Catalytic enantioselective hydrophosphinylation of in situ generated indole-derived vinylogous imines to access 3-(1-diphenylphosphoryl-arylmethyl)indoles

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Supporting Information

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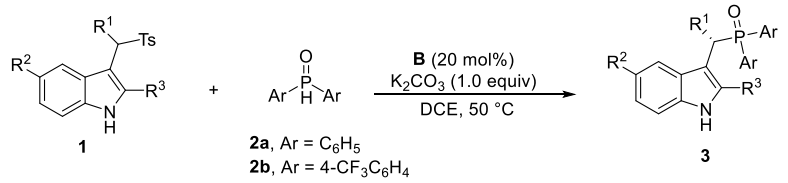
1. General information

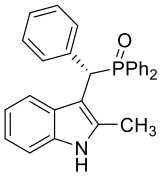
Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by TLC. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6. ^{1}H NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$ at 7.26 ppm, DMSO-d_6 at 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.16 ppm, DMSO-d_6 at 39.52 ppm). The enantiomeric excesses were determined by chiral HPLC analysis. HPLC analysis was performed on Shimadzu SCL-10AVP HPLC systems and Agilent 1260 Infinity Ⅱ consisting of the followings: pump, LC-10AD and G7129A; detector, SPD-10A and G7114A measured at 254 nm. Melting points products were recorded on a Büchi Melting Point B-545. The HRMS were recorded by Agilent 6545 LC/Q-TOF mass spectrometer.

2. General procedure for the synthesis of 3



In an ordinary vial equipped with a magnetic stirring bar, diarylphosphine oxides **2** (0.11mmol, 1.1 equiv) were added to a solution of arylsulfonyl indoles **1** (0.10 mmol, 1.0 equiv), catalyst **B** (20 mol%) and K_2CO_3 (0.10 mmol, 1.0 equiv) in 1,2-dichloroethane (1mL) at 50 ℃. And then, the mixture was stirred at the same temperature for the specified time. After completion of the reaction, as indicated by TLC, the products **3** were isolated by flash chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 6/1/1 ~ 2/1/1).

(S)-((2-methyl-1H-indol-3-yl)(phenyl)methyl)diphenylphosphine oxide (3a)



It was purified by flash chromatography (petroleum ether/EtOAc/DCM = 3:1:1) to afford white solid (31.6 mg, 75% yield, 87% ee); $[\alpha]_D^{20}$ = -1.8 (*c* 1.00, CH_2Cl_2); m.p. 140.7-141.1 ºC;

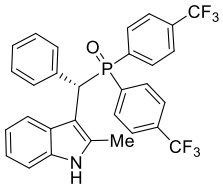
The ee was determined by HPLC (Chiralpak AD-H, *i*-PrOH/hexane = 25/75, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 10.0 min, t_{minor} = 19.7 min);

^{1}H NMR (300 MHz, DMSO-d_6) δ 10.74 (s, 1H), 8.35 – 8.27 (m, 1H), 8.01 – 7.91 (m, 2H), 7.78 – 7.68 (m, 2H), 7.60 – 7.53 (m, 2H), 7.42 (d, *J* = 6.8 Hz, 3H), 7.35 – 7.25 (m, 3H), 7.16 – 7.00 (m, 4H), 6.94 – 6.86 (m, 2H), 5.47 (d, *J* = 11.9 Hz, 1H), 2.42 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 137.4 (d, *J* = 2.8 Hz), 135.2, 133.6 (d, *J* = 7.9 Hz), 133.3 (d, *J* = 94.5 Hz), 133.1 (d, *J* = 99.7 Hz), 131.5 (d, *J* = 8.3 Hz), 131.4, 131.3 (d, *J* = 2.3 Hz), 131.1 (d, *J* = 8.8 Hz), 130.1 (d, *J* = 6.8 Hz), 128.5 (d, *J* = 11.2 Hz), 128.4, 128.3, 128.0 (d, *J* = 11.5 Hz), 126.6, 120.9, 119.7, 119.3, 110.2, 107.3 (d, *J* = 5.1 Hz), 45.0 (d, *J* = 69.8 Hz), 12.8.

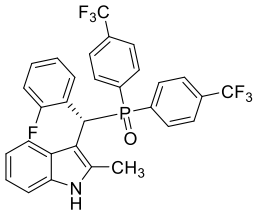
^{31}P NMR (243 MHz, DMSO-d_6) δ 27.16.
HRMS (ESI-TOF) calcd. for $C_{28}H_{24}NONaP$ $[M + Na]^+$ 444.1488; found: 444.1493.

(S)-((2-methyl-1H-indol-3-yl)(phenyl)methyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3b)



It was purified by flash chromatography (petroleum ether/EtOAc/DCM = 4:1:1) to afford white solid (46.6 mg, 84% yield, 97% ee); $[\alpha]_D^{20}$ = -19.9 (*c* 1.00, CH_2Cl_2); m.p. 156.2-156.6 ºC;
The ee was determined by HPLC (Chiralpak AD-H, *i*-PrOH/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 15.0 min, t_{minor} = 18.7 min);
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.82 (s, 1H), 8.30 – 8.21 (m, 3H), 8.05 – 7.95 (m, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 7.6 Hz, 2H), 7.20 – 7.14 (m, 2H), 7.13 – 7.02 (m, 2H), 6.91 (dd, *J* = 6.4, 3.3 Hz, 2H), 5.68 (d, *J* = 11.8 Hz, 1H), 2.44 (s, 3H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 138.1 (d, *J* = 90.5 Hz), 138.0 (d, *J* = 94.9 Hz), 137.7 (d, *J* = 2.1 Hz), 135.0, 134.1 (d, *J* = 9.4 Hz), 132.2 (d, *J* = 9.2 Hz), 131.6 (qd, *J* = 32.3, 2.6 Hz, 2C), 131.5 (d, *J* = 9.2 Hz), 129.6 (d, *J* = 7.2 Hz), 128.2, 127.5 (d, *J* = 4.0 Hz), 126.6, 125.4 – 124.9 (m, 2C), 123.7 (q, *J* = 273.0 Hz), 123.6 (q, *J* = 273.4 Hz), 120.5, 120.2, 118.4, 110.2, 105.9 (d, *J* = 4.6 Hz), 43.0 (d, *J* = 71.0 Hz), 12.1.
^{31}P NMR (162 MHz, DMSO-d_6) δ 28.92.
^{19}F NMR (376 MHz, DMSO-d_6) δ -61.69, -61.68.
HRMS (ESI-TOF) calcd. for $C_{30}H_{23}F_6NOP$ $[M + H]^+$ 558.1416; found: 558.1421.

(R)-((2-fluorophenyl)(2-methyl-1H-indol-3-yl)methyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3c)



It was purified by flash chromatography (petroleum ether/EtOAc/DCM = 4.5:1:1) to afford white solid (52.3 mg, 91% yield; 97% ee); $[\alpha]_D^{20}$ = -51.8 (*c* 1.00, CH_2Cl_2); m.p. 213.7-214.4 ºC;
The ee was determined by HPLC (Chiralpak AD-H, *i*-PrOH/hexane = 25/75, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 12.1 min, t_{minor} = 19.8 min);
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.88 (s, 1H), 8.29 – 8.11 (m, 4H), 8.08 – 7.98 (m, 2H), 7.84 (d, *J* = 7.6 Hz, 2H), 7.69 (d, *J* = 7.7 Hz, 2H), 7.20 – 7.05 (m, 3H), 7.05 – 6.97 (m, 1H), 6.91 (p, *J* = 7.0 Hz, 2H), 5.79 (d, *J* = 11.4 Hz, 1H), 2.37 (s, 3H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 159.6 (dd, *J* = 245.0, 8.8 Hz), 137.5 (d, *J* = 90.2 Hz), 137.2 (d, *J* = 96.9 Hz), 135.0, 134.4 (d, *J* = 9.0 Hz), 132.0 (d, *J* = 9.2 Hz), 131.7 (d, *J* = 9.3 Hz), 131.6 (qd, *J* = 31.3, 2.7 Hz, 2C), 131.4, 129.0 (d, *J* = 8.1 Hz), 127.4 (d, *J* = 2.8 Hz), 125.5 - 125.4 (m), 125.2

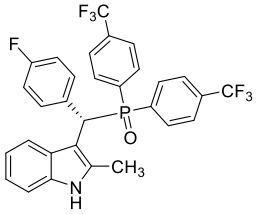
- 125.0 (m), 124.4 (d, *J* = 14.7 Hz), 124.1 (d, *J* = 3.0 Hz), 123.7 (q, *J* = 273.7 Hz), 123.6 (q, *J* = 273.7 Hz), 120.2, 120.1, 118.5, 115.3 (d, *J* = 22.3 Hz), 110.4, 104.2 (d, *J* = 4.6 Hz), 35.5 (d, *J* = 72.7 Hz), 11.9.

^{31}P NMR (162 MHz, DMSO-*d*$_6$) δ 28.84.

^{19}F NMR (376 MHz, CDCl$_3$) δ -63.20, -63.27, -117.76.

HRMS (ESI-TOF) calcd. for $C_{30}H_{22}F_7NOP$ $[M + H]^+$ 576.1322; found: 576.1317.

(S)-((4-fluorophenyl)(2-methyl-1H-indol-3-yl)methyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3d)



It was purified by flash chromatography (petroleum ether/EtOAc/DCM = 4:1:1) to afford white solid (55.4 mg, 96% yield; 97% ee); $[\alpha]_D^{20}$ = -20.1 (*c* 1.00, CH_2Cl_2); m.p. 192.2-192.5 ºC;

The ee was determined by HPLC (Chiralpak AD-H, EtOH/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 5.4 min, t_{minor} = 6.3 min);

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.85 (s, 1H), 8.30 – 8.17 (m, 3H), 8.04 – 7.93 (m, 2H), 7.83 (d, *J* = 7.9 Hz, 2H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.64 – 7.56 (m, 2H), 7.12 (d, *J* = 7.3 Hz, 1H), 7.06 – 6.97 (m, 2H), 6.96 – 6.86 (m, 2H), 5.70 (d, *J* = 11.9 Hz, 1H), 2.44 (s, 3H).

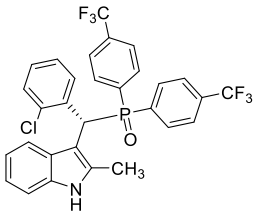
^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 160.9 (d, *J* = 242.9 Hz), 137.9 (d, *J* = 90.1 Hz), 137.7 (d, *J* = 95.3 Hz), 135.1, 134.2 (d, *J* = 9.4 Hz), 133.9, 132.3 (d, *J* = 9.3 Hz), 131.8 (qd, *J* = 31.8, 2.9 Hz, 2C),131.6, 131.5 (d, *J* = 4.1 Hz), 127.4 (d, *J* = 3.9 Hz), 125.6 – 125.0 (m, 2C), 123.7 (q, *J* = 274.7 Hz), 123.6 (q, *J* = 273.7 Hz), 120.3 (d, *J* = 14.0 Hz), 115.1 (d, *J* = 21.3 Hz), 114.9, 110.3, 105.8 (d, *J* = 4.4 Hz), 42.2 (d, *J* = 70.6 Hz), 12.1.

^{31}P NMR (162 MHz, DMSO-*d*$_6$) δ 29.11.

^{19}F NMR (376 MHz, CDCl$_3$) δ -63.17, -63.29, -115.02.

HRMS (ESI-TOF) calcd. for $C_{30}H_{22}F_7NOP$ $[M + H]^+$ 576.1322 ; found: 576.1318.

(R)-((2-chlorophenyl)(2-methyl-1H-indol-3-yl)methyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3e)



It was purified by flash chromatography (petroleum ether / EtOAc/DCM = 3:1:1) to afford white solid (47.9 mg, 81% yield; 98% ee); $[\alpha]_D^{20}$ = -128.5 (*c* 1.00, CH_2Cl_2); m.p. 222.8-223.4 ºC;

The ee was determined by HPLC (Chiralpak AD-H, EtOH/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 10.9 min, t_{minor} = 22.2 min);

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.88 (s, 1H), 8.40 (d, *J* = 7.8 Hz, 1H), 8.10 (m, 2H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.95 – 7.87 (m, 2H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 7.8 Hz, 2H), 7.38 – 7.23 (m, 2H), 7.15 (dd, *J* = 18.0, 8.0 Hz, 2H), 6.88 (dt, *J* = 24.5, 7.2 Hz, 2H), 5.71 (d, *J* = 11.2 Hz, 1H), 2.25 (s, 3H).

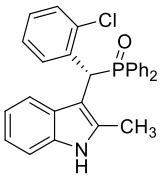
^{13}C NMR (101 MHz, $CDCl_3$) δ 137.2 (d, *J* = 89.1 Hz), 136.8 (d, *J* = 98.1 Hz), 135.0, 134.8 (d, *J* = 8.6 Hz), 134.6, 133.3 (d, *J* = 10.1 Hz), 132.0 (d, *J* = 9.1 Hz), 131.9 (d, *J* = 9.2 Hz), 131.7 (qd, J = 32.3, 2.8 Hz, 2C), 129.7, 128.8, 127.5 (d, *J* = 3.6 Hz), 126.9, 125.6 - 125.4 (m), 125.1 - 125.0 (m), 123.6 (q, *J* = 275.5 Hz), 123.5 (q, *J* = 271.5 Hz), 120.2, 120.0, 118.5, 110.4, 103.1 (d, *J* = 5.2 Hz), 40.2 (d, *J* = 79.8 Hz), 12.2.

^{31}P NMR (162 MHz, $CDCl_3$) δ 32.15.

^{19}F NMR (376 MHz, $CDCl_3$) δ -56.92, -56.99.

HRMS (ESI-TOF) calcd. for $C_{30}H_{22}{}^{35}Cl\ F_6NOP$ $[M + H]^+$ 592.1026, found: 592.1024; calcd. for $C_{30}H_{22}{}^{37}Cl\ F_6NOP$ $[M + H]^+$ 594.1011, found: 594.1007.

(R)-((2-chlorophenyl)(2-methyl-1H-indol-3-yl)methyl)diphenylphosphine oxide (3f)



It was purified by flash chromatography (petroleum ether/MTBE = 2:1) to afford white solid (25.9 mg, 57% yield; 94% ee); $[\alpha]_D{}^{20}$ = -79.1 (*c* 1.00, CH_2Cl_2); m.p. 133.2-133.7 ºC;

The ee was determined by HPLC (Chiralpak AD-H, *i*-PrOH/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 7.4 min, t_{minor} = 15.5 min);

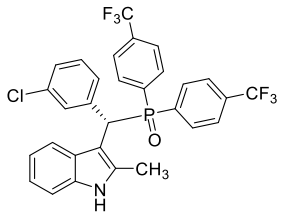
^{1}H NMR (300 MHz, DMSO-d_6) δ 10.81 (s, 1H), 8.47 (d, *J* = 7.2 Hz, 1H), 8.09 – 7.89 (m, 1H), 7.78 (dd, *J* = 9.8, 7.7 Hz, 2H), 7.67 – 7.54 (m, 2H), 7.51 – 7.36 (m, 4H), 7.36 – 7.18 (m, 4H), 7.13 (d, *J* = 7.3 Hz, 2H), 6.96 – 6.75 (m, 2H), 5.56 (d, *J* = 11.2 Hz, 1H), 2.22 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 135.5, 135.0, 133.9 (d, *J* = 94.8 Hz), 133.8 (d, *J* = 102.2 Hz), 133.2 (d, *J* = 5.6 Hz), 132.5, 132.3, 132.1 (d, *J* = 5.3 Hz), 131.5 (d, *J* = 11.4 Hz), 130.8 (d, *J* = 9.1 Hz), 130.7, 129.4, 128.5 (d, *J* = 11.0 Hz), 128.4, 128.2 (d, *J* = 11.3 Hz), 127.6 (d, *J* = 3.3 Hz), 126.7, 120.4, 119.9, 118.3, 110.2, 104.0 (d, *J* = 5.0 Hz), 40.4 (d, *J* = 71.1 Hz), 12.1.

^{31}P NMR (243 MHz, DMSO-d_6) δ 31.05.

HRMS (ESI-TOF) calcd. for $C_{28}H_{24}{}^{35}ClNOP$ $[M + H]^+$ 456.1284, found: 456.1281; calcd. for $C_{28}H_{24}{}^{37}ClNOP$ $[M + H]^+$458.1249, found: 458.1263.

(S)-((3-chlorophenyl)(2-methyl-1H-indol-3-yl)methyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3g)



It was purified by flash chromatography (petroleum ether/MTBE = 2:1) to afford white solid (57.3 mg, 97% yield; 95% ee); $[\alpha]_D^{20}$ = -23.53 (*c* 1.00, CH_2Cl_2); m.p. 126.6-127.0 ºC;

The ee was determined by HPLC (Chiralpak AD-H, EtOH/hexane = 25/75, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 7.6 min, t_{minor} = 5.2 min);

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.89 (s, 1H), 8.31 – 8.16 (m, 3H), 8.05 – 7.93 (m, 2H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.73 (d, *J* = 7.5 Hz, 2H), 7.55 (s, 2H), 7.24 – 7.18 (m, 1H), 7.18 – 7.10 (m, 2H), 6.98 – 6.87 (m, 2H), 5.72 (d, *J* = 11.6 Hz, 1H), 2.43 (s, 3H).

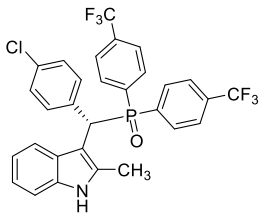
^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 140.1 (d, *J* = 1.9 Hz), 137.6 (d, *J* = 90.2 Hz), 137.4 (d, *J* = 95.5 Hz), 135.1, 134.5 (d, *J* = 9.3 Hz), 132.6, 132.3 (d, *J* = 9.2 Hz), 131.9 (qd, *J* = 30.9, 2.0 Hz, 2C), 131.5 (d, *J* = 9.0 Hz), 130.1, 129.4 (d, *J* = 7.3 Hz), 128.2 (d, *J* = 6.7 Hz), 127.4 (d, *J* = 3.6 Hz), 126.7, 125.6 – 125.0 (m, 2C), 123.7 (q, *J* = 273.7 Hz), 123.6 (q, *J* = 274.0 Hz), 120.3, 118.6, 110.4, 105.2 (d, *J* = 4.6 Hz), 42.7 (d, *J* = 70.3 Hz), 12.1.

^{31}P NMR (162 MHz, CDCl$_3$) δ 29.66.

^{19}F NMR (376 MHz, CDCl$_3$) δ -63.21, -63.30.

HRMS (ESI-TOF) calcd. for $C_{30}H_{22}{}^{35}Cl\ F_6NOP$ $[M + H]^+$ 592.1026, found: 592.1032; calcd. for $C_{30}H_{22}{}^{37}Cl\ F_6NOP$ $[M + H]^+$ 594.1011, found: 594.1015.

(S)-((4-chlorophenyl)(2-methyl-1H-indol-3-yl)methyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3h)



It was purified by flash chromatography (petroleum ether/EtOAc/DCM = 4:1:1) to afford white solid (48.5 mg, 82% yield; 97% ee); $[\alpha]_D^{20}$ = -15.9 (*c* 1.00, CH_2Cl_2); m.p. 134.4-134.8 ºC;

The ee was determined by HPLC (Chiralpak AD-H, EtOH/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 7.0 min, t_{minor} = 10.1 min);

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.87 (s, 1H), 8.37 – 8.18 (m, 3H), 8.02 – 7.93 (m, 2H), 7.84 (d, *J* = 7.7 Hz, 2H), 7.71 (d, *J* = 7.7 Hz, 2H), 7.59 (d, *J* = 6.9 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 5.9 Hz, 1H), 6.97 – 6.86 (m, 2H), 5.72 (d, *J* = 11.4 Hz, 1H), 2.43 (s, 3H).

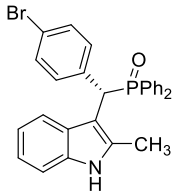
^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 137.8 (d, *J* = 90.3 Hz), 137.6 (d, *J* = 95.7 Hz), 136.8 (d, *J* = 1.8 Hz), 135.1, 134.3 (d, *J* = 9.2 Hz), 132.3 (d, *J* = 9.2 Hz), 131.8 (qd, *J* = 15.4, 3.8 Hz, 2C), 131.5, 131.4 (d, *J* = 7.3 Hz), 128.3, 127.4 (d, *J* = 3.5 Hz), 125.6 - 125.3 (m), 125.2 - 125.0 (m), 123.7 (q, *J* = 273.4 Hz), 123.6 (q, *J* = 273.4 Hz), 120.3, 118.5, 110.3, 105.4 (d, *J* = 4.5 Hz), 42.4 (d, *J* = 70.6 Hz), 12.1.

^{31}P NMR (162 MHz, DMSO-*d*$_6$) δ 28.93.

^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ -61.67, -61.76.

HRMS (ESI-TOF) calcd. for $C_{30}H_{22}{}^{35}Cl\ F_6NOP$ $[M + H]^+$ 592.1026, found: 592.1034; calcd. for $C_{30}H_{22}{}^{37}Cl\ F_6NOP$ $[M + H]^+$ 594.1011, found: 594.1016.

(S)-((4-bromophenyl)(2-methyl-1H-indol-3-yl)methyl)diphenylphosphine oxide (3i)



It was purified by flash chromatography (petroleum ether/EtOAc/DCM = 3:1:1) to afford white solid (31.0 mg, 62% yield; 84% ee); $[\alpha]_D^{20}$ = -5.8 (*c* 1.00, CH_2Cl_2); m.p. 155.8-156.3 ºC;

The ee was determined by HPLC (Chiralpak AD-H, *i*-PrOH/hexane = 25/75, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 11.1 min, t_{minor} = 21.4 min);

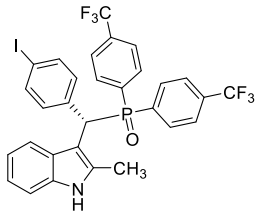
^{1}H NMR (600 MHz, DMSO-d_6) δ 10.80 (s, 1H), 8.26 (d, *J* = 7.6 Hz, 1H), 8.02 – 7.92 (m, 2H), 7.73 (dd, *J* = 10.0, 8.0 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.48 – 7.43 (m, 3H), 7.37 – 7.32 (m, 3H), 7.31 – 7.28 (m, 2H), 7.12 (d, *J* = 7.7 Hz, 1H), 6.91 (m, 2H), 5.49 (d, *J* = 11.6 Hz, 1H), 2.41 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 138.1 (d, *J* = 1.3 Hz), 135.1, 133.9, 133.6 (d, *J* = 83.4 Hz), 133.5 (d, *J* = 98.1 Hz), 131.9 (d, *J* = 6.6 Hz), 131.4, 131.3, 131.2 (d, *J* = 8.6 Hz), 130.9, 130.4 (d, *J* = 8.6 Hz), 128.9 (d, *J* = 12.7 Hz), 128.5 (d, *J* = 10.9 Hz), 128.2 (d, *J* = 11.2 Hz), 127.6, 120.1, 119.6, 118.4, 110.2, 106.3 (d, *J* = 4.3 Hz), 42.8 (d, *J* = 69.3 Hz), 12.1.

^{31}P NMR (243 MHz, DMSO-d_6) δ 29.94.

HRMS (ESI-TOF) calcd. for $C_{28}H_{24}{}^{79}BrNOP$ $[M + H]^+$ 500.0780, found: 500.0779; calcd. for $C_{28}H_{24}{}^{81}BrNOP$ $[M + H]^+$ 502.0753; found: 502.0763.

(S)-((4-iodophenyl)(2-methyl-1H-indol-3-yl)methyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3j)



It was purified by flash chromatography (petroleum ether/EtOAc/DCM = 5:1:1) to afford orange solid (63.6 mg, 93% yield; 99% ee); $[\alpha]_D^{20}$ = -7.9 (*c* 1.00, CH_2Cl_2); m.p. 141.2-141.5 ºC;

The ee was determined by HPLC (Chiralpak AD-H, EtOH/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 6.4 min, t_{minor} = 12.2 min);

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.85 (s, 1H), 8.33 – 8.22 (m, 2H), 8.19 (d, *J* = 7.2 Hz, 1H), 8.02 – 7.91 (m, 2H), 7.84 (d, *J* = 7.9 Hz, 2H), 7.70 (d, *J* = 7.9 Hz, 2H), 7.54 (d, *J* = 7.9 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.11 (d, *J* = 7.3 Hz, 1H), 6.90 (p, *J* = 7.0 Hz, 2H), 5.67 (d, *J* = 11.5 Hz, 1H), 2.40 (s, 3H).

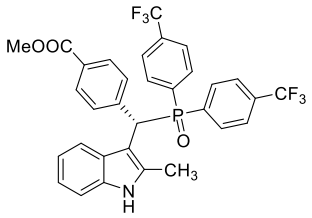
^{13}C NMR (101 MHz, DMSO-d_6) δ 137.8 (d, *J* = 89.9 Hz), 137.7 (d, *J* = 95.7 Hz), 137.6 (d, *J* = 1.8 Hz), 137.0, 135.1, 134.3 (d, *J* = 9.1 Hz), 132.2 (d, *J* = 9.2 Hz), 131.9 (d, *J* = 7.1 Hz), 131.7 (qd, *J* = 32.1, 2.5 Hz), 131.5 (d, *J* = 9.1 Hz), 127.4 (d, *J* = 3.8 Hz), 125.6 - 125.3 (m), 125.3 - 125.0 (m), 123.7 (q, *J* = 273.7 Hz), 123.6 (q, *J* = 274.0 Hz), 120.3, 118.5, 110.3, 105.4 (d, *J* = 4.7 Hz), 92.8, 42.4 (d, *J* = 70.2 Hz), 12.1.

^{31}P NMR (162 MHz, $CDCl_3$) δ 29.52.

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.15, -63.28.

HRMS (ESI-TOF) calcd. for $C_{30}H_{22}F_6INOP$ $[M + H]^+$ 684.0382; found: 684.0384.

Methyl (S)-4-((bis(4-(trifluoromethyl)phenyl)phosphoryl) (2-methyl-1H-indol-3-yl)methyl)benzate (3k)



It was purified by flash chromatography (petroleum ether/EtOAc/DCM = 4:1:1) to afford red solid (55.9 mg, 91% yield; 97% ee); $[\alpha]_D^{20}$ = -13.5 (*c* 1.00, CH_2Cl_2); m.p. 150.4-150.8 ºC;

The ee was determined by HPLC (Chiralpak AD-H, EtOH/hexane = 25/75, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 5.4 min, t_{minor} = 8.5 min);

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.88 (s, 1H), 8.29 – 8.15 (m, 3H), 8.05 – 7.95 (m, 2H), 7.82 (d, *J* = 7.7 Hz, 2H), 7.76 (d, *J* = 7.9 Hz, 2H), 7.74 – 7.67 (m, 4H), 7.12 (d, *J* = 7.0 Hz, 1H), 6.91 (p, *J* = 7.2 Hz, 2H), 5.80 (d, *J* = 11.3 Hz, 1H), 3.74 (s, 3H), 2.41 (s, 3H).

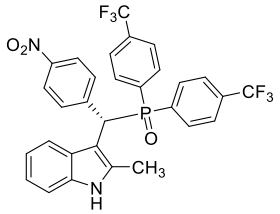
^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 166.0, 143.3, 137.7 (d, *J* = 89.7 Hz), 137.5 (d, *J* = 95.4 Hz), 135.1, 134.5 (d, *J* = 9.1 Hz), 132.3 (d, *J* = 9.3 Hz), 131.9 (qd, *J* = 32.3, 2.6 Hz, 2C), 131.6 (d, *J* = 9.2 Hz), 130.0 (d, *J* = 7.1 Hz), 129.1, 127.9, 127.5 (d, *J* = 3.4 Hz), 125.5 – 125.1 (m, 2C), 123.7 (q, *J* = 273.7Hz), 123.6 (q, *J* = 273.7 Hz) 120.3, 118.6, 110.3, 105.0 (d, *J* = 5.0 Hz), 52.1, 43.1 (d, *J* = 71.0 Hz), 12.2.

^{31}P NMR (162 MHz, DMSO-*d*$_6$) δ 28.78.

^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ -61.68, -61.75.

HRMS (ESI-TOF) calcd. for $C_{32}H_{25}F_6NO_3P$ $[M + H]^+$ 616.1471; found: 616.1472.

(S)-((2-methyl-1H-indol-3-yl)(4-nitrophenyl)methyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3l)



It was purified by flash chromatography (petroleum ether/EtOAc/DCM, 4:1:1) to afford yellow solid (56.1 mg, 93% yield; 90% ee); $[\alpha]_D^{20}$ = +5.1 (*c* 1.00, CH_2Cl_2); m.p. 132.1-132.3 ºC;

The ee was determined by HPLC (Chiralpak AD-H, EtOH/hexane = 25/75, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 5.5 min, t_{minor} = 11.5 min);

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.94 (s, 1H), 8.38 – 8.17 (m, 3H), 8.12 – 7.94 (m, 4H), 7.84 (d, *J* = 8.3 Hz, 4H), 7.72 (d, *J* = 7.9 Hz, 2H), 7.24 – 7.04 (m, 1H), 6.93 (dd, *J* = 6.5, 3.0 Hz, 2H), 5.91 (d, *J* = 11.5 Hz, 1H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 146.1, 145.6 (d, *J* = 1.8 Hz), 137.4 (d, *J* = 90.5 Hz), 137.2 (d, *J* = 96.8 Hz), 135.1, 134.8 (d, *J* = 8.9 Hz), 132.3 (d, *J* = 9.3 Hz), 131.9 (qd, *J* = 31.1, 3.4 Hz, 2C), 131.6 (d, *J* = 9.3 Hz), 130.8 (d, *J* = 6.9 Hz), 127.3 (d, *J* = 4.4 Hz), 125.8 - 125.4 (m), 125.4 - 125.1

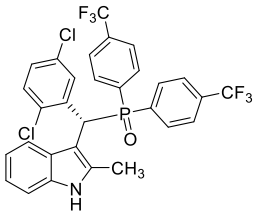
(m), 123.7 (q, *J* = 273.7 Hz), 123.6 (q, *J* = 273.7 Hz), 123.5, 122.3 (d, *J* = 8.3 Hz), 120.4, 118.7, 110.4, 104.7 (d, *J* = 4.8 Hz), 43.0 (d, *J* = 69.8 Hz), 12.1.

^{31}P NMR (162 MHz, DMSO-*d*$_6$) δ 28.73.

^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ -61.75, -61.81.

HRMS (ESI-TOF) calcd. for $C_{30}H_{22}F_6N_2O_3P$ $[M + H]^+$ 603.1267; found: 603.1274.

(R)-((2,5-dichlorophenyl)(2-methyl-1H-indol-3-yl)methyl)bis(4-(trifluoromethyl)phenyl) phosphine oxide (3m)



It was purified by flash chromatography (petroleum ether/EtOAc/DCM = 6:1:1) to afford white solid (55.9 mg, 89% yield; 99% ee); $[\alpha]_D^{20}$ = -69.7 (*c* 1.00, CH_2Cl_2); m.p. 137.1-137.5 ºC;

The ee was determined by HPLC (Chiralpak AD-H, EtOH/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 6.3 min, t_{minor} = 8.1 min);

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.43 (s, 1H), 8.07 (s, 1H), 7.94 – 7.79 (m, 3H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.63 (t, *J* = 9.4 Hz, 2H), 7.48 (d, *J* = 7.9 Hz, 2H), 7.19 – 7.13 (m, 2H), 7.11 – 6.99 (m, 3H), 5.53 (d, *J* = 11.4 Hz, 1H), 2.34 (s, 3H).

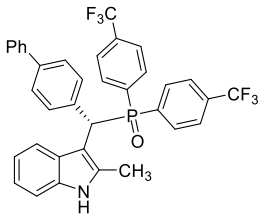
^{13}C NMR (101 MHz, CDCl$_3$) δ 136.5, 135.9 (d, *J* = 93.4 Hz), 135.5 (d, *J* = 93.6 Hz), 134.2 (d, *J* = 7.8 Hz), 133.9, 133.8 (qd, *J* = 35.3, 3.0 Hz, 2C), 133.1 (d, *J* = 1.2 Hz), 132.4 (d, *J* = 5.2 Hz), 132.2 (d, *J* = 9.6 Hz), 131.9 (d, *J* = 9.2 Hz), 131.6 (d, *J* = 9.2 Hz), 130.7, 129.0, 128.1 (d, *J* = 4.3 Hz), 125.7 (dq, *J* = 11.4, 3.7 Hz), 125.2 (dq, *J* = 11.6, 3.7 Hz), 123.7 (q, *J* = 273.7 Hz), 123.5 (q, *J* = 273.7 Hz), 121.7, 120.2, 119.7, 110.3, 104.3 (d, *J* = 5.4 Hz), 41.0 (d, *J* = 71.2 Hz), 13.1.

^{31}P NMR (162 MHz, CDCl$_3$) δ 30.36.

^{19}F NMR (376 MHz, CDCl$_3$) δ -63.21, -63.29.

HRMS (ESI-TOF) calcd. for $C_{30}H_{21}{}^{35}Cl_2F_6NOP$ $[M + H]^+$ 626.0637, found: 626.0639; calcd. for $C_{30}H_{21}{}^{35}Cl\ {}^{37}ClF_6NOP$ $[M + H]^+$ 628.0615, found: 628.0618; calcd. for $C_{30}H_{21}{}^{37}Cl_2F_6NOP$ $[M + H]^+$ 630.0602, found: 630.0602.

(S)-([1,1'-biphenyl]-4-yl(2-methyl-1H-indol-3-yl)methyl)bis(4-(trifluoromethyl)phenyl)p hosphine oxide (3n)

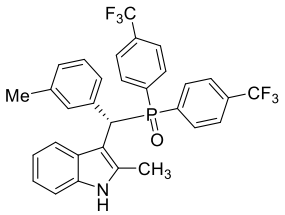


It was purified by flash chromatography (petroleum ether/EtOAc/DCM = 4:1:1) to afford white solid (62.5 mg, 99% yield; 97% ee); $[\alpha]_D^{20}$ = +8.1 (*c* 1.00, CH_2Cl_2); m.p. 130.2-130.6 ºC;

The ee was determined by HPLC (Chiralpak AD-H, *i*-PrOH/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 6.7 min, t_{minor} = 9.5 min);

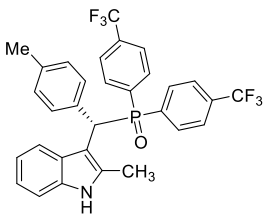
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.86 (s, 1H), 8.37 – 8.28 (m, 3H), 8.00 (d, *J* = 8.9 Hz, 2H), 7.84 (d, *J* = 7.6 Hz, 2H), 7.75 – 7.64 (m, 4H), 7.51 (dd, *J* = 19.0, 7.6 Hz, 4H), 7.41 – 7.32 (m, 2H), 7.29 (d, *J* = 7.1 Hz, 1H), 7.13 (s, 1H), 6.98 – 6.89 (m, 2H), 5.76 (d, *J* = 10.9 Hz, 1H), 2.49 (s, 3H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 139.4, 138.2, 138.1 (d, *J* = 89.6 Hz), 138.0 (d, *J* = 95.1 Hz), 137.0 (d, *J* = 2.0 Hz), 135.1, 134.2 (d, *J* = 9.4 Hz), 132.3 (d, *J* = 9.2 Hz), 131.7 (qd, *J* = 32.3, 3.0 Hz, 2C), 131.5 (d, *J* = 9.1 Hz), 130.2 (d, *J* = 7.0 Hz), 128.9, 127.5 (d, *J* = 3.8 Hz), 127.4, 126.5, 126.4, 125.5 – 125.3 (m), 125.2 – 125.0 (m), 123.7 (q, *J* = 273.7 Hz), 123.6 (q, *J* = 273.7 Hz), 120.5, 120.2, 118.5, 110.3, 105.9 (d, *J* = 4.4 Hz), 42.6 (d, *J* = 71.1 Hz), 12.2.
^{31}P NMR (162 MHz, $CDCl_3$) δ 29.93.
^{19}F NMR (376 MHz, $CDCl_3$) δ -63.12, -63.23.
HRMS (ESI-TOF) calcd. for $C_{36}H_{27}F_6NOP$ $[M + H]^+$ 634.1729; found: 634.1731.

(S)-((2-methyl-1H-indol-3-yl)(m-tolyl)methyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3o)



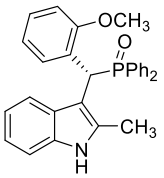
It was purified by flash chromatography (petroleum ether/EtOAc/DCM = 4:1:1) to afford white solid (57.0 mg, 99% yield; 97% ee);$[\alpha]_D^{20}$ = -34.4 (*c* 1.00, CH_2Cl_2); m.p. 124.4-124.9 ºC;
The ee was determined by HPLC (Chiralpak AD-H, *i*-PrOH/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 11.7 min, t_{minor} = 20.7 min);
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.82 (s, 1H), 8.39 – 8.13 (m, 3H), 8.04 – 7.94 (m, 2H), 7.81 (d, *J* = 7.3 Hz, 2H), 7.70 (d, *J* = 7.7 Hz, 2H), 7.43 (d, *J* = 6.8 Hz, 1H), 7.29 (s, 1H), 7.11 (d, *J* = 6.3 Hz, 1H), 7.08 – 6.99 (m, 1H), 6.95 – 6.82 (m, 3H), 5.63 (d, *J* = 11.6 Hz, 1H), 2.43 (s, 3H), 2.10 (s, 3H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 138.2 (d, *J* = 89.9 Hz), 138.0 (d, *J* = 89.9 Hz), 137.6 (d, *J* = 2.5 Hz), 137.1, 135.0, 134.1 (d, *J* = 9.3 Hz), 132.2 (d, *J* = 9.1 Hz), 131.6 (qd, *J* = 32.3, 2.0 Hz, 2C), 131.5 (d, *J* = 9.1 Hz), 130.4 (d, *J* = 7.5 Hz), 128.0, 127.6 (d, *J* = 3.2 Hz), 127.3, 126.7 (d, *J* = 6.8 Hz), 125.7 – 124.3 (m, 2C), 123.8 (q, *J* = 273.7), 123.7 (q, *J* = 273.7), 120.5, 120.2, 118.4, 110.2, 105.9 (d, *J* = 4.6 Hz), 43.0 (d, *J* = 70.8 Hz), 21.0, 12.2.
^{31}P NMR (162 MHz, $CDCl_3$) δ 30.05.
^{19}F NMR (376 MHz, $CDCl_3$) δ -63.17, -63.25.
HRMS (ESI-TOF) calcd. for $C_{31}H_{25}F_6NOP$ $[M + H]^+$ 572.1572; found: 572.1575.

(S)-((2-methyl-1H-indol-3-yl)(p-tolyl)methyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3p)



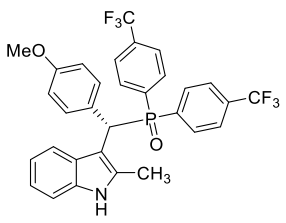
It was purified by flash chromatography (petroleum ether/EtOAc/DCM = 5:1:1) to afford white solid (42.7 mg, 75% yield; 91% ee); $[\alpha]_D^{20}$ = -25.9 (*c* 1.00, CH_2Cl_2); m.p. 134.0-134.4 ºC;
The ee was determined by HPLC (Chiralpak AD-H, *i*-PrOH/hexane = 25/75, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 9.5 min, t_{minor} = 12.4 min);
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.80 (s, 1H), 8.41 – 8.17 (m, 3H), 8.05 – 7.92 (m, 2H), 7.82 (d, *J* = 7.9 Hz, 2H), 7.69 (d, *J* = 7.9 Hz, 2H), 7.46 (d, *J* = 7.7 Hz, 2H), 7.10 (d, *J* = 7.3 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 2H), 6.94 – 6.81 (m, 2H), 5.64 (d, *J* = 11.7 Hz, 1H), 2.41 (s, 3H), 2.12 (s, 3H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 138.2 (d, *J* = 91.4 Hz), 138.1 (d, *J* = 94.4 Hz), 135.6, 135.0, 134.7 (d, *J* = 2.1 Hz), 134.0 (d, *J* = 9.4 Hz), 132.2 (d, *J* = 9.1 Hz), 131.5 (qd, *J* = 31.3, 2.5 Hz, 2C),131.4 (d, *J* = 9.0 Hz), 129.5 (d, *J* = 7.2 Hz), 128.8, 127.6 (d, *J* = 4.0 Hz), 125.6 – 124.7 (m, 2C), 123.7 (q, *J* = 273.7 Hz), 123.6 (q, *J* = 273.7 Hz), 120.5, 120.1, 118.4, 110.2, 106.1 (d, *J* = 4.4 Hz), 42.5 (d, *J* = 70.9 Hz), 20.5, 12.1.
^{31}P NMR (162 MHz, DMSO-d_6) δ 28.88.
^{19}F NMR (376 MHz, $CDCl_3$) δ -63.14, -63.25.
HRMS (ESI-TOF) calcd. for $C_{31}H_{24}F_6NOPNa$ $[M + Na]^+$ 594.1392; found: 594.1386.

(R)-((2-methoxyphenyl)(2-methyl-1H-indol-3-yl)methyl)diphenylphosphine oxide (3q)



It was purified by flash chromatography (petroleum ether/EtOAc/DCM = 4:1:1) to afford yellow solid (22.6 mg, 50% yield; 86% ee);$[\alpha]_D^{20}$ = -46.0 (*c* 1.00, CH_2Cl_2); m.p. 148.9-149.1 ºC;
The ee was determined by HPLC (Chiralpak AD-H, *i*-PrOH/hexane = 25/75, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 11.9 min, t_{minor} = 27.9 min);
^{1}H NMR (300 MHz, DMSO-d_6) δ 10.68 (s, 1H), 8.26 – 8.19 (m, 1H), 8.15 (d, *J* = 7.8 Hz, 1H), 7.78 – 7.68 (m, 2H), 7.66 – 7.57 (m, 2H), 7.45 – 7.35 (m, 3H), 7.35 – 7.26 (m, 3H), 7.12 – 7.01 (m, 2H), 6.92 – 6.86 (m, 2H), 6.84 – 6.75 (m, 2H), 5.75 (d, *J* = 12.0 Hz, 1H), 3.63 (s, 3H), 2.33 (s, 3H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 156.0 (d, *J* = 7.5 Hz), 135.1, 133.9 (d, *J* = 9.5 Hz), 133.8 (d, *J* = 93.8 Hz), 133.7 (d, *J* = 97.5 Hz).131.3, 130.9 (d, *J* = 5.1 Hz), 130.7 (d, *J* = 8.6 Hz), 130.5 (d, *J* = 8.6 Hz), 128.4, 128.3, 128.2, 127.9, 127.8, 126.3, 120.8, 120.7, 120.0 (d, *J* = 5.6 Hz), 118.3, 110.7, 110.2, 106.1 (d, *J* = 4.1 Hz), 55.5, 35.2 (d, *J* = 72.3 Hz), 11.9.
^{31}P NMR (162 MHz, DMSO-d_6) δ 30.99.
HRMS (ESI-TOF) calcd. for $C_{29}H_{27}NO_2P$ $[M + H]^+$ 452.1779; found: 452.1765.

(S)-((4-methoxyphenyl)(2-methyl-1H-indol-3-yl)methyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3r)



It was purified by flash chromatography (petroleum ether/EtOAc/DCM = 4:1:1) to afford white solid (58.0 mg, 99% yield; 91% ee); $[\alpha]_D^{20}$ = -51.8 (*c* 1.00, CH_2Cl_2); m.p. 213.7-213.9 ºC;

The ee was determined by HPLC (Chiralpak AD-H, EtOH/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 7.7 min, t_{minor} = 9.5 min);

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.81 (s, 1H), 8.35 – 8.18 (m, 3H), 8.07 – 7.94 (m, 2H), 7.82 (d, *J* = 7.7 Hz, 2H), 7.69 (d, *J* = 7.6 Hz, 2H), 7.51 (d, *J* = 6.7 Hz, 2H), 7.11 (s, 1H), 6.95 – 6.87 (m, 2H), 6.73 (d, *J* = 7.9 Hz, 2H), 5.63 (d, *J* = 11.7 Hz, 1H), 3.60 (s, 3H), 2.44 (s, 3H).

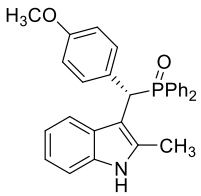
^{13}C NMR (101 MHz, DMSO-d_6) δ 157.8, 138.3 (d, *J* = 90.3 Hz), 138.1 (d, *J* = 93.9 Hz), 135.1, 133.9 (d, *J* = 9.5 Hz), 132.2 (d, *J* = 9.1 Hz), 131.6 (qd, *J* = 30.3, 2.0 Hz, 2C), 131.5 (d, *J* = 9.0 Hz), 130.7 (d, *J* = 7.1 Hz), 130.1, 129.6 (d, *J* = 2.2 Hz), 127.5 (d, *J* = 3.8 Hz), 125.6 – 124.9 (m, 2C), 123.7 (q, *J* = 273.7 Hz), 123.6 (q, *J* = 273.7 Hz), 120.2, 118.4, 113.6, 110.2, 106.3 (d, *J* = 4.2 Hz), 54.9, 42.1 (d, *J* = 71.1 Hz), 12.1.

^{31}P NMR (162 MHz, DMSO-d_6) δ 29.09.

^{19}F NMR (376 MHz, DMSO-d_6) δ -61.64, -61.73.

HRMS (ESI-TOF) calcd. for $C_{31}H_{24}F_6NO_2PNa$ $[M + Na]^+$ 610.1341; found: 610.1340.

(S)-((4-methoxyphenyl)(2-methyl-1H-indol-3-yl)methyl)diphenylphosphine oxide (3s)



It was purified by flash chromatography (petroleum ether/EtOAc/DCM, 4:1:1) to afford white solid (28.4 mg, 63% yield; 88% ee); $[\alpha]_D^{20}$ = -8.4 (*c* 1.00, CH_2Cl_2); m.p. 110.2-110.5 ºC;

The ee was determined by HPLC (Chiralpak AD-H, *i*-PrOH/hexane = 40/60, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 7.1 min, t_{minor} = 19.6 min);

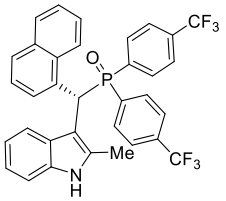
^{1}H NMR (300 MHz, DMSO-d_6) δ 10.74 (s, 1H), 8.37 – 8.25 (m, 1H), 8.08 – 7.90 (m, 2H), 7.80 – 7.67 (m, 2H), 7.56 – 7.40 (m, 5H), 7.37 – 7.21 (m, 3H), 7.15 – 7.08 (m, 1H), 6.95 – 6.87 (m, 2H), 6.71 (d, *J* = 8.6 Hz, 2H), 5.43 (d, *J* = 12.1 Hz, 1H), 3.59 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 157.6, 135.1, 134.1 (d, *J* = 93.3 Hz), 134.0 (d, *J* = 91.2 Hz), 133.4, 133.5, 131.2 (d, *J* = 8.7 Hz), 130.8 (d, *J* = 6.7 Hz), 130.5, 130.4 , 128.4 (d, *J* = 11.1 Hz), 128.1 (d, *J* = 11.2 Hz), 127.8 (d, *J* = 4.0 Hz), 120.7, 120.0, 118.3, 113.4, 110.1, 107.3 (d, *J* = 4.1 Hz), 54.9, 42.4 (d, *J* = 70.6 Hz), 12.2.

^{31}P NMR (243 MHz, $CDCl_3$) δ 31.81.

HRMS (ESI-TOF) calcd. for $C_{29}H_{27}NO_2P$ $[M + H]^+$ 452.1779; found: 452.1774.

(S)-((2-methyl-1H-indol-3-yl)(naphthalen-1-yl)methyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3t)



It was purified by flash chromatography (petroleum ether/EtOAc/DCM = 5:1:1) to afford colorless oil (51.5 mg, 85% yield; 95% ee); $[\alpha]_D^{20}$ = -354.8 (*c* 1.00, CH_2Cl_2);

The ee was determined by HPLC (Chiralpak AD-H, *i*-PrOH/hexane = 25/75, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 7.6 min, t_{minor} = 14.7 min);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 7.2 Hz, 1H), 8.45 (s, 1H), 7.89 – 7.82 (m, 3H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.70 (d, *J* = 8.3 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.48 – 7.39 (m, 2H), 7.38 – 7.29 (m, 4H), 7.29 – 7.22 (m, 2H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.97 – 6.89 (m, 1H), 6.84 – 6.76 (m, 1H), 5.73 (d, *J* = 11.0 Hz, 1H), 2.16 (s, 3H).

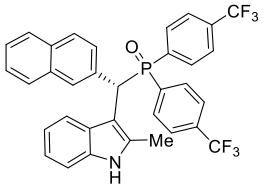
^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0 (d, *J* = 100.0 Hz), 136.6 (d, *J* = 89.9 Hz), 135.6 (d, *J* = 6.9 Hz), 134.5,134.2, 133.6 (qd, *J* = 32.6, 2.7 Hz, 2C), 132.2, 132.0 (d, *J* = 8.9 Hz), 131.9, 131.8 (d, *J* = 9.4 Hz), 129.3 (d, *J* = 9.9 Hz), 128.5 (d, *J* = 3.5 Hz), 128.3, 126.7, 125.7, 125.8 – 125.5 (m), 125.0 – 124.6 (m), 125.2, 123.5 (q, *J* = 273.7 Hz), 123.0, 122.2, 121.0, 119.7, 117.6, 110.3, 103.8 (d, *J* = 6.9 Hz), 40.1 (d, *J* = 72.7 Hz), 13.2.

^{31}P NMR (162 MHz, $CDCl_3$) δ 32.15.

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.22, -63.27.

HRMS (ESI-TOF) calcd. for $C_{34}H_{24}F_6NOPNa$ $[M + Na]^+$ 630.1392; found: 630.1398.

(S)-((2-methyl-1H-indol-3-yl)(naphthalen-2-yl)methyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3u)



It was purified by flash chromatography (petroleum ether/EtOAc/DCM = 4.5:1:1) to afford white soild (59.0 mg, 97% yield; 96% ee); $[\alpha]_D^{20}$ = -63.6 (*c* 1.00, CH_2Cl_2); m.p. 182.7-183.1 ºC

The ee was determined by HPLC (Chiralpak AD-H, EtOH/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 15.0 min, t_{minor} = 8.3 min);

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.88 (s, 1H), 8.40 – 8.25 (m, 3H), 8.15 (s, 1H), 8.09 – 7.97 (m, 2H), 7.79 (d, *J* = 7.5 Hz, 2H), 7.73 (d, *J* = 7.3 Hz, 5H), 7.70 – 7.64 (m, 1H), 7.45 – 7.32 (m, 2H), 7.13 (d, *J* = 7.7 Hz, 1H), 6.98 – 6.86 (m, 2H), 5.90 (d, *J* = 11.5 Hz, 1H), 2.48 (s, 3H).

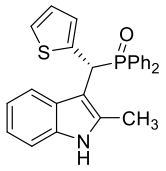
^{13}C NMR (101 MHz, DMSO-d_6) δ 138.1 (d, *J* = 89.8 Hz), 138.0 (d, *J* = 95.5 Hz), 135.5, 135.1, 134.3 (d, *J* = 9.0 Hz), 132.6, 132.3 (d, *J* = 9.2 Hz), 131.8 (qd, *J* = 32.3, 2.1 Hz, 2C), 131.6 (d, *J* = 8.7 Hz), 131.5, 128.2 (d, *J* = 7.3 Hz), 127.9 (d, *J* = 7.4 Hz), 127.7, 127.5 (d, *J* = 8.8 Hz), 126.3, 125.9, 125.6 – 124.6 (m, 2C), 125.0, 123.8 (q, *J* = 274.7 Hz), 123.7 (q, *J* = 273.7 Hz), 120.4, 120.2, 118.5, 110.3, 105.7 (d, *J* = 4.6 Hz), 43.0 (d, *J* = 70.9 Hz), 12.2.

^{31}P NMR (162 MHz, DMSO-d_6) δ 29.06.

^{19}F NMR (376 MHz, DMSO-d_6) δ -61.71, -61.78.

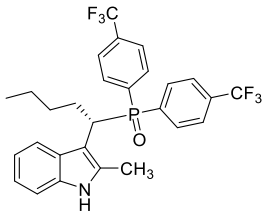
HRMS (ESI-TOF) calcd. for $C_{34}H_{24}F_6NOPNa$ $[M + Na]^+$ 630.1392; found: 630.1391.

(R)-((2-methyl-1H-indol-3-yl)(thiophen-2-yl)methyl)diphenylphosphine oxide (3v)



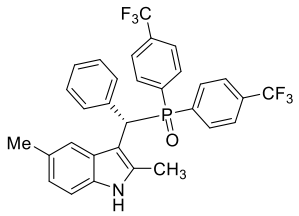
It was purified by flash chromatography (petroleum ether/EtOAc/DCM = 3:1:1) to afford yellow soild (28.2 mg, 66% yield; 83% ee); $[\alpha]_D^{20}$ = -55.9 (*c* 1.00, CH_2Cl_2); m.p. 113.7-114.2 ºC;
The ee was determined by HPLC (Chiralpak AD-H, *i*-PrOH/hexane = 25/75, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 10.5 min, t_{minor} = 23.5 min);
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.77 (s, 1H), 8.17 (d, *J* = 7.6 Hz, 1H), 8.15 – 8.03 (m, 2H), 7.76 – 7.59 (m, 2H), 7.51 (s, 3H), 7.31 (d, *J* = 6.6 Hz, 1H), 7.30 – 7.22 (m, 2H), 7.20 (d, *J* = 5.1 Hz, 1H), 7.14 – 7.07 (m, 2H), 6.96 – 6.86 (m, 2H), 6.78 (dd, *J* = 5.0, 3.6 Hz, 1H), 5.78 (d, *J* = 12.1 Hz, 1H), 2.38 (s, 3H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 140.3 (d, *J* = 1.4 Hz), 135.0, 133.9 (d, *J* = 8.2 Hz), 133.7 (d, *J* = 93.0 Hz), 133.3 (d, *J* = 98.3 Hz), 131.5 (d, *J* = 2.1 Hz), 131.3, 131.2, 130.4 (d, *J* = 8.7 Hz), 128.5 (d, *J* = 11.2 Hz), 128.0 (d, *J* = 11.1 Hz), 126.7 (d, *J* = 6.0 Hz), 127.5 (d, *J* = 3.2 Hz), 126.3, 125.0, 124.9, 120.1, 118.1, 110.0, 106.4 (d, *J* = 4.4 Hz), 38.7 (d, *J* = 66.9 Hz), 12.1.
^{31}P NMR (162 MHz, DMSO-d_6) δ 29.61.
HRMS (ESI-TOF) calcd. for $C_{26}H_{23}NOPS$ $[M + H]^+$ 428.1238; found: 428.1226.

(S)-(1-(2-methyl-1H-indol-3-yl)pentyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3w)



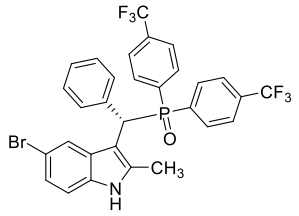
It was purified by flash chromatography (petroleum ether/EtOAc/DCM = 4:1:1) to afford white solid (46.2 mg, 86% yield; 95% ee); $[\alpha]_D^{20}$ = -151.3 (*c* 1.00, CH_2Cl_2); m.p. 142.7-143.1 ºC;
The ee was determined by HPLC (Chiralpak IA, EtOH/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 13.2 min, t_{minor} = 15.8 min);
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.91 (s, 1H), 8.69 – 8.52 (m, 2H), 8.26 – 8.12 (m, 3H), 8.06 – 7.96 (m, 2H), 7.88 (d, *J* = 7.3 Hz, 2H), 7.38 – 7.29 (m, 1H), 7.18 – 7.03 (m, 2H), 4.35 – 4.23 (m, 1H), 2.87 – 2.77 (m, 1H), 2.40 (s, 3H), 1.93 – 1.77 (m, 1H), 1.35 – 1.13 (m, 4H), 0.84 (t, *J* = 6.6 Hz, 3H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 139.0, 138.6 (d, *J* = 92.7 Hz), 135.9 (d, *J* = 2.9 Hz), 135.4 (d, *J* = 96.7 Hz), 132.6 (d, *J* = 8.7 Hz), 132.2 (qd, *J* = 31.8, 2.1 Hz, 2C), 131.7 (d, *J* = 9.1 Hz), 127.5, 126.2 – 125.9 (m), 125.5 – 125.1 (m), 124.3 (q, *J* = 273.7 Hz), 124.1 (q, *J* = 273.7 Hz), 121.7, 120.5, 118.5, 110.7, 103.8 (d, *J* = 6.4 Hz), 37.4 (d, *J* = 74.6 Hz), 29.7 (d, *J* = 13.1 Hz), 26.7, 21.9, 14.1.
^{31}P NMR (162 MHz, DMSO-d_6) δ 31.04.
^{19}F NMR (376 MHz, DMSO-d_6) δ -61.64, -61.71.
HRMS (ESI-TOF) calcd. for $C_{28}H_{27}F_6NOP$ $[M + H]^+$ 538.1729; found: 538.1732.

(S)-((2,5-dimethyl-1H-indol-3-yl)(phenyl)methyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3x)



It was purified by flash chromatography (petroleum ether/EtOAc/DCM = 4:1:1) to afford white solid (52.8 mg, 92% yield, 95% ee); $[\alpha]_D^{20}$ = -27.3 (*c* 1.00, CH_2Cl_2); m.p. 144.2-144.6 ºC;
The ee was determined by HPLC (Chiralpak AD-H, EtOH/hexane = 15/85, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 7.1 min, t_{minor} = 5.7 min);
^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.69 (s, 1H), 8.35 – 8.19 (m, 2H), 7.98 (s, 3H), 7.81 (d, *J* = 7.7 Hz, 2H), 7.70 (d, *J* = 7.6 Hz, 2H), 7.57 (s, 2H), 7.21 – 7.12 (m, 2H), 7.10 – 7.04 (m, 1H), 7.00 (d, *J* = 7.2 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 5.65 (d, *J* = 11.4 Hz, 1H), 2.41 (s, 3H), 2.33 (s, 3H).
^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 138.1(d, *J* = 94.4 Hz), 138.0 (d, *J* = 94.9 Hz), 137.8 (d, J = 2.5 Hz), 134.2 (d, *J* = 9.1 Hz), 133.4, 132.3 (d, *J* = 9.2 Hz), 131.6 (qd, *J* = 31.3, 2.6 Hz, 2C), 131.5 (d, *J* = 9.1 Hz), 129.7 (d, *J* = 7.1 Hz), 127.9 (d, *J* = 4.2 Hz), 128.2, 126.6 (d, *J* = 10.4 Hz), 125.4 – 124.9 (m, 2C), 123.8 (q, *J* = 272.7 Hz), 123.7 (q, *J* = 273.7 Hz), 122.4 (d, *J* = 9.5 Hz), 121.7, 120.0, 109.9, 105.3 (d, *J* = 4.7 Hz), 43.0 (d, *J* = 71.0 Hz), 21.6, 12.3.
^{31}P NMR (162 MHz, DMSO-*d*$_6$) δ 28.93.
^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ -61.66, -61.74.
HRMS (ESI-TOF) calcd. for $C_{31}H_{25}F_6NOP$ $[M + H]^+$ 572.1572; found: 572.1574.

(S)-((5-bromo-2-methyl-1H-indol-3-yl)(phenyl)methyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3y)



It was purified by flash chromatography (petroleum ether/EtOAc/DCM = 4:1:1) to afford white solid (60.5 mg, 95% yield; 95% ee); $[\alpha]_D^{20}$ = -11.2 (*c* 1.00, CH_2Cl_2); m.p. 260.6-260.9 ºC;
The ee was determined by HPLC (Chiralpak OJ, EtOH/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 10.3 min, t_{minor} = 7.1 min);
^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 11.08 (s, 1H), 8.42 (s, 1H), 8.33 – 8.19 (m, 2H), 8.05 – 7.92 (m, 2H), 7.82 (d, *J* = 7.8 Hz, 2H), 7.72 (d, *J* = 7.7 Hz, 2H), 7.54 (d, *J* = 7.4 Hz, 2H), 7.22 – 7.14 (m, 2H), 7.11 – 7.05 (m, 2H), 7.02 (d, *J* = 8.5 Hz, 1H), 5.70 (d, *J* = 11.6 Hz, 1H), 2.42 (s, 3H).
^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 137.8 (d, *J* = 92.8 Hz), 137.5 (d, *J* = 2.0 Hz), 136.2 (d, *J* = 9.2 Hz), 133.7, 132.3 (d, *J* = 9.3 Hz), 131.8 (qd, *J* = 32.3, 2.4 Hz, 2C), 131.5 (d, *J* = 9.2 Hz), 129.6 (d, *J* = 7.3 Hz), 129.4 (d, *J* = 3.8 Hz), 128.3, 126.7, 125.5 – 125.1 (m, 2C), 123.8 (q, *J* = 273.7 Hz),

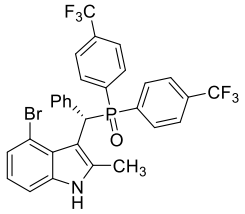
123.7 (q, *J* = 273.7 Hz), 122.7, 122.6, 112.2, 111.4, 105.8 (d, *J* = 4.7 Hz), 42.7 (d, *J* = 70.4 Hz), 12.2.

^{31}P NMR (162 MHz, DMSO-*d*$_6$) δ 29.23.

^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ -61.65, -61.73.

HRMS (ESI-TOF) calcd. for $C_{28}H_{22}{}^{79}BrF_6NOP$ $[M + H]^+$ 636.0521, found: 636.0525; calcd. for $C_{28}H_{22}{}^{81}BrF_6NOP$ $[M + H]^+$ 638.0505; found: 638.0510.

(S)-((4-bromo-2-methyl-1H-indol-3-yl)(phenyl)methyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide(3z)



It was purified by flash chromatography (petroleum ether/EtOAc/DCM = 3:1:1) to afford white solid (37.5 mg, 62% yield, 83% ee); $[\alpha]_D^{20}$ = 55.6 (*c* 1.00, CH_2Cl_2); m.p. 289.3-289.8 ºC;

The ee was determined by HPLC (Chiralpak AD-H, EtOH/hexane = 25/75, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 4.6 min, t_{minor} = 5.5 min);

^{1}H NMR (400 MHz, CDCl$_3$) δ 11.34 (s, 1H), 8.13 (dd, *J* = 10.1, 8.1 Hz, 2H), 7.92 (d, *J* = 7.1 Hz, 2H), 7.79 (dd, *J* = 10.5, 8.1 Hz, 2H), 7.57 (d, *J* = 7.0 Hz, 2H), 7.49 (d, *J* = 7.8 Hz, 2H), 7.25 – 7.15 (m, 3H), 7.14 (d, *J* = 7.3 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 6.87 – 6.80 (m, 2H), 2.61 (s, 3H).

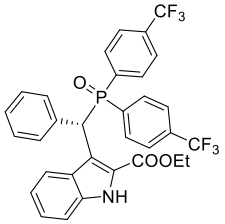
^{13}C NMR (101 MHz, CDCl$_3$) δ 137.7 (d, *J* = 90.2 Hz), 137.5 (d, *J* = 5.0 Hz), 137.4 (d, *J* = 97.1 Hz), 137.2 (d, *J* = 1.9 Hz), 136.3, 132.0 (d, *J* = 8.9 Hz), 131.8 (qd, *J* = 32.2, 2.8 Hz, 2C), 131.5 (d, *J* = 9.1 Hz), 129.6 (d, *J* = 7.2 Hz), 128.5, 126.8, 126.2 – 125.8 (m, 1C), 125.2 – 124.8 (m, 1C), 124.3 (d, *J* = 6.6 Hz), 124.0, 123.8 (q, J = 273.7 Hz), 123.6 (q, *J* = 274.0 Hz), 121.6, 111.3, 110.7, 105.7 (d, *J* = 4.9 Hz), 40.3 (d, *J* = 69.8 Hz), 14.0.

^{31}P NMR (162 MHz, CDCl$_3$) δ 33.80.

^{19}F NMR (376 MHz, CDCl$_3$) δ -57.01, -57.08.

HRMS (ESI-TOF) calcd. for $C_{28}H_{22}{}^{79}BrF_6NOP$ $[M + H]^+$ 636.0521, found: 636.0526; calcd. for $C_{28}H_{22}{}^{81}BrF_6NOP$ $[M + H]^+$ 638.0505; found: 638.0507.

ethyl (S)-3-((bis(4-(trifluoromethyl)phenyl)phosphoryl)(phenyl)methyl)-1H-indole-2-carboxylate (3a')

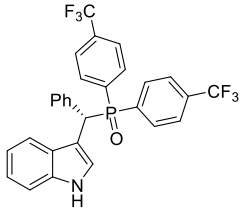


It was purified by flash chromatography (petroleum ether/EtOAc = 5:1) to afford white solid (42.8 mg, 71% yield; 45% ee); $[\alpha]_D^{20}$ = -36.4 (*c* 1.00, CH_2Cl_2); m.p. 133.6-133.9 ºC;

The ee was determined by HPLC (Chiralpak AD-H, EtOH/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 8.3 min, t_{minor} = 10.2 min);

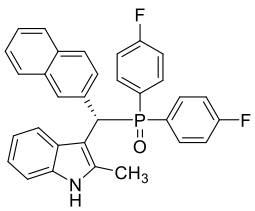
^{1}H NMR (400 MHz, DMSO-d_6) δ 11.76 (s, 1H), 8.53 (d, *J* = 8.3 Hz, 1H), 8.13 – 8.00 (m, 2H), 7.91 (d, *J* = 7.8 Hz, 2H), 7.82 – 7.73 (m, 2H), 7.69 (d, *J* = 7.8 Hz, 2H), 7.60 (d, *J* = 7.5 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 1H), 7.20 (q, *J* = 6.8 Hz, 3H), 7.16 – 7.01 (m, 2H), 6.85 (d, *J* = 11.1 Hz, 1H), 4.42 (q, *J* = 7.0 Hz, 2H), 1.39 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 161.8, 137.2 (d, *J* = 92.6 Hz), 136.9 (d, *J* = 95.7 Hz), 136.5 (d, *J* = 3.5 Hz), 136.3, 132.0 (qd, *J* = 32.5,2.3 Hz, 2C), 131.8 (d, *J* = 8.9 Hz), 131.2 (d, *J* = 9.0 Hz), 129.7 (d, *J* = 7.0 Hz), 128.6, 127.2, 126.1 – 125.8 (m), 126.0, 125.3 – 125.1 (m), 125.2, 124.0, 123.7 (q, *J* = 273.7 Hz), 123.5 (q, *J* = 273.7 Hz), 123.3 (d, *J* = 9.3 Hz), 120.2, 117.8 (d, *J* = 4.8 Hz), 112.5, 60.9, 42.5 (d, *J* = 70.1 Hz), 14.3.
^{31}P NMR (162 MHz, DMSO-d_6) δ 28.37.
^{19}F NMR (376 MHz, $CDCl_3$) δ -63.18, -63.26.
HRMS (ESI-TOF) calcd. for $C_{32}H_{25}F_6NO_3P$ $[M + H]^+$ 616.1471; found: 616.1474.

(S)-((1H-indol-3-yl)(phenyl)methyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3b`)



It was purified by flash chromatography (petroleum ether/EtOAc/DCM = 4:1:1) to afford white solid (28.9 mg, 53% yield, 5% ee); $[\alpha]_D^{20}$ = 1.4 (*c* 1.00, CH_2Cl_2); m.p. 109.8-110.3 ºC;
The ee was determined by HPLC (Chiralpak AD-H, EtOH/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 6.6 min, t_{minor} = 8.9min);
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (s, 1H), 7.86 (dd, *J* = 17.0, 8.2 Hz, 3H), 7.64 – 7.54 (m, 4H), 7.51 (d, *J* = 7.2 Hz, 2H), 7.43 (d, *J* = 7.9 Hz, 1H), 7.35 – 7.23 (m, 3H), 7.17 – 7.11 (m, 1H), 7.11 – 7.05 (m, 3H), 7.05 – 7.01 (m, 1H), 5.13 (d, *J* = 9.6 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 136.5 (d, *J* = 96.0 Hz), 136.5 (d, *J* = 95.2 Hz), 135.8,135.4 (d, *J* = 5.2 Hz), 133.7 (qd, *J* = 32.8, 2.9 Hz, 2C), 131.8 (d, *J* = 6.9 Hz), 131.7 (d, *J* = 6.7 Hz), 129.8 (d, *J* = 5.8 Hz), 128.5 (d, *J* = 1.8 Hz), 127.4 (d, *J* = 2.5 Hz), 127.0 (d, *J* = 9.9 Hz), 125.6 (dq, *J* = 11.3, 3.7 Hz), 125.2 (dq, *J* = 11.6, 3.6 Hz), 125.0 (d, *J* = 5.9 Hz),123.6 (q, *J* = 273.7 Hz), 123.5 (q, *J* = 273.7 Hz), 122.5, 119.9, 117.8, 111.7, 110.2 (d, *J* = 5.2 Hz), 43.7 (d, *J* = 68.0 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 31.22.
^{19}F NMR (376 MHz, $CDCl_3$) δ -63.20, -63.31.
HRMS (ESI-TOF) calcd. for $C_{29}H_{21}F_6NOP$ $[M + H]^+$ 544.1259; found: 544.1262.

(S)-bis(4-fluorophenyl)((2-methyl-1H-indol-3-yl)(naphthalen-2-yl)methyl)phosphine oxide (3c`)



It was purified by flash chromatography (petroleum ether/EtOAc = 2:1) to afford white solid (41.3 mg, 81% yield, 87% ee); $[\alpha]_D^{20}$ = -57.6 (*c* 1.00, CH_2Cl_2); m.p. 135.2-135.6ºC;

The ee was determined by HPLC (Chiralpak AD-H, *i*-PrOH/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm, t_{minor} = 13.3min, t_{major} = 18.2min);

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.85 (s, 1H), 8.30 (d, *J* = 6.3 Hz, 1H), 8.11 (d, *J* = 9.0 Hz, 3H), 7.87 – 7.78 (m, 2H), 7.76 – 7.66 (m, 4H), 7.42 – 7.34 (m, 2H), 7.30 – 7.22 (m, 2H), 7.22 – 7.10 (m, 3H), 6.97 – 6.86 (m, 2H), 5.70 (d, *J* = 11.6 Hz, 1H), 2.47 (s, 3H).

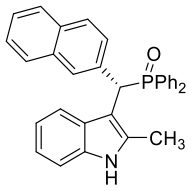
^{13}C NMR (101 MHz, DMSO-d_6) δ 164.1 (d, J_{C-F} = 250.2 Hz), 164.0 (d, J_{C-F} = 250.3 Hz), 135.7 (d, *J* = 87.3 Hz), 135.6 (d, *J* = 89.0 Hz), 134.1 (d, *J* = 9.4 Hz), 134.0, 133.4 (d, *J* = 9.3 Hz), 133.3, 132.7, 131.6, 130.3, 129.4 (dd, J_{C-P} = 7.4, J_{C-F} = 2.8 Hz), 128.4 (d, *J* = 6.3 Hz), 128.0 (dd, J_{C-P} = 7.3, J_{C-F} = 3.4 Hz), 127.8, 127.6, 127.4, 126.2, 125.8, 120.5, 120.2, 118.4 (d, *J* = 3.0 Hz), 115.8 (dd, J_{C-P} = 12.2 Hz, J_{C-F} = 21.5), 115.6 (dd, J_{C-P} = 12.2 Hz, J_{C-F} = 21.5), 110.3, 106.3 (d, *J* = 4.4 Hz), 43.6 (d, *J* = 73.9 Hz), 12.2.

^{31}P NMR (162 MHz, DMSO-d_6) δ 29.64.

^{19}F NMR (376 MHz, DMSO-d_6) δ -108.25, -108.29.

HRMS (ESI-TOF) calcd. for $C_{32}H_{25}F_2NOP$ $[M + H]^+$ 508.1636 found: 508.1640.

(S)-((2-methyl-1H-indol-3-yl)(naphthalen-2-yl)methyl)diphenylphosphine oxide (3d`)



It was purified by flash chromatography (petroleum ether/EtOAc = 2:1) to afford yellow solid (21.2 mg, 45% yield; 91% ee); $[\alpha]_D^{20}$ = -91.5 (*c* 1.00, THF); m.p. 149.4-150.2 ºC;

The ee was determined by HPLC (Chiralpak AD-H, *i*-PrOH/hexane = 25/75, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 16.3 min, t_{minor} = 23.1 min);

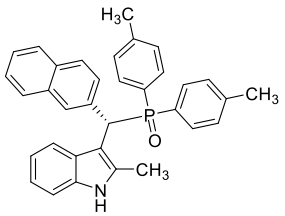
^{1}H NMR (300 MHz, DMSO-d_6) δ 10.76 (s, 1H), 8.39 – 8.25 (m, 1H), 8.11 (s, 1H), 8.06 – 7.95 (m, 2H), 7.81 – 7.70 (m, 3H), 7.70 – 7.64 (m, 3H), 7.43 – 7.36 (m, 5H), 7.36 – 7.28 (m, 3H), 7.15 – 7.05 (m, 1H), 6.95 – 6.81 (m, 2H), 5.66 (d, *J* = 11.7 Hz, 1H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 136.3 (d, *J* = 2.2 Hz), 135.0, 133.9 (d, *J* = 93.1 Hz), 133.9 (d, *J* = 8.8 Hz), 133.8 (d, *J* = 97.7 Hz), 132.6, 131.5, 131.3, 131.2, 131.1, 130.5 (d, *J* = 8.6 Hz), 128.5, 128.4, 128.3, 128.1 (d, *J* = 11.2 Hz), 127.9 (d, *J* = 7.4 Hz), 127.8 (d, *J* = 4.1 Hz), 127.5, 127.4, 126.1, 125.7, 120.6, 120.0, 118.3, 110.1, 106.7 (d, *J* = 4.5 Hz), 43.3 (d, *J* = 70.3 Hz), 12.2.

^{31}P NMR (162 MHz, DMSO-d_6) δ 30.11.

HRMS (ESI-TOF) calcd. for $C_{32}H_{27}NOP$ $[M + H]^+$ 472.1830; found: 472.1824.

(S)-((2-methyl-1H-indol-3-yl)(naphthalen-2-yl)methyl)di-p-tolylphosphine oxide (3e`)



It was purified by flash chromatography (petroleum ether/EtOAc = 2:1) to afford yellow solid (15.9 mg, 32% yield; 56% ee); $[\alpha]_D^{20}$ = -27.3 (*c* 1.00, THF); m.p. 144.2-144.8 ºC;

The ee was determined by HPLC (Chiralpak AD-H, EtOH/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 17.0 min, t_{minor} = 14.1 min);

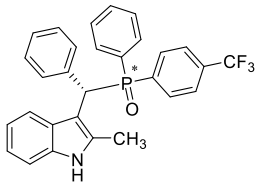
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.78 (s, 1H), 8.42 – 8.28 (m, 1H), 8.15 (s, 1H), 7.92 – 7.84 (m, 2H), 7.73 (d, *J* = 7.9 Hz, 2H), 7.70 – 7.62 (m, 4H), 7.42 – 7.33 (m, 2H), 7.18 (d, *J* = 7.2 Hz, 2H), 7.11 (d, *J* = 7.1 Hz, 3H), 6.96 – 6.87 (m, 2H), 5.62 (d, *J* = 11.5 Hz, 1H), 2.47 (s, 3H), 2.20 (d, *J* = 9.5 Hz, 6H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 142.7 (d, *J* = 2.7 Hz), 141.1 (d, *J* = 2.3 Hz), 141.0 (d, *J* = 2.3 Hz), 136.6 (d, *J* = 2.2 Hz), 135.1, 133.8 (d, *J* = 8.8 Hz), 132.7, 131.1 (d, *J* = 8.9 Hz), 131.0 (d, *J* = 94.9 Hz), 130.9 (d, *J* = 94.8 Hz), 130.4, 129.5 (d, *J* = 13.4 Hz), 129.0 (d, *J* = 11.4 Hz), 128.7 (d, *J* = 11.5 Hz), 128.5 (d, *J* = 6.7 Hz), 127.9, 127.8, 127.5, 127.4, 126.1, 125.6, 120.6, 120.0, 118.3, 110.1, 107.0 (d, *J* = 4.3 Hz), 43.4 (d, *J* = 70.1 Hz), 21.0, 20.9, 12.3.

^{31}P NMR (162 MHz, DMSO-d_6) δ 30.42.

HRMS (ESI-TOF) calcd. for $C_{34}H_{31}NOP$ $[M + H]^+$ 500.2138; found: 500.2143.

(2-methyl-1H-indol-3-yl)(phenyl)methyl)(phenyl)(4-(trifluoromethyl)phenyl)phosphine oxide (3f`)



It was purified by flash chromatography (petroleum ether/EtOAc = 3:1) to afford white solid (43.4 mg, 88%yield, 1.25:1 dr; isomer 1: 23.6 mg, 48% yield, 96% ee; $[\alpha]_D^{20}$ = 2.78 (*c* 1.00, CH_2Cl_2); m.p. 117.2-117.9 ºC; isomer 2: 19.8 mg, 40% yield, 97% ee); $[\alpha]_D^{20}$ = -45.2 (*c* 1.00, CH_2Cl_2); m.p. 119.6-120.0 ºC;

The ee was determined by HPLC (isomer 1 : Chiralpak AD-H, EtOH/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 16.5 min, t_{minor} = 22.5 min); (isomer 2: Chiralpak IA, EtOH/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm, t_{major} = 5.3 min, t_{minor} = 5.9 min).

^{1}H NMR (400 MHz, DMSO-d_6) isomer 1: δ 10.79 (s, 1H), 8.31 (d, *J* = 5.8 Hz, 1H), 8.24 – 8.15 (m, 2H), 7.84 – 7.73 (m, 4H), 7.57 (d, *J* = 7.1 Hz, 2H), 7.41 – 7.28 (m, 3H), 7.18 – 7.08 (m, 3H), 7.08 – 7.01 (m, 1H), 6.96 – 6.86 (m, 2H), 5.58 (d, *J* = 11.9 Hz, 1H), 2.45 (s, 3H). **isomer 2:** δ 10.78 (s, 1H), 8.26 (d, *J* = 7.1 Hz, 1H), 8.05 – 7.98 (m, 2H), 7.98 – 7.89 (m, 2H), 7.67 (d, *J* = 7.2 Hz, 2H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.47 (t, *J* = 6.7 Hz, 3H), 7.19 – 7.12 (m, 2H), 7.12 – 7.02 (m, 2H), 6.95 – 6.85 (m, 2H), 5.56 (d, *J* = 11.8 Hz, 1H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) isomer 1: δ 139.2 (d, *J* = 89.9 Hz), 138.2 (d, *J* = 2.0 Hz), 135.1, 133.9 (d, *J* = 9.3 Hz), 132.8 (d, *J* = 98.2 Hz), 132.1 (d, *J* = 9.0 Hz), 131.6 (d, *J* = 2.0 Hz), 131.1 (d, *J* = 2.0 Hz), 130.5 (d, *J* = 8.8 Hz), 129.7 (d, *J* = 6.8 Hz), 128.3 (d, *J* = 11.3 Hz), 128.1, 127.7 (d, *J* = 4.1 Hz), 126.4, 125.3 – 124.6 (m), 123.8 (q, *J* = 273.7 Hz), 120.6, 120.1, 118.4, 110.2, 106.5 (d, *J* = 4.5 Hz), 43.2 (d, *J* = 68.4 Hz), 12.2. **isomer 2:** δ 139.0 (d, *J* = 94.1 Hz), 138.1 (d, *J* = 2.1 Hz), 135.0, 133.9 (d, *J* = 9.2 Hz), 132.9 (d, *J* = 93.8 Hz), 131.7 (d, *J* = 2.2 Hz), 131.4 (d, *J* = 9.1 Hz), 131.2 (d, *J* = 8.9 Hz), 131.0 (d, *J* = 2.7 Hz), 129.7 (d, *J* = 7.0 Hz), 128.6 (d, *J* = 11.2 Hz), 128.1,

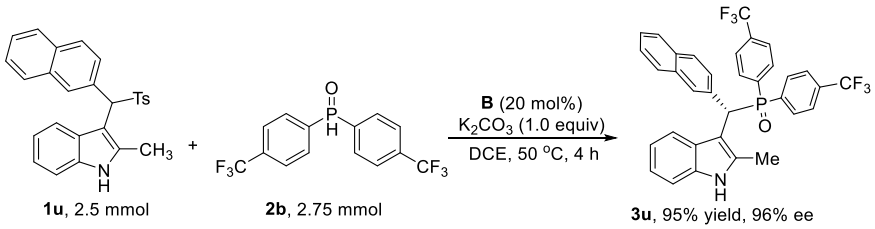
127.6 (d, *J* = 3.7 Hz), 126.4, 125.0 – 124.8 (m), 123.7 (q, *J* = 273.7 Hz), 120.6, 120.1, 118.4, 110.2, 106.4 (d, *J* = 4.7 Hz), 43.1 (d, *J* = 70.6 Hz), 12.1.

^{31}P NMR (162 MHz, $CDCl_3$) isomer 1 δ 30.82; isomer 2 δ 31.03. .

^{19}F NMR (376 MHz, $CDCl_3$) isomer 1 δ -63.05; isomer 2 δ -63.17.

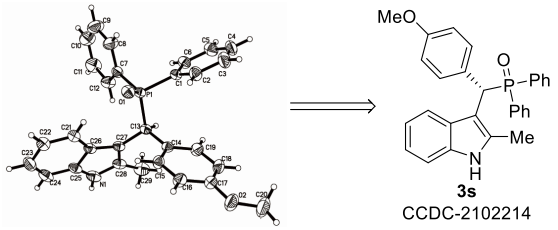
HRMS (ESI-TOF) calcd. for $C_{29}H_{23}F_3NOP$ $[M + H]^+$ 490.1542; found: 490.1543.

3. Scale-up experiment



In an ordinary vial equipped with a magnetic stirring bar, the bis(4-(trifluoromethyl)phenyl) -phosphine oxide **2b** (2.75 mmol, 930 mg) were added to a solution of arylsulfonyl indoles **1a** (2.5 mmol, 1.06 g), catalyst **B** (20 mol%) and K_2CO_3 (2.5 mmol, 1.0 equiv) in 1,2-dichloroethane (25 mL) at 50 ℃. And then, the whole was stirred for 5 h until the completion of the reaction, as indicated by TLC. Finally the reaction mixture was directly purified by flash chromatography on silica gel (PE/EA/DCM=4:1:1) and obtained the products **3u** (1.44 g, 95% yield, 96% ee).

4. X-ray crystal data for compound 3s

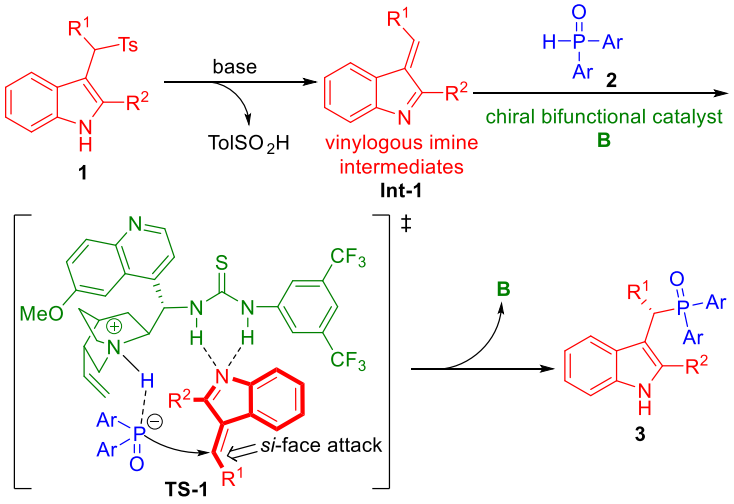


Identification code	202009174
Empirical formula	$C_{31}H_{32}NO_3P$
Formula weight	497.54
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	P212121
a/Å	10.45953(19)
b/Å	13.5092(3)
c/Å	19.3396(4)
α/°	90
β/°	90
γ/°	90
Volume/Å3	2732.69(10)
Z	4
ρcalcg/cm3	1.209

μ/mm-1	1.138
F(000)	1056.0
Crystal size/mm3	0.16 × 0.13 × 0.09
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.984 to 134.138
Index ranges	-12 ≤ h ≤ 12, -16 ≤ k ≤ 15, -22 ≤ l ≤ 23
Reflections collected	24771
Independent reflections	4884 [Rint = 0.0406, Rsigma = 0.0269]
Data/restraints/parameters	4884/1/333
Goodness-of-fit on F2	1.032
Final R indexes [I>=2σ (I)]	R1 = 0.0391, wR2 = 0.1048
Final R indexes [all data]	R1 = 0.0420, wR2 = 0.1077
Largest diff. peak/hole / e Å-3	0.22/-0.20
Flack parameter	-0.006(10)

5. Proposed reaction mechanism

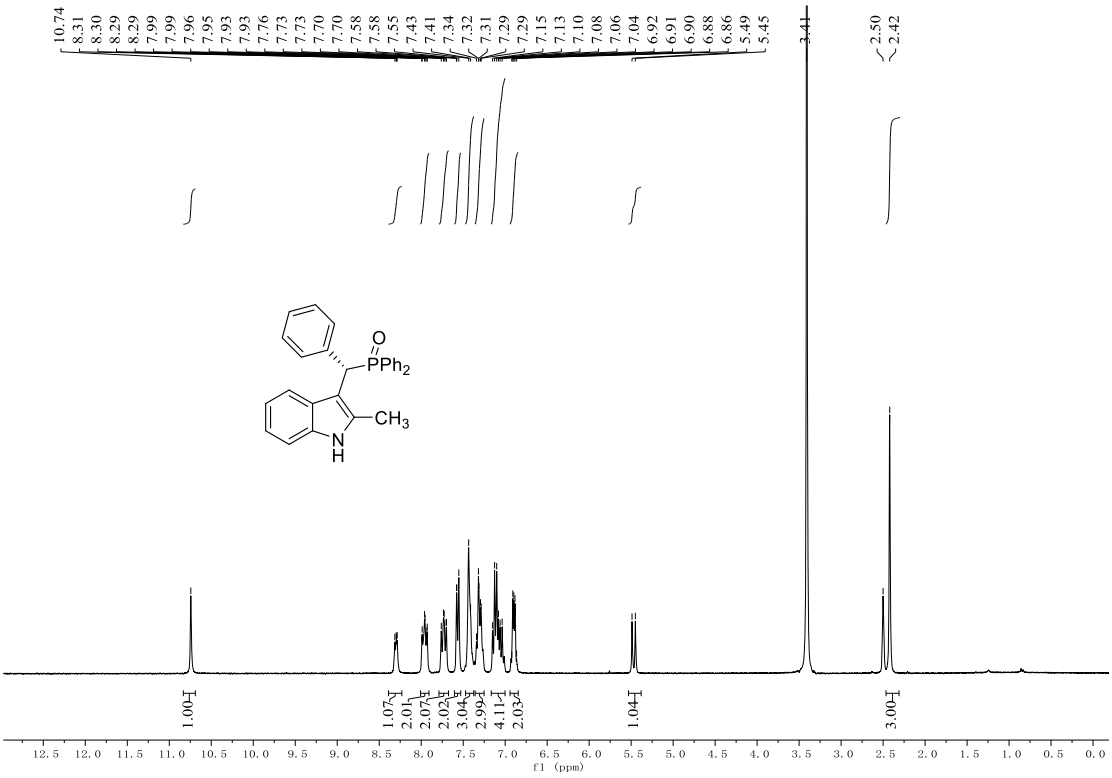
In the presence of base, an elimination of *p*-methyl benzenesulfinic acid from sulfonyl indoles **1** leads to the *in situ* generation of indole-derived vinylogous imine intermediates **Int-1**, which is oriented by the double hydrogen bonds of thiourea moiety of the catalyst **B**. Concurrently, the tertiary nitrogen of the quinine moiety in catalyst **B** would provide suitable basicity to enhance the nucleophilicity of the diarylphosphine oxides **2**. Under the stereoselective control via transition state **TS-1**, the phospha-Michael conjugated addition of diarylphosphine oxides **2** to the *Si*-face of intermediates **A** leads to the expected 3-(1-diphenylphosphoryl-arylmethyl)indole products **3** with stereospecific configuration.



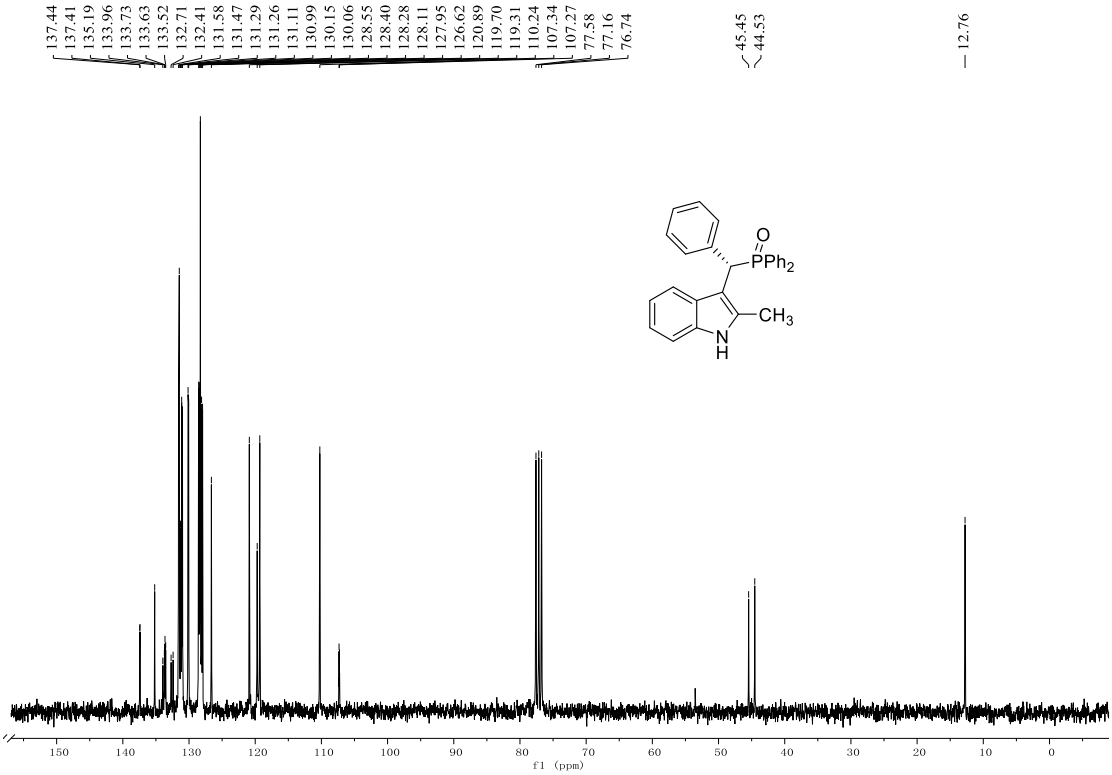
Proposed reaction mechanism

5. NMR and HPLC Spectra of compounds of 3

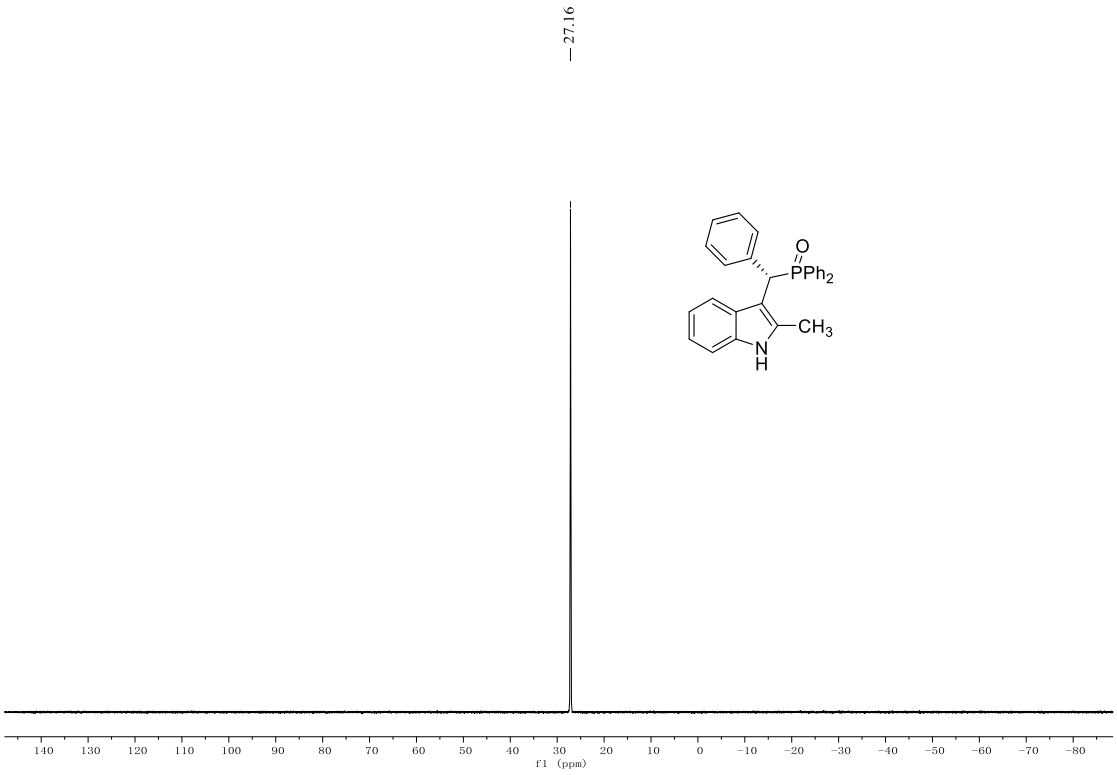
^{1}H NMR spectrum of compound 3a



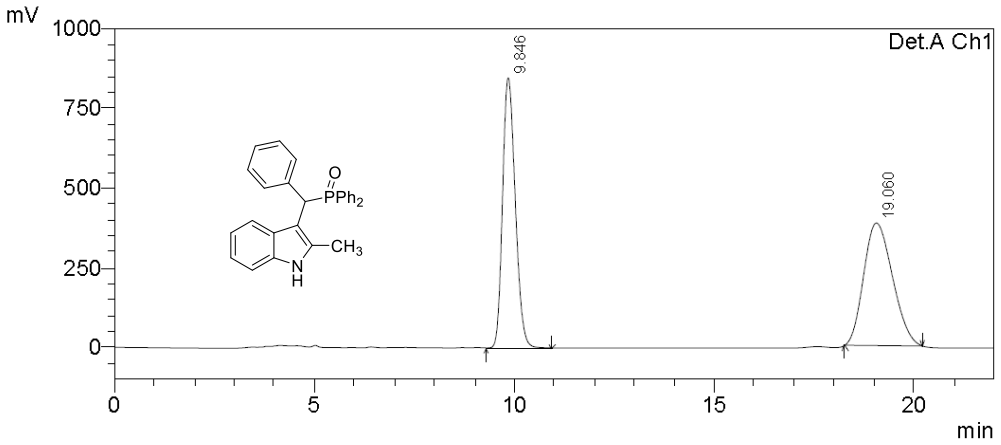
^{13}C NMR spectrum of compound 3a



^{31}P NMR spectrum of compound 3a



HPLC spectra of 3a



1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
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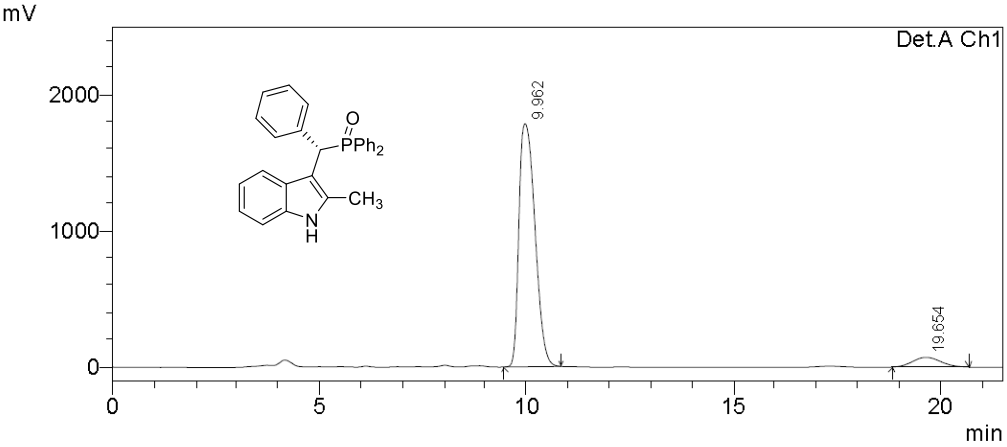
2	19.060	19264527	384045	50.291
Total		38305756		100.000



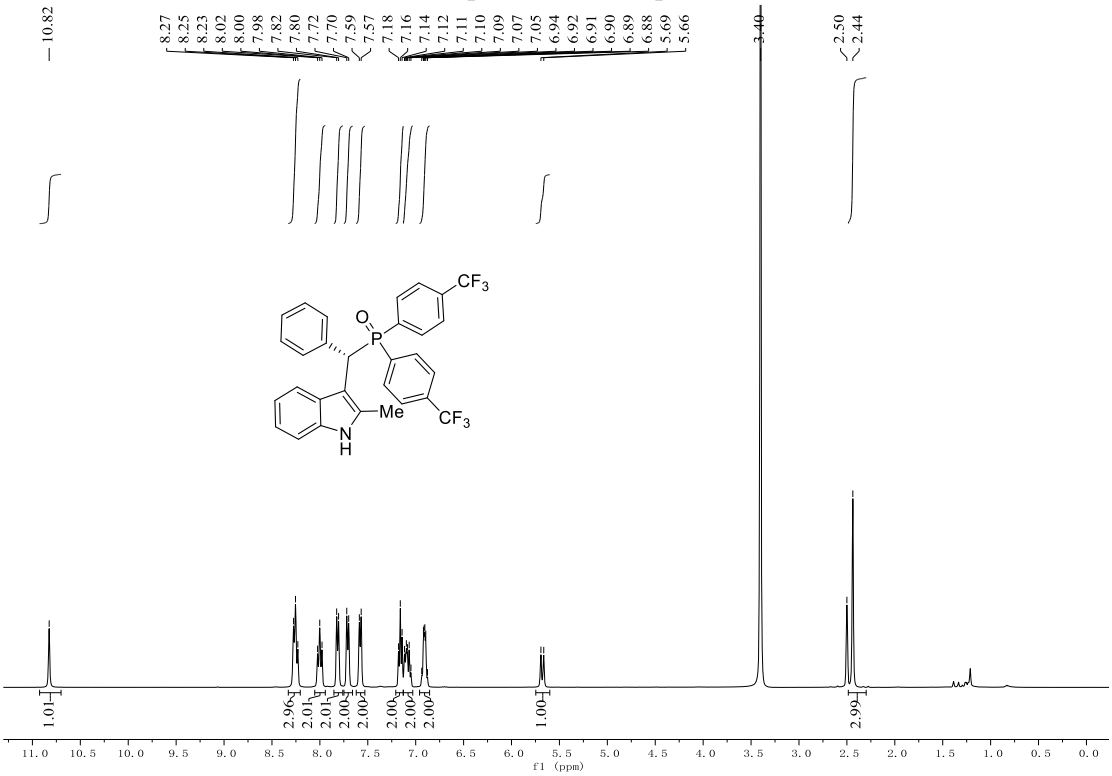
1 Det.A Ch1/254nm

PeakTable

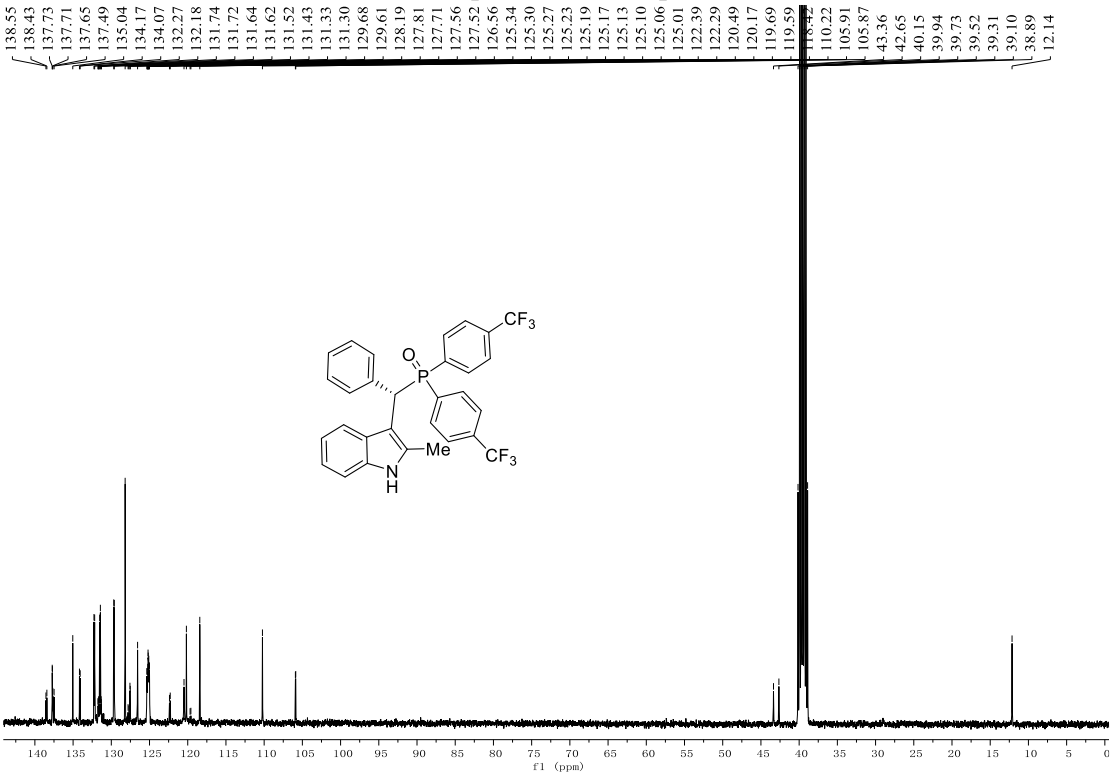
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	9.962	48032271	1782155	93.456
2	19.654	3363384	71124	6.544
Total		51395655		100.000

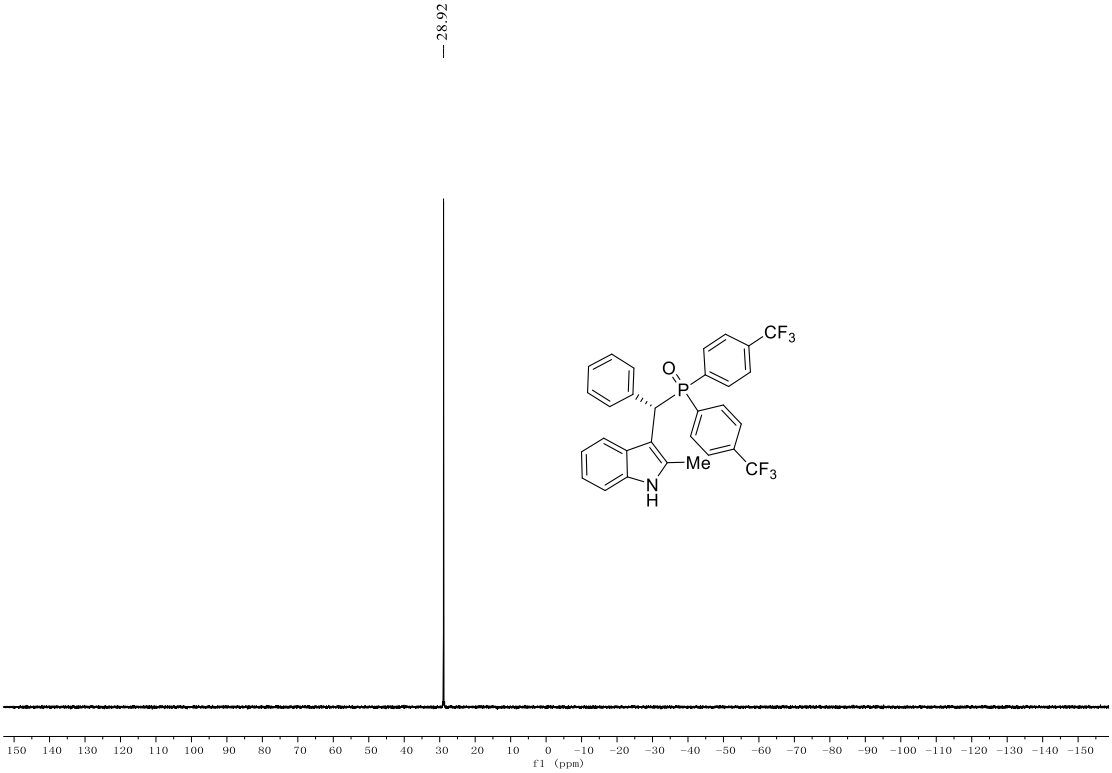
^{1}H NMR spectrum of compound 3b



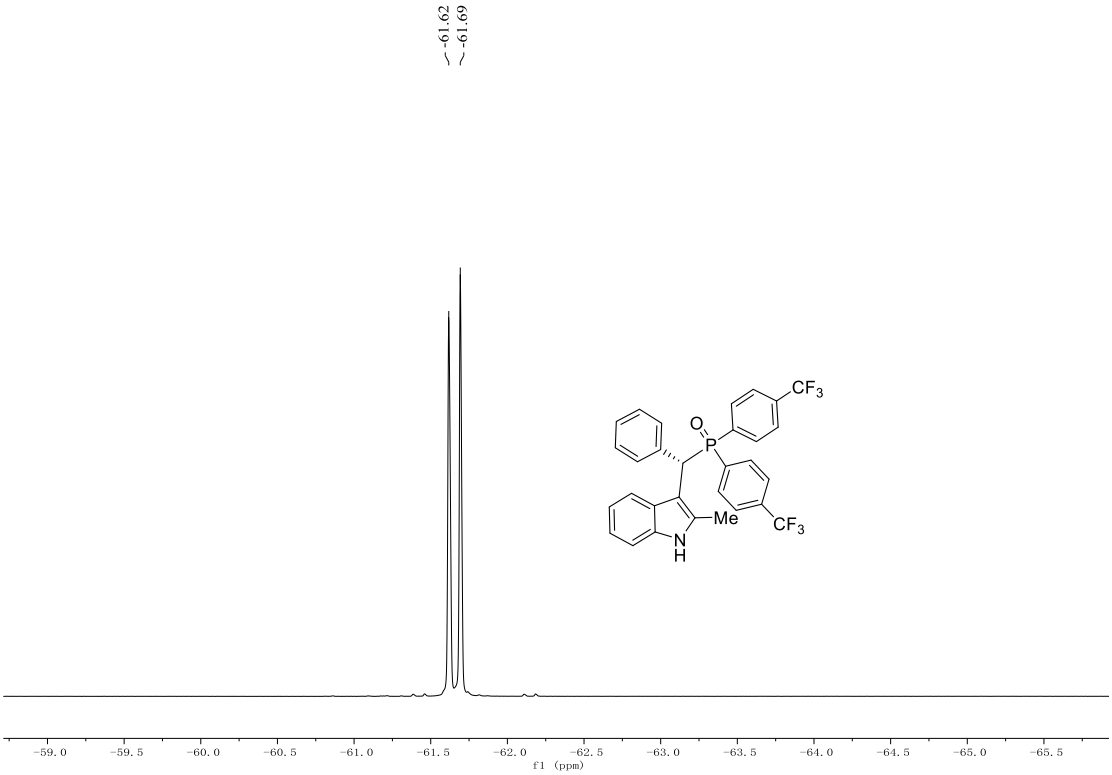
^{13}C NMR spectrum of compound 3b



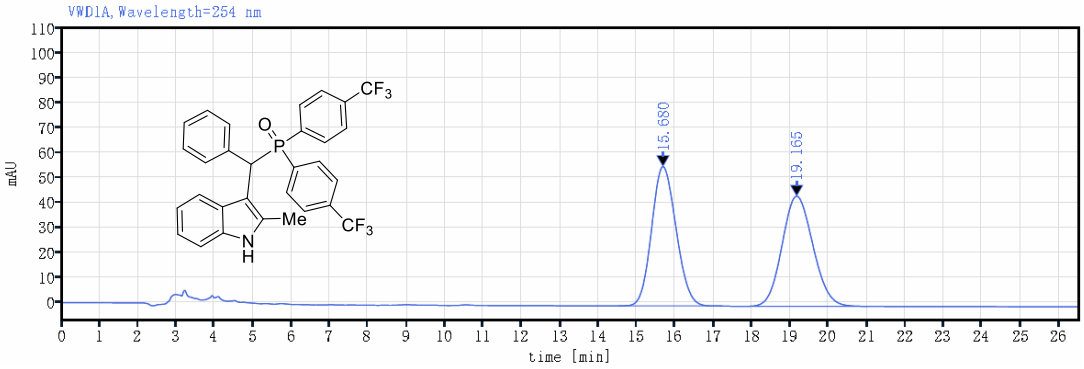
^{31}P NMR spectrum of compound 3b



^{19}F NMR spectrum of compound 3b

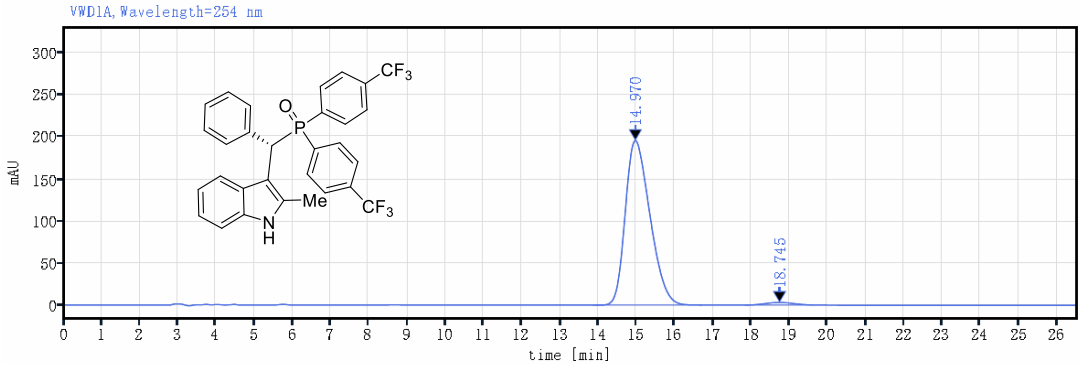


HPLC spectra of 3b



Detector VWD1A, Wavelength=254 nm

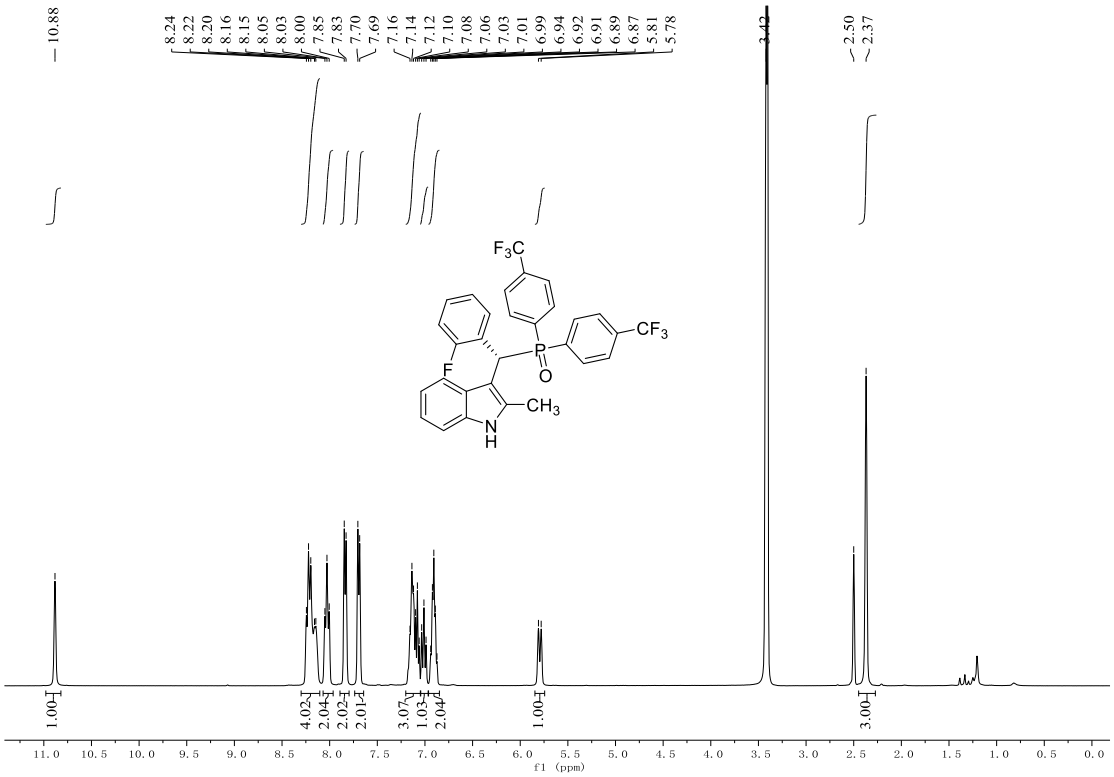
Peak	Ret.Time [min]	Area	Height	Area%
	15.680	2479.31	55.94	50.07
	19.165	2472.60	44.21	49.93
		4951.91		100.00



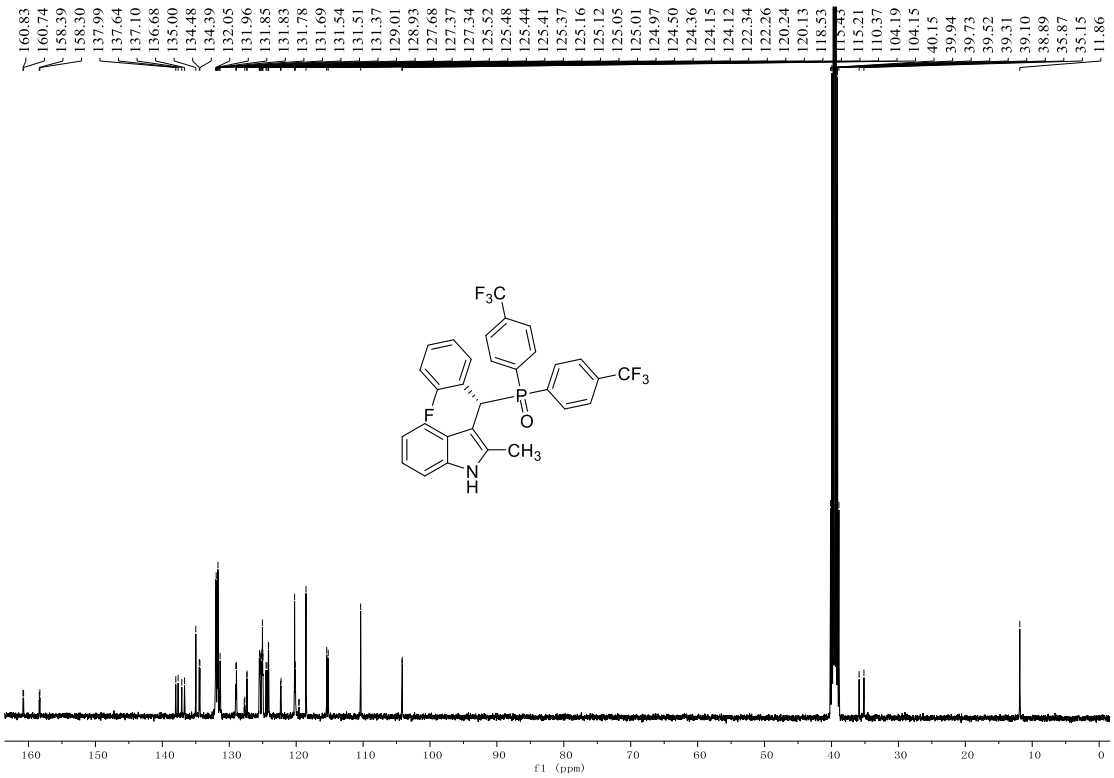
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	14.970	8776.53	195.98	98.27
	18.745	154.48	3.07	1.73
		8931.00		100.00

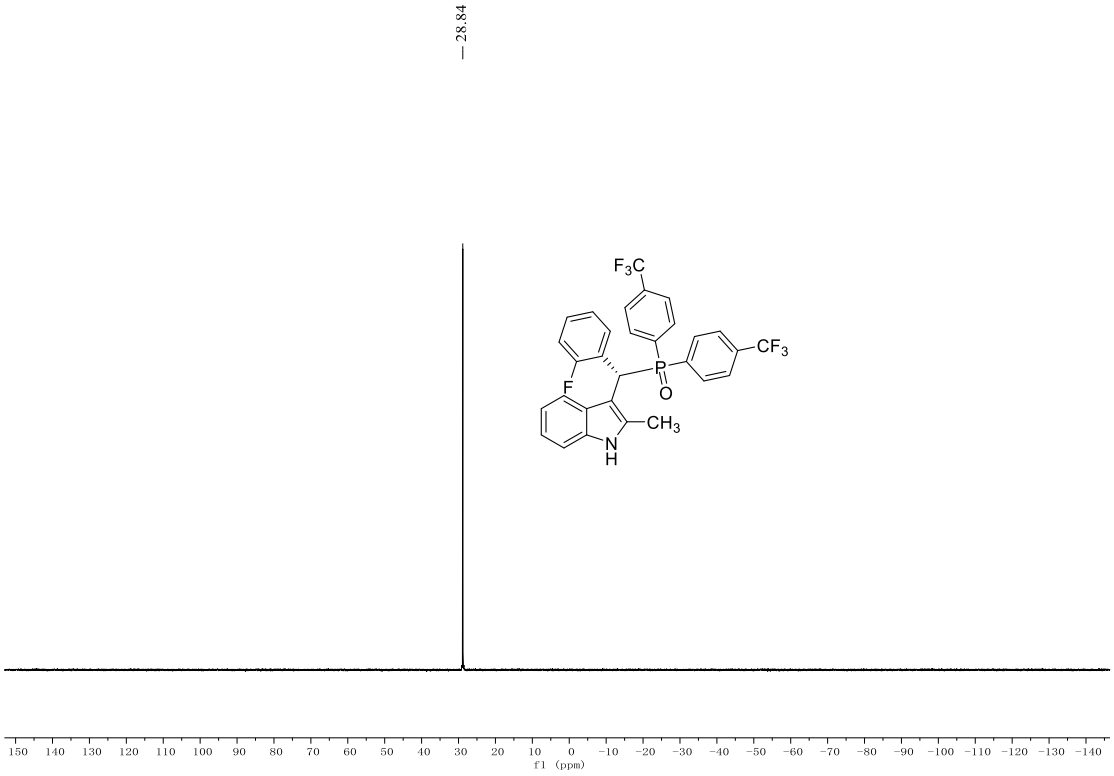
^{1}H NMR spectrum of compound of 3c



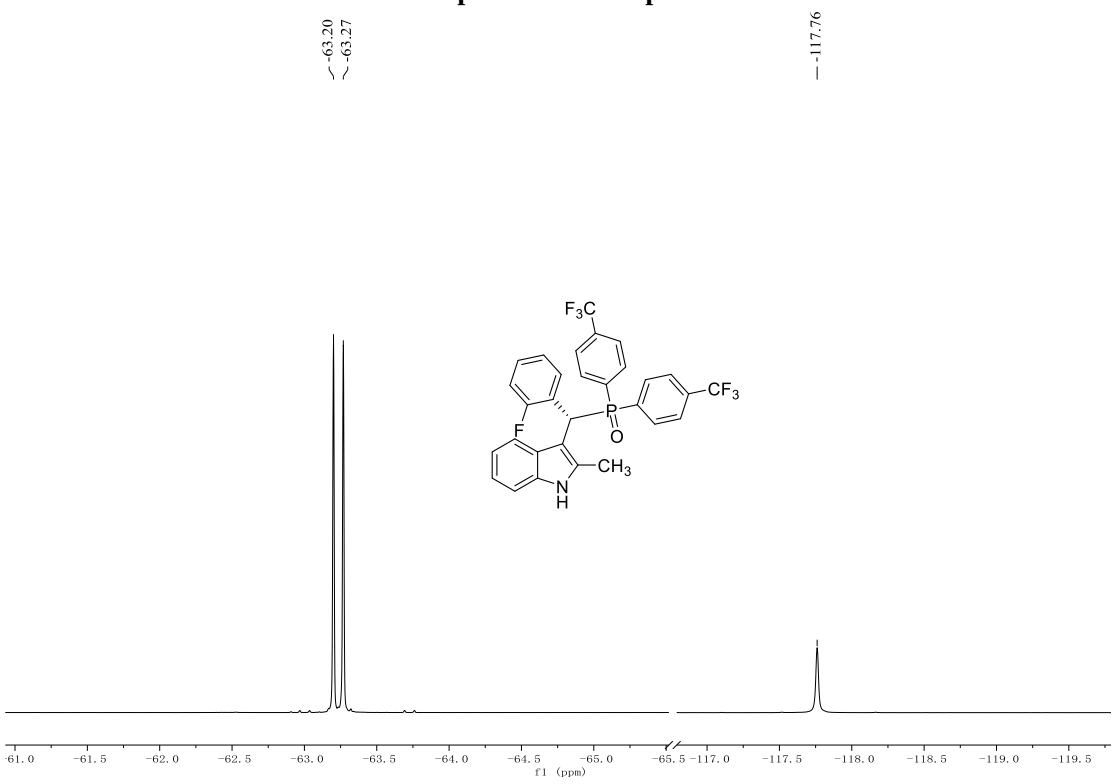
^{13}C NMR spectrum of compound of 3c



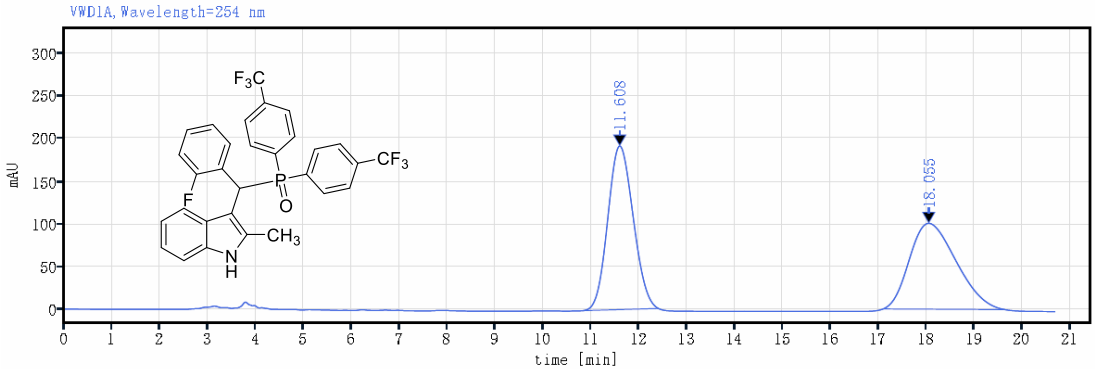
^{31}P NMR spectrum of compound of 3c



^{19}F NMR spectrum of compound of 3c

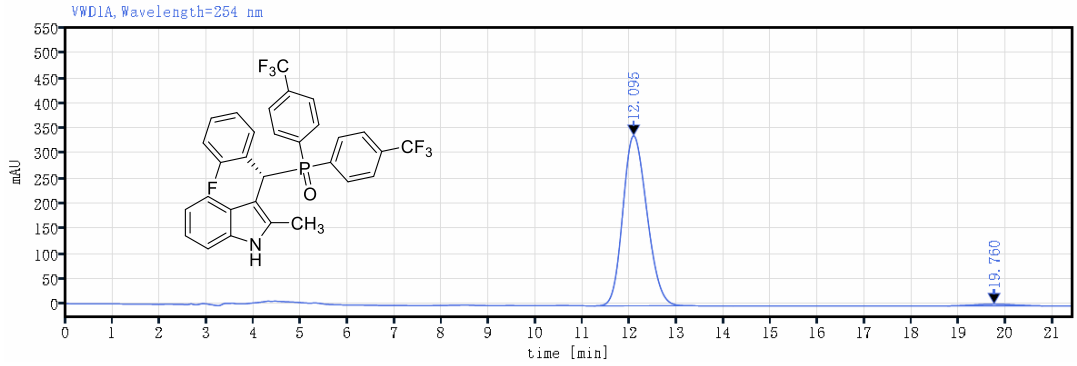


HPLC spectra of 3c



Detector VWD1A, Wavelength=254 nm

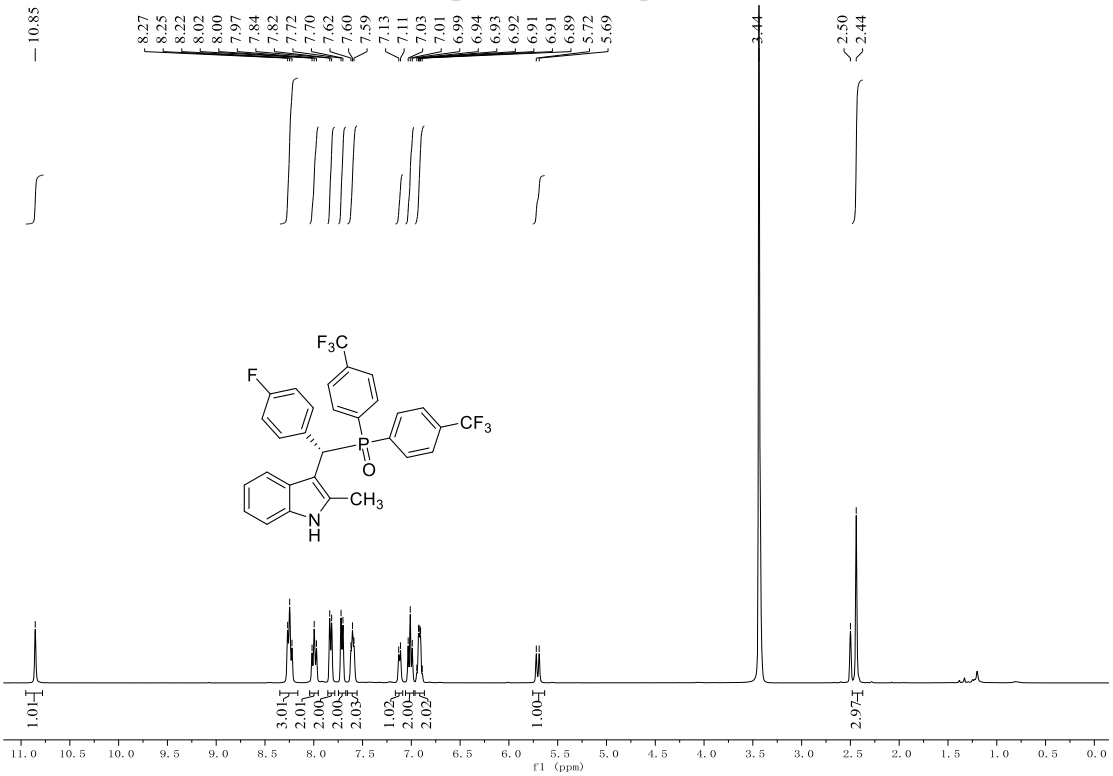
Peak	Ret.Time [min]	Area	Height	Area%
	11.608	7077.73	192.32	50.94
	18.055	6815.55	100.96	49.06
		13893.28		100.00



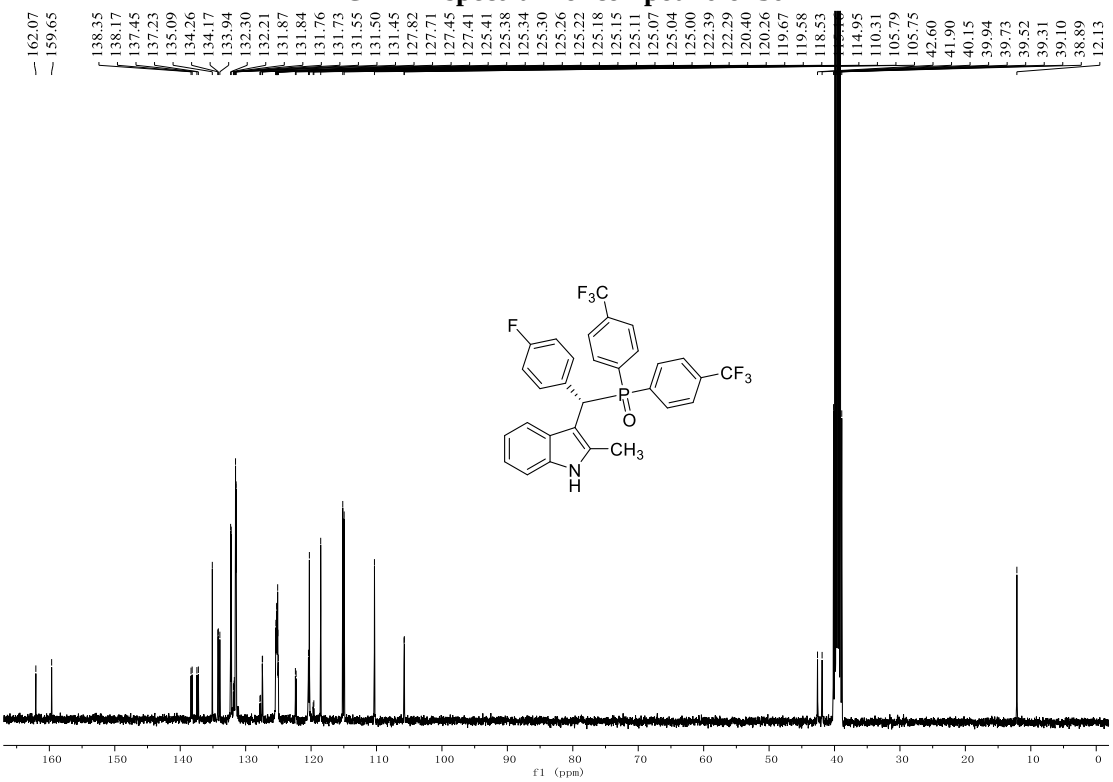
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	12.095	12038.19	338.44	98.41
	19.760	194.44	3.24	1.59
		12232.63		100.00

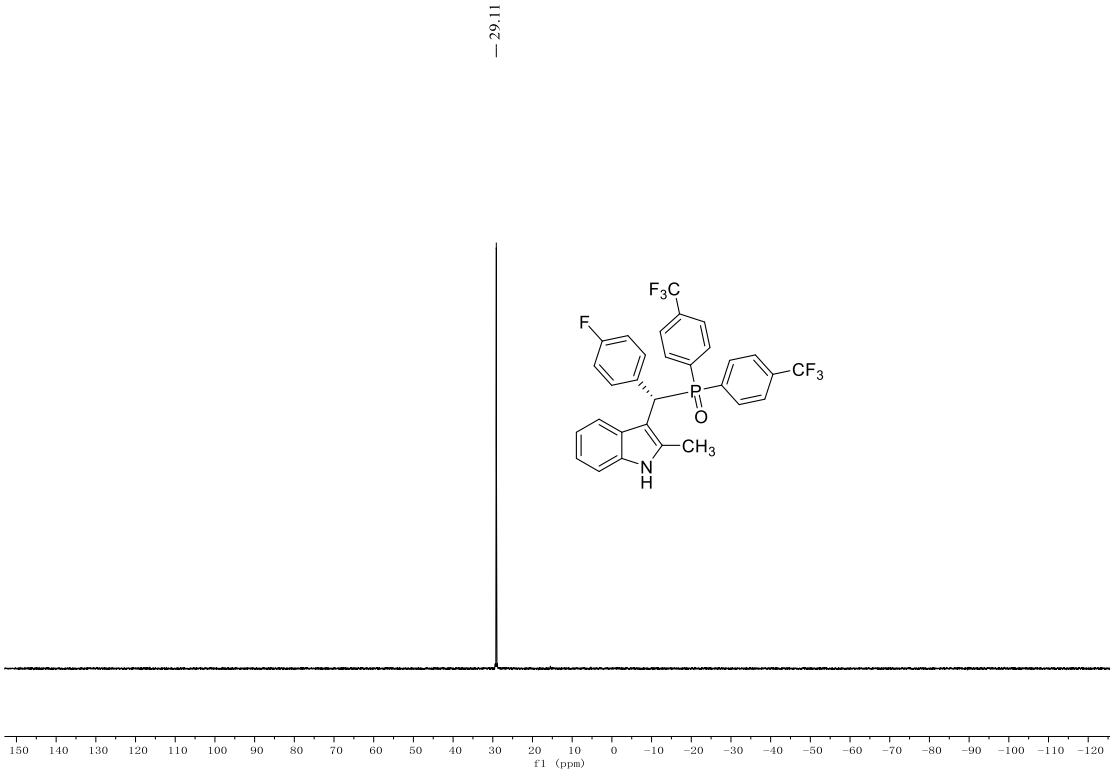
^{1}H NMR spectrum of compound of 3d



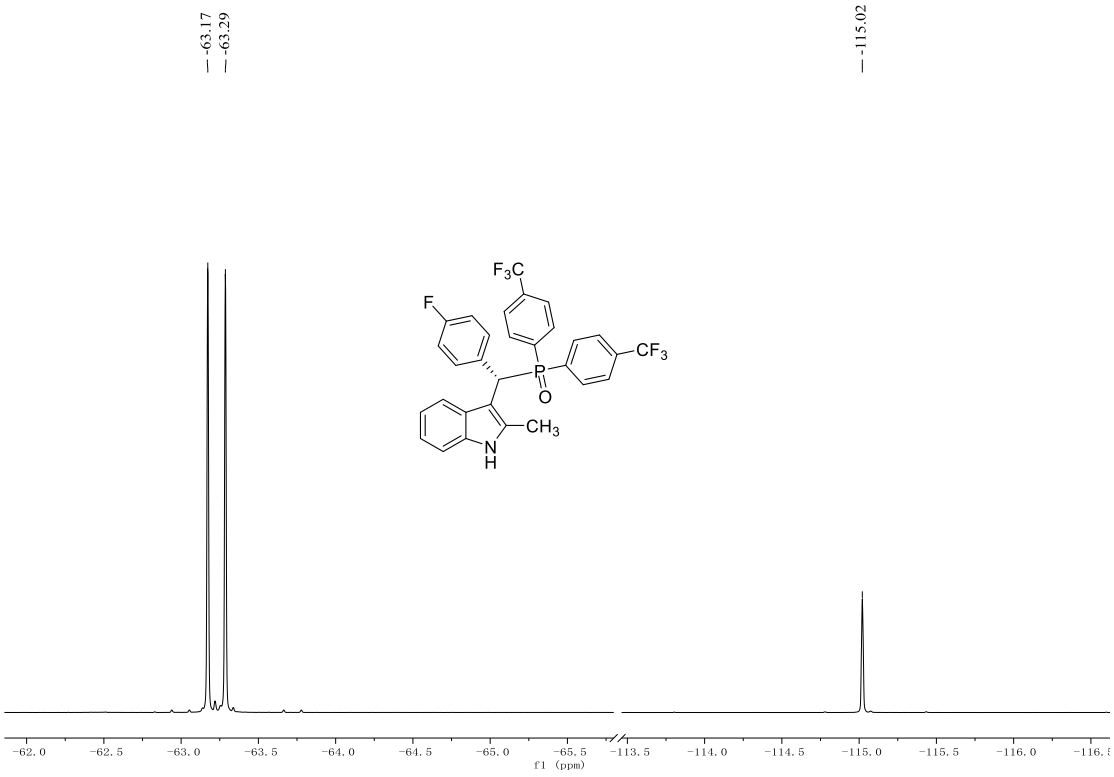
^{13}C NMR spectrum of compound of 3d



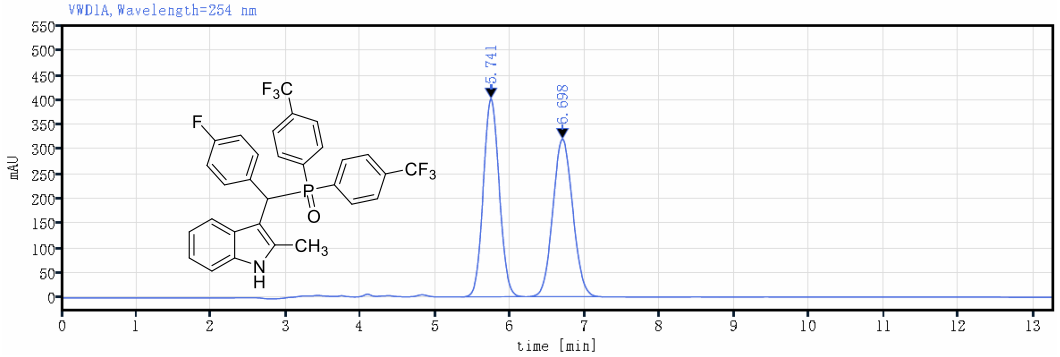
^{31}P NMR spectrum of compound of 3d



^{19}F NMR spectrum of compound of 3d

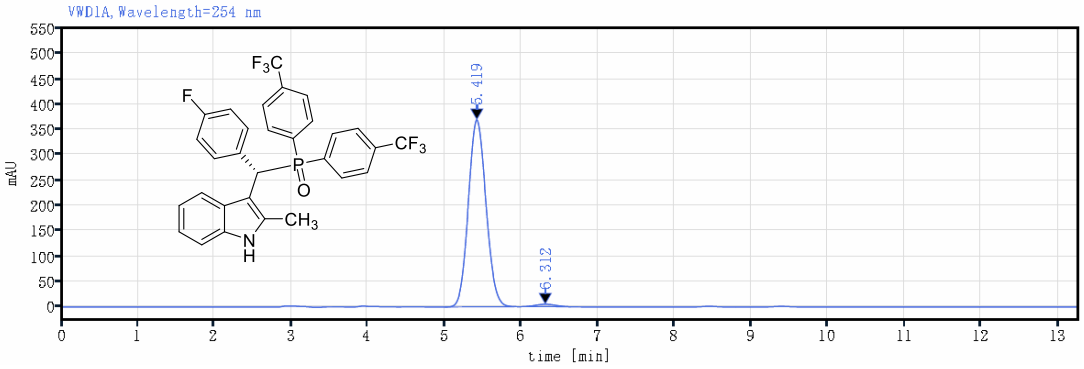


HPLC spectra of 3d



Detector VWD1A, Wavelength=254 nm

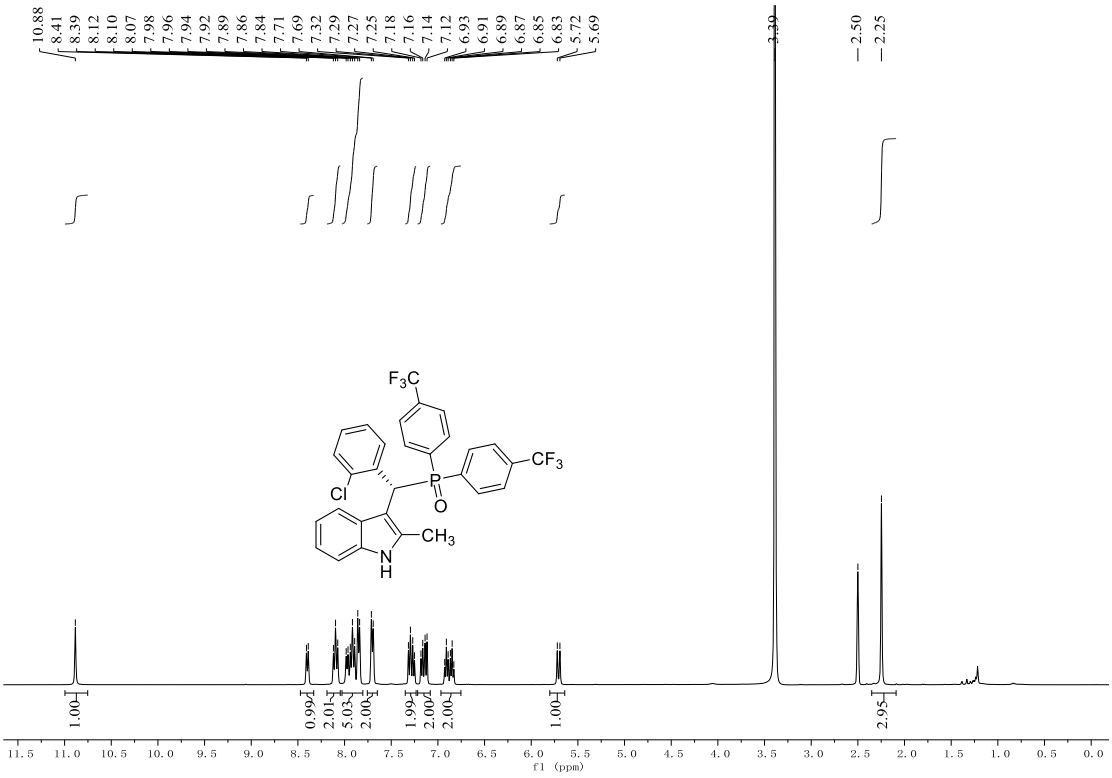
Peak	Ret.Time [min]	Area	Height	Area%
	5.741	5943.69	400.56	50.26
	6.698	5883.29	318.48	49.74
		11826.99		100.00



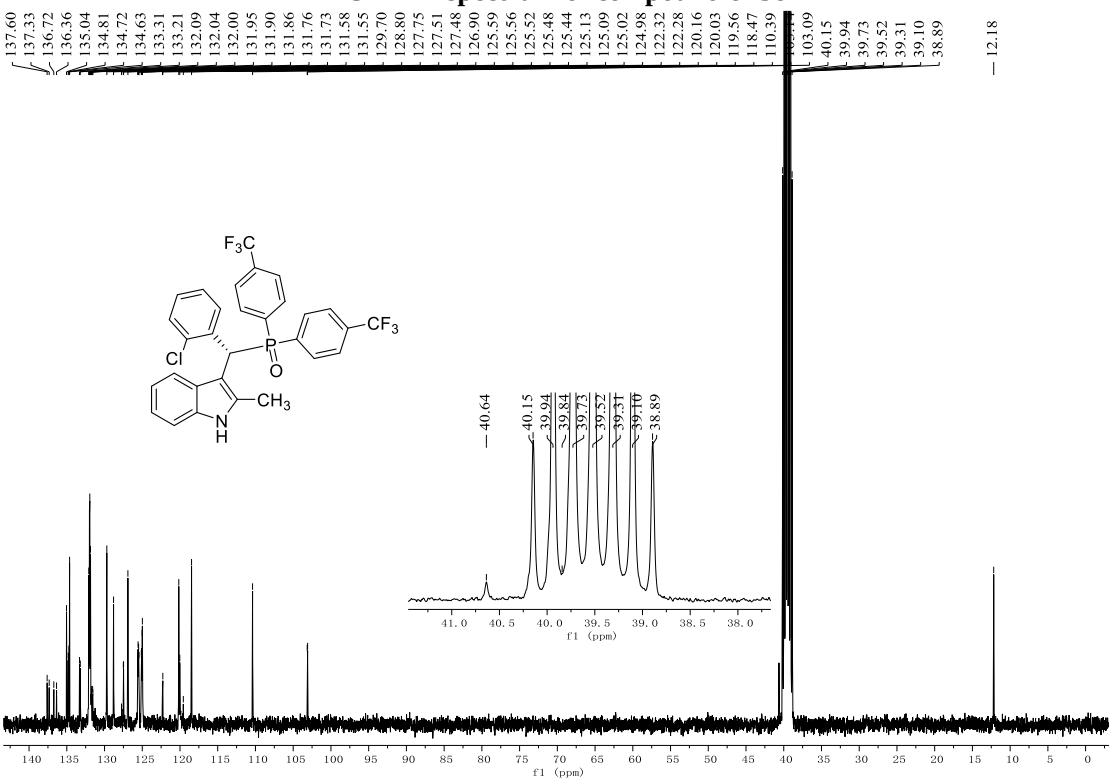
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	5.419	5908.84	369.02	98.64
	6.312	81.32	4.63	1.36
		5990.16		100.00

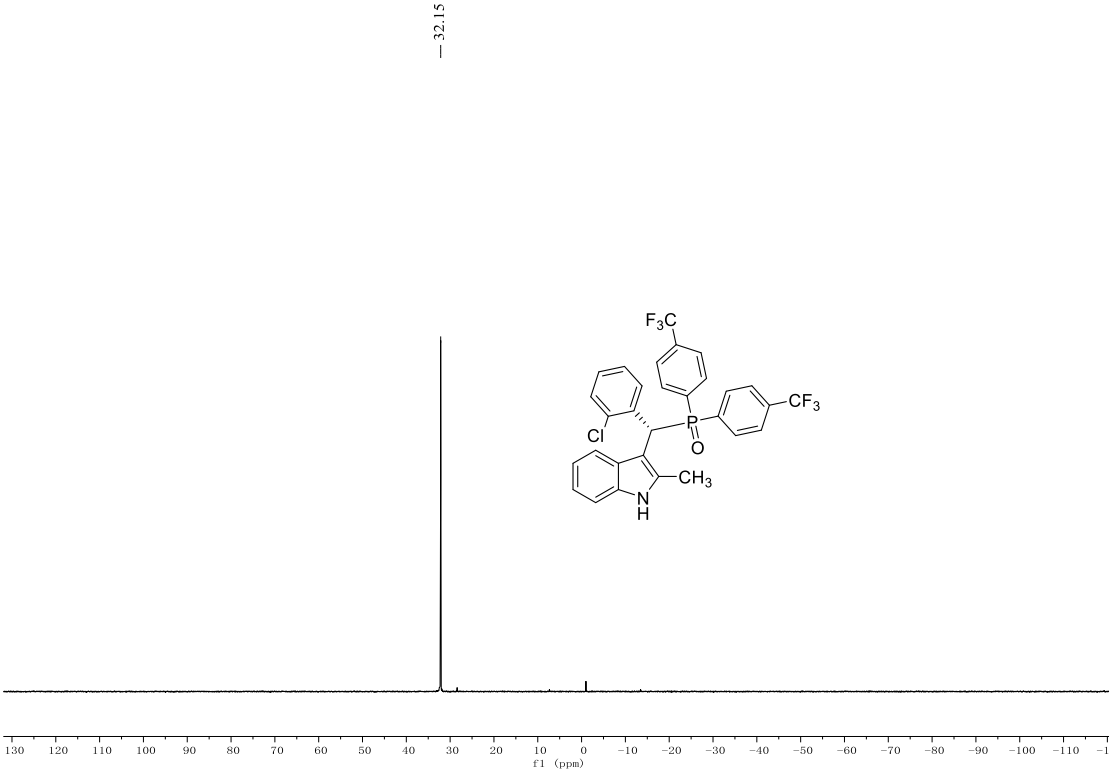
^{1}H NMR spectrum of compound of 3e



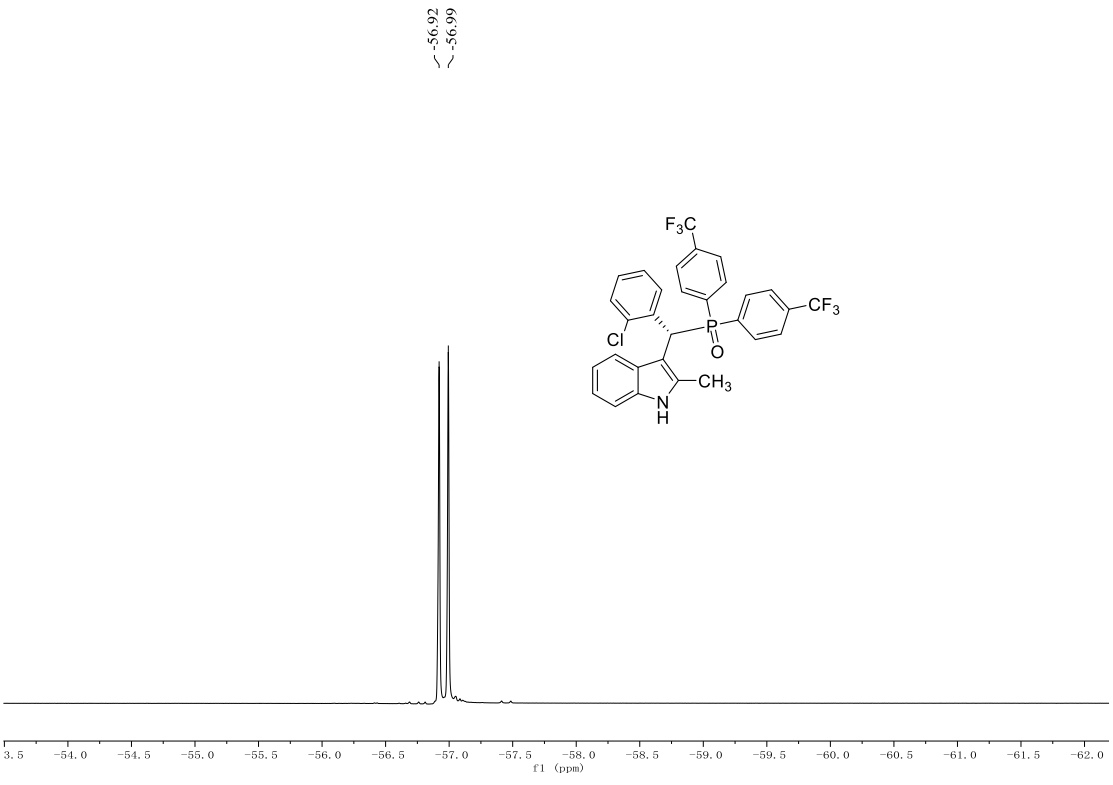
^{13}C NMR spectrum of compound of 3e



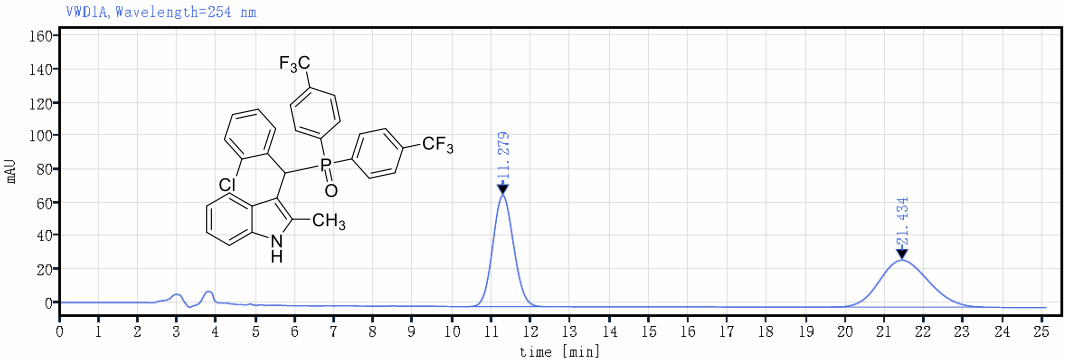
^{31}P NMR spectrum of compound of 3e



^{19}F NMR spectrum of compound of 3e

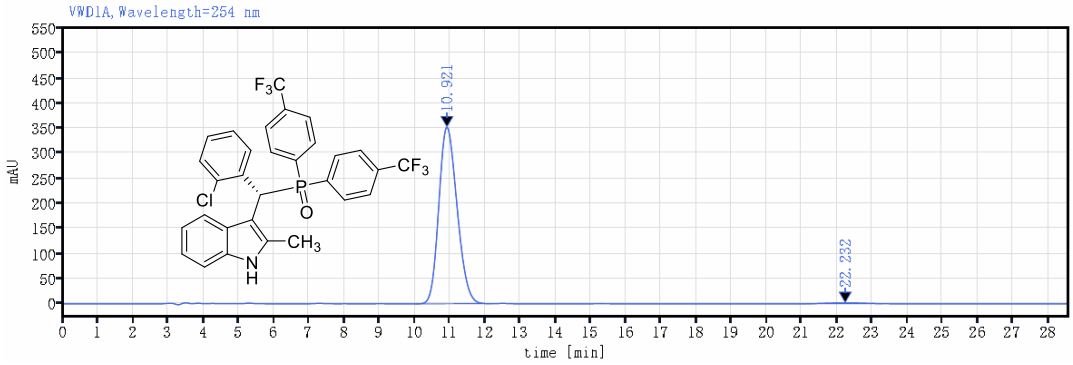


HPLC spectra of 3e



Detector VWD1A, Wavelength=254 nm

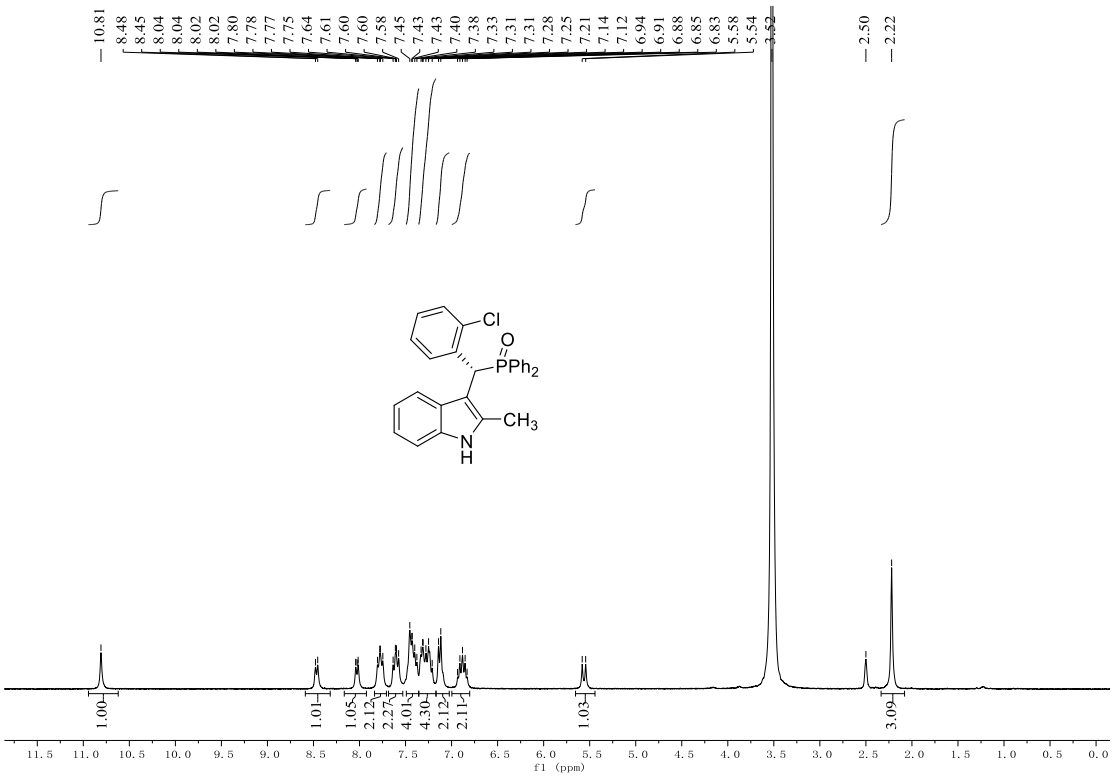
Peak	Ret.Time [min]	Area	Height	Area%
	11.279	2452.44	66.90	50.21
	21.434	2431.53	28.23	49.79
		4883.97		100.00



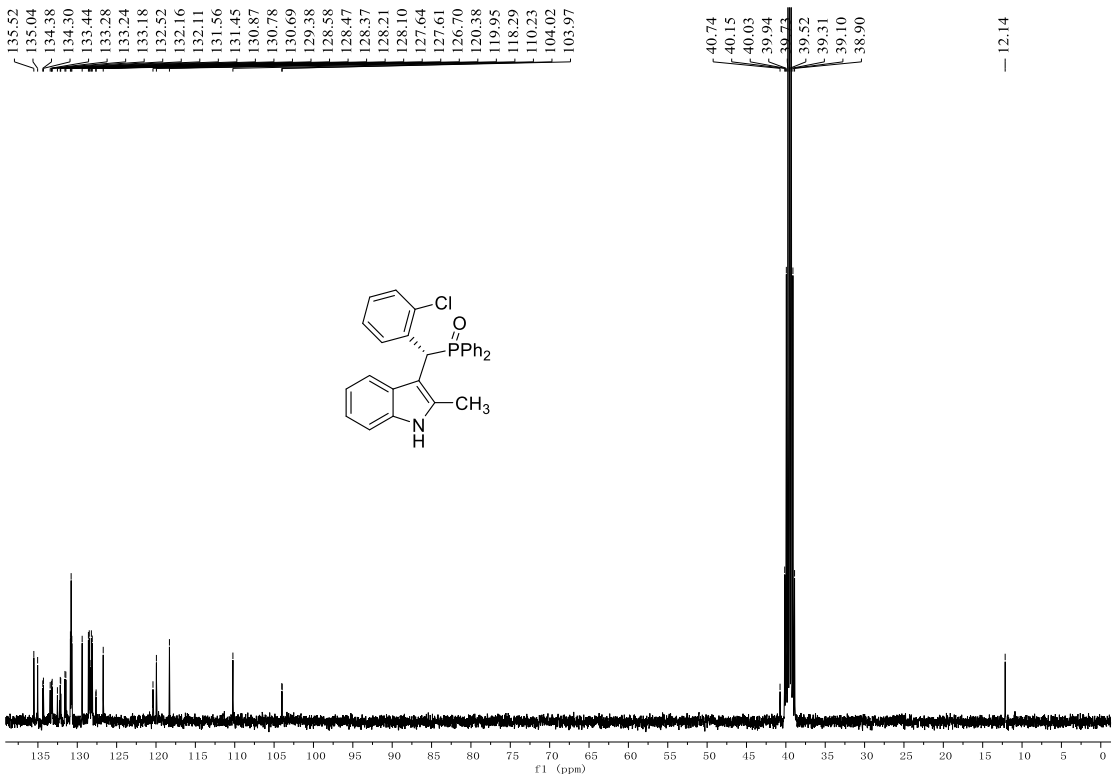
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	10.921	12689.30	352.10	99.08
	22.232	117.61	1.63	0.92
		12806.92		100.00

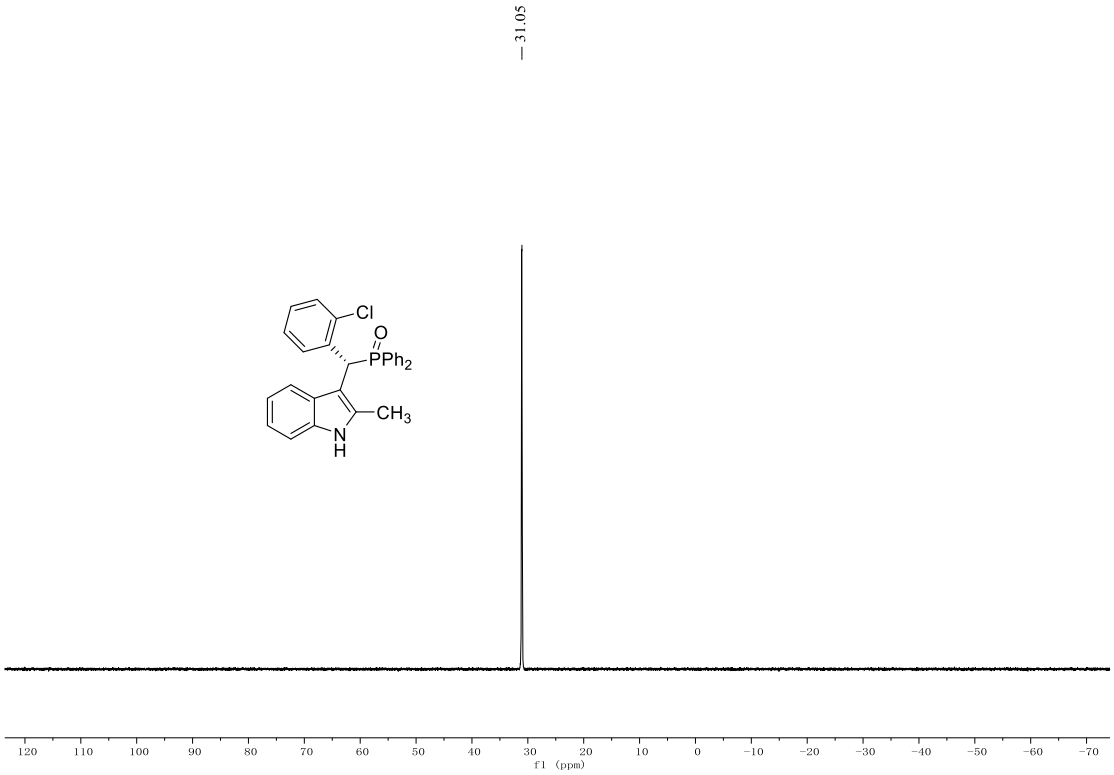
^{1}H NMR spectrum of compound of 3f



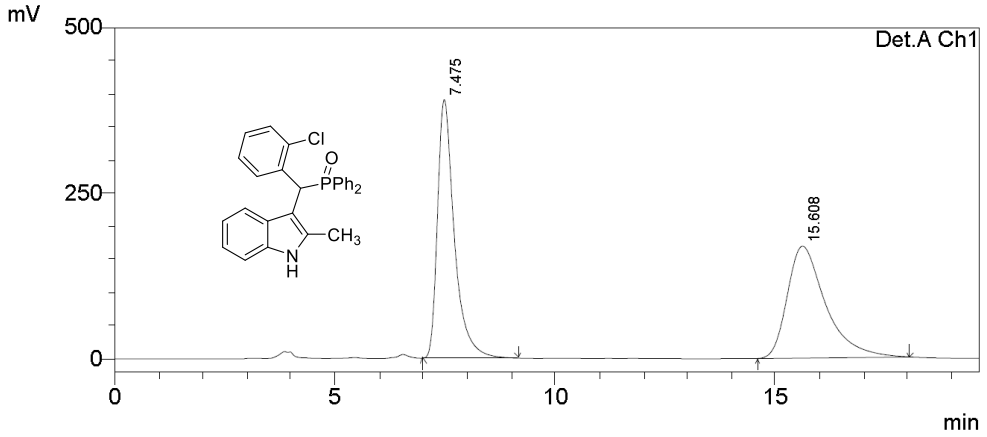
^{13}C NMR spectrum of compound of 3f



^{31}P NMR spectrum of compound of 3f



HPLC spectra of 3f

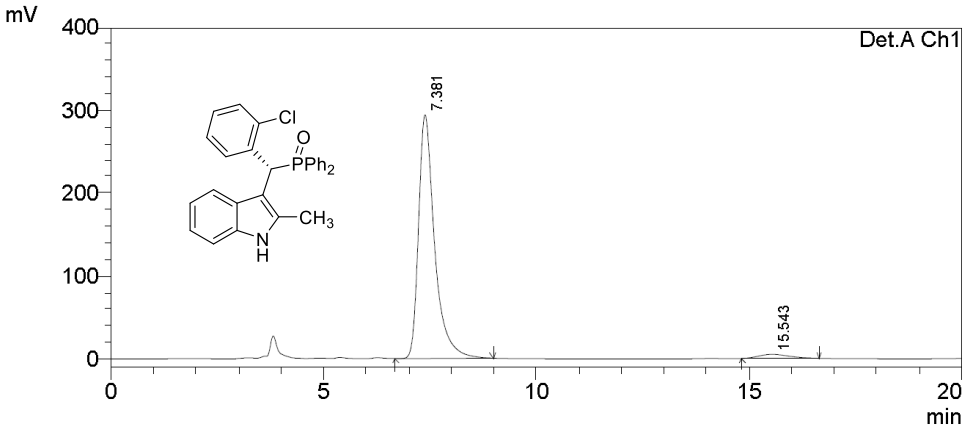


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.475	10358144	389612	50.371
2	15.608	10205365	168527	49.629
Total		20563508		100.000



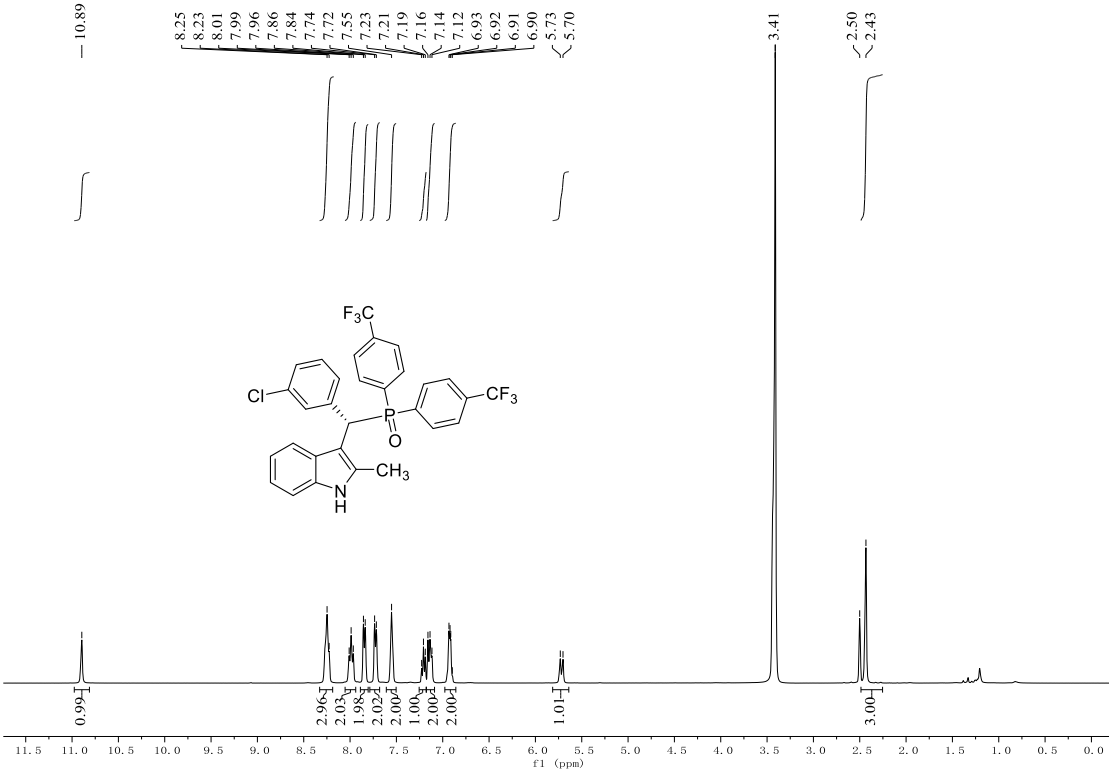
1 Det.A Ch1/254nm

PeakTable

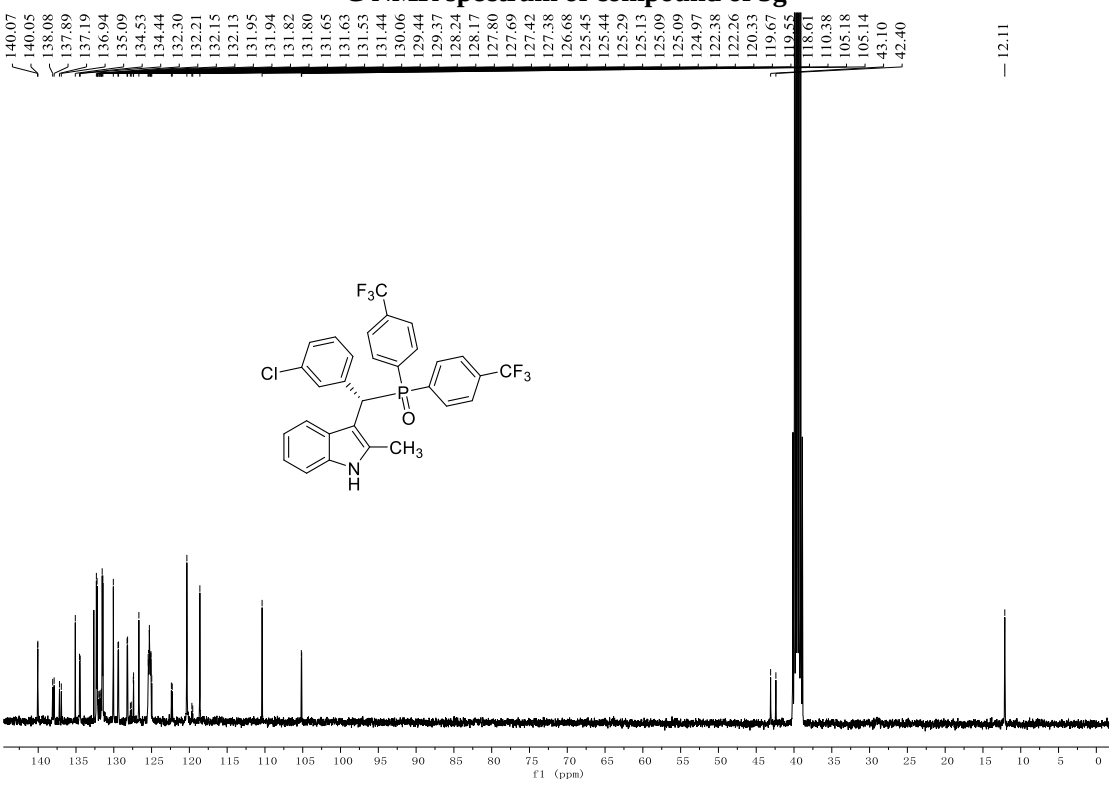
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.381	7710278	294015	96.915
2	15.543	245458	4860	3.085
Total		7955736		100.000

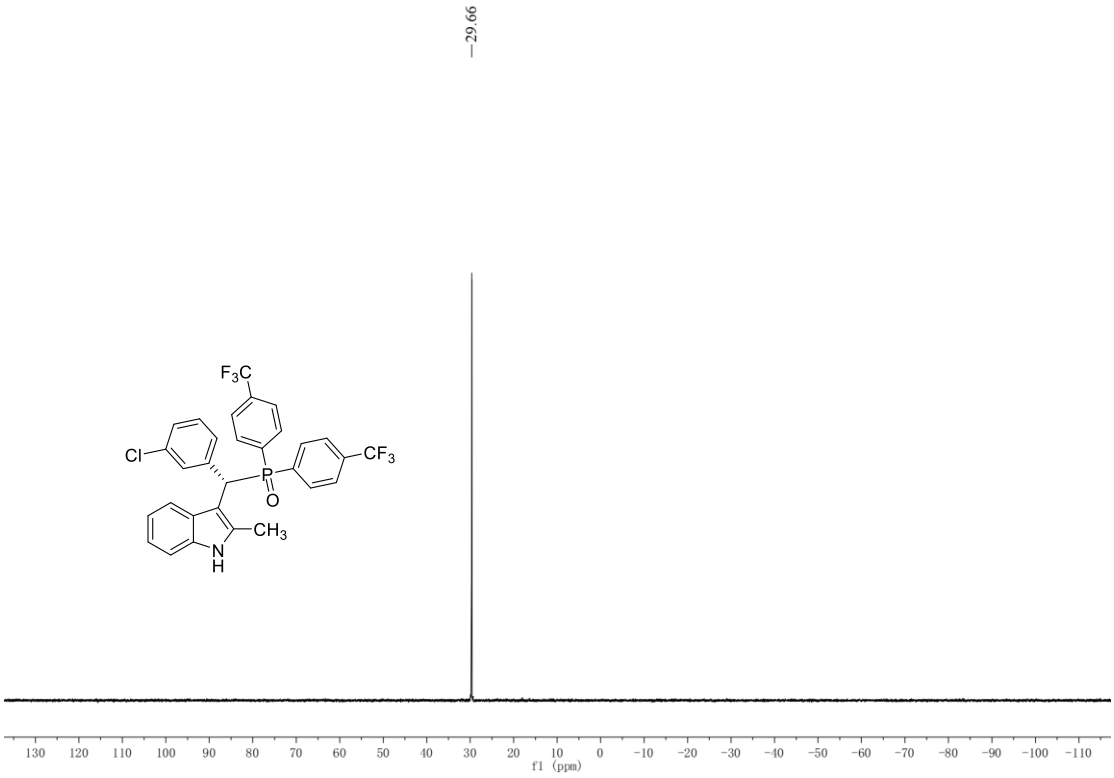
^{1}H NMR spectrum of compound of 3g



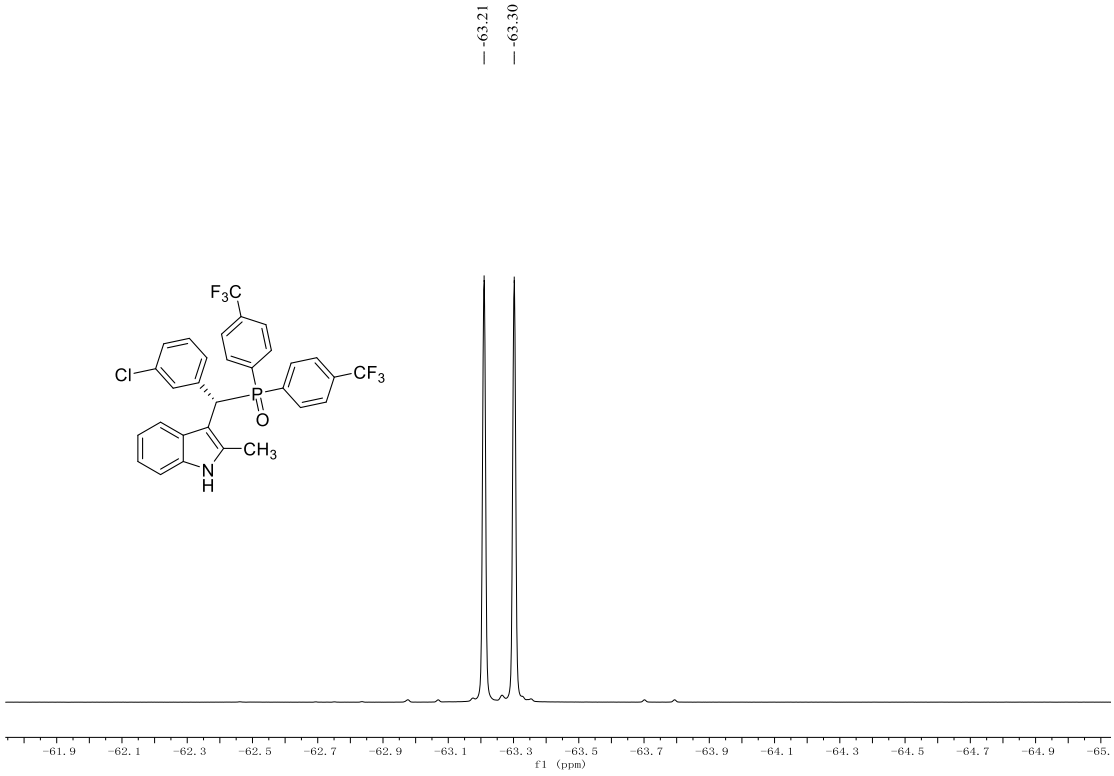
^{13}C NMR spectrum of compound of 3g



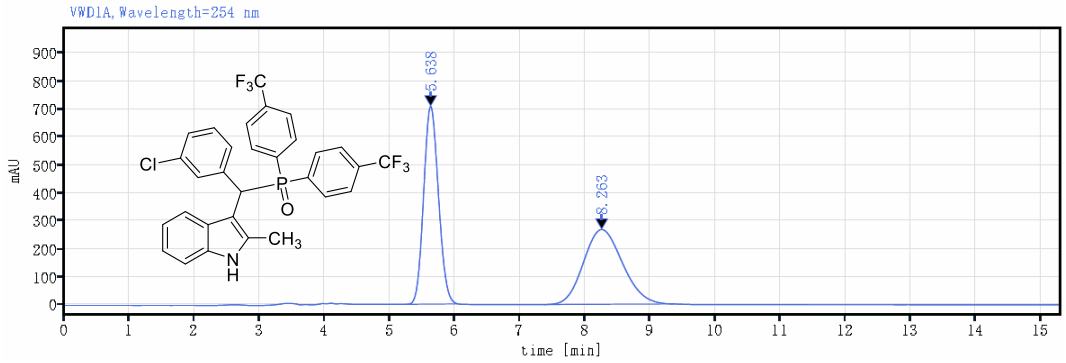
^{31}P NMR spectrum of compound of 3g



^{19}F NMR spectrum of compound of 3g

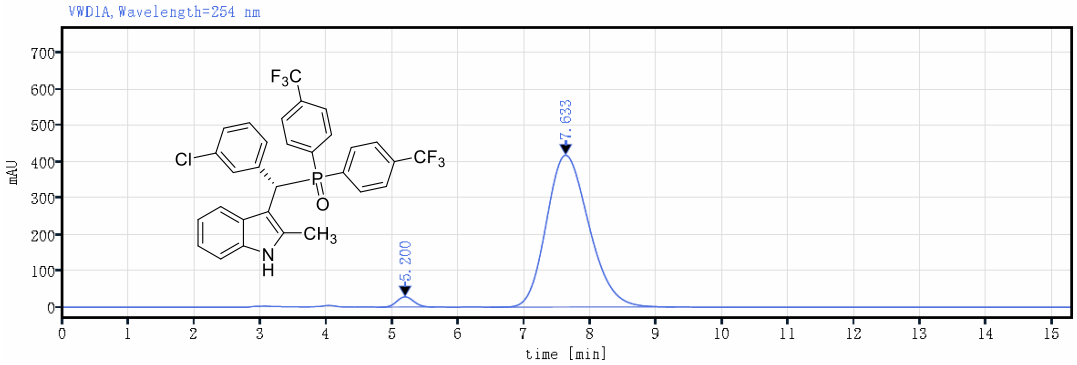


HPLC spectra of 3g



Detector VWD1A, Wavelength=254 nm

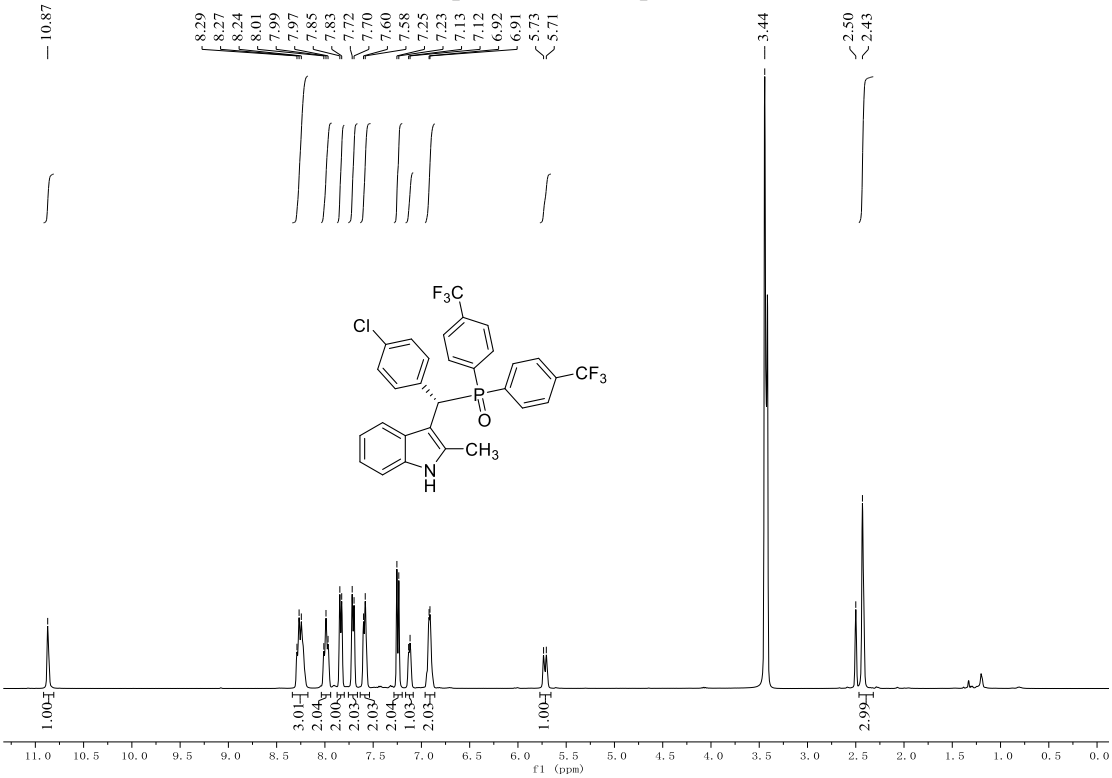
Peak	Ret.Time [min]	Area	Height	Area%
	5.638	11173.50	706.36	50.17
	8.263	11099.23	266.97	49.83
		22272.73		100.00



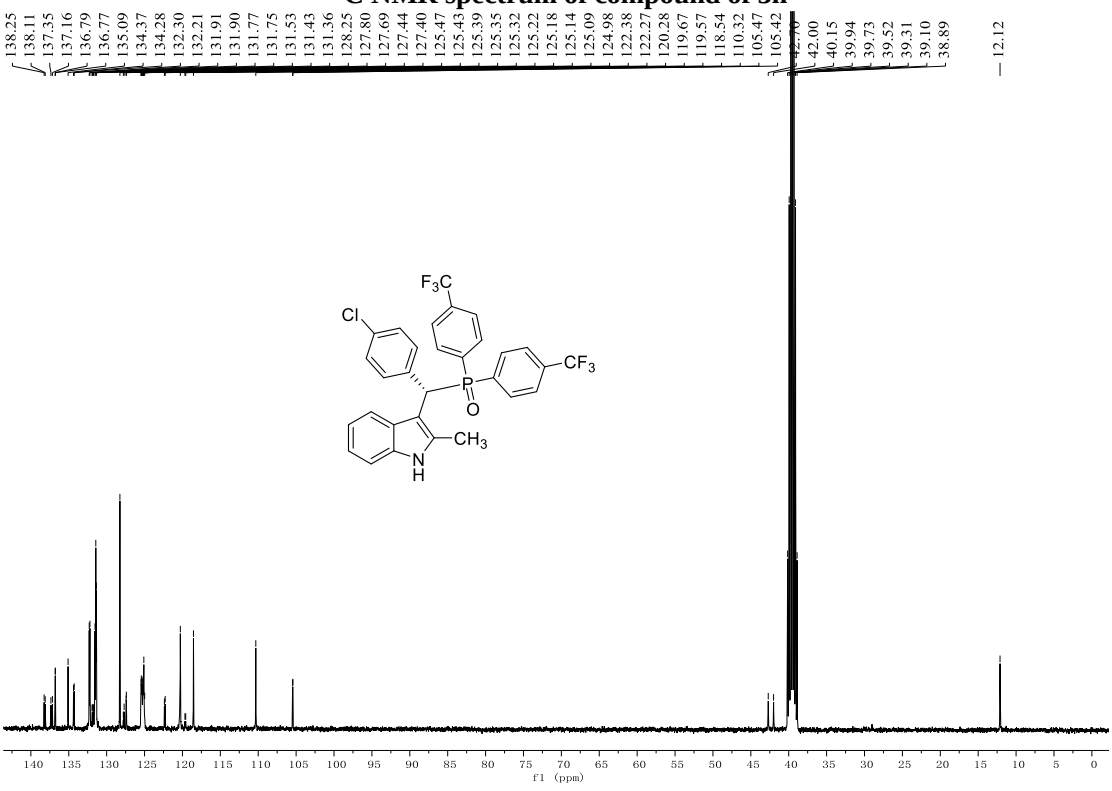
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	5.200	499.95	28.00	2.60
	7.633	18696.87	418.48	97.40
		19196.82		100.00

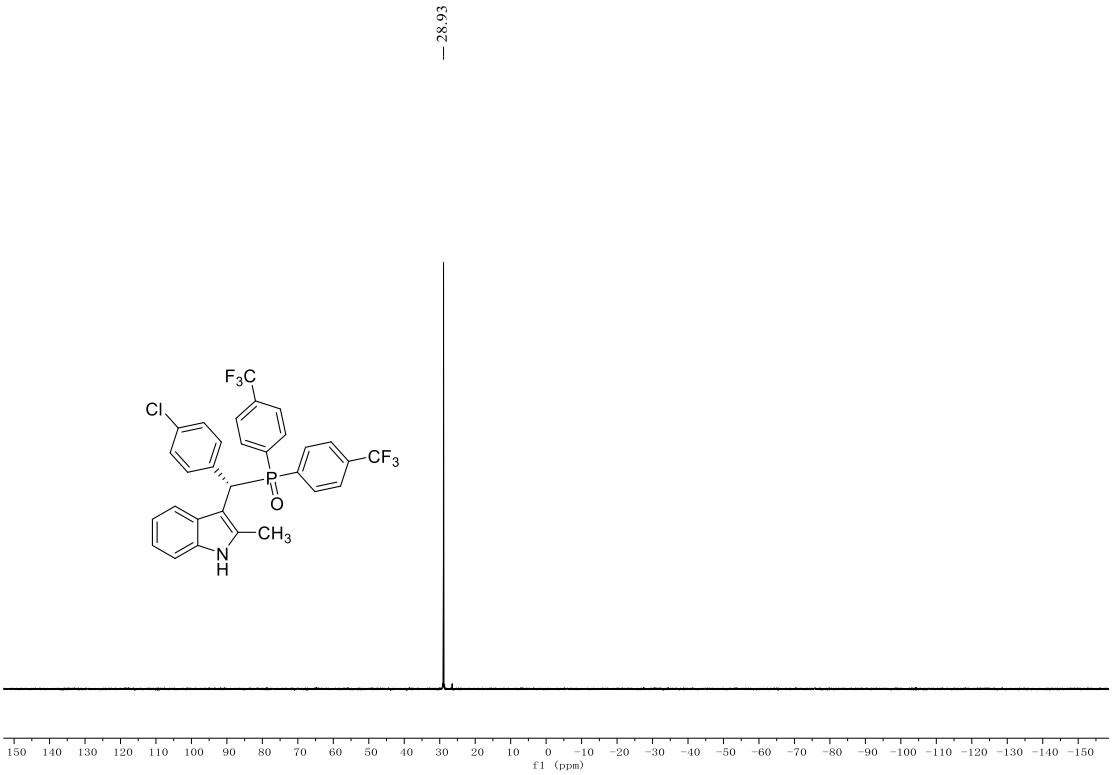
^{1}H NMR spectrum of compound of 3h



^{13}C NMR spectrum of compound of 3h

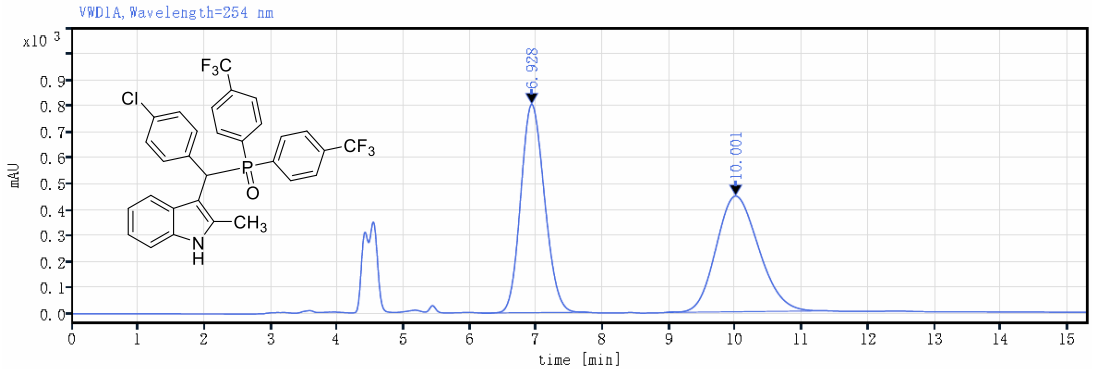


^{31}P NMR spectrum of compound of 3h



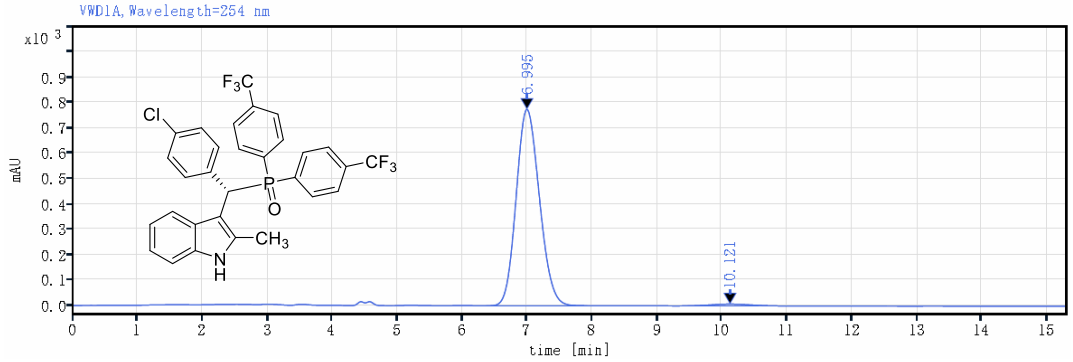
^{19}F NMR spectrum of compound of 3h

HPLC spectra of 3h



Detector VWD1A, Wavelength=254 nm

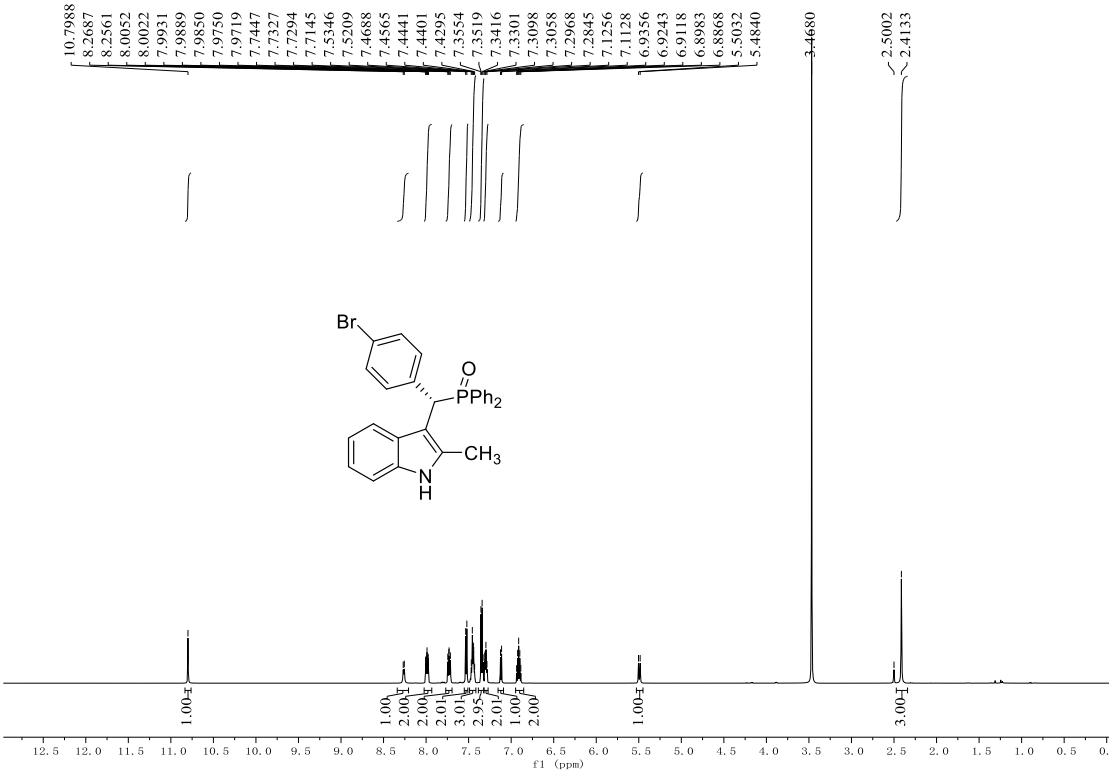
Peak	Ret.Time [min]	Area	Height	Area%
	6.928	20018.29	803.17	50.23
	10.001	19836.09	446.10	49.77
		39854.38		100.00



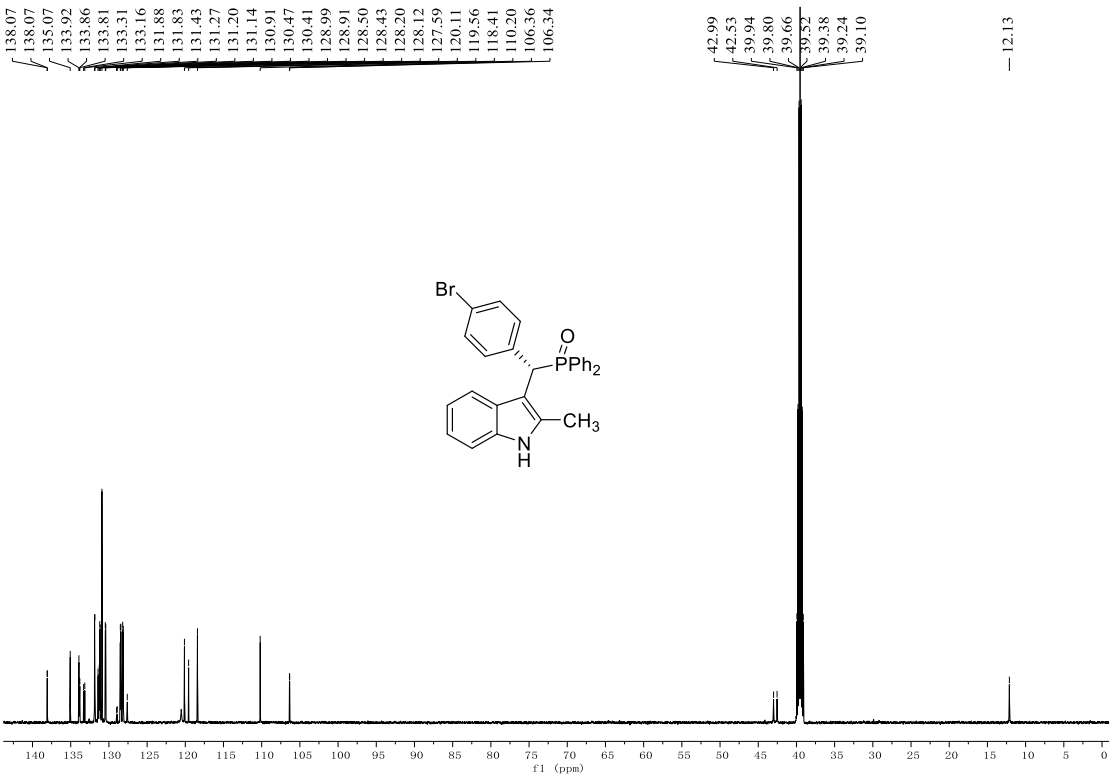
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	6.995	19282.07	775.14	98.69
	10.121	256.65	6.68	1.31
		19538.71		100.00

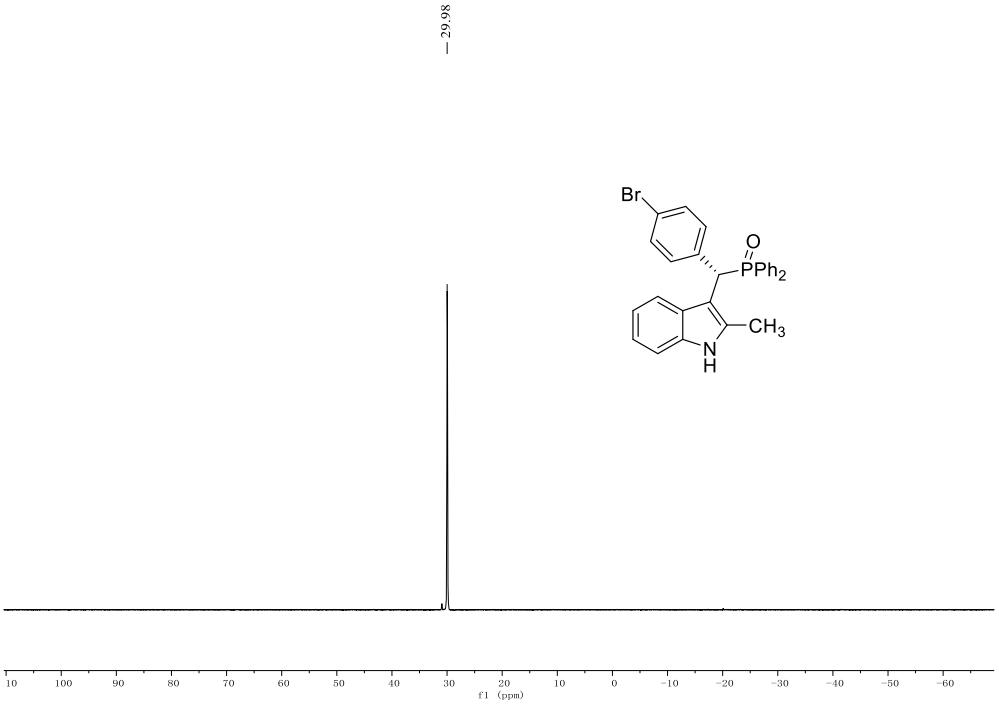
^{1}H NMR spectrum of compoundof 3i



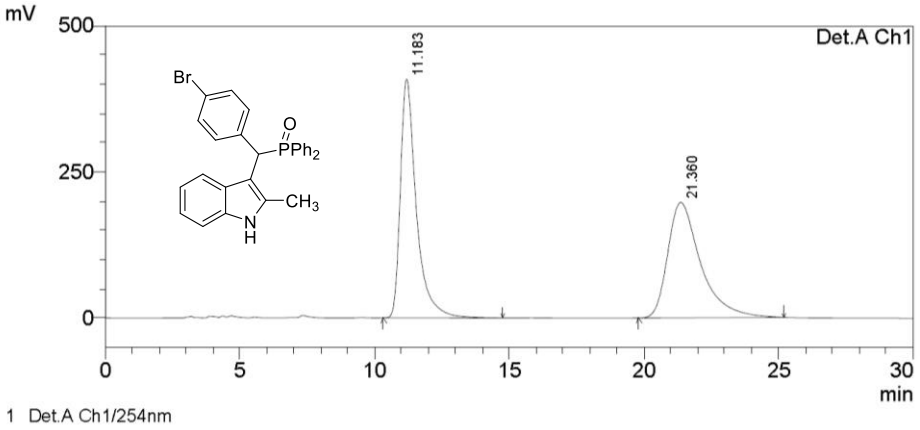
^{13}C NMR, ^{31}P NMR spectrum of compound of 3i



^{31}P NMR spectrum of compound of 3i



HPLC spectra of 3i

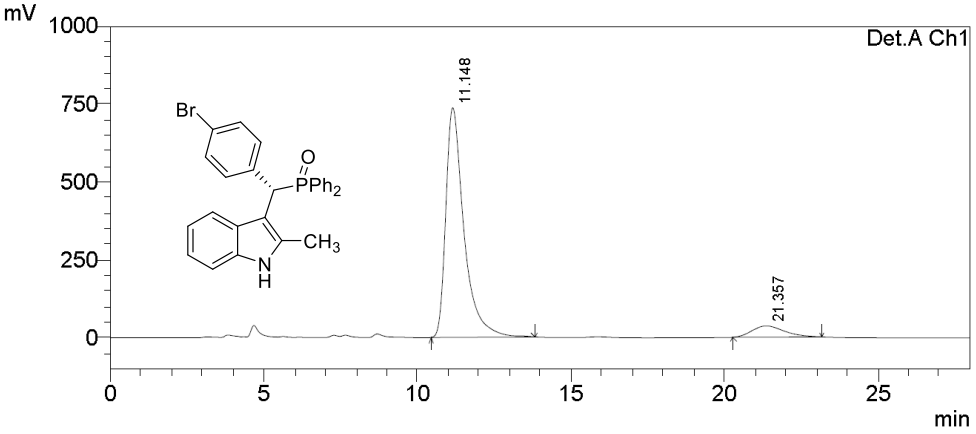


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	11.183	16759495	407762	50.003
2	21.360	16757151	197187	49.997
Total		33516646		100.000



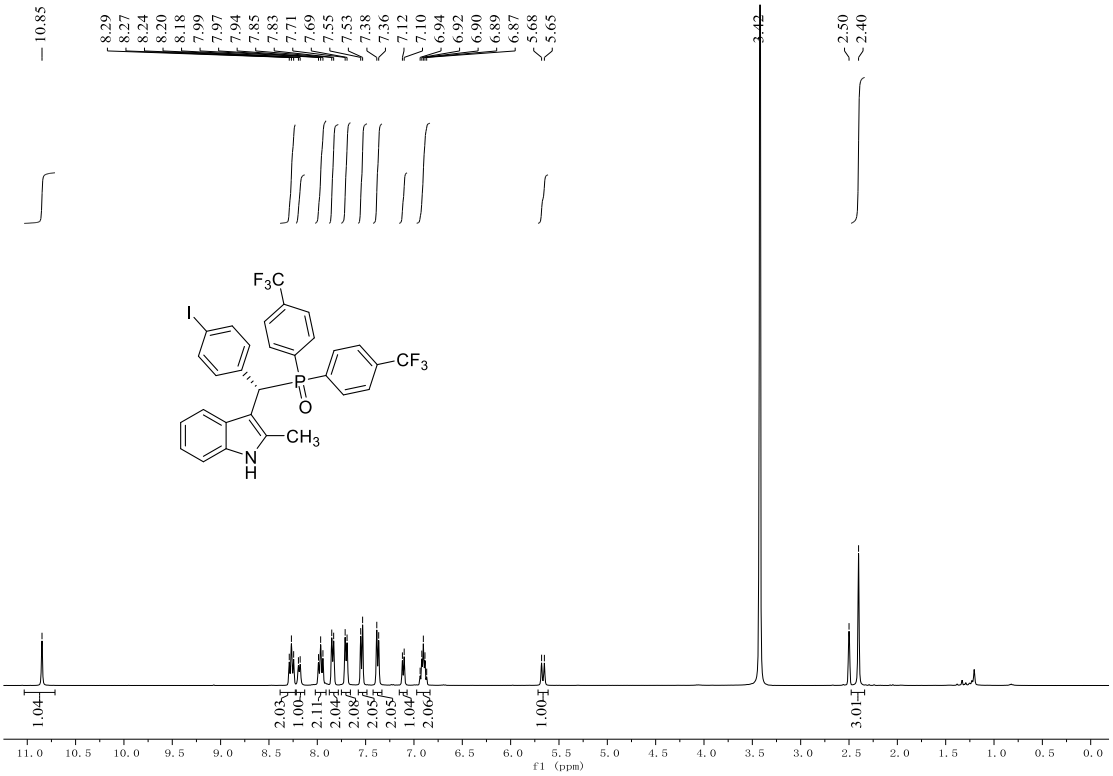
1 Det.A Ch1/254nm

PeakTable

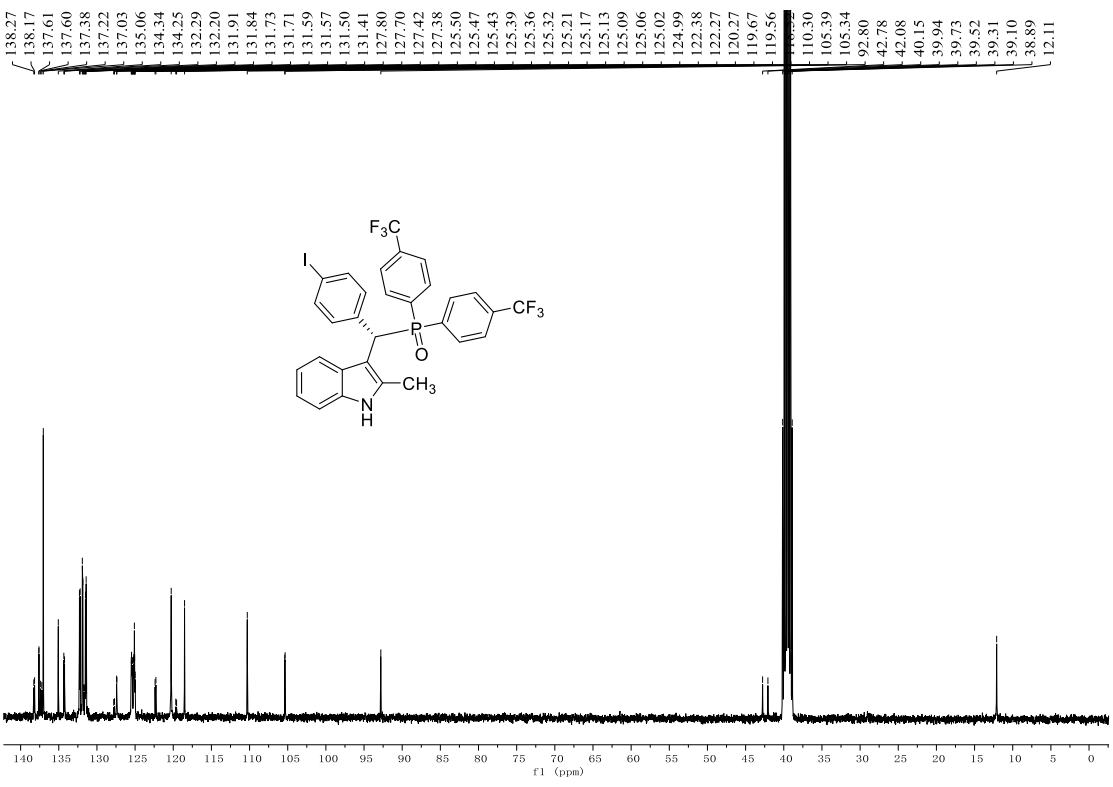
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	11.148	30379044	736268	92.033
2	21.357	2629828	36006	7.967
Total		33008871		100.000

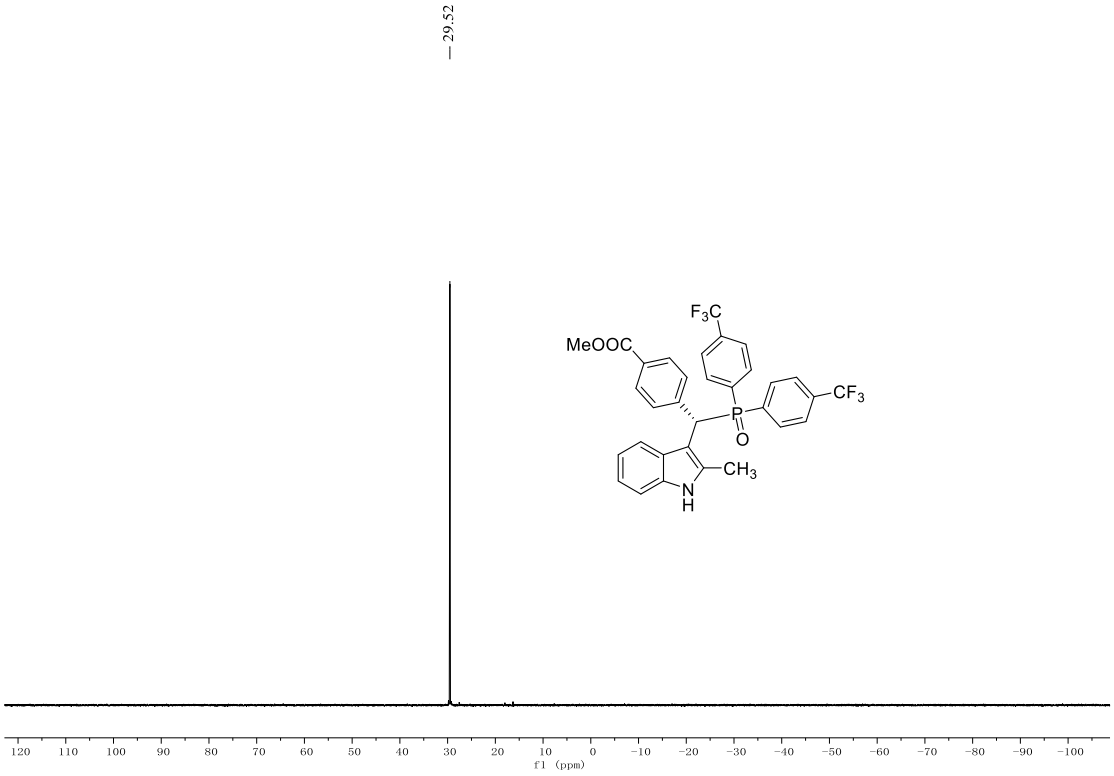
^{1}H NMR spectrum of compound of 3j



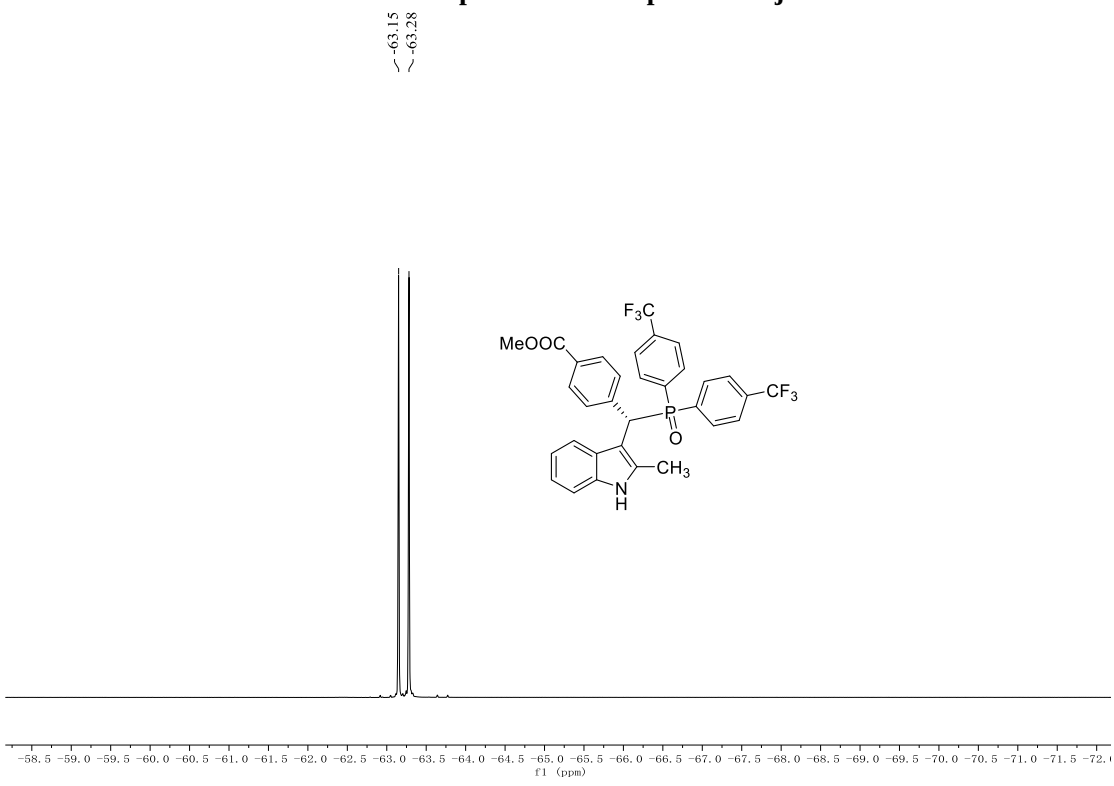
^{13}C NMR spectrum of compound of 3j



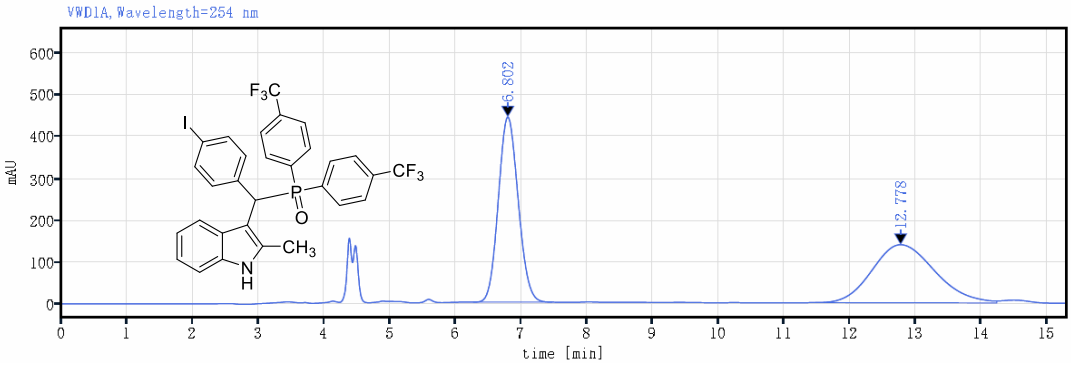
^{31}P NMR spectrum of compound of 3j



^{19}F NMR spectrum of compound of 3j

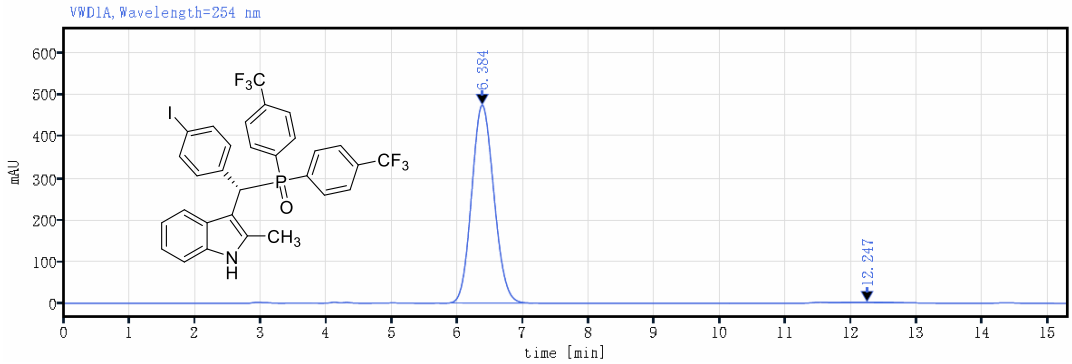


HPLC spectra of 3j



Detector VWD1A, Wavelength=254 nm

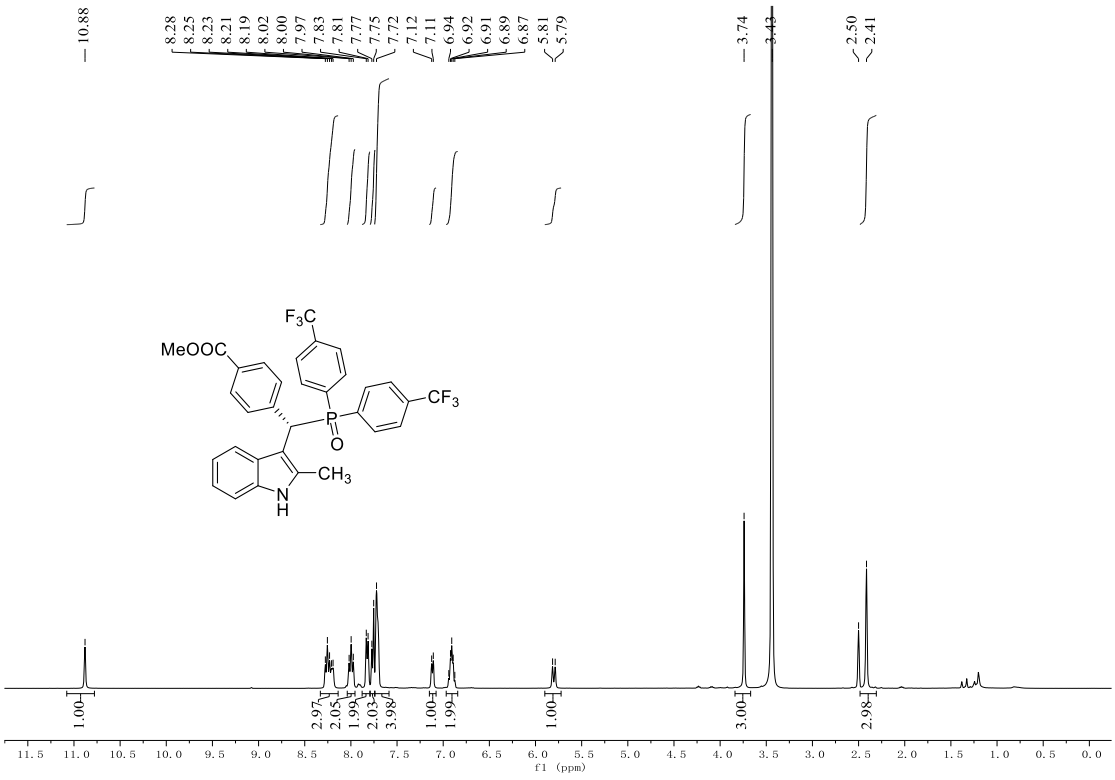
Peak	Ret.Time [min]	Area	Height	Area%
	6.802	9310.46	443.71	50.24
	12.778	9219.89	139.16	49.76
		18530.35		100.00



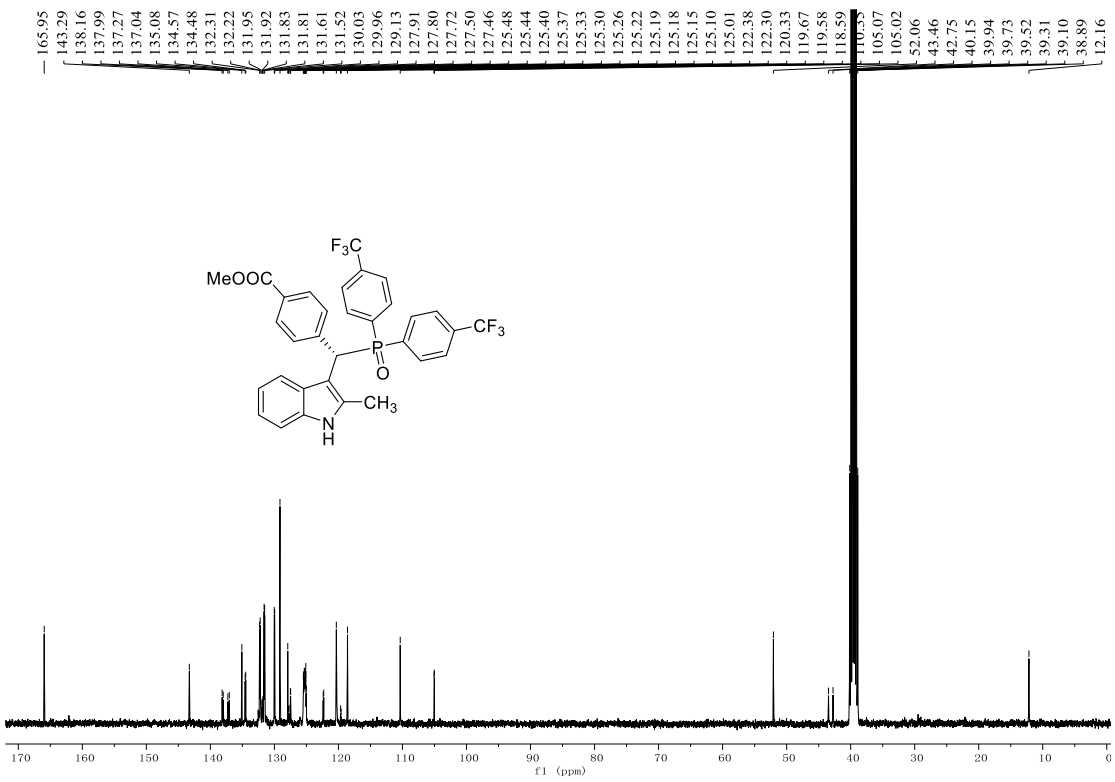
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	6.384	11166.38	475.56	99.48
	12.247	57.88	1.36	0.52
		11224.25		100.00

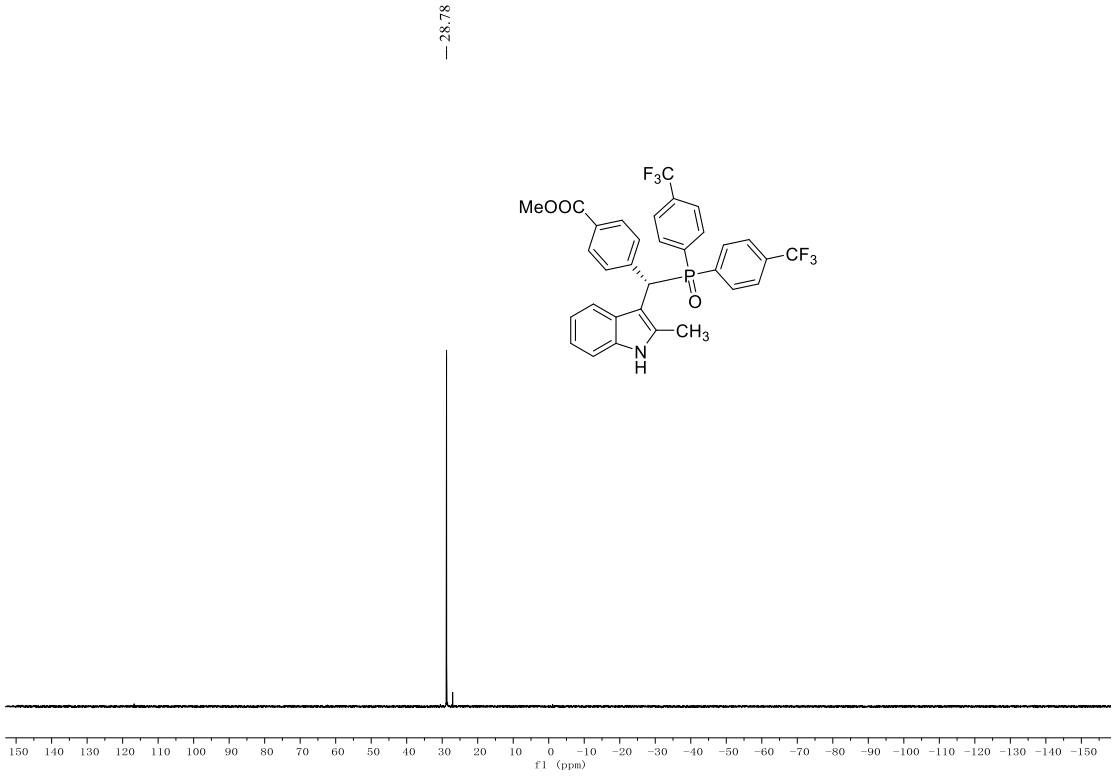
^{1}H NMR spectrum of compound of 3k



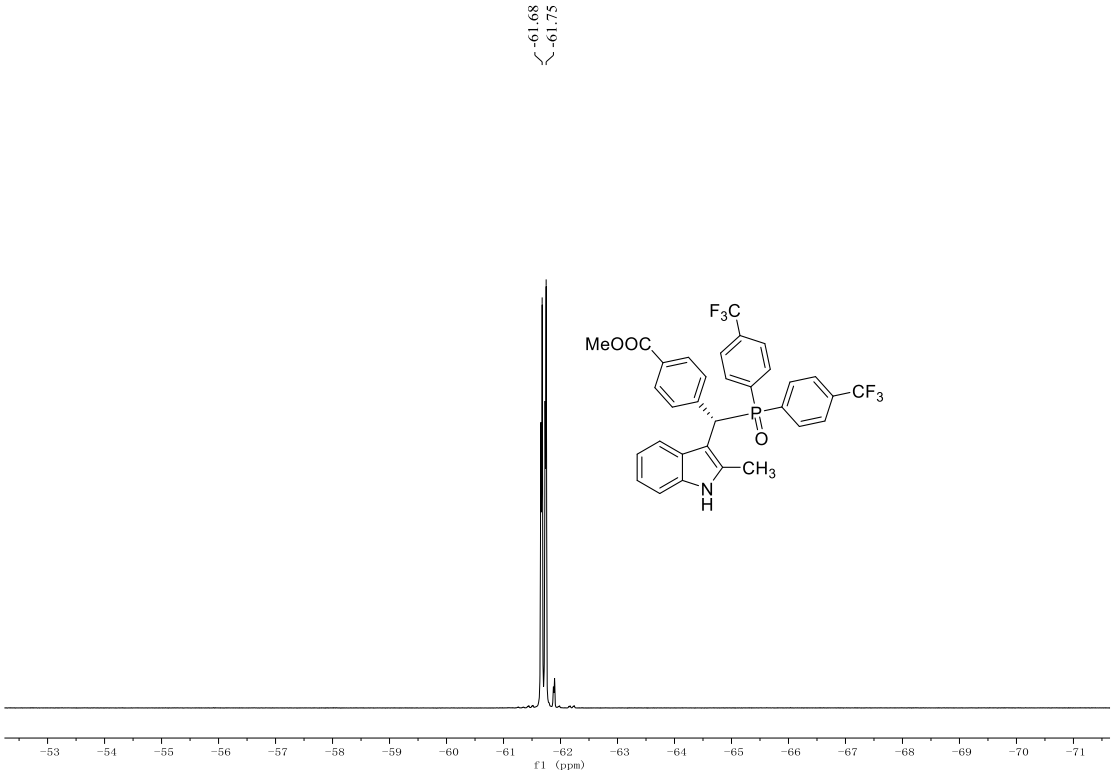
^{13}C NMR spectrum of compound of 3k



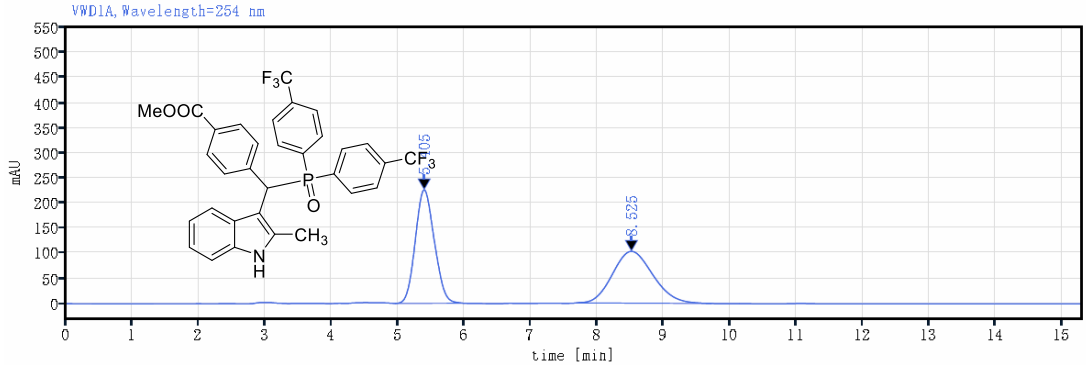
^{31}P NMR spectrum of compound of 3k



^{19}F NMR spectrum of compound of 3k

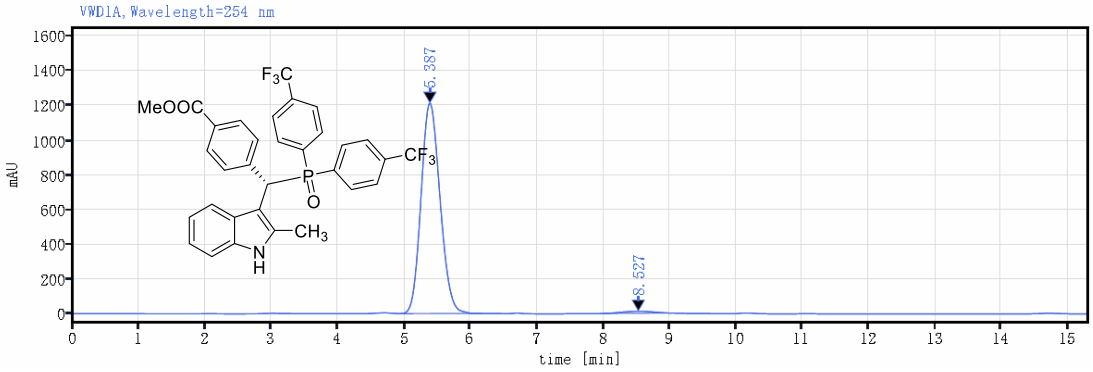


HPLC spectra of 3k



Detector VWD1A, Wavelength=254 nm

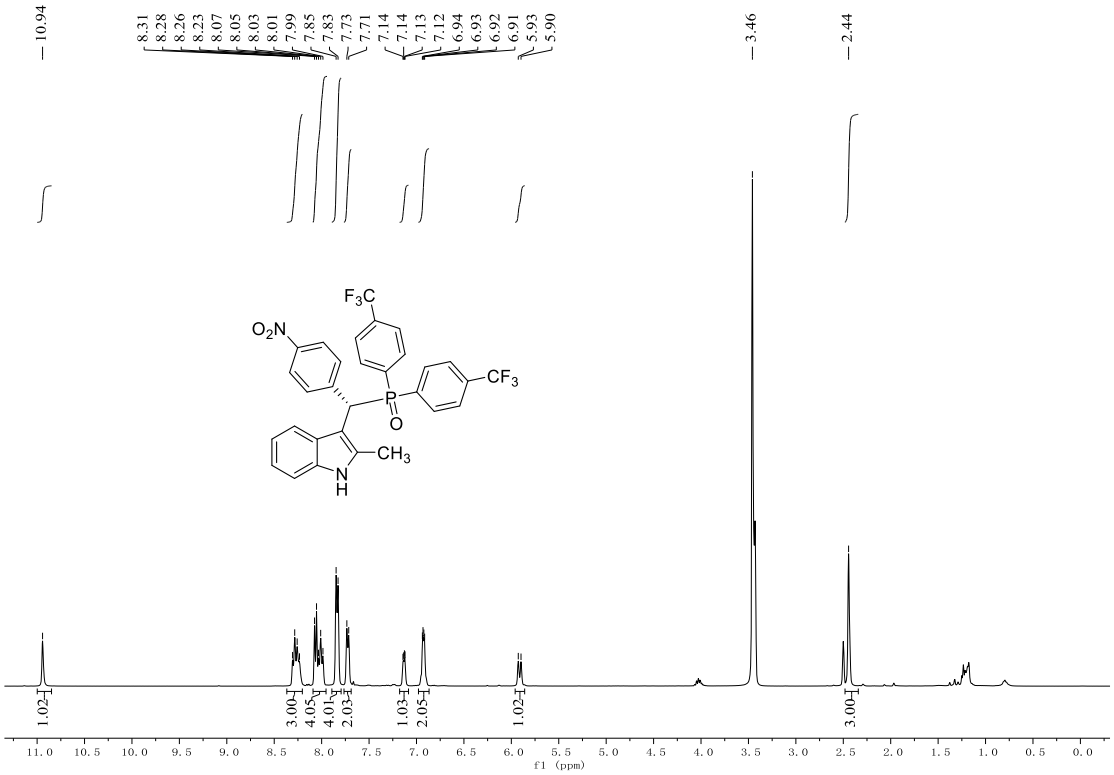
Peak	Ret.Time [min]	Area	Height	Area%
	5.405	4494.04	226.05	50.79
	8.525	4353.49	103.23	49.21
		8847.52		100.00



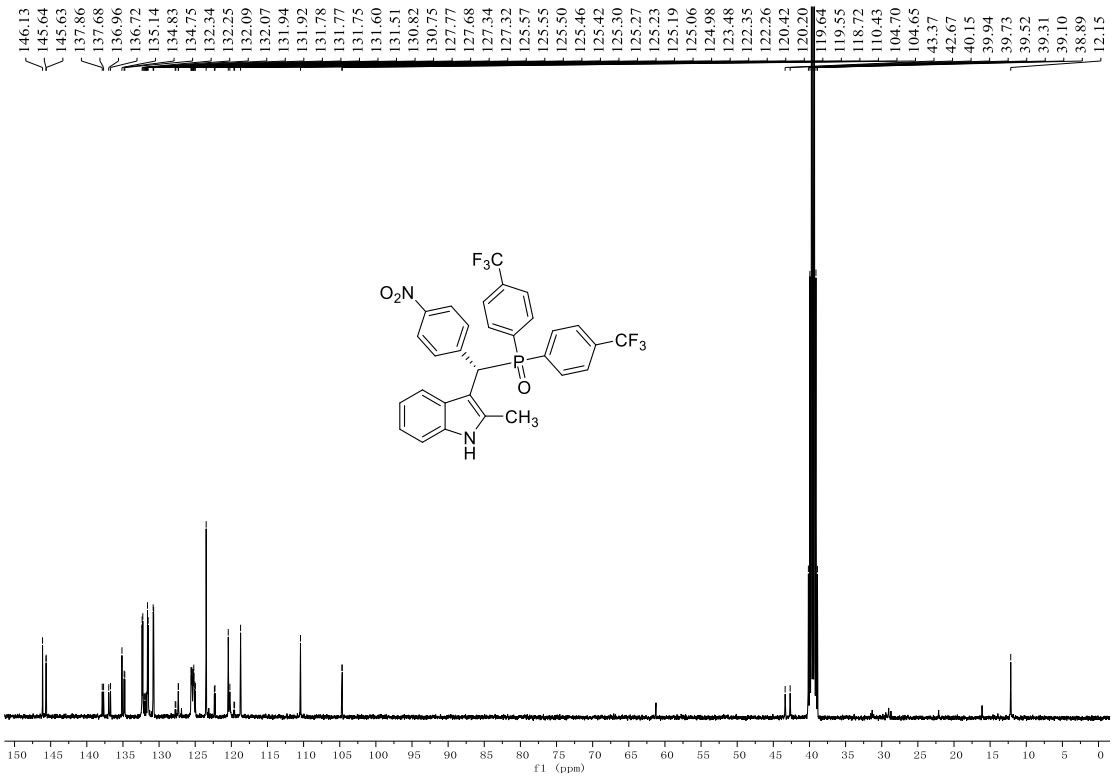
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	5.387	24134.97	1214.50	98.40
	8.527	391.67	11.97	1.60
		24526.64		100.00

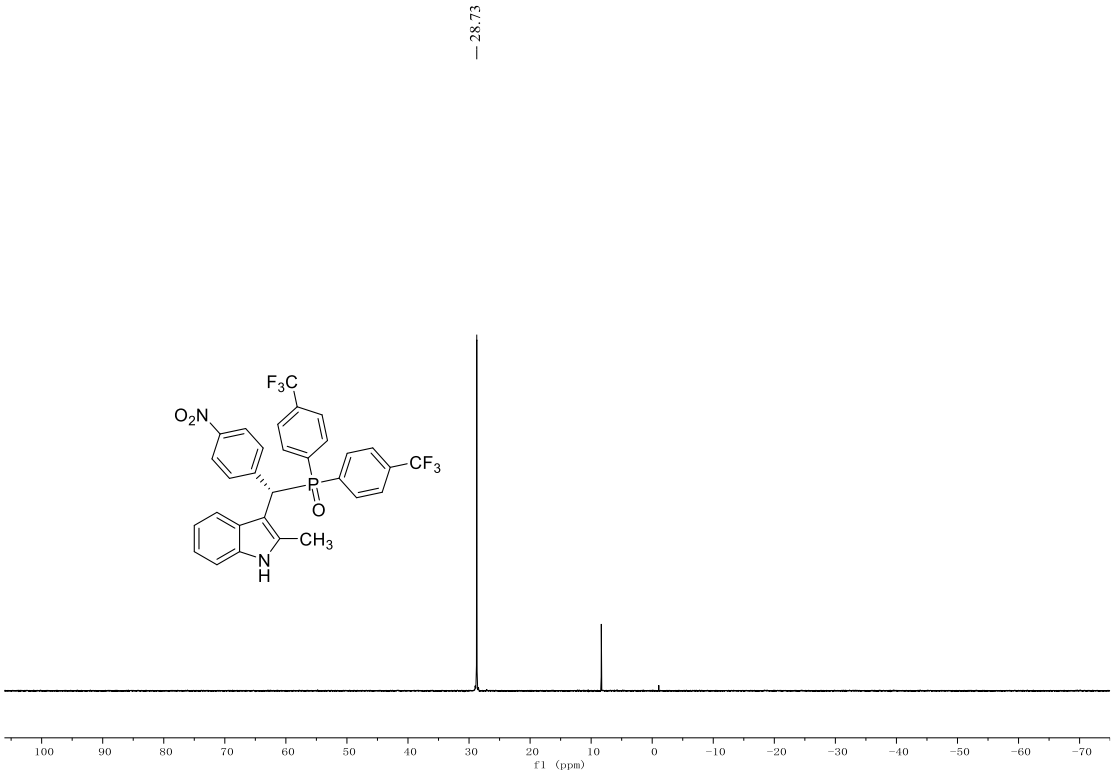
^{1}H NMR spectrum of compound of 3l



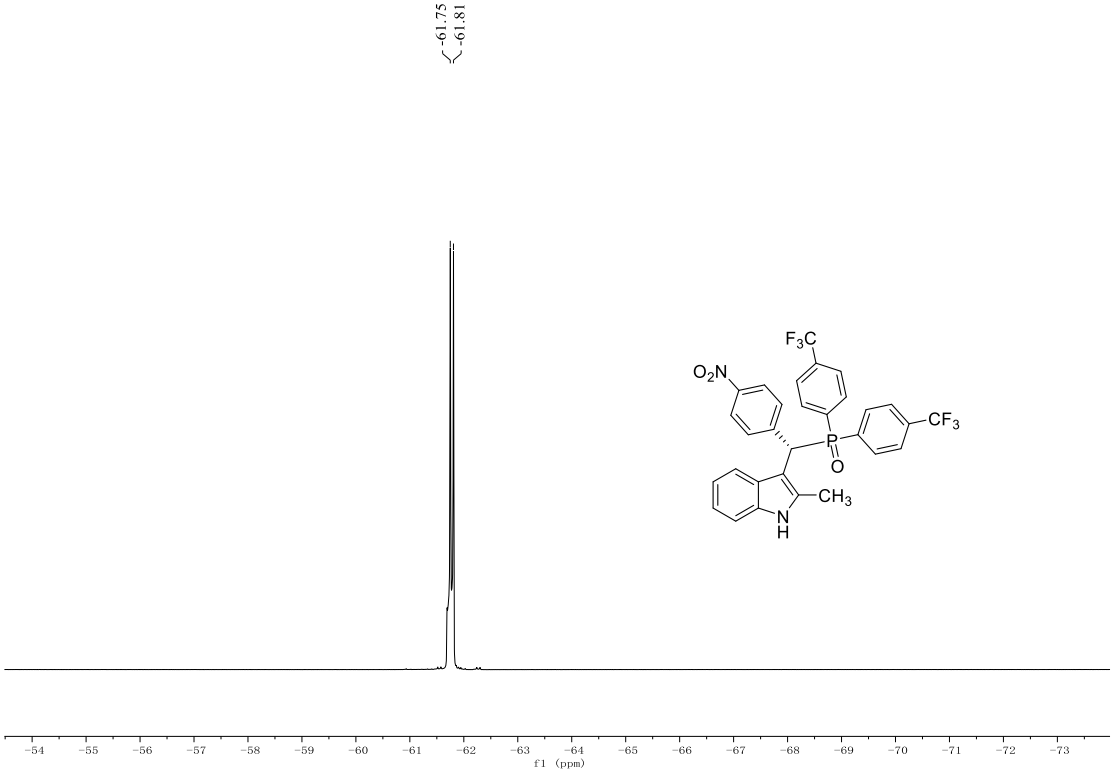
^{13}C NMR spectrum of compound of 3l



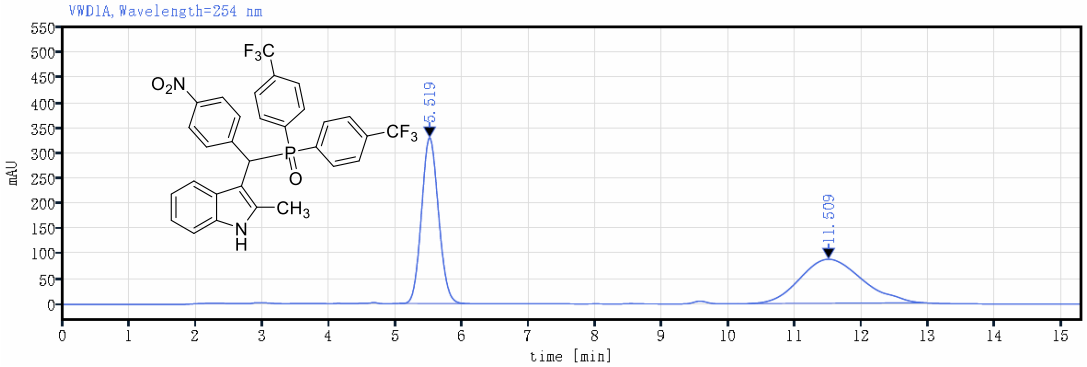
^{31}P NMR spectrum of compound of 3l



^{19}F NMR spectrum of compound of 3l

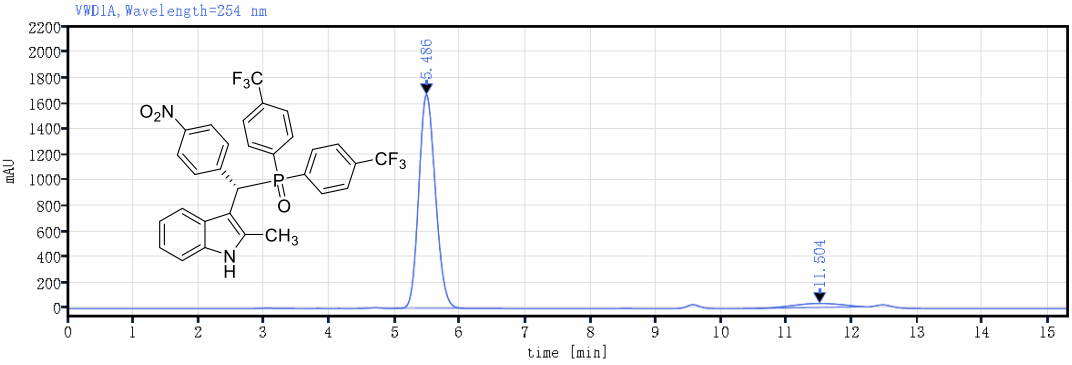


HPLC spectra of 3l



Detector VWD1A, Wavelength=254 nm

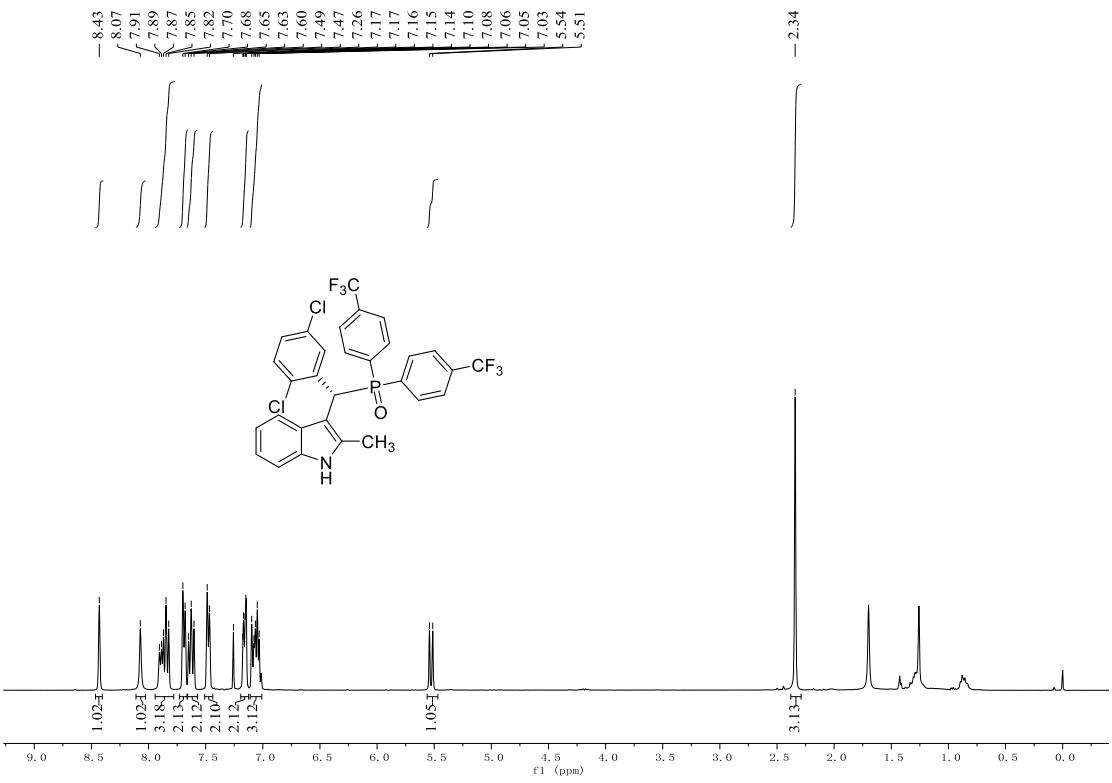
Peak	Ret.Time [min]	Area	Height	Area%
	5.519	5819.81	329.10	50.77
	11.509	5643.33	87.36	49.23
		11463.14		100.00



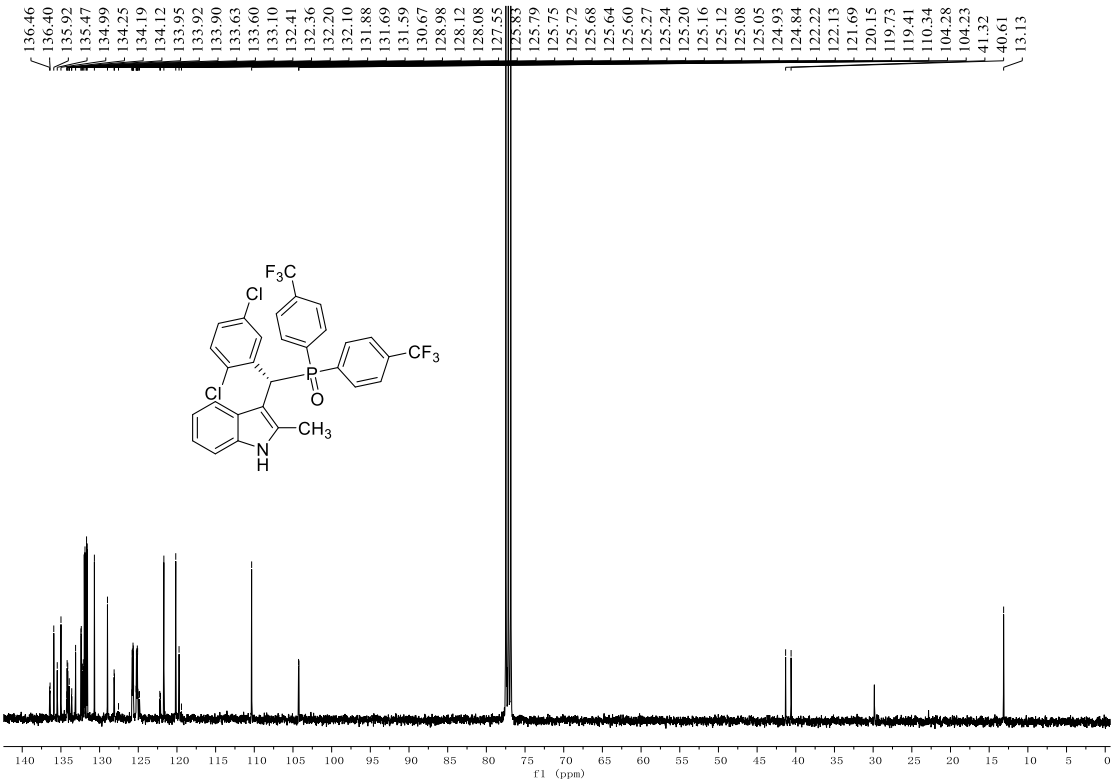
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	5.486	29429.58	1665.49	94.81
	11.504	1612.39	31.40	5.19
		31041.98		100.00

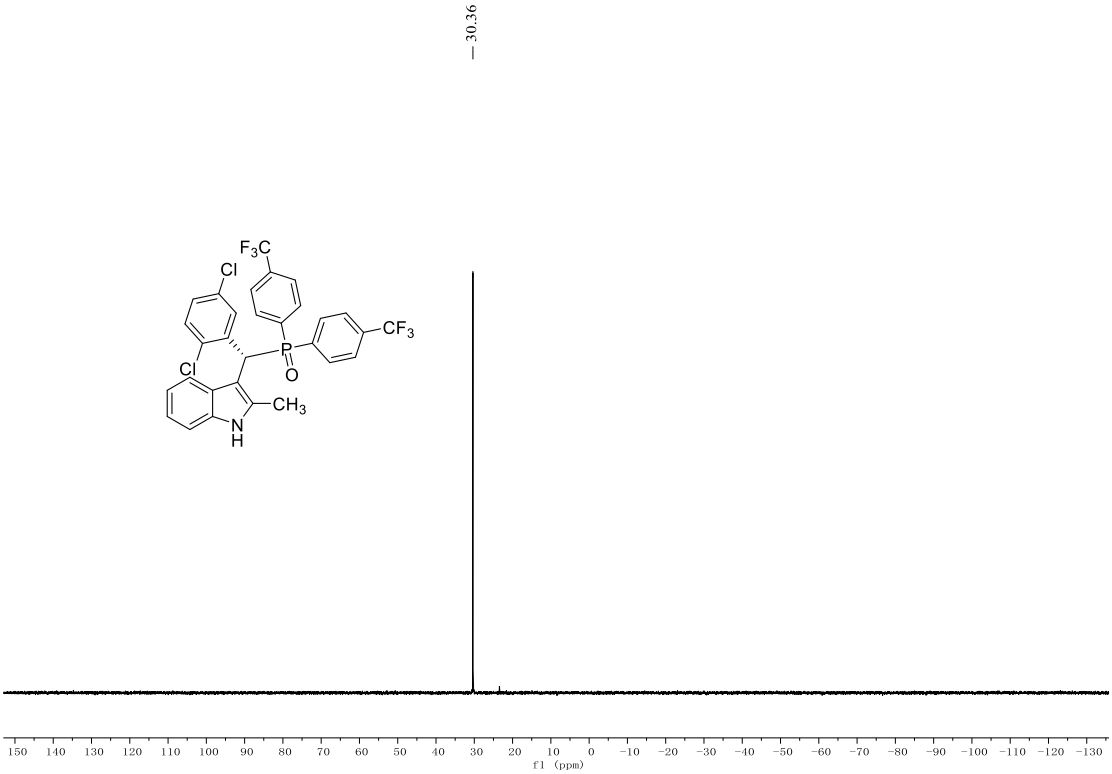
^{1}H NMR spectrum of compound of 3m



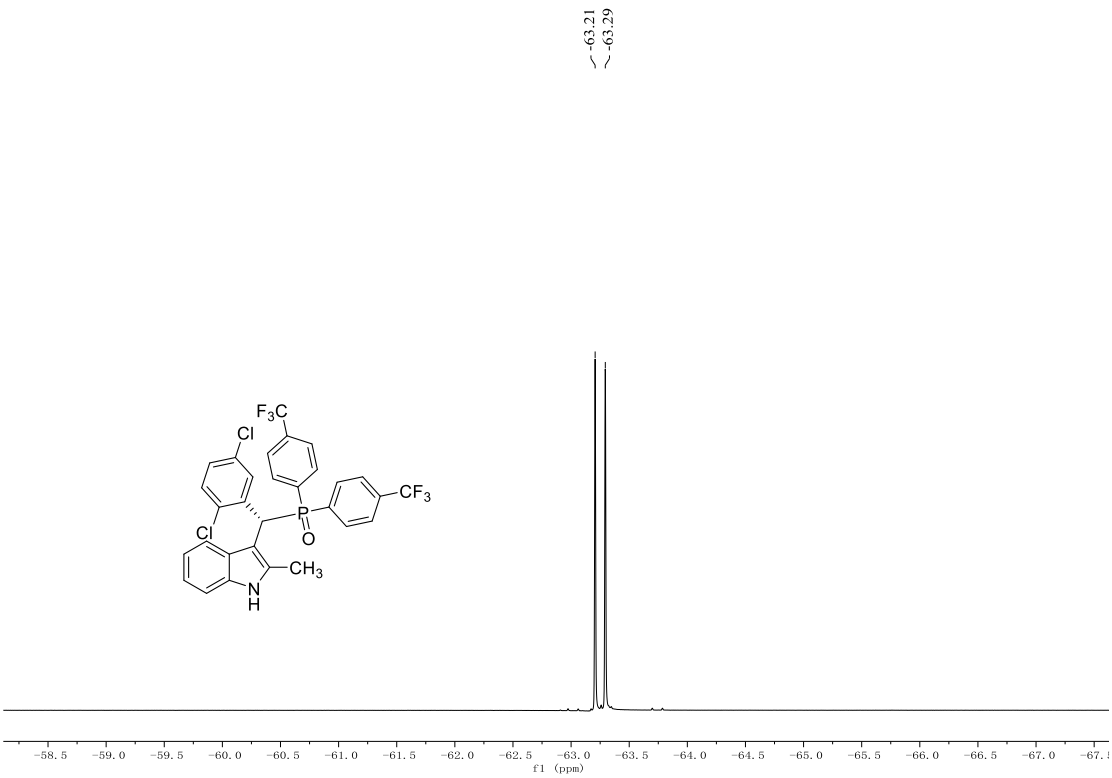
^{13}C NMR spectrum of compound of 3m



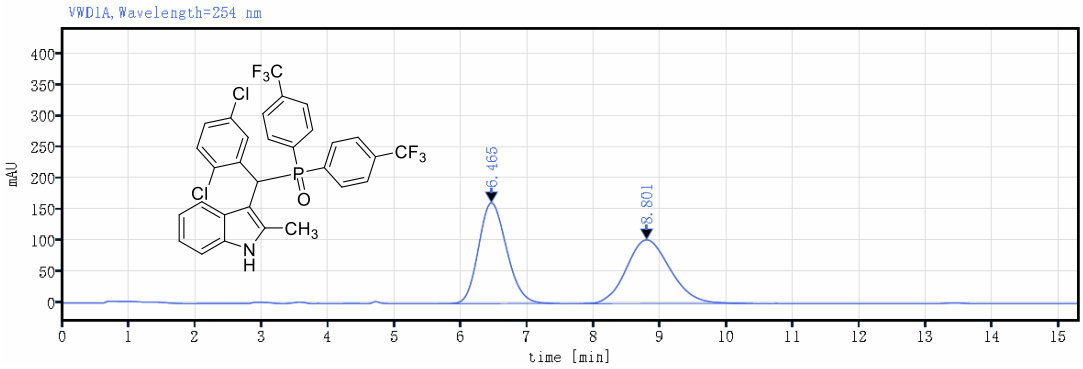
^{31}P NMR spectrum of compound of 3m



^{19}F NMR spectrum of compound of 3m

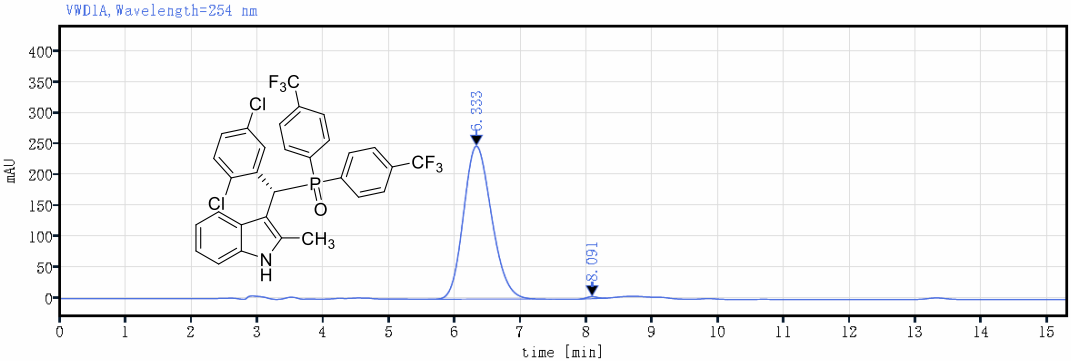


HPLC spectra of 3m



Detector VWD1A, Wavelength=254 nm

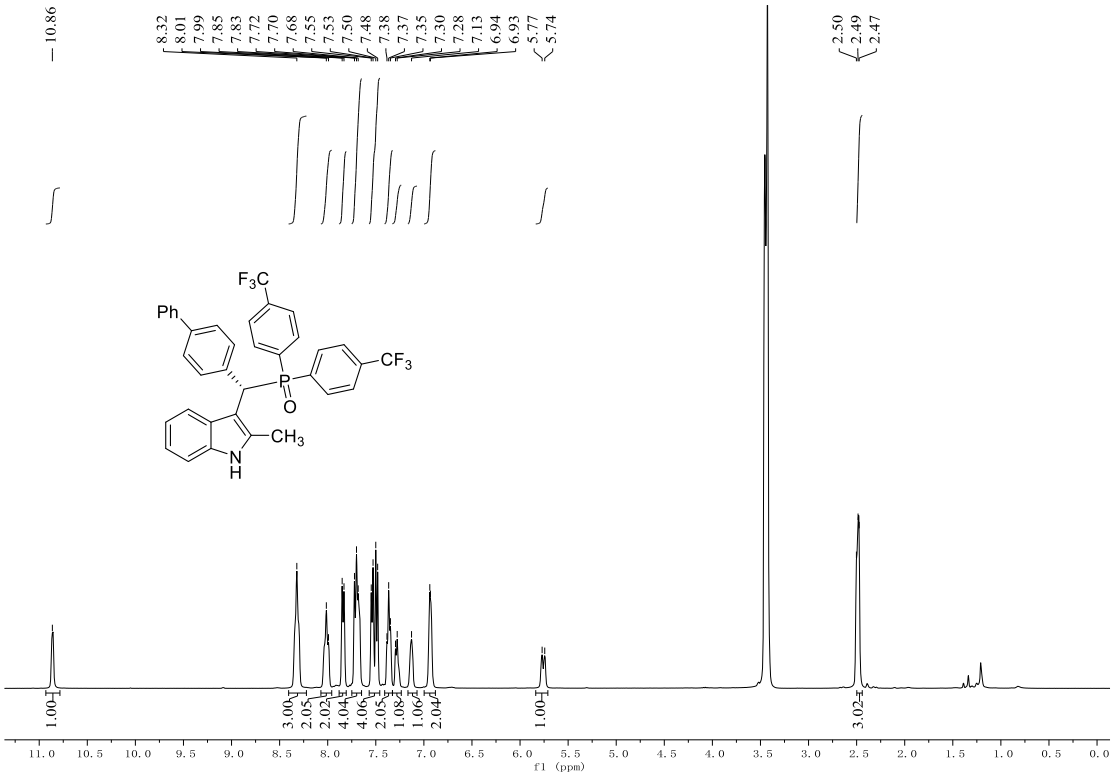
Peak	Ret.Time [min]	Area	Height	Area%
	6.465	4747.71	162.02	50.28
	8.801	4694.36	102.51	49.72
		9442.07		100.00



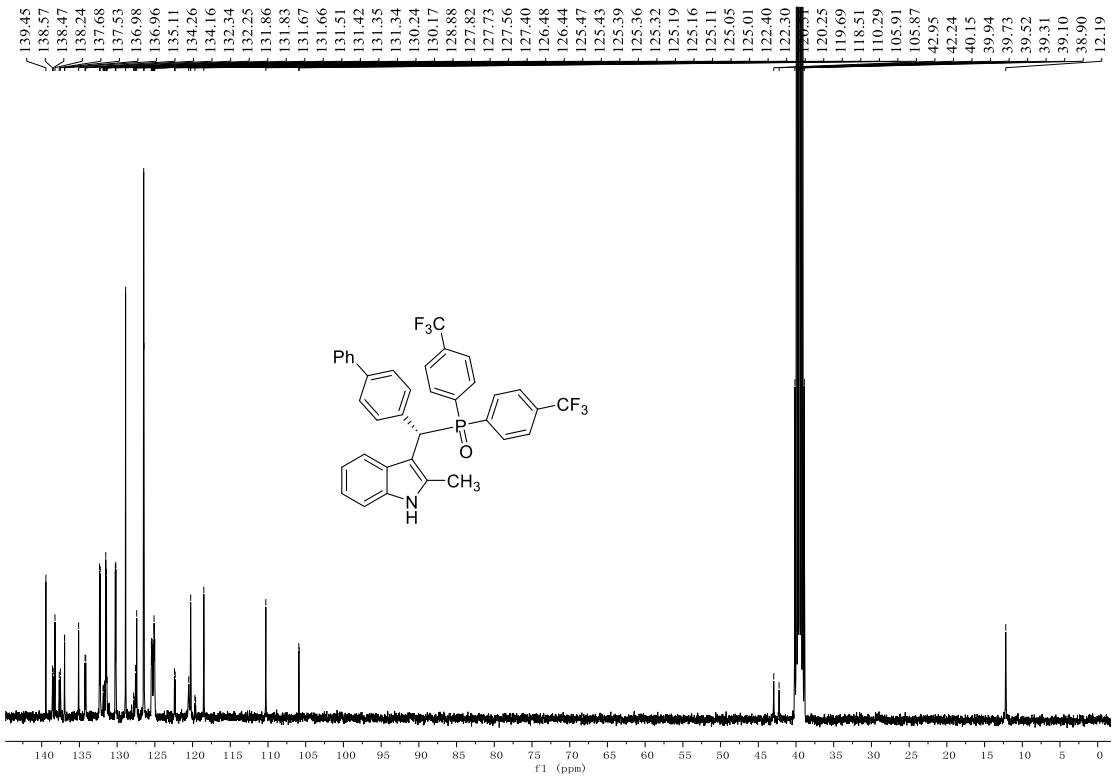
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	6.333	7326.90	248.08	99.49
	8.091	37.41	3.42	0.51
		7364.31		100.00

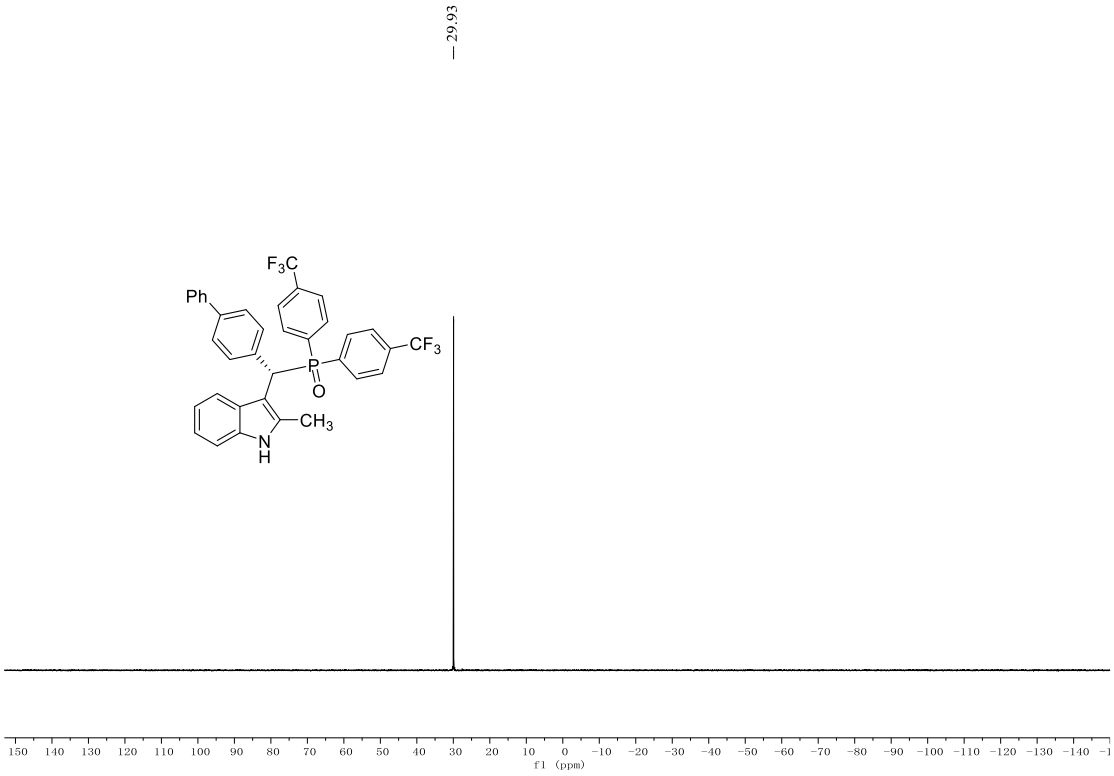
^{1}H NMR spectrum of compound of 3n



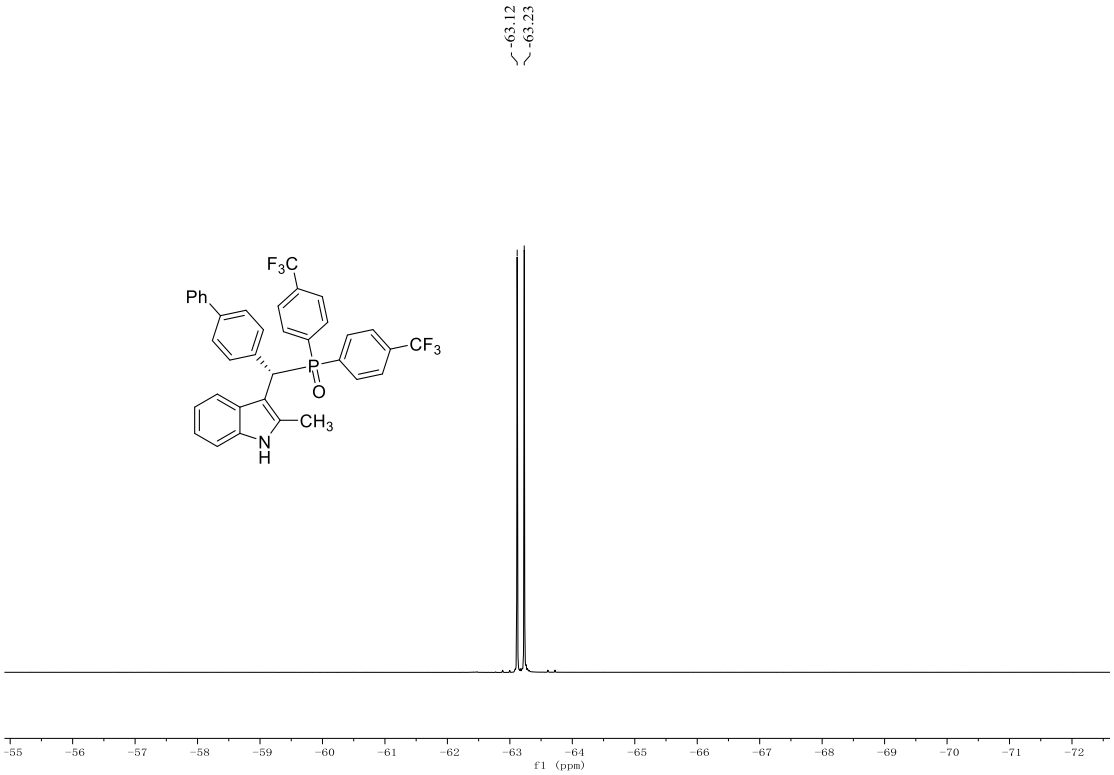
^{13}C NMR spectrum of compound of 3n



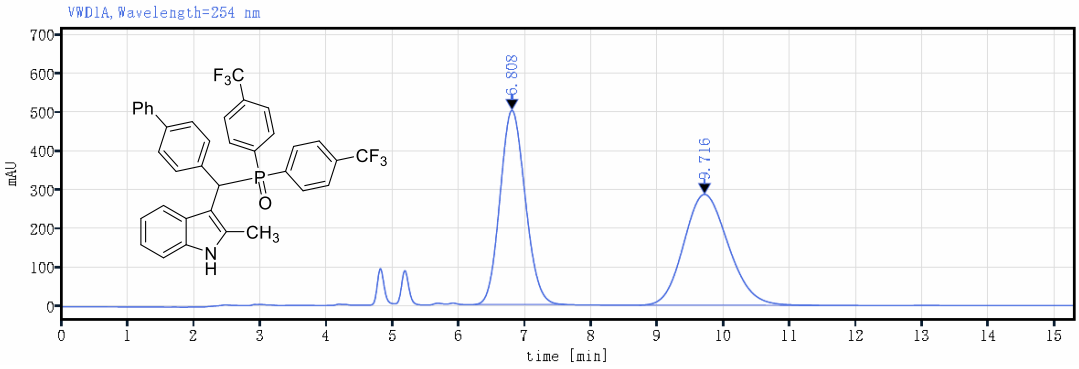
^{31}P NMR spectrum of compound of 3n



^{19}F NMR spectrum of compound of 3n

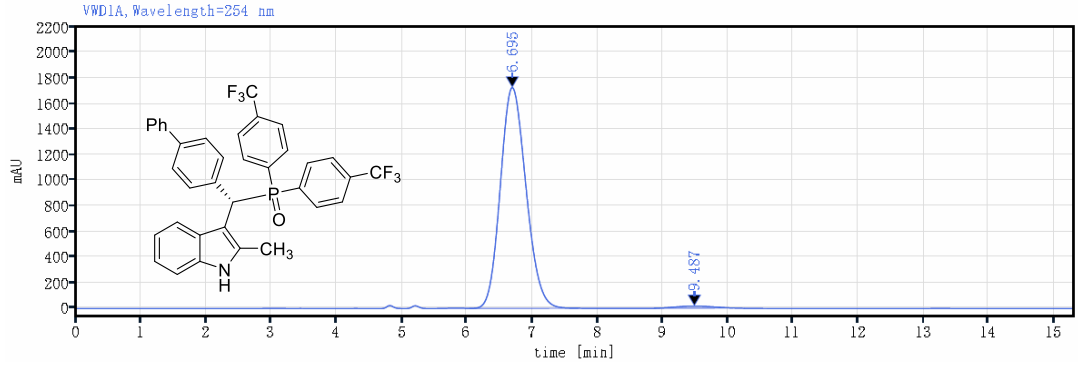


HPLC spectra of 3n



Detector VWD1A, Wavelength=254 nm

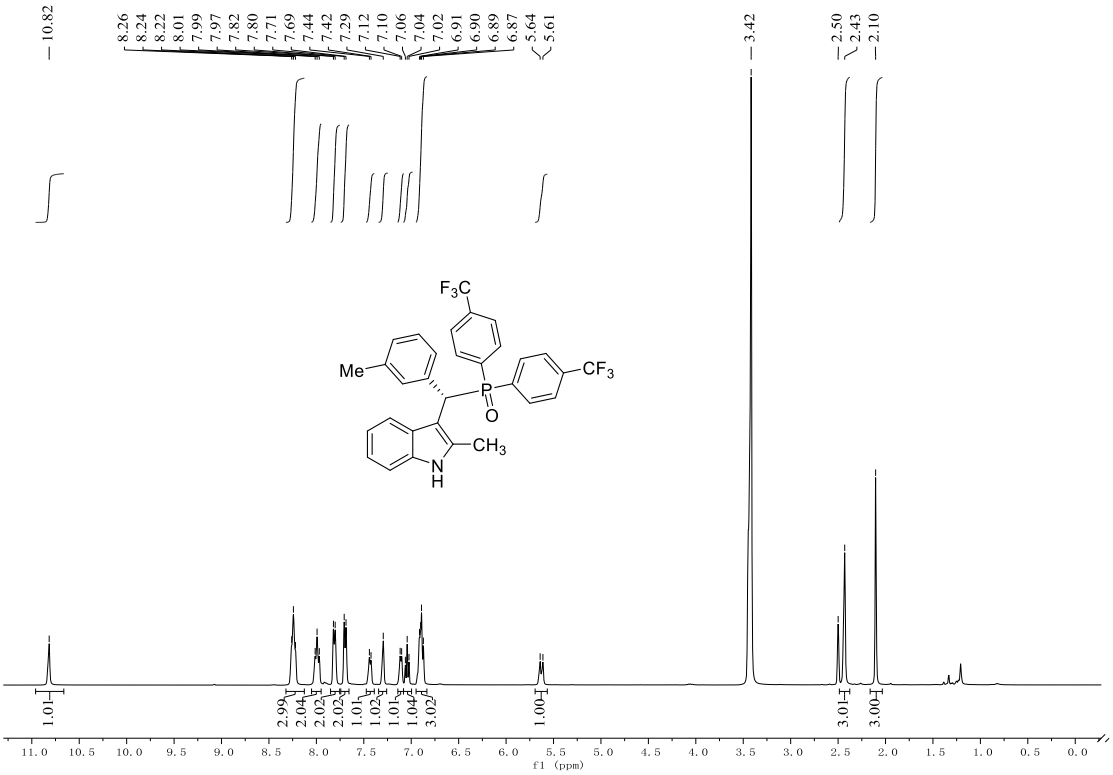
Peak	Ret.Time [min]	Area	Height	Area%
	6.808	13183.75	499.39	49.78
	9.716	13301.58	285.03	50.22
		26485.33		100.00



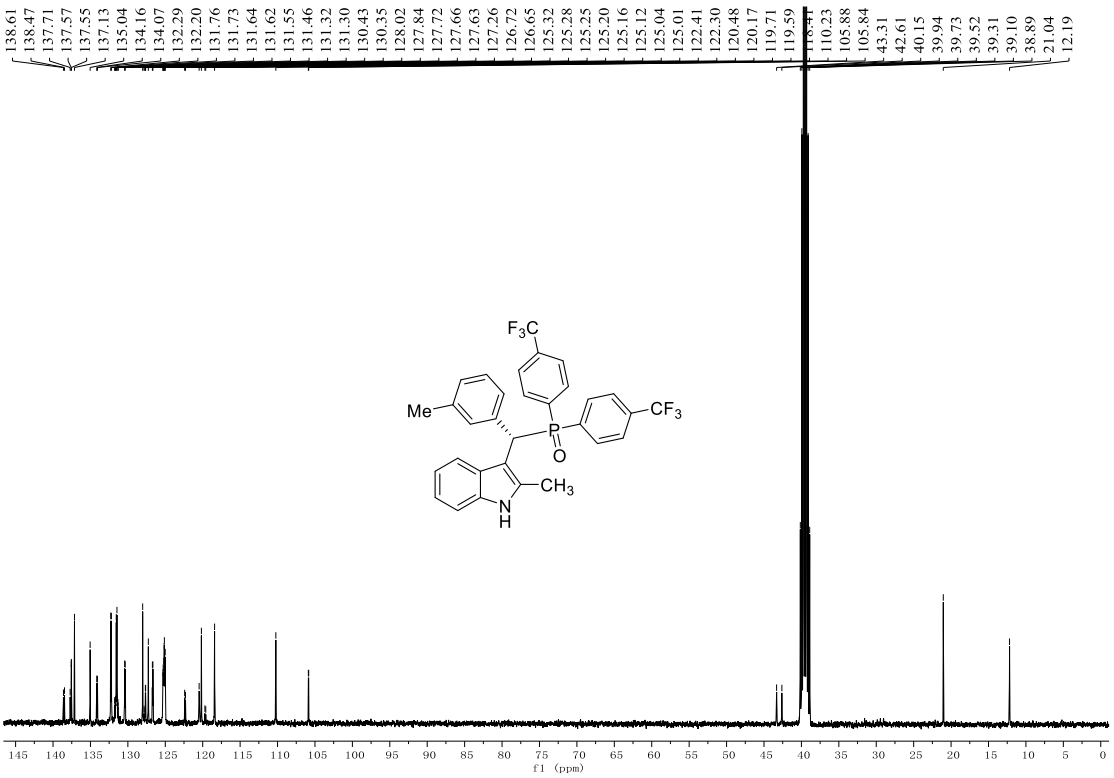
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	6.695	47059.85	1722.33	98.67
	9.487	632.90	16.23	1.33
		47692.75		100.00

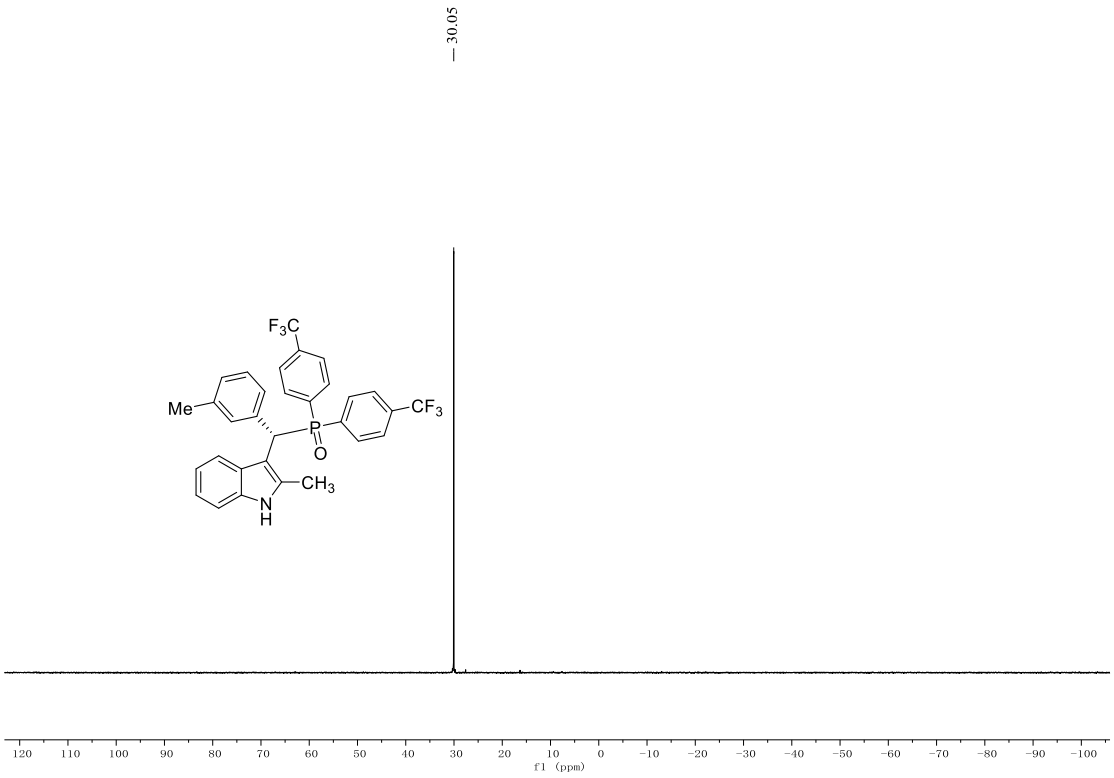
^{1}H NMR spectrum of compound of 3o



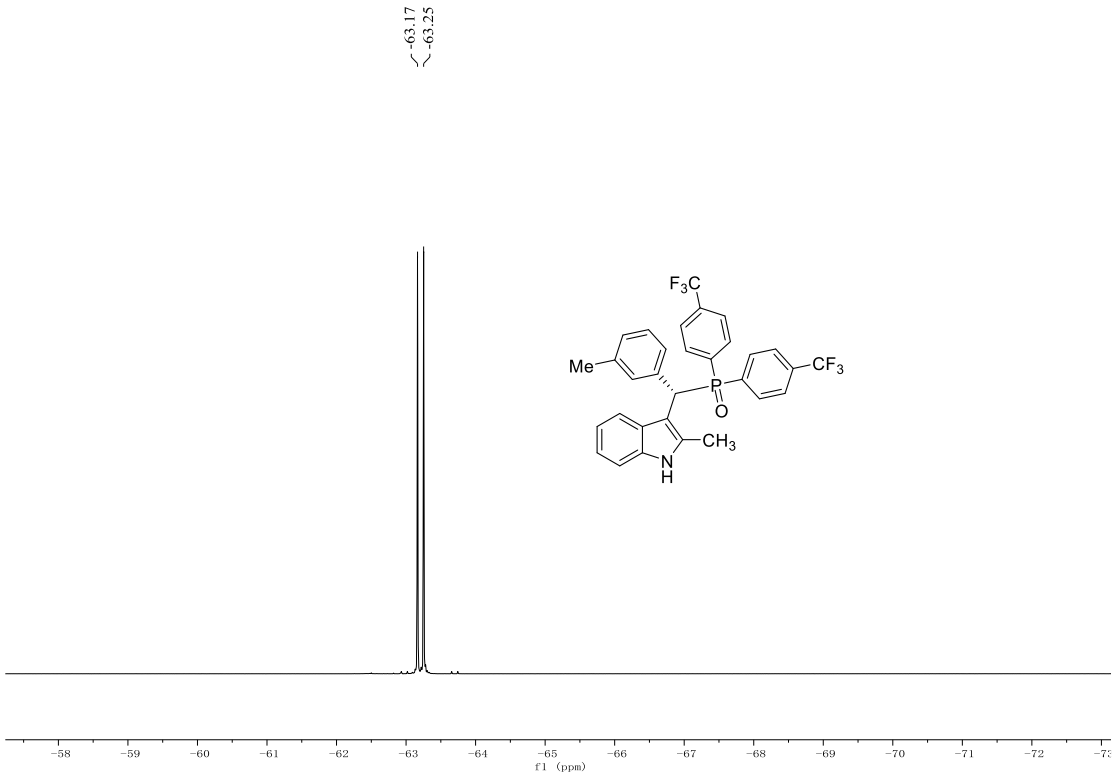
^{13}C NMR spectrum of compound of 3o



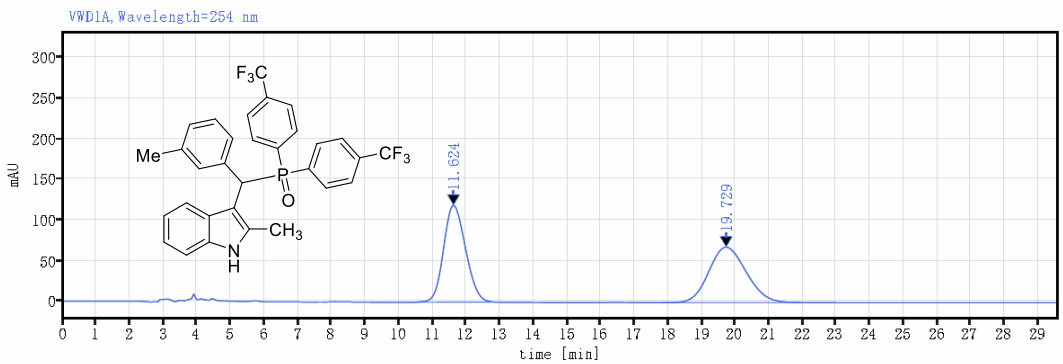
^{31}P NMR spectrum of compound of 3o



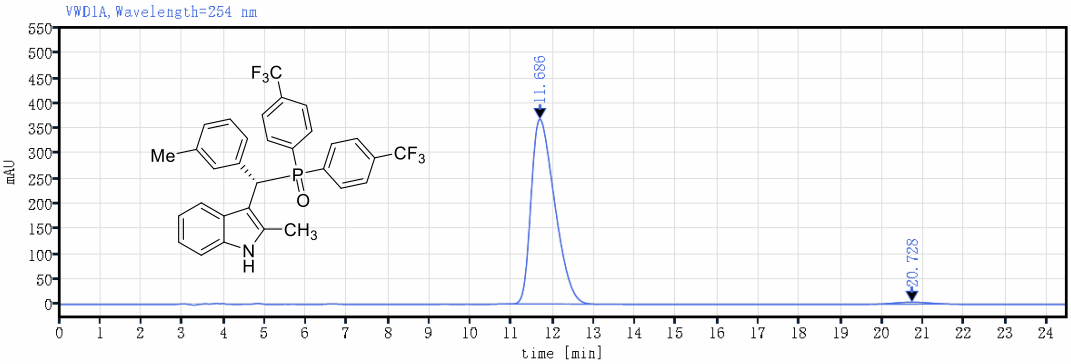
^{19}F NMR spectrum of compound of 3o



HPLC spectra of 3o

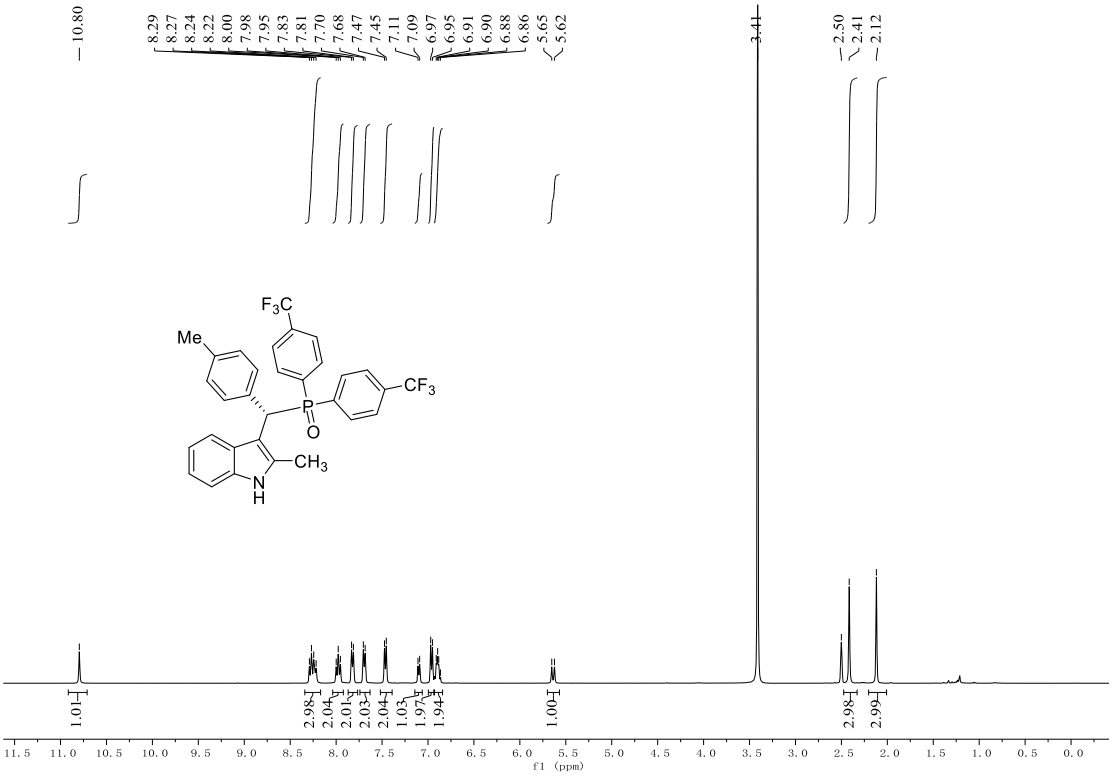


Detector	VWD1A, Wavelength=254 nm			
Peak	Ret.Time [min]	Area	Height	Area%
	11.624	5403.46	119.20	50.71
	19.729	5252.13	68.11	49.29
		10655.59		100.00

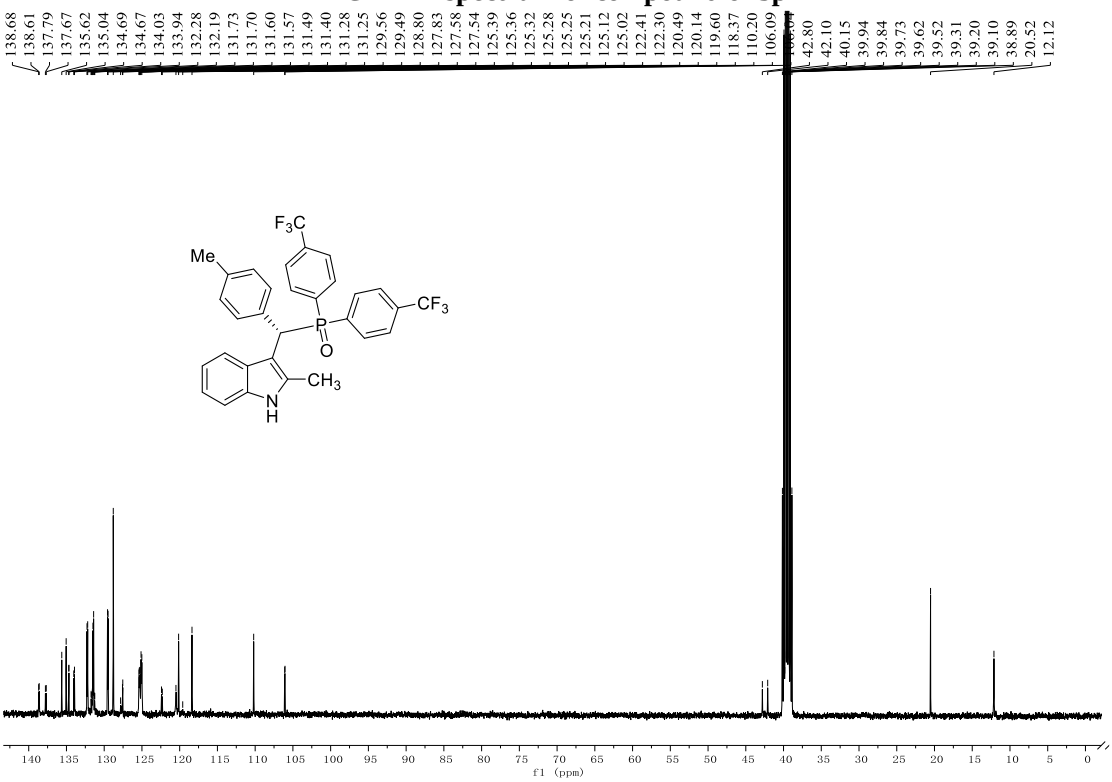


Detector	VWD1A, Wavelength=254 nm			
Peak	Ret.Time [min]	Area	Height	Area%
	11.686	14648.85	367.70	98.46
	20.728	229.82	3.99	1.54
		14878.67		100.00

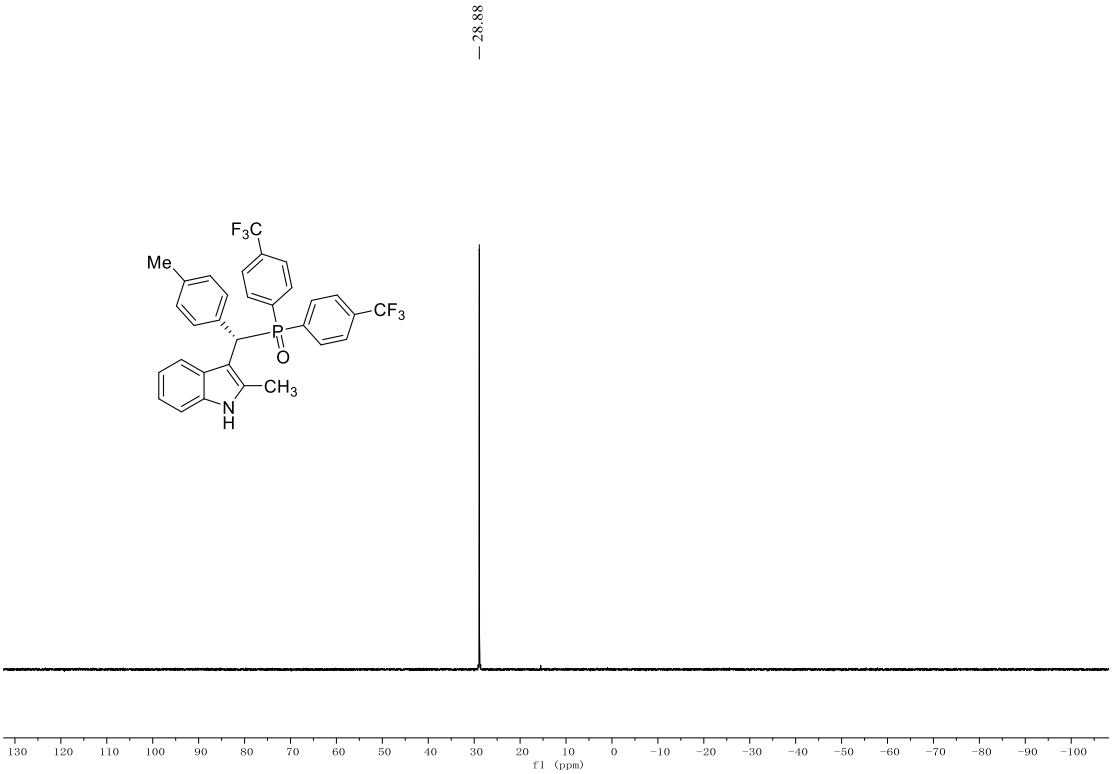
^{1}H NMR spectrum of compound of 3p



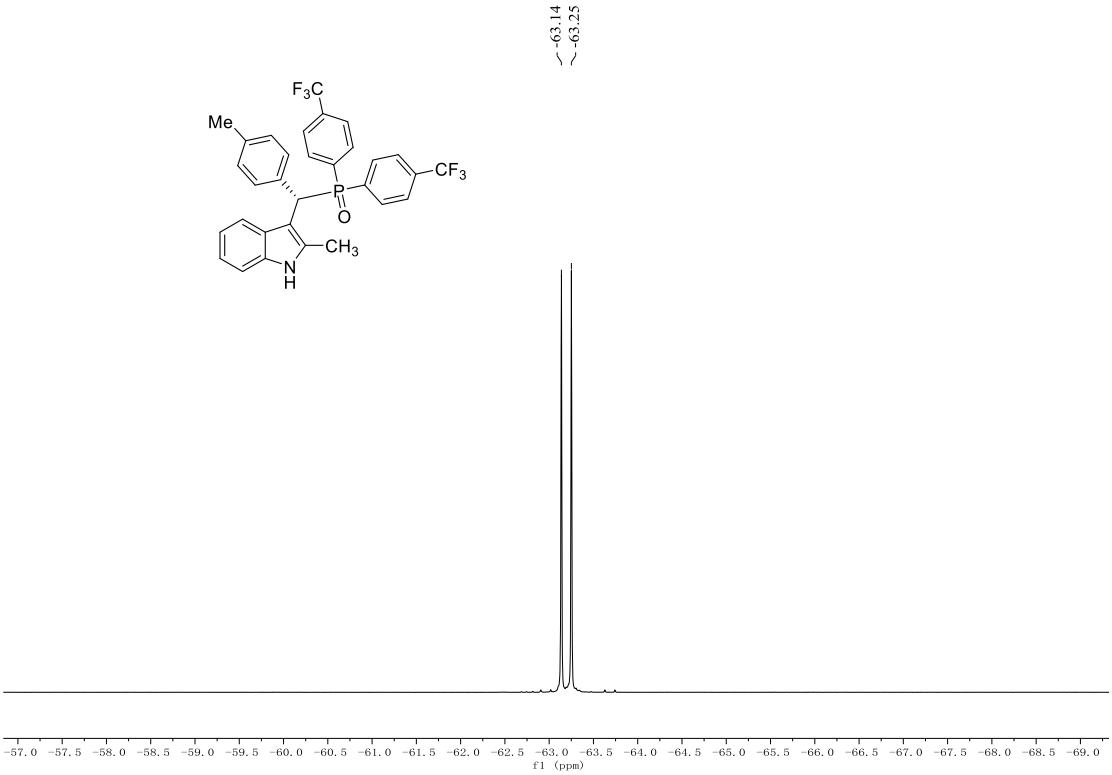
^{13}C NMR spectrum of compound of 3p



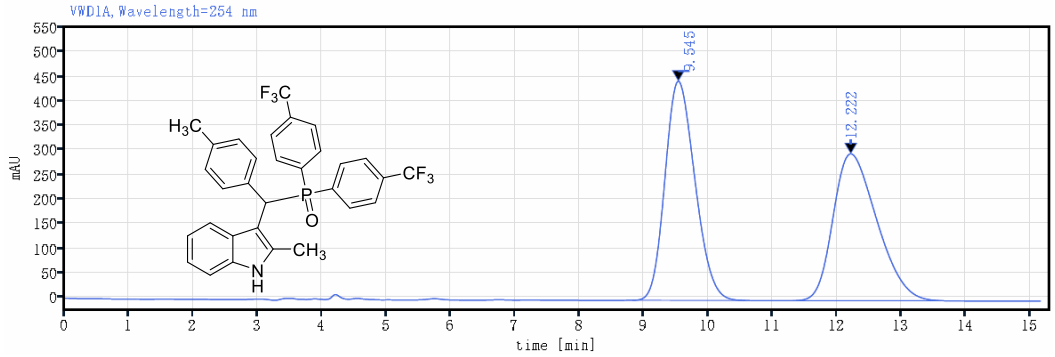
^{31}P NMR spectrum of compound of 3p



^{19}F NMR spectrum of compound of 3p

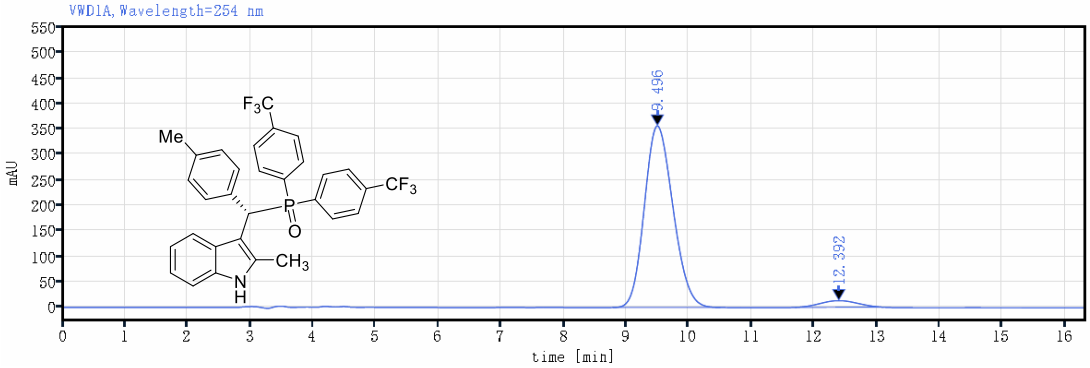


HPLC spectra of 3p



Detector VWD1A, Wavelength=254 nm

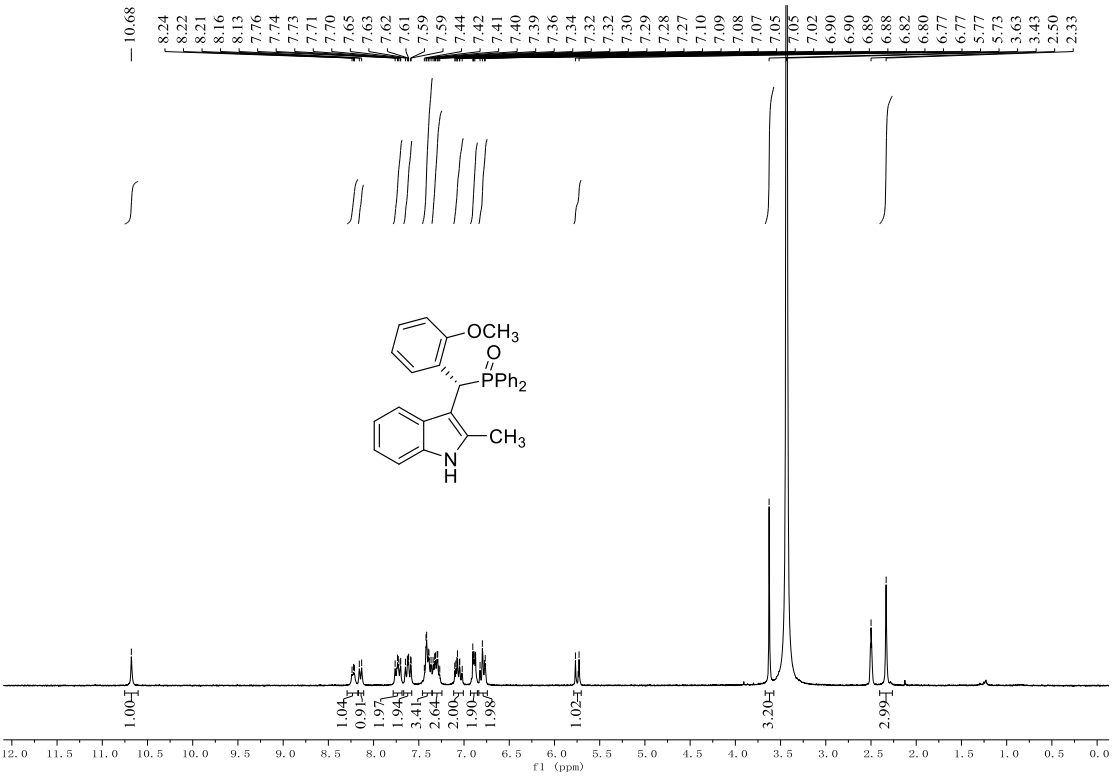
Peak	Ret.Time [min]	Area	Height	Area%
	9.545	14407.21	445.97	50.54
	12.222	14101.83	298.79	49.46
		28509.04		100.00



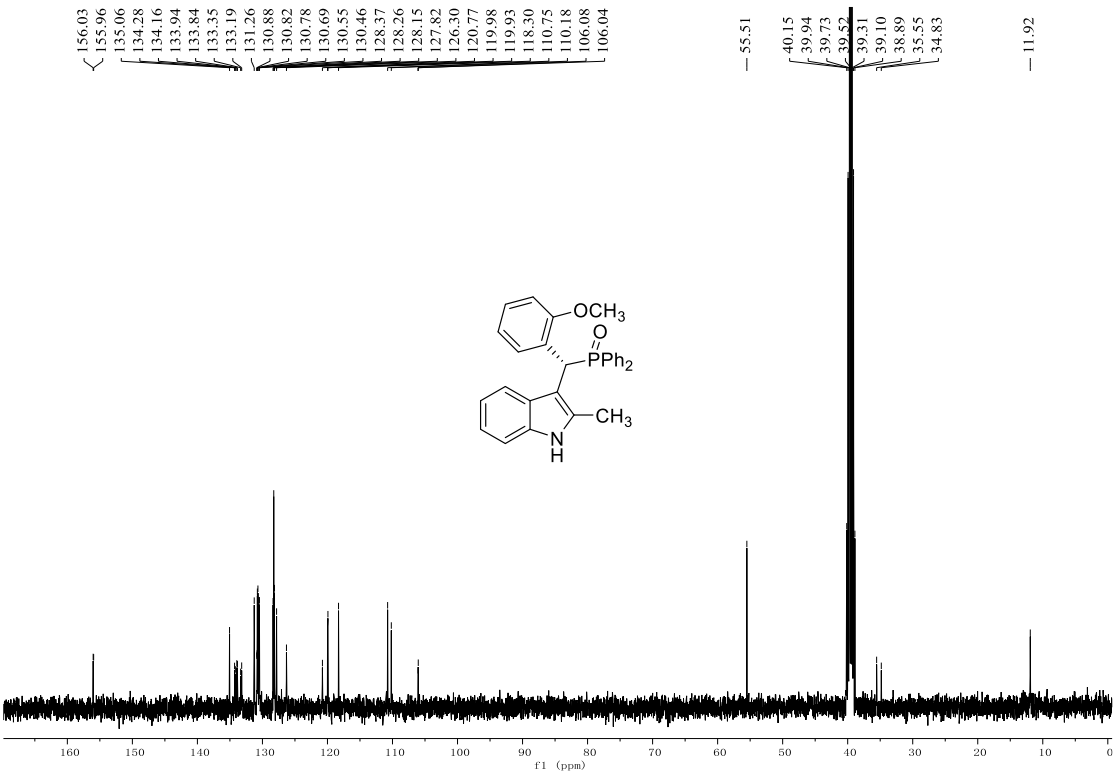
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	9.496	11307.76	356.38	95.44
	12.392	540.65	13.08	4.56
		11848.42		100.00

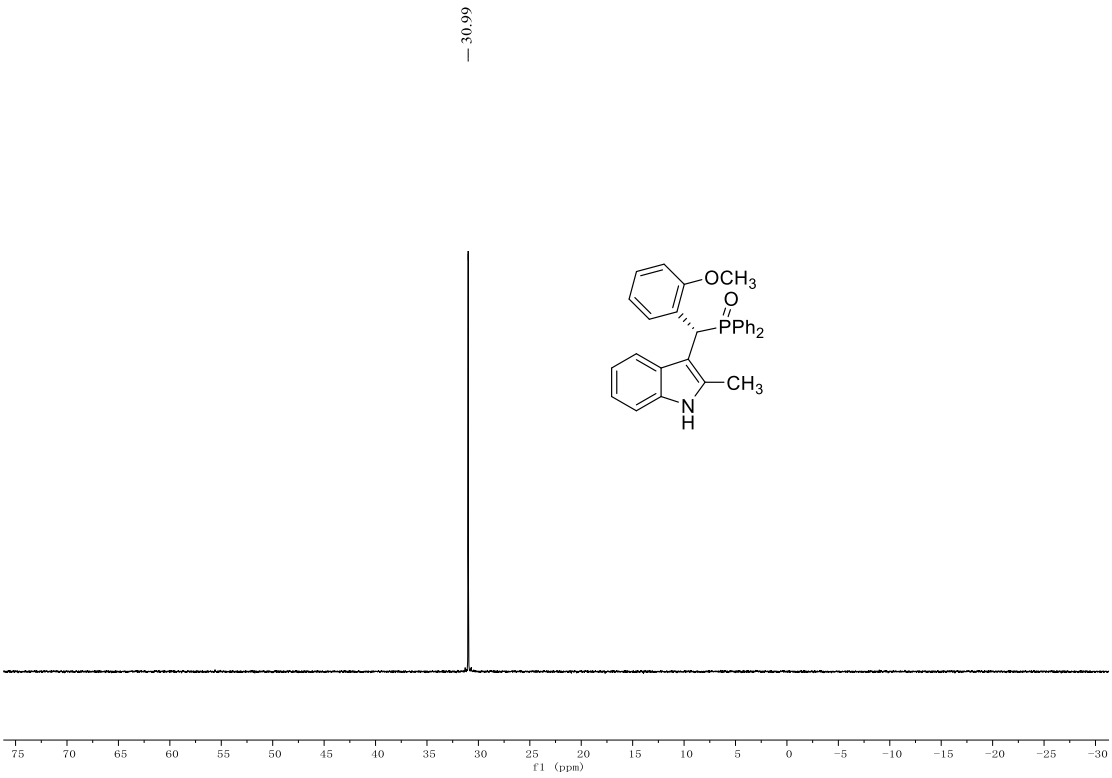
^{1}H NMR spectrum of compound of 3q



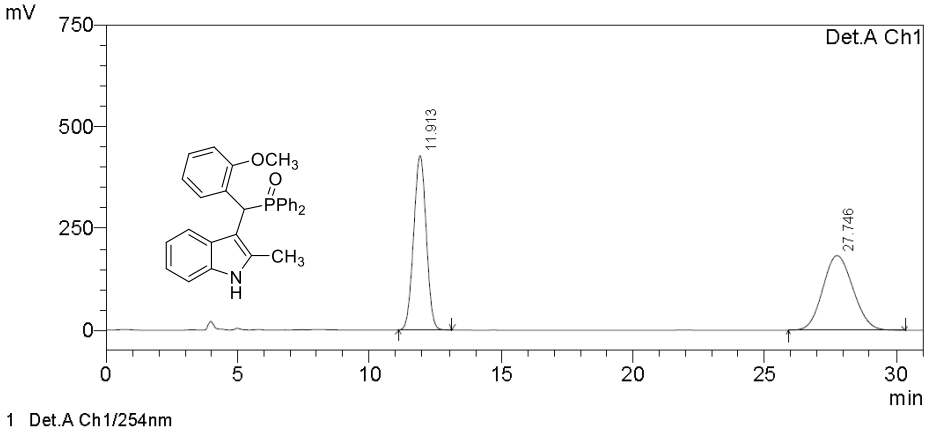
^{13}C NMR spectrum of compound of 3q



^{31}P NMR spectrum of compound of 3q



HPLC spectra of 3q

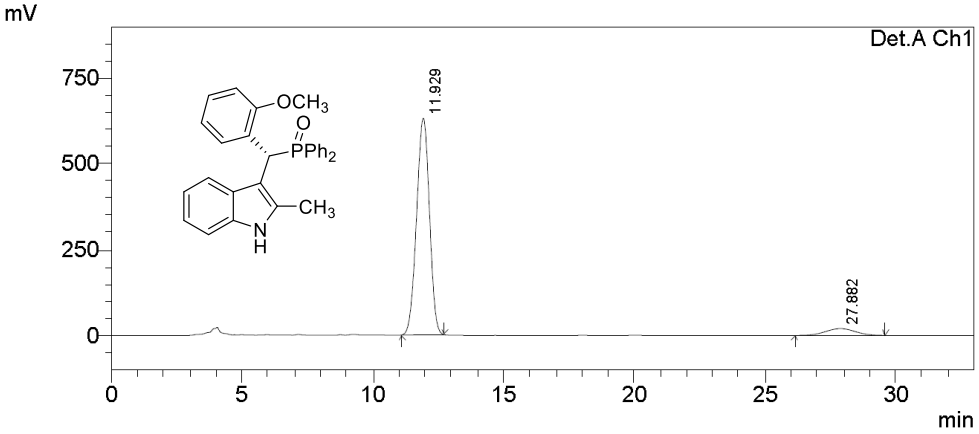


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	11.913	14245037	428304	49.435
2	27.746	14570404	183101	50.565
Total		28815440		100.000



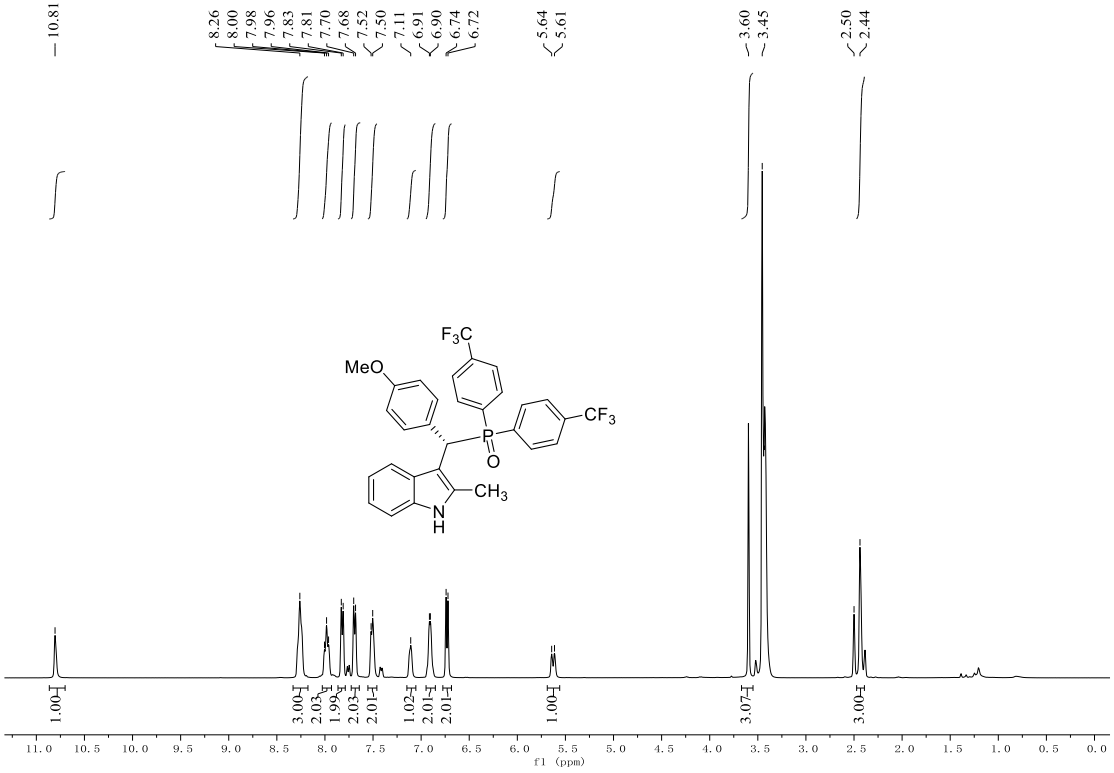
1 Det.A Ch1/254nm

PeakTable

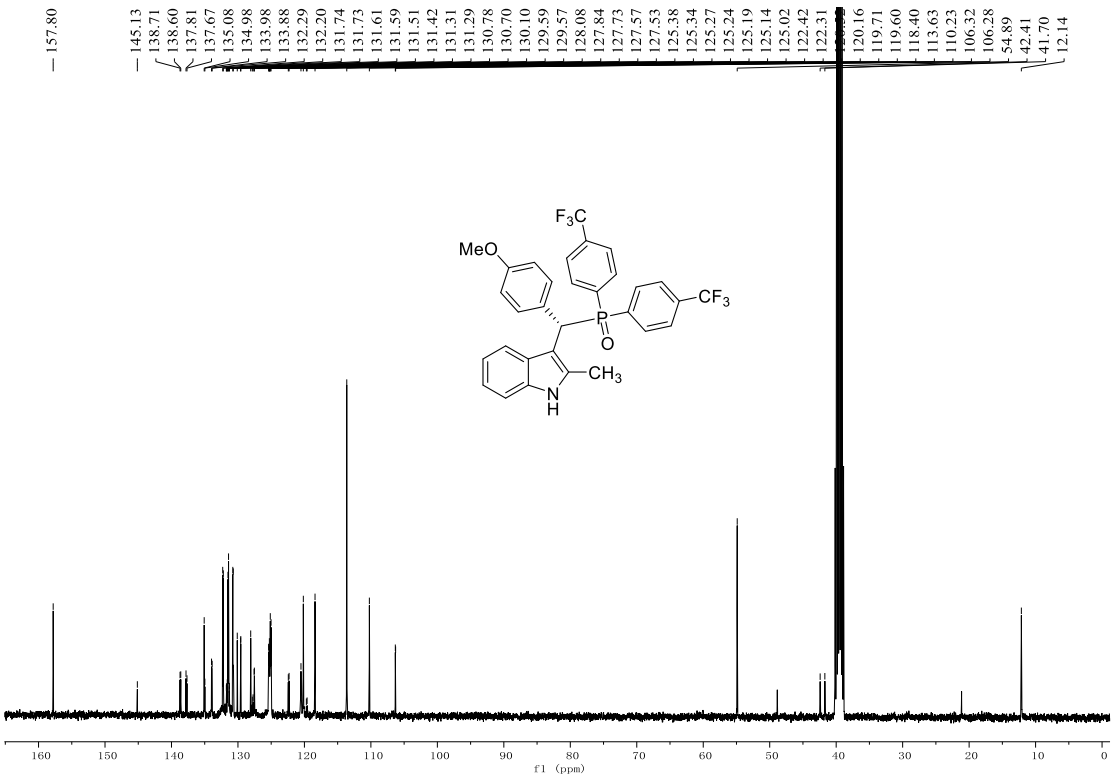
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	11.929	21612526	630238	93.245
2	27.882	1565803	19847	6.755
Total		23178329		100.000

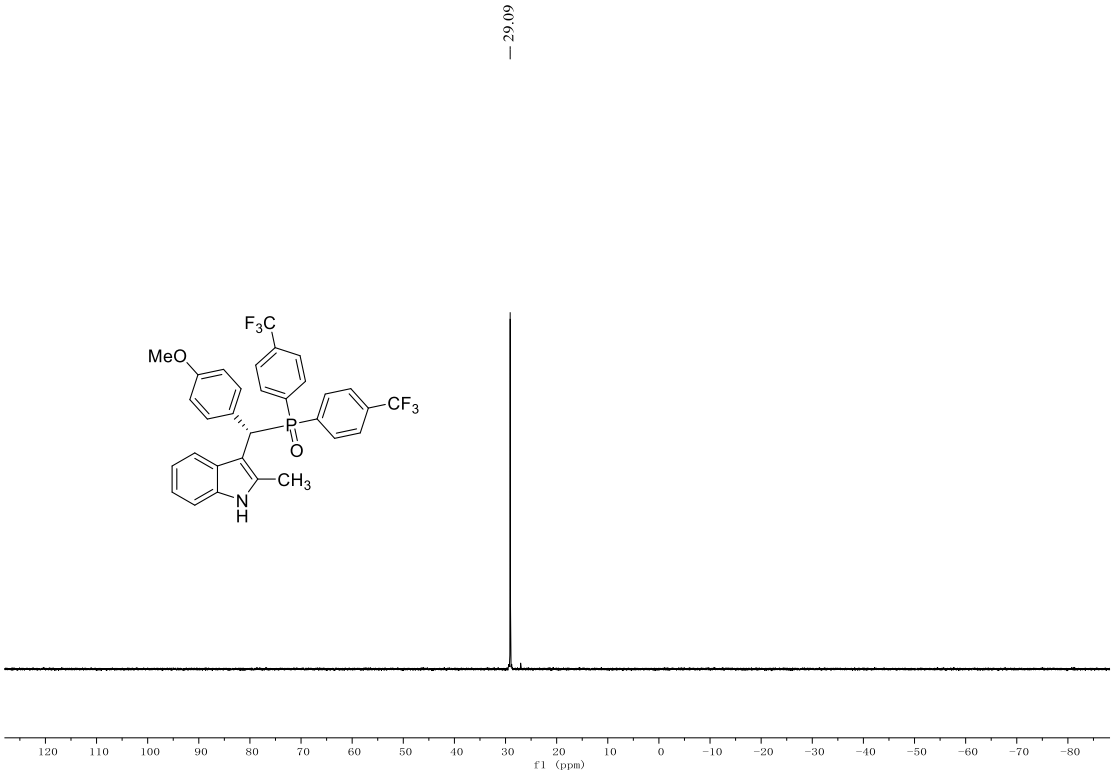
^{1}H NMR spectrum of compound of 3r



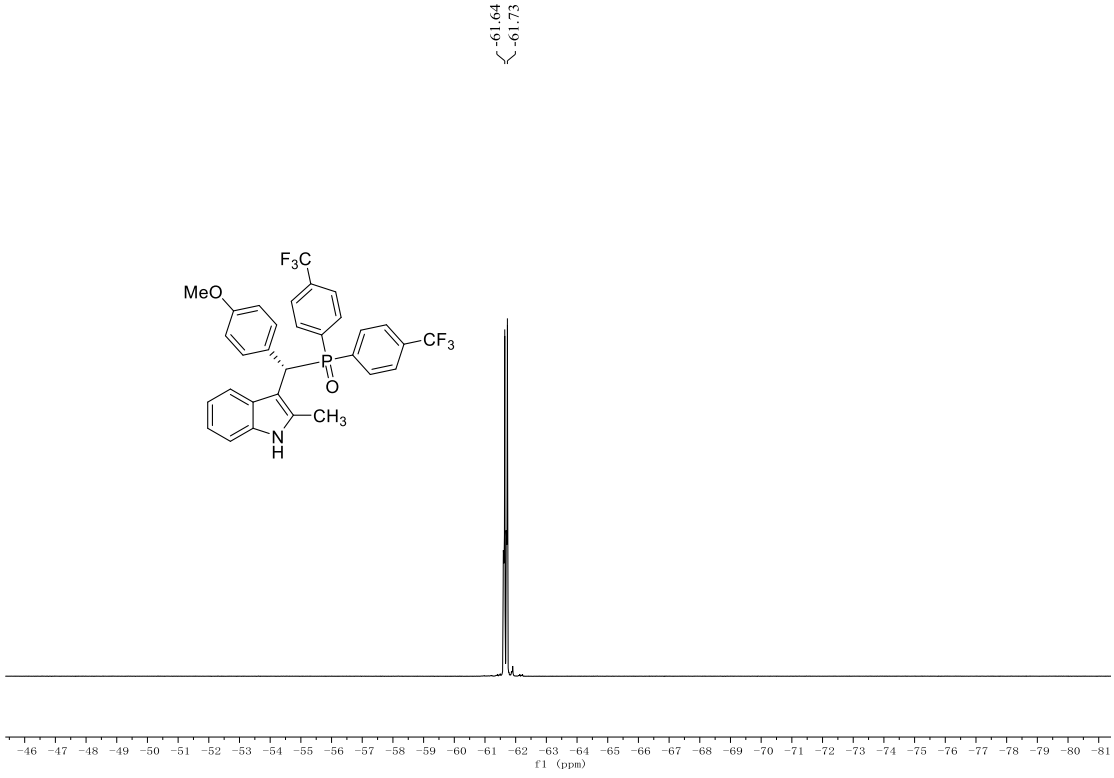
^{13}C NMR spectrum of compound of 3r



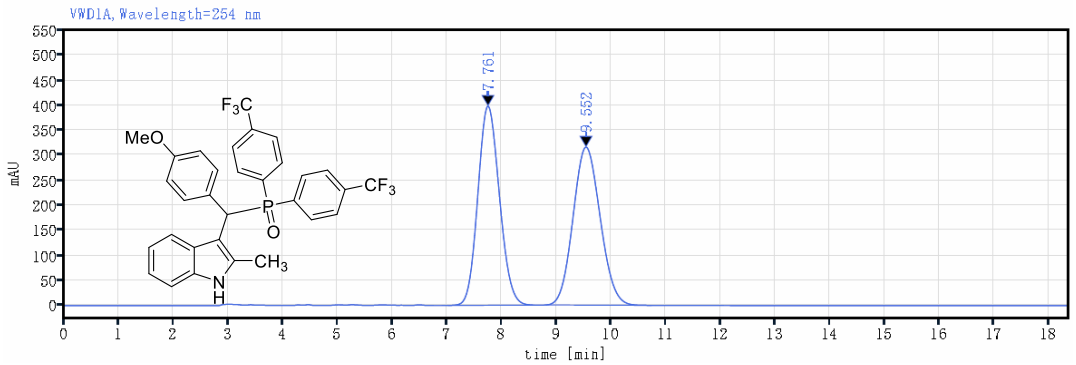
^{31}P NMR spectrum of compound of 3r



^{19}F NMR spectrum of compound of 3r

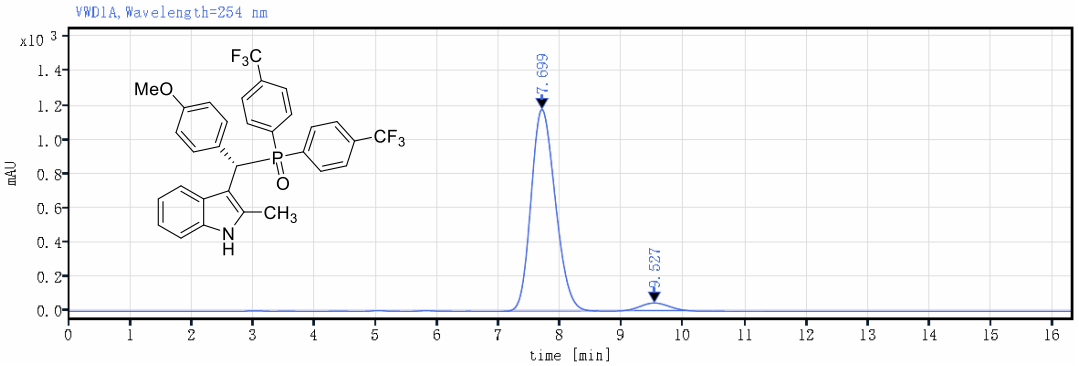


HPLC spectra of 3r



Detector VWD1A, Wavelength=254 nm

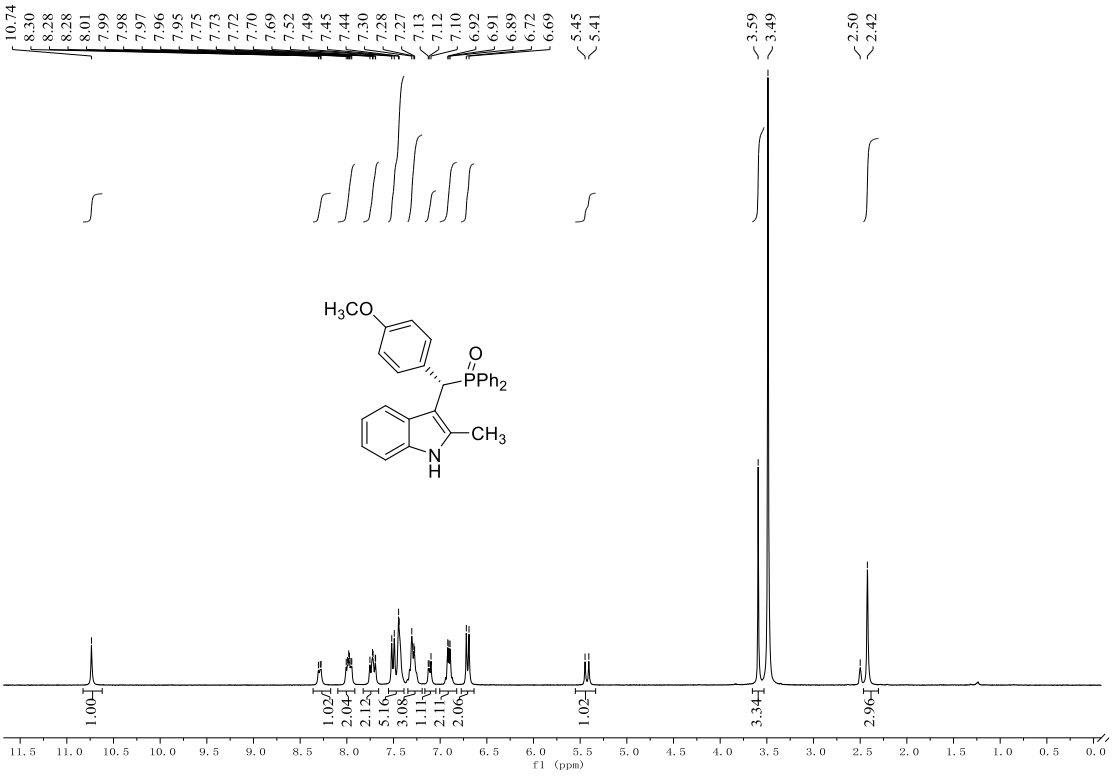
Peak	Ret.Time [min]	Area	Height	Area%
	7.761	10901.13	397.90	50.05
	9.552	10877.79	315.67	49.95
		21778.92		100.00



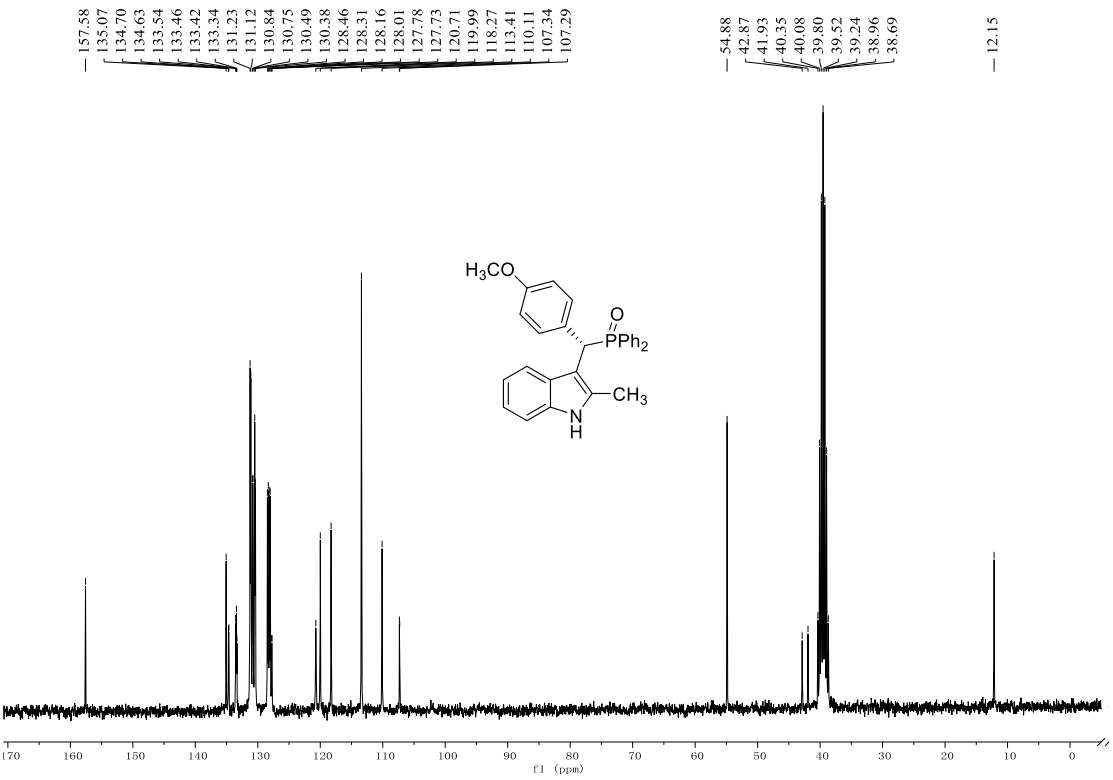
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	7.699	32252.72	1175.43	95.70
	9.527	1447.55	45.13	4.30
		33700.27		100.00

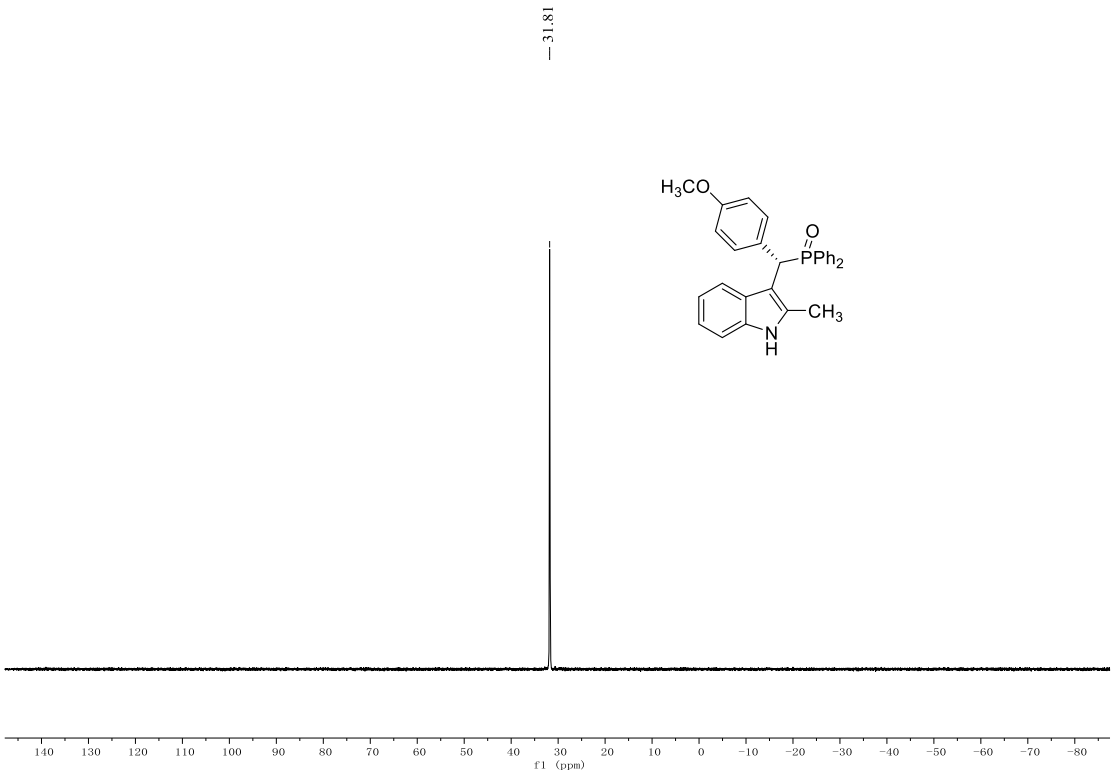
^{1}H NMR spectrum of compound of 3s



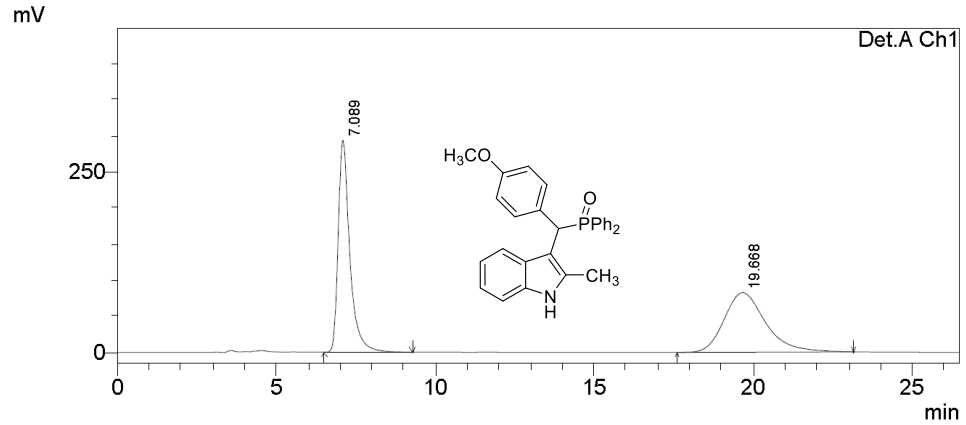
^{13}C NMR spectrum of compound of 3s



^{31}P NMR spectrum of compound of 3s



HPLC spectra of 3s

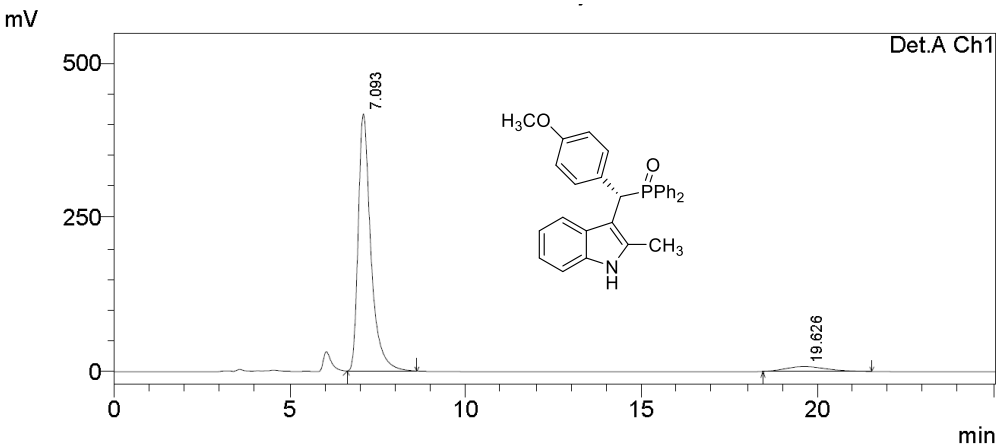


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.089	7441200	293311	50.058
2	19.668	7423923	82279	49.942
Total		14865122		100.000



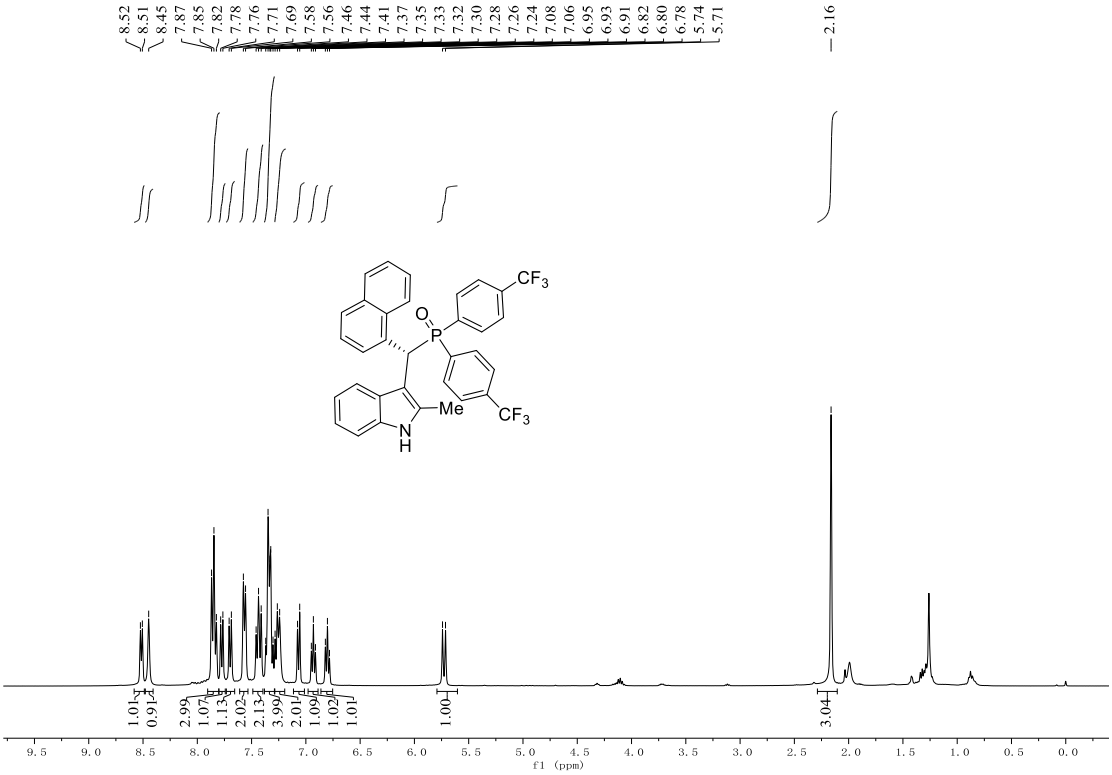
1 Det.A Ch1/254nm

PeakTable

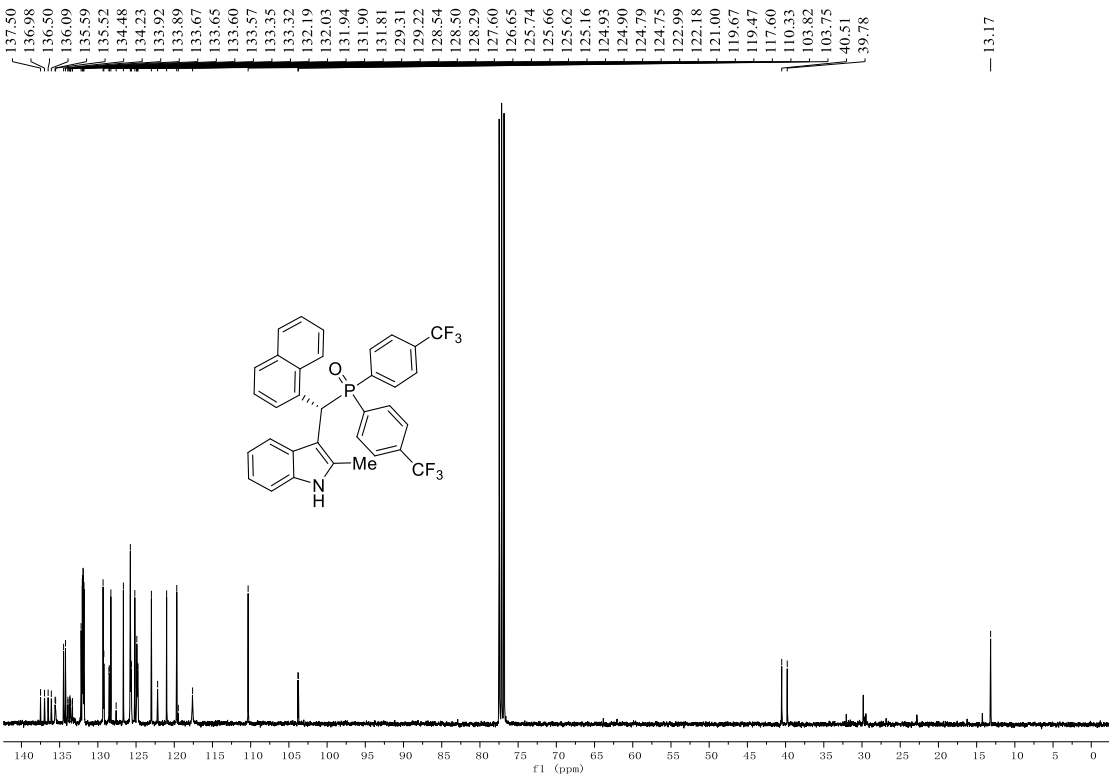
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.093	10407014	416400	94.197
2	19.626	641132	7943	5.803
Total		11048146		100.000

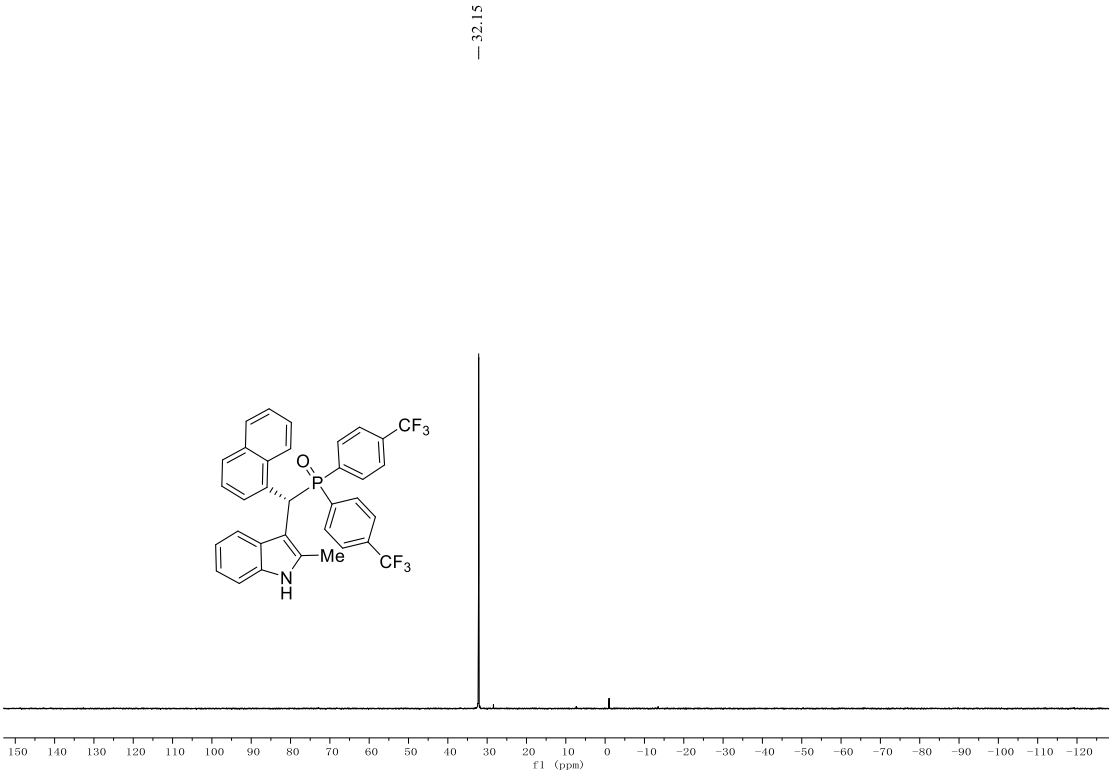
^{1}H NMR spectrum of compound of 3t



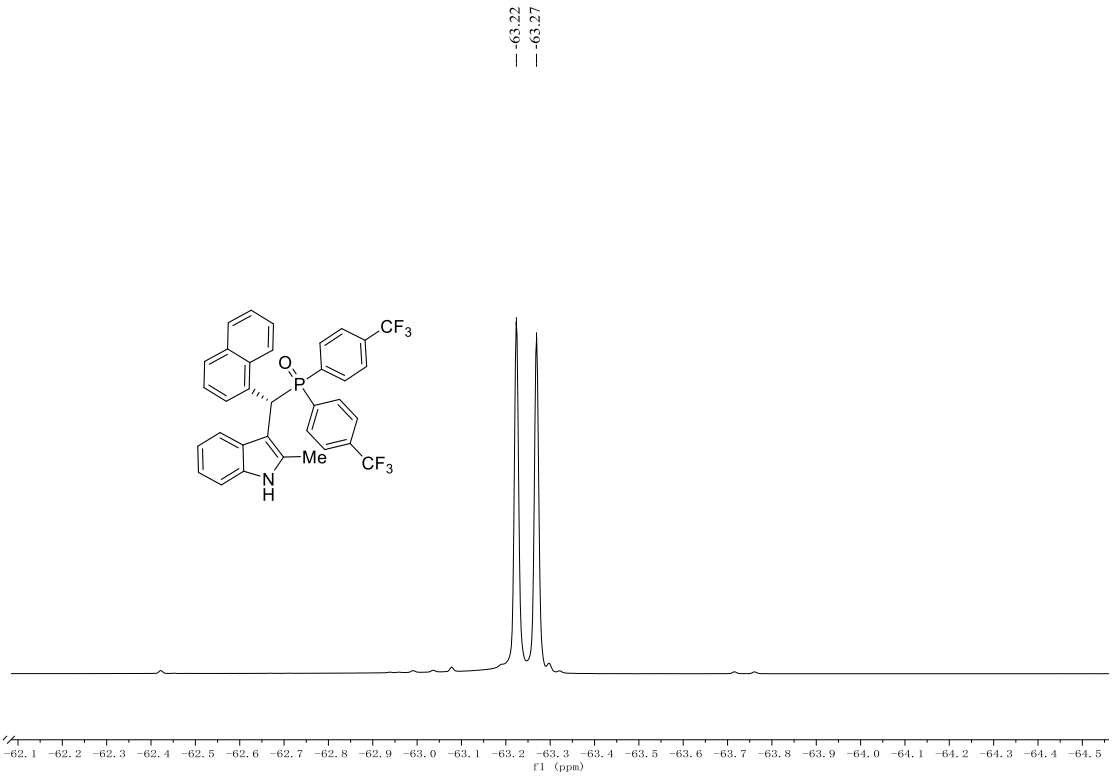
^{13}C NMR spectrum of compound of 3t



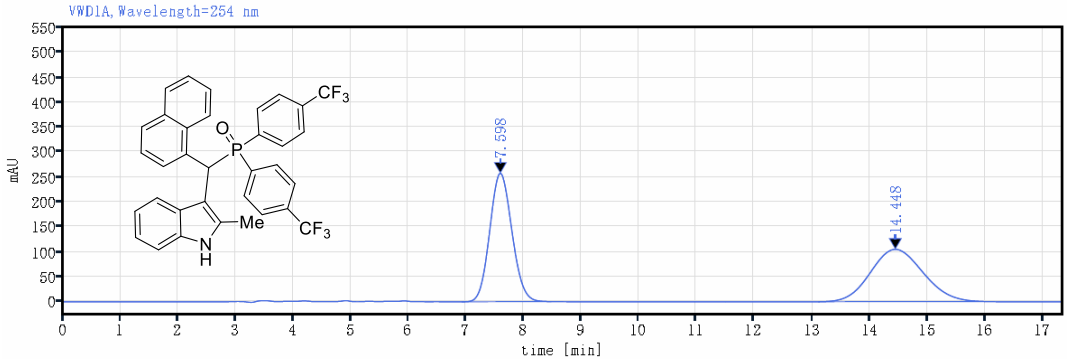
^{31}P NMR spectrum of compound of 3t



^{19}F NMR spectrum of compound of 3t

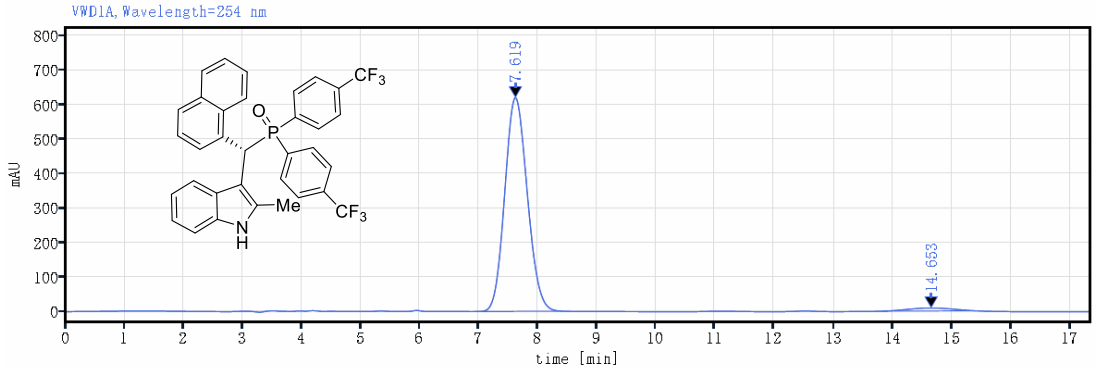


HPLC spectra of 3t



Detector VWD1A, Wavelength=254 nm

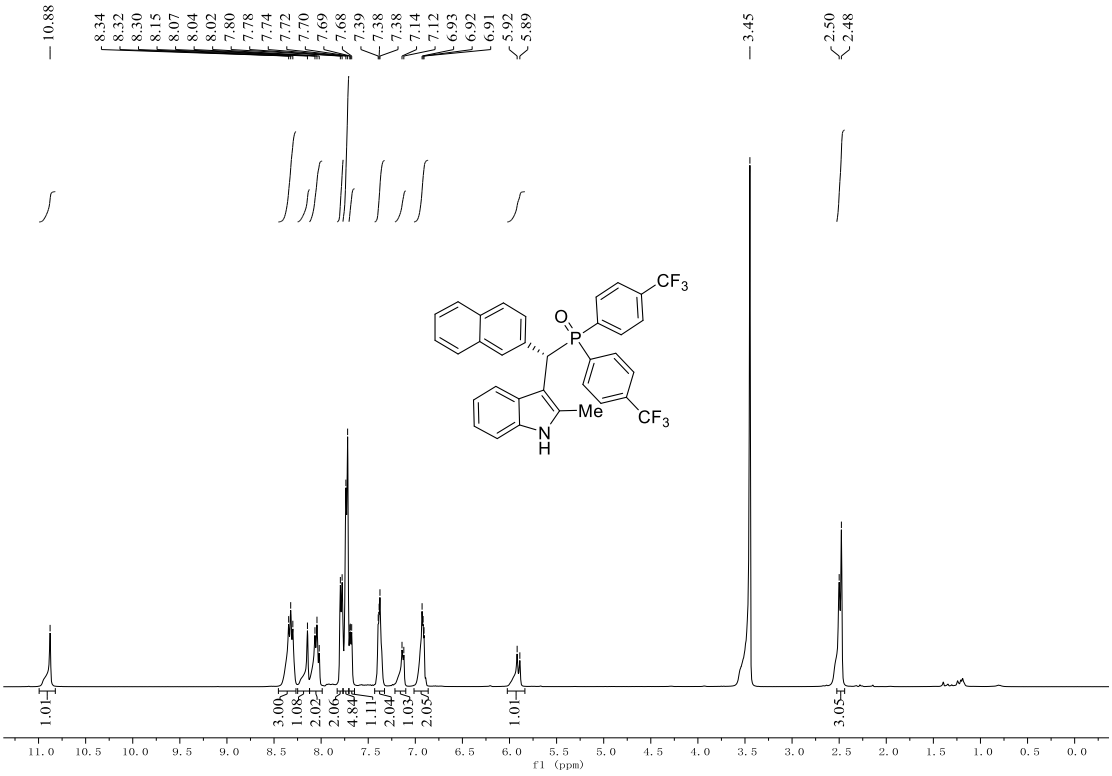
Peak	Ret.Time [min]	Area	Height	Area%
	7.598	6877.73	257.32	50.89
	14.448	6635.95	104.83	49.11
		13513.68		100.00



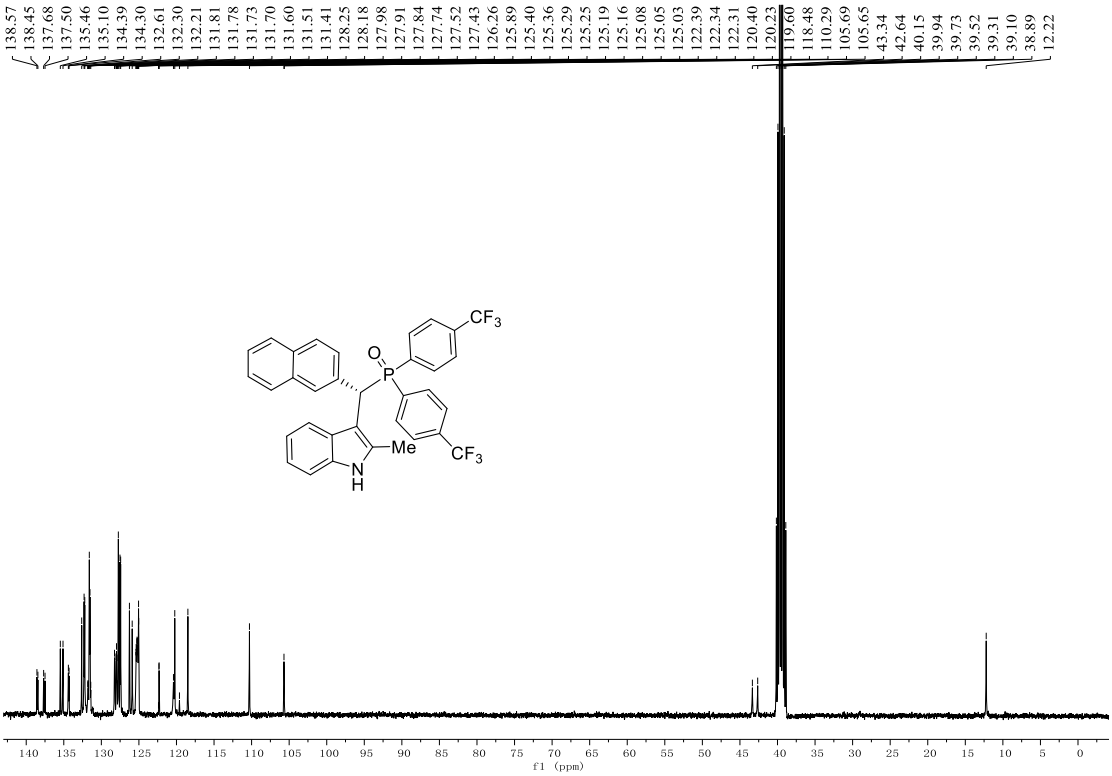
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	7.619	16455.83	621.14	97.33
	14.653	451.82	8.71	2.67
		16907.65		100.00

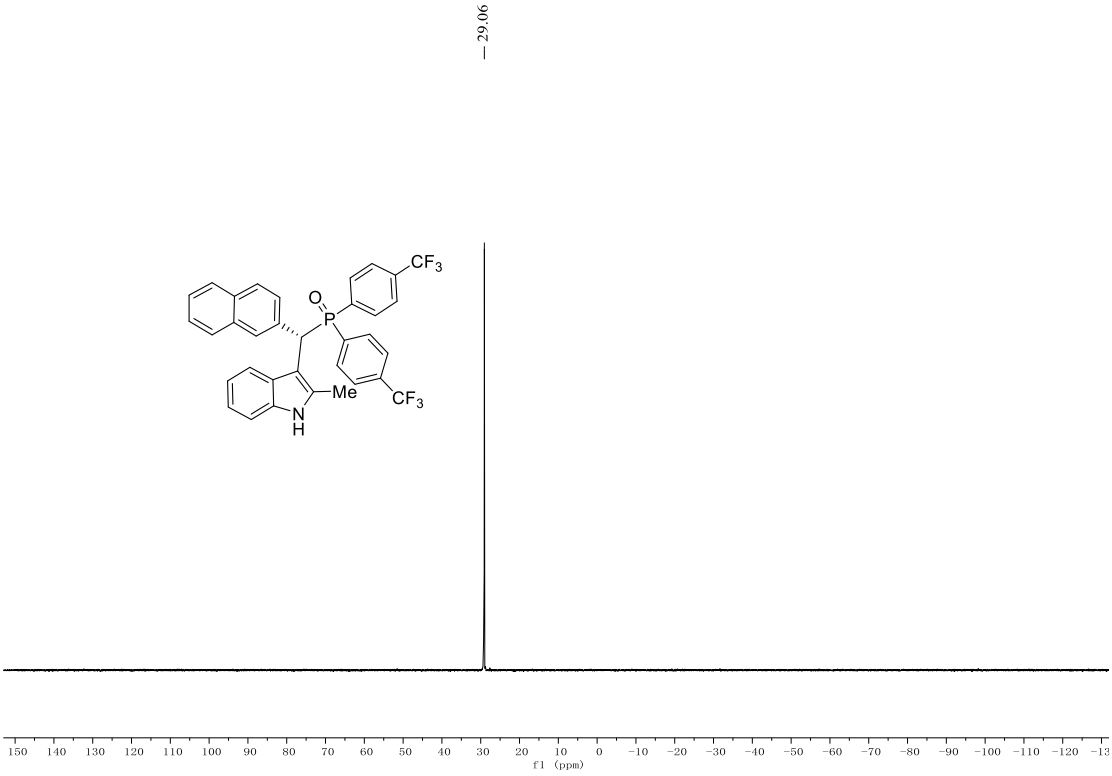
^{1}H NMR spectrum of compound of 3u



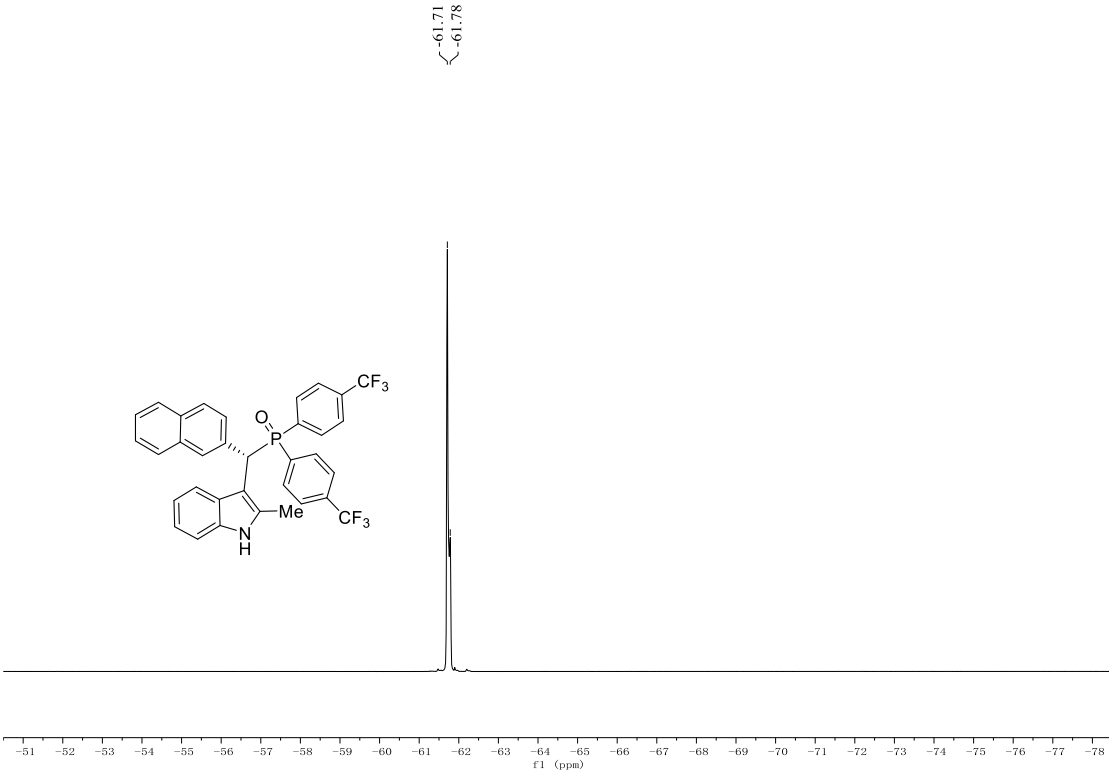
^{13}C NMR spectrum of compound of 3u



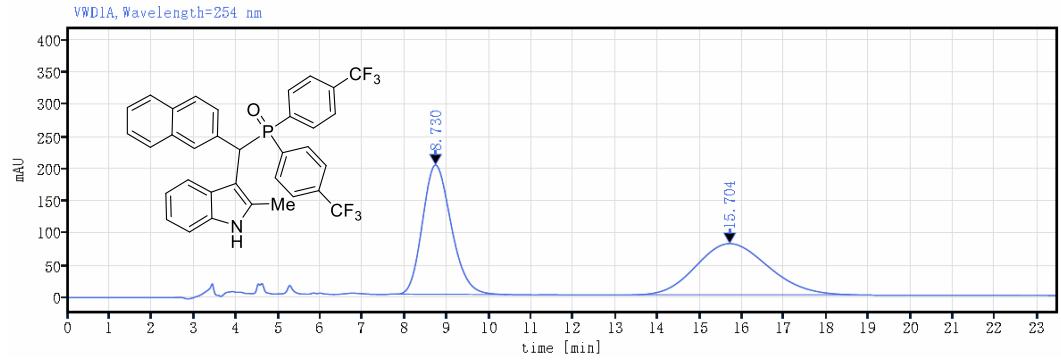
^{31}P NMR spectrum of compound of 3u



^{19}F NMR spectrum of compound of 3u

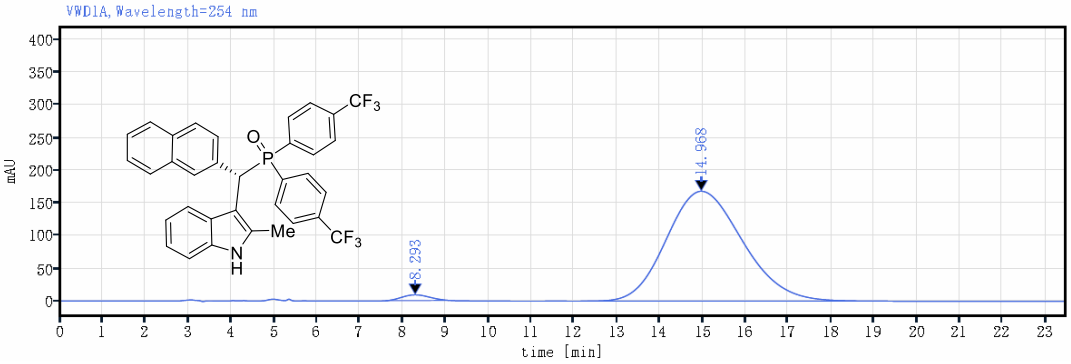


HPLC spectra of 3u



Detector VWD1A, Wavelength=254 nm

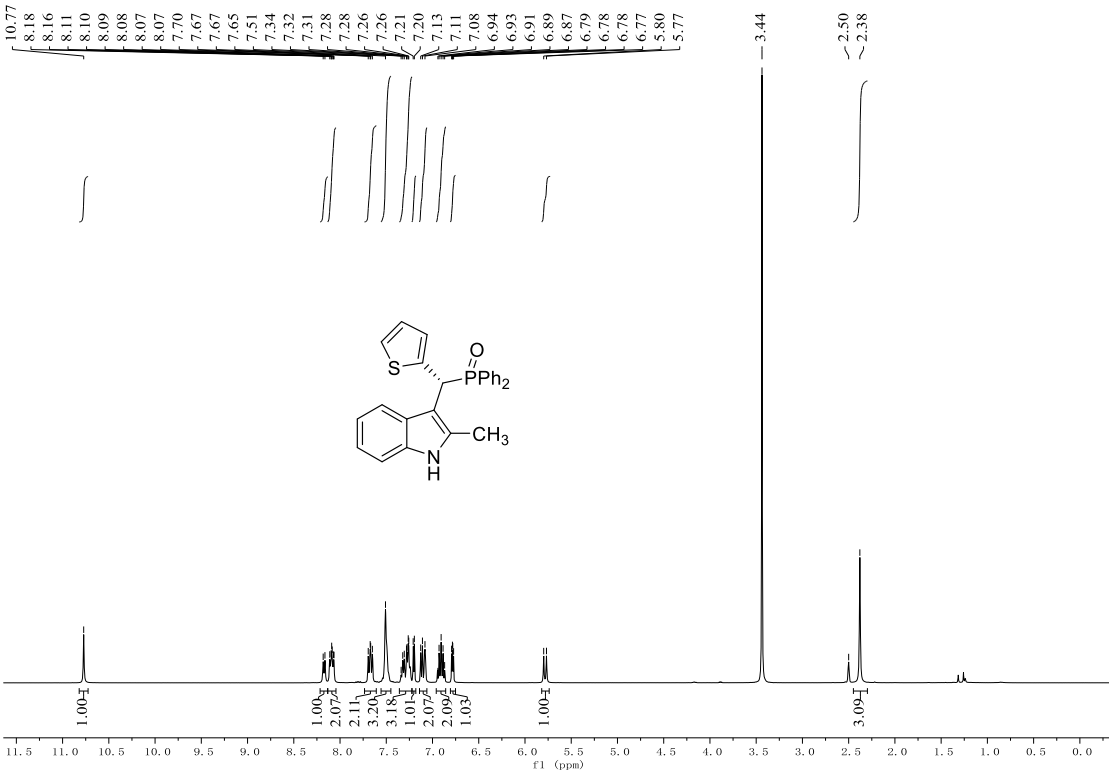
Peak	Ret.Time [min]	Area	Height	Area%
	8.730	9496.34	200.93	50.24
	15.704	9407.37	79.39	49.76
		18903.71		100.00



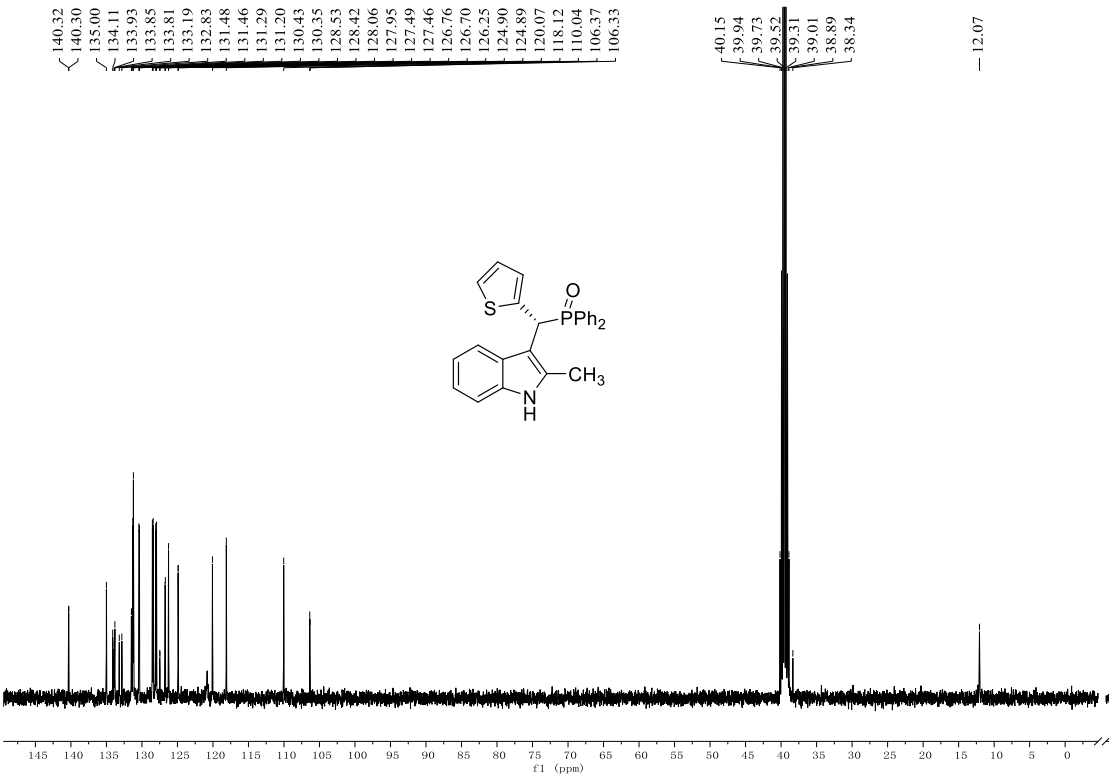
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	8.293	396.18	8.84	1.87
	14.968	20748.20	168.06	98.13
		21144.39		100.00

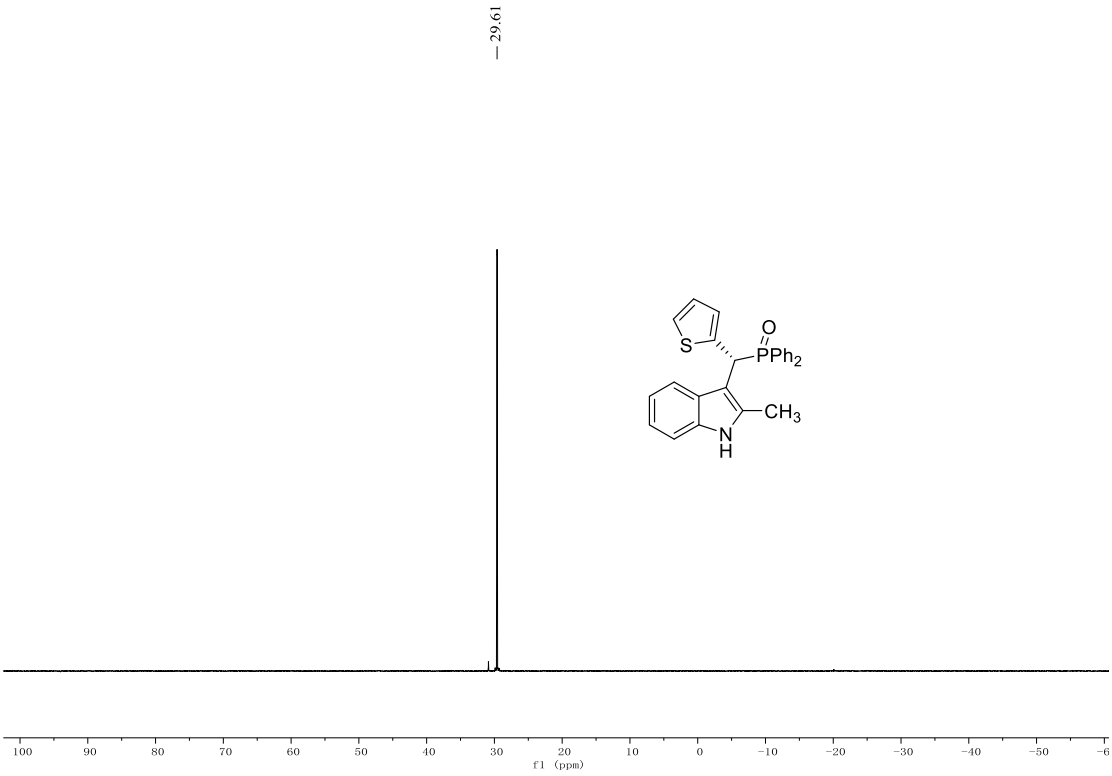
^{1}H NMR spectrum of compound of 3v



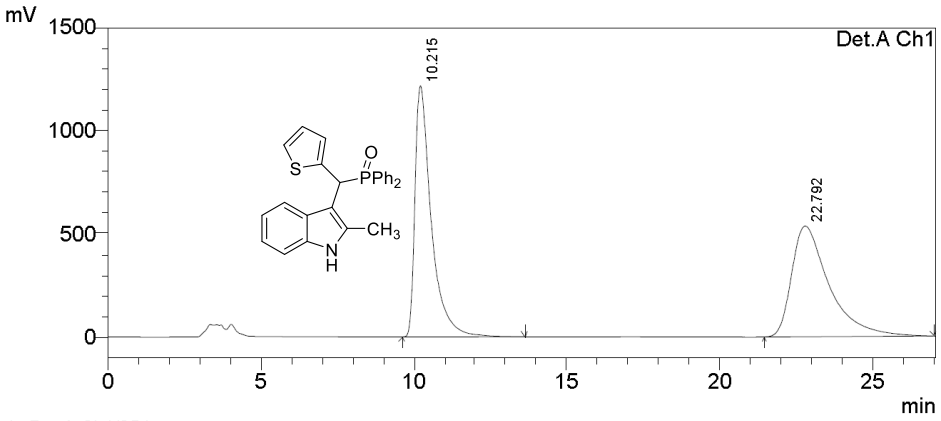
^{13}C NMR spectrum of compound of 3v



^{31}P NMR spectrum of compound of 3v



HPLC spectra of 3v

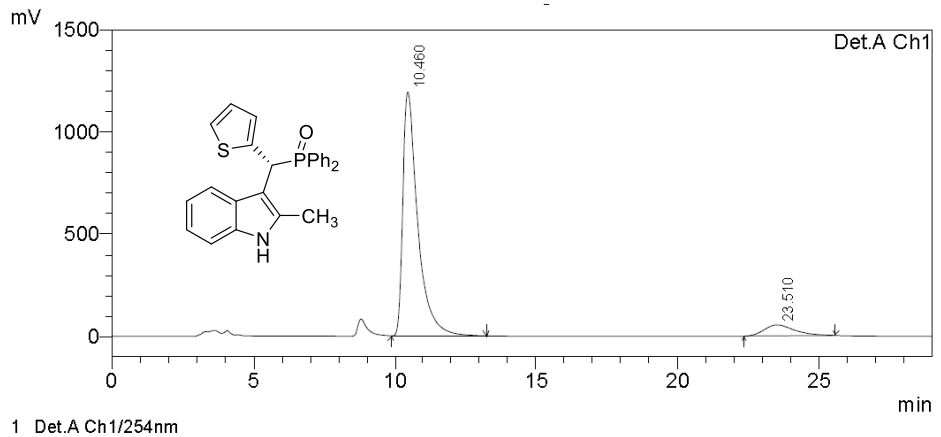


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	10.215	45131829	1215595	49.641
2	22.792	45783776	536250	50.359
Total		90915605		100.000



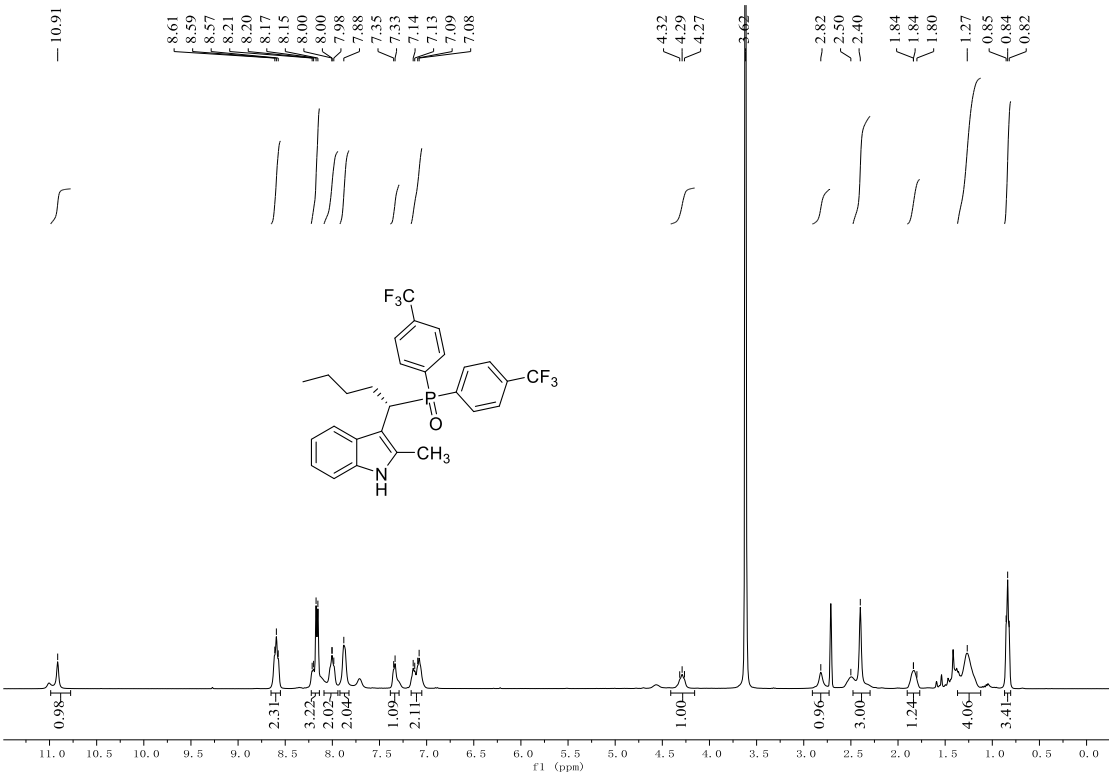
1 Det.A Ch1/254nm

PeakTable

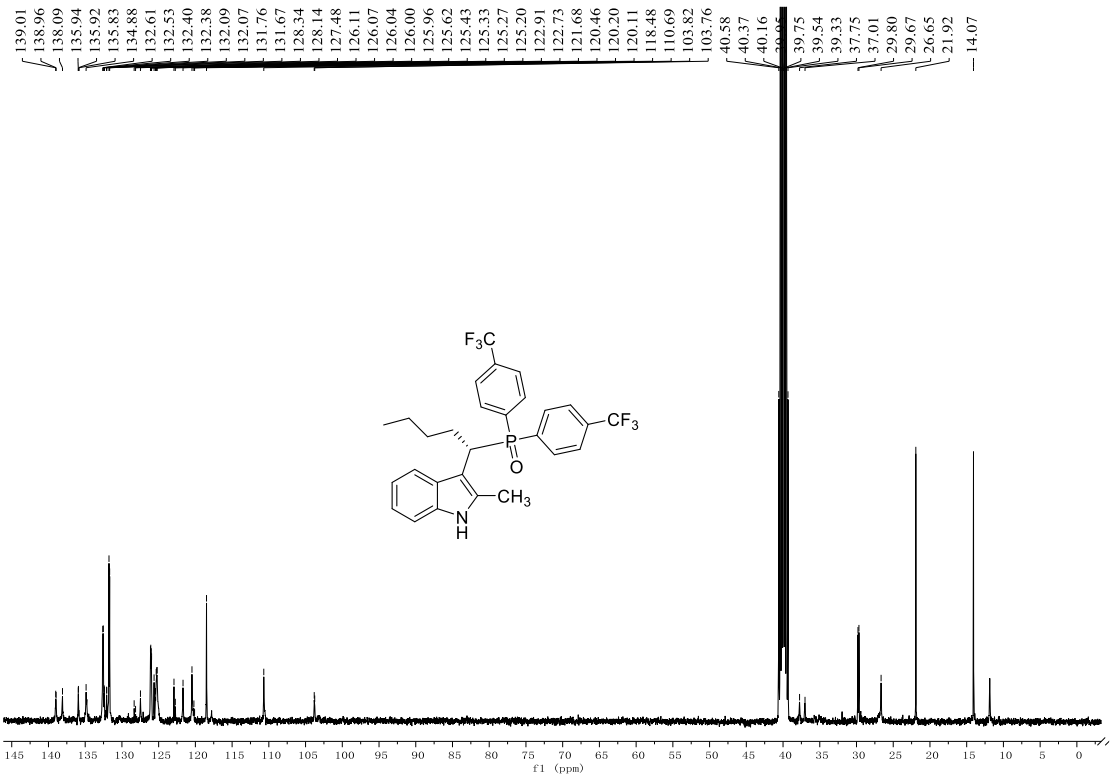
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	10.460	43612215	1192442	91.521
2	23.510	4040504	53477	8.479
Total		47652719		100.000

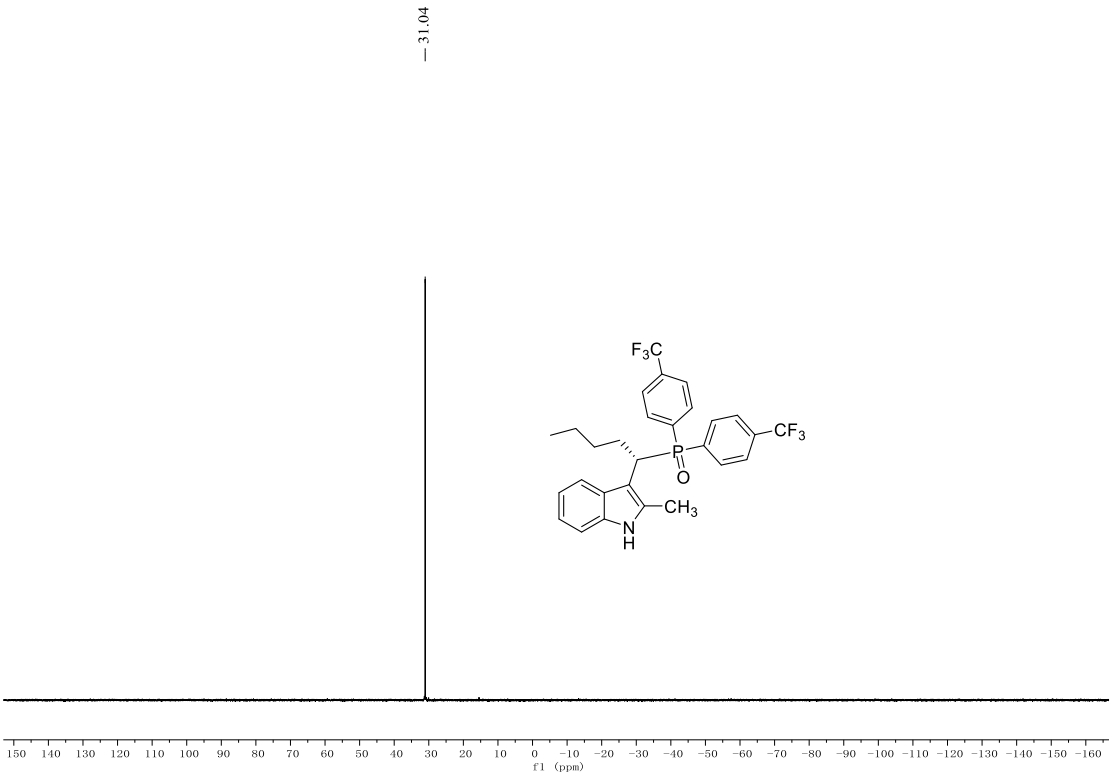
^{1}H NMR spectrum of compound of 3w



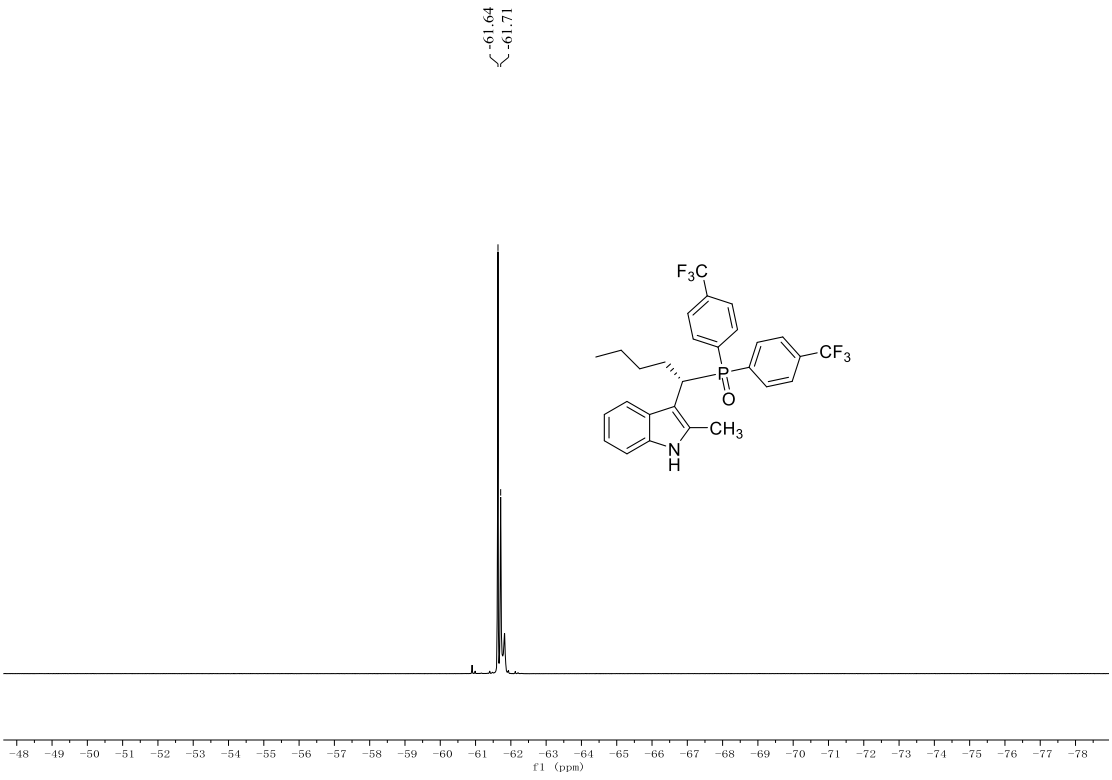
^{13}C NMR spectrum of compound of 3w



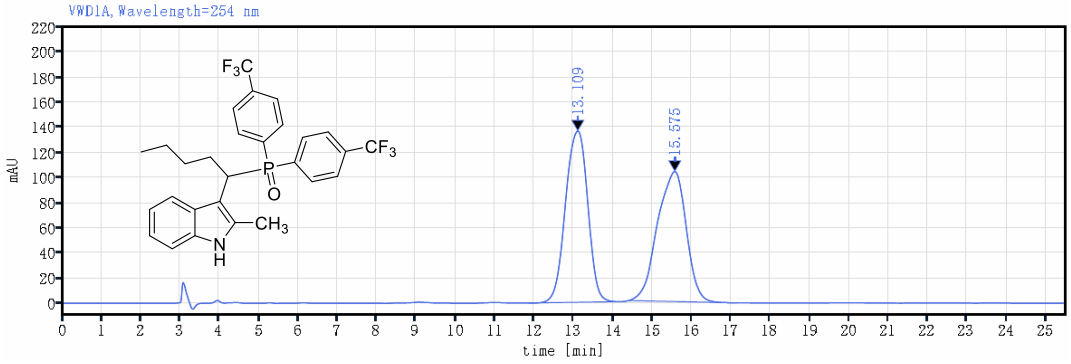
^{31}P NMR spectrum of compound of 3w



^{19}FNMR spectrum of compound of 3w

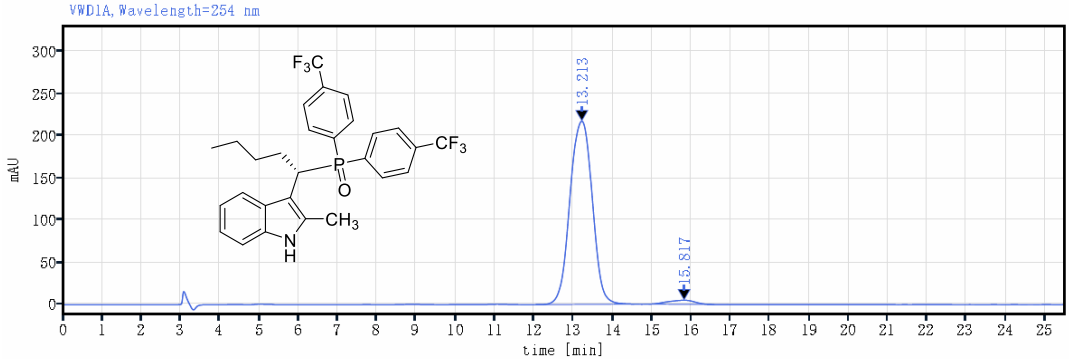


HPLC spectra of 3w



Detector VWD1A, Wavelength=254 nm

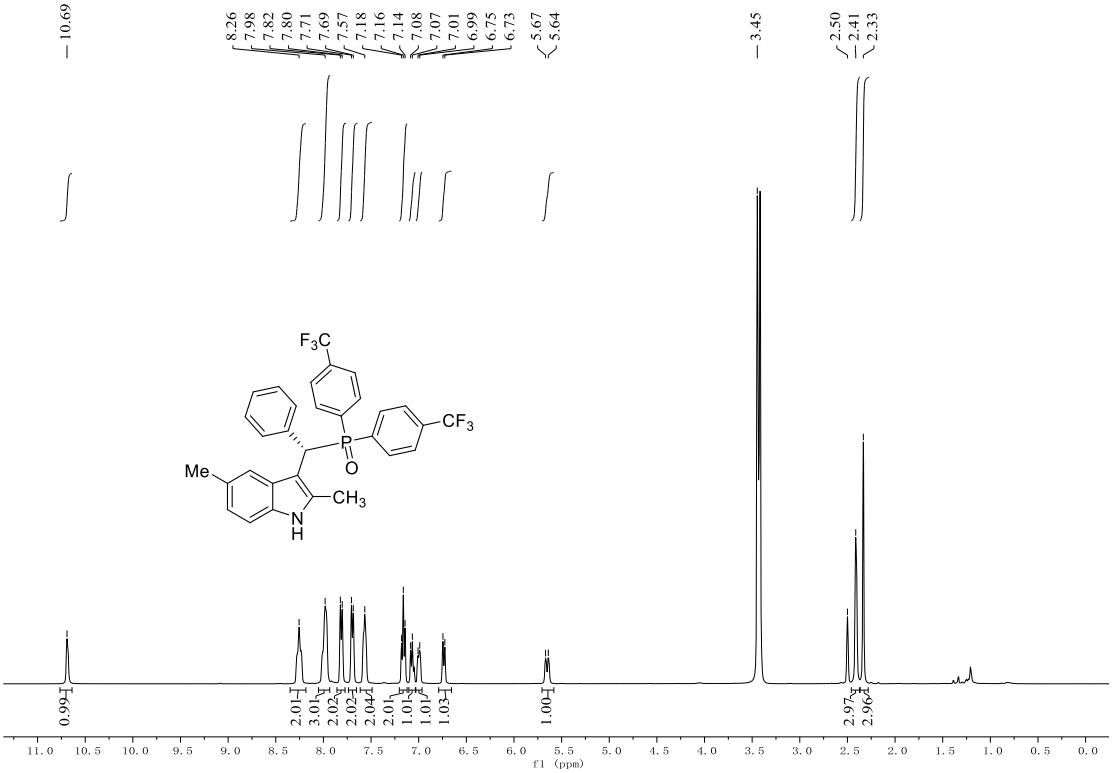
Peak	Ret.Time [min]	Area	Height	Area%
	13.109	5358.93	136.38	50.45
	15.575	5263.71	103.55	49.55
		10622.64		100.00



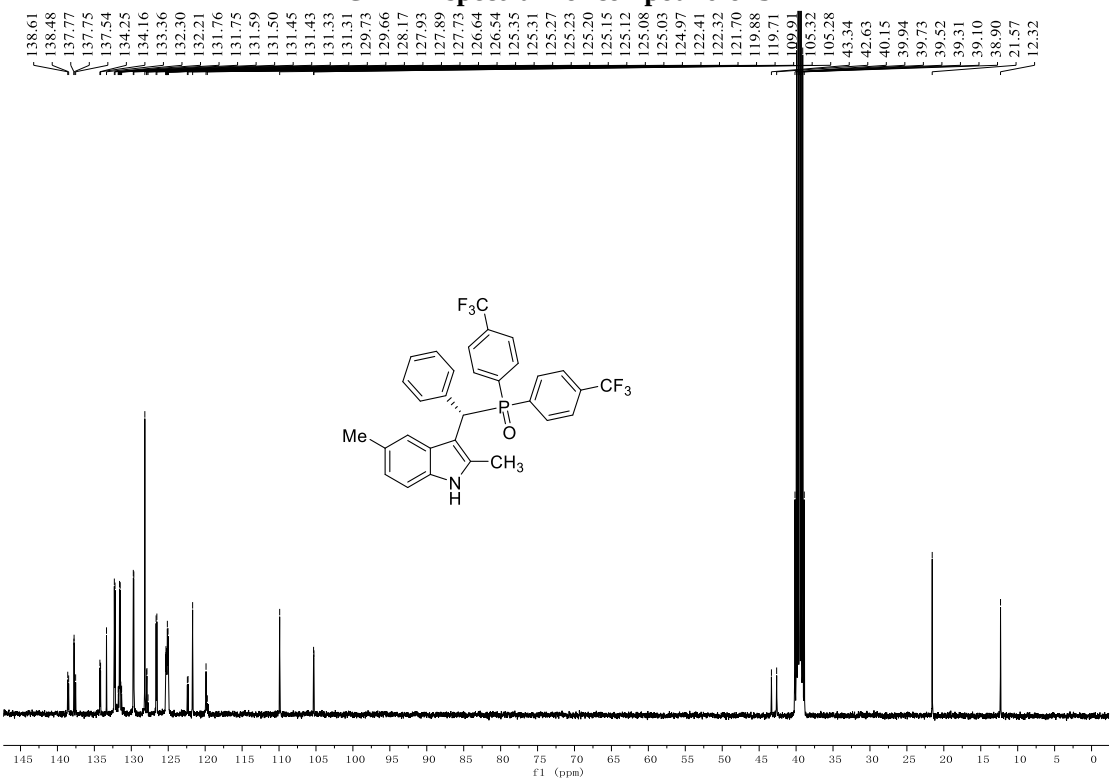
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	13.213	8595.05	217.05	97.40
	15.817	229.73	4.85	2.60
		8824.77		100.00

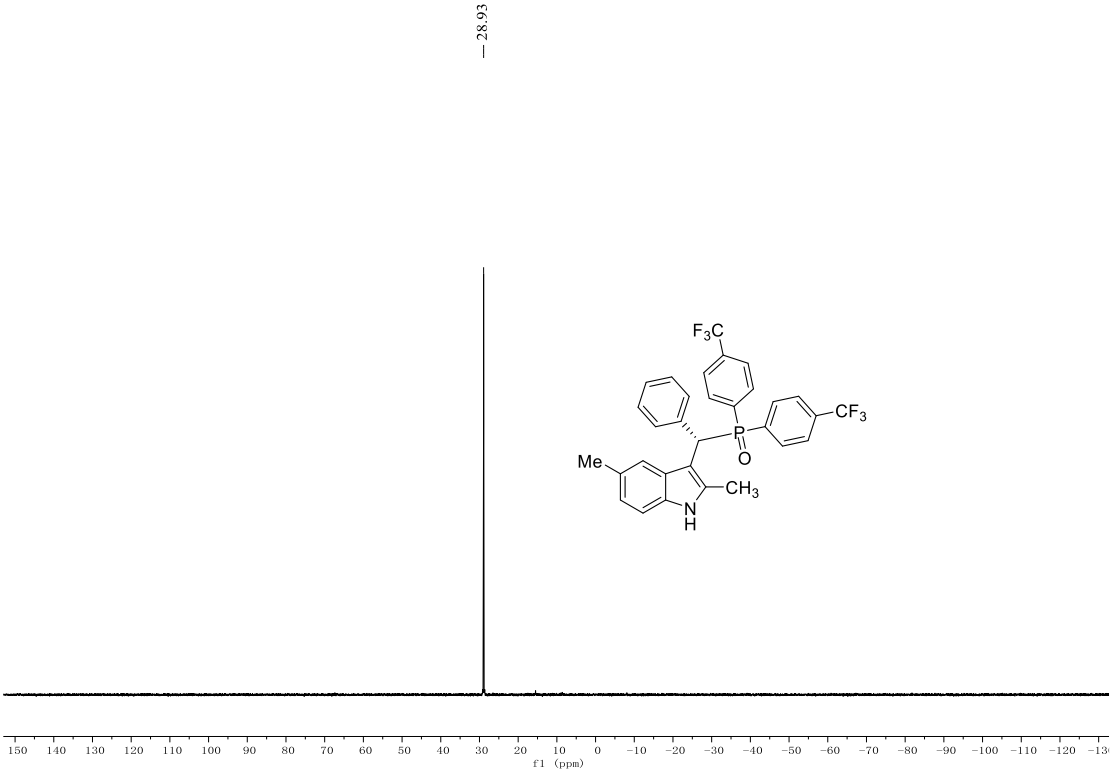
^{1}H NMR spectrum of compound of 3x



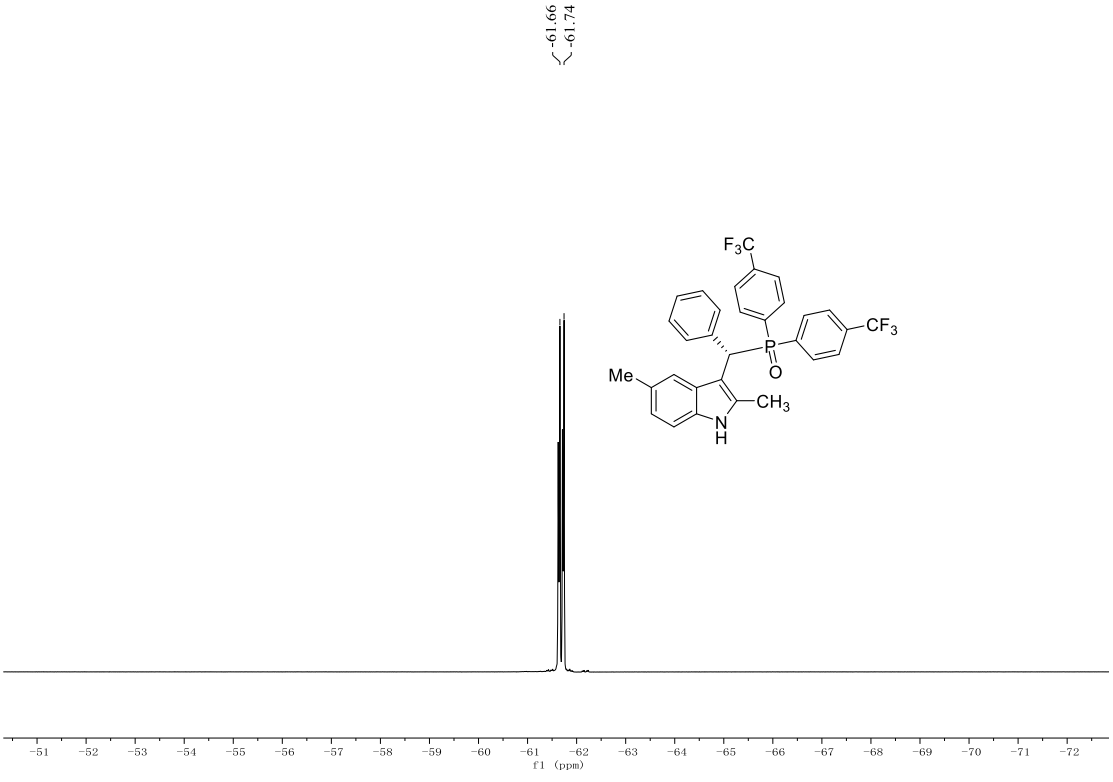
^{13}C NMR spectrum of compound of 3x



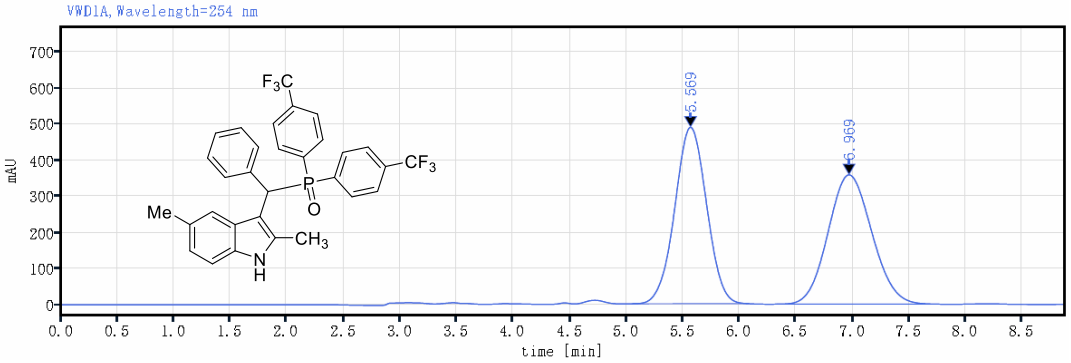
^{31}P NMR spectrum of compound of 3x



^{19}F NMR spectrum of compound of 3x

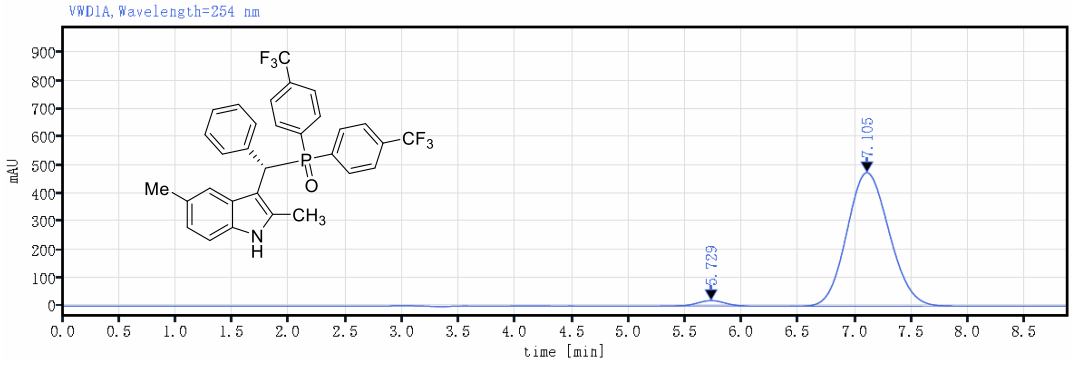


HPLC spectra of 3x



Detector VWD1A, Wavelength=254 nm

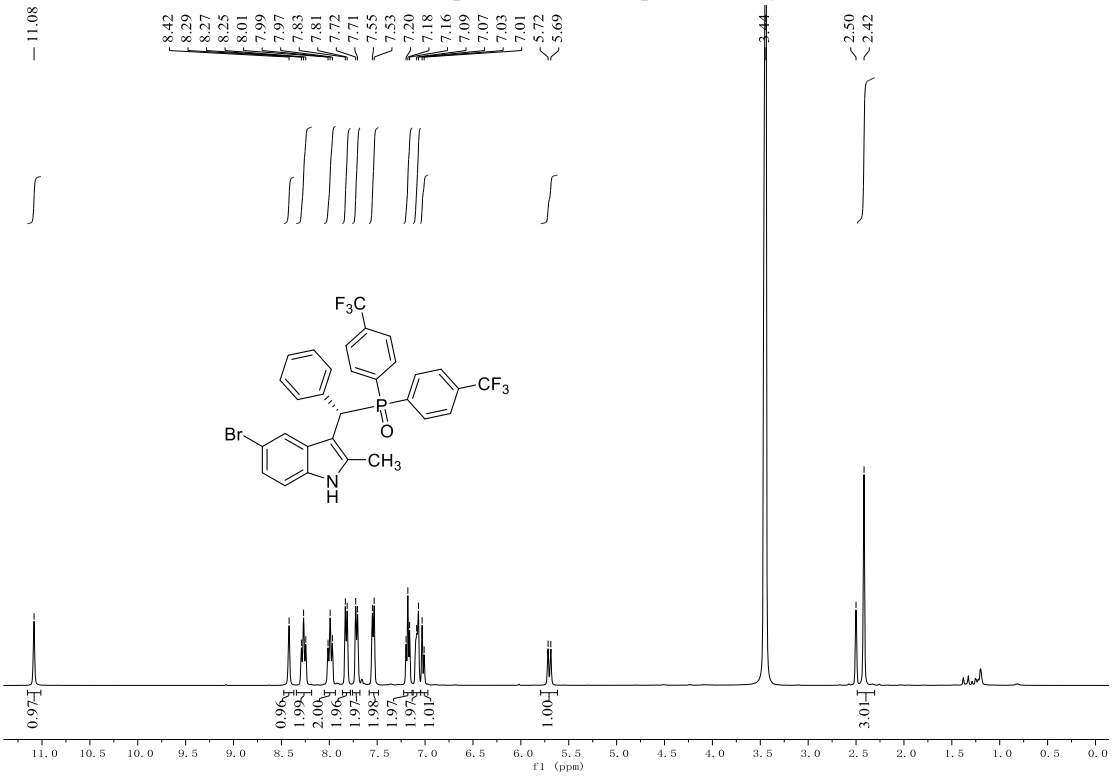
Peak	Ret.Time [min]	Area	Height	Area%
	5.569	9581.66	489.26	49.84
	6.969	9644.02	358.58	50.16
		19225.69		100.00



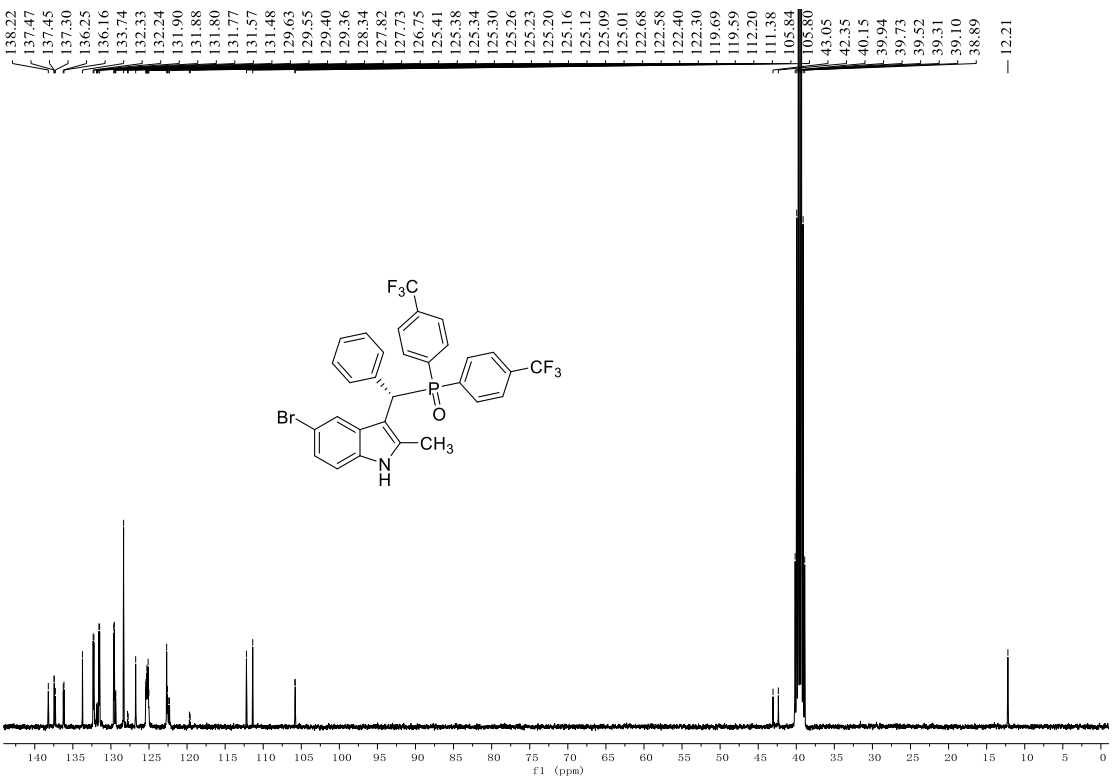
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	5.729	308.58	18.89	2.45
	7.105	12292.60	473.62	97.55
		12601.18		100.00

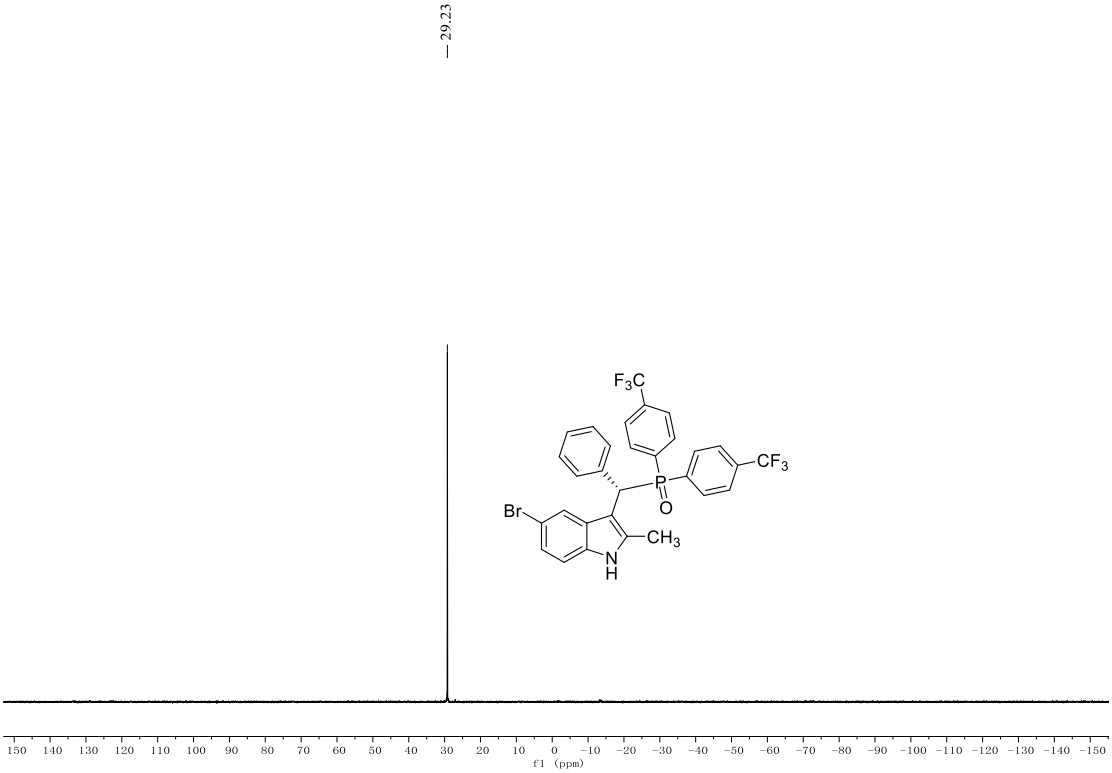
^{1}H NMR spectrum of compound of 3y



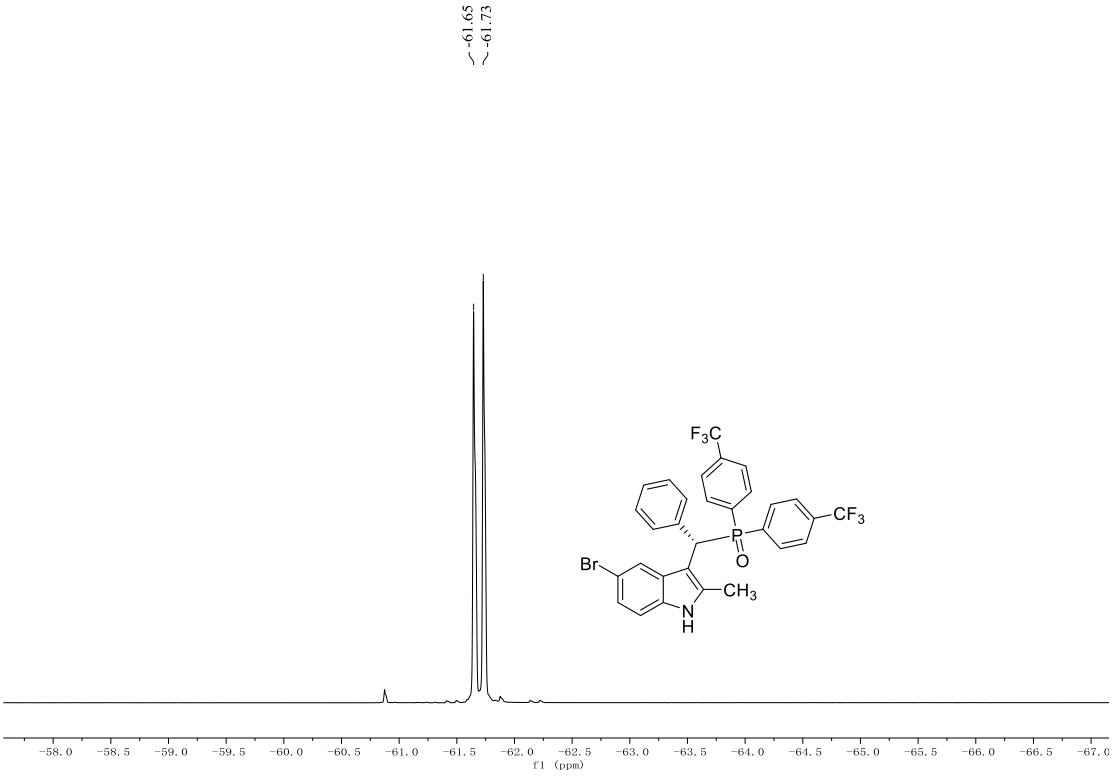
^{13}C NMR spectrum of compound of 3y



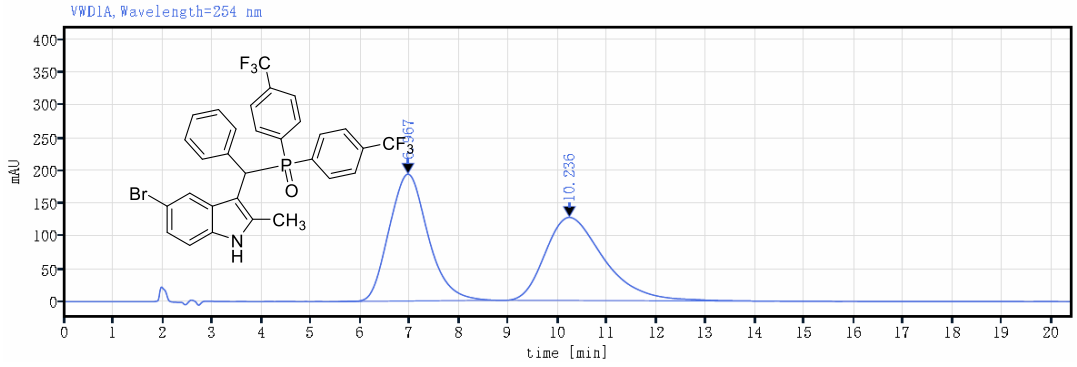
^{31}P NMR spectrum of compound of 3y



^{19}F NMR spectrum of compound of 3y

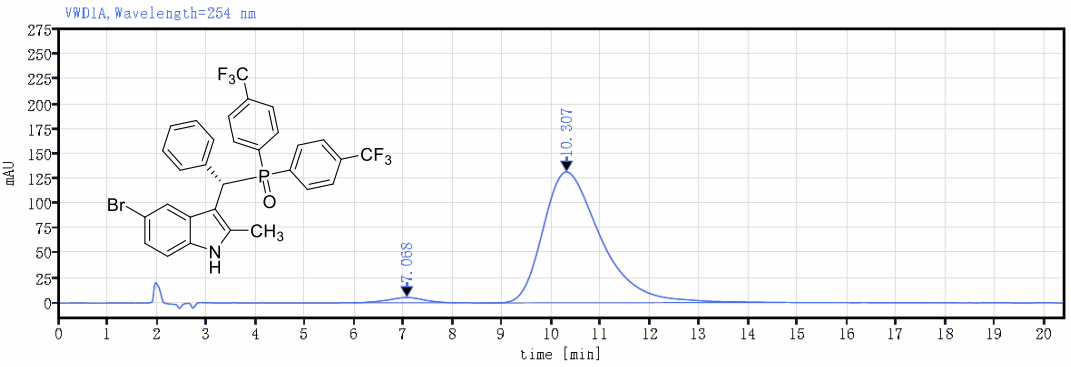


HPLC spectra of 3y



Detector VWD1A, Wavelength=254 nm

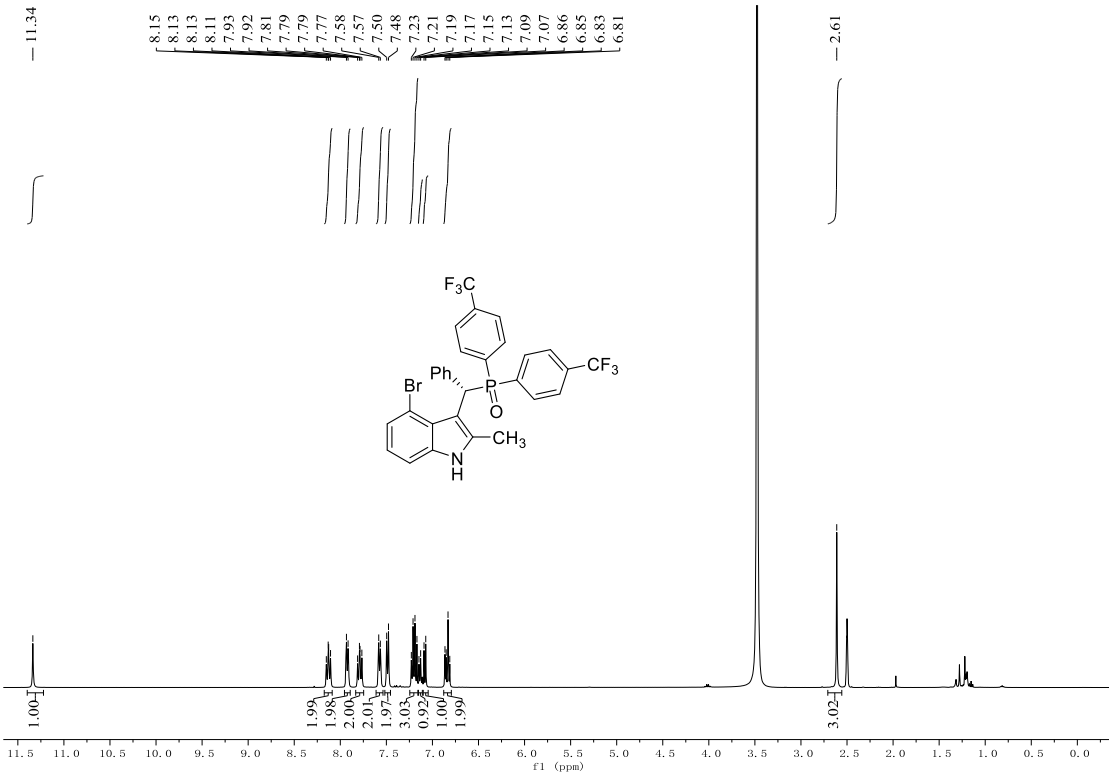
Peak	Ret.Time [min]	Area	Height	Area%
	6.967	10574.67	193.72	50.32
	10.236	10442.22	126.86	49.68
		21016.89		100.00



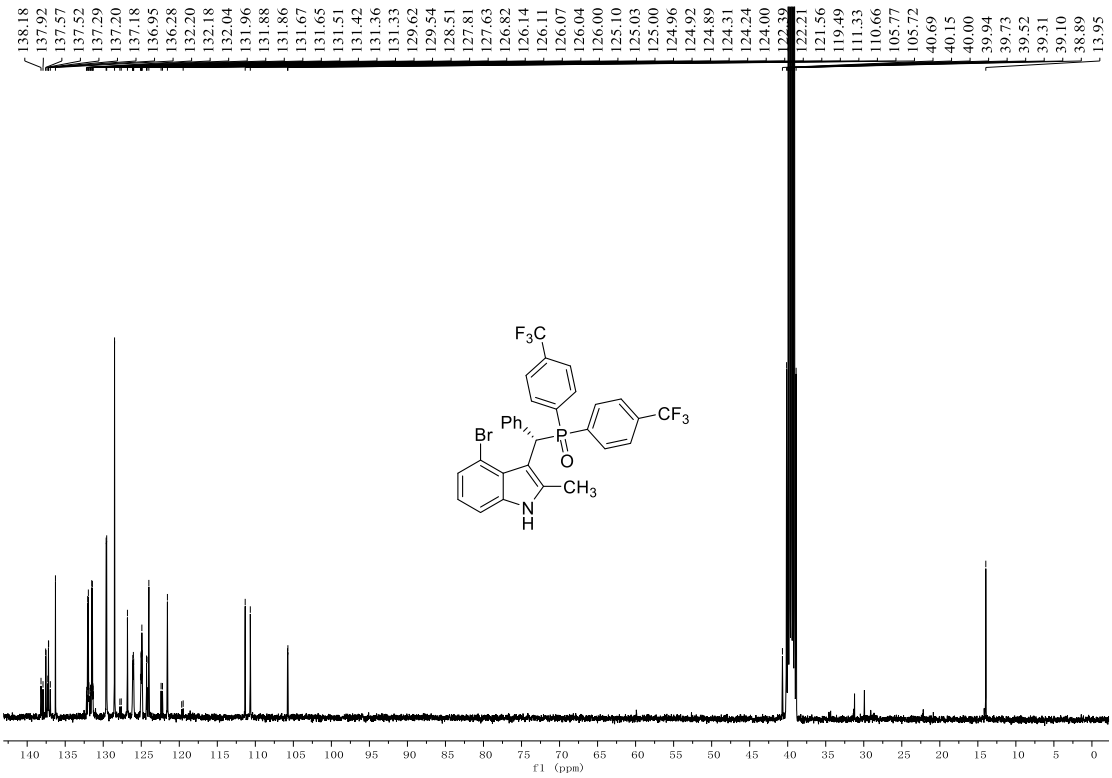
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	7.068	262.80	5.25	2.40
	10.307	10687.75	131.66	97.60
		10950.56		100.00

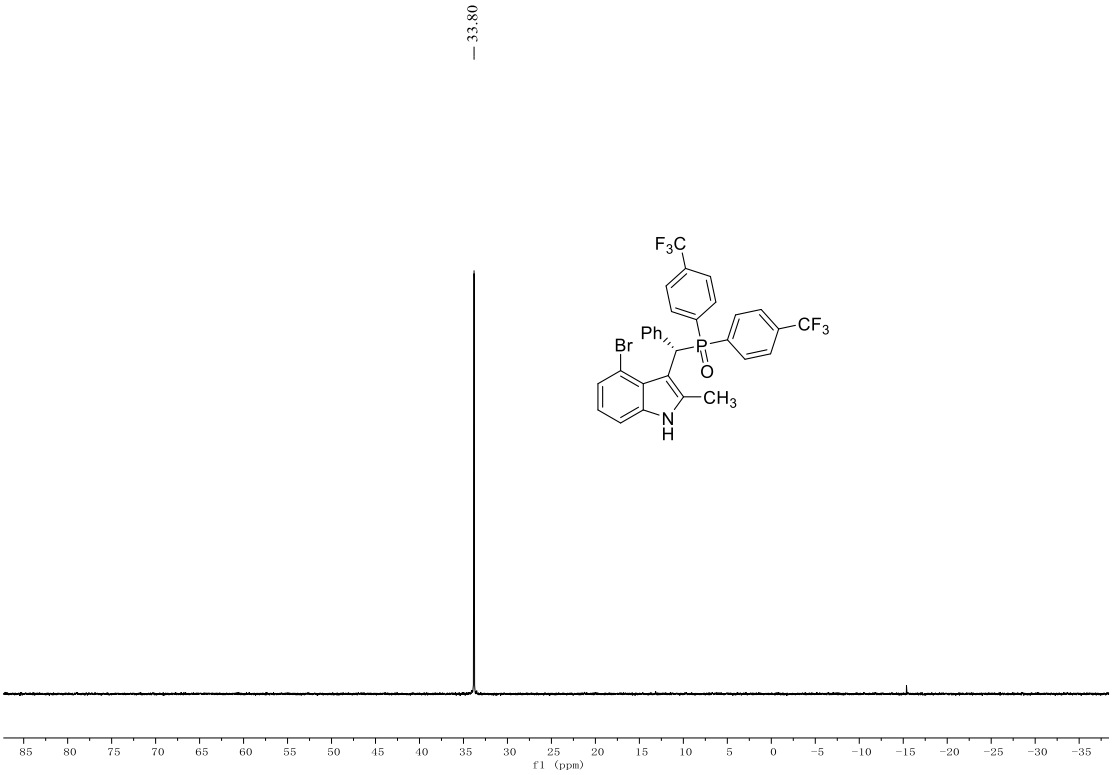
^{1}H NMR spectrum of compound of 3z



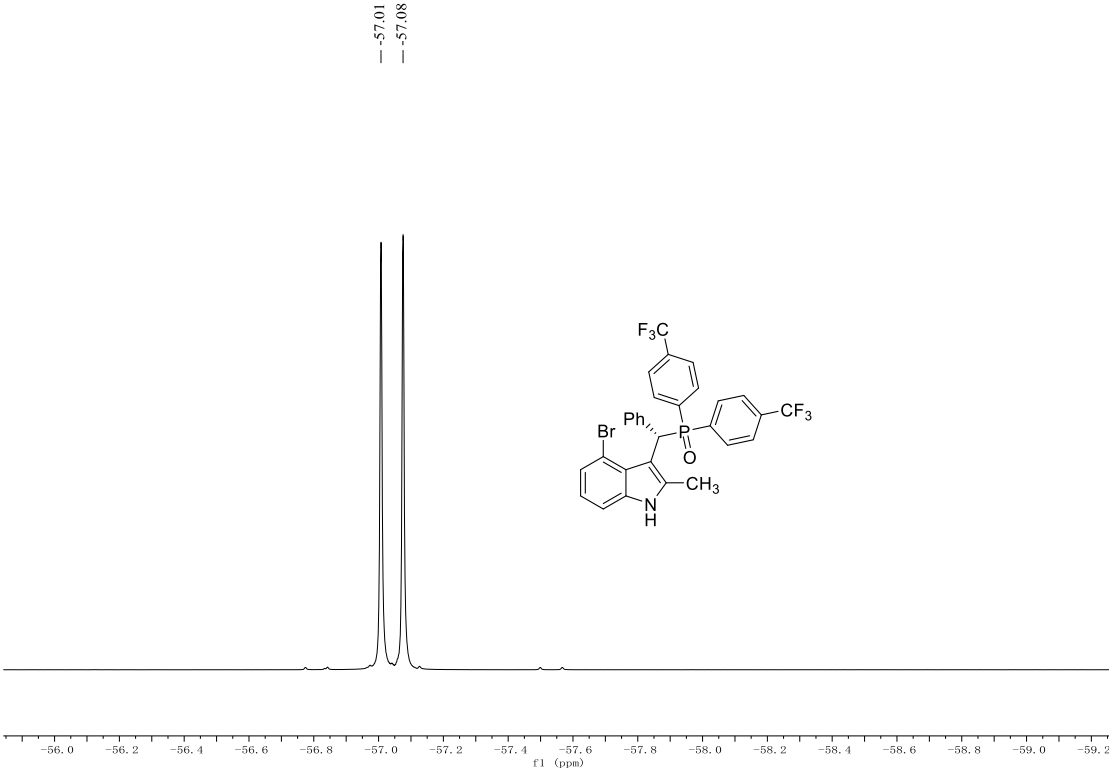
^{13}C NMR spectrum of compound of 3z



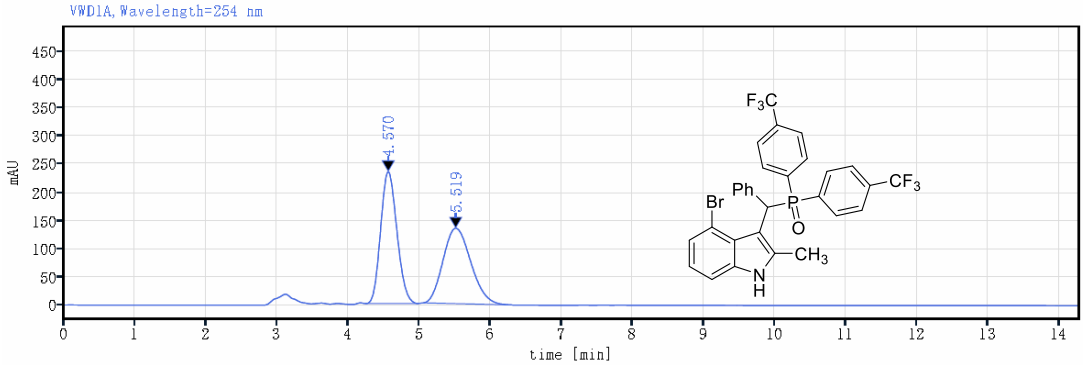
^{31}P NMR spectrum of compound of 3z



^{19}F NMR spectrum of compound of 3z

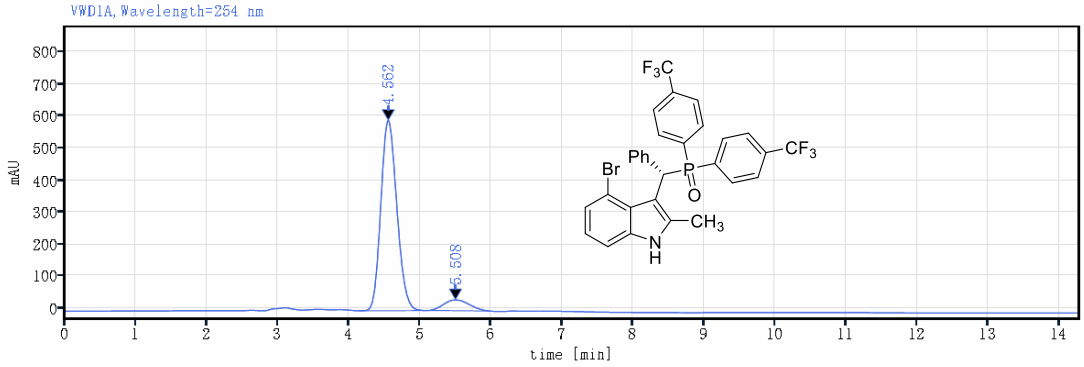


HPLC spectra of 3z



Detector VWD1A, Wavelength=254 nm

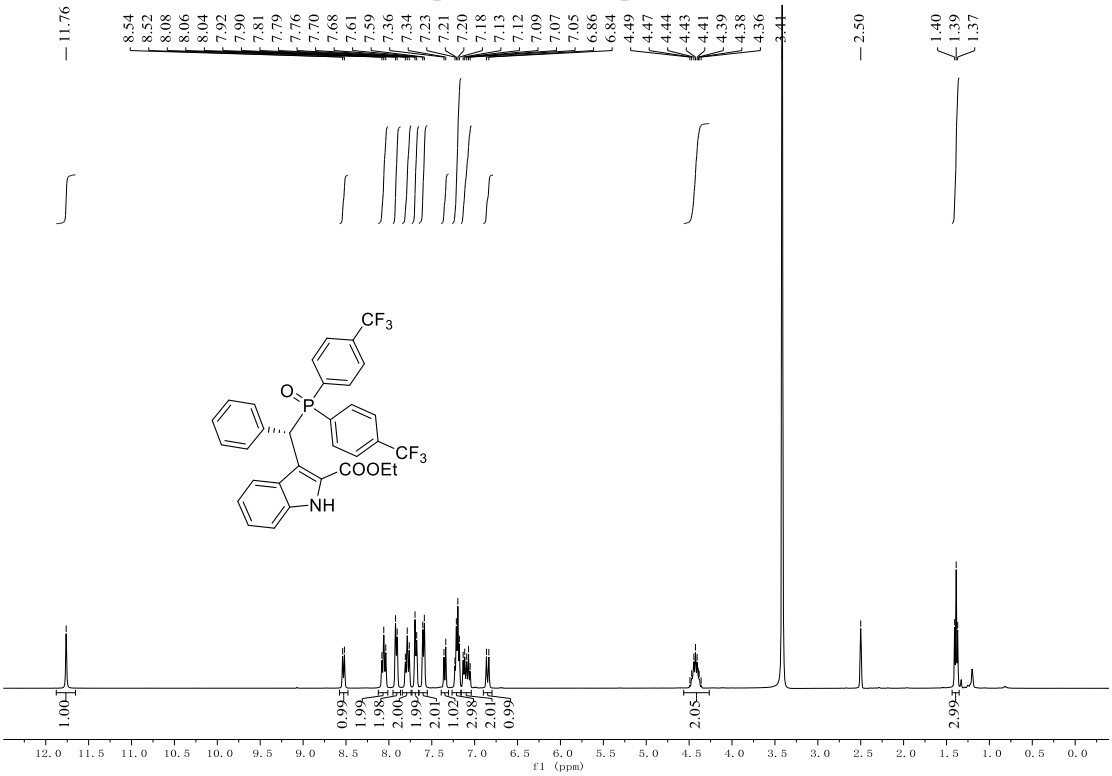
Peak	Ret.Time [min]	Area	Height	Area%
	4.570	3727.64	234.89	50.52
	5.519	3650.82	134.32	49.48
		7378.46		100.00



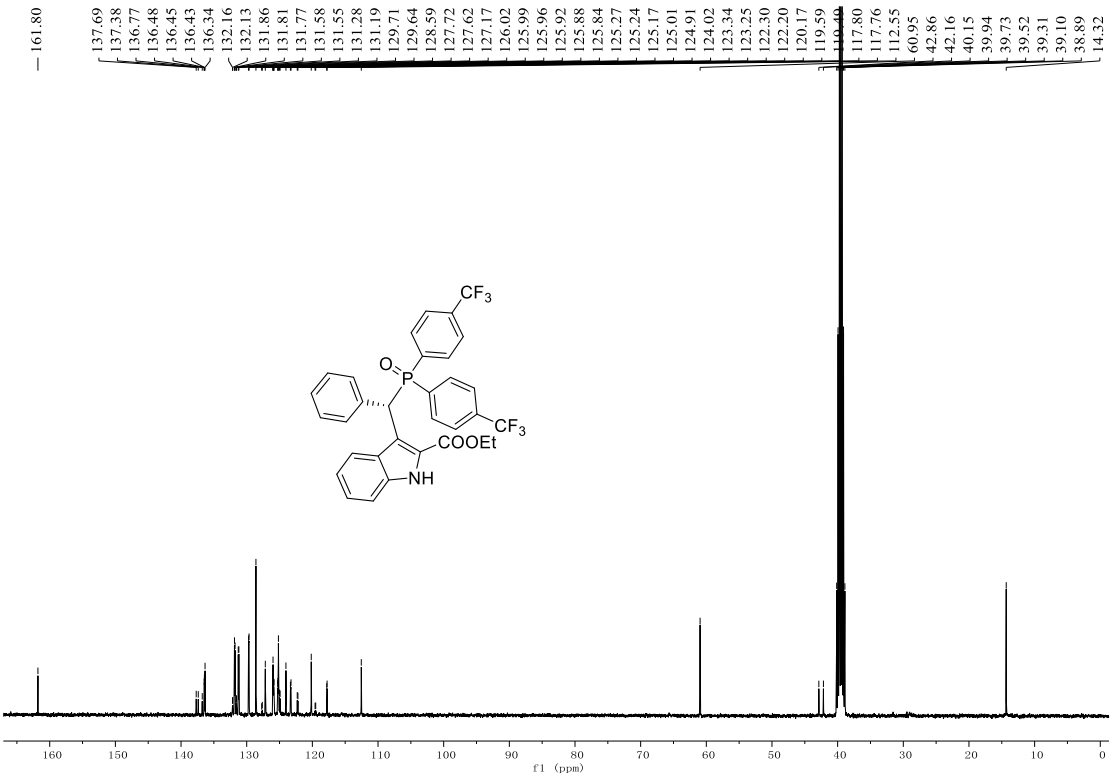
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	4.562	9303.56	593.87	91.71
	5.508	840.73	33.38	8.29
		10144.30		100.00

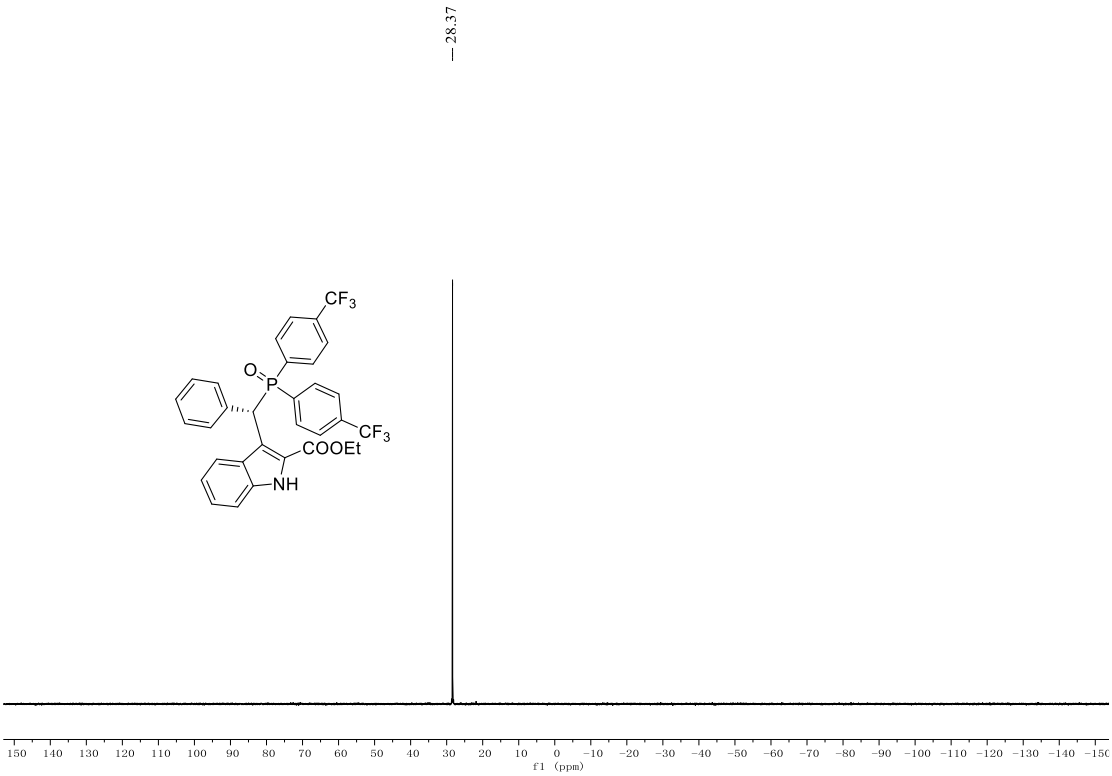
^{1}H NMR spectrum of compound of of 3a`



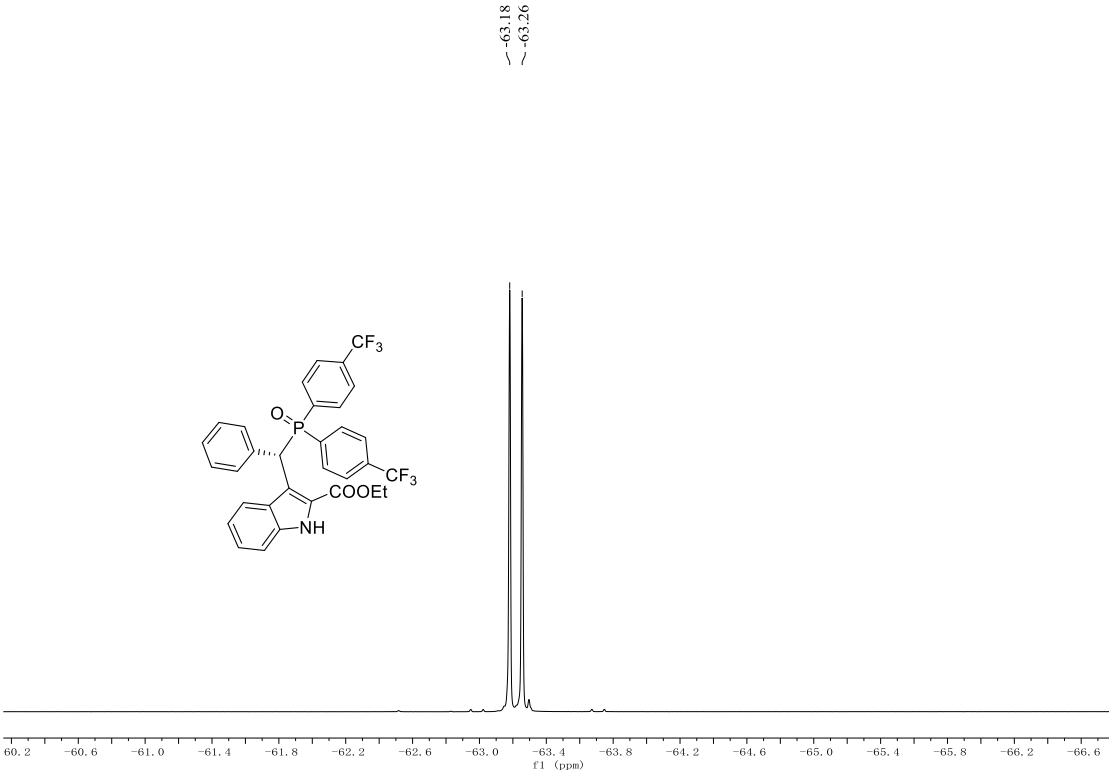
^{13}C NMR spectrum of compound of of 3a`



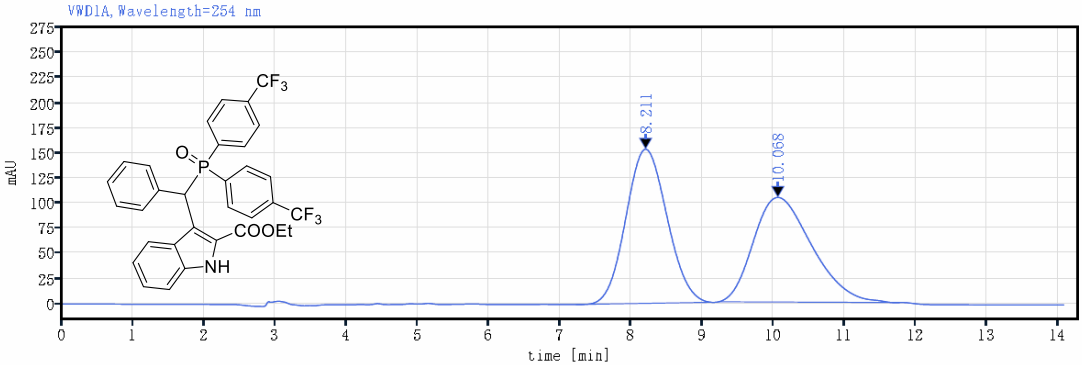
^{31}P NMR spectrum of compound of of 3a`



^{19}F NMR spectrum of compound of of 3a`

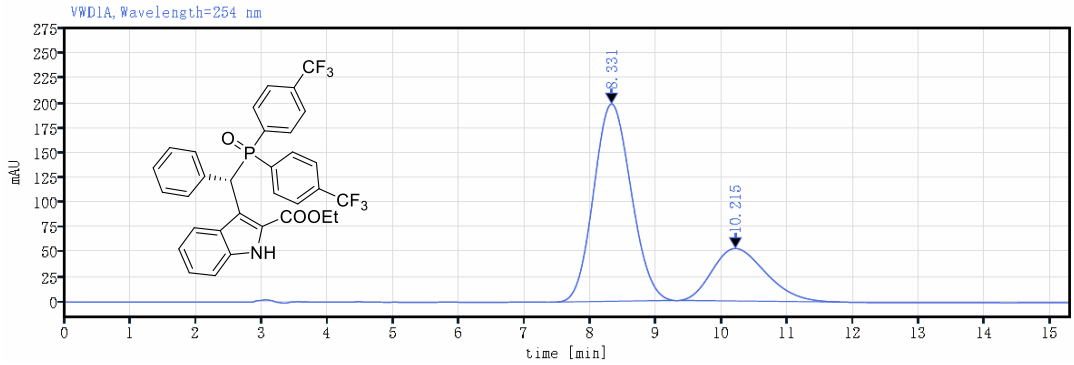


HPLC spectra of 3a`



Detector VWD1A, Wavelength=254 nm

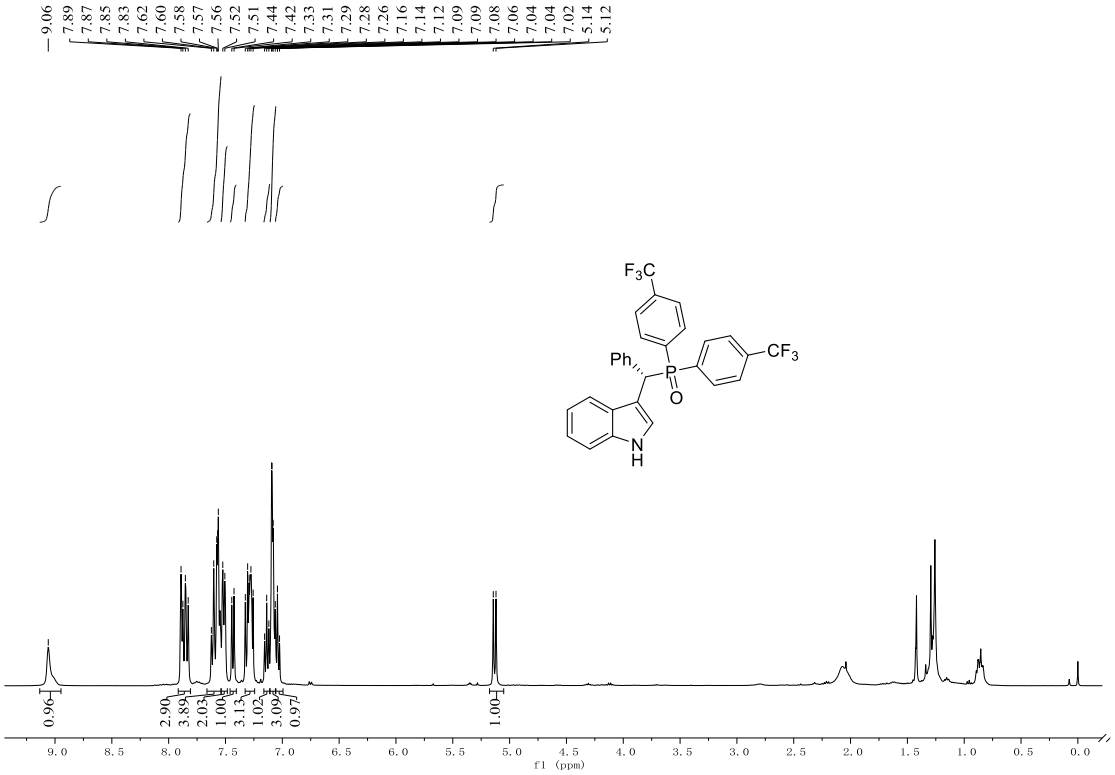
Peak	Ret.Time [min]	Area	Height	Area%
	8.211	6145.97	153.50	50.92
	10.068	5924.66	104.14	49.08
		12070.63		100.00



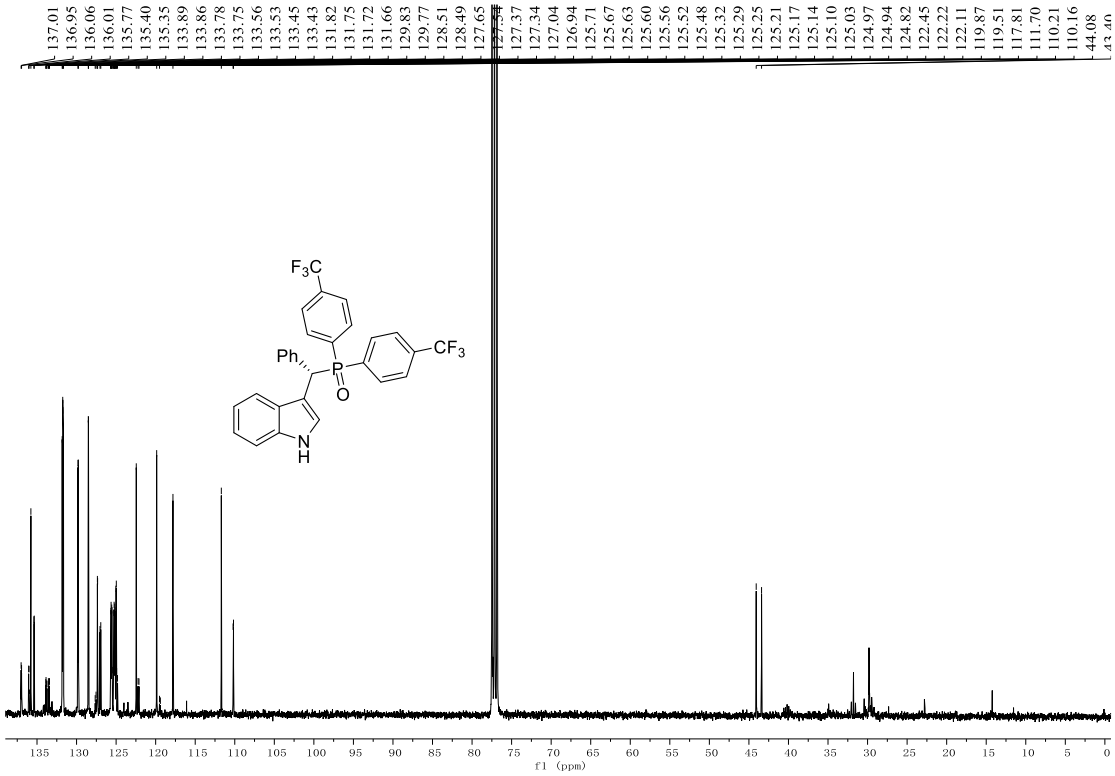
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	8.331	7853.37	198.64	72.51
	10.215	2976.79	52.77	27.49
		10830.16		100.00

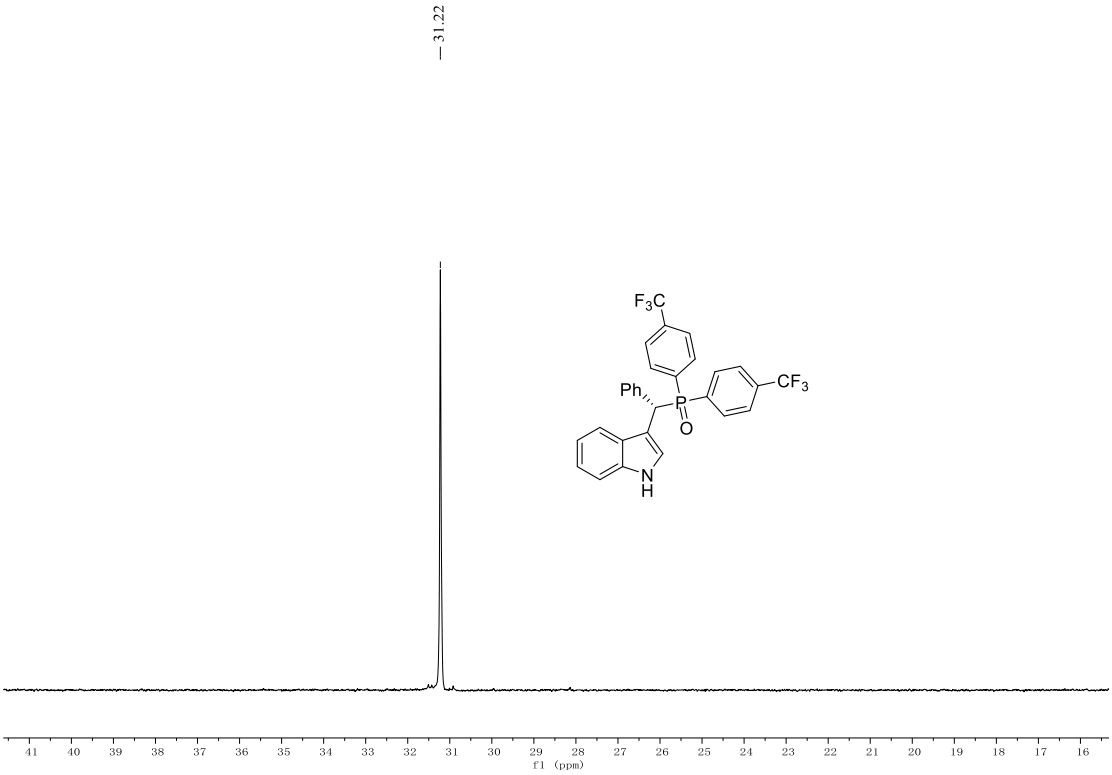
^{1}H NMR spectrum of compound of 3b`



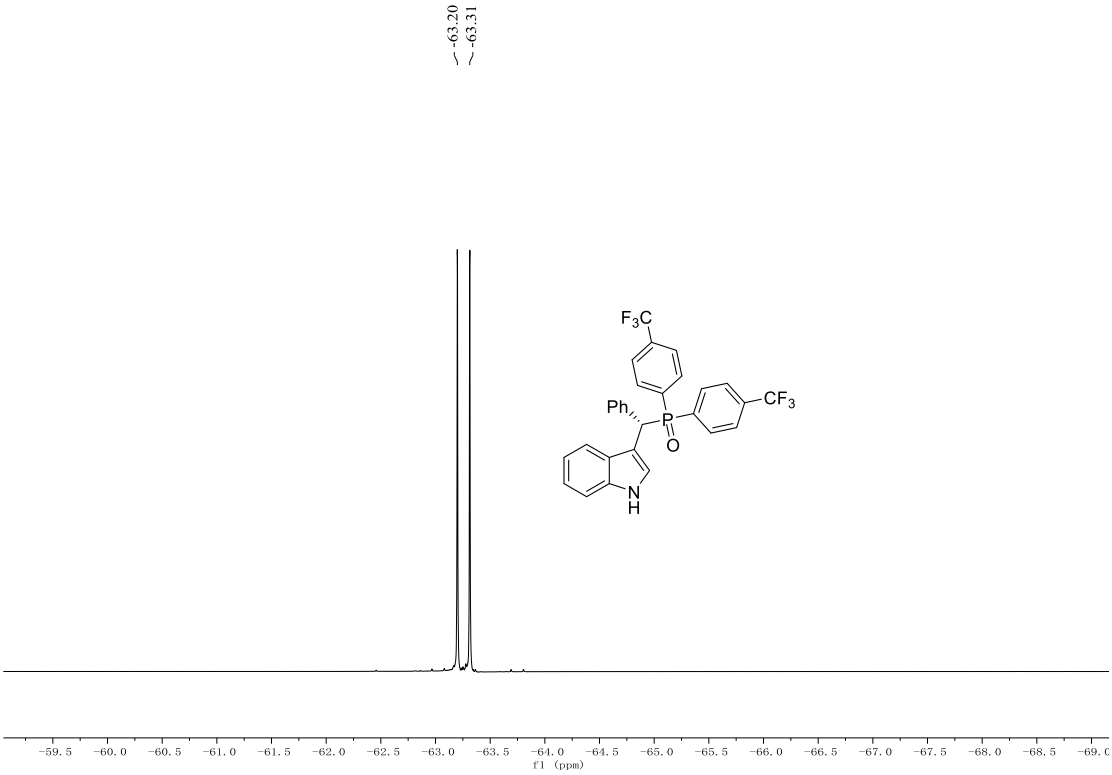
^{13}C NMR spectrum of compound of 3b`



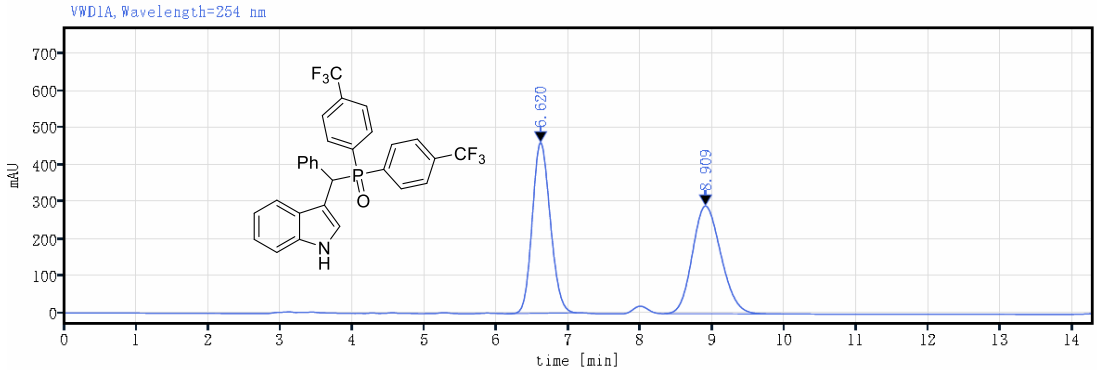
^{31}P NMR spectrum of compound of 3b`



^{19}F NMR spectrum of compound of 3b`

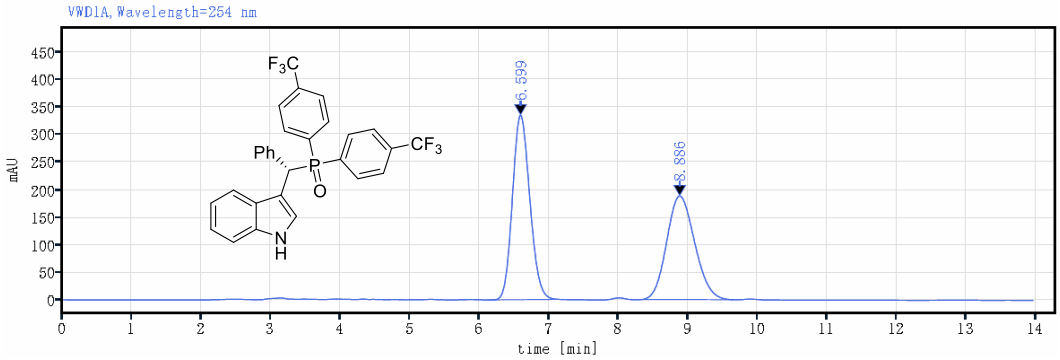


HPLC spectra of 3b`



Detector VWD1A, Wavelength=254 nm

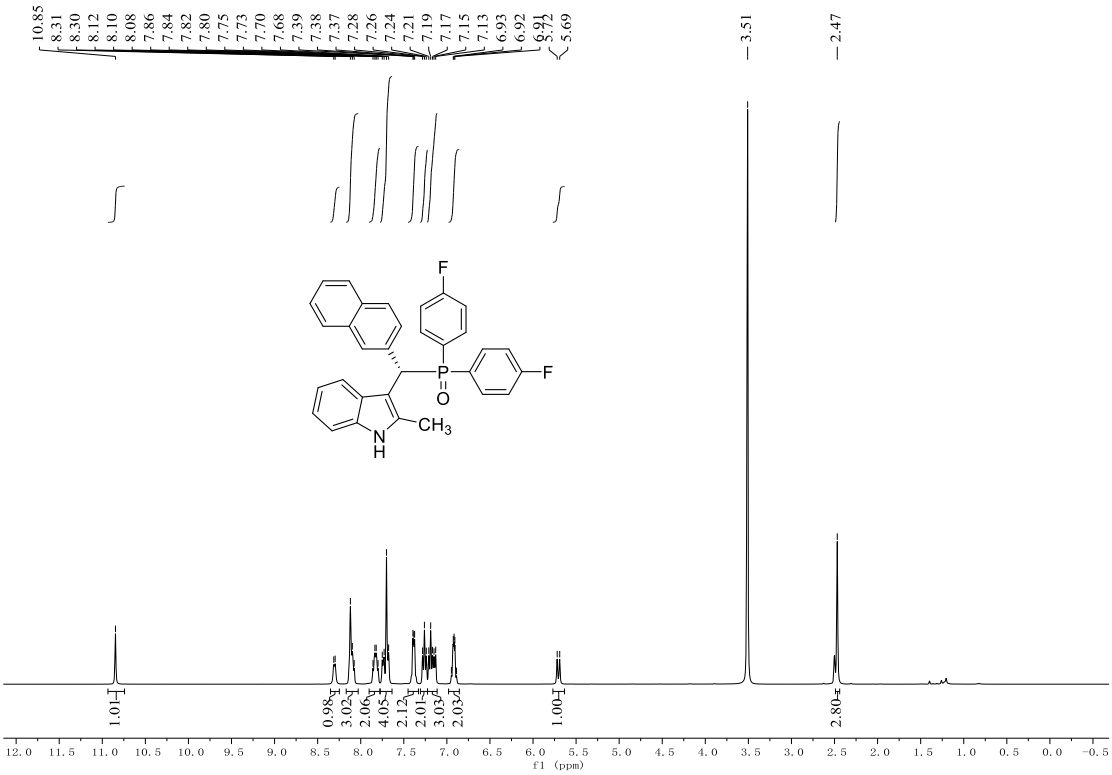
Peak	Ret.Time [min]	Area	Height	Area%
	6.620	8019.17	461.33	49.99
	8.909	8021.02	291.39	50.01
		16040.19		100.00



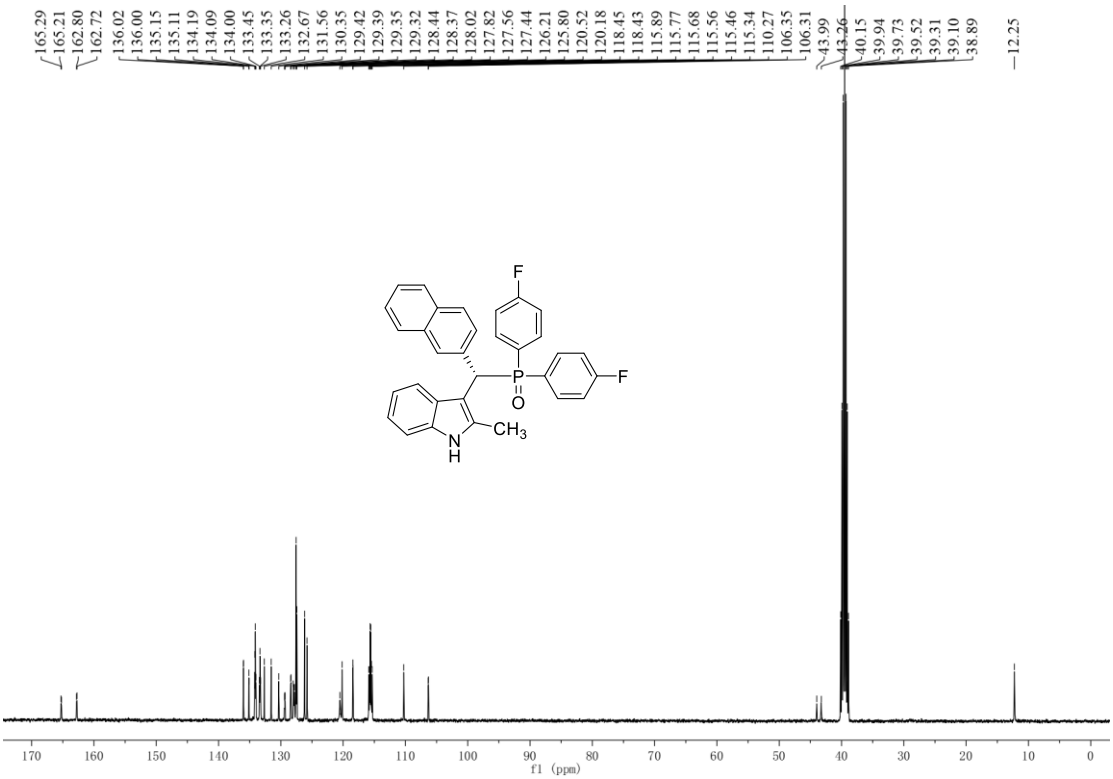
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	6.599	5827.97	335.86	52.52
	8.886	5267.86	188.62	47.48
		11095.83		100.00

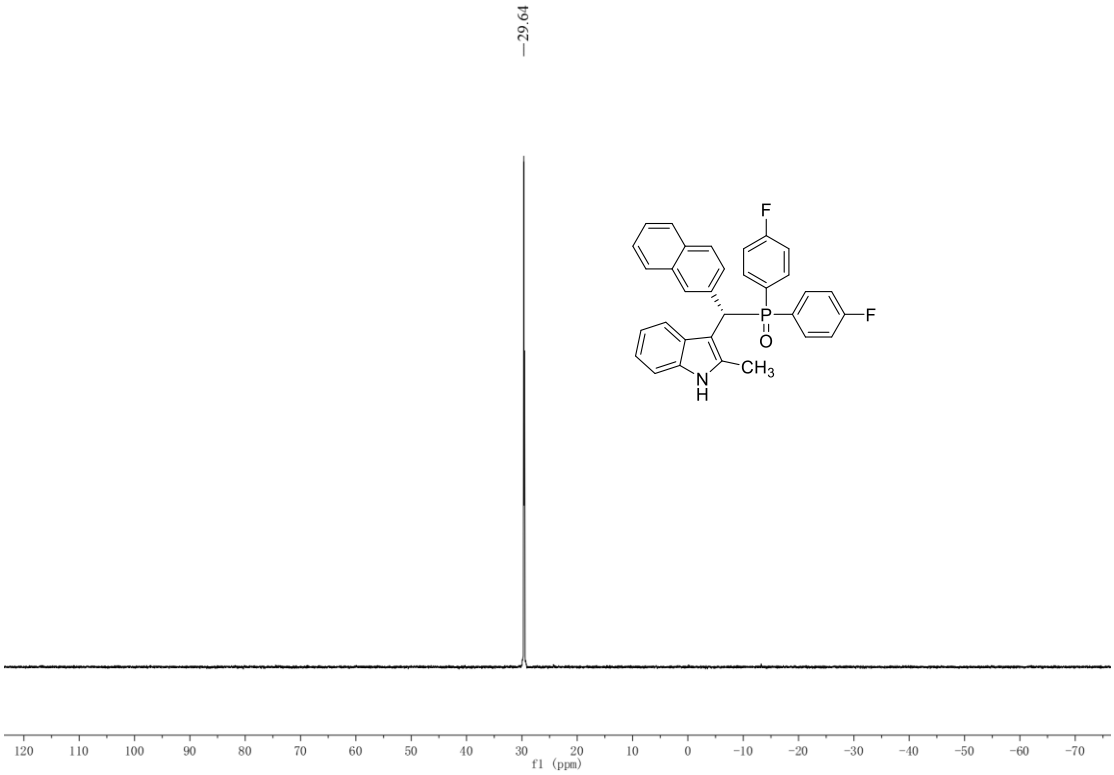
^{1}H NMR spectrum of compound of 3c`



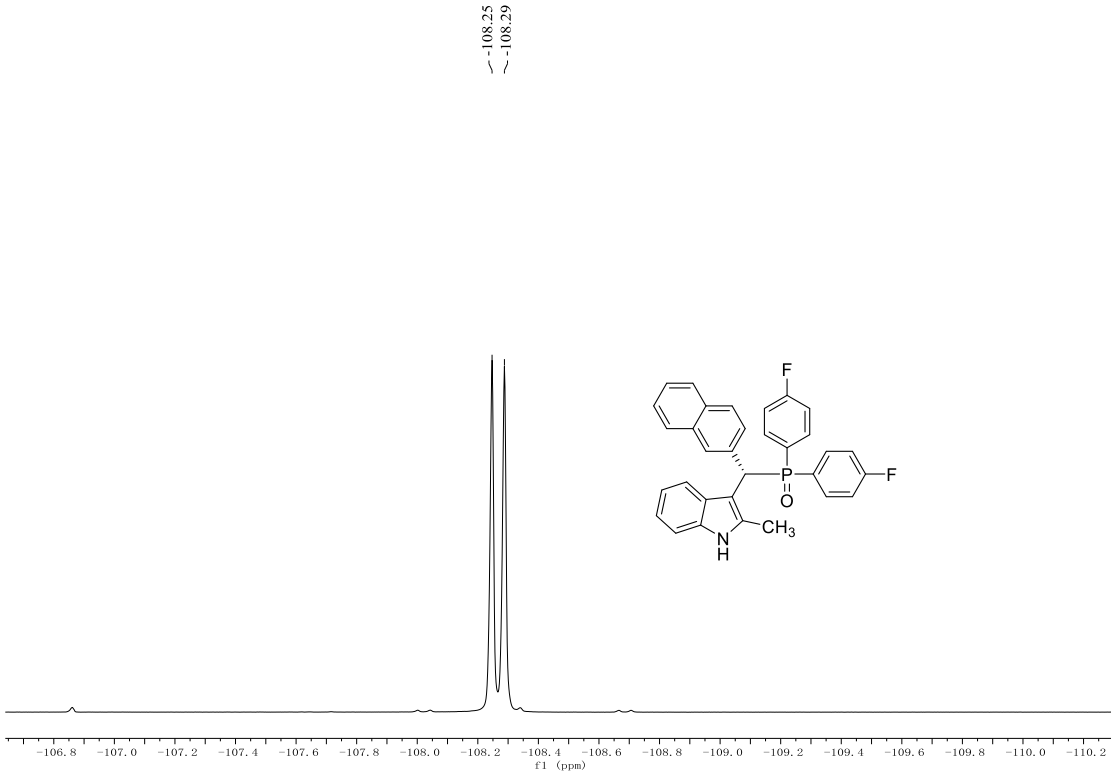
^{13}C NMR spectrum of compound of 3c`



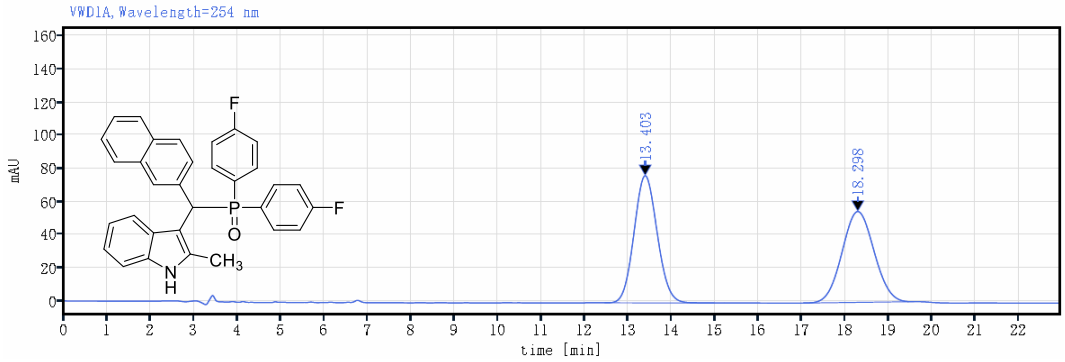
^{31}P NMR spectrum of compound of 3c`



^{19}F NMR spectrum of compound of 3c`

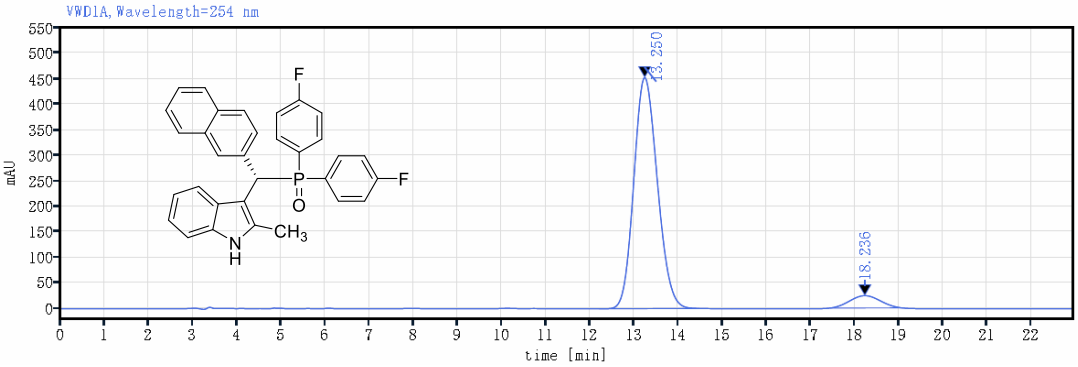


HPLC spectra of 3c`



Detector VWD1A, Wavelength=254 nm

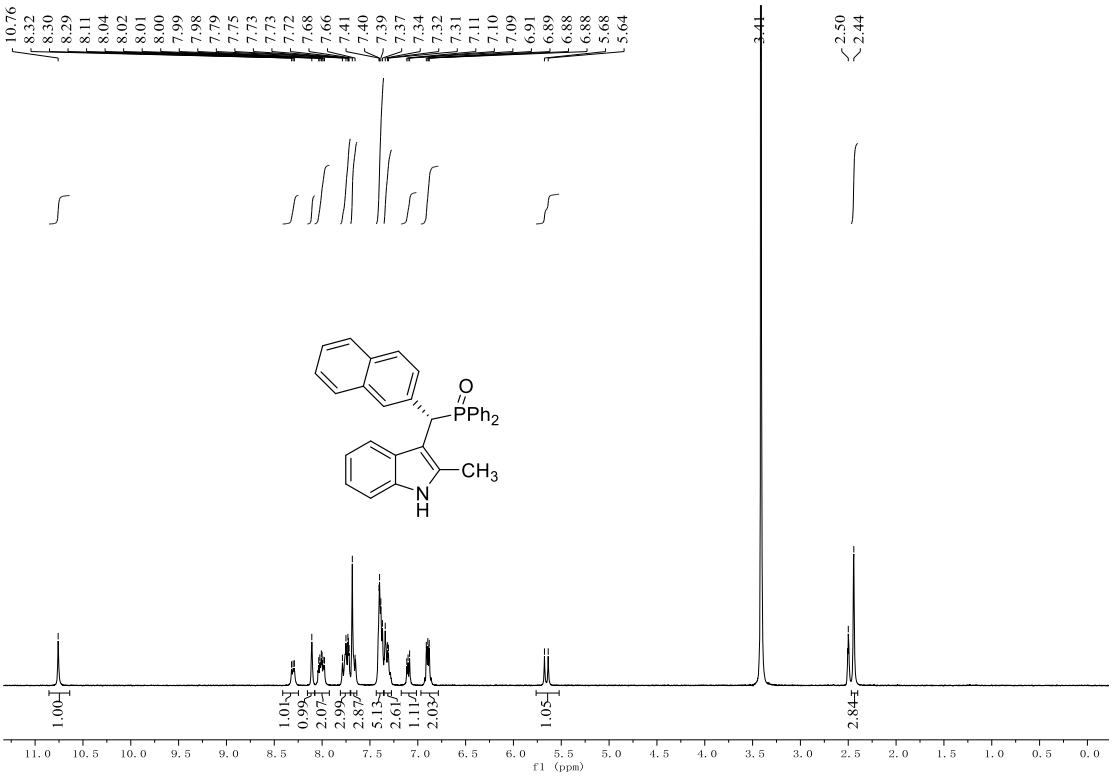
Peak	Ret.Time [min]	Area	Height	Area%
	13.403	2851.05	76.92	50.33
	18.298	2813.38	54.95	49.67
		5664.44		100.00



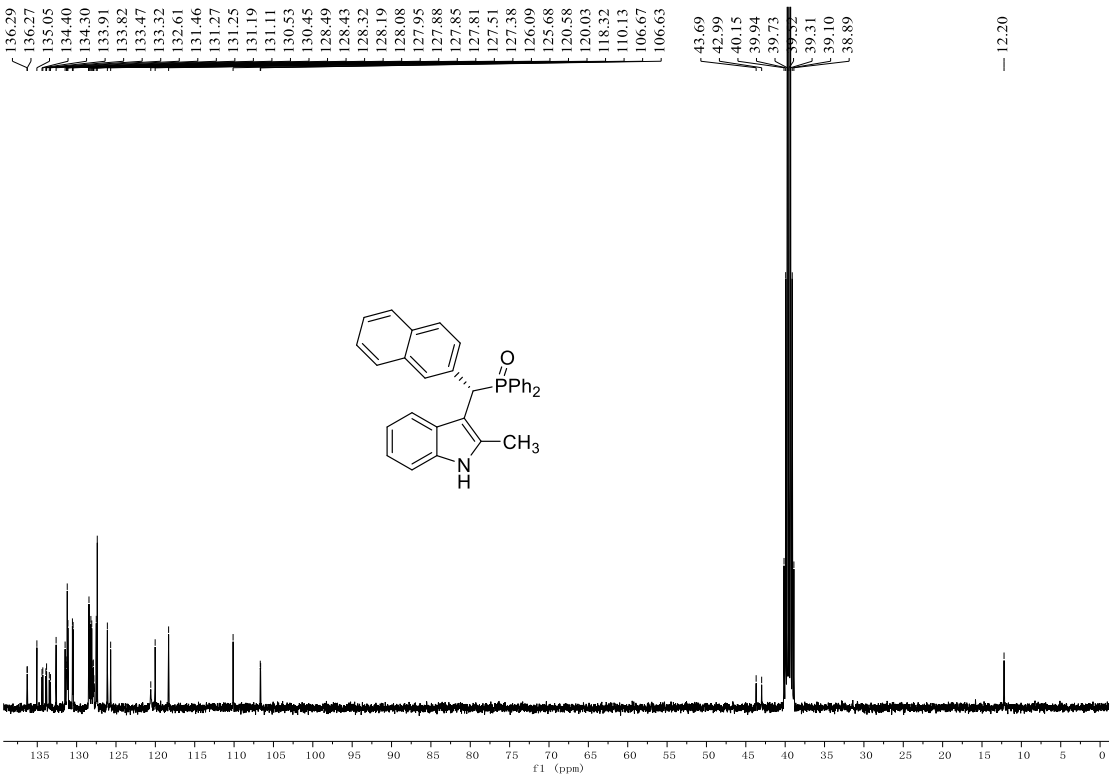
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	13.250	16760.02	452.28	93.60
	18.236	1145.47	24.03	6.40
		17905.49		100.00

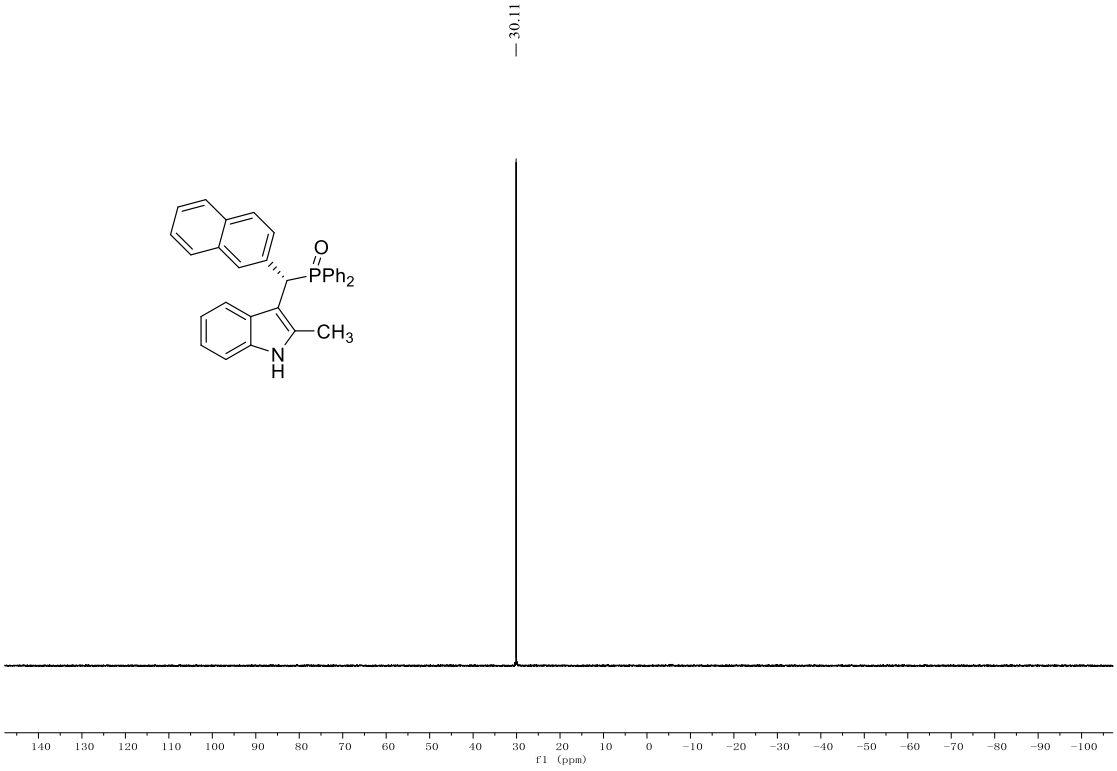
^{1}H NMR spectrum of compound of 3d`



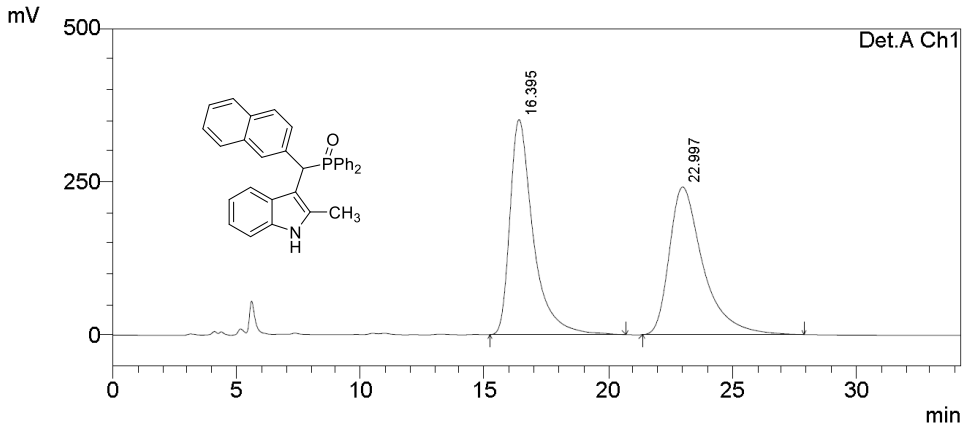
^{13}C NMR spectrum of compound of 3d`



^{31}P NMR spectrum of compound of 3d`



HPLC spectra of 3d`

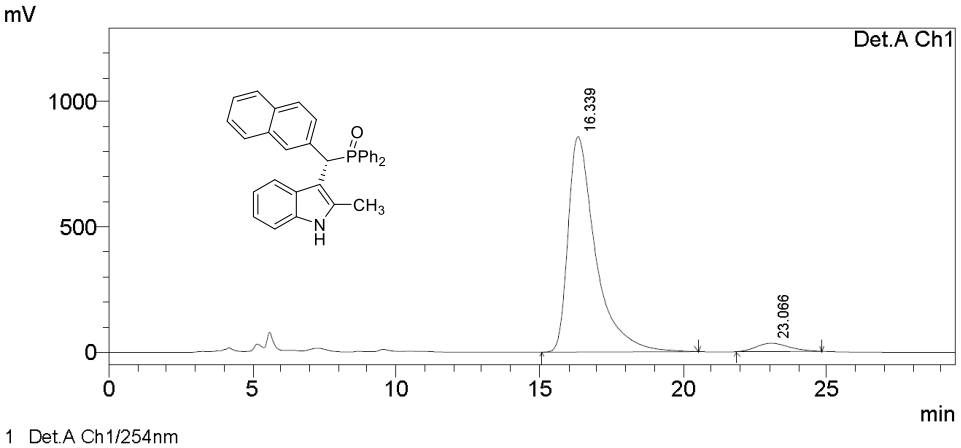


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	16.395	22910503	350204	50.112
2	22.997	22808415	240380	49.888
Total		45718918		100.000



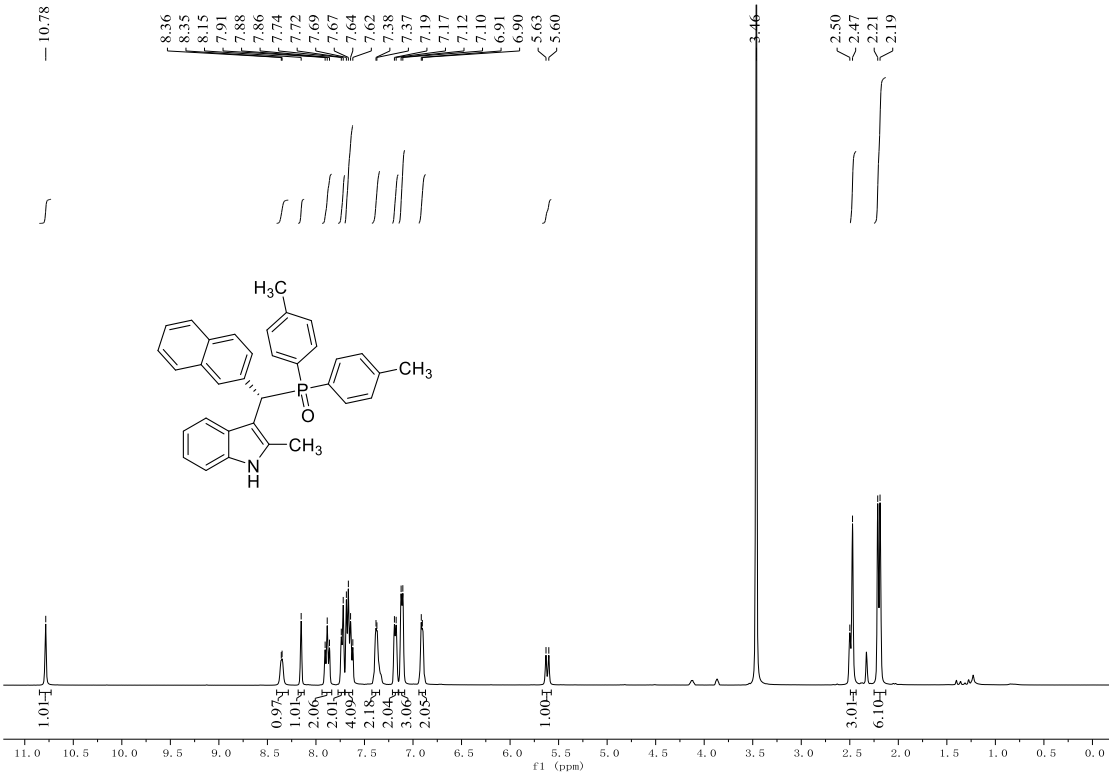
1 Det.A Ch1/254nm

PeakTable

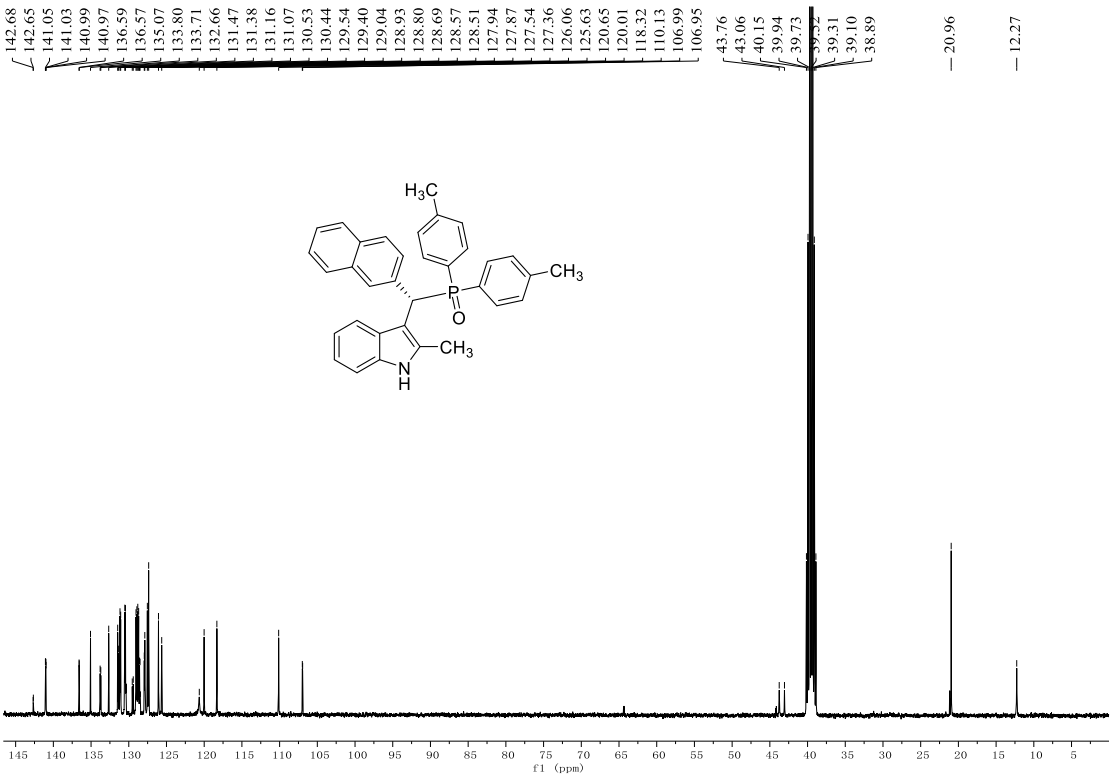
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	16.339	57395855	860938	95.633
2	23.066	2620900	32997	4.367
Total		60016754		100.000

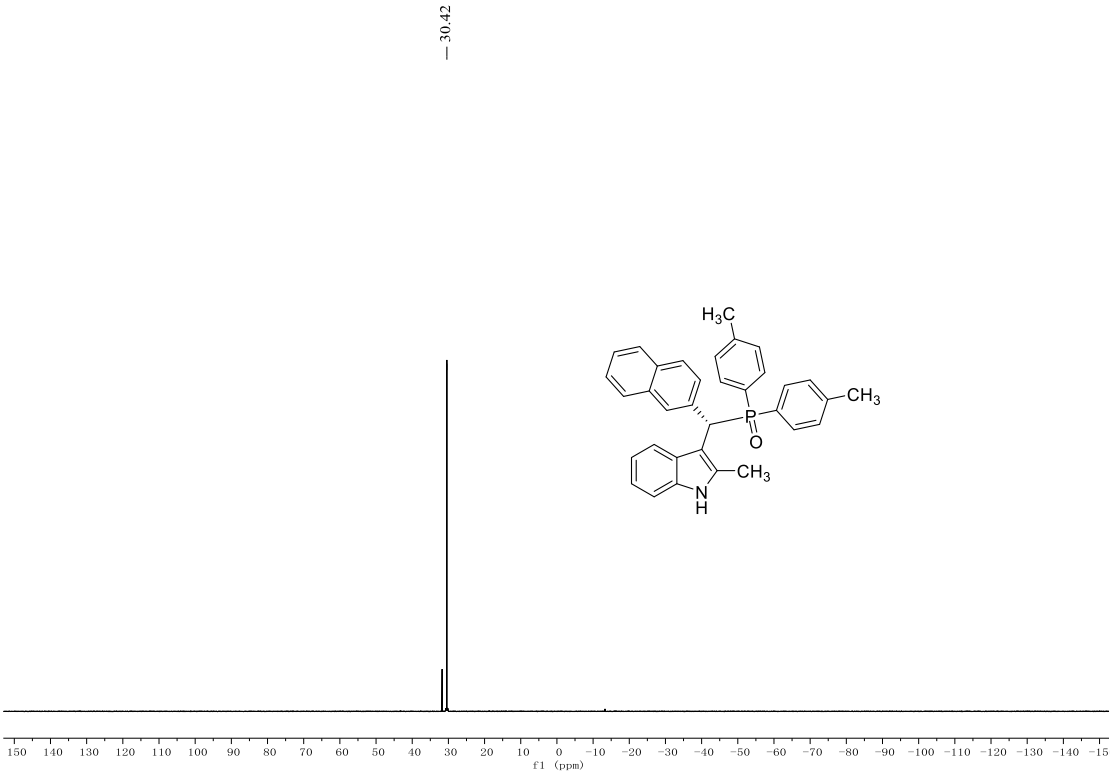
^{1}H NMR spectrum of compound of 3e`



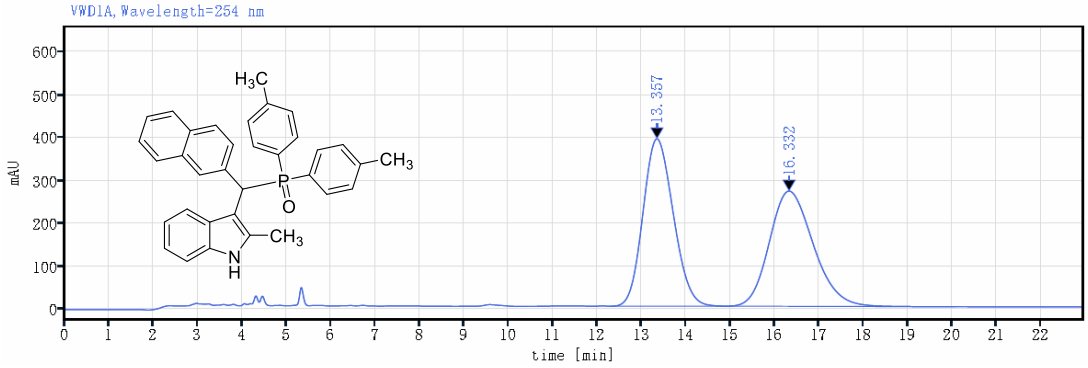
^{13}C NMR spectrum of compound of 3e`



^{31}P NMR spectrum of compound of 3e`

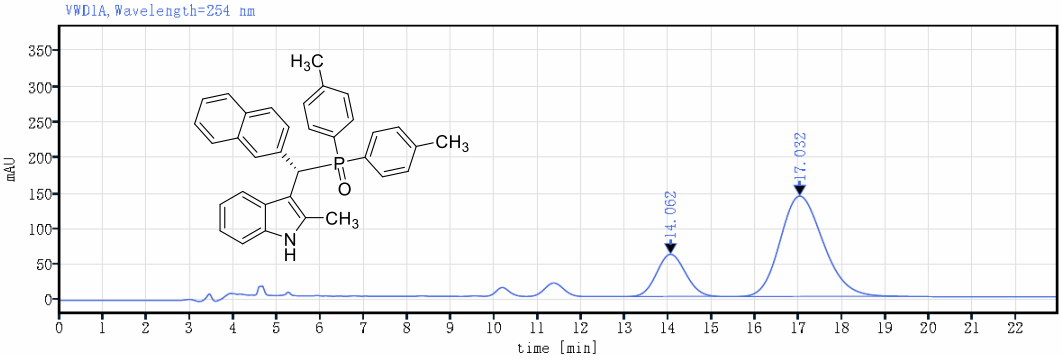


HPLC spectra of 3e`



Detector VWD1A, Wavelength=254 nm

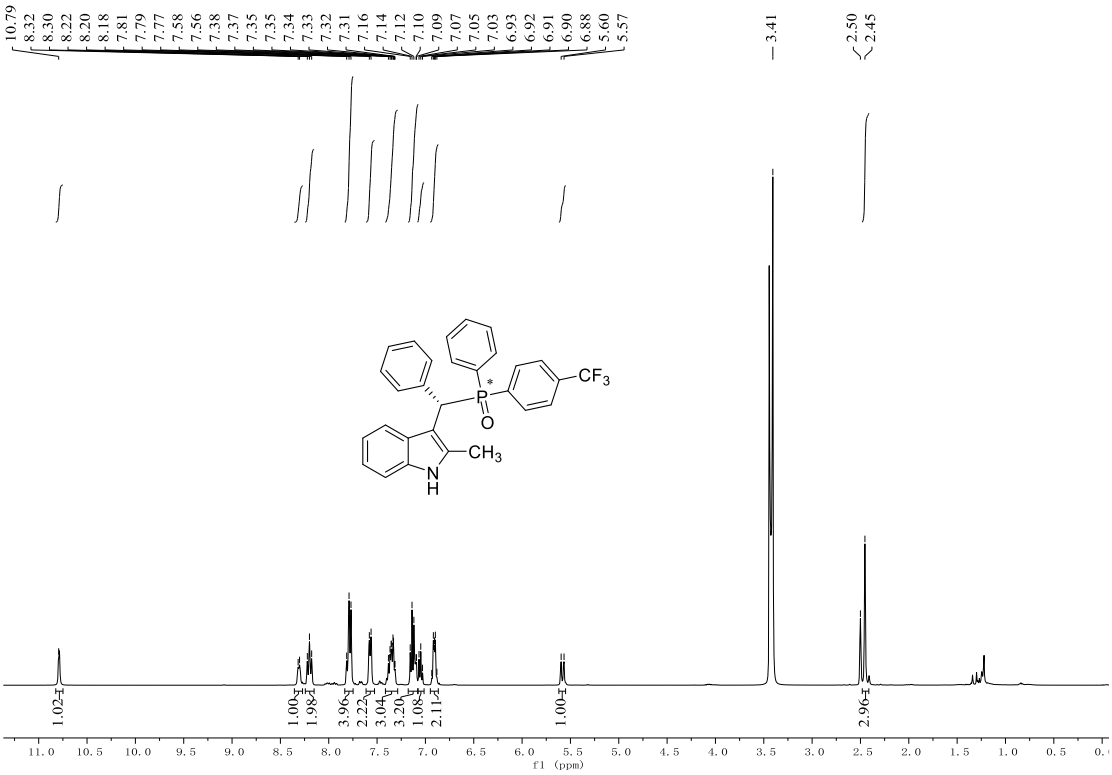
Peak	Ret.Time [min]	Area	Height	Area%
	13.357	18511.72	390.52	50.03
	16.332	18491.29	268.81	49.97
		37003.01		100.00



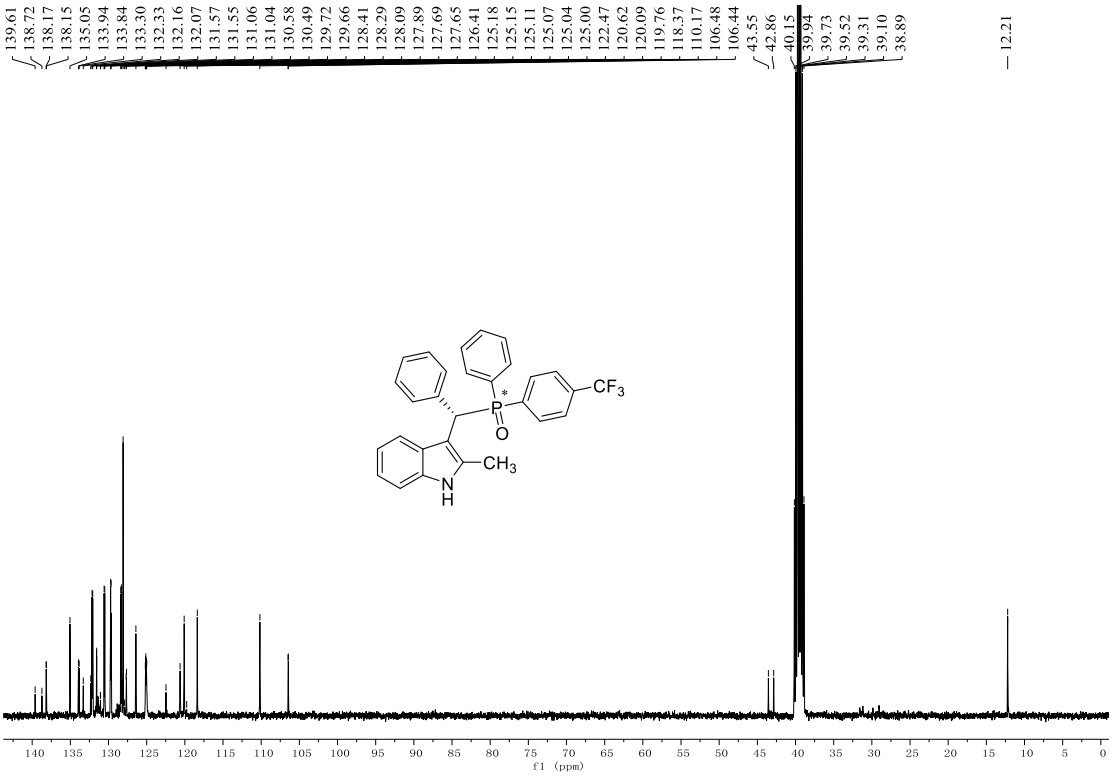
Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	14.062	2710.80	59.07	21.91
	17.032	9660.43	140.85	78.09
		12371.23		100.00

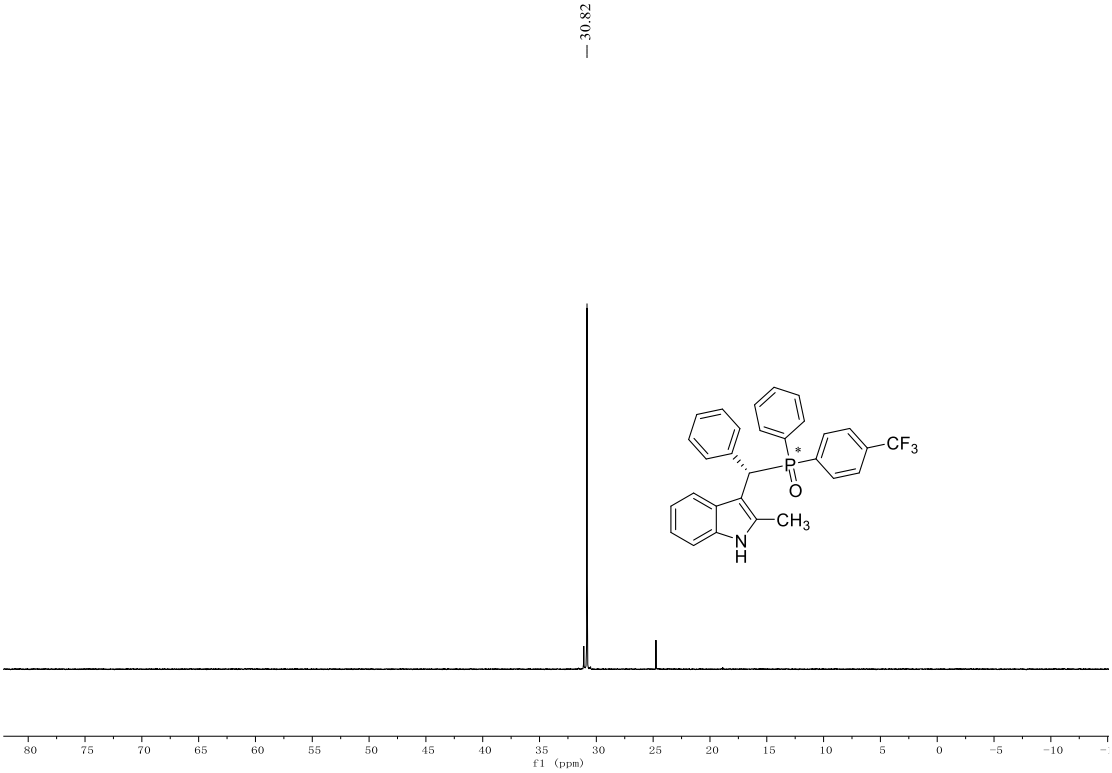
^{1}H NMR spectrum of compound of 3f`(isomer 1)



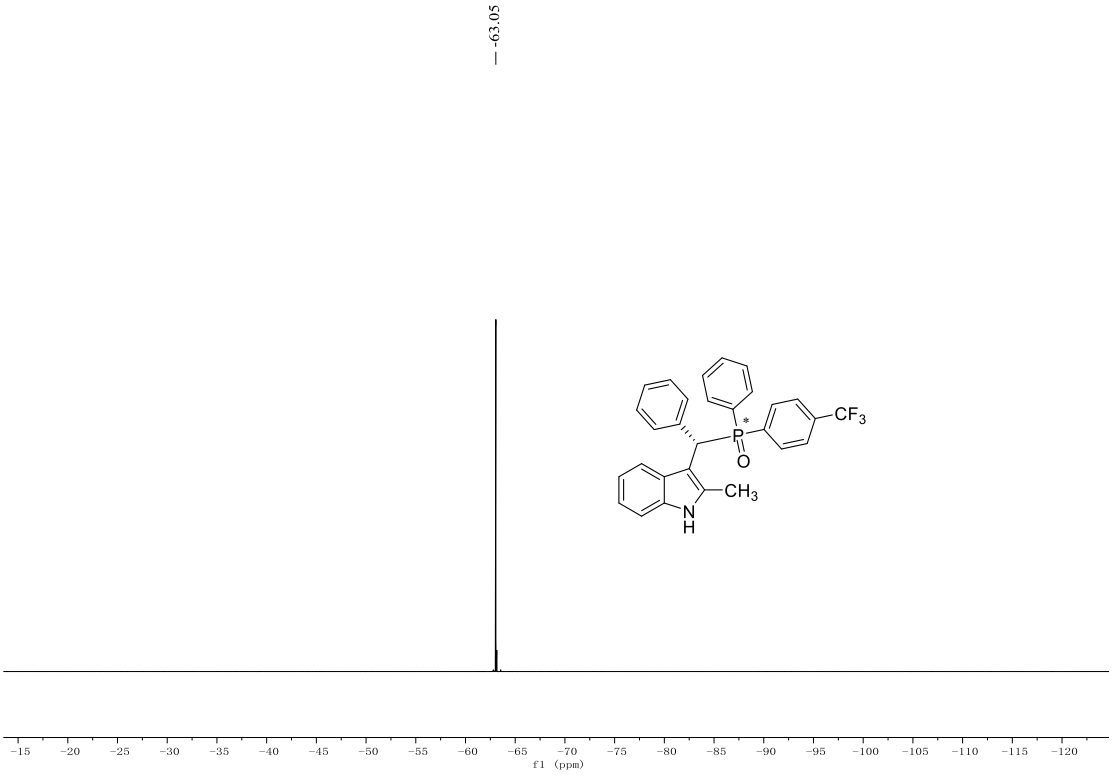
^{13}C NMR spectrum of compound of 3f`(isomer 1)



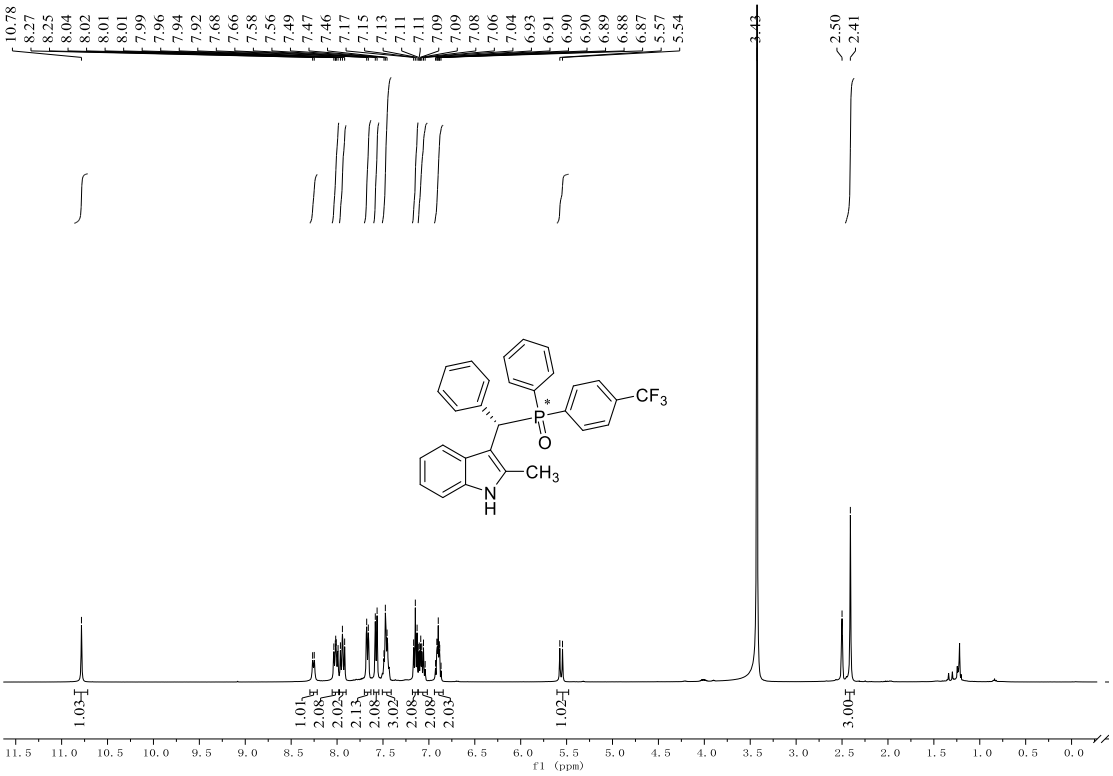
^{31}P NMR spectrum of compound of 3f`(isomer 1)



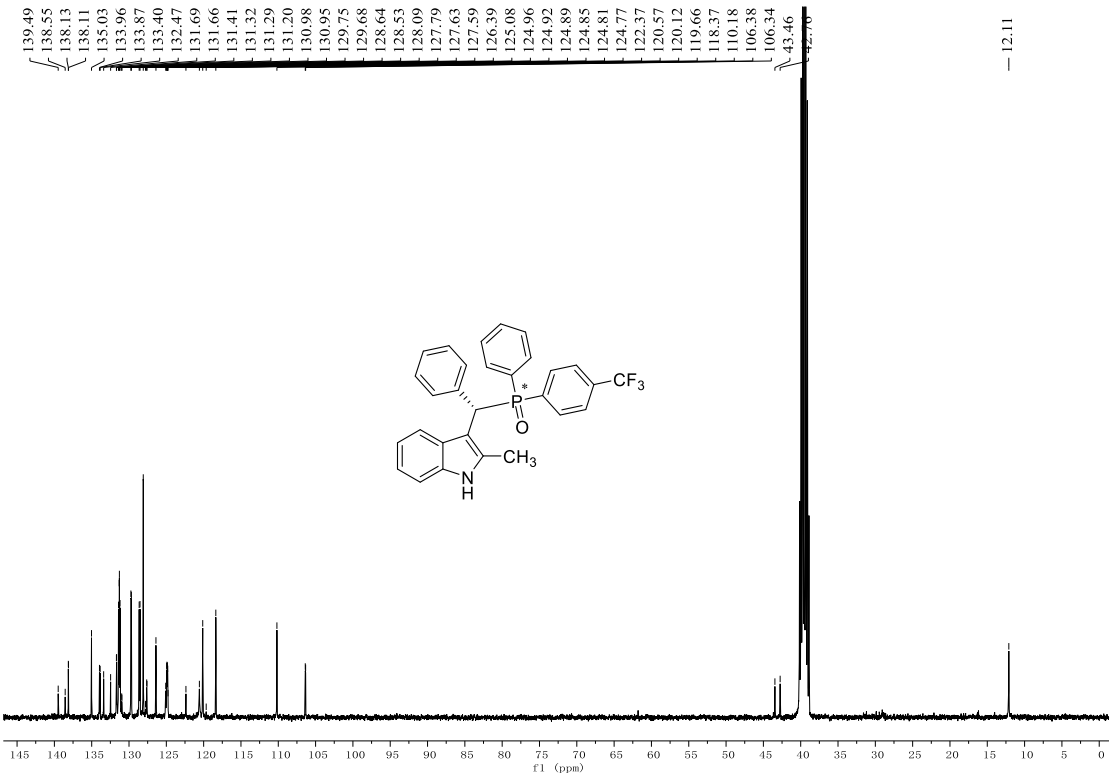
^{19}F NMR spectrum of compound of 3f`(isomer 1)



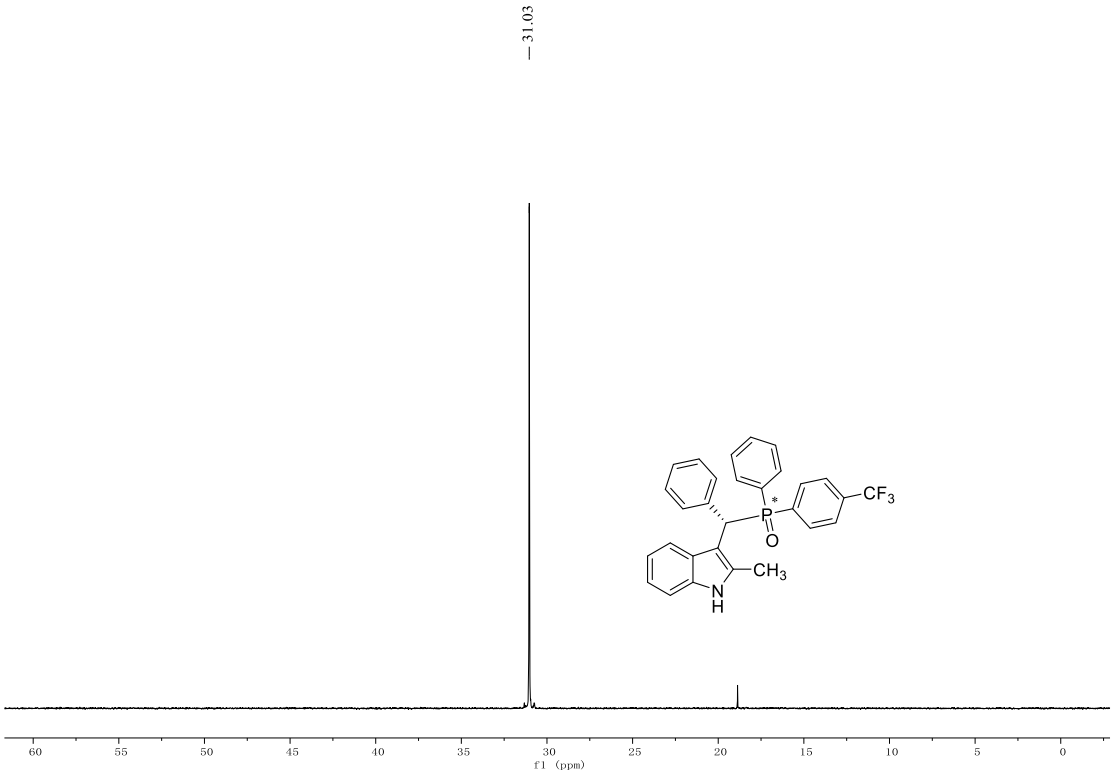
^{1}H NMR spectrum of compound of 3f`(isomer 2)



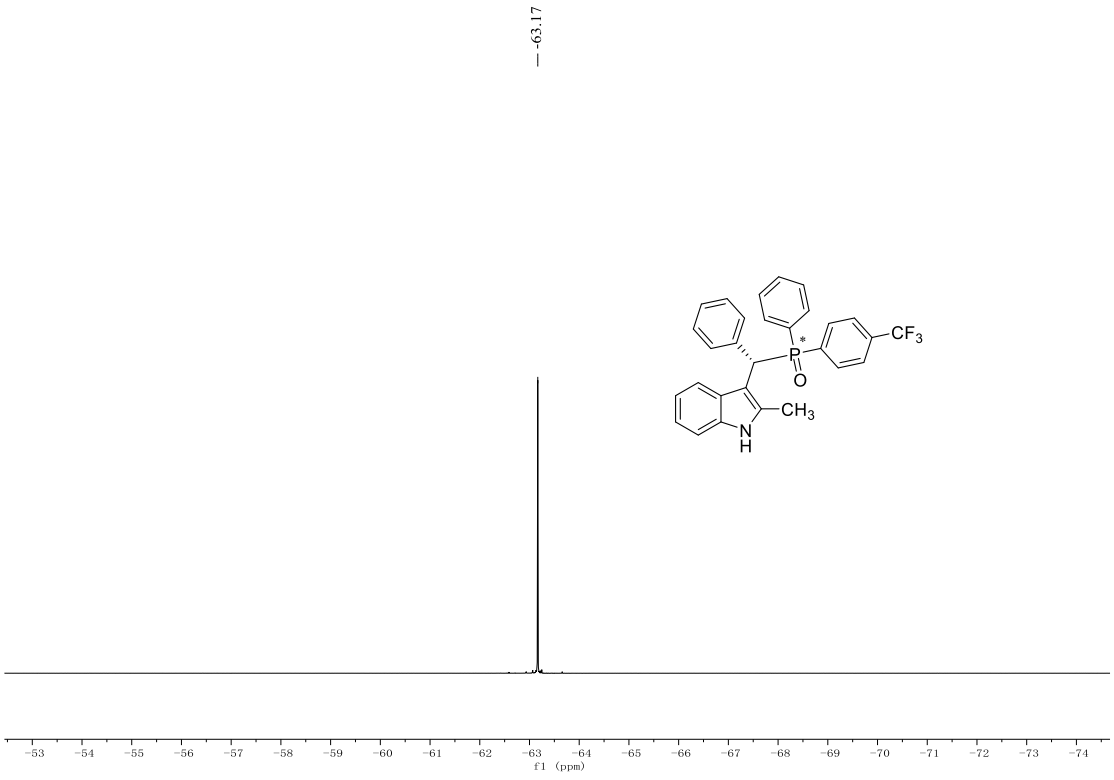
^{13}C NMR spectrum of compound of 3f`(isomer 2)



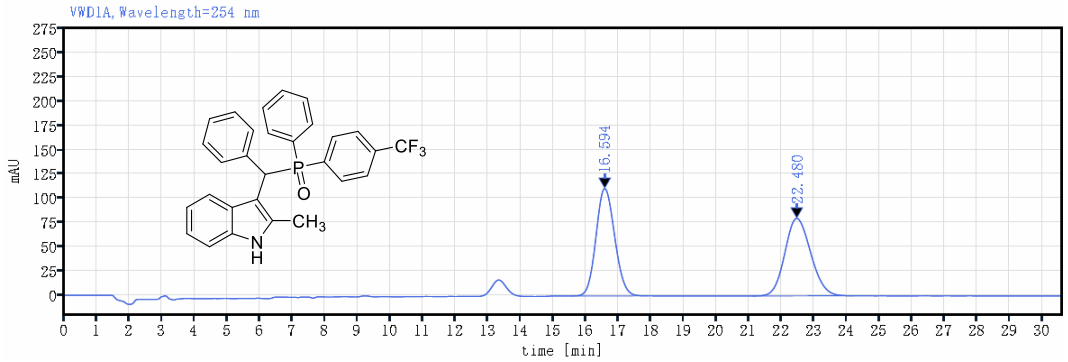
^{31}P NMR spectrum of compound of 3f`(isomer 2)



^{19}F NMR spectrum of compound of 3f`(isomer 2)

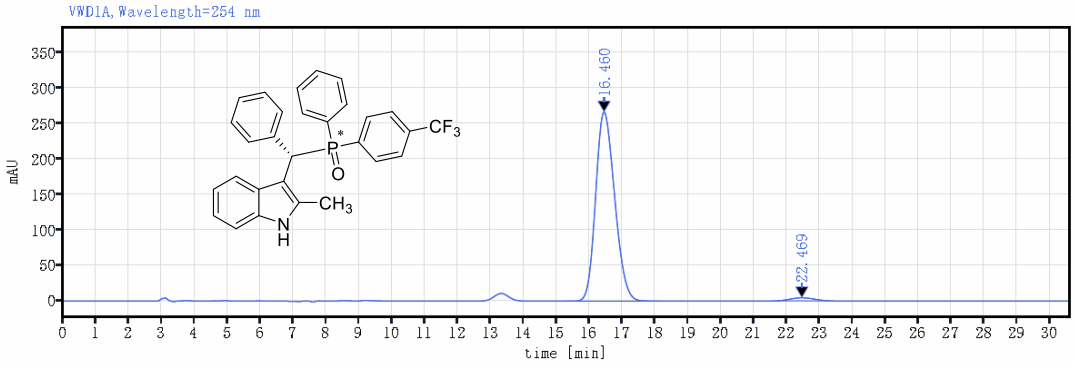


HPLC spectra of 3f`(isomer 1)



Detector VWD1A, Wavelength=254 nm

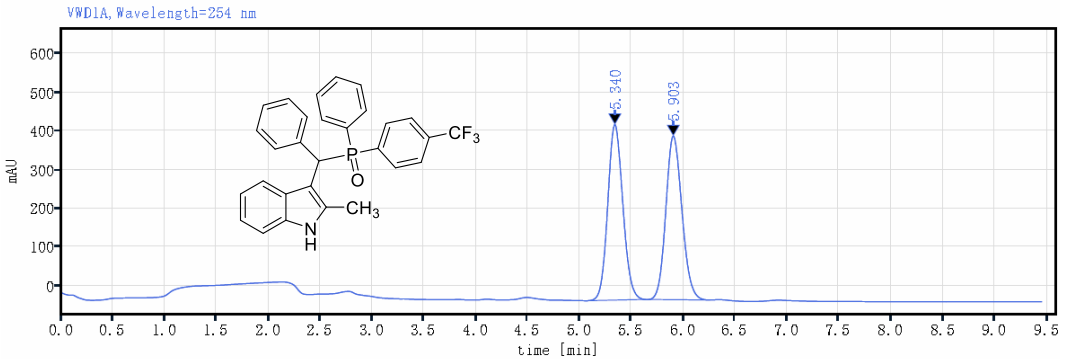
Peak	Ret.Time [min]	Area	Height	Area%
	16.594	4407.04	110.85	49.97
	22.480	4412.62	80.04	50.03
		8819.66		100.00



Detector VWD1A, Wavelength=254 nm

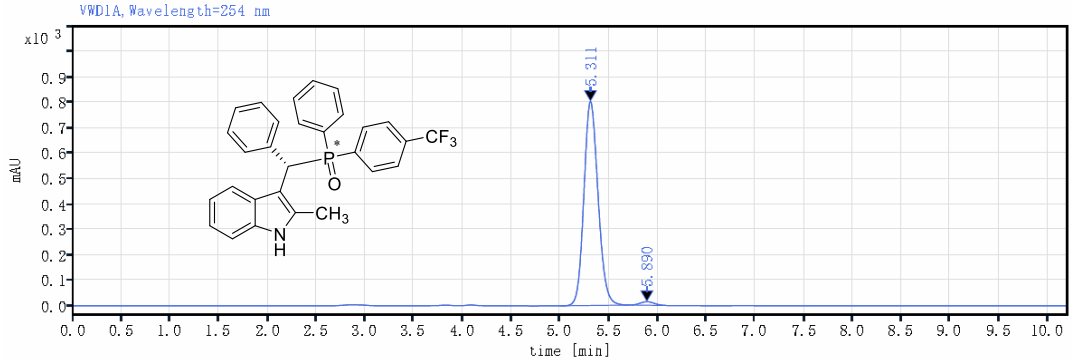
Peak	Ret.Time [min]	Area	Height	Area%
	16.460	10703.62	266.67	98.06
	22.469	211.84	4.32	1.94
		10915.46		100.00

HPLC spectra of 3f`(isomer 2)



Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	5.340	4580.27	453.26	50.10
	5.903	4561.89	422.84	49.90
		9142.15		100.00



Detector VWD1A, Wavelength=254 nm

Peak	Ret.Time [min]	Area	Height	Area%
	5.311	8131.50	803.39	98.36
	5.890	135.29	13.76	1.64
		8266.79		100.00