

Supporting information for

**Metal- and base-free reductive coupling reaction of P(O)-H with
aryl/alkyl sulfonyl chlorides: a novel protocol for the construction of
P-S-C bonds**

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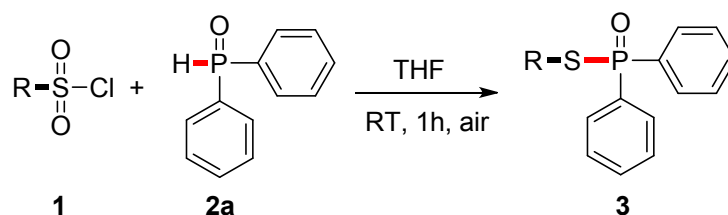
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1. General Information

All chemicals were obtained from commercial suppliers and used directly without further purification. ^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectras were recorded on Bruker AVANCE III (500 MHz) spectrometer with CDCl_3 or $\text{DMSO}-d_6$ as solvents. The chemical shifts δ are reported in ppm relative to tetra-methylsilane. Reference peaks for chloroform in ^1H NMR and ^{13}C NMR spectra were set at 7.26 ppm and 77.0 ppm, and for $\text{DMSO}-d_6$ (^1H NMR: TMS at 0.00 ppm, DMSO at 2.50 ppm; ^{13}C NMR: DMSO at 40.0 ppm). High resolution mass spectras (HRMS) were obtained on Bruker solariX 70 FT-MS apparatus. Melting points were determined on a WRS-1B melting point apparatus and were uncorrected.

2. Experimental Procedure:

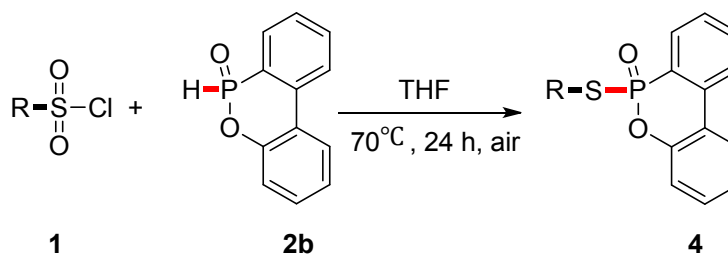
Typical Procedure for Method A



R = aryl, alkyl

Compound **1**, aryl/alkyl sulfonyl chlorides (0.5 mmol) and **2a**, diphenylphosphine oxide (1.5 mmol) were added to a glass tube, and then 1.5 mL of THF was added. The reaction mixture was stirred at room temperature for 1 h. After completion of the reaction, the mixture was concentrated under reduced pressure, and the residue was purified by flash column chromatography using petroleum ether/ethyl acetate as the eluent to give the pure product **3**.

Typical Procedure for Method B

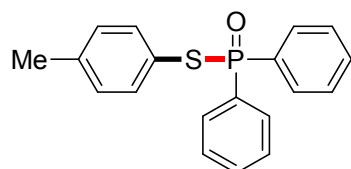


R = aryl, alkyl

Compound **1**, aryl/alkyl sulfonyl chlorides (0.5 mmol) and **2a**, 6H-dibenzo[c, e][1, 2]oxophosphinine 6-oxide (1.5 mmol) were added to a glass tube, and then 1.5 mL of THF was added. The reaction mixture was stirred at 70 °C for 24 h. After completion of

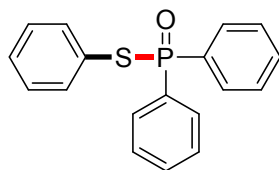
the reaction, the mixture was concentrated under reduced pressure, and the residue was purified by flash column chromatography using petroleum ether/ethyl acetate as the eluent to give the corresponding product **4**.

3. Characterization of products



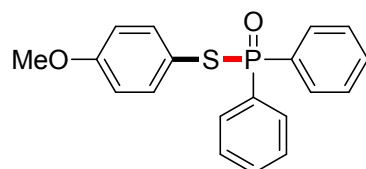
S-p-tolyl diphenylphosphinothioate

3a¹: White solid, m.p. 113.8-115.1 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.87-7.83 (m, 4H), 7.52-7.49 (m, 2H), 7.45-7.42 (m, 4H), 7.32 (d, *J* = 7.3 Hz, 2H), 7.00 (d, *J* = 7.9 Hz, 2H), 2.25 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 139.1 (d, *J* = 2.5 Hz), 135.3 (d, *J* = 3.8 Hz), 132.6 (d, *J* = 106.4 Hz), 132.2, 131.6 (d, *J* = 10.2 Hz), 129.9, 128.4 (d, *J* = 13.1 Hz), 122.2 (d, *J* = 5.0 Hz), 21.1; ³¹P NMR (202 MHz, CDCl₃): δ 41.28; HRMS: *m/z* [M+H]⁺ calcd for C₁₉H₁₈OPS⁺: 325.0810, found: 325.0811.



S-phenyl diphenylphosphinothioate

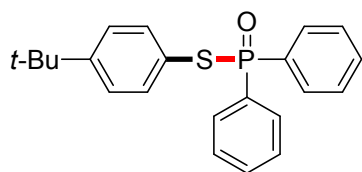
3b²: White solid, m.p. 86.6-87.5 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.88-7.82 (m, 4H), 7.48-7.38 (m, 8H), 7.22-7.15 (m, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 135.2 (d, *J* = 3.7 Hz), 132.4 (d, *J* = 106.3 Hz), 132.1 (d, *J* = 3.1 Hz), 131.4 (d, *J* = 10.1 Hz), 128.9, 128.7, 128.3 (d, *J* = 13.2 Hz), 126.0 (d, *J* = 4.6 Hz); ³¹P NMR (202 MHz, CDCl₃): δ 40.16; HRMS: *m/z* [M+H]⁺ calcd for C₁₈H₁₆OPS⁺: 311.0654, found: 311.0652.



S-(4-methoxyphenyl)diphenylphosphinothioate

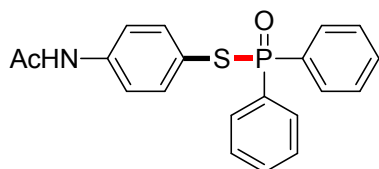
3c¹: White solid, m.p. 142.9-143.8 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.86-7.82 (m, 4H), 7.52-7.49 (m, 2H), 7.45-7.42 (m, 4H), 7.34-7.32 (m, 2H), 6.73 (d, *J* = 8.7 Hz, 2H), 3.72 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 160.4, 137.0 (d, *J* = 3.4 Hz), 132.6 (d, *J* = 107.8 Hz), 132.2 (d, *J* = 2.8 Hz), 131.6 (d, *J* = 10.2 Hz), 128.4 (d, *J* = 13.1 Hz), 116.0

(d, $J = 4.8$ Hz), 114.7 (d, $J = 1.7$ Hz), 55.2; ^{31}P NMR (202 MHz, CDCl_3): δ 41.34; HRMS: m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{18}\text{O}_2\text{PS}^+$: 341.0760, found: 341.0763.



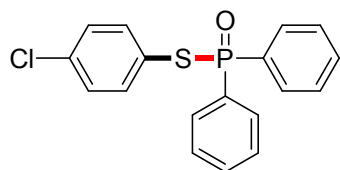
S-(4-(*tert*-butyl)phenyl)diphenylphosphinothioate

3d³: White solid, m.p. 123.4-124.4 °C; ^1H NMR (500 MHz, CDCl_3): δ 7.86-7.82 (m, 4H), 7.48-7.45 (m, 2H), 7.42-7.38 (m, 4H), 7.37-7.35 (m, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 1.22 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3): δ 152.0 (d, $J = 2.4$ Hz), 135.0 (d, $J = 3.5$ Hz), 132.6 (d, $J = 105.7$ Hz), 132.0, 131.4 (d, $J = 10.2$ Hz), 128.3 (d, $J = 13.1$ Hz), 126.1, 122.2, 34.4, 31.0; ^{31}P NMR (202 MHz, CDCl_3): δ 41.44; HRMS: m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{23}\text{OPS}^+$: 367.1280, found: 367.1282.



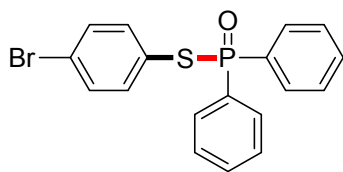
S-(4-acetamidophenyl)diphenylphosphinothioate

3e¹: White solid, m.p. 188.0-188.3 °C; ^1H NMR (500 MHz, CDCl_3): δ 9.86 (s, 1H), 7.85-7.81 (m, 4H), 7.58-7.54 (m, 2H), 7.49-7.44 (m, 6H), 7.20 (d, $J = 6.9$ Hz, 2H), 2.13 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 169.5, 140.4, 136.3 (d, $J = 3.2$ Hz), 132.6, 132.1 (d, $J = 104.5$ Hz), 131.4 (d, $J = 10.3$ Hz), 128.7 (d, $J = 13.0$ Hz), 120.3, 117.8 (d, $J = 2.2$ Hz), 24.5; ^{31}P NMR (202 MHz, CDCl_3): δ 42.73; HRMS: m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{19}\text{NO}_2\text{PS}^+$: 368.0869, found: 368.0864.



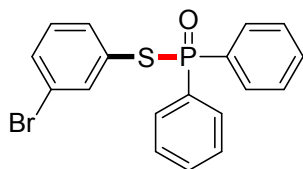
S-(4-chlorophenyl)diphenylphosphinothioate

3f⁴: White solid, m.p. 90.3-92.3 °C; ^1H NMR (500 MHz, CDCl_3): δ 7.86-7.82 (m, 4H), 7.54-7.51 (m, 2H), 7.47-7.43 (m, 4H), 7.39-7.37 (m, 2H), 7.18-7.16 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 136.4 (d, $J = 3.7$ Hz), 135.5 (d, $J = 2.5$ Hz), 132.4 (d, $J = 1.8$ Hz), 132.1 (d, $J = 106.1$ Hz), 131.5 (d, $J = 10.3$ Hz), 129.2, 128.6 (d, $J = 13.2$ Hz), 124.6 (d, $J = 5.0$ Hz); ^{31}P NMR (202 MHz, CDCl_3): δ 40.65; HRMS: m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{15}\text{ClOPS}^+$: 345.0264, found: 345.0268.



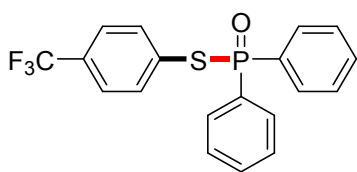
S-(4-bromophenyl)diphenylphosphinothioate

3g: White solid, m.p. 171.7-173.4 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.86-7.82 (m, 4H), 7.54-7.51 (m, 2H), 7.47-7.43 (m, 4H), 7.34-7.30 (m, 4H); ¹³C NMR (125 MHz, CDCl₃): δ 136.7 (d, *J* = 3.8 Hz), 132.5, 132.2, 132.1 (d, *J* = 105.9 Hz), 131.5 (d, *J* = 10.3 Hz), 128.6 (d, *J* = 13.2 Hz), 125.3 (d, *J* = 4.6 Hz), 123.7; ³¹P NMR (202 MHz, CDCl₃): δ 40.46; HRMS: *m/z* [M+H]⁺ calcd for C₁₈H₁₅BrOPS⁺: 390.9739, found: 390.9743.



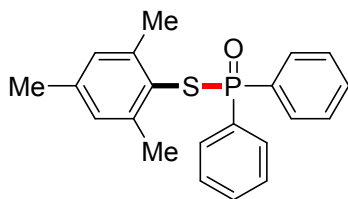
S-(3-bromophenyl)diphenylphosphinothioate.

3h⁴: White solid, m.p. 190.4-191.2 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.86-7.82 (m, 4H), 7.55-7.52 (m, 3H), 7.48-7.43 (m, 5H), 7.38-7.36 (m, 1H), 7.09-7.06 (m, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 137.6 (d, *J* = 3.9 Hz), 133.8 (d, *J* = 3.6 Hz), 132.5, 132.0 (d, *J* = 110.4 Hz), 132.0, 131.5 (d, *J* = 10.3 Hz), 130.2, 128.6 (d, *J* = 13.2 Hz), 128.3 (d, *J* = 4.9 Hz), 122.4 (d, *J* = 1.7 Hz); ³¹P NMR (202 MHz, CDCl₃): δ 40.75; HRMS: *m/z* [M+H]⁺ calcd for C₁₈H₁₅BrOPS⁺: 390.9739, found: 390.9742.



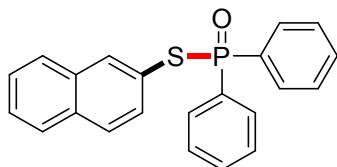
S-(4-(trifluoromethyl)phenyl)diphenylphosphinothioate

3i: White solid, m.p. 189.9-190.6 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.88-7.84 (m, 4H), 7.60 (d, *J* = 7.9 Hz, 2H), 7.55-7.52 (m, 2H), 7.48-7.44 (m, 6H); ¹³C NMR (125 MHz, CDCl₃): δ 135.9, 134.8, 132.3 (d, *J* = 107.3 Hz), 131.9 (d, *J* = 2.7 Hz), 131.4 (d, *J* = 10.0 Hz), 128.9 (d, *J* = 12.5 Hz), 127.3, 126.8 (d, *J* = 4.1 Hz), 124.5 (q, *J* = 270.0 Hz); ³¹P NMR (202 MHz, CDCl₃): δ 40.94; HRMS: *m/z* [M+H]⁺ calcd for C₁₉H₁₅F₃OPS⁺: 379.0528, found: 379.0530.



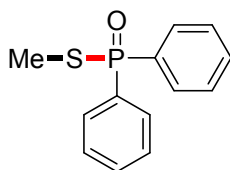
S-(2,4,6-trimethylphenyl)diphenylphosphinothioate

3j: White solid, m.p. 95.3-96.7°C; ^1H NMR (500 MHz, CDCl_3): δ 7.78-7.74 (m, 4H), 7.52-7.49 (m, 2H), 7.43-7.39 (m, 4H), 6.83(s, 2H), 2.25 (s, 6H), 2.22 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 144.7 (d, $J = 3.5$ Hz), 139.2 (d, $J = 2.0$ Hz), 133.3 (d, $J = 104.8$ Hz), 132.1, 131.2 (d, $J = 10.2$ Hz), 129.2 (d, $J = 2.1$ Hz), 128.3 (d, $J = 12.9$ Hz), 120.7 (d, $J = 5.5$ Hz), 22.3, 20.9; ^{31}P NMR (202 MHz, CDCl_3): δ 38.24; HRMS: m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{22}\text{OPS}^+$: 353.1124, found: 353.1119.



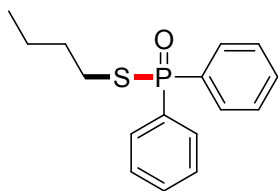
S-naphthalen-2-yl diphenylphosphinothioate

3k¹: White solid, m.p. 96.3-96.7°C; ^1H NMR (500 MHz, CDCl_3): δ 7.99 (s, 1H), 7.90-7.86 (m, 4H), 7.74-7.69 (m, 2H), 7.65 (d, $J = 8.5$ Hz, 1H), 7.51-7.47 (m, 3H), 7.45-7.41 (m, 6H); ^{13}C NMR (125 MHz, CDCl_3): δ 135.3 (d, $J = 4.9$ Hz), 133.5, 132.9, 132.5 (d, $J = 103.3$ Hz), 132.3 (d, $J = 2.6$ Hz), 131.6 (d, $J = 10.3$ Hz), 131.5 (d, $J = 3.0$ Hz), 128.6, 128.5 (d, $J = 13.1$ Hz), 127.8, 127.6, 126.8, 126.4, 123.5 (d, $J = 5.5$ Hz); ^{31}P NMR (202 MHz, CDCl_3): δ 41.48; HRMS: m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{18}\text{OPS}^+$: 361.0810, found: 361.0813.



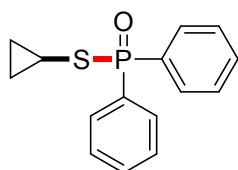
S-methyl diphenylphosphinothioate

3l: Colorless oil; ^1H NMR (500 MHz, CDCl_3): δ 7.91-7.86 (m, 4H), 7.53-7.49 (m, 2H), 7.48-7.44 (m, 4H), 2.21 (d, $J = 12.1$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 132.3 (d, $J = 106.4$ Hz), 132.0 (d, $J = 2.8$ Hz), 131.0 (d, $J = 10.4$ Hz), 128.3 (d, $J = 13.0$ Hz), 10.2 (d, $J = 2.6$ Hz); ^{31}P NMR (202 MHz, CDCl_3): δ 44.07; HRMS: m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{14}\text{OPS}^+$: 249.0497, found: 249.0496.



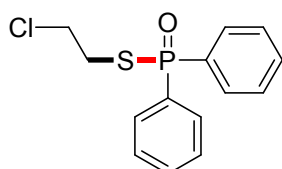
S-1-butyl diphenylphosphinothioate

3m⁴: Colorless oil; ¹H NMR (500 MHz, CDCl₃): δ 7.91-7.87 (m, 4H), 7.52-7.49 (m, 2H), 7.48-7.43 (m, 4H), 2.83-2.77 (m, 2H), 1.62-1.58 (m, 2H), 1.36-1.33 (m, 2H), 0.84-0.81 (m, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 133.3 (d, *J* = 106.5 Hz), 132.0 (d, *J* = 2.9 Hz), 131.2 (d, *J* = 10.4 Hz), 128.4 (d, *J* = 13.2 Hz), 32.4 (d, *J* = 4.8 Hz), 28.8 (d, *J* = 2.3 Hz), 21.5, 13.2; ³¹P NMR (202 MHz, CDCl₃): δ 41.65; HRMS: *m/z* [M+H]⁺ calcd for C₁₆H₂₀OPS⁺: 290.0967, found: 290.0967.



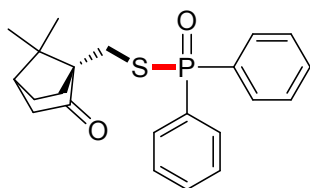
S-cyclopropyl diphenylphosphinothioate

3n: Colorless oil; ¹H NMR (500 MHz, CDCl₃): δ 7.90 (dd, *J* = 12.9, 7.6 Hz, 4H), 7.54-7.45 (m, 6H), 1.97-1.92 (m, 1H), 0.80-0.77 (m, 2H), 0.69-0.65 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 133.2 (d, *J* = 105.7 Hz), 132.1 (d, *J* = 2.9 Hz), 131.3 (d, *J* = 10.4 Hz), 128.5 (d, *J* = 13.0 Hz), 9.2 (d, *J* = 2.8 Hz), 7.5 (d, *J* = 5.5 Hz); ³¹P NMR (202 MHz, CDCl₃): δ 42.45; HRMS: *m/z* [M+H]⁺ calcd for C₁₅H₁₆OPS⁺: 275.0654, found: 275.0652.



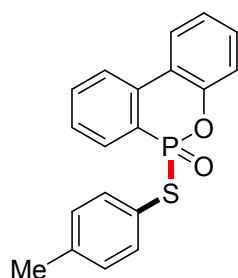
S-(2-chloroethyl) diphenylphosphinothioate

3o: Colorless oil; ¹H NMR (500 MHz, CDCl₃): δ 7.90-7.86 (m, 4H), 7.56-7.54 (m, 2H), 7.50-7.47 (m, 4H), 3.67 (t, *J* = 7.5 Hz, 2H), 3.11 (dt, *J* = 12.8, 7.5 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 132.5 (d, *J* = 105.4 Hz), 132.5 (d, *J* = 2.7 Hz), 131.3 (d, *J* = 10.6 Hz), 128.6 (d, *J* = 13.2 Hz), 43.3 (d, *J* = 2.6 Hz), 30.9 (d, *J* = 2.0 Hz); ³¹P NMR (202 MHz, CDCl₃): δ 43.53; HRMS: *m/z* [M+H]⁺ calcd for C₁₄H₁₅ClOPS⁺: 297.0264, found: 297.0265.



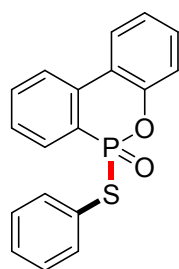
S-(((1S)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methyl)diphenylphosphinothioate

3p: Colorless oil; ^1H NMR (500 MHz, CDCl_3): δ 7.96-7.92 (m, 2H), 7.88-7.84 (m, 2H), 7.54-7.45 (m, 6H), 2.99-2.95 (m, 1H), 2.85-2.80 (m, 1H), 2.35-2.31 (m, 1H), 2.04-2.02 (m, 1H), 1.94-1.82 (m, 3H), 1.57-1.52 (m, 1H), 1.35-1.31 (m, 1H), 0.98 (s, 3H), 0.85 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 216.2 (d, $J = 8.8$ Hz), 133.0 (d, $J = 106.8$ Hz), 132.8 (d, $J = 106.9$ Hz), 132.0, 131.3 (d, $J = 10.4$ Hz), 131.1 (d, $J = 10.4$ Hz), 128.4 (d, $J = 12.5$ Hz), 128.3 (d, $J = 12.5$ Hz), 60.0 (d, $J = 4.1$ Hz), 47.8, 43.4, 42.7, 26.9, 26.4, 25.2 (d, $J = 1.5$ Hz), 19.8, 19.5; ^{31}P NMR (202 MHz, CDCl_3): δ 41.51; HRMS: m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{26}\text{ClO}_2\text{PS}^+$: 385.1386, found: 385.1384.



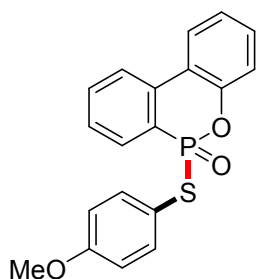
6-(p-tolylthio)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide

4a: Colorless oil; ^1H NMR (500 MHz, CDCl_3): δ 7.91-7.86 (m, 1H), 7.77-7.72 (m, 1H), 7.66-7.58 (m, 2H), 7.45-7.41 (m, 1H), 7.31-7.25 (m, 1H), 7.13-7.04 (m, 4H), 6.82-6.80 (m, 2H), 2.15 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 150.1 (d, $J = 9.6$ Hz), 139.4 (d, $J = 3.2$ Hz), 136.0 (d, $J = 7.2$ Hz), 135.5 (d, $J = 4.0$ Hz), 133.5 (d, $J = 1.9$ Hz), 130.3 (d, $J = 10.1$ Hz), 130.1, 129.5 (d, $J = 2.5$ Hz), 128.1 (d, $J = 14.9$ Hz), 124.6, 124.4 (d, $J = 132.9$ Hz), 124.1, 123.0 (d, $J = 11.4$ Hz), 121.3 (d, $J = 11.3$ Hz), 119.9 (d, $J = 5.7$ Hz), 119.6 (d, $J = 6.8$ Hz), 20.8; ^{31}P NMR (202 MHz, CDCl_3): δ 33.53; HRMS: m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{16}\text{O}_2\text{PS}^+$: 339.0603, found: 339.0613.



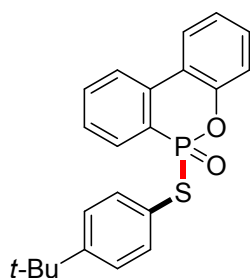
6-((phenyl)thio)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide

4b: Colorless oil; ^1H NMR (500 MHz, CDCl_3): δ 7.90-7.85 (m, 1H), 7.77-7.75 (m, 1H), 7.68-7.66 (m, 1H), 7.63-7.59 (m, 1H), 7.45-7.41 (m, 1H), 7.31-7.28 (m, 1H), 7.20-7.18 (m, 2H), 7.16-7.11 (m, 3H), 7.04-7.01 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 150.2 (d, $J = 9.6$ Hz), 136.0 (d, $J = 7.3$ Hz), 135.7 (d, $J = 4.2$ Hz), 133.6 (d, $J = 2.5$ Hz), 130.4 (d, $J = 10.3$ Hz), 130.2, 129.1 (d, $J = 2.9$ Hz), 128.8 (d, $J = 2.6$ Hz), 128.2 (d, $J = 15.0$ Hz), 124.7, 124.5, 124.4 (d, $J = 132.7$ Hz), 123.9 (d, $J = 5.6$ Hz), 123.1 (d, $J = 11.5$ Hz), 121.4 (d, $J = 11.6$ Hz), 119.6 (d, $J = 7.1$ Hz); ^{31}P NMR (202 MHz, CDCl_3): δ 30.16; HRMS: m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{14}\text{O}_2\text{PS}^+$: 325.0449, found: 325.0449.



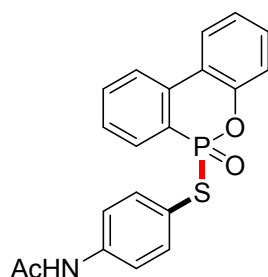
6-((4-methoxyphenyl)thio)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide

4c: White solid, m.p. 115.4-116.2 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.92-7.86 (m, 1H), 7.80-7.77 (m, 1H), 7.70-7.62 (m, 2H), 7.48-7.45 (m, 1H), 7.33-7.29 (m, 1H), 7.15-7.12 (m, 2H), 7.08-7.05 (m, 2H), 6.56-6.53 (m, 2H), 3.67 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 160.5 (d, *J* = 3.0 Hz), 150.4 (d, *J* = 9.7 Hz), 137.3 (d, *J* = 4.0 Hz), 136.2 (d, *J* = 7.2 Hz), 133.6 (d, *J* = 2.7 Hz), 130.5 (d, *J* = 10.4 Hz), 130.2, 128.3 (d, *J* = 14.9 Hz), 124.7, 124.6 (d, *J* = 131.6 Hz), 123.1 (d, *J* = 11.4 Hz), 121.5 (d, *J* = 11.4 Hz), 119.7 (d, *J* = 7.1 Hz), 114.9, 114.5 (d, *J* = 2.5 Hz), 113.9 (d, *J* = 5.8 Hz), 55.1; ³¹P NMR (202 MHz, CDCl₃): δ 33.30; HRMS: *m/z* [M+H]⁺ calcd for C₁₉H₁₆O₃PS⁺: 355.0552, found: 355.0551.



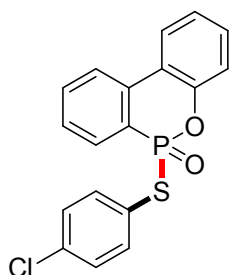
6-((4-(tert-butyl)phenyl)thio)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide

4d³: Colorless oil; ¹H NMR (500 MHz, CDCl₃): δ 7.95-7.91 (m, 1H), 7.76-7.74 (m, 1H), 7.64-7.61 (m, 2H), 7.48-7.44 (m, 1H), 7.30-7.27 (m, 1H), 7.13-6.99 (m, 6H), 1.17 (s, 9H); ¹³C NMR (125 MHz, CDCl₃): δ 152.5 (d, *J* = 3.4 Hz), 150.6 (d, *J* = 9.7 Hz), 136.2 (d, *J* = 7.1 Hz), 135.6 (d, *J* = 4.0 Hz), 133.6, 130.5 (d, *J* = 10.3 Hz), 130.2, 128.3 (d, *J* = 14.9 Hz), 125.8 (d, *J* = 2.4 Hz), 124.6 (d, *J* = 132.5 Hz), 124.6, 124.3, 122.8 (d, *J* = 11.4 Hz), 121.4 (d, *J* = 11.2 Hz), 120.1 (d, *J* = 5.0 Hz), 119.7 (d, *J* = 7.1 Hz), 34.3, 30.9; ³¹P NMR (202 MHz, CDCl₃): δ 34.70; HRMS: *m/z* [M+H]⁺ calcd for C₂₂H₂₂O₂PS⁺: 381.1074, found: 381.1073.



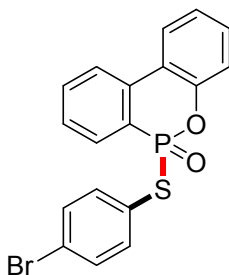
6-((4-acetamidophenyl)thio)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide

4e: White solid, m.p. 199.5-200.1 °C; ¹H NMR (500 MHz, DMSO-*d*₆): δ 11.39 (s, 1H), 9.48-9.45 (m, 1H), 9.36-9.35 (m, 1H), 9.20-9.13 (m, 2H), 9.02-8.94 (m, 1H), 8.81-8.78 (m, 1H), 8.74-8.72 (m, 2H), 8.65-8.60 (m, 2H), 8.44-8.42 (m, 2H), 3.36 (s, 3H); ¹³C NMR (125 MHz, DMSO-*d*₆): δ 169.0, 150.1 (d, *J* = 9.7 Hz), 141.1 (d, *J* = 2.8 Hz), 136.5 (d, *J* = 4.0 Hz), 136.2 (d, *J* = 7.4 Hz), 134.9, 131.4, 130.7 (d, *J* = 10.4 Hz), 129.4 (d, *J* = 14.3 Hz), 126.1, 125.5, 124.6 (d, *J* = 131.8 Hz), 124.5 (d, *J* = 10.9 Hz), 121.7 (d, *J* = 11.4 Hz), 120.2 (d, *J* = 6.7 Hz), 119.8, 116.5 (d, *J* = 5.3 Hz), 24.5; ³¹P NMR (202 MHz, DMSO-*d*₆): δ 33.65; HRMS: *m/z* [M+H]⁺ calcd for C₂₀H₁₇O₃PS⁺: 382.0661, found: 382.0657.



6-((4-chlorophenyl)thio)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide

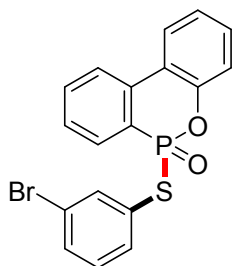
4f: White solid, m.p. 106.0-106.5 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.93-7.89 (m, 1H), 7.84-7.81 (m, 1H), 7.73-7.66 (m, 2H), 7.51-7.48 (m, 1H), 7.36-7.33 (m, 1H), 7.23-7.11 (m, 4H), 7.03-7.01 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 150.2 (d, *J* = 9.7 Hz), 137.1 (d, *J* = 4.3 Hz), 136.3 (d, *J* = 7.5 Hz), 136.0 (d, *J* = 3.5 Hz), 133.9, 130.6, 130.5, 129.1 (d, *J* = 2.6 Hz), 128.5 (d, *J* = 15.0 Hz), 124.9, 124.6, 124.4 (d, *J* = 132.4 Hz), 123.3 (d, *J* = 11.4 Hz), 122.6 (d, *J* = 7.6 Hz), 121.6 (d, *J* = 11.4 Hz), 119.8 (d, *J* = 7.2 Hz); ³¹P NMR (202 MHz, CDCl₃): δ 33.58; HRMS: *m/z* [M+H]⁺ calcd for C₁₈H₁₃ClO₂PS⁺: 359.0057, found: 359.0058.



6-((4-bromophenyl)thio)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide

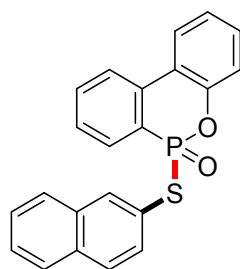
4g: White solid, m.p. 122.4-124.3 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.94-7.89 (m, 1H), 7.84-7.81 (m, 1H), 7.73-7.67 (m, 2H), 7.52-7.48 (m, 1H), 7.36-7.33 (m, 1H), 7.22-7.13 (m, 4H), 7.07-7.04 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): 150.3 (d, *J* = 9.5 Hz), 137.3 (d, *J* = 4.4 Hz), 136.4 (d, *J* = 7.5 Hz), 133.9 (d, *J* = 2.7 Hz), 132.1 (d, *J* = 2.7 Hz), 130.7, 130.6 (d, *J* = 6.0 Hz), 128.6 (d, *J* = 15.2 Hz), 125.0, 124.7, 124.5 (d, *J* = 133.9 Hz),

124.3 (d, $J = 3.7$ Hz), 123.4 (d, $J = 6.7$ Hz), 123.3 (d, $J = 11.5$ Hz), 121.7 (d, $J = 11.6$ Hz), 119.9 (d, $J = 7.0$ Hz); ^{31}P NMR (202 MHz, CDCl_3): δ 32.10; HRMS: m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{13}\text{BrO}_2\text{PS}^+$: 402.9552, found: 402.9548.



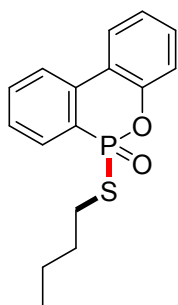
6-((3-bromophenyl)thio)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide

4h: White solid, m.p. 78.2-79.8°C; ^1H NMR (500 MHz, CDCl_3): δ 7.97-7.92 (m, 1H), 7.86-7.83 (m, 1H), 7.74-7.68 (m, 2H), 7.54-7.51 (m, 1H), 7.37-7.34 (m, 1H), 7.29-7.26 (m, 2H), 7.20-7.15 (m, 3H), 6.93-6.90 (m, 1H); ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$) δ 150.2 (d, $J = 9.8$ Hz), 137.9 (d, $J = 4.2$ Hz), 136.3 (d, $J = 7.2$ Hz), 135.2, 134.8 (d, $J = 4.2$ Hz), 133.0 (d, $J = 2.5$ Hz), 131.6, 131.4 (d, $J = 2.2$ Hz), 130.8 (d, $J = 10.4$ Hz), 129.6 (d, $J = 15.0$ Hz), 126.3 (d, $J = 6.0$ Hz), 126.0, 125.6, 124.5 (d, $J = 11.3$ Hz), 123.9 (d, $J = 134.0$ Hz), 122.2 (d, $J = 2.9$ Hz), 121.4 (d, $J = 11.2$ Hz), 120.0 (d, $J = 6.8$ Hz); ^{31}P NMR (202 MHz, CDCl_3): δ 32.88; HRMS: m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{13}\text{BrO}_2\text{PS}^+$: 402.9552, found: 402.9552.



6-(naphthalen-2-ylthio)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide

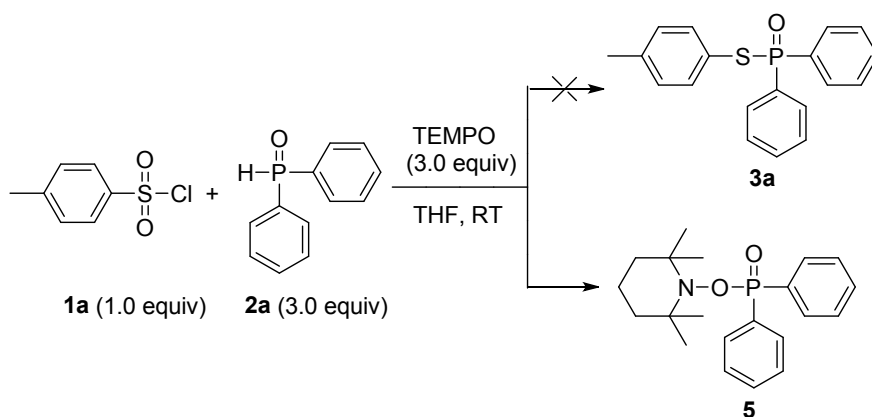
4i: White solid, m.p. 168.7-169.6°C; ^1H NMR (500 MHz, CDCl_3): δ 7.93-7.89 (m, 1H), 7.65-7.62 (m, 3H), 7.59-7.55 (m, 1H), 7.48-7.45 (m, 2H), 7.43-7.35 (m, 4H), 7.22-7.18 (m, 2H), 7.11-7.09 (m, 1H), 6.94-6.91 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 150.3 (d, $J = 9.7$ Hz), 136.3 (d, $J = 5.7$ Hz), 136.2 (d, $J = 7.2$ Hz), 133.6 (d, $J = 2.4$ Hz), 133.0 (d, $J = 2.8$ Hz), 132.8 (d, $J = 2.1$ Hz), 131.7 (d, $J = 3.0$ Hz), 130.5 (d, $J = 10.3$ Hz), 130.2, 128.4 (d, $J = 1.9$ Hz), 128.3 (d, $J = 15.0$ Hz), 127.5, 127.3, 127.0, 126.3, 124.5 (d, $J = 133.6$ Hz), 124.5, 124.3, 123.1 (d, $J = 11.4$ Hz), 121.3 (d, $J = 11.4$ Hz), 121.0 (d, $J = 7.3$ Hz), 119.6 (d, $J = 7.1$ Hz); ^{31}P NMR (202 MHz, CDCl_3): δ 32.96; HRMS: m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{16}\text{O}_2\text{PS}^+$: 375.0603, found: 375.0604.



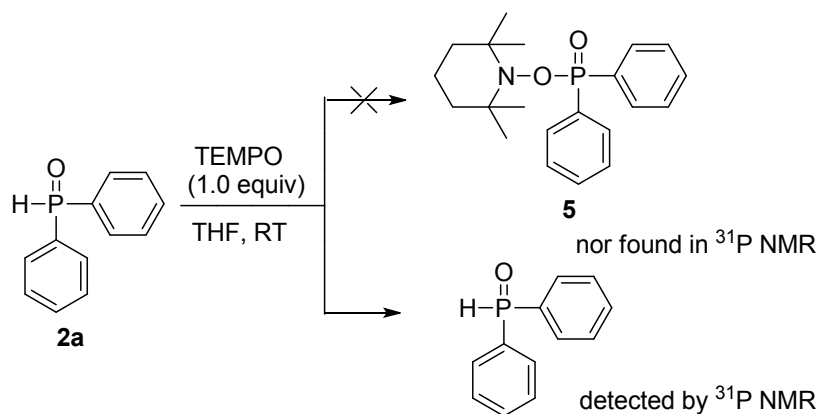
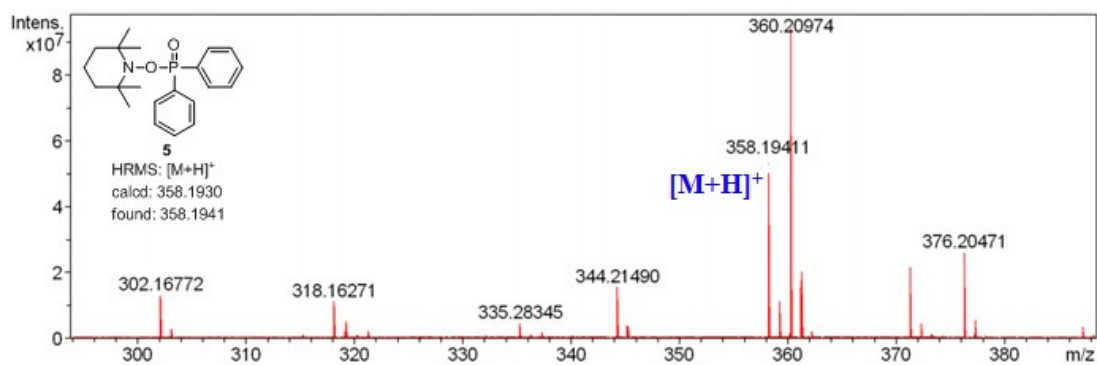
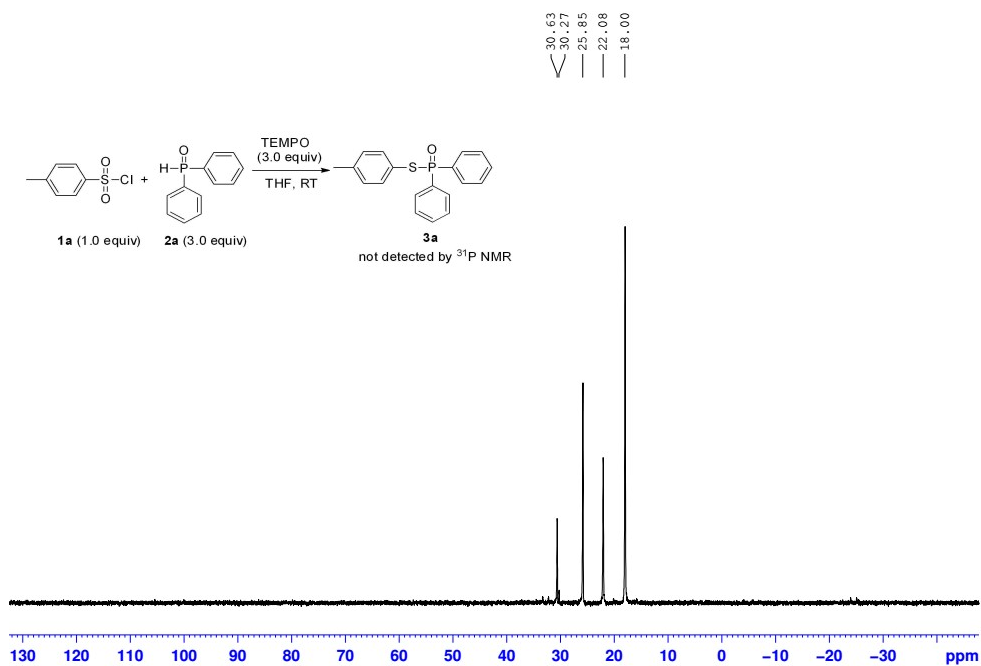
6-(1-butylthio)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide

4j: Colorless oil; ^1H NMR (500 MHz, CDCl_3): δ 8.02-7.98 (m, 1H), 7.95-7.90 (m, 2H), 7.71-7.68 (m, 1H), 7.54-7.50 (m, 1H), 7.40-7.37 (m, 1H), 7.29-7.22 (m, 2H), 2.95-2.80 (m, 2H), 1.66-1.60 (m, 2H), 1.37-1.32 (m, 2H), 0.85 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 149.5 (d, $J = 9.7$ Hz), 136.0 (d, $J = 7.3$ Hz), 133.6, 130.6, 130.3 (d, $J = 10.7$ Hz), 128.5 (d, $J = 14.9$ Hz), 126.0 (d, $J = 135.2$ Hz), 125.1, 124.8, 123.7 (d, $J = 11.2$ Hz), 122.3 (d, $J = 12.2$ Hz), 120.3 (d, $J = 6.7$ Hz), 32.8 (d, $J = 5.0$ Hz), 29.7 (d, $J = 3.6$ Hz), 21.5, 13.3; ^{31}P NMR (202 MHz, CDCl_3): δ 36.95; HRMS: m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{18}\text{O}_2\text{PS}^+$: 305.0758, found: 305.0758.

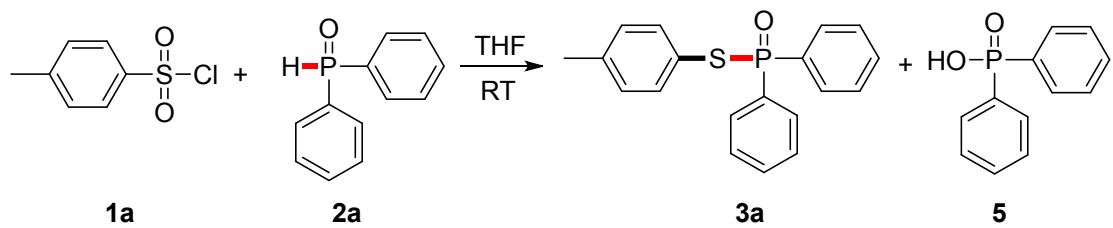
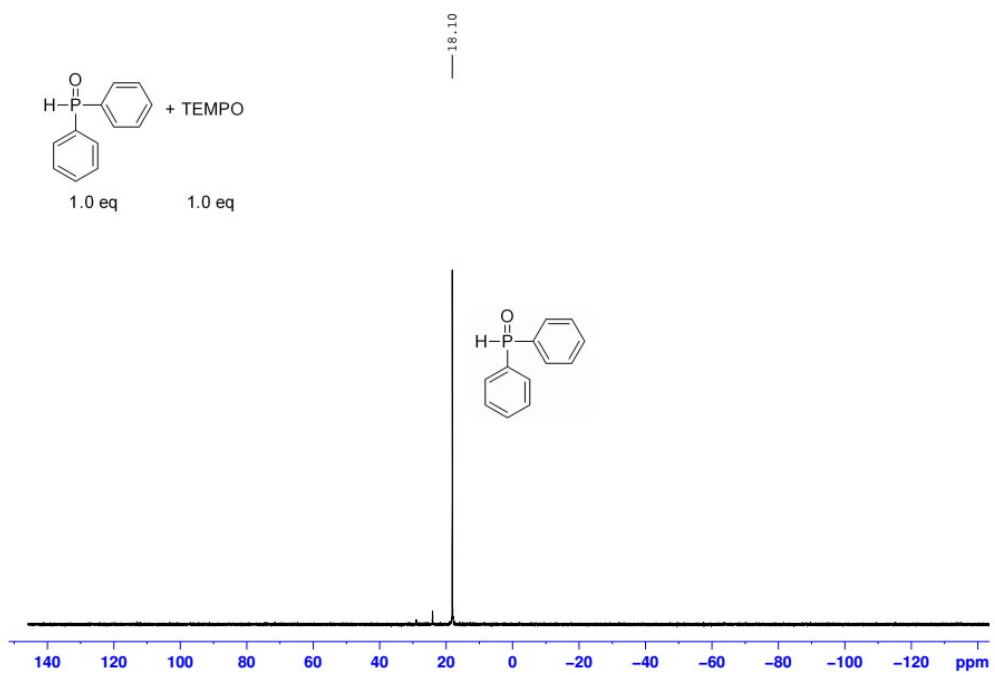
4. Mechanistic studies

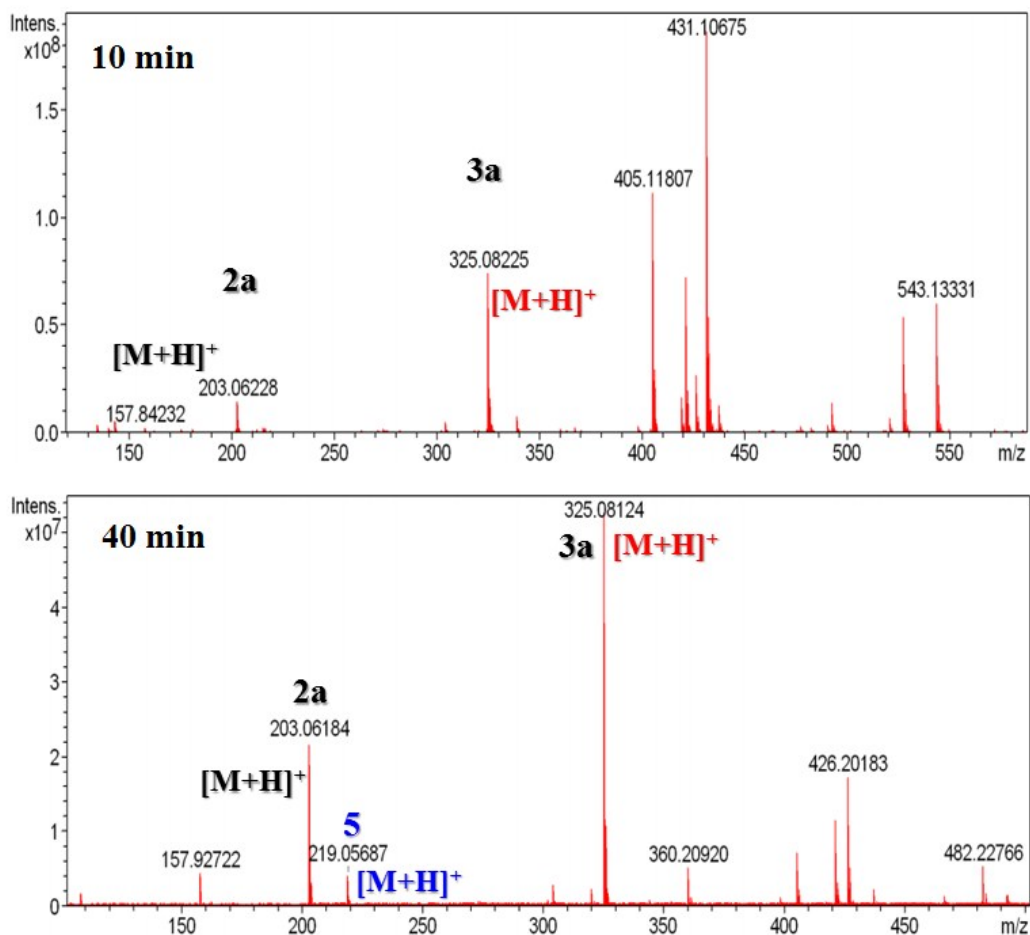


Compound **1a** (0.5 mmol), **2a** (1.5 mmol) and TEMPO (1.5 mmol) were added to a glass tube, and then 1.5 mL of THF was added. The reaction mixture was stirred at room temperature for 1 h. Compound **3a** was not found in ^{31}P NMR spectra. High-resolution mass spectra analysis of this reaction mixture showed that TEMPO-trapped product **5** was formed⁵. HRMS: m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{29}\text{NOP}^+$: 358.1930, found: 358.1941.



Compound **2a** (0.25 mmol) and TEMPO (0.25 mmol) were added to a glass tube, and then 1.0 mL of THF was added. The reaction mixture was stirred at room temperature for 1 h. TEMPO-trapped product **5** was not found in ^{31}P NMR spectra. The starting diphenylphosphine oxide (**2a**) in THF showed signal in the ^{31}P NMR spectrum at $\delta = 18.10$ ppm.





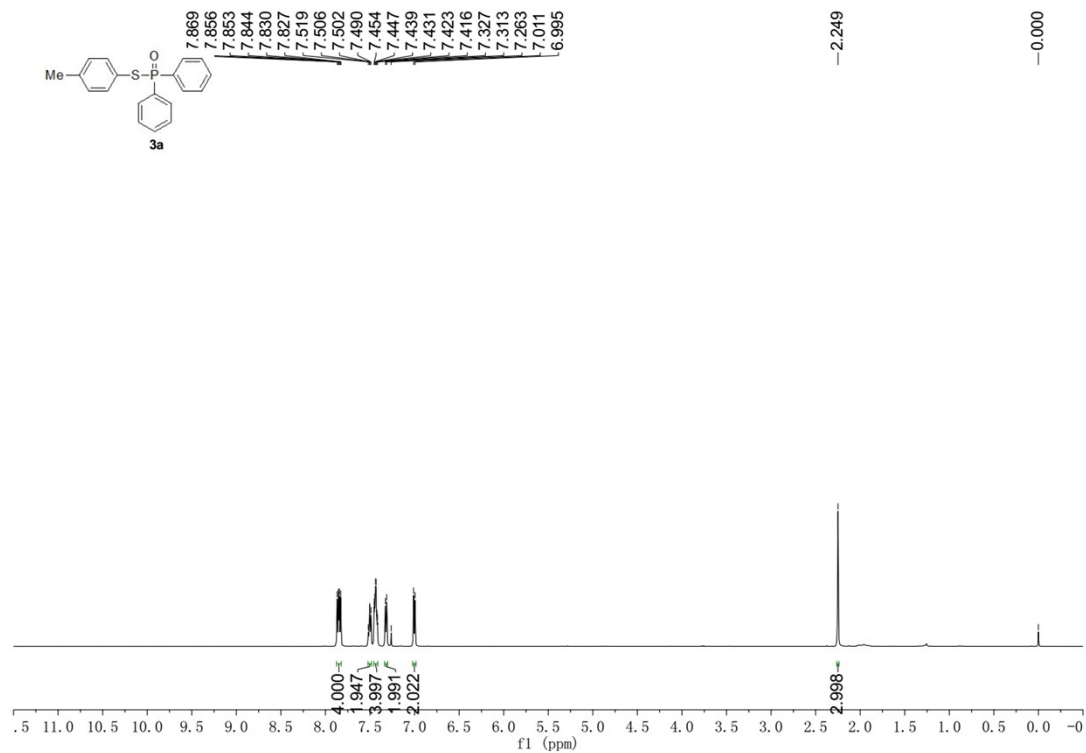
Compound **1a** (0.5 mmol), **2a** (1.5 mmol) were added to a glass tube, and then 1.5 mL of THF was added. The reaction mixture was stirred at room temperature and monitored by HRMS. Compound **2a** and **3a** were found in HRMS spectra after 10 minutes. HRMS: **2a**: m/z $[M+H]^+$ calcd for C₁₂H₁₂OP⁺: 203.0620, found: 203.0623; **3a**: m/z $[M+H]^+$ calcd for C₁₉H₁₈OPS⁺: 325.0811, found: 325.0823. As illustrated in figure above, the byproduct **5**, starting compound **2a** and corresponding product **3a** were all examined under the current reaction conditions after 40 minutes. HRMS: **2a**: m/z $[M+H]^+$ calcd for C₁₂H₁₂OP⁺: 203.0620, found: 203.0618; **3a**: m/z $[M+H]^+$ calcd for C₁₉H₁₈OPS⁺: 325.0811, found: 325.0812; **5**: m/z $[M+H]^+$ calcd for C₁₂H₁₂O₂P⁺: 219.0569, found: 219.0569.

5. References

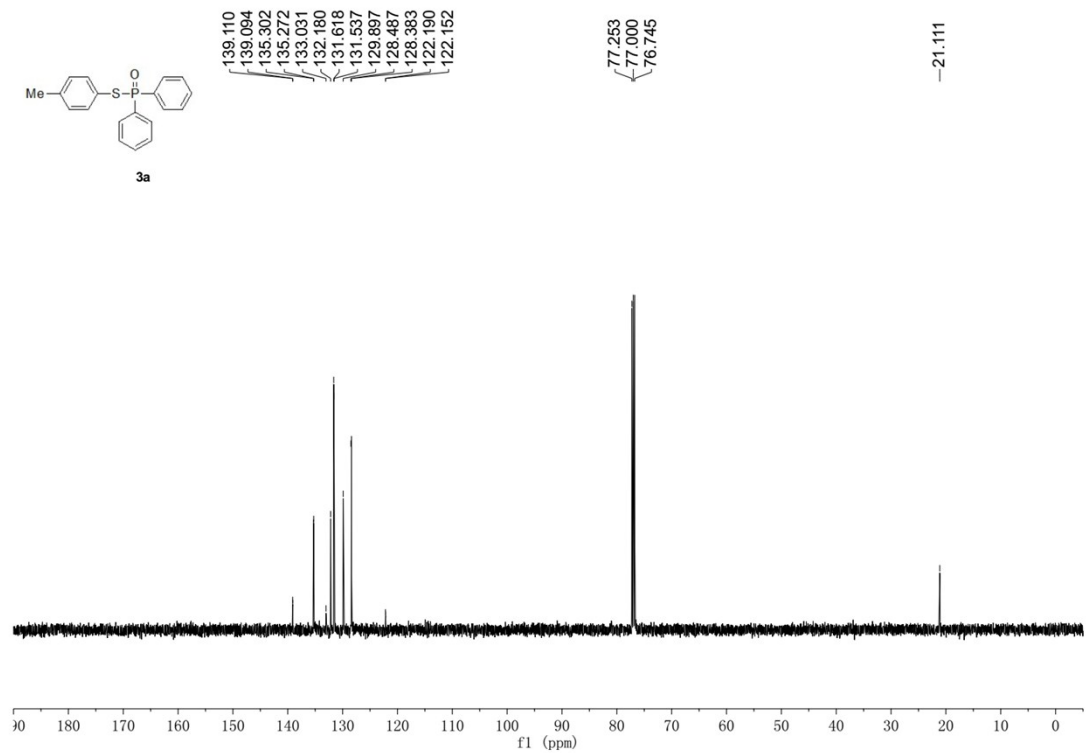
- 1 S. Li, T. Q. Chen, Y. Saga and L. B. Han, *RSC Adv.*, 2015, **5**, 71544.
- 2 L. L. Zhang, P. B. Zhang, X. Q. Li, J. Xu, G. Tang and Y. F. Zhao, *J. Org. Chem.*, 2016, **81**, 5588.
- 3 Y. Y. Zhu, T. Q. Chen, S. Li, S. Shimada and L. B. Han, *J. Am. Chem. Soc.*, 2016, **138**, 5825.

- 4 J. C. Wang, X. Huang, Z. Q. Ni, S. C. Wang, J. Wu and Y. J. Pan, *Green Chem.*, 2015, **17**, 314.
- 5 J. G. Sun, H. Yang, P. Li and B. Zhang, *Org. Lett.*, 2016, **18**, 5114.

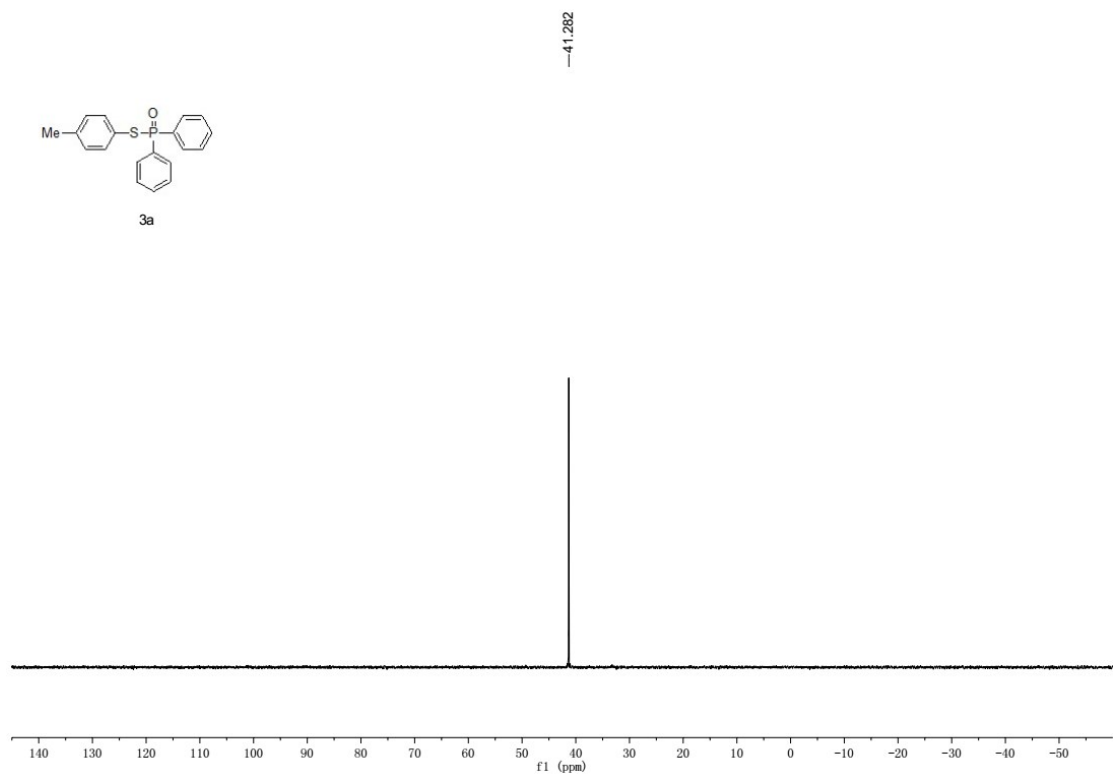
6. NMR Spectra



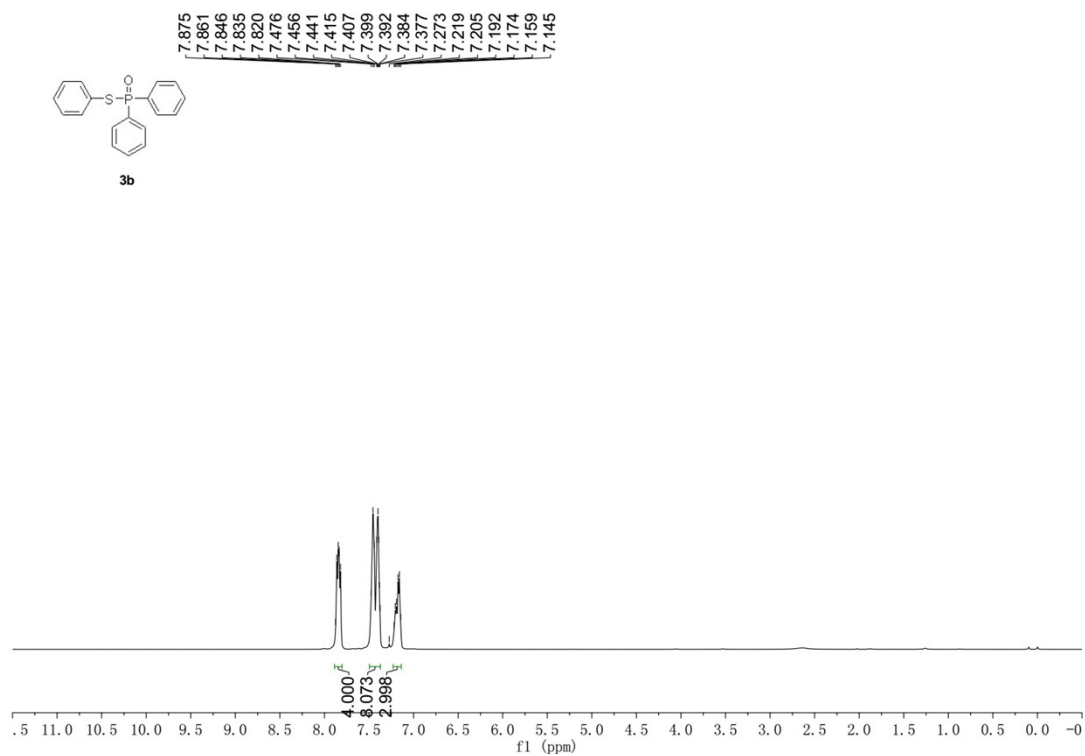
^1H NMR spectrum of compound **3a**



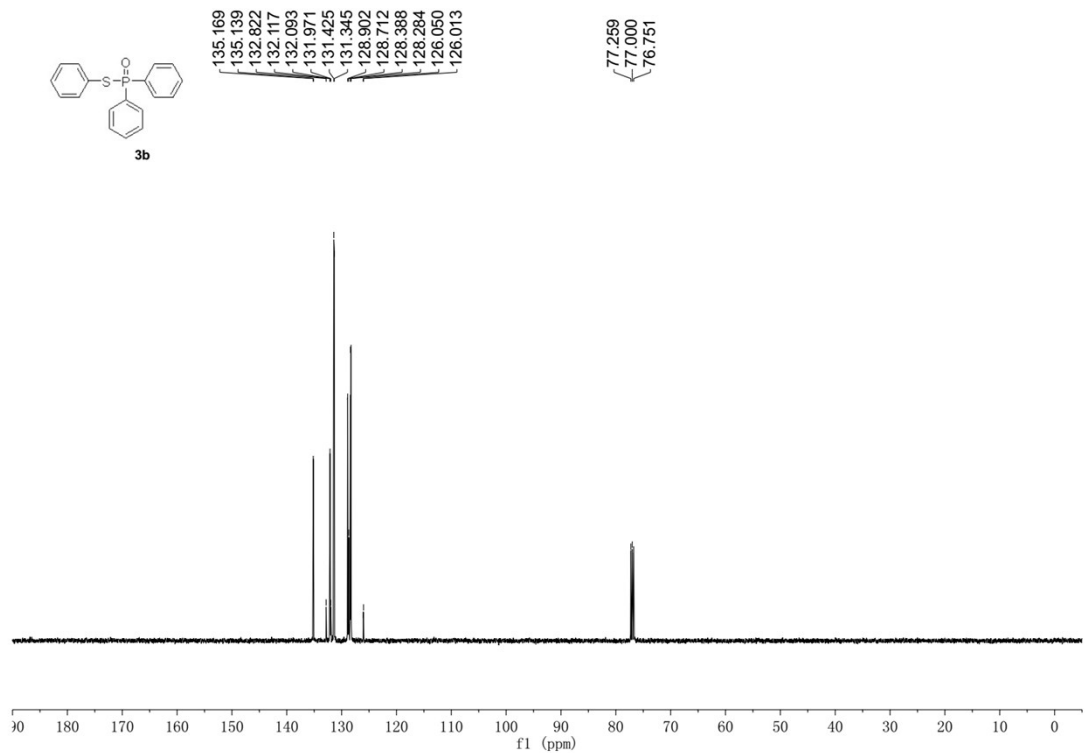
^{13}C NMR spectrum of compound **3a**



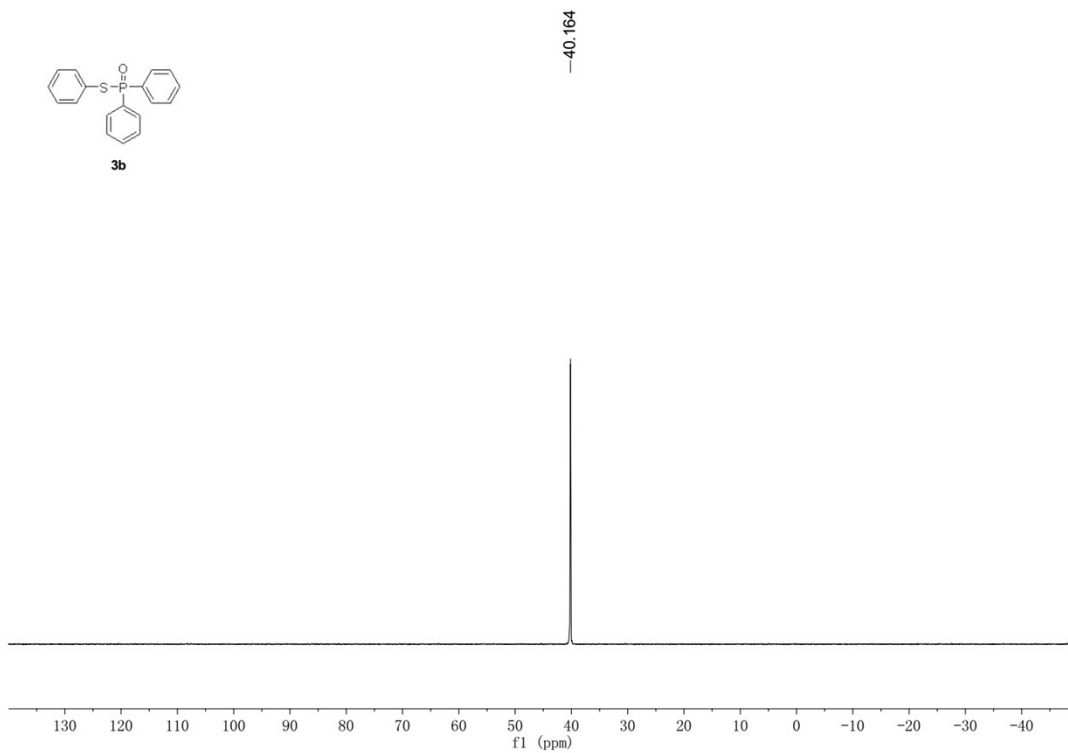
^{31}P NMR spectrum of compound **3a**



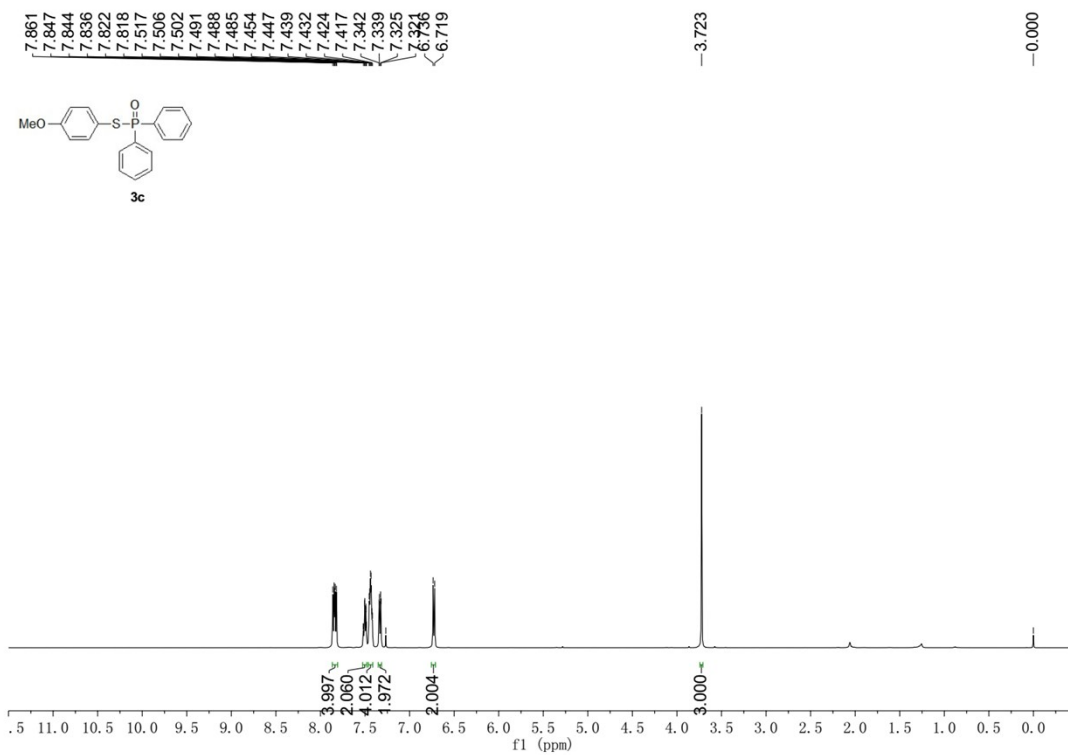
¹H NMR spectrum of compound **3b**



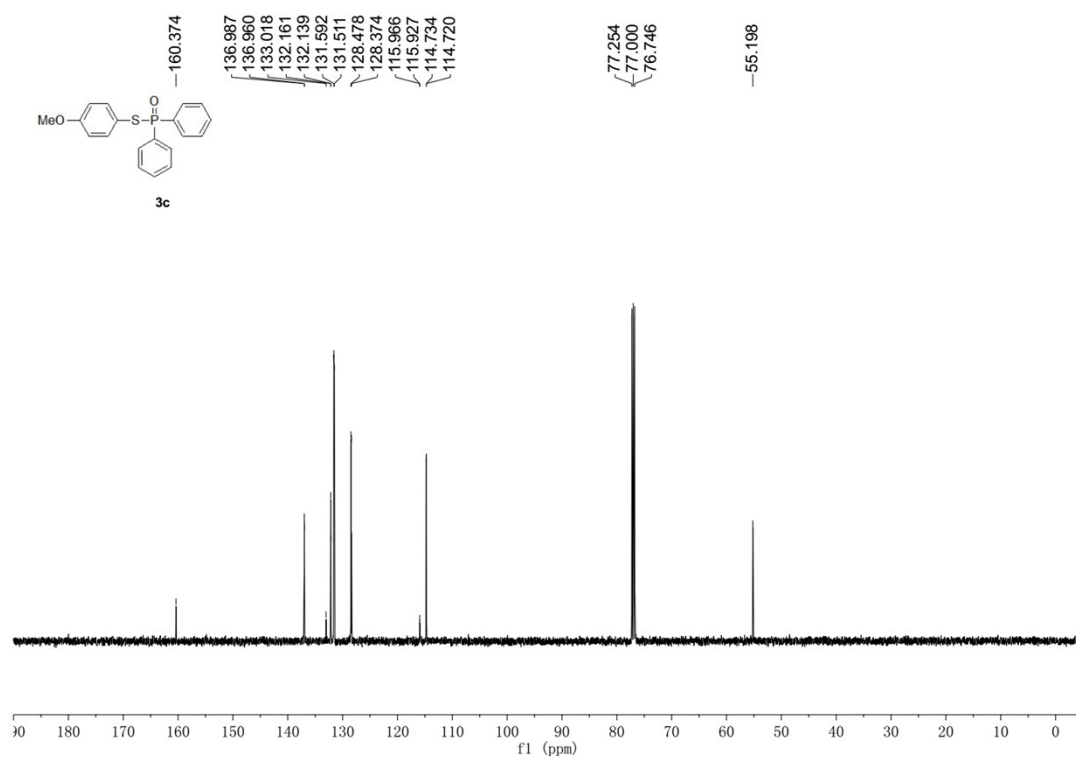
¹³C NMR spectrum of compound **3b**



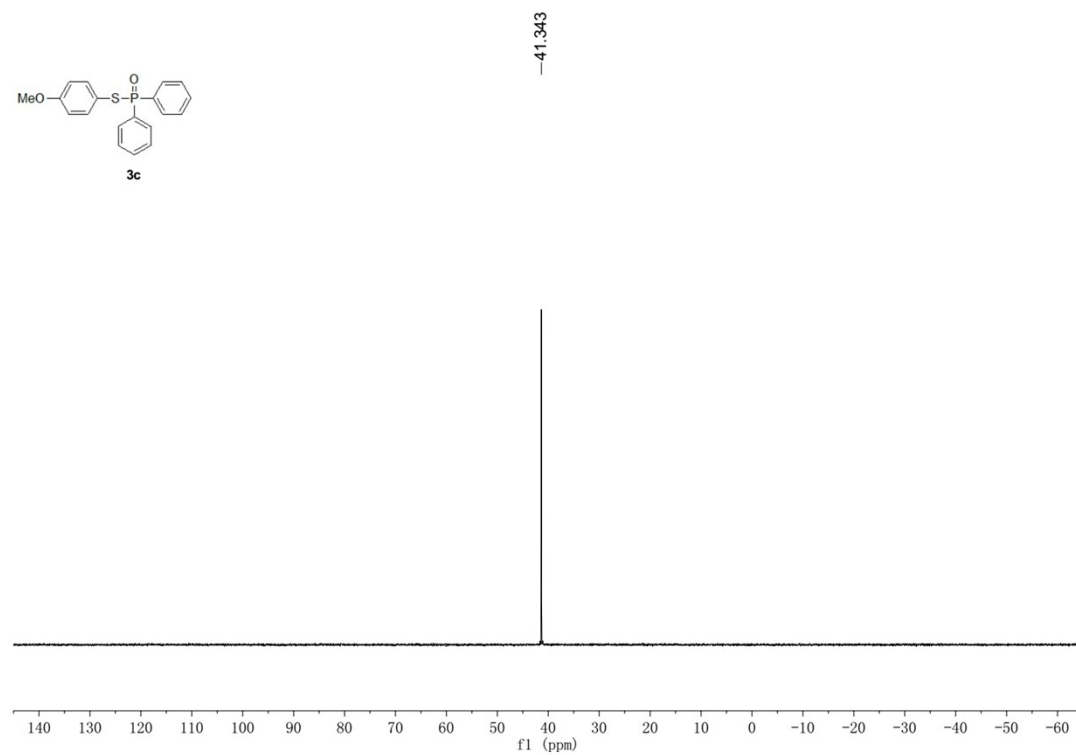
³¹P NMR spectrum of compound **3b**



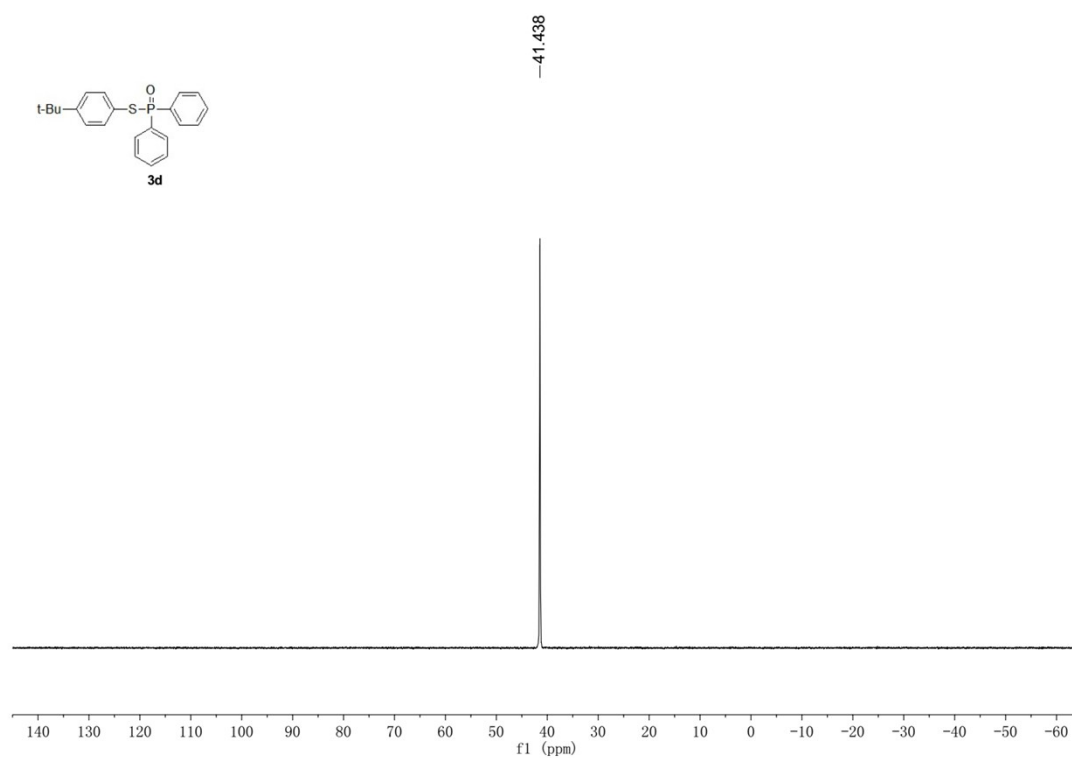
¹H NMR spectrum of compound **3c**



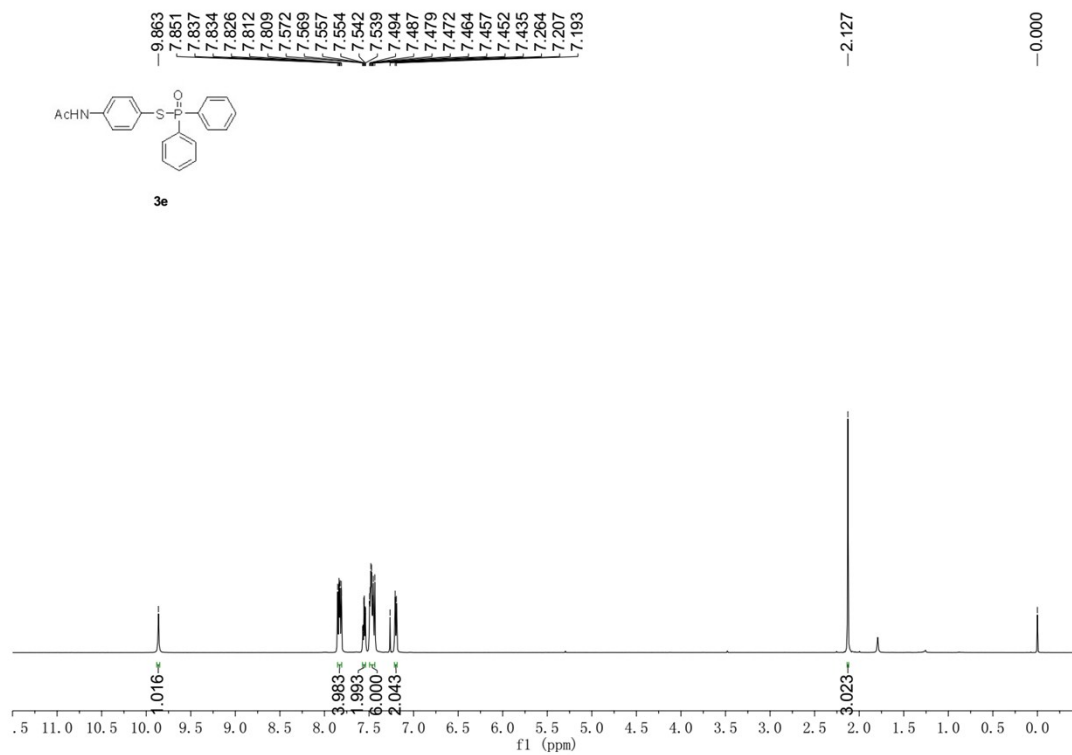
¹³C NMR spectrum of compound **3c**



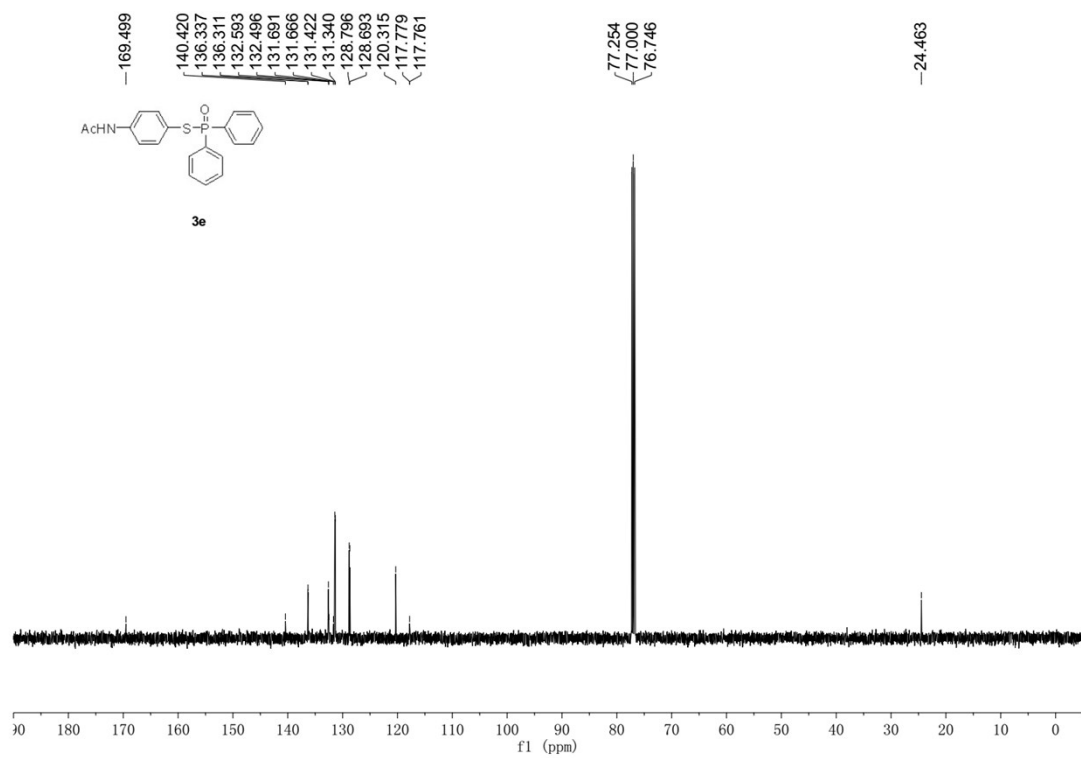
³¹P NMR spectrum of compound **3c**



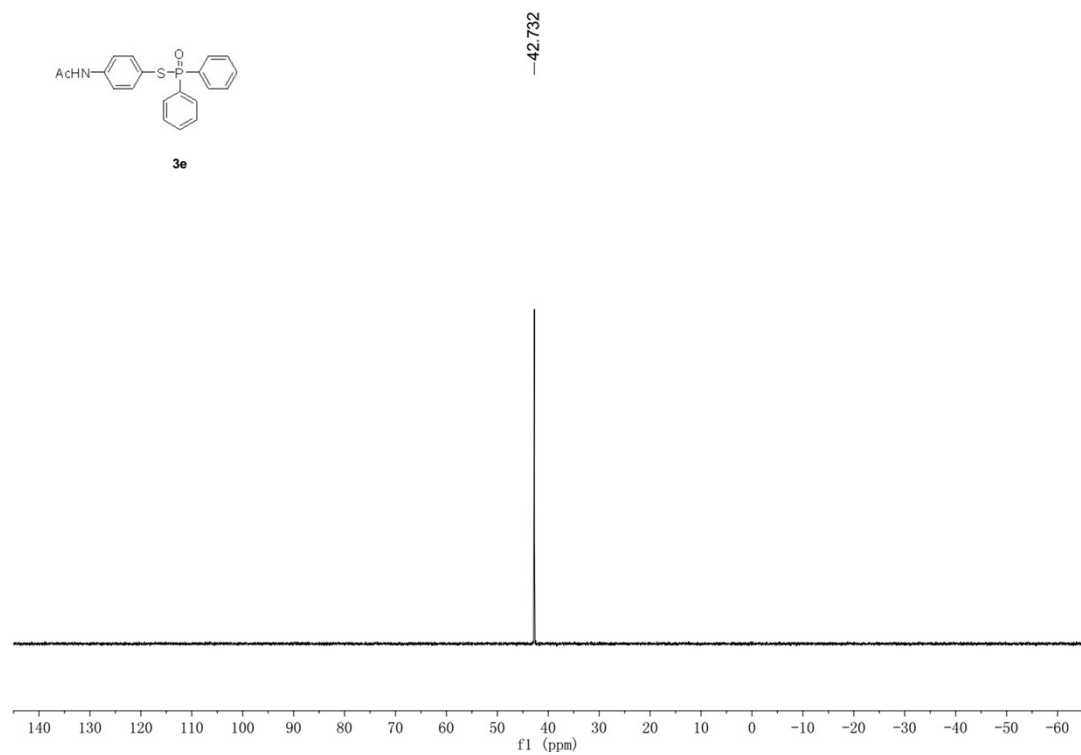
³¹P NMR spectrum of compound **3d**



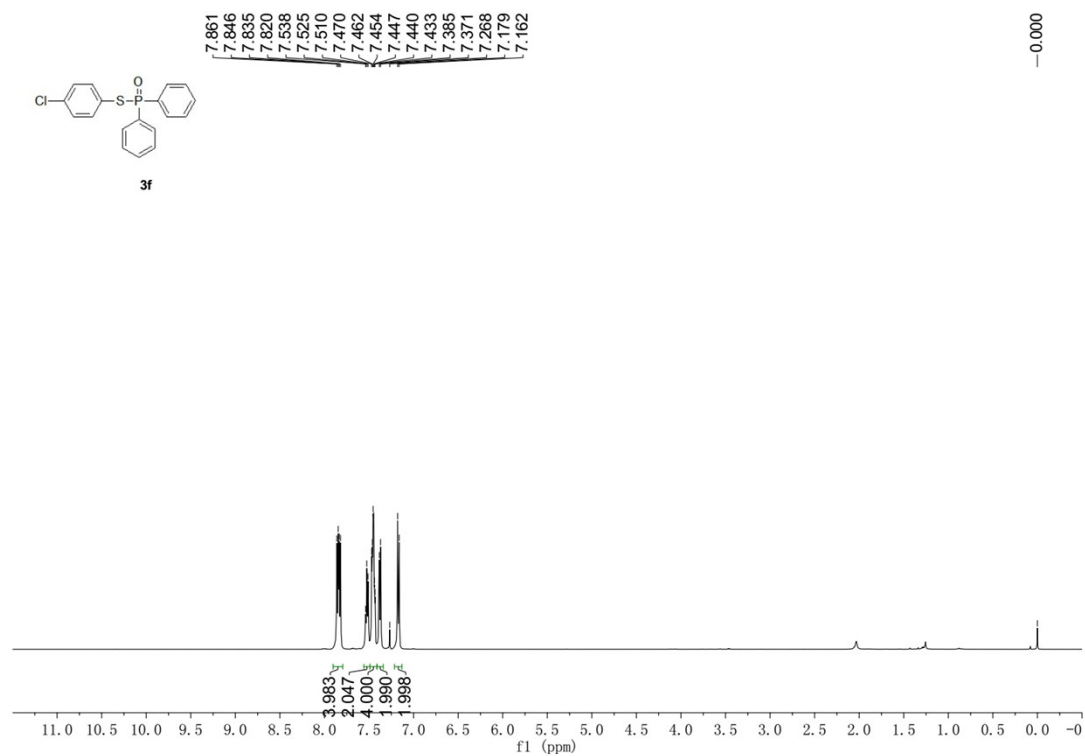
¹H NMR spectrum of compound **3e**



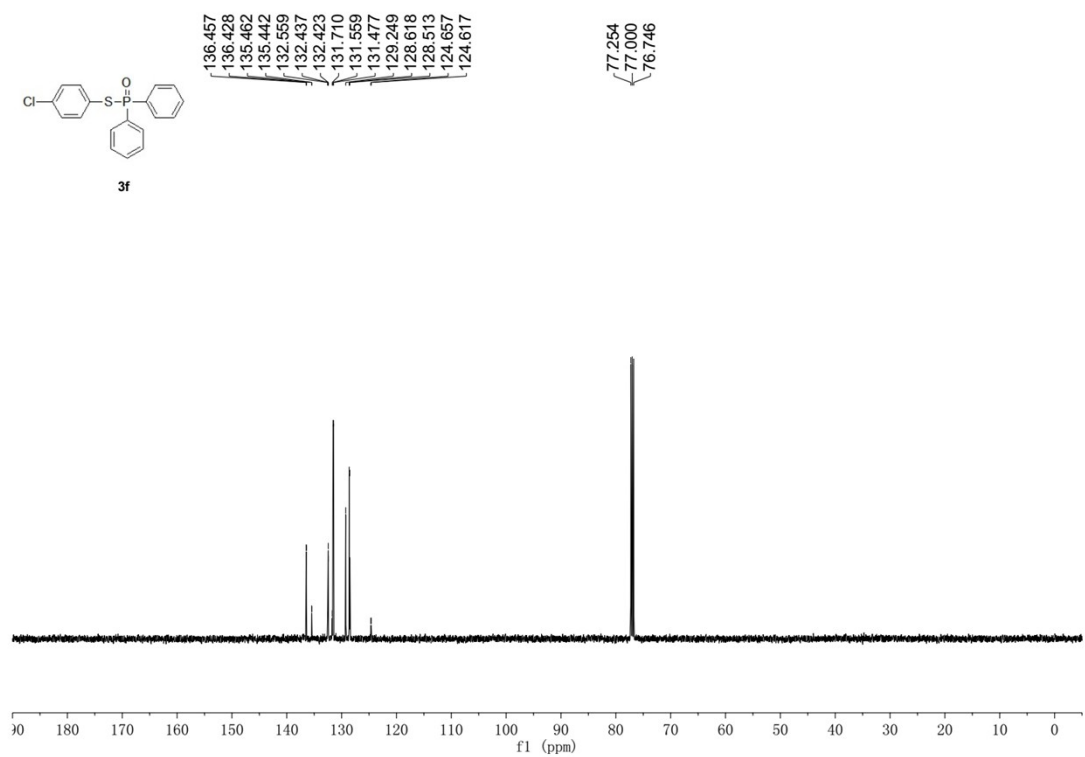
¹³C NMR spectrum of compound **3e**



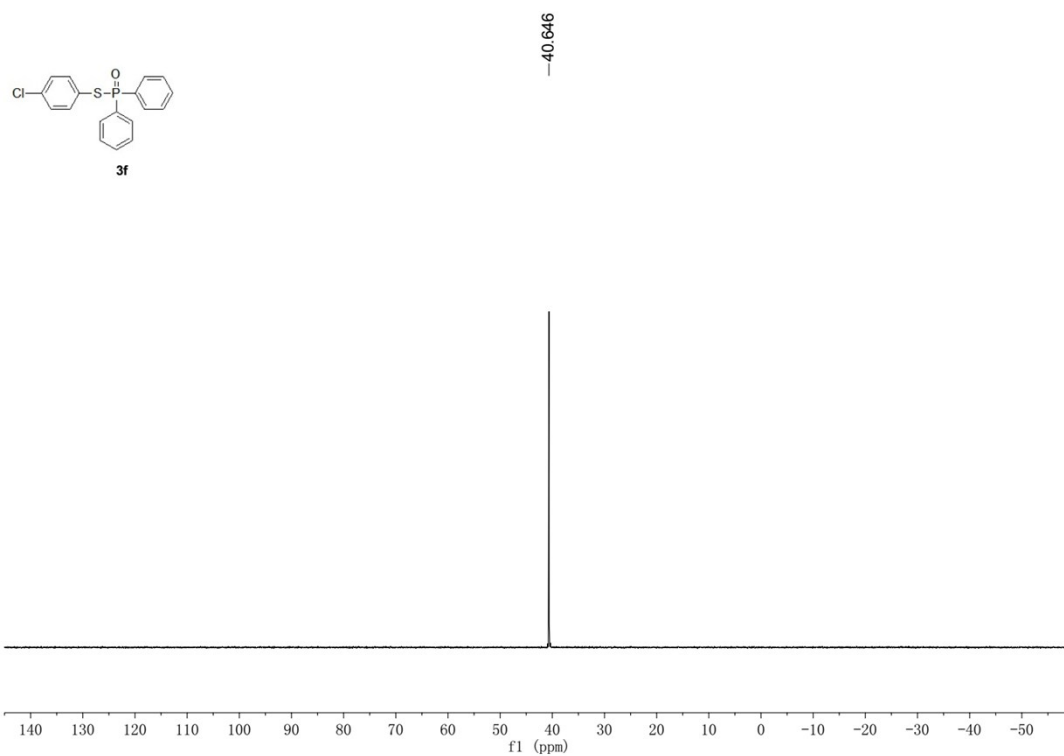
³¹P NMR spectrum of compound **3e**



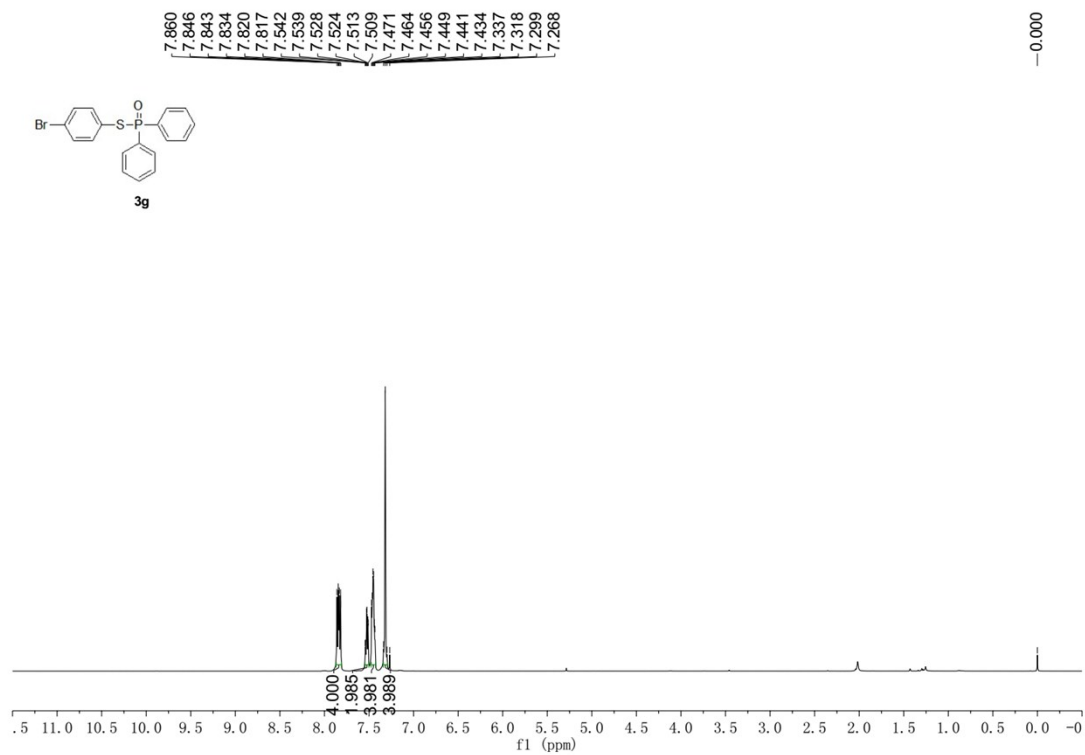
¹H NMR spectrum of compound **3f**



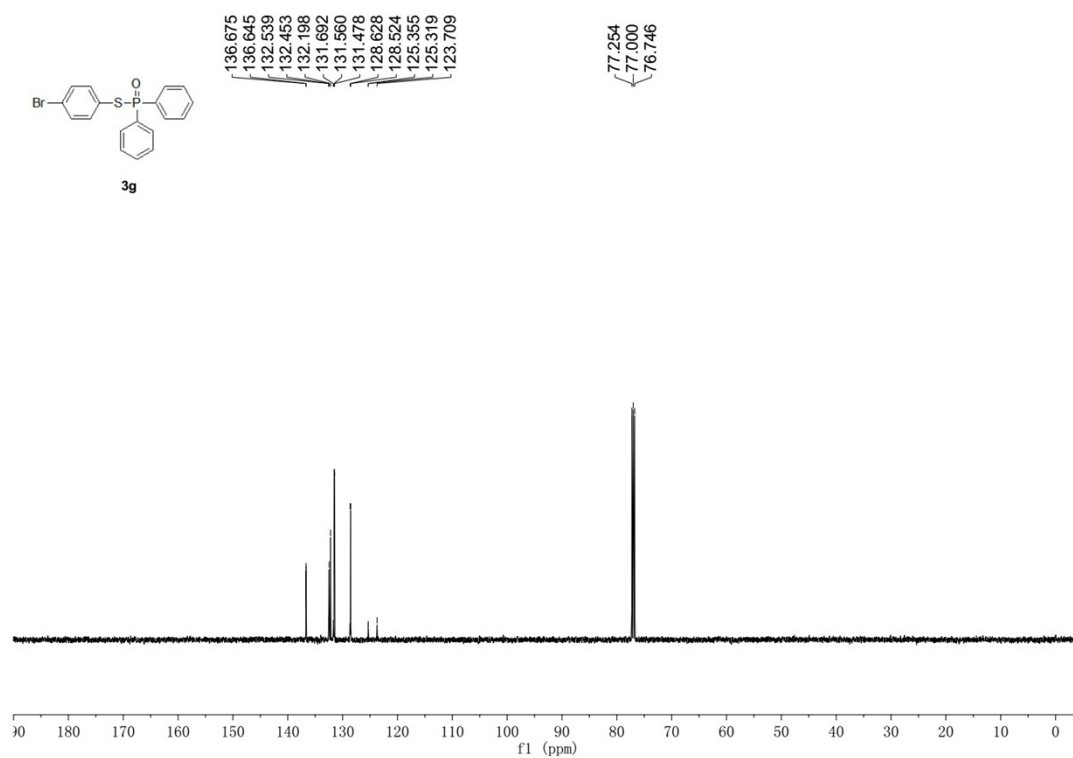
¹³C NMR spectrum of compound **3f**



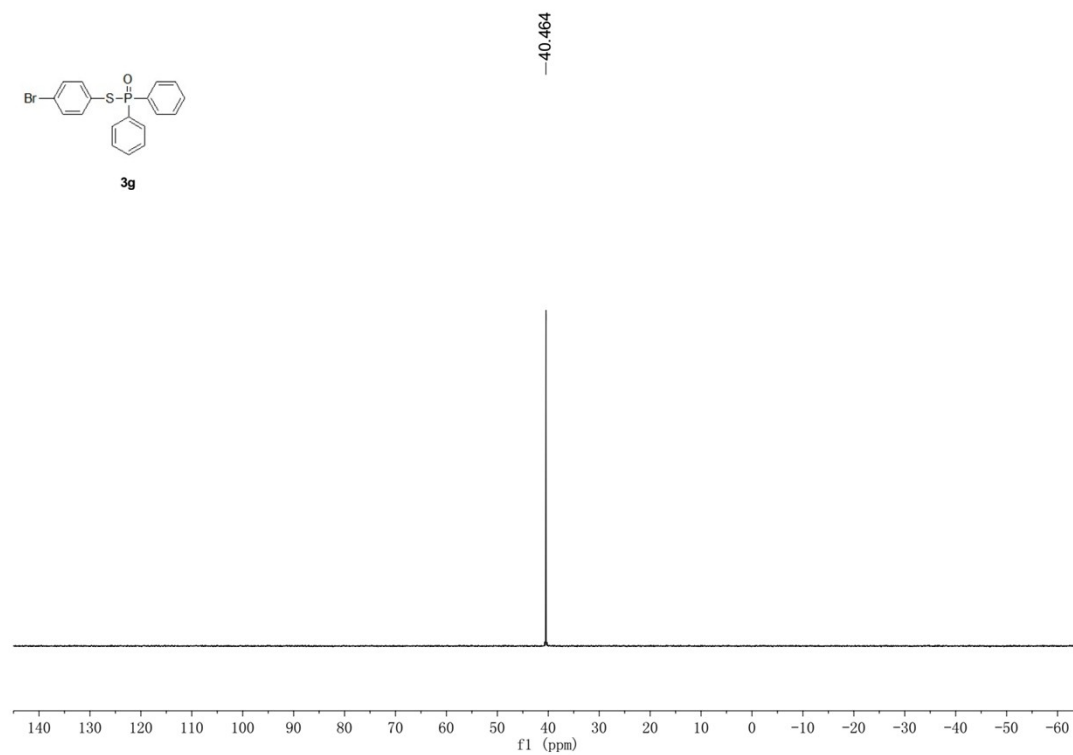
^{31}P NMR spectrum of compound **3f**



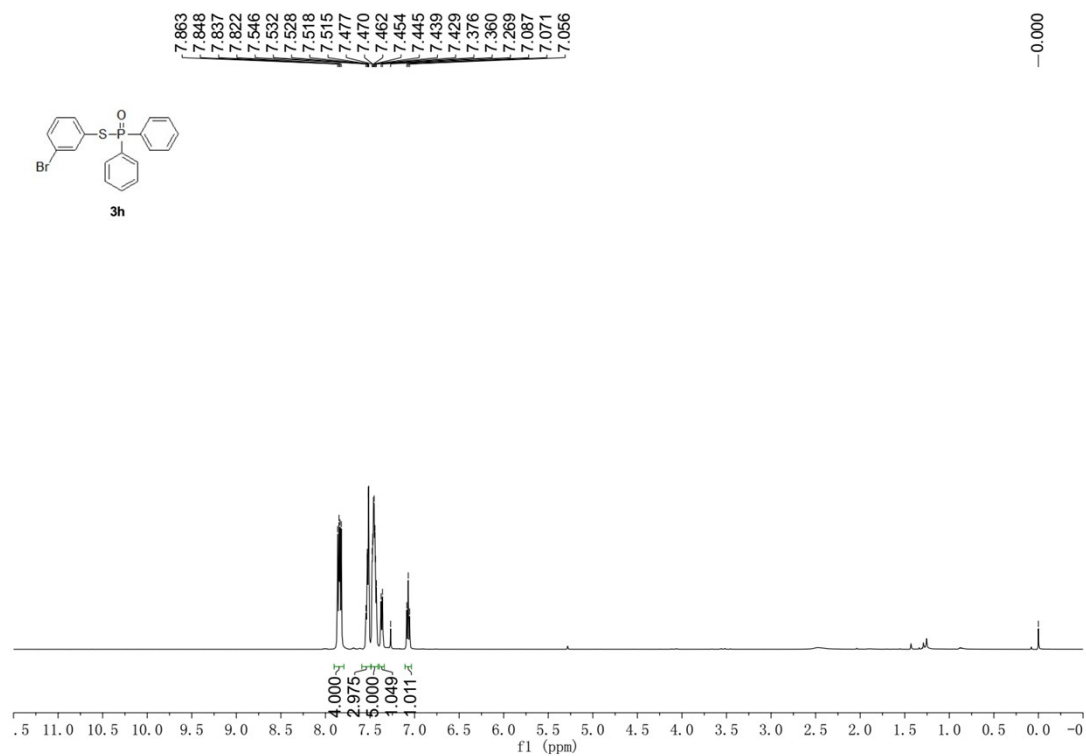
^1H NMR spectrum of compound **3g**



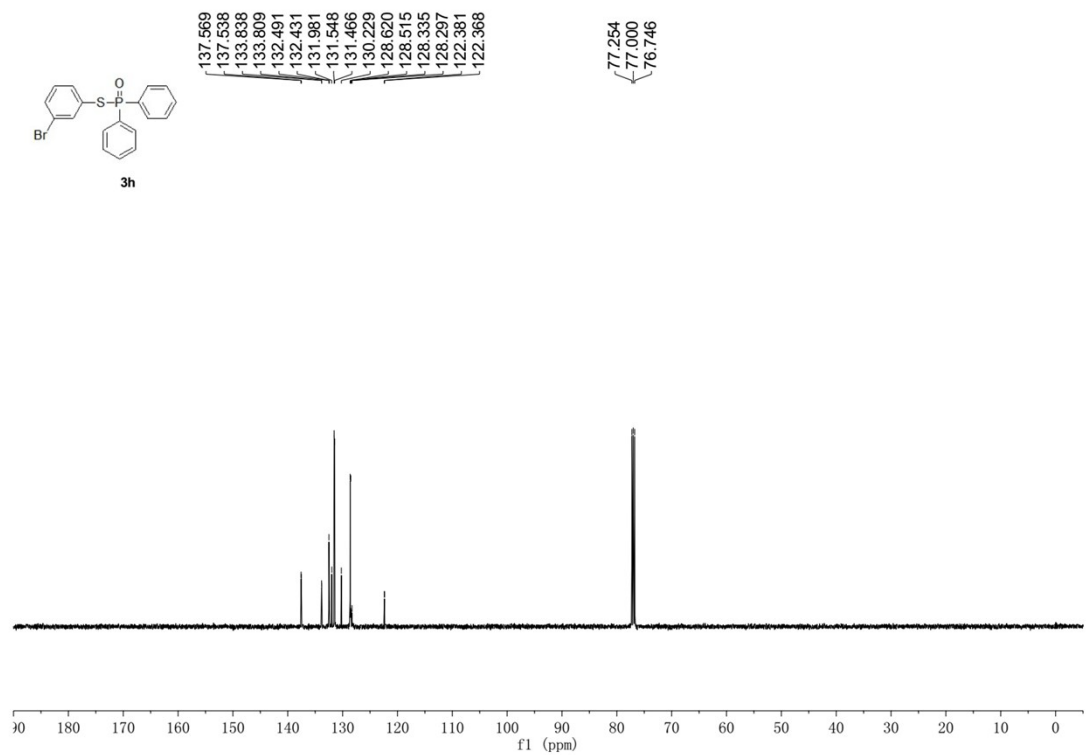
^{13}C NMR spectrum of compound **3g**



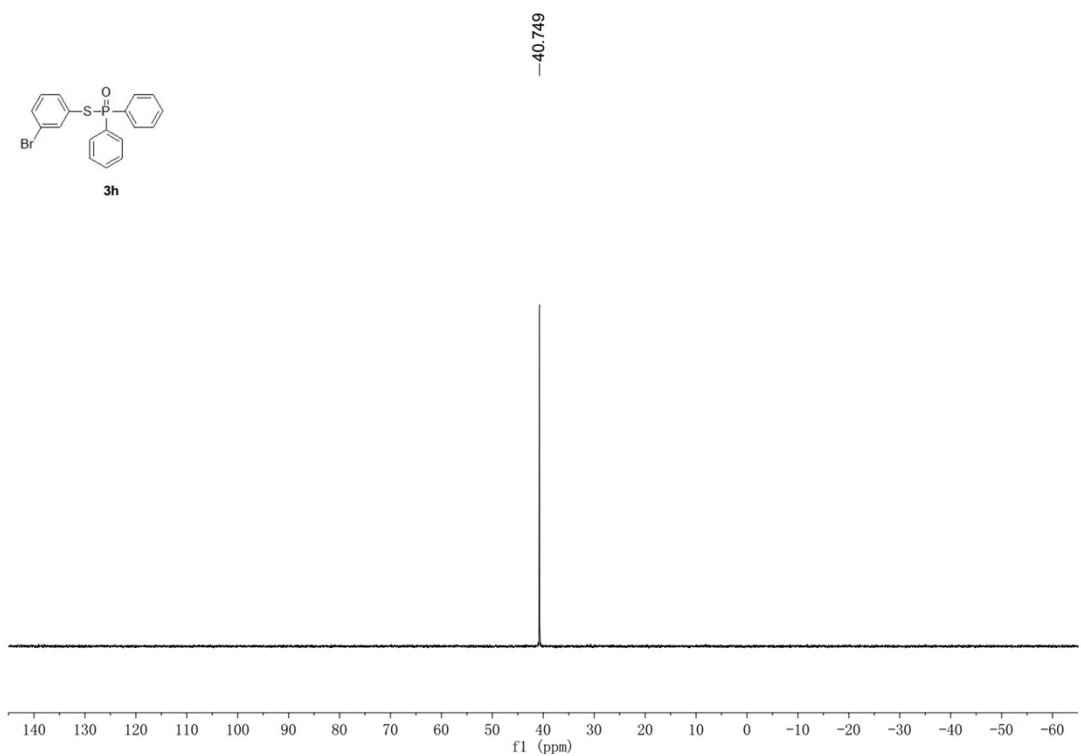
^{31}P NMR spectrum of compound **3g**



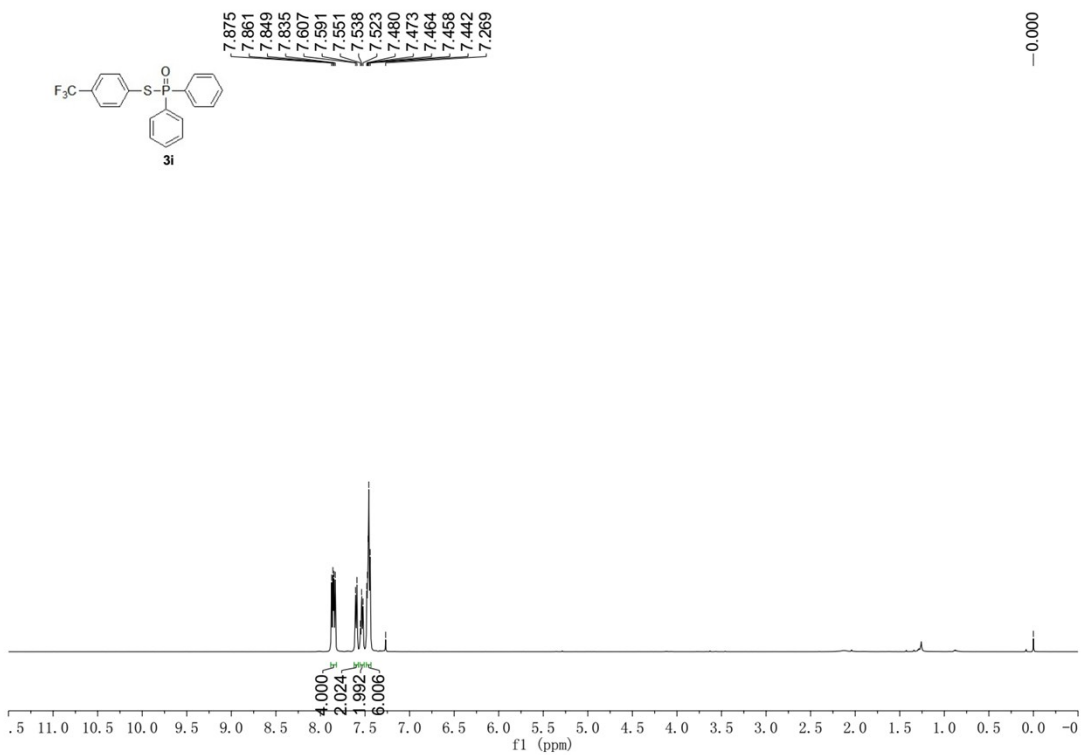
^1H NMR spectrum of compound **3h**



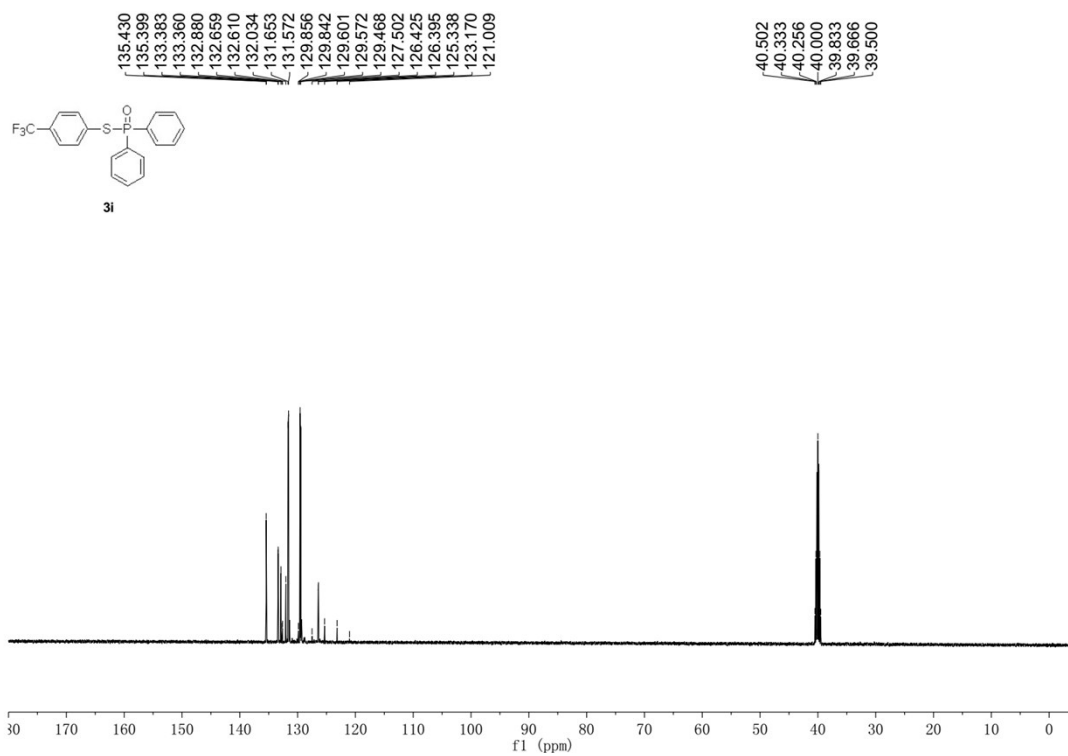
^{13}C NMR spectrum of compound **3h**



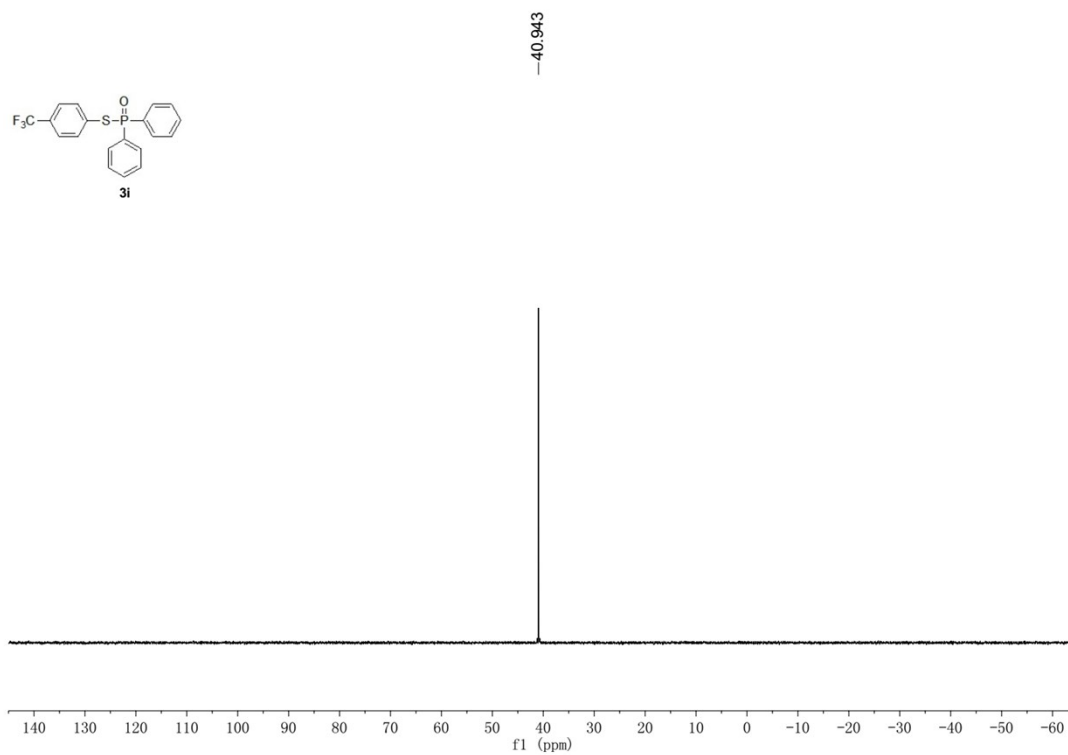
³¹P NMR spectrum of compound **3h**



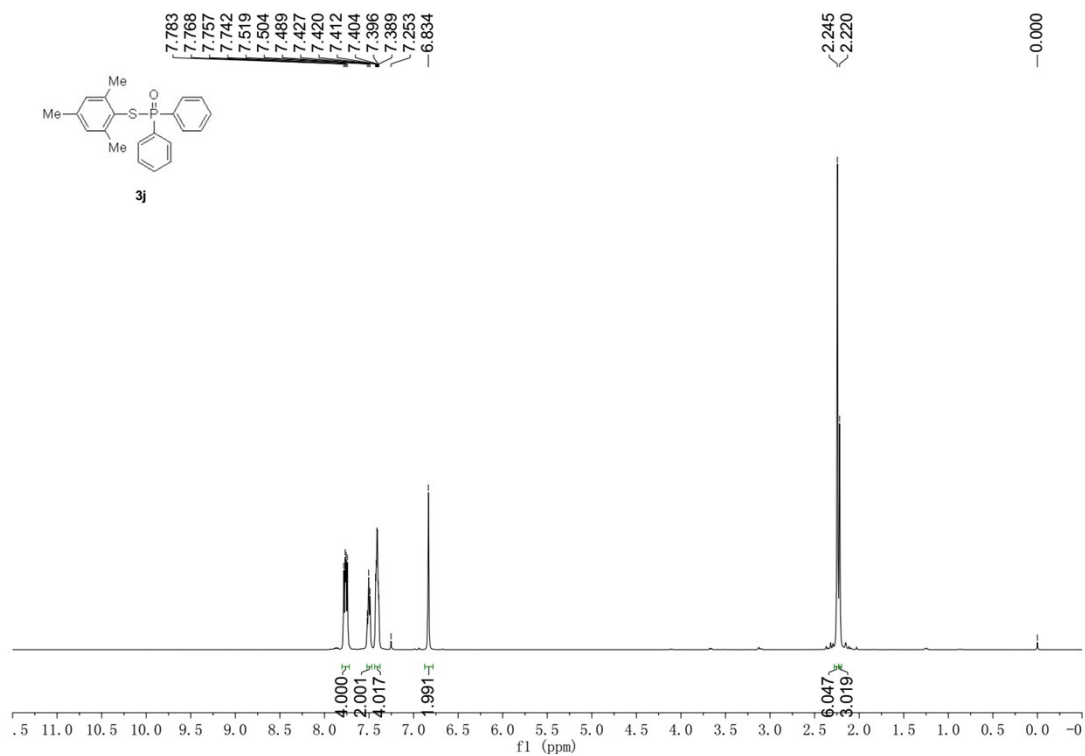
¹H NMR spectrum of compound **3i**



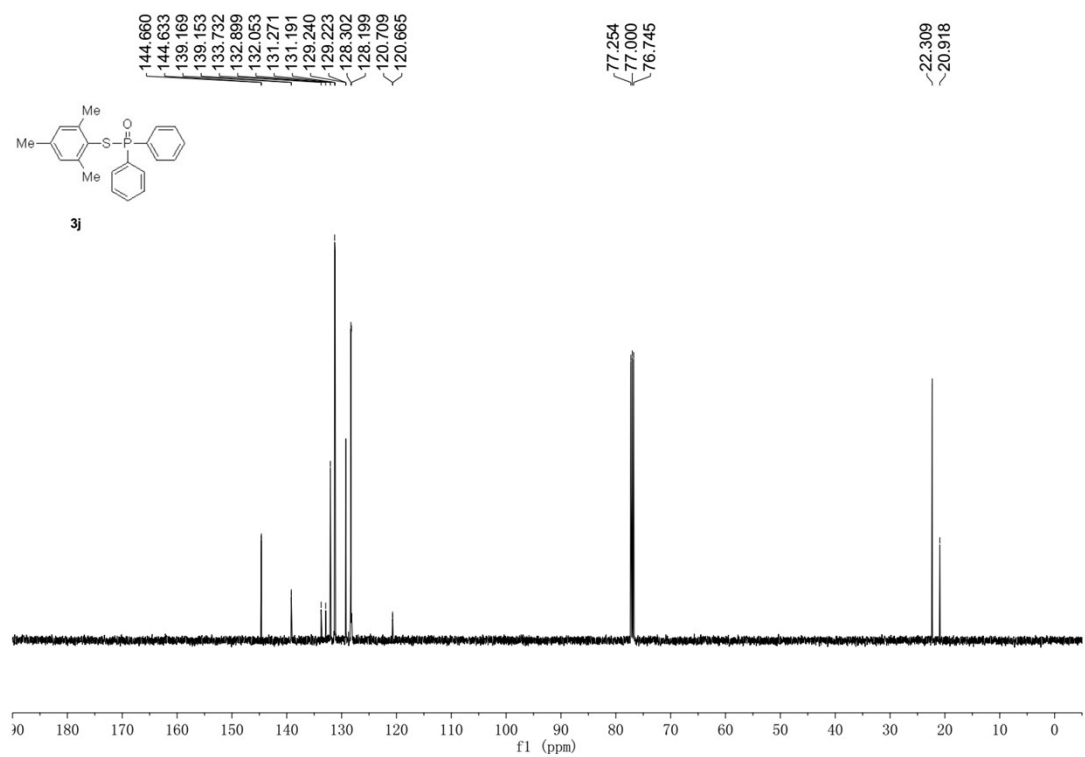
^{13}C NMR spectrum of compound **3i**



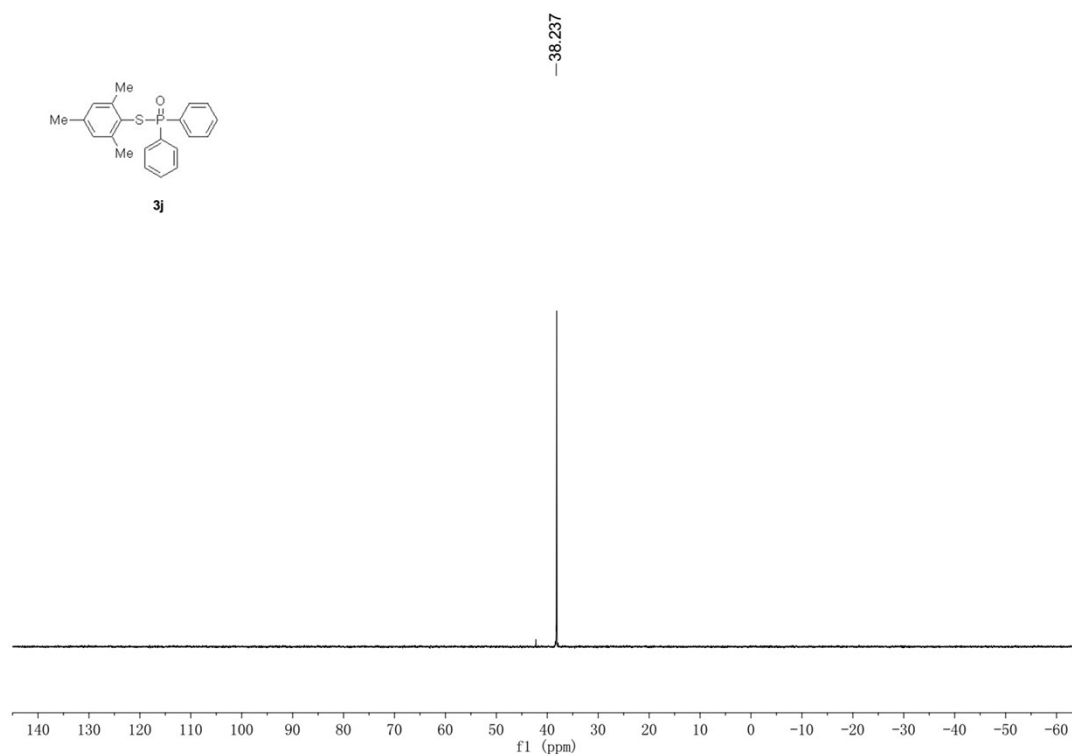
^{31}P NMR spectrum of compound **3i**



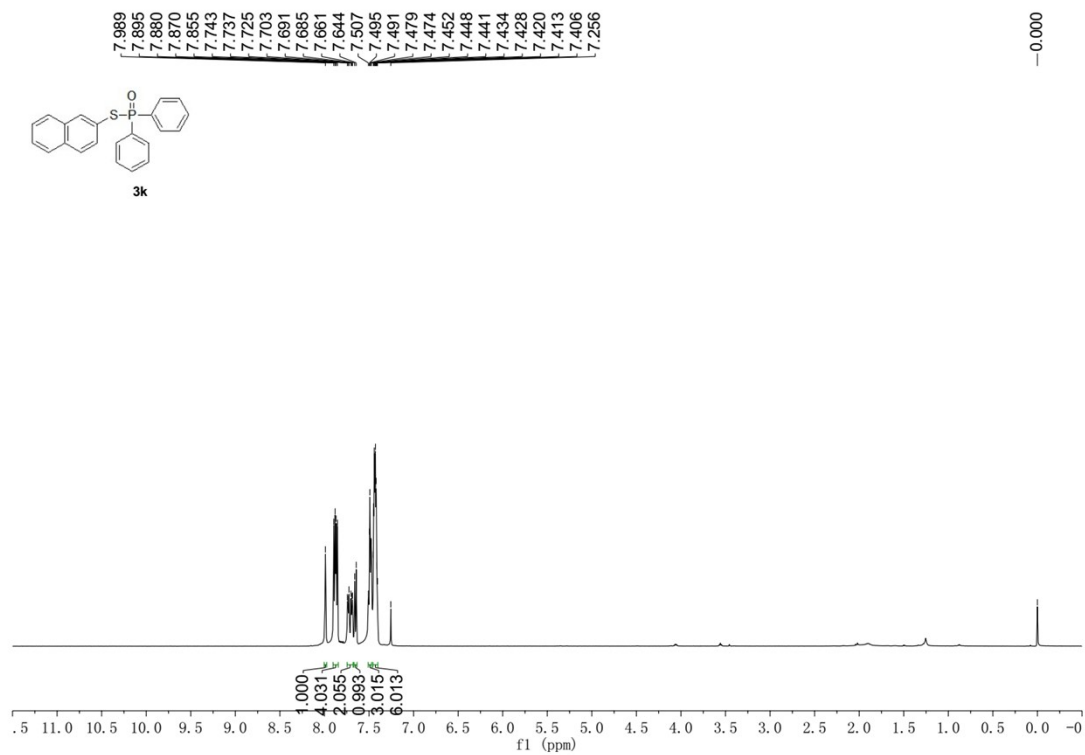
¹H NMR spectrum of compound **3j**



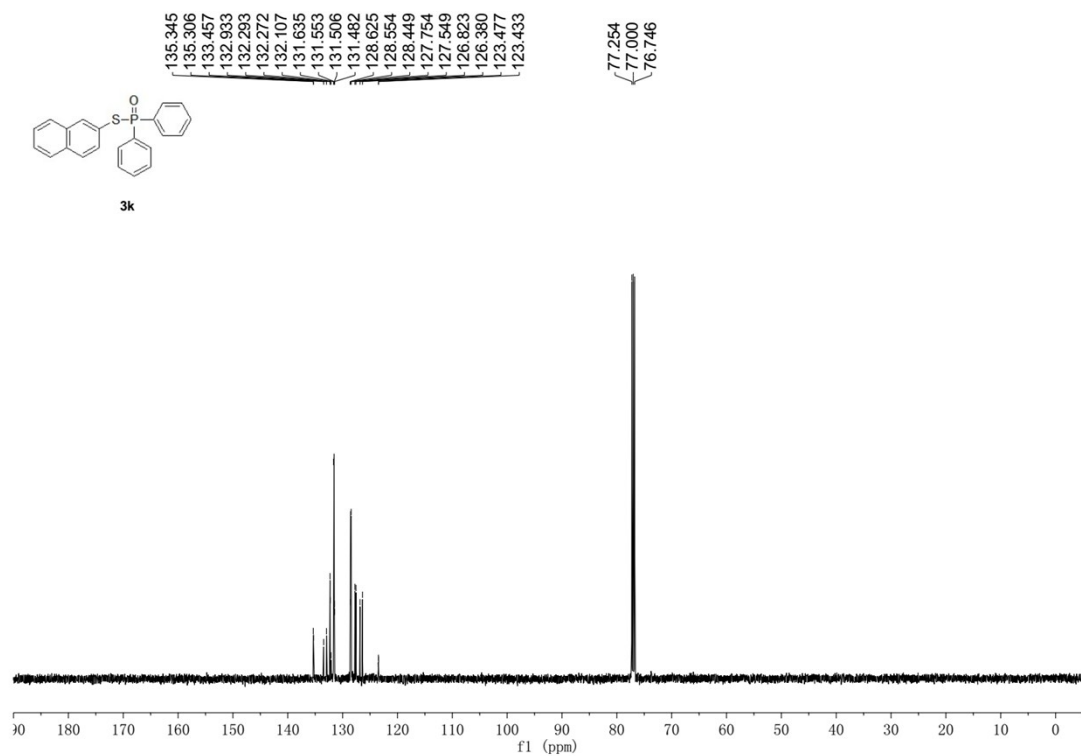
¹³C NMR spectrum of compound **3j**



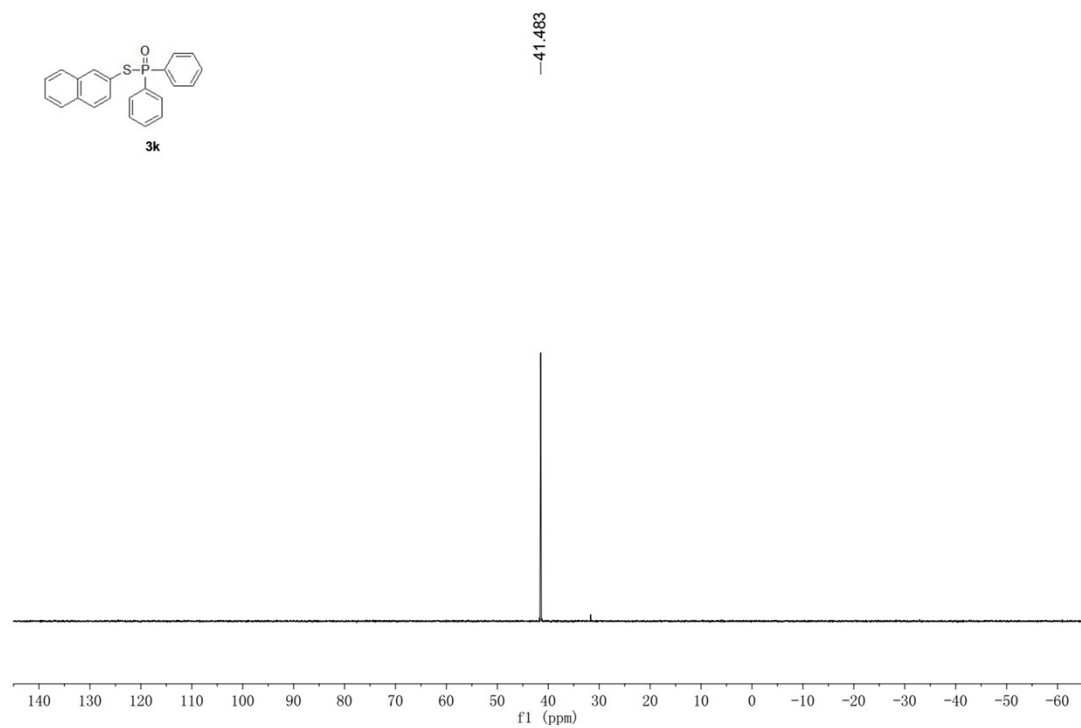
³¹P NMR spectrum of compound **3j**



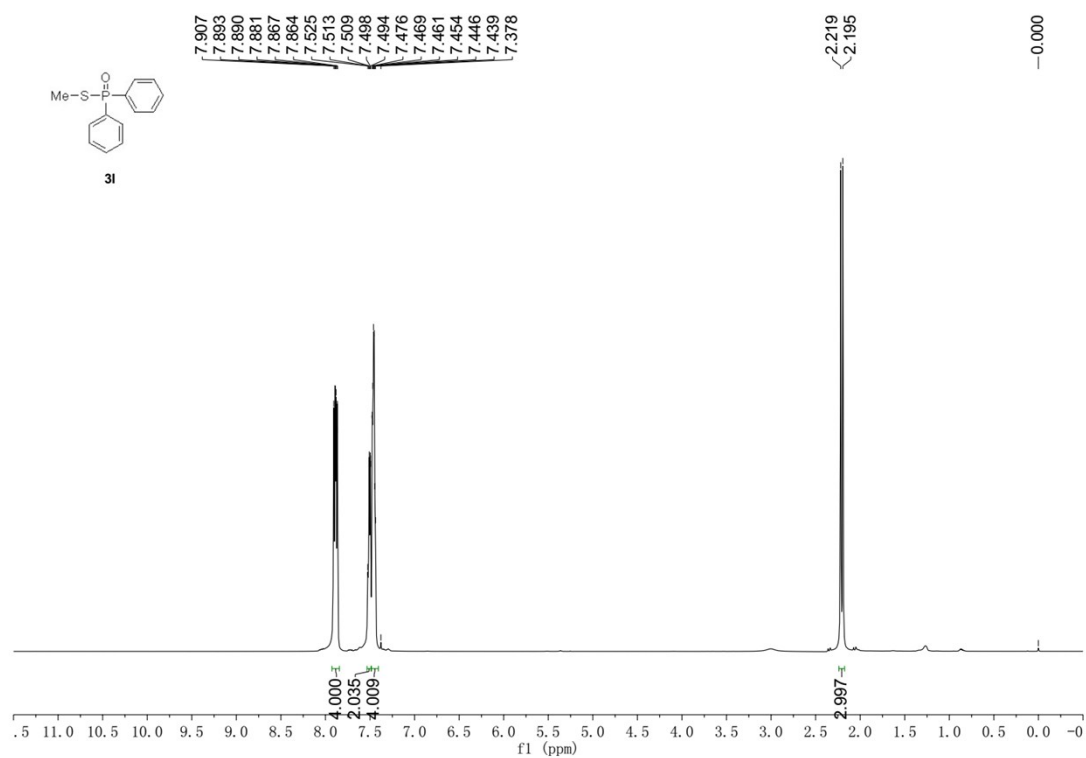
¹H NMR spectrum of compound **3k**



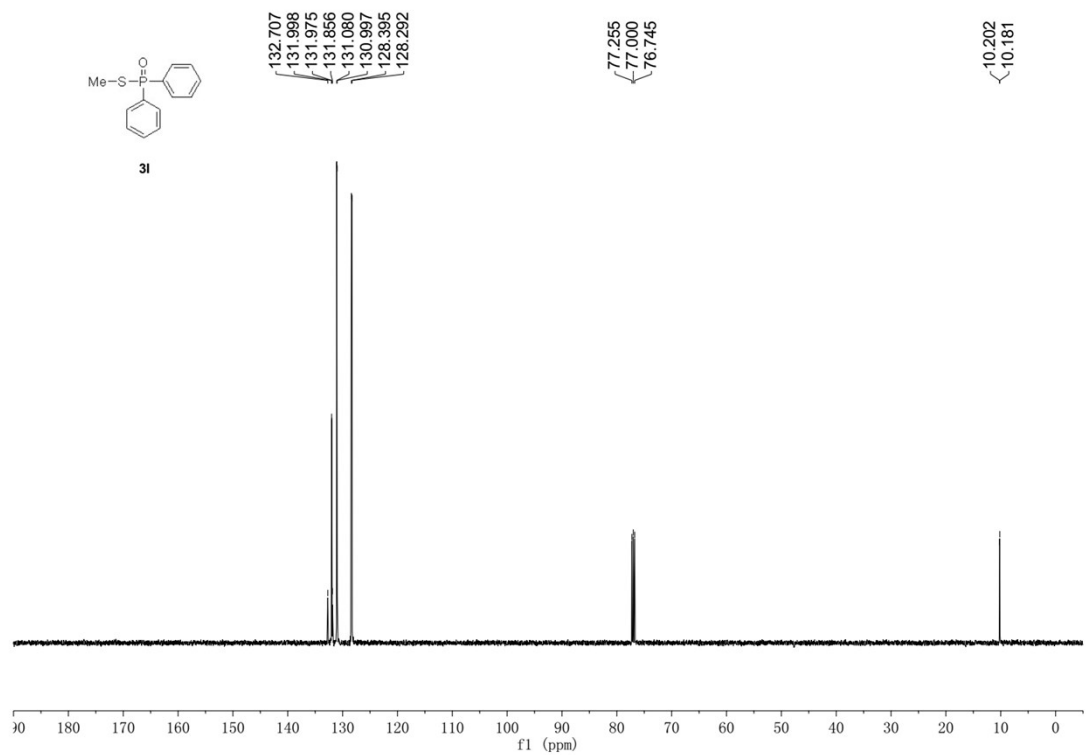
¹³C NMR spectrum of compound **3k**



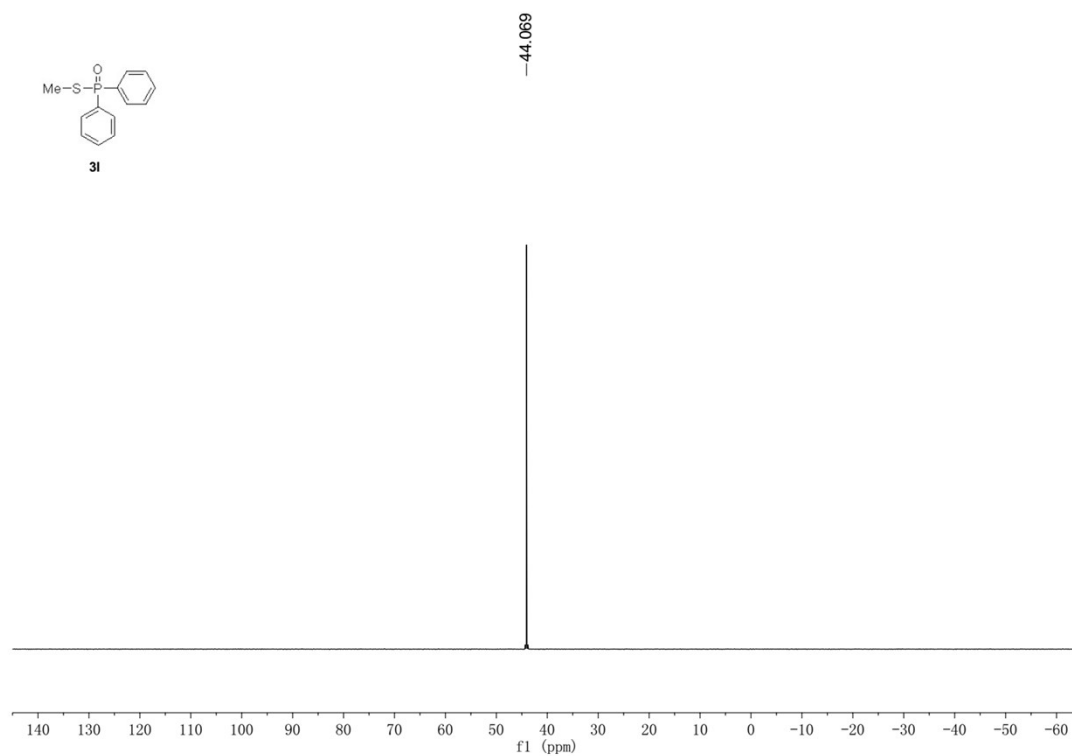
³¹P NMR spectrum of compound **3k**



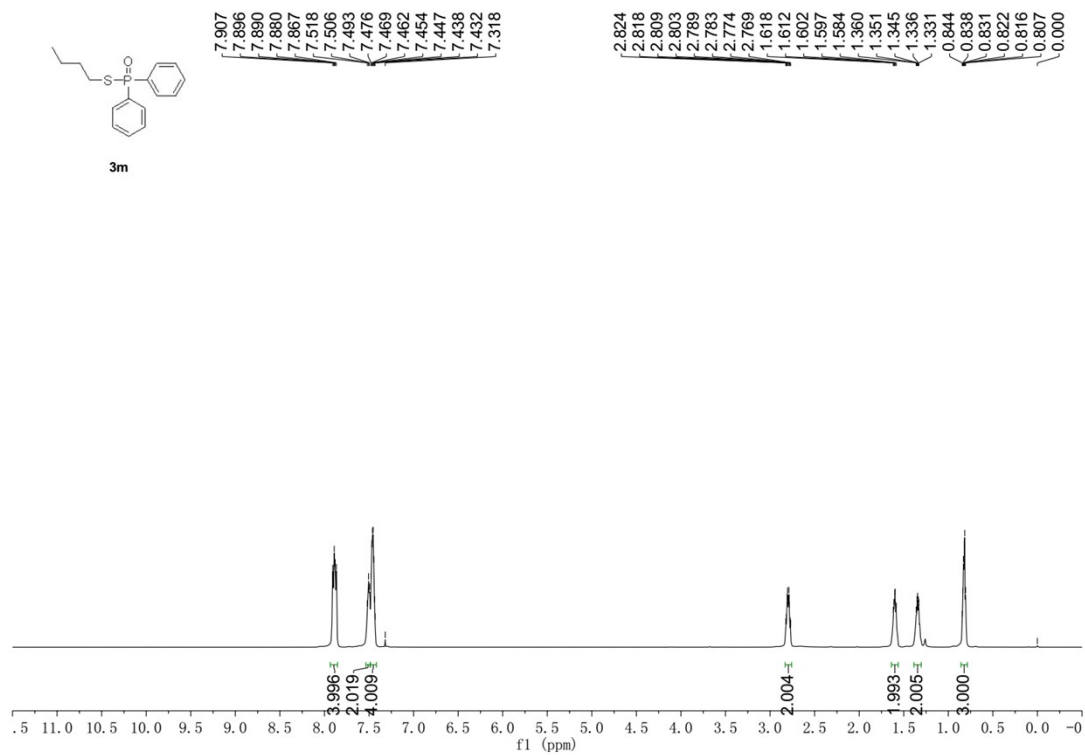
¹H NMR spectrum of compound **31**



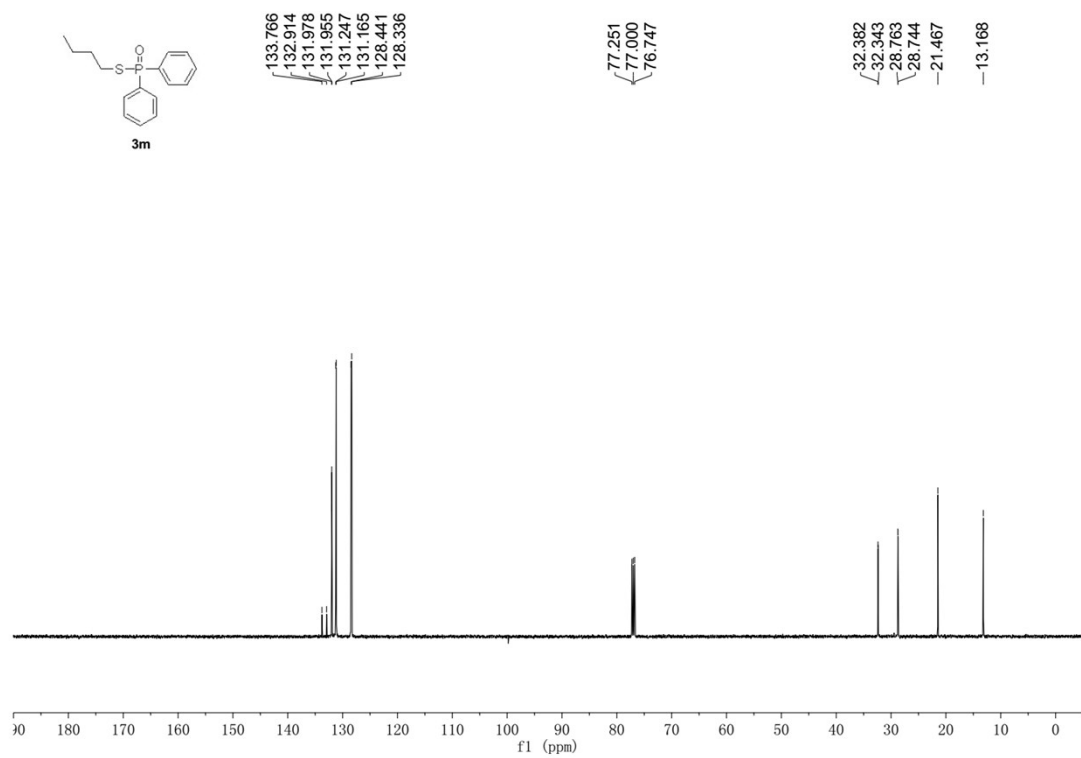
¹³C NMR spectrum of compound **31**



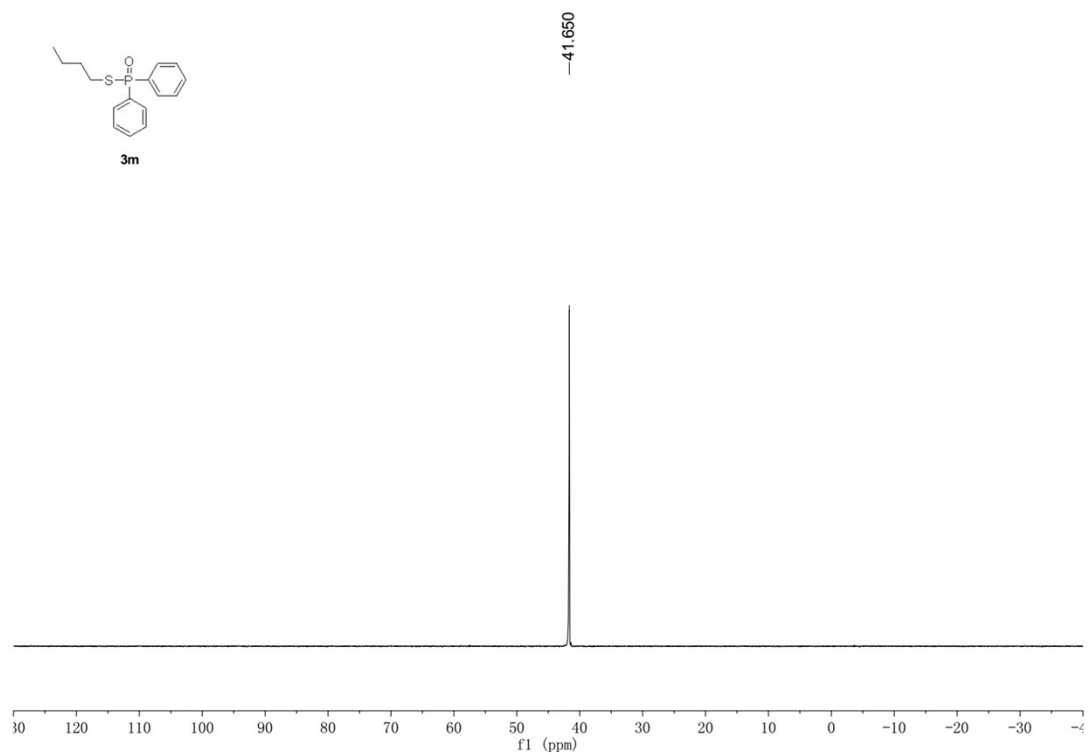
^{31}P NMR spectrum of compound **3l**



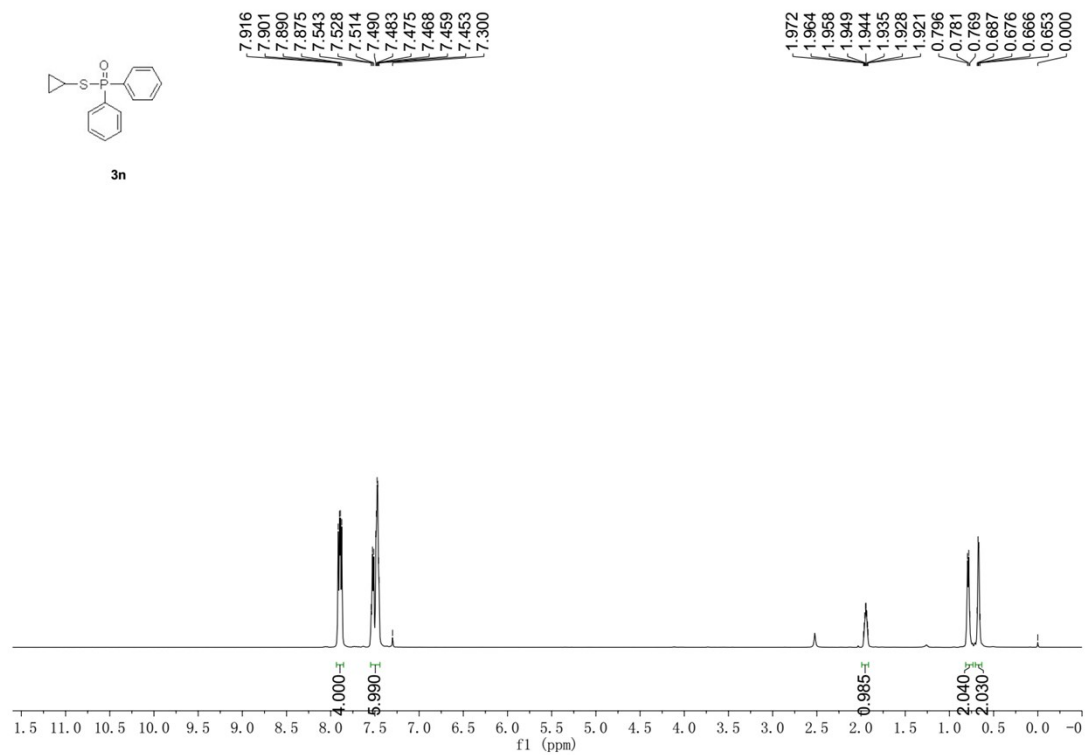
^1H NMR spectrum of compound **3m**



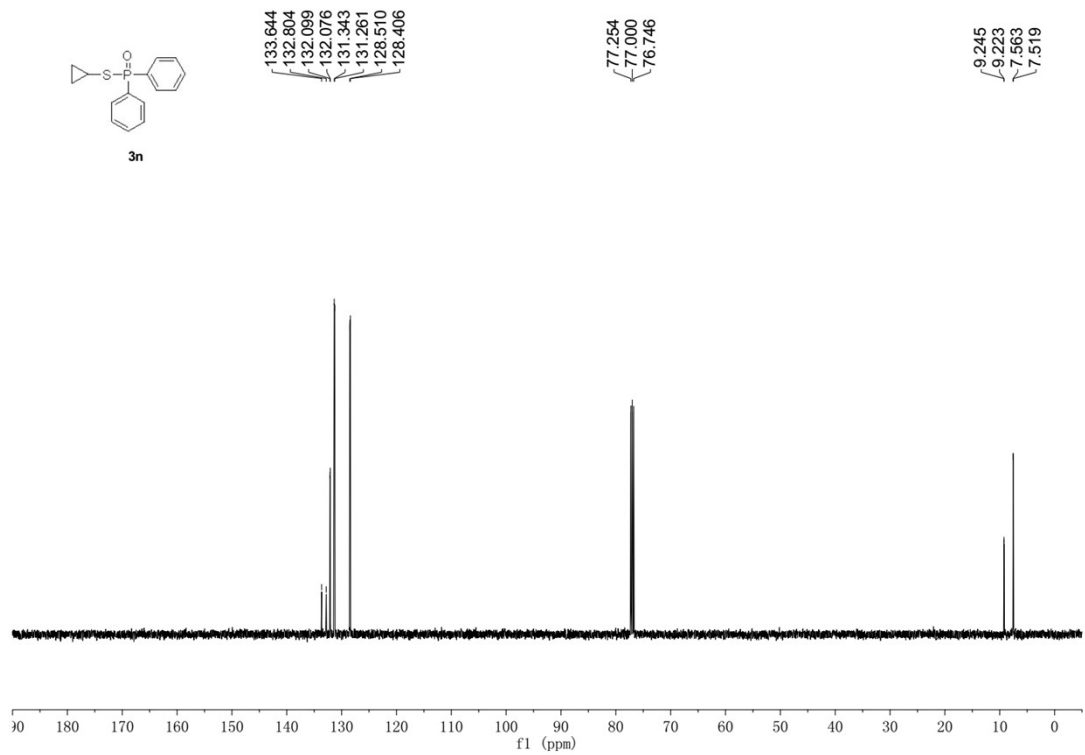
^{13}C NMR spectrum of compound **3m**



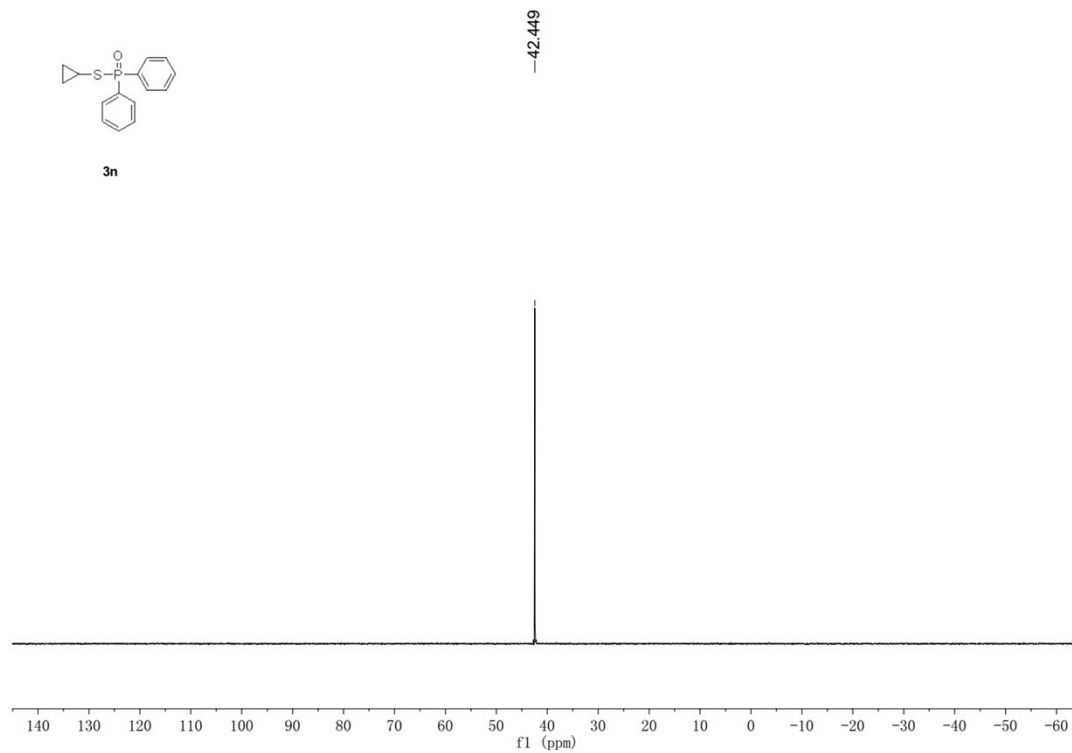
^{31}P NMR spectrum of compound **3m**



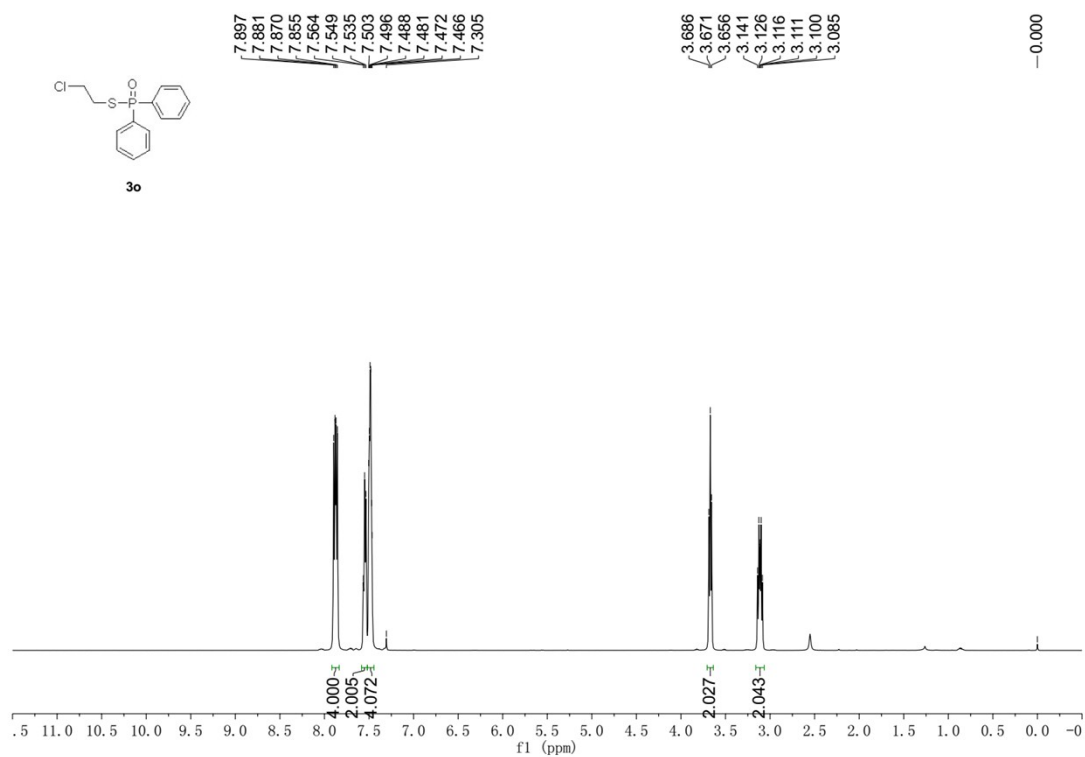
¹H NMR spectrum of compound **3n**



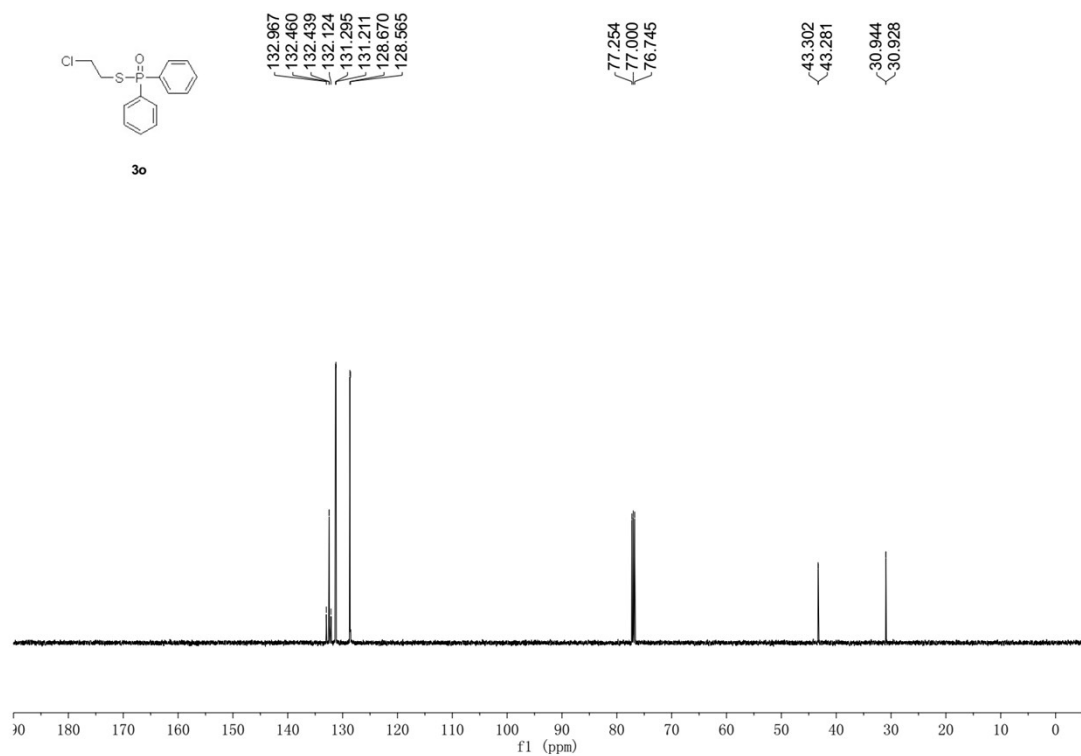
¹³C NMR spectrum of compound **3n**



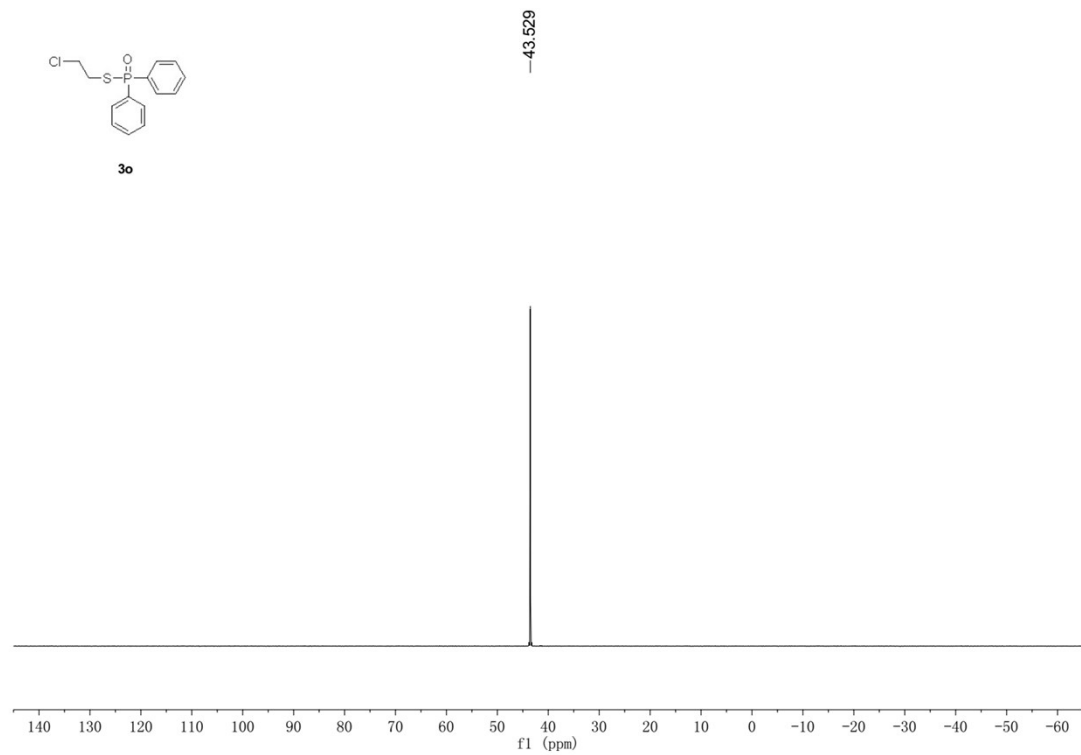
^{31}P NMR spectrum of compound **3n**



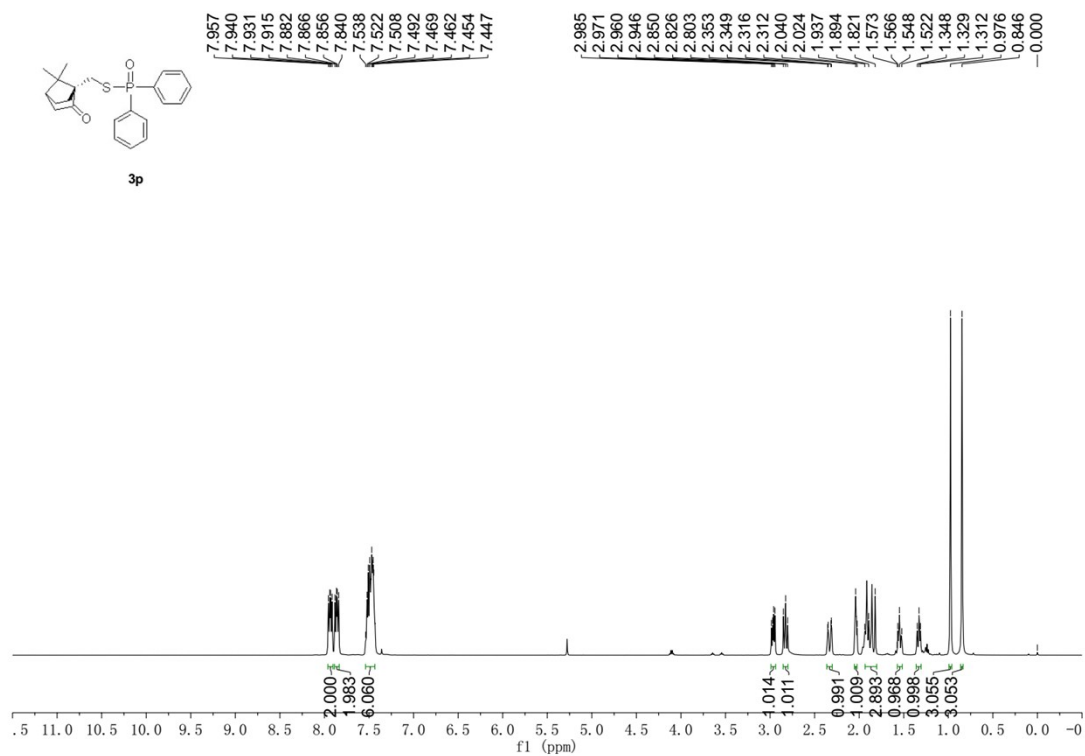
^1H NMR spectrum of compound **3o**



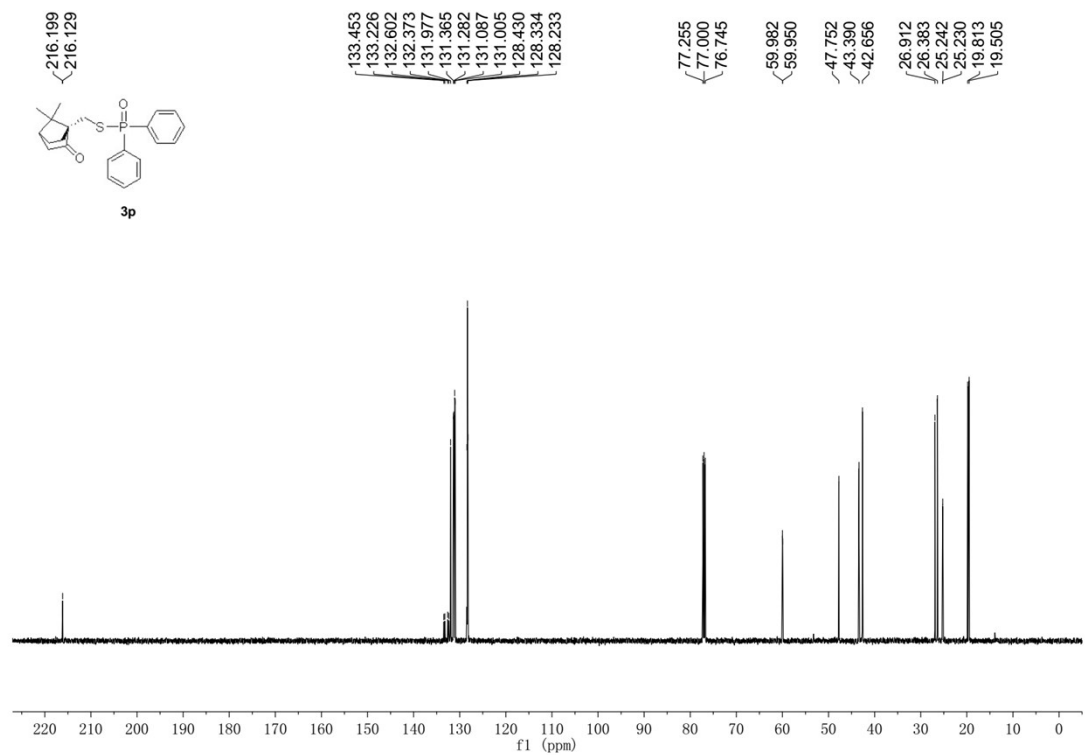
¹³C NMR spectrum of compound **3o**



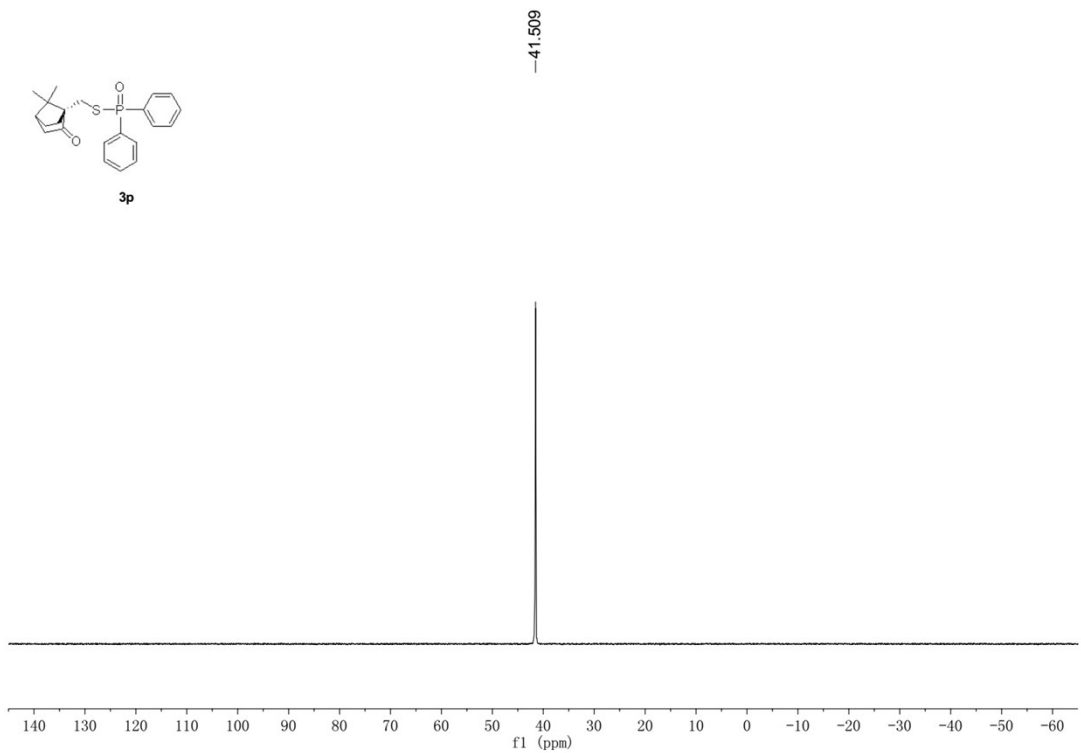
³¹P NMR spectrum of compound **3o**



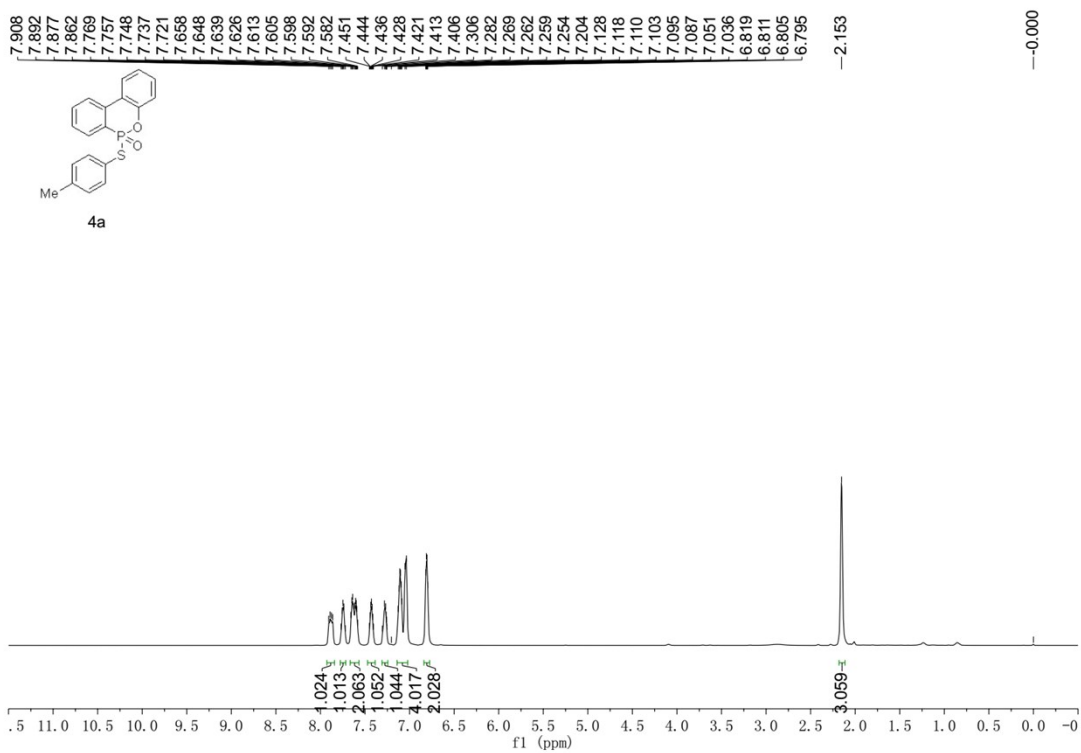
¹H NMR spectrum of compound 3p



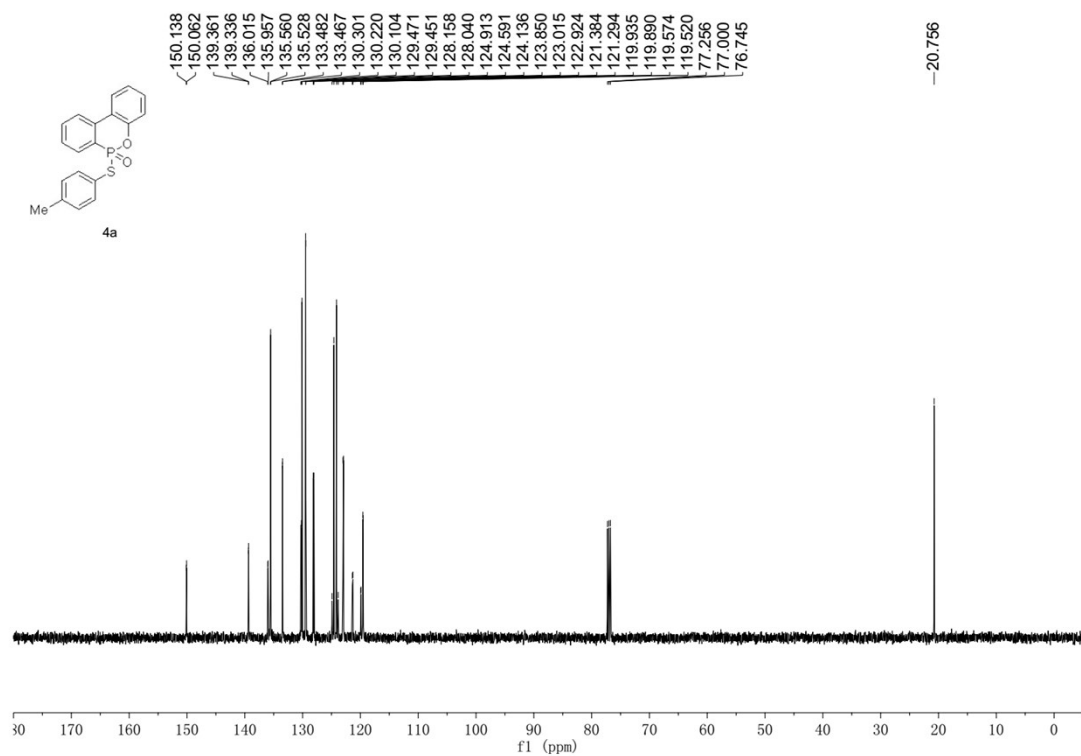
¹³C NMR spectrum of compound 3p



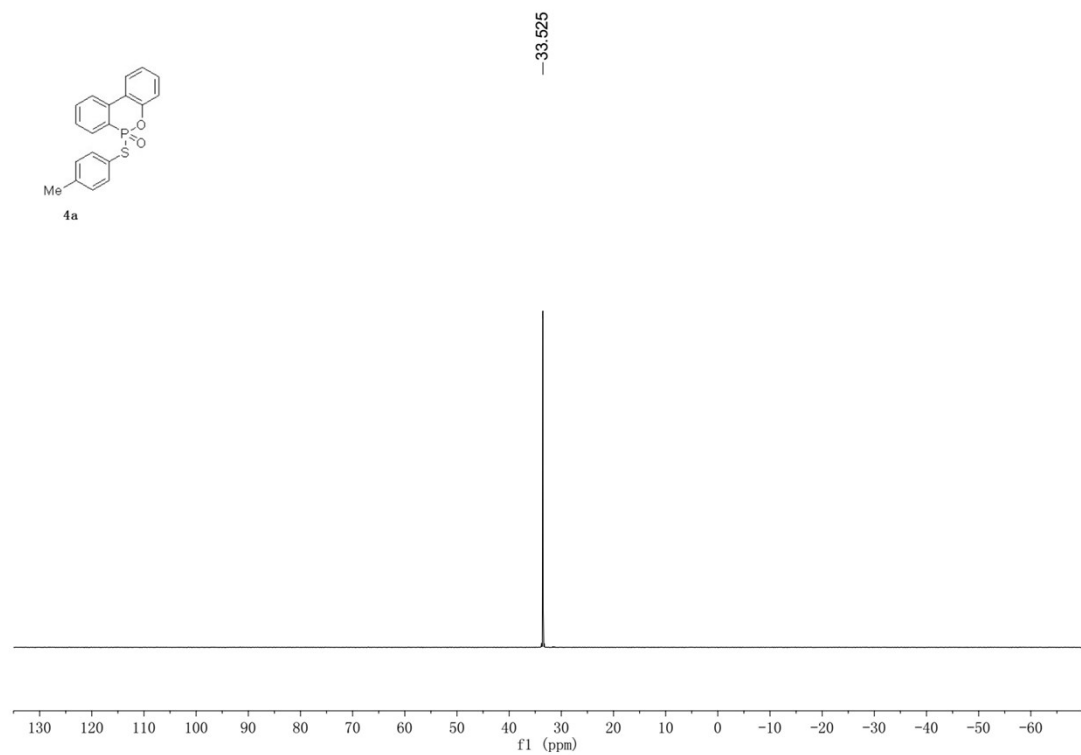
³¹P NMR spectrum of compound **3p**



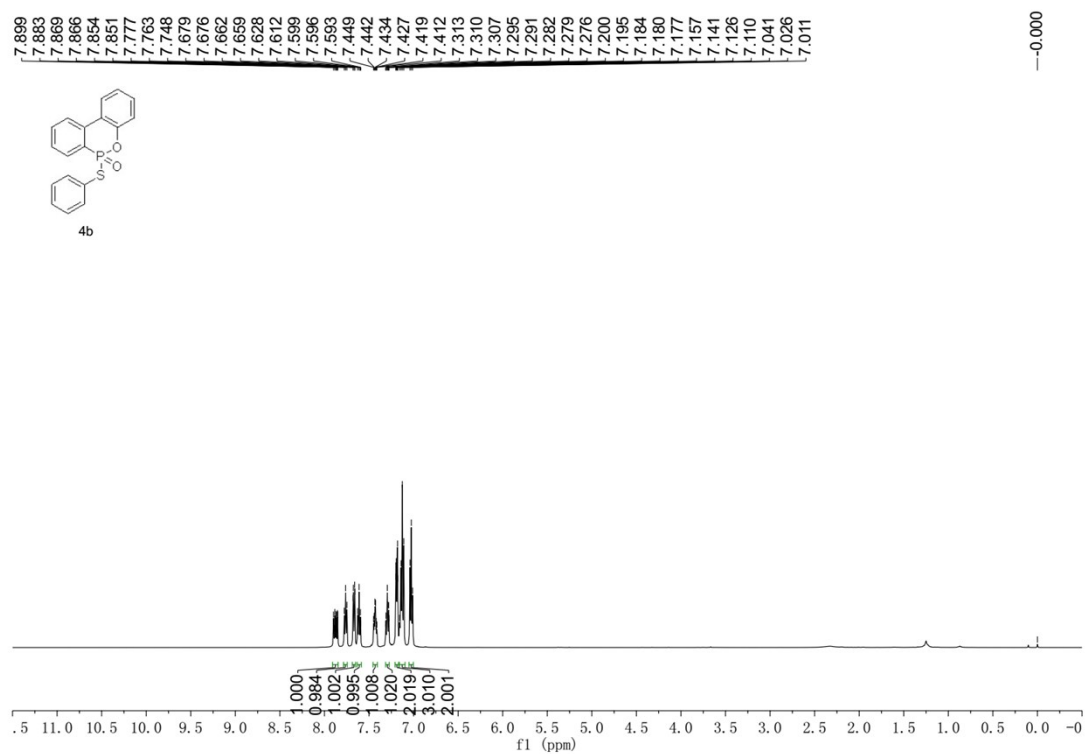
¹H NMR spectrum of compound **4a**



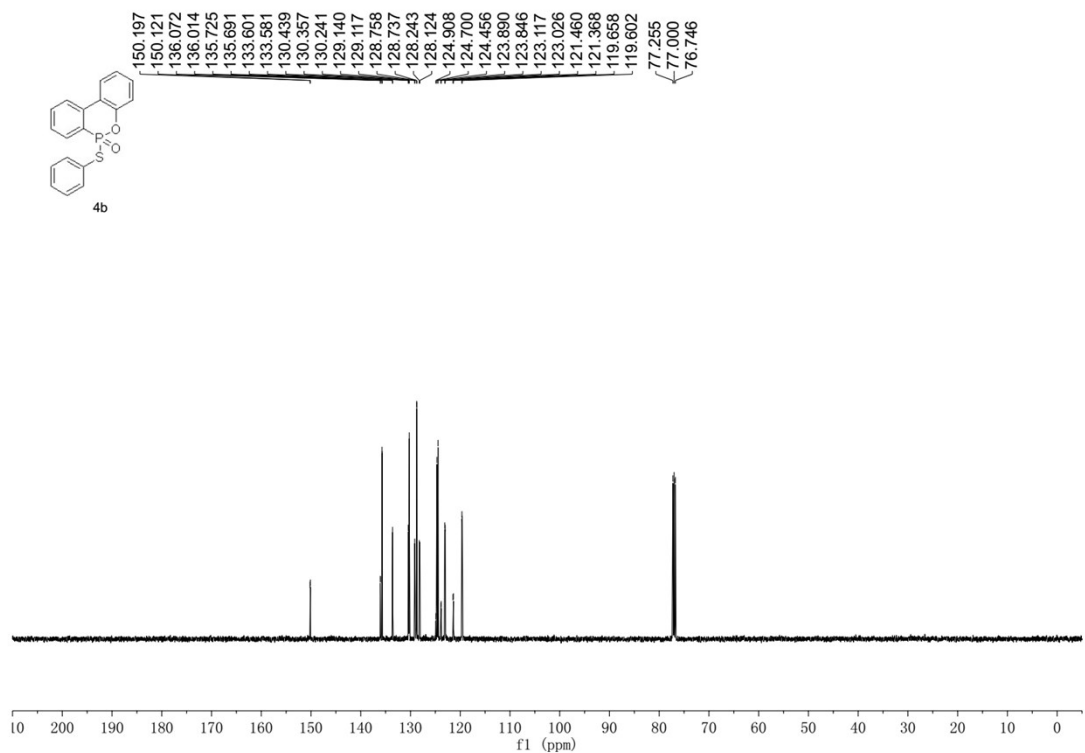
¹³C NMR spectrum of compound 4a



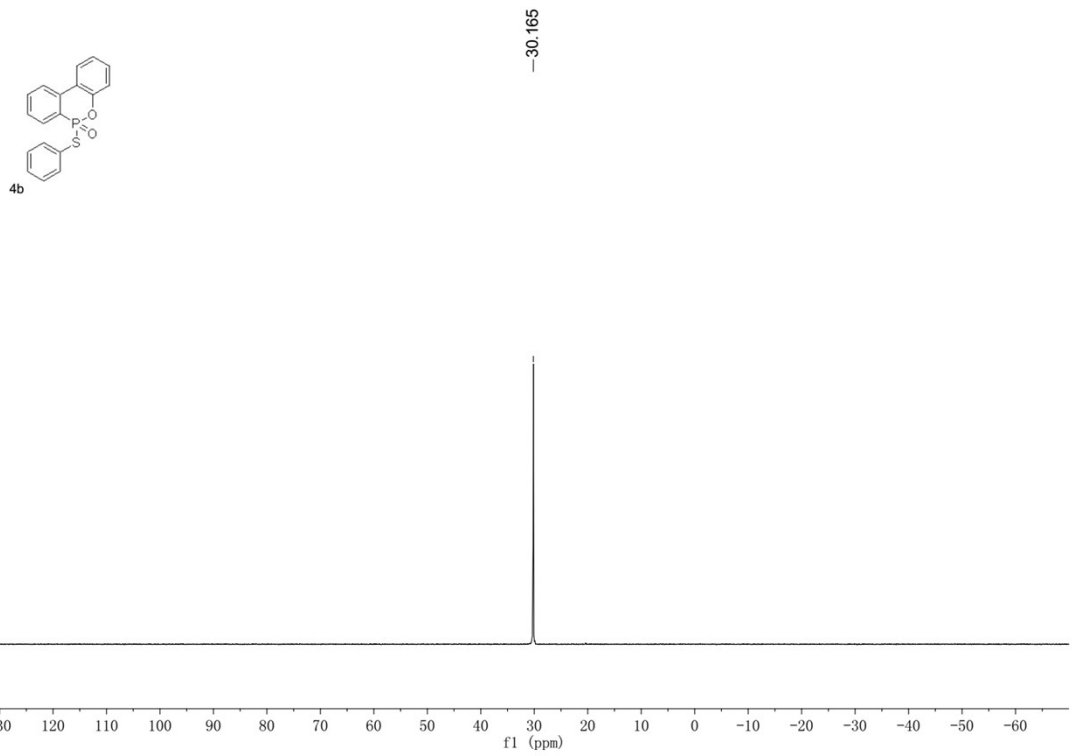
³¹P NMR spectrum of compound 4a



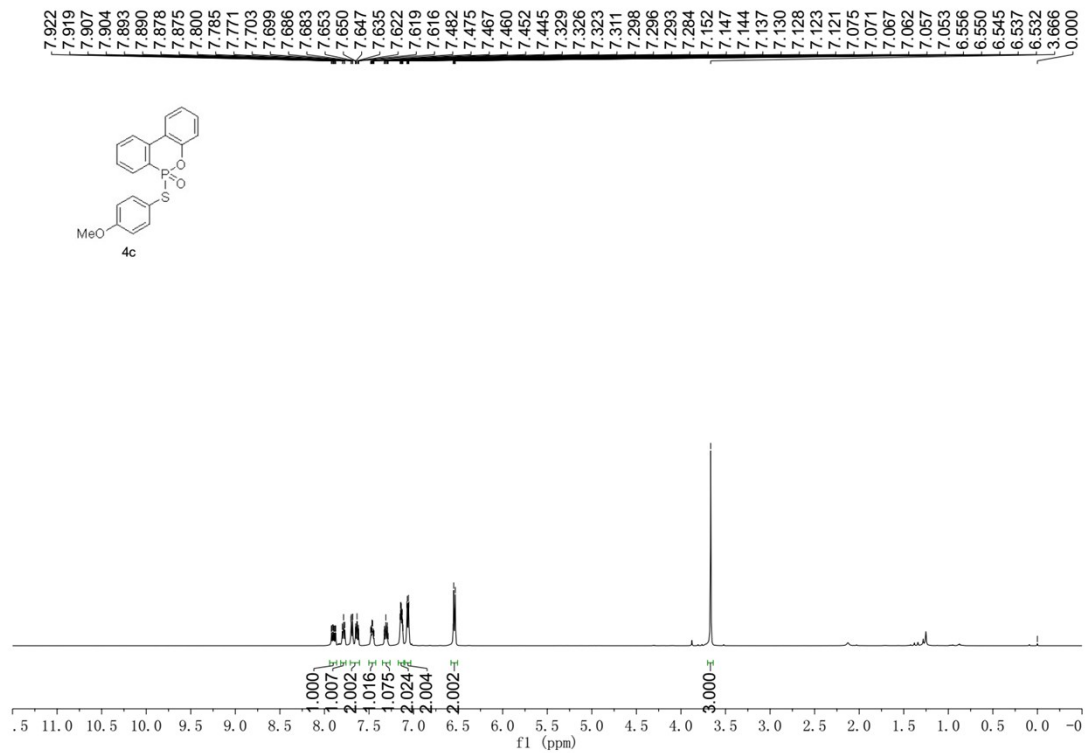
¹H NMR spectrum of compound **4b**



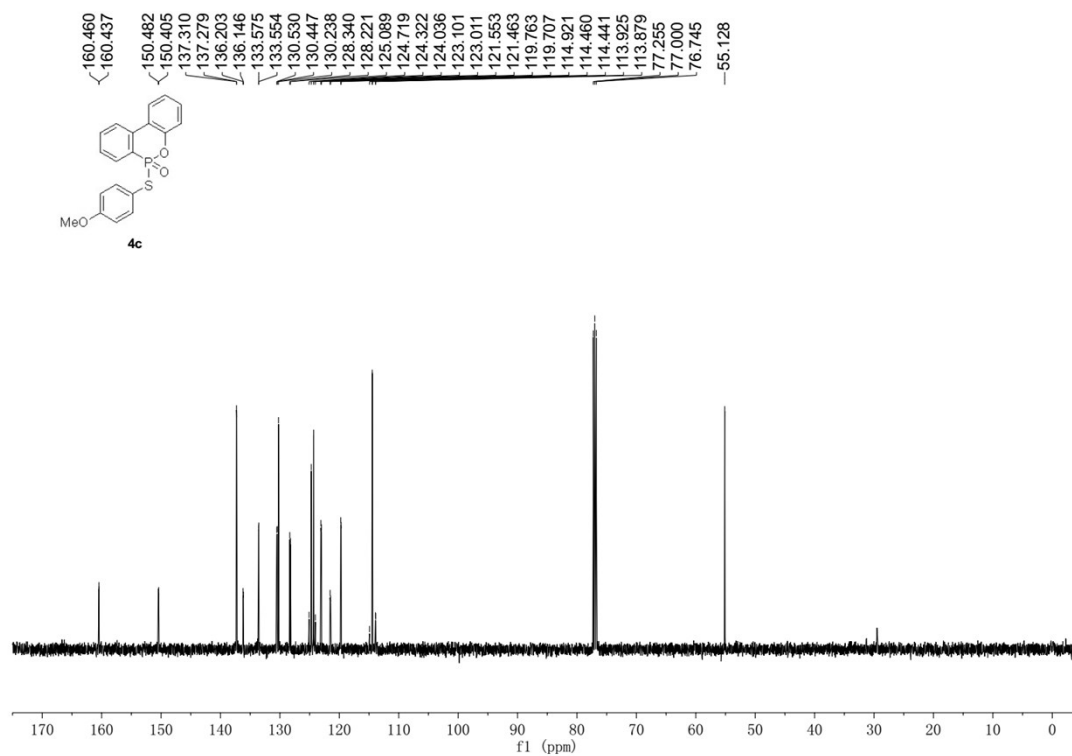
¹³C NMR spectrum of compound **4b**



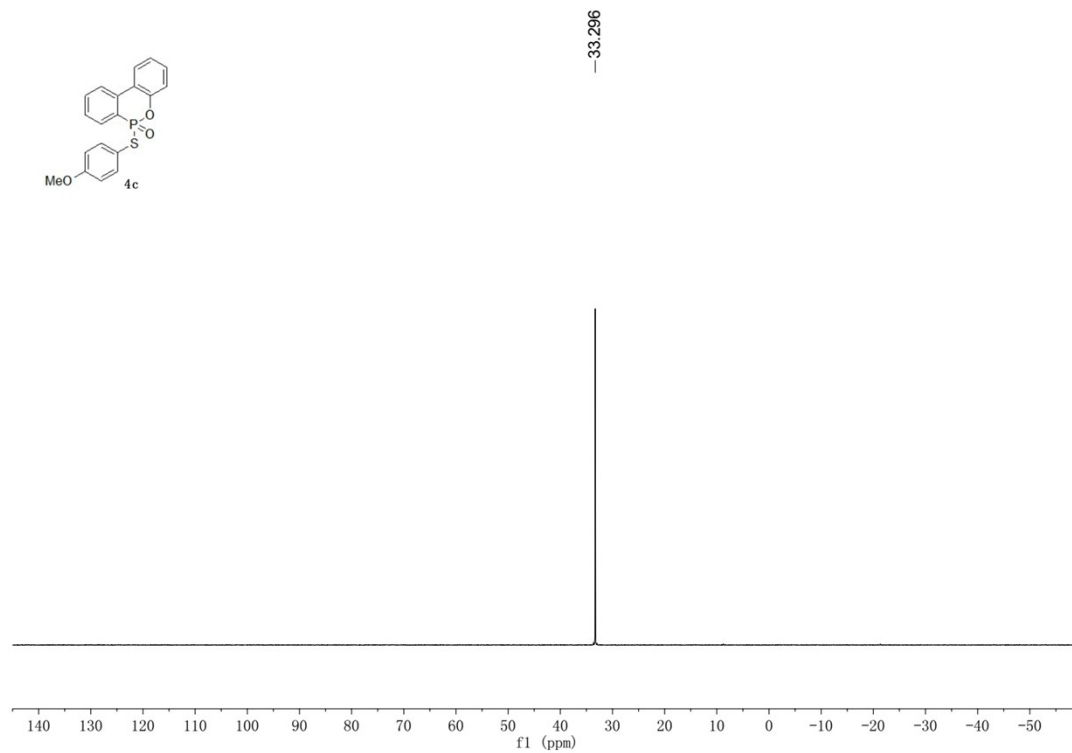
^{31}P NMR spectrum of compound **4b**



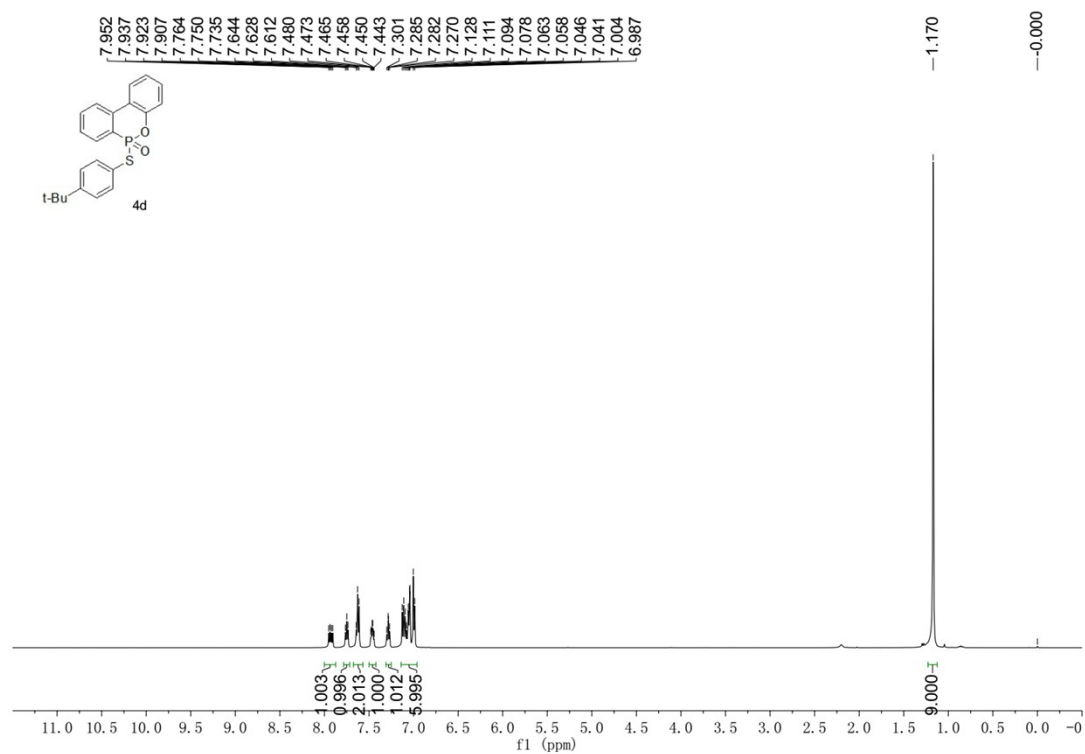
^1H NMR spectrum of compound **4c**



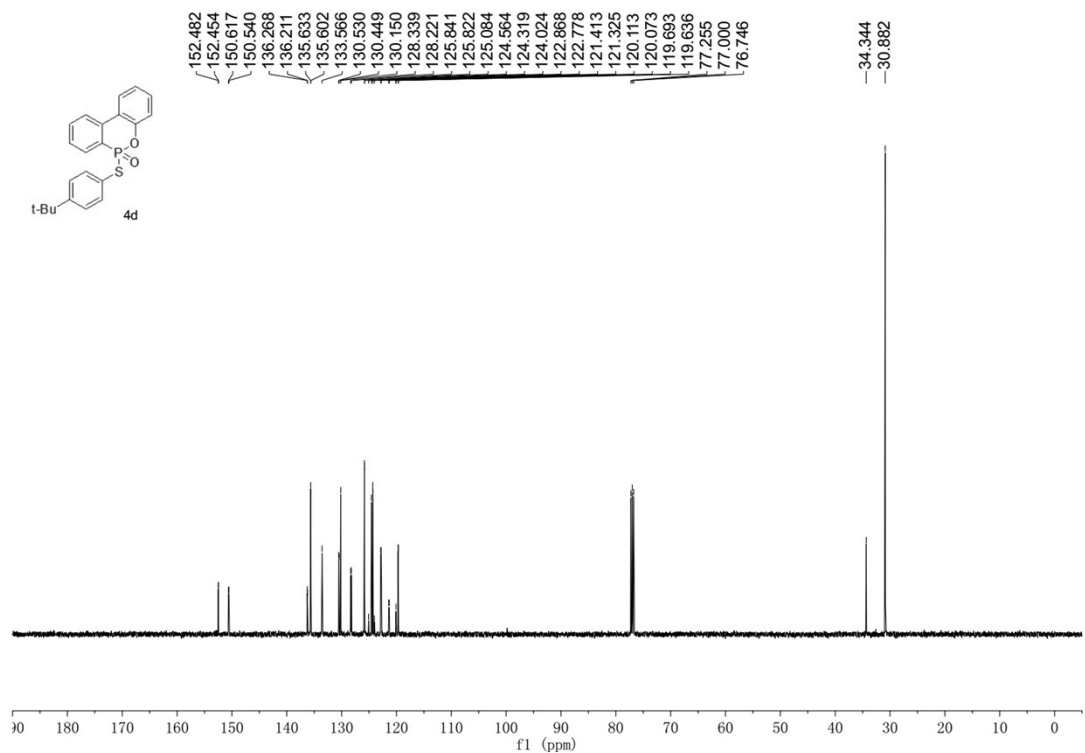
^{13}C NMR spectrum of compound **4c**



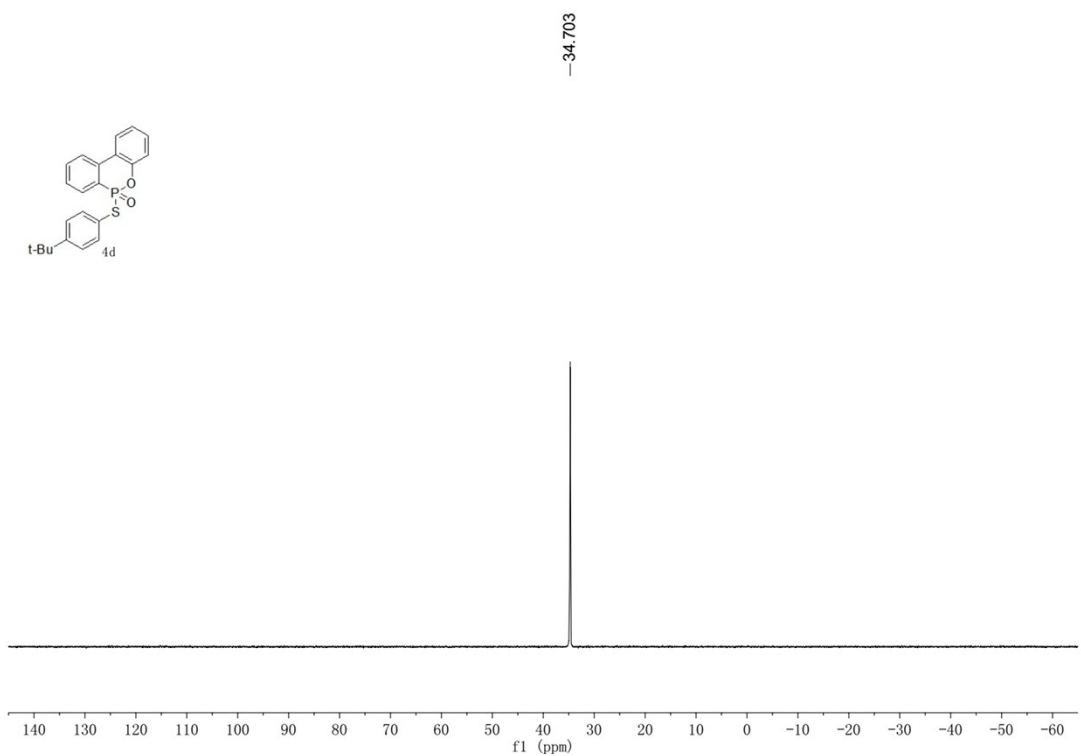
^{31}P NMR spectrum of compound **4c**



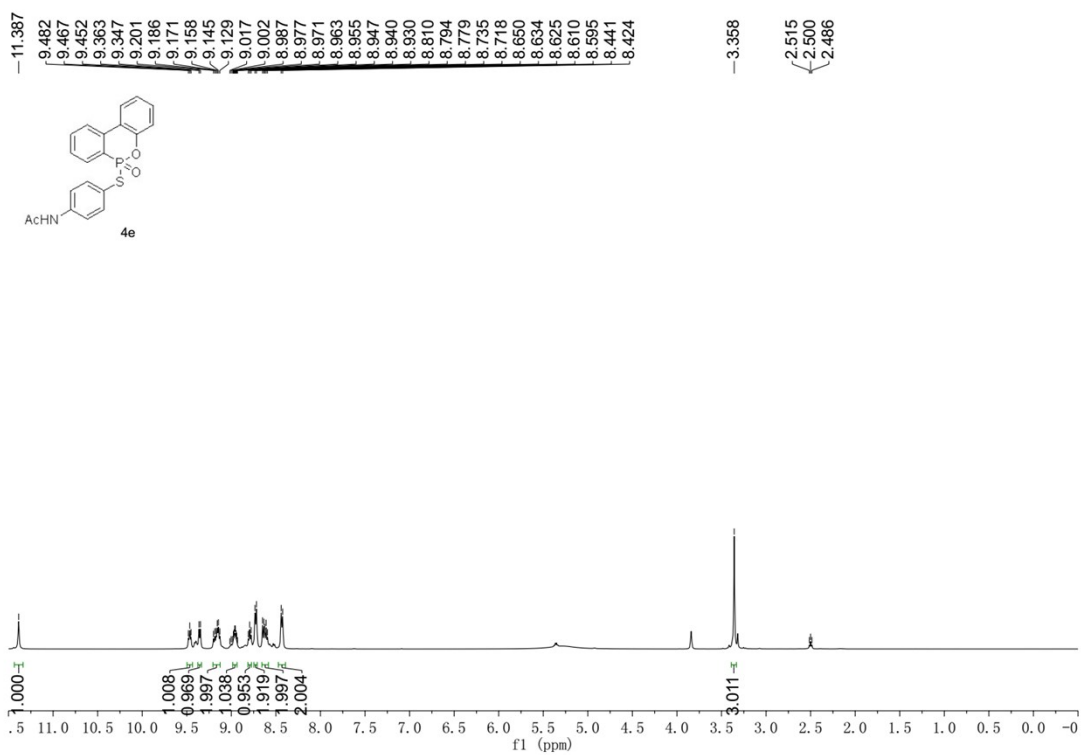
¹H NMR spectrum of compound **4d**



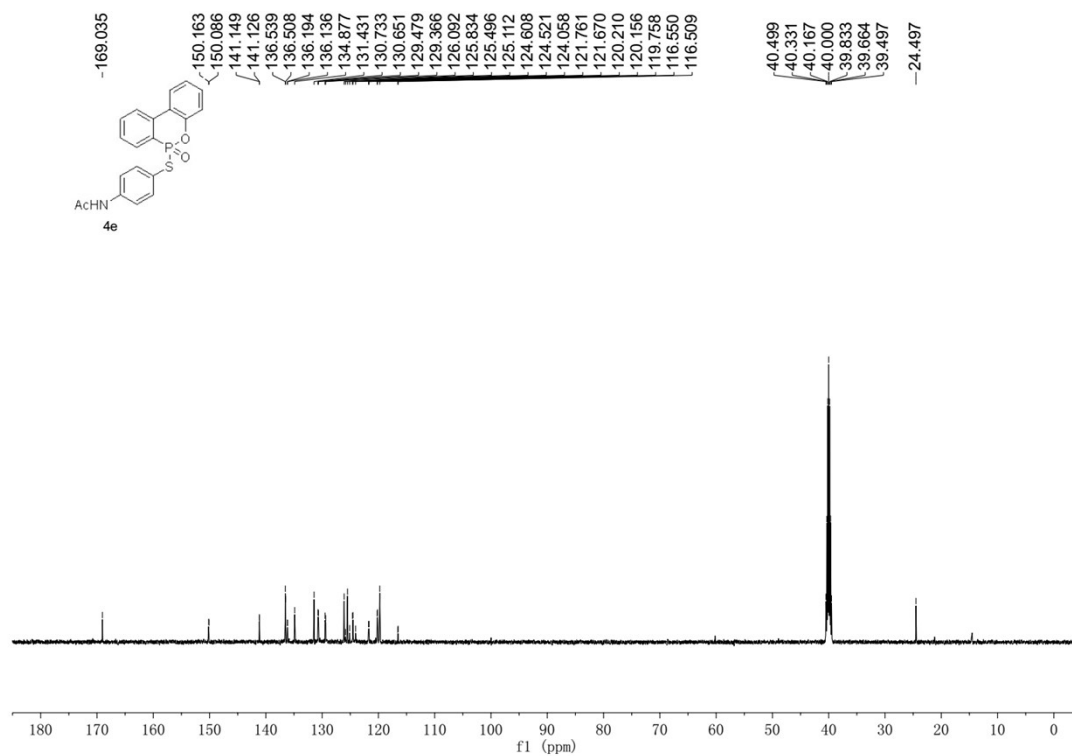
¹³C NMR spectrum of compound **4d**



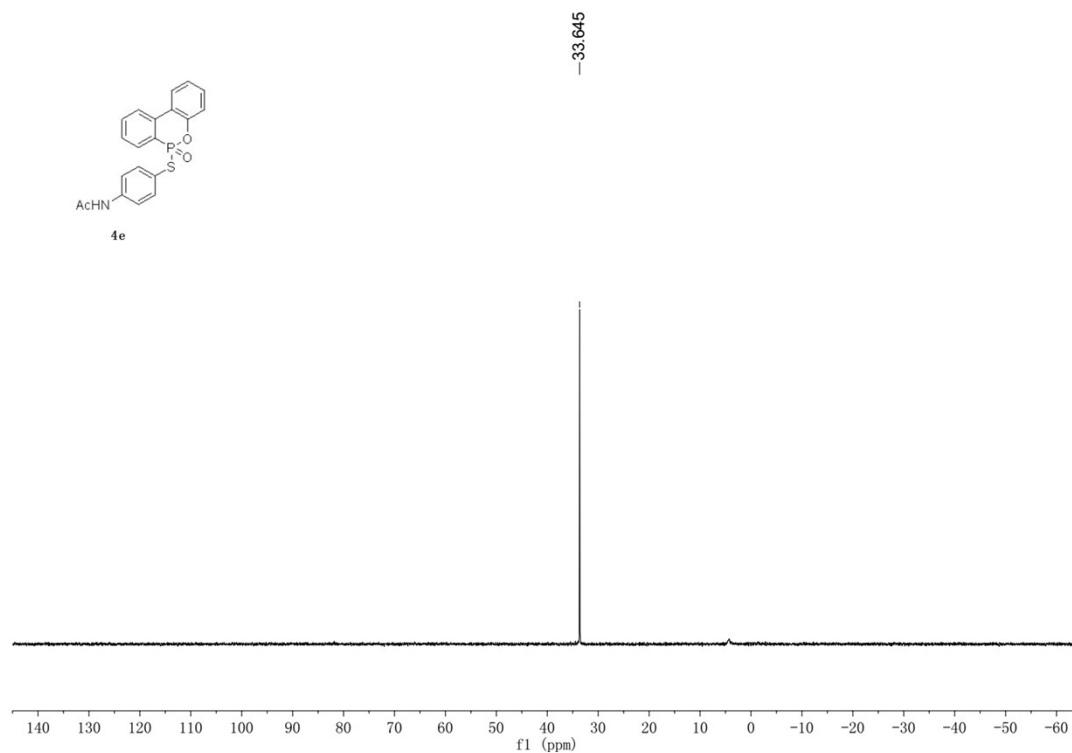
^{31}P NMR spectrum of compound **4d**



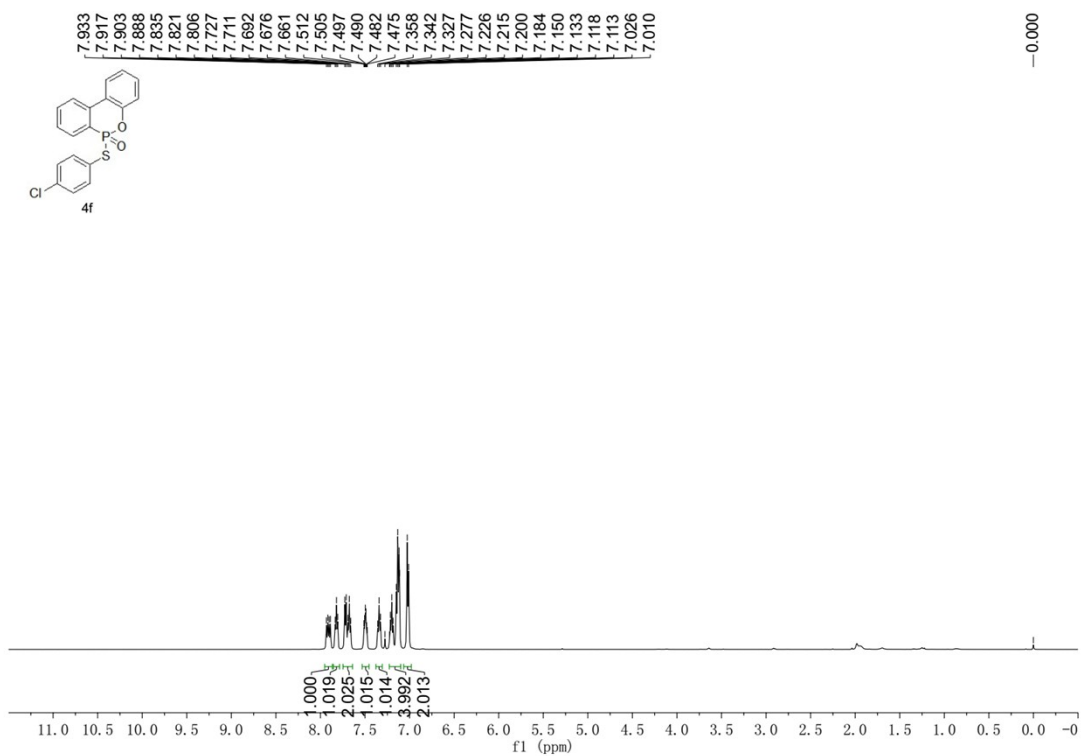
^1H NMR spectrum of compound **4e**



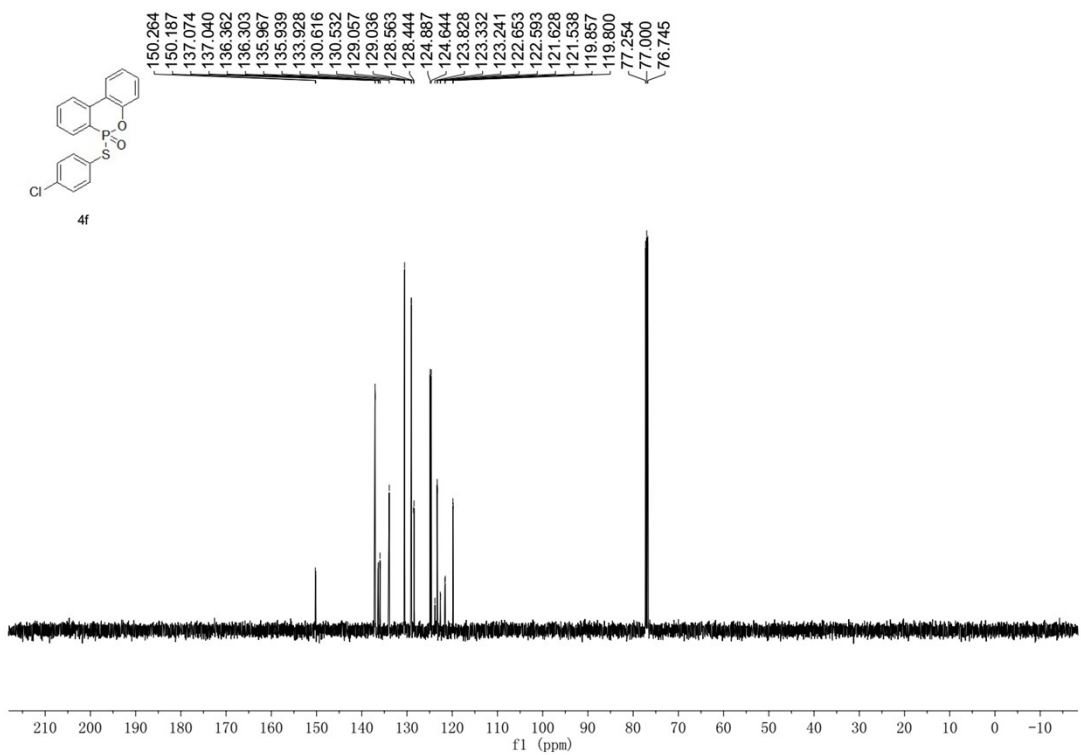
¹³C NMR spectrum of compound **4e**



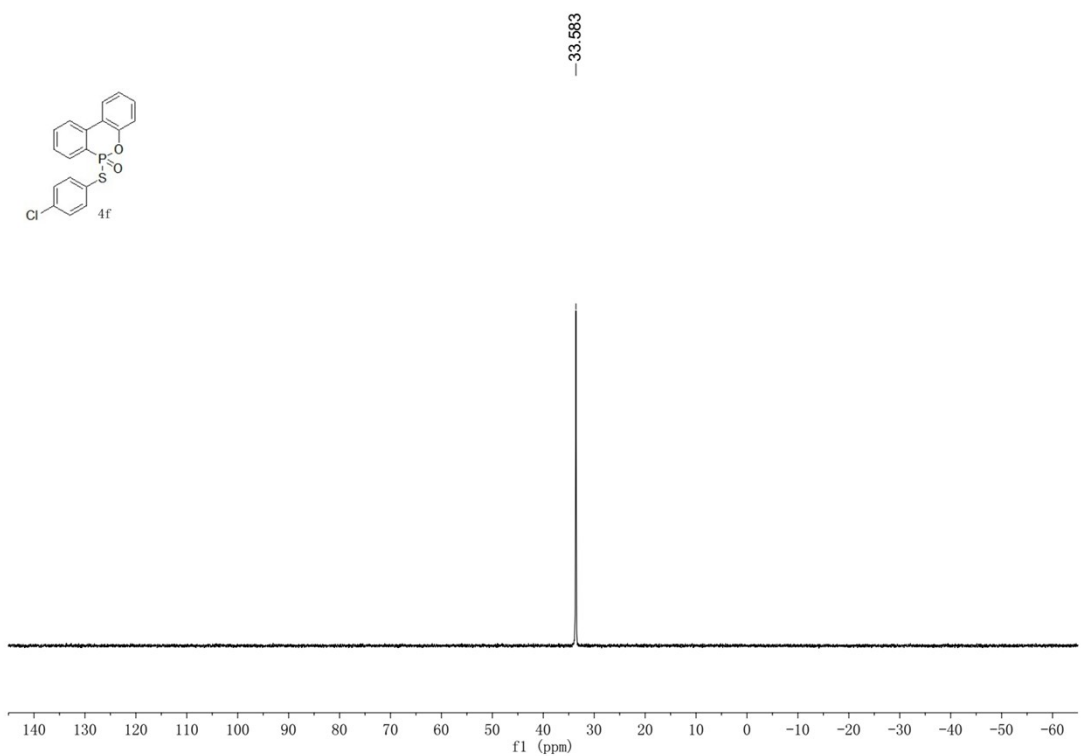
³¹P NMR spectrum of compound **4e**



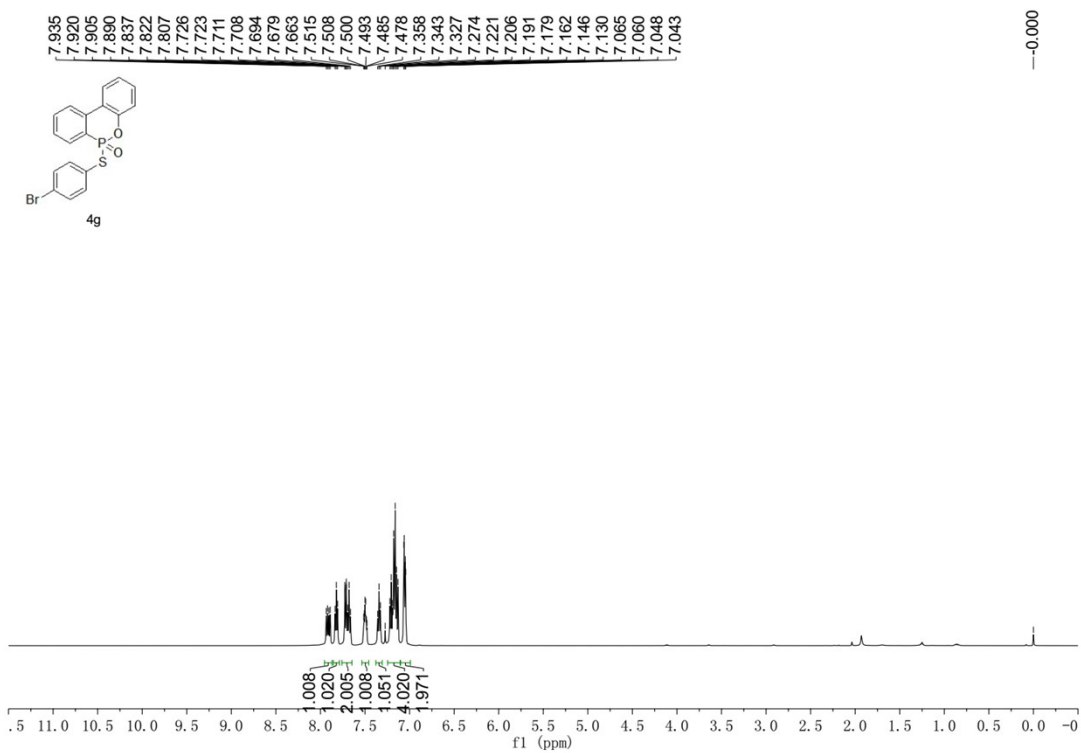
¹H NMR spectrum of compound **4f**



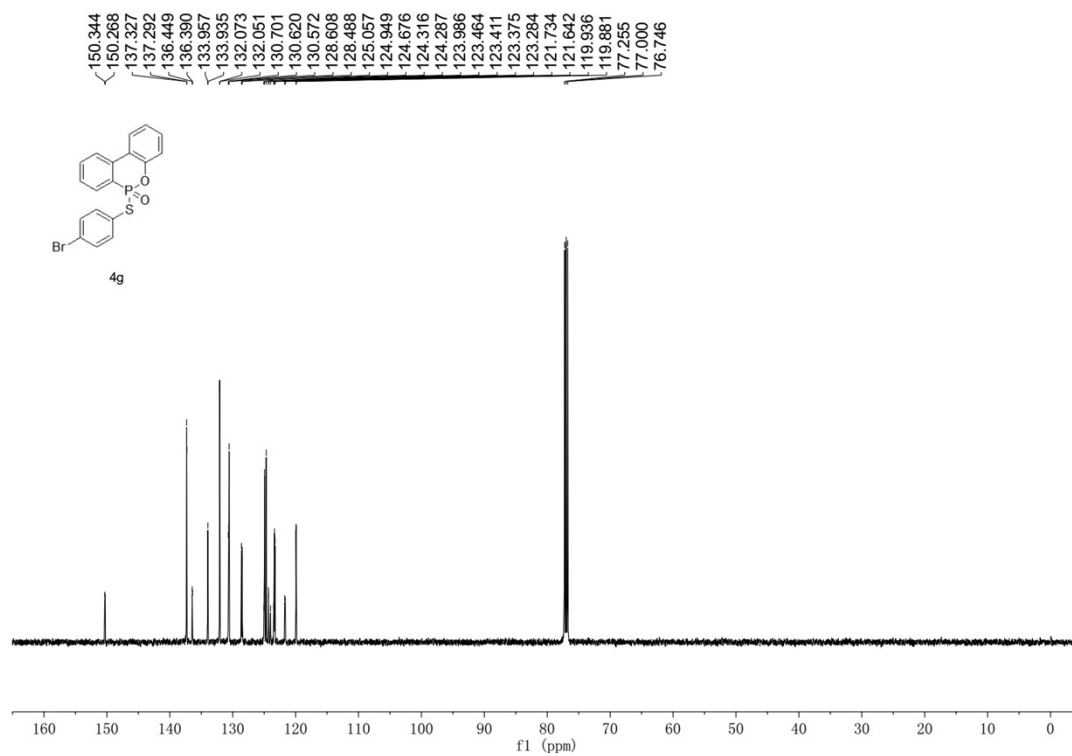
¹³C NMR spectrum of compound **4f**



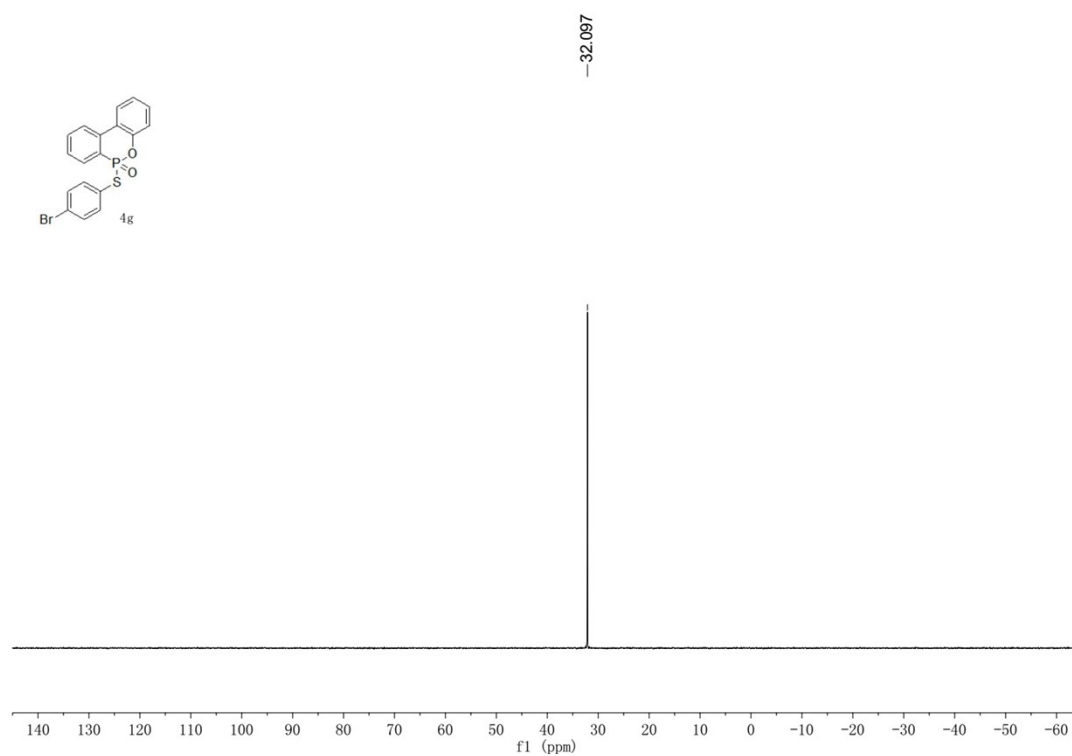
^{31}P NMR spectrum of compound **4f**



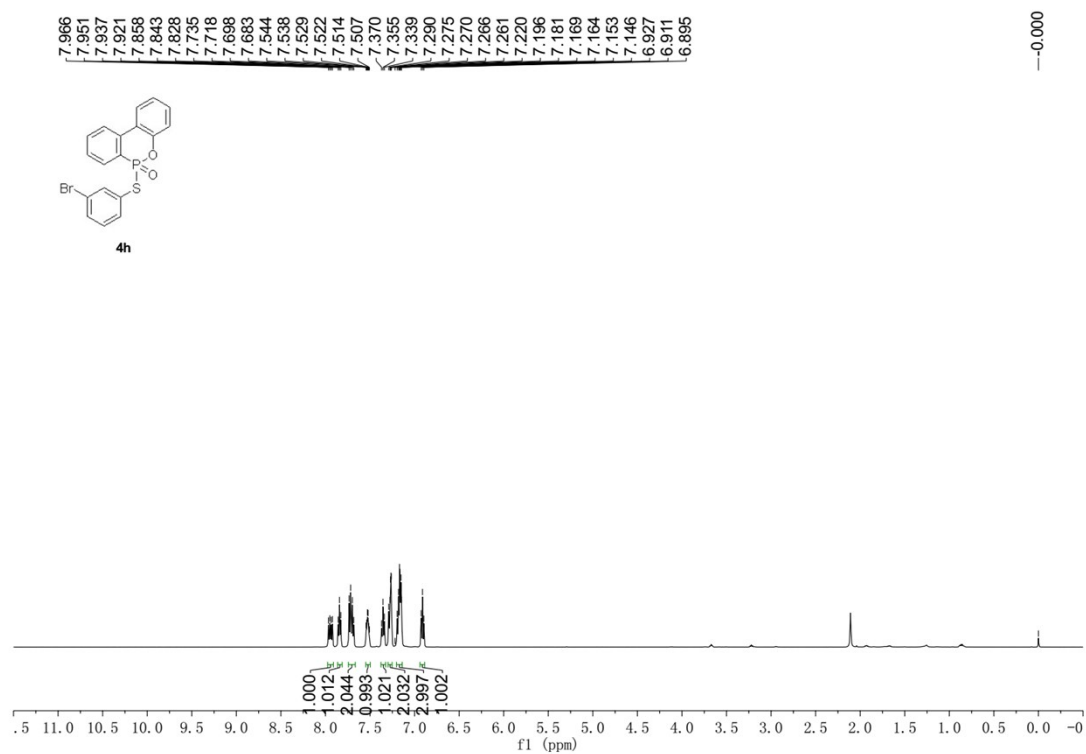
^1H NMR spectrum of compound **4g**



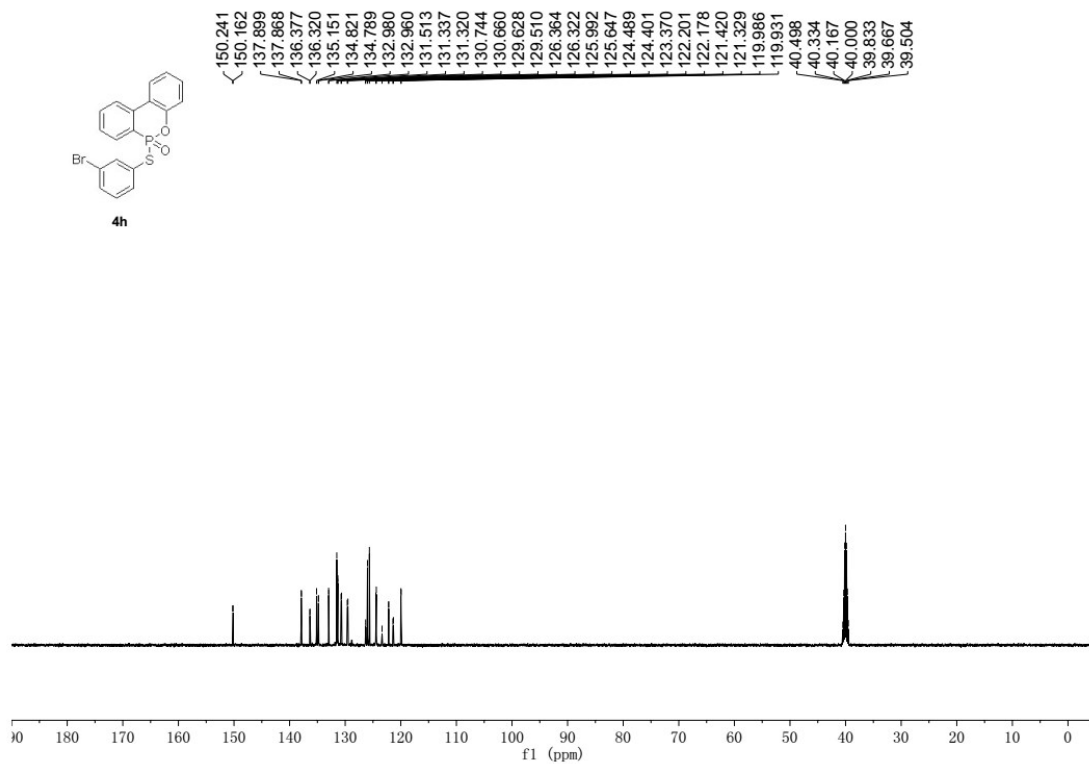
¹³C NMR spectrum of compound 4g



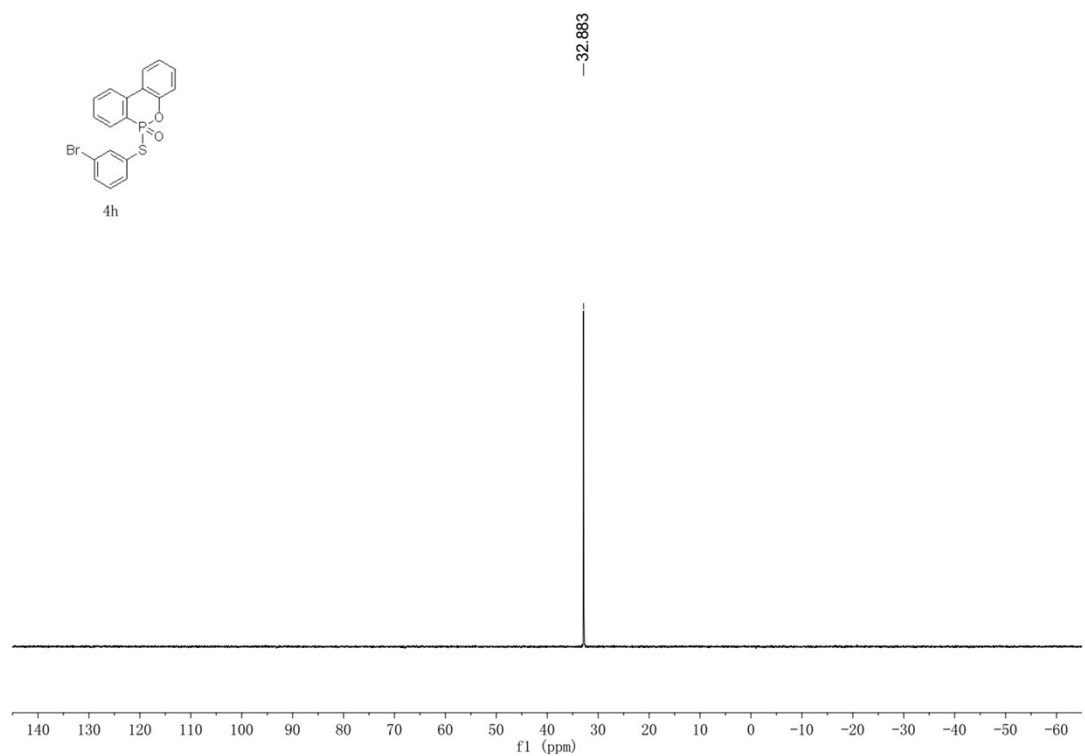
³¹P NMR spectrum of compound 4g



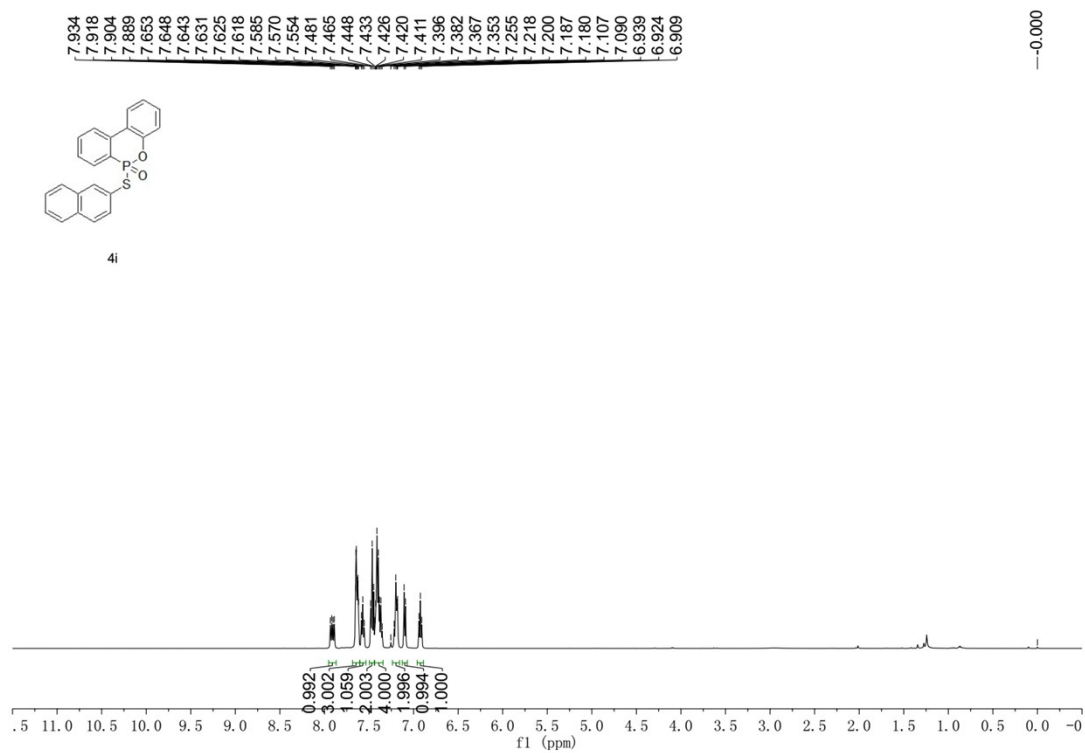
¹H NMR spectrum of compound **4h**



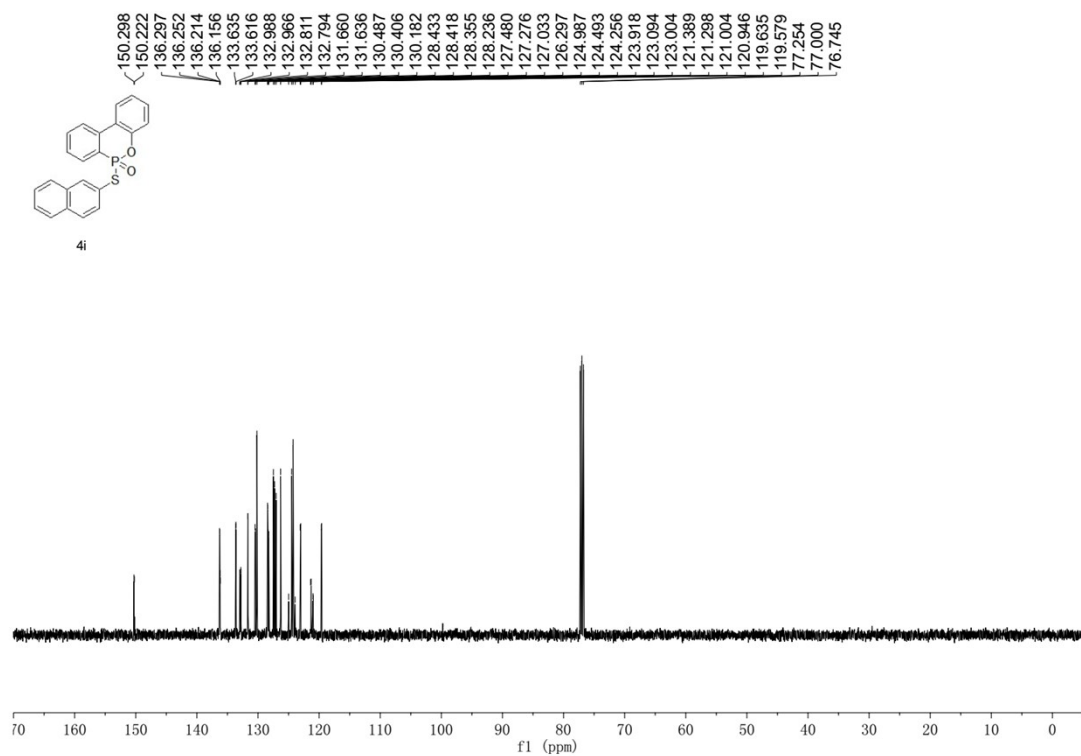
¹³C NMR spectrum of compound **4h**



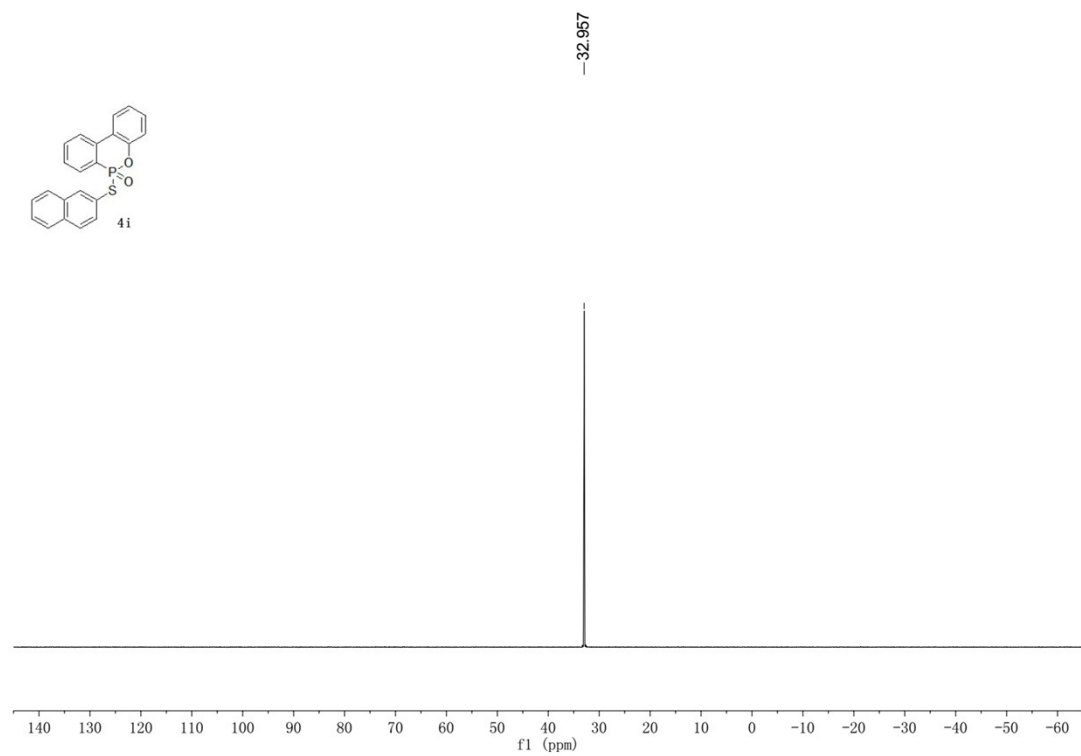
³¹P NMR spectrum of compound **4h**



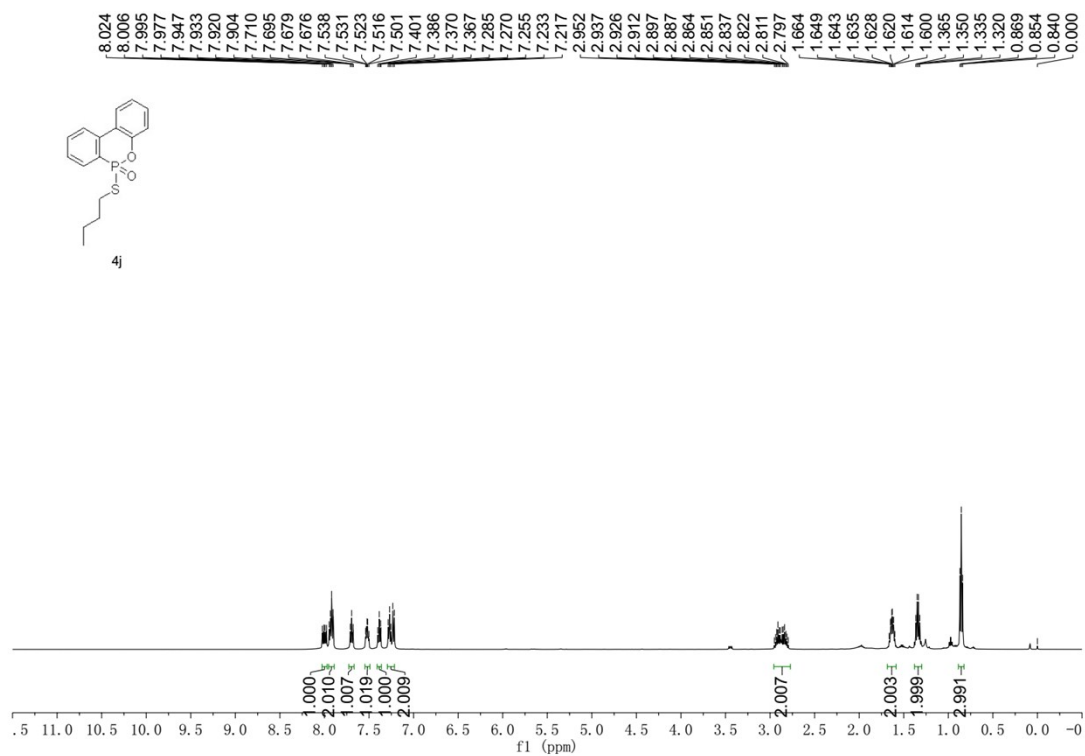
¹H NMR spectrum of compound **4i**



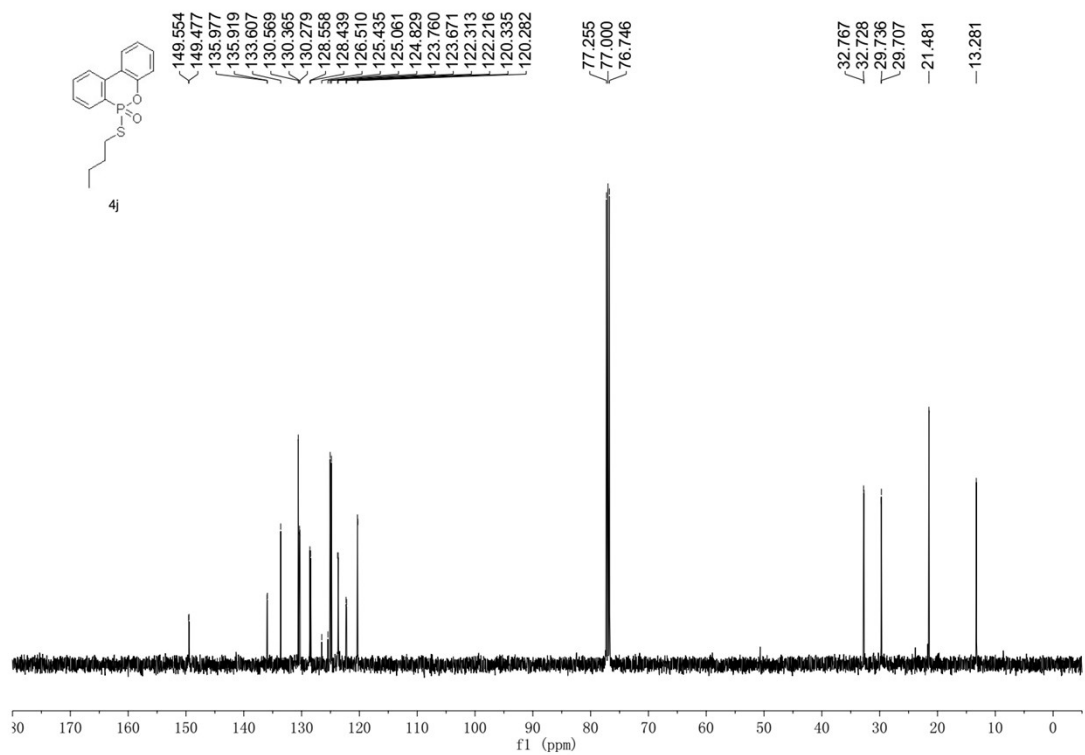
^{13}C NMR spectrum of compound **4i**



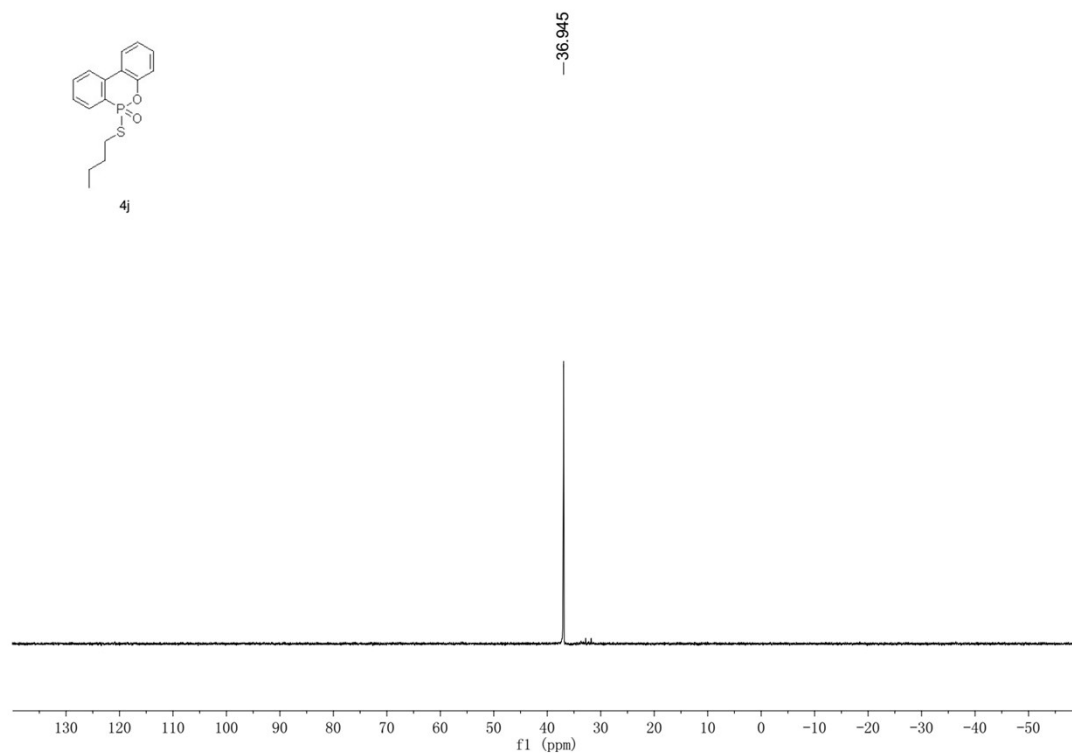
^{31}P NMR spectrum of compound **4i**



¹H NMR spectrum of compound **4j**



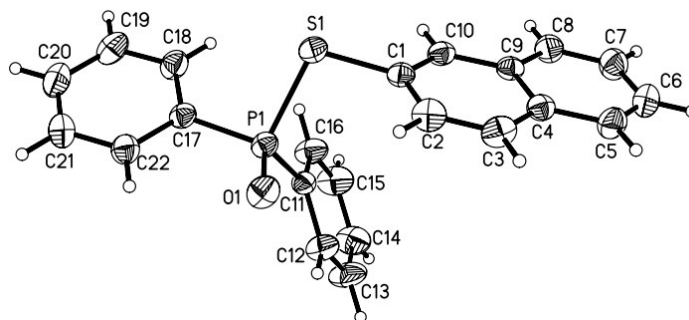
¹³C NMR spectrum of compound **4j**



^{31}P NMR spectrum of compound **4j**

6. Crystallographic detail of **3k** and **4i**

Detector with graphite-monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. All of the data were corrected for absorption effects using the multi-scan technique. The structures were solved by direct methods, expanded by difference Fourier syntheses and refined by full matrix least-squares on F2 using Bruker SHELXTL (Version 6.10) program package. Non-H atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were introduced at their geometric positions and refined as riding atoms unless otherwise stated.



X-ray crystal structure of **3k**

Crystal data for 3k: C₂₂H₁₇OPS, M = 360.39, monoclinic, space group P2(1)/c,

colorless plate, $a = 10.8152(5)$, $b = 8.5569(3)$, $c = 20.0431(9)$ Å, $\beta = 95.275(4)^\circ$, $V = 1847.02(14)$ Å³, $Z = 4$, $D_c = 1.296$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.268$ mm⁻¹, $T = 293(2)$ K. 3241 unique reflections [$R(\text{int}) = 0.0191$]. Final R [3241 with $I > 2\sigma(I)$] = 0.0418, $wR2$ (all data) = 0.1450. CCDC reference numbers 1513070.