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Supporting Information

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Chiara Portolani,[§,†] Giovanni Centonze,[§,†] Sara Luciani,[§] Andrea Pellegrini,[§,†] Paolo Righi,[§,†] Andrea Mazzanti,[§,†] Alessia Ciogli,[#] Andrea Sorato[#] and Giorgio Bencivenni[*,§,†]

[§]Department of Industrial Chemistry "Toso Montanari", University of Bologna, viale del Risorgimento 4, 40136, Bologna – Italy.

[†]Center for Chemical Catalysis – C^3, University of Bologna, Viale del Risorgimento 4, 40136, Bologna — Italy.

[#]Department of Chemistry and technologies of drug, Nuovo Edificio di Chimica, NEC- CU032, 3rd floor, room N° 1 Sapienza University of Rome piazzale A. Moro 5, 00185 Rome – Italy.

Contents

General

All the NMR spectra were recorded on Inova 300 MHz, Gemini 400 MHz or Mercury 600 MHz Varian spectrometers for ^{1}H, 101 MHz for ^{13}C. The chemical shifts (δ) for ^{1}H, ^{13}C are given in ppm relative to internal standard TMS (0.0 ppm) or residual signals of $CHCl_3$ (7.26 ppm). The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; bs, broad signal. Purification of reaction products was carried out by flash chromatography (FC) on silica gel (230-400 mesh). Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. X-ray data were acquired on a Bruker APEX-2 diffractometer. High Resolution Mass spectra were obtained from the Mass Facility of the Department of Chemistry and Drug Technology of the University of Rome on a Orbitrap Exactive, source: ESI (+): capillary temp: 250°C, spray voltage: 4.0 (kV), capillary voltage: 65 V, tube lens: 125 V. HPLC analysis on chiral stationary phase was performed on an Agilent 1100-series instrumentation. HPLC chromatograms of enantioenriched products were compared to racemic ones obtained with achiral catalysts. Optical rotations have not been determined since a mixture of diastereoisomers has been obtained in all cases. Infrared (ATR) spectra were recorded on a Perkin Elmer Spectrum Two FT-IR spectrometer equipped with an ATR probe. Signals are reported as strong (s), medium (m), and weak (w). Melting points (uncorrected) were determined with a Stuart Scientific SMP3 apparatus. All reactions were carried out in air; all evaporations were performed without heating to avoid rotation of the chiral axis. Starting materials **1a**, **2a-b**, **4a**, **4e-h**, **4j**, **4k**, **4l**, **a** and chiral catalyst **D** were purchased from suppliers. Aldehydes **1b-j**[1] and electrophiles **4b**,[2] **4c**,[2] **4d**,[2] **4i**,[2] **4m**,[2] **b**,[3] that are all commercially available, were prepared following literature procedures and their ^{1}H-NMR spectra were consistent with those previously reported. Primary amine catalysts **A** and ***ent*-A**,[4] and phase-transfer catalysts **B**-**Q**[5] were obtained following the reported literature procedures. Catalyst **G** was prepared following the described procedure[6] and ^{1}H-NMR spectrum was consistent with literature. The off-column HPLC experiments were made to determine the energy barrier of N-N rotation. The pure **5a** (peak 4) or **5a'** (peak 1) were dissolved in decalin and heated in oven at 88 °C. The diastereomerization process has been studied over time by HPLC on chiral stationary phase. Analytical conditions: Chiralpak IC 5μm

[1] T. Baumann, H. Vogt, S. Bräse, *Eur. J. Org. Chem.,* **2007**, 266 – 282.
[2] E. Doni, B. Mondal, S. O'Sullivan, T. Tuttle, J. A. Murphy *J. Am. Chem. Soc.* **2013**, *135*, 10934 – 10937.
[3] a) A. Varela, L. K. B. Garve, D. Leonori, V. K. Aggarwal, *Angew. Chem. Int. Ed.* **2017**, *56*, 2127 – 2131. b) X. H. Yang, J. P. Li, D. C. Wang, M. S. Xie, G. R. Qu, H. M. Guo *Chem. Commun.* **2019,** *55*, 9144 – 9147.
[4] C. Cassani, R. Martín-Rapún, E. Arceo, F. Bravo, P. Melchiorre *Nat. Protoc.* **2013**, *8*, 325 – 344.
[5] a) S.-S. Jew, M.-S. Yoo, B.-S. Jeong, I.-Y. Park, H.-G. Park *Org. Lett.* **2002**, *4*, 4245. b) M. Lian, Z. Li, J. Du, Q. Meng, Z. Gao, *Eur. J. Org. Chem*. **2010**, 6525 – 653. c) For catalysts P and Q: Chinchilla, R., Mazón, P., Nájera, C., & Ortega, F. J. *Tetrahedron Asymmetry.* **2004**, *15*, 2603 – 2607.
[6] Y.-C. Chan, X. Wang, Y.-P. Lam, J. Wong, Y.-L. S. Tse, Y.-Y. Yeung *J. Am. Chem. Soc.* **2021**, *143*, 12745 – 12754.

(150x4.6mm); Flow rate: 1.00 mL/min; Eluent: 98/2 hexane/i-PrOH, UV 267 nm (corresponding to an isosbestic point).

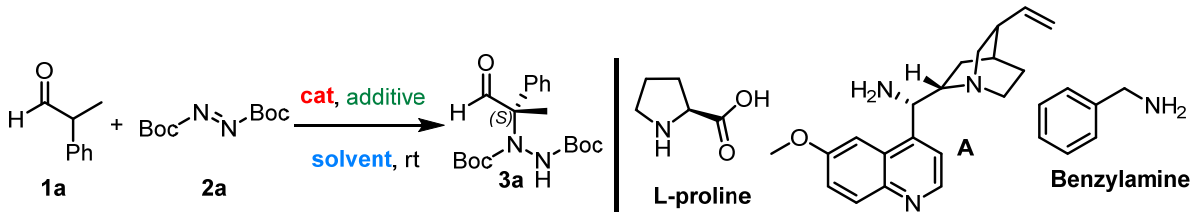
Optimization of the reaction conditions

The two steps were first studied separately. 2-Phenyl-propionaldehyde **1a**, di-*tert*-butyl azodicarboxylate **2a** and benzyl bromide **4a** were used as reagents for the optimization of the reaction conditions.

First step

L-Proline catalysis was first tested for the amination reaction following Bräse's procedure[1] (Table S1, entry 1); better results were obtained exploiting an amino quinine catalysis using the protocol reported by Greck,[7] with 9-epi-deoxy-amino-quinine (**A**) as catalyst, TFA as additive and chloroform as solvent (entry 2). The racemic product was obtained using benzylamine as catalyst (entry 3).

Table S1 – First step optimization.



Entry	Cat (mol%)	Additive	Solvent (M)	Yield[c] (time)	e.e.[d]
1[a]	**L-Proline** (50 mol%)	-	CH_2Cl_2 (0.1M)	61% (5 days)	88% (*R*)
2[b]	**A** (5 mol%)	TFA	$CHCl_3$ (0.6M)	90% (6 h)	94% (*S*)
3[b]	**$BnNH_2$** (10 mol%)	TFA	$CHCl_3$ (0.6M)	90% (1 day)	rac

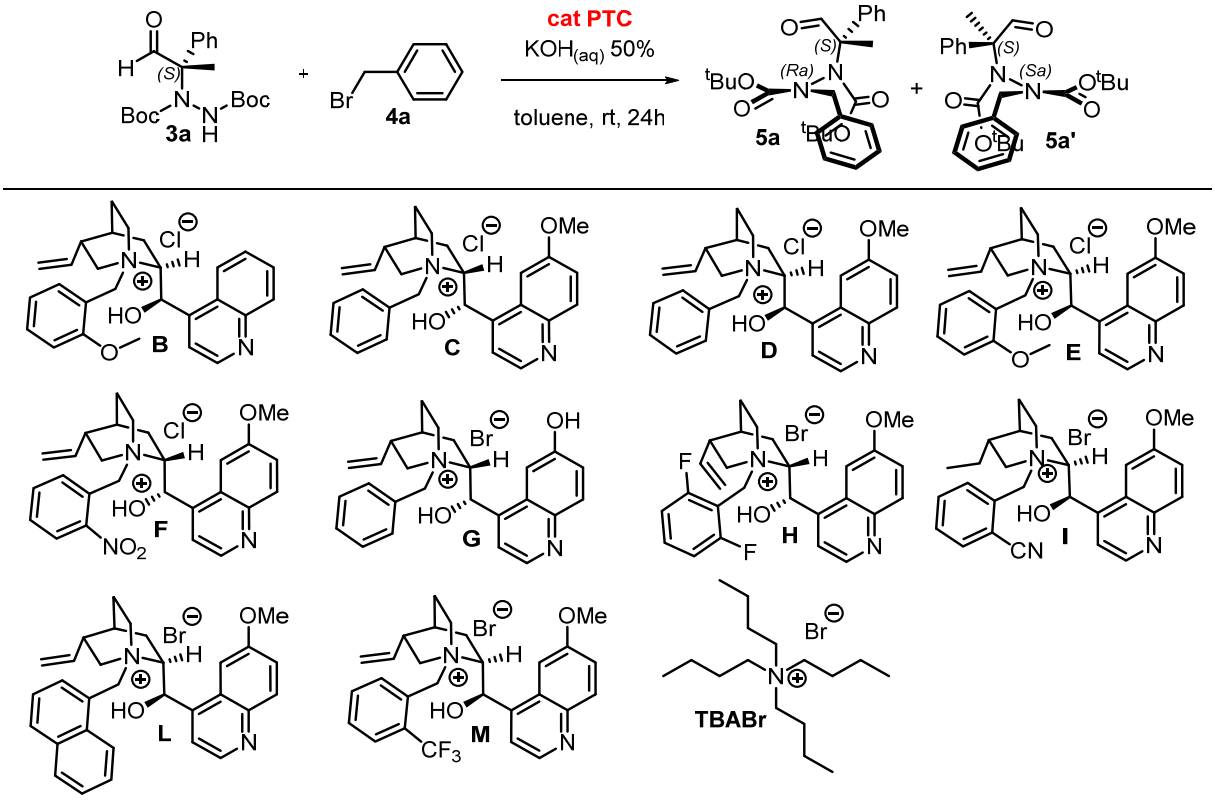
[a]The reaction was performed with 1 mmol of **1a**, 1.5 eq of **2a**, 50 mol% of catalyst in 10 mL of solvent. [b]The reaction was performed using 3 mmol of **2a**, 1.2 eq of **1a**, 5 mol% of catalyst, 0.15 eq of TFA and 6 mL of solvent. [c]Isolated yield. [d]Determined by HPLC using chiral stationary phase; absolute configuration known from literature.

[7] A. Desmarchelier, H. Yalgin, V. Coeffard, X. Moreau, C. Greck, *Tetrahedron Lett.* **2011**, *52*, 4430-4432.

Second step

Alkylation of the trisubstituted hydrazide **3a** (94% ee) was attempted exploiting a phase transfer catalysis using benzyl bromide **4a** with 10% mol of PTC catalyst, an aqueous solution of KOH (50% w/w) and toluene 0.05 M, as described in many PTC procedures[8].

Table S2 – Screening of PTC catalysts.[a]



Entry	Cat	Yield[b]	d.r.(5a:5a')[c]	e.e. (major)[c]
1	**B**	63%	1:3.4	98%
2	**C**	61%	6:1	98%
3	**D**	60%	1:6.3	99%
4	**E**	60%	1:4.5	99%
5	**F**	42%	3:1	97%
6	**G**	70%	2.6:1	90%

[8] a) K. Maruoka, T. Ooi *Chem. Rev*. **2003**, *103*, 3013–3028. b) K. Maruoka *Org. Process. Res. Dev*. **2006**, *12*, 679-697. c) S. S. Jew, H. G. Park, *Chem. Commun.* **2009**, *46*, 7090-7103.

7	**H**	42%	1.6:1	96%
8	**I**	18%	1:2.5	97%
9	**L**	38%	1:3.6	80%
10	**M**	21%	1:2.3	98%
11	**TBABr**	63%	1:1	94%[d]

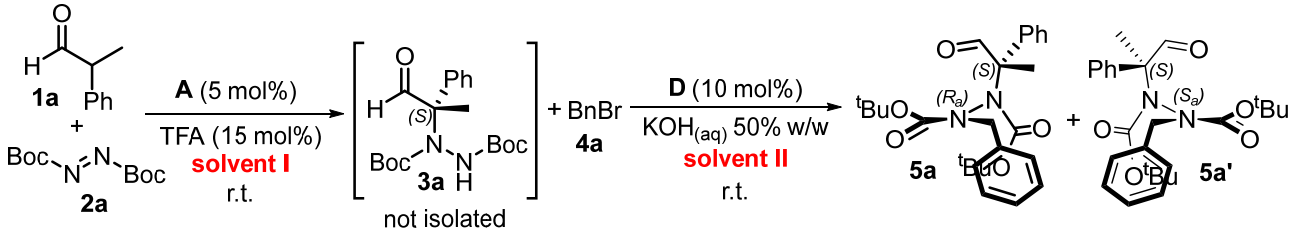
[a]The reactions were performed using 0.1 mmol of **3a**, 1.0 eq of **4a**, 10% mol of catalyst, 4 mL of an aqueous solution of KOH (50% w/w) and 2 mL of toluene. [b]Isolated yield as mixture of diastereoisomers. [c]Determined by HPLC using chiral stationary phase. [d]The ee% of the minor diastereoisomer is 94.

Quinidinium and quininium chloride **C** and **D** gave the best results, showing a similar behavior in terms of yield and atroposelectivity (with opposite d.r.); further tests were carried out using commercially available catalyst **D**.

One-pot Sequential Reaction

The two steps were carried out in sequence, without the isolation and purification of the intermediate. A first attempt was carried out directly adding the reagents for the second step to the flask, after the amination step was completed (Table S3- entry 1), but modest results were obtained. Evaporating chloroform before adding toluene led to the formation of **5a** + **5a'** with a yield and d.r. that are perfectly consistent with those obtained when the second step was performed separately, starting from **3a** (Table S3 - entry 2 vs Table S2 - entry 3); this suggests that the different conditions of the two steps are compatible when put together, except for the solvent: when traces of chloroform are present, lower yield and stereoselectivity are obtained. This was confirmed when, trying to use a common solvent for both steps, the whole reaction was run in chloroform (Table S3- entry 3). Promising results were obtained using 0.6 M toluene for the first step (entry 4) since it afforded the isolated trisubstituted hydrazide **3a** in 96% yield and 94% ee. In this case however it is necessary to change the reaction flask when switching from the first to the second step, as a higher volume is necessary. To bypass the problem, the first step was diluted to 0.1 M, surprisingly enhancing the enantioselectivity of the amination to 98%, with a 80% yield on **3a** obtained using 1,1 eq of **2a**; on the other hand, concentrating the second step to 0.1 M led to a lower d.r. (entry 5). Hence solvent concentrations were set as reported in entry 6.

Table S3 – Optimization of one-pot conditions.[a]

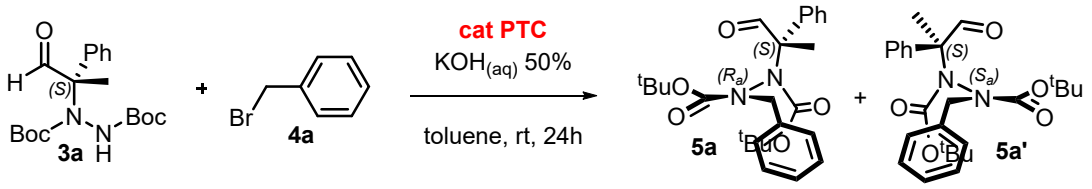


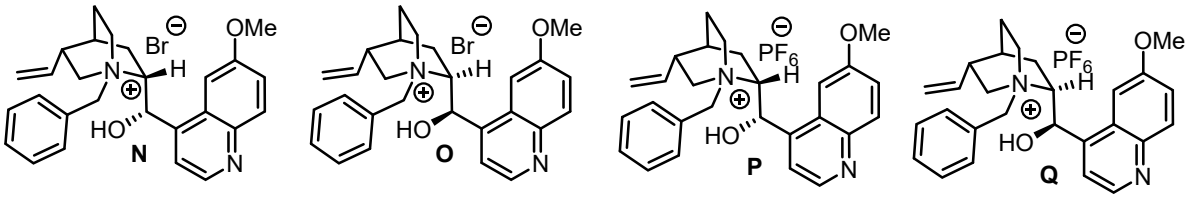
Entry	Solvent I	Solvent II	Yield[e]	d.r. (5a:5a')[f]	e.e. (major)[f]
1	$CHCl_3$ (0.6M)	Toluene (0.05M)	53%	1:5.4	97%
2[b]	$CHCl_3$ (0.6M)	Toluene (0.05M)	65%	1:6.2	99%
3	$CHCl_3$ (0.6M)	$CHCl_3$ (0.05M)	35%	1:1.2	96%
4[c]	Toluene (0.6M)	Toluene (0.05M)	60%	1:6.5	97%
5[d]	Toluene (0.1M)	Toluene (0.1M)	62%	1:5.5	98%
6[d]	Toluene (0.1M)	Toluene (0.05M)	65%	1:6.5	99%

[a]The reactions were performed using 0.1 mmol **1a**, 1.0 eq of **2a**, 5 mol% of catalyst **A**, 0.15 eq of TFA and solvent **I**; after 24 h, 1.0 eq of **4a** was added together with 10 mol% of catalyst **D**, 4 mL of an aqueous solutions of KOH (50% w/w) and solvent **II**. [b]The solution was concentrated before adding the reagents for the second step. [c]Intermediate **3a** was isolated with a yield of 96% and 94% ee. [d]First step conducted with 1.1 eq of **2a**; intermediate **3a** was isolated with a yield of 80% and 98% ee. [e]Isolated yield as mixture of diastereoisomers. [f]Determined by HPLC using chiral stationary phase.

Final optimization

Table S4 – Counterion screening.[a]





Entry	Catalyst	Yield[b]	d.r. (5a:5a')[c]	e.e. (major)[c]
1	**N**	80%	9:1	99%
2	**O**	49%	1:6	>99%
3	**P**	53%	7.5:1	98%
4	**Q**	50%	1:6	99%

[a]The reactions were performed using 0.1 mmol of **3a**, 1.0 eq of **4a**, 10% mol of catalyst, 4 mL of an aqueous solution of KOH (50% w/w) and 2 mL of toluene. [b]Isolated yield as mixture of diastereoisomers. [c]Determined by HPLC using chiral stationary phase.

Br^- and $PF6^-$ quininium and quinidinium catalysts were investigated instead of the chlorine correspondent **C** and **D**, obtaining equal to better results. Differences between quinine and quinidine scaffold were found in this case, leading to the choice of **N** as catalyst.

Table S5 – Screening of temperature.[a]

Entry	Cat	T (°C)	Yield[b]	d.r. (5a:5a')[c]	e.e. (major)[c]
1	**N**	0	64%	11:1	99%
2	**N**	-5	81%	13:1	98%
3	**N**	-20	63%	13:1	98%

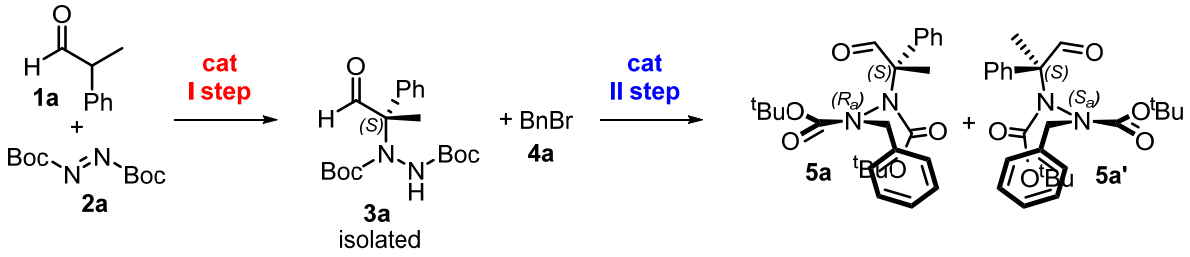
[a]The reactions were performed using 0.1 mmol of **3a**, 1.0 eq of **4a**, 10% mol of catalyst, 4 mL of an aqueous solution of KOH (50% w/w) and 2 mL of toluene. [b]Isolated yield as mixture of diastereoisomers. [c] Determined by HPLC using chiral stationary phase.

Role of the catalyst in the control of stereoselectivity

Tests with different catalyst combinations

Some tests were carried out to verify how the stereoselectivity is controlled, expecially in the second step, and if the substrate has any role in that. Different combinations of achiral catalysts **$BnNH_2$** and **TBABr**, and chiral ones **A** and **D** were used (Table S6).

Table S6 – Tests with different combination of racemic or chiral catalysts.[a]



Entry	Cat I step	e.e. (3a)	Cat II step	d.r. (5a:5a')[b]	e.e. (5a)[b]	e.e. (5a')[b]
1	**$BnNH_2$**	0%	**TBABr**	1:1	0%	0%
2	**$BnNH_2$**	0%	**D**	1:1	75%	77%
3	**A**	94%	**TBABr**	1:1	94%	94%
4	**A**	94%	**D**	1:6.3	73%	99%

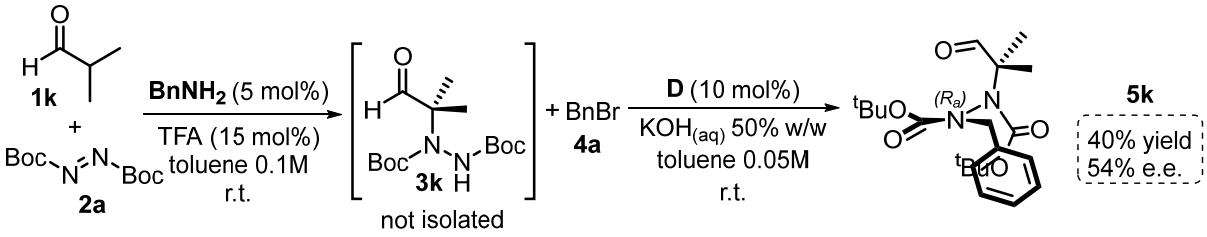
[a]The first step was performed using 0.1 mmol **1a**, 1.0 eq of **2a**, 5 mol% of catalyst, 0.15 eq of TFA and toluene 0.1M; after 24 h, the reaction was stopped and **3a** isolated by column chromatography. The second step was performed using 0.1 mmol of **3a**, 1.0 eq of **4a**, 10% mol of catalyst, 4 mL of an aqueous solution of KOH (50% w/w) and 2 mL of toluene. [b]Determined by HPLC using chiral stationary phase.

When catalyst **D** was used in the second step starting from racemic **3a** (entry 2), a 1:1 d.r was obtained, with both diastereoisomers having the same enantiomeric excess (small differences – 75%/77% - are due to imprecisions during HPLC peaks integration, as the first three peaks can not be perfectly separated). This result shows how catalyst **D** is able to control the formation of a specific axis configuration in the same way starting from (*R*)-**3a** and (*S*)-**3a**, independently by the chiral center.

When **TBABr** was employed for the alkylation of **3a** (94% e.e.), a 1:1 mixture of diastereoisomers was obtained (entry 3). This test confirmed that the stereogenic center on the trisubstituted hydrazide does not influence the choice of the chiral axis. Finally, using the two chiral catalysts (entry 4), a 1:6,3 d.r. was obtained, with a significant increase of the e.e. of the major diastereoisomer.

Synthesis of 5k

To better clarify this aspect, the enantioselective synthesis of **11** was carried out; the only stereogenic element in this case is the N-N axis, and catalyst **D** gave a 54% e.e., using the same reaction conditions as for the synthesis of **5a**. With no other stereogenic elements that could interfere, this result demonstrates that the catalyst is the only responsible of the stereoselectivity.



(R_a)-di-*tert*-butyl 1-benzyl-2-(2-methyl-1-oxopropan-2-yl)hydrazine-1,2-dicarboxylate (5k)

The reaction was performed starting from 0.3 mmol of **1k**. The crude mixture was purified by flash column chromatography (hexane:Et_2O = 8:2).

Yield= 40% (47 mg).

The e.e. was determined by HPLC analysis on a Daicel Chiralpak IC column: hexane/*i*-PrOH 98/2, flow rate 1 mL/min, 25 °C, λ = 220 nm: t_1= 11 min, t_2= 12 min.

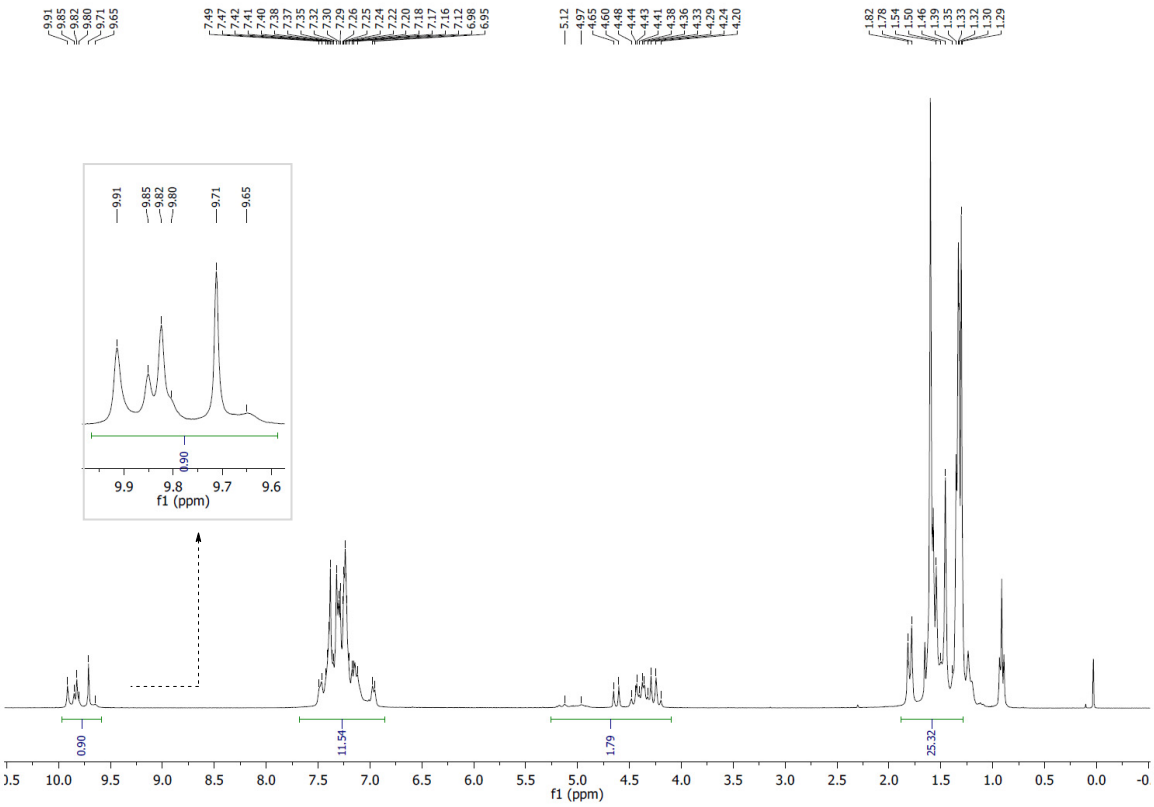
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.64 – 9.25 (m, 1H), 7.34 (m, 5H), 5.18 – 4.14 (m, 2H), 1.56 – 1.49 (m, 9H), 1.43 (s, 3H), 1.34 (s, 9H), 1.05 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 201.09, 200.26, 200.17, 199.31, 156.90, 156.43, 155.70, 155.50, 154.70, 153.98, 153.06, 152.68, 136.61, 136.47, 136.39, 136.34, 130.38, 130.28, 129.96, 129.89, 128.50, 128.46, 128.43, 128.32, 128.03, 83.37, 82.11, 82.07, 82.00, 81.98, 81.91, 67.18, 67.12, 66.83, 66.69, 56.39, 55.59, 54.97, 54.64, 53.40, 30.30, 29.67, 28.32, 28.28, 28.25, 28.10, 28.07, 27.99, 27.97, 26.36, 21.33, 21.24, 21.11, 20.95, 20.77, 20.23, 20.07.

Elucidations on ^{1}H NMR spectra

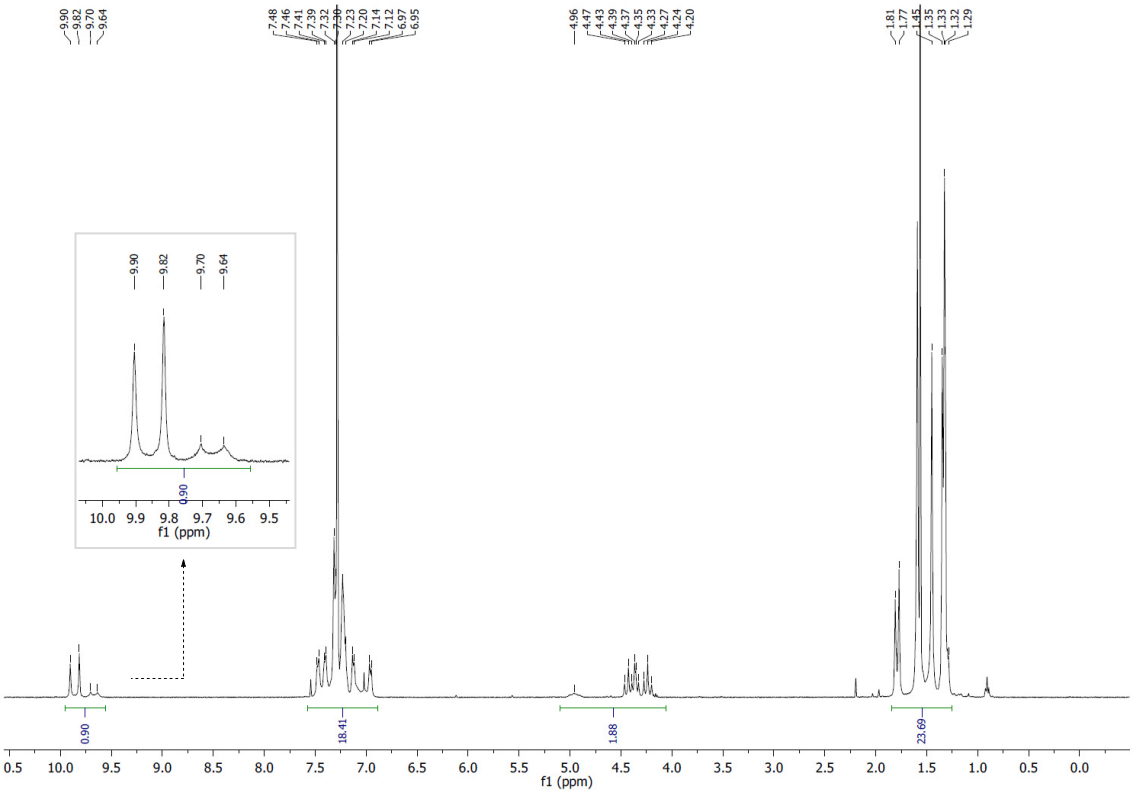
A certain complexity of ^{1}H NMR spectra was found for every pure product: beyond the peaks of the two diastereoisomers and those correspondent to diastereotopic protons, other peaks appear in every spectrum. We attributed this phenomenon to different conformations arising from the rotation of the amidic single bonds of NBoc groups. This behavior has been well described by Rinaldi on tetrasubstituted hydrazides.[9] We indeed calculated a $\Delta G^{\ddagger}_{rot}$ of 18 kcal/mol for NBoc groups on **5a**, a value making new visible rotamers for the NMR acquisition times. A representative peak of the ^{1}H NMR spectrum is the proton of the aldehyde at around 9-10 ppm: it corresponds to a single proton that does not have any coupling and it is not diastereotopic. For these reasons more than two diastereomeric peaks are present in each case, and it is not possible to calculate the d.r. Some examples are reported to clarify the problem, highlighting the 9-10 ppm area in each case. Remarkably, also the ^{1}H NMR of product **5k**, that is a mixture of enantiomers, shows the presence of at least four conformations due to the NBoc groups rotamers (Spectrum 5).

Spectrum 1 - ^{1}H NMR of racemic **5a+5a'**.

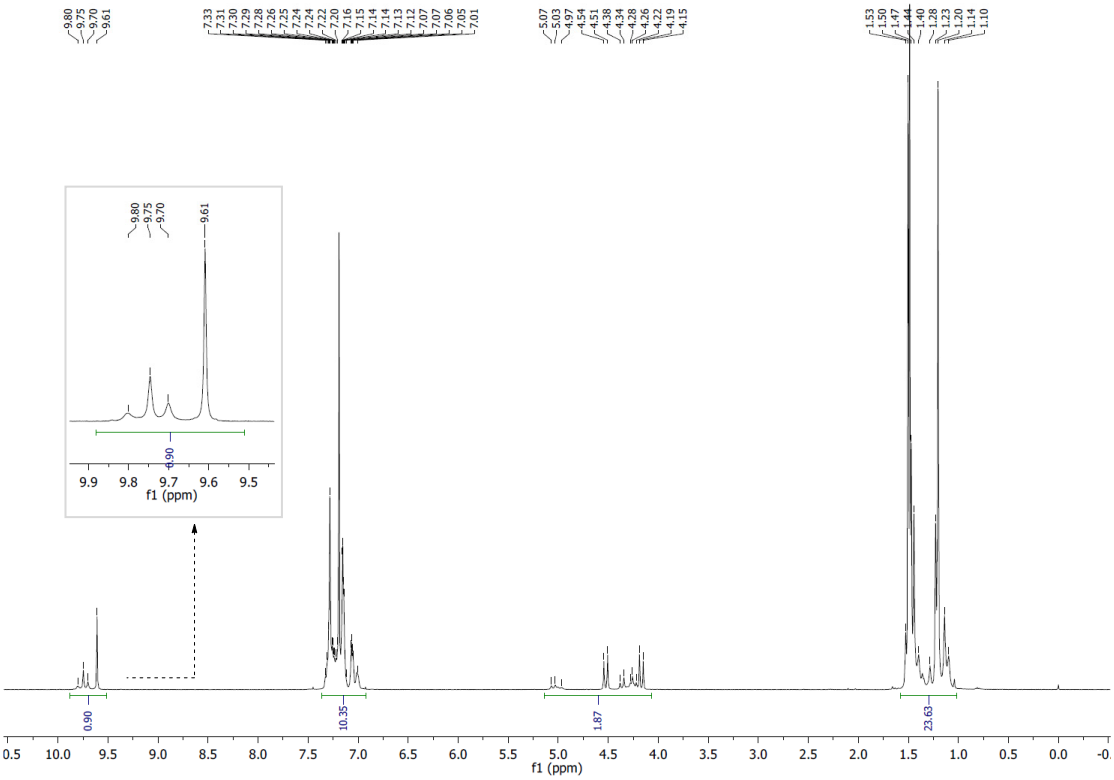


[9] P. Amabili, A. Amici, G. Campisi, G. Guerra, M. Monari, M. Orena, F. Piccinelli, S. Rinaldi, A. Tolomelli *Eur. J. Org. Chem*. **2018**, 6524.

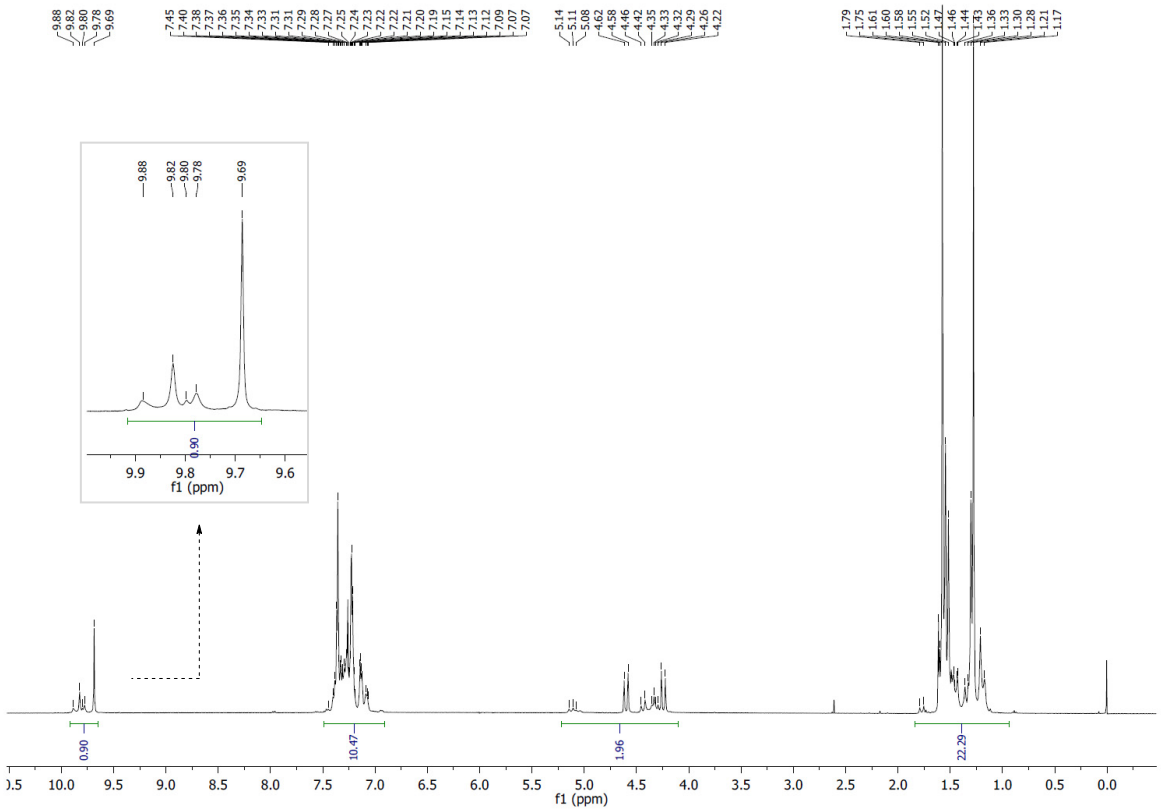
Spectrum 2 - ^{1}H NMR of pure **5a'** (*S*,*S*$_a$).



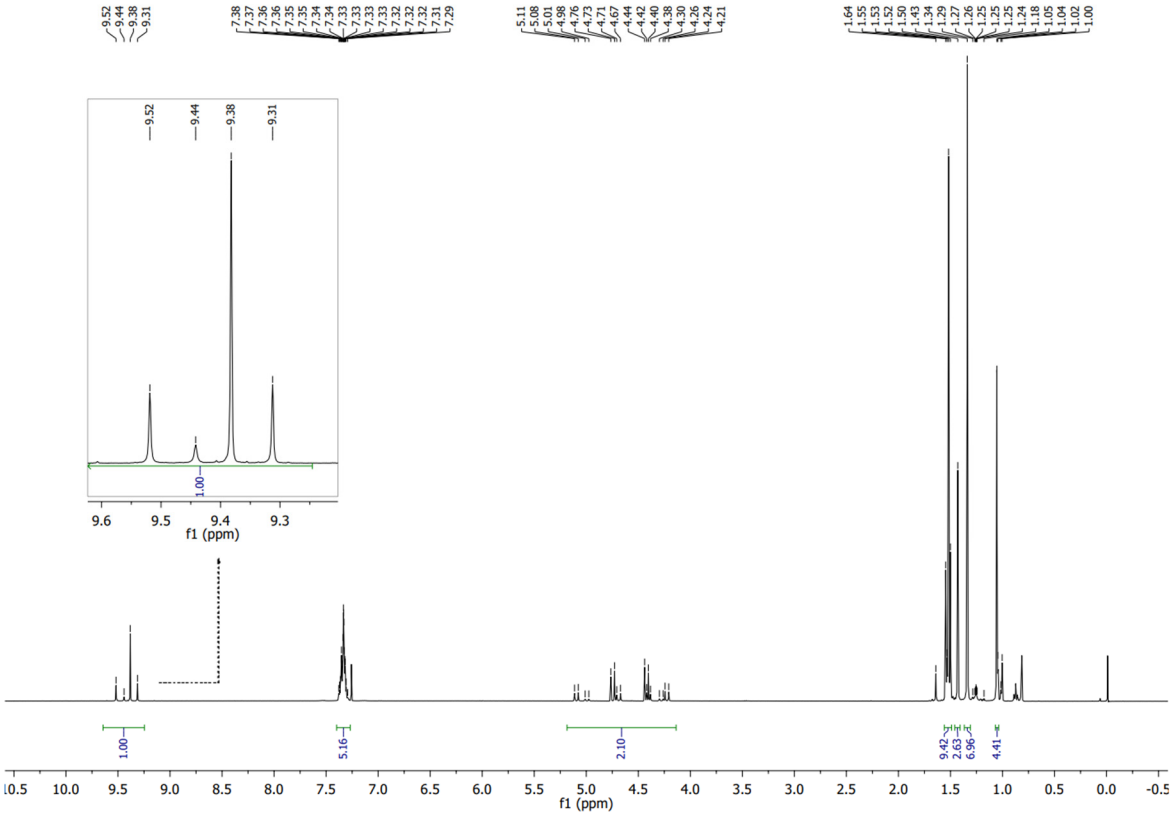
Spectrum 3 - ^{1}H NMR of pure **5a** (*S*,*R*$_a$).



Spectrum 4 - ^{1}H NMR of product mixture **5a:5a'** with a 13:1 d.r.

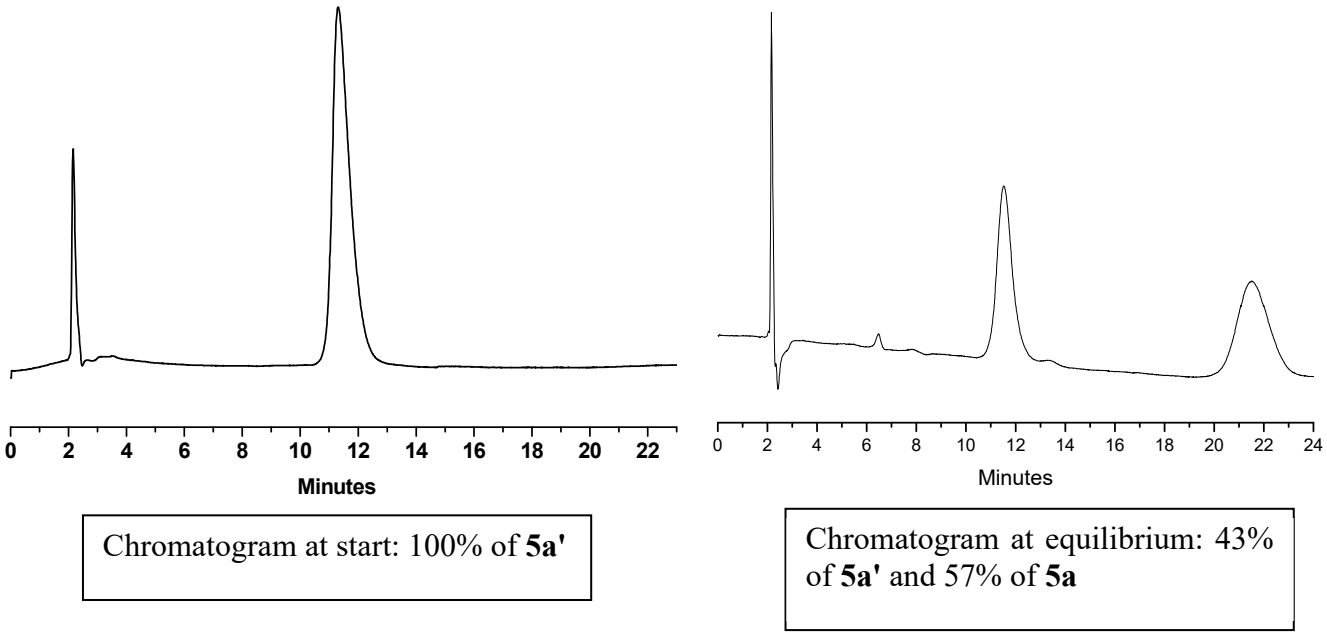


Spectrum 5 - ^{1}H NMR of product **5k** (racemic mixture).



Determination of the rotational energy barrier

The pure **5a'** (peak 1) or **5a** (peak 4) were dissolved in decalin in a close vial and heated in oven at 88 °C. The diastereomerization process has been studied over time by HPLC on chiral stationary phase. Analytical conditions: Chiralpak IC 5µm (150x4.6mm); Flow rate: 1.00 mL/min; Eluent: 98/2 hexane/i-PrOH, UV 267 nm (corresponding to an isosbestic point) (Figure S1). Column temperature: 25 °C. From equations, rate constants were 0.0028 min^{-1} for the interconversion of **5a'** to **5a** (Figure S2) and 0.0033 min^{-1} for the interconversion of **5a** to **5a'** (Figure S3).



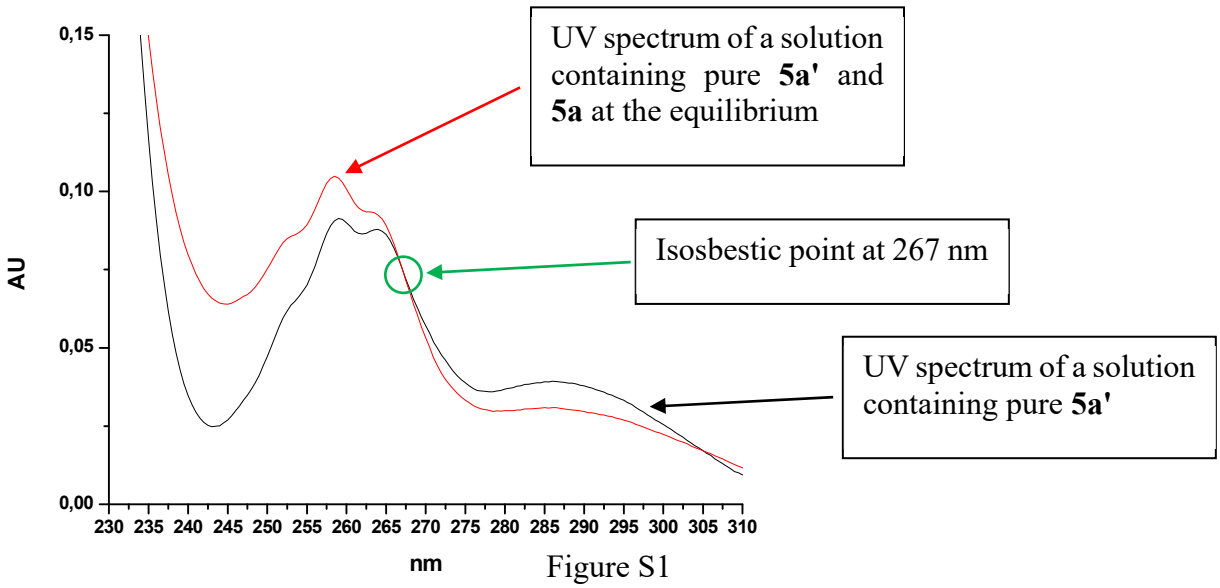
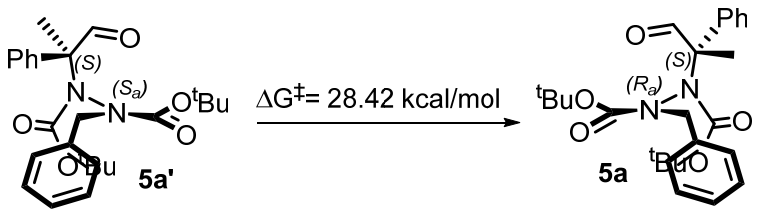
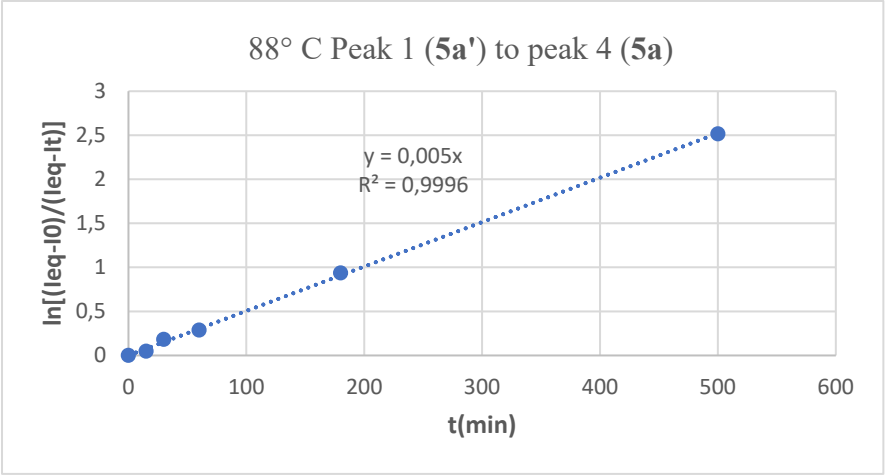


Figure S1

Peak 1 (5a') to peak 4 (5a)



Temp.(°C)	K_{eq}	$k+k_{-1}$(min^{-1})	k(min^{-1})	k_{-1}	$\Delta G_{1\text{-}4}$ (Kcal/mol)	$\Delta G_{1\text{-}4}$(KJ/mol)
88	1,31	0,0050	0,00284	0,00216	28,42	118,82



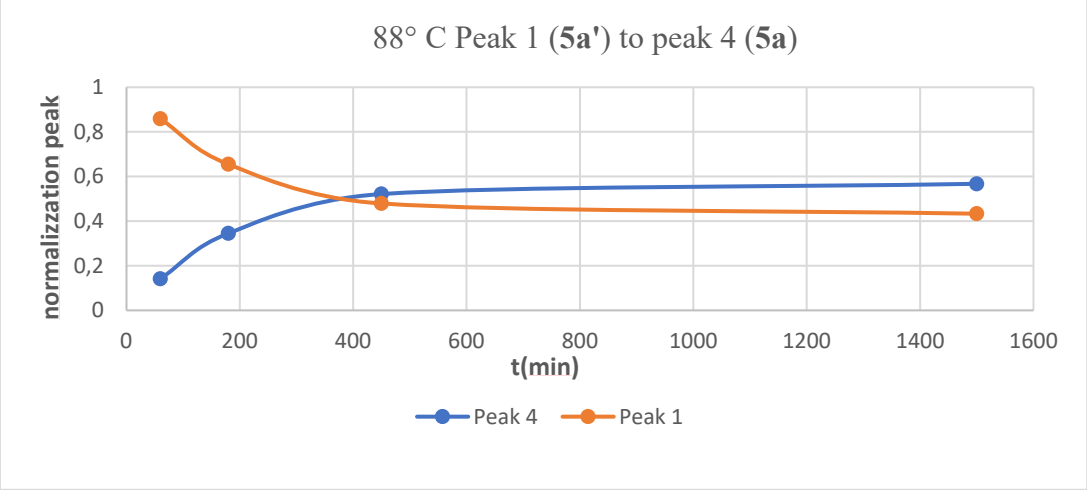
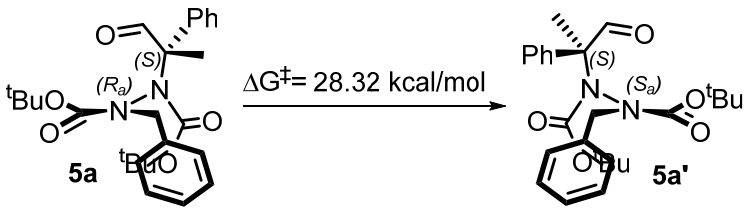
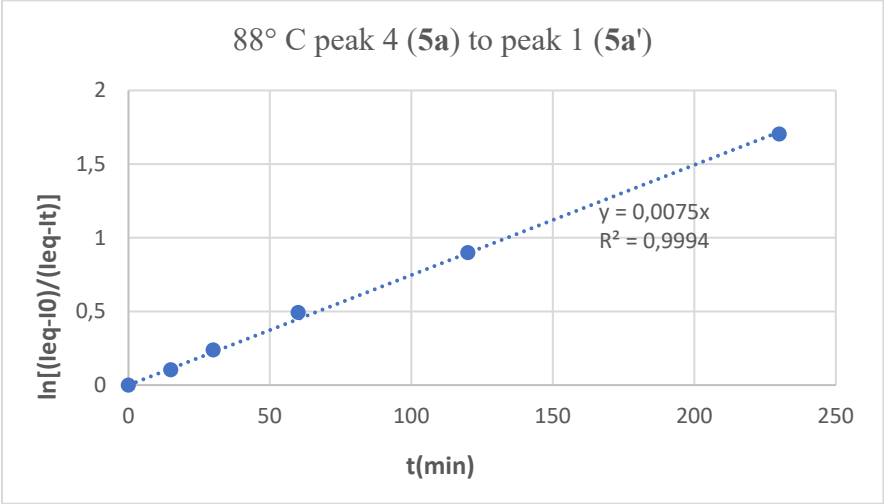


Figure S2: determination of the rotational energy barrier for the interconversion of **5a'** to **5a**.

Peak 4 (5a) to peak 1 (5a')



Temp. (°C)	K_{eq}	$k+k_{-1}$(min^{-1})	k (min^{-1})	k_{-1}	$\Delta G_{4\text{-}1}$(Kcal/mol)	$\Delta G_{4\text{-}1}$(KJ/mol)
88	0.78	0,0075	0,0033	0,0042	28,32	118,49



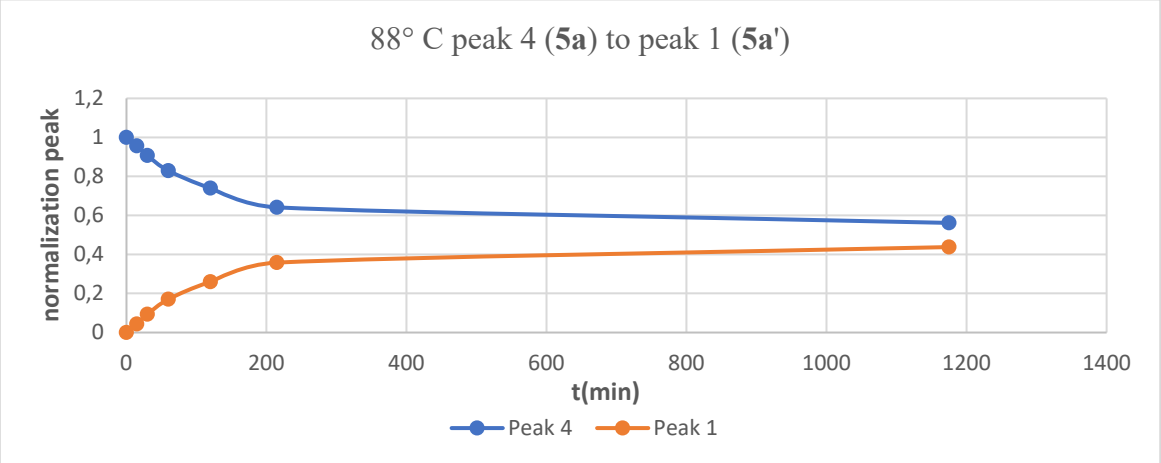
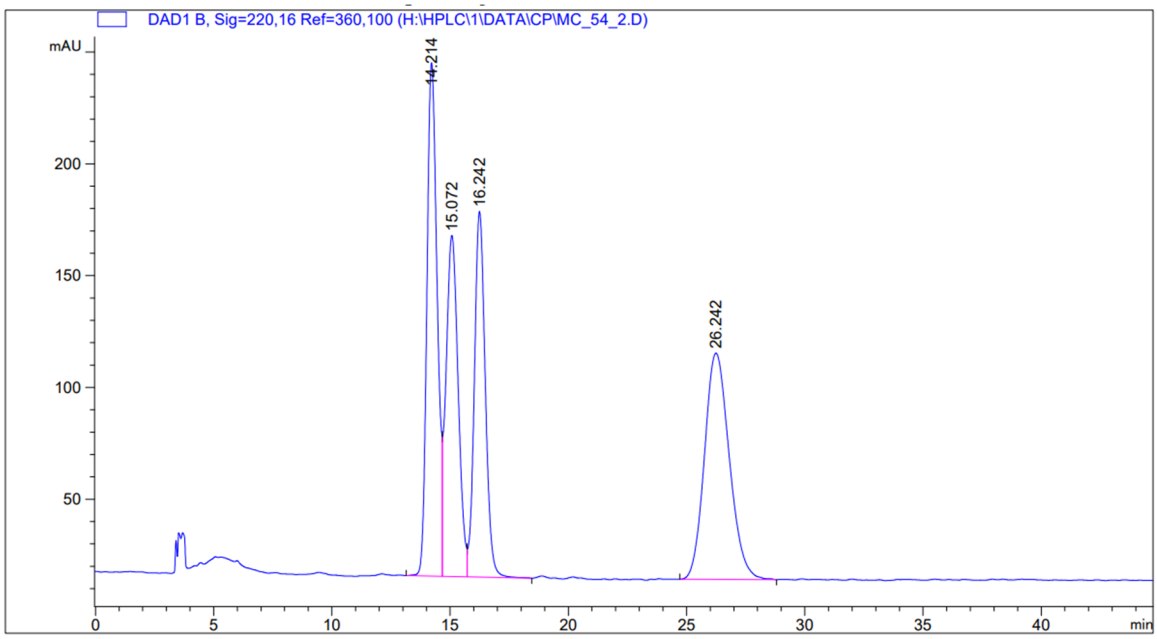


Figure S3: determination of the rotational energy barrier for the interconversion of **5a** to **5a'**.

Determination of the d.r. of 5a – HPLC peaks attribution

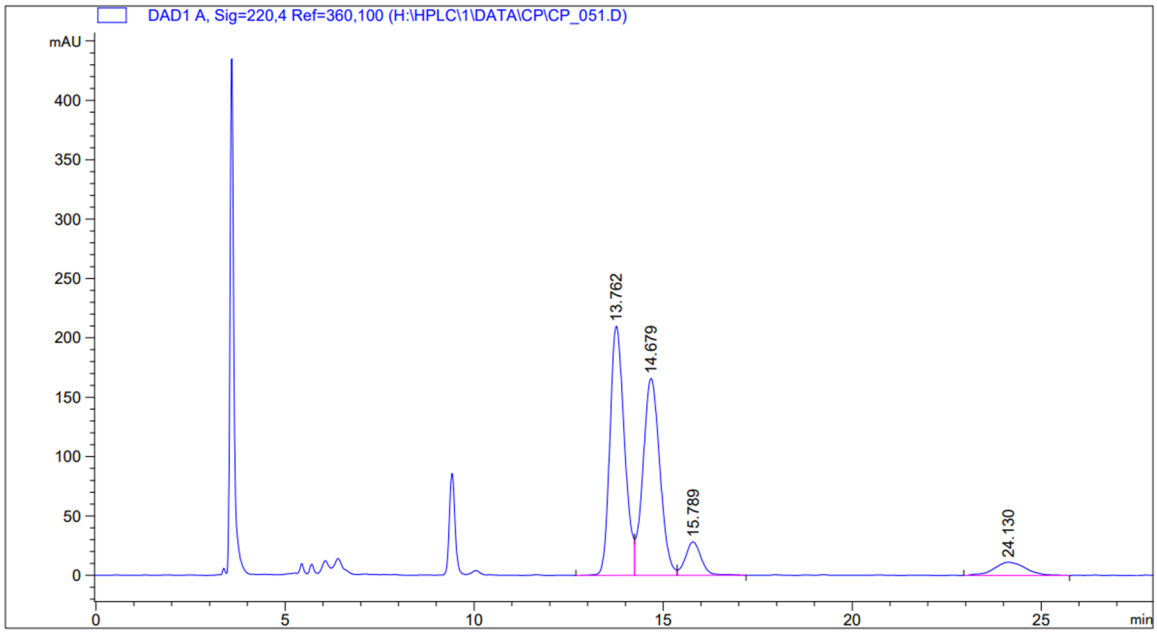
Racemic product **5a + 5a'** was obtained with benzylamine and tetrabutylammonium bromide as catalysts for the first and second step, respectively. HPLC chromatogram is reported, showing the peaks of the four diastereoisomers (IC column.: hexane/*i*-PrOH 98/2, flow rate 1 mL/min, 25 °C, λ = 220 nm. t_1= 14 min, t_2= 15 min, t_3= 16 min, t_4= 26 min). (Figure S4).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.214	BV	0.4635	6916.86572	229.59039	27.6327
2	15.072	VV	0.5485	5472.29736	152.55441	21.8617
3	16.242	VB	0.4950	5255.90186	163.52090	20.9972
4	26.242	BB	1.1154	7386.37988	101.21966	29.5084

Figure S4 – HPLC chromatogram of racemic product **5a + 5a'**.

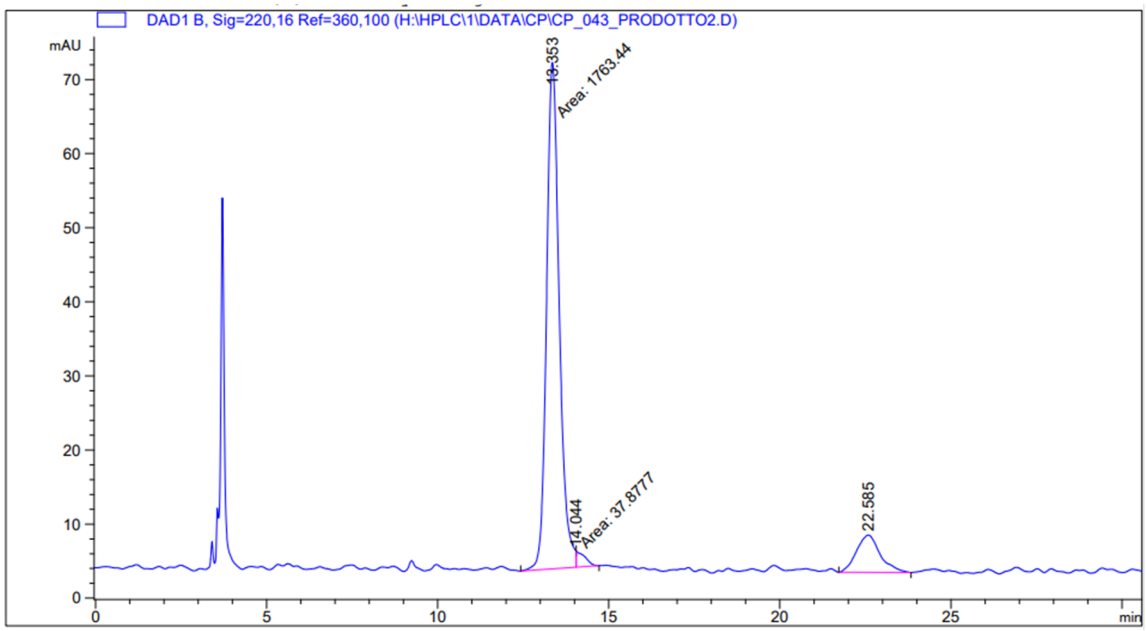
Catalyst **D** was tested with racemic trisubstituted hydrazide **3a**. Major peaks 1 and 2 were assigned as a diastereomeric couple of **5a** and **5a'** with same axis and different stereocenter (Figure S5).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.762	BV	0.4120	5613.02295	209.89731	45.8551
2	14.679	VV	0.4834	5165.57813	165.84851	42.1998
3	15.789	VB	0.4434	821.21252	28.23110	6.7088
4	24.130	BB	0.8786	640.96161	11.08535	5.2363

Figure S5 – HPLC chromatogram of **5a** + **5a'** obtained with benzylamine and **D**.

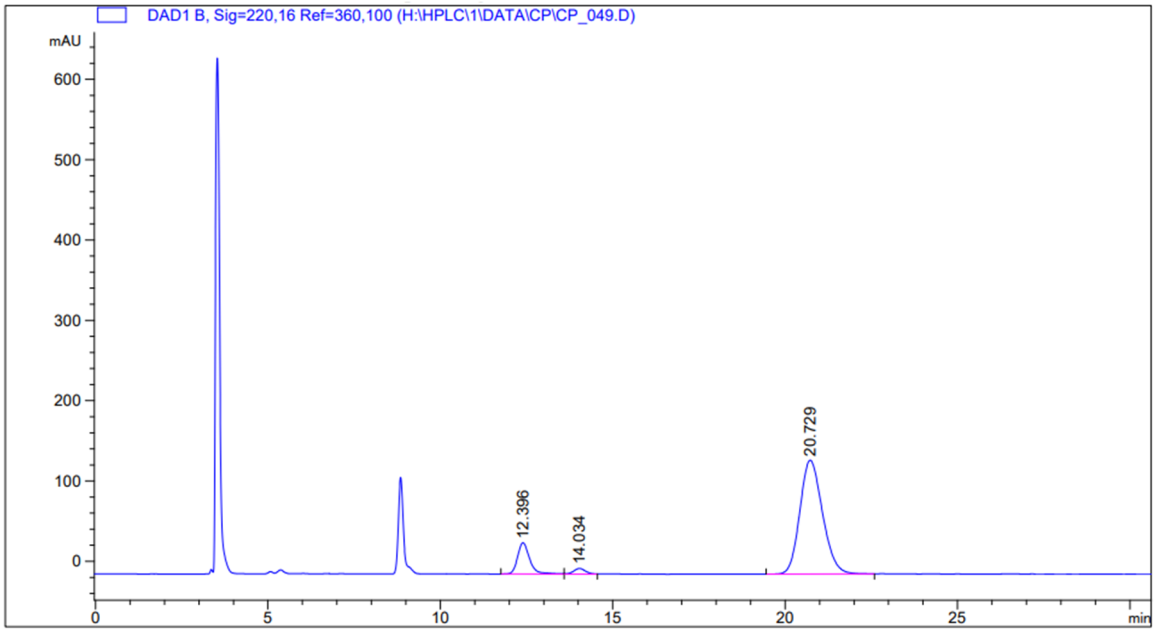
Catalyst **D** was tested with enantioenriched **3a** (94% ee); the third peak is absent and the second is minimal (Figure S6).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.353	MF	0.4299	1763.44080	68.35848	86.2826
2	14.044	FM	0.2888	37.87766	2.18614	1.8533
3	22.585	BB	0.7581	242.47900	5.03303	11.8641

Figure S6 – HPLC chromatogram of **5a** + **5a'** obtained with **A** and **D** at r.t.

Catalyst **C** was tested with enantioenriched **3a** (94% ee). The second peak is absent and the third is minimal (Figure S7). Peaks 1 and 4 are thus assigned as a diastereomeric couple of **5a** and **5a'** with same stereocenter and different chiral axis.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.396	BV	0.3704	947.06860	38.85221	12.4846
2	14.034	VV	0.3643	161.21207	6.85589	2.1252
3	20.729	BV	0.7053	6477.62744	141.69710	85.3903

Figure S7 – HPLC chromatogram of **5a** + **5a'**obtained with **A** and **C** at r.t.

The two couples of enantiomers are peaks 1-3 and 2-4, confirmed also by analysis of UV spectra and by experimental ECD. From the kinetic experiments, it can be observed that, under heating, peak 1 converts into peak 4 thus showing that 1 and 4 are diastereoisomers possessing the chiral center with the same absolute configuration and the chiral axis with opposite absolute configuration. The same holds also for peak 2 and peak 3 which interconvert into one another upon heating. Moreover, it is known from literature[7, 10] that the starting trisubstituted hydrazide **3a**, obtained under the same conditions, predominantly has the (*S*) configuration at the chiral center. Therefore, the major product of the two-step sequence, peak 4, must have the (*S*) configuration at the chiral center and then also peak 1 must have the same absolute configuration at the chiral center.

[10] C. Liu, Q. Zhu, K.-W. Huang, Y. Lu *Org. Lett*. **2011**, *13*, 2638-2641.

Having established that peaks 1 and 4 are axial epimers, the enantiomer of 1 must be either peak 2 or peak 3. Chiral HPLC (Chiralpak IC column.: hexane/*i*-PrOH 98/2, flow rate 1 mL/min) with CD detection at 285 nm does not help since both peaks 2 and 3 have opposite CD sign with respect to that of peak 1 (Figure S8).

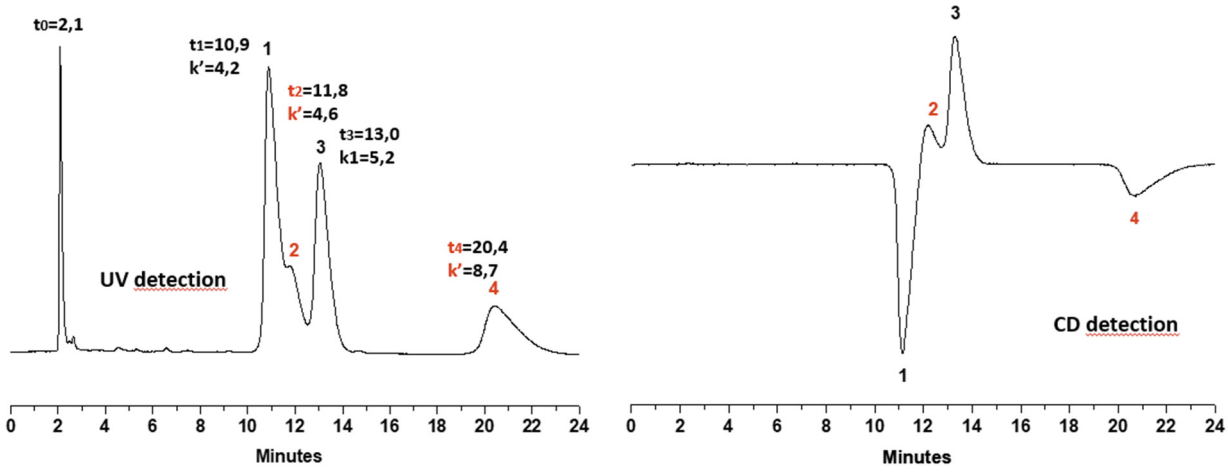


Figure S8: Chiral HPLC (Chiralpak I IC column.: hexane/*i*-PrOH 98/2, flow rate 1 mL/min) with CD detection at 285 nm.

The experimental ECD spectra of isolated peaks 1 and 3 show a nearly perfect inverted trend (below left) thus confirming that 1 (**5a'**) and 3 (*ent*-**5a'**) are enantiomers. The experimental ECD spectra of the two axial diastereoisomers [peak 1 (**5a'**) and peak 4 (**5a**), below right] are quite similar showing that the configuration at the chiral center is mainly responsible for the observed absorptions. However, it is possible to observe two main differences: a small peak around 250 nm present only in peak 4 (black circle), and a shoulder on the right at about 350 nm of only peak 1 (red circle) (Figure S9). Kinetic measurements in any case confirm that 1 and 4 are axial diastereoisomers.

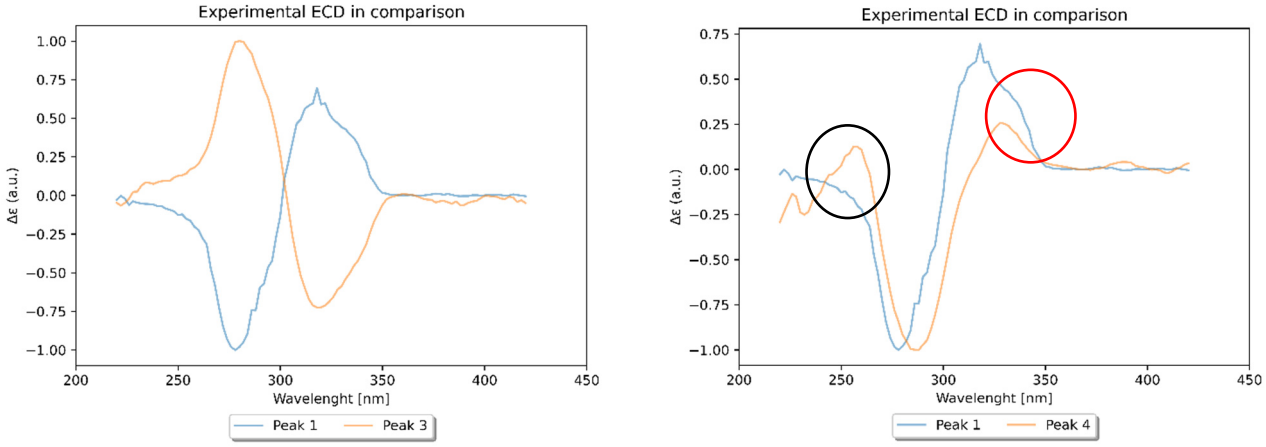
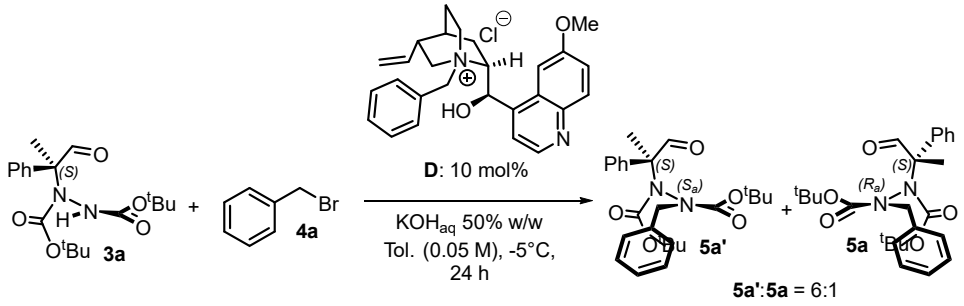


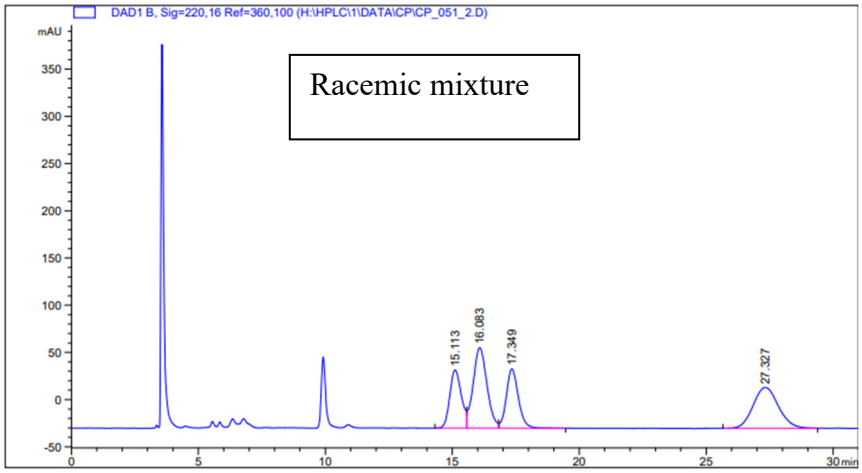
Figure S9. Experimental ECD comparison.

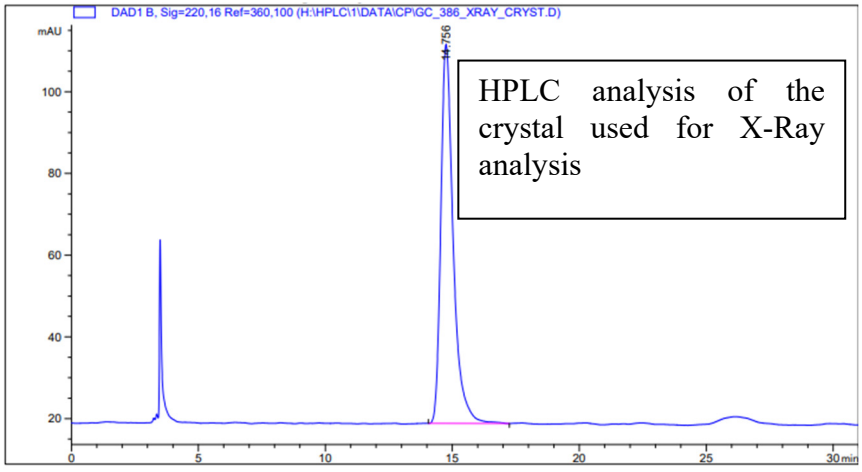
Determination of absolute configuration

A sample containing a mixture of **5a** and **5a'** in a d.r. of 1:6, obtained from the reaction of **3a** with **4a** using catalyst **D** (see reaction below), was dissolved in tert-butyl alcohol and let to slowly evaporate at r.t. Suitable crystals for X-Ray diffraction analysis were obtained.



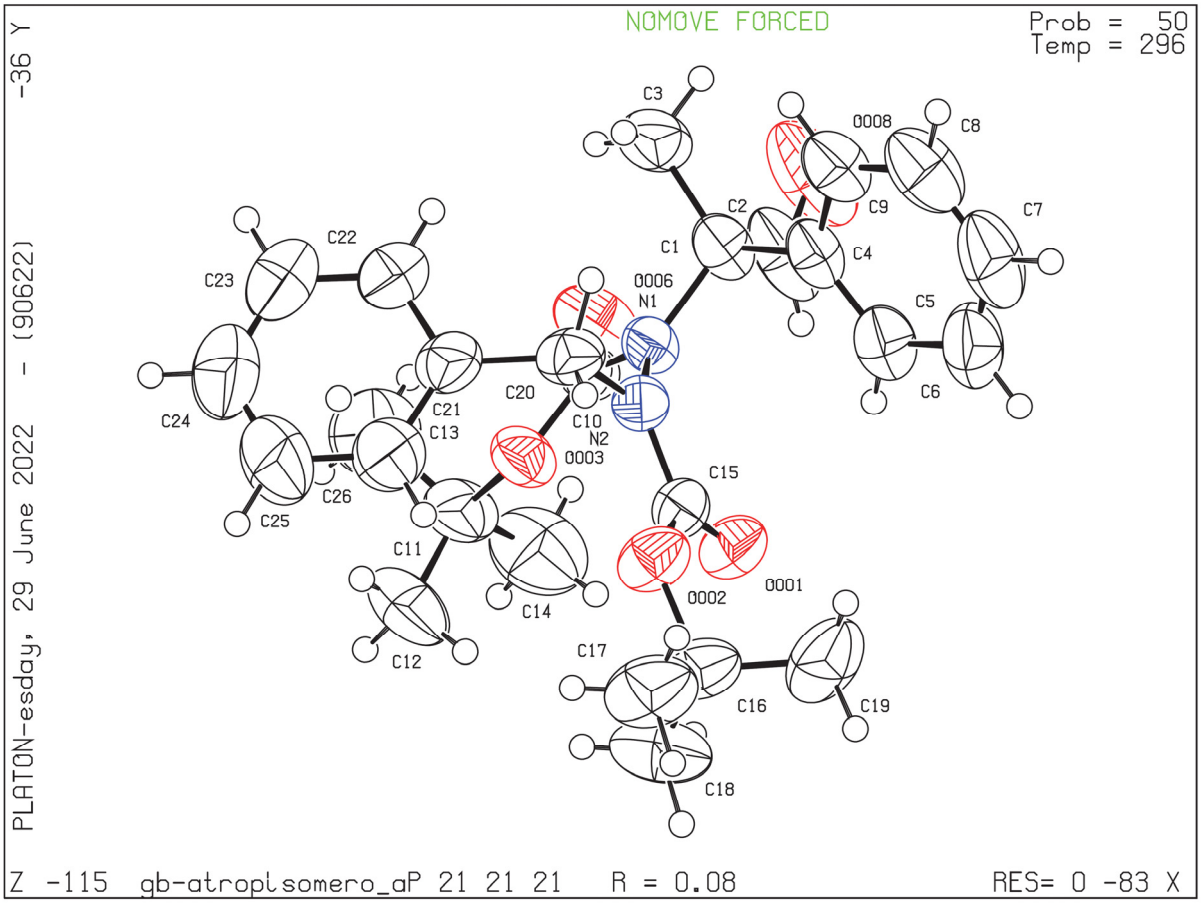
From X-Ray diffraction analysis the relative configuration of the crystalline compound was assigned as (*S**,*Sa**). The subsequent HPLC analysis on the analyzed crystal (IC column: hexane/i-PrOH 98/2, flow rate 1 mL/min, 25 °C, λ = 220 nm) associate the crystal to the first peak of the chromatogram. This peak is the axial-epimer of compound **5a** as revealed by kinetic epimerization studies.





Because the absolute configuration of the quaternary stereocenter on **3a** is known to be (*S*) from literature,[7,9] when hydrazide **3a** is prepared using catalyst **A**, the absolute configuration on compound **5a'** can be assigned to (*S*,*S*$_a$). Consequently, the absolute configuration of *S*,*R*$_a$ can be assigned to **5a**.

Crystal data for compound **5a'**



A specimen of $C_{26}H_{34}N_2O_5$ was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 0.71073 Å). The total exposure time was 27.11 hours. 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 31101reflections to a maximum θ angle of 25.00° (0.84 Å resolution), of which 4455 were independent (average redundancy 6.981, completeness = 97.9%, R_{int} = 5.37%, R_{sig} = 3.90%) and 3740 (83.95%) were greater than 2σ(F^2). The final cell constants of a = 10.3138(8) Å, b = 12.6890(12) Å, c = 20.1061(18) Å, volume = 2631.3(4) Å^3, are based upon the refinement of the XYZ-centroids of 9929 reflections above 20 σ(I) with 5.097° < 2θ < 54.28°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.924. 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, $C_{26}H_{34}N_2O_5$. The final anisotropic full-matrix least-squares refinement on F^2 with305 variables converged at R1 = 7.65%, for the observed data and wR2 = 14.59% for all data. The goodness-of-fit was 1.283. The largest peak in the final difference electron density synthesis was 0.220 $e^-/Å^3$ and the largest hole was -0.154 $e^-/Å^3$ with an RMS deviation of 0.029 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.147 g/cm^3 and F(000), 976 e^-.

Table 1. Sample and crystal data

Identification code	gb2201	
Chemical formula	$C_{26}H_{34}N_2O_5$	
Formula weight	454.55 g/mol	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 10.3138(8) Å	α = 90°
	b = 12.6890(12) Å	β = 90°
	c = 20.1061(18) Å	γ = 90°
Volume	2631.3(4) $Å^3$	
Z	4	
Density (calculated)	1.147 g/cm^3	
Absorption coefficient	0.079 mm^{-1}	
F(000)	976	

Table 2. Data collection and structure refinement.

Theta range for data collection	1.90 to 25.00°	
Index ranges	-12<=h<=12, -14<=k<=15, -23<=l<=23	
Reflections collected	31101	
Independent reflections	4455 [R(int) = 0.0537]	
Coverage of independent reflections	97.9%	
Absorption correction	Multi-Scan	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2017/1 (Sheldrick, 2017)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	4455 / 0 / 305	
Goodness-of-fit on F^2	1.283	
Final R indices	3740 data; I>2σ(I)	R1 = 0.0765, wR2 = 0.1416
	all data	R1 = 0.0970, wR2 = 0.1459

Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0347P)^2+1.0412P]$ where $P=(F_o^2+2F_c^2)/3$
Absolute structure parameter	0.4(4)
Largest diff. peak and hole	0.220 and -0.154 eÅ^{-3}
R.M.S. deviation from mean	0.029 eÅ^{-3}

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2).

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
O001	0.5134(3)	0.4471(3)	0.75160(18)	0.0637(9)
O002	0.6083(3)	0.2958(3)	0.78701(18)	0.0680(9)
O003	0.2892(3)	0.4072(3)	0.84172(15)	0.0666(9)
N1	0.2902(3)	0.3437(3)	0.73848(16)	0.0503(9)
N2	0.4037(3)	0.2916(3)	0.75475(17)	0.0493(9)
O006	0.1284(4)	0.4503(4)	0.77075(18)	0.0884(13)
C15	0.5108(5)	0.3542(4)	0.7638(2)	0.0527(11)
O008	0.0912(5)	0.4471(5)	0.6134(2)	0.129(2)
C4	0.3298(5)	0.2956(4)	0.6206(2)	0.0613(13)
C20	0.3942(5)	0.1802(4)	0.7730(2)	0.0632(13)
C9	0.3103(6)	0.2089(5)	0.5804(2)	0.0725(15)
C1	0.2293(5)	0.3279(4)	0.6721(2)	0.0616(13)
C10	0.2281(5)	0.4050(4)	0.7840(2)	0.0612(13)
C21	0.3342(5)	0.1613(4)	0.8402(3)	0.0700(15)
C5	0.4376(6)	0.3570(5)	0.6090(3)	0.0747(16)
C2	0.1857(7)	0.4349(6)	0.6483(3)	0.094(2)
C22	0.2046(6)	0.1393(5)	0.8475(3)	0.0926(19)
C11	0.2496(6)	0.4807(5)	0.8956(3)	0.0831(18)
C16	0.7403(5)	0.3408(5)	0.7922(3)	0.0759(15)
C7	0.5044(8)	0.2447(7)	0.5208(3)	0.103(2)
C3	0.1130(5)	0.2523(6)	0.6775(3)	0.0871(19)
C8	0.3987(8)	0.1837(6)	0.5307(3)	0.093(2)
C26	0.4070(7)	0.1658(6)	0.8974(3)	0.106(2)
C6	0.5247(6)	0.3309(6)	0.5592(3)	0.093(2)
C23	0.1485(8)	0.1222(7)	0.9087(4)	0.123(3)
C12	0.3542(8)	0.4591(7)	0.9468(3)	0.120(3)
C17	0.8168(6)	0.2485(6)	0.8182(4)	0.104(2)
C19	0.7849(6)	0.3751(6)	0.7239(3)	0.104(2)
C18	0.7379(7)	0.4312(6)	0.8419(4)	0.112(2)
C25	0.3508(10)	0.1495(8)	0.9593(4)	0.140(4)
C13	0.1188(8)	0.4485(9)	0.9208(4)	0.154(4)

	x/a	y/b	z/c	U(eq)
C24	0.2222(10)	0.1274(8)	0.9634(4)	0.149(4)
C14	0.2566(9)	0.5917(6)	0.8712(4)	0.125(3)

Table 4. Bond lengths (Å)

O001-C15	1.204(5)	O002-C15	1.334(6)
O002-C16	1.480(6)	O003-C10	1.320(5)
O003-C11	1.486(6)	N1-C10	1.362(6)
N1-N2	1.383(5)	N1-C1	1.489(6)
N2-C15	1.372(6)	N2-C20	1.464(6)
O006-C10	1.209(6)	O008-C2	1.211(7)
C4-C5	1.378(7)	C4-C9	1.379(7)
C4-C1	1.521(6)	C20-C21	1.505(7)
C20-H20A	0.97	C20-H20B	0.97
C9-C8	1.391(8)	C9-H9	0.93
C1-C2	1.507(8)	C1-C3	1.540(8)
C21-C22	1.373(8)	C21-C26	1.374(8)
C5-C6	1.384(8)	C5-H5	0.93
C2-H2	0.93	C22-C23	1.377(9)
C22-H22	0.93	C11-C14	1.493(9)
C11-C13	1.498(9)	C11-C12	1.517(9)
C16-C17	1.506(8)	C16-C19	1.512(8)
C16-C18	1.522(8)	C7-C8	1.351(10)
C7-C6	1.356(10)	C7-H7	0.93
C3-H3A	0.96	C3-H3B	0.96
C3-H3C	0.96	C8-H8	0.93
C26-C25	1.389(10)	C26-H26	0.93
C6-H6	0.93	C23-C24	1.339(11)
C23-H23	0.93	C12-H12A	0.96
C12-H12B	0.96	C12-H12C	0.96
C17-H17A	0.96	C17-H17B	0.96
C17-H17C	0.96	C19-H19A	0.96
C19-H19B	0.96	C19-H19C	0.96
C18-H18A	0.96	C18-H18B	0.96
C18-H18C	0.96	C25-C24	1.358(11)
C25-H25	0.93	C13-H13A	0.96
C13-H13B	0.96	C13-H13C	0.96
C24-H24	0.93	C14-H14A	0.96
C14-H14B	0.96	C14-H14C	0.96

Table 5. Bond angles (°).

C15-O002-C16	120.3(4)	C10-O003-C11	121.5(4)
C10-N1-N2	120.8(4)	C10-N1-C1	118.8(4)
N2-N1-C1	120.3(3)	C15-N2-N1	115.9(4)
C15-N2-C20	125.4(4)	N1-N2-C20	117.6(4)
O001-C15-O002	126.7(5)	O001-C15-N2	123.9(4)
O002-C15-N2	109.4(4)	C5-C4-C9	118.0(5)
C5-C4-C1	120.8(5)	C9-C4-C1	120.9(5)
N2-C20-C21	114.0(4)	N2-C20-H20A	108.8
C21-C20-H20A	108.8	N2-C20-H20B	108.8
C21-C20-H20B	108.8	H20A-C20-H20B	107.7
C4-C9-C8	120.5(6)	C4-C9-H9	119.7
C8-C9-H9	119.7	N1-C1-C2	106.8(4)
N1-C1-C4	111.0(4)	C2-C1-C4	103.3(4)
N1-C1-C3	110.4(4)	C2-C1-C3	110.5(5)
C4-C1-C3	114.2(4)	O006-C10-O003	126.2(5)
O006-C10-N1	121.6(4)	O003-C10-N1	112.3(4)
C22-C21-C26	116.8(6)	C22-C21-C20	122.0(5)
C26-C21-C20	121.2(5)	C4-C5-C6	120.7(6)
C4-C5-H5	119.6	C6-C5-H5	119.6
O008-C2-C1	122.7(7)	O008-C2-H2	118.7
C1-C2-H2	118.7	C21-C22-C23	122.4(6)
C21-C22-H22	118.8	C23-C22-H22	118.8
O003-C11-C14	109.9(5)	O003-C11-C13	108.8(5)
C14-C11-C13	114.3(7)	O003-C11-C12	100.8(5)
C14-C11-C12	111.0(6)	C13-C11-C12	111.2(6)
O002-C16-C17	101.9(4)	O002-C16-C19	109.1(5)
C17-C16-C19	112.3(5)	O002-C16-C18	108.8(5)
C17-C16-C18	111.5(5)	C19-C16-C18	112.6(6)
C8-C7-C6	120.2(6)	C8-C7-H7	119.9
C6-C7-H7	119.9	C1-C3-H3A	109.5
C1-C3-H3B	109.5	H3A-C3-H3B	109.5
C1-C3-H3C	109.5	H3A-C3-H3C	109.5
H3B-C3-H3C	109.5	C7-C8-C9	120.3(6)
C7-C8-H8	119.9	C9-C8-H8	119.9
C21-C26-C25	121.0(7)	C21-C26-H26	119.5
C25-C26-H26	119.5	C7-C6-C5	120.3(7)
C7-C6-H6	119.9	C5-C6-H6	119.9
C24-C23-C22	119.2(8)	C24-C23-H23	120.4
C22-C23-H23	120.4	C11-C12-H12A	109.5
C11-C12-H12B	109.5	H12A-C12-H12B	109.5

C11-C12-H12C	109.5	H12A-C12-H12C	109.5
H12B-C12-H12C	109.5	C16-C17-H17A	109.5
C16-C17-H17B	109.5	H17A-C17-H17B	109.5
C16-C17-H17C	109.5	H17A-C17-H17C	109.5
H17B-C17-H17C	109.5	C16-C19-H19A	109.5
C16-C19-H19B	109.5	H19A-C19-H19B	109.5
C16-C19-H19C	109.5	H19A-C19-H19C	109.5
H19B-C19-H19C	109.5	C16-C18-H18A	109.5
C16-C18-H18B	109.5	H18A-C18-H18B	109.5
C16-C18-H18C	109.5	H18A-C18-H18C	109.5
H18B-C18-H18C	109.5	C24-C25-C26	119.6(7)
C24-C25-H25	120.2	C26-C25-H25	120.2
C11-C13-H13A	109.5	C11-C13-H13B	109.5
H13A-C13-H13B	109.5	C11-C13-H13C	109.5
H13A-C13-H13C	109.5	H13B-C13-H13C	109.5
C23-C24-C25	121.0(8)	C23-C24-H24	119.5
C25-C24-H24	119.5	C11-C14-H14A	109.5
C11-C14-H14B	109.5	H14A-C14-H14B	109.5
C11-C14-H14C	109.5	H14A-C14-H14C	109.5
H14B-C14-H14C	109.5		

Table 6. Anisotropic atomic displacement parameters (Å^2)

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O001	0.0559(19)	0.054(2)	0.081(2)	0.0068(19)	-0.0008(17)	-0.0033(17)
O002	0.0448(19)	0.065(2)	0.094(2)	0.0134(19)	-0.0063(18)	0.0031(18)
O003	0.061(2)	0.089(3)	0.0499(18)	-0.0156(17)	-0.0001(16)	0.002(2)
N1	0.041(2)	0.065(2)	0.0448(18)	-0.0062(18)	0.0026(16)	0.0060(18)
N2	0.043(2)	0.055(2)	0.0509(19)	0.0023(18)	-0.0018(17)	0.0015(19)
O006	0.059(2)	0.130(4)	0.076(2)	-0.033(2)	-0.0056(19)	0.036(2)
C15	0.047(3)	0.055(3)	0.056(3)	0.000(2)	0.006(2)	0.001(3)
O008	0.129(4)	0.177(5)	0.080(3)	0.002(3)	-0.023(3)	0.083(4)
C4	0.062(3)	0.078(4)	0.043(2)	0.003(3)	-0.002(2)	0.017(3)
C20	0.067(3)	0.050(3)	0.073(3)	-0.002(2)	-0.010(3)	-0.008(3)
C9	0.073(4)	0.088(4)	0.057(3)	-0.006(3)	-0.006(3)	0.019(3)
C1	0.051(3)	0.087(4)	0.047(2)	-0.005(2)	-0.001(2)	0.015(3)
C10	0.049(3)	0.083(4)	0.052(3)	-0.011(3)	0.003(2)	-0.005(3)
C21	0.074(4)	0.057(3)	0.079(3)	0.017(3)	-0.012(3)	-0.016(3)
C5	0.080(4)	0.086(4)	0.058(3)	0.004(3)	0.005(3)	0.009(3)
C2	0.097(5)	0.134(6)	0.050(3)	-0.001(3)	-0.003(3)	0.056(4)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C22	0.090(5)	0.101(5)	0.088(4)	0.014(4)	-0.008(4)	-0.035(4)
C11	0.080(4)	0.106(5)	0.064(3)	-0.037(3)	0.007(3)	-0.011(4)
C16	0.044(3)	0.078(4)	0.105(4)	0.004(3)	-0.015(3)	0.001(3)
C7	0.099(5)	0.151(7)	0.057(4)	0.002(4)	0.021(4)	0.043(6)
C3	0.055(3)	0.139(6)	0.067(3)	-0.022(4)	0.000(3)	-0.008(4)
C8	0.107(5)	0.107(5)	0.064(3)	-0.022(3)	-0.003(4)	0.040(5)
C26	0.097(5)	0.126(6)	0.094(5)	0.039(4)	-0.027(4)	-0.025(4)
C6	0.082(4)	0.132(6)	0.067(4)	0.020(4)	0.018(3)	0.009(4)
C23	0.111(6)	0.146(7)	0.114(6)	0.032(5)	0.008(5)	-0.051(5)
C12	0.145(7)	0.156(7)	0.060(3)	-0.024(4)	-0.017(4)	-0.012(6)
C17	0.057(4)	0.111(5)	0.142(6)	0.014(5)	-0.024(4)	0.007(4)
C19	0.057(3)	0.124(6)	0.132(6)	0.024(5)	0.022(4)	-0.001(4)
C18	0.099(5)	0.109(5)	0.128(5)	-0.019(5)	-0.050(5)	0.000(5)
C25	0.134(7)	0.200(10)	0.087(5)	0.061(6)	-0.034(5)	-0.022(7)
C13	0.110(6)	0.239(11)	0.112(6)	-0.079(7)	0.061(5)	-0.036(7)
C24	0.151(9)	0.191(10)	0.105(6)	0.062(6)	0.000(6)	-0.052(8)
C14	0.162(8)	0.095(5)	0.118(6)	-0.036(4)	-0.011(6)	0.010(6)

Table 7. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$).

	x/a	y/b	z/c	U(eq)
H20A	0.4805	0.1497	0.7727	0.076
H20B	0.3432	0.1439	0.7397	0.076
H9	0.2373	0.1670	0.5866	0.087
H5	0.4519	0.4167	0.6348	0.09
H2	0.2332	0.4938	0.6610	0.113
H22	0.1527	0.1359	0.8097	0.111
H7	0.5633	0.2275	0.4875	0.123
H3A	0.1435	0.1825	0.6871	0.131
H3B	0.0664	0.2518	0.6361	0.131
H3C	0.0565	0.2755	0.7125	0.131
H8	0.3851	0.1247	0.5042	0.111
H26	0.4953	0.1799	0.8945	0.127
H6	0.5975	0.3727	0.5522	0.112
H23	0.0605	0.1072	0.9120	0.148
H12A	0.3496	0.3868	0.9606	0.18
H12B	0.3415	0.5042	0.9846	0.18
H12C	0.4378	0.4728	0.9277	0.18
H17A	0.7786	0.2239	0.8589	0.155
H17B	0.9046	0.2699	0.8264	0.155

	x/a	y/b	z/c	U(eq)
H17C	0.8160	0.1928	0.7860	0.155
H19A	0.7771	0.3172	0.6935	0.156
H19B	0.8738	0.3973	0.7261	0.156
H19C	0.7321	0.4327	0.7088	0.156
H18A	0.6895	0.4890	0.8237	0.168
H18B	0.8250	0.4537	0.8510	0.168
H18C	0.6977	0.4081	0.8824	0.168
H25	0.4009	0.1537	0.9977	0.168
H13A	0.0534	0.4706	0.8898	0.23
H13B	0.1033	0.4809	0.9632	0.23
H13C	0.1159	0.3732	0.9255	0.23
H24	0.1848	0.1158	1.0049	0.179
H14A	0.3388	0.6034	0.8501	0.188
H14B	0.2473	0.6391	0.9082	0.188
H14C	0.1881	0.6040	0.8399	0.188

Computational details

Structure of (*R,R*$_a$)-*ent*-**5a'** was subjected to conformational search, which was carried out using the recent CREST program.[11,12] at the GFN2-xTB[13,14] level of theory with the GBSA implicit solvation model. The conformational ensemble obtained from this search was visually inspected and it was noted that the ensemble contained members possessing an opposite axial configuration with respect to that of the input structure. Clearly, this axial rotation was induced by the metadynamic sampling performed by CREST. All the members of the ensemble presenting an inverted chiral axis were manually sorted out before the following step. Conformer ensemble obtained in the first step (457 conformers) was refined and sorted at the DFT level using the CENSO algorithm[15] interfaced with the ORCA quantum chemistry program package.[16] The refinement was performed in three parts with default thresholds. After each part, conformers lying outside the given threshold were discarded.

- Part0: cheap prescreening: single point energy at the B97-D3/def2-SV(P)//GFNn-xTB level

[11] P. Pracht, S. Grimme *Chem. Sci.*, **2021**, *12*, 6551–6568.

[12] P. Pracht , F. Bohle, S. Grimme *Phys. Chem. Chem. Phys.*, **2020**, *22* , 7169–7192

[13] C. Bannwarth, E. Caldeweyher, S. Ehlert, A. Hansen, P. Pracht, J. Seibert, S. Spicher, S. Grimme *WIREs Comput. Mol. Sci.*, **2020**, *11*, e01493.

[14] Bannwarth, C.; Ehlert, S.; Grimme, S. *J. Chem. Theory Comput.* **2019**, *15*, 1652–1671.

[15] Grimme, S.; Bohle, F.; Hansen, A.; Pracht, P.; Spicher, S.; Stahn, M. *J. Phys. Chem. A* **2021**, *125*, 4039–4054.

[16] Neese, F.; Wennmohs, F.; Becker, U.; Riplinger, C. *J. Chem. Phys.*, **2020**, *152*, 224108.

- Part1: prescreening: single point energy at the r2SCAN-3c/def2-mTZVPP/CPCM[toluene] + GmRRHO(GFN2[alpb]-bhess)//GFNn-xTB
- Part2: geometry optimization and free energy calculation at the r2SCAN -3c/def2-mTZVPP + CPCM[toluene] + GmRRHO(GFN2[alpb]-bhess) // r2SCAN -3c[SMD] /def2-mTZVPP

This gave final refined and optimized conformers ensembles (67 cumulative conformers). Part2 was also repeated at the ωb97x-d4/6-31g(d) + CPCM[hexane] + GmRRHO(GFN2[alpb]-bhess) // ωb97x-d4/6-31g(d)[SMD], with the aim to preoptimize the final ensemble for the following higher level DFT optimizations. Vibrational frequencies were computed at the same level with the default mRRHO approximation.[17]

Computation of the N–N rotational barriers of 5a and 3a

To determine the rotational barrier of **5a**, the lower energy conformer resulting from the conformational search already performed at the ωb97x-d4 level, has been used to explore the PES by using a relaxed scan about the N–N bond. This scan has been carried out at ωb97x-d4/3-21g + CPCM[toluene] level, taking 36 steps of 10°. Results are represented in Figure S10

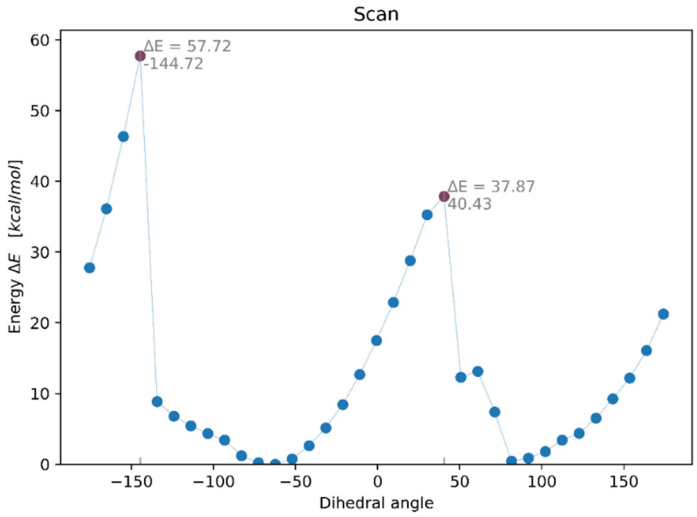
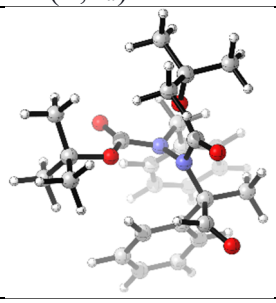
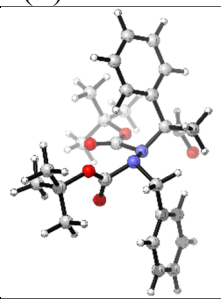
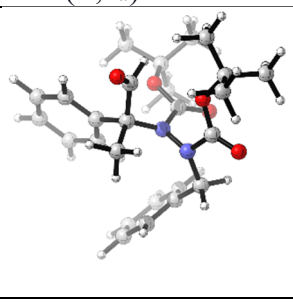
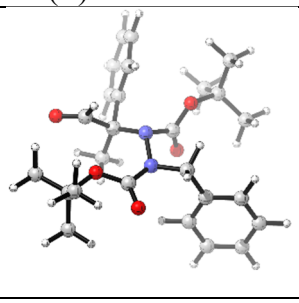


Figure S10. Clockwise N-N dihedral relaxed scan of (*R,R*$_a$)-*ent*-**5a'** at the ωB97x-d4/3-21g level.

[17] Grimme, S. Supramolecular Binding Thermodynamics by Dispersion-Corrected Density Functional Theory. *Chemistry – A European Journal* **2012**, *18* (32), 9955–9964.

Initial crude geometry of two TS - here called *cis* and *trans*, 40.34° and -144.72° respectively- have been pre-optimized by freezing the dihedral angle C-N-N-C (where carbon atoms are the Boc's ones), and then further optimized at the final ωB97x-d4/6-31g(d) level of theory, following the mode that represents the distortion on the bond. The same protocol has been followed to find the barrier of the tri-substituted hydrazide 3a. Vibrational frequency calculations were performed at the same level of theory to characterize all structures as either minima (no negative imaginary vibrational frequency) or saddle points (single negative imaginary frequency). Results for (R,Ra)-ent-5a' are shown in Table S9 and graphed in Figure S11, for molecule 3a in Table S10 and Figure S12.

Table S9. Optimized geometries[18] and rotational barriers [ΔG (kcal/mol)] calculated for (*R,Ra*)-*ent*-**5a'** at the ωb97x-d4/6-31g(d) CPCM[toluene] level of theory

(*R,Ra*)-*ent*-**5a'**	(*R*)-*cis*-TS-**5a**	(*R,Sa*)-*ent*-**5a**	(*R*)-*trans*-TS-**5a**
			
0.00	38.3	0.40	33.7

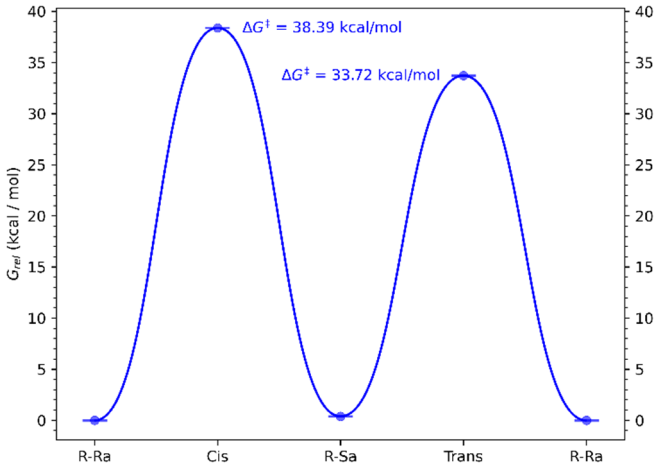
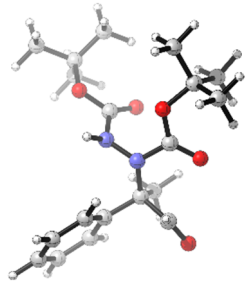
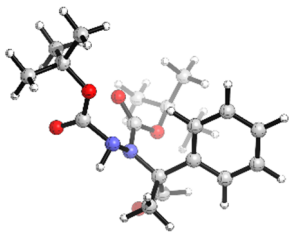
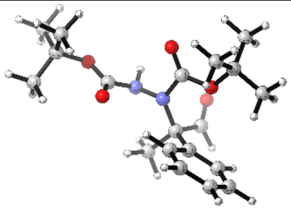
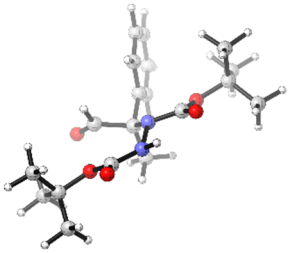


Figure S11. Rotational barriers of *ent*-**5a**.

The rotational barrier found is 33.7 kcal/mol, which is in fair agreement with the experimental one (28.32 kcal/mol). The energy separation between diastereomeric axial epimers of *ent*-**5a** was calculated to be 0.40 kcal/mol which corresponds to a Boltzmann population ratio of about **57:43 (*ent*-5a:*ent*-5a')**. This value is in very good agreement with the experimental value found during the kinetic equilibration experiments.

[18] CYLview, 1.0b; Legault, C. Y., Université de Sherbrooke, 2009 (http://www.cylview.org)

Table S10. Optimized geometries[18] and rotational barriers [ΔG (kcal/mol)] calculated for *ent*-**3a** at the ωb97x-d4/6-31g(d) CPCM[toluene] level of theory.

(*R*,*R*a)-*ent*-**3a**	(*R*)-*cis*-TS-**3a**	(*R*,*S*a)-*ent*-**3a**	(*R*)-*trans*-TS-**3a**
			
0.00	25.0	1.14	20.6

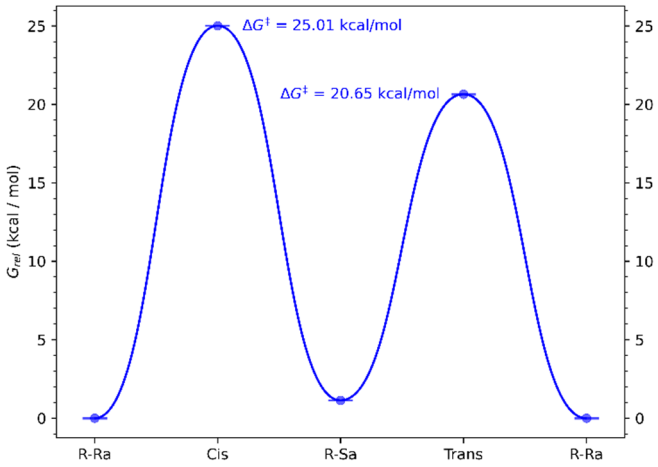


Figure S12. Rotational barrier of *ent*-**3a**.

The calculated rotational barrier of the trisubstituted hydrazide (*R*)-**3a** is of 20.6 kcal/mol, which corresponds to a half-life time of about two minutes at room temperature. This cannot be compared to any experimental value; however, it can be supported by two observations: the first is that the ^{1}H NMR spectrum shows two broadened peaks (Figure S13) for the aldehyde proton signal.

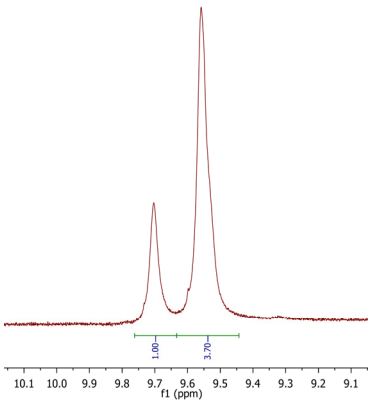


Figure S13. Broadened ^{1}H-NMR peaks attributed to the aldehyde's proton

(*R*,*R*$_a$)-*ent*-**5a'**

Zero Point Energy (Hartree)	0.5733011231
Inner Energy (Hartree)	-1496.9537316631
Enthalpy (Hartree)	-1496.9527874541
Rotational entropy	0.0171981631
Vibrational entropy	0.0533263995
Translational entropy	0.0171981631
Entropy	0.0915402877
Gibbs Energy (Hartree)	-1497.0443277418

N	-0.566527	0.791838	0.017796
N	-0.111998	-0.341807	-0.616904
C	-1.876725	1.184706	-0.168293
C	0.374478	1.756617	0.632045
C	-0.509027	-1.580106	-0.150541
C	0.365671	-0.226645	-1.999455
O	-2.327189	2.188345	0.363884
O	-0.246996	-2.607902	-0.754131
O	-2.530511	0.338880	-0.964272
C	-3.966314	0.509909	-1.222913
C	-4.745344	0.428049	0.088950
C	-4.205285	1.821247	-1.969419
C	-4.281413	-0.688703	-2.115535
H	-3.679062	-0.654388	-3.029982
H	-4.067069	-1.625967	-1.590548
H	-5.340804	-0.675986	-2.393116
H	-3.989270	2.683458	-1.335448
H	-3.573173	1.865315	-2.863937
H	-5.253238	1.869086	-2.286385
H	-4.543778	1.291031	0.726560
H	-5.818011	0.394579	-0.132713
H	-4.476373	-0.486826	0.629478
O	-1.180487	-1.484547	1.000537
C	-1.608268	-2.692184	1.715738
C	-2.631571	-3.456995	0.877719
C	-0.395438	-3.546669	2.085410
C	-2.262209	-2.113939	2.969525
H	0.339908	-2.945646	2.632308
H	-0.720082	-4.365095	2.737807
H	0.079708	-3.969951	1.198539
H	-2.643454	-2.925652	3.598164
H	-1.536504	-1.533864	3.550619
H	-3.096894	-1.457787	2.699018
H	-3.038857	-4.283107	1.471584
H	-3.458427	-2.794641	0.596734
H	-2.176343	-3.863493	-0.027407
C	-0.268243	2.260899	1.939044
C	0.635457	2.936784	-0.304561
O	-0.096866	3.374367	2.375196
H	-0.833698	1.489329	2.496948
H	1.219417	3.704854	0.207895
H	1.173754	2.610576	-1.198130
H	-0.318939	3.381578	-0.597791
C	2.674551	-0.727427	2.401569
C	1.535110	-0.076951	1.936927
C	1.641509	1.032945	1.089241
C	2.911103	1.489393	0.733351
C	4.052765	0.840258	1.201520
C	3.940382	-0.270219	2.033993
H	2.572458	-1.591684	3.054639
H	0.554873	-0.445372	2.221136
H	3.026574	2.343967	0.075943
H	5.033363	1.201700	0.902018
H	4.832385	-0.777409	2.394628
C	1.875525	-0.161433	-2.102691
H	-0.014303	-1.093533	-2.547424
H	-0.091587	0.671022	-2.426293
C	2.495370	0.857644	-2.826250
C	3.887494	0.914722	-2.924400
H	1.886767	1.615998	-3.317038
C	4.668548	-0.054134	-2.298673
H	5.753187	-0.011609	-2.370573
C	4.052093	-1.080849	-1.579371
H	4.357983	1.717143	-3.488541
C	2.665612	-1.135161	-1.482810
H	2.187578	-1.931740	-0.919337
H	4.656861	-1.838627	-1.086193

(*R*)-*cis*-TS-**5a**

Zero Point Energy (Hartree)	0.5735042962
Inner Energy (Hartree)	-1496.8953271407
Enthalpy (Hartree)	-1496.8943829316
Rotational entropy	0.0172875208
Vibrational entropy	0.0504665181
Translational entropy	0.0172875208
Entropy	0.0887697639
Gibbs Energy (Hartree)	-1496.9831526956
Imaginary frequency (cm^{-1})	-12.609945

N	-0.433124	-0.496758	0.885971
N	-1.103802	-0.707396	-0.382509
C	0.532892	0.524174	0.821292
C	-1.324173	-0.274211	2.080300
C	-0.184165	-0.532655	-1.506328
C	-1.604517	-2.106289	-0.584024
O	0.792497	1.179440	-0.168874
O	0.902841	-1.049429	-1.596811
O	1.100609	0.675417	2.019262
C	2.004544	1.809350	2.289764
C	3.276568	1.645514	1.460023
C	1.290984	3.134861	2.027885
C	2.301335	1.647354	3.778998
H	3.030436	2.402315	4.091485
H	1.389537	1.782037	4.371614
H	2.714779	0.653854	3.983484
H	1.944287	3.951310	2.356576
H	1.068442	3.270911	0.968249
H	0.357857	3.187006	2.598565
H	4.002742	2.408157	1.763322
H	3.717608	0.658119	1.636684
H	3.070675	1.757733	0.393884
O	-0.841280	0.134098	-2.450398
C	-0.224656	0.333885	-3.769720
C	-1.287959	1.142199	-4.510964
C	1.064335	1.142243	-3.625131
C	-0.001979	-1.017052	-4.450079
H	1.420305	1.428480	-4.621446
H	0.872384	2.052735	-3.047373
H	1.842245	0.564829	-3.122493
H	-0.938497	-1.587080	-4.471500
H	0.320317	-0.849687	-5.484117
H	0.761053	-1.603932	-3.935015
H	-0.947829	1.357577	-5.529535
H	-2.227738	0.581667	-4.566231
H	-1.475108	2.090577	-3.995578
C	-0.473463	-0.712112	3.301821
C	-2.576419	-1.161982	2.140316
O	-0.095386	-1.851523	3.446521
H	-0.276490	0.051913	4.070131
H	-3.268197	-0.918283	1.330584
H	-2.323499	-2.224396	2.139266
H	-3.086200	-0.940459	3.084310
C	-2.568202	3.044262	3.547042
C	-2.118957	1.728227	3.440451
C	-1.797805	1.179061	2.193338
C	-1.995311	1.958421	1.047813
C	-2.448932	3.272142	1.154813
C	-2.725078	3.826098	2.403682
H	-2.800631	3.454072	4.527343
H	-2.038561	1.134463	4.347845
H	-1.798960	1.540941	0.066273
H	-2.588946	3.863106	0.252527
H	-3.073326	4.853120	2.485047
C	-0.608940	-3.248802	-0.557612
H	-2.408505	-2.290622	0.120347
H	-2.076403	-2.060463	-1.571962
C	0.037164	-3.639304	0.619556
C	0.917020	-4.721057	0.611548
H	-0.127216	-3.092475	1.542655
C	1.153001	-5.433376	-0.564688
H	1.837209	-6.279181	-0.565009
C	0.504336	-5.055267	-1.739822
H	1.417613	-5.010993	1.533033
C	-0.368724	-3.968591	-1.731642
H	-0.868081	-3.671934	-2.652895

H	0.678800	-5.603660	-2.663057

(*R*,S_a)-*ent*-**5a**

Zero Point Energy (Hartree)	:	0.5736208847
Inner Energy (Hartree)	:	-1496.9529116618
Enthalpy (Hartree)	:	-1496.9519674528
Rotational entropy	:	0.0171658528
Vibrational entropy	:	0.0535404647
Translational entropy	:	0.0171658528
Entropy	:	0.0917220426
Gibbs Energy (Hartree)	:	-1497.0436894953

N	-0.041205	-0.178587	-0.384461
N	-0.079704	-0.984947	-1.506379
C	-0.314588	-0.841531	0.806718
C	-0.217308	1.286130	-0.575600
C	-1.306625	-1.453491	-1.945913
C	1.075144	-1.856039	-1.823861
O	-0.363839	-2.056561	0.881110
O	-1.396658	-2.313734	-2.802517
O	-0.478618	0.027971	1.801579
C	-0.466724	-0.402019	3.203375
C	-1.706635	-1.246932	3.489901
C	0.837942	-1.138538	3.505187
C	-0.518793	0.928835	3.951510
H	-0.517000	0.746164	5.031594
H	0.347963	1.546990	3.693268
H	-1.429646	1.479479	3.691465
H	0.908014	-1.316130	4.584201
H	0.881812	-2.100044	2.989015
H	1.693158	-0.525455	3.197811
H	-1.770860	-1.445988	4.565780
H	-2.608918	-0.703495	3.185348
H	-1.667133	-2.198119	2.955110
O	-2.314982	-0.816967	-1.336955
C	-3.711003	-1.136486	-1.672197
C	-4.503491	-0.271837	-0.692244
C	-3.988541	-0.718503	-3.114691
C	-3.987512	-2.618049	-1.415545
H	-5.055862	-0.842834	-3.329932
H	-3.727960	0.337016	-3.253997
H	-3.415449	-1.326679	-3.818194
H	-3.662779	-2.888243	-0.404018
H	-5.066021	-2.796903	-1.492050
H	-3.471711	-3.254569	-2.135798
H	-5.574762	-0.453971	-0.829211
H	-4.236121	-0.526672	0.340156
H	-4.304757	0.791105	-0.858704
C	-1.699047	1.628956	-0.342708
C	0.174450	1.685473	-2.000581
O	-2.319836	2.398178	-1.043954
H	-2.165235	1.145482	0.531393
H	1.214900	1.412091	-2.189568
H	-0.470669	1.215286	-2.746354
H	0.072433	2.769614	-2.090021
C	1.060976	4.112294	1.671109
C	0.249096	3.357119	0.822439
C	0.652394	2.088669	0.401301
C	1.889671	1.595889	0.821146
C	2.701670	2.349883	1.662942
C	2.287928	3.610446	2.099240
H	0.728990	5.096294	1.994535
H	-0.698945	3.773045	0.490122
H	2.213220	0.613663	0.501066
H	3.661855	1.946441	1.977980
H	2.920209	4.198260	2.760692
C	2.365528	-1.368225	-1.215024
H	0.854474	-2.869331	-1.472697
H	1.157848	-1.888987	-2.913379
C	2.778465	-1.839657	0.035190
C	3.973228	-1.394438	0.601125
H	2.152892	-2.551426	0.567549
C	4.770071	-0.474080	-0.081472
H	5.702501	-0.126779	0.357804
C	4.371152	-0.009367	-1.335212
H	4.282651	-1.768248	1.574735
C	3.178511	-0.460754	-1.899358
H	2.877494	-0.110251	-2.884828
H	4.992580	0.699240	-1.877589

(*R*)-*trans*-TS-**5a**

Zero Point Energy (Hartree)	:	0.5730411347
Inner Energy (Hartree)	:	-1496.9024024746
Enthalpy (Hartree)	:	-1496.9014582656
Rotational entropy	:	0.0173334465
Vibrational entropy	:	0.0507819683
Translational entropy	:	0.0173334465
Entropy	:	0.0891311398
Gibbs Energy (Hartree)	:	-1496.9905894054
Imaginary frequency (cm^{-1})	:	-5.464991

N	-0.716408	0.089342	0.446511
N	-0.584704	-0.996839	-0.514436
C	0.551240	0.086531	1.189590
C	-0.891752	1.478279	-0.090936
C	-1.390098	-1.225213	-1.610140
C	-0.108872	-2.241148	0.116564
O	1.635656	0.227483	0.678108
O	-1.333361	-2.300270	-2.189523
O	0.295530	-0.119615	2.471574
C	1.382848	-0.084045	3.468561
C	2.331551	-1.256506	3.226172
C	2.093561	1.268417	3.430802
C	0.621421	-0.257596	4.780654
H	1.325684	-0.260497	5.619374
H	-0.089587	0.563980	4.920307
H	0.070946	-1.204859	4.782855
H	2.787799	1.321183	4.277337
H	2.660710	1.400250	2.507340
H	1.369050	2.082955	3.526363
H	3.079362	-1.280293	4.026976
H	1.780204	-2.203258	3.244028
H	2.846606	-1.164197	2.267739
O	-2.165350	-0.198536	-1.980845
C	-2.950652	-0.326936	-3.233816
C	-3.646295	1.023711	-3.377770
C	-2.008343	-0.554245	-4.416780
C	-3.990585	-1.435665	-3.073003
H	-2.587129	-0.489248	-5.344983
H	-1.240905	0.228372	-4.439935
H	-1.525026	-1.530666	-4.370033
H	-4.586031	-1.258827	-2.169742
H	-4.665608	-1.416425	-3.936258
H	-3.524513	-2.419628	-3.009720
H	-4.245486	1.010474	-4.294764
H	-4.308731	1.222719	-2.530856
H	-2.918765	1.837362	-3.443971
C	-2.377995	1.729485	-0.386943
C	-0.019694	1.836072	-1.294793
O	-2.759685	2.691409	-1.012536
H	-3.075853	1.030409	0.110673
H	1.036731	1.857241	-1.023228
H	-0.157953	1.107983	-2.094854
H	-0.325253	2.815004	-1.672929
C	-1.325053	3.087542	3.357198
C	-1.427507	2.210798	2.281791
C	-0.685099	2.423997	1.110961
C	0.154050	3.536667	1.039106
C	0.258342	4.415388	2.118385
C	-0.480537	4.196175	3.278802
H	-1.906925	2.904371	4.257659
H	-2.070412	1.339152	2.359770
H	0.734214	3.732031	0.143672
H	0.920528	5.274980	2.046218
H	-0.400147	4.884063	4.117294
C	1.282967	-2.669640	-0.302417
H	-0.163044	-2.116070	1.201211
H	-0.814177	-3.035862	-0.138818
C	1.938259	-3.645162	0.453495
C	3.199897	-4.105375	0.079658
H	1.456445	-4.048686	1.343529
C	3.819693	-3.591435	-1.059861
H	4.804267	-3.947108	-1.355202

C	3.168199	-2.617793	-1.816862
H	3.699388	-4.863214	0.679371
C	1.905872	-2.159995	-1.440751
H	1.405354	-1.395471	-2.027126
H	3.644717	-2.211716	-2.706565

(*R*,*R*$_a$)-*ent*-**3a**

Zero Point Energy (Hartree):	0.4618930274
Inner Energy (Hartree) :	-1226.5618766876
Enthalpy (Hartree) :	-1226.5609324786
Rotational entropy :	0.0168393109
Vibrational entropy :	0.0432792945
Translational entropy :	0.0168393109
Entropy :	0.0808213659
Gibbs Energy (Hartree) :	-1226.6417538445

N	0.612038	0.615167	0.172126
N	0.030999	-0.577121	0.550319
C	-0.175292	1.755416	0.089328
C	1.797973	0.527016	-0.702217
C	-1.090622	-1.019084	-0.130058
O	0.180422	2.730016	-0.553615
O	-1.465546	-0.558313	-1.190627
O	-1.278306	1.640453	0.824014
C	-2.333773	2.662229	0.738407
C	-1.821089	3.991316	1.291713
C	-2.827330	2.770127	-0.703963
C	-3.423459	2.086142	1.640491
H	-3.760053	1.114544	1.263086
H	-3.049321	1.957327	2.662125
H	-4.279958	2.768100	1.666003
H	-2.071740	3.219263	-1.351959
H	-3.078696	1.775517	-1.087830
H	-3.727697	3.394139	-0.729283
H	-2.655536	4.699335	1.352371
H	-1.416850	3.849813	2.300702
H	-1.044541	4.414418	0.651932
O	-1.638817	-2.023630	0.562031
C	-2.790741	-2.757285	0.021400
C	-3.048995	-3.812073	1.095945
C	-3.990717	-1.820717	-0.113813
C	-2.411409	-3.419383	-1.302827
H	-3.819789	-1.063451	-0.881699
H	-4.875215	-2.407589	-0.386492
H	-4.189390	-1.324251	0.843045
H	-2.231115	-2.676234	-2.082071
H	-1.510680	-4.030225	-1.173209
H	-3.228426	-4.075447	-1.623425
H	-3.900018	-4.436845	0.804691
H	-2.170406	-4.453941	1.221911
H	-3.277255	-3.336188	2.055953
C	1.421252	0.224974	-2.149789
C	2.560117	1.861466	-0.607951
O	3.195180	2.325037	-1.525505
C	3.936137	-1.298621	1.889088
C	2.998535	-0.450143	1.305971
C	2.778600	-0.469411	-0.077794
C	3.529357	-1.343463	-0.866154
C	4.468947	-2.194298	-0.282563
C	4.675758	-2.176196	1.095282
H	4.090248	-1.273193	2.965486
H	2.425618	0.229849	1.932743
H	3.387160	-1.371392	-1.941687
H	5.040926	-2.872449	-0.911771
H	5.408155	-2.840130	1.548645
H	2.580087	2.306683	0.405610
H	0.665142	0.941547	-2.478496
H	1.013202	-0.784836	-2.241557
H	2.295220	0.330379	-2.796692
H	0.103461	-0.816123	1.530408

(*R*)-cis-TS-**3a**

Zero Point Energy (Hartree):	0.4617151138
Inner Energy (Hartree) :	-1226.5238383438
Enthalpy (Hartree) :	-1226.5228941348
Rotational entropy :	0.0167435930
Vibrational entropy :	0.0415536106
Translational entropy :	0.0167435930
Entropy :	0.0789999641
Gibbs Energy (Hartree) :	-1226.6018940989
Imaginary frequency (cm^{-1}) :	-58.657851

N	0.084483	-1.034805	1.383626
N	-0.583171	-1.563009	0.219085
C	1.057937	-0.088738	1.152879
C	-0.805880	-0.857161	2.547825
C	0.323963	-1.784792	-0.909025
H	-0.805389	-2.518550	0.499385
O	1.566076	0.110841	0.061731
O	1.180441	-2.637779	-0.908493
O	1.360278	0.539515	2.294087
C	2.314415	1.657666	2.325477
C	3.704418	1.159073	1.937464
C	1.816042	2.787520	1.424859
C	2.270789	2.076622	3.793408
H	2.951002	2.918853	3.958369
H	1.256399	2.384312	4.071448
H	2.577583	1.246097	4.438815
H	2.459584	3.663611	1.563996
H	1.840936	2.498556	0.372207
H	0.790931	3.063220	1.696380
H	4.430548	1.965401	2.091998
H	3.990322	0.310672	2.569035
H	3.735412	0.850825	0.890418
O	-0.083687	-1.042045	-1.925236
C	0.613641	-1.103617	-3.219250
C	-0.137721	-0.062114	-4.046701
C	2.078986	-0.704304	-3.051816
C	0.450932	-2.497268	-3.826342
H	2.536636	-0.621019	-4.044306
H	2.151637	0.263355	-2.546549
H	2.630864	-1.445669	-2.470637
H	-0.609838	-2.770519	-3.867404
H	0.844228	-2.490794	-4.849230
H	0.992276	-3.248541	-3.247634
H	0.283917	-0.015735	-5.056492
H	-1.199038	-0.323512	-4.121380
H	-0.051510	0.927360	-3.584894
C	0.092292	-0.955742	3.809038
C	-1.790003	-2.036684	2.656331
O	0.749620	-1.939738	4.048961
H	0.050647	-0.096434	4.502321
H	-2.509987	-2.020448	1.834122
H	-1.241192	-2.984379	2.670783
H	-2.347462	-1.952055	3.594010
C	-2.952210	2.105207	3.648148
C	-2.241205	0.905447	3.654771
C	-1.574615	0.461761	2.507307
C	-1.657793	1.228561	1.341458
C	-2.368946	2.427947	1.334125
C	-3.013845	2.874481	2.487201
H	-3.458478	2.436249	4.552054
H	-2.215778	0.313932	4.568197
H	-1.180335	0.890801	0.426558
H	-2.420081	3.012942	0.418638
H	-3.566664	3.810929	2.478964

(*R*,*S*$_a$)-*ent*-**3a**

Zero Point Energy (Hartree):	0.4616586453
Inner Energy (Hartree) :	-1226.5592501814
Enthalpy (Hartree) :	-1226.5583059724
Rotational entropy :	0.0167780746
Vibrational entropy :	0.0441492896
Translational entropy :	0.0167780746
Entropy :	0.0816301246
Gibbs Energy (Hartree) :	-1226.6399360970

N	0.093184	0.086623	-0.730045
N	-0.716205	-0.725340	-1.494050
C	-0.573634	1.104536	-0.063521
C	1.529998	0.112654	-1.019178
C	-1.359771	-1.750751	-0.811757
O	-1.787546	1.122456	0.040247

O	-0.973652	-2.208742	0.245700
O	0.289724	1.994772	0.420941
C	-0.139641	3.018311	1.379198
C	-1.105102	3.990746	0.702720
C	-0.743568	2.346822	2.611456
C	1.175891	3.708385	1.735644
H	1.641907	4.130286	0.838106
H	0.987126	4.520144	2.446674
H	1.872253	2.994072	2.187596
H	-0.933867	3.106106	3.378258
H	-1.684561	1.847165	2.371145
H	-0.040020	1.611712	3.018928
H	-2.052649	3.503576	0.464806
H	-1.297675	4.835657	1.373925
H	-0.661440	4.377218	-0.221969
O	-2.400674	-2.158572	-1.543029
C	-3.264684	-3.246254	-1.068772
C	-4.314434	-3.345248	-2.173969
C	-2.463627	-4.543997	-0.968423
C	-3.914042	-2.849086	0.256938
H	-3.146202	-5.371257	-0.743073
H	-1.969660	-4.756408	-1.923498
H	-1.709683	-4.484967	-0.180878
H	-4.399710	-1.871673	0.157869
H	-4.677609	-3.589743	0.520250
H	-3.177864	-2.799956	1.061591
H	-5.034701	-4.133392	-1.929898
H	-4.853269	-2.397041	-2.276859
H	-3.842634	-3.586844	-3.132720
C	1.948659	-1.200291	-1.712931
C	1.805757	1.231087	-2.029402
O	0.926508	1.891558	-2.534347
C	4.176752	1.086101	1.598600
C	3.459691	1.045820	0.400704
C	2.335397	0.228648	0.279092
C	1.942522	-0.557993	1.367448
C	2.655253	-0.512702	2.562617
C	3.776405	0.311300	2.684623
H	5.047669	1.732877	1.679574
H	3.788993	1.675505	-0.420938
H	1.061838	-1.189825	1.275906
H	2.333489	-1.124489	3.402624
H	4.332750	0.346622	3.618441
H	2.859711	1.353667	-2.343566
H	1.669715	-2.048657	-1.081211
H	3.036210	-1.199695	-1.838019
H	1.472970	-1.313411	-2.690986
H	-1.286231	-0.233918	-2.174800

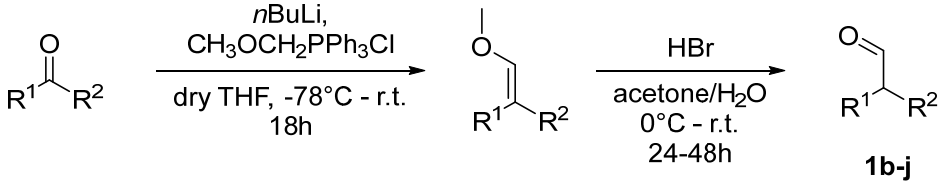
(*R*)-trans-TS--**3a**

Zero Point Energy (Hartree)	:	0.4616502236
Inner Energy (Hartree)	:	-1226.5311051827
Enthalpy (Hartree)	:	-1226.5301609737
Rotational entropy	:	0.0167413496
Vibrational entropy	:	0.0412363540
Translational entropy	:	0.0167413496
Entropy	:	0.0786804639
Gibbs Energy (Hartree)	:	-1226.6088414376
Imaginary frequency (cm^{-1})	:	-36.116356

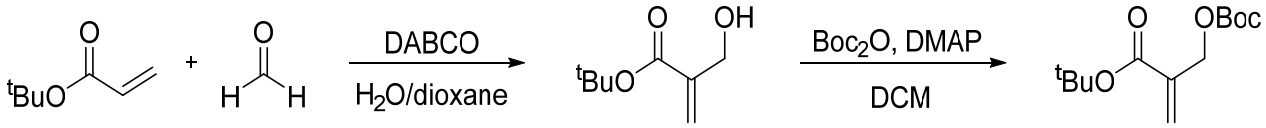
N	-0.491419	-0.068636	0.349666
N	-0.412398	-0.916346	-0.808172
C	0.597573	-0.414018	1.166411
C	-0.926547	1.334277	0.194012
C	-1.346867	-1.162875	-1.793421
H	0.006747	-1.786850	-0.497538
O	1.045885	-1.550314	1.170365
O	-1.415072	-2.272710	-2.293600
O	1.048762	0.604924	1.879007
C	1.982728	0.395000	2.998973
C	1.387569	-0.595558	3.998088
C	3.336014	-0.057454	2.454268
C	2.073606	1.790570	3.612151
H	2.772437	1.776383	4.455558
H	2.433796	2.512014	2.870416
H	1.091747	2.117475	3.968953
H	4.062206	-0.084735	3.274651
H	3.270579	-1.051140	2.006865
H	3.695170	0.651996	1.700190
H	2.026985	-0.628134	4.887248
H	0.388047	-0.266649	4.304015
H	1.323700	-1.601306	3.577390
O	-2.001164	-0.071185	-2.202284
C	-2.894306	-0.151700	-3.379953
C	-3.369804	1.286782	-3.573438
C	-2.094616	-0.602917	-4.603069
C	-4.072249	-1.071203	-3.063891
H	-2.727605	-0.505835	-5.492249
H	-1.218947	0.043144	-4.735700
H	-1.766696	-1.639068	-4.513875
H	-4.579005	-0.732069	-2.153074
H	-4.790483	-1.028586	-3.890688
H	-3.748212	-2.105379	-2.931888
H	-3.978755	1.339063	-4.482540
H	-3.967582	1.626873	-2.725425
H	-2.514596	1.961962	-3.686031
C	-2.406491	1.383721	-0.233262
C	-0.032041	2.109045	-0.768025
O	-2.900577	2.368923	-0.729637
H	-3.008413	0.511541	0.084276
H	0.950584	2.280855	-0.318181
H	0.090854	1.528333	-1.686411
H	-0.490085	3.065474	-1.029173
C	-2.026429	1.862740	3.824566
C	-1.752606	1.258671	2.600304
C	-1.115689	1.976371	1.580052
C	-0.795833	3.317004	1.792619
C	-1.074099	3.922368	3.017983
C	-1.686910	3.199325	4.039964
H	-2.511644	1.288227	4.610446
H	-2.013972	0.214882	2.444972
H	-0.319176	3.899435	1.010956
H	-0.809516	4.966206	3.170909
H	-1.904173	3.673498	4.994136

Synthesis of starting materials

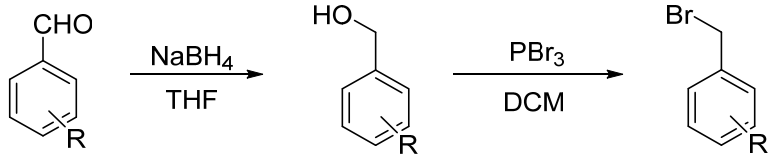
Aldehydes 1b-j[1]



Morita-Baylis-Hillman Reaction b[3]



General procedure for the synthesis of 4b, 4c, 4d, 4i and 4m.[2]

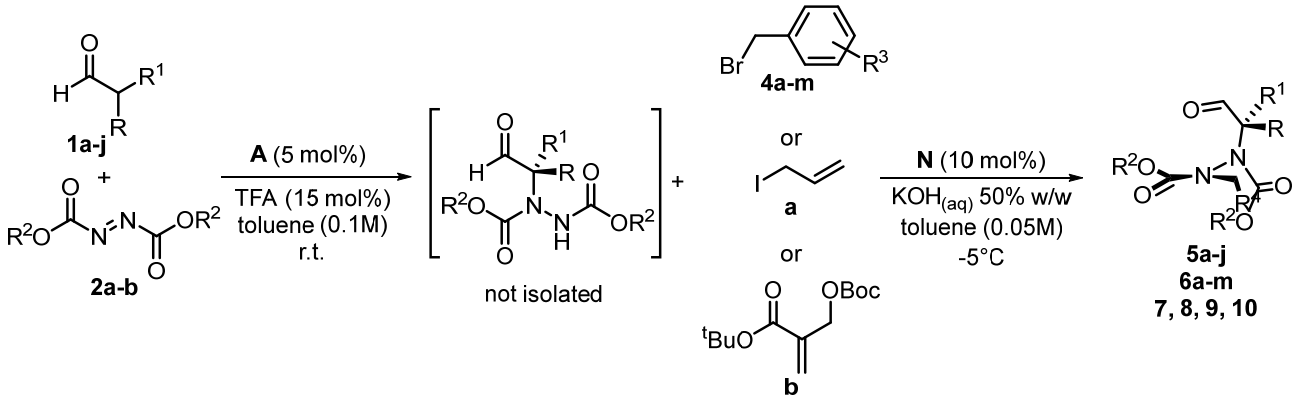


In a 10 mL round bottom flask equipped with a magnetic stirring bar 2 mmol of aldehyde, 4 mL of freshly distilled THF and 3 mmol of $NaBH_4$ were added. After three hours the reaction was quenched with a saturated solution of NH_4Cl and extracted three times with ethyl acetate. The organic fractions were collected, dried on Na_2SO_4, filtered, and concentrated with rotavapor. The crude product was pure enough to be used in the following step without further purification.

In a previously dried 10 mL two-necks round bottom flask, equipped with a magnetic stirring bar and flushed with nitrogen, the corresponding alcohol was added in DCM (0.5 M). After cooling the flask with an ice bath, 1.5 eq of PBr_3 were slowly added. The consumption of the starting compound was checked with TLC, then the reaction was stopped with the slow addition of distilled water. The two phases were separated, and the water phase was washed twice with fresh DCM. The organic phases were collected and washed twice with brine, dried on Na_2SO_4, filtered, and concentrated at low pressure. The crude product was purified through flash chromatography with a 9:1 hexane/diethyl ether mixture.

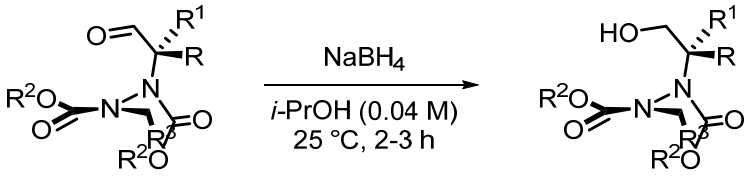
Experimental procedures

General procedure for the sequential catalysis one-pot reactions



The reactions were carried out on a 0.3 mmol scale of aldehyde. To a 25 mL round bottom flask with a Teflon coated magnetic stirrer, 5% mol of catalyst **A** was added and dissolved in 3 mL of toluene; 0.3 mmol of aldehyde **1a-j**, TFA (15 mol%) and **2a-b** (1.1 eq) were added, and the solution was left stirring for 24h at 25 °C. An equal amount of toluene was added together with 12 mL of a solution of $KOH_{(aq)}$ (50% w/w), PTC catalyst **N** (10 mol%) and electrophile **4a-m** / **a** / **b** (1 eq). The flask was cooled to -5 °C and left stirring vigorously at this temperature. Completion of the reaction was checked by TLC using a solvent mixture of hexane:diethyl ether – 4:1. After the appropriate time, the two phases were separated and the water phase was washed twice with diethyl ether; the organic parts were collected, dried over Na_2SO_4, filtered and concentrated with rotavapor without heating the bath; eventual traces of toluene were removed by high vacuum pump. Column chromatography was used with the proper solvent mixture to isolate the product as a single spot containing both diastereoisomers. To determine the diastereomeric ratio and enantiomeric excess of the major diastereoisomer, in most cases reduction to alcohols was necessary as the four peaks could not be separated by HPLC.

General procedure for reduction reactions



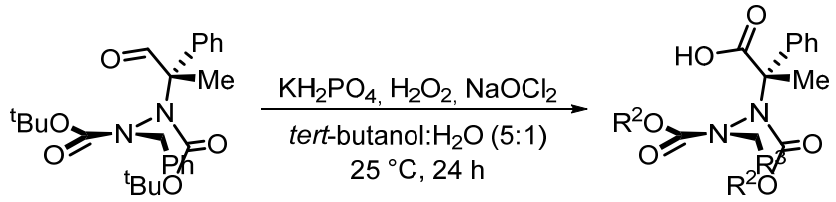
5a-j
6c, 6d, 6f, 6k, 6l
8, 10

5(a-j)r
6cr, 6dr, 6fr, 6kr, 6lr
8r, 10r

Reduction was performed with 1 eq of sodium borohydride in isopropanol (0.04 M) at r.t. After 2/3 hours, completion of the reaction was checked by TLC; a saturated solution of NH_4Cl was added and the solution was extracted with diethyl ether. Yield was quantitative in all cases. Crude mixture was directly analyzed through ^1H NMR and HPLC with chiral stationary phase.

The assignment of d.r. and e.e.% was done by identification of the enantiomeric couples by UV spectra.

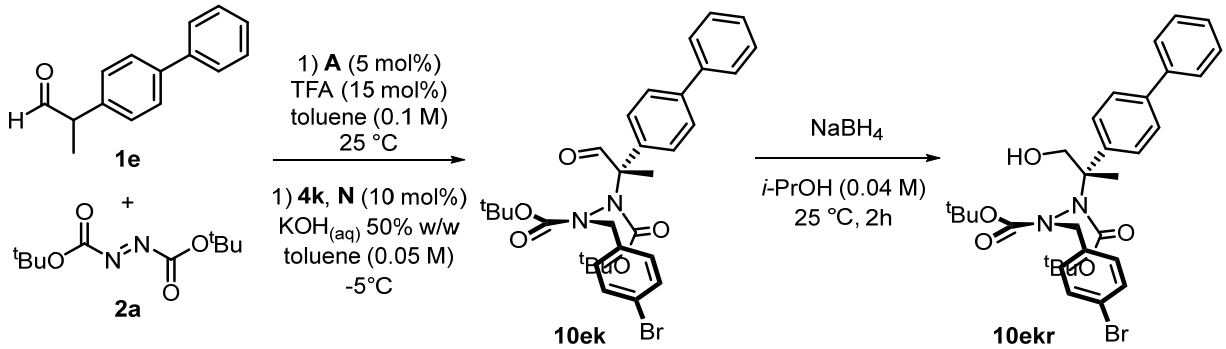
Oxidation reaction - 5ao



5a **5ao**

0.2 mmol of compound **5a** were dissolved in 3 mL of a mixture of *tert*-butanol:H_2O (5:1), then KH_2PO_4 (0.34 mmol, 46 mg), H_2O_2 (0.96 mmol, 0.1 mL of a 30% solution) and $NaOCl_2$ (0.69 mmol, 62 mg) were added. The solution was stirred at 25 °C for 24 hours, then water was added and EtOAc was used to extract. The organic parts were collected, dried over Na_2SO_4 and concentrated on the rotary evaporator. Crude ^1H NMR showed a mixture of diastereoisomers and complete conversion of the starting material. Column chromatography was used to get the clean final product **5ao**, that was obtained as a single diastereoisomer.

Three-step reaction process synthesis of 10ekr



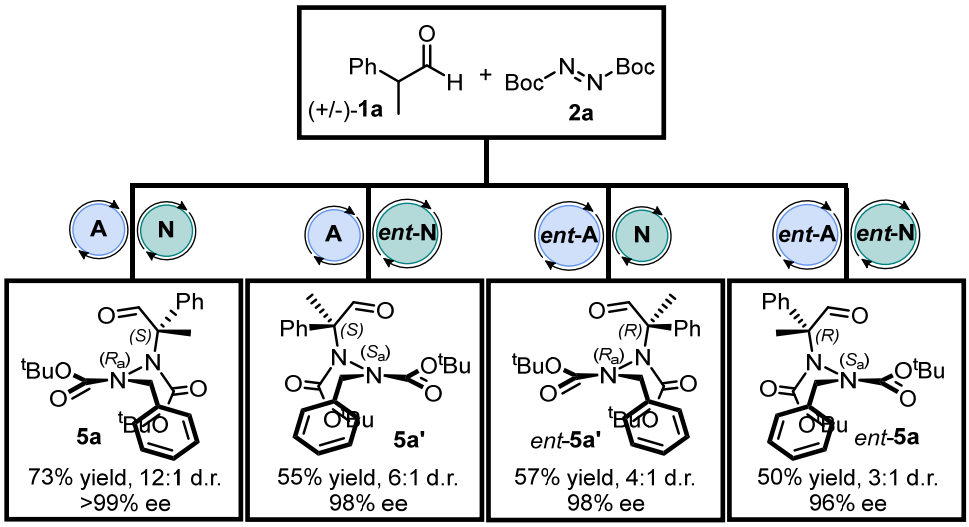
To a 25 mL round bottom flask with a Teflon coated magnetic stirrer, 5 mol % of catalyst **A** was added and dissolved in 3 mL of toluene; 0.3 mmol of aldehyde **1e**, TFA (15 mol %) and **2a** (1.1 eq) were added, and the solution was left stirring for 24h. An equal amount of toluene was added together with 12 mL of a solution of $KOH_{(aq)}$ (50% w/w), PTC catalyst **N** (10 mol%) and electrophile **4k** (1 eq). The flask was cooled to -5 °C and left stirring vigorously at this temperature. Completion of the reaction was checked by TLC using a solvent mixture of hexane:diethyl ether – 4:1. The two phases were separated and the water phase was washed twice with diethyl ether; the organic parts were collected, dried over Na_2SO_4, filtered and concentrated with rotavapor without heating the bath; eventual traces of toluene were removed by high vacuum pump. Reduction was then directly performed adding 1 eq of sodium borohydride in isopropanol (0.04 M) at r.t. After 2h, completion of the reaction was checked by TLC; a saturated solution of NH_4Cl was added and the solution was extracted with diethyl ether. Column chromatography was used to isolate the product as a single spot containing both diastereoisomers.

Large scale reaction for 5a and 6k

The reactions were carried out following the general procedure for the sequential catalysis one-pot reactions, using 3 mmol of aldehyde **1a** for compound **5a**, 2.5 mmol of aldehyde **1a** for compound **6k**.

Stereodivergent synthesis

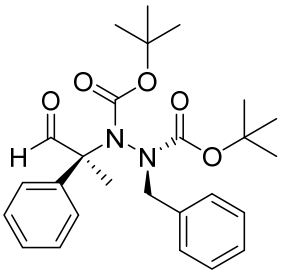
Reactions were performed in a 0.2 mmol scale of **1a**, following general procedure. To obtain the four diastereoisomers different combinations of catalysts **A** and **N** and their correspondent pseudoenantiomers ***ent*-A** (9-*epi*-deoxy-amino-quinidine) and ***ent*-N** (catalyst **O**) were exploited. Regarding the amination step, catalyst ***ent*-A** gave the trisubstituted hydrazide (*R*)-**3a** with a 72% yield and 68% ee, hence showing a lower reactivity and enantioselectivity with respect to **A**.



To better understand the diastereoselectivity, products **5a'**, ***ent*-5a'** and ***ent*-5a** were reduced following general procedure B.

Experimental details

(*S*, R_a)-di-tert-butyl 1-benzyl-2-(1-oxo-2-phenylpropan-2-yl)hydrazine-1,2-dicarboxylate (5a)



The reaction was carried out following the general procedure. Reaction time: 48h. The crude mixture was purified by flash column chromatography (hexane:Et_2O = 8:2). Yield= 73% (100 mg). Colorless oil. The d.r. and e.e. were determined by HPLC analysis on a Daicel Chiralpak IC column: hexane/*i*-PrOH 98/2, flow rate 1 mL/min, 25 °C, λ = 220 nm: t_1= 14 min, t_2= 15 min, t_3= 16 min, t_4= 26 min. d.r.= 13:1 and e.e. (major diastereoisomer) 99%. Peaks 1 and 3: minor diastereoisomer; peaks 2 and 4: major diastereoisomer.

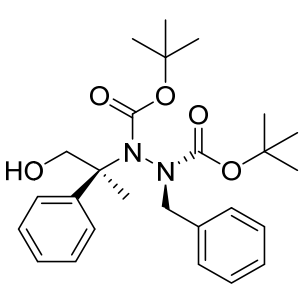
HRMS-ESI-ORBITRAP (+): calculated for $[C_{26}H_{34}N_2NaO_5]^+$ 477.2360, found 477.2359 $[M+Na]^+$.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 – 9.61 (m, 1H), 7.50 – 6.89 (m, 10H), 5.17 – 4.13 (m, 2H), 1.83 – 1.08 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.35, 196.25, 196.10, 195.94, 195.66, 155.49, 155.36, 155.10, 154.71, 154.39, 154.17, 152.79, 138.99, 138.84, 136.71, 136.59, 136.18, 135.89, 129.77, 129.17, 129.08, 128.49, 128.29, 128.25, 128.21, 128.18, 128.14, 127.87, 127.77, 127.72, 127.61, 127.50, 127.47, 127.45, 127.32, 127.29, 127.23, 126.81, 126.06, 82.59, 82.40, 82.32, 82.23, 82.13, 82.03, 81.94, 81.59, 72.78, 71.69, 71.54, 71.43, 56.41, 55.23, 54.44, 29.69, 29.65, 29.35, 28.34, 28.24, 28.14, 27.88, 27.82, 22.49, 20.27, 20.00, 19.69, 18.95, 18.42.

IR (ATR) ν(max)= 1735 (s) 1710 (s) 1681 (s) 1355 (s) 1150 (s) 1126 (s) cm^{-1}.

(*S*, R_a)-di-tert-butyl 1-benzyl-2-(1-hydroxy-2-phenylpropan-2-yl)hydrazine-1,2-dicarboxylate (5ar)



The reaction was carried out following the general reduction procedure. HPLC analysis were performed on a Daicel Chiralpak IC column: hexane/*i*-PrOH 98/2, flow rate 1 mL/min, 25 °C, λ =

220 nm: t_1= 14 min, t_2=18 min, t_3= 28 min, t_4= 43 min. The d.r. and e.e. values are consistent with those of **5a**. Peaks 1 and 2: couple of enantiomers; peaks 3 and 4: couple of enantiomers.

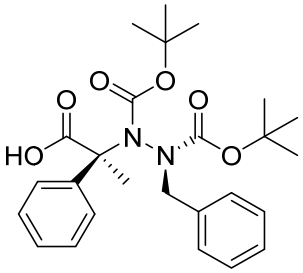
HRMS-ESI-ORBITRAP (+): calculated for $[C_{27}H_{36}N_2NaO_5]^+$ 479.2516, found 479.2509 $[M+Na]^+$.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.01 (m, 10H), 5.52 – 3.37 (m, 4H), 1.95 – 0.94 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.08, 157.54, 156.15, 155.41, 153.69, 153.31, 146.16, 145.93, 144.25, 142.81, 137.70, 137.22, 137.00, 129.45, 128.83, 128.45, 128.28, 128.19, 127.47, 127.38, 127.27, 126.69, 126.61, 126.28, 125.37, 125.23, 125.03, 83.36, 83.00, 82.25, 81.73, 81.33, 70.33, 70.01, 69.63, 69.17, 66.90, 66.44, 58.65, 57.91, 55.79, 31.91, 30.32, 29.68, 28.34, 28.22, 27.87, 27.81, 26.77, 25.51, 25.21, 23.88.

IR (ATR) ν(max)= 3406 (br, m) 1694 (s) 1367 (s) 1152 (s) cm^{-1}.

(*S*, R_a)-2-(2-benzyl-1,2-bis(tert-butoxycarbonyl)hydrazineyl)-2-phenylpropanoic acid (5ao)



The reaction was carried out following the oxidation procedure. The crude mixture was purified by flash column chromatography (hexane:EtOAc = 2:1). Yield= 56% (53 mg). White solid. m.p. = 90-92 °C. D.r. and e.e. were determined by HPLC analysis on a Daicel Chiralpak IC column: hexane/*i*-PrOH 98/2, flow rate 1 mL/min, 25 °C, λ = 220 nm: t_1= 18 min, t_2= 20 min, t_3= 48 min, t_4= 54 min. d.r.> 20:1 and e.e. (major diastereoisomer) > 99%. Peaks 3 and 4: minor diastereoisomer; peaks 1 and 2: major diastereoisomer.

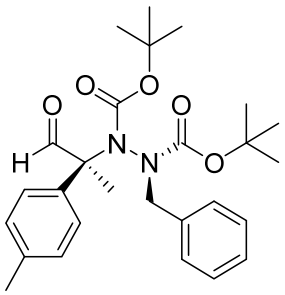
HRMS-ESI-ORBITRAP (+): calculated for $[C_{26}H_{34}N_2NaO_5]^+$ 493.2309, found 493.2304 $[M+Na]^+$.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.07 (m, 10H), 5.18 – 4.27 (m, 2H), 1.74 – 1.11 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.59, 171.98, 160.28, 158.92, 155.22, 153.56, 152.86, 140.06, 139.47, 136.98, 136.02, 135.76, 135.64, 130.00, 129.81, 129.46, 128.75, 128.40, 128.33, 128.22, 128.07, 127.84, 127.61, 127.46, 127.42, 127.32, 127.17, 127.12, 126.08, 125.50, 85.45, 84.95, 83.09, 71.50, 70.63, 65.83, 57.04, 56.40, 53.77, 34.21, 30.31, 29.24, 28.56, 28.24, 28.15, 27.82, 27.80, 27.64, 25.84, 24.59, 15.25.

IR (ATR) ν(max)= 3662 (br, m) 3444 (br, m) 1704 (s) 1367 (s) 1151 (s) 1127 (s) cm^{-1}.

(*S*, R_a)-di-tert-butyl 1-benzyl-2-(1-oxo-2-(p-tolyl)propan-2-yl)hydrazine-1,2-dicarboxylate (5b)



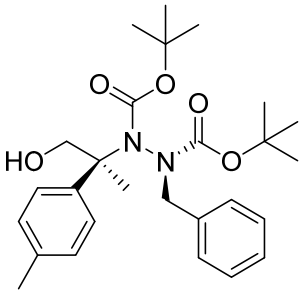
The reaction was carried out following the general procedure, at r.t. Reaction time: 32h. The crude mixture was purified by flash column chromatography (hexane:Et_2O = 8:2). Yield= 57% (53 mg). Colorless oil.

HRMS-ESI-ORBITRAP (+): calculated for $[C_{27}H_{36}N_2NaO_5]^+$ 491.2516, found 491.2515 $[M+Na]^+$.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (d, *J* = 51.6 Hz, 1H), 7.35 – 6.88 (m, 9H), 5.13 – 4.01 (m, 2H), 2.47 – 2.23 (m, 3H), 1.82 – 1.13 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.82, 197.28, 196.31, 196.03, 195.87, 155.52, 155.37, 155.07, 154.66, 143.85, 143.42, 138.14, 137.60, 137.43, 136.81, 136.64, 135.85, 135.74, 134.72, 130.50, 129.77, 129.22, 129.01, 128.58, 128.42, 128.24, 128.14, 128.06, 127.44, 127.34, 127.15, 127.12, 126.14, 83.32, 82.46, 82.27, 82.18, 82.05, 81.94, 72.57, 71.54, 71.29, 56.41, 54.95, 54.43, 30.31, 29.68, 28.34, 28.23, 27.85, 27.82, 27.79, 26.51, 22.12, 21.61, 20.99, 20.92, 19.92, 19.49, 18.85.

(*S*, R_a)-di-tert-butyl 1-benzyl-2-(1-hydroxy-2-(p-tolyl)propan-2-yl)hydrazine-1,2-dicarboxylate (5br)

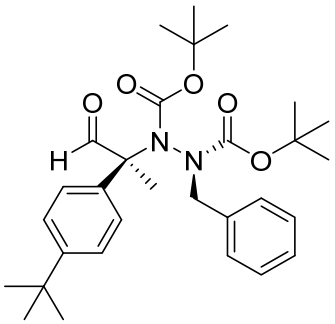


The reaction was carried out following the general reduction procedure. The dr and ee were determined by HPLC analysis on a Phenomenex Lux 5u Cellulose-2 column: hexane/*i*-PrOH 98/2, flow rate 1 mL/min, 25 °C, λ = 220 nm: t_1=17 min, t_2= 28 min, t_3= 30 min, t_4= 43 min. D.r.= 5:1 and e.e. (major diastereoisomer) >99%. Peaks 1 and 2: minor diastereoisomer; peaks 3 and 4: major diastereoisomer.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 6.90 (m, 9H), 5.36 – 3.34 (m, 4H), 2.32 (d, *J* = 7.3 Hz, 3H), 1.77 – 0.96 (m, 21H).

IR (ATR) ν(max)= 3406 (br, m) 1694 (s) 1367 (s) 1152 (s) 1067 (s) 1049 (s) cm^{-1}.

(*S*, R_a)-di-tert-butyl 1-benzyl-2-(2-(4-(tert-butyl)phenyl)-1-oxopropan-2-yl)hydrazine-1,2-dicarboxylate (5c)



The reaction was carried out following the general procedure. Reaction time: 5 days. The crude mixture was purified by flash column chromatography (hexane:Et_2O = 8:2). Yield= 67% (104 mg). Colorless oil.

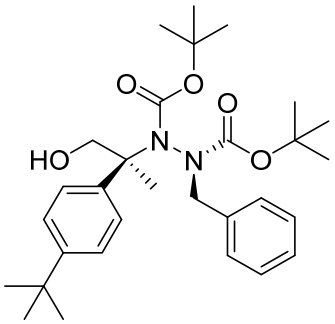
HRMS-ESI-ORBITRAP (+): calculated for $[C_{30}H_{42}N_2NaO_5]^+$ 533.2986, found 533.2984 $[M+Na]^+$.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 – 9.51 (m, 1H), 7.43 – 6.84 (m, 9H), 5.25 – 4.03 (m, 2H), 1.95 – 0.96 (m, 30H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.15, 196.02, 195.63, 156.79, 155.52, 155.36, 155.15, 154.77, 153.18, 151.15, 150.69, 150.50, 136.85, 136.58, 135.66, 129.81, 129.13, 129.02, 128.96, 128.28, 128.09, 128.03, 127.43, 127.37, 127.31, 127.05, 125.98, 125.49, 125.22, 125.16, 124.99, 83.24, 82.28, 82.18, 81.98, 81.91, 81.40, 72.52, 71.52, 71.29, 71.18, 56.68, 56.43, 54.22, 34.45, 34.41, 31.30, 31.08, 29.69, 28.35, 28.23, 27.92, 27.81, 21.86, 19.68, 19.27, 18.56.

IR (ATR) ν(max)= 1697 (s) 1366 (s) 1150 (s) 1124 (s) cm^{-1}.

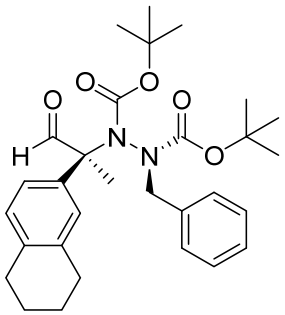
(*S*, R_a)-di-tert-butyl 1-benzyl-2-(2-(4-(tert-butyl)phenyl)-1-hydroxypropan-2-yl)hydrazine-1,2-dicarboxylate (5cr)



The reaction was carried out following the general reduction procedure. The d.r. and e.e. were determined by HPLC analysis on a Phenomenex Lux 5u Cellulose-2 column: hexane/*i*-PrOH 95/5, flow rate 1 mL/min, 25 °C, λ = 220 nm: t_1= 7 min, t_2= 9 min, t_3= 13 min, t_4= 15 min. D.r.= 10:1 and e.e. (major diastereoisomer) >99%. Peaks 1 and 3: minor diastereoisomer; peaks 2 and 4: major diastereoisomer.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.02 (m, 9H), 5.65 – 3.24 (m, 4H), 1.70 – 1.03 (m, 30H).

(*S*, R_a)-di-tert-butyl 1-benzyl-2-(1-oxo-2-(5,6,7,8-tetrahydronaphthalen-2-yl)propan-2-yl)hydrazine-1,2-dicarboxylate (5d)



The reaction was carried out following the general procedure. Reaction time: 48h. The crude mixture was purified by flash column chromatography (hexane:Et_2O = 8:2).

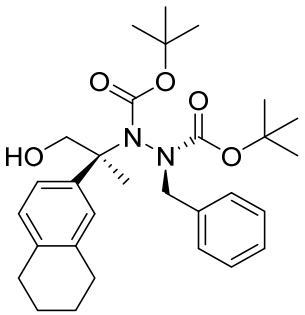
Yield= 60% (92 mg). Colorless oil.

HRMS-ESI-ORBITRAP (+): calculated for $[C_{30}H_{40}N_2NaO_5]^+$ 531.2829, found 531.2827 $[M+Na]^+$.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.73 (d, *J* = 48.1 Hz, 1H), 7.46 – 6.80 (m, 8H), 5.15 – 4.03 (m, 2H), 2.93 – 2.50 (m, 4H), 1.78 (dh, *J* = 10.6, 4.6 Hz, 4H), 1.66 – 1.09 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.28, 195.95, 156.78, 155.57, 155.45, 155.12, 154.68, 137.39, 136.90, 136.86, 136.72, 135.57, 129.70, 129.09, 128.80, 128.40, 128.08, 127.95, 127.78, 127.37, 127.21, 126.91, 124.29, 83.25, 82.20, 82.12, 82.01, 81.86, 71.64, 71.37, 56.57, 54.47, 29.62, 29.58, 28.98, 28.91, 28.34, 28.22, 27.84, 27.79, 23.15, 23.12, 19.94, 19.38.

(*S*, R_a)-di-tert-butyl 1-benzyl-2-(1-hydroxy-2-(5,6,7,8-tetrahydronaphthalen-2-yl)propan-2-yl)hydrazine-1,2-dicarboxylate (5dr)

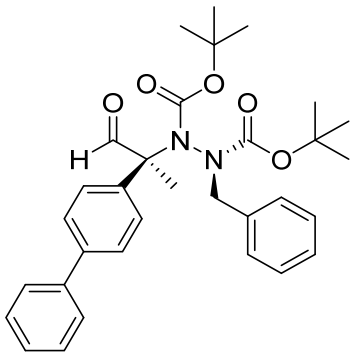


The reaction was carried out following the general reduction procedure.

The d.r. and e.e. were determined by HPLC analysis on a Daicel Chiralpak IC column.: hexane/*i*-PrOH 98/2, flow rate 1 mL/min, 25 °C, λ = 220 nm: t_1= 19 min, t_2= 21 min, t_3= 50 min, t_4= 55 min. D.r.= 13:1 and e.e. (major diastereoisomer) >99%. Peaks 1 and 2: minor diastereoisomer; peaks 3 and 4: major diastereoisomer.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 6.69 (m, 8H), 5.46 – 3.21 (m, 4H), 2.74 (q, *J* = 5.3 Hz, 4H), 1.80 (dh, *J* = 7.8, 4.3, 3.9 Hz, 4H), 1.70 – 1.15 (m, 21H). **IR** (ATR) ν(max)= 3407 (br, m) 1693 (s) 1367 (s) 1153 (s) 1058 (s) 1049 (s) cm^{-1}.

(*S*, R_a)-di-tert-butyl 1-(2-([1,1'-biphenyl]-4-yl)-1-oxopropan-2-yl)-2-benzylhydrazine-1,2-dicarboxylate (5e)



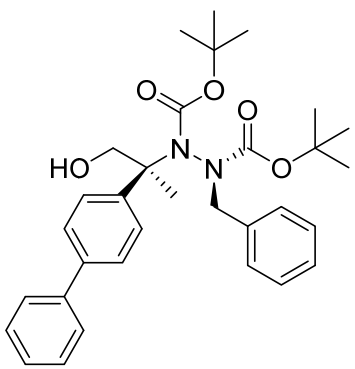
The reaction was carried out following the general procedure, at r.t. Reaction time: 32h. The crude mixture was purified by flash column chromatography (hexane:Et_2O = 6:1). Yield= 63% (100 mg). White solid.

HRMS-ESI-ORBITRAP (+): calculated for $[C_{32}H_{38}N_2NaO_5]^+$ 553.2673, found 553.2669 $[M+Na]^+$.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.08 – 9.60 (m, 1H), 7.66 – 7.11 (m, 14H), 5.61 – 3.98 (m, 2H), 1.93 – 1.11 (m, 21H).

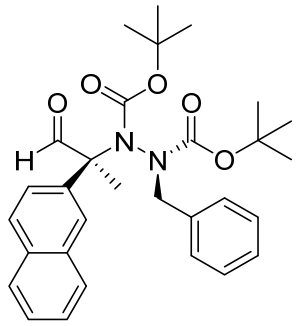
^{13}C NMR (101 MHz, $CDCl_3$) δ 197.73, 197.45, 195.60, 155.42, 154.75, 145.77, 145.49, 140.64, 139.87, 139.59, 137.78, 136.58, 135.85, 135.57, 129.70, 129.42, 128.94, 128.90, 128.76, 128.66, 128.62, 128.48, 128.21, 128.19, 127.93, 127.65, 127.37, 127.26, 127.21, 127.11, 126.98, 126.96, 126.93, 126.83, 126.68, 82.53, 82.20, 71.31, 54.60, 29.68, 28.36, 28.25, 28.08, 27.85, 27.58, 26.65, 26.37, 19.99. **IR** (ATR) ν(max)= 1699 (s) 1679 (s) 1367 (s) 1151 (s) cm^{-1}.

(*S*, R_a)-di-tert-butyl 1-(2-([1,1'-biphenyl]-4-yl)-1-hydroxypropan-2-yl)-2-benzylhydrazine-1,2-dicarboxylate (5er)



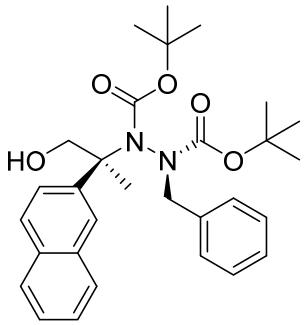
The reaction was carried out following the general reduction procedure. The d.r. and e.e. were determined by HPLC analysis on a Daicel Chiralpak IC column.: hexane/*i*-PrOH 98/2, flow rate 1 mL/min, 25 °C, λ = 220 nm: t_1= 19 min, t_2= 21 min, t_3= 38 min, t_4= 42 min. D.r.= 5:1 and e.e.(major diastereoisomer)= 99%. Peaks 1 and 2: minor diastereoisomer; peaks 3 and 4: major diastereoisomer.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 6.92 (m, 14H), 5.50 – 3.31 (m, 4H), 1.93 – 0.99 (m, 21H).

(*S*, R_a)-di-tert-butyl 1-benzyl-2-(2-(naphthalen-2-yl)-1-oxopropan-2-yl)hydrazine-1,2-dicarboxylate (5f)



The reaction was carried out following the general procedure. Reaction time: 5 days. The crude mixture was purified by flash column chromatography (hexane:Et_2O = 7:3). Yield= 72% (109 mg). Colorless oil.
HRMS-ESI-ORBITRAP (+): calculated for $[C_{30}H_{36}N_2NaO_5]^+$ 527.2516, found 527.2513 $[M+Na]^+$.
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.11 – 9.64 (m, 1H), 8.18 – 6.92 (m, 12H), 5.16 – 4.09 (m, 2H), 2.00 – 0.99 (m, 21H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.09, 197.52, 196.38, 195.72, 155.58, 155.47, 155.16, 154.79, 136.58, 136.39, 135.59, 134.50, 132.91, 132.81, 132.52, 132.39, 130.19, 129.70, 129.54, 129.30, 129.06, 128.82, 128.46, 128.42, 128.38, 128.13, 128.05, 127.95, 127.78, 127.66, 127.50, 127.41, 127.38, 126.77, 126.31, 126.28, 126.19, 126.07, 125.96, 125.29, 125.05, 124.30, 123.90, 83.48, 82.52, 82.38, 82.21, 82.09, 72.85, 71.77, 71.54, 56.36, 54.62, 29.69, 28.37, 28.27, 27.92, 27.86, 27.75, 26.68, 22.56, 20.05, 19.82.
IR (ATR) ν(max)= 1734 (s) 1710 (s) 1694 (s) 1367 (s) 1150 (s) cm^{-1}.

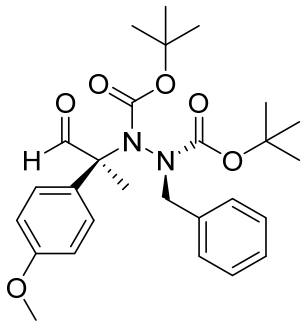
(*S*, R_a)-di-tert-butyl 1-benzyl-2-(1-hydroxy-2-(naphthalen-2-yl)propan-2-yl)hydrazine-1,2-dicarboxylate (5fr)



The reaction was carried out following the general reduction procedure. The dr and ee were determined by HPLC analysis on a Daicel Chiralpak IC column.: hexane/*i*-PrOH 98/2, flow rate 1 mL/min, 25 °C, λ = 220 nm: t_1= 17 min, t_2= 18 min, t_3= 37 min, t_4= 43 min. D.r.= 11:1 and e.e.(major diastereoisomer)= >99%. Peaks 1 and 2: minor diastereoisomer; peaks 3 and 4: major diastereoisomer.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 6.99 (m, 12H), 5.51 – 3.41 (m, 4H), 1.88 – 0.63 (m, 21H).

(*S*, R_a)-di-tert-butyl 1-benzyl-2-(2-(4-methoxyphenyl)-1-oxopropan-2-yl)hydrazine-1,2-dicarboxylate (5g)



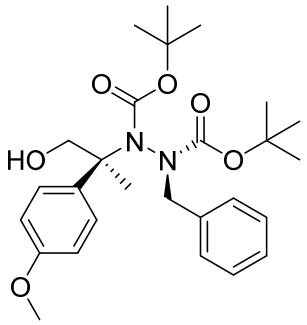
The reaction was carried out following the general procedure. Reaction time: 72h. The crude mixture was purified by flash column chromatography (hexane:Et_2O = 8:2). Yield= 65% (94 mg). Colorless oil.

HRMS-ESI-ORBITRAP (+): calculated for $[C_{27}H_{36}N_2NaO_6]^+$ 507.2466, found 507.2467 $[M+Na]^+$.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (d, *J* = 51.0 Hz, 1H), 7.41 – 6.66 (m, 9H), 5.12 – 4.08 (m, 2H), 3.88 – 3.69 (m, 3H), 1.86 – 1.03 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.07, 196.73, 196.19, 195.70, 163.47, 159.47, 159.14, 159.05, 158.80, 155.48, 155.36, 155.05, 154.68, 136.76, 136.58, 131.47, 130.77, 130.57, 130.33, 129.72, 129.14, 128.99, 128.66, 128.46, 128.13, 128.07, 127.63, 127.44, 127.35, 113.66, 113.64, 113.35, 83.37, 82.42, 82.28, 82.16, 82.00, 81.92, 81.55, 72.25, 71.21, 71.08, 71.00, 70.89, 56.36, 55.44, 55.24, 54.39, 30.30, 29.67, 28.33, 28.22, 28.15, 27.87, 27.82, 27.80, 26.31, 21.89, 19.61, 19.24.

(*S*, R_a)-di-tert-butyl 1-benzyl-2-(1-hydroxy-2-(4-methoxyphenyl)propan-2-yl)hydrazine-1,2-dicarboxylate (5gr)

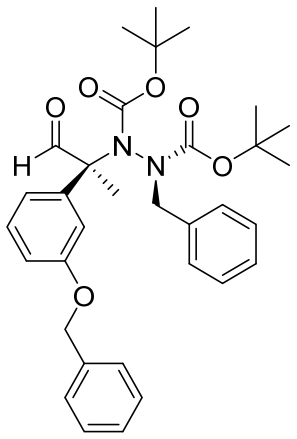


The reaction was carried out following the general reduction procedure. The d.r. and e.e. were determined by HPLC analysis on a Daicel Chiralpak IC column.: hexane/*i*-PrOH 98/2, flow rate 1 mL/min, 25 °C, λ = 220 nm: t_1= 27 min, t_2= 30 min, t_3= 51 min, t_4= 62 min. D.r.= 11:1 and e.e.(major diastereoisomer)= >99%. Peaks 1 and 2: minor diastereoisomer; peaks 3 and 4: major diastereoisomer.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 6.64 (m, 9H), 5.36 – 3.30 (m, 7H), 1.89 – 0.99 (m, 21H).

IR (ATR) ν(max)= 3406 (br, m) 1694 (s) 1367 (s) 1249 (s) 1152 (s) 1067 (s) 1032 (s) cm^{-1}.

(*S*, R_a)-di-tert-butyl 1-benzyl-2-(2-(3-(benzyloxy)phenyl)-1-oxopropan-2-yl)hydrazine-1,2-dicarboxylate (5h)



The reaction was carried out following the general procedure. Reaction time: 4 days. The crude mixture was purified by flash column chromatography (hexane:Et_2O = 7:3). Yield= 50% (84 mg). Colorless oil.

HRMS-ESI-ORBITRAP (+): calculated for $[C_{27}H_{36}N_2NaO_5]^+$ 583.2779, found 583.2772 $[M+Na]^+$.

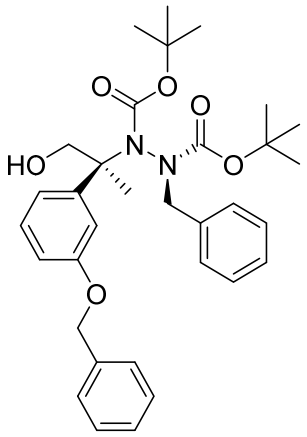
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (d, *J* = 51.7 Hz, 1H), 7.66 – 6.77 (m, 14H), 5.01 (d, *J* = 4.5 Hz, 2H), 4.67 – 4.06 (m, 2H), 1.80 – 1.21 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.16, 195.81, 195.30, 158.76, 156.71, 155.52, 155.34, 155.11, 154.77, 140.59, 137.00, 136.97, 136.75, 136.57, 129.75, 129.63, 129.28, 128.97, 128.56, 128.15,

128.08, 127.95, 127.47, 127.38, 121.31, 120.27, 119.86, 118.75, 114.45, 114.34, 114.15, 113.70, 113.58, 113.12, 83.41, 82.43, 82.32, 82.11, 82.05, 72.67, 71.63, 71.32, 70.18, 69.95, 56.42, 54.38, 29.69, 28.34, 28.24, 27.82, 26.71, 22.39, 19.84, 19.51.

IR (ATR) ν(max)= 1696 (s) 1367 (s) 1149 (s) 1056 (s) 1027 (s) cm^{-1}.

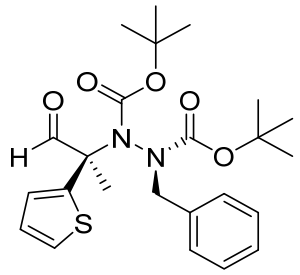
(*S*, R_a)-di-tert-butyl 1-benzyl-2-(2-(3-(benzyloxy)phenyl)-1-hydroxypropan-2-yl)hydrazine-1,2-dicarboxylate (5hr)



The reaction was carried out following the general reduction procedure. The d.r. and e.e. were determined by HPLC analysis on a Daicel Chiralpak IC column.: hexane/*i*-PrOH 98/2, flow rate 1 mL/min, 25 °C, λ = 220 nm: t_1= 20 min, t_2= 23 min, t_3= 46 min, t_4= 58 min. D.r.= 12:1 and e.e.(major diastereoisomer)= >99%. Peaks 1 and 2: minor diastereoisomer; peaks 3 and 4: major diastereoisomer.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 6.72 (m, 14H), 5.02 (d, *J* = 6.5 Hz, 2H), 4.82 – 3.78 (m, 4H), 1.81 – 0.71 (m, 21H).

(*S*, R_a)-di-tert-butyl 1-benzyl-2-(1-oxo-2-(thiophen-2-yl)propan-2-yl)hydrazine-1,2-dicarboxylate (5i)



The reaction was carried out following the general procedure. Reaction time: 72h. The crude mixture was purified by flash column chromatography (hexane:Et_2O = 7:3). Yield= 33% (46 mg). Colorless oil.

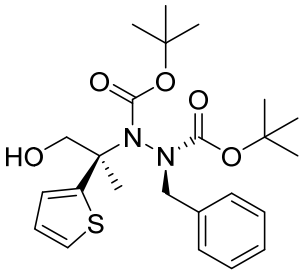
HRMS-ESI-ORBITRAP (+): calculated for $[C_{24}H_{32}N_2NaO_5S]^+$ 483.1924, found 483.1924 $[M+Na]^+$

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 – 9.47 (m, 1H), 7.39 – 6.85 (m, 8H), 5.03 – 4.06 (m, 2H), 1.77 – 1.12 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.54, 194.87, 194.43, 193.94, 192.24, 155.19, 154.87, 154.54, 154.22, 153.94, 142.63, 140.27, 140.15, 136.64, 136.57, 136.36, 136.09, 132.34, 132.32, 129.79, 129.22, 129.15, 128.59, 128.46, 128.28, 128.18, 127.50, 127.41, 127.32, 127.25, 126.96, 126.94, 126.73, 126.62, 126.38, 126.36, 125.56, 125.44, 125.32, 124.78, 124.58, 123.60, 123.42, 83.81, 82.38, 82.24, 81.91, 81.67, 69.73, 69.44, 69.07, 68.61, 56.35, 56.04, 55.20, 54.08, 29.67, 28.34, 28.26, 28.16, 28.01, 27.89, 27.76, 27.53, 27.51, 19.33, 19.10, 19.00.

IR (ATR) ν(max)= 1734 (s) 1692 (s) 1367 (s) 1150 (s) cm^{-1}.

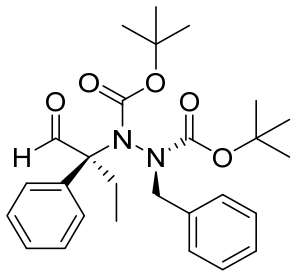
(*S*, R_a)-di-tert-butyl 1-benzyl-2-(1-hydroxy-2-(thiophen-2-yl)propan-2-yl)hydrazine-1,2-dicarboxylate (5ir)



The reaction was carried out following the general reduction procedure. The d.r. and e.e. were determined by HPLC analysis on a Daicel Chiralpak IC: hexane/*i*-PrOH 98/2, flow rate 0.5 mL/min, 25 °C, λ = 220 nm: t_1= 41 min, t_2= 43 min, t_3= 48 min, t_4= 66 min. D.r.= 1.3:1 and e.e.(major diastereoisomer)= 92%. Peaks 1 and 2: minor diastereoisomer; peaks 3 and 4: major diastereoisomer.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 6.85 (m, 7H), 5.13 – 3.30 (m, 4H), 1.82 – 1.10 (m, 21H).

(*S*, R_a)-di-tert-butyl 1-benzyl-2-(1-oxo-2-phenylbutan-2-yl)hydrazine-1,2-dicarboxylate (5j)



The reaction was carried out following the general procedure. (with 1.5 eq of **4a**). Reaction time: 7 days. The crude mixture was purified by flash column chromatography (hexane:Et_2O = 8:2).
Yield= 34% (32 mg). Colorless oil.

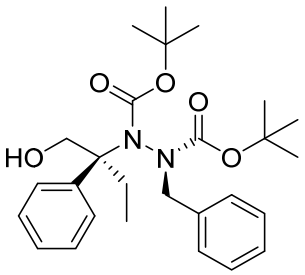
HRMS-ESI-ORBITRAP (+): calculated for $[C_{27}H_{36}N_2NaO_5]^+$ 491.2516, found 491.2516 $[M+Na]^+$.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.30 – 9.49 (m, 1H), 7.73 – 6.89 (m, 10H), 5.46 – 4.10 (m, 2H), 2.75 – 0.52 (m, 23H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.20, 197.40, 196.25, 195.15, 156.26, 155.65, 155.39, 154.92, 154.74, 154.40, 154.13, 152.95, 150.07, 138.07, 137.93, 137.36, 136.95, 136.79, 136.73, 136.45, 136.28, 135.59, 130.50, 130.29, 130.14, 129.93, 129.74, 129.65, 129.58, 129.39, 128.97, 128.77, 128.57, 128.41, 128.36, 128.34, 128.28, 128.26, 128.24, 128.21, 128.16, 128.12, 127.90, 127.60, 127.50, 127.43, 127.36, 127.32, 127.24, 126.95, 83.12, 82.84, 82.11, 82.00, 81.62, 81.34, 81.24, 80.93, 80.83, 80.72, 80.50, 75.14, 74.63, 74.50, 73.65, 73.50, 70.48, 57.01, 56.42, 54.55, 52.56, 28.40, 28.35, 28.33, 28.22, 28.18, 28.13, 27.98, 27.92, 27.81, 27.74, 27.71, 27.39, 26.93, 23.98, 23.64, 23.10, 10.81, 9.24, 9.00, 8.75, 8.58, 8.40.

IR (ATR) ν(max)= 1699 (s) 1367 (s) 1152 (s) cm^{-1}.

(*S*, R_a)-di-tert-butyl 1-benzyl-2-(1-hydroxy-2-phenylbutan-2-yl)hydrazine-1,2-dicarboxylate (5jr)

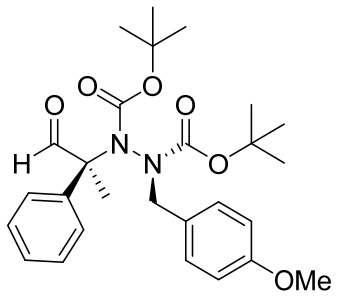


The reaction was carried out following the general reduction procedure, using 1.5 eq of **4a**. The d.r. and e.e. were determined by HPLC analysis on a Phenomenex Lux 5u Cellulose-2 column: hexane/*i*-PrOH 95/5, flow rate 1 mL/min, 25 °C, λ = 220 nm: t_1= 8 min, t_2= 18, t_3= 20, t_4= 27 min. D.r.= 2:1

and e.e.(major diastereoisomer)= >99%. Peaks 1 and 4: minor diastereoisomer; peaks 2 and 3: major diastereoisomer.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 6.66 (m, 10H), 5.47 – 3.64 (m, 4H), 2.65 – 0.42 (m, 23H).

(*S*, R_a)-di-tert-butyl (S)-1-(4-methoxybenzyl)-2-(1-oxo-2-phenylpropan-2-yl)hydrazine-1,2-dicarboxylate (6b)



The reaction was carried out following the general procedure. Reaction time: 48h. The crude mixture was purified by flash column chromatography (hexane:Et_2O = 3:1). Yield=76% (110 mg). Colorless oil. The d.r. and e.e. were determined by HPLC analysis on a Daicel Chiralpak IC column: hexane/*i*-PrOH 98/2, flow rate 1 mL/min, 25 °C, λ = 220 nm: t_1 = 21 min, t_2 = 23 min, t_3 = 25 min, t_4 = 37 min. d.r.= 9.6:1 and e.e.(major diastereoisomer)= >99%. Peaks 1 and 3: minor diastereoisomer; peaks 2 and 4: major diastereoisomer.

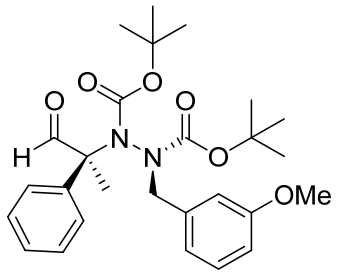
HRMS-ESI-ORBITRAP (+): calculated for $[C_{27}H_{36}N_2NaO_6]^+$ 507.2466, found 507.2457 $[M+Na]^+$.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95-955 (m 1H), 7.49 – 6.63 (m, 9H), 5.13 – 4.08 (m, 2H), 3.82 – 3.68 (m, 3H), 1.58 – 1.12 (m, 21H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 197.52, 196.46, 195.79, 159.04, 156.63, 155.52, 155.34, 155.13, 154.74, 153.15, 139.14, 138.90, 131.03, 130.70, 130.47, 130.19, 129.00, 128.78, 128.24, 128.20, 128.01, 127.83, 127.65, 127.44, 127.24, 126.71, 126.07, 113.52, 83.28, 82.48, 82.34, 82.20, 82.04, 81.95, 72.80, 71.64, 71.54, 71.42, 55.57, 55.28, 55.24, 55.18, 53.85, 29.26, 28.35, 28.31, 28.25, 27.90, 27.87, 27.75, 20.06, 19.84.

IR (ATR) ν(max)= 1695 (s) 1367 (s) 1248 (s) 1150 (s) 1125 (s) cm^{-1}.

(*S*, R_a)-di-tert-butyl (S)-1-(3-methoxybenzyl)-2-(1-oxo-2-phenylpropan-2-yl)hydrazine-1,2-dicarboxylate (6c)



The reaction was carried out following the general procedure. Reaction time: 48h. The crude mixture was purified by flash column chromatography (hexane:Et_2O = 3:1). Yield=70% (101 mg). Colorless oil.

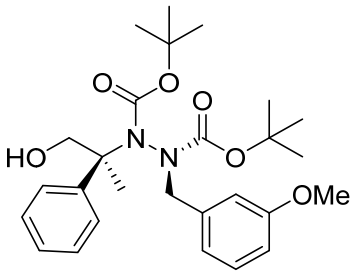
HRMS-ESI-ORBITRAP (+): calculated for $[C_{27}H_{36}N_2NaO_6]^+$ 507.2466, found 507.2451 $[M+Na]^+$.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92-9.62 (m, 1H), 7.43 – 6.46 (m, 9H), 5.17 – 4.09 (m, 2H), 3.68 (m, 3H), 1.62 – 1.10 (m, 21H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 210.82, 206.91, 197.36, 196.24, 195.65, 159.40, 156.73, 155.49, 155.35, 155.06, 154.70, 138.97, 138.78, 138.47, 138.16, 138.09, 129.17, 128.26, 128.21, 128.03, 127.85, 127.68, 127.28, 126.13, 122.06, 121.44, 114.82, 114.50, 114.32, 113.59, 113.27, 83.41, 82.40, 82.27, 82.14, 82.06, 71.63, 71.41, 69.49, 56.43, 56.28, 55.07, 54.99, 54.45, 53.79, 31.72, 30.91, 29.26, 28.33, 28.29, 28.22, 27.89, 27.82, 20.00, 19.69.

IR (ATR) ν(max)= 1696 (s) 1367 (s) 1260 (s) 1150 (s) 1125 (s) cm^{-1}.

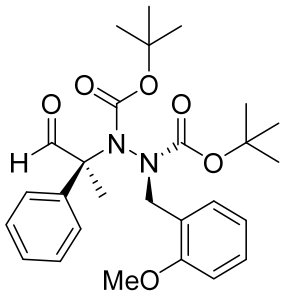
(*S*, R_a)-di-tert-butyl 1-(1-hydroxy-2-phenylpropan-2-yl)-2-(3-methoxybenzyl)hydrazine-1,2-dicarboxylate (6cr)



The reaction was carried out following the general reduction procedure. The d.r. and e.e. were determined by HPLC analysis on a Daicel Chiralpak IC column: hexane/*i*-PrOH 92/8, flow rate 1 mL/min, 25 °C, λ = 220 nm: t_1 = 9 min, t_2 = 11 min, t_3 = 15 min, t_4 = 18 min. D.r.= 7:1 and e.e.(major diastereoisomer)= 99%. Peaks 1 and 2: minor diastereoisomer; peaks 3 and 4: major diastereoisomer.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 6.72 (m, 9H), 5.32 – 3.38 (m, 7H), 1.78 – 1.02 (m, 21H).

(*S*, R_a)-di-tert-butyl (S)-1-(2-methoxybenzyl)-2-(1-oxo-2-phenylpropan-2-yl)hydrazine-1,2-dicarboxylate (6d)



The reaction was carried out following the general procedure, at -5 °C. Reaction time: 5 days. The crude mixture was purified by flash column chromatography (hexane:Et_2O = 3:1). Yield=48% (70 mg). Colorless oil.

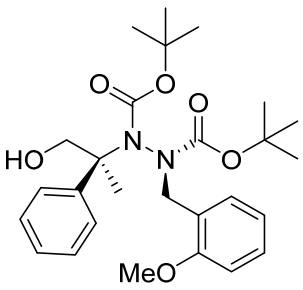
HRMS-ESI-ORBITRAP (+): calculated for $[C_{27}H_{36}N_2NaO_6]^+$ 507.2466, found 507.2452 $[M+Na]^+$.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 – 9.68 (m, 1H), 7.54 – 6.55 (m, 9H), 5.16 – 4.07 (m, 2H), 3.85 – 3.56 (m, 3H), 1.84 – 1.06 (m, 21H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 198.25, 197.56, 197.46, 196.66, 196.45, 157.50, 157.45, 157.32, 157.24, 156.82, 156.06, 155.53, 155.42, 155.34, 155.24, 154.65, 154.36, 153.37, 152.84, 140.46, 139.25, 139.04, 136.75, 136.37, 132.16, 131.68, 131.12, 130.53, 128.74, 128.52, 128.21, 128.17, 128.05, 128.01, 127.89, 127.52, 127.41, 127.32, 127.01, 126.84, 126.59, 125.88, 125.21, 125.14, 124.41, 120.46, 120.29, 120.02, 119.93, 109.93, 109.88, 109.73, 82.99, 82.92, 82.40, 82.04, 81.87, 81.81, 81.78, 81.76, 81.70, 81.61, 81.26, 73.10, 72.05, 71.65, 69.48, 55.02, 54.85, 54.76, 53.80, 51.21, 50.66, 50.27, 49.17, 48.94, 31.72, 31.58, 30.32, 29.69, 29.27, 28.32, 28.29, 28.26, 28.19, 27.78, 22.69, 22.64, 20.80, 20.18, 18.38, 17.88, 14.12.

IR (ATR) ν(max)= 1695 (s) 1367 (s) 1245 (s) 1152 (s) 1131 (s) cm^{-1}.

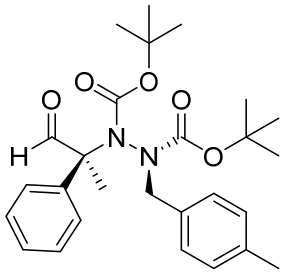
(*S*, R_a)-di-tert-butyl 1-(1-hydroxy-2-phenylpropan-2-yl)-2-(2-methoxybenzyl)hydrazine-1,2-dicarboxylate (6dr)



The reaction was carried out following the general reduction procedure. The d.r. and e.e. were determined by HPLC analysis on a Daicel Chiralpak IC column: hexane/*i*-PrOH 90/10, flow rate 1

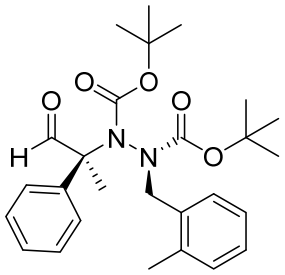
mL/min, 25 °C, λ = 220 nm: t_1 = 8 min, t_2 = 9 min, t_3 = 16 min, t_4 = 23 min. D.r.= 2.4:1 and e.e.(major diastereoisomer)= 97%. Peaks 1 and 2: minor diastereoisomer; peaks 3 and 4: major diastereoisomer.
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 – 6.68 (m, 9H), 5.26 – 3.43 (m, 7H), 1.90 – 0.96 (m, 21H).

(*S*, R_a)-di-tert-butyl (S)-1-(4-methylbenzyl)-2-(1-oxo-2-phenylpropan-2-yl)hydrazine-1,2-dicarboxylate (6e)



The reaction was carried out following the general procedure. Reaction time: 48h. The crude mixture was purified by flash column chromatography (hexane:Et_2O = 3:1). Yield=70% (98 mg). Colorless oil. The d.r. and e.e. were determined by HPLC analysis on a Daicel Chiralpak IC column: hexane/*i*-PrOH 98/2, flow rate 1 mL/min, 25 °C, λ = 220 nm: t_1 = 17 min, t_2 = 19 min, t_3 = 21, t_4 = 33 min. d.r.= 7:1 and e.e.(major diastereoisomer)= >99%. Peaks 1 and 3: minor diastereoisomer; peaks 2 and 4: major diastereoisomer.
HRMS-ESI-ORBITRAP (+): calculated for $[C_{27}H_{36}N_2NaO_5]^+$ 491.2516, found 491.2512 $[M+Na]^+$.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 – 9.63 (m, 1H), 7.41 – 6.76 (m, 9H), 5.13 – 4.08 (m, 2H), 2.30 (m, 3H), 1.79 – 1.09 (m, 21H).
^{13}C NMR (400 MHz, $CDCl_3$) δ 198.09, 197.53, 196.47, 196.18, 196.02, 195.82, 156.96, 156.71, 155.59, 155.37, 155.11, 154.72, 154.17, 153.18, 140.02, 139.12, 138.89, 137.10, 136.32, 135.97, 133.82, 133.58, 133.50, 133.09, 129.73, 129.31, 129.13, 128.90, 128.81, 128.78, 128.56, 128.51, 128.29, 128.23, 128.19, 128.02, 127.80, 127.61, 127.48, 127.21, 126.74, 126.02, 83.24, 82.50, 82.34, 82.21, 82.05, 81.95, 81.85, 81.49, 72.80, 71.67, 71.55, 71.45, 56.88, 56.04, 54.92, 54.23, 28.34, 28.27, 28.23, 28.16, 27.86, 27.82, 27.74, 26.58, 22.65, 22.18, 21.10, 21.08, 20.12, 19.90, 19.04, 18.46.
IR (ATR) ν(max)= 1697 (s) 1367 (s) 1150 (s) 1127 (s) cm^{-1}.

(*S*, R_a)-di-tert-butyl (S)-1-(2-methylbenzyl)-2-(1-oxo-2-phenylpropan-2-yl)hydrazine-1,2-dicarboxylate (6f)



The reaction was carried out following the general procedure. Reaction time: 48h. The crude mixture was purified by flash column chromatography (hexane:Et_2O = 3:1). Yield=69% (97 mg). Colorless oil.

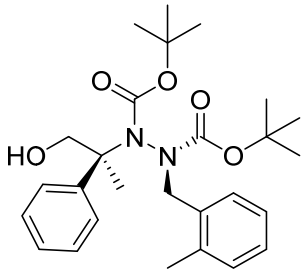
HRMS-ESI-ORBITRAP (+): calculated for $[C_{27}H_{36}N_2NaO_5]^+$ 491.2516, found 491.2514 $[M+Na]^+$.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97-9.74 (m, 1H), 7.43 – 6.58 (m, 9H), 5.18 – 4.02 (m, 2H), 2.33 – 1.87 (m, 3H), 1.68 – 1.04 (m, 21H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 197.85, 196.83, 195.93, 155.89, 155.28, 154.71, 138.85, 137.13, 136.89, 136.35, 134.47, 134.14, 133.09, 130.60, 130.18, 129.77, 128.56, 128.29, 128.24, 128.17, 128.00, 127.84, 127.68, 127.64, 127.39, 126.01, 125.53, 83.54, 83.31, 82.36, 82.15, 72.79, 71.66, 71.25, 65.83, 53.38, 51.20, 28.31, 28.10, 27.79, 19.70, 19.07, 18.38, 15.27.

IR (ATR) ν(max)= 1696 (s) 1367 (s) 1150 (s) cm^{-1}.

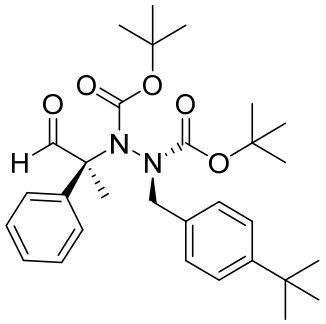
(*S*, R_a)-di-tert-butyl 1-(1-hydroxy-2-phenylpropan-2-yl)-2-(2-methylbenzyl)hydrazine-1,2-dicarboxylate (6fr)



The reaction was carried out following the general reduction procedure. The d.r. and e.e. were determined by HPLC analysis on a Daicel Chiralpak IC column: hexane/*i*-PrOH 95/5, flow rate 1 mL/min, 25 °C, λ = 220 nm: t_1 = 10 min, t_2 = 10.5 min, t_3 = 17 min, t_4 = 22 min. D.r.= 5:1 and e.e.(major diastereoisomer)= 98%. Peaks 1 and 2: minor diastereoisomer; peaks 3 and 4: major diastereoisomer.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.72 – 6.80 (m, 9H), 5.35 – 3.74 (m, 4H), 2.47 – 2.08 (m, 3H), 1.75 – 0.91 (m, 21H).

(*S*, R_a)-di-tert-butyl (S)-1-(4-(tert-butyl)benzyl)-2-(1-oxo-2-phenylpropan-2-yl)hydrazine-1,2-dicarboxylate (6g)



The reaction was carried out following the general procedure. Reaction time: 48h. The crude mixture was purified by flash column chromatography (hexane:Et_2O = 3:1). Yield=67% (104 mg). Colorless oil. The d.r.and e.e. were determined by HPLC analysis on a Daicel Chiralpak IC column: hexane/*i*-PrOH 98/2, flow rate 1 mL/min, 25 °C, λ = 220 nm: t_1 = 13 min, t_2 = 14 min, t_3 = 15 min, t_4 = 18 min. d.r.= 10:1 and e.e.(major diastereoisomer)= 98.6 %. Peaks 1 and 3: minor diastereoisomer; peaks 2 and 4: major diastereoisomer.

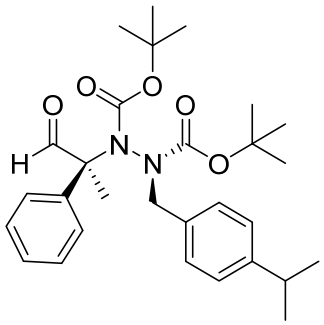
HRMS-ESI-ORBITRAP (+): calculated for $[C_{30}H_{42}N_2NaO_5]^+$ 533.2986, found 533.2980 $[M+Na]^+$.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96-9.61 (m, 1H), 7.48 – 6.98 (m, 9H), 5.09 – 3.91 (m, 2H), 1.64 – 1.07 (m, 30H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 198.07, 197.51, 196.36, 196.17, 195.69, 155.34, 155.16, 155.12, 154.77, 153.20, 150.47, 150.40, 150.27, 140.03, 139.19, 138.94, 137.13, 133.60, 133.54, 133.08, 129.66, 129.12, 128.61, 128.56, 128.29, 128.26, 128.21, 128.04, 127.88, 127.69, 127.31, 126.05, 125.09, 125.06, 83.21, 82.47, 82.24, 82.08, 81.96, 81.89, 81.77, 81.46, 72.84, 71.60, 71.48, 71.42, 55.90, 55.42, 54.27, 53.56, 34.46, 31.57, 31.34, 28.35, 28.30, 28.23, 27.79, 27.73, 26.90, 26.58, 22.64, 22.55, 19.98, 19.74, 19.14, 18.62, 14.12.

IR (ATR) ν(max)= 1695 (s) 1366 (s) 1152 (s) 1129 (s) cm^{-1}.

(*S*, R_a)-di-tert-butyl (S)-1-(4-isopropylbenzyl)-2-(1-oxo-2-phenylpropan-2-yl)hydrazine-1,2-dicarboxylate (6h)



The reaction was carried out following the general procedure. Reaction time: 48h. The crude mixture was purified by flash column chromatography (hexane:Et_2O = 3:1). Yield=70 % (104 mg). Colorless oil. The d.r.and e.e. were determined by HPLC analysis on a Daicel Chiralpak IC column: hexane/*i*-PrOH 98/2, flow rate 1 mL/min, 25 °C, λ = 220 nm: t_1 = 15 min, t_2 = 17 min, t_3 = 18 min, t_4 = 22 min. d.r.= 10:1 and e.e.(major diastereoisomer)= 98.5 %. Peaks 1 and 3: minor diastereoisomer; peaks 2 and 4: major diastereoisomer.

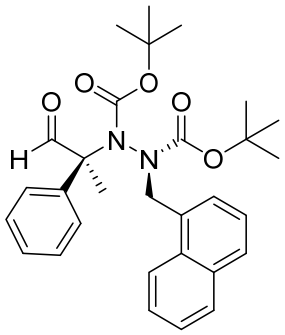
HRMS-ESI-ORBITRAP (+): calculated for $[C_{29}H_{40}N_2NaO_5]^+$ 519.2829, found 519.2823 $[M+Na]^+$.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.75 (m, 1H), 7.42 – 6.98 (m, 9H), 5.08 – 3.96 (m, 2H), 2.86 (m, 1H), 1.84 – 1.10 (m, 27H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 198.09, 197.54, 196.39, 195.72, 156.68, 155.38, 155.20, 155.11, 154.77, 153.18, 148.23, 148.20, 148.07, 140.01, 139.16, 138.93, 137.13, 133.98, 133.90, 133.08, 129.92, 129.36, 128.56, 128.29, 128.26, 128.21, 128.03, 127.87, 127.68, 127.29, 126.75, 126.23, 126.20, 126.05, 82.48, 82.26, 82.11, 81.98, 81.90, 81.79, 81.46, 72.83, 71.61, 71.49, 71.42, 56.86, 55.94, 55.61, 54.44, 53.73, 33.84, 33.75, 29.68, 28.35, 28.29, 28.23, 27.80, 27.74, 26.59, 24.06, 24.00, 23.97, 22.56, 19.99, 19.75.

IR (ATR) ν(max)= 1695 (s) 1367 (s) 1152 (s) 1131 (s) cm^{-1}.

(*S*, R_a)-di-tert-butyl (S)-1-(naphthalen-1-ylmethyl)-2-(1-oxo-2-phenylpropan-2-yl)hydrazine-1,2-dicarboxylate (6i)



The reaction was carried out following the general procedure. Reaction time: 48h. The crude mixture was purified by flash column chromatography (hexane:Et_2O = 3:1). Yield=68% (103 mg). Colorless oil.

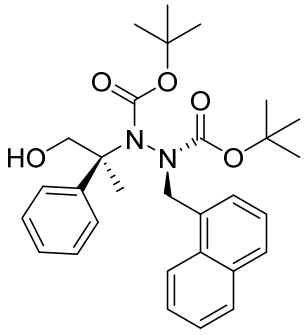
HRMS-ESI-ORBITRAP (+): calculated for $[C_{30}H_{36}N_2NaO_5]^+$ 527.2516, found 527.2508 $[M+Na]^+$.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 – 9.43 (m, 1H), 8.20 – 6.65 (m, 12H), 5.38 – 4.28 (m, 2H), 1.71 – 0.76 (m, 21H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 198.13, 196.79, 196.61, 195.71, 155.37, 155.17, 154.88, 154.74, 154.13, 139.06, 138.92, 137.13, 136.35, 133.63, 133.09, 132.66, 132.41, 132.28, 131.88, 129.34, 128.56, 128.38, 128.34, 128.30, 128.19, 128.06, 127.66, 127.47, 126.97, 126.62, 126.33, 125.95, 125.70, 125.59, 125.04, 124.96, 124.84, 124.34, 123.96, 123.40, 83.57, 82.26, 82.18, 82.15, 81.92, 72.85, 71.65, 71.56, 71.07, 69.48, 65.84, 53.78, 52.55, 52.26, 50.18, 29.27, 28.33, 28.27, 27.98, 27.81, 27.65, 27.46, 27.23, 26.60, 19.87, 19.09, 18.90, 18.68, 18.36, 15.28.

IR (ATR) ν(max)= 1736 (s) 1690 (s) 1367 (s) 1151 (s) cm^{-1}.

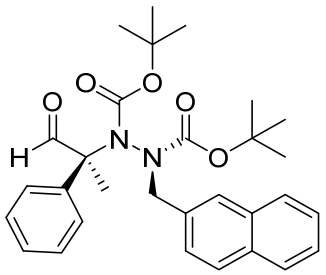
(*S*, R_a)-di-tert-butyl 1-(1-hydroxy-2-phenylpropan-2-yl)-2-(naphthalen-1-ylmethyl)hydrazine-1,2-dicarboxylate (6ir)



The reaction was carried out following the general reduction procedure. The d.r. and e.e. were determined by HPLC analysis on a Daicel Chiralpak IC column: hexane/*i*-PrOH 90/10, flow rate 1

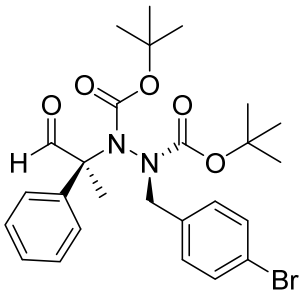
mL/min, 25 °C, λ = 220 nm: t_1 = 7 min, t_2 = 8 min, t_3 = 11 min, t_4 = 12 min. D.r.= 3:1 and e.e.(major diastereoisomer)= 96%. Peaks 1 and 2: minor diastereoisomer; peaks 3 and 4: major diastereoisomer.
^{1}H NMR of alcohol (600 MHz, Chloroform-*d*) δ 7.98 – 6.85 (m, 12H), 5.39 – 3.74 (m, 4H), 1.71 – 0.74 (m, 21H).

(*S*, R_a)-di-tert-butyl (S)-1-(naphthalen-2-ylmethyl)-2-(1-oxo-2-phenylpropan-2-yl)hydrazine-1,2-dicarboxylate (6j)



The reaction was carried out following the general procedure. Reaction time: 48h. The crude mixture was purified by flash column chromatography (hexane:Et_2O=3:1). Yield=66% (100 mg). Colorless oil. The d.r. and e.e. were determined by HPLC analysis on a Daicel Chiralpak OD-H column: hexane/*i*-PrOH 98/2, flow rate 0.5 mL/min, 25 °C, λ = 220 nm: t_1 = 13 min, t_2 = 14 min, t_3 = 18 min, t_4 = 21 min. D.r.= 6:1 and e.e.(major diastereoisomer)= >99%. Peaks 2 and 4: minor diastereoisomer; peaks 1 and 3: major diastereoisomer.
HRMS-ESI-ORBITRAP (+): calculated for $[C_{30}H_{36}N_2NaO_5]^+$ 527.2516, found 527.2509 $[M+Na]^+$.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 – 9.62 (m, 1H), 7.86 – 7.12 (m, 12H), 5.35 – 4.22 (m, 2H), 1.84 – 1.12 (m, 21H).
^{13}C NMR (400 MHz, $CDCl_3$) δ 197.32, 196.08, 195.61, 195.46, 156.81, 155.60, 155.45, 155.30, 155.17, 154.76, 154.51, 154.25, 153.18, 139.79, 138.96, 136.04, 135.78, 134.38, 134.17, 134.00, 133.87, 133.02, 132.76, 132.70, 128.61, 128.33, 128.30, 128.03, 127.96, 127.88, 127.78, 127.49, 127.44, 127.40, 126.99, 126.84, 126.13, 126.06, 125.94, 125.81, 83.46, 82.65, 82.44, 82.35, 82.19, 82.14, 82.06, 81.69, 72.76, 71.67, 71.34, 65.84, 57.41, 57.06, 56.64, 56.37, 55.84, 54.60, 53.43, 30.33, 29.70, 29.28, 28.36, 28.29, 28.26, 28.14, 27.84, 27.79, 22.44, 19.73, 19.47, 18.71, 18.16.
IR (ATR) *v*(max)= 1695 (s) 1367 (s) 1150 (s) cm^{-1}.

(*S*, R_a)-di-tert-butyl (S)-1-(4-bromobenzyl)-2-(1-oxo-2-phenylpropan-2-yl)hydrazine-1,2-dicarboxylate (6k)



The reaction was carried out following the general procedure. Reaction time: 48h. The crude mixture was purified by flash column chromatography (hexane:Et_2O = 3:1). Yield=70% (112 mg). Colorless oil.

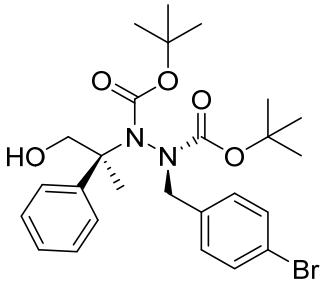
HRMS-ESI-ORBITRAP (+): calculated for $[C_{26}H_{36}BrN_2NaO_5]^+$ 555.1465, found 555.1458 $[M+Na]^+$.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.86 – 9.52 (m, 1H), 7.45 – 6.60 (m, 9H), 5.01 – 3.94 (m, 2H), 2.10 (s, 3H), 1.65 – 1.06 (m, 18H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 206.76, 196.69, 195.64, 195.10, 156.61, 155.40, 155.31, 155.03, 154.57, 154.30, 154.04, 153.38, 153.04, 139.94, 139.52, 138.69, 136.27, 135.96, 135.82, 135.77, 135.59, 131.30, 131.23, 131.20, 131.13, 130.80, 130.47, 130.18, 129.77, 128.33, 128.15, 127.97, 127.86, 127.41, 127.26, 127.23, 126.10, 121.44, 121.23, 121.13, 120.98, 83.52, 83.33, 82.71, 82.57, 82.48, 82.30, 82.23, 81.84, 72.92, 72.67, 71.66, 71.51, 71.29, 69.43, 56.20, 56.03, 55.77, 55.08, 54.03, 53.80, 30.83, 29.23, 28.26, 28.16, 27.90, 27.84, 27.72, 22.14, 21.62, 19.67, 19.21, 18.76, 18.27.

IR (ATR) ν(max)= 1697 (s) 1367 (s) 1149 (s) 1127 (s) cm^{-1}.

(*S*, R_a)-di-tert-butyl 1-(4-bromobenzyl)-2-(1-hydroxy-2-phenylpropan-2-yl)hydrazine-1,2-dicarboxylate (6kr)

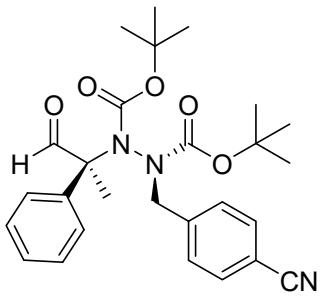


The reaction was carried out following the general reduction procedure. The d.r. and e.e. were determined by HPLC analysis on Phenomenex Lux 5u Cellulose-2 column: hexane/*i*-PrOH 90/10, flow rate 1 mL/min, 25 °C, λ = 220 nm: t_1 = 6 min, t_2 = 7 min, t_3 = 9 min, t_4 = 22 min. D.r.= 8.5:1 and e.e.(major diastereoisomer)= 99%. Peaks 1 and 2: minor diastereoisomer; peaks 3 and 4: major

diastereoisomer. The reported HPLC chromatogram is referred to the large-scale reaction (d.r.= 7:1, e.e.= 95.5%).

^{1}H NMR: (600 MHz, $CDCl_3$) δ 7.73 – 6.91 (m, 9H), 5.29 – 3.72 (m, 4H), 1.76 – 0.95 (m, 21H).

(*S*, R_a)-di-tert-butyl (S)-1-(4-cyanobenzyl)-2-(1-oxo-2-phenylpropan-2-yl)hydrazine-1,2-dicarboxylate (6l)



The reaction was carried out following the general procedure, at r.t. Reaction time: 48h. The crude mixture was purified by flash column chromatography (hexane:Et_2O = 2:1). Yield=42% (60 mg). Colorless oil. The d.r. and e.e. were determined by HPLC analysis on a Daicel Chiralpak IC column: hexane/*i*-PrOH 90/10, flow rate 1 mL/min, 25 °C, λ = 220 nm: t_1 = 24 min, t_2 = 28 min, t_3 = 31 min, t_4 = 36 min. D.r.= 4:1 and e.e.(major diastereoisomer)= 98%. Peaks 2 and 4: minor diastereoisomer; peaks 1 and 3: major diastereoisomer.

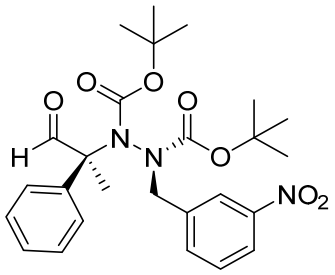
HRMS-ESI-ORBITRAP (+): calculated for $[C_{27}H_{33}N_3NaO_5]^+$ 502.2312, found 502.2305 $[M+Na]^+$.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 – 9.54 (m, 1H), 7.55 – 6.72 (m, 9H), 5.02 – 4.02 (m, 2H), 1.75 – 1.09 (m, 21H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 196.39, 196.02, 195.17, 194.89, 194.61, 156.61, 155.51, 154.98, 154.45, 153.03, 142.47, 142.03, 139.04, 138.38, 138.09, 131.94, 131.90, 131.77, 129.85, 129.26, 128.90, 128.68, 128.50, 128.33, 128.18, 127.76, 127.68, 127.43, 127.39, 127.22, 126.25, 118.66, 111.17, 110.92, 83.90, 83.08, 82.86, 82.75, 82.64, 82.60, 82.27, 72.69, 71.90, 71.65, 71.35, 69.47, 65.81, 57.06, 56.37, 55.99, 54.88, 53.78, 31.71, 30.30, 29.25, 28.26, 28.17, 28.07, 28.01, 27.95, 27.75, 21.58, 19.39, 18.59, 15.26.

IR (ATR) ν(max)= 2229 (s) 1697 (s) 1368 (s) 1149 (s) cm^{-1}.

(*S*, R_a)-di-tert-butyl (S)-1-(3-nitrobenzyl)-2-(1-oxo-2-phenylpropan-2-yl)hydrazine-1,2-dicarboxylate (6m)



The reaction was carried out following the general procedure. Reaction time: 48h. The crude mixture was purified by flash column chromatography (hexane:Et_2O = 2:1). Yield=65% (98 mg). Colorless oil. The d.r. and e.e. were determined by HPLC analysis on a Phenomenex Lux 5u Cellulose-2 column: hexane/*i*-PrOH 90/10, flow rate 1 mL/min, 25 °C, λ = 220 nm: t_1 = 10 min, t_2 = 11 min, t_3 = 12 min, t_4 = 15 min. D.r.= 6:1 and e.e.(major diastereoisomer)= 98%. Peaks 2 and 3: minor diastereoisomer; peaks 1 and 4: major diastereoisomer.

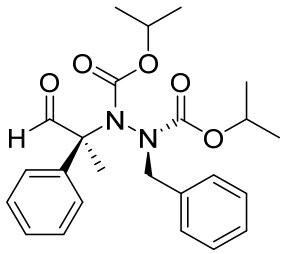
HRMS-ESI-ORBITRAP (+): calculated for $[C_{26}H_{33}N_3NaO_7]^+$ 522.2211, found 522.2202 $[M+Na]^+$.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 – 9.56 (m, 1H), 8.11 – 7.11 (m, 9H), 5.02 – 4.06 (m, 2H), 1.77 – 1.15 (m, 21H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 195.99, 195.53, 194.90, 194.41, 156.55, 156.24, 155.72, 155.51, 155.33, 155.03, 154.86, 154.52, 154.23, 154.02, 153.02, 148.20, 148.00, 139.12, 139.02, 138.89, 138.78, 138.31, 138.13, 135.43, 135.26, 135.05, 134.15, 133.71, 129.08, 128.93, 128.52, 128.41, 128.36, 128.23, 128.04, 127.79, 127.34, 127.19, 126.85, 126.31, 125.33, 123.93, 123.52, 123.28, 123.01, 122.34, 122.13, 122.08, 83.97, 83.07, 82.86, 82.78, 82.52, 72.92, 72.64, 71.80, 71.59, 71.29, 56.45, 55.73, 54.48, 31.54, 30.29, 29.24, 28.24, 28.15, 28.09, 27.93, 27.76, 25.21, 22.61, 21.49, 21.13, 19.21, 18.58, 18.42, 18.22, 14.09.

IR (ATR) ν(max)= 1698 (s) 1528 (s) 1368 (s) 1346 (s) 1148 (s) cm^{-1}.

(*S*, R_a)-diisopropyl 1-benzyl-2-(1-oxo-2-phenylpropan-2-yl)hydrazine-1,2-dicarboxylate (7)



The reaction was carried out following the general procedure. Reaction time: 48h. The crude mixture was purified by flash column chromatography (hexane:Et_2O = 8:2). Yield= 56% (48 mg). Colorless oil.

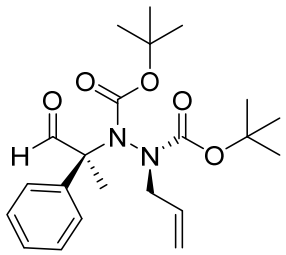
HRMS-ESI-ORBITRAP (+): calculated for $[C_{24}H_{30}N_2NaO_5]^+$ 449.2047, found 449.2047 $[M+Na]^+$. The d.r. and e.e. were determined by HPLC analysis on a Daicel Chiralpak IC: hexane/*i*-PrOH 90/10, flow rate 1 mL/min, 25 °C, λ = 220 nm: t_1= 16 min, t_2= 16 min, t_3= 23 min, t_4= 40 min. D.r.= 6.4:1 and e.e.(major)= >99%. Peaks 1 and 2: minor diastereoisomer; peaks 3 and 4: major diastereoisomer.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 – 9.50 (m, 1H), 7.59 – 6.93 (m, 10H), 5.21 – 4.23 (m, 4H), 1.81 – 0.74 (m, 15H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.13, 196.21, 195.79, 157.22, 156.58, 156.45, 156.27, 155.60, 155.34, 154.89, 145.91, 141.01, 138.77, 138.63, 136.60, 136.35, 136.29, 129.56, 129.15, 128.49, 128.44, 128.32, 128.29, 128.24, 128.16, 127.91, 127.80, 127.65, 127.52, 127.38, 127.21, 127.09, 126.98, 126.93, 126.17, 126.03, 125.36, 72.89, 72.05, 71.99, 71.87, 71.32, 71.01, 70.86, 70.75, 70.29, 65.23, 56.20, 56.02, 55.21, 29.68, 25.20, 22.20, 22.07, 21.92, 21.82, 21.46, 21.31, 20.27, 19.86, 19.61.

IR (ATR) ν(max)= 1699 (s) 1374 (s) 1105 (s) cm^{-1}.

(*S*, R_a)-di-tert-butyl (S)-1-allyl-2-(1-oxo-2-phenylpropan-2-yl)hydrazine-1,2-dicarboxylate (8)



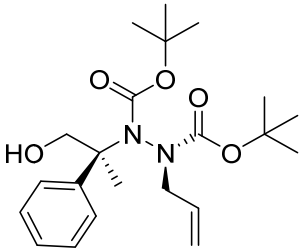
The reaction was carried out following the general procedure, at r.t. Reaction time: 6 days. The crude mixture was purified by flash column chromatography (hexane:Et_2O = 3:1). Yield=40% (50 mg). Colorless oil.

HRMS-ESI-ORBITRAP (+): calculated for $[C_{22}H_{32}N_2NaO_5]^+$ 427.2203, found 427.2202 $[M+Na]^+$.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 – 9.61 (m, 1H), 7.60 – 7.18 (m, 5H), 6.07 – 5.65 (m, 1H), 5.20 – 4.90 (m, 2H), 4.27 – 3.64 (m, 2H), 1.69 – 1.37 (m, 18H), 1.27 – 1.11 (m, 3H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 197.07, 196.38, 195.87, 155.36, 154.97, 154.86, 154.60, 153.20, 138.94, 138.66, 133.74, 133.58, 133.23, 128.22, 128.09, 127.78, 127.63, 127.41, 126.99, 126.90, 126.12, 118.11, 117.84, 117.57, 83.22, 82.58, 82.38, 82.09, 81.73, 72.73, 71.61, 71.47, 56.17, 55.01, 54.20, 30.30, 29.67, 28.32, 28.21, 28.10, 28.07, 27.70, 22.39, 20.50, 20.07.

(*S*, R_a)-di-tert-butyl 1-allyl-2-(1-hydroxy-2-phenylpropan-2-yl)hydrazine-1,2-dicarboxylate (8r)

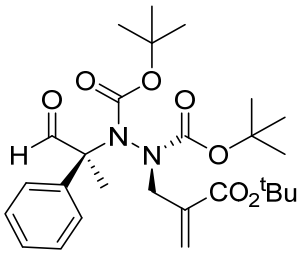


The reaction was carried out following the general reduction procedure. The d.r. and e.e. were determined by HPLC analysis on Daicel Chiralpak IC column: hexane/*i*-PrOH 97.5/2.5, flow rate 1 mL/min, 25 °C, λ = 220 nm: t_1 = 12 min, t_2 = 13 min, t_3 = 22 min, t_4 = 46 min. D.r.= 6:1 and e.e.(major diastereoisomer)= 96%. Peaks 1 and 2: minor diastereoisomer; peaks 3 and 4: major diastereoisomer. The reported HPLC chromatogram is referred to the reaction with the second step at -5°C (d.r.= 15:1, e.e.>99%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 6.97 (m, 6H), 6.18 – 3.43 (m, 8H), 1.92 – 0.86 (m, 21H).

IR (ATR) ν(max)= 3406 (br,m) 1715 (s) 1367 (s) 1144 (s) 1069 (s) cm^{-1}.

(*S*, R_a)-di-tert-butyl (S)-1-(2-(tert-butoxycarbonyl)allyl)-2-(1-oxo-2-phenylpropan-2-yl)hydrazine-1,2-dicarboxylate (9)



The reaction was carried out following the general procedure. Reaction time: 72h. The crude mixture was purified by flash column chromatography (hexane:Et_2O = 3:1). Yield=40% (60 mg). Colorless oil. The d.r. and e.e. were determined by HPLC analysis on a Daicel Chiralpak IC column: hexane/*i*-PrOH 98/2, flow rate 1 mL/min, 25 °C, λ = 220 nm: t_1 = 13 min, t_2 = 14 min, t_3 = 15 min, t_4 = 17 min. D.r.= 4.7:1 and e.e.(major diastereoisomer)= 90%. Peaks 1 and 4: minor diastereoisomer; peaks 2 and 3: major diastereoisomer.

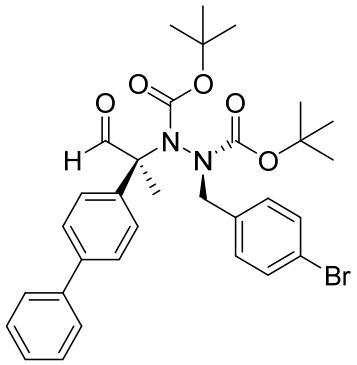
HRMS-ESI-ORBITRAP (+): calculated for $[C_{27}H_{40}N_2NaO_7]^+$ 527.2728, found 527.2717 $[M+Na]^+$.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 – 9.59 (m, 1H), 7.60 – 7.17 (m, 5H), 6.20 – 3.56 (m, 4H), 1.84 – 1.07 (m, 30H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 197.19, 195.30, 194.05, 193.72, 165.22, 155.71, 155.43, 154.69, 154.58, 154.36, 152.88, 138.22, 137.10, 136.25, 136.16, 135.61, 135.49, 133.07, 128.54, 128.51, 128.34, 128.27, 127.94, 127.37, 127.09, 126.94, 126.33, 126.01, 125.85, 125.34, 83.55, 83.15, 82.95, 82.81, 82.42, 82.07, 81.58, 81.02, 80.88, 80.81, 72.07, 71.99, 71.70, 54.38, 54.06, 53.01, 31.54, 29.65, 29.24, 28.19, 28.11, 28.02, 28.00, 27.93, 27.73, 26.57, 22.61, 19.62, 19.48, 18.71, 17.14, 17.01, 14.08.

IR (ATR) ν(max)= 1702 (s) 1367 (s) 1143 (s) cm^{-1}.

(*S*, R_a)-di-tert-butyl 1-(2-([1,1'-biphenyl]-4-yl)-1-oxopropan-2-yl)-2-(4-bromobenzyl)hydrazine-1,2-dicarboxylate (10ek)



The reaction was carried out following the general procedure. Reaction time: 72h. The crude mixture was purified by flash column chromatography (hexane:Et_2O = 8:2). Yield= 64% (117 mg). White solid.

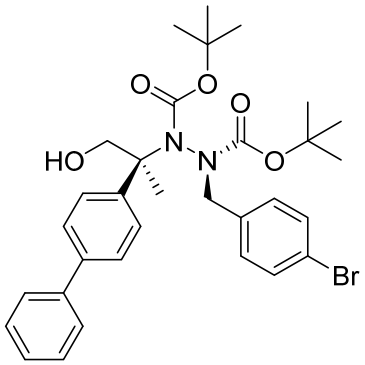
HRMS-ESI-ORBITRAP (+): calculated for $[C_{32}H_{37}BrN_2NaO_5]^+$ 631.1778, found 631.1775 $[M+Na]^+$.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 – 9.62 (m, 1H), 7.82 – 6.68 (m, 13H), 5.06 – 3.97 (m, 2H), 1.91 – 1.13 (m, 21H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.78, 195.57, 195.16, 155.64, 155.45, 155.12, 154.64, 154.31, 154.07, 141.08, 140.82, 140.41, 140.29, 140.17, 137.61, 135.90, 135.61, 134.81, 134.65, 131.26, 131.21, 131.17, 130.48, 129.76, 128.89, 128.81, 127.99, 127.81, 127.68, 127.64, 127.46, 127.11, 127.08, 127.03, 126.91, 126.75, 121.51, 121.20, 121.05, 82.76, 82.66, 82.44, 82.30, 81.99, 71.43, 71.23, 56.34, 55.31, 54.29, 30.91, 29.68, 28.35, 28.15, 27.98, 27.93, 19.87, 19.70, 18.85, 18.42.

IR (ATR) ν(max)= 1698 (s) 1366 (s) 1152 (s) cm^{-1}.

(*S*, R_a)-di-tert-butyl 1-(2-([1,1'-biphenyl]-4-yl)-1-hydroxypropan-2-yl)-2-(4-bromobenzyl)hydrazine-1,2-dicarboxylate (10ekr)

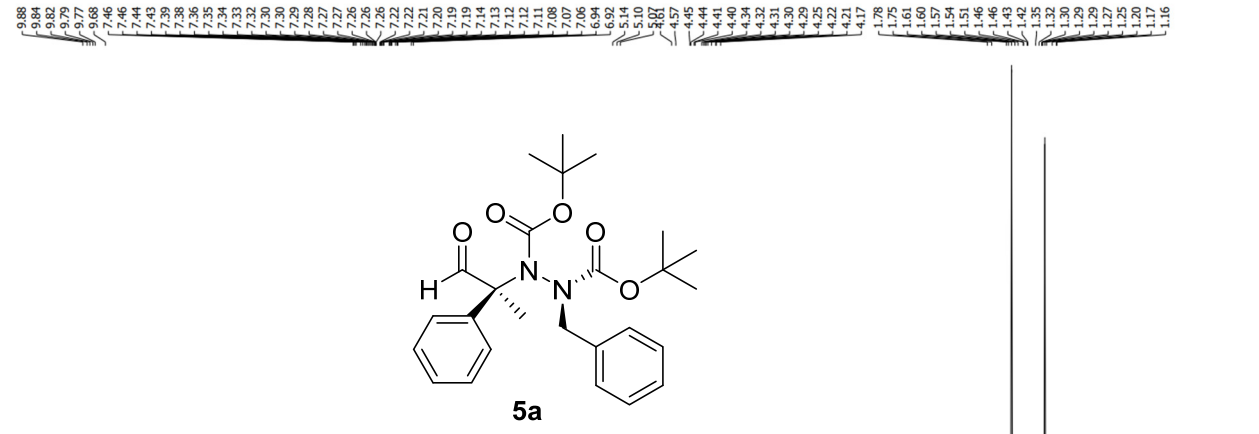


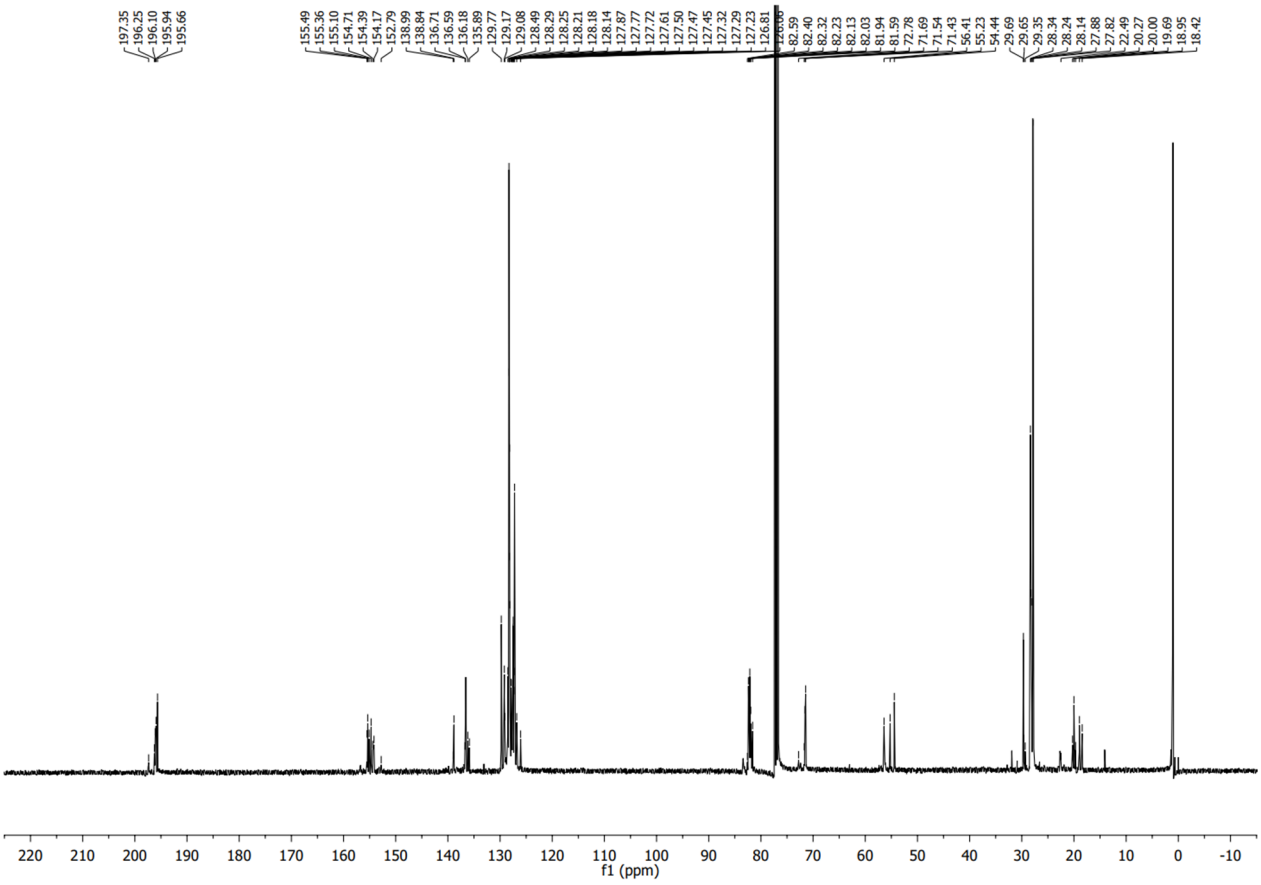
The reaction was carried out following the reported one-pot procedure. The crude mixture was purified by flash column chromatography (hexane:Et_2O = 8:2). Yield= 64% (117 mg). White solid.

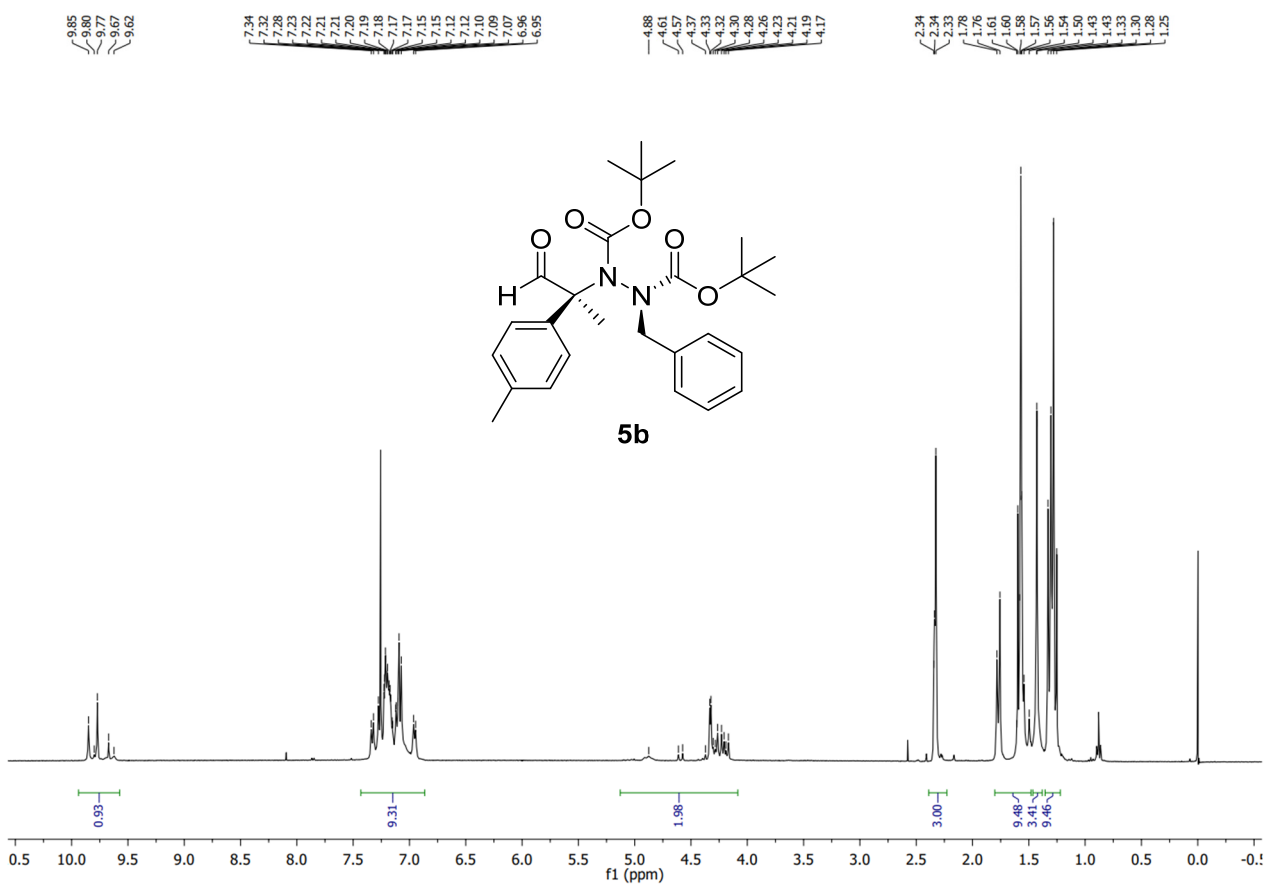
The d.r. and e.e. were determined by HPLC analysis on a Phenomenex Lux 5u Cellulose-2 column: hexane/*i*-PrOH 98/2, flow rate 1 mL/min, 25 °C, λ = 220 nm: t_1= 25 min, t_2= 42 min, t_3= 78 min, t_4= 99 min. D.r.= 8:1 and e.e.(major diastereoisomer)= >99%. Peaks 1 and 2: major diastereoisomer; peaks 3 and 4: minor diastereoisomer.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 6.80 (m, 13H), 5.23 – 3.15 (m, 4H), 1.89 – 0.96 (m, 21H).

NMR traces



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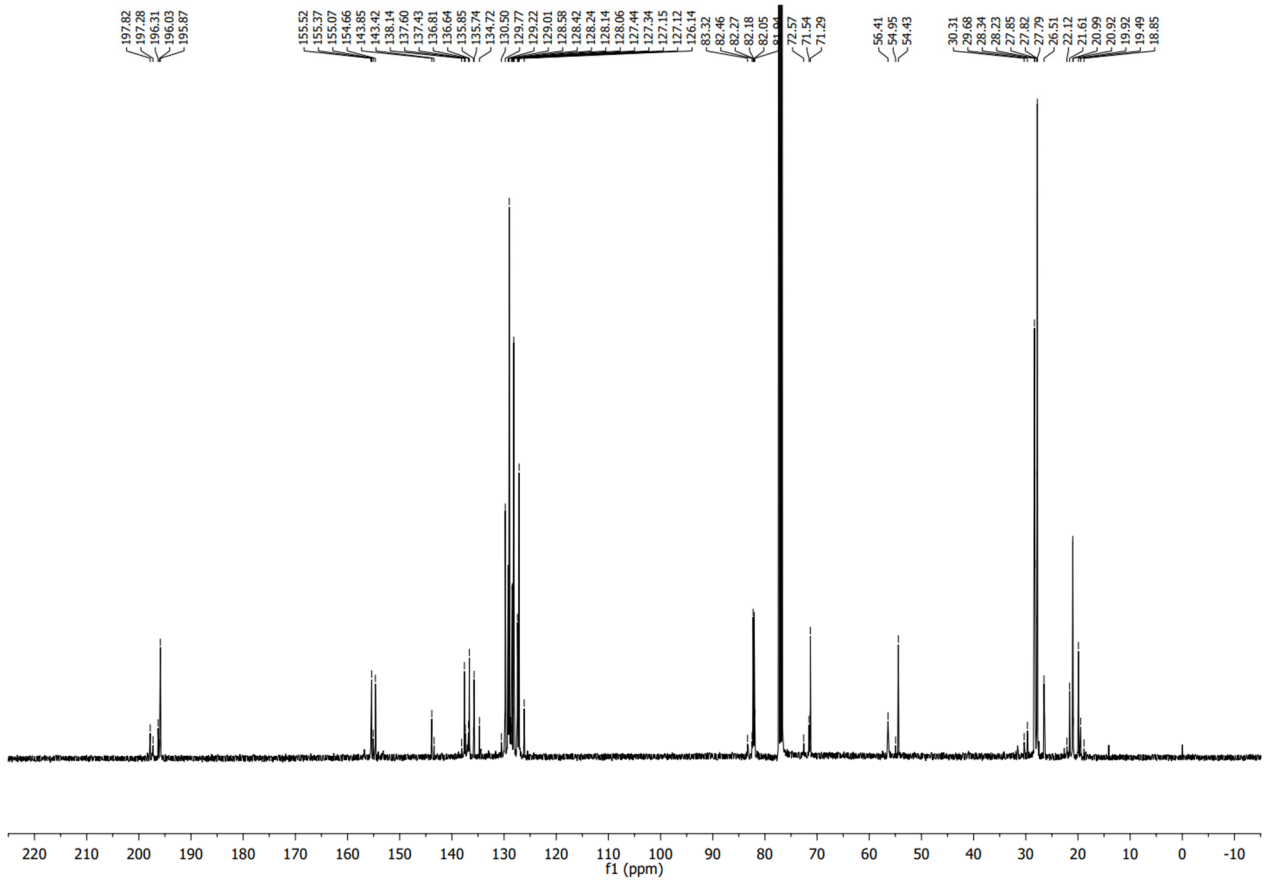
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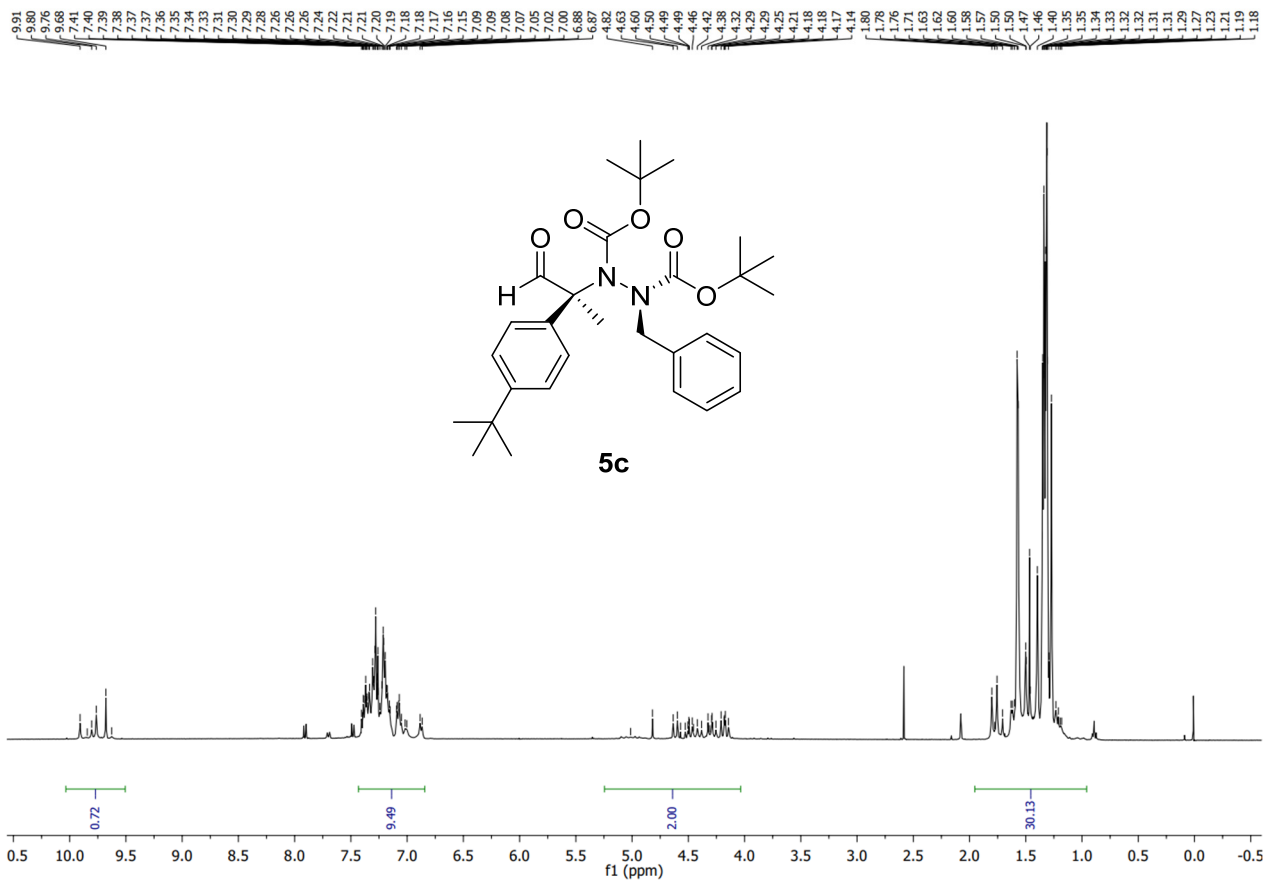
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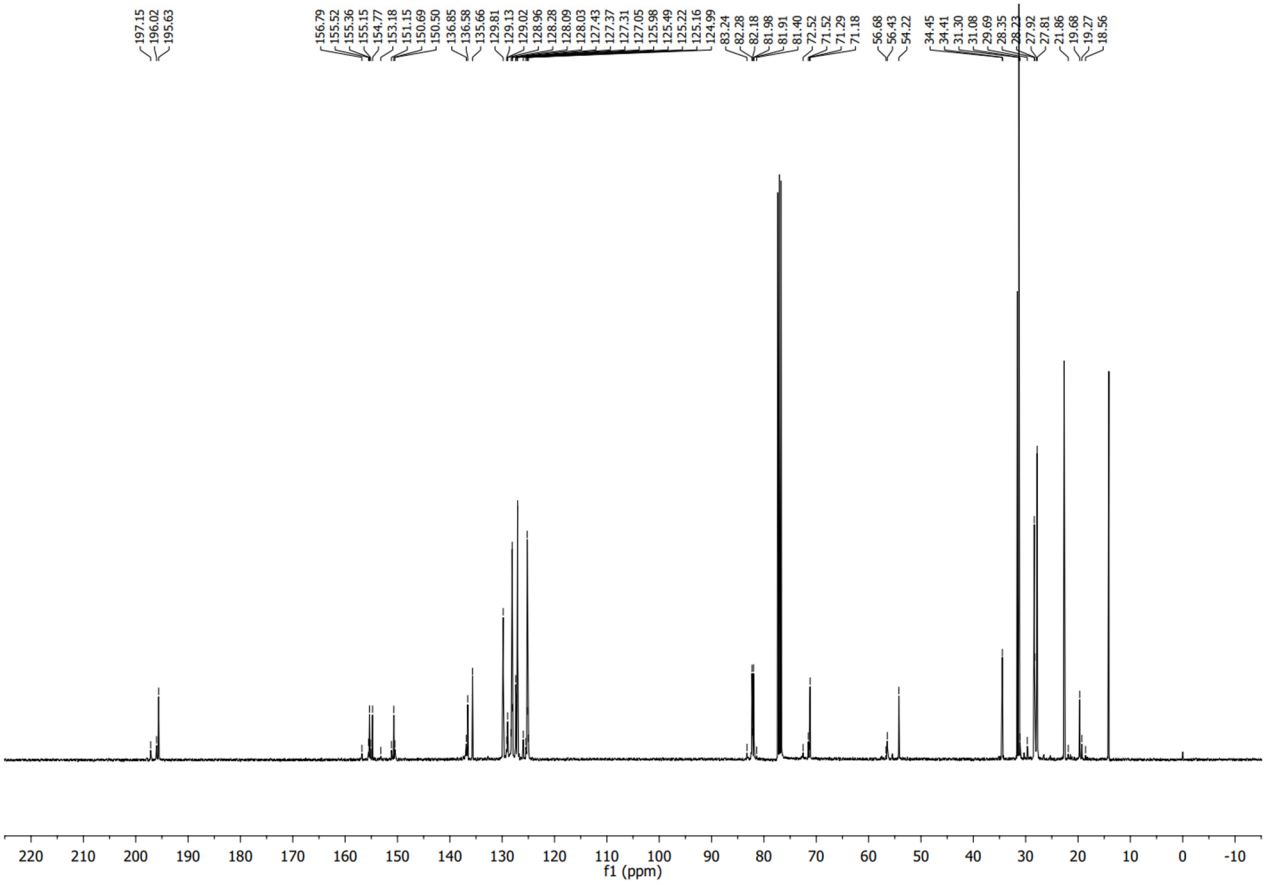
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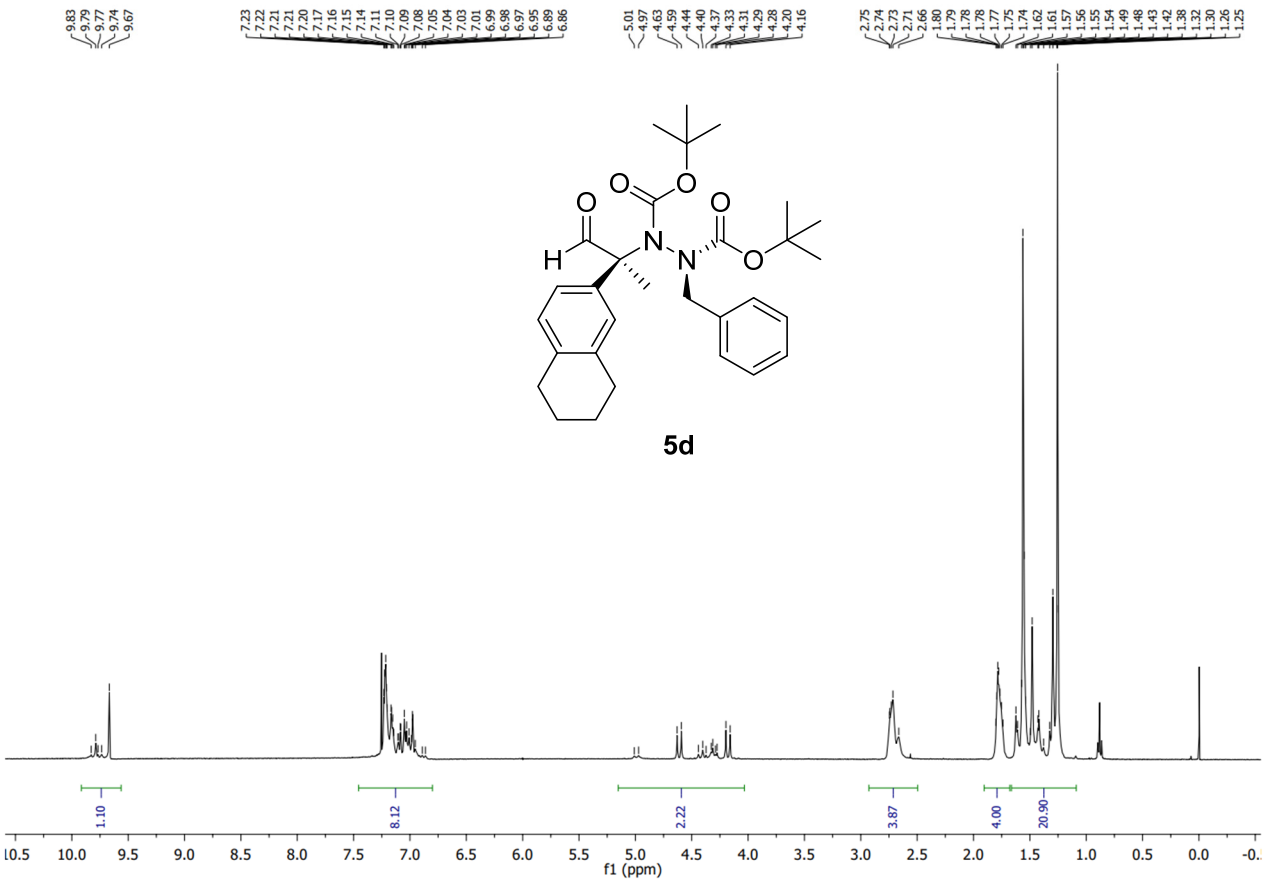
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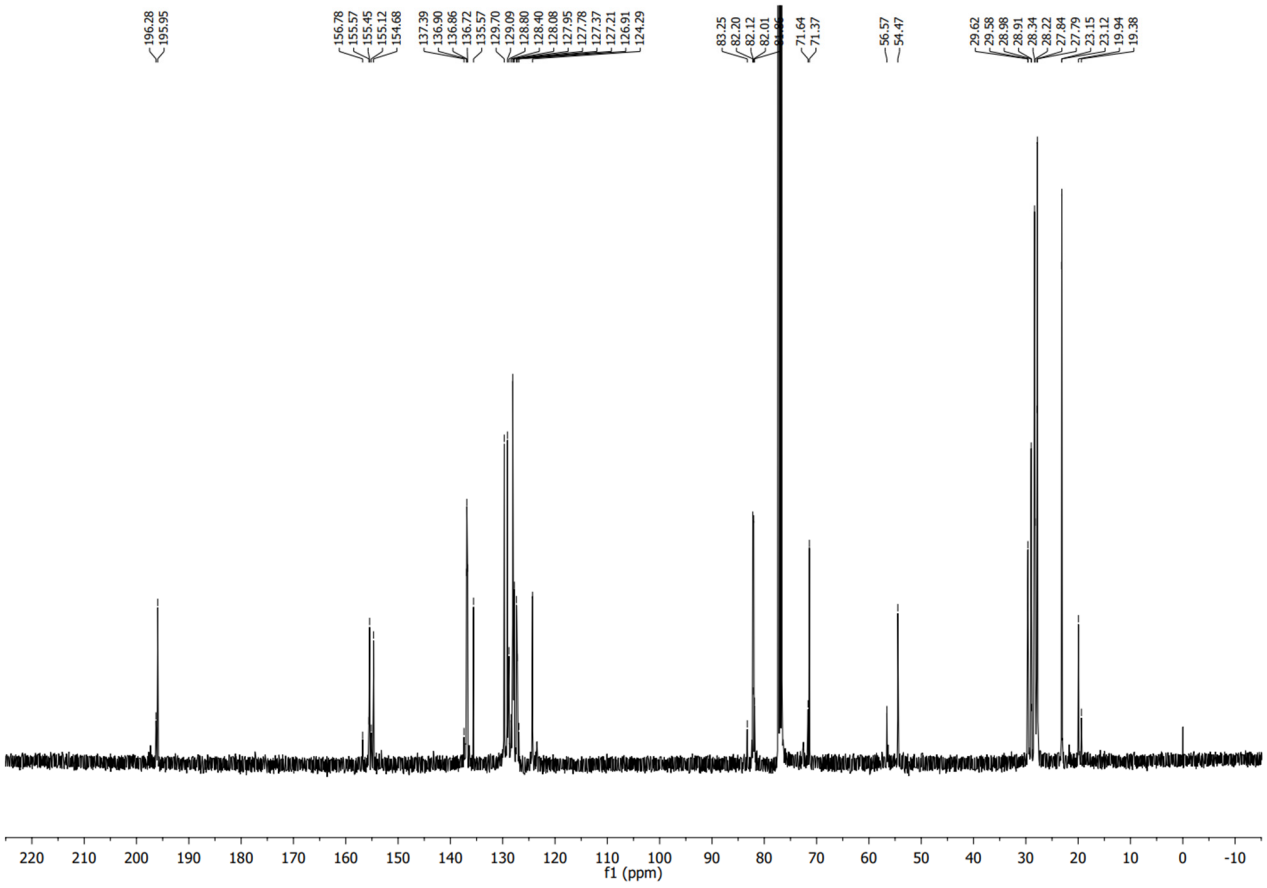
5d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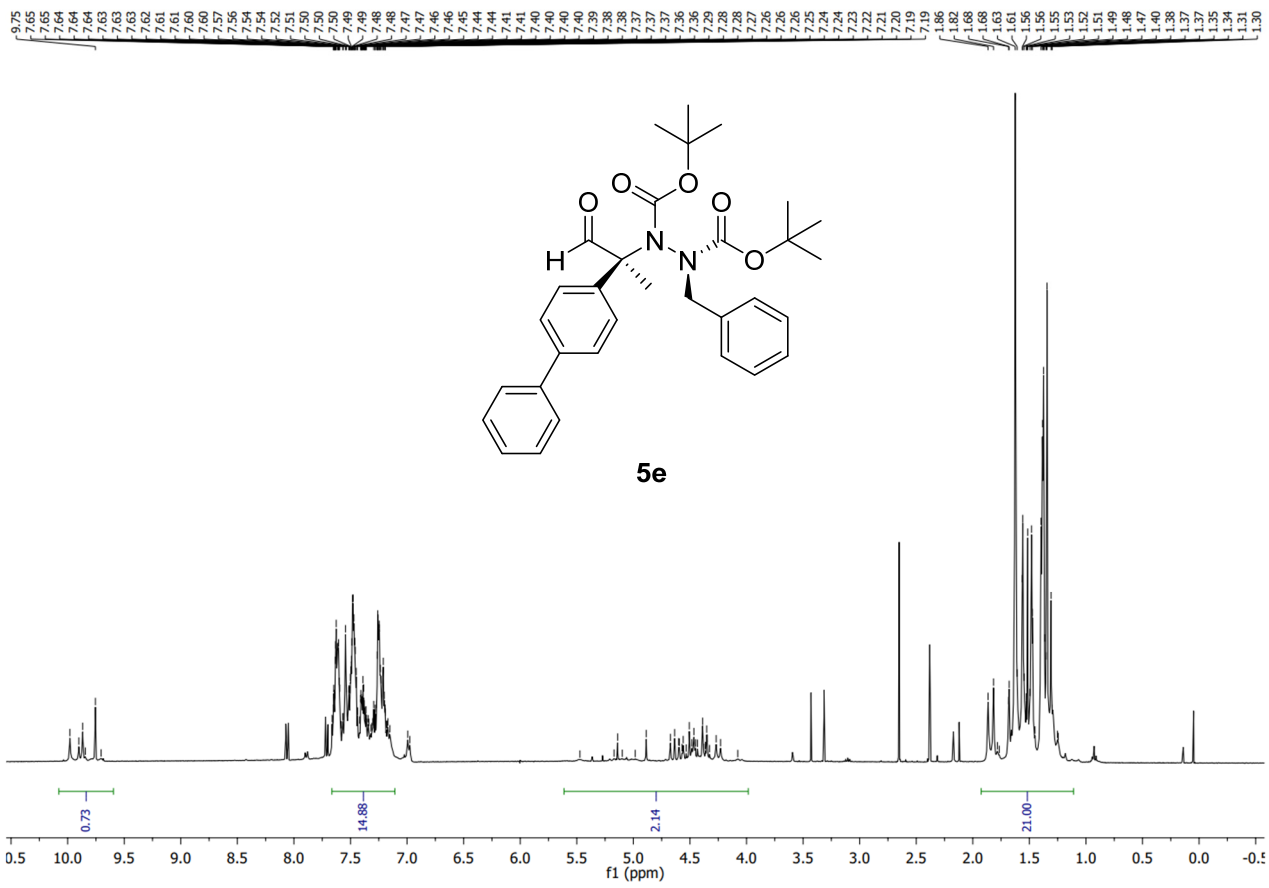
f1 (ppm)



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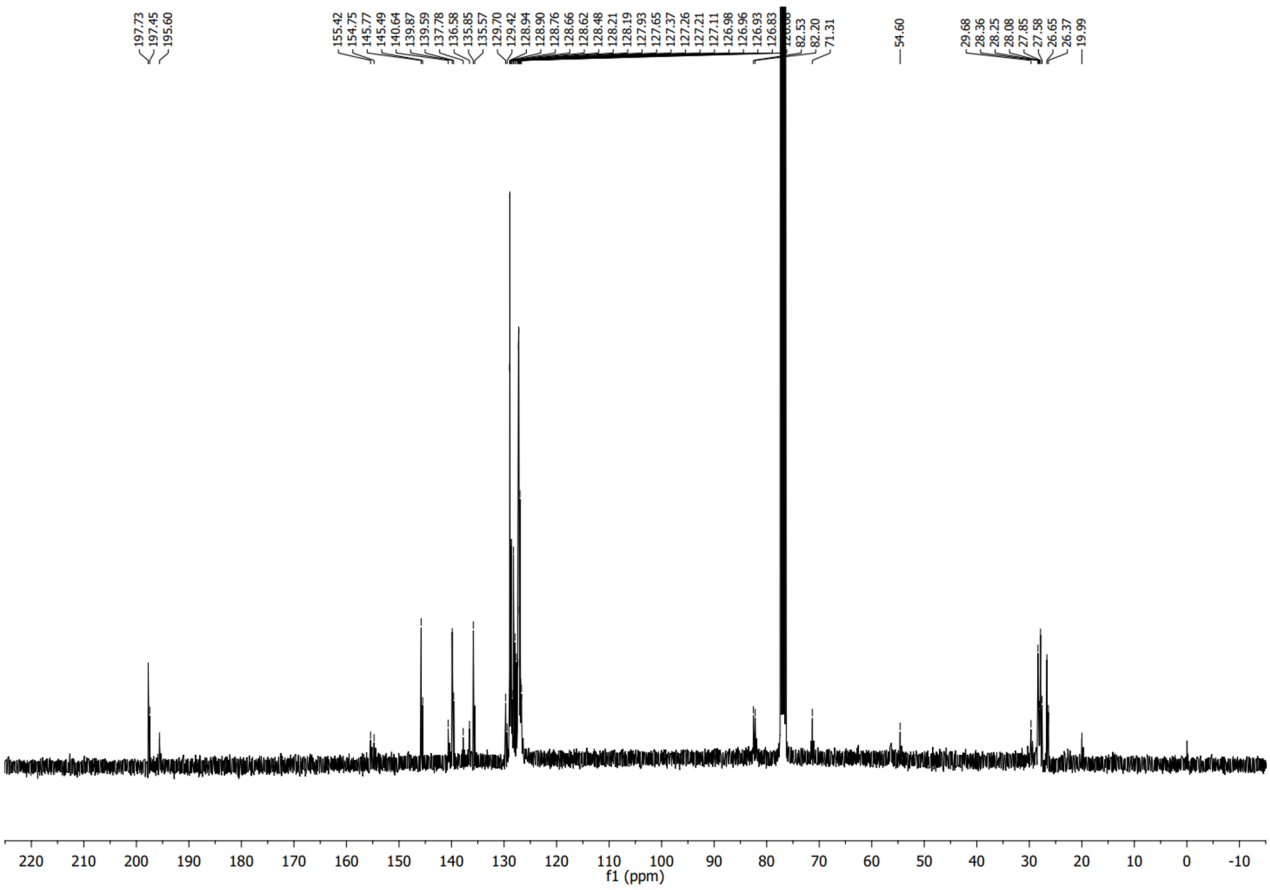

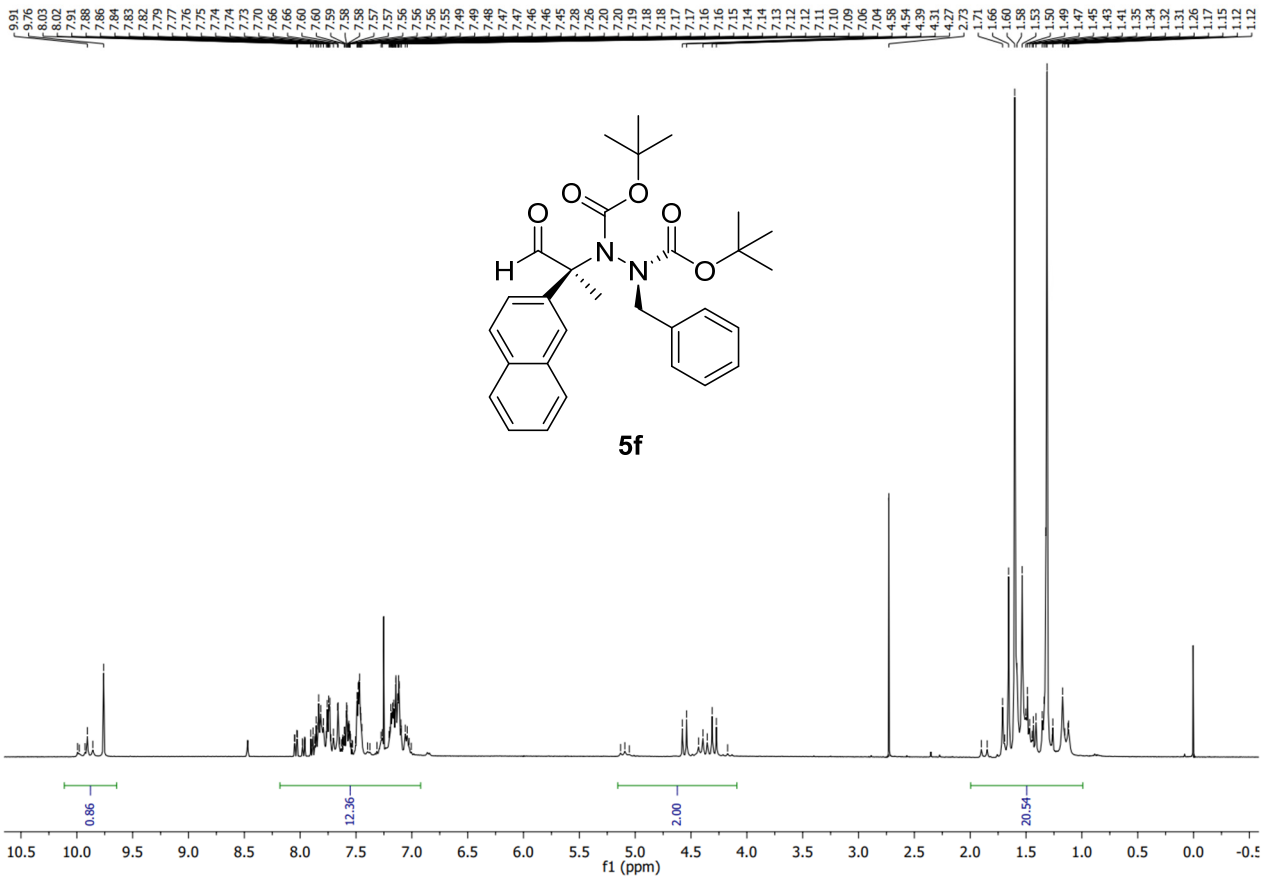
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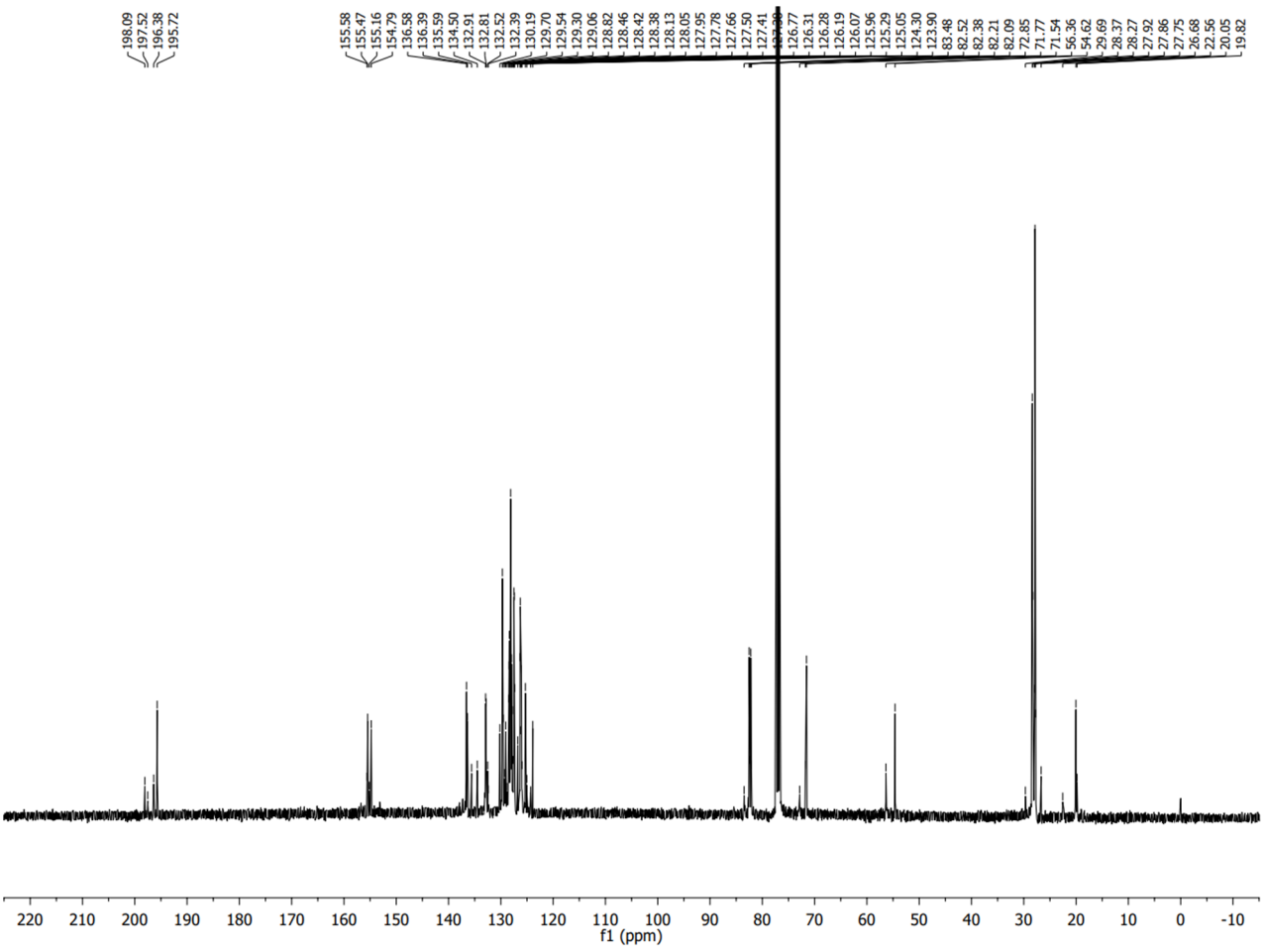
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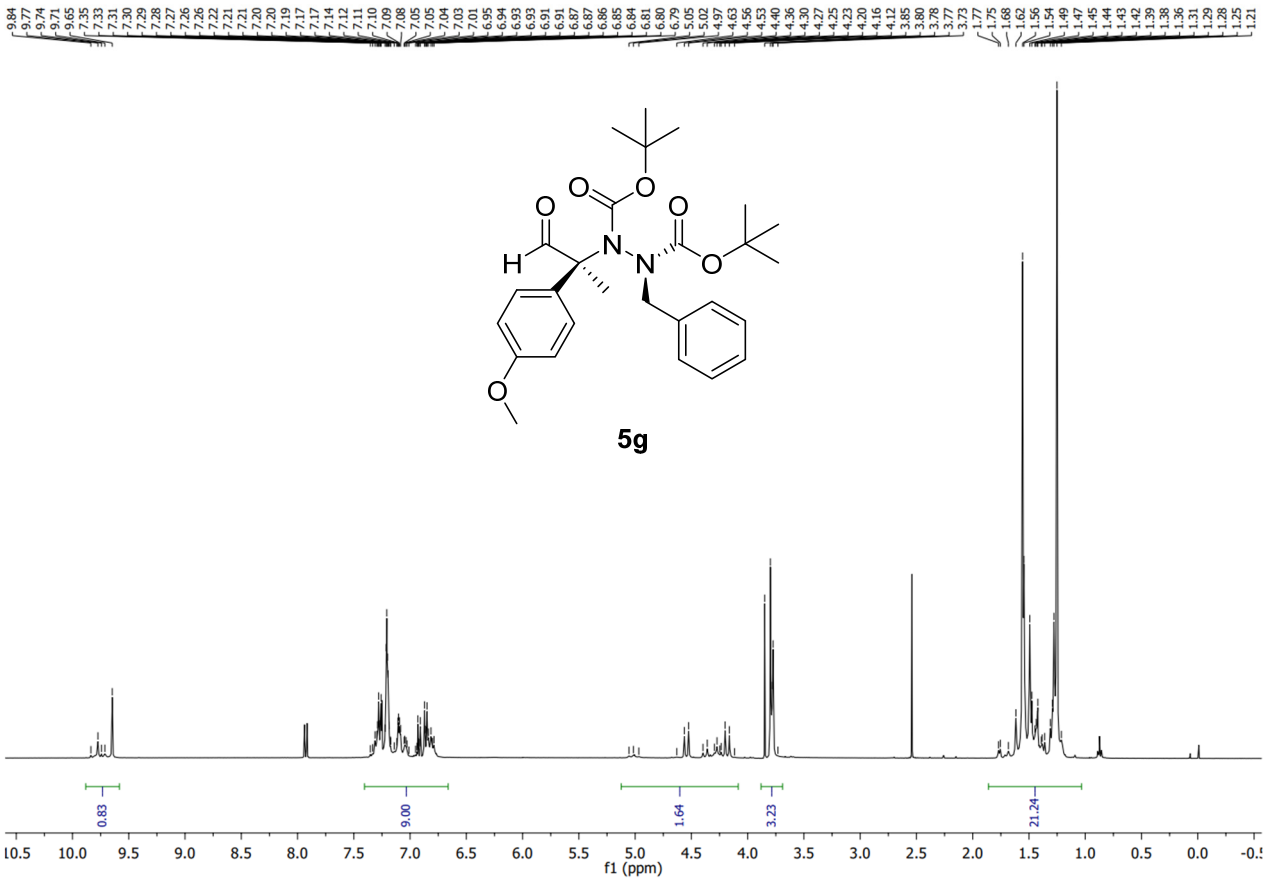
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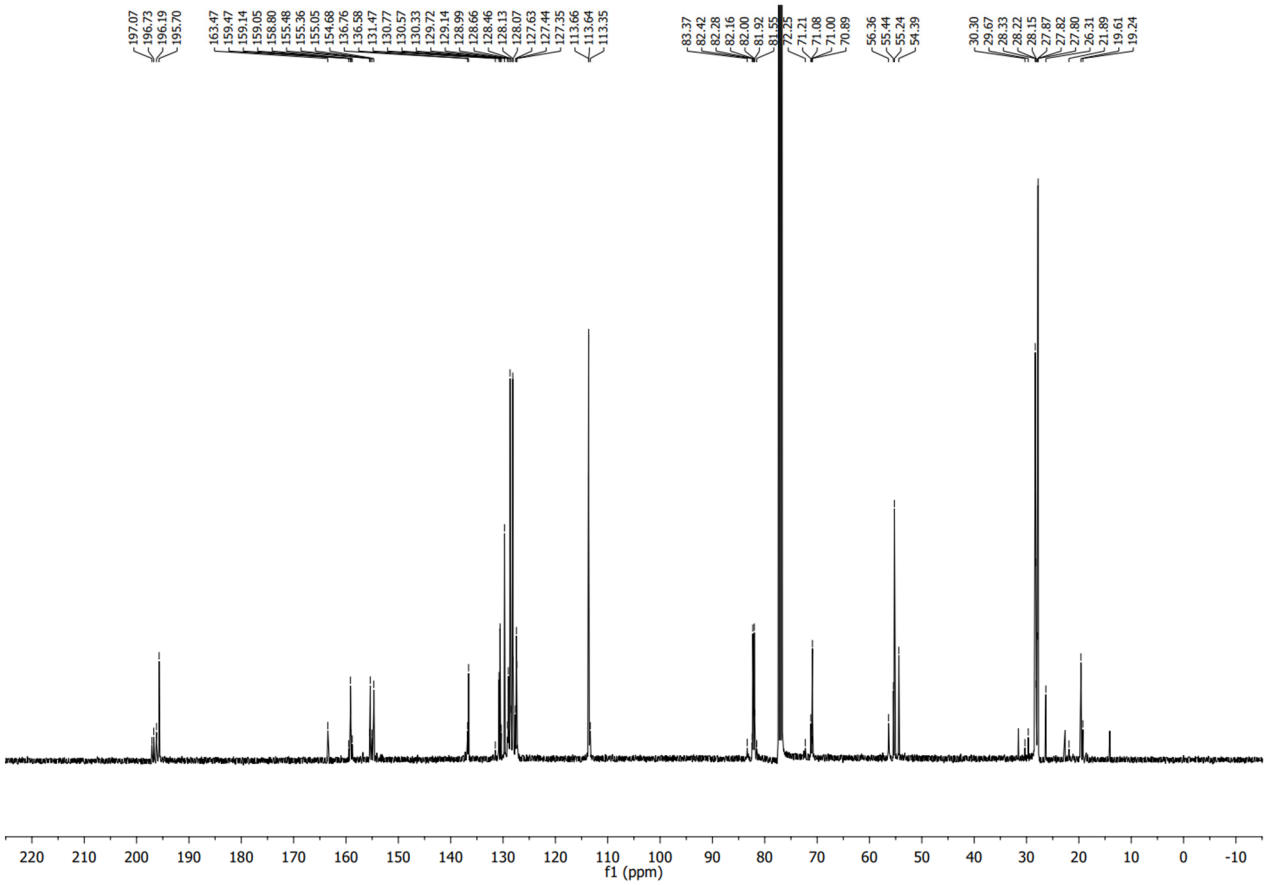
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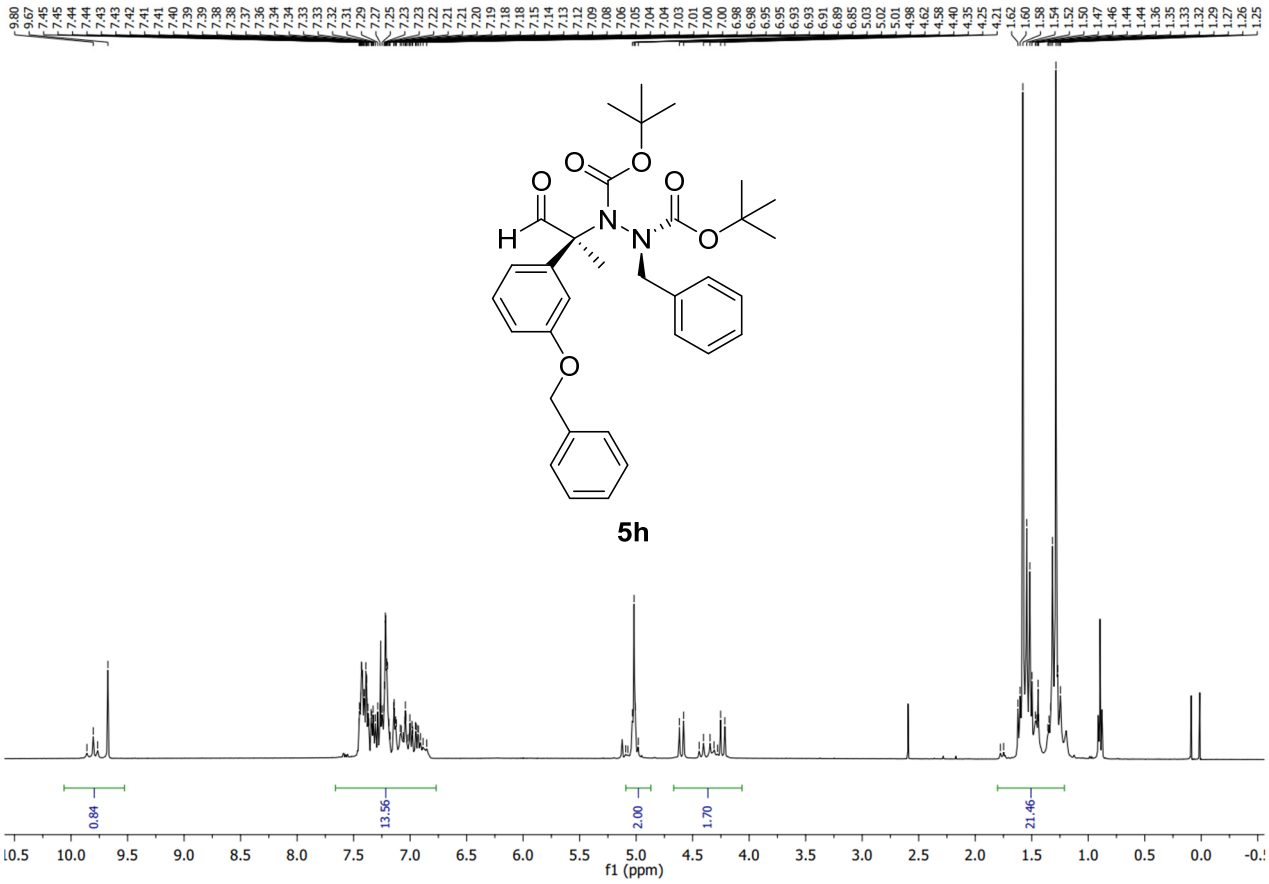
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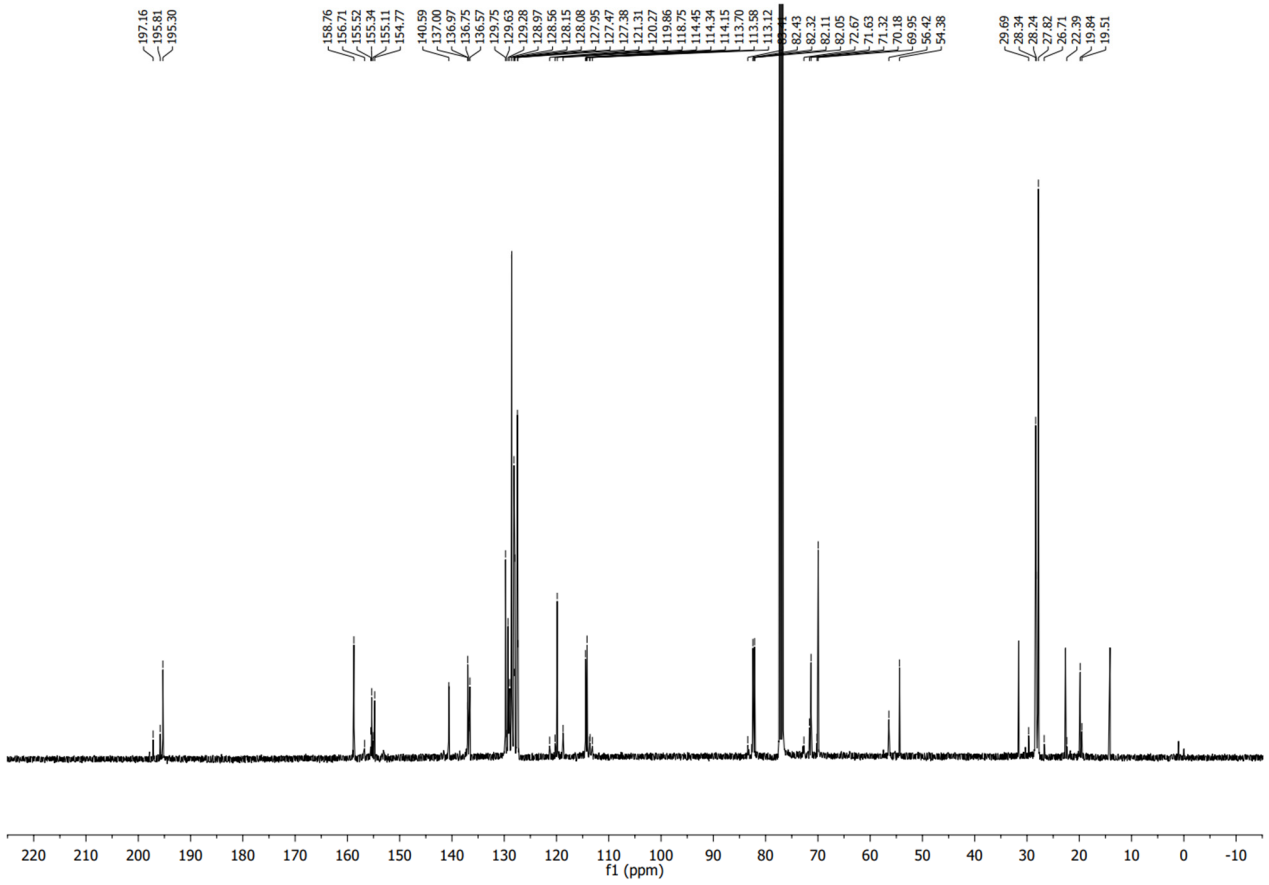
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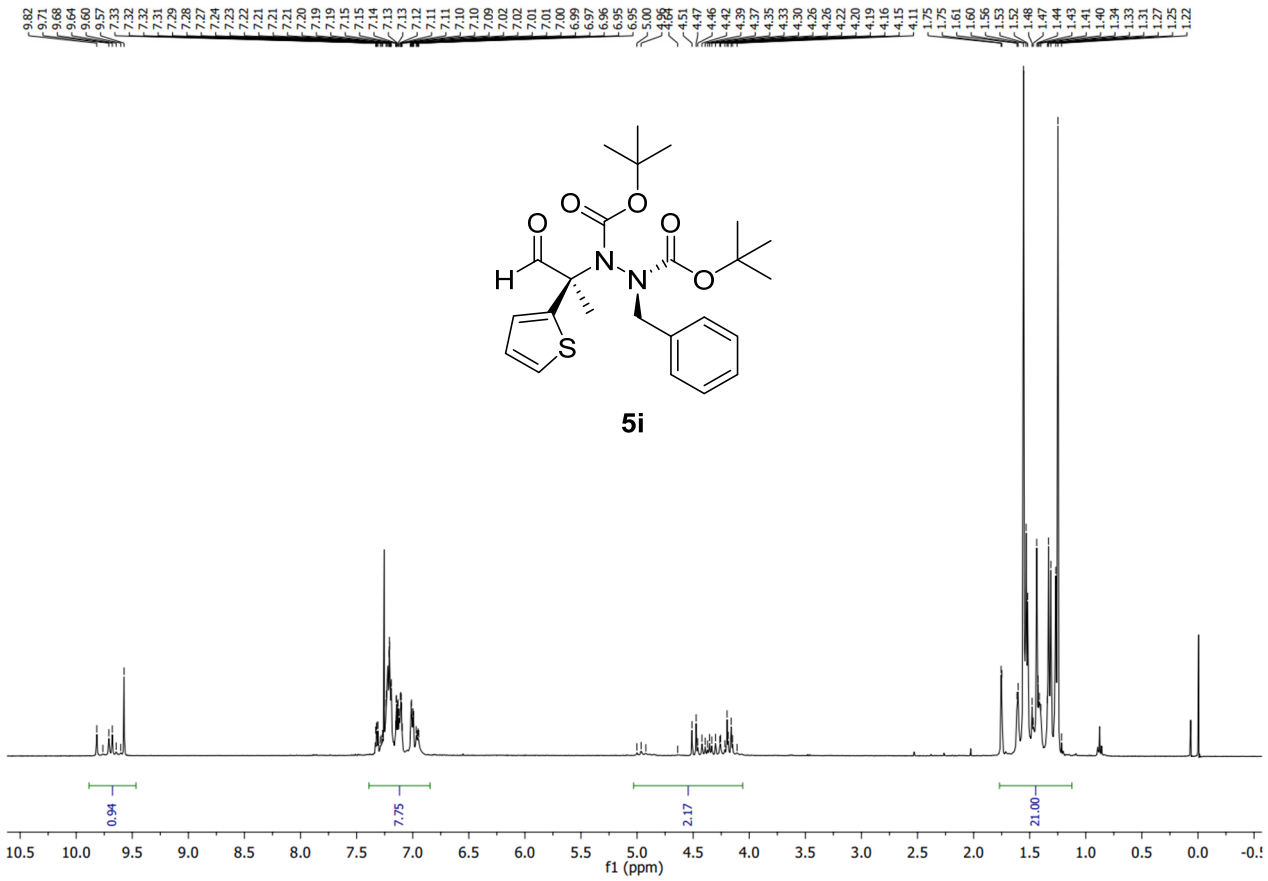

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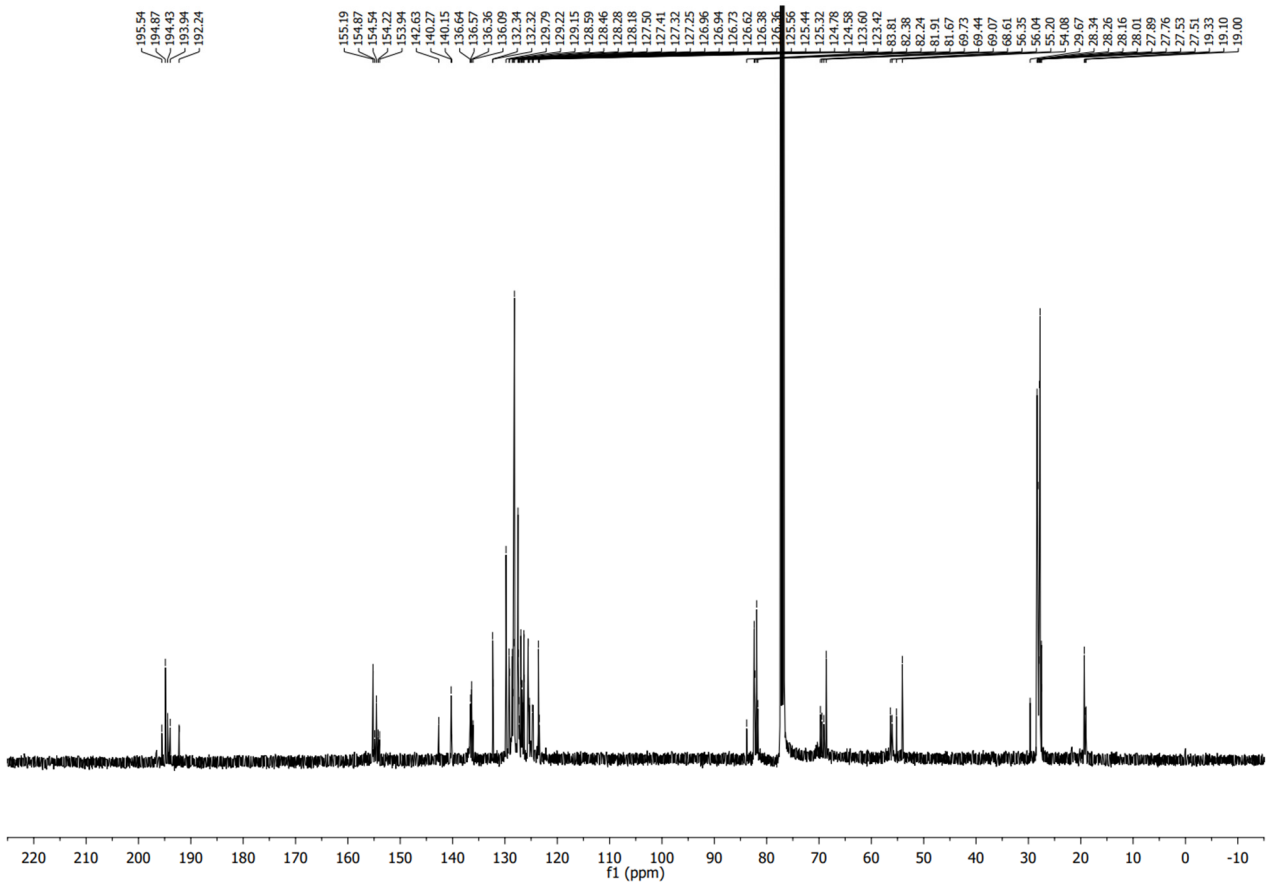

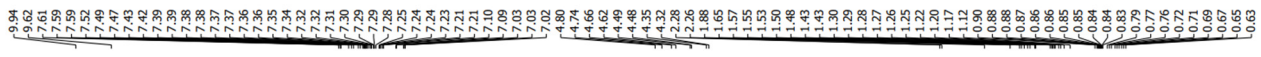

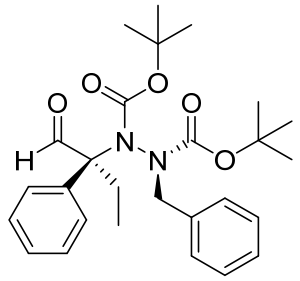

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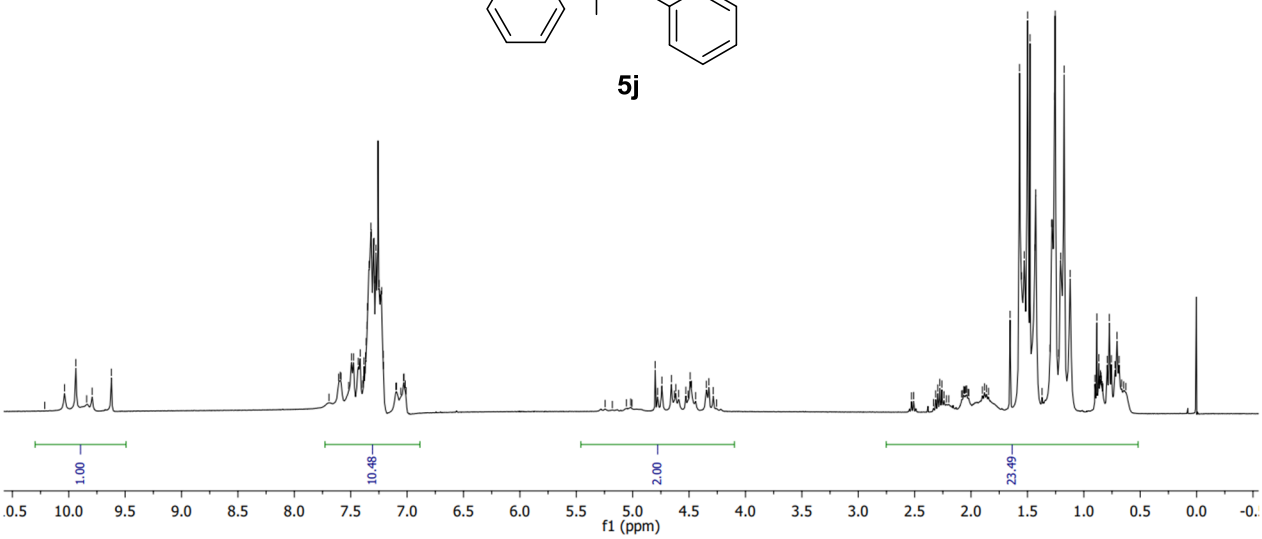

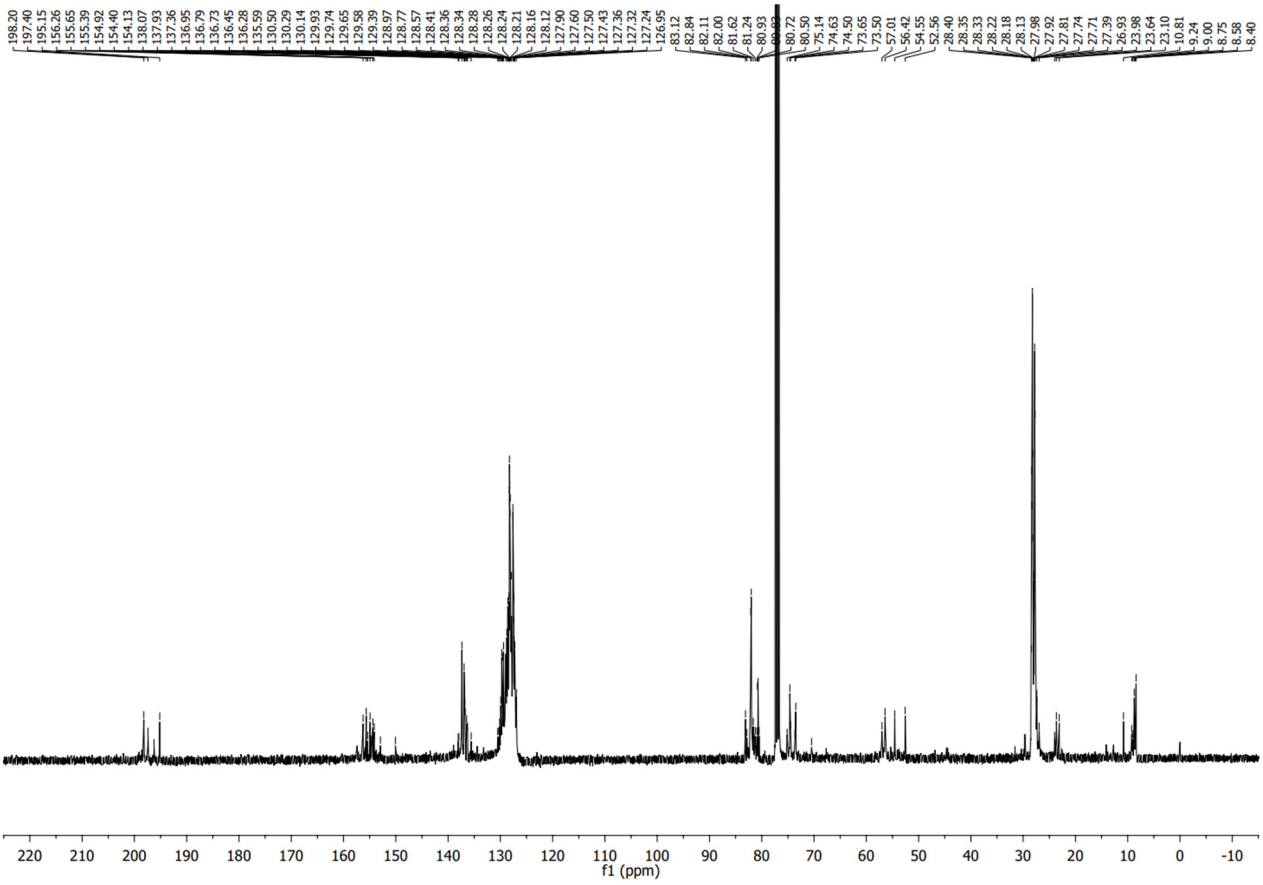

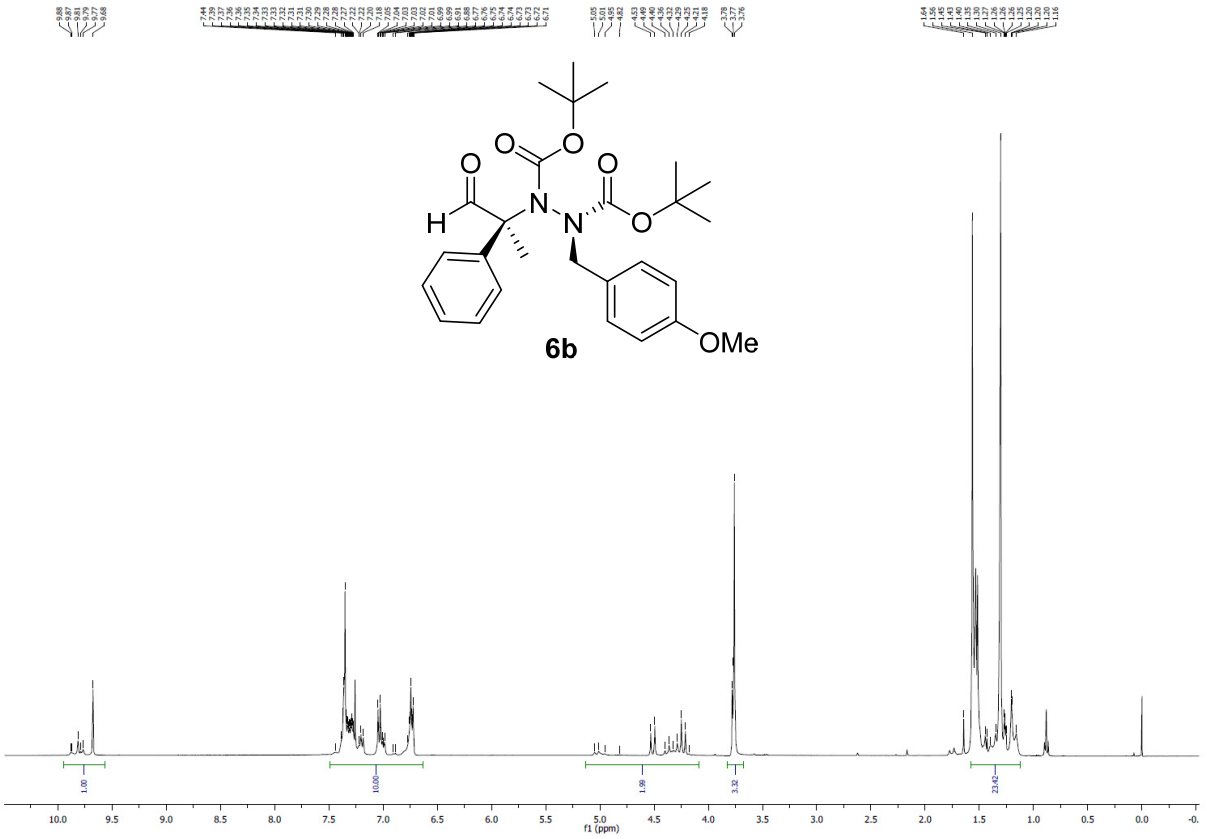
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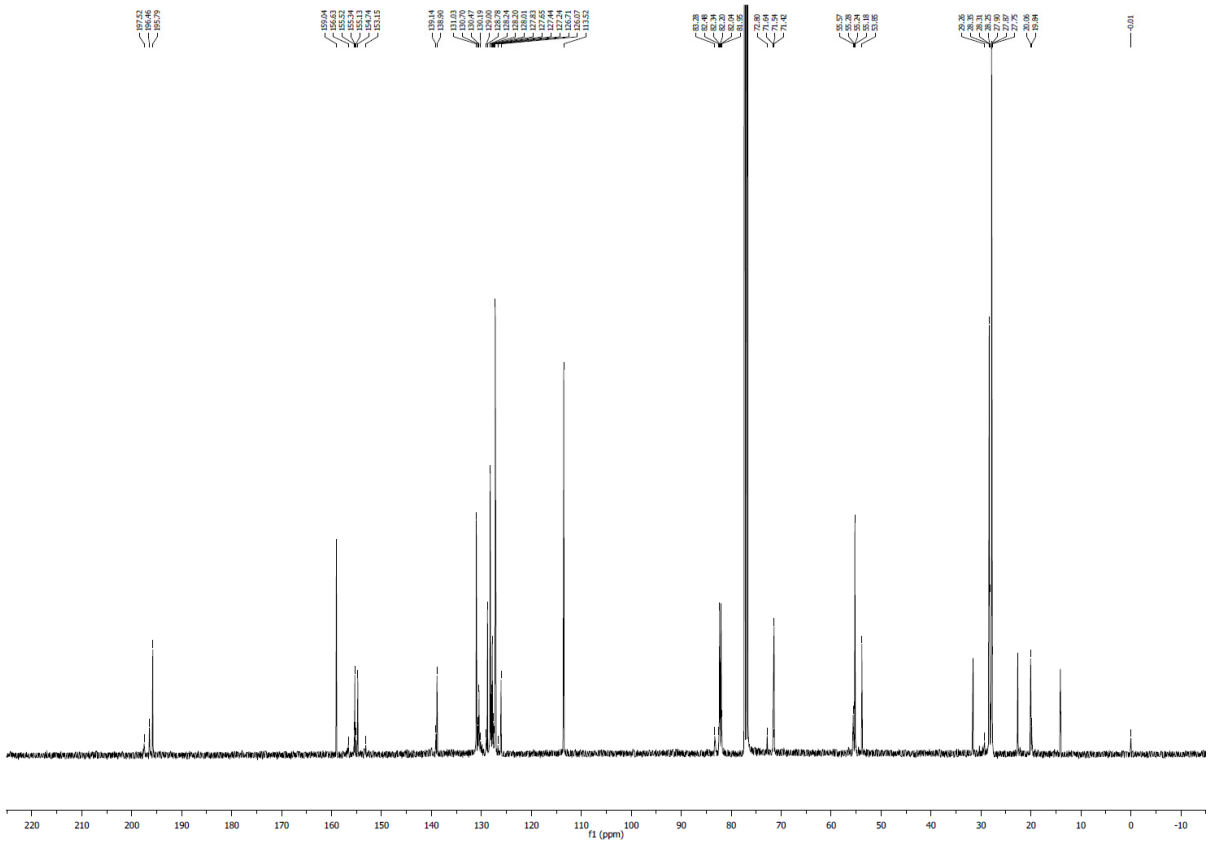
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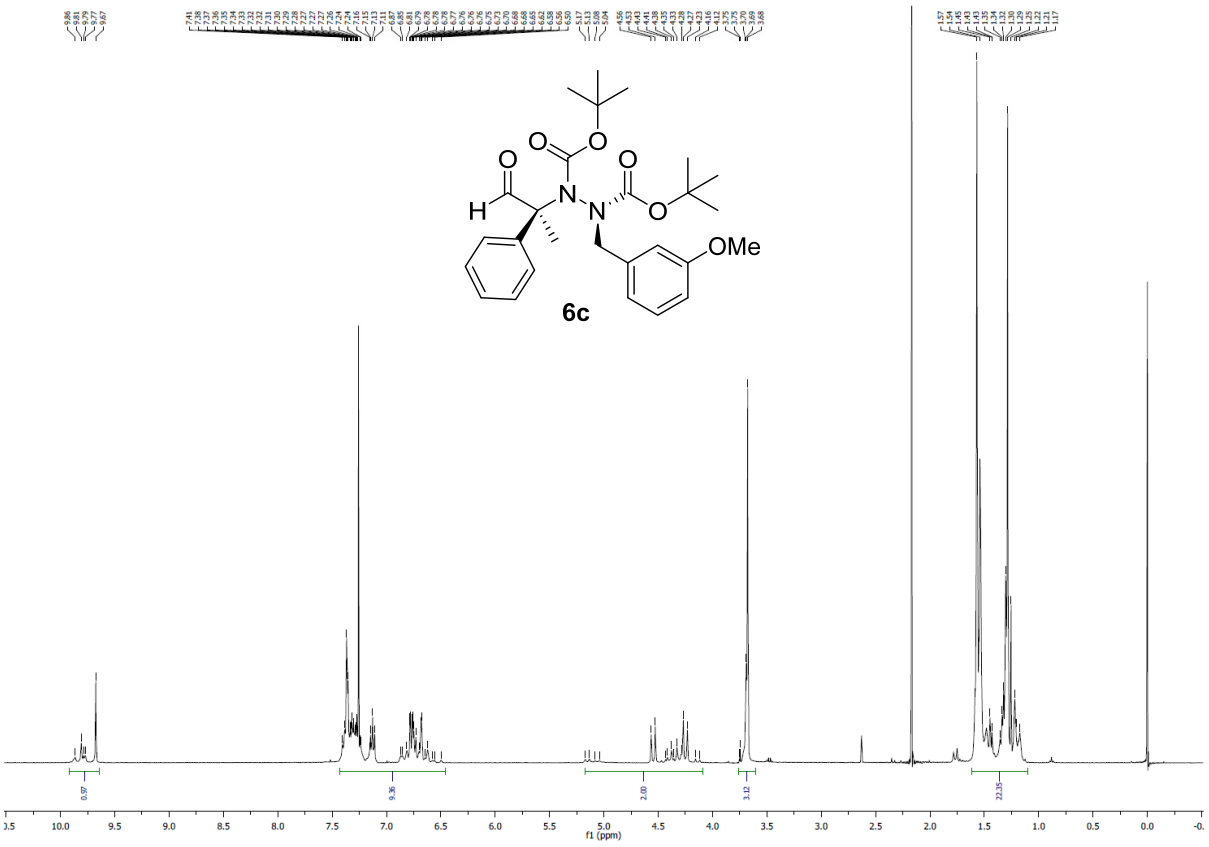

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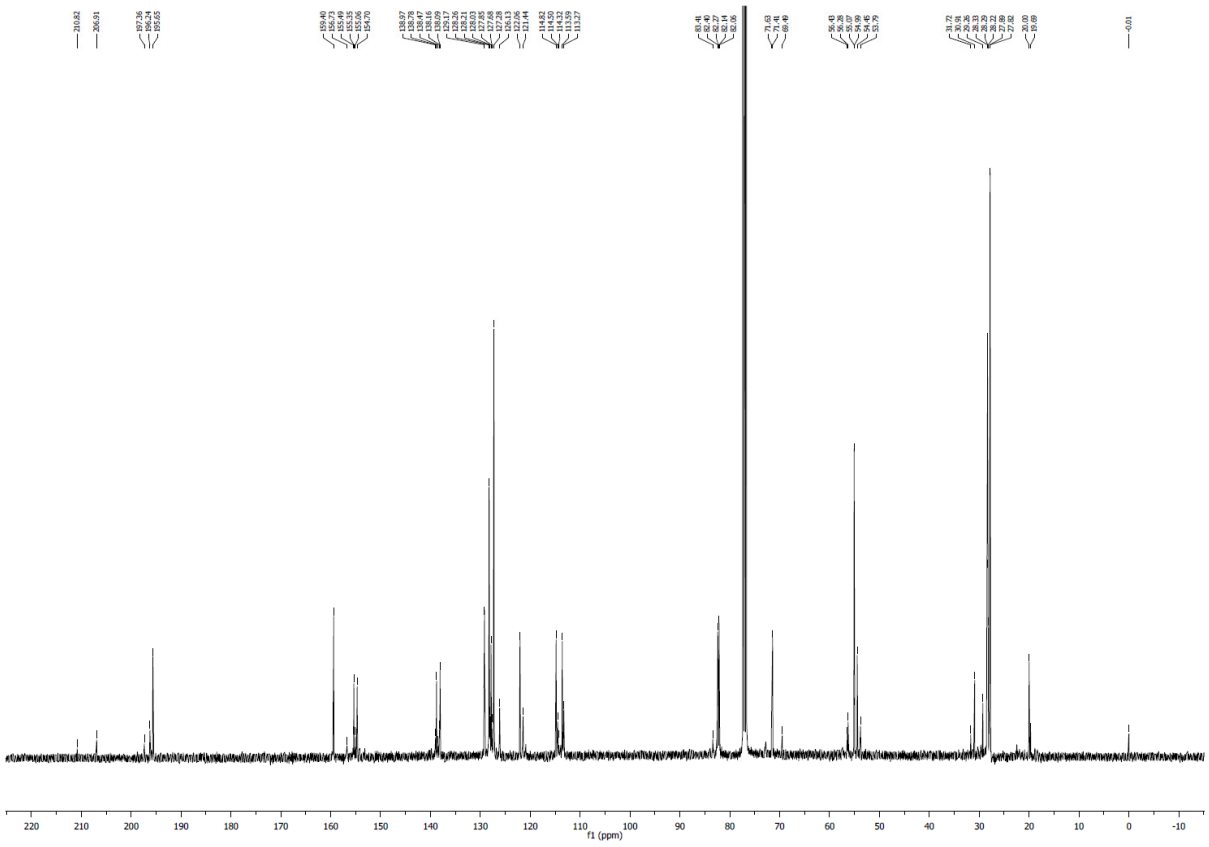

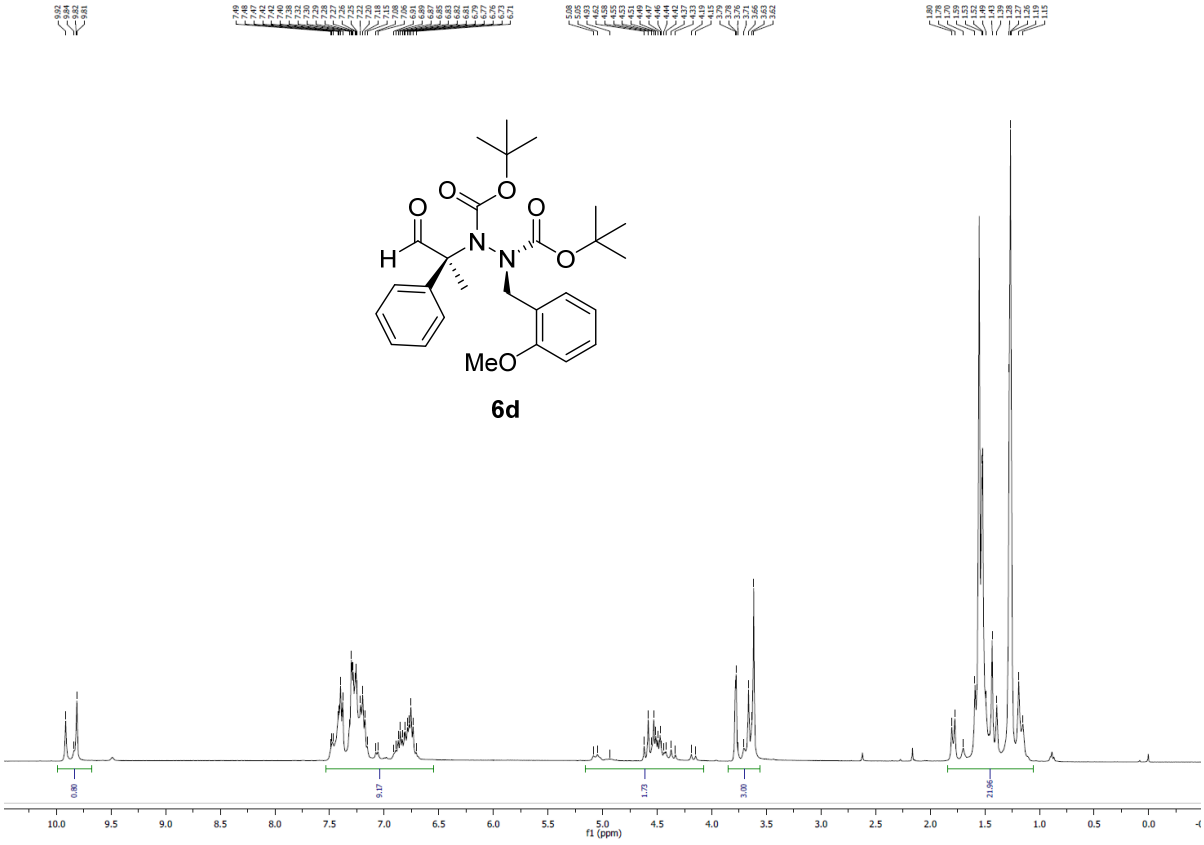

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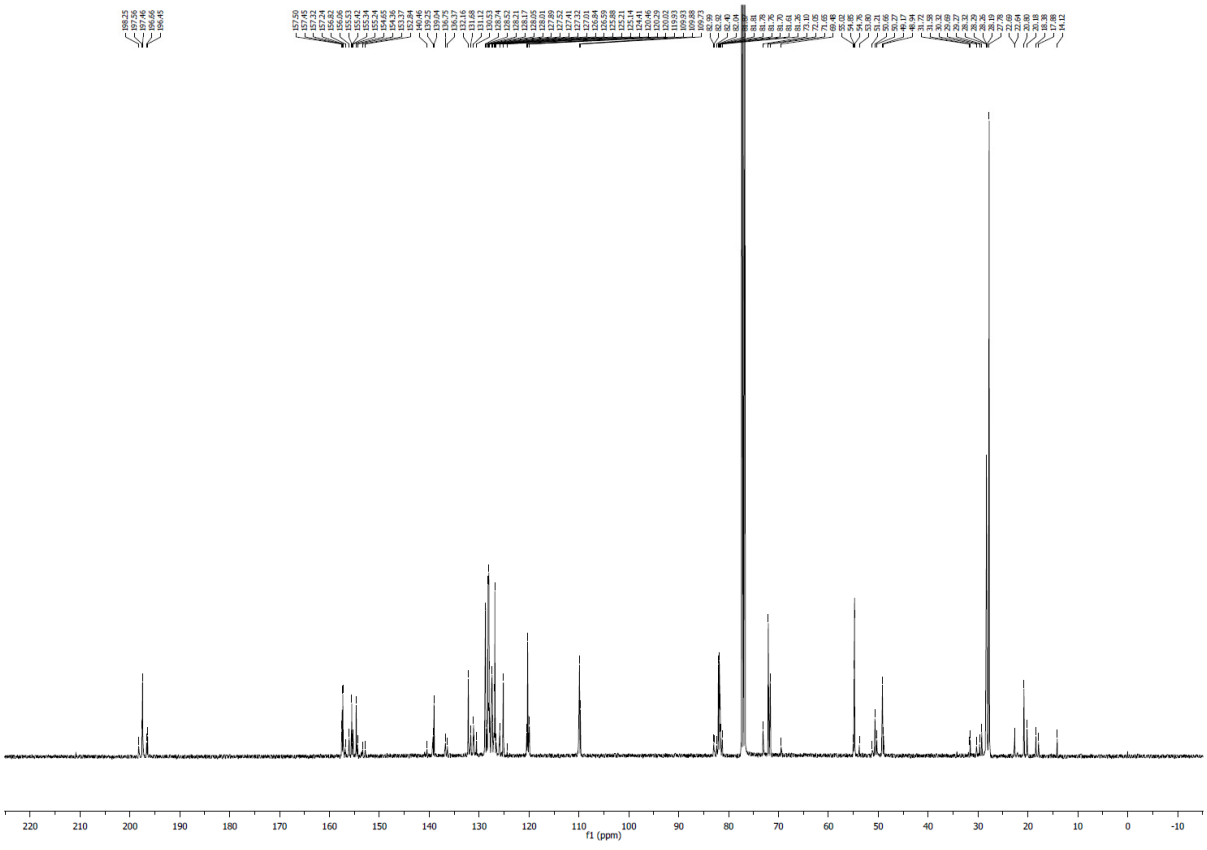

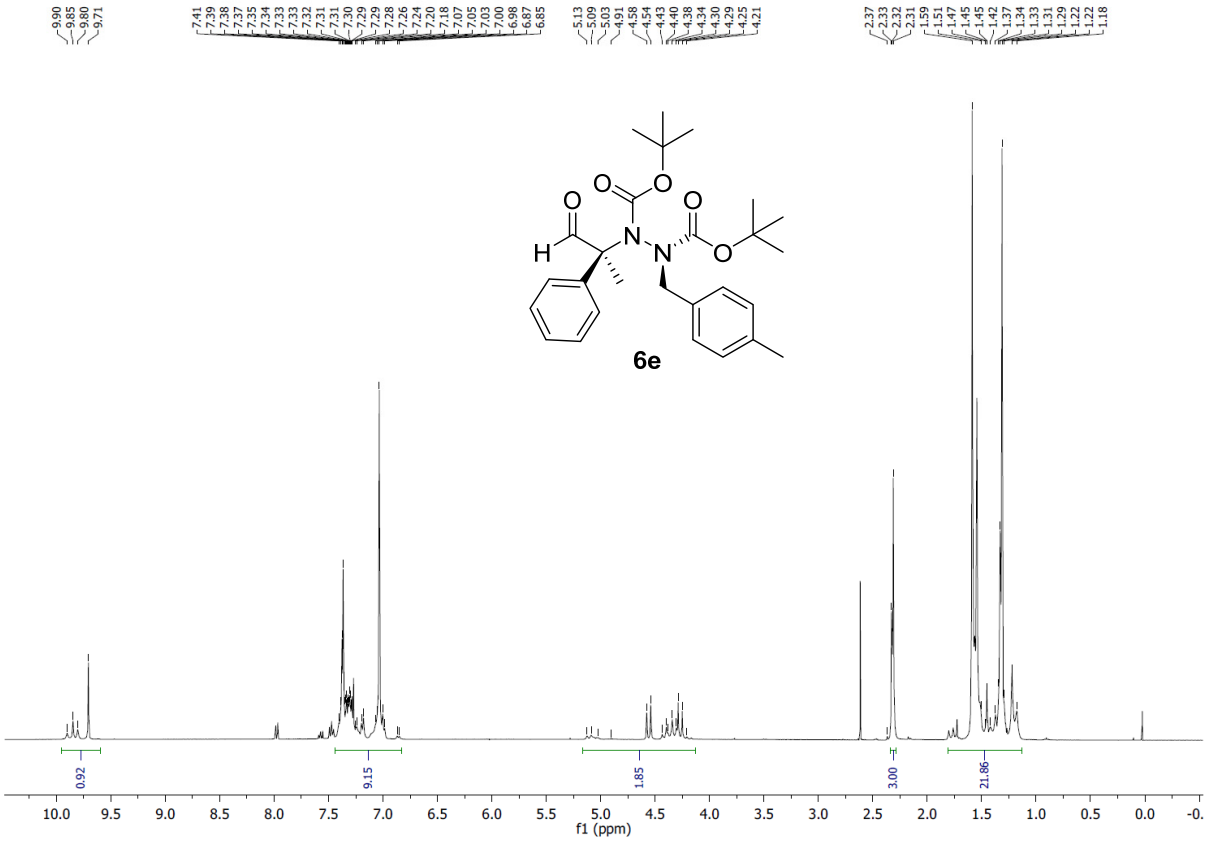
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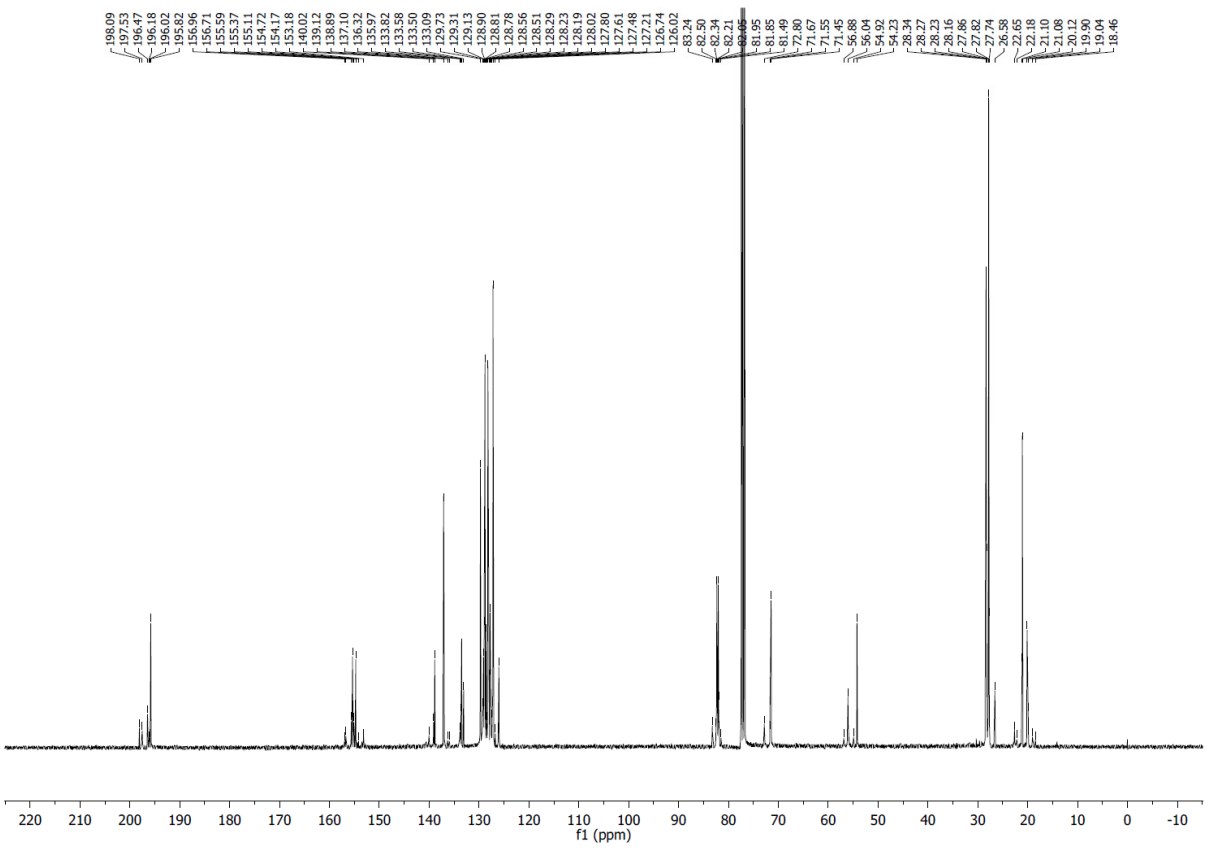
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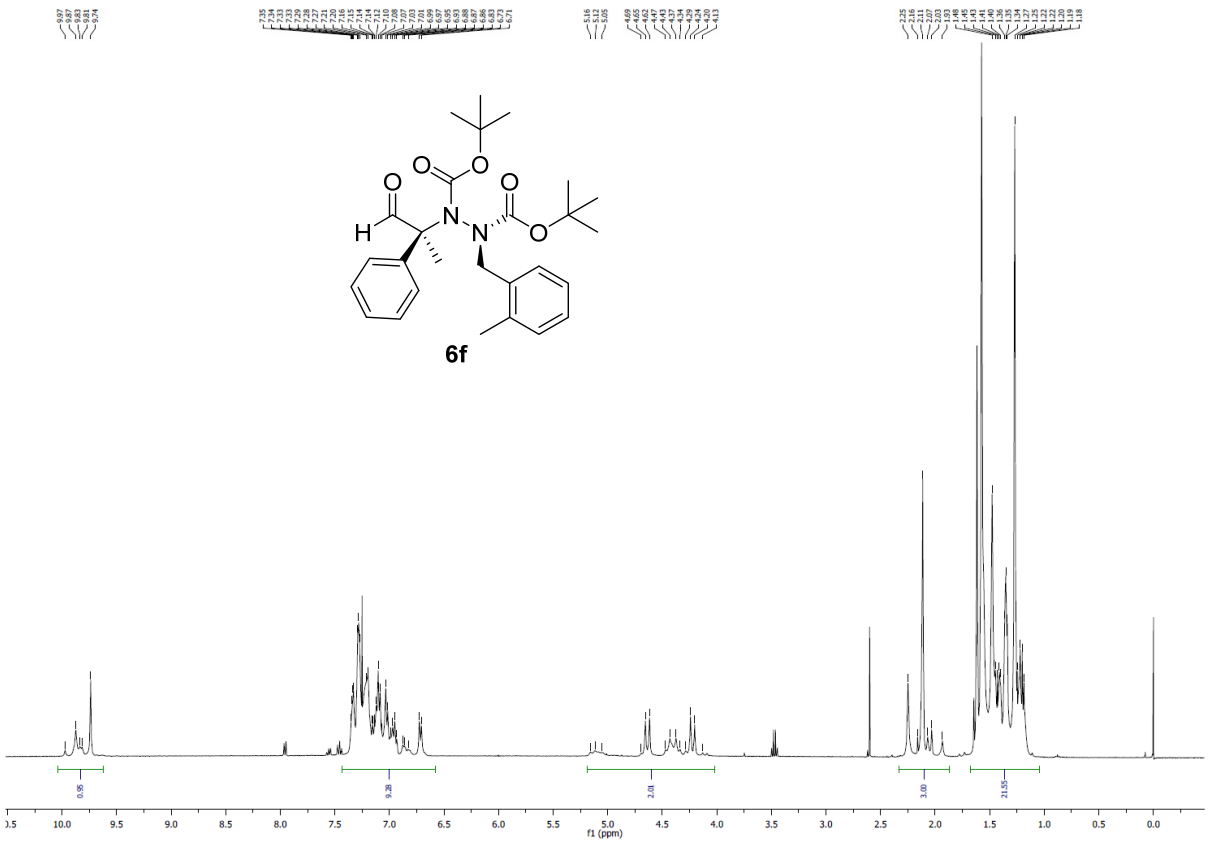
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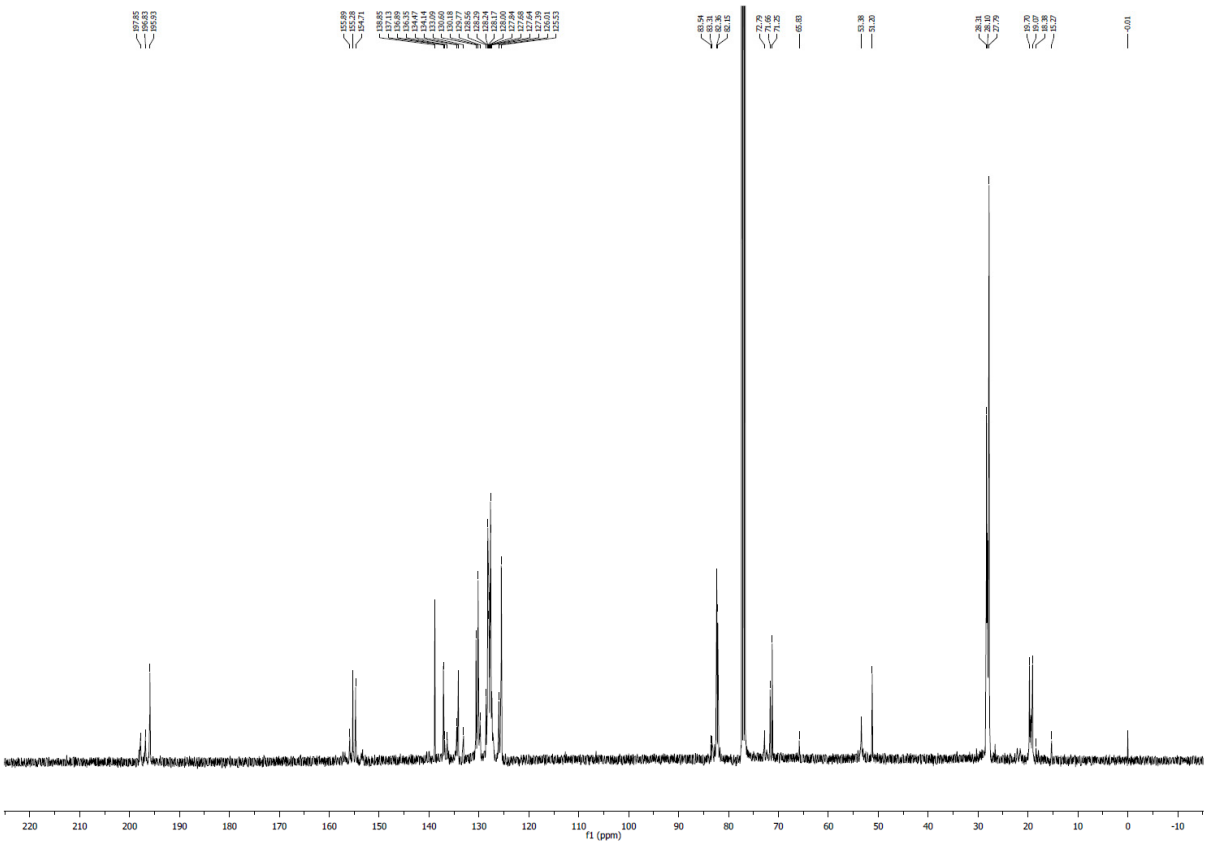
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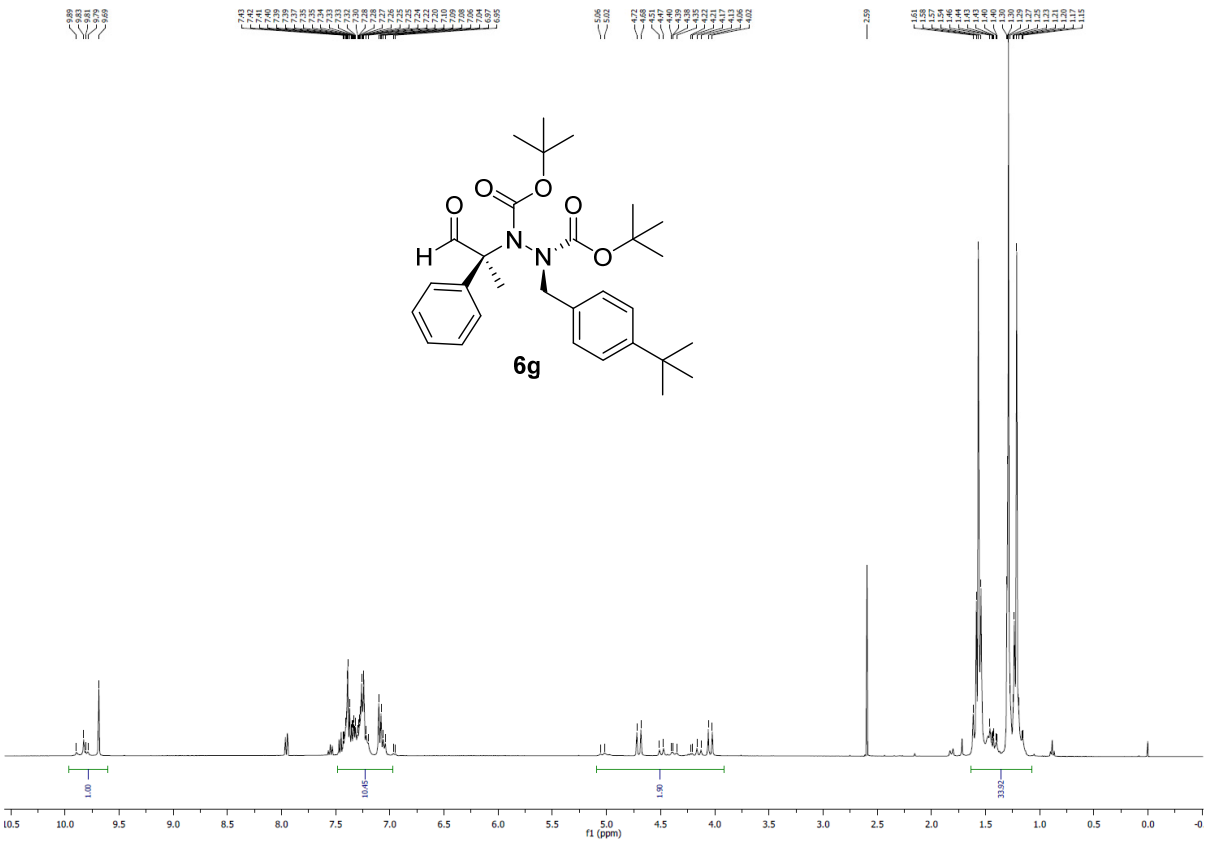
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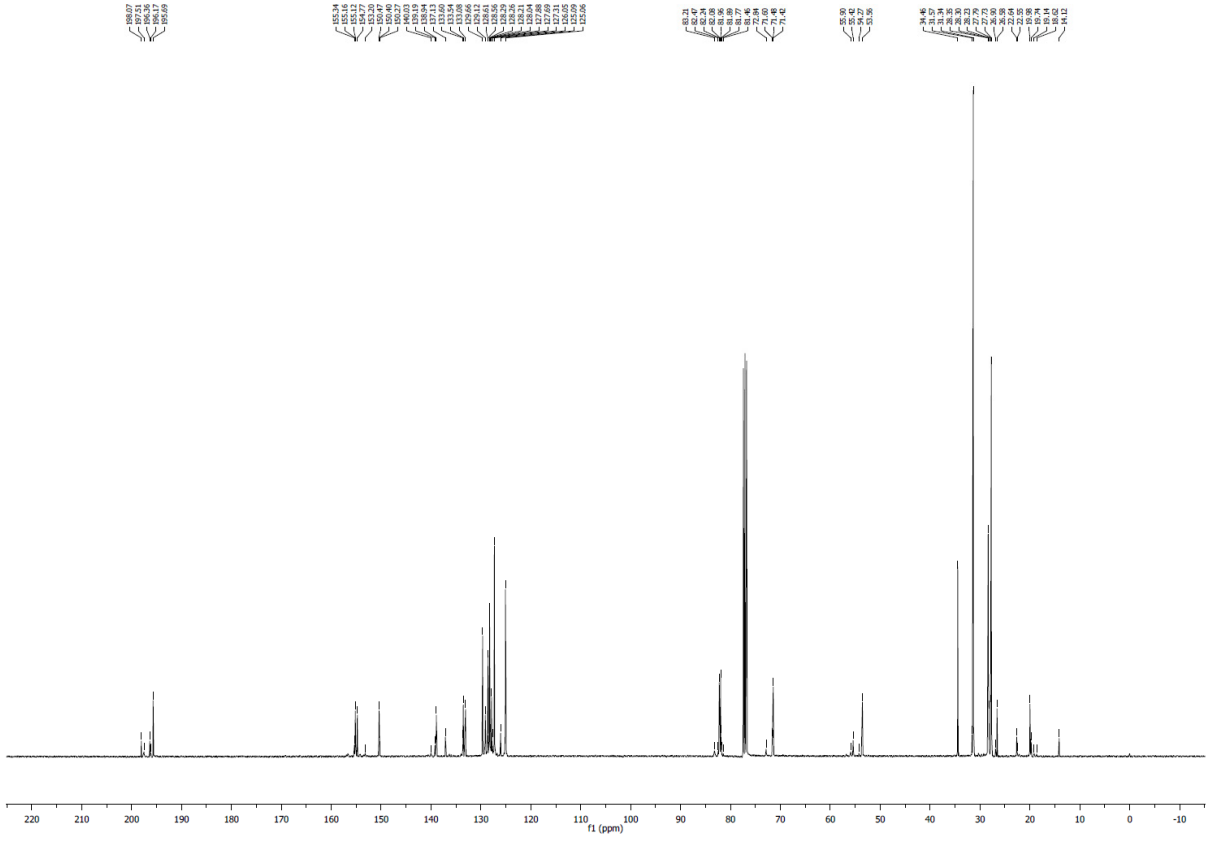
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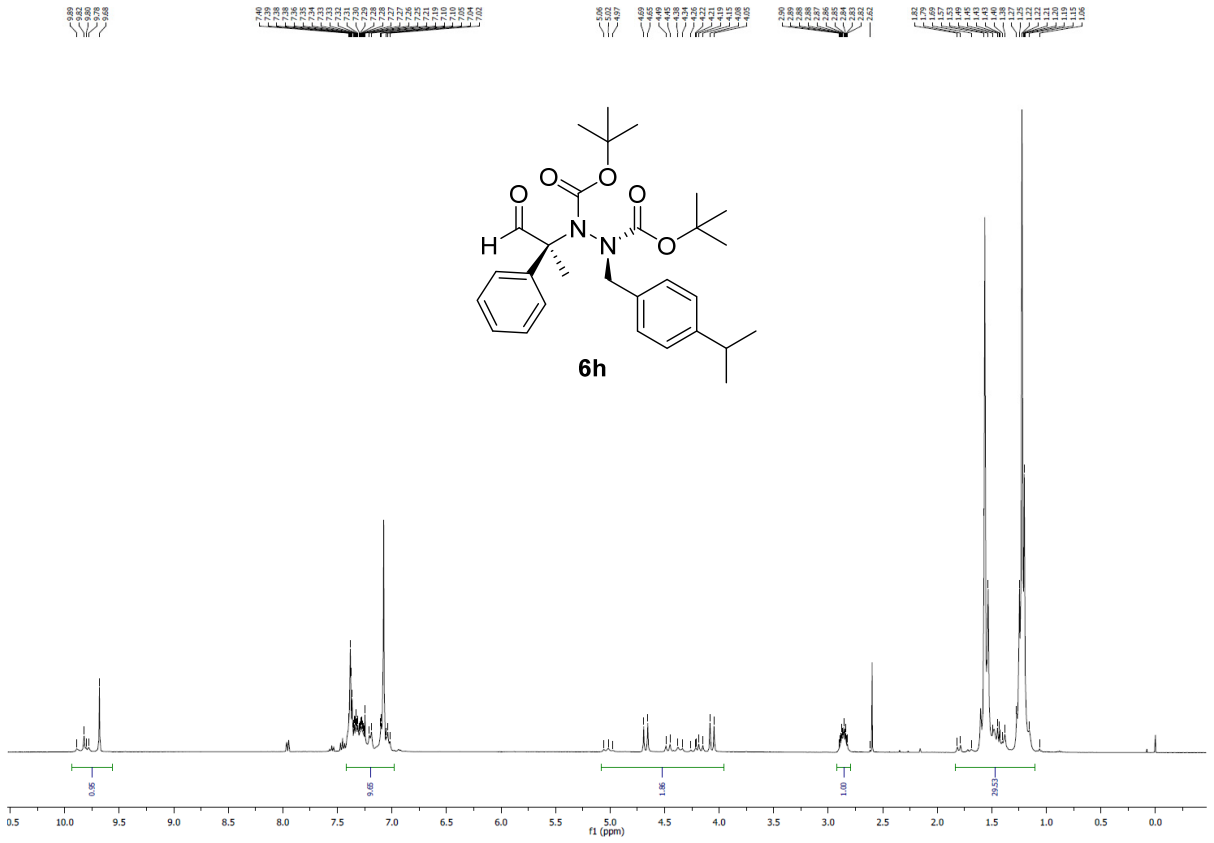
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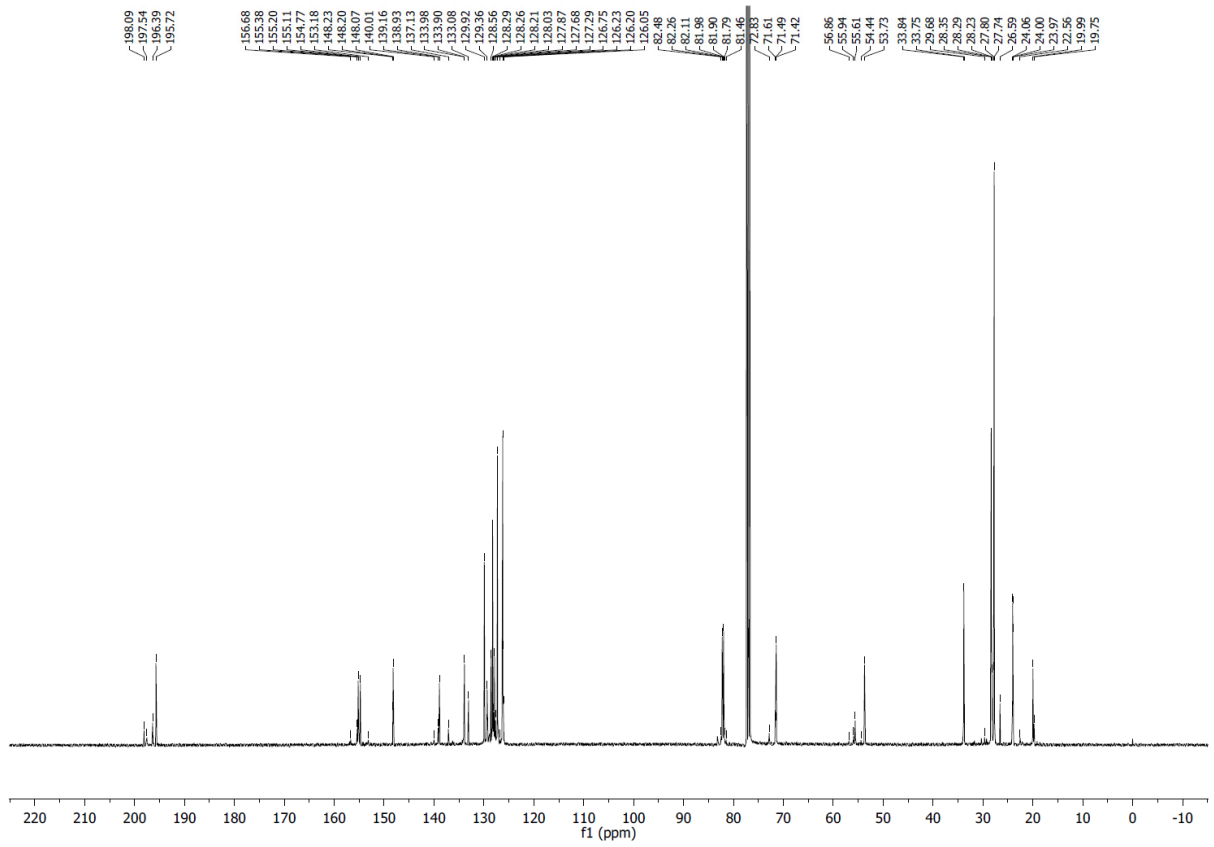
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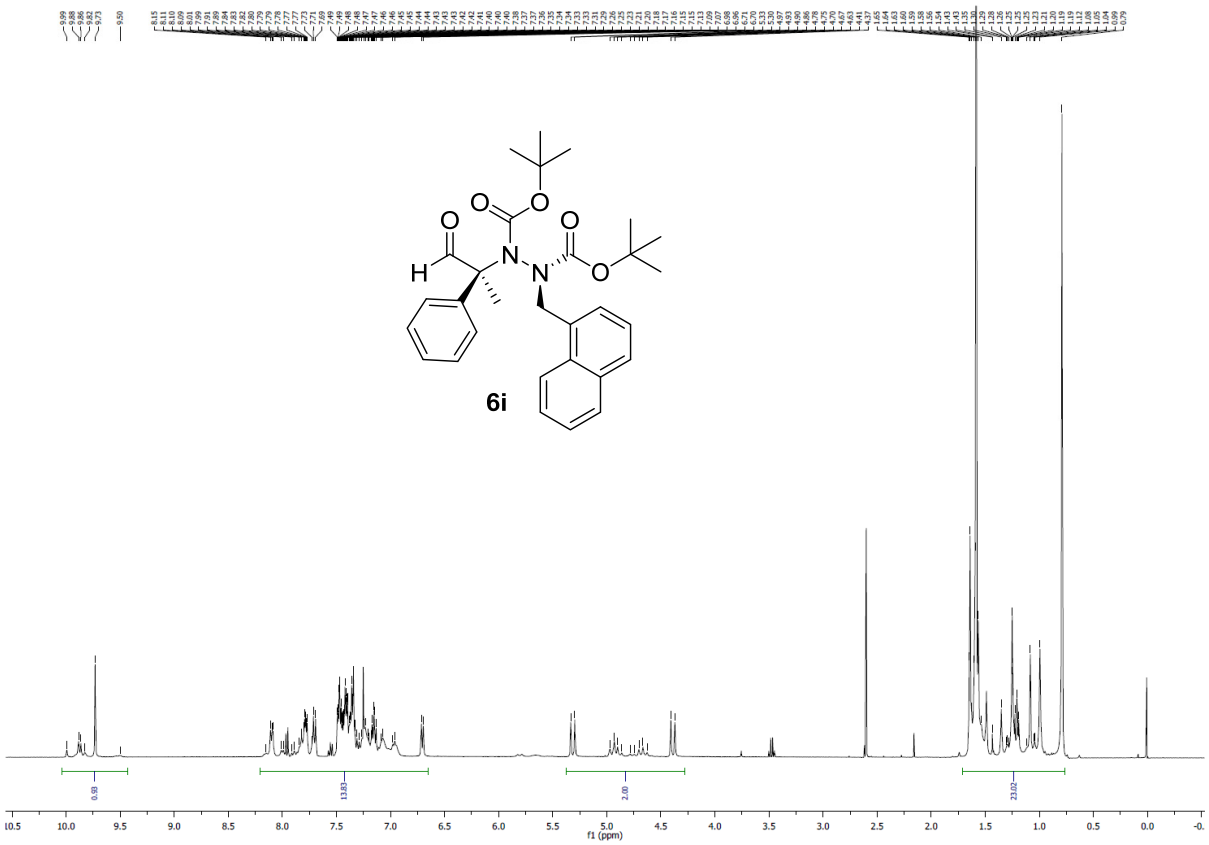
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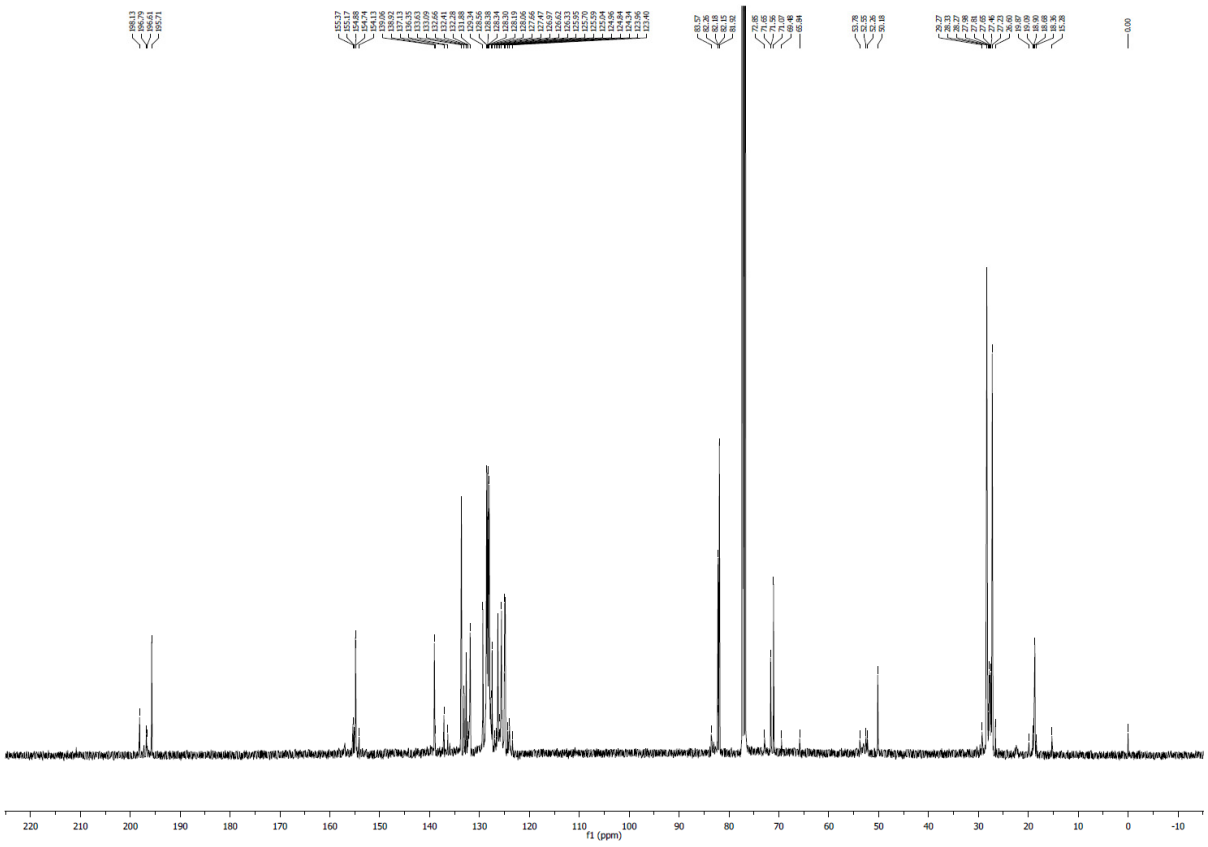
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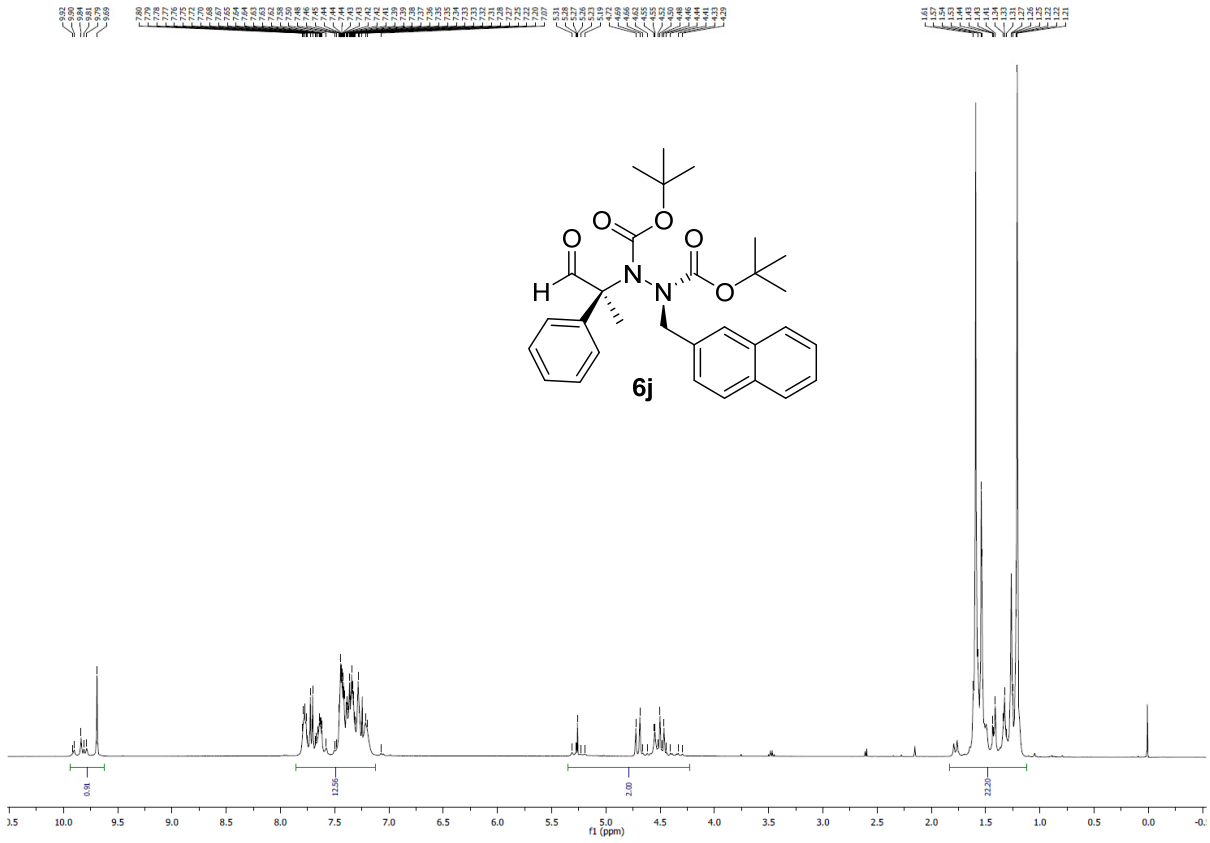
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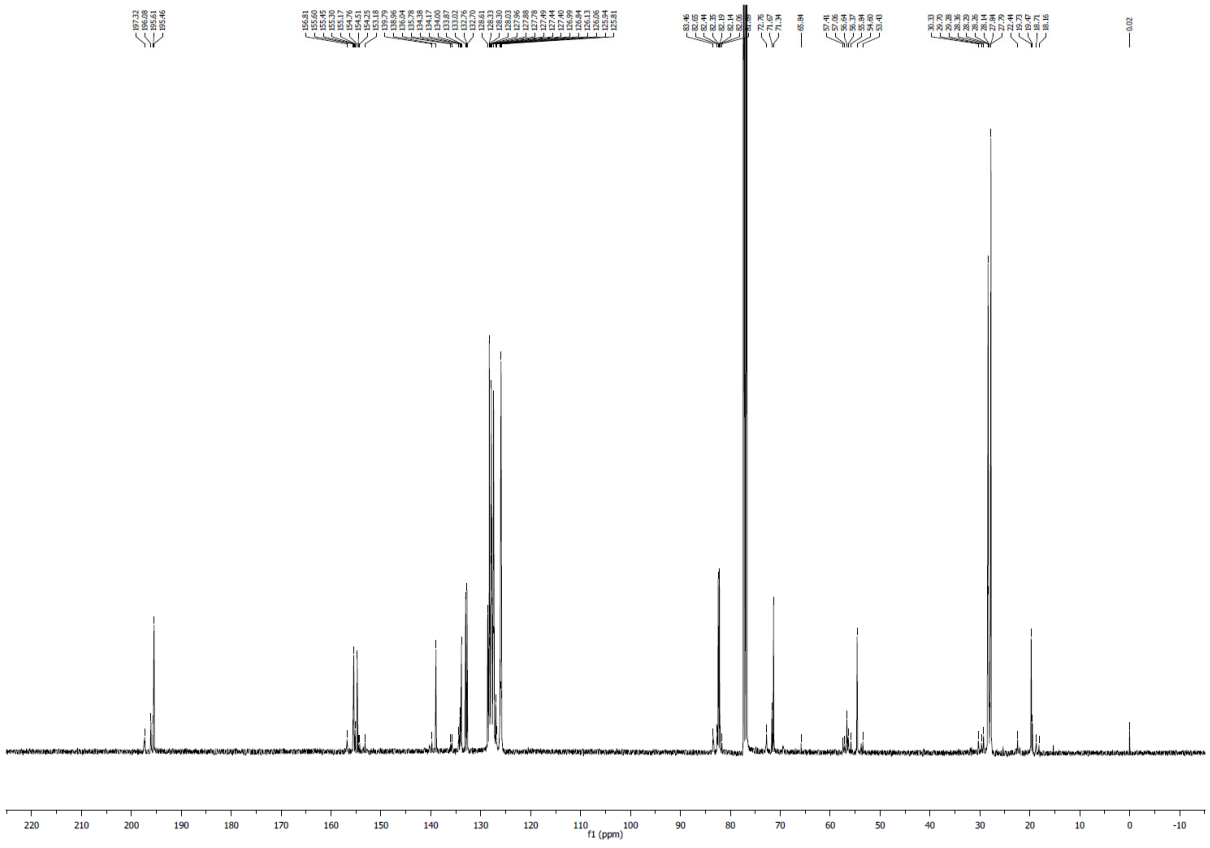
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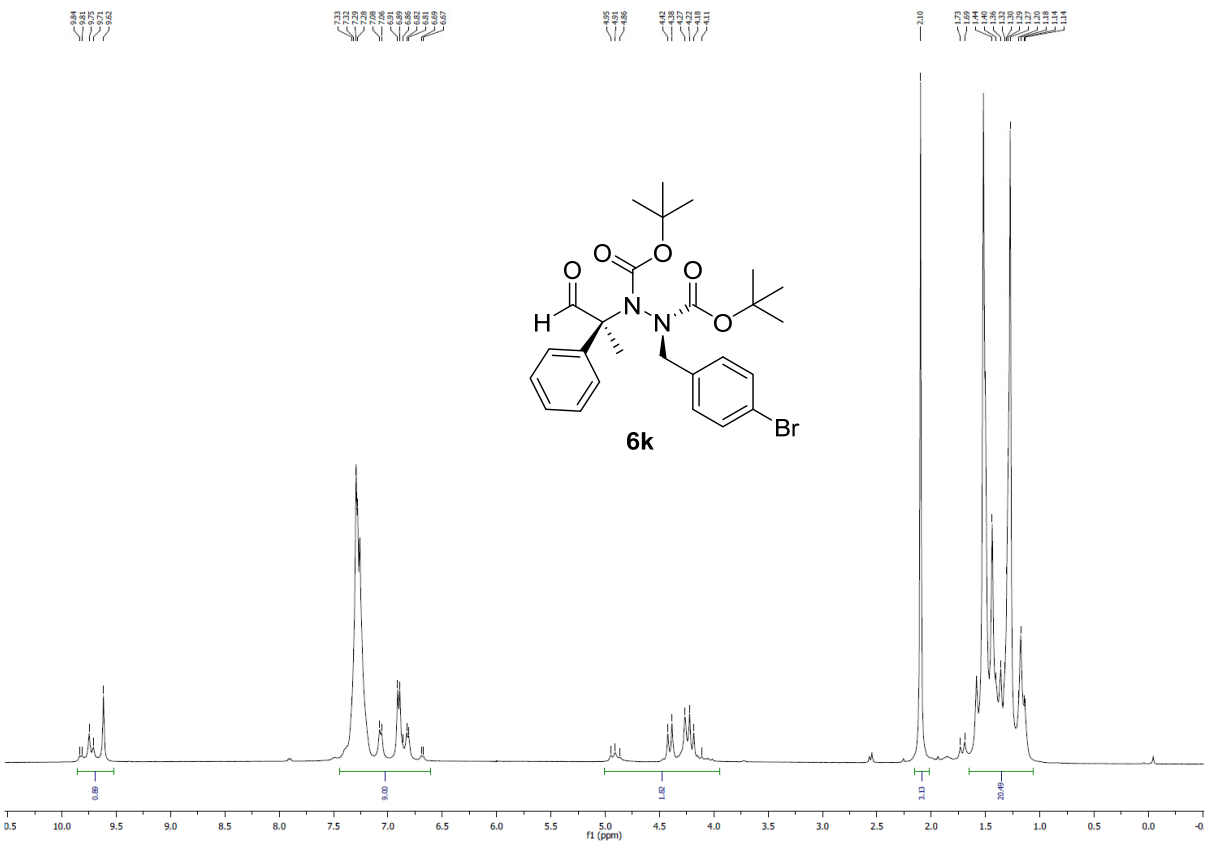
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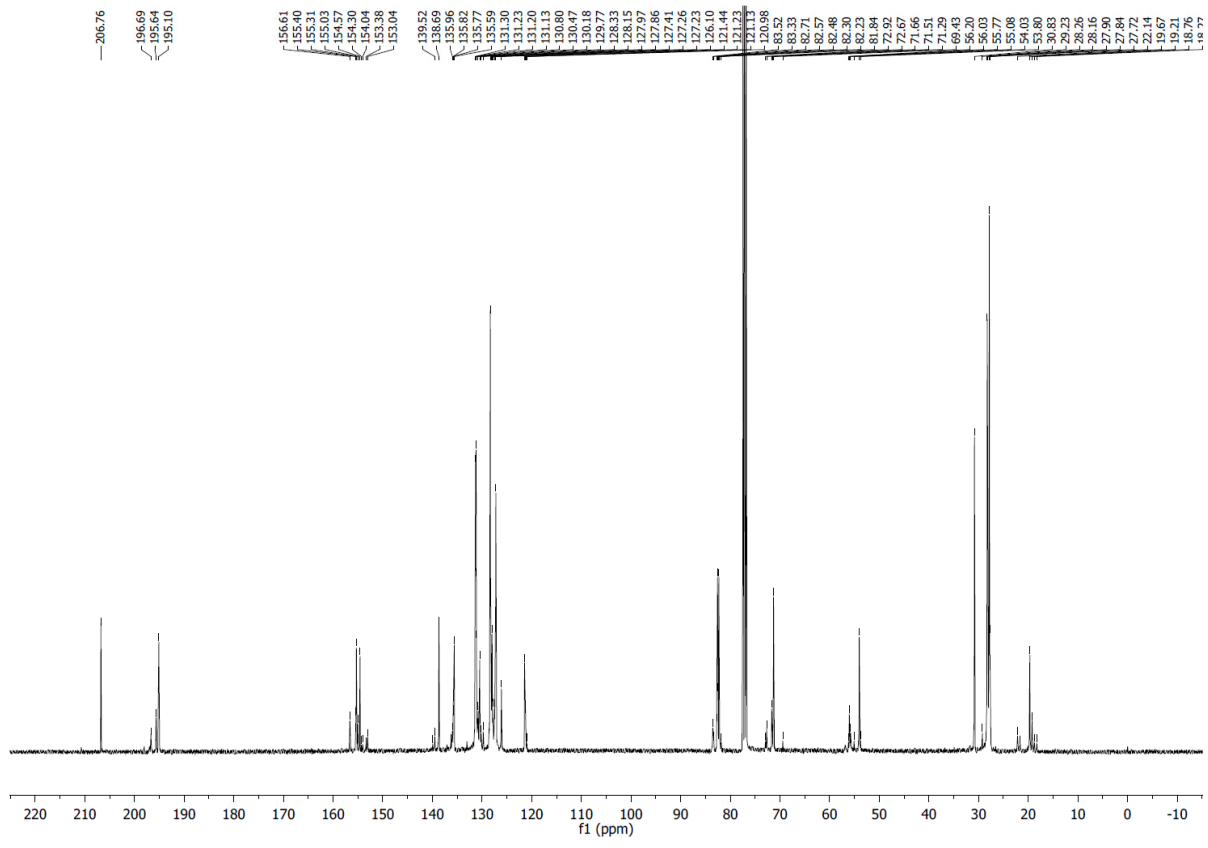
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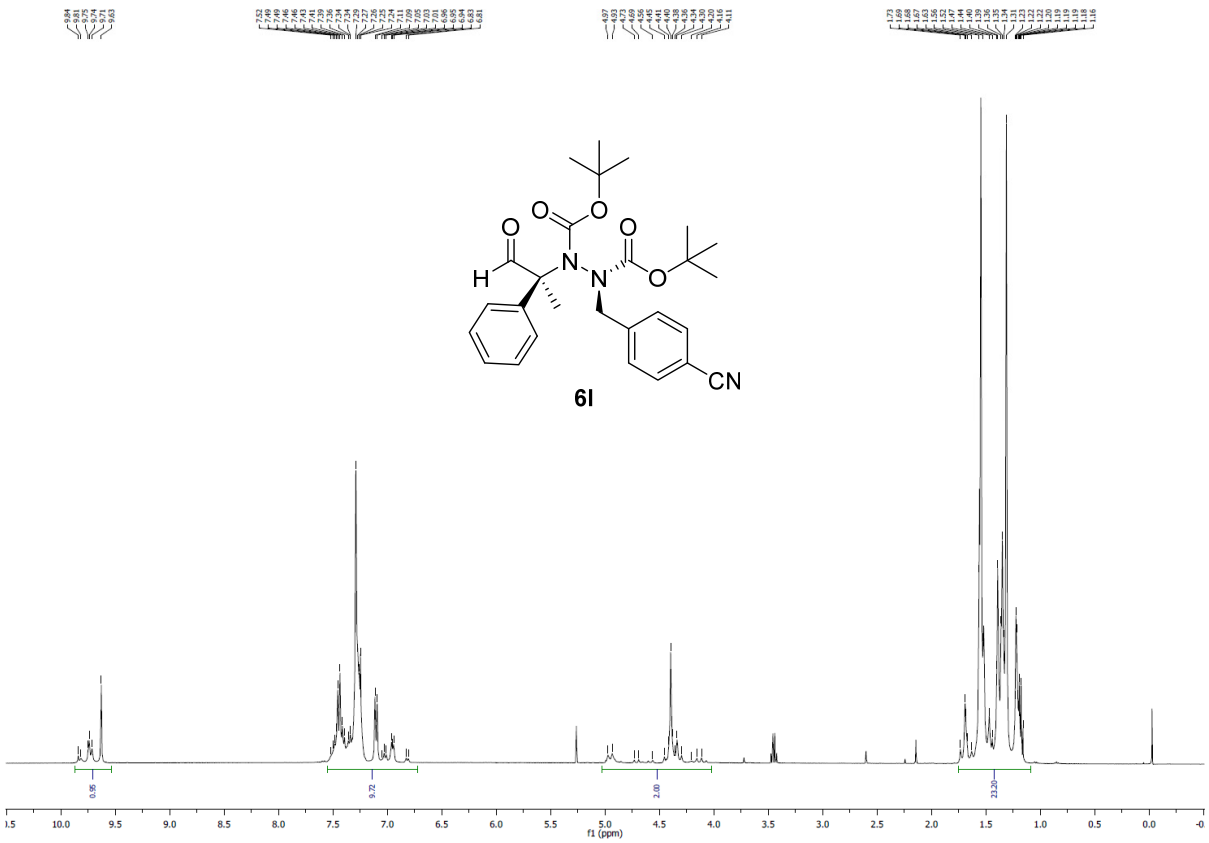
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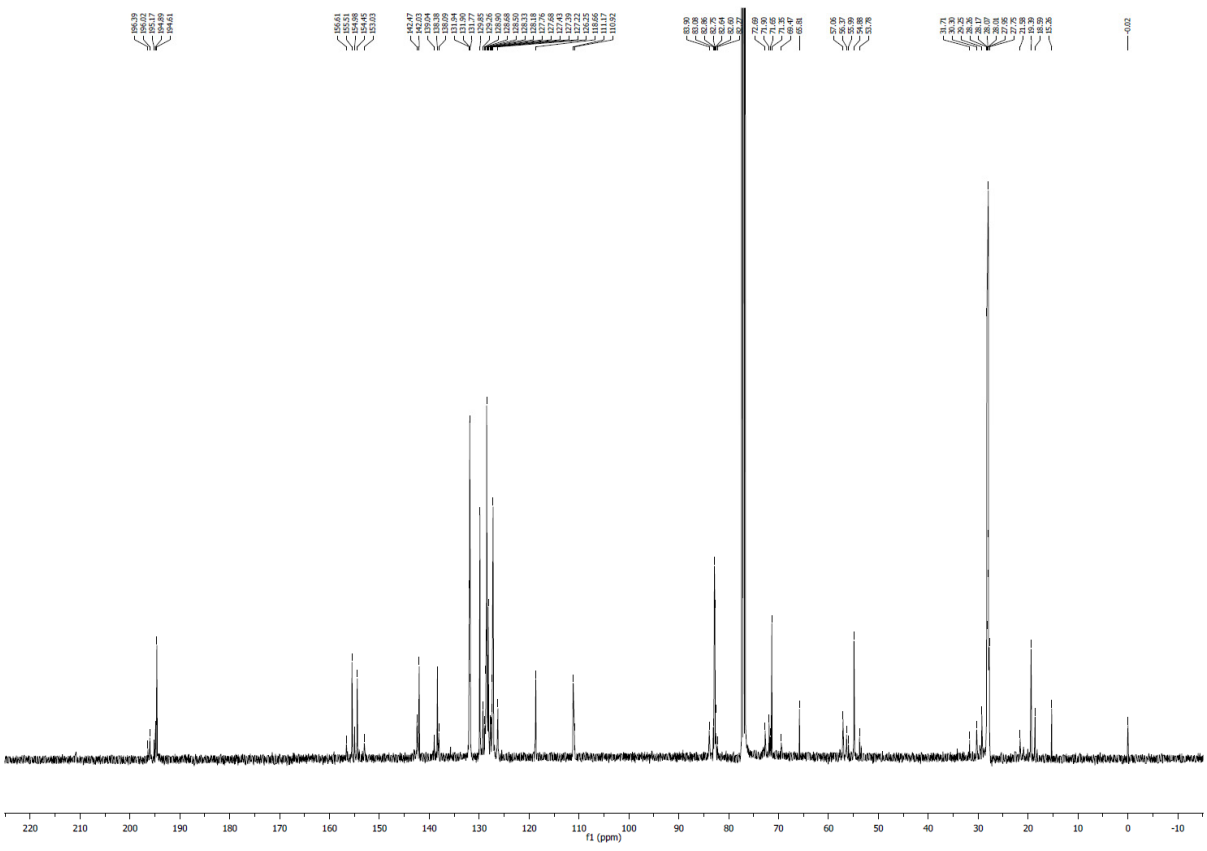
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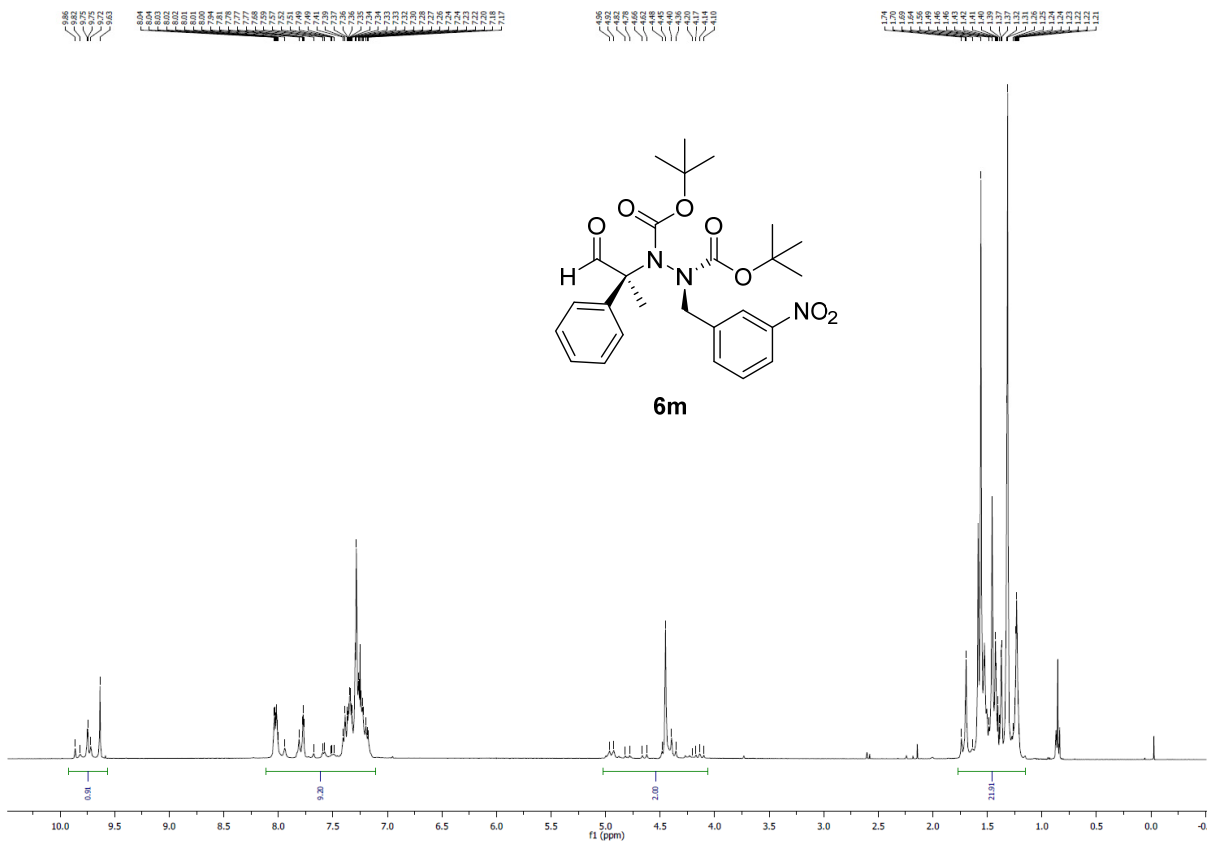

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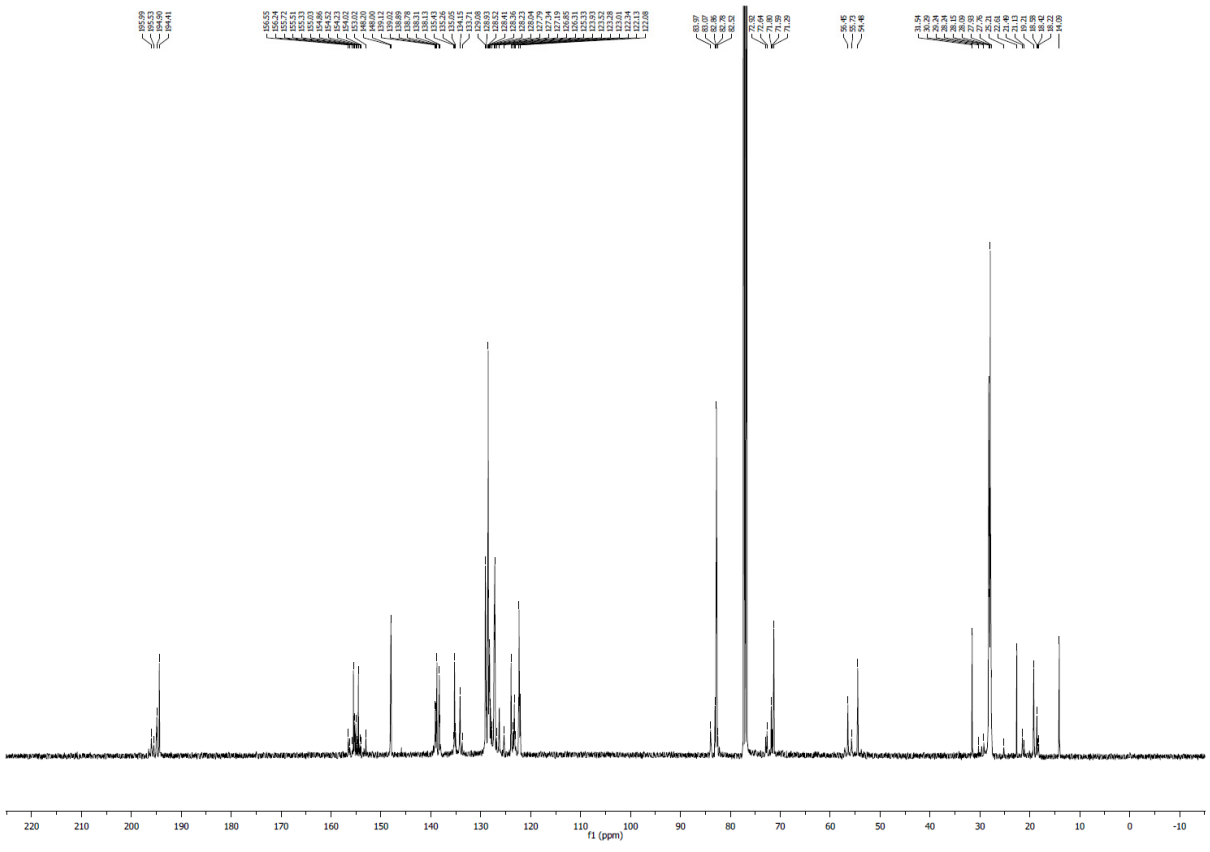
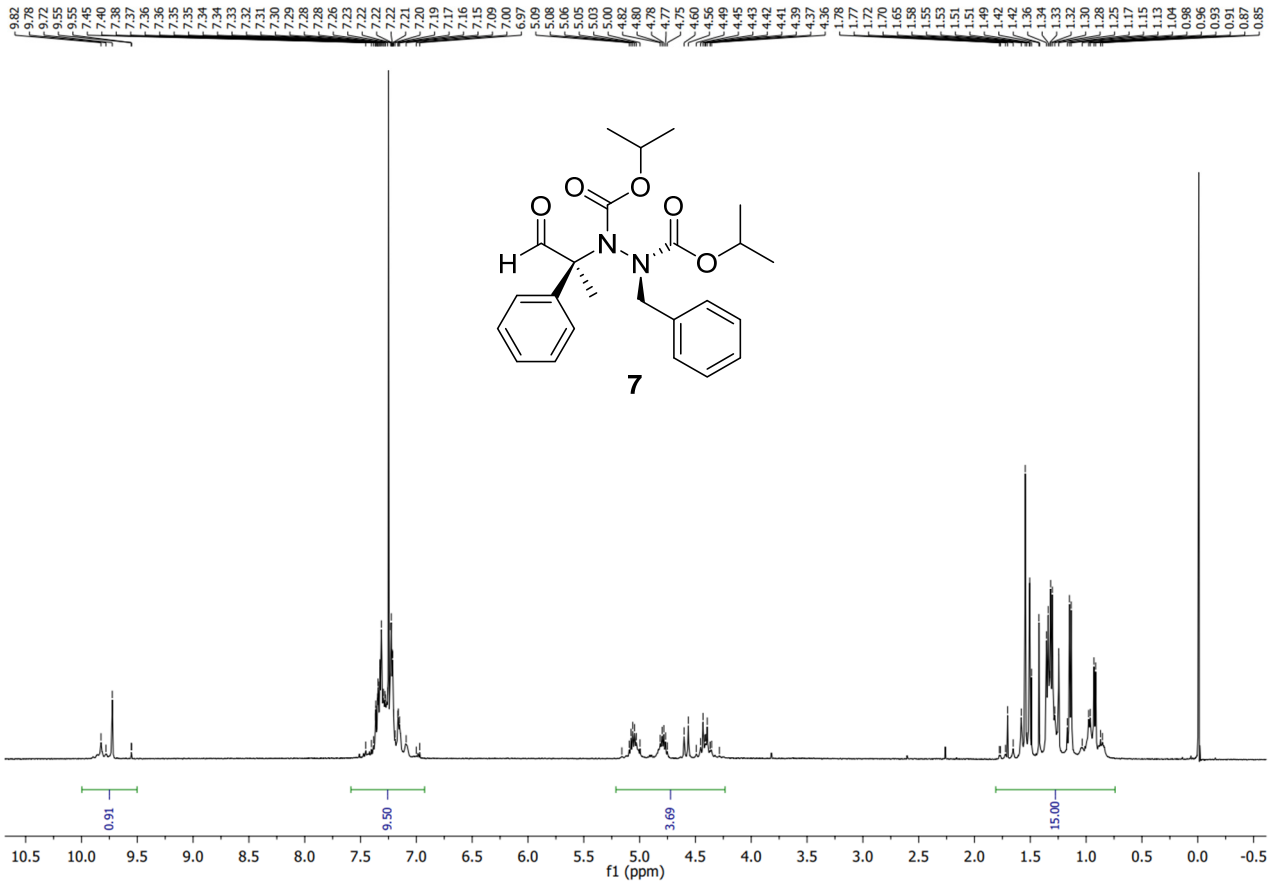
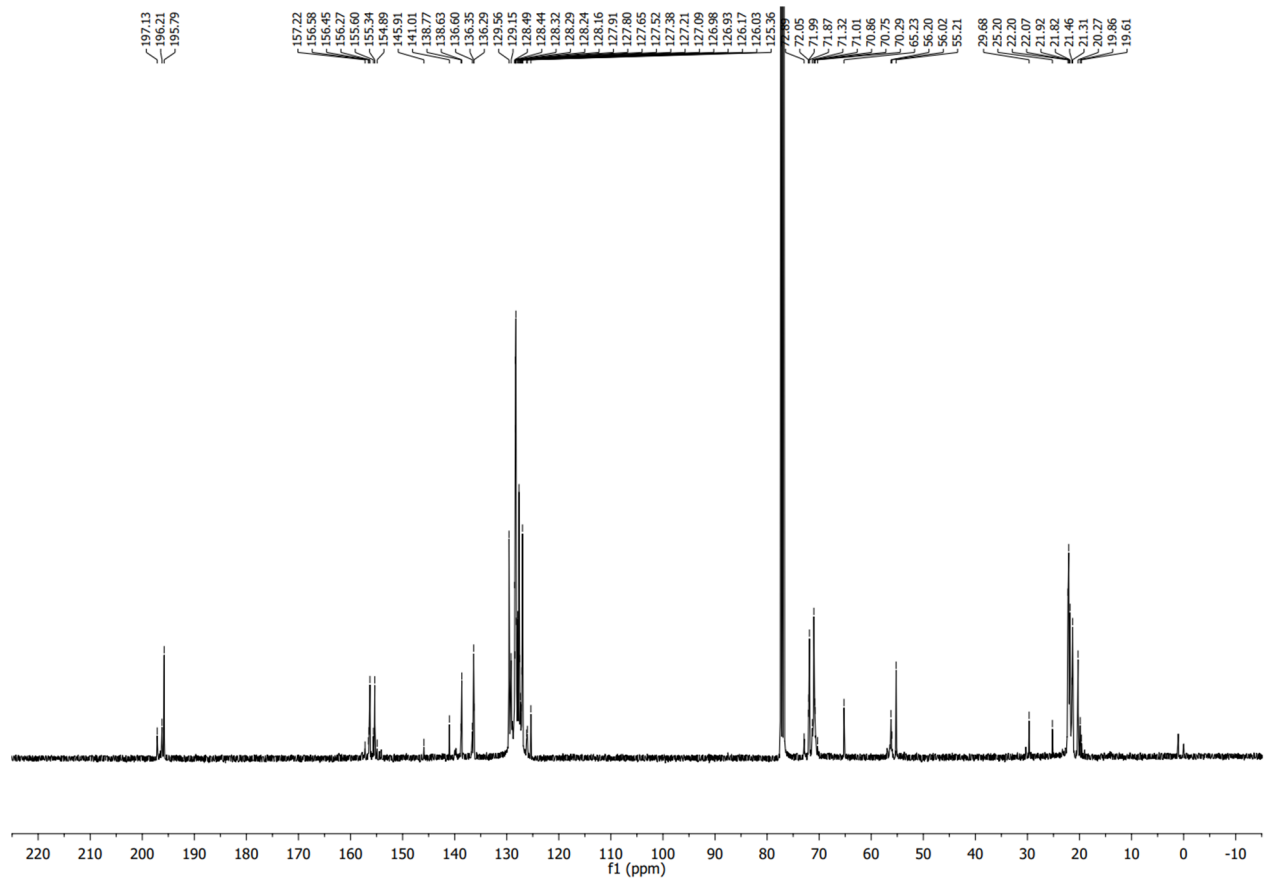
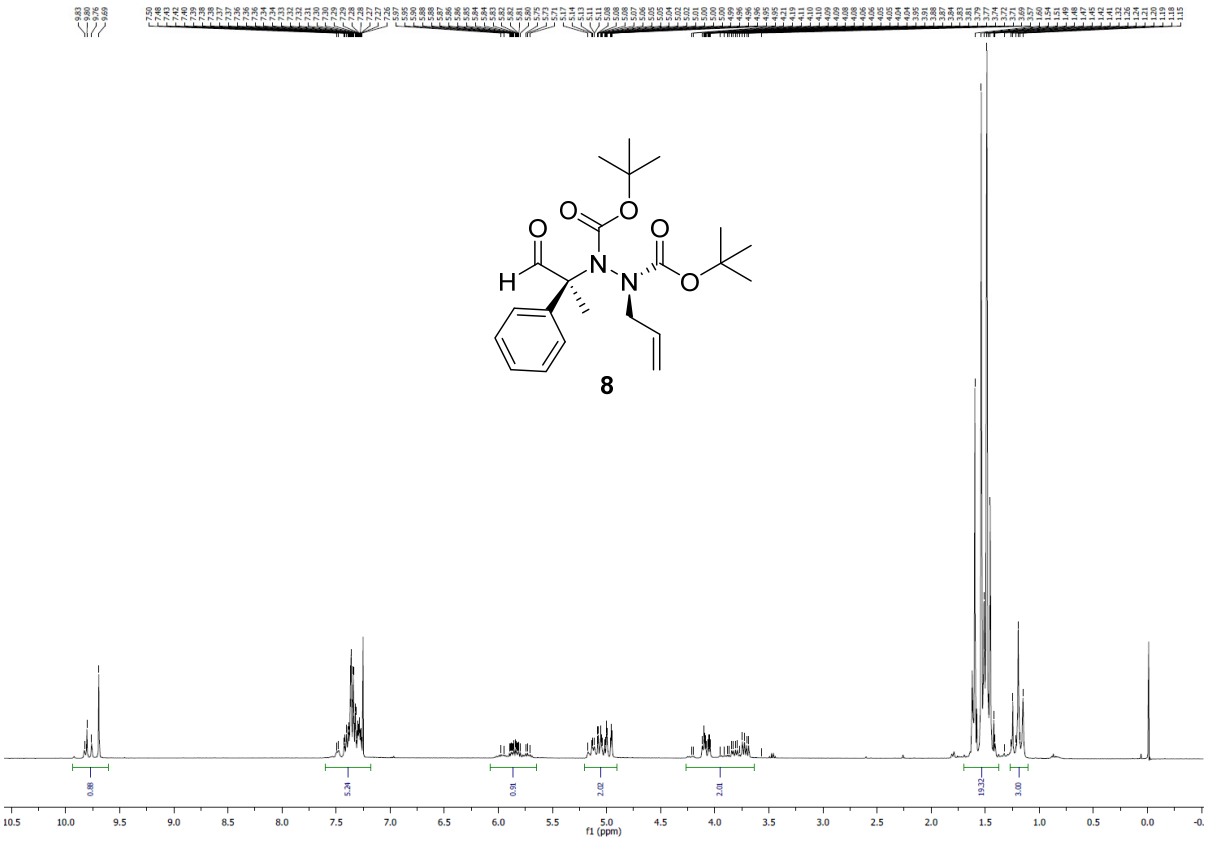
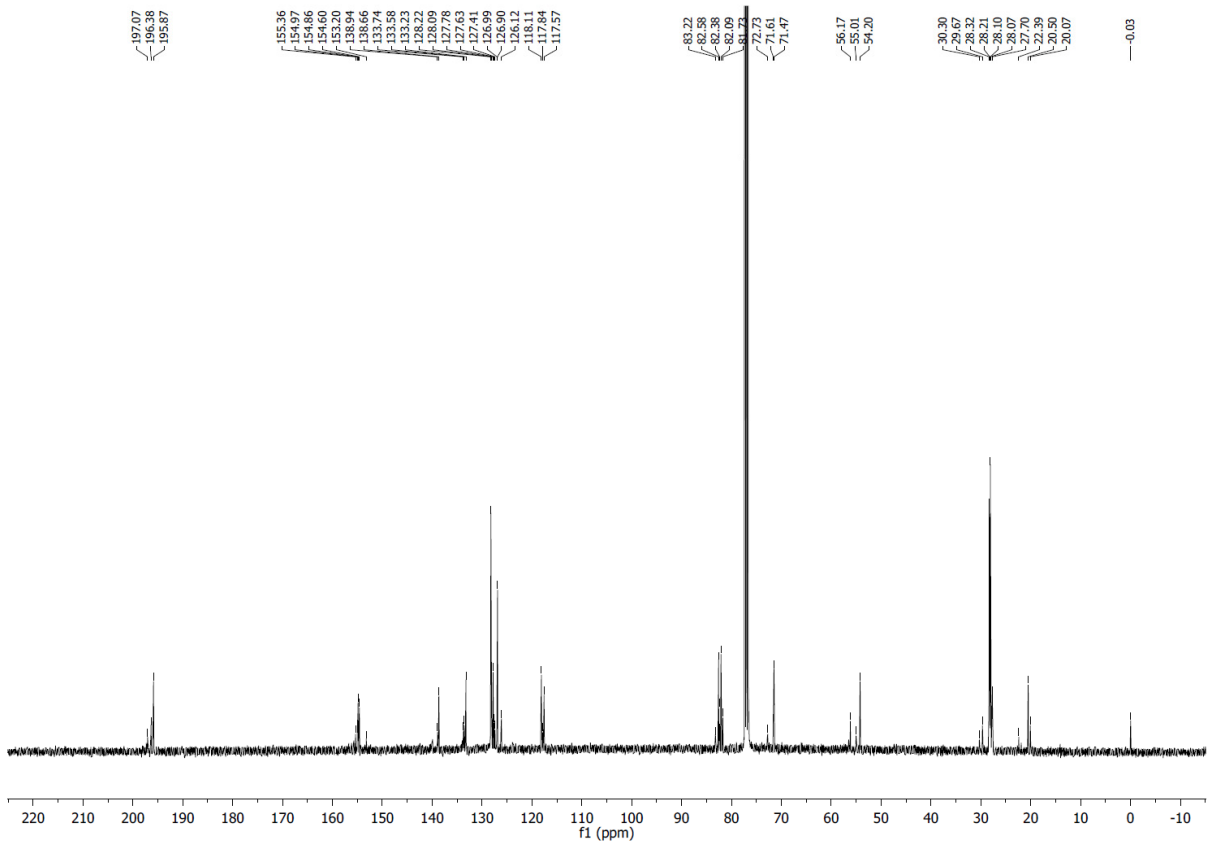


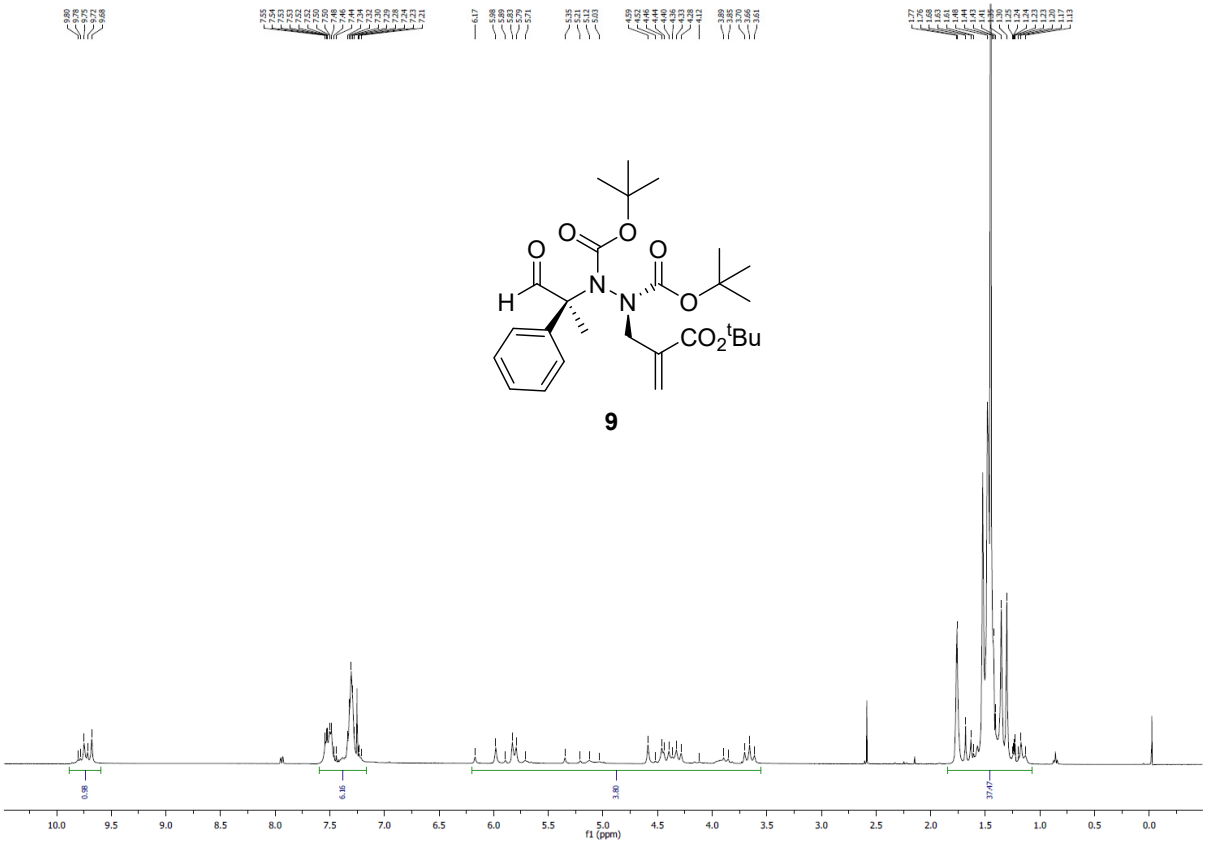


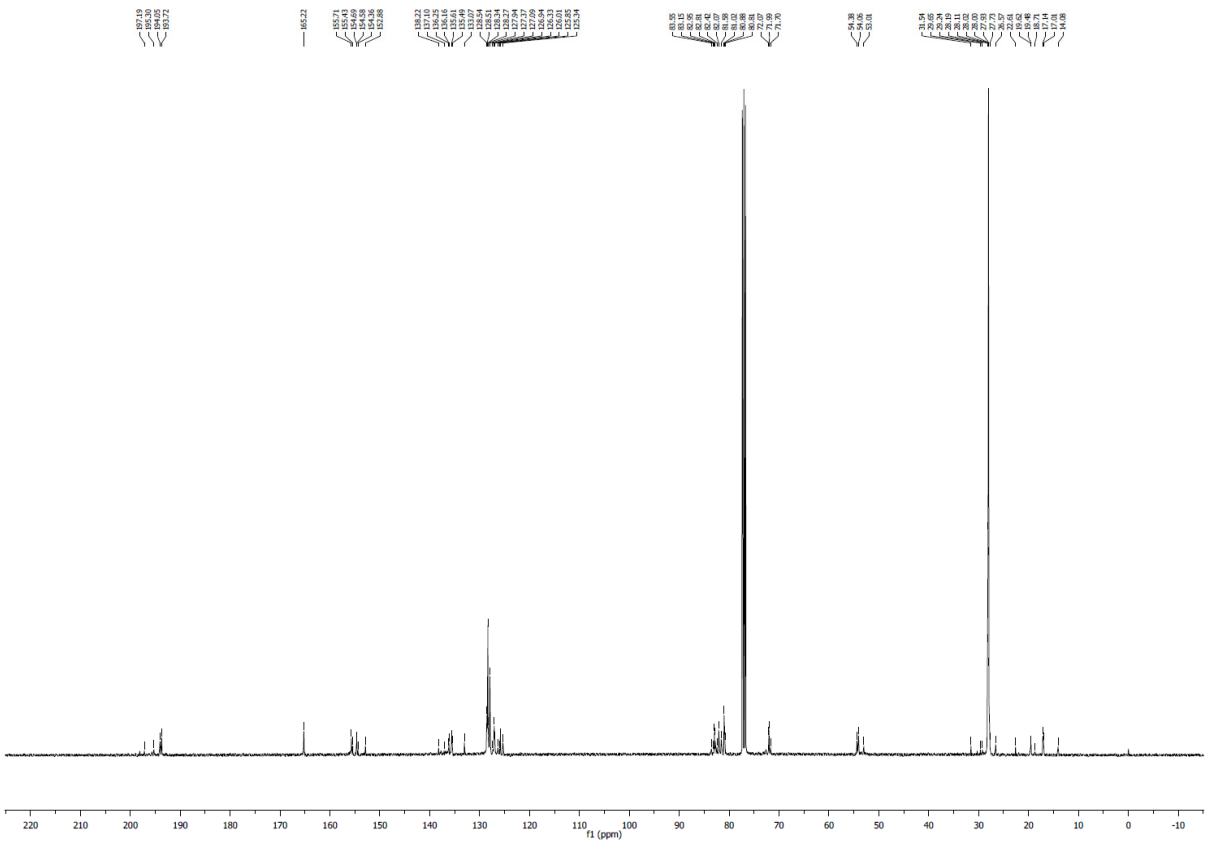
7

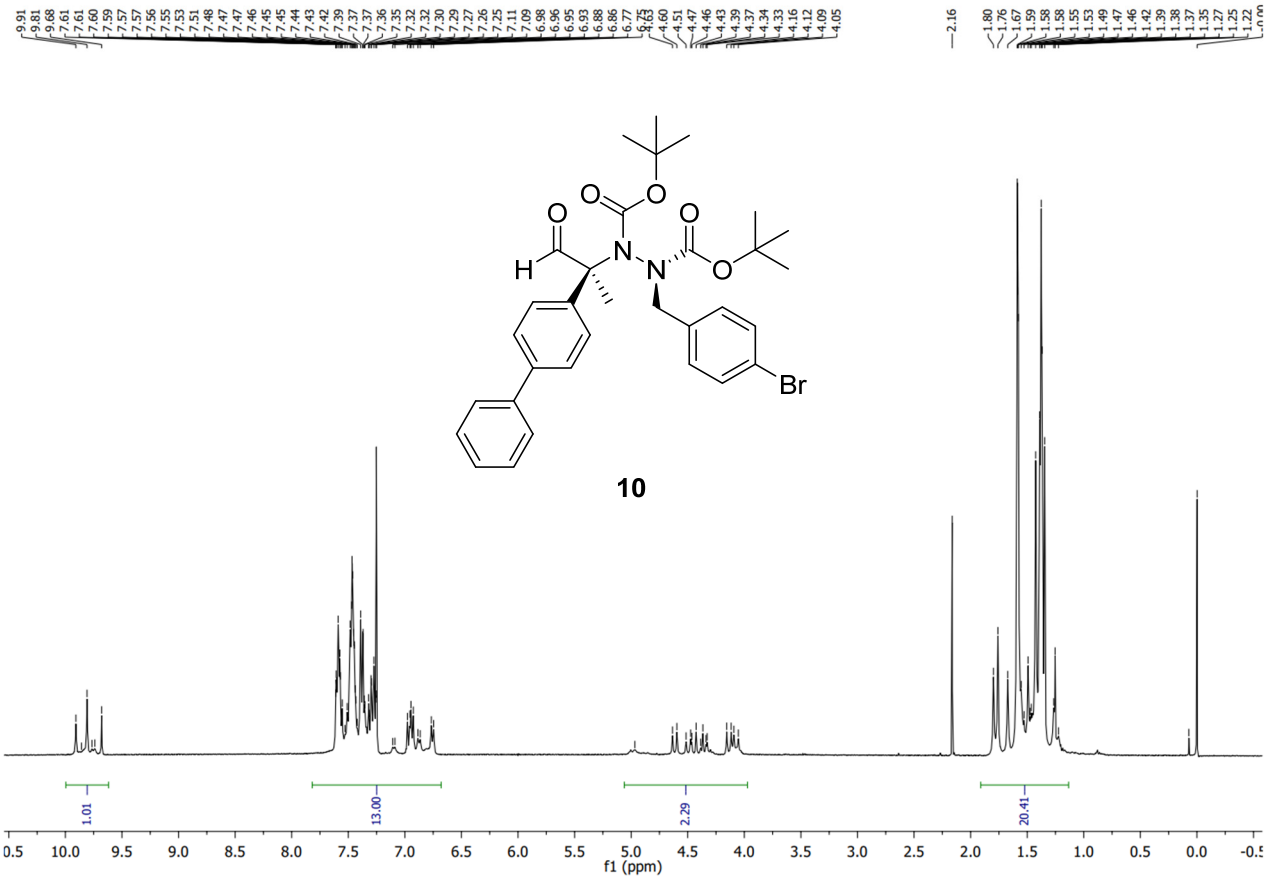


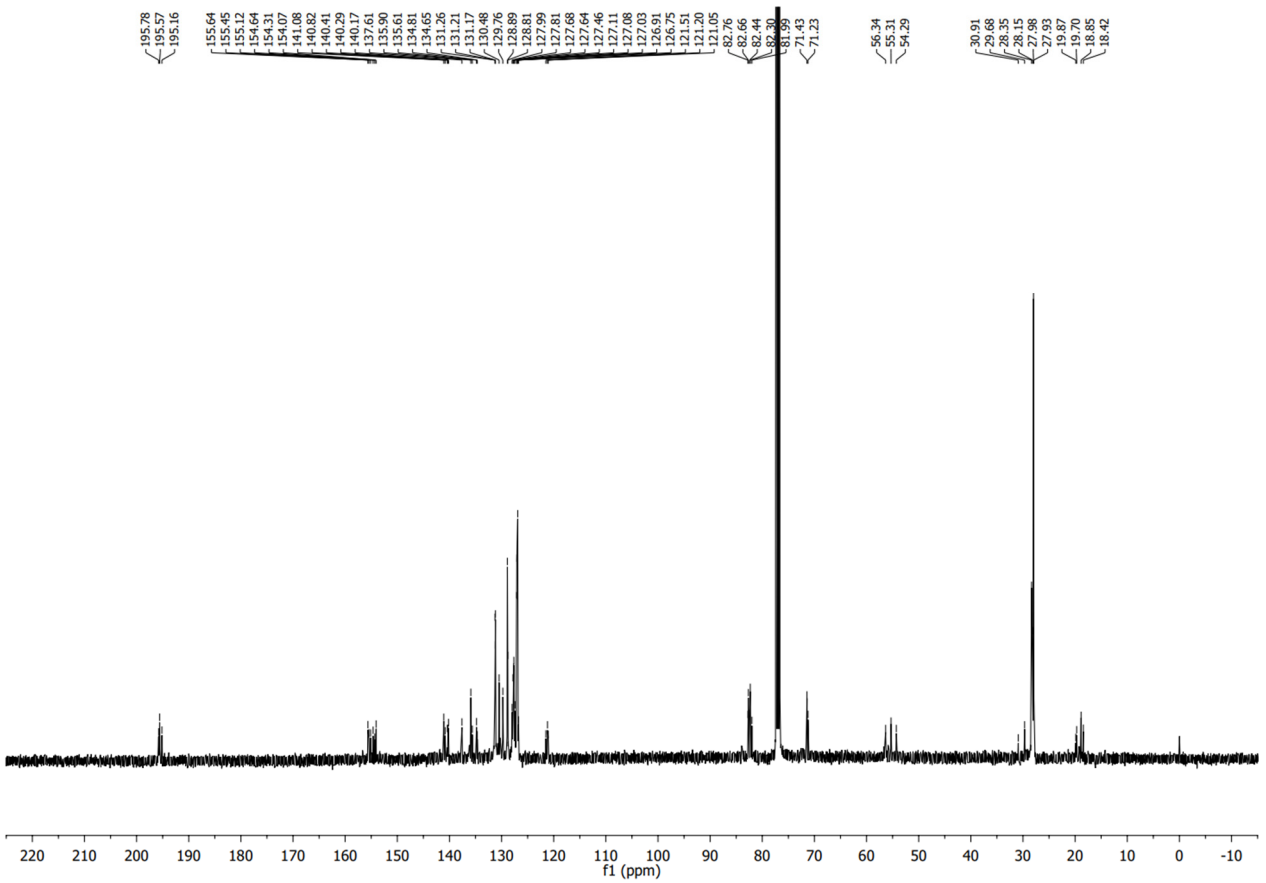

8
f1 (ppm)

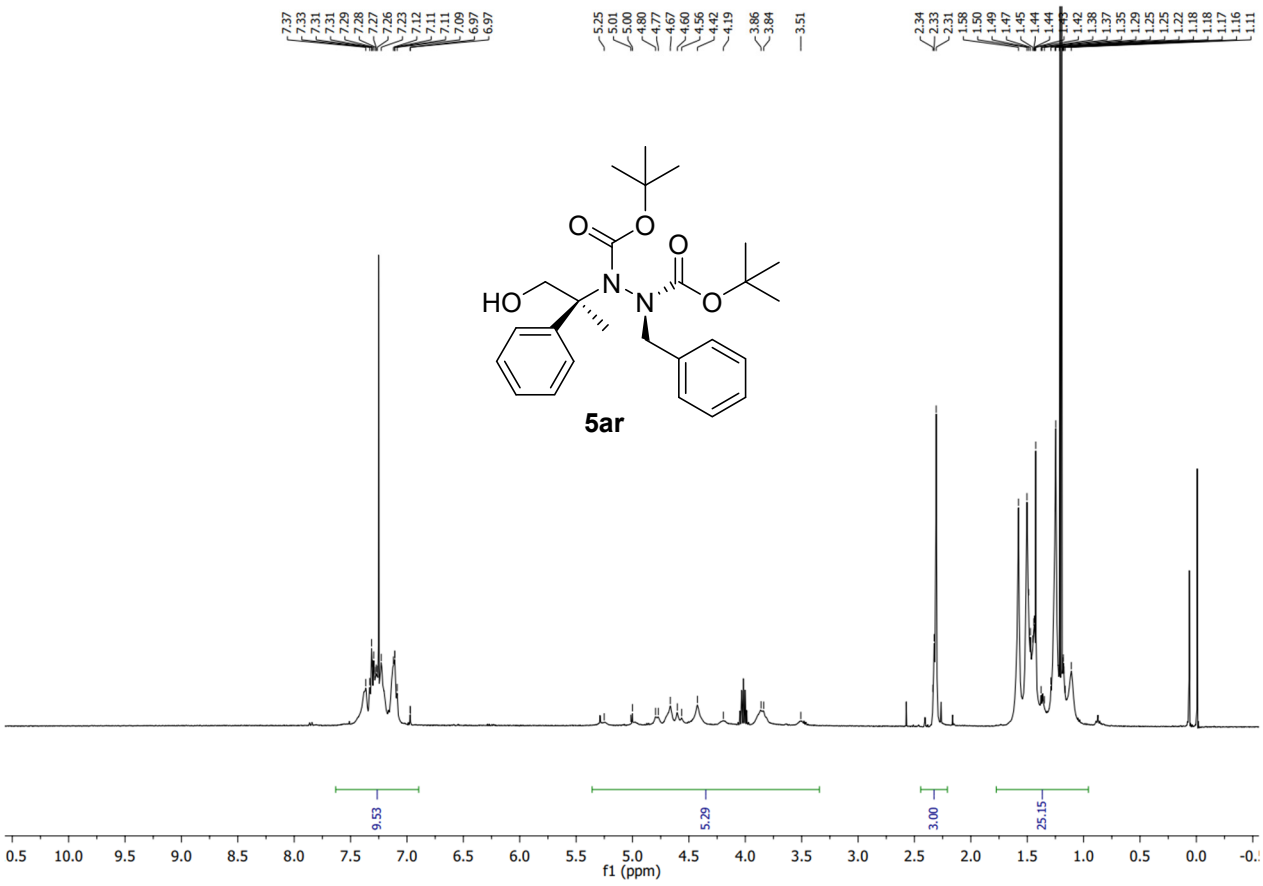

f1 (ppm)

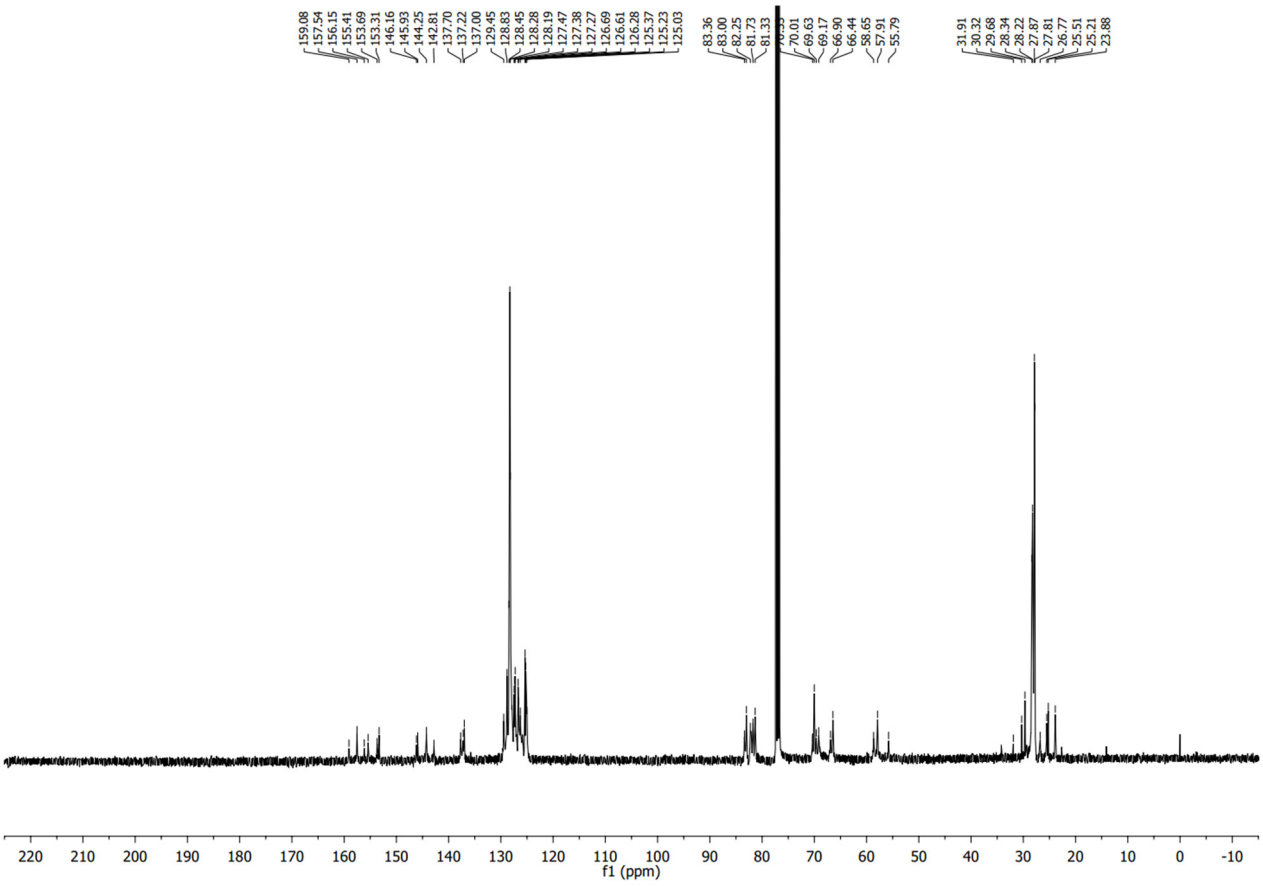

O
O
O
O
H
N
N
O
CO2tBu
9
0.98
6.16
3.80
37.47
f1 (ppm)

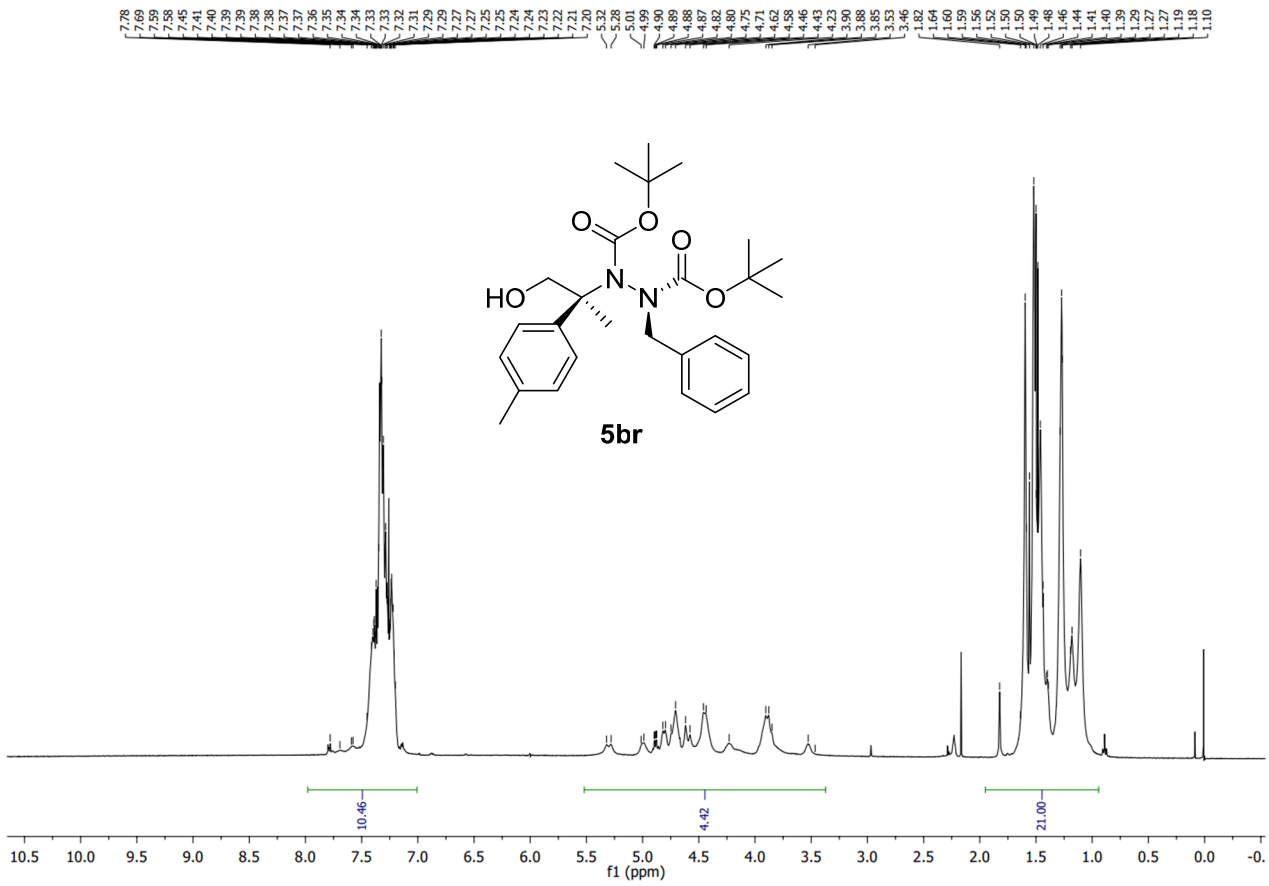

f1 (ppm)

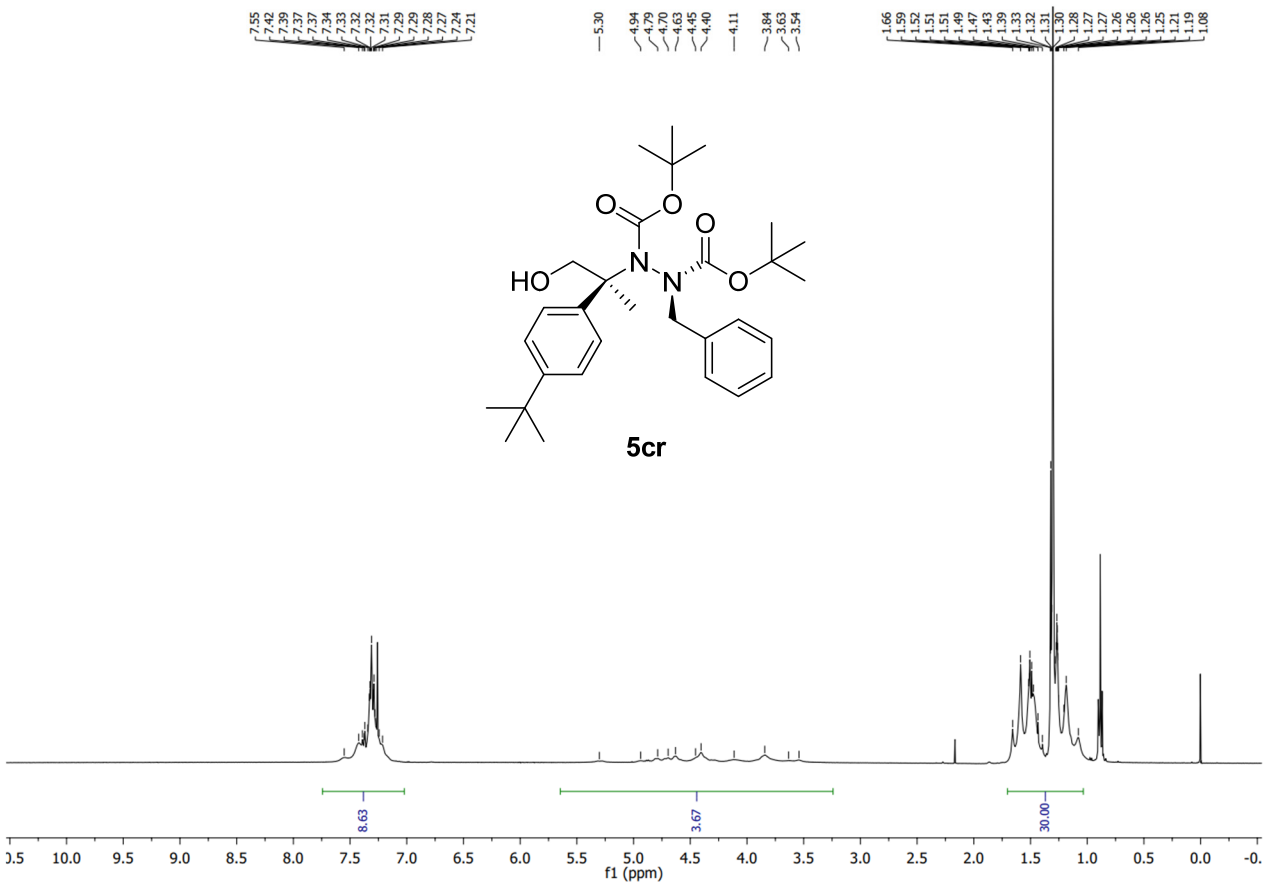

10
1.01
13.00
2.29
20.41
f1 (ppm)

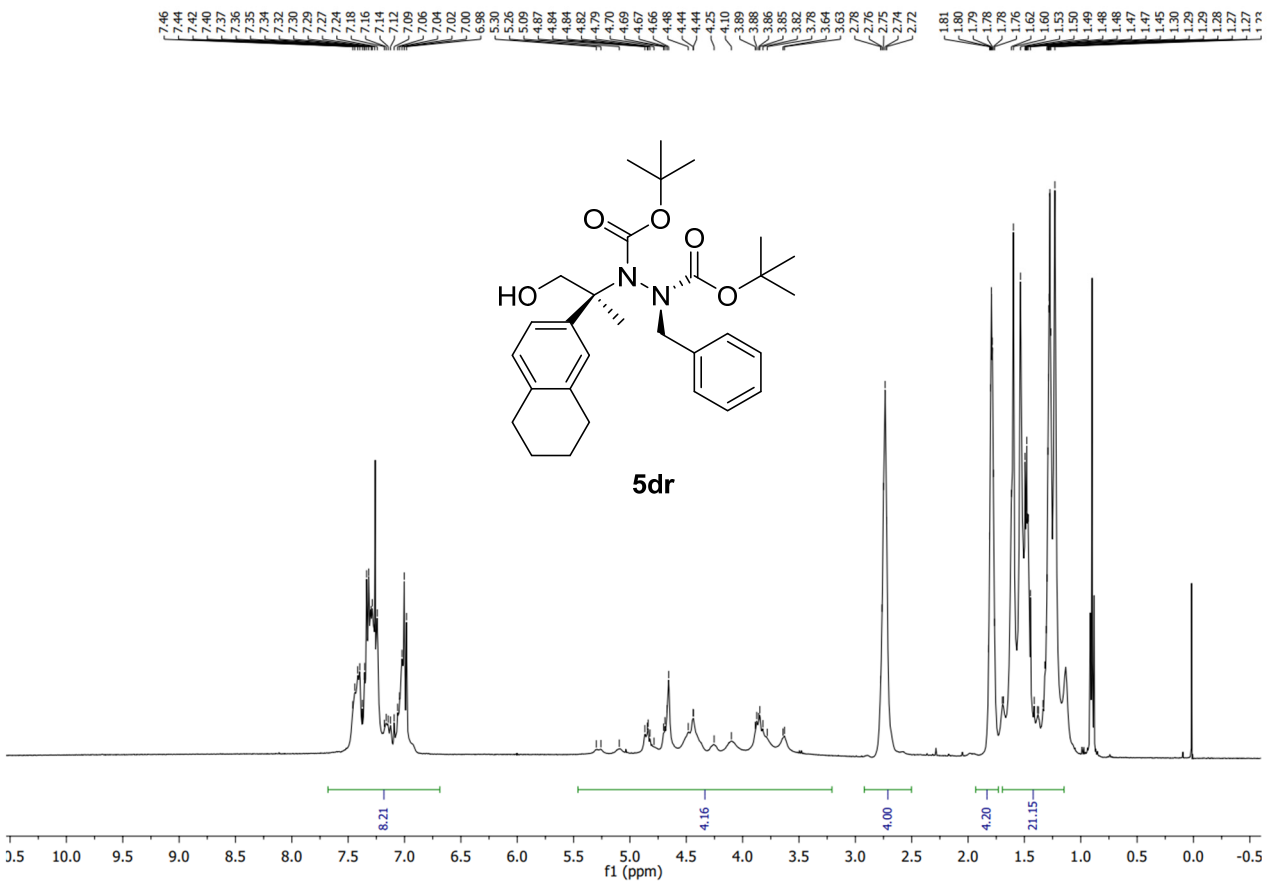

f1 (ppm)

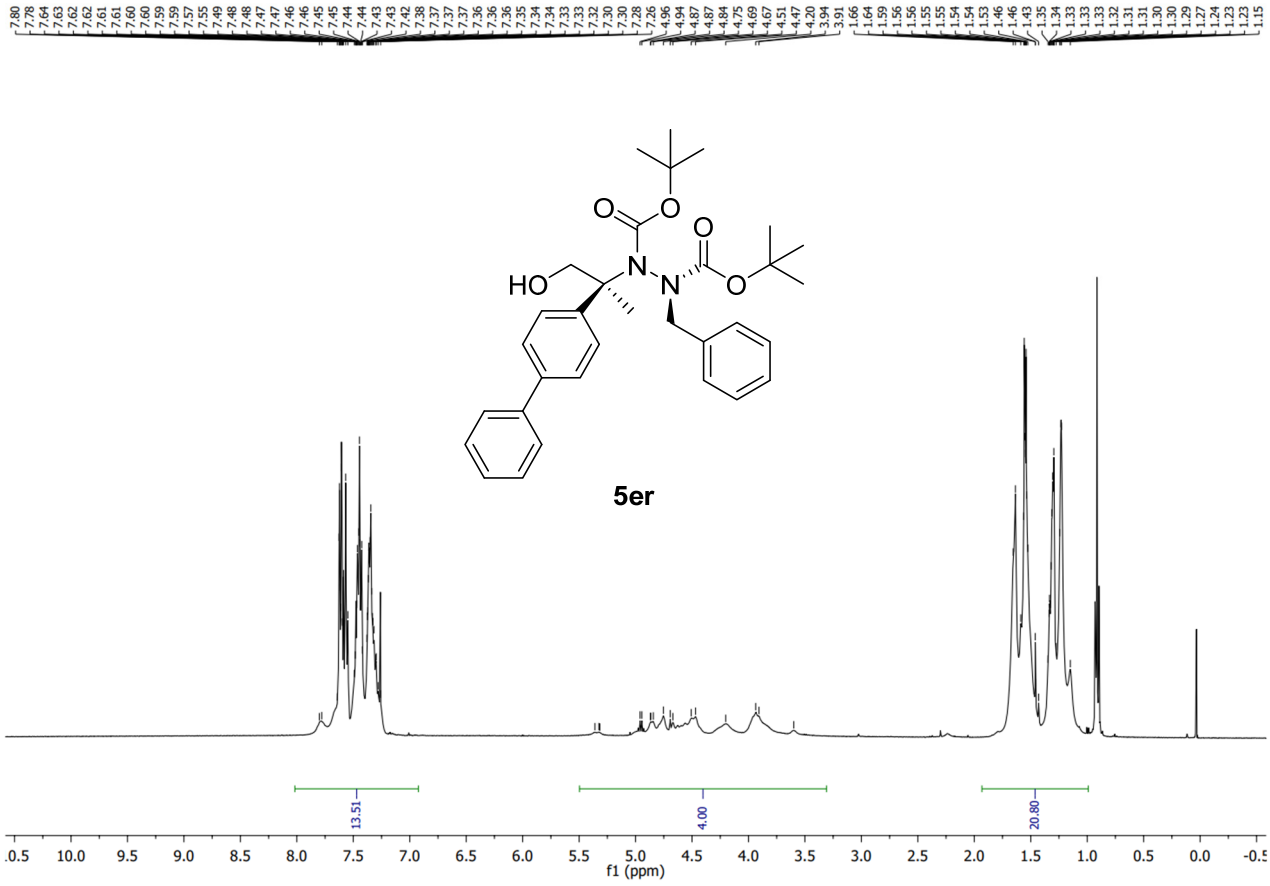

HO
N
N
O
O
O
O
O
5ar
9.53
5.29
3.00
25.15
f1 (ppm)

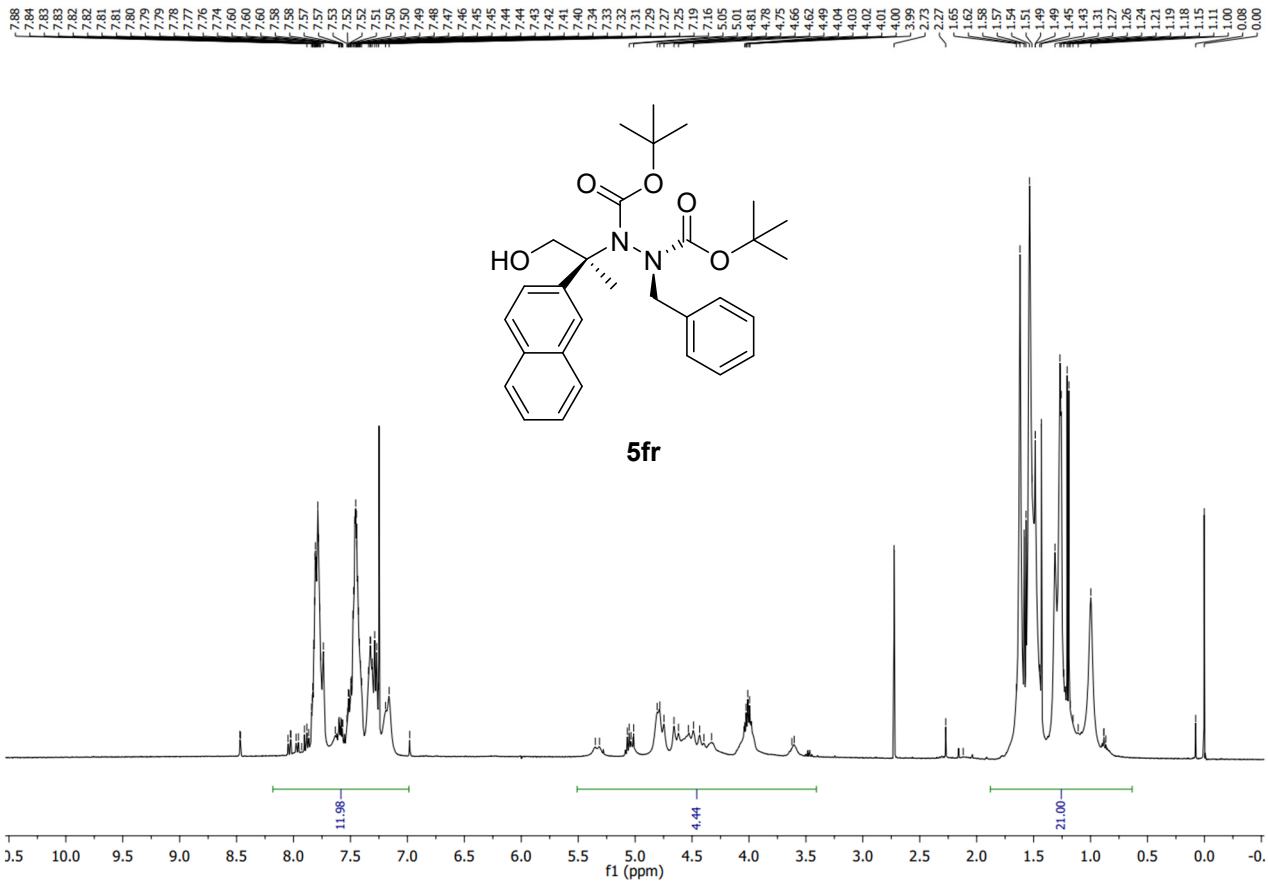

f1 (ppm)


HO
N
N
O
O
O
O
O
5br
10.46
4.42
21.00
f1 (ppm)

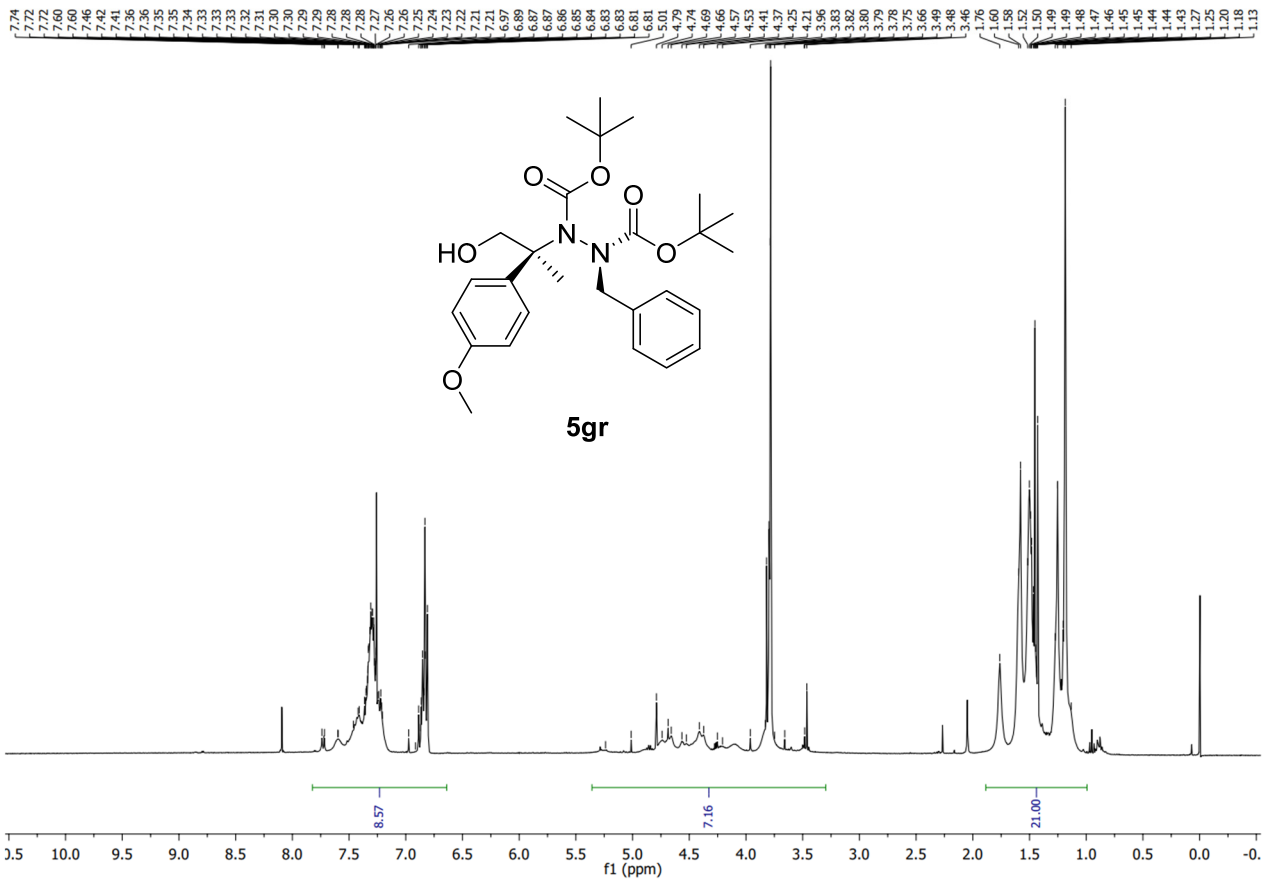

HO
N
N
O
O
O
O
O
5cr
8.63
3.67
30.00
f1 (ppm)


HO
N
N
O
O
O
O
O
5dr
8.21
4.16
4.00
4.20
21.15
f1 (ppm)

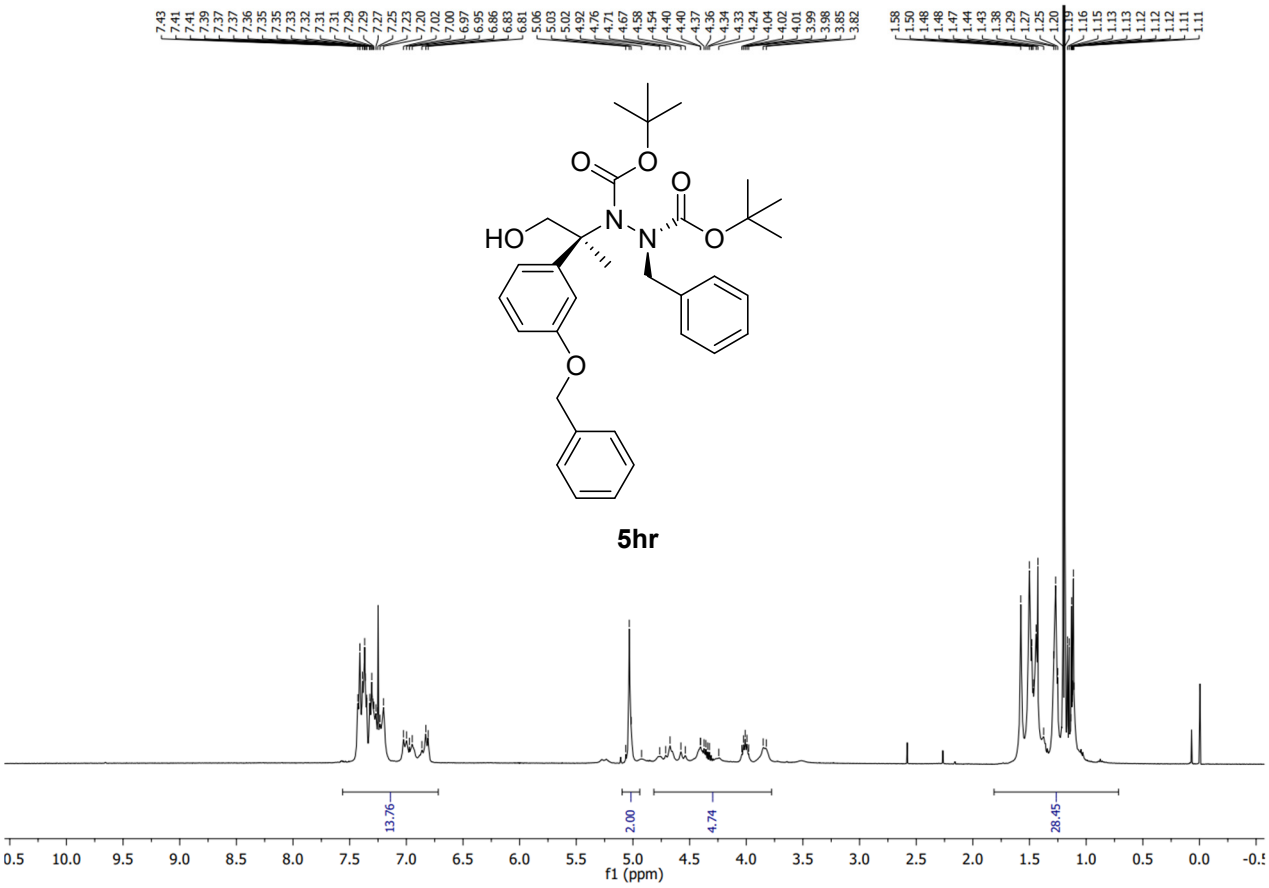

HO
N
N
O
O
O
O
O
5er
13.51
4.00
20.80
f1 (ppm)



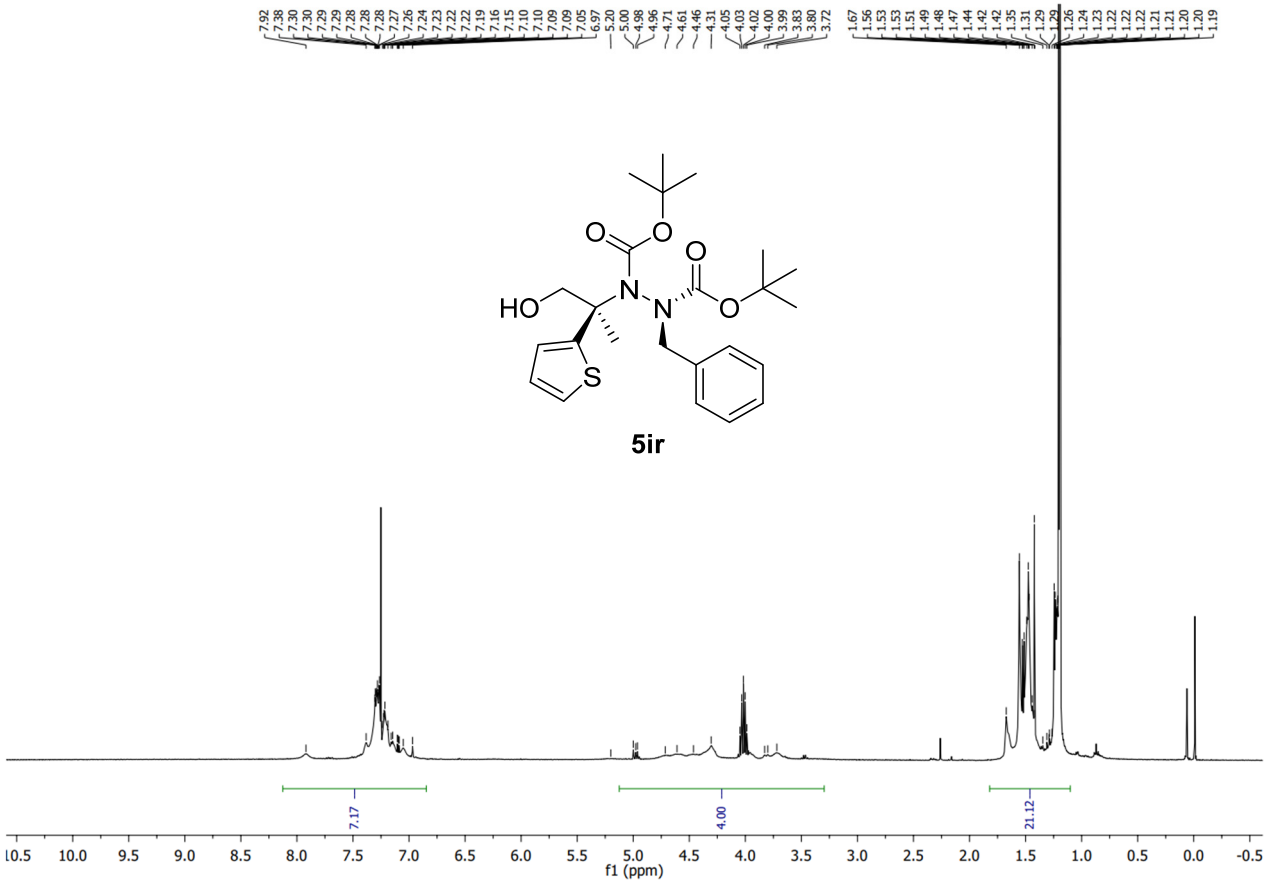
5fr



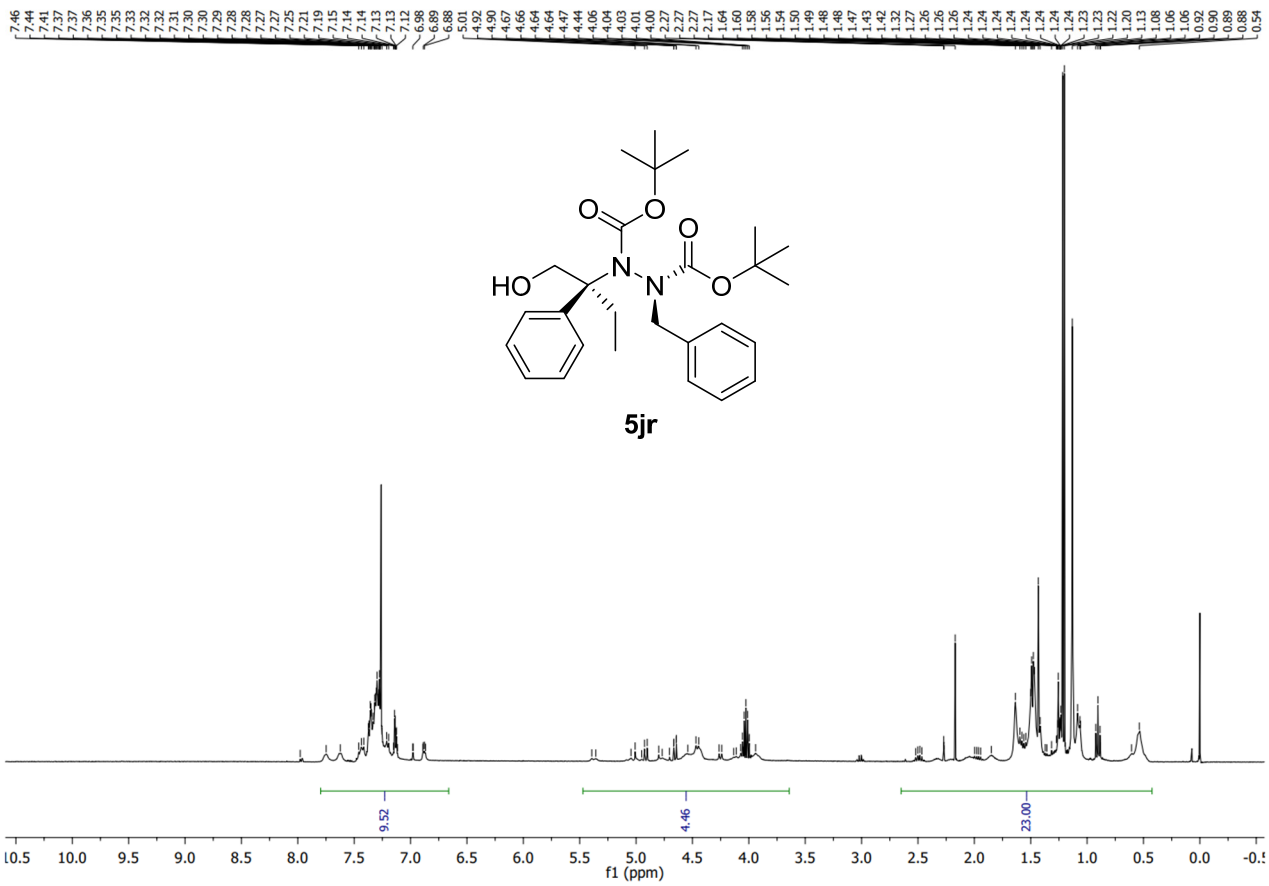
5gr


HO
O
N
N
O
O
O
O
O
13.76
2.00
4.74
28.45
f1 (ppm)

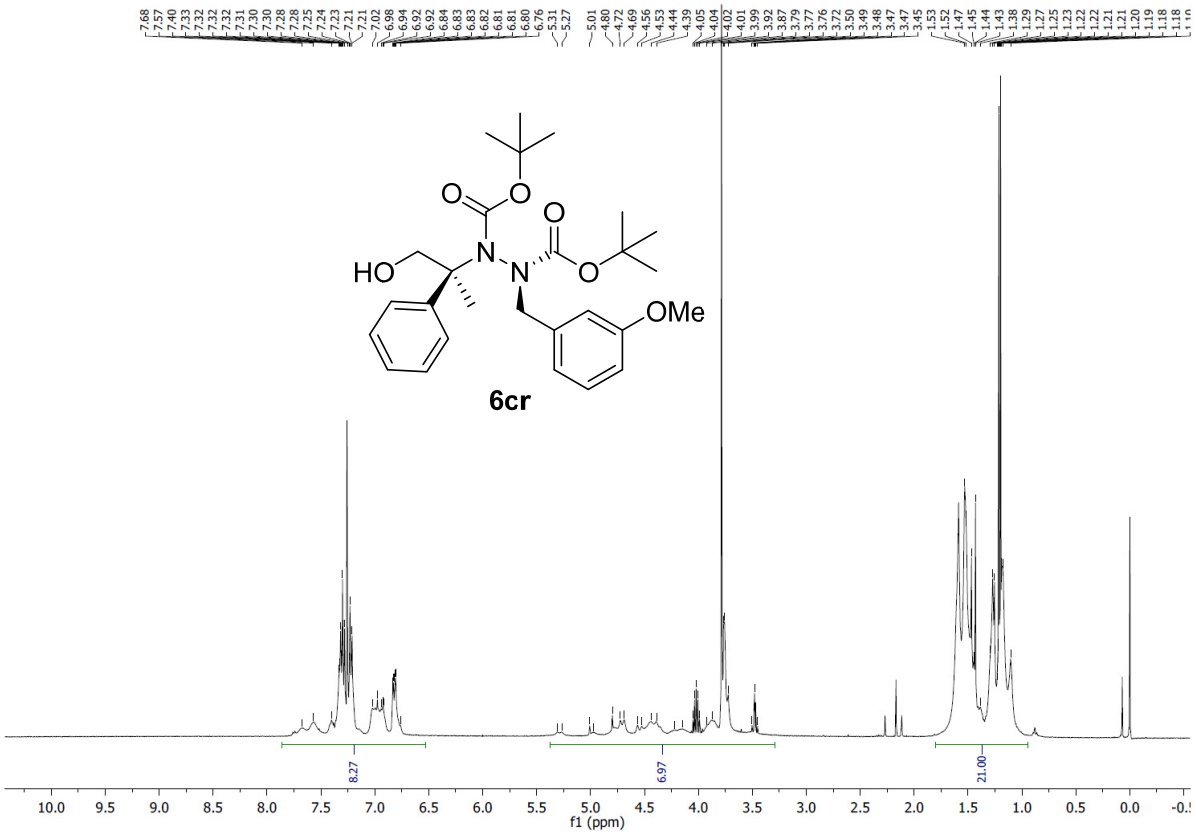
5hr


HO
O
N
N
O
O
O
S
7.17
4.00
21.12
f1 (ppm)

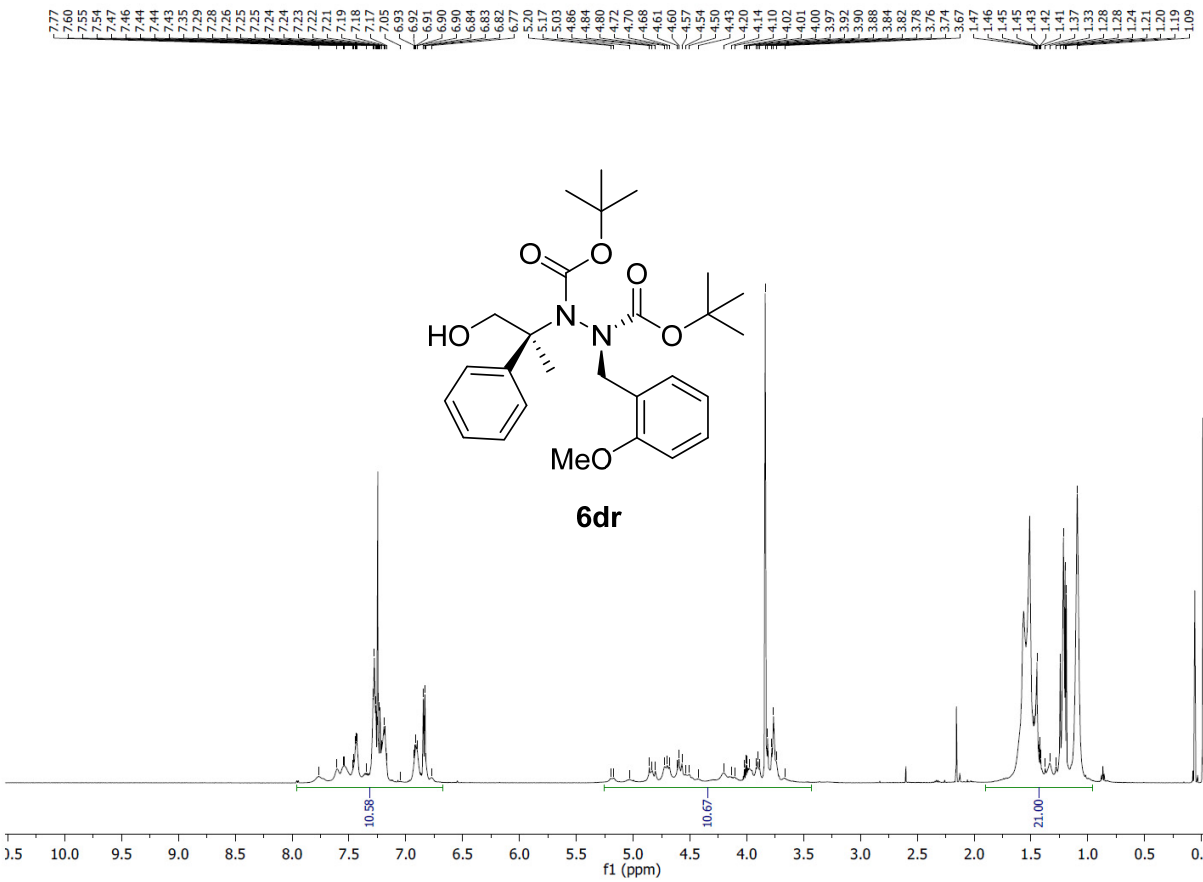
5ir


HO
N
N
O
O
O
O
O
9.52
4.46
23.00
f1 (ppm)

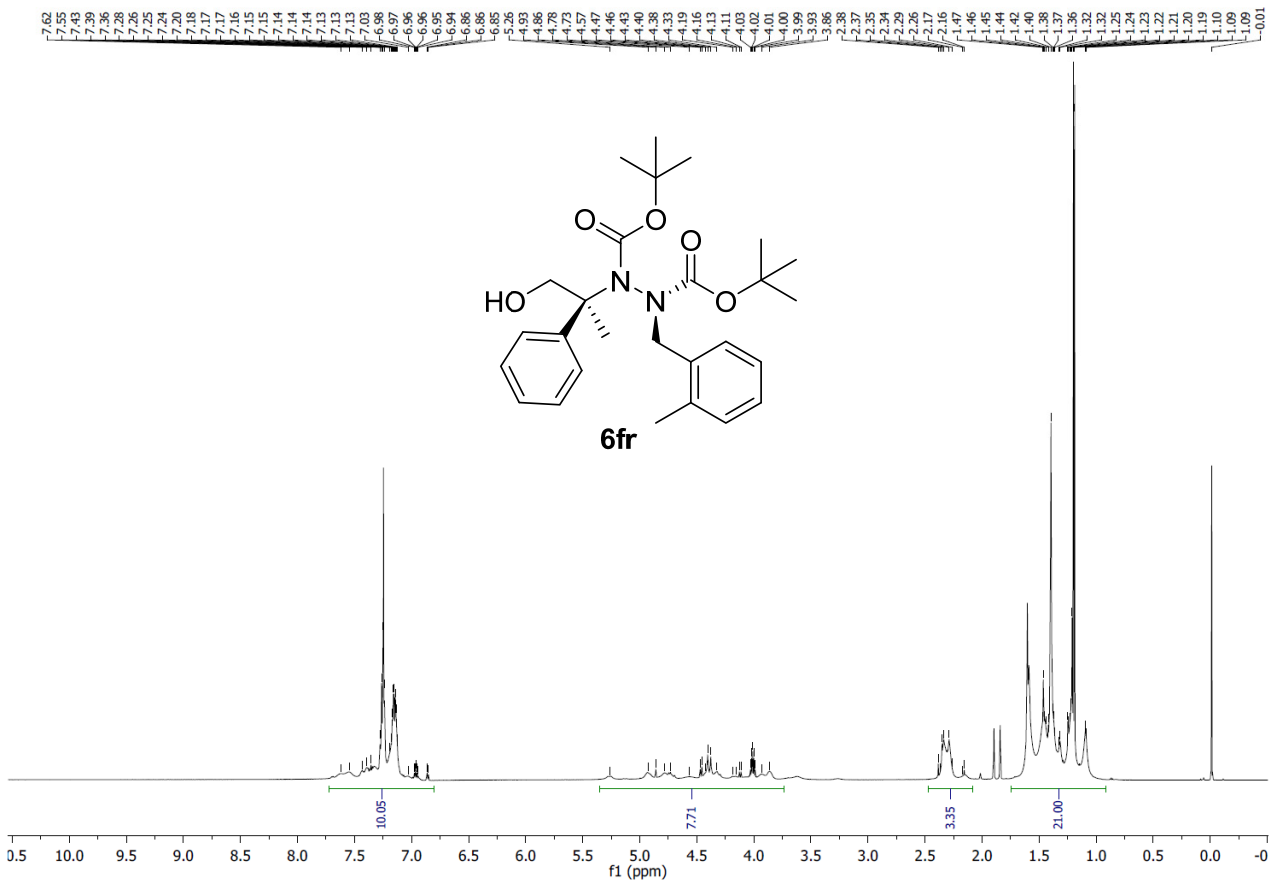
5jr


HO
N
N
O
O
O
O
O
OMe
8.27
6.97
21.00
f1 (ppm)

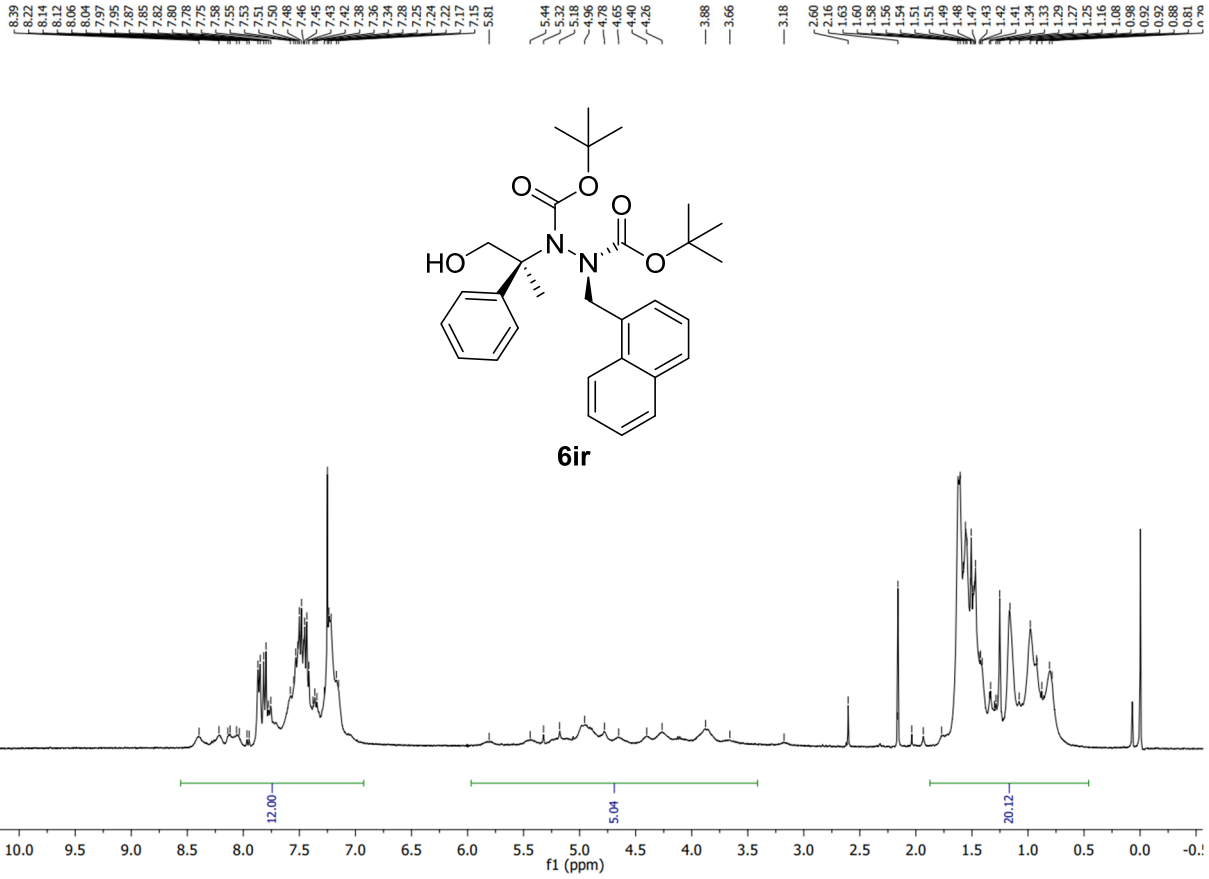
6cr

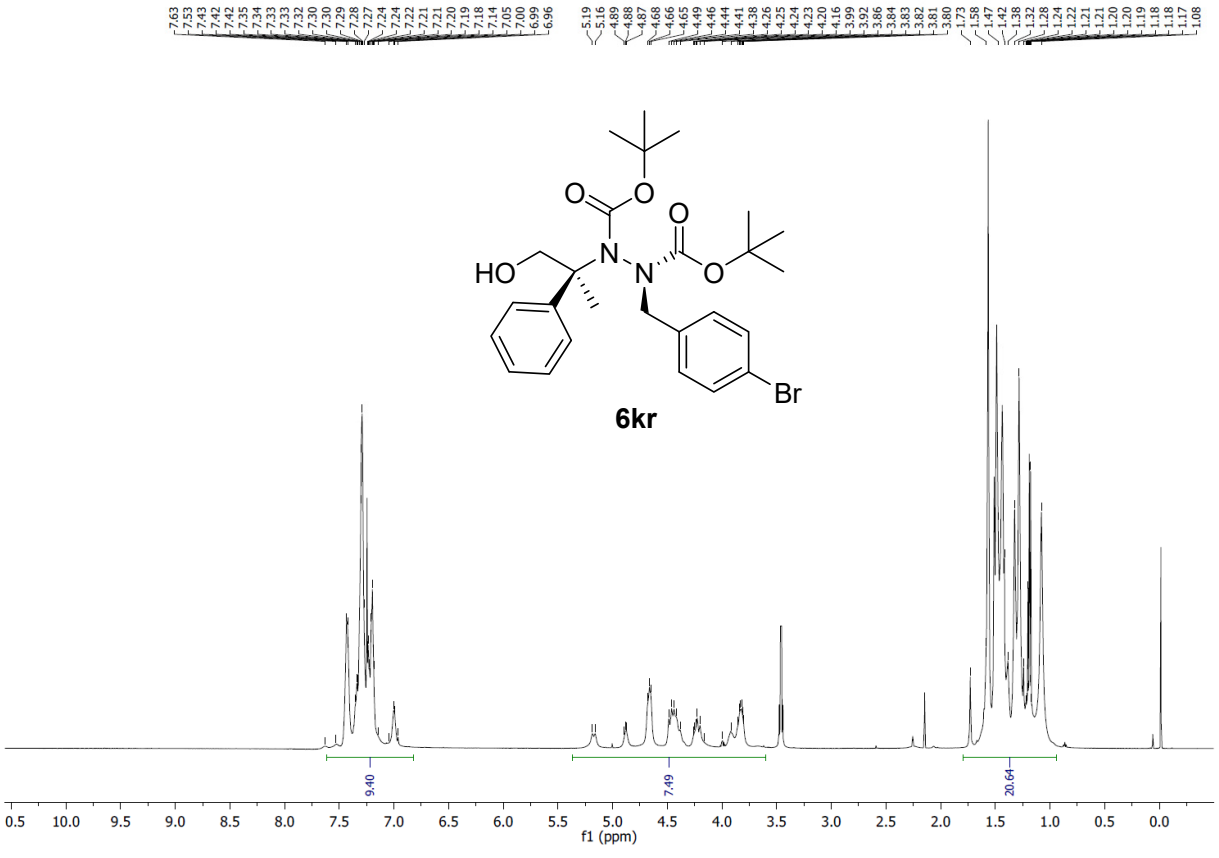

HO
N
N
O
O
O
O
O
MeO
10.58
10.67
21.00
f1 (ppm)

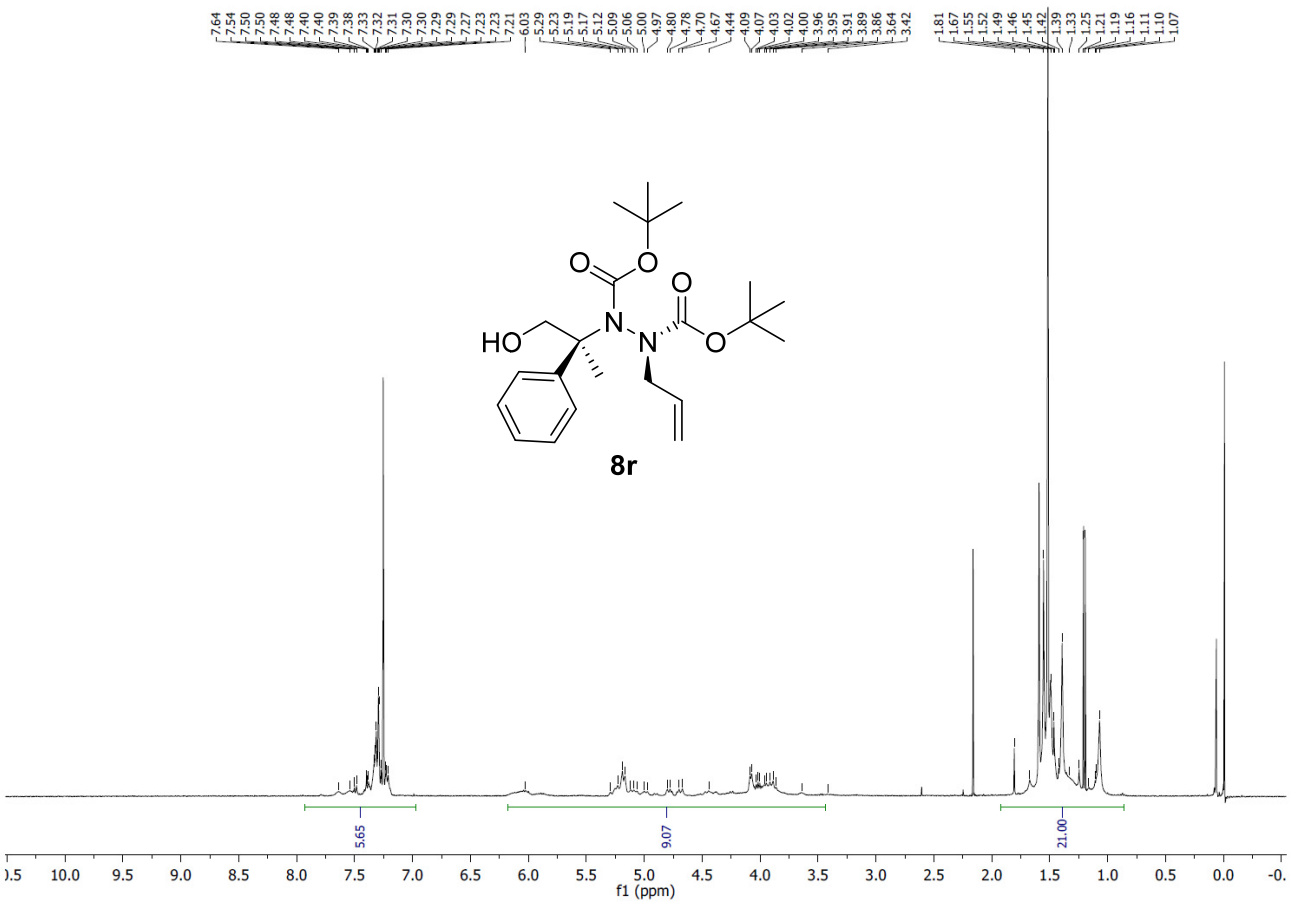
6dr

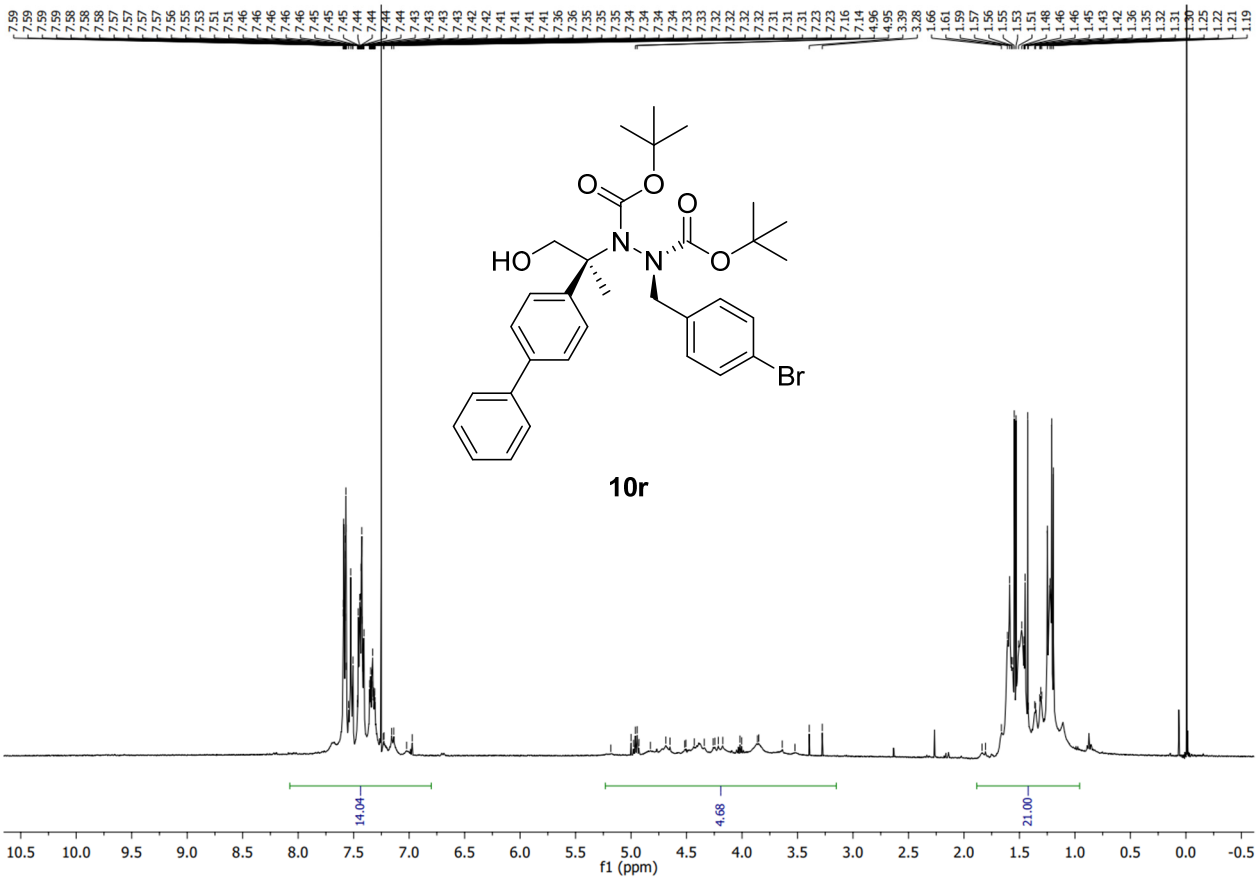

HO
N
N
O
O
O
O
O
10.05
7.71
3.35
21.00
f1 (ppm)

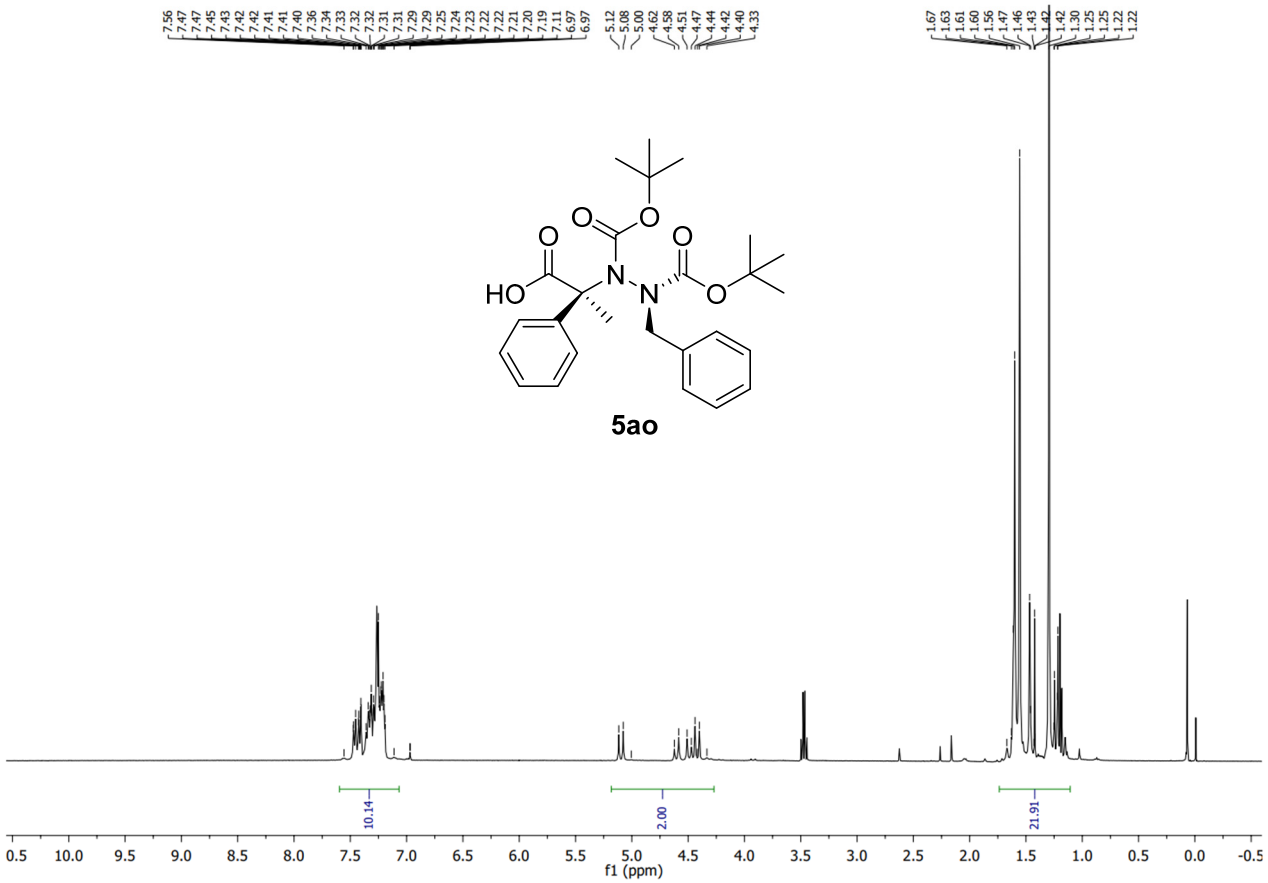
6fr

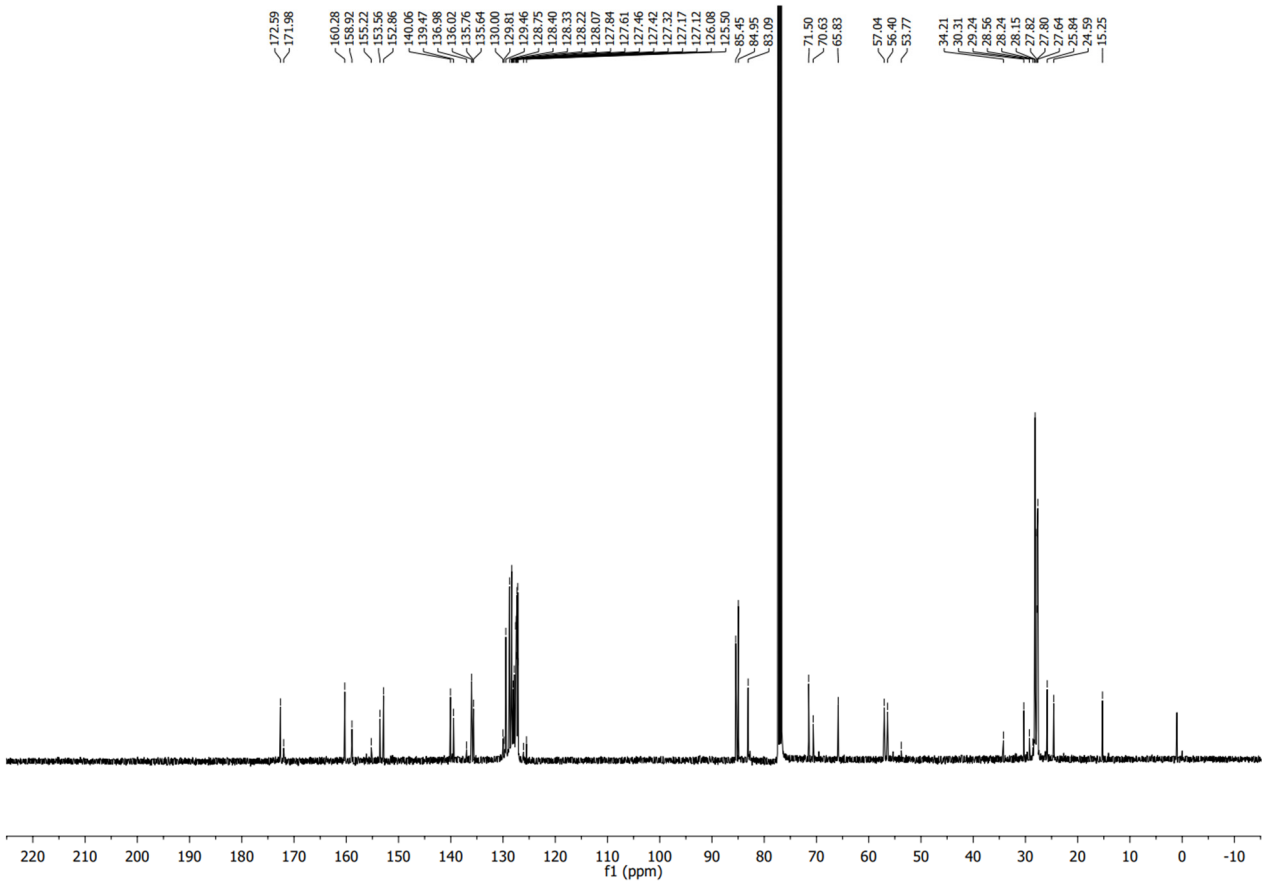

6ir
12.00
5.04
20.12
f1 (ppm)


6kr
9.40
7.49
20.64
f1 (ppm)


HO
O
O
N
N
O
O
8r
5.65
9.07
21.00
f1 (ppm)

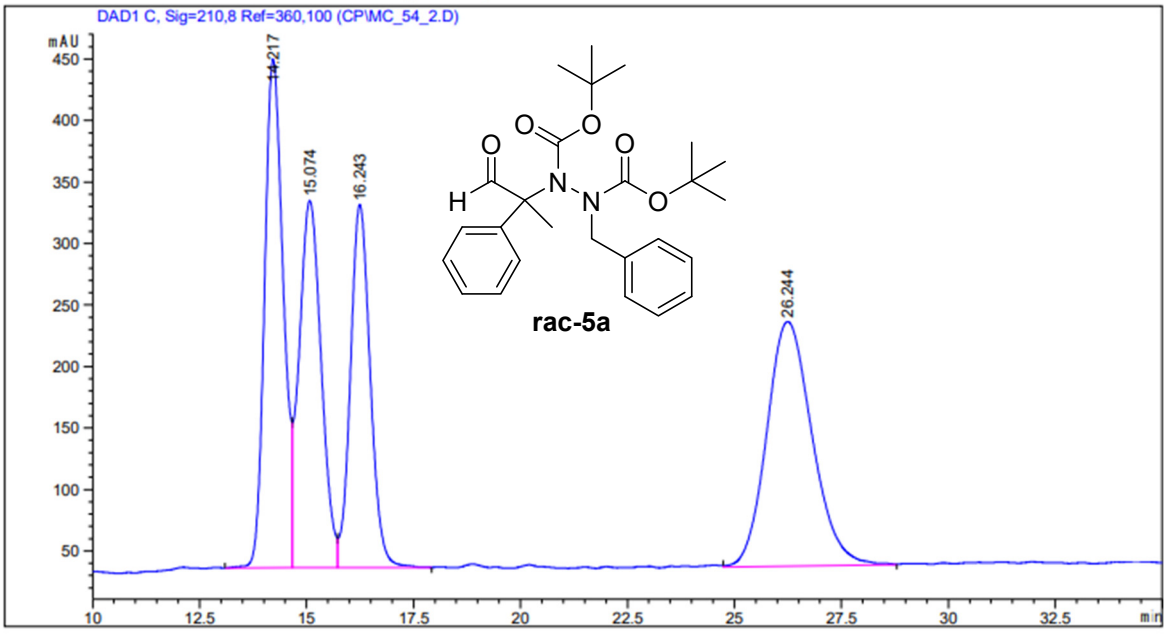

HO
O
O
N
N
O
O
Br
10r
14.04
4.68
21.00
f1 (ppm)


HO
O
O
O
O
O
N
N
5ao
10.14
2.00
21.91
f1 (ppm)


f1 (ppm)

HPCL traces

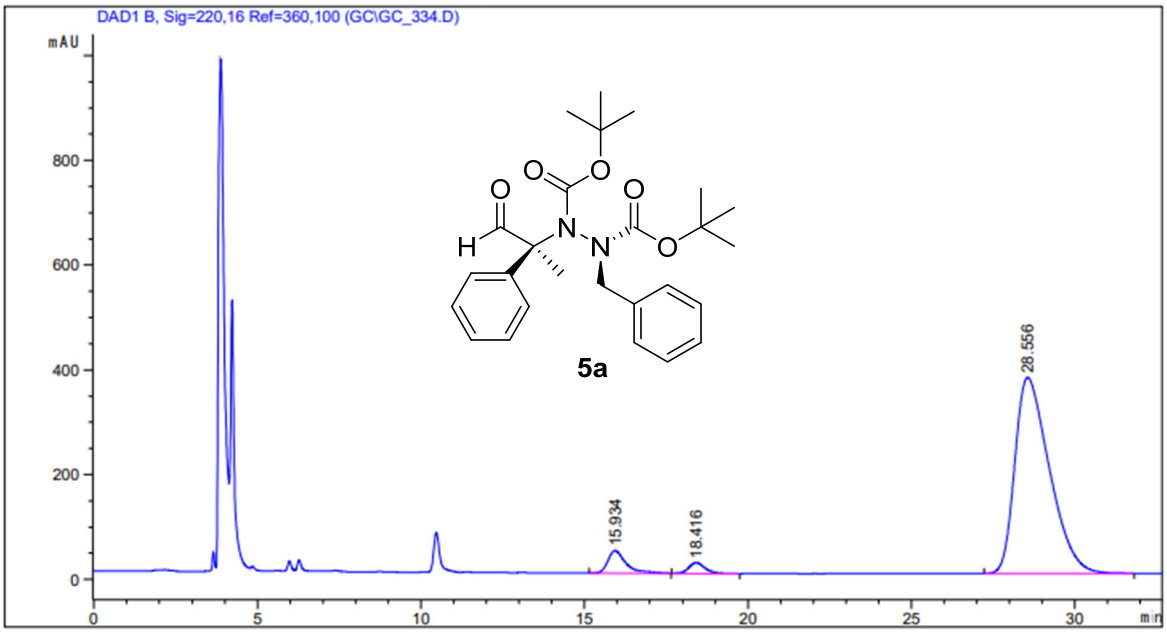
```
Data File C:\CHEM32\1\DATA\CP\MC_54_2.D
Sample Name: MC_54_2

    ======================================================================
    Acq. Operator    : Chiara
    Acq. Instrument : HPLC-1                          Location : Vial 1
    Injection Date   : 23/02/2021 13:39:21
    Acq. Method      : C:\CHEM32\1\METHODS\DEF_LC.M
    Last changed     : 23/02/2021 13:31:10 by Chiara
                       (modified after loading)
    Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
    Last changed     : 24/02/2021 18:09:49 by Chiara
                       (modified after loading)
    Sample Info      : MC_54_2, 1.0 mL/min, 98:2 hex:ipr, 25°C, IC


    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier:                   :      1.0000
    Dilution:                     :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 C, Sig=210,8 Ref=360,100

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]    [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  14.217 BV    0.4660 1.25196e4   412.61871  26.4103
       2  15.074 VV    0.5484 1.07350e4   297.93188  22.6456
       3  16.243 VB    0.5045 9504.39063  294.48352  20.0496
       4  26.244 VV    1.1159 1.46453e4   198.70433  30.8945

    Totals :                  4.74044e4  1203.73845
```

Data File C:\CHEM32\1\DATA\GC\GC_334.D
Sample Name: GC_334.D

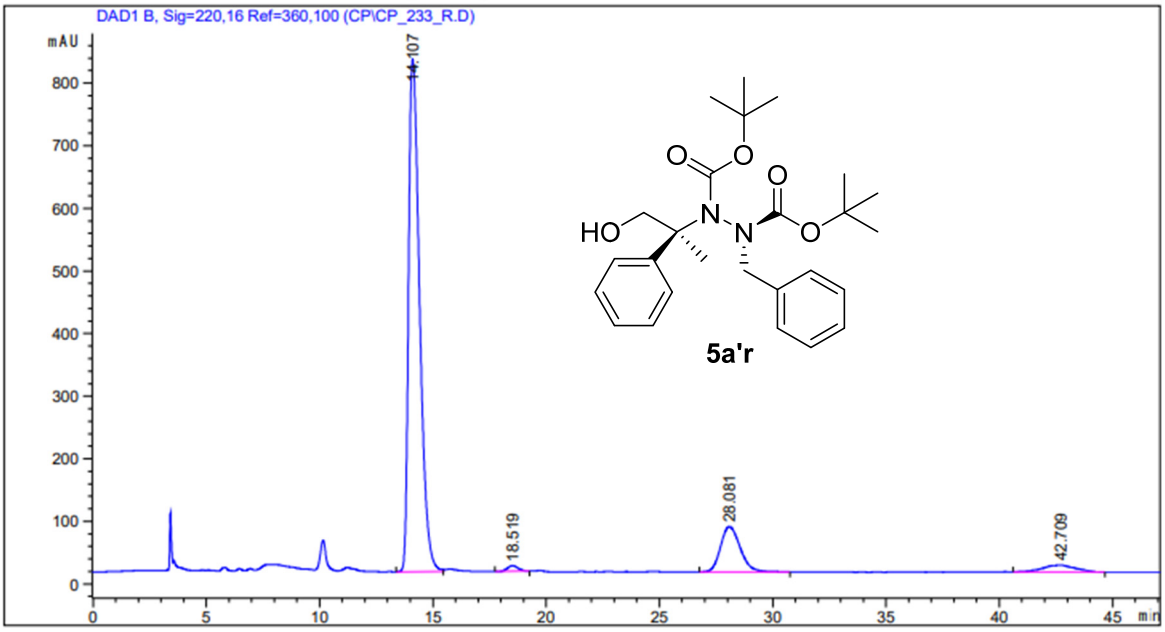
```
==========================================================================
Acq. Operator    : Chiara
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date   : 10/12/2021 15:04:47
Acq. Method      : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 10/12/2021 14:42:19 by Chiara
                   (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 18/05/2022 15:43:08 by Giovanni
                   (modified after loading)
Sample Info      : GC_334, 1 mL/min, 98:2 hex:ipr, 25°C, IC


Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  15.934 BB    0.5672 1646.84863   42.95967   5.5226
   2  18.416 BB    0.5263  704.22192   20.42389   2.3616
   3  28.556 BB    1.1208 2.74691e4   374.05396  92.1158


Totals :                  2.98201e4   437.43751
```

Data File C:\CHEM32\1\DATA\CP\CP_233_R.D
Sample Name: CP_233_R

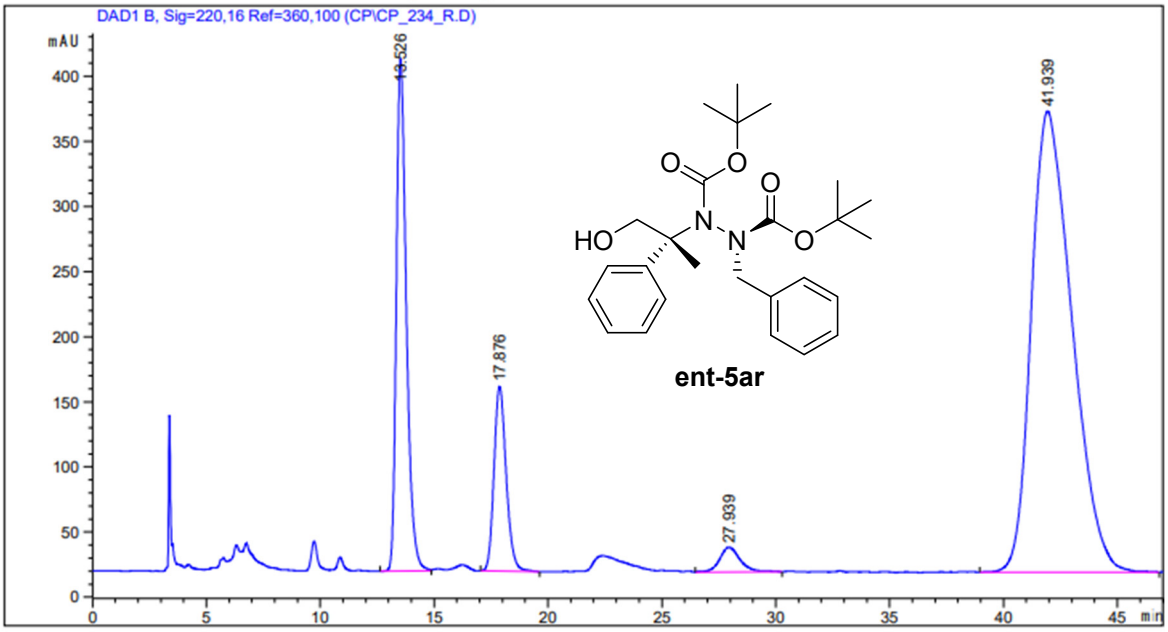
```
==========================================================================
Acq. Operator    : Chiara
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date   : 25/03/2022 16:38:16
Acq. Method      : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 25/03/2022 16:36:55 by Chiara
                   (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 18/05/2022 15:47:25 by Giovanni
                   (modified after loading)
Sample Info      : CP_233_R, 1 mL/min, 98:2 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  14.107 BV    0.5232 2.76049e4   819.14893  82.6333
   2  18.519 BB    0.5194  301.73871    8.94777   0.9032
   3  28.081 BB    0.9441 4370.65576   72.41911  13.0832
   4  42.709 BB    1.2980 1129.23645   11.03340   3.3803

Totals :                  3.34066e4   911.54920
```

ata File C:\CHEM32\1\DATA\CP\CP_234_R.D
ample Name: CP_234_R

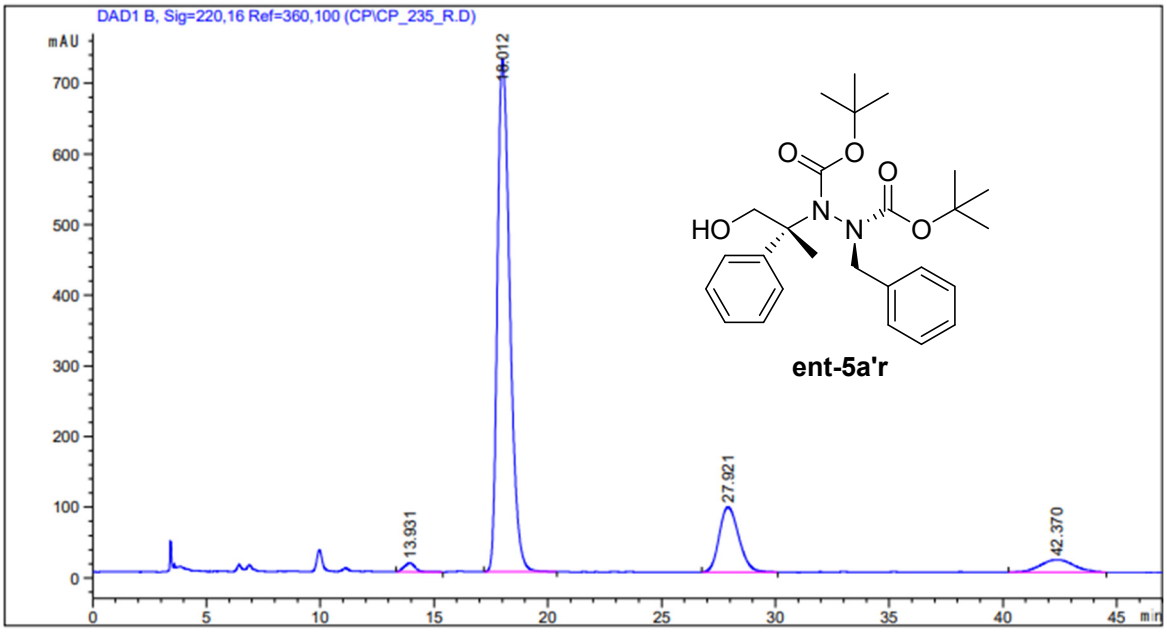
```
==========================================================================
Acq. Operator    : Chiara
Acq. Instrument  : HPLC-1                          Location : Vial 1
Injection Date   : 25/03/2022 14:46:52
Acq. Method      : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 25/03/2022 14:46:16 by Chiara
                   (modified after loading)
Analysis Method  : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 18/05/2022 15:56:19 by Giovanni
                   (modified after loading)
Sample Info      : CP_234_R, 1 mL/min, 98:2 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.526 BV    0.4639 1.19908e4   393.02396  19.2553
   2  17.876 BB    0.5690 5265.57910  141.88268   8.4557
   3  27.939 BB    0.9515 1178.91699   18.80141   1.8932
   4  41.939 VB    1.9417 4.38373e4   353.75073  70.3958

Totals :                  6.22725e4   907.45877
```

Data File C:\CHEM32\1\DATA\CP\CP_235_R.D
Sample Name: CP_235_R

```
==========================================================================
Acq. Operator    : Chiara
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date   : 28/03/2022 15:40:19
Acq. Method      : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 28/03/2022 14:41:27 by Alberto
                   (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 18/05/2022 15:55:24 by Giovanni
                   (modified after loading)
Sample Info      : CP_235_R, 1 mL/min, 98:2 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```

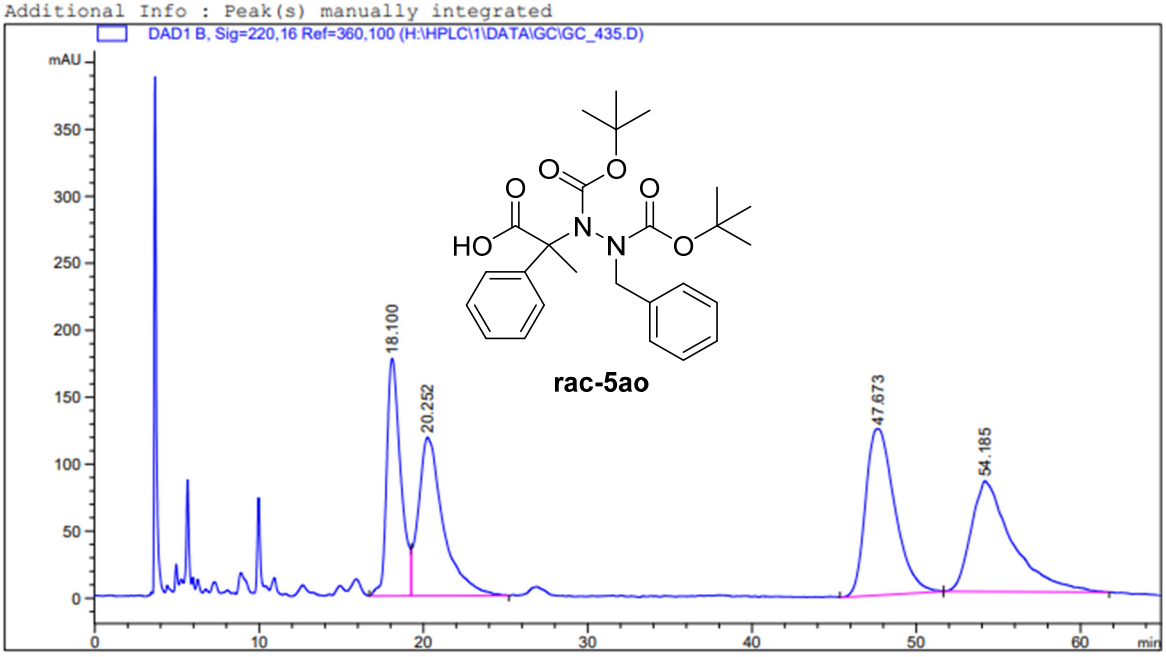


ent-5a'r

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.931 BB    0.4947  417.59653   12.47040   1.1816
   2  18.012 BB    0.5999 2.76104e4   725.60986  78.1230
   3  27.921 BB    0.9296 5496.96240   91.92726  15.5535
   4  42.370 BB    1.2393 1817.24609   17.44482   5.1419

Totals :                  3.53422e4   847.45235
```

Data File H:\HPLC\1\DATA\GC\GC_435.D
Sample Name: GC_435

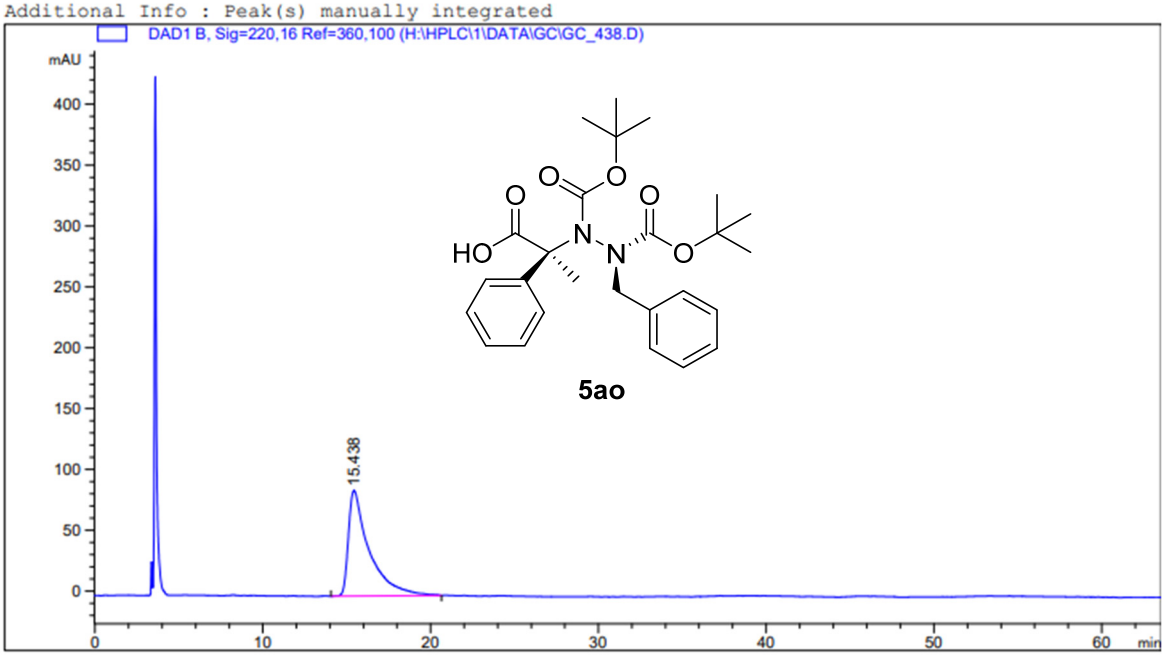
```
======================================================================
Acq. Operator    : Chiara
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date   : 09/06/2022 16:45:51
Acq. Method      : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 09/06/2022 16:45:02 by Chiara
                   (modified after loading)
Analysis Method : H:\HPLC\2\METHODS\DEF_LC.M
Last changed     : 21/06/2022 22:53:21
                   (modified after loading)
Sample Info      : GC_435, 1 mL/min, 98:2 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  18.100 BV    0.8961 1.04589e4   177.31779  19.8196
   2  20.252 VB    1.3715 1.24886e4   118.31341  23.6658
   3  47.673 BB    1.8663 1.53991e4   124.21582  29.1811
   4  54.185 BB    2.1390 1.44241e4    82.69429  27.3335

Totals :                  5.27707e4   502.54131
```

Data File H:\HPLC\1\DATA\GC\GC_438.D
Sample Name: GC_438

```
======================================================================
Acq. Operator   : Giovanni
Acq. Instrument : HPLC-1                        Location : Vial 1
Injection Date  : 10/06/2022 18:05:57
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 10/06/2022 18:05:30 by Giovanni
                  (modified after loading)
Analysis Method : H:\HPLC\2\METHODS\DEF_LC.M
Last changed    : 21/06/2022 22:55:20
                  (modified after loading)
Sample Info     : GC_438, 1 mL/min, 98:2 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```

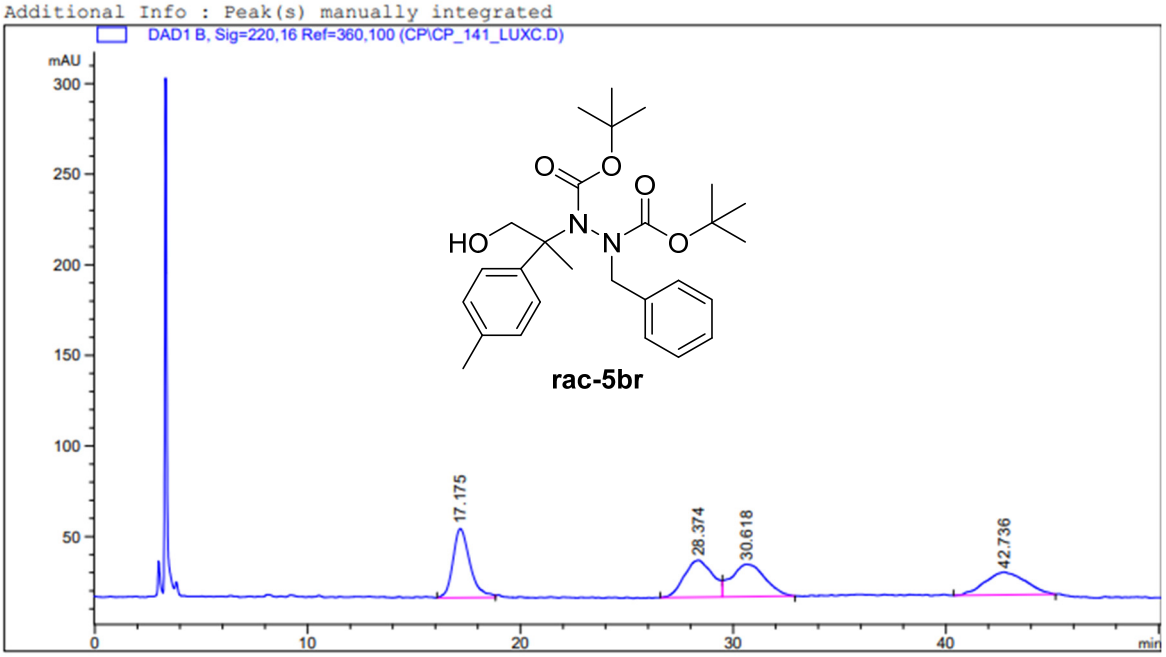


5ao

```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  15.438 BB    1.1907 7499.94482   86.74514 100.0000

Totals :                  7499.94482   86.74514
```

Data File C:\CHEM32\1\DATA\CP\CP_141_LUXC.D
Sample Name: CP_141_LuxC

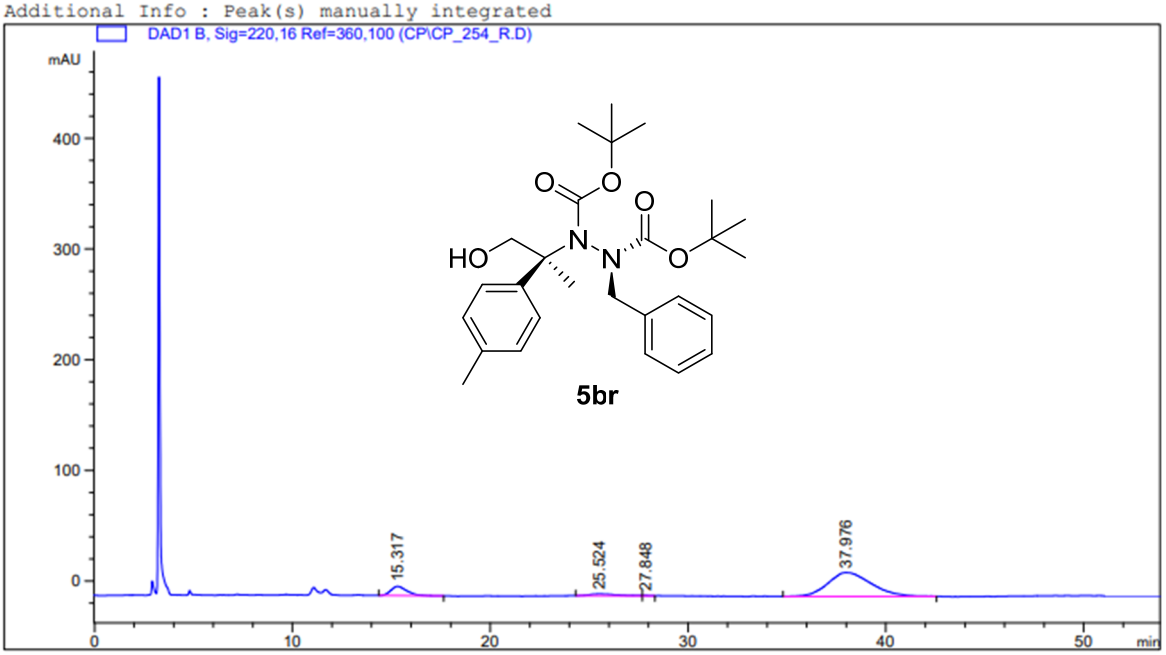
```
======================================================================
Acq. Operator    : Chiara
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date  : 17/03/2022 14:13:25
Acq. Method      : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 17/03/2022 14:12:55 by Chiara
                   (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 22/04/2022 17:39:59 by Chiara
                   (modified after loading)
Sample Info      : CP_141_LuxC, 1 mL/min, 98:2 hex:ipr, 25°C, Lux 5u Cellu
                   lose-2


Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.175 BV    0.8410 2130.24976   38.17538  27.7597
   2  28.374 BV    1.1798 1904.16736   20.42281  24.8136
   3  30.618 VB    1.4154 1975.45605   17.84628  25.7425
   4  42.736 BB    1.6009 1664.02673   12.61544  21.6842

Totals :                  7673.89990   89.05992
```

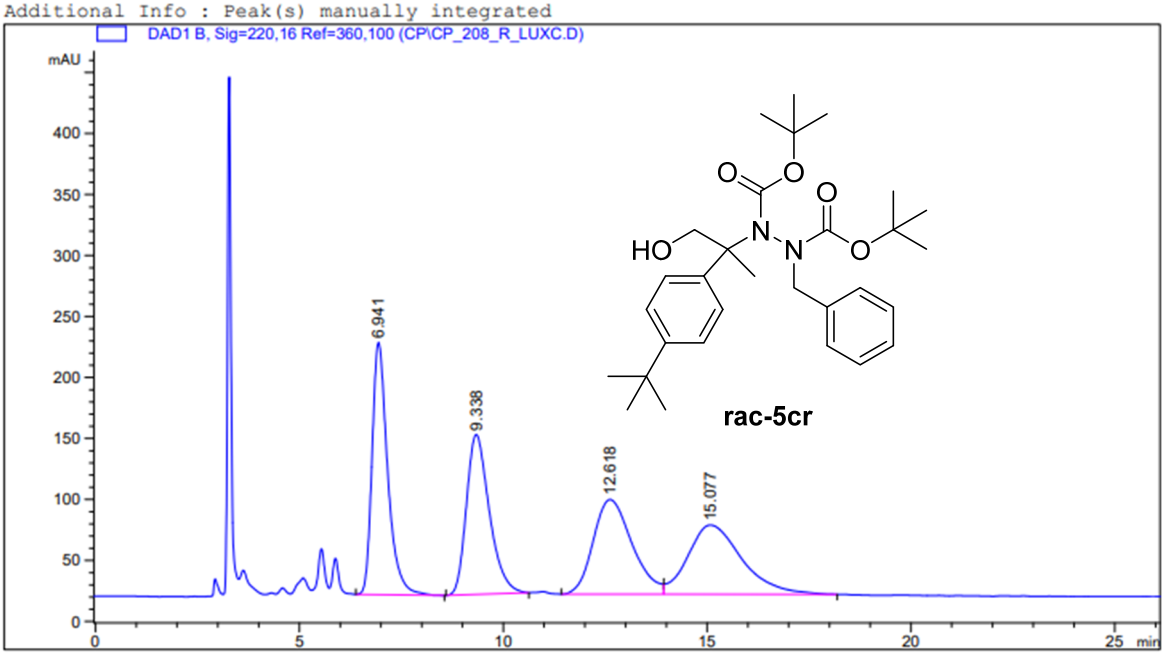
Data File C:\CHEM32\1\DATA\CP\CP_254_R.D
Sample Name: CP_254_R

```
======================================================================
Acq. Operator    : Chiara
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date   : 22/04/2022 11:31:14
Acq. Method      : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 22/04/2022 11:28:01 by Chiara
                   (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 22/04/2022 17:37:28 by Chiara
                   (modified after loading)
Sample Info      : CP_254_R, 1 mL/min, 98:2 hex:ipr, 25°C, Lux 5u Cellulos
                   e

Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  15.317 BB    0.8531  479.38226    8.30861  12.1362
   2  25.524 BV    1.1480  157.74081    1.67915   3.9934
   3  27.848 VB    0.2966    6.85585 3.21790e-1   0.1736
   4  37.976 BB    1.9262 3306.05005   21.54502  83.6969

Totals :                  3950.02898   31.85456
```

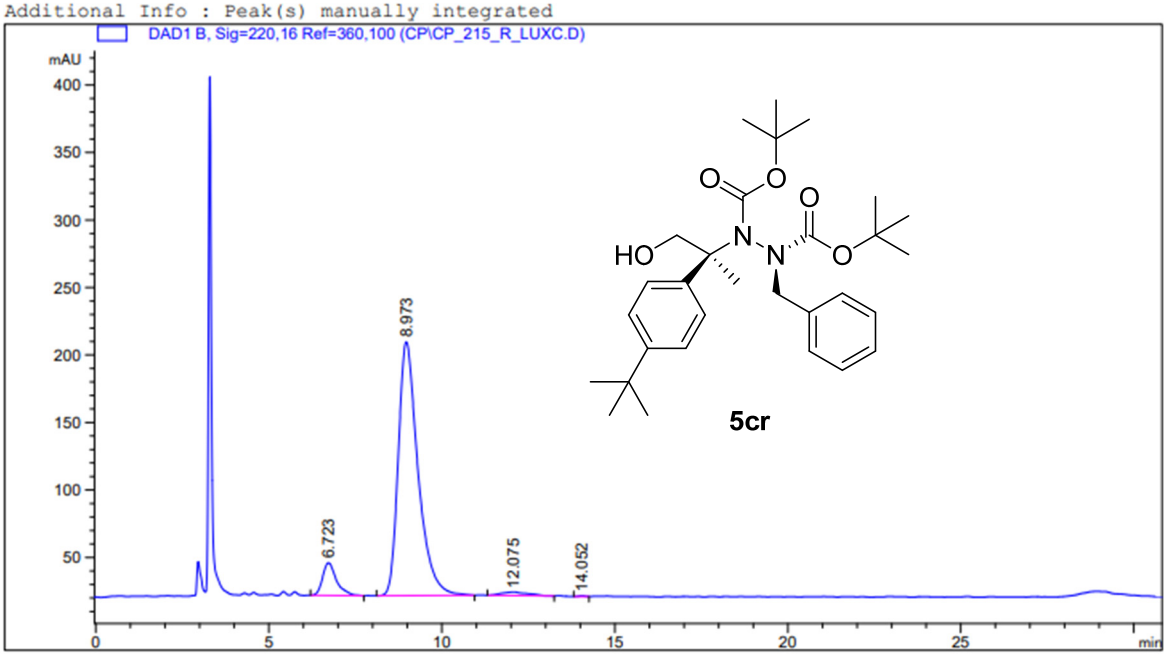
```
Data File C:\CHEM32\1\DATA\CP\CP_208_R_LUXC.D
Sample Name: CP_208_R_LuxC

    ======================================================================
    Acq. Operator    : Chiara
    Acq. Instrument : HPLC-1                          Location : Vial 1
    Injection Date   : 09/03/2022 12:27:27
    Acq. Method      : C:\CHEM32\1\METHODS\DEF_LC.M
    Last changed     : 09/03/2022 12:25:28 by Chiara
                       (modified after loading)
    Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
    Last changed     : 22/04/2022 17:56:54 by Chiara
                       (modified after loading)
    Sample Info      : CP_208_R_LuxC, 1 mL/min, 95:5 hex:ipr, 25°C, lux 5u cel
                       lulose-2

    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier:                   :      1.0000
    Dilution:                     :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 B, Sig=220,16 Ref=360,100

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]    [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   6.941 BB    0.4023 5497.83203  206.72803  26.1940
       2   9.338 BB    0.6018 5122.81299  131.12161  24.4072
       3  12.618 BV    1.0064 5136.26514   77.58142  24.4713
       4  15.077 VB    1.3805 5232.02393   56.70445  24.9275

    Totals :                  2.09889e4   472.13551
```

Data File C:\CHEM32\1\DATA\CP\CP_215_R_LUXC.D
Sample Name: CP_215_R_LuxC

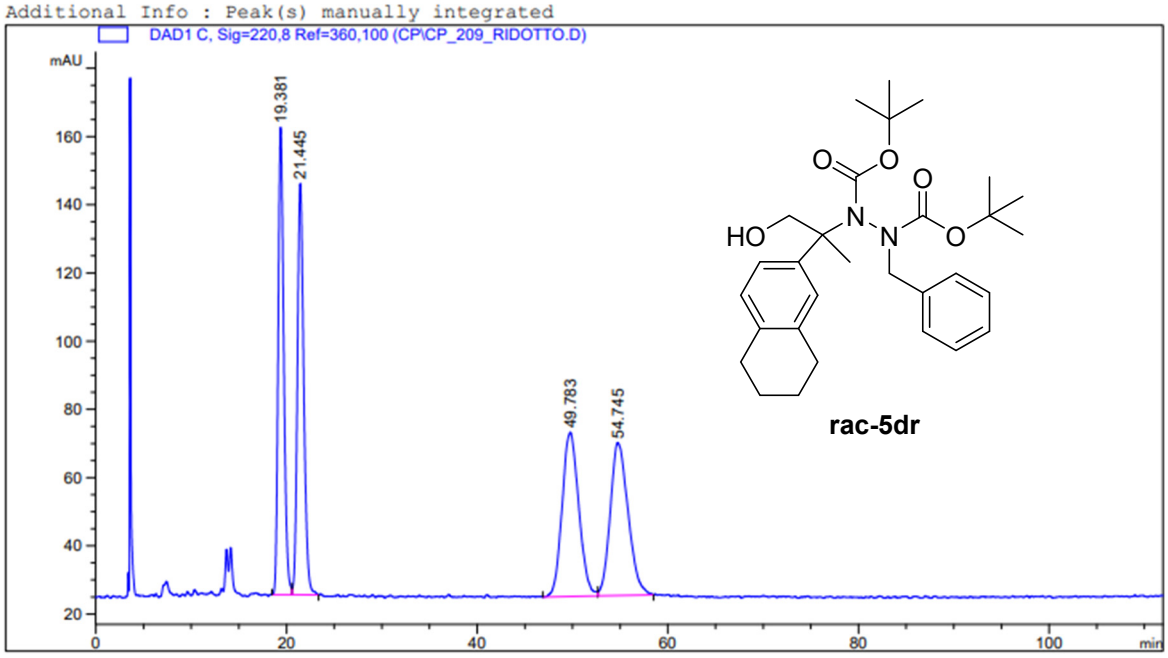
```
==========================================================================
Acq. Operator    : Chiara
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date  : 10/03/2022 15:36:51
Acq. Method      : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 10/03/2022 15:22:31 by Chiara
                   (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 22/04/2022 17:58:37 by Chiara
                   (modified after loading)
Sample Info      : CP_215_R_LuxC, 1 mL/min, 95:5 hex:ipr, 25°C, LuxC

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.723 BB    0.4193  675.41315   24.22640   8.1690
   2   8.973 BB    0.5939 7445.16797  188.05902  90.0482
   3  12.075 BB    0.6714  140.41481    2.65319   1.6983
   4  14.052 BB    0.1892    6.98399 5.85274e-1   0.0845

Totals :                  8267.97991  215.52389
```

Data File C:\CHEM32\1\DATA\CP\CP_209_RIDOTTO.D
Sample Name: CP_209_ridotto

```
==========================================================================
Acq. Operator   : Chiara
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date  : 02/02/2022 13:57:29
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 02/02/2022 13:56:41 by Giovanni
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 22/04/2022 18:00:41 by Chiara
                  (modified after loading)
Sample Info     : CP_209_ridotto, 1 mL/min, 98:2 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```

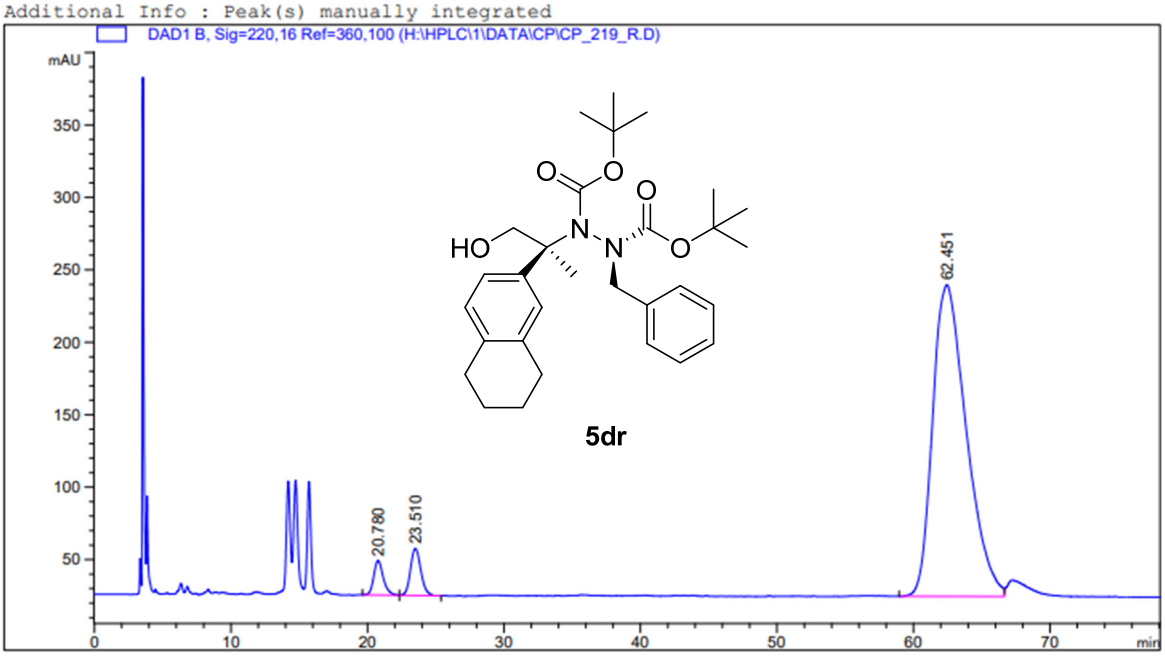


rac-5dr

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=220,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  19.381 BV    0.6305 5571.86377  137.00578  24.3925
   2  21.445 VB    0.7019 5559.34180  120.58350  24.3377
   3  49.783 BV    1.7572 5865.04834   48.14730  25.6760
   4  54.745 VB    1.6920 5846.29053   44.87307  25.5939

Totals :                  2.28425e4   350.60965
```

Data File H:\HPLC\1\DATA\CP\CP_219_R.D
Sample Name: CP_219_R

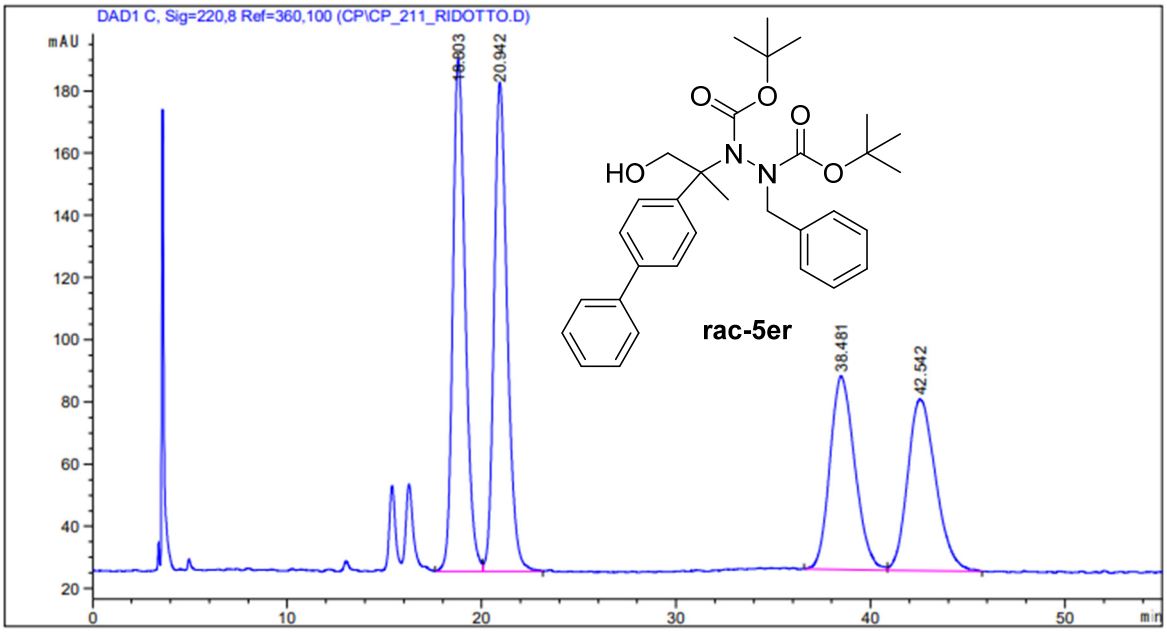
```
==========================================================================
Acq. Operator    : Chiara
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date   : 18/02/2022 12:55:07
Acq. Method      : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 18/02/2022 12:10:40 by Chiara
                   (modified after loading)
Analysis Method : H:\HPLC\2\METHODS\DEF_LC.M
Last changed     : 06/06/2022 10:31:47
                   (modified after loading)
Sample Info      : CP_219_R, 1 mL/min, 98:2 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  20.780 BB    0.7421 1154.79504   23.79881   2.9082
   2  23.510 BB    0.8194 1711.21057   32.44208   4.3095
   3  62.451 BV    2.5069 3.68421e4   215.02814  92.7823

Totals :                  3.97081e4   271.26903
```

Data File C:\CHEM32\1\DATA\CP\CP_211_RIDOTTO.D
Sample Name: CP_211_ridotto

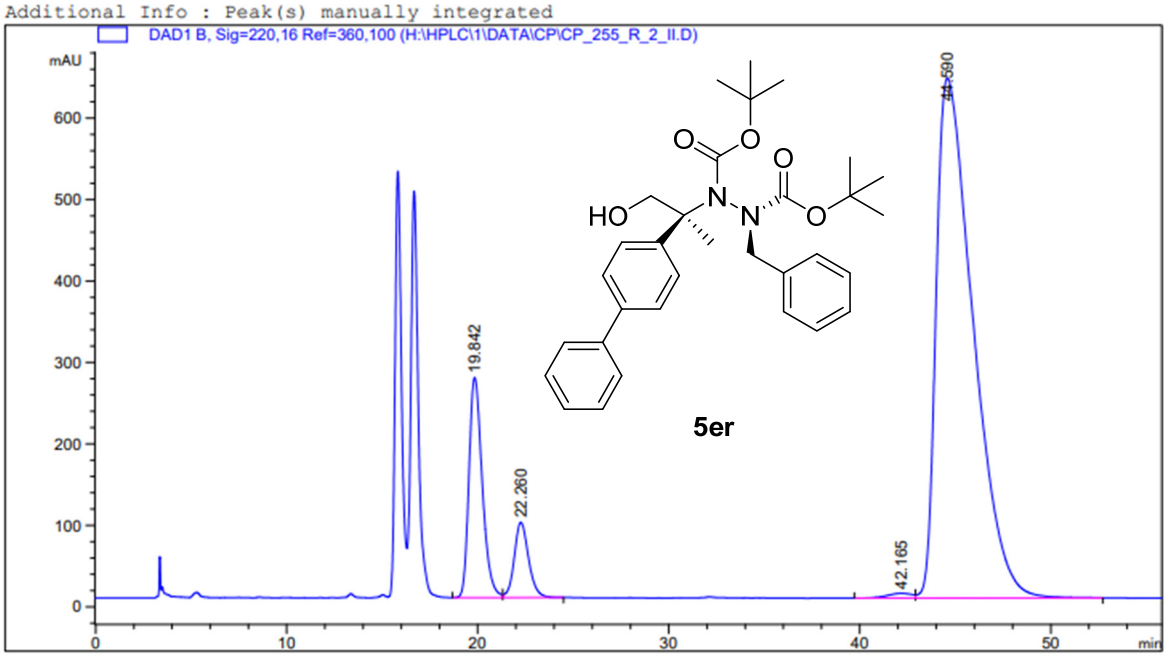
```
======================================================================
Acq. Operator    : Chiara
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date   : 02/02/2022 15:50:26
Acq. Method      : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 02/02/2022 15:49:49 by Chiara
                   (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 18/05/2022 17:12:22 by Giovanni
                   (modified after loading)
Sample Info      : CP_211_ridotto, 1 mL/min, 98:2 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=220,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  18.803 BV    0.6847 7347.02734  164.61923  28.4906
   2  20.942 VB    0.7152 7375.02051  157.24989  28.5992
   3  38.481 BV    1.3939 5540.93408   62.28122  21.4869
   4  42.542 VB    1.4545 5524.55664   55.06638  21.4234

Totals :                  2.57875e4   439.21672
```

Data File H:\HPLC\1\DATA\CP\CP_255_R_2_II.D
Sample Name: CP_255_R_2_II

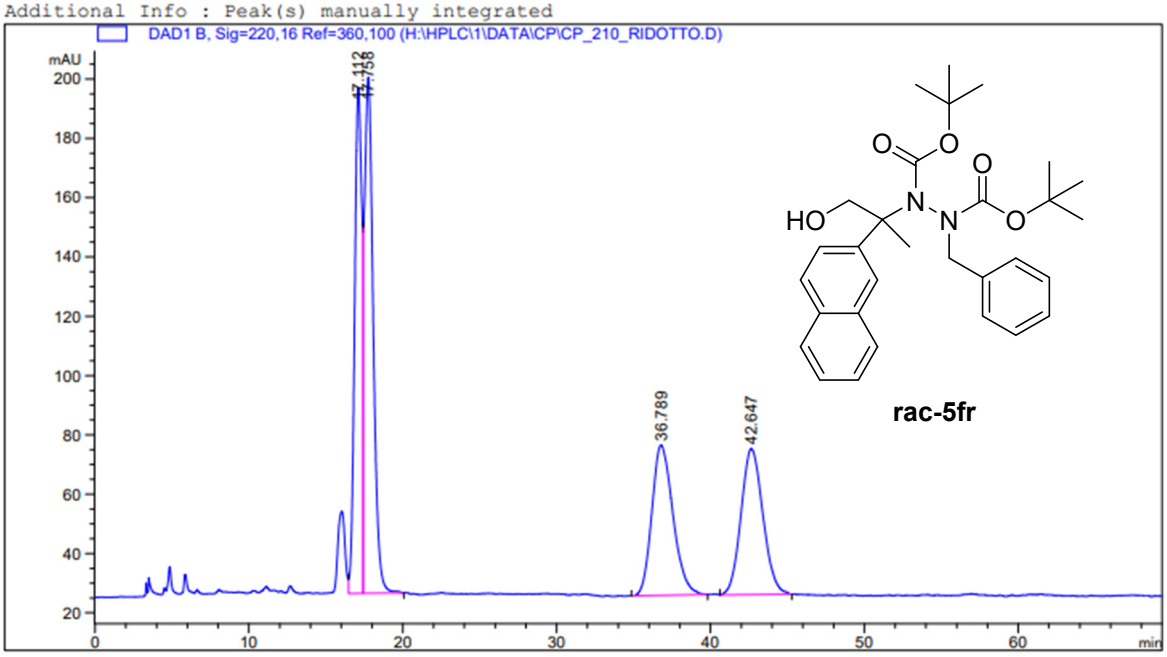
```
==========================================================================
Acq. Operator   : Chiara
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date  : 21/04/2022 18:01:06
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 21/04/2022 17:53:32 by Chiara
                  (modified after loading)
Analysis Method : H:\HPLC\2\METHODS\DEF_LC.M
Last changed    : 06/06/2022 10:36:40
                  (modified after loading)
Sample Info     : CP_255_R_2_II, pulito, 1 mL/min, 98:2 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  19.842 BV    0.7354 1.30479e4   270.18030  12.5910
   2  22.260 VB    0.7955 4814.13281   92.45843   4.6456
   3  42.165 BV    1.1949  513.15485    5.80731   0.4952
   4  44.590 VB    1.9701 8.52537e4   638.37128  82.2683

Totals :                  1.03629e5  1006.81731
```

Data File H:\HPLC\1\DATA\CP\CP_210_RIDOTTO.D
Sample Name: CP_210_ridotto

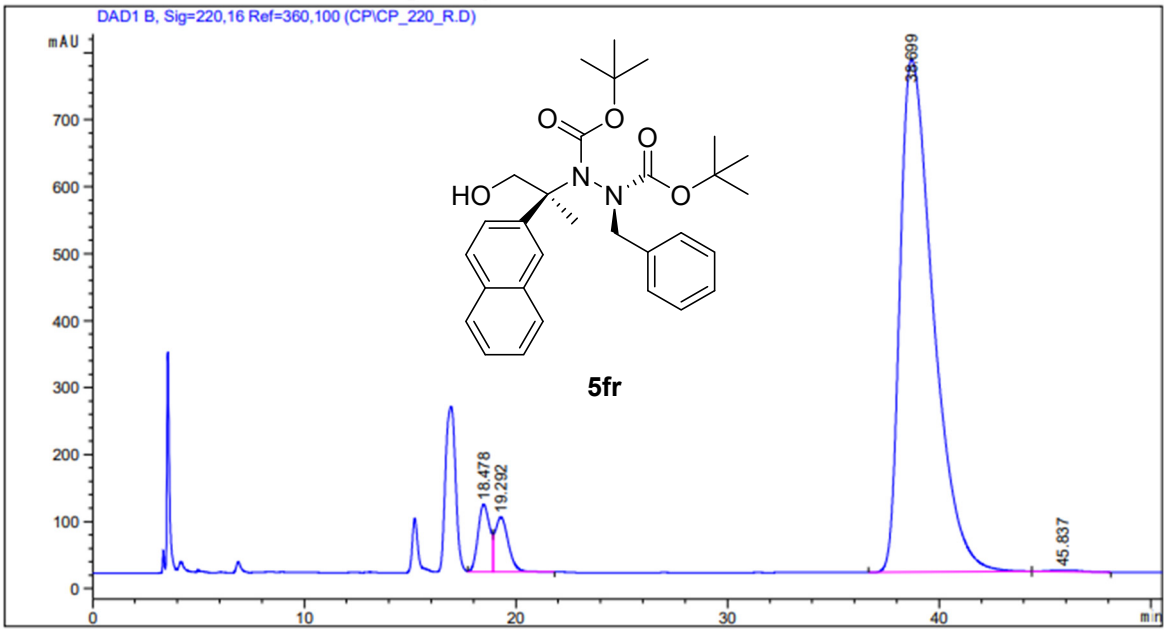
```
==========================================================================
Acq. Operator   : Chiara
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date  : 03/02/2022 10:57:51
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 03/02/2022 10:17:08 by Chiara
                  (modified after loading)
Analysis Method : H:\HPLC\2\METHODS\DEF_LC.M
Last changed    : 24/05/2022 10:41:02
                  (modified after loading)
Sample Info     : CP_210_ridotto, 1 mL/min, 98:2 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.112 VV    0.4985 5589.28711  170.49522  25.1286
   2  17.758 VB    0.5896 6943.39697  173.99034  31.2165
   3  36.789 BB    1.4424 4845.10547   50.72123  21.7829
   4  42.647 BB    1.5256 4864.94385   49.20243  21.8721

Totals :                  2.22427e4   444.40923
```

Data File C:\CHEM32\1\DATA\CP\CP_220_R.D
Sample Name: CP_220_R

```
==========================================================================
Acq. Operator    : Chiara
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date   : 15/02/2022 16:35:29
Acq. Method      : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 15/02/2022 16:07:22 by Giovanni
                   (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 18/05/2022 17:20:25 by Giovanni
                   (modified after loading)
Sample Info      : CP_220_R, 1 mL/min, 98:2 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```

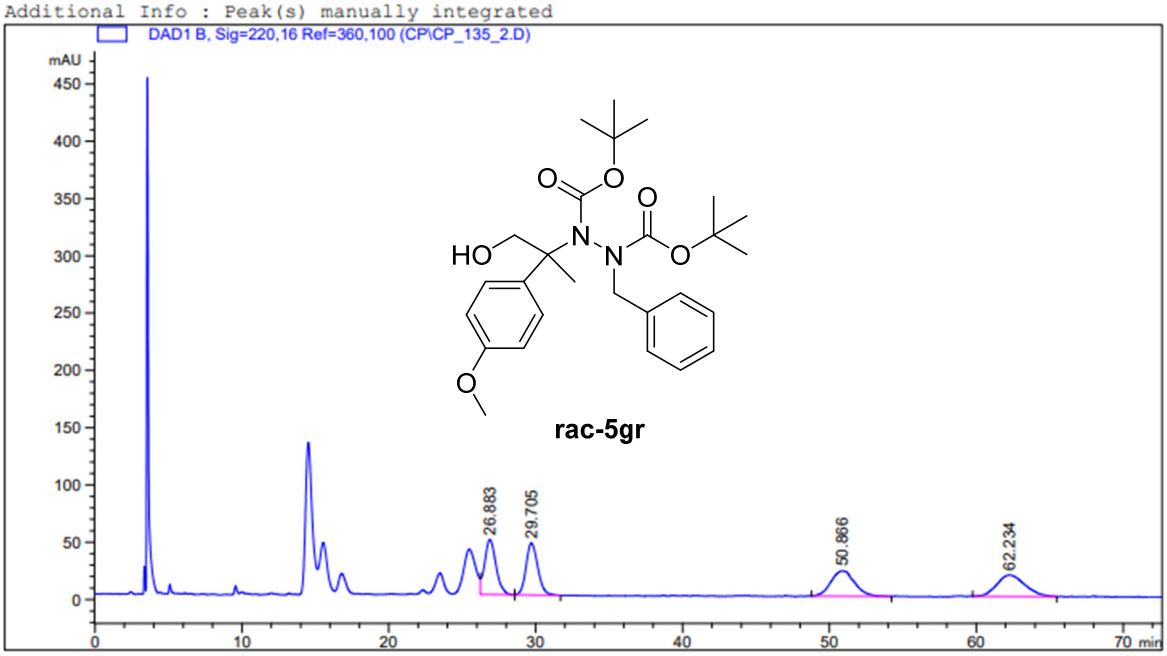


5fr

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  18.478 VV    0.5934 3920.14453  100.87508   4.3057
   2  19.292 VB    0.6568 3568.94238   81.83964   3.9200
   3  38.699 BB    1.6134 8.33232e4   765.81567  91.5181
   4  45.837 BB    1.2445  233.29845    2.29790   0.2562

Totals :                  9.10456e4   950.82829
```

Data File C:\CHEM32\1\DATA\CP\CP_135_2.D
Sample Name: CP_135_2

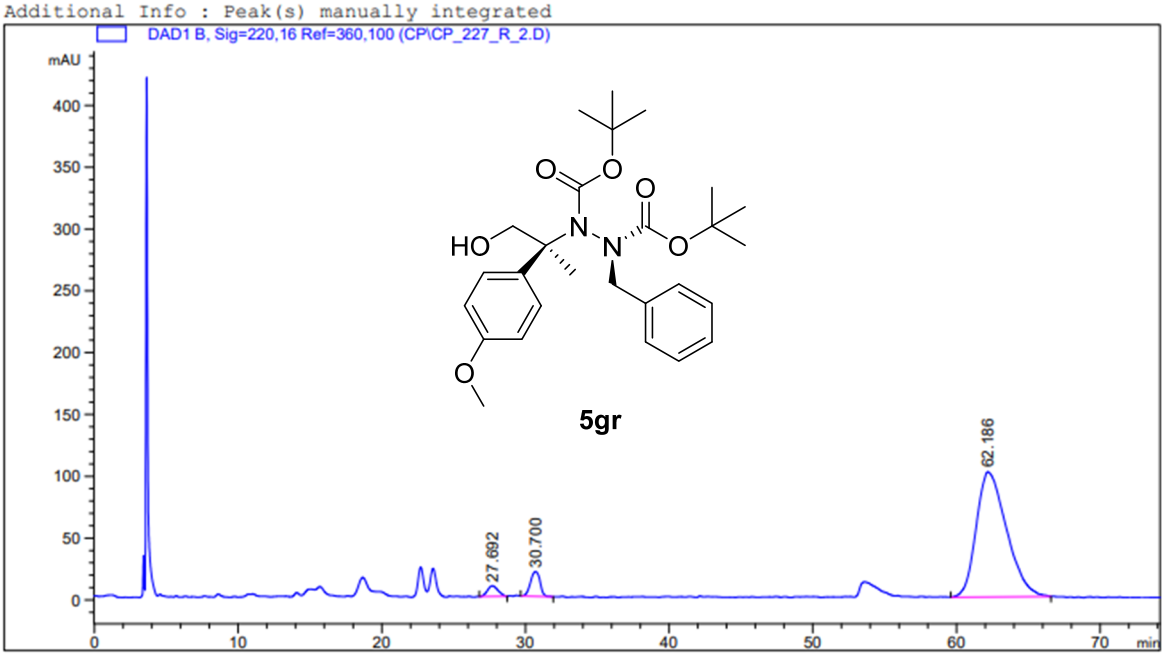
```
==========================================================================
Acq. Operator    : Chiara
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date   : 01/03/2022 14:06:01
Acq. Method      : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 01/03/2022 13:50:56 by Chiara
                   (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 22/04/2022 17:50:00 by Chiara
                   (modified after loading)
Sample Info      : CP_135_2, 1 mL/min, 98:2 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  26.883 VB    0.8266 2596.38647   48.03494  25.6748
   2  29.705 BB    0.8649 2526.40649   45.41959  24.9828
   3  50.866 BB    1.5147 2495.89844   22.21669  24.6811
   4  62.234 BB    1.8403 2493.91187   18.64765  24.6614

Totals :                  1.01126e4   134.31888
```

Data File C:\CHEM32\1\DATA\CP\CP_227_R_2.D
Sample Name: CP_227_R_2

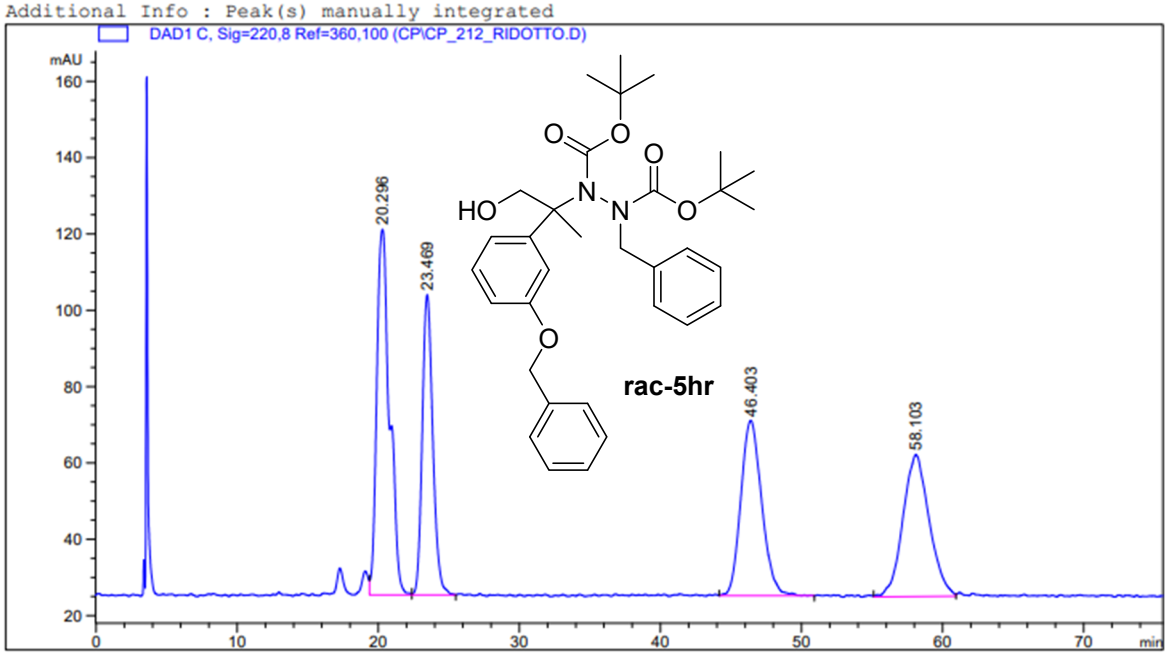
```
==========================================================================
Acq. Operator    : Chiara
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date   : 02/03/2022 16:25:59
Acq. Method      : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 02/03/2022 16:23:12 by Chiara
                   (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 22/04/2022 17:52:27 by Chiara
                   (modified after loading)
Sample Info      : CP_227_R_2, 1 mL/min, 98:2 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  27.692 BB    0.7806  443.52988    8.61513   2.7364
   2  30.700 BB    0.7476  930.21252   20.11050   5.7391
   3  62.186 BB    1.9470 1.48345e4   101.14850  91.5244

Totals :                  1.62083e4   129.87413
```

Data File C:\CHEM32\1\DATA\CP\CP_212_RIDOTTO.D
Sample Name: CP_212_ridotto

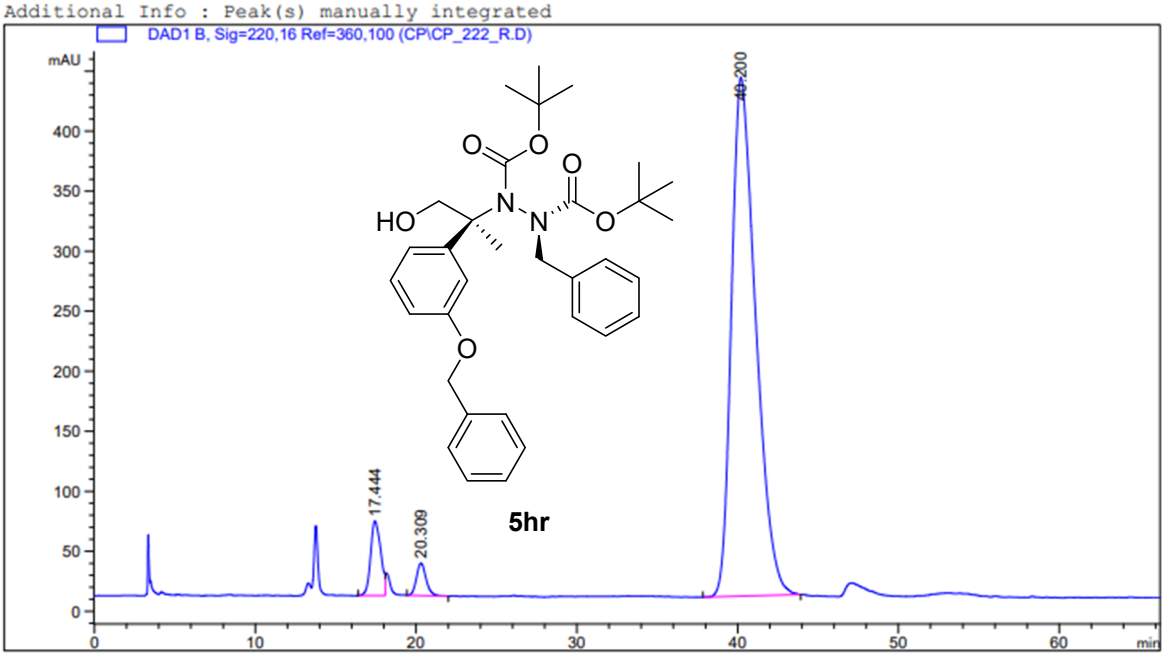
```
==========================================================================
Acq. Operator   : Chiara
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date  : 02/02/2022 16:51:27
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 02/02/2022 16:50:53 by Chiara
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 26/04/2022 12:59:23 by Chiara
                  (modified after loading)
Sample Info     : CP_212_ridotto, 1 mL/min, 98:2 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=220,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  20.296 VV    0.9441 6043.45605   95.78014  30.7125
   2  23.469 VV    0.7975 4082.83569   78.66629  20.7488
   3  46.403 BB    1.5139 4733.56543   45.94631  24.0557
   4  58.103 VV    1.6734 4817.63721   37.13958  24.4830

Totals :                  1.96775e4   257.53232
```

Data File C:\CHEM32\1\DATA\CP\CP_222_R.D
Sample Name: CP_222_R

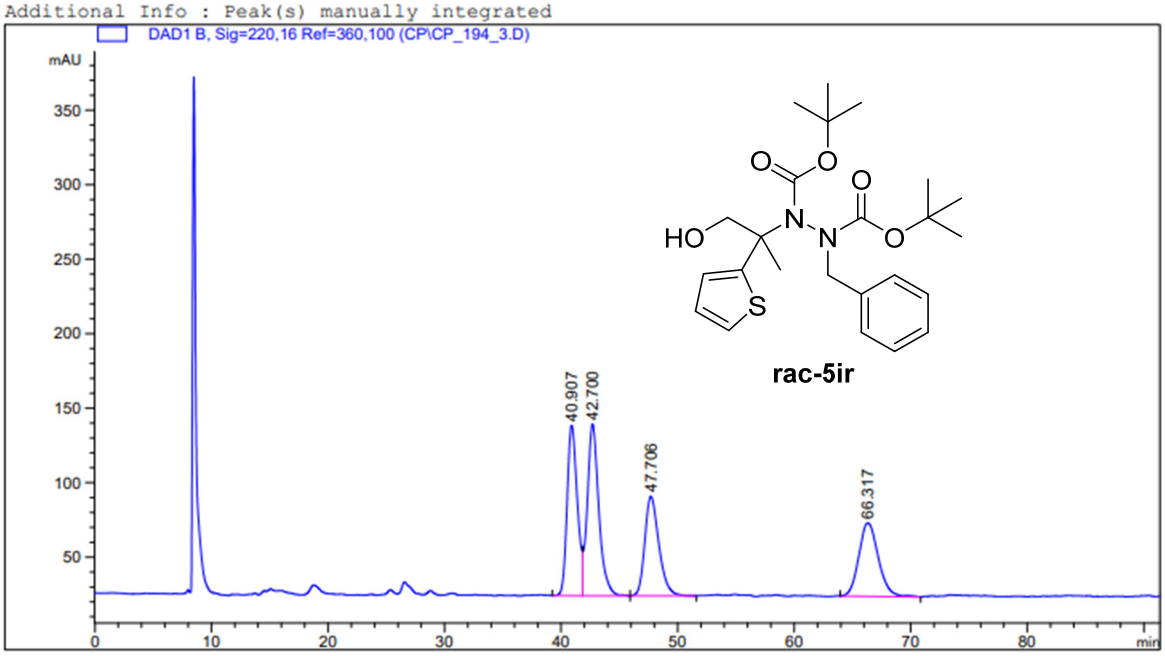
```
==========================================================================
Acq. Operator    : Chiara
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date   : 22/02/2022 15:02:32
Acq. Method      : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 22/02/2022 13:59:28 by Chiara
                   (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 26/04/2022 13:00:16 by Chiara
                   (modified after loading)
Sample Info      : CP_222_R, 1 mL/min, 90:10 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.444 BV    0.7011 2697.91357   62.06453   5.5046
   2  20.309 BB    0.6287 1121.28235   27.10343   2.2878
   3  40.200 BB    1.5004 4.51929e4   432.02646  92.2076

Totals :                  4.90121e4   521.19442
```

)ata File C:\CHEM32\1\DATA\CP\CP_194_3.D
Sample Name: CP_194_3

```
==========================================================================
Acq. Operator   : Chiara
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date  : 15/12/2021 12:33:24
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 15/12/2021 12:32:01 by Chiara
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 03/05/2022 17:55:16 by Chiara
                  (modified after loading)
Sample Info     : CP_194_3, 0.5 mL/min, 98:2 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```

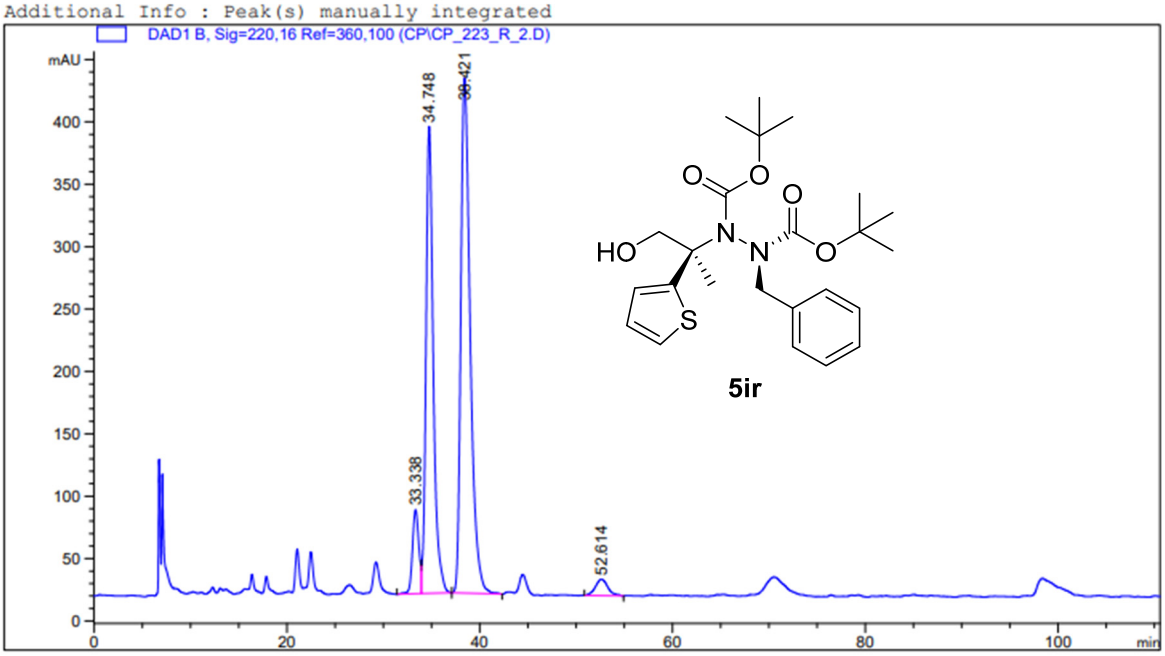


rac-5ir

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  40.907 BV    0.9332 6948.21289  114.29614  26.4888
   2  42.700 VB    1.0279 7934.87500  115.16032  30.2502
   3  47.706 BB    1.2773 5610.95996   66.70800  21.3907
   4  66.317 BB    1.7501 5736.73877   49.28159  21.8703

Totals :                  2.62308e4   345.44606
```

Data File C:\CHEM32\1\DATA\CP\CP_223_R_2.D
Sample Name: CP_223_R_2

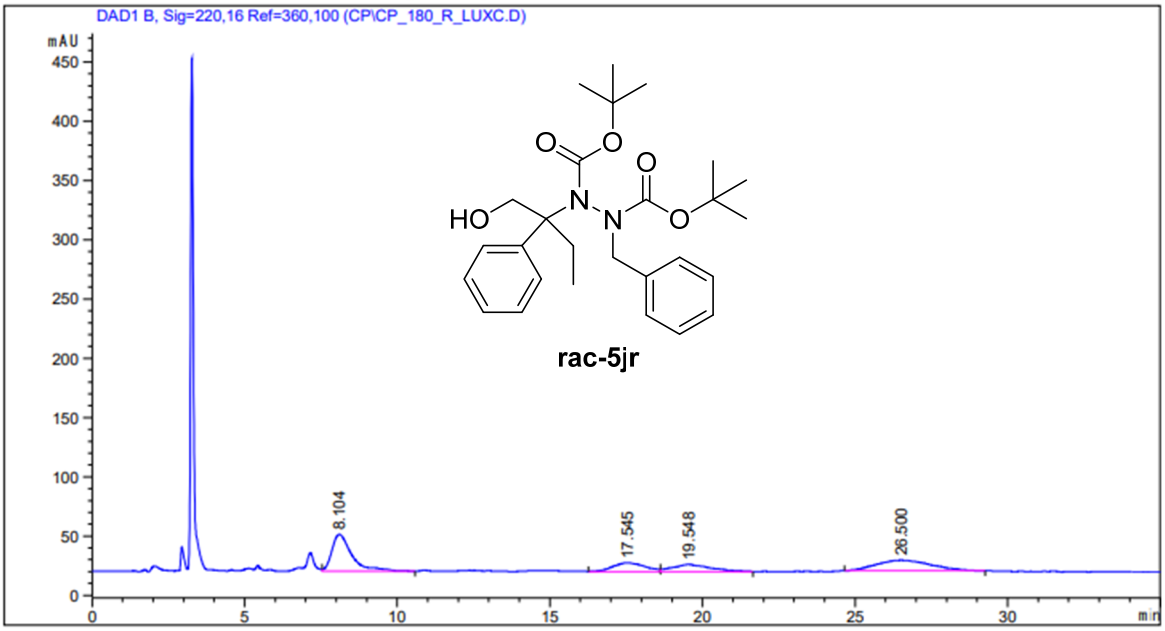
```
======================================================================
Acq. Operator    : Chiara
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date   : 23/02/2022 11:21:53
Acq. Method      : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 23/02/2022 11:20:57 by Chiara
                   (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 03/05/2022 17:57:02 by Chiara
                   (modified after loading)
Sample Info      : CP_223_R_2, 0.5 mL/min, 98:2 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  33.338 BV    0.6965 3097.83911   67.37090   5.9775
   2  34.748 VB    0.7969 1.96592e4   374.21191  37.9336
   3  38.421 BB    1.0200 2.78935e4   412.97580  53.8222
   4  52.614 BB    1.4086 1174.72314   13.06996   2.2667

Totals :                  5.18252e4   867.62857
```

Data File C:\CHEM32\1\DATA\CP\CP_180_R_LUXC.D
Sample Name: CP_180_R_LuxC

```
==========================================================================
Acq. Operator    : Chiara
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date   : 09/03/2022 13:01:50
Acq. Method      : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 09/03/2022 12:53:56 by Chiara
                   (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 18/05/2022 16:46:26 by Giovanni
                   (modified after loading)
Sample Info      : CP_180_R_LuxC, 1 mL/min, 95:5 hex:ipr, 25°C, lux 5u cel
                   lulose-2


Additional Info : Peak(s) manually integrated
```

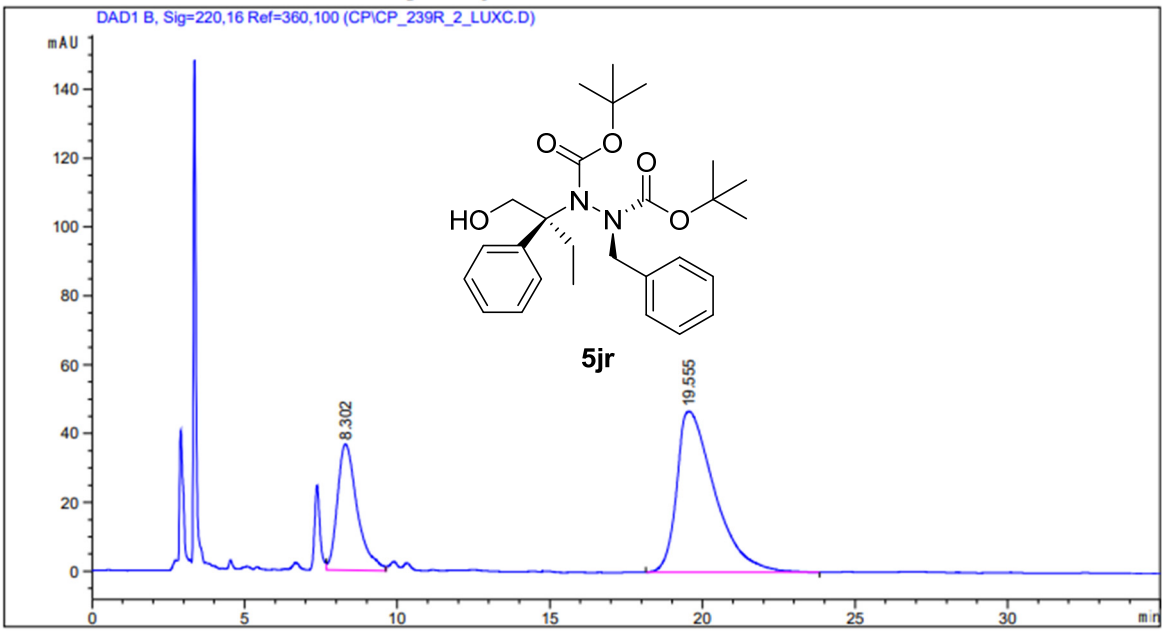


rac-5jr

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.104 VB    0.6820 1425.58569   31.03194  39.5513
   2  17.545 BV    0.9742  526.32788    7.25633  14.6024
   3  19.548 VB    1.1138  504.38864    5.89765  13.9937
   4  26.500 BB    1.5416 1148.09827    9.01617  31.8527

Totals :                  3604.40048   53.20209
```

Data File C:\CHEM32\1\DATA\CP\CP_239R_2_LUXC.D
Sample Name: CP_239R_2_LuxC

```
==========================================================================
Acq. Operator    : Chiara
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date   : 04/05/2022 15:28:50
Acq. Method      : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 04/05/2022 15:02:10 by Giovanni
                   (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 18/05/2022 16:53:41 by Giovanni
                   (modified after loading)
Sample Info      : CP_239R_2_LuxC, 1 mL/min, 95:5 hex:ipr, 25°C, LuxC


Additional Info : Peak(s) manually integrated
```

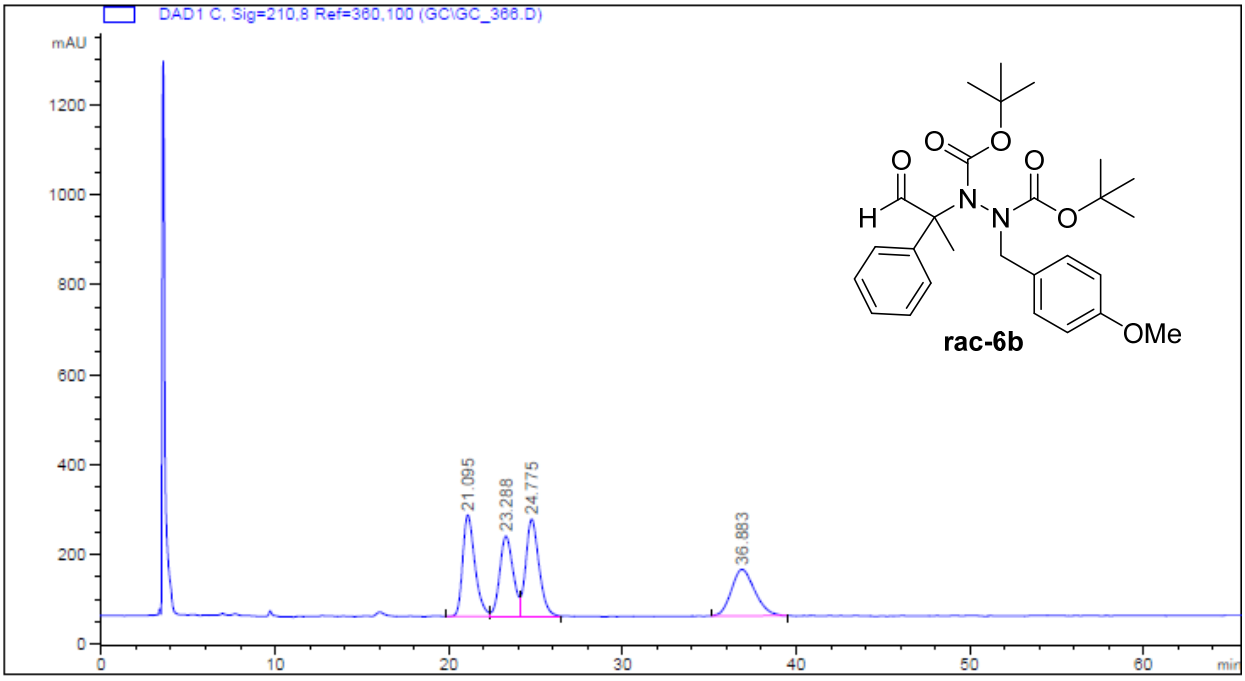


5jr

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.302 VV    0.6859 1657.85583   36.63976  29.0649
   2  19.555 BB    1.2258 4046.11426   46.74608  70.9351

Totals :                  5703.97009   83.38585
```

Data File H:\HPLC\1\DATA\GC\GC_366.D
Sample Name: GC_366

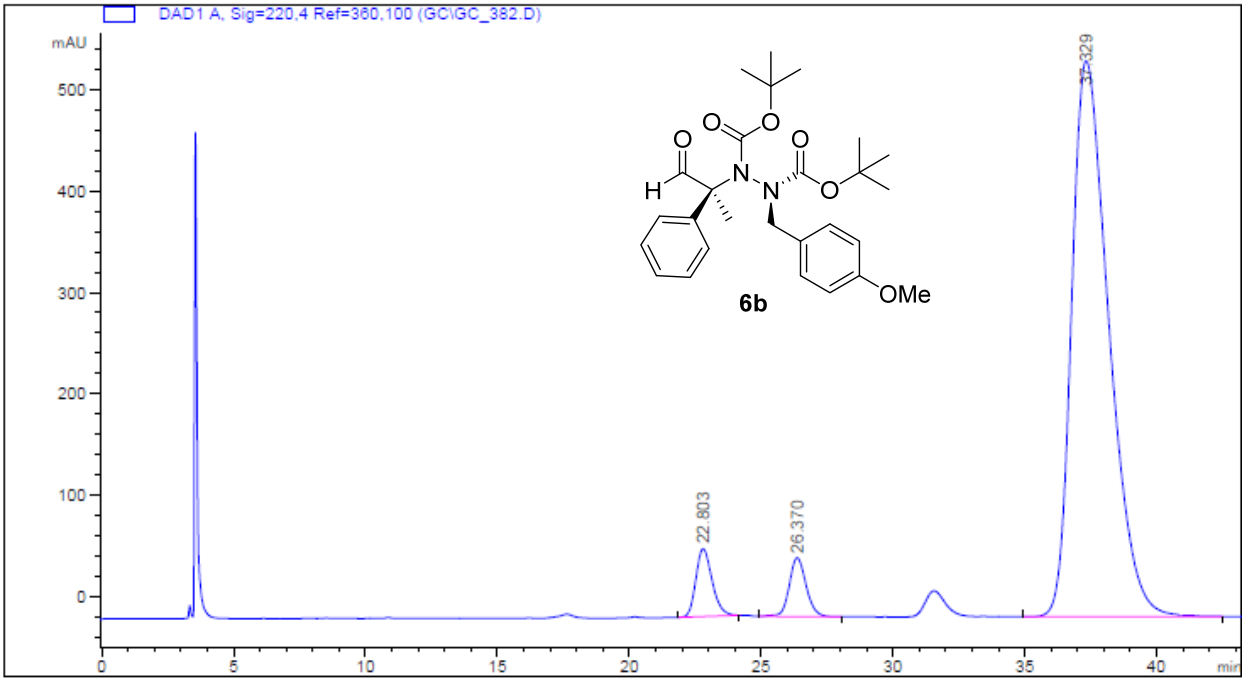
```
================================================================================
Acq. Operator   : Giovanni
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date  : 17/01/2022 10.41.51
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 17/01/2022 10.41.11 by Giovanni
                  (modified after loading)
Analysis Method : H:\HPLC\1\METHODS\DEF_LC.M
Last changed    : 07/05/2022 14.10.49
                  (modified after loading)
Sample Info     : GC_366, 1 mL/min, 98:2 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```




```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  21.095 BV    0.7440 1.10458e4   225.27597  26.4823
   2  23.288 VV    0.8205 9535.31738  178.14674  22.8610
   3  24.775 VB    0.8049 1.14462e4   215.75931  27.4423
   4  36.883 BB    1.3641 9682.70703  103.06392  23.2144

Totals :                  4.17100e4   722.24594
```

Data File H:\HPLC\1\DATA\GC\GC_382.D
Sample Name: GC_382

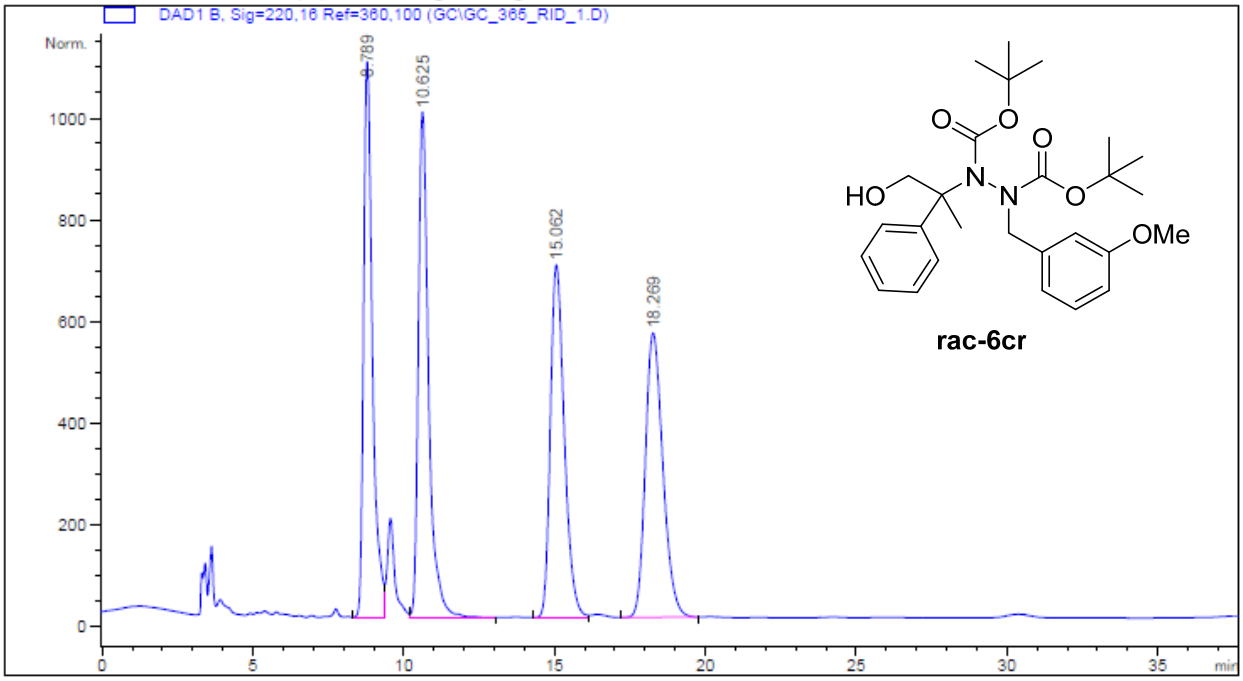
```
=====================================================================
Acq. Operator   : Giovanni
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date  : 18/02/2022 09.46.55
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 18/02/2022 09.29.14 by Giovanni
                  (modified after loading)
Analysis Method : H:\HPLC\1\METHODS\DEF_LC.M
Last changed    : 07/05/2022 14.02.09
                  (modified after loading)
Sample Info     : GC_382, 1 mL/min, 98:2 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=220,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  22.803 BB    0.6538 2857.00757   66.95844   4.8440
   2  26.370 BB    0.6817 2584.41187   58.02159   4.3819
   3  37.329 BB    1.4422 5.35383e4   548.79712  90.7741

Totals :                  5.89797e4   673.77714
```

Data File C:\CHEM32\1\DATA\GC\GC_365_RID_1.D
Sample Name: GC_365_rid

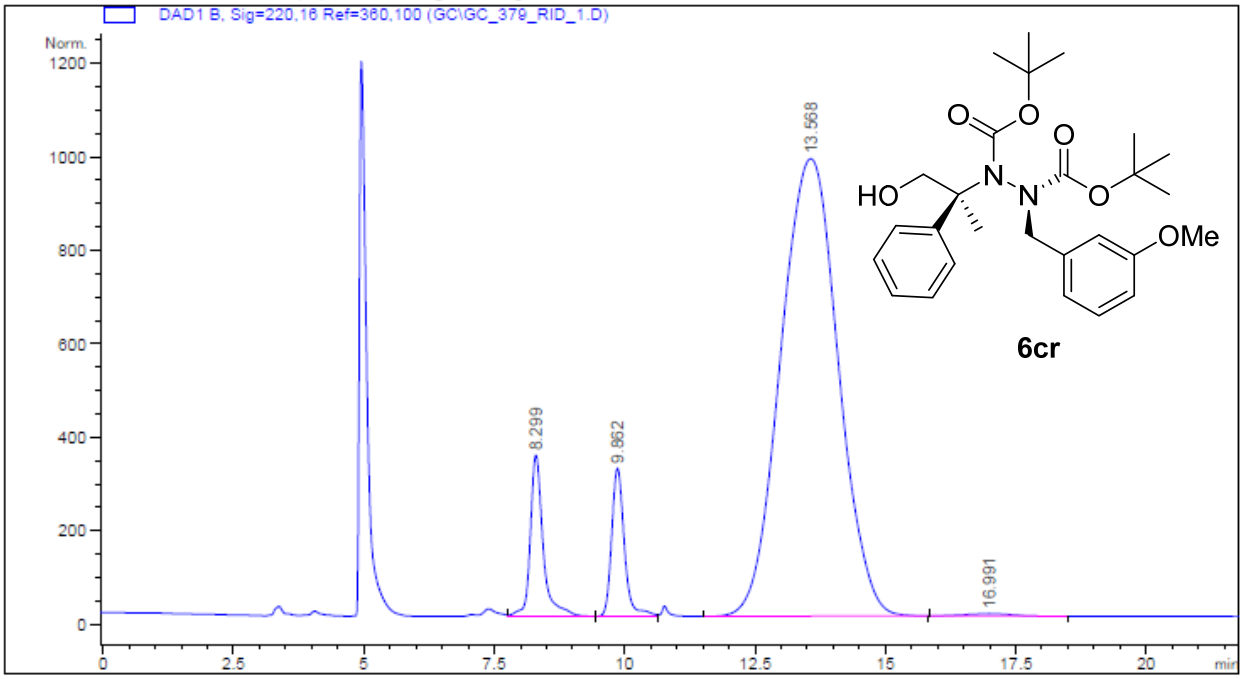
```
==========================================================================
Acq. Operator    : Giovanni
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date   : 21/02/2022 14:51:22
Acq. Method      : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 21/02/2022 14:46:01 by Giovanni
                   (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 03/05/2022 10:40:53 by Chiara
                   (modified after loading)
Sample Info      : GC_365_ridotto, 1 mL/min, 92:8 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.789 BV    0.3183 2.23275e4  1093.24707  24.5720
   2  10.625 VB    0.3571 2.36134e4   994.05261  25.9872
   3  15.062 BV    0.4949 2.22911e4   693.72565  24.5319
   4  18.269 BB    0.6238 2.26335e4   559.69019  24.9088

Totals :                  9.08655e4  3340.71552
```

Data File C:\CHEM32\1\DATA\GC\GC_379_RID_1.D
Sample Name: GC_379_rid

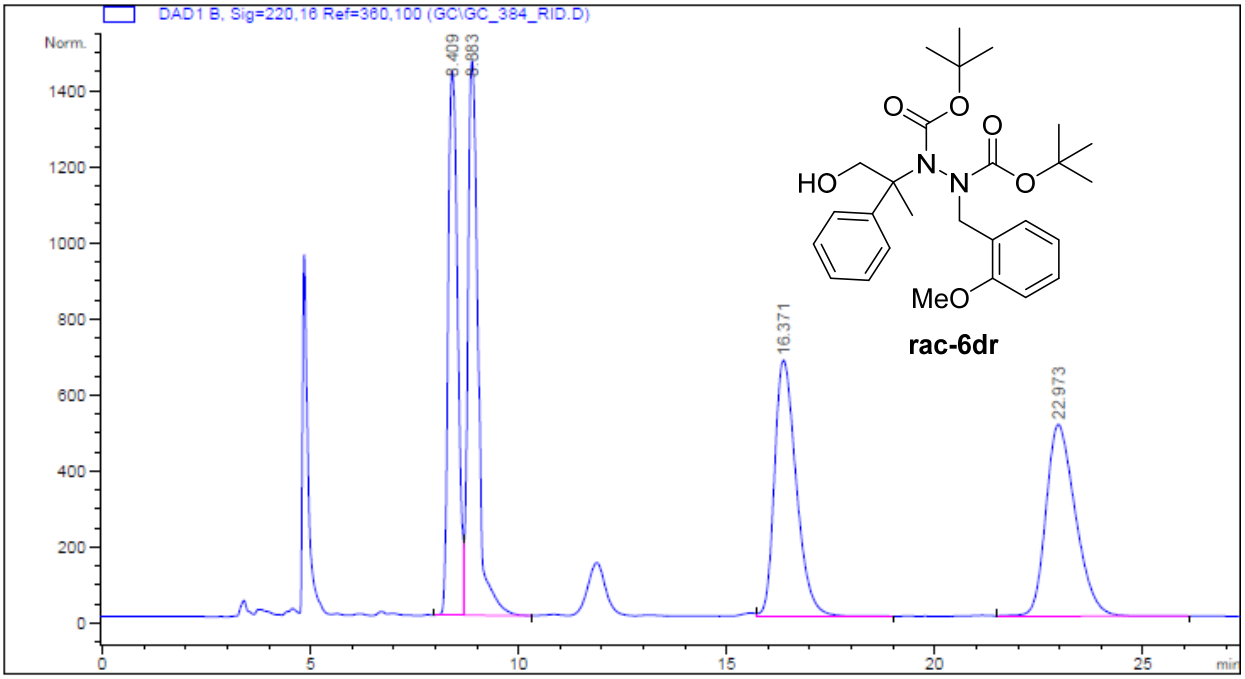
```
==========================================================================
Acq. Operator    : Giovanni
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date   : 21/02/2022 15:30:58
Acq. Method      : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 21/02/2022 15:29:27 by Giovanni
                   (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 03/05/2022 10:41:39 by Chiara
                   (modified after loading)
Sample Info      : GC_379_ridotto, 1 mL/min, 92:8 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.299 VB    0.2563 5916.02246  344.62469   6.8383
   2   9.862 BV    0.2575 5356.50049  316.45337   6.1916
   3  13.568 BB    1.2135 7.49478e4   978.63129  86.6318
   4  16.991 BB    0.8300  292.72147    5.00762   0.3384

Totals :                  8.65131e4  1644.71697
```

Data File C:\CHEM32\1\DATA\GC\GC_384_RID.D
Sample Name: GC_384_rid

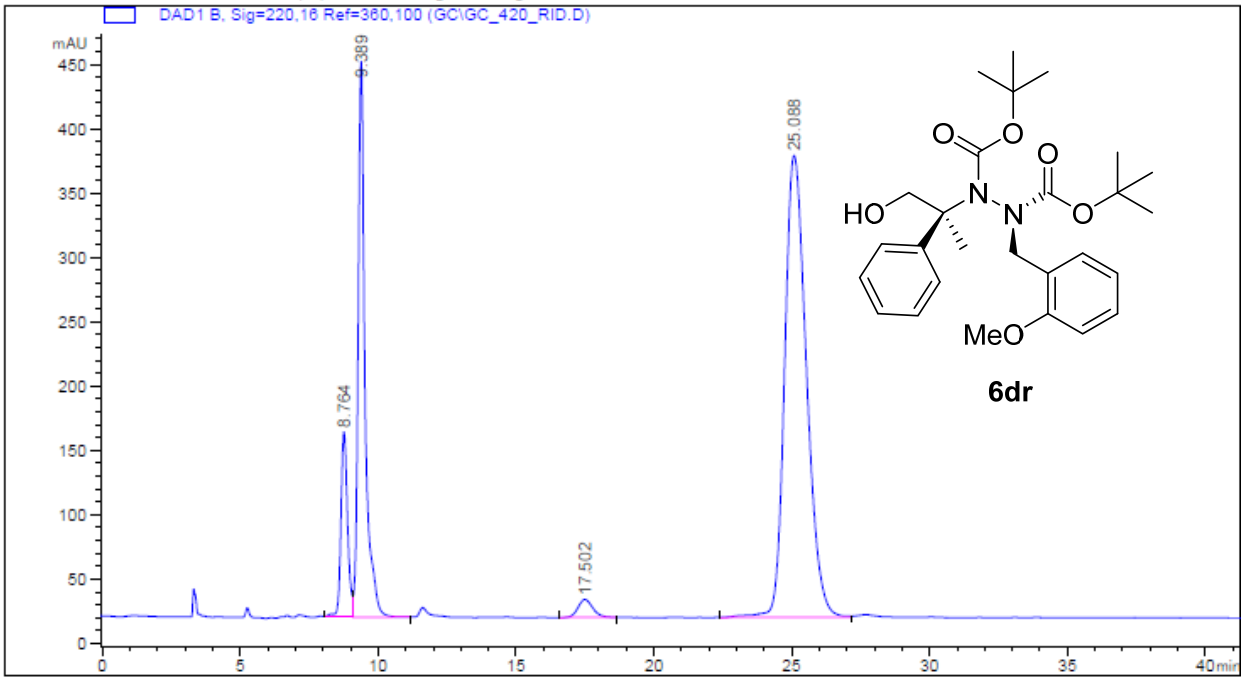
```
    ========================================================================
    Acq. Operator    : Giovanni
    Acq. Instrument  : HPLC-1                          Location : Vial 1
    Injection Date   : 18/02/2022 16:26:01
    Acq. Method      : C:\CHEM32\1\METHODS\DEF_LC.M
    Last changed     : 18/02/2022 16:15:56 by Chiara
                       (modified after loading)
    Analysis Method  : C:\CHEM32\1\METHODS\DEF_LC.M
    Last changed     : 03/05/2022 10:37:18 by Chiara
                       (modified after loading)
    Sample Info      : GC_384_ridotto, 1 mL/min, 90:10 hex:ipr, 25°C, IC

    Additional Info : Peak(s) manually integrated
```




```
    ========================================================================
                           Area Percent Report
    ========================================================================

    Sorted By             :      Signal
    Multiplier:                   :      1.0000
    Dilution:                     :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 B, Sig=220,16 Ref=360,100

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   8.409 BV    0.2541 2.28224e4  1430.49854  23.5122
       2   8.883 VB    0.2632 2.48792e4  1457.47778  25.6311
       3  16.371 VB    0.5598 2.44525e4   673.19305  25.1916
       4  22.973 VB    0.7641 2.49122e4   504.47980  25.6651

    Totals :                  9.70664e4  4065.64917
```

Data File H:\HPLC\1\DATA\GC\GC_420_RID.D
Sample Name: GC_420_RID

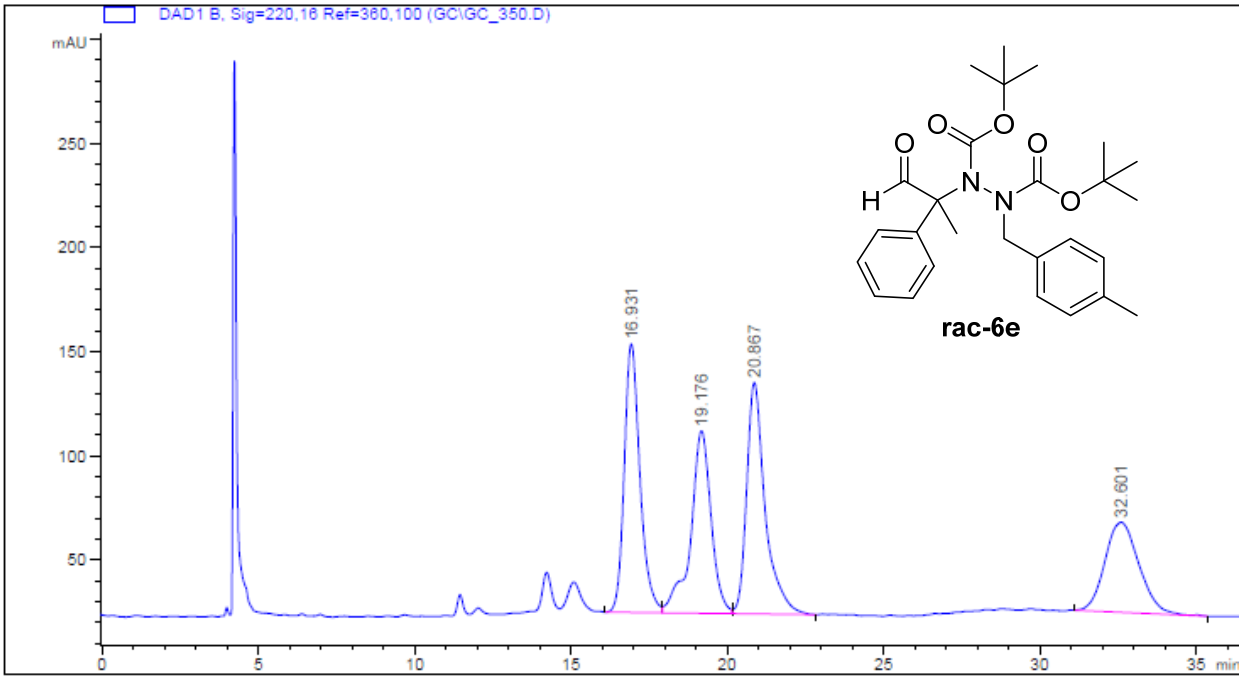
```
==========================================================================
Acq. Operator    : Giovanni
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date   : 13/05/2022 11.28.39
Acq. Method      : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 13/05/2022 10.42.01 by Giovanni
                   (modified after loading)
Analysis Method : H:\HPLC\1\METHODS\DEF_LC.M
Last changed     : 21/05/2022 14.11.49
                   (modified after loading)
Sample Info      : GC_420_RID,1 mL/min, 90:10 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.764 VV    0.2558 2416.99219  143.98268   8.0011
   2   9.389 VB    0.2570 7584.79053  431.60550  25.1084
   3  17.502 BB    0.5705  518.63452   13.92620   1.7169
   4  25.088 BV    0.8443 1.96877e4   358.70432  65.1736

Totals :                  3.02082e4   948.21870
```

Data File C:\CHEM32\1\DATA\GC\GC_350.D
Sample Name: GC_350

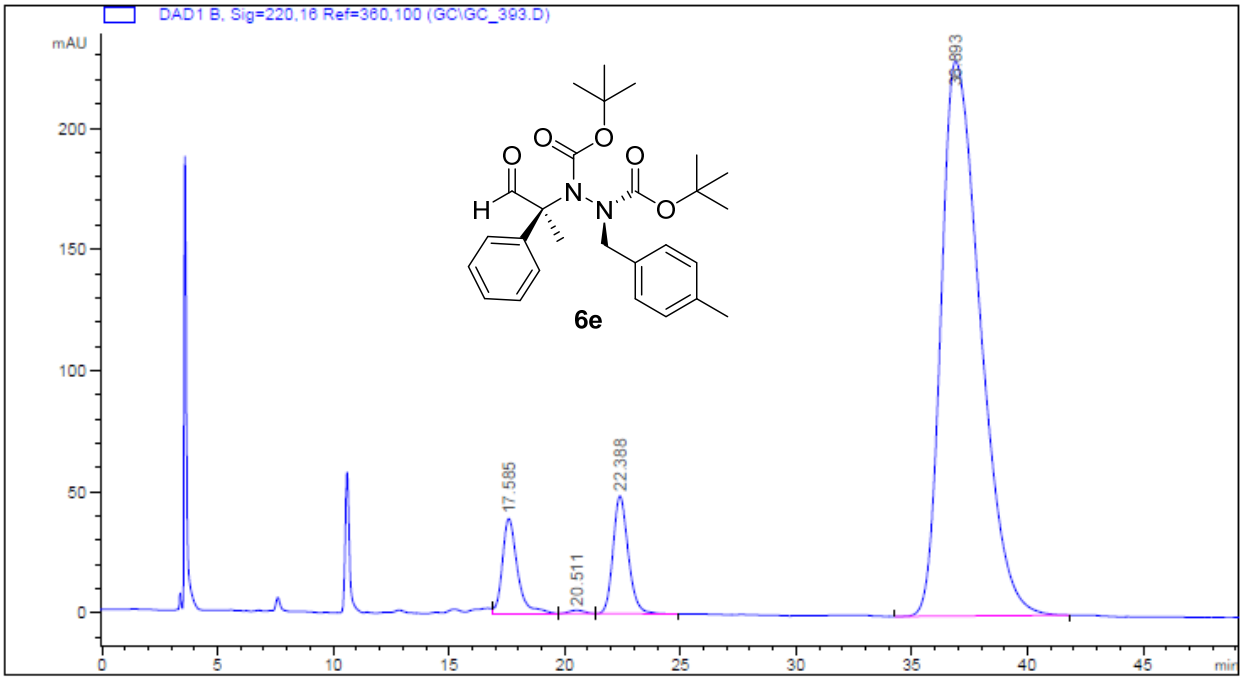
```
==========================================================================
Acq. Operator    : Giovanni
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date   : 15/12/2021 14:38:39
Acq. Method      : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 15/12/2021 14:37:53 by Giovanni
                   (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 03/05/2022 10:54:58 by Chiara
                   (modified after loading)
Sample Info      : GC_350, 1 mL/min, 98:2 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.931 BV    0.5319 4504.48096  128.84485  27.5521
   2  19.176 VV    0.6792 3986.21411   87.54908  24.3821
   3  20.867 VB    0.6094 4584.28516  111.11101  28.0403
   4  32.601 BB    1.1466 3273.95947   43.27497  20.0255

Totals :                  1.63489e4   370.77990
```

Data File C:\CHEM32\1\DATA\GC\GC_393.D
Sample Name: GC_393

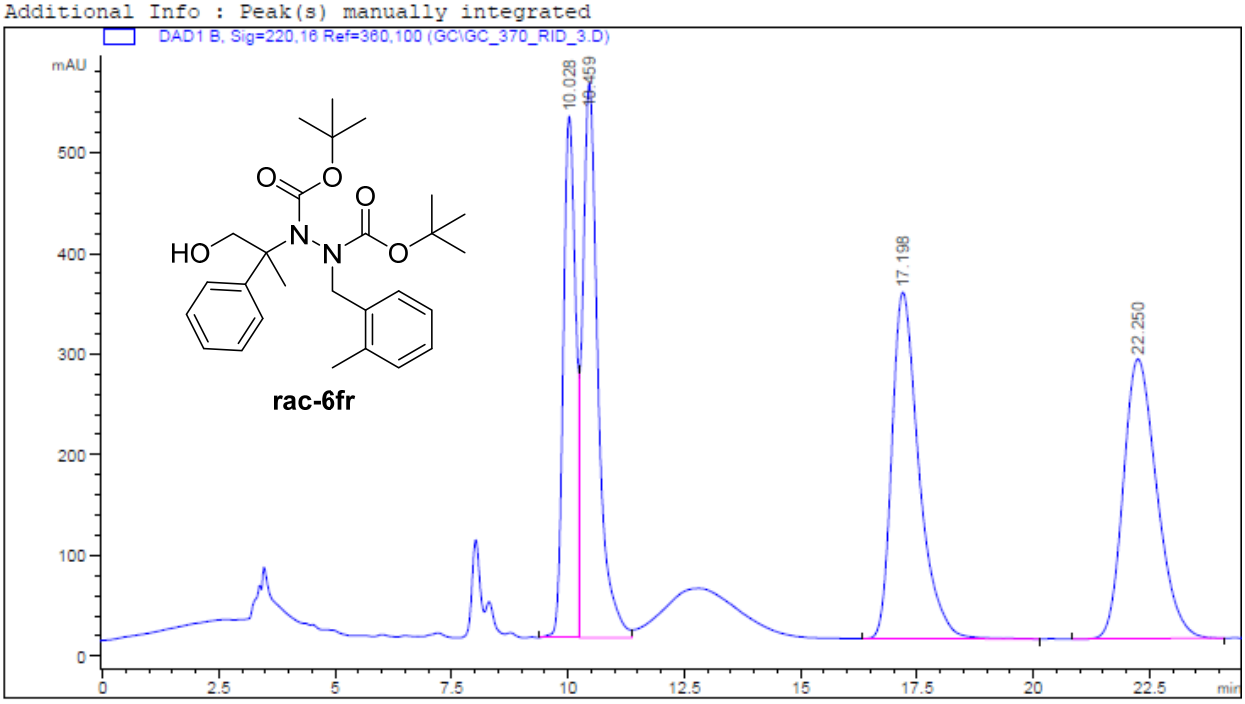
```
==========================================================================
Acq. Operator    : Giovanni
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date   : 04/03/2022 16:29:46
Acq. Method      : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 04/03/2022 16:07:44 by Chiara
                   (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 03/05/2022 10:55:58 by Chiara
                   (modified after loading)
Sample Info      : GC_393, 1 mL/min, 98:2 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  17.585 VB    0.6847 1772.01001   39.10073   5.7427
   2  20.511 BB    0.5879   63.37709    1.40055   0.2054
   3  22.388 BB    0.6957 2225.28589   48.64693   7.2117
   4  36.893 BB    1.7723 2.67961e4   228.81345  86.8402

Totals :                  3.08567e4   317.96165
```

Data File C:\CHEM32\1\DATA\GC\GC_370_RID_3.D
Sample Name: GC_370_RID

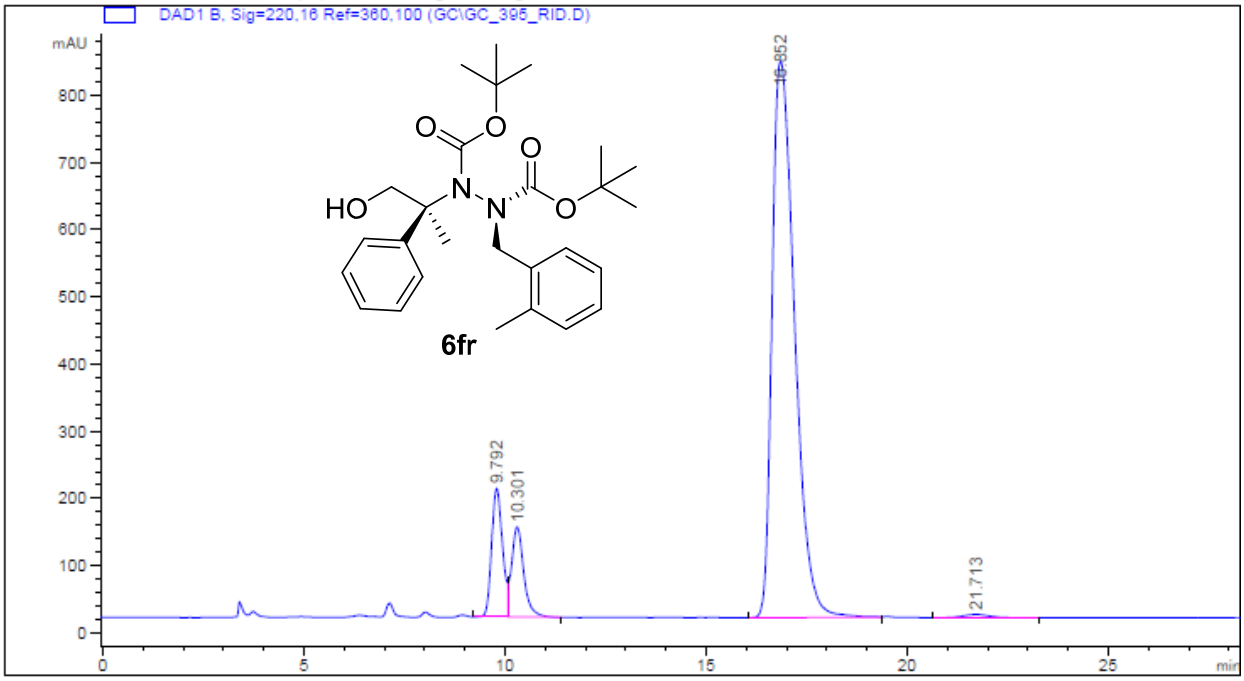
```
==========================================================================
Acq. Operator   : Giovanni
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date  : 15/03/2022 15:06:48
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 15/03/2022 15:05:36 by Giovanni
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 03/05/2022 11:00:48 by Chiara
                  (modified after loading)
Sample Info     : GC_370_RID, 1 mL/min, 95:5 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.028 BV    0.2824 9512.76367  517.73743  19.0280
   2  10.459 VV    0.3417 1.27222e4   550.32629  25.4477
   3  17.198 BB    0.6110 1.38877e4   343.98843  27.7791
   4  22.250 BBA   0.7709 1.38708e4   277.63614  27.7452

Totals :                  4.99935e4  1689.68829
```

Data File C:\CHEM32\1\DATA\GC\GC_395_RID.D
Sample Name: GC_395_rid

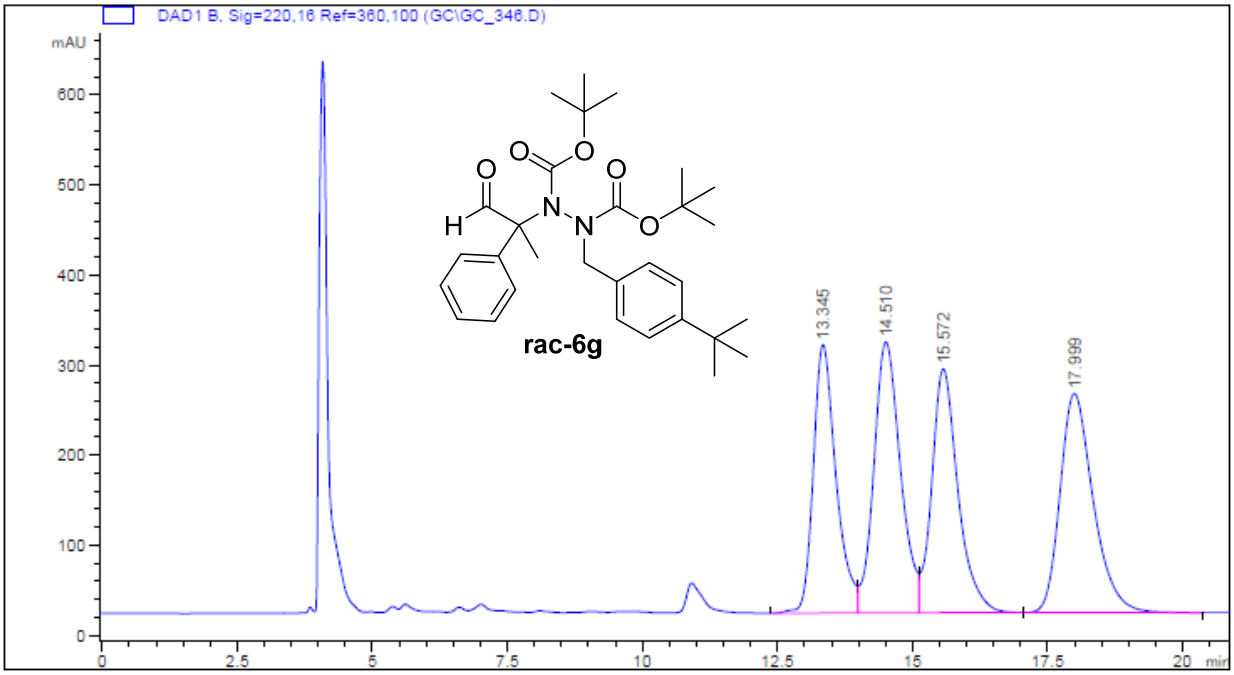
```
==========================================================================
Acq. Operator    : Giovanni
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date   : 17/03/2022 15:39:59
Acq. Method      : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 17/03/2022 15:17:43 by Chiara
                   (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 03/05/2022 11:01:34 by Chiara
                   (modified after loading)
Sample Info      : GC_395_rid, 1 mL/min, 95:5 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.792 BV    0.2904 3578.63208  191.15277   9.2112
   2  10.301 VB    0.3155 2844.47119  134.05757   7.3215
   3  16.852 BV    0.6057 3.21656e4   827.10956  82.7926
   4  21.713 BB    0.7931  262.08530    4.92326   0.6746

Totals :                  3.88508e4  1157.24316
```

Data File H:\HPLC\1\DATA\GC\GC_346.D
Sample Name: GC_346

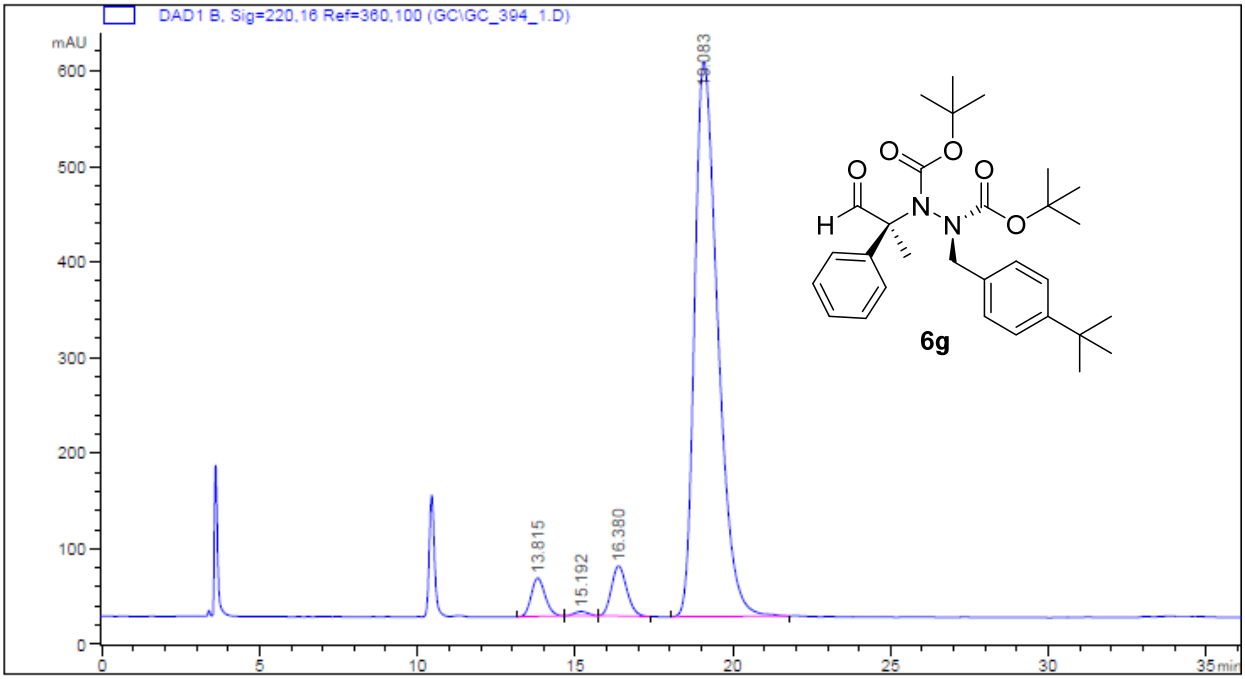
```
================================================================================
Acq. Operator   : Giovanni
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date  : 14/12/2021 12.44.25
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 14/12/2021 12.37.29 by Chiara
                  (modified after loading)
Analysis Method : H:\HPLC\1\METHODS\DEF_LC.M
Sample Info     : GC_346, 1 mL/min, 98:2 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```




```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]      %
----|-------|----|-------|----------|----------|--------|
   1  13.345 BV    0.4374 8722.36230  298.05161  22.6122
   2  14.510 VV    0.5216 1.03088e4   300.97156  26.7248
   3  15.572 VB    0.5064 9155.16895  270.81717  23.7342
   4  17.999 BB    0.6502 1.03874e4   243.27058  26.9288

Totals :                  3.85737e4  1113.11092
```

Data File H:\HPLC\1\DATA\GC\GC_394_1.D
Sample Name: GC_394

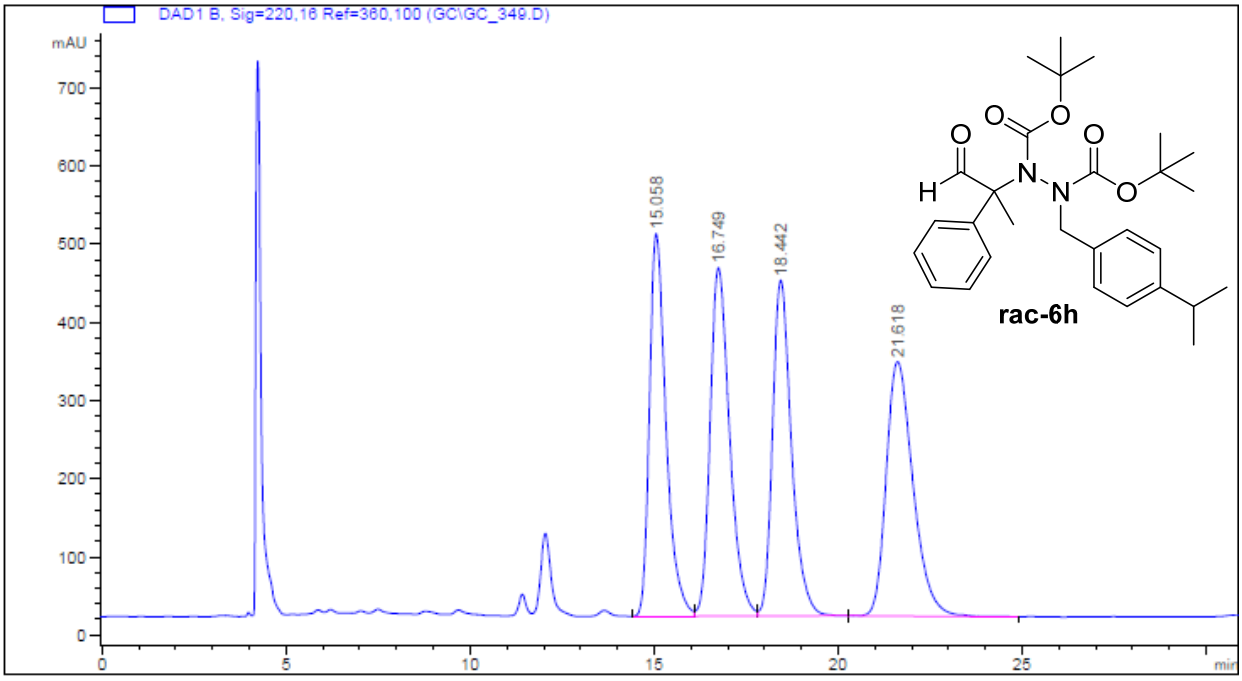
```
==========================================================================
Acq. Operator   : Giovanni
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date  : 07/03/2022 15.13.17
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 07/03/2022 15.10.35 by Giovanni
                  (modified after loading)
Analysis Method : H:\HPLC\1\METHODS\DEF_LC.M
Sample Info     : GC_394, 1 mL/min, 98:2 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.815 BB    0.4727 1235.50659   40.18773   3.7722
   2  15.192 BB    0.4528  130.51820    4.31615   0.3985
   3  16.380 BB    0.5252 1772.05920   52.31383   5.4104
   4  19.083 BB    0.7834 2.96147e4   580.30078  90.4189

Totals :                  3.27527e4   677.11849
```

Data File C:\CHEM32\1\DATA\GC\GC_349.D
Sample Name: GC_349

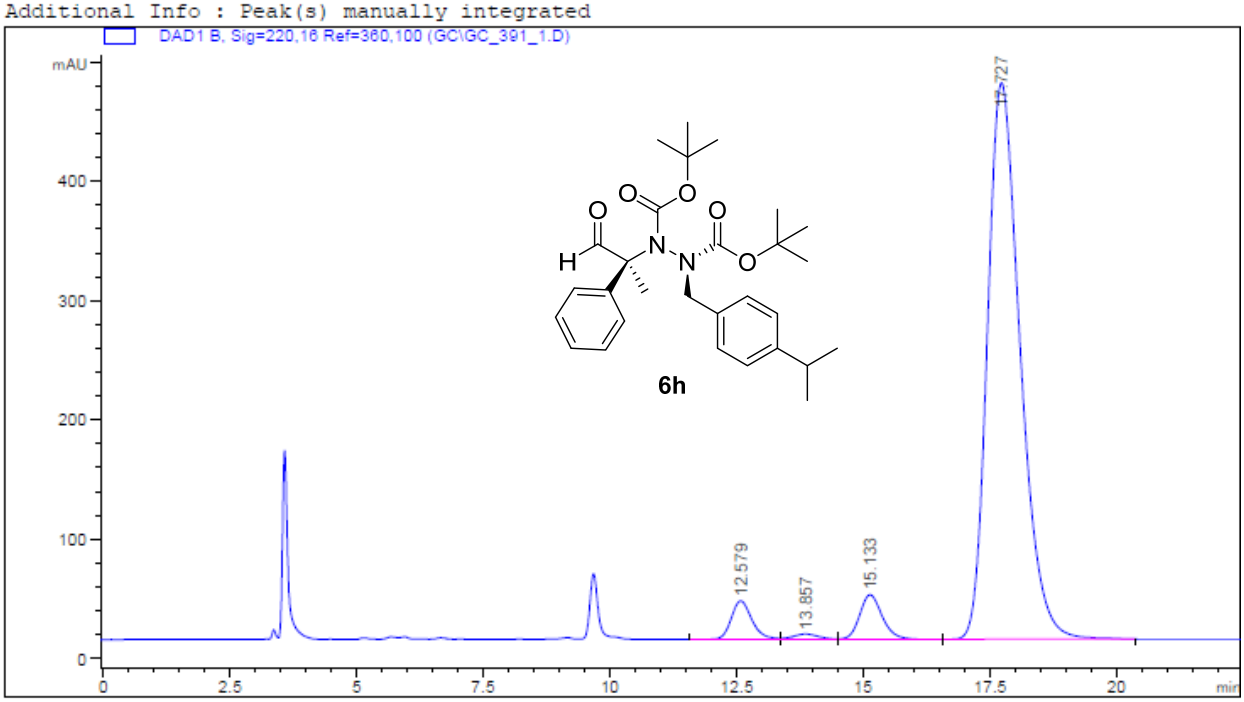
```
==========================================================================
Acq. Operator    : Giovanni
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date   : 15/12/2021 14:06:37
Acq. Method      : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 15/12/2021 14:05:14 by Chiara
                   (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 03/05/2022 10:57:34 by Chiara
                   (modified after loading)
Sample Info      : GC_349, 1 mL/min, 98:2 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  15.058 BV    0.4770 1.53105e4   489.37558  24.0669
   2  16.749 VV    0.5620 1.64188e4   445.48318  25.8092
   3  18.442 VB    0.5415 1.53625e4   429.32986  24.1488
   4  21.618 BB    0.7770 1.65244e4   325.08359  25.9751

Totals :                  6.36161e4  1689.27222
```

Data File C:\CHEM32\1\DATA\GC\GC_391_1.D
Sample Name: GC_391

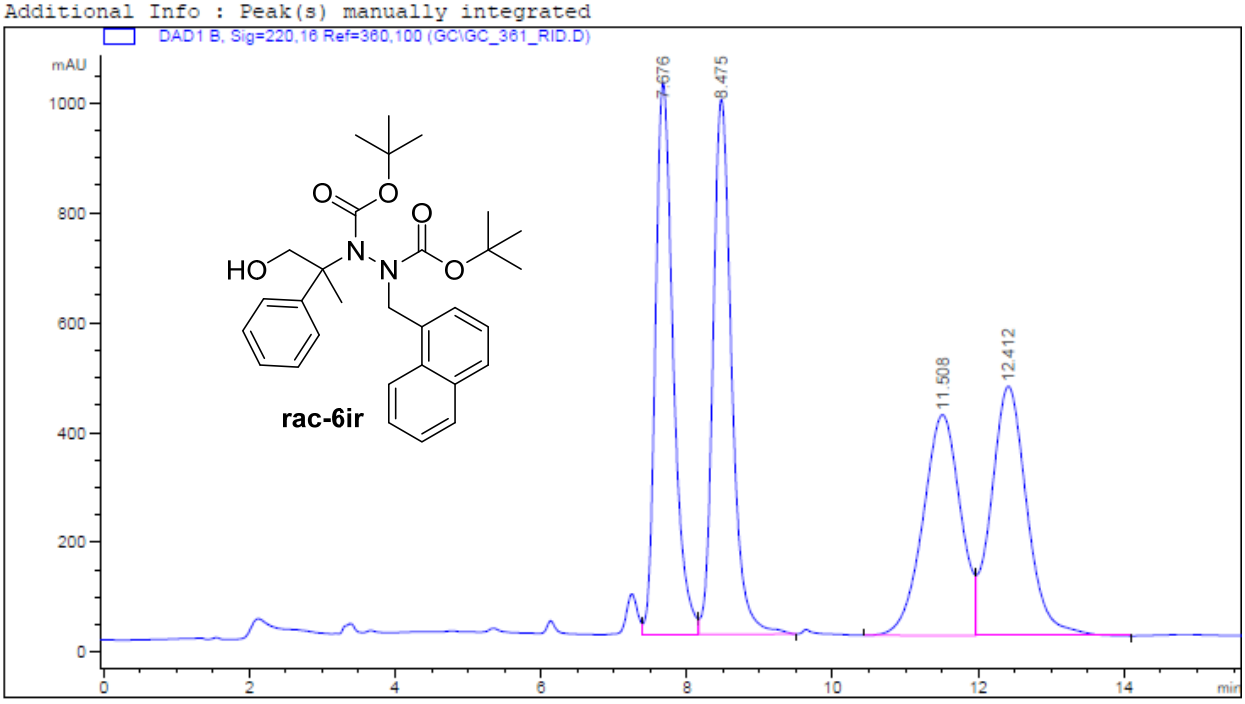
```
Acq. Operator   : Giovanni
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date  : 28/02/2022 15:33:21
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 28/02/2022 15:31:53 by Giovanni
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 03/05/2022 10:58:27 by Chiara
                  (modified after loading)
Sample Info     : GC_391, 1 mL/min, 98:2 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```




```
                        Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.579 BV    0.4320  908.97858   32.13691   3.9359
   2  13.857 VV    0.5014  154.03836    4.43269   0.6670
   3  15.133 VB    0.4727 1154.63843   37.34182   4.9996
   4  17.727 BB    0.6884 2.08769e4   466.26382  90.3975

Totals :                  2.30946e4   540.17524
```

Data File C:\CHEM32\1\DATA\GC\GC_361_RID.D
Sample Name: GC_361_rid

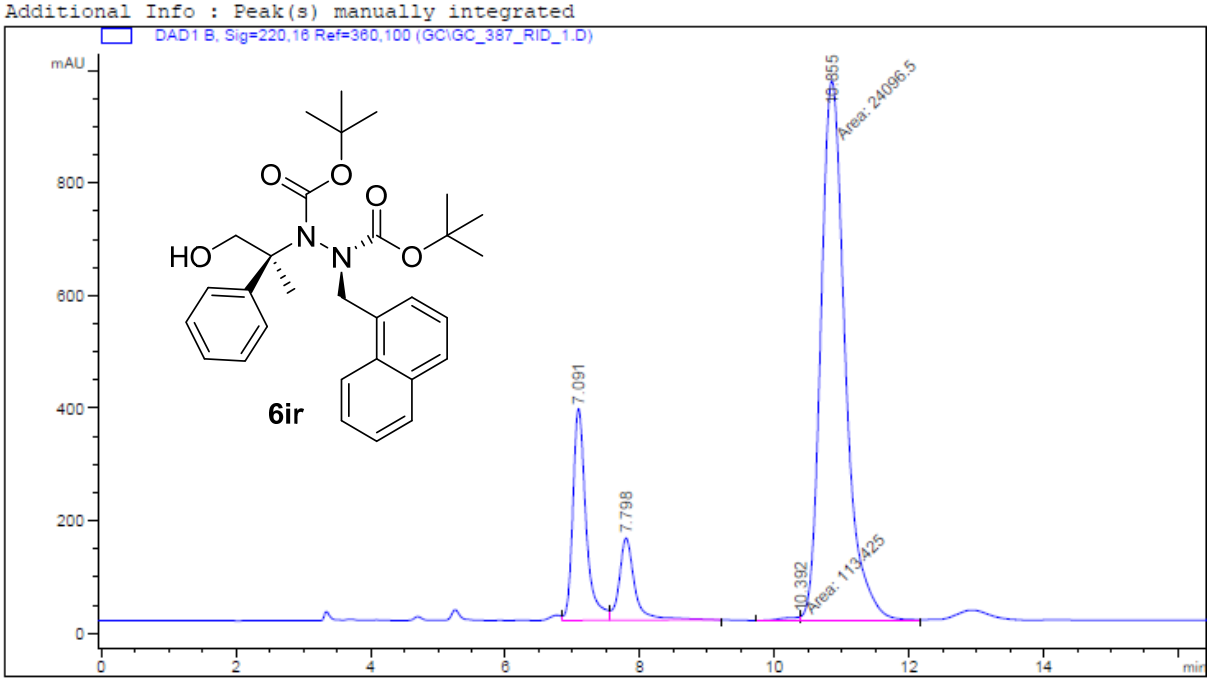
```
    ========================================================================
    Acq. Operator    : Giovanni
    Acq. Instrument  : HPLC-1                          Location : Vial 1
    Injection Date   : 22/02/2022 09:15:51
    Acq. Method      : C:\CHEM32\1\METHODS\DEF_LC.M
    Last changed     : 22/02/2022 09:13:58 by Chiara
                       (modified after loading)
    Analysis Method  : C:\CHEM32\1\METHODS\DEF_LC.M
    Last changed     : 03/05/2022 10:44:55 by Chiara
                       (modified after loading)
    Sample Info      : GC_361_ridotto, 1 mL/min, 90:10 hex:ipr, 25°C, IC


    Additional Info : Peak(s) manually integrated
```




```
    ========================================================================
                            Area Percent Report
    ========================================================================

    Sorted By             :      Signal
    Multiplier:                   :      1.0000
    Dilution:                     :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 B, Sig=220,16 Ref=360,100

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]    [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   7.676 VV    0.2601 1.70587e4  1004.81989  26.5610
       2   8.475 VB    0.2733 1.73305e4   975.15918  26.9842
       3  11.508 BV    0.5450 1.43717e4   402.06247  22.3772
       4  12.412 VB    0.5194 1.54638e4   453.99808  24.0776

    Totals :                  6.42247e4  2836.03961
```

Data File H:\HPLC\1\DATA\GC\GC_387_RID_1.D
Sample Name: GC_387_rid

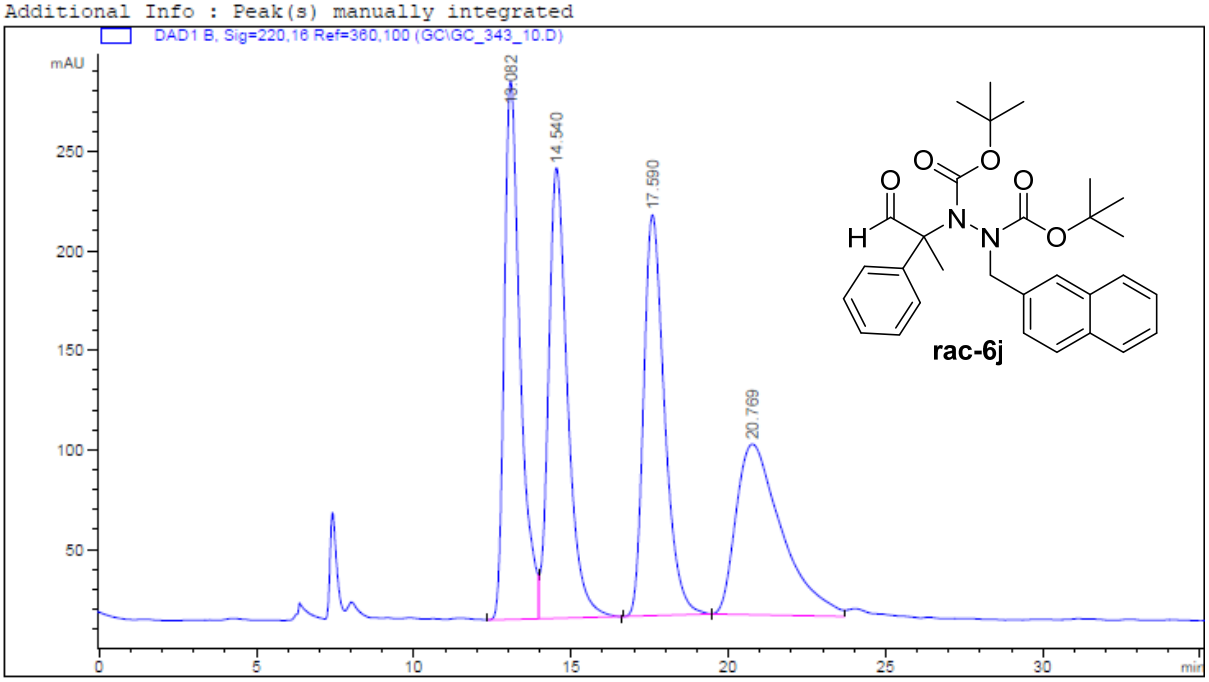
```
==========================================================================
Acq. Operator   : Giovanni
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date  : 01/03/2022 16.37.40
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 01/03/2022 16.28.33 by Giovanni
                  (modified after loading)
Analysis Method : H:\HPLC\1\METHODS\DEF_LC.M
Last changed    : 21/05/2022 14.11.49
                  (modified after loading)
Sample Info     : GC_387_rid, 1 mL/min, 90:10 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.091 VV    0.2050 5130.84180  376.39688  16.1940
   2   7.798 VB    0.2372 2342.85303  146.00117   7.3945
   3  10.392 MF    0.2664  113.42534    7.09741   0.3580
   4  10.855 FM    0.4188 2.40965e4   958.92871  76.0535

Totals :                  3.16836e4  1488.42417
```

Data File H:\HPLC\1\DATA\GC\GC_343_10.D
Sample Name: GC_343

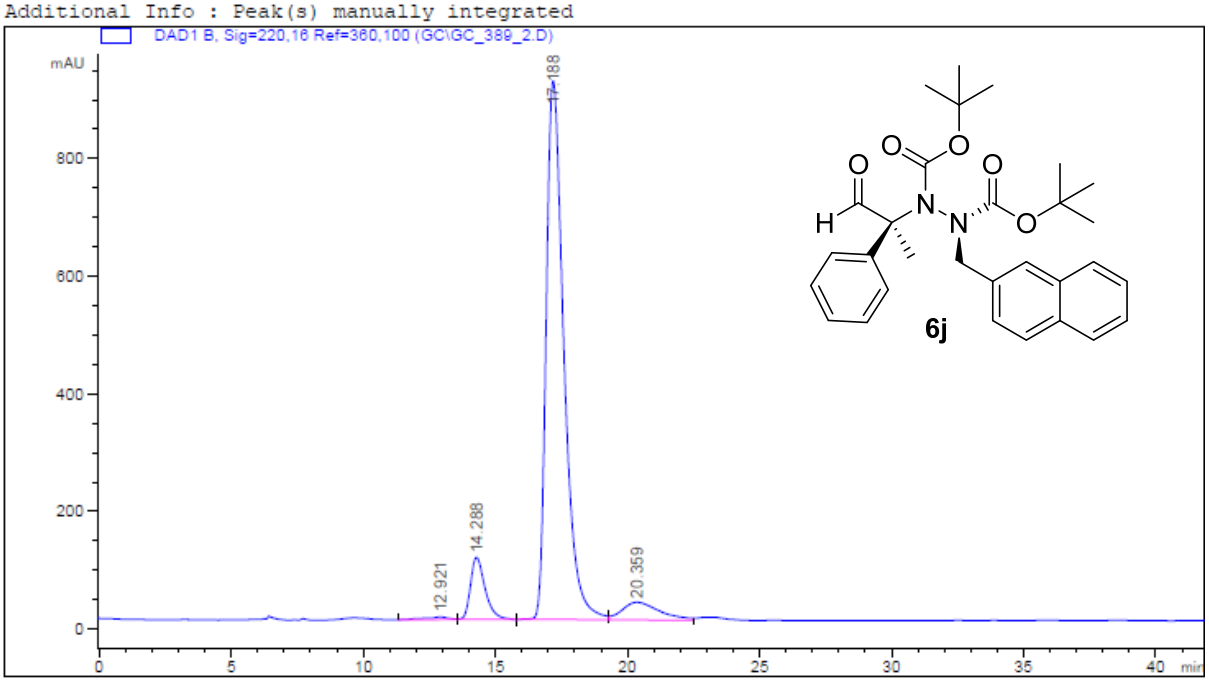
```
======================================================================
Acq. Operator   : Giovanni
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date  : 05/05/2022 15.46.17
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 05/05/2022 15.38.27 by Giovanni
                  (modified after loading)
Analysis Method : H:\HPLC\1\METHODS\DEF_LC.M
Last changed    : 21/05/2022 14.11.49
                  (modified after loading)
Sample Info     : GC_343, 0.5 mL/min, 98:2 hex:ipr, 25°C, OD-H


Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.082 BV    0.5315 9539.87891  270.45291  25.7755
   2  14.540 VB    0.6315 9531.51367  226.25156  25.7529
   3  17.590 BB    0.7061 9286.42773  201.33719  25.0907
   4  20.769 BV    1.4861 8653.54199   85.69472  23.3808

Totals :                  3.70114e4   783.73637
```

Data File H:\HPLC\1\DATA\GC\GC_389_2.D
Sample Name: GC_389

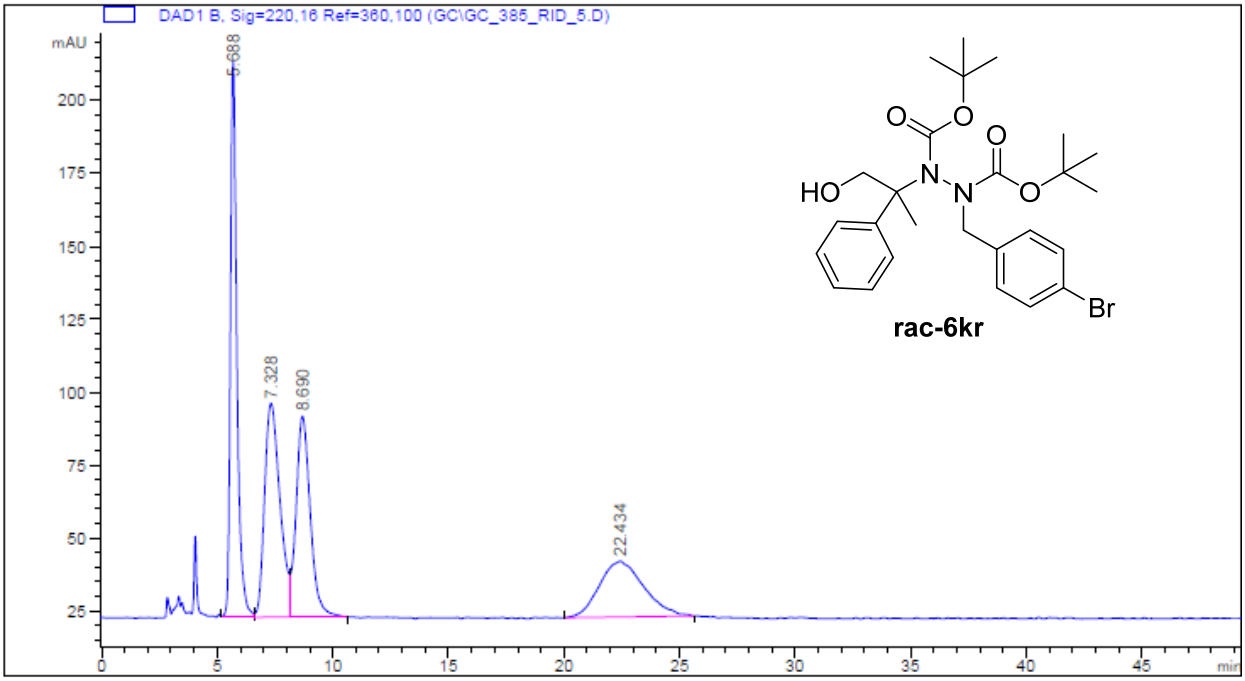
```
======================================================================
Acq. Operator   : Giovanni
Acq. Instrument : HPLC-1                        Location : Vial 1
Injection Date  : 05/05/2022 16.49.21
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 05/05/2022 16.49.02 by Giovanni
                  (modified after loading)
Analysis Method : H:\HPLC\1\METHODS\DEF_LC.M
Last changed    : 21/05/2022 14.11.49
                  (modified after loading)
Sample Info     : GC_389, 0.5 mL/min, 98:2 hex:ipr, 25°C, OD-H

Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.921 BV    0.7794  263.05069    4.55725   0.5297
   2  14.288 VB    0.5767 4019.73462  105.45032   8.0942
   3  17.188 BV    0.7050 4.24463e4   915.39722  85.4701
   4  20.359 VV    1.4307 2933.07007   29.84169   5.9061

Totals :                  4.96621e4  1055.24648
```

Data File H:\HPLC\1\DATA\GC\GC_385_RID_5.D
Sample Name: GC_385_rid

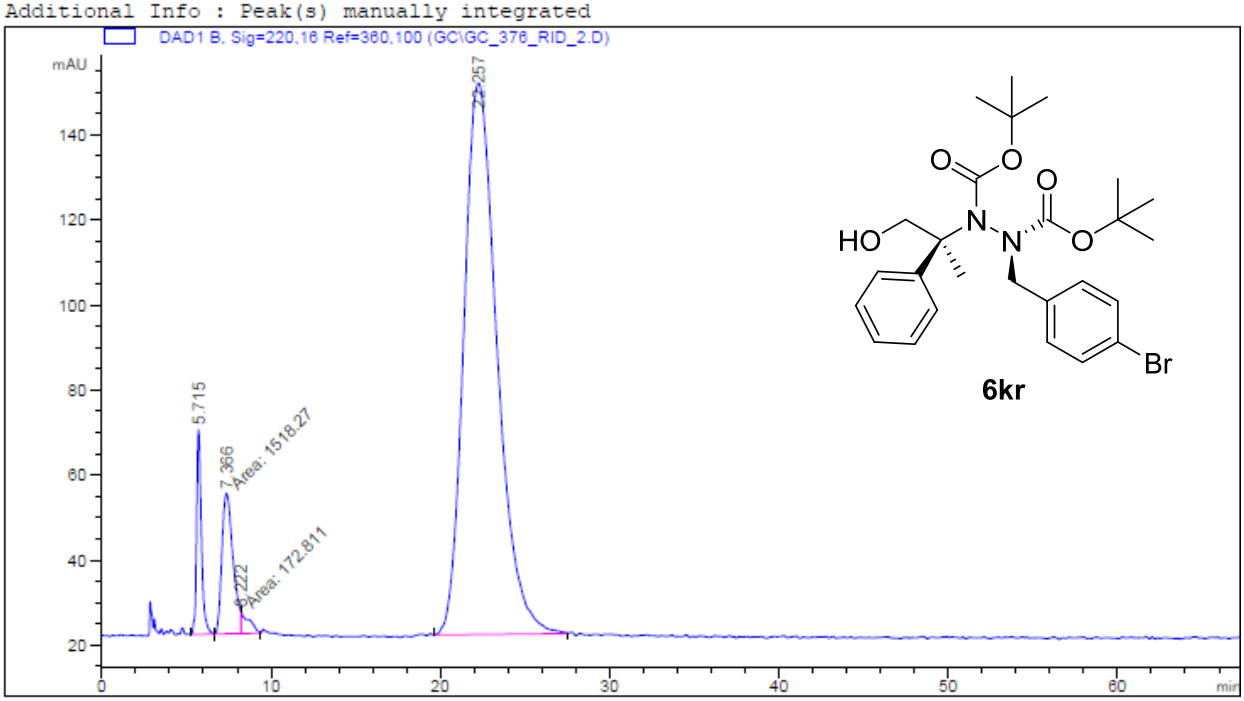
```
==========================================================================
Acq. Operator   : Giovanni
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date  : 29/03/2022 10.57.33
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 29/03/2022 10.05.29 by Giovanni
                  (modified after loading)
Analysis Method : H:\HPLC\1\METHODS\DEF_LC.M
Last changed    : 07/05/2022 14.02.09
                  (modified after loading)
Sample Info     : GC_385_rid, 1 mL/min, 90:10 hex:ipr, 25°C, Lux 5u cellu
                  lose-2

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.688 VV    0.2934 3714.81152  190.60124  29.4185
   2   7.328 VV    0.7050 3387.54224   73.32783  26.8268
   3   8.690 VB    0.6535 2960.59082   68.86859  23.4456
   4  22.434 BB    1.6152 2564.52075   19.18918  20.3091

Totals :                  1.26275e4   351.98684
```

Data File H:\HPLC\1\DATA\GC\GC_376_RID_2.D
Sample Name: GC_376_RID

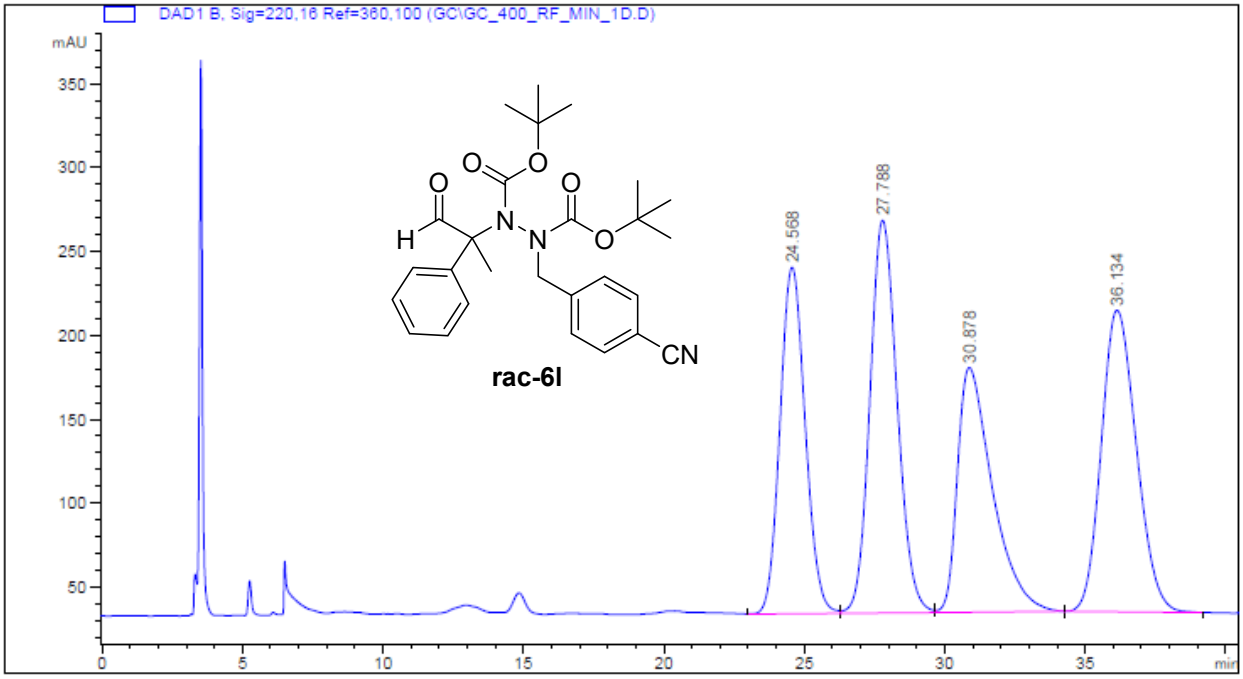
```
======================================================================
Acq. Operator   : Giovanni
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date  : 29/03/2022 13.01.29
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 29/03/2022 12.57.10 by Giovanni
                  (modified after loading)
Analysis Method : H:\HPLC\1\METHODS\DEF_LC.M
Last changed    : 07/05/2022 14.10.49
                  (modified after loading)
Sample Info     : GC_376_RID, 1 mL/min, 90:10 hex:ipr, 25°C, Lux 5u cellu
                  lose-2

Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   5.715 BB    0.2904  950.22357   48.12112   4.6728
   2   7.366 MF    0.7660 1518.27429   33.03587   7.4662
   3   8.222 FM    0.5561  172.81067    5.17892   0.8498
   4  22.257 BB    1.8979 1.76941e4   129.67358  87.0113

Totals :                  2.03354e4   216.00949
```

Data File C:\CHEM32\1\DATA\GC\GC_400_RF_MIN_1D.D
Sample Name: GC_400_rf_min

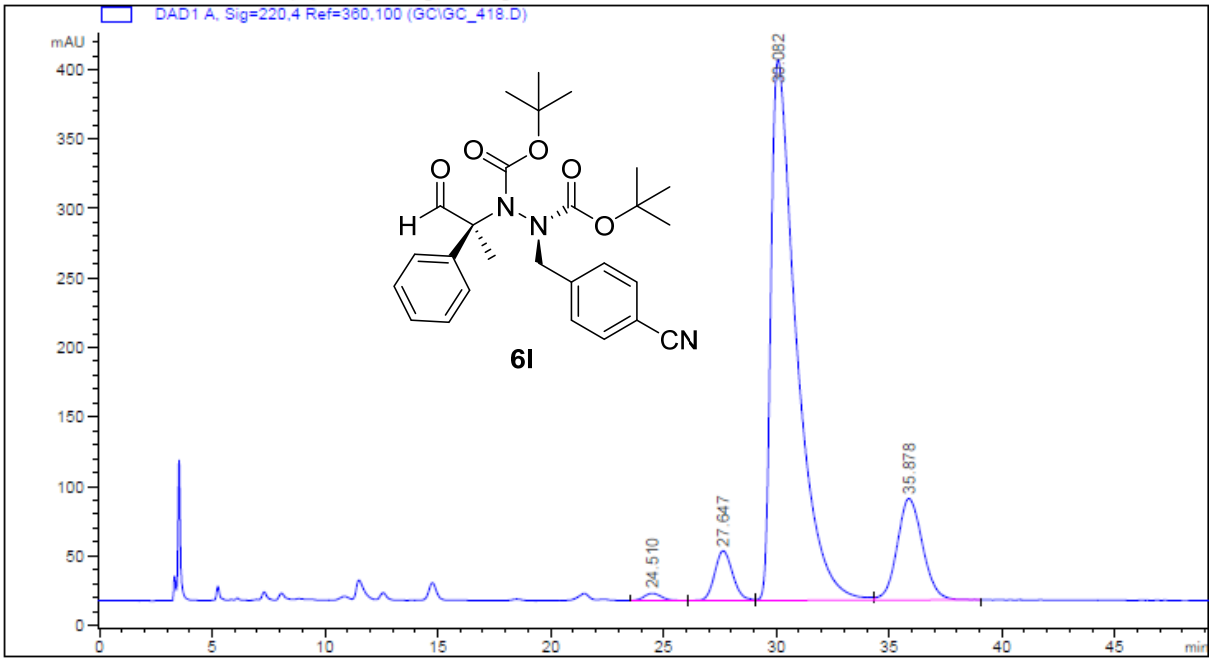
```
==========================================================================
Acq. Operator    : Giovanni
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date   : 18/03/2022 10:04:28
Acq. Method      : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 18/03/2022 09:31:54 by Giovanni
                   (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 03/05/2022 10:49:20 by Chiara
                   (modified after loading)
Sample Info      : GC_400_rf_min, 1 mL/min, 90:10 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|---------|--------|
   1  24.568 BV    0.9609 1.28655e4   206.47943  22.6232
   2  27.788 VV    1.0316 1.58008e4   234.06561  27.7847
   3  30.878 VB    1.2935 1.26204e4   145.85873  22.1921
   4  36.134 BB    1.3308 1.55820e4   179.84575  27.4000

Totals :                  5.68686e4   766.24953
```

Data File H:\HPLC\1\DATA\GC\GC_418.D
Sample Name: GC_418

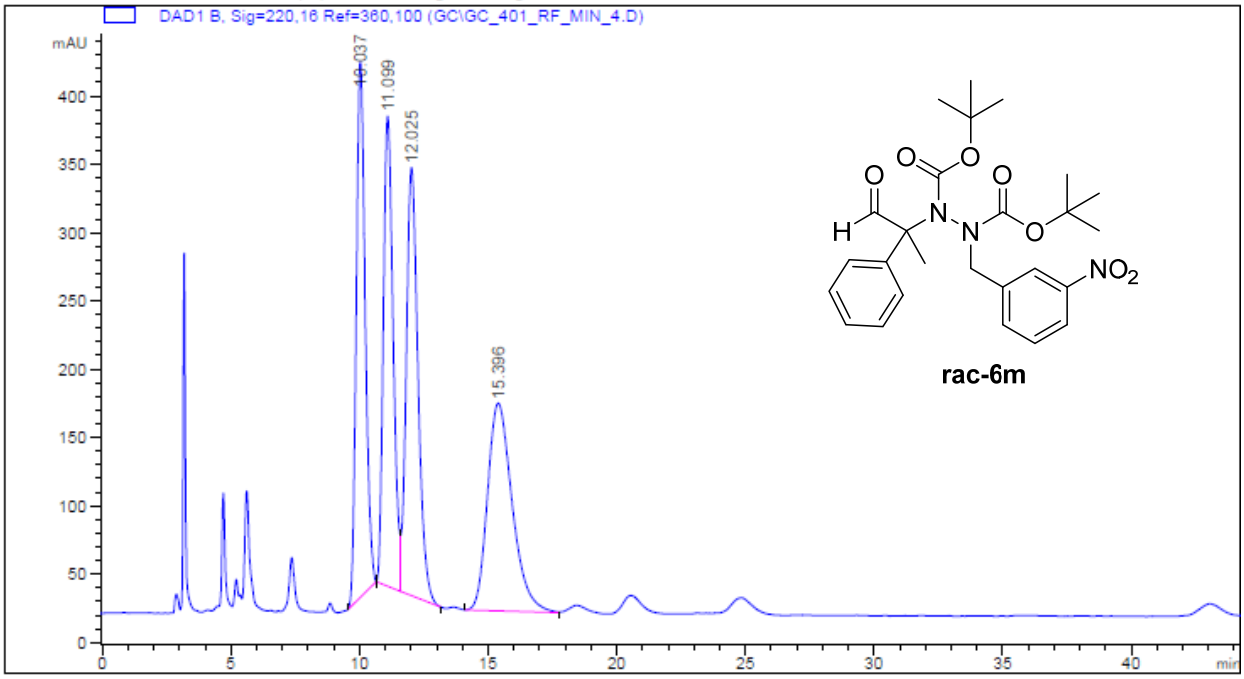
```
==========================================================================
Acq. Operator   : Giovanni
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date  : 06/05/2022 16.24.53
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 06/05/2022 16.23.51 by Giovanni
                  (modified after loading)
Analysis Method : H:\HPLC\1\METHODS\DEF_LC.M
Last changed    : 21/05/2022 14.11.49
                  (modified after loading)
Sample Info     : GC_418, 1 mL/min, 90:10 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=220,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  24.510 VB    0.8072  292.92017    5.31335   0.7620
   2  27.647 BV    0.8593 1989.95520   35.86528   5.1770
   3  30.082 VV    1.1524 3.04310e4   389.10516  79.1676
   4  35.878 VB    1.1941 5724.81250   73.06770  14.8934

Totals :                  3.84387e4   503.35150
```

Data File H:\HPLC\1\DATA\GC\GC_401_RF_MIN_4.D
Sample Name: GC_401_RF_MIN

```
==========================================================================
Acq. Operator    : Giovanni
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date   : 01/04/2022 12.30.28
Acq. Method      : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 01/04/2022 12.16.07 by Giovanni
                   (modified after loading)
Analysis Method : H:\HPLC\1\METHODS\DEF_LC.M
Last changed     : 07/05/2022 14.10.49
                   (modified after loading)
Sample Info      : GC_401_RF_MIN, 1 mL/min, 90:10 hex:ipr, 25°C, Lux 5u ce
                   llulose-2

Additional Info : Peak(s) manually integrated
```

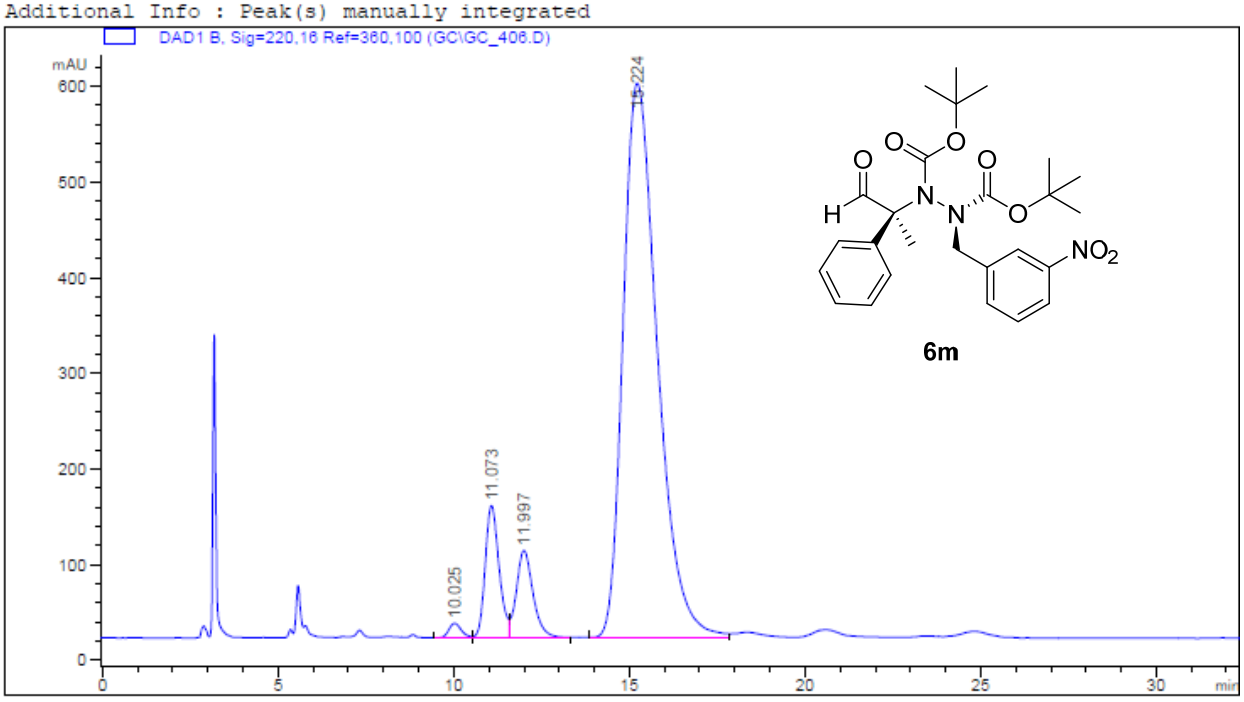


rac-6m

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.037 BB    0.3726 9422.60742  391.78265  24.4395
   2  11.099 BV    0.4078 9071.34180  343.88449  23.5284
   3  12.025 VB    0.4813 9911.47363  313.10593  25.7074
   4  15.396 BV    1.0271 1.01495e4   151.97836  26.3247

Totals :                  3.85549e4  1200.75143
```

Data File H:\HPLC\1\DATA\GC\GC_406.D
Sample Name: GC_406

```
======================================================================
Acq. Operator   : Giovanni
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date  : 05/04/2022 15.54.52
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 05/04/2022 15.14.26 by alberto
                  (modified after loading)
Analysis Method : H:\HPLC\1\METHODS\DEF_LC.M
Last changed    : 07/05/2022 14.10.49
                  (modified after loading)
Sample Info     : GC_406, 1 mL/min, 90:10 hex:ipr, 25°C, Lux 5u cellulose
                  -2

Additional Info : Peak(s) manually integrated
```

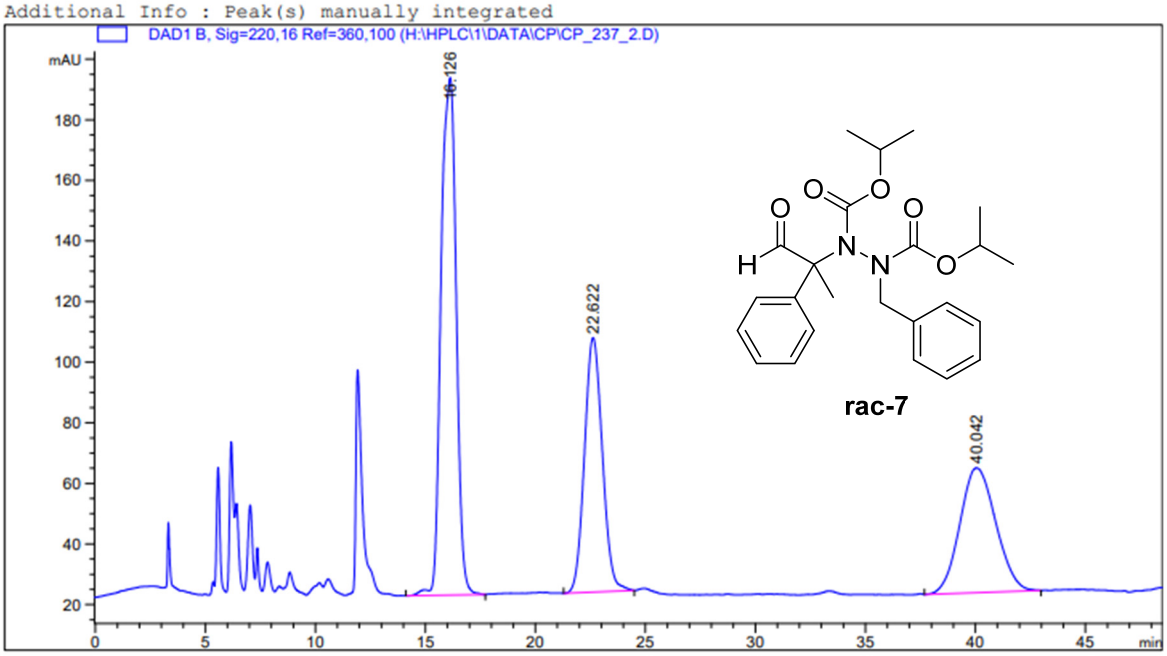


6m

```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.025 BV    0.3781  375.53873   15.20502   0.8082
   2  11.073 VV    0.4216 3810.45801  138.24240   8.2010
   3  11.997 VB    0.4963 3002.30493   91.13885   6.4617
   4  15.224 BV    1.0347 3.92751e4   579.49292  84.5291

Totals :                  4.64634e4   824.07919
```

Data File H:\HPLC\1\DATA\CP\CP_237_2.D
Sample Name: CP_237_2

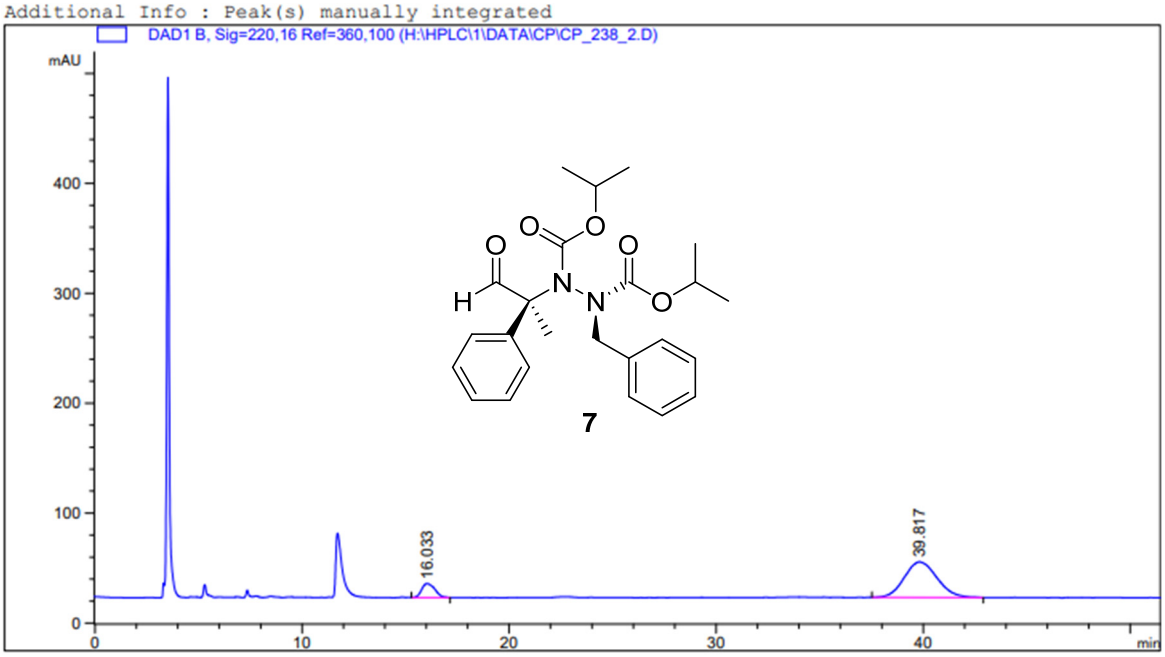
```
    ======================================================================
    Acq. Operator   : Chiara
    Acq. Instrument : HPLC-1                          Location : Vial 1
    Injection Date  : 21/03/2022 10:00:30
    Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
    Last changed    : 21/03/2022 09:40:25 by Chiara
                      (modified after loading)
    Analysis Method : H:\HPLC\2\METHODS\DEF_LC.M
    Last changed    : 06/06/2022 15:16:29
                      (modified after loading)
    Sample Info     : CP_237_2, 1 mL/min, 90:10 hex:ipr, 25°C, IC

    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier:                   :      1.0000
    Dilution:                     :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 B, Sig=220,16 Ref=360,100

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  16.126 BB    0.6750 8181.92627  170.75758  46.5221
       2  22.622 BB    0.8831 4731.23242   84.00115  26.9016
       3  40.042 BB    1.6944 4674.01611   41.17331  26.5763

    Totals :                  1.75872e4   295.93204
```

Data File H:\HPLC\1\DATA\CP\CP_238_2.D
Sample Name: CP_238_2

```
Acq. Operator    : Chiara
Acq. Instrument  : HPLC-1                          Location : Vial 1
Injection Date   : 21/03/2022 10:51:00
Acq. Method      : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 21/03/2022 10:49:26 by Chiara
                   (modified after loading)
Analysis Method  : H:\HPLC\2\METHODS\DEF_LC.M
Last changed     : 06/06/2022 15:17:37
                   (modified after loading)
Sample Info      : CP_238_2, 1 mL/min, 90:10 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```

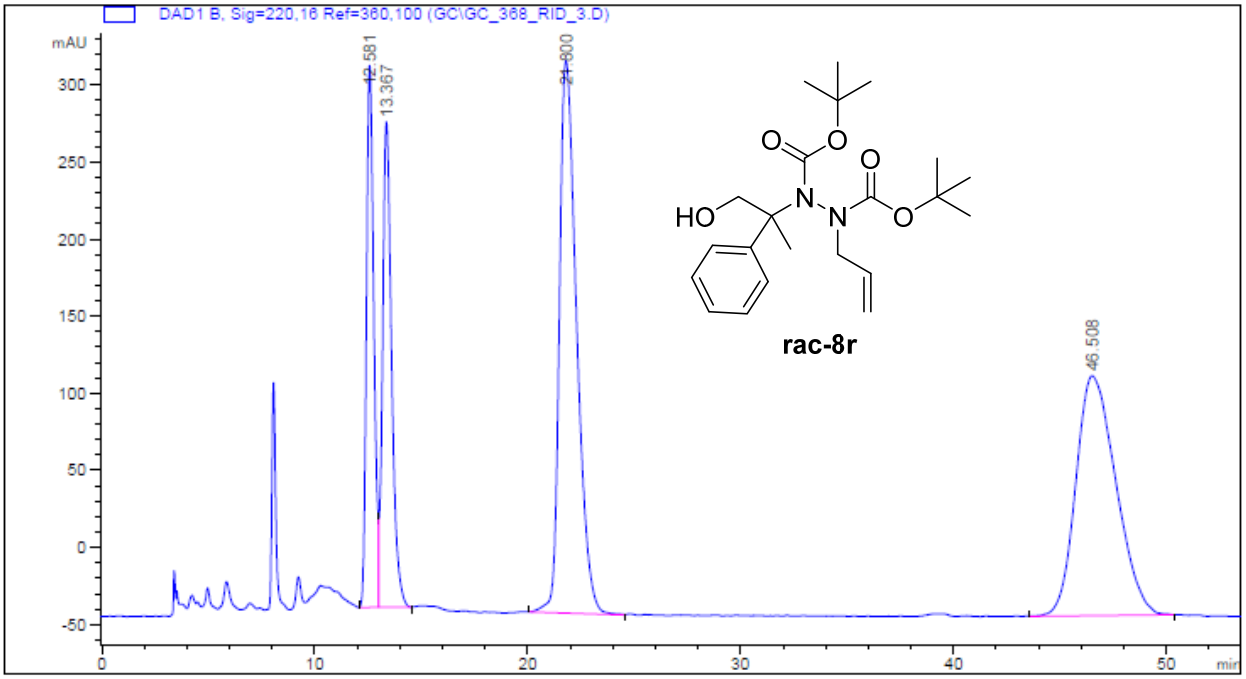


7

```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  16.033 BB    0.7152  556.44891   12.65098  13.5177
   2  39.817 BB    1.4642 3560.00342   32.39307  86.4823

Totals :                  4116.45233   45.04405
```

Data File C:\CHEM32\1\DATA\GC\GC_368_RID_3.D
Sample Name: GC_368_rid

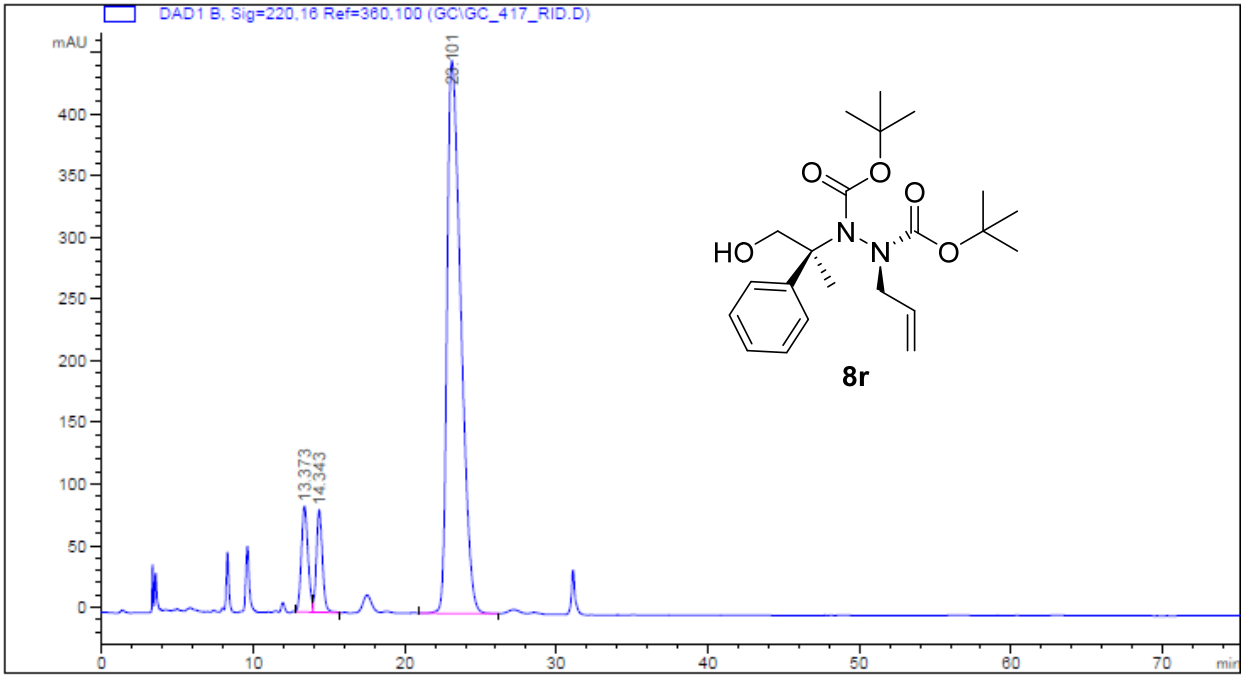
```
==========================================================================
Acq. Operator   : Giovanni
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date  : 22/03/2022 17:31:10
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 22/03/2022 17:06:28 by Giovanni
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 03/05/2022 10:51:32 by Chiara
                  (modified after loading)
Sample Info     : GC_368_rid, 1 mL/min, 97.5:2.5 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.581 BV    0.3729 8461.94434  351.49106  14.5415
   2  13.367 VB    0.4481 9285.16797  314.79404  15.9561
   3  21.800 BV    0.8519 2.01369e4   358.18231  34.6044
   4  46.508 BB    1.8148 2.03078e4   155.58533  34.8980

Totals :                  5.81918e4  1180.05273
```

Data File H:\HPLC\1\DATA\GC\GC_417_RID.D
Sample Name: GC_417_rid

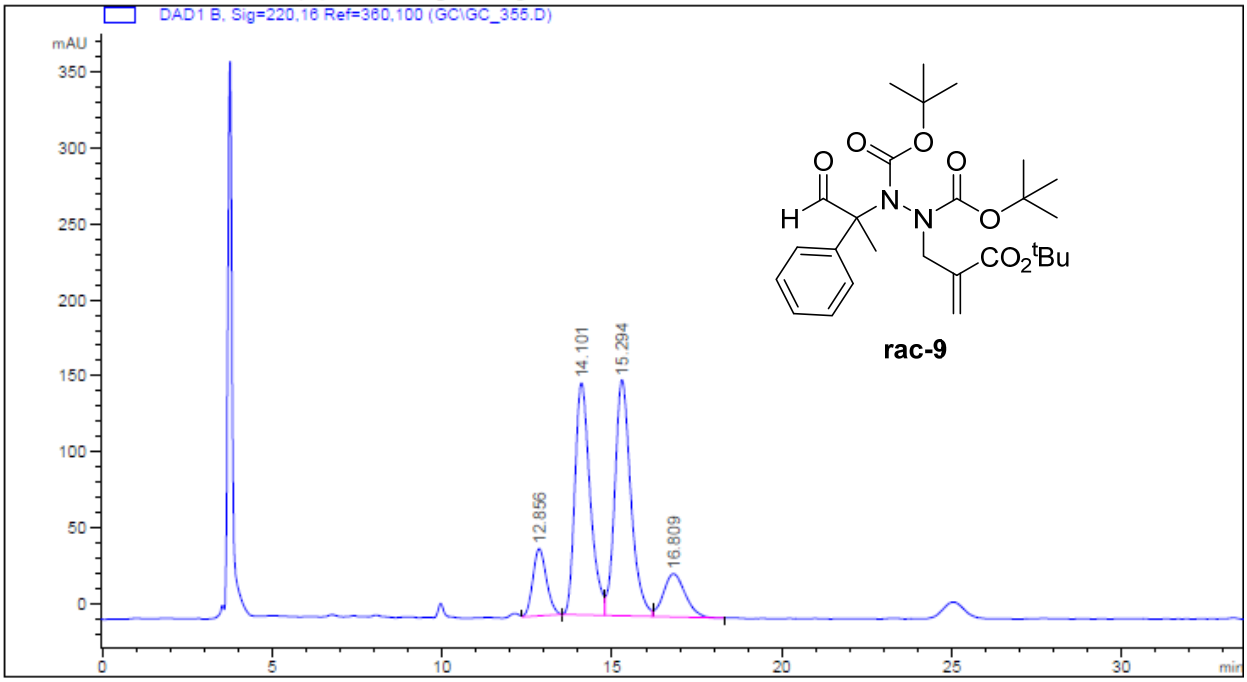
```
================================================================================
Acq. Operator   : Giovanni
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date  : 04/05/2022 12.55.12
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 04/05/2022 12.50.07 by Giovanni
                  (modified after loading)
Analysis Method : H:\HPLC\1\METHODS\DEF_LC.M
Last changed    : 21/05/2022 14.11.49
                  (modified after loading)
Sample Info     : GC_417_rid, 1 mL/min, 97.5:2.5 hex:ipr, 25°C, IA

Additional Info : Peak(s) manually integrated
```




```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.373 BV    0.4676 2614.81958   85.78152   7.8636
   2  14.343 VB    0.4280 2304.41504   82.99025   6.9301
   3  23.101 BB    0.9853 2.83329e4   448.30264  85.2063

Totals :                  3.32521e4   617.07441
```

Data File H:\HPLC\1\DATA\GC\GC_355.D
Sample Name: GC_355

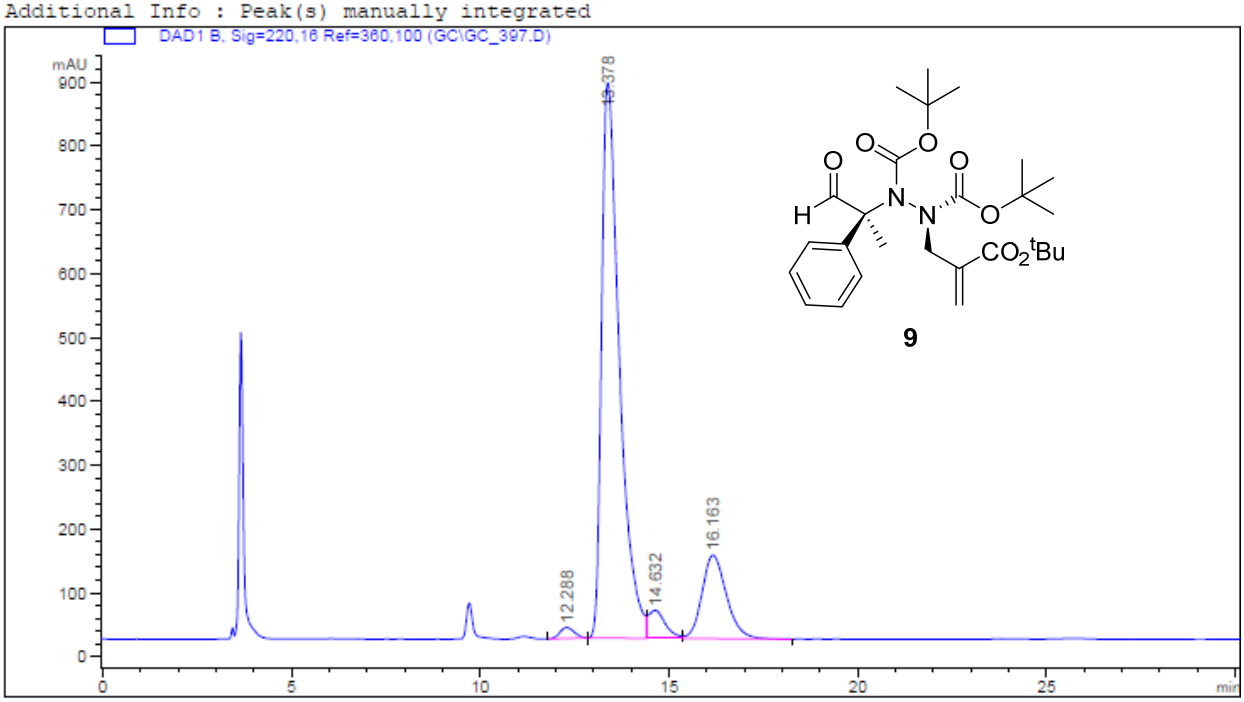
```
==========================================================================
Acq. Operator   : Giovanni
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date  : 17/12/2021 15.41.03
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 17/12/2021 14.54.51 by Giovanni
                  (modified after loading)
Analysis Method : H:\HPLC\1\METHODS\DEF_LC.M
Last changed    : 07/05/2022 14.10.49
                  (modified after loading)
Sample Info     : GC_355, 1 mL/min, 98:2 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.856 VB    0.4324 1228.60205   44.18421   9.9325
   2  14.101 BV    0.4758 4765.50781  152.84039  38.5261
   3  15.294 VV    0.4998 5114.30322  155.46941  41.3459
   4  16.809 VB    0.6908 1261.14856   28.36058  10.1956

Totals :                  1.23696e4   380.85459
```

Data File H:\HPLC\1\DATA\GC\GC_397.D
Sample Name: GC_397

```
======================================================================
Acq. Operator    : Giovanni
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date   : 11/03/2022 17.15.19
Acq. Method      : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 11/03/2022 17.10.50 by Giovanni
                   (modified after loading)
Analysis Method : H:\HPLC\1\METHODS\DEF_LC.M
Last changed     : 07/05/2022 14.10.49
                   (modified after loading)
Sample Info      : GC_397, 1 mL/min, 98:2 hex:ipr, 25°C, IC

Additional Info : Peak(s) manually integrated
```

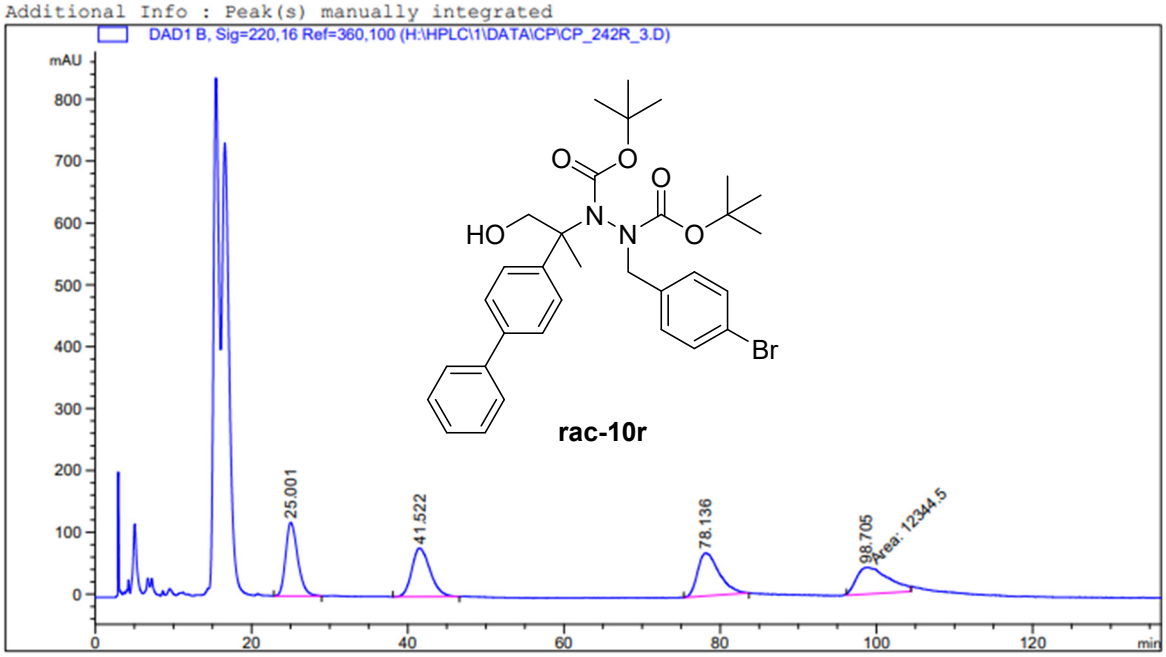


9

```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.288 BB    0.4159  454.48734   17.21891   1.2502
   2  13.378 BV    0.4958 2.86133e4   869.67395  78.7122
   3  14.632 VV    0.4677 1395.18188   43.79060   3.8380
   4  16.163 VB    0.6886 5888.84521  130.95662  16.1996

Totals :                  3.63518e4  1061.64008
```

Data File H:\HPLC\1\DATA\CP\CP_242R_3.D
Sample Name: CP_242R_3

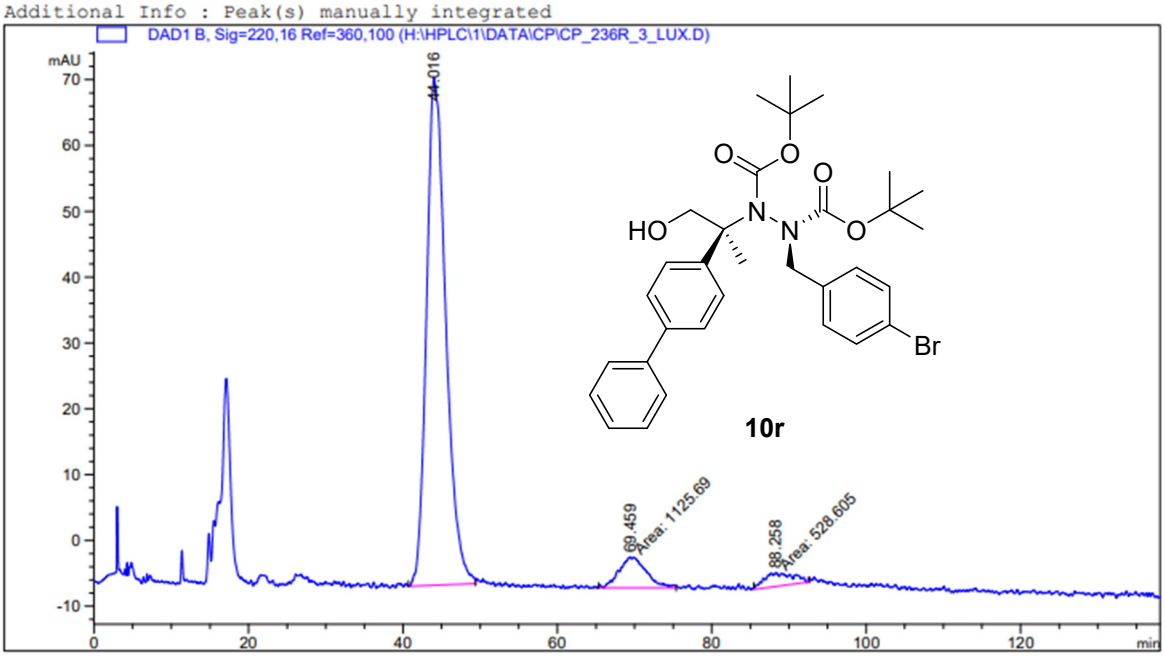
```
======================================================================
Acq. Operator   : Chiara
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date  : 17/05/2022 10:14:46
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 17/05/2022 09:44:18 by Chiara
                  (modified after loading)
Analysis Method : H:\HPLC\2\METHODS\DEF_LC.M
Last changed    : 01/06/2022 09:29:28
                  (modified after loading)
Sample Info     : CP_242R_3, pulito con colonna e ridotto, 1 mL/min, 98:2
                   hex:ipr, 25°C, Lux Cellulose

Additional Info : Peak(s) manually integrated
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  25.001 BB    1.6558 1.27946e4   118.86250  24.9910
   2  41.522 BB    2.1606 1.27472e4    78.33117  24.8982
   3  78.136 BB    2.3740 1.33108e4    69.32594  25.9991
   4  98.705 MM    4.7758 1.23445e4    43.07943  24.1117

Totals :                  5.11970e4   309.59903
```

Data File H:\HPLC\1\DATA\CP\CP_236R_3_LUX.D
Sample Name: CP_236R_3

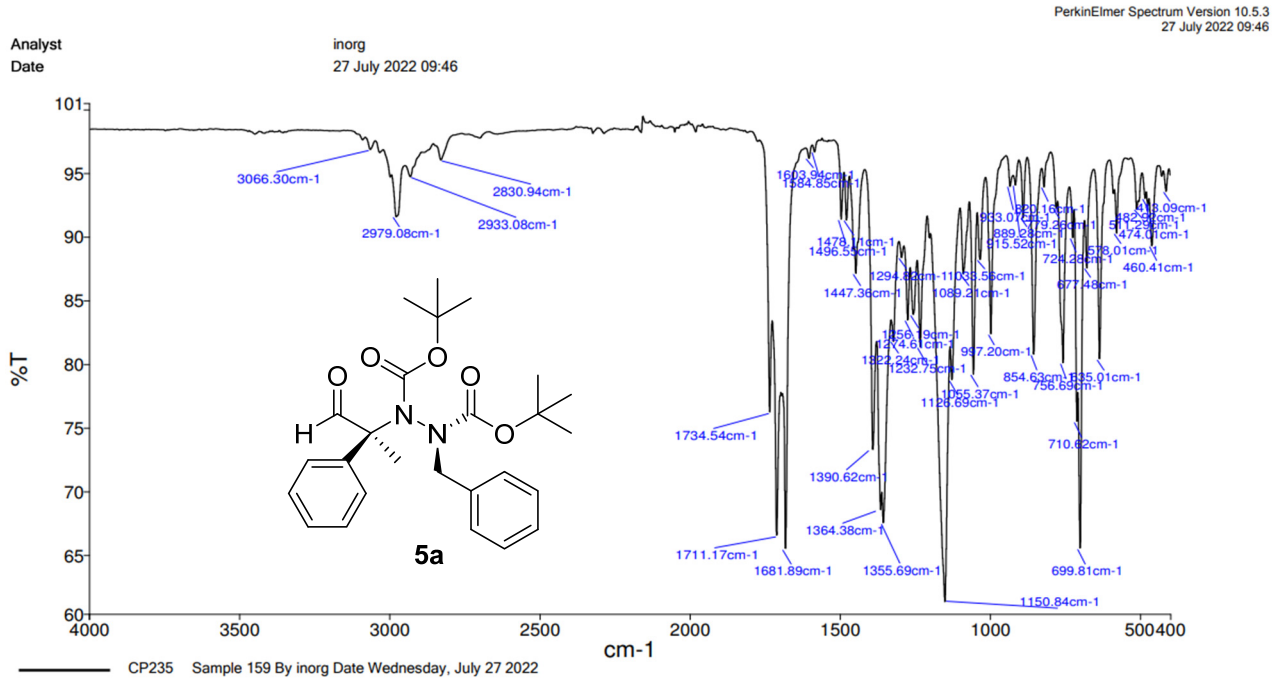
```
==========================================================================
Acq. Operator    : Chiara
Acq. Instrument : HPLC-1                          Location : Vial 1
Injection Date   : 17/05/2022 13:10:17
Acq. Method      : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed     : 17/05/2022 12:31:35 by Chiara
                   (modified after loading)
Analysis Method : H:\HPLC\2\METHODS\DEF_LC.M
Last changed     : 01/06/2022 09:31:13
                   (modified after loading)
Sample Info      : CP_236R_3, 1 mL/min, 98:2 hex:ipr, 25°C, Lux Cellulose

Additional Info : Peak(s) manually integrated
```

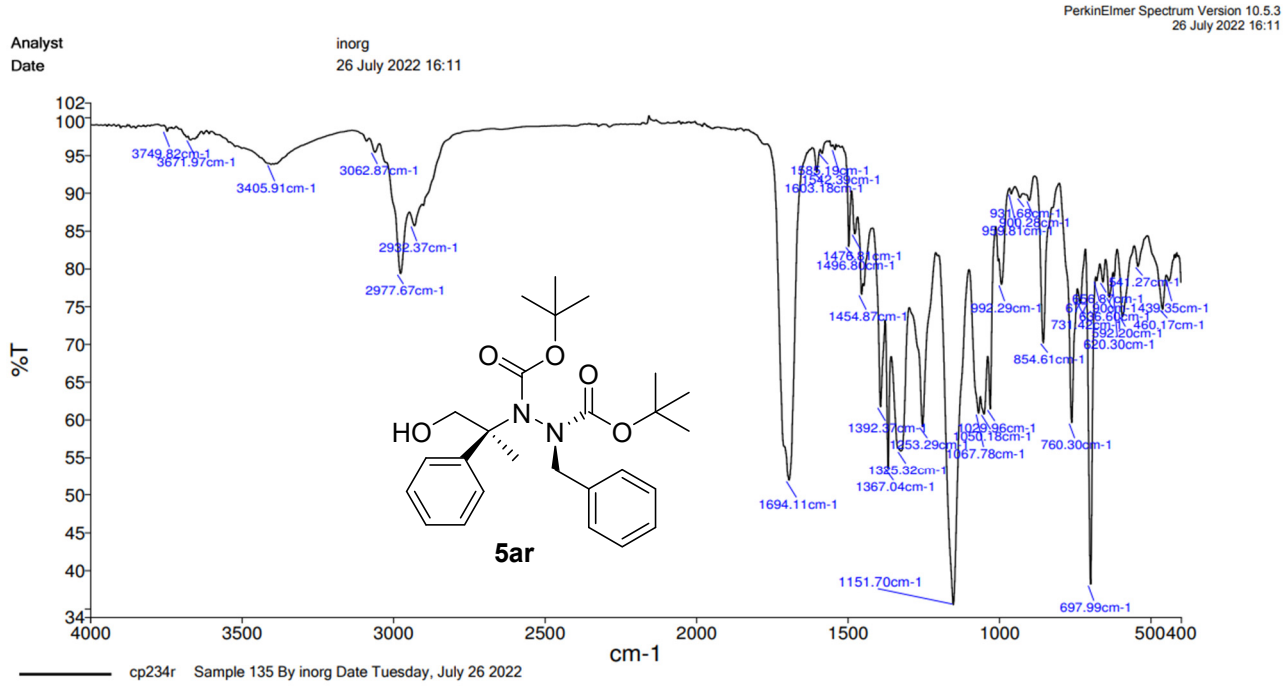


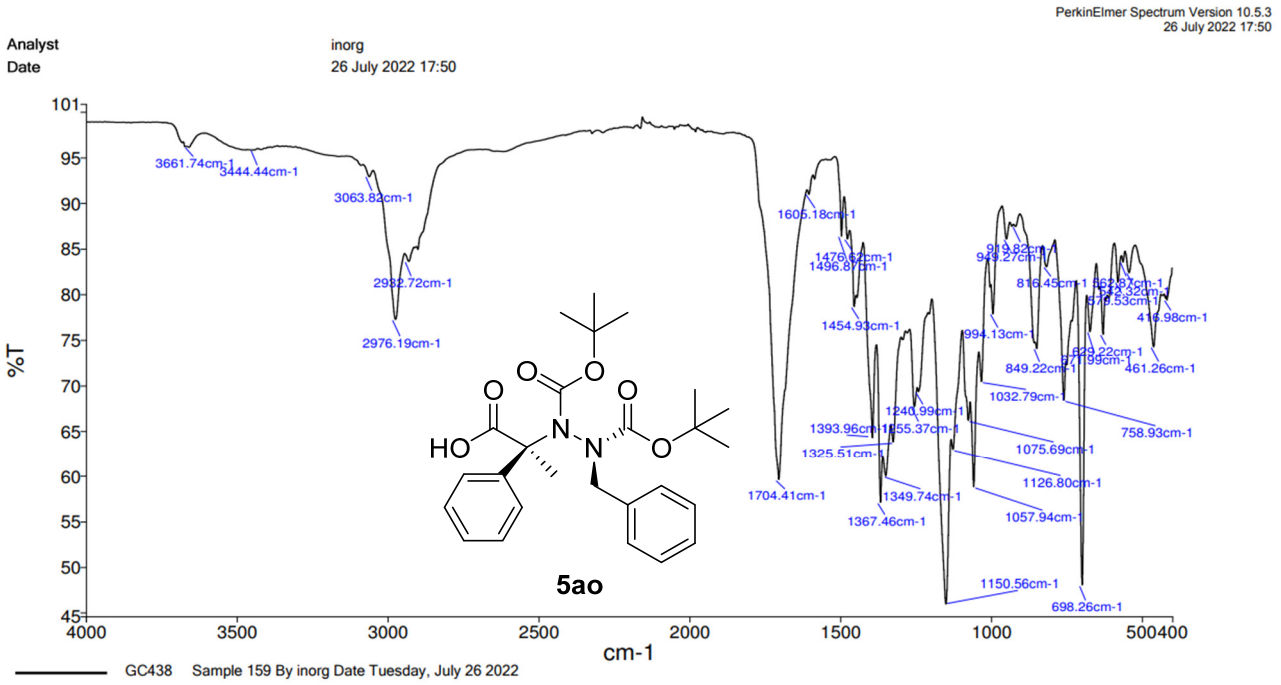

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  44.016 BV    2.2391 1.33638e4    77.06377  88.9847
   2  69.459 MM    4.0484 1125.68591    4.63424   7.4955
   3  88.258 MM    4.2324  528.60461    2.08156   3.5198

Totals :                  1.50181e4    83.77956
```

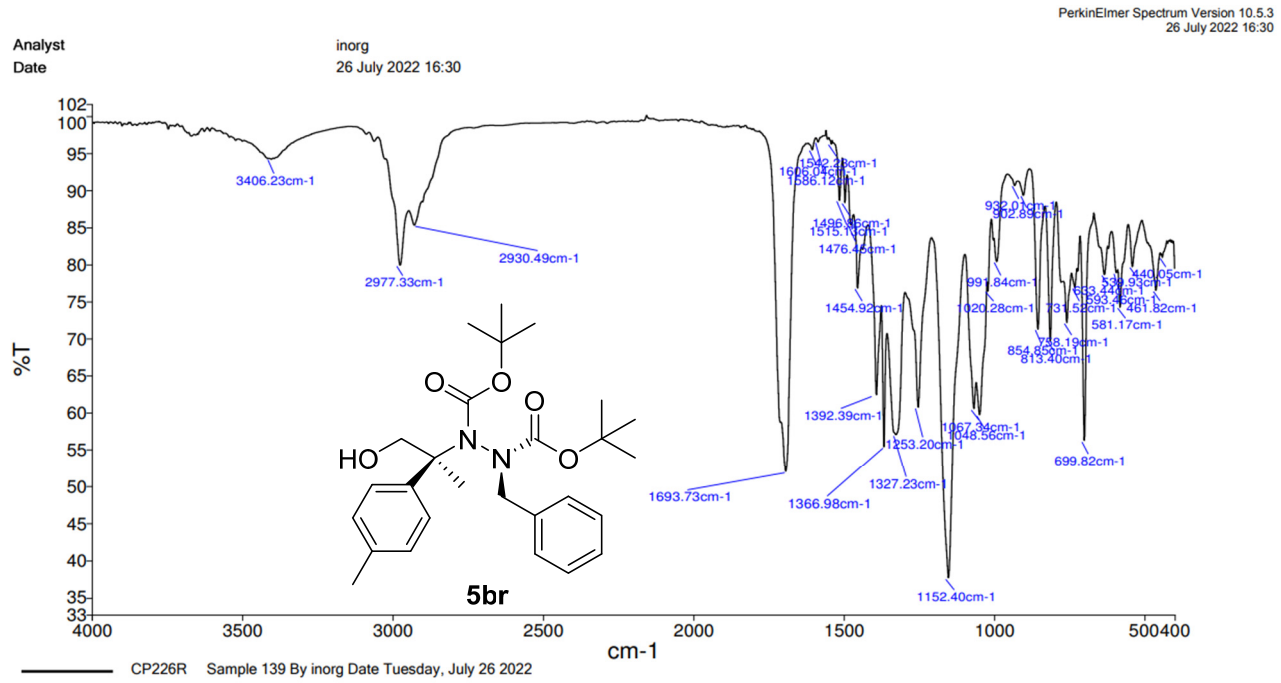
IR traces

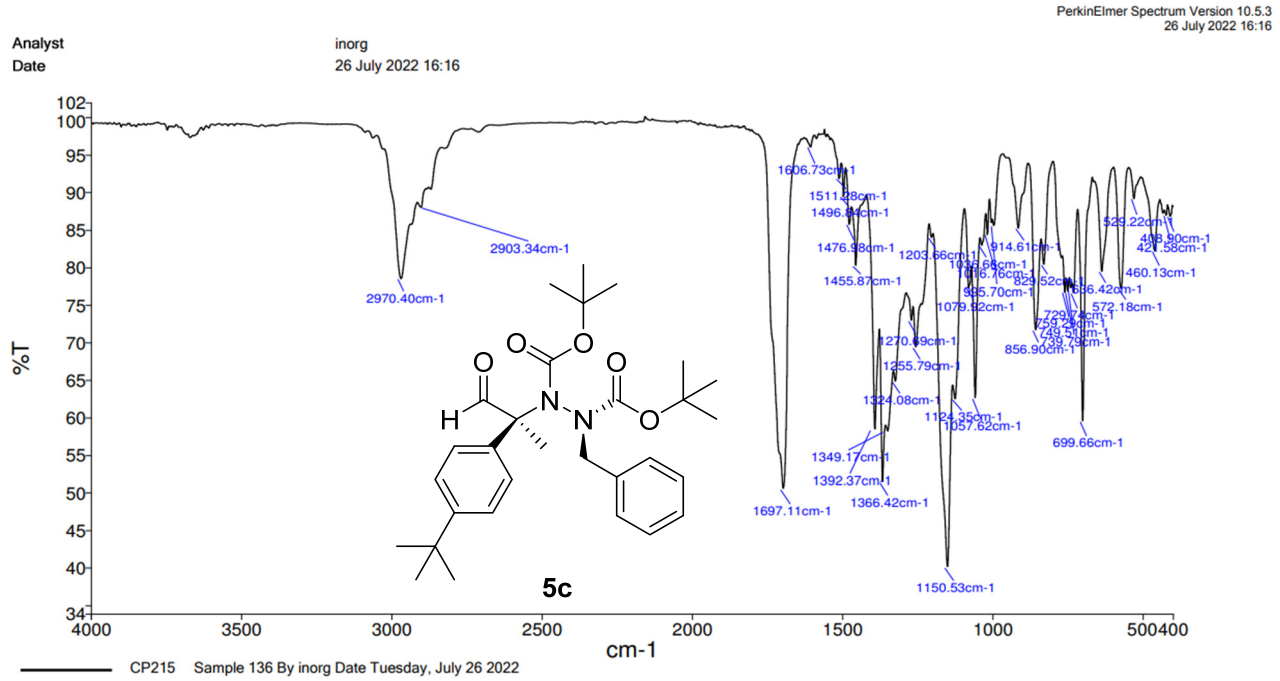
5a

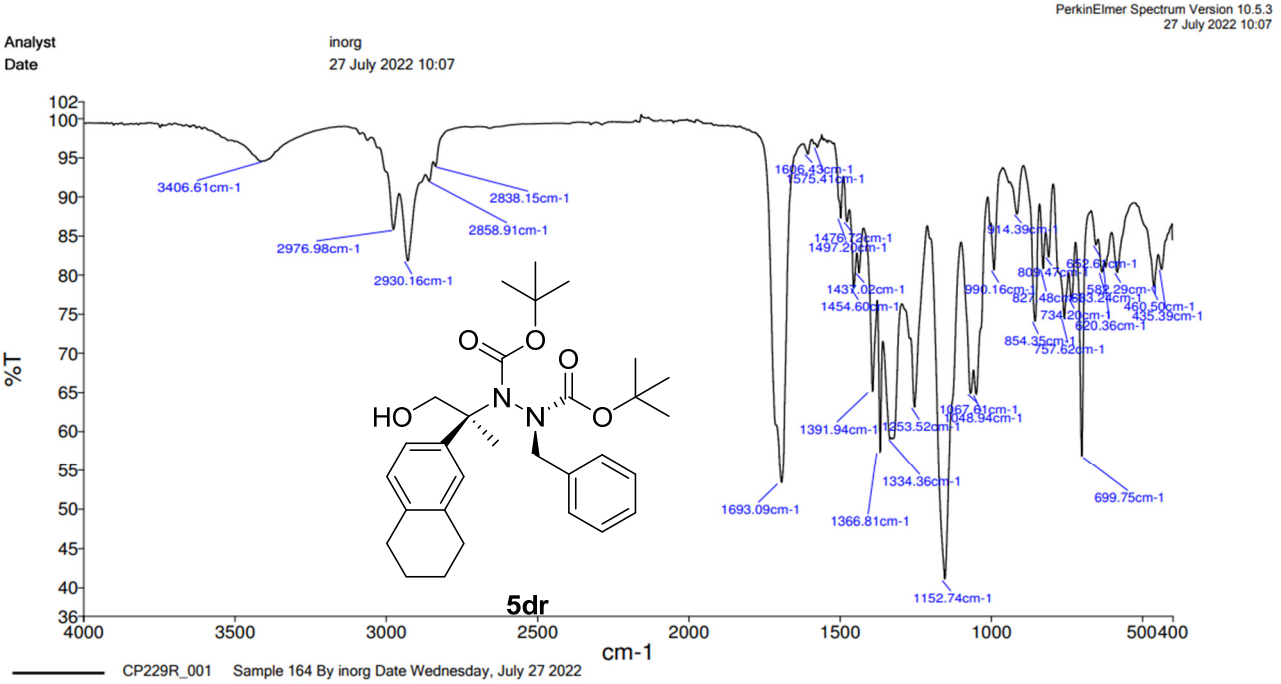

PerkinElmer Spectrum Version 10.5.3
27 July 2022 09:46
Analyst
inorg
Date
27 July 2022 09:46
%T
cm-1
3066.30cm-1
2979.08cm-1
2933.08cm-1
2830.94cm-1
1734.54cm-1
1711.17cm-1
1681.89cm-1
1390.62cm-1
1364.38cm-1
1355.69cm-1
1150.84cm-1
699.81cm-1
710.62cm-1
5a
CP235 Sample 159 By inorg Date Wednesday, July 27 2022

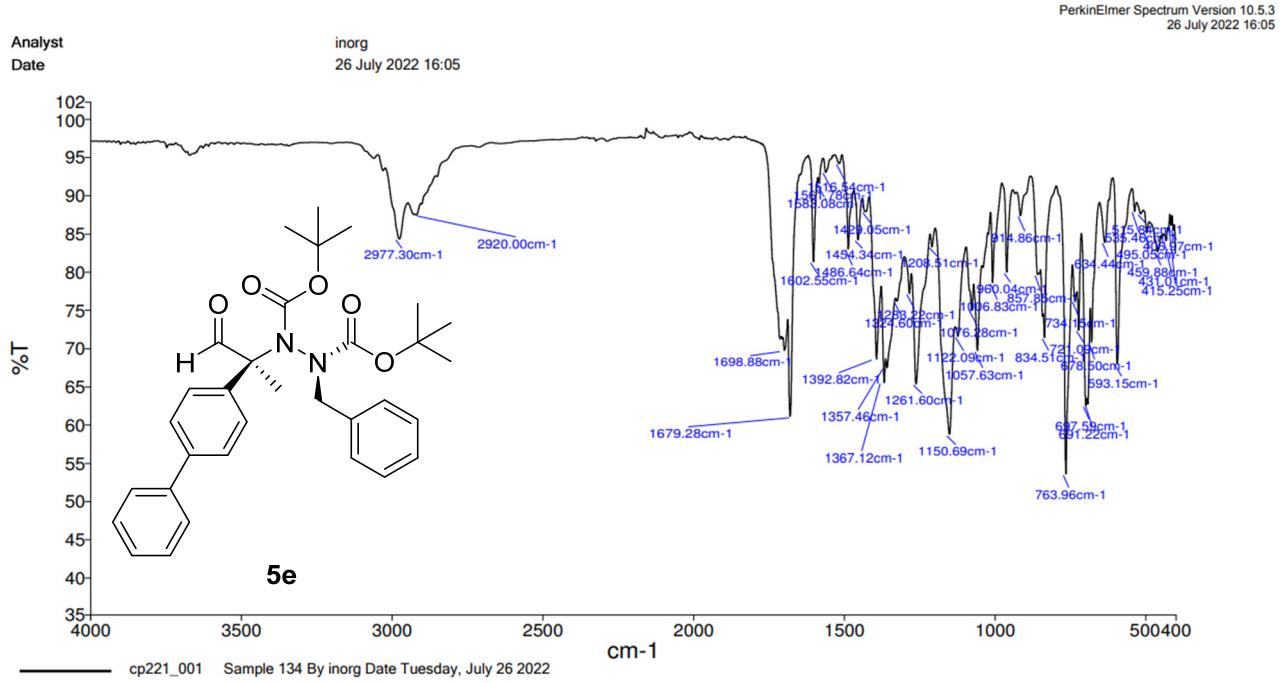

PerkinElmer Spectrum Version 10.5.3
26 July 2022 16:11
Analyst
inorg
Date
26 July 2022 16:11
%T
cm-1
3749.82cm-1
3671.97cm-1
3405.91cm-1
3062.87cm-1
2977.67cm-1
1694.11cm-1
1454.87cm-1
1392.37cm-1
1367.04cm-1
1325.32cm-1
1151.70cm-1
854.61cm-1
760.30cm-1
697.99cm-1
5ar
cp234r Sample 135 By inorg Date Tuesday, July 26 2022

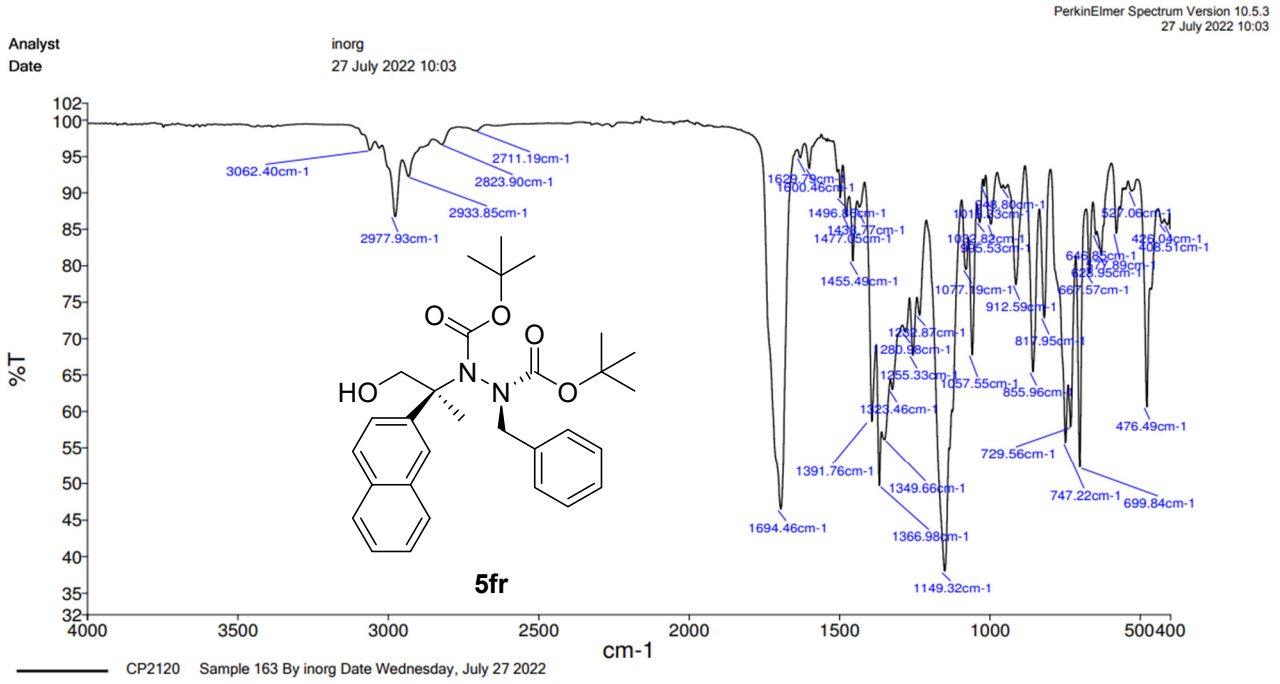

PerkinElmer Spectrum Version 10.5.3
26 July 2022 17:50
Analyst
inorg
Date
26 July 2022 17:50
%T
cm-1
3661.74cm-1
3444.44cm-1
3063.82cm-1
2932.72cm-1
2976.19cm-1
1605.18cm-1
1704.41cm-1
1454.93cm-1
1393.96cm-1
1325.51cm-1
1240.99cm-1
1155.37cm-1
1032.79cm-1
994.13cm-1
849.22cm-1
758.93cm-1
698.26cm-1
1150.56cm-1
1126.80cm-1
1075.69cm-1
1057.94cm-1
1367.46cm-1
1349.74cm-1
461.26cm-1
HO
O
N
5ao
GC438 Sample 159 By inorg Date Tuesday, July 26 2022

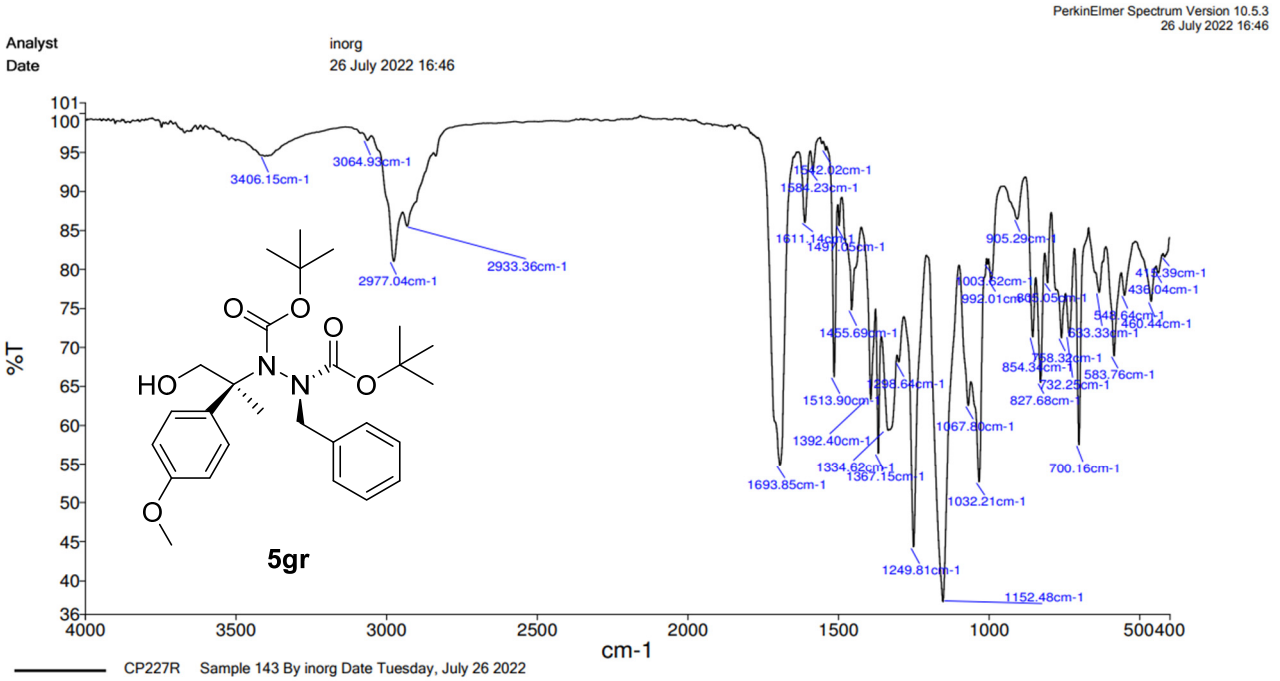

PerkinElmer Spectrum Version 10.5.3
26 July 2022 16:30
Analyst
inorg
Date
26 July 2022 16:30
%T
cm-1
3406.23cm-1
2977.33cm-1
2930.49cm-1
1693.73cm-1
1454.92cm-1
1392.39cm-1
1366.98cm-1
1327.23cm-1
1253.20cm-1
1152.40cm-1
1067.34cm-1
1048.56cm-1
1020.28cm-1
991.84cm-1
854.85cm-1
813.40cm-1
699.82cm-1
581.17cm-1
461.82cm-1
HO
O
N
5br
CP226R Sample 139 By inorg Date Tuesday, July 26 2022

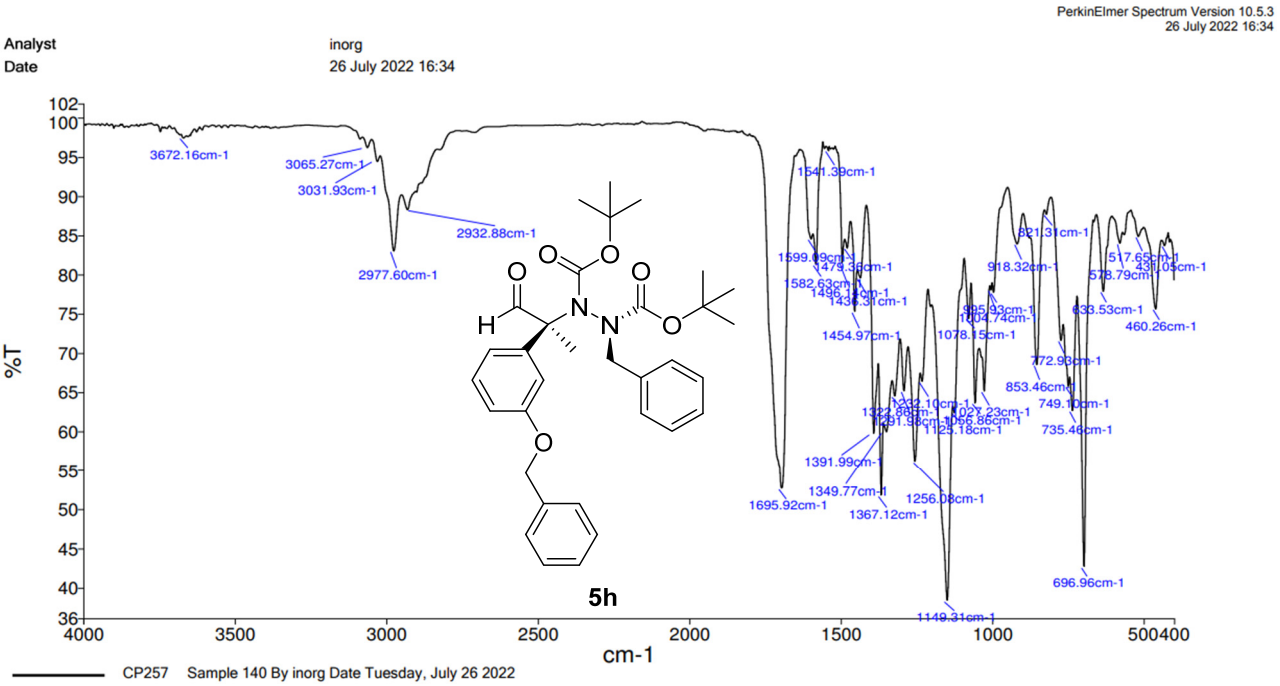

PerkinElmer Spectrum Version 10.5.3
26 July 2022 16:16
Analyst inorg
Date 26 July 2022 16:16
%T
cm-1
2970.40cm-1
2903.34cm-1
1697.11cm-1
1606.73cm-1
1511.08cm-1
1496.84cm-1
1476.98cm-1
1455.87cm-1
1349.17cm-1
1392.37cm-1
1366.42cm-1
1324.08cm-1
1270.09cm-1
1255.79cm-1
1203.66cm-1
1150.53cm-1
1124.35cm-1
1079.82cm-1
1057.62cm-1
995.70cm-1
914.61cm-1
856.90cm-1
699.66cm-1
572.18cm-1
460.13cm-1
5c
CP215 Sample 136 By inorg Date Tuesday, July 26 2022

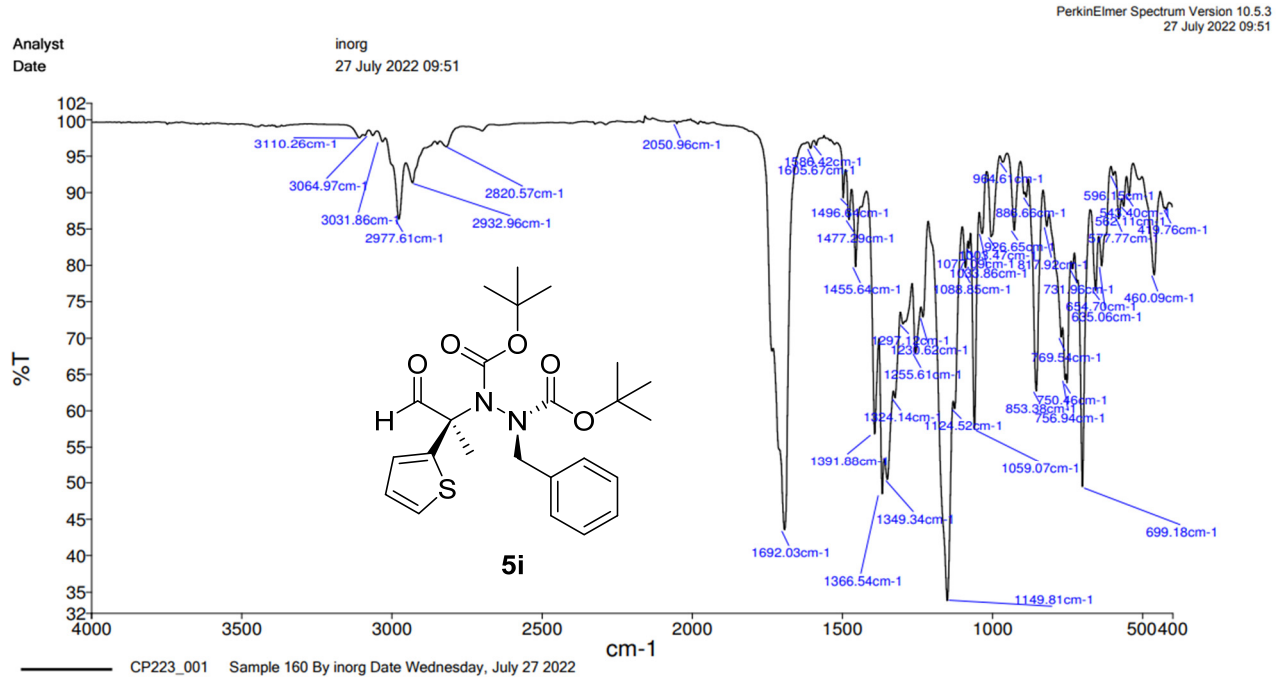

PerkinElmer Spectrum Version 10.5.3
27 July 2022 10:07
Analyst inorg
Date 27 July 2022 10:07
%T
cm-1
3406.61cm-1
2976.98cm-1
2930.16cm-1
2858.15cm-1
2838.91cm-1
1693.09cm-1
1606.43cm-1
1575.41cm-1
1497.20cm-1
1476.73cm-1
1454.60cm-1
1437.02cm-1
1391.94cm-1
1366.81cm-1
1353.52cm-1
1334.36cm-1
1152.74cm-1
1067.81cm-1
1048.94cm-1
990.16cm-1
914.39cm-1
854.35cm-1
757.62cm-1
699.75cm-1
5dr
CP229R_001 Sample 164 By inorg Date Wednesday, July 27 2022

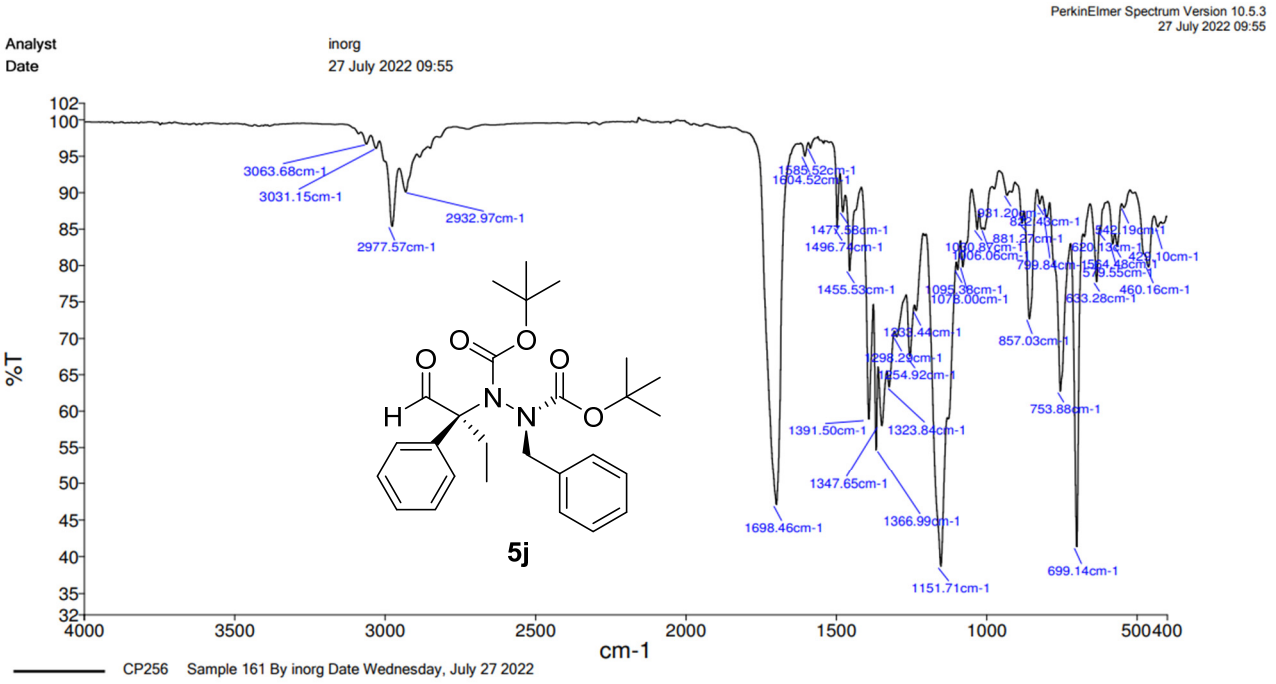

PerkinElmer Spectrum Version 10.5.3
26 July 2022 16:05
Analyst
inorg
Date
26 July 2022 16:05
%T
cm-1
2977.30cm-1
2920.00cm-1
1698.88cm-1
1679.28cm-1
1602.55cm-1
1486.64cm-1
1454.34cm-1
1429.05cm-1
1392.82cm-1
1357.46cm-1
1367.12cm-1
1261.60cm-1
1150.69cm-1
1122.09cm-1
1057.63cm-1
763.96cm-1
5e
cp221_001 Sample 134 By inorg Date Tuesday, July 26 2022

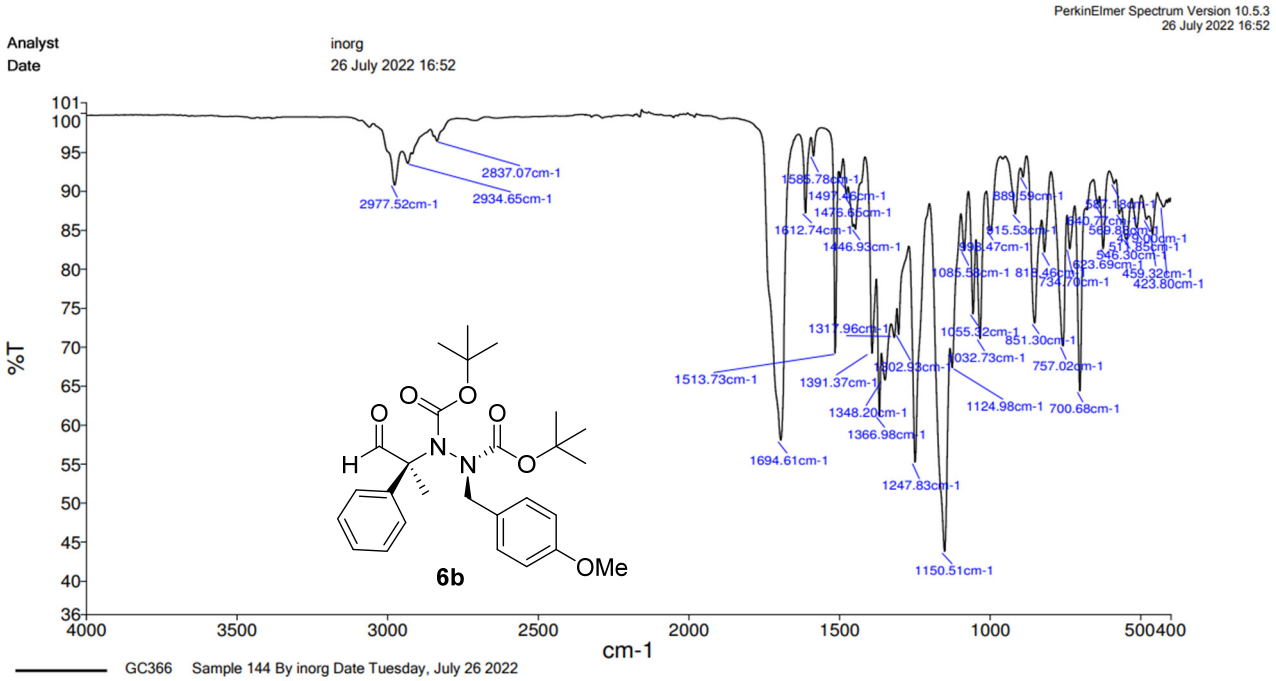

PerkinElmer Spectrum Version 10.5.3
27 July 2022 10:03
Analyst
inorg
Date
27 July 2022 10:03
%T
cm-1
3062.40cm-1
2977.93cm-1
2933.85cm-1
2823.90cm-1
2711.19cm-1
1694.46cm-1
1600.46cm-1
1455.49cm-1
1391.76cm-1
1366.98cm-1
1349.66cm-1
1323.46cm-1
1280.98cm-1
1255.33cm-1
1149.32cm-1
1077.19cm-1
1057.55cm-1
912.59cm-1
855.96cm-1
817.95cm-1
747.22cm-1
729.56cm-1
699.84cm-1
667.57cm-1
476.49cm-1
5fr
CP2120 Sample 163 By inorg Date Wednesday, July 27 2022

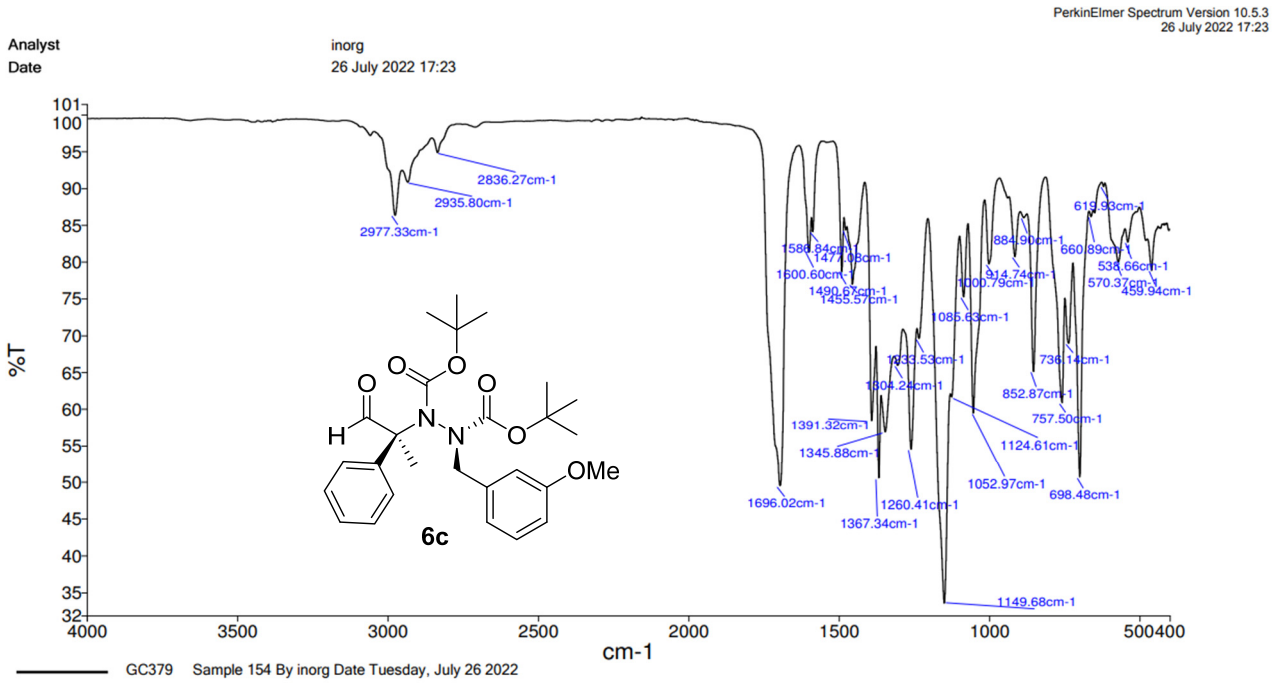

PerkinElmer Spectrum Version 10.5.3
26 July 2022 16:46
Analyst
inorg
Date
26 July 2022 16:46
%T
cm-1
3406.15cm-1
3064.93cm-1
2977.04cm-1
2933.36cm-1
1693.85cm-1
1513.90cm-1
1392.40cm-1
1249.81cm-1
1152.48cm-1
1032.21cm-1
700.16cm-1
5gr
CP227R Sample 143 By inorg Date Tuesday, July 26 2022

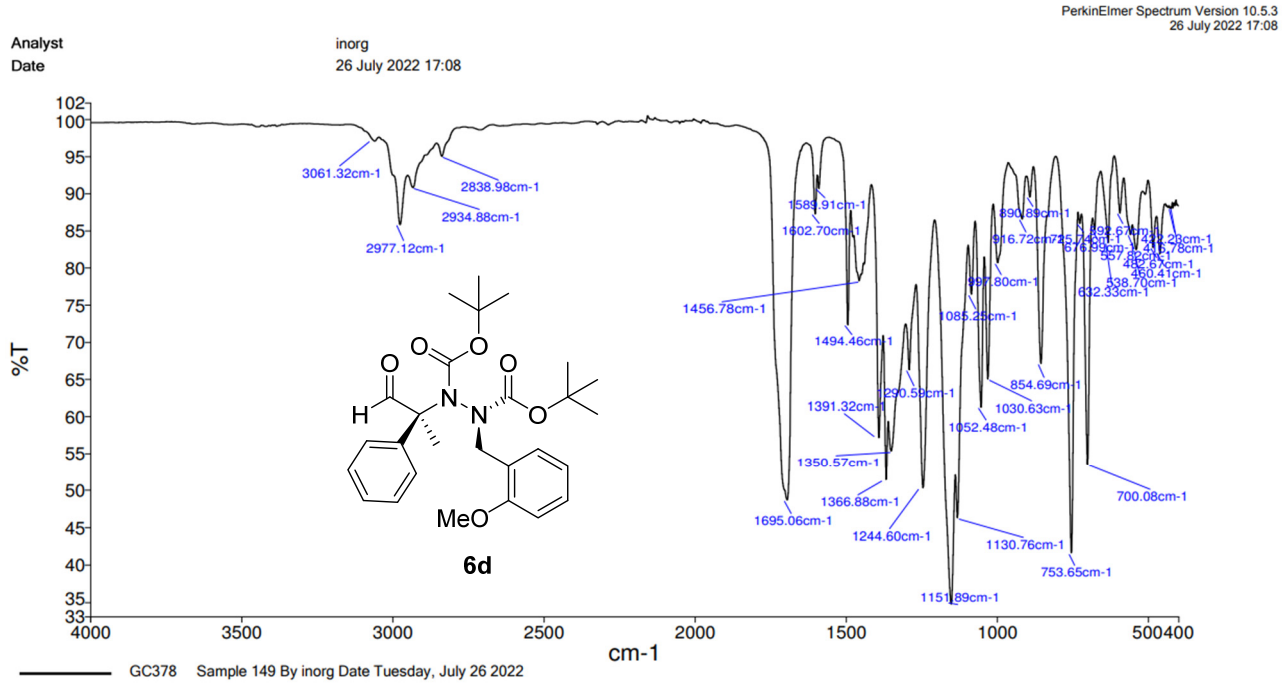

PerkinElmer Spectrum Version 10.5.3
26 July 2022 16:34
Analyst
inorg
Date
26 July 2022 16:34
%T
cm-1
3672.16cm-1
3065.27cm-1
3031.93cm-1
2977.60cm-1
2932.88cm-1
1695.92cm-1
1541.39cm-1
1454.97cm-1
1391.99cm-1
1349.77cm-1
1367.12cm-1
1256.08cm-1
1149.31cm-1
1078.15cm-1
696.96cm-1
5h
CP257 Sample 140 By inorg Date Tuesday, July 26 2022

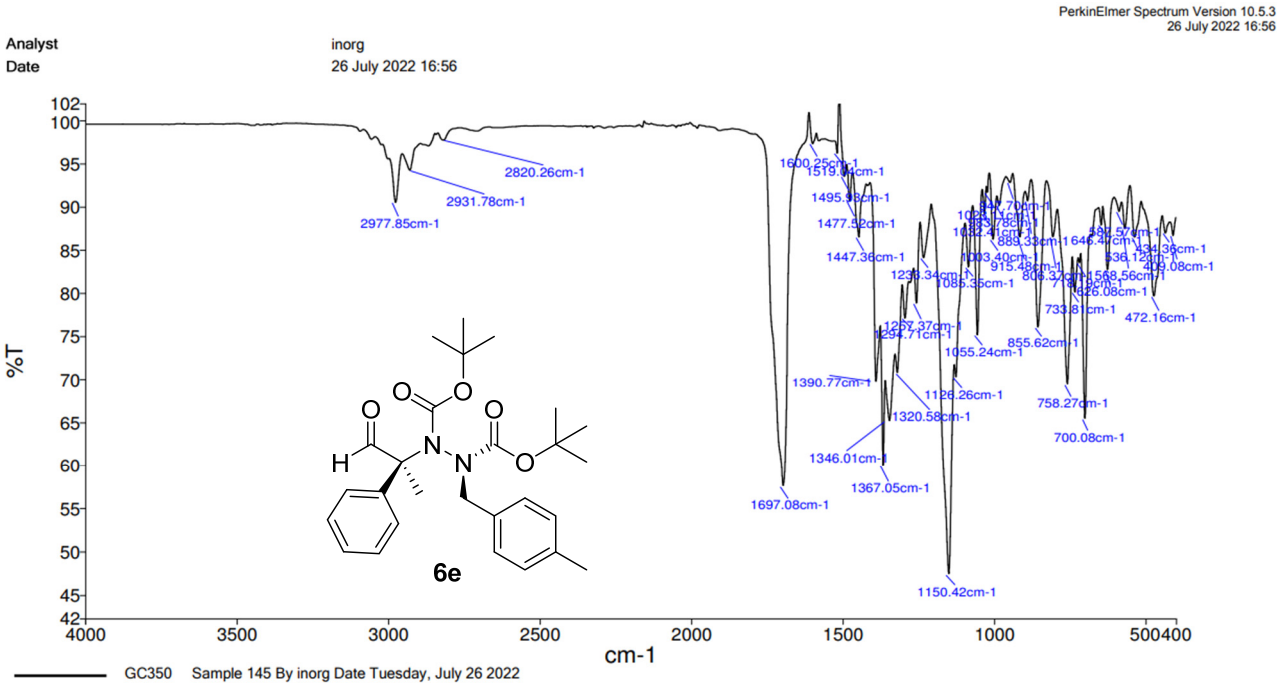

PerkinElmer Spectrum Version 10.5.3
27 July 2022 09:51
Analyst
Date
inorg
27 July 2022 09:51
%T
cm-1
3110.26cm-1
3064.97cm-1
3031.86cm-1
2977.61cm-1
2932.96cm-1
2820.57cm-1
2050.96cm-1
1692.03cm-1
1366.54cm-1
1149.81cm-1
1059.07cm-1
699.18cm-1
5i
CP223_001 Sample 160 By inorg Date Wednesday, July 27 2022

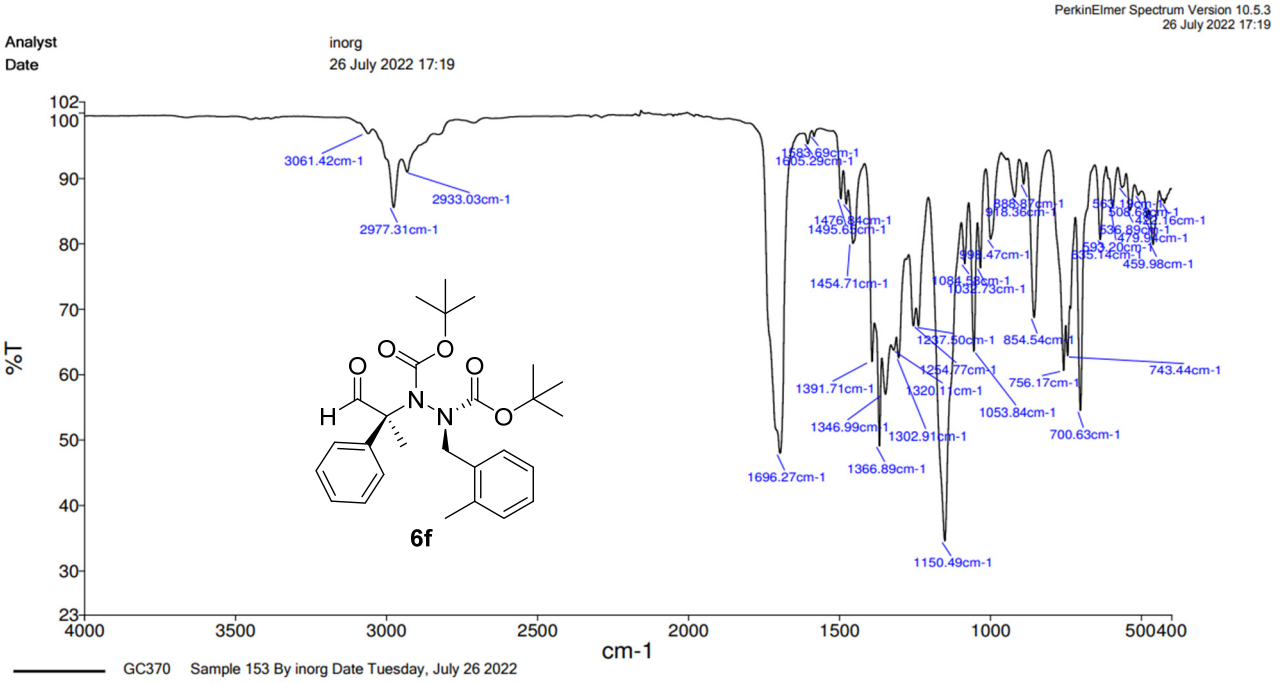

PerkinElmer Spectrum Version 10.5.3
27 July 2022 09:55
Analyst
Date
inorg
27 July 2022 09:55
%T
cm-1
3063.68cm-1
3031.15cm-1
2977.57cm-1
2932.97cm-1
1698.46cm-1
1391.50cm-1
1347.65cm-1
1323.84cm-1
1366.99cm-1
1151.71cm-1
857.03cm-1
753.88cm-1
699.14cm-1
5j
CP256 Sample 161 By inorg Date Wednesday, July 27 2022

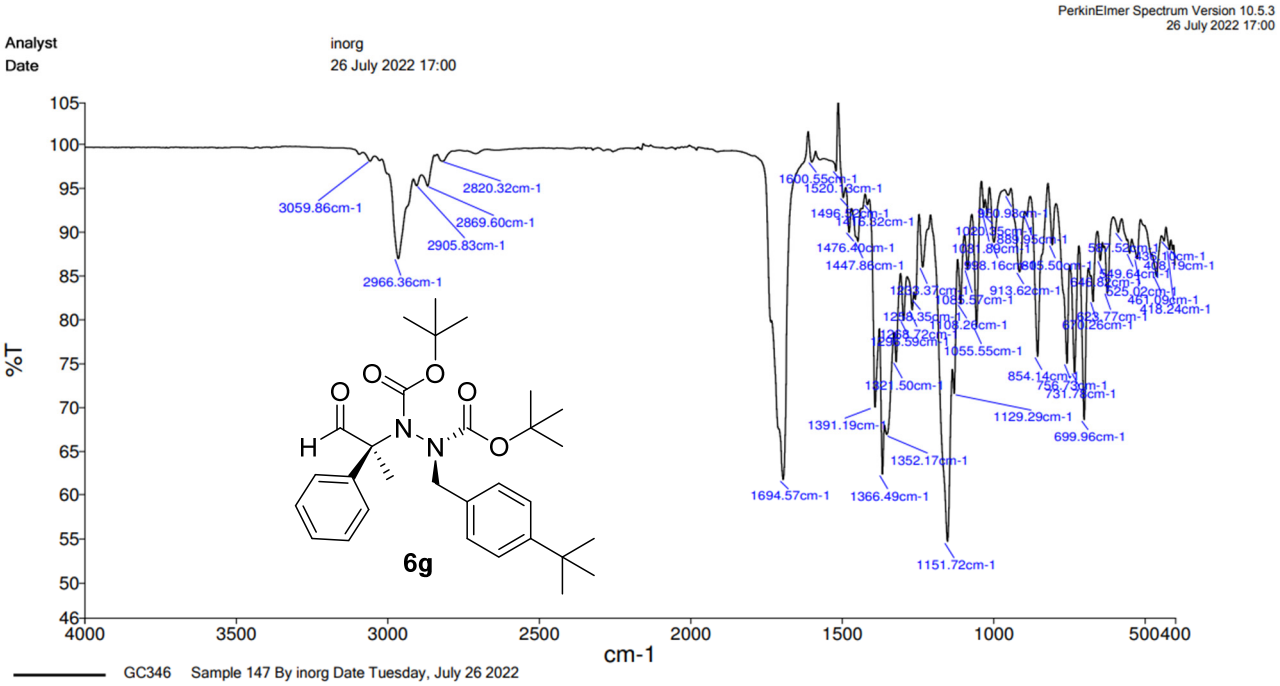

PerkinElmer Spectrum Version 10.5.3
26 July 2022 16:52
Analyst
inorg
Date
26 July 2022 16:52
%T
cm-1
2977.52cm-1
2934.65cm-1
2837.07cm-1
1694.61cm-1
1513.73cm-1
1391.37cm-1
1348.20cm-1
1366.98cm-1
1247.83cm-1
1150.51cm-1
1124.98cm-1
700.68cm-1
757.02cm-1
OMe
6b
GC366 Sample 144 By inorg Date Tuesday, July 26 2022

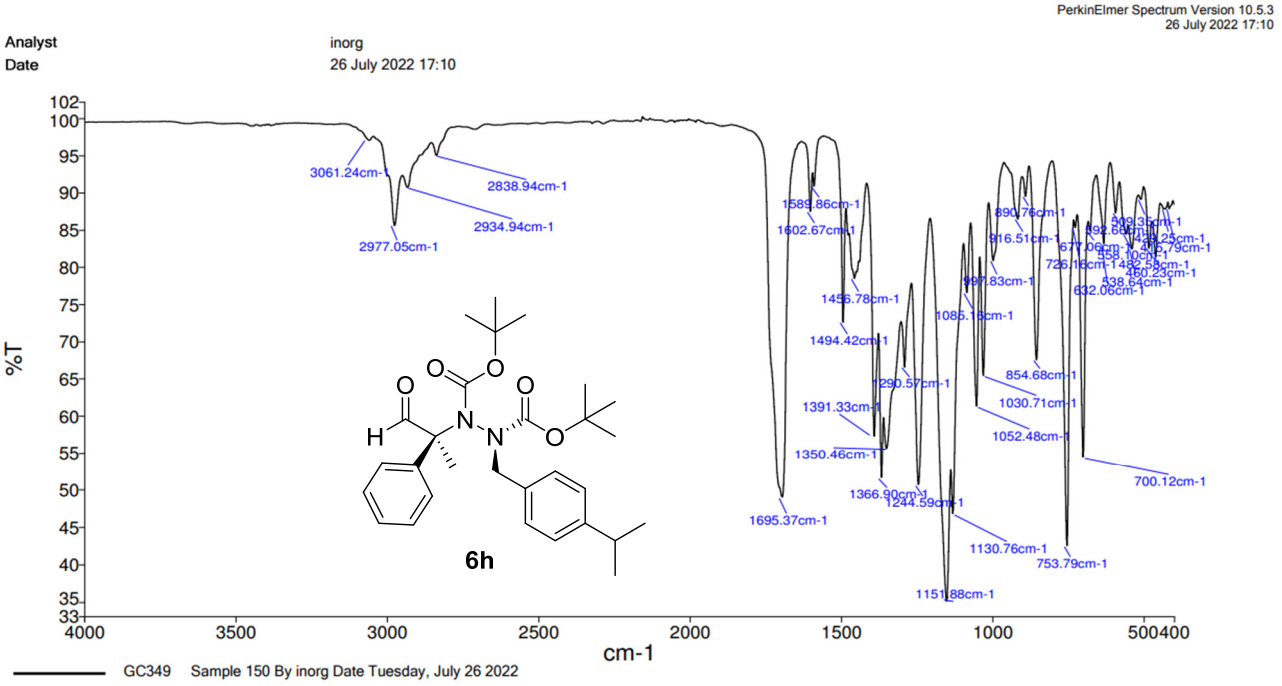

PerkinElmer Spectrum Version 10.5.3
26 July 2022 17:23
Analyst
inorg
Date
26 July 2022 17:23
%T
cm-1
2977.33cm-1
2935.80cm-1
2836.27cm-1
1696.02cm-1
1391.32cm-1
1345.88cm-1
1367.34cm-1
1260.41cm-1
1149.68cm-1
1124.61cm-1
1052.97cm-1
757.50cm-1
852.87cm-1
698.48cm-1
OMe
6c
GC379 Sample 154 By inorg Date Tuesday, July 26 2022

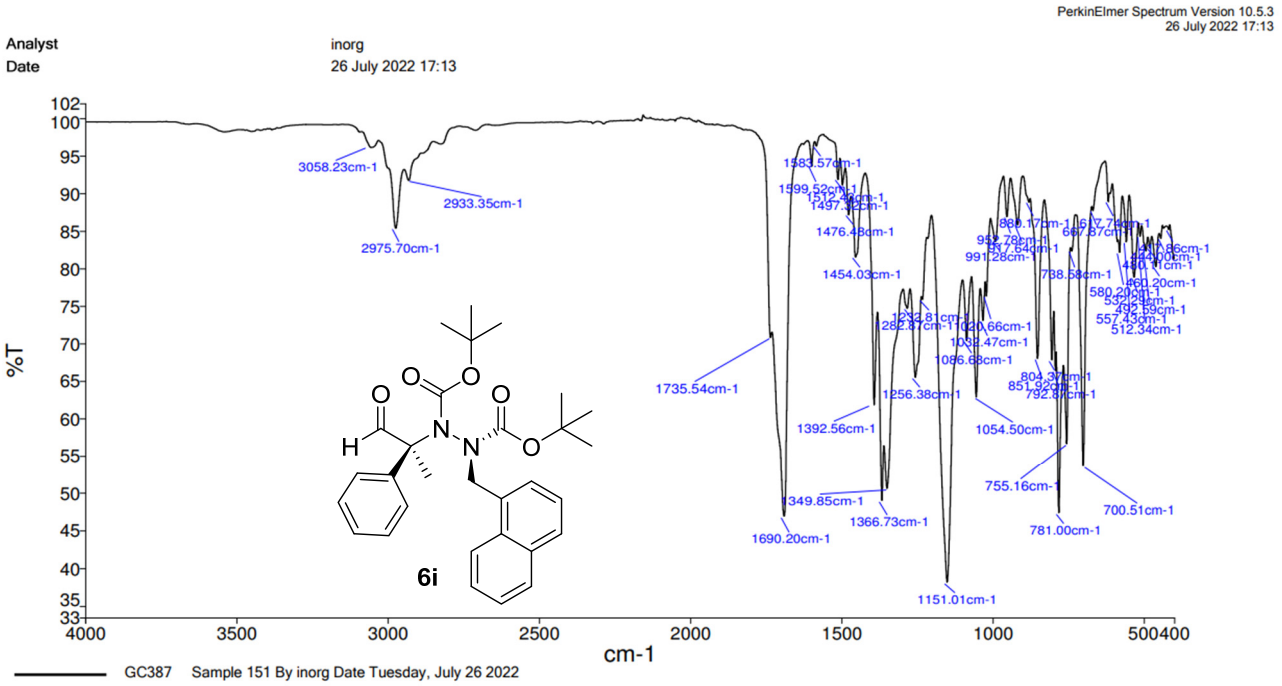

PerkinElmer Spectrum Version 10.5.3
26 July 2022 17:08
Analyst
inorg
Date
26 July 2022 17:08
%T
cm-1
3061.32cm-1
2838.98cm-1
2934.88cm-1
2977.12cm-1
1589.91cm-1
1602.70cm-1
1456.78cm-1
1494.46cm-1
1391.32cm-1
1350.57cm-1
1366.88cm-1
1695.06cm-1
1244.60cm-1
1290.59cm-1
1085.25cm-1
1151.89cm-1
1130.76cm-1
1052.48cm-1
1030.63cm-1
854.69cm-1
753.65cm-1
700.08cm-1
538.70cm-1
632.33cm-1
MeO
6d
GC378 Sample 149 By inorg Date Tuesday, July 26 2022

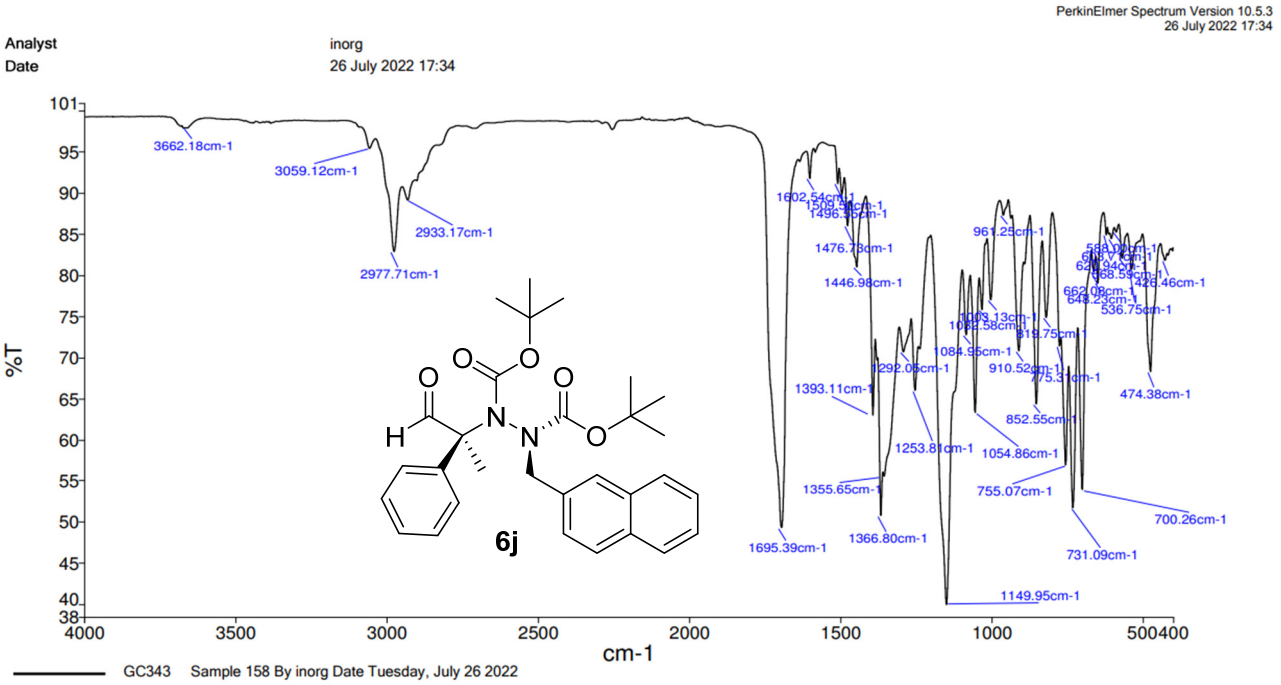

PerkinElmer Spectrum Version 10.5.3
26 July 2022 16:56
Analyst
inorg
Date
26 July 2022 16:56
%T
cm-1
2820.26cm-1
2931.78cm-1
2977.85cm-1
1600.25cm-1
1519.91cm-1
1495.93cm-1
1477.52cm-1
1447.36cm-1
1390.77cm-1
1320.58cm-1
1346.01cm-1
1367.05cm-1
1697.08cm-1
1150.42cm-1
1126.26cm-1
1055.24cm-1
1085.35cm-1
855.62cm-1
758.27cm-1
700.08cm-1
733.81cm-1
472.16cm-1
6e
GC350 Sample 145 By inorg Date Tuesday, July 26 2022

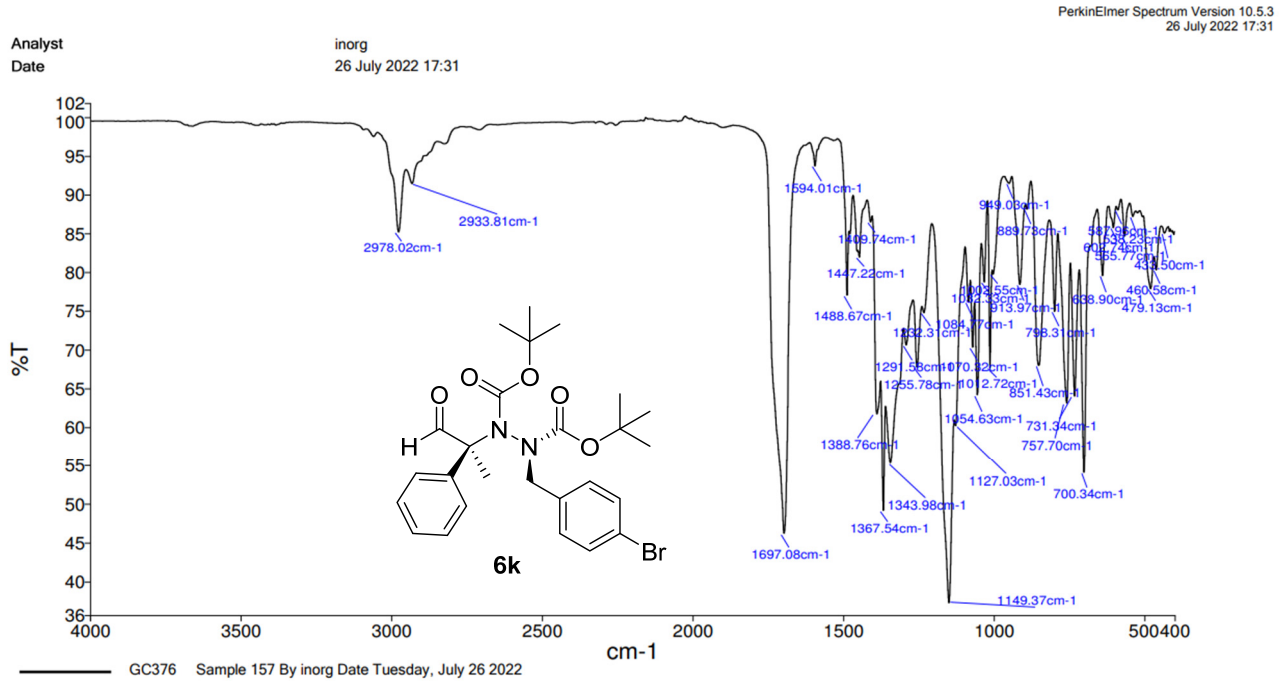

PerkinElmer Spectrum Version 10.5.3
26 July 2022 17:19
Analyst
inorg
Date
26 July 2022 17:19
%T
cm-1
3061.42cm-1
2977.31cm-1
2933.03cm-1
1696.27cm-1
1454.71cm-1
1391.71cm-1
1346.99cm-1
1366.89cm-1
1302.91cm-1
1150.49cm-1
1237.50cm-1
1254.77cm-1
1320.11cm-1
1053.84cm-1
854.54cm-1
756.17cm-1
743.44cm-1
700.63cm-1
6f
GC370 Sample 153 By inorg Date Tuesday, July 26 2022

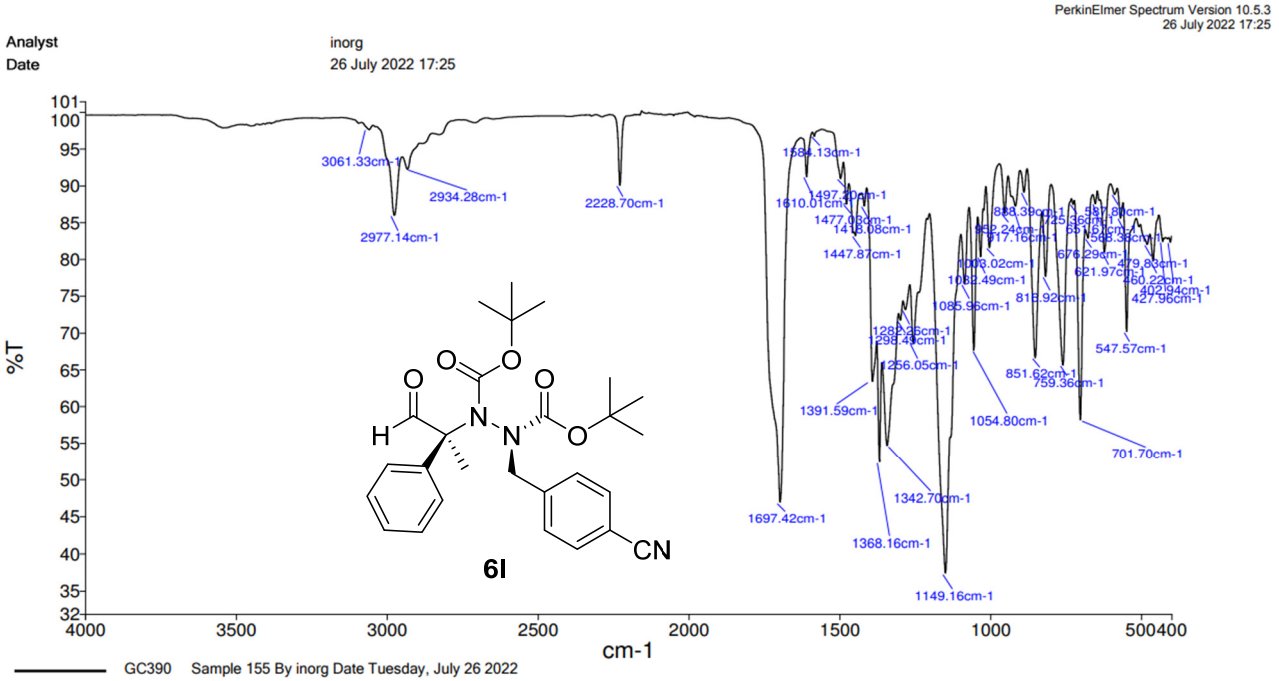

PerkinElmer Spectrum Version 10.5.3
26 July 2022 17:00
Analyst
inorg
Date
26 July 2022 17:00
%T
cm-1
3059.86cm-1
2966.36cm-1
2905.83cm-1
2869.60cm-1
2820.32cm-1
1694.57cm-1
1600.55cm-1
1447.86cm-1
1476.40cm-1
1391.19cm-1
1366.49cm-1
1352.17cm-1
1151.72cm-1
1129.29cm-1
1055.55cm-1
913.62cm-1
854.14cm-1
699.96cm-1
6g
GC346 Sample 147 By inorg Date Tuesday, July 26 2022

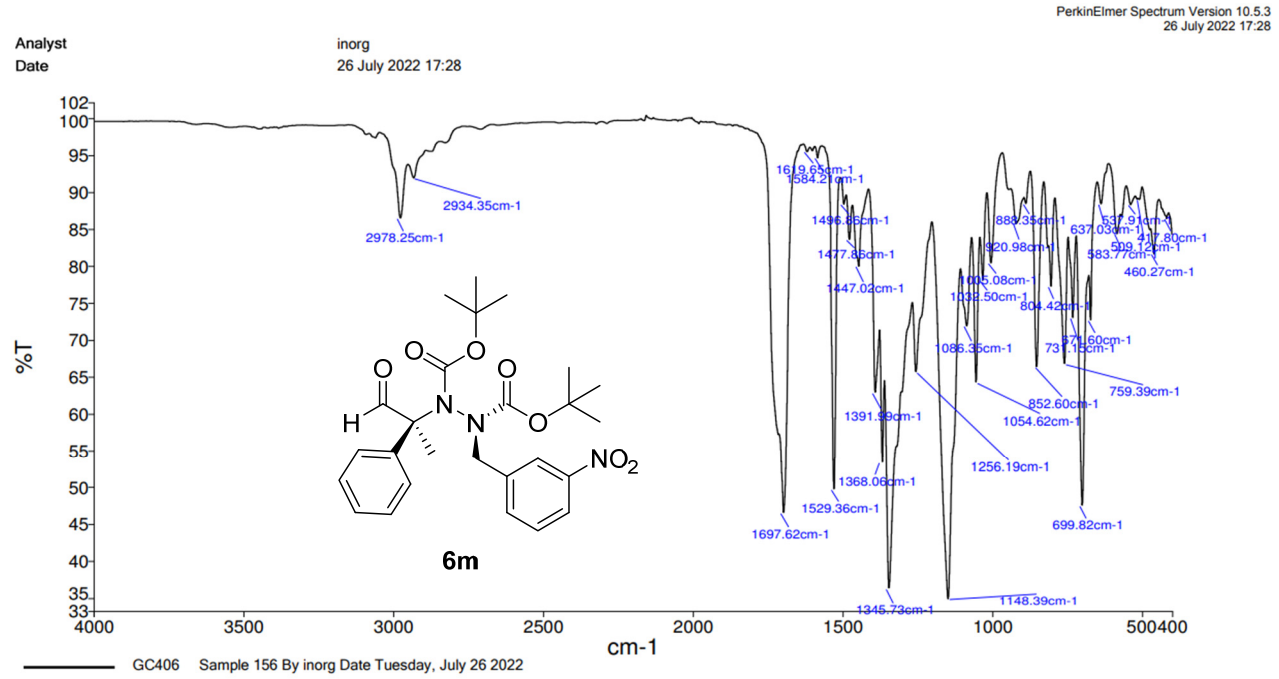

PerkinElmer Spectrum Version 10.5.3
26 July 2022 17:10
Analyst
inorg
Date
26 July 2022 17:10
%T
cm-1
3061.24cm-1
2977.05cm-1
2934.94cm-1
2838.94cm-1
1695.37cm-1
1602.67cm-1
1589.86cm-1
1494.42cm-1
1456.78cm-1
1391.33cm-1
1350.46cm-1
1290.57cm-1
1244.59cm-1
1151.88cm-1
1130.76cm-1
1085.18cm-1
1052.48cm-1
1030.71cm-1
997.83cm-1
916.51cm-1
890.76cm-1
854.68cm-1
753.79cm-1
700.12cm-1
632.06cm-1
538.64cm-1
6h
GC349 Sample 150 By inorg Date Tuesday, July 26 2022

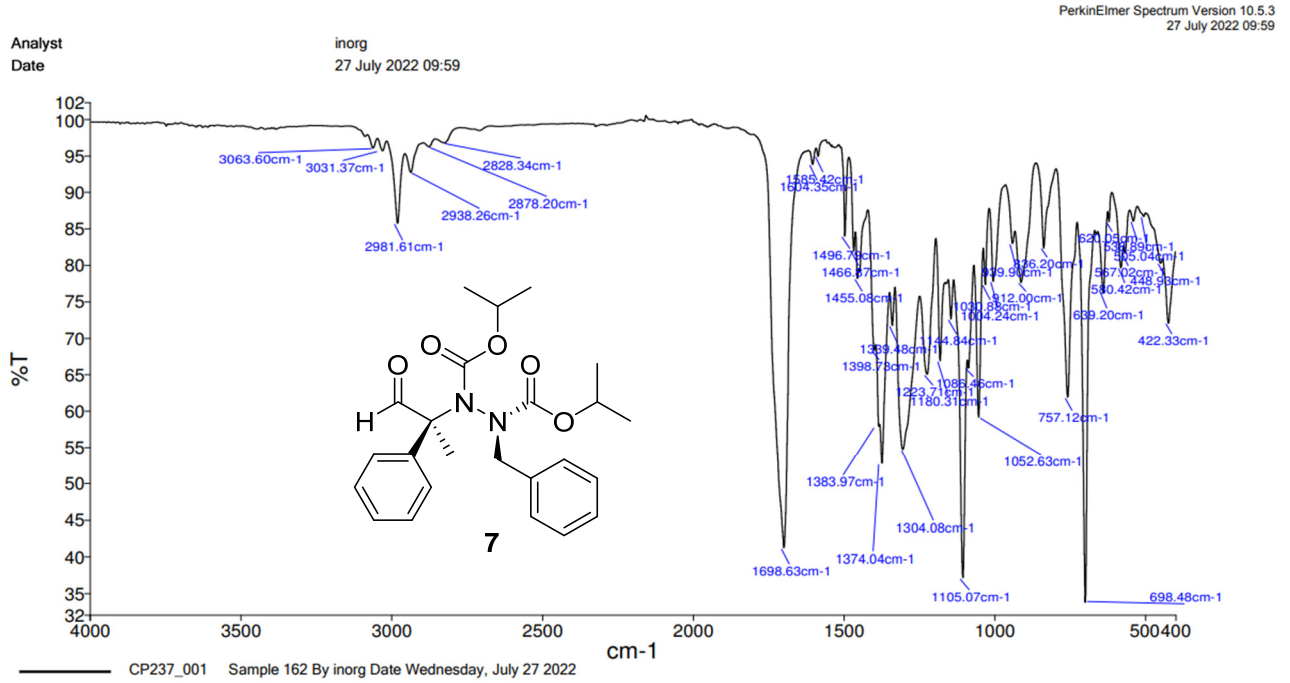

PerkinElmer Spectrum Version 10.5.3
26 July 2022 17:13
Analyst
inorg
Date
26 July 2022 17:13
%T
cm-1
3058.23cm-1
2975.70cm-1
2933.35cm-1
1735.54cm-1
1690.20cm-1
1599.52cm-1
1583.57cm-1
1497.02cm-1
1476.48cm-1
1454.03cm-1
1392.56cm-1
1366.73cm-1
1349.85cm-1
1256.38cm-1
1232.81cm-1
1151.01cm-1
1086.68cm-1
1054.50cm-1
1033.47cm-1
991.28cm-1
866.17cm-1
851.92cm-1
792.87cm-1
755.16cm-1
738.58cm-1
700.51cm-1
781.00cm-1
6i
GC387 Sample 151 By inorg Date Tuesday, July 26 2022

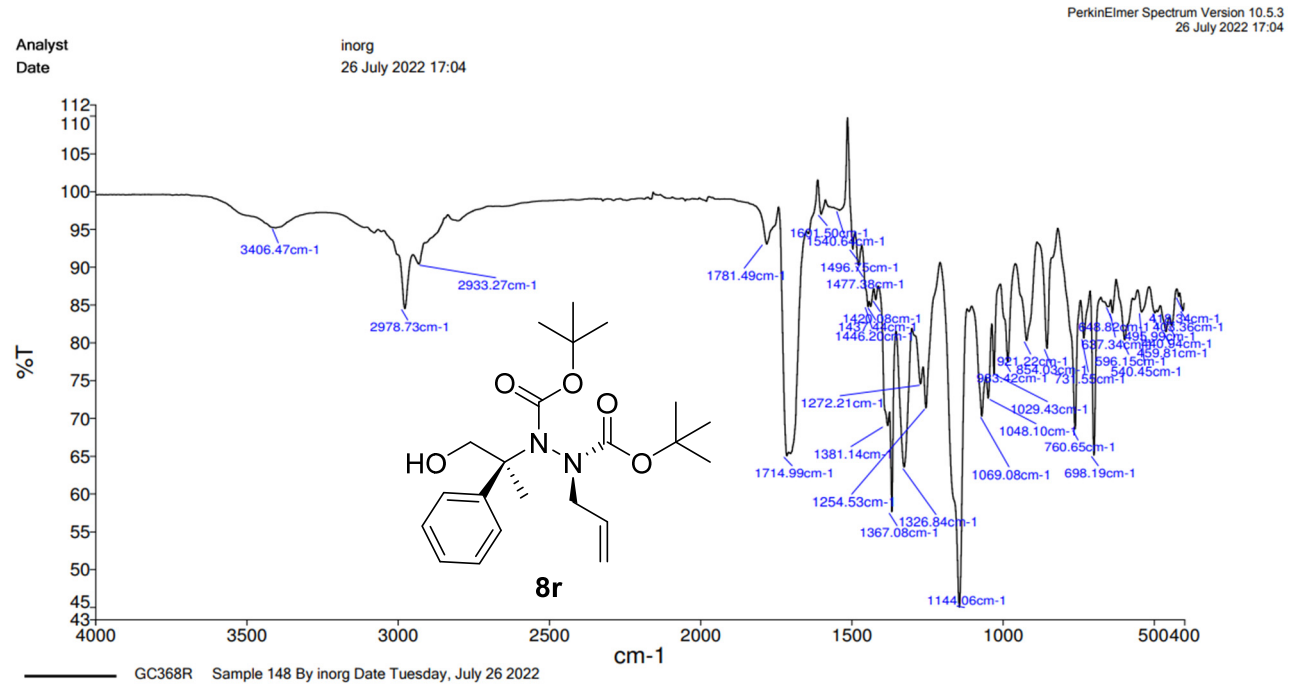

PerkinElmer Spectrum Version 10.5.3
26 July 2022 17:34
Analyst inorg
Date 26 July 2022 17:34
%T
cm-1
3662.18cm-1
3059.12cm-1
2977.71cm-1
2933.17cm-1
1695.39cm-1
1602.54cm-1
1476.73cm-1
1446.98cm-1
1393.11cm-1
1355.65cm-1
1366.80cm-1
1253.81cm-1
1149.95cm-1
1084.95cm-1
961.25cm-1
910.52cm-1
852.55cm-1
755.07cm-1
731.09cm-1
700.26cm-1
474.38cm-1
536.75cm-1
426.46cm-1
6j
GC343 Sample 158 By inorg Date Tuesday, July 26 2022

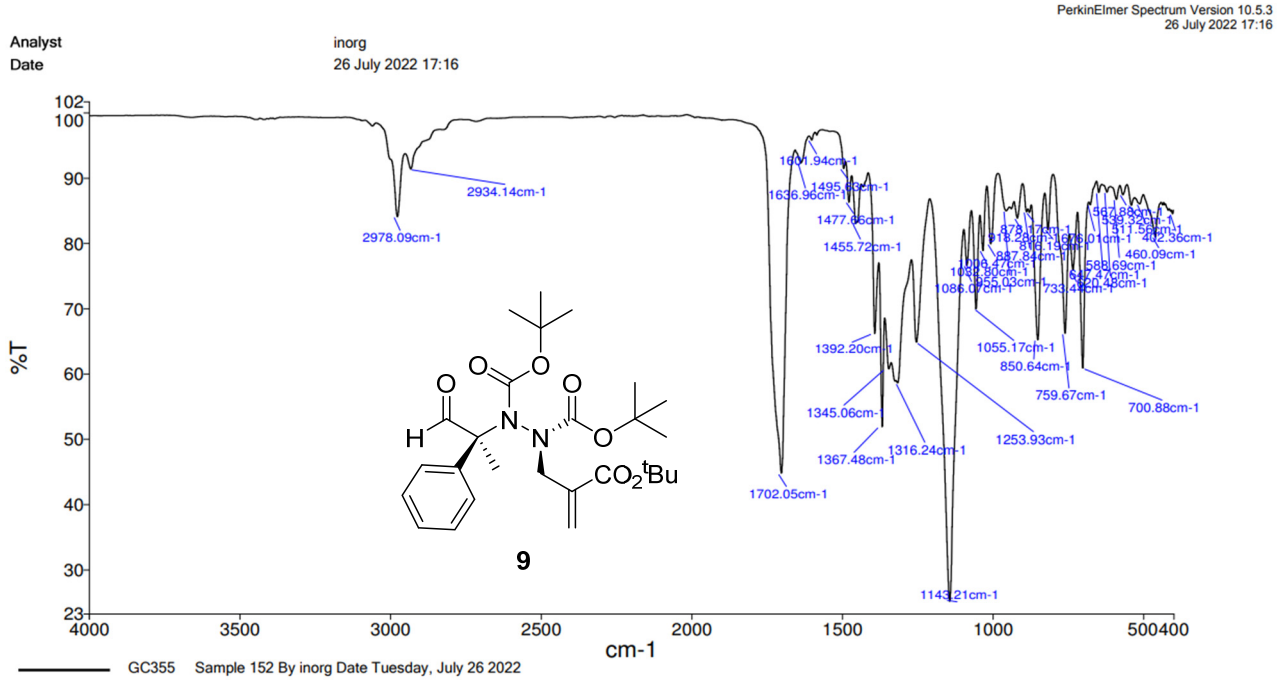

PerkinElmer Spectrum Version 10.5.3
26 July 2022 17:31
Analyst inorg
Date 26 July 2022 17:31
%T
cm-1
2978.02cm-1
2933.81cm-1
1697.08cm-1
1594.01cm-1
1488.67cm-1
1447.22cm-1
1409.74cm-1
1388.76cm-1
1343.98cm-1
1367.54cm-1
1149.37cm-1
1127.03cm-1
1054.63cm-1
913.97cm-1
889.78cm-1
851.43cm-1
757.70cm-1
731.34cm-1
700.34cm-1
479.13cm-1
460.58cm-1
6k
Br
GC376 Sample 157 By inorg Date Tuesday, July 26 2022

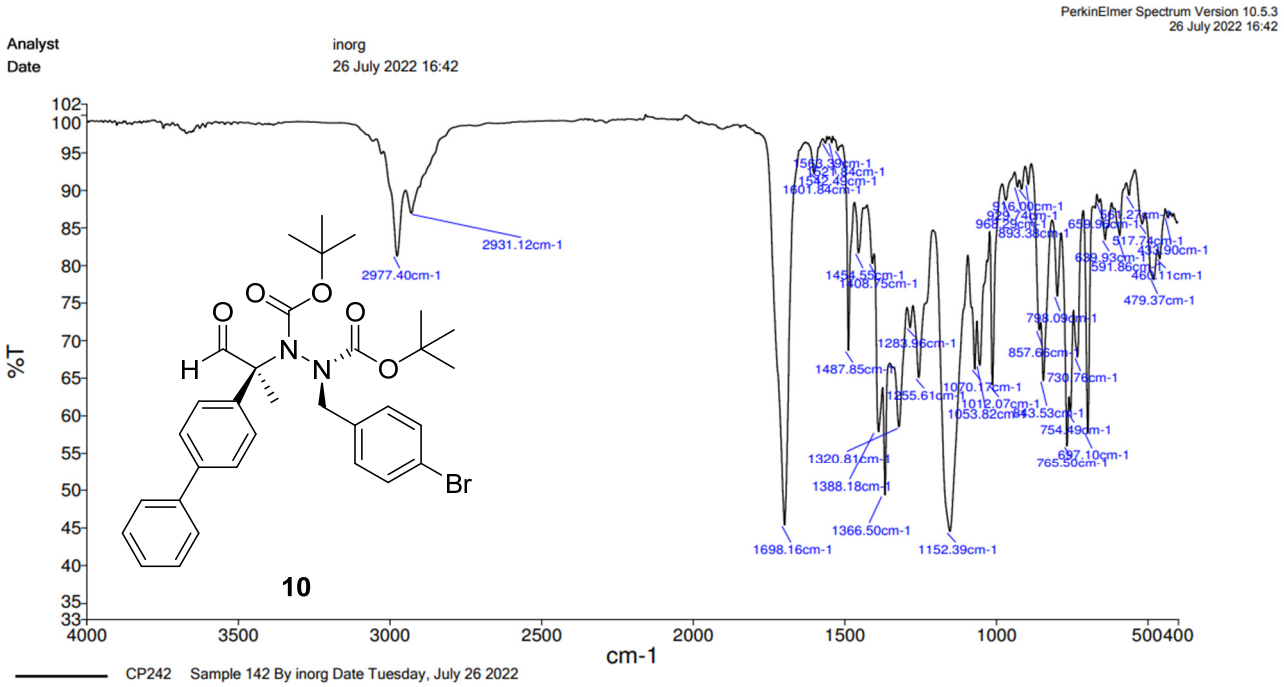

PerkinElmer Spectrum Version 10.5.3
26 July 2022 17:25
Analyst
inorg
Date
26 July 2022 17:25
%T
cm-1
3061.33cm-1
2934.28cm-1
2977.14cm-1
2228.70cm-1
1584.13cm-1
1610.01cm-1
1497.30cm-1
1477.08cm-1
1412.08cm-1
1447.87cm-1
1697.42cm-1
1391.59cm-1
1256.05cm-1
1342.70cm-1
1368.16cm-1
1149.16cm-1
1085.96cm-1
1054.80cm-1
851.62cm-1
759.36cm-1
701.70cm-1
547.57cm-1
427.96cm-1
6l
CN
GC390 Sample 155 By inorg Date Tuesday, July 26 2022


PerkinElmer Spectrum Version 10.5.3
26 July 2022 17:28
Analyst
inorg
Date
26 July 2022 17:28
%T
cm-1
2978.25cm-1
2934.35cm-1
1697.62cm-1
1529.36cm-1
1368.06cm-1
1345.73cm-1
1148.39cm-1
1256.19cm-1
1054.62cm-1
852.60cm-1
759.39cm-1
699.82cm-1
6m
NO2
GC406 Sample 156 By inorg Date Tuesday, July 26 2022


PerkinElmer Spectrum Version 10.5.3
27 July 2022 09:59
Analyst
inorg
Date
27 July 2022 09:59
%T
cm-1
3063.60cm-1
3031.37cm-1
2981.61cm-1
2938.26cm-1
2878.20cm-1
2828.34cm-1
1698.63cm-1
1604.35cm-1
1585.42cm-1
1496.78cm-1
1466.87cm-1
1455.08cm-1
1398.78cm-1
1383.97cm-1
1374.04cm-1
1304.08cm-1
1105.07cm-1
1052.63cm-1
757.12cm-1
698.48cm-1
422.33cm-1
7
CP237_001 Sample 162 By inorg Date Wednesday, July 27 2022


PerkinElmer Spectrum Version 10.5.3
26 July 2022 17:04
Analyst
inorg
Date
26 July 2022 17:04
%T
cm-1
3406.47cm-1
2978.73cm-1
2933.27cm-1
1781.49cm-1
1714.99cm-1
1496.75cm-1
1477.38cm-1
1446.20cm-1
1381.14cm
1272.21cm-1
1254.53cm-
1326.84cm-1
1367.08cm-1
1144.06cm-1
1069.08cm-1
1048.10cm-
1029.43cm-1
760.65cm-1
698.19cm-1
8r
GC368R Sample 148 By inorg Date Tuesday, July 26 2022


PerkinElmer Spectrum Version 10.5.3
26 July 2022 17:16
Analyst
inorg
Date
26 July 2022 17:16
%T
cm-1
2978.09cm-1
2934.14cm-1
1702.05cm-1
1636.96cm-1
1601.94cm-1
1495.43cm-1
1477.06cm-1
1455.72cm-1
1392.20cm-1
1345.06cm-1
1367.48cm-1
1316.24cm-1
1253.93cm-1
1143.21cm-1
1086.07cm-1
1055.17cm-1
850.64cm-1
759.67cm-1
700.88cm-1
9
GC355 Sample 152 By inorg Date Tuesday, July 26 2022


PerkinElmer Spectrum Version 10.5.3
26 July 2022 16:42
Analyst
inorg
Date
26 July 2022 16:42
%T
cm-1
2977.40cm-1
2931.12cm-1
1698.16cm-1
1601.84cm-1
1487.85cm-1
1450.55cm-1
1408.75cm-1
1366.50cm-1
1320.81cm-1
1388.18cm-1
1283.96cm-1
1255.61cm-1
1152.39cm-1
1070.17cm-1
1053.82cm-1
1012.07cm-1
916.00cm-1
893.38cm-1
857.66cm-1
798.09cm-1
754.49cm-1
730.76cm-1
697.10cm-1
765.50cm-1
591.86cm-1
517.78cm-1
479.37cm-1
10
CP242 Sample 142 By inorg Date Tuesday, July 26 2022