Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Competing Amination and C-H Arylation Pathways in Pd/Xantphos-Catalyzed Transformations of Binaphthyl Triflates: Switchable Routes to Chiral Amines and Helicene Derivatives

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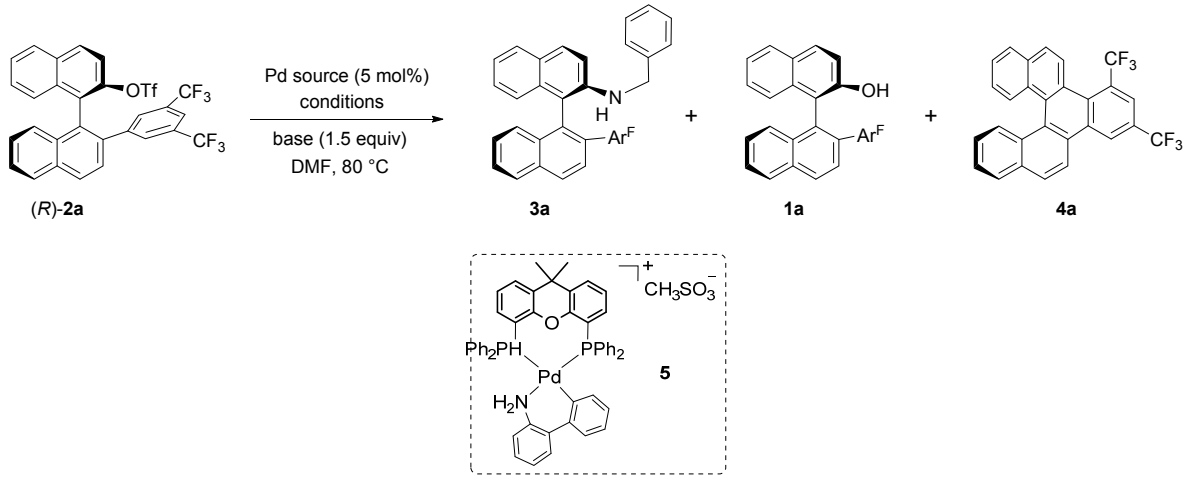
SUPPLEMENTARY INFORMATION

ADDITIONAL CATALYTIC RESULTS

Table S1 Variation of Pd source and base in catalytic intramolecular C-H arylation of **2a**[a]



entry	Pd source	mol% xantphos	equiv $PhCH_2NH_2$	base	t (h)	yield **3a** (%)[b]	yield **1a** (%)[b]	yield **4a** (%)[b]	recovered **2a** (%)[c]
1	$Pd(OAc)_2$	7.5	0	Cs_2CO_3	2	--	--	3	91
2	Pd_2dba_3[d]	7.5	0	Cs_2CO_3	3.5	--	89	5	<5
3	precatalyst **5**	--	0	Cs_2CO_3	3.5	--	21	64	8
4	$Pd(OAc)_2$	7.5	0.2	$CsHCO_3$	3.5	--	15	70	<5

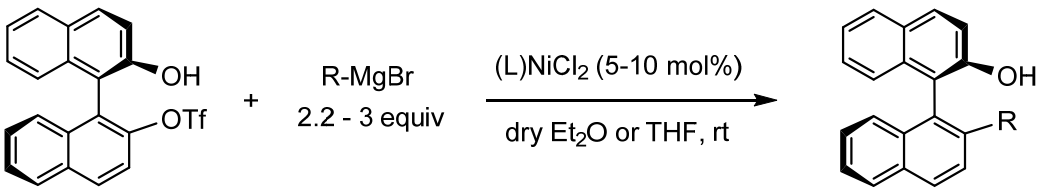
[a] Reaction conditions: **2a** (0.163 mmol), solvent (2.0 mL). [b] Isolated yields. [c] Remaining mass balance reflects losses during purification. [d] 2.5 mol% Pd_2dba_3; 5 mol% in Pd.

GENERAL EXPERIMENTAL CONSIDERATIONS

NMR spectra were recorded on Varian VNMRS 400 MHz or 500 MHz FT-NMR spectrometers. ^1H and ^{13}C NMR chemical shifts were referenced to solvent peaks.[1] ^{19}F NMR chemical shifts were referenced to *p*-fluoronitrobenzene at -103.0 ppm. Preparative flash column chromatography was performed on silica gel 60 (230-400 mesh) with solvent mixtures that gave optimal separations by TLC (specified along with R_f values in the characterization data given below).

SYNTHESIS OF BINAPHTHYL ALCOHOLS (1a-k, 7a/7b)

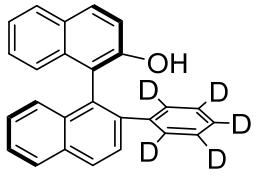
Alcohols **1a-e,i** were synthesized from (*R*)-BINOL monotriflate (*R*)-**11** according to Ni-catalyzed Kumada coupling procedures reported previously (Scheme S1).[2] Addition of a drop of 1,2-dibromoethane to the Mg/aryl bromide mixture was found to be beneficial for consistent initiation of Grignard formation. Alcohols **1f-h**,**k** and **7a/7b** were synthesized from (*R*)-**11** by modifications of these procedures as described below. Unsubstituted alcohol **1j** (R = H) was prepared according to the literature.[3]



(*R*)-**11** **1a-i,1k,7a/7b**

Scheme S1. Synthesis of binaphthyl alcohols.

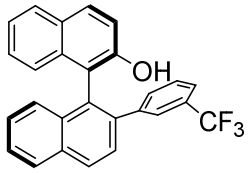
(*R*)-2'-Phenyl-*d*$_5$-[1,1'-binaphthalen]-2-ol (1b-*d*$_5$)



1b-*d*$_5$

The compound was prepared by the same procedure used to synthesize the perprotio analogue,[2] but with bromobenzene-*d*$_5$ (Cambridge Isotope Laboratories, 99.5% D) utilized in the Kumada coupling procedure. Optical rotation and melting point data were in agreement with published data for **1b**.[4] Yield 0.25 g, 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 9.2 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.8 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.63-7.58 (m, 2H), 7.47-7.41 (m, 2H), 7.38-7.32 (m, 2H), 7.30-7.24 (m, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 4.83 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.9, 146.3, 133.4, 133.4, 133.1, 131.8, 131.6, 129.3, 128.7, 128.5, 128.4, 127.8, 127.2, 126.6, 125.3, 124.4, 124.0, 120.0, 118.1, 116.8, 112.3. HRMS (ESI-orbitrap, $[C_{26}H_{13}D_5O + Na]^+$) calcd 374.1569, found m/z 374.1588.

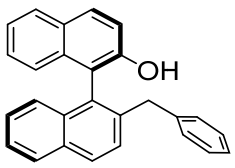
(*R*)-2′-[3-(Trifluoromethyl)phenyl]-[1,1′-binaphthalen]-2-ol (1f)



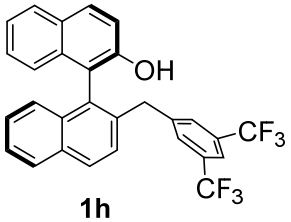
1f

Compound **1f** was prepared by the same Kumada coupling procedure used to synthesize **1a**, with 2.2 equiv of Grignard reagent and 5 mol% $NiCl_2$(dppe) catalyst in Et_2O at 25 °C.[2] R_f 0.56 (2:3 CH_2Cl_2/hexanes); white solid, mp = 143-144 °C, yield 1.03 g, 52%; $[\alpha]_D^{24}$ = +6.4 (*c* = 0.2, THF), *er* = 4.1(*S*):95.9(*R*), determined by chiral HPLC (Chiralpak IC column, 4.6 x 250 mm, 5 μm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 2.0 MPa, flow rate: 0.5 mL/min, t_R (*S*)= 8.2 min, t_R (*R*)= 10.2 min). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.5 Hz, 1H), 8.15 (d, *J* = 8.5 Hz, 1H) 8.05 (d, *J* = 8.0 Hz, 1H), 7.82–7.91 (m, 2H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.60–7.57 (m, 1H), 7.43 (s, 1H), 7.41–7.39 (m, 2H), 7.34–7.16 (m, 5H), 7.08 (d, *J* = 8.0 Hz, 1H), 4.82 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.3, 141.7, 140.2, 134.1, 133.6, 133.2, 132.0, 131.9, 130.6 (q, $^2J_{(C,F)}$ = 32 Hz), 130.3, 129.8, 129.4, 129.0, 128.4, 128.3, 128.2, 128.1, 127.6, 127.0, 127.0, 126.7 (q, $^1J_{(C,F)}$= 272 Hz), 126.5, 125.8 (q, $^3J_{(C,F)}$ = 3.7 Hz), 124.8, 123.9 (q, $^3J_{(C,F)}$ = 3.7Hz), 123.5, 117.3 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.9. Anal. Calcd for $C_{27}H_{17}F_3O$: C, 78.25; H, 4.13%. Found: C, 78.34; H, 4.17%.

Modified procedure for synthesis of 1g and 1h.



1g

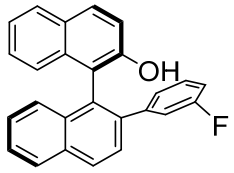


1h

The following was developed as a user-friendly alternative to the highly air-sensitive phosphinan-2-ol/Ni catalyst previously used for couplings of **11** with benzylic Grignard reagents.[2] The corresponding benzyl bromide (3.0 equiv) was added dropwise to a volume of dry diethyl ether (sufficient to give 0.1 *M* Grignard) containing magnesium turnings (3.1 equiv). Iodine (5 mol%) was added to initiate the reaction, and the mixture was stirred at 0 °C until consumption of magnesium was

complete. The freshly prepared Grignard reagent was allowed to warm to room temperature and then transferred by cannula into a diethyl ether solution of (*R*)-**11** (3.6 – 4.8 mmol) and $NiCl_2$(xantphos)[5] (10 mol%), and the reaction was stirred at room temperature. The reaction was monitored by TLC until complete consumption of starting material was observed. The reaction was quenched with aqueous NH_4Cl and extracted with diethyl ether. The combined organic extracts were dried over sodium sulfate and then concentrated under reduced pressure. The products were purified via column chromatography over silica. ^{1}H NMR spectral data and optical rotations matched those previously reported.[2] **1g**: Yield 1.01 g, 78%. **1h**: Yield 1.87 g, 79%.

(*R*)-2'-[3-(Fluoro)phenyl]-[1,1'-binaphthalen]-2-ol (1k)

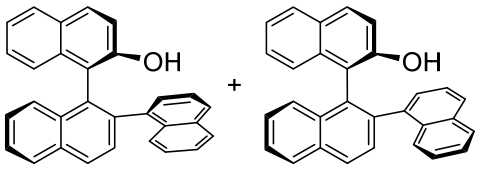


1k

3-Fluorobromobenzene (1.0 g, 3 equiv) was added dropwise to 60 mL of dry THF (sufficient to give 0.1 *M* Grignard) containing magnesium turnings (150 mg, 3.1 equiv).. A drop of 1,2-dibromoethane was added to initiate the reaction, and the mixture was heated to 50 °C and stirred until consumption of magnesium was complete. The freshly prepared Grignard reagent was allowed to cool to room temperature and then transferred by cannula into a THF solution of (*R*)-**11** (860 mg, 2.0 mmol) and $NiCl_2$(dppe) (10 mol%). The reaction mixture was stirred at room temperature and monitored by TLC until consumption of starting material was complete. The reaction was quenched with aqueous NH_4Cl and extracted with diethyl ether. The organic extracts were dried over sodium sulfate and then concentrated under reduced pressure. The product was purified via column chromatography over silica. R_f 0.48 (2:3 CH_2Cl_2/hexanes); white solid, mp = 152-153 °C, yield 0.57 g, 78%; $[\alpha]_D^{24}$ = +14.3 (*c* = 0.2, THF), *er* = 0.6(*S*):99.4(*R*), determined by chiral HPLC (Chiralpak IA column, 4.6 x 250 mm, 5 μm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.7 MPa, flow rate: 1.0 mL/min, t_R (*S*)= 9.7 min, t_R (*R*)= 15.3 min). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.5 Hz, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.81 (t, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.55-7.52 (m, 1H), 7.37-7.20 (m, 4H),

7.17 (d, J = 8.5 Hz, 1H), 7.04 (d, J = 8 Hz, 1H), 7.01-6.75 (m, 4H), 4.79 (bs, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.2 (d, $^1J_{(C,F)}$ = 246 Hz), 151.1, 143.2 (d, $^3J_{(C,F)}$ = 7.9 Hz), 140.4, 134.1, 133.5 (d, $^2J_{(C,F)}$ = 41 Hz), 130.2, 129.7, 129.3, 129.2, 128.9, 128.88, 128.4, 128.3, 128.28, 127.5, 126.9, 126.86, 126.5, 124.9, 124.6, 124.5, 123.5, 117.4, 117.3, 115.9, 115.7, 114.1, 114.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ –113.8 (m). Anal. Calcd for $C_{26}H_{17}FO$: C, 78.24; H, 4.14%. Found: C, 78.08; H, 4.31%.

(*R*,*S*)/(*R*/*R*)-[1,1':2',1''-Ternaphthalen]-2-ol (7a/7b):



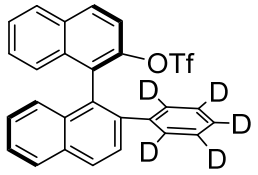
7a **7b**

A 1:1 diastereomeric mixture of **7a** and **7b** was obtained by the same Kumada coupling procedure used to synthesize **1a**, with 2.2 equiv of 1-naphthyl Grignard and 5 mol% $NiCl_2$(dppe) catalyst in Et_2O at 25 °C.[2]. R_f 0.47 (2:3 CH_2Cl_2/hexanes); white solid, mp = 130-131 °C, yield 0.90 g, 71%; $[\alpha]_D^{24}$ = +146.0 (c = 0.15, THF). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.4 Hz, 2H), 8.03 (dd, J = 8.4 and 3.6 Hz, 2H), 7.80-7.77 (m, 7H), 7.64-7.50 (m, 9H), 7.44-7.34 (m, 5H), 7.33-7.22 (m, 9H), 7.16 (d, J = 8.8 Hz, 1H), 7.07 (d, J = 8.4 Hz, 1H), 6.99-6.82 (m, 4H), 4.99 (s, 1H), 4.65 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.3, 151.0, 140.9, 139.9, 138.3, 137.8, 135.0, 133.9, 133.7, 133.5, 133.5, 133.4, 133.2, 132.0, 131.7, 130.7, 130.3, 130.2, 129.9, 129.8, 129.6, 128.9, 128.7, 128.6, 128.5, 128.5, 128.4, 128.2, 128.2, 127.8, 127.7, 127.6, 127.5, 127.2, 126.8, 126.8, 126.7, 126.7, 126.3, 126.3, 126.2, 125.9, 125.7, 125.6, 125.5, 125.4, 125.3, 125.2, 125.1, 124.4, 123.4, 123.2, 123.2, 118.1, 117.8, 117.6, 116.9. Anal. Calcd for $C_{30}H_{20}O$: C, 90.88; H, 5.08%. Found: C, 91.08; H, 5.27%.

CHARACTERIZATION DATA

Binaphthyl 2-triflates (2a-2k, 8a/8b). Compounds **2a**, **2b**, and **2j** were synthesized as reported in a prior communication,[6] and their characterization data matched those previously published.[6] Some of the triflates were prone to degradation upon extended workup, so the compounds were generally used immediately in subsequent reactions without chromatographic purification or recrystallization.

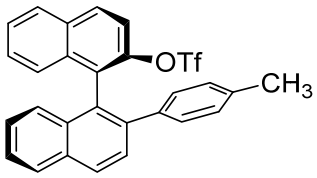
(*R*)-2'-Phenyl-*d*$_5$-[1,1'-binaphthalen]-2-yl trifluoromethanesulfonate (2b-*d*$_5$)



2b-*d*$_5$

White solid, yield 0.32 g, 93%. The phenyl group is 99.4% deuterated as determined by HRMS. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.98-7.88 (m, 3H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.57-7.41 (m, 4H), 7.32-7.26 (m, 2H), 7.16 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): 144.8, 141.2, 140.9, 134.7, 132.9, 132.8, 132.1, 130.5, 129.8, 129.6, 128.5, 128.3, 128.2, 128.1, 127.9, 127.5, 127.0, 127.0, 126.7, 126.7, 126.1, 122.0 (q, ^1J(C,F) = 319 Hz; CF_3), 119.6. HRMS (ESI-orbitrap, $[C_{27}H_{12}D_5F_3O_3S + Na]^+$) calcd 506.1062, found m/z 506.1063.

(*R*)-2′-[4-(Methyl)phenyl]-[1,1′-binaphthalen]-2-yl trifluoromethanesulfonate (2c)

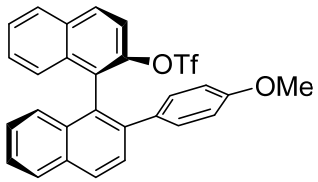


2c

R_f 0.69 (3:7 diethyl ether/hexanes); white solid, mp = 77-78 °C, yield 3.1 g, 93%; $[\alpha]_D^{24}$ = +28.5 (*c* = 0.70, THF). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.8 Hz, 1H), 7.96 (t, *J* = 8.0 Hz, 2H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.58-7.54 (m, 1H), 7.48 (t, *J* = 8.4 Hz, 1H), 7.44-7.40 (m, 1H), 7.31 (d, *J* = 8.8 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 8.4 Hz,

1H), 6.93 (d, J = 8.0 Hz, 2H), 6.86 (d, J = 8.4 Hz, 2H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 141.0, 138.4, 136.5, 134.7, 133.0, 132.7, 132.1, 130.4, 129.9, 129.5, 128.7, 128.5, 128.5, 128.4, 128.1, 127.9, 127.9, 127.5, 127.0, 126.6, 126.0, 119.7, 118.1 (q, $^1J_{(C,F)}$ = 320 Hz), 21.2. HRMS (ESI-orbitrap, $[C_{28}H_{19}F_3O_3S + H]^+$) calcd 493.1085, found m/z 493.1072.

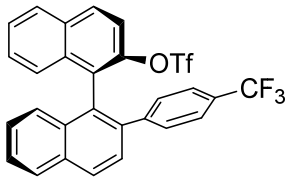
(*R*)-2′-[4-(Methoxy)phenyl]-[1,1′-binaphthalen]-2-yl trifluoromethanesulfonate (2d)



2d

R_f 0.52 (1:9 acetone/hexanes); white solid, mp = 90-91 °C, yield 3.1 g, 96%; $[\alpha]_D^{24}$ = +53.1 (c = 0.60, THF). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.4 Hz, 1H), 7.95 (dd, J = 8.4, 3.6 Hz, 2H), 7.91 (d, J = 9.2 Hz, 1H), 7.65 (d, J = 8.4 Hz, 1H), 7.58-7.54 (m, 1H), 7.50-7.46 (m, 2H), 7.44-7.40 (m, 1H), 7.32-7.27 (m, 2H), 7.15 (d, J = 8.8 Hz, 1H), 6.96-6.93 (m, 2H), 6.61-6.57 (m, 2H), 3.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 158.5, 144.7, 140.6, 134.6, 133.8, 133.0, 132.6, 132.1, 130.4, 130.0, 129.9, 129.5, 128.5, 128.1, 127.9, 127.5, 127.0, 126.9, 126.6, 125.9, 122.9 (q, $^1J_{(C,F)}$ = 320 Hz), 119.7, 116.6, 113.2, 55.2. HRMS (ESI-orbitrap, $[C_{28}H_{19}F_3O_4S + H]^+$) calcd 509.1034, found m/z 509.1051.

(*R*)-2′-[4-(Trifluoromethyl)phenyl]-[1,1′-binaphthalen]-2-yl trifluoromethanesulfonate (2e)

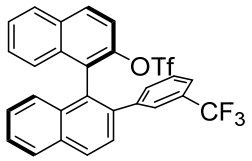


2e

R_f 0.55 (1:9 acetone/hexanes); sticky white solid, yield 3.5 g, 98%; $[\alpha]_D^{24}$ = +19.5 (c = 0.35, THF). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.4 Hz, 1H), 7.97 (t, J = 9.2 Hz, 2H), 7.94 (d, J = 9.2 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.60-7.56 (m, 1H), 7.55-7.50 (m, 1H), 7.46-7.42 (m, 2H), 7.35-7.28 (m, 4H), 7.18 (d, J = 8.4 Hz, 1H), 7.14 (d, J = 8.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 144.8, 139.5, 134.4, 133.1, 132.9, 132.1, 130.9, 129.9, 129.2, 129.1 (q, $^2J_{(C,F)}$ =

32.4 Hz), 128.6, 128.4, 128.2, 128.1, 127.7, 127.2, 127.2, 127.1, 127.0, 126.6, 124.7 (q, $^{3}J_{(C,F)}$ = 3.7 Hz), 124.2 (q, $^{1}J_{(C,F)}$ = 272 Hz), 119.6, 118.2 (q, $^{1}J_{(C,F)}$ = 320 Hz). HRMS (ESI-orbitrap, $[C_{28}H_{16}F_6O_3S + H]^+$) calcd 547.0804, found m/z 547.0851.

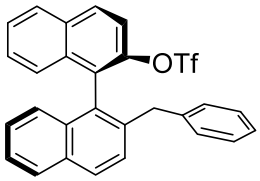
(*R*)-2'-[3-(Trifluoromethyl)phenyl)-[1,1'-binaphthalen]-2-ol (2f)



2f

R_f 0.62 (2:3 CH_2Cl_2/hexanes); white solid, mp = 116-117 °C, yield 0.58 g, 89%; $[\alpha]_D^{24}$ = +28.1 (*c* = 0.2 THF). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 9.0 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 9 Hz, 1H), 7.95 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 9.5 Hz, 1H), 7.68–7.26 (m, 9H), 7.19 (d, *J* = 8.5 Hz, 1H). Prone to degradation in solution or on standing as a solid; used as obtained without collecting further characterization data.

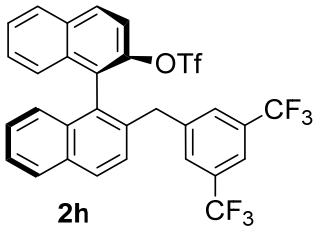
(*S*)-2′-Benzyl-[1,1′-binaphthalen]-2-yl trifluoromethanesulfonate (2g)



2g

R_f 0.49 (1:9 acetone/hexanes); sensitive viscous oil, yield 1.5 g, 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.8 Hz, 1H), 7.99-7.89 (m, 3H), 7.59-7.25 (m, 7H), 7.22 (d, *J* = 8.8 Hz, 1H), 7.12 (m, 4H), 6.90 (m, 2H), 3.87 (AB, *J* = 16 Hz, *C* = 27 Hz, 2H)[7]. Prone to degradation in solution or on standing; used as obtained without collecting further characterization data.

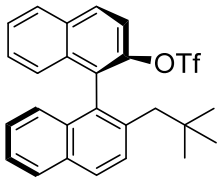
(*S*)-2'-[3,5-Bis(trifluoromethyl)benzyl]-[1,1'-binaphthalen]-2-yl trifluoromethanesulfonate (2h)



2h

R_f 0.60 (1:9 acetone/hexanes); sensitive viscous oil, yield 0.90 g, 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (m, 2H), 7.98 (t, *J* = 8.8 Hz, 2H), 7.61-7.47 (m, 5H), 7.33 (t, *J* = 8 Hz, 1H), 7.24 (m, 1H), 7.20 (s, 2H), 7.15 (d, *J* = 8 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 1H), 4.03 (AB, *J* = 16 Hz, *C* = 28 Hz, 2H).[7] Prone to degradation in solution or on standing; used as obtained without collecting further characterization data.

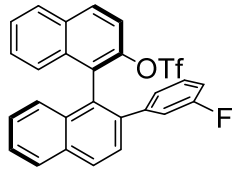
(*S*)-2′-Neopentyl-[1,1′-binaphthalen]-2-yl trifluoromethanesulfonate (2i)



2i

R_f 0.59 (1:9 acetone/hexanes); sensitive viscous oil, yield 1.5 g, 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 9.2 Hz, 1H), 7.98-7.88 (m, 3H), 7.62-7.51 (m, 3H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.33 (d, *J* = 8 Hz, 2H), 7.24 (m, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 2.57 (AB, *J* = 14 Hz, *C* = 21.1 Hz, 2H), 0.68 (s, 9H). Prone to degradation in solution or on standing; used as obtained without collecting further characterization data.

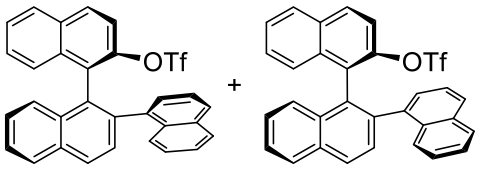
(*R*)-2'-[3-(Fluoro)phenyl]-[1,1'-binaphthalen]-2-ol (2k)



2k

R_f 0.59 (2:3 CH_2Cl_2/hexanes); white solid, mp = 111-112 °C, yield 0.63 g, 92%; $[\alpha]_D^{24}$ = +2.8 (*c* = 0.2, THF). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.5 Hz, 1H), 8.00 (m, 3H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.58-7.55 (m, 1H), 7.53 (t, *J* = 7 Hz, 1H), 7.46-6.77 (m, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.2, 161.2, 144.8, 143.6, 143.5, 139.6, 134.5, 132.9, 132.86, 132.1, 130.7, 129.8, 129.4, 129.2, 129.18, 128.6, 128.3, 128.2, 128.1, 127.9, 127.2, 127.1, 127.0, 126.9, 126.4, 124.7, 124.69, 122.0 (q, $^1J_{(C-F)}$ = 320 Hz), 119.6, 116.0, 115.8, 114.0, 113.9. HRMS [LDI-orbitrap, $[C_{27}H_{16}F_4SO_3]^+$] calcd 496.0756, found m/z 496.0751.

(*R*,*S*)/(*R*/*R*)-[1,1':2',1''-Ternaphthalen]-2-yl trifluoromethanesulfonate (8a/8b)

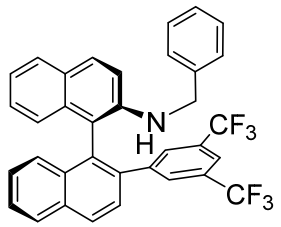


8a **8b**

Product was obtained as a 1:1 mixture of diastereomers. R_f 0.42 (1:9 acetone/hexanes); white solid, mp = 166-167 °C, yield 3.5 g, 98%; $[\alpha]_D^{24}$ +190 (*c* = 0.30, THF). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 8.4, 3.2 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.94-7.75 (m, 3H), 7.70-7.38 (m, 8H), 7.37-7.13 (m, 3H), 7.05-6.99 (m, 1H), 6.86 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.75 (dd, *J* = 7.2, 1.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 144.4, 139.6, 139.3, 138.6, 138.4, 134.8, 133.7, 133.4, 133.2, 133.1, 133.0, 132.9, 132.0, 132.0, 132.0, 131.5, 130.4, 130.2, 130.1, 129.9, 129.7, 129.6, 129.4, 129.2, 129.0, 128.7, 128.4, 128.2, 128.2, 127.9, 127.8, 127.6, 127.6, 127.6, 127.2, 127.1, 127.0, 126.9, 126.8, 126.8, 126.7, 126.7, 126.4, 126.3, 125.9, 125.4, 125.2, 124.8, 124.3, 119.5, 118.9, 118.2 (q, $^1J_{(C,F)}$ = 320 Hz), 118.2 (q, $^1J_{(C,F)}$ = 320 Hz). Anal. Calcd for $C_{31}H_{19}F_3O_3S$: C, 70.45; H, 3.62%. Found: C, 70.46; H, 3.72%.

2-Benzylamino binaphthyl derivatives (3a-j)

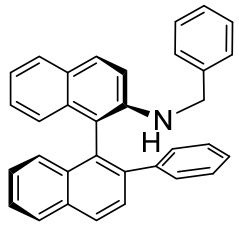
(*R*)-2-Benzylamino-2′-[3,5-bis(trifluoromethyl)phenyl]-1,1′-binaphthyl (3a)



3a

R_f 0.58 (2:3 CH_2Cl_2/hexanes); viscous oil, yield 0.28 g, 61%; *er* = 0.9(*S*):99.1(*R*), determined by chiral HPLC (Phenomenex Lux Cellulose-1 column, 4.6 x 250 mm, 3 μm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 6.5 MPa, flow rate: 1.0 mL/min, t_R (*S*)= 5.25 min, t_R (*R*)= 4.44 min). NMR and optical rotation data matched those previously reported.[6]

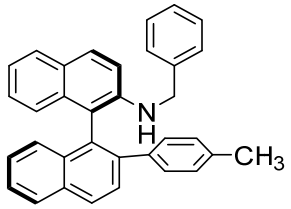
(*R*)-2-Benzylamino-2′-phenyl-1,1′-binaphthyl (3b)



3b

R_f 0.46 (2:3 CH_2Cl_2/hexanes); white solid, mp = 80-81 °C, yield 0.27 g, 69%; *er* = 0.7(*S*):99.3(*R*), determined by chiral HPLC (Phenomenex Lux Cellulose-1 column, 4.6 x 250 mm, 3 μm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 6.5 MPa, flow rate: 1.0 mL/min, t_R (*S*)= 6.6 min, t_R (*R*)= 6.0 min). NMR and optical rotation data matched those previously reported.[6]

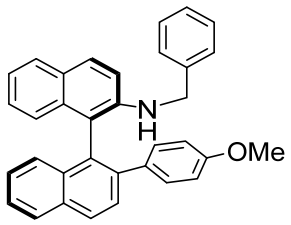
(*R*)-2-Benzylamino-2′-[4-(methyl)phenyl]-1,1′-binaphthyl (3c)



3c

R_f 0.47 (2:3 CH_2Cl_2/hexanes); viscous oil, yield 0.27 g, 63%; $[\alpha]_D^{24}$ = +58.8 (*c* = 0.50, $CHCl_3$), *er* = 0.5(*S*):99.5(*R*), determined by chiral HPLC (Chiralpak AD-H column, 4.6 x 250 mm, 5 μm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.9 MPa, flow rate: 1.0 mL/min, t_R (*S*)= 7.2 min, t_R (*R*)= 6.3 min). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.8 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.70-7.67 (m, 1H), 7.66 (d, *J* = 9.2 Hz, 1H), 7.49-7.45 (m, 1H), 7.29-7.25 (m, 2H), 7.16-7.10 (m, 5H), 7.07 (d, *J* = 8.4 Hz, 2H), 7.00-6.96 (m, 1H), 6.90-6.86 (m, 5H), 4.23 (s, 2H), 397 (bs, IH), 2.24 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 140.5, 139.7, 138.4, 136.4, 134.9, 133.4, 133.2, 131.4, 129.0, 129.0, 128.9, 128.9, 128.7, 128.5, 128.4, 128.1, 128.1, 127.0, 126.8, 126.7, 126.5, 126.1, 124.5, 121.6, 115.7, 113.8, 47.6, 21.2. HRMS (ESI-orbitrap, $[C_{34}H_{27}N + H]^+$) calcd 450.2222, found m/z 450.2220.

(*R*)-2-Benzylamino-2′-[4-(methoxy)phenyl]-1,1′-binaphthyl (3d)

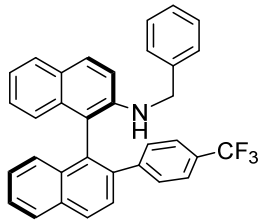


3d

R_f 0.57 (2:3 CH_2Cl_2/hexanes); off-white solid, mp 81-83 °C (decomp), yield 0.27 g, 76%; $[\alpha]_D^{24}$ = +23.8 (*c* = 0.55, $CHCl_3$), *er* = 0.5(*S*):99.5(*R*), determined by chiral HPLC (Chiralpak AD-H column, 4.6 x 250 mm, 5 μm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.9 MPa, flow rate: 1.0 mL/min, t_R (*S*)= 8.1 min, t_R (*R*)= 9.6 min). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.73-7.70 (m, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 9.2 Hz, 1H), 7.48 (septet, *J* = 4.0 Hz, 1H), 7.30-7.27 (m, 2H), 7.17-7.09 (m, 6H), 7.11 (d, *J* = 8.8 Hz, 1H), 6.99-6.95 (m, 1H), 6.89 (d, *J* = 9.2 Hz, 1H), 6.87-6.84 (m, 2H), 6.64-6.60 (m, 1H), 6.62

(d, J = 8.8 Hz, 1H), 4.25 (d, J = 6.0 Hz, 2H), 3.96 (t, J = 6.0 Hz, 1H), 3.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 143.1, 140.2, 139.8, 135.0, 133.8, 133.4, 133.3, 131.4, 130.3, 129.1, 129.0, 128.8, 128.5, 128.2, 127.1, 126.9, 126.8, 126.8, 126.7, 126.6, 126.1, 124.5, 121.6, 115.7, 113.9, 113.3, 55.2, 47.6. HRMS (ESI-orbitrap, $[C_{34}H_{27}NO + H]^+$) calcd 466.2173, found m/z 466.2185. Anal Calcd for $C_{34}H_{27}NO$: C, 87.70; H, 5.85; N, 3.01 %, Found: C, 87.65; H, 5.92; N, 3.00 %.

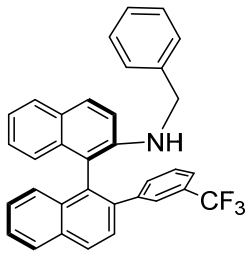
(*R*)-2-Benzylamino-2′-[4-(trifluoromethyl)phenyl]-1,1′-binaphthyl (3e)



3e

R_f 0.43 (2:3 CH_2Cl_2/hexanes); viscous oil, yield 0.19 g, 51%; $[\alpha]_D^{24}$ = +43.7 (c = 0.50, $CHCl_3$), *er* = 0.4(*S*):99.6(*R*), determined by chiral HPLC (Phenomenex Lux Cellulose-1 column, 4.6 x 250 mm, 3 μm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 6.5 MPa, flow rate: 1.0 mL/min, t_R (*S*)= 7.9 min, t_R (*R*)= 6.2 min). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.72-7.68 (m, 2H), 7.67 (d, J = 8.8 Hz, 1H), 7.56-7.50 (m, 1H), 7.36-7.32 (m, 4H), 7.28 (d, J = 8.4 Hz, 2H), 7.18-7.13 (m, 5H), 6.96-6.92 (m, 1H), 6.89 (d, J = 9.2 Hz, 2H), 6.88-6.85 (m, 1H), 4.25 (d, J = 6.0 Hz, 2H), 3.92 (t, J = 6.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 145.1, 143.2, 139.6, 139.3, 134.8, 133.8, 133.1, 132.1, 129.5, 129.4, 129.1, 128.7 (q, $^2J_{(C,F)}$ = 38 Hz), 128.5, 128.4, 128.3, 127.2, 127.0, 127.0, 126.8, 126.8, 126.7, 126.6, 124.6 (q, $^3J_{(C,F)}$ = 3.6 Hz), 124.4 (q, $^1J_{(C,F)}$ = 272 Hz), 124.0, 121.8, 114.8, 113.8, 47.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.7. HRMS (ESI-orbitrap, $[C_{34}H_{24}F_3N + H]^+$) calcd 504.1941, found m/z 504.1939.

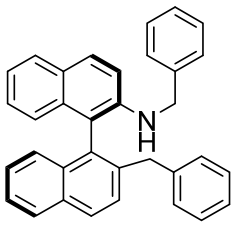
(*R*)-2'-[3-(Trifluoromethyl)phenyl]-1,1'-binaphthyl (3f)



3f

R_f 0.55 (2:3 CH_2Cl_2/hexanes); white solid, mp = 82-83 °C, yield 0.21 g, 57%; $[\alpha]_D^{24}$ = +36.1 (*c* = 0.1, THF), *er* = 0.4(*S*):99.6(*R*), determined by chiral HPLC (Chiralpak IB column, 4.6 x 250 mm, 5 μm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.7 MPa, flow rate: 1.0 mL/min, t_R (*S*)= 5.1 min, t_R (*R*)= 4.8 min). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H) 7.72-7.67 (m, 3H), 7.56-7.52 (m, 2H), 7.41-6.89 (m, 14H), 4.27(d, *J* = 6 Hz, 2H), 3.92 (t, *J* = 6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 142.1, 139.6, 139.2, 134.6, 133.8, 133.1, 132.2, 132.2, 130.1 (q, $^1J_{(C,F)}$ = 272 Hz), 129.8 (q, $^2J_{(C,F)}$ = 38 Hz), 129.5, 129.1, 128.6, 128.3, 128.3, 128.2, 128.0, 127.2, 127.1, 127.1, 126.8, 126.8, 126.7, 126.0 (q, $^3J_{(C,F)}$= 3.8 Hz), 125.5, 124.1, 123.6 (q, $^3J_{(C,F)}$= 3.7 Hz), 121.8, 114.9, 113.7, 47.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.7. HRMS [LDI-orbitrap, $[C_{34}H_{24}F_3N]^+$] calcd 503.1861, found m/z 503.1860.

(*S*)-2-Benzylamino-2′-benzyl-1,1′-binaphthyl (3g)

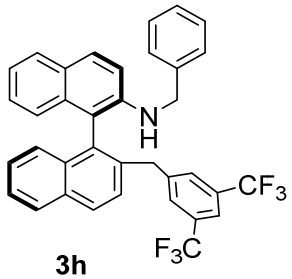


3g

R_f 0.61 (2:3 CH_2Cl_2/hexanes); viscous oil, yield 0.20 g, 83%; $[\alpha]_D^{24}$ = +102.7(*c* = 0.5, CH_2Cl_2), *er* = 99.4(*S*):0.4(*R*), determined by chiral HPLC (Phenomenex Lux Cellulose-1 column, 4.6 x 250 mm, 3 μm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 6.5 MPa, flow rate: 1.0 mL/min, t_R (*S*)= 5.8 min, t_R (*R*)= 6.8 min). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.8 Hz, 2H), 7.73 (d, *J* = 9.2 Hz, 1H), 7.68 (d, *J* = 9.2 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.38-7.34 (m,

1H), 7.22-7.18 (m, 2H), 7.16-7.08 (m, 4H), 7.07-7.00 (m, 7H), 6.86-6.84 (m, 2H), 6.79 (d, J = 8.0 Hz, 1H), 4.14 (AB, J = 16 Hz, C = 16 Hz, 2H),[7] 3.76 (bs, 1H), 3.69 (AB, J = 15 Hz, C = 9.4 Hz, 2H).[7] ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 140.9, 140.0, 139.6, 134.0, 133.1, 133.0, 132.3, 129.4, 129.3, 128.6, 128.5, 128.3, 128.2, 128.2, 128.1, 127.5, 127.0, 126.9, 126.6, 126.6, 126.2, 125.9, 125.8, 124.1, 121.9, 115.5, 114.0, 47.8, 39.8. HRMS (ESI-orbitrap, $[C_{34}H_{27}N + H]^+$) calcd 450.2223, found m/z 450.2219.

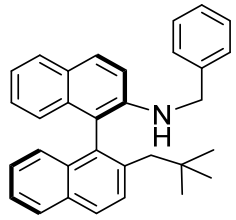
(*S*)-2-Benzylamino-2′-[3,5-bis(trifluoromethyl)benzyl]-1,1′-binaphthyl (3h)



3h

R_f 0.54 (2:3 CH_2Cl_2/hexanes); viscous oil, yield 0.23 g, 62%; $[\alpha]_D^{24}$ = –76.2 (c = 1.00, THF), *er* > 99.9(*S*):0.1(*R*), determined by chiral HPLC (Regis (R,R)-Whelk-O1 column, 4.6 x 250 mm, 5 μm particle size, 25 °C, hexanes/*i*PrOH 99:1, pressure = 3.7 MPa, flow rate: 1.0 mL/min, t_R (*S*)= 13.6 min, t_R (*R*)= 12.0 min). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 8.8 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.52-7.48 (m, 2H), 7.34-7.29 (m, 2H), 7.23-7.17 (m, 5H), 7.15-7.11(m, 1H), 7.10-7.07 (m, 3H), 7.06-7.01 (m, 1H), 6.66 (d, J = 8.4 Hz, 1H), 4.23 (AB, J = 16 Hz, C = 13 Hz, 1H),[7] 4.21 (AB, J = 16 Hz, C = 13 Hz, 1H), 3.89 (AB, J = 15 Hz, C = 10 Hz, 2H), 3.73 (t, J = 6.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 143.0, 139.7, 137.6, 133.6, 133.4, 133.2, 131.6 (q, $^2J_{(C,F)}$ = 33 Hz), 129.8, 129.1, 129.1, 129.0, 128.6, 128.5, 128.3, 127.2, 127.4, 127.1, 127.0, 126.8, 126.8, 126.4, 126.2, 123.5, 123.4 (q, $^1J_{(C,F)}$ = 272 Hz), 119.9 (septet, $^3J_{(C,F)}$ = 3.7 Hz), 119.3, 114.8, 113.9, 47.6, 40.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.8. HRMS (ESI-orbitrap, $[C_{36}H_{25}F_6N + H]^+$) calcd 586.1971, found m/z 586.1965.

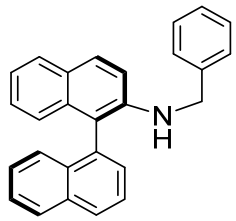
(*S*)-2-Benzylamino-2′-neopentyl-1,1′-binaphthyl (3i)



3i

R_f 0.40 (2:3 CH_2Cl_2/hexanes); off-white solid, mp = 91-92 °C, yield 0.24 g, 76%; $[\alpha]_D^{24}$ = +63.4 (*c* = 0.50, THF), *er* = 99.1(*S*):0.9(*R*), determined by chiral HPLC (Phenomenex Lux Cellulose-1 column, 4.6 x 250 mm, 3 μm particle size, 25 °C, hexanes/*i*PrOH 99:1, pressure = 3.3 MPa, flow rate: 0.5 mL/min, t_R (*S*)= 8.7 min, t_R (*R*)= 9.5 min). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.75-7.23 (m, 1H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.45-7.41 (m, 1H), 7.28-7.23 (m, 4H), 7.21-7.17 (m, 3H), 7.16-7.08 (m, 3H), 6.89 (d, *J* = 8.4 Hz, 1H), 4.41-4.29 (m, 2H), 3.93 (t, 1H), 2.51 (AB, *J* = 14 Hz, *C* = 16 Hz, 2H),[7] 0.76 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 140.1, 139.1, 134.2, 133.1, 133.0, 132.9, 130.3, 129.2, 128.6, 128.1, 128.0, 127.4, 127.0, 127.0, 127.0, 126.9, 126.3, 126.1, 125.5, 125.2, 121.7, 116.1, 113.9, 48.2, 47.0, 33.1, 30.6. Anal. Calcd for $C_{32}H_{31}N$: C, 89.46; H, 7.28; N, 3.26 %. Found: C, 89.21; H, 7.41; N, 3.16 %.

(*S*)-2-Benzylamino-1,1′-binaphthyl (3j)

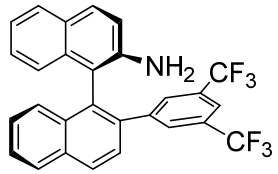


3j

Sensitive, viscous oil; purified by rapid filtration through a silica pad in Et_2O/hexanes (15:85). Yield 0.38 g (85%). *er* = 99.3(*S*):0.7(*R*), determined by chiral HPLC (Phenomenex Lux Cellulose-1 column, 4.6 x 250 mm, 3 μm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 6.5 MPa, flow rate: 1.0 mL/min, t_R (*S*)= 6.9 min, t_R (*R*)= 6.3 min). NMR data matched those previously reported.[6]

2-Amino binaphthyl derivatives (6a-j)

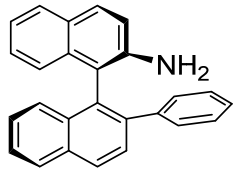
(*R*)-2-Amino-2′-[3,5-bis(trifluoromethyl)phenyl]-1,1′-binaphthyl (6a)



6a

R_f 0.58 (3:7 CH_2Cl_2/hexanes); white solid, mp = 123-124 °C, yield 2.4 g, 57%; *er* = 0.9(*S*):99.1(*R*), determined by chiral HPLC (Chiralpak IB column, 4.6 x 250 mm, 5 μm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 4.6 MPa, flow rate: 1.0 mL/min, t_R (*S*)= 6.5 min, t_R (*R*)= 5.4 min). NMR and optical rotation data matched those previously reported.[6]

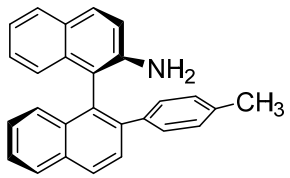
(*R*)-2-Amino-2′-phenyl-1,1′-binaphthyl (6b)



6b

R_f 0.57 (2:3 CH_2Cl_2/hexanes); waxy solid, mp = 26-27 °C, yield 2.1 g , 91%; *er* = 0.9(*S*):99.1(*R*), determined by chiral HPLC (Chiralpak IB column, 4.6 x 250 mm, 5 μm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.5 MPa, flow rate: 1.0 mL/min, t_R (*S*) = 8.2 min, t_R (*R*) = 9.2 min). NMR and optical rotation data matched those previously reported.[6]

(*R*)-2-Amino-2′-[4-(methyl)phenyl]-1,1′-binaphthyl (6c)

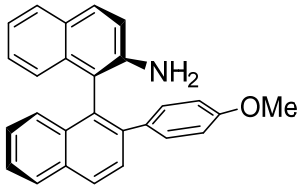


6c

R_f 0.45 (2:3 CH_2Cl_2/hexanes); off-white solid, mp = 80-82 °C (decomp), yield 1.3 g, 57%; $[\alpha]_D^{25}$ = +43.9 (*c* = 0.5, THF), *er* = 0.4(*S*):99.6(*R*), determined by chiral HPLC (Chiralpak IA column,

4.6 x 250 mm, 5 μm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.8 MPa, flow rate: 1.0 mL/min, t_R (*S*)= 10.8 min, t_R (*R*)= 8.3 min). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.8 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.70-7.65 (s, 3H), 7.47-7.43 (m, 1H), 7.28-7.26 (m, 3H), 7.16-7.10 (m, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.99-6.97 (m, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 2H), 3.50 (br s, 1H), and 2.17 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 140.6, 138.6, 136.4, 134.8, 133.4, 132.9, 131.5, 129.0, 129.0, 128.7, 128.6, 128.4, 128.2, 128.0, 127.9, 126.9, 126.5, 126.1, 124.7, 122.1, 118.0, 116.6, 21.2. Anal. Calcd for $C_{27}H_{21}N$: C, 90.21; H, 5.89; N, 3.90 %. Found: C, 88.36; H, 6.24; N, 3.84 %. HRMS (ESI-orbitrap, $[C_{27}H_{21}N + H]^+$) calcd 360.1754, found m/z 360.1738.

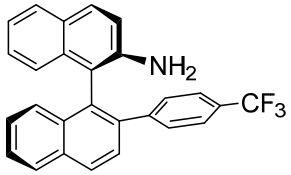
(*R*)-2-Amino-2′-[4-(methoxy)phenyl]-1,1′-binaphthyl (6d)



6d

R_f 0.42 (2:3 CH_2Cl_2/hexanes); viscous oil, yield 1.1 g , 91%; $[\alpha]_D^{25}$ = +72.3 (*c* = 0.5, THF), *er* = 0.3(*S*):99.7(*R*), determined by chiral HPLC (Chiralpak IA column, 4.6 x 250 mm, 5 μm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.8 MPa, flow rate: 1.0 mL/min, t_R (*S*)= 15.7 min, t_R (*R*)= 11.3 min). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.72-7.69 (m, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.48-7.44 (m, 1H), 7.30-7.27 (m, 2H), 7.19-7.11 (m, 4H), 6.99-6.97 (m, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 6.59 (dt, *J* = 8.4, 2.8 Hz, 2H), 3.67 (s, 3H), and 3.51 (bs, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 142.1, 140.9, 134.7, 134.0, 133.3, 133.0, 131.5, 130.0, 129.1, 128.9, 128.6, 128.2, 128.1, 128.0, 126.9, 126.5, 126.5, 126.0, 124.6, 122.1, 118.1, 116.6, 113.2, 55.1. HRMS (ESI-orbitrap, $[C_{27}H_{21}NO + H]^+$) calcd 376.1704, found m/z 376.1719.

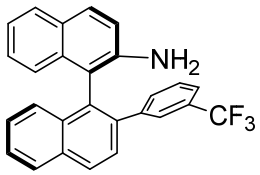
(*R*)-2-Amino-2′-[4-(trifluoromethyl)phenyl]-1,1′-binaphthyl (6e)



6e

R_f 0.55 (2:3 CH_2Cl_2/hexanes); off-white solid, mp = 125-126 °C, yield 1.3 g , 89%; $[\alpha]_D^{25}$ = –30.1 (*c* = 0.5, THF), *er* = 0.7(*S*):99.4(*R*), determined by chiral HPLC (Chiralpak IB column, 4.6 x 250 mm, 5 μm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.7 MPa, flow rate: 1.0 mL/min, t_R (*S*)= 10.1 min, t_R (*R*)= 8.3 min). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.12 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.75-7.72 (m, 2H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.58-7.54 (m, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.38-7.30 (m, 4H), 7.20-7.13 (m, 2H), 7.02 (d, *J* = 8.8 Hz, 1H), 6.93-6.90 (m, 1H), 3.67 (br s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 142.2, 139.2, 134.5, 133.7, 132.8, 132.2, 129.5, 129.1, 128.9, 128.6 (q, $^2J_{(C,F)}$ = 41 Hz), 128.4 (q, $^1J_{(C,F)}$ = 272 Hz) 128.3, 128.2, 127.9, 127.2, 126.8, 126.7, 126.6, 124.6 (q, $^3J_{(C,F)}$ = 3.6 Hz), 124.3, 124.2, 122.3, 117.9, 115.5 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.2 ppm. Anal. Calcd for $C_{27}H_{18}F_3N$: C, 78.42; H, 4.39; N, 3.39 %. Found: C, 78.23; H, 4.60; N, 3.41 %. HRMS (ESI-orbitrap, $[C_{27}H_{18}F_3N + H]^+$) calcd 415.1471, found m/z 415.1452.

(*R*)-2'-(3-(Trifluoromethyl)phenyl)-[1,1'-binaphthalen] (6f)

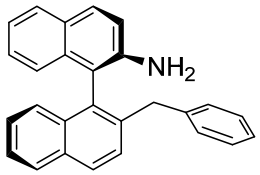


6f

R_f 0.48 (2:3 CH_2Cl_2/hexanes); white solid, mp = 120-121 °C, yield 0.48 g, 81%; $[\alpha]_D^{24}$ = +32.3 (*c* = 0.1, THF), *er* = 0.5(*S*):99.5(*R*), determined by chiral HPLC (Chiralpak IB column, 4.6 x 250 mm, 5 μm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.7 MPa, flow rate: 1.0 mL/min, t_R (*S*)= 7.8 min, t_R (*R*)= 6.9 min). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.8 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.71-7.67 (m, 3H), 7.55-7.52 (m, 2H), 7.43-7.29 (m, 4H), 7.16-7.12 (m, 3H), 6.95-6.92 (m, 2H), 3.29 (br s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 142.2, 139.2, 134.4,

133.7, 132.8, 132.4, 132.0, 130.3 (q, $^{2}J_{(C,F)}$ = 32 Hz), 129.5, 129.0, 128.4, 128.2, 128.2, 128.1, 128.0, 127.3, 126.7, 126.7, 126.6, 125.9 (q, $^{3}J_{(C,F)}$ = 4.5 Hz), 125.5 (q, $^{1}J_{(C,F)}$ = 272 Hz), 124.2, 123.6 (q, $^{3}J_{(C,F)}$ = 3.8 Hz), 122.3, 117.8, 115.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.8. HRMS [LDI-orbitrap, $[C_{27}H_{18}F_3N]^+$] calcd 413.1391, found m/z 413.1388.

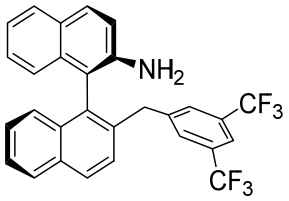
(*S*)-2-Amino-2′-benzyl-1,1′-binaphthyl (6g)



6g

R_f 0.51 (2:3 CH_2Cl_2/hexanes); waxy solid, yield 2.5 g, 88%; $[\alpha]_D^{25}$ = +94.8 (*c* = 0.5, THF), *er* = 99.6(*S*):0.4(*R*), determined by chiral HPLC (Chiralpak IB column, 4.6 x 250 mm, 5 μm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.7 MPa, flow rate: 1.0 mL/min, t_R (*S*)= 6.8 min, t_R (*R*)= 7.4 min). ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.89 (dd, *J* = 8.8, 2.0 Hz, 2H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.8 Hz, 1H), 7.45-7.41 (m, 1H), 7.28-7.26 (m, 2H), 7.24-7.20 (m, 1H), 7.18-7.06 (m, 5H), 6.96-6.91 (m, 3H), 3.77 (2H, AB, *J* = 15 Hz, *C* = 10 Hz),[7] 3.37 (br s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 140.9, 139.3, 134.2, 132.9, 132.4, 129.4, 129.3, 129.3, 128.5, 128.4, 128.3, 128.2, 128.2, 128.1, 126.7, 126.7, 126.1, 125.9, 125.8, 124.2, 122.4, 118.3, 115.9, 39.8. HRMS (ESI-orbitrap, $[C_{27}H_{21}N + H]^+$) calcd 360.1754, found m/z 360.1741.

(*S*)-2-Amino-2′-[3,5-bis(trifluoromethyl)benzyl]-1,1′-binaphthyl (6h)

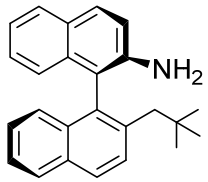


6h

R_f 0.46 (2:3 CH_2Cl_2/hexanes); waxy solid, yield 0.57 g, 86%; $[\alpha]_D^{25}$ = +28.2 (*c* = 0.1, THF), *er* = 99.5(*S*):0.5(*R*), determined by chiral HPLC (Chiralpak IB column, 4.6 x 250 mm, 5 μm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.7 MPa, flow rate: 1.0 mL/min, t_R (*S*)= 5.9 min, t_R

(*R*)= 7.7 min). ^{1}H NMR (400 MHz,$CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8 Hz, 1H), 7.63 (d, *J* = 8.4Hz, 1H), 7.56 (s, 1H), 7.54-7.31 (m, 3H), 7.29 (s, 2H), 7.25-7.10 (m, 2H), 7.07 (d, *J* = 8.4 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 3.97 (AB, *J*= 15 Hz, *C* = 10 Hz, 2H),[7] 3.41 (br s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 142.0, 137.4, 133.8, 133.34, 133.32, 133.1, 131.6 (q, $^{2}J_{(C,F)}$ = 33 Hz), 129.8, 129.1, 129.0, 128.5, 128.4, 128.3, 128.2, 127.5 (q, $^{1}J_{(C,F)}$= 273 Hz), 127.1, 126.9, 126.3, 126.1, 123.8, 122.5, 120.0 (sept, $^{3}J_{(C,F)}$= 3.8 Hz), 118.0, 115.0, 40.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.8 ppm. HRMS (ESI-orbitrap, $[C_{29}H_{19}F_6N + H]^+$) calcd 496.1500, found m/z 496.1495.

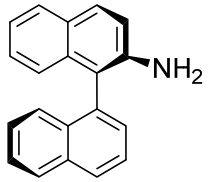
(*S*)-2-Amino-2′-neopentyl-1,1′-binaphthyl (6i)



6i

R_f 0.55 (2:3 CH_2Cl_2/hexanes); waxy solid, yield 1.5 g, 82%; $[\alpha]_D^{25}$ = +84.8 (*c* = 0.5, THF), *er* = 99.4(*S*):0.6(*R*), determined by chiral HPLC (Chiralpak IB column, 4.6 x 250 mm, 5 μm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.7 MPa, flow rate: 1.0 mL/min, t_R (*S*)= 5.2 min, t_R (*R*)= 5.7 min). ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 9.2 Hz, 1H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.45-7.40 (m, 1H), 7.27-7.25 (m, 2H), 7.21 (dt, *J* = 6.8, 1.2 Hz, 1H), 7.15 (dt, *J* = 6.8, 1.2 Hz, 1H), 7.10 (d, *J* = 8.8 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 3.55 (s, 2H), 2.50 (2H, AB, *J* = 14 Hz, *C* = 12.0 Hz),[7] 0.77 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 138.8, 134.4, 133.1, 132.8, 132.7, 130.3, 129.2, 128.2, 128.1, 128.0, 127.3, 126.7, 126.3, 126.3, 125.5, 125.2, 122.2, 118.2, 116.5, 46.9, 33.1, 30.6. HRMS (ESI-orbitrap, $[C_{25}H_{25}N + Na]^+$) calcd 362.1884, found m/z 362.1880.

(*S*)-2-Amino-1,1′-binaphthyl (6j)

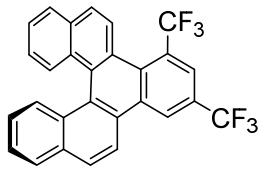


6j

R_f 0.59 (2:3 CH_2Cl_2/hexanes); white solid, mp = 190-191 °C, yield 2.1 g, 96%; *er* = 99.4(*S*):0.6(*R*), determined by chiral HPLC (Chiralpak IB column, 4.6 x 250 mm, 5 μm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.8 MPa, flow rate: 1.0 mL/min, t_R (*S*)= 8.3 min, t_R (*R*)= 9.6 min). NMR and optical rotation data matched those previously reported.[6]

[5]Helicene derivatives (4a-4e, 4k, 9). Note that enantiopure helicenes commonly exhibit very high optical rotation values ($[\alpha]_D > 1000°$).[8] Thus, the small $[\alpha]_D$ values reported below (4 - 26°) likely represent either a miniscule enantiomeric excess that is not detectable by chiral HPLC or small amounts of chiral impurities that are not visible in the NMR spectra.

1,3-Bis(trifluoromethyl)naphtho[1,2-*g*]chrysene (4a)

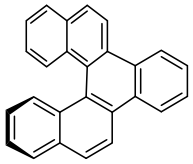


4a

R_f 0.70 (3:7 CH_2Cl_2/hexanes); yellow solid, mp = 184-185 °C, yield 0.21 g, 74%; $[\alpha]_D^{25}$ = +3.8 (*c* = 0.1, THF), *er* = 51.3:48.3 (absolute stereochemistries of enantiomers not known), determined by chiral HPLC (Chiralpak IB column, 4.6 x 250 mm, 5 μm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.7 MPa, flow rate: 1.0 mL/min, t_R (enantiomer 1)= 4.3 min, t_R (enantiomer 2)= 4.6 min). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.56 (d, *J* = 8.8 Hz, 1H), 8.54 (d, *J* = 8.8 Hz, 1H), 8.22 (s, 1H), 8.15 (d, *J* = 8.8 Hz, 2H), 8.08 (d, *J* = 8.8 Hz, 2H), 8.01 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.97 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.56 (m, 2H), 7.34 (dt, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.27-7.23 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.4, 132.8, 132.7, 132.5,

131.1, 129.9, 129.7, 129.6, 129.1, 128.4, 128.2 (q, $^{2}J_{C\text{-}F}$ = 36.7 Hz), 128.1, 128.0, 128.0, 127.9, 127.5, 127.4, 127.3 (q, $^{2}J_{C\text{-}F}$ = 32 Hz), 127.1, 127.0, 125.7, 125.3, 125.0 (q, $^{1}J_{C\text{-}F}$ = 274 Hz), 124.9 (q, $^{3}J_{C\text{-}F}$ = 6.6 Hz), 123.9 (q, $^{1}J_{C\text{-}F}$ = 273 Hz), 123.8 (septet, $^{3}J_{C\text{-}F}$ = 1.6 Hz), 123.0, 119.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.2, –53.2 ppm. HRMS [LDI-orbitrap, $[C_{28}H_{14}F_6]^+$] calcd 464.0999, found m/z 464.0993.

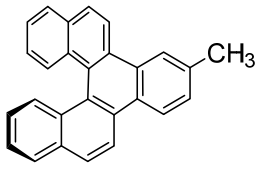
Naphtho[1,2-*g*]chrysene (4b)



4b

R_f 0.55 (3:7 CH_2Cl_2/hexanes); white solid, mp = 150-152 °C (decomp), yield 0.17 g, 82%; $[\alpha]_D^{25}$ = +4.97 (*c* = 0.2, THF), *er* = 50.0:50.0 (absolute stereochemistries of enantiomers not known), determined by chiral HPLC (Chiralpak IB column, 4.6 x 250 mm, 5 μm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 2.6 MPa, flow rate: 0.8 mL/min, t_R (enantiomer 1)= 9.7 min, t_R (enantiomer 2)= 10.7 min). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72-8.67 (m, 4H), 8.08 (d, *J* = 8.4 Hz, 2H), 8.07 (d, *J* = 8.8 Hz, 2H), 7.95 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.70 (d, *J* = 6.4 Hz, 1H), 7.69 (d, *J* = 6.4 Hz, 1H), 7.47 (dt, *J* = 6.8, 0.8 Hz, 2H), 7.24-7.19 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.4, 131.4, 130.4, 129.8, 129.4, 128.0, 127.7, 127.4, 126.1, 126.0, 124.8, 123.6, 120.6. HRMS [LDI-orbitrap, $[C_{26}H_{16}]^+$] calcd 328.1252, found m/z 328.1240.

2-Methylnaphtho[1,2-*g*]chrysene (4c)

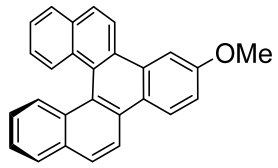


4c

R_f 0.60 (3:7 CH_2Cl_2/hexanes); white solid, mp = 170-172 °C (decomp), yield 56 mg, 79%; $[\alpha]_D^{25}$ = +25.5 (*c* = 0.2, THF), *er* = 50.1:49.9 (absolute stereochemistries of enantiomers not known), determined by chiral HPLC (Chiralpak IB column, 4.6 x 250 mm, 5 μm particle size, 25 °C, hexanes/*i*PrOH 98:2, pressure = 1.7 MPa, flow rate: 0.5 mL/min, t_R (enantiomer 1)= 12.6 min, t_R

(enantiomer 2)= 13.5 min). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 9.2 Hz, 1H), 8.69 (d, *J* = 9.2 Hz, 1H), 8.60 (d, *J* = 8.4 Hz, 1H), 8.51 (s, 1H), 8.11-8.06 (m, 4H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.54 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.51-7.46 (m, 2H), 7.22 (dt, *J* = 8.4, 1.2 Hz, 2H), 2.66 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.2, 132.4, 132.3, 131.4, 131.4, 130.4, 129.8, 129.7, 129.5, 129.2, 129.0, 128.2, 128.0, 127.8, 127.7, 127.7, 126.1, 126.0, 125.9, 125.4, 124.7, 124.7, 123.5, 123.5, 120.7, 120.6, 22.1. HRMS [LDI-orbitrap, $[C_{27}H_{18}]^+$] calcd 342.1409, found m/z 342.1396.

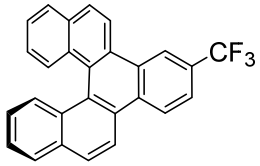
2-Methoxynaphtho[1,2-*g*]chrysene (4d)



4d

R_f 0.63 (1:9 CH_2Cl_2/hexanes); off-white solid, mp = 250-251 °C (decomp), yield 54 mg, 77%; $[\alpha]_D^{25}$ = +5.8 (*c* = 0.2, THF), *er* = 50.0:50.0 (absolute stereochemistries of enantiomers not known), determined by chiral HPLC (Chiralpak IB column, 4.6 x 250 mm, 5 μm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.8 MPa, flow rate: 1.0 mL/min, t_R (enantiomer 1)= 8.8 min, t_R (enantiomer 2)= 10.1 min). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 9.2 Hz, 3H), 8.13-8.04 (m, 5H), 7.96 (dt, *J* = 8.0 Hz & 1.2Hz, 2H), 7.51-7.45 (m, 2H), 7.34 (dd, *J* = 9.2 Hz, 2.8 Hz, 1H), 7.25-7.20 (m, 2H), 4.07 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 132.5, 132.0, 131.9, 131.5, 131.4, 130.0, 129.6, 129.5, 129.0, 128.1, 127.8, 127.8, 127.8, 127.7, 126.7, 126.2, 125.7, 125.2, 124.8, 124.7, 124.5, 120.7, 120.5, 116.5, 105.6, 55.7. HRMS [LDI-orbitrap, $[C_{27}H_{18}O]^+$] calcd 358.1358, found m/z 358.1344.

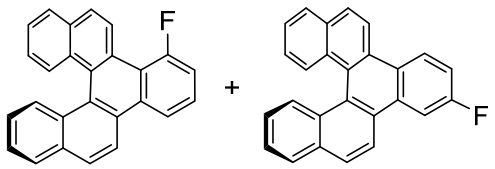
2-(Trifluoromethyl)naphtho[1,2-*g*]chrysene (4e)



4e

R_f 0.74 (1:9 acetone/hexanes); light yellow solid, mp = 277-278 °C, yield 0.12 g, 83%; $[\alpha]_D^{25}$ = +25.8 (*c* = 0.2, CH_2Cl_2), *er* = 49.9:50.1 (absolute stereochemistries of enantiomers not known), determined by chiral HPLC (Chiralpak IB column, 4.6 x 250 mm, 5 μm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.7 MPa, flow rate: 1.0 mL/min, t_R (enantiomer 1)= 5.2 min, t_R (enantiomer 2)= 5.7 min). ^{1}H NMR (400 MHz, C_6D_6) δ 8.85 (s, 1H), 8.31-8.23 (m, 3H), 8.10 (dd, *J* = 8.8 Hz, 4.0 Hz, 2H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.77-7.72 (m, 3H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.29-7.24 (m, 2H), 6.98 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, C_6D_6) δ 133.3, 133.2, 132.9, 131.8, 130.6, 130.3, 130.1, 129.1 (q, $^2J_{C\text{-}F}$ = 40 Hz), 128.7, 128.5, 128.4, 128.2, 128.1, 127.9, 127.7, 127.0, 126.8, 126.7, 125.5 (q, $^1J_{C\text{-}F}$ = 272.3 Hz), 125.2, 125.2, 124.7, 123.1 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 121.2 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 120.8, 120.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ –61.9. HRMS [LDI-orbitrap, $[C_{27}H_{15}F_3]^+$] Calcd: 396.1126; Found: m/z 396.1115.

1-(Fluoro)naphtho[1,2-*g*]chrysene (4k)/ 3-(Fluoro)naphtho[1,2-*g*]chrysene (4k')

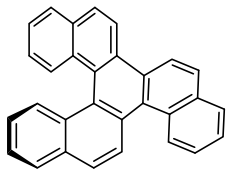


4k **4k'**

Obtained as an inseparable mixture of regioisomers (**4k**:**4k'** 89:11). R_f 0.71 (2:3 CH_2Cl_2/hexanes); white solid, mp = 176-178 °C (decomp), yield 63 mg, 91%; $[\alpha]_D^{24}$ = +18.8 (*c* = 0.1 THF). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (m, 1H, major), 8.89 (m, 1H, minor), 8.80 (m, 2H. minor), 8.74 (m, 3H), minor), 8.65 (d, *J*= 9.2Hz, 1H, major), 8.34 (m, 2H, minor), 8.12 -7.91 (m , 8H, major and minor), 7.66-7.17 (m, 8H, major and minor). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.8 (d, $^1J_{C\text{-}F}$ = 253 Hz), 133.3, 133.3, 132.7, 132.5, 132.3, 132.3, 131.4, 131.3, 130.9, 130.7, 130.6, 128.4, 128.2, 128.2, 128.1, 128.1, 127.8, 127.8, 127.6, 127.6, 127.4, 126.5, 126.5, 126.4, 126.3, 126.2, 125.9, 125.5, 125.1, 125.0, 124.9, 124.7, 124.4, 124.3, 124.1, 123.3, 122.1, 120.8,

120.6, 120.6, 120.5, 119.9, 119.8, 119.4, 119.4, 116.0, 115.8, 114.7, 114.6, 114.4, 109.0, 108.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ −108.7 (major), −112.8 (minor). HRMS [LDI-orbitrap, $[C_{26}H_{15}F]^+$] calcd 346.1158, found m/z 346.1145.

Naphtho[1,2-*s*]picene (9)



9

R_f 0.83 (1:4 acetone/hexanes); red solid, mp = 231-232 °C, yield 51 mg, 71%; $[\alpha]_D^{25}$ = +1.4 (*c* = 0.2, CH_2Cl_2), *er* = 50.5:49.5 (absolute stereochemistries of enantiomers not known), determined by chiral HPLC (Chiralpak IB column, 4.6 x 250 mm, 5 μm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.5 MPa, flow rate: 1.0 mL/min, t_R (enantiomer 1)= 5.6 min, t_R (enantiomer 2)= 6.5 min). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (t, *J* = 8.4 Hz, 2H), 8.65 (d, *J* = 8.8 Hz, 1H), 8.60 (d, *J* = 8.8 Hz, 1H), 8.35 (d, *J* = 8.8 Hz, 1H), 8.29 (d, *J* = 8.8 Hz, 1H), 8.11 (d, *J* = 8.8 Hz, 1H), 8.07 (d, *J* = 8.8 Hz, 1H), 8.05-7.96 (m, 4H), 7.70 (dt, *J* = 8.4 Hz, 1.6 Hz, 1H), 7.63 (dt, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.51 (dq, *J* = 7.6 Hz, 1.2 Hz, 2H), 7.32 (dt, *J* = 6.8 Hz, 1.2 Hz, 1H), 7.27-7.23 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.8, 132.3, 132.1, 131.4, 130.8, 129.9, 129.8, 129.7, 129.4, 129.3, 128.9, 128.7, 128.3, 128.2, 128.1, 128.1, 127.8, 126.3, 126.1, 126.1, 126.0, 125.9, 125.7, 125.1, 124.9, 120.7, 120.6. HRMS [LDI-orbitrap, $[C_{30}H_{18}]^+$] calcd 378.1409, found m/z 378.1391.

X-RAY CRYSTALLOGRAPHIC DATA AND PROCEDURES

General Considerations. X-ray diffraction data were collected on a Bruker SMART APEX II single crystal diffractometer using graphite-monochromated Mo *k*-α radiation (λ=0.71073 Å, sealed tube) and a combination of ϕ and ω scans. Unit cell determination and data collection utilized the Bruker SMART[9] and APEX2[10] software packages. Data integration employed SAINT.[11] Multiscan absorption corrections were implemented using SADABS.[12] Structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software suite.[13] Non-hydrogen atoms were assigned anisotropic temperature factors, and carbon-bound hydrogen atoms were included in calculated positions (riding model) with isotropic U fixed at 1.5 times the U_{eq} of the attached atom for -CH_3 groups and 1.2 times the U_{eq} of the attached carbon for other hydrogen atoms. CCDC 1479924-1479926 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

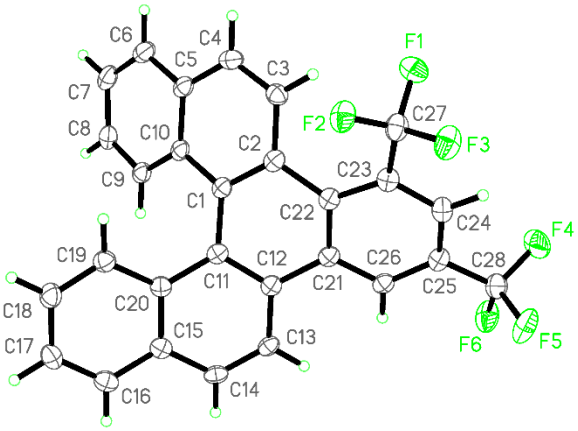


Figure S1. X-ray structure of **4a,** with displacement ellipsoids drawn at the 50% probability level. Note that the crystal is a racemate and belongs to a centrosymmetric space group.

X-ray Crystallographic Analysis of 4a. Thin yellow needles were obtained by slow diffusion of *n*-hexane into a THF solution of **4a**. A sample measuring 0.47 x 0.16 x 0.04 mm was cut from a longer needle and placed on the goniometer of the diffractometer, and reflection data were collected using 40 s scans. The sample was cooled to 115(2) K during data collection using a Bruker Kryoflex liquid nitrogen cooling device. $C_{28}H_{14}F_6$, M_r = 464.39 g mol^{-1}, monoclinic, space group $P2_1/c$, a = 9.81380(10), b = 22.8364(3), c = 9.09370(10) Å, β = 99.9067(7)°, V = 2007.62(4) Å^3, Z = 4, Z' = 1, ρ_{calcd} = 1.536 g cm^{-3}, μ = 0.127 mm^{-1}, T = 115(2) K, $2\theta_{max}$ = 52.68°, 38424 total reflections, 4088 independent (R_{int} = 0.044), 3187 observed [$I > 2\sigma(I)$]. Final $R1$ [$I > 2\sigma(I)$] = 0.0346, $wR2$ (all data) = 0.0826, largest difference peak (hole) 0.236 (-0.203) e Å^{-3}. CCDC 1479926.

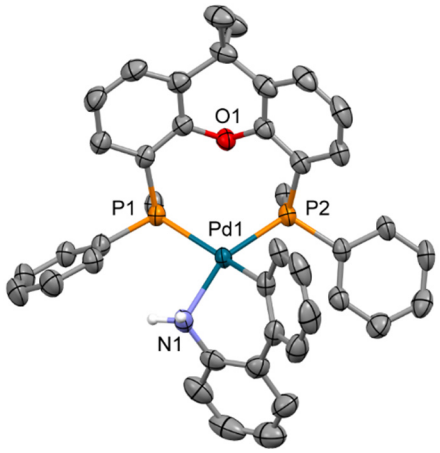


Figure S2. X-ray structure of xantphos-ligated palladacycle **5**, with 50% probability ellipsoids. The mesylate counterion, rear phenyl groups, three disordered CH_2Cl_2 molecules, and all non N-H hydrogen atoms are omitted for clarity.

X-ray Crystallographic Analysis of 5. Colorless plates were obtained by slow diffusion of pentane into a CH_2Cl_2 solution of **5**. A sample measuring 0.29 x 0.20 x 0.05 mm was placed on the goniometer of the diffractometer, and reflection data were collected. The sample was cooled to 200(2) K during data collection using an Oxford Cryostream liquid nitrogen cooling device. The NH_2 hydrogen atoms were located in the difference Fourier map and were allowed to refine freely. Three disordered CH_2Cl_2 solvent molecules were located in the difference map and refined using a two-part disorder model. Rotational disorder of the mesylate SO_3^- group was treated similarly. Appropriate least-squares restraints and constraints were employed to aid refinement of disordered moieties. $C_{51}H_{42}NOP_2Pd \cdot CH_3O_3S \cdot 3CH_2Cl_2$, M_r = 1203.07 g mol^{-1}, triclinic, space group $P\bar{1}$, a = 9.6010(12), b = 14.5905(18), c = 20.173(3) Å, α = 82.894(2), β = 81.824(2), γ = 77.999(2)°, V = 2723.1(6) Å^3, Z = 2, Z' = 1, ρ_{calcd} = 1.467 g cm^{-3}, μ = 0.778 mm^{-1}, T = 200(2) K, $2\theta_{max}$ = 54.20°, 27009 total reflections, 11840 independent (R_{int} = 0.041), 9219 observed [$I > 2\sigma(I)$]. Final $R1$ [$I > 2\sigma(I)$] = 0.0808, $wR2$ (all data) = 0.2373, largest difference peak (hole) 2.168 (-0.974) e Å^{-3}. CCDC 1479925.

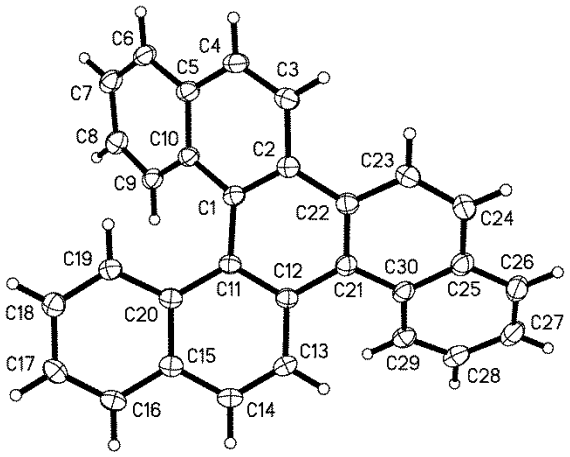


Figure S3. X-ray structure of **9,** with displacement ellipsoids drawn at the 50% probability level. Note that the crystal is a racemate and belongs to a space group containing glide planes.

X-ray Crystallographic Analysis of 9. Red-orange plates were obtained by slow diffusion of pentane into a CH_2Cl_2 solution of **9**. A sample measuring 0.45 x 0.40 x 0.15 mm was placed on the goniometer of the diffractometer, and reflection data were collected using 30 s scans. The sample was cooled to 115(2) K during data collection using a Bruker Kryoflex liquid nitrogen cooling device. $C_{30}H_{18}$, M_r = 378.44 g mol^{-1}, orthorhombic, space group $Pca2_1$, a = 11.2287(3), b = 21.5577(6), c = 7.6682(2) Å, V = 1856.20(9) Å^3, Z = 4, Z' = 1, ρ_{calcd} = 1.354 g cm^{-3}, μ = 0.077 mm^{-1}, T = 115(2) K, $2\theta_{max}$ = 57.06°, 24906 total reflections, 4649 independent (R_{int} = 0.031), 4324 observed [$I > 2\sigma(I)$]. Final $R1$ [$I > 2\sigma(I)$] = 0.0344, $wR2$ (all data) = 0.0867, largest difference peak (hole) 0.240 (-0.230) e Å^{-3}. CCDC 1479924.

SUPPLEMENTAL FIGURES

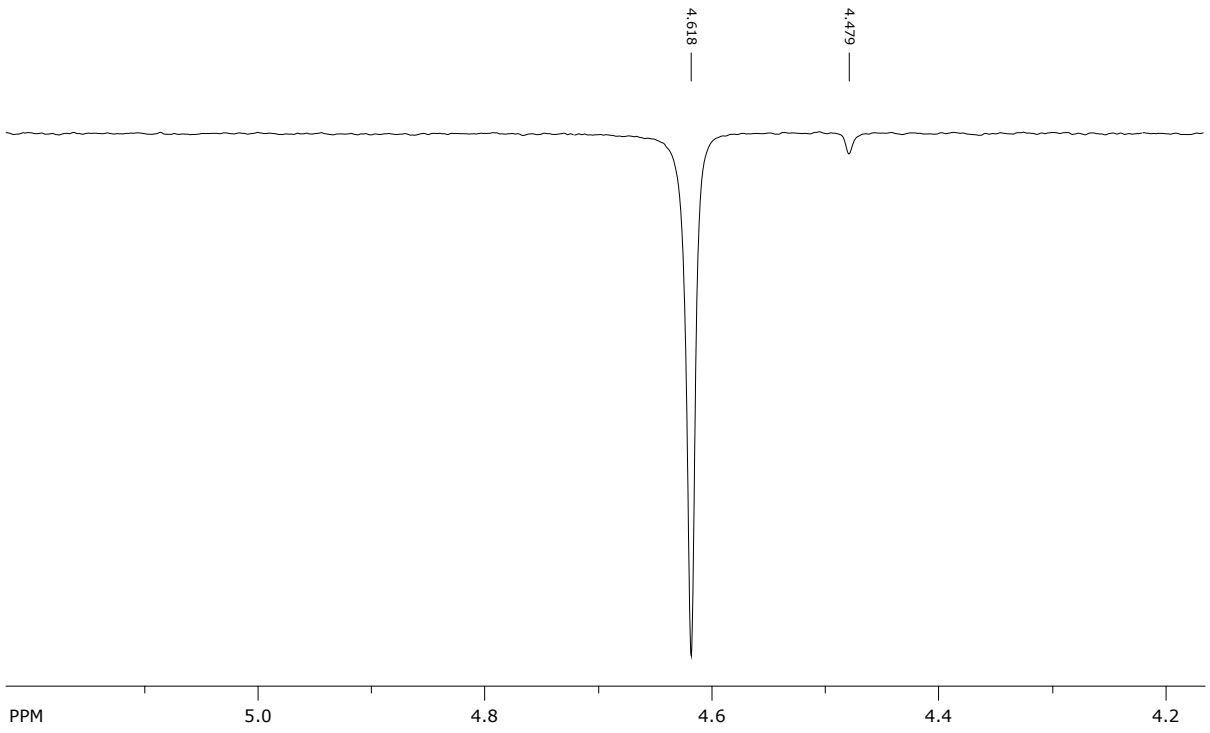


Figure S4. 1D-EXSY ^{1}H NMR experiment with a 1:1 diasteromeric mixture of **7a** and **7b**. The signal at 4.618 ppm was irradiated, and the 1D gradient NOE spectrum was acquired (^{1}H, 400 MHz, C_6D_6 solvent, acquisition time 2.556 s, mixing time 500 ms).

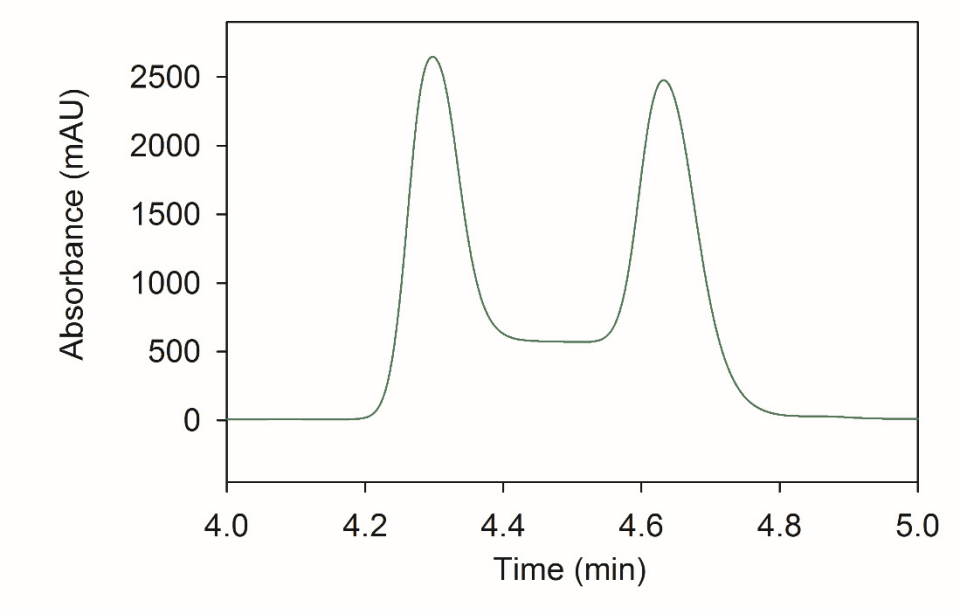


Figure S5. Chiral HPLC chromatogram indicating dynamic interconversion of enantiomers during analysis of helicene **4a** (Chiralpak IA column, diode array detector observing 254 nm).

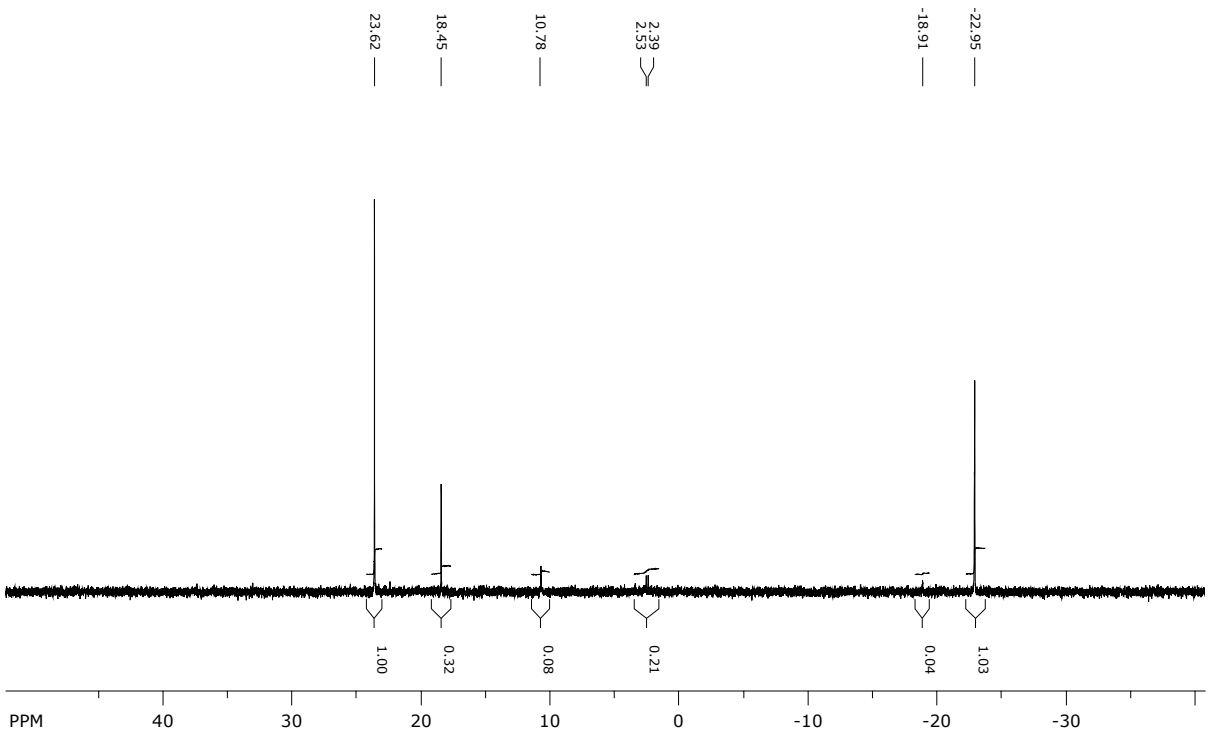


Figure S6. ^{31}P NMR spectrum of a catalytic reaction mixture for C-H arylation of **2b**, after 2 min at 80 °C followed by filtration, with integrations shown. Solvent: DMF with C_6D_6 added (5% v/v) to facilitate NMR locking and shimming.

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7. For an AB pattern, J corresponds to the chemical shift difference between the outer and inner peaks, and $2C$ denotes the difference between the midpoints of these two sets of peaks. See: R. S. Macomber, *A Complete Introduction to Modern NMR Spectroscopy*, Wiley, New York, 1998.

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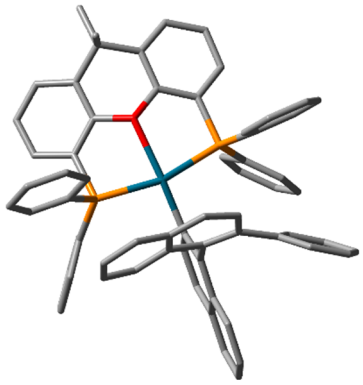
OPTIMIZED GEOMETRIES FROM DFT CALCULATIONS

Geometries are given in Cartesian coordinates (Å). Nonessential hydrogen atoms are not shown in the figures.

I1 P-O-P Tridentate (xantphos)Pd(binaphthyl) cation



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C	4.70209200	-1.49214300	1.21033100
C	5.96985800	-0.87745400	1.16279900
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C	5.00548300	1.07391500	-0.00129800
C	3.73333200	0.46260900	0.13972000
O	2.58008000	1.15737400	-0.31647800
C	2.63684700	2.57462500	-0.24075200
C	3.88362000	3.22550400	-0.43631500
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C	-1.78698700	3.90957400	4.32690700
C	-2.67354700	3.85695300	3.22444600
C	-2.21073200	3.43919900	1.95338000
C	-1.15399600	3.10819400	-1.21932200
C	-1.14597300	2.35125000	-2.41986800
C	-1.73006800	2.87694600	-3.59528000
C	-2.34085400	4.15368200	-3.57430800
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C	-5.43605300	-3.08274400	1.30485500
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C	-6.48574700	1.35470000	-1.57334200
C	-5.15124200	1.90514800	0.39151700
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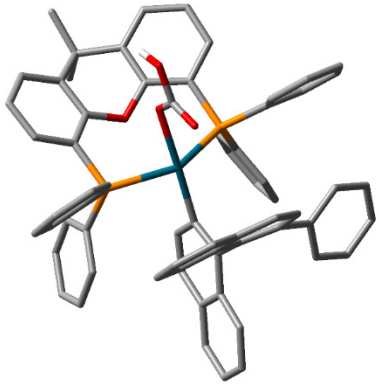
I2 Trans bidentate (xantphos)Pd(binaphthyl)(κ^1-HCO_3)



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C	-3.41145700	1.28886000	0.12598000
C	-4.47485900	2.17352200	-0.19842000
H	-4.25248900	3.20588200	-0.46676500
C	-5.81742900	1.73936500	-0.21218500
H	-6.61308000	2.44102800	-0.47497800
C	-6.13016500	0.40072800	0.11399700
H	-7.17236700	0.07805700	0.10736900
C	-5.10356400	-0.51606800	0.44681500
C	-3.75757600	-0.05769400	0.42620000
O	-2.74121900	-0.96865100	0.72722700
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C	-4.23499100	-2.80935800	0.23256900
C	-4.42388000	-4.10262900	-0.31298800
H	-5.42016900	-4.54671500	-0.33845100
C	-3.32853700	-4.83030000	-0.82972400
H	-3.48139200	-5.82458400	-1.25676600
C	-2.03182700	-4.27437300	-0.78951700
H	-1.19926300	-4.84666700	-1.19812300
C	-1.79523200	-2.98043000	-0.25478500
C	-5.34889000	-1.97081100	0.88065200

C	-6.76272500	-2.47017700	0.49974700
H	-6.93500500	-2.43394600	-0.58844400
H	-7.53452900	-1.86119300	0.99599900
H	-6.91257100	-3.50589800	0.84289400
C	-5.20206000	-2.06208400	2.43756300
H	-5.33790600	-3.10535600	2.77133100
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H	-4.20973800	-1.72178800	2.77149000
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C	-1.98403800	5.65460500	-2.65075000
H	-2.08145000	6.50771800	-3.32923900
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H	4.72619300	2.50173000	0.47970600
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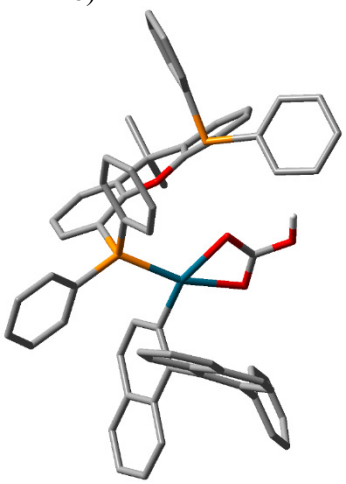
I3 (κ^1-xantphos)Pd(binaphthyl)(κ^2-HCO_3)



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C	7.62810500	-1.84334300	-0.82836500
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H	-0.47302000	-2.66422300	3.86739500
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C	2.34922100	-3.06649000	1.93871900
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C	-4.37087800	2.70678900	0.15461000
C	-5.63039300	3.24650000	-0.23211200
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H	-2.78090000	5.67711100	0.94363100
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P	0.02667700	-1.60553400	1.12055600
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C	-0.12891200	2.35250300	-0.99650200
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H	-1.53537000	3.59674000	-1.21370800
H	4.07888900	1.48064200	-4.71392100
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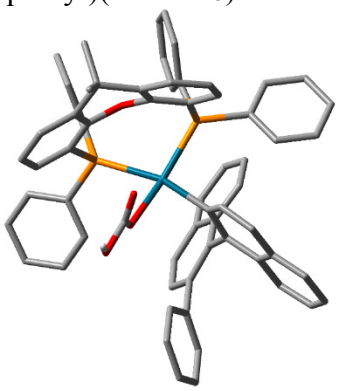
I4 cis-Bidentate (xantphos)Pd(binaphthyl)(κ^1-HCO_3)



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H	-2.88297700	2.75757300	-3.51143700
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C	3.41874500	-3.23955000	-3.14611800
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C	3.55730000	2.52524900	1.47481300
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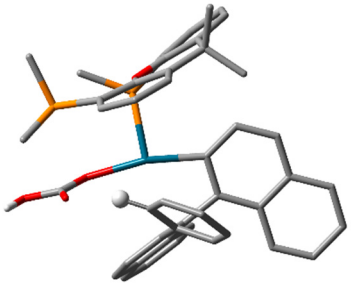
C	4.51137500	2.56370200	2.51882800
H	5.47047300	3.06481200	2.35873500
C	4.21871400	1.96336300	3.76840000
H	4.95310100	1.99527200	4.57898500
C	2.97694700	1.31243200	3.96121800
H	2.74786200	0.83606800	4.91717400
C	2.02743300	1.26791900	2.91439900
H	1.07089800	0.76603200	3.07200200
C	2.85671000	-1.82957200	1.75650100
C	4.22142400	-1.50559600	1.55631200
H	4.58526400	-1.24352900	0.56158600
C	5.13336900	-1.53960600	2.64004700
H	6.18480800	-1.29215100	2.46653400
C	4.69186600	-1.90194800	3.93444300

H	5.40136900	-1.94517000	4.76660500
C	3.32572000	-2.21314000	4.14405100
H	2.97244800	-2.50087300	5.13900300
C	2.41484100	-2.16948200	3.06599100
H	1.36642400	-2.42586400	3.24086300
C	0.65916000	4.37517800	1.93170200
H	1.55494900	4.06919200	2.47014100
C	0.03548700	5.59450700	2.29108000
H	0.46299800	6.19738600	3.09762100
C	-1.12955300	6.02975200	1.61505500
H	-1.61413500	6.96961900	1.89554900
C	-1.66064400	5.23357200	0.57106800
H	-2.56180100	5.54934400	0.03818800
C	-1.03955400	4.01411200	0.21222400
H	-1.46906700	3.42582200	-0.59589900
C	0.13120200	3.56851700	0.88593900
C	0.87512500	-3.52942500	0.67247400
C	1.71121600	-4.64365600	0.96986400
H	2.79526600	-4.51693100	1.02041700
C	1.15131800	-5.91791200	1.21589300
H	1.80653900	-6.76527700	1.43801100
C	-0.25653200	-6.09089800	1.18070600
H	-0.69325100	-7.07588500	1.37187500
C	-1.09234100	-4.98425400	0.90097500
H	-2.17812900	-5.10635400	0.87070000
C	-0.53147100	-3.70863700	0.64502200
H	-1.18724100	-2.87279300	0.41268500
O	2.95069800	0.31316600	-1.01547400
P	0.96325600	1.96617700	0.40817700
P	1.60874500	-1.85311100	0.38196600
Pd	-0.11447700	-0.07227500	-0.19197300
O	-0.74071100	-1.61987500	-1.51831700
C	-0.36112100	-1.41805600	-2.74329100
O	-0.86146400	-2.39334100	-3.59908500
O	0.35286900	-0.50599000	-3.19867200
H	-0.50726700	-2.14437200	-4.47383300
H	-4.24606600	-2.55821300	-3.65514300
H	-7.72278900	-3.02798500	-1.07741300

I5 (κ^1-xantphos)Pd(binaphthyl)(κ^1-HCO_3) intermediate preceding CMD TS1 (from IRC analysis). Xantphos phenyl rings have been removed for clarity in the figure.

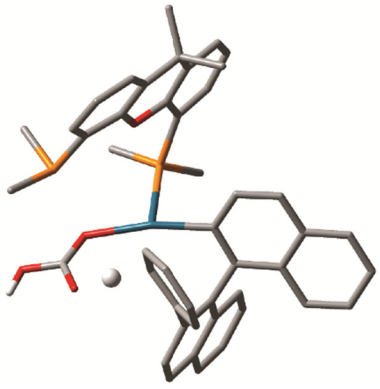


C	2.57217600	-0.48556600	0.82087700
C	3.61466700	-0.96575800	0.02067700
C	2.59583000	-0.74160800	2.23059900
C	4.74282200	-1.67944000	0.56043800
C	3.66327200	-1.45132500	2.79194900
H	1.80107600	-0.39077200	2.88413300
C	5.83264300	-2.16443800	-0.24527500
C	4.75801300	-1.92735900	1.98912900
H	3.67635900	-1.65178700	3.86800500
C	6.89511800	-2.86082500	0.33977100
H	5.82555700	-1.98025400	-1.32218500
C	5.86597400	-2.64834300	2.55976500
C	6.91473200	-3.10571500	1.75565200
H	7.71796900	-3.22235100	-0.28372100

H	5.87372200	-2.83511100	3.63804700
H	7.75102100	-3.65202800	2.20089800
C	3.39842400	-0.66504200	-1.44879200
C	4.16236100	0.38362700	-2.11536500
C	2.44522100	-1.42522300	-2.18136100
C	5.15503200	1.15562600	-1.42314900
C	3.91956400	0.66044000	-3.51028300
C	2.21641300	-1.11420800	-3.57207700
C	5.87484900	2.15623100	-2.08630900
H	5.34951800	0.95169400	-0.36888500
C	4.66652400	1.69587300	-4.16702000
C	2.92694300	-0.10946800	-4.21282900
H	1.46734200	-1.69268000	-4.11275900
C	5.62972400	2.43364300	-3.47034800
H	6.63098300	2.73088200	-1.54365600
H	4.46319200	1.90347900	-5.22147700
H	2.73945300	0.10947400	-5.26786200
H	6.19244300	3.22235200	-3.97730000
C	1.75027600	-2.63794500	-1.61477800
C	2.50860500	-3.74499900	-1.14938700
C	0.33197100	-2.71497200	-1.61112800
C	1.85841300	-4.90786700	-0.67279400
H	3.59891600	-3.71129600	-1.17674600
C	-0.31564100	-3.87186400	-1.11728900
H	-0.24631300	-1.86371600	-1.97509000
C	0.44322600	-4.97235900	-0.64902000
H	-0.06047400	-5.86826200	-0.27341300
C	-0.52300700	-3.34231800	3.88707100
H	0.03274700	-3.20692500	4.83053700
H	-0.93719800	-4.36436600	3.87957200
H	0.18851700	-3.25359200	3.05105800
C	-2.65701100	-2.44249500	4.95713600
H	-3.45993000	-1.68896600	4.90540300
H	-3.12252700	-3.44076100	4.95212100
H	-2.13820200	-2.32815300	5.92280600
C	-1.66567000	-2.28334600	3.76208900
C	-2.42727400	-2.49991800	2.44460900
C	-2.47522500	-1.51654800	1.42270400
C	-3.14467300	-3.70640100	2.23190100
H	-3.10412600	-4.49466400	2.98713500
C	-3.90881400	-3.90880700	1.06595800
H	-4.44225300	-4.85056600	0.91262200
C	-4.01434500	-2.86863200	0.11416100
H	-4.64976400	-3.00731500	-0.76113300
C	-3.32032200	-1.64404300	0.27841900
C	-1.03010200	-0.88416200	3.78672900
C	-0.98095000	-0.06540700	2.62797100
C	-0.18105400	1.12079400	2.58296800
C	0.44425700	1.55185300	3.77787800
H	1.05551700	2.45354500	3.77258600
C	0.31905200	0.81041600	4.97309500
H	0.79718700	1.16339300	5.88979300
C	-0.37561100	-0.41497500	4.95546000
H	-0.40578300	-1.02059900	5.86375100
C	-1.18239900	2.84087000	0.40787200
C	-2.33944200	2.93974500	1.22253500
H	-2.41743100	2.36622200	2.14768000
C	-3.40296400	3.79331200	0.84665000
H	-4.29188200	3.85789000	1.47868900
C	-3.31413700	4.55387900	-0.34247700
H	-4.13541800	5.21726900	-0.63105700
C	-2.16476500	4.44622700	-1.16462800
H	-2.09311000	5.02024300	-2.09247900
C	-1.09893800	3.59399800	-0.79551000
H	-0.22124700	3.50902400	-1.43592600
C	-5.04045600	0.60973600	-0.07465800
C	-5.58631600	0.23455700	1.18226500
H	-5.17988400	-0.62141300	1.72406400
C	-6.67284200	0.95237800	1.74473800
H	-7.07829800	0.64633500	2.71430900
C	-7.24251700	2.04769600	1.05165900

H	-8.08919900	2.59305600	1.47976200
C	-6.70683000	2.42849800	-0.20579100
H	-7.13838400	3.27181300	-0.75418200
C	-5.60727100	1.72841800	-0.75005800
H	-5.19025300	2.04654300	-1.71022900
C	0.93261900	4.48598200	1.99637100
H	-0.14386100	4.62451700	2.11522800
C	1.81266500	5.52548000	2.37817400
H	1.40676200	6.45423200	2.78914200
C	3.21252300	5.36727100	2.21688000
H	3.89304300	6.17420200	2.50473300
C	3.72451900	4.16493900	1.67196600
H	4.80168700	4.03797000	1.53345100
C	2.84380100	3.12346300	1.29217100
H	3.24426600	2.20497500	0.86109100
C	1.44273300	3.27233800	1.45831100
C	-4.38295500	-1.03214100	-2.32726800
C	-5.77609900	-1.31067400	-2.41519500
H	-6.44391600	-1.02349200	-1.59978200
C	-6.31167200	-1.95771500	-3.55559900
H	-7.38528800	-2.16378700	-3.60834100
C	-5.46061900	-2.33720700	-4.62459700
H	-5.87416800	-2.83882900	-5.50512700
C	-4.07392100	-2.05440300	-4.54913500
H	-3.41133200	-2.33338000	-5.37428400
C	-3.53749900	-1.39625800	-3.41399600
H	-2.47533600	-1.14553500	-3.37801500
O	-1.69568400	-0.35962800	1.48641800
P	0.29501200	1.89848000	0.97366700
P	-3.56272400	-0.19386900	-0.88010600
Pd	1.43084800	0.50728300	-0.52516100
O	0.74823800	1.61059600	-2.20527700
C	-0.09619100	1.15251300	-3.06185500
O	-0.63512500	0.02794200	-3.11683200
O	-0.40597800	2.09466100	-4.04161200
H	-1.05913100	1.64408000	-4.60969900
H	2.45566300	-5.75499000	-0.32259000
H	-1.40773700	-3.91053300	-1.10001300

TS1 Inner-sphere CMD transition state. Xantphos phenyl rings have been removed for clarity in the figure.

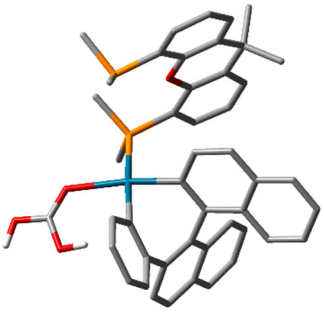


C	1.99549700	-0.01399000	-1.19377500
C	3.29305800	0.51925900	-1.09523300
C	1.68987700	-0.97664200	-2.21197800
C	4.33843800	0.05903200	-1.99628600
C	2.67791900	-1.45134100	-3.07529500
H	0.66683600	-1.33938900	-2.31960000
C	5.67870300	0.59203200	-1.97778400
C	4.02517200	-0.95993400	-2.98328000
H	2.43368900	-2.18990900	-3.84534200
C	6.65538600	0.12386700	-2.86260700

H	5.93386800	1.37800400	-1.26712400
C	5.05496800	-1.42799900	-3.87447500
C	6.34908600	-0.90316000	-3.81743200
H	7.66350100	0.54744700	-2.82656200
H	4.80064400	-2.19817100	-4.60943500
H	7.12252400	-1.26291100	-4.50203100
C	3.56406200	1.68149100	-0.16242100
C	4.47635200	1.59497400	0.95950900
C	2.96025800	2.91985800	-0.46468400
C	5.07445300	0.35216900	1.36593900
C	4.79031900	2.79173900	1.72045100
C	3.28691900	4.09889400	0.28638700
C	5.94803300	0.29502200	2.45455700
H	4.82878900	-0.55605700	0.81897800
C	5.69938400	2.70279500	2.83379900
C	4.18744700	4.04196000	1.34982800
H	2.80309300	5.04208000	0.02105700
C	6.27190500	1.48062500	3.19599200
H	6.38294000	-0.66495700	2.74598500
H	5.93018500	3.61299500	3.39563900
H	4.43109100	4.94193500	1.92181600
H	6.95938000	1.42420600	4.04488200
C	1.91151000	2.98830300	-1.53295000
C	2.17511500	3.59998000	-2.78218600
C	0.63830900	2.39258000	-1.24538200
C	1.19075700	3.57429100	-3.80166500
H	3.15012300	4.05702000	-2.97295300
C	-0.32439900	2.37673600	-2.30221000
H	0.08151900	2.95321700	-0.11494200
C	-0.05962300	2.94830700	-3.56738800
H	-0.81582400	2.91698800	-4.35767000
C	-1.77745500	-3.41036300	-4.33598200
H	-1.31536700	-4.40229200	-4.47258700
H	-2.43579000	-3.22126400	-5.20008700
H	-0.97646100	-2.65314700	-4.34477100
C	-3.71733900	-4.42706700	-3.03098000
H	-4.29537100	-4.41443600	-2.09266800
H	-4.41278200	-4.23951500	-3.86463000
H	-3.30380400	-5.43957000	-3.16702700
C	-2.58419800	-3.35199800	-2.99928900
C	-3.22308400	-1.96585900	-2.83906000
C	-2.93157900	-1.12357100	-1.73704700
C	-4.17764600	-1.50965700	-3.78801300
H	-4.40333700	-2.12766500	-4.66005600
C	-4.84304200	-0.27937800	-3.62592600
H	-5.56672500	0.05892700	-4.37199300
C	-4.59690500	0.49804700	-2.47003300
H	-5.15067000	1.42523900	-2.31980200
C	-3.65053400	0.08957000	-1.49800100
C	-1.62425700	-3.63785100	-1.83255500
C	-1.27827500	-2.64825000	-0.86929200
C	-0.23709000	-2.86993400	0.09007100
C	0.32334400	-4.17125700	0.16089000
H	1.08441000	-4.38770500	0.90886100
C	-0.06868900	-5.19774400	-0.72456600
H	0.37643800	-6.19210700	-0.64412200
C	-1.00369300	-4.90922500	-1.73658700
H	-1.25861500	-5.68489900	-2.46191100
C	-0.47932800	-1.63305900	2.73820500
C	-1.35159900	-2.72086400	3.00357500
H	-1.54202300	-3.47345700	2.23644400
C	-1.98192700	-2.84244700	4.26469900
H	-2.65742200	-3.68233000	4.45067300
C	-1.73831800	-1.88411800	5.27660100
H	-2.21509500	-1.98520100	6.25661000
C	-0.88067000	-0.78799600	5.01196400
H	-0.69617400	-0.03305100	5.78155900
C	-0.26321000	-0.65536000	3.74647500
H	0.37755800	0.20287100	3.54685800
C	-4.25626400	0.05657900	1.30229100
C	-5.25374100	-0.90410200	0.97949500

H	-5.49394600	-1.11517000	-0.06525300
C	-5.95408000	-1.58701700	2.00447300
H	-6.72189600	-2.32121600	1.74100400
C	-5.66790400	-1.31402300	3.36552400
H	-6.21279400	-1.83734500	4.15762300
C	-4.66703700	-0.36700500	3.69455700
H	-4.42906400	-0.15825000	4.74108300
C	-3.95835000	0.30616800	2.67122900
H	-3.17386100	1.02040700	2.93486100
C	2.47465400	-2.48590500	3.00681200
H	1.77905100	-2.22565200	3.80509500
C	3.72949000	-3.04819200	3.35025300
H	3.97881000	-3.19783200	4.40477600
C	4.64491300	-3.42399500	2.33979700
H	5.60728300	-3.87270400	2.60402500
C	4.29882000	-3.22287400	0.98038300
H	4.99357100	-3.50983000	0.18541800
C	3.05814200	-2.64033000	0.63726300
H	2.80996000	-2.50756200	-0.41586400
C	2.12222000	-2.27802300	1.64777600
C	-4.45121200	2.51851500	-0.17419500
C	-5.82743400	2.53563200	0.18447700
H	-6.29009700	1.64414000	0.61318500
C	-6.60752600	3.70316200	-0.00258400
H	-7.66439400	3.69991200	0.28138200
C	-6.02284200	4.87254300	-0.55123800
H	-6.62621900	5.77414100	-0.69491300
C	-4.64947600	4.87000700	-0.90194100
H	-4.18478600	5.77043400	-1.31471200
C	-3.86824200	3.70516900	-0.70292500
H	-2.80307800	3.72435900	-0.94729000
O	-1.93270800	-1.43160100	-0.81170200
P	0.48494500	-1.52519800	1.16347200
P	-3.31711300	1.06008400	0.05289800
Pd	0.63871200	0.64565100	0.12986000
O	-0.46231900	1.59896300	1.80714100
C	-0.74095500	2.81844200	1.74791400
O	-0.48129200	3.62947000	0.77408300
O	-1.39820400	3.36101800	2.81922200
H	-1.55318100	4.29994400	2.59834900
H	1.40423100	4.02833700	-4.77432100
H	-1.30227600	1.92167200	-2.12117800

I6 Palladacycle following inner-sphere CMD, with κ^1-xantphos and κ^1-HCO_3 (from IRC analysis). Xantphos phenyl rings have been removed for clarity in the figure.

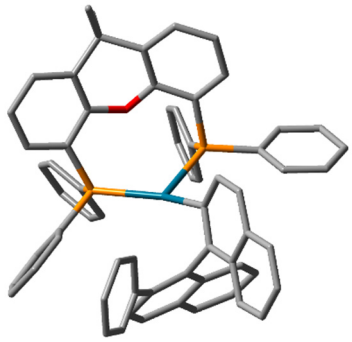


C	1.28994000	-0.92967300	-0.92398600
C	2.60693000	-1.41781600	-0.95835100
C	0.19301900	-1.84831100	-1.05314700
C	2.86133400	-2.84030700	-1.13747900
C	0.40225300	-3.21918000	-1.19031500
H	-0.82465300	-1.46003100	-1.04512300
C	4.18848300	-3.39099100	-1.25657000
C	1.73608100	-3.75158900	-1.24354200
H	-0.44807200	-3.90075000	-1.29031600
C	4.38926800	-4.76275900	-1.44431700

H	5.05197500	-2.72657800	-1.21687200
C	1.97432300	-5.15926500	-1.42540000
C	3.27491900	-5.66334600	-1.52006200
H	5.40793700	-5.15120000	-1.53712300
H	1.11262400	-5.82999500	-1.50154000
H	3.44446000	-6.73450300	-1.66265100
C	3.76170000	-0.45437800	-0.87851300
C	4.68719700	-0.49746500	0.23756000
C	3.97221700	0.47451300	-1.92088000
C	4.47098600	-1.35510400	1.37415500
C	5.85563900	0.36335700	0.24096300
C	5.13857200	1.31765200	-1.90307500
C	5.36973100	-1.37387600	2.44366200
H	3.58263400	-1.98609700	1.40230600
C	6.76971900	0.31508800	1.35245400
C	6.06419200	1.26012600	-0.86170100
H	5.28671300	2.02410200	-2.72398500
C	6.53806700	-0.53953500	2.43313000
H	5.18162300	-2.03223300	3.29663500
H	7.65260800	0.96170500	1.33459700
H	6.94656500	1.90669600	-0.86576700
H	7.23891300	-0.56964300	3.27242900
C	2.99400100	0.63198800	-3.05075000
C	3.46692700	0.57688700	-4.39401200
C	1.61185600	0.88358100	-2.77540800
C	2.57652600	0.73757800	-5.48115800
H	4.52613100	0.38027000	-4.58299100
C	0.73752500	1.04326100	-3.88971500
H	2.08485200	2.81140500	-2.74369200
C	1.20299200	0.97323500	-5.22746100
H	0.50174200	1.10244800	-6.05789500
C	-1.05239900	-5.05257200	2.26401500
H	-0.37859200	-5.39663400	3.06530600
H	-1.76812800	-5.86615600	2.06277100
H	-0.44962100	-4.88607600	1.35747000
C	-2.62052600	-4.01095700	3.98162500
H	-3.15848200	-3.10325100	4.30100000
H	-3.36353400	-4.80911500	3.81610600
H	-1.96129800	-4.32753600	4.80724400
C	-1.79412400	-3.74386100	2.68292200
C	-2.75021700	-3.31211100	1.55730100
C	-2.69815400	-2.02028900	0.96910700
C	-3.73573000	-4.21199300	1.07403000
H	-3.80945900	-5.21062500	1.51085200
C	-4.62181600	-3.85254400	0.03680500
H	-5.36531700	-4.56764900	-0.32442800
C	-4.53654800	-2.56306300	-0.53522100
H	-5.21379200	-2.28829400	-1.34583500
C	-3.58690700	-1.61680600	-0.07470000
C	-0.75607900	-2.64350000	2.95778500
C	-0.78319000	-1.39633200	2.28426600
C	0.18831600	-0.37748100	2.52252300
C	1.20403700	-0.63693600	3.47337600
H	1.96474100	0.11733900	3.67294800
C	1.25065800	-1.86755000	4.16735500
H	2.03768100	-2.04976500	4.90318700
C	0.27893800	-2.85375200	3.90688000
H	0.32643500	-3.80176900	4.44767500
C	-1.35197700	2.06338800	2.05253600
C	-2.15646400	1.62100300	3.13406600
H	-1.90066100	0.70574900	3.67135600
C	-3.29302600	2.36562300	3.53423700
H	-3.91055200	2.00639300	4.36269300
C	-3.62981300	3.56509300	2.86341600
H	-4.51157800	4.13613300	3.16782800
C	-2.82424600	4.01524700	1.78884500
H	-3.07571600	4.94240100	1.26492400
C	-1.69900000	3.26546300	1.37681700
H	-1.08935100	3.61683600	0.54344600
C	-4.93032100	0.94389800	-0.07520500
C	-5.86590100	0.33363400	0.80338800

H	-5.75298700	-0.71622000	1.08014900
C	-6.95489400	1.07513300	1.32651600
H	-7.66398000	0.58844900	2.00340700
C	-7.13371200	2.43375600	0.96864500
H	-7.98195000	3.00127600	1.36389500
C	-6.20422800	3.05309100	0.09564000
H	-6.32834200	4.10362100	-0.18508200
C	-5.10374700	2.31875300	-0.40350300
H	-4.37795200	2.81304200	-1.05636400
C	1.23284500	2.97102300	3.54130700
H	0.22534300	3.00249100	3.96070500
C	2.26855100	3.71032500	4.16131400
H	2.05008600	4.30456300	5.05358400
C	3.58159900	3.68392700	3.62641700
H	4.38141400	4.25587800	4.10682900
C	3.85311500	2.91552000	2.46823500
H	4.86138600	2.88271500	2.04763900
C	2.81461700	2.18217500	1.84522500
H	3.02493600	1.60105300	0.94625200
C	1.49896800	2.19786900	2.37916400
C	-4.04328500	-0.24271400	-2.54507000
C	-5.37201600	-0.02982100	-3.00477400
H	-6.13619600	0.33855900	-2.31704700
C	-5.71915700	-0.29162100	-4.35411900
H	-6.74664900	-0.12225800	-4.69079300
C	-4.74420800	-0.77193600	-5.26300100
H	-5.01394700	-0.97600600	-6.30370000
C	-3.41450400	-0.98110100	-4.81608400
H	-2.65097100	-1.34677200	-5.50917400
C	-3.06555300	-0.70670900	-3.47244900
H	-2.03271400	-0.85873600	-3.14609600
O	-1.77389400	-1.06965000	1.37483800
P	0.19413500	1.18762400	1.52862200
P	-3.45078200	0.09427900	-0.81130000
Pd	0.87665900	1.03857700	-0.84938900
O	0.56961600	3.33406300	-0.98020400
C	1.24482200	4.11936100	-1.64582300
O	2.12313300	3.80312400	-2.60377700
O	1.14635100	5.45260500	-1.45307100
H	1.74762200	5.89454000	-2.08448200
H	2.94892600	0.67595600	-6.50788600
H	-0.32579300	1.23421400	-3.71396600

I7 cis-Bidentate (xantphos)Pd(binaphthyl) cation



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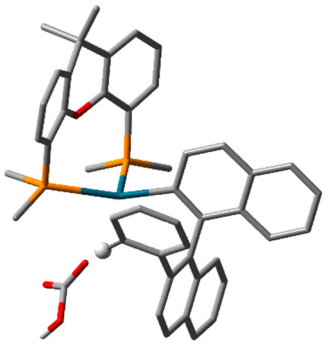
C	-2.90599600	1.00872400	-0.28139400
C	-1.56663100	2.02987900	-2.08902500
C	-4.12191700	1.52998300	-0.86072500
C	-2.73562600	2.51293500	-2.68913100
H	-0.59647500	2.21020900	-2.55742200
C	-5.41563900	1.30222700	-0.27511200
C	-4.02422900	2.30486700	-2.08369600
H	-2.67615000	3.07067500	-3.62827900
C	-6.56234200	1.84170900	-0.86394600

H	-5.49189700	0.71662900	0.64314700
C	-5.22699500	2.83731000	-2.67009100
C	-6.47007500	2.61382000	-2.07217200
H	-7.54006200	1.67292500	-0.40474200
H	-5.15237200	3.42054000	-3.59222400
H	-7.37723900	3.02375400	-2.52361500
C	-2.87630800	0.02048600	0.86640000
C	-2.48704600	0.46367900	2.19647500
C	-3.24164500	-1.33540000	0.64955800
C	-2.25237900	1.84933200	2.49987400
C	-2.37301500	-0.49782200	3.27060100
C	-3.10119400	-2.27112600	1.73839800
C	-1.91435300	2.25897700	3.79239900
H	-2.37407100	2.59339700	1.71402300
C	-1.99157200	-0.05608100	4.58527800
C	-2.66679200	-1.87580400	2.99797900
H	-3.32922100	-3.32110700	1.55427000
C	-1.76734100	1.29856100	4.84733600
H	-1.76862300	3.32233600	4.00099600
H	-1.90950600	-0.79760400	5.38520400
H	-2.55928500	-2.61324400	3.79820600
H	-1.50422500	1.62964800	5.85543500
C	-3.86126600	-1.86121300	-0.61931800
C	-4.98765000	-2.72355500	-0.49377200
C	-3.39110000	-1.56065600	-1.92841500
C	-5.61931500	-3.27545700	-1.63272000
H	-5.39173500	-2.94365400	0.49720700
C	-4.01134900	-2.12300900	-3.06663700
C	-5.12893200	-2.98306800	-2.92825800
H	-5.61181200	-3.40841600	-3.81225100
C	4.56272400	-0.17377600	-5.05986900
H	5.13099900	0.70273400	-5.40698100
H	5.15953000	-1.05645100	-5.33480800
H	3.60732800	-0.21254000	-5.60811100
C	5.73920000	-0.06039000	-2.81752900
H	5.63330200	-0.02457100	-1.72094400
H	6.33091300	-0.95556300	-3.07287800
H	6.29940600	0.83393000	-3.13907600
C	4.34338000	-0.11429400	-3.52698800
C	3.58965000	-1.35532600	-3.00373900
C	2.85515000	-1.25078600	-1.79660500
C	3.65225000	-2.64138800	-3.59938000
H	4.20690600	-2.78733400	-4.52754900
C	3.01440200	-3.75474000	-3.00137400
H	3.08916900	-4.73850500	-3.47063400
C	2.27402600	-3.60260000	-1.80653700
H	1.77004200	-4.46599500	-1.37076400
C	2.16723700	-2.32984100	-1.18568800
C	3.55074100	1.14166800	-3.11022800
C	2.83901100	1.11545500	-1.88749500
C	2.15793100	2.23560100	-1.34515500
C	2.19446400	3.45326900	-2.07399400
H	1.68335100	4.33754800	-1.69203400
C	2.88754800	3.51451300	-3.30481500
H	2.91294500	4.45212400	-3.86488200
C	3.55355000	2.37388500	-3.81550100
H	4.08350500	2.45647900	-4.76569700
C	2.31308400	1.65542500	1.57354300
C	3.71959700	1.58482500	1.41428800
H	4.17237600	1.67488400	0.42613100
C	4.55033700	1.42433800	2.54947100
H	5.63503300	1.37438400	2.42231800
C	3.98040200	1.34282400	3.84312200
H	4.62544900	1.22698900	4.71848400
C	2.57375500	1.41423700	4.00064600
H	2.12802200	1.35670400	4.99737800
C	1.74096300	1.56052800	2.87141400
H	0.65799600	1.62894100	3.00304600
C	2.23399900	-2.28845300	1.75087700
C	3.48817100	-2.94117900	1.62248800
H	3.86258900	-3.22749600	0.63763300

C	4.25824800	-3.23501400	2.77345900
H	5.22270000	-3.73875200	2.66528000
C	3.77502900	-2.88952100	4.06009800
H	4.36500600	-3.12751700	4.94973800
C	2.52516300	-2.23522900	4.19031500
H	2.14871100	-1.96177300	5.17997300
C	1.76327500	-1.92458500	3.03990000
H	0.80301900	-1.41377200	3.14931100
C	1.53953300	4.57902000	1.25689600
H	2.52432200	4.20742300	1.54257800
C	1.20850800	5.92336000	1.54574800
H	1.94180100	6.56148700	2.04586600
C	-0.06572500	6.43507100	1.19633200
H	-0.32472000	7.47225600	1.42631700
C	-0.99983500	5.59341300	0.54622200
H	-1.98603100	5.97503700	0.26887100
C	-0.66702600	4.24981500	0.24765300
H	-1.39382200	3.62792500	-0.26613300
C	0.60314600	3.72679900	0.60253600
C	0.02785700	-3.49994100	0.32118000
C	0.06330200	-4.47355900	1.35302300
H	0.76898900	-4.38030800	2.17964800
C	-0.81242900	-5.58634000	1.31116600
H	-0.76974200	-6.33534300	2.10686800
C	-1.72885000	-5.73608400	0.24189400
H	-2.39878600	-6.60001700	0.20885700
C	-1.77031400	-4.76429400	-0.78882200
H	-2.47293400	-4.86651800	-1.61931300
C	-0.90084600	-3.65256600	-0.74378500
H	-0.93620300	-2.91935400	-1.55305900
O	2.78698200	-0.03702600	-1.12374600
P	1.16293200	2.00680500	0.18378600
P	1.12151700	-2.00481900	0.31151200
Pd	-0.25408500	0.14818300	-0.02277600
H	-6.49119600	-3.92322800	-1.50660900
H	-3.62544000	-1.88252000	-4.06123700
H	-2.53360300	-0.90465600	-2.07141500

I8 cis-Bidentate (xantphos)Pd(binaphthyl) cation with noncovalently associated bicarbonate. This intermediate precedes outer-sphere CMD TS2 according to IRC analysis. Xantphos phenyl rings have been removed for clarity in the figure.



C	-1.74873700	0.78659300	-1.06596400
C	-3.05228900	0.26350300	-1.08708400
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C	-4.12369800	1.06185800	-1.66386400
C	-2.47460500	2.84214100	-2.21115200
H	-0.43502600	2.43986100	-1.66132300
C	-5.48184600	0.58296400	-1.74628600
C	-3.83093500	2.37339400	-2.21174700
H	-2.24315600	3.81353300	-2.65831300
C	-6.49273500	1.37007100	-2.30617900
H	-5.72411100	-0.40813000	-1.36382400
C	-4.89439400	3.16397300	-2.77745500

C	-6.20347300	2.67809300	-2.82266400
H	-7.51492000	0.98317700	-2.35104600
H	-4.65438600	4.15220600	-3.18169100
H	-7.00345400	3.28450000	-3.25670000
C	-3.30997800	-1.18511400	-0.74238100
C	-4.10522300	-1.62270500	0.38282900
C	-2.77749900	-2.13981900	-1.62910700
C	-4.68108200	-0.70442100	1.32768400
C	-4.33666900	-3.04382700	0.57160900
C	-2.99511500	-3.54027000	-1.42174000
C	-5.46419700	-1.16429100	2.38920700
H	-4.50924700	0.36331500	1.20201600
C	-5.13858600	-3.48635400	1.68221300
C	-3.76419100	-3.98398300	-0.34940500
H	-2.53504400	-4.25682000	-2.10490400
C	-5.69828200	-2.56799100	2.57376800
H	-5.89690900	-0.44518200	3.09017800
H	-5.29865000	-4.56021400	1.81650100
H	-3.92107800	-5.05325200	-0.18587700
H	-6.30774800	-2.91502800	3.41301600
C	-1.88759100	-1.68271300	-2.74795300
C	-2.39151800	-1.09884300	-3.93270200
C	-0.48142500	-1.78247400	-2.55905000
C	-1.49959900	-0.59466300	-4.91068200
H	-3.47068000	-1.02228000	-4.08399000
C	0.40795600	-1.27652800	-3.54294900
H	-0.13325900	-2.35616300	-1.69446500
C	-0.09830100	-0.67002500	-4.71379700
H	0.58597400	-0.27384800	-5.46933800
C	3.68991500	5.38868600	-1.79071400
H	3.69098000	6.32674800	-1.21434900
H	4.64329400	5.36082400	-2.34083000
H	2.86502300	5.42730000	-2.52099300
C	4.76653800	4.17498000	0.15451500
H	4.71175500	3.32580000	0.85443000
H	5.72417700	4.11157000	-0.39037600
H	4.75873200	5.10615700	0.74721100
C	3.56578100	4.16279700	-0.85176800
C	3.61410800	2.83296200	-1.63015700
C	3.09053200	1.67354900	-1.00908700
C	4.26266100	2.64750800	-2.87853700
H	4.67969100	3.50248700	-3.41348100
C	4.38201200	1.35597500	-3.44424300
H	4.87143500	1.23234500	-4.41383700
C	3.90229300	0.21795300	-2.75244400
H	4.02948900	-0.77038100	-3.19473800
C	3.25493800	0.35360500	-1.49792100
C	2.25882000	4.19388700	-0.03590800
C	1.71945000	2.96710000	0.42889200
C	0.51462100	2.86715100	1.17544500
C	-0.09707000	4.08332600	1.57762100
H	-0.99956300	4.06506200	2.18651200
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H	-0.04088600	6.25377100	1.50275800
C	1.59051900	5.38093900	0.35706200
H	1.96896300	6.35326200	0.03663800
C	0.61795300	0.45804200	2.89586000
C	1.31111300	1.26116700	3.84042300
H	1.47686600	2.32433500	3.65059000
C	1.77777400	0.67988100	5.04184200
H	2.31467600	1.29600100	5.76907300
C	1.54420400	-0.69562000	5.30322200
H	1.89832700	-1.13841100	6.23954800
C	0.87551800	-1.49641300	4.34751800
H	0.71976300	-2.56626700	4.50088900
C	0.41715800	-0.92345300	3.13899900
H	-0.06713900	-1.56472800	2.39883000
C	3.61084200	-1.04489000	1.02668900
C	4.76894700	-0.23729400	1.17251700
H	5.01663100	0.51783900	0.42404600
C	5.63022100	-0.41295300	2.28240700

H	6.52133300	0.21482000	2.38053300
C	5.34467900	-1.40442000	3.25285100
H	6.01325900	-1.54726900	4.10742500
C	4.18754900	-2.20872600	3.10978400
H	3.95004800	-2.97276300	3.85516100
C	3.31855800	-2.03170300	2.00742900
H	2.43264000	-2.66667500	1.92392200
C	-2.25843300	1.16789900	3.47851100
H	-1.59386800	0.50707700	4.03342900
C	-3.48648000	1.55059600	4.06970200
H	-3.73812000	1.17589800	5.06577300
C	-4.37317400	2.41219800	3.38476200
H	-5.31577100	2.71956800	3.84767700
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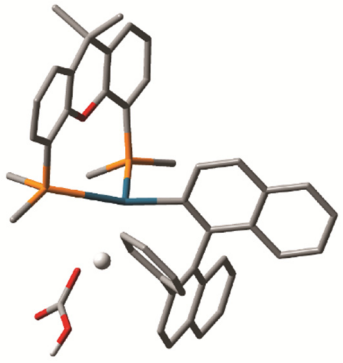
H	-4.70703000	3.53246800	1.54024500
C	-2.81226000	2.47995000	1.49147500
H	-2.56959400	2.85888600	0.50005000
C	-1.90004400	1.63702300	2.18691900
C	3.17103500	-2.55667300	-1.28732500
C	4.56148600	-2.68500700	-1.57327600
H	5.24508800	-1.86282100	-1.35117900
C	5.07895200	-3.88049300	-2.11998400
H	6.14862800	-3.95919000	-2.33587400
C	4.21628800	-4.98052800	-2.36571000
H	4.61633900	-5.91048000	-2.78127300
C	2.84344400	-4.87502800	-2.04416300
H	2.17206000	-5.72497200	-2.19206100
C	2.32151200	-3.67211700	-1.50511400
H	1.27537600	-3.63606500	-1.20953500
O	2.37713700	1.77823600	0.17997000
P	-0.24299000	1.19441900	1.45723200
P	2.51280100	-1.01306000	-0.47453200
Pd	-0.11375100	-0.23317800	-0.43840500
O	0.42226200	-3.97947500	2.31963400
C	0.03225700	-3.87965700	1.12546100
O	-0.16783200	-2.84719400	0.41679700
O	-0.19747800	-5.09857200	0.43405000
H	0.01339600	-5.78077600	1.09942900
H	-1.89914300	-0.13677600	-5.82058100
H	1.48527600	-1.38261400	-3.40740300

TS2 Outer-sphere CMD transition state. Xantphos phenyl rings have been removed for clarity in the figure.

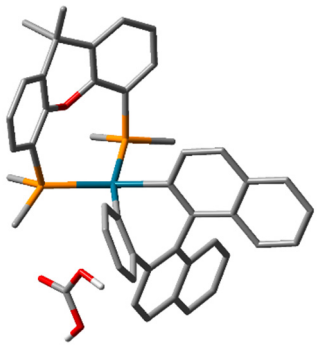


C	-1.77614000	0.43711400	-1.38836800
C	-3.08366200	-0.03860300	-1.22252500
C	-1.48755300	1.47482700	-2.34057100
C	-4.15960800	0.54223400	-2.01871100
C	-2.50389200	2.06075400	-3.09374400
H	-0.45627400	1.80839900	-2.48237900
C	-5.51873500	0.06491600	-1.95561000
C	-3.86303000	1.61845000	-2.94690000

H	-2.27443000	2.84895300	-3.81757400
C	-6.52590400	0.64067800	-2.73716400
H	-5.76630700	-0.76492700	-1.29478700
C	-4.92250100	2.19888100	-3.73018000
C	-6.23382200	1.72643400	-3.62814700
H	-7.54748900	0.25545700	-2.66798200
H	-4.67747800	3.01232600	-4.42023300
H	-7.03084200	2.17093200	-4.23093600
C	-3.35765200	-1.24682700	-0.35940900
C	-4.23243000	-1.21432900	0.79594200
C	-2.81167800	-2.47517000	-0.77761400
C	-4.80486800	0.00615500	1.29783200
C	-4.55484100	-2.45575600	1.47828200
C	-3.14120800	-3.69597300	-0.09832900
C	-5.66747400	-0.00335700	2.39673100
H	-4.56471700	0.94714100	0.80586900
C	-5.43900200	-2.43126800	2.61416800
C	-3.99491300	-3.68998400	1.00217100
H	-2.69133500	-4.62602200	-0.44892300
C	-5.99235800	-1.23041400	3.06550000
H	-6.09359500	0.93818800	2.75352200
H	-5.66992000	-3.37473400	3.11784300
H	-4.23912000	-4.62069600	1.52188600
H	-6.66669300	-1.22250500	3.92662000
C	-1.86484300	-2.52316400	-1.93963100
C	-2.30830000	-3.02500700	-3.18613400
C	-0.51294400	-2.07247000	-1.75171500
C	-1.44357500	-3.00775700	-4.30818000
H	-3.33347400	-3.39062300	-3.29075600
C	0.32732800	-2.07076100	-2.90941700
H	-0.11625800	-2.52108900	-0.51243400
C	-0.12501400	-2.50951500	-4.17458500
H	0.54301100	-2.47725500	-5.04048900
C	3.33469600	4.79830100	-2.94584300
H	3.16881300	5.86792300	-2.73942900
H	4.16713500	4.72846100	-3.66438800
H	2.42879200	4.39542500	-3.42697600
C	4.95582900	4.61138200	-0.99111600
H	5.20806100	4.08434100	-0.05646500
H	5.81194300	4.51652400	-1.68015800
H	4.82130300	5.68085900	-0.75580100
C	3.66129100	4.01970500	-1.63499300
C	3.90495500	2.53081600	-1.95493900
C	3.27402900	1.50329700	-1.21609200
C	4.82949000	2.11235700	-2.94991000
H	5.35115200	2.85909200	-3.55337200
C	5.09598100	0.74326100	-3.17401400
H	5.80222200	0.44769100	-3.95406000
C	4.47361100	-0.24980300	-2.37662800
H	4.70861900	-1.30187000	-2.54114500
C	3.55490900	0.11884300	-1.36468400
C	2.48490900	4.17031900	-0.64760000
C	1.84878200	3.04269000	-0.07107400
C	0.68216500	3.12110000	0.73955200
C	0.22093600	4.41493200	1.09133600
H	-0.65799800	4.52763900	1.72579300
C	0.88480300	5.56885100	0.61150000
H	0.52830100	6.56032600	0.90120500
C	1.98056900	5.44246200	-0.27172800
H	2.44900300	6.34713400	-0.66700800
C	0.31661400	0.93044400	2.74648600
C	1.06089500	1.72088100	3.65878800
H	1.41993800	2.71003300	3.36468600
C	1.33588300	1.22902400	4.95713000
H	1.91548700	1.83934100	5.65575200
C	0.85711000	-0.04514300	5.35072000
H	1.05978900	-0.41713800	6.35992400
C	0.13307600	-0.84405000	4.43286500
H	-0.21466000	-1.84129300	4.71445500
C	-0.12741800	-0.36406800	3.12932300
H	-0.66710700	-0.99710000	2.42092000

C	3.45688500	-0.74649400	1.40511800
C	4.51423400	0.17632700	1.61474000
H	4.86229300	0.81293000	0.79902100
C	5.14764000	0.26596100	2.87859900
H	5.96574300	0.97806800	3.02489200
C	4.73372200	-0.57314100	3.94139900
H	5.22904200	-0.51268900	4.91553600
C	3.67387500	-1.49062700	3.73601900
H	3.34085900	-2.13994600	4.54996300
C	3.03280400	-1.57616200	2.47877300
H	2.22037000	-2.29241600	2.33415400
C	-2.40315800	2.28425300	2.88126700
H	-1.85523600	1.76871000	3.66988700
C	-3.61236900	2.94533800	3.20800900
H	-3.97134400	2.92496000	4.24097800
C	-4.34509500	3.62978900	2.21123000
H	-5.27389500	4.14923800	2.46600600
C	-3.86505100	3.63833000	0.87790100
H	-4.42354700	4.15568000	0.09266100
C	-2.66237900	2.97355400	0.54972400
H	-2.30468400	3.00593600	-0.47921600
C	-1.90971200	2.29948900	1.55158400
C	3.45786200	-2.67017000	-0.65461600
C	4.84515000	-2.84769100	-0.38383300
H	5.42104800	-2.03828400	0.06900200
C	5.49386300	-4.06611400	-0.68779300
H	6.56007700	-4.18037200	-0.47083300
C	4.75997800	-5.13945700	-1.25482300
H	5.25722100	-6.08728400	-1.48252000
C	3.37810900	-4.97863600	-1.50961800
H	2.79347700	-5.80177900	-1.92951100
C	2.73033000	-3.75403400	-1.21018000
H	1.66407700	-3.67164500	-1.39859500
O	2.33015200	1.77008100	-0.24491900
P	-0.25835000	1.55834900	1.11559100
P	2.63642300	-1.04398100	-0.23578300
Pd	-0.11973000	-0.27631600	-0.48335800
O	0.34933400	-4.50883400	2.27110500
C	0.15535300	-4.12236300	1.11058000
O	0.16946900	-2.89330000	0.68538200
O	-0.09282400	-5.05418200	0.09879200
H	-0.04963700	-5.91587600	0.55630800
H	-1.80093200	-3.36933900	-5.27728800
H	1.35740300	-1.71496400	-2.83030100

I9 Palladacycle following inner-sphere CMD, with κ^2-xantphos and noncovalently associated HCO_3^- (from IRC analysis). Xantphos phenyl rings have been removed for clarity in the figure.

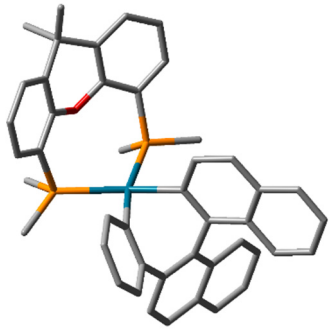


C	1.64150200	-1.23895200	-1.30909400
C	2.94768100	-0.72148200	-1.28701500
C	1.41475300	-2.56359500	-1.82262400
C	4.06941200	-1.52100500	-1.75800600
C	2.46952700	-3.36776500	-2.25059800

H	0.39193500	-2.94630300	-1.88271100
C	5.42216700	-1.02591700	-1.82152800
C	3.82032800	-2.87360500	-2.22519400
H	2.28160000	-4.37524200	-2.63582800
C	6.46817500	-1.83061700	-2.28558100
H	5.63486100	-0.00160500	-1.51575200
C	4.91857500	-3.68114500	-2.68747000
C	6.22258900	-3.17754600	-2.71427300
H	7.48374200	-1.42538100	-2.32477300
H	4.71021900	-4.69924800	-3.03135900
H	7.04882000	-3.79892500	-3.07144200
C	3.14396500	0.71883400	-0.89085800
C	3.96641900	1.09979600	0.24187100
C	2.53821100	1.72377300	-1.68290600
C	4.52082700	0.12516300	1.14459400
C	4.23776200	2.50307800	0.50045900
C	2.81121100	3.10799600	-1.40216200
C	5.32745700	0.51371000	2.21634300
H	4.29465600	-0.92803200	0.99064800
C	5.07621800	2.87417800	1.61079000
C	3.64789500	3.49566500	-0.35452300
H	2.35073900	3.86903900	-2.03755500
C	5.62094300	1.89916800	2.45013300
H	5.73176000	-0.24829100	2.88788900
H	5.27469600	3.93560200	1.78528800
H	3.86941000	4.55247800	-0.17964100
H	6.25914300	2.18885700	3.28984200
C	1.61777000	1.38716300	-2.81942000
C	1.86705600	1.94505500	-4.10420700
C	0.48194600	0.54889400	-2.60314400
C	1.02828900	1.63796600	-5.20141700
H	2.74156000	2.58631700	-4.25178100
C	-0.32831100	0.22597000	-3.72348100
H	1.85292000	3.52920800	0.88085400
C	-0.06711200	0.76245600	-5.00844200
H	-0.71507400	0.49811900	-5.85062800
C	-4.91086300	-4.77913000	-1.48784500
H	-5.04820700	-5.69017200	-0.88472200
H	-5.89006900	-4.55122700	-1.93724000
H	-4.19637300	-4.99986100	-2.29774700
C	-5.49217300	-3.35283100	0.52002500
H	-5.18696500	-2.52877000	1.18454500
H	-6.46773700	-3.09302200	0.07390700
H	-5.61609600	-4.25971000	1.13679300
C	-4.42949000	-3.60310700	-0.60340100
C	-4.27133100	-2.29870600	-1.41099900
C	-3.45737000	-1.27415500	-0.86747800
C	-4.95068000	-2.00333800	-2.62083000
H	-5.58461300	-2.75628600	-3.09254400
C	-4.81942200	-0.73343400	-3.23125000
H	-5.34436800	-0.52463400	-4.16703600
C	-4.01968700	0.27214200	-2.63893800
H	-3.92389900	1.24175300	-3.12779300
C	-3.31890800	0.01959600	-1.43114100
C	-3.07813400	-3.90318500	0.07473600
C	-2.29231600	-2.80724100	0.50882700
C	-1.04765700	-2.93589300	1.17834800
C	-0.61209900	-4.25158500	1.48013000
H	0.32685000	-4.40427100	2.01266500
C	-1.37831100	-5.37283000	1.08228600
H	-1.02562600	-6.38003700	1.31896400
C	-2.58997600	-5.20151400	0.37206200
H	-3.15373900	-6.08346000	0.06264100
C	-0.86866400	-0.65007700	2.96915400
C	-1.61272000	-1.42717000	3.89590100
H	-1.81514800	-2.48124700	3.69190000
C	-2.08646300	-0.84425600	5.09483100
H	-2.65885800	-1.45006500	5.80373500
C	-1.81451800	0.51854600	5.37811500
H	-2.17854900	0.96865100	6.30681200
C	-1.08099400	1.29825700	4.45206900

H	-0.87972500	2.35437700	4.64586000
C	-0.61406800	0.71498200	3.24980400
H	-0.05346000	1.32563000	2.53839600
C	-2.99002900	1.77735400	0.89118400
C	-4.17763600	1.19815900	1.40391300
H	-4.62267700	0.32669400	0.92156200
C	-4.81459600	1.76052500	2.53832500
H	-5.73147500	1.30373700	2.92308300
C	-4.27534000	2.91033600	3.16382600
H	-4.77436900	3.34713300	4.03440400
C	-3.08541000	3.48899800	2.65810100
H	-2.64376500	4.36804700	3.13478000
C	-2.44599200	2.92119700	1.53549800
H	-1.52661200	3.37742000	1.16166800
C	1.92360700	-1.66042800	3.52784400
H	1.30952900	-0.98813100	4.12667500
C	3.13445000	-2.14721500	4.07757700
H	3.42628400	-1.83922700	5.08600200
C	3.95403800	-3.02993400	3.33573200
H	4.88334300	-3.41659200	3.76526300
C	3.55625000	-3.41076700	2.03094200
H	4.17923300	-4.08708300	1.43823200
C	2.35706500	-2.91019400	1.47376200
H	2.07861000	-3.21745500	0.46733500
C	1.51356600	-2.04062800	2.22120700
C	-2.36830200	2.75304500	-1.65264500
C	-3.63532600	3.40302300	-1.63730000
H	-4.45935900	2.98023100	-1.05850900
C	-3.84341600	4.60143000	-2.35675100
H	-4.82510000	5.08361000	-2.33386100
C	-2.77760800	5.18189100	-3.09152100
H	-2.93300400	6.11379600	-3.64379800
C	-1.51266500	4.54904100	-3.10124300
H	-0.68302000	4.98430700	-3.66560600
C	-1.30961500	3.33878900	-2.39133000
H	-0.33298200	2.86265900	-2.41691700
O	-2.74094800	-1.50948200	0.30022100
P	-0.06772100	-1.38402100	1.47652600
P	-2.11722800	1.20210700	-0.64737300
Pd	0.03825800	-0.11795900	-0.69530500
O	0.26187200	4.73368200	3.21838000
C	1.10440800	4.54299900	2.35550100
O	1.06613700	3.52658300	1.48166700
O	2.19808400	5.34887500	2.15942000
H	2.13362500	6.04613300	2.84131500
H	1.24042900	2.05612900	-6.18972300
H	-1.18101400	-0.44765100	-3.60051700

I10 Palladacycle with κ^2-xantphos. This intermediate precedes reductive elimination according to the IRC analysis. Xantphos phenyl rings have been removed for clarity in the figure.

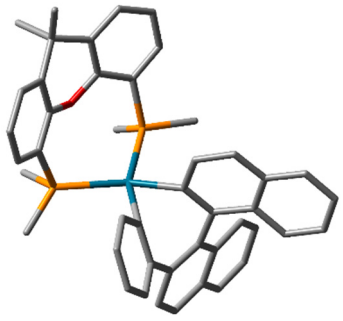


C	1.83149100	0.08240500	-1.51166400
C	3.07896600	0.52806500	-1.04499800
C	1.75020300	-0.61077900	-2.76966000
C	4.28812500	0.27260000	-1.81256100

C	2.89386700	-0.90208800	-3.51186400
H	0.77172700	-0.90894900	-3.15691000
C	5.58754000	0.75826300	-1.41961200
C	4.18923000	-0.47566600	-3.05368500
H	2.81835600	-1.43468300	-4.46551800
C	6.72421100	0.49120700	-2.19000800
H	5.68449600	1.35578600	-0.51303800
C	5.37812600	-0.74288200	-3.81997000
C	6.62693900	-0.27587200	-3.39884600
H	7.69671100	0.87599200	-1.86853300
H	5.28355300	-1.31087400	-4.75095900
H	7.52302000	-0.48076500	-3.99174900
C	3.11370200	1.38704500	0.19259800
C	3.82920100	0.98796900	1.38889100
C	2.44695800	2.63441900	0.16253400
C	4.45175500	-0.30498700	1.51543700
C	3.91475300	1.90084300	2.51575000
C	2.55131500	3.52734400	1.28578400
C	5.13879300	-0.66447900	2.67761400
H	4.37577600	-1.01402800	0.69268500
C	4.63400900	1.50399800	3.69883900
C	3.27165900	3.18220900	2.42817000
H	2.04269900	4.49354100	1.23534000
C	5.24127400	0.24801900	3.78123100
H	5.59713000	-1.65496800	2.74638500
H	4.69563200	2.20755900	4.53490500
H	3.34181500	3.87397300	3.27277700
H	5.78713900	-0.04307200	4.68339000
C	1.61056200	3.05112700	-1.01277500
C	1.84280300	4.31137200	-1.62934400
C	0.55717700	2.20592700	-1.47756100
C	1.07178300	4.72606300	-2.74142500
H	2.65232300	4.94850100	-1.26021000
C	-0.18396200	2.62246500	-2.61354100
C	0.06230200	3.86913600	-3.24125200
H	-0.52967700	4.16639500	-4.11321000
C	-4.58320000	-3.25664400	-3.82677200
H	-4.72420400	-4.34833600	-3.79877700
H	-5.53645700	-2.82747700	-4.17308200
H	-3.80355200	-3.02322000	-4.57018700
C	-5.36296400	-3.08811900	-1.42417200
H	-5.13941100	-2.73026200	-0.40635000
H	-6.31694500	-2.63620400	-1.74655500
H	-5.48884500	-4.18390200	-1.38102700
C	-4.21660600	-2.71364800	-2.42333000
C	-4.06487800	-1.17851200	-2.42121500
C	-3.32048000	-0.58512200	-1.37411500
C	-4.69763900	-0.29131700	-3.33077500
H	-5.27828000	-0.68484200	-4.16717700
C	-4.58992100	1.11127500	-3.16945500
H	-5.07825900	1.77693500	-3.88589700
C	-3.86709500	1.66135600	-2.08335000
H	-3.79629700	2.74382300	-1.96941800
C	-3.21642000	0.81032400	-1.15526800
C	-2.90105300	-3.32335400	-1.89602600
C	-2.16413600	-2.59900000	-0.92538200
C	-0.93609800	-3.03668200	-0.36434400
C	-0.48321100	-4.32813000	-0.74390600
H	0.44838600	-4.71924400	-0.33527700
C	-1.21487000	-5.10474300	-1.67233400
H	-0.85099400	-6.09662400	-1.95251800
C	-2.39753100	-4.59778300	-2.26147200
H	-2.92421000	-5.20491800	-3.00012400
C	-0.54093100	-1.89861300	2.34392400
C	-1.56489900	-2.77917000	2.77102100
H	-2.07292100	-3.42195100	2.04824100
C	-1.92550300	-2.84447500	4.13988900
H	-2.72215800	-3.52350100	4.45735500
C	-1.24823000	-2.04747300	5.09363000
H	-1.51333600	-2.11497400	6.15331700
C	-0.22779400	-1.16036100	4.66951500

H	0.30236800	-0.54005600	5.39823500
C	0.10999200	-1.07316800	3.30068100
H	0.90387300	-0.39043000	2.98313300
C	-3.11038700	0.80959500	1.74137500
C	-4.40671600	0.23581800	1.68109700
H	-4.87073500	0.02272600	0.71633400
C	-5.12386900	-0.04831900	2.86881500
H	-6.12509200	-0.48525900	2.80426500
C	-4.55395600	0.24176100	4.13196900
H	-5.10996300	0.02814700	5.04997200
C	-3.25756300	0.80863500	4.19869700
H	-2.80194300	1.02794500	5.16806500
C	-2.54103500	1.08589600	3.01241100
H	-1.54441100	1.53082500	3.07809700
C	2.05790700	-3.41968400	1.99912200
H	1.42960000	-3.33626500	2.88545300
C	3.25689900	-4.16910800	2.08494000
H	3.52615100	-4.64290700	3.03352400
C	4.09672400	-4.30676500	0.95441000
H	5.02232300	-4.88681500	1.01952900
C	3.72287900	-3.69083000	-0.26519900
H	4.35799800	-3.78564600	-1.15051400
C	2.53013200	-2.93549300	-0.34766700
H	2.26293700	-2.47902800	-1.29884800
C	1.67964500	-2.79049400	0.78280700
C	-2.51433800	3.18267500	0.37257300
C	-3.84677100	3.62376000	0.61347200
H	-4.65935000	2.89779100	0.68553700
C	-4.13558800	4.99844100	0.76874000
H	-5.16574900	5.31904700	0.94995200
C	-3.08948600	5.95478400	0.70496000
H	-3.30895300	7.01925700	0.83244800
C	-1.76172500	5.52244700	0.47884200
H	-0.94682600	6.24975800	0.42406400
C	-1.47502500	4.14498000	0.30839300
H	-0.45093600	3.82998100	0.12422600
O	-2.63969900	-1.38247400	-0.46334700
P	0.09091900	-1.82436500	0.60915900
P	-2.14184600	1.36232700	0.25035400
Pd	0.12413300	0.46601400	-0.44295600
H	1.27161500	5.68922300	-3.22020700
H	-0.96699000	1.97494800	-3.01861000

TS3 Reductive elimination transition state. Xantphos phenyl rings have been removed for clarity in the figure.

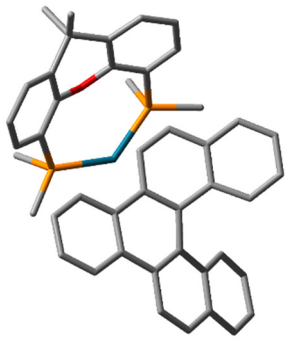


C	1.78007800	0.33559400	-1.60782500
C	3.05821200	0.62030200	-1.07405700
C	1.66928600	-0.39995400	-2.84409600
C	4.25585300	0.19846200	-1.78763900
C	2.79527400	-0.87485600	-3.50415500
H	0.67808600	-0.58281300	-3.26753000
C	5.58996900	0.55890100	-1.37737000
C	4.11474900	-0.58706900	-3.00100200
H	2.69614700	-1.44589500	-4.43286900

C	6.71281400	0.12877300	-2.09347500
H	5.72993500	1.19217400	-0.50223600
C	5.28629500	-1.02763300	-3.70771900
C	6.56861700	-0.68686200	-3.26354200
H	7.71102000	0.42446900	-1.75707600
H	5.15490100	-1.62402500	-4.61623300
H	7.45288100	-1.02271200	-3.81255800
C	3.11571500	1.50601300	0.13323500
C	3.84758800	1.16225200	1.33998900
C	2.43768600	2.75238200	0.06531200
C	4.43855800	-0.13555400	1.53966800
C	3.96297600	2.13514400	2.41222100
C	2.56992700	3.70201300	1.13799100
C	5.13606300	-0.43981900	2.71169500
H	4.33004000	-0.89512900	0.76779200
C	4.69474600	1.79617100	3.60493000
C	3.32307700	3.41489300	2.27334600
H	2.04633400	4.65788200	1.06048500
C	5.27954400	0.53550300	3.75436200
H	5.56824400	-1.43671400	2.83508900
H	4.77992200	2.54638700	4.39712800
H	3.41232800	4.14620500	3.08183800
H	5.83401300	0.28796100	4.66415900
C	1.57903200	3.08643000	-1.10518600
C	1.63251900	4.37407300	-1.70583400
C	0.69349400	2.08712500	-1.62408600
C	0.84176000	4.67909300	-2.83665400
H	2.32816300	5.12107800	-1.31234100
C	-0.07097700	2.40237600	-2.78520300
C	-0.00823300	3.68147400	-3.38043700
H	-0.61724000	3.90000700	-4.26349700
C	-4.60091400	-3.39444900	-3.69275800
H	-4.71090600	-4.48923200	-3.64841200
H	-5.57525400	-2.99531000	-4.01567000
H	-3.85003200	-3.14898500	-4.46157300
C	-5.31670100	-3.21800600	-1.27155700
H	-5.07452200	-2.84122600	-0.26497600
H	-6.29115000	-2.79577100	-1.57242700
H	-5.41145400	-4.31618200	-1.21211300
C	-4.20929100	-2.82519500	-2.30690400
C	-4.09809600	-1.28671300	-2.32512300
C	-3.34883800	-0.66388500	-1.29841800
C	-4.76898900	-0.42656600	-3.23366500
H	-5.35464800	-0.84472200	-4.05456500
C	-4.69459900	0.98000000	-3.08887900
H	-5.21530600	1.62519100	-3.80138500
C	-3.96529300	1.55987400	-2.02247000
H	-3.92430600	2.64501100	-1.91808200
C	-3.27257500	0.73681700	-1.09927900
C	-2.86333300	-3.39160700	-1.80951200
C	-2.13075900	-2.64076800	-0.85561500
C	-0.87850300	-3.03770700	-0.31825600
C	-0.38963600	-4.31271400	-0.70870500
H	0.56302900	-4.67131400	-0.31885700
C	-1.11267200	-5.11376200	-1.62310000
H	-0.72059800	-6.09243700	-1.91185100
C	-2.32505900	-4.64843500	-2.18609500
H	-2.84679000	-5.27347200	-2.91323200
C	-0.47196000	-1.91859100	2.38824500
C	-1.46563600	-2.83150800	2.82005300
H	-1.96489400	-3.48148500	2.09761500
C	-1.80878600	-2.91876900	4.19229500
H	-2.58173600	-3.62353400	4.51252000
C	-1.14490900	-2.10999700	5.14570000
H	-1.39715800	-2.19289500	6.20745500
C	-0.15404100	-1.19150800	4.71794300
H	0.36599500	-0.56186800	5.44603600
C	0.16588300	-1.08403500	3.34610000
H	0.93422300	-0.37431400	3.02462500
C	-3.11277600	0.80451100	1.79161700
C	-4.40712800	0.22277500	1.76765800

H	-4.89654300	0.00913000	0.81541900
C	-5.08776200	-0.07023400	2.97470500
H	-6.08743000	-0.51388400	2.93801700
C	-4.48210500	0.21791200	4.22179600
H	-5.00877900	-0.00433300	5.15493100
C	-3.18708300	0.79119700	4.25285400
H	-2.70326600	1.00660800	5.20933700
C	-2.50722600	1.07691000	3.04680200
H	-1.50771000	1.51919100	3.08451200
C	2.18599800	-3.34202600	1.95212900
H	1.56993700	-3.32119500	2.85123400
C	3.42574600	-4.02604500	1.98908500
H	3.74114500	-4.51716800	2.91443200
C	4.24759500	-4.07788600	0.83765300
H	5.20548300	-4.60632400	0.86522200
C	3.81671400	-3.44318600	-0.35306500
H	4.43942800	-3.47125300	-1.25146800
C	2.58255600	-2.75356800	-0.38637700
H	2.26493000	-2.28410800	-1.31607200
C	1.74980400	-2.69623300	0.76444100
C	-2.59562600	3.16159100	0.32432700
C	-3.88962200	3.60595200	0.71948700
H	-4.66014900	2.88121400	0.98904200
C	-4.19414600	4.98531000	0.77372300
H	-5.19401500	5.30782700	1.07918600
C	-3.20239600	5.94519200	0.44531700
H	-3.43360700	7.01375400	0.49320400
C	-1.91233000	5.51075800	0.06023000
H	-1.13798700	6.23903900	-0.19678100
C	-1.61012400	4.12744700	-0.00294000
H	-0.61133300	3.81342300	-0.29484900
O	-2.63525300	-1.43641700	-0.39103700
P	0.12263900	-1.79366400	0.64255300
P	-2.18353400	1.34561000	0.27364000
Pd	0.09058100	0.48139200	-0.40881600
H	0.90709100	5.66644200	-3.30263900
H	-0.72775200	1.64492200	-3.22247100

Pd^0/4b (xantphos)Pd^0 with noncovalently associated helicene **4b** (shortest Pd···C distance 4.6 Å). This intermediate follows reductive elimination according to an IRC analysis. Xantphos phenyl rings have been removed for clarity in the figure.

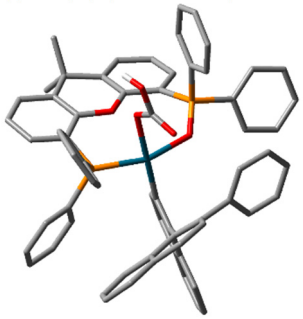


C	2.99487800	0.26252700	-1.61758900
C	3.65577600	-0.81330300	-0.94710400
C	1.77398500	-0.00539600	-2.34701800
C	3.28730300	-2.18810200	-1.30986000
C	1.29253700	-1.29308700	-2.50821900
H	1.20606700	0.81906500	-2.77573100
C	4.13936100	-3.32005700	-1.05785200
C	2.07549500	-2.41977700	-2.06684200
H	0.35418700	-1.47263000	-3.03812300
C	3.77023000	-4.61112300	-1.45399500
H	5.10775800	-3.17202300	-0.58422500
C	1.69573400	-3.75867300	-2.42259300

C	2.52195500	-4.84419800	-2.11582500
H	4.45014600	-5.44653300	-1.26354300
H	0.75933900	-3.90562100	-2.96785800
H	2.23332300	-5.85854000	-2.40503300
C	4.70923000	-0.48362600	0.03361000
C	5.01829100	-1.31828600	1.20204000
C	5.43512000	0.73698900	-0.13574100
C	4.10258400	-2.29523300	1.72785800
C	6.23867800	-1.07986000	1.94358100
C	6.65048600	0.94548400	0.62299100
C	4.41924700	-3.05495800	2.85942900
H	3.12515100	-2.42019800	1.26629200
C	6.56434000	-1.90465900	3.07472500
C	7.07598700	0.03620600	1.57869800
H	7.25750400	1.83165500	0.44136900
C	5.67687900	-2.88832300	3.52371500
H	3.69065000	-3.77361300	3.24504100
H	7.50631700	-1.72350100	3.60071000
H	8.01290100	0.19746600	2.11892000
H	5.92394100	-3.50110500	4.39499500
C	4.89037100	1.80033000	-1.00263600
C	5.54884800	3.06237900	-1.16258700
C	3.60983500	1.60413500	-1.63476500
C	4.95733800	4.11193900	-1.88165500
H	6.52820100	3.23086100	-0.71489200
C	3.01407400	2.69960600	-2.33733800
C	3.66998400	3.93266700	-2.46193000
H	3.19326900	4.74973600	-3.01025500
C	-2.58485800	1.03336900	-5.38738700
H	-3.22462700	0.33754800	-5.95247900
H	-2.80035300	2.04099100	-5.77580400
H	-1.53080800	0.79281100	-5.60410300
C	-4.40878200	1.31558100	-3.66318600
H	-4.68645100	1.27966200	-2.59856900
H	-4.61306700	2.33327400	-4.03878900
H	-5.04971800	0.60281000	-4.21046100
C	-2.89855900	0.95555800	-3.87383500
C	-2.04801500	1.93895200	-3.04849700
C	-1.94756700	1.70930600	-1.64973200
C	-1.41843700	3.09368400	-3.57922400
H	-1.47113000	3.30485200	-4.64864400
C	-0.72699300	3.98879900	-2.73067500
H	-0.25584900	4.88304100	-3.14771300
C	-0.64730400	3.73467000	-1.34279700
H	-0.09640900	4.42723500	-0.70535000
C	-1.25004900	2.58510900	-0.76517800
C	-2.65539900	-0.45141200	-3.29691500
C	-2.54334100	-0.57103700	-1.88649100
C	-2.42131200	-1.82405800	-1.21695200
C	-2.40025000	-2.98793200	-2.03085700
H	-2.30794000	-3.96853100	-1.56190200
C	-2.48398000	-2.90046900	-3.43959100
H	-2.46312400	-3.81171300	-4.04358500
C	-2.61043400	-1.64034600	-4.06853800
H	-2.68502600	-1.59191300	-5.15627700
C	-3.99547700	-1.79700400	1.20628000
C	-5.09989700	-2.13734200	0.38049500
H	-4.93475900	-2.45823400	-0.65055200
C	-6.42317900	-2.06006400	0.88105300
H	-7.26474800	-2.31941100	0.23154200
C	-6.65603900	-1.64798100	2.21670500
H	-7.67807000	-1.58719700	2.60312900
C	-5.55894400	-1.30624800	3.04698900
H	-5.73005800	-0.97816200	4.07645000
C	-4.23926600	-1.37095200	2.54003500
H	-3.39405900	-1.08192700	3.17111300
C	-2.58915600	2.94770300	1.78321400
C	-3.41119200	3.87689900	1.09313900
H	-3.17001000	4.16671400	0.06805500
C	-4.55256800	4.43415600	1.72250400
H	-5.18007300	5.14419800	1.17528300

C	-4.87889300	4.07592700	3.05339100
H	-5.75888600	4.50785400	3.53975100
C	-4.06301800	3.14764700	3.74951100
H	-4.31074700	2.85961300	4.77553000
C	-2.93460100	2.57948500	3.11319600
H	-2.32045800	1.84480300	3.64240700
C	-2.75617400	-4.67851800	1.28591600
H	-3.80722700	-4.41383300	1.41754000
C	-2.34084000	-6.01543800	1.50972900
H	-3.07609300	-6.76638200	1.81440800
C	-0.98226200	-6.37877600	1.33905700
H	-0.66318900	-7.41141500	1.51042100
C	-0.03630000	-5.39544300	0.95104300
H	1.01543000	-5.66253600	0.81438600
C	-0.44892100	-4.05793400	0.74969100
H	0.28711400	-3.29814100	0.47217300
C	-1.81421900	-3.68812600	0.90062400
C	0.26483700	3.37995200	1.55718200
C	0.01310900	4.66460800	2.10766300
H	-1.01334100	5.01092400	2.24659300
C	1.08979500	5.50521200	2.48620700
H	0.88251900	6.49005600	2.91587000
C	2.42763500	5.07342300	2.30933000
H	3.25821000	5.72394500	2.60004900
C	2.68635800	3.79170500	1.76040200
H	3.71465000	3.44681200	1.62386500
C	1.61069800	2.94702700	1.40097400
H	1.81322800	1.94757300	1.00630900
O	-2.56519500	0.58413000	-1.10972300
P	-2.23121000	-1.89696200	0.63784400
P	-1.06410800	2.18598300	1.05026900
Pd	-0.97240200	-0.10238200	1.36567300
H	5.48281600	5.06535000	-1.98543800
H	2.03679500	2.58573200	-2.80317600

I11 Trans bidentate (xantPO)Pd(binaphthyl)(κ^1-HCO_3)

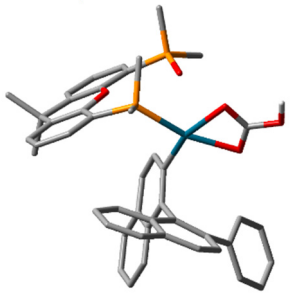


P	-1.37444900	1.95075000	0.17971200
P	3.01004200	-0.90361900	0.11224500
O	1.72568900	1.89884500	-0.78856500
O	1.53898100	-1.27126000	0.18758800
C	-2.80183300	2.24051700	-0.96797800
C	-3.98122000	2.91499700	-0.55957300
C	-5.00518400	3.19774200	-1.49449200
C	-4.86524300	2.80371000	-2.84596900
C	-3.69298100	2.12076000	-3.25763600
C	-2.67001900	1.83895600	-2.32431300
C	-1.99389500	2.50780200	1.82610800
C	-2.96931300	1.68540200	2.45021300
C	-3.47035900	2.01818200	3.72908000
C	-2.98642100	3.16264300	4.40838500
C	-1.99455400	3.96982500	3.80105600
C	-1.49858900	3.64308500	2.51626500
C	3.72201500	-0.29819200	1.67904500
C	4.79560800	0.62886800	1.72624400
C	5.34449000	1.00738200	2.97574500
C	4.81458300	0.46887800	4.17475100

C	3.73604800	-0.44992400	4.12485700
C	3.19504800	-0.84104200	2.88068800
C	3.91046000	-2.44525500	-0.29510700
C	5.19435200	-2.74355700	0.22982200
C	5.83708000	-3.95604600	-0.11798100
C	5.19553900	-4.87282800	-0.98870700
C	3.90556800	-4.58193600	-1.49873900
C	3.25822400	-3.37459400	-1.14813500
C	3.52364500	0.33129600	-1.17022200
C	4.70955800	0.00567600	-1.87995700
C	5.34298300	0.93006400	-2.73752600
C	4.80282500	2.22155300	-2.86206000
C	3.60798900	2.59641000	-2.19461400
C	2.94539400	1.63170700	-1.38680000
C	-0.23067800	3.29684000	-0.43146900
C	-0.82434800	4.58296100	-0.52491700
C	-0.15002600	5.68284200	-1.08963300
C	1.12766600	5.47887700	-1.64246000
C	1.76102900	4.21189200	-1.60151100
C	1.09949200	3.13395600	-0.94551900
C	3.10783200	4.04118200	-2.31919300
C	4.16895200	4.99356600	-1.67937200
C	2.92272600	4.40321600	-3.82833700
H	-4.10947700	3.22077800	0.47981100
H	-5.90699200	3.72123400	-1.16336200
H	-5.65603400	3.02409300	-3.56950600
H	-3.57622700	1.80445600	-4.29816500
H	-1.77511500	1.31131400	-2.65584200
H	-3.33755700	0.78834500	1.94966600
H	-4.21853100	1.37238100	4.19595200
H	-3.36341800	3.41126900	5.40487200
H	-1.59783800	4.84321500	4.32662300
H	-0.71768800	4.26142300	2.07198700
H	5.20122300	1.05849500	0.80762000
H	6.17190800	1.72211500	3.01142100
H	5.22949000	0.77186100	5.14068400
H	3.30093000	-0.84035300	5.04802800
H	2.34452400	-1.52299000	2.84229500
H	5.68784000	-2.04520800	0.90991100
H	6.82486300	-4.18483900	0.29198000
H	5.69212000	-5.81005600	-1.25773400
H	3.40032000	-5.29522700	-2.15583400
H	2.24974400	-3.16347100	-1.50881200
H	5.15428700	-0.98067300	-1.75799000
H	6.25108400	0.64927000	-3.27554900
H	5.31550300	2.95359800	-3.48923700
H	-1.84200200	4.72268900	-0.15852400
H	-0.62661200	6.66486200	-1.12899300
H	1.63733100	6.31540400	-2.12509600
H	4.30911500	4.76258200	-0.61086800
H	5.14411000	4.89285400	-2.18394800
H	3.85416000	6.04663800	-1.76365500
H	3.87213700	4.31023400	-4.37994400
H	2.18273600	3.73802200	-4.30207600
H	2.57386700	5.44134500	-3.94565100
Pd	-0.19454900	0.03355100	0.36681700
C	-0.96986000	-0.96882400	-1.20015500
C	-2.02434900	-1.89308100	-1.08896200
C	-0.27526500	-0.84127400	-2.45641700
C	-2.41699900	-2.69418200	-2.23715800
C	-0.63164300	-1.59641700	-3.57440700
H	0.55762300	-0.13773700	-2.53413300
C	-3.48464600	-3.65996900	-2.17180300
C	-1.71246300	-2.54102200	-3.49604900
H	-0.09019600	-1.48338100	-4.51929400
C	-3.84040100	-4.42303400	-3.28928900
H	-4.02383200	-3.79636700	-1.23282000
C	-2.10151700	-3.33805700	-4.63003200
C	-3.14619100	-4.26286300	-4.53521100
H	-4.65605700	-5.14807000	-3.21170100
H	-1.55961900	-3.20860900	-5.57231300

H	-3.43294900	-4.86393000	-5.40291500
C	-2.76873900	-2.04565700	0.21833600
C	-4.07775800	-1.42845600	0.35486200
C	-2.21489800	-2.75308900	1.30746900
C	-4.72193300	-0.75054900	-0.74046800
C	-4.78481100	-1.50009700	1.61838500
C	-2.91896000	-2.77175300	2.56662900
C	-5.99240000	-0.18787100	-0.59650400
H	-4.21274900	-0.68495300	-1.70059600
C	-6.08606900	-0.89944900	1.74328600
C	-4.16006900	-2.16688000	2.72539500
H	-2.46320000	-3.29820500	3.40722600
C	-6.68656200	-0.25793400	0.65633900
H	-6.45998600	0.30857500	-1.45064300
H	-6.60238200	-0.96388100	2.70618400
H	-4.67903300	-2.20954400	3.68747500
H	-7.68022100	0.18806900	0.75839600
C	-0.94491300	-3.55669100	1.24719500
C	0.01159100	-3.44412800	2.29247200
C	-0.73328100	-4.52602400	0.23019100
C	1.15107600	-4.28078500	2.31581300
H	-0.12353900	-2.67809800	3.05852200
C	0.40412200	-5.36572900	0.25881900
H	-1.46836200	-4.65094800	-0.56556800
C	1.35268600	-5.24778300	1.30243600
H	1.87765100	-4.18142900	3.12843400
H	0.53679300	-6.11916100	-0.52419500
H	2.23173000	-5.89902000	1.32587400
O	0.71916600	1.13551400	1.99021900
C	0.45473300	0.65886600	3.17508300
O	-0.11522900	-0.40002000	3.46688800
O	0.90912000	1.47480900	4.20832800
H	1.32253700	2.23956600	3.76562200

I12 (κ^1-P-xantPO)Pd(binaphthyl)(κ^2-HCO_3)



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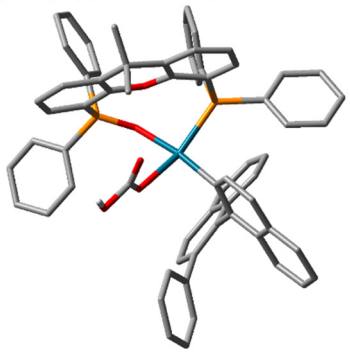
C	-2.73385700	1.10006300	0.57766100
C	-0.31936100	1.55192400	0.69770700
C	-2.95185200	2.08919700	1.62249300
C	-0.50839800	2.53094900	1.67300400
H	0.67413200	1.35727700	0.29847700
C	-4.26623900	2.38444500	2.13347100
C	-1.82274200	2.80772900	2.18130400
H	0.34344000	3.10360000	2.05302800
C	-4.45008700	3.32687000	3.14998100
H	-5.12812500	1.85277700	1.72816100
C	-2.04411100	3.78078800	3.21872900
C	-3.33139300	4.03838900	3.69923400
H	-5.45788200	3.52797500	3.52545600
H	-1.18212500	4.32078500	3.62325400
H	-3.48880400	4.77993700	4.48791800
C	-3.93694700	0.44742600	-0.05844200
C	-4.36747100	-0.85912200	0.40272400
C	-4.70490200	1.13041400	-1.02960700
C	-3.73122000	-1.51704000	1.51370400
C	-5.50864900	-1.51006700	-0.21157400
C	-5.81499000	0.44835200	-1.65114700

C	-4.20300800	-2.74089700	1.99279300
H	-2.88730100	-1.02908800	2.00242900
C	-5.94770700	-2.78988600	0.27830900
C	-6.19411100	-0.83873700	-1.27982400
H	-6.35807100	0.96479300	-2.44579800
C	-5.31582400	-3.39383700	1.36785500
H	-3.72157200	-3.20507700	2.85822300
H	-6.80691100	-3.26830800	-0.20202400
H	-7.03372700	-1.33531200	-1.77497200
H	-5.66837100	-4.35736100	1.74702100
C	-4.52655800	2.58311200	-1.38487900
C	-5.67721200	3.42088100	-1.31495300
C	-3.28998400	3.16027500	-1.78331600
C	-5.59816300	4.79909300	-1.62550200
H	-6.63275500	2.99608900	-0.99514600
C	-3.21466900	4.53633500	-2.10115100
C	-4.36154500	5.36439900	-2.02173300
H	-4.29354100	6.42890000	-2.26626600
C	1.14377500	0.96154100	5.35717000
H	0.56722300	0.39873400	6.10886000
H	1.76224100	1.69721800	5.89676900
H	0.43213000	1.50690400	4.71748700
C	3.02715100	-0.75960600	5.43555300
H	3.66565300	-1.44587700	4.85519600
H	3.68207900	-0.05367000	5.97264300
H	2.48271800	-1.35312700	6.18831300
C	2.03245700	0.00212300	4.50276900
C	2.83188000	0.82603600	3.48035900
C	2.75896500	0.58157400	2.08210500
C	3.68608400	1.86558500	3.93051200
H	3.76319900	2.06671500	5.00134200
C	4.43396100	2.65310600	3.03282100
H	5.07467200	3.45728800	3.40196100
C	4.33670700	2.39783400	1.64777200
H	4.90132700	3.01995000	0.95254800
C	3.51538900	1.35606300	1.14550700
C	1.12624100	-1.01111300	3.78635200
C	1.10309800	-1.13734100	2.37389800
C	0.21959900	-2.04386200	1.70955000
C	-0.61921500	-2.85862500	2.50879400
H	-1.29716900	-3.56224900	2.02953800
C	-0.59612700	-2.77086300	3.91774000
H	-1.24657100	-3.41167800	4.51782900
C	0.26300400	-1.84669300	4.54166500
H	0.26390200	-1.77372400	5.63141400
C	1.66999700	-2.66408700	-0.78228500
C	2.71340200	-3.11121000	0.06637200
H	2.61032000	-3.04991700	1.15107600
C	3.89788100	-3.65710100	-0.48486600
H	4.69940700	-3.99281100	0.17963600
C	4.04184400	-3.76837500	-1.88715000
H	4.95596100	-4.19313500	-2.31176700
C	2.99947500	-3.32323500	-2.73656200
H	3.10194200	-3.40626500	-3.82287700
C	1.82177900	-2.76466200	-2.19197600
H	1.02913500	-2.41580500	-2.85565900
C	5.00087400	0.03523200	-1.00818300
C	5.98353200	-0.25410400	-0.02625100
H	5.85589100	0.09561500	1.00033100
C	7.13888400	-0.99700700	-0.37247300
H	7.89211900	-1.21682900	0.38986800
C	7.32188000	-1.44545000	-1.70355800
H	8.22059200	-2.00876000	-1.97310100
C	6.33906400	-1.16413100	-2.68555400
H	6.47369100	-1.51361100	-3.71347500
C	5.17858100	-0.43741000	-2.33760400
H	4.41082700	-0.23698700	-3.08874200
C	-0.41943100	-4.93480900	-0.15413300
H	0.58317100	-5.02738200	0.26901600
C	-1.16664600	-6.10257600	-0.42865300
H	-0.73826200	-7.08486900	-0.20914800

C	-2.45983600	-5.99841600	-1.00385000
H	-3.03496700	-6.90221100	-1.22707700
C	-2.99930100	-4.72323300	-1.29277700
H	-3.99293300	-4.63022400	-1.73824700
C	-2.25521900	-3.55327900	-1.00578700
H	-2.67306200	-2.57425500	-1.24254700
C	-0.96254600	-3.64944300	-0.43306700
C	3.89011900	2.69011600	-1.42781500
C	5.20592300	3.14054200	-1.71639400
H	6.06757300	2.50653300	-1.49300400
C	5.40862300	4.41172600	-2.30781200
H	6.42403300	4.75209500	-2.53082800
C	4.29718400	5.23390500	-2.62053300
H	4.45389500	6.21362000	-3.08192600
C	2.98152700	4.78141900	-2.34588600
H	2.12101100	5.40740200	-2.59803700
C	2.77674500	3.51286900	-1.75357100
H	1.76374100	3.14937000	-1.56643800
O	1.95774600	-0.41451700	1.55758800
P	0.03001100	-2.10995100	-0.13214900
P	3.51049300	1.05448700	-0.67883100
Pd	-0.97017600	-0.41838400	-1.37626900
O	-0.78008000	-1.24708600	-3.46406700
C	-1.35181800	-0.17444100	-3.86961200
O	-1.73924000	0.74384000	-3.07986500
O	-1.56421000	0.00260600	-5.20510300
H	-1.20713100	-0.79751400	-5.63703300
H	-6.49367600	5.42381200	-1.55327400
H	-2.25668400	4.95808400	-2.42000600
O	2.22815700	0.50231700	-1.23357700
H	-2.40891900	2.53514100	-1.88725800

I13 cis-Bidentate (xantPO)Pd(binaphthyl)(κ^1-HCO_3)



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O	-2.32906700	-0.78462700	-1.29098000
O	-1.47824700	0.77198500	0.97262700
C	0.84281400	-3.65244900	0.73682200
C	0.47080700	-4.63388000	1.69468000
C	1.33278700	-5.71895900	1.98731900
C	2.58084900	-5.83759700	1.32918800
C	2.95566000	-4.86465500	0.36933500
C	2.09578700	-3.78044600	0.07660900
C	-1.59351600	-2.39825500	1.61777500
C	-1.34214900	-1.84768900	2.90175100
C	-2.25378800	-2.06596900	3.95793000
C	-3.43975500	-2.80871500	3.73420200
C	-3.70745000	-3.33571400	2.44781000
C	-2.78111800	-3.13769400	1.39408100
C	-4.18231000	1.02451700	1.54088200
C	-5.46266500	0.85441800	0.95326500
C	-6.57640600	0.51449000	1.75988100

C	-6.41580800	0.34951500	3.15753300
C	-5.13648600	0.51392200	3.74649800
C	-4.02199900	0.84288800	2.94157300
C	-2.53558500	3.34317800	0.91913400
C	-3.57823900	4.10707100	1.51078000
C	-3.39105700	5.48855400	1.75771000
C	-2.16159400	6.10760400	1.41995700
C	-1.12066900	5.34362100	0.83432800
C	-1.29973800	3.96295300	0.58208100
C	-3.20677000	1.41954900	-1.18510300
C	-3.87516900	2.50607900	-1.80311800
C	-4.35125700	2.39624600	-3.12778200
C	-4.14030200	1.19797400	-3.84388900
C	-3.45201300	0.09664300	-3.27638500
C	-2.99524400	0.23048300	-1.94170400
C	-1.06808100	-2.79286700	-1.25409100
C	-0.72576500	-4.02711000	-1.85875600
C	-1.20988800	-4.36213500	-3.14463900
C	-2.00786500	-3.44113300	-3.85379900
C	-2.38316000	-2.19485300	-3.28781300
C	-1.93565600	-1.91758300	-1.97494700
C	-3.18335300	-1.16863400	-4.10877000
C	-4.53790100	-1.79287900	-4.56514500
C	-2.32951200	-0.76721100	-5.35547600
H	-0.48517000	-4.56585800	2.21416400
H	1.02649200	-6.46426500	2.72719300
H	3.24944000	-6.67260900	1.55865700
H	3.91667800	-4.93924100	-0.14701100
H	2.40213900	-3.04789200	-0.66943800
H	-0.43890900	-1.26076200	3.07616700
H	-2.04082200	-1.65234600	4.94825300
H	-4.15072600	-2.96811600	4.55057100
H	-4.62473600	-3.90252500	2.26431400
H	-2.98435500	-3.56557200	0.40972600
H	-5.59622900	0.98585000	-0.12230900
H	-7.55979000	0.38273400	1.29958200
H	-7.27751900	0.09436000	3.78181200
H	-5.00761300	0.38228800	4.82472000
H	-3.03468800	0.96099900	3.39271000
H	-4.52558500	3.63675800	1.78262300
H	-4.19541600	6.07221600	2.21471100
H	-2.01555400	7.17477800	1.61343800
H	-0.17062500	5.81651300	0.57113200
H	-0.49730600	3.37894000	0.12566600
H	-4.01895400	3.43737600	-1.25307800
H	-4.86870800	3.23599700	-3.59746700
H	-4.50510600	1.12652100	-4.87131300
H	-0.07375000	-4.72547900	-1.33476600
H	-0.94337200	-5.32142600	-3.59488600
H	-2.34000900	-3.69280100	-4.86359400
H	-5.14949500	-2.09027700	-3.69720600
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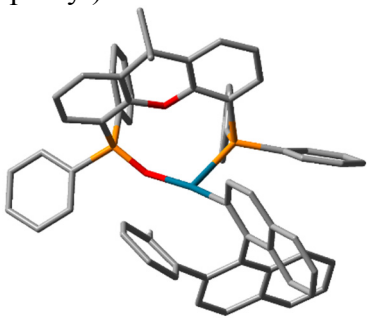
H	-4.36936000	-2.68638000	-5.18888500
H	-2.87919100	-0.05190900	-5.99047400
H	-1.38823700	-0.29880600	-5.03058700
H	-2.09748100	-1.65214400	-5.97131700
C	2.16638400	-0.43633100	-0.76877000
C	3.31370300	-0.05114500	-0.04887500
C	2.29272300	-1.04544600	-2.06231400
C	4.62803000	-0.40639100	-0.55878400
C	3.54730100	-1.35064800	-2.59081900
H	1.39117800	-1.24065000	-2.64514900
C	5.83510900	-0.13147700	0.17727500
C	4.74257600	-1.07171700	-1.84324900
H	3.63348300	-1.80722000	-3.58178300
C	7.08534100	-0.50837400	-0.32235600
H	5.76418500	0.36016200	1.14862100
C	6.04509200	-1.43301100	-2.33907300
C	7.19751500	-1.16077300	-1.59602700
H	7.98718600	-0.29786700	0.26021900
H	6.11689100	-1.92690300	-3.31316400

H	8.18191300	-1.44165800	-1.98154300
C	3.19572700	0.77099000	1.21784000
C	2.78210600	0.14404500	2.46048900
C	3.50743100	2.15045800	1.21564100
C	2.64141300	-1.28140100	2.57804700
C	2.55948400	0.94588800	3.64632500
C	3.28764900	2.92784600	2.41074200
C	2.27591300	-1.88077100	3.78595400
H	2.86357800	-1.90301600	1.71375700
C	2.14705300	0.30978500	4.86987300
C	2.79389800	2.35972200	3.58157800
H	3.49545200	3.99965000	2.37189800
C	2.00646500	-1.07889100	4.94443200
H	2.19708500	-2.96969700	3.84475300
H	1.97037000	0.93515600	5.75044500
H	2.60802800	2.97674100	4.46547900
H	1.71374400	-1.55506900	5.88479500
C	4.13674700	2.88113600	0.05950600
C	5.36844900	3.55793600	0.28676100
C	3.53992300	2.95765400	-1.22662900
C	6.00155800	4.28108800	-0.75206500
H	5.83948900	3.50280800	1.27252600
C	4.16807200	3.69011600	-2.26159300
H	2.57523900	2.48584400	-1.39534500
C	5.40191200	4.34873800	-2.03416400
H	6.95492700	4.78333000	-0.56139500
H	3.68376700	3.74986400	-3.24032400
H	5.88610000	4.90892600	-2.84011600
O	0.46161300	1.86002900	-1.09829300
C	0.15778100	1.81720900	-2.35621700
O	-0.21800700	0.84979200	-3.04740400
O	0.28624400	3.06974500	-2.95463100
H	0.01934400	2.92072900	-3.88140500

I14 cis-Bidentate (xantPO)Pd(binaphthyl) cation

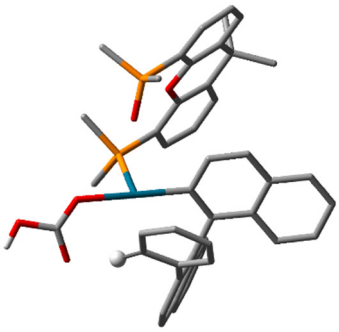


C	2.07289400	-0.44540700	-1.13766200
C	3.29720400	0.23428500	-1.04341300
C	1.96333100	-1.68983900	-1.83920600
C	4.47848500	-0.35005300	-1.66037600
C	3.08685100	-2.26815600	-2.43358100
H	0.99558200	-2.19226300	-1.91207100
C	5.76154800	0.30794800	-1.65170900
C	4.36826900	-1.62537600	-2.34657800
H	3.00100500	-3.21527500	-2.97421800
C	6.87538400	-0.28062900	-2.25835300
H	5.86632500	1.27805600	-1.16646200
C	5.53602800	-2.20869600	-2.95635000
C	6.76947400	-1.55463300	-2.91137600
H	7.83822700	0.23718500	-2.23563700
H	5.43676700	-3.17160600	-3.46590600
H	7.64976100	-2.00315900	-3.37913800
C	3.35036200	1.64091800	-0.49176400
C	4.07597600	1.99363400	0.71009200
C	2.68632600	2.64968700	-1.22207200
C	4.74460900	1.01184700	1.52229000

C	4.12896200	3.38595000	1.12289600
C	2.72979800	4.01893200	-0.79634700
C	5.45036900	1.39132400	2.66636400
H	4.70187200	-0.03731500	1.23278900
C	4.86430300	3.74409400	2.30834500
C	3.44734400	4.38232000	0.34381400
H	2.21102700	4.77760600	-1.38754500
C	5.51800100	2.76864400	3.06497400
H	5.95740400	0.62952700	3.26431800
H	4.90468900	4.79635200	2.60388000
H	3.49718600	5.42870400	0.65698500
H	6.07965600	3.05067900	3.95947100
C	1.83736300	2.25112700	-2.39453000
C	2.38548900	1.83238400	-3.62788500
C	0.42781300	2.17353400	-2.19942300
C	1.54375700	1.31360400	-4.64145900
H	3.46380400	1.89106600	-3.78897100
C	-0.41158200	1.63162500	-3.21135800
C	0.14804900	1.18919600	-4.43004400
H	-0.49145200	0.76950900	-5.21085300
C	-2.52091600	-4.65646900	-2.87825300
H	-2.20022800	-5.69091900	-2.67750500
H	-3.29575400	-4.69715400	-3.66056200
H	-1.65758200	-4.09966800	-3.27744500
C	-4.29949900	-4.79166300	-1.05613100
H	-4.70415600	-4.34467400	-0.13337700
H	-5.10420900	-4.81459700	-1.80906100
H	-4.01635500	-5.83377300	-0.83556400
C	-3.07060100	-3.98329300	-1.58163900
C	-3.52185200	-2.54463400	-1.89431100
C	-3.04882900	-1.43306500	-1.15615900
C	-4.49072300	-2.28189800	-2.89998800
H	-4.88097700	-3.11035200	-3.49514200
C	-4.97062100	-0.97847100	-3.15083200
H	-5.70566300	-0.80746900	-3.94025800
C	-4.52105300	0.10105400	-2.35530200
H	-4.92006900	1.10178000	-2.52454500
C	-3.55872200	-0.11425700	-1.33780800
C	-1.96144800	-3.97520000	-0.51242200
C	-1.47249200	-2.77404200	0.05648600
C	-0.34557000	-2.73193800	0.93089400
C	0.21470300	-3.96736500	1.34290600
H	1.06218500	-3.97921600	2.02725700
C	-0.30859000	-5.19064700	0.86409900
H	0.12208800	-6.13598000	1.20116500
C	-1.35978100	-5.18552600	-0.07645700
H	-1.71939400	-6.13753400	-0.47316500
C	-0.46359200	-0.37324000	2.75561500
C	-1.27256900	-1.16012700	3.61367000
H	-1.48563500	-2.20316900	3.36840900
C	-1.79056700	-0.59956400	4.80583900
H	-2.41405500	-1.20987000	5.46446900
C	-1.48797000	0.74007000	5.15047700
H	-1.86690700	1.16304000	6.08546400
C	-0.69662400	1.53310200	4.28317600
H	-0.46318700	2.56928500	4.54308200
C	-0.19611300	0.98257300	3.08206300
H	0.41794100	1.59507600	2.41686700
C	-3.99396100	0.83211300	1.38292600
C	-4.93563200	-0.22675600	1.47453400
H	-5.09105300	-0.90548100	0.63416400
C	-5.69611300	-0.40006900	2.65643400
H	-6.42240400	-1.21486900	2.71963600
C	-5.52556700	0.48836300	3.74578000
H	-6.12375200	0.36336800	4.65294300
C	-4.58425900	1.54433600	3.65709800
H	-4.45071300	2.23270600	4.49581200
C	-3.81876700	1.71648200	2.48271800
H	-3.10188800	2.53807400	2.41646900
C	2.34501400	-1.28396700	3.46976800
H	1.63241900	-0.72061000	4.07105100

C	3.56141700	-1.69472100	4.06664800
H	3.75761900	-1.43893700	5.11132900
C	4.50850400	-2.43564300	3.32280200
H	5.44264400	-2.76295100	3.78807600
C	4.23393800	-2.75747600	1.97035800
H	4.95628500	-3.32960500	1.38173100
C	3.02662000	-2.33914700	1.36782400
H	2.83470100	-2.60847700	0.33015300
C	2.06158800	-1.60711900	2.11583500
C	-3.85703000	2.75698800	-0.76368000
C	-5.24954000	2.99548400	-0.59506000
H	-5.87957100	2.26234000	-0.08602800
C	-5.82776300	4.19191300	-1.07941000
H	-6.89845000	4.36895600	-0.94796600
C	-5.01791700	5.16378100	-1.72056800
H	-5.46515900	6.09143800	-2.08830900
C	-3.62792200	4.93725100	-1.87399100
H	-2.99825500	5.68976500	-2.35597800
C	-3.04851800	3.73672800	-1.39758200
H	-1.97504400	3.57689500	-1.49736400
O	-2.06659000	-1.55007300	-0.19139200
P	0.44871200	-1.11213800	1.34509400
P	-3.09108800	1.21007500	-0.15969400
Pd	0.36054800	0.35655100	-0.47878500
H	1.98120800	0.98945500	-5.58989100
H	-1.49059700	1.57795600	-3.05170900
O	-1.58515500	1.39709000	0.01317900
H	-0.00591200	2.64631500	-1.31389400

I15 (κ^1-P-xantPO)Pd(binaphthyl)(κ^1-HCO_3) intermediate preceding CMD TS4 (from IRC analysis). XantPO phenyl rings have been removed for clarity in the figure.

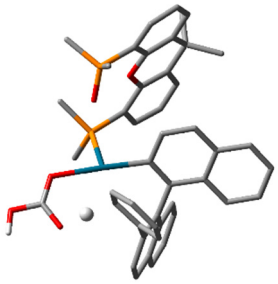


C	1.24815500	1.06054400	0.75517200
C	2.53502100	1.62971000	0.69701500
C	0.09240200	1.90753400	0.66442800
C	2.68726300	3.06762200	0.52749200
C	0.21055500	3.28484800	0.48333000
H	-0.88973100	1.44608300	0.75414100
C	3.97406300	3.71982700	0.52222900
C	1.50524300	3.90021800	0.39808700
H	-0.68306400	3.91450200	0.42550100
C	4.08466200	5.10518700	0.36134200
H	4.87881400	3.12540800	0.64984200
C	1.65075500	5.32224200	0.22557100
C	2.91427300	5.91984900	0.20128600
H	5.07472700	5.57078300	0.36011900
H	0.74707900	5.93209300	0.12706700
H	3.01283300	7.00172400	0.07365300
C	3.75449800	0.79431000	1.00198200
C	4.78260100	0.52968700	0.01927800
C	3.89043100	0.27404400	2.30627700
C	4.67723200	0.99099800	-1.33974600
C	5.94860400	-0.24666700	0.39784600

C	5.03698200	-0.50903100	2.66474100
C	5.68048200	0.71413800	-2.27168500
H	3.79657700	1.56102000	-1.63704700
C	6.96785300	-0.51233900	-0.58393500
C	6.05213800	-0.75089700	1.73906600
H	5.10432100	-0.91849100	3.67543600
C	6.84183300	-0.04073100	-1.89279700
H	5.58278500	1.07746700	-3.29891900
H	7.84526100	-1.09414800	-0.28537100
H	6.92839700	-1.34181400	2.02040600
H	7.62203900	-0.24869700	-2.63061500
C	2.74627700	0.43461700	3.26779200
C	2.41130600	1.67431400	3.85575400
C	1.89452400	-0.69135800	3.47081700
C	1.21713300	1.80342900	4.60817000
H	3.06008300	2.54019800	3.70618400
C	0.67780900	-0.54413700	4.19031400
H	2.24603100	-1.68281900	3.16435600
C	0.33277700	0.70798200	4.75267300
H	-0.60314500	0.82182200	5.30667100
C	-0.98027300	4.35923700	-3.45890500
H	-0.23004900	4.54766000	-4.24334200
H	-1.76253100	5.12884100	-3.55980700
H	-0.49051700	4.48528700	-2.48056900
C	-2.23446100	2.76198300	-5.00338600
H	-2.66972900	1.75627300	-5.12295000
H	-3.03793100	3.50283400	-5.15188400
H	-1.48681800	2.90882500	-5.80042900
C	-1.58057000	2.92376000	-3.59393500
C	-2.65458100	2.71784600	-2.51259800
C	-2.60435200	1.63942600	-1.58691800
C	-3.74556000	3.62042400	-2.42371600
H	-3.81353600	4.44770500	-3.13377900
C	-4.74363100	3.48520800	-1.43811100
H	-5.56884600	4.19909400	-1.38358800
C	-4.65320500	2.42715200	-0.50812800
H	-5.40731700	2.34400800	0.27558600
C	-3.59808700	1.48021400	-0.56802400
C	-0.45381800	1.89066900	-3.43599200
C	-0.51124300	0.85520300	-2.47021400
C	0.53367700	-0.10745700	-2.32508500
C	1.65839300	-0.00007000	-3.17770100
H	2.47593700	-0.71322900	-3.08515900
C	1.74064800	1.02164000	-4.15003500
H	2.61398800	1.08453900	-4.80354200
C	0.69036500	1.95079400	-4.27417400
H	0.76012000	2.73508900	-5.03116400
C	-0.98952800	-2.45718800	-1.48605500
C	-1.66048800	-2.27809300	-2.72451700
H	-1.37492900	-1.47078900	-3.40030800
C	-2.69987000	-3.15863300	-3.11058100
H	-3.20954900	-3.00584700	-4.06661100
C	-3.07086600	-4.23154100	-2.26593600
H	-3.87289800	-4.91373000	-2.56329000
C	-2.40071200	-4.41147700	-1.03149100
H	-2.67905400	-5.23737100	-0.37016500
C	-1.37182700	-3.52826500	-0.63337000
H	-0.87543500	-3.66168300	0.32838700
C	-4.74866800	-1.15595000	0.06949200
C	-5.71282200	-0.91775400	-0.94483500
H	-5.74253500	0.04269900	-1.46423400
C	-6.64050400	-1.92958500	-1.29379800
H	-7.37961400	-1.74167500	-2.07809200
C	-6.61168600	-3.17956000	-0.62707400
H	-7.33518000	-3.95719100	-0.89076700
C	-5.64187300	-3.42382300	0.37697200
H	-5.60866400	-4.39168900	0.88557100
C	-4.70709800	-2.41992300	0.71898500
H	-3.94217600	-2.61113600	1.47521300
C	1.76921100	-3.39177000	-2.68684100
H	0.84971800	-3.40043800	-3.27564500

C	2.84630500	-4.22199700	-3.07115900
H	2.75005900	-4.85973200	-3.95475800
C	4.04103800	-4.23599300	-2.30515200
H	4.87226400	-4.88465500	-2.59828400
C	4.14782500	-3.42038800	-1.15505000
H	5.05297100	-3.43700300	-0.54344500
C	3.06980300	-2.58635400	-0.77129200
H	3.14814600	-1.99454700	0.13966900
C	1.87882100	-2.55817100	-1.53869900
C	-4.42328000	0.85033400	2.15083500
C	-5.80916800	0.70198100	2.42019500
H	-6.44448800	0.12998700	1.73977200
C	-6.37613300	1.28475900	3.58076600
H	-7.44423000	1.16346000	3.78332800
C	-5.55897400	2.01261000	4.48054700
H	-5.99619900	2.46067100	5.37797400
C	-4.17098400	2.15033900	4.22209700
H	-3.53581400	2.70362800	4.91996100
C	-3.60288400	1.56807800	3.06489800
H	-2.52948100	1.65167700	2.87864400
O	-1.60008400	0.69379200	-1.62700500
P	0.49104200	-1.43904300	-1.03547500
P	-3.58552000	0.11915600	0.68350300
Pd	0.87255900	-0.87359100	1.21223100
O	0.39213000	-2.88892100	1.81060900
C	1.29483000	-3.75599300	2.12213800
O	2.51736600	-3.58483400	2.32072300
O	0.76428400	-5.03949200	2.25122100
H	1.53371800	-5.59216500	2.48659600
H	0.96671400	2.77068600	5.05459900
H	0.02261300	-1.40980900	4.31090500
O	-2.22671500	-0.40149400	1.05835400

TS4 Inner-sphere CMD transition state with mono-oxidized xantPO ligand on Pd. XantPO phenyl rings have been removed for clarity in the figure.

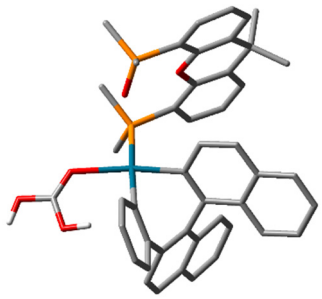


C	1.28630300	1.07512100	0.63773100
C	2.56769800	1.63184800	0.50303200
C	0.12774100	1.91487700	0.50976900
C	2.72448200	3.04942200	0.20927700
C	0.24567500	3.26945400	0.20424600
H	-0.85201800	1.46699300	0.66884700
C	4.01212900	3.69115300	0.11498900
C	1.54025500	3.87215300	0.03973900
H	-0.64698200	3.89709800	0.11689900
C	4.12163500	5.05838300	-0.16229700
H	4.91783300	3.10479100	0.27176400
C	1.68506900	5.27371900	-0.25352100
C	2.94945200	5.86170600	-0.35920600
H	5.11221600	5.51869900	-0.22635600
H	0.78084800	5.87803200	-0.37901000
H	3.04694500	6.92892400	-0.57872300
C	3.78265600	0.79206700	0.80351300
C	4.76694100	0.46799800	-0.20783400
C	3.98279600	0.36611900	2.13199700
C	4.58990100	0.83083700	-1.58917400
C	5.96198600	-0.26566700	0.16704900

C	5.17461900	-0.34913100	2.49359500
C	5.54807300	0.49410100	-2.54867200
H	3.68898400	1.37031800	-1.88323200
C	6.93308300	-0.59533400	-0.84405900
C	6.14516700	-0.65501100	1.53856200
H	5.30450900	-0.66600100	3.53137400
C	6.73530600	-0.22238400	-2.17599100
H	5.39425200	0.78087100	-3.59304600
H	7.83346200	-1.14298000	-0.54868000
H	7.04846900	-1.20360300	1.82090800
H	7.48050600	-0.47644700	-2.93541100
C	2.92725000	0.62424700	3.16937000
C	3.13188300	1.60523600	4.17035000
C	1.71800400	-0.14823100	3.12444800
C	2.10901800	1.88026500	5.11254200
H	4.06583600	2.17372600	4.19620100
C	0.70820500	0.15839700	4.08902400
H	2.04228300	-1.49972100	3.15040100
C	0.88682200	1.16368000	5.06780300
H	0.09672700	1.37719600	5.79446500
C	-1.05772300	4.11740600	-3.70900900
H	-0.35211500	4.23629900	-4.54672400
H	-1.81336700	4.91475600	-3.79873100
H	-0.50177400	4.26674700	-2.77030000
C	-2.47228300	2.50855000	-5.09413700
H	-2.95441100	1.51817600	-5.13942100
H	-3.25270900	3.27636200	-5.22783500
H	-1.77162400	2.58741600	-5.94182200
C	-1.72330200	2.70474700	-3.73721900
C	-2.73409100	2.59477300	-2.58336700
C	-2.66858800	1.55887100	-1.61104300
C	-3.78169800	3.54511800	-2.47432600
H	-3.85920200	4.34108700	-3.21832700
C	-4.72377200	3.49652000	-1.42743700
H	-5.51509700	4.24659400	-1.35838800
C	-4.62060800	2.47692200	-0.45685900
H	-5.33143400	2.45877800	0.37027600
C	-3.60798100	1.48562600	-0.53261600
C	-0.63188400	1.63202100	-3.59979800
C	-0.66357500	0.65159900	-2.57669800
C	0.35147700	-0.34418600	-2.44459500
C	1.41759200	-0.32980500	-3.37602900
H	2.21342200	-1.06905300	-3.29733300
C	1.47222300	0.63333800	-4.40838100
H	2.30064700	0.62413600	-5.12083500
C	0.45386500	1.59964700	-4.51375700
H	0.50352600	2.34048900	-5.31481300
C	-1.14364900	-2.60586100	-1.34525800
C	-1.91650500	-2.50114600	-2.53048400
H	-1.68178200	-1.74310000	-3.27981300
C	-2.99286200	-3.39120200	-2.76700600
H	-3.58280500	-3.29433900	-3.68336100
C	-3.29867700	-4.40158300	-1.82504000
H	-4.12927800	-5.09000400	-2.00708000
C	-2.52568000	-4.51096300	-0.64306500
H	-2.75117700	-5.29134400	0.09031300
C	-1.46201400	-3.61445600	-0.39507700
H	-0.87773300	-3.70314500	0.52086100
C	-4.83588600	-1.06852200	0.25245100
C	-5.82228200	-0.82581800	-0.73926100
H	-5.82684800	0.11467800	-1.29453300
C	-6.80494300	-1.80679500	-1.01919400
H	-7.56080200	-1.61471200	-1.78632600
C	-6.80930400	-3.03128600	-0.30624800
H	-7.57426800	-3.78491800	-0.51735600
C	-5.81883900	-3.28091600	0.67601300
H	-5.81197600	-4.22931100	1.22114400
C	-4.83009200	-2.30790900	0.94854600
H	-4.05097800	-2.50511800	1.68842600
C	1.50279100	-3.75660500	-2.53232200
H	0.52192900	-3.88184500	-2.99515700

C	2.56177100	-4.61788500	-2.90502600
H	2.38770800	-5.39781000	-3.65228300
C	3.83947400	-4.47640200	-2.30601200
H	4.65705800	-5.14500700	-2.59261200
C	4.05068600	-3.47108100	-1.33196000
H	5.02969500	-3.35210600	-0.86063300
C	2.98870800	-2.61335200	-0.95693200
H	3.14997000	-1.85426200	-0.19036800
C	1.70997700	-2.74280500	-1.55798600
C	-4.32495100	0.99521600	2.24243100
C	-5.69542900	0.89426100	2.59850500
H	-6.38261500	0.30684800	1.98489200
C	-6.17981300	1.54726400	3.75922400
H	-7.23659700	1.46297900	4.02897800
C	-5.29533600	2.29868300	4.57187700
H	-5.66924400	2.80154700	5.46893100
C	-3.92246400	2.39033400	4.22658700
H	-3.23432900	2.96184600	4.85597500
C	-3.43685100	1.73826800	3.06914100
H	-2.37501900	1.78999200	2.81653800
O	-1.70247500	0.57564500	-1.65980600
P	0.36243600	-1.56876900	-1.05044300
P	-3.58954200	0.17339300	0.76842000
Pd	0.96342200	-0.83553000	1.17013500
O	0.67700100	-2.95125800	1.83193900
C	1.46234900	-3.38907900	2.70718800
O	2.30936500	-2.69331200	3.39579700
O	1.42453300	-4.72809600	2.97607100
H	2.08191600	-4.88135300	3.68215800
H	2.26573900	2.65281500	5.87196900
H	-0.22328000	-0.41667600	4.07928500
O	-2.23939200	-0.39666900	1.10092600

I16 Palladacycle following inner-sphere CMD, with κ^1-P-xantPO and κ^1-HCO_3 (from IRC analysis). XantPO phenyl rings have been removed for clarity in the figure.



C	1.31025500	1.00357900	0.85985900
C	2.60831500	1.54091700	0.86859000
C	0.17719800	1.88750000	0.90278900
C	2.80877600	2.98198800	0.92930700
C	0.33627900	3.27191800	0.92224100
H	-0.81905800	1.44794600	0.92794700
C	4.11307700	3.58948800	1.01941600
C	1.64976600	3.85666600	0.94183300
H	-0.53786000	3.93027900	0.95704200
C	4.26258300	4.97885500	1.09076000
H	4.99954400	2.95541300	1.05075900
C	1.83564200	5.28233300	1.00386100
C	3.11585900	5.84082600	1.07231600
H	5.26520800	5.41082200	1.16455800
H	0.94944100	5.92517300	1.00990600
H	3.24450100	6.92594700	1.12371300
C	3.79697200	0.61644500	0.88752100
C	4.73967700	0.59739900	-0.21466400

C	4.01951700	-0.21668600	2.00619600
C	4.51353000	1.34705600	-1.42362900
C	5.93704600	-0.21875600	-0.12916400
C	5.21471000	-1.01551600	2.07624200
C	5.42831100	1.30620300	-2.47889400
H	3.60405300	1.94053400	-1.51775300
C	6.86758200	-0.23208800	-1.22794100
C	6.15691700	-1.01187100	1.04818100
H	5.37076500	-1.64750500	2.95441300
C	6.62473800	0.51849800	-2.38105700
H	5.23141200	1.88206800	-3.38784600
H	7.77105600	-0.84404100	-1.14278300
H	7.06043500	-1.62457500	1.11934800
H	7.33793500	0.50187700	-3.21033400
C	3.02547200	-0.31871800	3.12846800
C	3.46900700	-0.14406900	4.47188600
C	1.65767900	-0.63537100	2.85025700
C	2.56150800	-0.24715800	5.55182400
H	4.51750100	0.10085800	4.66476700
C	0.76365300	-0.72917700	3.95682000
H	2.18644400	-2.54252300	2.96855100
C	1.19995200	-0.54185100	5.29291400
H	0.48655300	-0.62501000	6.11915700
C	-1.06630600	4.80169500	-2.80154200
H	-0.37160200	5.06679500	-3.61450400
H	-1.79785000	5.62142200	-2.71260600
H	-0.49058800	4.74444400	-1.86447900
C	-2.57730400	3.55071300	-4.43340800
H	-3.08985500	2.60220700	-4.66358700
H	-3.33871400	4.34654900	-4.37372800
H	-1.90430500	3.78873900	-5.27363600
C	-1.77650200	3.44214800	-3.09653000
C	-2.74953200	3.11826300	-1.95089900
C	-2.68191400	1.90170600	-1.21706300
C	-3.76259600	4.04897800	-1.60500100
H	-3.83997700	4.98356000	-2.16500000
C	-4.66908700	3.80610900	-0.55356500
H	-5.43356900	4.54389100	-0.29893700
C	-4.56617900	2.60345300	0.17839600
H	-5.25071000	2.42642700	1.00902700
C	-3.58711400	1.62764600	-0.14211700
C	-0.71688100	2.33788700	-3.22813700
C	-0.74028000	1.16816500	-2.42817000
C	0.24883900	0.14444100	-2.54581600
C	1.27766000	0.32790800	-3.50116800
H	2.05398700	-0.42847600	-3.60924400
C	1.32286200	1.48168700	-4.31582500
H	2.12324100	1.60073600	-5.05015000
C	0.33171600	2.47127400	-4.17577800
H	0.37351400	3.36025300	-4.80911400
C	-1.22176700	-2.29719200	-1.89730400
C	-2.01061900	-1.97335900	-3.02987500
H	-1.77765700	-1.08972000	-3.62705600
C	-3.09836700	-2.79853600	-3.40866600
H	-3.70200500	-2.53206000	-4.28144900
C	-3.39750400	-3.96420200	-2.66451000
H	-4.23611800	-4.60321300	-2.95690100
C	-2.60911800	-4.29324100	-1.53405400
H	-2.83139200	-5.19360300	-0.95278200
C	-1.53690900	-3.46019400	-1.14317700
H	-0.94325700	-3.71482400	-0.26448400
C	-4.86762700	-1.00297500	0.09568600
C	-5.87922100	-0.51608200	-0.77330400
H	-5.87822200	0.52927400	-1.08928700
C	-6.89346300	-1.38652900	-1.24218000
H	-7.66840200	-1.00567900	-1.91385600
C	-6.90372900	-2.74565200	-0.84163100
H	-7.69217900	-3.41558900	-1.19831100
C	-5.88858800	-3.23740900	0.01621000
H	-5.88656400	-4.28867700	0.31882800
C	-4.86896700	-2.37248500	0.47628900

H	-4.07139900	-2.75147000	1.11925800
C	1.41160500	-3.22903100	-3.27224100
H	0.41612400	-3.31757400	-3.71195100
C	2.47970800	-3.98351300	-3.81418300
H	2.29743700	-4.64504300	-4.66642900
C	3.77845500	-3.88495300	-3.25329800
H	4.60380400	-4.46804100	-3.67348200
C	4.00169400	-3.03022500	-2.14652100
H	4.99810700	-2.94142000	-1.70594200
C	2.93035300	-2.28172100	-1.60155900
H	3.10322200	-1.63566700	-0.73931500
C	1.62871300	-2.36749100	-2.16304800
C	-4.24456400	0.55757000	2.47897800
C	-5.60119900	0.38530500	2.85952600
H	-6.31850100	-0.05365800	2.16202100
C	-6.03283100	0.77364200	4.15242400
H	-7.07910200	0.63483700	4.44020600
C	-5.10997700	1.33176700	5.07114700
H	-5.44342600	1.63022200	6.06970900
C	-3.75116300	1.49598200	4.69774200
H	-3.03301900	1.91909300	5.40589100
C	-3.31815400	1.10719700	3.40861500
H	-2.26724100	1.21476600	3.12943400
O	-1.74658200	0.92929600	-1.50111300
P	0.28205000	-1.32911900	-1.41153700
P	-3.57234400	0.06276500	0.83881200
Pd	0.93738000	-0.96967900	0.94608600
O	0.68307500	-3.26299400	1.26794200
C	1.38133600	-3.96583000	1.99653600
O	2.25426100	-3.54131400	2.91787900
O	1.32136200	-5.31497700	1.92635100
H	1.93752800	-5.67787400	2.59260600
H	2.91137800	-0.09474200	6.57714800
H	-0.28973800	-0.95954400	3.76897500
O	-2.23373100	-0.60263700	0.99283400

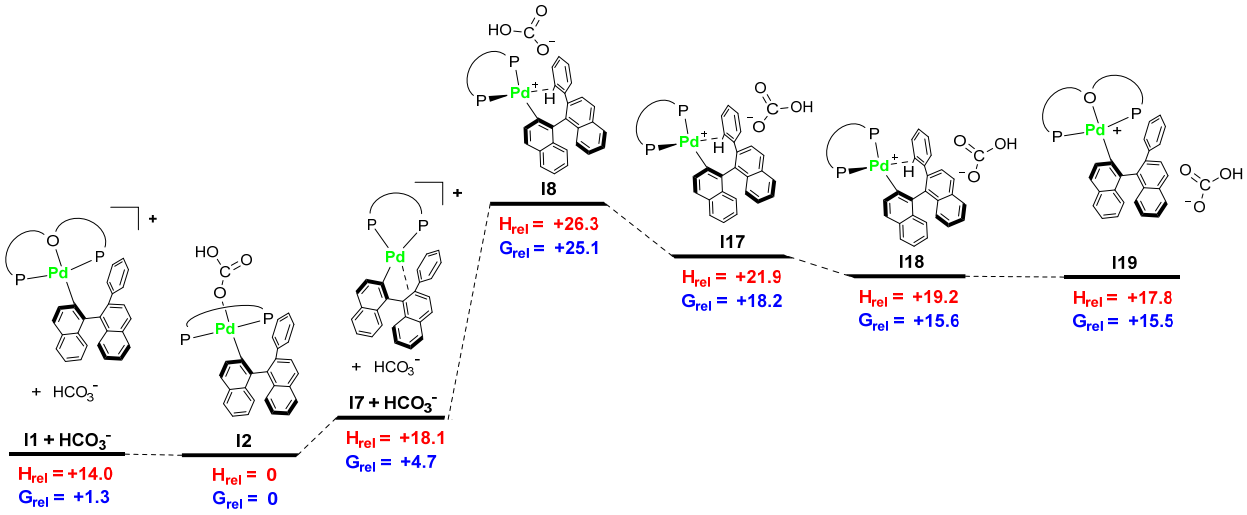
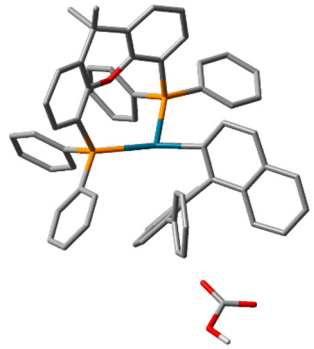


Figure S7. Relative energies of (xantphos)Pd(2'-phenylbinaphthyl) cationic intermediates with noncovalently pre-associated bicarbonate counterions (**I8**, **I17**-**I19**). Note that **I8**, **I17**, and **I18** differ primarily in the location of the bicarbonate anion (see geometries below).

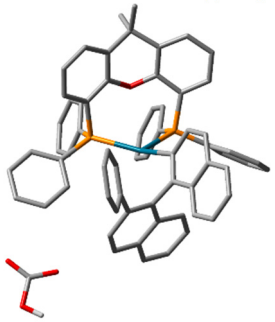
I17 cis-Bidentate (xantphos)Pd(binaphthyl) cation with noncovalently associated bicarbonate. Alternative to I8, with bicarbonate located on other side of 2'-Ph group.



C	-1.06681900	1.64965300	-1.02176300
C	-2.35360900	1.40684900	-0.56266400
C	-0.79611300	2.50791600	-2.13070900
C	-3.48852800	2.07621500	-1.14856400
C	-1.88195700	3.15980900	-2.73207900
H	0.21688400	2.65481500	-2.51193900
C	-4.83211600	1.85012200	-0.69279400
C	-3.22965900	2.98568700	-2.25315000
H	-1.70874700	3.82174500	-3.58663400
C	-5.88942900	2.53943400	-1.29558200
H	-5.04148800	1.14424000	0.11748000
C	-4.34484600	3.67283800	-2.84944100
C	-5.64436100	3.45488300	-2.37569900
H	-6.89846000	2.34334900	-0.92538300
H	-4.16160800	4.35991300	-3.68145700
H	-6.48498400	3.98041900	-2.83898800
C	-2.43239600	0.30899600	0.48042200
C	-2.20450300	0.61628400	1.88725700
C	-2.85349400	-0.99451000	0.09947200
C	-1.91208400	1.94483400	2.34416300
C	-2.31552800	-0.43260500	2.87279000
C	-2.97742100	-2.00701500	1.11156300
C	-1.70775600	2.21840600	3.70047700
H	-1.88740800	2.75949000	1.62203300
C	-2.07367700	-0.13566900	4.25752600
C	-2.70246800	-1.74606700	2.44465700
H	-3.32106600	-2.99640300	0.81465700
C	-1.77070600	1.16598600	4.67102500
H	-1.51568400	3.24631800	4.02152600
H	-2.17018600	-0.94250800	4.99020000
H	-2.81823300	-2.53530200	3.19232000
H	-1.61659200	1.38743500	5.73088600
C	-3.29220100	-1.36017400	-1.29184700
C	-4.54900900	-2.01455200	-1.43104900
C	-2.51741900	-1.10774500	-2.45688900
C	-5.00478400	-2.41930100	-2.70757000
C	-2.97205500	-1.52013900	-3.73018400
C	-4.21927600	-2.18103000	-3.86211200
H	-4.57592900	-2.49186900	-4.84889800
C	5.46602600	-0.70224800	-4.56982900
H	6.16314900	0.10371200	-4.84699500
H	5.99270700	-1.64856800	-4.76656900
H	4.58575600	-0.64754100	-5.23077200
C	6.36446800	-0.67673200	-2.20125100
H	6.12763200	-0.61468200	-1.12663300
H	6.88554000	-1.63288400	-2.37994600
H	7.05066900	0.15063900	-2.45112300
C	5.06802400	-0.59345600	-3.07605700
C	4.12594400	-1.73764300	-2.64645800
C	3.25754100	-1.53261300	-1.54427600
C	4.12733100	-3.03210800	-3.22597900
H	4.77703400	-3.25120700	-4.07490500
C	3.30142400	-4.05912600	-2.71140700

H	3.32751100	-5.05423800	-3.16214500
C	2.43106400	-3.80467400	-1.62649100
H	1.78259600	-4.60089600	-1.26085500
C	2.37630400	-2.51771600	-1.02847800
C	4.37253000	0.74701600	-2.76527900
C	3.52852900	0.81904600	-1.63149500
C	2.93148700	2.01599500	-1.16232800
C	3.18071400	3.20680800	-1.89243600
H	2.73299600	4.14818900	-1.57245900
C	3.99942900	3.17121100	-3.04518800
H	4.18153600	4.09040600	-3.60727800
C	4.58998500	1.95788100	-3.47326900
H	5.22597700	1.96534600	-4.36008400
C	2.72261000	1.43923900	1.74568900
C	4.11120400	1.15842700	1.72909700
H	4.66547600	1.15434100	0.78975100
C	4.79691300	0.90172800	2.94120000
H	5.86896300	0.68605600	2.91985800
C	4.10110400	0.93361400	4.17351200
H	4.63373900	0.73984800	5.10905600
C	2.71236900	1.21448200	4.18987800
H	2.16618800	1.24126300	5.13687300
C	2.02260600	1.45656800	2.98283200
H	0.95214400	1.67812800	3.00926300
C	2.06985600	-2.42003800	1.88357900
C	3.25305500	-3.20315900	1.92514300
H	3.71199300	-3.55370800	0.99845300
C	3.83806100	-3.54556200	3.16779300
H	4.74907600	-4.15065500	3.18943600
C	3.23769200	-3.11749600	4.37828400
H	3.68273500	-3.39255700	5.33918300
C	2.06013700	-2.33153200	4.33916300
H	1.59346600	-1.99111100	5.26781000
C	1.48569500	-1.97288500	3.09717100
H	0.58021300	-1.36126200	3.07822000
C	2.49336400	4.45212600	1.18463400
H	3.46462200	3.98462100	1.35707800
C	2.32428400	5.81741800	1.50780900
H	3.16530500	6.38277900	1.91877900
C	1.06706300	6.44359200	1.31175000
H	0.93046400	7.49770100	1.57006000
C	-0.00963900	5.69388300	0.78335300
H	-0.98562900	6.16163500	0.62866800
C	0.16256900	4.32751800	0.44927400
H	-0.67372700	3.77609100	0.03130800
C	1.41457200	3.69276600	0.64545100
C	-0.00866700	-3.49589900	0.20101800
C	-0.19466200	-4.42254300	1.25893300
H	0.37968800	-4.33417400	2.18200200
C	-1.13119600	-5.47664500	1.12590300
H	-1.26656200	-6.18331300	1.94974200
C	-1.88850800	-5.61586500	-0.06209300
H	-2.61605500	-6.42679200	-0.15958600
C	-1.70407000	-4.69385800	-1.12202000
H	-2.28984300	-4.77882700	-2.04065900
C	-0.77525500	-3.63952300	-0.98594300
H	-0.64542900	-2.94159900	-1.81430900
O	3.24833900	-0.31175400	-0.88464300
P	1.74914400	1.90602300	0.24802300
P	1.16577800	-2.06396500	0.31369700
Pd	0.07697400	0.27921900	-0.09304800
H	-5.98252800	-2.90127100	-2.79419900
H	-2.35839800	-1.31899600	-4.61342000
H	-1.55225900	-0.60404100	-2.37788100
O	-5.68454900	-0.66215000	1.15268100
H	-5.17947600	-2.14684200	-0.54964300
C	-6.89341500	-0.52222000	0.81274000
O	-7.57954700	0.51547400	0.59708400
O	-7.58054300	-1.76704300	0.60690100
H	-8.47600800	-1.47772600	0.34927300

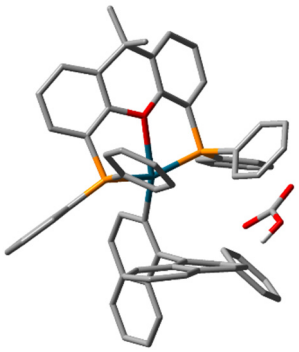
I18 cis-Bidentate (xantphos)Pd(binaphthyl) cation with noncovalently associated bicarbonate. Alternative to **I8** and **I17**, with bicarbonate located on periphery.



C	-0.08226600	2.20952500	-0.47468300
C	-1.37815400	2.62456200	-0.17233800
C	0.77051200	2.96827800	-1.33732100
C	-1.84318800	3.91563400	-0.64104800
C	0.32286000	4.19358900	-1.84026400
H	1.75819400	2.60002300	-1.61833700
C	-3.14250600	4.43236600	-0.30227400
C	-0.96902600	4.71228900	-1.48148400
H	0.96167100	4.77529300	-2.51162900
C	-3.54673800	5.69097700	-0.75608900
H	-3.80536500	3.83892700	0.32935900
C	-1.42158000	5.99811800	-1.94584600
C	-2.68361400	6.48077700	-1.58919000
H	-4.53232800	6.07577900	-0.47982000
H	-0.76078000	6.59097900	-2.58523400
H	-3.01879600	7.45866900	-1.94574700
C	-2.31360700	1.66281100	0.53179700
C	-2.24598200	1.46719400	1.96979400
C	-3.35661600	1.05011600	-0.21379500
C	-1.24901900	2.10154000	2.78902200
C	-3.22714200	0.61833500	2.61751300
C	-4.34746300	0.26240000	0.46305900
C	-1.19684900	1.87754200	4.16788900
H	-0.53682800	2.78370500	2.32816100
C	-3.14085600	0.39372000	4.03717000
C	-4.27864500	0.03433900	1.83541300
H	-5.14885000	-0.22687300	-0.09147400
C	-2.14271600	1.00393600	4.80212200
H	-0.43047700	2.37865100	4.76631600
H	-3.88366200	-0.25829100	4.50486600
H	-5.03363700	-0.61461300	2.28435900
H	-2.09096400	0.83178500	5.88080900
C	-3.49606500	1.18912800	-1.70357400
C	-4.73778200	1.62037800	-2.24696400
C	-2.45068000	0.83960800	-2.60136800
C	-4.91884800	1.72876900	-3.64583100
H	-5.55910200	1.87216400	-1.57147100
C	-2.62834300	0.94323000	-3.99948200
C	-3.86273200	1.39495200	-4.52859300
H	-4.00370700	1.47041300	-5.61076800
C	4.93848300	-0.27424600	-4.78025400
H	5.94564000	0.16999800	-4.74787600
H	4.99006900	-1.11259700	-5.49185200
H	4.23581300	0.47746700	-5.17535800
C	5.55776900	-1.83783900	-2.88919500
H	5.30543200	-2.21712800	-1.88599600
H	5.58336500	-2.69492700	-3.58310200
H	6.56616800	-1.39174800	-2.84288400
C	4.51557900	-0.77618000	-3.37786800
C	3.12099000	-1.43900400	-3.39406300
C	2.42346600	-1.56313600	-2.16816100
C	2.50616500	-2.01273200	-4.53670600
H	2.98932600	-1.94457200	-5.51284500

C	1.26051400	-2.67623300	-4.43014000
H	0.79570000	-3.10236400	-5.32267400
C	0.61094100	-2.80083000	-3.17952300
H	-0.35515500	-3.30232200	-3.11858700
C	1.19179900	-2.24805000	-2.00687900
C	4.47541900	0.36859000	-2.34534000
C	3.67149800	0.19352900	-1.19316000
C	3.54136000	1.16869400	-0.17013200
C	4.32520100	2.34622700	-0.27411800
H	4.26358700	3.11361200	0.49828400
C	5.17046800	2.53701400	-1.39164300
H	5.77267000	3.44572500	-1.46572700
C	5.22643000	1.57012500	-2.42491400
H	5.86595000	1.75705500	-3.28931300
C	2.81151900	-0.43807300	2.18137000
C	4.18208900	-0.80093500	2.23042100
H	4.90324700	-0.32527200	1.56225600
C	4.62234100	-1.77156200	3.15982900
H	5.67982800	-2.04811000	3.19505500
C	3.69552700	-2.38120000	4.04051300
H	4.03356000	-3.13825600	4.75361900
C	2.32750100	-2.01916300	3.99034500
H	1.60738600	-2.49554300	4.65952500
C	1.88405000	-1.05056100	3.06196900
H	0.82715200	-0.77339400	3.02872500
C	1.28702400	-3.50237200	0.66088500
C	2.63678700	-3.86200800	0.41893600
H	3.20372000	-3.38481000	-0.38037900
C	3.26179900	-4.86610900	1.19880400
H	4.29975700	-5.14160500	0.98892800
C	2.54705700	-5.51935900	2.23053800
H	3.02584500	-6.30739300	2.81966100
C	1.20142200	-5.15539000	2.48533800
H	0.63166300	-5.66229700	3.26971300
C	0.57634800	-4.15495300	1.70881400
H	-0.47010700	-3.90655700	1.90076300
C	2.91917900	2.27818000	3.49440300
H	3.27217800	1.31187500	3.85206200
C	3.03881200	3.40400900	4.34435900
H	3.47905100	3.28051500	5.33764300
C	2.59079700	4.67572000	3.91444500
H	2.67882800	5.54427100	4.57329600
C	2.02409500	4.81275200	2.62309300
H	1.66823400	5.78679400	2.27683300
C	1.90016200	3.68980700	1.77290500
H	1.45646200	3.82282200	0.78808100
C	2.34996300	2.40836900	2.19731000
C	-1.23484700	-3.11710800	-0.58574400
C	-1.29609600	-4.47140500	-1.02817000
H	-0.38101500	-5.00970600	-1.28988800
C	-2.54433900	-5.13109100	-1.09797900
H	-2.58536400	-6.16999200	-1.43923600
C	-3.73422300	-4.46005800	-0.70591600
H	-4.71396000	-4.94365700	-0.72268400
C	-3.67734300	-3.12054500	-0.24995300
H	-4.60260500	-2.63370600	0.07703900
C	-2.42782400	-2.45487200	-0.19774700
H	-2.38333000	-1.42717800	0.16625100
O	2.95535600	-0.97672200	-1.01468600
P	2.22769300	0.91786300	1.09574500
P	0.35461800	-2.24596600	-0.34356100
Pd	0.21896000	0.29024700	0.05293900
H	-5.88148300	2.06450100	-4.04152700
H	-1.81257200	0.65832200	-4.67009400
O	-6.71941700	-3.99182900	0.10554700
C	-7.10007300	-2.93336000	0.65394500
O	-6.45476700	-1.85471200	0.89718300
O	-8.45852500	-2.91527200	1.07907900
H	-8.55843700	-2.02511200	1.46447400
H	-1.50456200	0.45460000	-2.21205800

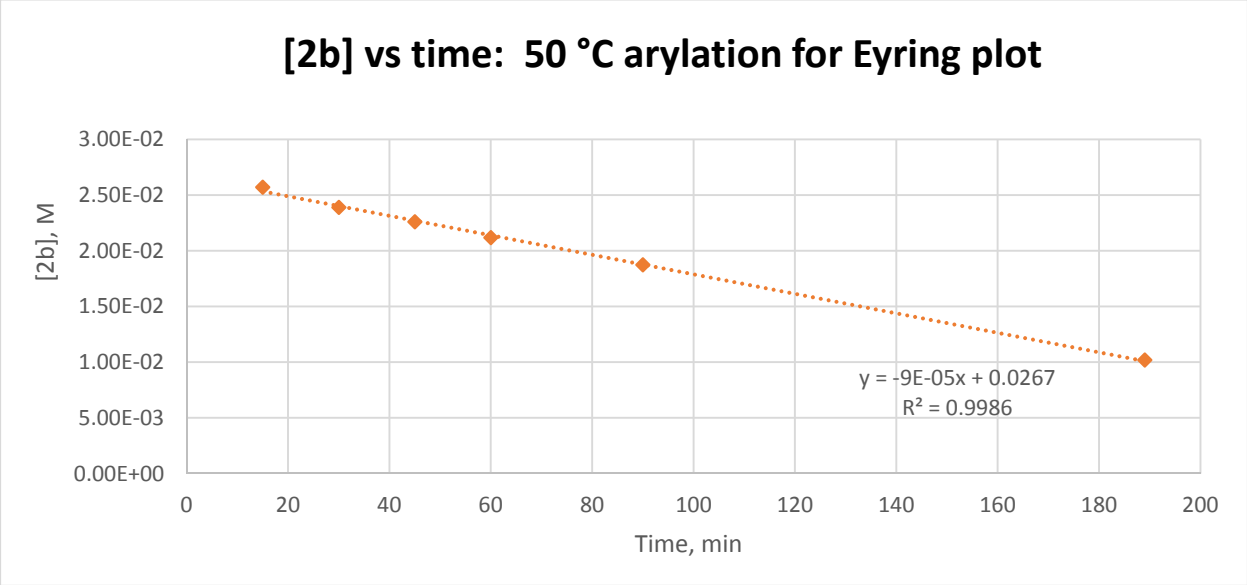
I19 P-O-P-Tridentate (xantphos)Pd(binaphthyl) cation with noncovalently associated bicarbonate.

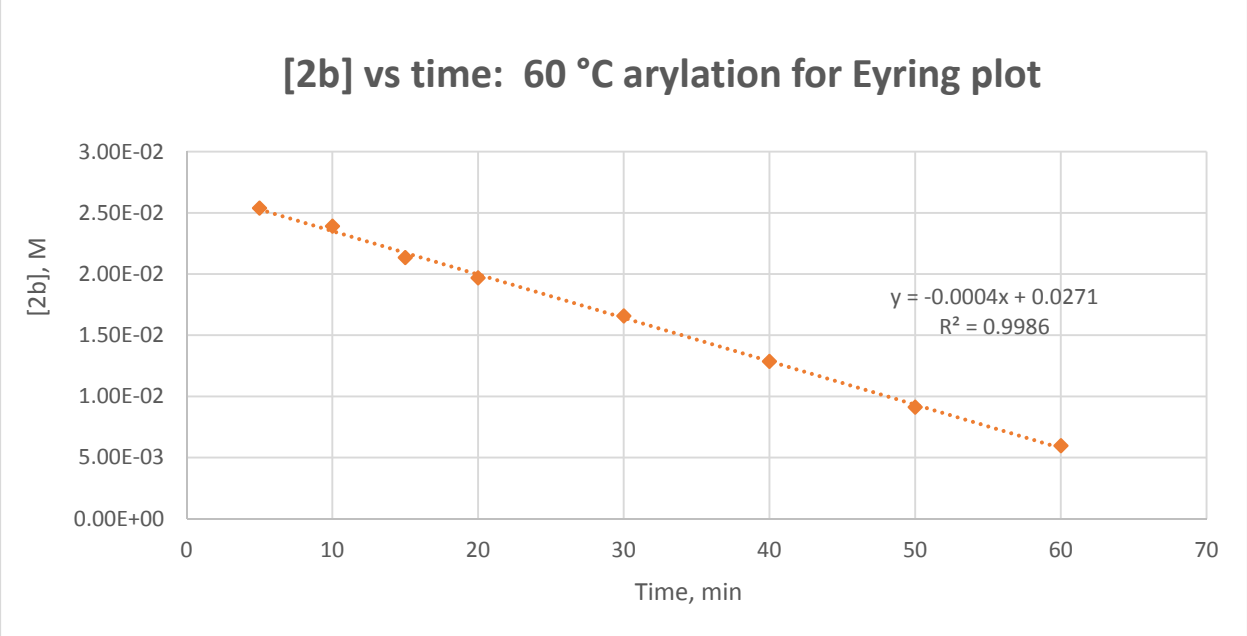


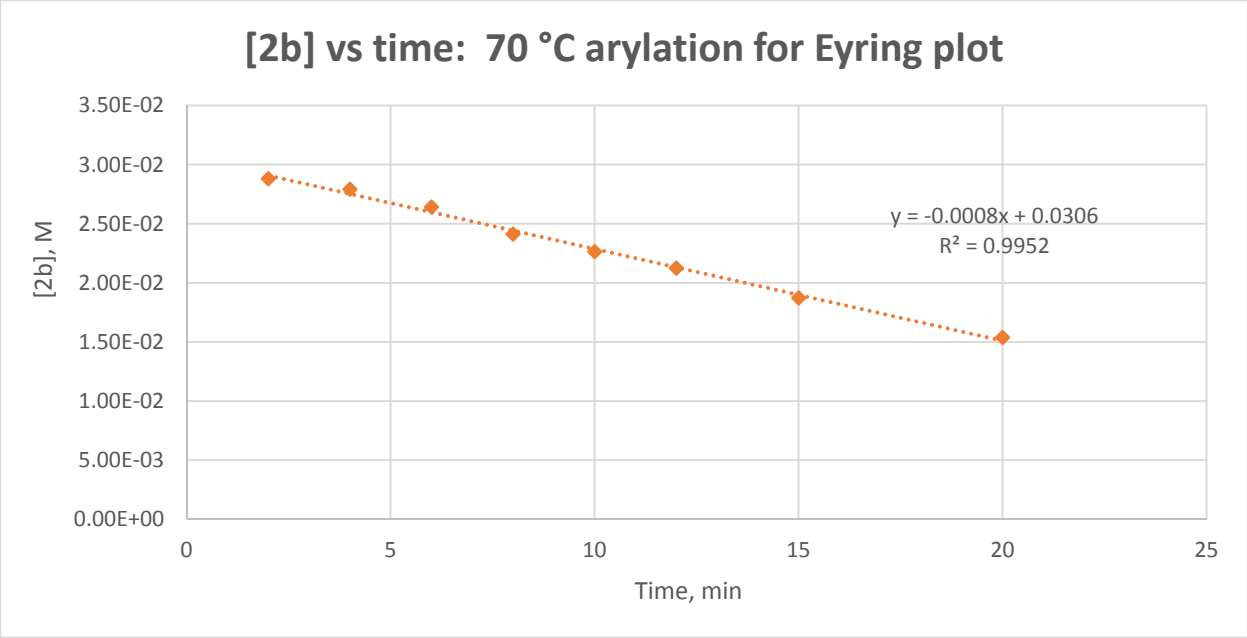
Pd	-0.43480300	0.33270600	-0.71181200
P	-1.85031500	-1.51470800	-1.20816300
P	0.13892300	2.39855700	0.29383400
C	-3.33041100	-0.56917000	-1.79603700
C	-4.26790500	-1.11349800	-2.71025300
H	-4.05504200	-2.07033600	-3.18973700
C	-5.47051600	-0.43073700	-2.99998600
H	-6.17890400	-0.85161700	-3.71773700
C	-5.77442800	0.77627800	-2.33171300
H	-6.72691500	1.26811200	-2.53272900
C	-4.86632800	1.35118300	-1.40370600
C	-3.63011700	0.68868600	-1.20631400
O	-2.64694900	1.27485300	-0.37128400
C	-2.65787600	2.68850600	-0.27335100
C	-3.88622800	3.38512200	-0.40891400
C	-3.84794800	4.80206700	-0.35448400
H	-4.76996200	5.37285000	-0.46952900
C	-2.63319200	5.49244000	-0.14973500
H	-2.62348700	6.58439000	-0.11080700
C	-1.43330200	4.76934600	0.01818700
H	-0.49885000	5.30620900	0.18603100
C	-1.42173400	3.35004400	-0.03802200
C	-5.18386500	2.57427900	-0.53207500
C	-6.35653800	3.41337100	-1.09365600
H	-6.58412400	4.25605900	-0.42332000
H	-7.27296500	2.80599200	-1.14773500
H	-6.13909900	3.81211000	-2.09831200
C	-5.58058000	2.06273300	0.89592700
H	-5.78039200	2.91892500	1.56214500
H	-4.78115900	1.45689600	1.34970900
H	-6.49015400	1.44126700	0.83690100
C	-1.67241700	-2.86580100	-2.43389200
C	-1.04166500	-2.57485100	-3.67384100
H	-0.65605700	-1.57318600	-3.87281100
C	-0.90609100	-3.58473000	-4.65488800
H	-0.41676400	-3.35460600	-5.60509100
C	-1.38912900	-4.89289900	-4.39866200
H	-1.27820900	-5.67559200	-5.15462200
C	-2.00664700	-5.18695000	-3.15762100
H	-2.37380700	-6.19617600	-2.95159400
C	-2.14626800	-4.17780900	-2.17457700
H	-2.60585900	-4.41545800	-1.21372400
C	-2.47912800	-2.19780400	0.37946800
C	-3.82714100	-2.63692000	0.52254900
H	-4.51511500	-2.61662400	-0.32573300
C	-4.28381500	-3.09116400	1.78088400
H	-5.31784000	-3.43199700	1.88895400
C	-3.41152000	-3.08845100	2.90218500
H	-3.77550400	-3.42501800	3.87733700
C	-2.07430300	-2.64367800	2.77120600
H	-1.38719000	-2.63303500	3.62692500
C	-1.61621200	-2.20632400	1.50446400
H	-0.58743700	-1.86956200	1.39784100

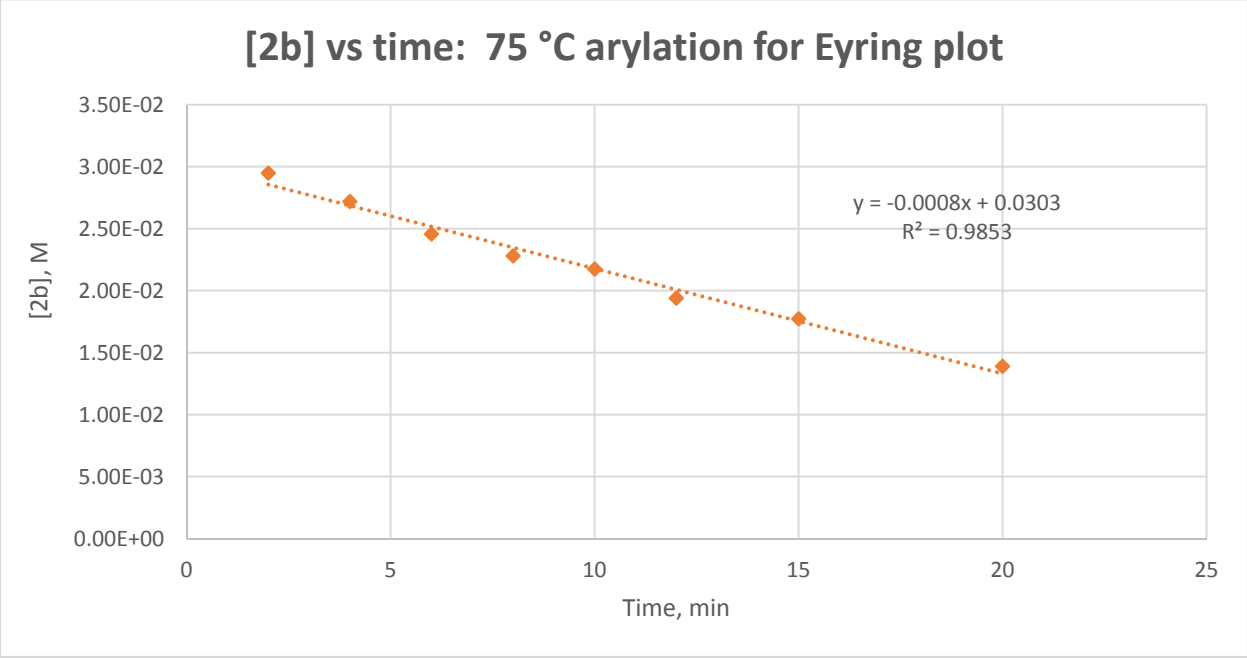
C	1.44147300	3.61134100	-0.15029200
C	1.60871100	3.95423600	-1.52032600
H	0.99449800	3.47360200	-2.28694000
C	2.56001600	4.92925400	-1.89542100
H	2.67788400	5.19587100	-2.94943600
C	3.35972400	5.55685100	-0.90597400
H	4.09558700	6.31252000	-1.19622000
C	3.21259100	5.19640700	0.45358900
H	3.83810600	5.66438600	1.21848400
C	2.25622200	4.22416800	0.83391600
H	2.15610200	3.94206400	1.88347400
C	0.10905000	2.15323200	2.10575000
C	0.35874300	0.84534100	2.60172500
H	0.64572900	0.05337200	1.91016200
C	0.21752800	0.55816000	3.97910500
H	0.36550100	-0.45268900	4.36876300
C	-0.15517200	1.59019300	4.87341400
H	-0.27166500	1.33024600	5.92800500
C	-0.38480200	2.90589500	4.38880800
H	-0.67320700	3.70440000	5.07905600
C	-0.26942100	3.18945200	3.00788300
H	-0.48412700	4.19652200	2.64205200
C	1.25587600	-0.16416900	-1.72737800
C	2.38447600	-0.87708600	-1.29486100
C	1.16846100	0.32092300	-3.08144200
C	3.42963000	-1.18906400	-2.26029200
C	2.18359500	0.06307100	-4.00448300
H	0.29908500	0.90481100	-3.39627000
C	4.58423100	-1.96368900	-1.88870100
C	3.33085900	-0.71193400	-3.62376200
H	2.10744600	0.44364900	-5.02766200
C	5.58070400	-2.25843000	-2.82366700
H	4.67122100	-2.33089200	-0.86589900
C	4.37732800	-1.02074000	-4.56265000
C	5.48320200	-1.78162500	-4.17366000
H	6.44622000	-2.85454200	-2.52081100
H	4.29054300	-0.64962900	-5.58841600
H	6.27320400	-2.01420700	-4.89321200
C	2.55020600	-1.31958600	0.13677700
C	1.87313600	-2.52881400	0.56350200
C	3.38452900	-0.62591700	1.04810900
C	1.21692300	-3.40684300	-0.37078800
C	1.89503400	-2.91359200	1.95845900
C	3.35272100	-1.01260300	2.44085400
C	0.62662200	-4.59663200	0.06224700
H	1.22634800	-3.16237400	-1.43369900
C	1.21297100	-4.10318800	2.38809200
C	2.59299600	-2.08300700	2.89803900
H	3.90373800	-0.40584000	3.16185800
C	0.60943700	-4.94499400	1.45197400
H	0.17216000	-5.26779400	-0.67181100
H	1.18282100	-4.31756000	3.45764700
H	2.51218200	-2.31483500	3.96136200
H	0.11151800	-5.86244700	1.77814800
C	4.39134300	0.42475000	0.65717600
C	5.66476900	0.39252200	1.30257900
C	4.18779400	1.40451900	-0.35393500
C	6.68906200	1.30376000	0.95728300
H	5.86701800	-0.37096500	2.05651200
C	5.20997600	2.31682100	-0.69867600
H	3.23528100	1.46571100	-0.87153100
C	6.46728200	2.27400800	-0.05043400
H	7.65674400	1.24507900	1.46431400
H	5.02306100	3.05063400	-1.48633900
H	7.25883300	2.97673300	-0.32746900
O	0.23324600	-2.67359200	5.07402200
C	-0.02336200	-2.21464000	6.24563100
O	-0.14145700	-3.20866700	7.25521400
H	0.02286200	-4.04039100	6.77363300
O	-0.18396200	-1.03471600	6.62583300

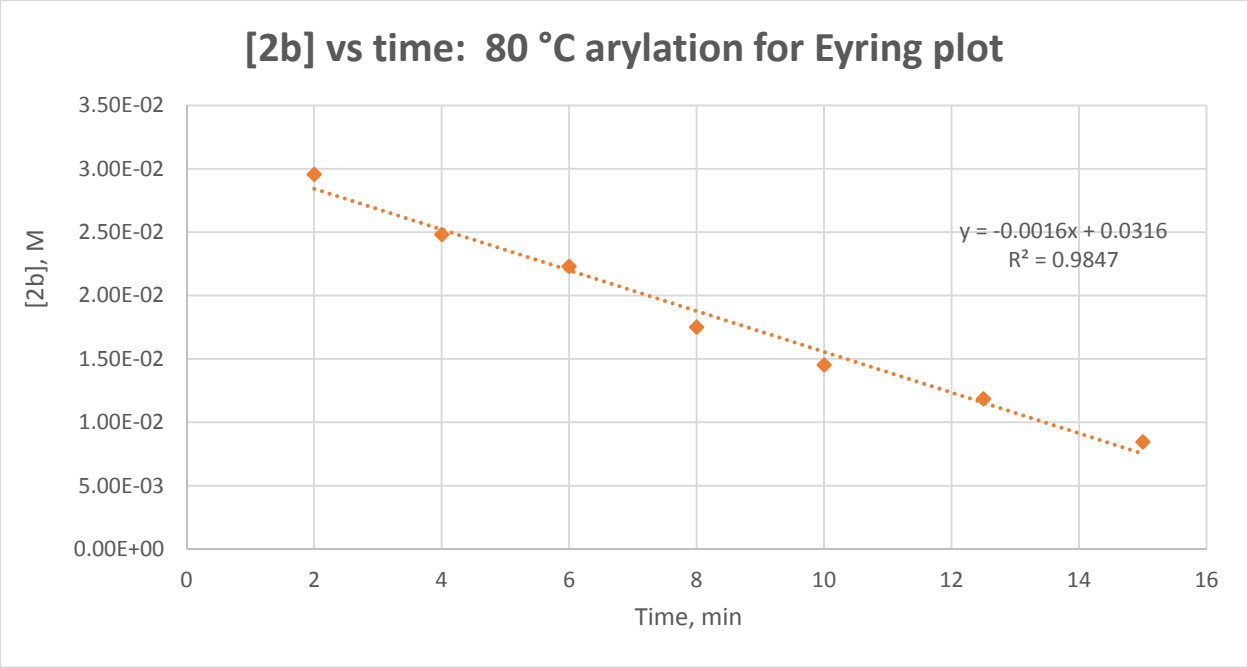
KINETIC PLOTS

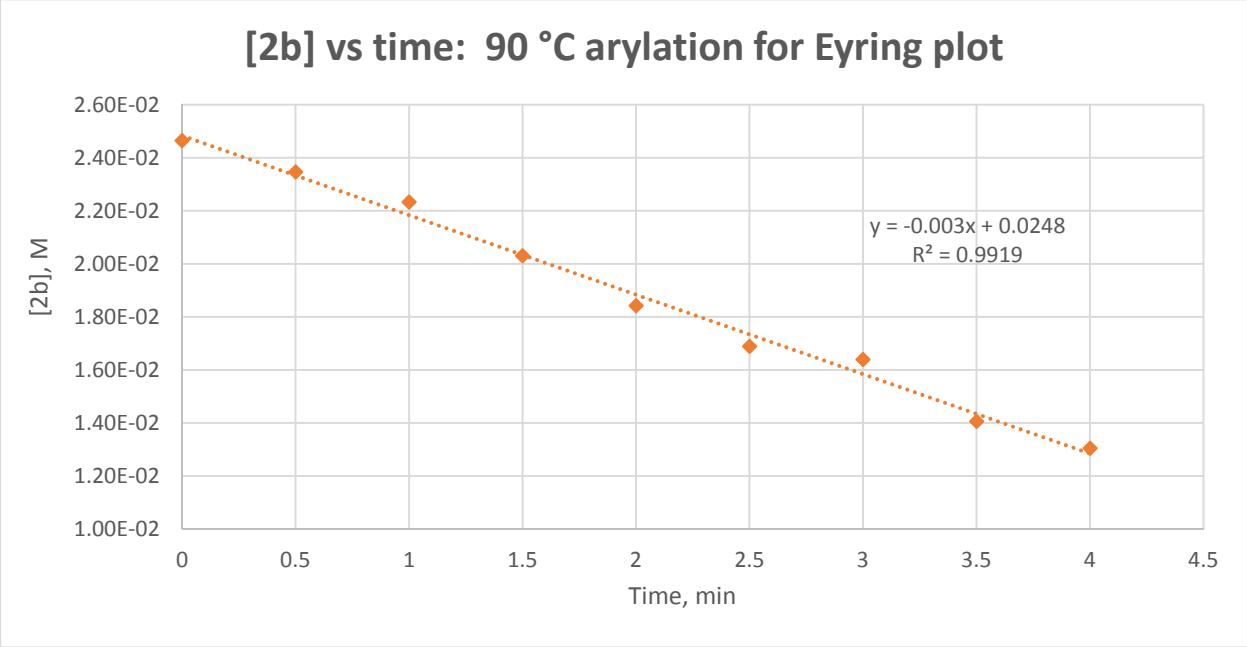


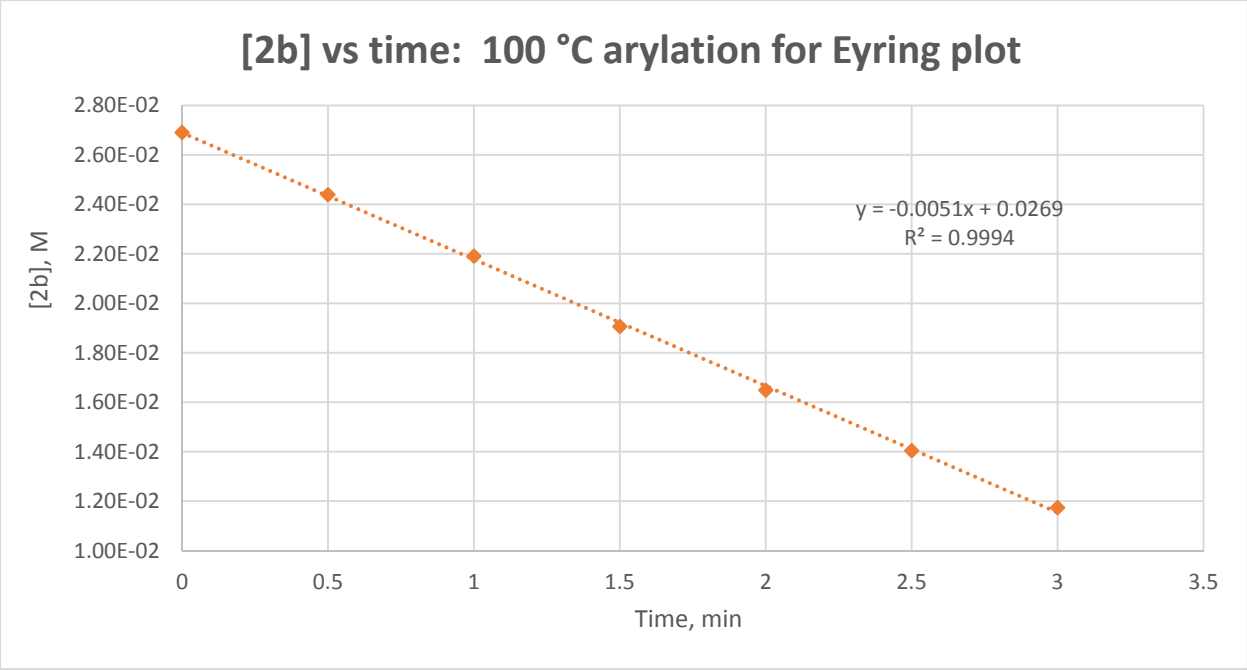


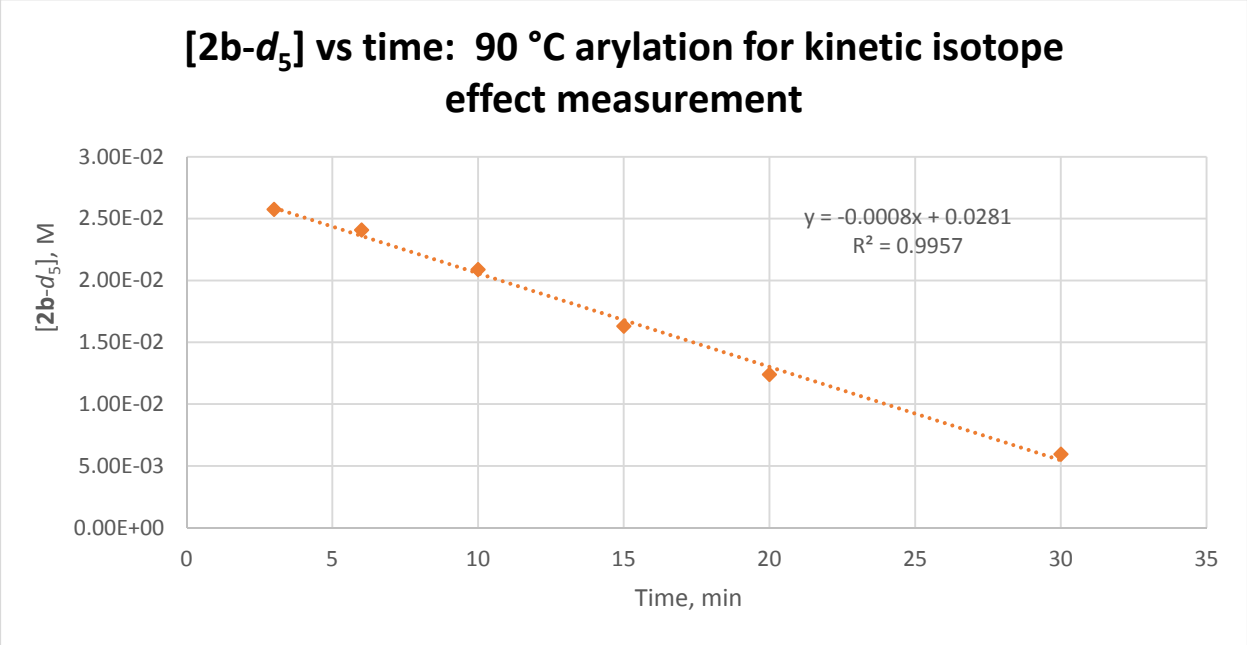

[2b] vs time: 70 °C arylation for Eyring plot
[2b], M
3.50E-02
3.00E-02
2.50E-02
2.00E-02
1.50E-02
1.00E-02
5.00E-03
0.00E+00
0
5
10
15
20
25
Time, min
y = -0.0008x + 0.0306
R² = 0.9952


[2b] vs time: 75 °C arylation for Eyring plot
[2b], M
3.50E-02
3.00E-02
2.50E-02
2.00E-02
1.50E-02
1.00E-02
5.00E-03
0.00E+00
0
5
10
15
20
25
Time, min
y = -0.0008x + 0.0303
R² = 0.9853


[2b] vs time: 80 °C arylation for Eyring plot
[2b], M
3.50E-02
3.00E-02
2.50E-02
2.00E-02
1.50E-02
1.00E-02
5.00E-03
0.00E+00
0
2
4
6
8
10
12
14
16
Time, min
y = -0.0016x + 0.0316
R² = 0.9847


[2b] vs time: 90 °C arylation for Eyring plot
[2b], M
2.60E-02
2.40E-02
2.20E-02
2.00E-02
1.80E-02
1.60E-02
1.40E-02
1.20E-02
1.00E-02
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
Time, min
y = -0.003x + 0.0248
R² = 0.9919


[2b] vs time: 100 °C arylation for Eyring plot
2.80E-02
2.60E-02
2.40E-02
2.20E-02
2.00E-02
1.80E-02
1.60E-02
1.40E-02
1.20E-02
1.00E-02
[2b], M
y = -0.0051x + 0.0269
R² = 0.9994
0
0.5
1
1.5
2
2.5
3
3.5
Time, min

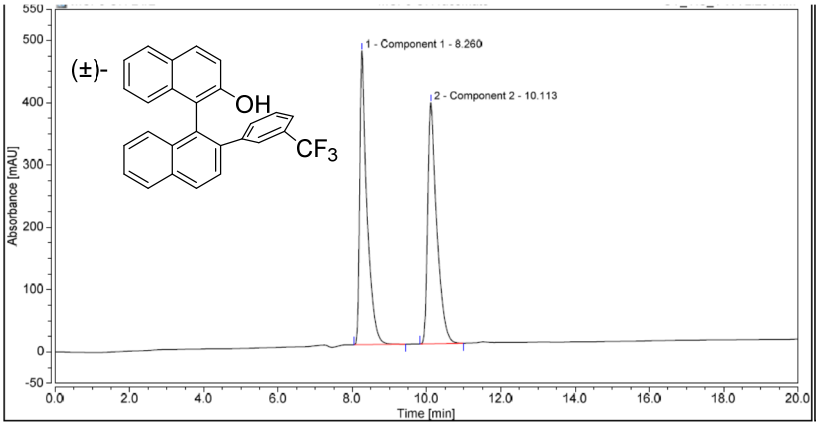

[2b-d_5] vs time: 90 °C arylation for kinetic isotope effect measurement
3.00E-02
2.50E-02
2.00E-02
1.50E-02
1.00E-02
5.00E-03
0.00E+00
[2b-d_5], M
y = -0.0008x + 0.0281
R² = 0.9957
0
5
10
15
20
25
30
35
Time, min

CHIRAL HPLC CHROMATOGRAMS

Note: Detector channel was set to 254 nm for all chromatograms.

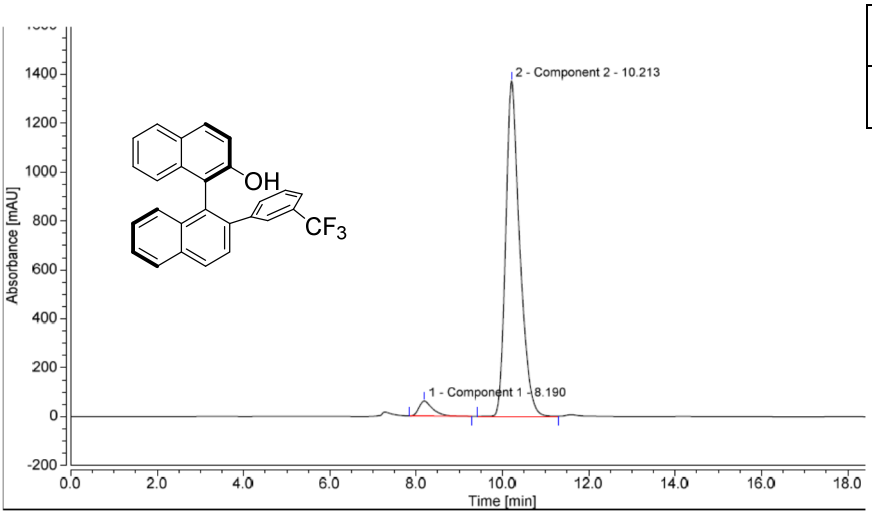
rac-2′-[3-(Trifluoromethyl)phenyl]-[1,1′-binaphthalen]-2-ol [(±)-1f]

Chiralpak IC column, 4.6 x 250 mm, 5 µm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 2.0 MPa, flow rate: 0.5 mL/min



	r_t / min	Area %
R	10.113	50.48
S	8.260	49.52

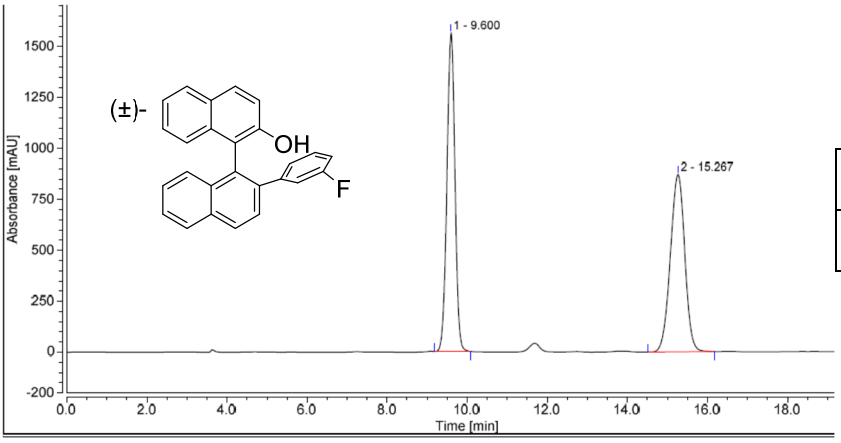
(*R*)-2′-[3-(Trifluoromethyl)phenyl]-[1,1′-binaphthalen]-2-ol (1f)



	r_t / min	Area %
R	10.213	95.86
S	8.190	4.14

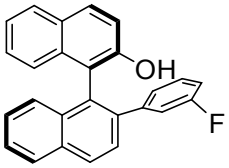
(*rac*)-2'-[3-(Fluoro)phenyl]-[1,1'-binaphthalen]-2-ol [(±)-1k]

Chiralpak IA column, 4.6 x 250 mm, 5 µm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.7 MPa, flow rate: 1.0 mL/min

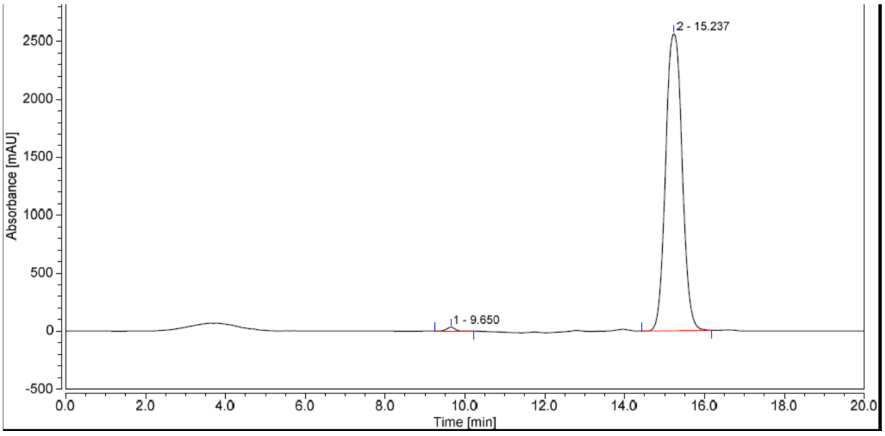


	r_t / min	Area %
R	15.267	49.97
S	9.600	50.03

(*R*)-2'-[3-(Fluoro)phenyl]-[1,1'-binaphthalen]-2-ol (1k)



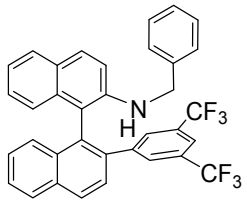
	r_t / min	Area %
R	15.237	99.36
S	9.650	0.64



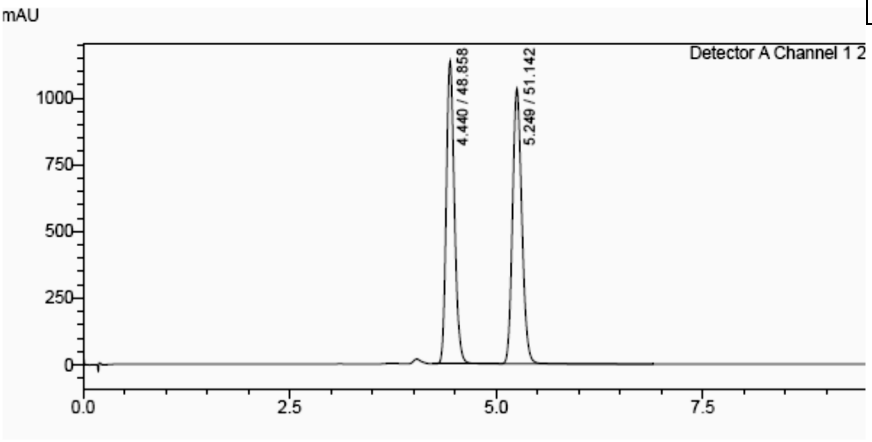
***rac*-2-Benzylamino-2′-[3,5-bis(trifluoromethyl)phenyl]-1,1′-binaphthyl [(±)-3a]**

Phenomenex Lux Cellulose-1 column, 4.6 x 250 mm, 3 µm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 6.5 MPa, flow rate: 1.0 mL/min

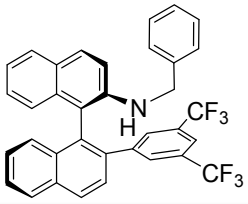
(±)-



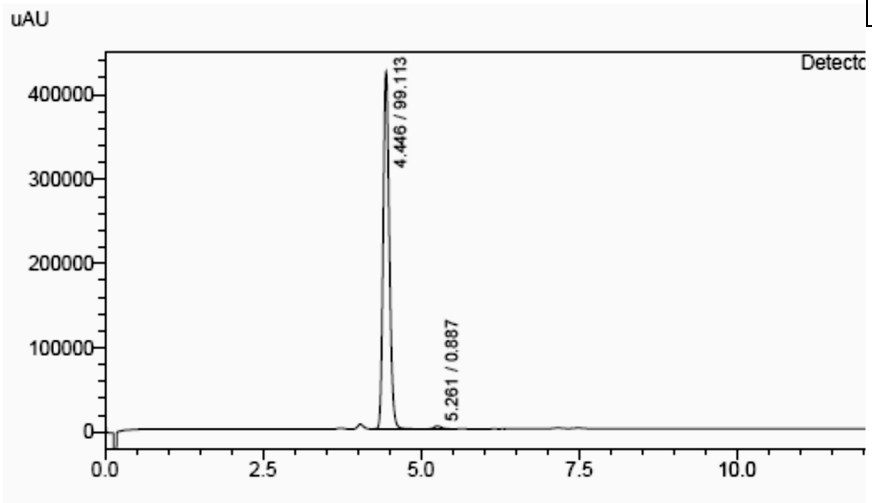
	r_t / min	Area %
R	4.440	48.858
S	5.249	51.142



(*R*)-2-Benzylamino-2′-[3,5-bis(trifluoromethyl)phenyl]-1,1′-binaphthyl (3a)

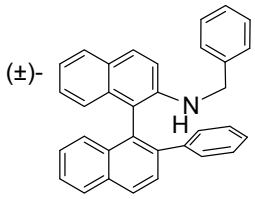


	r_t / min	Area %
R	4.446	99.113
S	5.261	0.887

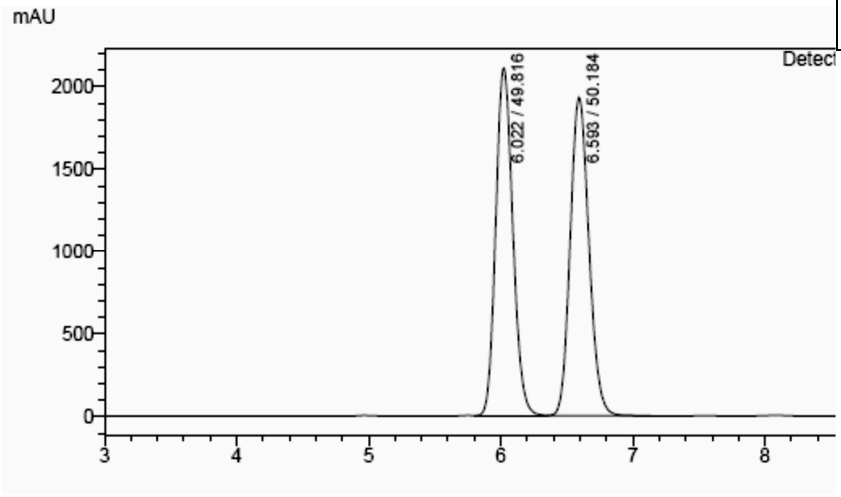


***rac*-2-Benzylamino-2′-phenyl-1,1′-binaphthyl [(±)-3b]**

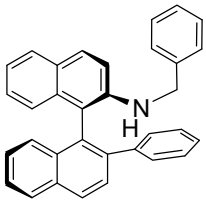
Phenomenex Lux Cellulose-1 column, 4.6 x 250 mm, 3 µm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 6.5 MPa, flow rate: 1.0 mL/min



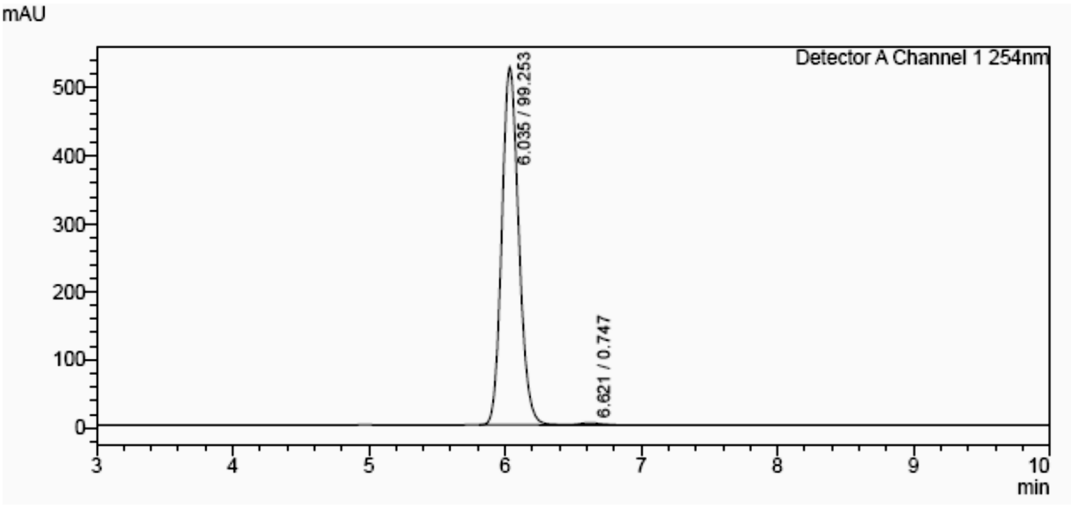
	r_t / min	Area %
R	6.022	49.816
S	6.593	50.184



(*R*)-2-Benzylamino-2′-phenyl-1,1′-binaphthyl (3b)

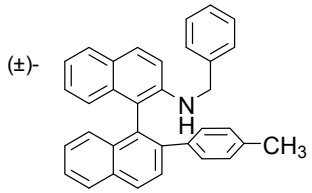


	r_t / min	Area %
R	6.035	99.253
S	6.621	0.747

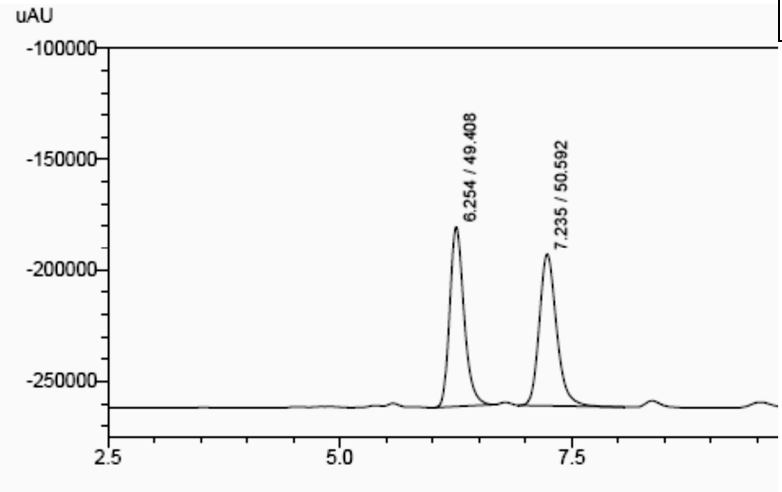


***rac*-2-Benzylamino-2′-[4-(methyl)phenyl]-1,1′-binaphthyl [(±)-3c]**

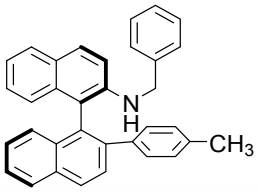
Chiralpak AD-H column, 4.6 x 250 mm, 5 μm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.9 MPa, flow rate: 1.0 mL/min



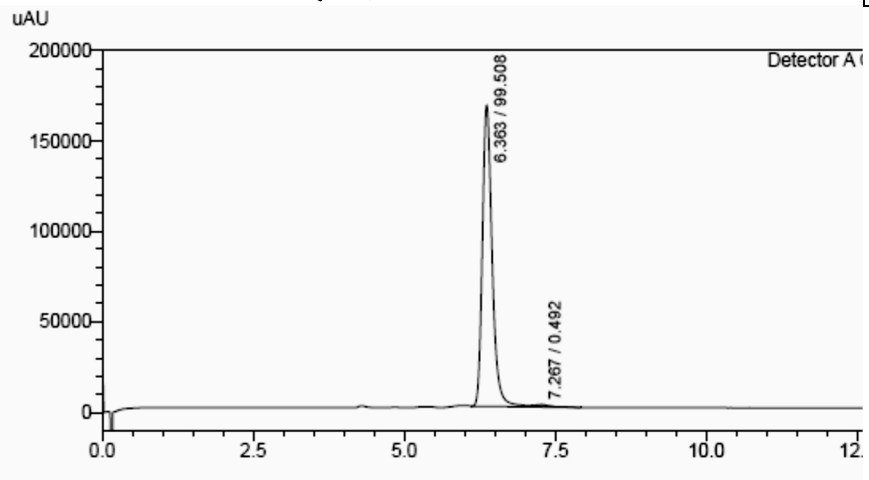
	r_t / min	Area %
R	6.254	49.408
S	7.235	50.592



(*R*)-2-Benzylamino-2′-[4-(methyl)phenyl]-1,1′-binaphthyl (3c)

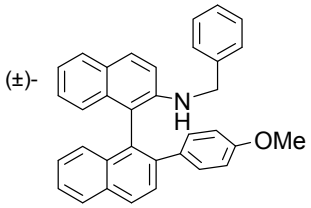


	r_t / min	Area %
R	6.363	99.508
S	7.267	0.492

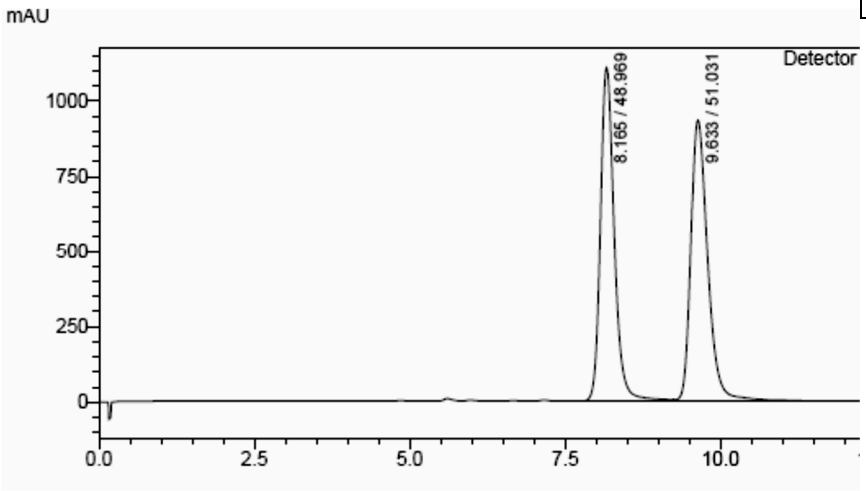


***rac*-2-Benzylamino-2′-[4-(methoxy)phenyl]-1,1′-binaphthyl (3d)**

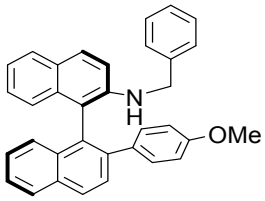
Chiralpak AD-H column, 4.6 x 250 mm, 5 μm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.9 MPa, flow rate: 1.0 mL/min



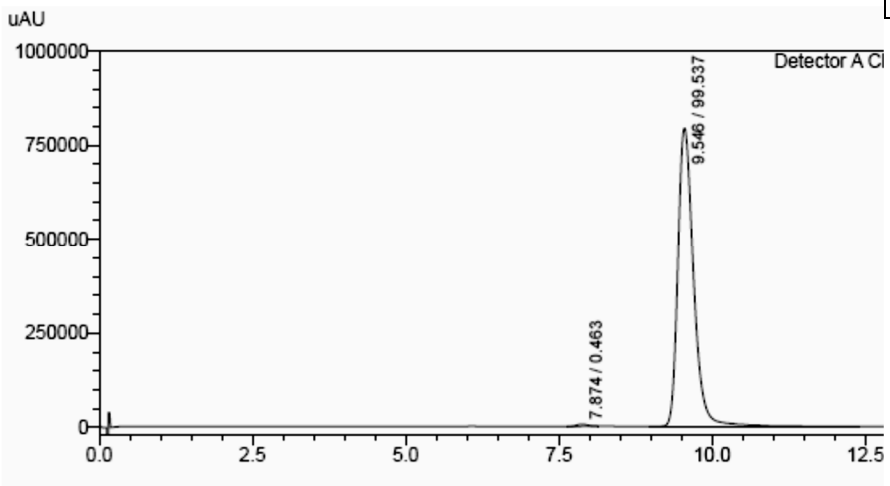
	r_t / min	Area %
R	9.633	51.031
S	8.165	48.969



(*R*)-2-Benzylamino-2′-[4-(methoxy)phenyl]-1,1′-binaphthyl (3d)

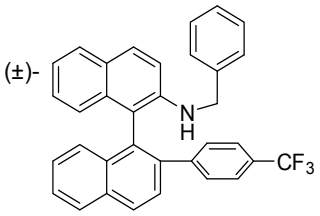


	r_t / min	Area %
R	9.546	99.537
S	7.874	0.463

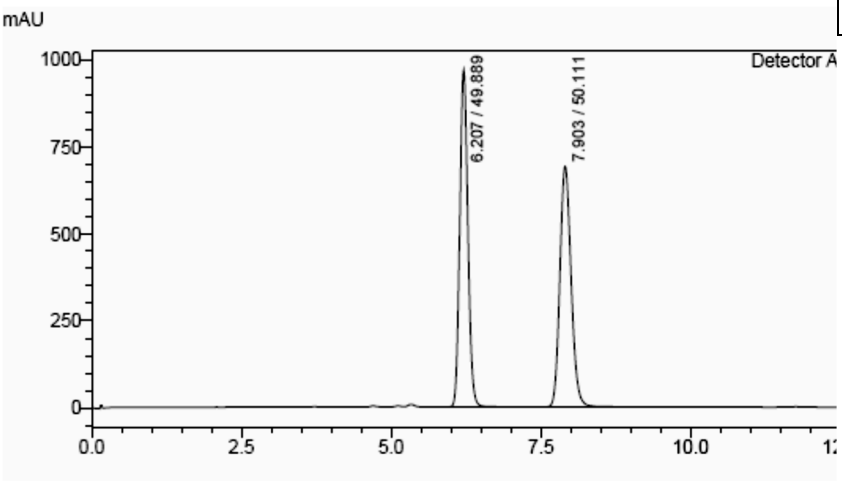


***rac*-2-Benzylamino-2′-[4-(trifluoromethyl)phenyl]-1,1′-binaphthyl [(±)-3e]**

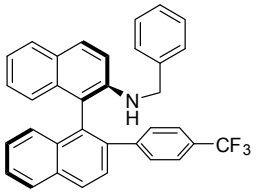
Phenomenex Lux Cellulose-1 column, 4.6 x 250 mm, 3 µm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 6.5 MPa, flow rate: 1.0 mL/min



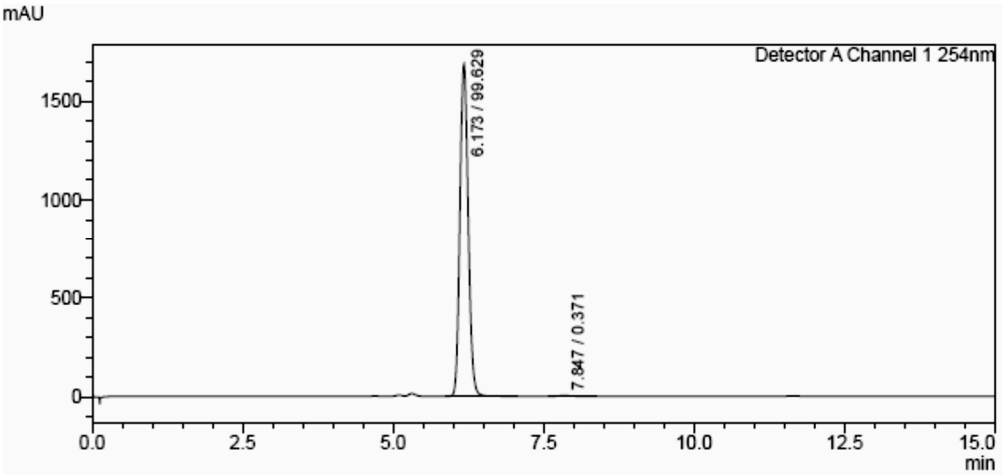
	r_t / min	Area %
R	6.207	49.889
S	7.903	50.111



(*R*)-2-Benzylamino-2′-[4-(trifluoromethyl)phenyl]-1,1′-binaphthyl (3e)

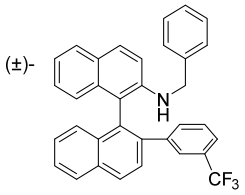


	r_t / min	Area %
R	6.173	99.629
S	7.847	0.371

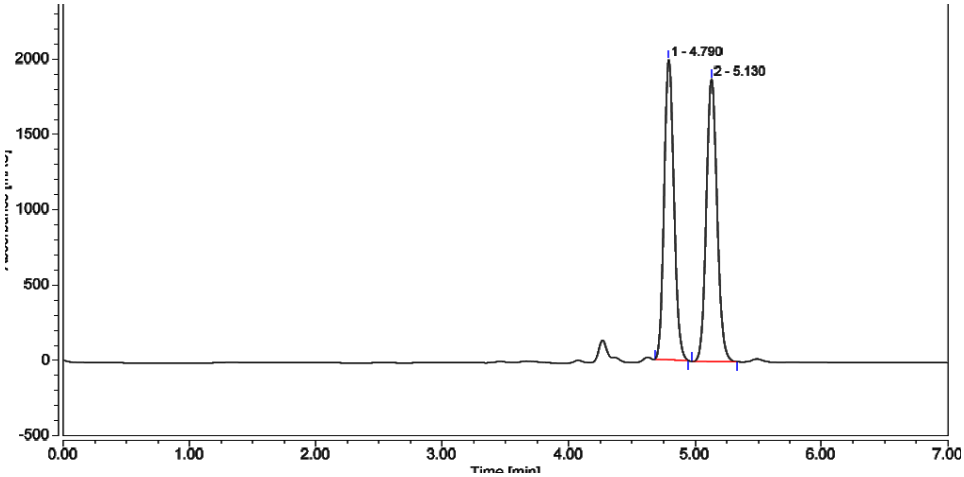


***rac*-2'-[3-(Trifluoromethyl)phenyl]-1,1'-binaphthyl (3f)**

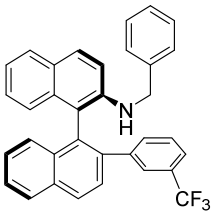
Chiralpak IB column, 4.6 x 250 mm, 5 µm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.7 MPa, flow rate: 1.0 mL/min



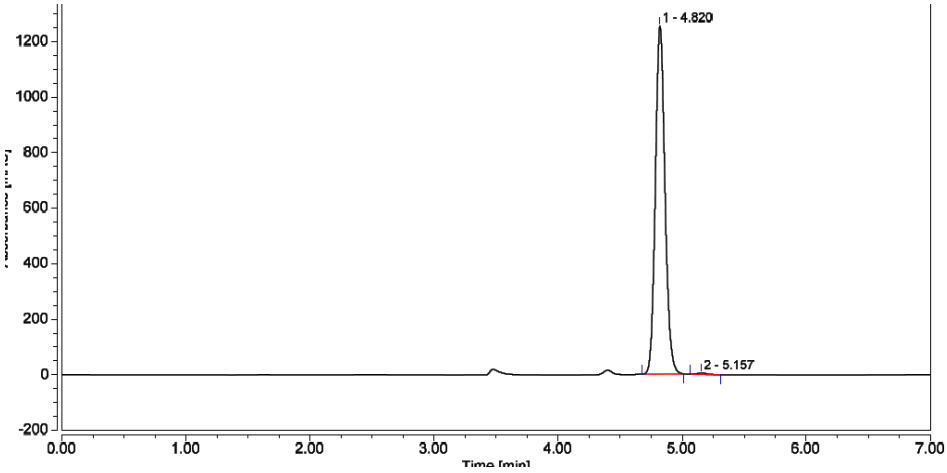
	r_t / min	Area %
R	4.790	49.09
S	5.130	50.91



(*R*)-2'-[3-(Trifluoromethyl)phenyl]-1,1'-binaphthyl (3f)



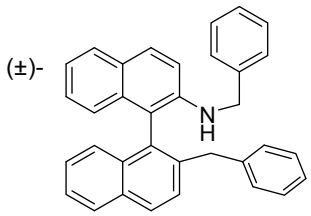
	r_t / min	Area %
R	4.820	99.58
S	5.157	0.42



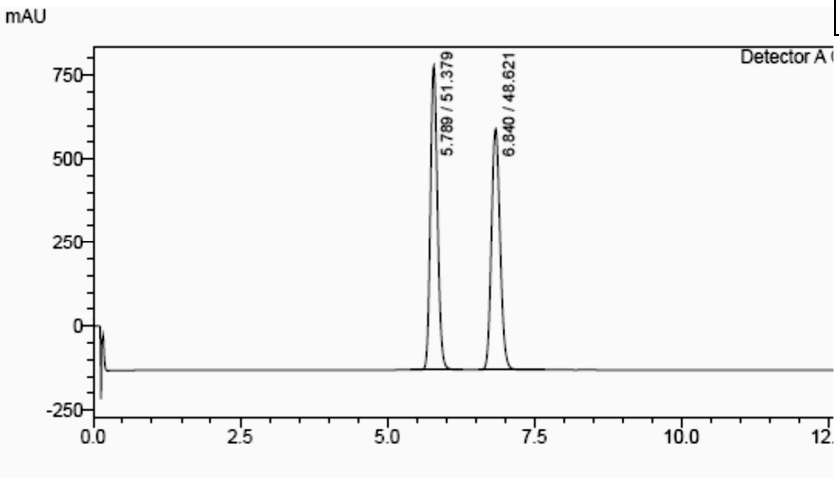
***rac*-2-Benzylamino-2′-benzyl-1,1′-binaphthyl [(±)-3g]**

Phenomenex Lux Cellulose-1 column, 4.6 x 250 mm, 3 µm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 6.5 MPa, flow rate: 1.0 mL/min

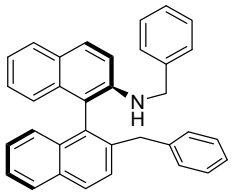
(±)-



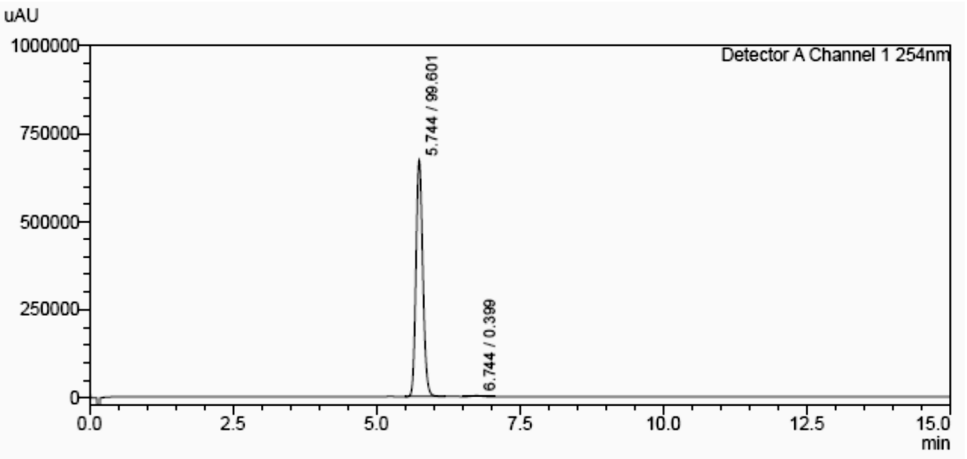
	r_t / min	Area %
R	6.840	48.621
S	5.789	51.379



(*S*)-2-Benzylamino-2′-benzyl-1,1′-binaphthyl (3g)

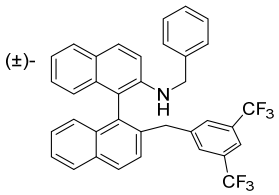


	r_t / min	Area %
R	6.744	0.399
S	5.744	99.601

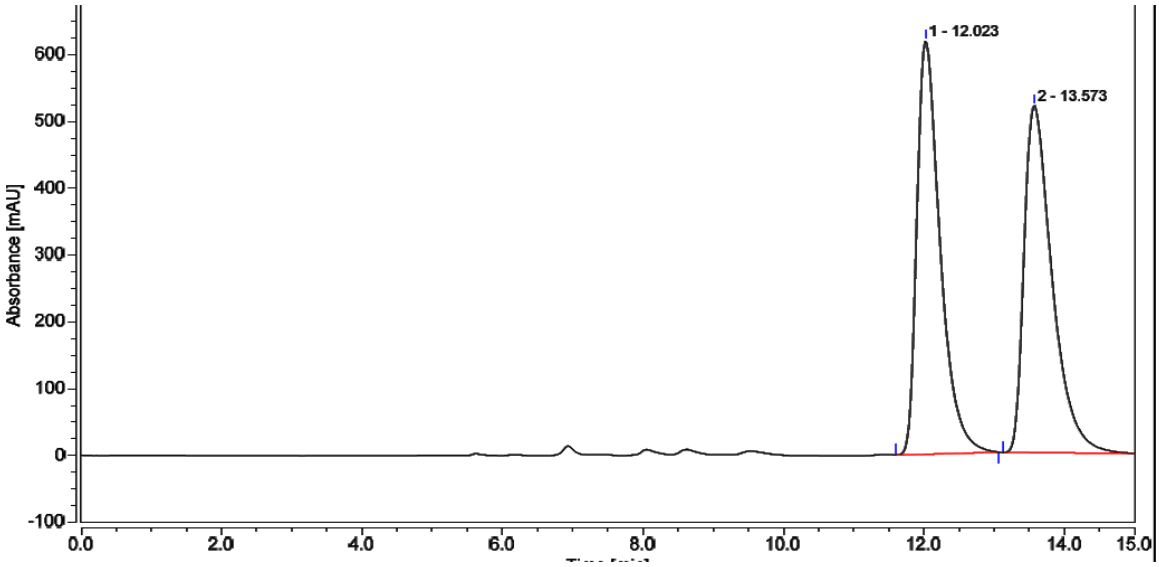


***rac*-2-Benzylamino-2′-[3,5-bis(trifluoromethyl)benzyl]-1,1′-binaphthyl [(±)-3h]**

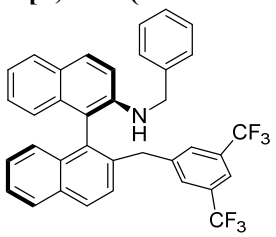
Regis (R,R)-Whelk-O1 column, 4.6 x 250 mm, 5 µm particle size, 25 °C, hexanes/*i*PrOH 99:1, pressure = 3.7 MPa, flow rate: 1.0 mL/min



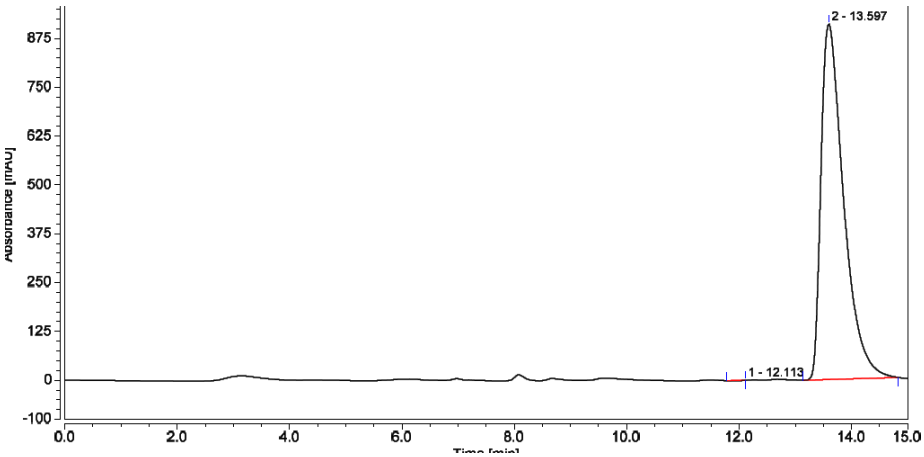
	r_t / min	Area %
R	12.023	49.65
S	13.573	50.35



(*S*)-2-Benzylamino-2′-[3,5-bis(trifluoromethyl)benzyl]-1,1′-binaphthyl (3h)



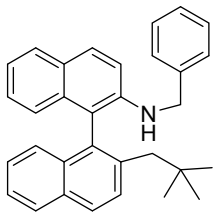
	r_t / min	Area %
R	12.113	0.04
S	13.597	99.96



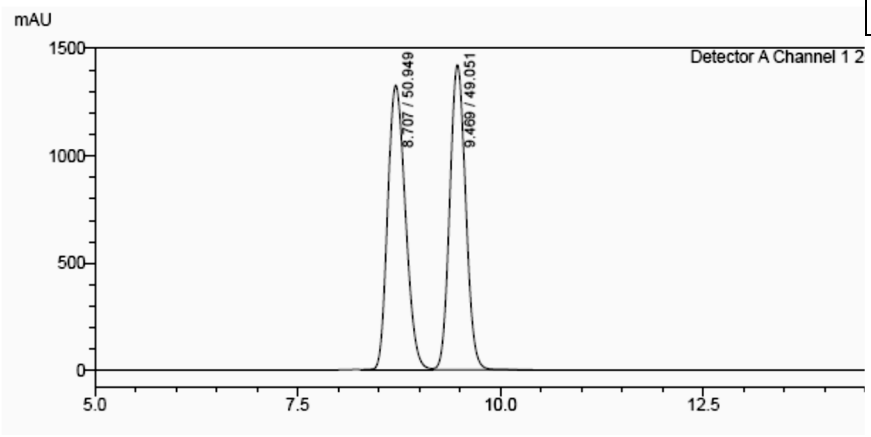
***rac*-2-Benzylamino-2′-neopentyl-1,1′-binaphthyl [(±)-3i]**

Phenomenex Lux Cellulose-1 column, 4.6 x 250 mm, 3 µm particle size, 25 °C, hexanes/*i*PrOH 99:1, pressure = 3.3 MPa, flow rate: 0.5 mL/min

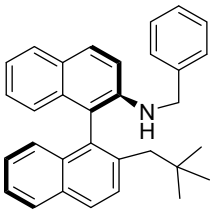
(±)-



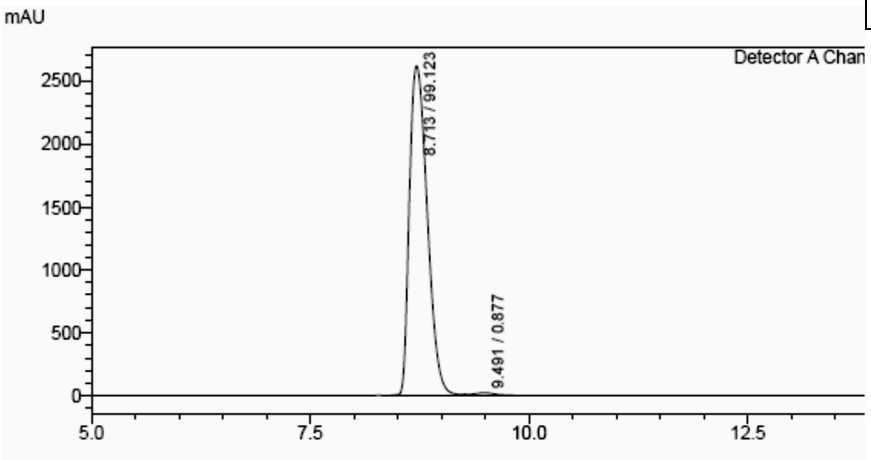
	r_t / min	Area %
R	9.469	49.051
S	8.707	50.949



(*S*)-2-Benzylamino-2′-neopentyl-1,1′-binaphthyl (3i)

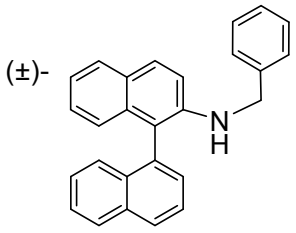


	r_t / min	Area %
R	9.491	0.877
S	8.713	99.123

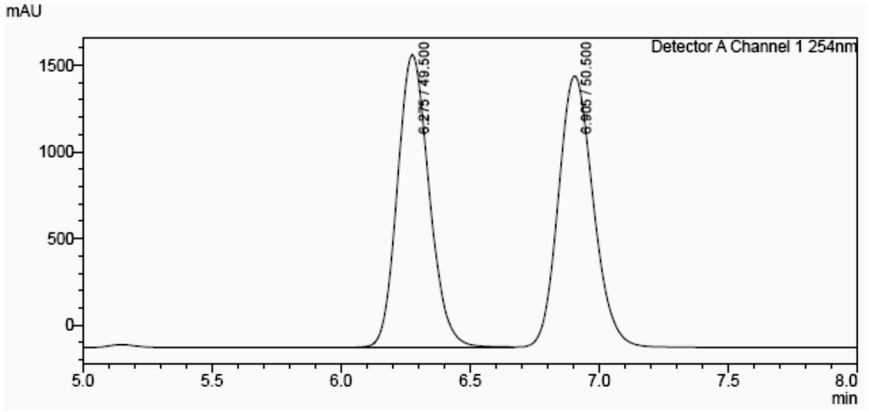


***rac*-2-Benzylamino-1,1′-binaphthyl [(±)-3j]**

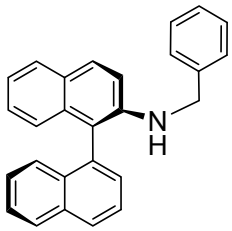
Phenomenex Lux Cellulose-1 column, 4.6 x 250 mm, 3 µm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 6.5 MPa, flow rate: 1.0 mL/min



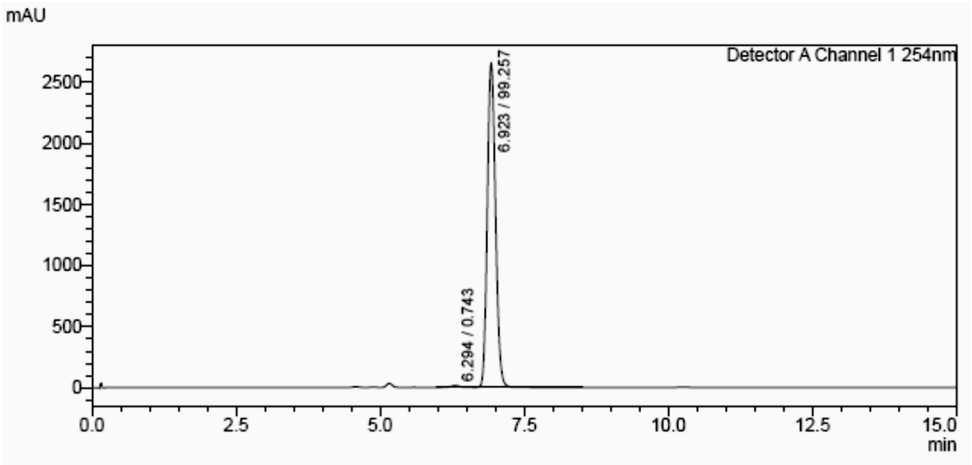
	r_t / min	Area %
R	6.275	49.50
S	6.905	50.50



(*S*)-2-Benzylamino-1,1′-binaphthyl (3j)

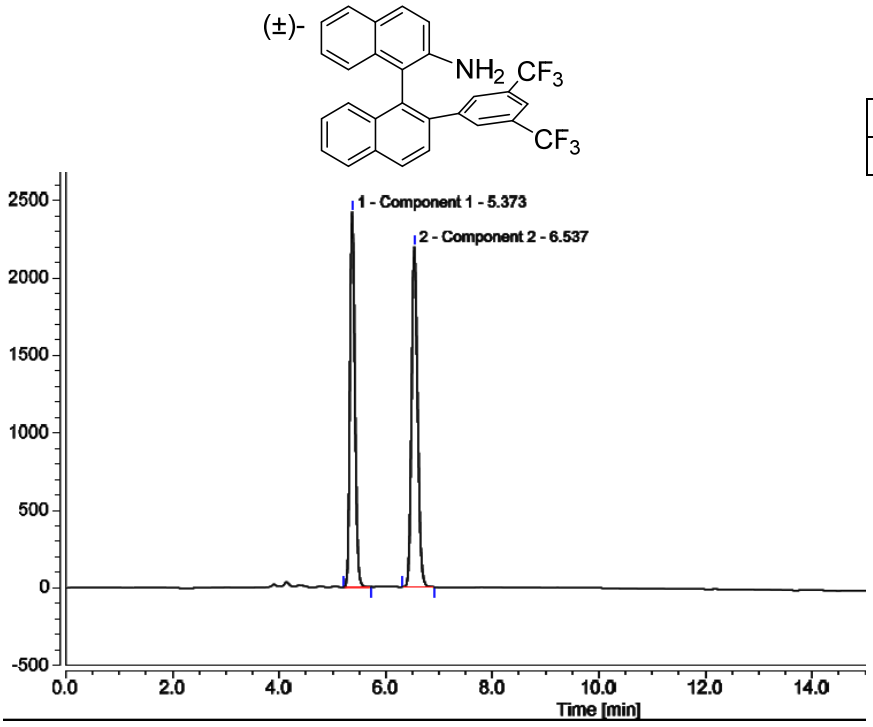


	r_t / min	Area %
R	6.294	0.743
S	6.923	99.257



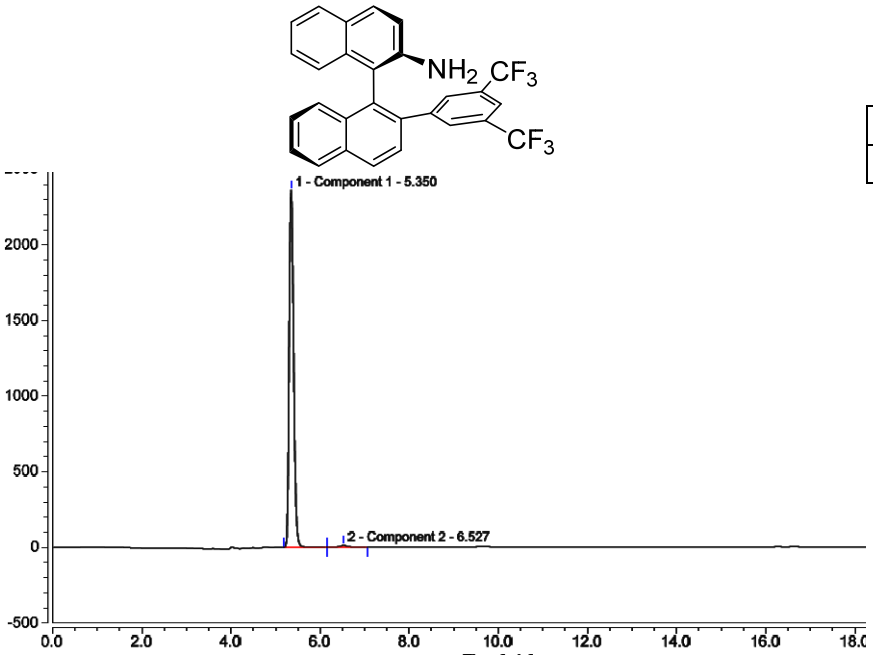
***rac*-2-Amino-2′-[3,5-bis(trifluoromethyl)phenyl]-1,1′-binaphthyl [(±)-6a]**

Chiralpak IB column, 4.6 x 250 mm, 5 µm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 4.6 MPa, flow rate: 1.0 mL/min



	r_t / min	Area %
R	5.373	47.72
S	6.537	52.28

(*R*)-2-Amino-2′-[3,5-bis(trifluoromethyl)phenyl]-1,1′-binaphthyl (6a)

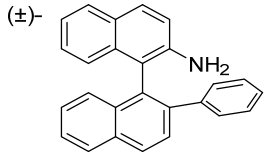


	r_t / min	Area %
R	5.350	99.14
S	6.527	0.86

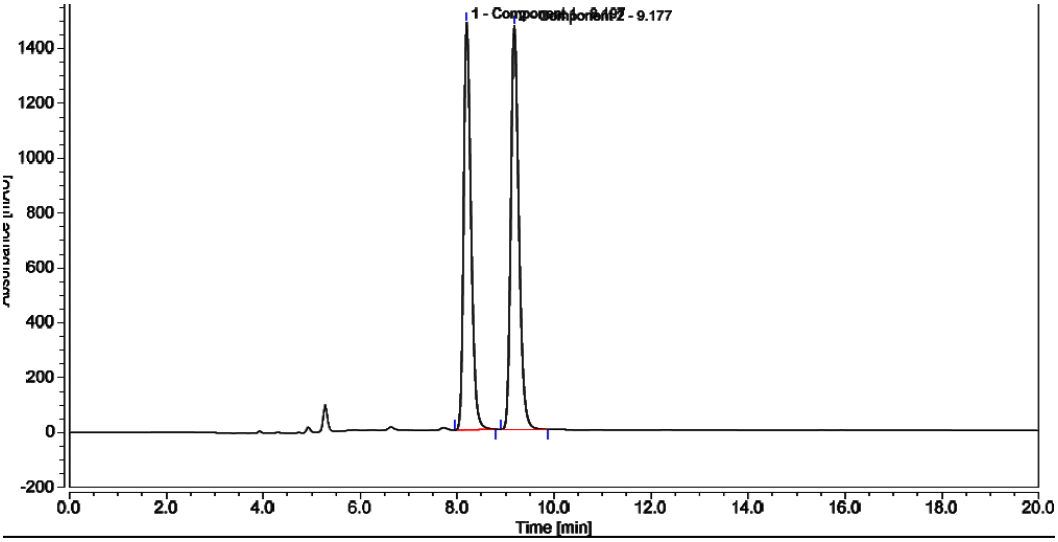
***rac*-2-Amino-2′-phenyl-1,1′-binaphthyl [(±)-6b]**

Chiralpak IB column, 4.6 x 250 mm, 5 µm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.5 MPa, flow rate: 1.0 mL/min

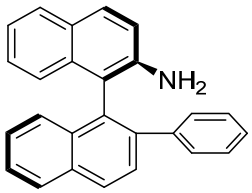
(±)-



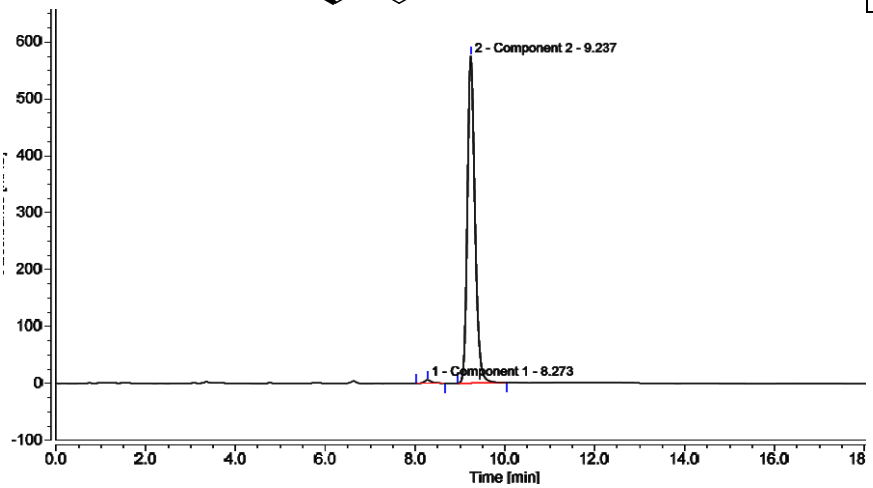
	r_t / min	Area %
S	8.197	47.71
R	9.177	52.29



(*R*)-2-Amino-2′-phenyl-1,1′-binaphthyl (6b)



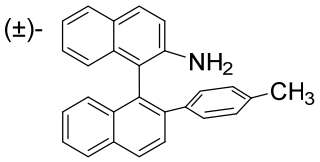
	r_t / min	Area %
S	8.273	0.98
R	9.237	99.02



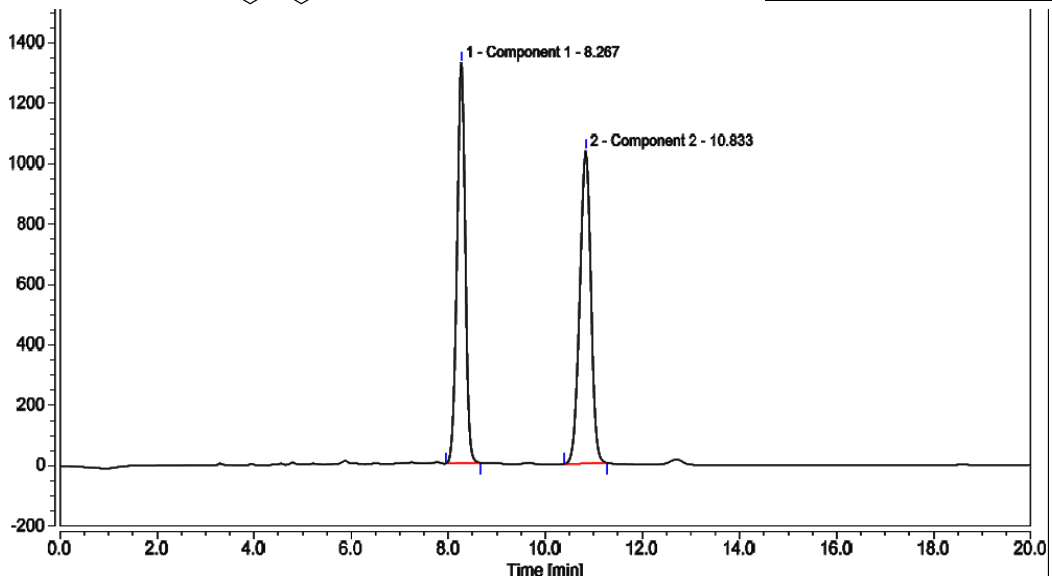
***rac*-2-Amino-2′-[4-(methyl)phenyl]-1,1′-binaphthyl [(±)-6c]**

Chiralpak IA column, 4.6 x 250 mm, 5 µm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.8 MPa, flow rate: 1.0 mL/min

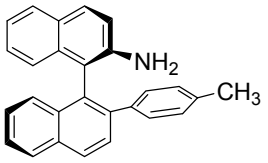
(±)-



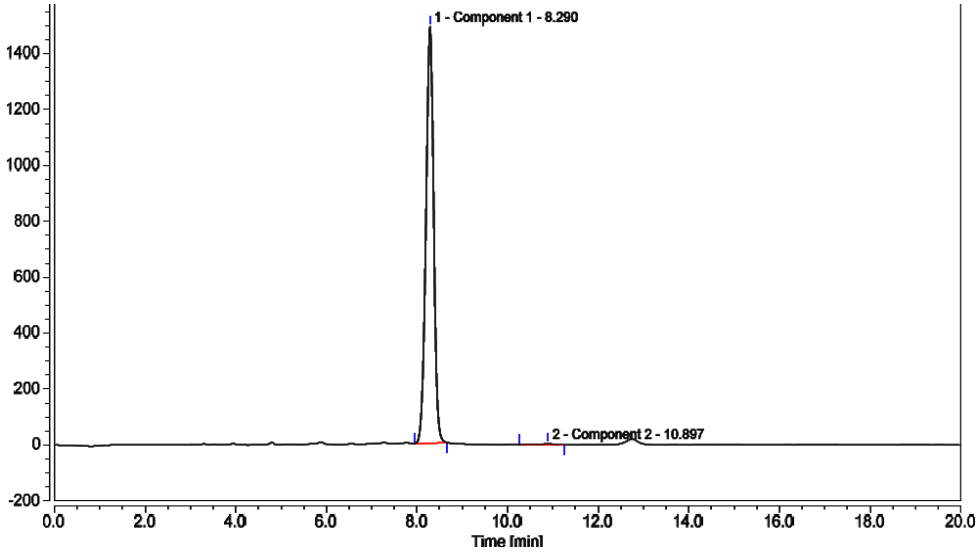
	r_t / min	Area %
R	8.267	48.54
S	10.833	51.46



(*R*)-2-Amino-2′-[4-(methyl)phenyl]-1,1′-binaphthyl (6c)



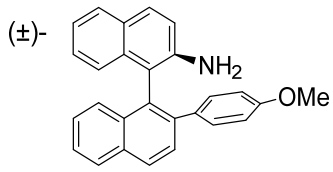
	r_t / min	Area %
R	8.290	99.60
S	10.897	0.40



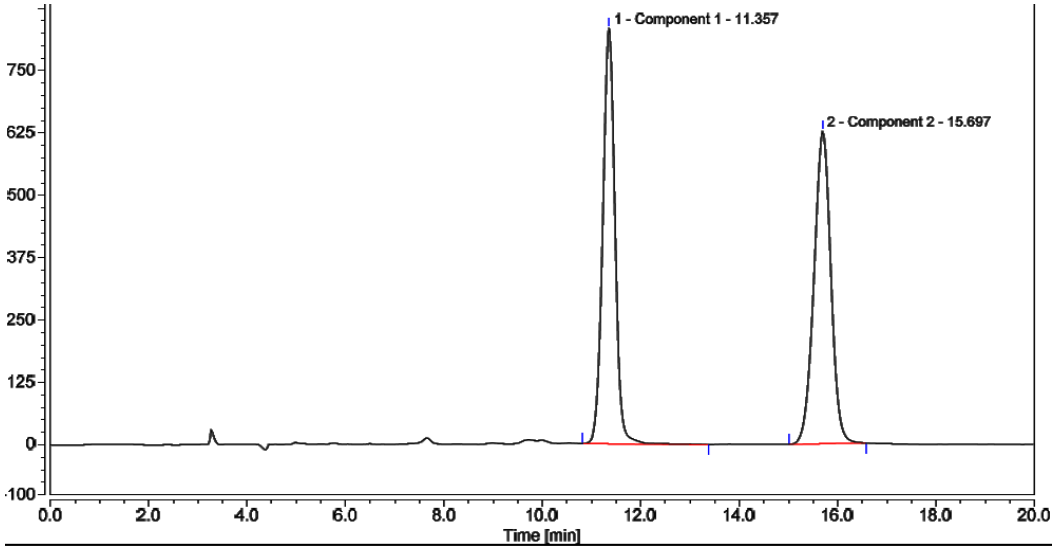
***rac*-2-Amino-2′-[4-(methoxy)phenyl]-1,1′-binaphthyl [(±)-6d]**

Chiralpak IA column, 4.6 x 250 mm, 5 µm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.8 MPa, flow rate: 1.0 mL/min

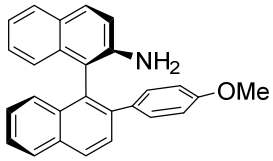
(±)-



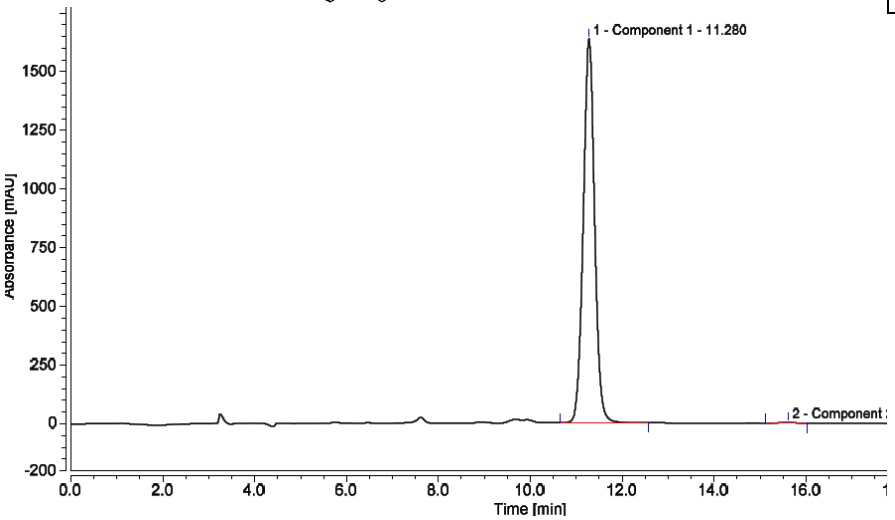
	r_t / min	Area %
R	11.357	48.94
S	15.697	51.06



(*R*)-2-Amino-2′-[4-(methoxy)phenyl]-1,1′-binaphthyl (6d)

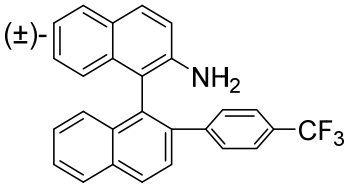


	r_t / min	Area %
R	11.280	99.67
S	15.609	0.33

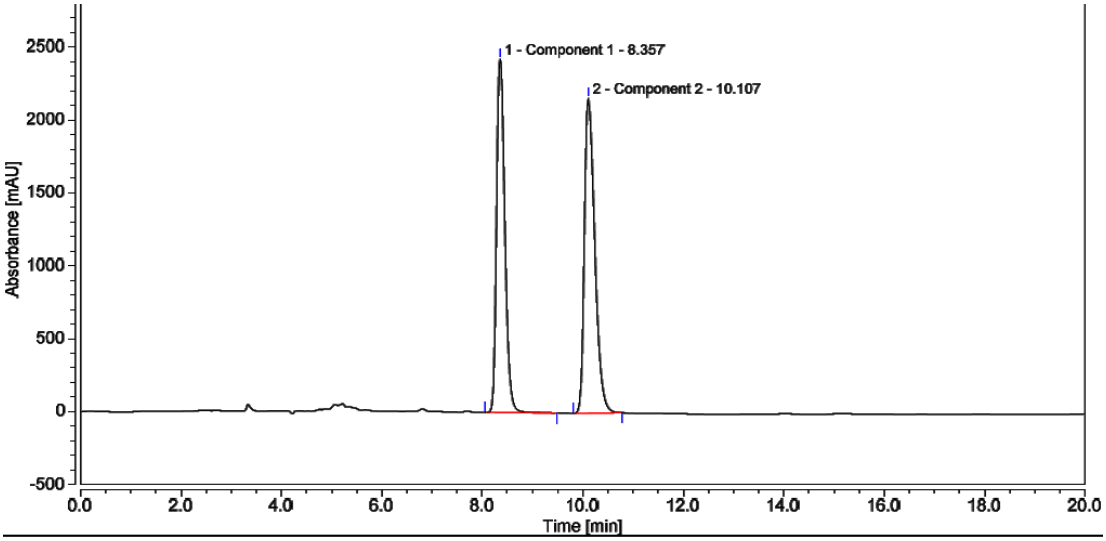


***rac*-2-Amino-2′-[4-(trifluoromethyl)phenyl]-1,1′-binaphthyl [(±)-6e]**

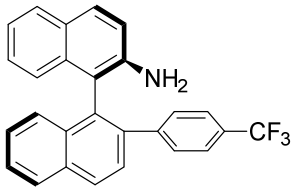
Chiralpak IB column, 4.6 x 250 mm, 5 µm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.7 MPa, flow rate: 1.0 mL/min



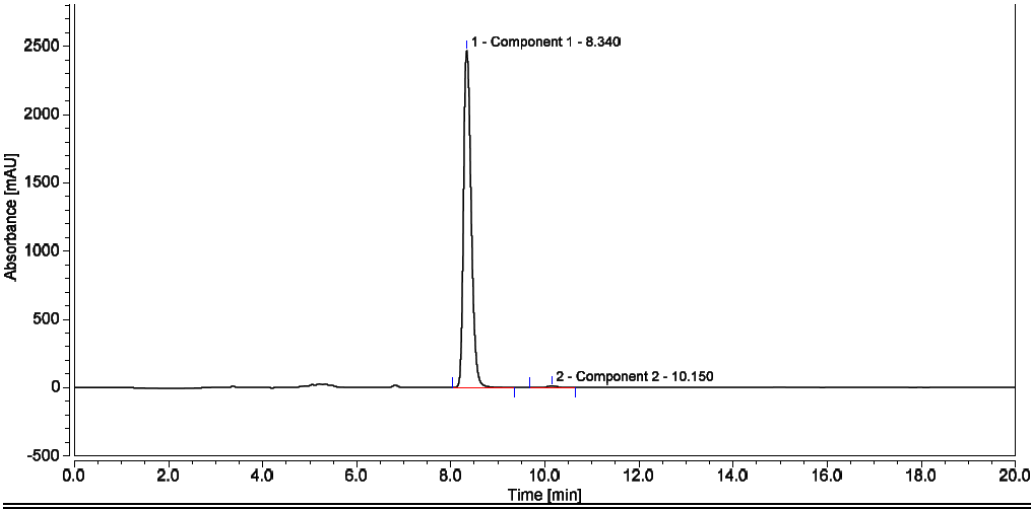
	r_t / min	Area %
R	8.357	47.47
S	10.107	52.53



(*R*)-2-Amino-2′-[4-(trifluoromethyl)phenyl]-1,1′-binaphthyl (6e)

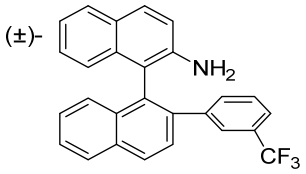


	r_t / min	Area %
R	8.340	99.35
S	10.150	0.65

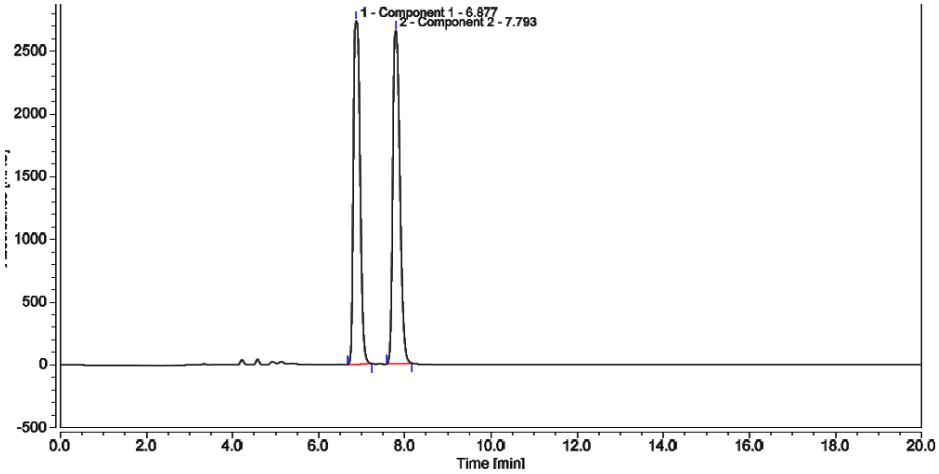


***rac*-2'-(3-(Trifluoromethyl)phenyl)-[1,1'-binaphthalen] [(±)-6f]**

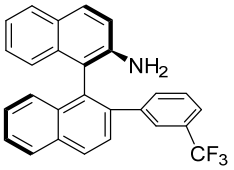
Chiralpak IB column, 4.6 x 250 mm, 5 µm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.7 MPa



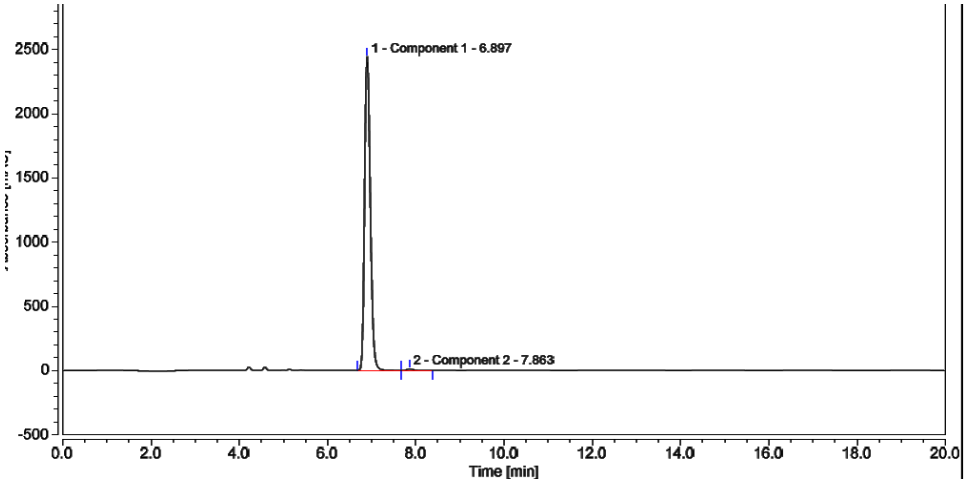
	r_t / min	Area %
R	6.877	49.33
S	7.793	50.67



(*R*)-2'-(3-(Trifluoromethyl)phenyl)-[1,1'-binaphthalen] (6f)



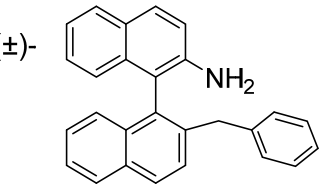
	r_t / min	Area %
R	6.897	99.39
S	7.863	0.49



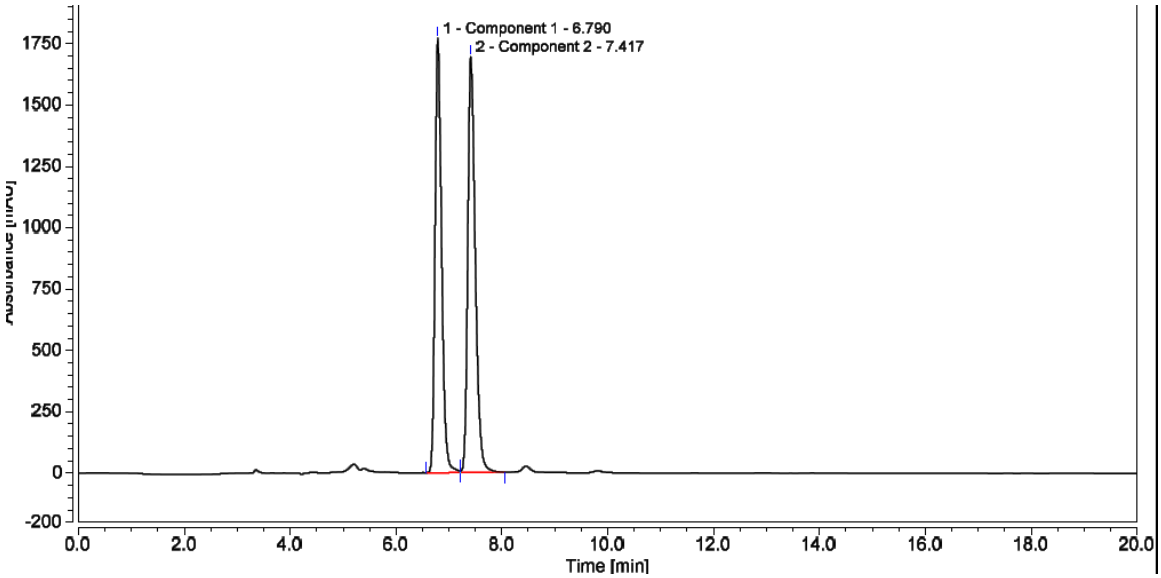
rac-2-Amino-2′-benzyl-1,1′-binaphthyl [(±)-6g)

Chiralpak IB column, 4.6 x 250 mm, 5 µm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.7 MPa, flow rate: 1.0 mL/min

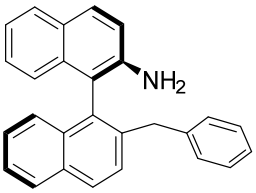
(±)-



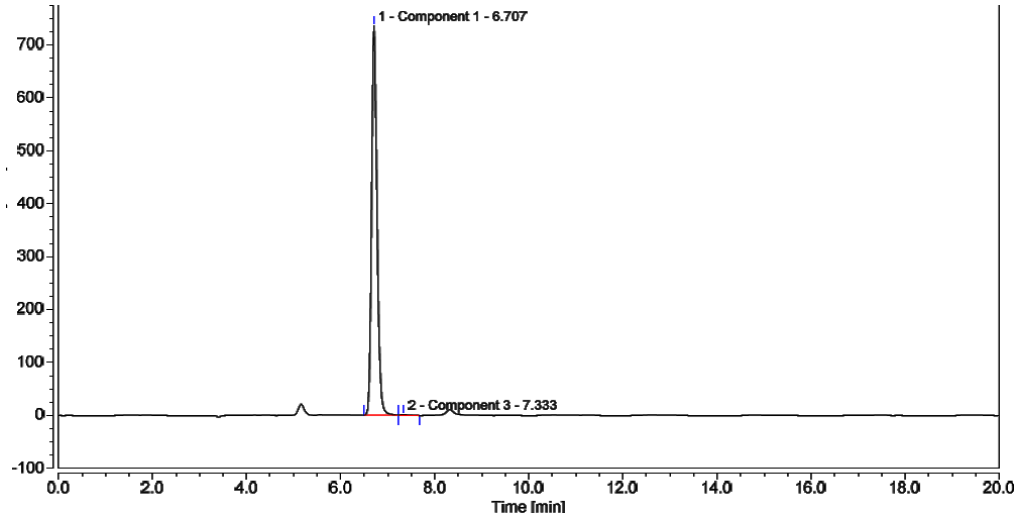
	r_t / min	Area %
S	6.790	47.71
R	7.417	52.29



(*S*)-2-Amino-2′-benzyl-1,1′-binaphthyl (6g)

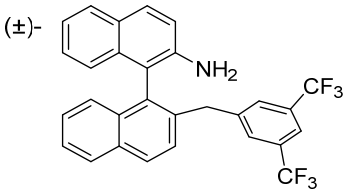


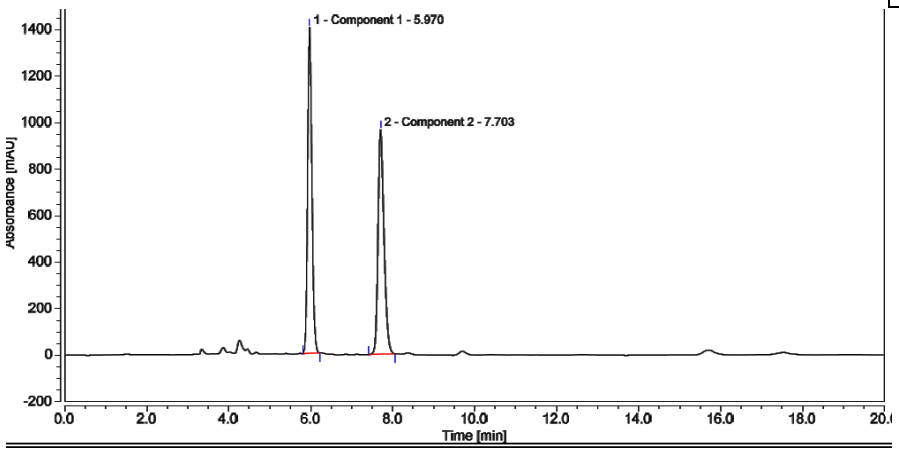
	r_t / min	Area %
S	6.707	99.62
R	7.333	0.38



***rac*-2-Amino-2′-[3,5-bis(trifluoromethyl)benzyl]-1,1′-binaphthyl [(±)-6h]**

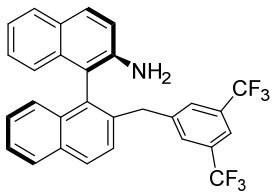
Chiralpak IB column, 4.6 x 250 mm, 5 µm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.7 MPa, flow rate: 1.0 mL/min

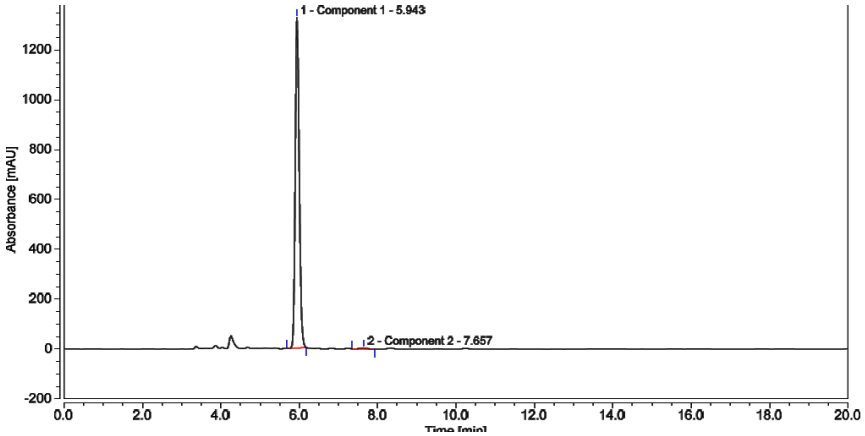




	r_t / min	Area %
S	5.970	50.66
R	7.703	49.34

(*S*)-2-Amino-2′-[3,5-bis(trifluoromethyl)benzyl]-1,1′-binaphthyl (6h)

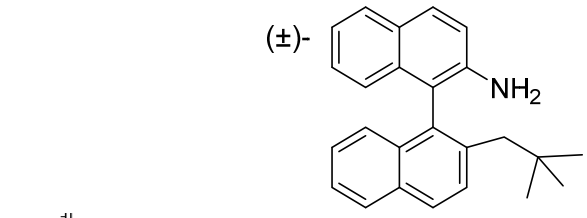




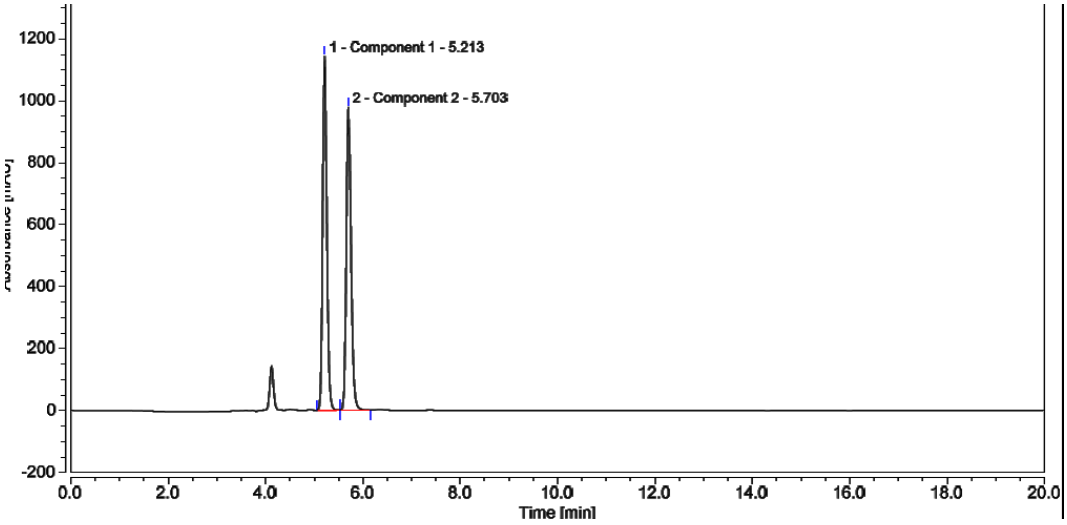
	r_t / min	Area %
S	5.943	99.54
R	7.657	0.46

***rac*-2-Amino-2′-neopentyl-1,1′-binaphthyl [(±)-6i]**

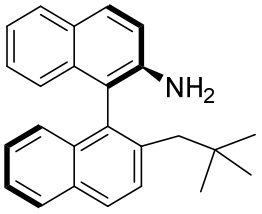
Chiralpak IB column, 4.6 x 250 mm, 5 µm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.7 MPa, flow rate: 1.0 mL/min



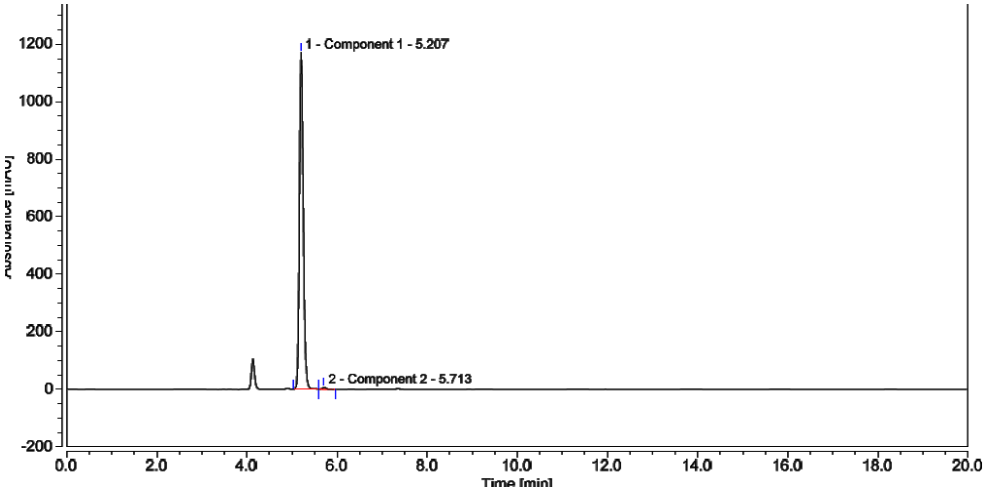
	r_t / min	Area %
S	5.213	50.49
R	5.703	49.51



(*S*)-2-Amino-2′-neopentyl-1,1′-binaphthyl (6i)



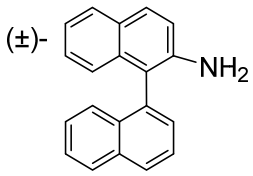
	r_t / min	Area %
S	5.207	99.43
R	5.713	0.57

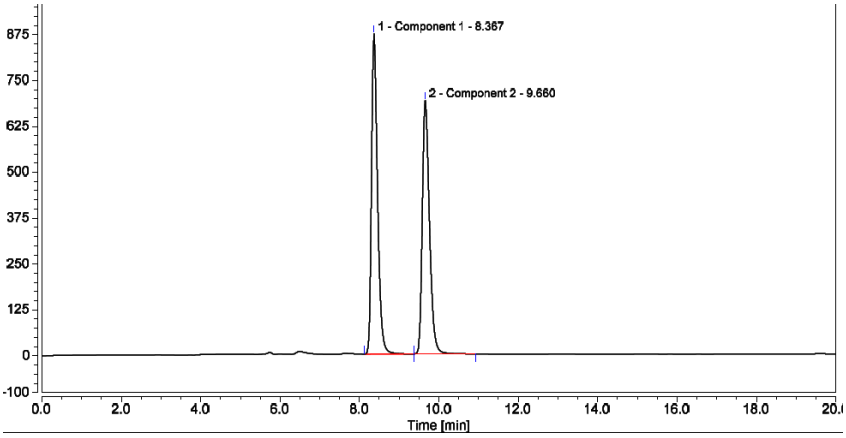


rac-2-Amino-1,1′-binaphthyl [(±)-6j]

Chiralpak IB column, 4.6 x 250 mm, 5 µm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.8 MPa, flow rate: 1.0 mL/min

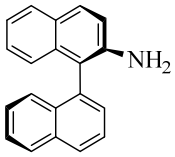
(±)-



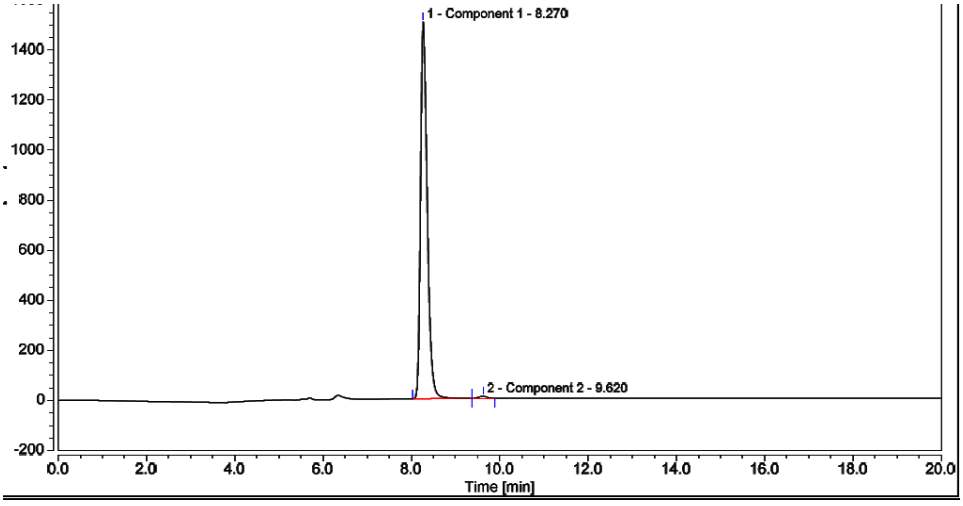


	r_t / min	Area %
S	8.367	51.91
R	9.660	48.09

(*S*)-2-Amino-1,1′-binaphthyl (6j)



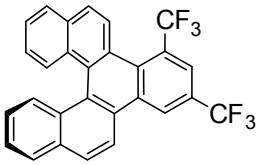
	r_t / min	Area %
S	8.270	99.41
R	9.620	0.59



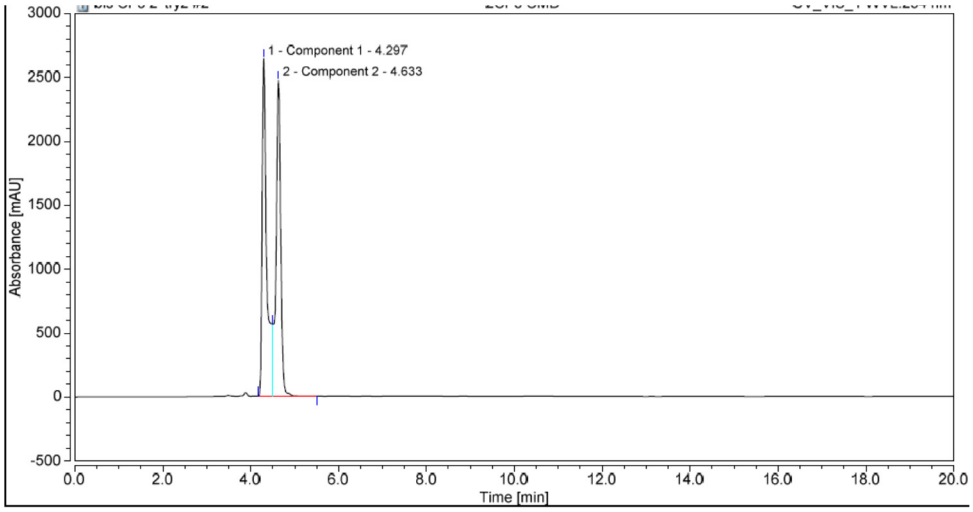
1,3-Bis(trifluoromethyl)naphtho[1,2-*g*]chrysene (4a)

Chiralpak IB column, 4.6 x 250 mm, 5 µm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.7 MPa, flow rate: 1.0 mL/min, t_R (enantiomer 1)= 4.3 min, t_R (enantiomer 2)= 4.6 min)

(+/-)-



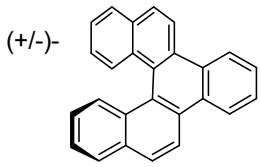
	r_t / min	Area %
	4.297	51.28
	4.633	48.72



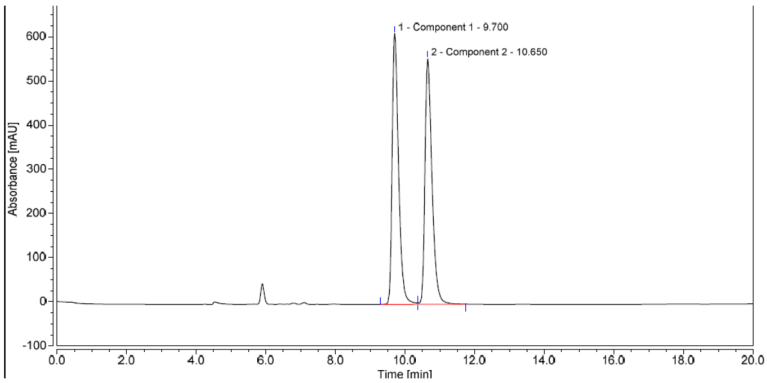
Naphtho[1,2-*g*]chrysene (4b)

Chiralpak IB column, 4.6 x 250 mm, 5 µm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 2.6 MPa, flow rate: 0.8 mL/min

(+/-)-

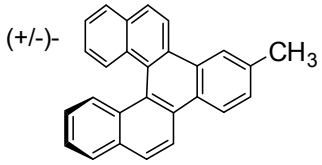


	r_t / min	Area %
	9.700	49.99
	10.650	50.01

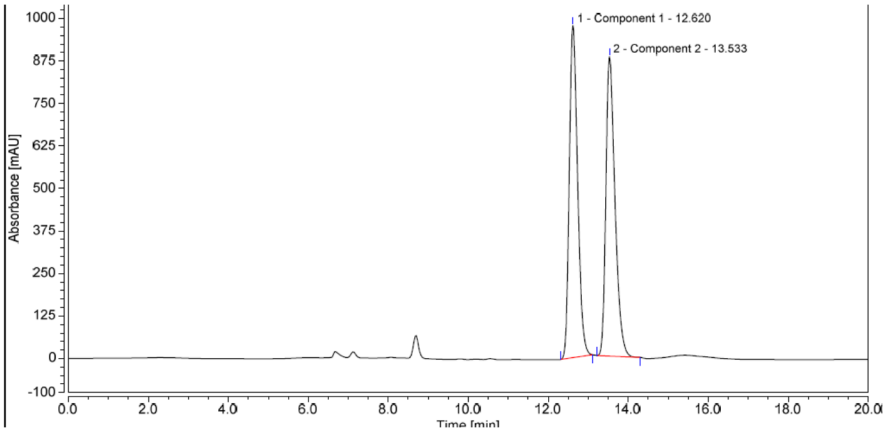


2-Methylnaphtho[1,2-*g*]chrysene (4c)

Chiralpak IB column, 4.6 x 250 mm, 5 µm particle size, 25 °C, hexanes/*i*PrOH 98:2, pressure = 1.7 MPa, flow rate: 0.5 mL/min

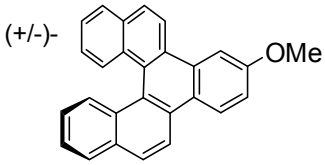


	r_t / min	Area %
	12.620	50.13
	13.533	49.87

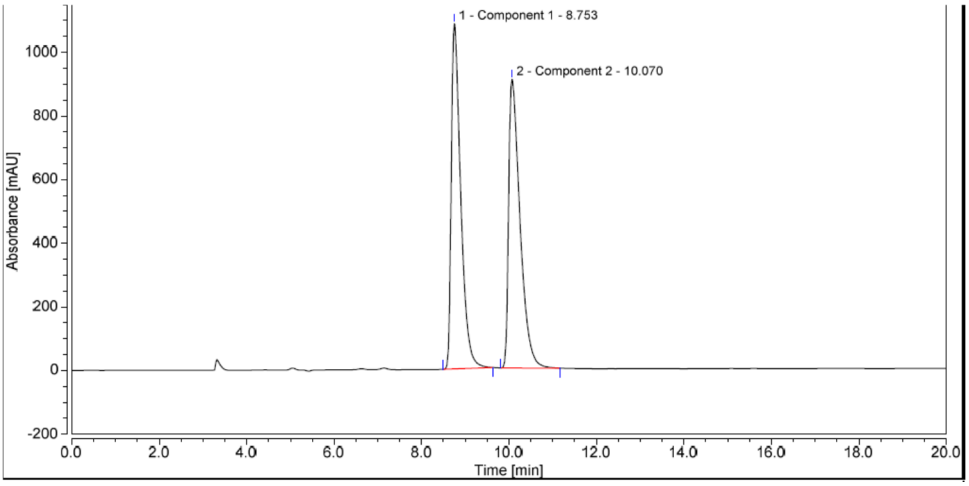


2-Methoxynaphtho[1,2-*g*]chrysene (4d)

Chiralpak IB column, 4.6 x 250 mm, 5 µm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.8 MPa, flow rate: 1.0 mL/min

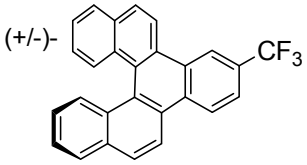


	r_t / min	Area %
	8.753	49.96
	10.070	50.04

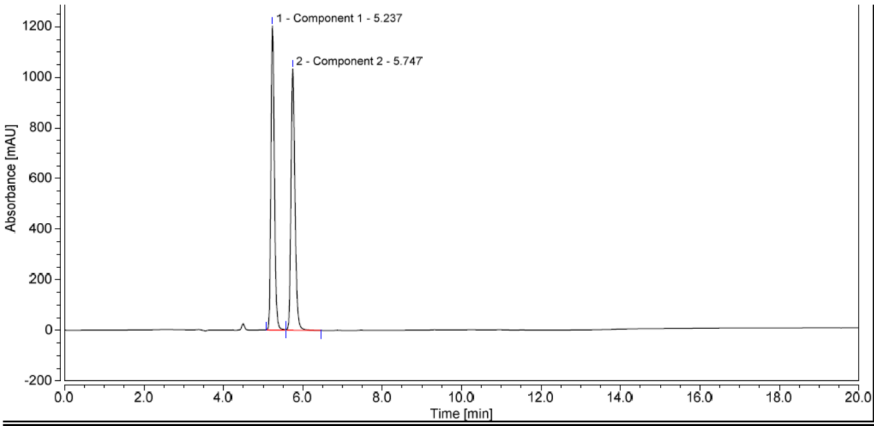


2-(Trifluoromethyl)naphtho[1,2-*g*]chrysene (4e)

Chiralpak IB column, 4.6 x 250 mm, 5 µm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.7 MPa, flow rate: 1.0 mL/min

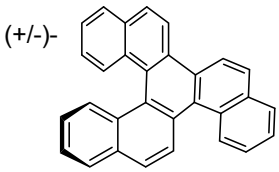


	r_t / min	Area %
	5.237	49.86
	5.747	50.14

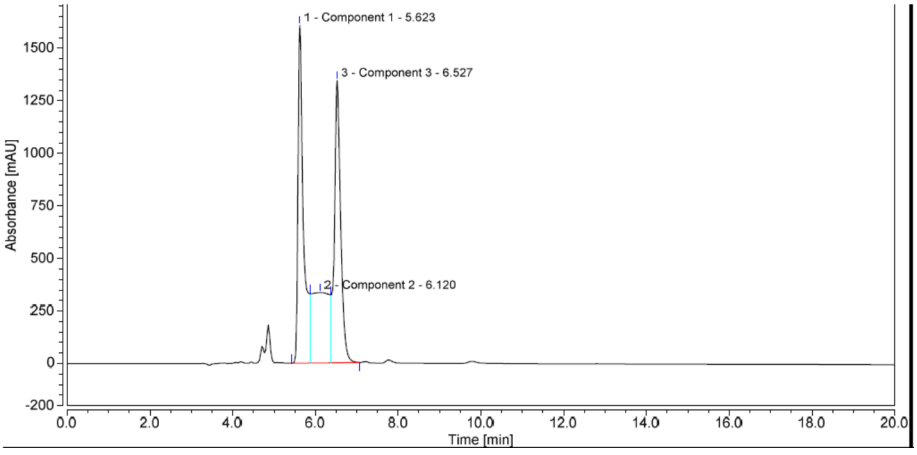


Naphtho[1,2-*s*]picene (9)

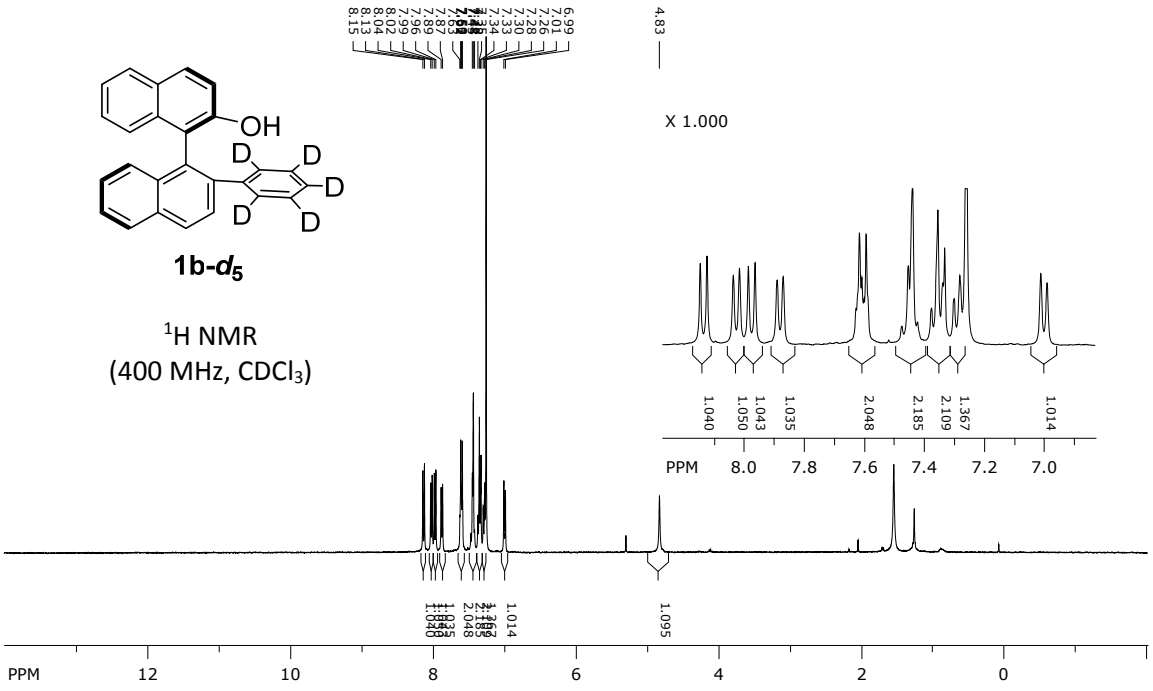
Chiralpak IB column, 4.6 x 250 mm, 5 µm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.5 MPa, flow rate: 1.0 mL/min

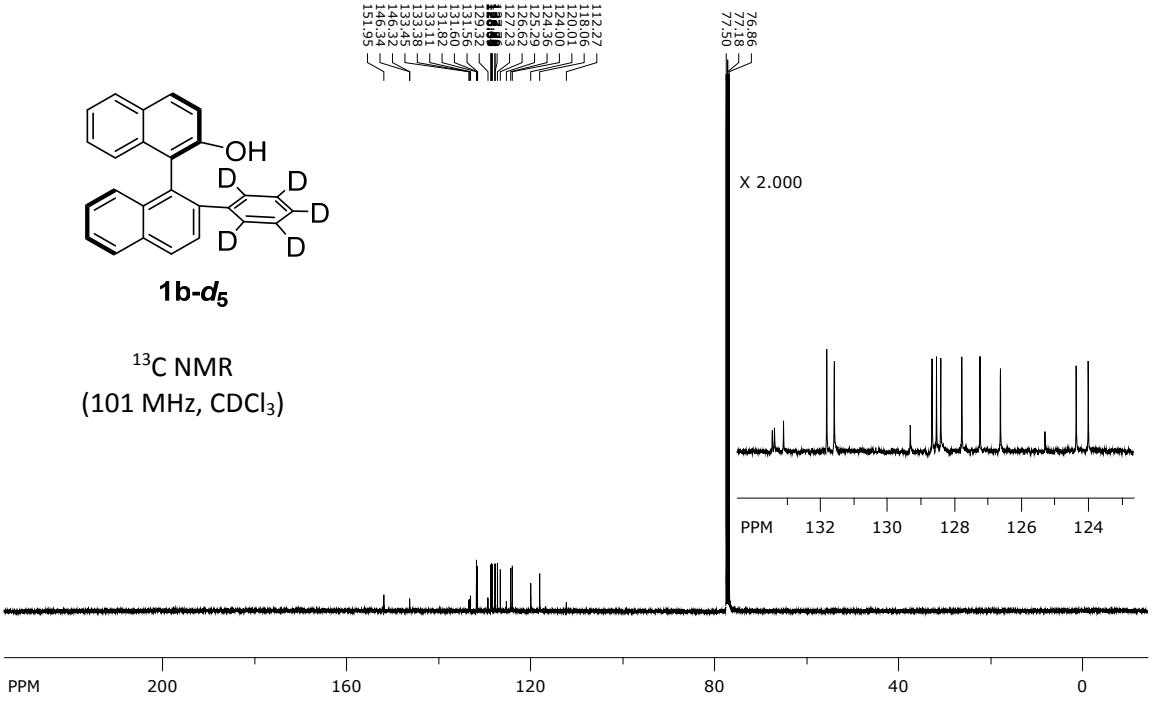


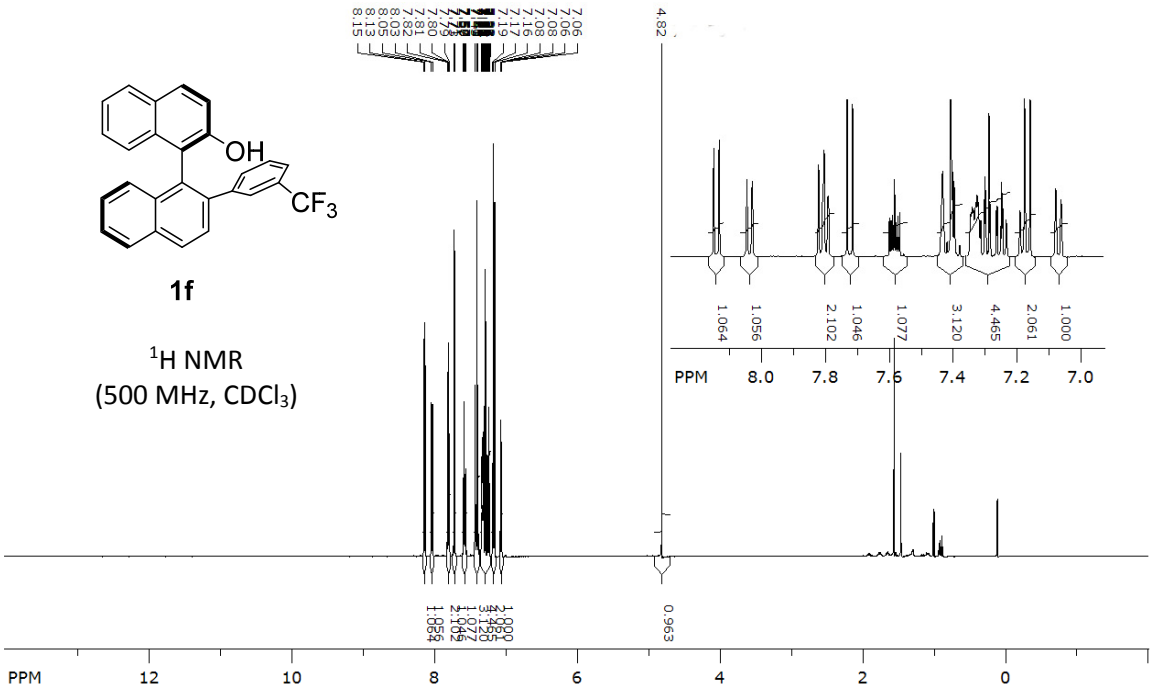
	r_t / min	Area %
	5.623	50.48
	6.527	49.52

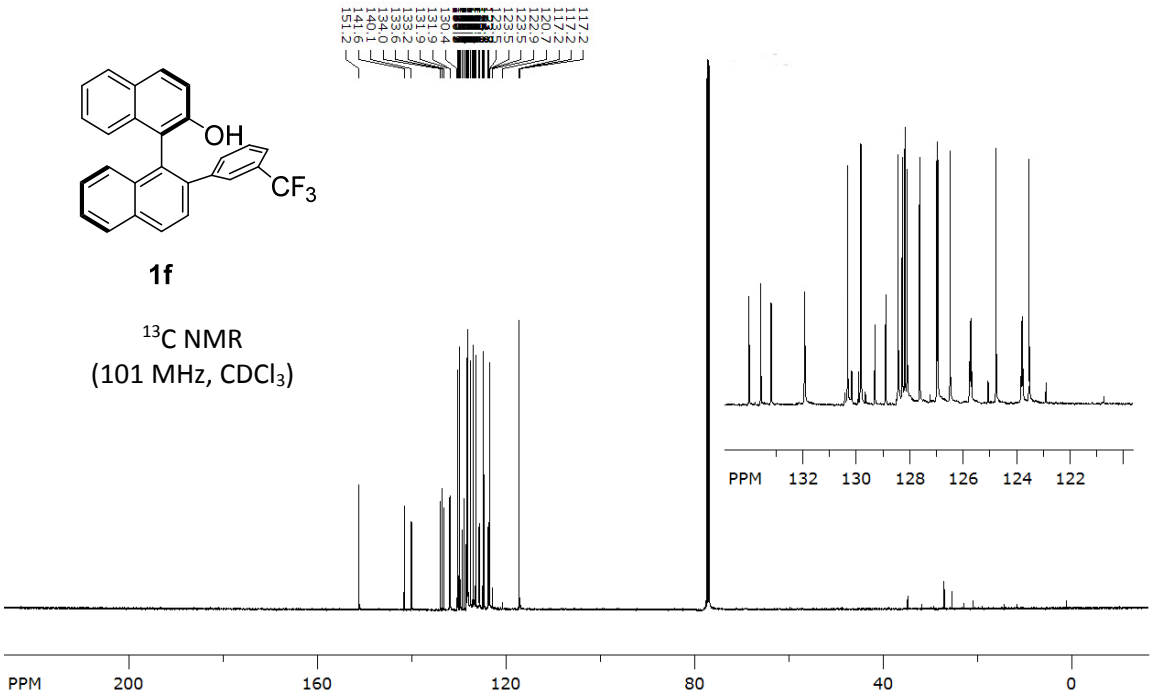


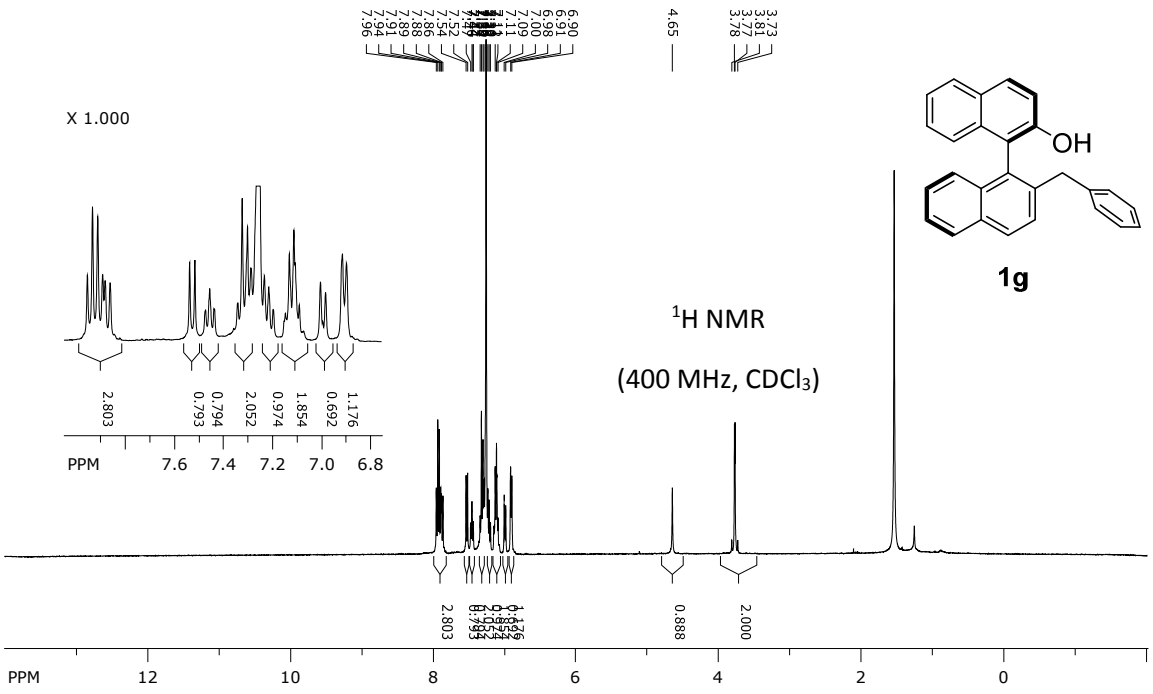
^{1}H AND ^{13}C NMR SPECTRA

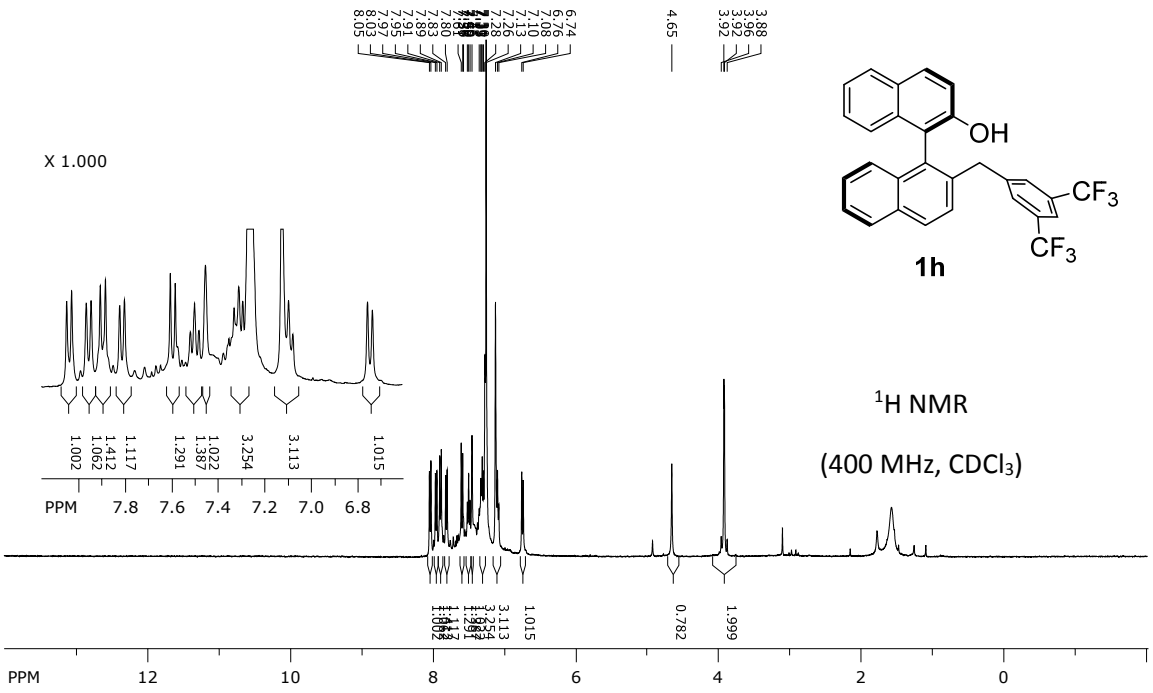


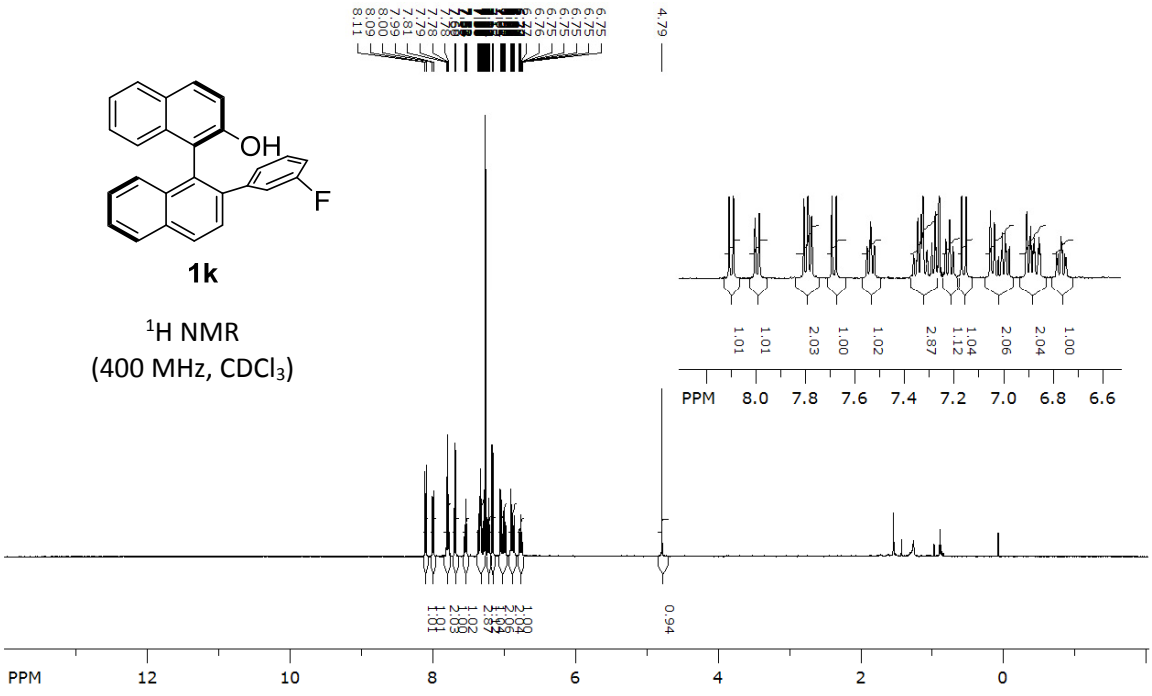


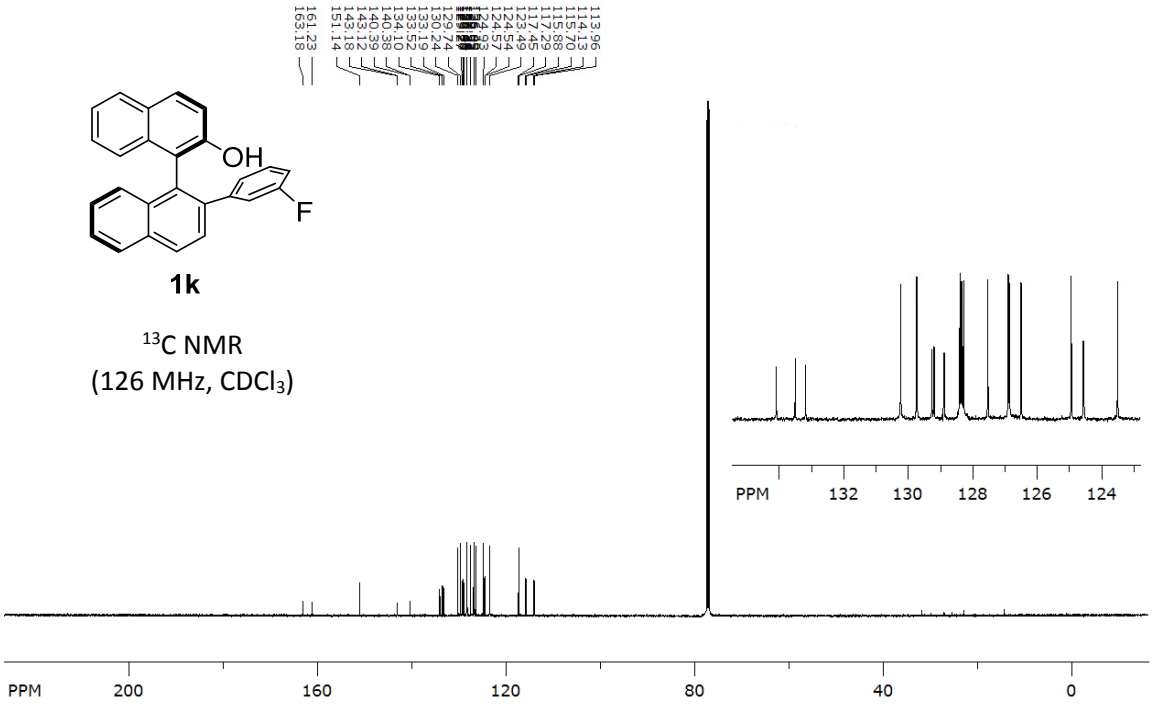

OH
CF3
1f
1H NMR
(500 MHz, CDCl3)
PPM
12
10
8
6
4
2
0
8.0
7.8
7.6
7.4
7.2
7.0

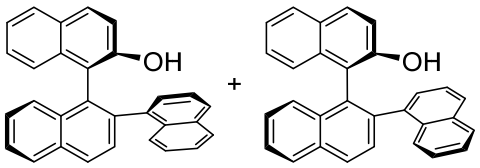

OH
CF3
1f
13C NMR
(101 MHz, CDCl3)
PPM
200
160
120
80
40
0
132
130
128
126
124
122


X 1.000
OH
1g
^{1}H NMR
(400 MHz, CDCl$_3$)
PPM


X 1.000
OH
CF$_3$
CF$_3$
1h
^{1}H NMR
(400 MHz, CDCl$_3$)
PPM

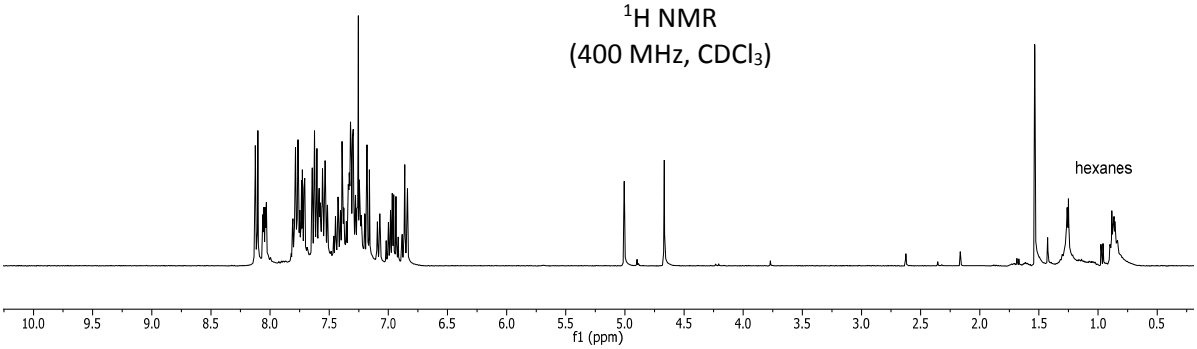

OH
F
1k
1H NMR
(400 MHz, CDCl3)
PPM
12
10
8
6
4
2
0
PPM
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6

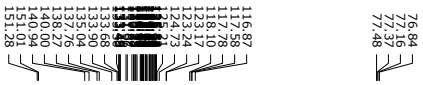

OH
F
1k
13C NMR
(126 MHz, CDCl3)
PPM
200
160
120
80
40
0
PPM
132
130
128
126
124

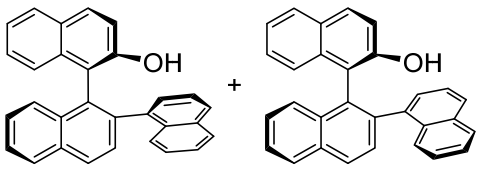


7a **7b**

^{1}H NMR
(400 MHz, $CDCl_3$)

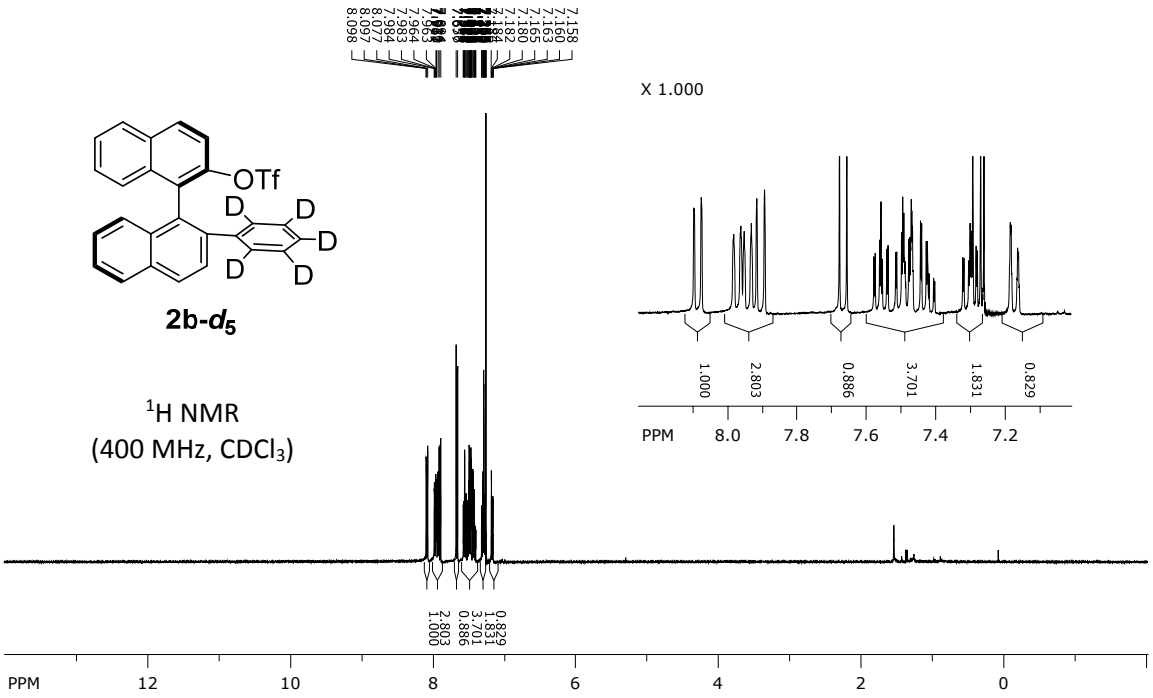


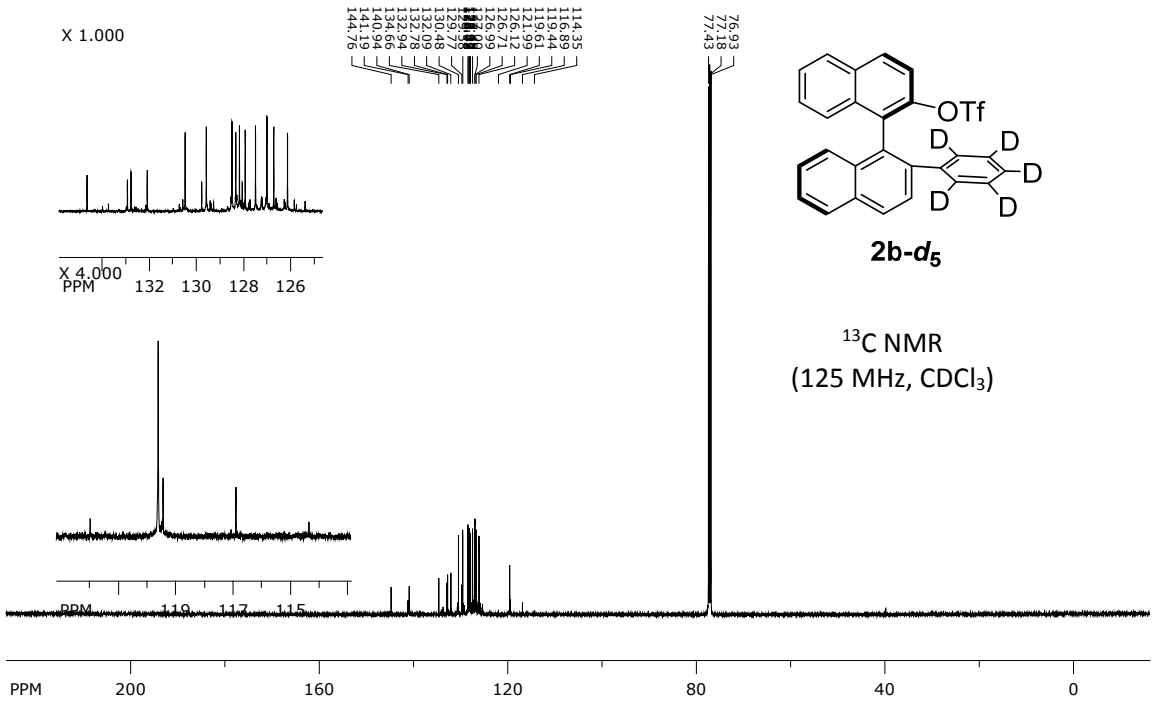


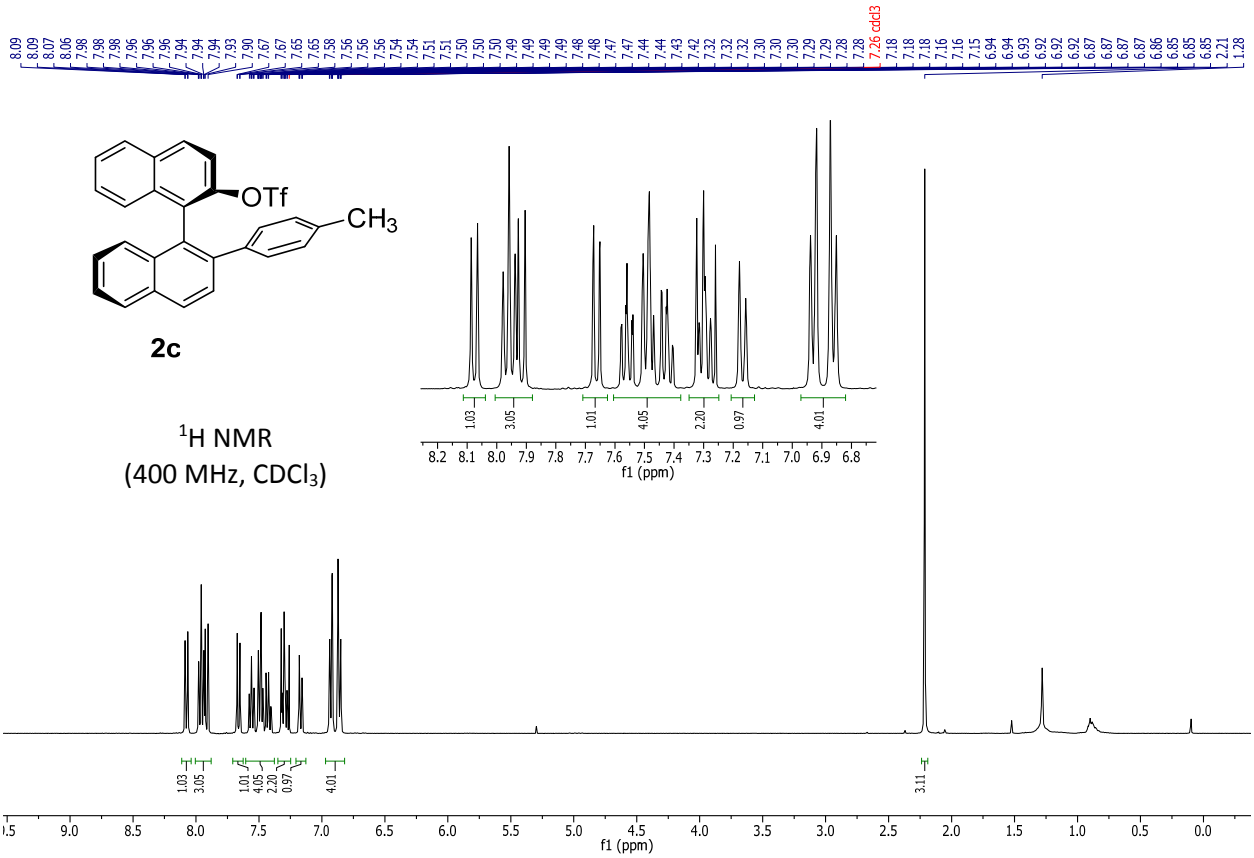


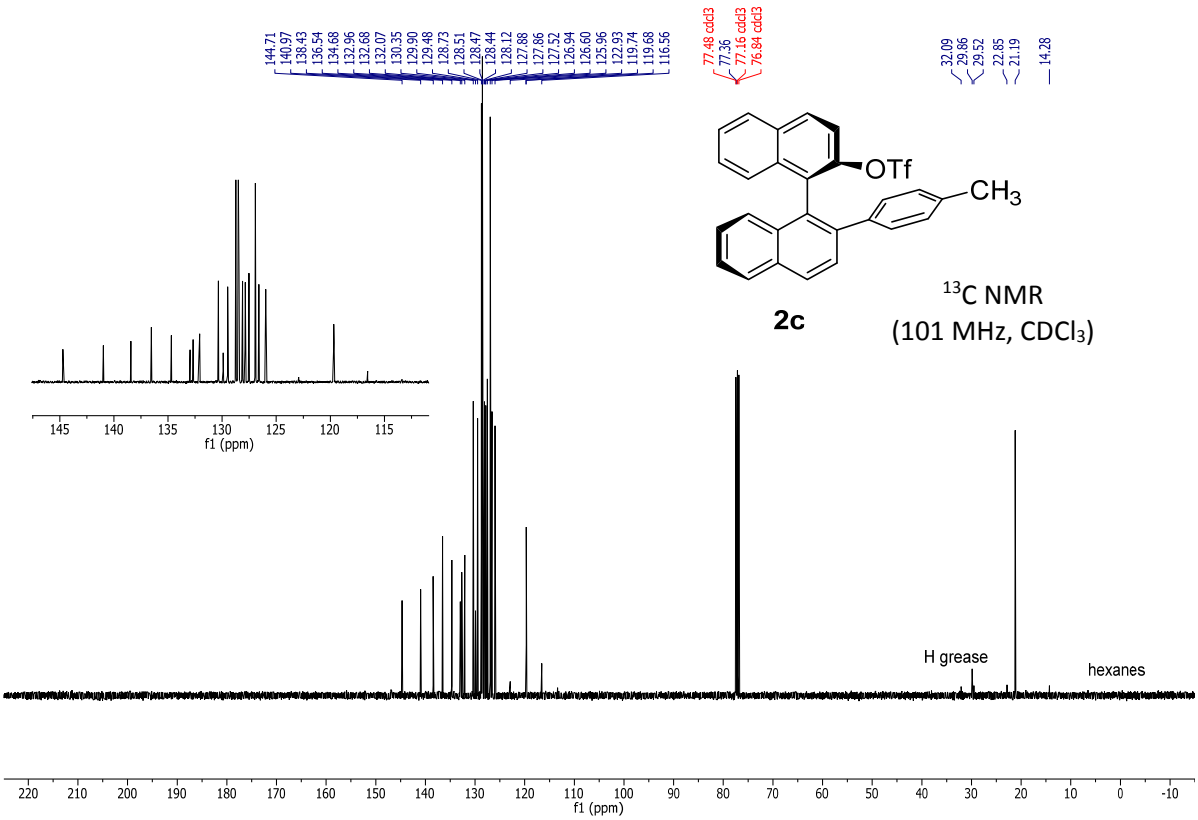
7a **7b**

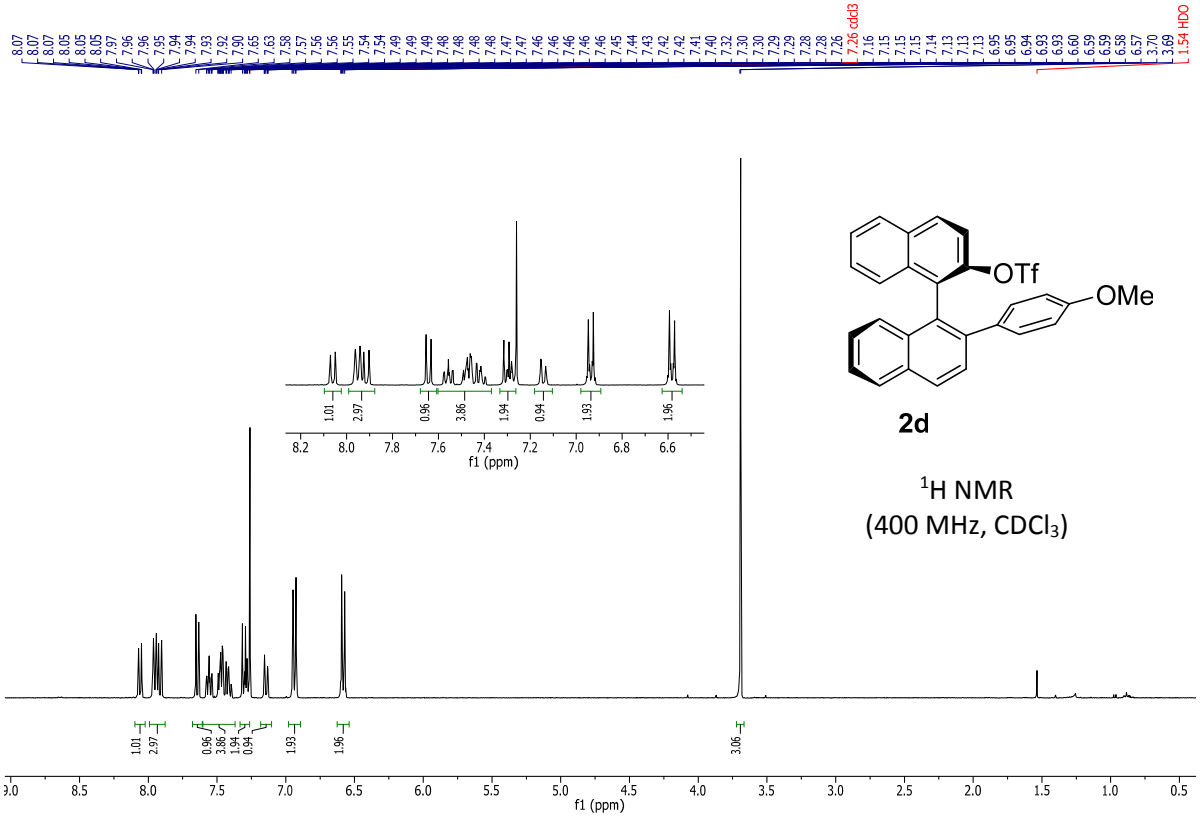
^{13}C NMR
(101 MHz, $CDCl_3$)

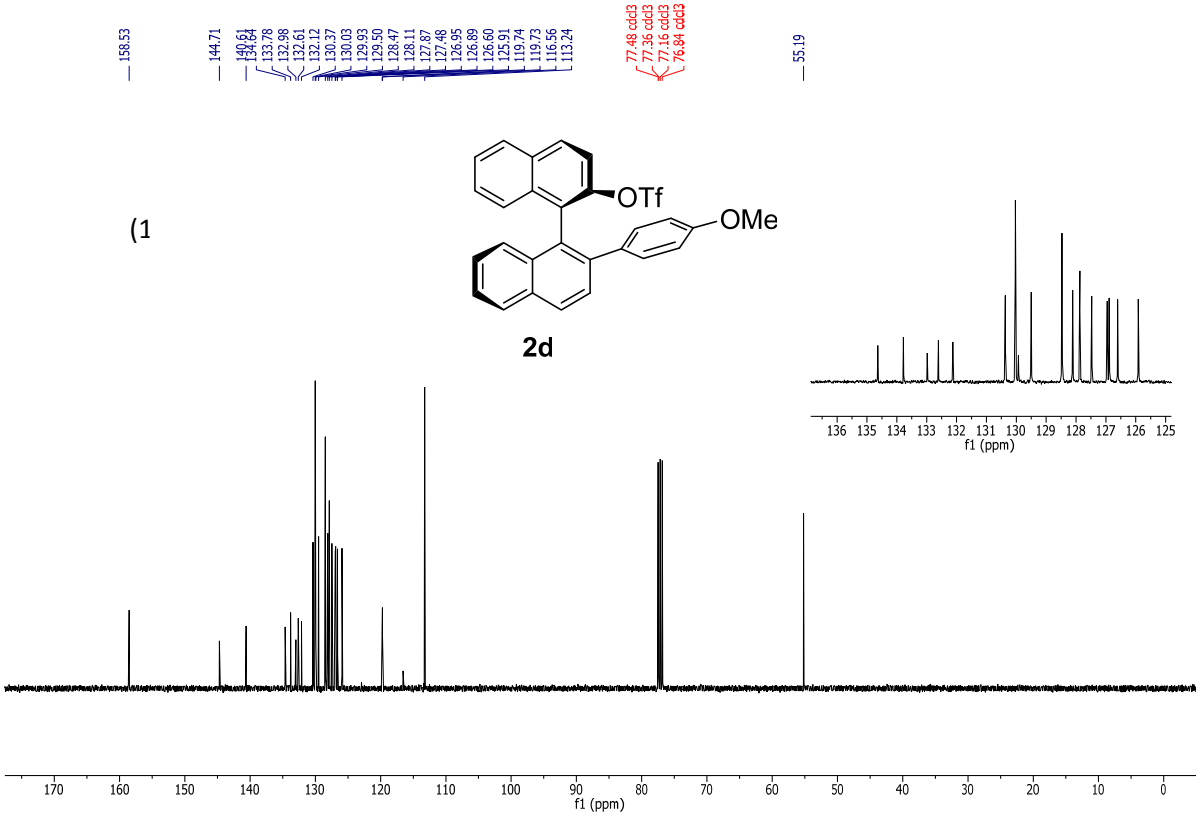

OTf
D
D
D
D
D
2b-d_5
^{1}H NMR
(400 MHz, $CDCl_3$)
X 1.000
1.000
2.803
0.886
3.701
1.831
0.829
PPM
8.0
7.8
7.6
7.4
7.2
12
10
8
6
4
2
0

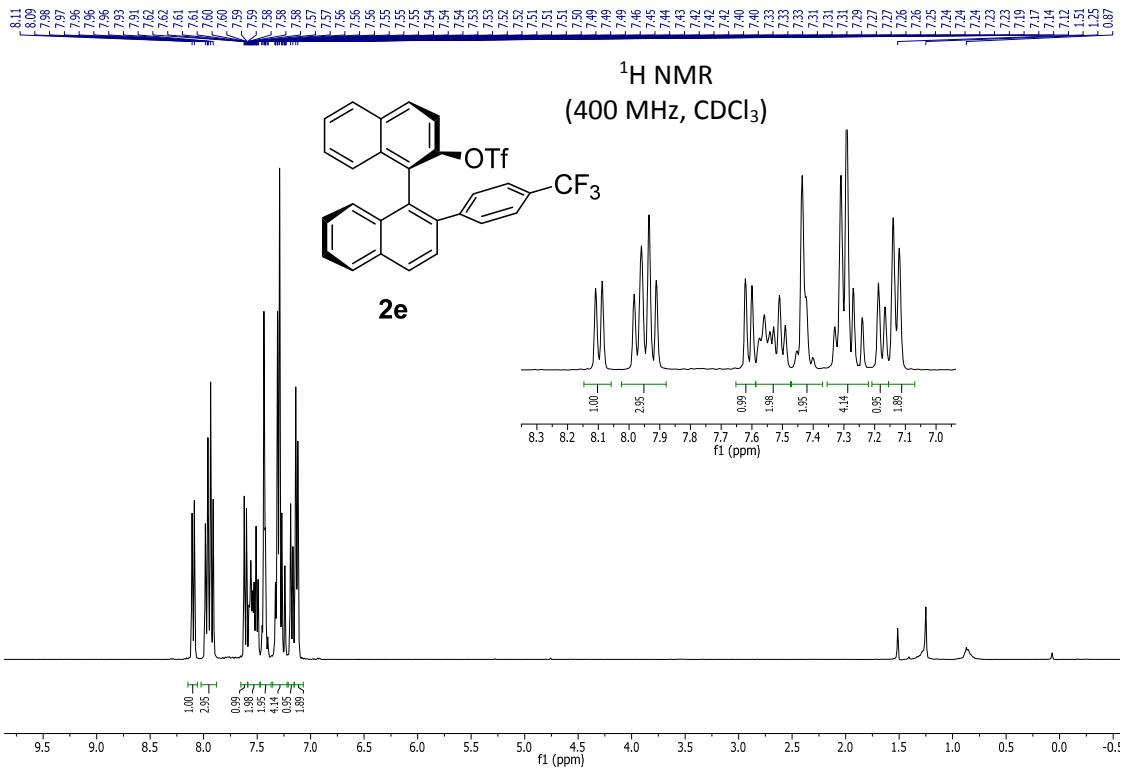

X 1.000
X 4.000
PPM
132
130
128
126
OTf
D
D
D
D
D
2b-d_5
^{13}C NMR
(125 MHz, $CDCl_3$)
PPM
200
160
120
80
40
0

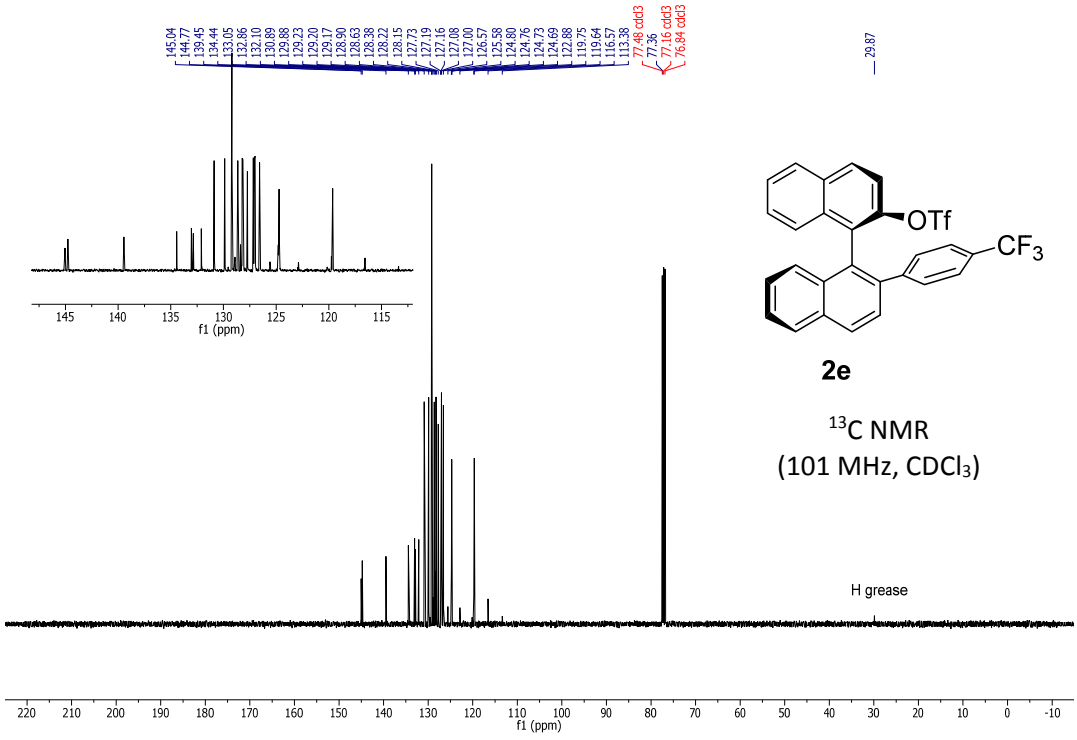

OTf
CH3
2c
1H NMR
(400 MHz, CDCl3)
f1 (ppm)

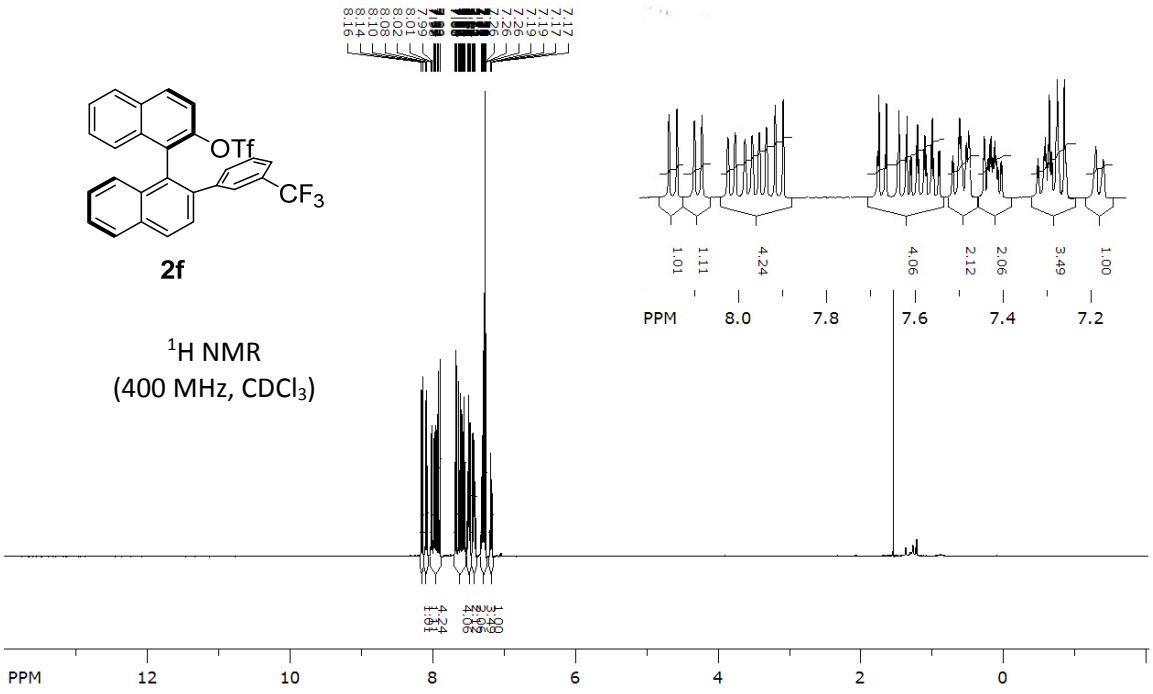

OTf
CH3
2c
13C NMR
(101 MHz, CDCl3)
H grease
hexanes
f1 (ppm)

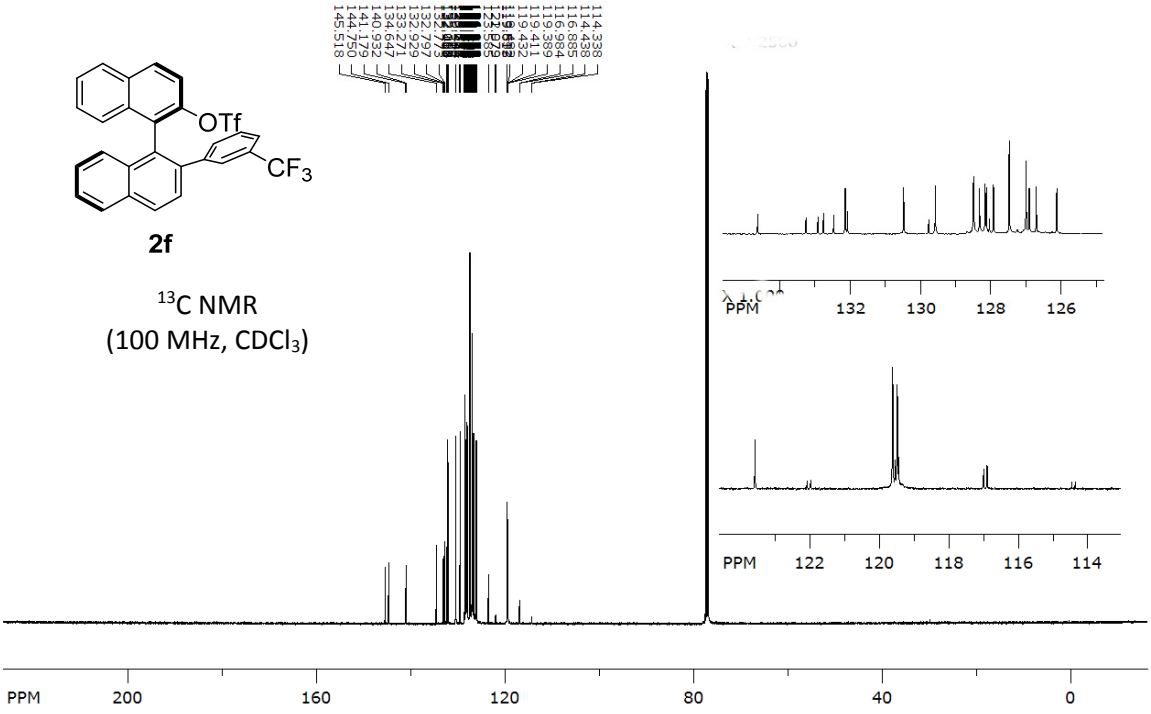

OTf
OMe
2d
^{1}H NMR
(400 MHz, $CDCl_3$)
f1 (ppm)

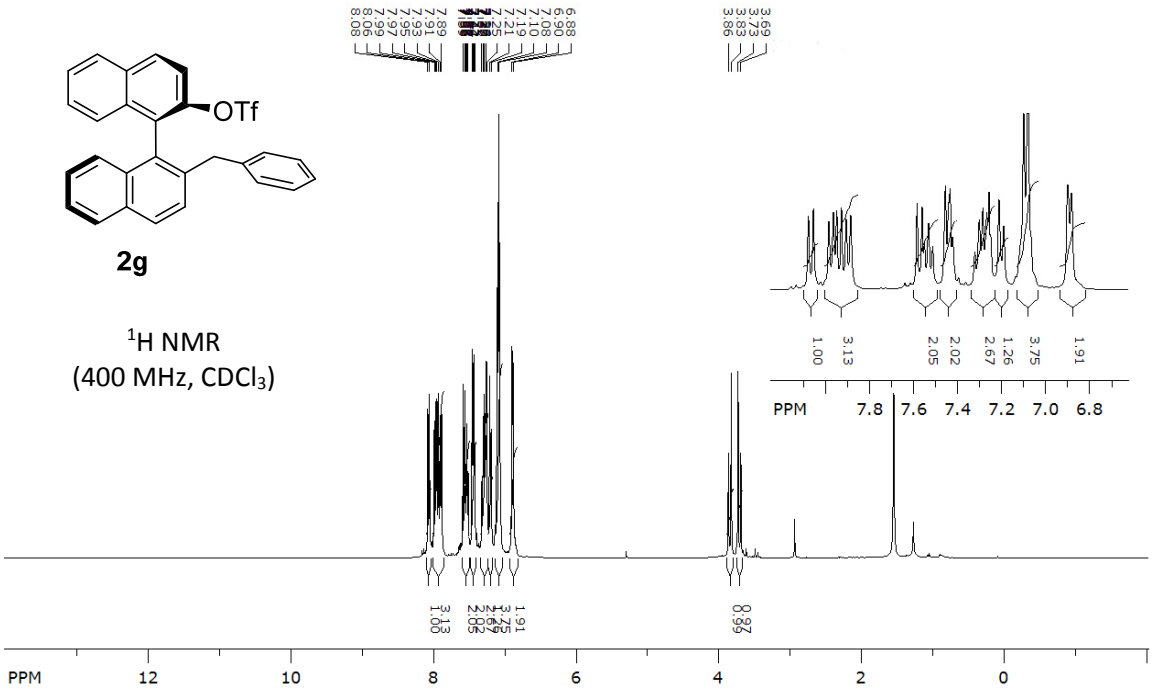

OTf
OMe
2d
f1 (ppm)

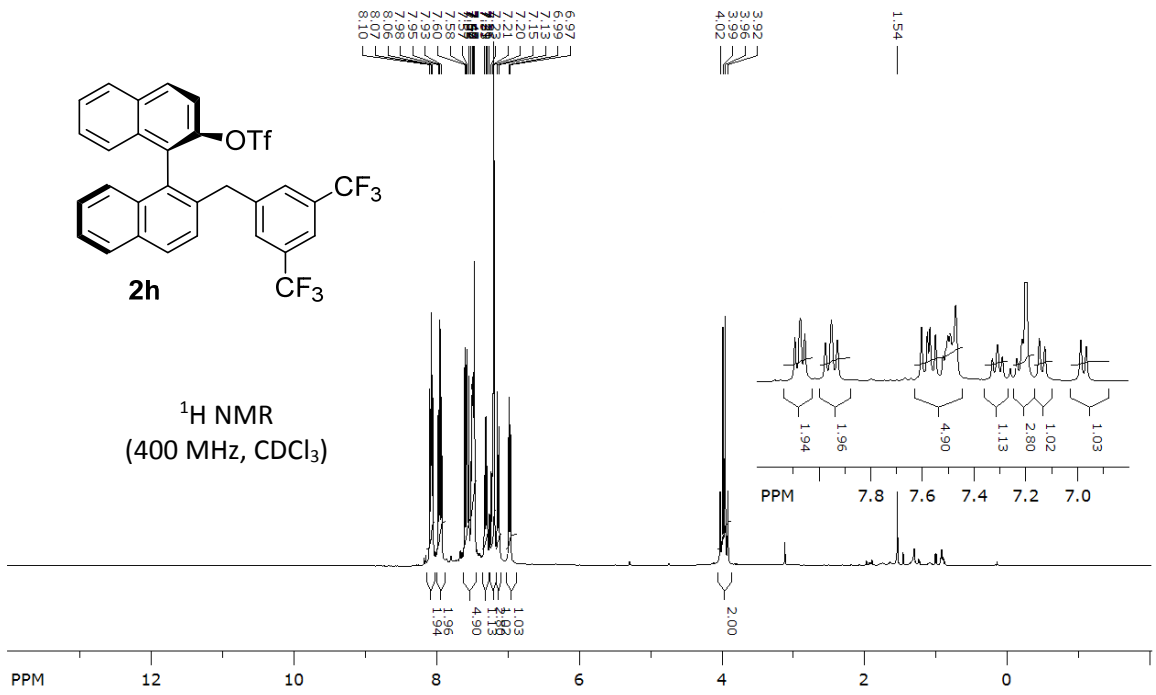

^{1}H NMR
(400 MHz, $CDCl_3$)
OTf
CF_3
2e
f1 (ppm)

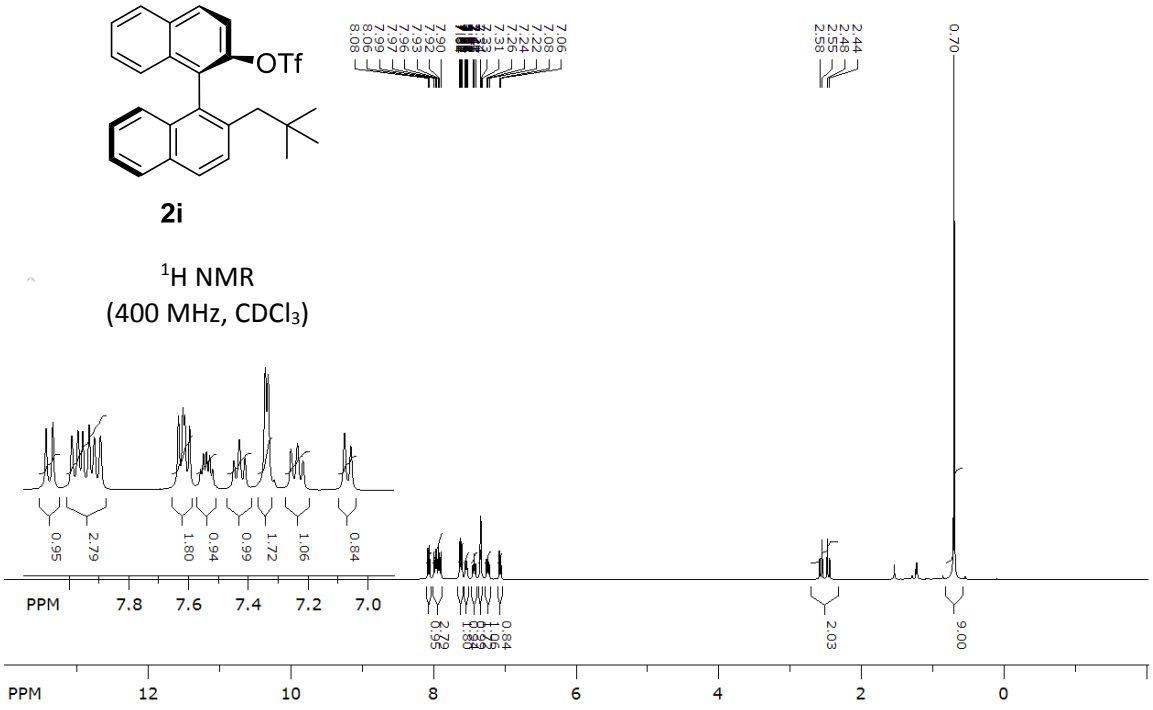

OTf
CF_3
2e
^{13}C NMR
(101 MHz, $CDCl_3$)
H grease
f1 (ppm)

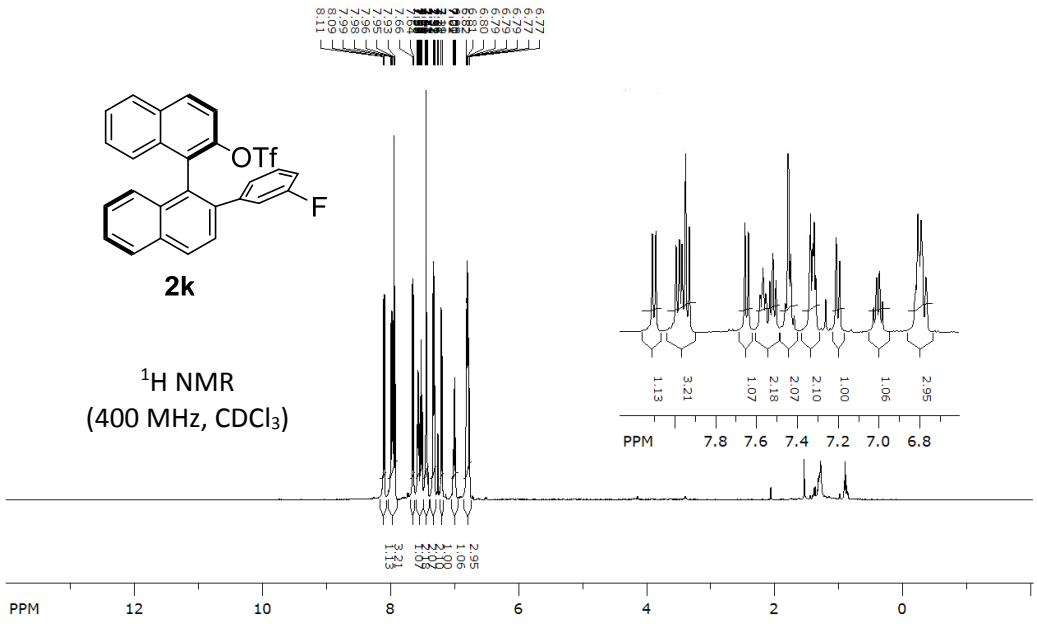

OTf
CF3
2f
1H NMR
(400 MHz, CDCl3)
PPM
12
10
8
6
4
2
0
PPM
8.0
7.8
7.6
7.4
7.2

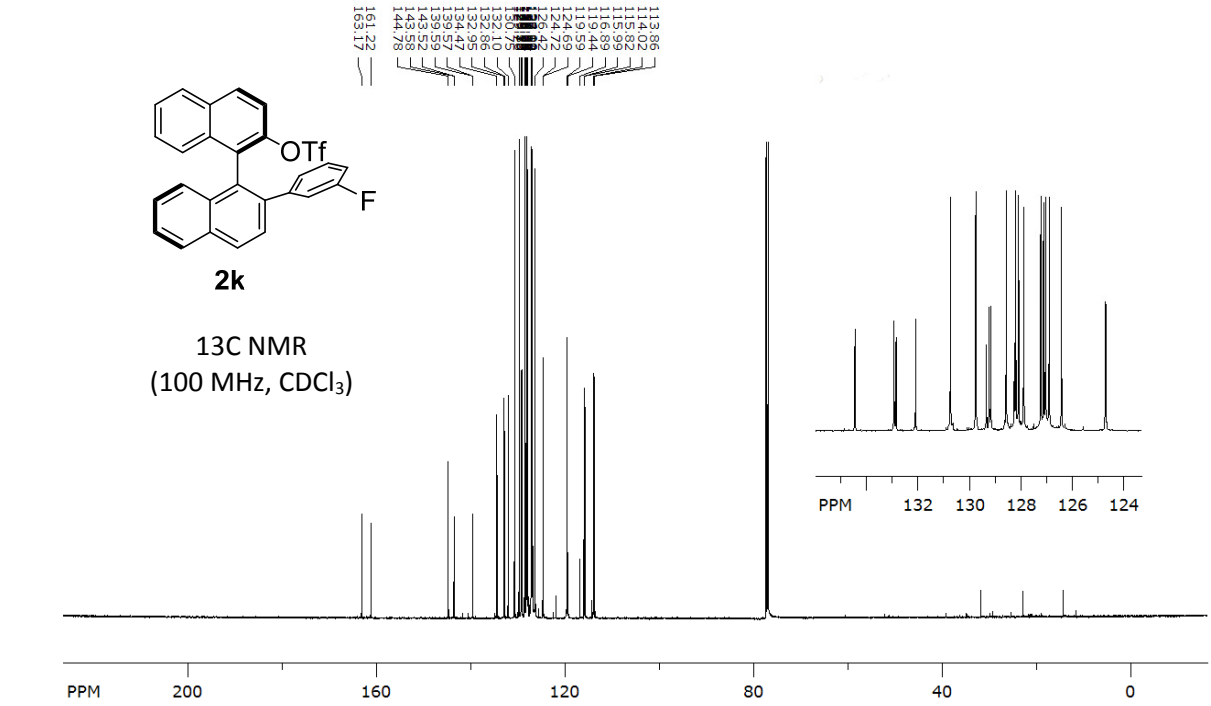

OTf
CF3
2f
13C NMR
(100 MHz, CDCl3)
PPM
200
160
120
80
40
0
PPM
132
130
128
126
PPM
122
120
118
116
114

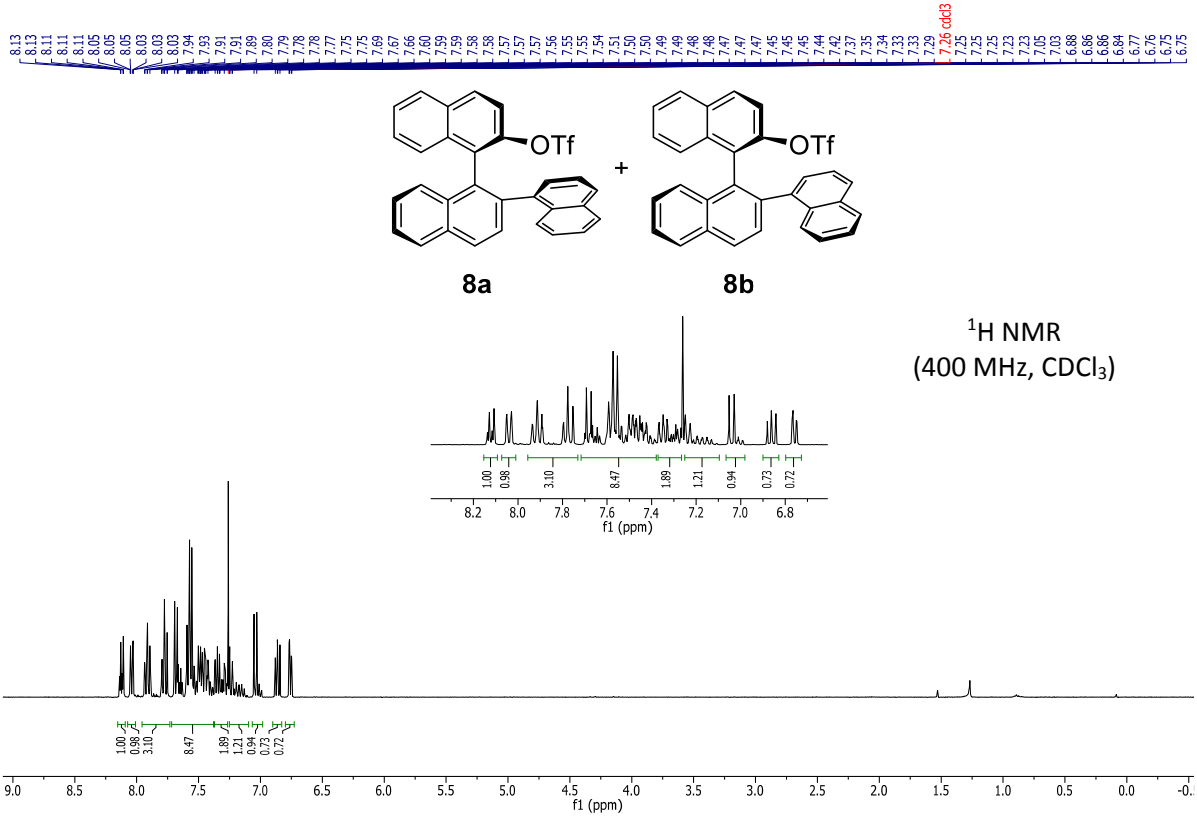

OTf
2g
1H NMR
(400 MHz, CDCl3)
PPM
12
10
8
6
4
2
0
7.8
7.6
7.4
7.2
7.0
6.8

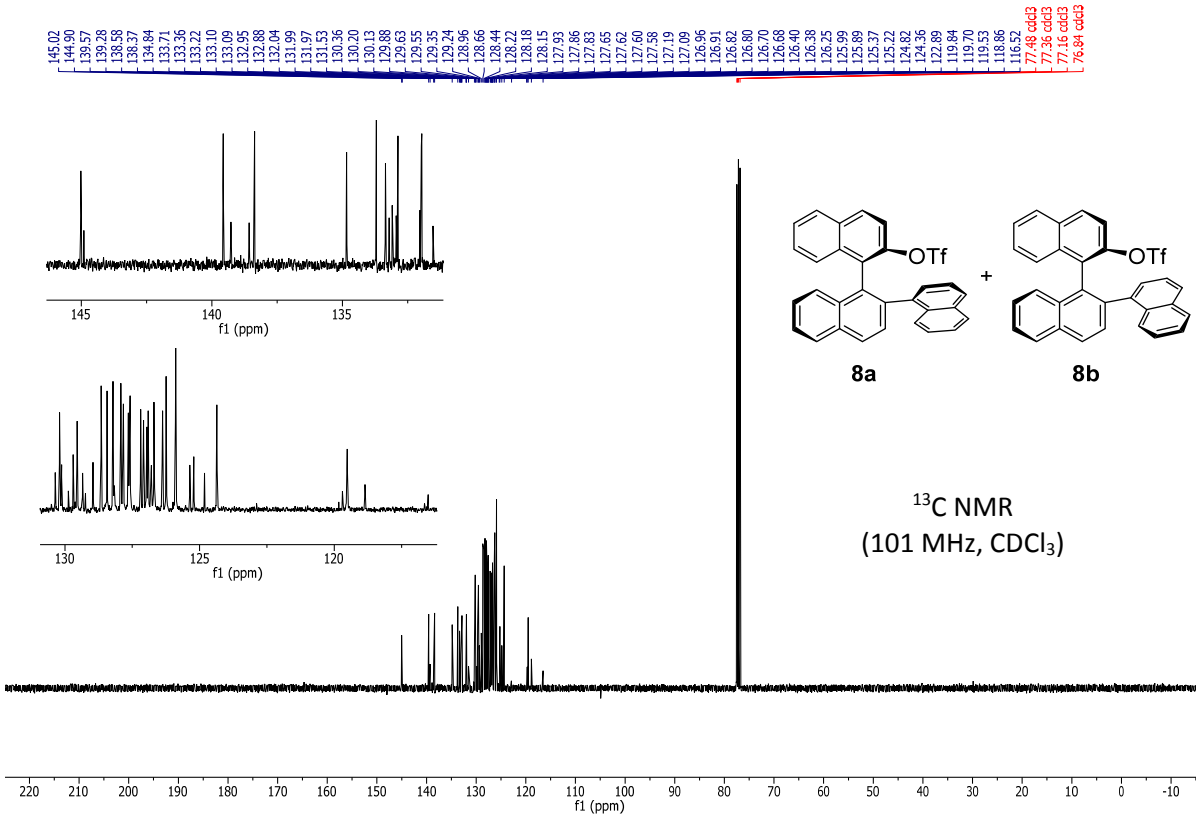

OTf
CF3
CF3
2h
1H NMR
(400 MHz, CDCl3)
PPM
12
10
8
6
4
2
0
7.8
7.6
7.4
7.2
7.0

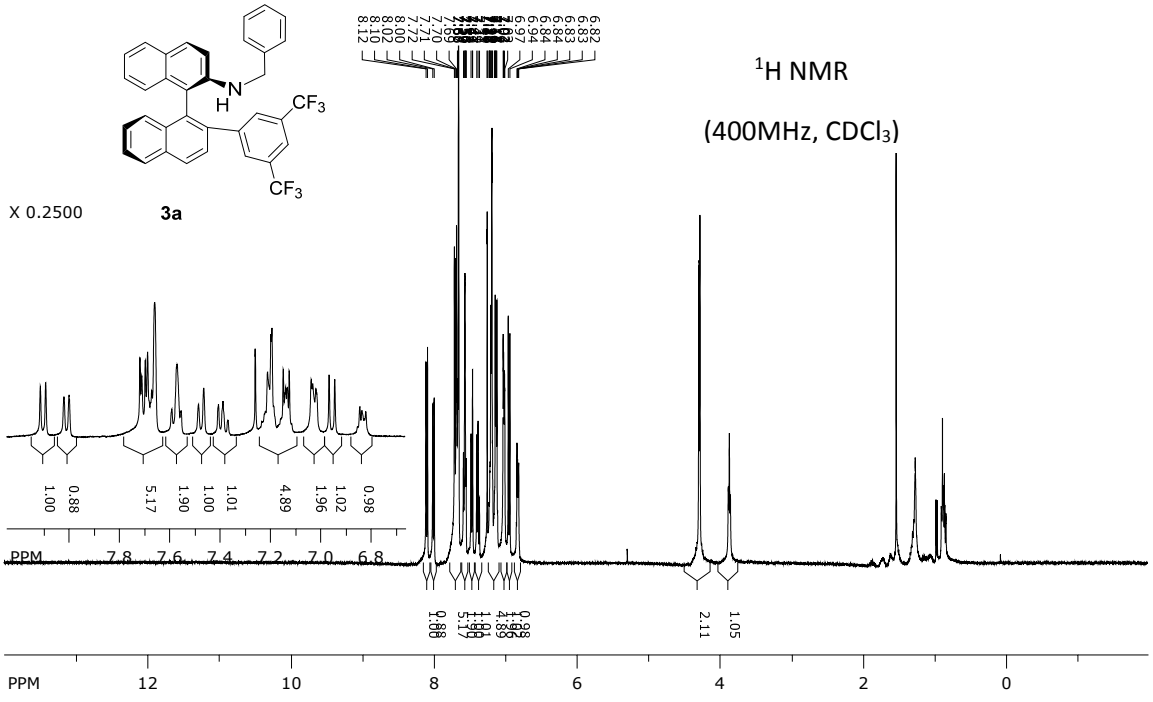

OTf
2i
1H NMR
(400 MHz, CDCl3)
PPM
12
10
8
6
4
2
0
7.8
7.6
7.4
7.2
7.0

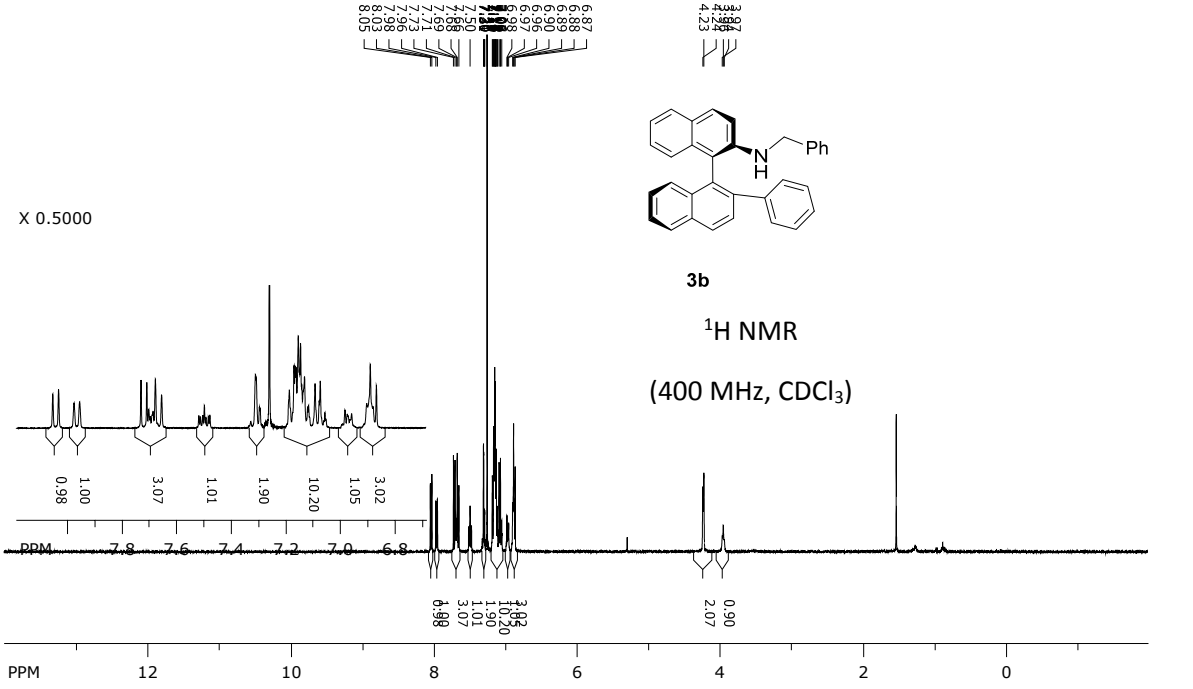

OTf
F
2k
1H NMR
(400 MHz, CDCl3)
PPM
12
10
8
6
4
2
0
7.8
7.6
7.4
7.2
7.0
6.8

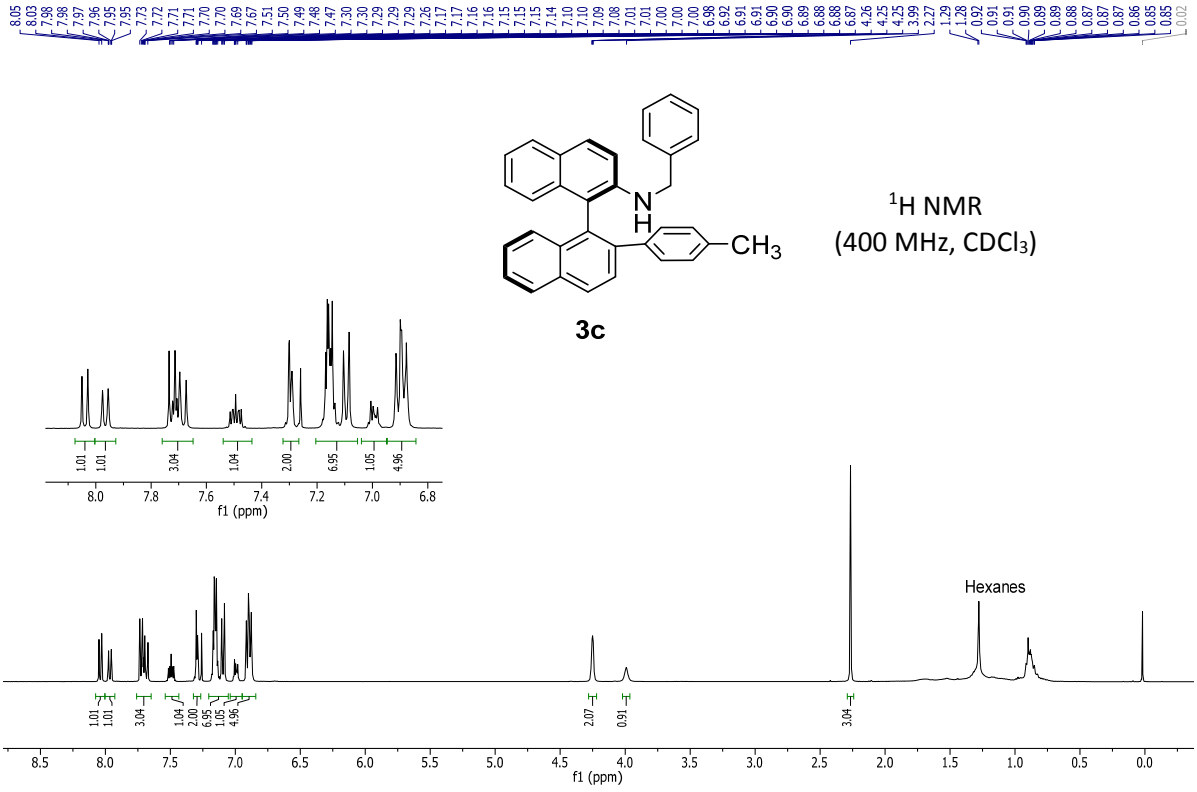

OTf
F
2k
13C NMR
(100 MHz, CDCl3)
PPM
200
160
120
80
40
0
132
130
128
126
124

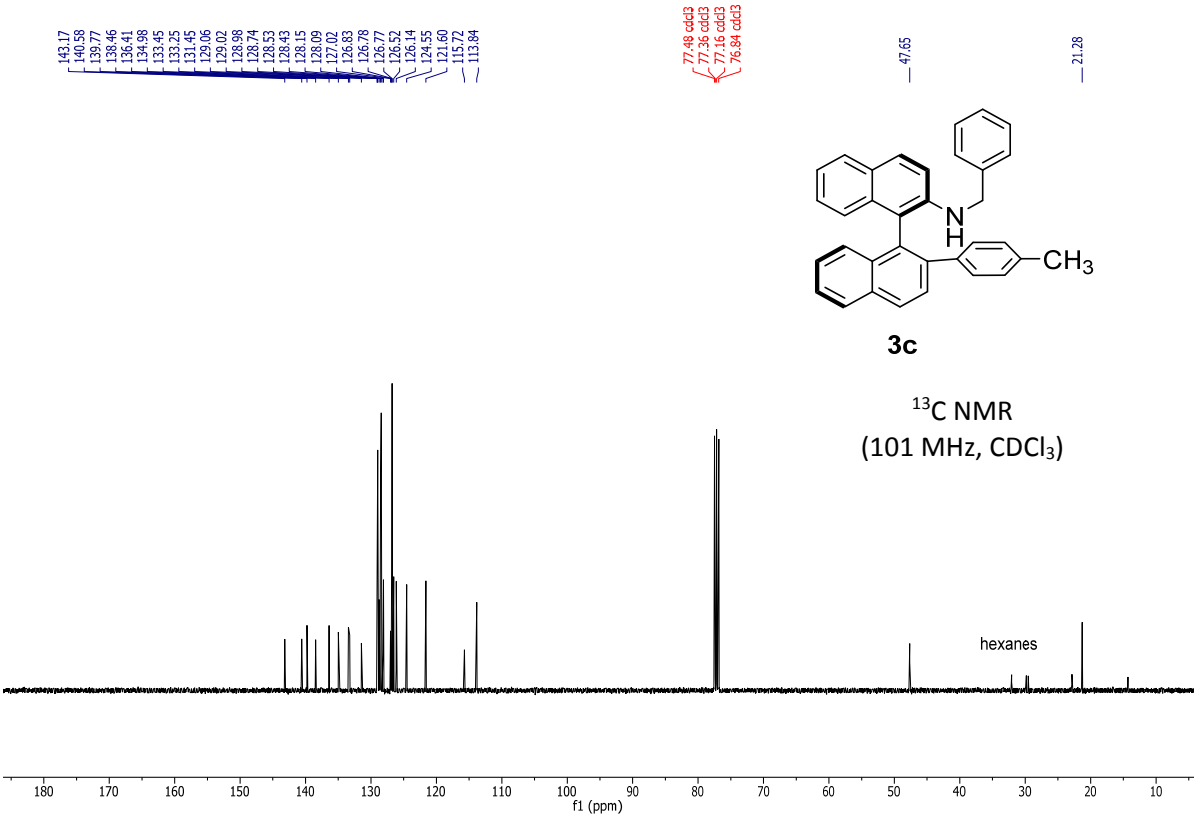

OTf
OTf
+
8a
8b
1H NMR
(400 MHz, CDCl3)
f1 (ppm)


OTf
OTf
+
8a
8b
^{13}C NMR
(101 MHz, CDCl$_3$)
f1 (ppm)


N
H
CF$_3$
CF$_3$
3a
X 0.2500
^{1}H NMR
(400MHz, CDCl$_3$)
PPM

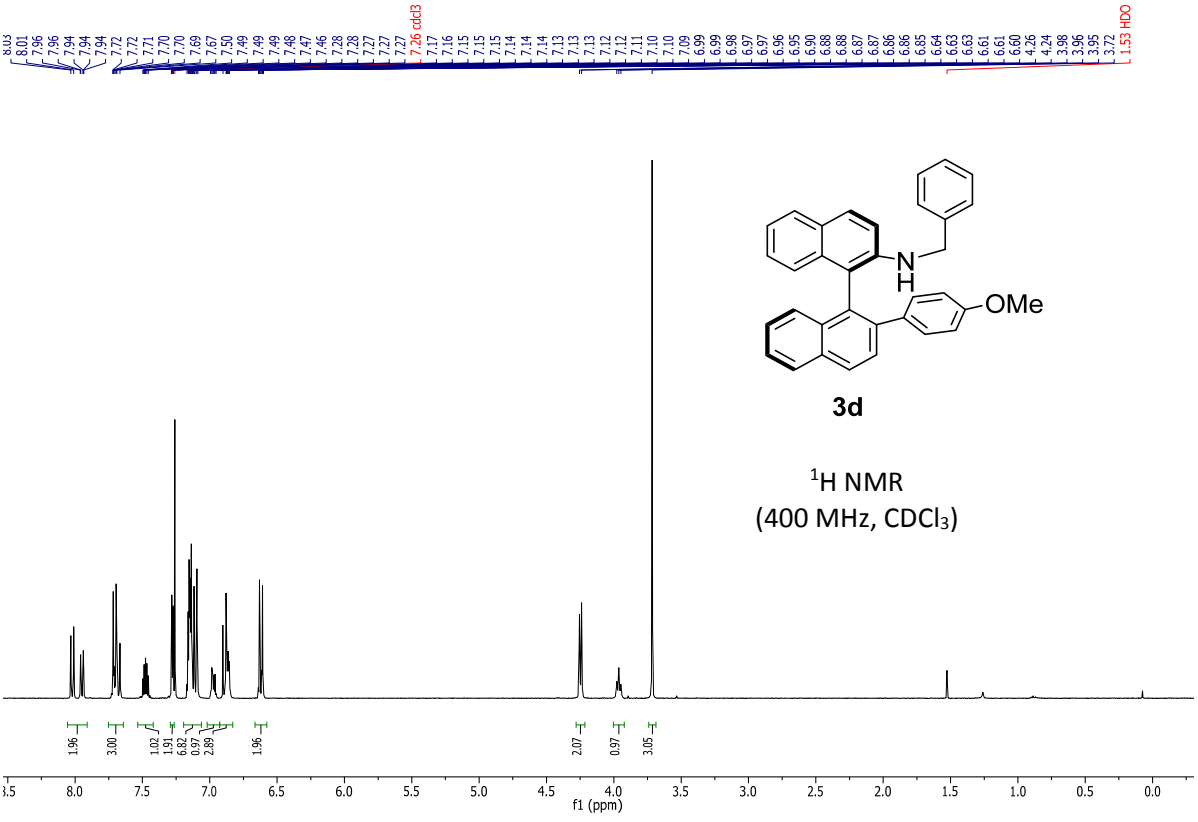

X 0.5000
Ph
N
H
3b
^{1}H NMR
(400 MHz, $CDCl_3$)
PPM
12
10
8
6
4
2
0


N
H
CH_3
3c
^{1}H NMR
(400 MHz, $CDCl_3$)
Hexanes
f1 (ppm)



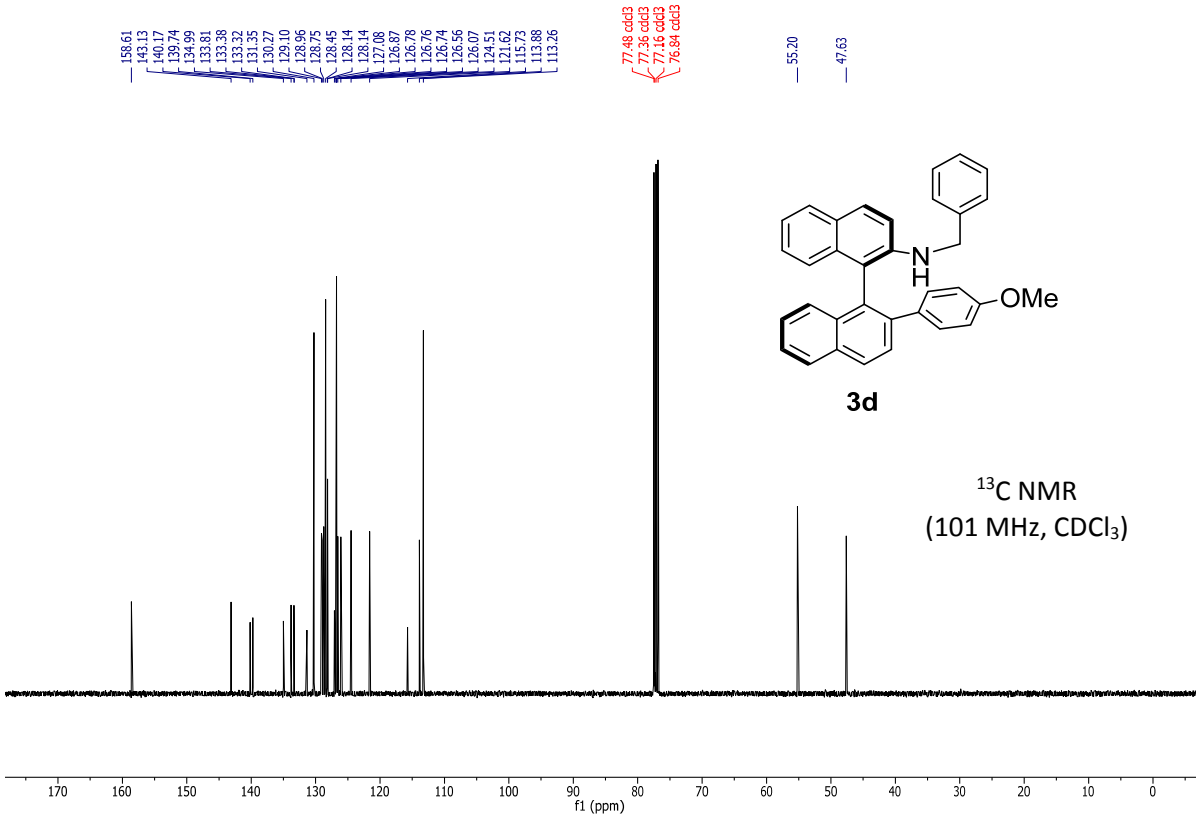
3c

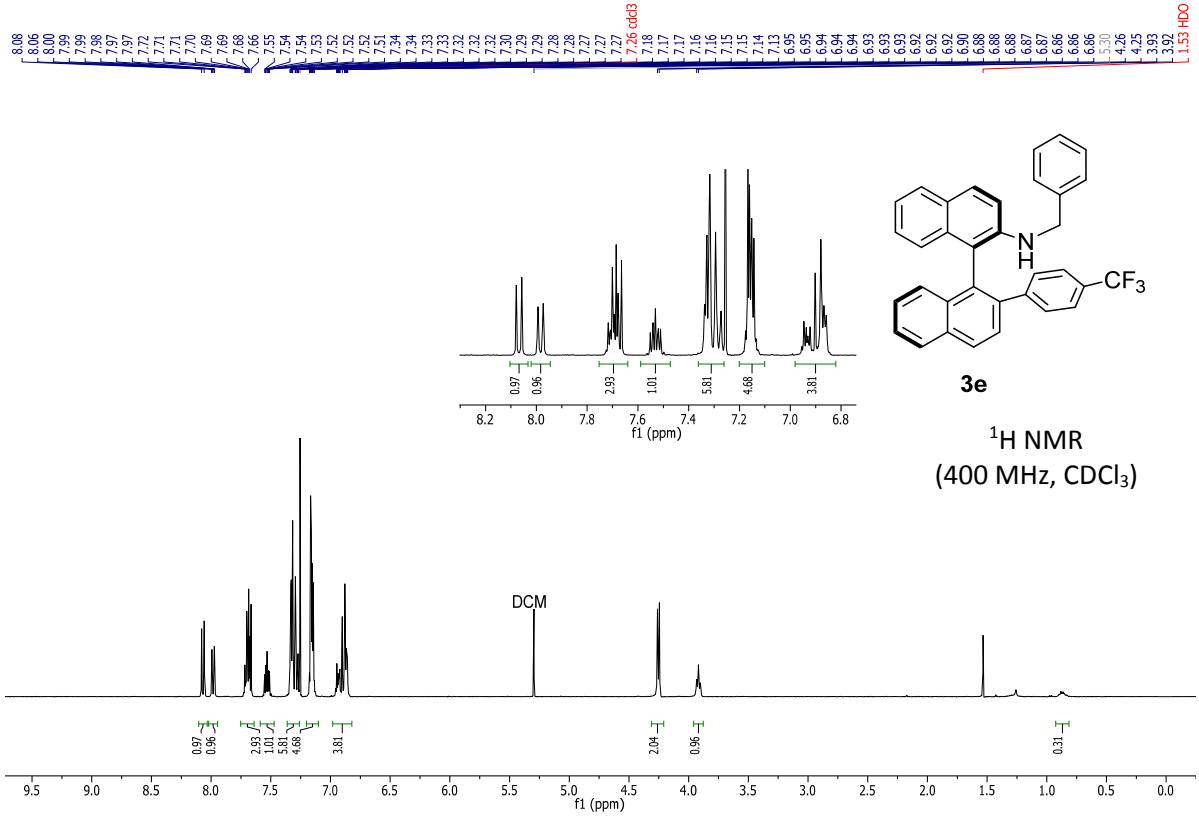
^{13}C NMR
(101 MHz, $CDCl_3$)

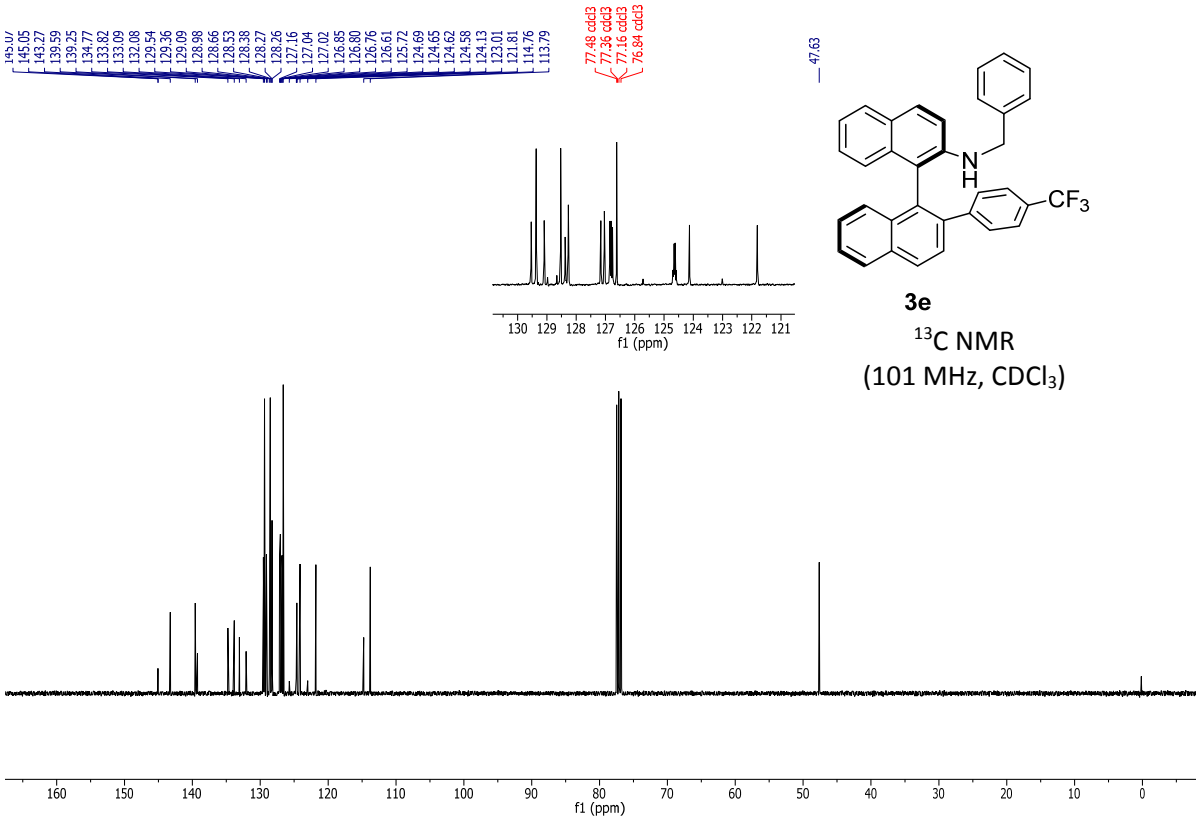


3d

^{1}H NMR
(400 MHz, $CDCl_3$)

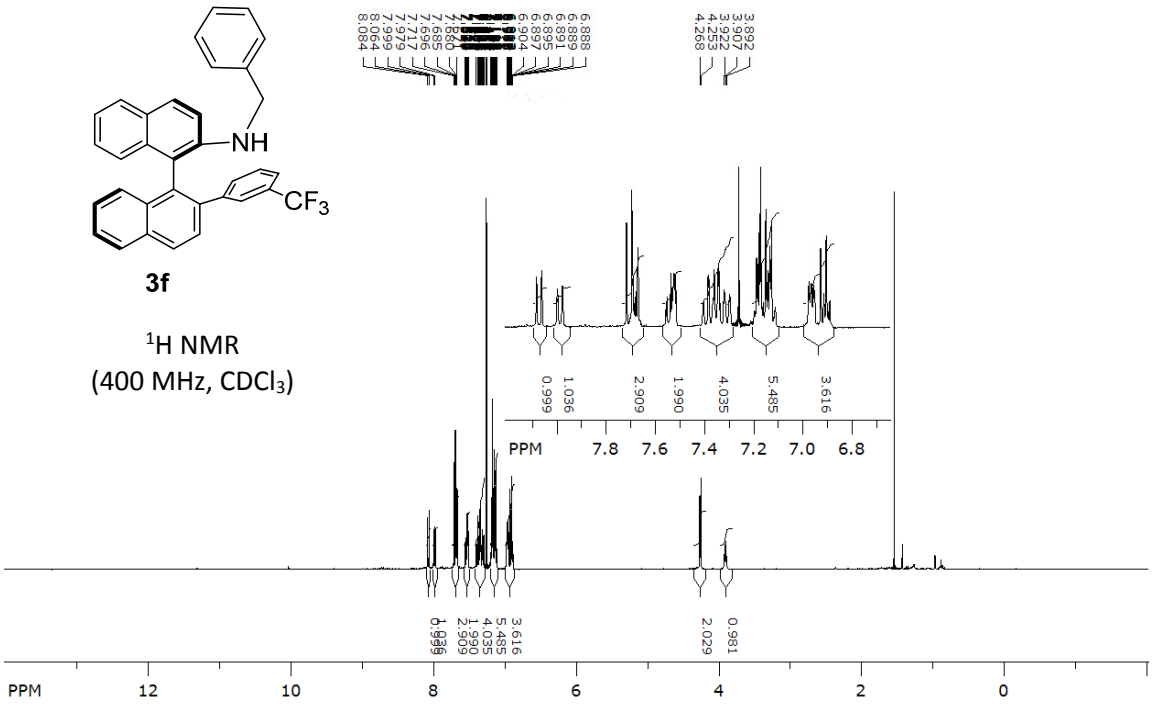

158.61
143.13
140.17
139.74
134.99
133.81
133.38
133.32
131.35
130.27
129.10
128.96
128.75
128.45
128.14
128.14
127.08
126.87
126.78
126.76
126.74
126.56
126.07
124.51
121.62
115.73
113.88
113.26
77.48 cdcl3
77.36 cdcl3
77.16 cdcl3
76.84 cdcl3
55.20
47.63
N
H
OMe
3d
13C NMR
(101 MHz, CDCl3)
f1 (ppm)


7.26 cdcl3
1.53 HDO
0.97
0.96
2.93
1.01
5.81
4.68
3.81
f1 (ppm)
N
H
CF3
3e
1H NMR
(400 MHz, CDCl3)
DCM
2.04
0.96
0.31



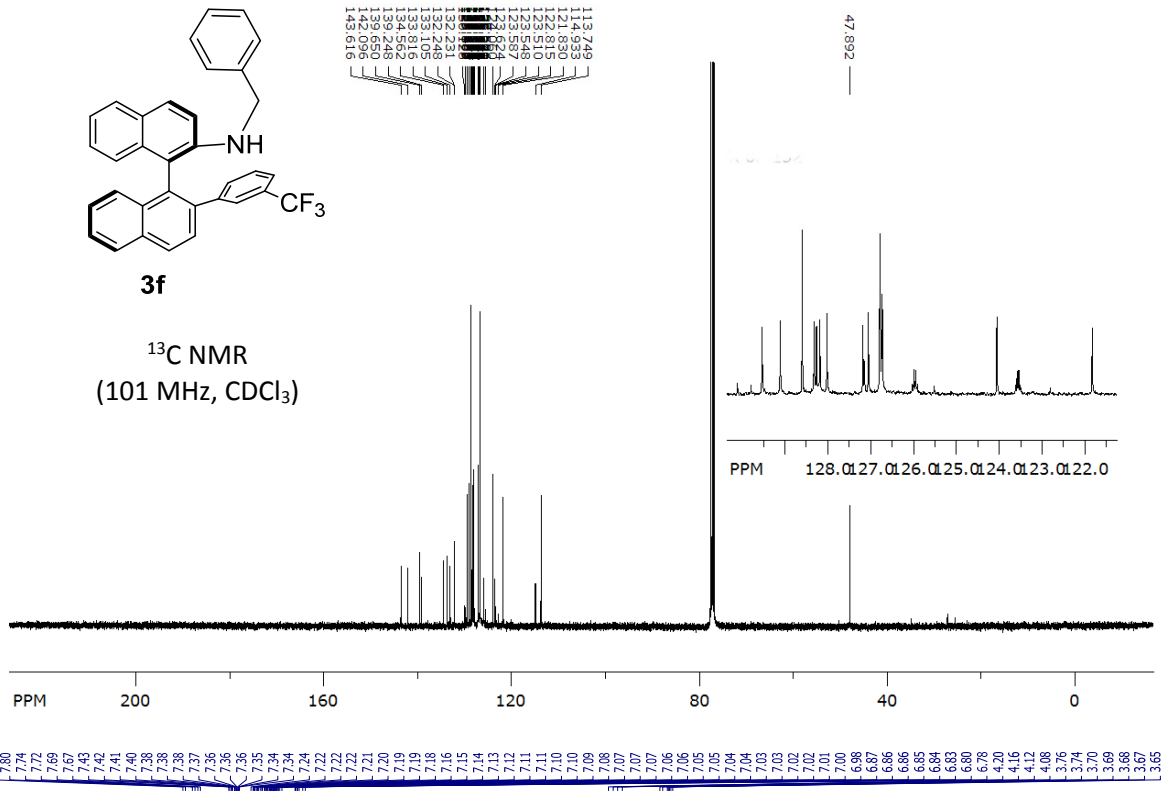
3e

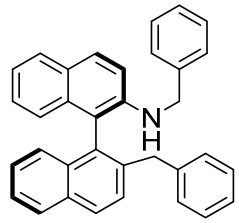
^{13}C NMR
(101 MHz, $CDCl_3$)



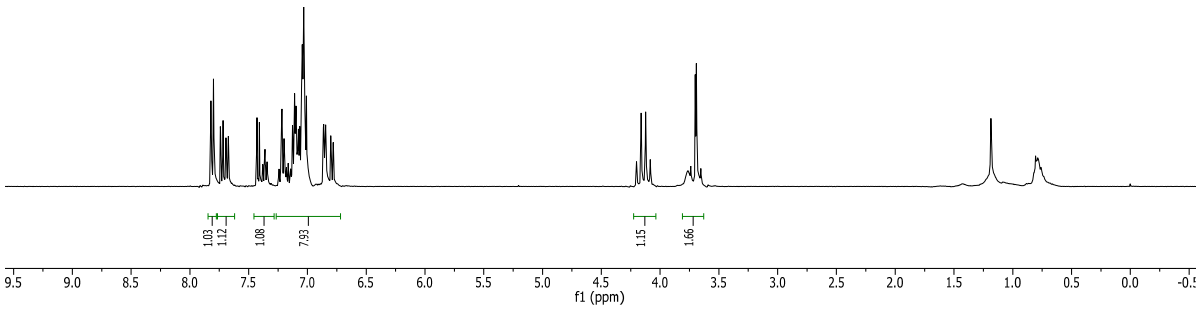
3f

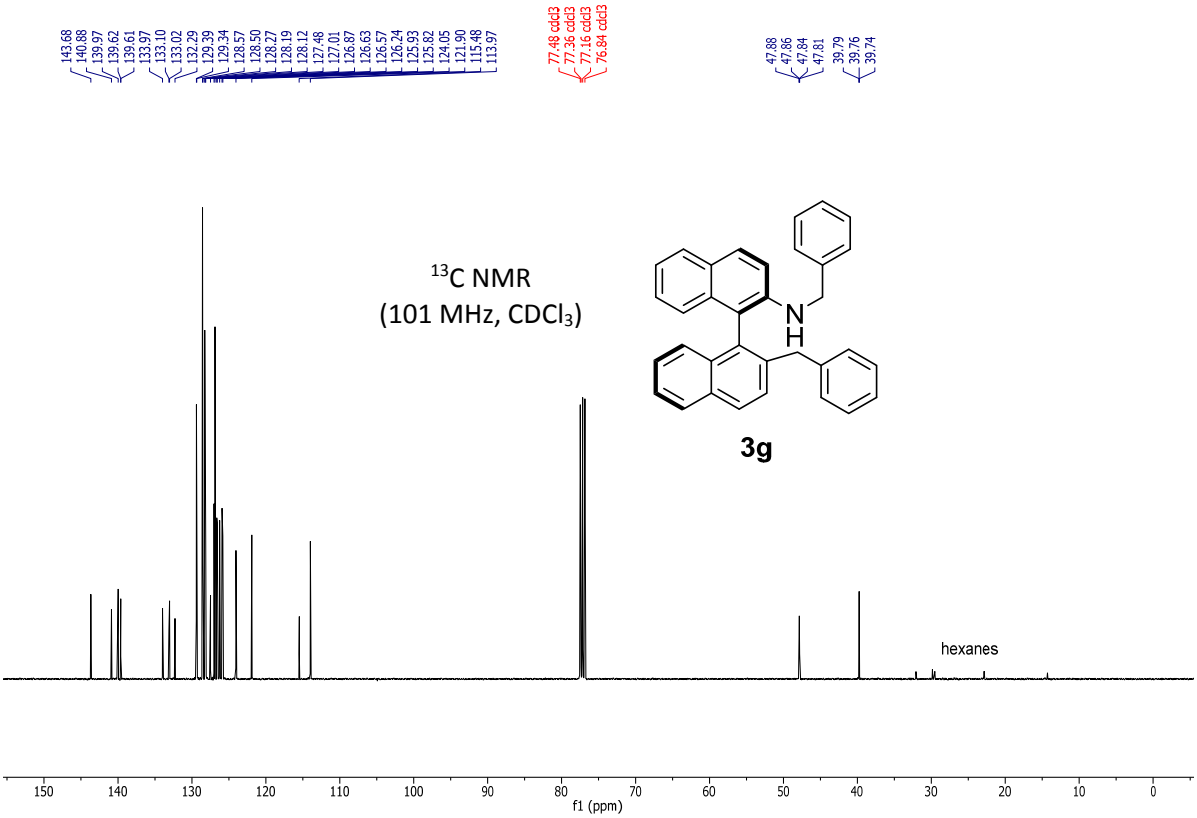
^{1}H NMR
(400 MHz, $CDCl_3$)

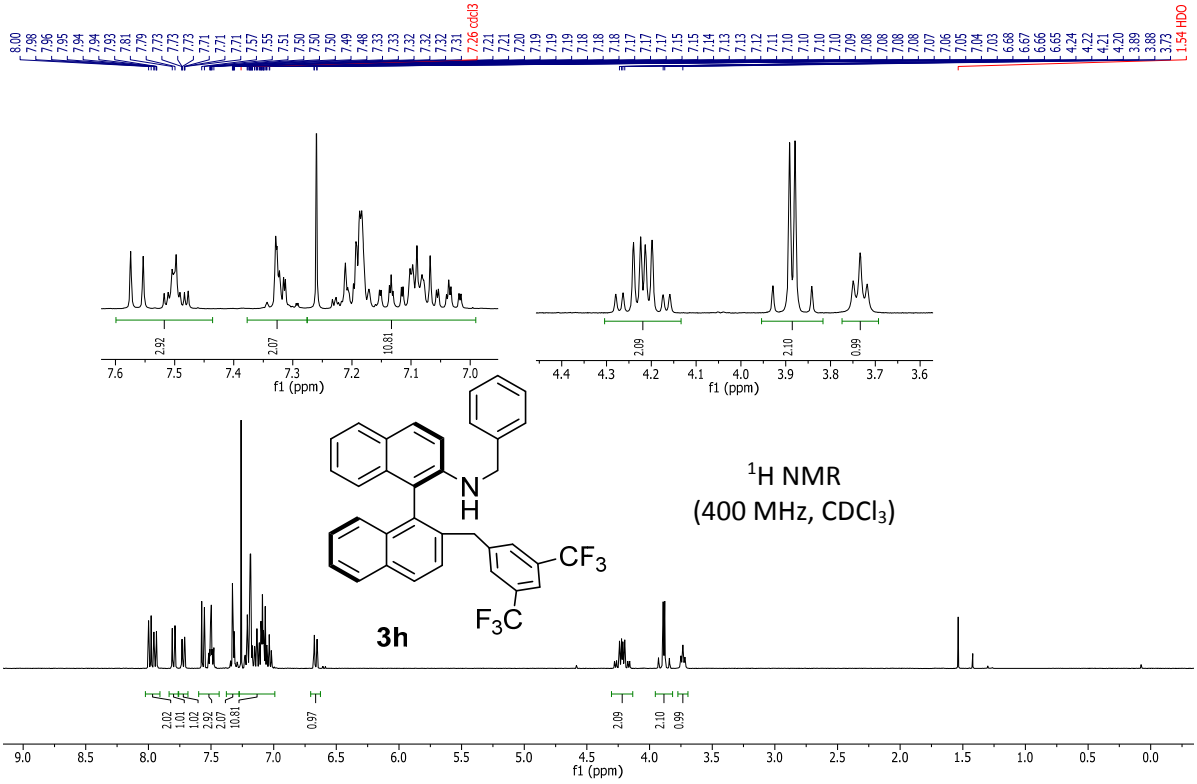


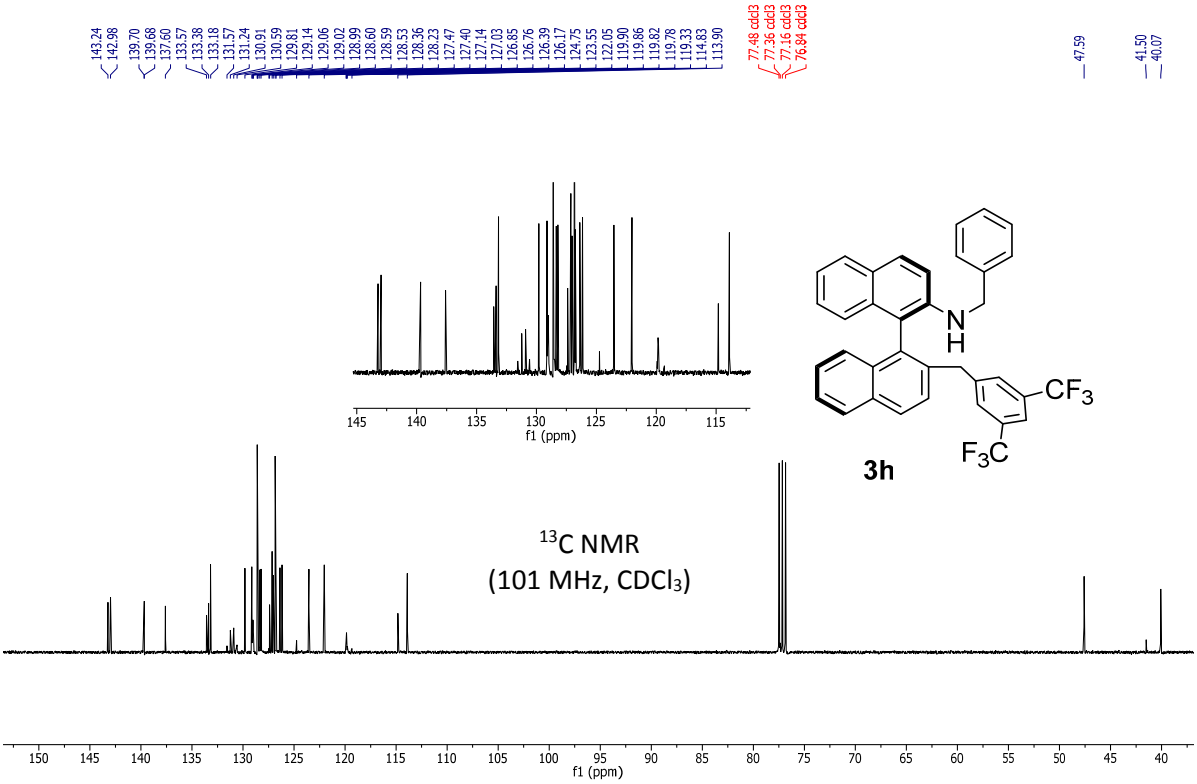


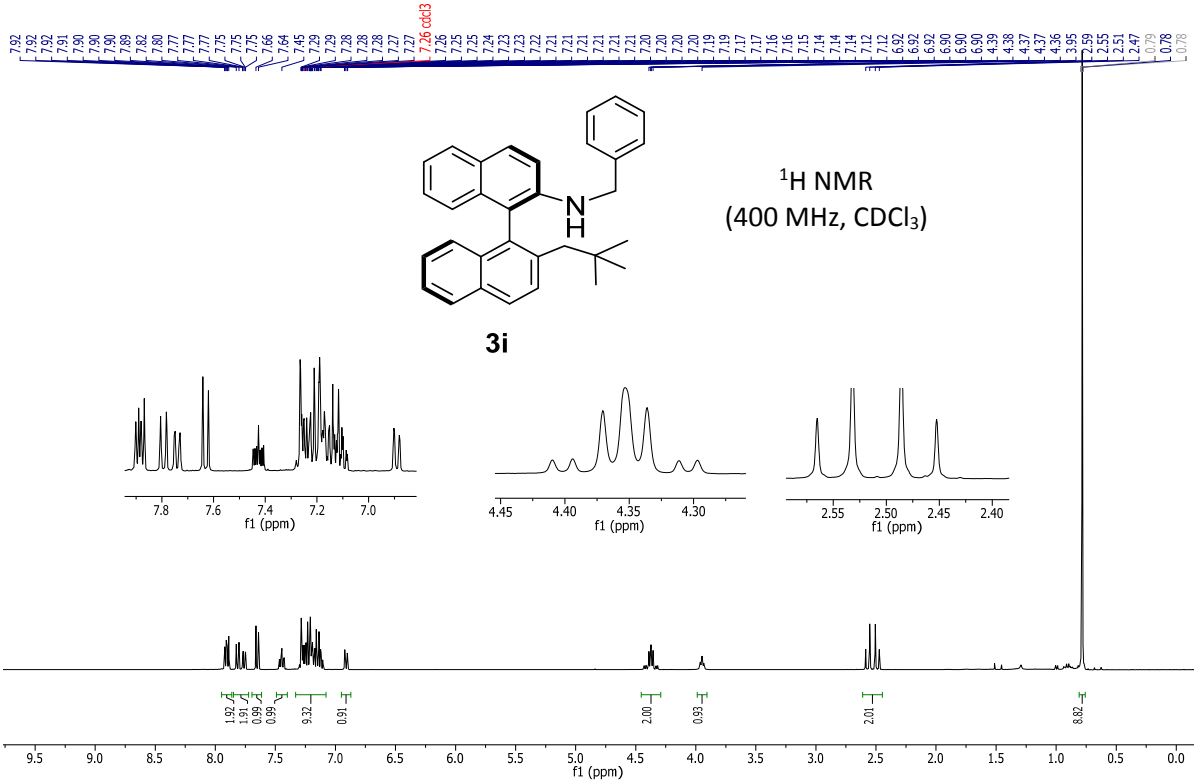
^{1}H NMR
(400 MHz, CDCl$_3$)

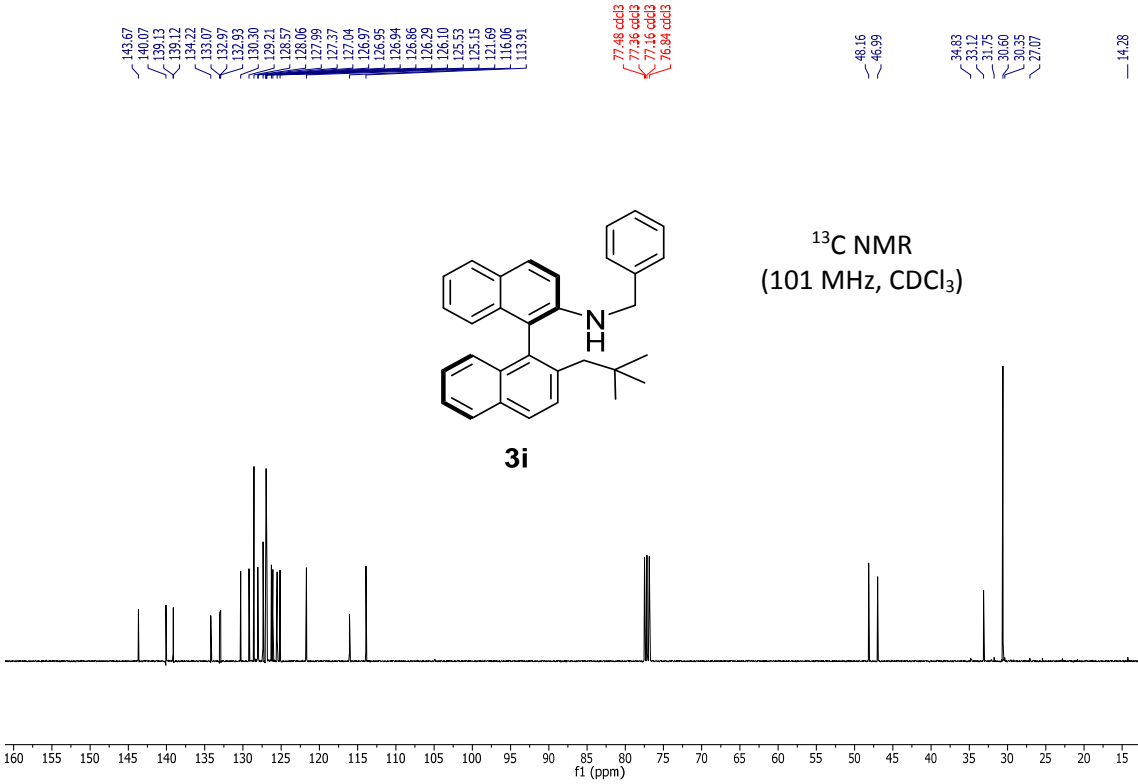


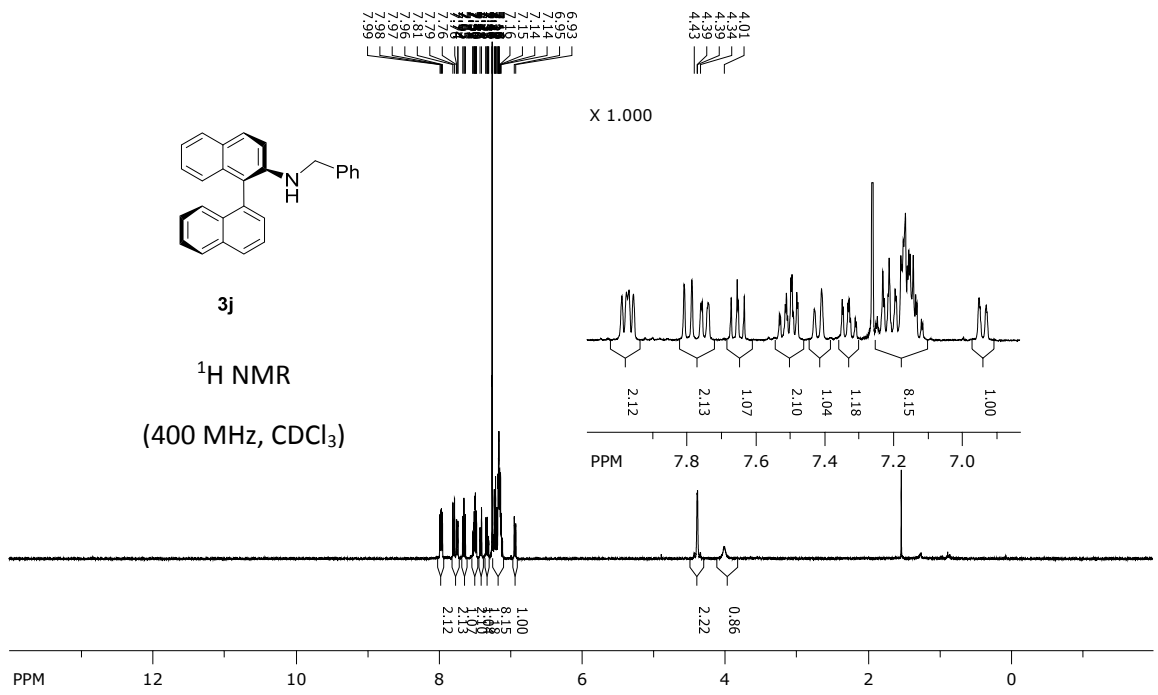

143.68
140.88
139.97
139.62
139.61
133.97
133.10
133.02
132.29
129.39
129.34
128.57
128.50
128.27
128.19
128.12
127.48
127.01
126.87
126.63
126.57
126.24
125.93
125.82
124.05
121.90
115.48
113.97
77.48 cdcl3
77.36 cdcl3
77.16 cdcl3
76.84 cdcl3
47.88
47.86
47.84
47.81
39.79
39.76
39.74
^{13}C NMR
(101 MHz, $CDCl_3$)
N
H
3g
hexanes
f1 (ppm)

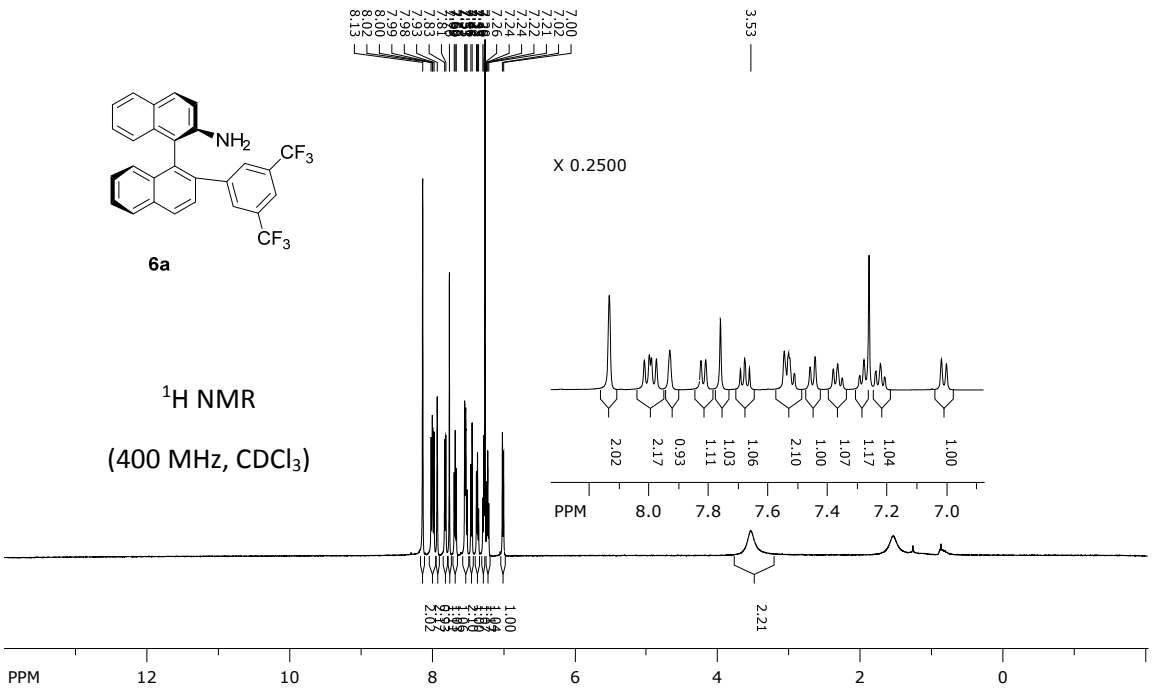

8.00
7.98
7.96
7.95
7.94
7.94
7.93
7.81
7.79
7.73
7.73
7.73
7.71
7.71
7.71
7.57
7.55
7.51
7.50
7.50
7.50
7.49
7.48
7.33
7.33
7.32
7.32
7.32
7.31
7.26 cdcl3
7.21
7.21
7.20
7.19
7.19
7.19
7.18
7.18
7.18
7.17
7.17
7.17
7.15
7.15
7.14
7.13
7.12
7.11
7.10
7.10
7.10
7.10
7.09
7.08
7.08
7.08
7.08
7.07
7.06
7.05
7.04
7.03
6.68
6.67
6.66
6.65
4.24
4.22
4.21
4.20
3.89
3.88
3.73
1.54 HDO
2.92
2.07
10.81
2.09
2.10
0.99
f1 (ppm)
N
H
CF_3
F_3C
3h
^{1}H NMR
(400 MHz, $CDCl_3$)
2.02
1.01
1.02
2.92
2.07
10.81
0.97
2.09
2.10
0.99
f1 (ppm)

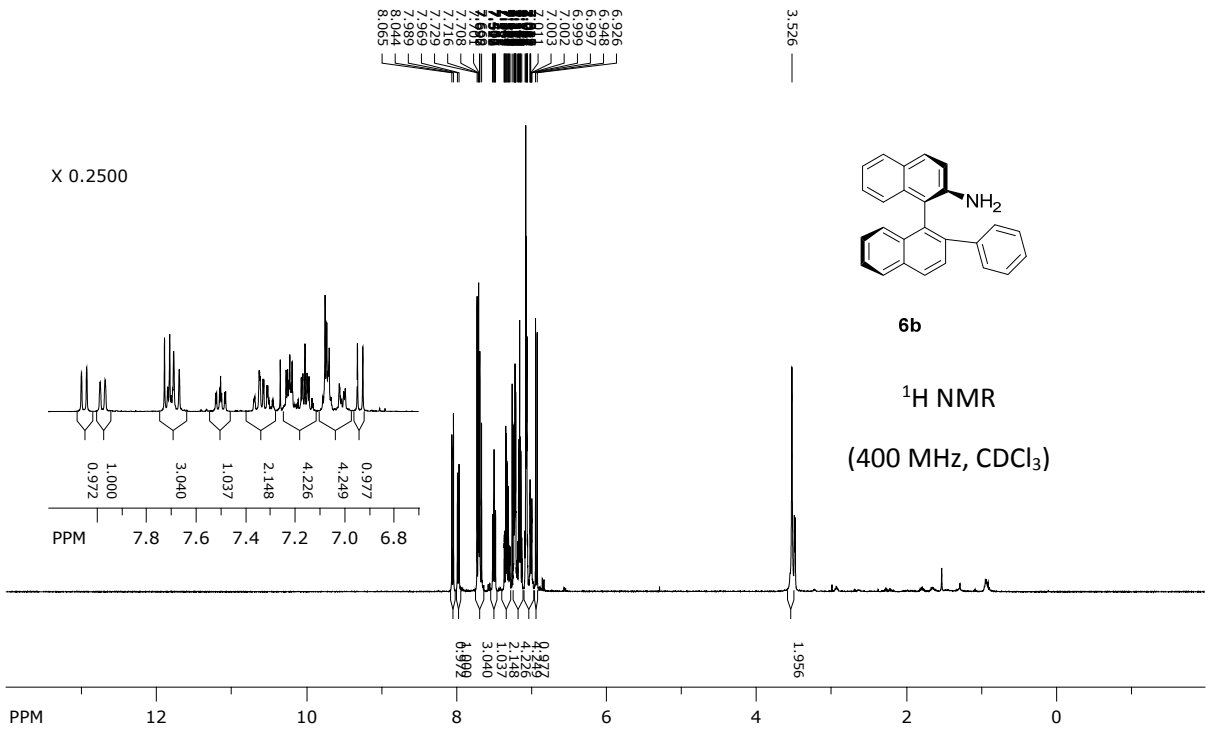

143.24
142.98
139.70
139.68
137.60
133.57
133.38
133.18
131.57
131.24
130.91
130.59
129.81
129.14
129.06
129.02
128.99
128.60
128.59
128.53
128.36
128.23
127.47
127.40
127.14
127.03
126.85
126.76
126.39
126.17
124.75
123.55
122.05
119.90
119.66
119.82
119.78
119.33
114.83
113.90
77.48 cdcl3
77.36 cdcl3
77.16 cdcl3
76.84 cdcl3
47.59
41.50
40.07
f1 (ppm)
N
H
CF3
F3C
3h
13C NMR
(101 MHz, CDCl3)

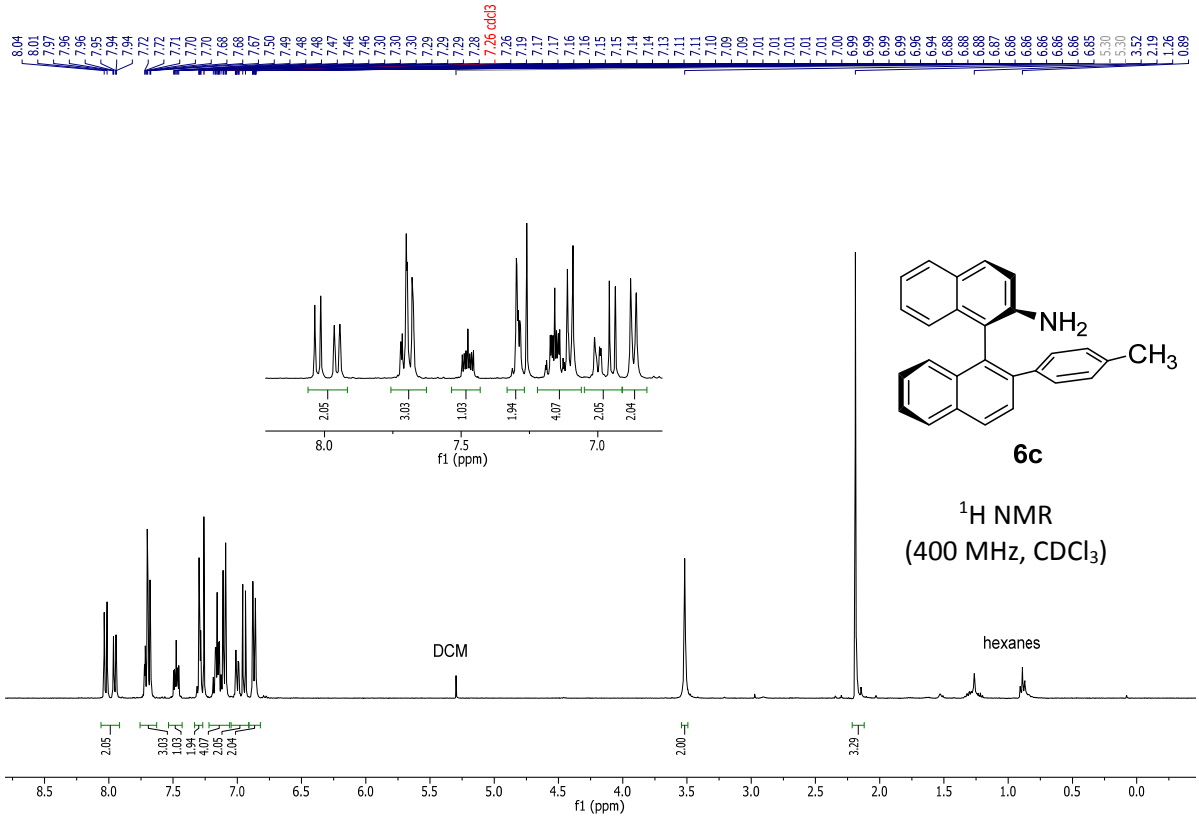

7.26 cdcl3
f1 (ppm)
N
H
3i
1H NMR
(400 MHz, CDCl3)
1.92
1.91
0.99
0.99
9.32
0.91
2.00
0.93
2.01
8.82

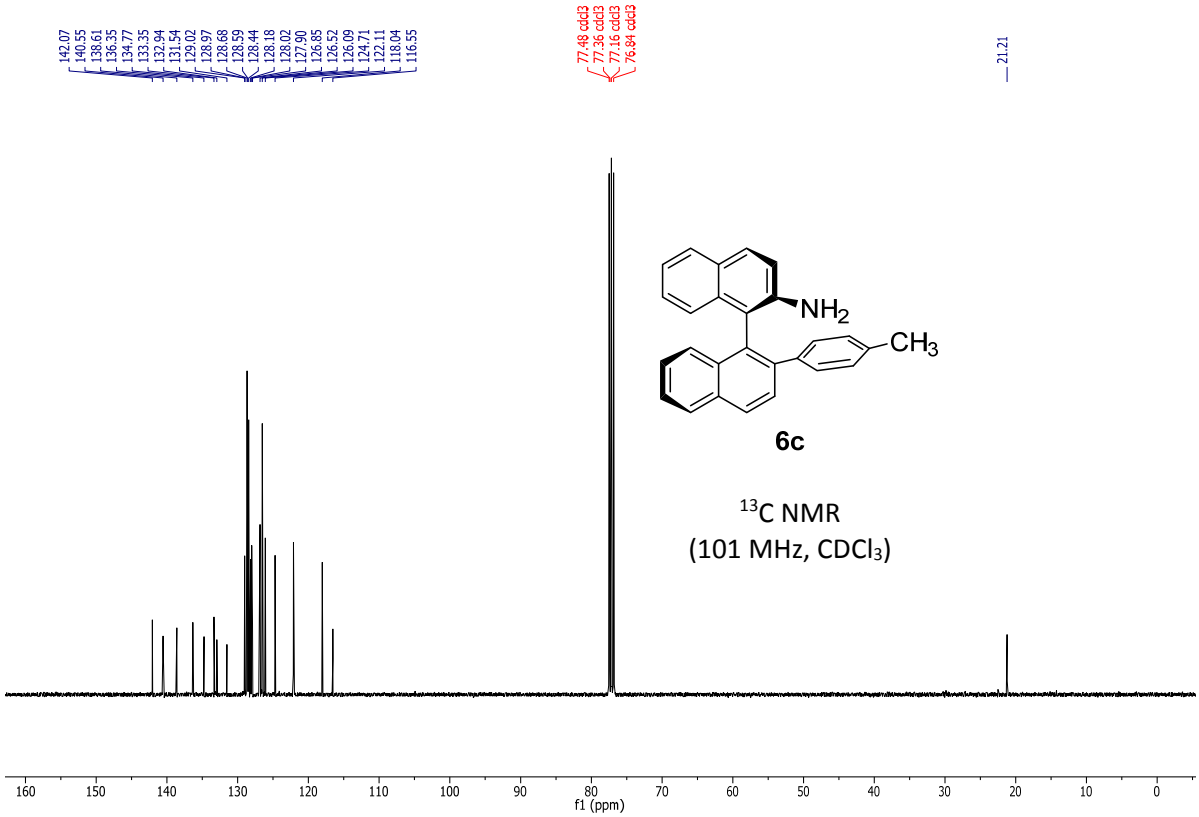

143.67
140.07
139.13
139.12
134.22
133.07
132.97
132.93
130.30
129.21
128.57
128.06
127.99
127.37
127.04
126.97
126.95
126.94
126.86
126.29
126.10
125.53
125.15
121.69
116.06
113.91
77.48 cdcl3
77.36 cdcl3
77.16 cdcl3
76.84 cdcl3
48.16
46.99
34.83
33.12
31.75
30.60
30.35
27.07
14.28
N
H
3i
^{13}C NMR
(101 MHz, $CDCl_3$)
160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)

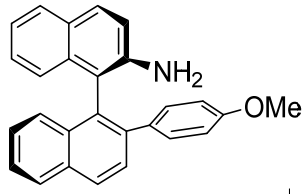

7.99
7.98
7.97
7.96
7.81
7.79
7.78
7.15
7.14
6.95
6.93
4.43
4.39
4.34
4.01
X 1.000
N
H
Ph
3j
^{1}H NMR
(400 MHz, $CDCl_3$)
2.12
2.13
1.07
2.10
1.04
1.18
8.15
1.00
PPM
7.8
7.6
7.4
7.2
7.0
2.12
2.13
8.15
1.00
2.22
0.86
PPM
12
10
8
6
4
2
0


NH2
CF3
CF3
6a
X 0.2500
1H NMR
(400 MHz, CDCl3)
PPM


X 0.2500
NH2
6b
1H NMR
(400 MHz, CDCl3)
PPM

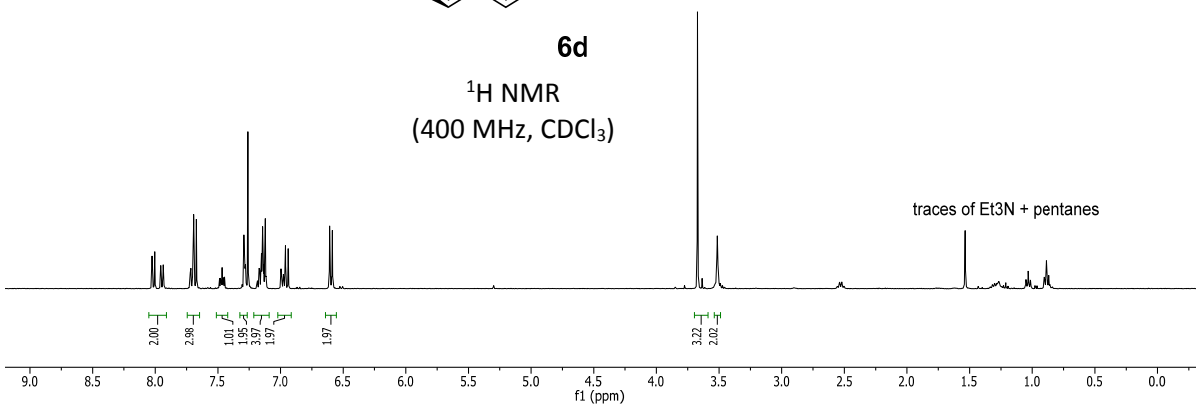

NH2
CH3
6c
1H NMR
(400 MHz, CDCl3)
DCM
hexanes
f1 (ppm)

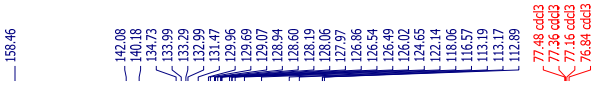

NH2
CH3
6c
13C NMR
(101 MHz, CDCl3)
f1 (ppm)

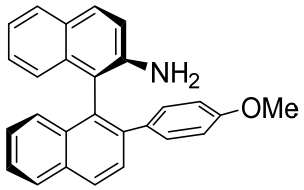


6d

^{1}H NMR
(400 MHz, $CDCl_3$)

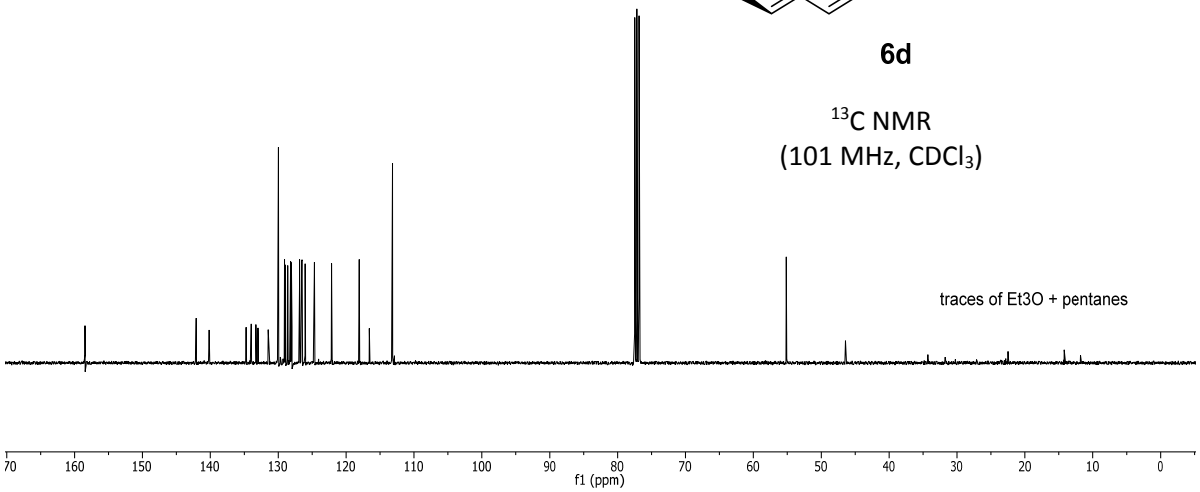


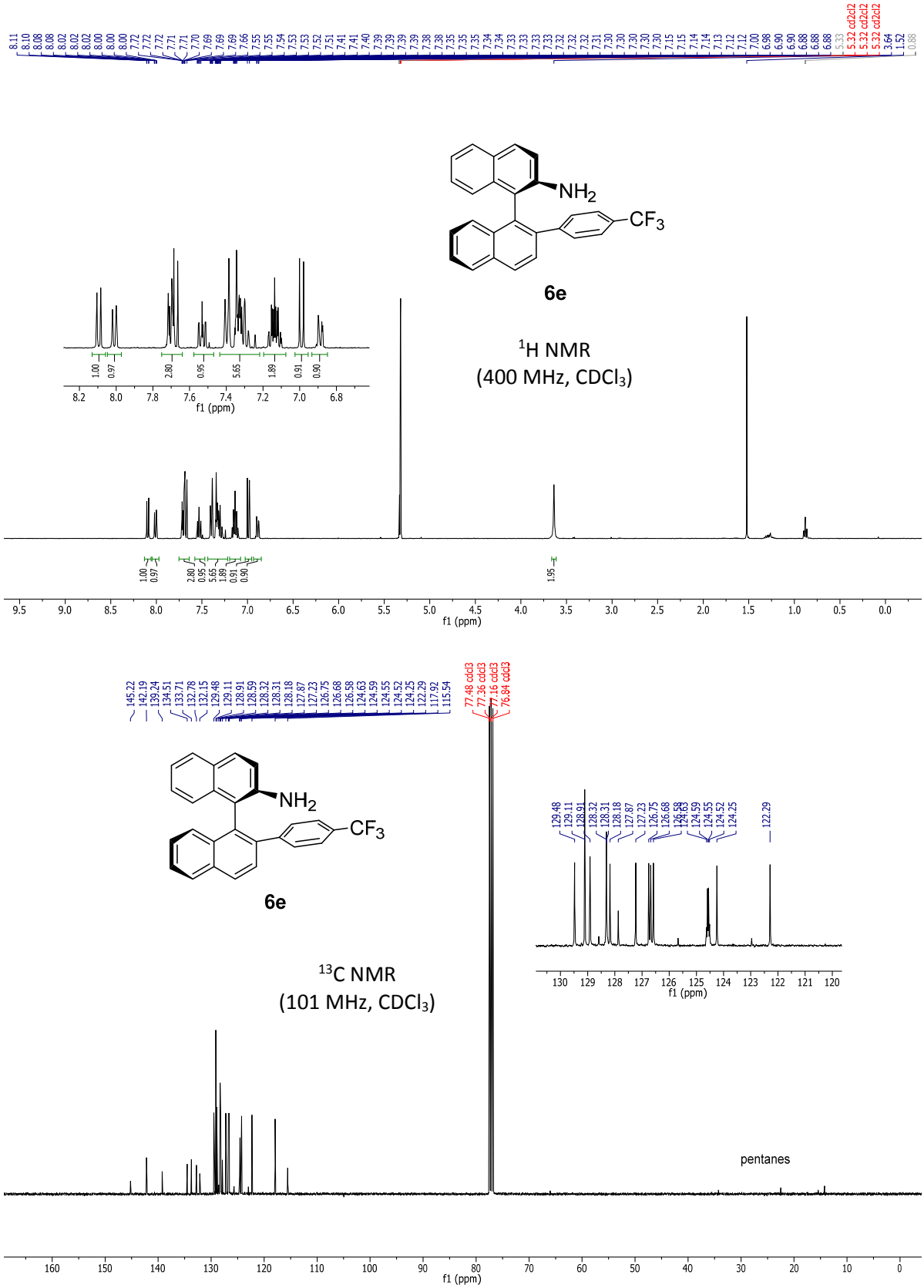


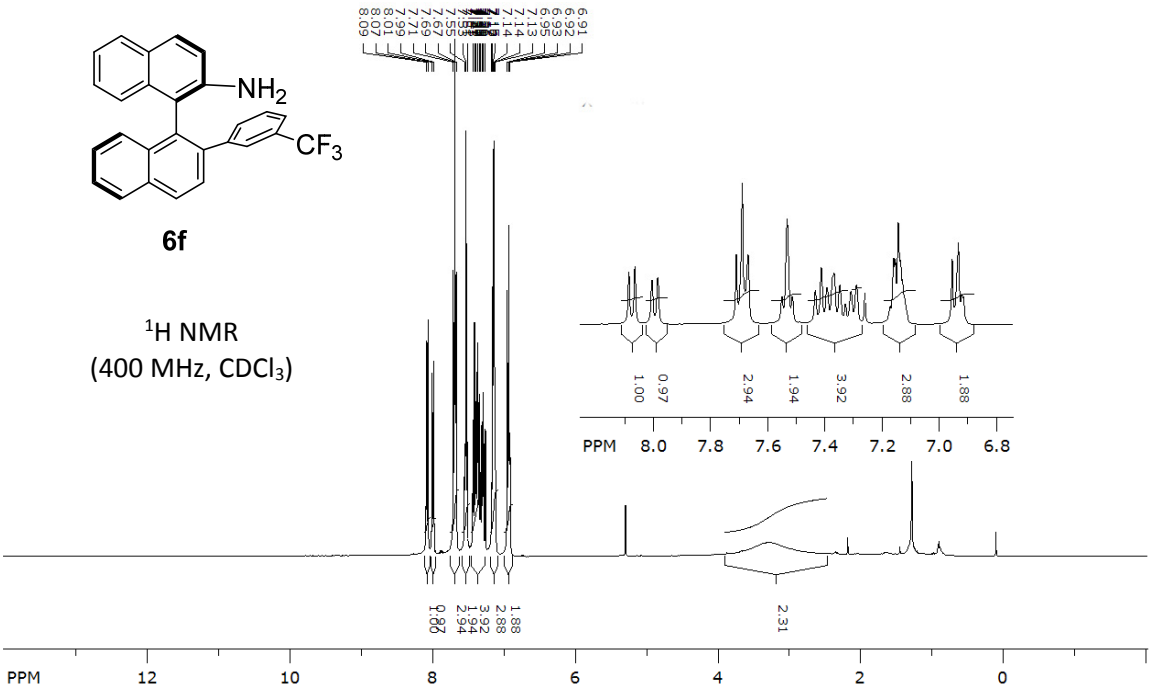


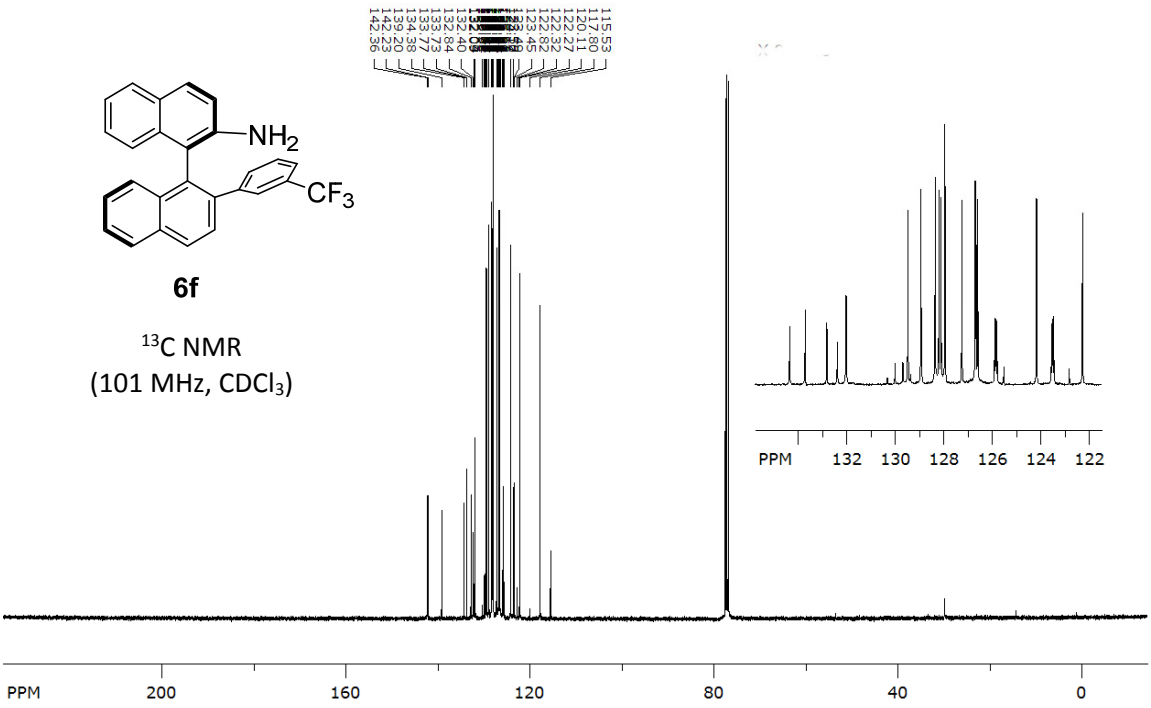
6d

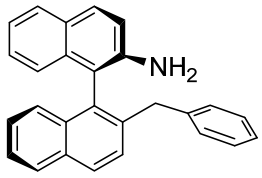
^{13}C NMR
(101 MHz, $CDCl_3$)




NH2
CF3
6e
1H NMR
(400 MHz, CDCl3)
f1 (ppm)
13C NMR
(101 MHz, CDCl3)
pentanes

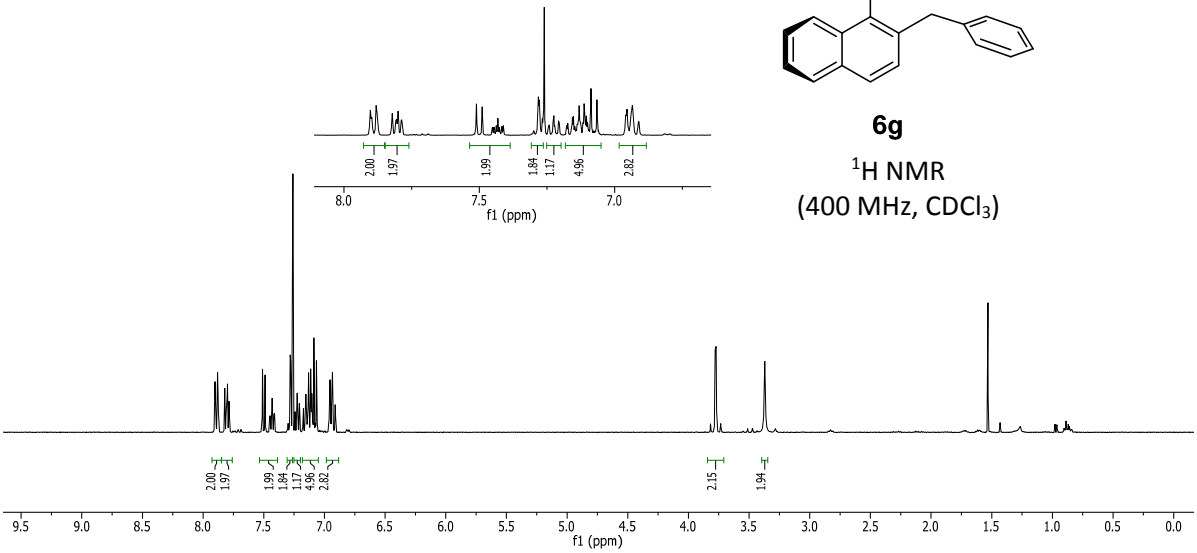

NH2
CF3
6f
1H NMR
(400 MHz, CDCl3)
PPM 12 10 8 6 4 2 0
PPM 8.0 7.8 7.6 7.4 7.2 7.0 6.8

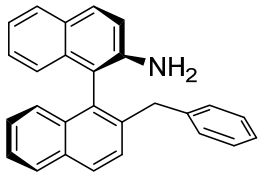

NH2
CF3
6f
13C NMR
(101 MHz, CDCl3)
PPM 200 160 120 80 40 0
PPM 132 130 128 126 124 122



6g

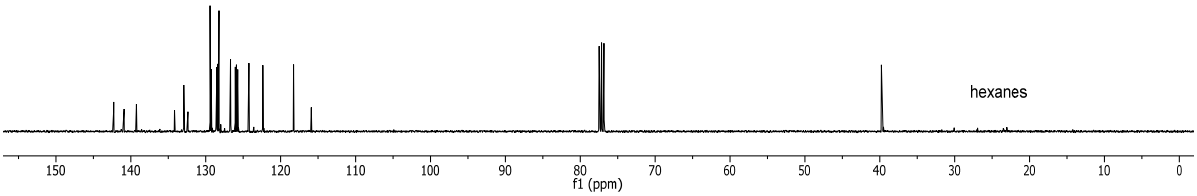
^{1}H NMR
(400 MHz, $CDCl_3$)

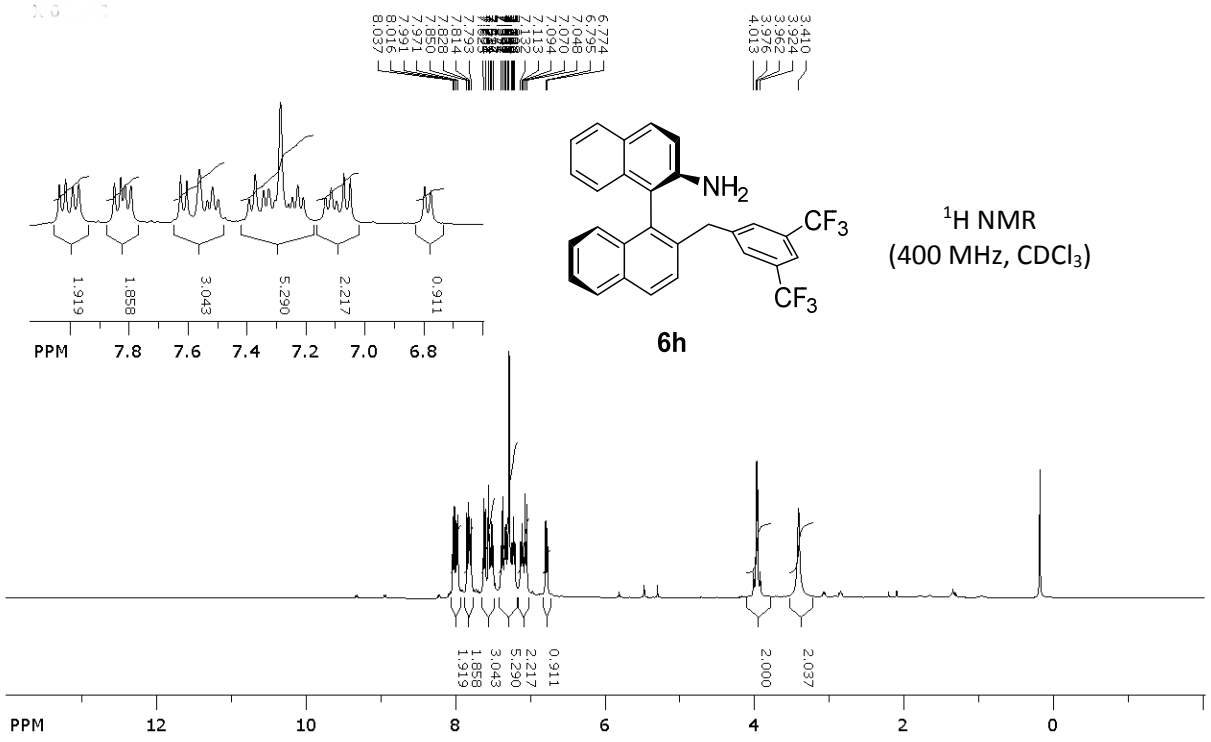


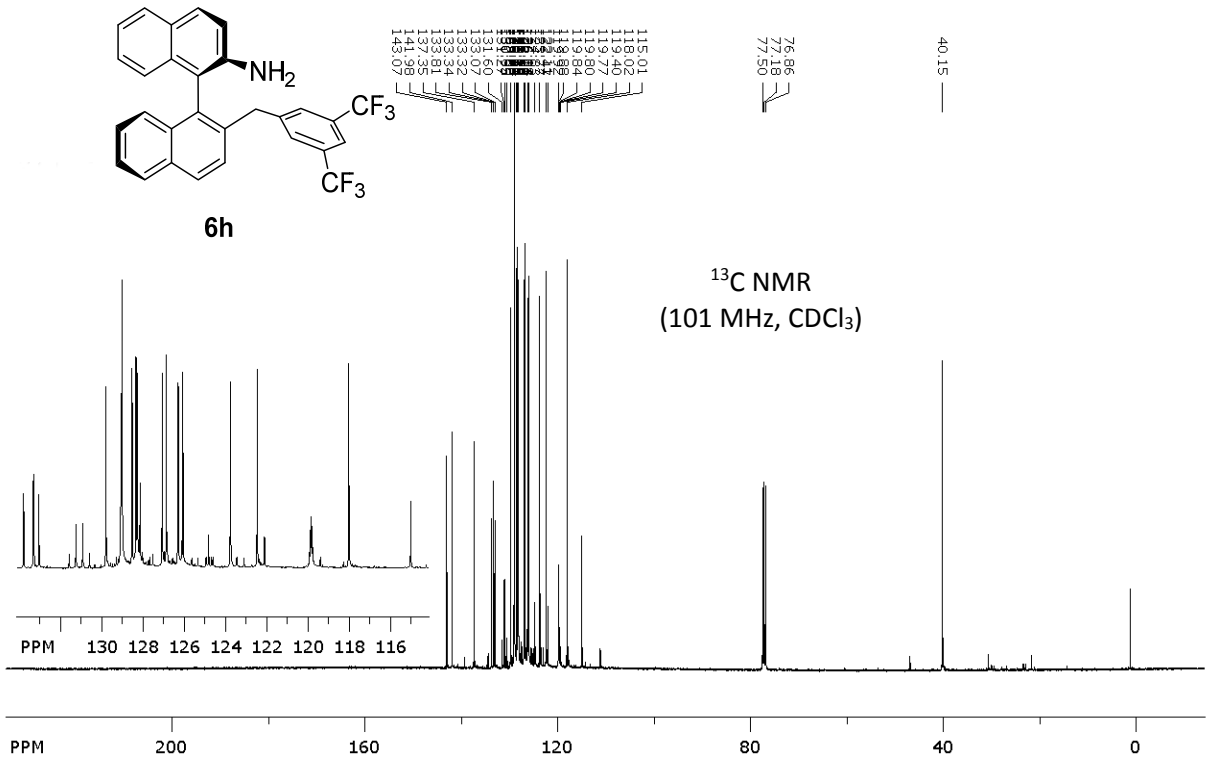


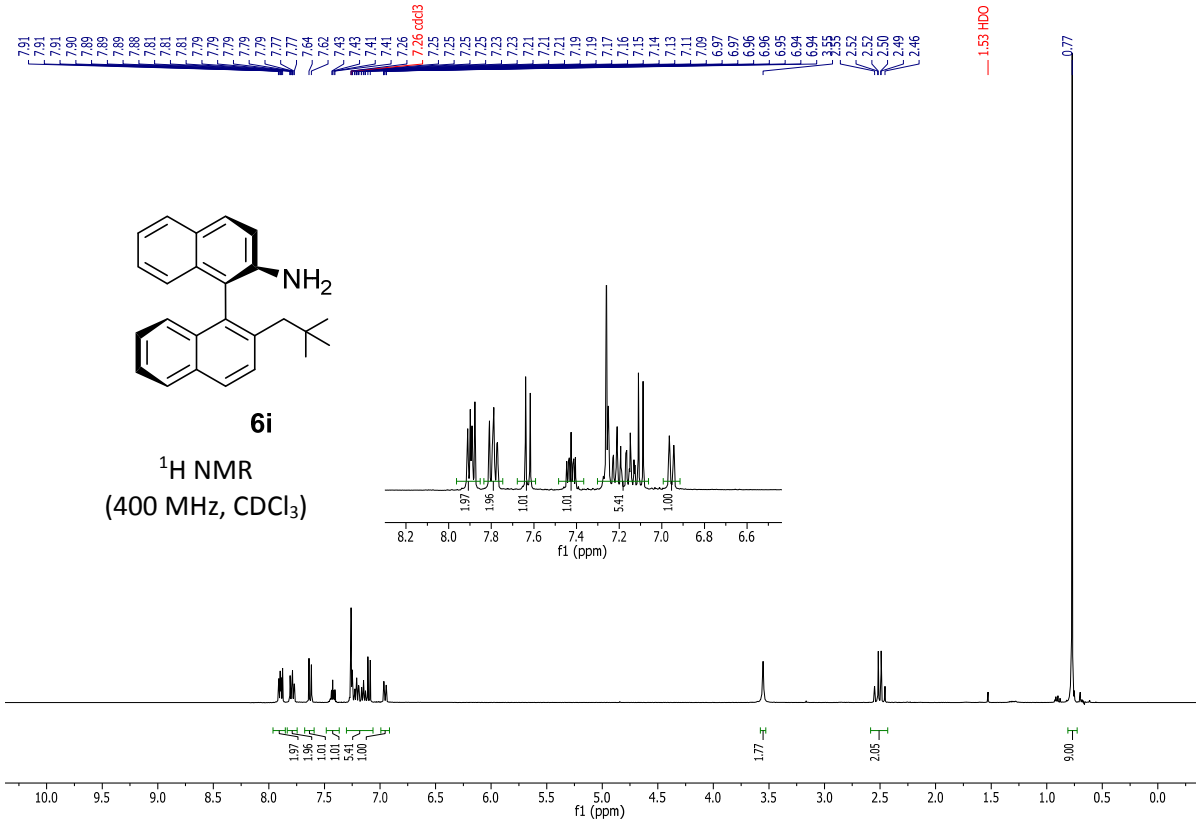
6g

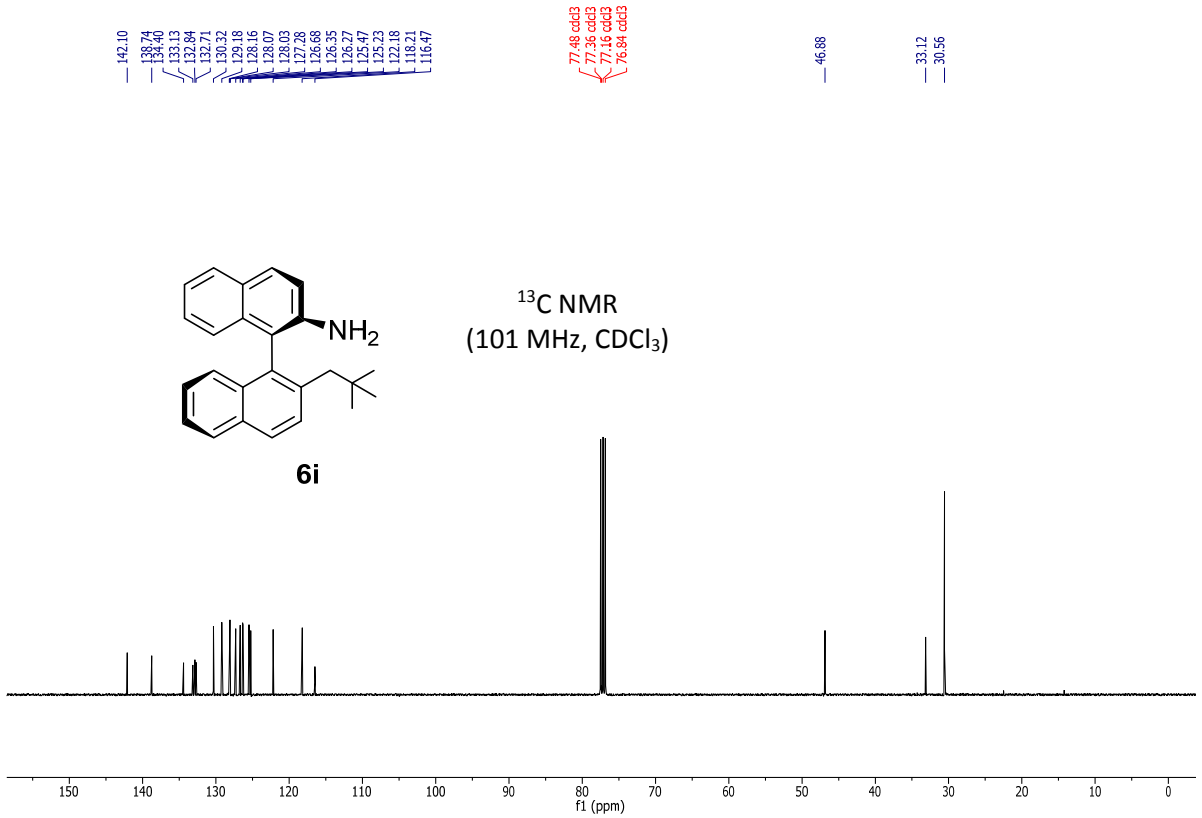
^{13}C NMR
(101 MHz, $CDCl_3$)

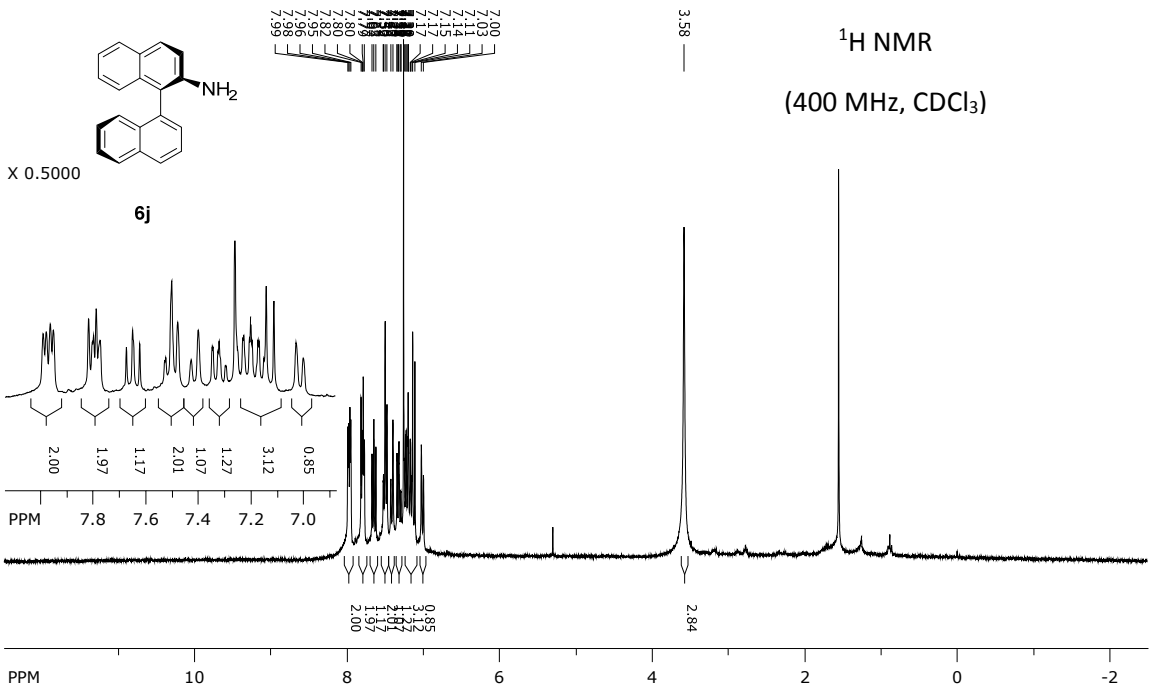


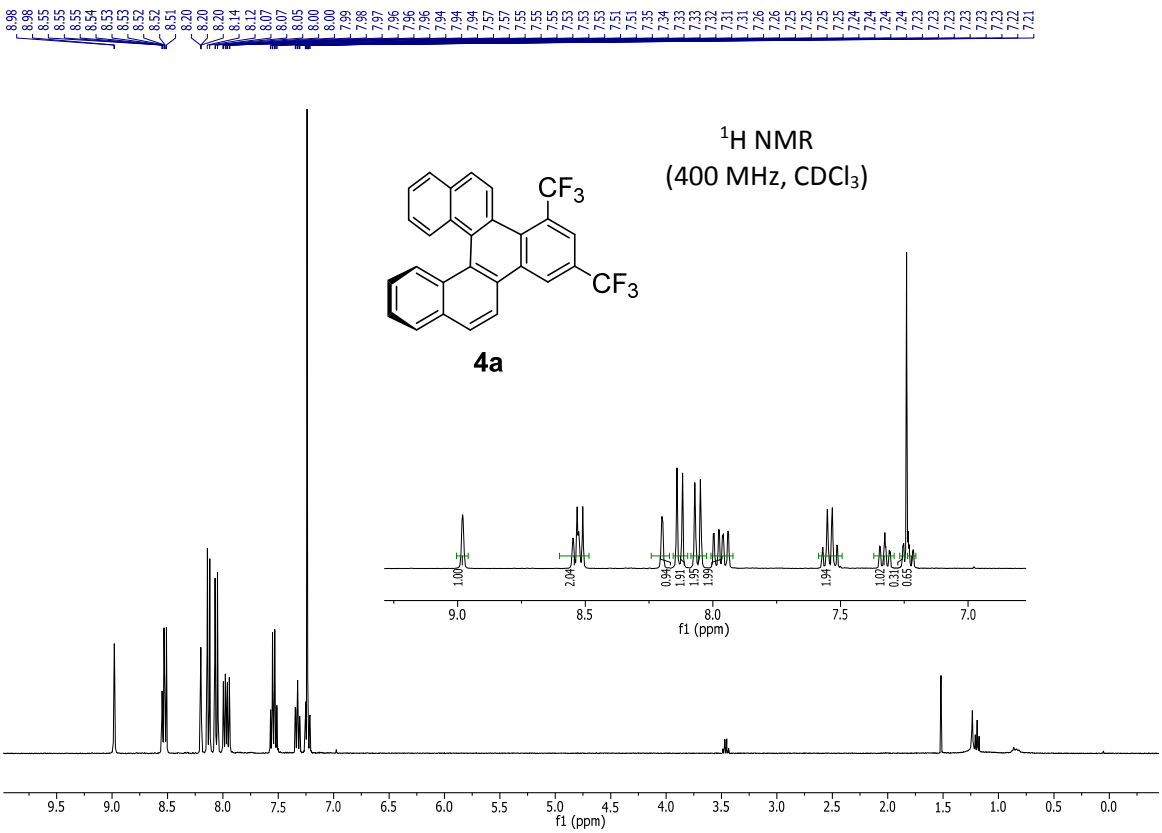

NH2
CF3
CF3
6h
1H NMR
(400 MHz, CDCl3)
PPM
12
10
8
6
4
2
0

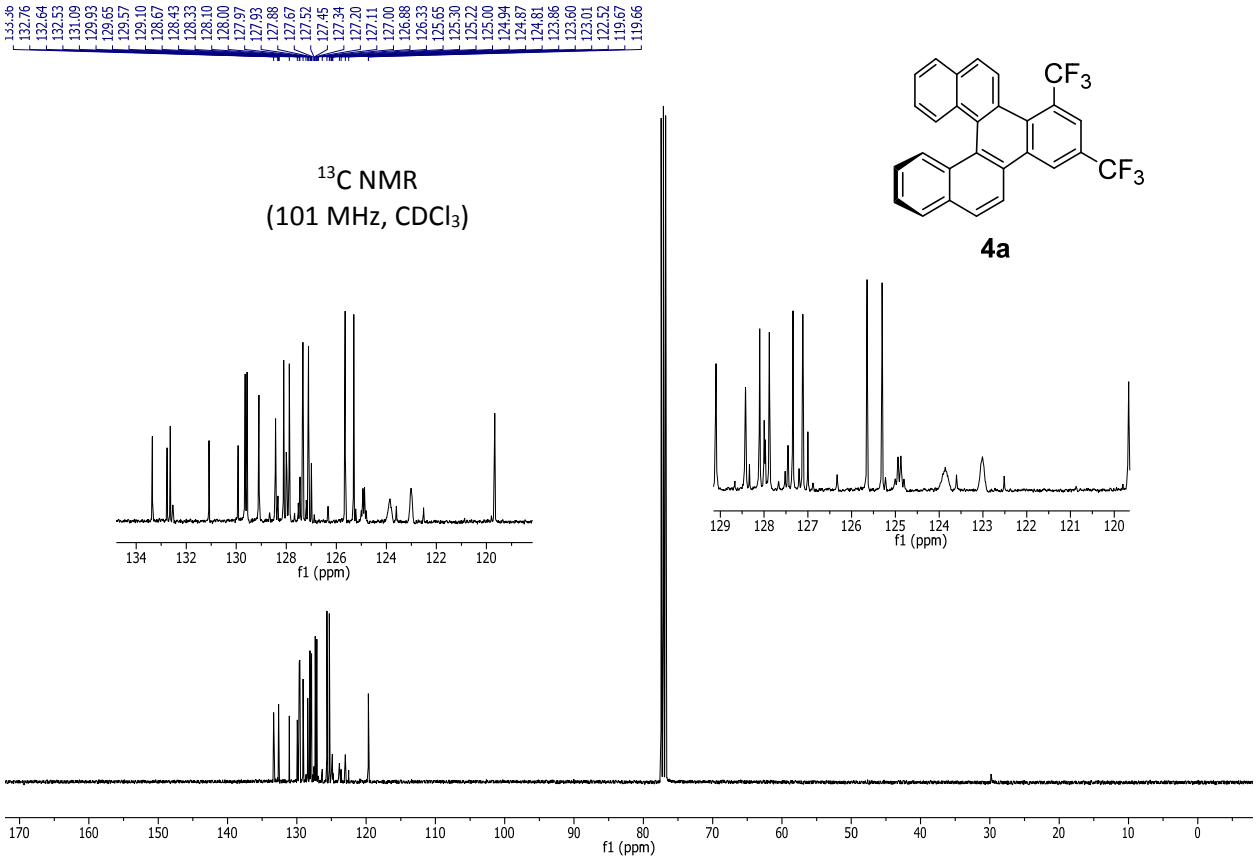

NH2
CF3
CF3
6h
13C NMR
(101 MHz, CDCl3)
PPM
200
160
120
80
40
0

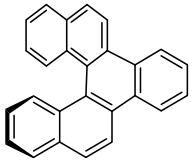

NH2
6i
1H NMR
(400 MHz, CDCl3)
f1 (ppm)


NH2
6i
13C NMR
(101 MHz, CDCl3)
f1 (ppm)


^{1}H NMR
(400 MHz, $CDCl_3$)
NH2
X 0.5000
6j
7.99
7.98
7.96
7.95
7.80
7.80
7.79
7.17
7.15
7.14
7.11
7.03
7.00
3.58
2.00
1.97
1.17
2.01
1.07
1.27
3.12
0.85
PPM
7.8
7.6
7.4
7.2
7.0
0.85
3.12
2.84
PPM
10
8
6
4
2
0
-2

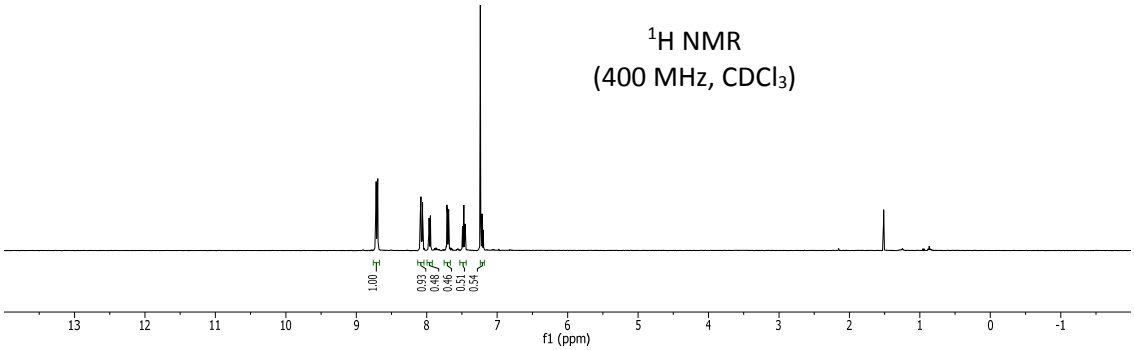

^{1}H NMR
(400 MHz, $CDCl_3$)
CF_3
CF_3
4a
f1 (ppm)

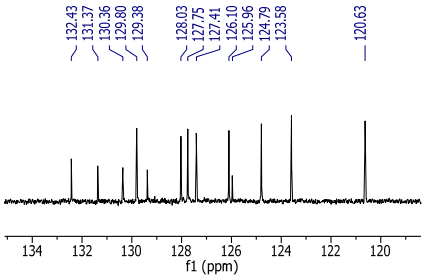

^{13}C NMR
(101 MHz, $CDCl_3$)
CF_3
CF_3
4a
f1 (ppm)

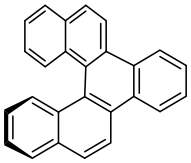


4b

^{1}H NMR
(400 MHz, $CDCl_3$)

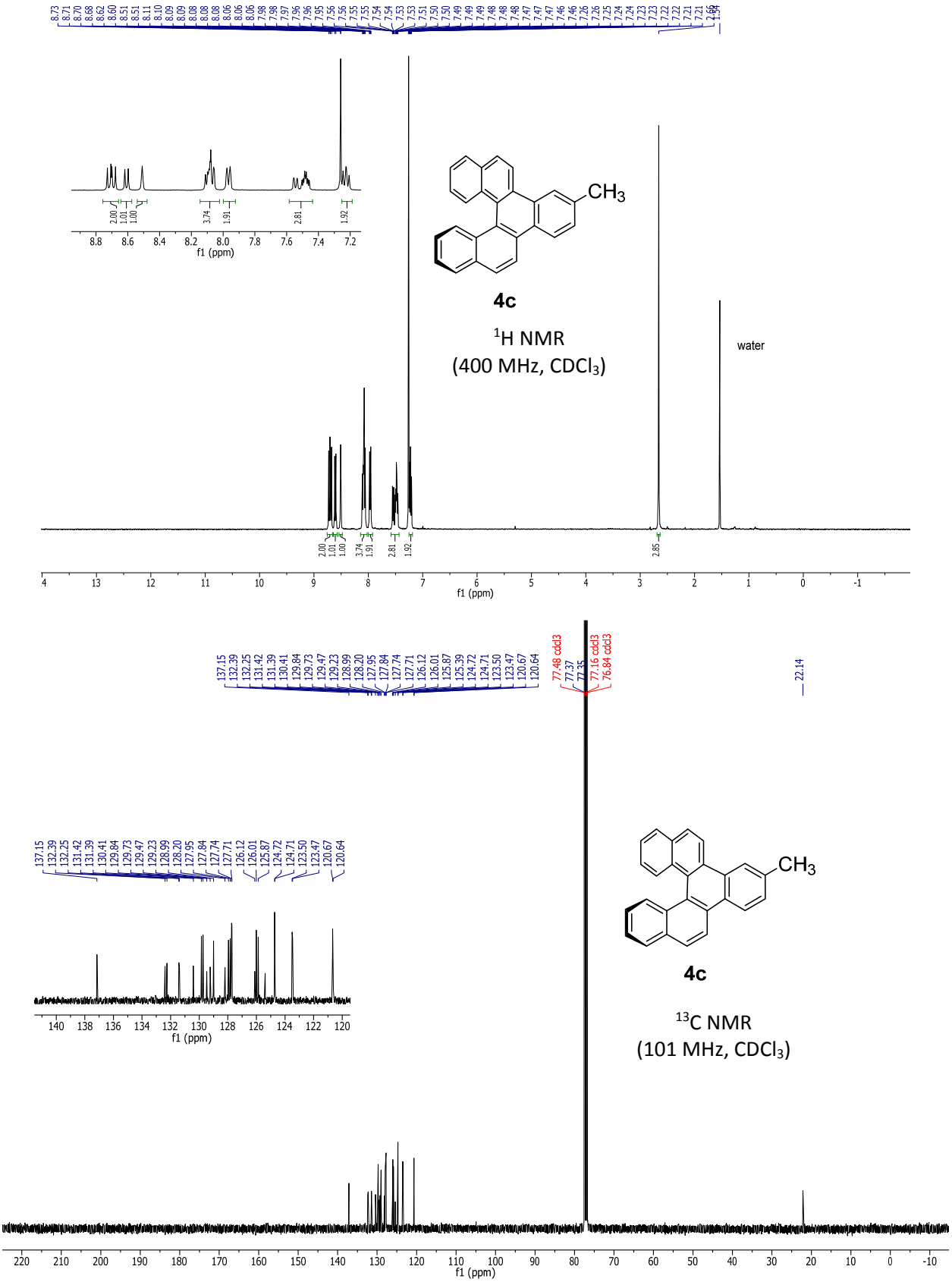


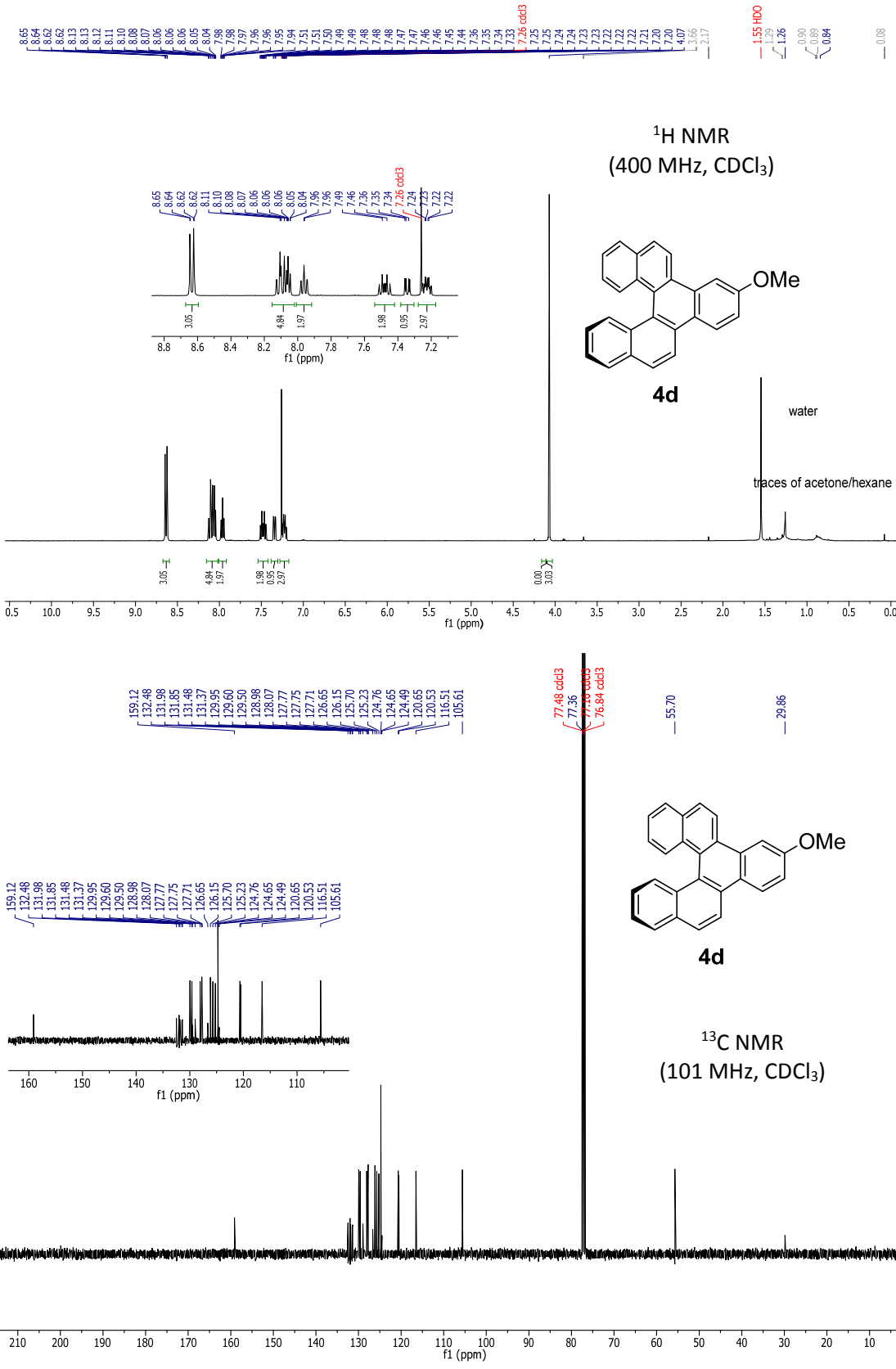


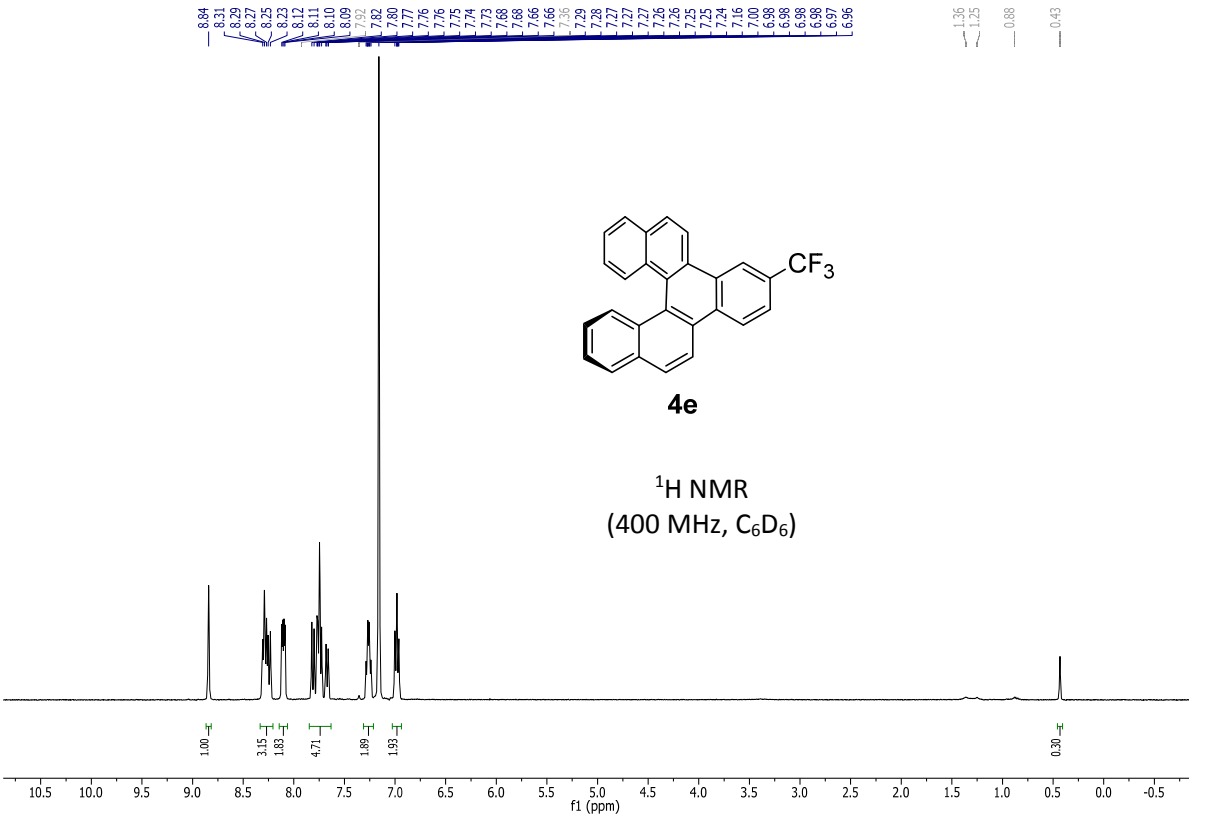


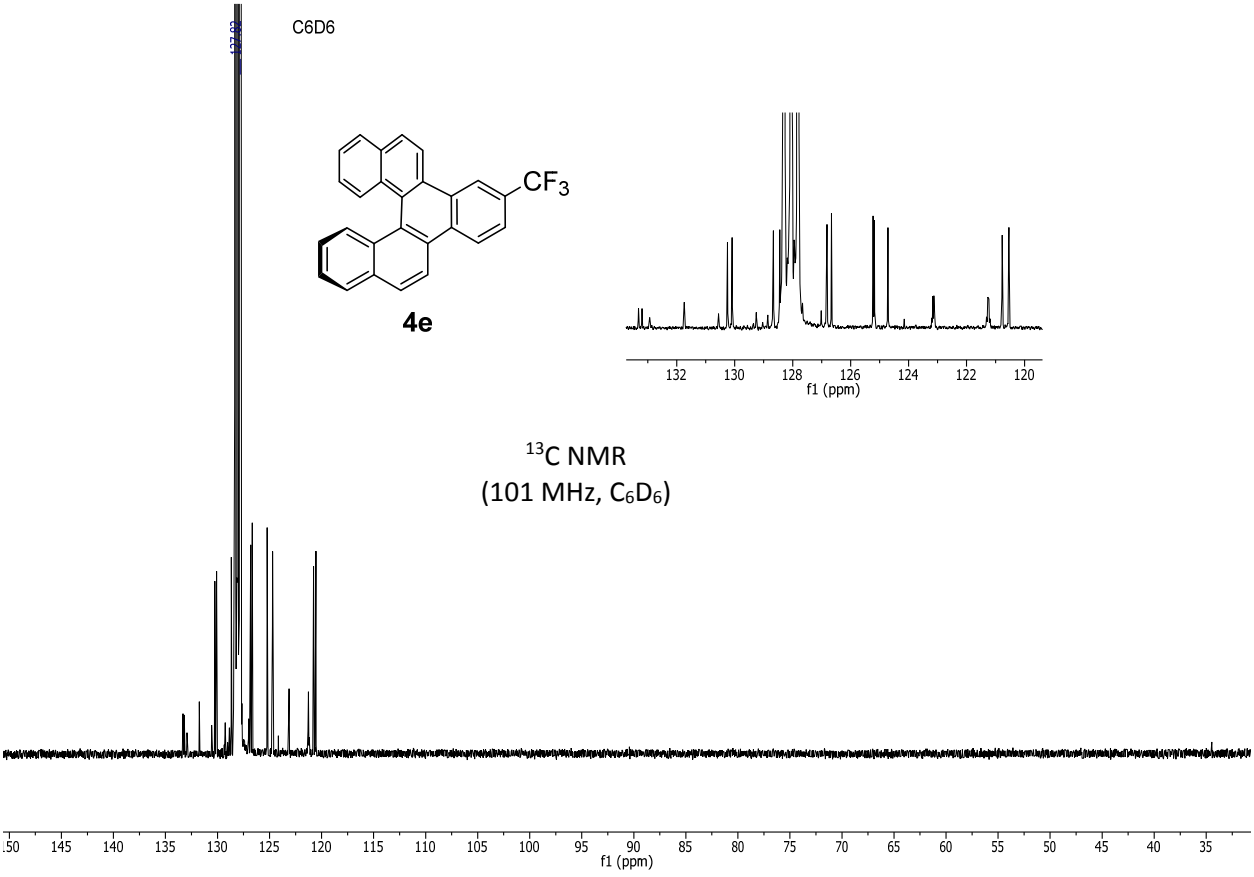
4b

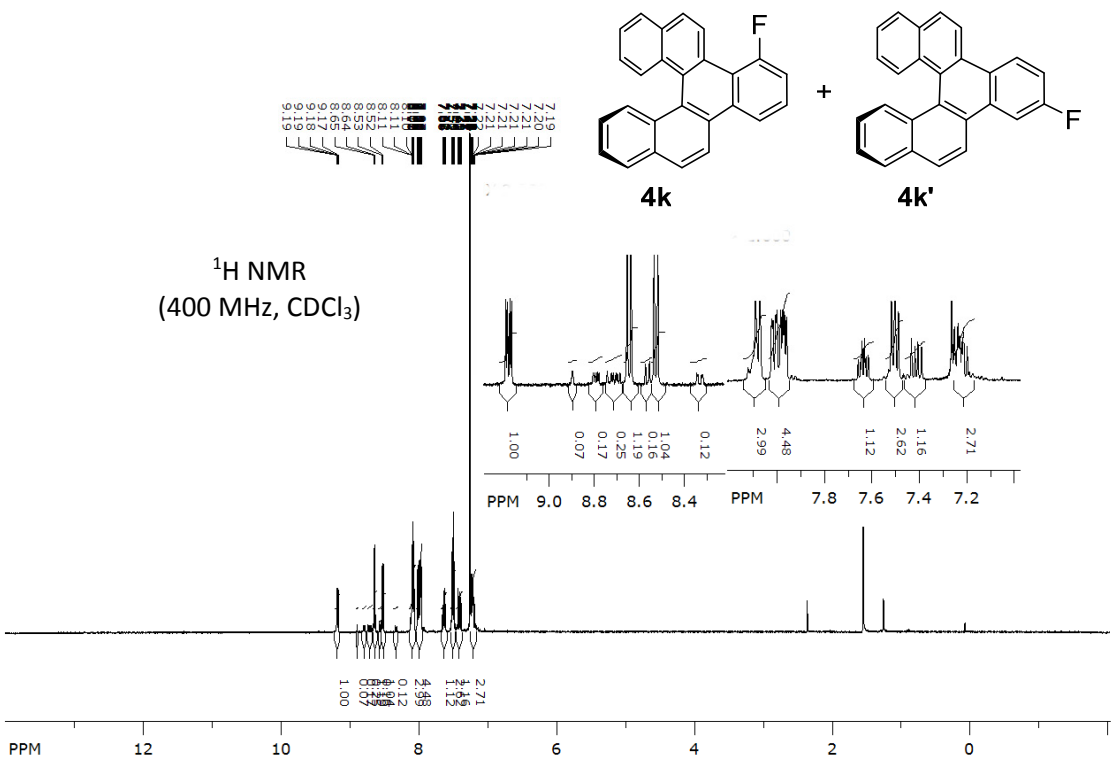
^{13}C NMR
(101 MHz, $CDCl_3$)

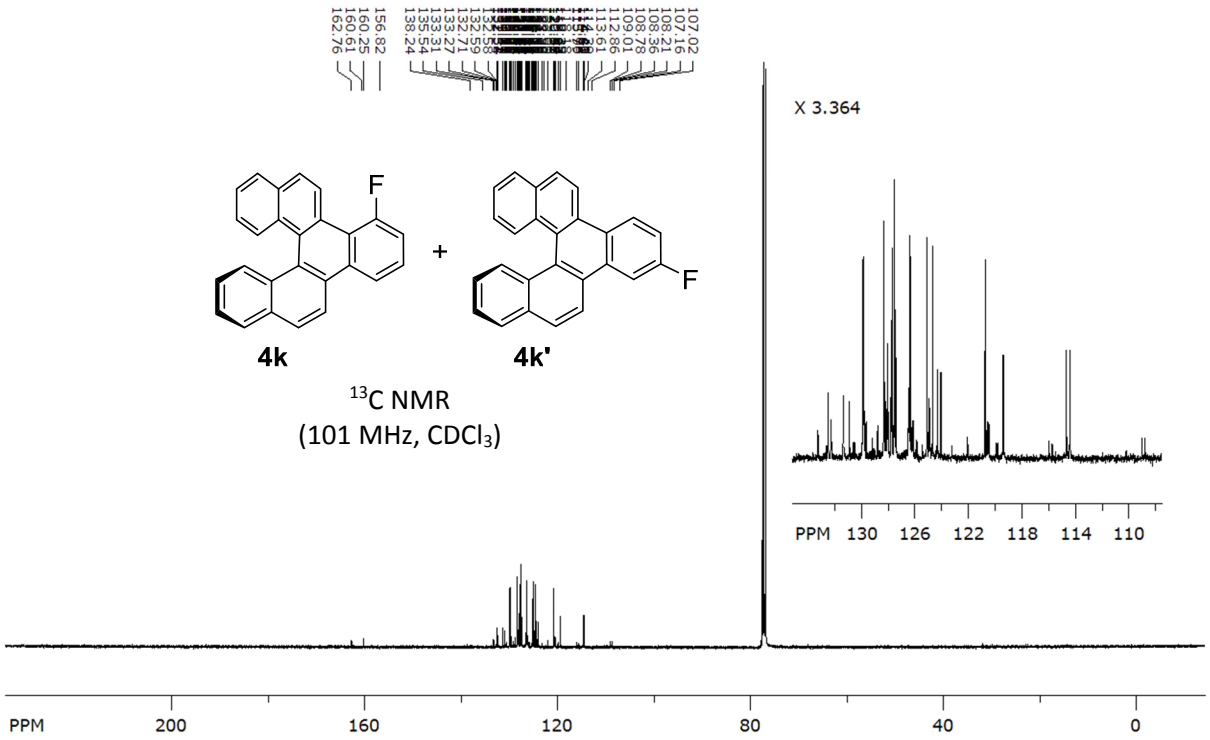

CH3
4c
1H NMR
(400 MHz, CDCl3)
water
f1 (ppm)
CH3
4c
13C NMR
(101 MHz, CDCl3)
f1 (ppm)

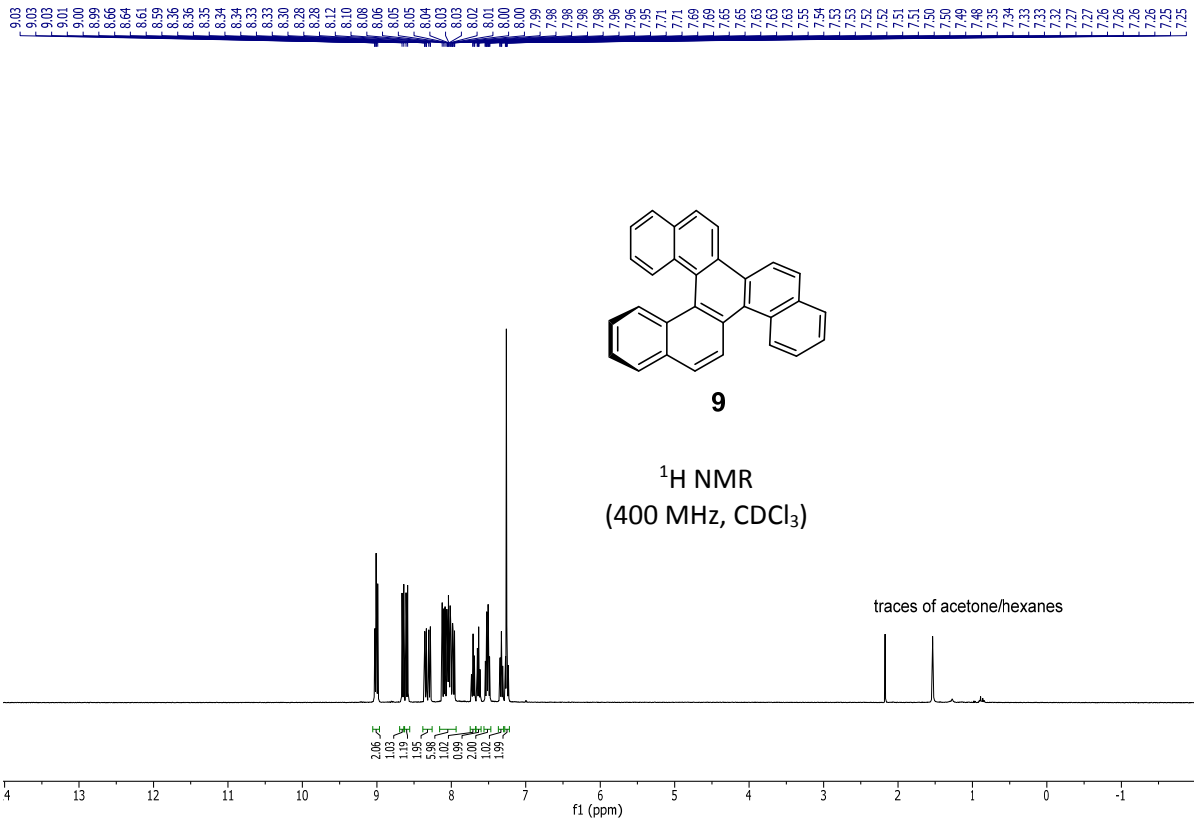

^{1}H NMR
(400 MHz, $CDCl_3$)
OMe
4d
water
traces of acetone/hexane
f1 (ppm)
^{13}C NMR
(101 MHz, $CDCl_3$)
OMe
4d
f1 (ppm)

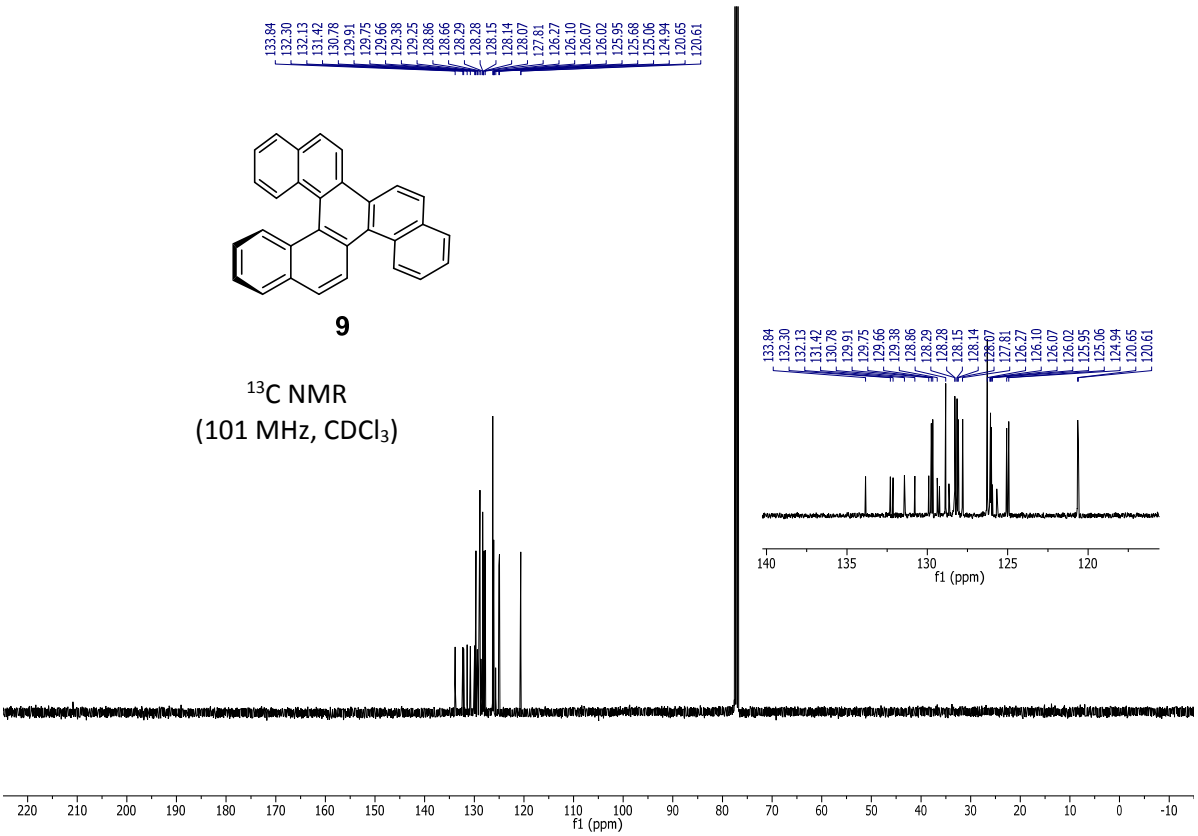

8.84
8.31
8.29
8.27
8.25
8.23
8.12
8.11
8.10
8.09
7.92
7.82
7.80
7.77
7.76
7.76
7.75
7.74
7.73
7.68
7.68
7.66
7.66
7.36
7.29
7.28
7.27
7.27
7.27
7.26
7.26
7.25
7.25
7.24
7.16
7.00
6.98
6.98
6.98
6.98
6.97
6.96
1.36
1.25
0.88
0.43
CF3
4e
1H NMR
(400 MHz, C6D6)
1.00
3.15
1.83
4.71
1.89
1.93
0.30
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


C6D6
CF3
4e
132
130
128
126
124
122
120
f1 (ppm)
13C NMR
(101 MHz, C6D6)
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
f1 (ppm)


F
+
F
4k
4k'
^{1}H NMR
(400 MHz, CDCl$_3$)
PPM 9.0 8.8 8.6 8.4
PPM 7.8 7.6 7.4 7.2
PPM 12 10 8 6 4 2 0


X 3.364
F
+
F
4k
4k'
^{13}C NMR
(101 MHz, CDCl$_3$)
PPM 130 126 122 118 114 110
PPM 200 160 120 80 40 0


9
^{1}H NMR
(400 MHz, $CDCl_3$)
traces of acetone/hexanes
f1 (ppm)


9
^{13}C NMR
(101 MHz, $CDCl_3$)
f1 (ppm)