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

Metal-free electrophilic phosphination of electron-rich arenes, arenols and aromatic thiols with diarylphosphine oxides

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1 Experimental

1.1 General remarks

All chemical reagents were obtained from commercial suppliers and used without further purification. All known compounds were identified by using appropriate techniques such as ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and GC-MS. All unknown compounds were characterized by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, GC-MS and elemental analyses. Analytical thin-layer chromatography was performed on glass plates precoated with silica gel impregnated with a fluorescence indicator (254 nm). GC analyses were performed on an Agilent 7890A instrument (column: Agilent 19091J-413: 30 m × 320 μm × 0.25 μm, H. FID). All NMR spectra were recorded on an AVANCE 500 Bruker spectrometer operating at 500 MHz and 125 MHz in $CDCl_3$, respectively, and chemical shifts were reported in ppm and using TMS as an internal standard. GC-MS data was recorded on a 5975C Mass Selective Detector, coupled with a 7890A Gas Chromatograph (Agilent Technologies). Elemental analyses were performed on a Yanagimoto MT3CHN recorder.

1.2 Experimental procedures

General procedures for electrophilic phosphination of electron-rich arenes with diarylphosphine oxides: A mixture of electron-rich arenes **1** 0.25 mmol, diarylphosphine oxide **2** 0.5 mmol, OTf_2 0.50 mmol in MeCN (2 mL) was stirred at 60 ^{o}C for 4 h. Upon completion, the reaction mixture was poured into sat. $NaHCO_3$ aqueous solution, and oxidized with H_2O_2 (30% aq, ca. 0.5 mL) for 15 min under open air. The resulting mixture was quenched with sat. $Na_2S_2O_3$ aqueous solution and extracted with ethyl acetate (20 mL x 3). The combined organic layer was dried over Na_2SO_4 and volatiles were removed under reduced pressure. Further column chromatography on silica gel (EtOAc/petroleum ether) was needed to afford the pure desired products **3**.

General procedures for electrophilic phosphination of arenols or arylthiols with diarylphosphine oxides: A mixture of arenols **4** or arylthiols **7** 0.25 mmol, diarylphosphine oxide **2** 0.50 mmol, OTf_2 0.50 mmol in MeCN (2 mL) was stirred at rt for 4 h. Upon completion, the reaction mixture was poured into sat. $NaHCO_3$ aqueous solution, and oxidized with H_2O_2 (30% aq, ca. 0.5 mL) for 15 min under open air. The resulting mixture was quenched with sat. $Na_2S_2O_3$ aqueous solution and extracted with ethyl acetate (20 mL x 3). The combined organic layer was dried over Na_2SO_4 and volatiles were removed under reduced pressure. Further column chromatography on silica gel (EtOAc/petroleum ether) was needed to afford the pure desired products **5** or **6**.

1.3 Tentative pathway

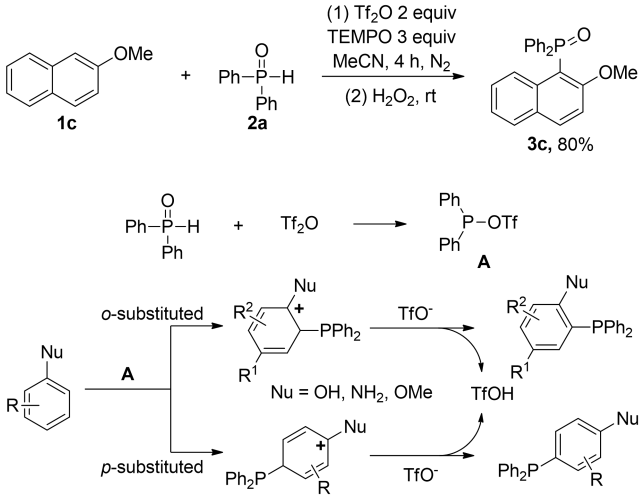
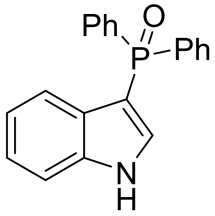


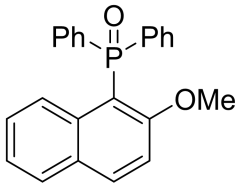
Figure S1. A tentative pathway for electrophilc phosphination of arenes from diphenyl phosphine oxide

2 Characterization Data



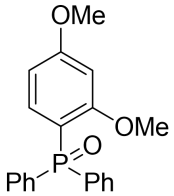
Chemical Formula: $C_{20}H_{16}NOP$
Mass: 317

(1*H*-indol-3-yl)diphenylphosphine oxide[1] **3a**, light brown solid, m.p. 250-253 °C (97%, 76 mg). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 11.36 (s, 1H), 7.73 (dd, *J* = 12.4, 7.6 Hz, 4H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.42 (td, *J* = 7.7, 2.6 Hz, 4H), 7.28 (s, 1H), 7.24 (d, *J* = 8.3 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.95 (t, *J* = 3.4 Hz, 1H), 6.90 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 136.83, 133.46, 133.30, 132.87, 132.01, 130.78, 127.57, 127.48, 127.47, 127.00, 121.71, 119.89, 119.50, 111.38. ^{31}P NMR (202 MHz, Chloroform-*d*) δ 23.32. GC-MS (EI) *m/z*: 317.



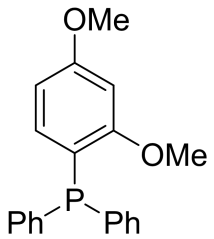
Chemical Formula: $C_{23}H_{19}O_2P$
Mass: 358

(2-Methoxynaphthalen-1-yl)diphenylphosphine oxide **3b**, CAS 294671-36-6, light brown soild, m.p. 196-199 °C (87%, 77.8 mg). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.52 (d, *J* = 8.8 Hz, 1H), 8.03 (d, *J* = 9.0 Hz, 1H), 7.85–7.69 (m, 5H), 7.57–7.39 (m, 8H), 7.16 (dd, *J* = 9.1, 4.8 Hz, 1H), 3.27 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 161.58, 158.73, 135.68, 134.81, 134.11, 130.34, 130.26, 130.13, 128.84, 127.42, 127.17, 127.07, 126.86, 125.55, 123.41, 112.20, 54.56, ^{31}P NMR (202 MHz, Chloroform-*d*) δ 32.11. GC-MS (EI) *m/z*: 358.



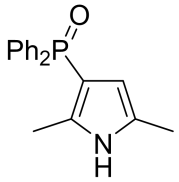
Chemical Formula: $C_{20}H_{19}O_3P$
Exact Mass: 338.1072
Elemental Analysis: C, 71.00; H, 5.66; O, 14.19; P, 9.15

(2,4-Dimethoxyphenyl)diphenylphosphine oxide **3c**, light yellow solid, m.p. 162-165 °C (91% 76.9 mg). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82–7.70 (m, 4H), 7.69–7.40 (m, 7H), 6.63 (dt, *J* = 8.5, 1.9 Hz, 1H), 6.49 (dd, *J* = 4.7, 2.2 Hz, 1H), 3.89 (s, 3H), 3.59 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 164.01, 161.36, 135.46, 130.87, 130.78, 130.39, 127.16, 127.06, 104.21, 98.06, 54.55, 54.26. ^{31}P NMR (202 MHz, Chloroform-*d*) δ 34.70. GC-MS (EI) *m/z*: 338. Anal. Calcd for $C_{20}H_{19}O_3P$: C, 71.00%; H, 5.66%. Found: C, 71.36%; H, 5.43%.



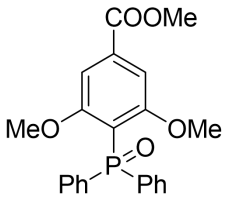
Chemical Formula: $C_{20}H_{19}O_2P$
Mass: 322

(2,4-Dimethoxyphenyl)diphenylphosphane[2] **3c'**, white solid, m.p. 121-124 °C (93%, 74.9 mg). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.35–7.26 (m, 10H), 6.61 (dd, *J* = 8.4, 4.8 Hz, 1H), 6.49 (dd, *J* = 4.4, 2.3 Hz, 1H), 6.41 (dd, *J* = 8.4, 2.3 Hz, 1H), 3.80 (s, 3H), 3.74 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.90, 160.49, 135.59, 133.20, 132.14, 131.98, 126.74, 126.66, 103.50, 96.65, 54.04, 53.67. ^{31}P NMR (202 MHz, Chloroform-*d*) δ -18.18. GC-MS (EI) *m/z*: 322.

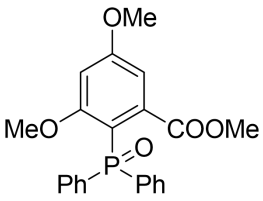


Chemical Formula: $C_{18}H_{18}NOP$
Mass: 295

(2,5-Dimethyl-1H-pyrrol-3-yl)diphenylphosphine oxide **3d**, CAS 785792-24-7, white solid, m.p. 253-256 °C (60%, 44.2 mg). ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.02 (s, 1H), 7.57–7.50 (m, 4H), 7.50–7.40 (m, 7H), 5.45–5.28 (m, 1H), 2.07–2.02 (m, 6H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 135.58, 134.75, 133.87, 133.74, 130.51, 130.43, 129.93, 127.98, 127.82, 127.73, 127.27, 125.93, 125.83, 108.87, 108.77, 106.81, 105.80, 11.95, 11.66. ^{31}P NMR (202 MHz, Chloroform-*d*) δ 25.29. GC-MS (EI) *m/z*: 295.



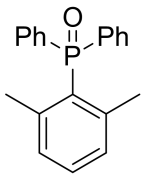
3e



3e'

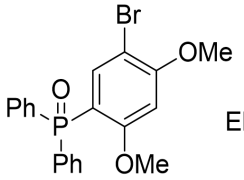
Chemical Formula: $C_{22}H_{21}O_5P$
Mass: 396

Methyl-4-(diphenylphosphoryl)-3,5-dimethoxybenzoate **3e,** Methyl-2-(diphenylphosphoryl)-3,5-dimethoxybenzoate **3e',** brown oil (a mixture of **3e**+**3e'**, 61%+17%, 77.2 mg). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.75–7.63 (m, 4H), 7.52–7.35 (m, 6H), 6.76 (dt, *J* = 7.6, 2.2 Hz, 1H), 6.42 (td, *J* = 5.1, 4.7, 2.3 Hz, 1H), 3.80 (d, *J* = 39.1 Hz, 6H), 3.29 (d, *J* = 10.8 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 163.17, 160.88, 141.44, 133.67, 133.67, 132.80, 130.50, 130.41, 130.22, 127.03, 126.93, 105.34, 99.55, 54.78, 54.30, 51.76. ^{31}P NMR (202 MHz, Chloroform-*d*) δ 27.58, 27.09. GC-MS (EI) *m/z*: 396.



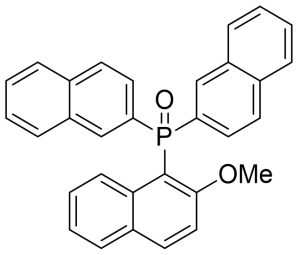
Chemical Formula: $C_{20}H_{19}OP$
Mass: 306

(2,6-Dimethylphenyl)diphenylphosphine oxide **3f**, CAS: 67754-88-5, yellow oil (81%, 61.9 mg). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89 (ddd, *J* = 12.6, 8.3, 1.4 Hz, 1H), 7.59–7.52 (m, 0H), 7.47 (td, *J* = 7.6, 3.6 Hz, 1H), 7.00–6.90 (m, 1H), 2.02 (s, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 147.28, 131.73, 131.33, 130.69, 130.61, 129.75, 128.07, 127.59, 127.48, 123.87, 28.37, 17.21. ^{31}P NMR (202 MHz, Chloroform-*d*) δ 29.55. GC-MS (EI) *m/z*: 306.



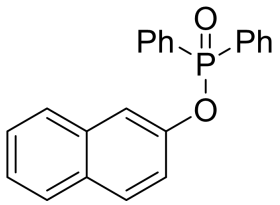
Chemical Formula: $C_{20}H_{18}BrO_3P$
Exact Mass: 416.0177
Elemental Analysis: C, 57.57; H, 4.35; Br, 19.15; O, 11.50; P, 7.42

(5-Bromo-2,4-dimethoxyphenyl)diphenylphosphine oxide **3g**, brown solid, m.p. 2 31-234 °C (88%, 91.7 mg). ^{1}H NMR (500 MHz, Methanol-d_4) δ 7.68–7.42 (m, 12H), 6.72 (d, *J* = 5.0 Hz, 1H), 3.93 (s, 3H), 3.58 (s, 3H). ^{13}C NMR (126 MHz, Methanol-d_4) δ 162.72, 161.81, 137.60, 132.59, 132.38, 131.80, 131.72, 1 28.69, 128.59, 112.11, 111.23, 102.69, 102.57, 97.44, 56.20, 55.33. ^{31}P NMR (202 MHz, Chloroform-*d*) δ 31.94. GC-MS (EI) *m/z*: 416. Anal. Calcd for $C_{20}H_{18}BrO_3P$: C, 57.57%; H, 4.35%. Found: C, 57.48%; H, 4.19%.



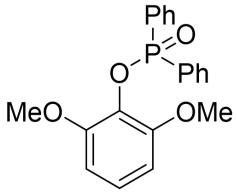
Chemical Formula: $C_{31}H_{23}O_2P$
Exact Mass: 458.1436
Elemental Analysis: C, 81.21; H, 5.06; O, 6.98; P, 6.76

(2-Methoxynaphthalen-1-yl)di(naphthalen-2-yl)phosphine oxide **3j**, yellow solid, m.p. 131-133 °C (58%, 53.1 mg). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.54 (d, *J* = 8.8 Hz, 1H), 8.42 (d, *J* = 14.5 Hz, 1H), 8.12 (d, *J* = 9.0 Hz, 1H), 7.95–7.78 (m, 10H), 7.64–7.54 (m, 5H), 7.46 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1H), 7.23 (ddd, *J* = 9.1, 4.9, 1.4 Hz, 1H), 3.25 (d, *J* = 1.5 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.98, 135.59, 135.04, 133.54, 132.22, 131.81, 131.73, 131.58, 131.36, 128.93, 128.86, 128.01, 127.54, 127.00, 126.83, 125.99, 125.91, 125.64, 123.53, 112.19, 54.69. ^{31}P NMR (202 MHz, Chloroform-*d*) δ 37.42. GC-MS (EI) *m/z*: 458. Anal. Calcd for $C_{31}H_{23}O_2P$: C, 81.21%; H, 5.06%. Found: C, 81.49%; H, 4.56%.



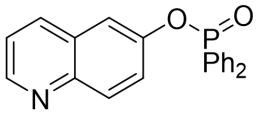
Chemical Formula: $C_{22}H_{17}O_2P$
Mass: 344

Naphthalen-2-yl diphenylphosphinate[3] **5a**, white solid, m.p. 127-128 °C (75%, 64.5 mg). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.96 (dd, *J* = 12.6, 7.5 Hz, 3H), 7.75 (dd, *J* = 17.5, 8.4 Hz, 3H), 7.61–7.33 (m, 7H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 147.70, 132.99, 131.55, 130.92, 130.84, 129.71, 129.43, 128.79, 127.73, 127.62, 126.66, 126.55, 125.59, 124.29, 119.78, 116.24. ^{31}P NMR (202 MHz, Chloroform-*d*) δ 30.94. GC-MS (EI) *m/z*: 344.



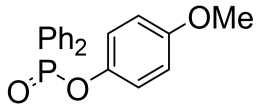
Chemical Formula: $C_{20}H_{19}O_4P$
Exact Mass: 354.1021
Elemental Analysis: C, 67.79; H, 5.40; O, 18.06; P, 8.74

2,6-Dimethoxyphenyl diphenylphosphinate **5b**, white soild, m.p. 98-111°C (70%, 61.9 mg). ^{1}H NMR (500 MHz, Methanol-d_4) δ 7.93–7.80 (m, 4H), 7.57–7.43 (m, 6H), 6.99 (td, *J* = 8.4, 1.2 Hz, 1H), 6.56 (d, *J* = 8.4 Hz, 2H), 3.61 (s, 6H). ^{13}C NMR (126 MHz, Methanol-d_4) δ 151.23, 131.24,130.71, 130.55, 130.47, 129.60, 127.94, 127.05, 126.94, 124.15, 103.62, 53.84. ^{31}P NMR (202 MHz, Methanol-d_4) δ 33.90. GC-MS (EI) *m/z*: 354. Anal. Calcd for $C_{20}H_{19}O_4P$: C, 67.79%; H, 5.40%. Found: C, 67.84%; H, 5.03%.



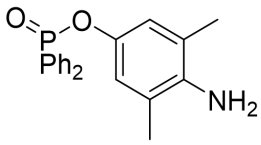
Chemical Formula: $C_{21}H_{16}NO_2P$
Exact Mass: 345.0919
Elemental Analysis: C, 73.04; H, 4.67; N, 4.06; O, 9.27; P, 8.97

Quinolin-6-yl diphenylphosphinate **5c**, brown solid, m.p. 127-131 °C (75%, 64.6 mg). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.79 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.00 (t, *J* = 8.0 Hz, 2H), 7.92 (ddt, *J* = 12.6, 6.8, 1.4 Hz, 4H), 7.72 (t, *J* = 2.0 Hz, 1H), 7.52 (td, *J* = 8.5, 7.3, 2.2 Hz, 3H), 7.45 (td, *J* = 7.4, 3.6 Hz, 4H), 7.31 (dd, *J* = 8.3, 4.2 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 148.77, 147.85, 144.57, 134.77, 131.73, 130.85, 130.77, 130.32, 130.15, 129.06, 127.81, 127.70, 123.30, 120.62, 116.00. ^{31}P NMR (202 MHz, Chloroform-*d*) δ 31.66. GC-MS (EI) *m/z*: 345. Anal. Calcd for $C_{21}H_{16}NO_2P$: C, 73.04%; H, 4.67%; N, 4.06%. Found: C, 72.89%; H, 4.92%; N, 3.86%.



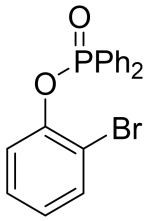
Chemical Formula: $C_{19}H_{17}O_3P$
Exact Mass: 324

4-Methoxyphenyl diphenylphosphinate[3] **5d**, white solid, m.p. 94-97 °C (85%, 68.9 mg). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.96–7.80 (m, 4H), 7.57–7.49 (m, 2H), 7.45 (td, *J* = 7.8, 2.3 Hz, 4H), 7.14–7.04 (m, 2H), 6.79–6.69 (m, 2H), 3.71 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.41, 143.38, 131.42, 130.92, 130.84, 129.53, 127.64, 127.53, 120.69, 113.64, 54.57. ^{31}P NMR (202 MHz, Chloroform-*d*) δ 30.64. GC-MS (EI) *m/z*: 324.



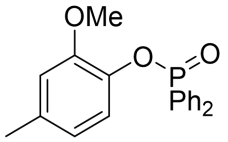
Chemical Formula: $C_{20}H_{20}NO_2P$
Exact Mass: 337.1232
Elemental Analysis: C, 71.21; H, 5.98; N, 4.15; O, 9.48; P, 9.18

4-Amino-3,5-dimethylphenyl diphenylphosphinate **5e**, light brown solid, m.p. 118-120 °C (76%, 64 mg). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.99–7.74 (m, 4H), 7.48 (dtd, *J* = 36.5, 7.5, 2.5 Hz, 6H), 6.79 (s, 2H), 3.37 (s, 2H), 2.07 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.26, 138.53, 131.21, 131.06, 130.93, 130.85, 129.96, 127.54, 127.43, 121.79, 119.29, 28.73, 16.73. ^{31}P NMR (202 MHz, Chloroform-*d*) δ 29.85. GC-MS (EI) *m/z*: 337. Anal. Calcd for $C_{20}H_{20}NO_2P$: C, 71.21%; H, 5.98%; N, 4.15%. Found: C, 71.49%; H, 5.72%; N, 3.86%.



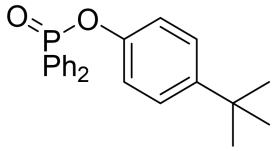
Chemical Formula: $C_{18}H_{14}BrO_2P$
Mass: 372

2-Bromophenyl diphenylphosphinate[4] **5f**, light yellow oil (90%, 83.4 mg). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.05–7.92 (m, 4H), 7.63–7.57 (m, 1H), 7.54–7.47 (m, 3H), 7.47–7.41 (m, 4H), 7.16–7.11 (m, 1H), 6.94–6.87 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 147.41, 132.58, 131.69, 130.97, 130.89,130.13, 129.03, 127.74, 127.64, 124.63, 120.60, 113.35. ^{31}P NMR (202 MHz, Chloroform-*d*) δ 31.94. GC-MS (EI) *m/z*: 372.



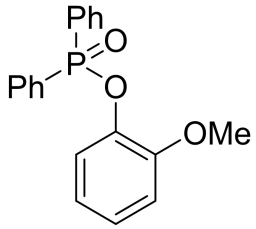
Chemical Formula: $C_{20}H_{19}O_3P$
Exact Mass: 338.1072
Elemental Analysis: C, 71.00; H, 5.66; O, 14.19; P, 9.15

2-Methoxy-4-methylphenyl diphenylphosphinate **5g**, light yellow oil (90%, 76 mg). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.93 (ddd, *J* = 12.5, 8.4, 1.5 Hz, 4H), 7.49 (td, *J* = 7.4, 1.6 Hz, 2H), 7.42 (td, *J* = 7.4, 3.6 Hz, 4H), 7.28–7.22 (m, 1H), 6.64 (d, *J* = 1.9 Hz, 1H), 6.58 (dd, *J* = 8.1, 1.8 Hz, 1H), 3.73 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 149.25, 136.72, 134.19, 131.26, 131.01, 130.92, 129.81, 127.43, 127.32, 120.71, 120.15, 112.44, 54.73, 20.29. ^{31}P NMR (202 MHz, Chloroform-*d*) δ 31.14. GC-MS (EI) *m/z*: 338. Anal. Calcd for $C_{20}H_{19}O_3P$: C, 71.00%; H, 5.66%. Found: C, 71.08%; H, 5.47%.



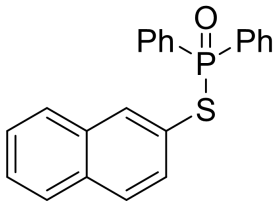
Chemical Formula: $C_{22}H_{23}O_2P$
Mass: 350

4-(Tert-butyl)phenyl diphenylphosphinate[3] **5h**, white solid, m.p. 163-165 °C (77%, 67.3 mg). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 (ddd, *J* = 12.5, 7.9, 1.4 Hz, 4H), 7.63–7.55 (m, 2H), 7.51 (td, *J* = 7.6, 3.5 Hz, 4H), 7.33–7.25 (m, 2H), 7.19–7.10 (m, 2H), 1.30 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 147.46, 131.40, 130.88, 130.80, 129.74, 127.66, 127.55, 125.53, 119.12, 33.33, 30.40. ^{31}P NMR (202 MHz, Chloroform-*d*) δ 36.21. GC-MS (EI) *m/z*: 350.



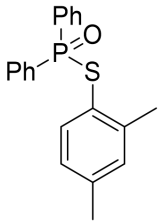
Chemical Formula: $C_{19}H_{17}O_3P$
Mass: 324

2-Methoxyphenyl diphenylphosphinate **5i**, CAS 213137-01-0, yellow oil (83%, 67.2 mg). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 (ddd, *J* = 12.6, 8.3, 1.4 Hz, 4H), 7.55–7.35 (m, 7H), 7.06–6.97 (m, 1H), 6.90–6.74 (m, 2H), 3.76 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 149.69, 139.08, 131.30, 130.99, 130.91, 129.74, 127.44, 127.33, 124.33, 121.16, 119.85, 111.56, 54.78. ^{31}P NMR (202 MHz, Chloroform-*d*) δ 31.27. GC-MS (EI) *m/z*: 324.



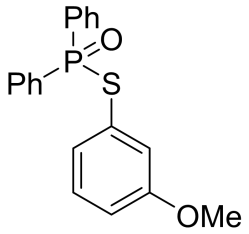
Chemical Formula: $C_{22}H_{17}OPS$
Mass: 360

S-(Naphthalen-2-yl)diphenylphosphinothioate[3] **6a**, white solid, m.p. 167-170 °C (79%, 71.1 mg). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 2.1 Hz, 1H), 7.97–7.88 (m, 4H), 7.83–7.78 (m, 1H), 7.77–7.73 (m, 1H), 7.71 (d, *J* = 8.6 Hz, 1H), 7.60–7.44 (m, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 134.46, 132.55, 132.03, 131.39, 131.16, 130.73, 130.64, 127.66, 127.55, 126.85, 126.64, 125.92, 125.48, 122.49. ^{31}P NMR (202 MHz, Chloroform-*d*) δ 47.57. GC-MS (EI) *m/z*: 360.



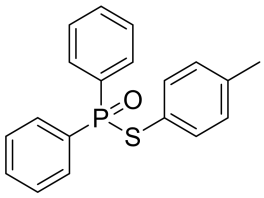
Chemical Formula: $C_{20}H_{19}OPS$
Exact Mass: 338.0894
Elemental Analysis: C, 70.98; H, 5.66; O, 4.73; P, 9.15; S, 9.48

S-(2,4-dimethylphenyl)diphenylphosphinothioate **6b**, white solid, m.p. 73-76 °C(89%, 75.2 mg). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 (ddt, *J* = 12.8, 7.0, 1.4 Hz, 4H), 7.55–7.49 (m, 2H), 7.43 (td, *J* = 7.6, 3.6 Hz, 4H), 7.29 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.96 (d, *J* = 1.9 Hz, 1H), 6.82 (dd, *J* = 8.0, 1.9 Hz, 1H), 2.31 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.81,138.55, 135.79, 132.41, 131.56, 131.26, 130.60, 130.52, 127.53, 127.42, 126.37, 120.54, 20.37, 20.10. ^{31}P NMR (202 MHz, Chloroform-*d*) δ 41.13. GC-MS (EI) *m/z*: 338. Anal. Calcd for $C_{20}H_{19}OPS$: C, 70.98%; H, 5.66%. Found: C, 70.74%; H, 5.40%.



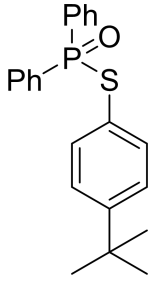
Chemical Formula: $C_{19}H_{17}O_2PS$
Mass: 340

S-(3-methoxyphenyl)diphenylphosphinothioate[5] **6c**, white solid, m.p. 175-178 °C (95%, 80.7 mg). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.85 (ddt, *J* = 12.9, 7.1, 1.4 Hz, 4H), 7.54–7.41 (m, 6H), 7.10 (t, *J* = 7.9 Hz, 1H), 7.03 (dq, *J* = 7.7, 1.4 Hz, 1H), 6.97 (dt, *J* = 2.9, 1.5 Hz, 1H), 6.79 (ddt, *J* = 8.1, 2.5, 1.2 Hz, 1H), 3.66 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 158.66, 132.00, 131.35, 131.15, 130.70, 130.62, 128.79, 127.63, 127.53, 126.61, 126.10, 118.80, 114.78, 54.31. ^{31}P NMR (202 MHz, Chloroform-*d*) δ 41.69. GC-MS (EI) *m/z*: 340.



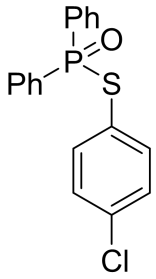
Chemical Formula: $C_{19}H_{17}OPS$
Mass: 324

S-*p*-tolyl diphenylphosphinothioate[6] **6d**, white solid, m.p. 110-112 °C (lit. 112-113 °C, 80%, 65 mg). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.84–7.65 (m, 4H), 7.38–7.32 (m, 2H), 7.31–7.25 (m, 4H), 7.22 (dd, *J* = 8.1, 1.5 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 2.08 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 138.59, 134.78, 132.29, 131.70, 131.44, 131.04, 130.96, 129.35, 127.97, 127.87, 127.57, 121.53, 20.52. ^{31}P NMR ($CDCl_3$, 202 MHz): δ 42.23. GC-MS (EI) *m/z*: 324.



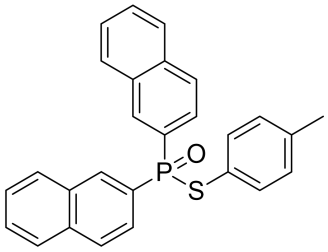
Chemical Formula: $C_{22}H_{23}OPS$
Mass: 366

S-(4-(Tert-butyl)phenyl)diphenylphosphinothioate[5] **6e**, white soild, m.p. 131-134 °C (90%, 82.3 mg). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.84 (dd, *J* = 13.1, 7.3 Hz, 4H), 7.49 (d, *J* = 7.4 Hz, 2H), 7.42 (td, *J* = 7.4, 3.4 Hz, 4H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 7.7 Hz, 2H), 1.23 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.32, 134.26, 131.28, 130.71, 130.63, 127.57, 127.47, 125.33, 33.63, 30.17. ^{31}P NMR (202 MHz, Chloroform-*d*) δ 41.82. GC-MS (EI) *m/z*: 366.



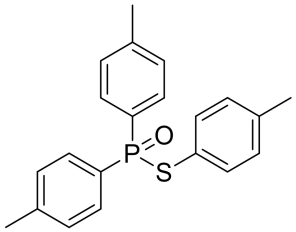
Chemical Formula: $C_{18}H_{14}ClOPS$
Mass: 344

S-(4-chlorophenyl)diphenylphosphinothioate[5] **6f**, white soild, m.p. 184-187 °C (81%, 68.8 mg). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.88–7.80 (m, 4H), 7.53 (td, *J* = 7.2, 1.7 Hz, 2H), 7.45 (td, *J* = 7.7, 3.6 Hz, 4H), 7.37 (dd, *J* = 8.5, 1.7 Hz, 2H), 7.18 (t, *J* = 9.1 Hz, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 135.56, 134.60, 131.53, 130.68, 130.59, 128.36, 127.72, 127.62, 127.31, 123.70. ^{31}P NMR (202 MHz, Chloroform-*d*) δ 41.78. GC-MS (EI) *m/z*: 344.



Chemical Formula: $C_{27}H_{21}OPS$
Mass: 424

S-*p*-tolyl di(naphthalen-2-yl)phosphinothioate[7] **6g,** white solid, 167-169 °C (lit. 159-161 °C, 67%, 71 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.94–8.81 (m, 2H), 8.03 (dd, *J* = 17.3, 7.1 Hz, 2H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.85–7.76 (m, 2H), 7.50–7.41 (m, 4H), 7.37 (dd, *J* = 10.1, 5.2 Hz, 4H), 6.93 (d, *J* = 8.0 Hz, 2H), 2.17 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.22 (s), 135.51 (s), 136.26–133.81 (m), 133.54 (dd, *J* = 25.9, 9.9 Hz), 130.11 (s), 129.85 (d, *J* = 49.9 Hz), 129.07 (s), 128.93 (d, *J* = 23.2 Hz), 127.44 (d, *J* = 11.0 Hz), 126.66 (s), 124.55 (d, *J* = 15.1 Hz), 123.27 (s), 21.30 (s). ^{31}P NMR (202 MHz, Chloroform-*d*) δ 45.53. GC-MS (EI) *m/z*: 424.



Chemical Formula: $C_{21}H_{21}OPS$
Mass: 352

S-*p*-tolyl di-*p*-tolylphosphinothioate[7] **6h**. white solid, m.p. 148-150 °C (lit. 145-147 °C, 78%, 68.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 12.7, 8.1 Hz, 4H), 7.32 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.22 (dd, *J* = 7.9, 2.9 Hz, 4H), 6.99 (d, *J* = 7.9 Hz, 2H), 2.36 (s, 7H), 2.24 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.36, 139.58, 135.84, 132.27, 132.19, 130.51, 129.88, 129.78, 123.29, 22.20, 21.75. ^{31}P NMR (202 MHz, Chloroform-*d*) δ 42.23. GC-MS (EI) *m/z*: 352.

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[4] Revol, G.; McCallum, T.; Morin, M.; Gagosz, F.; Barriault, L. *Angew. Chem. Int. Ed.* **2013,** *52*, 13342-13345.

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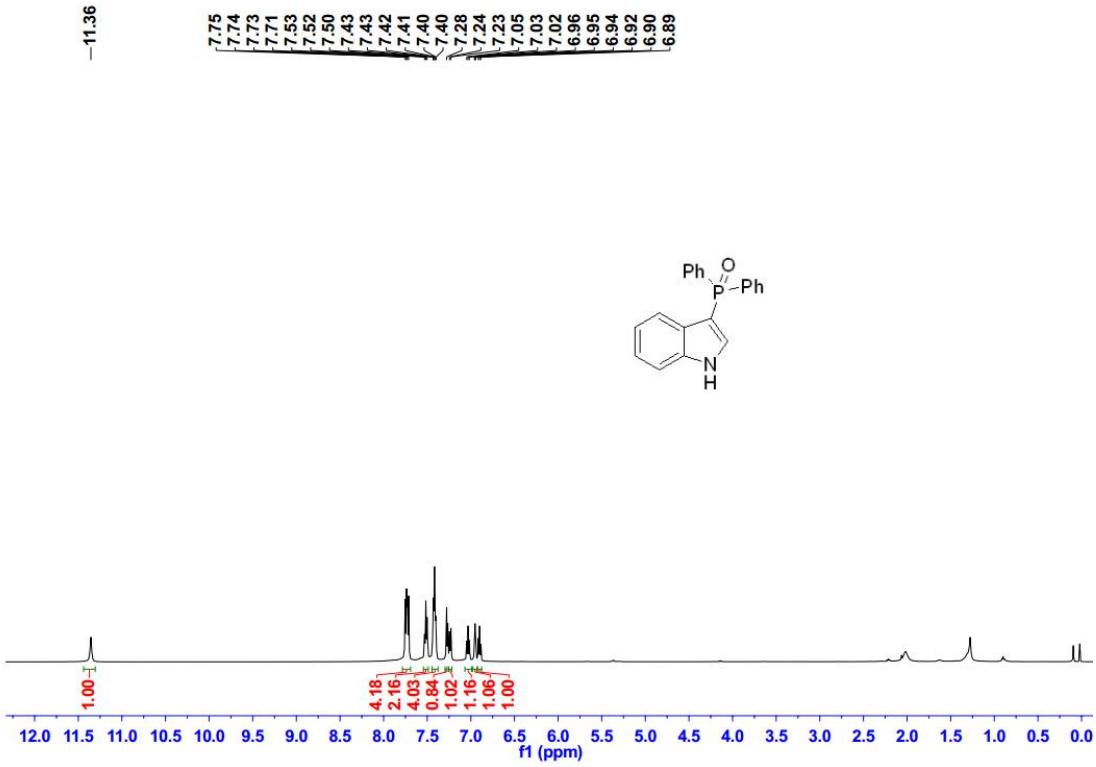
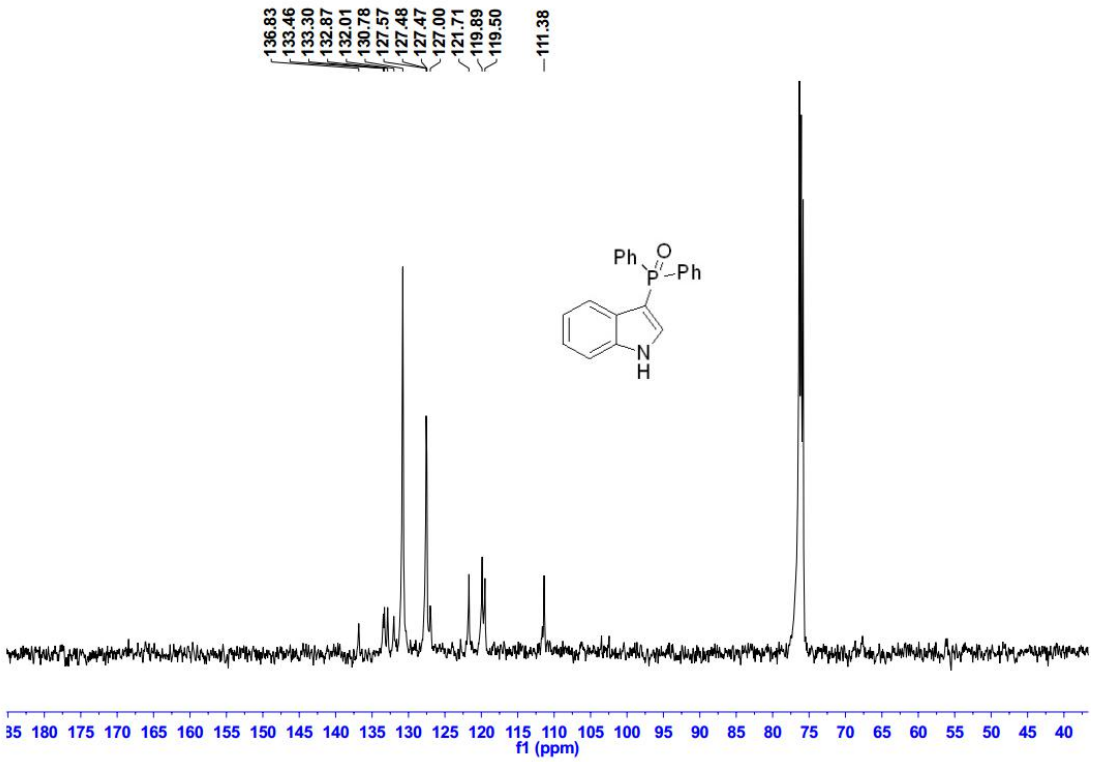
[6] Kumaraswamy, G.; Raju, R. *Adv. Syn. Catal.* **2014,** *356*, 2591-2598.

[7] Lin, Y.-m.; Lu, G.-p.; Wang, G.-x.; Yi, W.-b. *J. Org. Chem.* **2017,** *82*, 382-389.

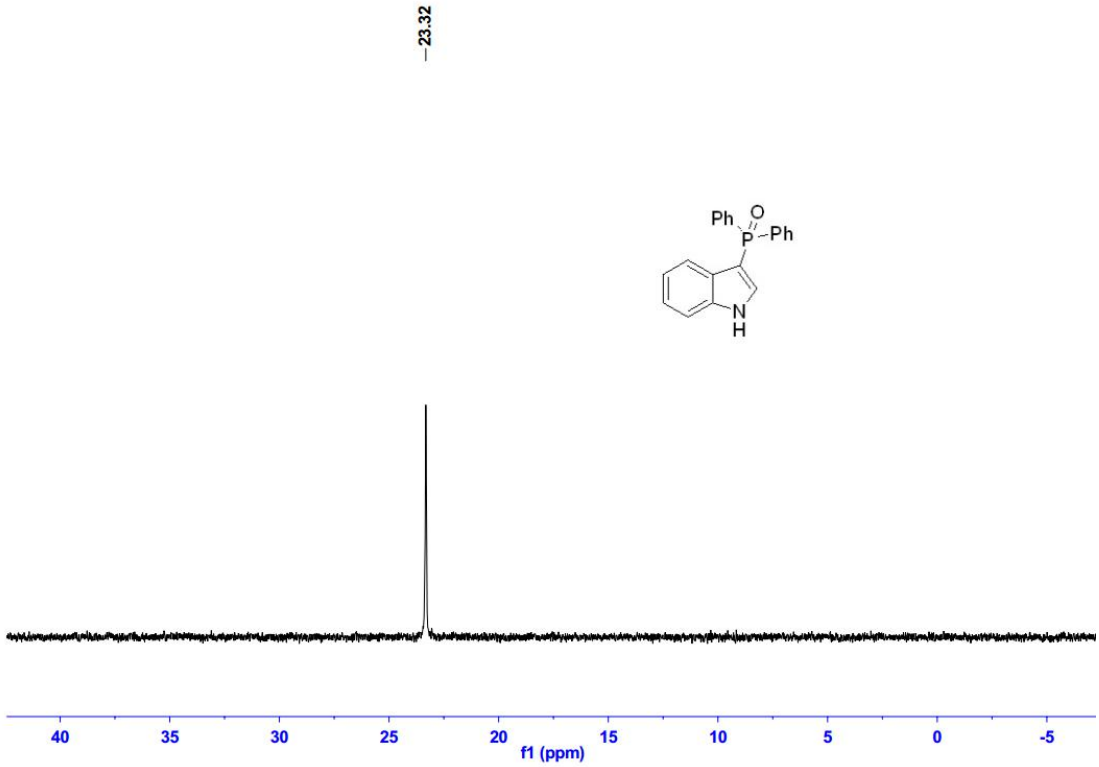
3 NMR Spectra of All Products



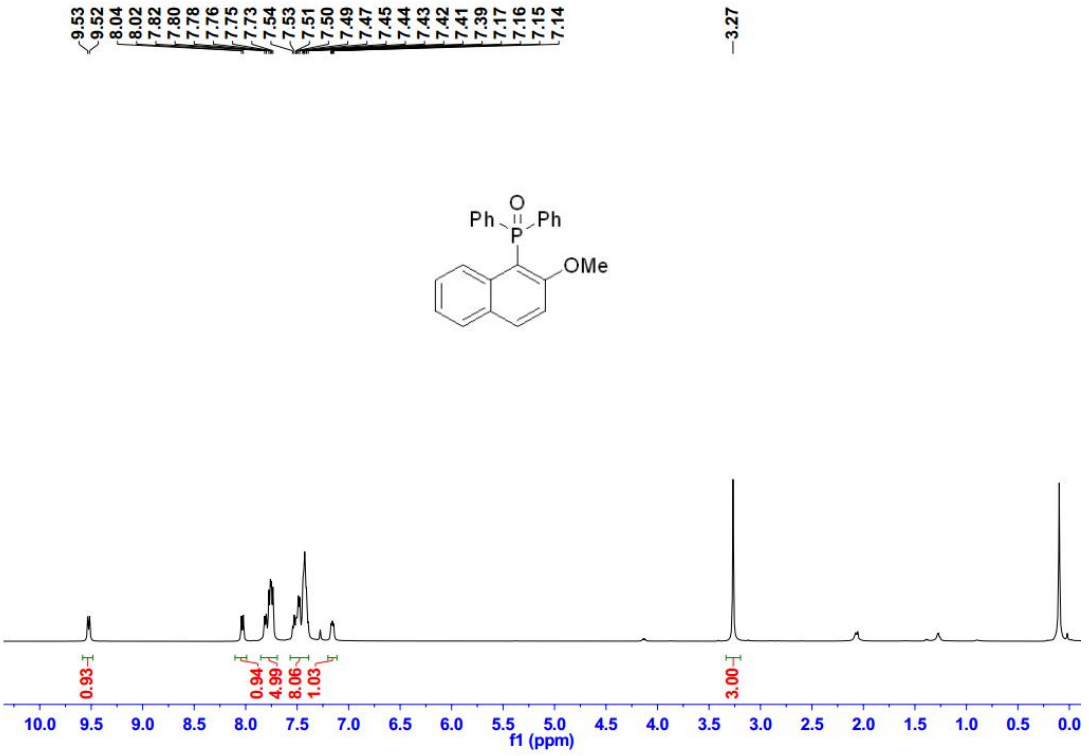
^{1}H NMR of **3a**



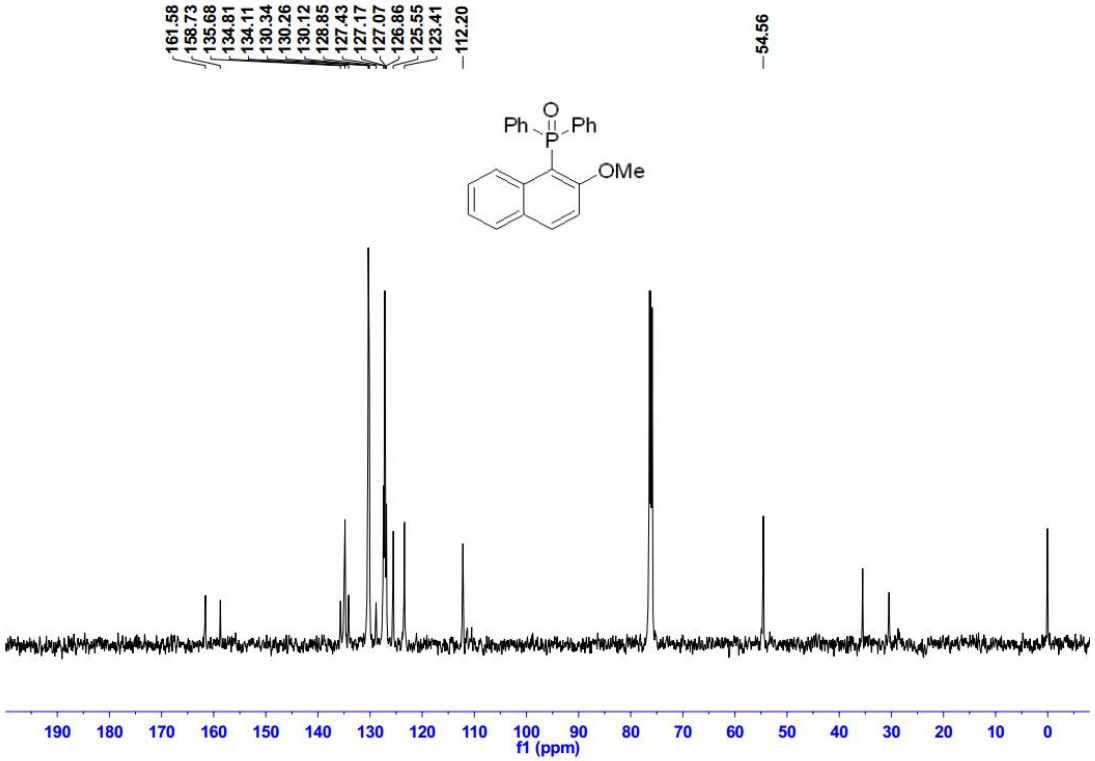
^{13}C NMR of **3a**



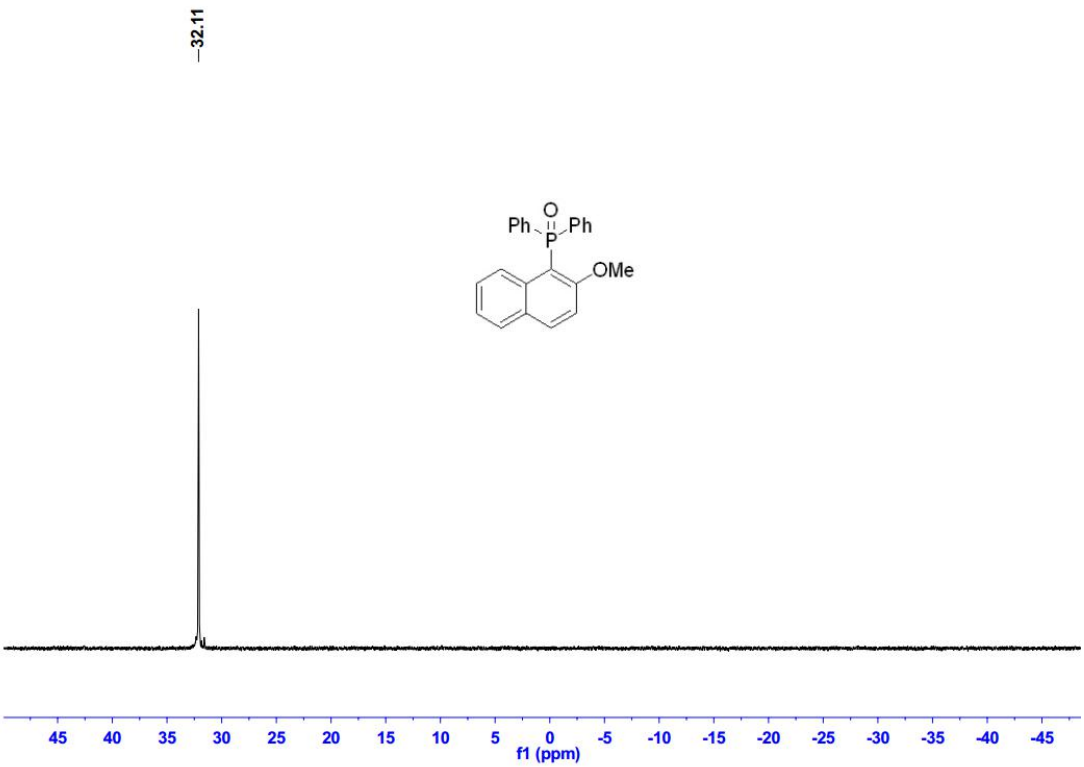
^{31}P NMR of **3a**



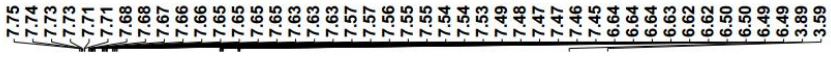
^{1}H NMR of **3b**

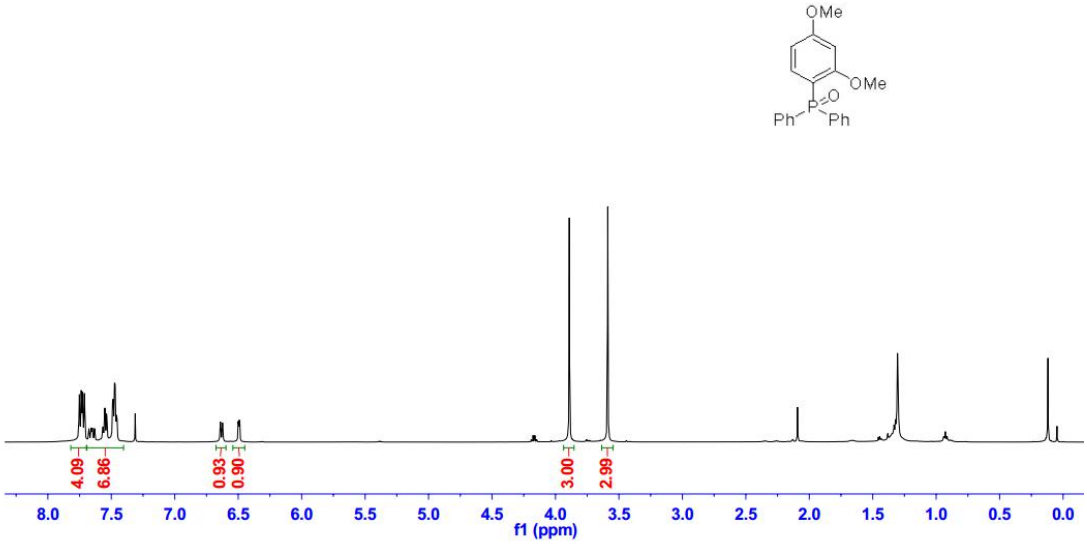


^{13}C NMR of **3b**

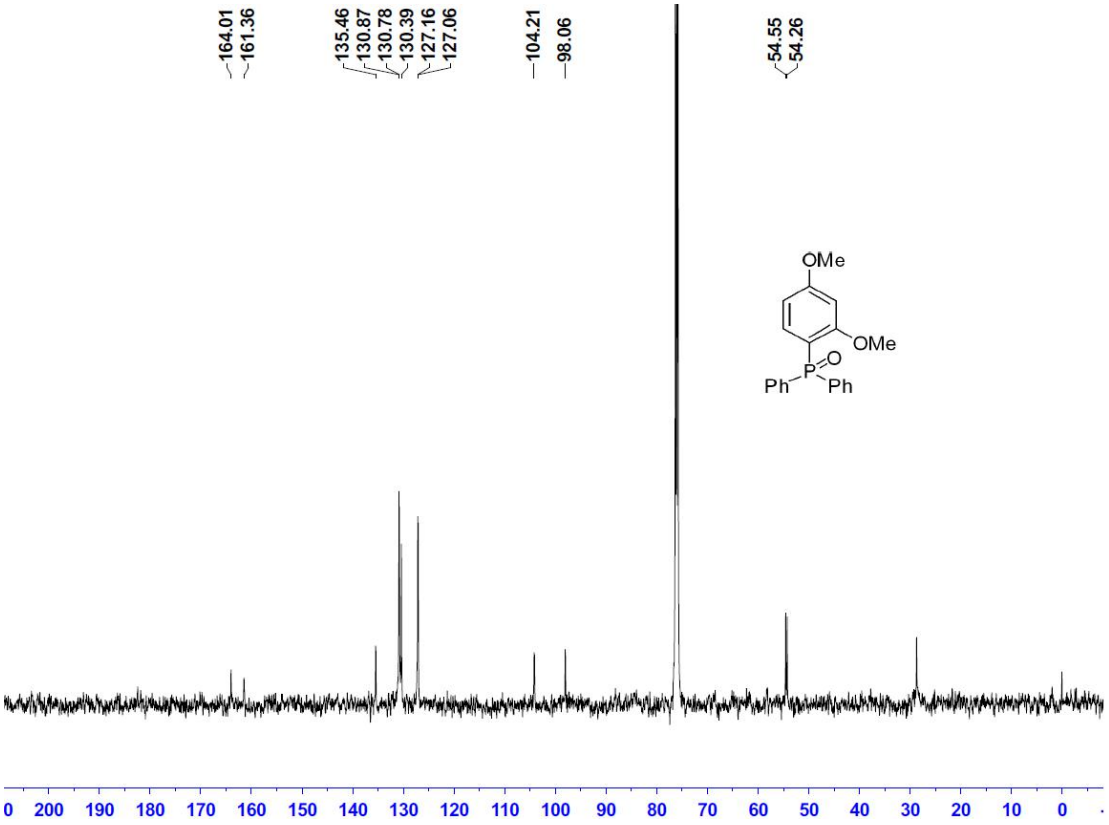

32.11
O
Ph
P
Ph
OMe
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
f1 (ppm)

^{31}P NMR of **3b**

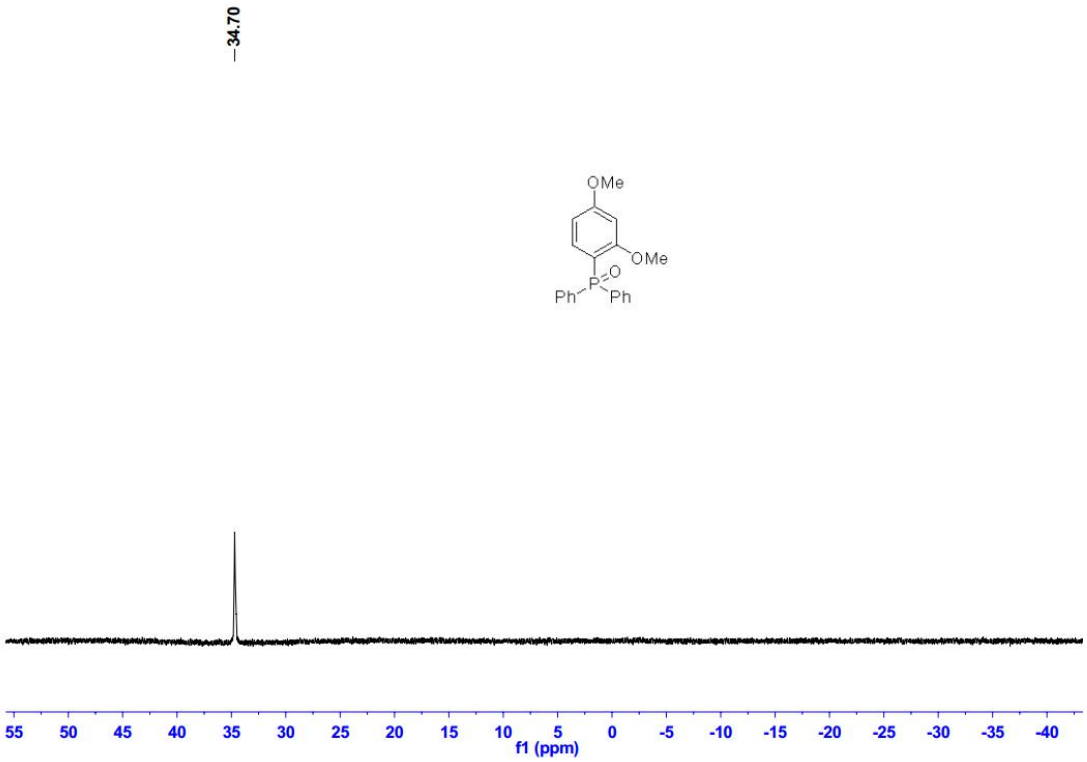




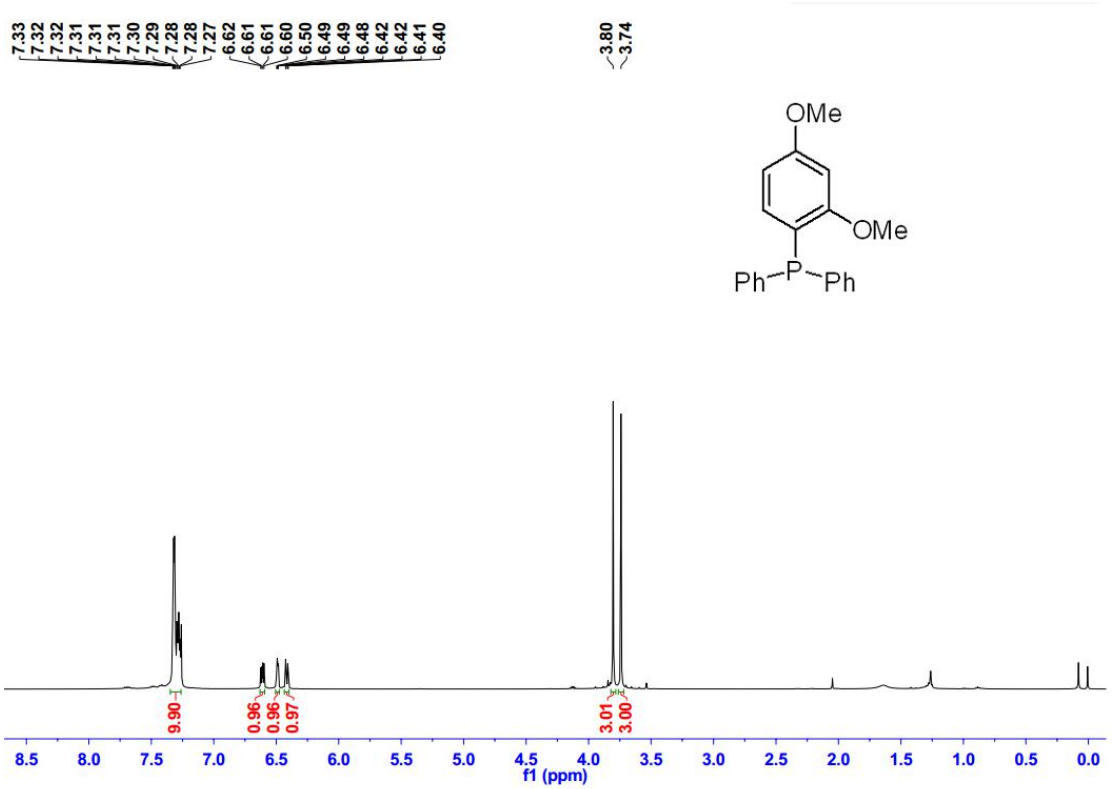
^{1}H NMR of **3c**



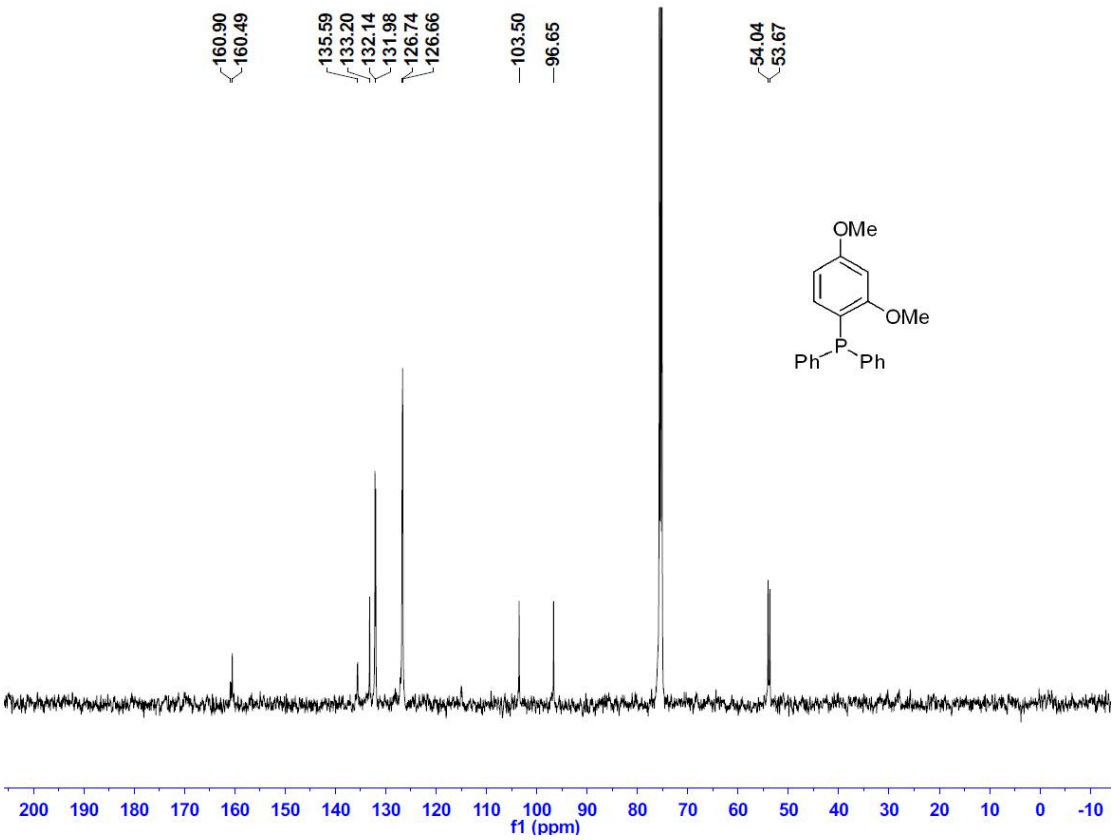
^{13}C NMR of **3c**


34.70
OMe
OMe
P
O
Ph
Ph
55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40
f1 (ppm)

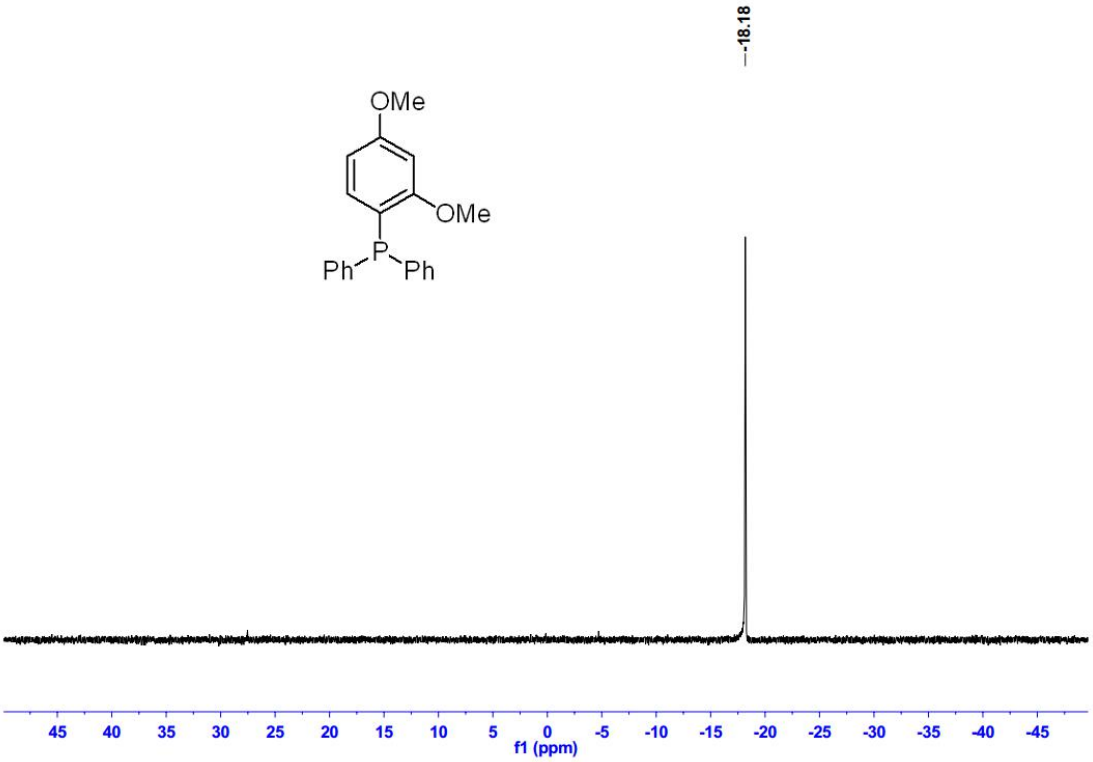
^{31}P NMR of **3c**



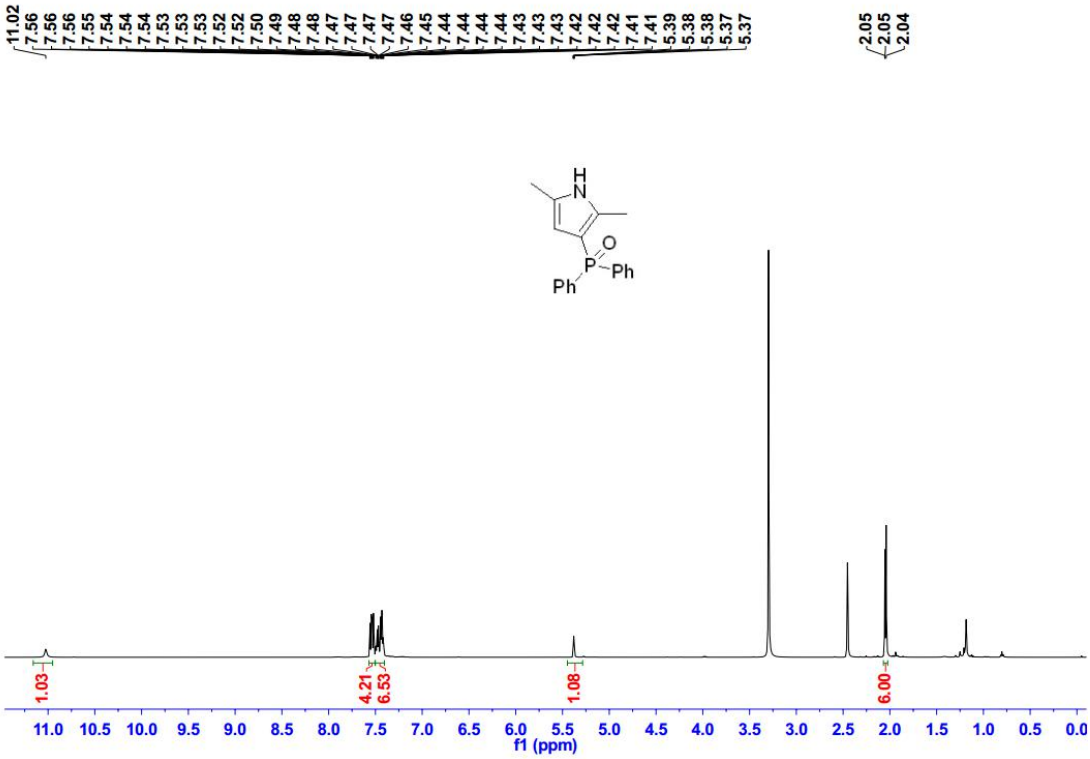
^{1}H NMR of **3c'**



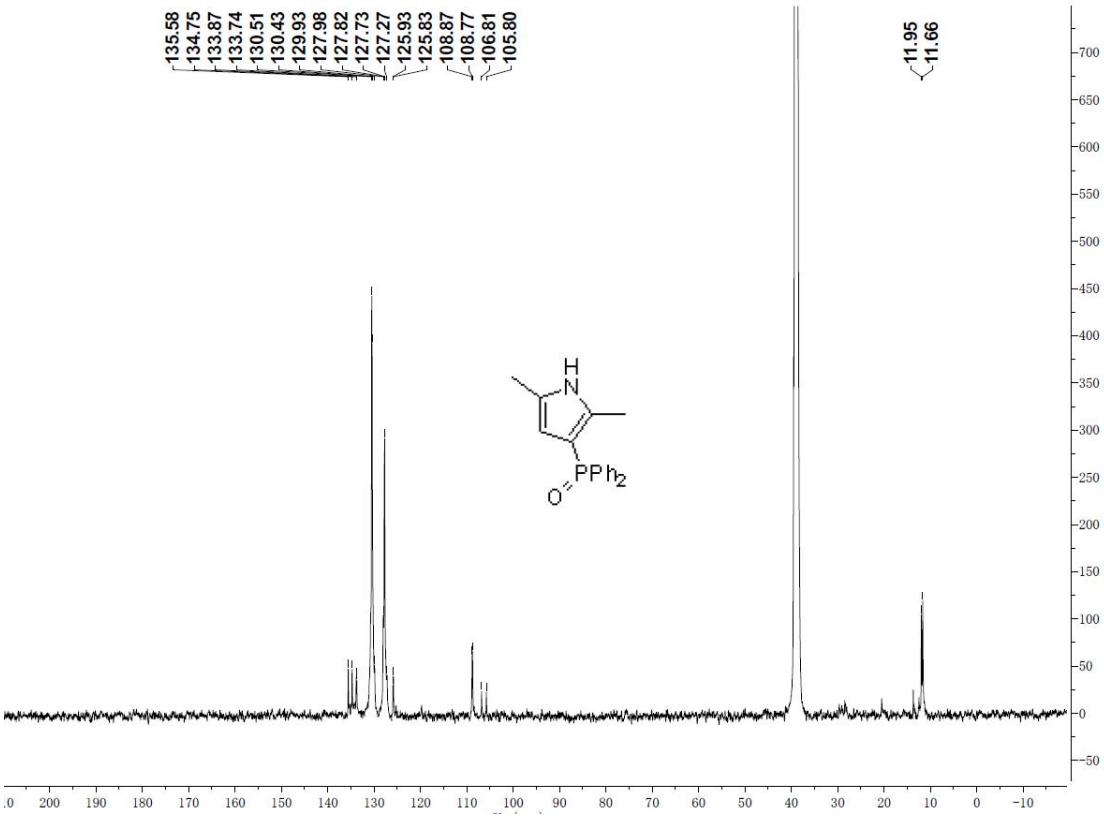
^{13}C NMR of **3c'**


-18.18
OMe
OMe
P
Ph
Ph
45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45
f1 (ppm)

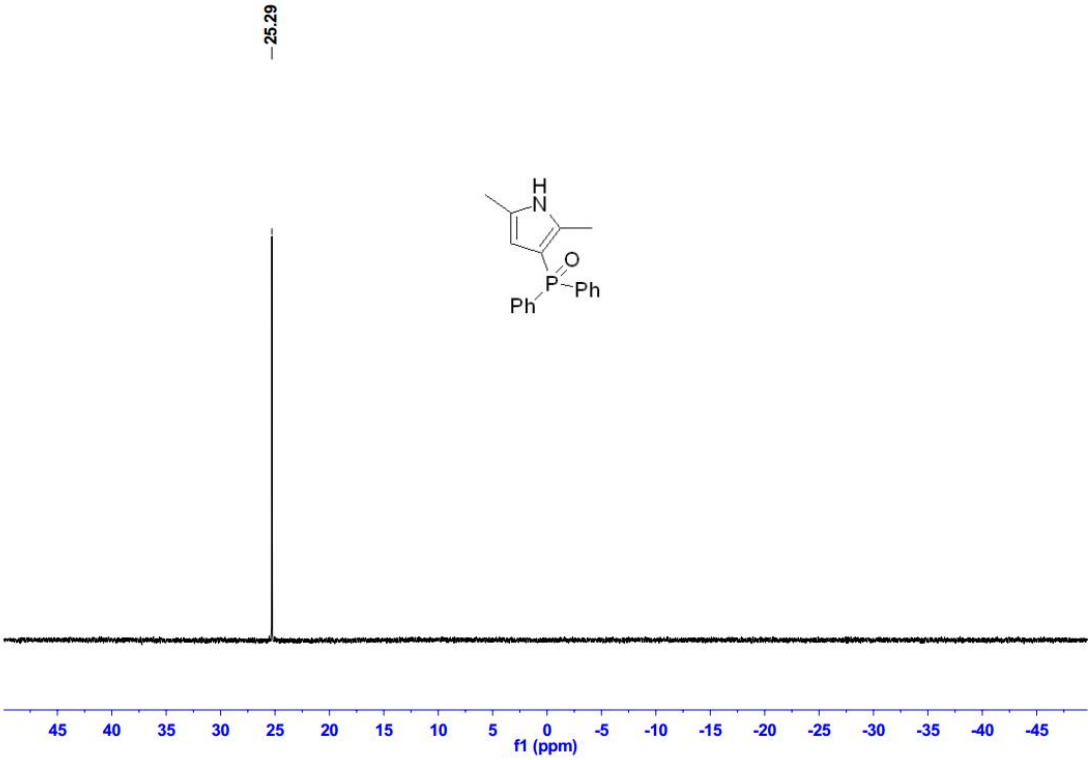
^{31}P NMR of **3c'**



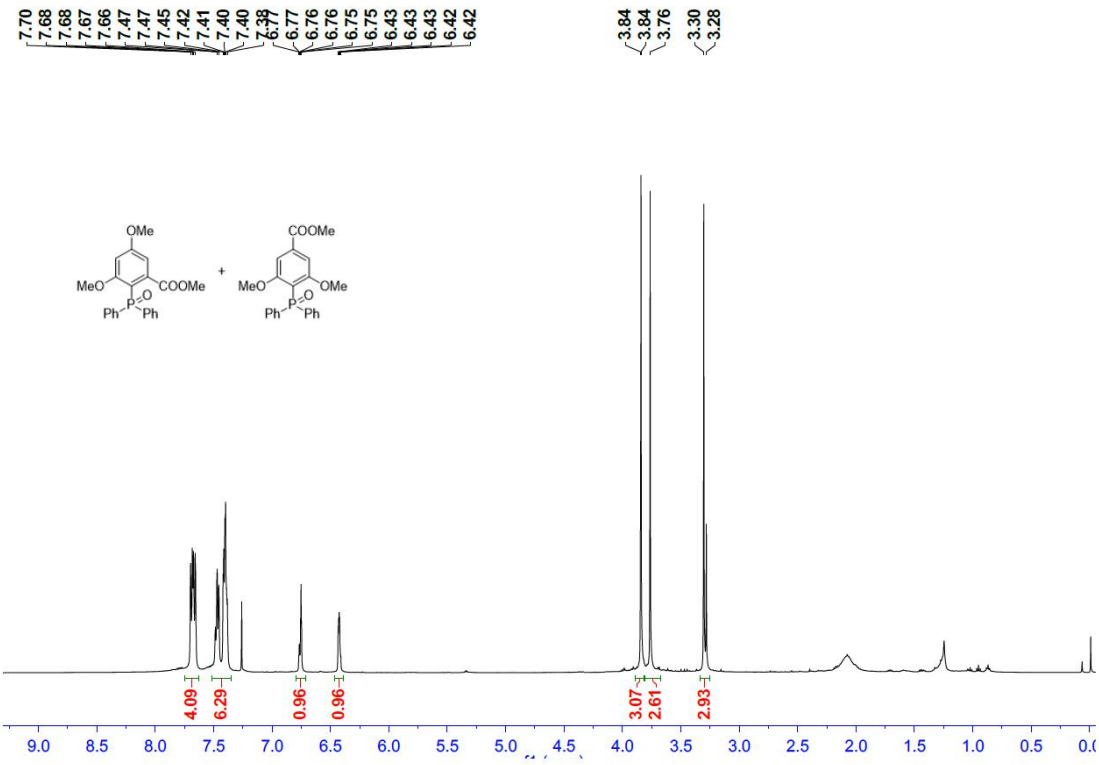
^{1}H NMR of **3d**



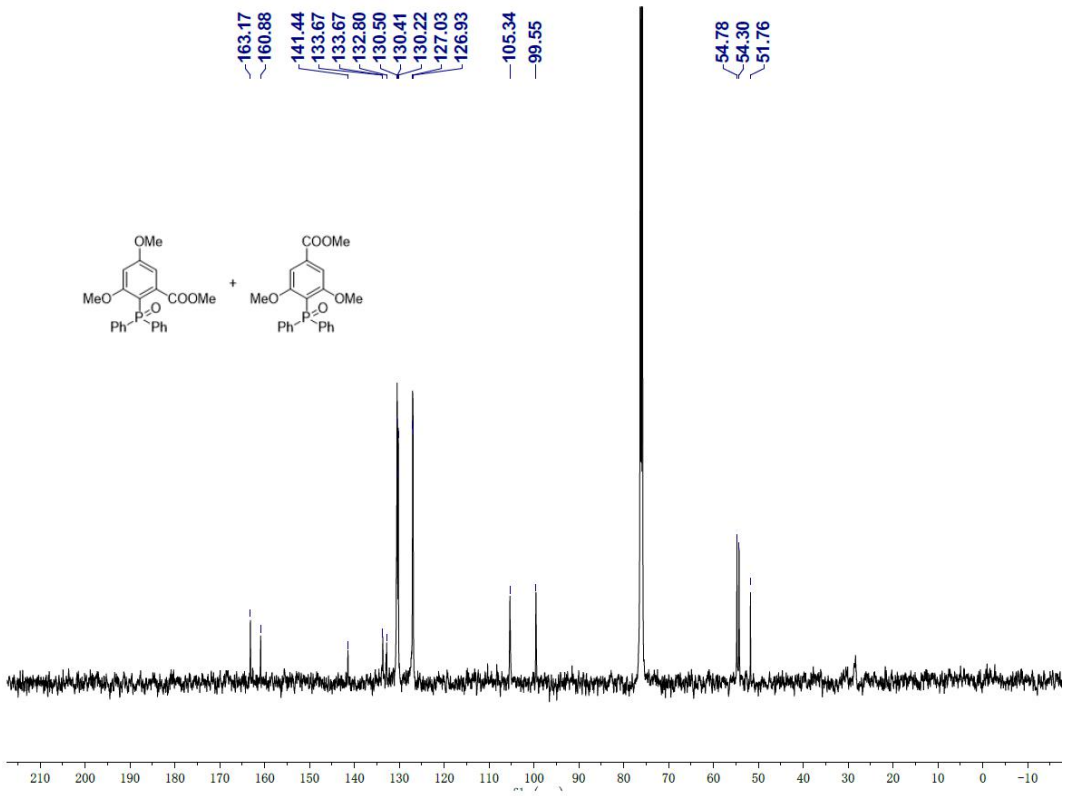
^{13}C NMR of **3d**


25.29
H
N
O
P
Ph
Ph
45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45
f1 (ppm)

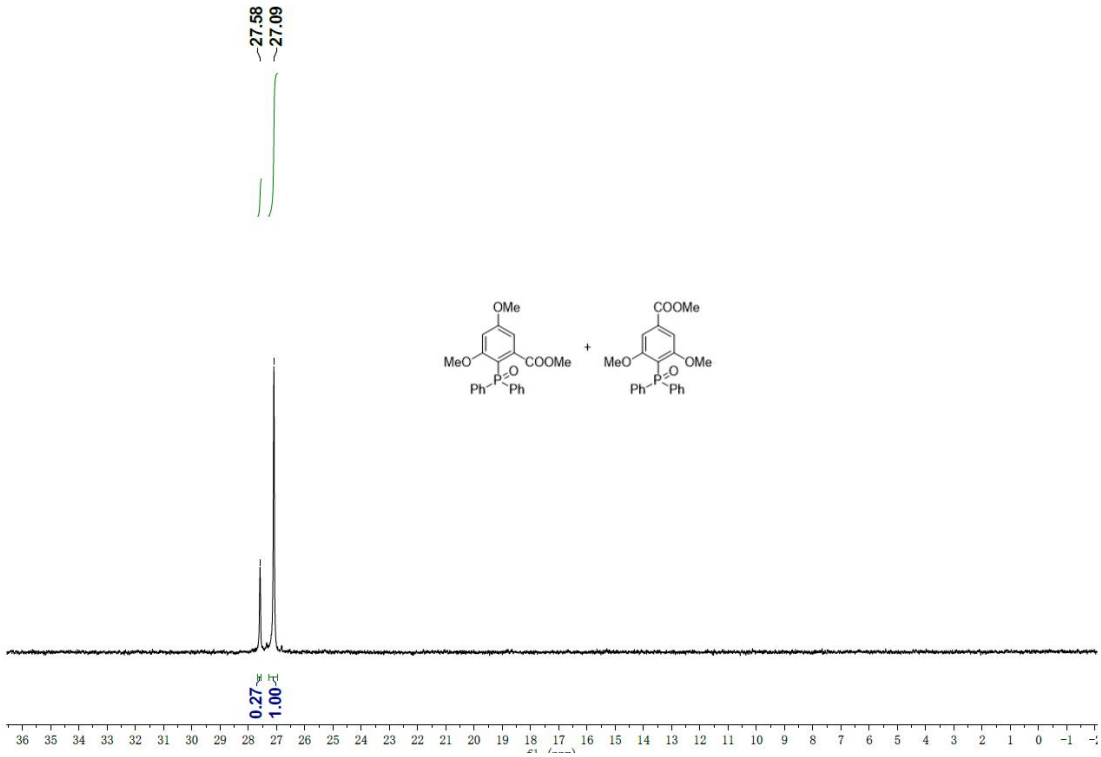
^{31}P NMR of **3d**



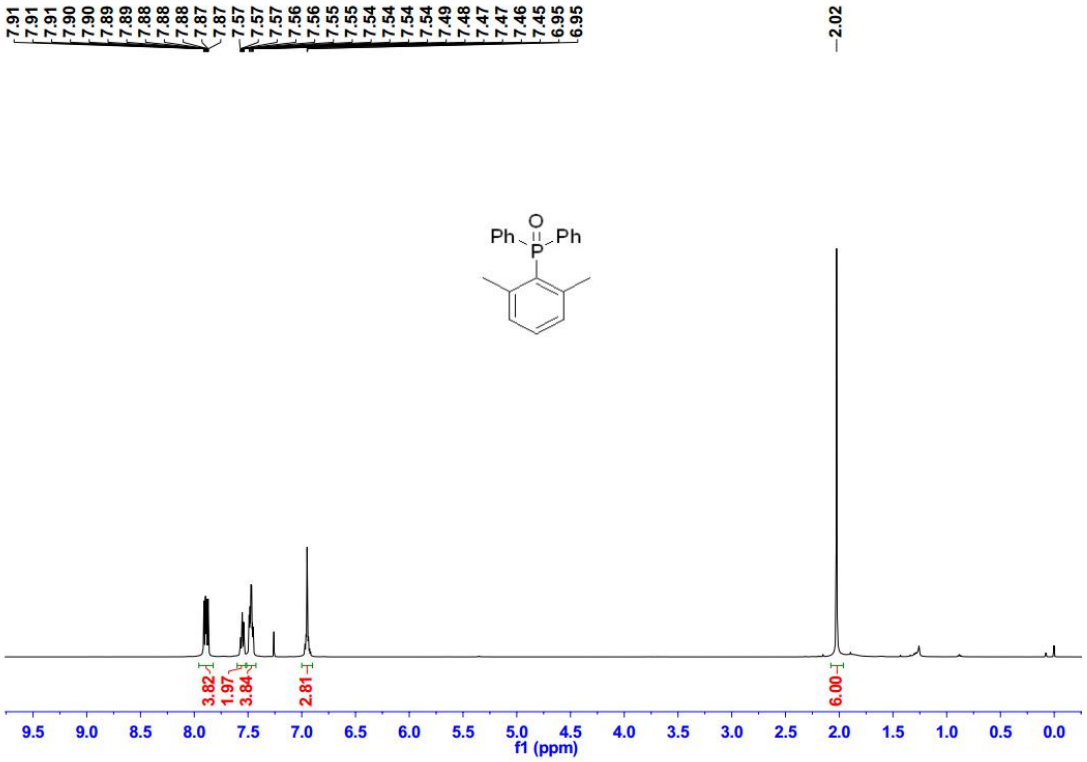
^{1}H NMR of **3e+3e'**



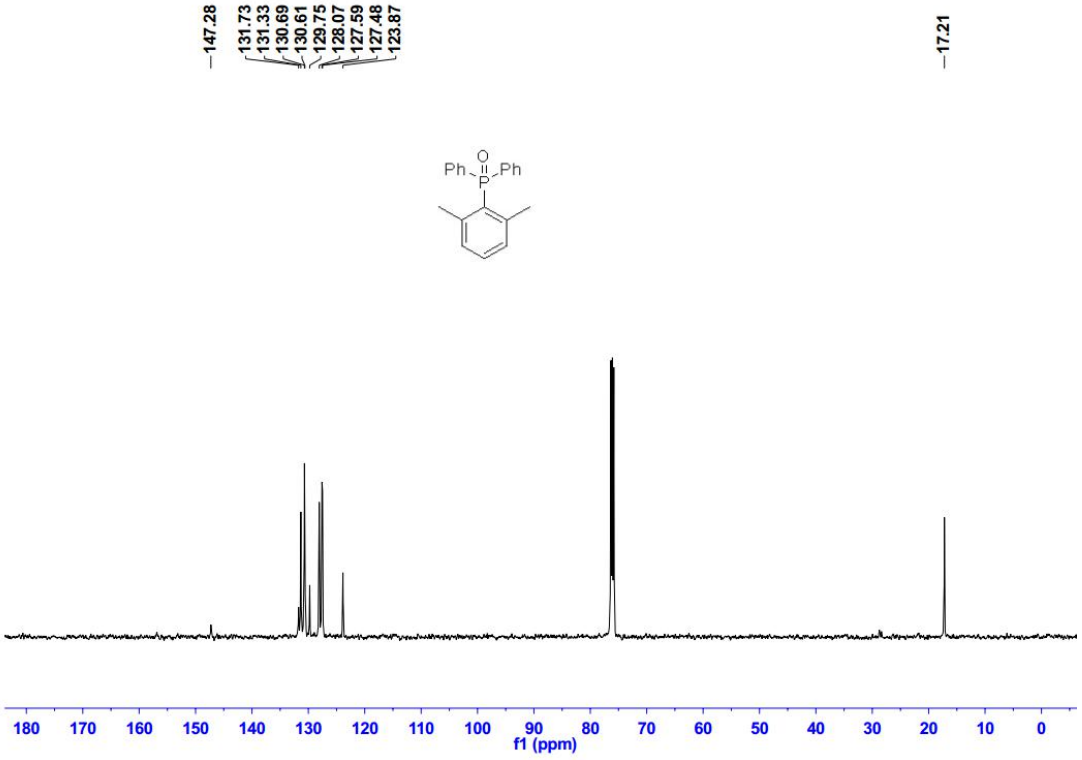
^{13}C NMR of **3e+3e'**



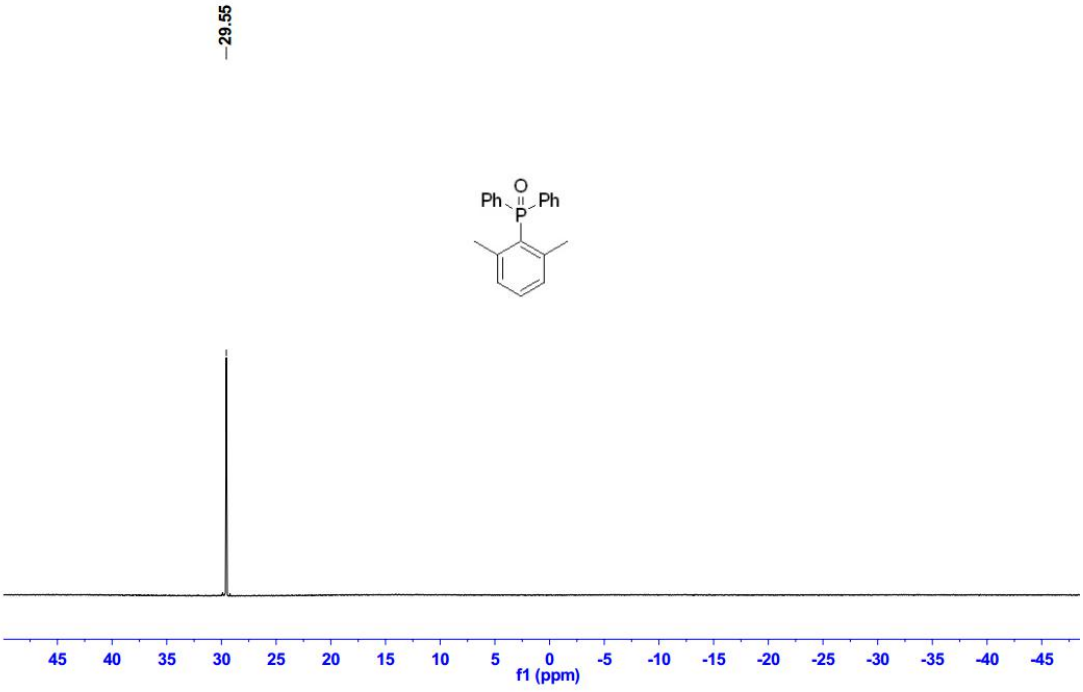
^{31}P NMR of **3e+3e'**



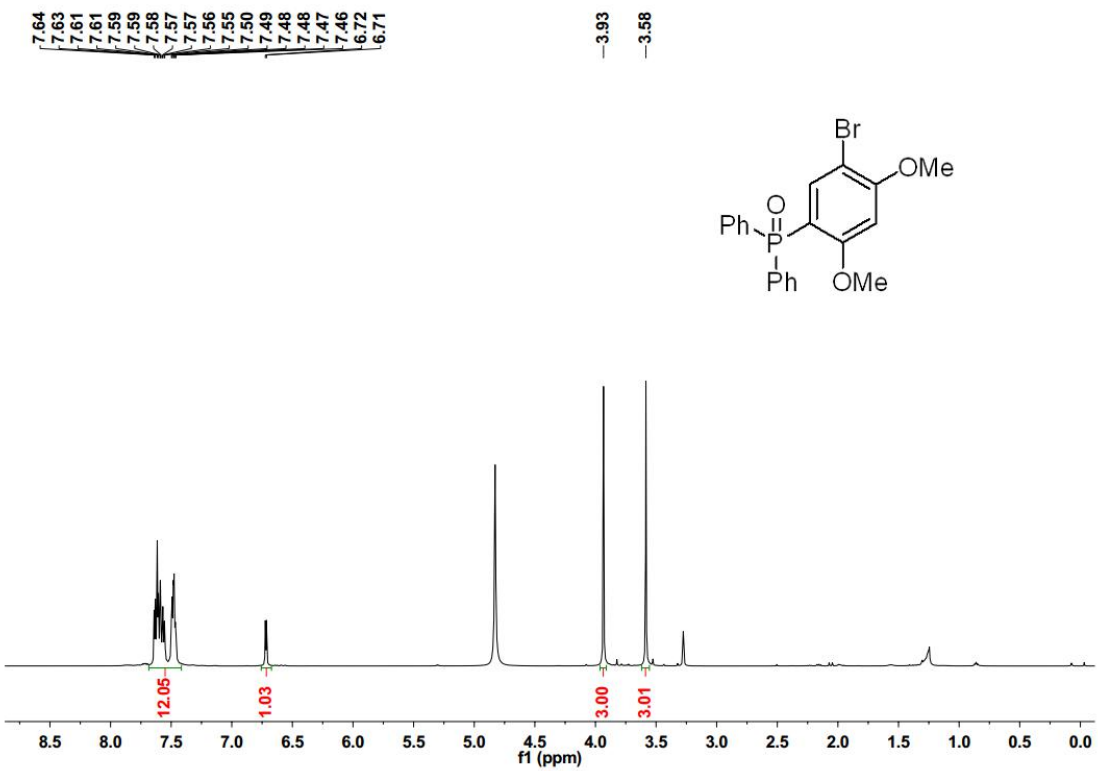
^{1}H NMR of **3f**



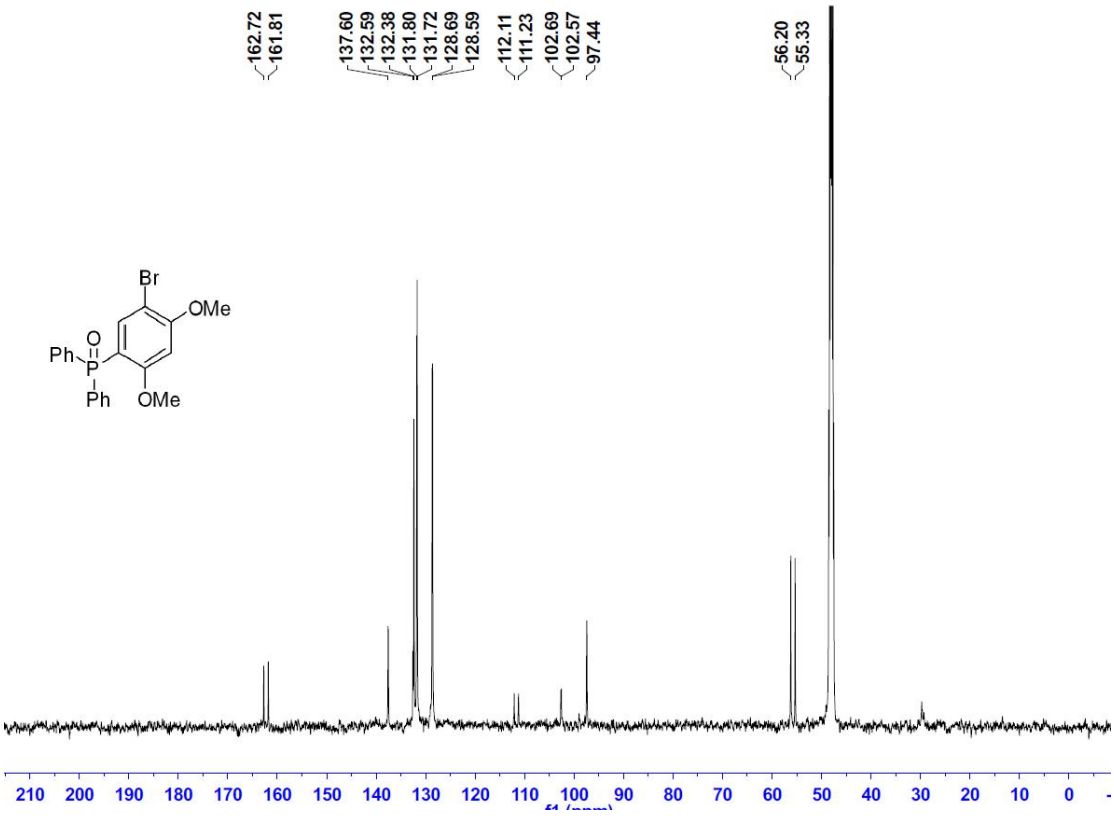
^{13}C NMR of **3f**


29.55
Ph
O
P
Ph
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
f1 (ppm)

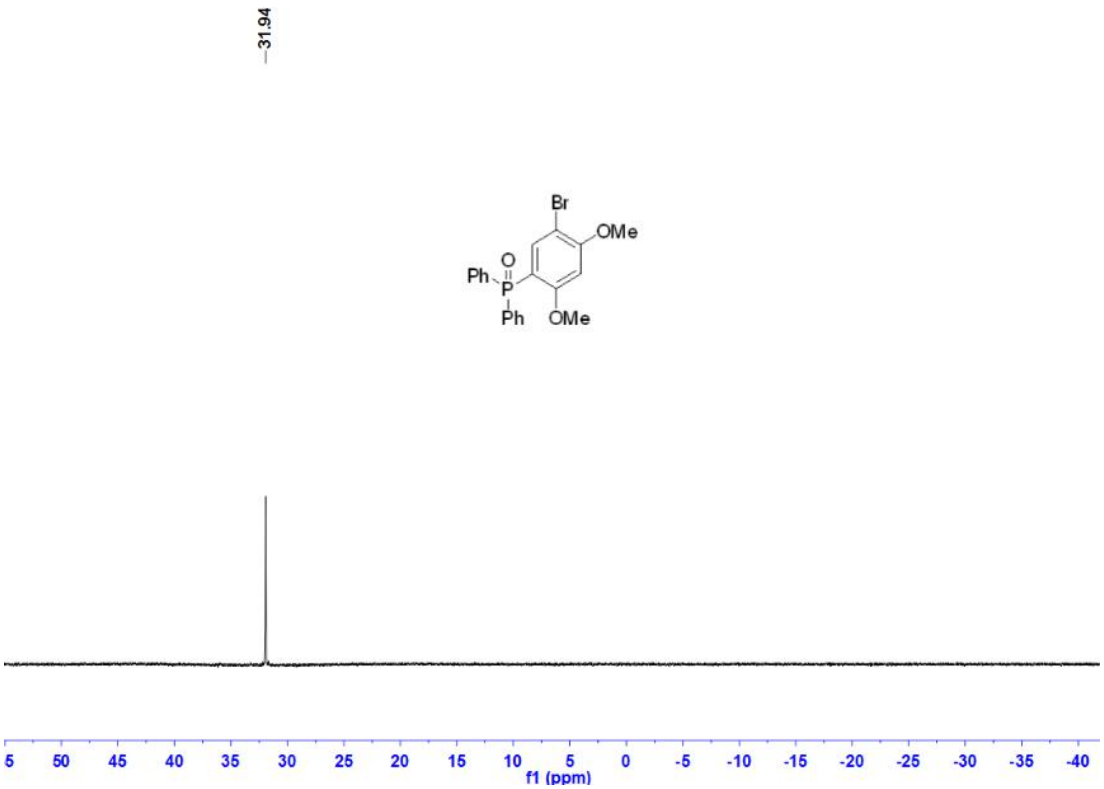
^{31}P NMR of **3f**



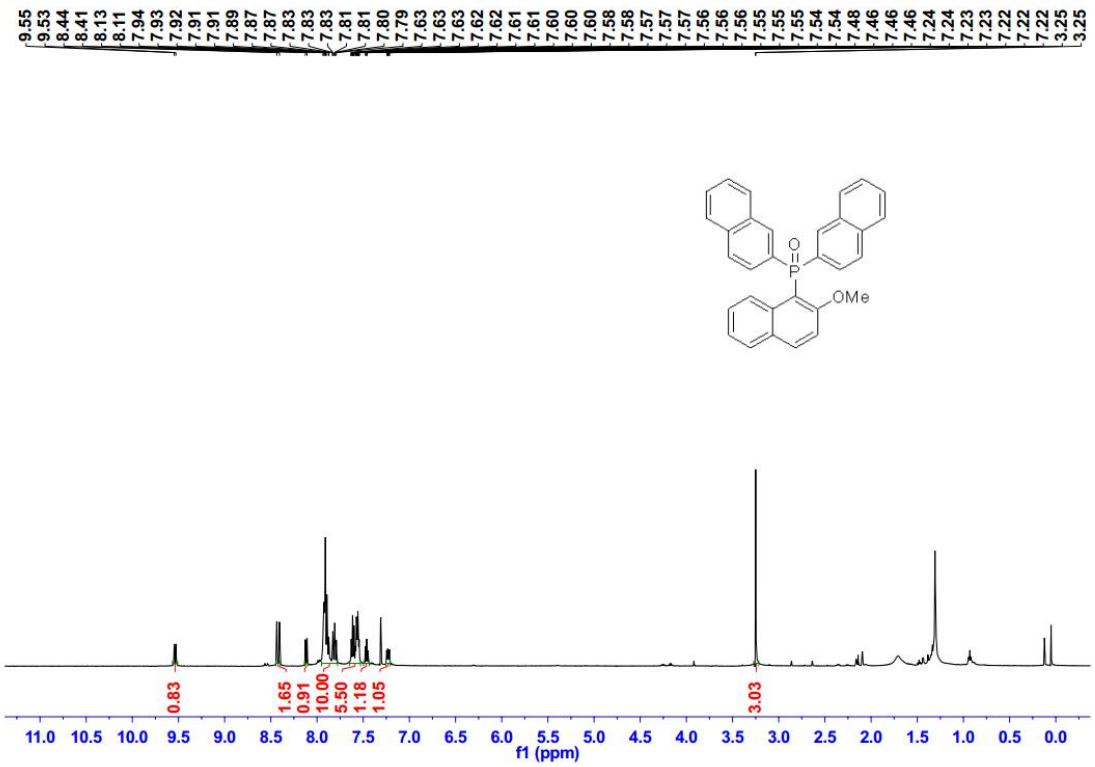
^{1}H NMR of **3g**



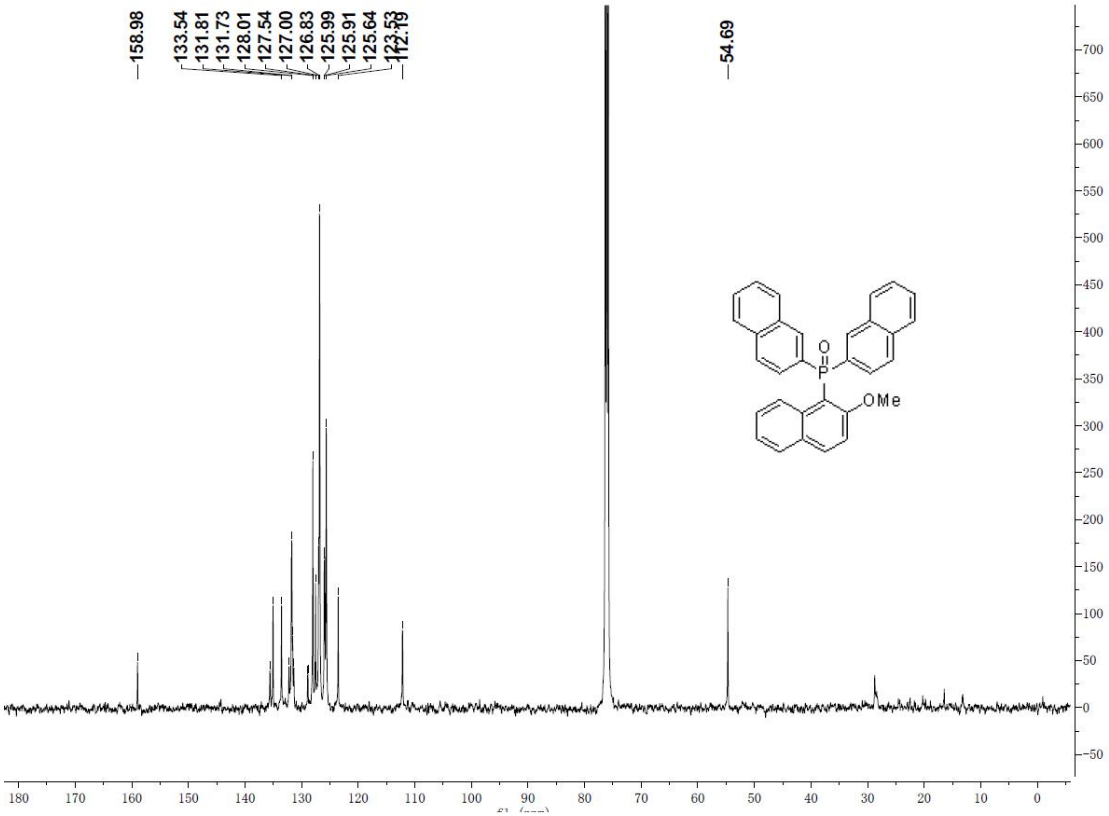
^{13}C NMR of **3g**


31.94
Br
OMe
O
Ph
P
Ph
OMe
5 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40
f1 (ppm)

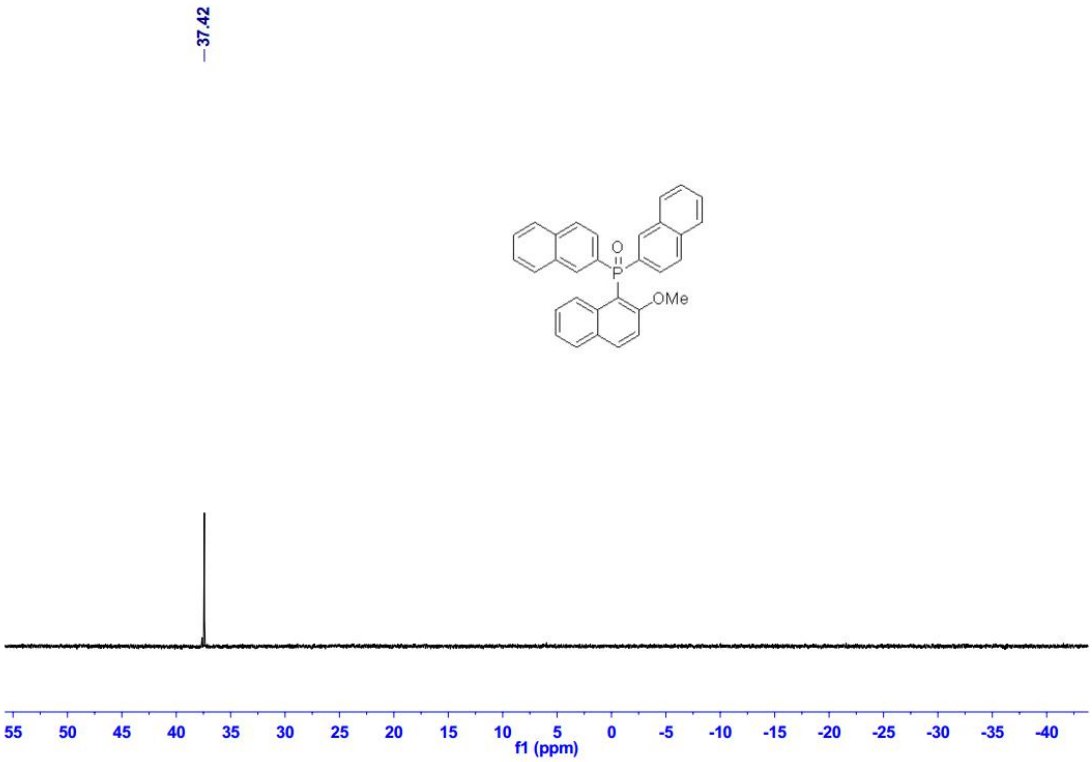
^{31}P NMR of **3g**



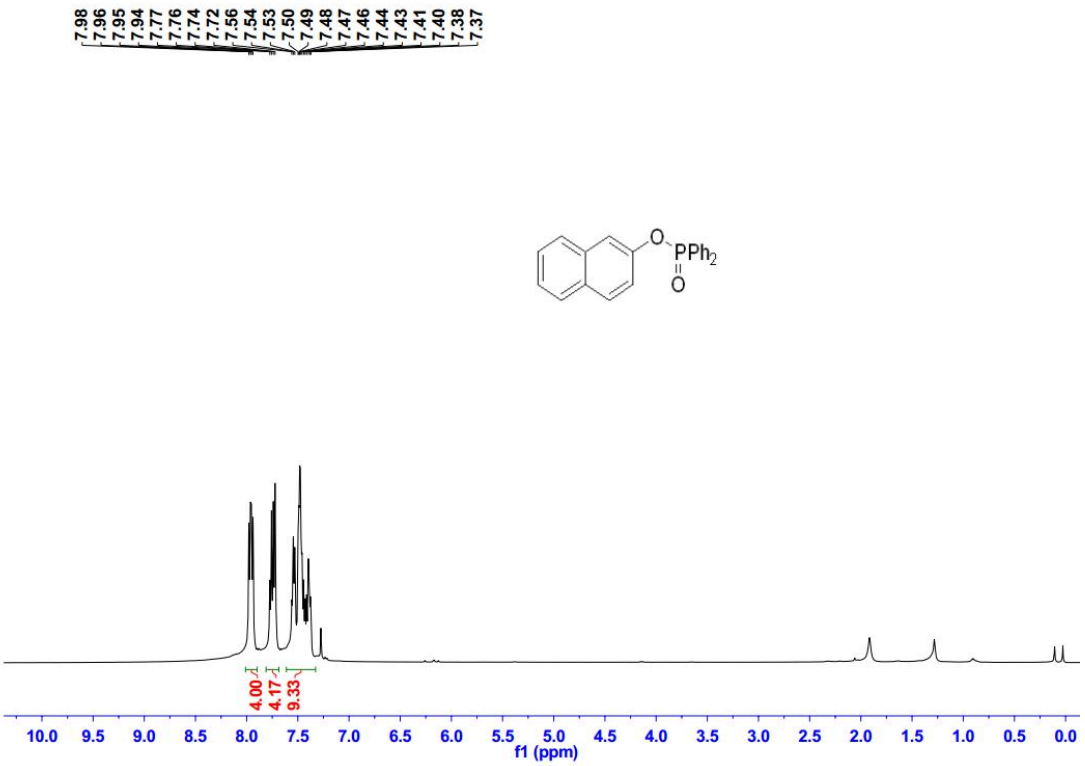
^{1}H NMR of **3j**



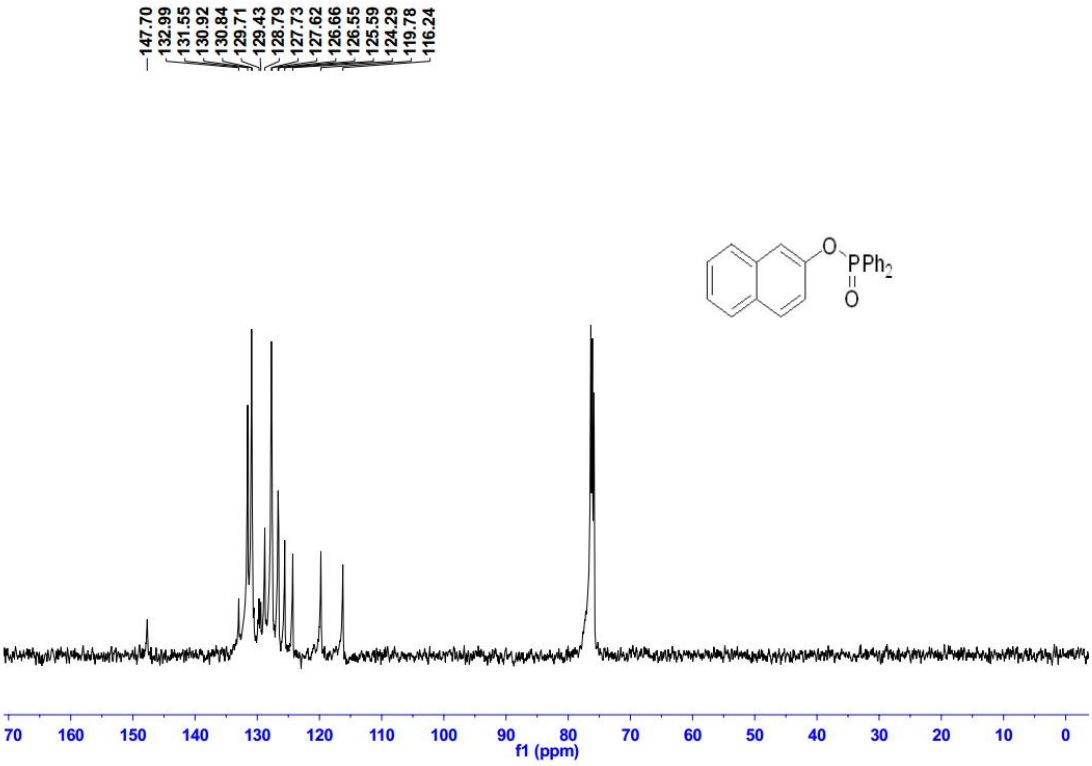
^{13}C NMR of **3j**


37.42
O
P
OMe
55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40
f1 (ppm)

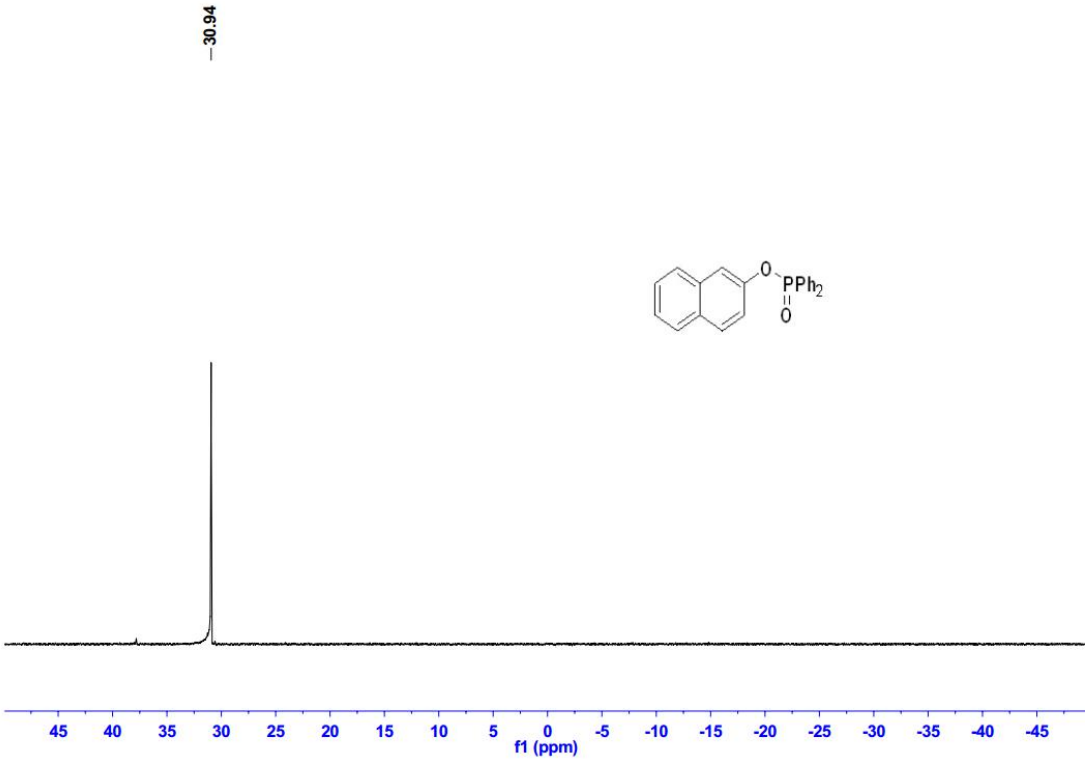
^{31}P NMR of **3j**



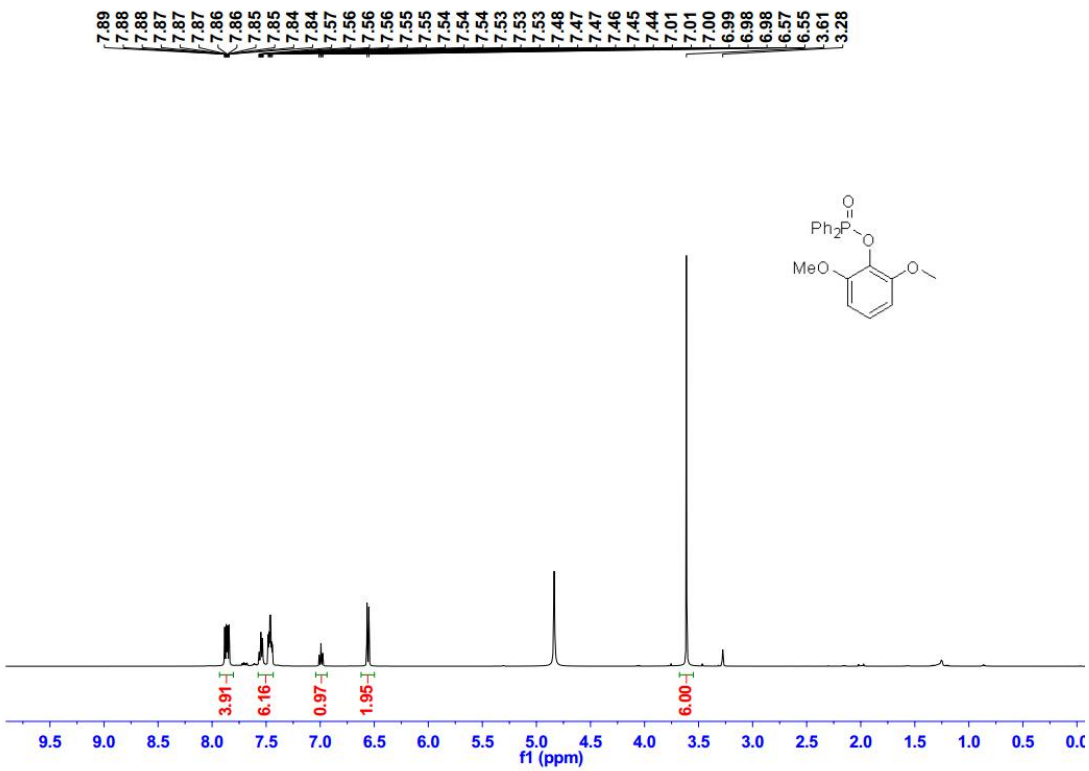
^{1}H NMR of **5a**



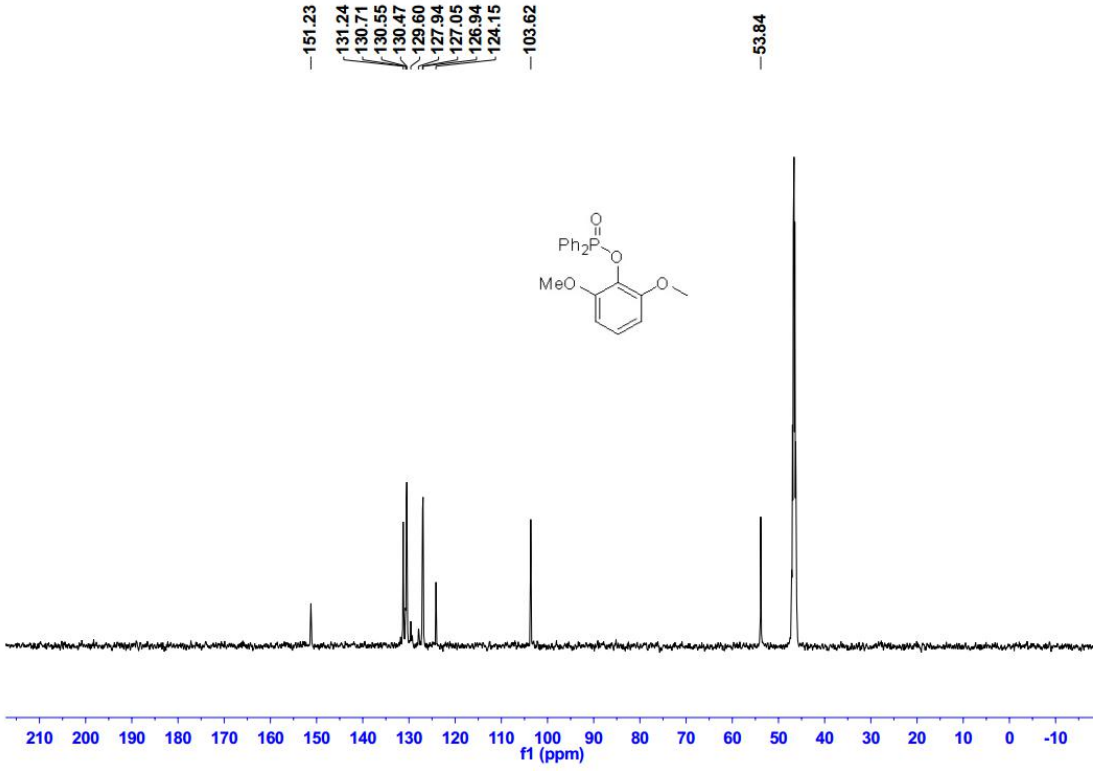
^{13}C NMR of **5a**


30.94
O
PPh2
O
45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45
f1 (ppm)

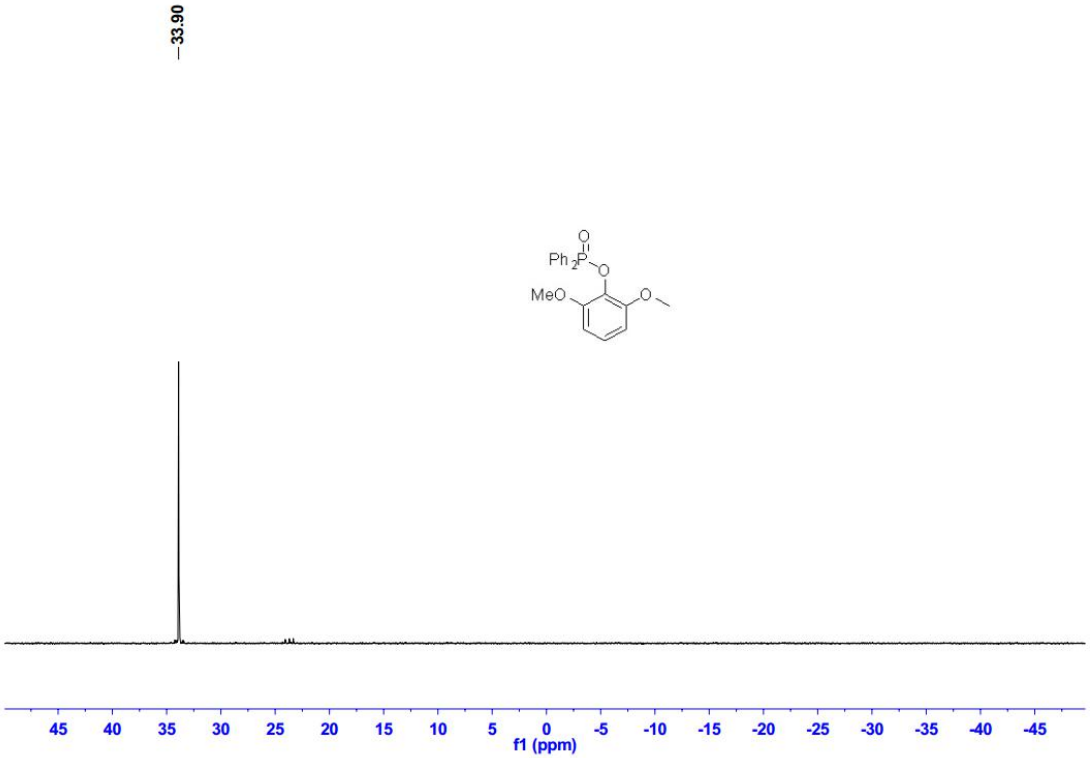
^{31}P NMR of **5a**



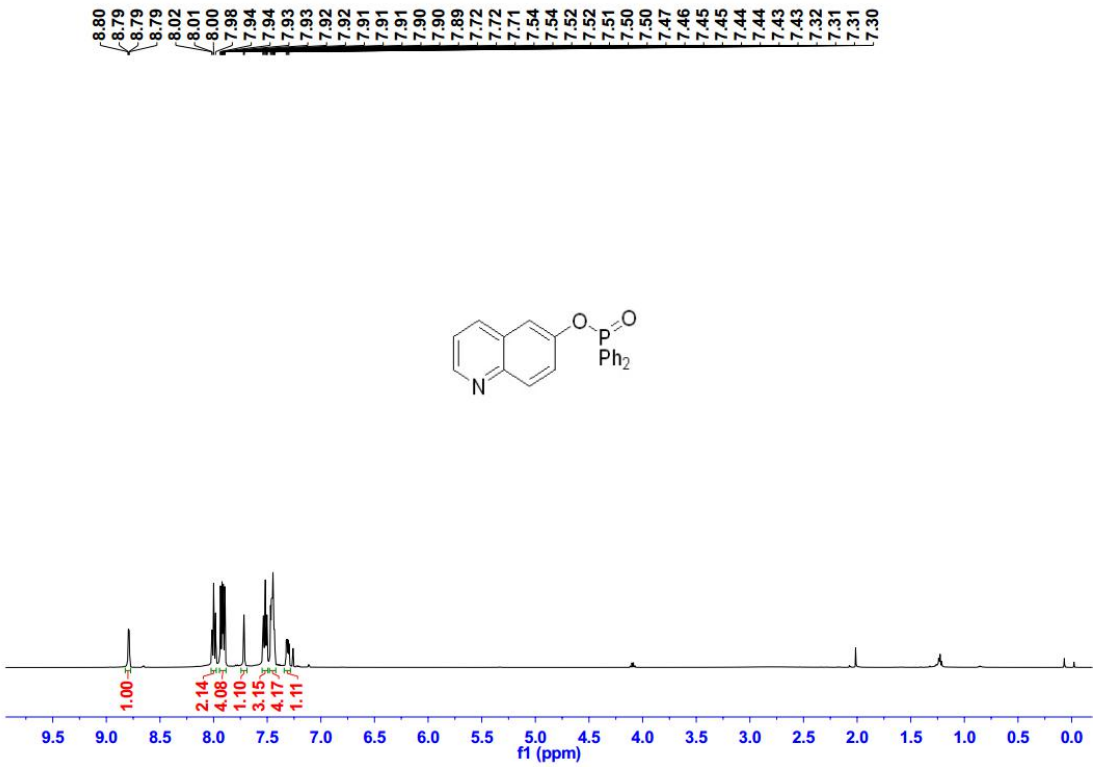
^{1}H NMR of **5b**



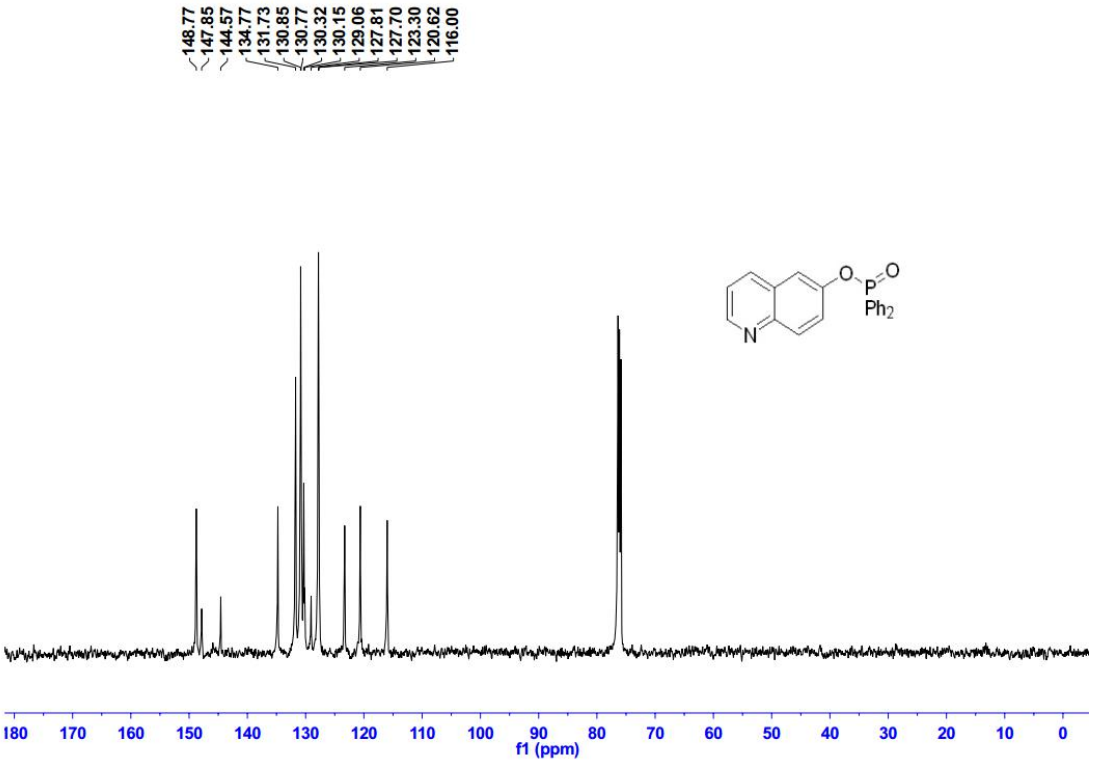
^{13}C NMR of **5b**


33.90
Ph2P
O
MeO
O
45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45
f1 (ppm)

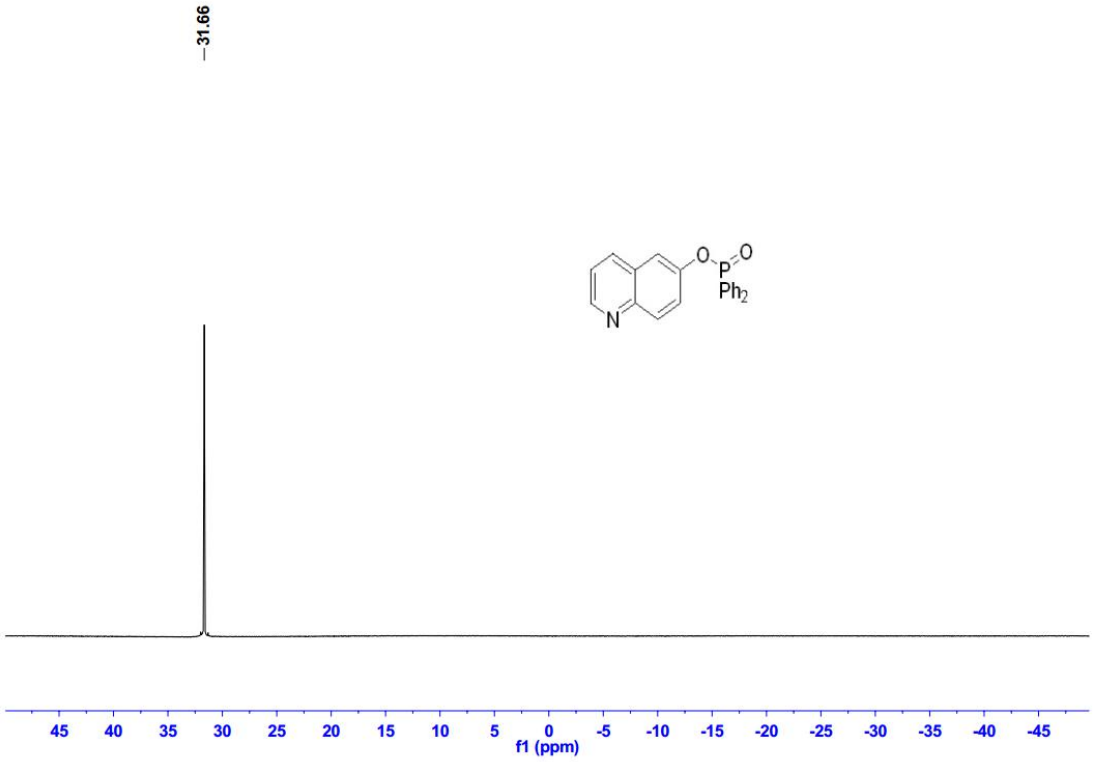
^{31}P NMR of **5b**



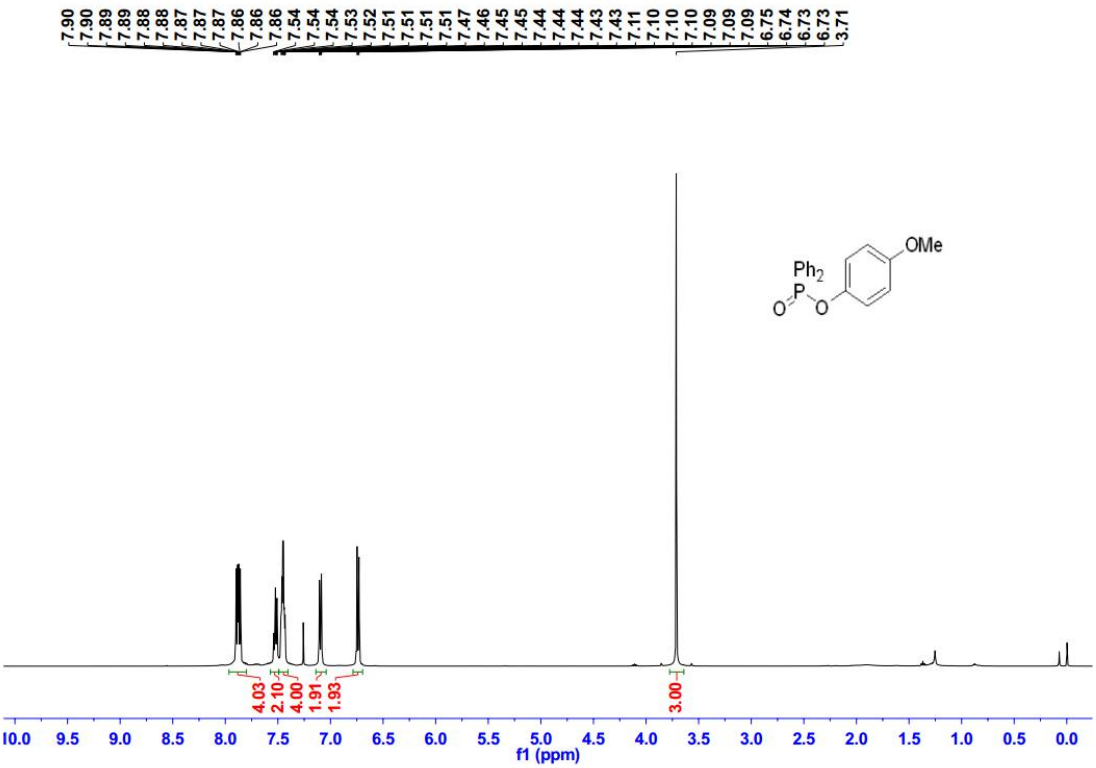
^{1}H NMR of **5c**



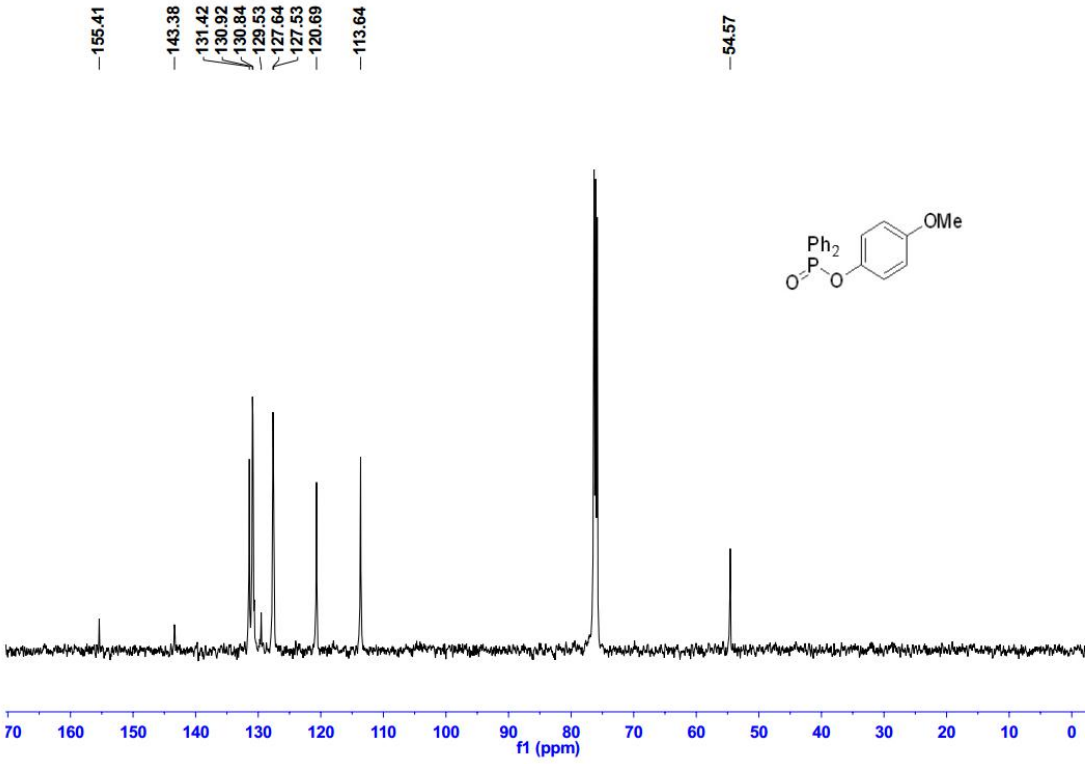
^{13}C NMR of **5c**


31.66
O
P
O
Ph2
N
45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45
f1 (ppm)

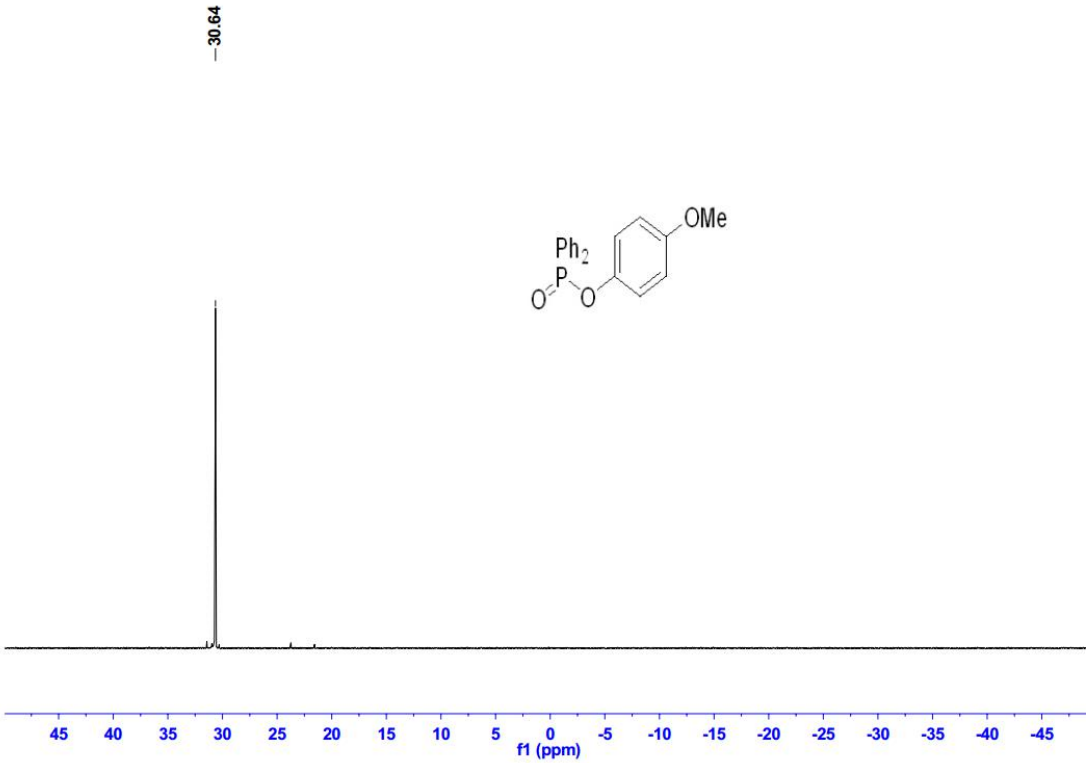
^{31}P NMR of **5c**



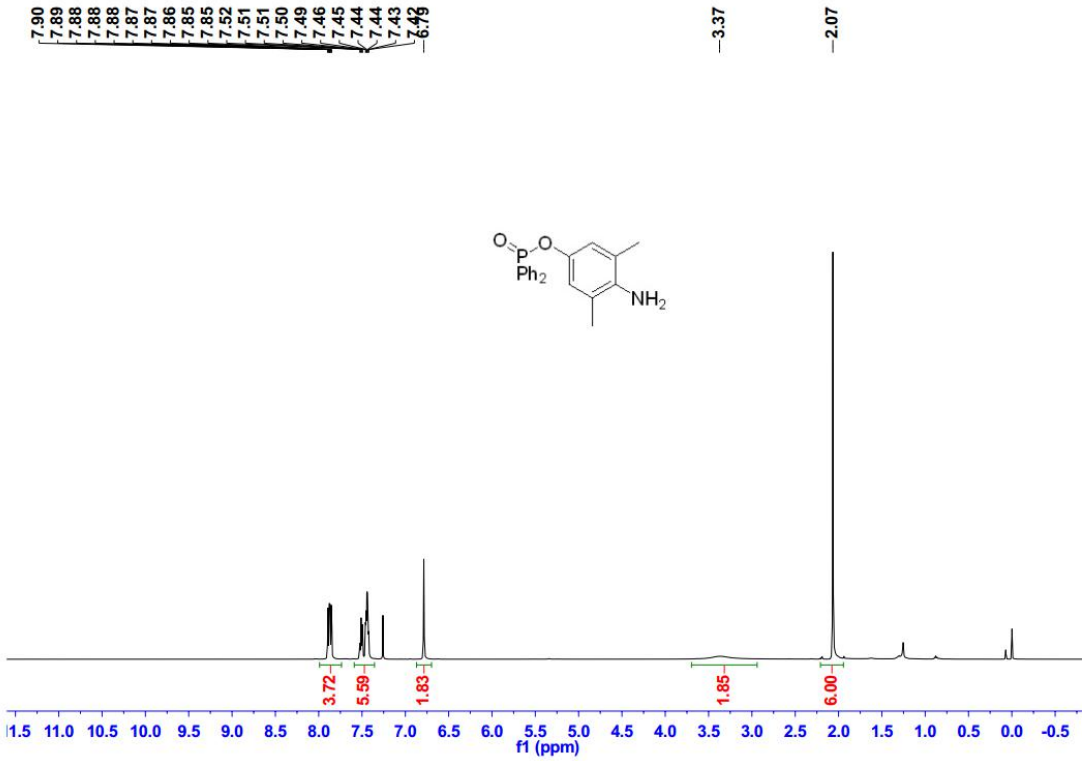
^{1}H NMR of **5d**



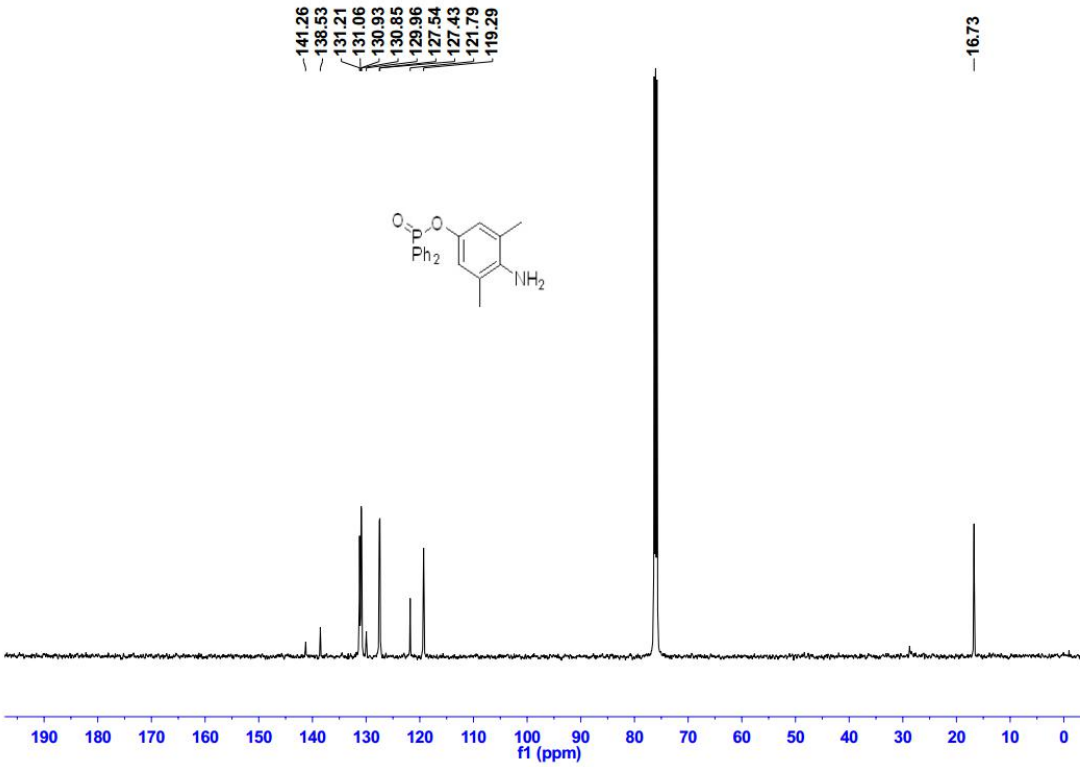
^{13}C NMR of **5d**


30.64
OMe
Ph2
P
O
O
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
f1 (ppm)

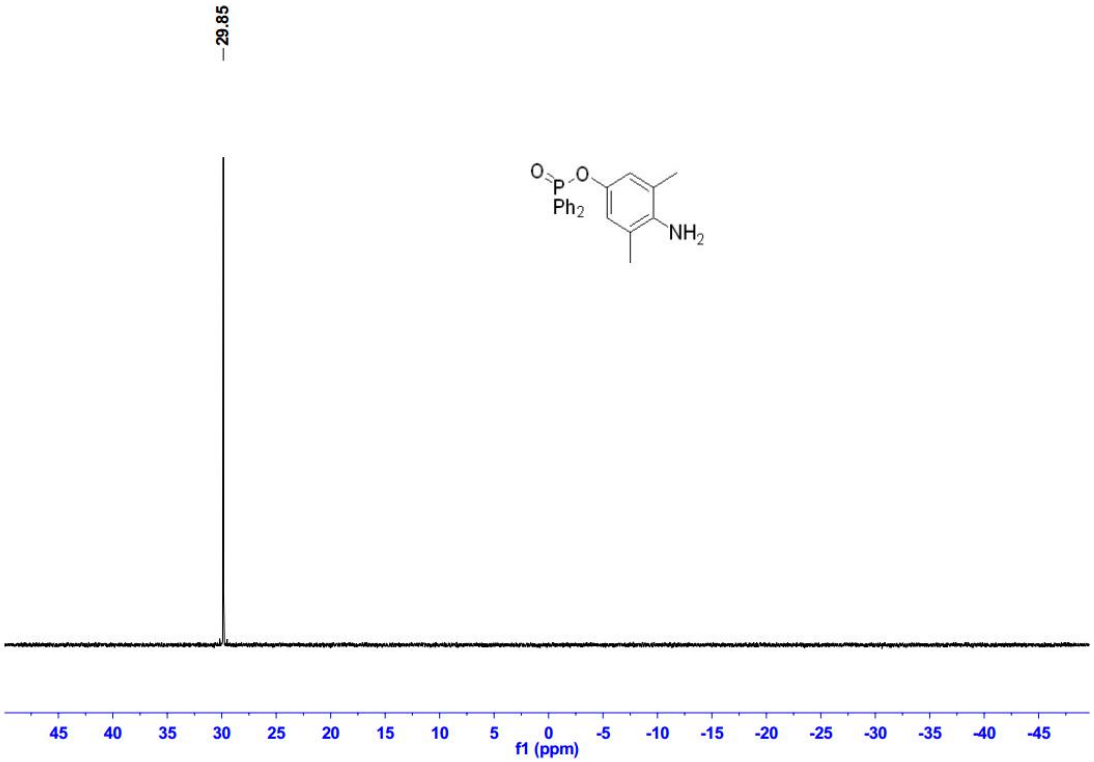
^{31}P NMR of **5d**



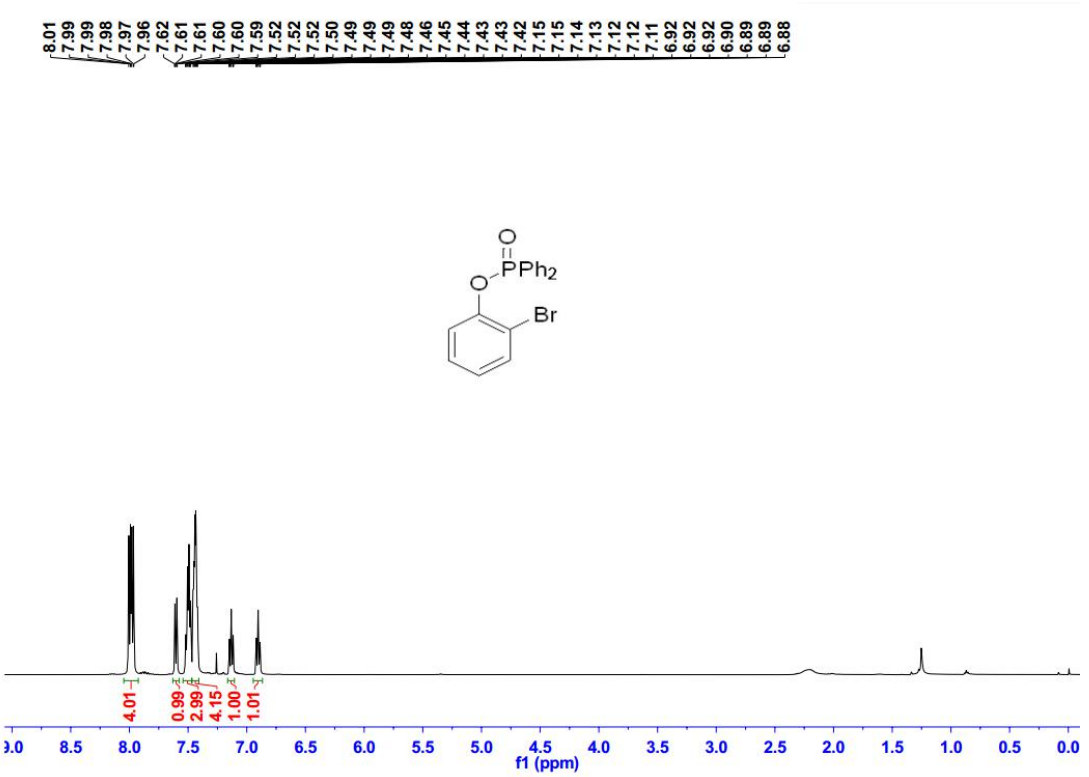
^{1}H NMR of **5e**



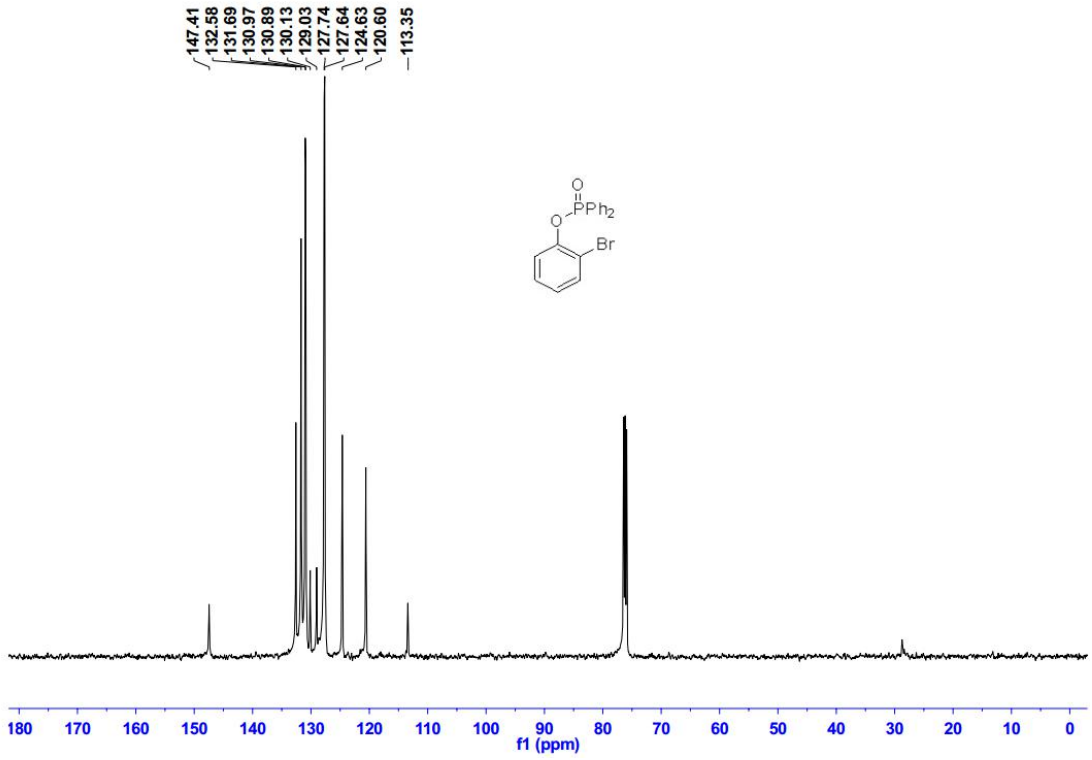
^{13}C NMR of **5e**


29.85
O
P
O
Ph2
NH2
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
f1 (ppm)

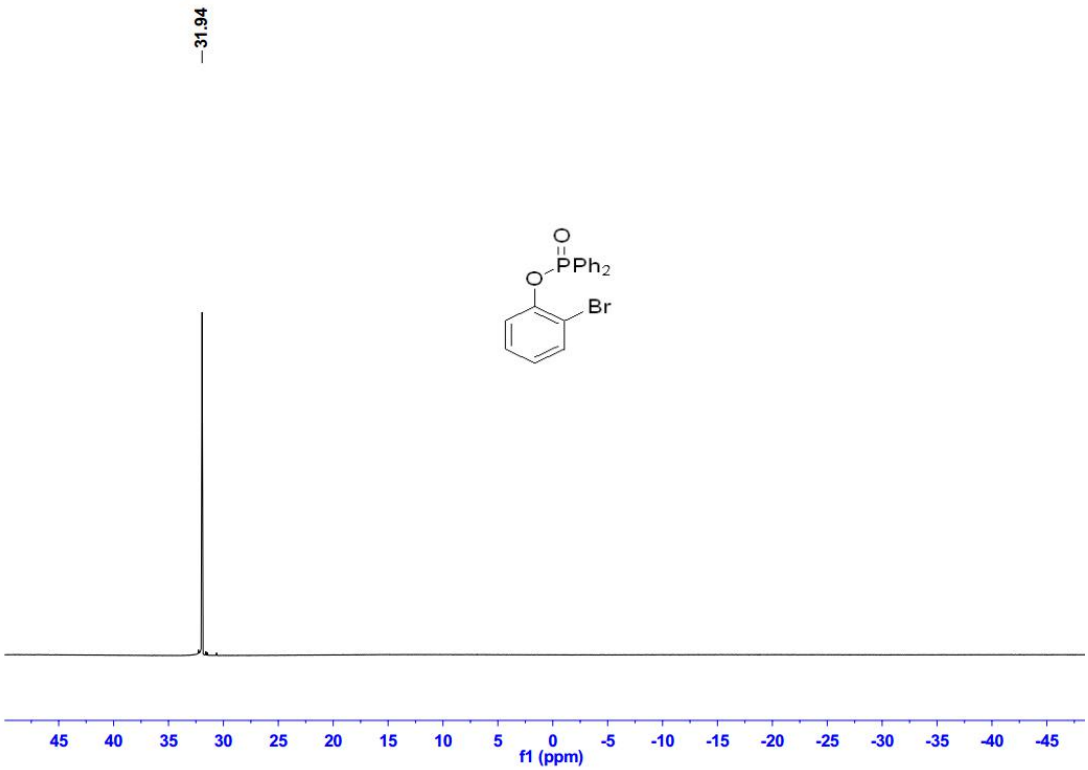
^{31}P NMR of **5e**



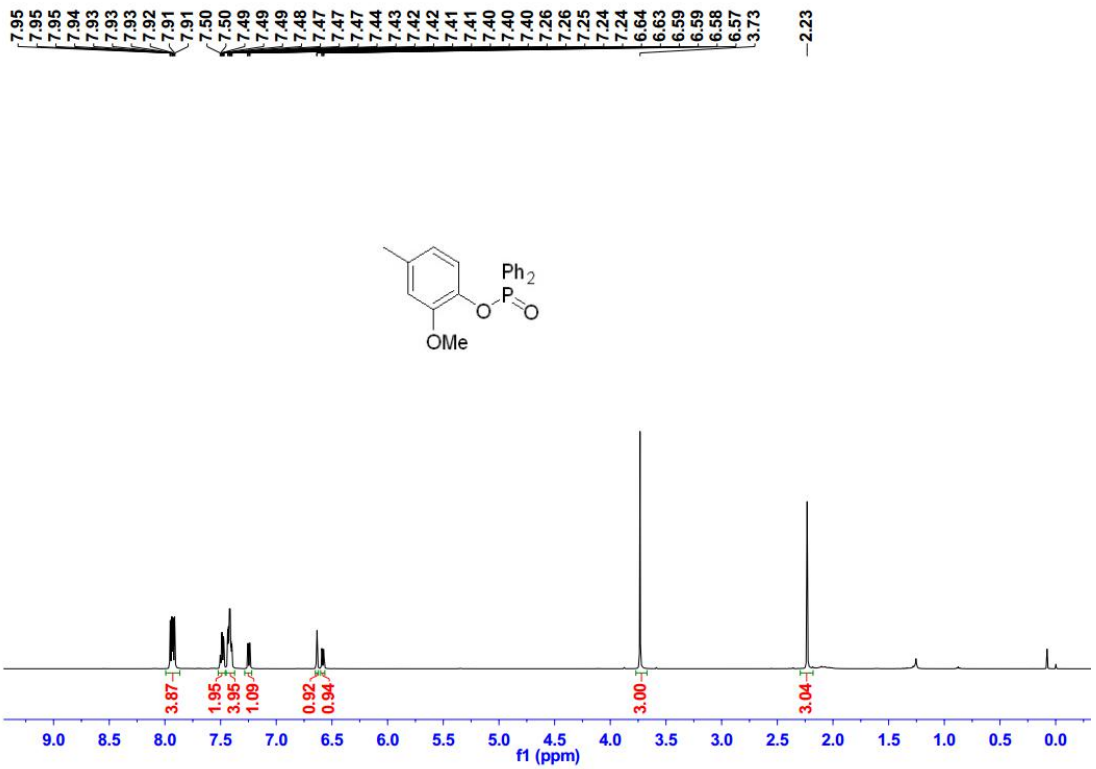
^{1}H NMR of **5f**



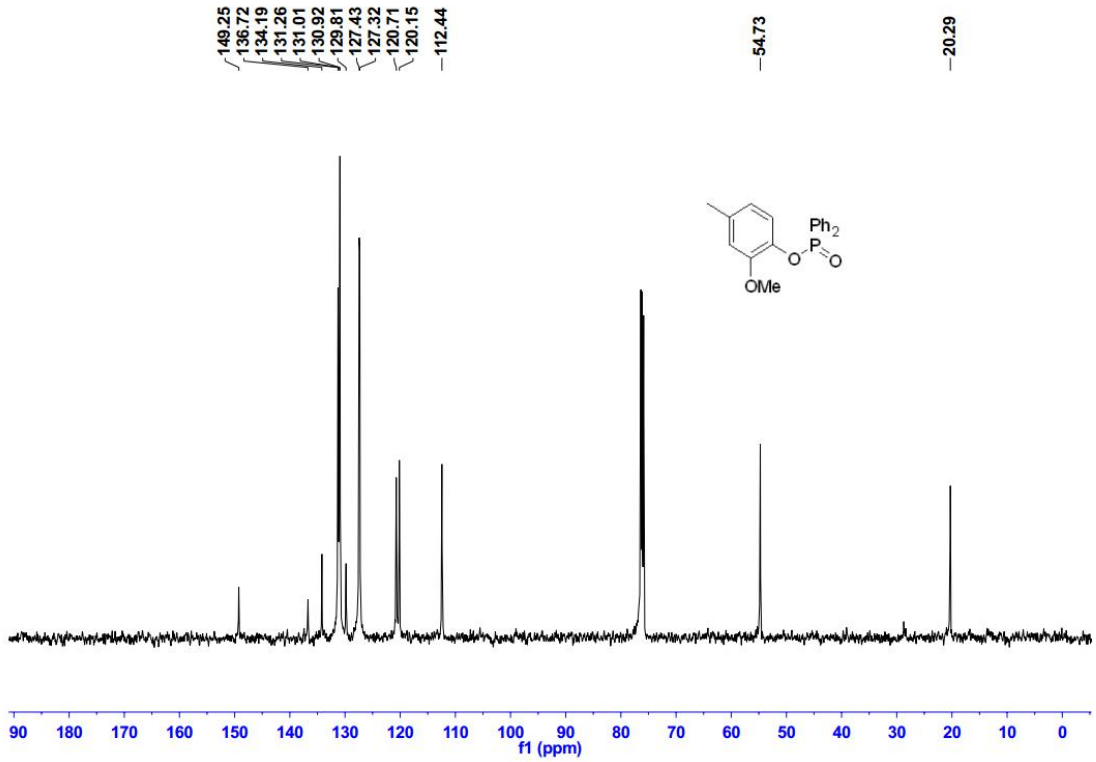
^{13}C NMR of **5f**


31.94
O
PPh2
O
Br
45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45
f1 (ppm)

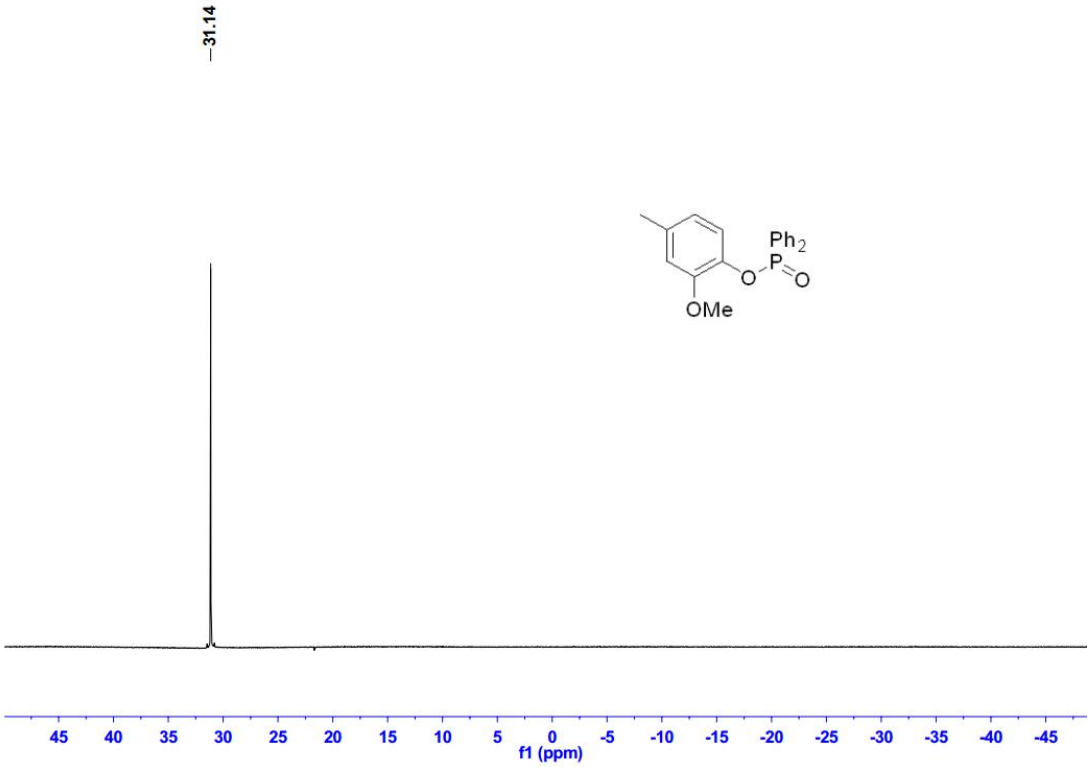
^{31}P NMR of **5f**



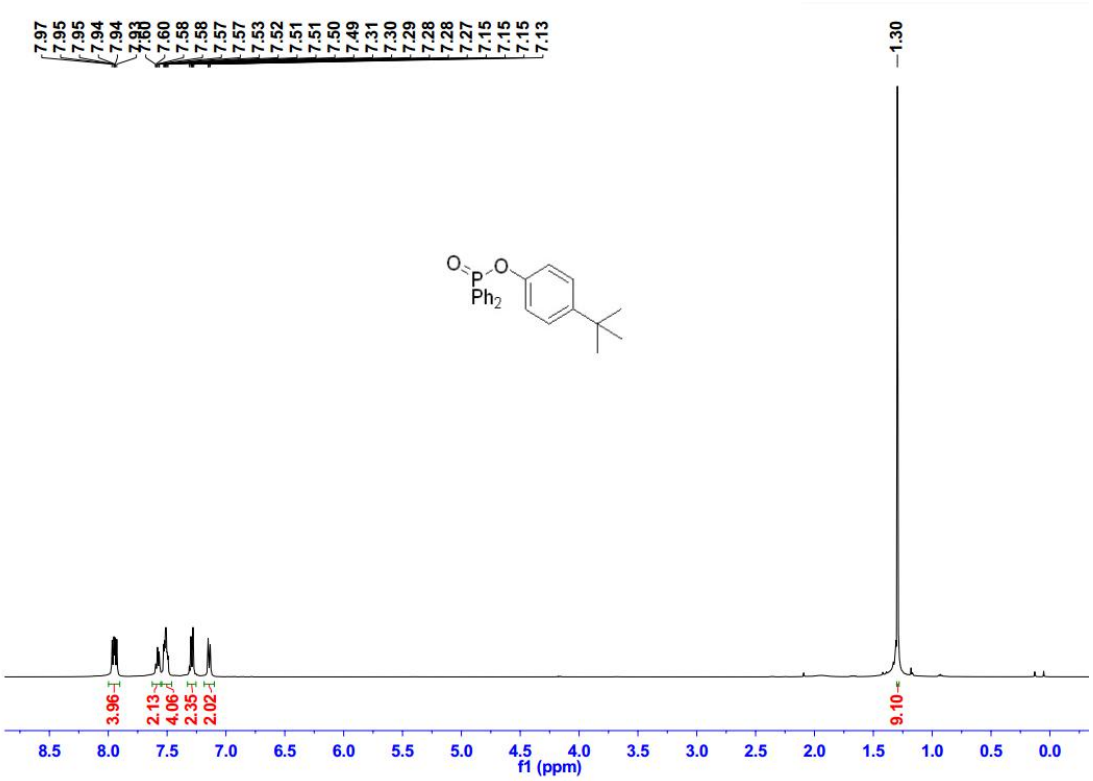
^{1}H NMR of **5g**



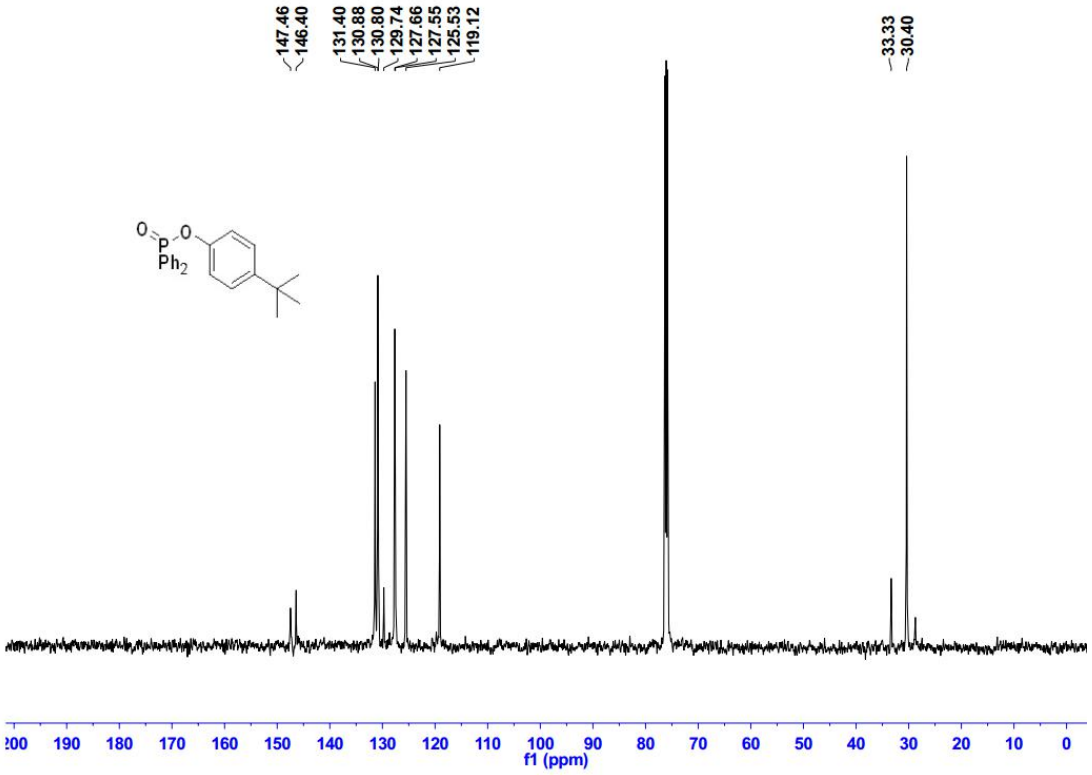
^{13}C NMR of **5g**


31.14
Ph2
P
O
O
OMe
45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45
f1 (ppm)

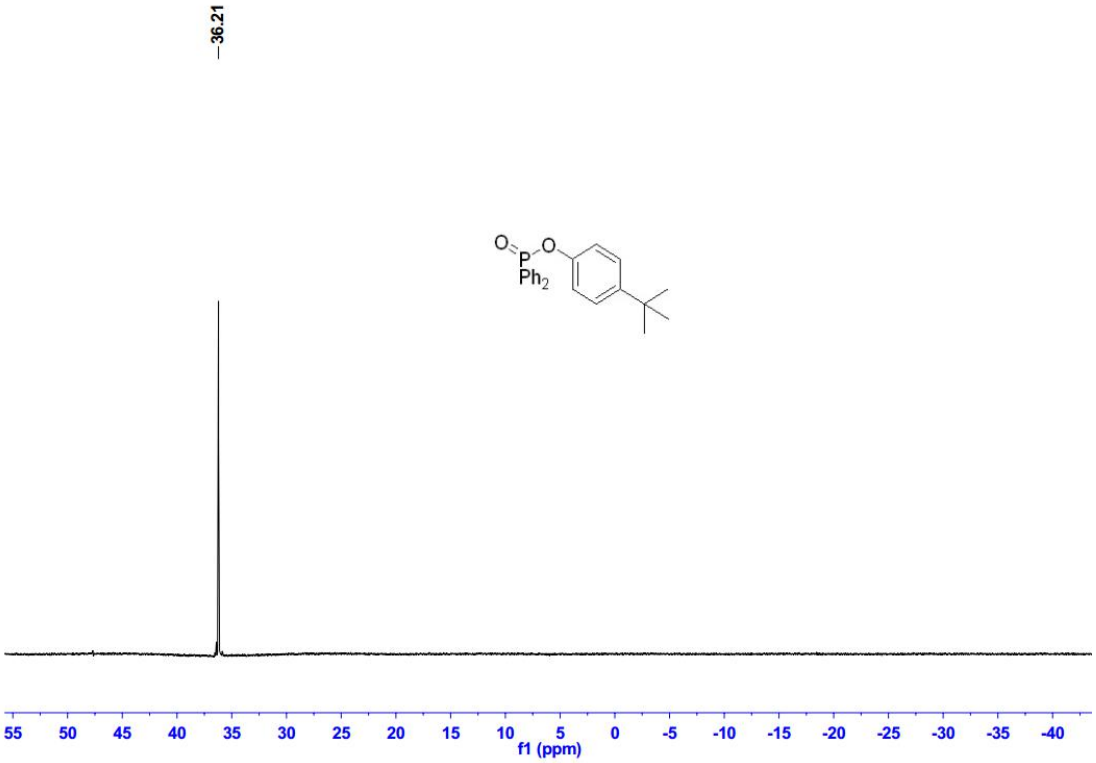
^{31}P NMR of **5g**



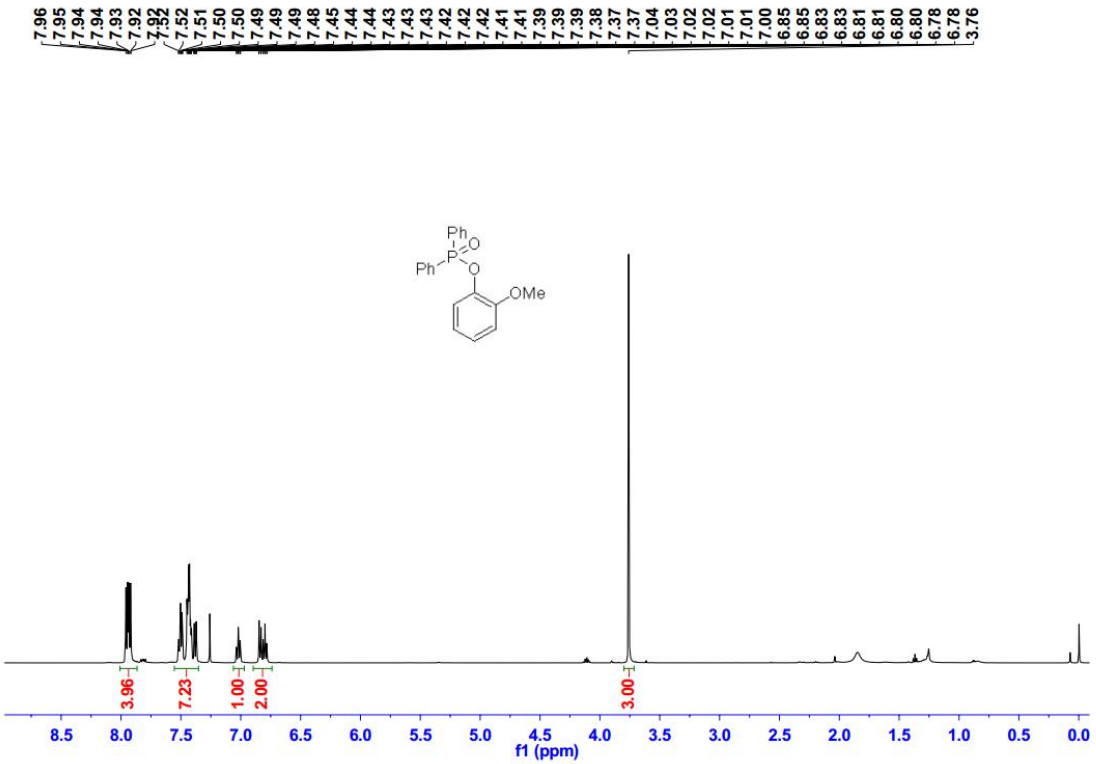
^{1}H NMR of **5h**



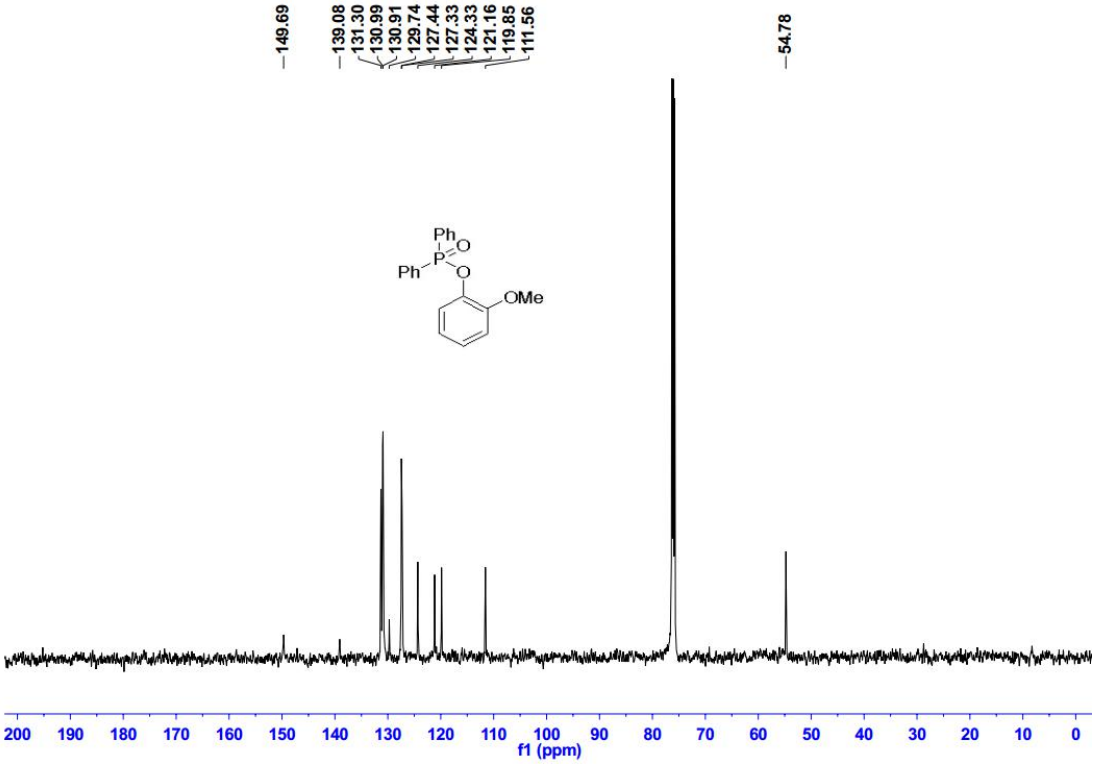
^{13}C NMR of **5h**


36.21
O
P
O
Ph2
55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40
f1 (ppm)

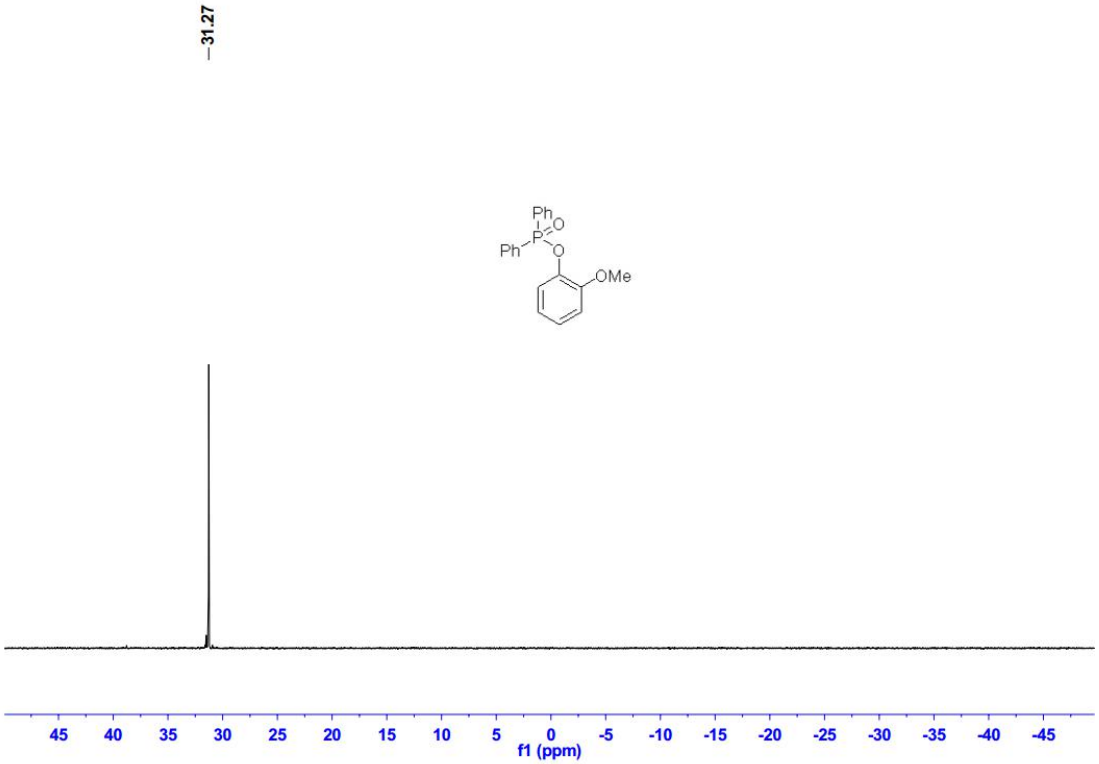
^{31}P NMR of **5h**



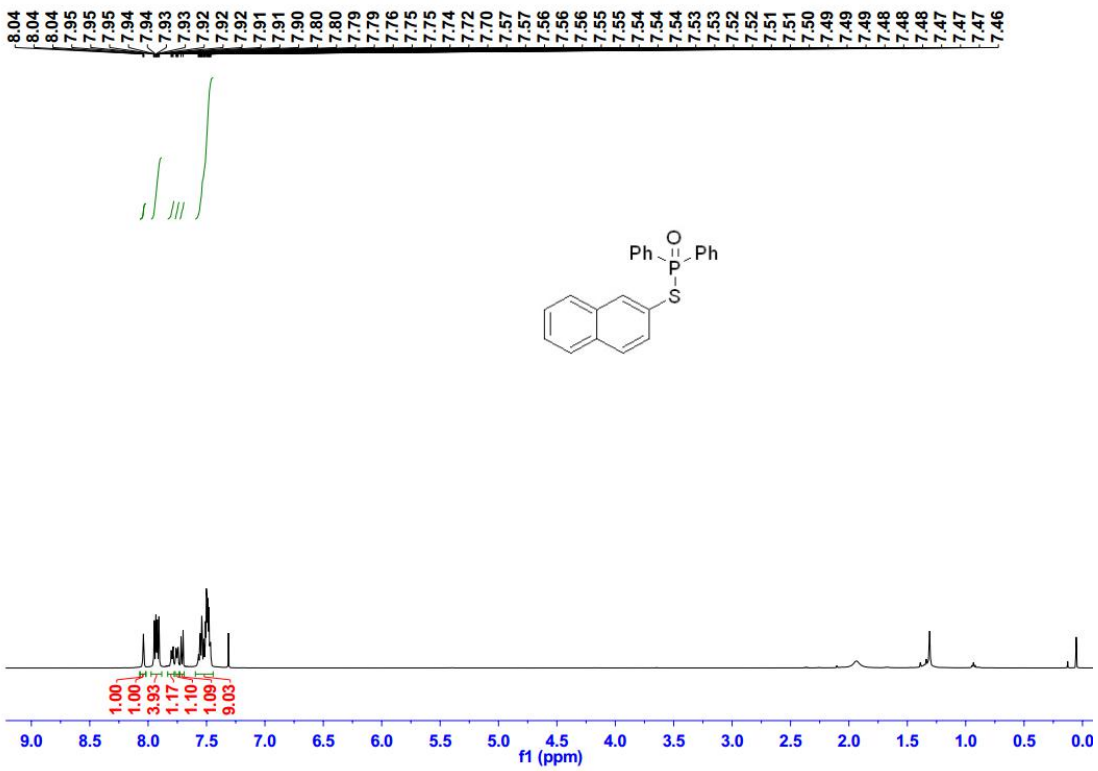
^{1}H NMR of **5i**



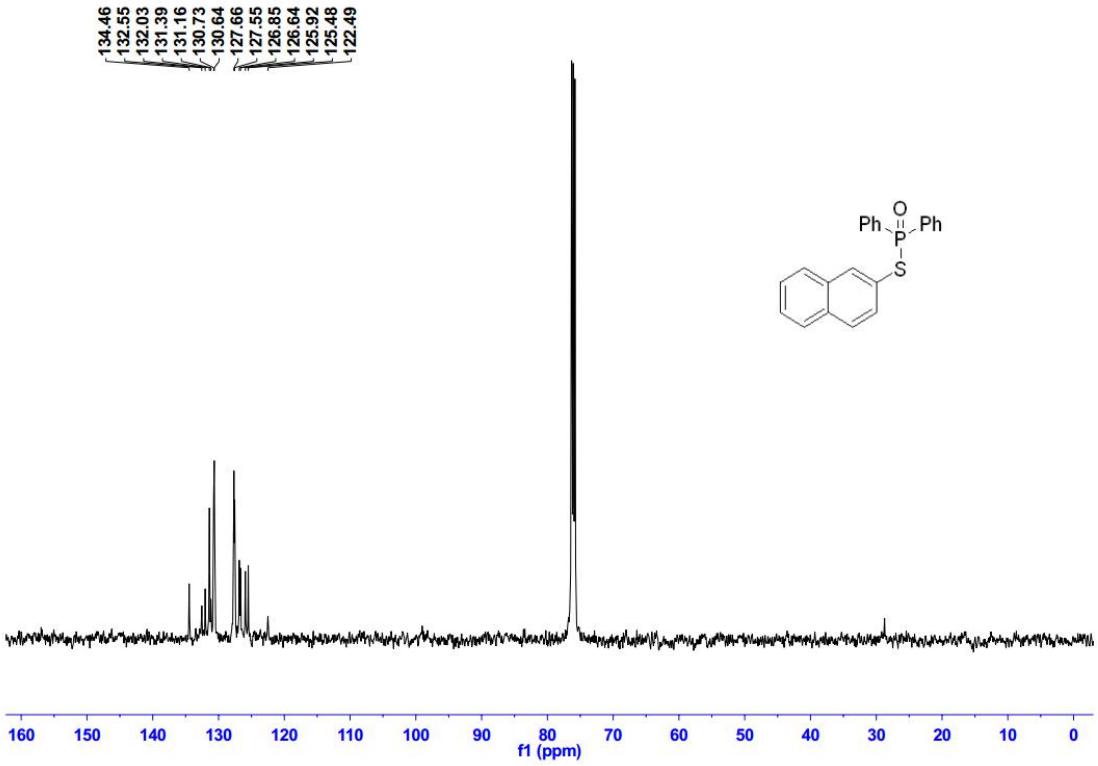
^{13}C NMR of **5i**


31.27
Ph
P
O
Ph
O
OMe
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
f1 (ppm)

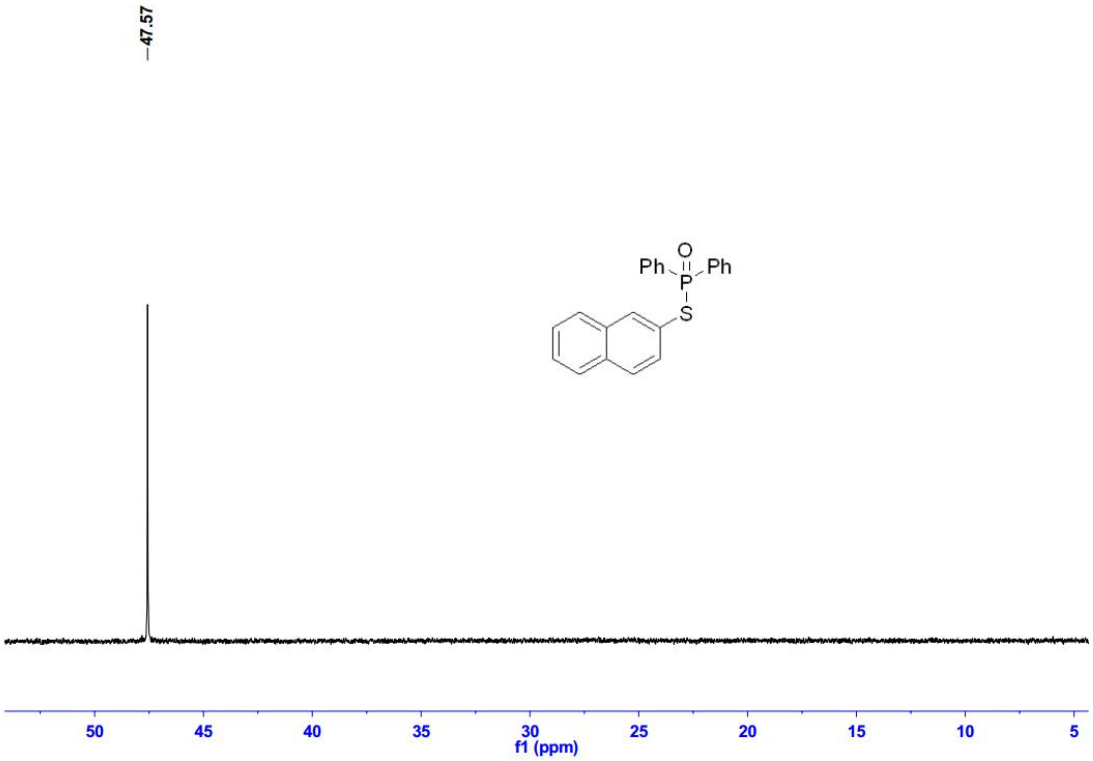
^{31}P NMR of **5i**



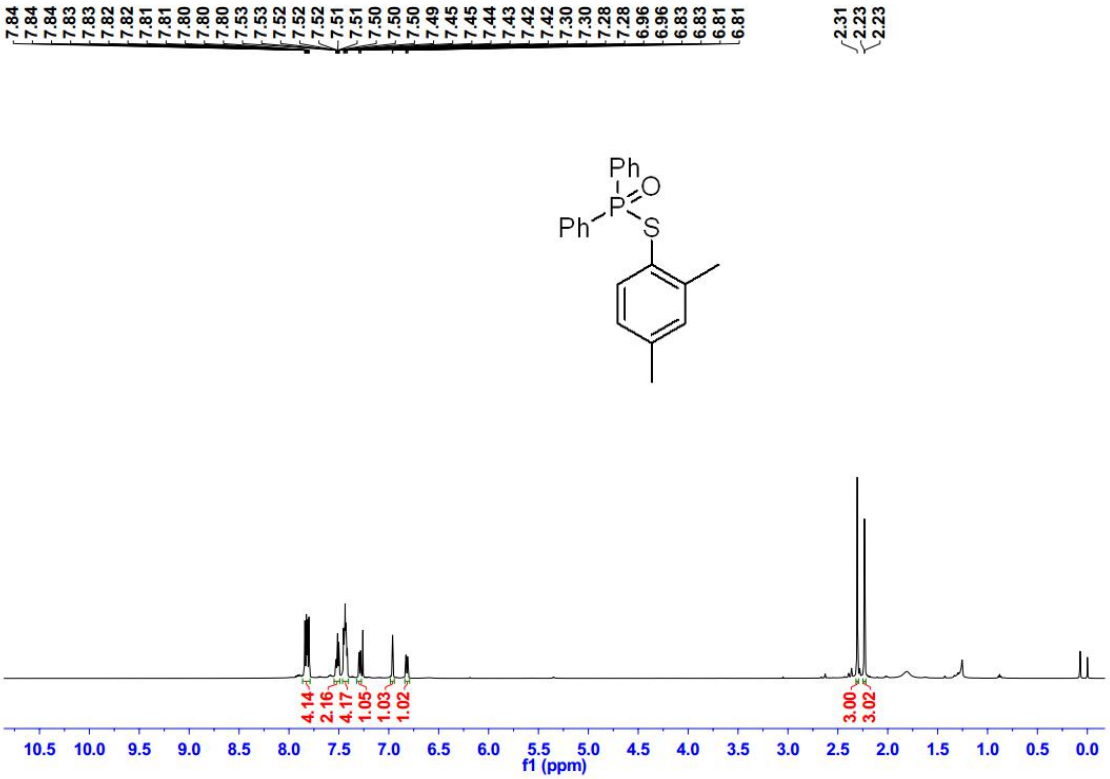
^{1}H NMR of **6a**



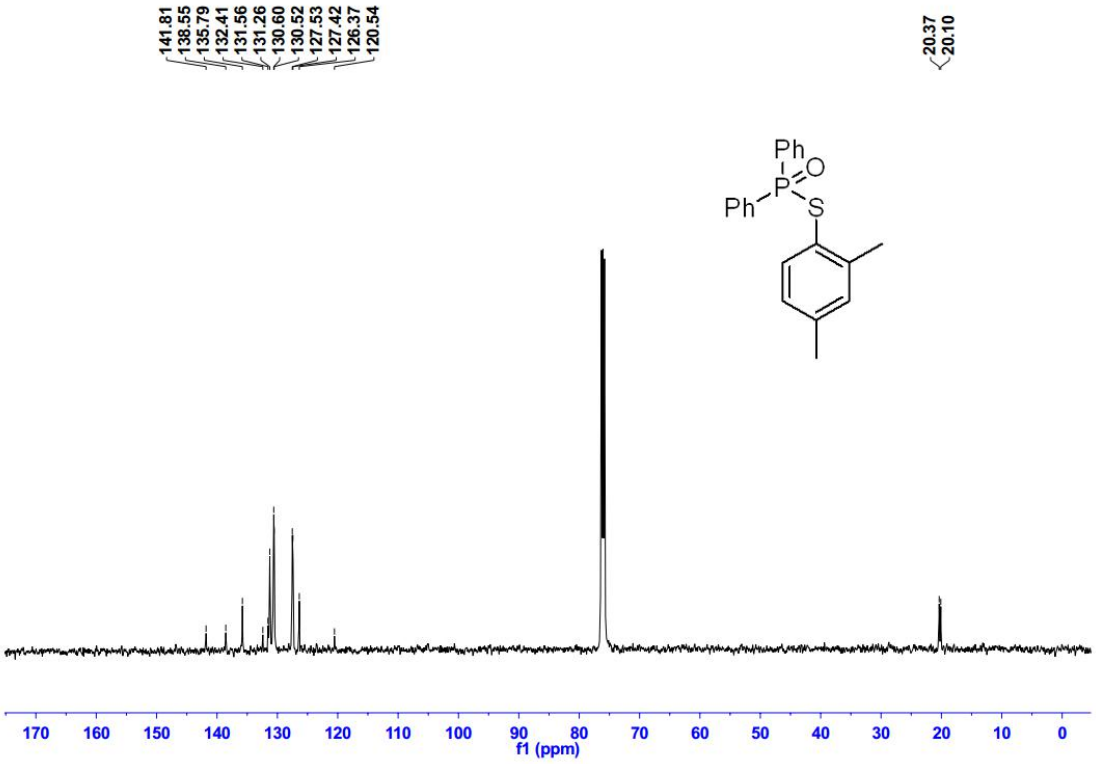
^{13}C NMR of **6a**



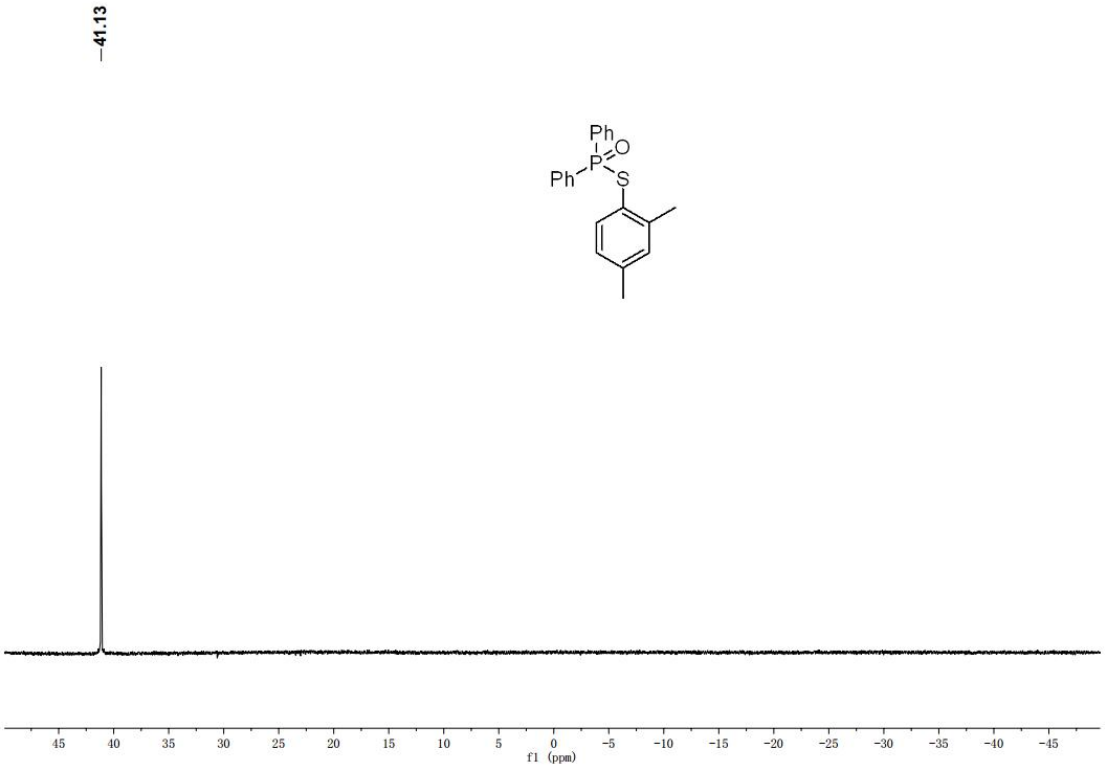
^{31}P NMR of **6a**



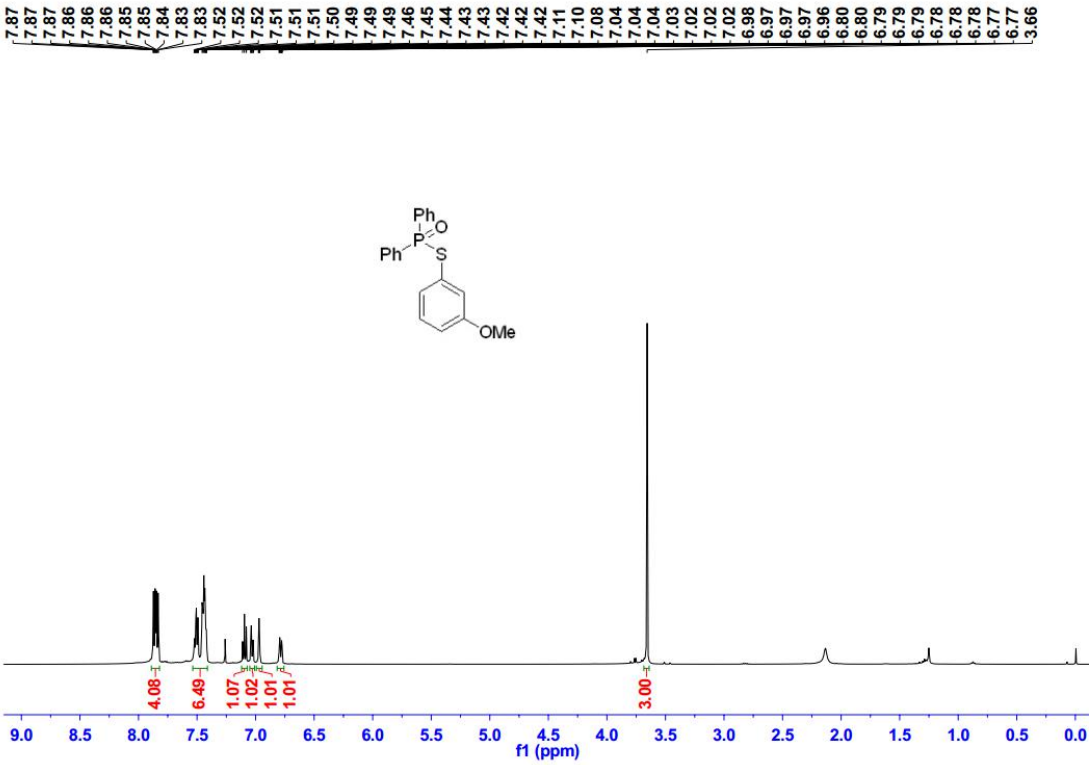
^{1}H NMR of **6b**



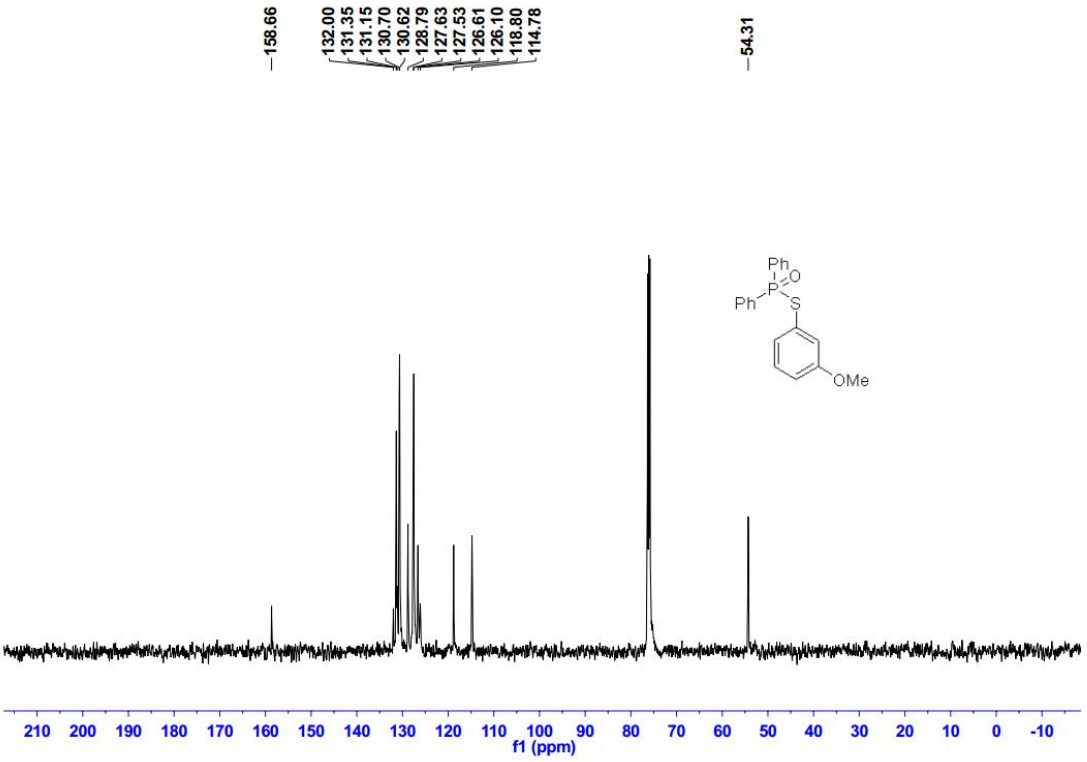
^{13}C NMR of **6b**


41.13
Ph
O
P
Ph
S
45
40
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−40
−45
f1 (ppm)

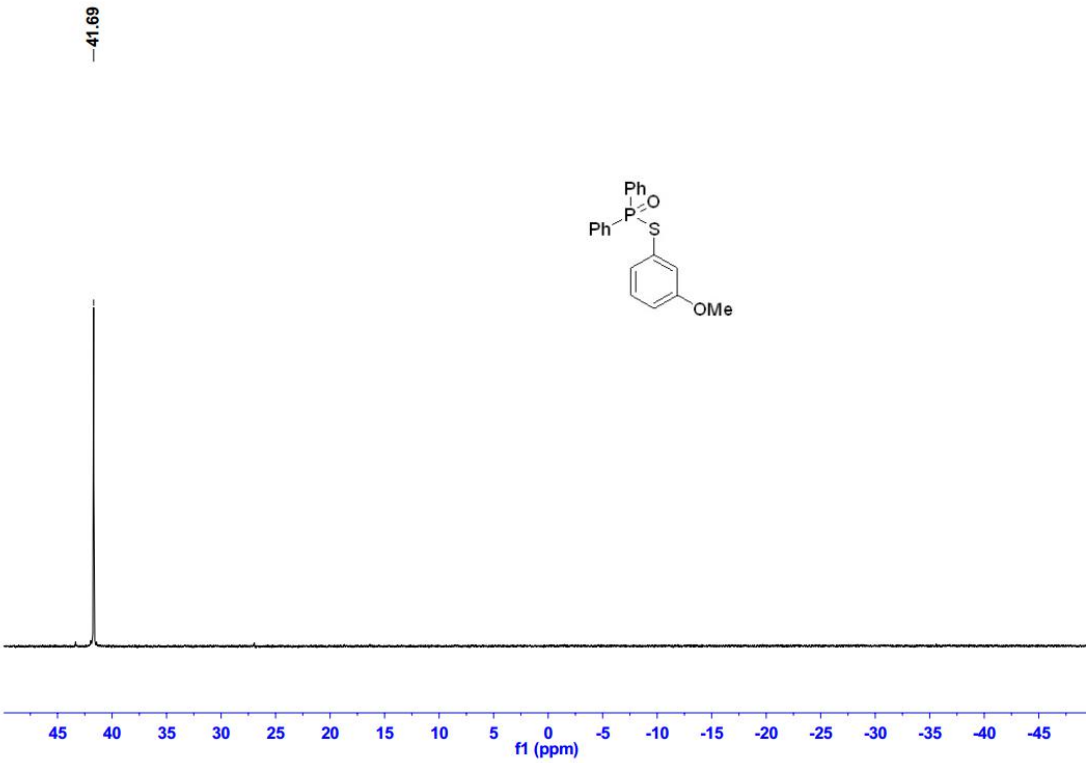
^{31}P NMR of **6b**



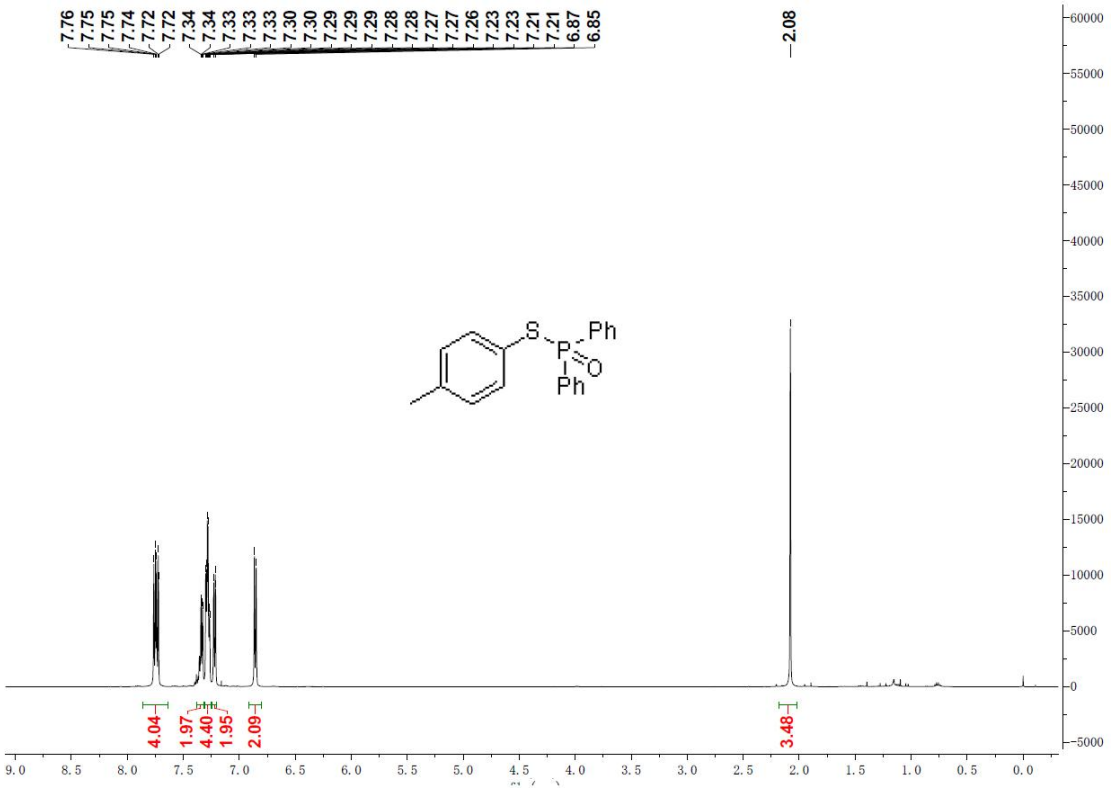
^{1}H NMR of **6c**



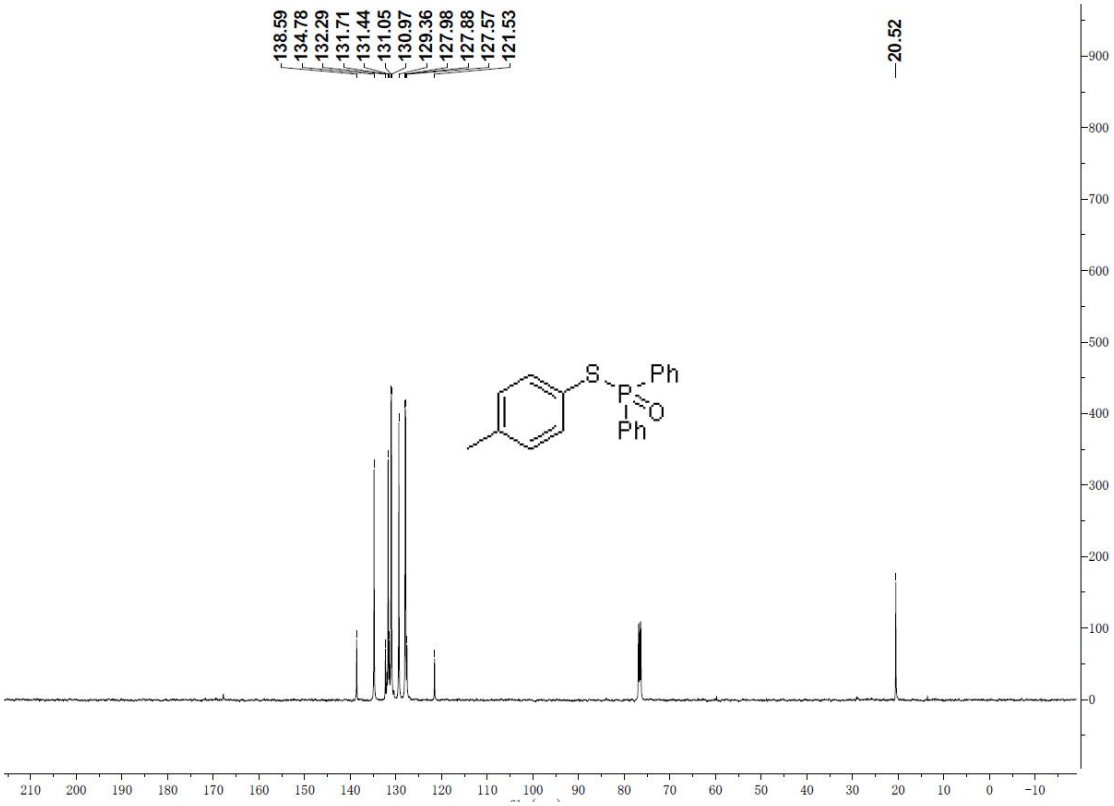
^{13}C NMR of **6c**


41.69
Ph
O
P
Ph
S
OMe
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
f1 (ppm)

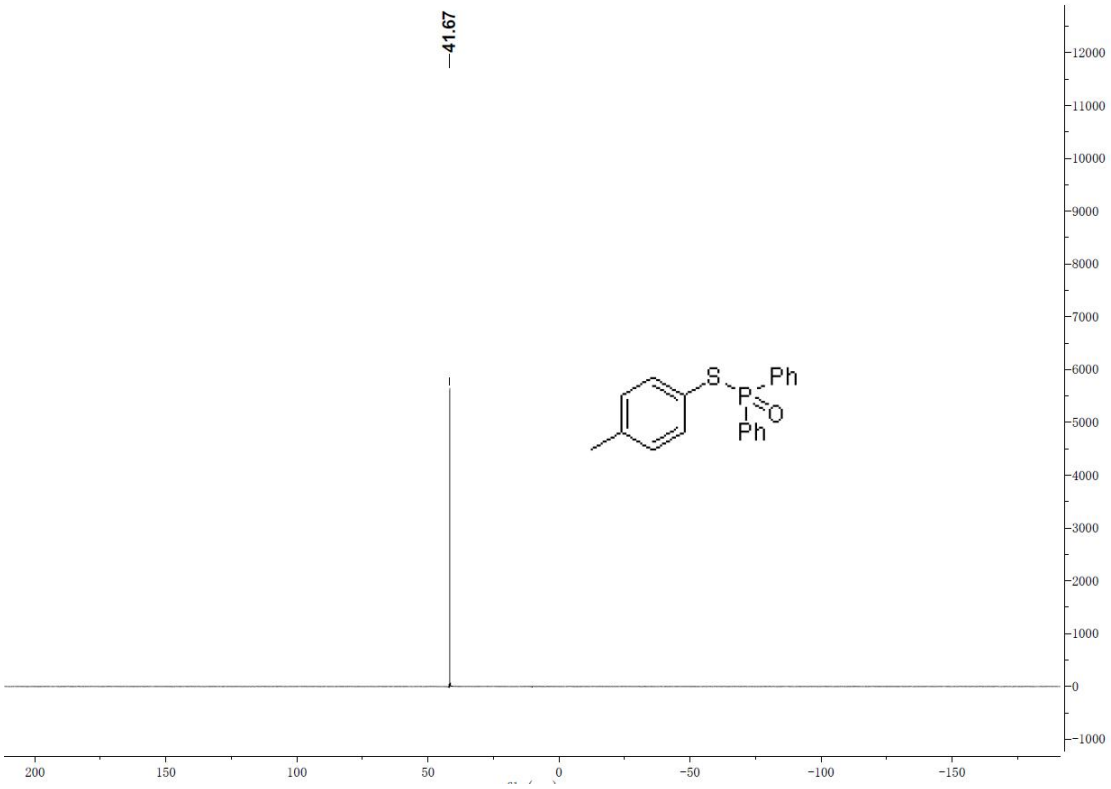
^{31}P NMR of **6c**



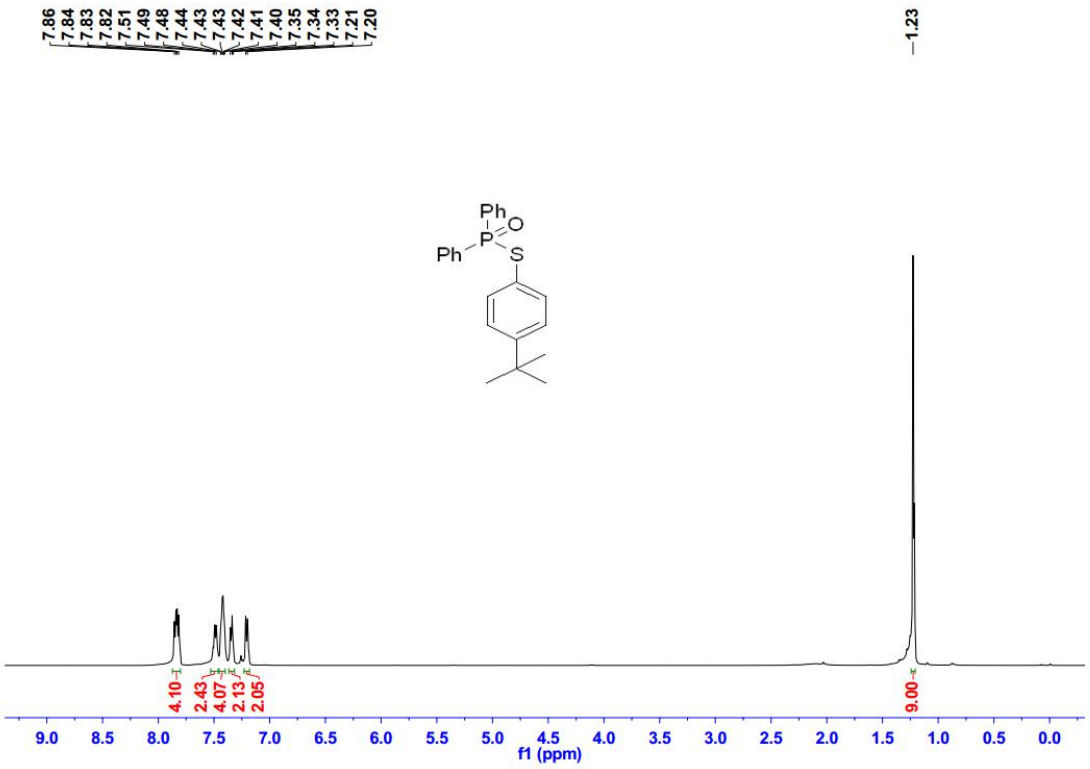
^{1}H NMR of **6d**



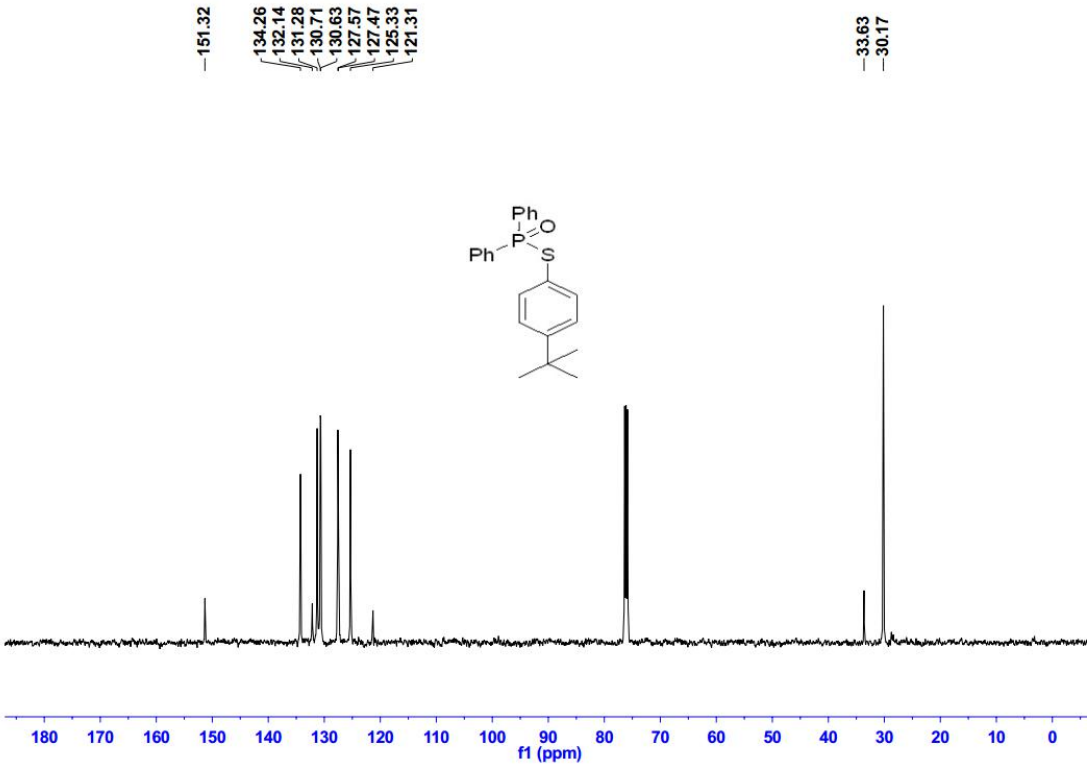
^{13}C NMR of **6d**


41.67
S
Ph
P
O
Ph
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
200
150
100
50
0
−50
−100
−150

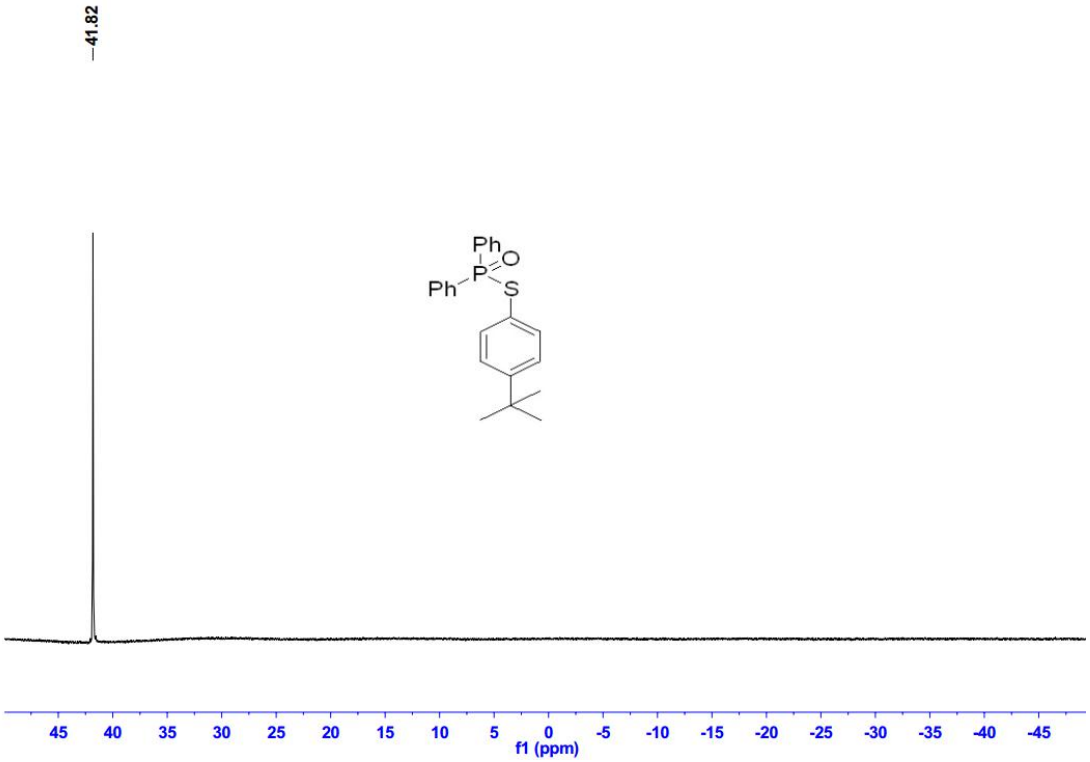
^{31}P NMR of **6d**



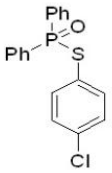
^{1}H NMR of **6e**

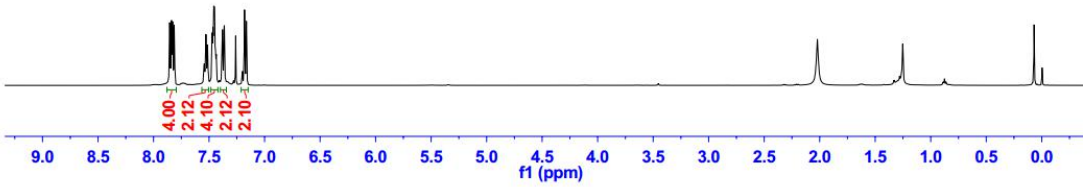


^{13}C NMR of **6e**

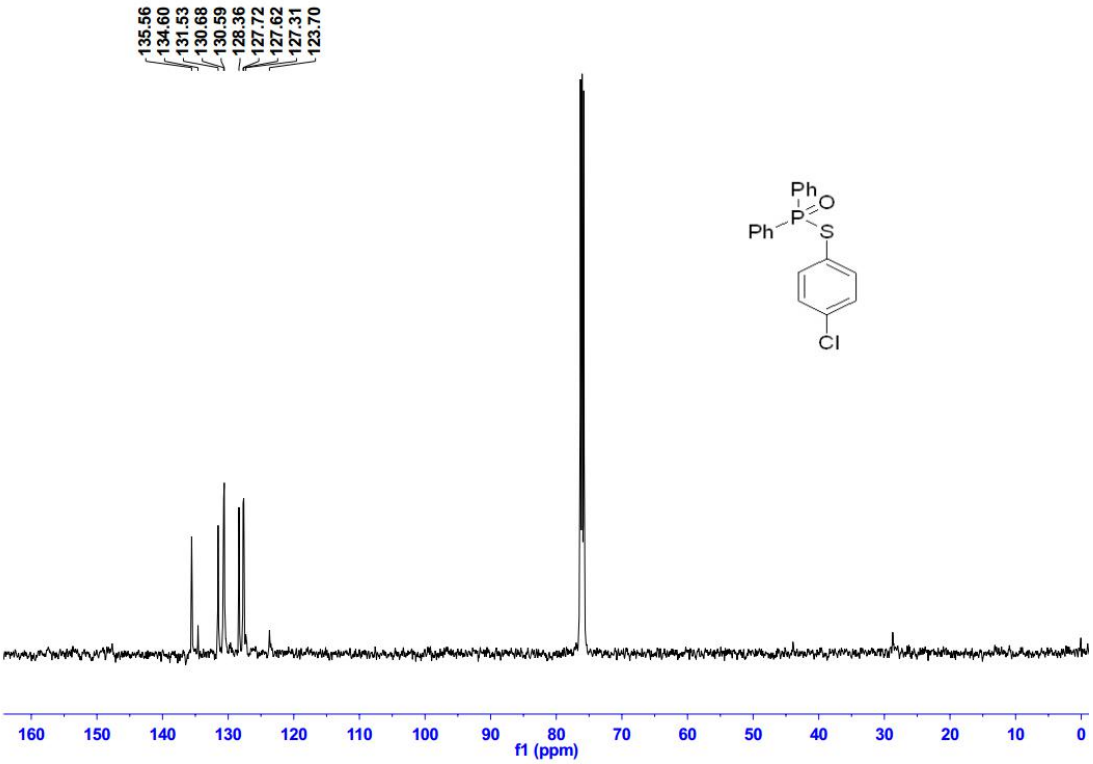

41.82
Ph
O
P
Ph
S
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
f1 (ppm)

^{31}P NMR of **6e**

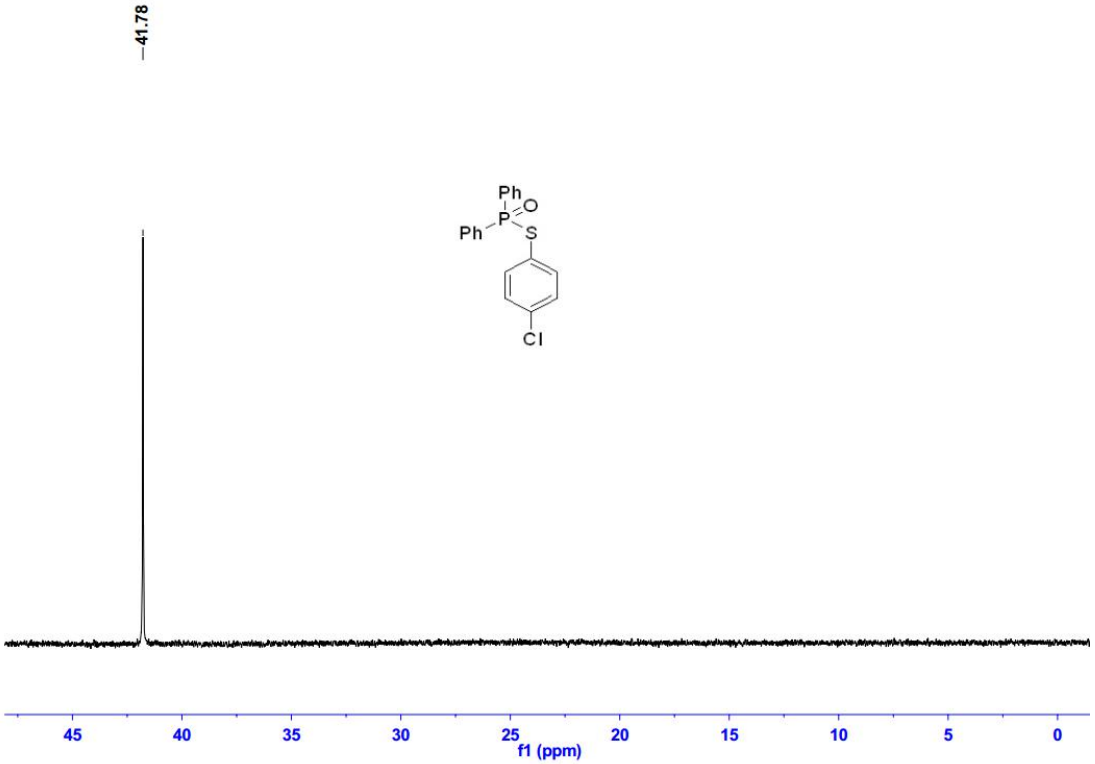




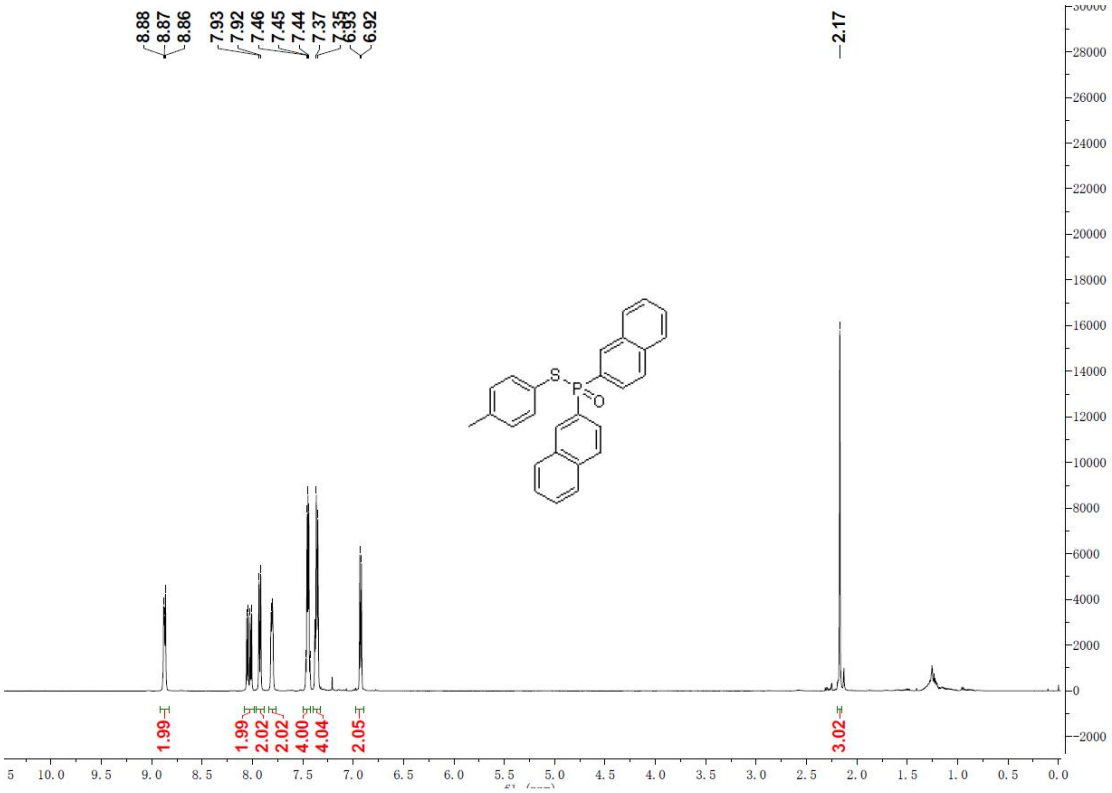
^{1}H NMR of **6f**



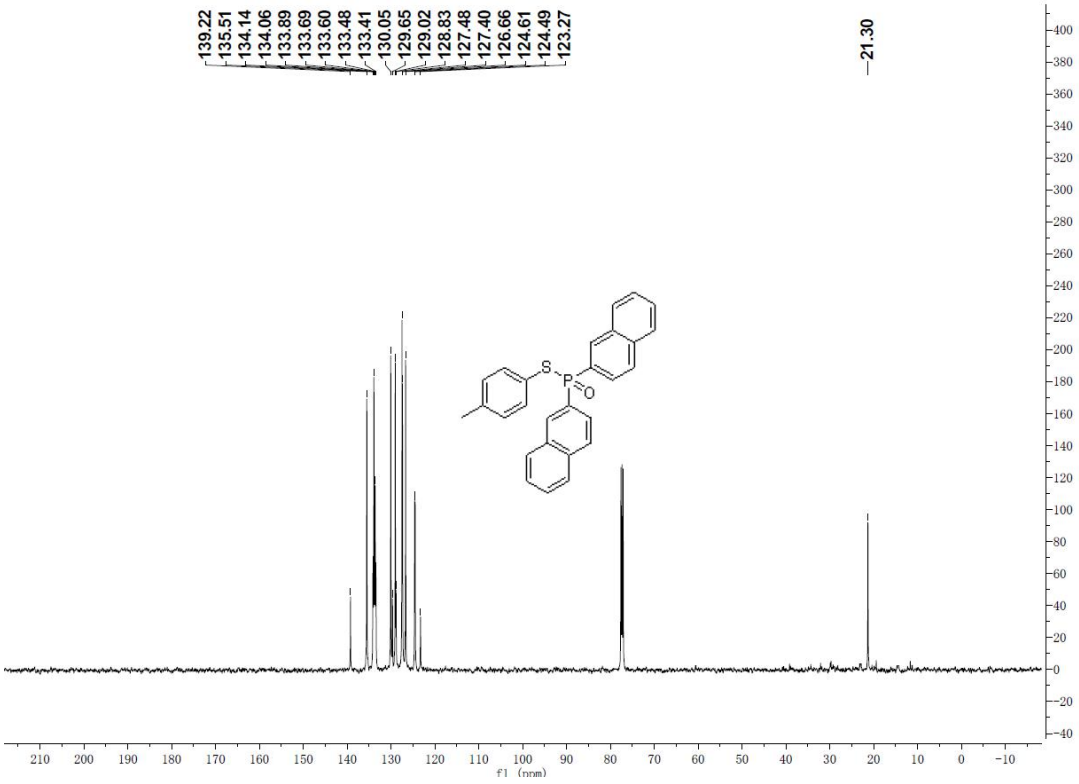
^{13}C NMR of **6f**



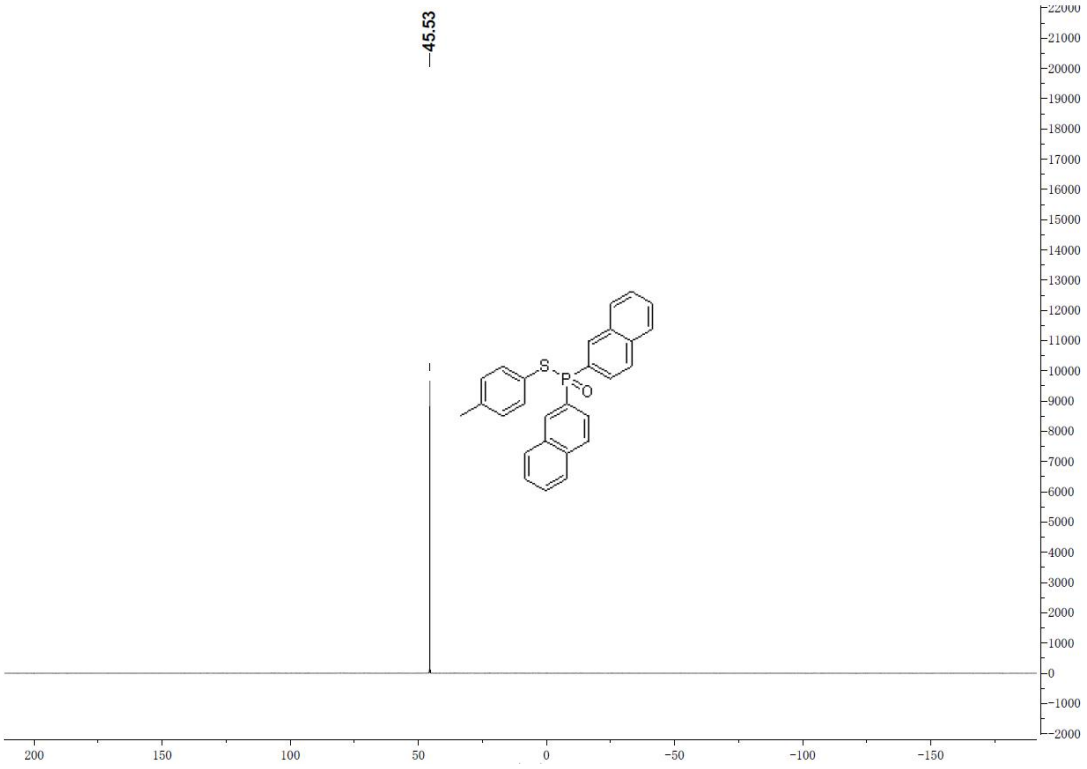
^{31}P NMR of **6f**



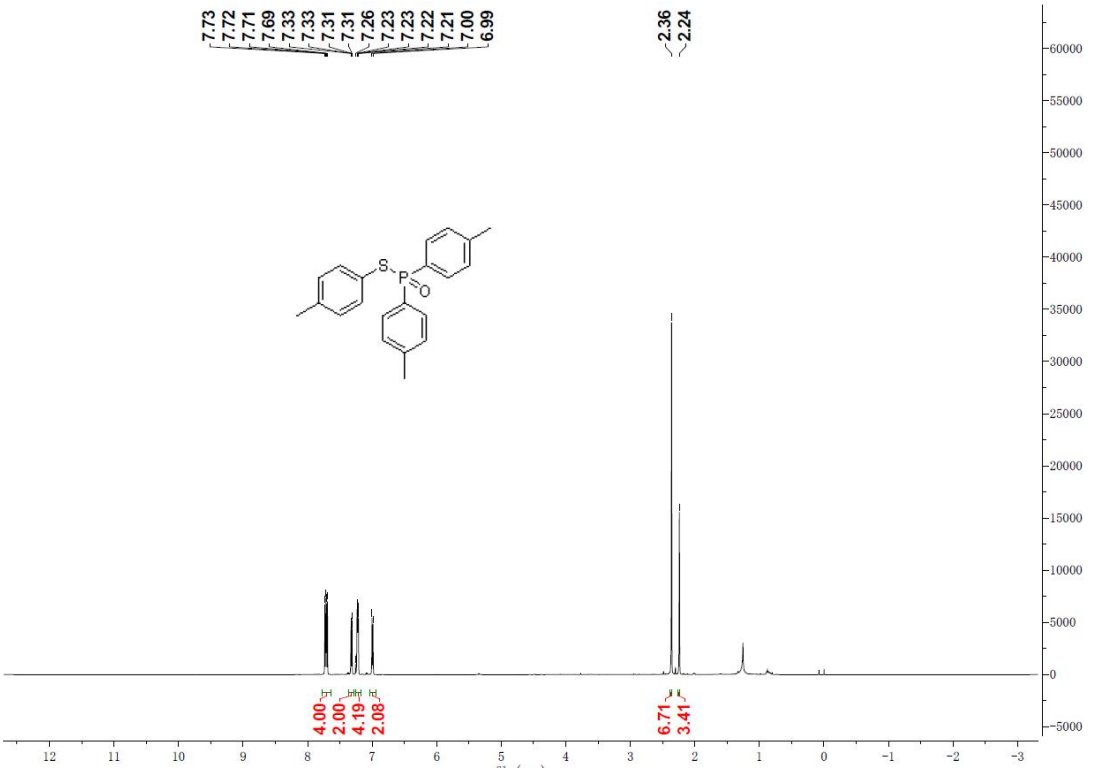
^{1}H NMR of **6g**



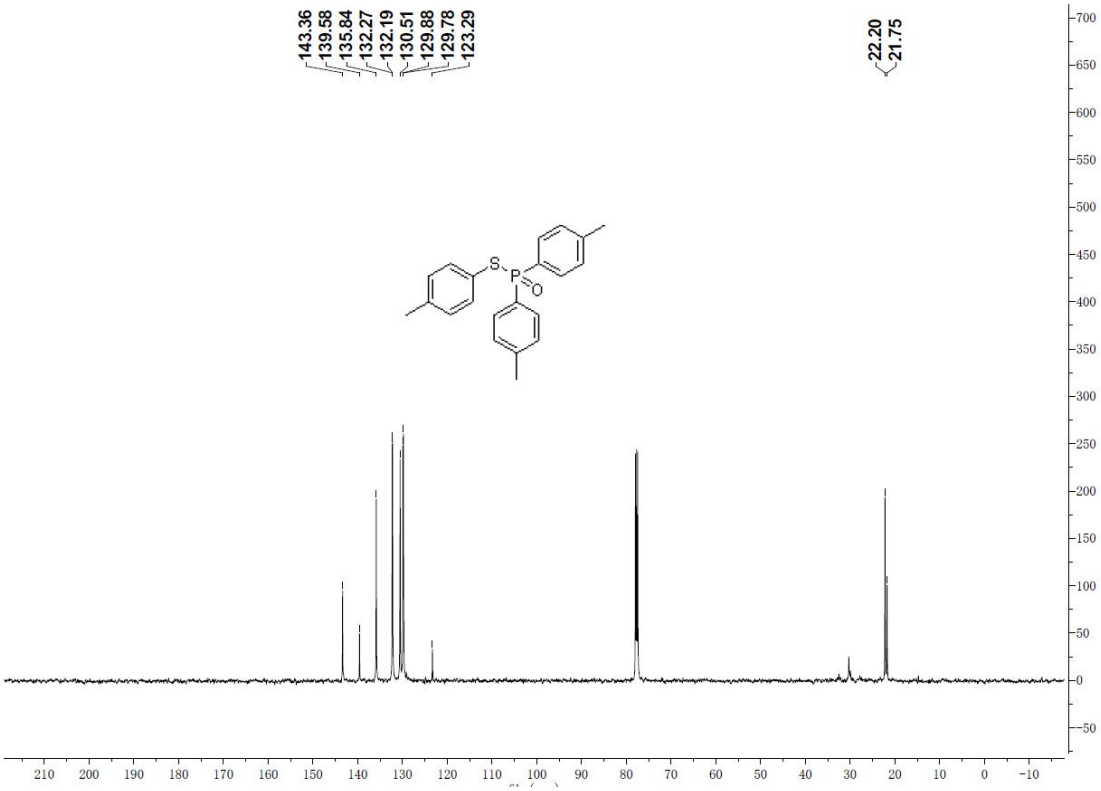
^{13}C NMR of **6g**



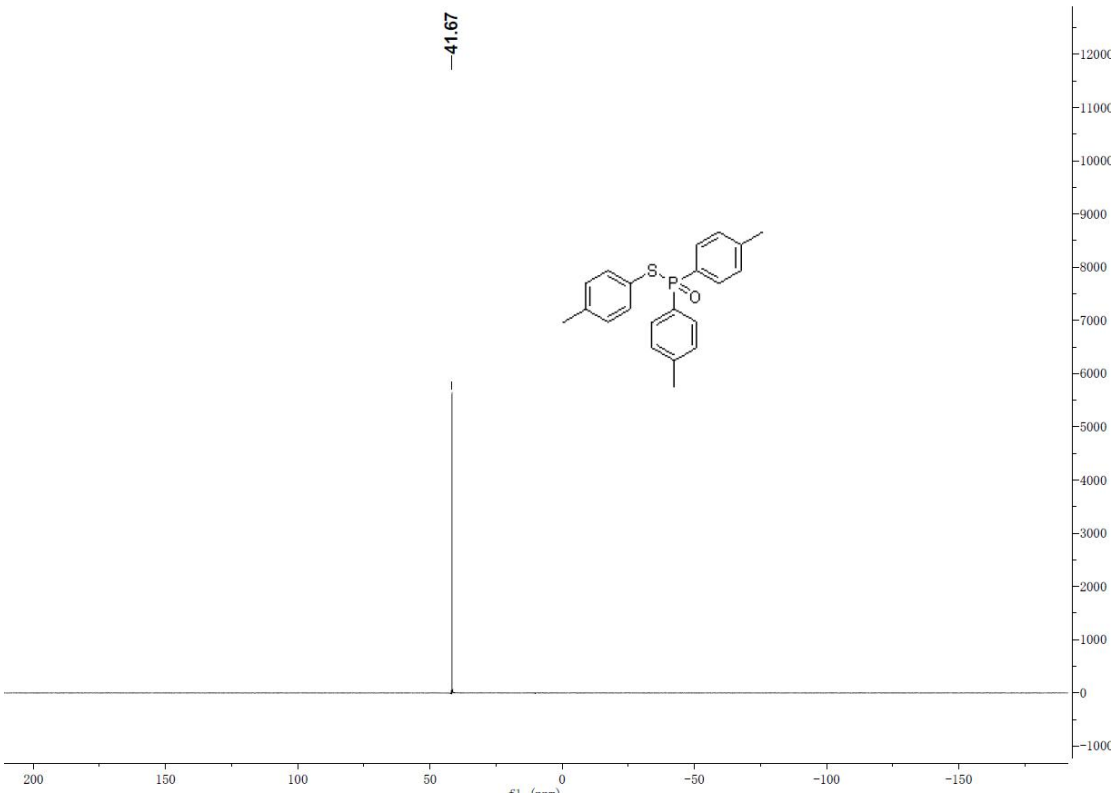
^{31}P NMR of **6g**



^{1}H NMR of **6h**



^{13}C NMR of **6h**



^{31}P NMR of **6h**