64 h, CH_2Cl_2 added) from tetrahydroquinoline **3ec**, product **4ec** was obtained as a white solid in 69% yield after column chromatography on silica gel (CH_2Cl_2/Et_2O = 50:1). $[\alpha]_D^{25}$ = +67 (c = 0.27 in $CHCl_3$) for 90% *ee*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.26 (d, *J* = 2.4 Hz, 1H), 7.45 – 7.37 (m, 3H), 7.37 – 7.27 (m, 4H), 7.23 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.04 (t, *J* = 7.9 Hz, 1H), 7.00 – 6.95 (m, 3H), 6.69 (d, *J* = 2.5 Hz, 1H), 6.60 – 6.51 (m, 2H), 4.05 (d, *J* = 16.1 Hz, 1H), 3.99 (s, 3H), 3.85 (s, 3H), 3.79 (d, *J* = 16.1 Hz, 1H), 3.13 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 160.2, 155.1, 149.3, 144.7, 142.6, 141.8, 141.5, 140.2, 136.2, 131.8, 128.6 (2C), 128.1 (2C), 128.0 (2C), 127.7, 127.6 (2C), 125.9, 125.1, 124.0, 123.4, 122.8, 120.4, 115.7, 114.7, 110.5, 104.9, 61.0, 60.7, 56.0, 36.4. **ESI-MS**: 579 [M(^{79}Br) + H^+], 581 [M(^{81}Br) + H^+]. **HPLC**: OD-H (*n*-hexane/iPrOH 90:10, flow-rate 0.75 mL/min; t_{major} = 12.9; t_{minor} = 22.7 min).

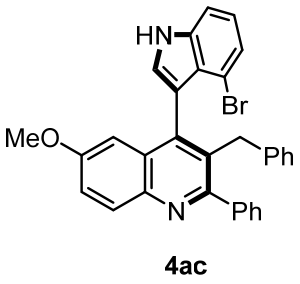
(*aS*)-3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-5,7-dichloro-2-phenylquinoline 4fc



4fc

Following the general procedure but running the reaction at room temperature (64 h, CH_2Cl_2 added) from tetrahydroquinoline **3fc**, product **4fc** was obtained as a white solid in 70% yield after column chromatography on silica gel (*n*-hexane/Et_2O = 1:1). $[\alpha]_D^{25}$ = -157 (c = 0.2 in $CHCl_3$) for 86% ee. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.31 (bs, 1H), 8.15 (d, *J* = 2.2 Hz, 1H), 7.51 (d, *J* = 2.2 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.38 – 7.32 (m, 4H), 7.28 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.08 (t, *J* = 7.9 Hz, 1H), 7.02 – 6.96 (m, 3H), 6.64 (d, *J* = 2.5 Hz, 1H), 6.54 – 6.48 (m, 2H), 4.12 (d, *J* = 15.9 Hz, 1H), 3.87 (d, *J* = 15.9 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 162.3, 147.9, 141.8, 141.0, 140.6, 136.3, 135.4, 133.5, 132.3, 130.0, 128.6 (2C), 128.5, 128.3, 128.2 (2C), 128.0 (2C), 127.8 (2C), 126.4, 125.4, 125.3, 125.0, 124.4, 123.4, 114.6, 113.5, 110.7, 36.8. **ESI-MS**: 557 [M(^{79}Br,^{35}Cl,^{35}Cl) + H^+], 559 [M(^{79}Br,^{37}Cl,^{35}Cl) and M(^{81}Br,^{35}Cl,^{35}Cl) + H^+], 561 [M(^{81}Br,^{37}Cl,^{35}Cl) and M(^{79}Br,^{37}Cl,^{37}Cl) + H^+], 563 [M(^{81}Br,^{37}Cl,^{37}Cl) + H^+]. **HPLC**: ODH (*n*-hexane/i-PrOH 90:10, flow-rate 0.75 mL/min; t_{minor} = 11.3; t_{major} = 19.1 min).

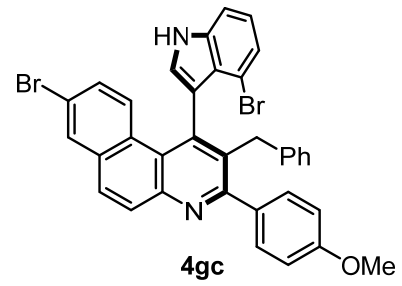
(*aS*)-3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-6-methoxy-2-phenylquinoline 4ac



4ac

Following the general procedure (48 h) but running the reaction at room temperature from tetrahydroquinoline **3ac**, product **4ac** was obtained as a white solid in 87% yield after column chromatography on silica gel (*n*-hexane/Et_2O = 1:1). $[\alpha]_D^{25}$ = -120 (c = 0.2 in $CHCl_3$) for 90% *ee*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.59 (bs, 1H), 8.11 (d, *J* = 9.1 Hz, 1H), 7.48 – 7.40 (m, 2H), 7.40 – 7.29 (m, 5H), 7.29 – 7.27 (m, 1H), 7.10 (t, *J* = 7.9 Hz, 1H), 7.01 – 6.95 (m, 3H), 6.87 (d, *J* = 2.6 Hz, 1H), 6.83 (d, *J* = 2.8 Hz, 1H), 6.60 – 6.52 (m, 2H), 4.15 (d, *J* = 15.8 Hz, 1H), 3.88 (d, *J* = 15.8 Hz, 1H), 3.67 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 154.0, 152.9, 137.6, 136.8, 136.6, 132.0, 128.5, 126.0, 125.2, 124.1 (2C), 123.5, 123.4 (2C), 123.3 (2C), 122.9 (2C), 122.1, 120.7, 120.5, 120.4, 119.9, 118.7, 116.1, 109.7, 107.6, 106.0, 100.3, 50.7, 32.3. **ESI-MS**: 519 [M(^{79}Br) + H^+], 521 [M(^{81}Br) + H^+]. **HPLC**: OD-H (*n*-hexane/iPrOH 90:10, flow-rate 0.75 mL/min; t_{major} = 14.1; t_{minor} = 24.6 min).

(*aS*)-2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(4-methoxyphenyl)benzo[*f*] quinoline 4gc

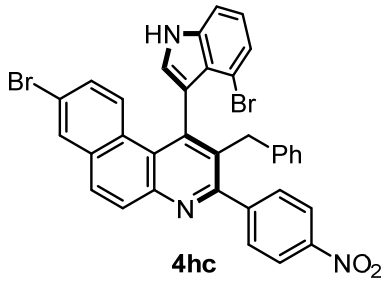


4gc

Following the general procedure (64 h, CH_2Cl_2 added) from tetrahydroquinoline **3gc**, product **4gc** was obtained as a white solid in 53% yield after column chromatography on silica gel (*n*-hexane/Et_2O = 1:1). $[\alpha]_D^{25}$ = +108 (c = 0.2 in $CHCl_3$) for 97% *ee*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.42 (d, *J* = 2.4 Hz, 1H), 8.09 (d, *J* = 9.0 Hz, 1H), 7.97 (d, *J* = 2.3 Hz, 1H), 7.87 – 7.80 (m, 1H), 7.56 – 7.50 (m, 3H), 7.43 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.33 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.16 (t, *J* = 7.9 Hz, 1H), 7.08 (dd, *J* = 9.2, 2.3 Hz, 1H), 7.00 – 6.88 (m, 5H), 6.49 – 6.42 (m, 2H), 6.41 (d, *J* = 2.5 Hz, 1H), 4.28 (d, *J* = 15.9 Hz, 1H), 3.86 (d, *J* = 15.9 Hz, 1H), 3.81 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ = 159.6 (2C), 147.0, 142.1, 141.5, 136.9, 134.8, 134.7, 133.7, 130.6, 130.4 (2C), 130.1, 129.7, 129.4, 128.8, 128.7, 127.8 (2C), 127.7 (2C), 125.8, 125.3, 124.8, 124.6, 123.9, 123.8, 120.2, 116.1, 114.5, 113.8 (2C), 111.0, 55.4, 36.8.

ESI-MS: 647 [M(^{79}Br, ^{79}Br) + H$^+$], 649 [M(^{81}Br, ^{79}Br) + H$^+$], 651 [M(^{81}Br,^{81}Br) + H$^+$]. **HPLC**: OD-H (*n*-hexane/iPrOH 90:10, flow-rate 0.75 mL/min; t_{major} = 17.3 min; t_{minor} = 23.0 min).

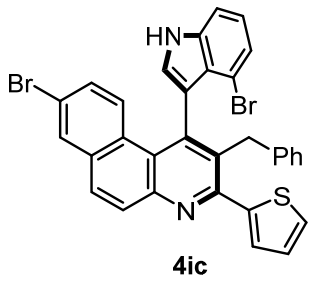
(*aS*)-2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(4-nitrophenyl)benzo[*f*]quinoline 4hc



4hc

Following the general procedure (64 h) from tetrahydroquinoline **3hc**, product **4hc** was obtained as a white solid in 61% yield after column chromatography on silica gel (*n*-hexane/Et$_2$O = 1:1). $[\alpha]_D^{25}$ = +116 (c = 0.2 in CHCl$_3$) for 81% *ee*. **^{1}H NMR** (400 MHz, CDCl$_3$) δ = 8.53 (d, *J* = 2.6 Hz, 1H), 8.26 – 8.18 (m, 2H), 8.07 (d, *J* = 9.0 Hz, 1H), 8.01 (d, *J* = 2.2 Hz, 1H), 7.88 (dt, *J* = 8.9, 0.7 Hz, 1H), 7.73 – 7.65 (m, 2H), 7.56 (dt, *J* = 9.3, 0.6 Hz, 1H), 7.46 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.35 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.21 – 7.15 (m, 1H), 7.12 (dd, *J* = 9.2, 2.3 Hz, 1H), 7.02 – 6.93 (m, 3H), 6.61 (d, *J* = 2.5 Hz, 1H), 6.48 – 6.42 (m, 2H), 4.09 (d, *J* = 16.2 Hz, 1H), 3.94 (d, *J* = 16.1 Hz, 1H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ = 157.4, 147.7, 147.5, 147.1, 142.7, 140.6, 136.9, 134.9, 134.4, 130.7 (2C), 130.4, 130.1, 129.8, 129.2, 129.0, 128.9, 128.0 (2C), 127.8 (2C), 126.5, 125.7, 125.0, 124.6, 124.2, 123.6, 123.4 (2C), 120.9, 115.7, 114.4, 111.2, 36.5. **ESI-MS**: 662 [M(^{79}Br, ^{79}Br) + H$^+$], 664 [M(^{81}Br, ^{79}Br) + H$^+$], 666 [M(^{81}Br,^{81}Br) + H$^+$]. **HPLC**: OD-H (*n*-hexane/iPrOH 90:10, flow-rate 0.75 mL/min; t_{major} = 25.7 min; t_{minor} = 54.2 min).

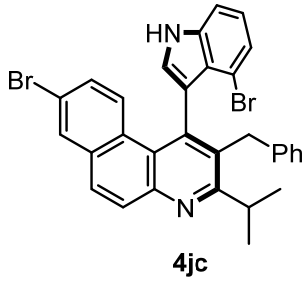
(*aS*)-2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(thiophen-2-yl)benzo[*f*]quinoline 4ic



4ic

Following the general procedure but running the reaction at room temperature (64 h) from tetrahydroquinoline **3ic**, product **4ic** was obtained as a white solid in 65% yield after column chromatography on silica gel (*n*-hexane/Et$_2$O = 1:1). $[\alpha]_D^{25}$ = +101 (c = 0.2 in CHCl$_3$) for 63% *ee*. **^{1}H NMR** (400 MHz, CDCl$_3$) δ = 8.36 (bs, 1H), 8.10 (d, *J* = 9.0 Hz, 1H), 7.96 (d, *J* = 2.3 Hz, 1H), 7.84 (d, *J* = 9.1 Hz, 1H), 7.51 – 7.38 (m, 3H), 7.32 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.14 – 7.02 (m, 5H), 7.00 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.80 – 6.65 (m, 2H), 6.51 (d, *J* = 2.6 Hz, 1H), 4.53 (d, *J* = 16.5 Hz, 1H), 4.02 (d, *J* = 16.5 Hz, 1H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ = 152.3, 147.2, 144.4, 143.1, 141.3, 136.8, 134.7, 133.0, 130.7, 130.1, 129.3 (2C), 128.9, 128.5, 128.1 (2C), 128.05, 128.0 (2C), 127.7, 127.6, 126.0, 125.6, 124.8, 124.4, 124.0, 123.7, 120.4, 115.7, 114.6, 110.9, 37.1. **ESI-MS**: 623 [M(^{79}Br, ^{79}Br) + H$^+$], 625 [M(^{81}Br, ^{79}Br) + H$^+$], 627 [M(^{81}Br,^{81}Br) + H$^+$]. **HPLC**: OD-H (*n*-hexane/iPrOH 90:10, flow-rate 0.75 mL/min; t_{major} = 14.5 min; t_{minor} = 18.2 min).

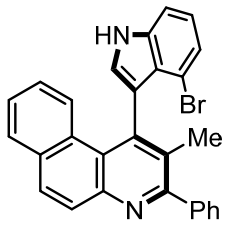
(*aS*)-2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-isopropylbenzo[*f*]quinoline 4jc



4jc

Following the general procedure (64 h) from tetrahydroquinoline **3jc**, product **4jc** was obtained as a white solid in 64% yield after column chromatography on silica gel (*n*-hexane/Et_2O = 1:1). $[\alpha]_D^{25}$ = +122 (c = 0.2 in $CHCl_3$) for 60% *ee*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.37 (s, 1H), 8.06 (d, *J* = 9.0 Hz, 1H), 7.96 (d, *J* = 2.3 Hz, 1H), 7.80 (d, *J* = 9.0 Hz, 1H), 7.48 – 7.39 (m, 2H), 7.29 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.18 – 7.01 (m, 5H), 6.79 – 6.74 (m, 2H), 6.63 (d, *J* = 2.5 Hz, 1H), 4.20 (d, *J* = 16.5 Hz, 1H), 3.96 (d, *J* = 16.5 Hz, 1H), 3.39 (sept, *J* = 6.9 Hz, 1H), 1.33 (d, *J* = 6.9 Hz, 3H), 1.32 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 165.4, 147.4, 141.1, 141.0, 136.9, 134.5, 133.3, 130.5, 130.4, 129.6, 129.0, 128.5, 128.4, 128.1 (2C), 127.9 (2C), 125.6, 125.1, 124.9, 124.7, 124.0, 123.2, 119.8, 116.7, 114.7, 110.9, 35.3, 32.4, 23.2, 21.2. **ESI-MS**: 583 [M(^{79}Br, ^{79}Br) + H^+], 585 [M(^{81}Br, ^{79}Br) + H^+], 587 [M(^{81}Br,^{81}Br) + H^+]. **HPLC**: OD-H (*n*-hexane/iPrOH 90:10, flow-rate 0.75 mL/min; t_{major} = 9.0 min; t_{minor} = 12.1 min).

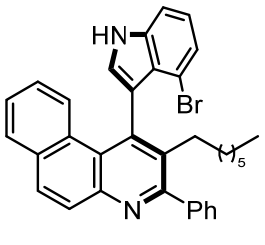
(*aS*)-1-(4-bromo-1*H*-indol-3-yl)-2-methyl-3-phenylbenzo[*f*]quinoline 4bd



4bd

Following the general procedure (48 h) from tetrahydroquinoline **3bd**, product **4bd** was obtained as a white solid in 75% yield after column chromatography on silica gel (*n*-hexane/Et_2O = 1:1). $[\alpha]_D^{25}$ = +10 (c = 0.2 in $CHCl_3$) for 89% *ee*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 9.07 (bs, 1H), 8.08 (d, *J* = 9.0 Hz, 1H), 7.92 (d, *J* = 9.0 Hz, 1H), 7.85 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.75 (dd, *J* = 8.6, 1.0 Hz, 1H), 7.74 – 7.68 (m, 2H), 7.51 – 7.43 (m, 3H), 7.43 – 7.36 (m, 2H), 7.35 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.16 (t, *J* = 7.9 Hz, 1H), 7.04 (ddd, *J* = 8.6, 6.9, 1.5 Hz, 1H), 6.86 (d, *J* = 2.5 Hz, 1H), 2.13 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.4, 146.6, 141.9, 141.4, 137.3, 133.2, 132.0, 130.7, 130.5, 129.3 (2C), 128.6, 128.5, 128.3 (2C), 128.0, 127.3, 126.1, 125.7, 125.6, 125.3, 124.5, 123.8, 122.6, 117.6, 114.7, 111.1, 19.1. **ESI-MS**: 463 [M(^{79}Br) + H^+], 465 [M(^{81}Br) + H^+]. **HPLC**: AD-H (*n*-hexane /iPrOH 90:10, flow-rate 0.75 mL/min; t_{minor} = 7.1 min; t_{major} = 9.2 min).

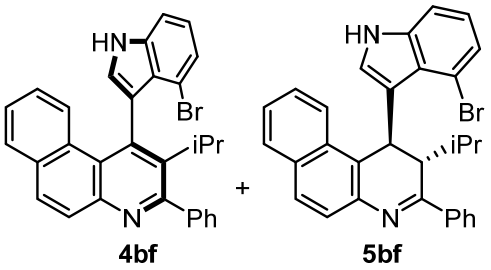
(*aS*)-1-(4-bromo-1*H*-indol-3-yl)-2-heptyl-3-phenylbenzo[*f*]quinoline 4be



4be

Following the general procedure (48 h) from tetrahydroquinoline **3be**, product **4be** was obtained as a white solid in 99% yield after column chromatography on silica gel (*n*-hexane/Et_2O = 1:1). $[\alpha]_D^{25}$ = +37 (c = 0.2 in $CHCl_3$) for 90% *ee*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = δ 9.59 (bs, 1H), 8.13 – 8.03 (m, 1H), 7.91 (d, *J* = 9.0 Hz, 1H), 7.85 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.74 – 7.62 (m, 3H), 7.48 – 7.34 (m, 5H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.12 (td, *J* = 7.9, 1.4 Hz, 1H), 7.05 (dddd, *J* = 8.5, 6.9, 2.7, 1.4 Hz, 1H), 6.85 (dd, *J* = 4.1, 2.4 Hz, 1H), 2.75 (ddd, *J* = 13.3, 11.1, 4.9 Hz, 1H), 2.58 – 2.43 (m, 1H), 1.19 – 0.95 (m, 4H), 0.95 – 0.63 (m, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 159.0, 146.3, 141.5, 137.2, 137.0, 136.9, 133.2, 130.8, 130.7, 129.0 (2C), 128.6, 128.3, 128.2 (2C), 127.9, 127.3, 126.2, 126.1, 125.7, 125.4, 124.5, 123.62, 123.57, 116.3, 114.8, 111.2, 31.3, 30.5, 29.7, 29.4, 28.1, 22.5, 14.0. **ESI-MS**: 547 [M(^{79}Br) + H^+], 549 [M(^{81}Br) + H^+]. **HPLC**: OD-H (*n*-hexane/iPrOH 90:10, flow-rate 0.75 mL/min; t_{major} = 10.5; t_{minor} = 52.5 min).

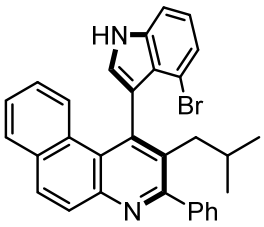
(*aS*)-1-(4-bromo-1*H*-indol-3-yl)-2-isopropyl-3-phenylbenzo[*f*]quinoline 4bf and (1*R*,2*S*)-1-(4-bromo-1*H*-indol-3-yl)-2-isopropyl-3-phenyl-1,2-dihydrobenzo[*f*]quinoline 5bf



4bf **5bf**

Following the general procedure but running the reaction at room temperature (64 h, CH_2Cl_2 added) from tetrahydroquinoline **3bf**, product **4bf** was obtained as a white solid in 50% yield (82% combined yield with **5bf**, 1:0.64 **4bf**/**5bf**, inseparable mixture) after column chromatography on silica gel (*n*-hexane/Et_2O = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 9.38 (bs, 1H **4bf**), 8.17 – 8.08 (m, 1H **5bf**), 8.02 (d, *J* = 8.9 Hz, 1H **4bf**), 7.93 (bd, *J* = 2.5 Hz, 1H **5bf**), 7.91 – 7.88 (m, 1H **4bf**), 7.88 – 7.81 (m, 2H **5bf** + 1H **4bf**), 7.78 (d, *J* = 8.6 Hz, 1H **5bf**), 7.70 – 7.65 (m, 2H **5bf**), 7.58 – 7.52 (m, 2H **4bf**), 7.49 (dd, *J* = 8.7, 1.0 Hz, 1H **4bf**), 7.47 – 7.33 (m, 4H **4bf** + 4H **5bf**), 7.33 – 7.23 (m, 2H **4bf** + 2H **5bf**), 7.11 (t, *J* = 7.9 Hz, 1H **4bf**), 7.06 (dd, *J* = 8.1, 1.1 Hz, 1H **5bf**), 7.02 – 6.93 (m, 1H **4bf** + 1H **5bf**), 6.86 (d, *J* = 2.4 Hz, 1H **4bf**), 6.14 (d, *J* = 2.6 Hz, 1H **5bf**), 5.92 (s, 1H **5bf**), 3.71 (dd, *J* = 8.3, 1.4 Hz, 1H **5bf**), 3.26 (sept, *J* = 7.2 Hz, 1H **4bf**), 1.90 (sept, *J* = 7.3 Hz, 1H **5bf**), 1.04 (d, *J* = 6.8 Hz, 3H **5bf**), 0.91 (d, *J* = 7.2 Hz, 3H **4bf**), 0.88 (d, *J* = 7.2 Hz, 3H **4bf**), 0.73 (d, *J* = 6.8 Hz, 3H **5bf**). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 171.6, 159.3, 145.8, 143.1, 141.9, 141.7, 141.0, 140.7, 137.8, 137.0, 133.3, 133.19, 131.14, 130.8 (2C), 130.1, 129.4 (2C), 128.7, 128.5 (2C), 128.4, 127.8, 127.78 (2C), 127.72, 127.2 (2C), 127.1, 126.6, 126.2, 126.1, 126.0, 125.7 (2C), 125.6, 125.3, 124.6, 124.5, 124.3, 124.1, 124.0, 123.7, 123.5, 122.4, 116.7, 115.1, 115.0, 113.4, 111.0, 110.7, 48.9, 31.5, 30.7, 30.7, 30.6, 23.1, 22.9, 22.8, 22.5 (all peaks are given without assignment). **ESI-MS**: 491 [M(**4bf**, ^{79}Br) + H^+], 493 [M(**4bf**, ^{81}Br) or M(**5bf**, ^{81}Br) + H^+], 495 [M(**5bf**, ^{81}Br) + H^+]. **HPLC**: OD-H (*n*-hexane/iPrOH 90:10, flow-rate 0.75 mL/min; t_{major} = 14.6; t_{minor} = 55.3 min), 99% *ee*.

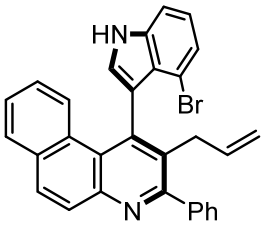
(*aS*)-1-(4-bromo-1*H*-indol-3-yl)-2-isobutyl-3-phenylbenzo[*f*]quinoline 4bg



4bg

Following the general procedure (48 h) from tetrahydroquinoline **3bg**, product **4bg** was obtained as a white solid in 80% yield after column chromatography on silica gel (*n*-hexane/Et_2O = 1:1). $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = +42 (c = 0.2 in $CHCl_3$) for 97% *ee*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 9.32 (bs, 1H), 8.04 (d, *J* = 9.0 Hz, 1H), 7.90 (d, *J* = 8.9 Hz, 1H), 7.84 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.73 (dd, *J* = 5.1, 3.2 Hz, 2H), 7.55 (d, *J* = 8.7 Hz, 1H), 7.49 – 7.31 (m, 6H), 7.14 (t, *J* = 7.9 Hz, 1H), 7.01 (ddd, *J* = 8.6, 7.0, 1.5 Hz, 1H), 6.85 (d, *J* = 2.5 Hz, 1H), 2.93 (dd, *J* = 13.9, 6.5 Hz, 1H), 2.51 (dd, *J* = 13.9, 7.6 Hz, 1H), 1.40 – 1.25 (m, 1H), 0.39 (d, *J* = 6.7 Hz, 3H), 0.34 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 159.1, 146.4, 141.8, 141.7, 137.1, 135.3, 133.3, 130.8, 130.6, 129.4 (2C), 128.5, 128.4, 128.3 (2C), 127.9, 127.5, 126.0, 125.8, 125.4, 125.3, 124.7, 124.2, 123.6, 116.7, 114.8, 111.1, 38.9, 28.9, 22.7, 22.3. **ESI-MS**: 505 [M(^{79}Br) + H^+], 507 [M(^{81}Br) + H^+]. **HPLC**: OD-H (*n*-hexane/iPrOH 90:10, flow-rate 0.75 mL/min; t_{major} = 10.3; t_{minor} = 63.1 min).

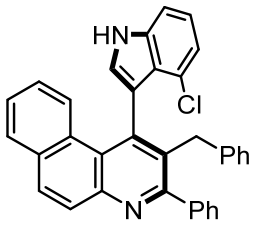
(*aS*)-2-allyl-1-(4-bromo-1*H*-indol-3-yl)-3-phenylbenzo[*f*]quinoline 4bh



4bh

Following the general procedure (48 h) from tetrahydroquinoline **3bh**, product **4bh** was obtained as a white solid in 83% yield after column chromatography on silica gel (*n*-hexane/Et_2O = 1:1). $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = +64 (c = 0.2 in $CHCl_3$) for 96% *ee*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 9.23 (bs, 1H), 8.08 (d, *J* = 9.0 Hz, 1H), 7.94 (d, *J* = 9.0 Hz, 1H), 7.85 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.70 (dd, *J* = 8.7, 1.0 Hz, 1H), 7.68 – 7.61 (m, 2H), 7.50 – 7.34 (m, 5H), 7.30 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.13 (t, *J* = 7.9 Hz, 1H), 7.04 (ddd, *J* = 8.7, 7.0, 1.5 Hz, 1H), 6.90 (d, *J* = 2.5 Hz, 1H), 5.49 (ddt, *J* = 17.2, 10.1, 5.9 Hz, 1H), 4.67 (dq, *J* = 10.1, 1.6 Hz, 1H), 4.27 (dq, *J* = 17.1, 1.8 Hz, 1H), 3.52 (ddt, *J* = 15.7, 5.9, 1.7 Hz, 1H), 3.28 (ddt, *J* = 15.7, 6.1, 1.7 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 159.2, 146.9, 142.1, 141.3, 137.1, 136.6, 133.3, 133.2, 131.0, 130.7, 129.1 (2C), 128.6, 128.5, 128.2 (2C), 128.0, 127.2, 126.2 (2C), 125.8, 125.1, 124.5, 123.9, 123.7, 116.1, 115.2, 114.7, 111.1, 35.2. **ESI-MS**: 489 [M(^{79}Br) + H^+], 491 [M(^{81}Br) + H^+]. **HPLC**: OD-H (*n*-hexane/iPrOH 90:10, flow-rate 0.75 mL/min; t_{major} = 13.3; t_{minor} = 42.2 min).

(*aS*)-2-benzyl-1-(4-chloro-1*H*-indol-3-yl)-3-phenylbenzo[*f*]quinoline 4bi

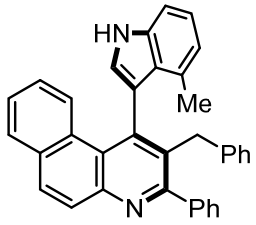


4bi

Following the general procedure (48 h) from tetrahydroquinoline **3bi**, product **4bi** was obtained as a white solid in 97% yield after column chromatography on silica gel (*n*-hexane/Et_2O = 1:1). $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = +206 (c = 0.2 in $CHCl_3$) for 91% *ee*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.86 (bs, 1H), 8.09 (d, *J* = 9.0 Hz, 1H), 7.95 (d, *J* = 8.9 Hz, 1H), 7.85 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.59 – 7.51 (m, 2H), 7.45 – 7.38 (m, 1H), 7.38 – 7.27 (m, 4H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.12 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.02 (ddd, *J* = 8.6, 7.0, 1.5 Hz, 1H), 6.97 – 6.91 (m, 3H), 6.49 – 6.34 (m, 3H), 4.25 (d, *J* = 15.9 Hz, 1H), 3.95 (d, *J* = 15.9 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 159.5, 147.2, 142.7, 141.5, 141.3, 137.3, 134.1, 133.2, 131.1, 130.7, 129.1 (2C), 128.58, 128.55, 128.2 (2C), 127.93, 127.89 (2C), 127.6 (2C), 127.3, 126.6, 126.2, 126.0, 125.7, 125.2, 123.8, 123.6, 123.3, 121.1, 115.3, 110.4, 36.6. **ESI-MS**: 495 [M(^{35}Cl) + H^+], 497 [M(^{37}Cl) +

H^+]. **HPLC**: OD-H (*n*-hexane/iPrOH 80:20, flow-rate 0.75 mL/min; t_{major} = 7.1 min; t_{minor} = 14.8 min).

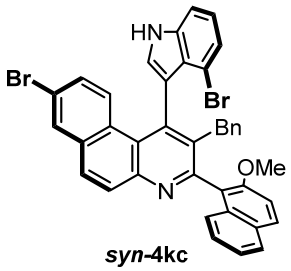
(*aS*)-2-benzyl-1-(4-methyl-1*H*-indol-3-yl)-3-phenylbenzo[*f*]quinoline 4bj



4bj

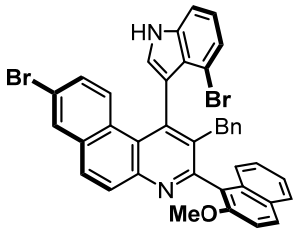
Following the general procedure (48 h) from tetrahydroquinoline **3bj**, product **4bj** was obtained as a white solid in 92% yield after column chromatography on silica gel (*n*-hexane/Et_2O = 1:1). $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$ = +116 (c = 0.2 in $CHCl_3$) for 75% *ee*. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.32 (bs, 1H), 8.11 (d, *J* = 9.0 Hz, 1H), 7.97 (d, *J* = 8.9 Hz, 1H), 7.85 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.45 – 7.33 (m, 4H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.23 – 7.15 (m, 1H), 7.05 – 6.93 (m, 4H), 6.88 (dd, *J* = 7.1, 0.9 Hz, 1H), 6.52 – 6.46 (m, 2H), 6.44 (d, *J* = 2.5 Hz, 1H), 4.18 (d, *J* = 15.7 Hz, 1H), 3.93 (d, *J* = 15.7 Hz, 1H), 2.03 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 159.6, 147.4, 144.3, 141.6, 141.3, 136.4, 133.7, 133.2, 131.3, 131.2, 130.7, 129.0 (2C), 128.9, 128.6, 128.2 (2C), 127.97 (2C), 127.94, 127.7 (2C), 127.3, 126.3, 125.9, 125.8, 125.2, 125.0, 122.9, 121.9, 121.5, 115.9, 109.4, 36.4, 19.3. **ESI-MS**: 475 [M + H^+]. **HPLC**: OD-H (*n*-hexane/iPrOH 90:10, flow-rate 0.75 mL/min; t_{major} = 6.8 min; t_{minor} = 16.4 min).

(1*aR*,3*aR*)-*2*-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(2-methoxynaphthalen-1-yl)benzo[*f*]quinoline *syn*-4kc and (1*aR*,3*aS*)-2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(2-methoxynaphthalen-1-yl)benzo[*f*]quinoline *anti*-4kc



***syn*-4kc**

Following the general procedure (64 h, CH_2Cl_2 added) from tetrahydroquinoline **3kc**, product ***syn*-4kc** and ***anti*-4kc** (dr = 3:1 in the crude mixture) were obtained in 62% combined yield after column chromatography on silica gel (CH_2Cl_2/Et_2O = 50:1). This mixture was separated by performing a second column chromatography (*n*-hexane/Et_2O = 1:1). Product ***syn*-4kc** was isolated as the second eluting fraction and was obtained in 44% yield as a white solid. $[\alpha]_D^{25}$ = -61 (c = 0.2 in $CHCl_3$) for 95% *ee*. **^{1}H NMR** (600 MHz, CD_2Cl_2) δ = 8.61 (bs, 1H), 8.09 – 8.02 (m, 2H), 7.93 – 7.87 (m, 2H), 7.85 (dt, *J* = 7.2, 1.6 Hz, 1H), 7.66 (d, *J* = 9.2 Hz, 1H), 7.48 (dt, *J* = 8.2, 1.0 Hz, 1H), 7.33 (tt, *J* = 6.8, 5.0 Hz, 2H), 7.30 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.23 (d, *J* = 9.1 Hz, 1H) 7.14 (t, *J* = 8.0 Hz, 1H) partially overlapped with 7.13 (dd, *J* = 9.3, 2.3 Hz, 1H), 6.96 – 6.89 (m, 3H), 6.66 (t, *J* = 2.4 Hz, 1H), 6.46 (dd, *J* = 7.3, 2.2 Hz, 2H), 3.70 (d, *J* = 15.8 Hz, 1H), 3.63 (d, *J* = 15.8 Hz, 1H), 3.57 (s, 3H). **^{13}C NMR** (151 MHz, CD_2Cl_2) δ = 156.7, 154.4, 147.8, 142.1, 140.9, 137.2, 137.1, 134.8, 132.9, 130.6, 129.9, 129.6, 128.8, 128.64, 128.62, 128.04 (2C), 128.01, 127.7, 127.6, 127.3 (2C), 126.8, 126.1, 125.0, 124.54, 124.51, 124.3, 124.0, 123.8, 123.5, 123.0, 120.2, 115.6, 114.2, 113.0, 111.2, 55.6, 36.8. **ESI-MS**: 697 [M(^{79}Br, ^{79}Br) + H$^+$], 699 [M(^{81}Br, ^{79}Br) + H$^+$], 701 [M(^{81}Br,^{81}Br) + H$^+$]. **HPLC**: AD-H (*n*-hexane/iPrOH 80:20, flow-rate 0.75 mL/min; t_{major} = 6.0 min; t_{minor} = 7.6 min).



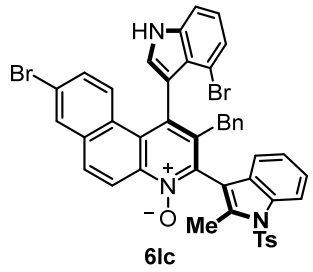
***anti*-4kc**

Product ***anti*-4kc** was obtained as the first eluting fraction and was obtained in 15% yield as a white solid. $[\alpha]_D^{25}$ = -142 (c = 0.17 in $CHCl_3$) for 96% *ee*. **^{1}H NMR** (600 MHz, CD_2Cl_2) δ = 8.66 (bs, 1H), 8.06 – 8.02 (m, 2H), 7.94 – 7.91 (m, 1H), 7.87 (d, *J* = 9.0 Hz, 1H), 7.79 – 7.72 (m, 1H), 7.62 (d, *J* = 9.3 Hz, 1H), 7.48 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.42 – 7.39 (m, 1H), 7.37 (d, *J* = 9.0 Hz, 1H), 7.34 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.26 (ddd, *J* = 8.1, 6.7, 1.4 Hz, 1H), 7.22 (ddd, *J* = 8.2, 6.8, 1.5 Hz, 1H), 7.16 (t, *J* = 7.9 Hz, 1H), 7.11 (dd, *J* = 9.2, 2.3 Hz, 1H), 6.71 – 6.64 (m, 3H), 6.63 (d, *J* = 2.6 Hz, 1H), 6.30 – 6.24 (m, 2H), 3.93 (d, *J* = 15.7 Hz, 1H), 3.87 (s, 3H), 3.83 (d, *J* = 15.7 Hz, 1H). **^{13}C NMR** (151 MHz, CD_2Cl_2) δ = 156.6, 153.9, 147.4, 141.7, 140.5, 138.2, 137.1, 134.8, 133.3, 130.6, 130.3, 130.2, 129.6, 129.3, 129.0, 128.9, 128.5, 127.8 (2C), 127.6, 127.1 (2C), 126.2, 125.8, 125.0, 124.9, 124.8, 124.4, 124.0, 123.8, 123.3, 123.2, 120.1, 116.0, 114.4, 112.7, 111.1, 56.1, 36.8. **ESI-MS**: 697 [M(^{79}Br, ^{79}Br) + H$^+$], 699 [M(^{81}Br, ^{79}Br) + H$^+$], 701 [M(^{81}Br,^{81}Br) + H$^+$]. **HPLC**: AD-H (*n*-hexane/iPrOH 80:20, flow-rate 0.75 mL/min; t_{major} = 5.7 min; t_{minor} = 8.1 min).

The rotational barrier of the quinoline-methoxynaphthalene axis was determined as follows. A solution of pure ***anti*-4kc** in $C_2D_2Cl_4$ was heated into an NMR tube at 100 °C for 2 h after which the ^{1}H NMR spectrum showed ***anti*-4kc**/***syn*-4kc** ratio being 94.5:5.5. By applying the initial rates method the kinetic constant for the rotation of the axis is 7.6x10^{-6} s^{-1} at +100°C, corresponding to a $\Delta G^{\ddagger}_{rot}$ = 30.7 kcal/mol, according to the Eyring equation. The rotation of this axis was also followed over time giving: after 4 h (91:9), after 6 h (86:14) and after 48 h (68:32), which should be the thermodynamic ratio, being the $t_{1/2}$ approximately 25 h). The observed barrier has to be related to methoxynaphthalene rotation and not to the indole-quinoline one, as the latter is calculated to be too high to show any appreciable rotation at 100 °C. By boiling **4bc**

in toluene (110 °C) for one week no detriment in the enantiomeric excess was observed, indicating that the rotation of the indole-quinoline axis has a lower limit value of 36 kcal/mol).

(1*aS*,3*aS*)-2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(2-methyl-1-tosyl-1*H*-indol-3-yl)benzo[*f*]quinoline 4-oxide *syn*-6lc



6lc

Following the general procedure (64 h) from tetrahydroquinoline **3lc**, product **4lc** was obtained as a white solid in 60% yield after column chromatography on silica gel (CH_2Cl_2/Et_2O = 50:1). This product was turned into the desire *N*-oxide without further characterization, as follows. In a test tube, **4lc** (82.3 mg, 0.1 mmol) was suspended in CH_2Cl_2 (1.5 mL) and the resulting suspension was cooled to 0 °C. Then, *m*-CPBA (54.6 mg, 50% wt., 0.17 mmol) was added in one portion and the reaction mixture was stirred at 0 °C for 30 min and at room temperature for 3 h, after which a dark solution was obtained and TLC indicated complete disappearance of **4lc**. The solvent was partially evaporated under a stream of N_2 and the crude product (9.2:1 dr, from ^{1}H NMR) was directly purified by column chromatography on silica gel (from CH_2Cl_2/Et_2O = 50:1 to CH_2Cl_2/Et_2O = 20:1). Product **6lc** was thus obtained as a dark yellow solid in 91% yield (9.4:1 dr). The following NMR and HPLC characterizations refer to the major diastereoisomer only. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 9.12 (d, *J* = 2.6 Hz, 1H), 8.95 (d, *J* = 9.5 Hz, 1H), 8.14 – 8.09 (m, 1H), 8.01 (d, *J* = 2.3 Hz, 1H), 7.92 – 7.87 (m, 1H), 7.73 – 7.66 (m, 1H), 7.62 (d, *J* = 9.3 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.34 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.31 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.25 – 7.19 (m, 2H), 7.17 – 7.07 (m, 3H), 7.03 – 6.99 (m, 2H), 6.98 – 6.91 (m, 2H), 6.66 (d, *J* = 2.5 Hz, 1H), 6.36 – 6.29 (m, 2H), 3.77 (d, *J* = 15.7 Hz, 1H), 3.63 (d, *J* = 15.7 Hz, 1H), 2.20 (s, 3H), 2.15 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ = 167.7, 144.7, 141.2, 140.9, 139.6, 139.5, 138.8, 137.1, 136.3, 135.9, 135.1, 132.7, 132.5, 131.5, 130.9, 129.8 (2C), 129.4, 129.1, 128.9, 128.3, 128.0 (2C), 127.4 (2C), 126.3 (2C), 125.9, 124.81, 124.80, 124.3, 124.25, 124.18, 124.0, 121.9, 119.2, 118.7, 114.7, 114.2, 113.3, 111.5, 36.9, 21.5, 14.5. **ESI-MS**: 862 [M(^{79}Br, ^{79}Br) + Na^+], 864 [M(^{81}Br, ^{79}Br) + Na^+], 866 [M(^{81}Br,^{81}Br) + Na^+]. **HRMS**: calculated for [$C_{44}H_{31}Br_2N_3O_3S$ + H^+]: 840.0526 [M(^{79}Br, ^{79}Br) + H^+], 842.0505 [M(^{81}Br, ^{79}Br) + H^+], 844.0485 [M(^{81}Br,^{81}Br) + H^+]; found 840.0531 [M(^{79}Br, ^{79}Br) + H^+], 842.0515 [M(^{81}Br, ^{79}Br) + H^+], 844.0505 [M(^{81}Br,^{81}Br) + H^+]. **HPLC**: Every attempt to separate the two diastereoisomes by column chromatography on silica gel falied. Separation by chiral stationary phase HPLC of a racemic sample containing the two diastereoisomers falied as well. Thus, preparative HPLC was used to isolate a small aliquot of the major diastereoisomer (Phenomenex-Luna C_{18} CH_3CN/H_2O = 81:19, flow rate 5 mL/min; t = 18 min). Separation of the enantiomers of this diastereoisomer was possible in AD-H (*n*-hexane/iPrOH 80:20, flow-rate 0.75 mL/min; t_{minor} = 18.4 min; t_{major} = 24.9 min), 90 % *ee*.

Relative configuration of compounds 4kc and 6lc

Due to the existence of two chiral axes, two diastereoisomers are observable for compounds **4kc** and **6lc**. The relative configuration of the major and minor diastereoisomer was determined by NOE-NMR. Full assignments of the aromatic hydrogen signals was obtained by 2D-HSQC, 2D-COSY and 2D-HMBC NMR. Saturation[16] of the *ortho*-hydrogens of the benzyl group of the minor isomer (Figure S3) yields similar NOE on the H2" signal of indole and on the H8'

[16] DPFGSE-NOE Sequence. J. Stonehouse, P. Adell, J. Keeler, A. J. Shaka, *J. Am. Chem. Soc.* **1995**, *116*,6037.

signal of the 2-methoxynaphthalene ring. This implies that the 4-bromoindole ring and the 2-methoxynaphthalene are in the *anti*-disposition. On the contrary, when the *ortho*-hydrogens of the benzyl are saturated in the major isomer, NOEs were observed again for the H2'' signal of indole and on the OMe signal, thus confirming that the bromo-indole and the 2-methoxynaphthalene are in the *syn* disposition (Figure S4). In an analogous way the *syn* relationship was assigned to the major diastereoisomer of **6lc**.

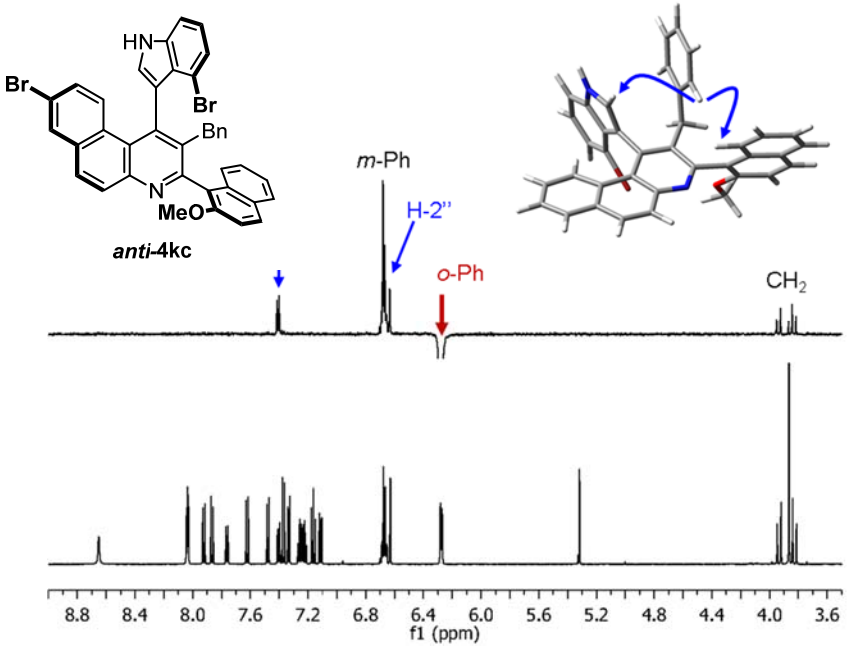


Figure S3. NOE-NMR spectra (600 MHz in CD_2Cl_2) of the minor diastereoisomer of **4kc**. Bottom: control spectrum. Top: NOE spectrum on saturation of the *ortho*-hydrogens of the benzyl group. Black label are control NOEs, whereas blue labels indicates diagnostic NOEs.

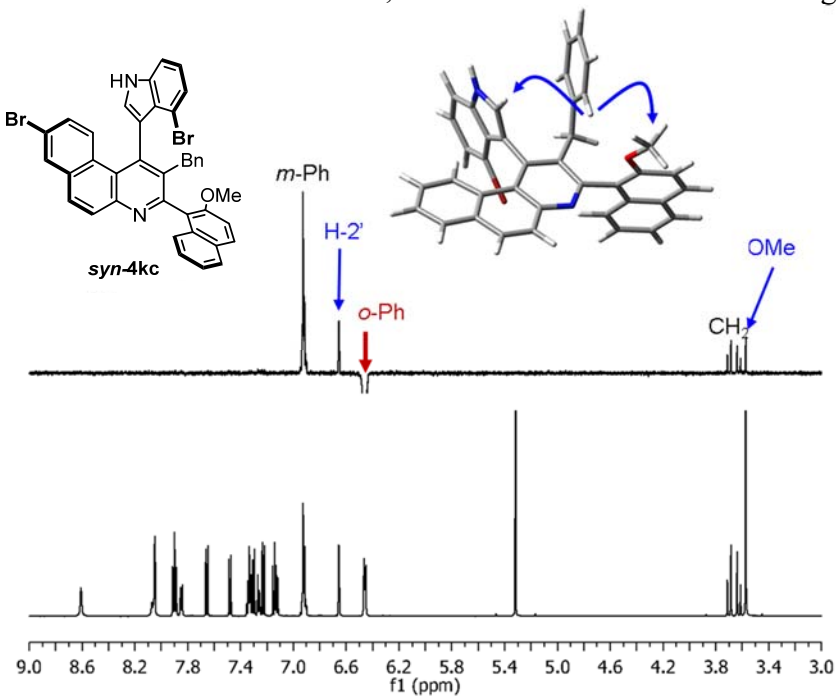
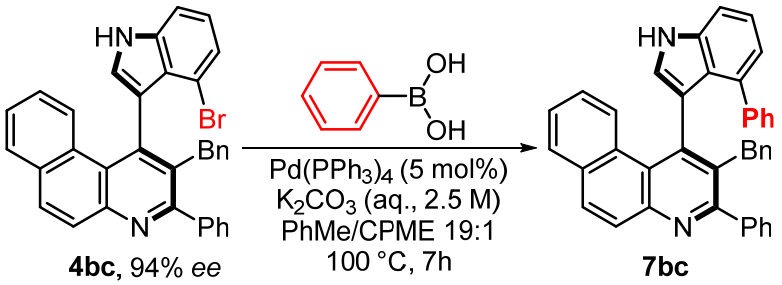


Figure S4. NOE-NMR spectra (600 MHz in CD_2Cl_2) of the major diastereoisomer of **4kc**. Bottom: control spectrum. Top: NOE spectrum on saturation of the *ortho*-hydrogens of the benzyl group. Black label are control NOEs, whereas blue labels indicates diagnostic NOEs.

It should be noted that a different disposition of the benzyl group (the one with the CH_2 on the same side of the H-2" of the indole) with respect to the 4-bromoindole could lead to different conclusions. However, there are both experimental and computational data that strongly suggest that there is only a populated conformation of the benzyl group. When the H-2" signal was saturated the NOE enhancement was observed only on the *ortho* hydrogens of the benzyl group, and not on the CH_2. On the other hand, DFT calculations on the second conformation suggested that it is 2.6 kcal/mol higher in energy.

Suzuki coupling to (a*S*)-2-benzyl-1-(4-phenyl-1*H*-indol-3-yl)-3-phenylbenzo[*f*]quinoline 7bc.

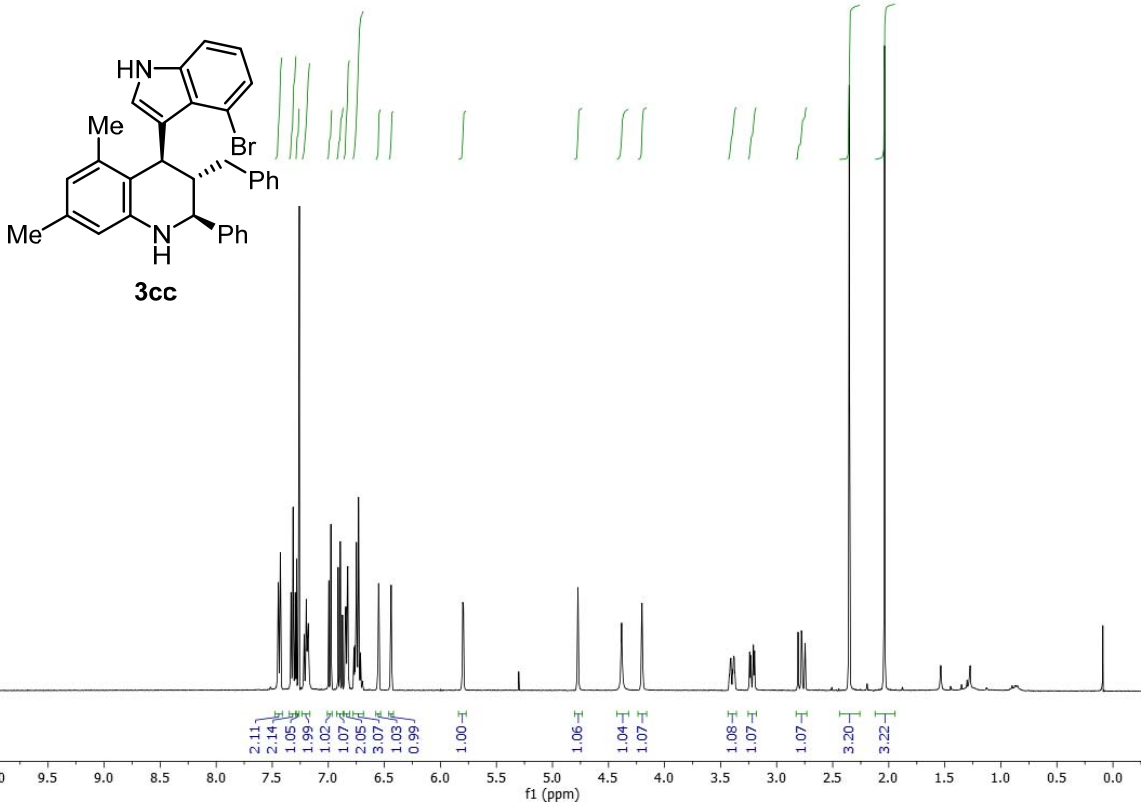


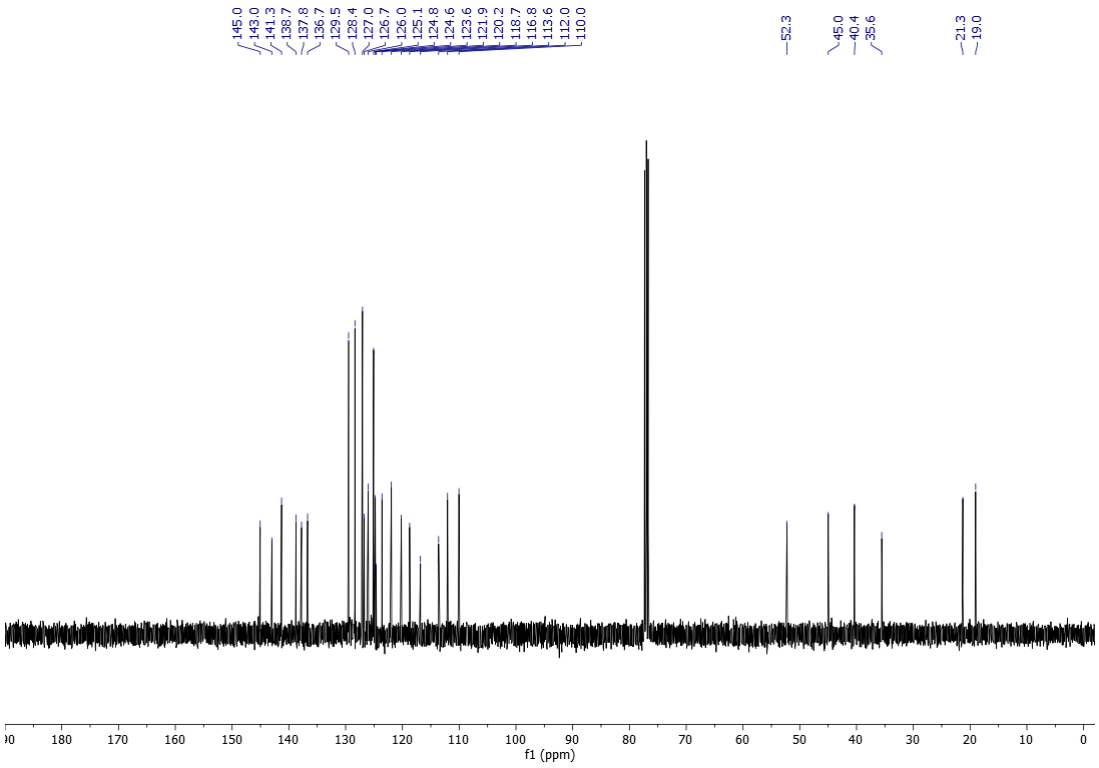
4bc, 94% *ee* — **7bc**, 80% yield, 90% *ee*

In a small Schlenk tube equipped with a magnetic stirring bar, compound **4bc** (54 mg, 1.0 equiv, 0.1 mmol, 94% *ee*), toluene (365 µL), CPME (cyclopentyl methyl ether, 20 µL), phenylboronic acid (25 mg, 2.0 equiv, 0.2 mmol) and K_2CO_3 (2M aqueous solution, 125 µL, 2.5 equiv, 0.25 mmol) were added in this order. The whole reaction mixture was then degassed using the freezing-pump method (3 times) and $Pd(PPh_3)_4$ (5.8 mg, 5 mol%) was added. The resulting biphasic mixture was vigorously stirred under nitrogen atmosphere at 100 °C for 7 h and then cooled to room temperature. The crude mixture was passed through a short plug of SiO_2 eluted with CH_2Cl_2 (10 mL) and Et_2O (3x5 mL), evaporated *in vacuo* and purified by column chromatography on silica gel (*n*-hexane/Et_2O = 3:1) to afford product **7bc** in 80% yield as a light yellow powder. $[\alpha]_D^{25}$ = +207 (c = 0.2 in $CHCl_3$) for 90% *ee*. Similarly to products **3** and **4**, **6bc** was found to be sensitive to traces of DCl in $CDCl_3$. In order to record the spectra in $CDCl_3$ the solvent had to be filtered over basic alumina prior to use. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.37 (s, 1H), 7.93 (d, *J* = 9.0 Hz, 1H), 7.89 (d, *J* = 9.1 Hz, 1H), 7.87 – 7.81 (m, 2H), 7.52 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.44 (ddd, *J* = 7.9, 6.9, 1.1 Hz, 1H), 7.38 (dd, *J* = 8.2, 7.2 Hz, 1H), 7.31 – 7.27 (m, 3H), 7.20 – 7.15 (m, 2H), 7.14 – 7.04 (m, 2H), 7.03 – 6.96 (m, 3H), 6.96 – 6.88 (m, 3H), 6.77 (t, *J* = 7.3 Hz, 2H), 6.51 (d, *J* = 2.5 Hz, 1H), 6.39 – 6.30 (m, 2H), 3.72 (d, *J* = 15.9 Hz, 1H), 3.67 (d, *J* = 15.9 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 159.3, 147.2, 143.1, 141.8, 141.2, 139.8, 136.9, 136.5, 133.3, 133.0, 130.6, 130.5, 129.0, 128.9 (2C), 128.8 (2C), 128.6, 127.94 (2C), 127.91 (2C), 127.7, 127.6 (2C), 127.4, 126.8, 126.7 (2C), 126.0, 125.5, 125.1, 124.9, 123.5, 123.5, 122.8, 121.9, 115.9, 110.7, 36.4. **ESI-MS**: 537 [M + H$^+$]. **HRMS**: calculated for [$C_{40}H_{28}N_2$ + H$^+$]: 537.2325; found 537.2331. **HPLC**: AD-H (*n*-hexane/iPrOH 80:20, flow-rate 0.75 mL/min; t_{major} = 5.0 min; t_{minor} = 7.3 min).

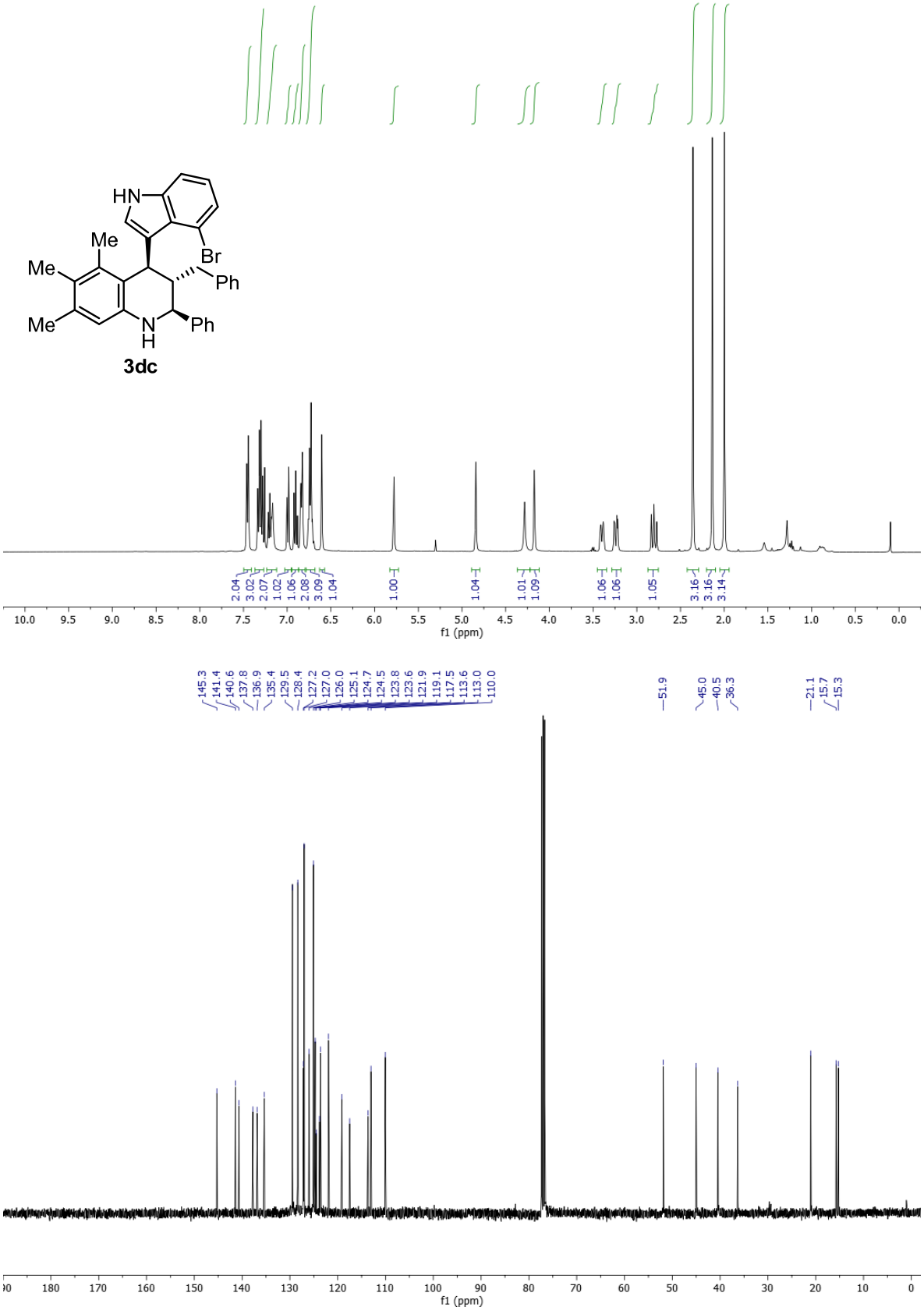
Copies of ^{1}H and ^{13}C NMR spectra of products 3 (in $CDCl_3$ unless otherwise stated)

(*2S,3S,4R*)-3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-5,6,7-dimethyl-2-phenyl-1,2,3,4-tetrahydroquinoline 3cc

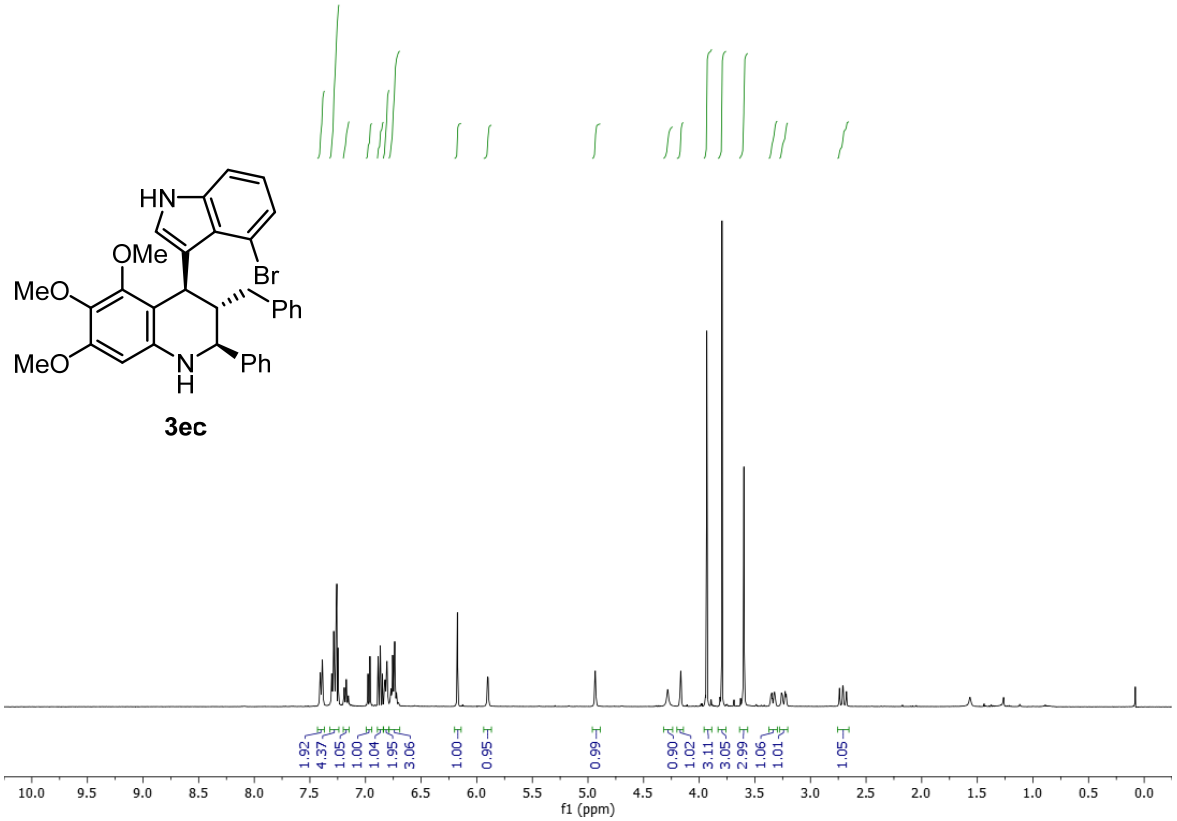


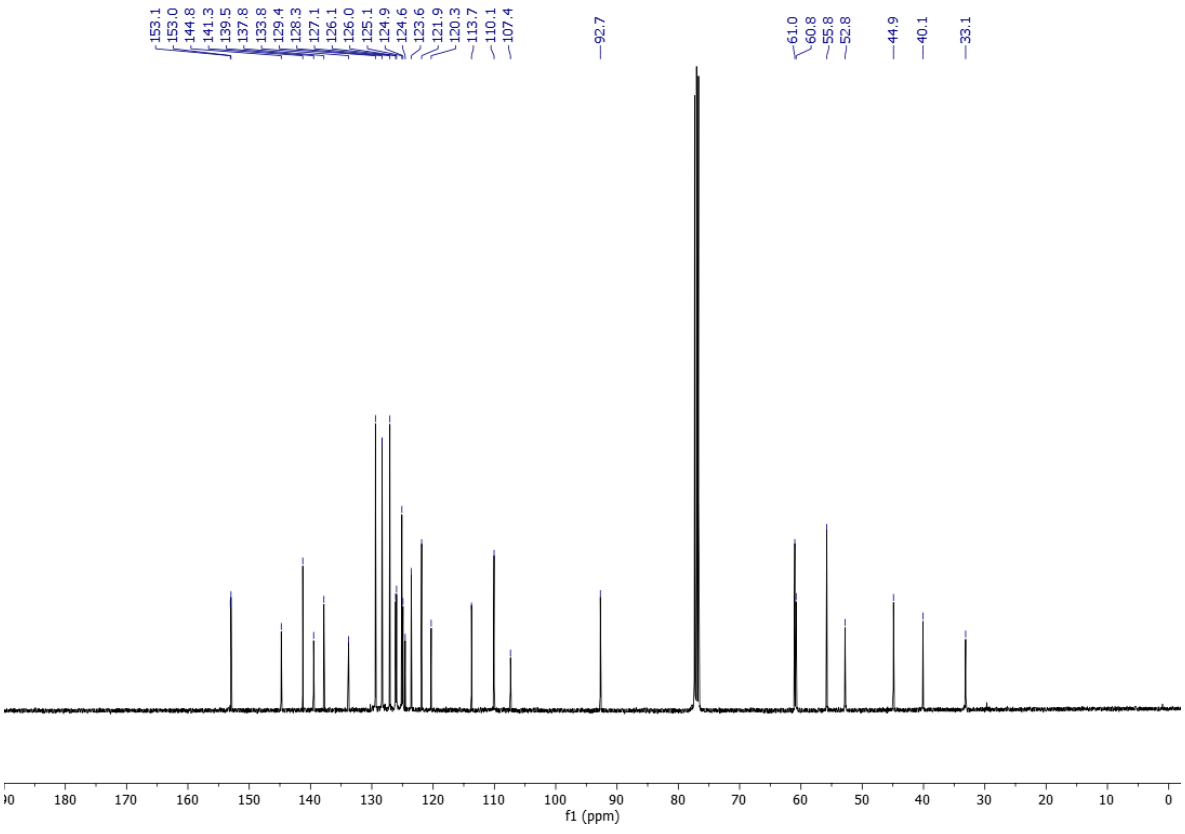


(*2S,3S,4R*)-3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-5,6,7-trimethyl-2-phenyl-1,2,3,4-tetrahydroquinoline 3dc

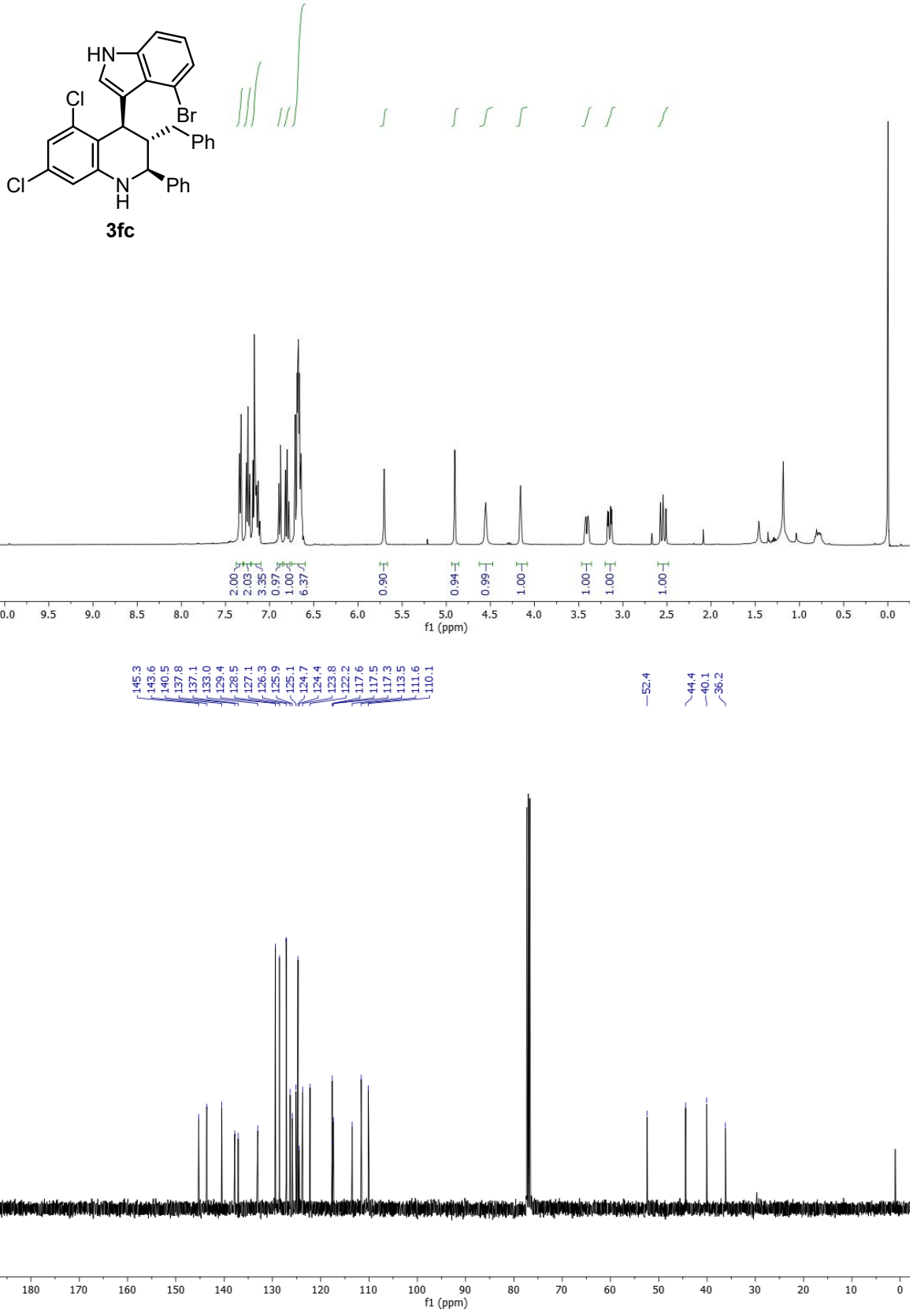


(*2S,3S,4R*)-3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-5,6,7-trimethoxy-2-phenyl-1,2,3,4-tetrahydroquinoline 3ec

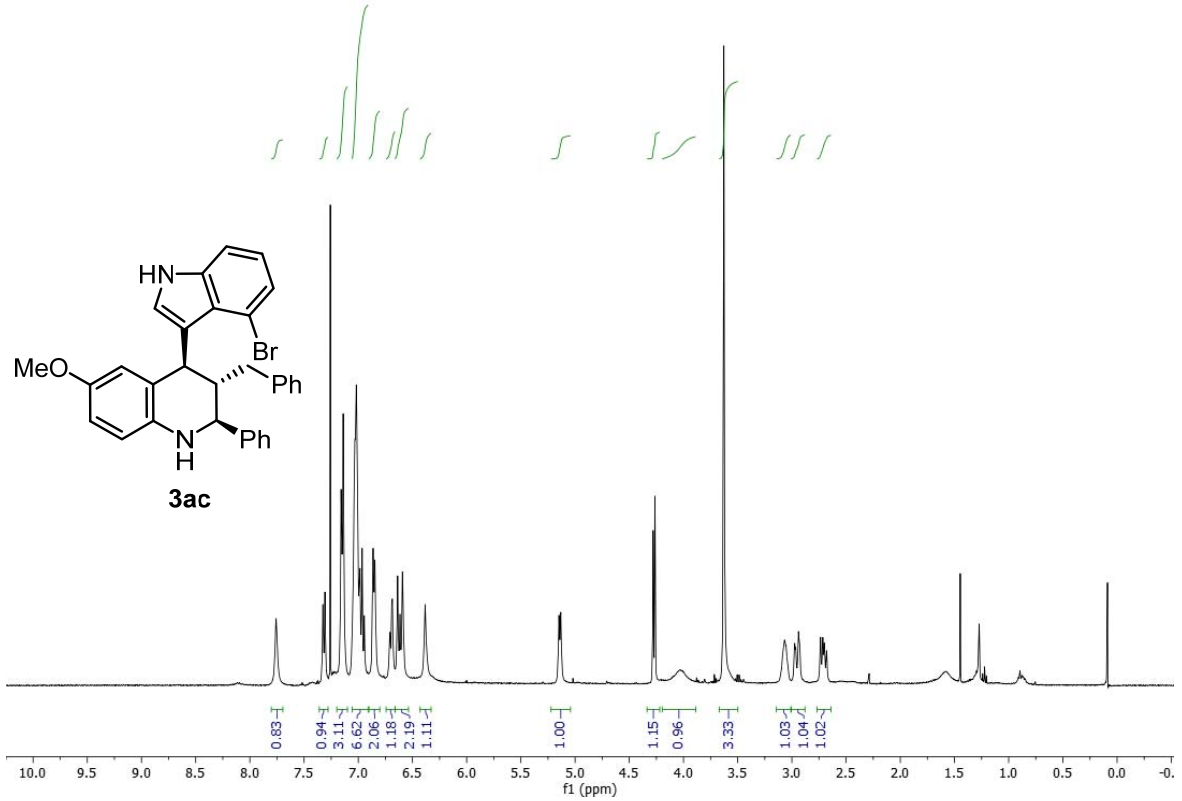


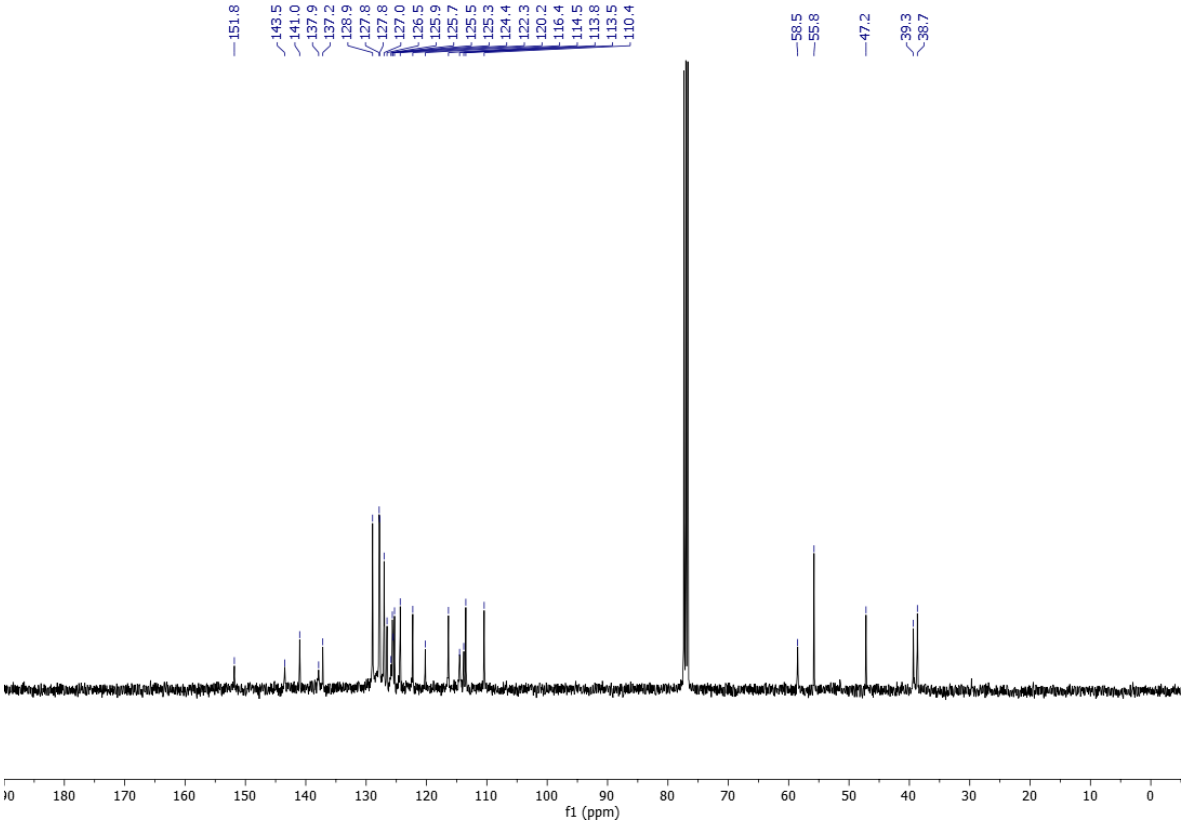


(*2S,3S,4R*)-3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-5,7-dichloro-2-phenyl-1,2,3,4-tetrahydroquinoline 3fc

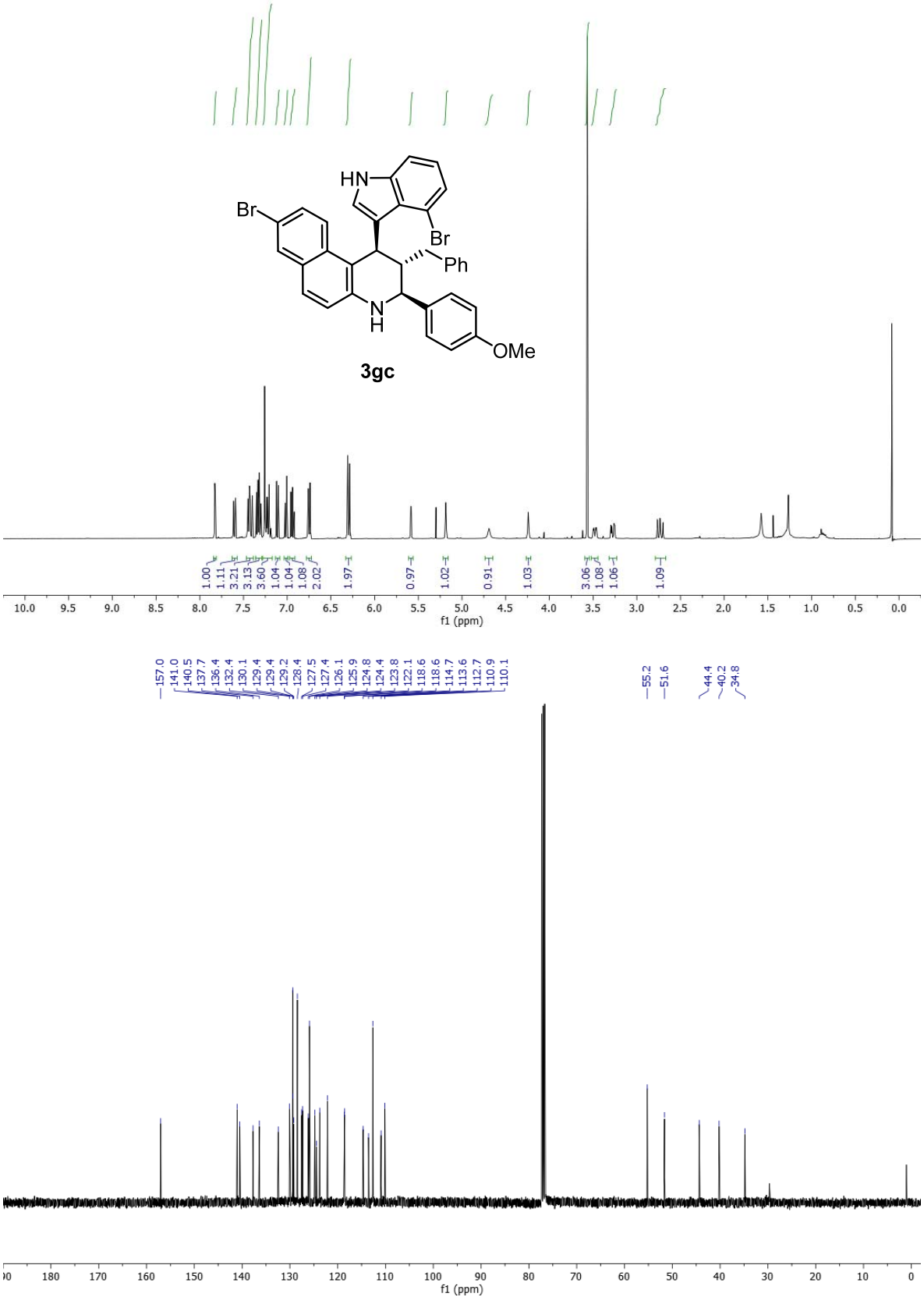


(*2S,3S,4R*)-3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-6-methoxy-2-phenyl-1,2,3,4-tetrahydroquinoline 3ac

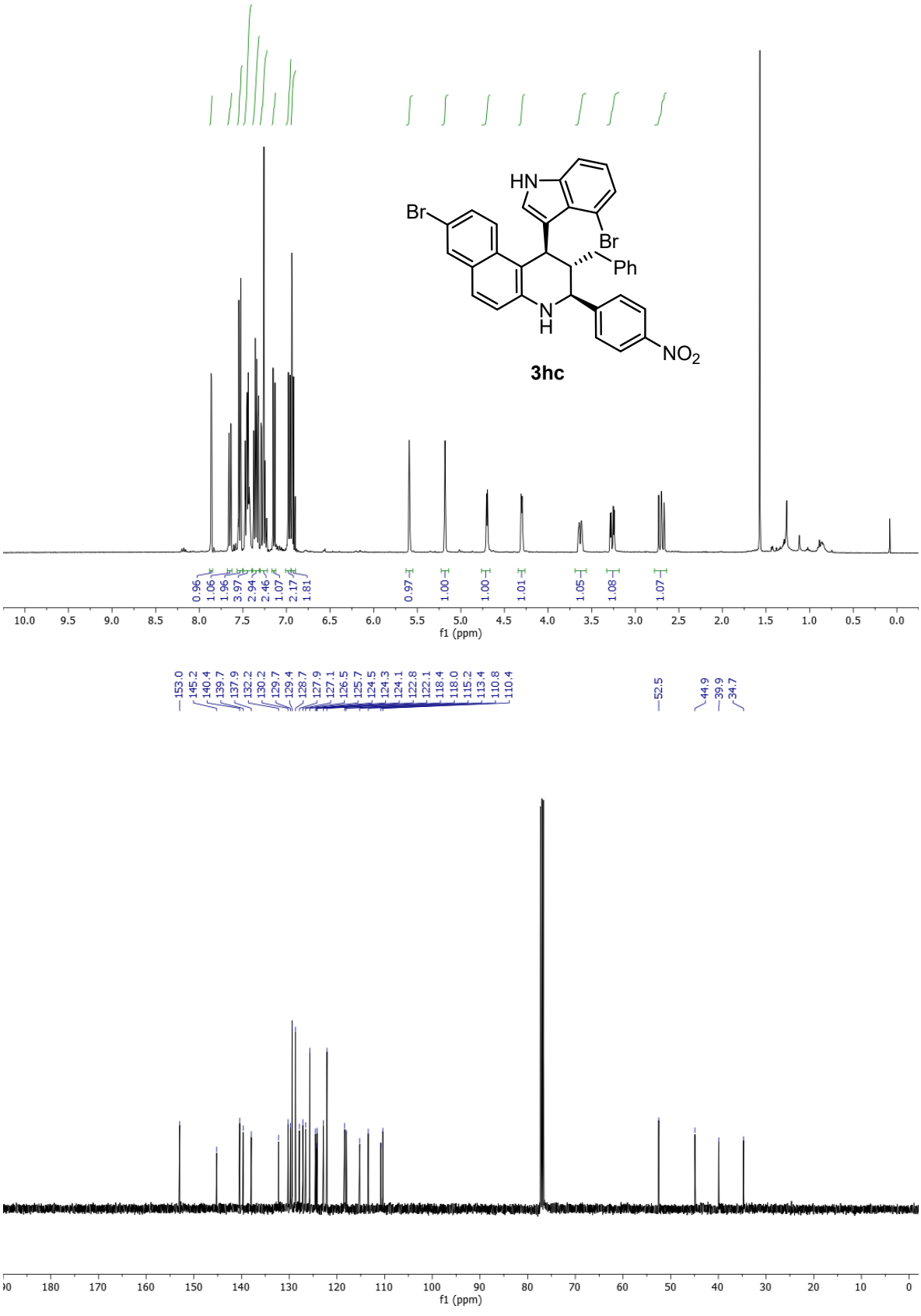




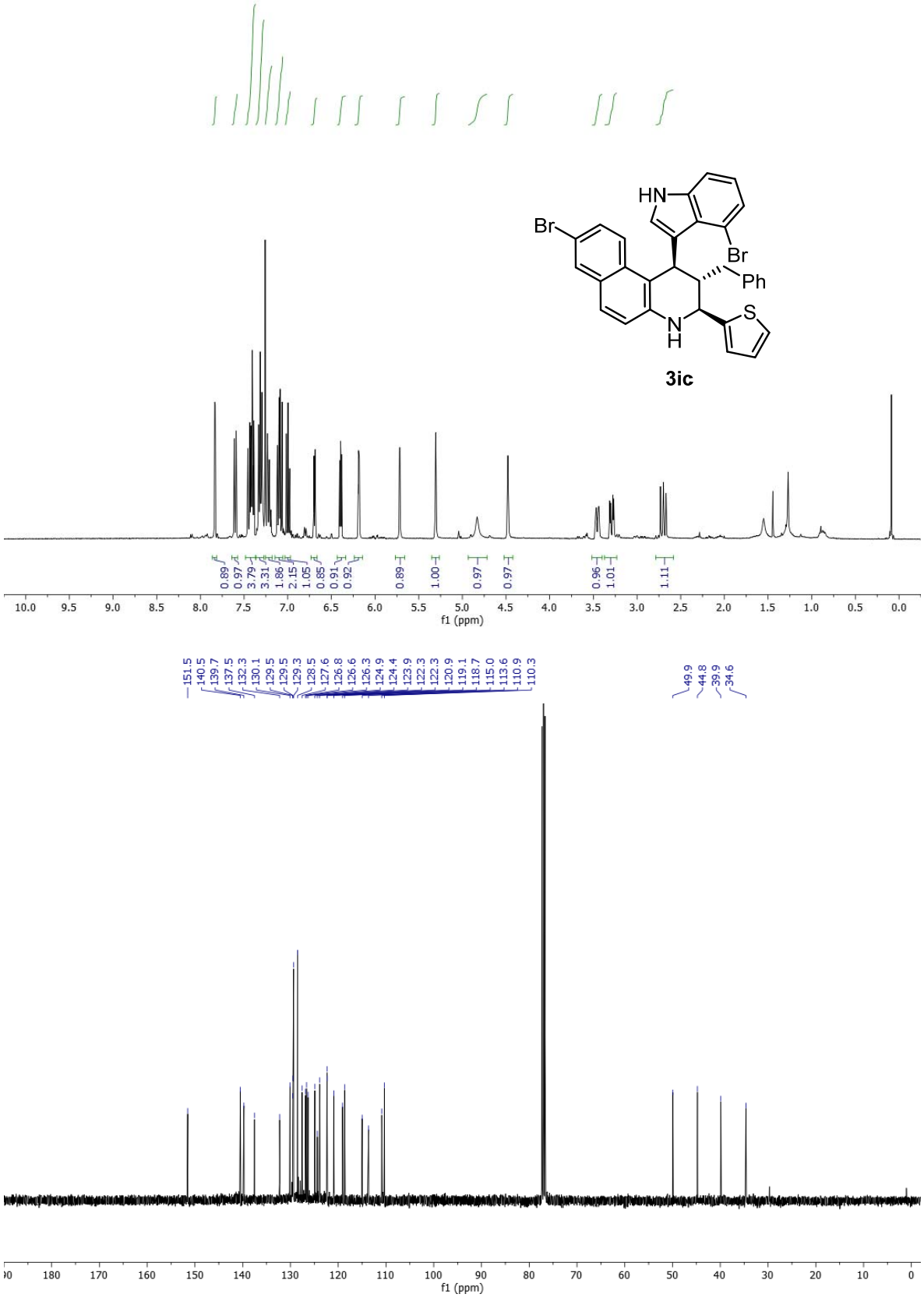
(*1R*,*2S*,*3S*)-2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(4-methoxyphenyl)-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3gc



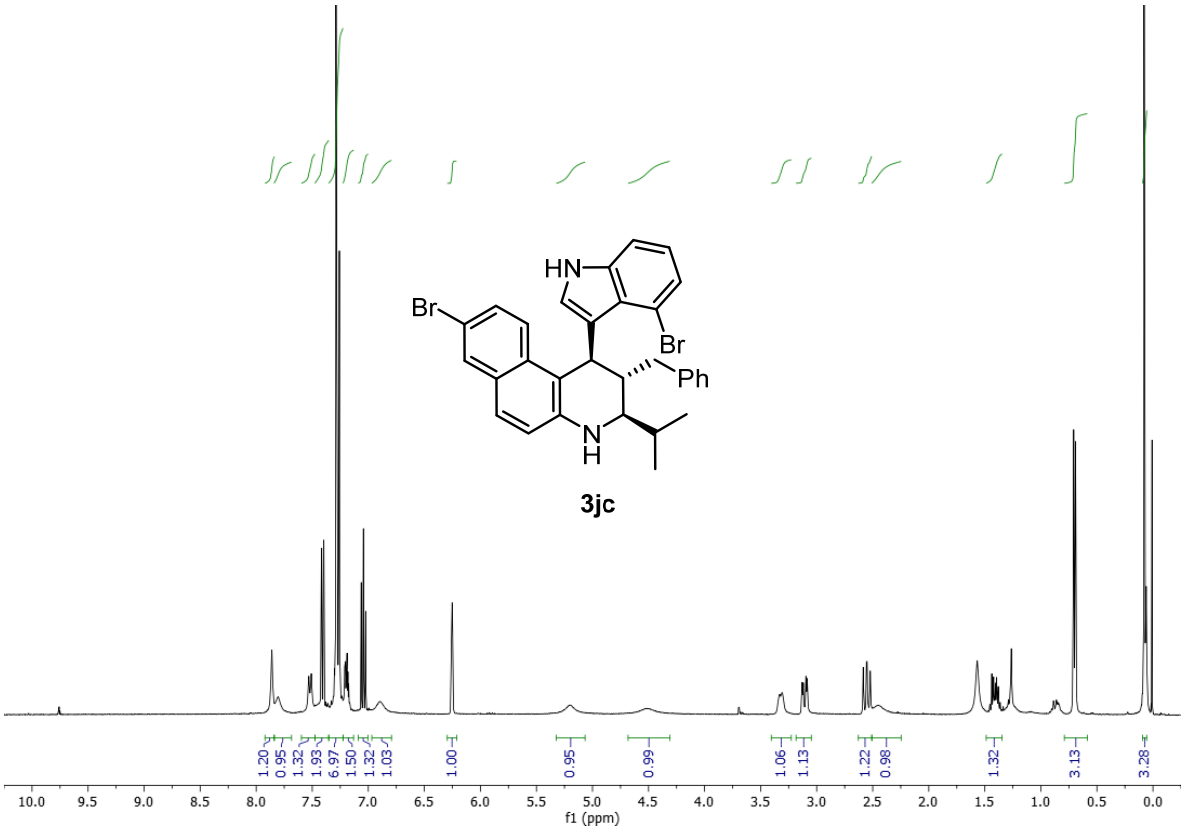
(*1R,2S,3S*)-2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(4-nitrophenyl)-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3hc

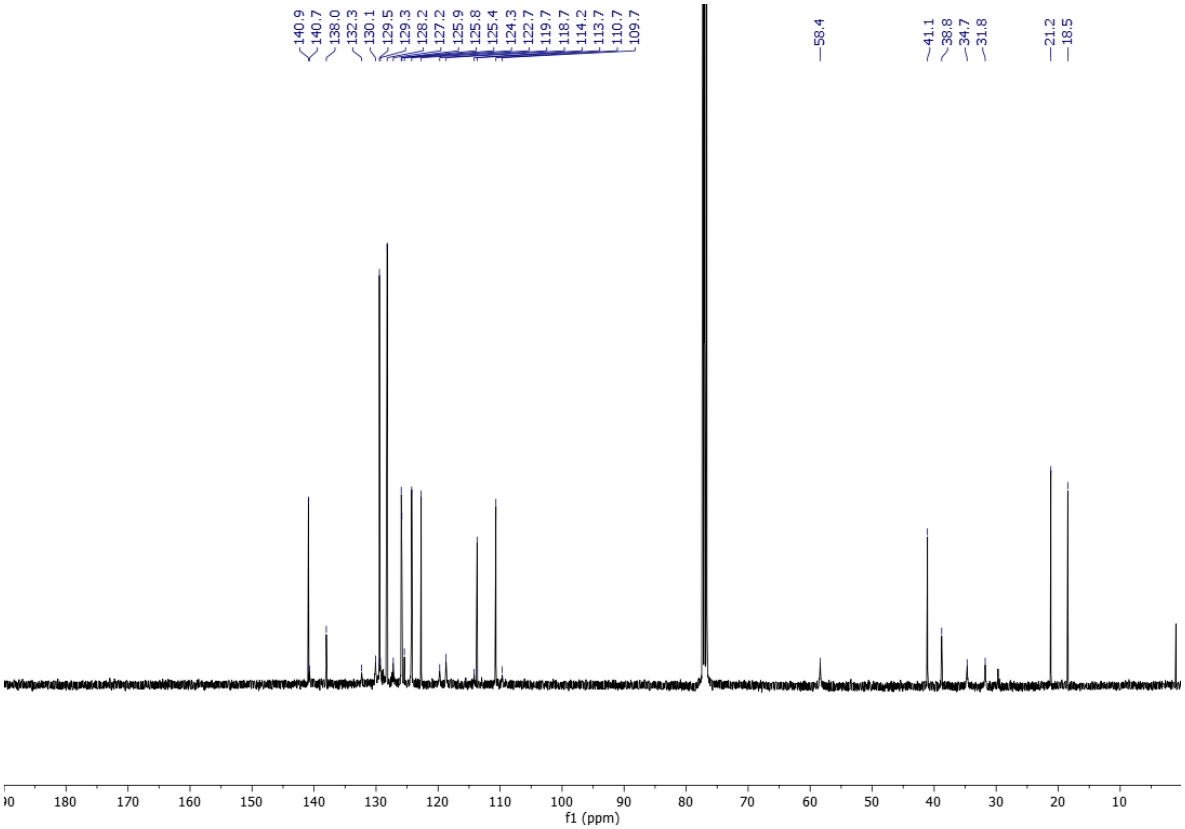


(*1R,2S,3S*)-2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(thiophen-2-yl)-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3ic

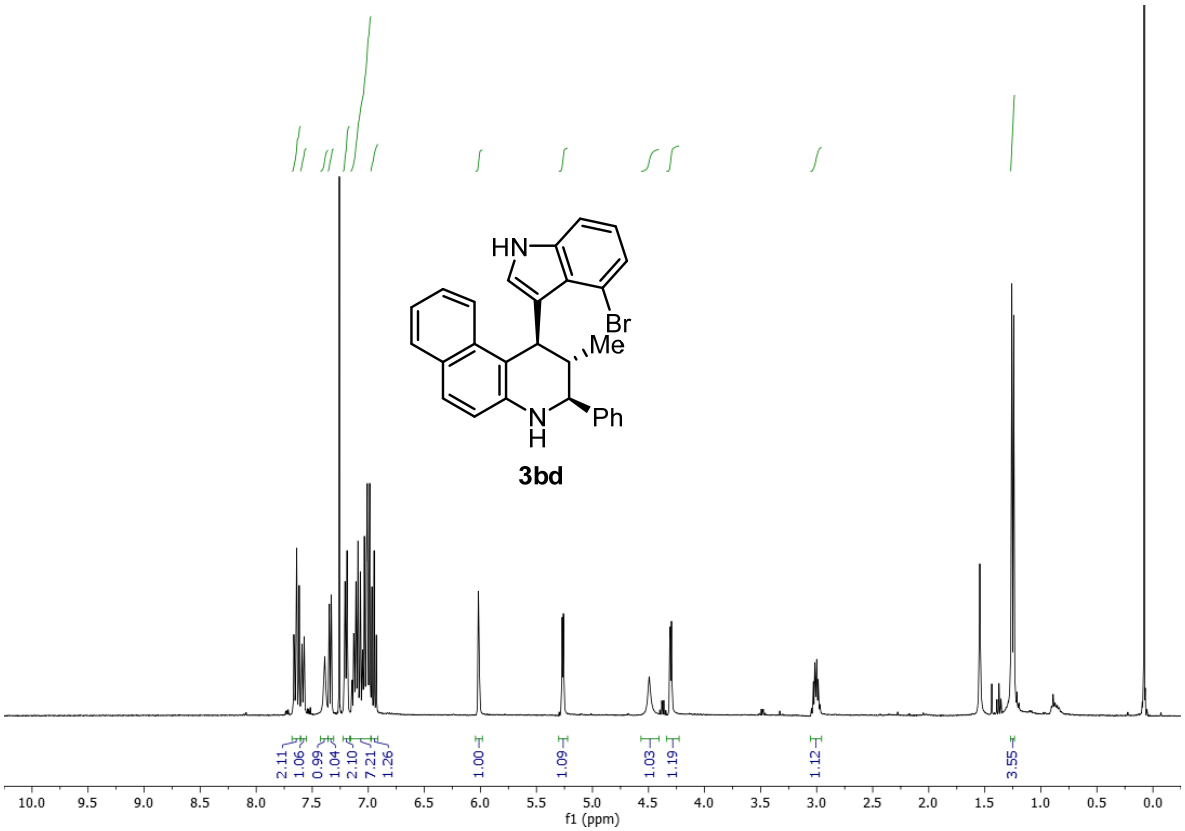


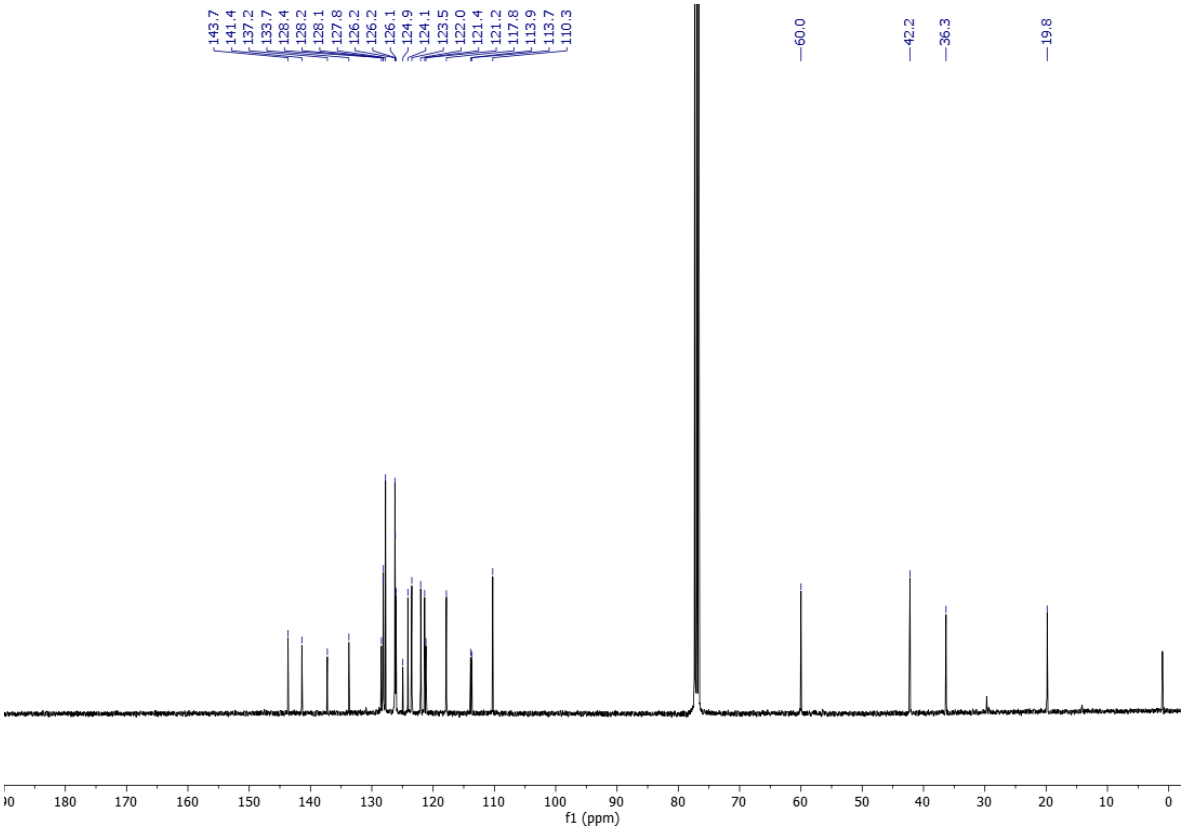
(*1R*,*2S*,*3R*)-2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-isopropyl-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3jc



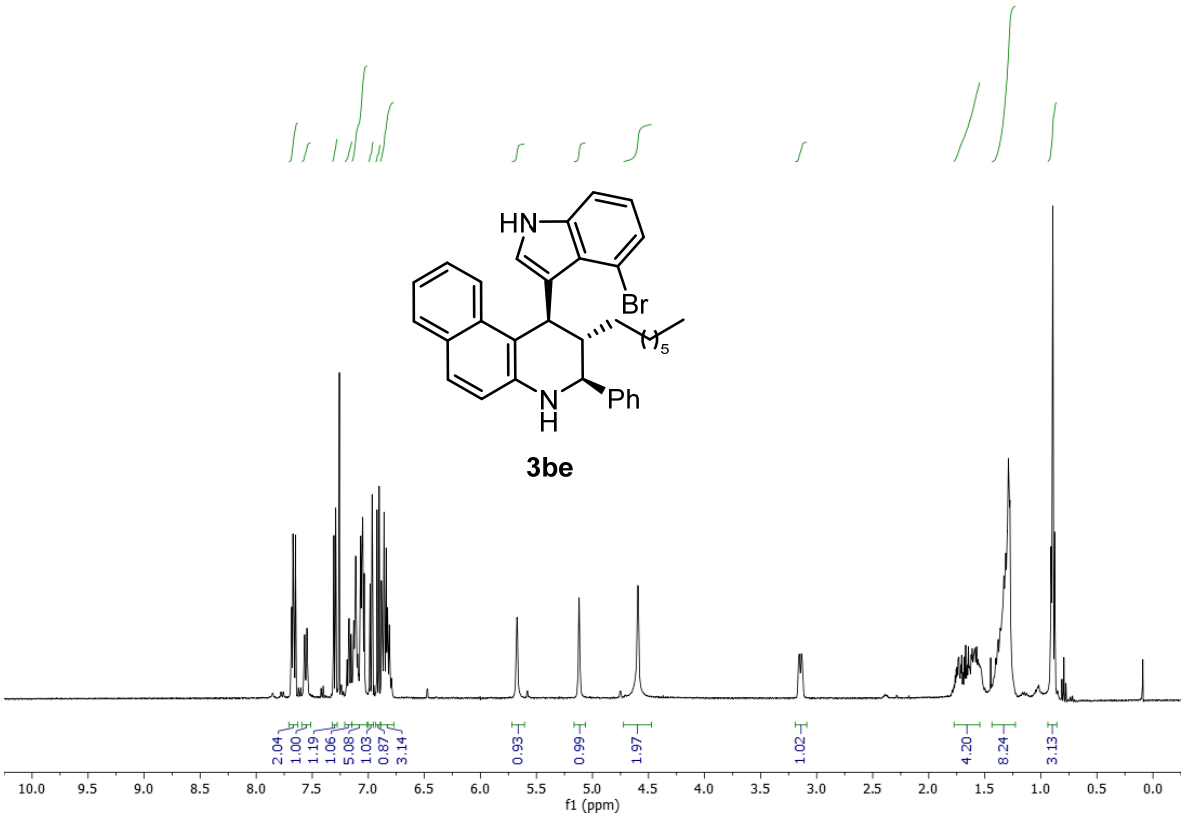


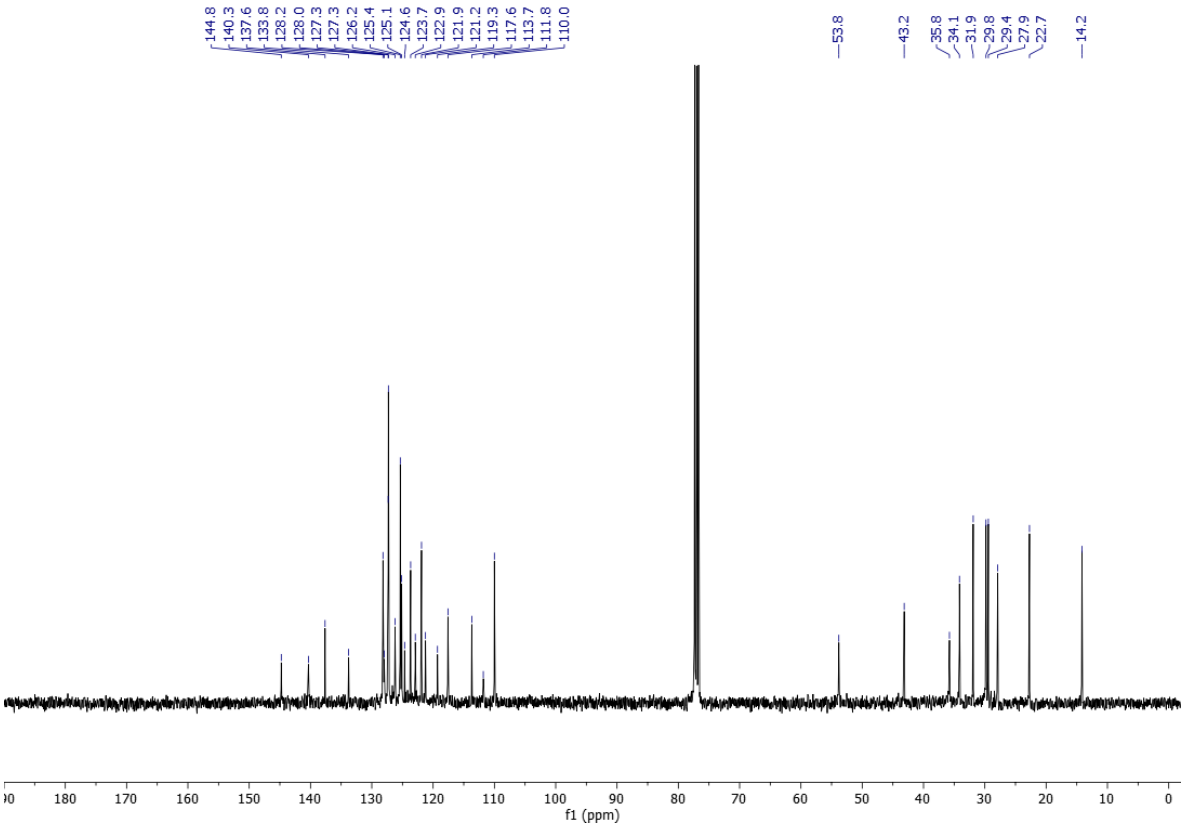
(*1R*,*2S*,*3S*)-1-(4-bromo-1*H*-indol-3-yl)-2-methyl-3-phenyl-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3bd



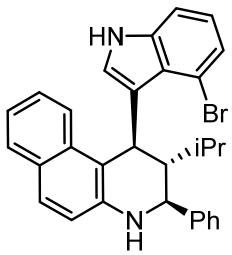


(1*R*,2*S*,3*S*)-1-(4-bromo-1*H*-indol-3-yl)-3-phenyl-2-propyl-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3be

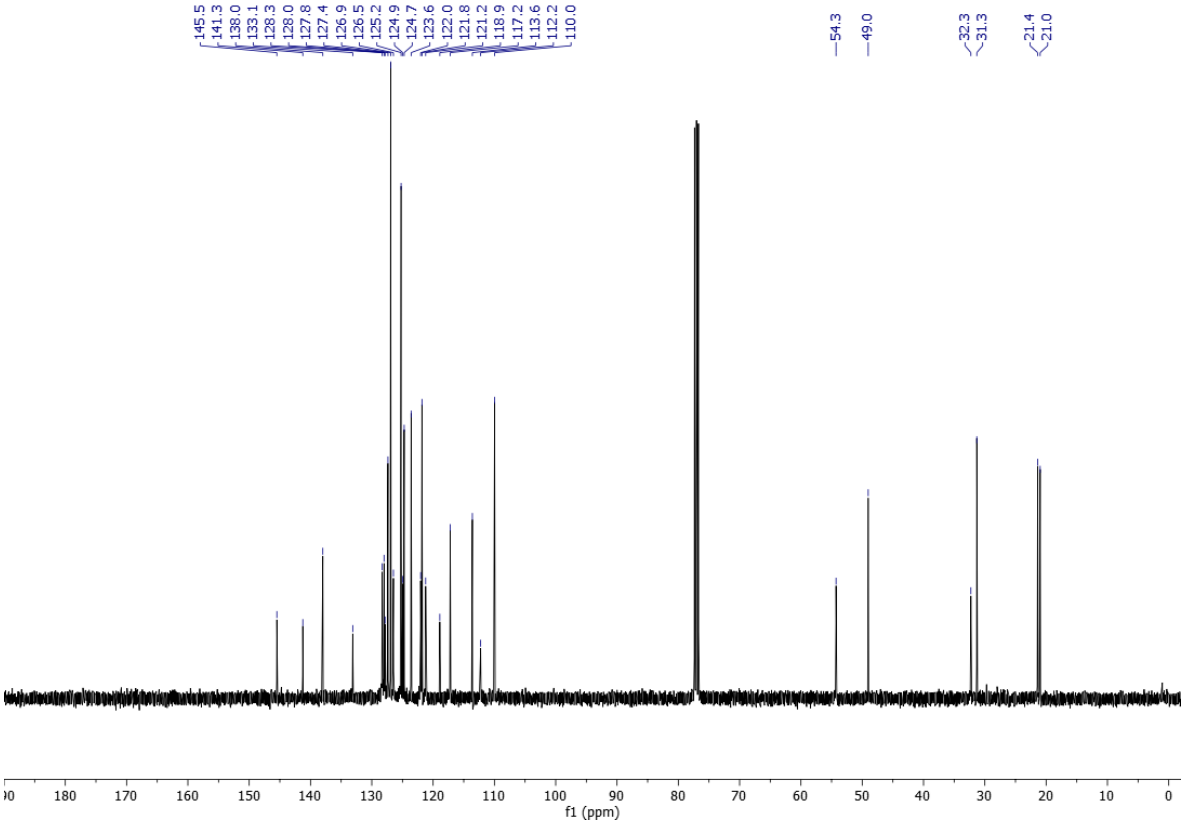




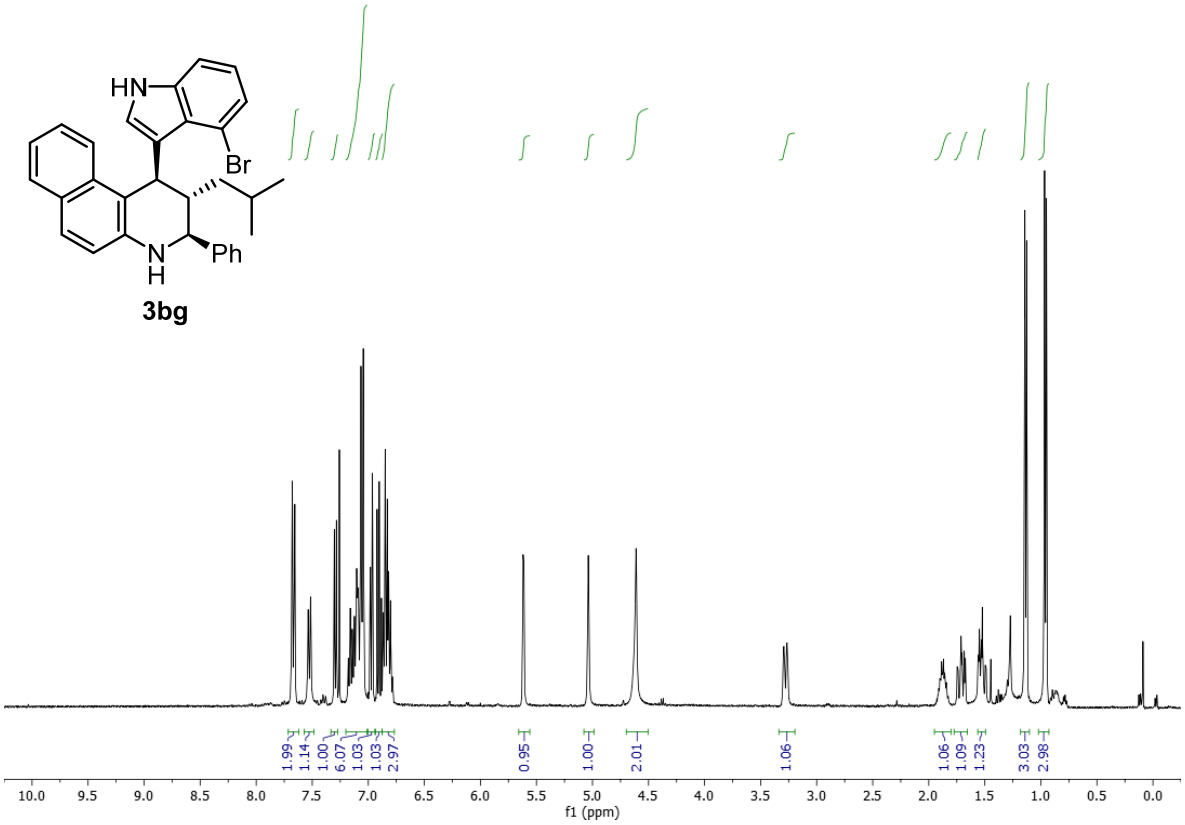
(*1R,2S,3S*)-1-(4-bromo-1*H*-indol-3-yl)-2-isopropyl-3-phenyl-1,2,3,4-tetrahydrobenzo[*f*] quinoline3bf

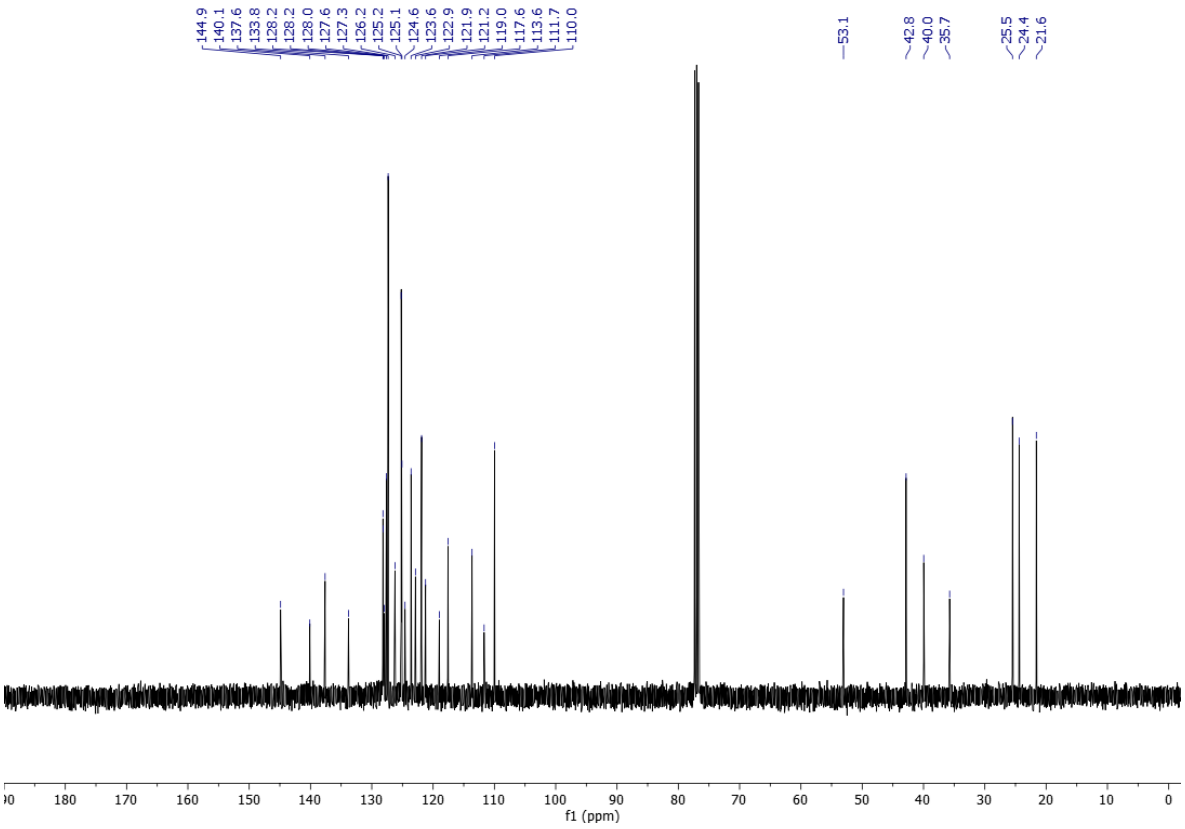


3bf

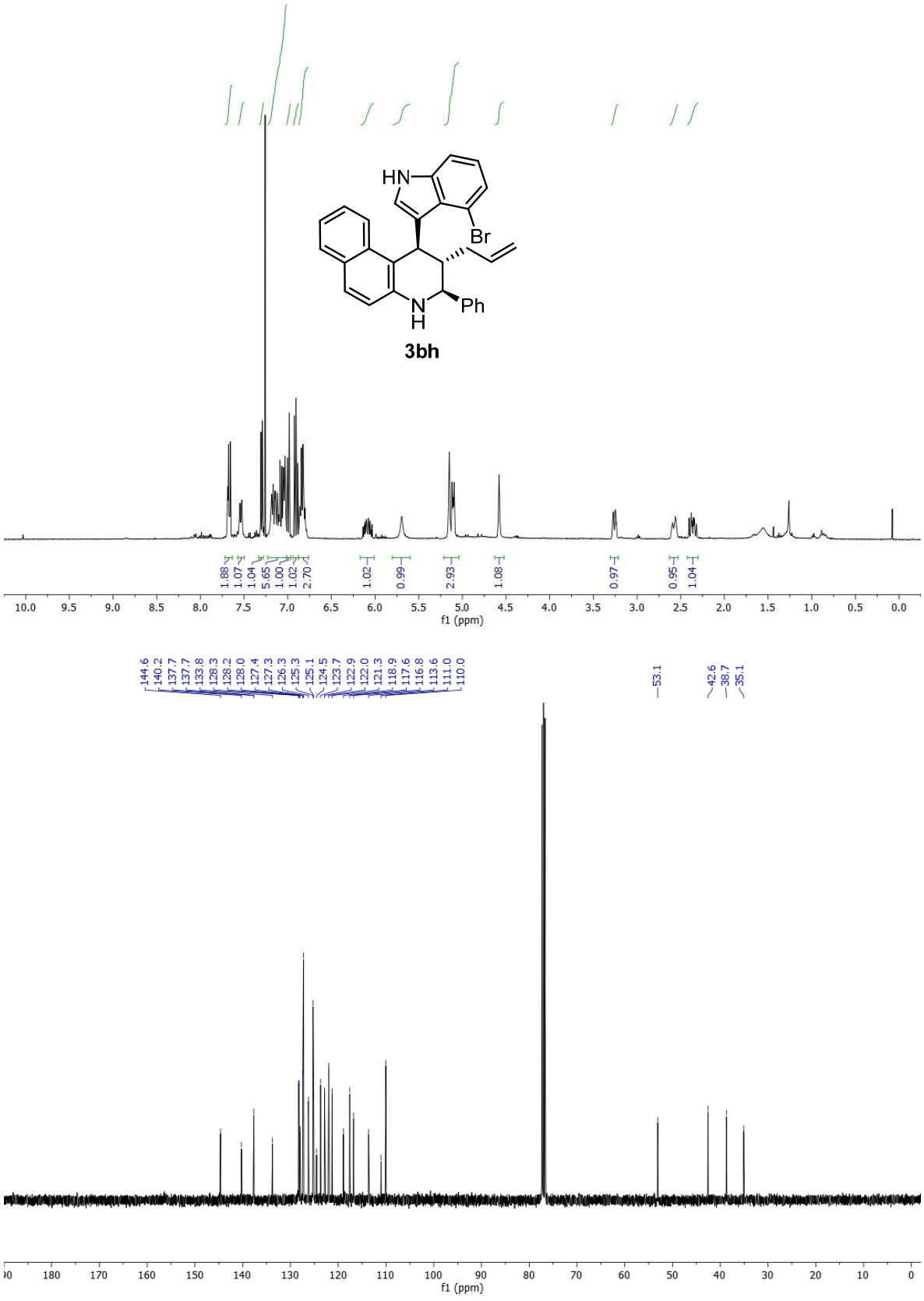


(*1R,2S,3S*)-1-(4-bromo-1*H*-indol-3-yl)-2-isobutyl-3-phenyl-1,2,3,4-tetrahydrobenzo[*f*] quinoline 3bg

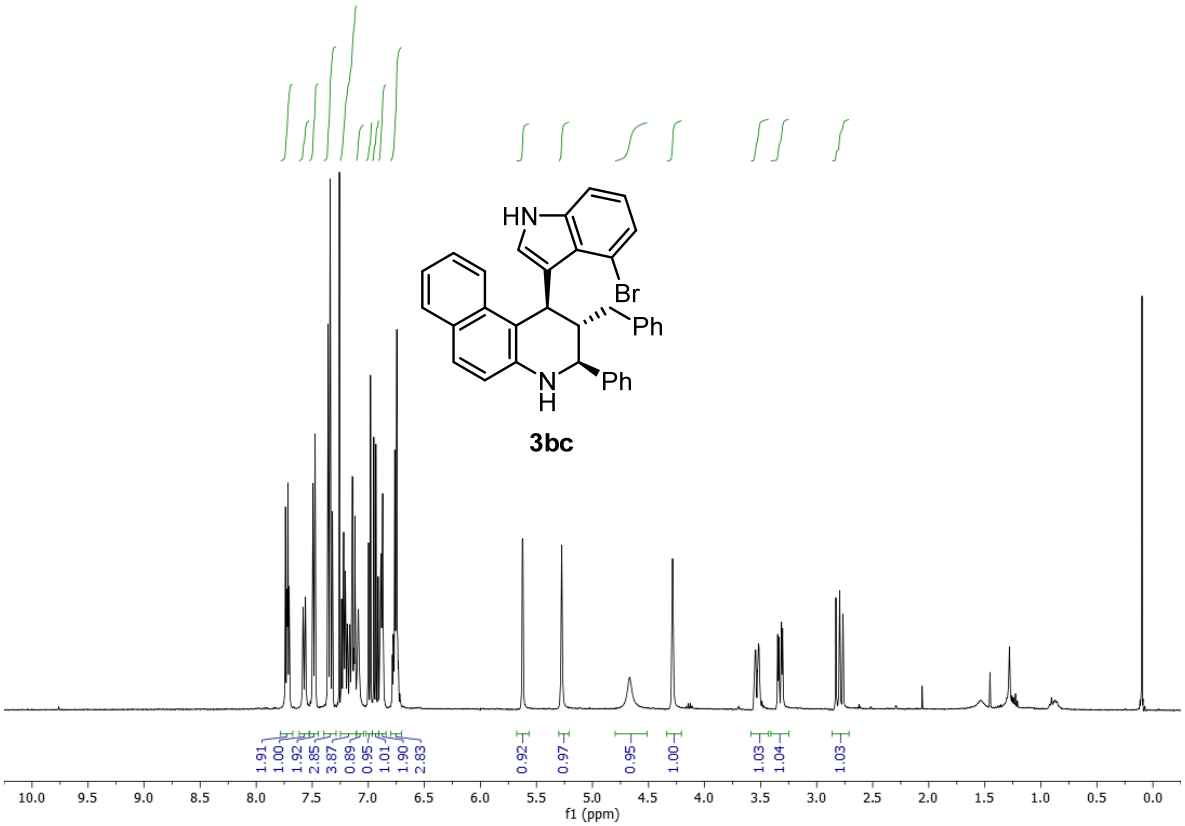


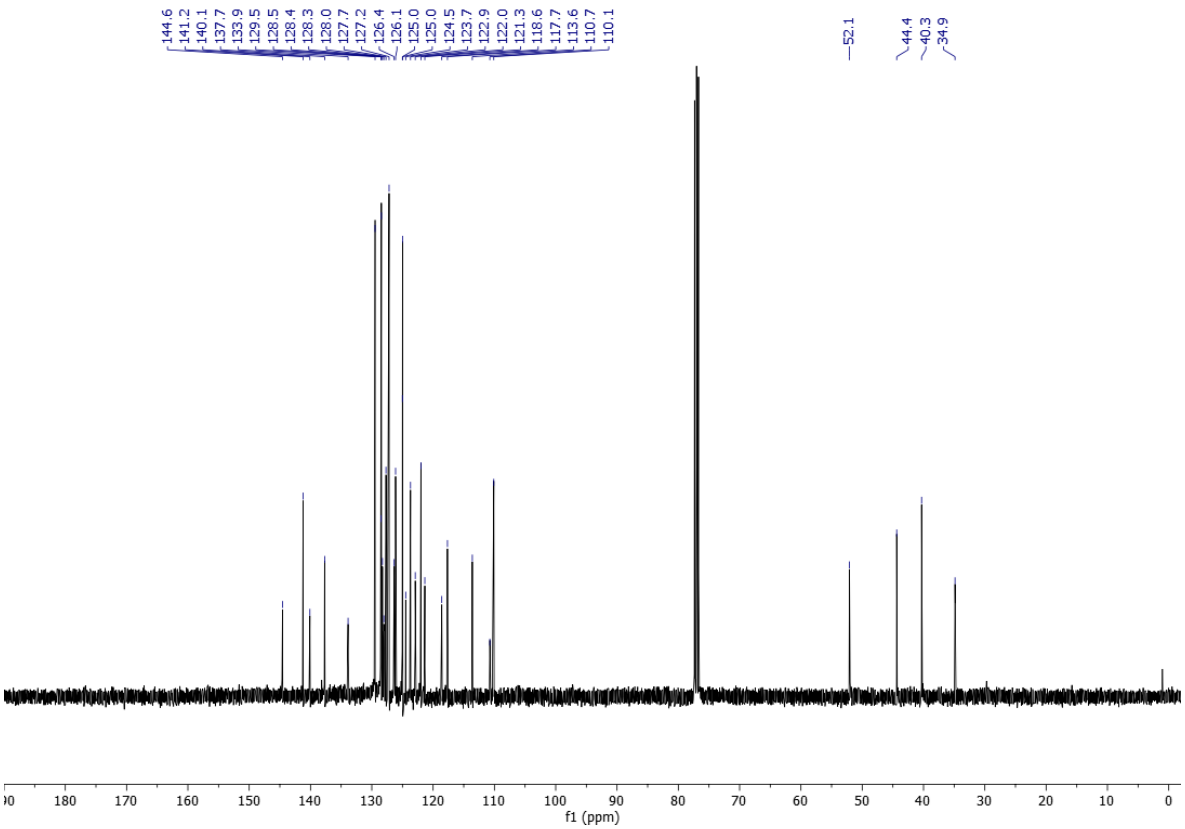


(*1R*,*2S*,*3S*)-2-allyl-1-(4-bromo-1*H*-indol-3-yl)-3-phenyl-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3bh

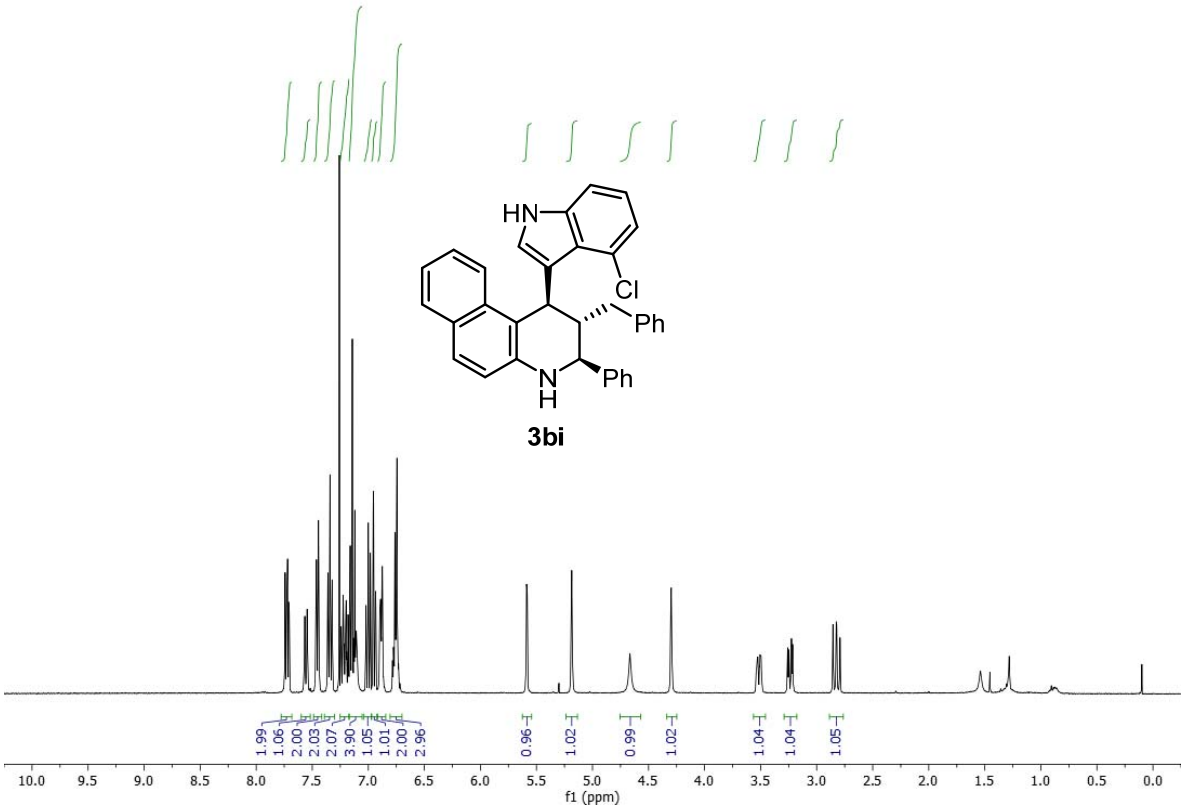


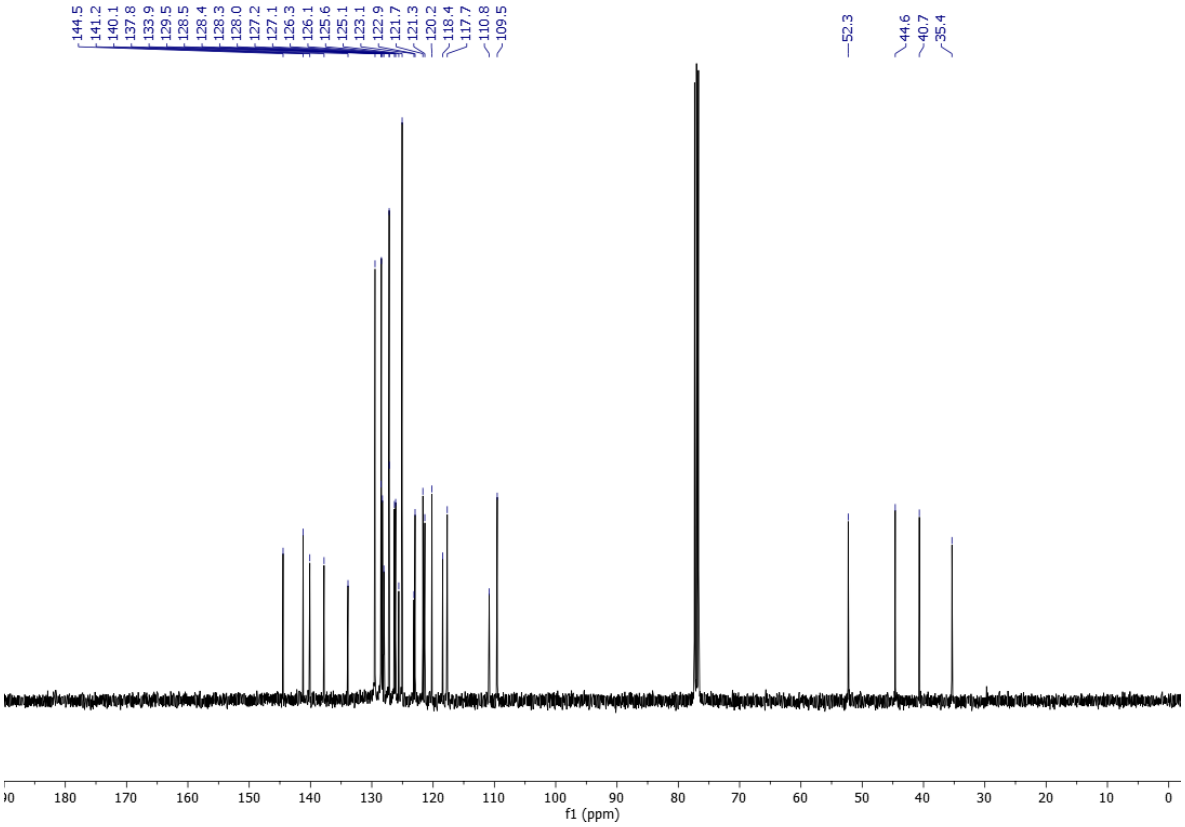
(*1R*,*2S*,*3S*)-2-benzyl-1-(4-bromo-1*H*-indol-3-yl)-3-phenyl-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3bc



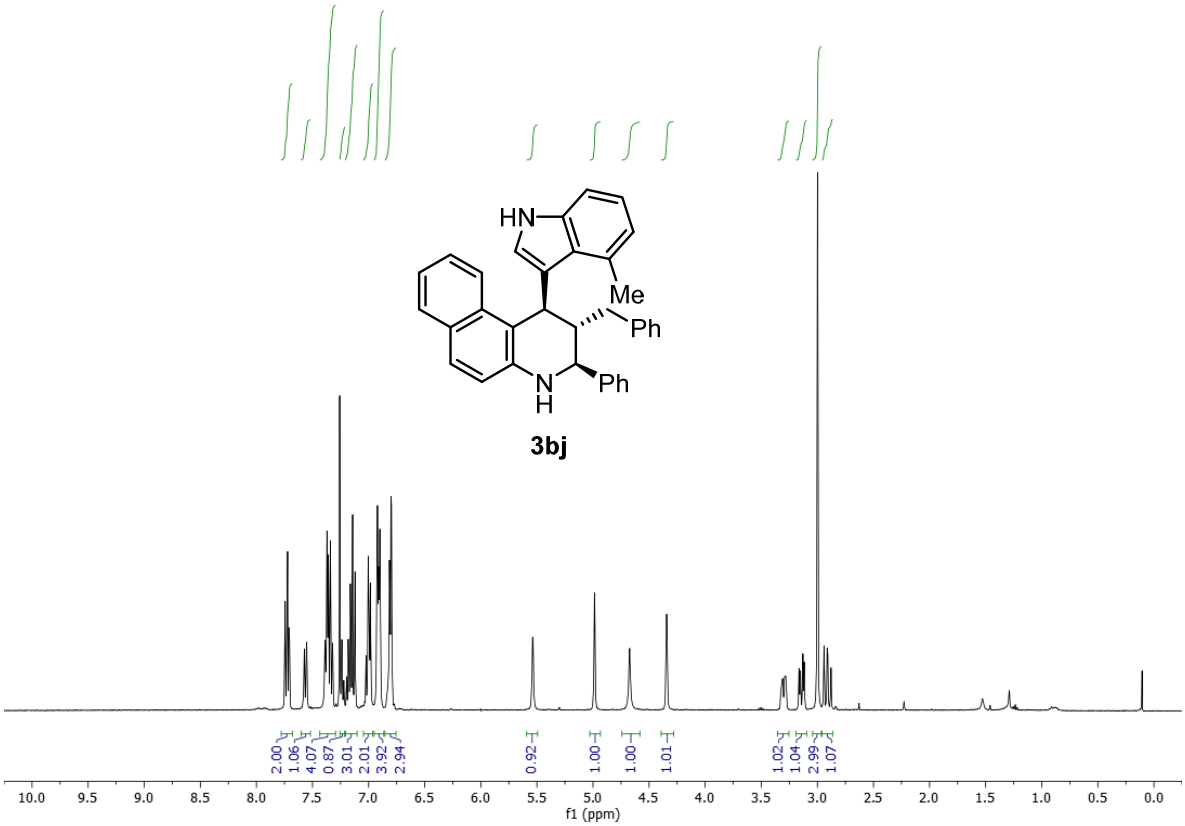


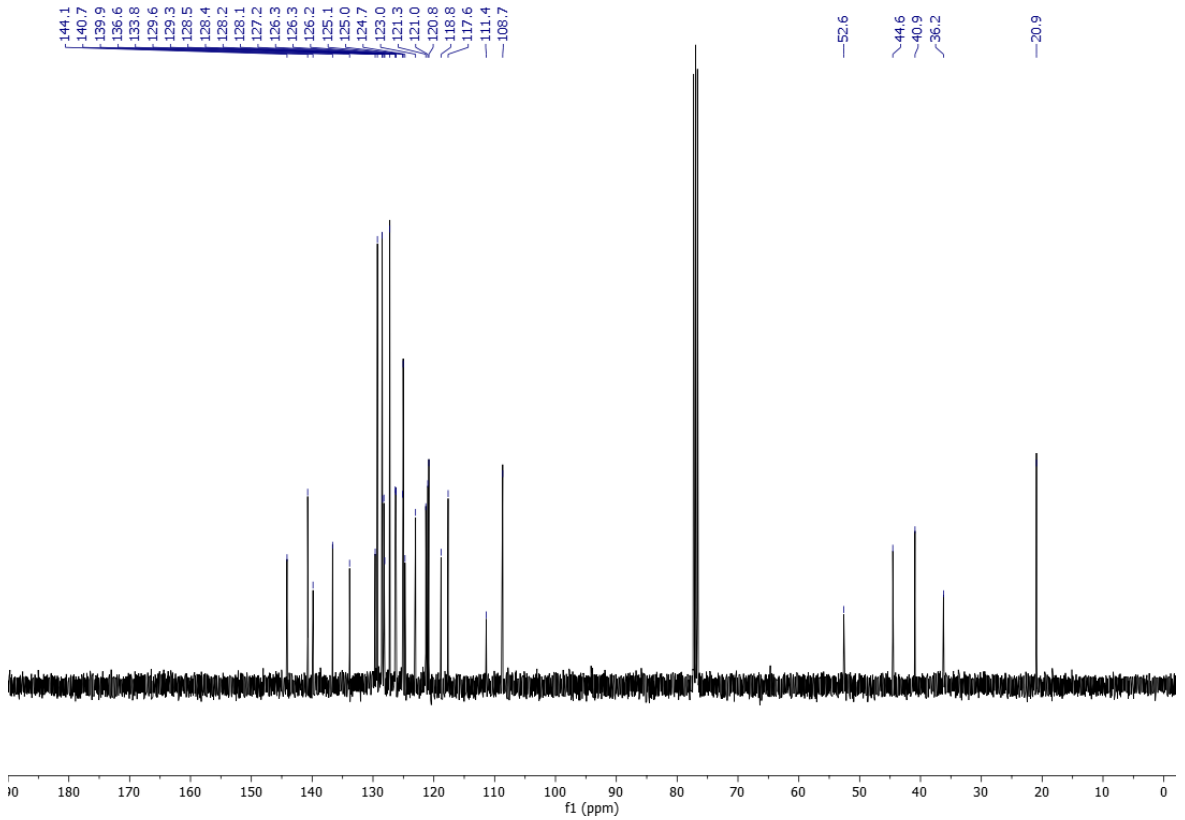
(1*R*,2*S*,3*S*)-2-benzyl-1-(4-chloro-1*H*-indol-3-yl)-3-phenyl-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3bi



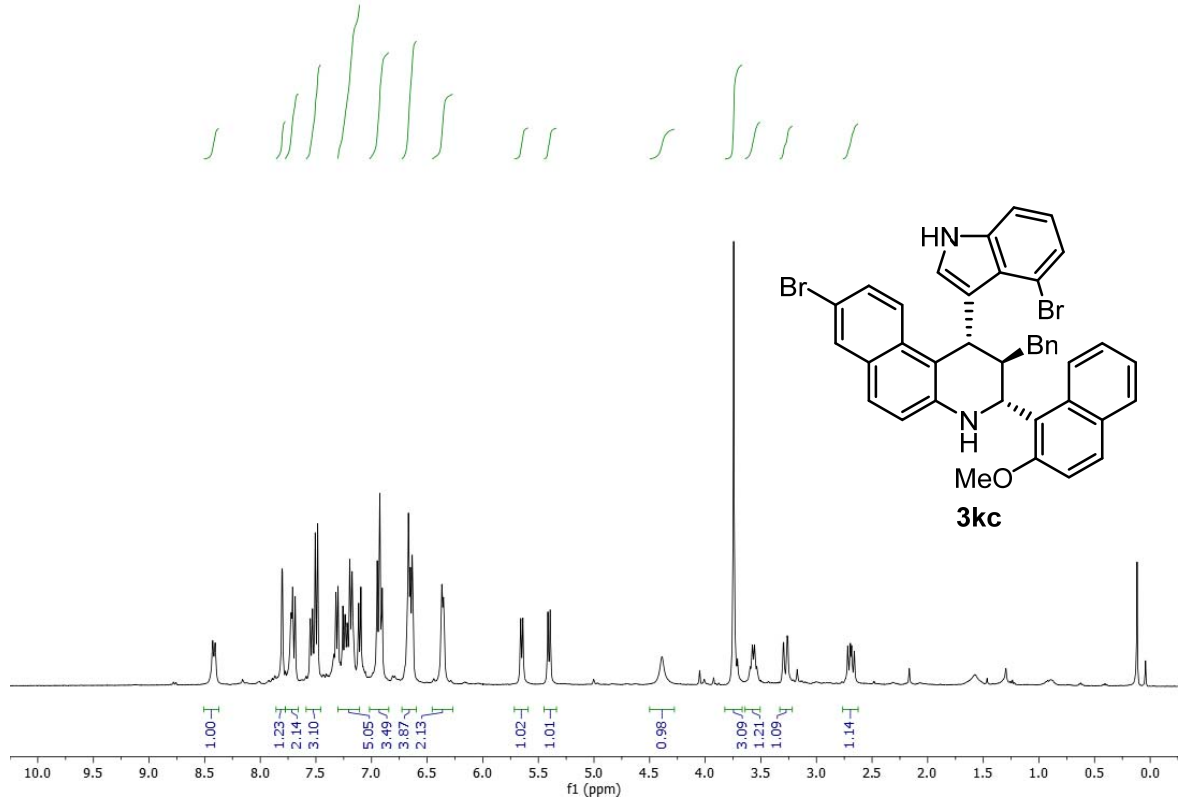


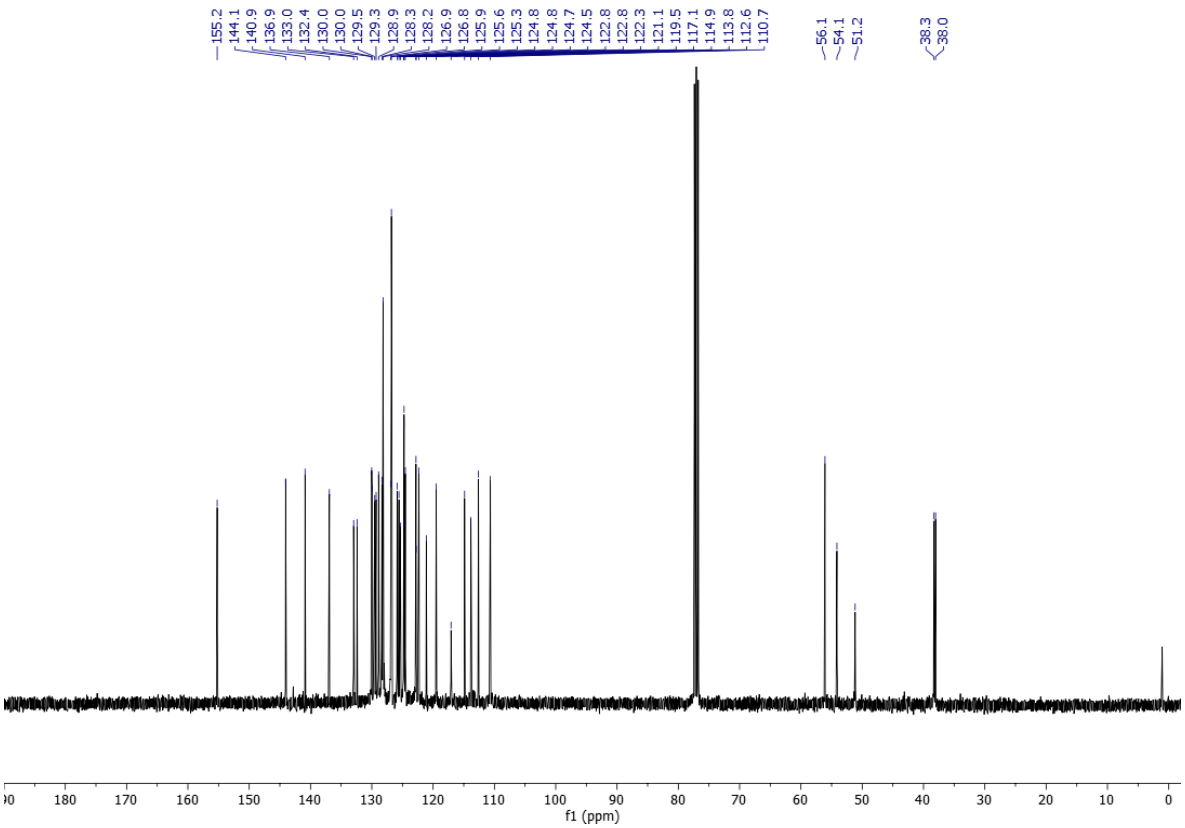
(*1R*,*2S*,*3S*)-2-benzyl-1-(4-methyl-1*H*-indol-3-yl)-3-phenyl-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3bj



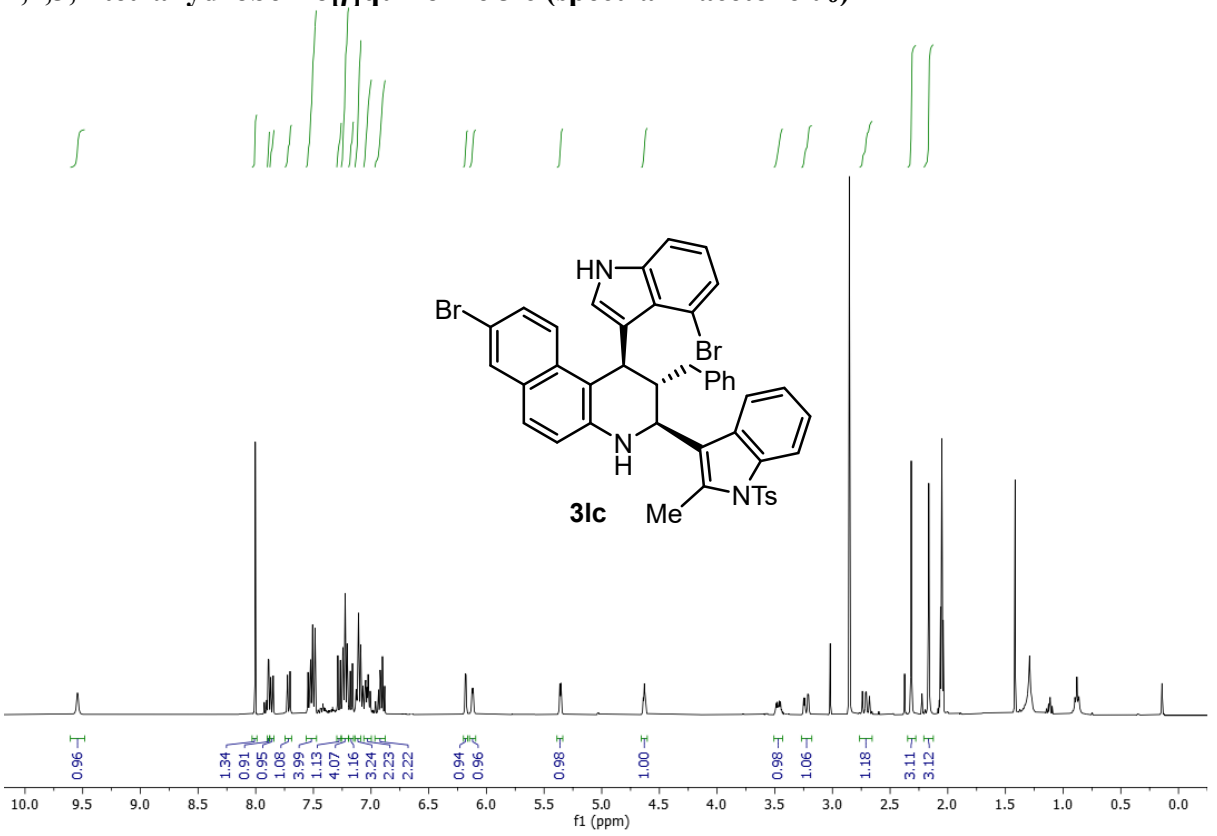


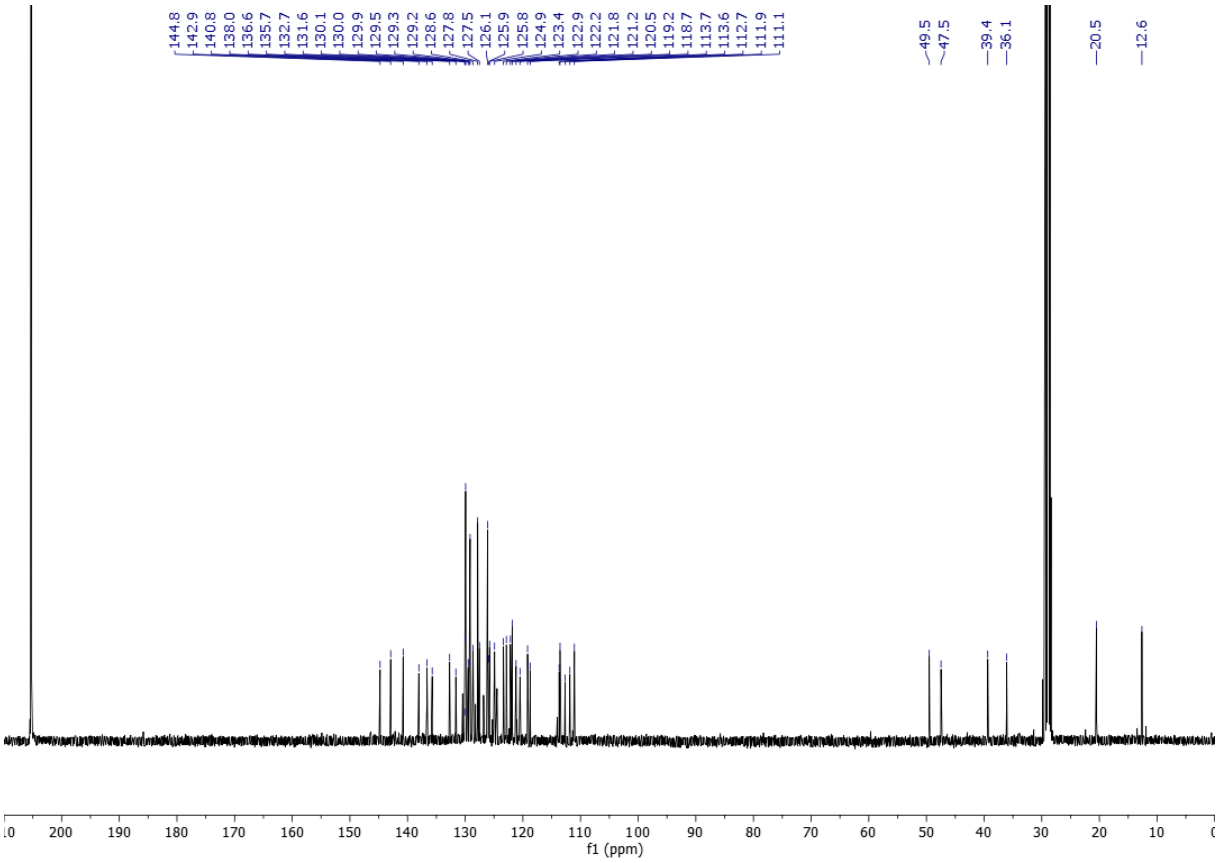
(1*S*,2*R*,3*R*)-2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(2-methoxynaphthalen-1-yl)-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3kc





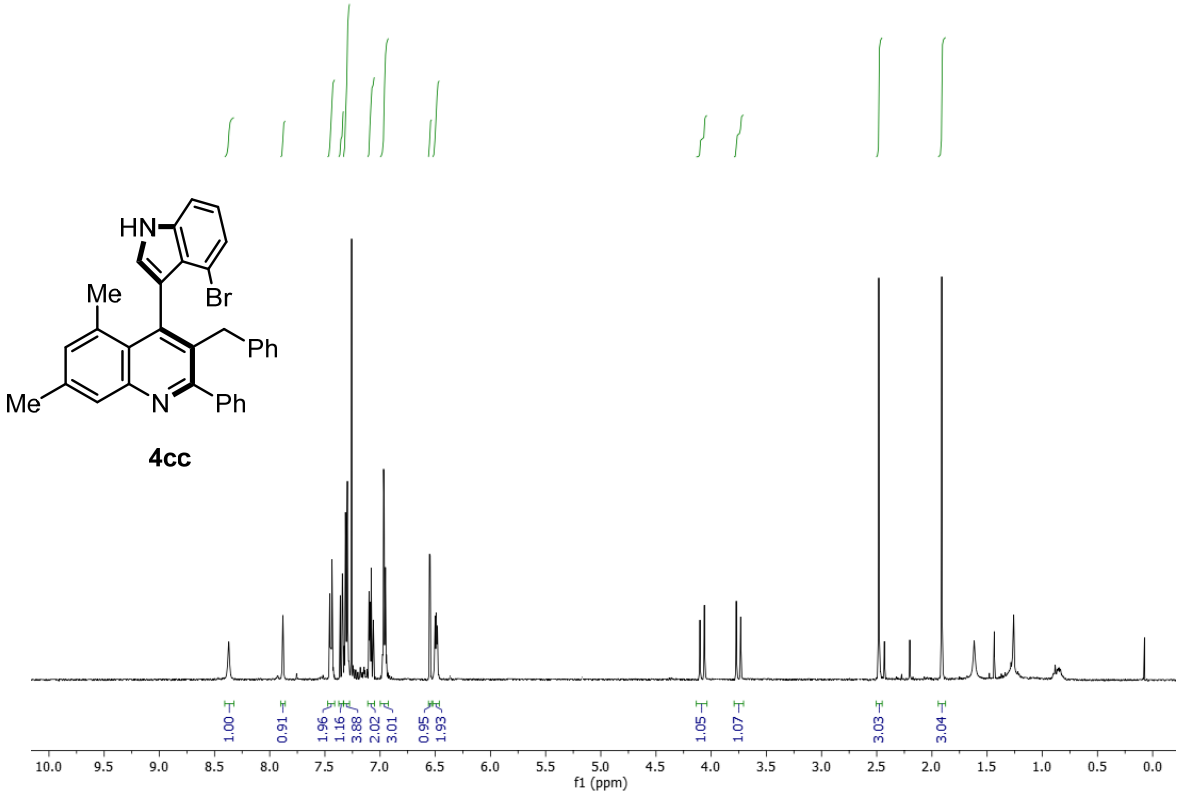
(1*R*,2*S*,3*S*)-2-benzyl-3-(2-methyl-1-tosyl-1*H*-indol-3-yl)-1-(4-methyl-1*H*-indol-3-yl)-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3lc (spectra in acetone-d_6)

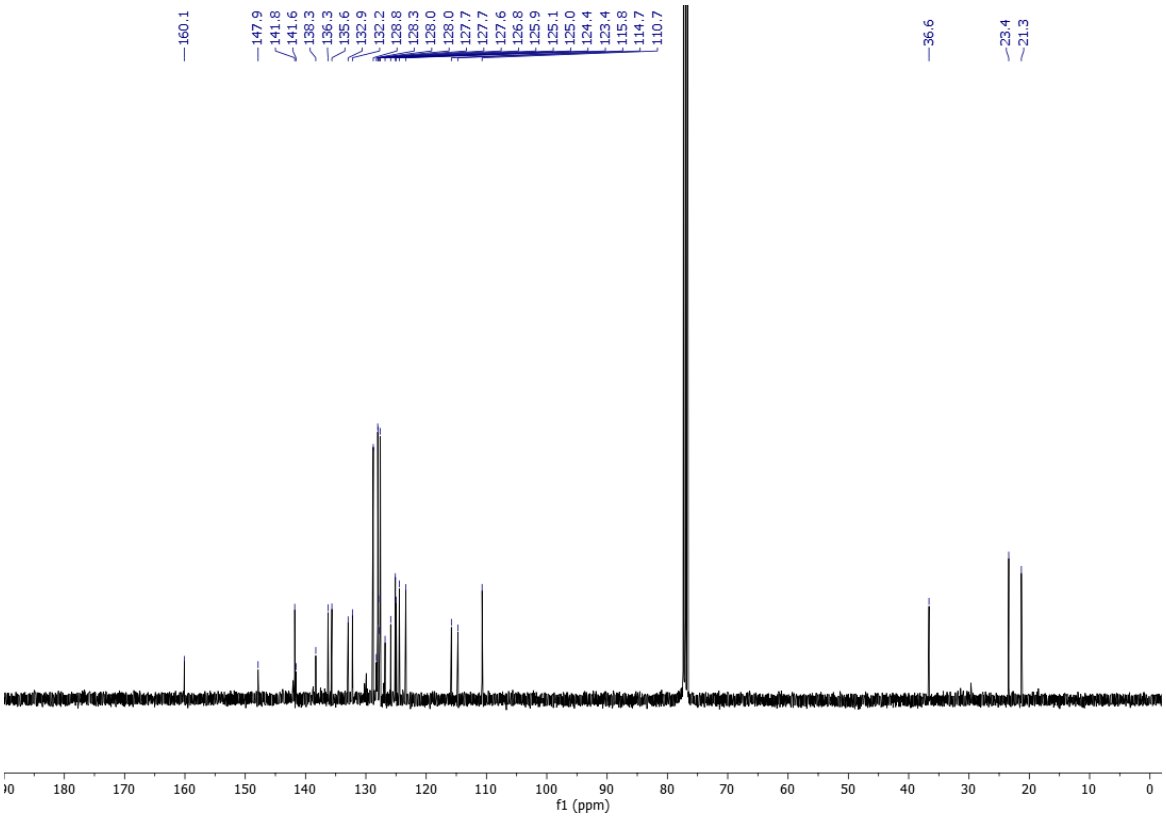




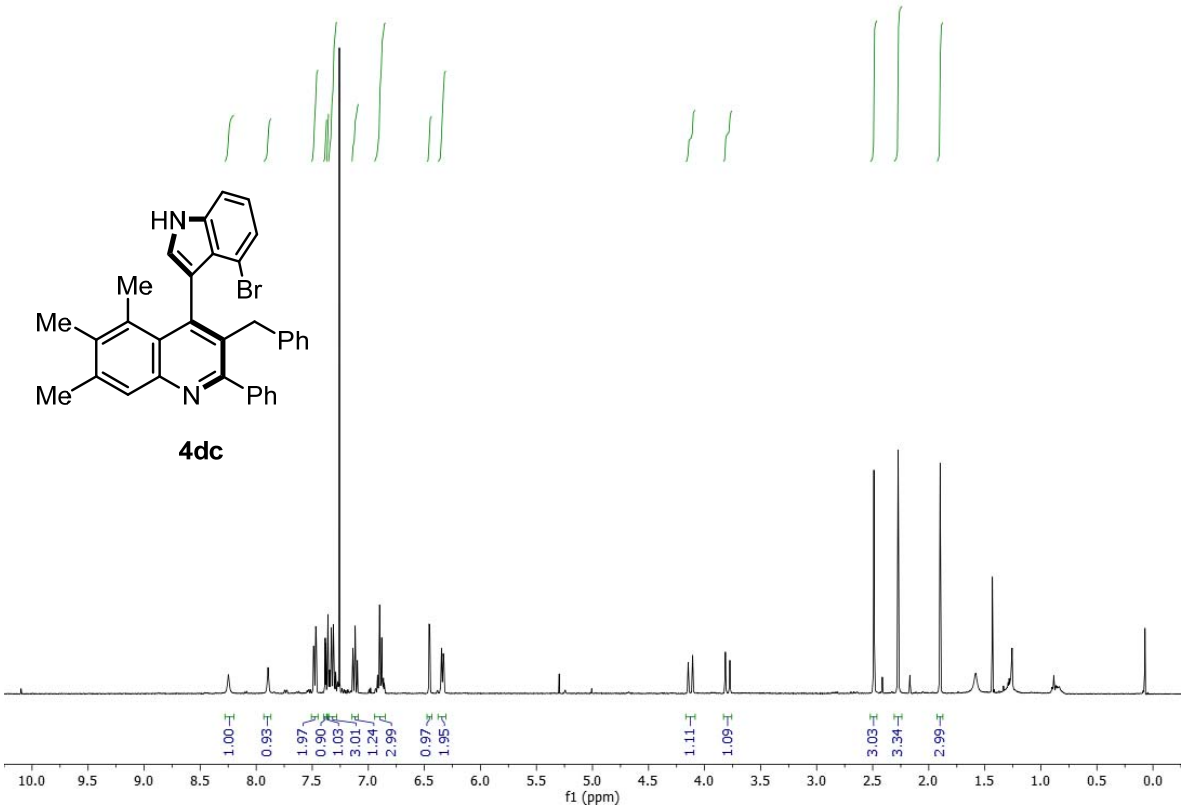
Copies of ^{1}H and ^{13}C NMR spectra of compounds 4 (in $CDCl_3$ unless otherwise stated)

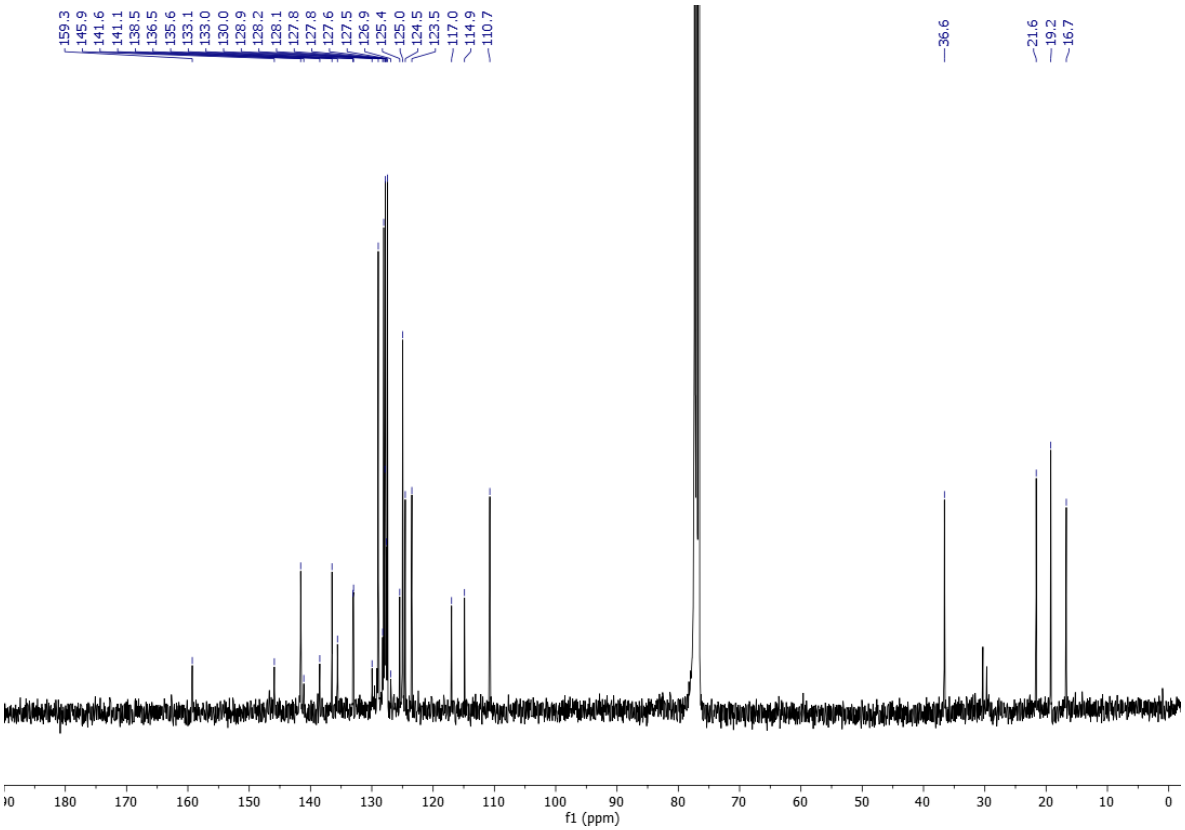
(*aS*)-3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-5,7-dimethyl-2-phenylquinoline 4cc



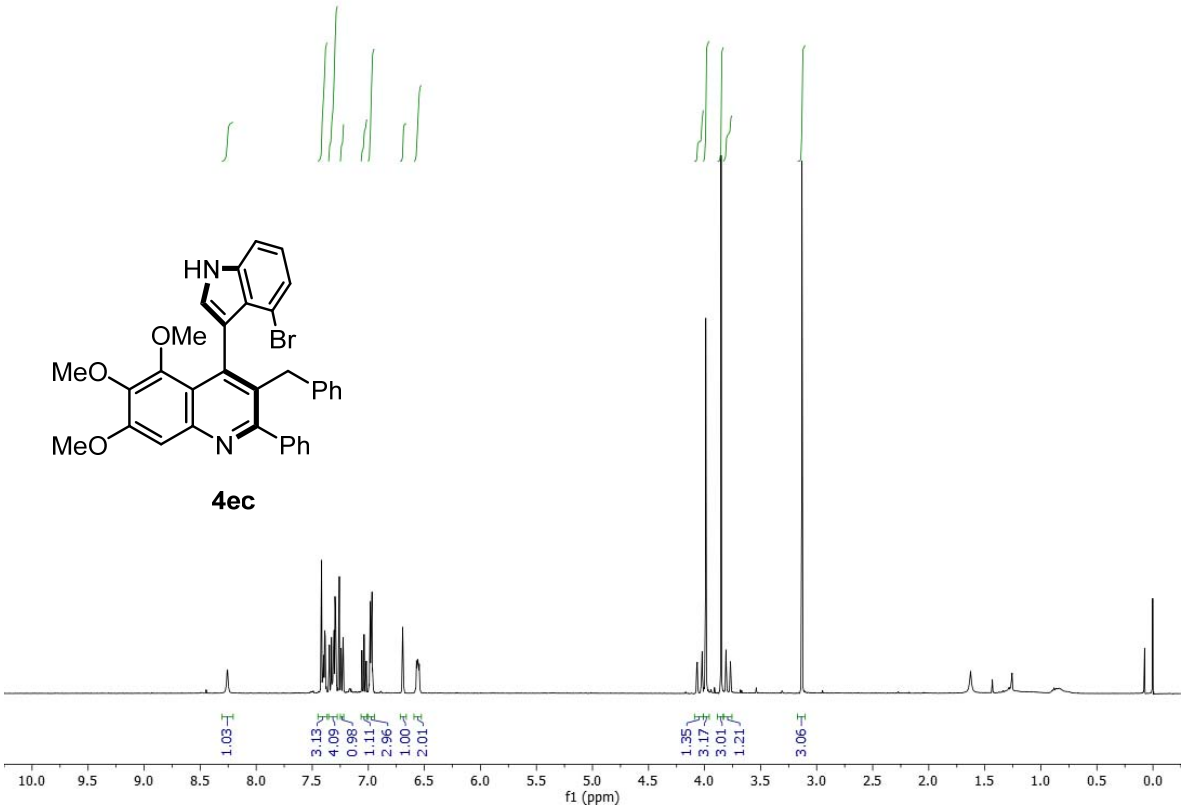


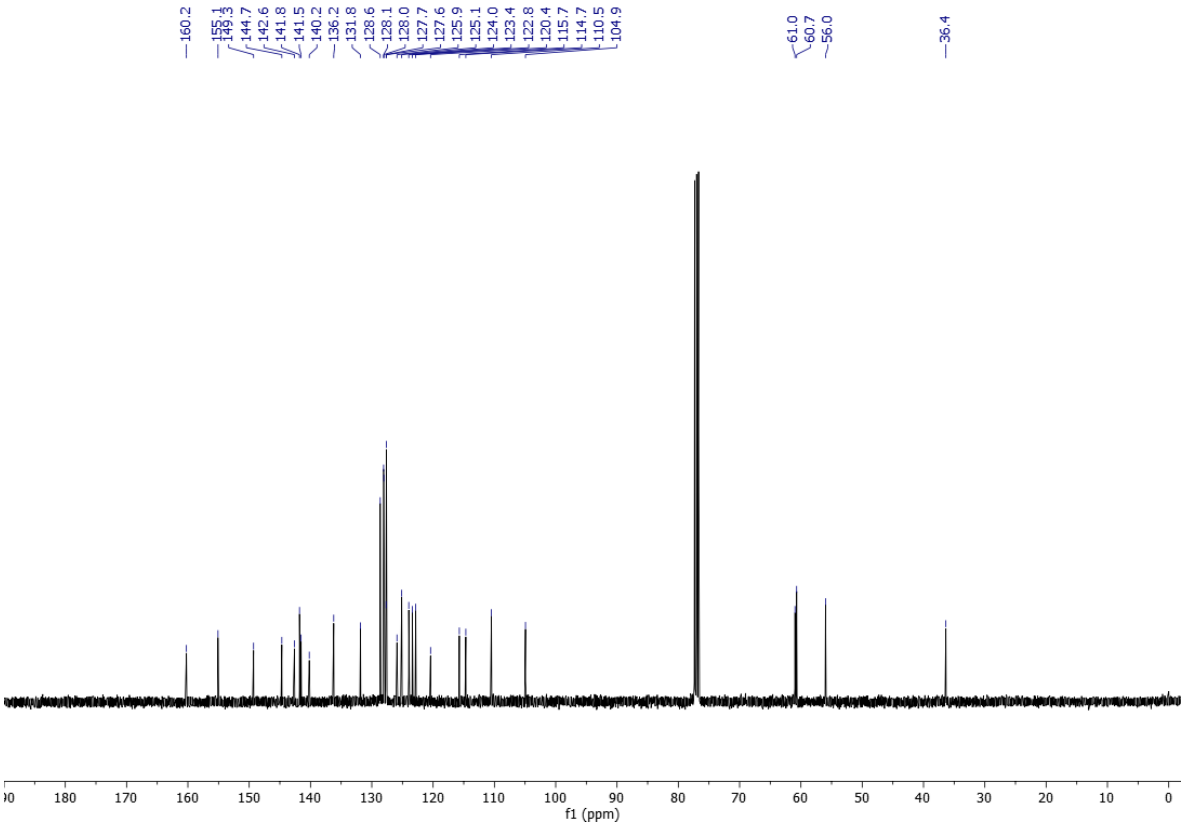
(*aS*)-3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-5,6,7-trimethyl-2-phenylquinoline 4dc



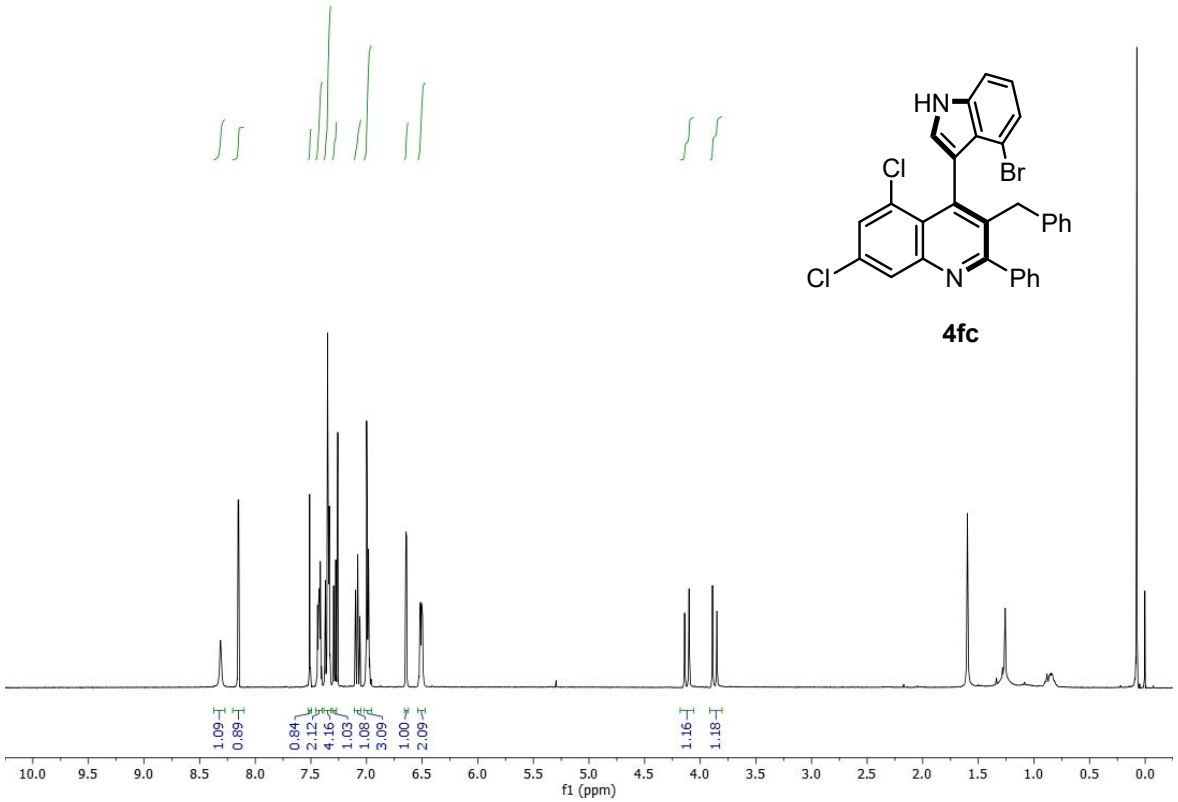


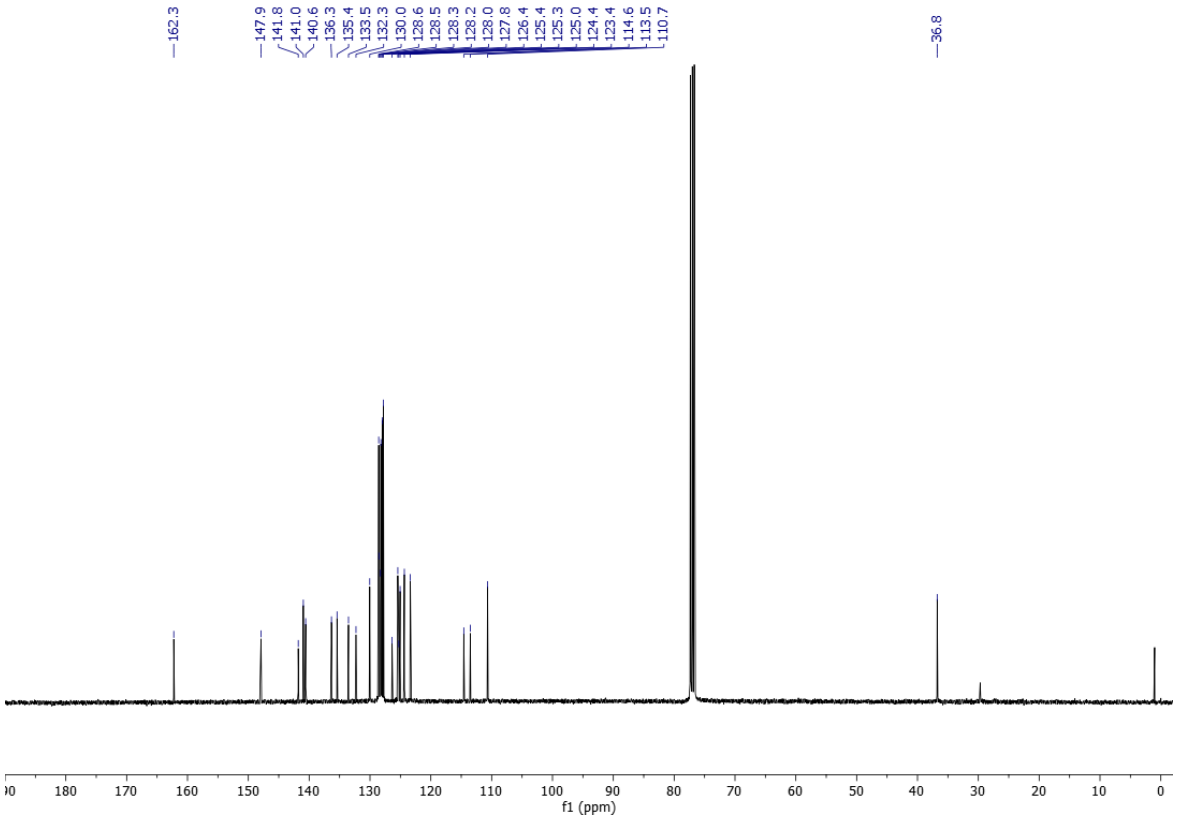
(*aS*)-3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-5,6,7-trimethoxy-2-phenylquinoline 4ec



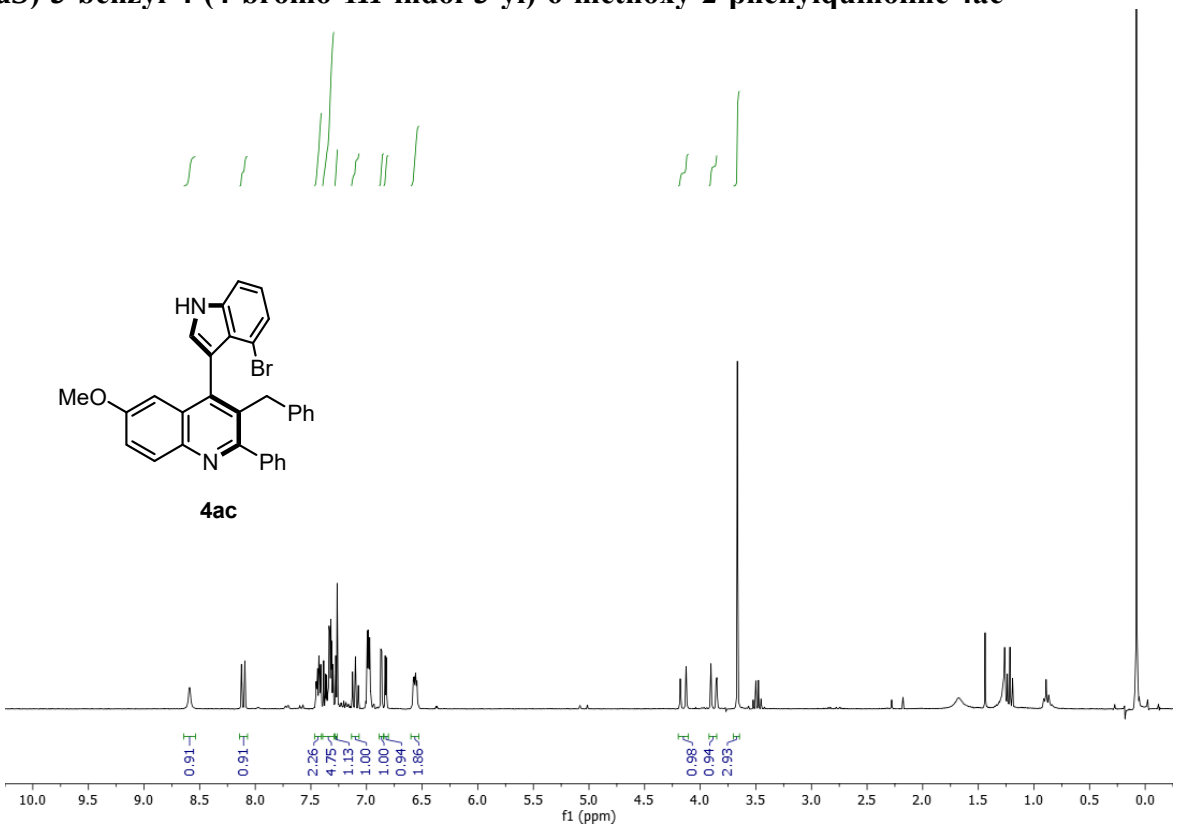


(*aS*)-3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-5,7-dichloro-2-phenylquinoline 4fc

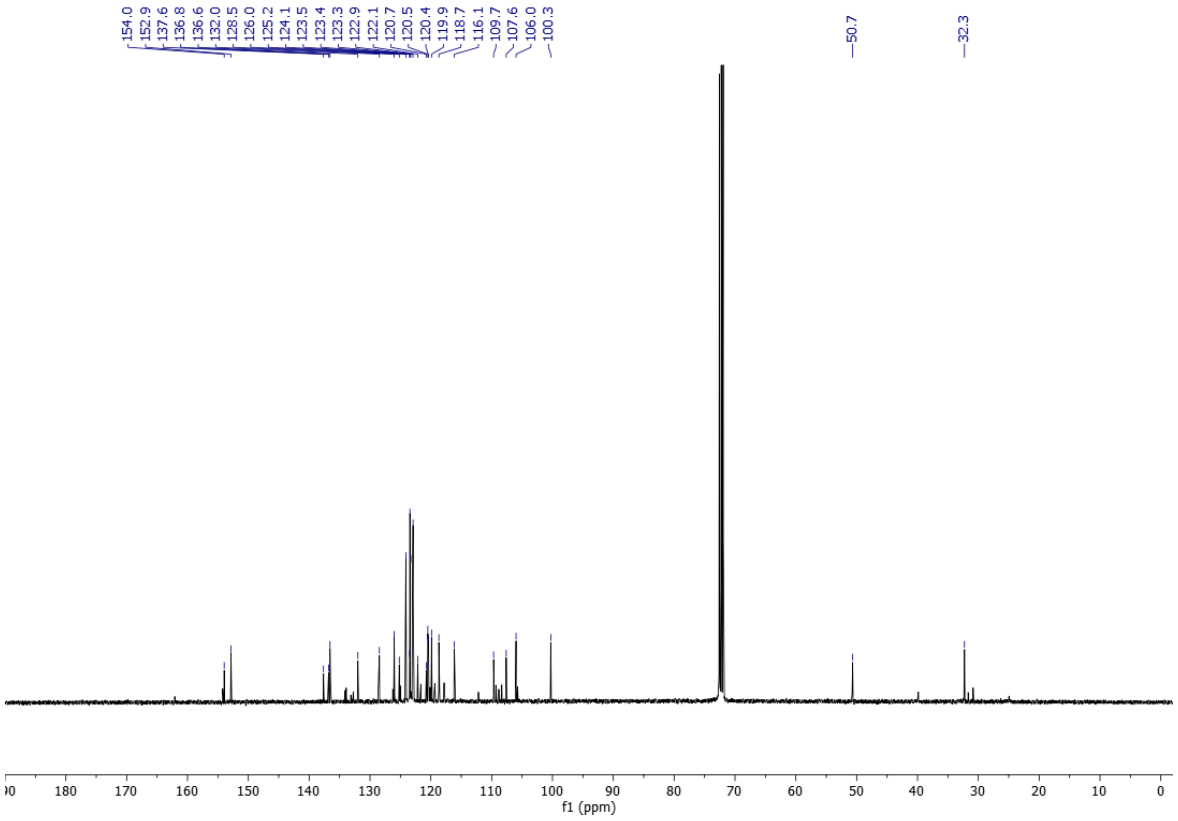




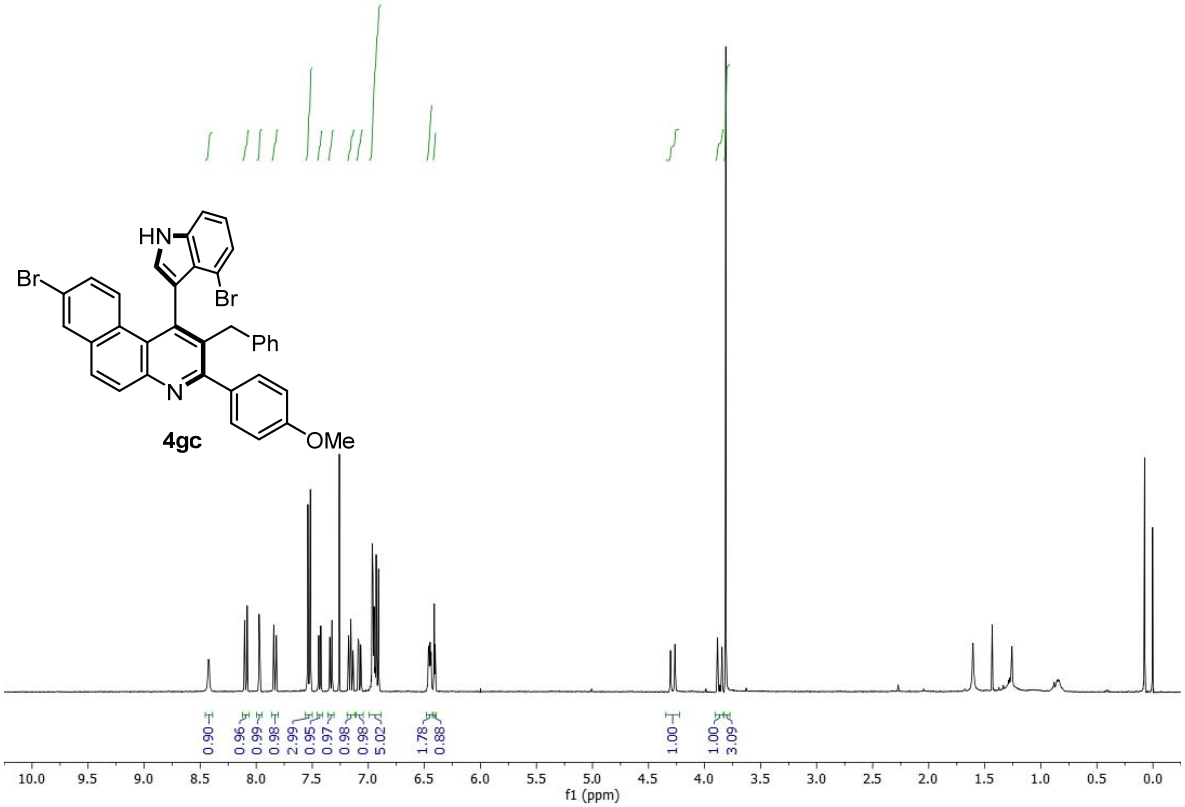
(*aS*)-3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-6-methoxy-2-phenylquinoline 4ac

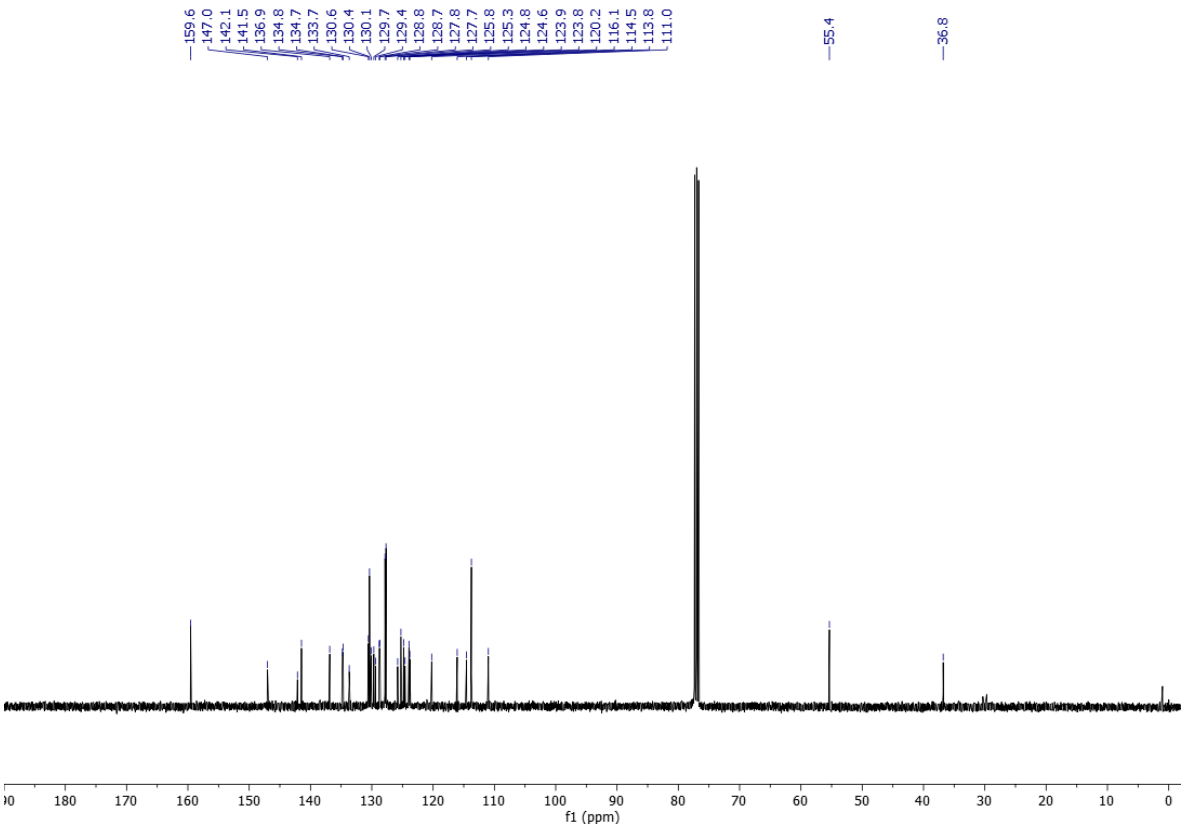


4ac

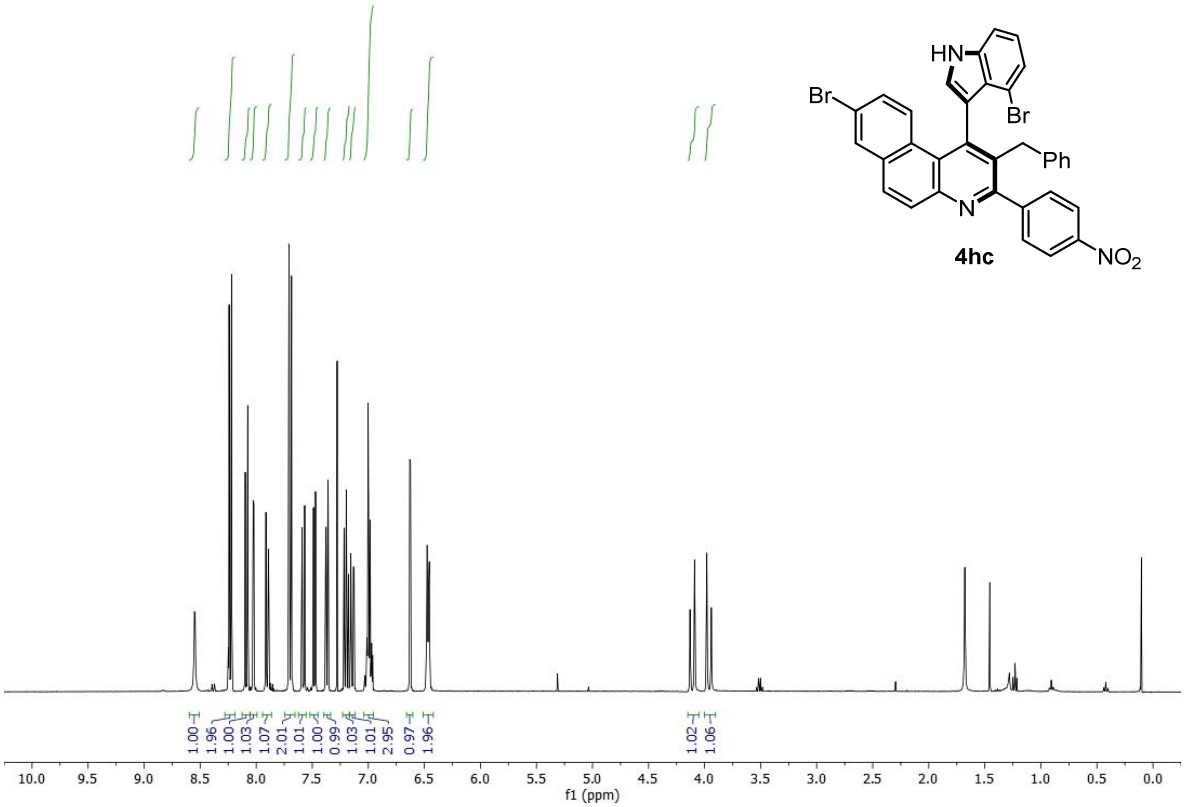


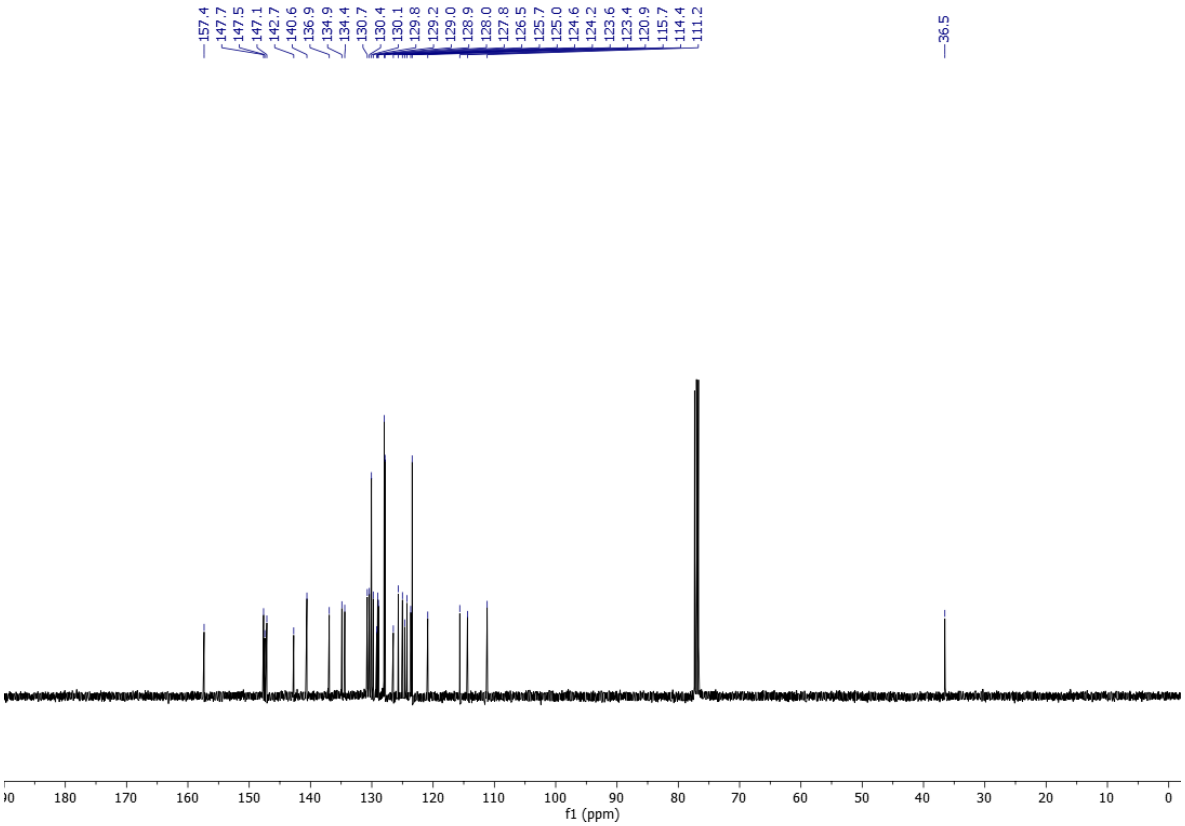
(*aS*)-2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(4-methoxyphenyl)benzo[*f*]quinoline 4gc



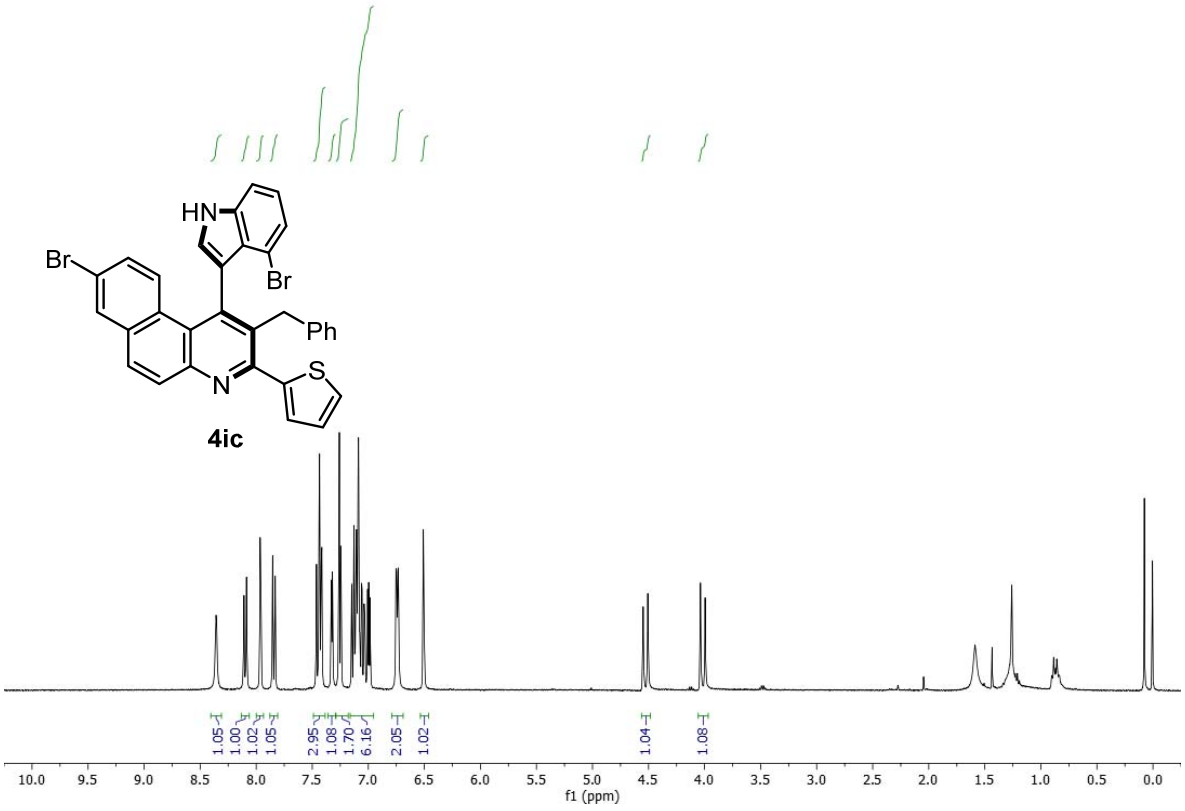


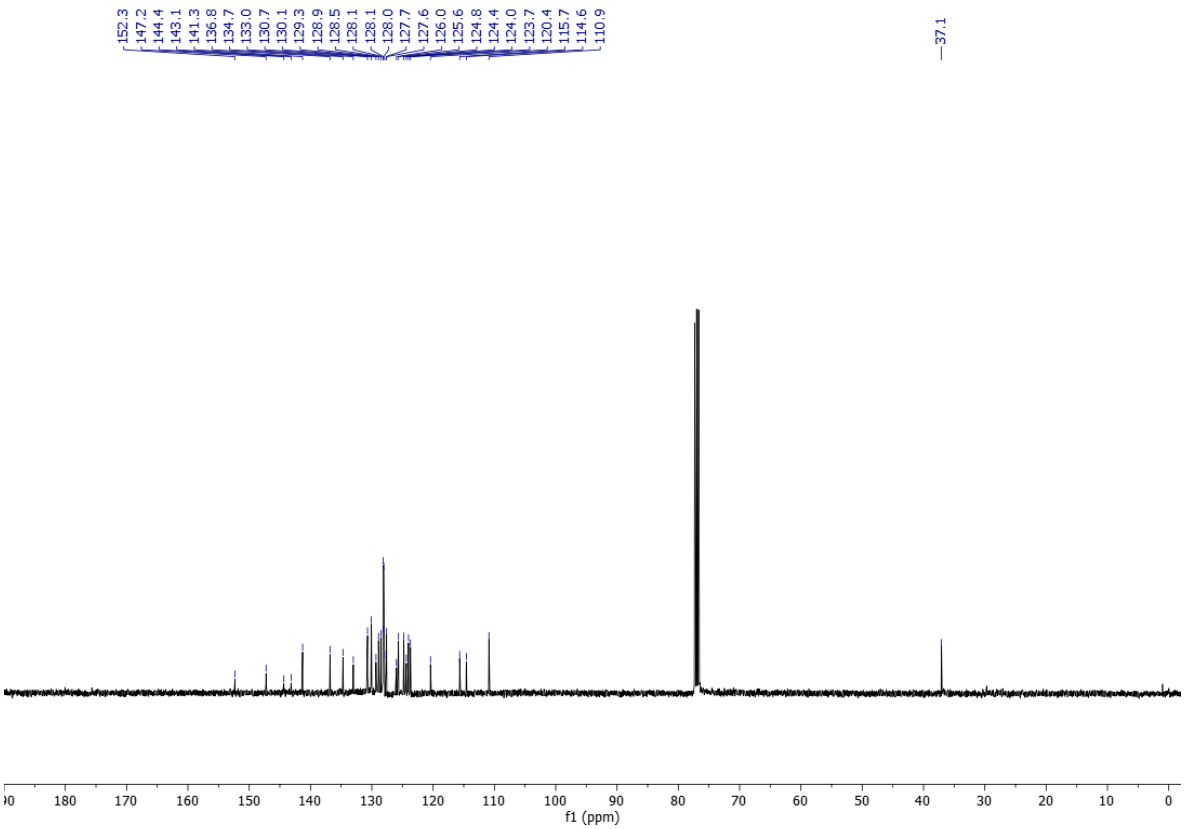
(*aS*)-2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(4-nitrophenyl)benzo[*f*]quinoline 4hc



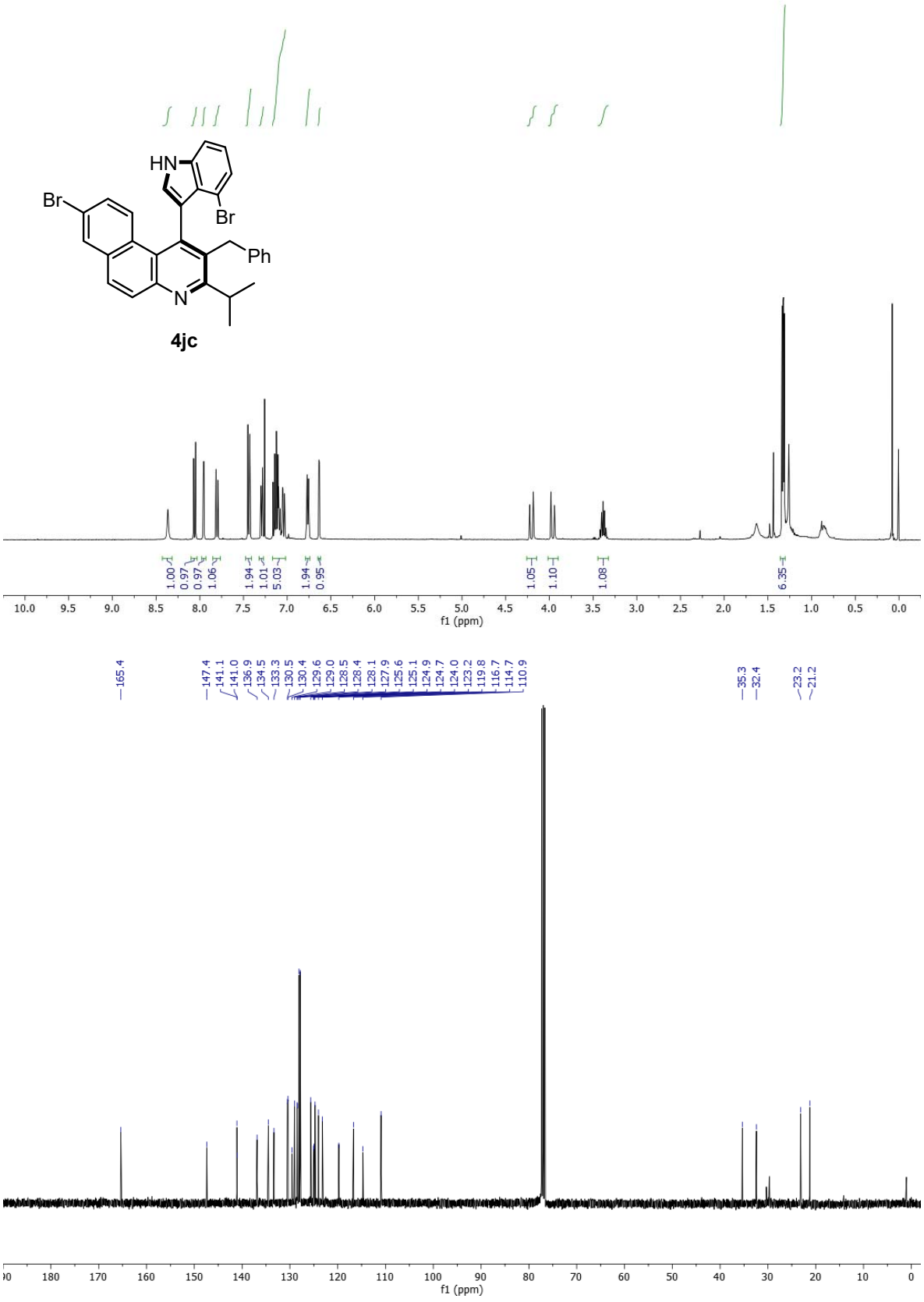


(*aS*)-2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(thiophen-2-yl)benzo[*f*]quinoline 4ic

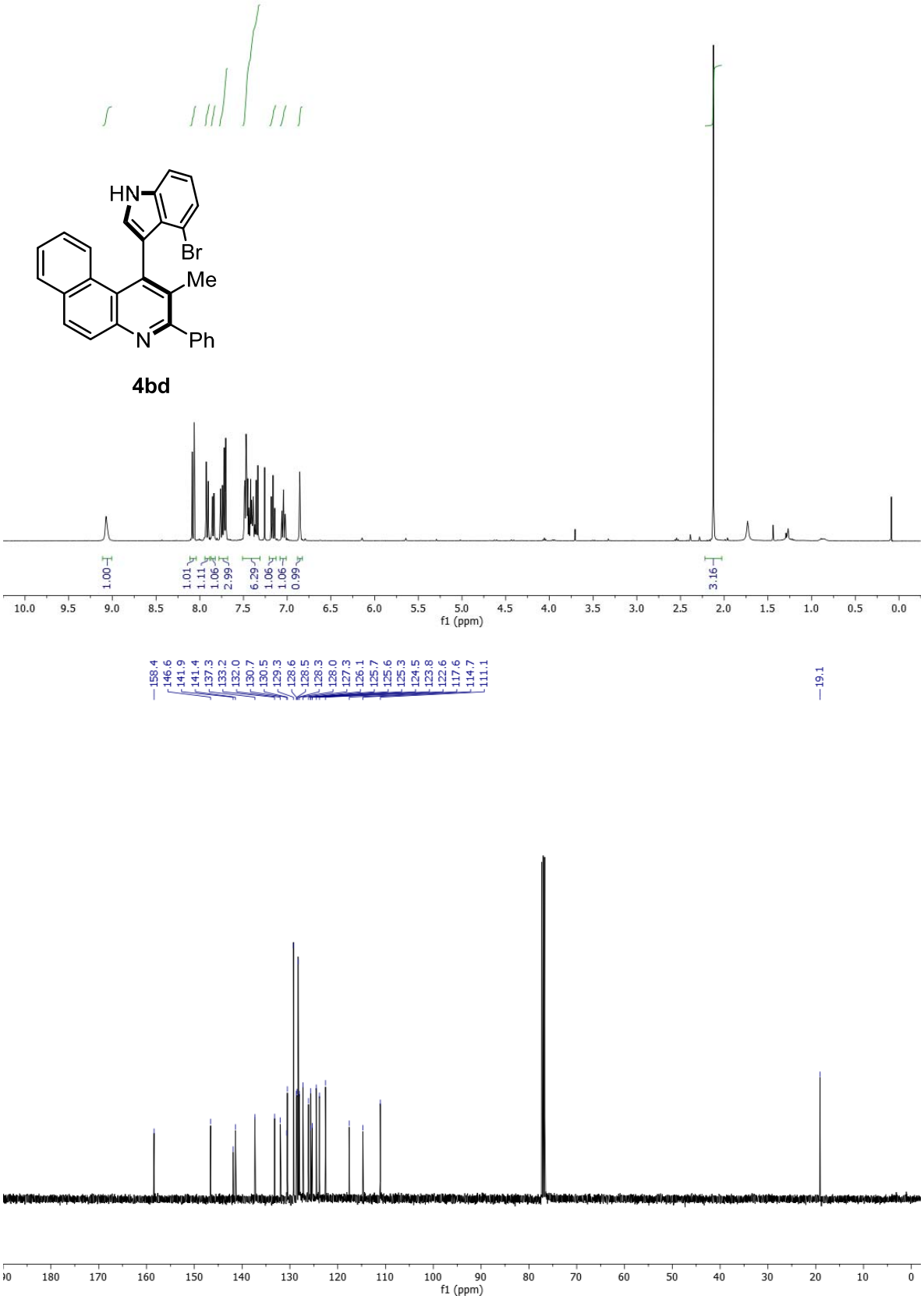




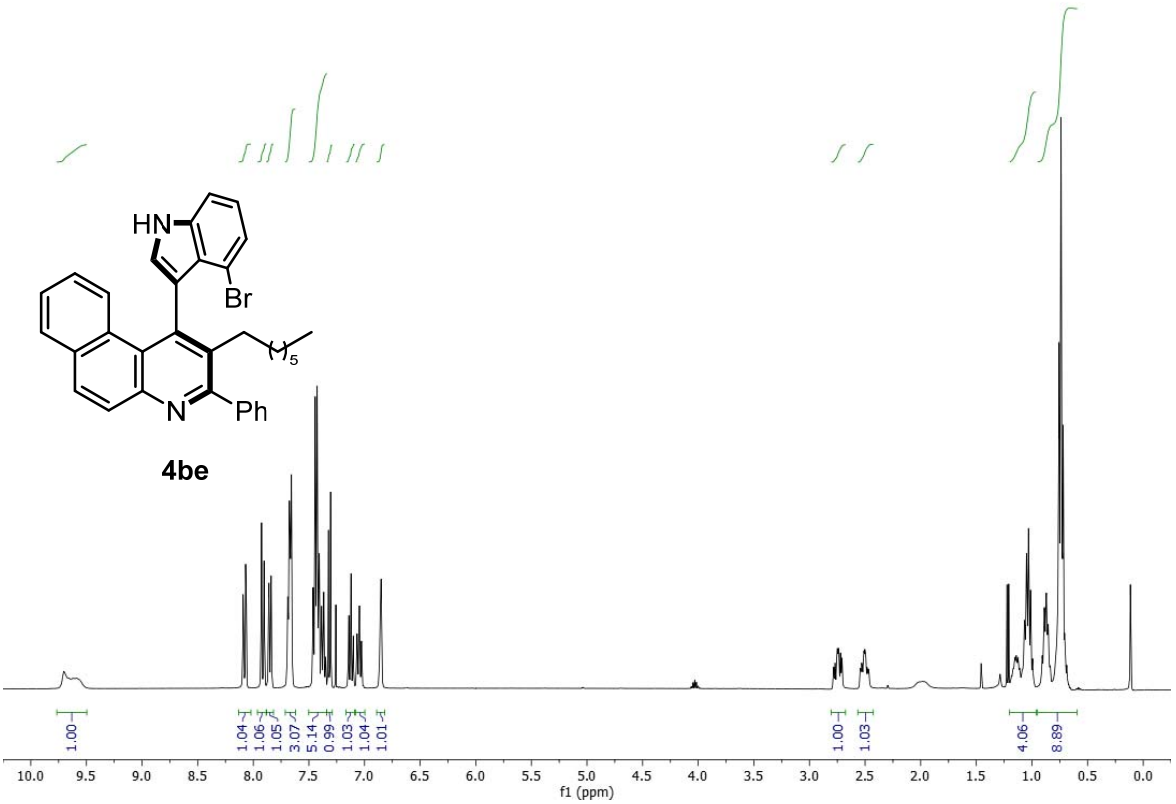
(*aS*)-2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-isopropylbenzo[*f*]quinoline 4jc

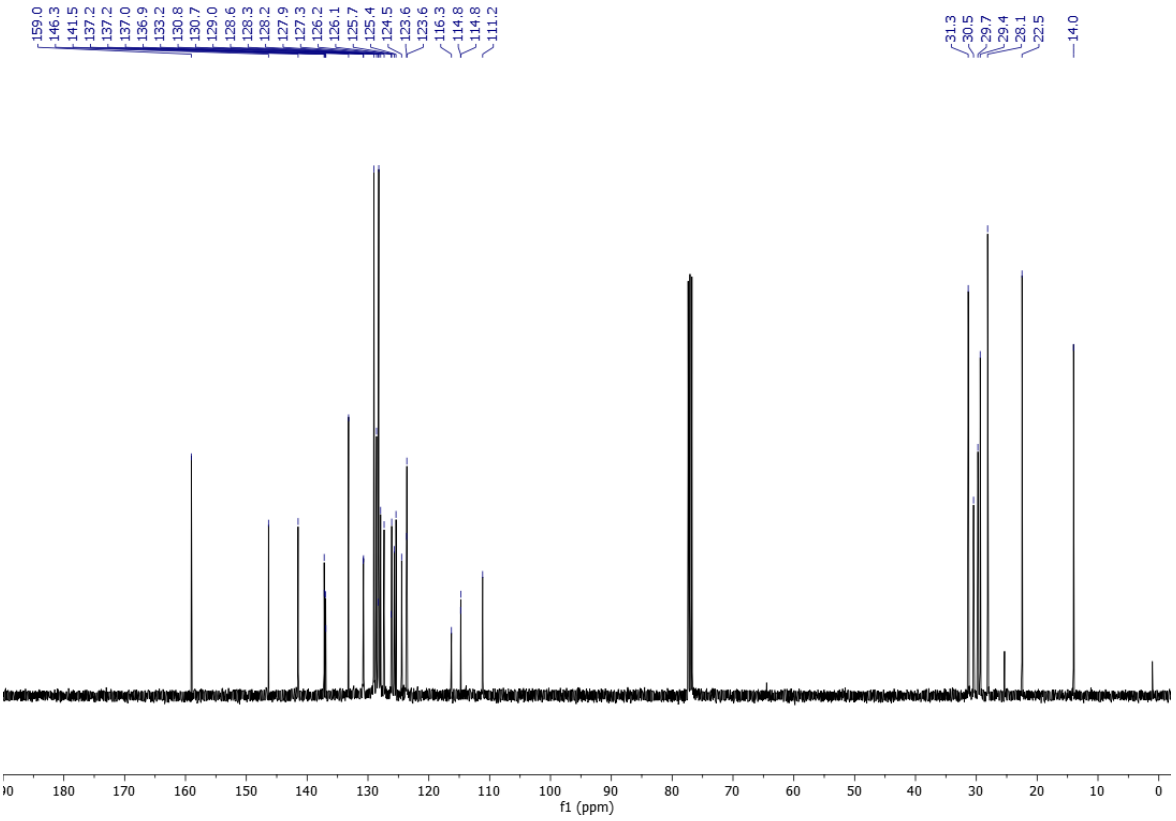


(*aS*)-1-(4-bromo-1*H*-indol-3-yl)-2-methyl-3-phenylbenzo[*f*]quinoline 4bd

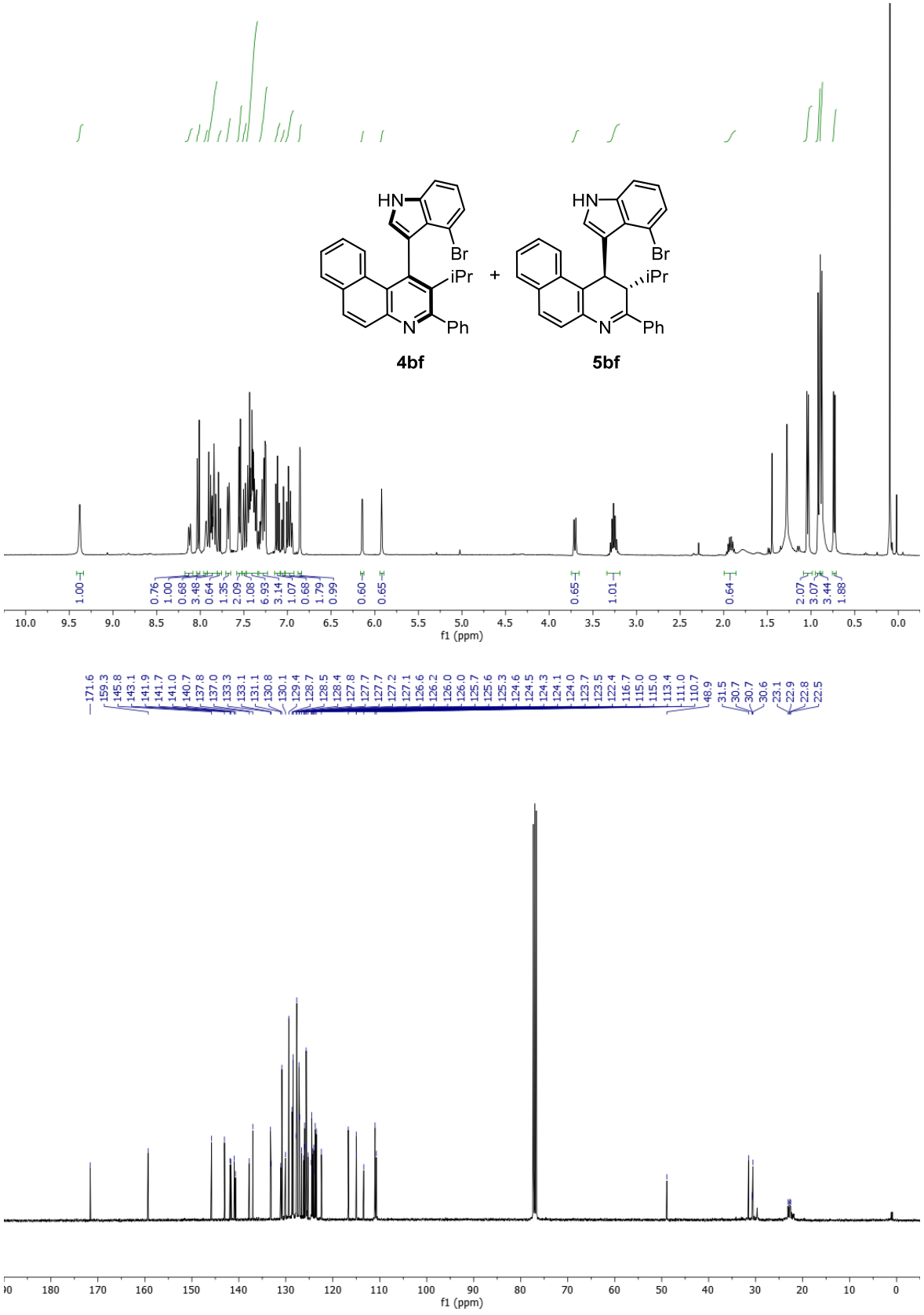


(*aS*)-1-(4-bromo-1*H*-indol-3-yl)-2-heptyl-3-phenylbenzo[*f*]quinoline 4be

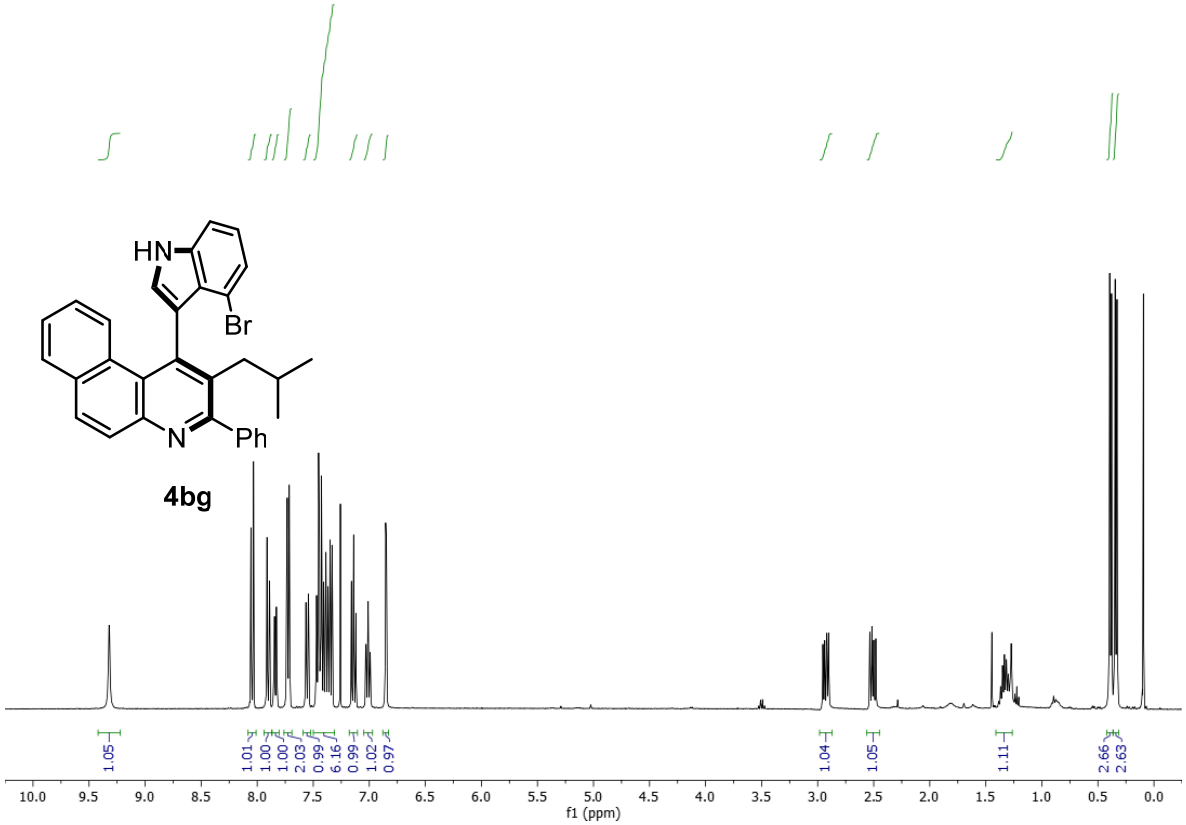


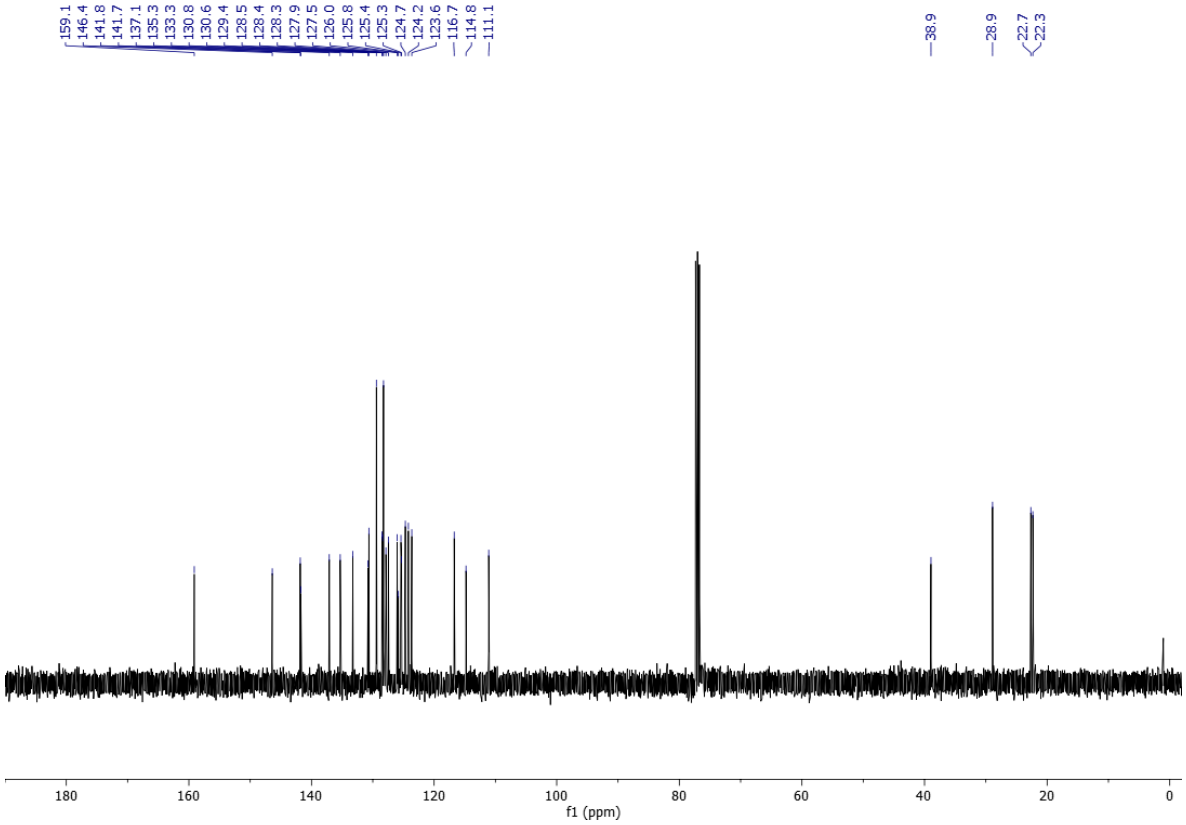


(*aS*)-1-(4-bromo-1*H*-indol-3-yl)-2-isopropyl-3-phenylbenzo[*f*]quinoline 4bf and (1*R*,2*S*)-1-(4-bromo-1*H*-indol-3-yl)-2-isopropyl-3-phenyl-1,2-dihydrobenzo[*f*]quinoline 5bf

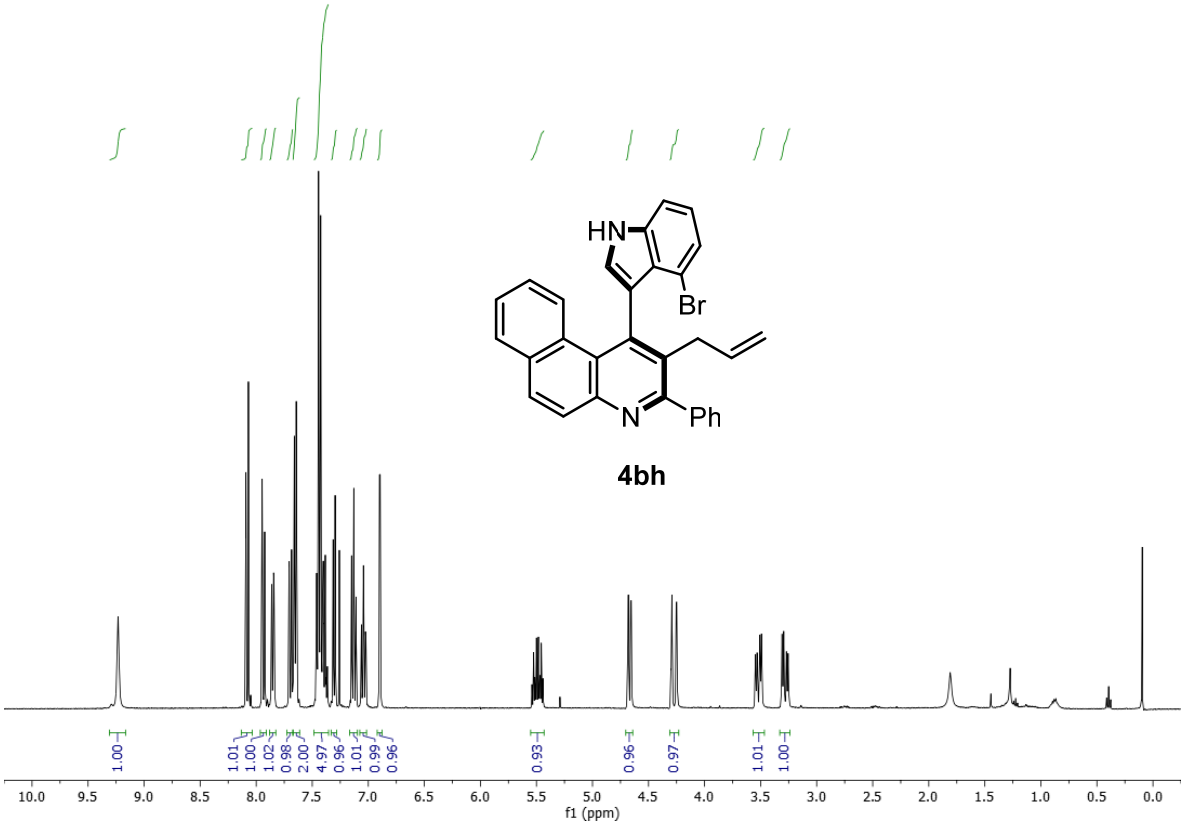


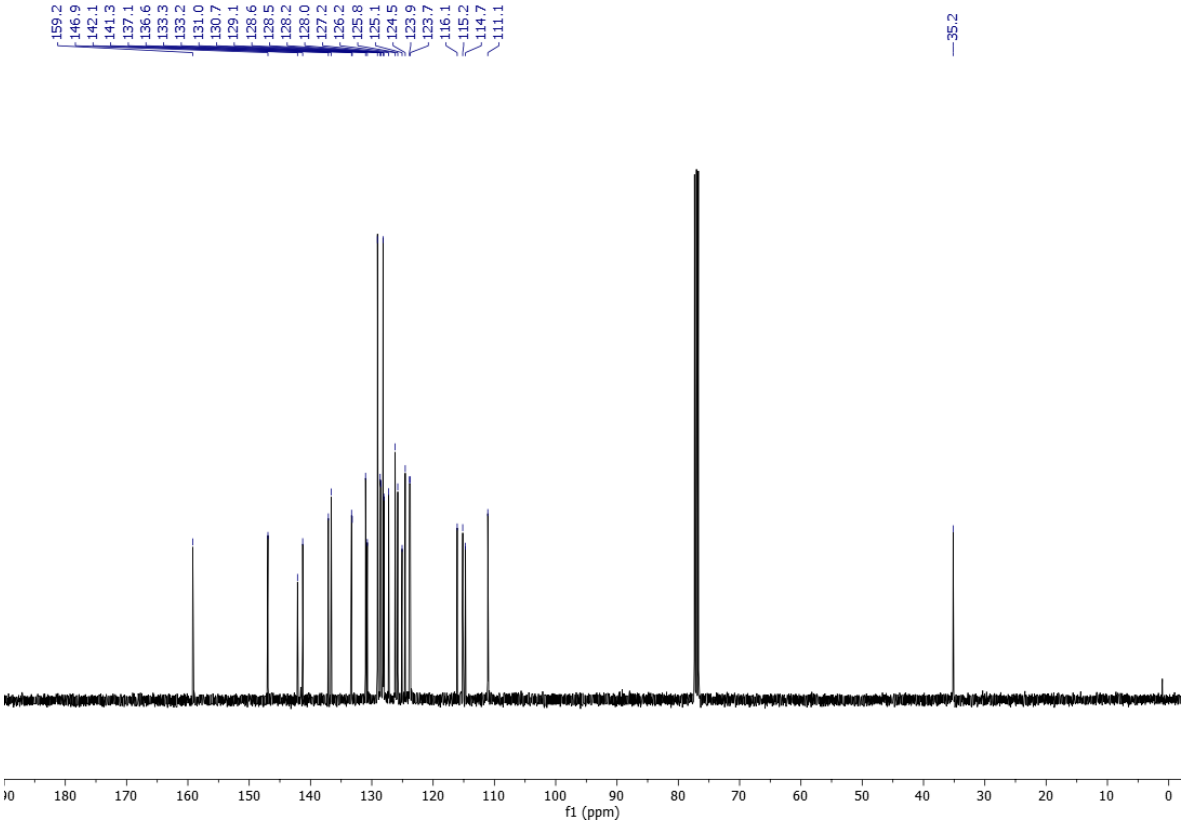
(*aS*)-1-(4-bromo-1*H*-indol-3-yl)-2-isobutyl-3-phenylbenzo[*f*]quinoline 4bg



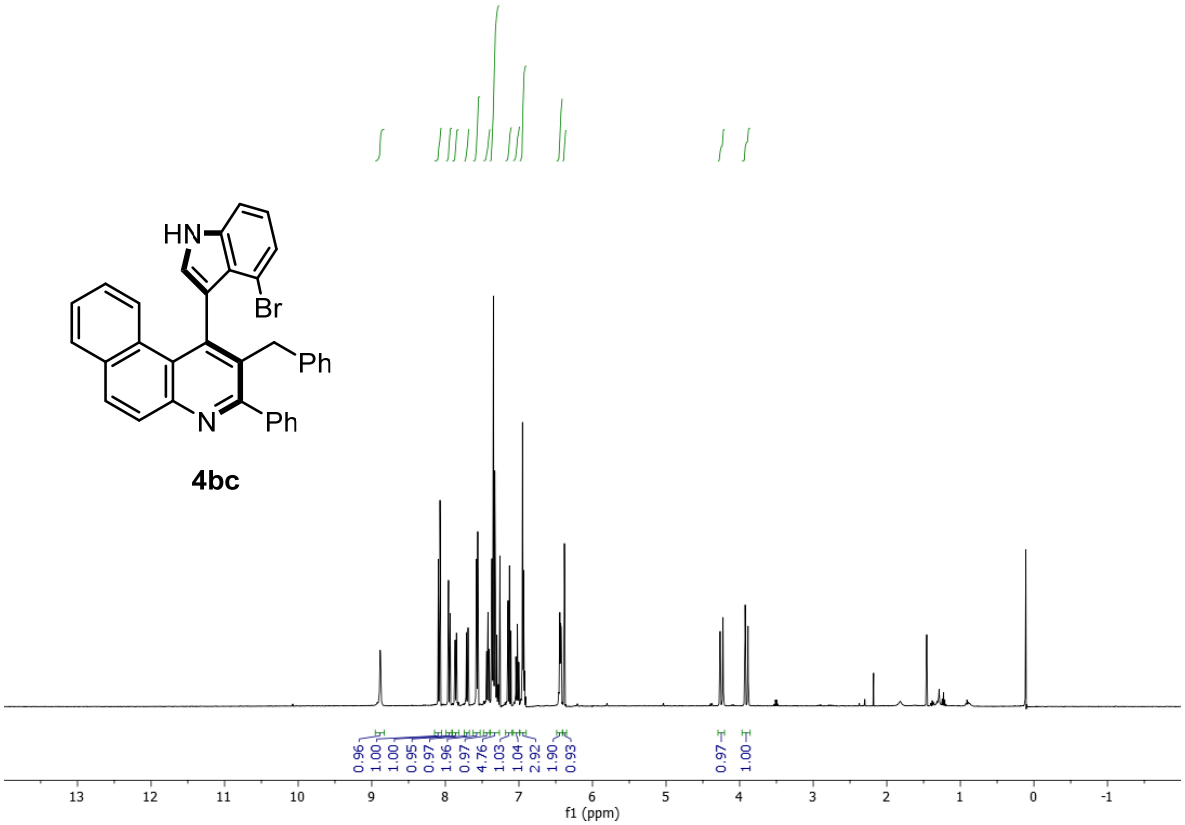


(*aS*)-2-allyl-1-(4-bromo-1*H*-indol-3-yl)-3-phenylbenzo[*f*]quinoline 4bh

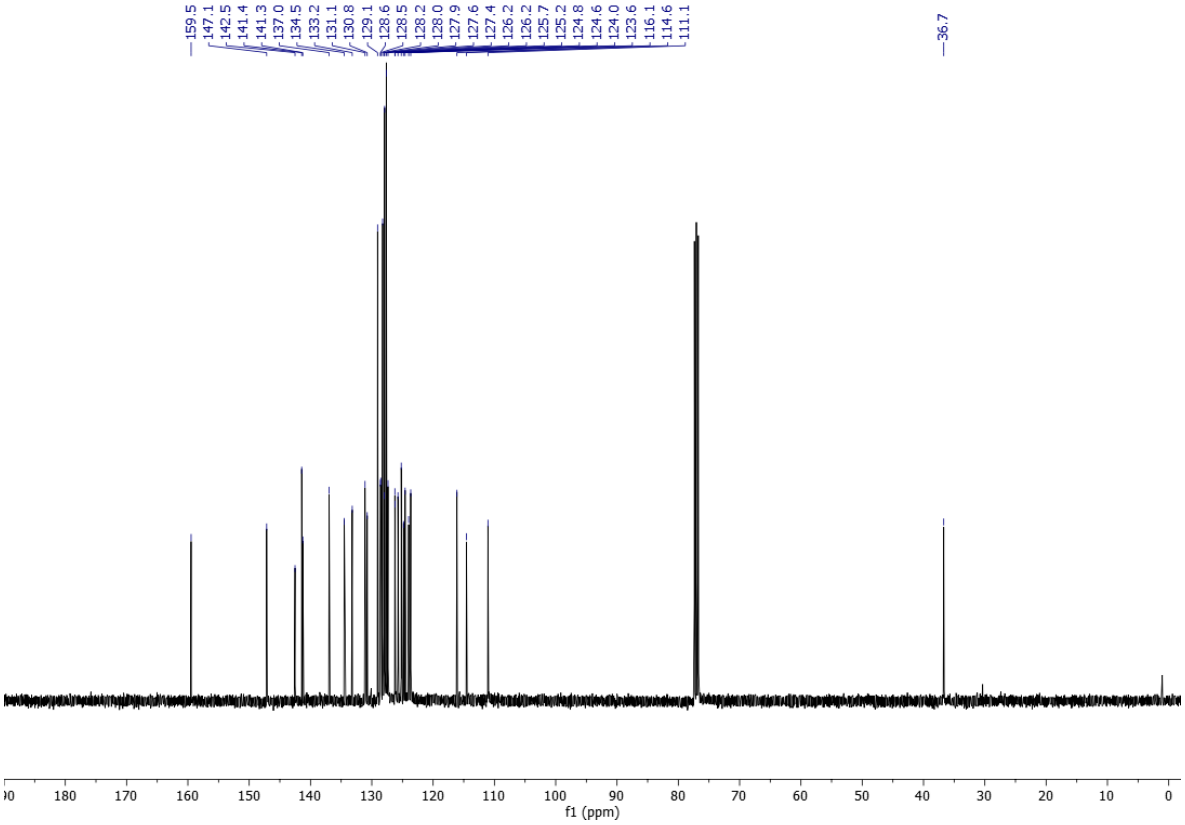




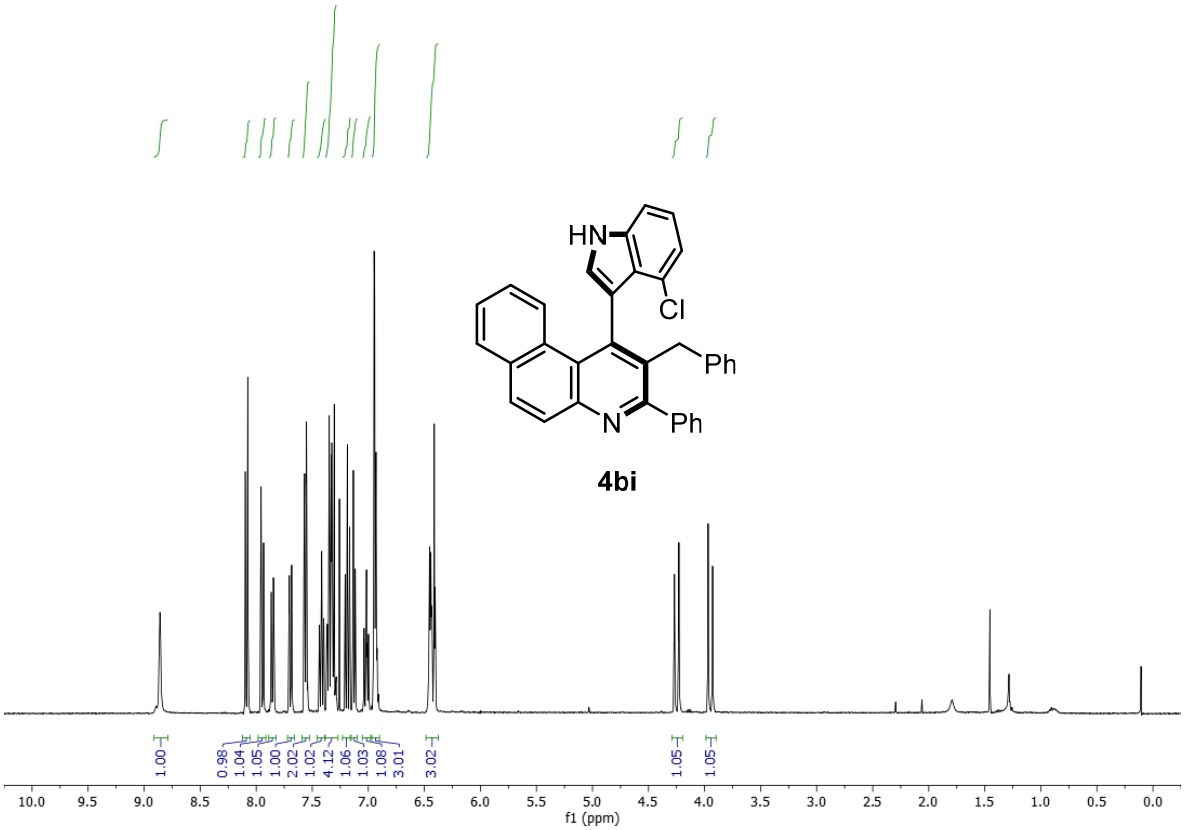
(*aS*)-2-benzyl-1-(4-bromo-1*H*-indol-3-yl)-3-phenylbenzo[*f*]quinoline 4bc

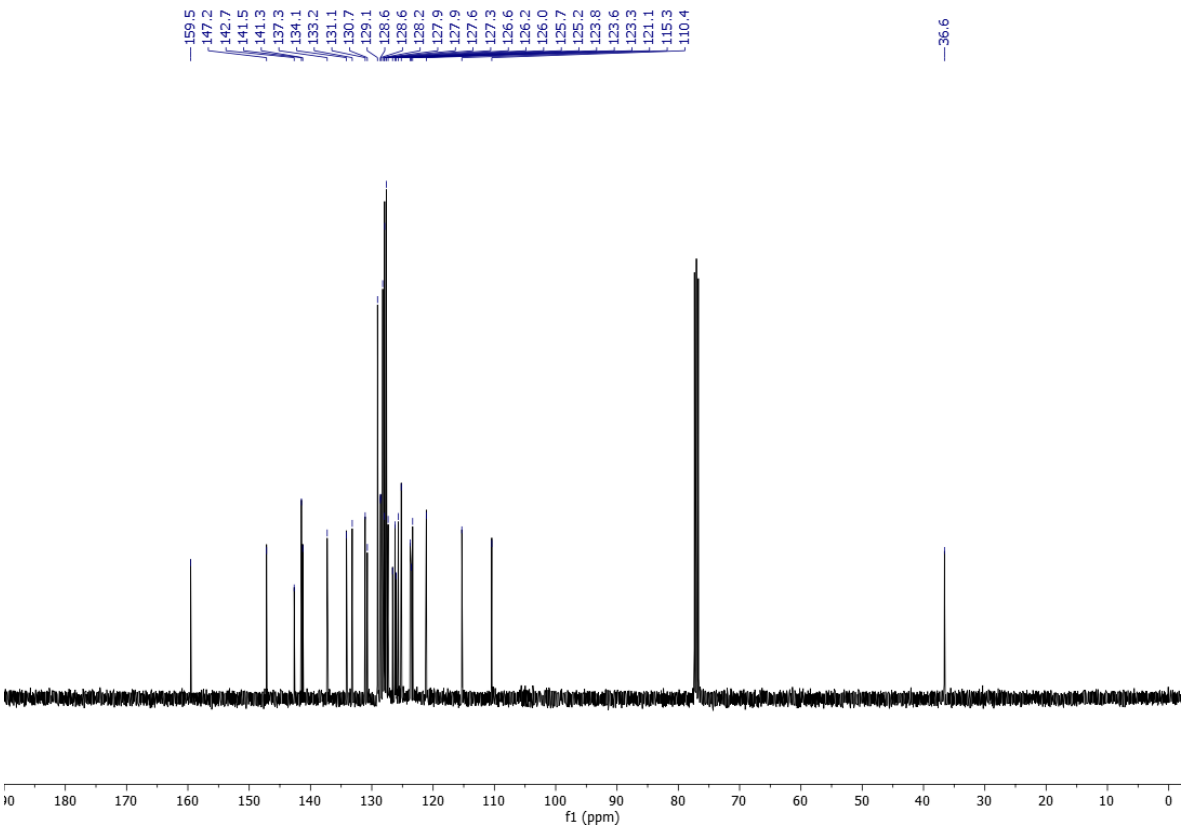


4bc

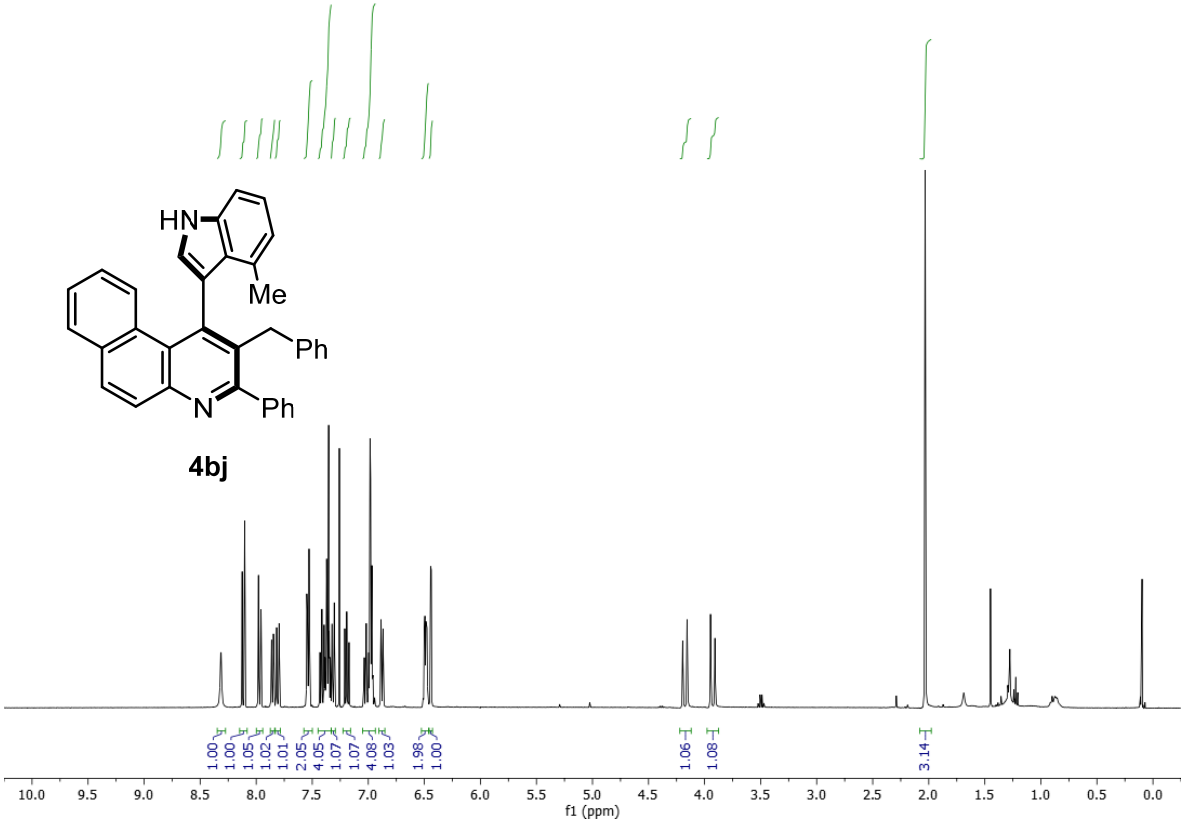


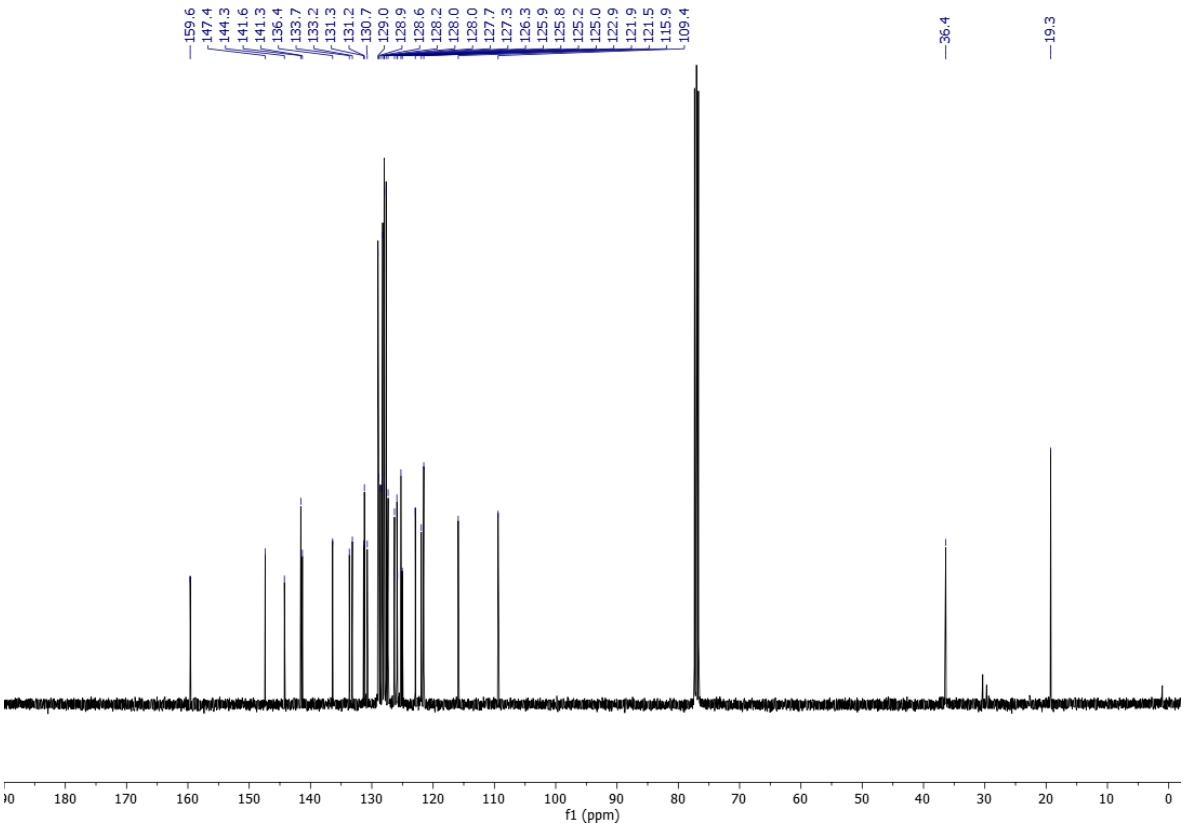
(*aS*)-2-benzyl-1-(4-chloro-1*H*-indol-3-yl)-3-phenylbenzo[*f*]quinoline 4bi



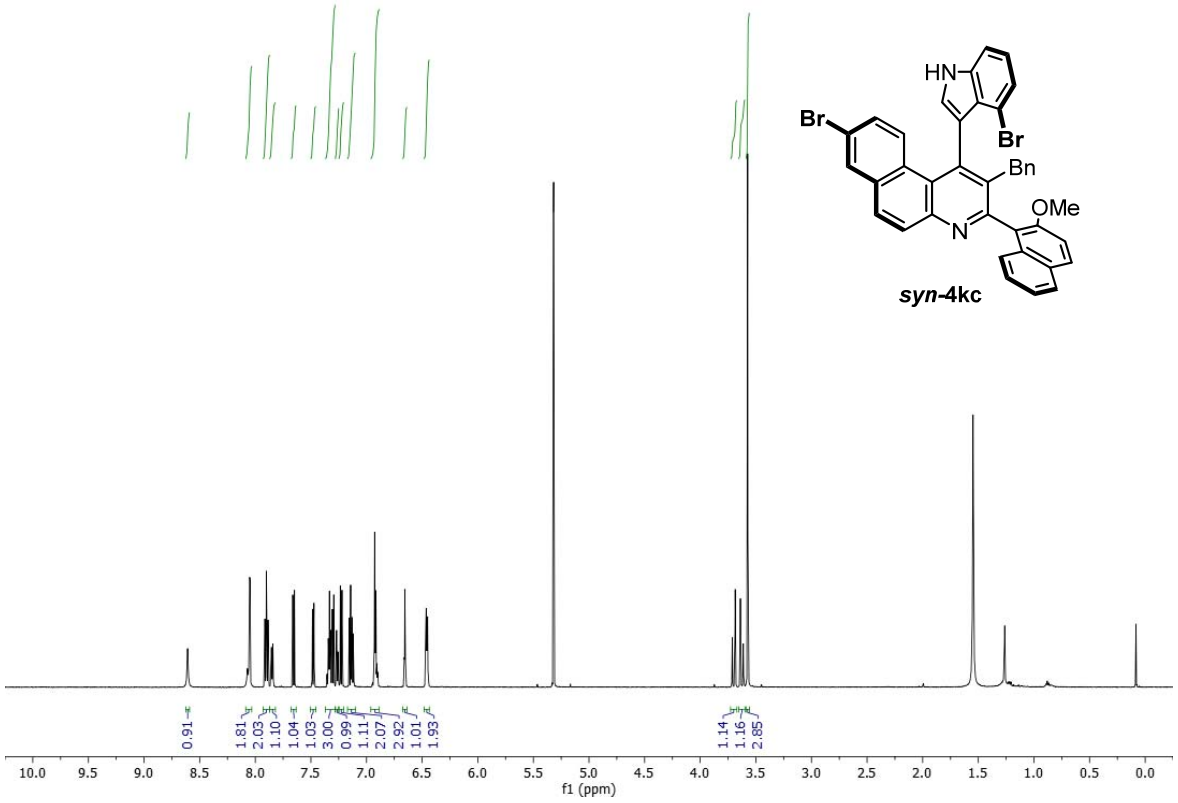


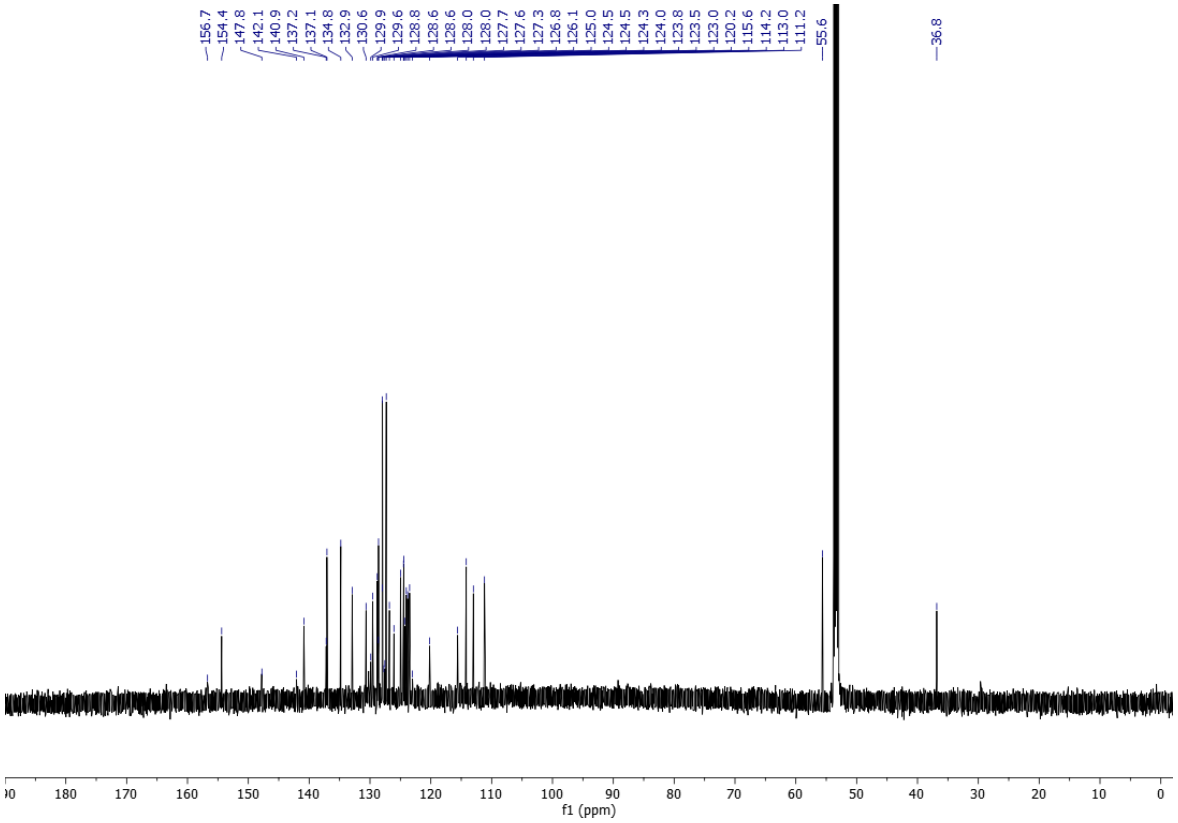
(*aS*)-2-benzyl-1-(4-methyl-1*H*-indol-3-yl)-3-phenylbenzo[*f*]quinoline 4bj



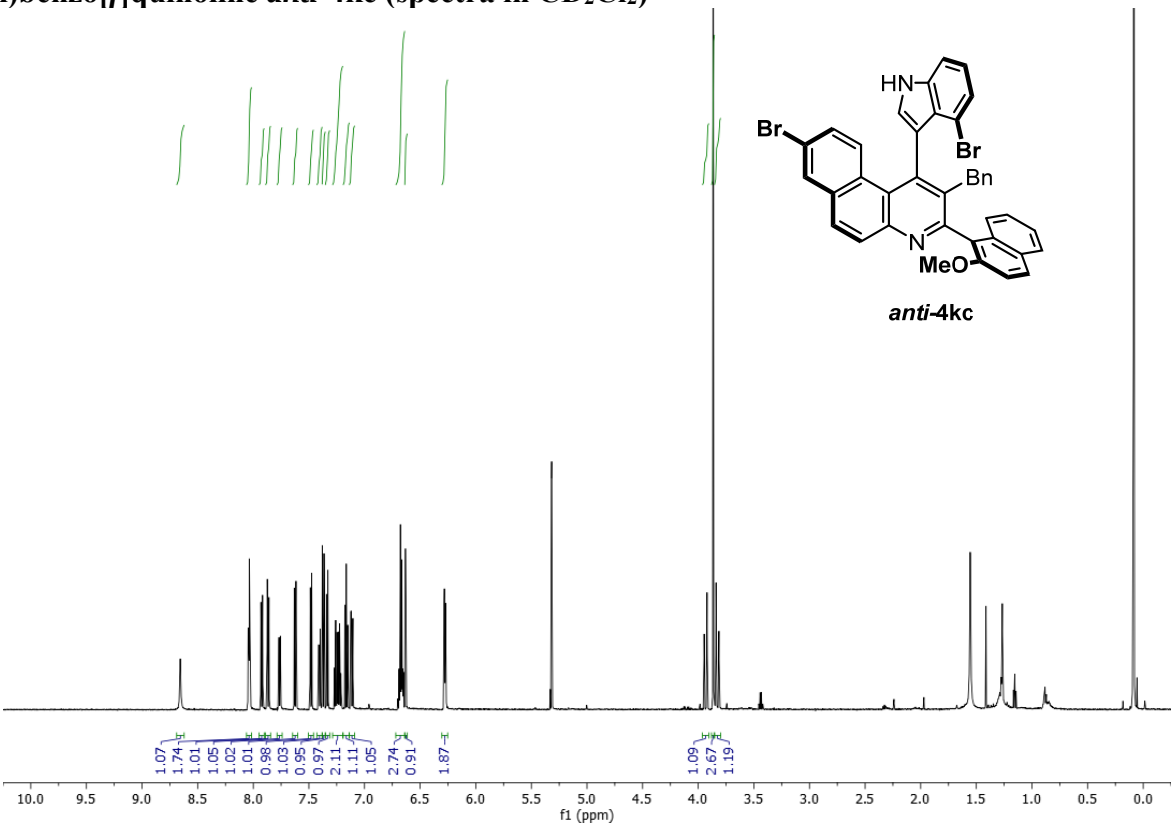


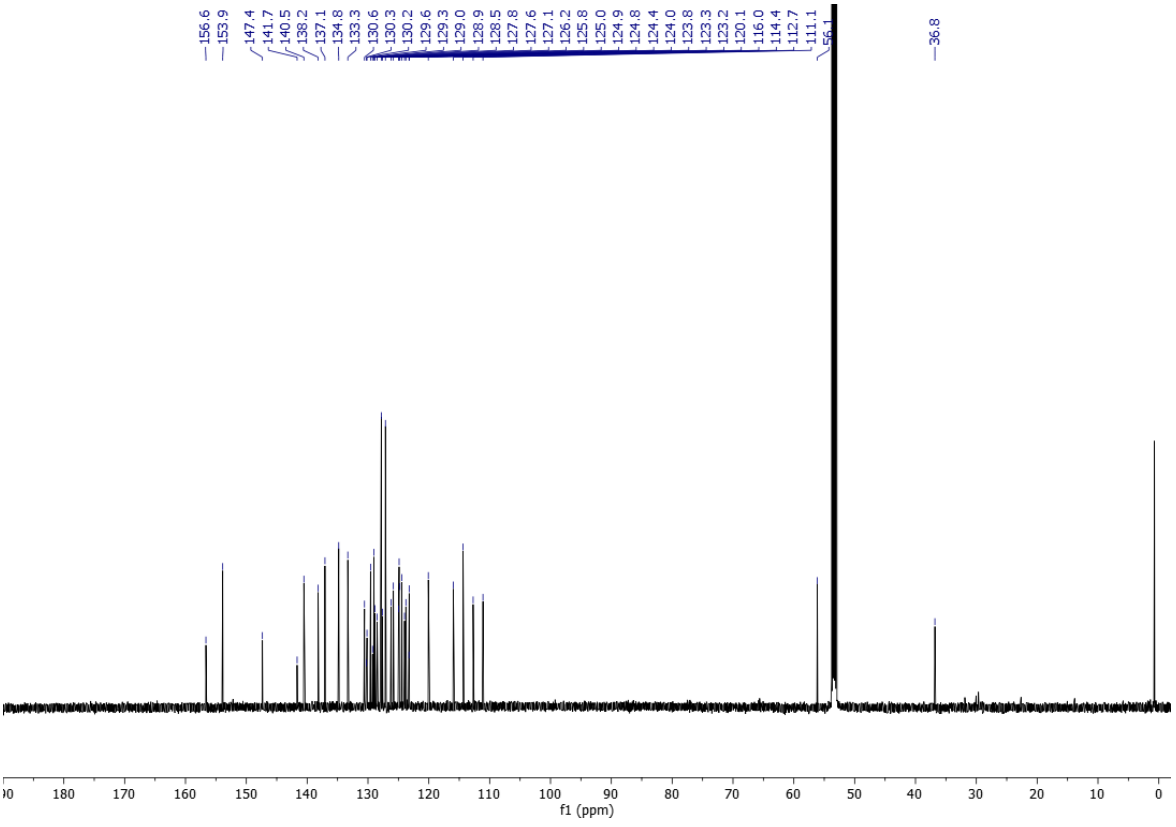
(1*aR*,3*aR*)-2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(2-methoxynaphthalen-1-yl)benzo[*f*]quinoline *syn*-4kc (spectra in CD_2Cl_2)



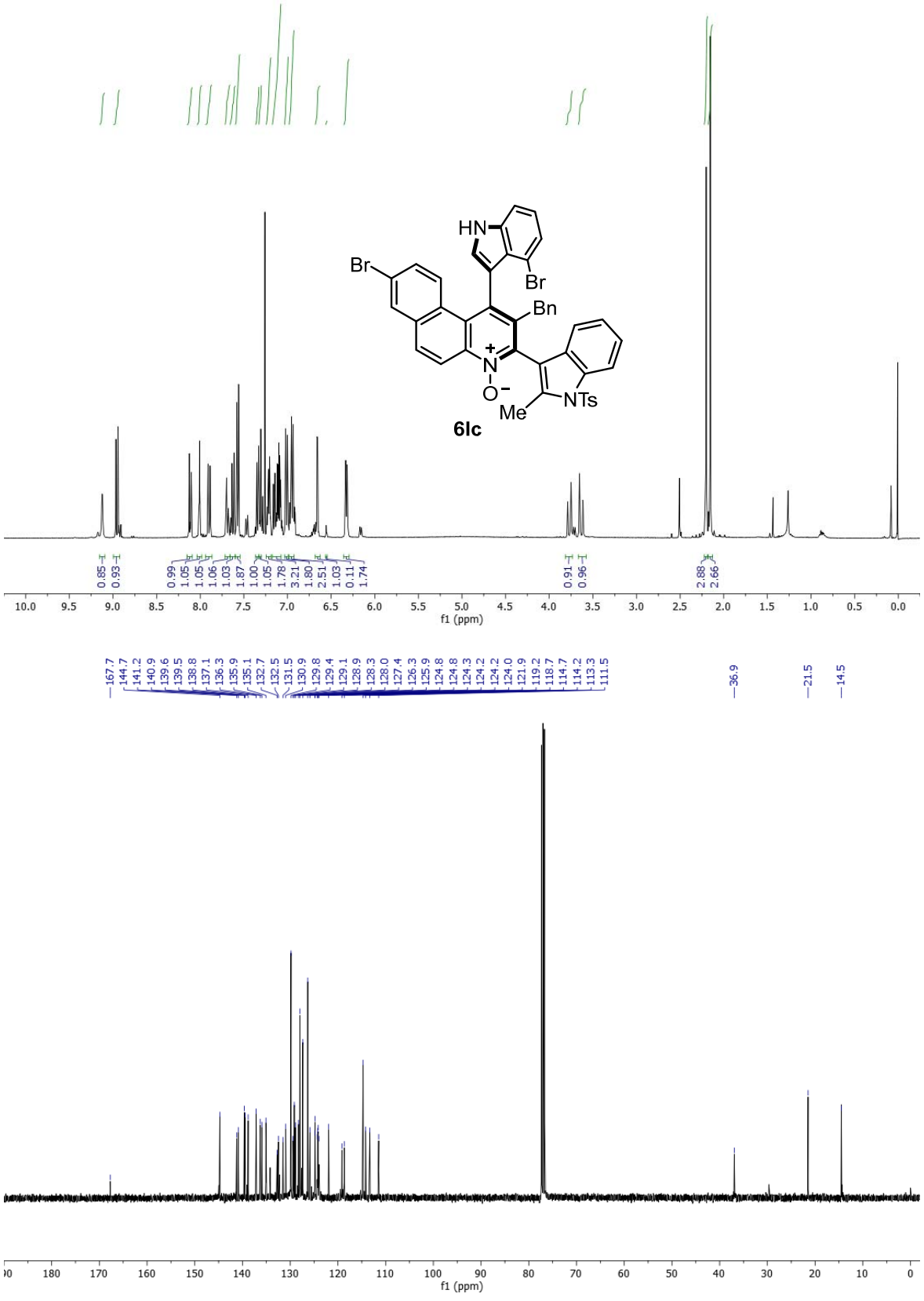


(1*aR*,3*aS*)-2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(2-methoxynaphthalen-1-yl)benzo[*f*]quinoline *anti*-4kc (spectra in CD_2Cl_2)

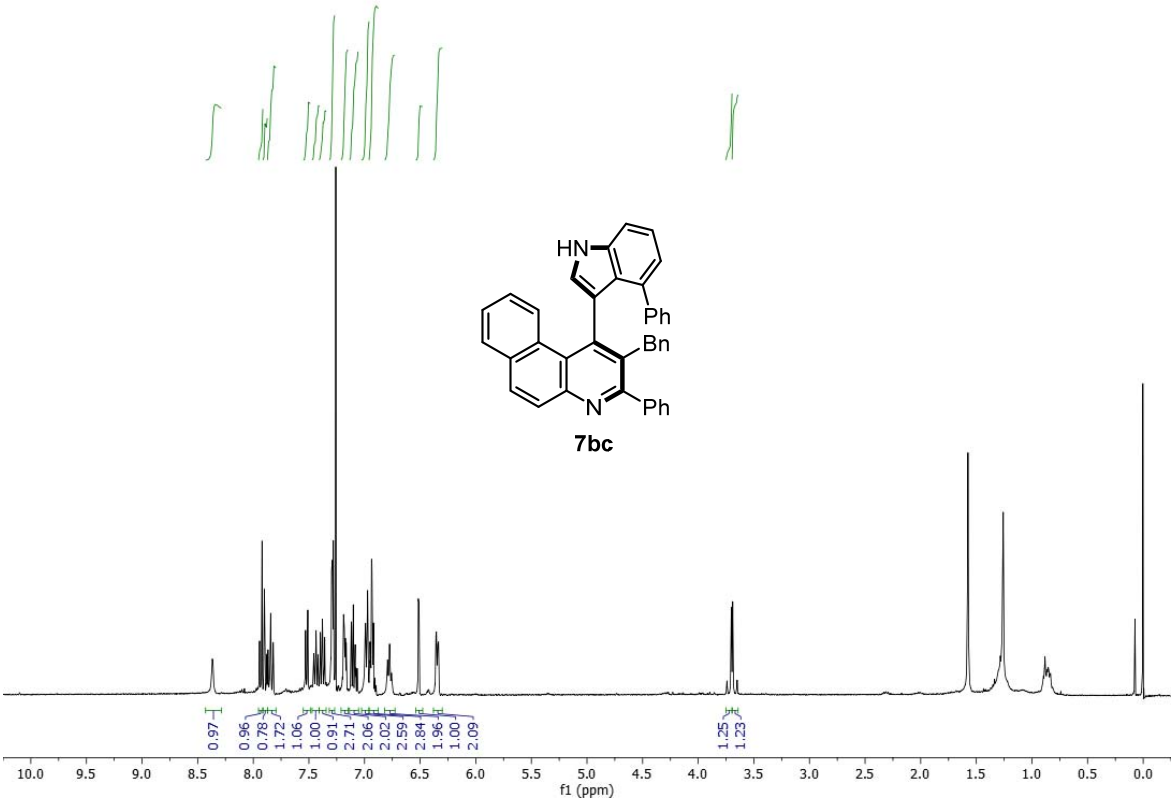


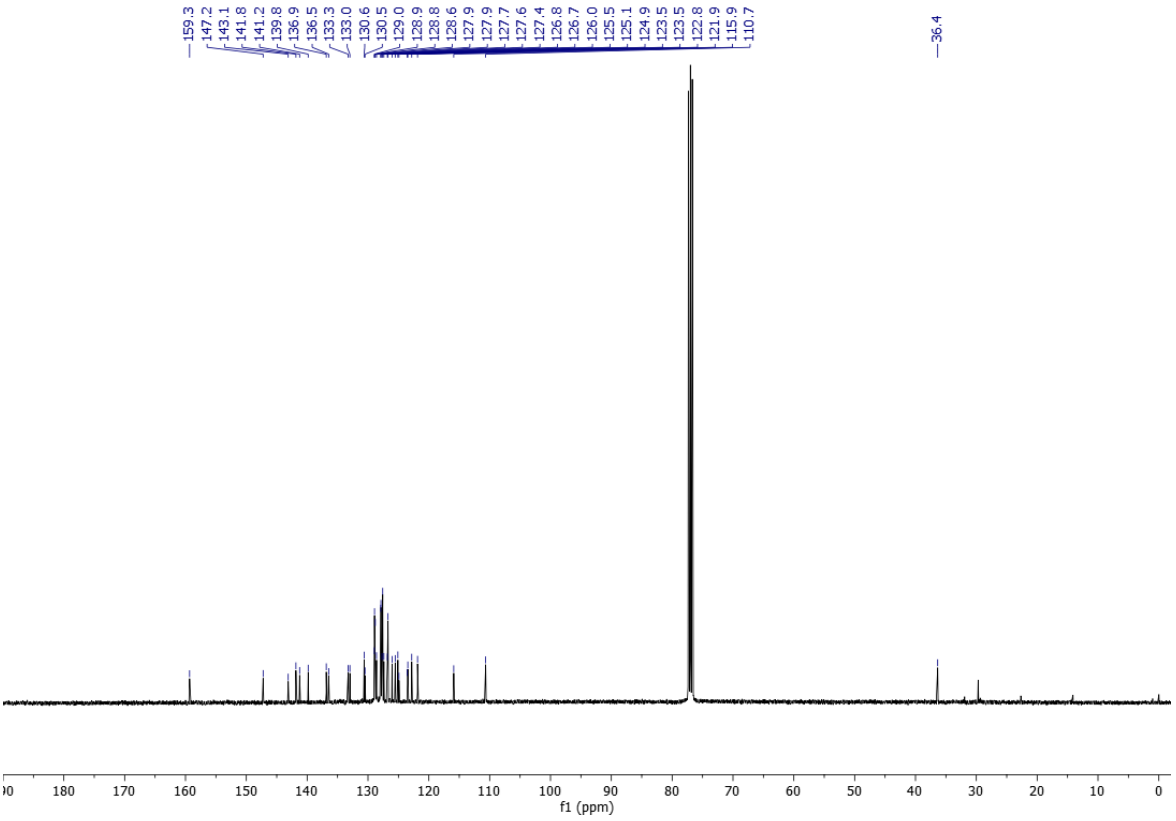


(1*aS*,3*aS*)-2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(2-methyl-1-tosyl-1*H*-indol-3-yl)benzo[*f*]quinoline 4-oxide 6lc



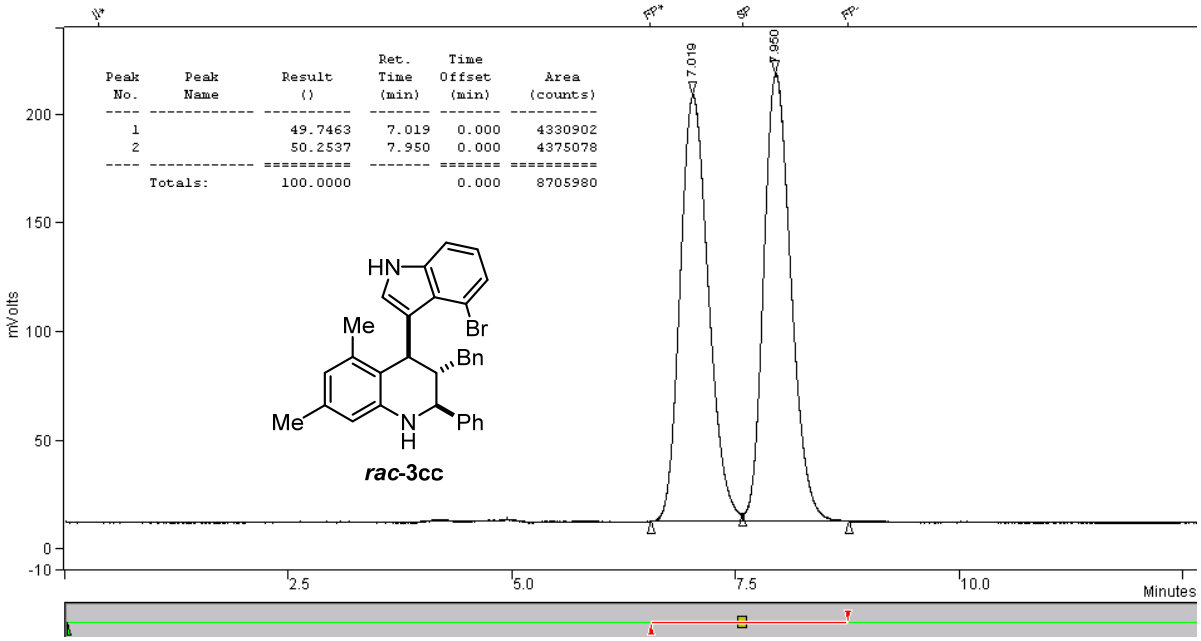
(a*S*)-2-benzyl-1-(4-phenyl-1*H*-indol-3-yl)-3-phenylbenzo[*f*]quinoline 7bc.



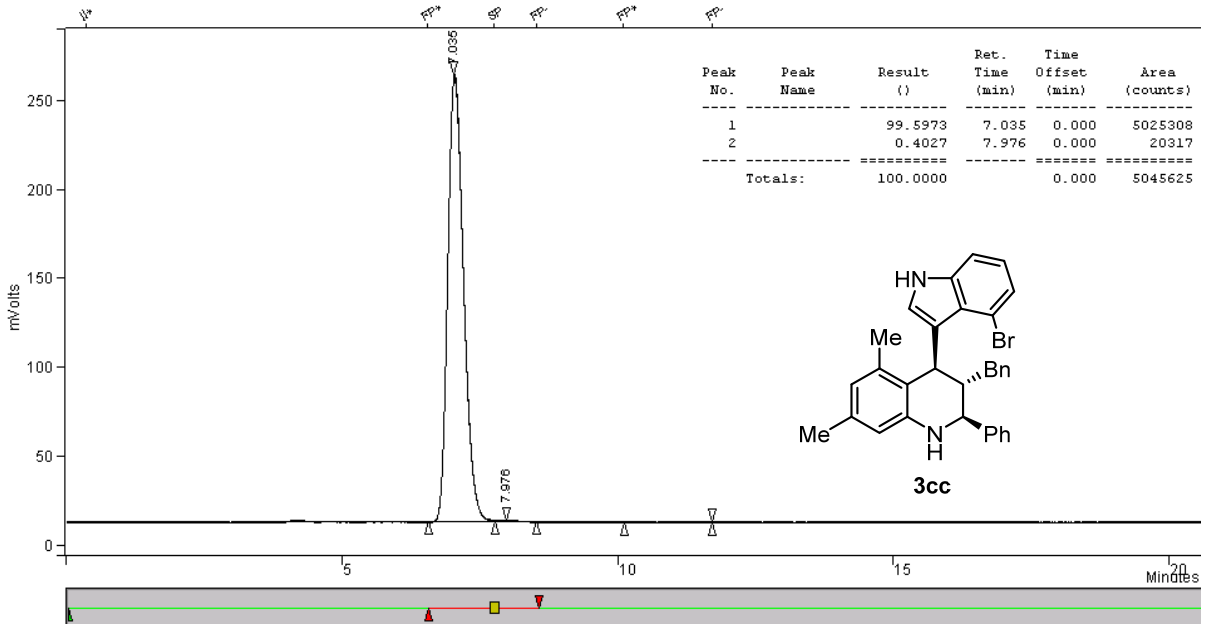


Copies of HPLC traces of products 3

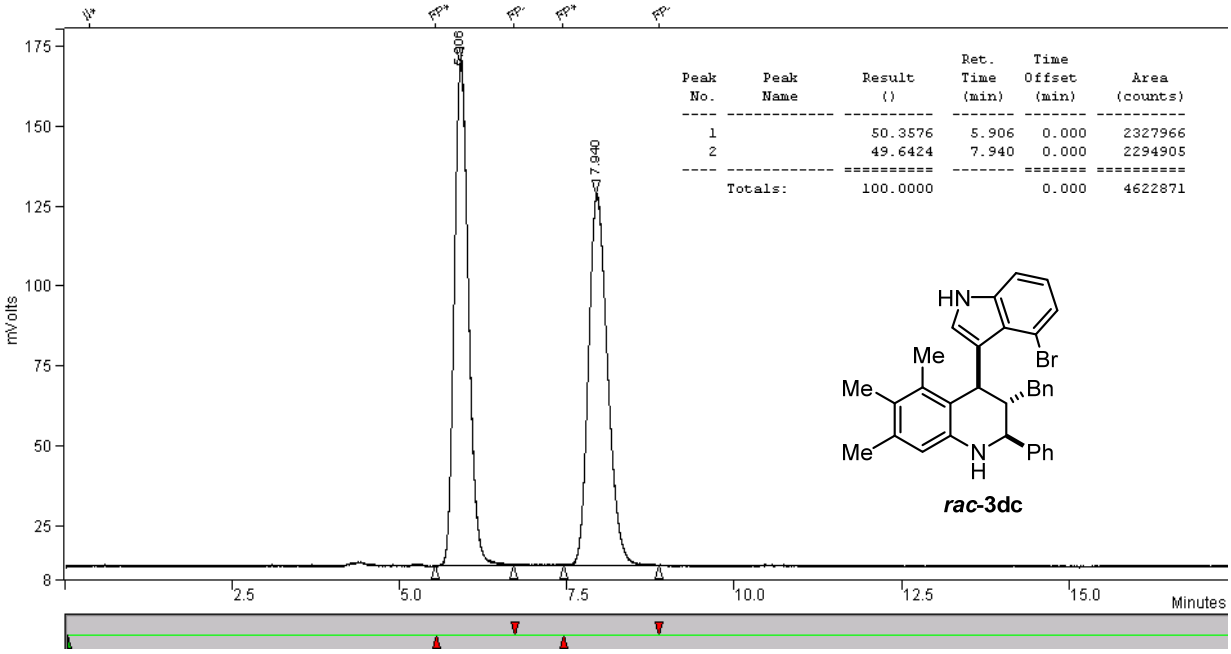
3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-5,6,7-dimethyl-2-phenyl-1,2,3,4-tetrahydroquinoline 3cc



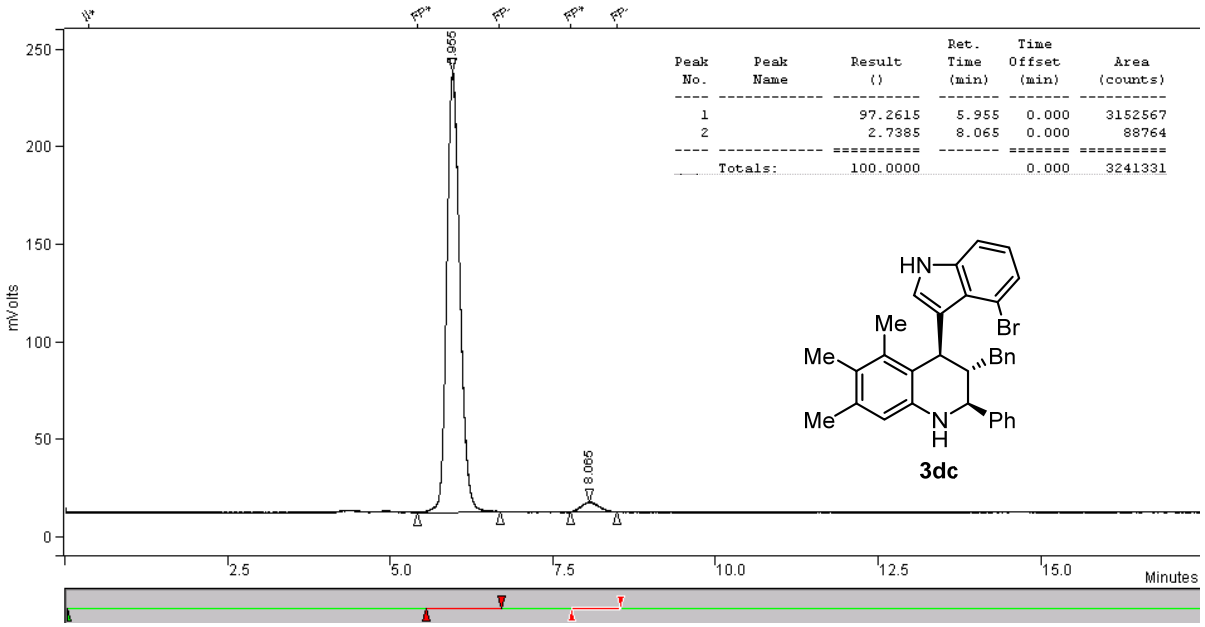
(*2S,3S,4R*)-3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-5,6,7-dimethyl-2-phenyl-1,2,3,4-tetrahydroquinoline 3cc



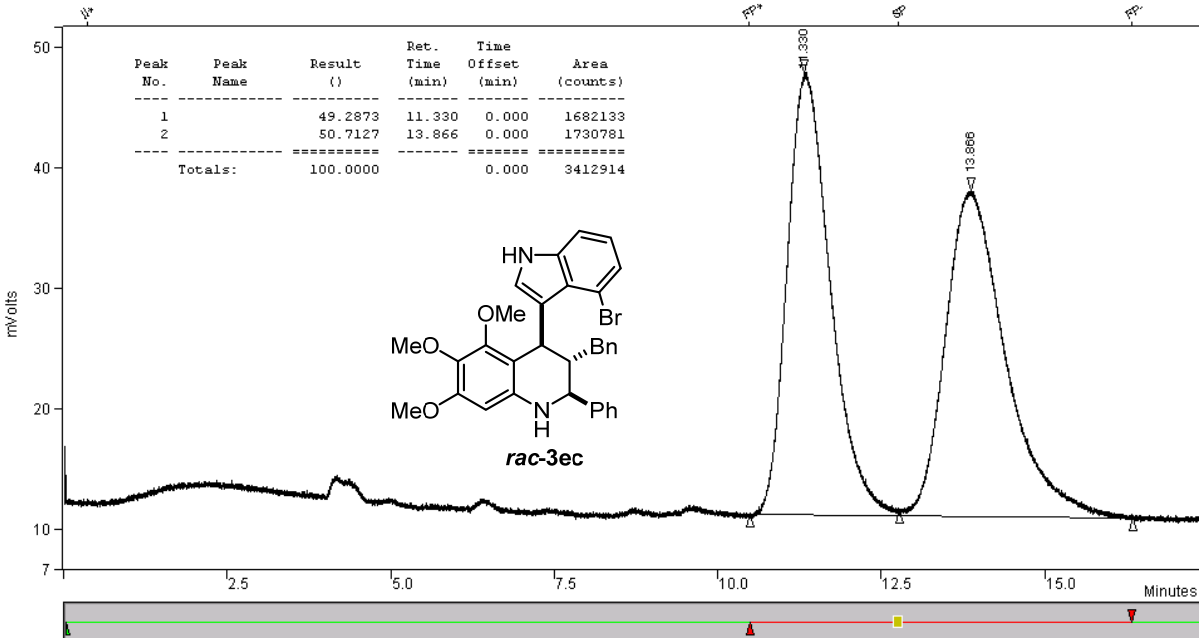
3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-5,6,7-trimethyl-2-phenyl-1,2,3,4-tetrahydroquinoline 3dc



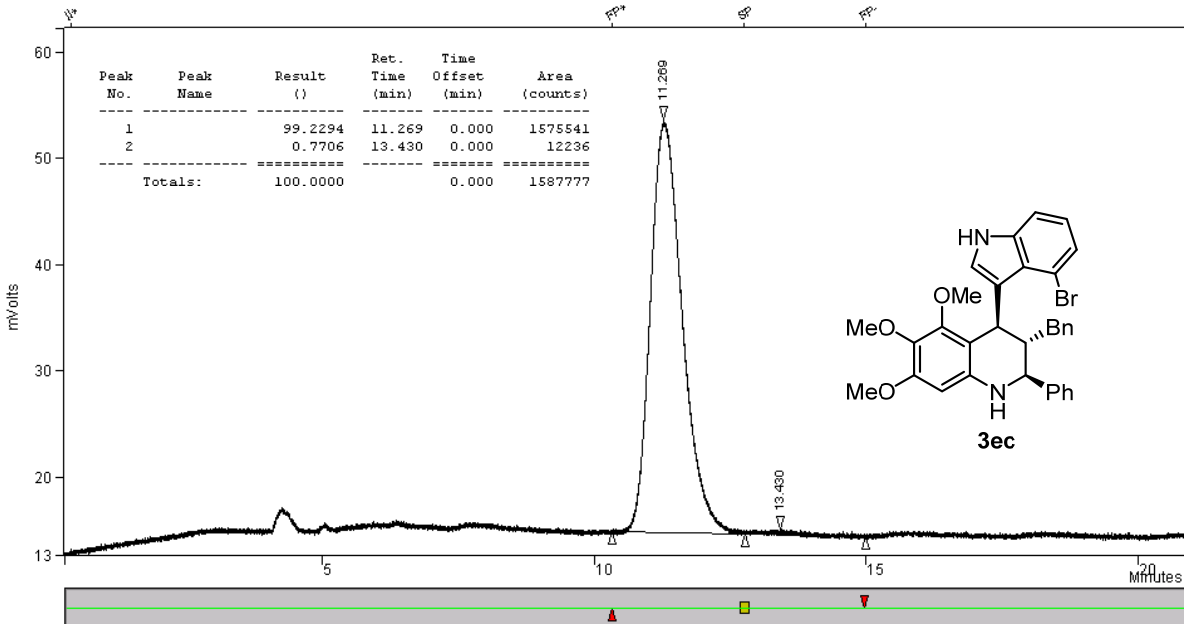
(*2S,3S,4R*)-3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-5,6,7-trimethyl-2-phenyl-1,2,3,4-tetrahydroquinoline 3dc



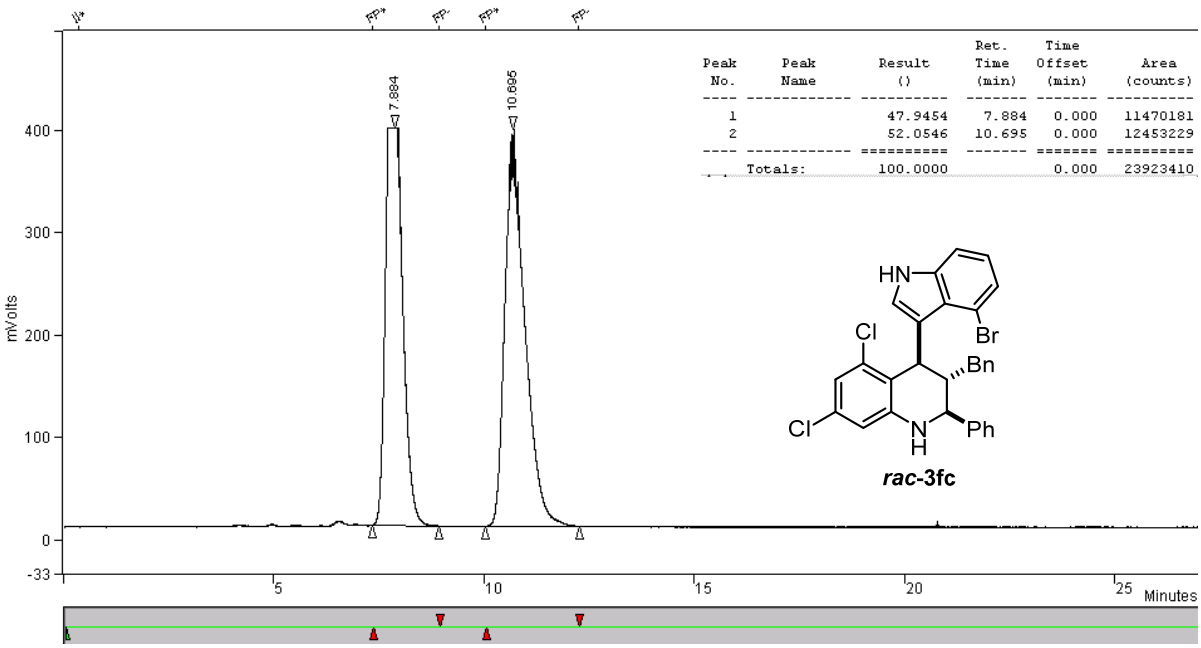
3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-5,6,7-trimethoxy-2-phenyl-1,2,3,4-tetrahydroquinoline 3ec



(*2S,3S,4R*)-3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-5,6,7-trimethoxy-2-phenyl-1,2,3,4-tetrahydroquinoline 3ec

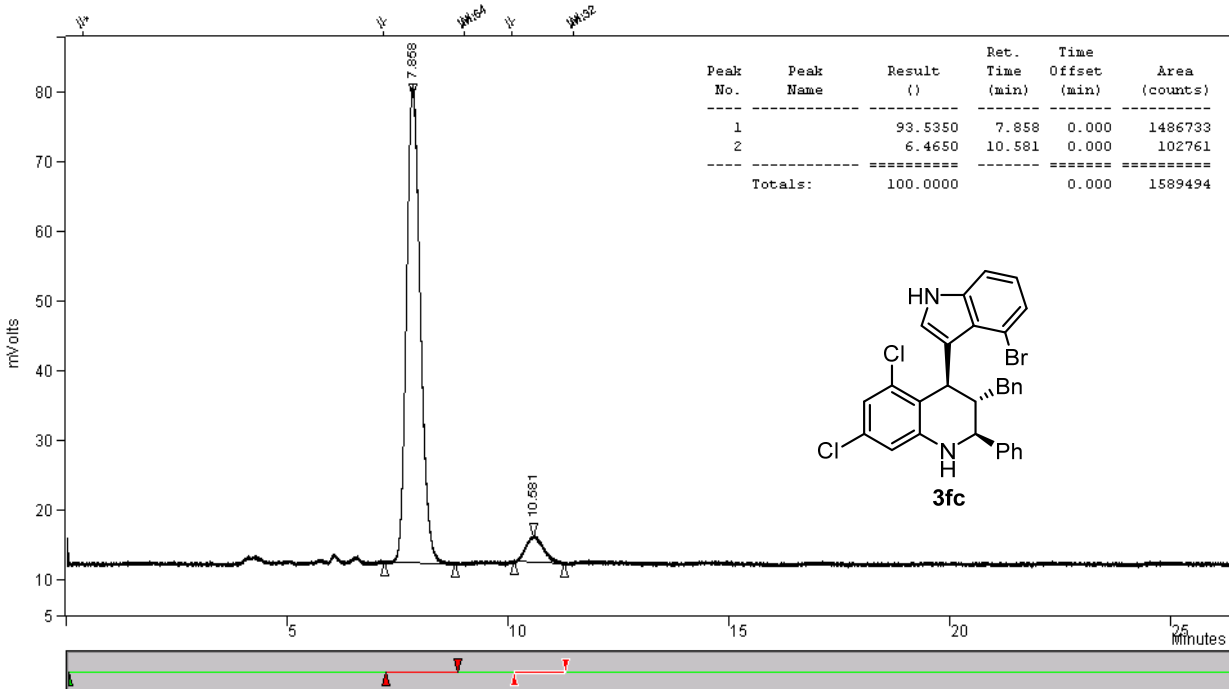


3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-5,7-dichloro-2-phenyl-1,2,3,4-tetrahydroquinoline 3fc



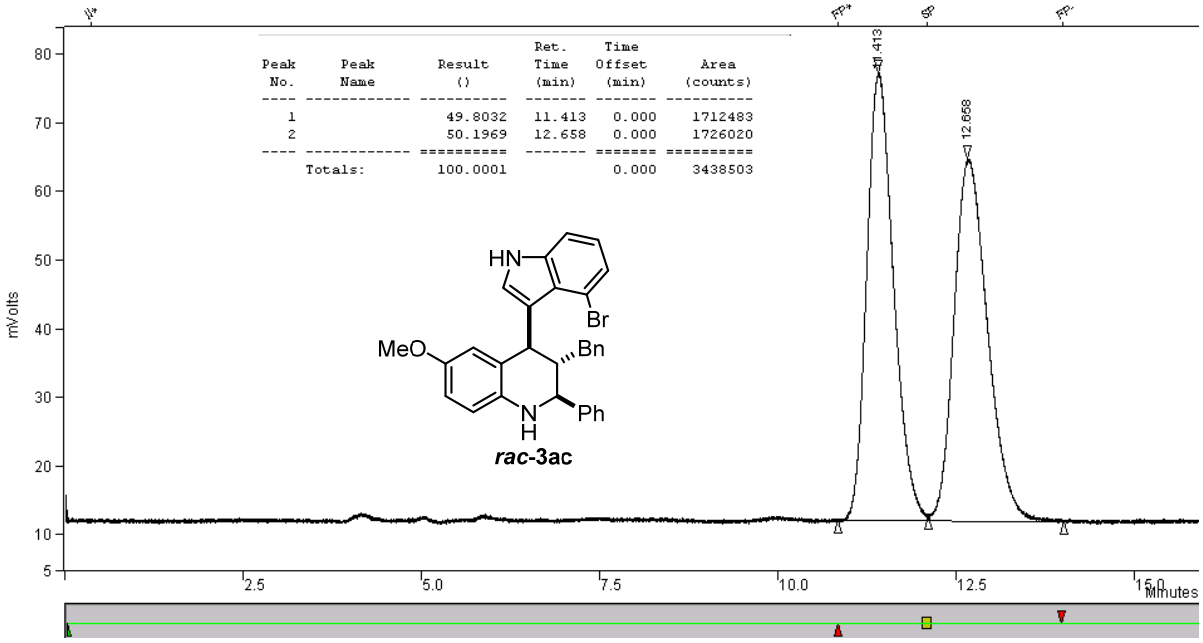
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)
1		47.9454	7.884	0.000	11470181
2		52.0546	10.695	0.000	12453229
	Totals:	100.0000		0.000	23923410

(*2S,3S,4R*)-3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-5,7-dichloro-2-phenyl-1,2,3,4-tetrahydroquinoline 3fc

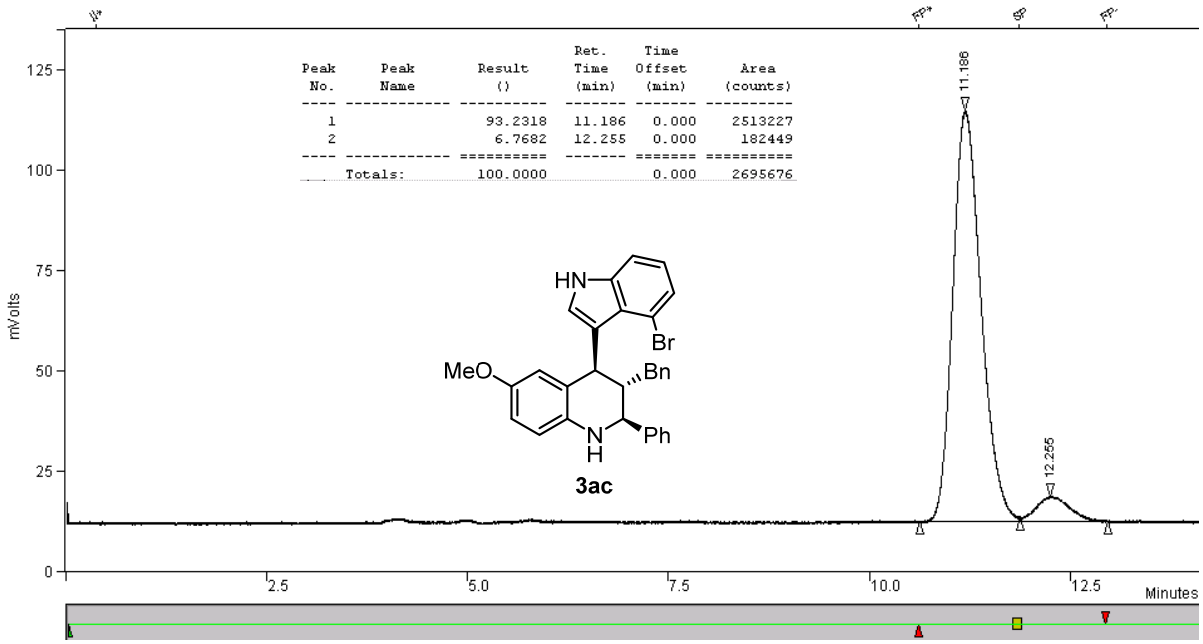


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)
1		93.5350	7.858	0.000	1486733
2		6.4650	10.581	0.000	102761
	Totals:	100.0000		0.000	1589494

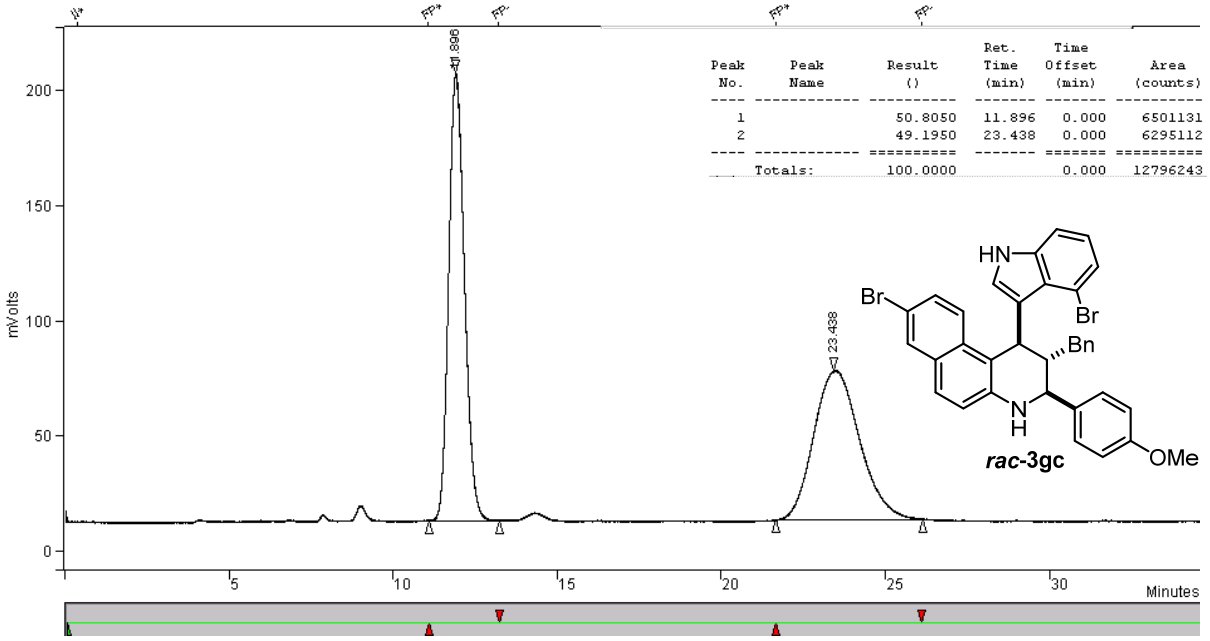
3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-6-methoxy-2-phenyl-1,2,3,4-tetrahydroquinoline 3ac



(*2S,3S,4R*)-3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-6-methoxy-2-phenyl-1,2,3,4-tetrahydroquinoline 3ac

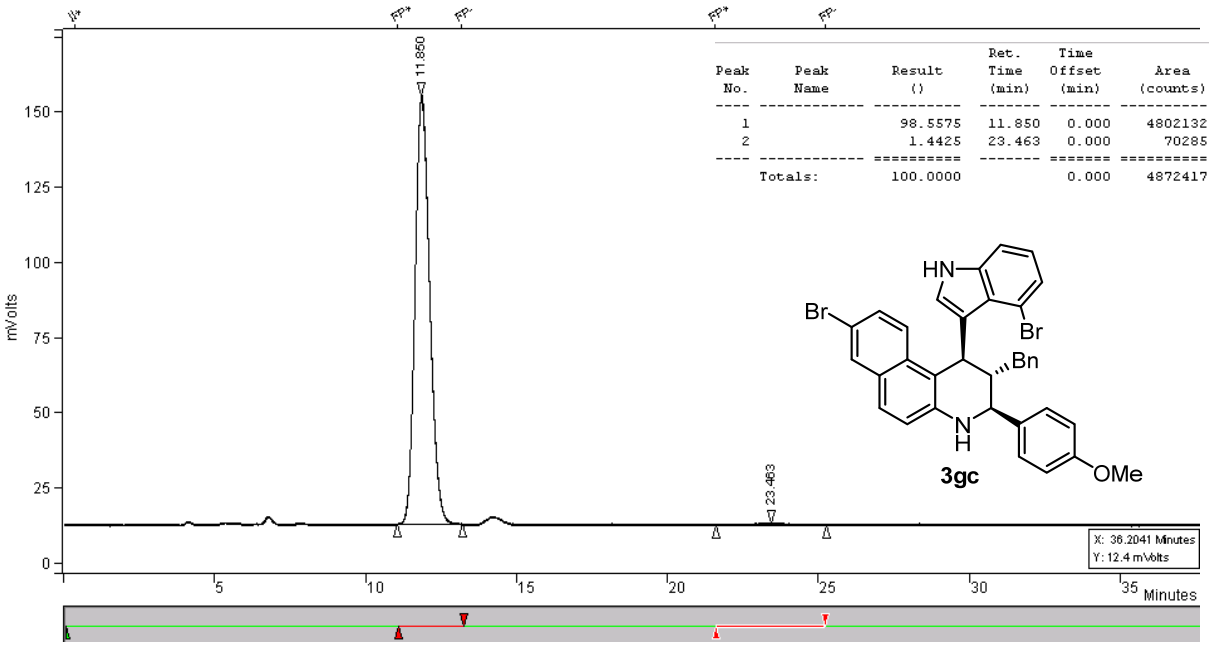


2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(4-methoxyphenyl)-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3gc



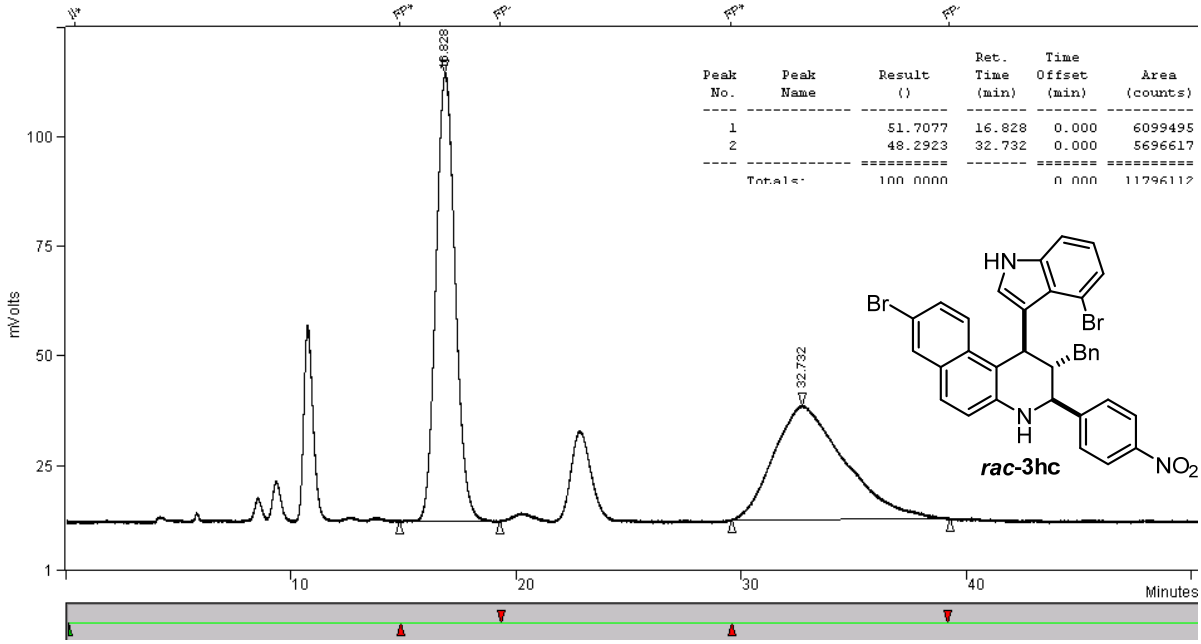
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)
1		50.8050	11.896	0.000	6501131
2		49.1950	23.438	0.000	6295112
	Totals:	100.0000		0.000	12796243

(*1R,2S,3S*)-2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(4-methoxyphenyl)-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3gc

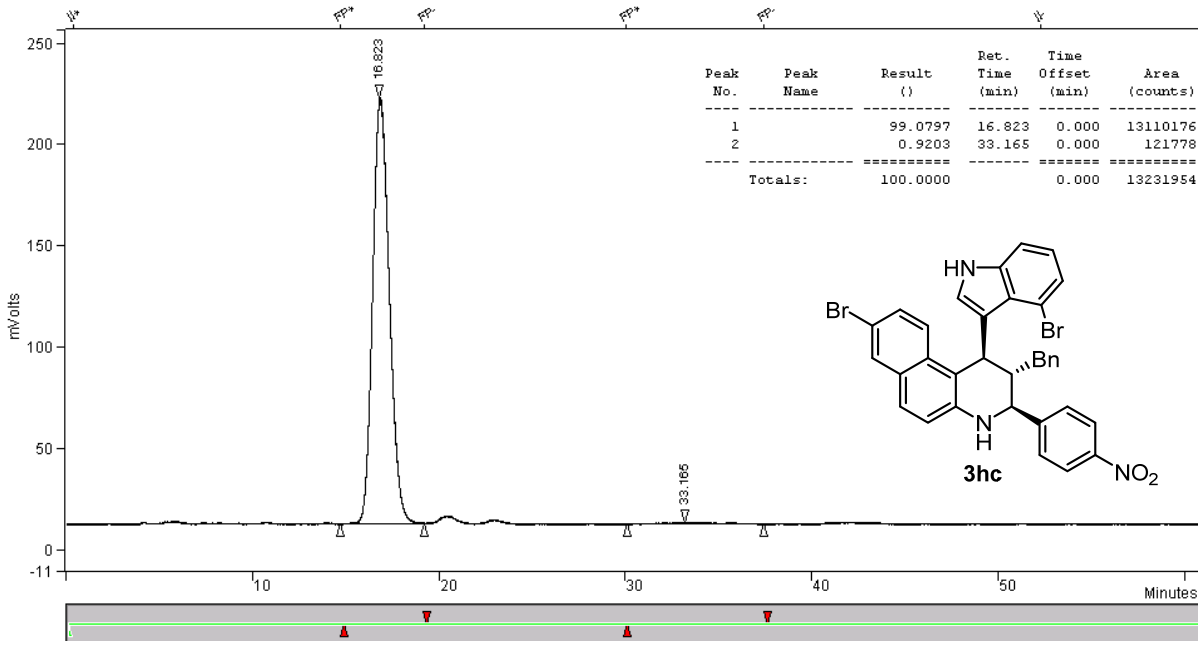


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)
1		98.5575	11.850	0.000	4802132
2		1.4425	23.463	0.000	70285
	Totals:	100.0000		0.000	4872417

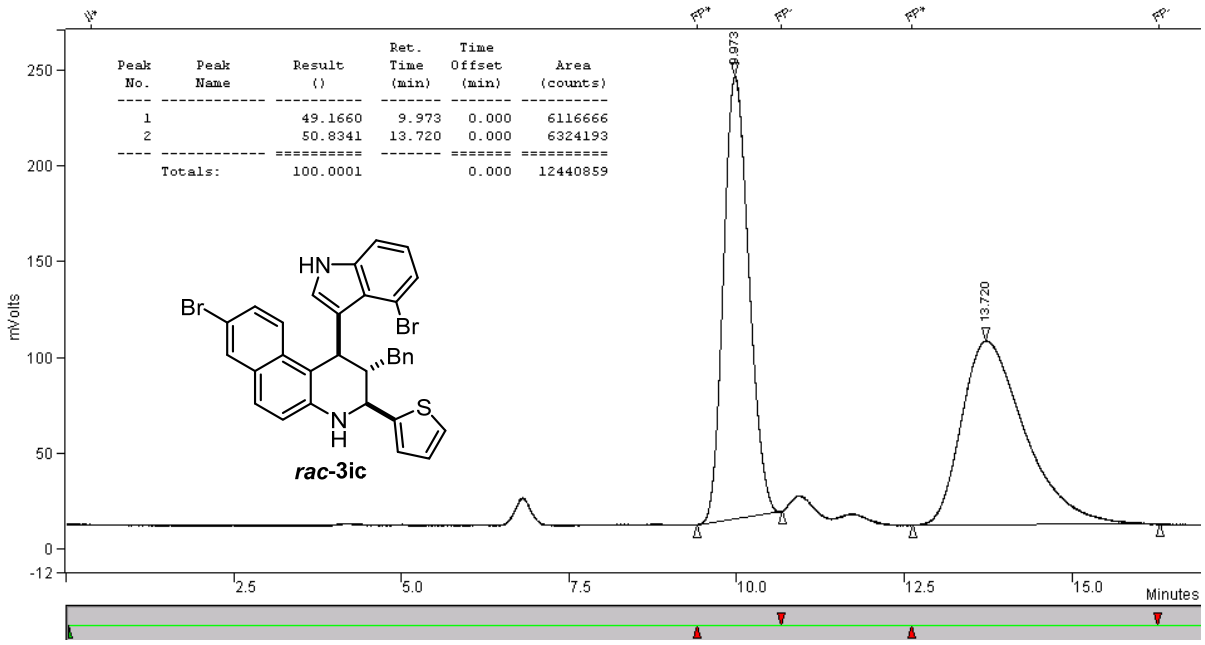
2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(4-nitrophenyl)-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3hc



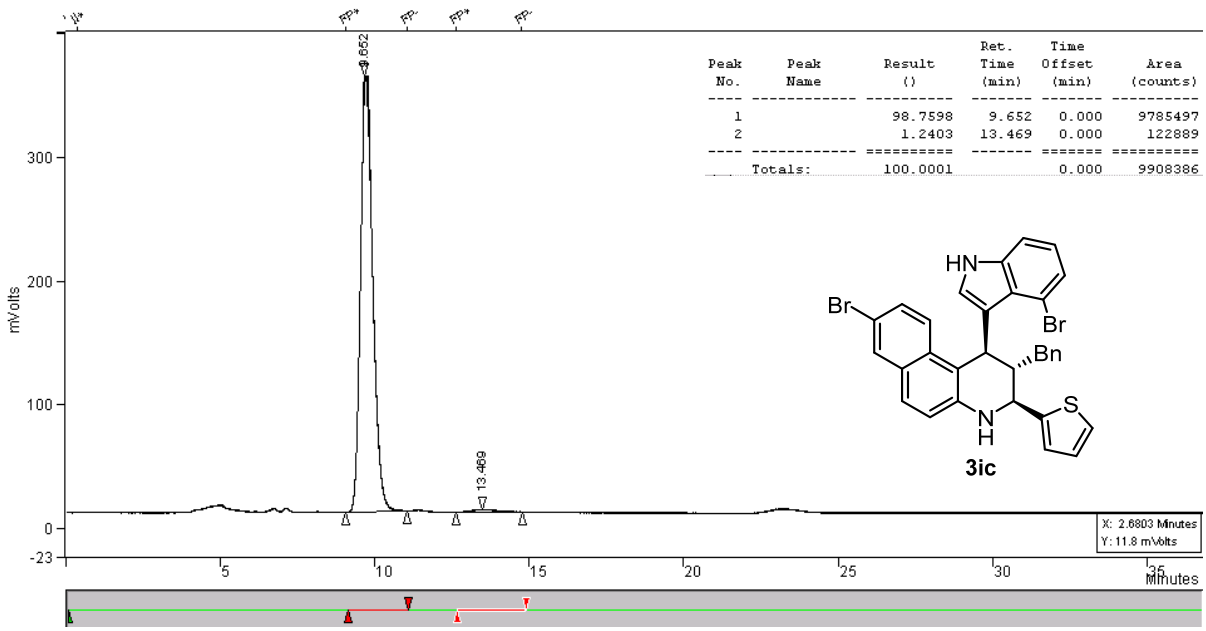
(*1R,2S,3S*)-2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(4-nitrophenyl)-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3hc



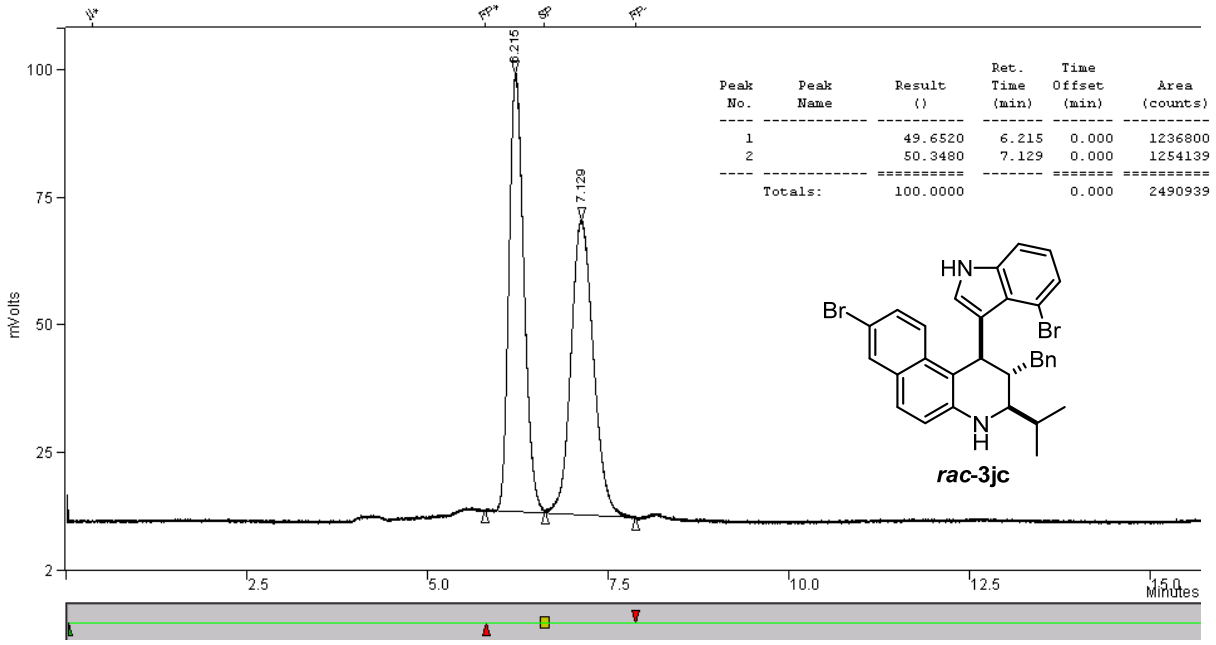
2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(thiophen-2-yl)-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3ic



(*1R,2S,3S*)-2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(thiophen-2-yl)-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3ic

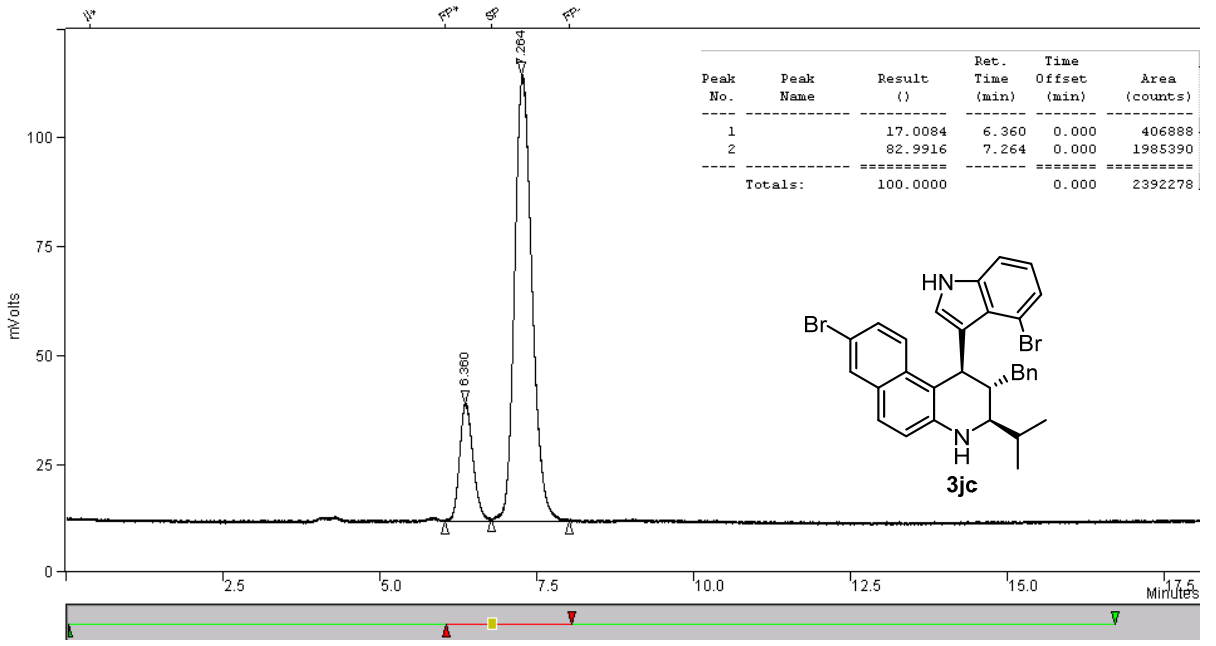


2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-isopropyl-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3jc



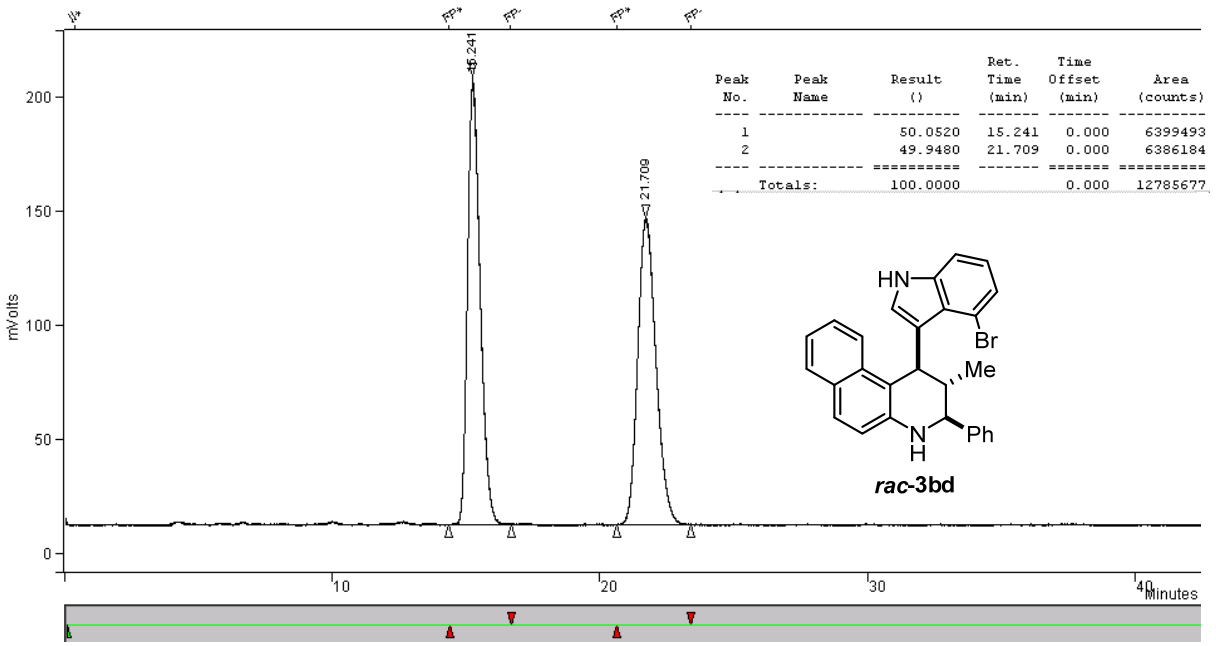
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)
1		49.6520	6.215	0.000	1236800
2		50.3480	7.129	0.000	1254139
Totals:		100.0000		0.000	2490939

(*1R,2S,3R*)-2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-isopropyl-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3jc

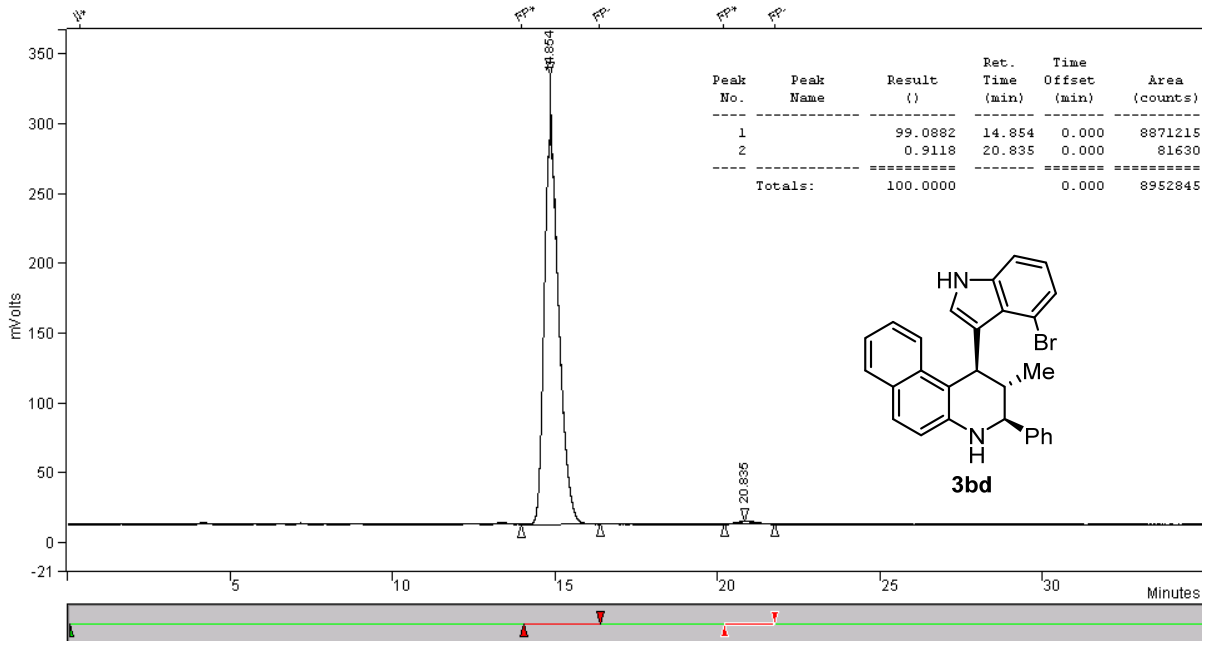


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)
1		17.0084	6.360	0.000	406888
2		82.9916	7.264	0.000	1985390
Totals:		100.0000		0.000	2392278

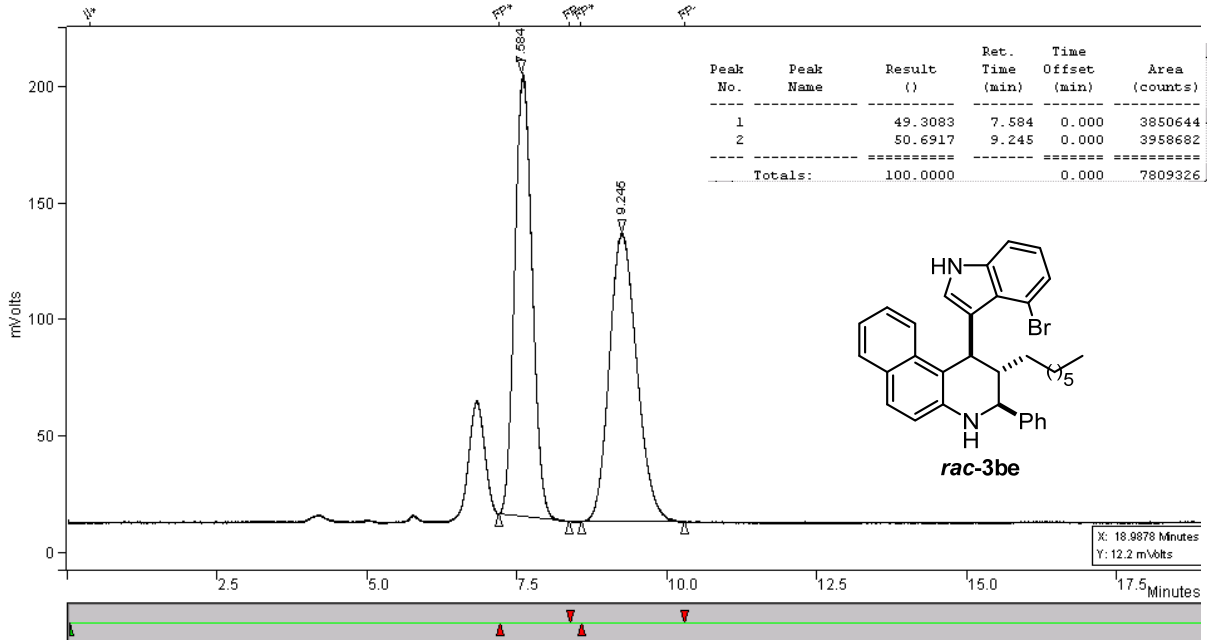
1-(4-bromo-1*H*-indol-3-yl)-2-methyl-3-phenyl-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3bd



(*1R,2S,3S*)-1-(4-bromo-1*H*-indol-3-yl)-2-methyl-3-phenyl-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3bd

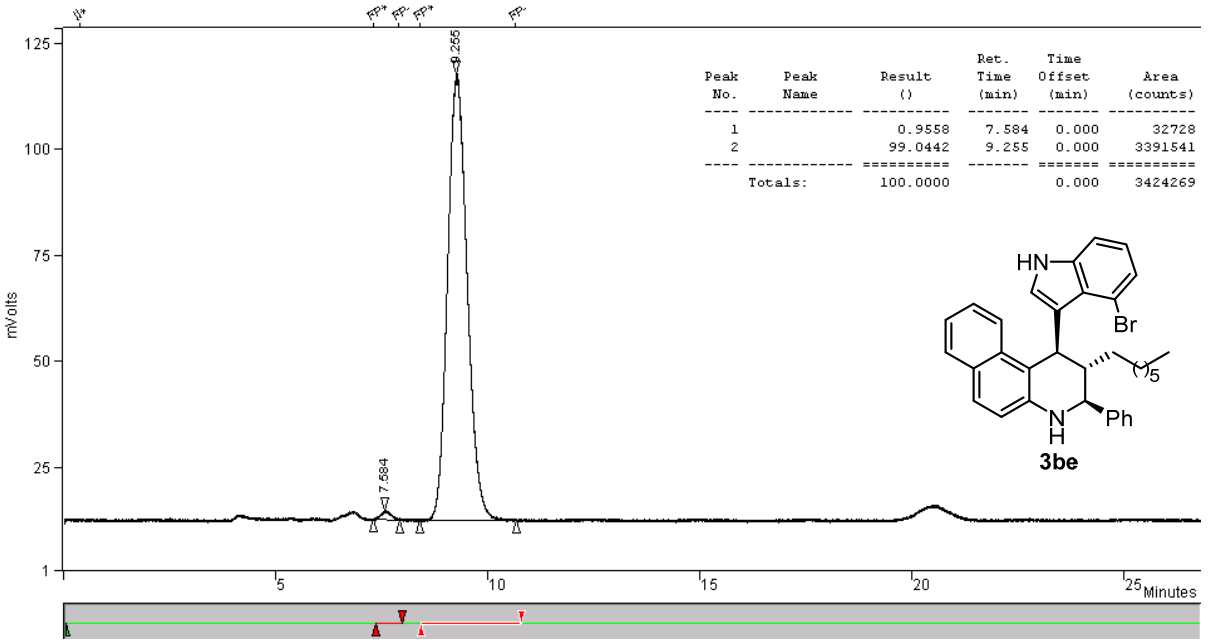


1-(4-bromo-1*H*-indol-3-yl)-3-phenyl-2-propyl-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3be



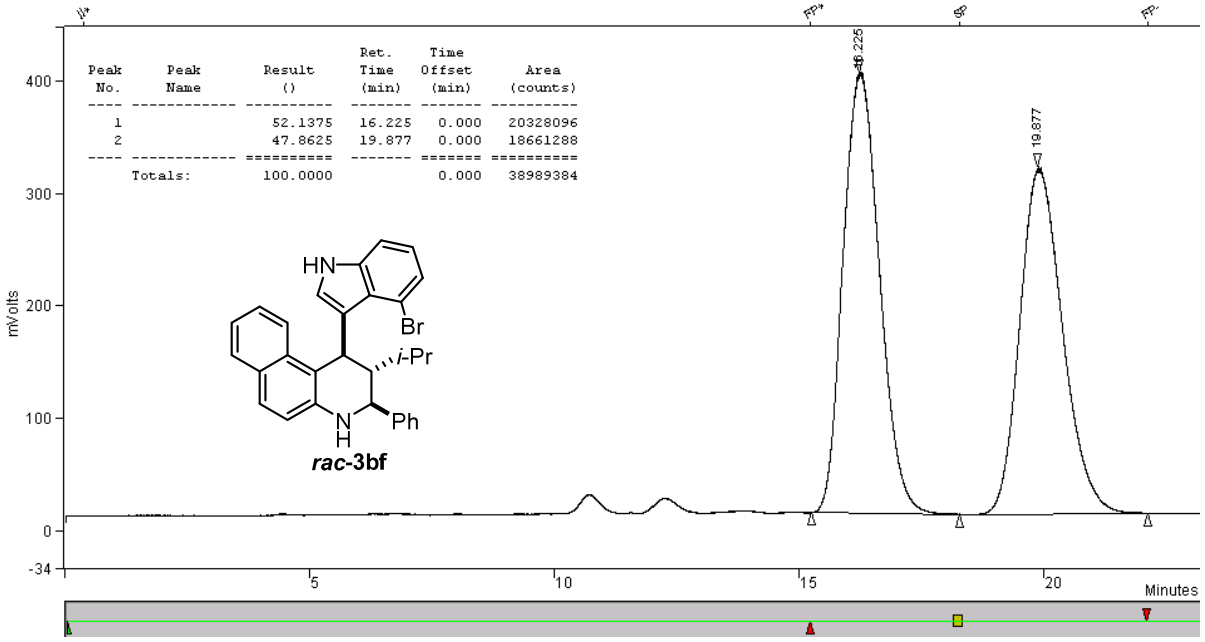
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)
1		49.3083	7.584	0.000	3850644
2		50.6917	9.245	0.000	3958682
Totals:		100.0000		0.000	7809326

(1R,2S,3S)-1-(4-bromo-1*H*-indol-3-yl)-3-phenyl-2-propyl-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3be

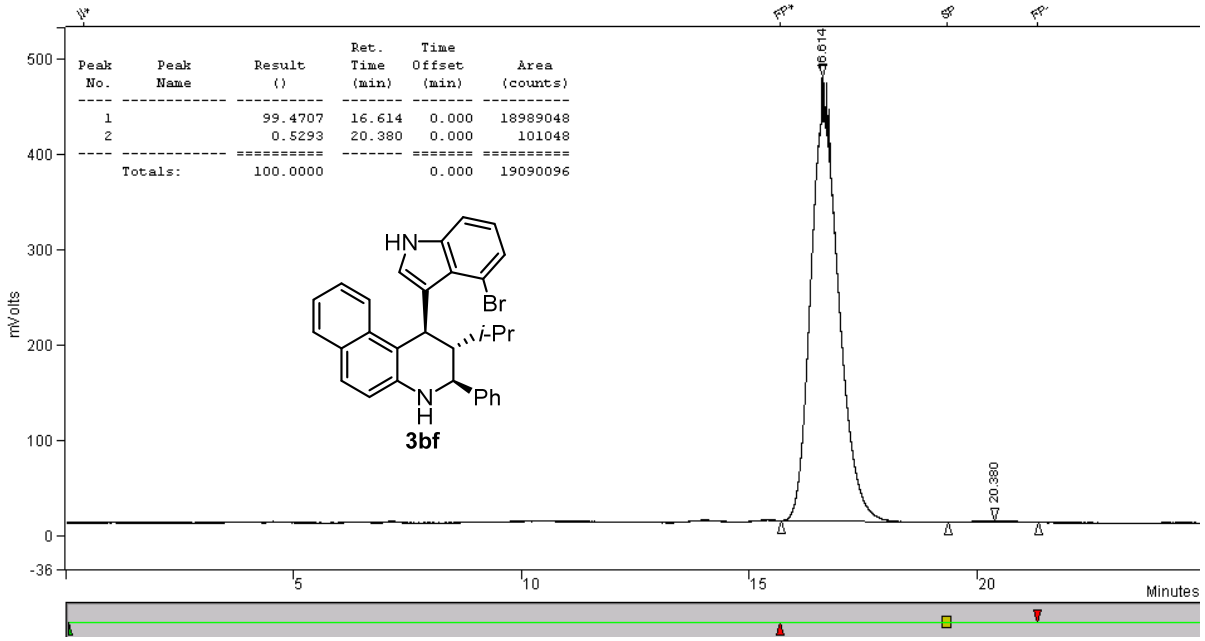


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)
1		0.9558	7.584	0.000	32728
2		99.0442	9.255	0.000	3391541
Totals:		100.0000		0.000	3424269

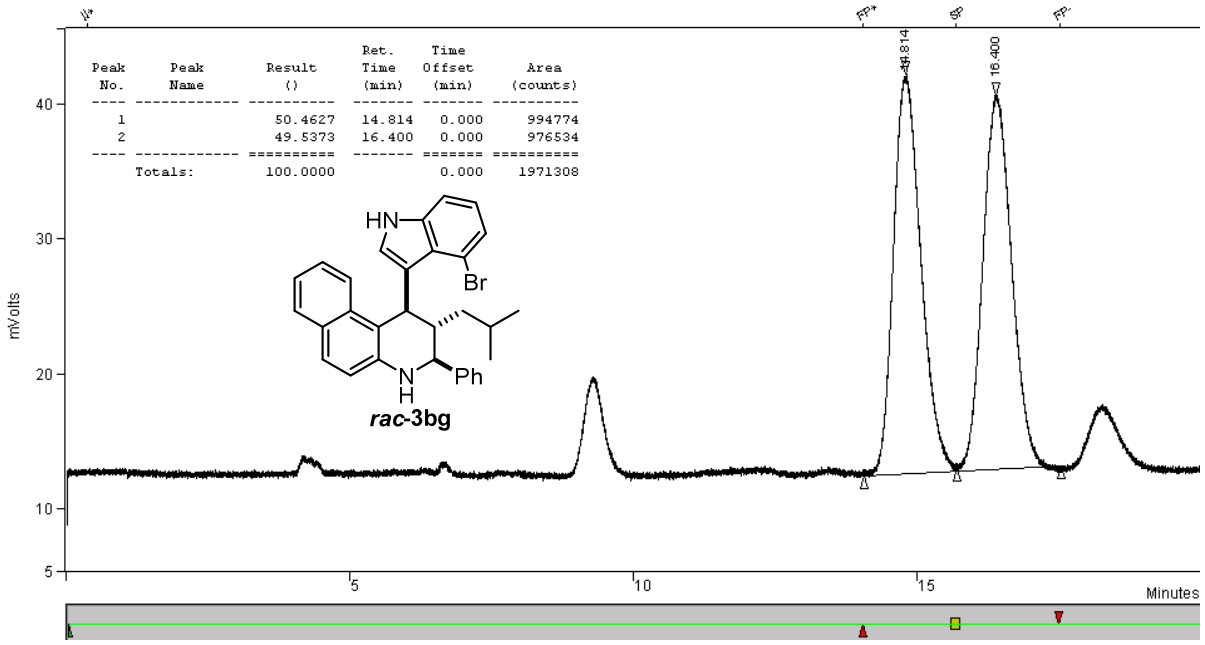
1-(4-bromo-1*H*-indol-3-yl)-2-isopropyl-3-phenyl-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3bf



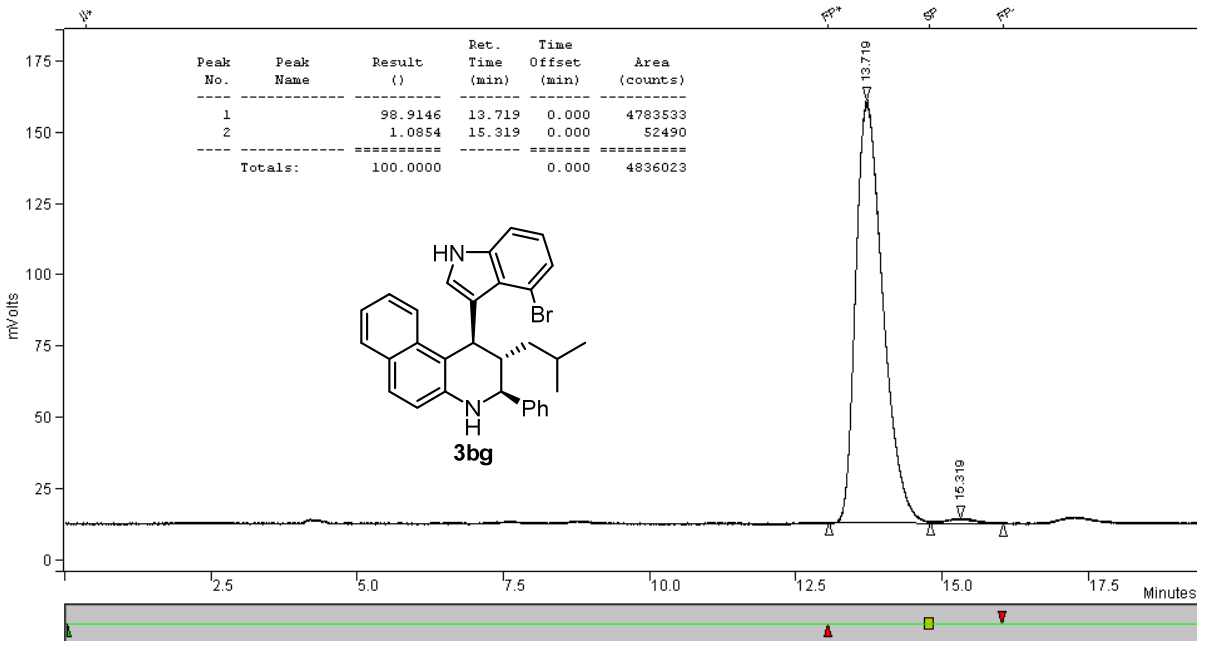
(*1R,2S,3S*)-1-(4-bromo-1*H*-indol-3-yl)-2-isopropyl-3-phenyl-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3bf



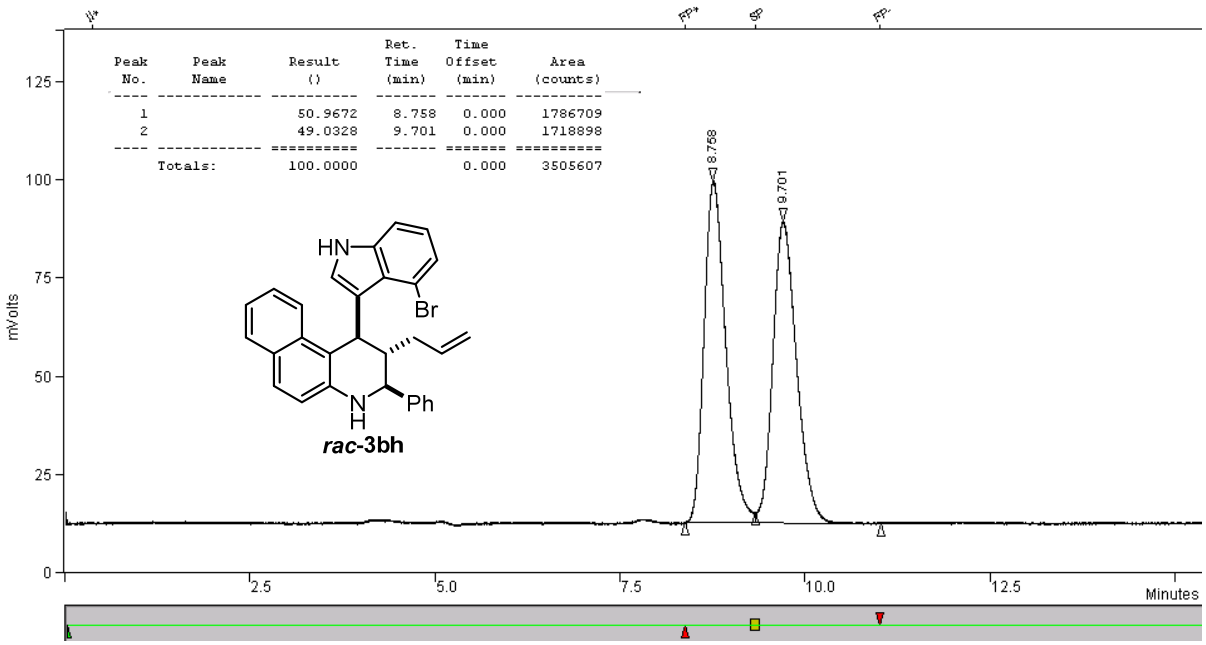
1-(4-bromo-1*H*-indol-3-yl)-2-isobutyl-3-phenyl-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3bg



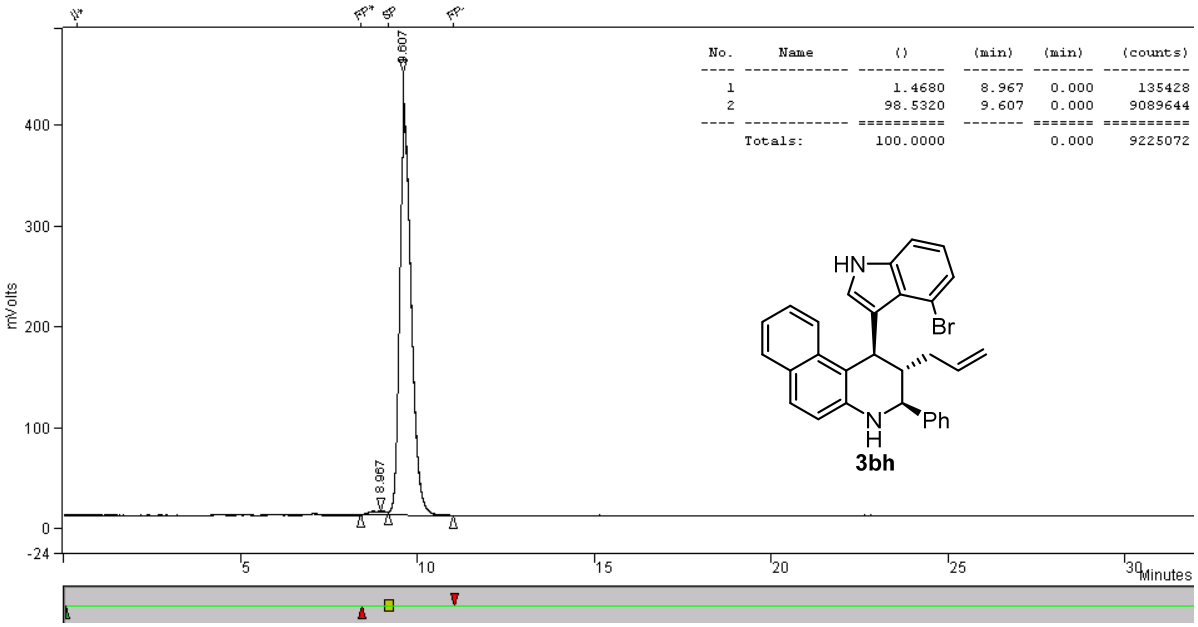
(*1R,2S,3S*)-1-(4-bromo-1*H*-indol-3-yl)-2-isobutyl-3-phenyl-1,2,3,4-tetrahydrobenzo[*f*] quinoline 3bg



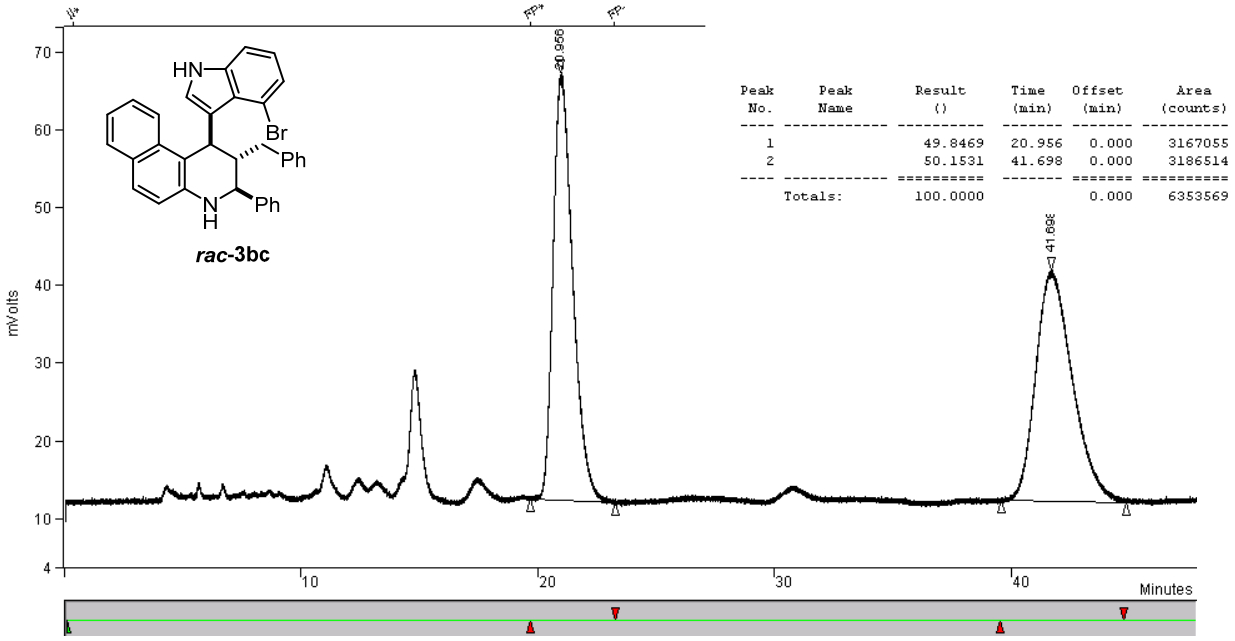
2-allyl-1-(4-bromo-1*H*-indol-3-yl)-3-phenyl-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3bh



(*1R,2S,3S*)-2-allyl-1-(4-bromo-1*H*-indol-3-yl)-3-phenyl-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3bh

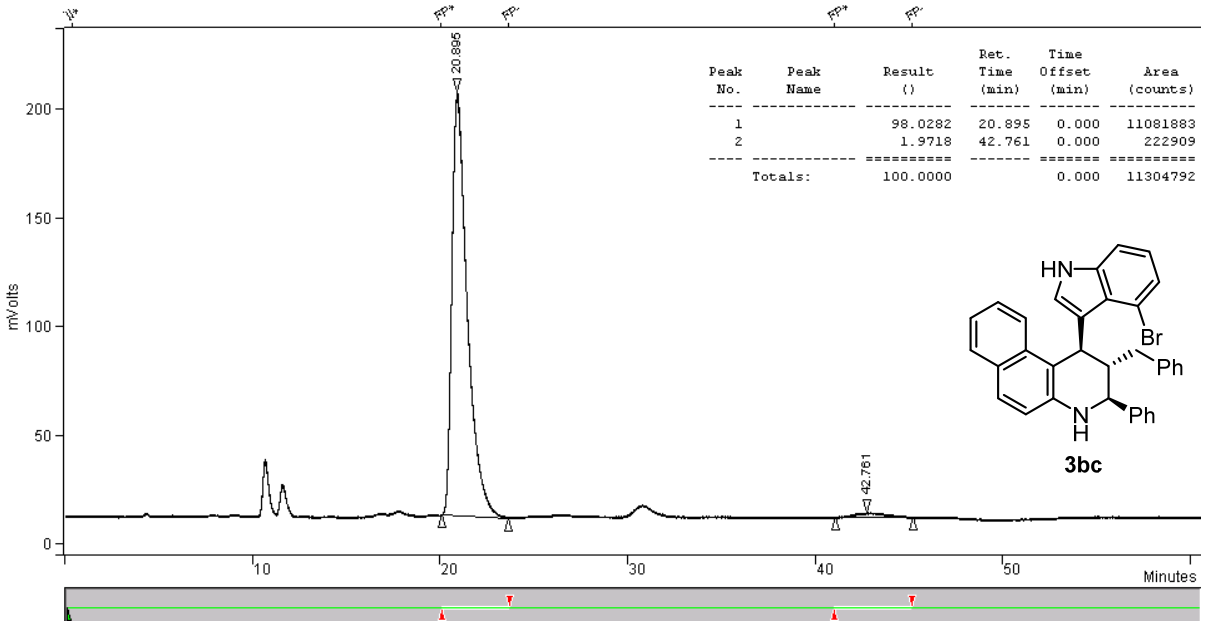


2-benzyl-1-(4-bromo-1*H*-indol-3-yl)-3-phenyl-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3bc



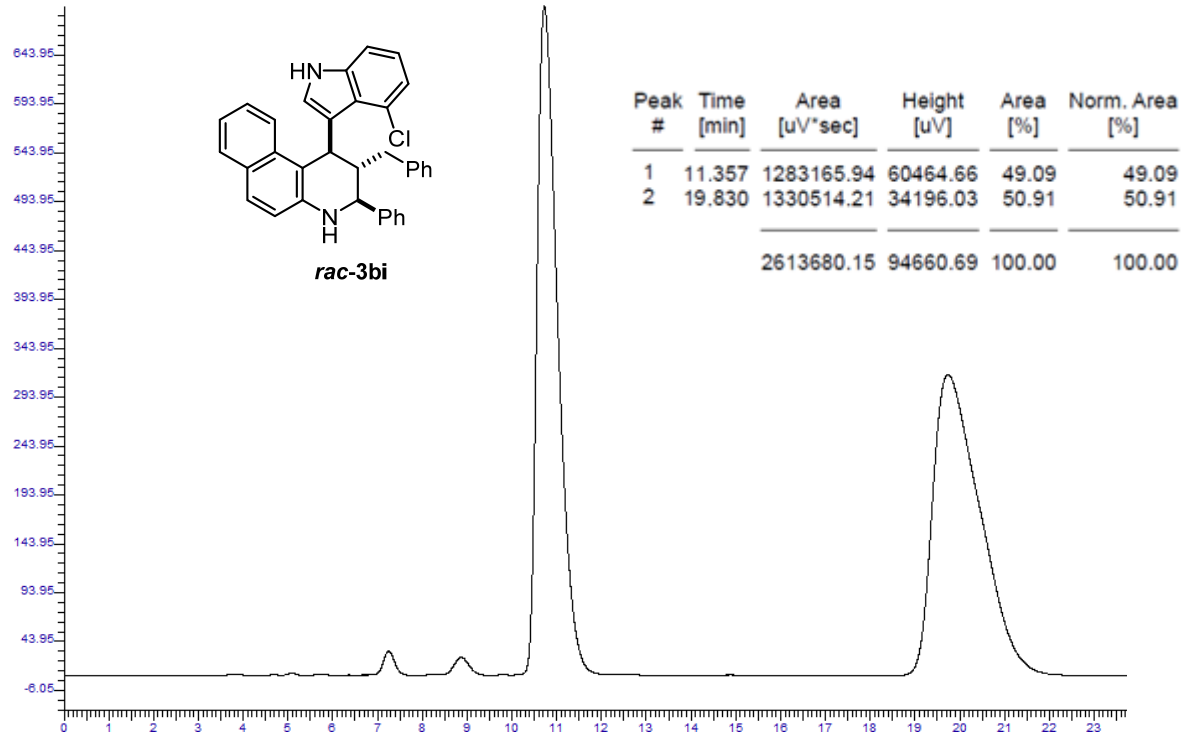
Peak No.	Peak Name	Result ()	Time (min)	Offset (min)	Area (counts)
1		49.8469	20.956	0.000	3167055
2		50.1531	41.698	0.000	3186514
	Totals:	100.0000		0.000	6353569

(*1R,2S,3S*)-2-benzyl-1-(4-bromo-1*H*-indol-3-yl)-3-phenyl-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3bc



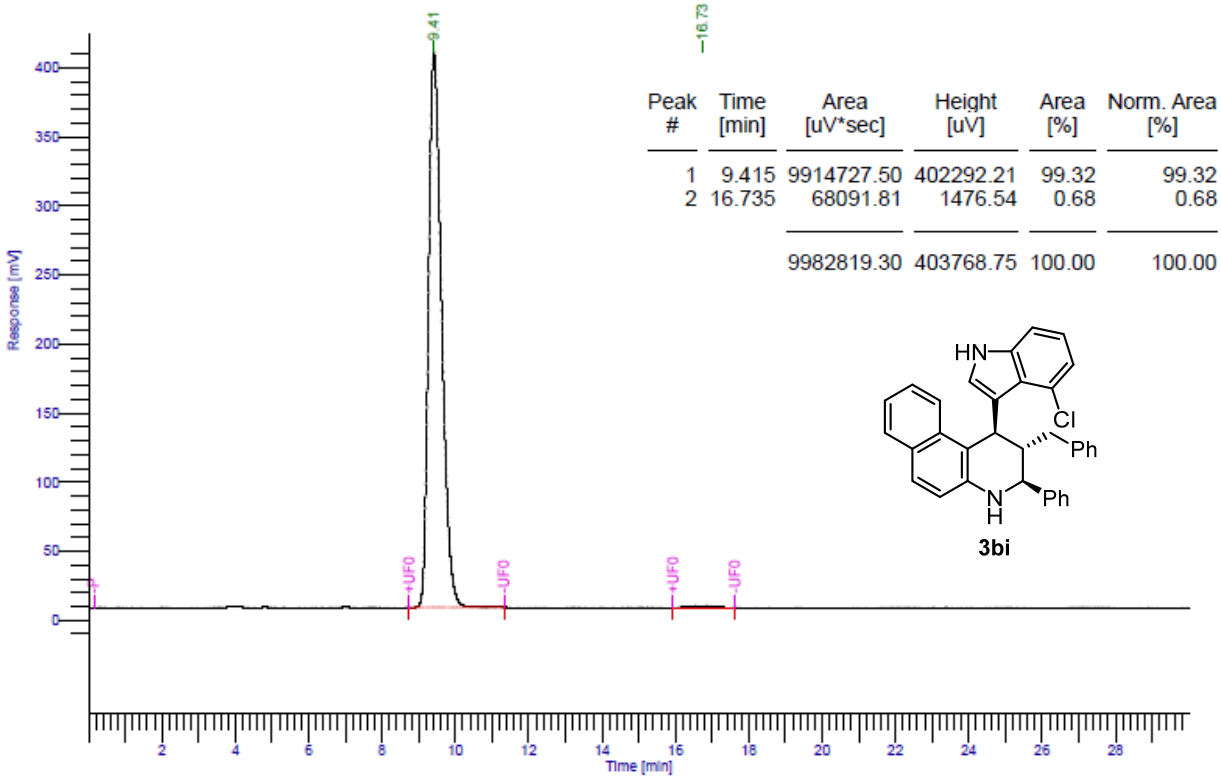
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)
1		98.0282	20.895	0.000	11081883
2		1.9718	42.761	0.000	222909
	Totals:	100.0000		0.000	11304792

2-benzyl-1-(4-chloro-1*H*-indol-3-yl)-3-phenyl-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3bi



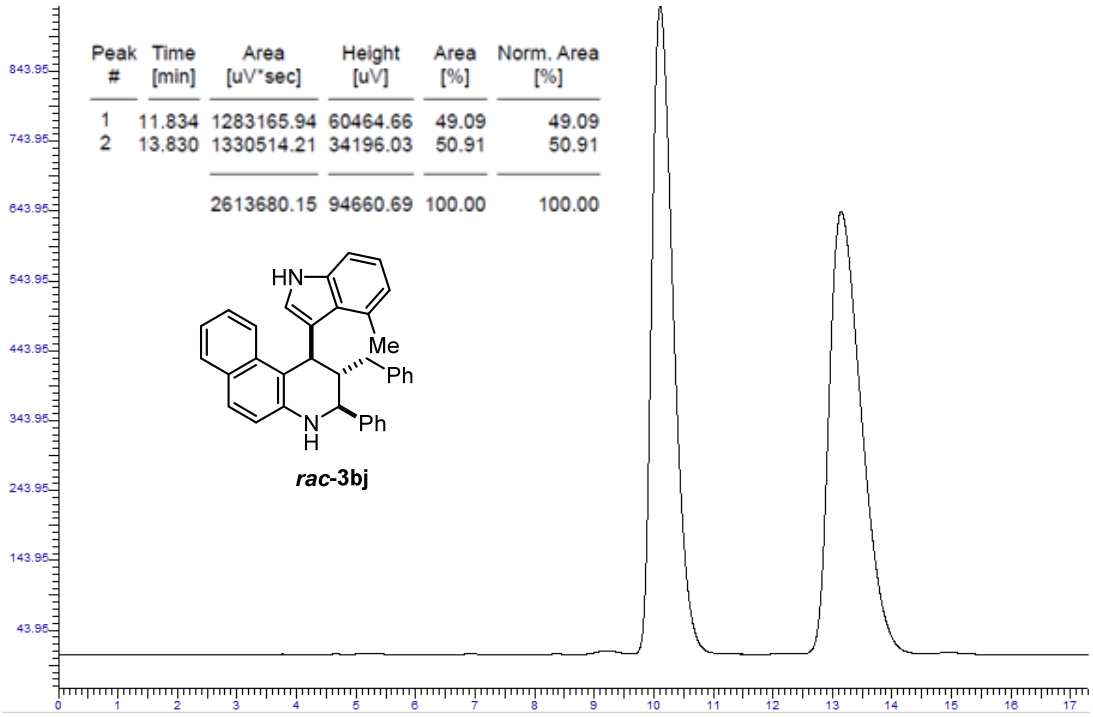
Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1	11.357	1283165.94	60464.66	49.09	49.09
2	19.830	1330514.21	34196.03	50.91	50.91
		2613680.15	94660.69	100.00	100.00

(1*R*,2*S*,3*S*)-2-benzyl-1-(4-chloro-1*H*-indol-3-yl)-3-phenyl-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3bi



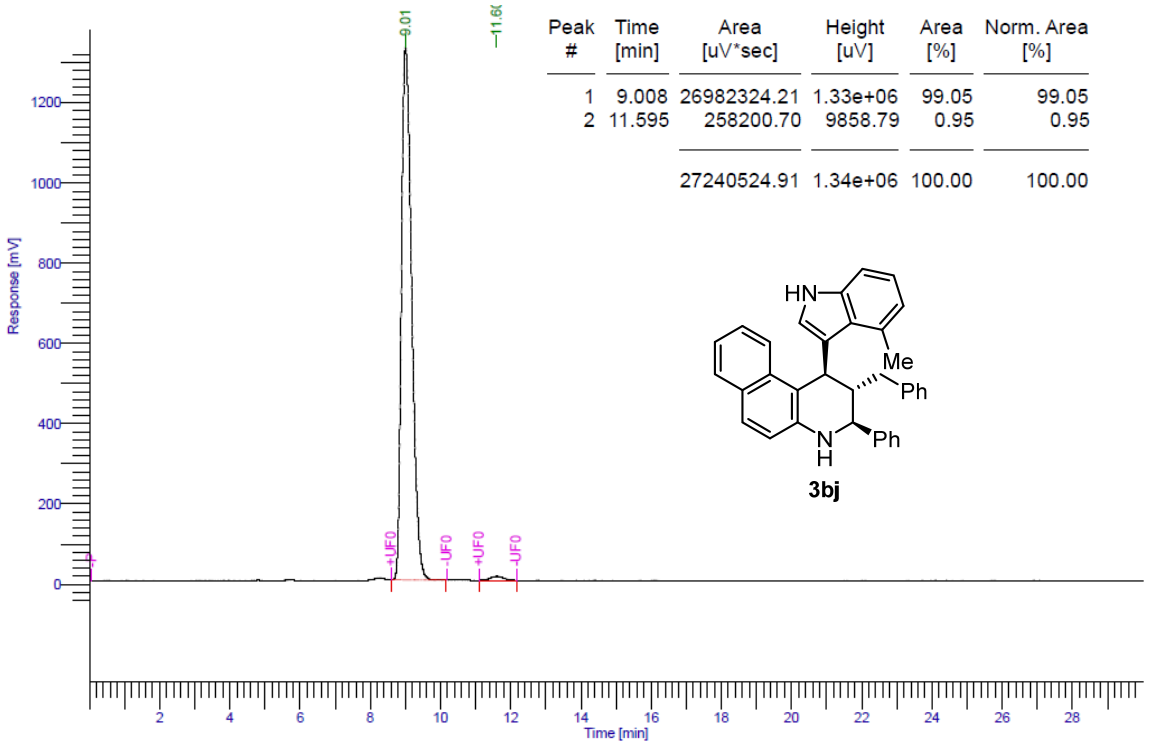
Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1	9.415	9914727.50	402292.21	99.32	99.32
2	16.735	68091.81	1476.54	0.68	0.68
		9982819.30	403768.75	100.00	100.00

2-benzyl-1-(4-methyl-1*H*-indol-3-yl)-3-phenyl-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3bj

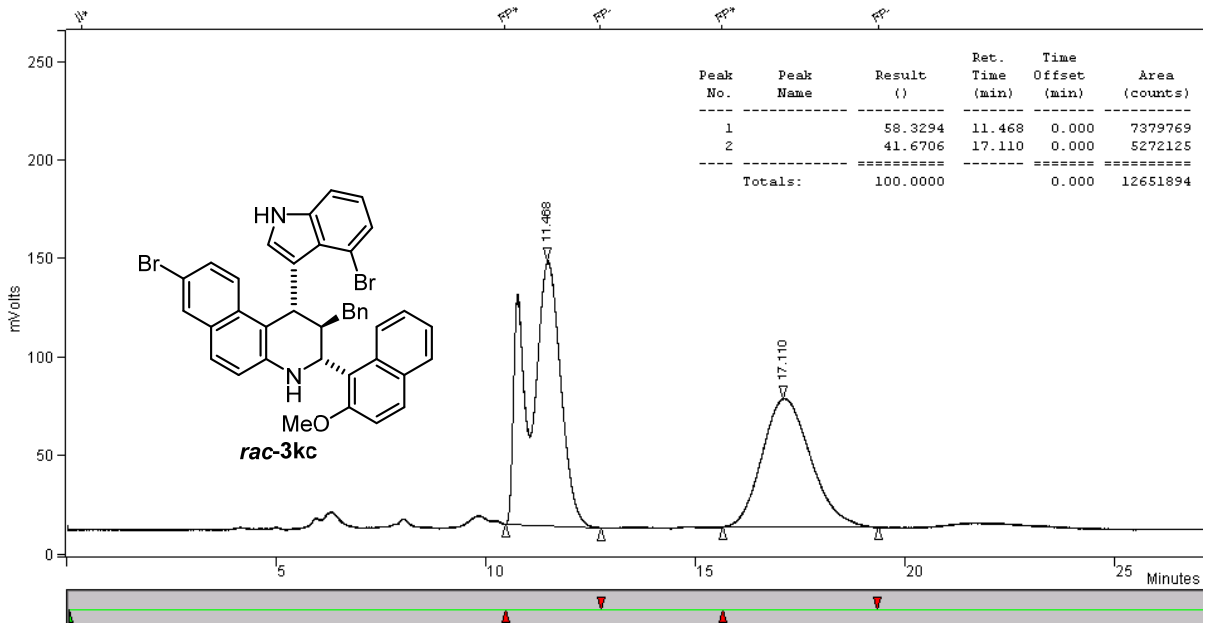


***rac*-3bj**

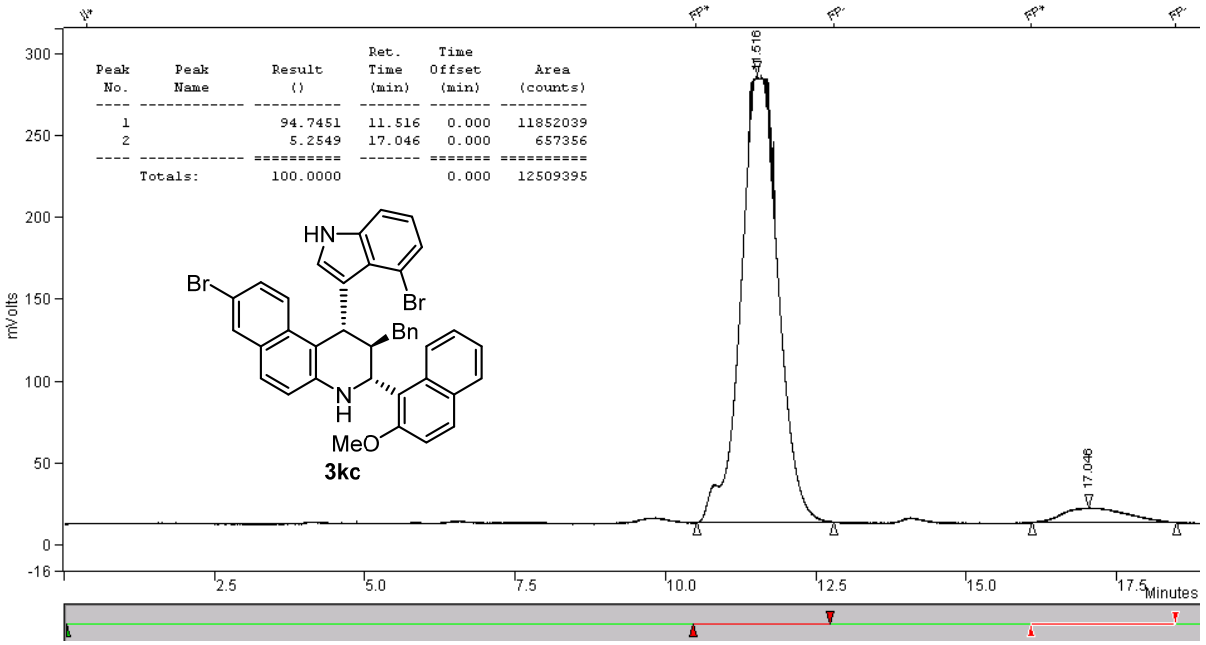
(*1R,2S,3S*)-2-benzyl-1-(4-methyl-1*H*-indol-3-yl)-3-phenyl-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3bj



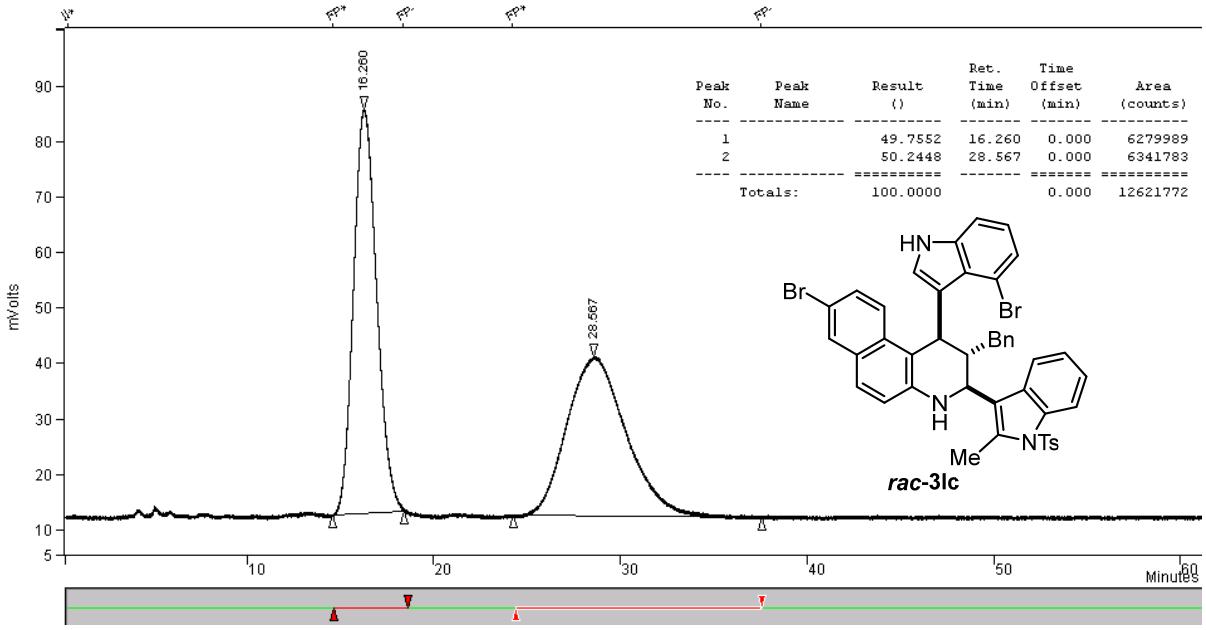
2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(2-methoxynaphthalen-1-yl)-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3kc



(1*S*,2*R*,3*R*)-2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(2-methoxynaphthalen-1-yl)-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3kc

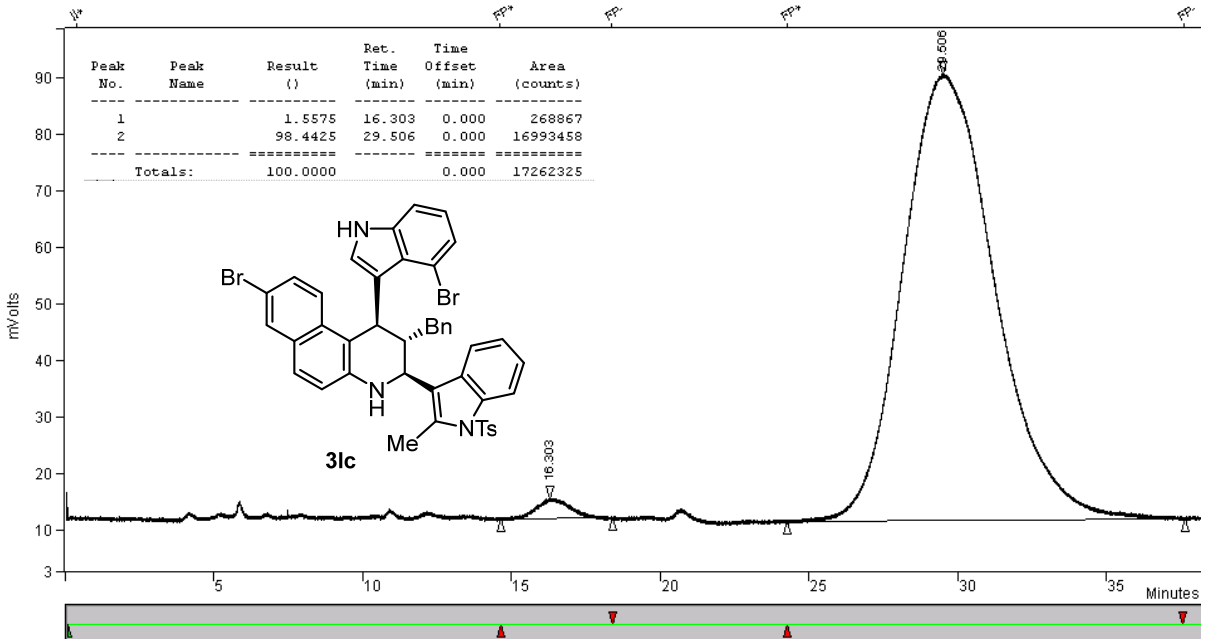


2-benzyl-3-(2-methyl-1-tosyl-1*H*-indol-3-yl)-1-(4-methyl-1*H*-indol-3-yl)-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3lc



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)
1		49.7552	16.260	0.000	6279989
2		50.2448	28.567	0.000	6341783
Totals:		100.0000		0.000	12621772

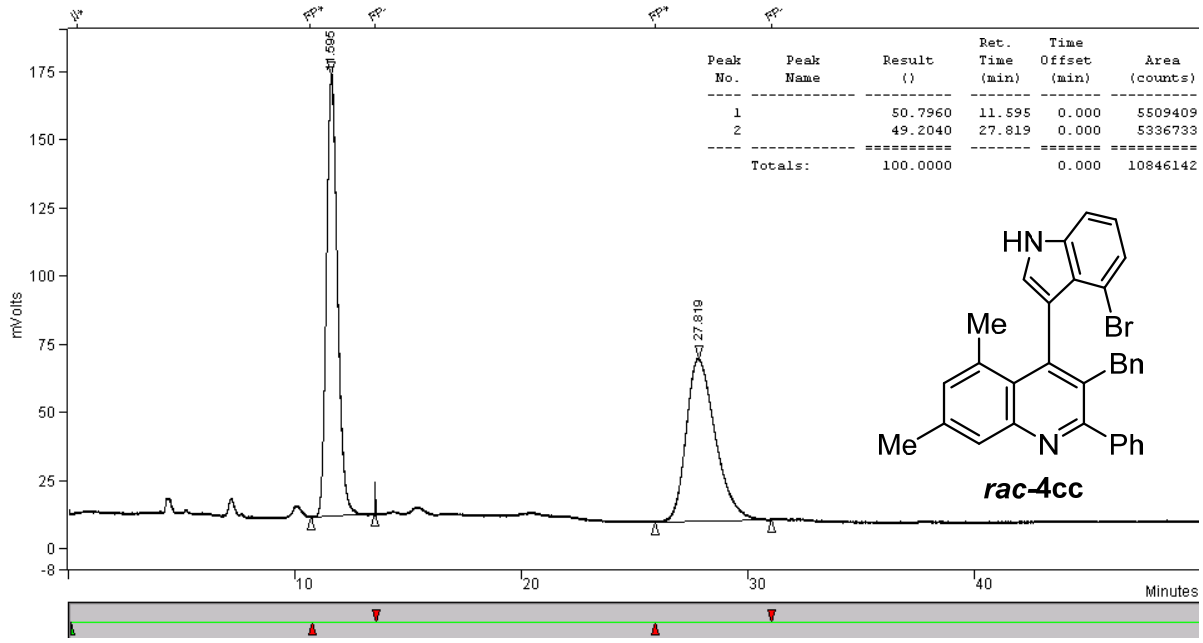
(1*R*,2*S*,3*S*)-2-benzyl-3-(2-methyl-1-tosyl-1*H*-indol-3-yl)-1-(4-methyl-1*H*-indol-3-yl)-1,2,3,4-tetrahydrobenzo[*f*]quinoline 3lc



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)
1		1.5575	16.303	0.000	268867
2		98.4425	29.506	0.000	16993458
Totals:		100.0000		0.000	17262325

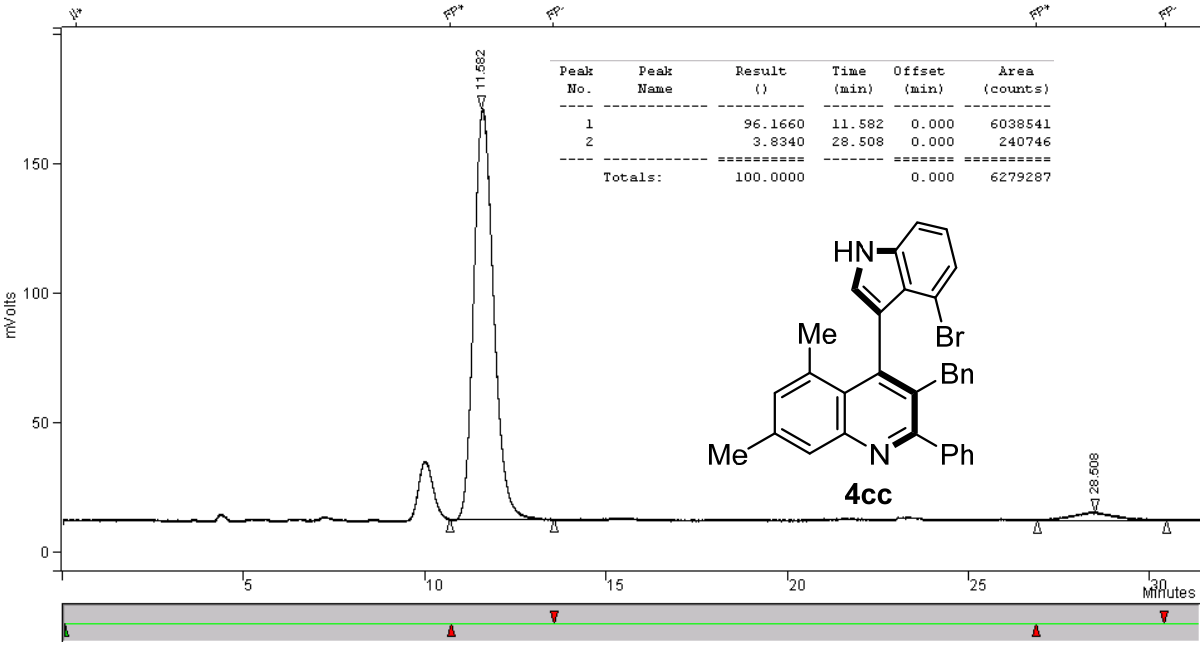
Copies of HPLC traces of products 4

3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-5,7-dimethyl-2-phenylquinoline 4cc



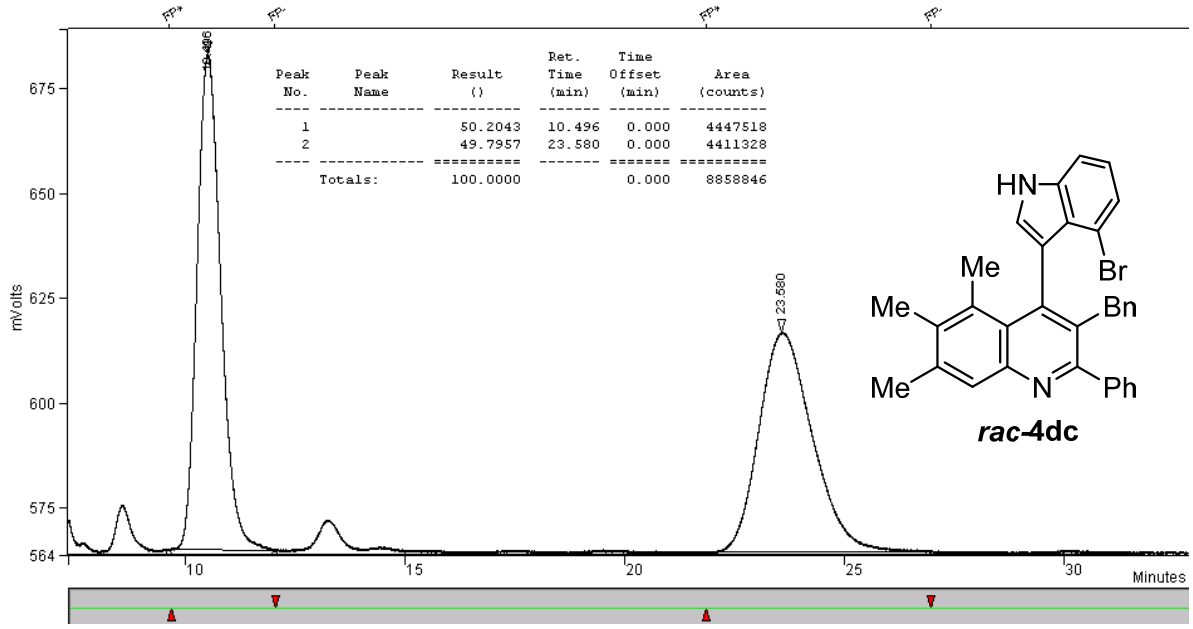
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)
1		50.7960	11.595	0.000	5509409
2		49.2040	27.819	0.000	5336733
	Totals:	100.0000		0.000	10846142

(*aS*)-3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-5,7-dimethyl-2-phenylquinoline 4cc

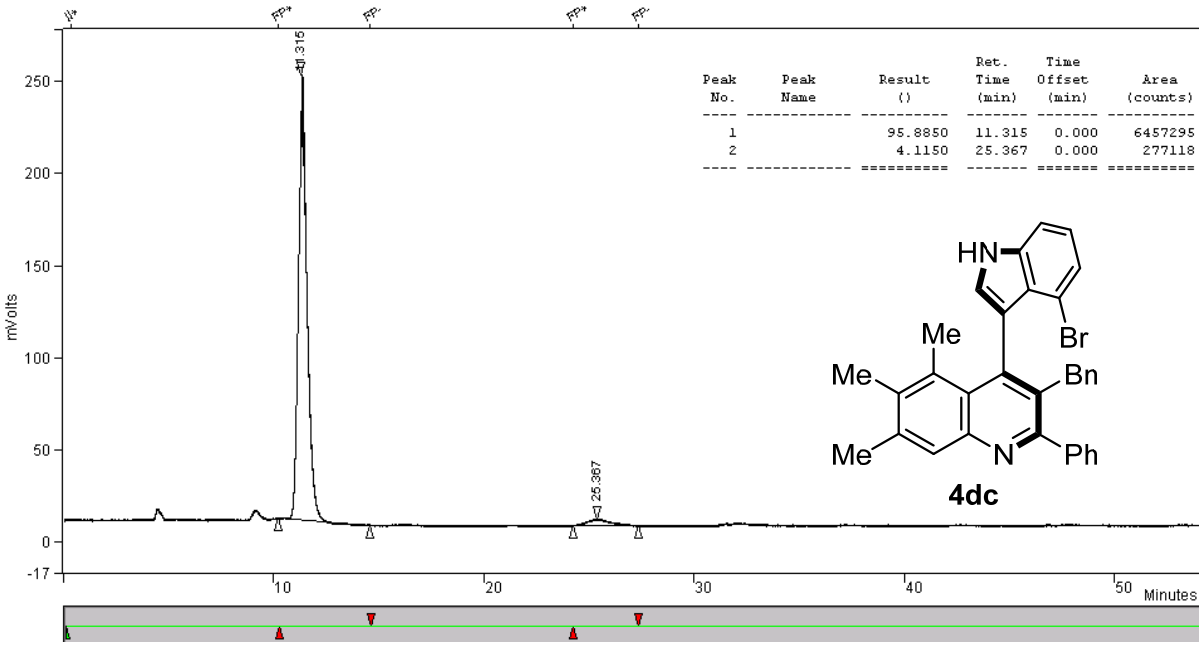


Peak No.	Peak Name	Result ()	Time (min)	Offset (min)	Area (counts)
1		96.1660	11.582	0.000	6038541
2		3.8340	28.508	0.000	240746
	Totals:	100.0000		0.000	6279287

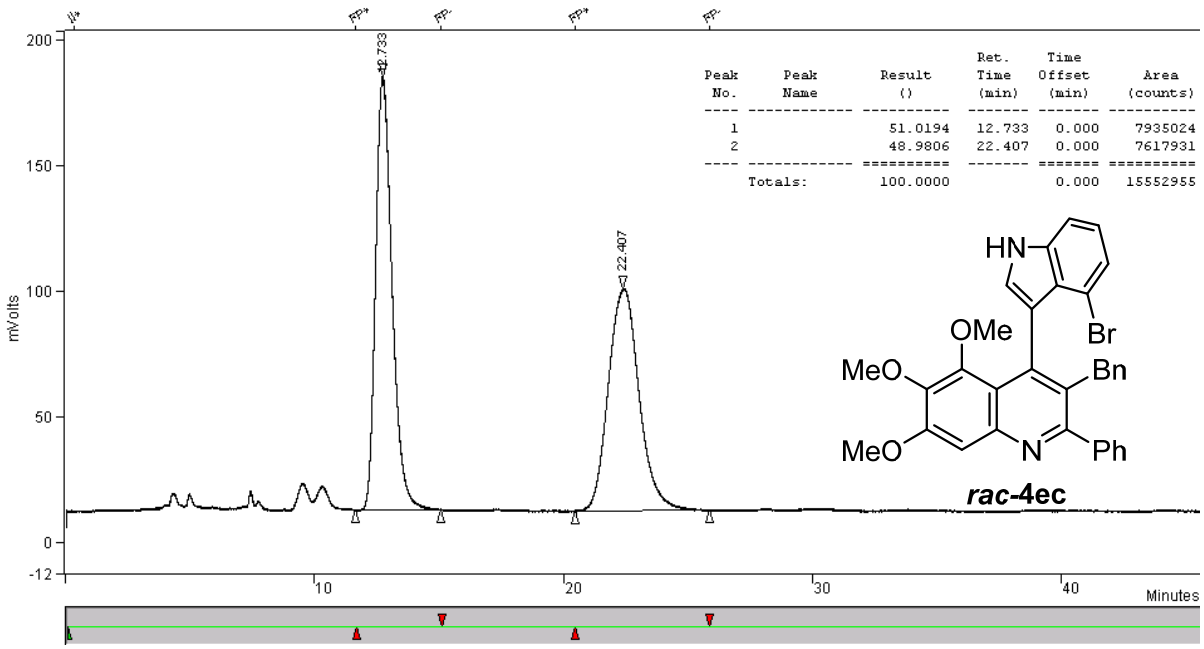
3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-5,6,7-trimethyl-2-phenylquinoline 4dc



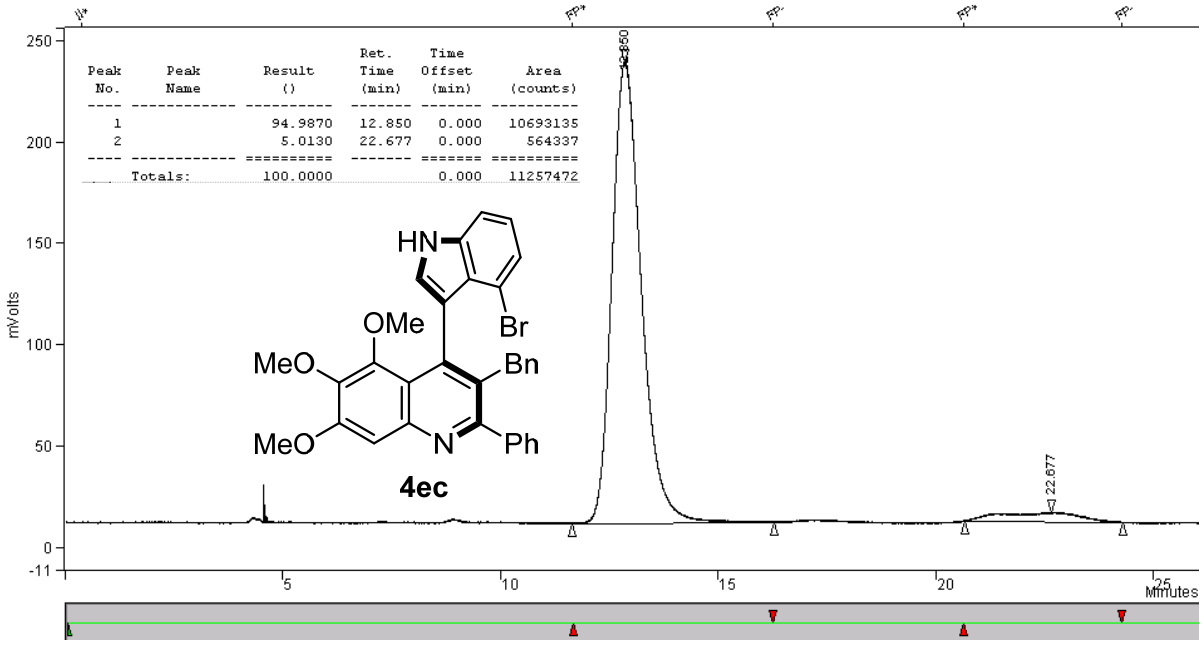
(*aS*)-3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-5,6,7-trimethyl-2-phenylquinoline 4dc



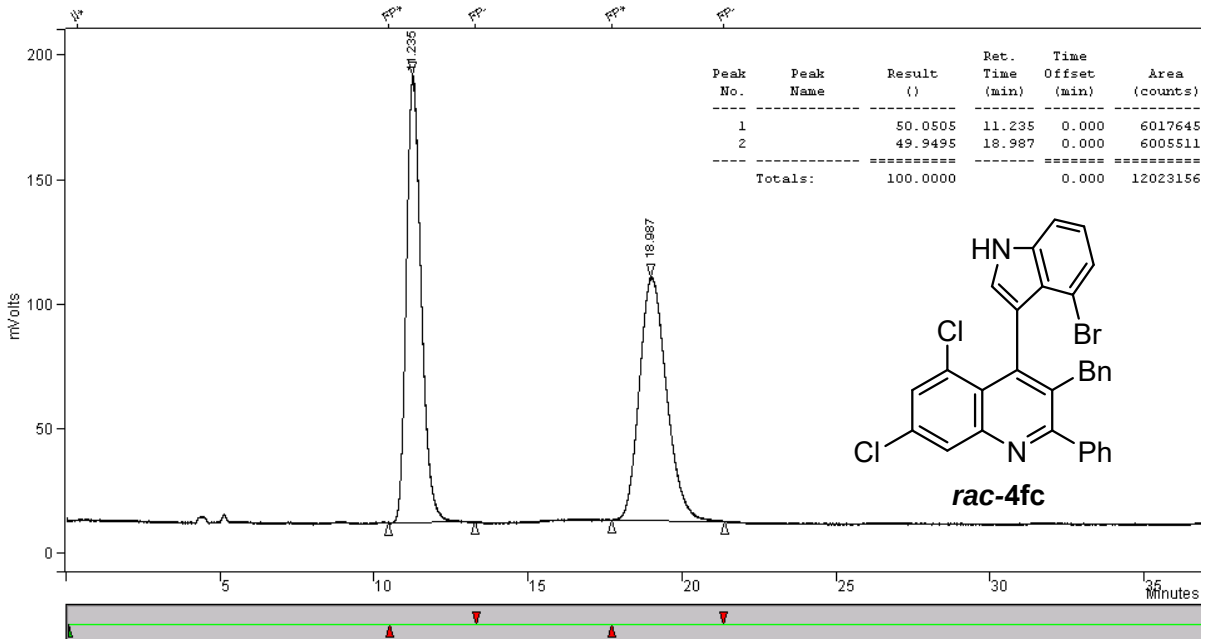
3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-5,6,7-trimethoxy-2-phenylquinoline 4ec



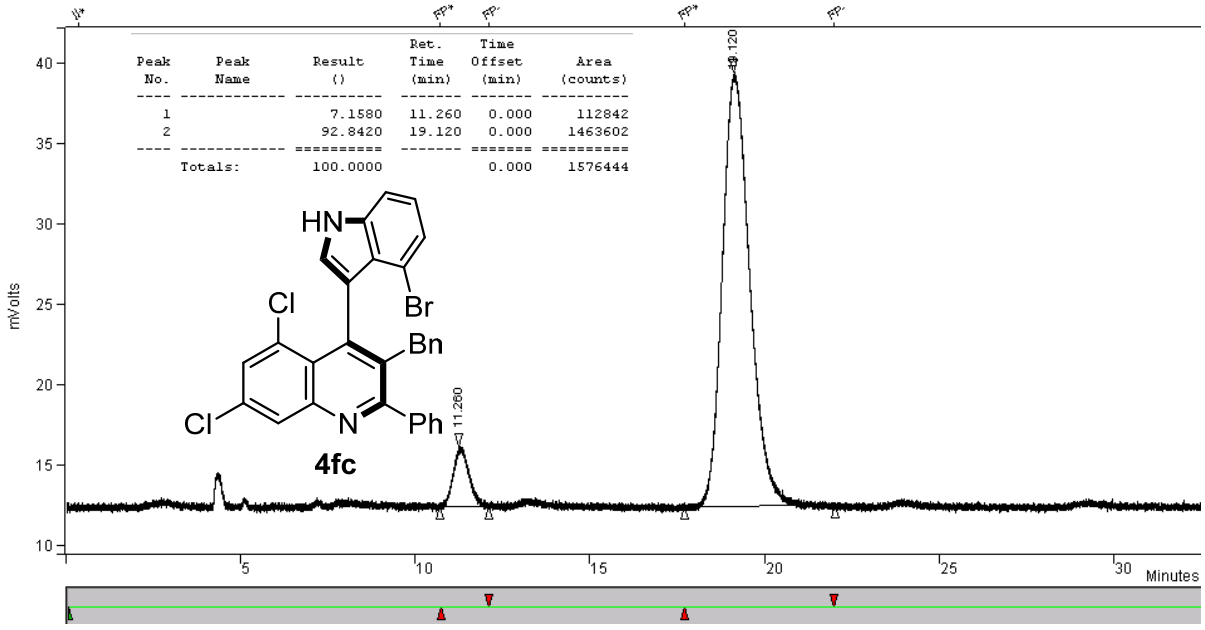
(*aS*)-3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-5,6,7-trimethoxy-2-phenylquinoline 4ec



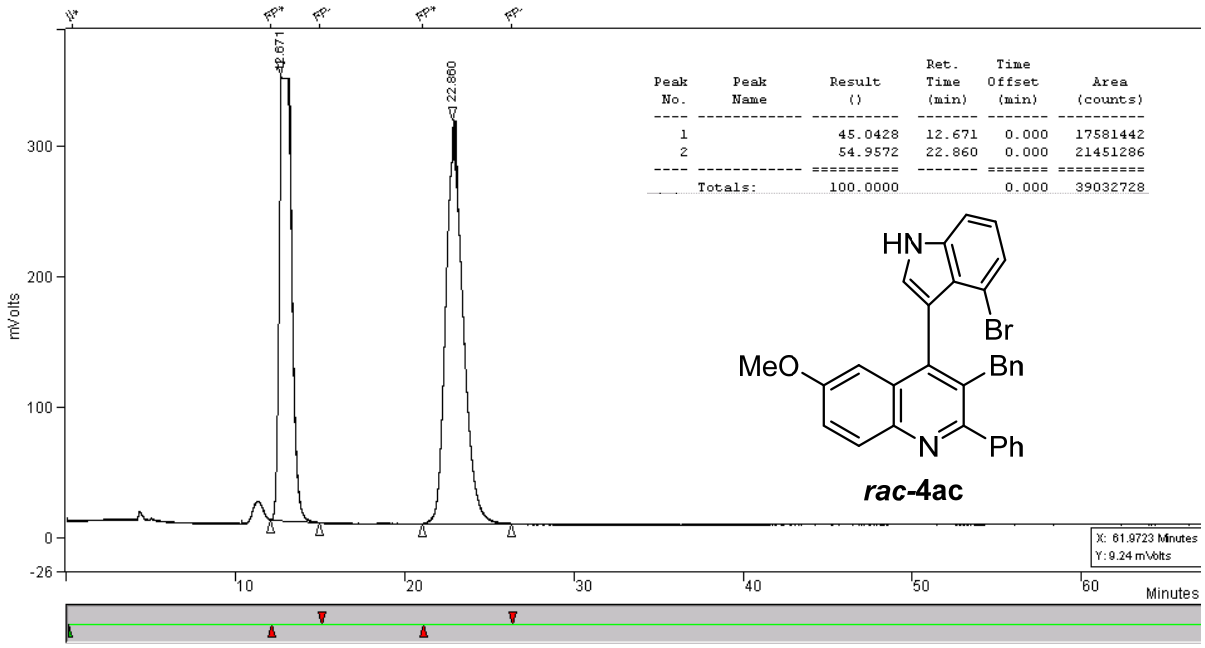
3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-5,7-dichloro-2-phenylquinoline 4fc



(*aS*)-3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-5,7-dichloro-2-phenylquinoline 4fc

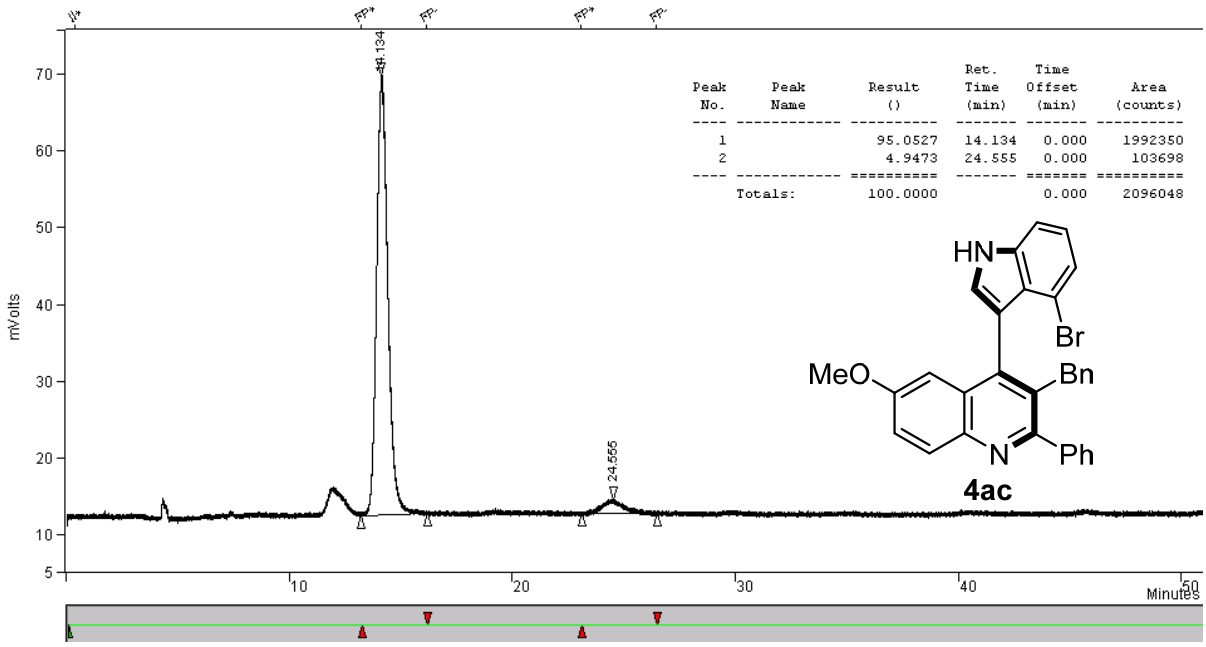


3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-6-methoxy-2-phenylquinoline 4ac



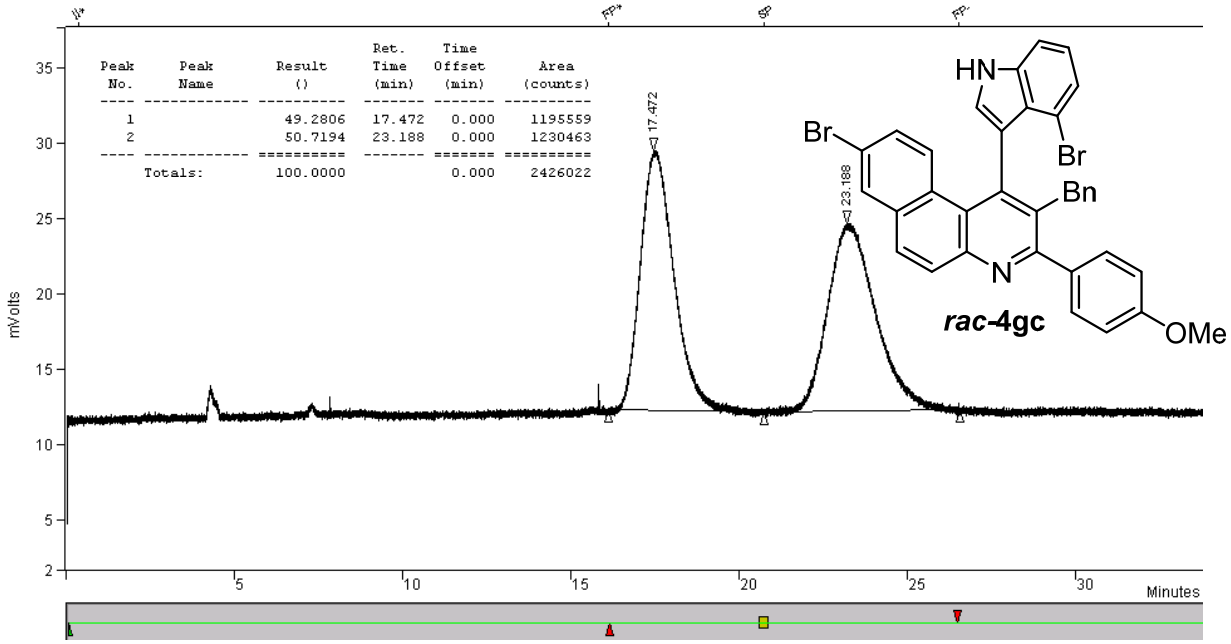
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)
1		45.0428	12.671	0.000	17581442
2		54.9572	22.860	0.000	21451286
	Totals:	100.0000		0.000	39032728

(*aS*)-3-benzyl-4-(4-bromo-1*H*-indol-3-yl)-6-methoxy-2-phenylquinoline 4ac

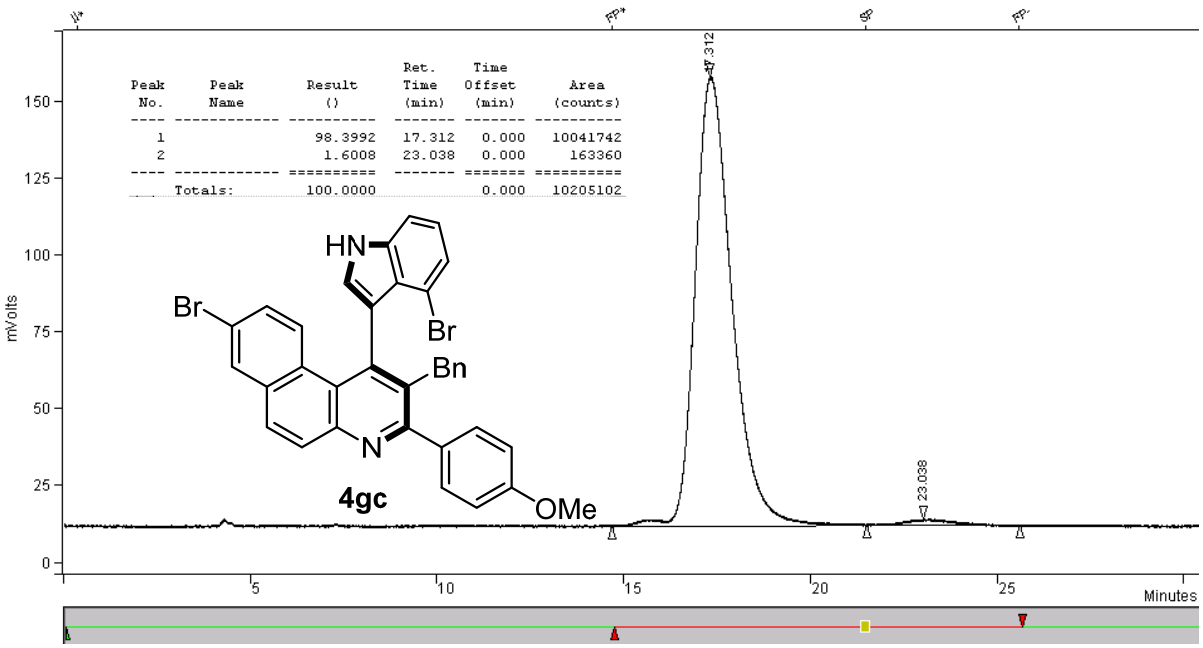


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)
1		95.0527	14.134	0.000	1992350
2		4.9473	24.555	0.000	103698
	Totals:	100.0000		0.000	2096048

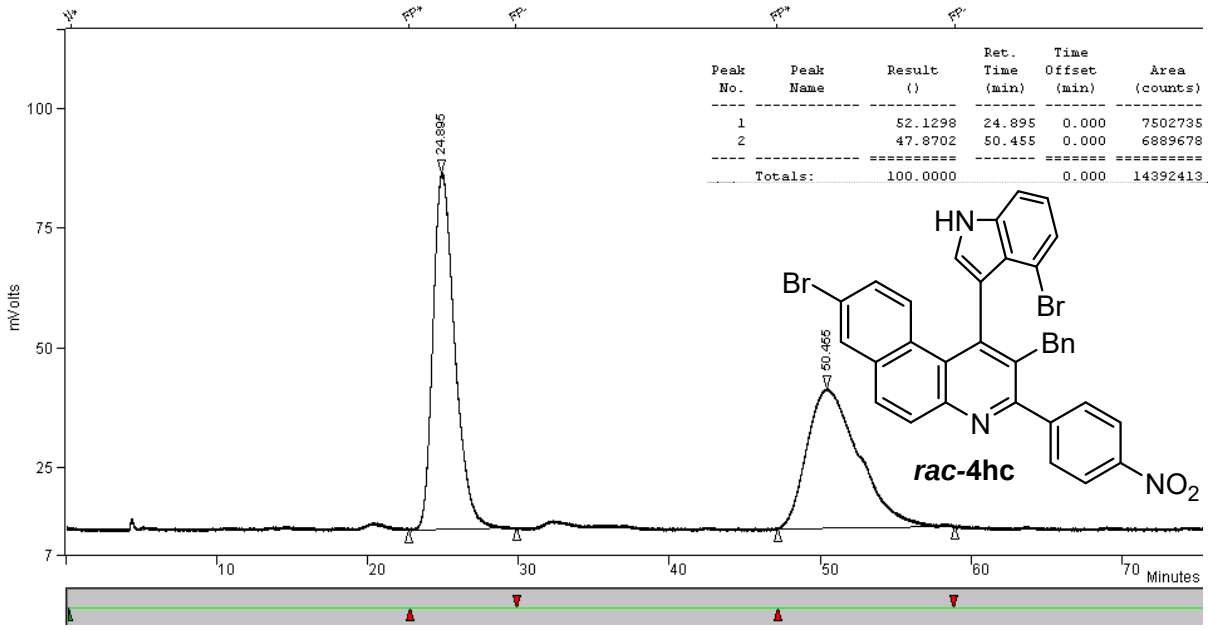
2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(4-methoxyphenyl)benzo[*f*]quinoline 4gc



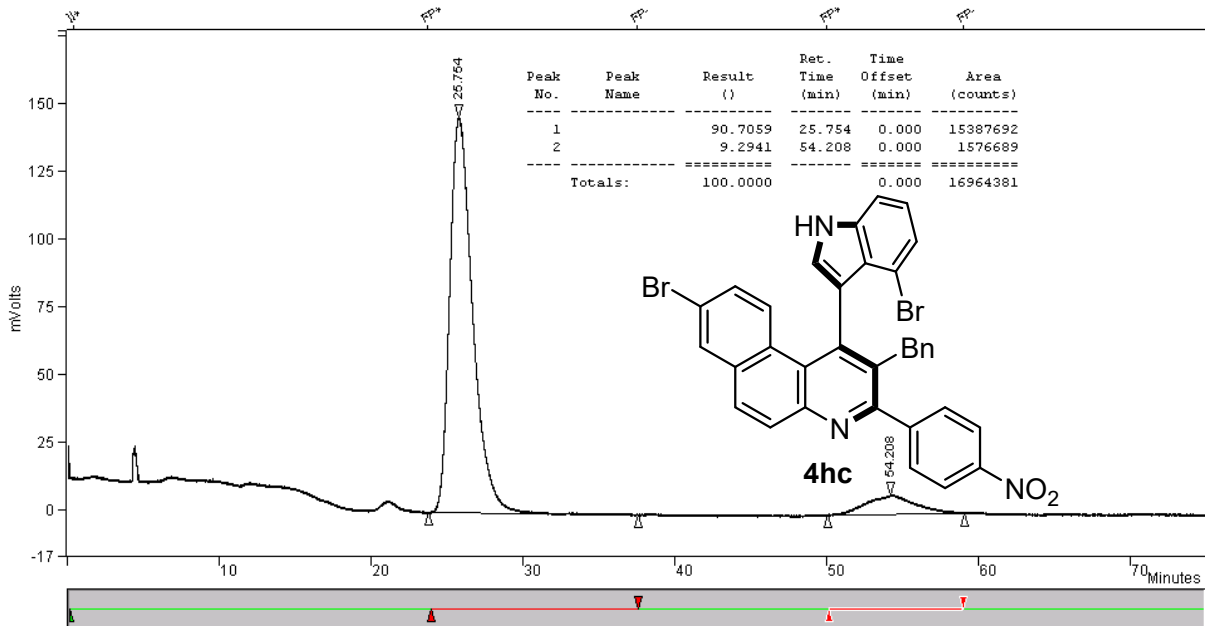
(*aS*)-2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(4-methoxyphenyl)benzo[*f*]quinoline 4gc



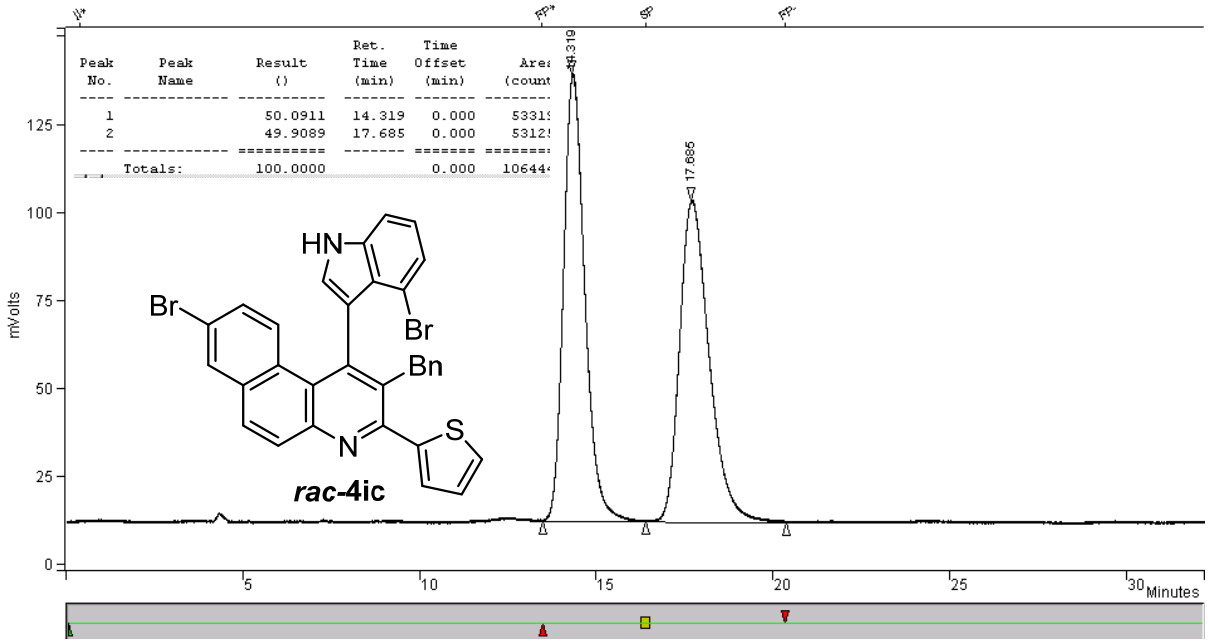
2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(4-nitrophenyl)benzo[*f*]quinoline 4hc



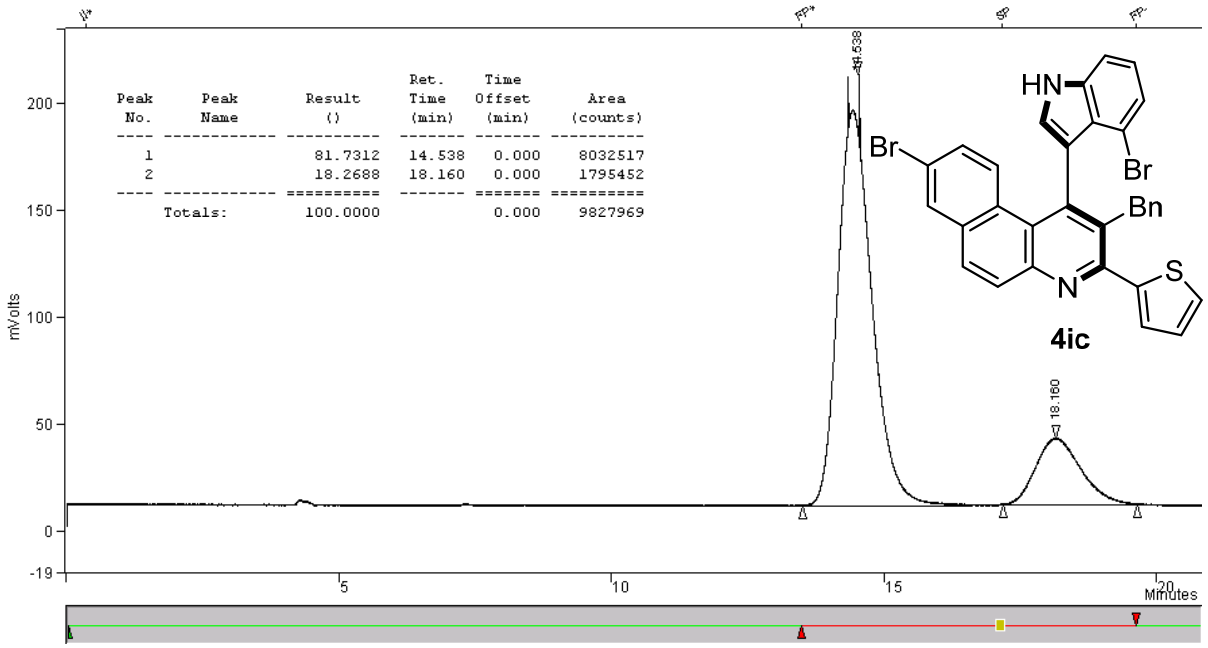
(*aS*)-2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(4-nitrophenyl)benzo[*f*]quinoline 4hc



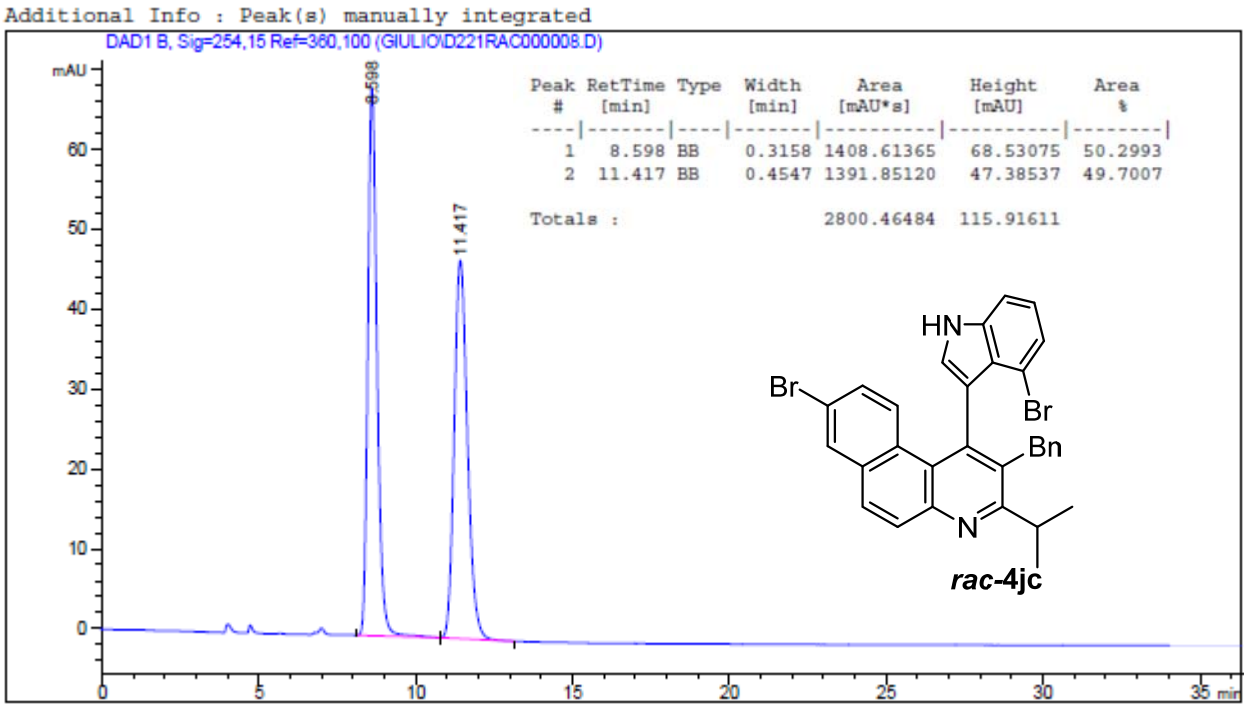
2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(thiophen-2-yl)benzo[*f*]quinoline 4ic



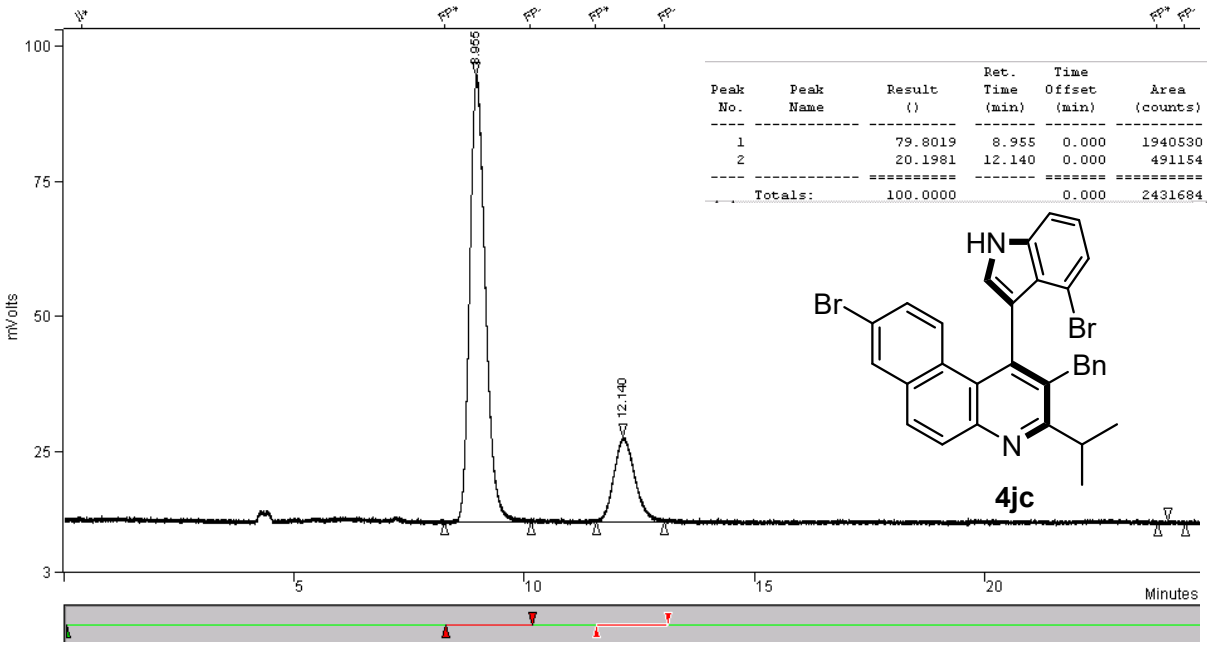
(*aS*)-2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(thiophen-2-yl)benzo[*f*]quinoline 4ic



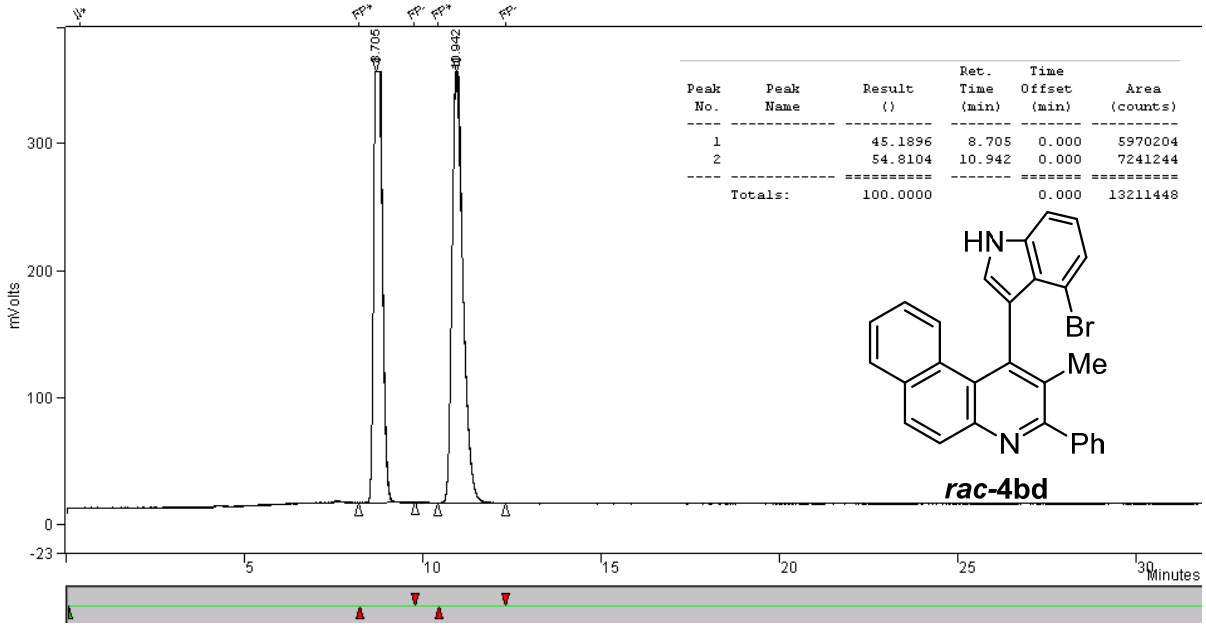
2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-isopropylbenzo[*f*]quinoline 4jc



(*aS*)-2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-isopropylbenzo[*f*]quinoline 4jc

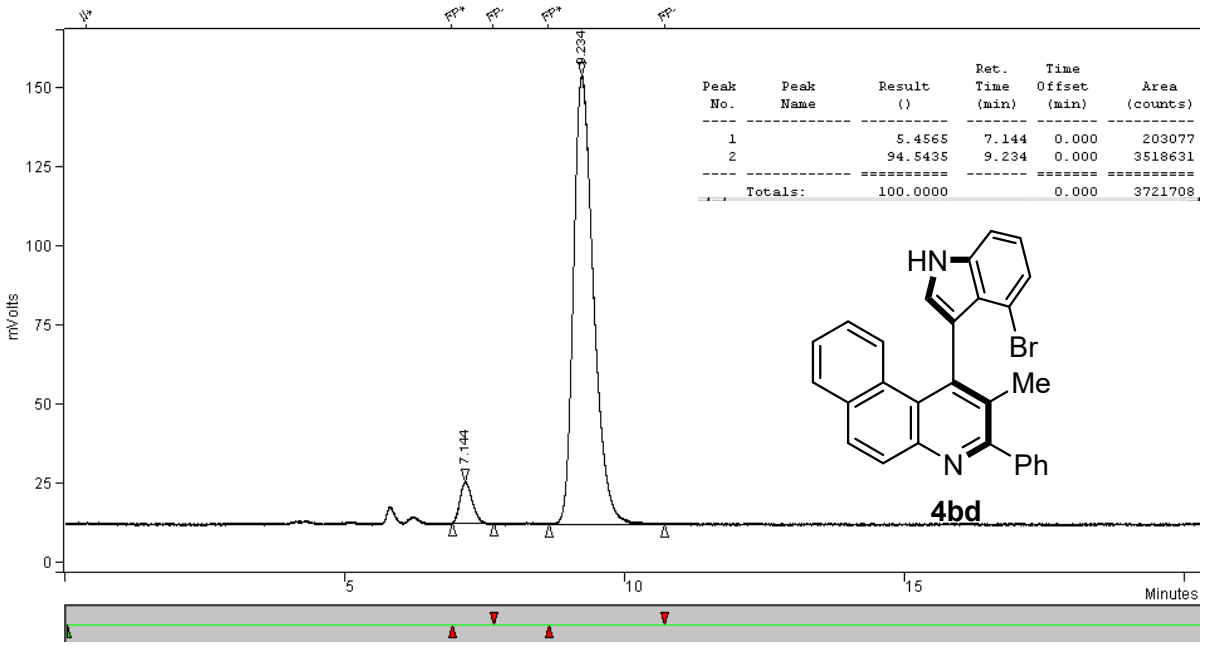


1-(4-bromo-1*H*-indol-3-yl)-2-methyl-3-phenylbenzo[*f*]quinoline 4bd



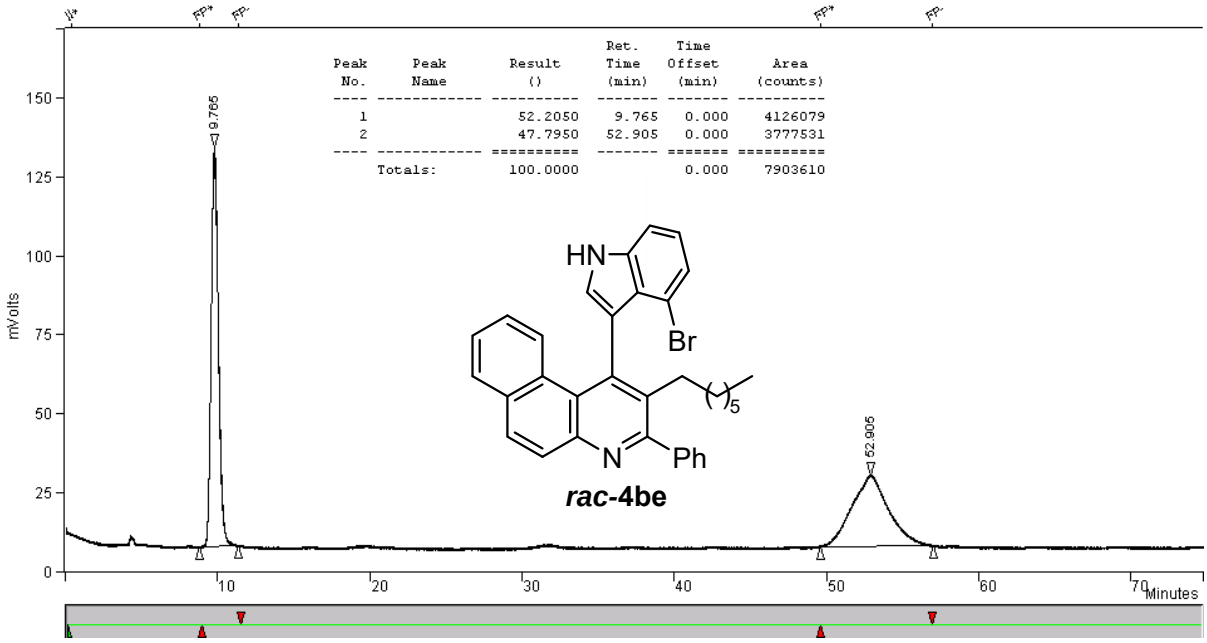
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)
1		45.1896	8.705	0.000	5970204
2		54.8104	10.942	0.000	7241244
Totals:		100.0000		0.000	13211448

(*aS*)-1-(4-bromo-1*H*-indol-3-yl)-2-methyl-3-phenylbenzo[*f*]quinoline 4bd

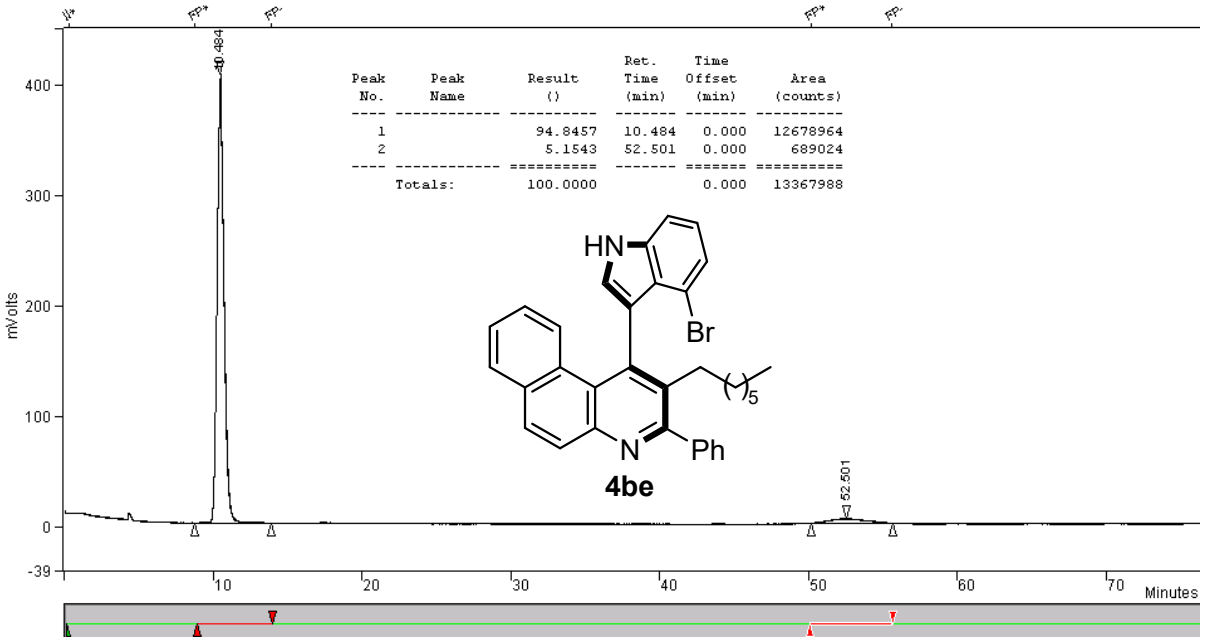


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)
1		5.4565	7.144	0.000	203077
2		94.5435	9.234	0.000	3518631
Totals:		100.0000		0.000	3721708

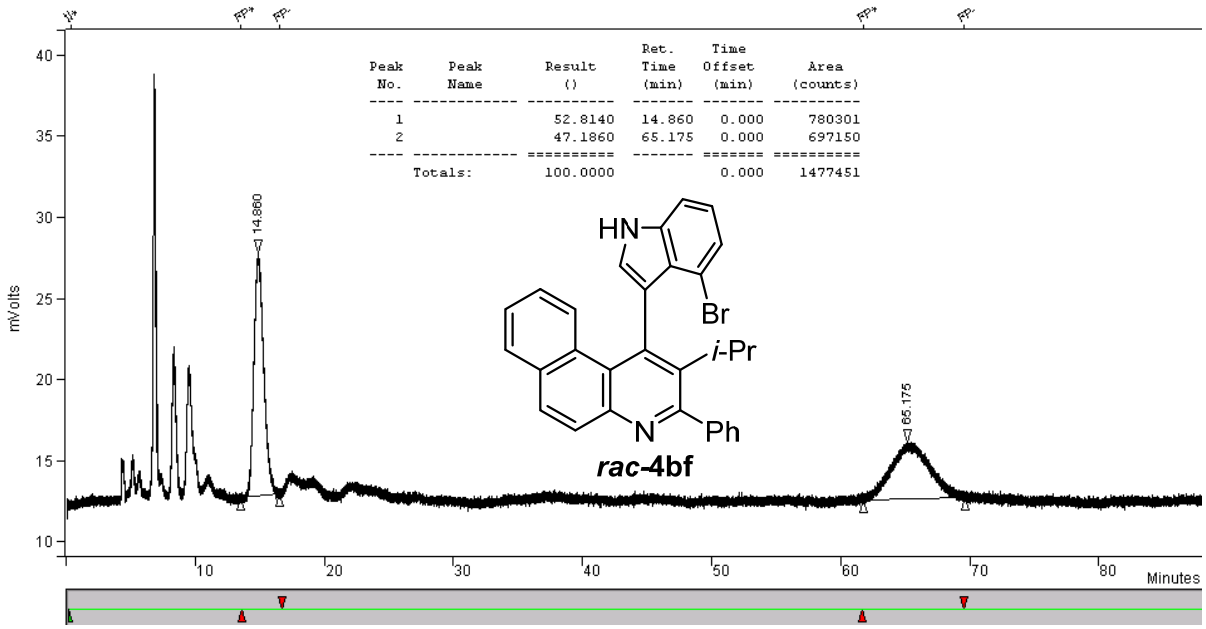
1-(4-bromo-1*H*-indol-3-yl)-2-heptyl-3-phenylbenzo[*f*]quinoline 4be



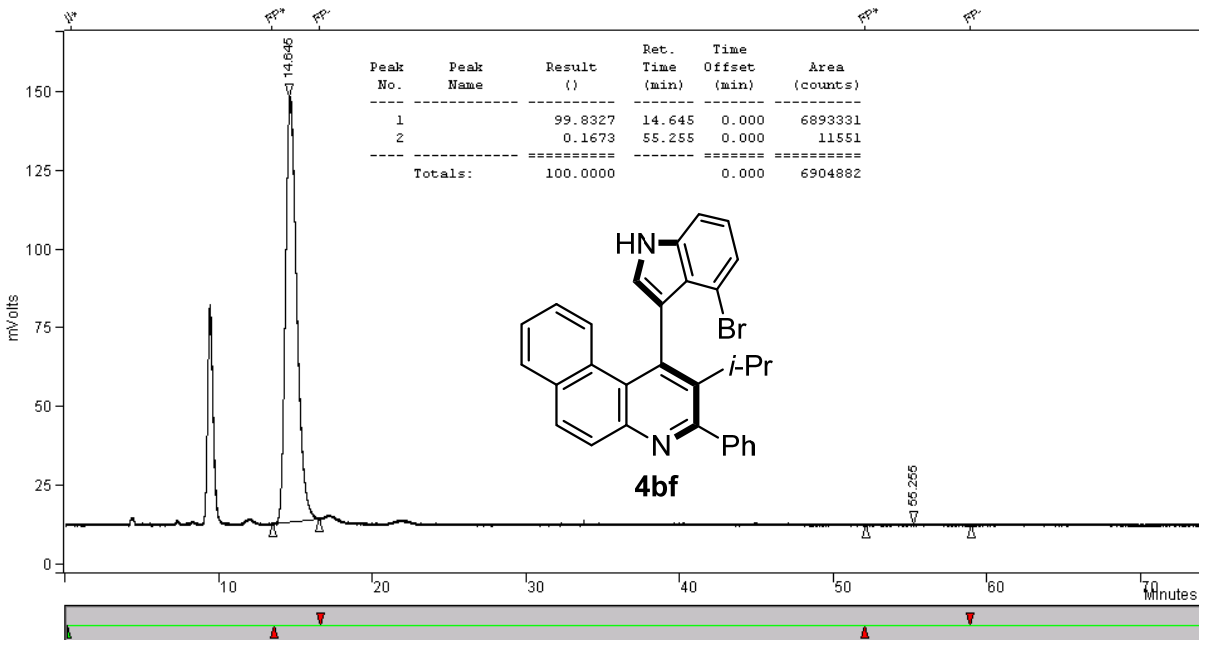
(*aS*)-1-(4-bromo-1*H*-indol-3-yl)-2-heptyl-3-phenylbenzo[*f*]quinoline 4be



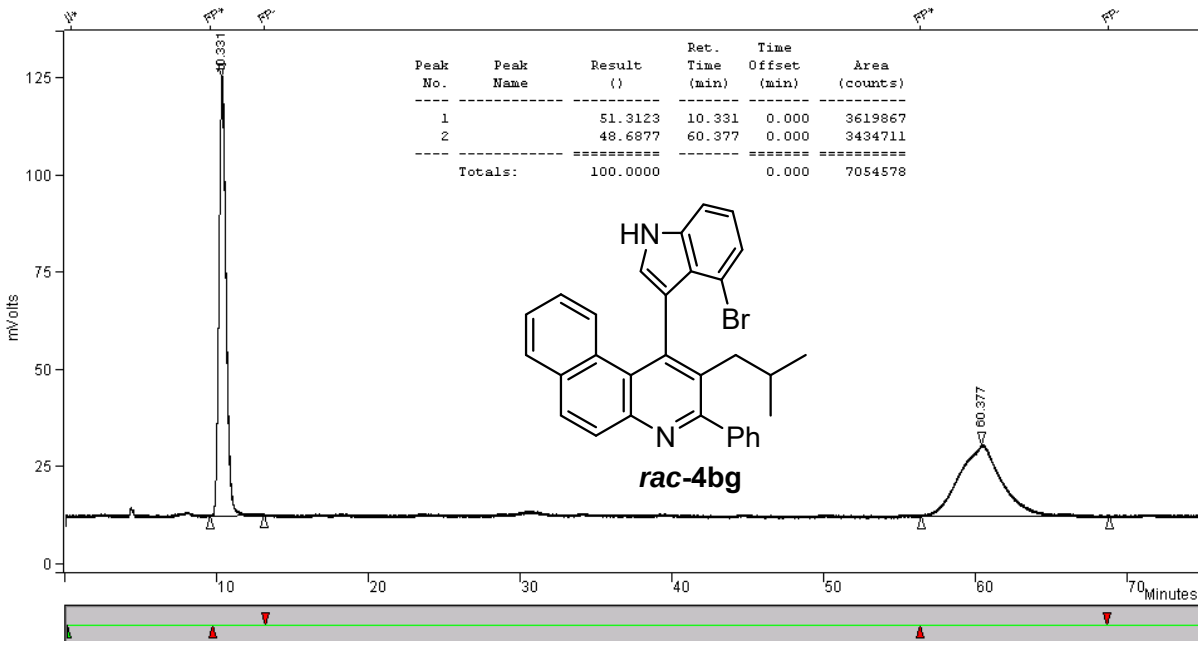
1-(4-bromo-1*H*-indol-3-yl)-2-isopropyl-3-phenylbenzo[*f*]quinoline 4bf



(*aS*)-1-(4-bromo-1*H*-indol-3-yl)-2-isopropyl-3-phenylbenzo[*f*]quinoline 4bf

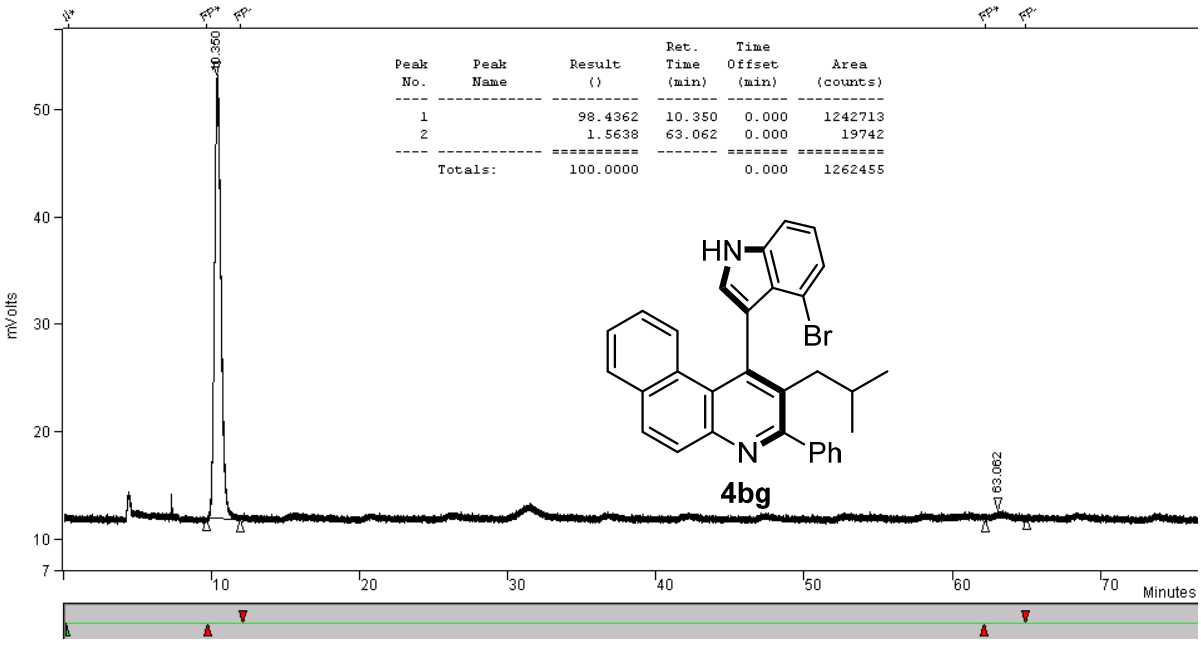


1-(4-bromo-1*H*-indol-3-yl)-2-isobutyl-3-phenylbenzo[*f*]quinoline 4bg



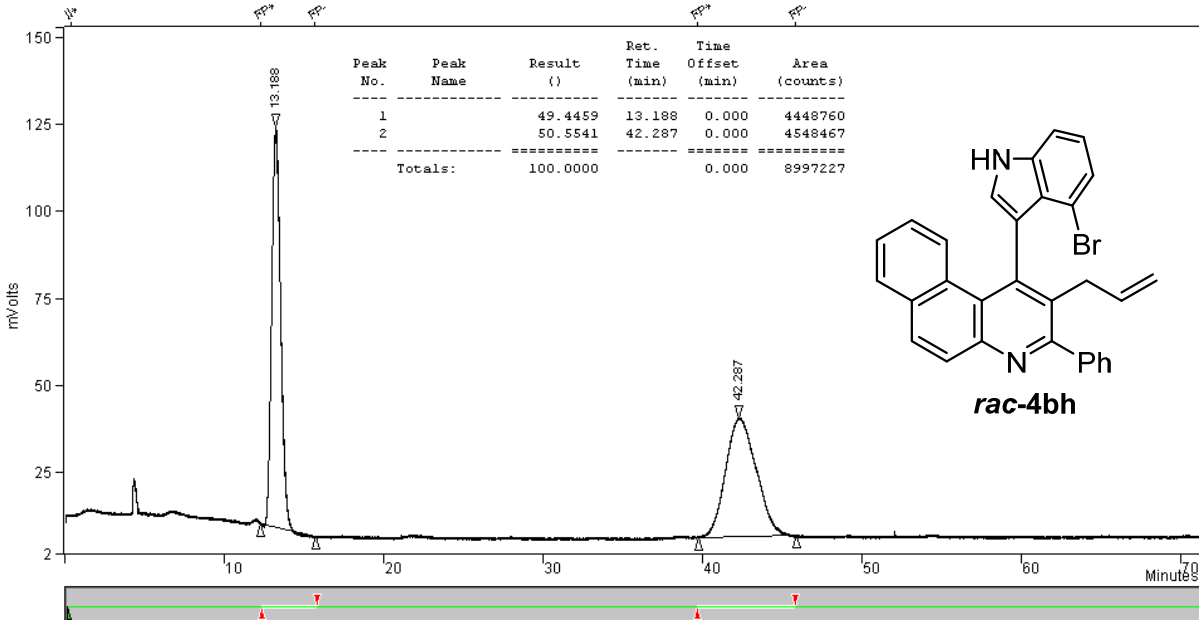
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)
1		51.3123	10.331	0.000	3619867
2		48.6877	60.377	0.000	3434711
Totals:		100.0000		0.000	7054578

(*aS*)-1-(4-bromo-1*H*-indol-3-yl)-2-isobutyl-3-phenylbenzo[*f*]quinoline 4bg

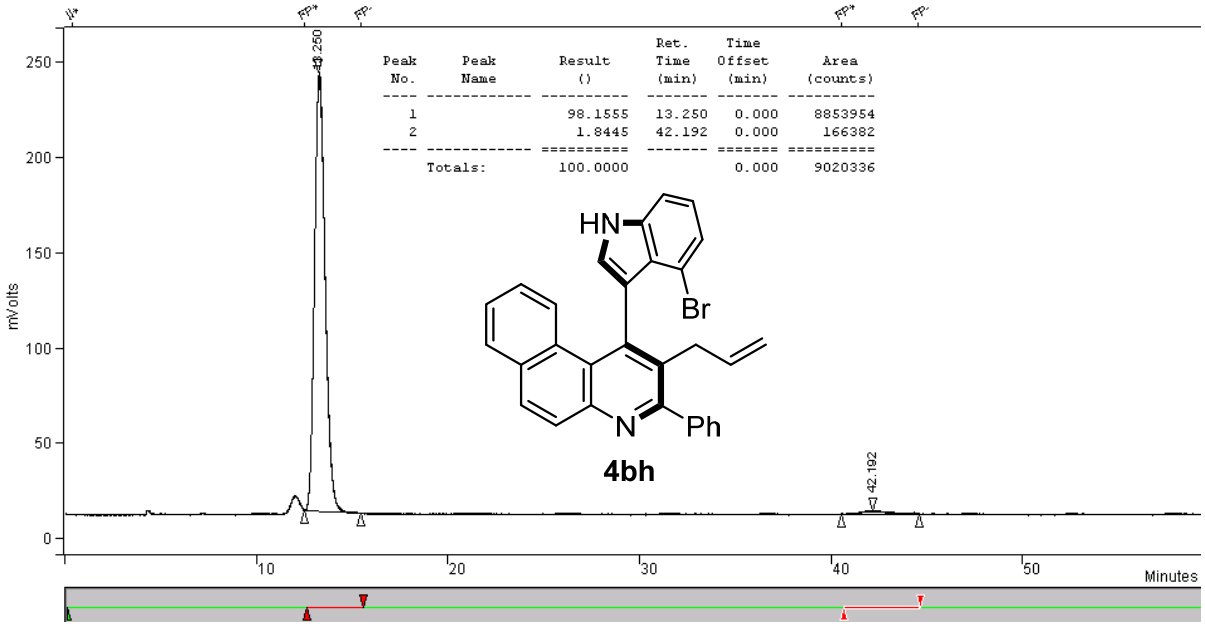


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)
1		98.4362	10.350	0.000	1242713
2		1.5638	63.062	0.000	19742
Totals:		100.0000		0.000	1262455

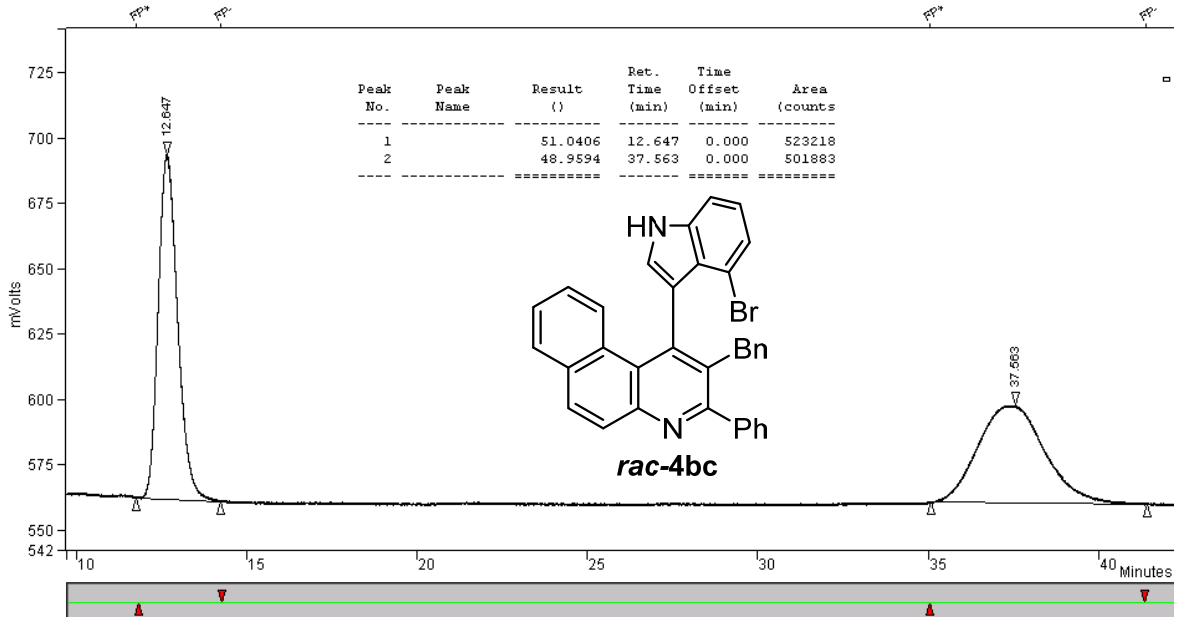
2-allyl-1-(4-bromo-1*H*-indol-3-yl)-3-phenylbenzo[*f*]quinoline 4bh



(*aS*)-2-allyl-1-(4-bromo-1*H*-indol-3-yl)-3-phenylbenzo[*f*]quinoline 4bh

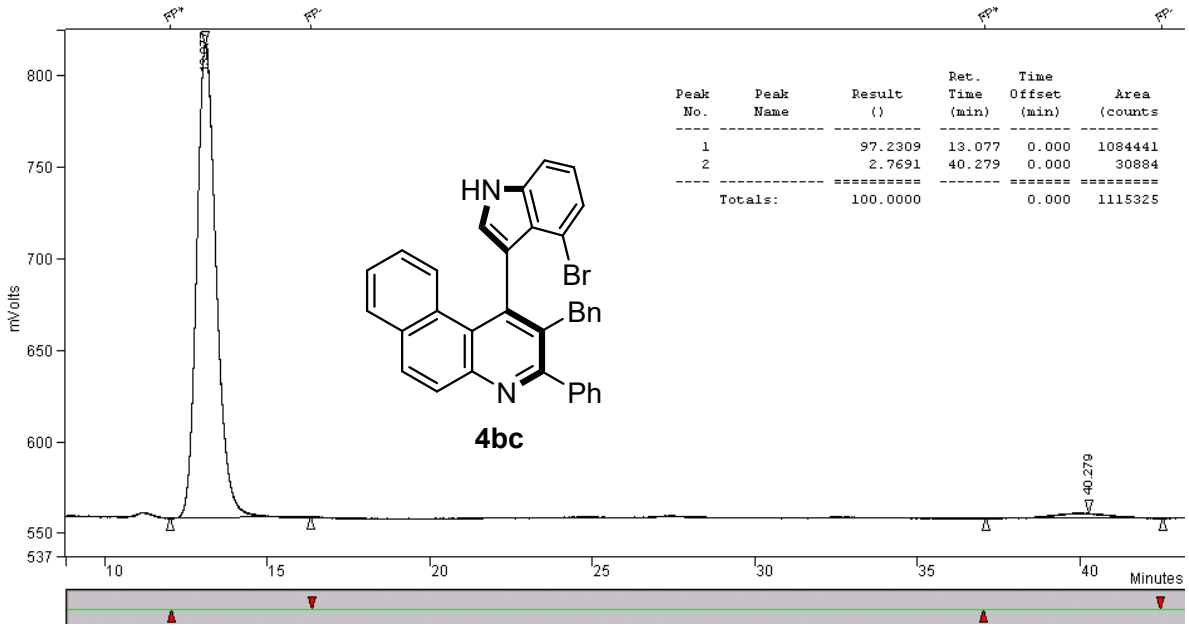


2-benzyl-1-(4-bromo-1*H*-indol-3-yl)-3-phenylbenzo[*f*]quinoline 4bc



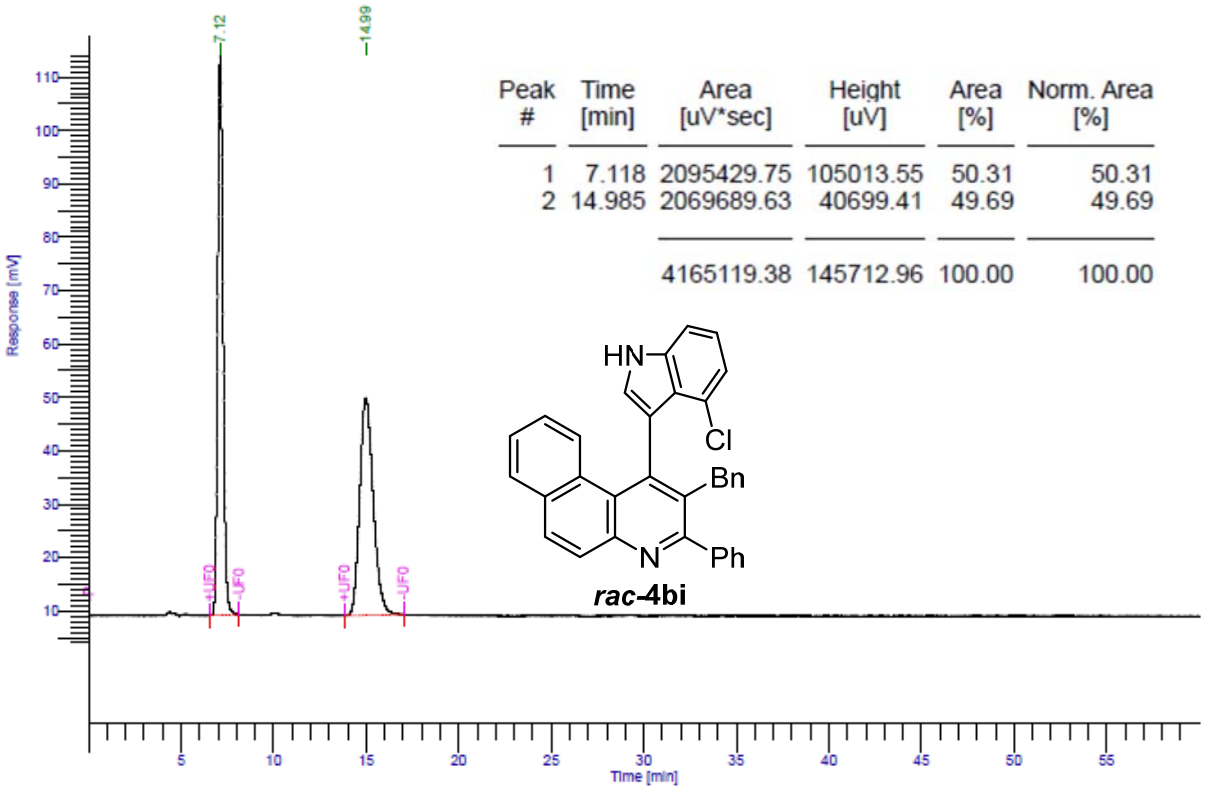
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts
1		51.0406	12.647	0.000	523218
2		48.9594	37.563	0.000	501883

(*aS*)-2-benzyl-1-(4-bromo-1*H*-indol-3-yl)-3-phenylbenzo[*f*]quinoline 4bc



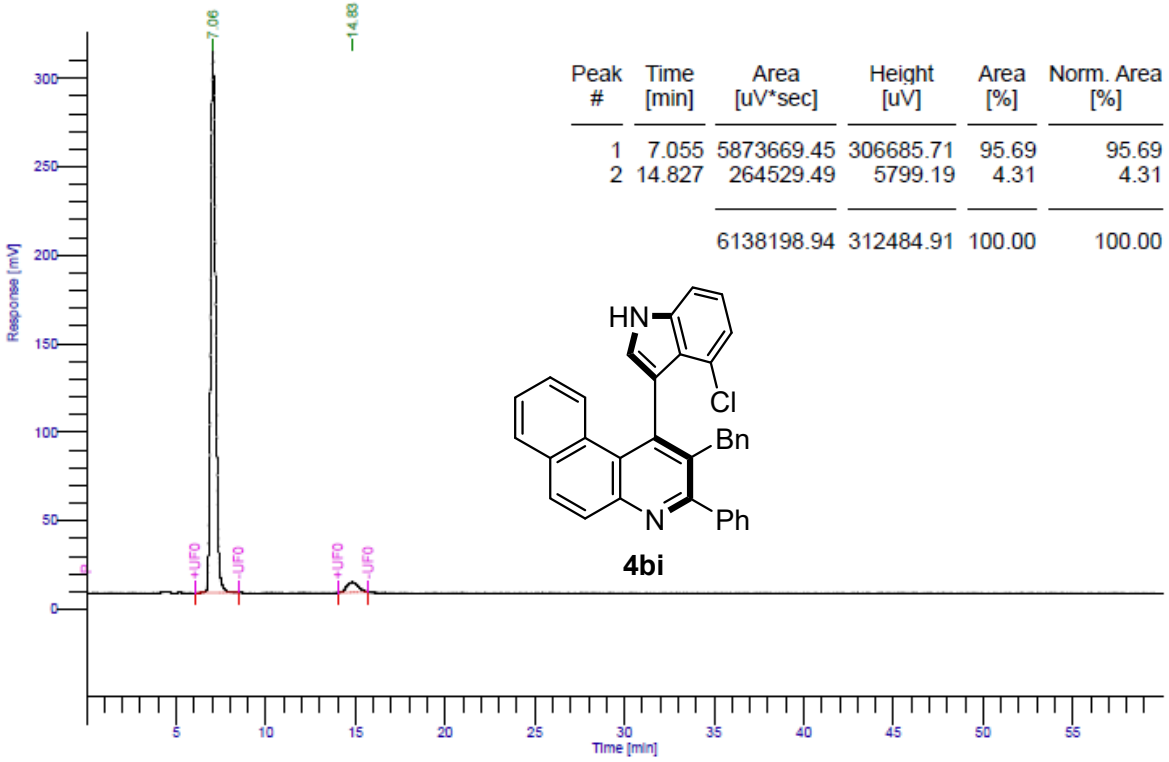
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts
1		97.2309	13.077	0.000	1084441
2		2.7691	40.279	0.000	30884
	Totals:	100.0000		0.000	1115325

2-benzyl-1-(4-chloro-1*H*-indol-3-yl)-3-phenylbenzo[*f*]quinoline 4bi



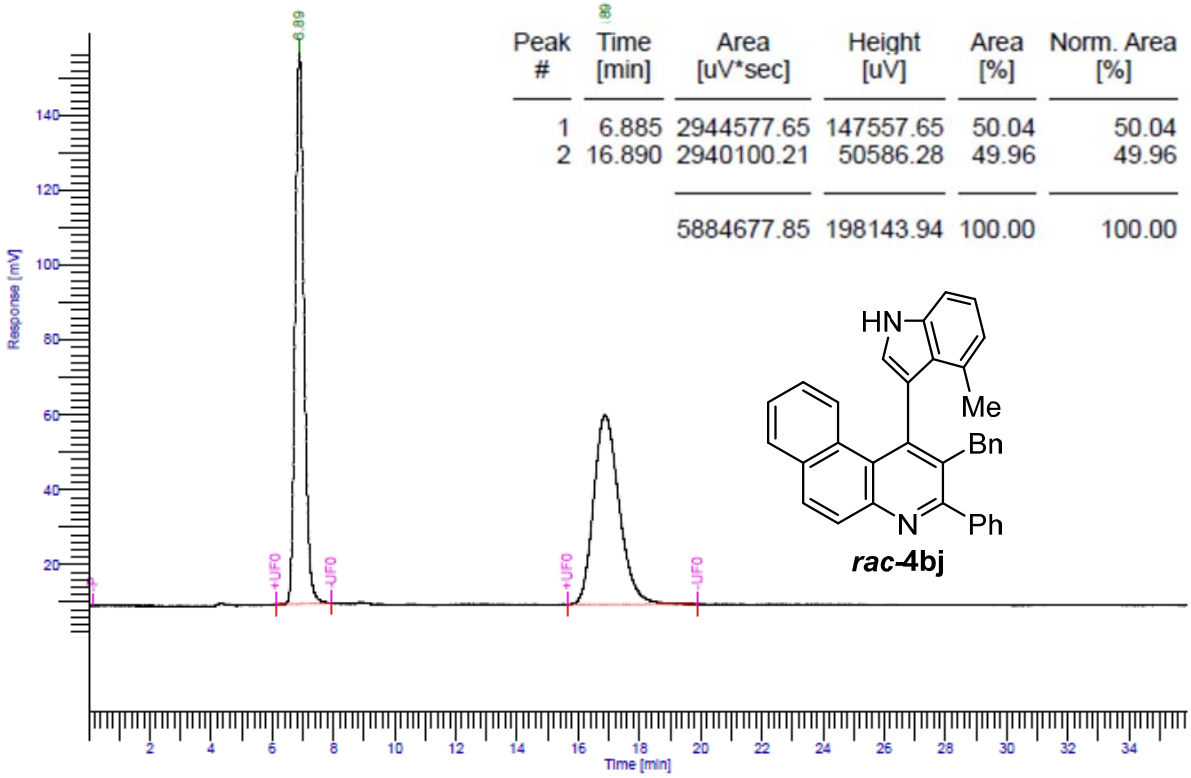
Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1	7.118	2095429.75	105013.55	50.31	50.31
2	14.985	2069689.63	40699.41	49.69	49.69
		4165119.38	145712.96	100.00	100.00

(*aS*)-2-benzyl-1-(4-chloro-1*H*-indol-3-yl)-3-phenylbenzo[*f*]quinoline 4bi



Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1	7.055	5873669.45	306685.71	95.69	95.69
2	14.827	264529.49	5799.19	4.31	4.31
		6138198.94	312484.91	100.00	100.00

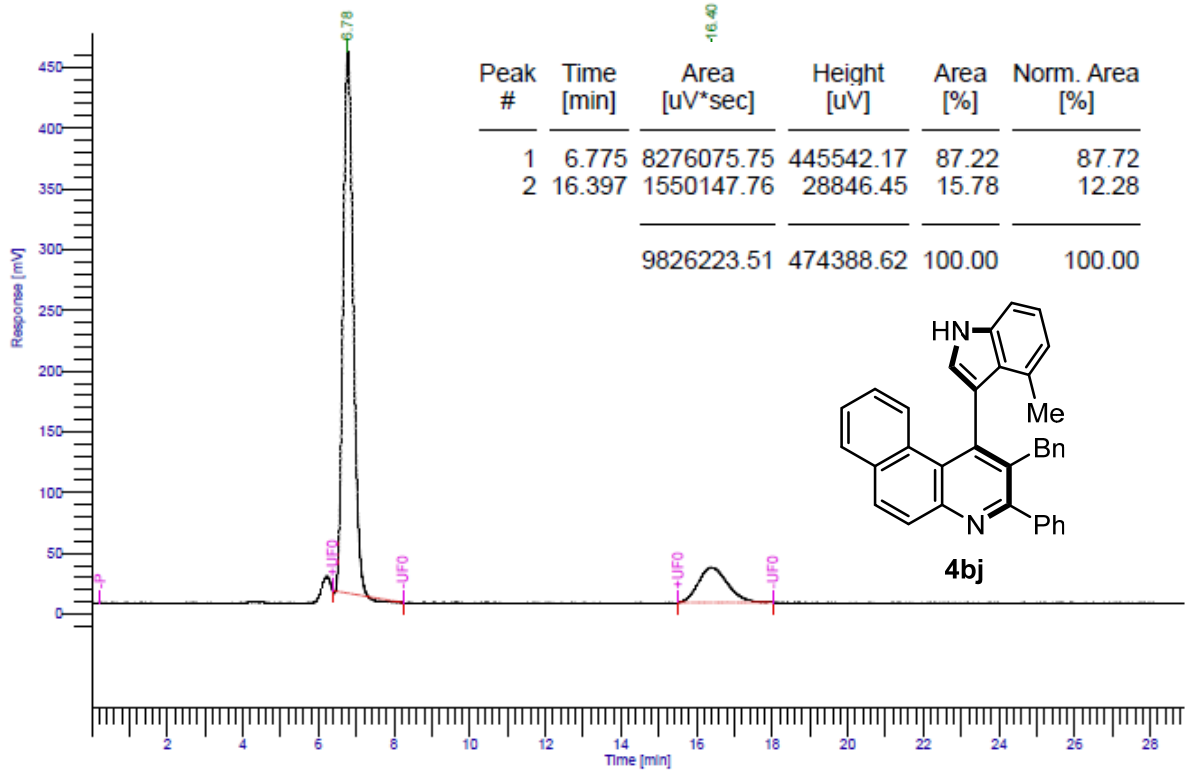
2-benzyl-1-(4-methyl-1*H*-indol-3-yl)-3-phenylbenzo[*f*]quinoline 4bj



Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1	6.885	2944577.65	147557.65	50.04	50.04
2	16.890	2940100.21	50586.28	49.96	49.96
		5884677.85	198143.94	100.00	100.00

***rac*-4bj**

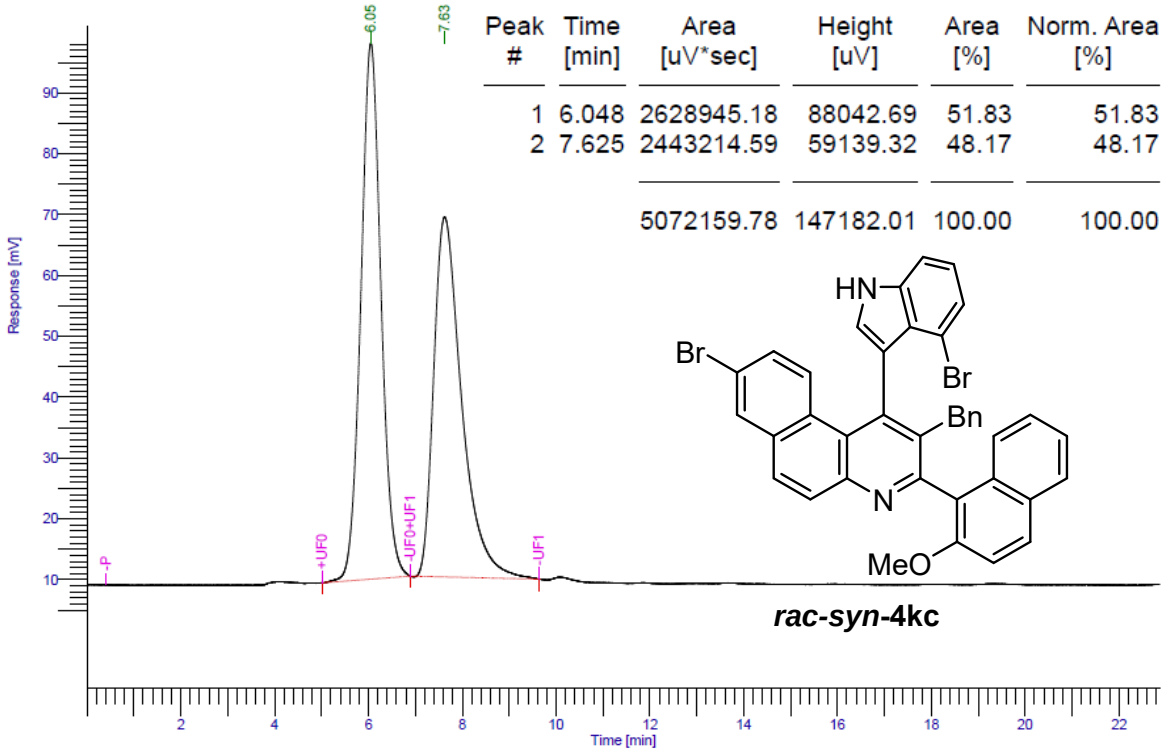
(*aS*)-2-benzyl-1-(4-methyl-1*H*-indol-3-yl)-3-phenylbenzo[*f*]quinoline 4bj



Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1	6.775	8276075.75	445542.17	87.22	87.72
2	16.397	1550147.76	28846.45	15.78	12.28
		9826223.51	474388.62	100.00	100.00

4bj

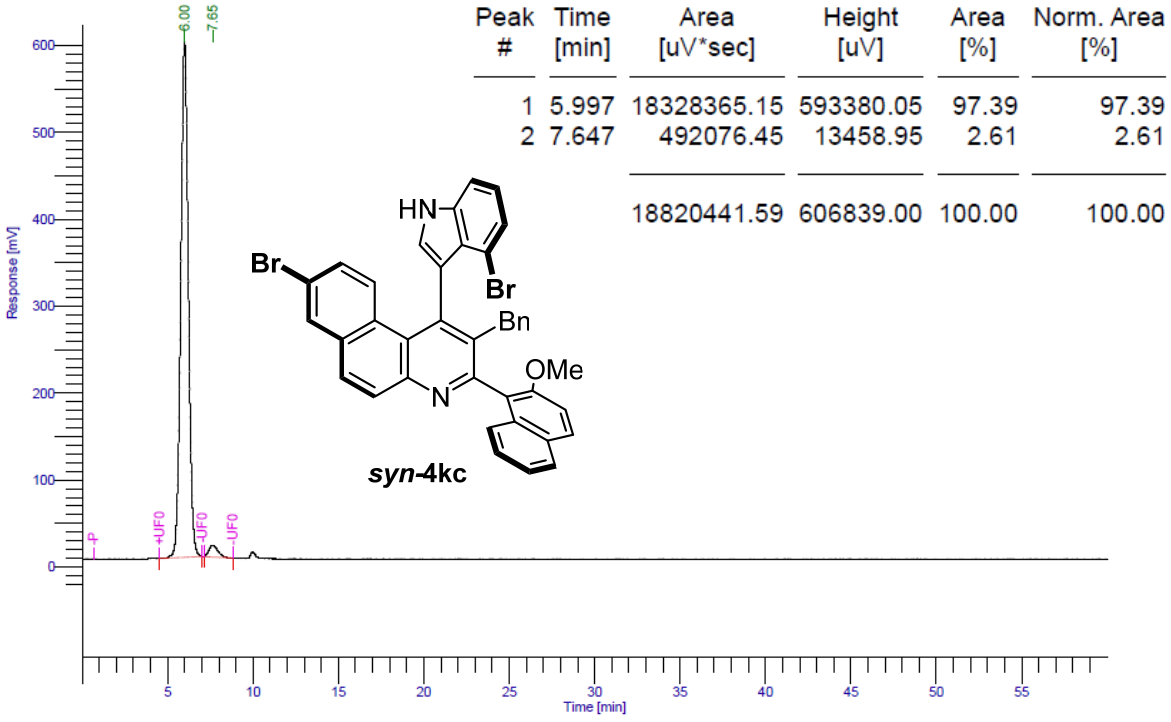
2-benzyl-1-(4-bromo-1*H*-indol-3-yl)-3-(2-methoxynaphthalen-1-yl)benzo[*f*]quinoline 4kc



Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1	6.048	2628945.18	88042.69	51.83	51.83
2	7.625	2443214.59	59139.32	48.17	48.17
		5072159.78	147182.01	100.00	100.00

***rac-syn*-4kc**

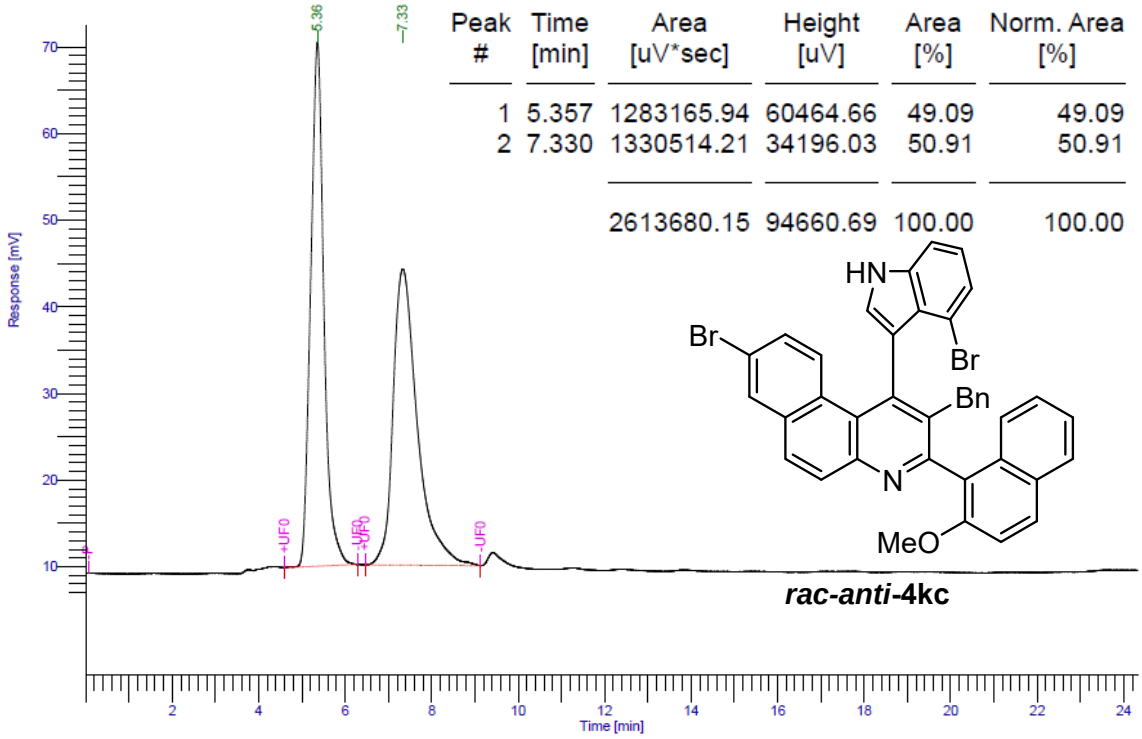
(1*aR*,3*aR*)-2-benzyl-1-(4-bromo-1*H*-indol-3-yl)-3-(2-methoxynaphthalen-1-yl)benzo[*f*]quinoline 4kc



Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1	5.997	18328365.15	593380.05	97.39	97.39
2	7.647	492076.45	13458.95	2.61	2.61
		18820441.59	606839.00	100.00	100.00

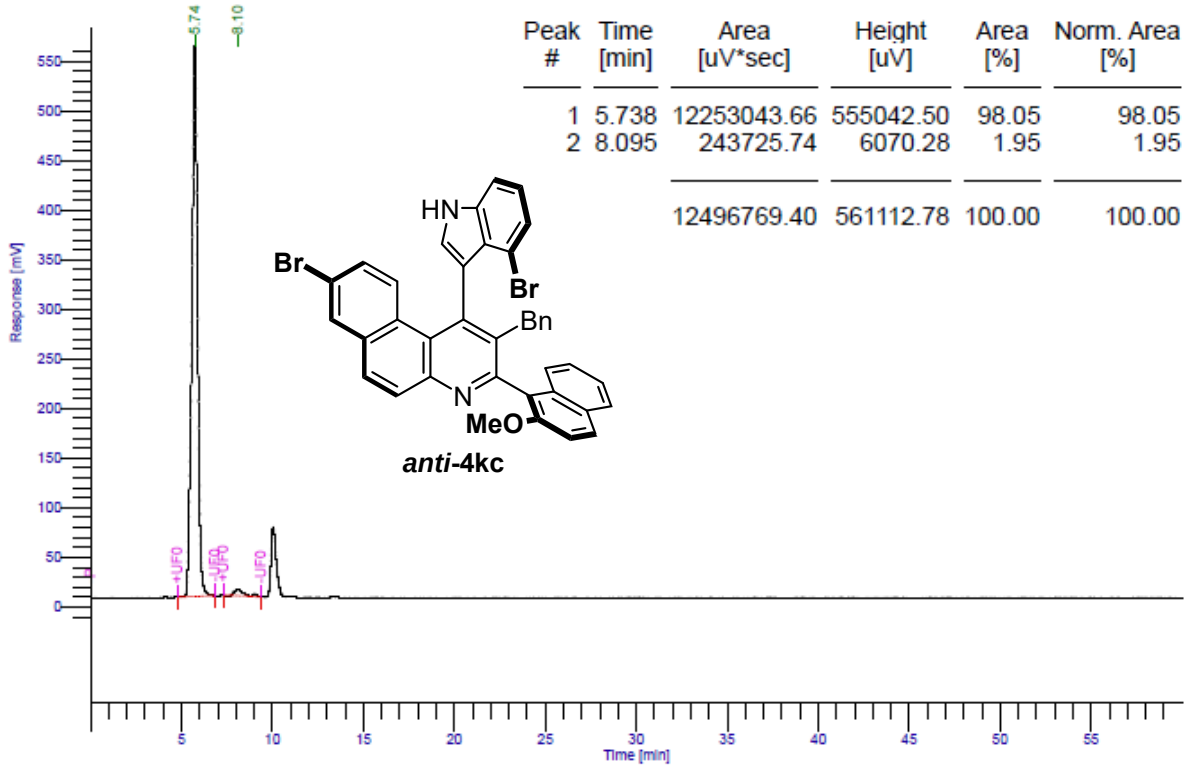
***syn*-4kc**

2-benzyl-1-(4-bromo-1*H*-indol-3-yl)-3-(2-methoxynaphthalen-1-yl)benzo[*f*]quinoline 4kc



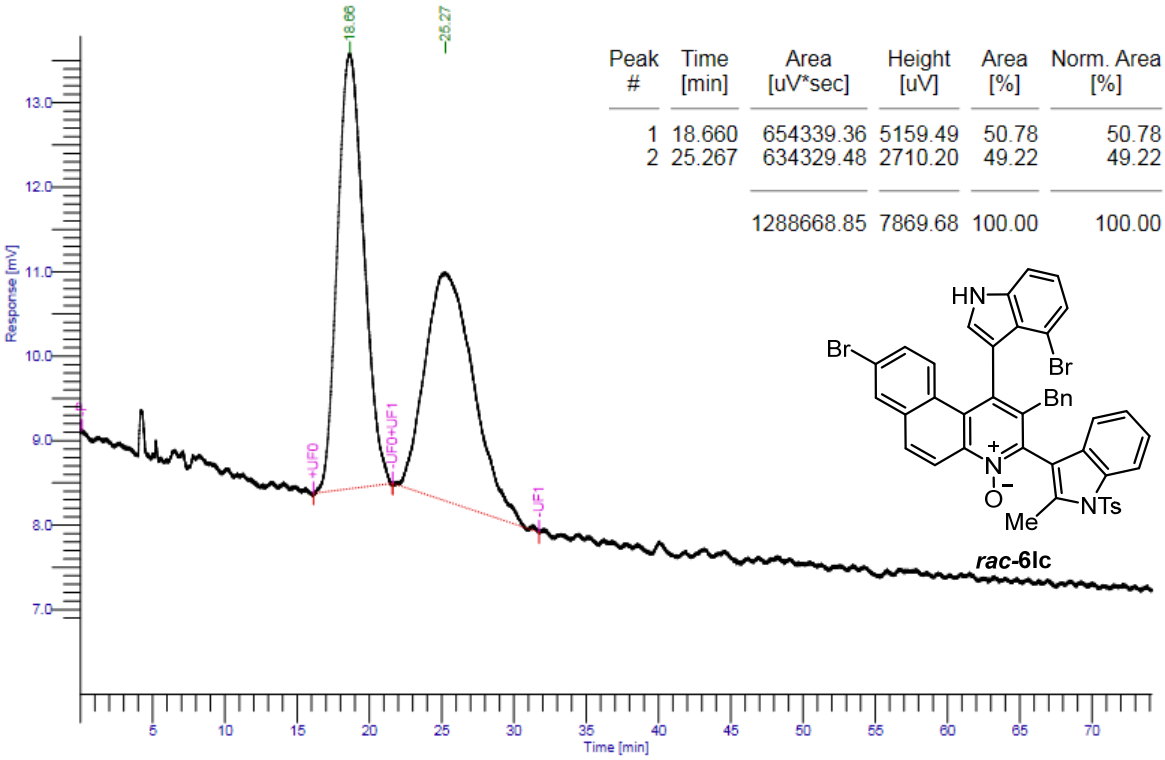
Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1	5.357	1283165.94	60464.66	49.09	49.09
2	7.330	1330514.21	34196.03	50.91	50.91
		2613680.15	94660.69	100.00	100.00

(1*aR*,3*aS*)-2-benzyl-1-(4-bromo-1*H*-indol-3-yl)-3-(2-methoxynaphthalen-1-yl)benzo[*f*] quinoline 4kc



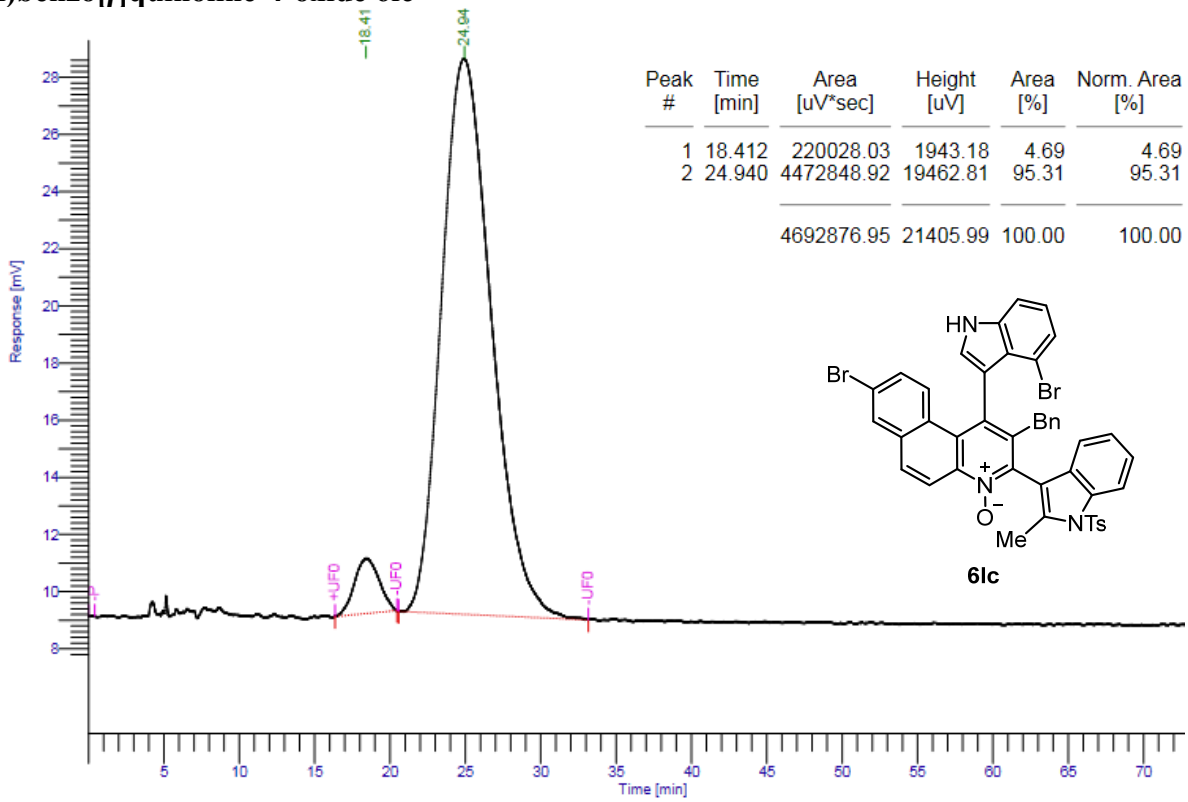
Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1	5.738	12253043.66	555042.50	98.05	98.05
2	8.095	243725.74	6070.28	1.95	1.95
		12496769.40	561112.78	100.00	100.00

2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(2-methyl-1-tosyl-1*H*-indol-3-yl)benzo[*f*]quinoline-4-oxide 6lc



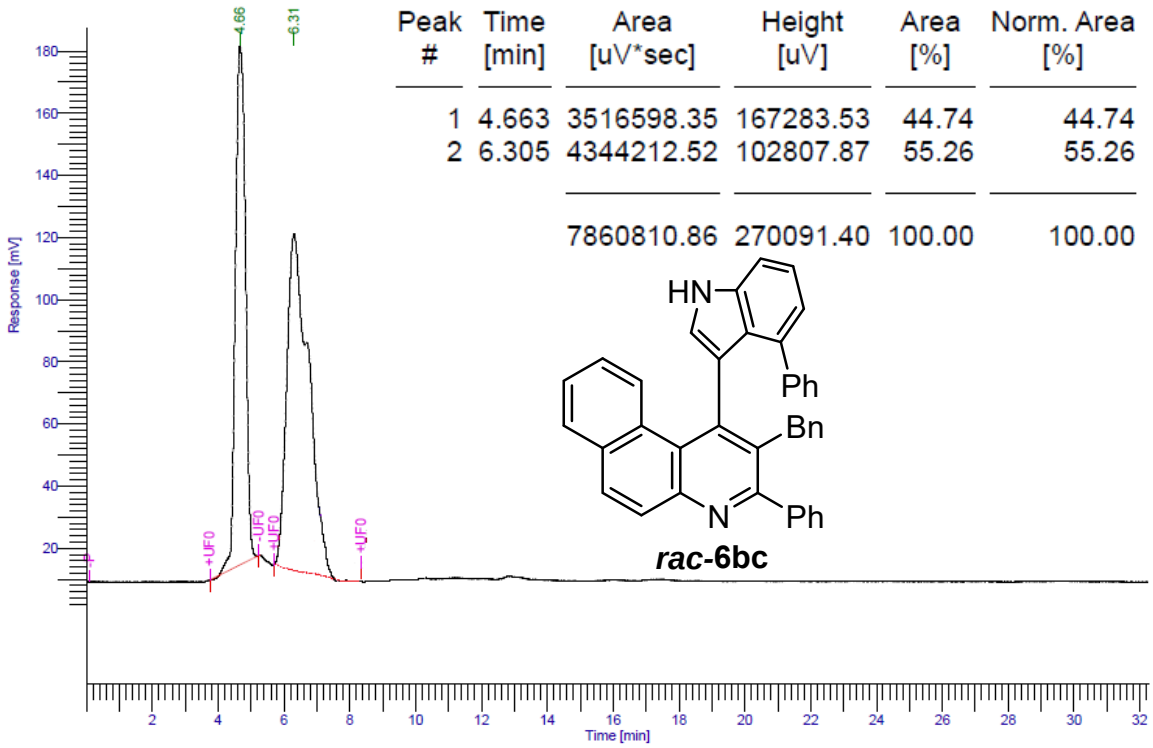
Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1	18.660	654339.36	5159.49	50.78	50.78
2	25.267	634329.48	2710.20	49.22	49.22
		1288668.85	7869.68	100.00	100.00

(1*aR*,3*aS*)-2-benzyl-8-bromo-1-(4-bromo-1*H*-indol-3-yl)-3-(2-methyl-1-tosyl-1*H*-indol-3-yl)benzo[*f*]quinoline-4-oxide 6lc



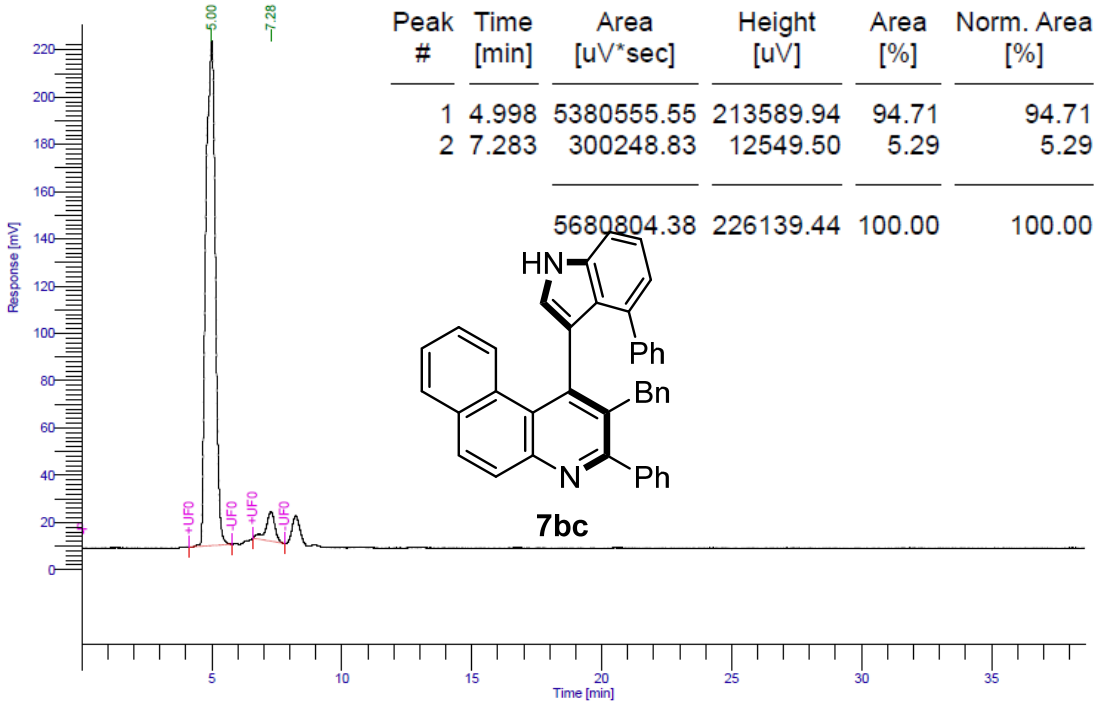
Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1	18.412	220028.03	1943.18	4.69	4.69
2	24.940	4472848.92	19462.81	95.31	95.31
		4692876.95	21405.99	100.00	100.00

2-benzyl-3-phenyl-1-(4-phenyl-1*H*-indol-3-yl)benzo[*f*]quinoline 7bc



Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1	4.663	3516598.35	167283.53	44.74	44.74
2	6.305	4344212.52	102807.87	55.26	55.26
		7860810.86	270091.40	100.00	100.00

(*aS*)-2-benzyl-3-phenyl-1-(4-phenyl-1*H*-indol-3-yl)benzo[*f*]quinoline 7bc



Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1	4.998	5380555.55	213589.94	94.71	94.71
2	7.283	300248.83	12549.50	5.29	5.29
		5680804.38	226139.44	100.00	100.00

Energetic Profile Coordinates and Energies

4aa GS

0 1

C	-1.21324600	4.92545400	0.90113700
C	-0.02998600	4.34640300	0.50284600
C	0.03763600	2.95326100	0.23736100
C	-1.12659000	2.14427100	0.40717900
C	-2.33700900	2.77696700	0.79940200
C	-2.37770700	4.13329500	1.04098800
H	-1.26041500	5.99305300	1.09878100
H	0.87845600	4.92521700	0.36807700
C	-0.99574100	0.73201700	0.18350200
H	-3.23446700	2.17709300	0.90355900
H	-3.31322800	4.60048200	1.33718600
C	0.23403300	0.22440000	-0.22958100
C	1.31027400	1.15386600	-0.45806400
N	1.22198400	2.44637800	-0.20211600
C	-2.17147800	-0.15115900	0.39203500
C	-2.92517500	-0.84870600	-0.62748800
C	-3.96698000	-1.55784500	0.02921300
C	-2.82338700	-0.93160600	-2.02704600
C	-4.89188000	-2.34269500	-0.66784100
C	-3.73900700	-1.70940300	-2.72310000
H	-2.04000700	-0.39121400	-2.55142200
C	-4.76210800	-2.40937600	-2.04982900
H	-5.68265700	-2.87898800	-0.14970100
H	-3.67036600	-1.78101400	-3.80503600
H	-5.46338500	-3.01029400	-2.62211300
C	-2.77752700	-0.45207900	1.59002300
C	0.48219600	-1.27530500	-0.32086300
H	-0.47923600	-1.79423200	-0.27734100
H	0.92589400	-1.53667500	-1.28467900
N	-3.84954900	-1.29511900	1.37959600
H	-4.43557000	-1.67996500	2.10393200
H	-2.51931300	-0.12902100	2.58916700
C	2.63468100	0.71930500	-1.00481200
C	3.81052900	1.03465400	-0.31012200
C	2.73794200	0.07157900	-2.24441500
C	5.05674500	0.68179900	-0.82539600
H	3.73543800	1.55933500	0.63715100
C	3.98548700	-0.27141500	-2.76708400
H	1.83929000	-0.13766400	-2.81894000
C	5.14850400	0.02486100	-2.05435300
H	5.95820600	0.92341900	-0.26833000
H	4.04817500	-0.76157000	-3.73528200
H	6.12041800	-0.24621400	-2.45833900
C	1.38057300	-1.81786800	0.78618200
C	1.10747200	-1.55002800	2.13483100
C	2.47590700	-2.63397800	0.47956200
C	1.90329500	-2.08636400	3.14678700
H	0.26443700	-0.91447100	2.39275800

C	3.27467600	-3.17377700	1.48932900
H	2.71128000	-2.84113700	-0.56141800
C	2.99121700	-2.90196300	2.82793400
H	1.67408400	-1.86635000	4.18665000
H	4.12244900	-3.80170500	1.22719300
H	3.61339700	-3.31829100	3.61588300

4aa TS0

0 1

C	0.51276200	5.04776300	0.24437500
C	-0.40466300	4.24458800	-0.39461100
C	-0.23239600	2.83741100	-0.44743800
C	0.95816400	2.24079400	0.07346000
C	1.84756600	3.09662800	0.78242200
C	1.62936200	4.45745900	0.87296500
H	0.36010700	6.12220700	0.29961900
H	-1.30758200	4.64677000	-0.84341900
C	1.10394700	0.79256200	-0.02846600
H	2.67657800	2.66390700	1.33010800
H	2.31465900	5.07174000	1.45107200
C	-0.10857000	0.09976100	-0.19151200
C	-1.20201700	0.79789700	-0.81666100
N	-1.23955300	2.10423700	-0.99730700
C	2.46211200	0.19206900	-0.04419000
C	3.00799400	-1.18380800	-0.09180800
C	4.41888800	-1.06072600	-0.26944200
C	2.52168300	-2.51062400	-0.07151400
C	5.30764300	-2.13454400	-0.35364400
C	3.39296600	-3.59019800	-0.16506600
H	1.46963200	-2.73031700	-0.00596200
C	4.78046500	-3.41506200	-0.29201000
H	6.37381800	-1.96264300	-0.47778100
H	2.98124600	-4.59546300	-0.14580800
H	5.43651400	-4.27815200	-0.35802100
C	-0.36282000	-1.26615900	0.43417700
H	-0.50831200	-2.06650600	-0.29836000
N	4.71466800	0.28016500	-0.37597400
H	5.62515500	0.66253700	-0.58053200
C	-2.36480500	0.05338000	-1.39088600
C	-3.66648900	0.53453700	-1.18807900
C	-2.18365100	-1.07445200	-2.20513300
C	-4.76061300	-0.11564100	-1.75483200
H	-3.80507300	1.42239600	-0.57999000
C	-3.27786700	-1.72036900	-2.78160300
H	-1.17814900	-1.42896900	-2.41523800
C	-4.57092500	-1.24793000	-2.55072200
H	-5.76390100	0.26316100	-1.57762300
H	-3.11857900	-2.58554400	-3.42024000
H	-5.42443800	-1.75266900	-2.99594800
H	0.51279400	-1.52364800	1.03014300

C	-1.54864400	-1.26046200	1.39565100
C	-2.56635900	-2.21408000	1.28483400
C	-1.60552100	-0.34088400	2.45275200
C	-3.61554000	-2.25248800	2.20517600
H	-2.54443300	-2.92578000	0.46347500
C	-2.65321900	-0.37470400	3.37229100
H	-0.82375800	0.40805000	2.55361400
C	-3.66305600	-1.33234600	3.25238400
H	-4.39805100	-2.99944600	2.09849900
H	-2.67971200	0.34677300	4.18504100
H	-4.48019200	-1.35862100	3.96854000
C	3.56882000	1.00617800	-0.27203900
H	3.60458300	2.07009700	-0.43320900

4aa TS180

0 1

C	2.10004800	-0.68826500	-0.30873100
C	3.56958800	-0.68843800	-0.13186900
C	4.03561400	-1.96211100	-0.57870800
C	5.37020500	-2.37307500	-0.56257700
C	5.91882200	-0.17945300	0.27709600
C	6.31905900	-1.46711000	-0.11547100
H	5.64791900	-3.36598700	-0.90718900
H	6.67008000	0.54182400	0.58663100
H	7.36885900	-1.74455700	-0.09135400
N	2.95051900	-2.66779500	-1.05096300
H	2.99256000	-3.56967200	-1.50033800
C	1.83014400	-1.90716500	-0.92336000
H	0.90252500	-2.26581700	-1.33715900
C	0.98721500	0.28162500	-0.13855200
C	1.14742000	1.70466200	0.08082900
C	-0.35445000	-0.13977200	-0.28535900
C	0.09440900	2.57507500	-0.34515200
C	2.19992400	2.29002900	0.82785000
C	-1.31182000	0.81938100	-0.76655100
C	-0.85559200	-1.51038900	0.18322900
C	0.23757800	3.97982300	-0.20180900
N	-1.07468800	2.11489900	-0.86659200
C	2.28670000	3.65473200	1.01772300
H	2.88379000	1.64307900	1.35470400
C	-2.65368600	0.39637100	-1.27860500
H	-1.23786300	-2.13588100	-0.63111100
H	-0.01434500	-2.05504400	0.62042000
C	-1.93292000	-1.40235500	1.25710700
C	1.32134300	4.51721800	0.45516000
H	-0.56718500	4.59850700	-0.58656700
H	3.09057900	4.06213100	1.62512900
C	-3.80328600	1.08483400	-0.86561100
C	-2.78781200	-0.61948700	-2.23607900
C	-3.13770200	-2.10487400	1.14206600

C	-1.70736000	-0.64623300	2.41617000
H	1.40950600	5.59261900	0.58363100
C	-5.05689900	0.74180600	-1.36820900
H	-3.69960100	1.89029600	-0.14591600
C	-4.04077700	-0.95700000	-2.74911400
H	-1.90156500	-1.12751700	-2.60729600
C	-4.09425300	-2.05781400	2.15769100
H	-3.33418800	-2.68377000	0.24299700
C	-2.66104500	-0.59566600	3.43226500
H	-0.77853000	-0.09077700	2.51969100
C	-5.18115300	-0.28292800	-2.30921100
H	-5.93900400	1.27788300	-1.02771500
H	-4.12402600	-1.73807500	-3.50068700
C	-3.85905900	-1.30288300	3.30708700
H	-5.02555700	-2.60726200	2.04623600
H	-2.46783200	-0.00392200	4.32347700
H	-6.15854600	-0.54704500	-2.70459500
H	-4.60330400	-1.26315200	4.09816500
C	4.58461100	0.21094200	0.26672300
H	4.36570900	1.23353200	0.52553600

4ab GS

0 1

C	1.30398700	4.90845600	-0.69528700
C	0.09037300	4.35558500	-0.35500200
C	-0.02531300	2.96038600	-0.11774500
C	1.12261500	2.12310400	-0.25681100
C	2.36450000	2.72856200	-0.58877200
C	2.45175000	4.08725500	-0.80351900
H	1.38776000	5.97770400	-0.87065800
H	-0.80654800	4.95720200	-0.24507400
C	0.94843000	0.71066500	-0.06429300
H	3.24858400	2.10453000	-0.66469800
H	3.41073800	4.53390600	-1.05255900
C	-0.30821000	0.23106000	0.30011300
C	-1.36864900	1.18499200	0.50239200
N	-1.23848000	2.47823300	0.26758900
C	2.10989200	-0.19966000	-0.23864900
C	2.81176000	-0.89303100	0.81979300
C	3.85607500	-1.63877200	0.21210400
C	2.66294000	-0.94487700	2.21570100
C	4.73943400	-2.42896100	0.95308500
C	3.53764100	-1.72952900	2.95750400
H	1.87604300	-0.37619500	2.70383700
C	4.56468000	-2.46526600	2.33256900
H	5.53358900	-2.99365500	0.47134700
H	3.43181700	-1.77717100	4.03783600
H	5.23360100	-3.07022600	2.93841400
C	2.73927000	-0.53300800	-1.42224600

C	2.43920000	-0.12819400	-2.82987000
H	1.65906800	0.63603700	-2.84649700
H	3.32457000	0.28950500	-3.32676200
H	2.09383800	-0.97925600	-3.43189400
C	-0.59037900	-1.26242000	0.38239100
H	-1.01777000	-1.52241200	1.35455300
H	0.36049400	-1.79922000	0.31922900
N	3.78451900	-1.39929000	-1.14585100
H	4.38654100	-1.80991400	-1.84322700
C	-2.72388400	0.77718600	0.99104300
C	-3.86262400	1.13714800	0.25715700
C	-2.89314900	0.11021700	2.21285200
C	-5.13702900	0.80815800	0.71576900
H	-3.73609100	1.67702300	-0.67599800
C	-4.16901000	-0.20909200	2.67893100
H	-2.02409400	-0.13312900	2.81849100
C	-5.29458300	0.13104300	1.92690300
H	-6.00906900	1.08412500	0.12861800
H	-4.28296100	-0.71551400	3.63399500
H	-6.28849200	-0.12222700	2.28650800
C	-1.51875200	-1.78937200	-0.70684600
C	-2.54810600	-2.68321800	-0.38747200
C	-1.33569000	-1.44086700	-2.05187500
C	-3.36790600	-3.22093000	-1.38078300
H	-2.71448700	-2.95406800	0.65231300
C	-2.15381800	-1.97425100	-3.04809200
H	-0.55032700	-0.73953700	-2.32022900
C	-3.17334500	-2.86881700	-2.71679100
H	-4.16341600	-3.90970400	-1.10787500
H	-1.99564500	-1.68876700	-4.08529100
H	-3.81262300	-3.28295000	-3.49207900

4ab TS0

0 1

C	0.12825400	4.85058300	-0.61107400
C	-0.67193100	3.91045700	-1.22342000
C	-0.42444700	2.52454300	-1.05468500
C	0.75420100	2.09228300	-0.37036400
C	1.50390900	3.08406200	0.31278800
C	1.19775300	4.42683300	0.20593900
H	-0.09129400	5.90980300	-0.71482500
H	-1.55054400	4.18991600	-1.79660000
C	0.98334000	0.65978800	-0.22990400
H	2.29030500	2.77046600	0.98842600
H	1.77461900	5.15633500	0.76834000
C	-0.21487800	-0.09005700	-0.24288100
C	-1.29961600	0.41668300	-1.04532000
N	-1.36174300	1.64978400	-1.51584500
C	2.32668200	0.07074600	-0.09206600

C	2.68148700	-1.36116700	0.00157900
C	4.09199200	-1.44237400	0.12313800
C	2.00938100	-2.59105300	-0.15654700
C	4.80905000	-2.63481700	0.23443000
C	2.70882500	-3.79117300	-0.07484100
H	0.95740900	-2.62874100	-0.39115800
C	4.09479000	-3.82237900	0.15131200
H	5.89004300	-2.62757300	0.34816500
H	2.16741500	-4.72438400	-0.20292300
H	4.61354400	-4.77386300	0.22450500
C	3.56611200	0.73843100	-0.20107000
C	4.02220000	2.08693500	-0.68889400
H	4.93313400	1.95164000	-1.28562800
H	3.27662800	2.56119200	-1.32446100
H	4.26329700	2.78899500	0.11753000
C	-0.50413600	-1.19836300	0.77130200
H	-0.89351100	-2.11417200	0.32028900
N	4.58127700	-0.16105200	0.01458900
H	5.55719100	0.06759100	-0.10406200
C	-2.42510600	-0.47447300	-1.46196200
C	-3.73991600	0.01468900	-1.44820600
C	-2.19789700	-1.77440600	-1.93937300
C	-4.80061900	-0.78450300	-1.87060900
H	-3.91390700	1.02832600	-1.10281800
C	-3.25789000	-2.57299600	-2.36933300
H	-1.17995900	-2.14981200	-2.00505200
C	-4.56459600	-2.08279100	-2.32890900
H	-5.81425000	-0.39284300	-1.84363600
H	-3.06130400	-3.57330500	-2.74668700
H	-5.39189100	-2.70473800	-2.66084900
H	0.41254600	-1.46161900	1.30042700
C	-1.51596600	-0.71477100	1.80838700
C	-2.75104500	-1.35650100	1.95672300
C	-1.21316600	0.35885600	2.65809900
C	-3.66024800	-0.94203400	2.93266000
H	-3.00417900	-2.18541800	1.30061700
C	-2.11864900	0.77544200	3.63268100
H	-0.26202900	0.87443900	2.55106000
C	-3.34732400	0.12545800	3.77385400
H	-4.61402900	-1.45414100	3.03155000
H	-1.86507600	1.60878800	4.28308400
H	-4.05416600	0.45041000	4.53288200

4ab TS180

0 1

C	2.05976100	-0.86561400	0.09175800
C	3.48362500	-0.49696500	-0.08621000
C	4.25522400	-1.66653400	0.12739200
C	4.19574400	0.63137300	-0.55058100

C	5.64795100	-1.72615900	0.03473800
C	5.57982500	0.58441300	-0.67286300
H	3.68188100	1.53651600	-0.83884700
C	6.31233600	-0.57346000	-0.35763600
H	6.18123400	-2.65249200	0.23269800
H	6.10391500	1.46566500	-1.03240300
H	7.39455200	-0.57591100	-0.45155300
C	2.07277600	-2.26715000	0.24313000
C	1.05757800	-3.36943600	0.13337000
H	1.55588100	-4.27612600	-0.22990400
H	0.28280500	-3.11640400	-0.59123200
H	0.56613600	-3.62757700	1.07745000
N	3.37273000	-2.69831800	0.34247200
H	3.63181200	-3.67263200	0.38731200
C	0.90256500	0.04266200	-0.05922200
C	1.08666200	1.48885700	-0.09158400
C	-0.45162900	-0.33990100	-0.18914900
C	0.10767400	2.28758800	-0.75836300
C	2.06063700	2.17032000	0.68589900
C	-1.30213100	0.50845200	-0.98709900
C	-1.10842100	-1.40358300	0.69144400
C	0.25115100	3.69759100	-0.79600700
N	-1.00371800	1.74693000	-1.33244800
C	2.13321200	3.54964300	0.70183500
H	2.73257100	1.59604500	1.31214400
C	-2.59417100	-0.00699300	-1.53436700
H	-1.57078000	-2.22567600	0.13966600
H	-0.34223900	-1.83404100	1.33579000
C	-2.16227200	-0.79149600	1.61203100
C	1.24830200	4.32276100	-0.08004900
H	-0.49061100	4.25636100	-1.35824400
H	2.87328600	4.03950500	1.32900900
C	-3.72708400	0.82056200	-1.53446800
C	-2.69328800	-1.27893000	-2.11830200
C	-3.47096100	-1.28678900	1.62887700
C	-1.82606400	0.24374200	2.49627000
H	1.33020900	5.40641600	-0.08369100
C	-4.93239300	0.37657900	-2.07424600
H	-3.64502100	1.81305900	-1.10427800
C	-3.89731400	-1.72212400	-2.66650100
H	-1.81201600	-1.91279100	-2.17362000
C	-4.42150900	-0.76829100	2.51081200
H	-3.75107400	-2.07891600	0.93880200
C	-2.77333700	0.76502100	3.37647500
H	-0.81654700	0.64731600	2.49032100
C	-5.02371300	-0.89793100	-2.63887700
H	-5.80301600	1.02710600	-2.05582200
H	-3.95168200	-2.70581700	-3.12610300
C	-4.07562000	0.25926900	3.38821900
H	-5.43332800	-1.16561300	2.50637400
H	-2.49415500	1.56734800	4.05469900

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 H                -5.96328300   -1.24257700   -3.06298100
 H                -4.81428900    0.66608000    4.07390900
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4ac GS

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0 1
 C                 0.19315600   -3.84182800    3.28432100
 C                 1.25200100   -3.39051000    2.53059000
 C                 1.09971000   -2.26518100    1.67570800
 C                -0.15851900   -1.59202200    1.61632300
 H                 0.31306100   -4.70575600    3.93259900
 H                 2.22336800   -3.87466000    2.55261900
 C                 2.04799200   -0.83882300    0.11782300
 N                 2.16466900   -1.88328600    0.92355600
 C                -1.51895000    0.34167100    0.74436000
 C                -2.62074700    0.27138800   -0.19357700
 C                -3.58029400    1.24716000    0.21870100
 C                -2.94465500   -0.48736100   -1.33511700
 C                -4.78556100    1.47314300   -0.45223200
 C                -4.13526300   -0.27641400   -2.01637200
 C                -5.04822100    0.70093400   -1.57492000
 H                -5.48954100    2.22463900   -0.10579200
 H                -4.36342000   -0.87220000   -2.89337400
 H                -5.97271700    0.84455800   -2.12631500
 C                -1.85106300    1.31785100    1.65297000
 C                 0.81349000    1.26332500   -0.75303300
 H                 1.63281100    1.27934600   -1.47592300
 H                -0.11192200    1.29802300   -1.33813000
 N                -3.07934400    1.85764500    1.34738700
 H                -3.51945800    2.61765100    1.84225000
 H                -1.27791800    1.68274200    2.49308400
 C                 3.26671500   -0.56553900   -0.70874300
 C                 4.51851300   -0.47046200   -0.08276400
 C                 3.20709500   -0.48416700   -2.10870400
 C                 5.67595400   -0.26480900   -0.83259900
 H                 4.57361000   -0.56991400    0.99704000
 C                 4.36682100   -0.28946500   -2.86063200
 H                 2.25189000   -0.60278800   -2.61382300
 C                 5.60367200   -0.17009500   -2.22434700
 H                 6.63641400   -0.18370800   -0.33024800
 H                 4.30315900   -0.23919400   -3.94442300
 H                 6.50605900   -0.01337900   -2.80933100
 C                 0.90818000    2.53548900    0.08419900
 C                 0.15116700    3.66192600   -0.26582100
 C                 1.78156000    2.63546300    1.17607700
 C                 0.26042100    4.85435200    0.45164500
 H                -0.53303400    3.60172600   -1.10942500
 C                 1.89164800    3.82551700    1.89815900
 H                 2.38044000    1.77611400    1.46490700
 C                 1.13109600    4.94051900    1.53988700
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H	-0.33695300	5.71513000	0.16095800
H	2.57609100	3.88114600	2.74102100
H	1.21797000	5.86703100	2.10140400
C	-0.25042500	-0.43682500	0.78032700
C	0.85926300	-0.03234700	0.04394000
Br	-1.75831700	-1.84919500	-1.99190400
C	-1.06218900	-3.18761000	3.21328300
H	-1.89445300	-3.55773500	3.80599600
C	-1.23514800	-2.08864200	2.40085200
H	-2.19614700	-1.58728400	2.35311100

4ac TS0

0 1

C	-0.84290400	5.28182000	0.42841400
C	-1.65449800	4.36336600	-0.19692200
C	-1.23130100	3.02096700	-0.38265100
C	0.09584100	2.62732100	-0.02318400
H	-1.18513800	6.30045400	0.58963300
H	-2.65637200	4.61309100	-0.53186000
C	0.49633600	1.23475900	-0.24287000
C	-0.58595400	0.34632200	-0.33096600
C	-1.84568600	0.86193700	-0.80753100
N	-2.13737600	2.14470500	-0.89476400
C	1.96948500	0.97800800	-0.40112400
C	3.02789200	-0.05227400	-0.17602700
C	4.28222800	0.64145800	-0.32772600
C	3.22937400	-1.45103300	0.03334300
C	5.55291600	0.13428100	-0.05622400
C	4.48405800	-1.97289600	0.34615300
C	5.64132200	-1.18382900	0.34895900
H	6.43130200	0.76357600	-0.16979600
H	4.57166900	-3.03898100	0.52058600
H	6.59946700	-1.63086400	0.59446600
C	-0.54957900	-1.04677500	0.26372900
H	-0.74662900	-1.84095400	-0.45724600
N	4.01665800	1.90624700	-0.79389500
H	4.71395900	2.58782200	-1.05103700
C	-2.90650500	-0.06055700	-1.31751300
C	-4.24742700	0.16802200	-0.97405500
C	-2.60768700	-1.10668900	-2.20411200
C	-5.25879200	-0.64904700	-1.47605700
H	-4.48191200	0.99272600	-0.30924300
C	-3.62076100	-1.91957000	-2.71446400
H	-1.58041900	-1.26567600	-2.52079500
C	-4.94913900	-1.69843100	-2.34503200
H	-6.29136400	-0.46550700	-1.19047300
H	-3.37257100	-2.71796000	-3.40908400
H	-5.73851600	-2.33334200	-2.73894400
H	0.44801500	-1.21800000	0.65884500

C	-1.52340900	-1.18128700	1.43217000
C	-2.50175200	-2.18274300	1.43965100
C	-1.42360900	-0.33481200	2.54638100
C	-3.35496900	-2.34180000	2.53418300
H	-2.60182200	-2.83747000	0.57780100
C	-2.27495800	-0.48988300	3.63995800
H	-0.67411000	0.45301700	2.55440500
C	-3.24477600	-1.49594300	3.63815200
H	-4.10813300	-3.12550900	2.51967500
H	-2.18082900	0.17501900	4.49486700
H	-3.90894000	-1.61720900	4.48991600
C	2.67575800	2.08743700	-0.85783300
H	2.27854200	3.01967300	-1.22217000
Br	1.98916400	-2.86658200	-0.41313800
C	0.42462400	4.87610900	0.90088900
H	1.04302500	5.57151600	1.46224200
C	0.88100300	3.59377600	0.67229000
H	1.84228300	3.30021200	1.07875700

4ac TS180

0 1

C	1.35637700	-0.78751800	-0.67224600
C	2.74597700	-1.21614200	-0.33725000
C	2.83599700	-2.59429900	-0.74589600
C	4.00321500	-0.71996600	0.12068900
C	3.89795400	-3.46404200	-0.49766400
C	5.06315700	-1.57647700	0.41643000
C	5.00339200	-2.95170100	0.15585300
H	3.84714600	-4.50083400	-0.81841500
H	5.98748700	-1.14820700	0.78669900
H	5.85253300	-3.58380400	0.39596200
N	1.69133300	-2.90915200	-1.44155400
H	1.52980300	-3.77943900	-1.92471000
C	0.85403400	-1.84321000	-1.42637000
H	-0.08482600	-1.88494300	-1.95380700
Br	4.59199600	1.12046800	0.03986700
C	0.32567200	0.25540000	-0.36293100
C	0.51987300	1.65967100	-0.07948300
C	-1.03488000	-0.13960400	-0.42040300
C	-0.55243600	2.56547500	-0.36316500
C	1.63480100	2.17966800	0.61211200
C	-2.01302200	0.85542900	-0.78129100
C	-1.54061000	-1.50380800	0.06939900
C	-0.38209000	3.95431800	-0.13117200
N	-1.76349700	2.14971000	-0.82488800
C	1.75479000	3.52600600	0.89356200
H	2.36602700	1.49144600	0.99972500
C	-3.39742800	0.47465300	-1.20516300
H	-2.07487100	-2.06925900	-0.70040400

H	-0.68154200	-2.11502700	0.35807500
C	-2.44864800	-1.37203900	1.28780900
C	0.75654200	4.43315200	0.47915500
H	-1.20609000	4.60538700	-0.40579900
H	2.61623000	3.88125000	1.45307300
C	-4.49697400	1.17275100	-0.68416000
C	-3.62841100	-0.50836500	-2.17912700
C	-3.70924400	-1.98032700	1.31300800
C	-2.01448100	-0.68401200	2.43030100
H	0.86708000	5.49532500	0.68036400
C	-5.79311400	0.87178800	-1.09915000
H	-4.31910200	1.95198100	0.04958800
C	-4.92448700	-0.80475000	-2.60343700
H	-2.78569400	-1.02293800	-2.63392000
C	-4.51602700	-1.91072300	2.45063800
H	-4.06686500	-2.50398800	0.42980500
C	-2.81833100	-0.61067700	3.56779000
H	-1.04160100	-0.19877600	2.42518500
C	-6.01245200	-0.12082200	-2.05752700
H	-6.63405800	1.41514600	-0.67619800
H	-5.08286700	-1.56036900	-3.36877500
C	-4.07295200	-1.22542900	3.58259200
H	-5.49318800	-2.38693600	2.44812100
H	-2.46442300	-0.07294800	4.44370400
H	-7.02287000	-0.35240200	-2.38420500
H	-4.70019000	-1.16735600	4.46828000

4ba GS

0 1

C	-2.15410700	4.13220200	0.55226500
C	-0.85011100	3.89987500	0.25888800
C	-0.39108400	2.57501900	-0.04446900
C	-1.28281500	1.46328900	-0.00017600
H	-2.49866300	5.13252700	0.80342200
H	-0.10516000	4.68893300	0.24951500
C	-0.66692400	0.16819400	-0.06318700
C	0.70438400	0.06644500	-0.34508900
C	1.43939200	1.26738100	-0.57905700
N	0.91936700	2.46553700	-0.36084800
C	-1.42235200	-1.07512100	0.25043400
C	-1.82637000	-2.12104000	-0.66328300
C	-2.51356100	-3.10463500	0.10008800
C	-1.68588900	-2.31126200	-2.04954600
C	-3.04249100	-4.26345300	-0.47851300
C	-2.21079300	-3.45953100	-2.62761500
H	-1.17325200	-1.56799600	-2.65422200
C	-2.88036900	-4.42680900	-1.84911700
H	-3.56219100	-5.00747900	0.11957100
H	-2.10709400	-3.61812800	-3.69739500

H	-3.27922000	-5.31566000	-2.32999000
C	-1.86508800	-1.45798400	1.49350300
C	1.44026100	-1.26528300	-0.26874600
H	0.71013200	-2.07638800	-0.21495400
H	2.01300500	-1.43698100	-1.18351400
N	-2.52516200	-2.66734300	1.40924500
H	-2.90902800	-3.17358600	2.19195100
H	-1.77586400	-0.94426300	2.44049300
C	2.86225700	1.27790000	-1.03795900
C	3.81093100	2.03863700	-0.33989000
C	3.26166500	0.60977800	-2.20480000
C	5.13221900	2.10305800	-0.77837200
H	3.49834000	2.57742200	0.54884000
C	4.58164400	0.68283100	-2.65088100
H	2.52882800	0.05582100	-2.78558500
C	5.52310300	1.42308100	-1.93389600
H	5.85772300	2.68799900	-0.21904700
H	4.87132200	0.16906800	-3.56393800
H	6.55268900	1.47652700	-2.27798100
C	2.38902200	-1.38613500	0.91932200
C	1.99529000	-1.00351700	2.20886500
C	3.66745000	-1.93196500	0.75026200
C	2.85187500	-1.16749700	3.29760200
H	1.01125200	-0.56816200	2.35951000
C	4.52707900	-2.09979000	1.83696400
H	3.99617400	-2.22019900	-0.24539600
C	4.12207100	-1.71826800	3.11648000
H	2.52719200	-0.86199600	4.28932700
H	5.51670400	-2.52168400	1.68062000
H	4.79109500	-1.84367900	3.96380700
C	-4.49275900	3.37385800	0.66385500
C	-3.74419000	0.79410500	-0.06581900
C	-5.08014400	1.11566800	0.09952700
H	-5.83616600	0.35765300	-0.08766200
C	-5.46443800	2.40920000	0.49256600
H	-6.51409200	2.65266300	0.63324500
C	-3.12282400	3.07777600	0.47452000
C	-2.71407000	1.74396600	0.15058900
H	-4.76848300	4.39251300	0.92681500
H	-3.49425900	-0.20213400	-0.39811900

4ba TS0

0 1

C	-2.03668200	-3.94020500	-1.30093200
C	-0.83013600	-3.44598400	-1.68356500
C	-0.38206200	-2.15609400	-1.24307600
C	-1.25366100	-1.30837800	-0.50684800
C	-2.45079500	-1.91888800	0.06909600
C	-2.84870200	-3.22248100	-0.36404600

H	-2.37211100	-4.91744900	-1.63961800
H	-0.15136200	-4.00264900	-2.32182700
C	-0.80961900	0.05940700	-0.30203100
C	0.59439300	0.22321400	-0.29266800
C	1.37552900	-0.70202300	-1.05095500
N	0.87965600	-1.80540700	-1.59400400
C	-1.79232500	1.17352300	-0.29368300
C	-1.72144700	2.64294500	-0.14643800
C	-3.01789600	3.14934200	-0.46515700
C	-0.75119100	3.62462900	0.15543000
C	-3.37337500	4.49887800	-0.43616700
C	-1.08865200	4.97354900	0.17950700
H	0.27510300	3.36740600	0.35728100
C	-2.39086200	5.41814800	-0.10076000
H	-4.38524200	4.81088800	-0.68209700
H	-0.31632400	5.70002500	0.41672100
H	-2.62484700	6.47827900	-0.06940100
C	1.28084600	1.21397500	0.64030500
H	1.85828900	1.98210500	0.11717200
N	-3.80926700	2.08044000	-0.82773100
H	-4.75897300	2.14282100	-1.16161900
C	2.81249000	-0.43938600	-1.36984500
C	3.75354000	-1.46948700	-1.22892500
C	3.23721300	0.79313100	-1.88783000
C	5.09065600	-1.26117400	-1.56136500
H	3.42167200	-2.43217900	-0.85393900
C	4.57388200	0.99977600	-2.23087400
H	2.51124500	1.58459800	-2.05385400
C	5.50682100	-0.02447500	-2.05978800
H	5.80935900	-2.06668100	-1.43449500
H	4.88330800	1.95710600	-2.64263500
H	6.54900400	0.13631100	-2.32331500
H	0.50847300	1.72181800	1.21868400
C	2.19089900	0.51755500	1.64985900
C	3.53129500	0.89362400	1.78860100
C	1.68210500	-0.47414200	2.50058700
C	4.34501500	0.29898900	2.75504800
H	3.94544500	1.65006800	1.12699700
C	2.49209800	-1.07088500	3.46586000
H	0.64424400	-0.78324600	2.40225600
C	3.82827900	-0.68512000	3.59766700
H	5.38470100	0.60352900	2.84416200
H	2.07887000	-1.83735800	4.11662300
H	4.46067400	-1.15042600	4.34922500
C	-3.08329700	0.93442500	-0.75299300
H	-3.52787500	0.00262600	-1.05896900
C	-4.00037100	-3.82902800	0.19544000
C	-4.71265700	-3.21856600	1.20612600
H	-5.58580200	-3.70267000	1.63494100
C	-4.27198200	-1.97610400	1.70436200
H	-4.79114100	-1.51081500	2.53820200

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 C                -3.17356800   -1.34780900    1.15037400
 H                -2.84974700   -0.39817200    1.55944100
 H                -4.29436500   -4.81047300   -0.16969500
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4ba TS180

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0 1
 C                 1.72378400    3.89582700   -1.29031500
 C                 0.51013300    3.40469300   -1.65420100
 C                 0.05369100    2.12067100   -1.19137400
 C                 0.95283200    1.27297000   -0.48329600
 C                 2.09785400    1.91357000    0.13823200
 C                 2.51011100    3.20841000   -0.30499900
 H                 2.06613000    4.86248500   -1.65139800
 H                -0.16919700    3.95597200   -2.29677800
 C                 0.57231400   -0.11181200   -0.38748400
 C                -0.83131100   -0.35222700   -0.40891700
 C                -1.67386500    0.62483600   -1.00843600
 N                -1.21584800    1.77445100   -1.49812100
 C                -1.44272300   -1.57441200    0.28247100
 H                -2.06547600   -2.17032800   -0.39128900
 C                -3.13959300    0.40328900   -1.22521900
 C                -4.05745800    1.34457600   -0.73880000
 C                -3.62282200   -0.68111700   -1.97107000
 C                -5.42447900    1.18777400   -0.96212600
 H                -3.68706100    2.19997800   -0.18252200
 C                -4.98995900   -0.83457200   -2.20526000
 H                -2.92289400   -1.39513800   -2.39775400
 C                -5.89613400    0.09561800   -1.69331500
 H                -6.12254000    1.92184800   -0.56818900
 H                -5.34549200   -1.67496500   -2.79616700
 H                -6.96154600   -0.02453000   -1.87159000
 H                -0.63299300   -2.23146400    0.61022000
 C                -2.27529800   -1.19916900    1.50449800
 C                -3.58290500   -1.67506500    1.65466500
 C                -1.72900100   -0.41457700    2.52997800
 C                -4.32535700   -1.38308700    2.80033600
 H                -4.02815400   -2.27046400    0.86148000
 C                -2.46732100   -0.11965200    3.67553700
 H                -0.71808600   -0.02795900    2.42678500
 C                -3.76968200   -0.60460400    3.81583800
 H                -5.34065300   -1.75991200    2.89461200
 H                -2.02504300    0.48954700    4.45981700
 H                -4.34659500   -0.37397100    4.70762800
 C                 3.59662600    3.84633800    0.33294400
 C                 4.19551700    3.29096700    1.44965100
 H                 5.01092800    3.80824500    1.94772800
 C                 3.69807200    2.08585500    1.97540900
 H                 4.10794100    1.68433900    2.89843500
 C                 2.67225000    1.41456400    1.32861100
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H	2.26132600	0.51000400	1.76638200
H	3.92008900	4.81651300	-0.03707300
C	1.46125700	-1.29699600	-0.57450700
C	2.83991300	-1.73836400	-0.29993100
C	0.92951200	-2.30084600	-1.37639300
C	2.99468300	-3.01439000	-0.92192000
N	1.81221100	-3.32065300	-1.56170800
H	-0.03152800	-2.32090400	-1.86700300
C	4.16430600	-3.77658200	-0.87986200
C	5.15370400	-1.98642800	0.40572300
H	1.66228200	-4.11943400	-2.15878400
C	5.25255300	-3.25011200	-0.20074500
H	4.21412000	-4.74441200	-1.37243100
H	6.01737500	-1.57193500	0.91862100
H	6.18230700	-3.80938800	-0.14795600
C	3.98206500	-1.24036900	0.35952600
H	3.98059800	-0.26417400	0.81452600

4bc GS

0 1

C	-1.11446200	4.52568700	-1.22027500
C	0.13589800	4.12988600	-0.87543000
C	0.39417000	2.77439600	-0.47891900
C	-0.64955000	1.79901000	-0.47852400
C	-2.02094900	2.26584600	-0.71144800
C	-2.22534400	3.62284900	-1.12158400
H	-1.30746200	5.54801600	-1.53653000
H	0.98564600	4.80469900	-0.88813000
C	2.00939300	1.25841500	0.19483900
N	1.66625100	2.50207400	-0.12031300
C	-1.13027300	-0.71428900	-0.53469800
C	-1.77763300	-1.61388600	0.39748200
C	-2.45808400	-2.60130100	-0.38102100
C	-1.90740600	-1.71410400	1.79662200
C	-3.20007500	-3.64469500	0.17979200
C	-2.63769000	-2.74470600	2.37247400
C	-3.27539600	-3.70588300	1.56442600
H	-3.70130300	-4.37770700	-0.44609500
H	-2.72171200	-2.80420600	3.45205800
H	-3.84053200	-4.50174400	2.04044100
C	-1.43619800	-1.18009200	-1.79006100
C	1.60912100	-1.27261100	0.08351800
H	2.57631800	-1.29636900	0.59178000
H	0.93304500	-1.88174100	0.69117400
N	-2.23660200	-2.29595200	-1.70563800
H	-2.54158400	-2.85137400	-2.48975200
H	-1.12213700	-0.79426500	-2.74903100
C	3.40934400	1.11440600	0.70147900
C	4.46307300	1.73565900	0.01413900

C	3.69259700	0.44324100	1.90167600
C	5.76937200	1.65965200	0.49499900
H	4.24237600	2.28578400	-0.89529100
C	4.99870200	0.37630800	2.38900400
H	2.88244500	-0.00550600	2.47069200
C	6.04245400	0.97706900	1.68300700
H	6.57518700	2.13803800	-0.05568000
H	5.19785400	-0.13912400	3.32487100
H	7.06026200	0.92101900	2.05987300
C	1.78712400	-1.94818200	-1.27367400
C	1.48836400	-3.30976200	-1.42067900
C	2.30449400	-1.25864500	-2.37897700
C	1.69607900	-3.96520300	-2.63548700
H	1.08569000	-3.86053200	-0.57337400
C	2.51081200	-1.91001400	-3.59671300
H	2.54633100	-0.20331700	-2.28791800
C	2.20692500	-3.26634300	-3.73116300
H	1.45698100	-5.02213700	-2.72557900
H	2.91346600	-1.35579100	-4.44096100
H	2.36935600	-3.77354800	-4.67863200
C	-3.53135900	4.09660700	-1.38449200
C	-3.18192900	1.47807700	-0.50947500
C	-4.45280000	1.97216300	-0.75204900
H	-5.31386900	1.33370500	-0.57314300
C	-4.63614500	3.28642200	-1.21387900
H	-3.08949400	0.47122000	-0.13293900
H	-5.63470000	3.66624600	-1.41221900
H	-3.65003100	5.12817300	-1.70783800
C	-0.22788000	0.44581900	-0.28891200
C	1.11167000	0.16551000	0.02663800
Br	-1.10023400	-0.41532100	2.96023000

4bc TS0

0 1

C	-1.02932500	-4.73166000	-0.97632200
C	0.08554600	-4.08245300	-1.40159800
C	0.27740700	-2.68578700	-1.13430600
C	-0.76320500	-1.91746800	-0.54524100
C	-1.87010200	-2.65082900	0.07496200
C	-2.00467100	-4.05194500	-0.17518200
H	-1.16899300	-5.79086000	-1.17847200
H	0.88086800	-4.58703700	-1.94092300
C	-0.57012000	-0.47423100	-0.49182400
C	0.78622700	-0.08761000	-0.41687900
C	1.74485700	-0.93673300	-1.05571600
N	1.47102300	-2.15741200	-1.49529500
C	-1.79267500	0.37420100	-0.67855700
C	-2.37855100	1.70721000	-0.36346800
C	-3.77137200	1.61439700	-0.71992000

C	-2.02768000	3.02043300	0.06068700
C	-4.75237300	2.57783600	-0.48914100
C	-2.99331600	3.98935600	0.32654300
C	-4.35570300	3.76654200	0.09461600
H	-5.78463400	2.39032300	-0.77150500
H	-2.66188100	4.96301500	0.66767600
H	-5.07574100	4.54879500	0.31343000
C	1.26830800	1.01815300	0.50600700
H	1.83009500	1.80260100	-0.00119700
N	-3.96880700	0.40997700	-1.35199000
H	-4.83821900	0.10543500	-1.76272900
C	3.12647000	-0.45365800	-1.35782700
C	4.22089100	-1.30453400	-1.14400400
C	3.35631100	0.80783400	-1.92814100
C	5.51395500	-0.89258900	-1.46063100
H	4.04188900	-2.28995400	-0.72670700
C	4.64954900	1.21740000	-2.25364500
H	2.51462100	1.45900200	-2.14746000
C	5.73376500	0.37140300	-2.01287000
H	6.35208400	-1.56019700	-1.27808100
H	4.80822300	2.19318500	-2.70562700
H	6.74204800	0.69105800	-2.26317100
H	0.40170600	1.49560000	0.95793600
C	2.11765900	0.45128500	1.64162600
C	3.41354400	0.92777900	1.87102100
C	1.59771500	-0.51714100	2.51263100
C	4.17081600	0.45515900	2.94487900
H	3.83599600	1.67090300	1.19965800
C	2.35150700	-0.99232400	3.58491100
H	0.59506800	-0.90419500	2.34742200
C	3.64258800	-0.50666700	3.80586500
H	5.17563100	0.83812000	3.10434400
H	1.92976300	-1.74223300	4.24943800
H	4.23111800	-0.87713700	4.64118400
C	-2.81283600	-0.29190400	-1.35143400
H	-2.77390200	-1.26116700	-1.81857000
C	-3.06460600	-4.77564700	0.42413400
C	-3.94304800	-4.17036500	1.29817800
H	-4.74331600	-4.74213800	1.75993600
C	-3.76778500	-2.80865900	1.61371200
H	-4.42053500	-2.33138700	2.34000300
C	-2.76260100	-2.07229600	1.01637800
H	-2.64488600	-1.03021300	1.28888800
H	-3.15442100	-5.83629400	0.20045700
Br	-0.25631300	3.76171100	0.07252500

4bc TS180

0 1

C	-0.47800400	0.91063500	-1.02234200

C	-1.86924600	1.43549500	-1.07755600
C	-1.78652700	2.70973300	-1.73910900
C	-3.20763300	1.06943200	-0.77774500
C	-2.83446300	3.60985800	-1.93172100
C	-4.26874800	1.95923700	-0.93797600
C	-4.08822100	3.23688700	-1.48233500
H	-2.65944300	4.56112500	-2.42678400
H	-5.26705200	1.62588400	-0.67838400
H	-4.93997400	3.90049500	-1.59542500
N	-0.49115900	2.88662300	-2.16946700
H	-0.18229900	3.62949200	-2.77764900
C	0.25176400	1.82023800	-1.78320300
H	1.28633000	1.74502200	-2.07710700
Br	-3.76490400	-0.70961700	-0.36075000
C	0.44036400	-0.14462900	-0.46331900
C	0.34395400	-1.57809600	-0.47142800
C	1.75367900	0.34142500	-0.15746700
C	1.50791600	-2.25891800	-0.94433700
C	-0.69596200	-2.41735000	0.09770700
C	2.86919400	-0.47030600	-0.50340800
C	1.95056000	1.65264400	0.62441000
C	1.38626500	-3.63146100	-1.36923700
N	2.72456400	-1.68838800	-1.03486400
C	-0.75111800	-3.80225400	-0.24932300
C	-1.46375300	-1.97703000	1.19798500
C	4.29055700	-0.01965500	-0.38526800
H	2.93998200	1.59199600	1.09007600
H	1.98401800	2.54538300	-0.00909100
C	0.92514900	1.88124900	1.72464400
C	0.26704500	-4.35377600	-1.10234700
H	2.24639000	-4.05896900	-1.87519800
C	-1.69741800	-4.63682300	0.38320700
C	-2.32108600	-2.83769100	1.86553300
H	-1.34194800	-0.95698200	1.54875300
C	5.25596400	-0.93971300	0.05764500
C	4.72026400	1.26344000	-0.75977500
C	0.79927700	0.96831500	2.78313400
C	0.11496600	3.02163200	1.73171800
H	0.18462300	-5.39213900	-1.41388500
C	-2.47557300	-4.16386900	1.42779500
H	-1.75352500	-5.68151100	0.08614800
H	-2.88325000	-2.47817800	2.72301500
C	6.59868700	-0.57945200	0.15112200
H	4.93529300	-1.94264300	0.31938800
C	6.06579300	1.62381100	-0.67453300
H	4.00254000	1.98222000	-1.14414200
C	-0.11524700	1.18823300	3.81285800
H	1.42228800	0.07708400	2.79724100
C	-0.80363500	3.24666900	2.76071400
H	0.19913000	3.74048100	0.91991500
H	-3.16726100	-4.82958500	1.93717400

C	7.00952500	0.70571200	-0.21188800
H	7.32723700	-1.30430900	0.50500200
H	6.37644500	2.62030900	-0.97783900
C	-0.92294800	2.32945600	3.80461800
H	-0.19452400	0.47044000	4.62535000
H	-1.42632500	4.13735000	2.74231700
H	8.05705300	0.98645400	-0.14146900
H	-1.63596700	2.50104600	4.60653600

4kc GS SYN

0 1

C	1.48047700	-4.50416900	-1.32409300
C	0.23868800	-4.02332600	-1.07269800
C	0.03617500	-2.64058500	-0.74481900
C	1.13433300	-1.72630300	-0.68708300
C	2.48731700	-2.27424600	-0.86345400
C	2.63205400	-3.65694700	-1.21222200
H	1.63173100	-5.54819200	-1.58788200
H	-0.64894700	-4.64576400	-1.11661300
C	-1.54122800	-1.02350400	-0.26387100
N	-1.24842600	-2.29033900	-0.51483200
C	1.76867500	0.76437200	-0.53982500
C	2.44587500	1.47840500	0.52307200
C	3.19733400	2.52727500	-0.09239500
C	2.54786400	1.36757900	1.92329800
C	3.98228200	3.43377900	0.62614000
C	3.31924900	2.25985600	2.65493600
C	4.02803700	3.28946500	2.00579100
H	4.53695000	4.21987400	0.12148900
H	3.37981400	2.15798100	3.73291700
H	4.62400400	3.97434900	2.60173800
C	2.12398900	1.39270800	-1.70816200
C	-0.96579900	1.45341700	-0.05884500
H	-1.97086800	1.46717800	0.37526500
H	-0.30921500	1.90864900	0.68990800
N	2.98958500	2.43130200	-1.45053200
H	3.32745500	3.08688000	-2.13784200
H	1.80446200	1.17520500	-2.71682500
C	-0.97263100	2.34371000	-1.29776600
C	-0.57382400	3.68343900	-1.19231000
C	-1.41724300	1.87732100	-2.54300600
C	-0.61115900	4.53556500	-2.29741000
H	-0.22610200	4.06135600	-0.23327500
C	-1.45097100	2.72707000	-3.65111900
H	-1.74146400	0.84582500	-2.64486800
C	-1.04771700	4.05912400	-3.53519700
H	-0.29702400	5.57117300	-2.19072100
H	-1.79737000	2.34611900	-4.60907600
H	-1.07686800	4.71906700	-4.39848000

C	3.91683100	-4.21147800	-1.41538500
C	3.68671300	-1.54024500	-0.68119200
C	4.93485400	-2.11034500	-0.86984300
H	5.82330300	-1.50526500	-0.70951200
C	5.06001400	-3.45481500	-1.25552300
H	3.64448000	-0.51013800	-0.36828100
H	6.04101200	-3.89612900	-1.40932800
H	3.98570600	-5.26179200	-1.68906100
C	0.78489400	-0.35494700	-0.47429900
C	-0.55906200	0.00251400	-0.27333200
Br	1.64371000	-0.03726800	2.87237600
C	-2.99336500	-0.75590600	0.02031900
C	-3.90840500	-0.75512000	-1.02795600
C	-3.46111900	-0.57781100	1.35805700
C	-5.29172700	-0.55590000	-0.78739100
C	-4.86156500	-0.37553100	1.60013700
C	-2.58563100	-0.59948000	2.48284900
C	-5.74862800	-0.36987700	0.49680500
H	-5.99475500	-0.54615900	-1.61194200
C	-5.32285400	-0.19397900	2.93222800
C	-3.06600400	-0.41988400	3.76061700
H	-1.52489900	-0.76447700	2.32485800
H	-6.81015200	-0.21566200	0.67531600
C	-4.44796100	-0.21216200	3.99333000
H	-6.38741300	-0.04150700	3.09603000
H	-2.37685400	-0.44091400	4.60087400
H	-4.81148500	-0.07229300	5.00764000
O	-3.39733000	-0.93669200	-2.28480300
C	-4.28867700	-1.03716000	-3.38287000
H	-4.99832000	-1.86424600	-3.25260000
H	-4.84455200	-0.10406400	-3.54553300
H	-3.66248500	-1.23714000	-4.25448600

4kc GS ANTI

0 1

C	-0.94597500	4.72103600	-0.77055900
C	0.19431500	4.09360900	-0.39157500
C	0.22193800	2.67170500	-0.19758000
C	-0.94190900	1.87370600	-0.41988900
C	-2.20081500	2.57213400	-0.71353200
C	-2.17045100	3.98987500	-0.92118000
H	-0.96318900	5.79587700	-0.93445900
H	1.12682600	4.62431200	-0.22957800
C	1.55674400	0.85609000	0.32591800
N	1.41494400	2.16674000	0.18716100
C	-1.78325700	-0.52824700	-0.76115200
C	-2.66348200	-1.34688300	0.04663000
C	-3.39343200	-2.18594800	-0.85181600
C	-2.96642200	-1.47489900	1.41642500

C	-4.34228500	-3.12177300	-0.42960100
C	-3.90435200	-2.39951900	1.85529200
C	-4.58221300	-3.22135700	0.93387400
H	-4.87377200	-3.74464100	-1.14364900
H	-4.12040100	-2.48260600	2.91482900
H	-5.31052100	-3.93698600	1.30385100
C	-2.01110000	-0.89514500	-2.06469100
C	0.76888800	-1.55823400	0.03072300
H	1.69449300	-1.74012900	0.58319700
H	-0.02512100	-2.05054900	0.60072900
N	-2.98113500	-1.86918500	-2.12713200
H	-3.26352100	-2.35152500	-2.96613800
H	-1.53187000	-0.53269400	-2.96248100
C	0.89271200	-2.24316400	-1.32606200
C	0.26491600	-3.47604700	-1.55015600
C	1.67922500	-1.70289300	-2.35322200
C	0.41025200	-4.14878900	-2.76490600
H	-0.35010000	-3.90943200	-0.76464700
C	1.82399300	-2.37036300	-3.57078400
H	2.18943100	-0.75622500	-2.19946600
C	1.18928000	-3.59629200	-3.78339200
H	-0.08566900	-5.10502000	-2.91444900
H	2.44082400	-1.93348200	-4.35223800
H	1.30529100	-4.11726300	-4.73030000
C	-3.35800500	4.68988100	-1.23646900
C	-3.47422500	1.95095100	-0.77068900
C	-4.62653700	2.66183900	-1.06238000
H	-5.57956200	2.13998400	-1.08623500
C	-4.57419000	4.04222200	-1.31666900
H	-3.56869800	0.89729500	-0.56410700
H	-5.47961400	4.59435800	-1.55360100
H	-3.29441500	5.76332400	-1.39924900
C	-0.73994600	0.45807900	-0.35769900
C	0.51616800	-0.05723200	0.00100000
Br	-2.11052700	-0.35523200	2.72079600
C	2.90286800	0.41617600	0.82559200
C	3.01017300	-0.15145600	2.09385900
C	4.08750600	0.63375600	0.05577900
C	4.26865500	-0.53977200	2.61816300
C	5.35964800	0.22817500	0.58408000
C	4.06722400	1.23106500	-1.23902000
C	5.40993900	-0.35556900	1.87283000
H	4.33745600	-0.97738600	3.60718000
C	6.53645200	0.42162000	-0.18963100
C	5.22619600	1.40280000	-1.96211000
H	3.12319500	1.57613700	-1.64408800
H	6.37334300	-0.65763300	2.27663700
C	6.47727900	0.99415800	-1.43829500
H	7.48930300	0.10597200	0.22958300
H	5.18174200	1.86409100	-2.94536700
H	7.38275000	1.13779300	-2.02141100

O	1.84198300	-0.30576600	2.78683600
C	1.87035400	-0.90627800	4.07180200
H	2.27649000	-1.92584000	4.03522600
H	2.45420700	-0.30925300	4.78458300
H	0.83025300	-0.94621800	4.39944900

4kc TS0 rac

0 1

C	1.92178200	4.46102400	-1.70391300
C	0.71057300	3.88246500	-1.91518000
C	0.40360800	2.58647700	-1.37852100
C	1.41974000	1.81140400	-0.75521100
C	2.64303100	2.51097600	-0.35609700
C	2.89345800	3.82357600	-0.86302900
H	2.14769000	5.44576200	-2.10592100
H	-0.08112200	4.37694800	-2.46896300
C	1.10030100	0.41948000	-0.46884300
C	-0.26932700	0.19909600	-0.21366400
C	-1.21371400	1.07994900	-0.82407200
N	-0.87694100	2.16417200	-1.50627800
C	2.21791200	-0.57264300	-0.61714400
C	2.70523800	-1.88976800	-0.11614500
C	4.09507900	-1.95721900	-0.49015000
C	2.26106500	-3.11013400	0.47613900
C	5.01004000	-2.93604600	-0.10299900
C	3.16158300	-4.08215500	0.91017900
C	4.53822000	-3.98149100	0.66959000
H	6.04956900	-2.87091700	-0.41210700
H	2.77040900	-4.97811600	1.37835300
H	5.20586200	-4.76237300	1.01992700
C	-0.76027500	-0.84426200	0.76220500
H	-1.46212500	-1.54493500	0.30303900
N	4.36338200	-0.89020300	-1.31546000
H	5.24584400	-0.71600100	-1.77156700
H	0.09346300	-1.42752700	1.09704100
C	-1.39845200	-0.24676100	2.01396500
C	-2.60764500	-0.75956400	2.50043100
C	-0.75842800	0.76237400	2.74744000
C	-3.16087000	-0.28534300	3.69207400
H	-3.12241100	-1.53405300	1.93703300
C	-1.30746900	1.23885900	3.93804700
H	0.17626100	1.18012700	2.38237800
C	-2.51182400	0.71604100	4.41673900
H	-4.09910200	-0.69994600	4.05247400
H	-0.79250300	2.01854400	4.49393800
H	-2.93784700	1.08366000	5.34685600
C	3.26291400	-0.10880200	-1.41125800
H	3.28687800	0.77793200	-2.02121500
C	4.06865700	4.51396700	-0.47608900

C	4.95363700	3.97106900	0.43254600
H	5.84364200	4.51894400	0.72982500
C	4.67107900	2.71221400	0.99970600
H	5.33260700	2.29646800	1.75532200
C	3.54950100	2.00340300	0.61251100
H	3.34874200	1.04335700	1.07393400
H	4.24531500	5.50352400	-0.89160700
Br	0.45463600	-3.79762300	0.42580700
C	-2.68125800	0.76420100	-0.80086000
C	-3.22826800	-0.30025700	-1.57887600
C	-3.52997600	1.56343500	-0.03803700
C	-2.42663600	-1.13527100	-2.41179100
C	-4.64153200	-0.55329500	-1.54085900
C	-4.92607000	1.31371100	-0.00657700
C	-2.98436600	-2.16279000	-3.13952200
H	-1.35994200	-0.94665800	-2.47529600
C	-5.18399300	-1.62119800	-2.30605600
C	-5.45964200	0.27865200	-0.73866900
H	-5.57712400	1.93487300	0.59730100
C	-4.37758000	-2.41565000	-3.08726500
H	-2.34918800	-2.78217900	-3.76746200
H	-6.25675200	-1.79680800	-2.26215900
H	-6.53044600	0.09086100	-0.70777500
H	-4.80311700	-3.22942600	-3.66795000
O	-2.94334300	2.56519800	0.67249300
C	-3.72890900	3.32913700	1.57178900
H	-4.19012100	2.69698200	2.34070800
H	-3.03560200	4.02380300	2.04930500
H	-4.50659100	3.90143800	1.04836100

4kc TS180 rac

0 1

C	1.05163700	-1.18297900	-0.70888700
C	2.38671000	-1.83656400	-0.67885100
C	2.15293800	-3.23056000	-0.94591300
C	3.76945700	-1.53352400	-0.56794200
C	3.10748900	-4.24737900	-0.91683700
C	4.73987100	-2.53259400	-0.50963800
C	4.41597600	-3.88831400	-0.64830300
H	2.82108400	-5.27758800	-1.10996400
H	5.77875600	-2.23984300	-0.40878500
H	5.20007000	-4.63777100	-0.60132700
N	0.82163300	-3.38887200	-1.25510700
H	0.40431600	-4.24123200	-1.59614700
C	0.19761000	-2.18900800	-1.15121500
H	-0.84757400	-2.10064500	-1.40125300
Br	4.49924900	0.22429500	-0.74313900
C	0.27258900	0.07338900	-0.41244000
C	0.49673500	1.43244800	-0.82842900

C	-1.04907100	-0.15679800	0.07913800
C	-0.62723300	2.07690300	-1.42856500
C	1.64570100	2.27625100	-0.55818900
C	-2.09823600	0.66729700	-0.40751000
C	-1.35466900	-1.21908800	1.14600600
C	-0.40783400	3.25617900	-2.22638300
N	-1.89977600	1.64566400	-1.28909600
C	1.80557400	3.49921000	-1.27913100
C	2.44546200	2.06844900	0.58759300
H	-2.35636100	-1.00287600	1.52918800
H	-1.41055800	-2.23701600	0.75022500
C	-0.37572500	-1.19882600	2.31010900
C	0.78877700	3.90107600	-2.21285400
H	-1.25721600	3.62121200	-2.79557900
C	2.86807700	4.36601800	-0.94204700
C	3.42399200	2.97848100	0.95354100
H	2.25386700	1.20050600	1.21112700
C	-0.23516800	-0.04428000	3.09567600
C	0.38658300	-2.32521200	2.63698800
H	0.94525500	4.80008600	-2.80396000
C	3.66964800	4.11180500	0.15912500
H	3.00108400	5.27802700	-1.51945300
H	4.01044000	2.80562700	1.85172100
C	0.64728000	-0.01930400	4.17505100
H	-0.82518000	0.83489400	2.84941400
C	1.27132000	-2.30479600	3.71908800
H	0.29095500	-3.22728900	2.03695300
H	4.45457000	4.81115800	0.43483200
C	1.40577200	-1.15093200	4.49091500
H	0.74253100	0.88351700	4.77337400
H	1.85683000	-3.19008700	3.95372500
H	2.09406300	-1.13144100	5.33179000
C	-3.53656700	0.39988800	-0.06410100
C	-4.35786600	-0.38373400	-0.92791900
C	-4.09003100	0.95861100	1.08326400
C	-3.86334400	-0.96295300	-2.13326400
C	-5.73452900	-0.60841200	-0.58908600
C	-5.45281600	0.74571400	1.41296300
O	-3.24313300	1.69690700	1.86583900
C	-4.67559700	-1.72837100	-2.93928000
H	-2.83793700	-0.76480300	-2.42744000
C	-6.54426700	-1.40508900	-1.44369200
C	-6.24769000	-0.02296000	0.59361200
H	-5.87430600	1.18405000	2.30992800
C	-3.76481200	2.36070900	3.00643600
C	-6.03019700	-1.95922200	-2.59284400
H	-4.27778500	-2.15280800	-3.85762700
H	-7.58472600	-1.56634600	-1.17028400
H	-7.29084500	-0.18695500	0.85305300
H	-4.14717800	1.65097300	3.75190100
H	-2.92759900	2.91392100	3.43573600

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 H                -4.56060600    3.06566600    2.73378900
 H                -6.65885600   -2.56521700   -3.23945500
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4kc TS0 diast

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0 1
 C                 2.07342400    4.19271600    1.41389300
 C                 0.78900400    3.78900100    1.23453100
 C                 0.50587200    2.47548600    0.72558800
 C                 1.55459800    1.53802100    0.52556800
 H                 2.29547900    5.18522200    1.79918600
 H                -0.05820600    4.43345800    1.44845600
 C                -1.15949300    0.97899900    0.00515800
 N                -0.76499300    2.18432600    0.42660300
 C                -0.67874500   -1.53752500    0.70427700
 H                 0.22659600   -2.03503600    1.05989600
 H                -0.99719900   -2.15562400   -0.13732400
 C                -1.68908300   -1.64721800    1.84210100
 C                -2.39419700   -2.84795800    2.01250600
 C                -1.86429000   -0.63743000    2.79688800
 C                -3.24982700   -3.03572700    3.09659900
 H                -2.27031300   -3.64570900    1.28320200
 C                -2.72520500   -0.81997800    3.88232100
 H                -1.33130200    0.30235900    2.69356300
 C                -3.42120700   -2.01836800    4.03849200
 H                -3.78817900   -3.97434500    3.20234600
 H                -2.84992300   -0.01875200    4.60653900
 H                -4.09214800   -2.15856000    4.88196400
 C                 1.10563700    0.18606800    0.44614200
 C                -0.26538000   -0.12589100    0.30164900
 C                 3.17364500    3.35121800    1.02971200
 C                 2.93003000    2.02714200    0.54223700
 C                -2.52413200    1.06974900   -0.65174400
 C                -3.57448100    0.06944600   -0.75413400
 C                -2.88234000    2.34846100   -1.15179700
 C                -3.35139200   -1.32395400   -0.89880500
 C                -4.95039900    0.48792800   -0.84378200
 C                -4.23746000    2.75148800   -1.25990800
 C                -4.38196500   -2.23780600   -0.98124500
 H                -2.34413700   -1.67185400   -1.04400600
 C                -5.99586400   -0.47256300   -0.86288500
 C                -5.24964800    1.85959500   -1.02136000
 H                -4.46993200    3.77447100   -1.53118900
 C                -5.72710600   -1.82059100   -0.91176500
 H                -4.14871800   -3.29004400   -1.12230300
 H                -7.02150400   -0.11119400   -0.89004300
 H                -6.28843500    2.17787100   -1.06202000
 H                -6.53338200   -2.54756400   -0.95075700
 O                -1.89916200    3.17939400   -1.58246100
 C                -2.11152700    4.58116300   -1.61438800
```

H	-2.78532100	4.87661900	-2.42974800
H	-1.12933400	5.02415000	-1.79074000
H	-2.50893100	4.94823600	-0.66031000
C	2.08675000	-0.91250800	0.67881100
C	2.57949400	-1.94477100	-0.21312600
C	2.71282600	-1.12133900	1.88552800
C	3.49698000	-2.74149900	0.54021800
N	3.55232900	-2.20825500	1.80923500
H	2.61264400	-0.56015100	2.80369000
H	4.10825900	-2.57028100	2.56836700
C	2.40061200	-2.30254100	-1.56471500
C	4.17871300	-3.84180100	0.01267300
C	3.06748500	-3.39327200	-2.10631800
H	2.91242800	-3.65112000	-3.14821600
C	3.94753300	-4.15935200	-1.31801600
H	4.45587400	-5.00669200	-1.76857000
H	4.86529400	-4.42259700	0.62222200
C	4.49640100	3.84718500	1.08513000
C	4.04186900	1.29934900	0.05056800
C	5.56338700	3.09438600	0.63358100
H	6.57355300	3.49292600	0.67406700
C	5.32481900	1.81842800	0.09246000
H	6.15037600	1.23458200	-0.30599600
H	4.65741400	4.85023700	1.47393000
H	3.88859300	0.32509900	-0.39328300
Br	1.25658200	-1.28616500	-2.72599900

4kc TS180 diast

0 1

C	0.84657400	4.37043500	1.65312200
C	-0.28011300	3.64944500	1.41848300
C	-0.19105600	2.33134600	0.85398700
C	1.06852500	1.71933000	0.62940200
H	0.78911500	5.36680400	2.08506600
H	-1.27322000	4.03170800	1.63240200
C	-1.41424600	0.48021500	0.06006700
N	-1.34220200	1.72495100	0.53317700
C	-0.22973700	-1.86594000	0.41645800
H	-0.50052900	-2.36642000	-0.51127100
H	0.79777900	-2.16725400	0.62630100
C	-1.07477200	-2.42573300	1.55700200
C	-1.23275700	-3.81913200	1.64675900
C	-1.64025800	-1.63669700	2.56606800
C	-1.94110800	-4.40386300	2.69539900
H	-0.78488400	-4.45292700	0.88327800
C	-2.35358500	-2.21878600	3.61886000
H	-1.53112400	-0.55754400	2.53451500
C	-2.50996800	-3.60220100	3.68915000
H	-2.04744100	-5.48525800	2.73864400

H	-2.78805800	-1.58183700	4.38536200
H	-3.06549500	-4.05269200	4.50748200
C	0.99744200	0.30357600	0.44299100
C	-0.23550500	-0.35513600	0.24566100
C	2.13702600	3.86876200	1.27031100
C	2.26395900	2.55476400	0.71433800
C	-2.79188800	0.18814300	-0.49536800
C	-3.70609200	1.31085700	-0.73485700
C	-3.34120600	-1.08127600	-0.76909000
C	-3.28553900	2.64447500	-1.02308400
C	-5.12356200	1.08702100	-0.79715300
C	-4.74492800	-1.29136800	-0.82295400
C	-4.18394900	3.66960700	-1.23394000
H	-2.23376400	2.86021700	-1.11961300
C	-6.03008200	2.17002500	-0.96038900
C	-5.61562000	-0.23839600	-0.76509100
H	-5.12942100	-2.30100500	-0.88781600
C	-5.57682800	3.45105400	-1.15855700
H	-3.80602400	4.65993200	-1.47515100
H	-7.09522400	1.94950900	-0.96268800
H	-6.68893600	-0.41119600	-0.76743400
H	-6.27317300	4.27336700	-1.29833300
O	-2.50676900	-2.12715100	-0.99142300
C	-3.02847800	-3.41800900	-1.27057300
H	-3.67481700	-3.40371100	-2.15638300
H	-2.15787600	-4.04491100	-1.47244800
H	-3.57394500	-3.83028900	-0.41381100
C	2.24042400	-0.50201400	0.63485500
C	3.04485500	-1.25227800	-0.30997300
C	2.84529000	-0.66037100	1.85894600
C	4.11721200	-1.84016300	0.43075600
N	3.96262600	-1.45586500	1.74420100
H	2.54883000	-0.25460400	2.81576100
H	4.56476600	-1.72906400	2.50516300
C	3.03166400	-1.49629200	-1.69771000
C	5.10521500	-2.64242900	-0.14732600
C	4.00357400	-2.29141700	-2.29004900
H	3.97236200	-2.46675600	-3.35981600
C	5.03090000	-2.86331600	-1.51520400
H	5.77807100	-3.48076800	-2.00502400
H	5.90198100	-3.07299400	0.45274700
C	3.27839300	4.69427100	1.39398000
C	3.53979700	2.17825200	0.22567100
C	4.51612400	4.27798300	0.94390000
H	5.38234300	4.92750300	1.03695500
C	4.63638300	3.01630300	0.33454800
H	5.59486900	2.69486500	-0.06437700
H	3.15715900	5.68148900	1.83415600
H	3.66273400	1.22613100	-0.27075700
Br	1.69007500	-0.72128500	-2.83255900

6lc GS SYN

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0 1
 C                  1.85740100    4.53584300    0.54883500
 C                  0.55929500    4.14802200    0.45604100
 C                  0.23833100    2.76490200    0.34148800
 C                  1.22291000    1.74266800    0.33954800
 C                  2.62448200    2.18683900    0.32424200
 C                  2.91882100    3.58141300    0.46712700
 H                  2.11065100    5.58751800    0.65590600
 H                 -0.26530900    4.84677700    0.47530800
 C                 -1.55597000    1.16943300    0.17831500
 C                  1.66407200   -0.77691900    0.62912400
 C                  2.20460900   -1.75262300   -0.29709100
 C                  2.92788700   -2.71005900    0.47951100
 C                  2.20146900   -1.94508900   -1.69222700
 C                  3.58959400   -3.80867000   -0.07653600
 C                  2.85007500   -3.03138200   -2.26353500
 C                  3.53593700   -3.95871000   -1.45534000
 H                  4.12676500   -4.51672000    0.54829000
 H                  2.83155600   -3.16157600   -3.34000100
 H                  4.03467900   -4.79998400   -1.92746100
 C                  2.06622600   -1.17792200    1.88000100
 C                 -1.12718000   -1.29674400    0.46722600
 H                 -2.11951400   -1.36885400    0.01627700
 H                 -0.48889500   -1.98167200   -0.09749400
 N                  2.83179400   -2.31885400    1.79678200
 H                  3.19384500   -2.83361000    2.58436100
 H                  1.84705100   -0.72700900    2.83690200
 C                 -1.22397100   -1.80253800    1.90426700
 C                 -1.12043200   -3.17881200    2.15339300
 C                 -1.46484000   -0.95034100    2.99005700
 C                 -1.25749600   -3.69051500    3.44418800
 H                 -0.92988900   -3.85577200    1.32334800
 C                 -1.59774300   -1.45801000    4.28498500
 H                 -1.53985400    0.12051500    2.82519100
 C                 -1.49615200   -2.83036000    4.51857100
 H                 -1.17414700   -4.76173000    3.61083200
 H                 -1.78203700   -0.77696600    5.11235900
 H                 -1.60133300   -3.22536500    5.52560400
 C                  4.26050700    4.03035100    0.48876600
 C                  3.73197000    1.32234900    0.13179100
 C                  5.03561300    1.78818800    0.13619100
 H                  5.84930700    1.08608600   -0.02458900
 C                  5.31238000    3.15158400    0.33493800
 H                  3.57086000    0.27210300   -0.04698500
 H                  6.33810100    3.50991400    0.34634000
 H                  4.44422600    5.09492300    0.61278000
 C                  0.76575000    0.38702000    0.38646600
 C                 -0.61073700    0.12660300    0.31703800
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Br	1.32007000	-0.69965700	-2.86018100
C	-2.99300700	0.95159700	-0.05845100
C	-3.56600100	0.27317700	-1.20284100
C	-4.04928500	1.37625200	0.72910300
C	-4.97668000	0.31067300	-1.04394500
C	-3.03309200	-0.33889400	-2.35095700
N	-5.22997800	0.97870600	0.13876400
C	-4.04818600	2.12577500	2.02139100
C	-5.85389100	-0.24580100	-1.97826500
C	-3.90115400	-0.89592600	-3.28377400
H	-6.14509400	1.17609600	0.51409300
H	-3.34934400	2.96459900	1.94116000
H	-5.04422300	2.52016800	2.25305300
H	-3.74083900	1.48807900	2.86021900
C	-5.29753400	-0.85268400	-3.10004600
H	-6.93088500	-0.20355300	-1.83654900
H	-3.49621800	-1.37051300	-4.17353800
H	-5.95064700	-1.29550200	-3.84693600
N	-1.12595500	2.47106900	0.24350400
O	-1.96596200	3.44152700	0.21455500
H	-1.95845000	-0.37280000	-2.50952700

6lc GS ANTI

0 1

C	-0.92244100	-4.61104500	-1.03492700
C	0.21749300	-4.02524700	-0.58669900
C	0.23034300	-2.63117800	-0.29587200
C	-0.90204000	-1.79305500	-0.46914800
C	-2.15863400	-2.46741300	-0.83244700
C	-2.13705000	-3.86434600	-1.14889800
H	-0.93732700	-5.66939000	-1.28243900
H	1.14311100	-4.56688300	-0.44832700
C	1.59990300	-0.78385600	0.41245700
C	-1.74465400	0.62681200	-0.66625400
C	-2.64038900	1.40214100	0.16837000
C	-3.35287700	2.29073200	-0.69576900
C	-2.96642200	1.45874300	1.53706000
C	-4.30800400	3.20421800	-0.24049200
C	-3.91018300	2.36028200	2.00979300
C	-4.57173200	3.23093500	1.12208000
H	-4.82586000	3.86607000	-0.92901900
H	-4.14274400	2.38823300	3.06870800
H	-5.30538000	3.92724800	1.51736000
C	-1.94769000	1.06716000	-1.95158100
C	0.77104500	1.59698900	0.25897700
H	-0.07315200	2.05429800	0.78255400
H	1.65012000	1.75599900	0.88811500
N	-2.91603400	2.04434000	-1.97872300
H	-3.18854700	2.56758000	-2.79627100

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 H                -1.45246600    0.75227000   -2.85868700
 C                 0.99452400    2.34351800   -1.05246500
 C                 0.38080800    3.58563900   -1.26412000
 C                 1.85593600    1.84934500   -2.04154100
 C                 0.61522600    4.31406900   -2.43184100
 H                -0.29193500    3.98262400   -0.50708100
 C                 2.08980500    2.57345100   -3.21195600
 H                 2.35601400    0.89681800   -1.89330800
 C                 1.46979300    3.80857100   -3.41344300
 H                 0.12927900    5.27649900   -2.57381300
 H                 2.76434600    2.17295200   -3.96449400
 H                 1.65494100    4.37311700   -4.32361700
 C                -3.32595500   -4.52776700   -1.53411000
 C                -3.42709600   -1.83383200   -0.84927600
 C                -4.58075600   -2.51003800   -1.20817200
 H                -5.53011200   -1.98138900   -1.19604200
 C                -4.53529600   -3.86565800   -1.57514600
 H                -3.51721000   -0.80137100   -0.55442600
 H                -5.44213400   -4.38894700   -1.86578700
 H                -3.26738900   -5.58517900   -1.78087300
 C                -0.71630300   -0.38494200   -0.29762500
 C                 0.53393500    0.09657000    0.12671300
 Br               -2.13616100    0.27145000    2.80123200
 C                 2.92401900   -0.38445700    0.92441100
 C                 4.18966200   -0.48943200    0.23109800
 C                 3.18798600    0.15882600    2.16784000
 C                 5.18254100    0.03248900    1.09841000
 C                 4.57610200   -0.97173700   -1.02946800
 N                 4.54355200    0.41416500    2.26397400
 C                 2.27961300    0.44016200    3.32167300
 C                 6.53121200    0.10351700    0.73839400
 C                 5.91561500   -0.90353300   -1.39518000
 H                 4.99771000    0.78877700    3.08263000
 H                 1.25079400    0.16578300    3.07716900
 H                 2.57653300   -0.13332700    4.20972200
 H                 2.28716000    1.50321000    3.59825800
 C                 6.88391800   -0.36949800   -0.52161200
 H                 7.27712000    0.51006600    1.41672500
 H                 6.22611700   -1.27910000   -2.36645500
 H                 7.92411000   -0.33181300   -0.83351300
 N                 1.45051600   -2.12565100    0.16365200
 O                 2.42780700   -2.92800300    0.35356900
 H                 3.84211100   -1.41367800   -1.69649600
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6lc TS0 rac

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0 1
 C                -2.22971100   -4.41791500   -1.25553200
 C                -0.96668000   -3.98736500   -1.51980000
 C                -0.56947300   -2.67254900   -1.13962400
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C	-1.47721900	-1.72854800	-0.61275800
C	-2.76229900	-2.26765700	-0.15175700
C	-3.13795400	-3.59841100	-0.51099900
H	-2.54375900	-5.41752000	-1.54458900
H	-0.22229300	-4.60205200	-2.00860400
C	-1.03781500	-0.35369900	-0.44257300
C	0.35032800	-0.24496500	-0.19714500
C	1.25083400	-1.20631900	-0.71822100
C	-2.05197800	0.71763700	-0.69308400
C	-2.42694000	2.10375200	-0.29893600
C	-3.78698000	2.28078100	-0.74173600
C	-1.88536200	3.30687900	0.24305100
C	-4.60869700	3.37434600	-0.46773000
C	-2.69503500	4.39616100	0.56066900
C	-4.06196000	4.42068200	0.25218100
H	-5.63604200	3.39285200	-0.82083100
H	-2.23358600	5.27671400	0.99279400
H	-4.65788500	5.28979600	0.51268000
C	0.89790200	0.74932000	0.80974800
H	1.67154500	1.39560000	0.39383300
N	-4.13225500	1.18694700	-1.49859100
H	-5.00687100	1.07183600	-1.98713400
H	0.08033800	1.39171900	1.12903200
C	1.44379600	0.05781000	2.05695200
C	2.71838100	0.37879800	2.54113100
C	0.66714100	-0.86082700	2.77818200
C	3.20551700	-0.19880300	3.71580300
H	3.33532000	1.08276200	1.98821800
C	1.15257400	-1.44278400	3.95014800
H	-0.32491100	-1.12373100	2.41935100
C	2.42494600	-1.11354500	4.42436300
H	4.19724400	0.06558400	4.07441700
H	0.53421600	-2.15174300	4.49505500
H	2.80251800	-1.56520900	5.33804000
C	-3.10869600	0.29842600	-1.49650000
H	-3.19802300	-0.62450200	-2.04436900
C	-4.37806600	-4.12336300	-0.06860900
C	-5.20924400	-3.39636500	0.75741400
H	-6.15098900	-3.81672400	1.09937400
C	-4.80615700	-2.11495500	1.18398300
H	-5.42720300	-1.55335500	1.87677500
C	-3.61848100	-1.56691800	0.73823400
H	-3.32808000	-0.58485900	1.09155600
H	-4.64866400	-5.13158300	-0.37350500
Br	-0.01243400	3.77733300	0.28129400
C	2.70317000	-1.00167800	-0.72409600
C	3.41428600	0.14464500	-1.24655300
C	3.65623400	-1.88395500	-0.24160600
C	4.79880400	-0.09719200	-1.03914300
C	3.03094600	1.33153000	-1.89547700
N	4.90367700	-1.33231900	-0.42666300

C	3.48215400	-3.22107300	0.39800200
C	5.78899400	0.80565800	-1.43382700
C	4.01195000	2.23545100	-2.29104100
H	5.76608600	-1.77861200	-0.15382500
H	2.89734000	-3.14144900	1.32194000
H	2.93882800	-3.87688100	-0.29238200
H	4.44657600	-3.67737700	0.64703700
C	5.37787400	1.97930400	-2.05889600
H	6.84257500	0.59732800	-1.26503200
H	3.72080700	3.15268300	-2.79589500
H	6.12169600	2.70362800	-2.37897700
O	1.54126900	-3.15362000	-1.95795100
N	0.77188400	-2.33757500	-1.32964800
H	1.98260200	1.53426100	-2.09763600

6lc TS180 rac

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C	0.89065300	-0.96540500	-0.90229000
C	2.18095000	-1.70284300	-0.98010000
C	1.87006600	-2.99030300	-1.54234900
C	3.57390000	-1.52900200	-0.77075400
C	2.76037600	-4.04949800	-1.72008800
C	4.48072900	-2.57698800	-0.91878900
C	4.08019200	-3.84396100	-1.36165200
H	2.41713000	-4.99281300	-2.13608500
H	5.53070100	-2.38436800	-0.73036900
H	4.81568500	-4.63528900	-1.46924500
N	0.54120000	-2.99514700	-1.89573300
H	0.08730500	-3.72358200	-2.42509200
C	-0.00867900	-1.80052600	-1.55852900
H	-1.03347100	-1.58558400	-1.81410600
Br	4.41221100	0.16714000	-0.49824600
C	0.17461000	0.24274700	-0.36101500
C	0.45017200	1.65003900	-0.50752200
C	-1.16877500	-0.01976400	0.04895000
C	-0.60160500	2.47363800	-0.97347500
C	1.62819700	2.37206700	-0.05162000
C	-2.21650500	0.87363900	-0.27059000
C	-1.51638400	-1.22969500	0.93388200
C	-0.35192700	3.78838400	-1.47276600
C	1.85708100	3.71295000	-0.48917500
C	2.39853500	1.88362700	1.02616300
H	-2.42814700	-0.95544900	1.47600700
H	-1.78854800	-2.11863300	0.35755700
C	-0.44882900	-1.60185300	1.94887200
C	0.87457100	4.35665200	-1.31218000
H	-1.17899200	4.29512500	-1.95306400
C	2.95547400	4.43330100	0.03134300
C	3.41109400	2.64535400	1.58653200

H	2.15640300	0.91241900	1.44508600
C	-0.05420300	-0.68621000	2.93655600
C	0.12974700	-2.87538600	1.95685700
H	1.07562700	5.35477800	-1.69244300
C	3.72440400	3.90914200	1.05635600
H	3.14069000	5.43976100	-0.33631700
H	3.97217600	2.25472800	2.43089700
C	0.89670900	-1.03188300	3.89633500
H	-0.49698600	0.30707100	2.95074000
C	1.08292400	-3.22773600	2.91637200
H	-0.16445300	-3.59962400	1.20090200
H	4.53718100	4.49218900	1.48121100
C	1.47157200	-2.30641100	3.88855500
H	1.18536500	-0.30830600	4.65454400
H	1.52226200	-4.22176500	2.89975300
H	2.21259500	-2.57732500	4.63581000
C	-3.63870700	0.62668600	0.01203800
C	-4.45128900	-0.50166200	-0.38866700
C	-4.47067800	1.49593600	0.69938400
C	-5.76316300	-0.26528000	0.10544900
C	-4.22743500	-1.66703000	-1.14165200
N	-5.73392200	0.95136500	0.75954200
C	-4.17632400	2.84278900	1.27114000
C	-6.82046800	-1.15464500	-0.10007700
C	-5.27515000	-2.55581700	-1.35536400
H	-3.24947400	-1.86536300	-1.57043700
H	-6.52359600	1.39550200	1.20303600
H	-4.99745400	3.20733400	1.89781900
H	-3.26818600	2.82085700	1.88362300
H	-3.99915000	3.55093900	0.45222600
C	-6.55990500	-2.30728700	-0.83430400
H	-7.81348700	-0.94967500	0.29180900
H	-5.10407100	-3.45575000	-1.94017700
H	-7.36011700	-3.01920200	-1.01576400
O	-2.84038900	2.76407700	-1.48004700
N	-1.92197200	2.02848300	-0.96522000

6lc TS0 diast

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C	1.70206400	4.57029300	0.55823100
C	0.47650200	4.08537900	0.90295900
C	0.15571900	2.72568400	0.62924200
C	1.10179500	1.82022800	0.10189400
C	2.35628600	2.37766900	-0.38739700
C	2.65754400	3.75189900	-0.12249500
H	1.95589300	5.60821900	0.75894500
H	-0.28141200	4.69242600	1.37932300
C	-1.58524000	1.06399800	0.49653000
C	1.82604900	-0.61628500	0.20887500

C	2.04388500	-1.73319200	-0.68961400
C	3.16834300	-2.45885400	-0.18411700
C	1.47536300	-2.21702200	-1.88519100
C	3.67958900	-3.61123100	-0.78634700
C	1.96640200	-3.36321100	-2.49681000
C	3.05832500	-4.05886500	-1.94398600
H	4.53463000	-4.13300300	-0.36547300
H	1.50864800	-3.71725900	-3.41404400
H	3.42155400	-4.95215200	-2.44344600
C	2.80281200	-0.70726700	1.17263800
C	-0.85021200	-1.30791600	1.08088300
H	-1.90990100	-1.34596700	1.32149800
H	-0.64377400	-2.11460900	0.36923400
N	3.60760000	-1.79526300	0.94067000
H	4.34973000	-2.10823800	1.54701100
H	2.96133000	-0.07313500	2.03273600
C	-0.12611000	-1.59635900	2.39402000
C	0.49119100	-2.83524900	2.60466000
C	-0.14061500	-0.66844400	3.44554800
C	1.09189500	-3.13890400	3.82840100
H	0.51020100	-3.56520300	1.79873700
C	0.46313000	-0.96714100	4.66766100
H	-0.62629200	0.29426800	3.30750800
C	1.08385200	-2.20365300	4.86444200
H	1.56557600	-4.10739900	3.97030400
H	0.44175100	-0.23441000	5.47043100
H	1.54989500	-2.43703400	5.81827100
C	3.88094200	4.30440100	-0.57281400
C	3.28295500	1.64617700	-1.17373200
C	4.45979500	2.21776400	-1.62198800
H	5.13904000	1.63021900	-2.23389000
C	4.77721200	3.55256500	-1.30407200
H	3.05730800	0.62670400	-1.45419700
H	5.70883800	3.99125800	-1.65110000
H	4.09224100	5.34668500	-0.34511900
C	0.77036000	0.42817700	0.21227300
C	-0.54402800	0.06836500	0.50129600
Br	0.02496400	-1.29702600	-2.74827000
C	-2.99062600	0.92578300	0.10488900
C	-3.86520700	-0.24533400	-0.13698100
C	-3.75168500	2.04320500	-0.30578300
C	-5.13040700	0.26861000	-0.54209000
C	-3.76260200	-1.65539900	-0.16288600
N	-5.01505400	1.63586900	-0.62763100
C	-3.40951600	3.46973400	-0.57537000
C	-6.24898700	-0.50797600	-0.84655900
C	-4.86456700	-2.44622700	-0.47803200
H	-5.71986200	2.25210000	-1.00360500
H	-3.29021900	4.03188400	0.35559300
H	-2.45103000	3.54687500	-1.09974200
H	-4.17732700	3.92988200	-1.20827400

C	-6.11137000	-1.88796100	-0.79818900
H	-7.18707800	-0.03846700	-1.13189900
H	-4.74305200	-3.52588700	-0.48763600
H	-6.95548500	-2.52963400	-1.03356000
N	-1.14699100	2.30918400	0.92684400
O	-1.91468700	3.11069400	1.58489600
H	-2.83138100	-2.16694300	0.01359000

6lc TS180 diast

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C	-0.57822200	4.44364600	1.17816700
C	-1.38910800	3.38060300	1.43896700
C	-1.01655700	2.08451900	0.98313100
C	0.22329500	1.83270000	0.35661100
C	1.01606000	2.99059700	-0.03828500
C	0.61818300	4.29109800	0.40858400
H	-0.85400900	5.43870700	1.51826900
H	-2.31957200	3.47241900	1.98294500
C	-1.72535200	-0.19162800	0.62127100
C	2.04832700	0.07491900	0.14359000
C	2.73593300	-0.66856000	-0.89399900
C	4.09772800	-0.80294900	-0.47578400
C	2.41320700	-1.22097900	-2.14989900
C	5.07360800	-1.46972100	-1.22082300
C	3.36757300	-1.89093500	-2.90426900
C	4.68913600	-2.01895800	-2.43613700
H	6.09617500	-1.54981500	-0.86254500
H	3.09248200	-2.30812200	-3.86679500
H	5.41567900	-2.54712800	-3.04644600
C	2.99552100	0.35610200	1.10013200
C	0.12640700	-1.94612000	0.85118100
H	-0.74899200	-2.56274400	1.02066600
H	0.70175500	-2.41326400	0.04561100
N	4.21603400	-0.15644700	0.73492100
H	5.05040800	-0.12923900	1.30013600
H	2.86949000	0.87633500	2.03849900
C	0.93073900	-2.01633200	2.14838100
C	2.08357200	-2.80808300	2.22169000
C	0.48794300	-1.37020600	3.31162700
C	2.78549600	-2.94446900	3.42132900
H	2.43938500	-3.31622700	1.32823100
C	1.18994200	-1.50114100	4.51069100
H	-0.41082000	-0.75973400	3.28028600
C	2.34290600	-2.28811300	4.57099200
H	3.67857600	-3.56391900	3.45562100
H	0.83074800	-0.99161900	5.40122800
H	2.88683100	-2.39238500	5.50622000
C	1.38784500	5.42440900	0.05116600
C	2.13839800	2.91230000	-0.90189700

C	2.85795300	4.03907300	-1.25612500
H	3.70375200	3.94162400	-1.93150600
C	2.49680900	5.30699100	-0.76121700
H	2.42657200	1.95704200	-1.31819600
H	3.07305300	6.18640200	-1.03578300
H	1.07260200	6.39921000	0.41610500
C	0.61909400	0.45712600	0.27406200
C	-0.33411400	-0.53764700	0.49412000
Br	0.65128200	-1.03866000	-2.90121300
C	-2.92723300	-0.92980800	0.19377300
C	-4.22507200	-0.28121100	-0.10015700
C	-3.08213900	-2.26600200	-0.23181000
C	-5.09217900	-1.27898100	-0.60372600
C	-4.72584300	1.03856600	-0.10106500
N	-4.37844900	-2.45270700	-0.64538100
C	-2.20899000	-3.47754800	-0.42809700
C	-6.40362200	-1.05104200	-1.02788900
C	-6.02551300	1.28537200	-0.53151500
H	-4.71526000	-3.31755100	-1.03980200
H	-1.95469900	-3.99316100	0.50496700
H	-2.74489700	-4.20349100	-1.05057600
H	-1.28182600	-3.23635900	-0.95190500
C	-6.86979100	0.25507200	-0.98141000
H	-7.02138000	-1.86570400	-1.39749500
H	-6.39553600	2.30709900	-0.51722600
H	-7.88157000	0.48210900	-1.30586700
N	-1.92880700	1.04788300	1.20363800
O	-2.97131200	1.27899700	1.91923000
H	-4.12640200	1.86356600	0.24953600

Imine *sp* conformer GS

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C	2.93513200	-3.96803400	0.45904100
C	1.66044600	-3.72125900	0.88214600
C	1.05657200	-2.45422400	0.65467000
C	1.75209100	-1.45569700	-0.00124300
C	3.10271800	-1.67437000	-0.40242100
C	3.69448900	-2.95207500	-0.18414700
H	3.39546800	-4.93865100	0.62382600
H	1.07238900	-4.47227400	1.39970300
C	-0.94530400	-1.27763700	0.78747500
N	-0.23379800	-2.27116600	1.18428200
C	1.39651900	0.86748800	0.85054400
C	1.16982400	2.29308400	0.83024200
C	1.56363300	2.79655300	2.09867700
C	0.69262800	3.23014900	-0.09960000
C	1.48346600	4.14840800	2.44388600
C	0.59817000	4.56989300	0.22022300
C	0.99291000	5.02241500	1.49219100

H	1.79433800	4.49590700	3.42398200
H	0.22460700	5.27071500	-0.51733100
H	0.91222700	6.07978800	1.72110100
C	1.90203300	0.58042800	2.08803400
C	-0.88199900	-0.91972500	-1.69340100
H	-0.40396100	-0.29794400	-2.46062800
H	-0.48814100	-1.93717500	-1.79940500
N	2.00552700	1.72831000	2.83668900
H	2.35359900	1.77844700	3.78100600
H	2.19687600	-0.37814700	2.49222000
C	-2.30411900	-1.12606200	1.37523000
C	-3.08311000	0.02017800	1.18475600
C	-2.84356200	-2.18937300	2.11393500
C	-4.37389700	0.09321300	1.70021600
H	-2.70099200	0.86355200	0.62113500
C	-4.12814100	-2.11311600	2.63186300
H	-2.23471100	-3.07513700	2.25657800
C	-4.90209300	-0.97177600	2.42195700
H	-4.96716500	0.98627400	1.53014600
H	-4.53312200	-2.94908700	3.19427700
H	-5.91157300	-0.91571400	2.81808500
C	-2.37895600	-0.89786200	-1.87272000
C	-3.01980000	0.30370700	-2.18718500
C	-3.15529300	-2.02920200	-1.62037100
C	-4.40820700	0.37589600	-2.23480800
H	-2.41766000	1.19462100	-2.35868500
C	-4.54518500	-1.95958500	-1.66004200
H	-2.66397800	-2.96391800	-1.35910700
C	-5.17499400	-0.75613800	-1.96548400
H	-4.89268400	1.31737000	-2.47650700
H	-5.13631600	-2.84432500	-1.44413100
H	-6.25887900	-0.69990000	-1.99377700
C	5.03209000	-3.17740000	-0.59746800
C	3.89112200	-0.65756000	-1.00872400
C	5.18575500	-0.90469100	-1.38970100
H	5.77374700	-0.11546900	-1.84791600
C	5.76392900	-2.18017700	-1.18943000
H	3.46861000	0.33202600	-1.15351000
H	6.78743900	-2.36332400	-1.50110500
H	5.46769100	-4.15933600	-0.43066800
C	1.05547600	-0.13497300	-0.22296800
H	1.36942500	0.27113900	-1.18927200
C	-0.46847900	-0.34800100	-0.31443200
H	-0.94344400	0.63070800	-0.21649500
Br	0.18396900	2.68842900	-1.85159900

Imine *ap* conformer GS

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C	1.80206700	-3.86244200	-1.54414100

C	0.47912300	-3.57608200	-1.39148800
C	0.04459500	-2.24723200	-1.13992500
C	0.94848000	-1.20728000	-1.01918700
C	2.33914100	-1.48009200	-1.23882500
C	2.76428600	-2.82121000	-1.48442100
H	2.13776500	-4.87933800	-1.72847600
H	-0.28718700	-4.34224500	-1.44410600
C	-1.87015700	-0.98530400	-0.73007200
N	-1.34555100	-2.12505600	-0.96934100
C	1.07523800	1.02837800	0.31491000
C	1.14146900	0.84804600	1.74940700
C	1.82380400	1.97610100	2.28168600
C	0.68350900	-0.09675800	2.68306500
C	2.09438700	2.14644800	3.64215700
C	0.93686700	0.05133700	4.03273100
C	1.65106500	1.16531600	4.50725300
H	2.62939600	3.02040800	4.00024400
H	0.56826800	-0.69591800	4.72587000
H	1.83987200	1.25627700	5.57179400
C	1.66565000	2.23995900	0.06872600
C	-1.65600100	1.22146500	-1.86836300
H	-1.43788500	0.72073200	-2.81969800
H	-2.74587200	1.29465400	-1.79056700
N	2.12374100	2.80406200	1.23085100
H	2.58687000	3.69581700	1.30398000
H	1.77603700	2.75698700	-0.87709800
C	-3.33656100	-0.96551300	-0.45467000
C	-3.95475400	0.08359300	0.23515600
C	-4.12193600	-2.04834700	-0.87136800
C	-5.32066500	0.05104900	0.50250000
H	-3.37232900	0.93058500	0.58518700
C	-5.48533700	-2.07631200	-0.61231300
H	-3.63420700	-2.86264000	-1.39563200
C	-6.09105000	-1.02599700	0.07649500
H	-5.78086100	0.86960500	1.04717500
H	-6.08001500	-2.92034900	-0.94818400
H	-7.15712600	-1.04878100	0.28051300
C	-1.04855100	2.60382500	-1.86740200
C	-0.17762700	3.01322200	-2.87861100
C	-1.31445800	3.49023600	-0.81856600
C	0.42644100	4.27022700	-2.83981100
H	0.03169700	2.33805300	-3.70517000
C	-0.71357000	4.74264700	-0.77164100
H	-1.99058700	3.18700500	-0.02179500
C	0.16483200	5.13578100	-1.78188900
H	1.09947300	4.57036900	-3.63744300
H	-0.93021900	5.41480900	0.05320500
H	0.63187500	6.11542000	-1.74899000
C	4.13836300	-3.10087800	-1.69530300
C	3.33823200	-0.46593900	-1.26920700
C	4.65874800	-0.76470500	-1.49337900

H	5.39326100	0.03485000	-1.51283800
C	5.07329100	-2.09942100	-1.69778300
H	3.05445300	0.56466900	-1.11042800
H	6.12204400	-2.32453300	-1.86441500
H	4.43161000	-4.13349600	-1.86680100
C	0.43731000	0.21414700	-0.79818200
H	0.73517700	0.75179300	-1.71098800
C	-1.11738000	0.32950900	-0.71775500
H	-1.35541600	0.82163900	0.23298600
Br	-0.35961500	-1.56045900	2.11121200

Imine *sp/ap* rotation TS1

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C	-2.03804300	0.35876000	3.22836200
C	-0.72477700	-0.01215600	3.15638200
C	-0.03888000	0.03878100	1.91673500
C	-0.70709600	0.36708600	0.74967200
C	-2.06342100	0.79826800	0.80929800
C	-2.73170200	0.79782900	2.06902800
H	-2.56823200	0.33743500	4.17674000
H	-0.16546300	-0.32128700	4.03323500
C	2.06236100	0.32633400	1.01908300
N	1.35048800	-0.19795800	1.95067100
C	0.52702700	-0.99331100	-1.10317300
C	-0.10273600	-2.31199400	-1.20537000
C	0.79842100	-3.13520500	-1.94661400
C	-1.28161600	-2.97846300	-0.79420200
C	0.59100400	-4.47765400	-2.27037000
C	-1.50759100	-4.30823200	-1.10583400
C	-0.58016900	-5.06043400	-1.84053800
H	1.33379500	-5.02874900	-2.83881600
H	-2.42711700	-4.76930500	-0.76557200
H	-0.79307000	-6.10061200	-2.06308900
C	1.72583900	-1.12127300	-1.76404800
C	1.18348700	2.58796400	0.36434400
H	0.59777100	2.59298200	1.28866700
H	2.16365600	3.01918300	0.60455600
N	1.88631000	-2.37679900	-2.27249100
H	2.70539300	-2.71304100	-2.75329500
H	2.51346900	-0.40039700	-1.91737600
C	3.53625800	0.15390500	1.07352600
C	4.39832400	0.89160900	0.25417700
C	4.08776300	-0.76312000	1.97914000
C	5.77797900	0.72019700	0.33862300
H	4.00276700	1.62260400	-0.44548900
C	5.46164100	-0.94111200	2.05421800
H	3.41138700	-1.32582600	2.61310300
C	6.31312400	-0.19952800	1.23422200
H	6.43310900	1.30791400	-0.29699900

H	5.87412500	-1.66030000	2.75521200
H	7.38813600	-0.33825200	1.29582500
C	0.49457500	3.41943900	-0.68974800
C	-0.83175700	3.82409000	-0.52950300
C	1.16054300	3.76185500	-1.87102900
C	-1.48292400	4.54326700	-1.52977100
H	-1.36178800	3.56398100	0.38292800
C	0.51652000	4.48434800	-2.86990000
H	2.19947900	3.46446500	-2.00454200
C	-0.81134000	4.87453800	-2.70258600
H	-2.51773900	4.84064100	-1.38827000
H	1.05030400	4.74575500	-3.77869000
H	-1.31658900	5.43616900	-3.48223000
C	-4.08655300	1.21528300	2.14036200
C	-2.80213400	1.19789700	-0.33995100
C	-4.10809000	1.60150200	-0.23792100
H	-4.64960800	1.90316300	-1.12928400
C	-4.76289600	1.61279100	1.01689300
H	-2.32988100	1.17804900	-1.31607200
H	-5.79887700	1.92994000	1.08351900
H	-4.57869400	1.20844000	3.10961500
C	0.13402400	0.37392100	-0.51009700
H	-0.36527500	0.96151100	-1.28558100
C	1.41824100	1.13015600	-0.10204500
H	2.08067000	1.19263100	-0.96481900
Br	-2.64833600	-2.15108000	0.21117900

Imine *sp/ap* rotation TS2

0 1

C	2.65727300	-2.69521800	2.51823700
C	1.52194200	-1.94742600	2.63358800
C	0.97746300	-1.28024800	1.50357000
C	1.62280300	-1.31683400	0.28137000
C	2.73642200	-2.19774600	0.11042400
C	3.27110600	-2.87241600	1.24944200
H	3.08390000	-3.19851700	3.38157500
H	0.99396900	-1.84259300	3.57573000
C	-0.96844300	-0.30139800	0.69409400
N	-0.27078200	-0.66962600	1.70652700
C	1.94441300	0.90277600	-0.84242500
C	1.85456000	2.31946100	-0.49203200
C	3.14374300	2.88599100	-0.73056600
C	0.89641600	3.25344300	-0.04474300
C	3.48974500	4.22182800	-0.51574000
C	1.21363500	4.58040300	0.18045000
C	2.50939600	5.06758200	-0.04482400
H	4.49818800	4.56888100	-0.71872400
H	0.43574800	5.24988000	0.52862700
H	2.72717600	6.11368800	0.14188100

C	3.23878700	0.73462700	-1.27606600
C	-0.90572400	-1.77607000	-1.34305300
H	-0.45439900	-1.85228800	-2.33986500
H	-0.46888500	-2.57746000	-0.73458600
N	3.95133700	1.89433300	-1.20911900
H	4.92348800	2.00067700	-1.45184000
H	3.72618100	-0.16713900	-1.61265900
C	-2.38479800	0.09459400	0.96519300
C	-3.22370900	0.63865600	-0.01598100
C	-2.91765700	-0.14453900	2.23793400
C	-4.55820900	0.91318600	0.25965500
H	-2.84769800	0.83658900	-1.01370700
C	-4.24930200	0.13718600	2.51611200
H	-2.26686900	-0.56631100	2.99516200
C	-5.07789100	0.66162500	1.52657100
H	-5.19240200	1.31823800	-0.52279600
H	-4.64415600	-0.05994700	3.50828800
H	-6.12122400	0.87257100	1.74097800
C	-2.39454800	-1.97587700	-1.46270200
C	-3.08533000	-1.47654300	-2.56864100
C	-3.11733200	-2.61469500	-0.45306800
C	-4.47080500	-1.58262200	-2.65108100
H	-2.53004800	-0.98573600	-3.36586500
C	-4.50233800	-2.71966600	-0.52741600
H	-2.58806700	-3.00260300	0.41457800
C	-5.18349100	-2.19882000	-1.62533000
H	-4.99379000	-1.18484000	-3.51574900
H	-5.05089400	-3.20161600	0.27595500
H	-6.26474000	-2.27761000	-1.68368200
C	4.38513300	-3.73676100	1.09457100
C	3.30702000	-2.50383800	-1.15865400
C	4.36889900	-3.36440500	-1.28138700
H	4.76964400	-3.58877400	-2.26524500
C	4.93369700	-3.97528300	-0.13860100
H	2.87520500	-2.07667200	-2.05842400
H	5.78019000	-4.64615600	-0.24451900
H	4.78568100	-4.22276100	1.98060400
C	1.09443400	-0.39214000	-0.81037500
H	1.31335500	-0.85192200	-1.77885300
C	-0.45004400	-0.40928100	-0.73752900
H	-0.85192000	0.40368800	-1.34796400
Br	-0.89900400	2.76538800	0.23780800

Enamine *sp* conformer GS

0 1

C	-0.06074100	4.73075300	0.27559300
C	-1.08511800	4.04108900	-0.30451600
C	-1.01735300	2.62496600	-0.41633700
C	0.08039200	1.92663400	0.04474400

C	1.15956100	2.63611100	0.65204400
C	1.08645900	4.05377700	0.77401300
H	-0.11106700	5.81255300	0.36684700
H	-1.96338000	4.56078800	-0.68001800
C	-2.25370500	0.56608300	-0.75442300
C	0.99400400	0.10718400	-1.40199900
C	2.00604300	-0.89778000	-1.62669900
C	2.42227600	-0.78000000	-2.98107600
C	2.64502600	-1.88750500	-0.86210700
C	3.40273900	-1.59150500	-3.55878200
C	3.61571300	-2.70167300	-1.41025400
C	3.98976800	-2.55228700	-2.75795800
H	3.69065500	-1.46746600	-4.59805900
H	4.08935300	-3.45523300	-0.79161200
H	4.75541700	-3.20312500	-3.16697400
C	0.85197300	0.76765400	-2.59294300
C	-1.35308300	-1.61120100	0.14802600
H	-2.30063900	-2.04701000	-0.18471100
H	-0.55084400	-2.20677800	-0.31227200
N	1.69537200	0.23950800	-3.53942800
H	1.79756300	0.57544600	-4.48388200
H	0.19299700	1.59183900	-2.83123700
C	-3.63652100	0.08211200	-1.00547300
C	-4.71839500	0.68290300	-0.35278400
C	-3.88293300	-0.94928500	-1.91648200
C	-6.01898200	0.25182700	-0.59525800
H	-4.53219500	1.47664200	0.36698800
C	-5.18321800	-1.38225100	-2.15743400
H	-3.04393600	-1.40014000	-2.43909100
C	-6.25363700	-0.78261000	-1.49788400
H	-6.84889300	0.71808200	-0.07328200
H	-5.36171800	-2.18420400	-2.86709700
H	-7.26784400	-1.12020600	-1.68703800
C	-1.25066800	-1.77913500	1.65876500
C	-0.85837100	-3.01267500	2.18885700
C	-1.56029600	-0.74431100	2.54088500
C	-0.78462400	-3.21040900	3.56273400
H	-0.59511700	-3.82051800	1.50955000
C	-1.48186300	-0.93635900	3.91977300
H	-1.85479200	0.22350700	2.14265400
C	-1.09637300	-2.16874300	4.43563900
H	-0.47564300	-4.17536100	3.95378700
H	-1.72007300	-0.11605500	4.59042500
H	-1.03275700	-2.31762500	5.50922200
C	2.15558100	4.76212400	1.37530300
C	2.32795200	1.98001900	1.13049700
C	3.34726100	2.69663700	1.70793200
H	4.22910500	2.17614000	2.06883900
C	3.26586500	4.10156300	1.83652600
H	2.42371900	0.90157800	1.04389000
H	4.08120800	4.65154900	2.29570000

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 H                  2.07756300    5.84313100    1.46273700
 C                 -1.23141100   -0.18235100   -0.30383200
 Br                 2.18815400   -2.12275600    0.96121600
 C                  0.15517600    0.42940200   -0.17447700
 H                  0.62034000   -0.02587400    0.70232800
 N                 -2.07422400    1.93447400   -1.00196300
 H                 -2.90342400    2.46240200   -1.23420800
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Enamine *ap* conformer GS

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0 1
 C                  2.53254300   -2.21068700   -2.95938600
 C                  1.24665000   -2.45877400   -2.58815300
 C                  0.52542100   -1.51216400   -1.81017700
 C                  1.10654500   -0.33268800   -1.38185200
 C                  2.43976300   -0.04124100   -1.81530600
 C                  3.16209100   -0.99016400   -2.59859300
 H                  3.08687100   -2.93557500   -3.54942800
 H                  0.75369000   -3.38599800   -2.86988100
 C                 -1.60571500   -0.93377500   -0.80821300
 C                  0.92248000    1.06826600    0.79911300
 C                  1.23768400    0.33835700    2.01137200
 C                  1.66900400    1.29716800    2.97136400
 C                  1.20651000   -0.99792300    2.45185900
 C                  2.07243400    0.97539300    4.26987500
 C                  1.59668000   -1.33804900    3.73323100
 C                  2.03336200   -0.35478700    4.63680500
 H                  2.39968900    1.74696700    4.95977200
 H                  1.56058000   -2.37777600    4.03696100
 H                  2.33688500   -0.65215900    5.63512000
 C                  1.14705900    2.38662200    1.09359900
 C                 -1.98936500    1.17535100    0.47769900
 H                 -3.00050500    0.76956400    0.58156400
 H                 -1.58026300    1.24891100    1.49372100
 N                  1.59566000    2.53238500    2.38128900
 H                  1.85976300    3.40154400    2.81704500
 H                  0.99111300    3.25028700    0.45940000
 C                 -2.98294600   -1.45886400   -0.60289000
 C                 -4.10242500   -0.82686100   -1.14924300
 C                 -3.15013800   -2.63670400    0.13308200
 C                 -5.37299700   -1.36323500   -0.95934000
 H                 -3.97045400    0.08868900   -1.72028000
 C                 -4.42057500   -3.17229900    0.31982400
 H                 -2.27587700   -3.10127600    0.58208000
 C                 -5.53344200   -2.53815100   -0.22860100
 H                 -6.23787100   -0.86540700   -1.38684400
 H                 -4.54295900   -4.08115000    0.90100500
 H                 -6.52460400   -2.95651100   -0.08300400
 C                 -2.07331200    2.57578800   -0.10196900
 C                 -2.06670100    3.69276800    0.73703400
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C	-2.17345000	2.78056400	-1.48062700
C	-2.17281000	4.98000900	0.21684900
H	-1.97284800	3.54538400	1.81088400
C	-2.27656000	4.06565300	-2.00664400
H	-2.14989600	1.91775800	-2.14362300
C	-2.27900400	5.17071200	-1.15889700
H	-2.16921900	5.83563600	0.88598900
H	-2.34982500	4.20447500	-3.08123800
H	-2.35746800	6.17340400	-1.56764600
C	4.48027500	-0.70239900	-3.02773200
C	3.08717900	1.19386900	-1.53357500
C	4.36127600	1.45294600	-1.97646100
H	4.82346700	2.40847500	-1.74657800
C	5.07801700	0.49413100	-2.72445800
H	2.56722500	1.94637700	-0.95682200
H	6.08772200	0.70783500	-3.06030700
H	5.00636000	-1.45176500	-3.61419400
C	-1.13795700	0.23427900	-0.33584100
Br	0.61696500	-2.38323300	1.31248400
C	0.31263100	0.66244100	-0.53814800
H	0.28900200	1.61166700	-1.10246300
N	-0.77832200	-1.83375400	-1.47122200
H	-1.22696300	-2.57993600	-1.98221600

Enamine *sp/ap* rotation TS1

0 1

C	1.00507100	4.01285700	1.91204300
C	1.05574800	2.72879800	2.37669000
C	0.57221400	1.66776300	1.56903000
C	0.00898400	1.90927100	0.32530000
C	-0.03646600	3.24262300	-0.17625700
C	0.47636300	4.30621600	0.62556400
H	1.38272500	4.83038600	2.52032700
H	1.47953600	2.50593000	3.35276200
C	0.84173700	-0.64768700	1.03822900
C	-2.00138100	0.47637200	0.36182900
C	-3.01140600	-0.55202900	0.19435700
C	-4.06127700	-0.26477700	1.11114000
C	-3.20949000	-1.68454200	-0.61238800
C	-5.21433500	-1.04120900	1.24961600
C	-4.33927700	-2.47145400	-0.49576700
C	-5.33836300	-2.15132000	0.43816300
H	-5.98170400	-0.77432400	1.96960200
H	-4.45029200	-3.33674400	-1.13885000
H	-6.21676900	-2.78384300	0.51121500
C	-2.49171800	1.30971500	1.33378300
C	1.00089500	-1.06086100	-1.42140200
H	0.88032200	-2.14734200	-1.45299300
H	0.49637000	-0.67740400	-2.31514100

N	-3.71239200	0.87561100	1.78251200
H	-4.26316300	1.32104600	2.49878900
H	-2.04733900	2.20194700	1.74950600
C	1.70288300	-1.79353000	1.39872100
C	1.28088800	-3.08904900	1.08056900
C	2.94323200	-1.60775100	2.01553300
C	2.09570400	-4.18011500	1.36157300
H	0.30867800	-3.21686600	0.60949700
C	3.75754800	-2.70052500	2.29661600
H	3.28860900	-0.59879800	2.22789100
C	3.33614900	-3.98712400	1.96888800
H	1.76169300	-5.18279700	1.11280900
H	4.72788200	-2.54689700	2.75868000
H	3.97269700	-4.83920700	2.18700900
C	2.47865400	-0.72428300	-1.49245000
C	3.44711800	-1.72549200	-1.42800300
C	2.89603600	0.60719500	-1.58914900
C	4.80446800	-1.40873000	-1.45959500
H	3.13421800	-2.76263100	-1.32732700
C	4.24804800	0.92732500	-1.62702000
H	2.14983700	1.39963400	-1.62162300
C	5.20882900	-0.08205700	-1.56134200
H	5.54377000	-2.20203800	-1.39825300
H	4.55423500	1.96637900	-1.70521100
H	6.26527300	0.16779500	-1.58645700
C	0.42995000	5.63617100	0.13681000
C	-0.60401700	3.57356700	-1.43772900
C	-0.63491900	4.87152100	-1.88242400
H	-1.06978600	5.09735700	-2.85129900
C	-0.10928300	5.91918100	-1.09167900
H	-1.02102800	2.78794800	-2.05858300
H	-0.13839400	6.94062500	-1.45724200
H	0.83304500	6.43059900	0.76019900
C	-0.65398100	0.70716200	-0.32863200
H	-0.82939100	0.88373400	-1.39445100
C	0.33776500	-0.44372000	-0.19722500
Br	-1.93735200	-2.16807300	-1.92354900
H	1.05709700	0.17768600	2.91770500
N	0.66310400	0.34774700	2.00252700

Enamine *sp/ap* rotation TS2

0 1

C	-1.35962300	-2.83719000	2.00701100
C	-0.63156900	-1.73570100	2.35280900
C	-0.23656500	-0.81460400	1.34980500
C	-0.64545100	-0.95808000	0.03752600
C	-1.36368500	-2.13024900	-0.34727900
C	-1.71747200	-3.08339600	0.65257000
H	-1.66003700	-3.55575000	2.76498000

H	-0.32857200	-1.56668600	3.38303100
C	1.55397100	0.60372900	0.65601300
C	-1.08000700	1.46378600	-0.88310200
C	-2.41904000	1.89949500	-0.49508400
C	-2.51779200	3.27565700	-0.86806700
C	-3.57731800	1.38447500	0.13355700
C	-3.63805100	4.08576900	-0.66950300
C	-4.69821000	2.17091300	0.33569900
C	-4.73609000	3.51471300	-0.06471900
H	-3.63099700	5.12478900	-0.98446900
H	-5.56007000	1.72835100	0.82095600
H	-5.63317100	4.09865400	0.11193100
C	-0.48466500	2.57013000	-1.43362700
C	2.20889300	0.56733900	-1.76843000
H	2.55237300	1.59857000	-1.93002900
H	1.70445600	0.27183000	-2.69758600
N	-1.33050500	3.64307600	-1.43779000
H	-1.10994200	4.56787000	-1.77080100
H	0.51234500	2.66398400	-1.84001000
C	2.89901600	1.03452100	1.11026300
C	3.36991700	2.31064400	0.79575300
C	3.73036700	0.14680500	1.79985900
C	4.66064500	2.69179300	1.15087000
H	2.71208100	2.99796200	0.26977300
C	5.02390100	0.52330300	2.14499500
H	3.37326200	-0.85693600	2.01636800
C	5.49108300	1.79540000	1.81938500
H	5.01944200	3.68678400	0.90513800
H	5.67342900	-0.18060300	2.65597900
H	6.50184700	2.08749400	2.08742800
C	3.42396600	-0.31709900	-1.55498500
C	4.71496800	0.20558400	-1.59358700
C	3.25474600	-1.67337700	-1.26096800
C	5.81947300	-0.60342000	-1.33257600
H	4.85582300	1.26453500	-1.79715900
C	4.35409900	-2.48620300	-1.00971400
H	2.24730100	-2.08150800	-1.20171300
C	5.64215400	-1.95157400	-1.03993100
H	6.81710200	-0.17444300	-1.34810000
H	4.20661500	-3.53793200	-0.78247300
H	6.50030700	-2.58373800	-0.83276800
C	-2.45952600	-4.23572400	0.29383200
C	-1.81791100	-2.36364600	-1.67258500
C	-2.53693300	-3.48914500	-1.99059700
H	-2.87180000	-3.64131100	-3.01219700
C	-2.86027400	-4.44392300	-1.00112000
H	-1.61220100	-1.63551800	-2.44941200
H	-3.43128400	-5.32814500	-1.26558600
H	-2.71333400	-4.95033900	1.07306000
C	-0.26465600	0.15389600	-0.91433100
H	-0.32839100	-0.23188500	-1.93647500

C	1.20135400	0.47584100	-0.63705900
Br	-3.70929600	-0.38819500	0.77319000
H	0.97959100	0.28007300	2.60255100
N	0.64863700	0.21948400	1.64919100

Imine-DDQ *sp* conformer GS

0 1

C	1.93357500	-2.25499400	-2.62055100
C	0.60264900	-2.50425400	-2.43124100
C	-0.24634900	-1.52425500	-1.84908500
C	0.25813000	-0.28904100	-1.46921900
C	1.67102300	-0.05809900	-1.54600700
C	2.50545000	-1.03215300	-2.17122800
H	2.57754100	-2.99929200	-3.08282800
H	0.14981900	-3.44900600	-2.71484800
C	-2.47026600	-1.05693300	-1.35089700
C	-0.43431000	2.14905600	-1.50677100
C	-0.25280400	3.41166800	-0.83015100
C	-0.11730800	4.40842400	-1.83293500
C	-0.14491100	3.84142100	0.50474300
C	0.07254800	5.76398800	-1.54833700
C	0.04327300	5.17477500	0.80816600
C	0.14290500	6.13152700	-0.21860500
H	0.16463200	6.49602200	-2.34432400
H	0.12112500	5.47767900	1.84601600
H	0.28854500	7.17338600	0.04645400
C	-0.38670700	2.43021200	-2.84549300
C	-3.09538300	1.14816100	-0.15499900
H	-4.01398600	1.49190800	-0.63830400
H	-2.56527000	2.05195000	0.17339100
N	-0.20084800	3.77559800	-3.04639600
H	-0.12364000	4.22688100	-3.94422800
H	-0.46320600	1.75130600	-3.68441200
C	-3.87143800	-1.53293100	-1.20389900
C	-4.93125700	-0.83467100	-1.78856100
C	-4.13104400	-2.67655300	-0.44460000
C	-6.24068000	-1.26889200	-1.60770200
H	-4.73371700	0.04652100	-2.39444300
C	-5.44224700	-3.09301500	-0.24588300
H	-3.29766700	-3.20181900	0.01179800
C	-6.49850300	-2.39092200	-0.82393100
H	-7.05910400	-0.72878000	-2.07407600
H	-5.64127100	-3.96602800	0.36797400
H	-7.52134100	-2.71968000	-0.66660400
C	-3.47774800	0.32106900	1.05454600
C	-4.81590600	0.23976200	1.44645100
C	-2.52936700	-0.41057300	1.77178500
C	-5.20127800	-0.56123800	2.51640700
H	-5.56906700	0.78372000	0.88133400

C	-2.91071400	-1.21641200	2.84109200
H	-1.48392000	-0.39118000	1.48502600
C	-4.24815300	-1.29655700	3.21714800
H	-6.24990000	-0.62306000	2.79213900
H	-2.15509300	-1.79043500	3.36921900
H	-4.54716800	-1.93180400	4.04528400
C	3.89800000	-0.78420000	-2.29991700
C	2.29734500	1.09389200	-0.98582100
C	3.64837900	1.30006400	-1.11759200
H	4.10209300	2.17788900	-0.66770300
C	4.45762200	0.36649100	-1.80537100
H	1.70878900	1.79525100	-0.40461400
H	5.52366800	0.54356600	-1.90563400
H	4.51462400	-1.53718700	-2.78424600
C	-0.69608700	0.76679600	-0.93920500
H	-0.54155900	0.81471800	0.14236100
Br	-0.19988400	2.58389200	1.92145200
C	3.05987500	-0.60051200	1.59364500
C	4.06770600	-1.31110700	1.05538300
C	2.41045000	-3.12382200	0.34454500
C	1.40379900	-2.42452300	0.90650300
C	3.81957900	-2.60622900	0.34580600
O	4.70369500	-3.23349300	-0.18046600
C	1.64849800	-1.09229100	1.54589600
O	0.73966800	-0.46803700	2.03787500
C	2.21073300	-4.40870200	-0.25867700
N	2.05437500	-5.44957600	-0.73739100
C	0.06451300	-2.92616900	0.97279700
N	-1.00856800	-3.34870500	1.06182000
Cl	5.70050700	-0.81800000	1.13579100
Cl	3.27638100	0.89191600	2.39438200
N	-1.58535100	-1.92321700	-1.67459400
C	-2.19370100	0.43030400	-1.19810700
H	-2.43957200	0.85683000	-2.18260500

Imine-DDQ *ap* conformer GS

0 1

C	1.87407900	-0.49452600	-2.73511700
C	0.55330400	-0.83419100	-2.65346300
C	-0.22961100	-0.43615800	-1.54215500
C	0.31449300	0.31439300	-0.50413900
C	1.71989400	0.61604200	-0.53750600
C	2.48941700	0.23110400	-1.68095700
H	2.47443100	-0.79052600	-3.59189800
H	0.05794900	-1.41337500	-3.42586800
C	-2.44843800	-0.29524700	-0.86295900
C	-0.33238300	2.09507300	1.24531400
C	-0.17500200	3.40800900	0.65894000
C	0.08598900	4.30688300	1.72844500

C	-0.21232700	3.96522200	-0.63279300
C	0.30496800	5.67616800	1.55248800
C	0.00359300	5.31524500	-0.82809900
C	0.26324700	6.16472400	0.26198500
H	0.50005100	6.32522300	2.40019200
H	-0.03331300	5.71684800	-1.83398900
H	0.42870200	7.22094200	0.07762900
C	-0.18227500	2.26251700	2.59538000
C	-3.05926600	0.66034900	1.43678600
H	-3.95083000	1.26854800	1.26072300
H	-2.53547300	1.14163300	2.27105000
N	0.07812100	3.57781000	2.89051600
H	0.20198600	3.95798000	3.81560700
H	-0.21311100	1.51150200	3.37424900
C	-3.86385600	-0.69731900	-1.07305700
C	-4.88096300	0.25906000	-1.12210200
C	-4.17792000	-2.05241600	-1.20486200
C	-6.20447500	-0.13648200	-1.29093700
H	-4.63709600	1.31582100	-1.04114900
C	-5.50324700	-2.44478500	-1.34964700
H	-3.37490300	-2.78192500	-1.15378400
C	-6.51820400	-1.48976400	-1.39068700
H	-6.99024400	0.61121100	-1.34150000
H	-5.74655100	-3.50017500	-1.42436600
H	-7.55256000	-1.79988200	-1.50485700
C	-3.51815900	-0.72714800	1.84073700
C	-4.88158500	-0.96476300	2.03672600
C	-2.63267000	-1.79804700	1.98285000
C	-5.35344800	-2.23535000	2.34657300
H	-5.58602600	-0.14710700	1.90421700
C	-3.10173700	-3.07427000	2.28571600
H	-1.56519900	-1.66197500	1.83778300
C	-4.46269600	-3.29932200	2.46608800
H	-6.41957000	-2.39710700	2.47541000
H	-2.39524700	-3.89486000	2.36428200
H	-4.82722800	-4.29655500	2.69266600
C	3.87338400	0.54193300	-1.74837700
C	2.42452600	1.26088100	0.52317300
C	3.76544500	1.54131800	0.43198600
H	4.26650800	2.02232900	1.26654800
C	4.50262700	1.19651100	-0.72220200
H	1.90276700	1.51449000	1.43448400
H	5.56195100	1.42453900	-0.78189900
H	4.42588200	0.23248500	-2.63182700
C	-0.63013800	0.75759700	0.61151900
H	-0.51033700	0.01799100	1.41876200
Br	-0.58773000	2.90115900	-2.15242900
C	3.22486800	-1.64526800	1.50884300
C	4.15945000	-1.90703600	0.57759600
C	2.37347600	-2.95525000	-0.91621200
C	1.43906600	-2.70754200	0.02692400

C	3.79938600	-2.53035200	-0.73689400
O	4.61532200	-2.71936200	-1.60336300
C	1.78217600	-1.97466100	1.28590600
O	0.93122200	-1.69799800	2.09913100
C	2.07378700	-3.66390700	-2.12535100
N	1.83747600	-4.24664700	-3.09579900
C	0.08800500	-3.16350700	-0.10514500
N	-0.99068700	-3.56941200	-0.20692400
Cl	5.81922300	-1.57819400	0.80399800
Cl	3.58741600	-0.93904300	3.02329200
C	-2.13372700	0.75013700	0.19194100
H	-2.32742100	1.71926600	-0.29015300
N	-1.57463600	-0.83333600	-1.62592000

Enamine-DDQ *sp* conformer GS

0 1

C	-2.13408400	-2.05942300	2.73138900
C	-0.79722400	-2.31829400	2.64974500
C	0.07093600	-1.41506600	1.97174600
C	-0.43423400	-0.26805300	1.35852400
C	-1.83075200	0.02272900	1.46695900
C	-2.69144300	-0.87944300	2.15666300
H	-2.79500400	-2.75994500	3.23594000
H	-0.38189200	-3.22402700	3.08374100
C	2.29465300	-0.96323500	1.11140700
C	0.60629100	2.02590100	1.36199600
C	0.47901600	3.37437300	0.86241100
C	0.74900200	4.24835600	1.95017400
C	0.15738300	3.98091500	-0.36444900
C	0.71791100	5.64162000	1.84353400
C	0.12153200	5.35471200	-0.49323000
C	0.40481800	6.17990400	0.61029300
H	0.93179800	6.27369700	2.69960800
H	-0.12936400	5.79243300	-1.45251800
H	0.37094200	7.25681300	0.48362700
C	0.93828500	2.14164500	2.68433100
C	2.78143700	0.89314000	-0.51468700
H	3.47345600	1.54263700	0.03718100
H	2.13917400	1.56664400	-1.09785500
N	1.02408500	3.46433400	3.04167300
H	1.23727800	3.80858000	3.96453100
H	1.12259300	1.35615500	3.40523600
C	3.69815300	-1.45922900	1.11802800
C	4.67981700	-0.69572600	1.75399600
C	4.05270800	-2.65330100	0.48484700
C	6.00813500	-1.11032900	1.74529700
H	4.39224300	0.23154700	2.24359400
C	5.38349300	-3.06046300	0.47024300
H	3.29161600	-3.22901400	-0.03308200

C	6.36151800	-2.29119700	1.09688000
H	6.76692000	-0.51039100	2.23874600
H	5.65916100	-3.97468000	-0.04634300
H	7.39904600	-2.61098800	1.07823800
C	3.55883400	0.00723100	-1.46650500
C	4.94984000	0.05611900	-1.53460400
C	2.87570200	-0.91204900	-2.26779000
C	5.65249300	-0.81125800	-2.36839100
H	5.49038100	0.75723900	-0.90323700
C	3.57325100	-1.77868100	-3.10152000
H	1.79050800	-0.95925200	-2.21275200
C	4.96617600	-1.73499200	-3.15052200
H	6.73762000	-0.77228600	-2.39469800
H	3.02899500	-2.49604700	-3.70885500
H	5.51171600	-2.41821900	-3.79456500
C	-4.07652900	-0.59613700	2.25839700
C	-2.41169400	1.18427100	0.88270600
C	-3.75782400	1.43380200	1.00202000
H	-4.17852000	2.32108200	0.53867200
C	-4.60278500	0.54327400	1.70162800
H	-1.79874600	1.87061300	0.30747300
H	-5.66477600	0.75161600	1.78025400
H	-4.71501400	-1.30624400	2.77783500
C	0.49370600	0.69153200	0.63993900
H	0.07047900	0.88373500	-0.35202400
C	1.88419800	0.12314800	0.43894300
Br	-0.26801700	2.91996200	-1.87894400
C	-3.04726300	-0.63073600	-1.63015700
C	-4.07875300	-1.30517000	-1.08940800
C	-2.46600100	-3.06239800	-0.19715100
C	-1.42761500	-2.38731400	-0.74447000
C	-3.86892800	-2.55726100	-0.29534900
O	-4.78222300	-3.15305200	0.22128100
C	-1.63622400	-1.10656400	-1.48589000
O	-0.70771500	-0.50136600	-1.97068200
C	-2.28393800	-4.30648500	0.49033700
N	-2.12564800	-5.31089800	1.04174100
C	-0.09385600	-2.90414900	-0.69767100
N	0.96539100	-3.36783700	-0.65914800
Cl	-5.70447700	-0.81107300	-1.26365000
Cl	-3.23900600	0.81087700	-2.52669400
H	1.73436300	-2.58833400	2.25686100
N	1.41238500	-1.69098100	1.92068300

Enamine-DDQ *ap* conformer GS

0 1

C	2.27641700	0.22558900	-2.75751000
C	1.02458400	-0.30928100	-2.77739400
C	0.16421300	-0.17165200	-1.65271500

C	0.56626000	0.52615700	-0.50679500
C	1.88365900	1.09120500	-0.48870500
C	2.74459400	0.93970800	-1.61770700
H	2.93946000	0.10223400	-3.61018600
H	0.67333200	-0.86802200	-3.64079700
C	-1.97476800	-0.72357000	-0.66493200
C	-0.67344100	2.04335200	1.21033900
C	-1.34096600	3.19399100	0.63598100
C	-1.40915000	4.18447700	1.65520000
C	-1.91612700	3.54428400	-0.59881100
C	-1.98239500	5.44685000	1.47976800
C	-2.49137400	4.78491400	-0.79422700
C	-2.51967900	5.73438300	0.24142900
H	-2.00409600	6.16740000	2.29119600
H	-2.92550600	5.01892900	-1.75928600
H	-2.97599300	6.70150600	0.05868000
C	-0.40832600	2.38305800	2.51119800
C	-2.60133900	-0.18991600	1.69424800
H	-3.43613400	0.51401100	1.57954500
H	-2.04142200	0.16025600	2.57051200
N	-0.83227500	3.65721000	2.78161900
H	-0.74705500	4.13028100	3.66733000
H	0.06977600	1.78339600	3.27584900
C	-3.29326100	-1.34256300	-0.96666400
C	-4.39568100	-0.50429600	-1.14954700
C	-3.44388300	-2.72818100	-1.05962800
C	-5.65251900	-1.05180100	-1.39127400
H	-4.24878300	0.57227000	-1.10990800
C	-4.70373200	-3.26962300	-1.29610500
H	-2.58315300	-3.37068200	-0.89787300
C	-5.80804600	-2.43458700	-1.45548000
H	-6.50942300	-0.39928100	-1.52918800
H	-4.82562900	-4.34750600	-1.34056600
H	-6.79031100	-2.86213900	-1.63338500
C	-3.13514300	-1.57862900	1.97920200
C	-4.50351300	-1.82460900	2.07169900
C	-2.24458900	-2.64690900	2.12157200
C	-4.98059700	-3.11680600	2.28152400
H	-5.20318000	-1.00263900	1.94038100
C	-2.71712400	-3.93742300	2.33105600
H	-1.17521800	-2.46442300	2.03433500
C	-4.08889400	-4.17749800	2.40719600
H	-6.05092000	-3.29440500	2.33127500
H	-2.01364500	-4.75945100	2.42554300
H	-4.45853900	-5.18683500	2.56128600
C	4.05113300	1.48820600	-1.59846600
C	2.41235800	1.77675000	0.64190000
C	3.68476200	2.29553900	0.63458500
H	4.05751200	2.80609600	1.51752800
C	4.51672600	2.16346200	-0.49825400
H	1.80260800	1.89126400	1.52694900

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 H                  5.52009600    2.57622900   -0.48969600
 H                  4.68219100    1.34846500   -2.47242000
 C                 -0.37279700    0.64036600    0.69141600
 H                  0.15098300    0.16160300    1.54301400
 C                 -1.67112800   -0.12479300    0.49688100
 Br                -1.94578200    2.32314800   -2.03648000
 C                  3.68012300   -1.02716800    1.47923500
 C                  4.67182800   -1.04824300    0.56998000
 C                  3.13962600   -2.23723000   -1.07567600
 C                  2.14147400   -2.21849900   -0.15782700
 C                  4.46754900   -1.61622600   -0.80185400
 O                  5.33791600   -1.60175700   -1.63846200
 C                  2.32764300   -1.58735000    1.17987100
 O                  1.43212200   -1.56224100    1.99586100
 C                  2.97882300   -2.86214100   -2.35446300
 N                  2.83483400   -3.36877900   -3.38443000
 C                  0.88729100   -2.86639600   -0.39243500
 N                 -0.11074300   -3.41531600   -0.59653400
 Cl                 6.24072100   -0.45429000    0.89060800
 Cl                 3.87086900   -0.38369300    3.05329900
 H                 -1.32441800   -1.27433000   -2.54449400
 N                 -1.07481600   -0.73855800   -1.72512600
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Imine-DDQ *sp/ap* rotation TS1

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0 1
 C                  1.50588800    1.00248200    3.12499200
 C                  0.25630300    0.45440600    3.06634700
 C                 -0.44892000    0.37975700    1.83569300
 C                  0.09383600    0.90419000    0.67229500
 C                  1.44856600    1.34620600    0.68728800
 C                  2.14344000    1.44177100    1.93451700
 H                  2.04502500    1.07076100    4.06574000
 H                 -0.23492800    0.04984700    3.94474000
 C                 -2.22840600   -0.67692200    0.78151400
 N                 -1.66842600   -0.30575500    1.87827400
 C                 -1.44829600    2.43107400   -0.56314800
 C                 -2.74919300    3.10119000   -0.54809400
 C                 -2.49175300    4.50143000   -0.66553400
 C                 -4.12143300    2.78354600   -0.45259400
 C                 -3.46427800    5.50335800   -0.69179400
 C                 -5.10412100    3.75602000   -0.47808700
 C                 -4.78255600    5.11584300   -0.59766900
 H                 -3.17725800    6.54629800   -0.78387100
 H                 -6.14067500    3.44984400   -0.39874500
 H                 -5.57710900    5.85404100   -0.61305200
 C                 -0.53453300    3.45214100   -0.68499000
 C                 -0.71952500   -1.41591800   -1.10757700
 H                 -0.30825200   -1.07058800   -2.06410600
 H                  0.12431500   -1.49496800   -0.41625200
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N	-1.13961000	4.67087100	-0.74741800
H	-0.66684000	5.55849400	-0.81101700
H	0.54231000	3.39570100	-0.72575600
C	-3.36928700	-1.63261900	0.90950300
C	-4.12968100	-2.06127500	-0.18666400
C	-3.65016000	-2.17838300	2.16843500
C	-5.12638400	-3.01720400	-0.03268000
H	-3.93635600	-1.66853500	-1.17845300
C	-4.65251800	-3.12753400	2.32424700
H	-3.05577600	-1.85252100	3.01389400
C	-5.39185200	-3.55524900	1.22388400
H	-5.68890400	-3.34617100	-0.90080200
H	-4.85151000	-3.54164800	3.30803900
H	-6.16802200	-4.30502000	1.34401100
C	-1.34192600	-2.77416200	-1.30079400
C	-1.99639800	-3.08900900	-2.49337500
C	-1.31604900	-3.72281300	-0.27574700
C	-2.64389000	-4.31149500	-2.64930600
H	-2.00969400	-2.36040000	-3.30202800
C	-1.96462000	-4.94447300	-0.42595600
H	-0.80454300	-3.48496200	0.65433900
C	-2.63573400	-5.23956100	-1.61069600
H	-3.15298400	-4.54002600	-3.58107600
H	-1.95132600	-5.66480800	0.38629200
H	-3.14449100	-6.19175500	-1.72690300
C	3.46823900	1.94856200	1.95947100
C	2.17977000	1.66874900	-0.49838800
C	3.47034300	2.13708900	-0.44429700
H	3.99768800	2.37488500	-1.36456200
C	4.12305300	2.29850900	0.80076200
H	1.70634300	1.53922600	-1.46794900
H	5.13794400	2.68429500	0.83799500
H	3.96750300	2.03824600	2.92142000
C	-0.83598100	1.00405000	-0.53274600
H	-0.23323700	0.96224000	-1.44543600
C	-1.67389000	-0.29445200	-0.58786900
H	-2.49023900	-0.16841200	-1.30220700
Br	-4.71793200	1.00899700	-0.26284500
C	5.75217000	-0.24216600	-0.82808900
C	4.69849400	-0.64849000	-1.55856400
C	3.46382500	-1.29731500	0.57710900
C	4.51558700	-0.87659400	1.30912500
C	3.47353400	-1.22716500	-0.91901600
O	2.53619600	-1.62265600	-1.56582600
C	5.75720100	-0.34014800	0.66615000
O	6.70779900	-0.01160600	1.33034300
C	2.28684000	-1.84497600	1.18184700
N	1.34401700	-2.30665400	1.66788200
C	4.50285400	-0.91241800	2.74185400
N	4.47146400	-0.92619700	3.89774100
Cl	4.63162900	-0.50731500	-3.25946900

Cl	7.14973600	0.46020200	-1.51549000

Imine-DDQ *sp/ap* rotation TS2

0 1

C	1.50588800	1.00248200	3.12499200
C	0.25630300	0.45440600	3.06634700
C	-0.44892000	0.37975700	1.83569300
C	0.09383600	0.90419000	0.67229500
C	1.44856600	1.34620600	0.68728800
C	2.14344000	1.44177100	1.93451700
H	2.04502500	1.07076100	4.06574000
H	-0.23492800	0.04984700	3.94474000
C	-2.22840600	-0.67692200	0.78151400
N	-1.66842600	-0.30575500	1.87827400
C	-1.44829600	2.43107400	-0.56314800
C	-1.12130426	3.80735890	-0.18827290
C	-2.27014208	4.60021566	-0.49206459
C	-0.05041444	4.54762643	0.35785856
C	-2.38004784	5.97721424	-0.28676037
C	-0.13408300	5.91098320	0.57300774
C	-1.29467231	6.63057783	0.25357309
H	-3.29432138	6.50109330	-0.54798273
H	0.72267600	6.42446715	0.99346147
H	-1.32758705	7.69973999	0.43328477
C	-2.73299089	2.50103817	-1.05002597
C	-0.71952500	-1.41591800	-1.10757700
H	-0.30825200	-1.07058800	-2.06410600
H	0.12431500	-1.49496800	-0.41625200
N	-3.22316275	3.77125451	-1.01002303
H	-4.13046412	4.06105464	-1.33903823
H	-3.35216036	1.70936355	-1.44286011
C	-3.36928700	-1.63261900	0.90950300
C	-4.12968100	-2.06127500	-0.18666400
C	-3.65016000	-2.17838300	2.16843500
C	-5.12638400	-3.01720400	-0.03268000
H	-3.93635600	-1.66853500	-1.17845300
C	-4.65251800	-3.12753400	2.32424700
H	-3.05577600	-1.85252100	3.01389400
C	-5.39185200	-3.55524900	1.22388400
H	-5.68890400	-3.34617100	-0.90080200
H	-4.85151000	-3.54164800	3.30803900
H	-6.16802200	-4.30502000	1.34401100
C	-1.34192600	-2.77416200	-1.30079400
C	-1.99639800	-3.08900900	-2.49337500
C	-1.31604900	-3.72281300	-0.27574700
C	-2.64389000	-4.31149500	-2.64930600
H	-2.00969400	-2.36040000	-3.30202800
C	-1.96462000	-4.94447300	-0.42595600
H	-0.80454300	-3.48496200	0.65433900

C	-2.63573400	-5.23956100	-1.61069600
H	-3.15298400	-4.54002600	-3.58107600
H	-1.95132600	-5.66480800	0.38629200
H	-3.14449100	-6.19175500	-1.72690300
C	3.46823900	1.94856200	1.95947100
C	2.17977000	1.66874900	-0.49838800
C	3.47034300	2.13708900	-0.44429700
H	3.99768800	2.37488500	-1.36456200
C	4.12305300	2.29850900	0.80076200
H	1.70634300	1.53922600	-1.46794900
H	5.13794400	2.68429500	0.83799500
H	3.96750300	2.03824600	2.92142000
C	-0.83598100	1.00405000	-0.53274600
H	-0.23323700	0.96224000	-1.44543600
C	-1.67389000	-0.29445200	-0.58786900
H	-2.49023900	-0.16841200	-1.30220700
Br	1.58393065	3.73604560	0.81730667
C	5.75217000	-0.24216600	-0.82808900
C	4.69849400	-0.64849000	-1.55856400
C	3.46382500	-1.29731500	0.57710900
C	4.51558700	-0.87659400	1.30912500
C	3.47353400	-1.22716500	-0.91901600
O	2.53619600	-1.62265600	-1.56582600
C	5.75720100	-0.34014800	0.66615000
O	6.70779900	-0.01160600	1.33034300
C	2.28684000	-1.84497600	1.18184700
N	1.34401700	-2.30665400	1.66788200
C	4.50285400	-0.91241800	2.74185400
N	4.47146400	-0.92619700	3.89774100
Cl	4.63162900	-0.50731500	-3.25946900
Cl	7.14973600	0.46020200	-1.51549000

Enamine-DDQ *sp/ap* rotation TS1

0 1

C	2.91242800	1.18946100	2.58988400
C	1.72021100	0.57405500	2.80757500
C	0.78054000	0.44225300	1.73776900
C	1.02671900	1.00025100	0.48180400
C	2.32694400	1.52077200	0.21680200
C	3.27327800	1.64355500	1.28356400
H	3.63271500	1.29567700	3.39622000
H	1.46912600	0.16449300	3.78207900
C	-1.20781100	-0.67966900	0.87954100
C	-0.73854000	2.61163200	-0.32966700
C	-2.01748300	3.28016100	-0.07325100
C	-1.77764100	4.68396900	-0.20157600
C	-3.35651700	2.96882200	0.25340900
C	-2.73165900	5.69065600	-0.04030500
C	-4.32220800	3.94686900	0.41356800

C	-4.01780500	5.30735600	0.26734800
H	-2.45484600	6.73382900	-0.15757400
H	-5.33175100	3.64323400	0.66407900
H	-4.79867200	6.04803500	0.40172500
C	0.14458900	3.63575200	-0.58037300
C	-1.83052300	-0.32556800	-1.61012900
H	-2.44423500	0.55690100	-1.84141500
H	-1.05465400	-0.34425300	-2.38886800
N	-0.45910100	4.85468900	-0.50730500
H	-0.00123200	5.74372100	-0.63200100
H	1.19687400	3.58862300	-0.80778100
C	-2.00130500	-1.88396000	1.29132500
C	-3.37980200	-2.03101900	1.10263900
C	-1.31959300	-2.91893100	1.94903900
C	-4.04272100	-3.17923700	1.51969100
H	-3.94880400	-1.27490400	0.58568600
C	-1.98218900	-4.06719300	2.37032400
H	-0.24905200	-2.84639600	2.10058400
C	-3.34894900	-4.20498800	2.15450700
H	-5.10899800	-3.26858800	1.33662300
H	-1.42002700	-4.85497700	2.86203700
H	-3.86873400	-5.10199900	2.47692800
C	-2.67165100	-1.56669800	-1.77154100
C	-4.03516400	-1.45954400	-2.04696200
C	-2.09897700	-2.83782700	-1.66593500
C	-4.82277000	-2.60046200	-2.18933200
H	-4.48775300	-0.47232000	-2.11039600
C	-2.88306700	-3.97695000	-1.80628600
H	-1.04261400	-2.92901300	-1.42482700
C	-4.24843000	-3.86209700	-2.06545700
H	-5.88467400	-2.50185500	-2.39485200
H	-2.42997800	-4.95801900	-1.70031700
H	-4.86055100	-4.75289200	-2.17032300
C	4.54787400	2.20600200	1.04098000
C	2.76084800	1.91975100	-1.08285800
C	4.00978400	2.45333500	-1.29172100
H	4.31246000	2.73018300	-2.29674100
C	4.91584700	2.61096800	-0.22002800
H	2.08945700	1.79568900	-1.92908600
H	5.90334600	3.02161000	-0.39941200
H	5.24472800	2.28102000	1.87168900
C	-0.17397800	1.16091300	-0.44516000
H	0.19182700	1.09963000	-1.47848200
C	-1.11588500	-0.03700100	-0.30581700
Br	-3.95514000	1.20167900	0.52506300
C	2.37922000	-1.55860400	-1.52901500
C	3.57493800	-0.96399900	-1.70864600
C	4.07191100	-1.21240200	0.77368200
C	2.88602100	-1.83901900	0.94421500
C	4.51709300	-0.73592500	-0.57126100
O	5.59610600	-0.21243900	-0.71733000

C	1.96317200	-2.09663500	-0.20185700
O	0.96812700	-2.76790600	-0.05397700
C	4.99284600	-1.00410100	1.85319700
N	5.73460900	-0.83336900	2.72401500
C	2.45826600	-2.34773200	2.21422300
N	2.08675100	-2.75711000	3.23076100
Cl	4.13695100	-0.45447800	-3.24250200
Cl	1.27910700	-1.82851300	-2.81144100
H	-0.52904000	-0.67786100	2.83712400
N	-0.37783000	-0.24514500	1.93540500

Enamine-DDQ *sp/ap* rotation TS2

0 1

C	1.99058800	-0.42108300	-2.52277600
C	0.64433700	-0.27587800	-2.70322700
C	-0.17602900	0.17876700	-1.63295600
C	0.36950600	0.47757300	-0.39287400
C	1.78056500	0.34132100	-0.19891500
C	2.60087600	-0.11893800	-1.27098600
H	2.61484800	-0.77335600	-3.34047300
H	0.18423300	-0.52068700	-3.65692700
C	-2.40212800	0.29000600	-0.71387800
C	-0.47763100	2.49519200	1.02823400
C	0.35678600	3.64566400	0.66427800
C	-0.11051900	4.74232500	1.45461500
C	1.35882500	4.01683600	-0.26937800
C	0.46476200	6.01460700	1.49917000
C	1.95692700	5.26496600	-0.22909900
C	1.54186200	6.25301900	0.67544600
H	0.06163500	6.77890300	2.15637900
H	2.72616000	5.49168800	-0.95774200
H	2.03550300	7.21892500	0.67607100
C	-1.45188600	3.01101600	1.84705600
C	-2.82414700	0.19407200	1.75927400
H	-3.44626200	1.06457100	2.00507700
H	-2.15181300	0.04452400	2.61572900
N	-1.22092800	4.32629900	2.13177600
H	-1.75854400	4.89322800	2.76805600
H	-2.26106300	2.50274000	2.34296500
C	-3.84063800	0.14138700	-1.06708000
C	-4.69071800	1.22394600	-0.82541700
C	-4.35502700	-1.02925700	-1.62998100
C	-6.04633900	1.13432800	-1.12532500
H	-4.27431800	2.13259600	-0.39717800
C	-5.71407100	-1.12012200	-1.91606300
H	-3.69907400	-1.87865500	-1.79225400
C	-6.56058900	-0.04257700	-1.66422000
H	-6.70075000	1.98012300	-0.93665700
H	-6.11504400	-2.04199400	-2.32599500

H	-7.62014700	-0.11988900	-1.88892800
C	-3.76224200	-0.99391800	1.65023900
C	-5.14329300	-0.81612800	1.73766300
C	-3.26597300	-2.28029600	1.43559500
C	-6.01414400	-1.89082600	1.58009700
H	-5.54382100	0.18285200	1.89369600
C	-4.13132600	-3.35755800	1.27591600
H	-2.19332700	-2.42578600	1.37784300
C	-5.50992100	-3.16593400	1.34062300
H	-7.08662200	-1.72708700	1.63032600
H	-3.72696600	-4.34909500	1.09354700
H	-6.18588200	-4.00509800	1.20650200
C	4.00348400	-0.20492600	-1.09984000
C	2.42479300	0.73518600	1.00630900
C	3.79112600	0.65124800	1.14000700
H	4.25801300	0.96378400	2.06903100
C	4.59362800	0.17301500	0.08232000
H	1.84034300	1.14252600	1.82501100
H	5.67006900	0.10911300	0.20268000
H	4.60670600	-0.56934800	-1.92796900
C	-0.52237500	0.97369100	0.73250100
H	-0.02884400	0.50140200	1.59656000
C	-1.94390600	0.46180000	0.54259100
Br	1.82497500	2.98742200	-1.78939100
C	2.36543000	-2.41926800	1.64670200
C	3.40179700	-2.81534200	0.88585900
C	1.81767500	-3.15207300	-1.08486900
C	0.77383700	-2.76914400	-0.31795000
C	3.21815600	-3.18093400	-0.55332000
O	4.13707300	-3.51429200	-1.25871100
C	0.97187700	-2.34272000	1.10340700
O	0.04329800	-1.98548100	1.78800400
C	1.65137800	-3.56558100	-2.44729900
N	1.51208300	-3.90052500	-3.54537500
C	-0.55747900	-2.78897000	-0.84187800
N	-1.60688800	-2.86237300	-1.32308100
Cl	4.99601100	-2.95730900	1.48081100
Cl	2.52687900	-1.99814800	3.29496300
H	-1.93004600	0.03852400	-2.70087800
N	-1.53401100	0.29885000	-1.80784600

Imine-DDQ HTO TS *sp* conformer

0 1

C	-1.21760800	-3.78099000	1.77991500
C	0.13593600	-3.62156400	1.61642800
C	0.67721200	-2.35004600	1.36160300
C	-0.15476600	-1.22071700	1.23894200
C	-1.56523000	-1.35131600	1.56253100
C	-2.08612300	-2.66492600	1.80289000

H	-1.63885100	-4.76861100	1.94433500
H	0.82229600	-4.45772000	1.69470900
C	2.63888600	-1.19776800	0.92102700
N	2.07048400	-2.23583800	1.41716400
C	0.32272100	1.22940300	1.52540600
C	0.53863200	2.62918400	1.20309000
C	0.35733200	3.35983100	2.40462600
C	0.80338500	3.38245100	0.04824000
C	0.46323600	4.74633100	2.49661200
C	0.91113200	4.76103600	0.11356000
C	0.75052300	5.43656900	1.33269300
H	0.31782300	5.25955600	3.44144500
H	1.11684500	5.31700000	-0.79378700
H	0.84211000	6.51707700	1.35300000
C	0.02708300	1.19934700	2.87962600
C	1.76580600	-0.85744600	-1.36109500
H	1.17899300	-0.20316100	-2.00535000
H	1.23736700	-1.81554500	-1.30074500
N	0.05049600	2.45105300	3.39731800
H	-0.09564900	2.68181200	4.36898300
H	-0.16999500	0.33481900	3.49845600
C	4.10230900	-1.03970100	1.10271400
C	4.79444500	0.10536300	0.69455600
C	4.82258500	-2.08980800	1.69330000
C	6.17328700	0.19419800	0.86217900
H	4.27399300	0.93377500	0.22768600
C	6.19520500	-1.99684700	1.86293100
H	4.27996400	-2.97568200	2.00337300
C	6.87749900	-0.85381800	1.44449600
H	6.69577800	1.08592900	0.53073000
H	6.73898100	-2.81953900	2.31683500
H	7.95361600	-0.78400000	1.57037500
C	3.14684000	-1.03333600	-1.94116900
C	3.81125100	0.06143400	-2.50073900
C	3.81488200	-2.25580400	-1.85751300
C	5.12172500	-0.05803800	-2.95212600
H	3.30010800	1.02070200	-2.55733200
C	5.12785800	-2.37798400	-2.30371100
H	3.30531600	-3.11029700	-1.41773400
C	5.78576800	-1.27844800	-2.84846400
H	5.62572900	0.80207100	-3.38291300
H	5.63854400	-3.33257200	-2.22201400
H	6.81047900	-1.37269600	-3.19444600
C	-3.46982300	-2.84434200	2.07079500
C	-2.48156000	-0.26730400	1.63225500
C	-3.81400800	-0.47314800	1.90219200
H	-4.48723600	0.37924400	1.93711200
C	-4.32283400	-1.77526200	2.12174500
H	-2.13661900	0.74324000	1.44241500
H	-5.38311500	-1.91909000	2.30099000
H	-3.83847700	-3.85570100	2.21617600

C	0.48441100	-0.00242600	0.75830700
H	-0.41887600	0.16788800	-0.47502100
C	1.83227200	-0.22444900	0.06708000
H	2.33502800	0.73882800	-0.01580900
Br	0.97317600	2.55757100	-1.63686100
C	-3.20851100	0.91804600	-1.18009200
C	-4.53731400	0.65741300	-1.03844000
C	-4.05695300	-1.78853900	-1.18251000
C	-2.72408100	-1.49593500	-1.34285900
C	-5.06472300	-0.72915600	-0.99793200
O	-6.24228300	-0.97462500	-0.80497900
C	-2.25459400	-0.14451900	-1.33303900
O	-0.98638000	0.11645100	-1.43236400
C	-4.51061400	-3.13970100	-1.08930100
N	-4.85709200	-4.23887800	-0.97696300
C	-1.73677000	-2.53258300	-1.46835800
N	-0.93625800	-3.36297400	-1.56277100
Cl	-5.69805400	1.90023000	-0.83029200
Cl	-2.56604400	2.51632600	-1.10089300

Imine-DDQ HTO TS *ap* conformer

0 1

C	3.17942100	-0.36045400	-1.97226700
C	2.09033400	-1.18412200	-1.90773500
C	0.91198300	-0.76381700	-1.25480900
C	0.82360500	0.52911600	-0.64858200
C	1.89973900	1.47676000	-0.91721900
C	3.08805200	1.00251200	-1.54293300
H	4.10700800	-0.70369100	-2.42485300
H	2.10043700	-2.18852500	-2.31919500
C	-1.29560800	-1.32209000	-0.81628200
N	-0.16635800	-1.63022500	-1.35758900
C	-0.56274900	1.97158700	0.98378600
C	-1.41318200	3.03066400	0.49362100
C	-1.53718600	3.98121000	1.53781100
C	-2.04263000	3.32157000	-0.72683800
C	-2.28997800	5.15256300	1.40988600
C	-2.79319800	4.47079700	-0.87263600
C	-2.91921900	5.37454700	0.19913400
H	-2.37259400	5.86031300	2.22825900
H	-3.27451600	4.67782500	-1.82143000
H	-3.51440000	6.27075200	0.05988900
C	-0.22151300	2.31499000	2.26458000
C	-1.91400600	-0.76736100	1.57565200
H	-1.72490100	0.03363100	2.30001300
H	-1.27321100	-1.60780100	1.84969100
N	-0.79282100	3.51856100	2.59587200
H	-0.70892700	3.97369700	3.49160300
H	0.39801000	1.77113700	2.96539200

C	-2.46795100	-2.14388400	-1.18179700
C	-3.71453100	-1.55000500	-1.41427000
C	-2.32467100	-3.53007100	-1.30017900
C	-4.81182800	-2.34006900	-1.73090000
H	-3.82285300	-0.47005500	-1.36356600
C	-3.43061900	-4.31737800	-1.59878200
H	-1.35062400	-3.97376800	-1.12265300
C	-4.67424700	-3.72503200	-1.80903100
H	-5.77692500	-1.87531100	-1.90535700
H	-3.32180300	-5.39525600	-1.66472400
H	-5.53735000	-4.34268400	-2.03841200
C	-3.36505800	-1.16753700	1.64277800
C	-4.36411500	-0.19399900	1.56436100
C	-3.73289200	-2.51030000	1.74169800
C	-5.70762100	-0.55540400	1.56147600
H	-4.08182900	0.85626000	1.49292000
C	-5.07622400	-2.87504600	1.73750800
H	-2.95683100	-3.27076200	1.79071600
C	-6.06615100	-1.89974600	1.64276300
H	-6.47493900	0.21043800	1.49699300
H	-5.34877300	-3.92438600	1.79749600
H	-7.11383800	-2.18482800	1.63514700
C	4.16927100	1.87713000	-1.76864400
C	1.82114100	2.85582200	-0.62965000
C	2.88605300	3.70016100	-0.88312300
H	2.78921900	4.75730800	-0.65705300
C	4.07845700	3.21106600	-1.43356700
H	0.91355600	3.27576900	-0.22291100
H	4.91295900	3.88025300	-1.61547600
H	5.06992800	1.47974300	-2.22782300
C	-0.23537900	0.68885700	0.30122800
H	0.45623000	0.03973500	1.29722800
C	-1.47298700	-0.21119400	0.18200400
H	-2.29662400	0.42888100	-0.16263300
Br	-1.82742400	2.16340400	-2.21225800
C	3.34774500	-0.37218100	1.36293100
C	4.42600000	-0.89381900	0.70883800
C	3.18434600	-3.03867600	0.39062100
C	2.10021500	-2.47214700	1.00444900
C	4.42831900	-2.27307200	0.16052700
O	5.38181000	-2.74599200	-0.42775400
C	2.12317100	-1.11510700	1.50264000
O	1.09005500	-0.61945400	2.09138400
C	3.14217600	-4.37561000	-0.11422500
N	3.09103400	-5.45451800	-0.53019700
C	0.87414100	-3.20172500	1.17081800
N	-0.12344300	-3.77300400	1.30283300
Cl	5.88882600	-0.02389800	0.51932000
Cl	3.37504800	1.21230900	2.03894000

Enamine-DDQ HTO TS *sp* conformer

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0 1
 C                 -2.35909100   -2.71417300    2.14525300
 C                 -1.02897700   -2.96621100    2.04269700
 C                 -0.14303000   -1.91407900    1.68312200
 C                 -0.58684500   -0.59405000    1.44586300
 C                 -2.00729600   -0.33079900    1.58740600
 C                 -2.88210400   -1.40309700    1.93184800
 H                 -3.05117600   -3.52009700    2.37394400
 H                 -0.63284400   -3.96790700    2.18195100
 C                  2.14807700   -1.31614000    1.19270300
 C                  0.23175900    1.79472600    1.53817800
 C                  0.20230600    3.12864300    0.97580400
 C                 -0.06012800    4.01996100    2.05166100
 C                  0.36274000    3.71479300   -0.29497100
 C                 -0.18029500    5.40432000    1.90218700
 C                  0.24266500    5.08074900   -0.46325300
 C                 -0.03358500    5.91987900    0.63012700
 H                 -0.38202300    6.04297700    2.75612200
 H                  0.37550500    5.50199100   -1.45297300
 H                 -0.12090900    6.98856000    0.46547900
 C                  0.01978400    1.94840000    2.88393900
 C                  2.88726400    0.94312000    0.46800400
 H                  3.56850700    1.14039600    1.30414700
 H                  2.43041700    1.90247500    0.21712200
 N                 -0.16170600    3.26751800    3.19461800
 H                 -0.33882600    3.63319600    4.11722700
 H                 -0.05021500    1.18149000    3.64317000
 C                  3.53750000   -1.84608300    1.16913700
 C                  4.45921800   -1.42490700    2.12968300
 C                  3.93050500   -2.73157900    0.16185000
 C                  5.77631400   -1.86996900    2.07292400
 H                  4.14179100   -0.74251700    2.91392500
 C                  5.25100900   -3.16679300    0.10602300
 H                  3.20915600   -3.04237300   -0.58869600
 C                  6.17393100   -2.73444100    1.05573700
 H                  6.49165900   -1.53986600    2.81981600
 H                  5.56107800   -3.83635900   -0.68981100
 H                  7.20433000   -3.07245000    1.00411500
 C                  3.69185300    0.44641200   -0.71917500
 C                  5.08513900    0.49883700   -0.69694800
 C                  3.05239100   -0.09962300   -1.83640000
 C                  5.83306600    0.00773700   -1.76383600
 H                  5.59005900    0.90146000    0.17812000
 C                  3.79887800   -0.58849300   -2.90417900
 H                  1.96821000   -0.18186400   -1.85354700
 C                  5.19105700   -0.53920700   -2.87108400
 H                  6.91774500    0.04283200   -1.72310500
 H                  3.28942200   -1.01986100   -3.76062800
 H                  5.77136200   -0.92999100   -3.70139000
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C	-4.27719400	-1.18814700	2.04298200
C	-2.60863700	0.93398500	1.33822200
C	-3.96740700	1.11375700	1.44793000
H	-4.38948600	2.08810400	1.22204500
C	-4.81810500	0.05111600	1.81403500
H	-2.00557100	1.77100000	1.01504700
H	-5.88956900	0.20592600	1.88110400
H	-4.91166600	-2.03644800	2.28270200
C	0.39883800	0.40412700	0.97101400
H	0.03008400	0.37326700	-0.31417300
C	1.80818800	-0.02999700	0.90411400
Br	0.80537800	2.66381300	-1.79406000
C	-2.73409100	-0.09620600	-1.58832900
C	-3.90315800	-0.76381800	-1.42276300
C	-2.63987200	-2.86830900	-0.97955300
C	-1.46332800	-2.17148700	-1.16334900
C	-3.94668500	-2.19887200	-1.03083600
O	-4.99231800	-2.77074200	-0.77601700
C	-1.44954900	-0.75614800	-1.40666000
O	-0.36197000	-0.09362500	-1.46360400
C	-2.62305300	-4.25994900	-0.65825300
N	-2.57561800	-5.37803100	-0.35820300
C	-0.19363400	-2.83439500	-1.13252100
N	0.83317600	-3.36838000	-1.09562100
Cl	-5.42802600	-0.00427400	-1.61542600
Cl	-2.66440500	1.57998600	-1.97258100
H	1.46284800	-3.17696100	1.69068600
N	1.17828700	-2.21169600	1.56788800

Enamine-DDQ HTO TS *ap* conformer

0 1

C	2.27450600	-0.87511500	-2.80387000
C	0.97015400	-1.24364700	-2.74859700
C	0.13085900	-0.68690100	-1.74794200
C	0.59125000	0.25040000	-0.78936200
C	1.95204600	0.72839100	-0.94259600
C	2.79175700	0.12839500	-1.93142100
H	2.94670100	-1.34043600	-3.51974400
H	0.56958400	-2.00348200	-3.41321600
C	-2.08714300	-0.73014900	-0.78358900
C	-0.24724100	1.91486200	1.00534300
C	-0.68931100	3.18470300	0.48582600
C	-0.45889900	4.14615700	1.50384900
C	-1.26082000	3.64395200	-0.71192700
C	-0.76387400	5.50260100	1.35628100
C	-1.57113700	4.97852600	-0.87696700
C	-1.31920800	5.90095100	0.15581800
H	-0.57310200	6.21146800	2.15548900
H	-2.01179200	5.31197000	-1.80934600

H	-1.57141200	6.94428300	-0.00116800
C	0.19102200	2.14536300	2.28119500
C	-2.69513500	0.39301600	1.35407700
H	-3.44068800	1.11675300	0.99990800
H	-2.15391300	0.89275000	2.16256700
N	0.08068200	3.48045300	2.57770800
H	0.33092100	3.90356500	3.45795900
H	0.60053200	1.43656100	2.98901900
C	-3.46800200	-1.21728200	-1.02184300
C	-4.44986000	-0.29613500	-1.39279900
C	-3.78424400	-2.56871900	-0.86498100
C	-5.75991500	-0.72489400	-1.58247500
H	-4.17111500	0.74608100	-1.53216900
C	-5.09813900	-2.98756200	-1.05058500
H	-3.01067000	-3.26627100	-0.55335700
C	-6.08443100	-2.06811500	-1.40315600
H	-6.52632700	-0.01171200	-1.86977000
H	-5.35447100	-4.03220900	-0.90548300
H	-7.10894500	-2.39996600	-1.54121200
C	-3.38897900	-0.83892300	1.90205000
C	-4.77873500	-0.90676900	1.98256700
C	-2.62983700	-1.94167000	2.30410100
C	-5.40641500	-2.06351000	2.43834900
H	-5.37539300	-0.05961300	1.65268900
C	-3.25489300	-3.09864600	2.75699800
H	-1.54432100	-1.90423400	2.23322100
C	-4.64596100	-3.16466500	2.82134000
H	-6.49074800	-2.10748100	2.47934400
H	-2.65323800	-3.95329700	3.05105400
H	-5.13352200	-4.07124500	3.16667700
C	4.14323700	0.52170800	-2.07183400
C	2.54221000	1.75060600	-0.14965500
C	3.85726700	2.12027800	-0.31269400
H	4.26699300	2.89879000	0.32325500
C	4.67782200	1.50193400	-1.27478300
H	1.96204300	2.25339800	0.60643800
H	5.71848100	1.79026800	-1.37672700
H	4.75208300	0.01289900	-2.81339800
C	-0.32145400	0.57278200	0.33710600
H	0.17781100	-0.17548100	1.22220700
C	-1.71148800	0.07355100	0.24492800
Br	-1.63320900	2.44664900	-2.13464800
C	3.25016800	-0.85059600	1.61610500
C	4.33667800	-1.20520700	0.88513300
C	2.93165500	-2.78021300	-0.44046100
C	1.84303300	-2.41507000	0.32598600
C	4.24930100	-2.16239600	-0.25135600
O	5.20426400	-2.40492800	-0.96926600
C	1.93297100	-1.41533600	1.35670600
O	0.90374000	-1.02295300	1.99434800
C	2.79435500	-3.72751200	-1.50085400

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 N                  2.64392800   -4.46989500   -2.37750300
 C                  0.55607500   -3.01342100    0.11846100
 N                 -0.48834700   -3.47922500   -0.06584800
 Cl                 5.89867300   -0.56776700    1.18902200
 Cl                 3.34746700    0.30217400    2.89501500
 H                 -1.45959600   -1.76990800   -2.42343200
 N                 -1.16190200   -1.09881200   -1.72410700
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Pyridinium-salt-DDQ *sp* conformer

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0 1
 C                 -2.65057700   -2.18413500    2.14106800
 C                 -1.38672100   -2.64776300    1.99233700
 C                 -0.36047300   -1.72698500    1.64571000
 C                 -0.56215500   -0.33119100    1.53630900
 C                 -1.95214600    0.13116000    1.57951900
 C                 -2.97079000   -0.80802300    1.90515200
 H                 -3.45951400   -2.87531300    2.36144200
 H                 -1.15672200   -3.70634800    2.06631100
 C                  1.98387600   -1.49320300    1.17392300
 C                  0.50390600    1.92237400    1.72242900
 C                  0.58570400    3.15353500    0.97083800
 C                  0.28222400    4.20701400    1.87146200
 C                  0.82976600    3.51545600   -0.36369700
 C                  0.23633600    5.55194000    1.49416400
 C                  0.78042700    4.83605000   -0.76145600
 C                  0.48593600    5.84896900    0.16874700
 H                  0.00314900    6.32806900    2.21561600
 H                  0.97529900    5.08691100   -1.79766500
 H                  0.45456800    6.87913000   -0.16899300
 C                  0.16736900    2.28255500    3.00288100
 C                  3.09043400    0.75387200    0.86203000
 H                  3.74001400    0.76326400    1.74529000
 H                  2.76959200    1.79016400    0.73085500
 N                  0.04141300    3.63904800    3.09843000
 H                 -0.19112700    4.14569900    3.93892400
 H                 -0.01714800    1.64272900    3.85456900
 C                  3.22264900   -2.29078800    1.00251800
 C                  4.36454300   -2.01598700    1.75914800
 C                  3.21993700   -3.36135900    0.10183200
 C                  5.50296200   -2.79675900    1.60361300
 H                  4.35766700   -1.20465100    2.48042500
 C                  4.36639000   -4.13461900   -0.05177200
 H                  2.33132200   -3.57391900   -0.48917100
 C                  5.50743300   -3.85220400    0.69370100
 H                  6.38677400   -2.58308400    2.19582800
 H                  4.36479900   -4.95658700   -0.75990700
 H                  6.40044200   -4.45644500    0.56976000
 C                  3.91576400    0.35173400   -0.35031200
 C                  5.26528900    0.70277800   -0.38600800
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C	3.36745000	-0.31901000	-1.44697100
C	6.05366900	0.40212200	-1.49313000
H	5.70546600	1.21686700	0.46584400
C	4.15475000	-0.62586900	-2.55274900
H	2.32167900	-0.62261800	-1.43613800
C	5.49916200	-0.26384300	-2.58197800
H	7.10213300	0.68399600	-1.50108200
H	3.71293800	-1.15354400	-3.39233300
H	6.11126200	-0.50511500	-3.44524700
C	-4.32950100	-0.42626600	1.90449900
C	-2.36824700	1.42778400	1.20034900
C	-3.70373400	1.77226600	1.18490900
H	-3.98766400	2.76188900	0.84109400
C	-4.69648500	0.85191300	1.55674200
H	-1.65031700	2.15436600	0.84845700
H	-5.74439400	1.12673700	1.50960400
H	-5.08187700	-1.18301500	2.10289900
C	0.60196100	0.47848600	1.37871300
H	-0.21688500	0.22607900	-1.74394400
C	1.86661600	-0.09806500	1.13436800
Br	1.29553500	2.20070600	-1.63408600
C	-2.66205400	-0.14248500	-1.71798400
C	-3.97593200	-0.48373700	-1.50128900
C	-3.29354900	-2.72578200	-0.87000900
C	-1.95349200	-2.35709600	-1.13929800
C	-4.38635700	-1.78831900	-0.95755500
O	-5.54434400	-2.02004000	-0.59366500
C	-1.60960500	-1.06553500	-1.50394800
O	-0.29012300	-0.73440700	-1.61275700
C	-3.55111100	-4.00075700	-0.29087700
N	-3.70165900	-5.01909700	0.24672300
C	-0.88730200	-3.29140100	-0.93695800
N	-0.00919300	-4.01743500	-0.71947000
Cl	-5.24801500	0.64460000	-1.78756900
Cl	-2.20730900	1.46168400	-2.23521400
H	0.98512700	-3.23233200	1.43395800
N	0.88800700	-2.21706600	1.44853100

Pyridinium-salt-DDQ *ap* conformer

0 1

C	2.54356400	-1.07353600	-2.50222100
C	1.31492800	-1.64673300	-2.50131400
C	0.26512800	-0.99164100	-1.80660600
C	0.41072400	0.26294700	-1.16250900
C	1.68573900	0.95665600	-1.35997000
C	2.75528200	0.23323500	-1.95524000
H	3.40241900	-1.60395200	-2.90885600
H	1.15841000	-2.64237900	-2.90651900
C	-1.98786800	-1.20747000	-1.01630900

C	-0.54398300	1.88614500	0.52617600
C	-1.22985700	3.14877100	0.42571900
C	-0.75018900	3.96021800	1.48544400
C	-2.18530500	3.71017300	-0.43551900
C	-1.19668300	5.26664500	1.70322600
C	-2.64273700	4.99660800	-0.23508700
C	-2.14676300	5.76737100	0.83314800
H	-0.81037900	5.86261700	2.52351200
H	-3.38308000	5.41127900	-0.90937000
H	-2.52033500	6.77676800	0.96759600
C	0.28880700	1.97426300	1.61220000
C	-3.00094800	0.33371400	0.67349400
H	-3.89248700	0.60825200	0.10046500
H	-2.71566200	1.22335900	1.23912800
N	0.17061000	3.21219400	2.17952100
H	0.67134800	3.51478000	3.00157300
H	0.96098700	1.22912200	2.01728300
C	-3.20494000	-2.04854300	-1.06529100
C	-4.37815000	-1.51570800	-1.60510200
C	-3.17978200	-3.34556500	-0.54684500
C	-5.53576500	-2.28503500	-1.62160500
H	-4.37277100	-0.50545800	-2.00807600
C	-4.34782700	-4.10242700	-0.55780100
H	-2.26729900	-3.72476500	-0.09191700
C	-5.52113000	-3.57461400	-1.09156800
H	-6.44862200	-1.87920500	-2.04561400
H	-4.34192400	-5.10241300	-0.13660800
H	-6.42909400	-4.16950300	-1.09511000
C	-3.32356000	-0.80162300	1.62560300
C	-4.63712000	-1.22491100	1.82283200
C	-2.28982400	-1.47394000	2.28038300
C	-4.91286600	-2.31221100	2.64754800
H	-5.44595100	-0.71888000	1.30132900
C	-2.56020500	-2.56518700	3.09919700
H	-1.26300300	-1.15552700	2.11170800
C	-3.87459000	-2.98935200	3.28224000
H	-5.93927600	-2.64043700	2.78072000
H	-1.74427800	-3.09562000	3.58081600
H	-4.08713000	-3.84671400	3.91308400
C	4.04335200	0.80210600	-2.05211200
C	1.92689700	2.31237300	-1.03623300
C	3.18232600	2.86515400	-1.18474200
H	3.33130700	3.90943600	-0.92884500
C	4.26248400	2.09901700	-1.65068400
H	1.12266300	2.94663900	-0.69404600
H	5.25692400	2.52863700	-1.70747300
H	4.85586900	0.17621600	-2.41259100
C	-0.66939900	0.69622000	-0.34057400
H	0.92977200	-1.55206200	2.63803800
C	-1.87008200	-0.03392600	-0.27050600
Br	-2.85549300	2.71478500	-1.90399500

C	3.70523100	-0.43437700	1.56759800
C	4.71461200	-0.75874100	0.68794500
C	3.41787800	-2.63837500	-0.13808700
C	2.38230400	-2.26199300	0.74867800
C	4.60711300	-1.84257200	-0.29923000
O	5.43510400	-2.00668300	-1.20653000
C	2.50924800	-1.18395800	1.60935200
O	1.51496500	-0.79648600	2.47115600
C	3.18461000	-3.70107100	-1.05482600
N	2.91963900	-4.53308300	-1.82050800
C	1.10475700	-2.90812900	0.71739700
N	0.02871900	-3.34363700	0.71254200
Cl	6.17015900	0.16146200	0.62906500
Cl	3.83636200	0.91971700	2.65004900
H	-1.01071200	-2.53841200	-2.17644000
N	-0.93029800	-1.63316400	-1.71799800