Supporting Information

Design of Phosphinic Acid Catalysts with the Closest Stereogenicity at α-Position: Synthesis and Application of α-Stereogenic Perfluoroalkyl Phosphinic Acid Catalysts

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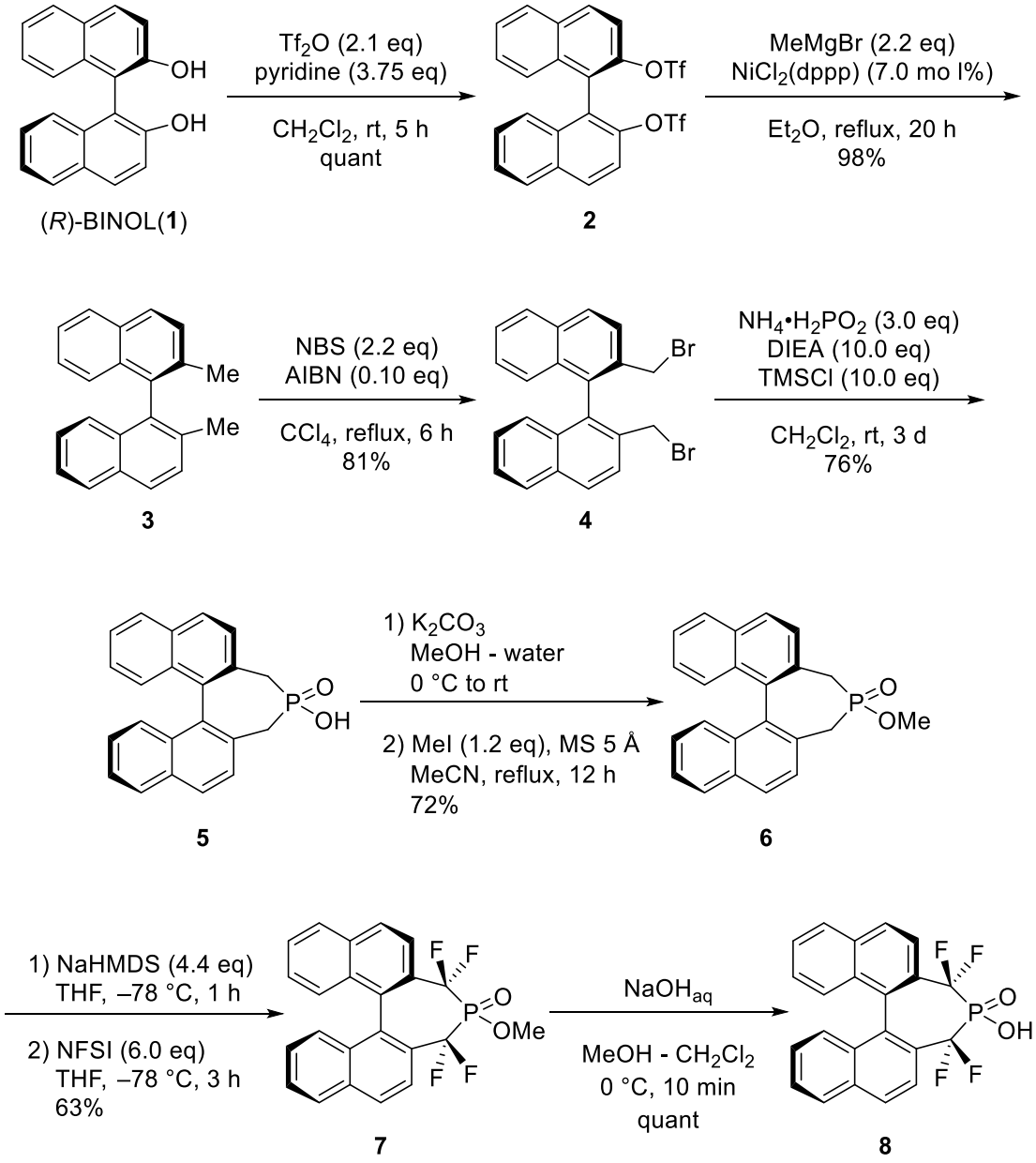
General Information:

^{1}H, ^{13}C, ^{31}P and ^{19}F NMR spectra were measured on Bruker AV300M (300 MHz) spectrometers. Chemical shifts of ^{1}H NMR were expressed in parts per million relative to the singlet (δ = 7.26) for $CDCl_3$, central line of quintet (δ = 2.50) for DMSO-d_6. Chemical shifts of ^{13}C NMR were expressed in parts per million relative to the central line of the triplet (δ = 77.0) for $CDCl_3$ central line of the septet (δ = 39.52) for DMSO-d_6. Chemical shifts of ^{31}P NMR were expressed in parts per million downfield from 85% H_3PO_4 as an external standard (δ = 0.00) in $CDCl_3$. Chemical shifts of ^{19}F NMR were expressed in parts per million downfield from BTF as an external standard (δ = -63.24) in $CDCl_3$. Analytical thin layer chromatography (TLC) was performed on glass plates pre-coated with silica-gel (Merck Kieselgel 60 F254, layer thickness 0.25 mm). Visualization was accomplished by UV light (254 nm), anisaldehyde, $KMnO_4$, phosphomolybdic acid and 2,4-dinitrophenylhydrazine. Column chromatography was performed on KANTO Silica Gel 60N (spherical, neutral). IR spectra were measured on a JASCO FT/IR-4200 spectrometer. High performance liquid chromatography (HPLC) was conducted on JASCO PU-980, LG-980-02, DG-980-50, MD-2010, and CO-966 instrument equipped with model UV-975 spectrometers as an ultra violet light. Peak areas were calculated by JASCO chrom NAV (Windows 7) as an automatic integrator. DAICEL CHIRALPAK DAICEL CHIRALCEL OD-3 was used as chiral columns. Mass spectra were measured on a JEOL JMS-T100CS (Accu-TOF) spectrometer. Optical rotations were measured on a JASCO P-1020. All experiments were carried out under argon atmosphere unless otherwise noted.

Reagents:

Pyridine (dehydrate), dichloromethane (dehydrate), diethyl ether (dehydrate), CCl_4, DMSO (dehydrate), TBME (dehydrate), acetone (dehydrate) MeOH (dehydrate), MeI, acetonitrile (dehydrate) and THF (dehydrate) were purchased from Kanto Chemical Co. Acetylacetone, diisopropylethylamine, indole, $BF_3{\cdot}(OEt_2)$, $B(C_6F_5)_3$, $AlEt_3$, $AlEt_2Cl$, K_2CO_3, phosphinic acid, oxalyl chloride and NaI were purchased from TCI. $NiCl_2$(dppp), MeMgBr, TMSCl, Ammonium hypohosphite, Xtalfluor®-E, TEA·3HF, NFSI, MeLi, NBS, triethylamine and were purchased from Aldrich. $Ti(OiPr_4)_4$, AIBN, $AgNO_3$ and trimethyl orthoformate were perchaced from FUJIFILM Wako Pure Chemical Corporation, TBAF (R)-BINOL and Tf_2O were provided from Takasago International Co. $TMSCF_3$ and C_2F_5I was gifted from TOSOH F-TECH, Inc. Chiral phosphoric acid **21**, **22**[1] and *N*-tosylimine **18**[2] was synthesized according to the reported procedure.

Synthesis of [F4]-Phosphinic acid (8)



(*R*)-2,2'-bis(trifluoromethanesulfonyl)-1,1'-binaphthalene (2)[3]

To a stirred mixture of (*R*)-BINOL (**1**) (2.86 g, 10 mmol) in dichloromethane (80 mL) were added pyridine (3.0 mL, 37.5 mmol) at room temperature followed by trifluoromethanesulfonic anhydride (3.5 mL, 21 mmol) upon slow addition at 0 °C. After stirred for 5 h at room temperature, the reaction mixture was quenched with 1 M HCl_{aq} at 0 °C. After extraction with ethyl acetate, the organic layer was washed with sat. aqueous $NaHCO_3$ and brine. The solvent was dried over $MgSO_4$ and removed *in vacuo*. The resultant residue was purified by flash chromatography on silica gel (hexane/ethyl acetate = 10/1) to give (*R*)-2,2'-bis(trifluoromethanesulfonyl)-1,1'-binaphthalene (**2**) as a white solid (5.55 g, quantitative yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, 2H, *J* = 9.3 Hz), 8.01 (d, 2H, *J* = 8.1 Hz), 7.85 (d, 2H, *J* = 9.1 Hz), 7.62 (d, 2H, *J* = 6.0 Hz), 7.59 (t, 2H, *J* = 7.8 Hz), 7.26 (d, 2H, *J* = 7.8 Hz)

^{13}C NMR (75 MHz, $CDCl_3$) δ 145.4, 133.1, 132.4, 132.0, 128.4, 128.0, 127.3, 126.8, 123.5, 119.3, 118.1 (q, $^1J_{CF}$ = 318.0 Hz)
^{19}F NMR (282 MHz, $CDCl_3$) δ -74.6

(*R*)-2,2'-dimethyl-1,1'-binaphthalene (3) [4]

To a stirred mixture of (*R*)-2,2'-bis(trifluoromethanesulfonyl)-1,1'-binaphthalene (**2**) (5.55g, 10 mmol) and $NiCl_2$(dppp) (379.4 mg, 0.7 mmol) in diethyl ether (80 mL) was added methyl magnesium bromide (13.3 mL, 3.0 M in diethyl ether solution, 40 mmol) at 0 °C over a period of 30 min. The reaction mixture was refluxed for 20 h, and then cooled to room temperature. The reaction was quenched slowly with water and diluted with 1 M HCl_{aq} at 0 °C. After extraction with hexane, the organic layer was washed with sat. aqueous $NaHCO_3$ and brine. The solvent was dried over $MgSO_4$ and removed *in vacuo*. The resultant residue was purified by silica gel column chromatography (hexane/EtOAc = 50/1) to give (*R*)-2,2'-dimethyl-1,1'-binaphthalene (**3**) as a white solid (2.76 g, 98%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.40-8.36 (m, 4H), 8.00 (d, 2H, *J* = 8.4 Hz), 7.88 (t, 2H, *J* = 6.8 Hz), 7.70 (d, 2H, *J* = 8.1 Hz), 7.56 (t, 2H, *J* = 8.5 Hz), 2.54 (s, 6H)
^{13}C NMR (75 MHz, $CDCl_3$) δ 135.2, 134.4, 132.9, 132.3, 128.9, 128.1, 127.6, 126.2, 125.8, 125.0, 20.2

(*R*)-2,2'-bis(bromomethyl)-1,1'-binaphthalene (4) [4]

To a stirred mixture of 2,2'-dimethyl-1,1'-binaphthalene (**3**) (1.80 g, 6.36 mmol) and *N*-Bromosuccinimide (2.26 g, 12.72 mmol) in CCl_4 (60 mL) were added AIBN (104.4 mg, 0.64 mmol) at room temperature. The reaction mixture was refluxed for 2 h, and then cooled to room temperature. The solvent was filtered and removed under reduced pressure. The residue was diluted with ethyl acetate and washed with water and brine. The solvent was dried over $MgSO_4$ and removed *in vacuo*. The residual solid was recrystalized from EtOH/$CHCl_3$ to afford (*R*)-2,2'-bis(bromomethyl)-1,1'-binaphthalene (**4**) (2.27 g, 81%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, 2H, *J* = 8.5 Hz), 7.93 (d, 2H, *J* = 8.1 Hz), 7.76 (d, 2H, *J* = 8.6 Hz), 7.50 (ddd, 2H, *J* = 9.3 , 6.8, 1.1 Hz), 7.28 (ddd, 2H, *J* = 9.7, 6.9, 1.2 Hz), 7.08 (d, 2H, *J* = 8.4 Hz), 4.26 (s, 4H)
^{13}C NMR (75 MHz, $CDCl_3$) δ 134.3, 134.2, 133.3, 132.6, 129.5, 128.1, 127.8, 127.0, 126.9, 126.8, 32.7

(*R*)-4,5-Dihydro-5-hydroxy-3H-dinaphtho-[1,2-c:2′,1′-e]−phosphepine-5-Oxide (5)[5]

To a stirred mixture of $NH_4H_2PO_2$ (2.10 g, 6.10 mmol) in dichloromethane (80 mL) was added DIEA (11.9 mL, 68.14 mmol) at 0 °C. The reaction solution was stirred for 30 min and TMSCl (8.6 mL, 68.08 mmol) was added at 0 °C. The mixture was stirred for 2 h at room temperature and cooled to 0 °C. (*R*)-bis(bromomethyl)-1,1'-binaphthalene (**4**) (3.01 g, 6.84 mmol) in dichloromethane (30 mL) was added. The reaction mixture was stirred for 3 d at room temperature and quenched with water. After extraction with dichloromethane, the organic layer was washed with brine. The solvent was dried over $MgSO_4$ and removed *in vacuo*. The resultant residue was purified

by silica gel column chromatography (dichloromethane to dichloromethane/methanol = 10/1) to give the corresponding phosphinic acid (**5**) (1.82 g, 78%).

^{1}H NMR (300 MHz, DMSO-d^{6}) δ 8.04 (d, 2H, *J* = 7.4 Hz), 8.02 (d, 2H, *J* = 6.8 Hz), 7.62 (d, 2H, *J* = 8.3 Hz), 7.46 (t, 2H, *J* = 7.2 Hz), 7.26 (t, 2H, *J* = 8.1 Hz), 7.01 (d, 2H, *J* = 8.5 Hz), 3.07 (dd, 2H, $^{2}J_{HP}$ = 18.8 Hz, $^{2}J_{HH}$ = 13.9 Hz), 2.67 (dd, 2H, $^{2}J_{HP}$ = 16.0 Hz, $^{2}J_{HH}$ = 14.0 Hz)

^{13}C{^{1}H} NMR (75 MHz, DMSO-d^{6}) δ 132.8, 132.7, 132.1 (d, $^{3}J_{CP}$ = 2.3 Hz), 131.7 (d, $^{2}J_{CP}$ = 9.0 Hz), 131.5 (d, $^{3}J_{CP}$ = 2.3 Hz), 128.6, 128.4, 128.3, 126.1, 125.4, 35.5 (d, $^{1}J_{CP}$ = 86.8 Hz)

^{31}P{^{1}H} NMR (122 MHz, DMSO-d^{6}) δ 61.2

(*R*)- 4-methoxy-3,5-dihydrodinaphtho-[2,1-c:1',2'-e]−phosphepine 4-oxide (6)

To a stirred mixture of phosphinic acid (**5**) (2.1 g, 20.4 mmol) in dichloromethane (25 mL) and methanol (25 mL) were added saturated K_2CO_3 aq (10 mL) at 0 °C. The reaction mixture was stirred for 30 min at room temperature, and solvent was removed. MS 5 Å (5.0 g) and acetonitrile (30 mL) was added to the residue. The mixture was stirred for 1 h at room temperature, and MeI (6.0 mL 36.9 mmol) was added. The reaction mixture was refluxed for 2 h, and then cooled to room temperature. The solvent was filtered and removed *in vacuo*. The resultant residue was purified by silica gel column chromatography (dichloromethane/ethyl acetate = 7/1 to 4/1) to give the corresponding methyl phosphinate (**6**) (1.57 g, 72%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (t, 2H, *J* = 7.9 Hz), 7.93 (d, 2H, *J* = 7.5 Hz), 7.62 (dd, 1H, *J* = 8.4, 1.1 Hz), 7.48-7.42 (m, 3H), 7.27-7.16 (m, 4H), 3.78 (d, 3H, $^{3}J_{HP}$ = 10.8 Hz), 3.22-2.96 (m, 4H)

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 133.6 (d, $^{3}J_{CP}$ = 4.5 Hz), 133.4 (d, $^{3}J_{CP}$ = 3.8 Hz), 132.7 (d, $^{4}J_{CP}$ = 3.0 Hz), 132.5 (d, $^{4}J_{CP}$ = 3.0 Hz), 132.0 (d, $^{4}J_{CP}$ = 2.3 Hz), 132.0 (d, $^{4}J_{CP}$ = 2.3 Hz), 130.1 (d, $^{2}J_{CP}$ = 9.7 Hz), 129.32, 129.29, 129.1, 129.0, 128.1 (d, $^{2}J_{CP}$ = 7.5 Hz), 128.0 (d, $^{3}J_{CP}$ = 4.5 Hz), 127.5 (d, $^{3}J_{CP}$ = 4.5 Hz), 126.8, 126.6, 126.3, 126.2, 125.6, 125.5, 51.2 (d, $^{2}J_{CP}$ = 6.8 Hz), 34.0 (d, $^{1}J_{CP}$ = 87.8 Hz), 33.3 (d, $^{1}J_{CP}$ = 86.2 Hz)

^{31}P{^{1}H} NMR (122 MHz, $CDCl_3$) δ 66.6

FT-IR (KBr pellet, cm^{-1}) 3658, 3470, 3052, 3007, 2950, 2916, 2845, 2229, 1955, 1922, 1594, 1254, 1232, 1037, 848, 836.

HRMS(ESI-TOF) Calcd for $C_{23}H_{19}NaO_2P$ $[M+Na]^+$: 381.1020, Found: 381.1023.

$[\alpha]_D^{25}$ -177.7 (*c* 1.48, $CHCl_3$)

(*R*)- 3,3,5,5-tetrafluoro-4-methoxy-3,5-dihydrodinaphtho[2,1-c:1',2'-e]phosphepine 4-oxide (7)

To a stirred mixture of methyl phosphinate (**6**) (179.2 mg, 0.50 mmol) in THF (15 mL) and was added NaHMDS (2.2 mL in THF, 2.20 mmol) at -78 °C, and the solution was stirred for 1 h. NFSI (946.0 mg, 3.00 mmol) in THF (20 mL) was added to the solution at -78 °C, and then stirred for 3 h. The reaction was quenched with sat. aqueous NH_4Cl at 0 °C. After extraction with ethyl acetate, the organic layer was washed with sat. aqueous $NaHCO_3$ and brine. The solvent was dried over $MgSO_4$, then removed *in vacuo*. The resultant residue was purified bysilica gel column chromatography (dichloromethane/methanol = 50/1 to 30/1) to give the corresponding methyl phosphinate (**7**) (135.1

mg, 63%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, 1H, *J* = 8.5 Hz), 8.13 (d, 1H, *J* = 8.1 Hz), 7.98 (d, 2H, *J* = 8.3 Hz), 7.94 (d, 1H, *J* = 8.8 Hz), 7.84 (d, 1H, *J* = 8.7 Hz), 7.58-7.54 (m, 2H), 7.32-7.27 (m, 2H), 7.16 (d, 1H, *J* = 8.5 Hz), 7.15 (d, 1H, *J* = 8.5 Hz), 4.04 (d, 3H, $^{3}J_{HP}$ = 10.4 Hz)

^{13}C{^{1}H} NMR δ 135.9, 134.7, 134.6, 134.4, 134.3, 132.6, 130.4, 130.1, 129.8, 129.5, 128.5, 128.4, 128.0, 127.4, 127.3, 127.2, 126.9~125.8 (m, 2C), 121.8 (dt, $^{3}J_{CP}$ = 13.6 Hz, $^{3}J_{CF}$ = 2.7 Hz), 121.3 (dt, $^{3}J_{CP}$ = 13.4 Hz, $^{3}J_{CF}$ = 2.7 Hz), 117.88 (tdd, $^{1}J_{CF}$ = 274.4 Hz, $^{1}J_{CP}$ = 142.3 Hz, $^{3}J_{CF}$ = 8.9 Hz), 117.87 (tdd, $^{1}J_{CF}$ = 269.0 Hz, $^{1}J_{CP}$ = 145.3 Hz, $^{3}J_{CF}$ = 9.4 Hz), 55.0 (d, $^{2}J_{CP}$ = 7.6 Hz)

^{19}F NMR (282 MHz, $CDCl_3$) δ -91.2 (dd, 1F, $^{2}J_{FF}$ = 281.4, $^{2}J_{FP}$ = 88.3 Hz), -92.6 (dd, 1F, $^{2}J_{FF}$ = 296.7, $^{2}J_{FP}$ = 115.1 Hz), δ -120.5 (ddd, 1F, $^{2}J_{FF}$ = 280.6 Hz, $^{2}J_{FP}$ = 98.4 Hz, $^{4}J_{FF}$ = 10.0 Hz) -123.4 (ddd, 1F, $^{2}J_{FF}$ = 294.7, $^{2}J_{FP}$ = 92.5 Hz, $^{4}J_{FF}$ = 13.9 Hz,)

^{31}P{^{1}H} NMR (122 MHz, $CDCl_3$) δ 28.3-25.0 (m)

FT-IR (KBr pellet, cm^{-1}) 3658, 3470, 3052, 3007, 2950, 2916, 2845, 2229, 1955, 1922, 1594, 1254, 1232, 1037, 848, 836.

HRMS(ESI-TOF) Calcd for $C_{23}H_{16}F_4O_2P$ $[M+H]^+$: 431.0824, Found: 431.0843.

$[\alpha]_D^{24}$ -177.4 (*c* 12.3, $CHCl_3$)

(*R*)-3,3,5,5-tetrafluoro-4-hydroxy-3,5-dihydrodinaphtho[2,1-c:1',2'-e]phosphepine 4-oxide (8)

To a stirred mixture of methyl phosphinate (**7**) (168.9 mg, 0.39 mmol) in dichloromethane (5 mL) and methanol (5 mL) was added 2 M $NaOH_{aq}$ (5 mL) at 0 °C, and then stirred for 1 h at room temperature. The reaction mixture was quenched with 1 M HCl_{aq} (10 mL) at 0 °C. After extraction with ethyl acetate, the organic layer was washed with brine. The solvent was dried over $MgSO_4$ and removed *in vacuo*. The resultant residue was purified by silica gel column chromatography (dichloromethane to dichloromethane/methanol = 10/1). The solid was dissolved in dichloromethane and washed with 3 M HCl_{aq}. The solvent was removed *in vacuo* to give the corresponding phosphinic acid (**8**) (163.0 mg, quantitative yield).

^{1}H NMR (300 MHz, DMSO-d^6) δ 8.20 (d, 2H, *J* = 8.3 Hz), 8.09 (d, 2H, *J* = 8.1 Hz), 7.77 (d, 2H, *J* = 8.4 Hz), 7.57 (t, 2H, *J* = 7.2 Hz), 7.33 (t, 2H, *J* = 7.9 Hz), 7.00 (d, 2H, *J* = 8.4 Hz), 5.47 (brs, 1H)

^{13}C{^{1}H} NMR (75 MHz, DMSO-d^6) δ 133.8, 133.7 (d, $^{3}J_{CP}$ = 6.0 Hz), 132.3, 130.1, 129.6, 128.8, 127.5 (d, $^{2}J_{CP}$ = 12.9 Hz), 126.9, 122.3, 122.1, 119.8 (tdt, $^{1}J_{CF}$ = 272.3 Hz, $^{1}J_{CP}$ = 135.9 Hz, $^{3}J_{CF}$ = 10.6 Hz,)

^{19}F NMR (282 MHz, DMSO-d^6) δ -85.9 (dd, 2F, $^{2}J_{FF}$ = 279.5, $^{2}J_{FP}$ = 83.2 Hz), -119.4 (dd, 2F, $^{2}J_{FF}$ = 280.0, $^{2}J_{FP}$ = 87.7 Hz)

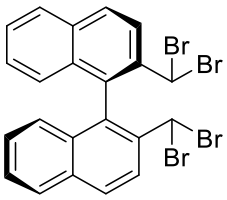
^{31}P{^{1}H} NMR (122 MHz, $CDCl_3$) δ 21.6 (tt, J_{FP} = 86.3 Hz, 85.1 Hz)

FT-IR (KBr pellet, cm^{-1}) 3650, 3347, 3068, 2216, 1929, 1647, 1333, 1249, 1150, 1063, 819, 655, 561.

HRMS(ESI-TOF) $C_{22}H_{12}F_4O_2P$ $[M-H]^-$: 415.0511, Found: 415.0497.

$[\alpha]_D^{23}$ = -130.9 (*c* 0.43, $CHCl_3$)

(*R*)-2,2'-bis(dibromomethyl)-1,1'-binaphthalene (9)[4]

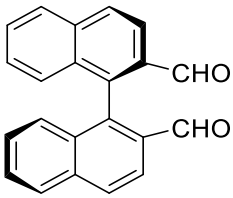


To a stirred mixture of (*R*)-2,2'-dimethyl-1,1'-binaphthalene (**3**) (2.24 g, 7.93 mmol) and *N*-bromosuccinimide (15.7 g, 88 mmol) in CCl_4 (40 mL) was added AIBN (65.6 mg, 0.4 mmol) at room temperature. The reaction mixture was refluxed 12 h, and then cooled to room temperature. The solvent was filtered and removed under reduced pressure. The residue was diluted with ethyl acetate and washed with water and brine. The solvent was dried over $MgSO_4$ and removed *in vacuo*. The residual solid was recrystalized from EtOH/$CHCl_3$ to afford (*R*)-2,2'-bis(dibromomethyl)-1,1'-binaphthalene (**9**) as a white solid (4.17g, 88%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (d, 2H, *J* = 8.7 Hz), 8.17 (d, 2H, *J* = 8.7 Hz), 7.97 (d, 2H, *J* = 8.1 Hz), 7.55 (ddd, 2H, *J* = 8.0, 6.9, 1.1 Hz), 7.32 (ddd, 2H, *J* = 8.3, 7.0, 1.2 Hz), 7.04 (d, 2H, *J* = 8.4 Hz), 6.26 (s, 2H)

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 138.2, 133.7, 130.8, 130.7, 128.2, 127.9, 127.8, 127.6, 127.5, 126.5, 39.1

(*R*)-1,1'-binaphthl-2,2'-dicarbaldehyde (10)[4]

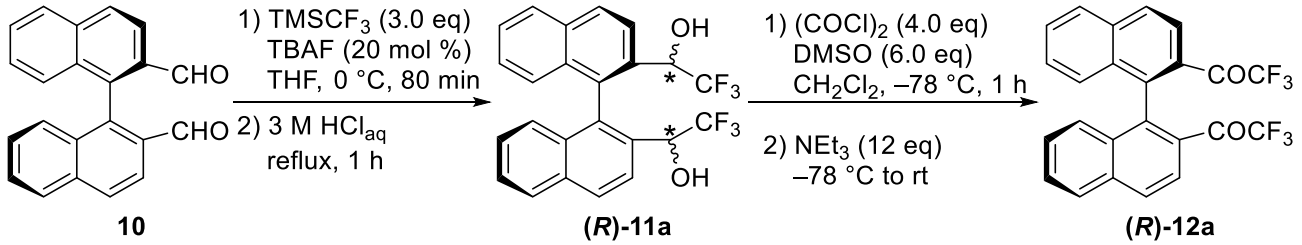


To a stirred mixture of (*R*)-2,2'-bis(dibromomethyl)-1,1'-binaphthalene (**9**) (4.17 g, 6.97 mmol) in THF (70 mL) and water (35 mL) was added $AgNO_3$ (5.95 g, 35 mmol) at room temperature. The reaction mixture was refluxed for 4 h, and then cooled to room temperature. The reaction mixture was filtered and quenched with brine at 0 °C. After extraction with ethyl acetate, the organic layer was washed with sat. aqueous $NaHCO_3$ and brine. The solvent was dried over $MgSO_4$ and removed *in vacuo.* The resultant residue was purified by silica gel column chromatography (hexane/EtOAc = 50/1 to 30/1) to give (*R*)-1,1'-binaphthl-2,2'-dicarbaldehyde (**10**) as a yellow solid (2.12 g, 98%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.62 (s, 2H), 8.21 (d, 2H, *J* = 8.4 Hz), 8.13 (d, 2H, *J* = 8.4 Hz), 8.02 (d, 2H, *J* = 8.1 Hz), 7.64 (ddd, 2H, *J* = 8.1, 6.9, 1.1 Hz), 7.37 (ddd, 2H, *J* = 8.4, 6.9, 1.2 Hz), 7.24 (d, 2H, *J* = 8.4 Hz)

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 191.3, 139.8, 136.1, 133.6, 133.4, 129.9, 129.6, 128.7, 128.1, 127.4, 122.4

(*R*)-1,1′-(1,1′-binaphthalene-2,2′-diyl)-bis(2,2,2-trifluoroethanone) (12a)[6]



To a stirred mixture of (*R*)-1,1’-binaphthl-2,2’-dicarbaldehyde (**10**) (1.02 g, 3.3 mmol) and $TMSCF_3$ (1.5 mL, 9.9 mmol) in THF (35 mL) were added terabutylammonium fluoride (660 µL, 0.66 mmol) at 0 °C. After stirred for 80 min at 0 °C, the reaction mixture was quenched with 3 M HCl_{aq}, and refluxed for 3 h. After cooling to room temperature, the solution was extracted with ethyl acetate and the organic layer was washed with sat. aqueous $NaHCO_3$ and brine. The solvent was dried over Na_2SO_4 and removed *in vacuo*.

To a solution of oxalyl chroride (1.13 mL, 13.2 mmol) in CH_2Cl_2 (6.6 mL) was added DMSO (1.40 mL, 19.8 mmol) slowly at -78 °C and stirred for 5 min. To the reaction mixture was added the solution of obtained diol in CH_2Cl_2 (6.6 mL) slowly at -78 °C. After stirred for 1h, triethylamine (5.50 mL, 39.6 mmol) was added to this mixture. After warmed to room temperature, the reaction mixture was diluted with CH_2Cl_2 and quenched with sat. aqueous NH_4Cl. The organic layer was separated, and then the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine twice and dried over $MgSO_4$. The solvent was removed *in vacuo*, and the resultant residue was purified by silica gel column chromatography (hexane/EtOAc = 100/1) to give (*R*)-1,1′-(1,1′-binaphthalene-2,2′-diyl)-bis(2,2,2-trifluoroethanone) as a yellow solid (**(*R*)-12a**) (1.08 g, 73% in two steps).

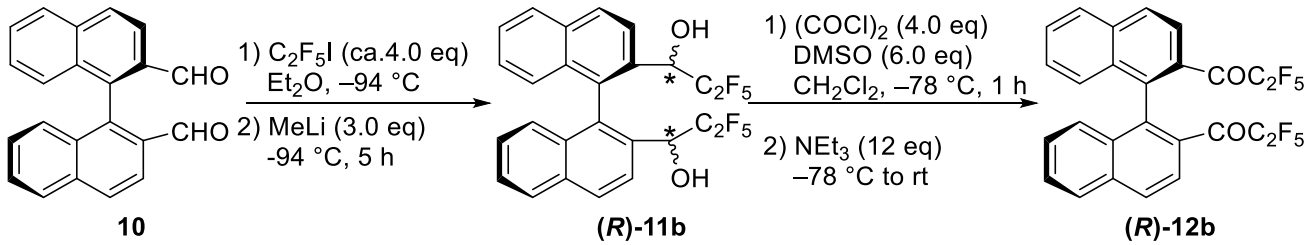
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16-8.12 (m, 4H), 8.01 (d, 2H, J = 8.3 Hz), 7.62 (ddd, 2H, J = 8.0, 6.9, 1.0 Hz), 7.32 (ddd, 2H, J = 8.3, 6.9, 1.2 Hz), 7.06 (d, 2H, J = 8.6 Hz)

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 181.4 (q, $^2J_{CF}$ = 34.5 Hz), 141.2, 135.7, 132.9, 129.5, 128.9, 128.4, 127.9, 127.3, 127.1, 124.1 (q, $^3J_{CF}$ = 4.5 Hz), 116.4 (q, $^1J_{CF}$ = 291.0 Hz)

^{19}F NMR (282 MHz, $CDCl_3$) δ -71.6

$[\alpha]_D^{26}$ -65.7 (*c* 0.74, $CHCl_3$)

(*R*)-1,1'-([1,1'-binaphthalene]-2,2'-diyl)bis(2,2,3,3,3-pentafluoropropan-1-one) (12b)[7]



To a stirred mixture of (*R*)-1,1'-binaphthl-2,2'-dicarbaldehyde (**10**) (1.40 g, 4.52 mmol) in Et_2O (35 mL) was added pentafluoroethyl iodide (ca. 18.1 mmol) at -94 °C. After stirred for 5min at -94 °C, methyllitium/lithium bromide solution (1.5 M in diethyl ether, 12.1 mL, 18.1 mmol) was added slowly. After stirred for 5 h, the reaction mixture was quenched with 1 M HCl_{aq}. The organic layer was extracted with ethyl acetate and washed with and brine. The solvent was dried over Na_2SO_4 and removed *in vacuo*.

To a solution of oxalyl chroride (1.55 mL, 18.1 mmol) in CH_2Cl_2 was added DMSO (1.85 mL, 26.12 mmol) slowly at –78 °C and stirred for 5 min. To the reaction mixture was added the solution of obtained diol in CH_2Cl_2 (23 mL) slowly at -78 °C. After stirred for 1h, triethylamine (7.56 mL,54.2 mmol) was added to this mixture. After warmed to room temperature, the reaction mixture was diluted with CH_2Cl_2 and quenched with sat. aqueous NH_4Cl. The organic layer was separated, and then the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine twice and dried over $MgSO_4$. The solvent was removed *in vacuo*, and the resultant residue was purified by silica gel column chromatography (hexane/EtOAc = 100/1) to give (*R*)-1,1'-([1,1'-binaphthalene]-2,2'-diyl)bis(2,2,3,3,3-pentafluoropropan-1-one)as a yellow solid (**(*R*)-12b**) (2.01 g, 82% in two steps).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14-8.08 (m, 4H), 7.995 (d, 2H, *J* = 8.2 Hz), 7.61 (ddd, 2H, *J* = 8.0, 7.6, 1.0 Hz), 7.33 (ddd, 2H, *J* = 8.5, 6.9, 1.2 Hz), 7.08 (d, 2H, *J* = 8.6 Hz)

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 184.9 (t, $^2J_{CF}$ = 26.3 Hz), 140.2, 135.5, 133.1, 129.4, 128.9, 128.8, 127.9, 127.4, 123.7(t, $^3J_{CF}$ = 5.3 Hz), 118.0 (qt, $^1J_{CF}$ = 285.0 Hz $^2J_{CF}$ = 33.8Hz), 108.1 (tq, $^1J_{CF}$ = 288.8 Hz $^2J_{CF}$ = 36.8 Hz)

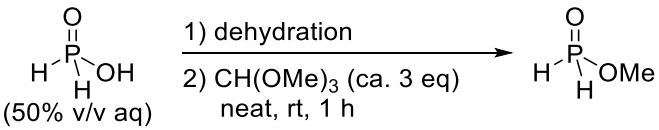
^{19}F NMR (282 MHz, $CDCl_3$) δ -81.4, 114.9

FT-IR (KBr pellet, cm^{-1}) 3415, 3068, 2360, 2341, 1718, 1620, 1591, 1349, 1315, 1220, 1180, 1140, 1092, 968, 951, 924, 828, 802, 794, 760, 741, 731, 654

HRMS(APCI-TOF) Calcd for $C_{26}H_{12}F_{10}O_2$ $[M-H]^+$: 547.07559, Found: 547.07626

$[\alpha]_D^{21}$ = -2532.6 (*c* 0.01, $CHCl_3$)

Preparation of methyl phosphinate (13)



To prepare anhydrous phosphinic acid, the stirring mixture of aqueous phosphinic acid (15.0 mL, 50% v/v aq) was evacuated for 30 min at 40 °C, and then azeotroped with anhydrous toluene.

To the anhydrous phosphinic acid was added trimethyl orthoformate (40.0 mL) at room temperature, and the solution was stirred for 1 h at room temperature.

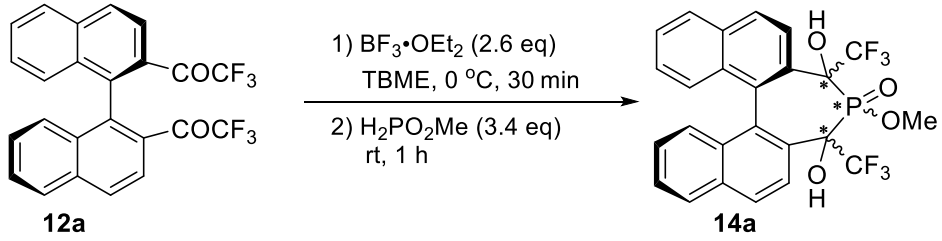
Remaining trimethyl orthoformate and methanol was removed under reduced pressure (This process is performed just before carrying out the next cycloaddition reaction, due to avoid the decomposition of methyl phosphinate (**13**)). After removed trimethyl orthoformate and methanol, methyl phosphinate was collected in a cold trap under reduced pressure. Solvent (10 mL) was added

to obtain the solution of methyl phosphinate (**13**). The conversion of phosphinic acid (>99%) and the concentration of methyl phosphinate (**13**) was determined by ^{1}H and ^{31}P NMR analysis using dichloromethane (10 μL, 0.157 mmol) as an internal standard in solution (0.5 mL sample) and sealed capillary filled with benzene-d_6 for signal lock.

^{1}H NMR (300 MHz, THF, benzene-d_6 for signal lock) δ 7.55 (d, 2H, $^{1}J_{HP}$ = 564.5 Hz), 4.29 (d, 3H, $^{3}J_{HP}$ = 12.8 Hz)

$^{31}P\{^{1}H\}$ NMR (122 MHz, THF, benzene-d_6 for signal lock) δ 17.4

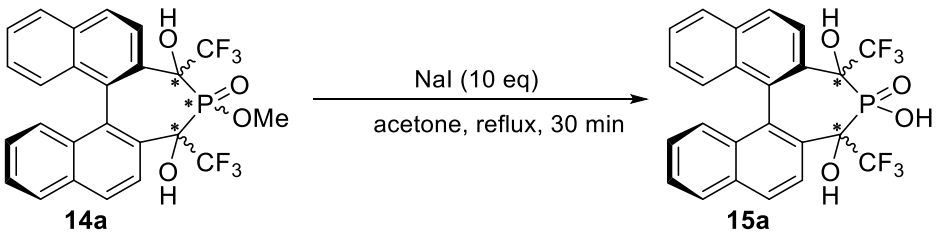
Synthesis of diol (14a)



12a **14a**

To a stirred mixture of diketone **12a** (34.6 mg, 0.08 mmol) in TBME (1.0 mL) was added BF_3·OEt_2 (24.7 μL, 0.2 mmol) at 0 °C, and then the mixture was stirred for 30 min. After methyl phosphinate (16a) or (16b) (96.7 μL, 2.7 M in TBME, 0.3 mmol) was added at 0 °C, the reaction mixture was stirred for 1 h at room temperature. After confirming the completion of reaction by TLC analysis, the reaction mixture was quenched with 1 M $HCl_{aq.}$ The reaction mixture was extracted with ethyl acetate, and organic layer was washed with brine. The solvent was dried over Na_2SO_4 and removed *in vacuo* to give the corresponding diastereomer of diol (**14a**) (84%, *dr* = 9.5:1:2.4:1.6). The yields and diastereoratio of diastereomer was determined by ^{19}F and ^{31}P NMR analysis.

Deprotection of diol(14a)

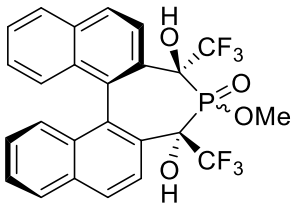


14a **15a**

To a stirred mixture of methyl phosphinate (**14a**) (0.0655 mmol, d1:d2:d3:d4 = 9.5:1:2.4:1.6) in acetone (2.0 mL) was added sodium iodide (108.1 mg, 0.655 mmol) at room temperature. The reaction mixture was stirred for 30 min at room temperature, and quenched with 1 M HCl_{aq}. The organic layer was extracted with dichloromethane and washed with 1 M $HCl_{aq.}$ The solvent was dried over $MgSO_4$ and removed in vacuo. (79.4 mg, 77%). The yield was determined by ^{19}F NMR analysis using benzotrifluoride (10 μL, 0.0814 mmol) as an internal standard.

Isolation of diastereomer 1 and 2

diastereomer d2



Purification of diol (**14a**) by silica gel column chromatography (hexane/ethyl acetate = 10/1) and recrystallization (chloroform/hexane) gives the corresponding isomer of diol **d2**.

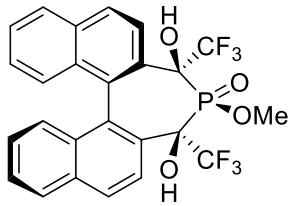
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, 2H, *J* = 8.9 Hz), 7.92 (d, 2H, *J* = 8.3 Hz), 7.81 (t, 2H, *J* = 9.5 Hz), 7.50 (t, 2H, *J* = 7.1 Hz), 7.30-7.22 (m, 2H), 7.09 (d, 1H, *J* = 14.5 Hz), 7.06 (d, 1H, *J* = 14.4 Hz), 3.98 (d, 3H, *J* = 10.2 Hz), 3.37 (d, 1H, *J* = 9.1 Hz), 2.55 (d, 1H, *J* = 11.9 Hz)

^{19}F NMR (282MHz, $CDCl_3$) δ -67.7 (s, 3F), -67.8 (s, 3F)

^{31}P{^{1}H} NMR (122MHz, $CDCl_3$) δ 40.3

HRMS(ESI-TOF) Calcd for $C_{25}H_{17}F_6NaO_4P$ $[M+Na]^+$: 549.0666, Found: 549.0677.

diastereomer d3



Purification of diol (**14a**) by silica gel column chromatography (hexane/ethyl acetate = 10/1) and recrystallization (chloroform/hexane) gives the corresponding isomer of diol **d3**.

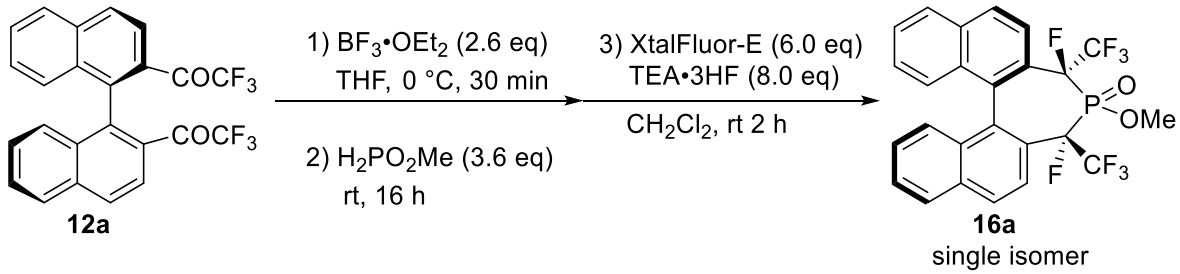
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (dd, 1H, *J* = 9.0, 1.5 Hz), 8.04 (q, 2H, *J* = 4.5 Hz), 7.91 (dd, 2H, *J* = 7.8, 3.3 Hz), 7.77 (d, 1H, *J* = 8.7 Hz), 7.49 (dd, 2H, *J* = 11.7, 7.5 Hz), 7.22-7.16 (m, 2H), 6.98 (d, 1H, *J* = 8.4 Hz), 6.84 (d, 1H, *J* = 8.4 Hz), 4.99 (d, 1H, *J* = 10.8 Hz), 3.88 (d, 3H, *J* = 10.8 Hz), 3.28 (d, 1H, *J* = 8.7 Hz)

^{19}F NMR (282MHz, $CDCl_3$) δ -67.9 (s, 3F), -70.5 (s, 3F)

^{31}P{^{1}H} NMR (122MHz, $CDCl_3$) δ 46.7

HRMS(ESI-TOF) Calcd for $C_{25}H_{17}F_6NaO_4P$ $[M+Na]^+$: 549.0666, Found: 549.0649.

(3*R*,5*R*)-3,5-difluoro-4-methoxy-3,5-bis(perfluoroethyl)-3,5-dihydrodinaphtho[2,1-c:1',2'-e]phosphepine 4-oxide(16a)



To a stirred mixture of (*R*)-diketone **12a** (446.4 mg, 1.0 mmol) in THF (0.25 mL) was treated with addition/cyclization sequence (described above), to obtain the diastereomer of diol (**14a**) (94%, *dr* = 58:6:18:11). The yields and diastereoratio of diastereomer was determined by ^{31}P NMR analysis.

To a stirred mixture of the corresponding diol in CH_2Cl_2 (30 mL) were added XtalFluor-E® (1.4 g, 6.0 mmol) and TEA·3HF (666 µL, 4.0 mmol) at 0 °C, and then the reaction mixture was stirred for 30 min at room temperature. The reaction mixture was quenched with water at 0 °C. The organic layer was extracted with CH_2Cl_2 and washed with brine. The solvent was dried over Na_2SO_4 and removed *in vacuo*. The resultant residue was purified by silica gel column chromatography (hexane/ethyl acetate =20/1 to 10/1) to give the corresponding methyl phosphinate (**16a**) (299.4 mg, 57% in two steps).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, 2H, *J* = 8.8 Hz), 7.96 (d, 2H, *J* = 8.2 Hz), 7.78 (d, 1H, *J* = 7.9 Hz), 7.75 (d, 1H, *J* = 9.0 Hz), 7.58-7.52 (m, 2H), 7.32-7.25 (m, 2H), 7.11 (t, 2H, *J* = 9.5 Hz), 3.98 (d, 3H, $^3J_{HP}$ = 10.7 Hz)

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 137.7 (d, $^3J_{CF}$ = 3.0 Hz), 137.4 (d, $^3J_{CF}$ = 1.5 Hz), 133.9, 133.7, 133.1 (d, $^3J_{CF}$ = 1.5 Hz), 133.1 (d, $^3J_{CF}$ = 1.5 Hz), 131.0, 130.3, 130.0, 129.8, 128.9, 128.2, 128.1, 127.5, 127.3, 122.23 (qdd, $^1J_{CF}$ = 287.7 Hz $^2J_{CF}$ = 27.6 Hz $^2J_{CP}$ = 4.2 Hz), 122.21 (qdd, $^1J_{CF}$ = 286.9 Hz $^2J_{CF}$ = 27.0 Hz $^2J_{CP}$ = 5.1 Hz), 122.3-121.9 (m), 97.4-92.2 (m, 2C), 54.9 (d, $^2J_{CP}$ = 7.6 Hz)

^{19}F NMR (282 MHz, $CDCl_3$) δ -67.3 (d, 3F, $^3J_{FF}$ = 8.5 Hz), -67.4 (d, 3F, $^3J_{FF}$ = 6.8 Hz), -151.9 (d, 1F, $^2J_{FP}$ = 60.1 Hz), -159.2 (d, 1F, $^2J_{FP}$ = 84.6 Hz)

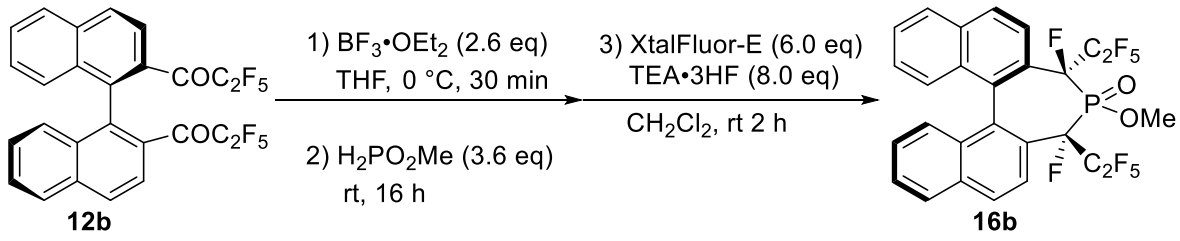
^{31}P{^{1}H} NMR (122 MHz, $CDCl_3$) δ 30.9 (dd, $^2J_{PF}$ = 86.3, 63.8 Hz)

FT-IR (KBr pellet, cm^{-1}) 3068, 2965, 2928, 2860, 2254, 1915, 1820, 1728, 1597, 1510, 1465, 1377, 1197, 1062, 1032, 967, 810, 746

HRMS(ESI-TOF) Calcd for $C_{25}H_{15}F_8NaO_2P$ $[M+Na]^+$: 553.0580, Found: 553.0582.

$[\alpha]_D^{23}$ = -105.2 (*c* 4.17, $CHCl_3$)

(3*R*,5*R*)-3,5-difluoro-4-methoxy-3,5-bis(perfluoroethyl)-3,5-dihydrodinaphtho[2,1-c:1',2'-e]phosphepine 4-oxide(16b)



To a stirred mixture of (*R*)-diketone **12b** (34.6 mg, 0.21 mmol) in THF (0.25 mL) was added $BF_3{\cdot}OEt_2$ (68 μL, 0.54 mmol) at 0 °C, and then the mixture was stirred for 30 min. After methyl phosphinate (**13**) (1.1 mL, 0.66 M in THF, 0.73 mmol) was added at 0 °C, the reaction mixture was stirred for 1 h at room temperature. After confirming the completion of reaction by TLC analysis, the reaction mixture was quenched with 1 M $HCl_{aq.}$ The reaction mixture was extracted with ethyl acetate, and organic layer was washed with brine. The solvent was dried over Na_2SO_4 and removed *in vacuo* to give the corresponding diastereomer of diol (**13b**) (84%, *dr* = 80: <1:2:2). The yields and diastereoratio of diastereomer was determined by ^{31}P NMR analysis.

To a stirred mixture of the corresponding diol in CH_2Cl_2 (2.0 mL) were added XtalFluor-E® (286 mg, 1.26 mmol) and TEA·3HF (274 μL, 1.68 mmol) at 0 °C, and then the reaction mixture was stirred for 30 min at room temperature. The reaction mixture was quenched with water at 0 °C. The organic layer was extracted with CH_2Cl_2 and washed with brine. The solvent was dried over Na_2SO_4 and removed *in vacuo*. The resultant residue was purified by silica gel column chromatography (hexane/ethyl acetate =20/1 to 10/1) to give the corresponding methyl phosphinate (**16b**) (27.8 mg, 21% in two steps).

13b d1

^1H NMR (300 MHz, acetone -d_6) δ 8.31 (d, 1H, *J* = 8.9 Hz), 8.26 (d, 2H, *J* = 9.5 Hz), 8.21 (d, 1H, *J* = 9.2 Hz), 8.04-8.01 (m, 2H), 7.51 (dt, 2H, *J* = 7.1, 6.6 Hz), 7.22-7.17 (m, 2H), 7.15 (d, 1H, *J* = 7.4 Hz), 6.84 (d, 1H, *J* = 8.6 Hz), 6.73 (d, 1H, *J* = 8.6 Hz), 3.94 (d, 3H, $^3J_{HP}$ = 10.4 Hz)

^{19}F NMR (282 MHz, acetone -d_6) δ -78.4 (s, 3F), -78.7 (d, 3F), -110.5--114.6 (m, 4F)

$^{31}P\{^1H\}$ NMR (122 MHz, acetone-d_6 δ 47.7

16b

^1H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, 1H, *J* = 8.9 Hz), 8.05 (d, 1H, *J* = 8.5 Hz), 7.95 (d, 2H, *J* = 8.4 Hz), 7.92 (d, 1H, *J* = 9.9 Hz), 7.82 (d, 1H, *J* = 8.7 Hz), 7.56 (t, 2H, *J* = 6.9 Hz), 7.34-7.19 (m, 4H), 4.01 (d, 3H, $^3J_{HP}$ = 10.8 Hz)

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 137.4, 137.2, 133.8, 133.6, 132.99, 132.96, 132.0-107.8 (m, 4C, pentafluoroethyl groups), 129.8, 129.4, 128.1 (d, $^2J_{CF}$ = 6.0 Hz), 127.5 (d, $^2J_{CF}$ = 5.3 Hz), 122.8-122.5 (m), 99.2-91.2 (m, 2C), 54.9 (t, $^2J_{CP}$ = 6.8 Hz)

^{19}F NMR (282 MHz, $CDCl_3$) δ -76.8 (d, 3F, $^3J_{FF}$ = 14.7 Hz), -77.3 (d, 3F, $^3J_{FF}$ = 17.2 Hz),-107.0--113.1 (m, 4F), -155.6 (dt, 1F, $^2J_{FP}$ = 61.8, $^3J_{FF}$ = 14.1 Hz), -160.0 (d, 1F, $^2J_{FP}$ = 83.8 Hz)

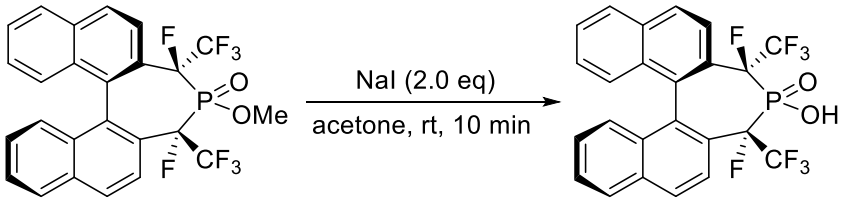
$^{31}P\{^1H\}$ NMR (122 MHz, $CDCl_3$) δ 31.6 (dd, $^2J_{PF}$ = 81.9, 60.9 Hz)

FT-IR (KBr pellet, cm^{-1}) 3067, 2968, 2929, 2862, 2254, 1596, 1509, 1464, 1375, 1359, 1322, 1279, 1227, 1190, 1160, 1087, 1058, 1030, 994, 955, 910, 868, 814, 779, 736, 699, 680, 648.

HRMS(ESI-TOF) Calcd for $C_{27}H_{15}F_{12}O_2P$ $[M-H]^+$: 653.0516, Found: 653.0505

$[\alpha]_D^{22}$ = -670.8 (*c* 0.01, $CHCl_3$)

(3*R*,5*R*)-3,5-difluoro-4-hydroxy-3,5-bis(trifluoromethyl)-3,5-dihydrodi-naphtho[2,1-c:1',2'-e]phosphepine 4-oxide (17a)



16a **17a**

To a stirred mixture of methyl phosphinate (**16a**) (106.1 mg, 0.2 mmol) in acetone (6.0 mL) was added sodium iodide (66.0 mg, 0.4 mmol) at room temperature. The reaction mixture was stirred for 10 min at room temperature, and quenched with 1 M HCl_{aq}. The organic layer was extracted with dichloromethane and washed with 1 M $HCl_{aq.}$ After the solvent was dried over Na_2SO_4 and removed *in vacuo*. The resultant residue was purified by silica gel column chromatography on silica gel (dichrolomethane/methanol =20/1 to 10/1). The solution was treated with cation exchange resin (Muromac®, 50W-X8). After the solution was filtered, the solvent was removed *in vacuo* to give the corresponding phosphinic acid (**17a**) (79.4 mg, 77%).

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.11 (d, 2H, *J* = 9.0 Hz), 8.02 (d, 2H, *J* = 9.0 Hz), 7.71 (d, 2H, *J* = 12.0 Hz), 7.51 (t, 2H, *J* = 7.5 Hz), 7.28 (t, 2H, *J* = 7.5 Hz), 7.00 (d, 2H, *J* = 9.0 Hz)

^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6) δ 135.6, 132.5, 132.4, 128.3, 127.9, 127.2 (dd, $^2J_{CF}$ = 8.3 Hz, $^3J_{CF}$ = 3.7 Hz), 127.0 (d, $^2J_{CF}$ = 3.7 Hz), 126.8, 126.7, 123.4 (qdd, $^1J_{CF}$ = 292.2 Hz, $^2J_{CF}$ = 29.4 Hz, $^2J_{CP}$ = 4.5 Hz, 2C), 122.4, 97.7-93.4 (m, 2C)

^{19}F NMR (282 MHz, DMSO-d_6) δ -86.4 (s, 6F), -154.66 (d, 2F, $^2J_{FP}$ = 59.6 Hz)

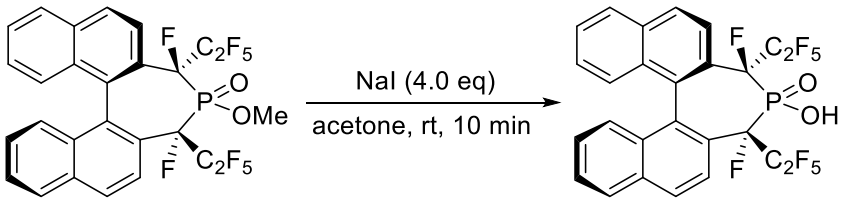
^{31}P{^{1}H} NMR (122 MHz, DMSO-d_6) δ 18.0 (t, $^2J_{PF}$ = 60.1 Hz)

FT-IR (KBr pellet, cm^{-1}) 3666, 3198, 3067, 2250, 1908, 1623, 1507, 1256, 1189, 1038, 908, 806, 736, 560, 524

HRMS(ESI-TOF) Calcd for $C_{24}H_{12}F_8O_2P$ $[M-H]^-$: 515.0447, Found: 515.0453

$[\alpha]_D^{23}$ = 114.9 (*c* 0.45, $CHCl_3$)

(3*R*,5*R*,11b*R*)-3,5-difluoro-4-hydroxy-3,5-bis(perfluoroethyl)-3,5-dihydrodinaphtho[2,1-c:1',2'-e]phosphepine 4-oxide (17b)



16b **17b**

To a stirred mixture of methyl phosphinate (**16b**) (11.0 mg, 0.018 mmol) in acetone (1.5 mL) was added sodium iodide (10.8 mg, 0.072 mmol) at room temperature. The reaction mixture was stirred for 10 min at room temperature, and quenched with 1 M HCl_{aq}. The organic layer was extracted with dichloromethane and washed with 1 M $HCl_{aq.}$ After the solvent was dried over Na_2SO_4, the solution was treated with cation exchange resin (Muromac®, 50W-X8). After the solution was filtered, the solvent was removed *in vacuo* to give the corresponding phosphinic acid (**17b**) (10.0 mg, 93%).

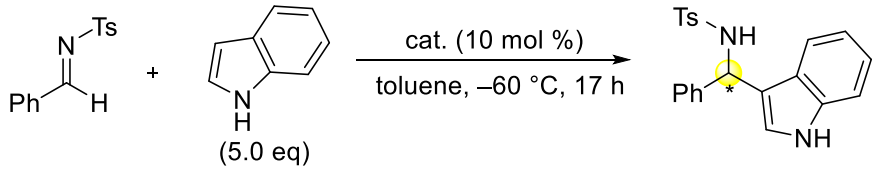
^{1}H NMR (300 MHz, acetone-d_6) δ 8.04 (d, 2H, *J* = 9.2 Hz), 8.01 (d, 2H, *J* = 8.5 Hz), 7.89 (d,

2H, J = 9.0 Hz), 7.53 (t, 2H, J = 7.3 Hz), 7.29 (t, 2H, J = 7.6 Hz), 7.19 (d, 2H, J = 9.0 Hz)

^{19}F NMR (282 MHz, acetone -d_6) δ -78.1 (s, 6F), -110.7 (d, 2F, $^2J_{FF}$ = 288.2 Hz), -112.7 (d, 2F, $^2J_{FF}$ = 288.5 Hz) -157.40 (d, 2F, $^2J_{FP}$ = 61.5 Hz)

^{31}P{^{1}H} NMR (122 MHz, acetone -d_6) δ 20.4 (t, $^2J_{PF}$ = 57.6 Hz)

Typical procedure for catalytic asymmetric Friedel-Crafts reaction[8,9]



18 **19** **20**

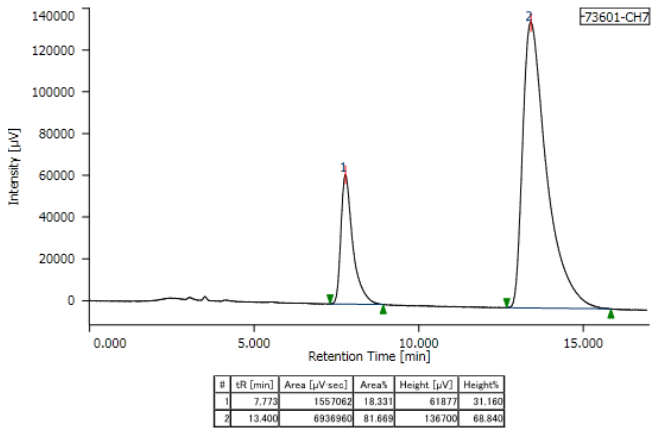
To a stirred mixture of (*E*)-*N*-Benzylidene-4-methylbenzensulfonamide (**18**) (25.9 mg, 0.10 mmol) in toluene (0.4 mL) was added chiral catalyst (0.01 mmol) at -60 °C. After stirred for 10 min, indole (58.6 mg, 0.50 mmol) was added in one portion. The reaction mixture was stirred for 17 h at -60 °C and quenched with sat. aqueous NH_4Cl at 0 °C. After extraction with ethyl acetate. The organic layer was washed with brine. The solvent was dried over Na_2SO_4 and removed *in vacuo*. The resultant residue was purified by silica gel column chromatography (hexane/ethyl acetate = 2/1) to give the corresponding tosylamide (**20**).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.55 (d, 2H, J = 8.3 Hz), 7.29 (d, 1H, J = 8.2 Hz), 7.26 (s, 1H), 7.26-7.13 (m, 6H), 7.09 (d, 2H, J = 8.0 Hz), 7.00 (ddd, 1H, J = 8.8, 7.0, 0.9 Hz), 6.66 (d, 1H, J = 2.0 Hz), 5.85 (d, 1H, J = 6.9 Hz), 5.13 (d, 1H, J = 6.9 Hz), 2.36 (s, 3H)

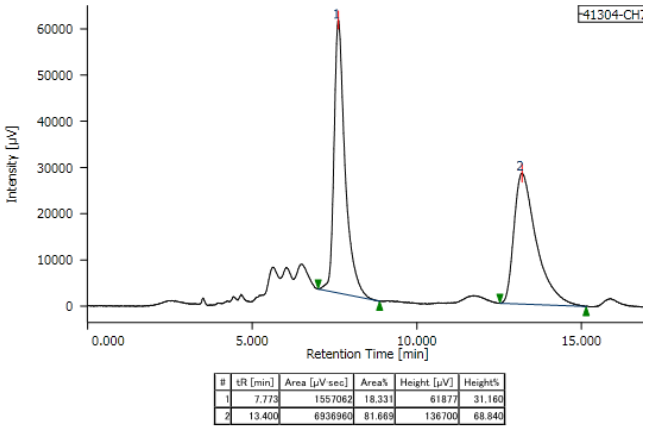
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.1, 140.3, 137.5, 136.6, 132.3, 129.3, 128.4, 127.5, 127.3, 125.4, 123.9, 122.7, 120.1, 119.4, 116.5, 111.3, 55.1, 21.6

HPLC (column, CHIRALPAK OD-3, Hexane/2-propanol = 70/30, flow rate 1.0 mL/min, 20°C, detection UV 254 nm) t_R of major isomer 13.1 min, t_R of minor isomer 8.7 min.

$[\alpha]_D^{21}$ = -833.1 (*c* 0.003, $CHCl_3$, 64% *ee*)



#	tR [min]	Area [μV·sec]	Area%	Height [μV]	Height%
1	7.773	1557062	18.331	61877	31.160
2	13.400	6936960	81.669	136700	68.840



#	tR [min]	Area [μV·sec]	Area%	Height [μV]	Height%
1	7.773	1557062	18.331	61877	31.160
2	13.400	6936960	81.669	136700	68.840

X-ray crystallography of 16b (racemic):

X-ray diffraction data were collected on a Rigaku RAXIS-Rapid diffractometer. The structures were solved by a direct method (SHELXL-2014).[10] The X-ray structure solution and refinement were carried out using the Yadokari-XG software.[11]

$C_{27}H_{15}F_{12}O_2P_2$, colorless prisms (CH_2Cl_2, 20 °C), M_W = 630.36, crystal dimensions = 0.300 × 0.280 × 0.220 mm^3, triclinic, space group *P*-1 (#2), a = 10.0113(6), b = 11.5797(7), c = 12.0978(7) Å, α = 77.512(2), β = 84.456(2), γ = 64.458(1)°, V = 1235.46(13) Å^3, Z = 2, λ = 0.71073 Å, T = 128 K, ρ_{calcd} = 1.694 g cm^{-3}, $\mu_{MoK\alpha}$ = 0.229 mm^{-1}, F_{000} = 632, 12050 total reflections ($2\theta_{max}$ = 54.88°), index ranges = $-12 \le h \le 12$, $-15 \le k \le 15$, $-15 \le l \le 15$, 5521 unique reflections (R_{int} = 0.0283), $R1$ = 0.0465 ($I > 2\sigma(I)$), 0.0575 (all data), $wR2$ = 0.1335 ($I > 2\sigma(I)$), 0.1459 (all data), S = 1.069 (439 parameters).

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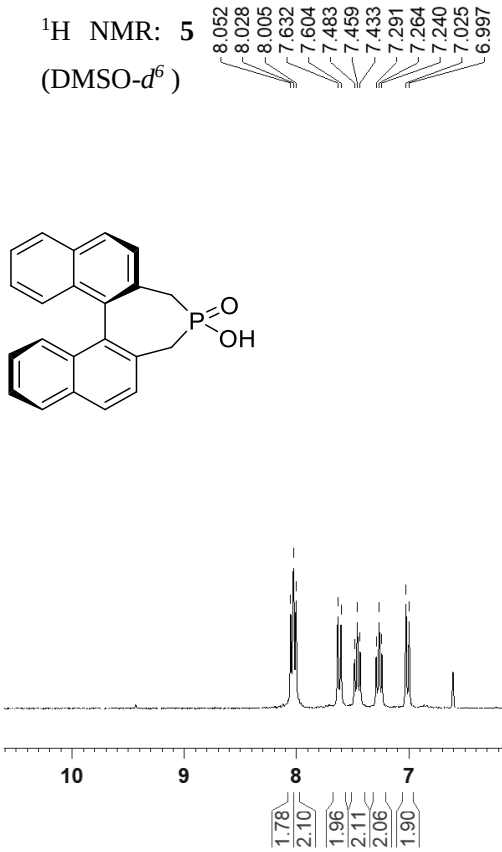
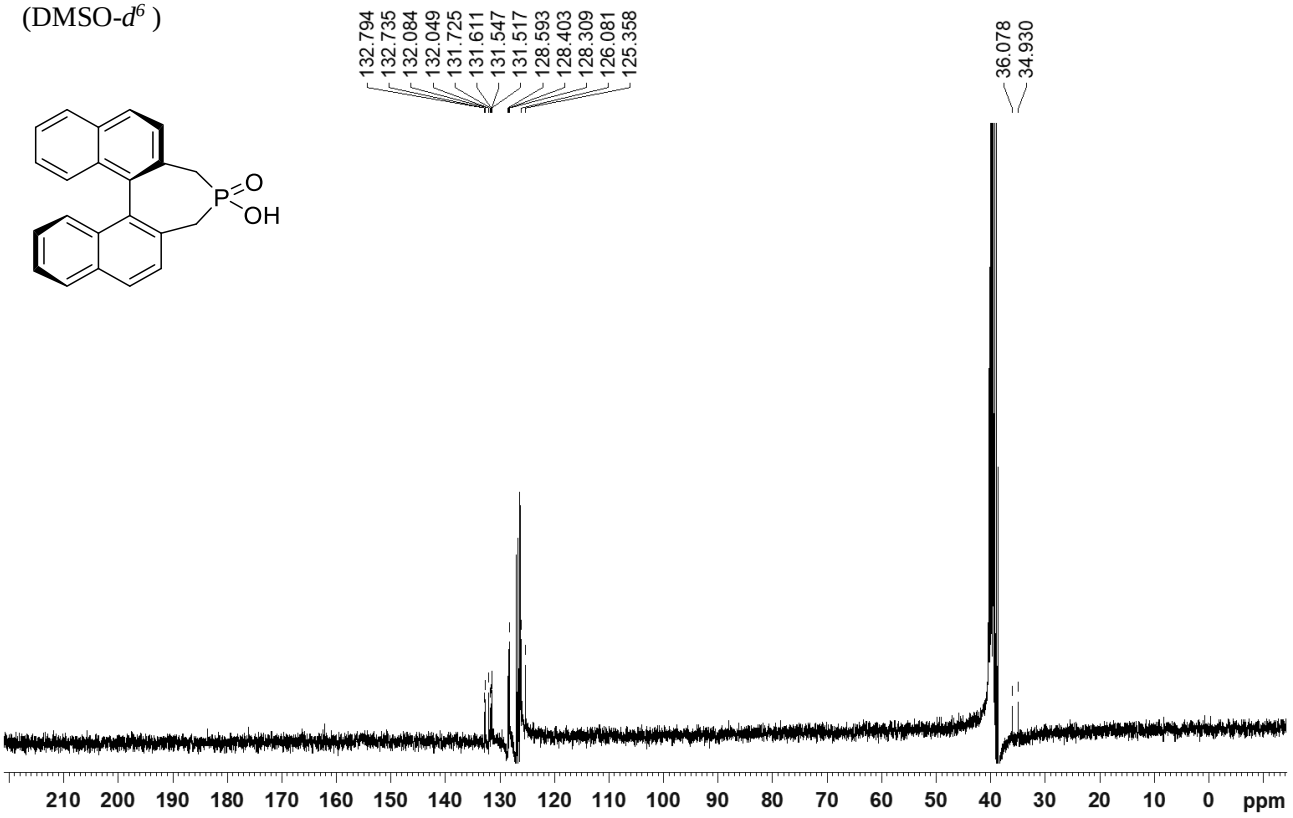
^{1}H NMR: **5**
(DMSO-d^{6})

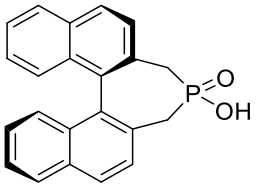


^{13}C{^{1}H} NMR: **5**
(DMSO-d^{6})

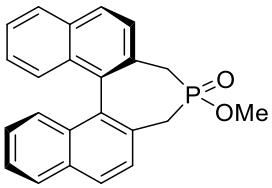


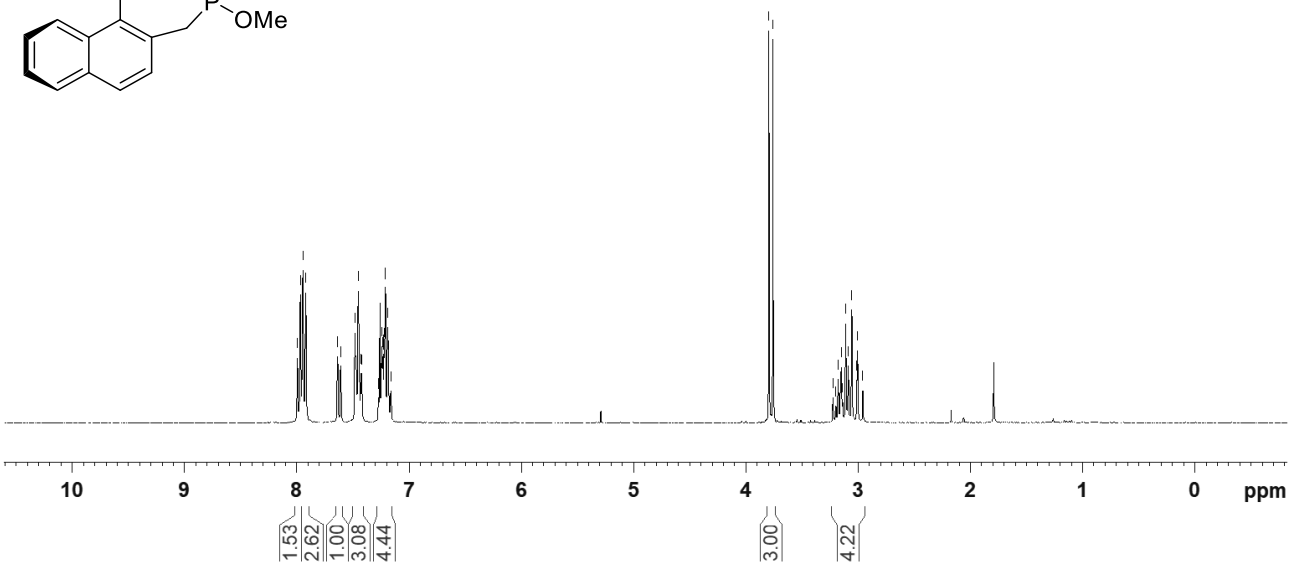
$^{31}P\{^{1}H\}$ NMR: **5**

(DMSO-d^6)



^{1}H NMR: **6**





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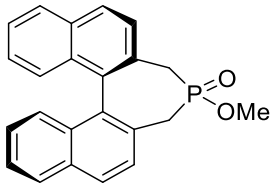

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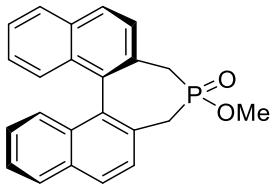

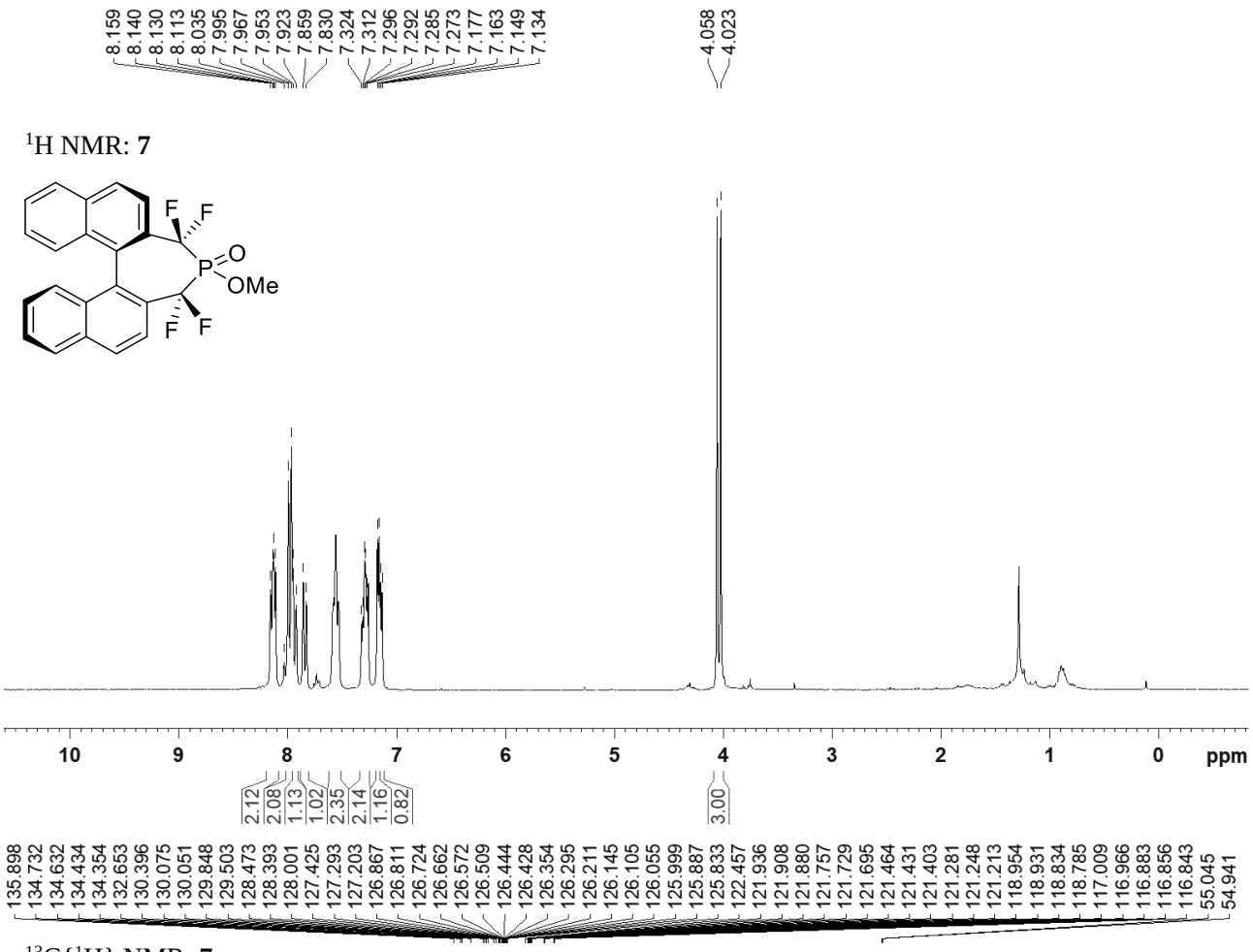

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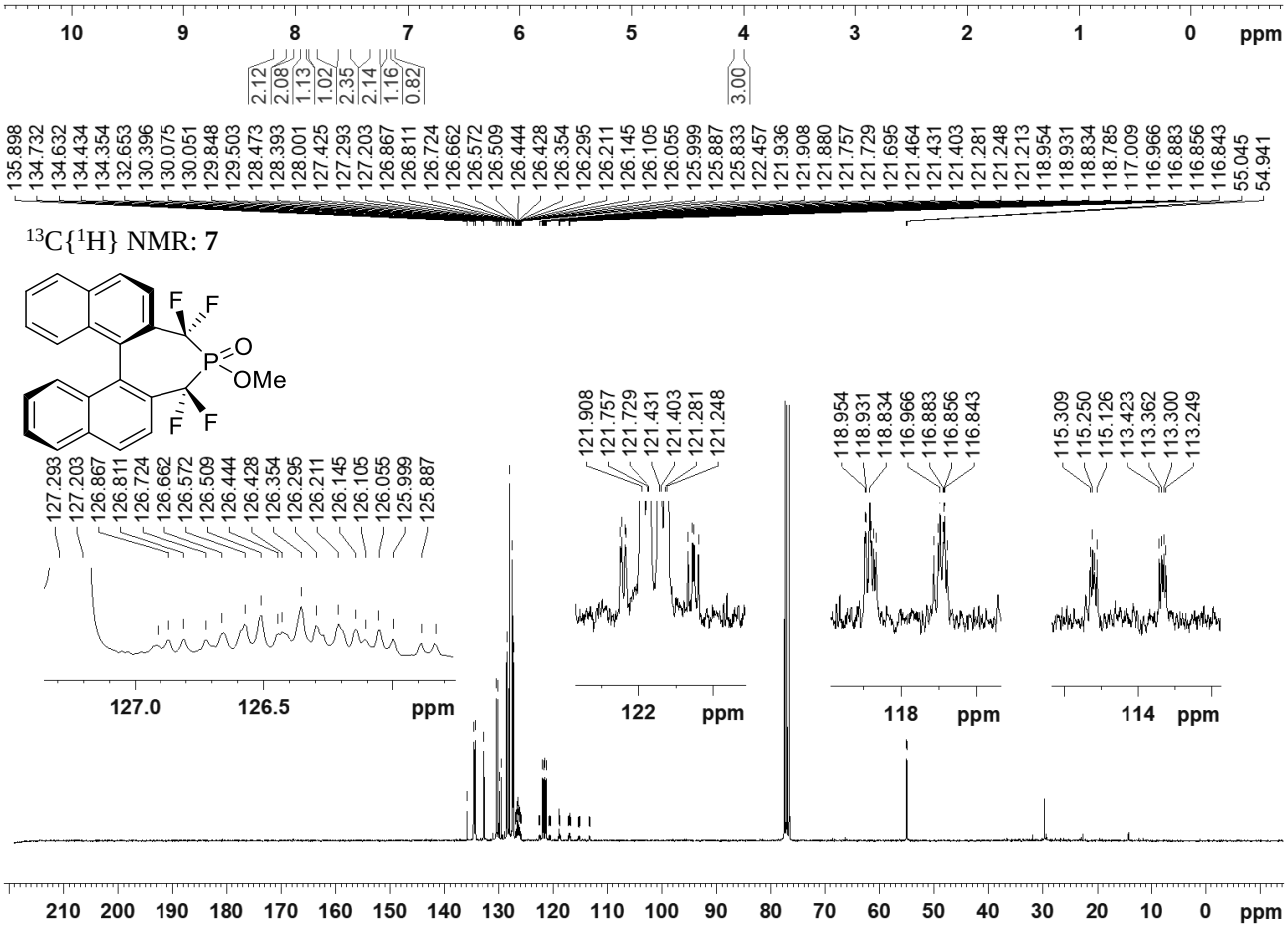
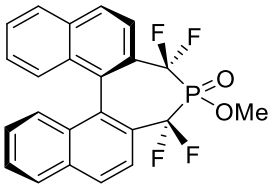


^{13}C{^{1}H} NMR: **7**

^{19}F NMR: **7**



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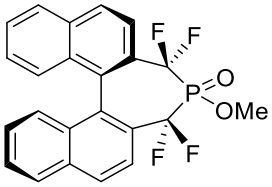
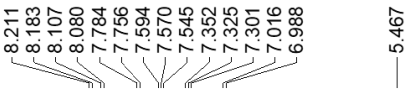
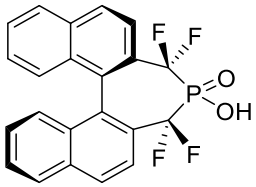
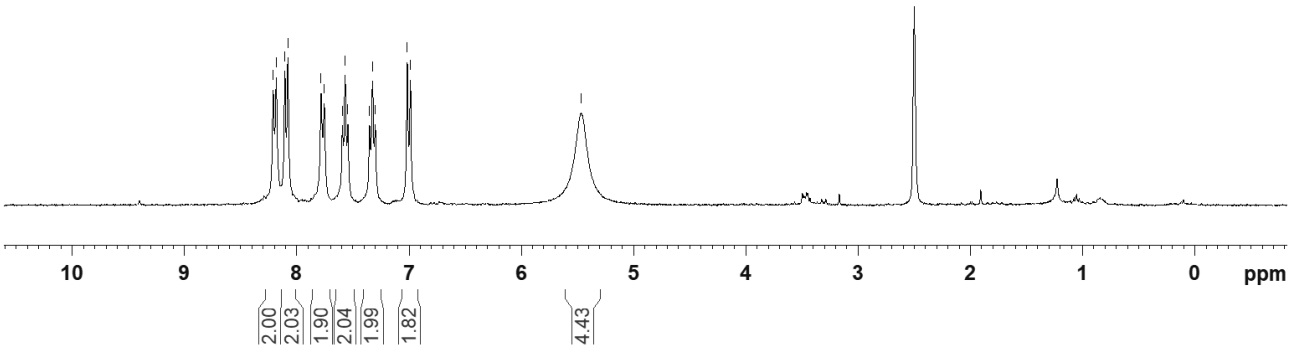


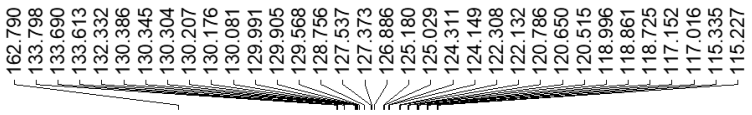


^{1}H NMR: **8**

(DMSO-d^6)

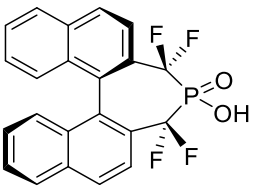






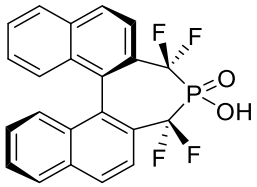
^{13}C{^{1}H} NMR: **8**

(DMSO-d^6)



^{19}F NMR: **8**

(DMSO-d^6)



^{31}P{^{1}H} NMR: **8**

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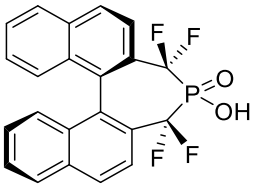
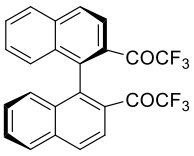
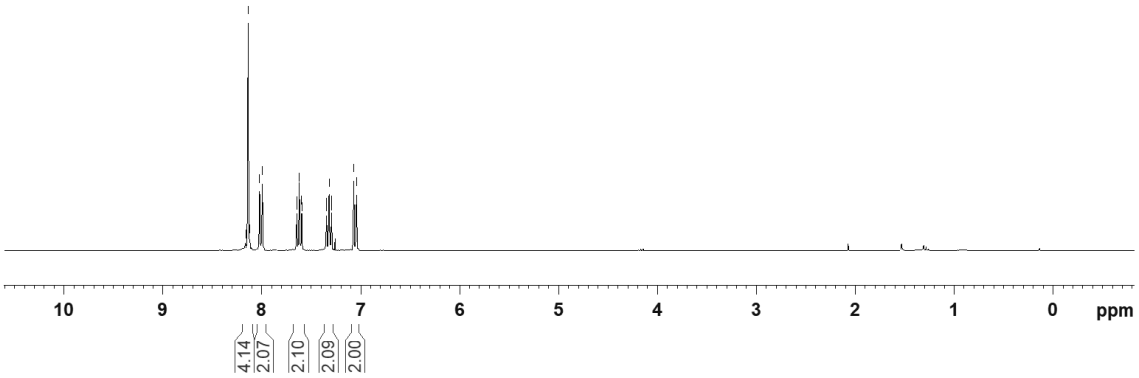
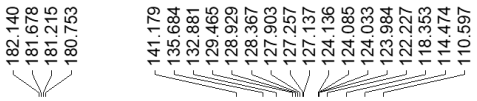


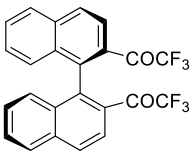
^{1}H NMR: **12a**



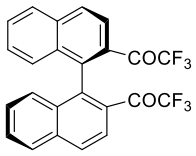


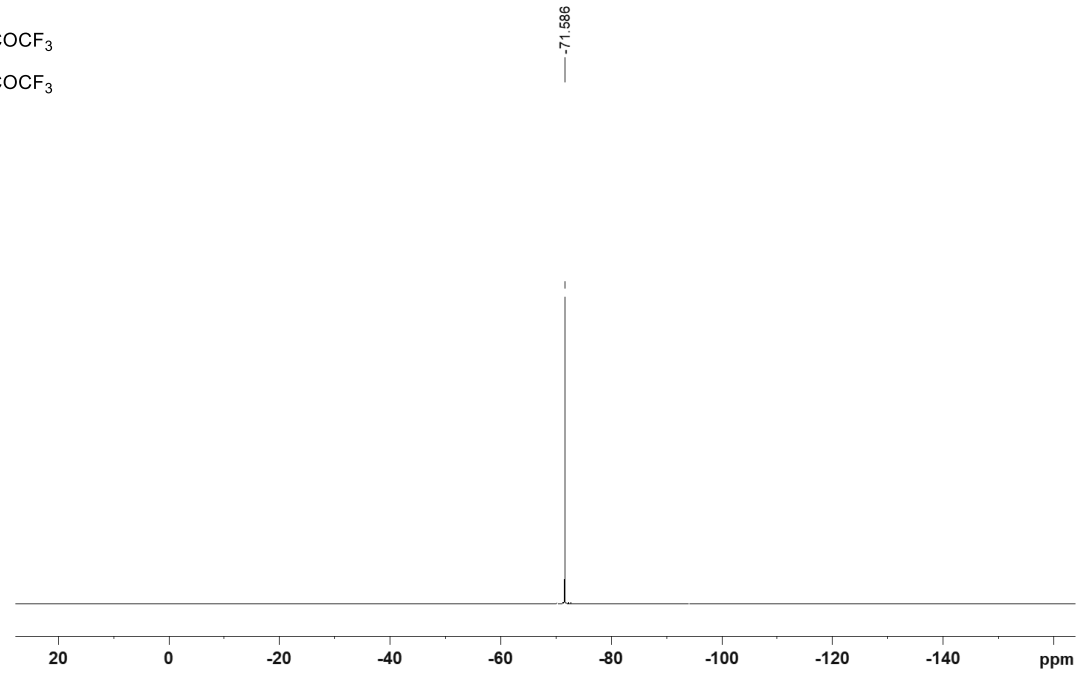


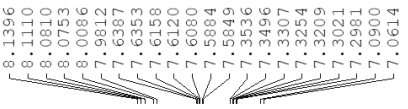
^{13}C{^{1}H} NMR: **12a**



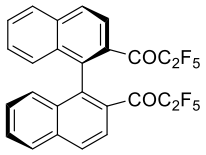
^{19}F NMR: **12a**



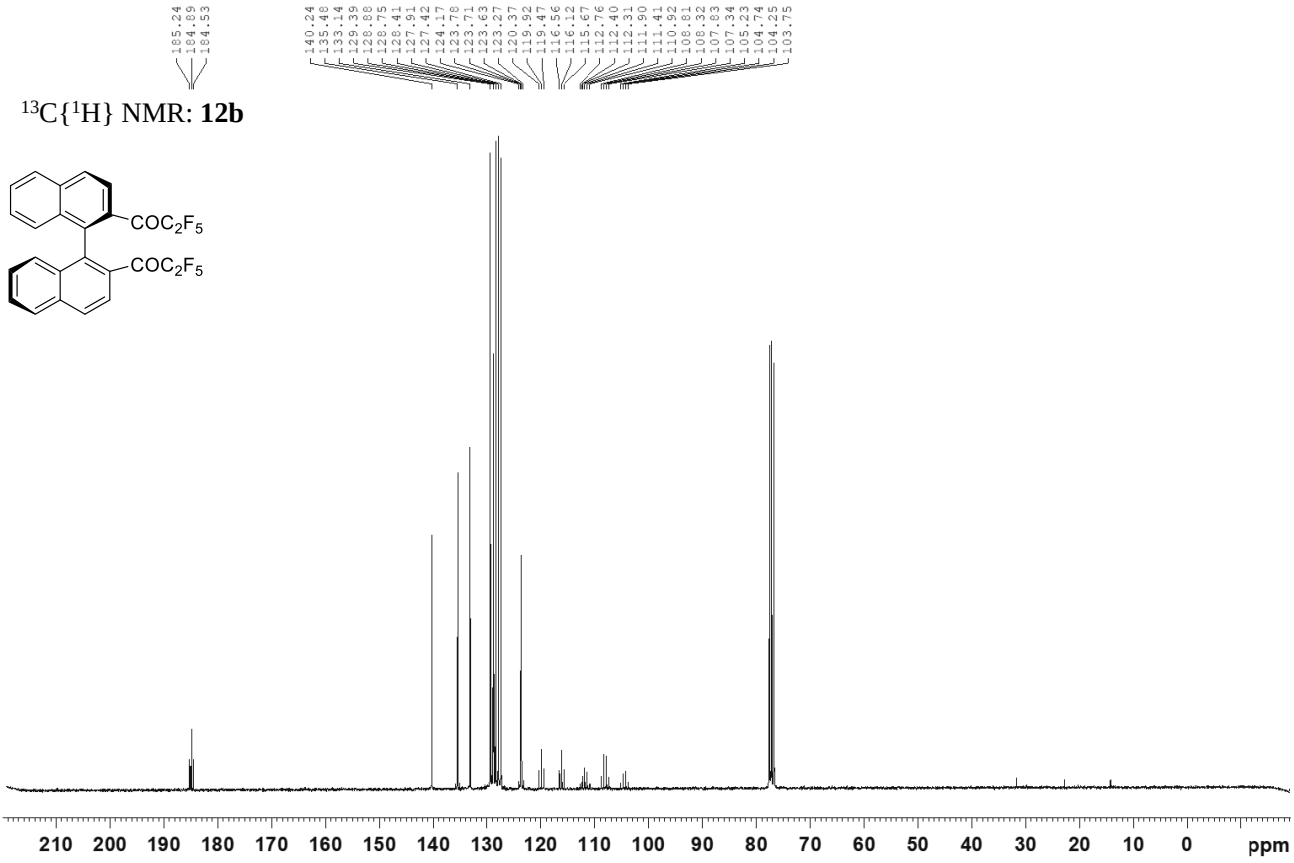




^{1}H NMR: **12b**



$^{13}C\{^{1}H\}$ NMR: **12b**



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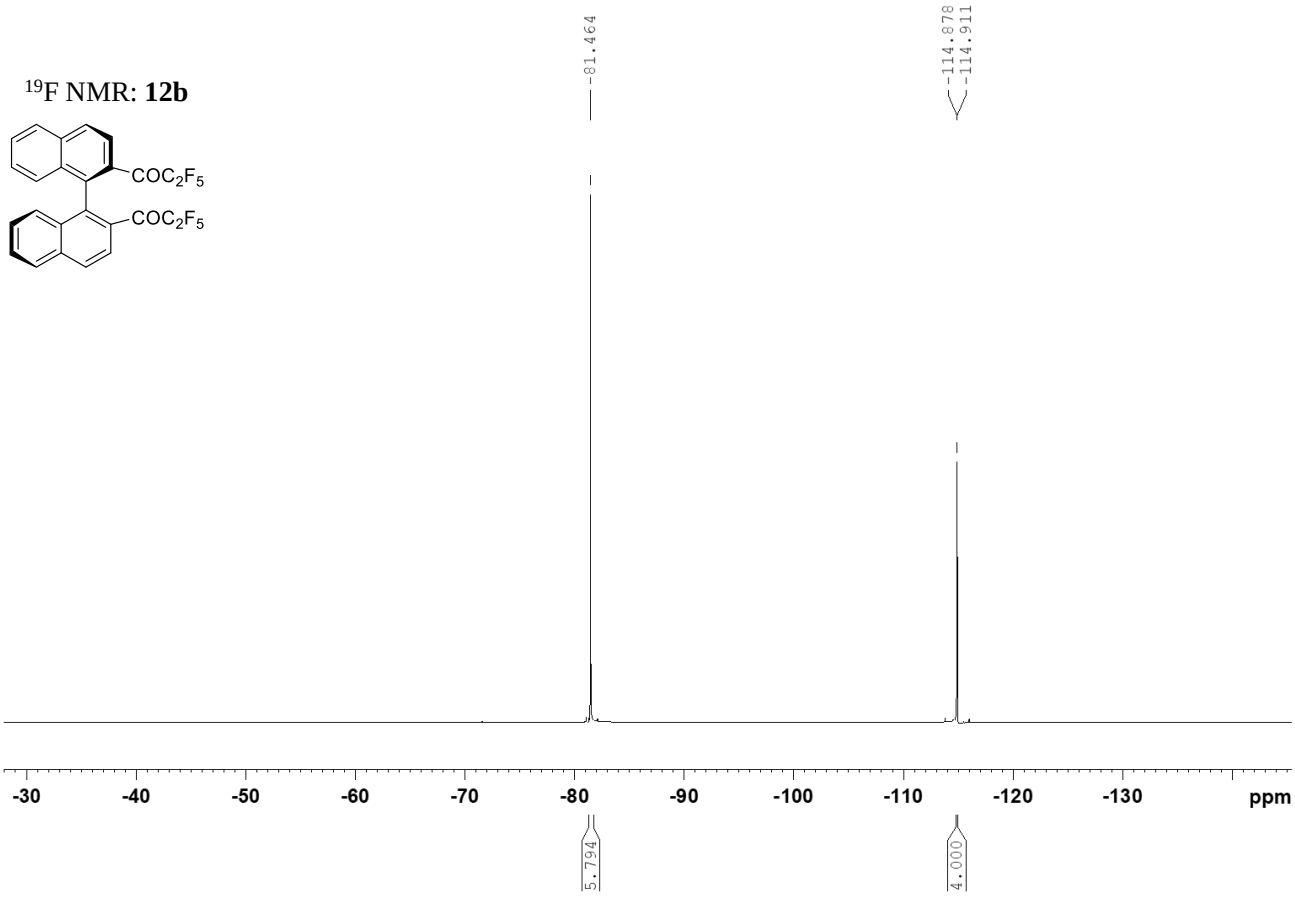
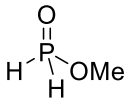
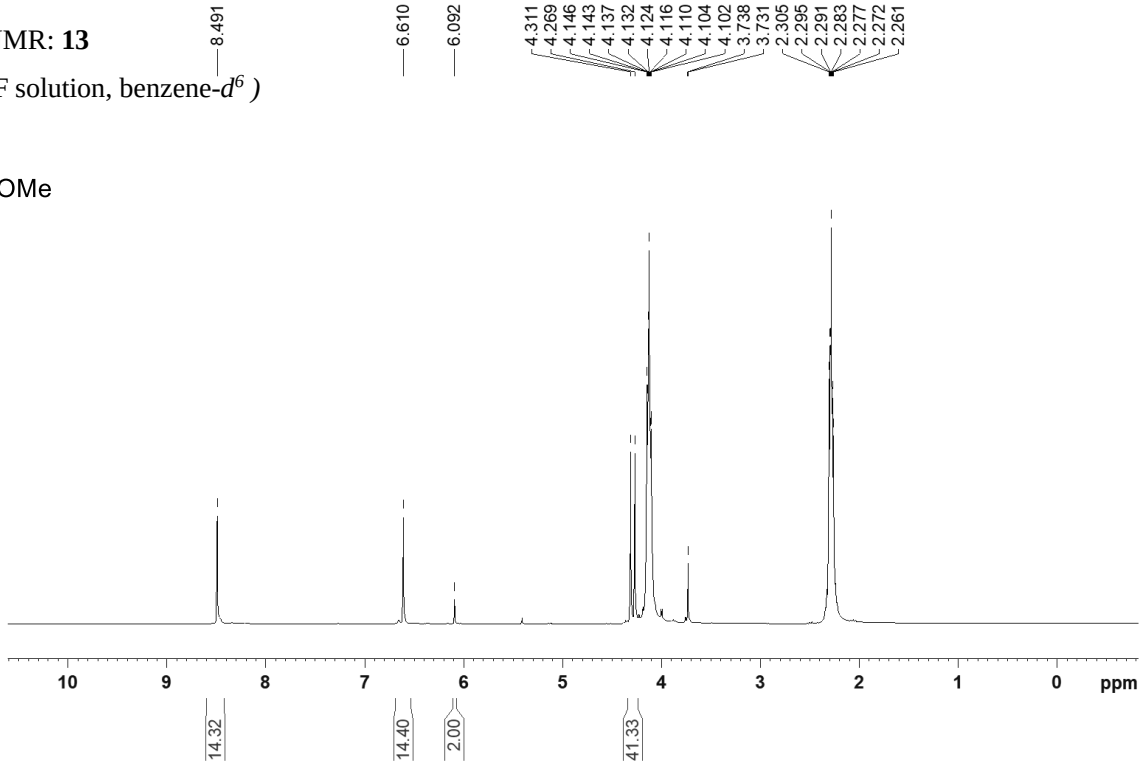


^{1}H NMR: **13**

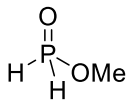
(THF solution, benzene-d^6)

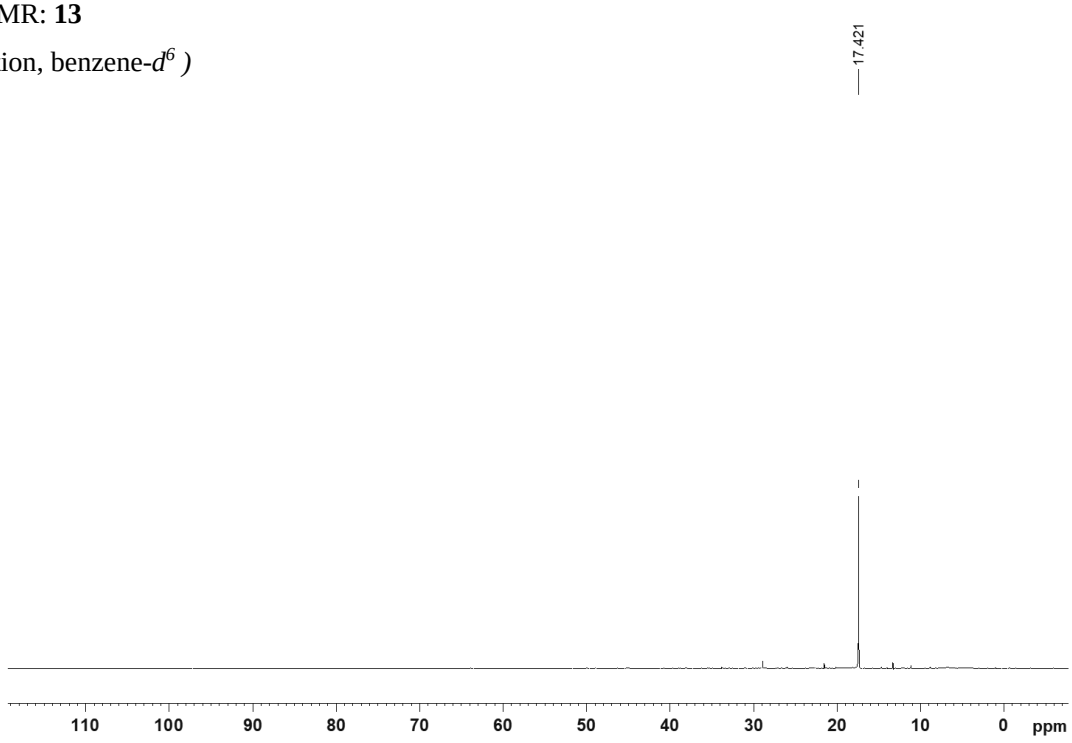


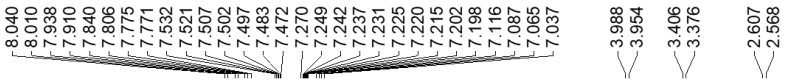


^{31}P{^{1}H} NMR: **13**

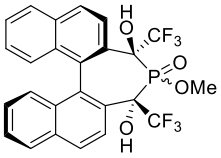
(THF solution, benzene-d^6)

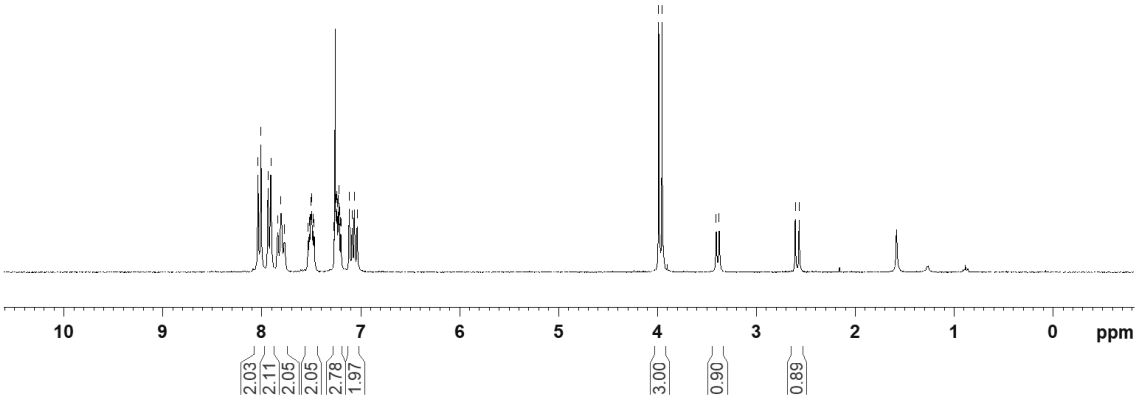




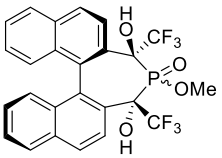


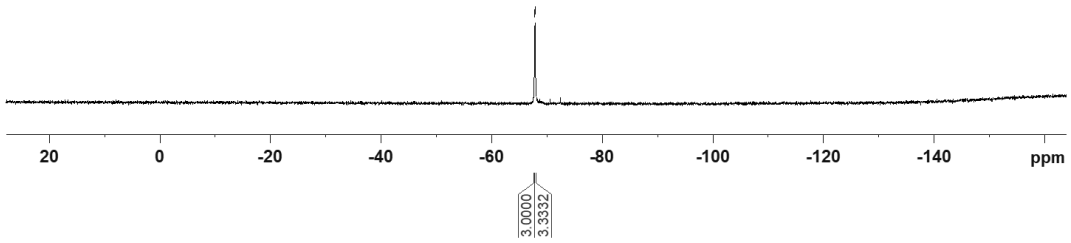
^{1}H NMR: **14a d2**



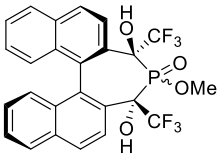


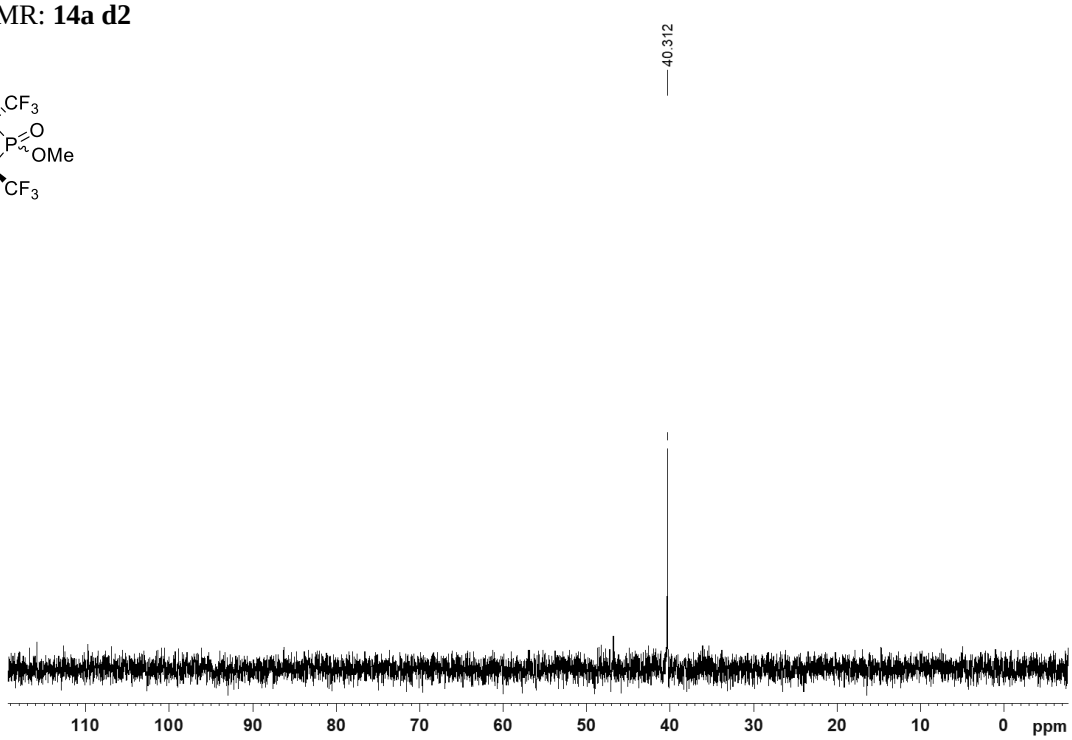
^{19}F NMR: **14a d2**

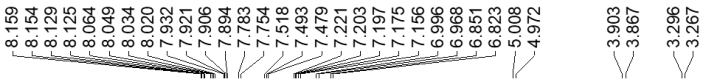




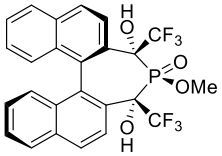
$^{31}P\{^{1}H\}$ NMR: **14a d2**

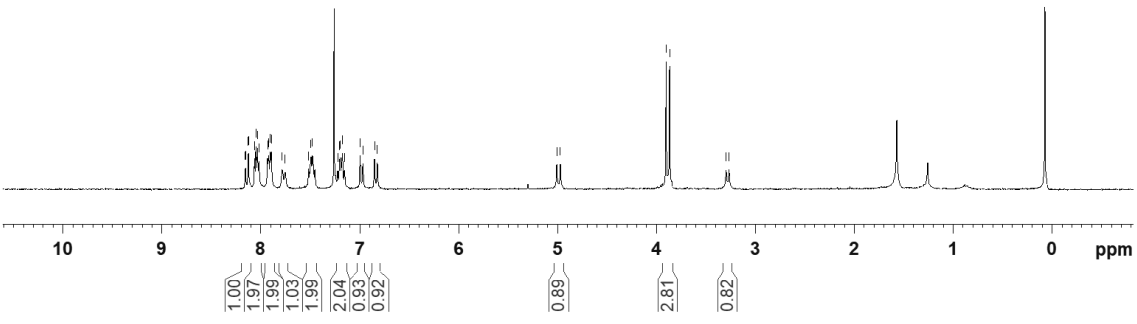




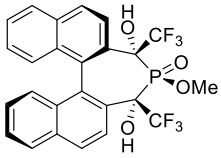


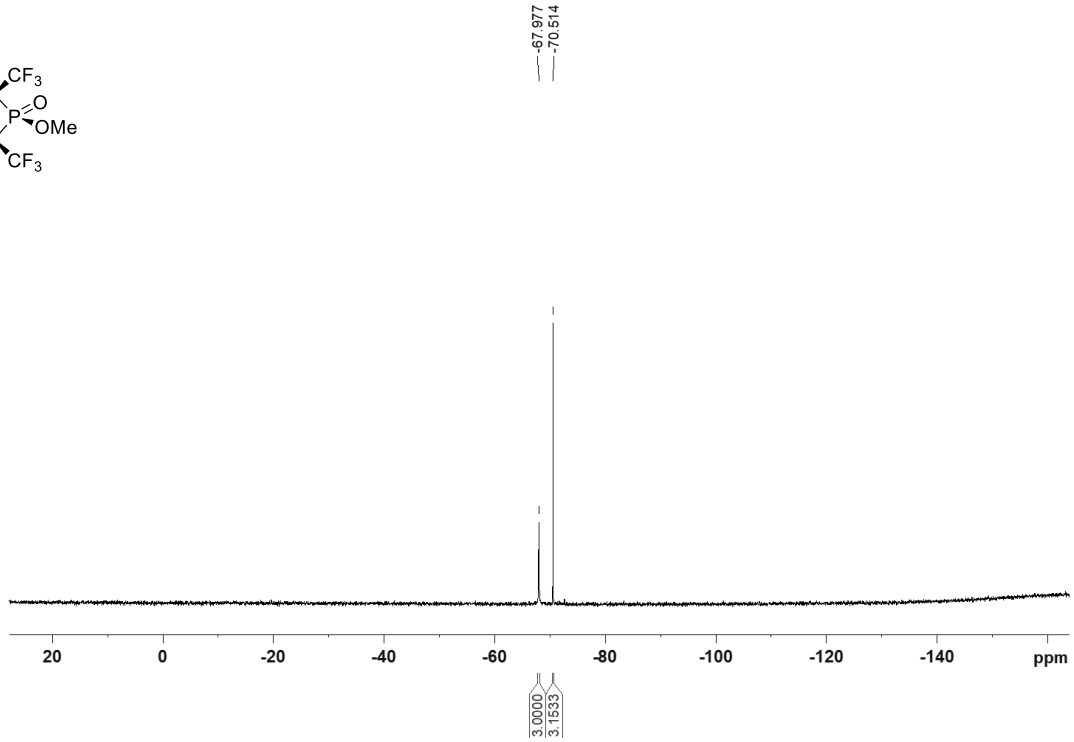
^{1}H NMR: **14a d3**



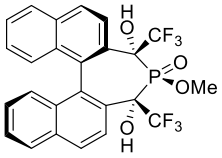


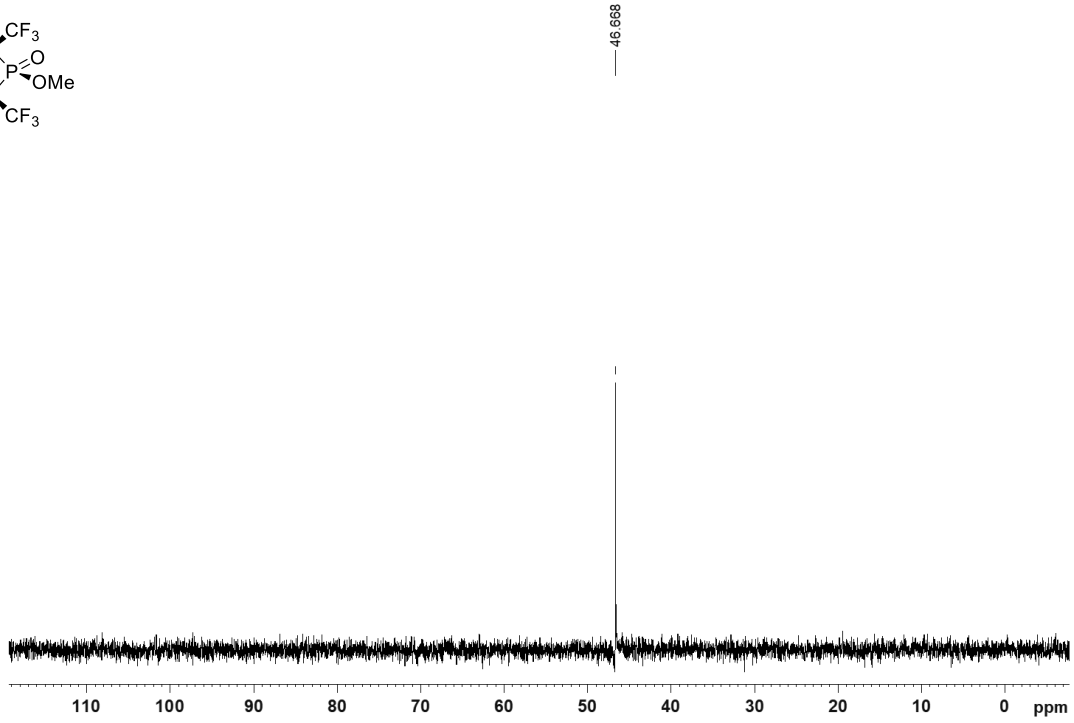
^{19}F NMR: **14a d3**



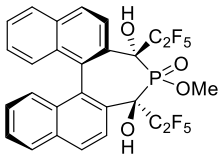


^{31}P{^{1}H} NMR: **14a d3**

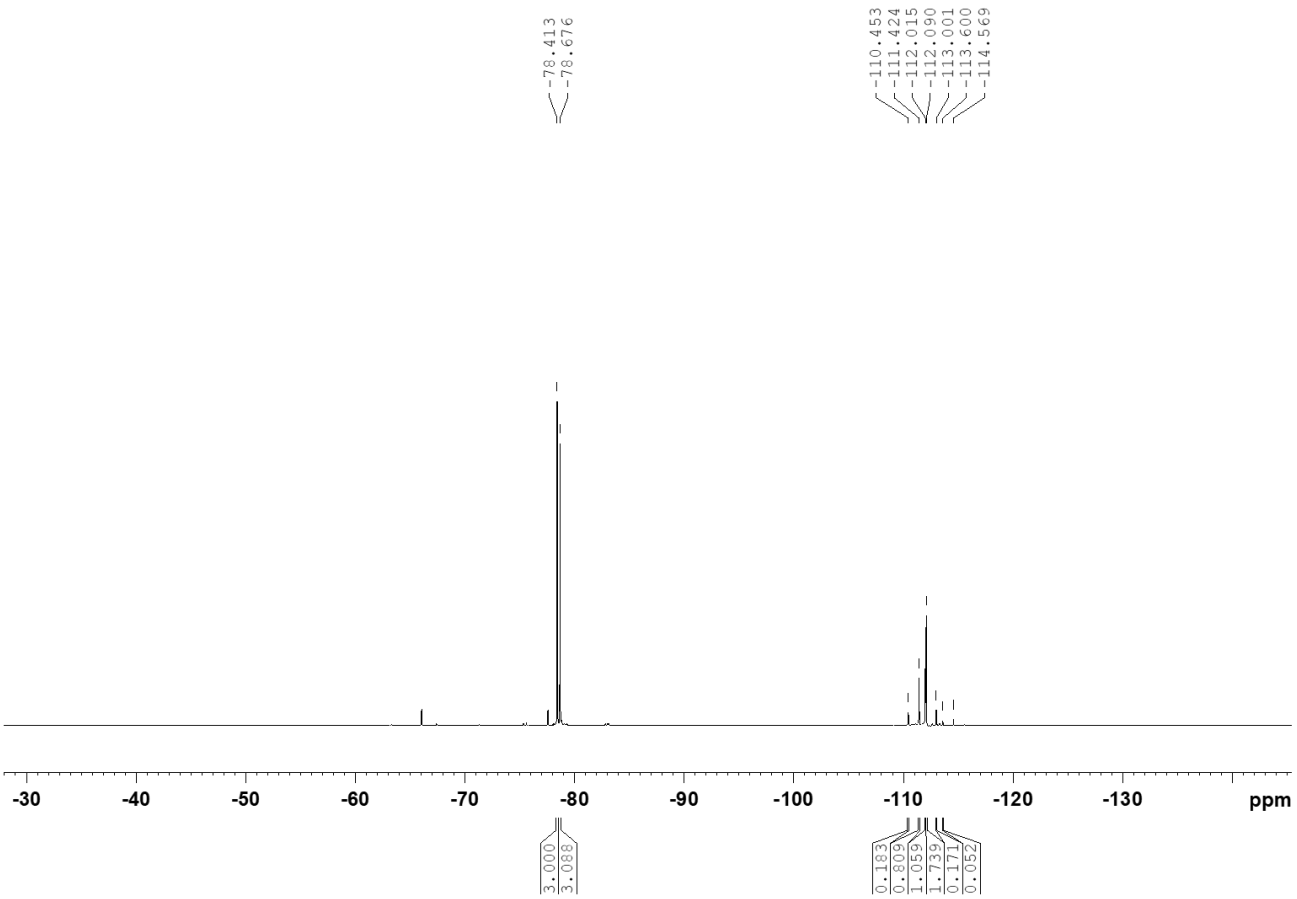




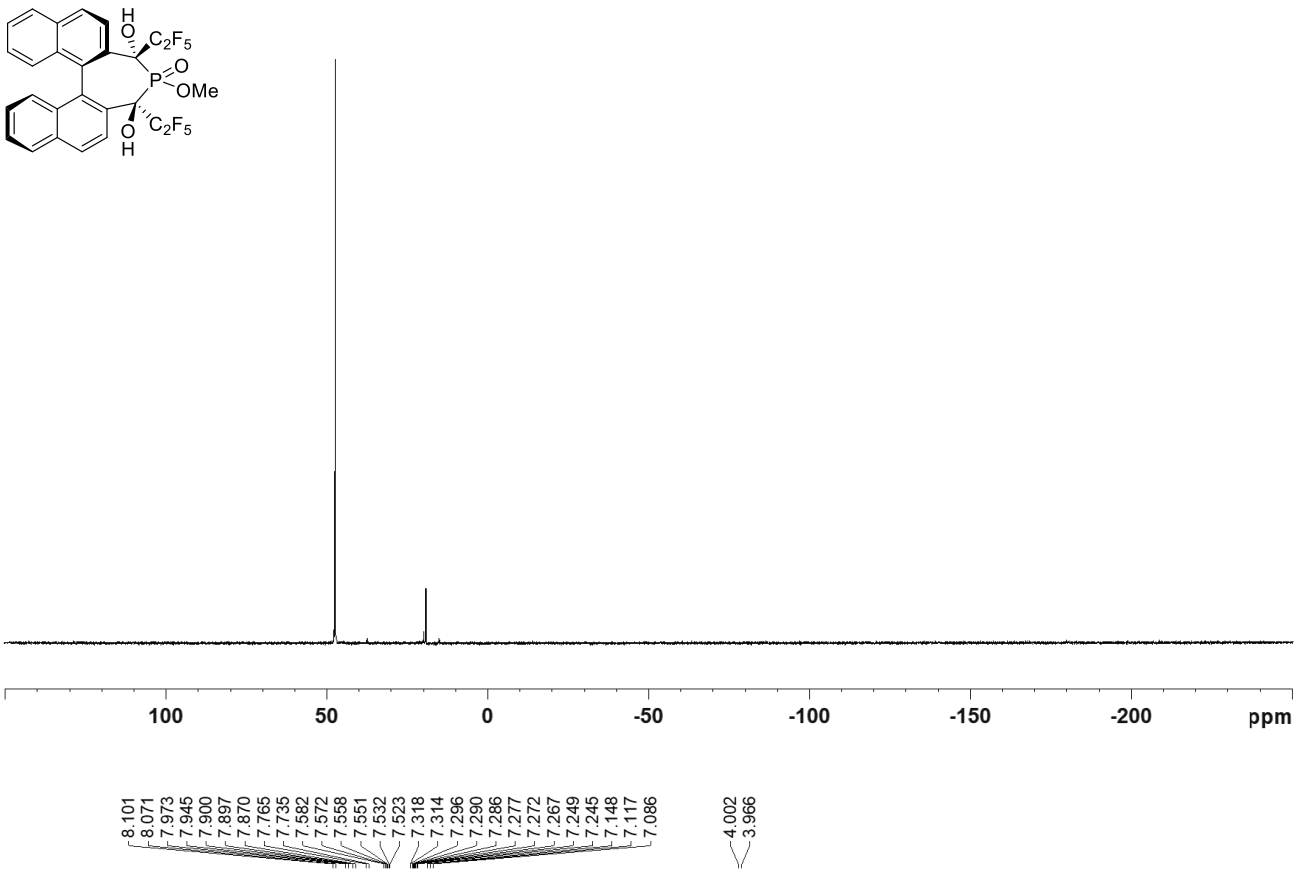
^{1}H NMR: **13b d1**



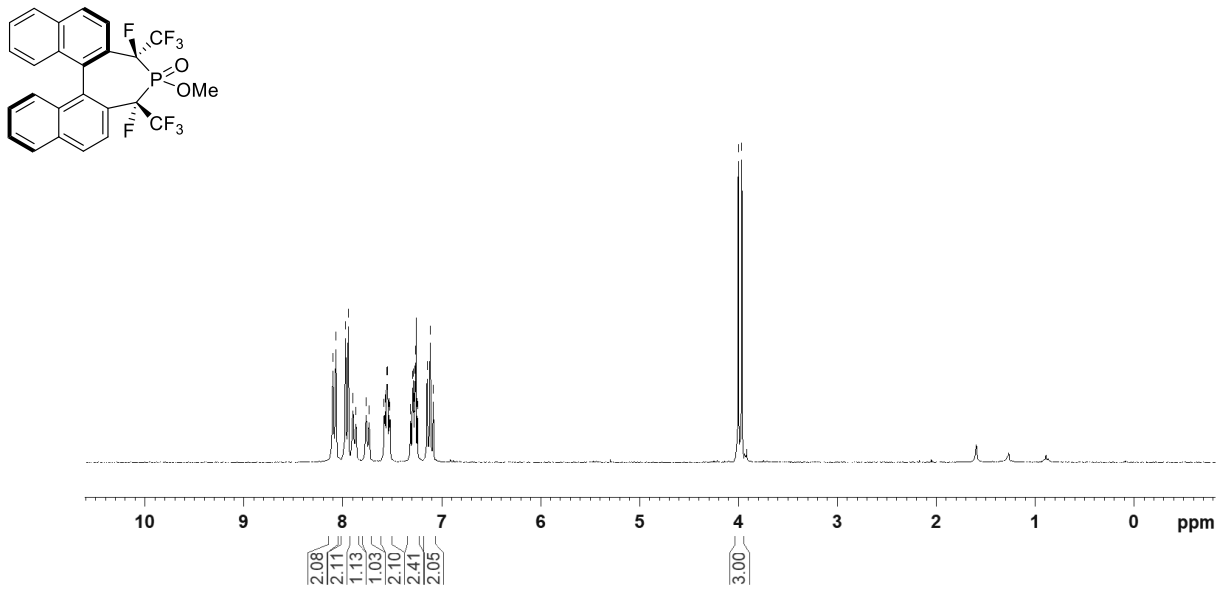
8.3267
8.2968
8.2399
8.2209
8.1905
8.0439
8.0304
8.0114
7.5459
7.5239
7.5001
7.4774
7.2176
7.2071
7.1981
7.1697
7.1592
7.1347
6.8524
6.8235
6.7416
6.7127
6.4133
6.3830
3.9529
3.9183
10
9
8
7
6
5
4
3
2
1
ppm
1.11
1.89
1.27
2.52
2.11
2.08
1.02
1.03
0.98
0.95
3.00

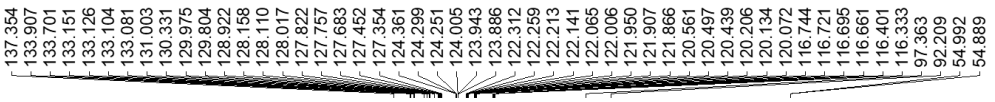

-78.413
-78.676
-110.453
-111.424
-112.015
-112.090
-113.001
-113.600
-114.569
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
ppm
3.000
3.088
0.183
0.809
1.059
1.739
0.171
0.052

$^{31}P\{^{1}H\}$ NMR: **13b d1**

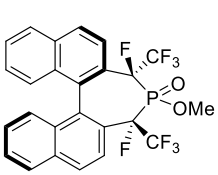


^{1}H NMR: **16a**

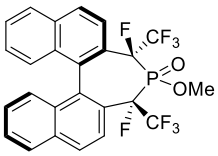


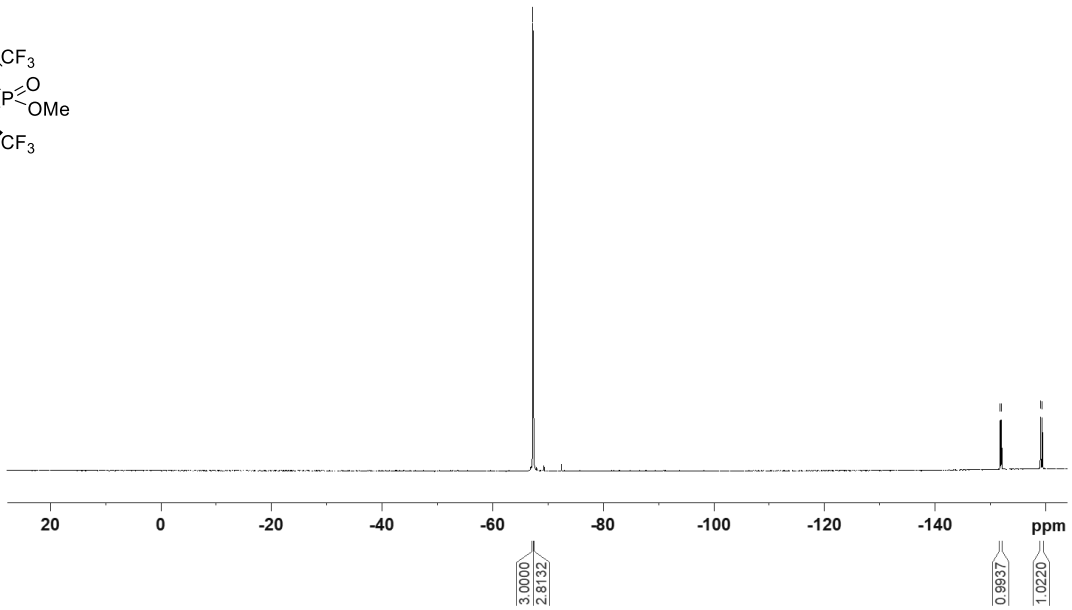


$^{13}C\{^{1}H\}$ NMR: **16a**

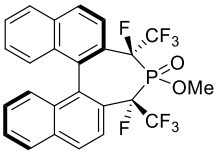


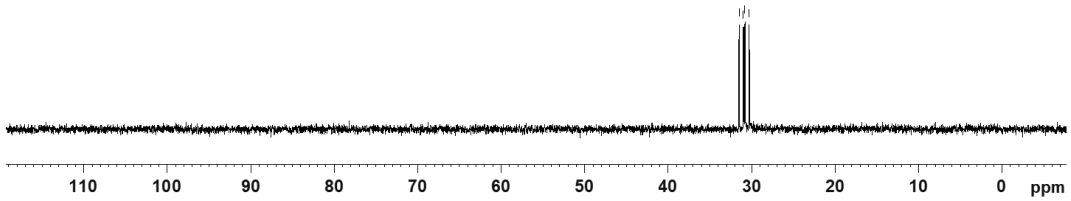
^{19}F NMR: **16a**



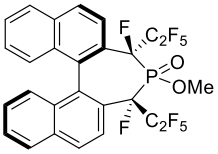


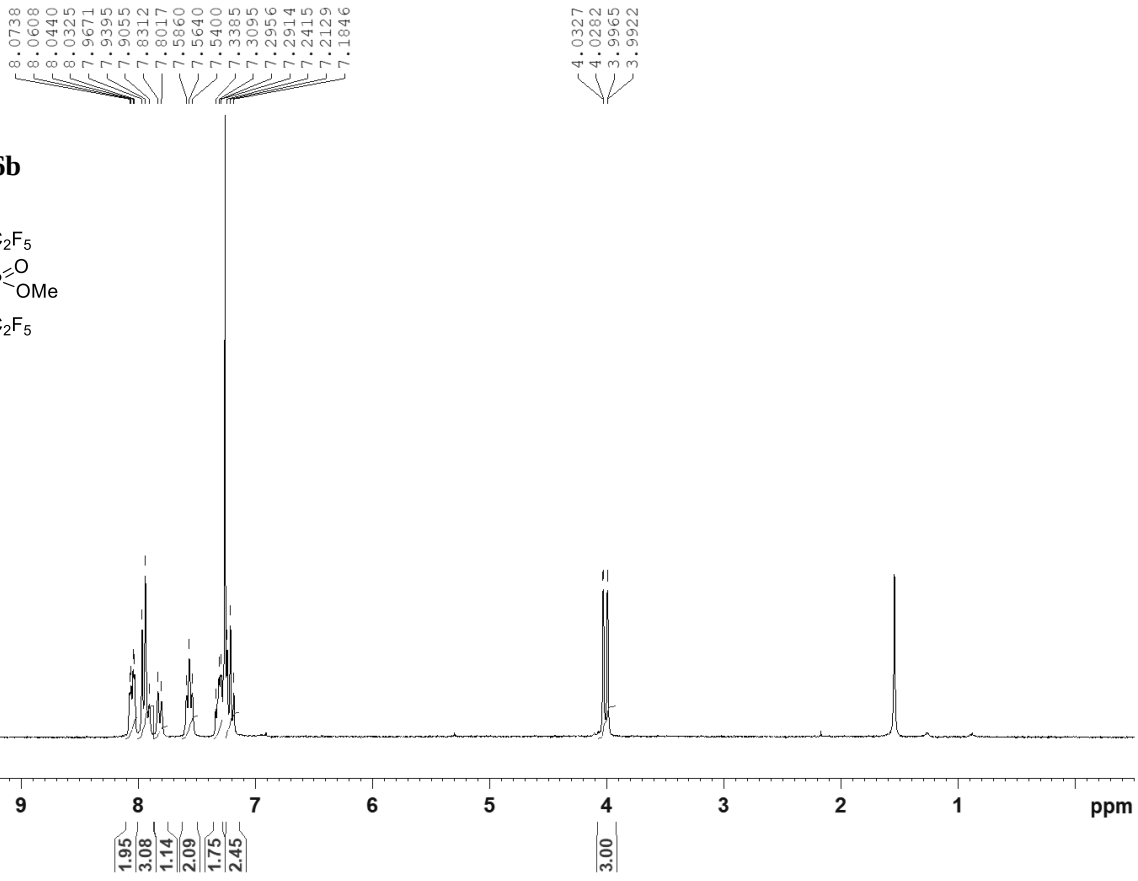
$^{31}P\{^{1}H\}$ NMR: **16a**



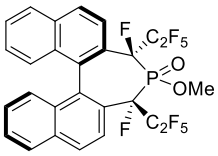


^{1}H NMR: **16b**

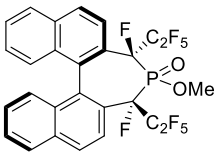




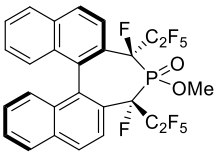
$^{13}C\{^{1}H\}$ NMR: **16b**

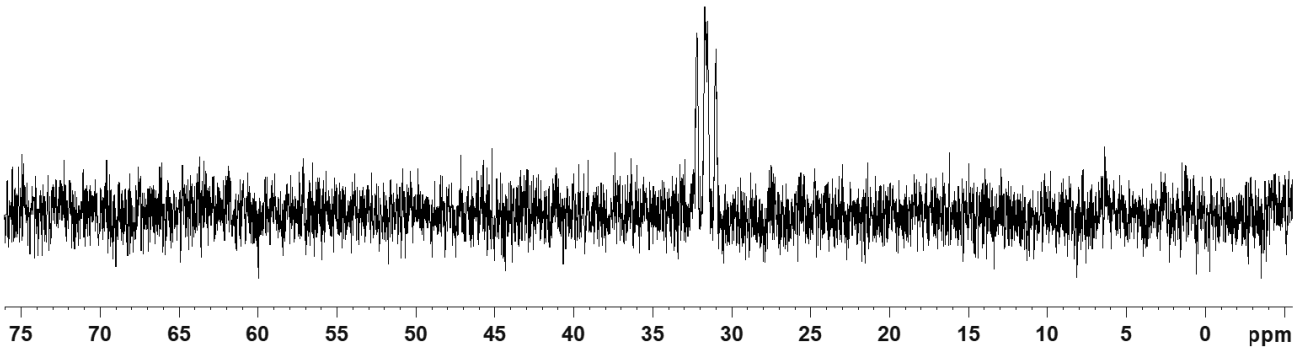


^{19}F NMR: **16b**



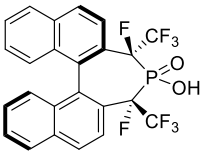
$^{31}P\{^{1}H\}$ NMR: **16b**

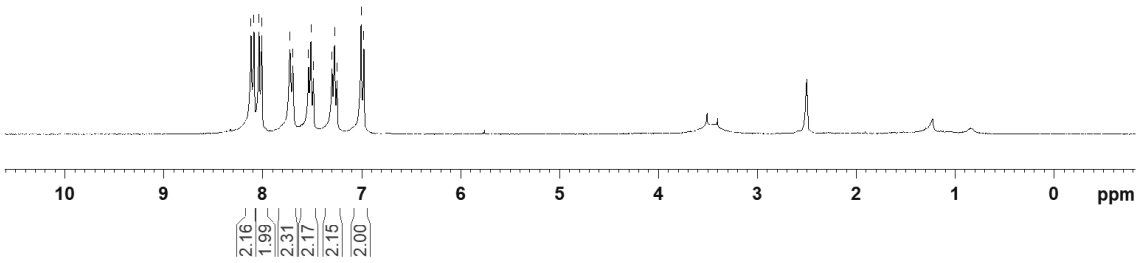




^{1}H NMR: **17a**

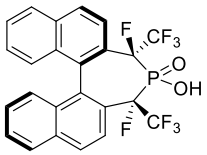
(DMSO-d^6)





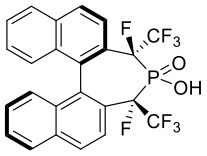
$^{13}C\{^{1}H\}$ NMR: **17a**

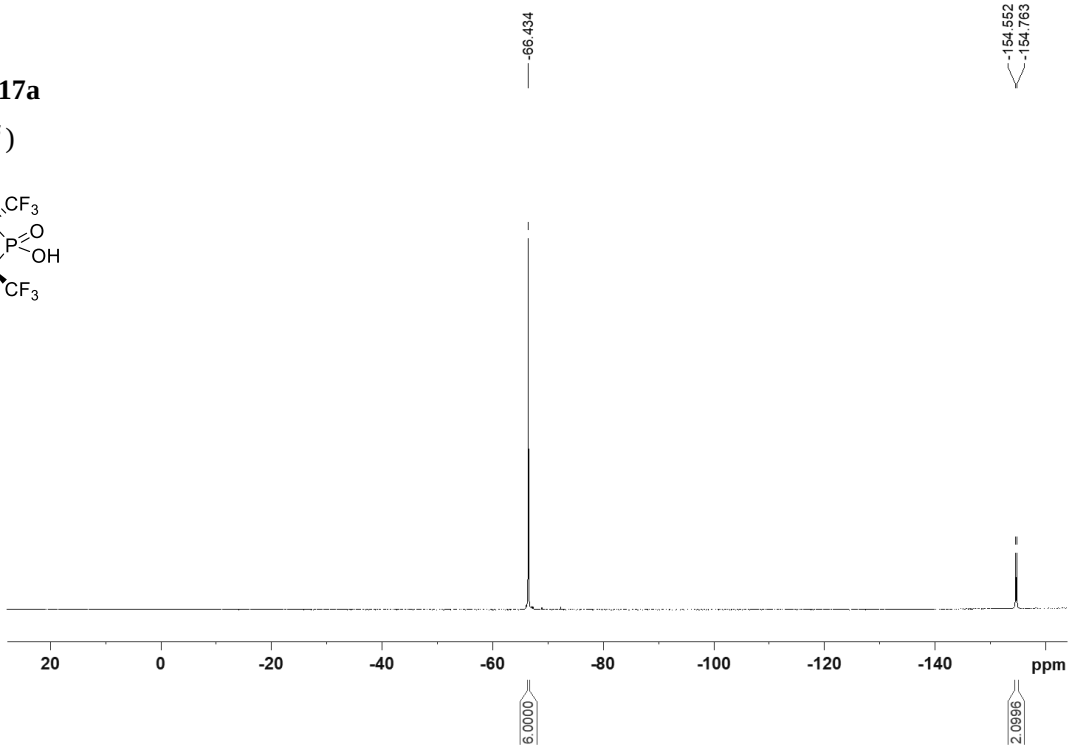
(DMSO-d^6)



^{19}F NMR: **17a**

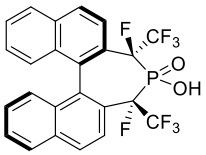
(DMSO-d^6)

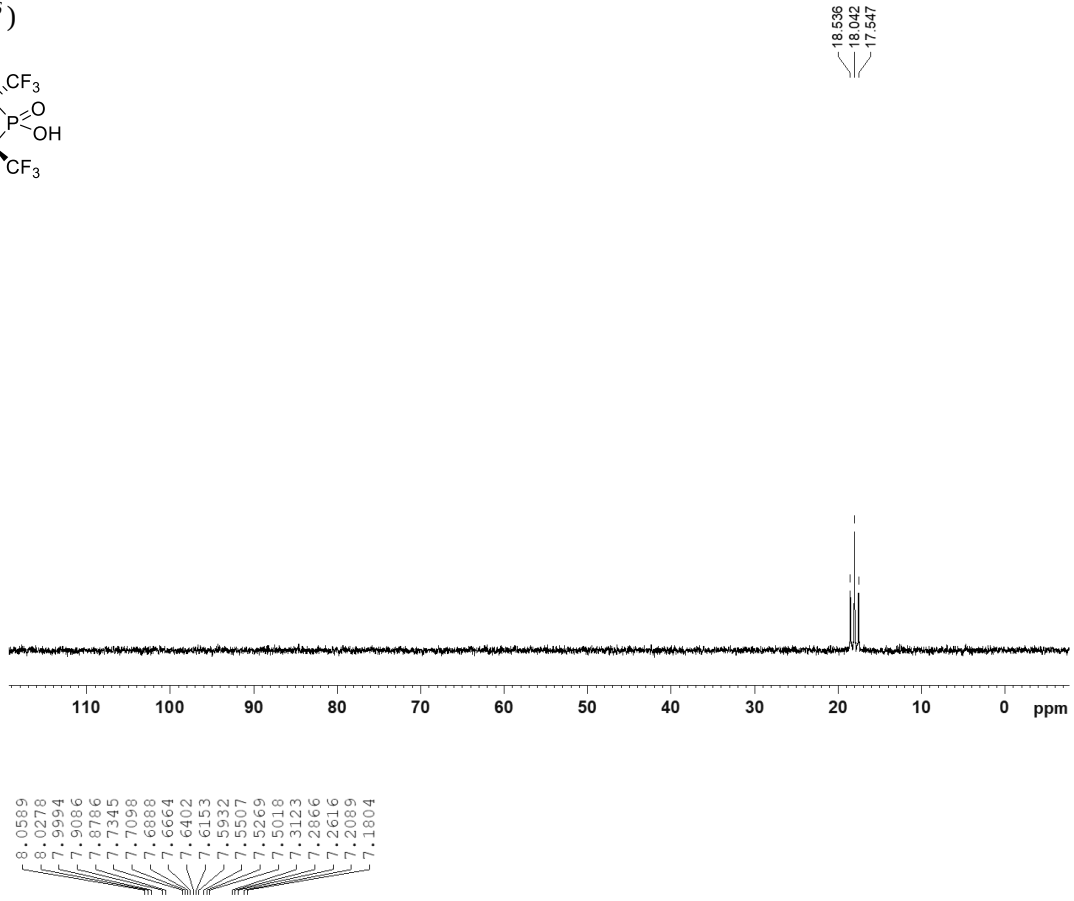




$^{31}P\{^{1}H\}$ NMR: **17a**

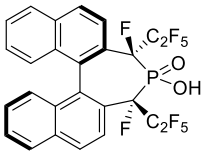
(DMSO-d^6)





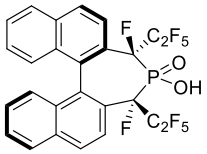
^{1}H NMR: **17b**

(acetone-d^6)



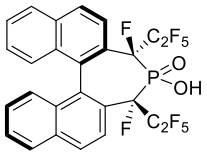
^{19}F NMR: **17b**

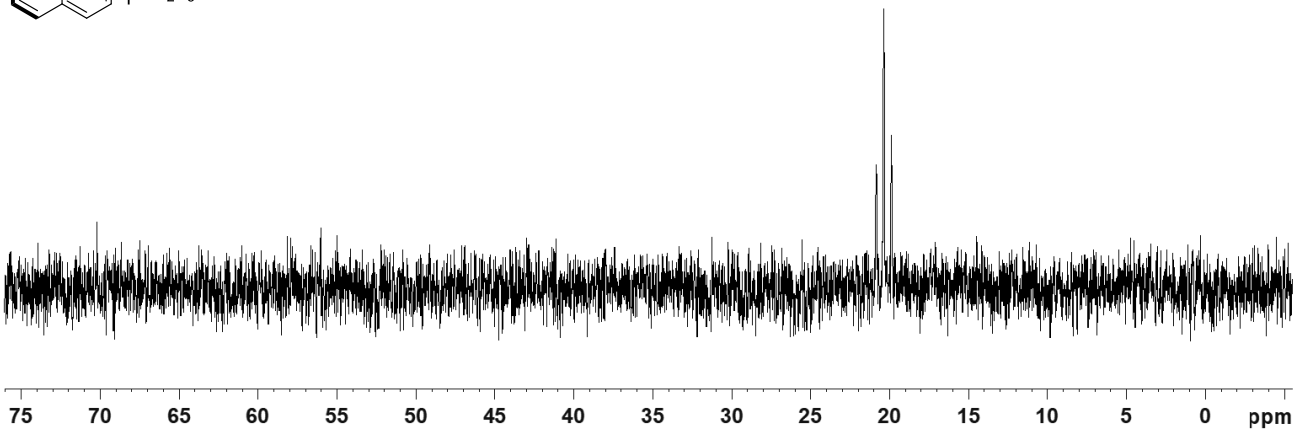
(acetone-d^6)

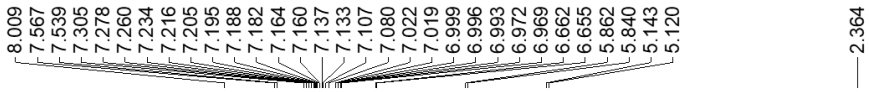


^{31}P{^{1}H} NMR: **17b**

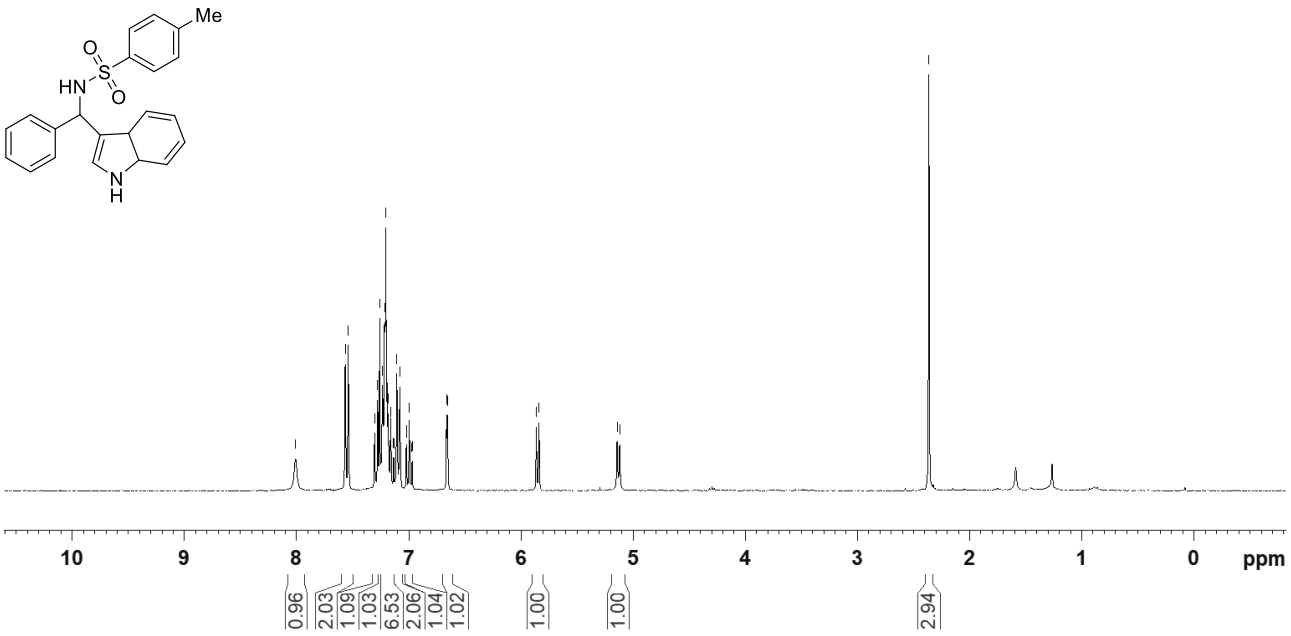
(acetone-d^6)

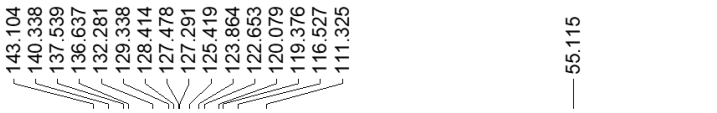






^{1}H NMR: **20**





^{13}C{^{1}H} NMR: **20**