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SUPPORTING INFORMATION

General methods

¹H-NMR spectra were recorded on Varian 400 (400 MHz) spectrometers. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (deuteriochloroform: 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sext = sextet, sept = septet, p = pseudo, b = broad, m = multiplet), coupling constants (Hz). ¹³C-NMR spectra were recorded on Varian 400 (100 MHz) spectrometers with complete proton decoupling. Chemical shifts are reported in ppm from TMS with the solvent as the internal standard (deuteriochloroform: 77.0 ppm). ¹⁹F-NMR spectra were recorded on Varian 400 (377 MHz). ³¹P-NMR spectra were recorded on Varian 400 (162 MHz) having as reference 31P-PPh₃: -4.7 ppm (*d*⁸-toluene).

Chromatographic purification was done with 240-400 mesh silica gel.

Anhydrous solvents were supplied by Sigma Aldrich in Sureseal® bottles and used without any further purification.

Commercially available chemicals were purchased from Sigma Aldrich, Fluorochem and TCI and used without any further purification.

Analytical high-performance liquid chromatography (HPLC) was performed on a liquid chromatograph equipped with a variable wavelength UV detector (deuterium lamp 190-600 nm), using a Daicel Chiracel™ IC (0.46 cm I.D. x 25 cm Daicel Inc) and Daicel Chiracel™ IA (0.46 cm I.D. x 25 cm Daicel Inc). HPLC grade isopropanol and n-hexane were used as the eluting solvents.

Compound **4** was synthesized following the known literature.^[1]

Naphthols **1a-f** were synthesized following the known literature.^[2]

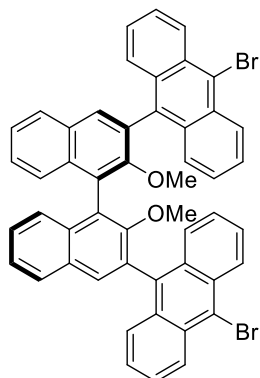
Allenamides **2a**, **2b** and **2c** were synthesized following the known literature.^[3]

SUPPORTING INFORMATION

Experimental Procedures

Synthesis of 6

Following reported literature^[4], product **6** was isolated and characterized.



(*R_a*)-10,10'-(2,2'-dimethoxy-[1,1'-binaphthalene]-3,3'-diyl)bis(9-bromoanthracene). White powder, Y = 62%.

M.p. = decomposition.

¹H NMR (400 MHz, CDCl₃) δ = 8.61 (ddt, *J* = 18.6, 8.8, 0.9 Hz, 1H), 7.94 (s, 0H), 7.91 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.75 (dt, *J* = 8.7, 1.0 Hz, 0H), 7.66 – 7.54 (m, 1H), 7.54 – 7.42 (m, 2H), 7.21 (ddd, *J* = 8.8, 6.5, 1.2 Hz, 1H), 2.92 (s, 1H).

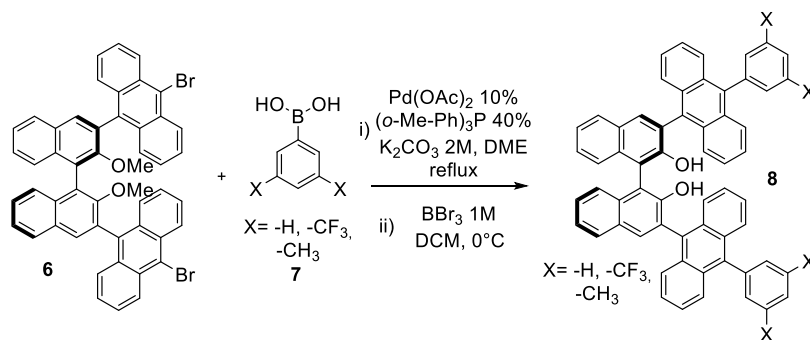
¹³C NMR (101 MHz, CDCl₃) δ = 155.35, 134.32, 134.24, 132.83, 131.71, 131.39, 131.26, 130.58, 130.30, 128.19, 128.02, 127.89, 127.31, 127.18, 126.99, 126.95, 126.92, 125.97, 125.84, 125.75, 125.48, 125.30, 123.25, 60.98.

Anal. Calc. for (C₅₀H₃₂Br₂O₂: 822.08): C, 72.83; H, 3.91; found: C, 72.65, H, 3.80.

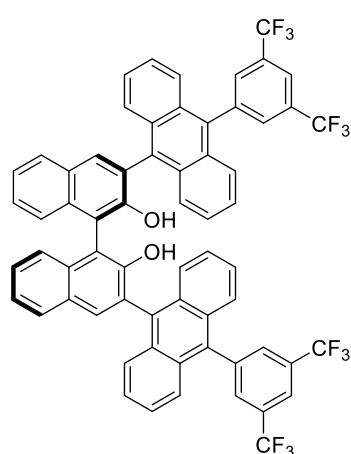
Synthesis of 8a-c.

For compound **10b**, data were in accordance with literature.^[5]

In oven dried Schlenk tube **6** (1 eq) and aryl boronic acid **7** (4 eq) were introduced, then 1:1 ratio of DME and K₂CO₃ 2M in water (10 eq) were added and the mixture was degassed for 3 minutes with N₂. Pd(OAc)₂ (0.1 eq) and tri(*o*-methoxyphenyl)phosphine (0.4 eq) were added. The reaction mixture was heated at 80 °C for 12h. After TLC, the reaction was extracted 3xDCM and washed once with water. The organic phase was dried over Na₂SO₄ and solvent evaporated. The crude was filtered with DCM through silica to remove palladium salts. Then crude mixture was transferred to a Schlenk tube under inert atmosphere and dissolved in dry DCM and cooled to 0 °C. then a 1.0 M solution of BBr₃ in DCM (6 eq) was added dropwise. The reaction mixture was stirred at the same temperature for 30 minutes and then warmed up to room temperature. After the intermediate was completely consumed, by TLC checking, the reaction was quenched at 0 °C by slowly addition of cold water (HBr gas develops). The mixture was extracted CH₂Cl₂ (3 x 15 mL) and the organic phase were washed 2 x 10 mL NaHCO₃ saturated solution, dried over Na₂SO₄ and evaporated. Product **8** was purified by FC with *c*Hex/AcOEt from 40/1 to 20/1.



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(*R_a*)-3,3'-bis(10-(3,5-bis(trifluoromethyl)phenyl)anthracen-9-yl)-[1,1'-binaphthalene]-2,2'-diol (**8a**).

Yellow powder, Y = 38%. M.p. = decomposition.

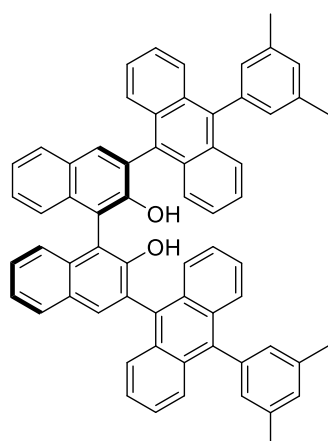
¹H-NMR (400 MHz, CDCl₃) δ = δ 8.16 (d, *J* = 1.8 Hz, 2H), 8.12 (s, 2H), 8.05 (d, *J* = 1.7 Hz, 4H), 8.04 – 7.97 (m, 4H), 7.81 (dt, *J* = 8.8, 1.0 Hz, 2H), 7.70 – 7.64 (m, 2H), 7.62 – 7.47 (m, 10H), 7.41 (ddd, *J* = 8.8, 6.5, 1.3 Hz, 2H), 7.33 (ddd, *J* = 8.8, 6.5, 1.3 Hz, 2H), 5.28 (s, 2H).

¹³C-NMR (100 MHz, CDCl₃) δ = 151.08, 141.34, 134.10, 133.96, 133.42, 132.88, 132.32, 132.29, 131.99, 131.96, 131.63, 131.53, 130.45, 130.42, 129.95, 129.89, 129.42, 128.66, 127.79, 127.09, 126.76, 126.66, 126.42, 126.15, 126.14, 126.08, 125.99, 124.86, 124.79, 124.76, 124.62, 122.08, 122.05, 121.87, 113.26.

¹⁹F-NMR (377 MHz, CDCl₃) δ = -62.60 (s, 6F), -62.63 (s, 6F).

[α]_D²⁰ = + 31.87 (DCM, *c* = 4.6).

Anal. Calc. for (C₆₄H₃₄F₁₂O₂: 1062.24): C, 72.32; H, 3.22; found: C, 72.15, H, 3.00.



(*R_a*)-3,3'-bis(10-(3,5-dimethylphenyl)anthracen-9-yl)-[1,1'-binaphthalene]-2,2'-diol (**8c**). Pale yellow powder, Y = 52%. M.p. = decomposition.

¹H-NMR (400 MHz, CDCl₃) δ = 8.15 (dt, *J* = 2.0, 1.1 Hz, 2H), 8.12 (s, 2H), 8.05 – 8.03 (m, 4H), 8.03 – 7.98 (m, 4H), 7.80 (dt, *J* = 8.7, 1.0 Hz, 2H), 7.68 – 7.64 (m, 2H), 7.60 – 7.46 (m, 12H), 7.41 (ddd, *J* = 8.9, 6.5, 1.3 Hz, 2H), 7.32 (ddd, *J* = 8.9, 6.4, 1.2 Hz, 2H), 5.22 (s, 2H), 1.45 (s, 12H).

¹³C-NMR (100 MHz, CDCl₃) δ = 151.07, 141.34, 134.09, 133.96, 133.41, 132.87, 132.32, 132.30, 131.99, 131.97, 131.52, 130.44, 130.41, 129.94, 129.89, 129.42, 128.66, 127.79, 127.08, 126.75, 126.66, 126.42, 126.15, 126.13, 126.07, 125.99, 124.86, 124.62, 121.86, 113.25, 26.93.

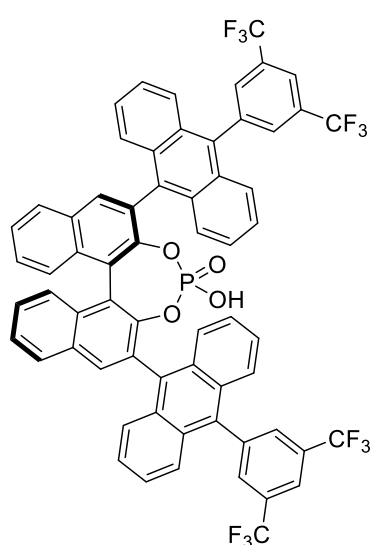
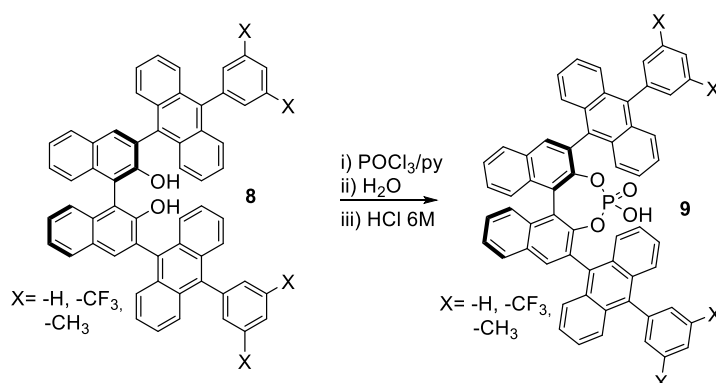
[α]_D²⁰ = +33.47 (DCM, *c* = 12.6).

Anal. Calc. for (C₆₄H₄₆O₂: 846.35): C, 90.75; H, 5.47; found: C, 90.65, H, 5.33.

SUPPORTING INFORMATION

Synthesis of phosphoric acid **9a-c**

A Schlenk tube, under inert atmosphere, was charged with **8** (1 eq) and dissolved in pyridine (0.05 M). Then, freshly distilled POCl₃ (3 eq) was added dropwise. The reaction mixture was stirred at 100 °C for 24 h, then a volume of H₂O equal to initial pyridine was added. The reaction was stirred at the same temperature for 6 h. The reaction was cooled to room temperature and acidified to pH = 2 with HCl 6 M. The mixture was extracted CH₂Cl₂ (3 x 10 mL), dried over Na₂SO₄ and the organic phase evaporated. The phosphoric acid **9** was purified by flash chromatography (DCM:MeOH = 100:1). Compound **9b** was isolated in 92% yield as a white solid.^[5]



(*R_a*)-3,3'-bis(10-(3,5-bis(trifluoromethyl)phenyl)anthracen-9-yl)-1,1'-binaphthyl-2,2'-diyl hydrogenphosphate (**9a**). Yellow powder, Y = 38%. M.p. = decomposition.

¹H-NMR (400 MHz, CDCl₃) δ = 8.04 (s, 4H), 8.02 – 7.96 (m, 2H), 7.93 (d, J = 8.9 Hz, 2H), 7.87 (s, 2H), 7.80 (d, J = 8.3 Hz, 3H), 7.68 (d, J = 8.4 Hz, 2H), 7.63 (s, 2H), 7.61 – 7.47 (m, 5H), 7.30 – 7.14 (m, 8H), 6.89 (t, J = 7.8 Hz, 2H), 6.82 (bs, 1H), 6.62 (d, J = 8.7 Hz, 2H).

¹³C-NMR (100 MHz, CDCl₃) δ = 147.71, 141.36, 134.30, 133.06, 132.26, 131.93, 131.51, 131.13, 130.78, 130.36, 129.95, 129.45, 129.19, 128.53, 127.07, 126.76, 125.91, 125.82, 125.70, 124.63, 124.37, 123.75, 123.03, 121.69.

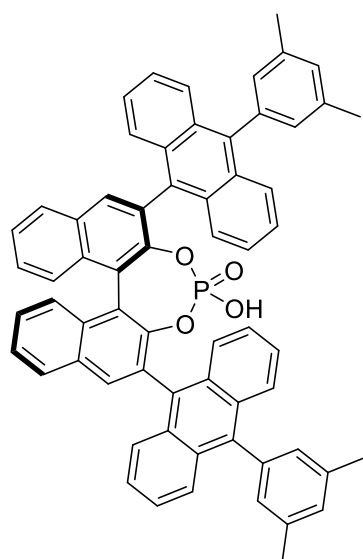
¹⁹F-NMR (377 MHz, CDCl₃) δ = -62.69 (s, 12F).

³¹P NMR (162 MHz, CDCl₃) δ = 4.30 (s).

[α]^D = +89.99 (DCM, c = 10.6).

Anal. Calc. for (C₆₄H₃₃F₁₂O₄P: 1124.19): C, 68.33; H, 2.96; found: C, 68.15, H, 2.66.

SUPPORTING INFORMATION



(*R_a*)-3,3'-bis(10-(3,5-bis(trifluoromethyl)phenyl)anthracen-9-yl)-1,1'-binaphthyl-2,2'-diylhydrogenphosphate (**9c**). White powder. Y = 52%. M.p. = decomposition.

¹H-NMR (400 MHz, CDCl₃) δ = 8.07 (s, 2H), 7.96 (dd, *J* = 7.3, 2.0 Hz, 2H), 7.93 – 7.88 (m, 2H), 7.83 – 7.69 (m, 6H), 7.62 (dd, *J* = 7.9, 1.8 Hz, 2H), 7.55 – 7.47 (m, 4H), 7.47 – 7.42 (m, 2H), 7.38 (ddd, *J* = 7.9, 6.5, 1.3 Hz, 2H), 7.30 (ddd, *J* = 8.6, 6.5, 1.4 Hz, 2H), 7.26 – 7.21 (m, 2H), 7.19 (s, 2H), 7.12 (d, *J* = 1.7 Hz, 4H), 2.46 (s, 6H), 2.45 (s, 6H).

¹³C-NMR (100 MHz, CDCl₃) δ = 148.34, 143.96, 138.73, 137.72, 137.58, 133.31, 133.08, 132.66, 131.68, 131.09, 130.54, 130.04, 129.64, 129.41, 129.03, 128.93, 128.70, 128.42, 127.31, 127.04, 126.55, 126.16, 125.52, 125.41, 124.79, 124.71, 124.62, 124.18, 123.08, 21.38.

³¹P NMR (162 MHz, CDCl₃) δ = 3.87.

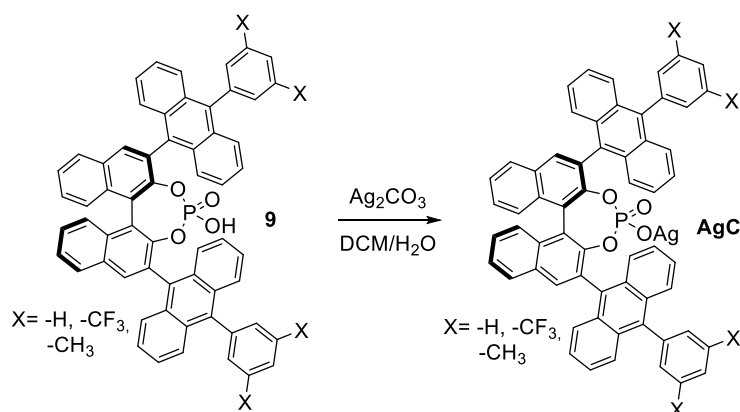
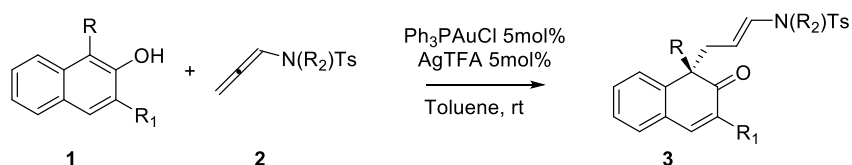
[α]_D²⁰ = +69.73 (DCM, *c* = 9.3).

Anal. Calc. for (C₆₄H₄₅O₄P: 908.31): C, 84.56; H, 4.99; found: C, 84.41, H, 4.65.

SUPPORTING INFORMATION

Synthesis of silver phosphate AgC4-6

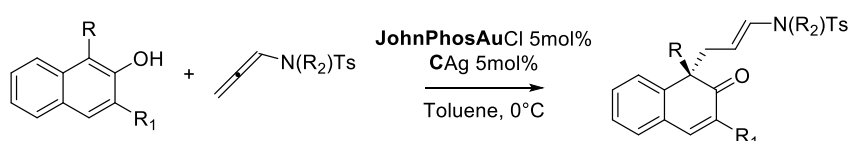
In a Schlenk tube, **9** (1 eq) was charged and dissolved a mixture 1:1 DCM/H₂O mixture (0.1 M), then the glassware was covered with aluminium foil to provide darkness. Ag₂CO₃ (0.5 eq) was added and the reaction mixture stirred at room temperature until **9** was completely consumed (DCM/MeOH = 10 : 1). The reaction was extracted with CH₂Cl₂ (3 x 10 mL) and evaporated. The silver salts were obtained in over 90% yields and employed without further purification.

General procedure for gold-catalyzed dearomatization of 2-naphthols with *N*-allenyl amides.

An oven dried two-necked flask was charged with 1 mL of anhydrous toluene, Ph₃PAuCl (1.2 mg, 5 mol%) and AgTFA (0.6 mg, 5 mol%). After stirring for 15 min in the dark, the desired naphthol (0.05 mmol) and *N*-allenyl amide (0.1 mmol) were added and the reaction was kept stirring at room temperature until **1** was completely consumed (TLC). Then, the reaction mixture was directly transferred into silica gel column chromatography (*n*-Hex:AcOEt = 10:1) to afford the dearomatized compound **3**.

General procedure for enantioselective gold(I)-catalysed reaction

A 2-necked dry flask, under N₂ atmosphere, was charged with JohnPhosAuCl (1.3 mg, 2.5 · 10⁻³ mmol, 5 mol%), 0.5 mL of dry toluene and the silver phosphate (2.5 · 10⁻³ mmol, 5 mol%). The flask was covered with aluminium foil to darkness and stirred at room temperature for 15 minutes. The reaction was cooled to 0 °C with an ice bath and naphthol (5 · 10⁻² mmol, 1 eq) and allenamide (7.5 · 10⁻², 1.5 eq) were added. The mixture was stirred at the same temperature for 16 h. After this time the reaction was charged directly on silica-gel and was purified by flash chromatography (*n*-hex:EtOAc = 10:1).

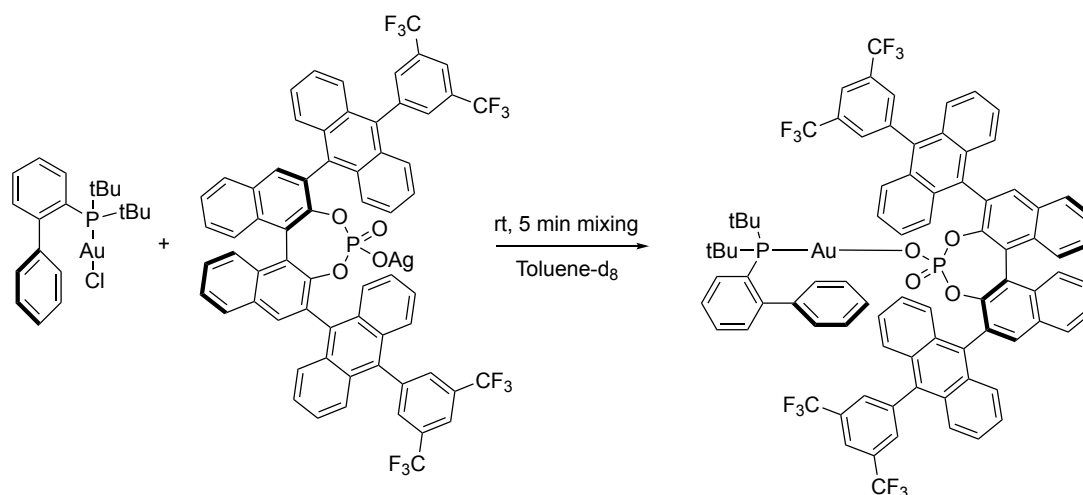


For ¹H-NMR and ¹³C-NMR spectra of compound **3aa-3fa** and **3ac** see ref [6].

SUPPORTING INFORMATION

³¹P-NMR experiments

All ³¹P-NMR experiments were carried in reagent grade *d*⁸-toluene.



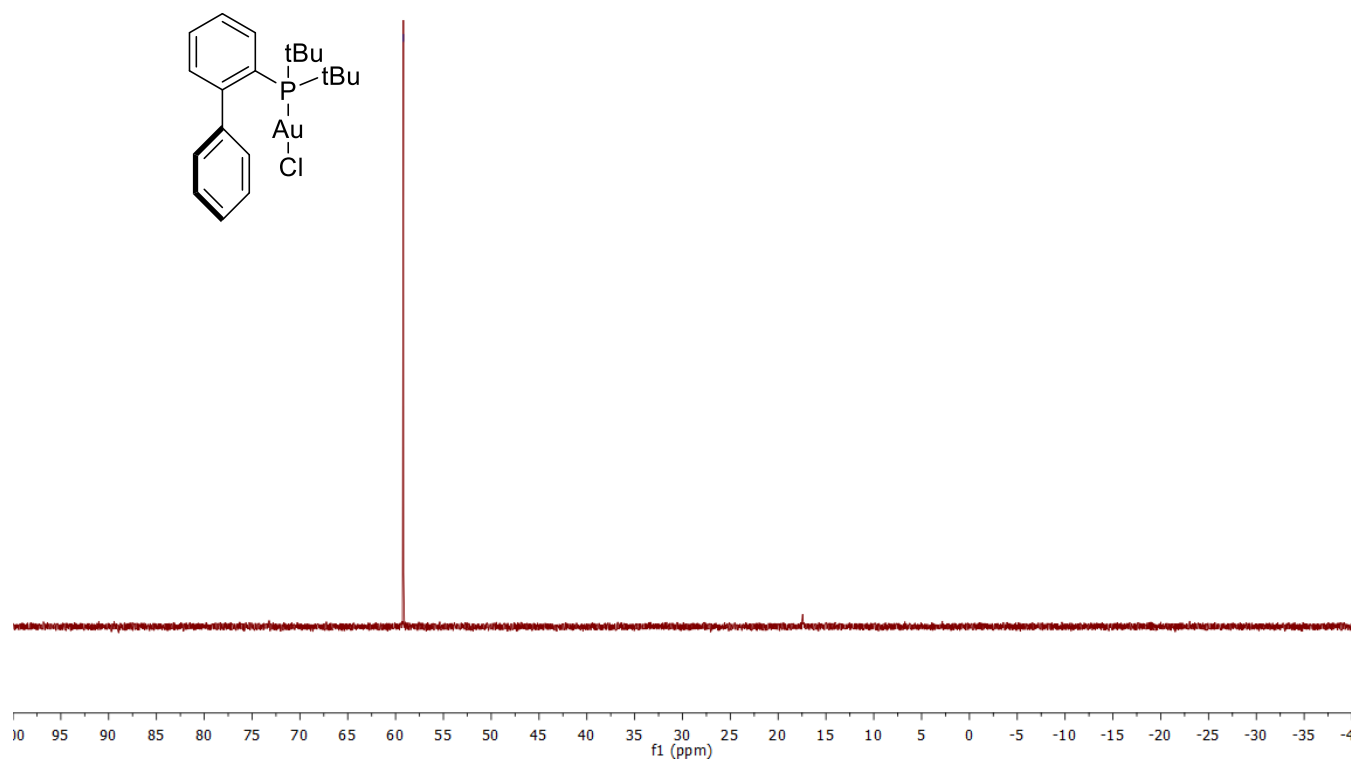
NMR experiment: JohnphosAuCl (10.6 mg, 0.02 mmol) and C4Ag (12.3 mg, 0.01 mmol) were mixed for 5 minutes in 1 mL of *d*⁸-toluene before acquisition.

JohnphosAuCl: ³¹P-NMR (162 MHz, *d*⁸-toluene) δ = 59.19 ppm.

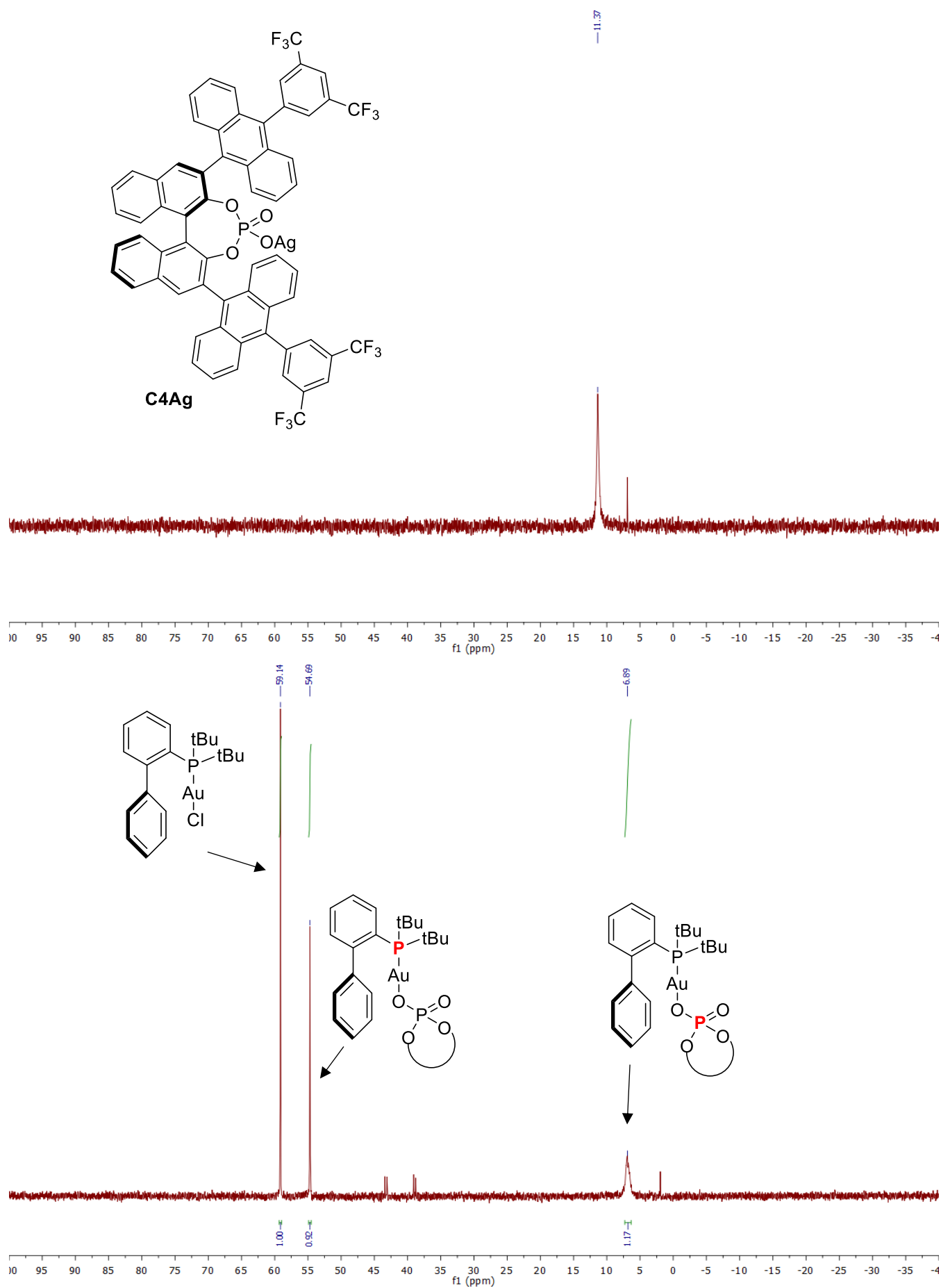
C4Ag: ³¹P-NMR (162 MHz, *d*⁸-toluene) δ = 11.37 ppm (brs).

JhonphosAuC4: ³¹P-NMR (162 MHz, *d*⁸-toluene) δ 59.14 (s, 1P), 6.89 (brs, 1P)

— 59.19



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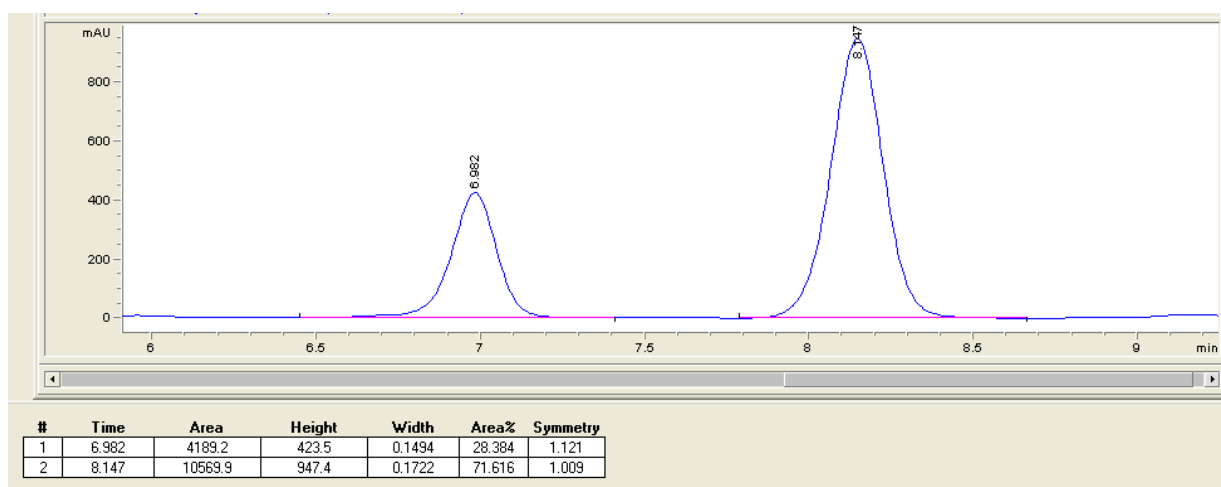
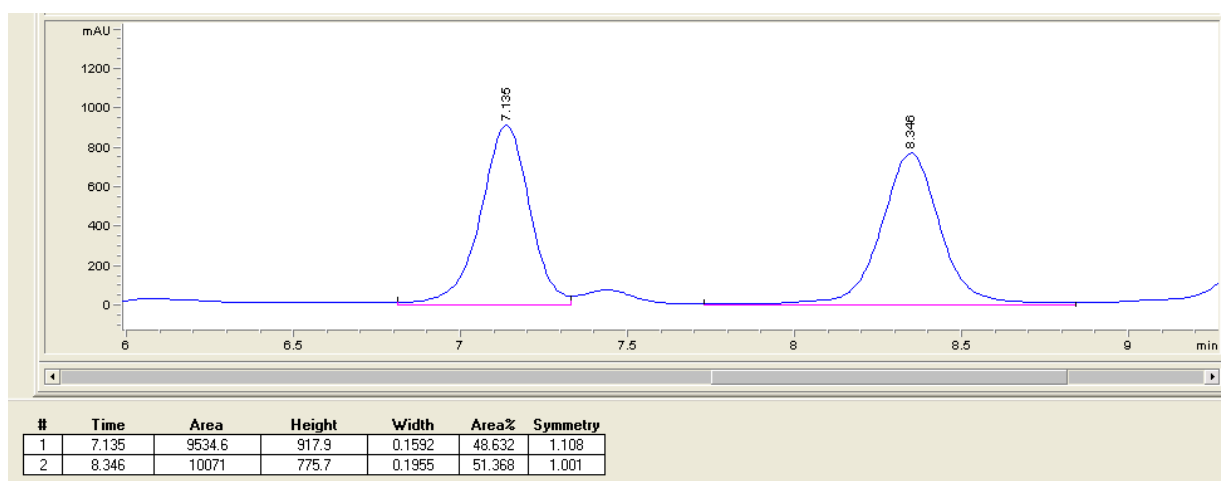
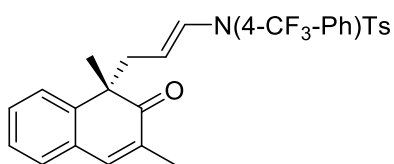
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Determination of absolute configuration

Determination of absolute configuration was done by comparison of compound **3ab** with known literature.^[7] The references reported for (S)-**3ab** an e.e.=90.6% and $[\alpha]^{20}_D = +16.0$ (c 1.0, CHCl₃). For determination of the absolute configuration, we carried the general procedure for enantioselective gold(I)-catalysed reaction using **C2-Ag** as chiral phosphate and resulted in an e.e.= 43%. Polarized light analysis shown the same direction of $[\alpha]^{20}_D$ of reported one, thus for similarity we attributed the absolute configuration of the major enantiomer as S and extended it to all the product.

(S)-**3ab**, Y = 40%, e.e. = 43%.

IA column, *n*-Hex:IPA 80:20, 1 mL/min, 30 °C. Rt(*R*): 7.13 min, Rt(*S*): 8.35 min

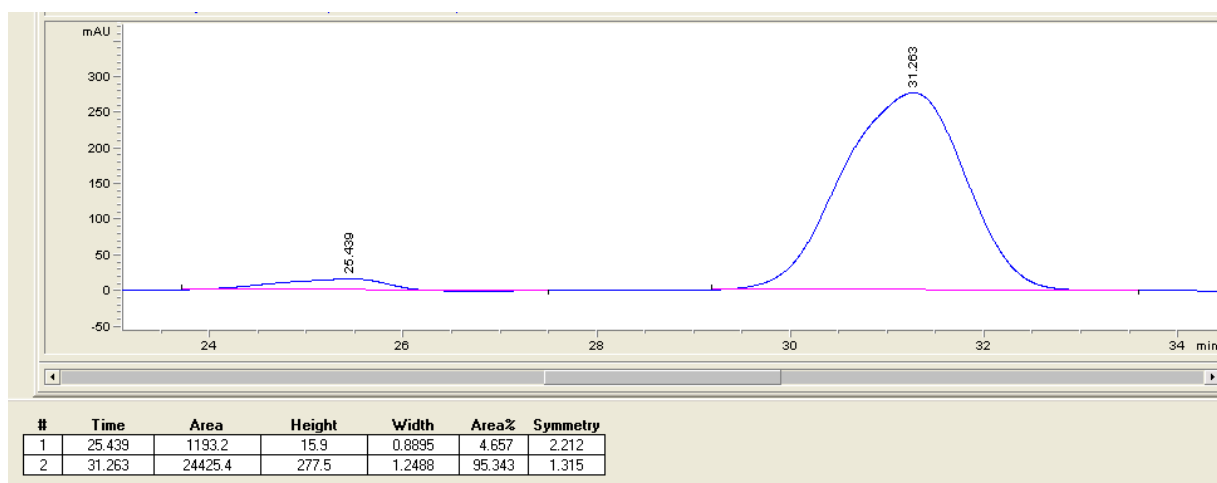
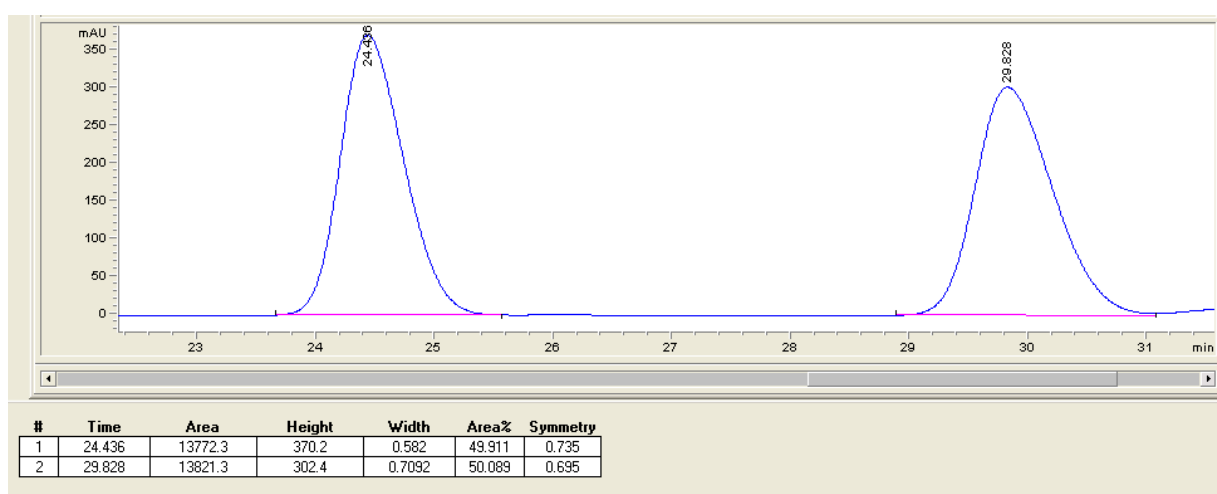
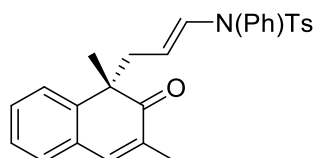


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Chiral HPLC analysis

(S)-**3aa**, Y = 99%, e.e. = 91%.

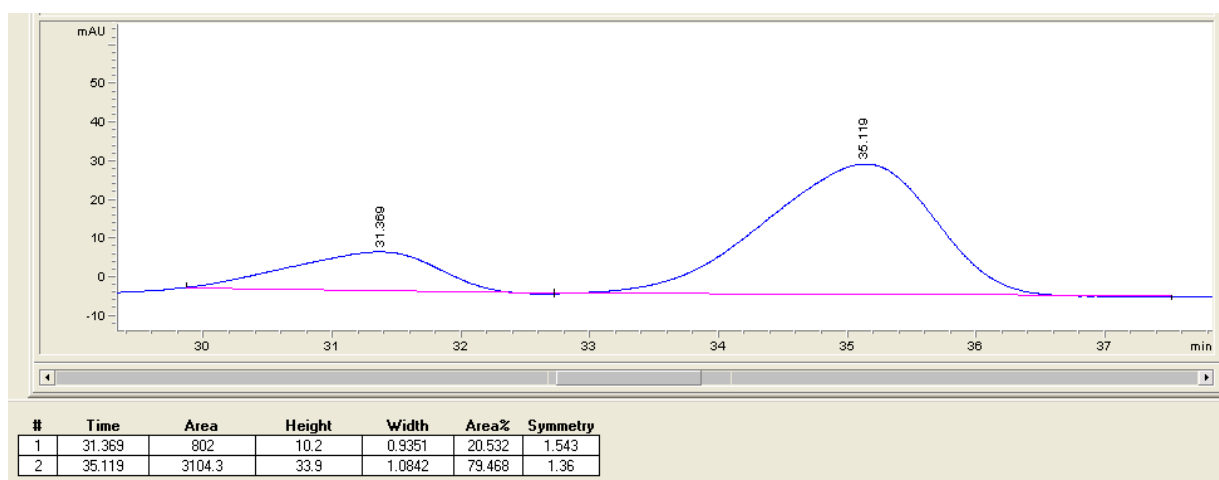
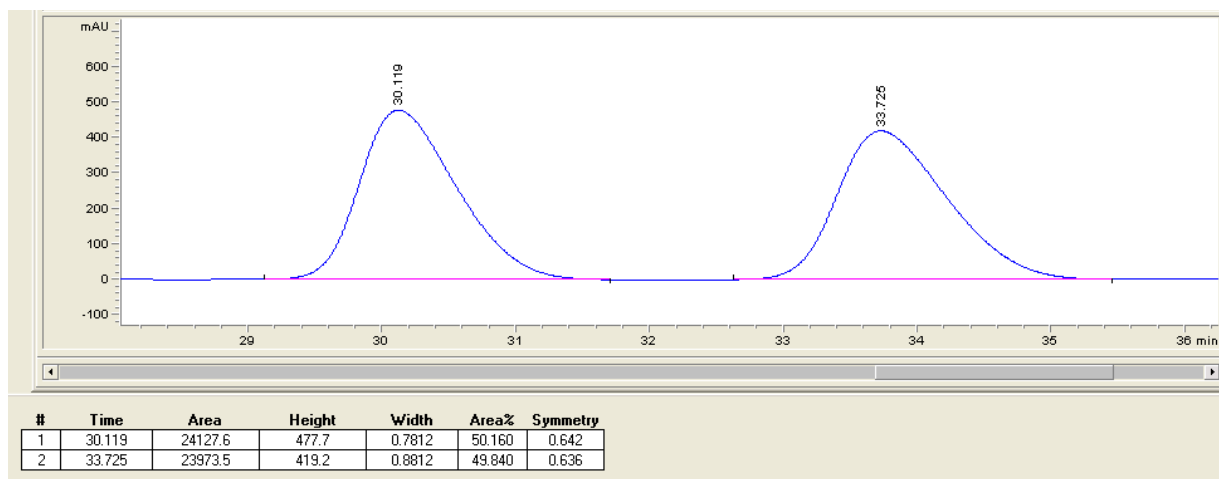
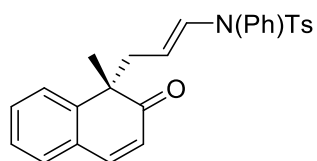
IC column, *n*-Hex:IPA 80:20, 1 mL/min, 30 °C. Rt(*R*): 24.43 min, Rt(*S*): 29.83 min



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(S)-**3ba**, Y = 60%, e.e. = 59%.

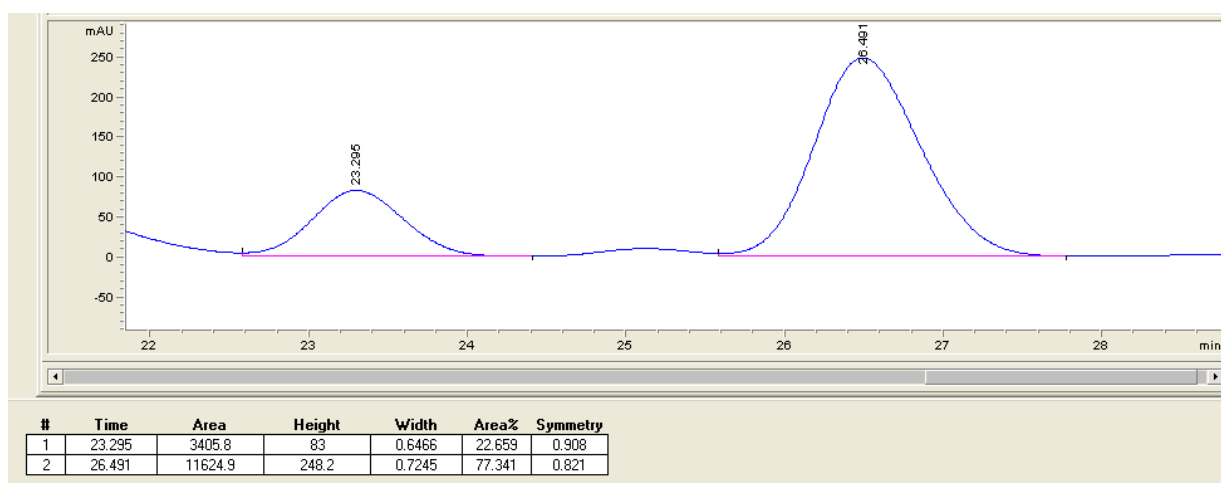
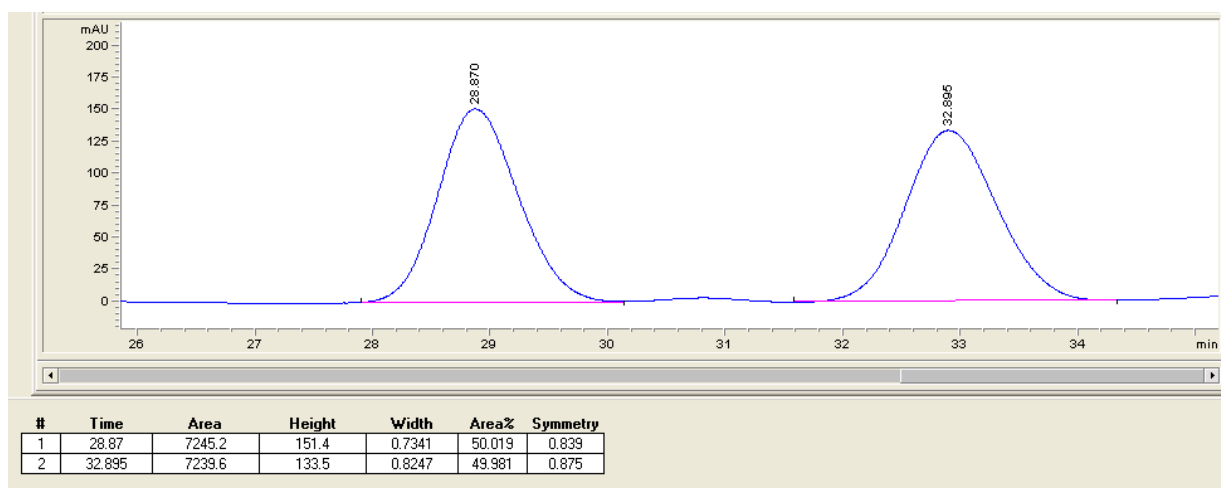
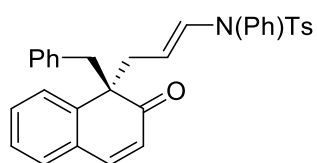
IC column, *n*-Hex:IPA 70:30, 1mL/min, 30°C. Rt(*R*): 30.12 min, Rt(*S*): 33.73 min



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(S)-**3ca**, Y = 47%, e.e. = 55%.

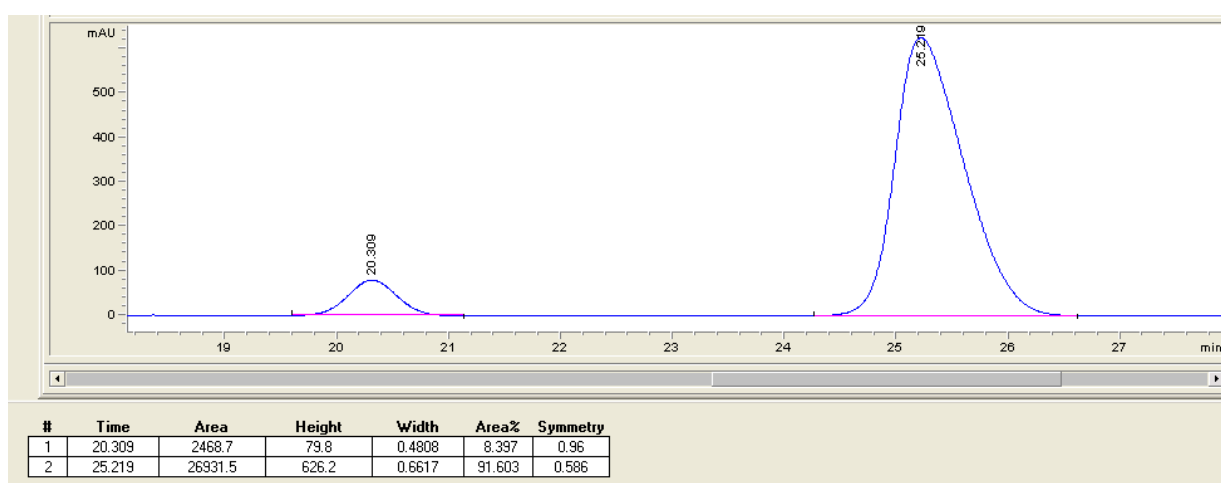
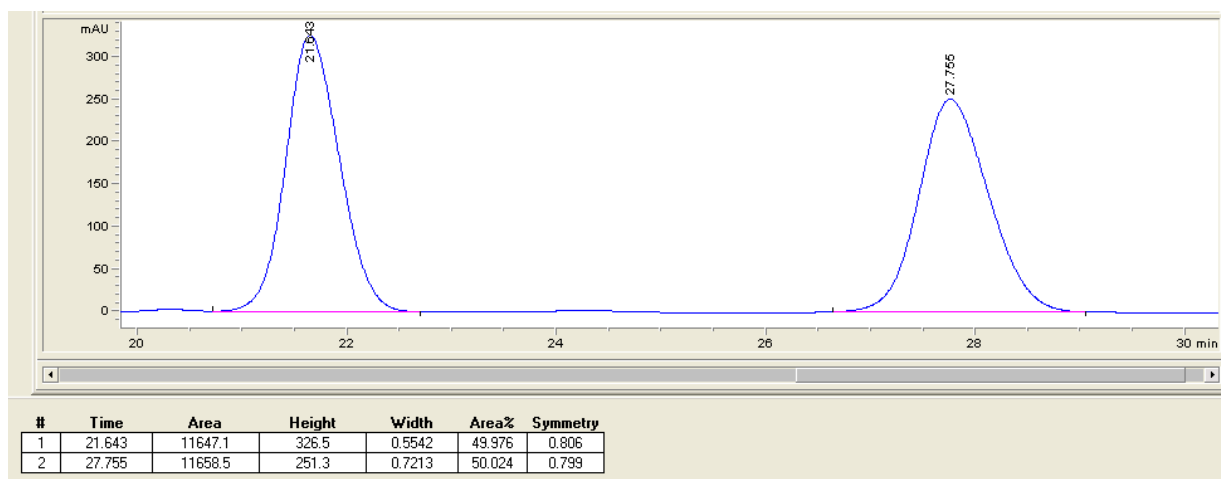
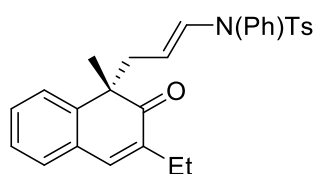
IC column, *n*-Hex:IPA 70:30, 1 mL/min, 30 °C. Rt(*R*): 28.87 min, Rt(*S*): 32.90 min



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(S)-**3da**, Y = 76%, e.e. = 83%.

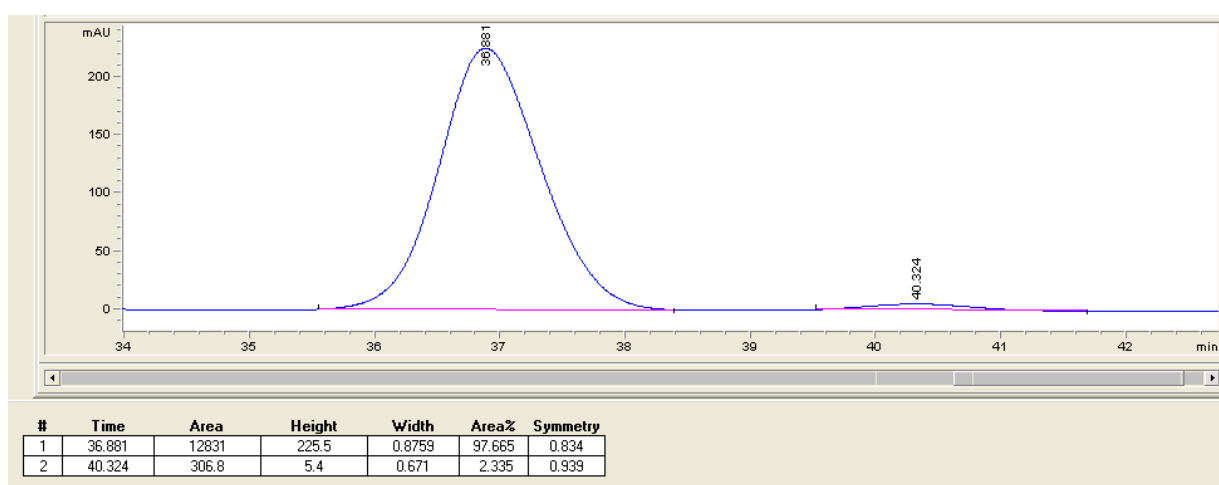
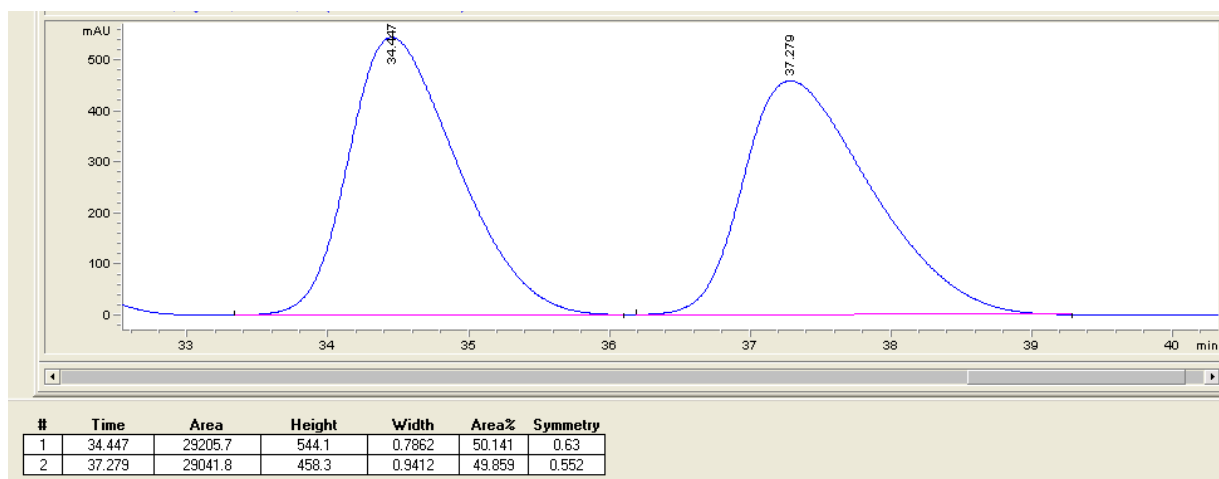
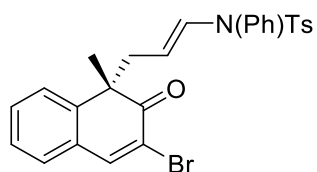
IC column, *n*-Hex:IPA 80:20, 1 mL/min, 30 °C. Rt(*R*): 21.64 min, Rt(*S*): 27.76 min



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(S)-**3ea**, Y = 24%, e.e. = 95%.

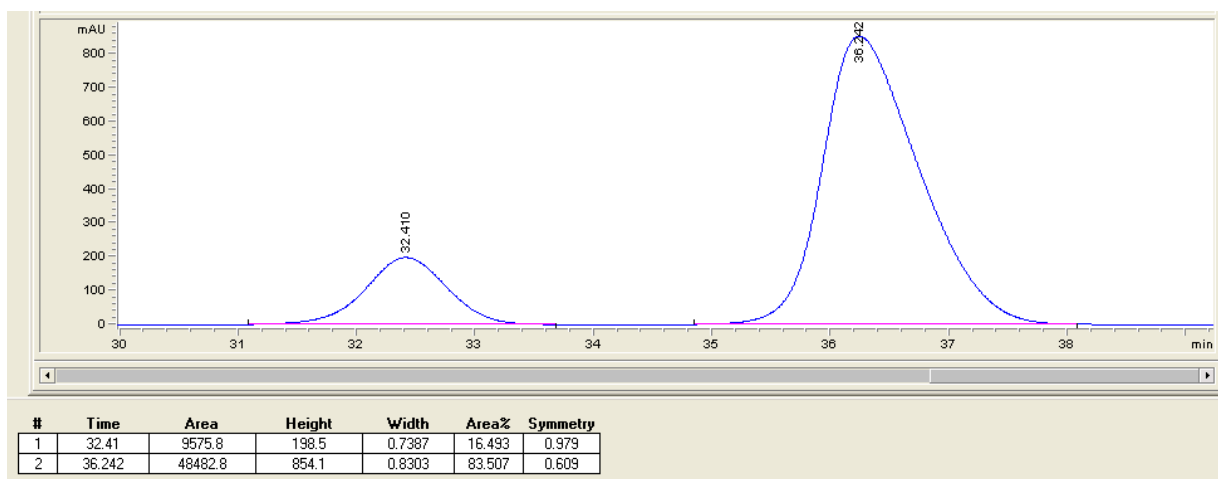
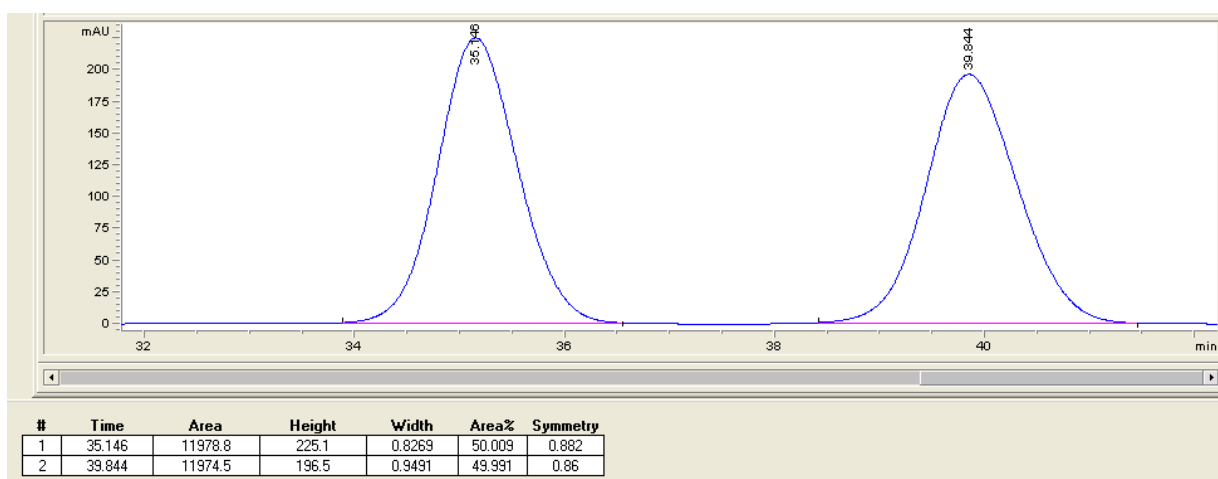
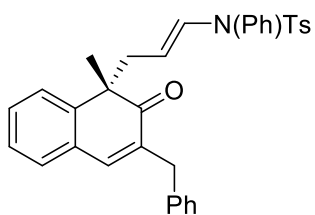
IC column, *n*-Hex:IPA 80:20, 1mL/min, 30°C. Rt(S): 34.44 min, Rt(R): 37.28 min



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(S)-**3fa**, Y = 49%, e.e. = 67%.

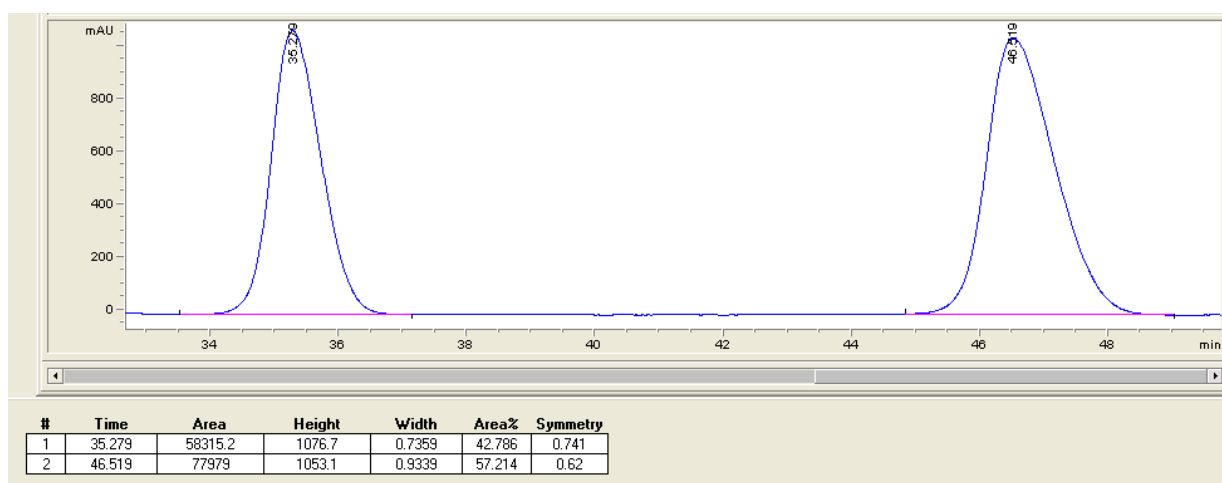
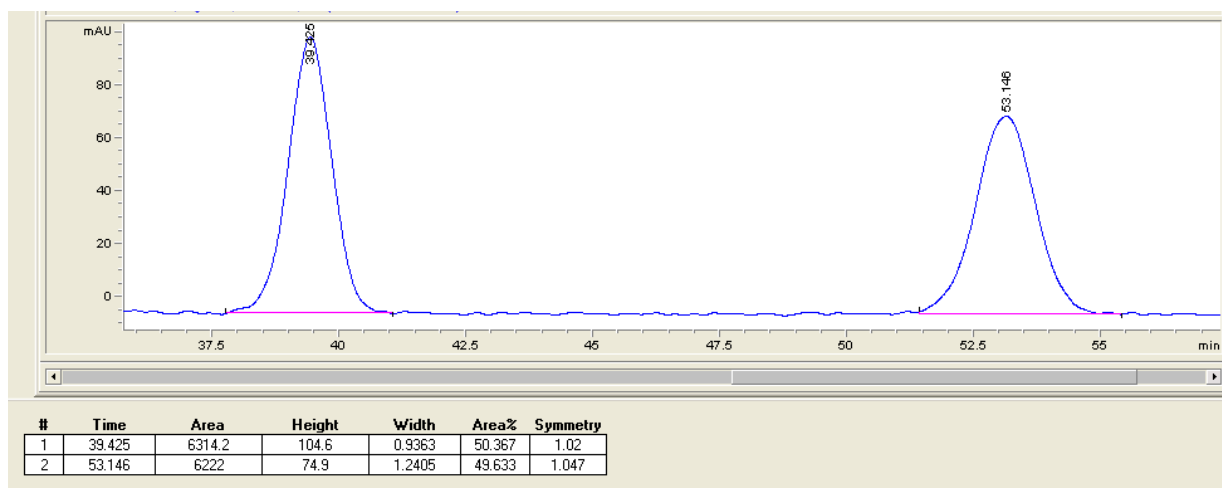
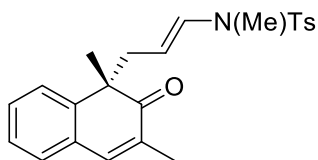
IC column, *n*-Hex:IPA 80:20, 0.7 mL/min, 30 °C. Rt(*R*): 35.15 min, Rt(*S*): 39.84 min



SUPPORTING INFORMATION

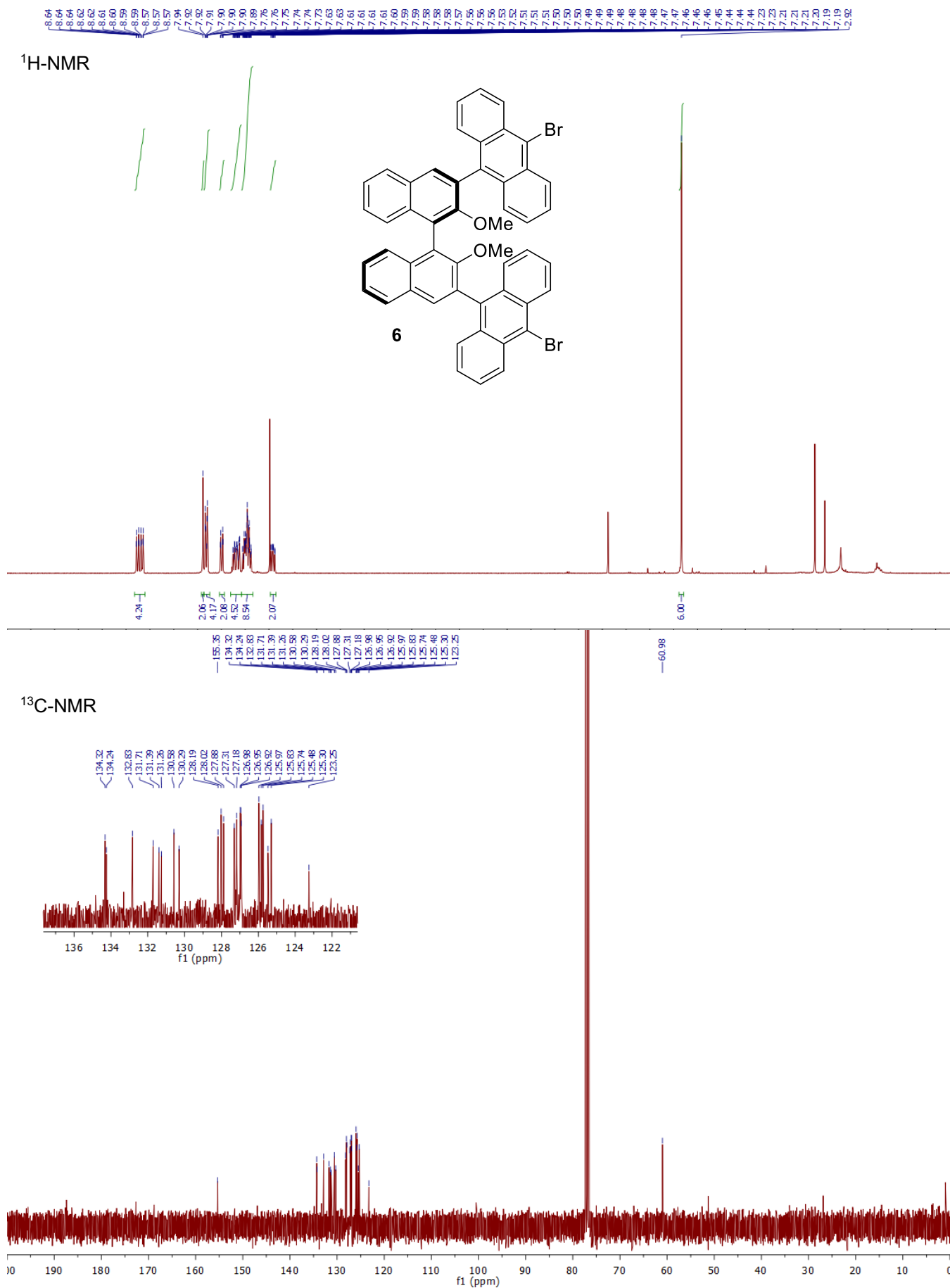
(S)-**3ac**, Y = 50%, e.e. = 5%.

IC column, *n*-Hex:IPA 80:20, 1 mL/min, 30 °C. Rt(*R*): 39.43 min, Rt(*S*): 53.14 min

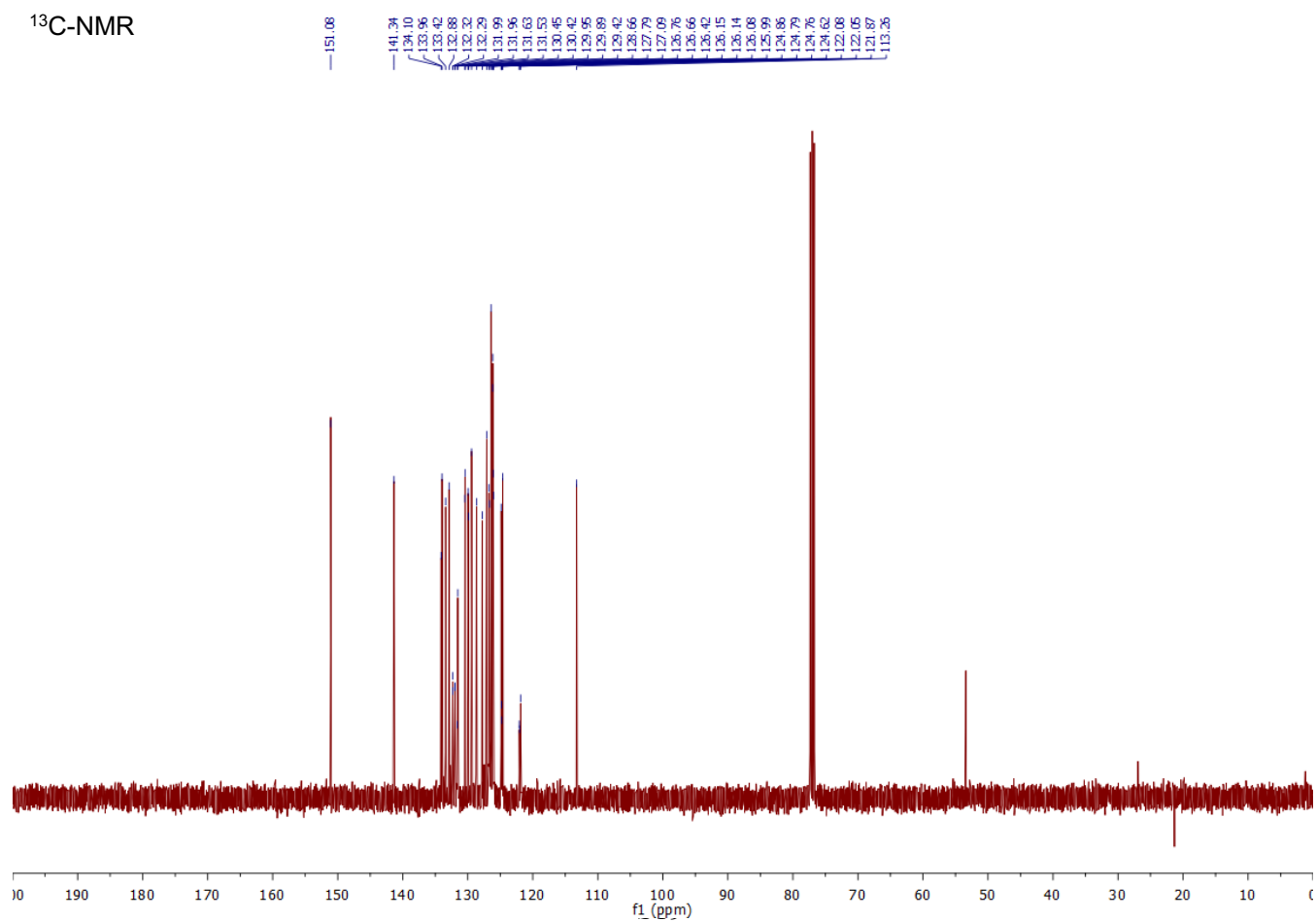
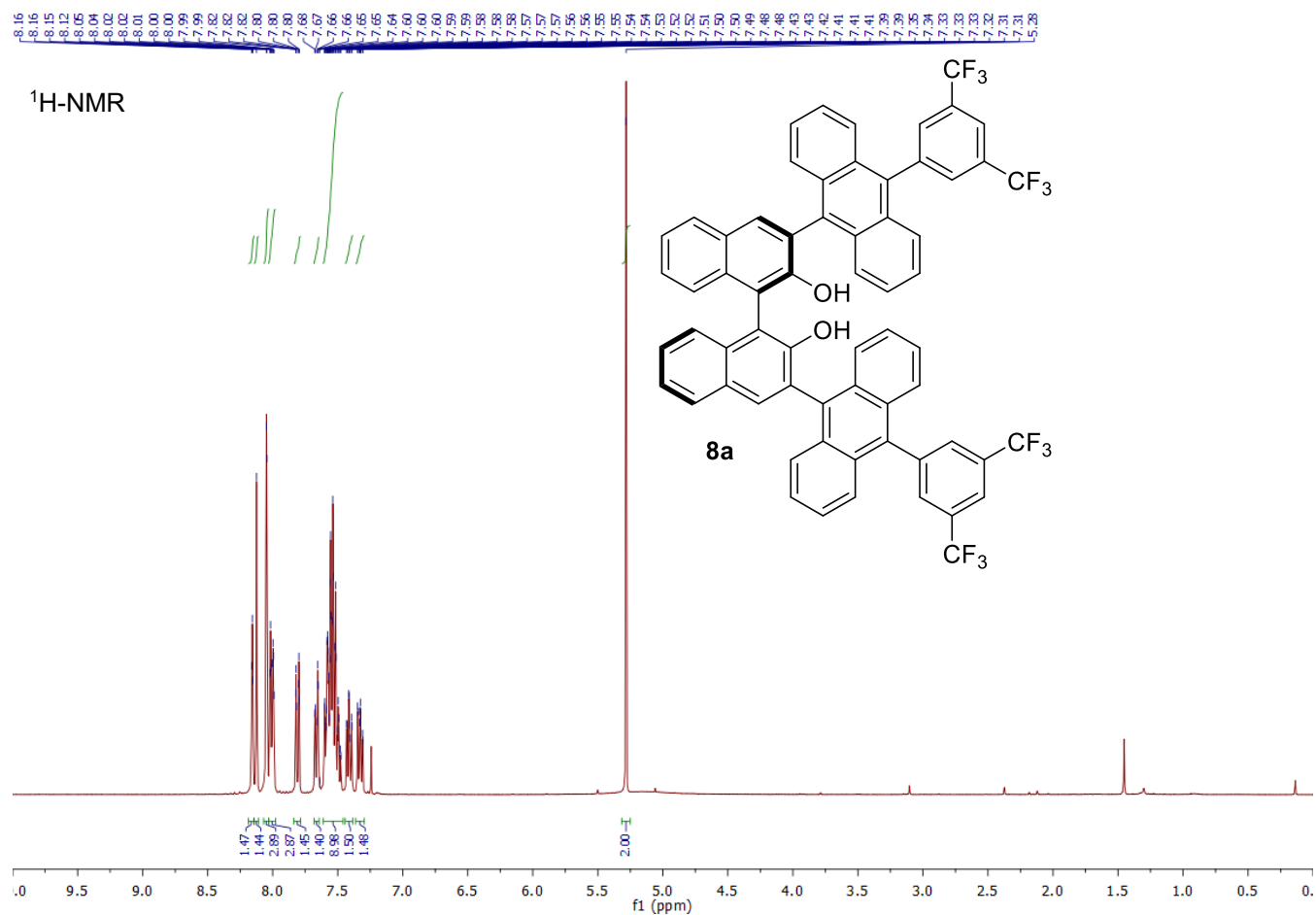


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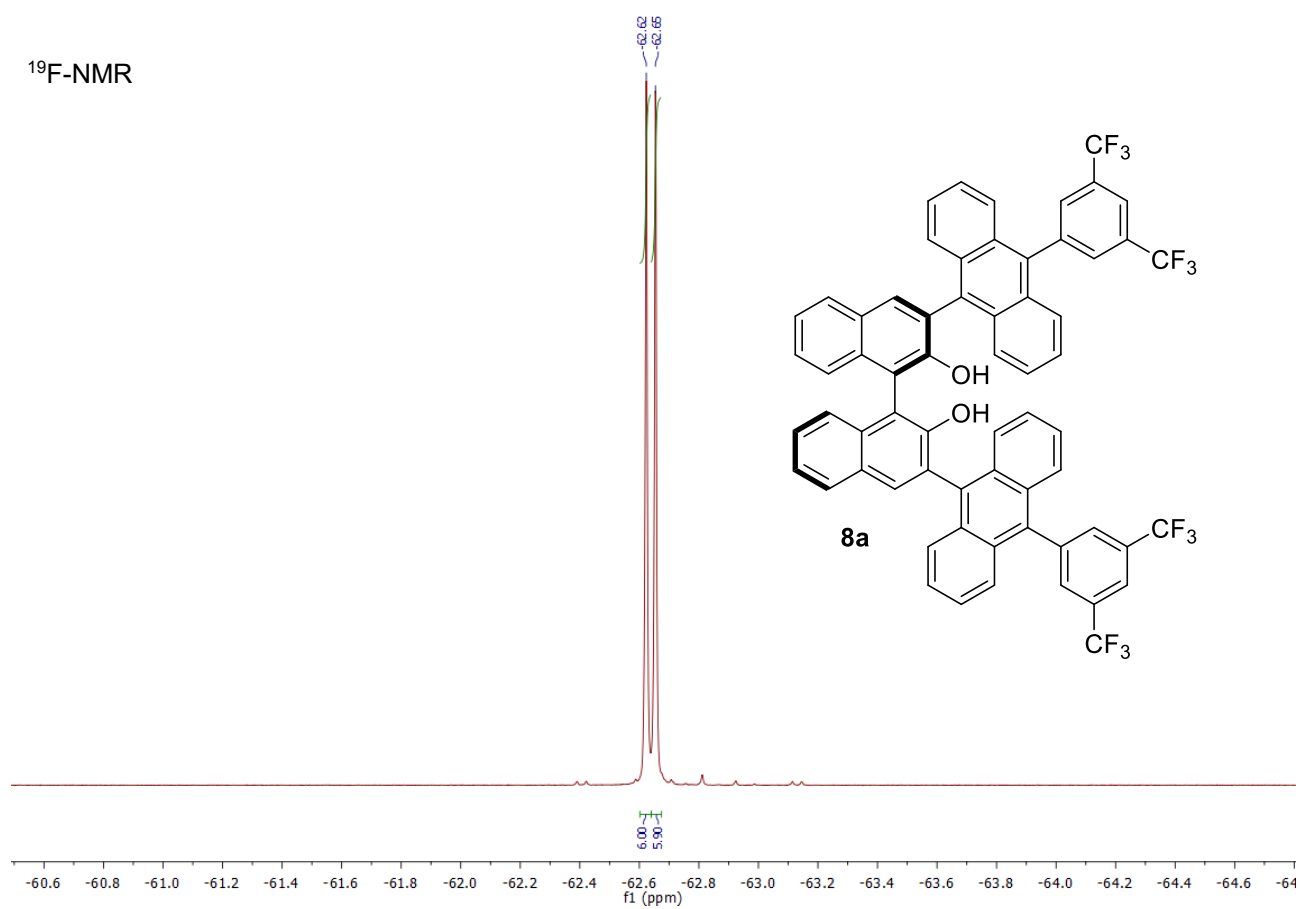
NMR Spectra

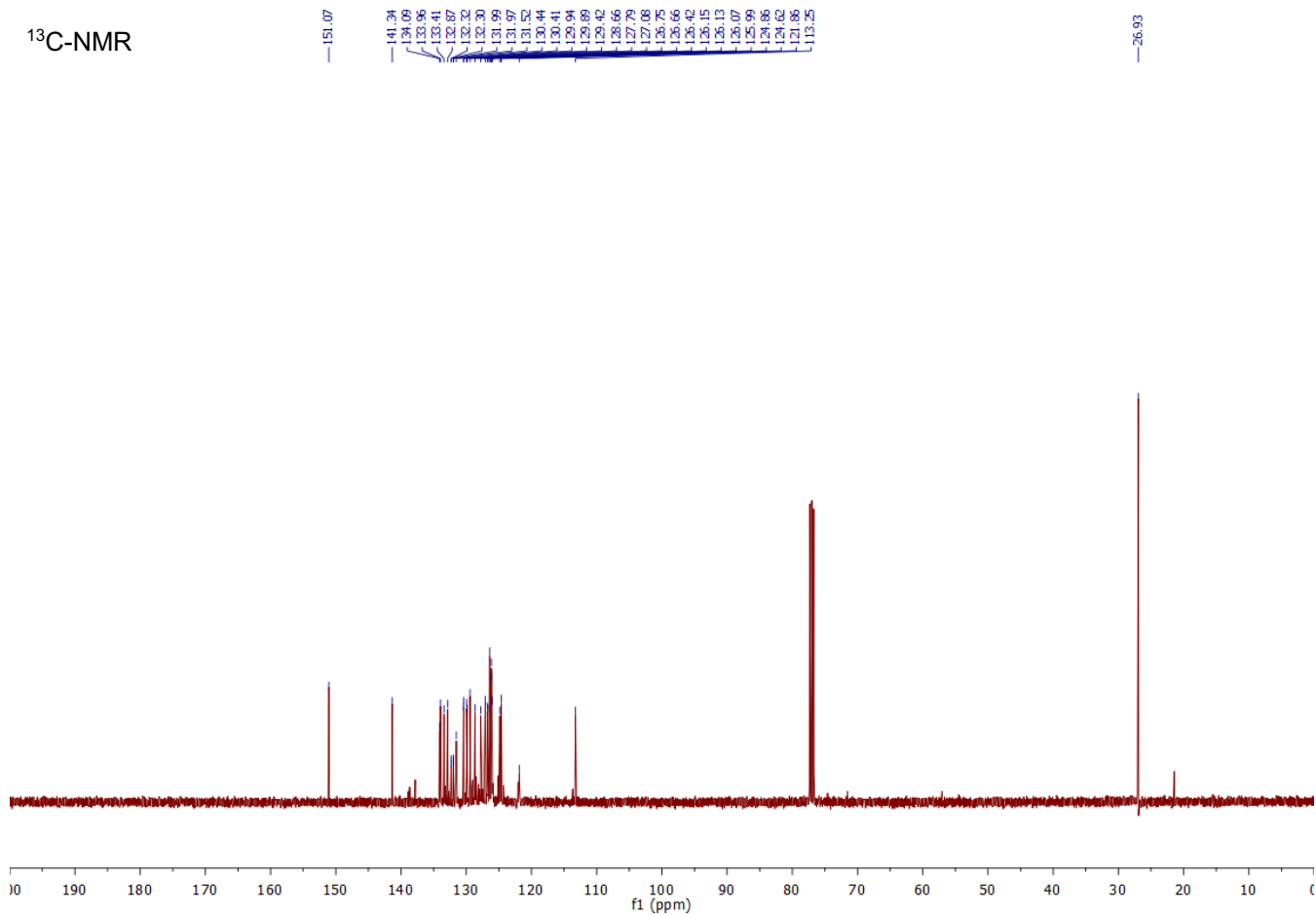
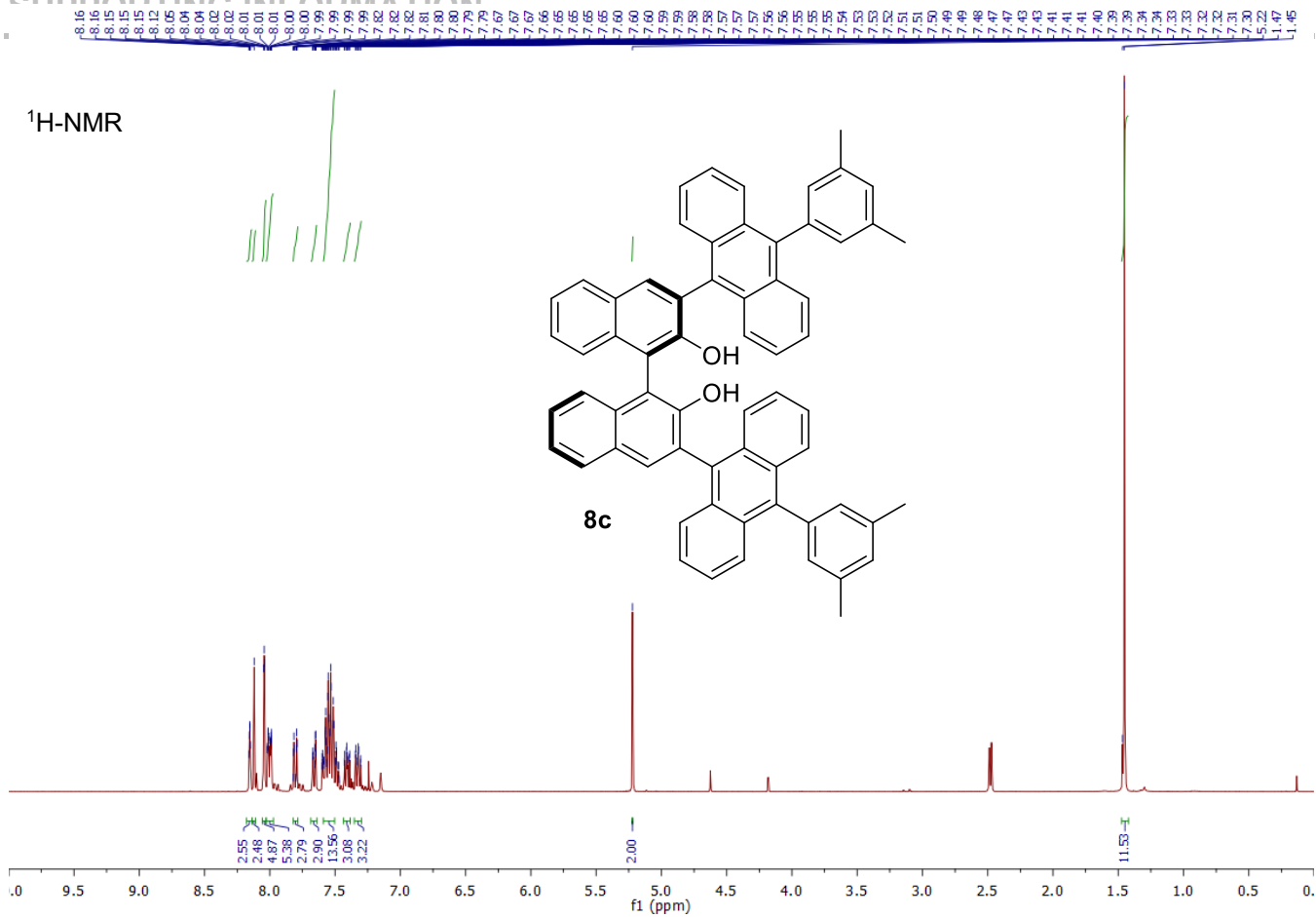


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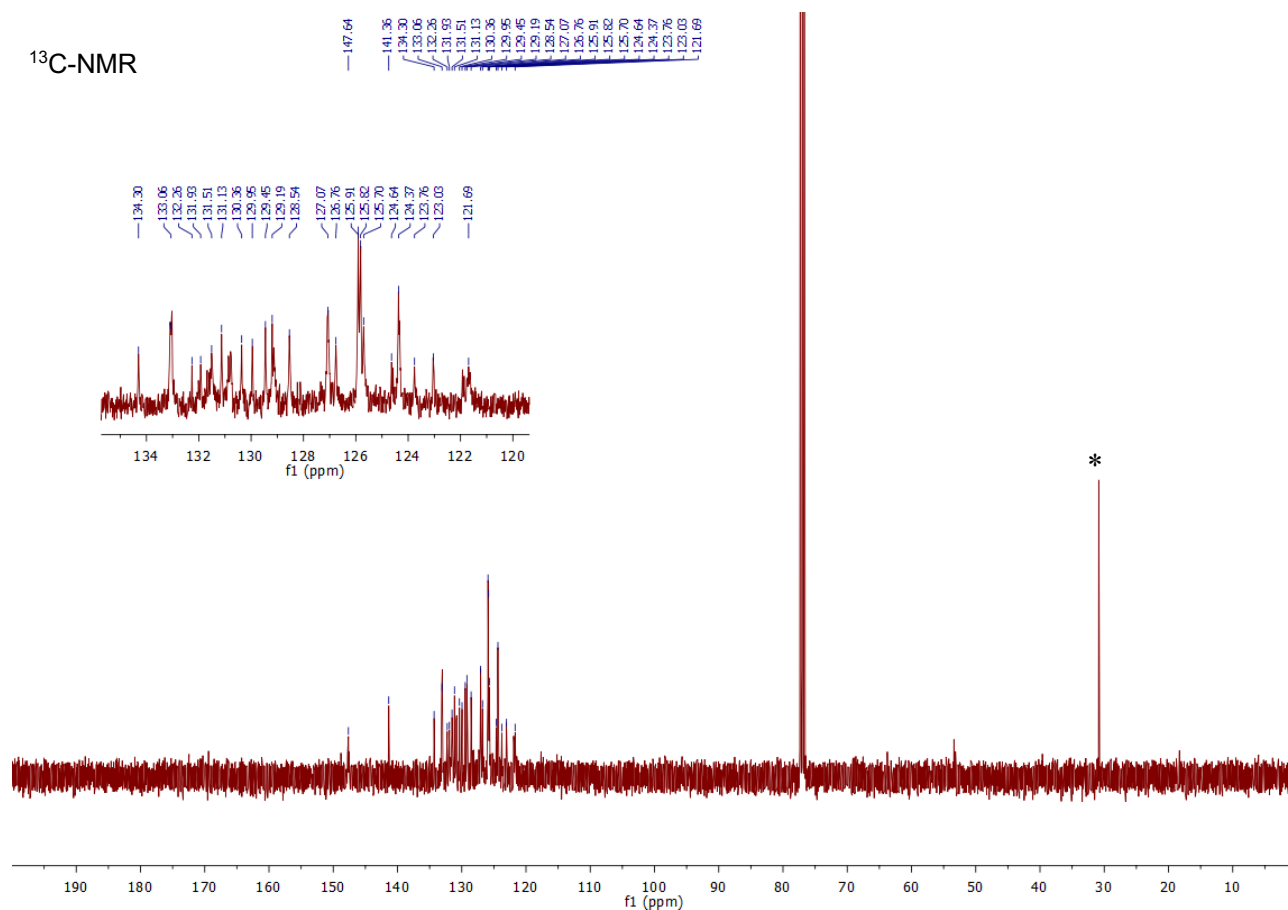
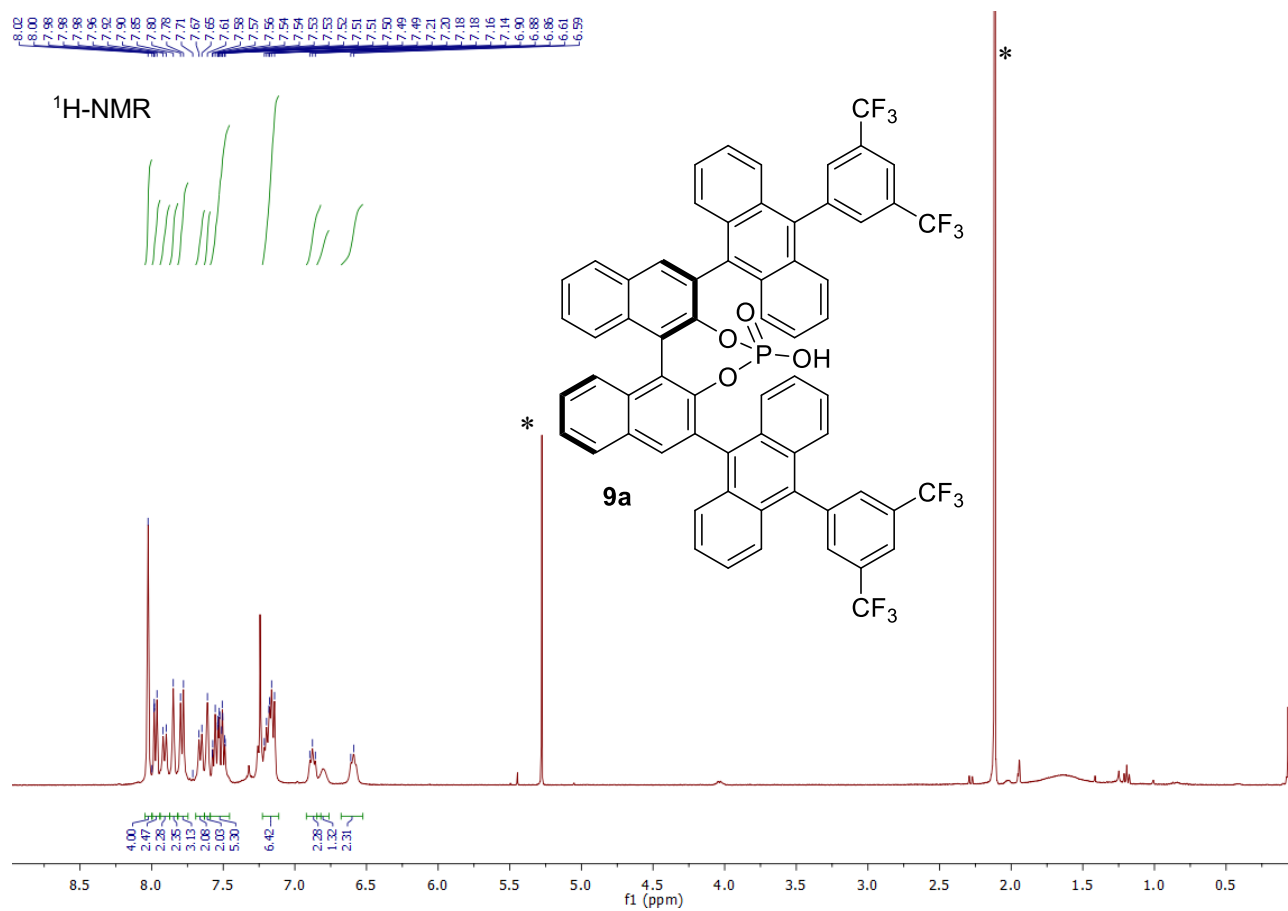


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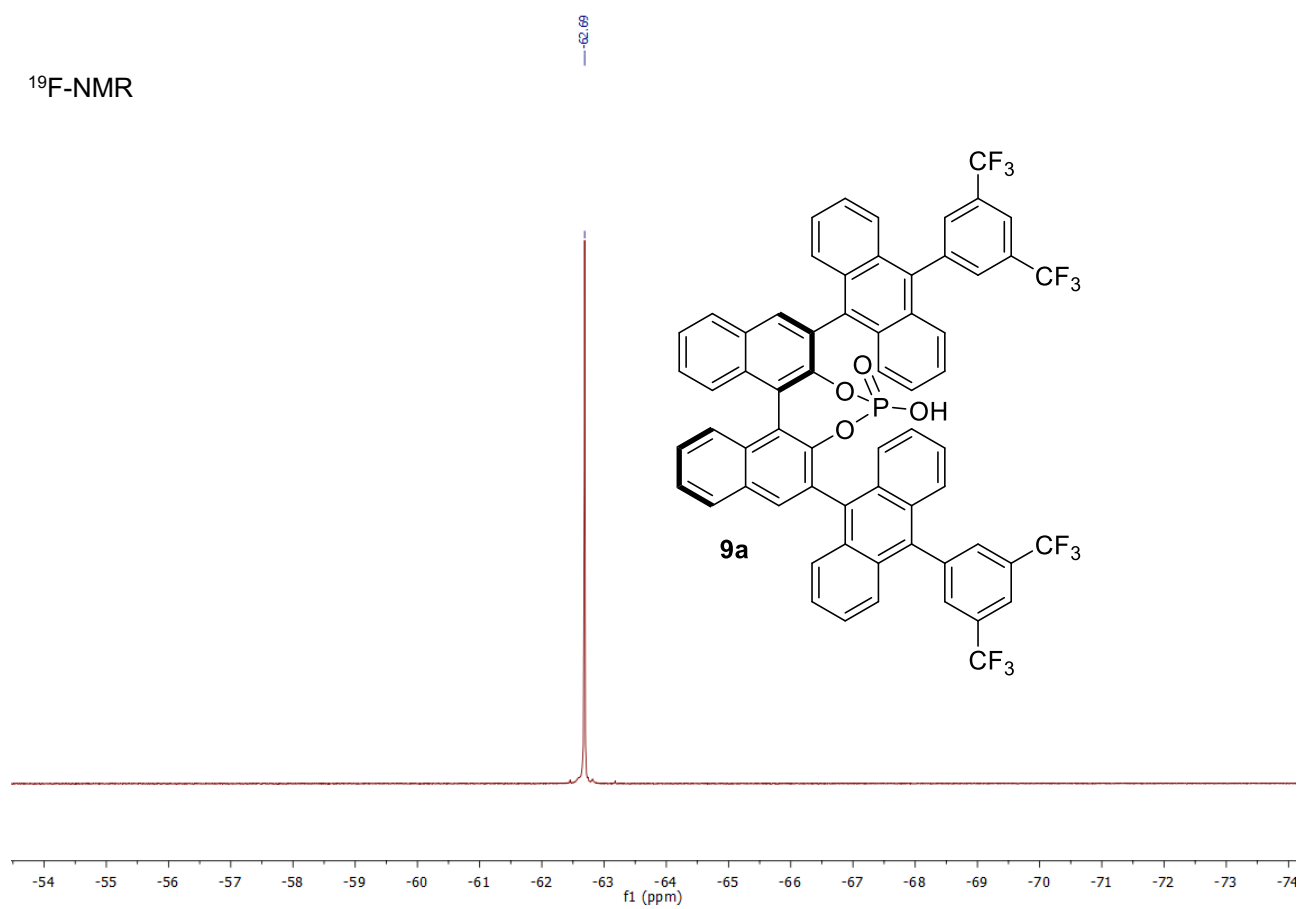
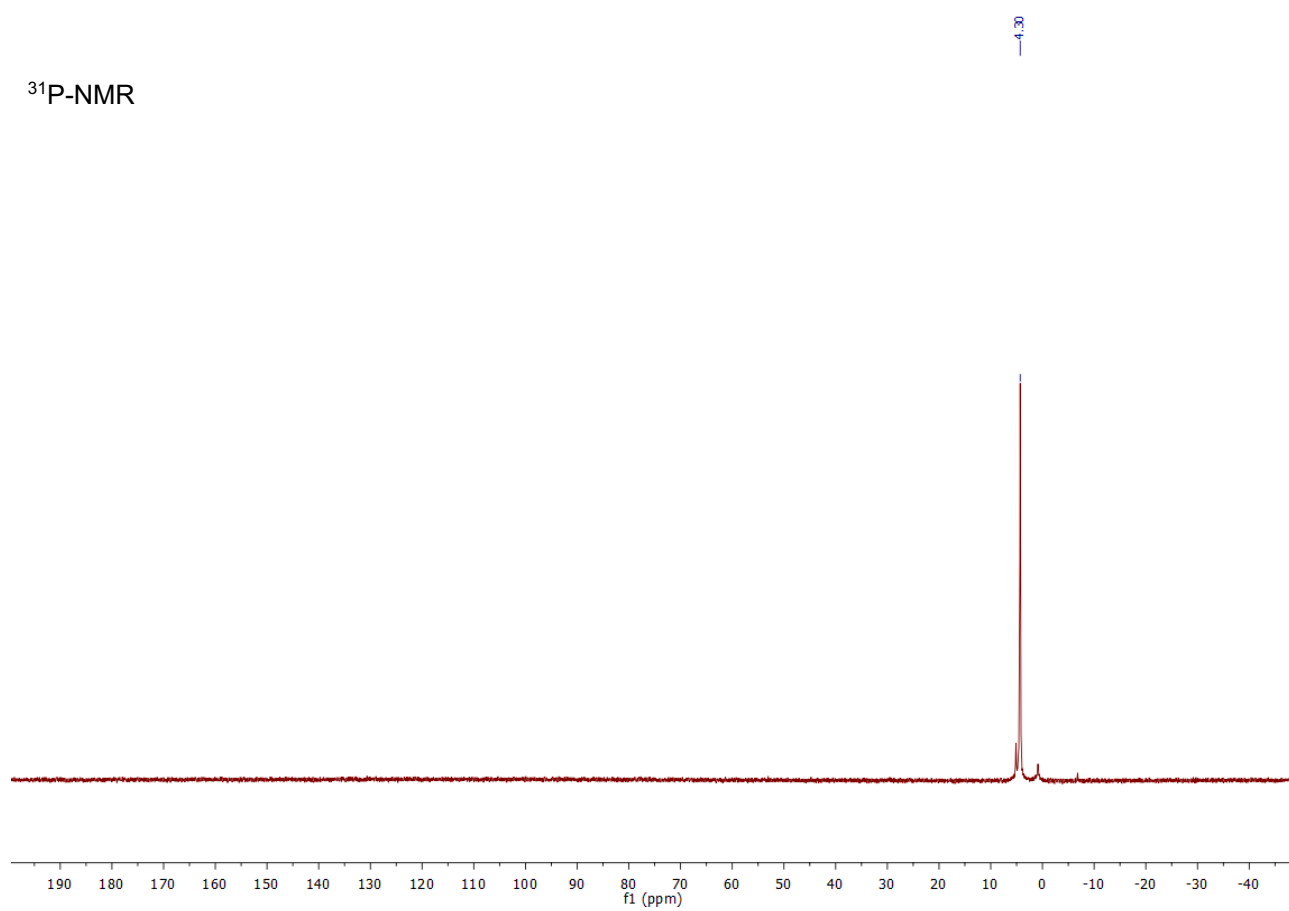
¹⁹F-NMR



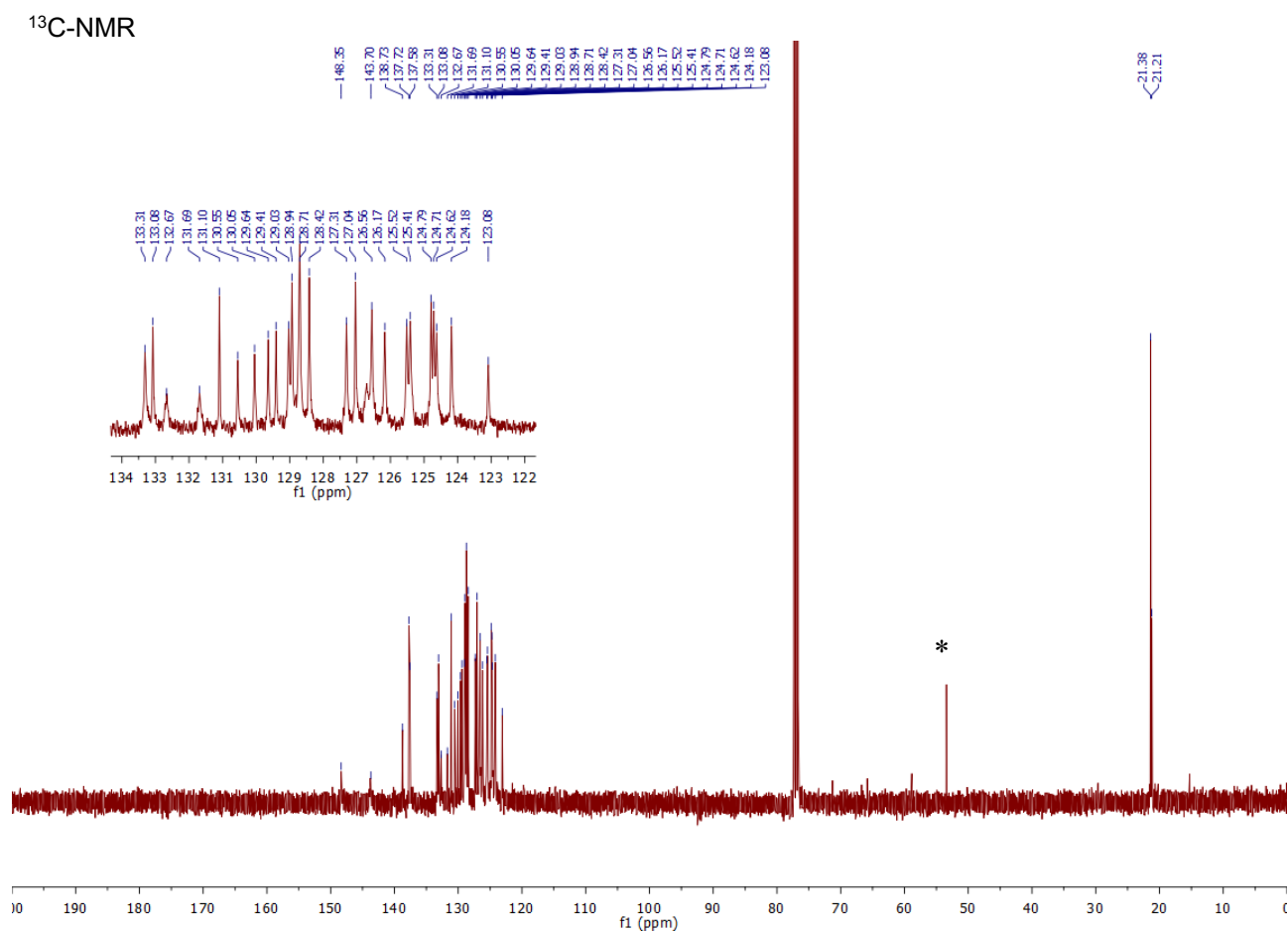
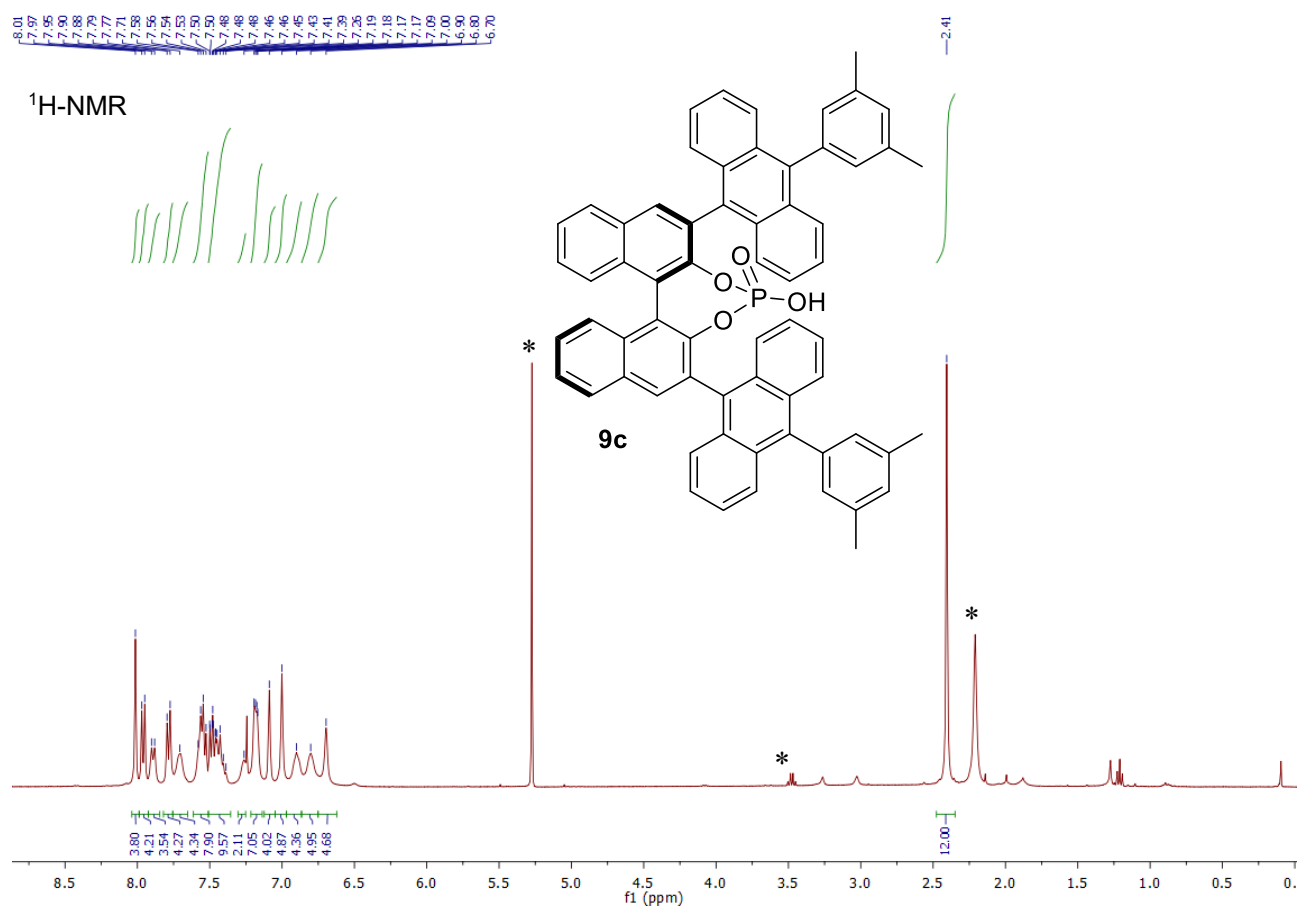
SUPPORTING INFORMATION



SUPPORTING INFORMATION

¹⁹F-NMR³¹P-NMR

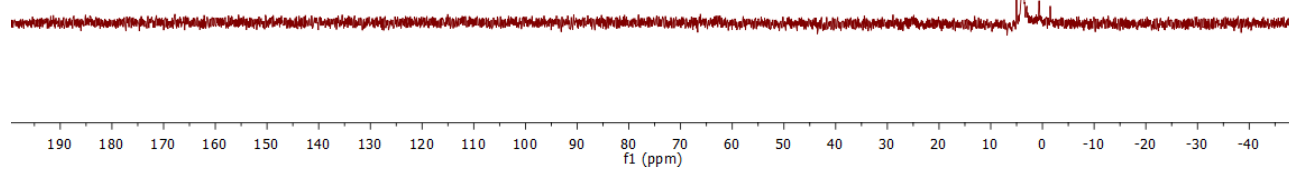
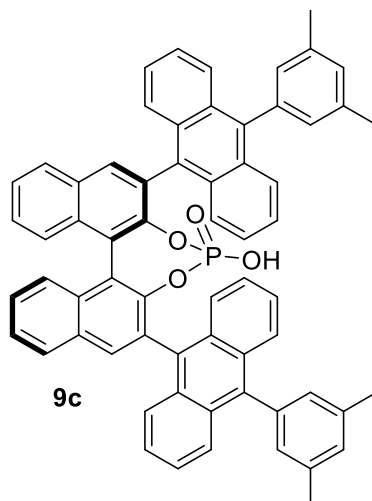
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 ^{31}P -NMR

-3.88



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References

- [1] F. Romanov-Michailidis, L. Guénée, A. Alexakis, *Angew. Chem. Int. Ed.*, **2013**, *52*, 35, 9266-9270
- [2] a) B. Heid, B. Plietker, *Synthesis* **2016**, *48*, 340-350; b) J. Nan, J. Liu, H. Zheng, Z. Zou, L. Hou, H. Hu, Y. Wang, X. Luan, *Angew. Chem., Int. Ed.* **2015**, *54*, 2356-2360.
- [3] A. González-Gómez, L. Añorbe, A. Poblador, G. Domínguez, J. Pérez-Castells, *Eur. J. Org. Chem.*, **2008**, 1370-1377.
- [4] Z.L. Xia, C. Zheng, X.W. Liang, Y. Cai, S.L. You, *Angew. Chem. Int. Ed.*, **2019**, *58*, 4, 1158-1162.
- [5] G. Lu, V.B. Birman, *Org. Lett.*, **2011**, *13*, 356-358.
- [6] J. An, L. Lombardi, S. Grilli, M. Bandini, *Org. Lett.* **2018**, *20*, 7380-7383
- [7] B. Yang, X. Zhai, S. Feng, D. Hu, Y. Deng, Z. Shao, *Org. Lett.* **2019**, *21*, 1, 330-334