Highly Efficient Synthesis of a Class of Novel Chiral-Bridged Atropisomeric Monophosphine Ligands via Simple Desymmetrization and Their Applications in Asymmetric Suzuki-Miyaura Coupling Reaction

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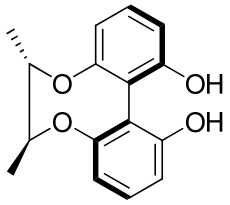
General Considerations: Anhydrous toluene, DMF, DME, DMSO, and pyridine were refluxed and distilled from CaH_2. Anhydrous THF was fleshly distilled from sodium and benzophenone before used. Acetone was refluxed and distilled from P_2O_5. Aryl boronic acids were purified by passing through a silica gel column before used. If not mentioned, all reagents were purchased from commercial sources and used without further purification. All reactions were carried out under an inert atmosphere of dry nitrogen and were monitored by TLC. Glassware was flame dried before use. Standard syringe techniques were applied to transfer dry solvents and reagents. The preparation of samples was carried out in a nitrogen-filled continuously purge glovebox or using standard Schlenk-type techniques. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded on a Varian Mercury-Plus 300 spectrometer at 300, 75 and 121.4 MHz respectively. Chemical shifts (δ) are given in ppm and are referenced to residual solvent peaks (^{1}H NMR and ^{13}C NMR) or to an external standard (85% H_3PO_4, ^{31}P NMR). HR-MS were carried out on a Bruker APEX 47e ESI FT-ICR mass spectrometer and Thermo MAT95XP EI-FAB-CI mass spectro-meter. Optical rotations were recorded on a Perkin-Elmer Model 341 polarimeter in a 10-cm cell at 20 ℃. HPLC analysis was performed on an Agilent 1200 series system using a Daicel Chiralpak OD-H or AD-H column. GC analysis was performed on an Agilent 7890 series system using a DB-5 column (30 m × 250 μm × 0.25μm).

Experimental section:

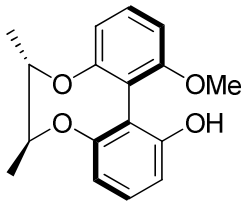
(1) The preparation of ligands 7a-7d

(*R*)-[6,6'-(2*S*,3*S*-butadioxy)]-(2,2')-dihydroxy-(1,1')-biphenyl (3)



Under N_2 atmosphere and at 80 ℃, a mixture of 2,2',6,6'-tetrahydroxybiphenyl [1] (1.06 g, 4.88 mmol) and Cs_2CO_3 (3.04 g, 9.36 mmol) in DMF (120 mL) was stirred for 1 h, then a solution of compound **2** (1.00 g, 4.07 mmol) in DMF (100 mL) was added dropwise into this mixture over a period of 4 h. The resulting suspension was stirred further for 24 h at this temperature. The resultant solution was concentrated *in vacuo* to give a crude product. The residue was poured into water and extracted three times with ethyl acetate. The extract was washed successively with 1N HCl solution, water and brine. The organic layer was separated, dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the residue by flash chromatography (20% ethyl acetate in petroleum ether) gave colorless crystals **3** (0.58 g 53%). $[\alpha]_D^{20}$-103.5 (c = 2.0 mg/mL, $CHCl_3$); ^{1}H NMR (300 MHz, d_6-DMSO): δ 1.28 (d, J = 5.4 Hz, 6H), 3.72-3.74 (m, 2H), 6.63 (d, J = 7.6 Hz, 2H), 6.67 (d, J = 7.6 Hz, 2H), 7.13 (t, J = 7.6 Hz, 2H), 9.15 (s, 2H) ppm. ^{13}C NMR (75 MHz, d_6-DMSO): δ 18.70, 85.46, 111.18, 112.33, 115.80, 128.54, 155.19, 159.79 ppm. MS (EI): $[M]^+$ 271.1; $C_{16}H_{16}O_4$.

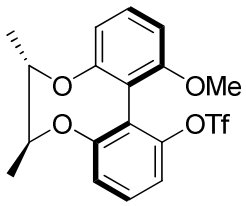
(*R*)-[6,6'-(2*S*,3*S*-butadioxy)]-2-hydroxy-2'-methoxy-(1,1')-biphenyl (4)



A mixture of **3** (0.70 g, 2.57 mmol) and K_2CO_3 (2.72 g, 5.22 mmol) in acetone (50 mL) was stirred at room temperature for 1 h under N_2 atmosphere, and then a

solution of iodomethane in acetone (50 mL) was added dropwise into this mixture over a period of 4 h. The mixture was stirred at room temperature for 18 h and then was filtered through a pad of celite, and the solid was washed with Et_2O. The combined organic layer was concentrated under reduced pressure. The residue was purified on silica gel (using 5% ethyl acetate in petroleum ether as eluent) to give 0.70 g (91%) of **4**. $[\alpha]_D^{20}$-105.5 (c = 2.0 mg/mL, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.38 (d, J = 6.0 Hz, 3H), 1.39 (d, J = 6.0 Hz, 3H), 3.86-3.96 (m, 2H), 3.90 (s, 3H), 6.74 (dd, J = 8.2 Hz, J = 1.2 Hz, 1H), 6.82-6.87 (m, 3H), 7.25 (t, J = 8.1 Hz, 1H), 7.35 (t, J = 8.1 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.83, 18.92, 56.45, 85.84, 86.00, 107.07, 107.21, 113.49, 114.06, 116.02, 116.44, 129.64, 129.82, 154.57, 155.80, 159.82, 160.50 ppm. MS (EI): $[M]^+$ 286; HRMS (EI): calcd for $C_{17}H_{18}O_4$ 286.1205, found 286.1199.

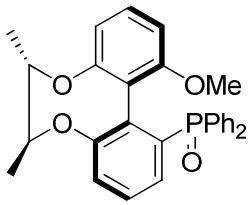
(*R*)-[6,6'-(2*S*,3*S*-butadioxy)]-2-trifluoromethanesulfonyloxy-2'-methoxy-(1,1')-biphenyl (5)



Trifluoromethanesulfonic anhydride (1.38 g, 4.90 mmol) was added dropwise to a solution of **4** (0.70 g, 2.45 mmol) in pyridine (5 mL) at 0 ℃. Then the mixture was allowed to warm to room temperature and stirred for 12 h. After removal of the solvent *in vacuo*, the residue was diluted with EtOAc and was then washed successively with aqueous HCl (10%), saturated $NaHCO_3$ and brine. The organic layer was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (using 5% ethyl acetate in petroleum ether as eluent) to give compound **5** as a yellowish solid (0.94 g, 92% yield). $[\alpha]_D^{20}$-55.5 (c = 2.0 mg/mL, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.38 (d, J = 6.0 Hz, 3H), 1.39 (d, J = 6.0 Hz, 3H), 3.80 (s, 3H), 3.84-3.89 (m, 2H), 6.76-6.80 (m, 2H), 7.13-7.17 (m, 2H), 7.34-7.41 (m, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.89,

55.54, 85.72, 86.52, 106.59, 114.13, 114.39, 116.61, 121.42, 121.81， 122.62, 129.16, 130.78 ppm. MS (EI): $[M]^+$ 418; HRMS (EI): calcd for $C_{18}H_{17}O_6F_3S$ 418.0698, found 418.0698.

(*R*)-[6,6'-(2*S*,3*S*-butadioxy)]-2-diphenylphosphoryl-2'-methoxy-(1,1')-biphenyl (6a)



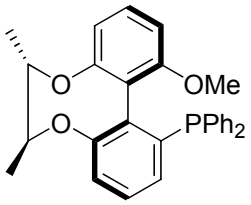
Under N_2 atmosphere, to a mixture of **5** (0.90 g, 2.15 mmol), diphenylphosphine oxide (0.87 g, 4.30 mmol), palladium acetate (96 mg, 0.43 mmol) and 1,3-bis(diphenylphosphino)propane (dppp) (184 mg, 0.43 mmol) were added dry dimethyl sulfoxide (10 mL) and diisopropylethylamine (1.5 mL). The mixture was heated with stirring at 110 ℃ for 24 h. After being cooled to room temperature, the reaction mixture was concentrated under reduced pressure to give a dark brown residue, which was diluted with EtOAc. The EtOAc solution was washed with aqueous HCl (10%) and dried over anhydrous $MgSO_4$. Removal of the solvent and flash column chromatography on silica gel (petroleum ether: ethyl acetate = 2:1) provided **6a** as a white solid (0.96 g, 95%). $[\alpha]_D^{20}$-117.0 (c = 2.0 mg/mL, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 1.35 (d, J = 8.4 Hz, 6H), 3.21 (s, 3H), 3.84-3.86 (m, 2H), 6.20 (d, J = 8.1 Hz, 1H), 6.54 (d, J = 8.1 Hz, 1H), 7.02 (t, 1H), 7.19-7.38 (m, 9H), 7.43-7.48 (m, 2H), 7.63-7.70(m, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.90, 19.02, 54.10, 85.29, 86.84, 105.10, 113.16, 117.67, 125.39, 127.30, 127.46, 127.65, 127.81, 128.06, 128.26, 129.85, 130.16, 130.31, 130.48, 130.68, 131.32, 131.39, 131.44, 131.50, 131.68, 131.77, 133.04, 133.70, 134.10, 135.09, 135.48, 156.88, 159.05, 159.17, 159.36 ppm (observed complexity due to P-C splitting). ^{31}P NMR (121.4 MHz, $CDCl_3$): δ 27.28 ppm. MS (EI): $[M]^+$ 470; HRMS (EI): calcd for $C_{29}H_{27}O_4P$ 470.1647, found 470.1653.

6b-6d was synthesized according to the general procedure of **6a**.

(*R*)-[6,6'-(2*S*,3*S*-butadioxy)]-2-di-(3,5-di-tert-butyl-phenyl)phosphoryl-2'-methoxy-(1,1')-biphenyl (6d)

81% yield, a white solid, $[\alpha]_D^{20}$-55.3 (c = 2.0 mg/mL, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.24 (s, 18H), 1.29 (s, 18H), 1.31-1.35 (m, 6H), 3.52 (s, 3H), 3.74-3.90 (m, 2H), 6.27 (d, J = 7.8 Hz 1H), 6.31 (d, J = 8.4 Hz 1H), 6.91 (t, J = 8.4 Hz 1H), 7.26-7.35 (m, 6H), 7.47 (s, 1H), 7.58 (d, J = 1.8 Hz 1H), 7.62 (d, J = 1.8 Hz 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.00, 19.07, 31.24, 31.35, 31.41, 34.82, 35.01, 54.71, 85.36, 86.85, 105.37, 113.03, 117.94, 124.95, 125.54, 125.64, 125.97, 126.10, 127.94, 128.13, 129.77, 129.85, 130.63, 130.78, 131.04, 131.93, 132.04, 132.42, 132.57, 132.76, 133.95, 134,11, 149.31, 149.53, 149.94, 150.09, 157.27, 158.90, 159.06, 159.24 ppm (observed complexity due to P-C splitting). ^{31}P NMR (121.4 MHz, $CDCl_3$): δ 31.47 ppm. MS (ESI): $[M+H]^+$ 695; HRMS (ESI) $[M+H]^+$: calcd for $C_{45}H_{59}O_4P$, 695.4252, found 695.4224.

(*R*)-[6,6'-(2*S*,3*S*-butadioxy)]-2-diphenylphosphino-2'-methoxy-(1,1')-biphenyl (7a)



A 100 mL, two-necked flask equipped with a magnetic stirring bar and a reflux condenser was charged with **6a** (0.60 g, 1.27 mmol) and the system was flushed with nitrogen. Dry and degassed toluene (50 mL), diisopropylethylamine (6.88 mL, 38.1 mmol) and trichlorosilane (1.70 g, 12.8 mmol) were added to the flask. The mixture was stirred and refluxed overnight. After the solution was cooled to 0 ℃, a 30% aqueous sodium hydroxide solution (17.5 mL) was carefully added. The mixture was then stirred at 60 ℃ until the organic and aqueous layers become clear. The organic product was extracted with EtOAc, and the extract was washed successively with water and brine and dried over anhydrous $MgSO_4$. The organic layer was concentrated under reduced pressure to give a crude product. The residue was purified

by silica gel column chromatography (using 5% ethyl acetate in petroleum ether as eluent) to give compound **7a** as a white solid (0.55 g, 95%). $[\alpha]_D^{20}$-128.5 (c = 2.0 mg/mL, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.40 (d, J = 6.0 Hz, 6H), 3.13 (s, 3H), 3.87-3.94 (m, 2H), 6.64-6.67 (m, 1H), 6.78-6.81 (m, 1H), 7.05-7.10 (m, 1H), 7.11-7.15 (m, 2H), 7.17-7.21 (m, 4H), 7.27 (d, J=7.5 Hz, 1H), 7.30-7.48(m, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.03, 19.09, 54.23, 85.74, 86.45, 105.60,114.07, 119.41, 122.72, 127.54, 127.90, 127.99, 128.70, 129.70, 131.42, 132.82, 133.02, 133.27, 134.21, 134.66, 137.82, 138.02, 138.20, 140.16, 140.34 ppm. ^{31}P NMR (121.4 MHz, $CDCl_3$): δ -9.68 ppm. MS (EI): $[M]^+$ 454; HRMS (EI): calcd for $C_{29}H_{27}O_3P$ 454.1698, found 454.1694.

7b-7d was synthesized according to the general procedure of **7a**.

(*R*)-[6,6'-(2*S*,3*S*-butadioxy)]-2-di-(4-methy-phenyl)phosphino -2'-methoxy-(1,1')-biphenyl (7b)

93% yield, a white solid, $[\alpha]_D^{20}$-119.5 (c = 2.0 mg/mL, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.36-1.38 (m, 6H), 2.27 (s, 3H), 2.39 (s, 3H), 3.20 (s, 3H), 3.86-3.88 (m, 2H), 6.62-6.65 (m, 1H), 6.73-6.77 (m, 1H), 6.97-7.02 (m, 4H), 7.05-7.09 (m, 1H), 7.11-7.18 (m, 3H), 7.24 (d, J = 7.8 Hz), 7.23-7.36 (m, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.96, 19.07, 21.16, 21.27, 54.24, 85.63, 86.34, 105.57, 113.88, 119.45, 119.54, 128.53, 128.60, 129.47, 130.99, 132.74, 132.90, 133.00, 133.15, 134.00, 134.45, 134.73, 134.88, 136.71, 136.88, 137.03, 137.16, 138.76, 138.95, 157.20, 158.61, 158.75, 159.80ppm (observed complexity due to P-C splitting). ^{31}P NMR (121.4 MHz, $CDCl_3$): δ -10.60 ppm. MS (ESI): $[M+H]^+$ 483; HRMS (ESI) $[M+H]^+$: calcd for $C_{31}H_{31}O_3P$, 483.2102, found 483.2084.

(*R*)-[6,6'-(2*S*,3*S*-butadioxy)]-2-di-(3,5-di-methy-phenyl)phosphino-2'-methoxy-(1,1')-biphenyl (7c)

89% yield, a white solid, $[\alpha]_D^{20}$-166.7 (c = 2.0 mg/mL, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42-1.43 (m, 6H), 2.24 (m, 6H), 2.37 (m, 6H), 3.92-3.94 (m, 2H), 6.62 (dd, J = 8.1, Hz, J = 0.9 Hz, 1H), 6.68-6.71 (m, 3H), 6.78 (s, 1H), 6.94 (s, 1H),

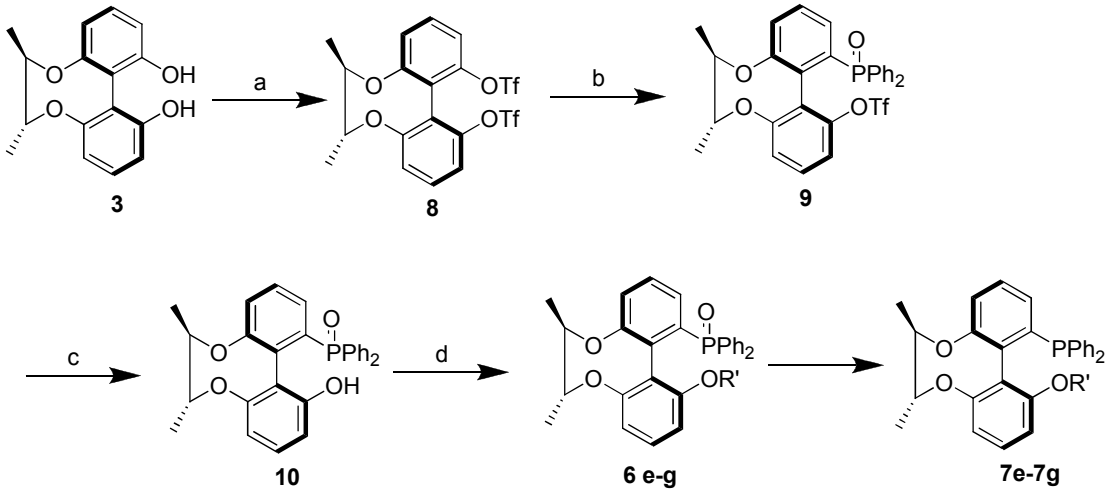
7.01-7.07 (m, 3H), 7.11 (dd, J = 8.1, Hz, J = 1.5 Hz, 1H), 7.22-7.28 (m, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.10, 21.25, 21.45, 54.46, 85.57, 86.44, 105.86, 113.95, 119.49, 119.58, 122.27, 128.61, 129.44, 130.60, 130.72, 130.86, 130.98, 131.21, 131.30, 133.70, 134.13, 136.83, 136.92, 137.05, 137.14, 137.83, 137.99, 138.88, 138.13, 139.30, 157.10, 158.65, 158.78, 159.85 ppm (observed complexity due to P-C splitting). ^{31}P NMR (121.4 MHz, $CDCl_3$): δ -7.73 ppm. MS (ESI): $[M+H]^+$ 511; HRMS (ESI) $[M+H]^+$: calcd for $C_{33}H_{35}O_3P$, 511.2418, found 511.2397.

(*R*)-[6,6'-(2*S*,3*S*-butadioxy)]-2-di-(3,5-di-tert-butyl-phenyl)phosphino-2'-methoxy -(1,1')-biphenyl (7d)

90% yield, a white solid, $[\alpha]_D^{20}$-113.2 (c = 2.0 mg/mL, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 1.18 (s, 18H), 1.29 (s, 18H), 1.32-1.37 (m, 6H), 3.57 (s, 3H), 3.82-3.84 (m, 2H), 6.20 (dd, J = 7.8 Hz J = 0.9 Hz 1H), 6.67 (d, J = 8.4 Hz, 1H), 6.94-6.98 (m, 1H), 7.11 (dd, J = 7.8 Hz J = 1.2 Hz 1H), 7.17-7.23 (m, 3H), 7.29-7.36 (m, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 31.42, 31.56, 34.78, 34.95, 54.98, 85.63, 86.67, 106.09, 113.95, 119.74, 119.81, 121.30, 121.50, 121.98, 127.07, 127.33, 127.62, 127.89, 128.40, 129.42, 130.11, 133.43, 133.84, 137.40, 137.58, 137.95, 138.11, 140.33, 140.53, 149.22, 149.29, 149.77, 149.85, 157.02, 158.67, 158.79, 160.01 ppm (observed complexity due to P-C splitting). ^{31}P NMR (121.4 MHz, $CDCl_3$): δ -4.00 ppm. MS (ESI): $[M+H]^+$ 679; HRMS (ESI) $[M+H]^+$: calcd for $C_{33}H_{35}O_3P$, 679.4309, found 679.4275.

(2) The preparation of ligands 7e-7g:

Ligands **7e-7g** were prepared according to the synthetic route in Scheme 1.



Scheme 1. Synthetic route to ligands **7e**-**7g** a) Tf_2O, pyridine, 90%; b) $Pd(OAc)_2$, dppb, $EtN(i\text{-}Pr)_2$, $Ph_2P(O)H$, DMSO, 110 ℃, 95%; c) NaOH, H_2O, EtOH, 92%; d) K_2CO_3, acetone, EtI; or *i*-Pr-Br, Bn-Br, THF, acetone reflux; e) $HSiCl_3$, $EtN(i\text{-}Pr)_2$, toluene, 110 ℃.

(*R*)-[6,6'-(2*S*,3*S*-butadioxy)]-2-diphenylphosphino-2'-ethoxy-(1,1')-biphenyl (7e)

92% yield, a white solid, $[\alpha]_D^{20}$-141.83 (c = 2.0 mg/mL, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 0.91 (t, J = 6.9 Hz, 3H), 1.32-1.37 (m, 6H), 3.67-3.89 (m, 4H), 6.65-6.68 (m, 2H), 6.99-7.06 (m, 3H), 7.09-7.15 (m, 4H), 7.21-7.27 (m, 2H), 7.32-7.38 (m, 3H), 7.40-7.46 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 14.25, 19.00, 19.09, 66.36, 85.73, 86.45, 107.13, 113.67, 119.78, 119.87, 122.34, 127.42, 127.68, 127.87, 127.94, 128.50, 129.43, 130.47, 132.57, 132.84, 133.20, 133.45, 134.17, 134.61, 138.00, 138.19, 138.57, 138.75, 139.56, 139.75, 156.55, 158.70, 158.83, 160.00 ppm (observed complexity due to P-C splitting). ^{31}P NMR (121.4 MHz, $CDCl_3$): δ -8.20 ppm. MS (ESI): $[M+H]^+$ 469; HRMS (ESI) $[M+H]^+$: calcd for $C_{30}H_{29}O_3P$, 469.1925, found 469.1927.

(*R*)-[6,6'-(2*S*,3*S*-butadioxy)]-2-diphenylphosphino-2'-isopropoxy-(1,1')-biphenyl (7f)

90% yield, a white solid, $[\alpha]_D^{20}$-173.83 (c = 2.0 mg/mL, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 0.90 (d, J = 6.3 Hz, 3H), 1. 02 (d, J = 6.0 Hz, 3H), 1.32 (d, J = 6.0 Hz,

3H), 1.36 (d, J = 6.0 Hz, 3H), 3.75-3.88 (m, 2H), 4.19-4.27 (m, 1H), 6.66 (d, J = 8.1 Hz, 1H), 6.20 (d, J = 8.1 Hz, 1H), 6.96-7.09 (m, 3H), 7.11-7.15 (m, 3H), 7.20-7.26 (m, 3H), 7.31-7.35 (m, 3H), 7.30-7.46 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 19.02, 19.12, 21.47, 22.25, 71.98, 85.81, 86.55, 110.26, 113.95, 121.56, 122.22, 127.42, 127.59, 127.68, 127.80, 127.88, 128.52, 129.29, 130.33, 132.59, 132.85, 133.26, 133.51, 134.44, 134.87, 138.15, 138.34, 138.72, 138.90, 139.47, 139.66, 156.00, 158.71, 158.83, 160.19 ppm (observed complexity due to P-C splitting). ^{31}P NMR (121.4 MHz, $CDCl_3$): δ -8.27 ppm. MS (ESI): $[M+H]^+$ 483; HRMS (ESI) $[M+H]^+$: calcd for $C_{31}H_{31}O_3P$, 483.2104, found 483.2084.

(*R*)-[6,6'-(2*S*,3*S*-butadioxy)]-2-diphenylphosphino-2'-beneyloxy-(1,1')-biphenyl (7g)

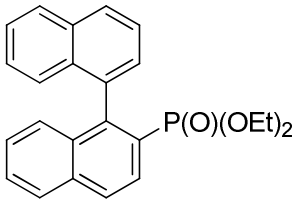
88% yield, a white solid, $[\alpha]_D^{20}$-148.83 (c = 2.0 mg/mL, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.33 (d, J = 5.7 Hz, 3H), 1.38 (d, J = 5.7 Hz, 3H), 3.80-3.88 (m, 2H), 4.70 (d, J = 12.6 Hz, 1H), 4.93 (d, J = 12.6 Hz, 1H), 6.65-6.72 (m, 2H), 6.89-6.93 (m, 1H), 7.03-7.07 (m, 2H), 7.13-7.27 (m, 16H). ^{13}C NMR (75 MHz, $CDCl_3$): 19.03, 19.14, 70.10, 85.70, 86.48, 108.32, 114.36, 120.21, 120.29, 122.37, 126.54, 126.97, 127.55, 127.65, 127.74, 127.85, 127.97, 128.70, 129.46, 130.07, 132.72, 132.99, 133.11, 133.36, 133.81, 134.24, 137.34, 137.89, 138.07, 138.77, 138.88, 138.95, 139.06, 156.31, 158.74, 158.87, 160.08 ppm (observed complexity due to P-C splitting). ^{31}P NMR (121.4 MHz, $CDCl_3$): δ -7.21 ppm. MS (ESI): $[M+H]^+$ 531; HRMS (ESI) $[M+H]^+$: calcd for $C_{35}H_{31}O_3P$, 531.2090, found 531.2084.

(3) General procedure for asymmetric Suzuki coupling

An oven-dried one-necked flask (10 mL) was charged with aryl halide (1.0 mmol, 1.0 equiv), $Pd_2(dba)_3$ (2 mol%), ligand **7a-7g** (L:Pd = 1.2:1), arylboronic acid (2.0 equiv), and K_3PO_4 (3 equiv) in glovebox, then 5 mL toluene was injected into the flask. The racemic products were prepared by using S-phos as the ligand and all the racemic reactions were performed at 100 ℃ for 24 h. For the asymmetric catalytic reaction,

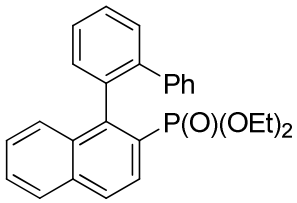
the mixture was stirred vigorously at the indicated temperature (20-70 ℃) for 48-120 h. The reaction was monitored by TLC or GC analysis. After reaction completion, the reaction mixture was cooled to room temperature, diluted with ethyl acetate and water, extracted, the combined organic layers was then dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified by flash chromatography on silica gel.

(*R*)-(+)-Diethyl 2-(1,1'-binaphthyl)phosphonate[2] (table 2, entry 1)



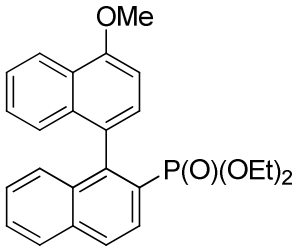
The reaction was conducted for 48 h at 40 ℃ according to the general procedure using 171 mg diethyl 1-bromo-2-naphthylphosphonate(1.0 equiv), 9.1mg $Pd_2(dba)_3$ (4.0 mol% Pd), 16.3 mg ligand **7d** (4.8 mol%), 172 mg 1-Naphthylboric acid (2.0 equiv), 318 mg K_3PO_4 (3.0 equiv) and 5 mL toluene on a 0.5 mmol scale. The product was purified by flash chromatography to give 122 mg the title compound as a white solid (62% yield). Ee value was determined by Chiral HPLC (AD-H column, flow rate 1.0 mL/min, 10% *i*-PrOH, 90% hexane, T_{major} = 8.5 min T_{minor} = 10.6 min) (88% ee). $[\alpha]_D^{20}$+45.8 (c = 2.0 mg/mL, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.74 (t, J = 6.9Hz, 3H), 0.99 (t, J = 6.9 Hz, 3H), 3.54-3.83 (m, 4H), 7.08-7.25 (m, 4H), 7.40-7.45 (m, 1H), 7.49-7.55 (m, 2H), 7.57-7.62 (m, 1H), 7.90-8.04 (m, 4H), 8.19-8.26 (m, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.47, 15.56, 15.94, 16.03, 61.47, 61.54, 61.65, 61.73, 124.76, 125.42, 125.68, 126.52, 127.32, 127.40, 127.64, 127.73, 127.82, 128.07, 128.42, 128.53, 132.95, 133.18, 134.73, 135.68, 135.74, 143.22, 143.35 ppm (observed complexity due to P-C splitting). ^{31}P NMR (121.4 MHz, $CDCl_3$): δ 18.95 ppm. MS (EI): $[M]^+$ 390.1.

Diethyl 1-(2'-biphenyl)-2-naphthylphosphonate[2] (table 2, entry 2)



The reaction was conducted for 48 h at 60 ℃ according to the general procedure using 171 mg diethyl 1-bromo-2-naphthylphosphonate(1.0 equiv), 9.1mg $Pd_2(dba)_3$ (4.0 mol% Pd), 16.3 mg ligand **7d** (4.8 mol%), 254 mg 2-Biphenylboronic acid (2.0 equiv), 318 mg K_3PO_4 (3.0 equiv) and 5 mL toluene on a 0.5 mmol scale. The product was purified by flash chromatography to give 135 mg title product as a colorless oil (65% yield). Ee value was determined by Chiral HPLC (OD-H column, flow rate 0.5 mL/min, 10% *i*-PrOH, 90% hexane, T_{minor} = 11.5 min T_{major} = 12.1min) (79% ee). $[\alpha]_D^{20}$-10.1 (c = 2.0 mg/mL, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$):1.16 (t, J = 7.2 Hz, 3H), 1.7 (t, J = 7.2 Hz, 3H), 3.64-3.77 (m, 1H), 3.88 (m, 3H), 6.92-6.96 (m, 3H), 7.15-7.26 (m, 3H), 7.32-7.55 (m, 5H), 7.70-7.82 (m, 2H), 7.94-8.01 (m, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.16, 16.25, 16.34, 61.77, 124.39, 126.15, 126.32, 126.89, 127.15, 127.26, 127.34, 127.54, 127.68, 128.14, 128.92, 129.48, 131.48, 132.09, 132.31, 134.38, 136.65, 136.71, 141.04, 141.82, 144.47, 144.61 ppm (observed complexity due to P-C splitting). ^{31}P NMR (121.4 MHz, $CDCl_3$): δ 18.92 ppm. MS (ESI): $[M+H]^+$ 417.1.

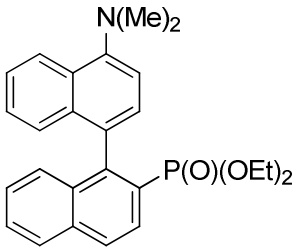
Diethyl 2-(4'-methoxy-1,1'-binaphthyl)phosphonate[2] (table 2, entry 3)



The reaction was conducted for 120 h at 20 ℃ according to the general procedure using 171 mg diethyl 1-bromo-2-naphthylphosphonate(1.0 equiv), 9.1mg $Pd_2(dba)_3$ (4.0 mol% Pd), 16.3 mg ligand **7d** (4.8 mol%), 202 mg 4-methoxy-1-Naphthylboric acid (2.0 equiv), 318 mg K_3PO_4 (3.0 equiv) and 5 mL

toluene on a 0.5 mmol scale. The product was purified by flash chromatography to give 202 mg title product as a colorless oil (96% yield). Ee value was determined by Chiral HPLC (OD-H column, flow rate 0.5 mL/min, 5% *i*-PrOH, 95% hexane, T_{minor} = 21.9 min T_{major} = 26.4 min) (97% ee). $[\alpha]_D^{20}$+13.8 (c = 2.0 mg/mL, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.79 (t, J = 6.9 Hz, 3H), 0.93 (t, J = 6.9 Hz, 3H), 3.47-3.78 (m, 4H), 4.08 (s, 3H), 6.91-7.00 (m, 2H), 7.18-7.24 (m, 3H), 7.37-7.52 (m, 3H), 7.89-7.99 (m, 2H), 8.12-8.19 (m, 1H), 8.31-8.34 (m, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.53, 15.62, 15.84, 15.93, 55.42, 61.41, 61.48, 61.62, 61.70, 102.74, 121.74, 124.61, 124.99, 125.13, 126.08, 126.24, 126.34, 127.18, 127.37, 127.50, 127.64, 128.30, 128.43, 128.58, 133.39, 133.60, 134.00, 134.70, 143.51, 143.64, 155.23 ppm (observed complexity due to P-C splitting). ^{31}P NMR (121.4 MHz, $CDCl_3$): δ 19.27 ppm. MS (ESI): $[M+H]^+$ 421.1.

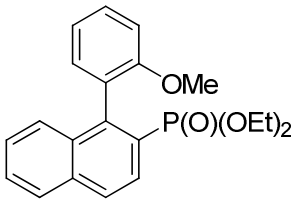
Diethyl 2-(4'-N,N-dimethyl-1,1'-binaphthyl)phosphonate (table 2, entry 4)



The reaction was conducted for 120 h at 20 □ according to the general procedure using 171 mg diethyl 1-bromo-2-naphthylphosphonate (1.0 equiv), 9.1 mg $Pd_2(dba)_3$ (4.0 mol% Pd), 16.3 mg ligand **7d** (4.8 mol%), 215 mg 4-dimethylamino-1-Naphthylboronic acid (2.0 equiv), 318 mg K_3PO_4 (3.0 equiv) and 5 mL toluene on a 0.5 mmol scale. The product was purified by flash chromatography gave 201 mg desired product as a colorless oil (93% yield). Ee value was determined by Chiral HPLC (OD-H column, flow rate 0.5 mL/min, 10% *i*-PrOH, 90% hexane, T_{minor} = 10.4 min T_{major} = 12.1 min) (97% ee). $[\alpha]_D^{20}$+8.3 (c = 2.0 mg/mL, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.79 (t, J = 6.9 Hz, 3H), 0.92 (t, J = 6.9 Hz, 3H), 3.00 (s, 6H), 3.44-3.79 (m, 4H), 7.05(d, J = 8.4 Hz, 1H), 7.16-7.25 (m, 4H), 7.39-7.53 (m, 3H), 7.91 (d, J = 8.1 Hz, 1H), 7.97-8.01 (m, 1H), 8.14-8.21 (m, 1H), 8.32 (d, J=8.7 Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.60, 15.69, 15.92, 16.01, 45.32, 61.52, 61.59,

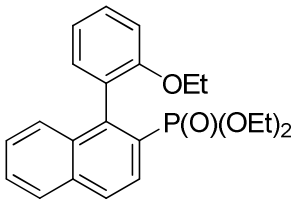
61.69, 61.77, 112.90, 124.00, 124.59, 125.04, 125.46, 126.43, 127.14, 127.24, 127.44, 127.59, 127.70, 127.86, 128.19, 128.36, 128.49, 128.58, 130.17, 130.24, 133.39, 133.60, 134.43, 134.77, 143.77, 143.90, 150.82 ppm (observed complexity due to P-C splitting). ^{31}P NMR (121.4 MHz, $CDCl_3$): δ 19.16 ppm. MS (ESI): $[M+H]^+$ 434; HRMS (ESI) $[M+H]^+$: calcd for $C_{26}H_{28}O_3NP$, 434.1880, found 434.1913.

Diethyl 1-(2'-methoxyphenyl)-2-naphthylphosphonate (table 2, entry 5)



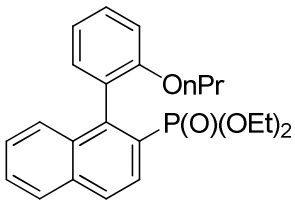
The reaction was conducted for 120 h at 20 □ according to the general procedure using 171 mg diethyl 1-bromo-2-naphthylphosphonate (1.0 equiv), 9.1 mg $Pd_2(dba)_3$ (4.0 mol% Pd), 16.3 mg ligand **7d** (4.8 mol%), 152 mg 2-methoxyphenyl boronic acid (2.0 equiv), 318 mg K_3PO_4 (3.0 equiv) and 5 mL toluene on a 0.5 mmol scale. The product was purified by flash chromatography to give 181 mg desired product as a white solid (98% yield). Ee value was determined by Chiral HPLC (OD-H column, flow rate 0.5 mL/min, 10% *i*-PrOH, 90% hexane, T_{major} = 15.4 min T_{minor} = 16.7 min) (78% ee). $[\alpha]_D^{20}$-42.0 (c = 2.0 mg/mL, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.19 (t, J = 7.2 Hz, 3H), 1.20 (t, J = 7.2 Hz, 3H), 3.66 (s, 3H), 3.81-4.00 (m, 4H), 7.00-7.03 (m, 1H), 7.04-7.09 (m, 1H), 7.21-7.24 (m, 1H), 7.34-7.56 (m, 4H), 7.87-7.94 (m, 2H), 8.06-8.13 (m, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.01, 16.07, 16.09, 16.16, 55.11, 61.35, 61.43, 61.48, 61.55, 109.96, 119.55, 123.58, 126.11, 126.80, 126.86, 126.98, 127.05, 127.31, 127.54, 128.13, 128.27, 129.19, 131.85, 132.41, 132.62, 134.54, 134.57, 142.10, 142.22, 157.18 ppm (observed complexity due to P-C splitting). ^{31}P NMR (121.4 MHz, $CDCl_3$): δ 19.35 ppm. MS (ESI): $[M+H]^+$ 371; HRMS (ESI) $[M+H]^+$: calcd for $C_{21}H_{23}O_4P$, 371.1407, found 371.1430.

Diethyl 1-(2'-ethoxy phenyl)-2-naphthylphosphonate (table 2, entry 6)



The reaction was conducted for 120 h at 20 □ according to the general procedure using 171 mg diethyl 1-bromo-2-naphthylphosphonate (1.0 equiv), 9.1 mg $Pd_2(dba)_3$ (4.0 mol% Pd), 16.3 mg ligand **7d** (4.8 mol%), 166 mg 2-ethoxyphenyl boronic acid (2.0 equiv), 318 mg K_3PO_4 (3.0 equiv) and 5 mL toluene on a 0.5 mmol scale. The product was purified by flash chromatography to give 188 mg desired product as a colorless oil (98% yield). Ee value was determined by Chiral HPLC (AD-H column, flow rate 0.5 mL/min, 10% *i*-PrOH, 90% hexane, T_{major} = 12.2 min T_{minor} = 13.3 min) (92% ee). **7a** $[\alpha]_D^{20}$-77.0 (c = 2.0 mg/mL, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.00 (t, J = 6.9 Hz, 3H), 1.16-1.23 (m, 6H), 3.82-4.00 (m, 6H), 6.97-7.00 (m, 1H), 7.02-7.07 (m, 1H), 7.25-7.25 (m, 1H), 7.33-7.45 (m, 3H), 7.50-7.56 (m, 1H), 7.86-7.93 (m, 2H), 8.07-8.13 (m, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.88, 16.45, 16.55, 16.65, 61.84, 61.92, 62.01, 63.78, 111.45, 119.89, 123.92, 126.40, 127.23, 127.42, 127.59, 127.70, 127.95, 128.63, 128.76, 129.58, 132.36, 132.89, 133.10, 134.98, 142.87, 142.99, 157.00 ppm (observed complexity due to P-C splitting). ^{31}P NMR (121.4 MHz, $CDCl_3$): δ 19.55 ppm. MS (ESI): $[M+H]^+$ 385; HRMS (ESI) $[M+H]^+$: calcd for $C_{22}H_{25}O_4P$, 385.1563, found 385.1582.

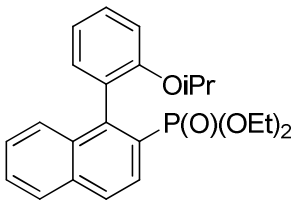
Diethyl 1-(2'-propoxy phenyl)-2-naphthylphosphonate (table 2, entry 7)



The reaction was conducted for 120 h at 20 □ according to the general procedure using 171 mg diethyl 1-bromo-2-naphthylphosphonate (1.0 equiv), 9.1 mg $Pd_2(dba)_3$ (4.0 mol% Pd), 16.3 mg ligand **7d** (4.8 mol%), 180 mg 2-propoxyphenyl boronic acid (2.0 equiv), 318 mg K_3PO_4 (3.0 equiv) and 5 mL toluene on a 0.5 mmol scale. The

product was purified by flash chromatography to give 185 mg desired product as a colorless oil (93% yield). Ee value was determined by Chiral HPLC (AD-H column, flow rate 0.5 mL/min, 5% *i*-PrOH, 95% hexane, T_{major} = 20.4 min, T_{minor} = 21.7 min) (92% ee). $[\alpha]_D^{20}$-105.7 (c = 2.0 mg/mL, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): 0.46 (t, J = 7.5 Hz, 3H), 1.14-1.23 (m, 6H), 1.32-1.39 (m, 2H), 3.72-3.99 (m, 6H), 6.98 (d, J = 8.4 Hz, 1H), 7.05 (dt, J = 7.5 Hz, J = 0.6 Hz, 1H), 7.24-7.45 (m, 4H), 7.52 (dt, J = 6.3 Hz, J = 1.8 Hz, 1H), 7.86-7.93 (m, 2H), 8.07-8.14 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 10.11, 16.03, 16.13, 16.17, 16.26, 22.26, 61.54, 61.62, 61.70, 69.29, 110.89, 119.50, 123.21, 125.70, 126.02, 126.84, 127.03, 127.14, 127.25, 127.34, 127.53, 127.91, 128.06, 128.24, 128.38, 128.52, 128.71, 129.22, 131.85, 132.50, 132.71, 134.56, 142.51, 142.63, 156.72 ppm (observed complexity due to P-C splitting). ^{31}P NMR (121.4 MHz, $CDCl_3$): δ 19.72 ppm. MS (ESI): $[M+H]^+$ 399; HRMS (ESI) $[M+H]^+$: calcd for $C_{23}H_{23}O_4P$, 339.1720, found 339.1720.

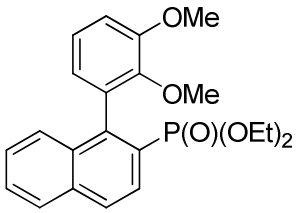
Diethyl 1-(2'-isopropoxy phenyl)-2-naphthylphosphonate (table 2, entry 8)



The reaction was conducted for 120 h at 20 □ according to the general procedure using 171 mg diethyl 1-bromo-2-naphthylphosphonate (1.0 equiv), 9.1 mg $Pd_2(dba)_3$ (4.0 mol% Pd), 16.3 mg ligand **7d** (4.8 mol%), 180 mg 2-isopropoxyphenyl boronic acid (2.0 equiv), 318 mg K_3PO_4 (3.0 equiv) and 5 mL toluene on a 0.5 mmol scale. The product was purified by flash chromatography to give 183 mg desired product as a colorless oil (92% yield). Ee value was determined by Chiral HPLC (AD-H column, flow rate 0.5 mL/min, 5% *i*-PrOH, 95% hexane, T_{major} = 20.4 min T_{minor} = 24.0 min) (93% ee). $[\alpha]_D^{20}$-89.5 (c = 2.0 mg/mL, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.94 (d, J = 5.7 Hz, 3H), 1.02 (d, J = 6.0 Hz, 3H), 1.19 (q, J = 7.2 Hz, 6H), 3.79-4.01 (m, 4H), 4.40-4.48 (m, 1H), 6.99 (d, J = 8.1 Hz, 1H), 7.04 (dd, J = 7.5 Hz J = 1.2 Hz 1H), 7.24-7.27 (m, 1H), 7.32-7.43 (m, 3H), 7.50-7.55 (m, 1H), 7.86-7.92 (m, 2H),

8.07-8.14 (m, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.45, 16.55, 16.58, 16.68, 21.92, 22.60, 61.85, 61.97, 62.05, 70.10, 112.58, 119.75, 123.78, 126.23, 127.16, 127.35, 127.70, 127.89, 128.29, 128.36, 128.73, 128.86, 129.44, 132,56, 132.79, 133.00, 134.94, 143.06, 143.18, 156.08 ppm (observed complexity due to P-C splitting). ^{31}P NMR (121.4 MHz, $CDCl_3$): δ 19.79 ppm. MS (ESI): $[M+H]^+$ 399; HRMS (ESI) $[M+H]^+$: calcd for $C_{23}H_{23}O_4P$, 339.1698, found 339.1696.

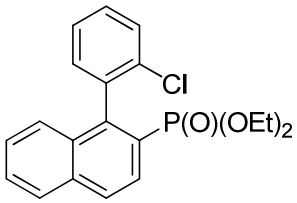
Diethyl 1-(2',3'-dimethoxyphenyl)-2-naphthylphosphonate (table 2, entry 9)



The reaction was conducted for 120 h at 20 □ according to the general procedure using 171 mg diethyl 1-bromo-2-naphthylphosphonate (1.0 equiv), 9.1 mg $Pd_2(dba)_3$ (4.0 mol% Pd), 16.3 mg ligand **7a** or **7d** (4.8 mol%), 182 mg 2,3-dimethoxyphenyl boronic acid (2.0 equiv), 318 mg K_3PO_4 (3.0 equiv) and 5 mL toluene on a 0.5 mmol scale. The product was purified by flash chromatography to give 190 mg desired product as a colorless oil (95% yield). Ee value was determined by Chiral HPLC (OD-H column, flow rate 0.5 mL/min, 10% *i*-PrOH, 90% hexane, T_{minor} = 12.5 min T_{major} = 14.1 min) (78% ee). **7a** $[\alpha]_D^{20}$-57.5 (c = 2.0 mg/mL, $CHCl_3$); **7d** $[\alpha]_D^{20}$-39.5 (c = 2.0 mg/mL, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 1.21 (t, J = 6.9Hz, 3H), 1.23 (t, J = 6.9Hz, 3H), 3.51 (s, 3H), 3.80-3.89 (m, 1H), 3.95 (s, 3H), 3.96-4.03 (m, 3H), 6.87 (dd, J = 7.5Hz, J = 1.5Hz, 1H), 7.05 (dd, J = 7.5Hz, J = 1.5Hz, 1H), 7.13 (dd, J = 7.5Hz, J = 1.5Hz, 1H), 7.36-7.42 (m, 1H), 7.47-7.56 (m,), 7.87-7.94 (m, 2H), 8.53(dd, J = 8.7Hz, J = 1.5Hz,) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.82, 15.91, 15.96, 16.04, 55.47, 59.81, 61.36, 61.44, 61.50, 61.56, 112.14, 122.48, 123.49, 125.91, 126.04, 126.87, 127.06, 127.11, 127.30, 127.37, 127.66, 127.79, 132.05, 132.12, 132.24, 132.45, 134.31, 134.35, 141.71, 141.84, 146.77, 151.87 ppm (observed complexity due to P-C splitting). ^{31}P NMR (121.4 MHz, $CDCl_3$): δ 18.95 ppm. MS (ESI):

$[M+H]^+$ 401; HRMS (ESI) $[M+H]^+$: calcd for $C_{22}H_{25}O_5P$, 401.1512 , found 401.1551.

Diethyl 1-(2'-chlorophenyl)-2-naphthylphosphonate (table 2, entry 10)



The reaction was conducted for 72 h at 50 □ according to the general procedure using 171 mg diethyl 1-bromo-2-naphthylphosphonate (1.0 equiv), 9.1 mg $Pd_2(dba)_3$ (4.0 mol% Pd), 16.3 mg ligand **7d** (4.8 mol%), 156 mg 2-chlorophenyl boronic acid (2.0 equiv), 318 mg K_3PO_4 (3.0 equiv) and 5 mL toluene on a 0.5 mmol scale. The product was purified by flash chromatography to give 121 mg the title compound as a colorless oil (65% yield). Ee value was determined by chiral HPLC (OD-H column, flow rate 1.0 mL/min, 10% *i*-PrOH, 90% hexane, T_{minor} = 12.2 min T_{major} = 15.3 min) (90% ee). $[\alpha]_D^{20}$-69.8 (c = 2.0 mg/mL, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 1.18-1.25 (m, 6H), 3.81-4.05 (m, 4H), 7.26-7.32 (m, 1H), 7.36-7.45 (m, 4H), 7.50-7.59 (m, 2H), 7.90-7.99 (m, 2H), 8.06-8.14 (m, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.92, 16.00, 16.09, 61.50, 61.58, 61.87, 61.94, 123.54, 125.61, 126.03, 126.42, 126.60, 127.55, 127.71, 127.91, 128.51, 129.05, 131.66, 131.86, 132.22, 134.27, 134.53, 136.77, 136.84, 141.80, 141.92 ppm (observed complexity due to P-C splitting). ^{31}P NMR (121.4 MHz, $CDCl_3$): δ 18.54 ppm. MS (ESI): $[M+H]^+$ 375; HRMS (ESI) $[M+H]^+$: calcd for $C_{20}H_{20}O_3PCl$, 375.0911, found 375.0929.

Referance

[1] Lindsten, G.; Wennerström, O.; Isaksson, R. *J. Org. Chem.*, **1987**, *52,* 547.

[2] Based on a literature procedure with slight modification: Yin，J.；Buchwald, S. L. *J. Am. Chem. Soc.*, **2000**, *122*, 12051.

X-ray data of ligand 7a

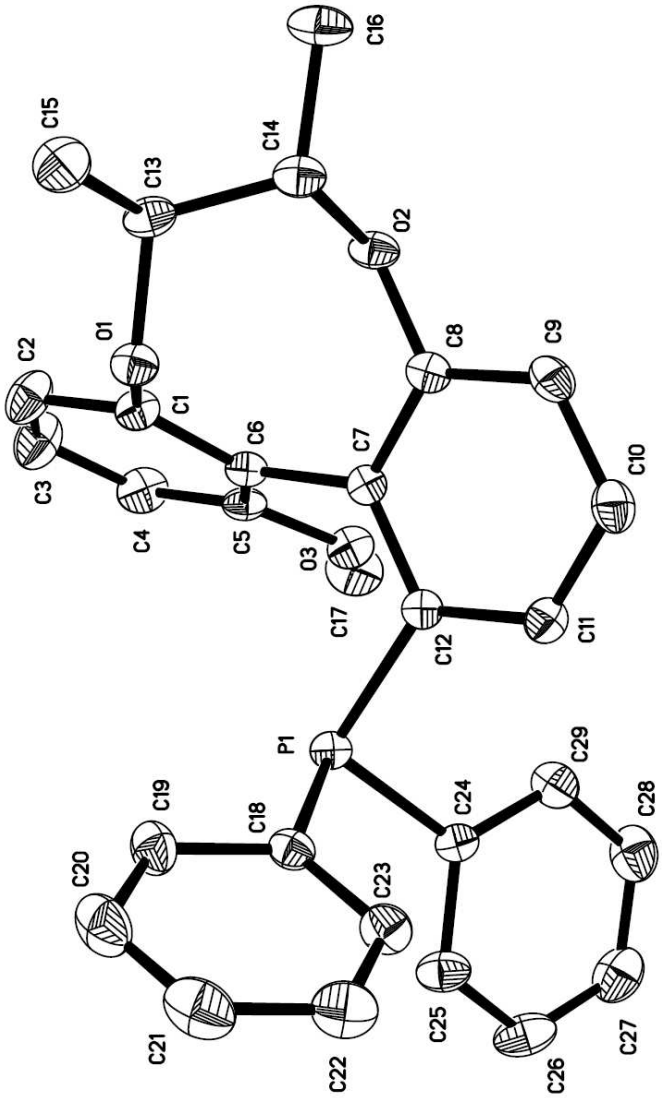


Table 1. Crystal data and structure refinement for ZSUQLQ12 (21 July 2011).

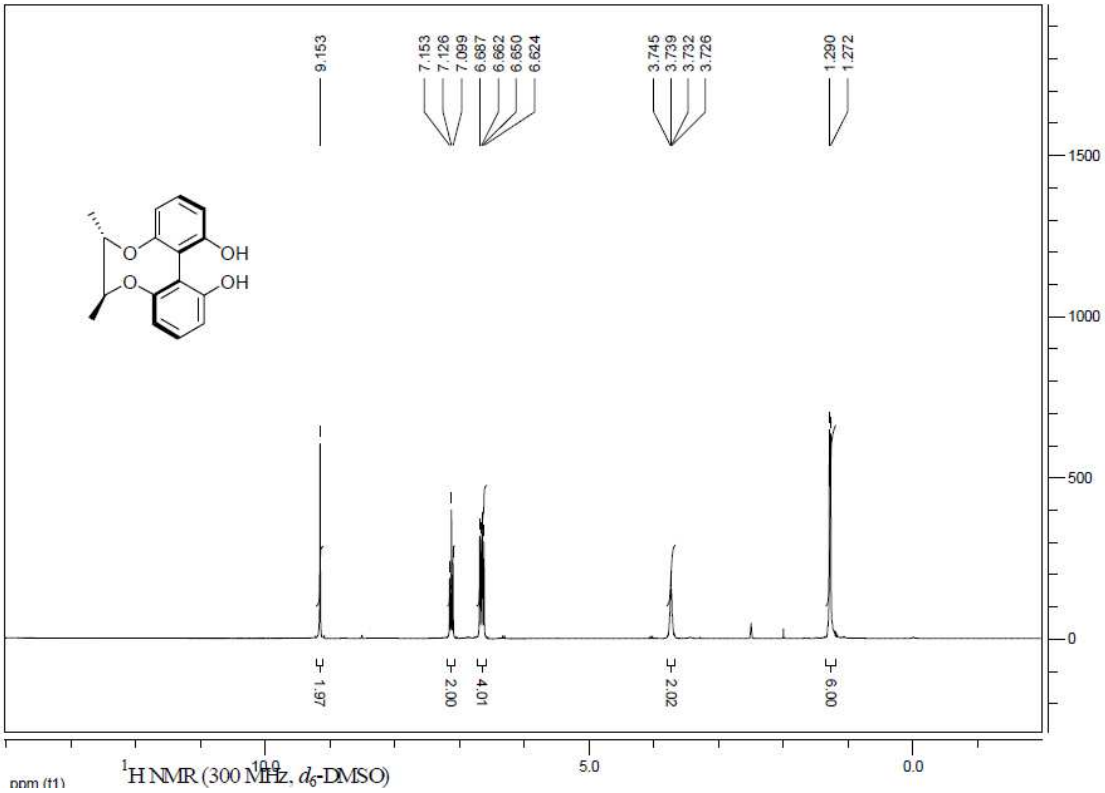
Identification code	qlq12	
Empirical formula	C_{29} H_{27} O_3 P	
Formula weight	454.48	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 8.0559(3) Å	□= 90°.
	b = 14.2981(5) Å	□= 90°.
	c = 21.0979(7) Å	□ = 90°.
Volume	2430.14(15) $Å^3$	
Z	4	
Density (calculated)	1.242 Mg/m^3	
Absorption coefficient	0.141 mm^{-1}	
F(000)	960	
Crystal size	0.42 x 0.38 x 0.32 mm^3	
Theta range for data collection	1.72 to 27.48°.	
Index ranges	-10<=h<=10, -18<=k<=18, -27<=l<=27	
Reflections collected	31203	
Independent reflections	5565 [R(int) = 0.0848]	
Completeness to theta = 27.48°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6116	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5565 / 0 / 298	
Goodness-of-fit on F^2	1.001	
Final R indices [I>2sigma(I)]	R1 = 0.0499, wR2 = 0.0992	
R indices (all data)	R1 = 0.0859, wR2 = 0.1139	
Absolute structure parameter	-0.03(11)	
Largest diff. peak and hole	0.202 and -0.207 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for qlq12. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

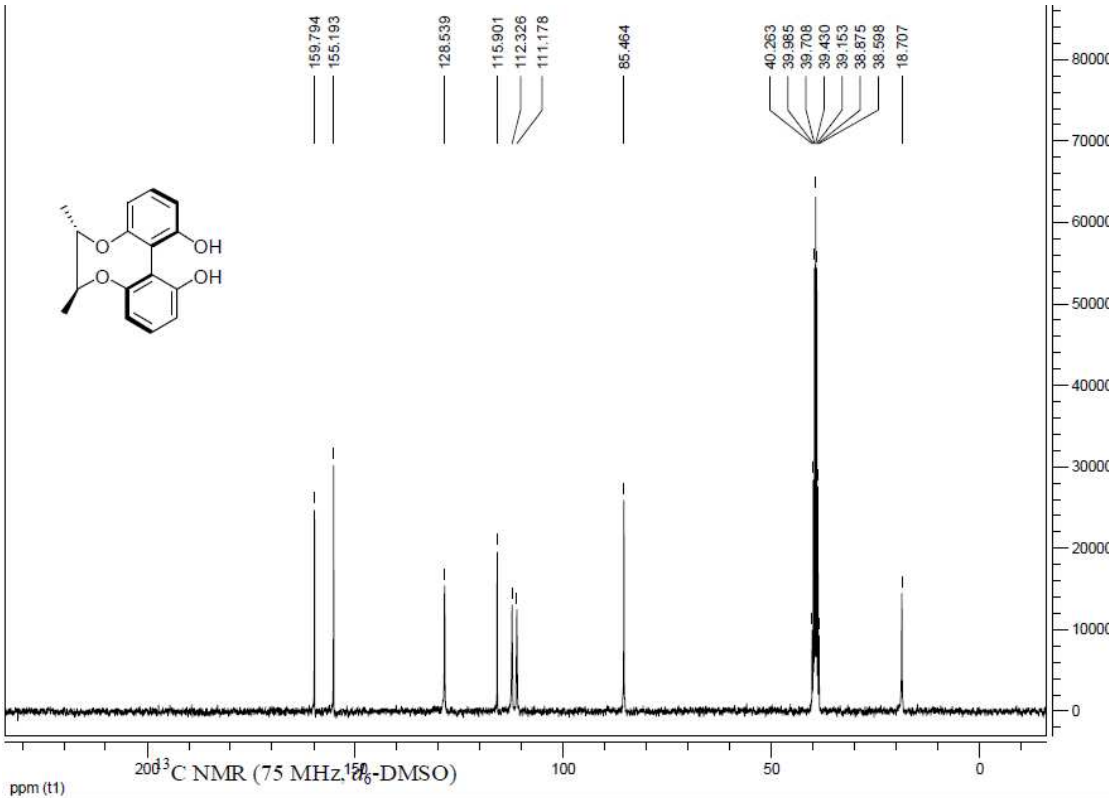
	x	y	z	U(eq)
P(1)	5333(1)	6238(1)	7878(1)	40(1)
O(1)	3537(2)	5564(1)	5851(1)	45(1)
O(2)	4657(2)	7342(1)	5554(1)	46(1)
O(3)	8226(2)	6667(1)	6962(1)	52(1)
C(1)	5177(3)	5433(2)	6040(1)	44(1)
C(2)	6015(4)	4636(2)	5848(2)	64(1)
C(3)	7635(4)	4518(2)	6051(2)	76(1)
C(4)	8412(4)	5175(2)	6422(1)	61(1)
C(5)	7561(3)	5958(2)	6611(1)	42(1)
C(6)	5890(3)	6081(2)	6440(1)	37(1)
C(7)	4945(3)	6921(2)	6645(1)	35(1)
C(8)	4319(3)	7523(2)	6185(1)	41(1)
C(9)	3475(3)	8325(2)	6350(1)	50(1)
C(10)	3230(3)	8532(2)	6985(1)	52(1)
C(11)	3790(3)	7929(2)	7446(1)	46(1)
C(12)	4649(3)	7110(2)	7286(1)	38(1)
C(13)	3346(3)	5898(2)	5207(1)	49(1)
C(14)	3311(3)	6954(2)	5181(1)	47(1)
C(15)	1719(4)	5478(2)	4956(2)	68(1)
C(16)	3554(4)	7319(2)	4516(1)	65(1)
C(17)	9951(4)	6634(2)	7108(2)	77(1)
C(18)	3325(3)	5875(2)	8213(1)	44(1)
C(19)	2769(4)	4988(2)	8041(1)	59(1)
C(20)	1249(5)	4657(2)	8254(2)	76(1)
C(21)	280(4)	5202(3)	8638(2)	79(1)
C(22)	810(4)	6068(3)	8816(2)	70(1)
C(23)	2329(3)	6405(2)	8610(1)	55(1)
C(24)	6204(3)	6973(2)	8507(1)	42(1)
C(25)	6208(4)	6663(2)	9128(1)	59(1)
C(26)	7033(4)	7147(3)	9599(1)	78(1)
C(27)	7846(5)	7953(3)	9461(2)	79(1)
C(28)	7870(4)	8279(2)	8856(2)	76(1)
C(29)	7062(4)	7789(2)	8373(2)	59(1)

Copies of ^{1}H NMR, ^{13}C NMR and chiral HPLC Spectra for all products

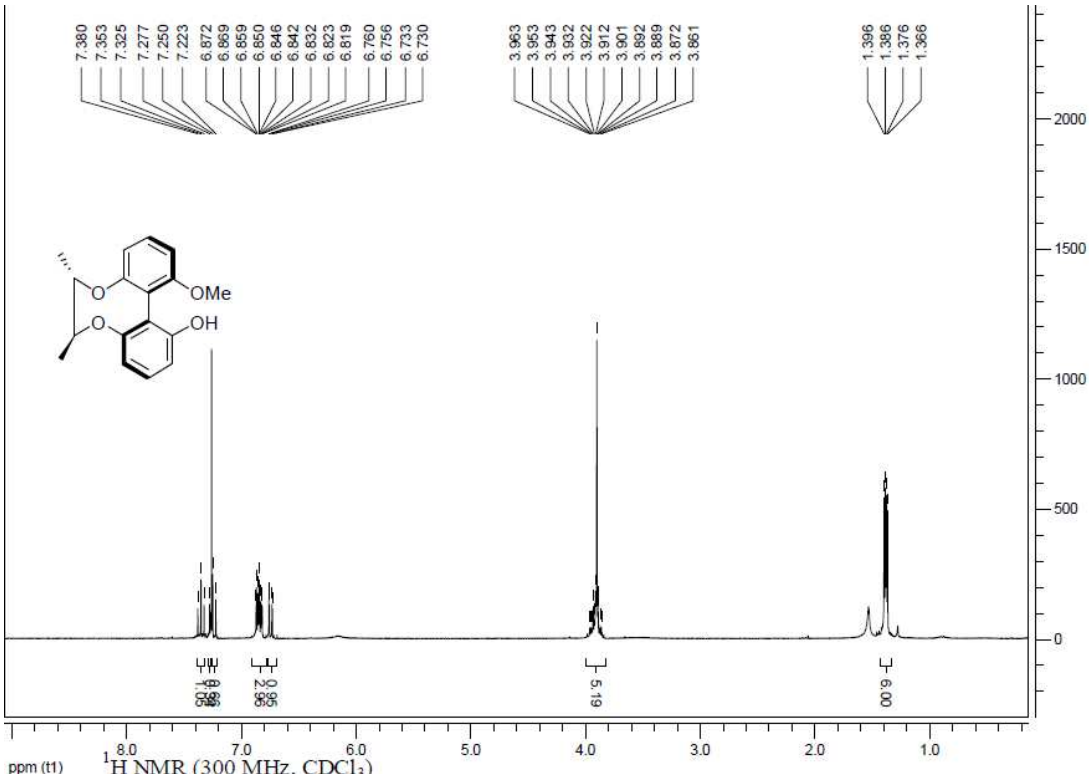
^{1}H NMR (300 MHz, d_6-DMSO) of **3**



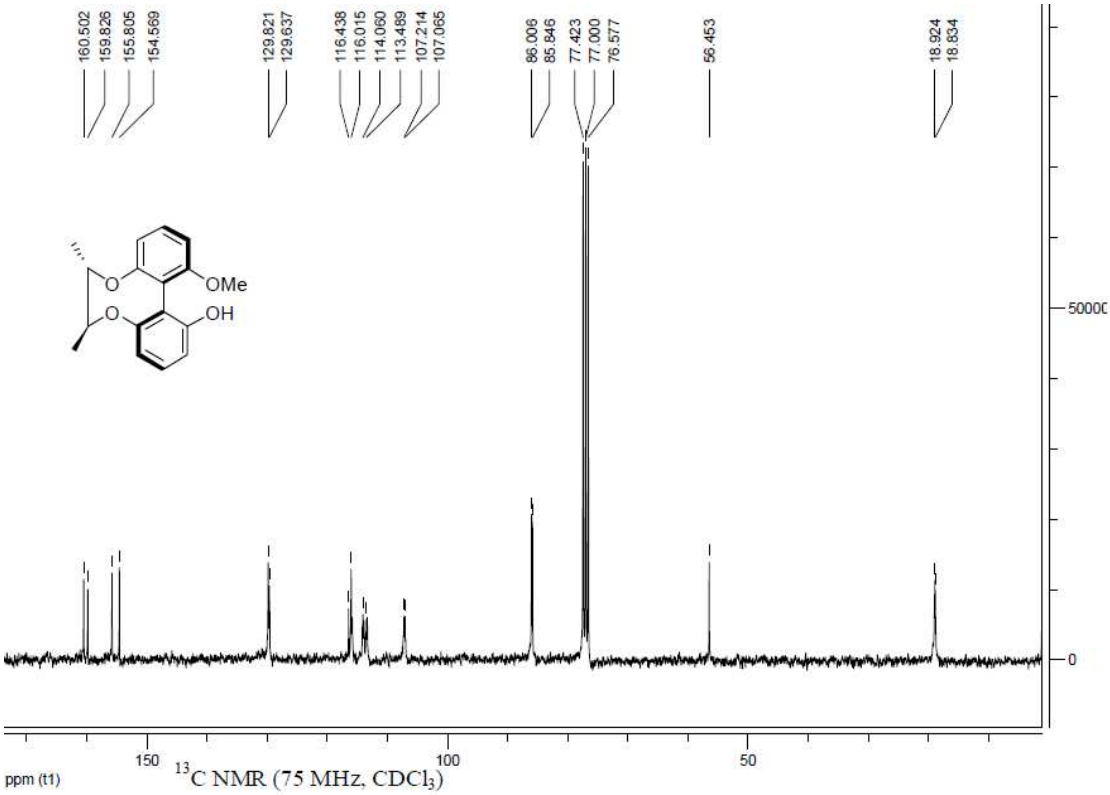
^{13}C NMR (75 MHz, d_6-DMSO) of **3**



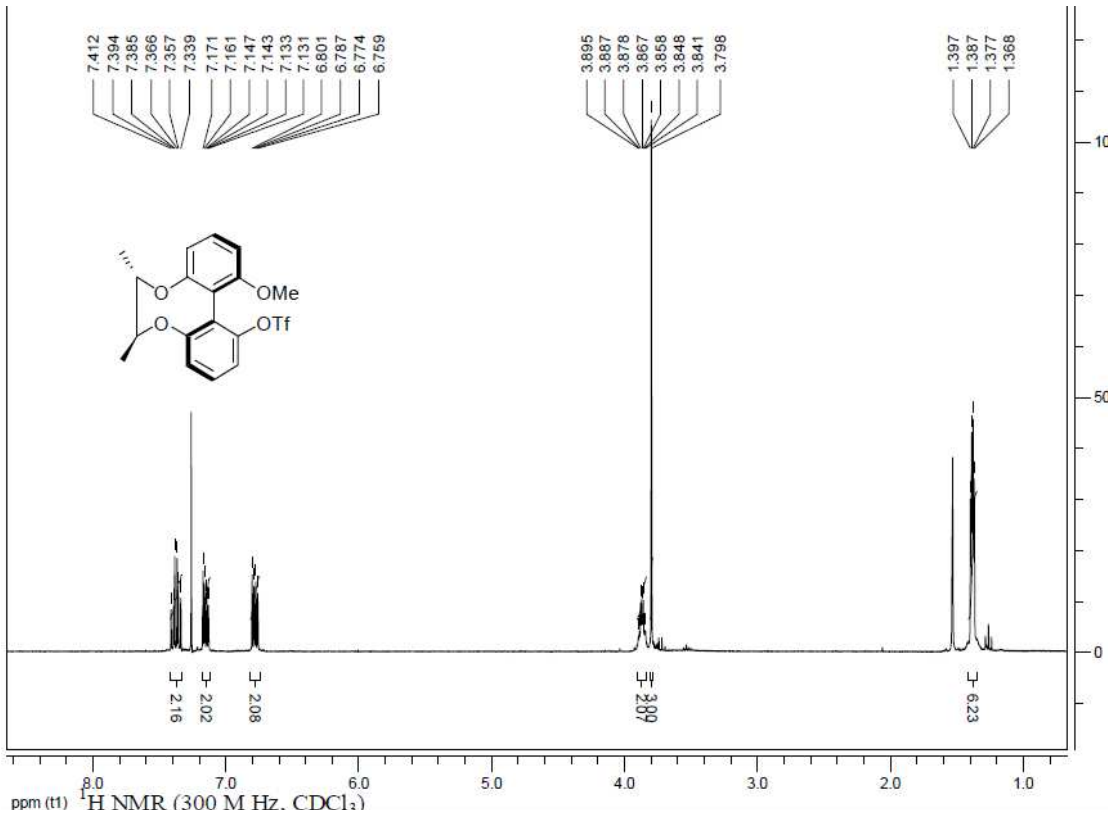
^{1}H NMR (300 MHz, $CDCl_3$) of **4**



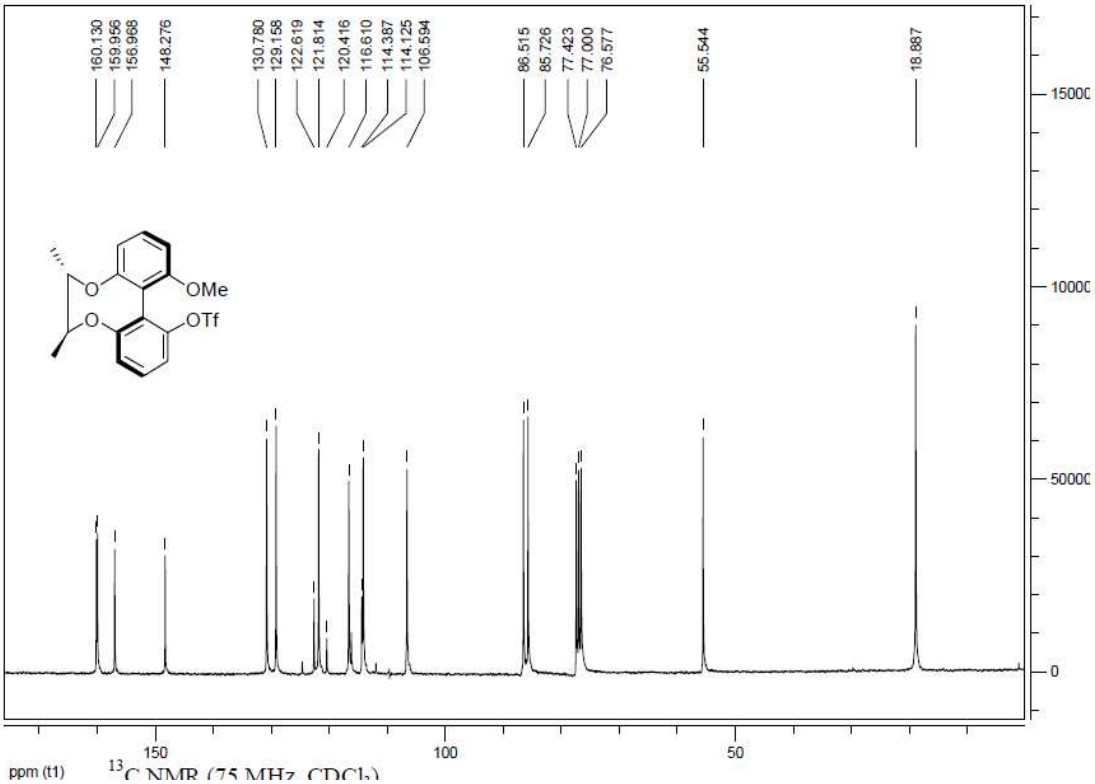
^{13}C NMR (75 MHz, $CDCl_3$) of **4**



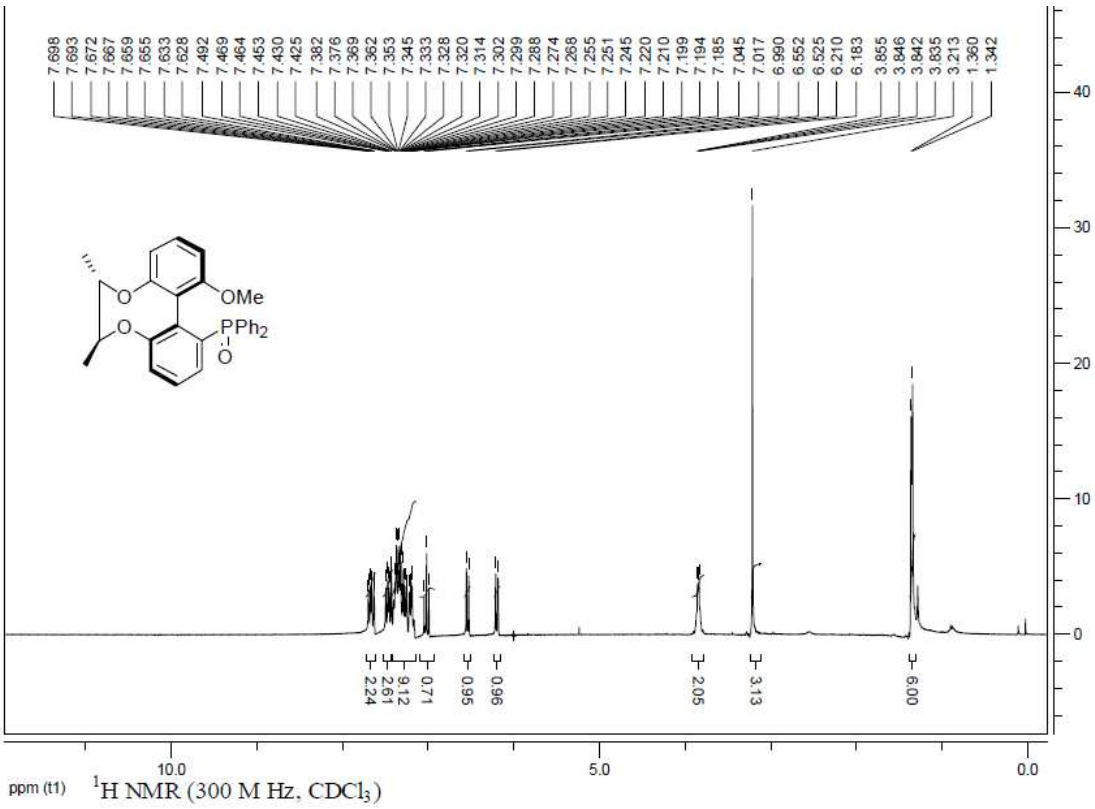
^{1}H NMR (300 MHz, $CDCl_3$) of **5**



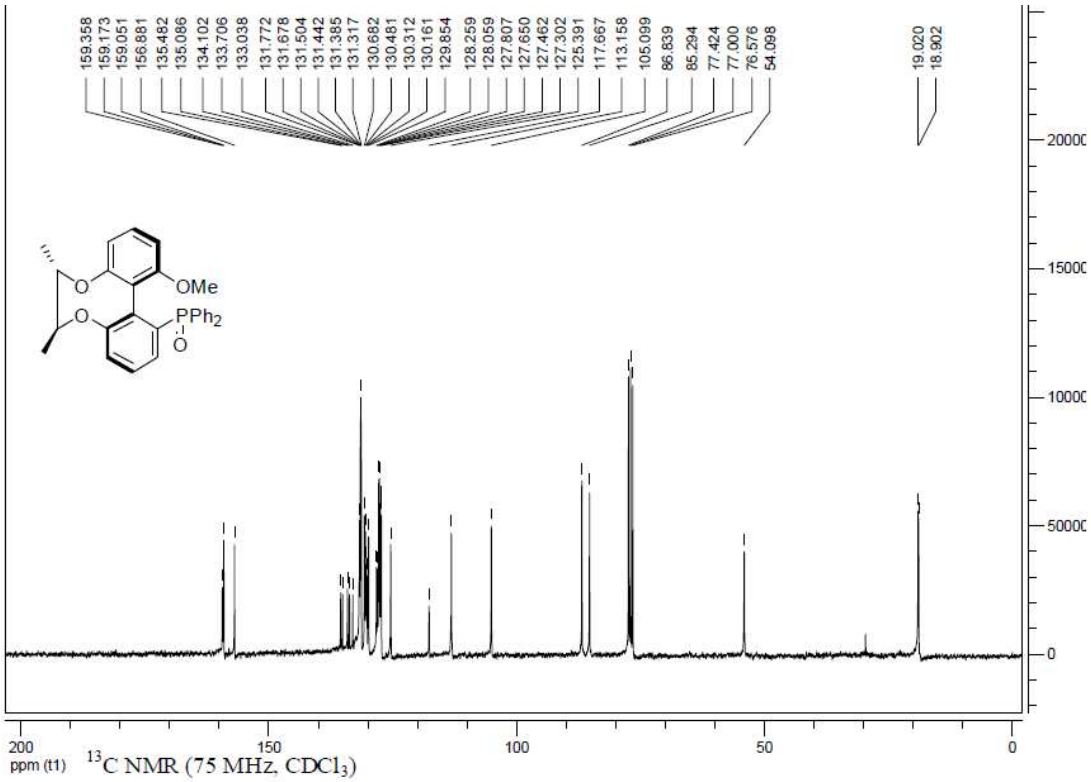
^{13}C NMR (75 MHz, $CDCl_3$) of **5**



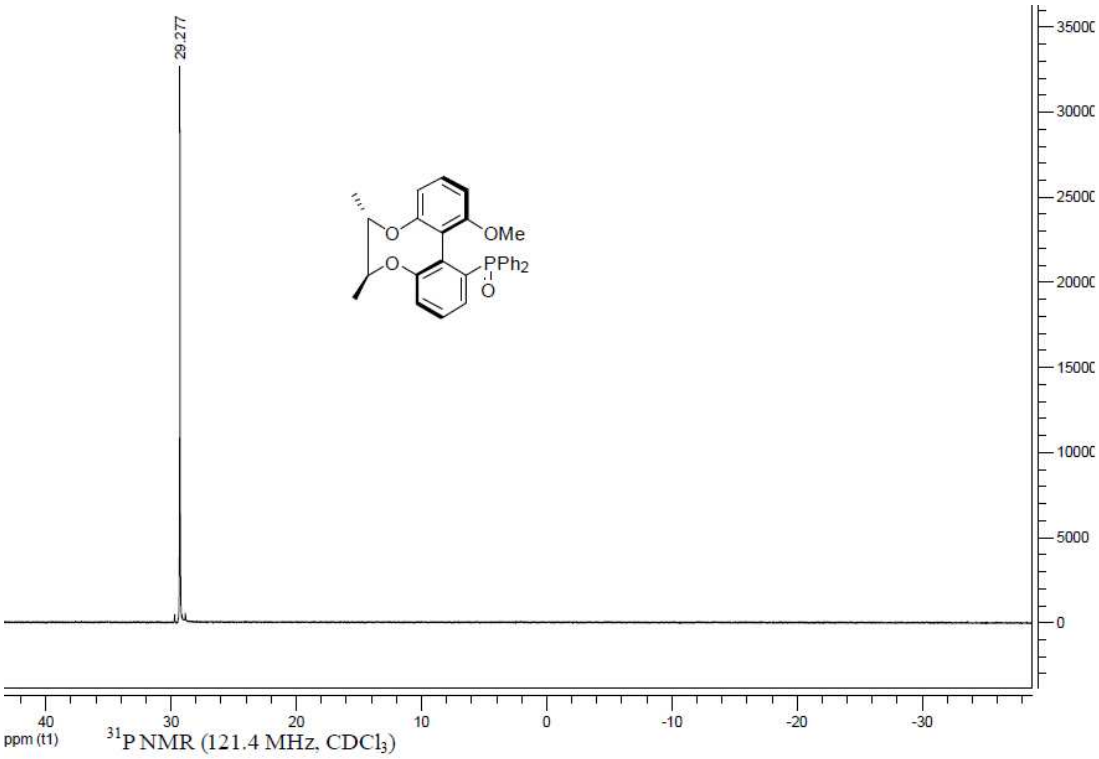
^{1}H NMR (300 MHz, $CDCl_3$) of **6a**



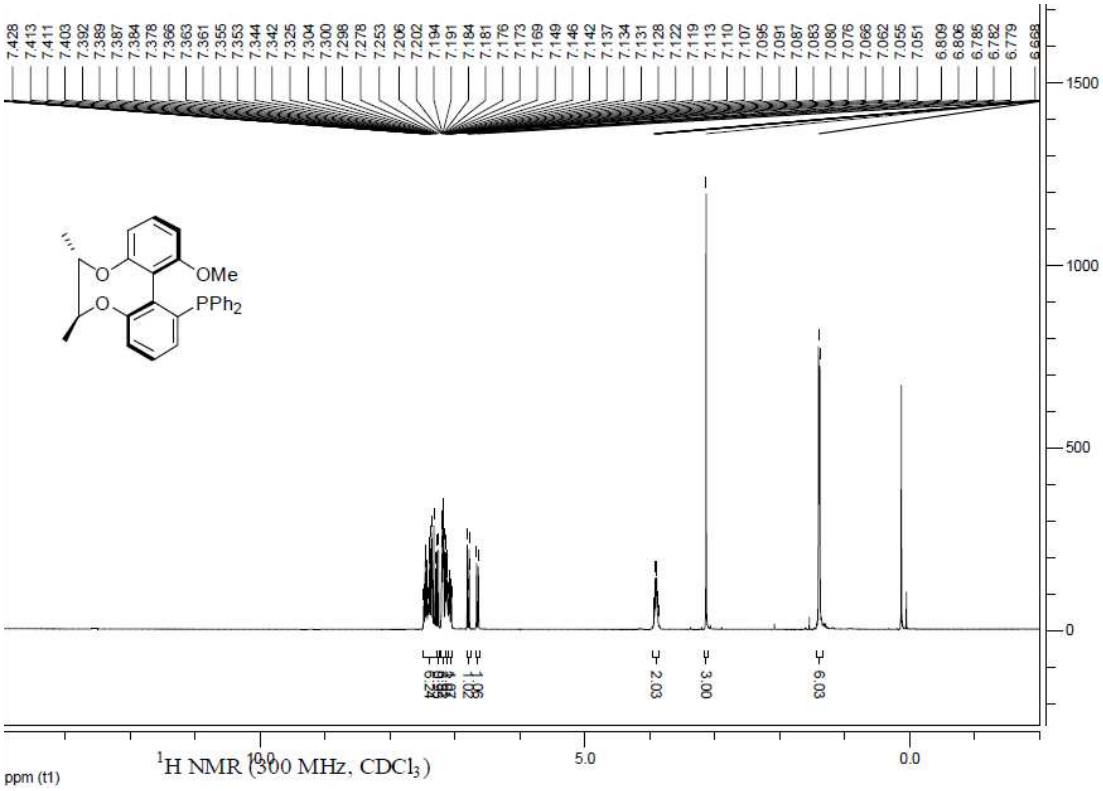
^{13}C NMR (75 MHz, $CDCl_3$) of **6a**



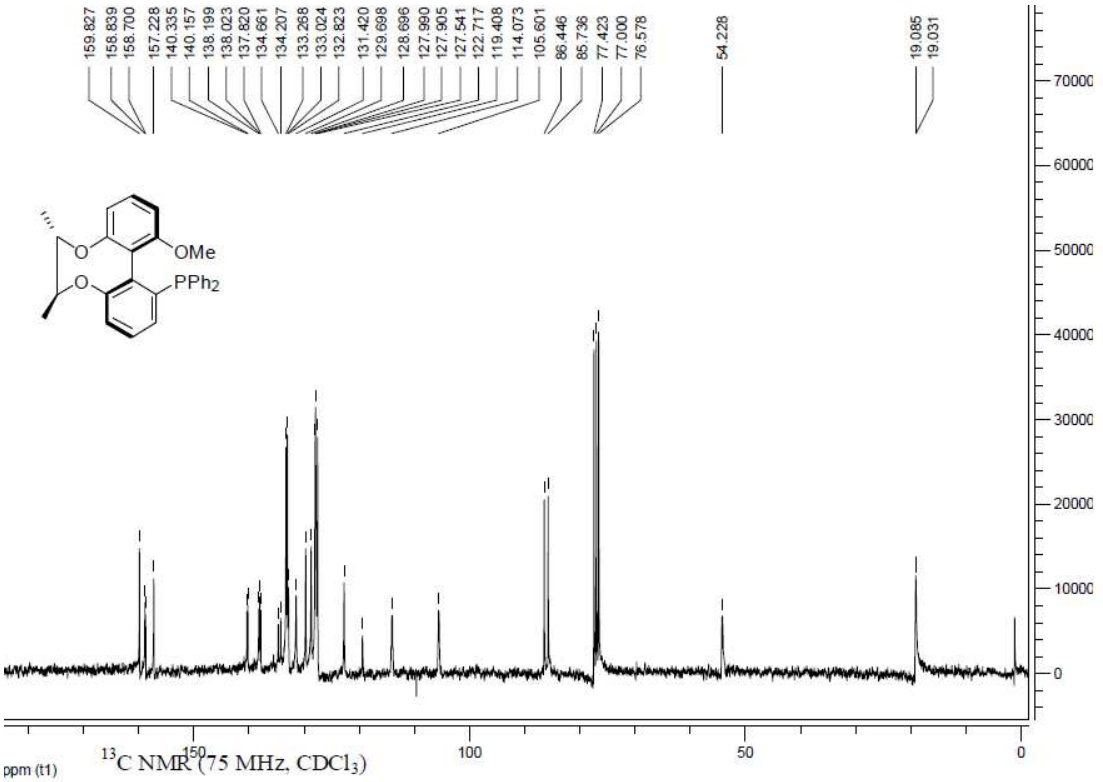
^{31}P NMR (121.4 MHz, $CDCl_3$) of **6a**



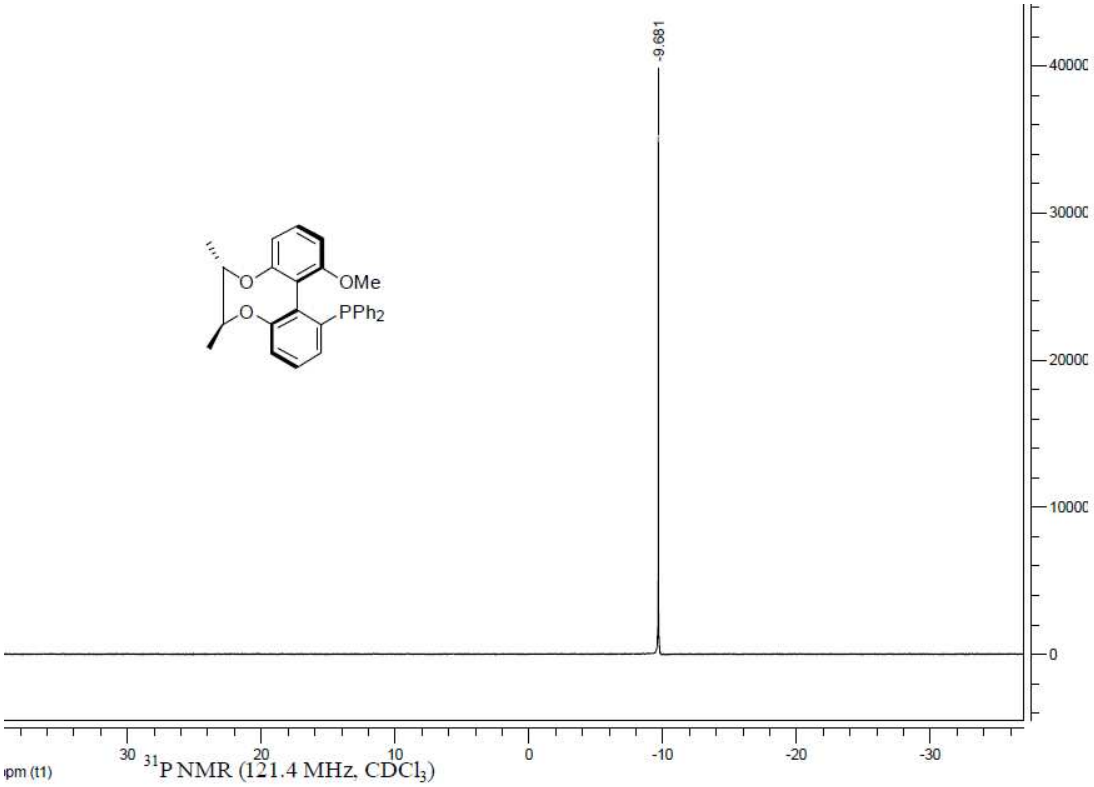
^{1}H NMR (300 MHz, $CDCl_3$) of **7a**



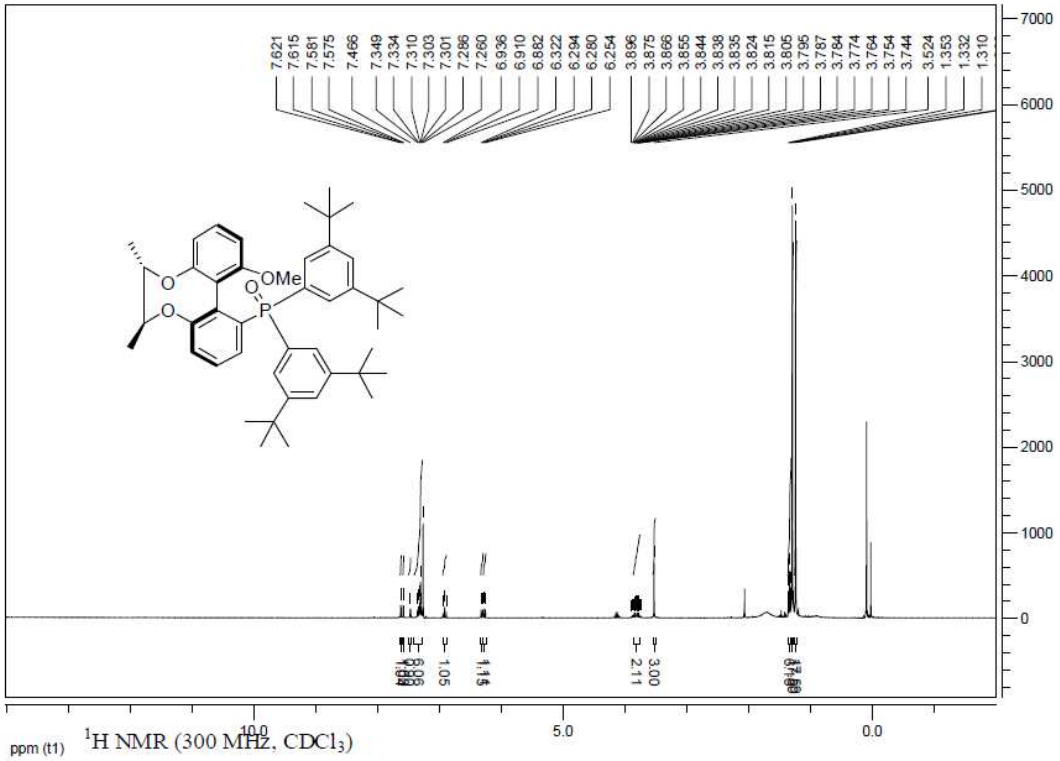
^{13}C NMR (75 MHz, $CDCl_3$) of **7a**



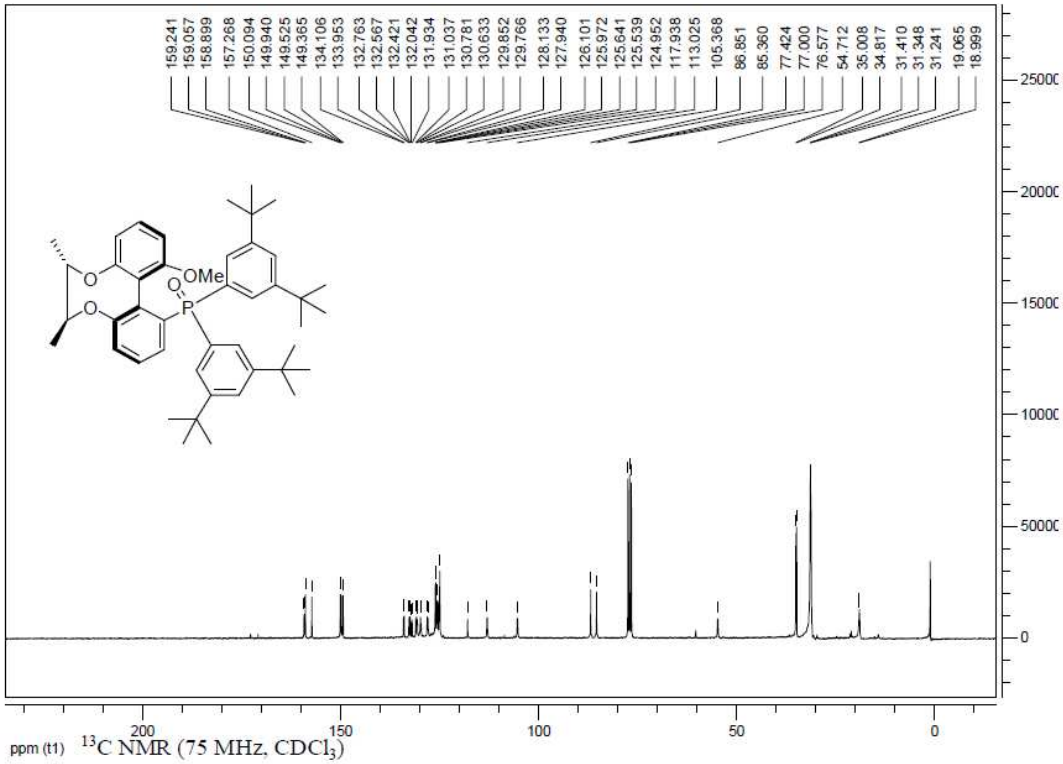
^{31}P NMR (121.4 MHz, $CDCl_3$) of **7a**



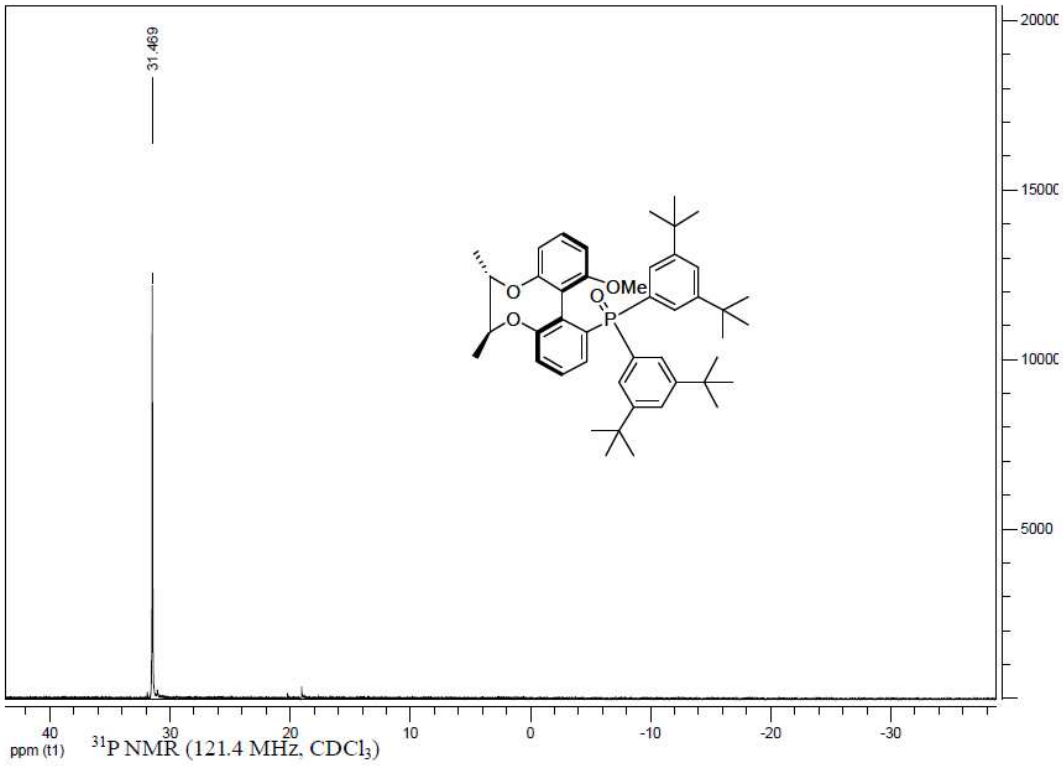
^{1}H NMR (300 MHz, $CDCl_3$) of **6d**



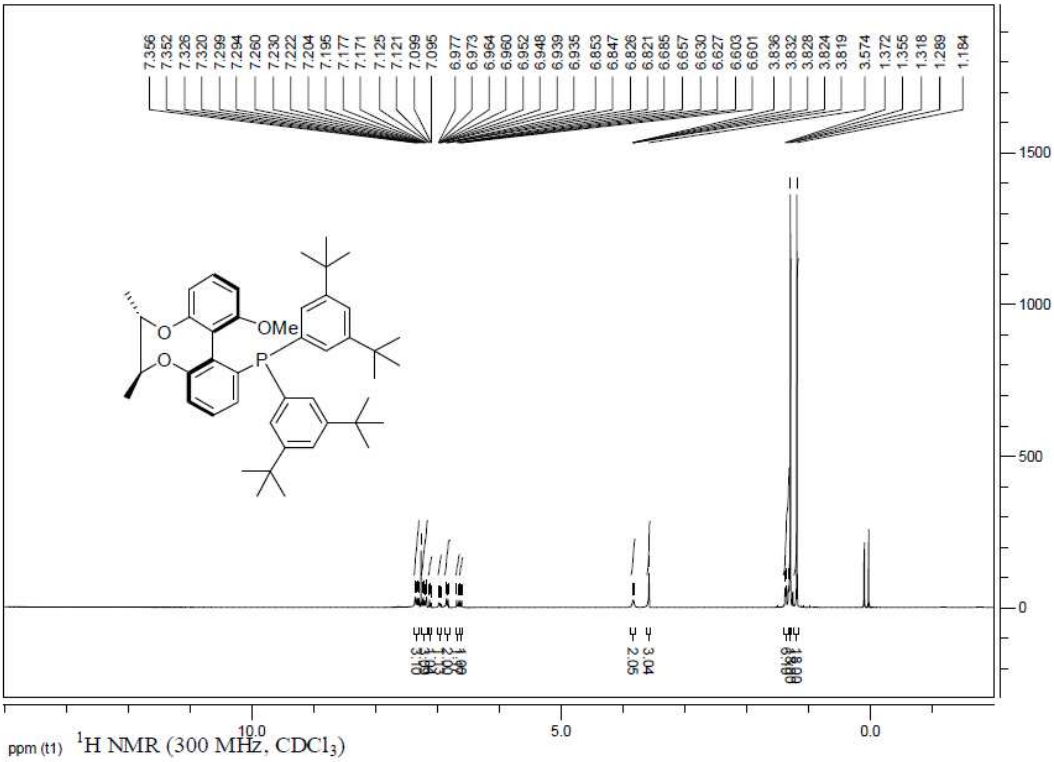
^{13}C NMR (75 MHz, $CDCl_3$) of **6d**



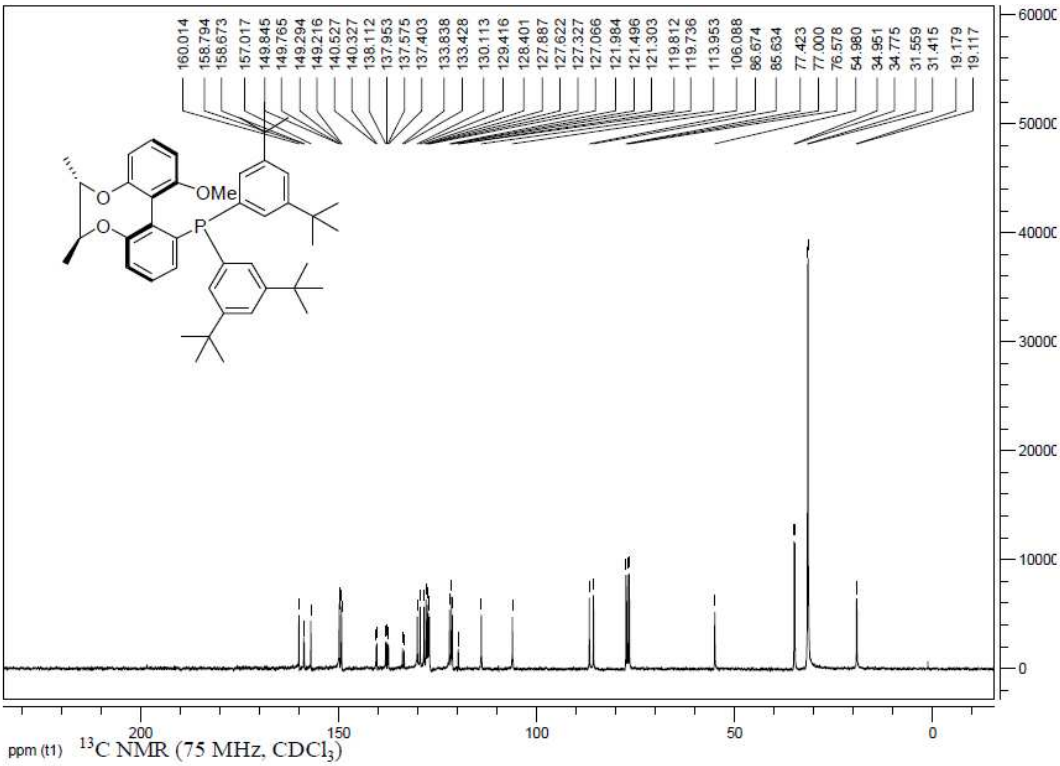
^{31}P NMR (121.4 MHz, $CDCl_3$) of **6d**



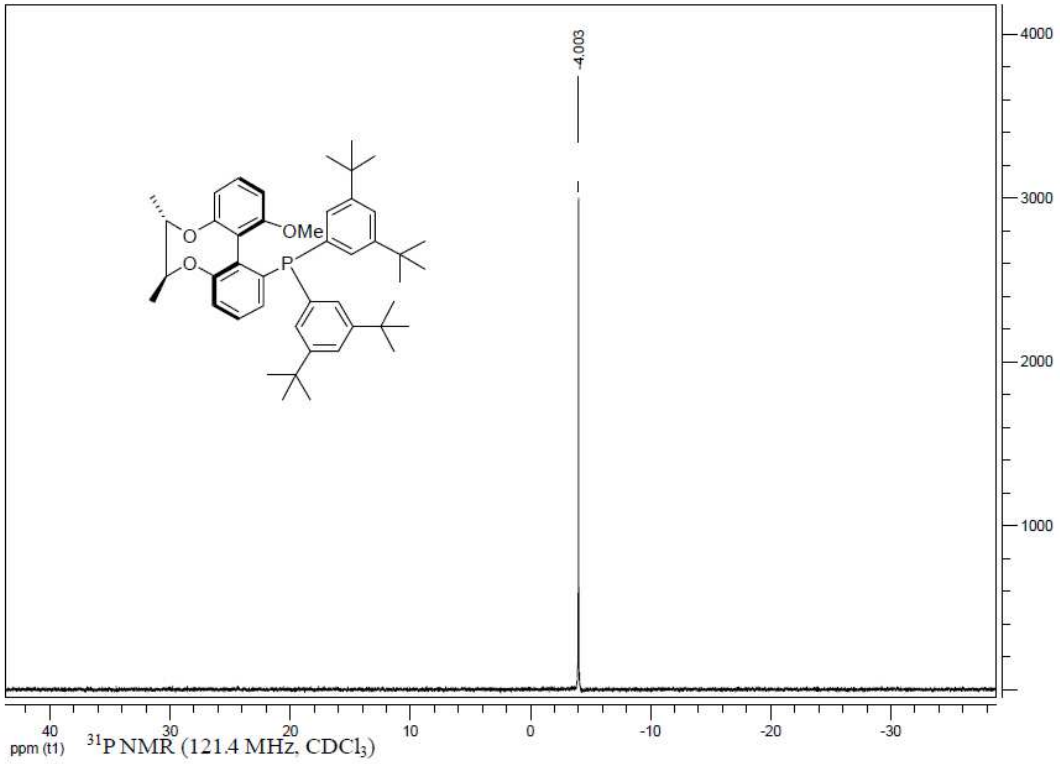
^{1}H NMR (300 MHz, $CDCl_3$) of **7d**



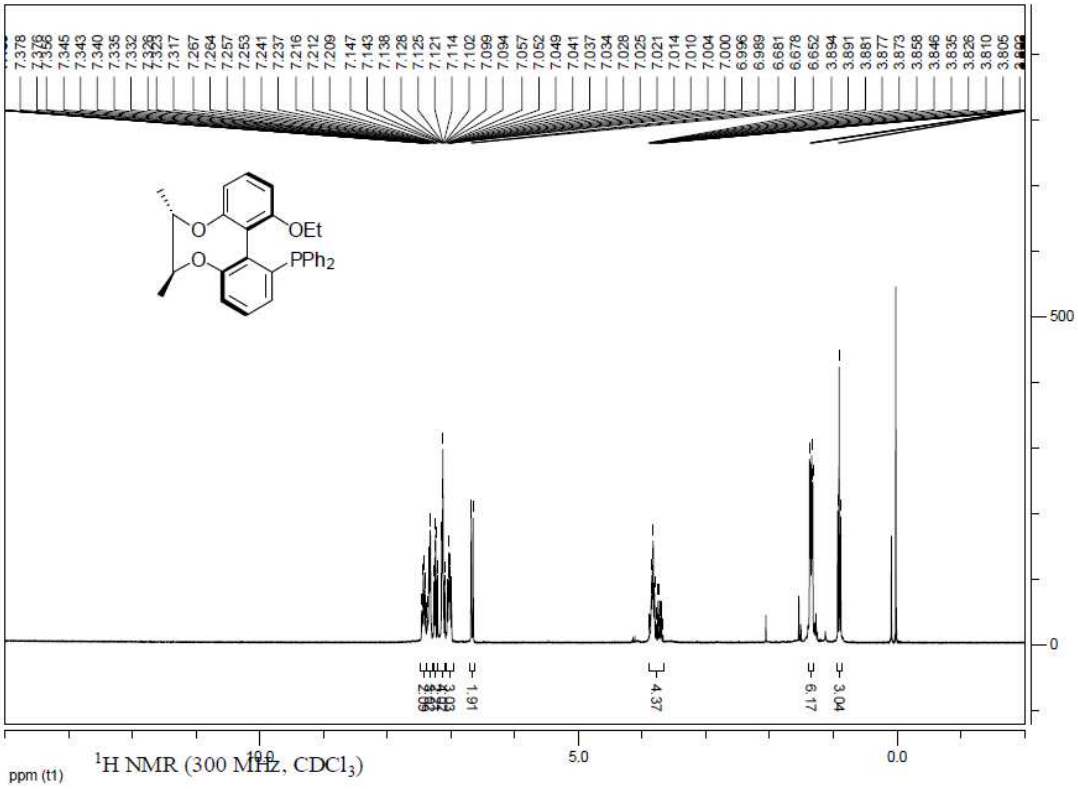
^{13}C NMR (75 MHz, $CDCl_3$) of **7d**



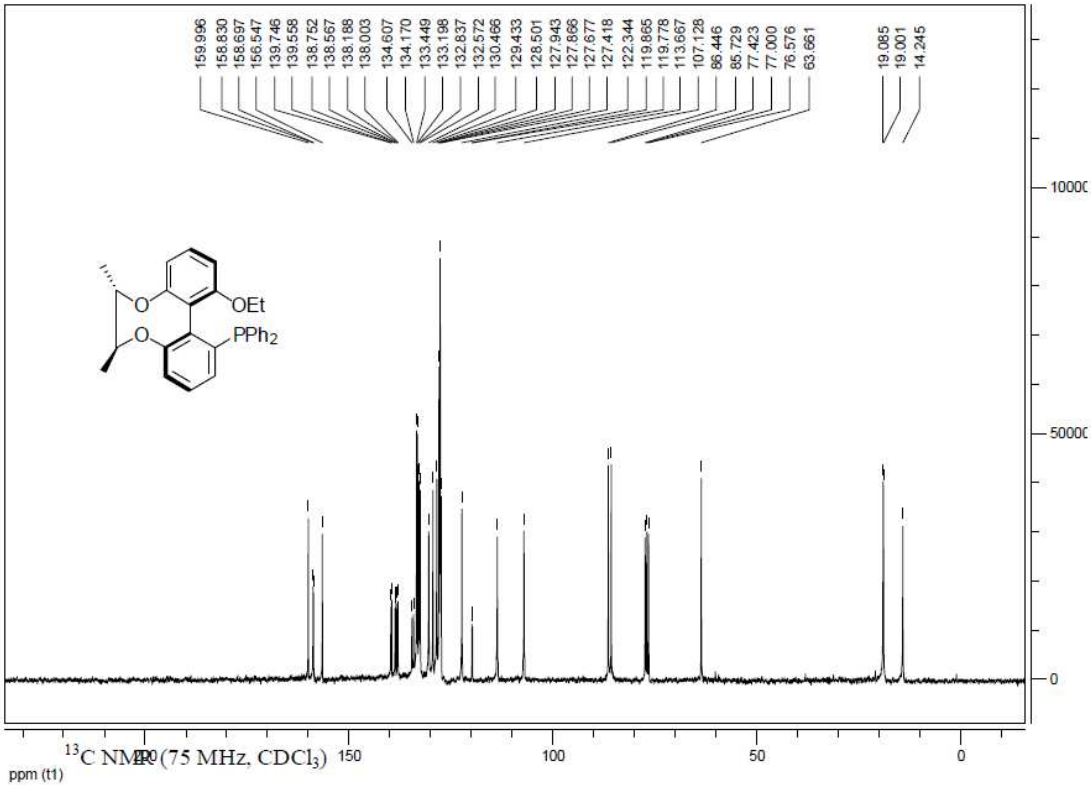
^{31}P NMR (121.4 MHz, $CDCl_3$) of **7d**



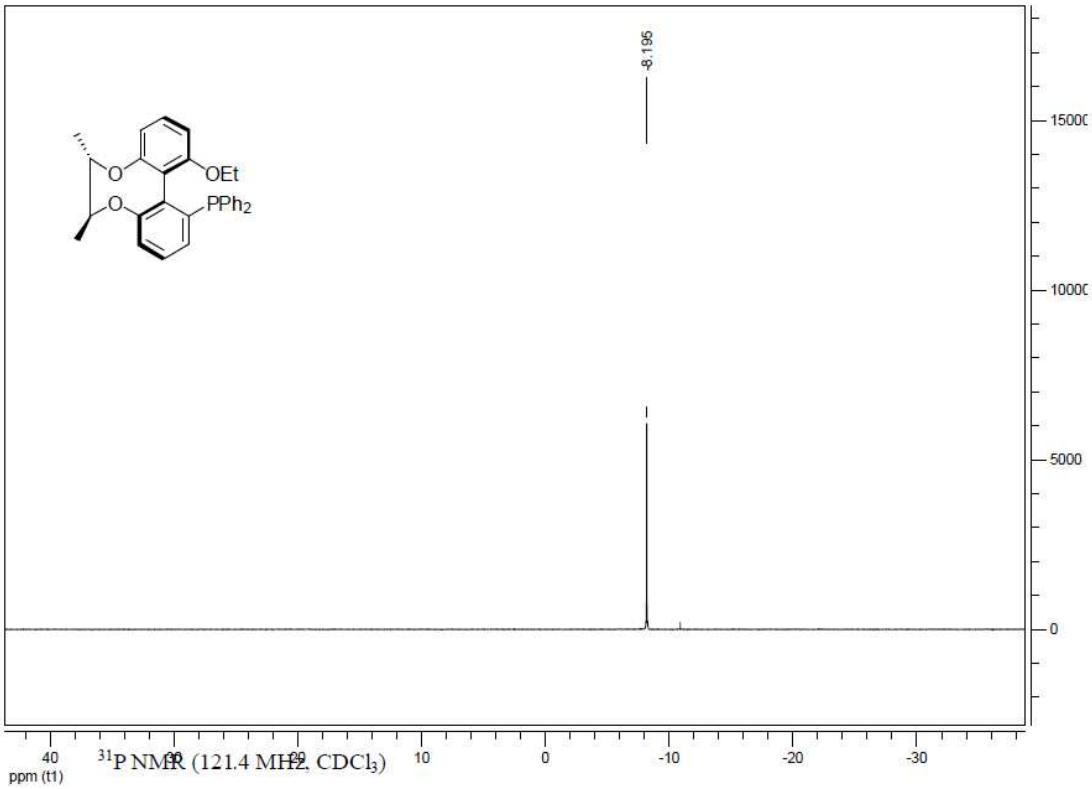
^{1}H NMR (300 MHz, $CDCl_3$) of **7e**



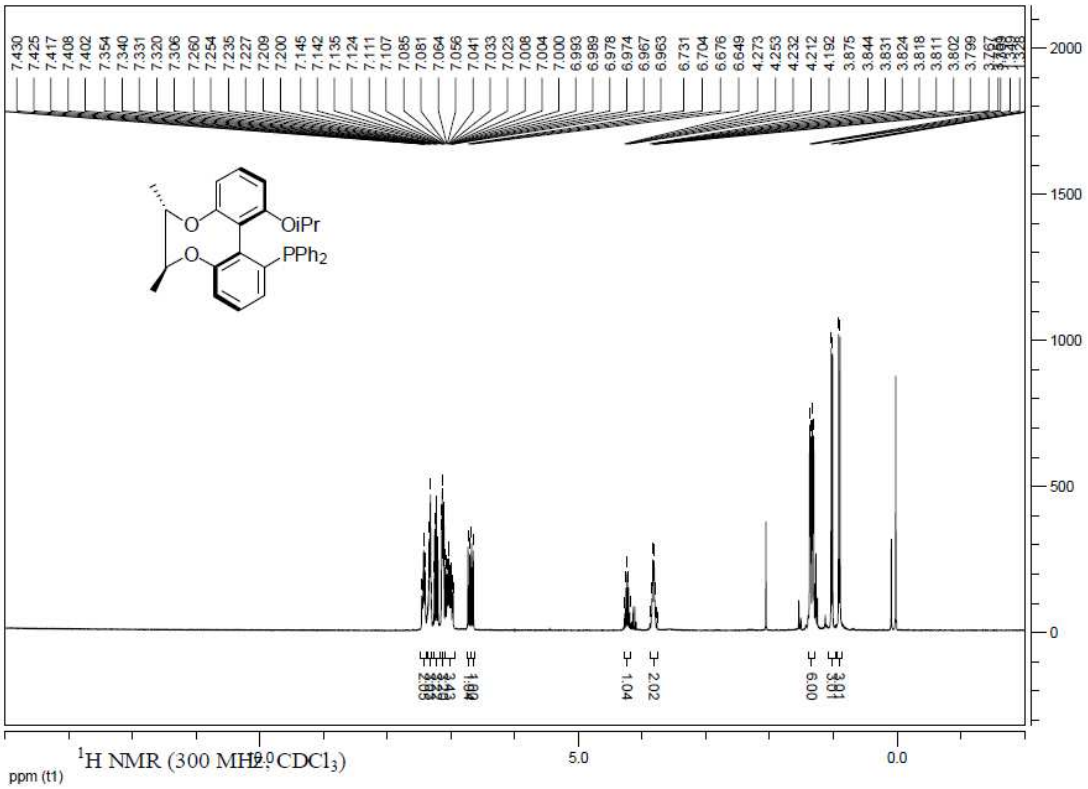
^{13}C NMR (75 MHz, $CDCl_3$) of **7e**



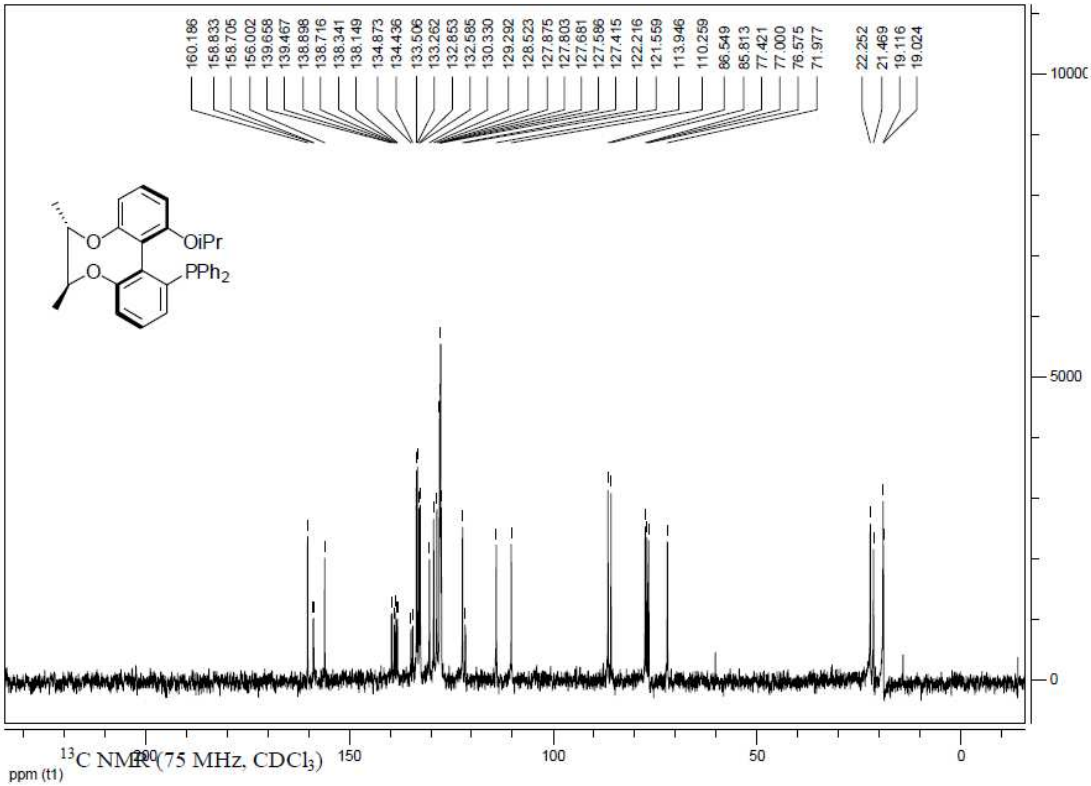
^{31}P NMR (121.4 MHz, $CDCl_3$) of **7e**



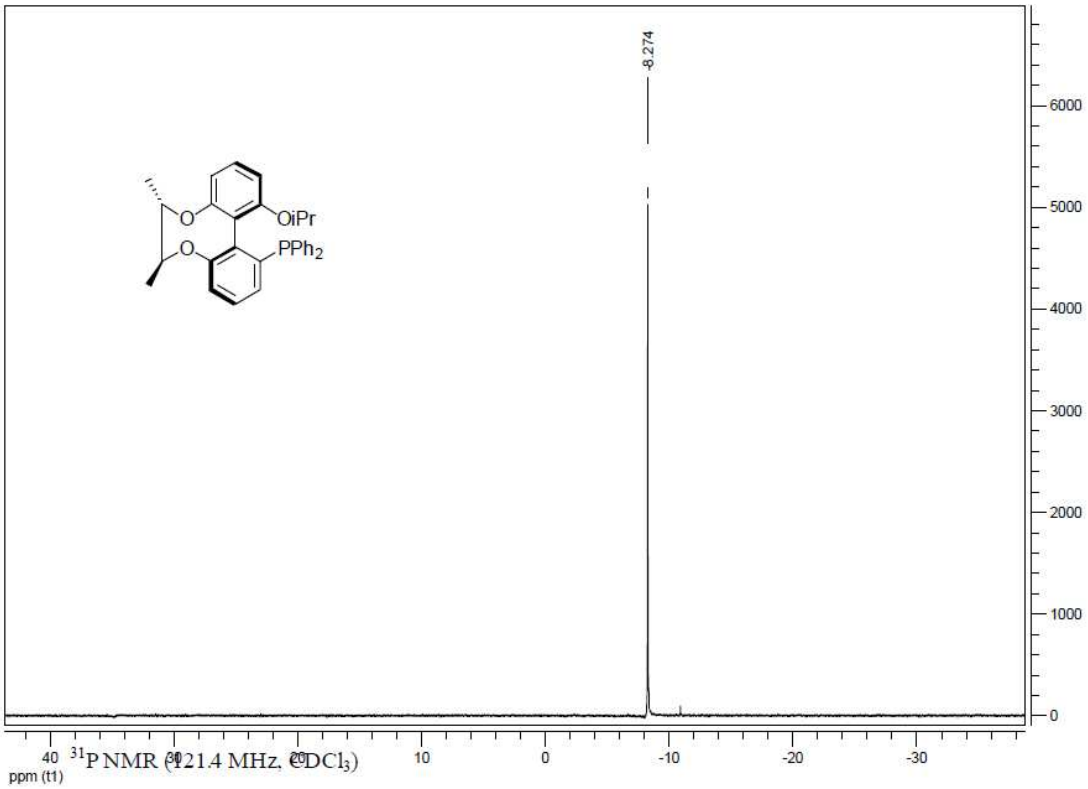
^{1}H NMR (300 MHz, $CDCl_3$) of **7f**



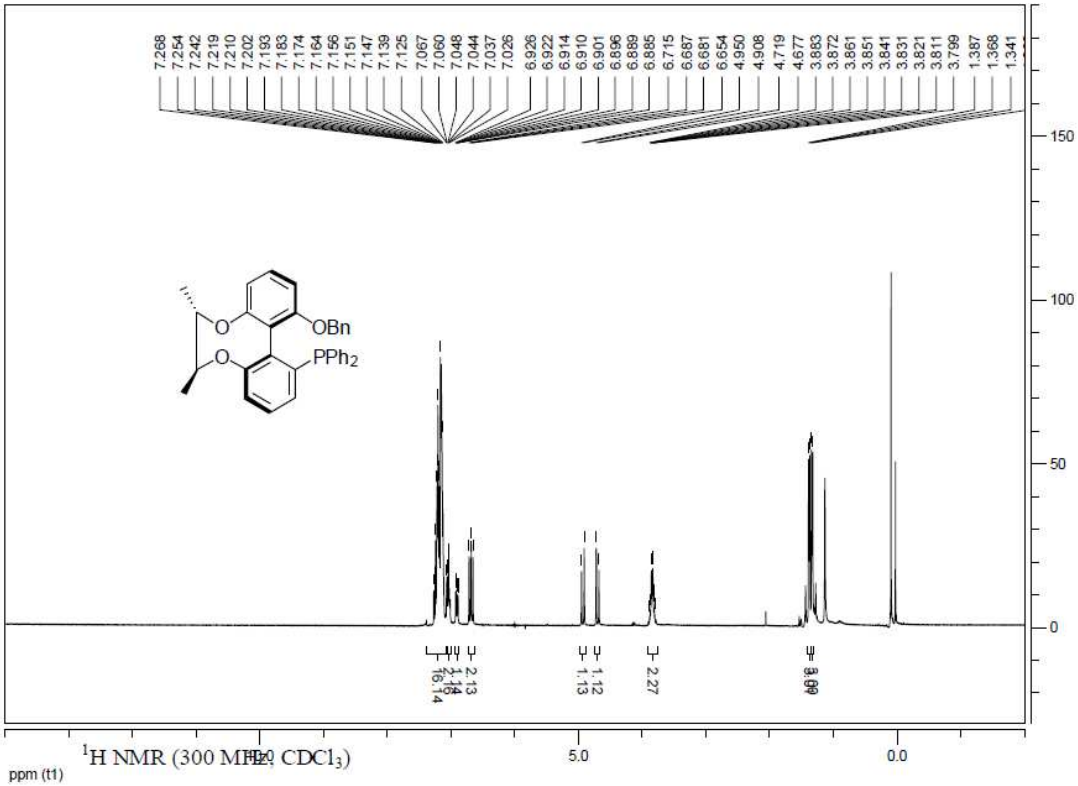
^{13}C NMR (75 MHz, $CDCl_3$) of **7f**



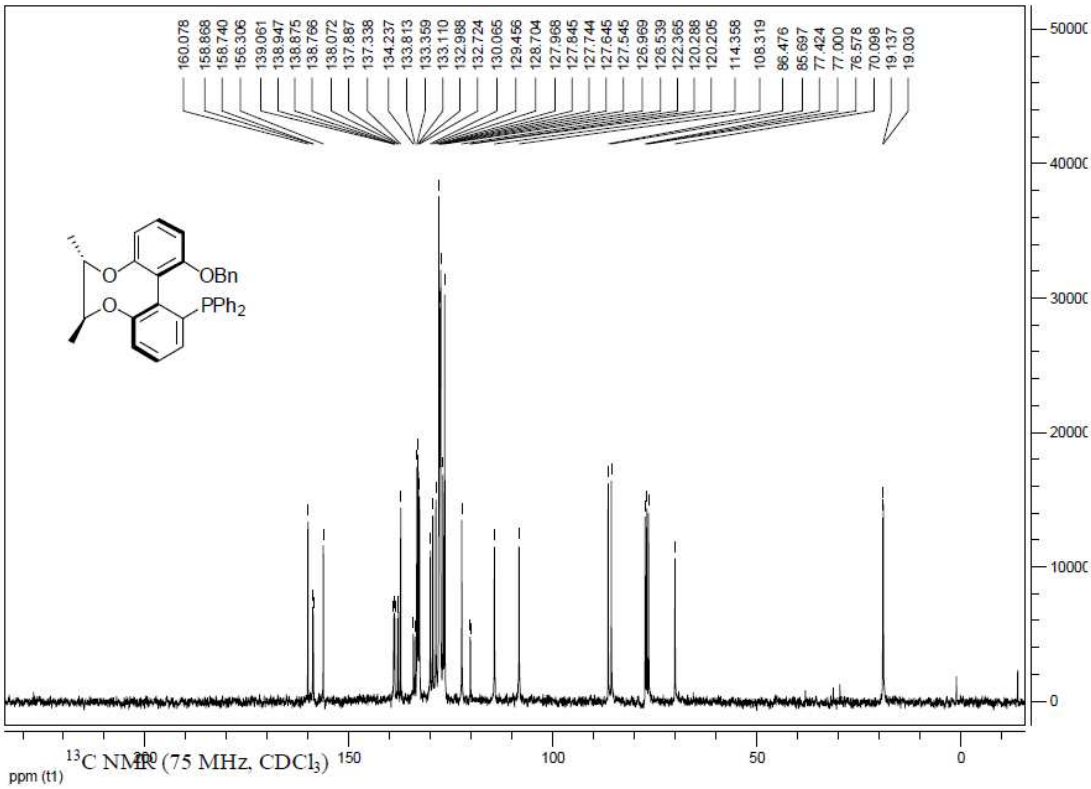
^{31}P NMR (121.4 MHz, $CDCl_3$) of **7f**



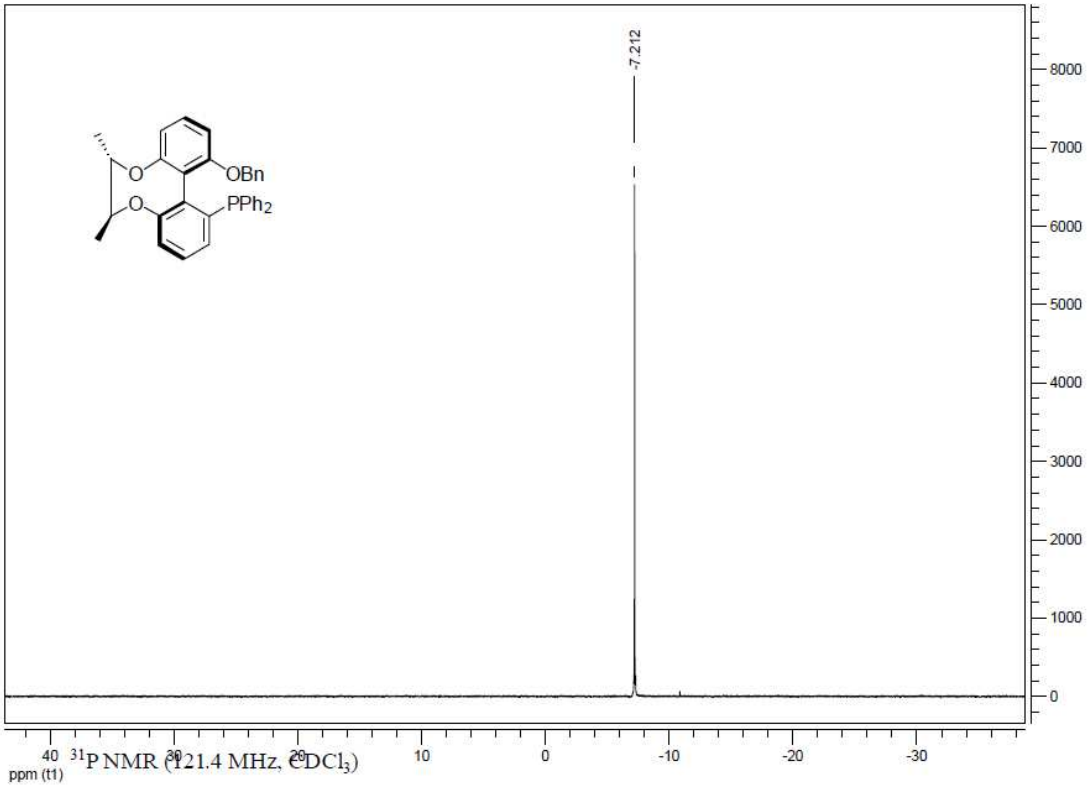
^{1}H NMR (300 MHz, $CDCl_3$) of **7g**



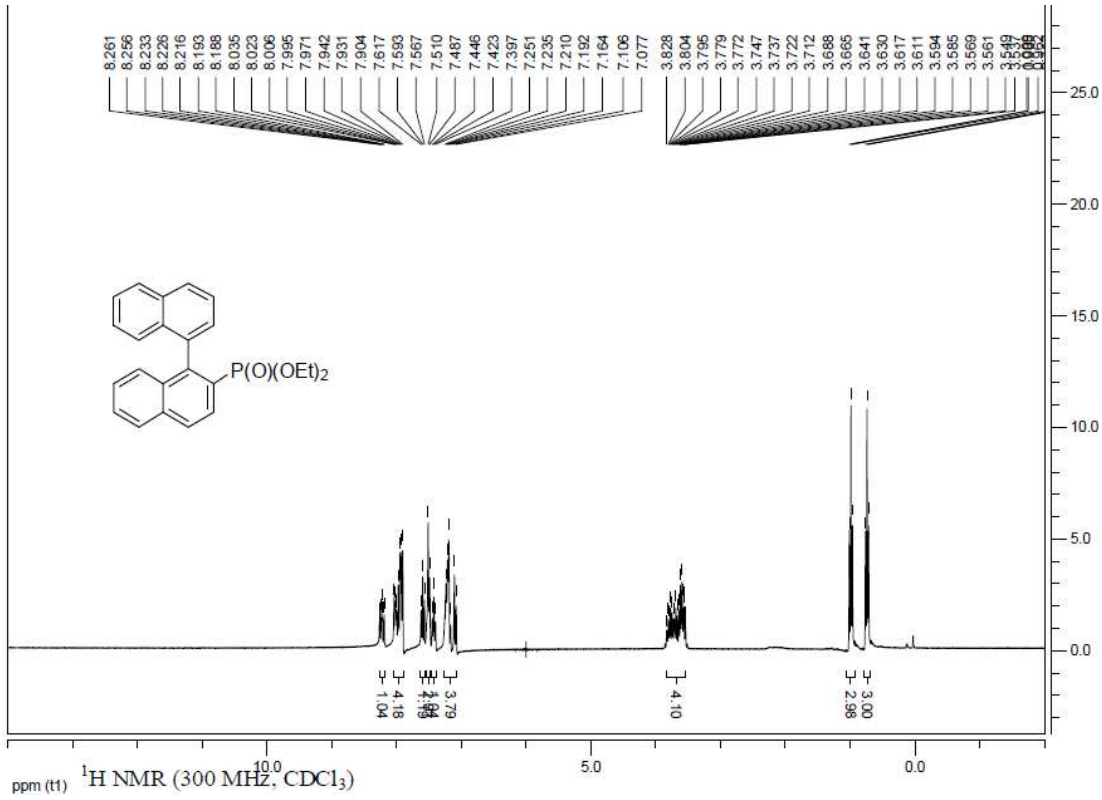
^{13}C NMR (75 MHz, $CDCl_3$) of **7g**



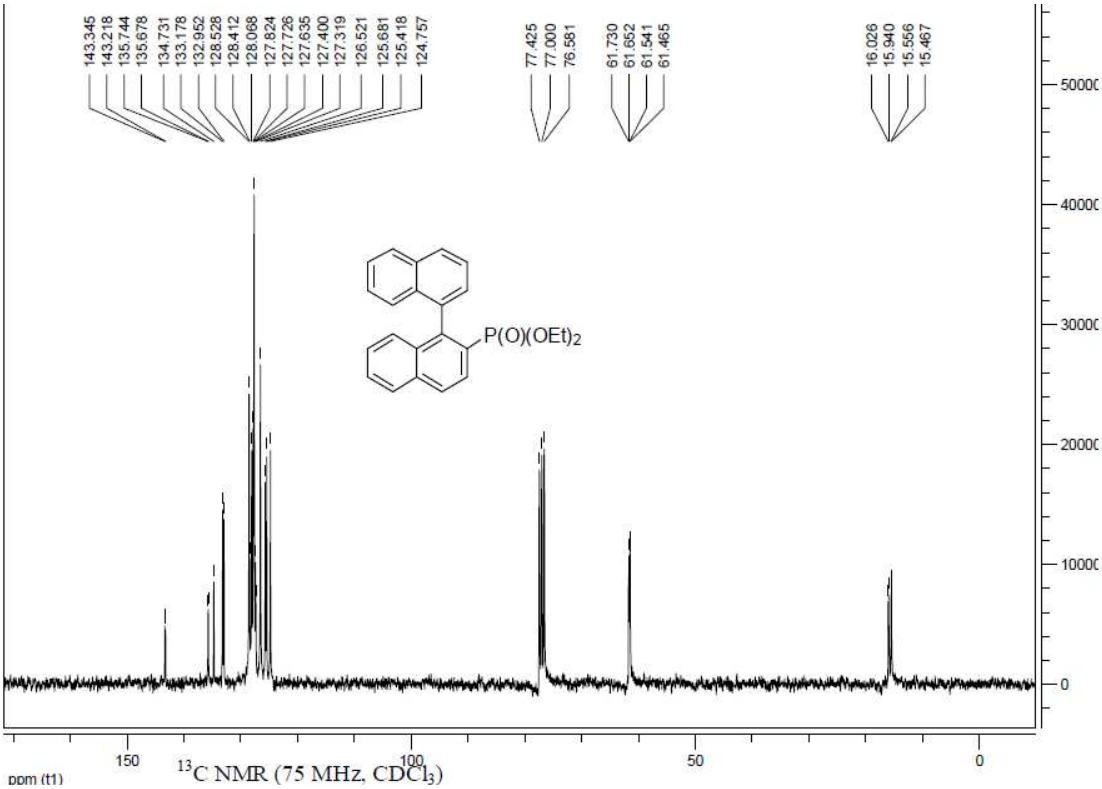
^{31}P NMR (121.4 MHz, $CDCl_3$) of **7g**



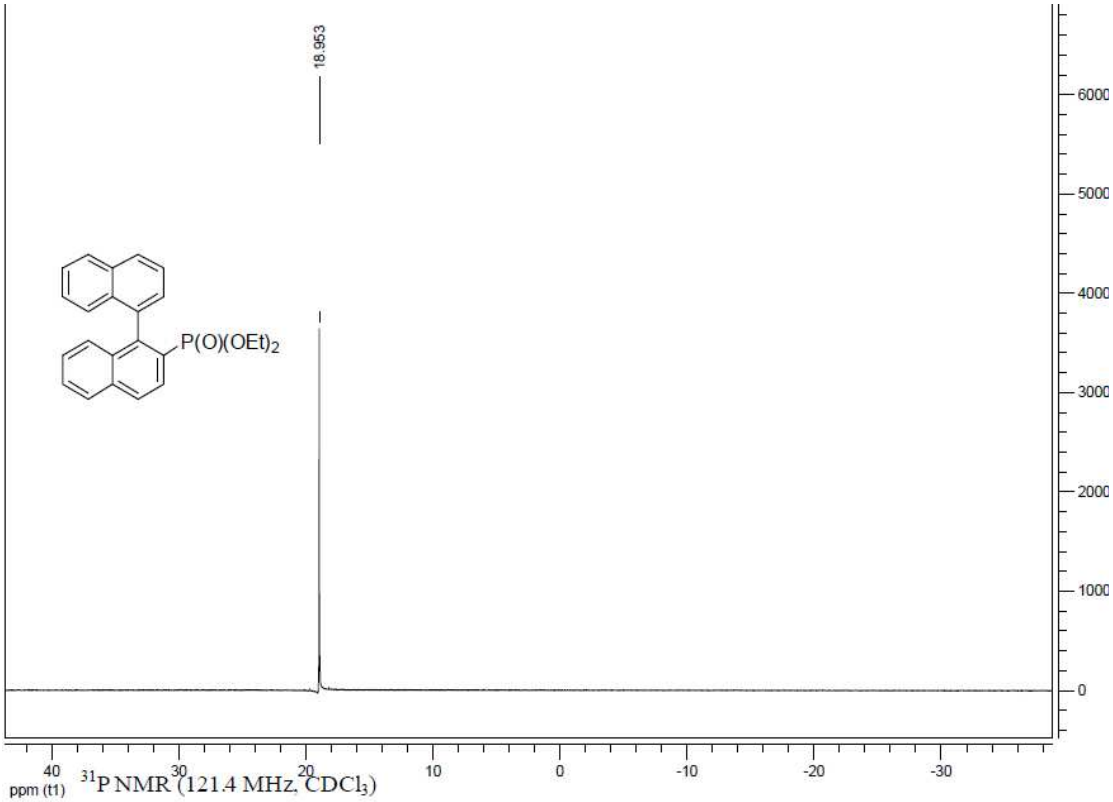
^{1}H NMR (300 MHz, $CDCl_3$) of product **1**



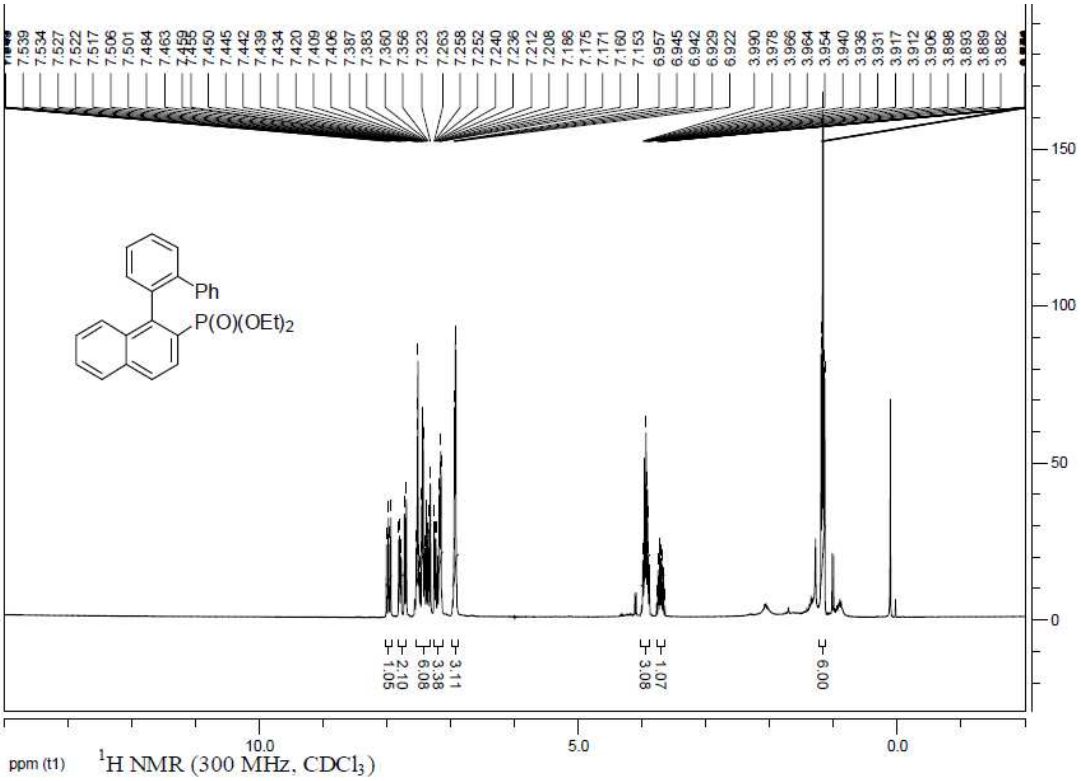
^{13}C NMR (75 MHz, $CDCl_3$) of product **1**



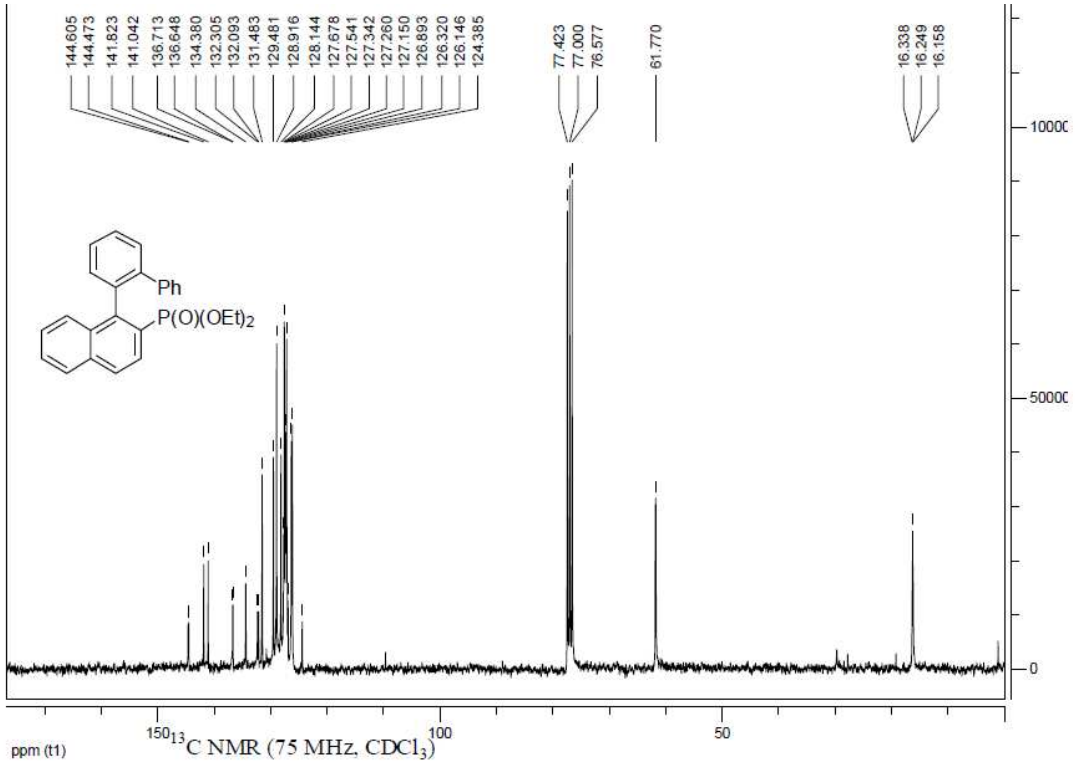
^{31}P NMR (121.4 MHz, $CDCl_3$) of product **1**



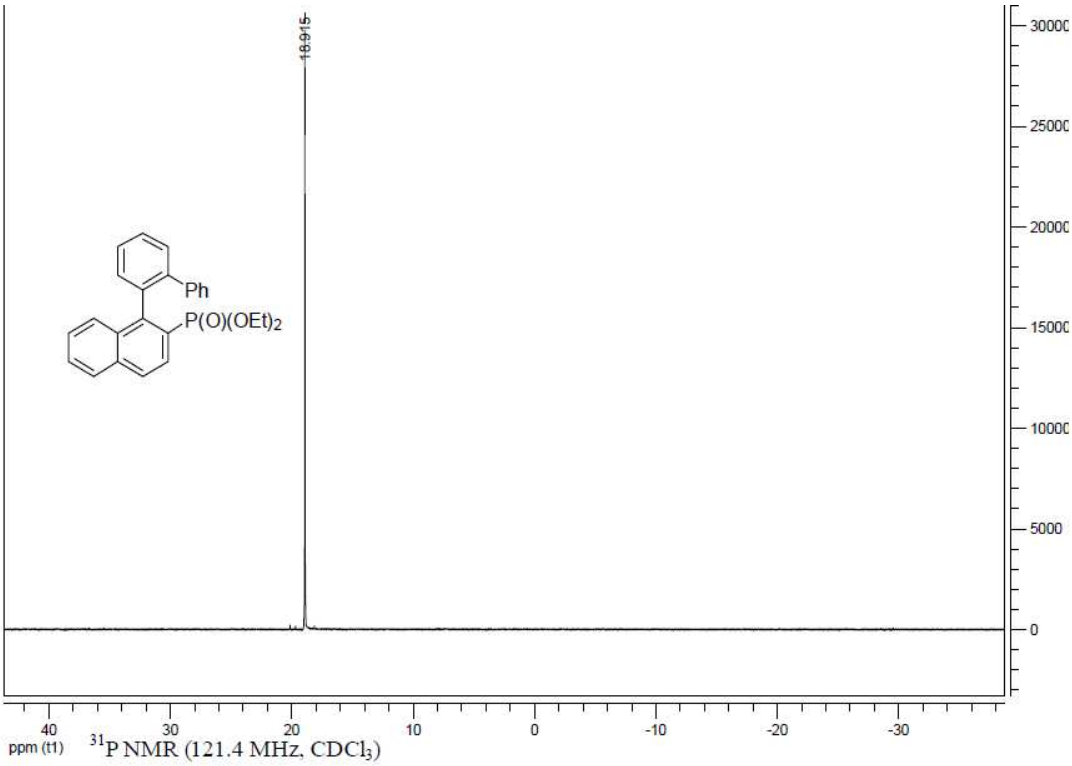
^{1}H NMR (300 MHz, $CDCl_3$) of product **2**



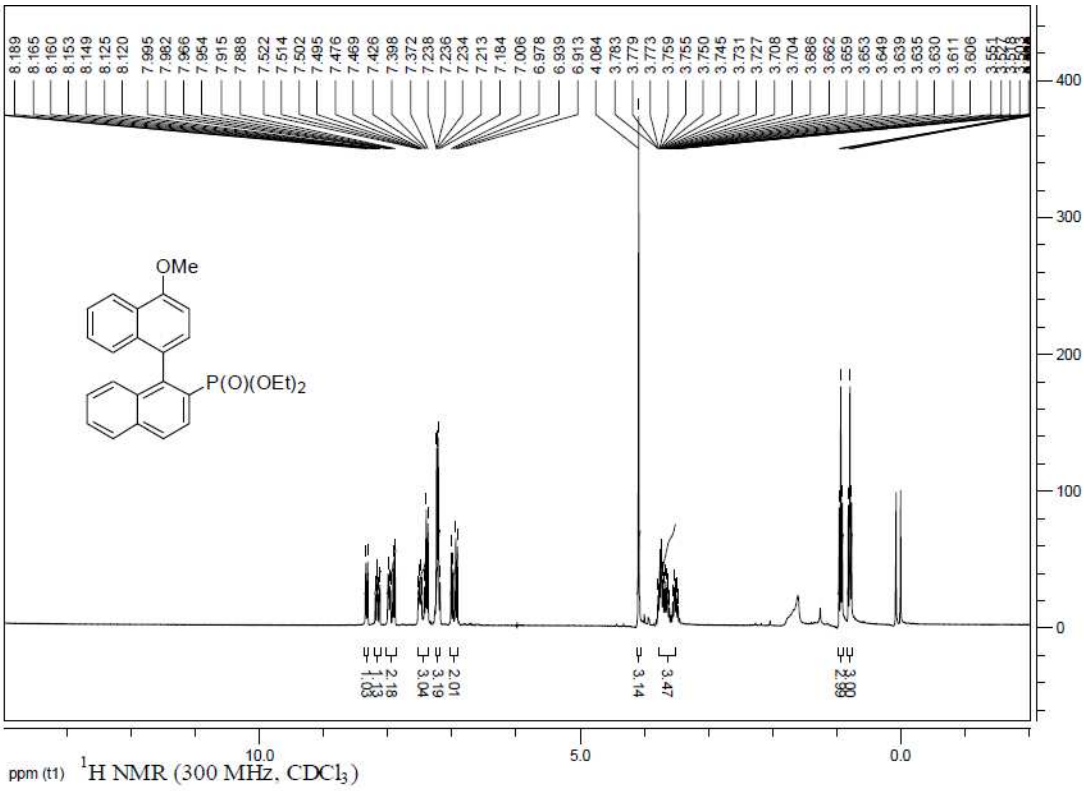
^{13}C NMR (75 MHz, $CDCl_3$) of product **2**



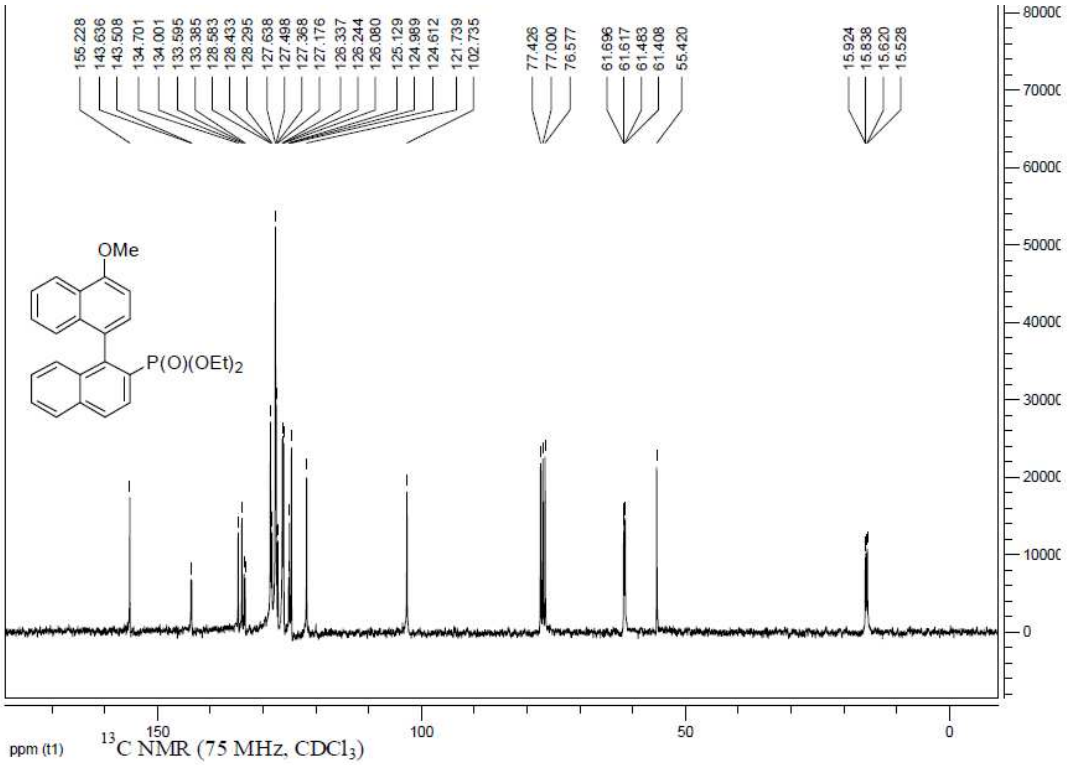
^{31}P NMR (121.4 MHz, $CDCl_3$) of product **2**



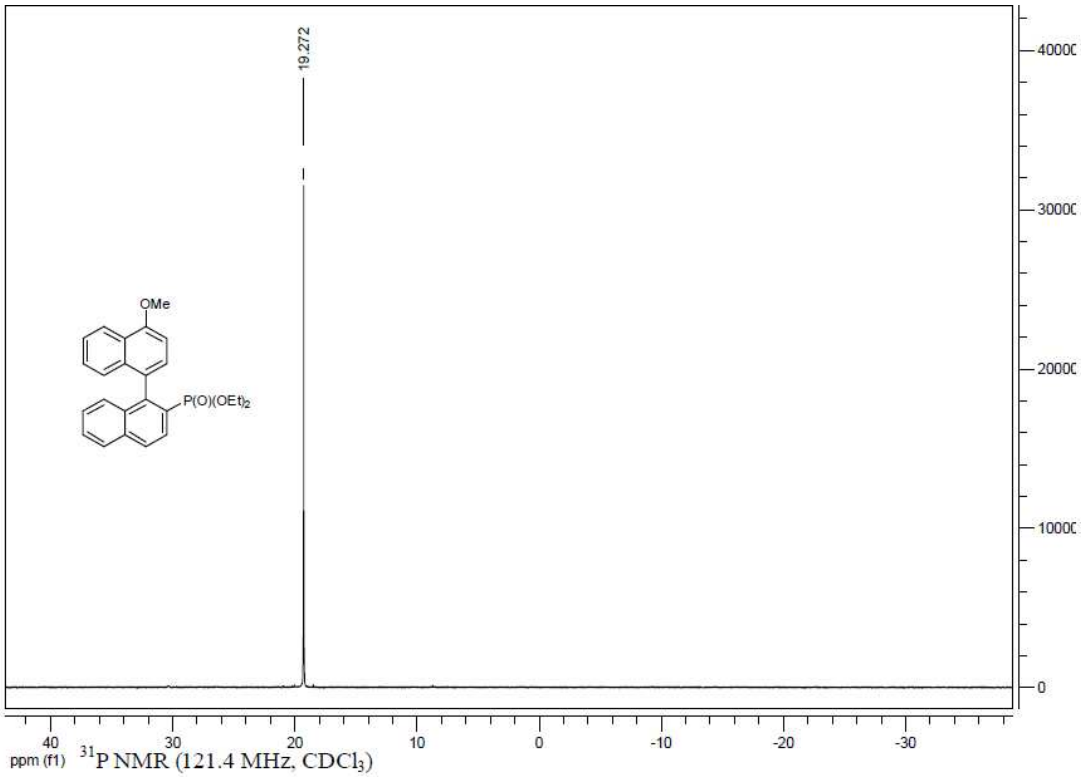
^{1}H NMR (300 MHz, $CDCl_3$) of product **3**



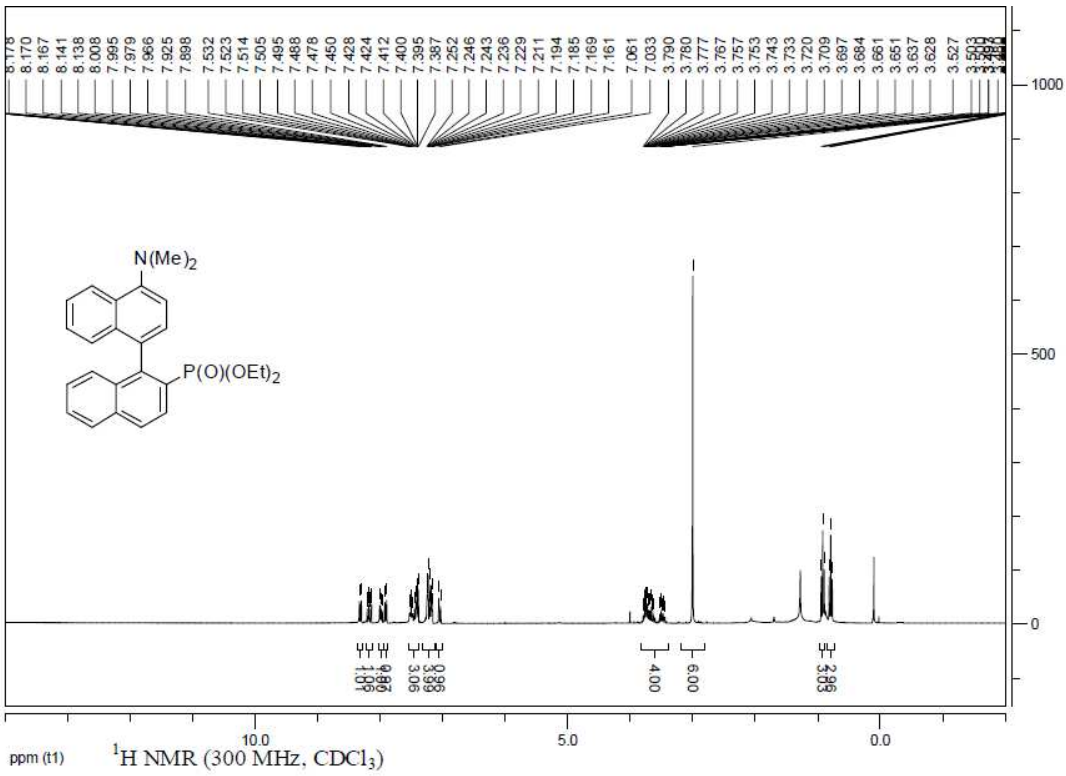
^{13}C NMR (75 MHz, $CDCl_3$) of product **3**



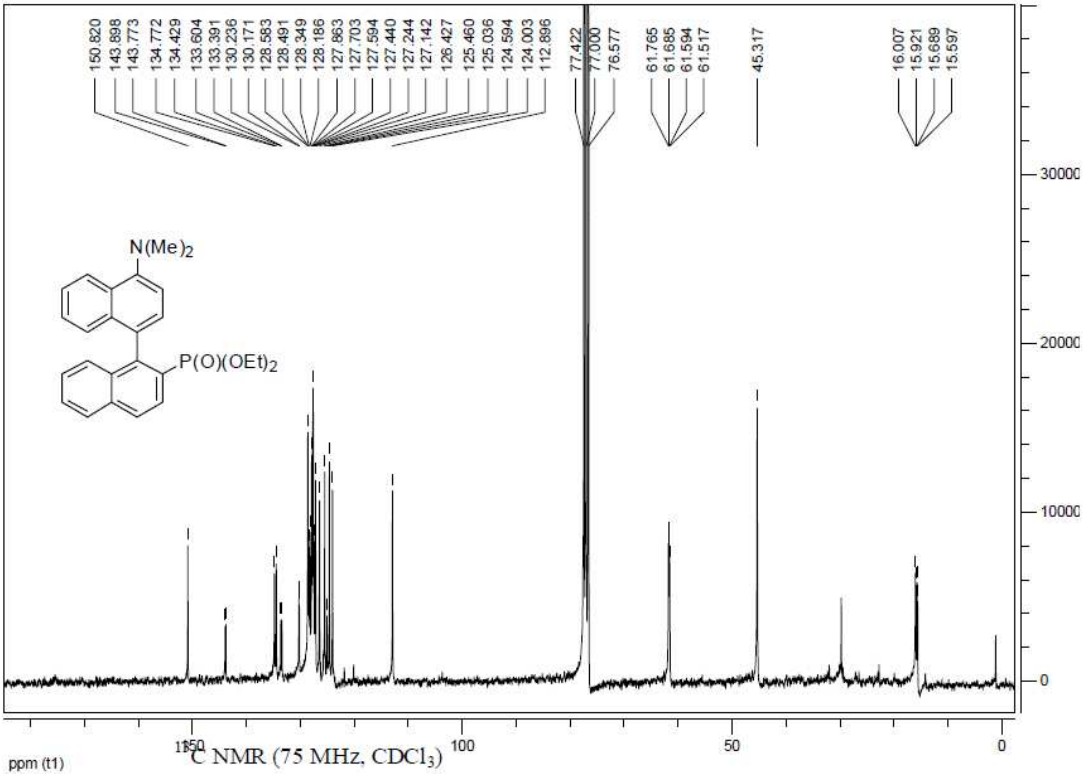
^{31}P NMR (121.4 MHz, $CDCl_3$) of product **3**



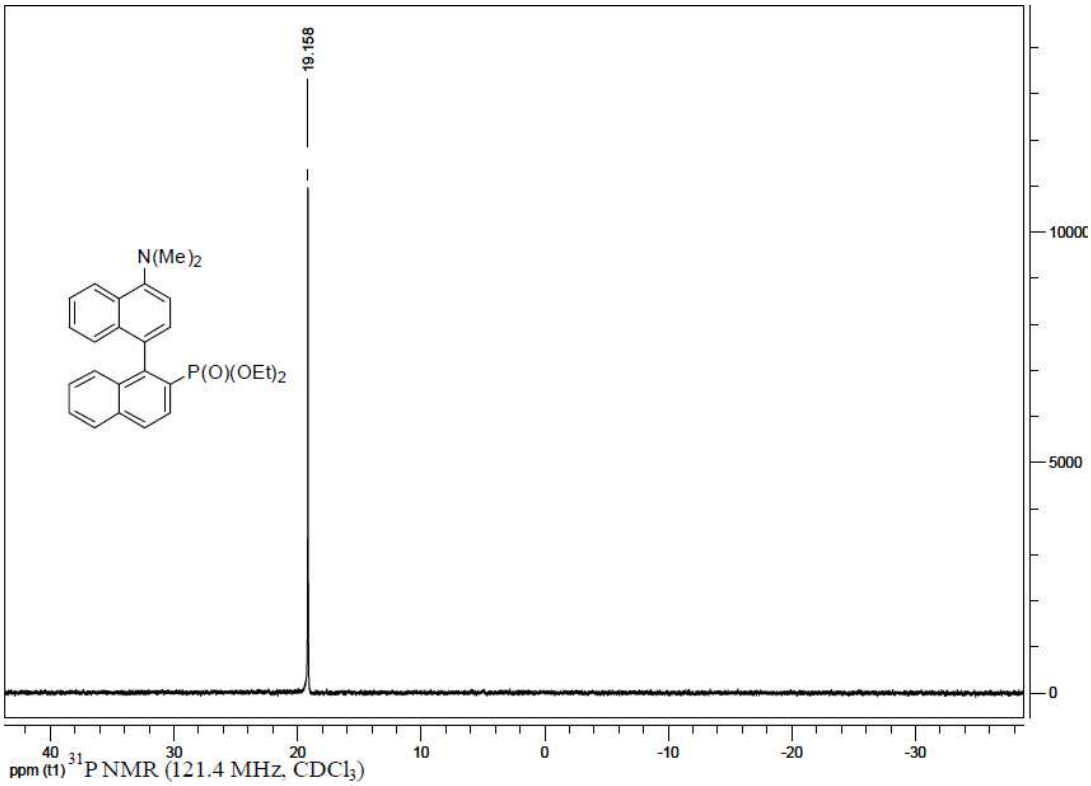
^{1}H NMR (300 MHz, $CDCl_3$) of product **4**



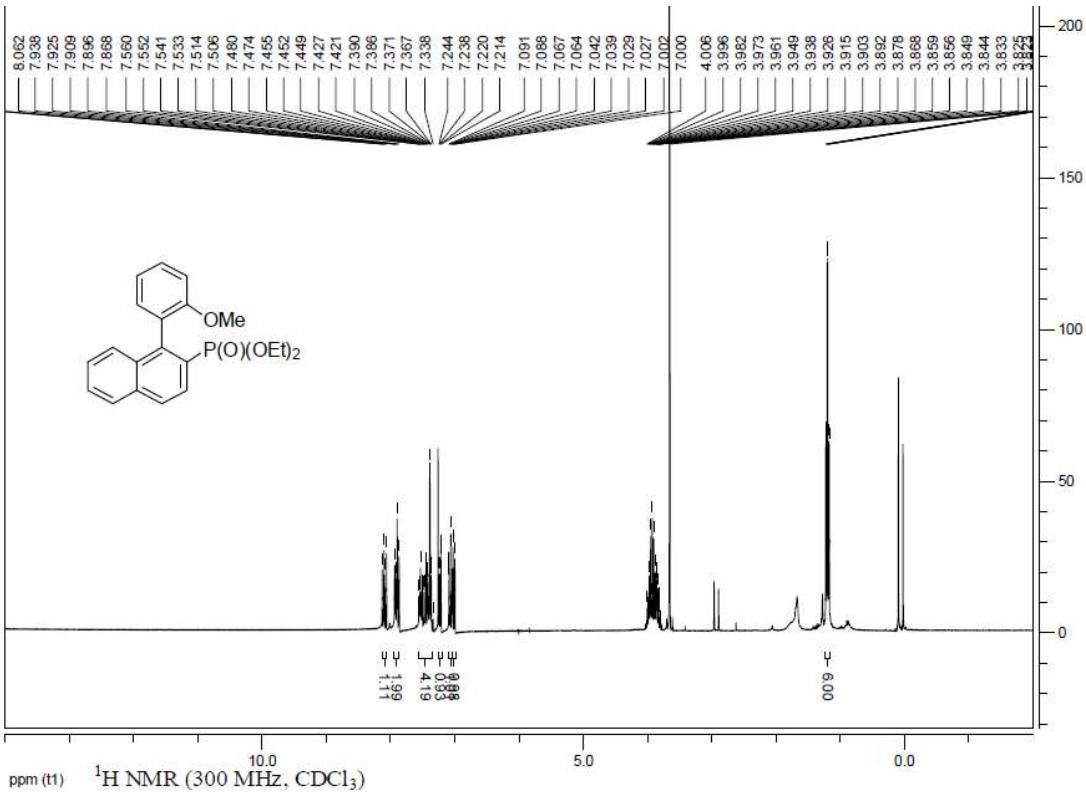
^{13}C NMR (75 MHz, $CDCl_3$) of product **4**



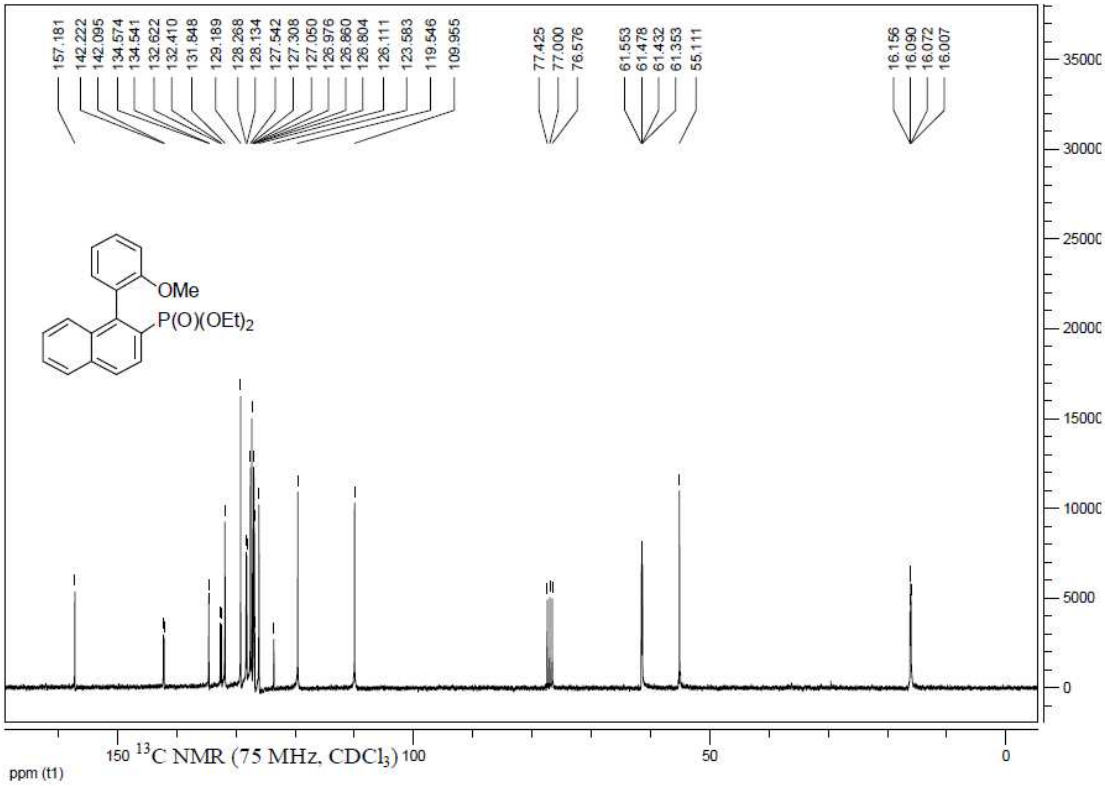
^{31}P NMR (121.4 MHz, $CDCl_3$) of product **4**



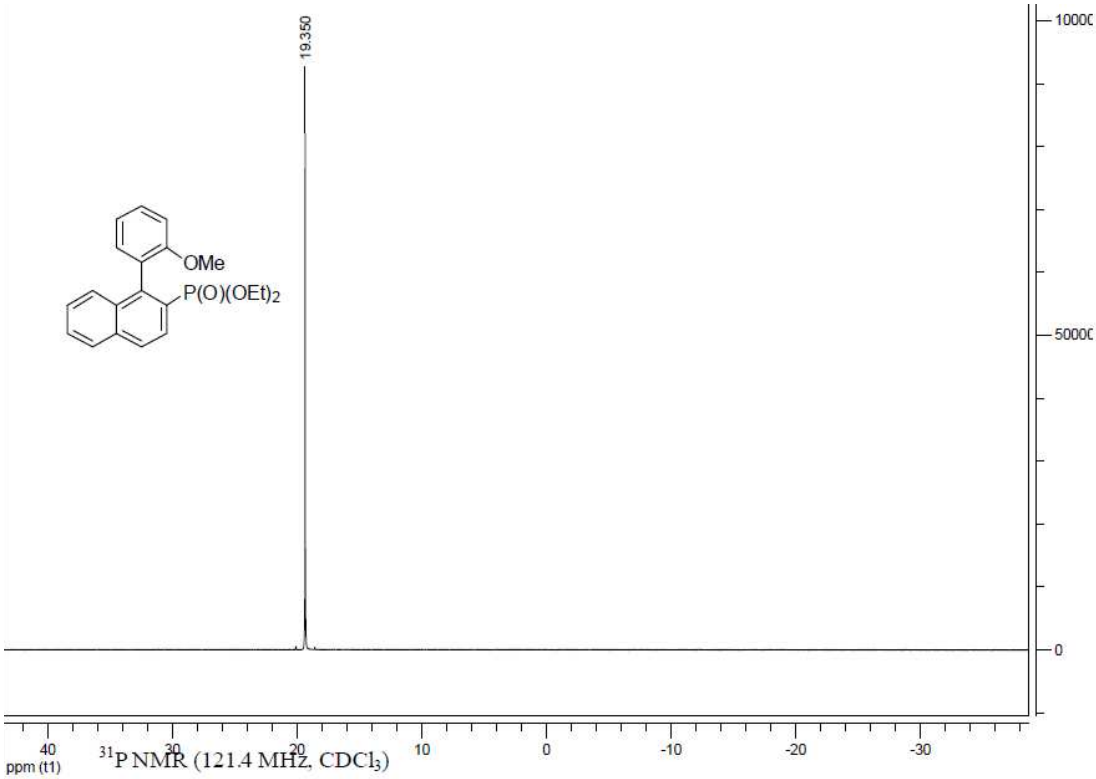
^{1}H NMR (300 MHz, $CDCl_3$) of product **5**



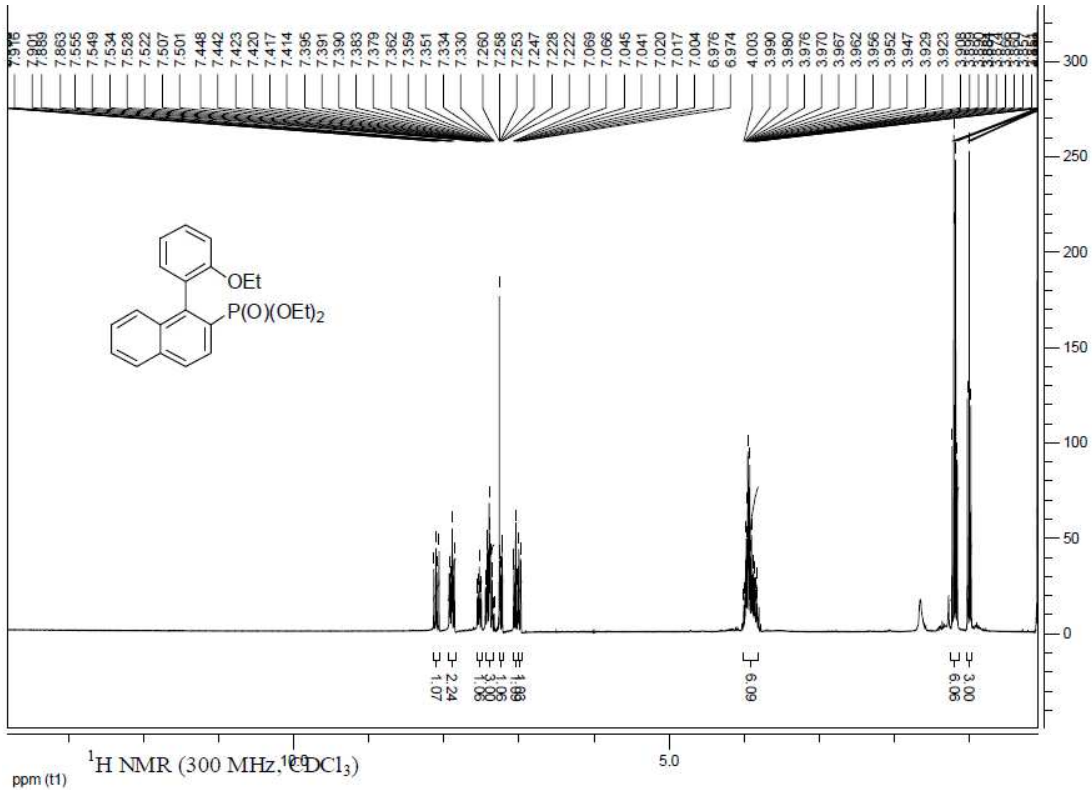
^{13}C NMR (75 MHz, $CDCl_3$) of product **5**



^{31}P NMR (121.4 MHz, $CDCl_3$) of product **5**

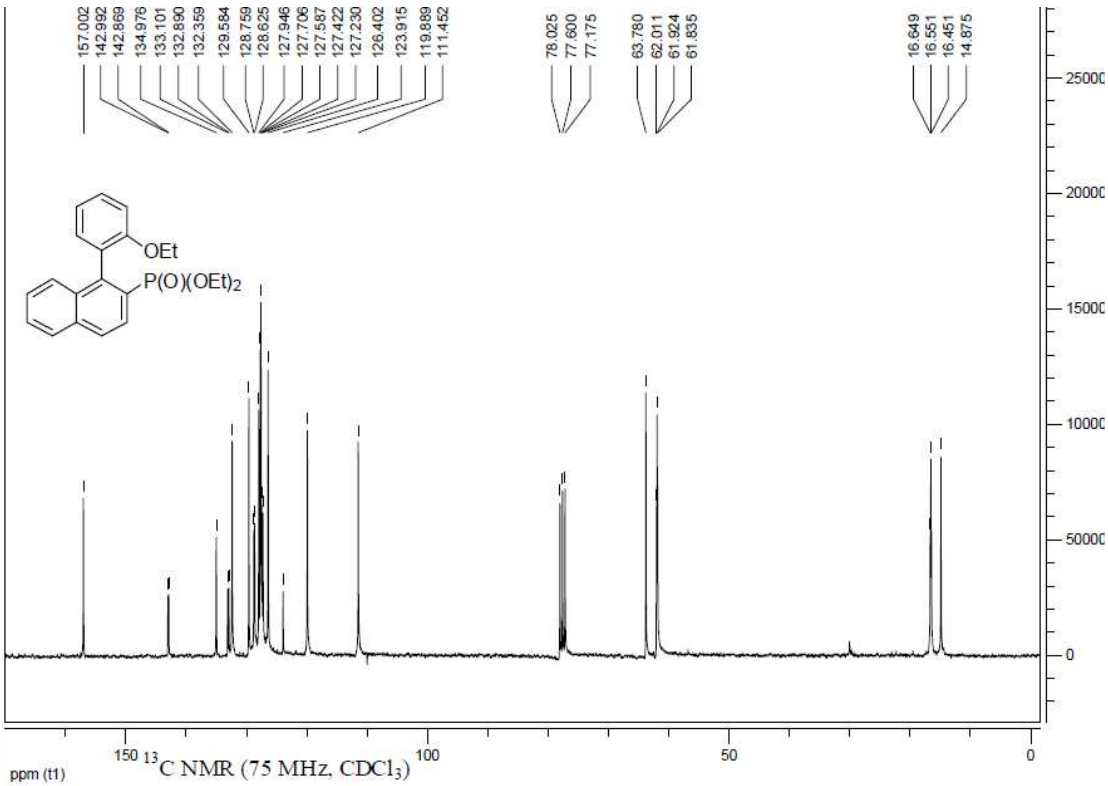


^{1}H NMR (300 MHz, $CDCl_3$) of product **6**



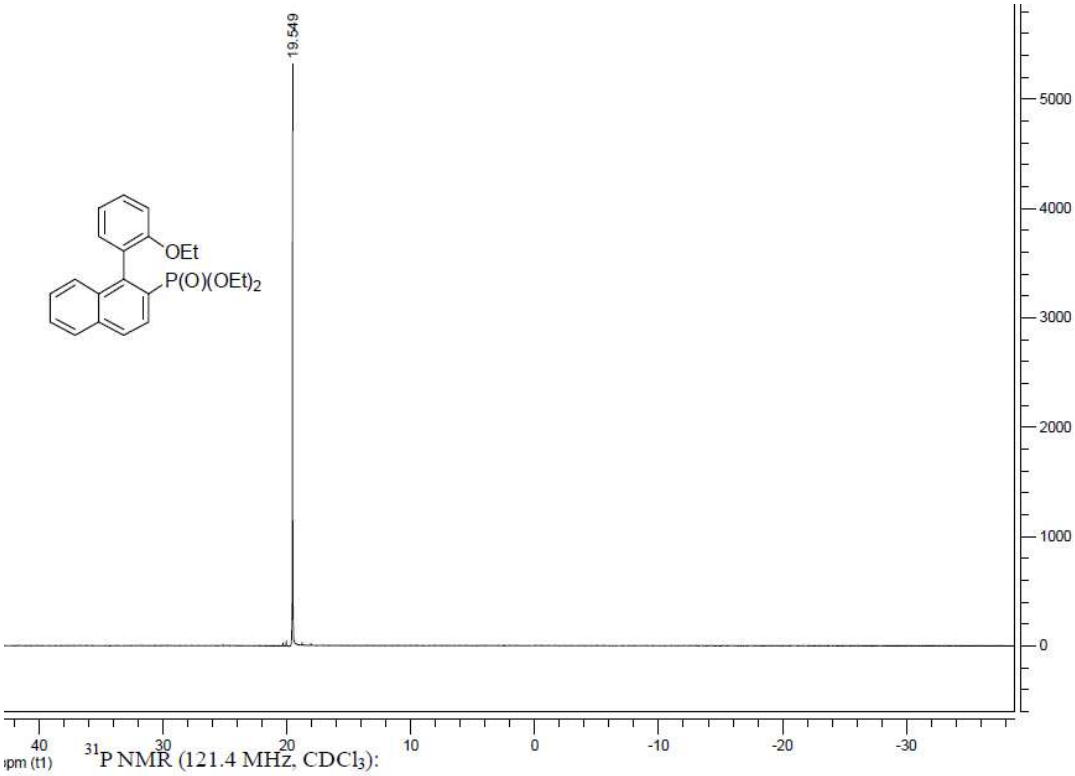
^{1}H NMR (300 MHz, $CDCl_3$)

^{13}C NMR (75 MHz, $CDCl_3$) of product **6**



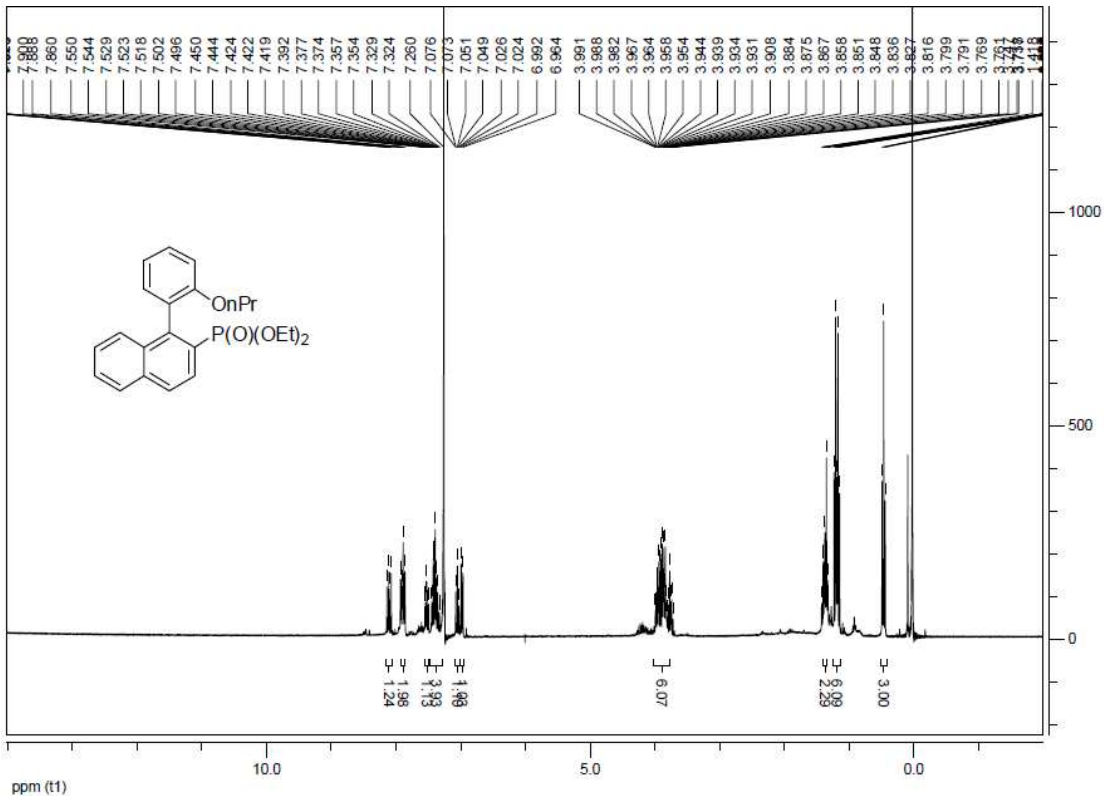
^{13}C NMR (75 MHz, $CDCl_3$)

^{31}P NMR (121.4 MHz, $CDCl_3$) of product **6**

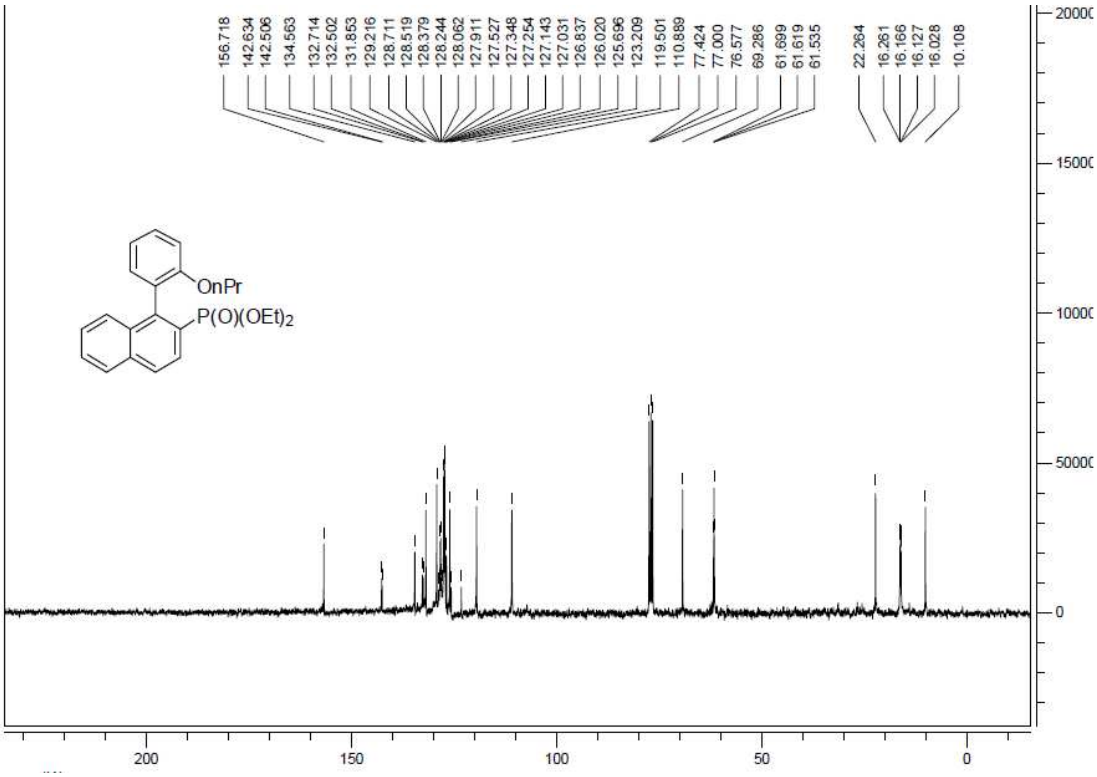


^{31}P NMR (121.4 MHz, $CDCl_3$):

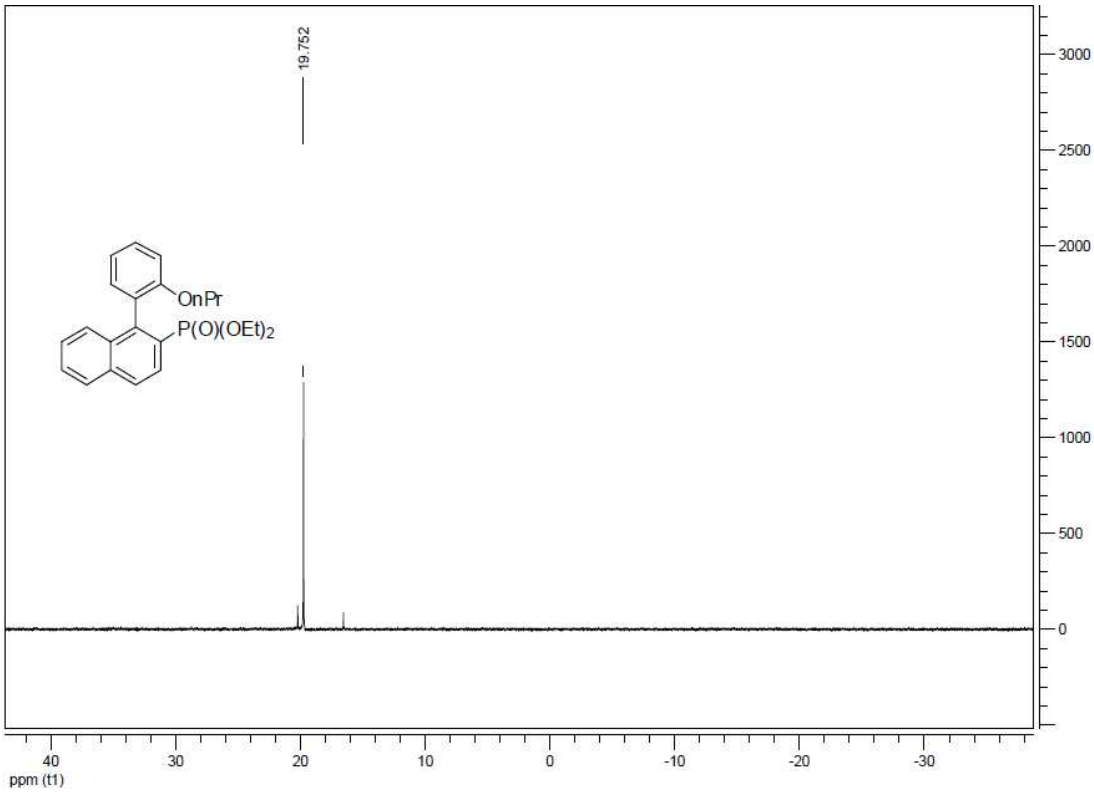
^{1}H NMR (300 MHz, $CDCl_3$) of product **7**



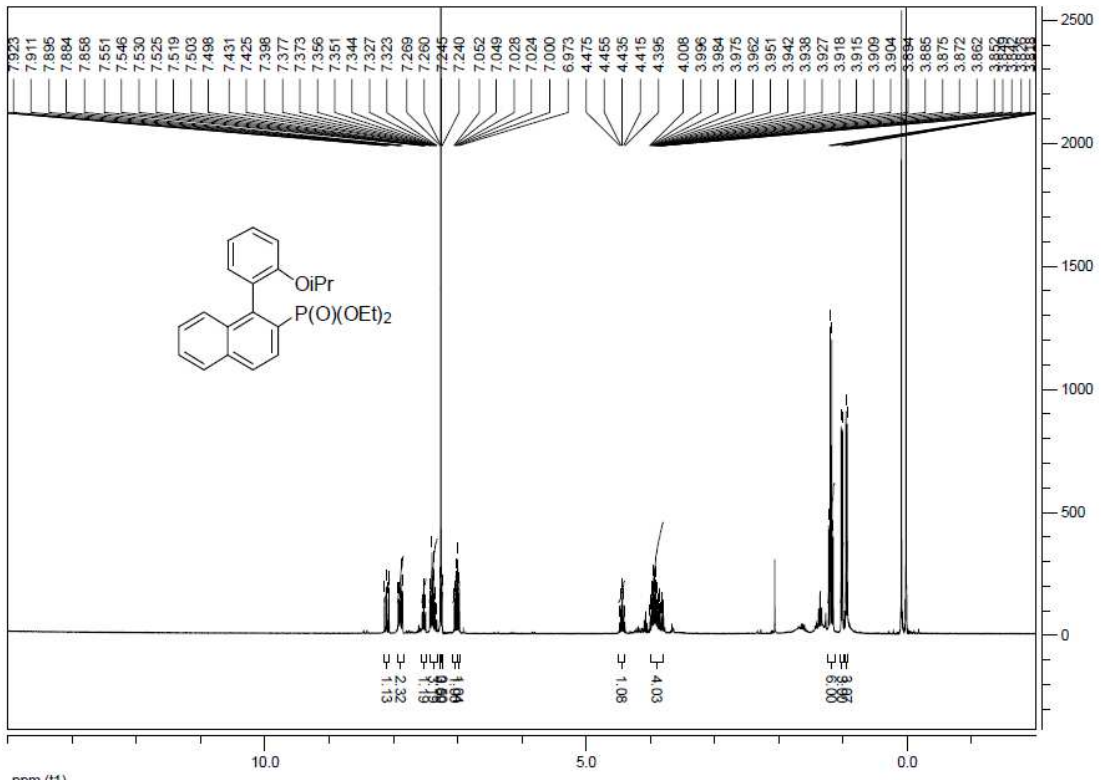
^{1}H NMR (300 MHz, $CDCl_3$) of product **7**



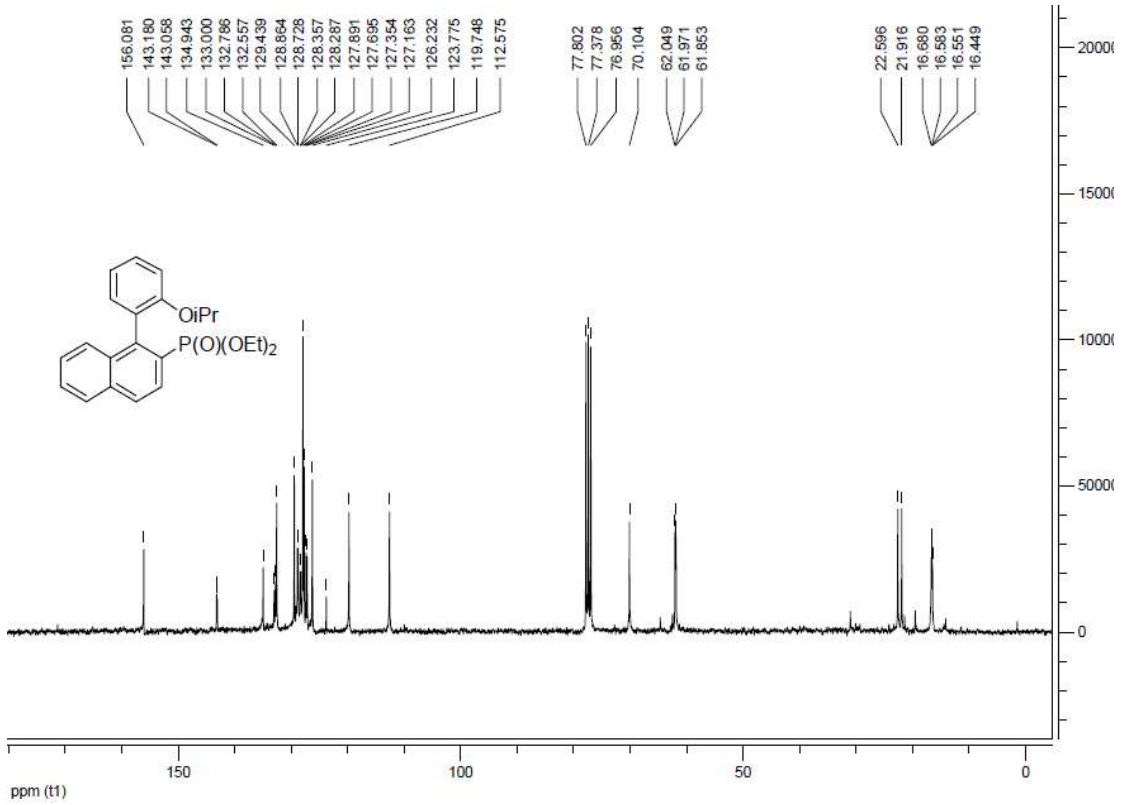
^{31}P NMR (121.4 MHz, $CDCl_3$) of product **7**



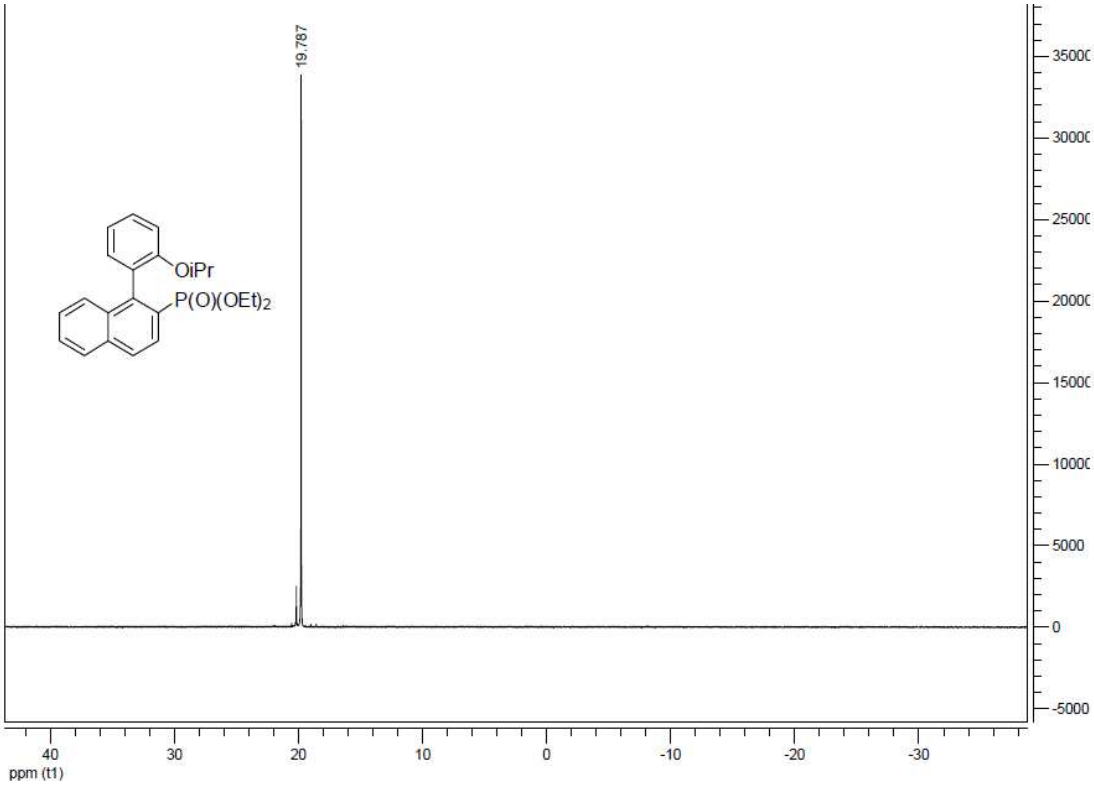
^{1}H NMR (300 MHz, $CDCl_3$) of product **8**



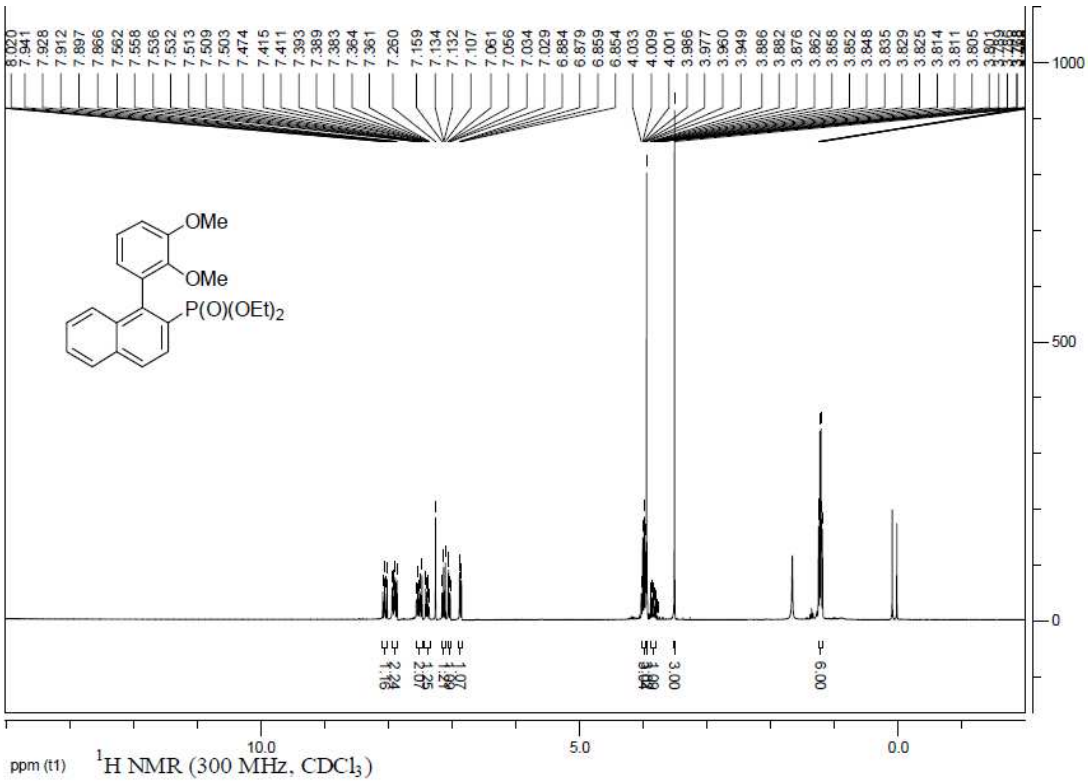
^{13}C NMR (75 MHz, $CDCl_3$) of product **8**



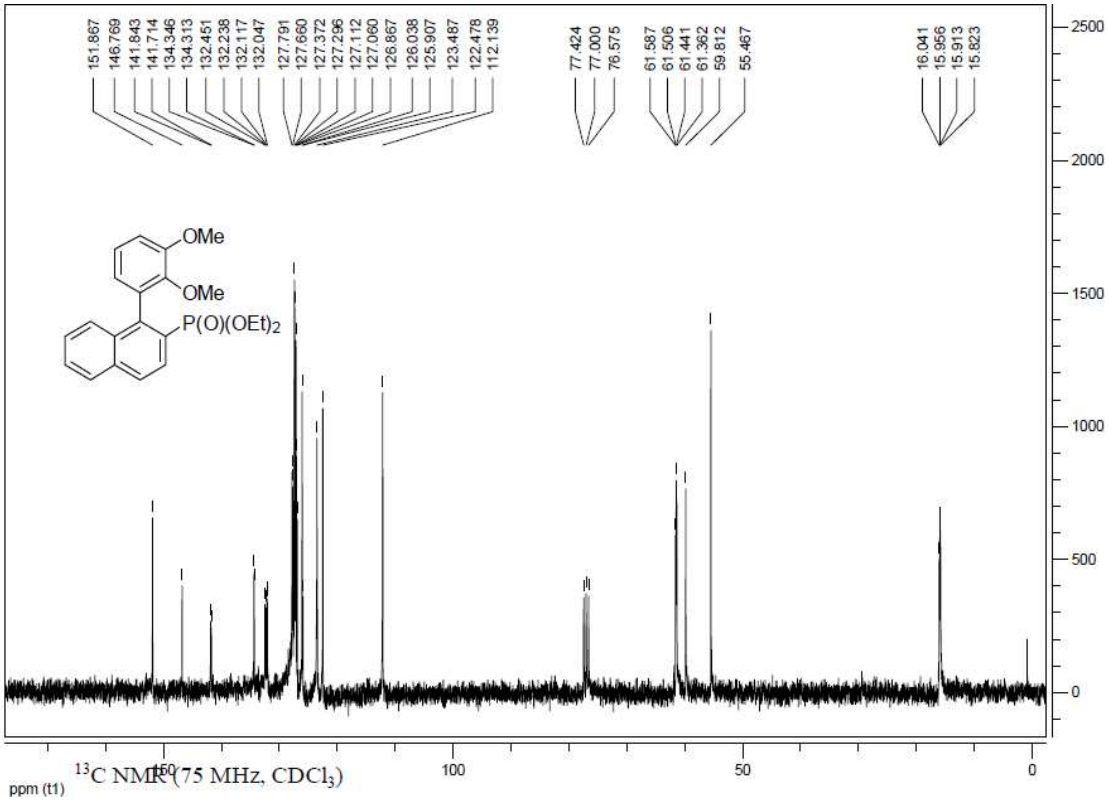
^{31}P NMR (121.4 MHz, $CDCl_3$) of product **8**



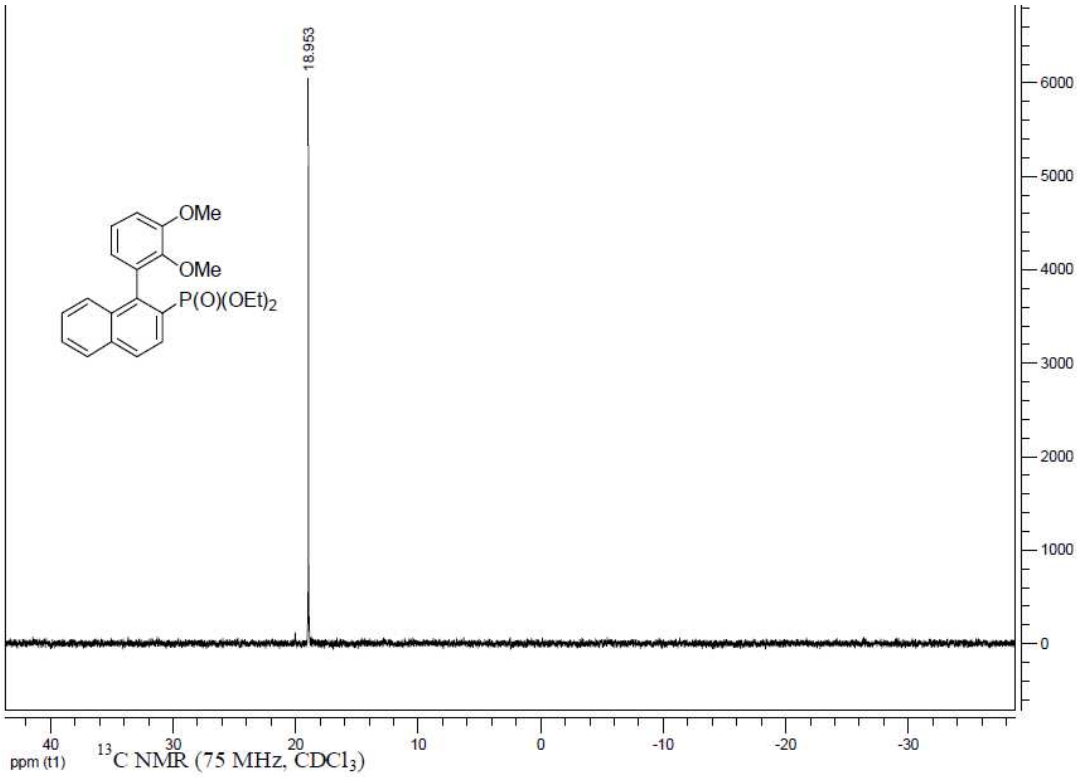
^{1}H NMR (300 MHz, $CDCl_3$) of product **9**



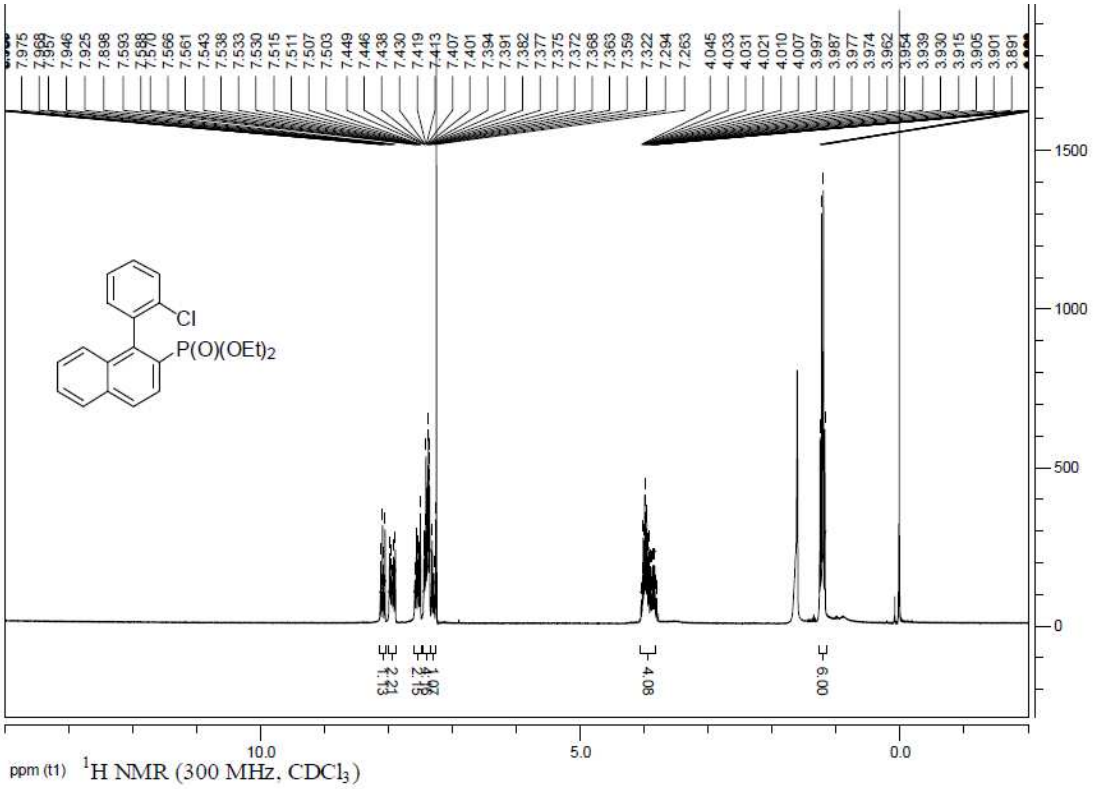
^{13}C NMR (75 MHz, $CDCl_3$) of product **9**



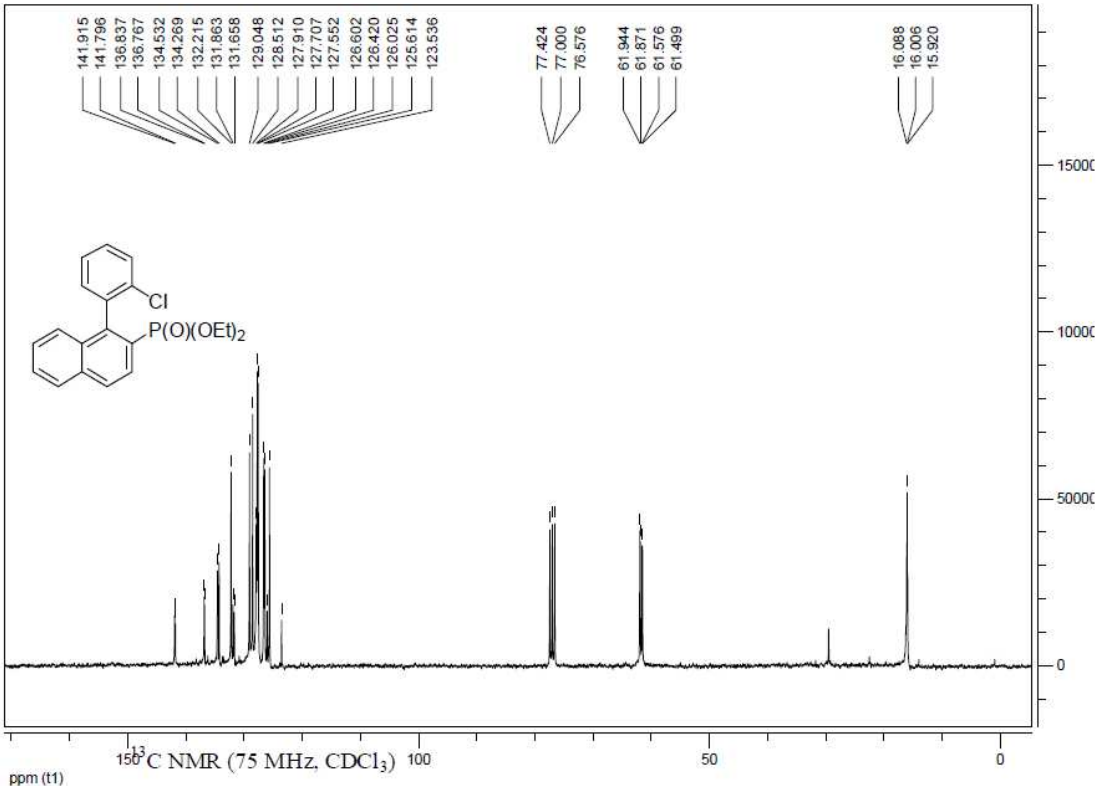
^{31}P NMR (121.4 MHz, $CDCl_3$) of product **9**



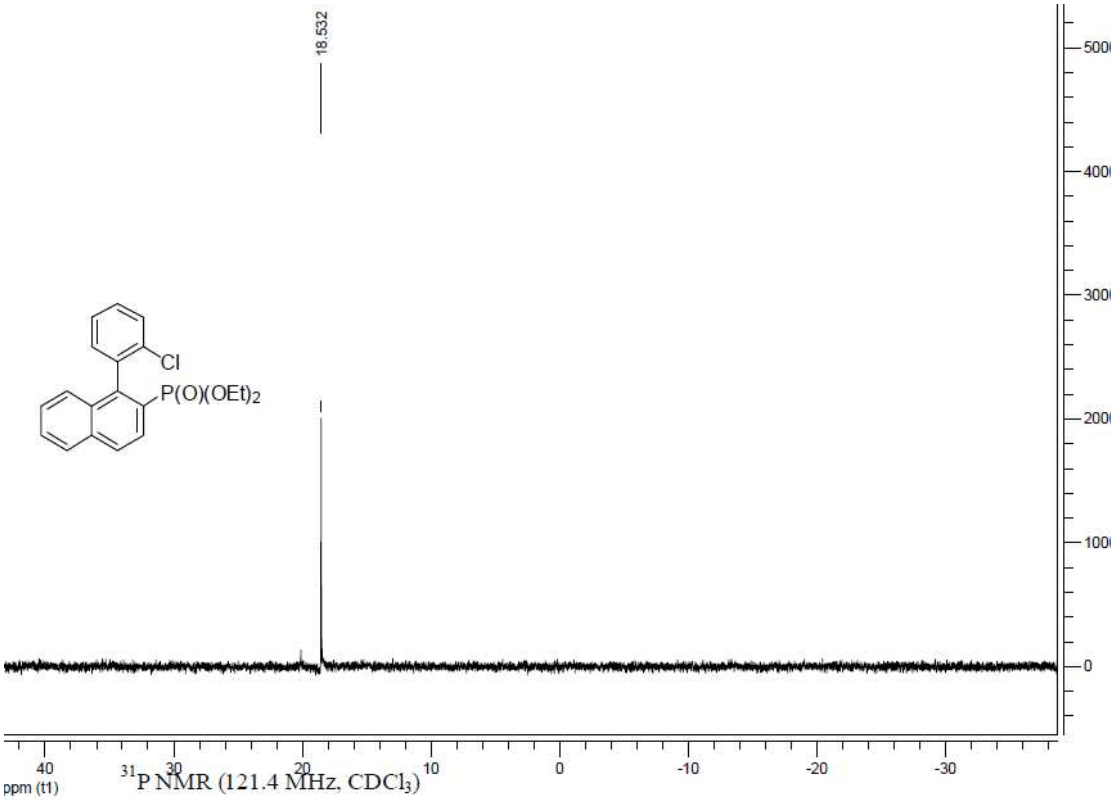
^{1}H NMR (300 MHz, $CDCl_3$) of product **10**



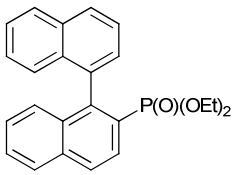
^{13}C NMR (75 MHz, $CDCl_3$) of product **10**



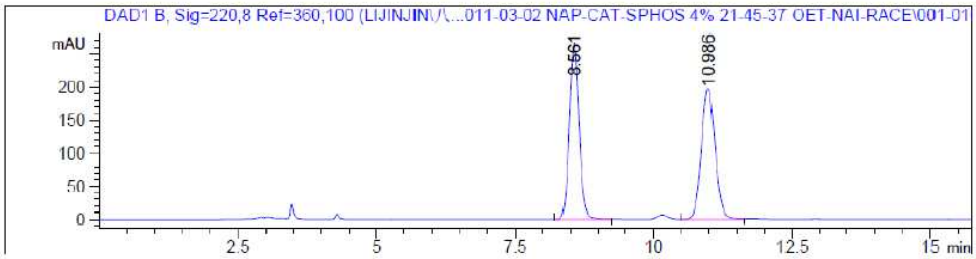
^{31}P NMR (121.4 MHz, $CDCl_3$) of product **10**



HPLC spectra.



The top one is racemic, the bottom one is the sample catalyzed by **7d**.
Conditions: column, AD-H, n-hexane : isopropanol = 90:10, 1.0 mL / min



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面积百分比报告

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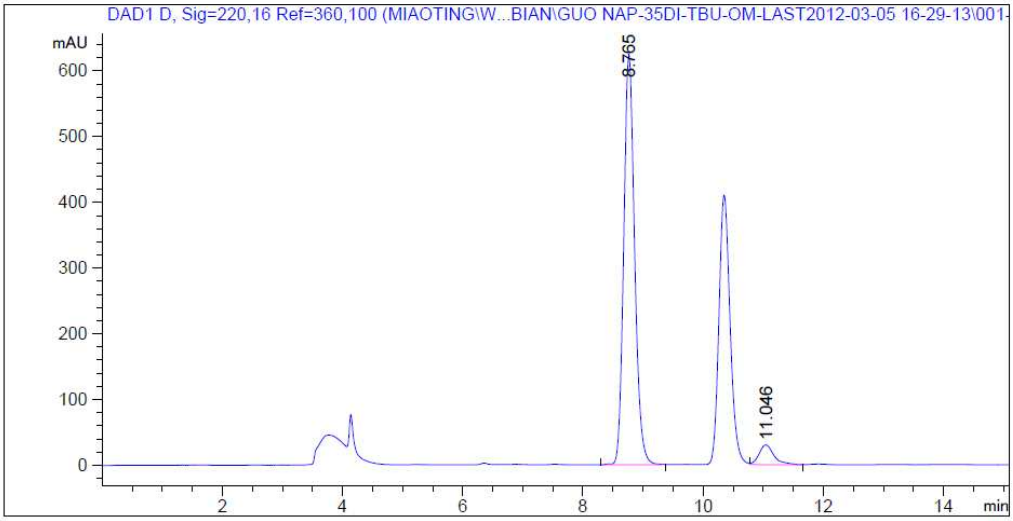
排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

信号 1: DAD1 B, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.561	VB	0.1914	3266.39624	265.82068	49.8705
2	10.986	VB	0.2581	3283.35986	197.30727	50.1295

总量 : 6549.75610 463.12794



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面积百分比报告

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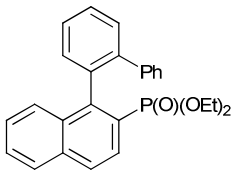
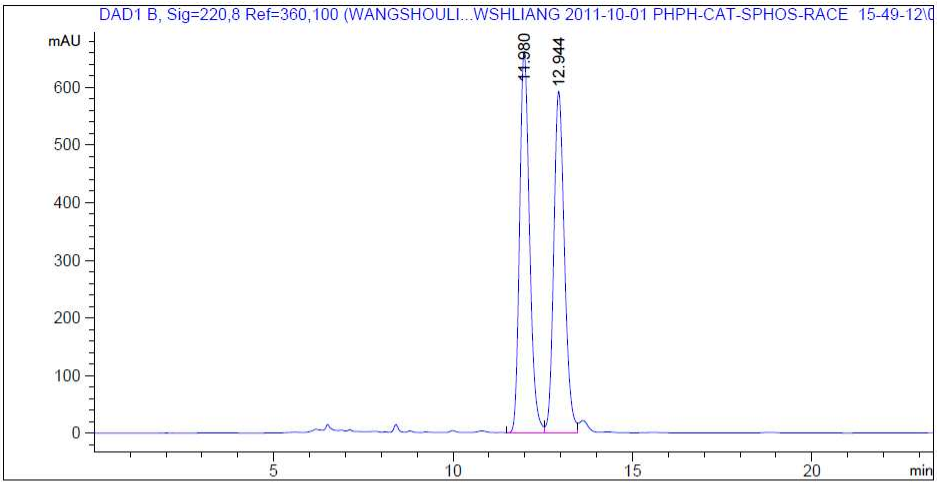
排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

信号 1: DAD1 D, Sig=220,16 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.765	BB	0.1937	7856.33838	624.68420	93.7472
2	11.046	VB	0.2648	524.00439	30.14992	6.2528



The top one is racemic, the bottom one is the sample catalyzed by **7d**.
Conditions: column, OD-H, n-hexane : isopropanol = 90:10, 0.5 mL / min



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面积百分比报告
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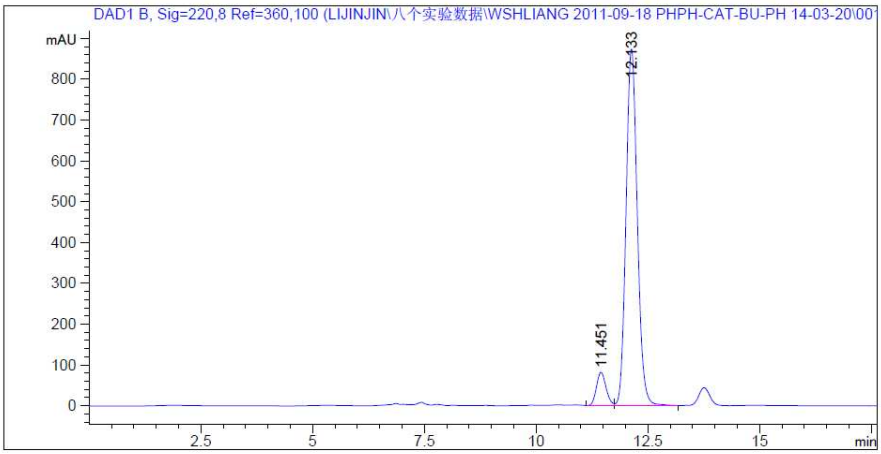
排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

信号 1: DAD1 B, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.980	VV	0.3007	1.27342e4	661.02637	50.9028
2	12.944	VV	0.3220	1.22825e4	592.06250	49.0972

总量 : 2.50167e4 1253.08887



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面积百分比报告

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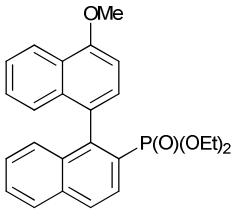
排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

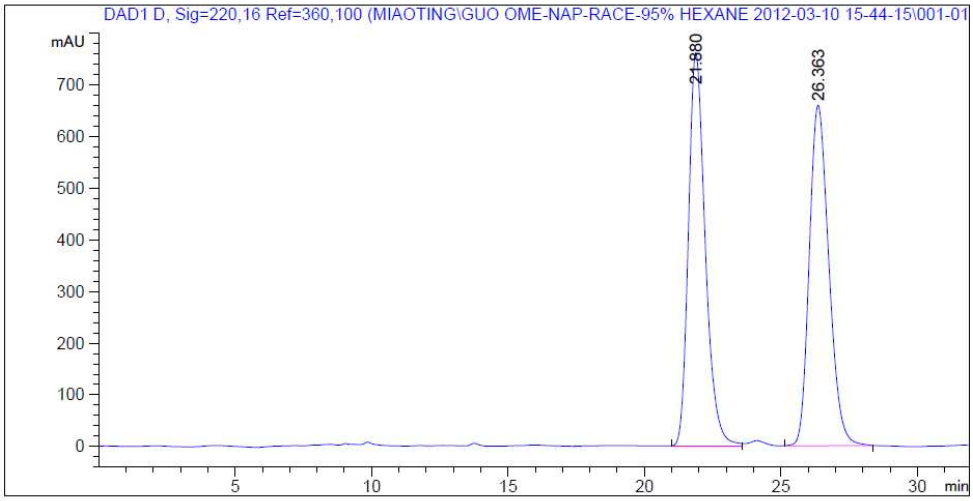
信号 1: DAD1 B, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.451	VV	0.2317	1238.85352	82.24255	7.4820
2	12.133	VB	0.2645	1.53190e4	873.93658	92.5180

总量 : 1.65579e4 956.17913



The top one is racemic, the bottom one is the sample catalyzed by **7d**.
Conditions: column, OD-H, n-hexane : isopropanol = 95:5, 0.5 mL / min



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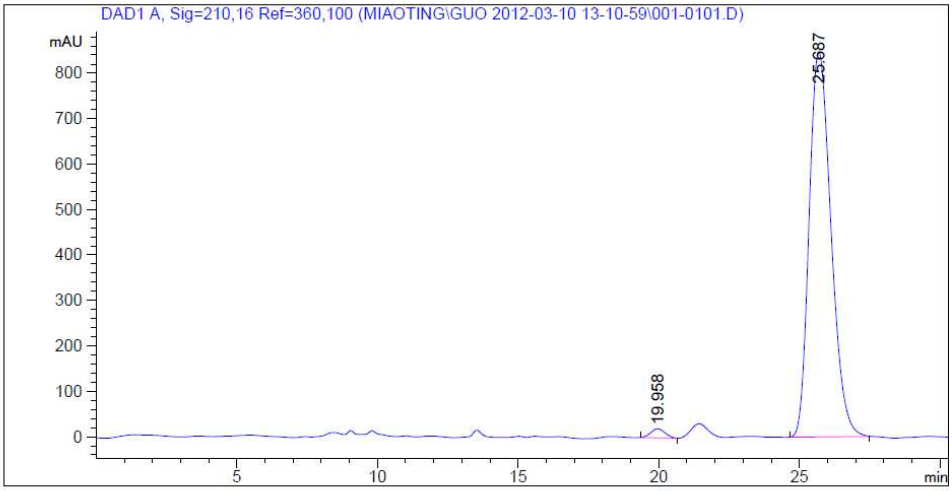
面积百分比报告
==========

排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

信号 1: DAD1 D, Sig=220,16 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	21.880	BB	0.6502	3.26266e4	761.02710	49.8291
2	26.363	BB	0.7605	3.28504e4	659.06409	50.1709

总量 : 6.54770e4 1420.09119



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面积百分比报告

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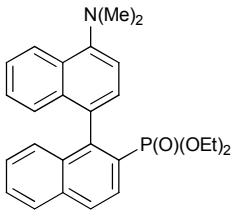
排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

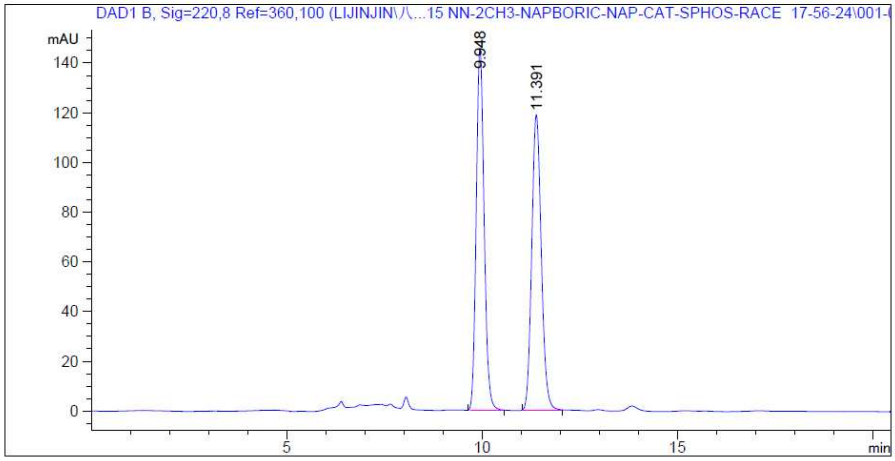
信号 1: DAD1 A, Sig=210,16 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	19.958	BV	0.4840	705.60571	20.02951	1.5158
2	25.687	BB	0.8407	4.58459e4	848.05408	98.4842

总量 : 4.65515e4 868.08359



The top one is racemic, the bottom one is the sample catalyzed by **7d**.
Conditions: column, OD-H, n-hexane : isopropanol = 90:10, 0.5 mL / min

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==========================================================================
                                面积百分比报告
==========================================================================

排序                    :      信号
乘积因子:                       :      1.0000
稀释因子:                       :      1.0000
内标使用乘积因子和稀释因子


信号 1: DAD1 B, Sig=220,8 Ref=360,100

 峰 保留时间 类型  峰宽      峰面积       峰高      峰面积
  #   [min]        [min]    [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   9.948 BB    0.2160 2045.36328  145.52280  50.2645
   2  11.391 BB    0.2645 2023.83972  118.95242  49.7355

总量 :                    4069.20300  264.47521
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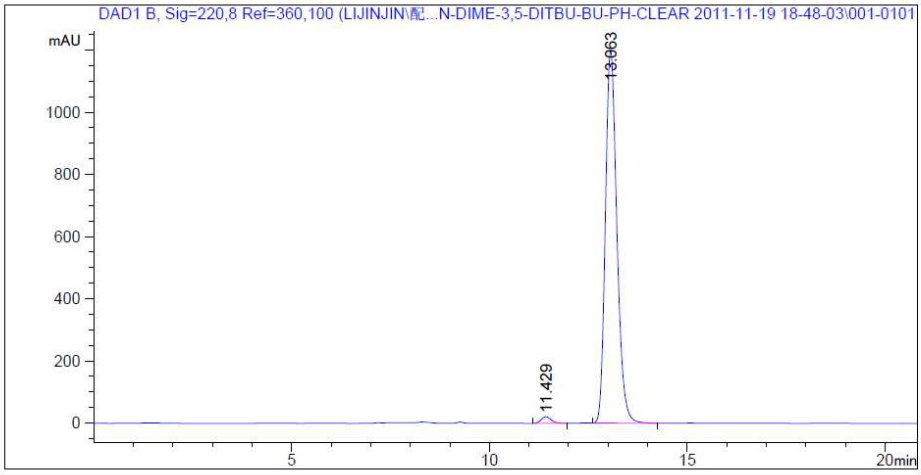

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面积百分比报告

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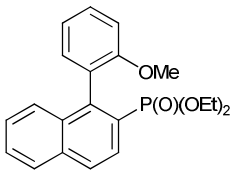
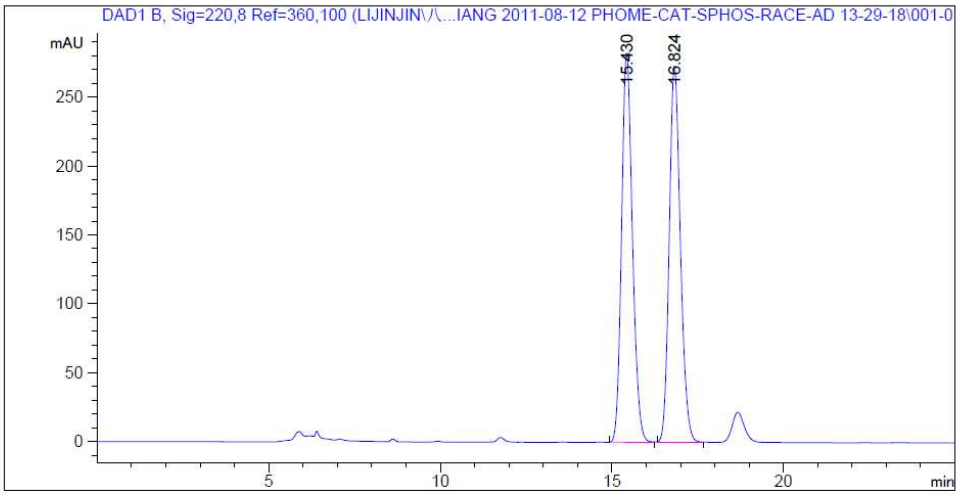
排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

信号 1: DAD1 B, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.429	BB	0.2743	367.95605	21.01375	1.4996
2	13.063	BB	0.3091	2.41698e4	1199.27502	98.5004



The top one is racemic, the bottom one is the sample catalyzed by **7d**.
Conditions: column, OD-H, n-hexane : isopropanol = 90:10, 0.5 mL / min



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面积百分比报告
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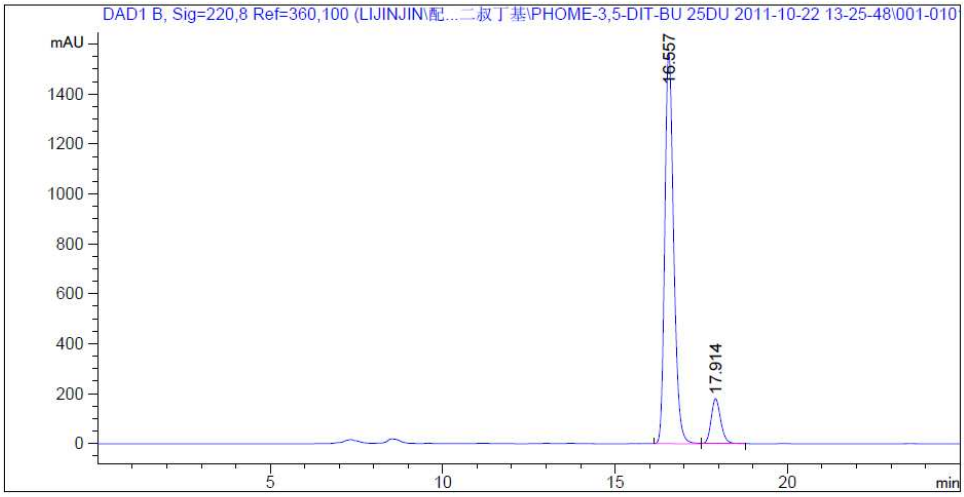
排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

信号 1: DAD1 B, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.430	BB	0.3364	6210.56934	282.54993	50.1221
2	16.824	BB	0.3478	6180.32178	273.35486	49.8779

总量 : 1.23909e4 555.90479



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面积百分比报告

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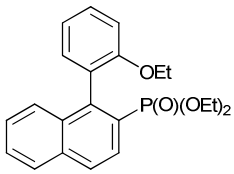
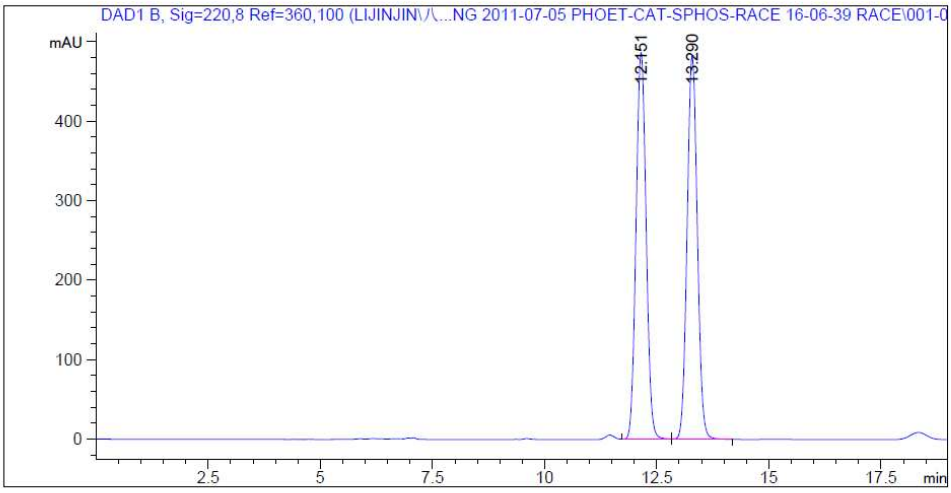
排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

信号 1: DAD1 B, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	16.557	BV	0.2747	2.80259e4	1566.43872	88.9090
2	17.914	VB	0.2962	3496.10718	180.33018	11.0910



The top one is racemic, the bottom one is the sample catalyzed by **7d**.
Conditions: column, AD-H, n-hexane : isopropanol = 90:10, 0.5 mL / min

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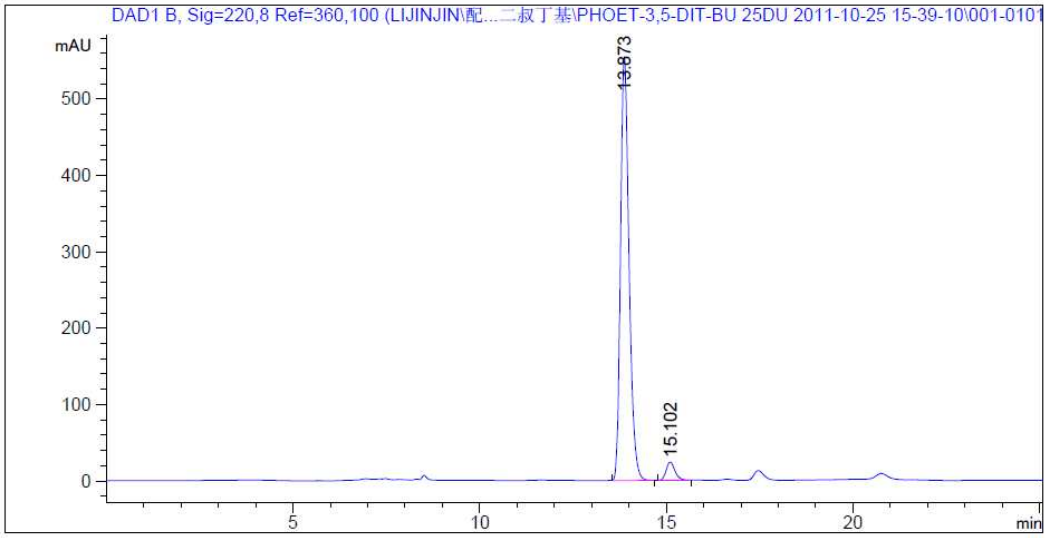
==========================================================================
                              面积百分比报告
==========================================================================

排序                    :      信号
乘积因子:                       :      1.0000
稀释因子:                       :      1.0000
内标使用乘积因子和稀释因子


信号 1: DAD1 B, Sig=220,8 Ref=360,100

 峰 保留时间 类型  峰宽      峰面积       峰高      峰面积
  #   [min]         [min]    [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  12.151 VV    0.2469 7630.65820  486.79492  49.9247
   2  13.290 VB    0.2470 7653.67041  482.53772  50.0753

总量 :                    1.52843e4   969.33264
```



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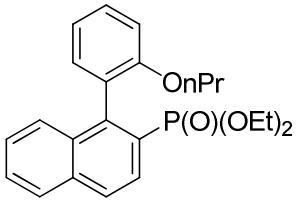
面积百分比报告

==========

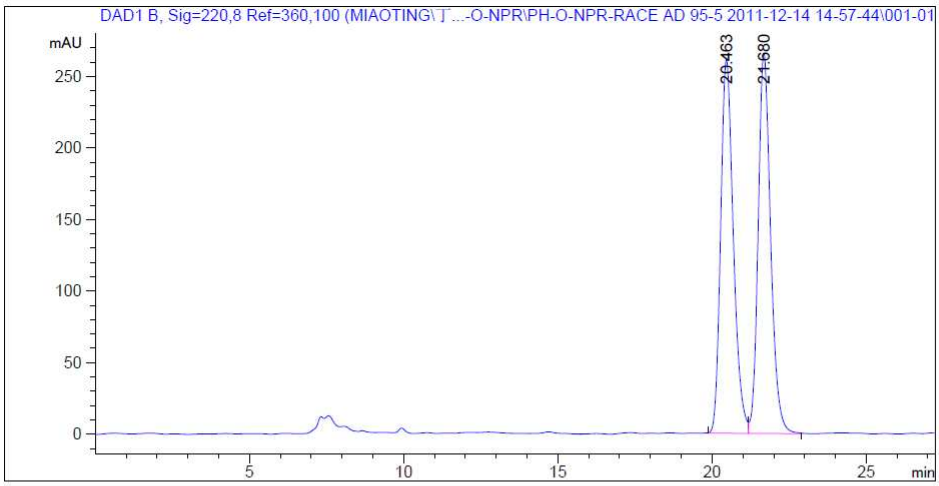
排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

信号 1: DAD1 B, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	13.873	BB	0.2388	8790.99609	555.06305	95.7227
2	15.102	BB	0.2558	392.81958	23.89570	4.2773



The top one is racemic, the bottom one is the sample catalyzed by **7d**.
Conditions: column, AD-H, n-hexane : isopropanol = 95:5, 0.5 mL / min



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面积百分比报告
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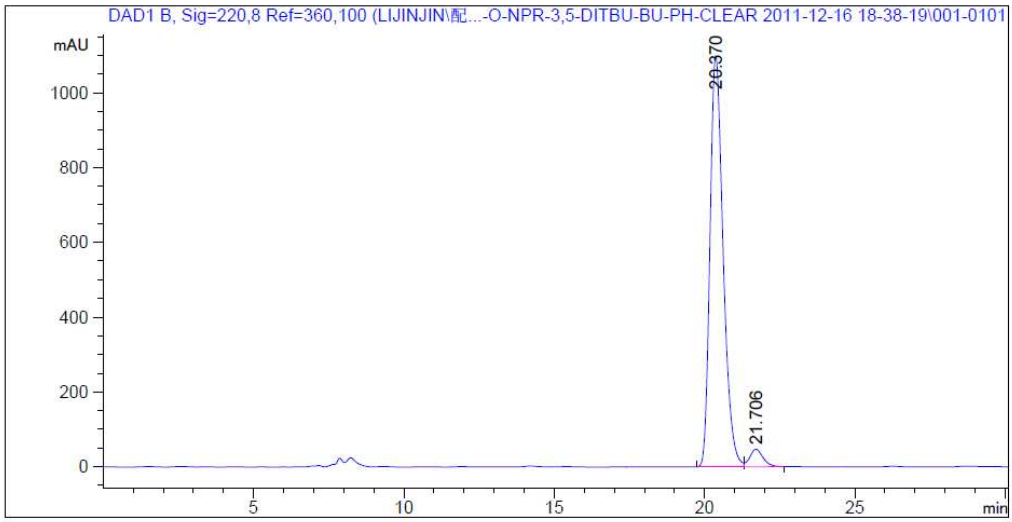
排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

信号 1: DAD1 B, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	20.463	BV	0.4363	7482.44775	261.15927	50.0597
2	21.680	VB	0.4275	7464.61426	265.95532	49.9403

总量 : 1.49471e4 527.11459



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面积百分比报告

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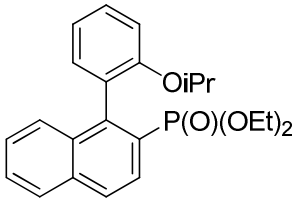
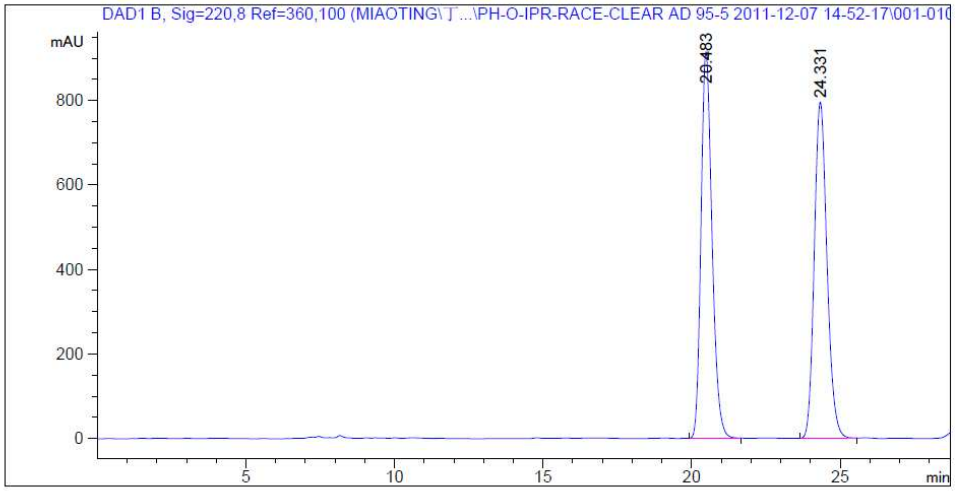
排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

信号 1: DAD1 B, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	20.370	BV	0.4639	3.33438e4	1099.07324	95.8565
2	21.706	VB	0.4634	1441.30823	46.79234	4.1435



The top one is racemic, the bottom one is the sample catalyzed by **7d**.
Conditions: column, AD-H, n-hexane : isopropanol = 95:5, 0.5 mL / min



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面积百分比报告
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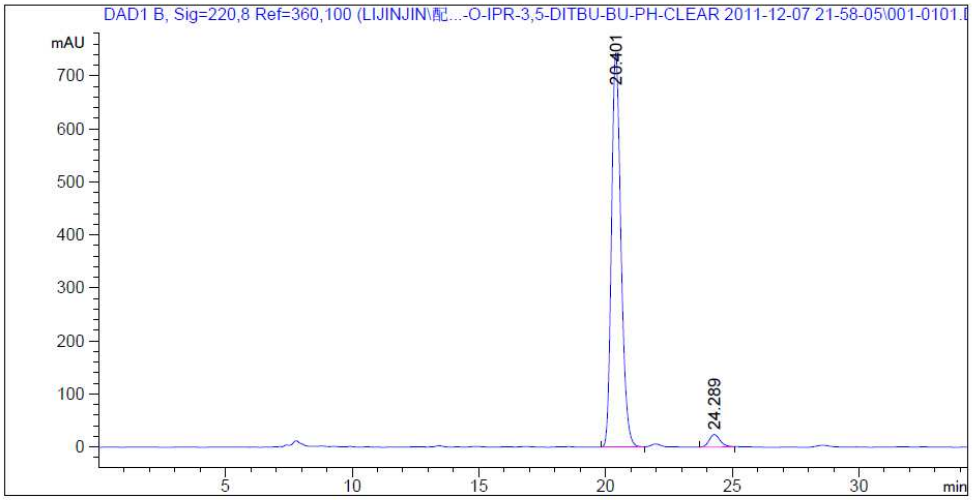
排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

信号 1: DAD1 B, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	20.483	BB	0.4028	2.35906e4	915.05127	49.9178
2	24.331	BB	0.4551	2.36683e4	795.60730	50.0822

总量 : 4.72590e4 1710.65857



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面积百分比报告

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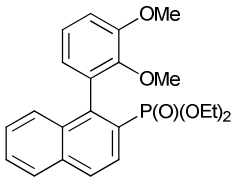
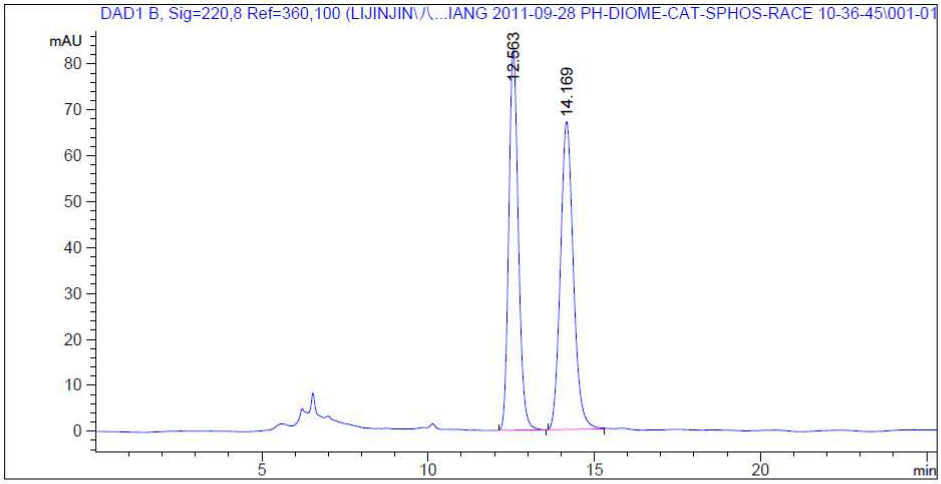
排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

信号 1: DAD1 B, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	20.401	BB	0.3950	1.93128e4	743.54913	96.4625
2	24.289	BB	0.4675	708.25385	23.50751	3.5375



The top one is racemic, the bottom one is the sample catalyzed by **7d**.
Conditions: column, OD-H, n-hexane : isopropanol = 90:10, 0.5 mL / min



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面积百分比报告
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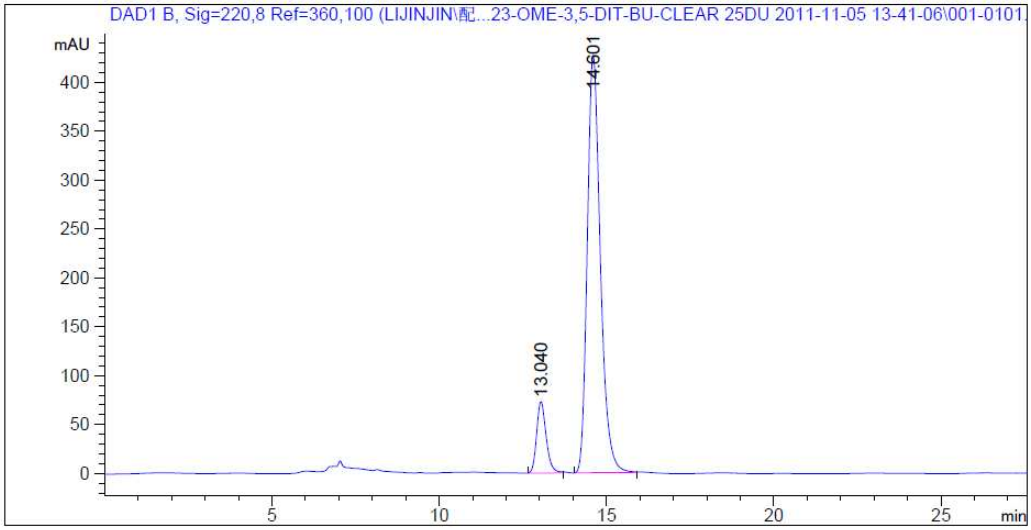
排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

信号 1: DAD1 B, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.563	BB	0.3098	1655.21033	82.59341	47.6816
2	14.169	BB	0.4119	1816.17358	67.06493	52.3184

总量 : 3471.38391 149.65834



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面积百分比报告

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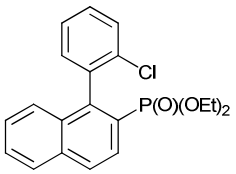
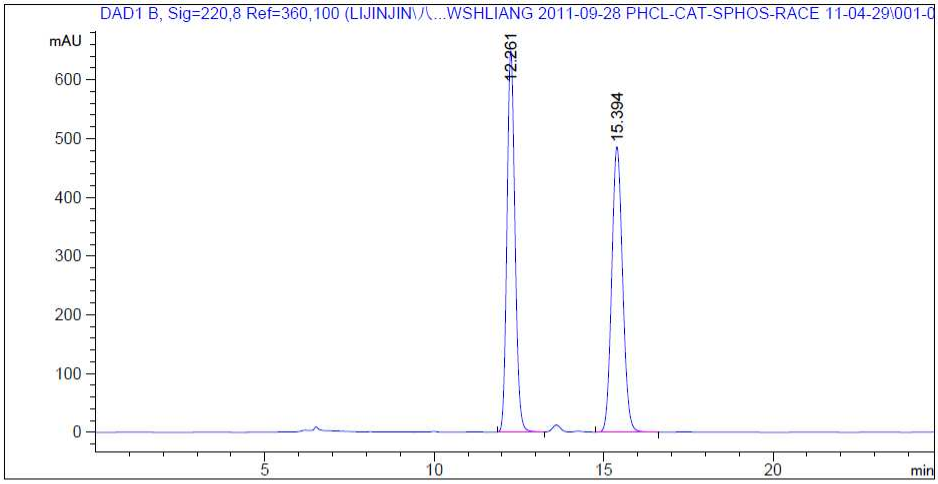
排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

信号 1: DAD1 B, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	13.040	BB	0.3030	1442.46423	72.86708	11.0447
2	14.601	BB	0.4214	1.16178e4	427.04147	88.9553



The top one is racemic, the bottom one is the sample catalyzed by **7d**.
Conditions: column, OD-H, n-hexane : isopropanol = 90:10, 0.5 mL / min



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面积百分比报告
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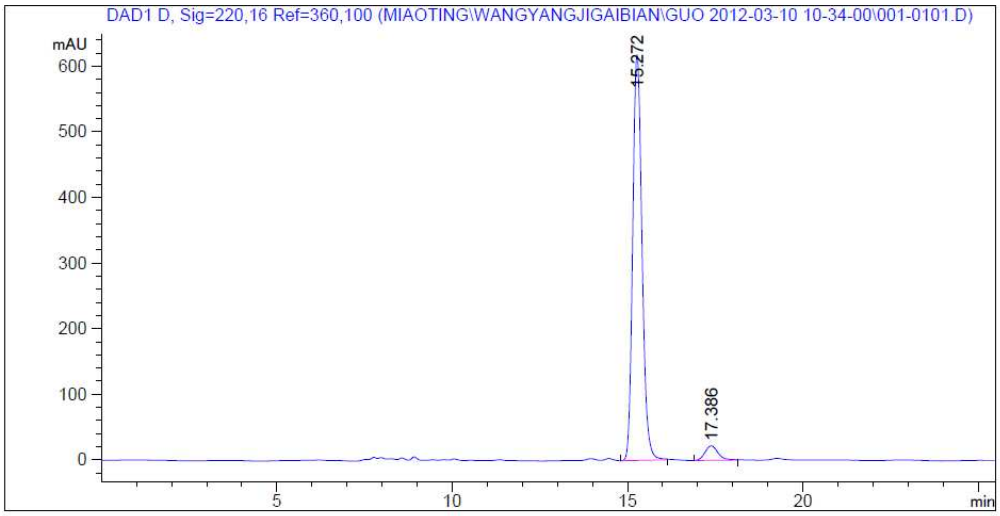
排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

信号 1: DAD1 B, Sig=220,8 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.261	BV	0.2599	1.06710e4	648.66760	49.5658
2	15.394	VB	0.3448	1.08580e4	485.74472	50.4342

总量 : 2.15291e4 1134.41232



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面积百分比报告

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排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

信号 1: DAD1 D, Sig=220,16 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.272	VB	0.2733	1.14073e4	618.15814	95.2179
2	17.386	BB	0.3964	572.90918	22.10405	4.7821

总量 : 1.19802e4 640.26219