Supplementary information for

TBPB-promoted metal-free synthesis of thiophosphinate/phosphonothioate by direct P-S bond coupling

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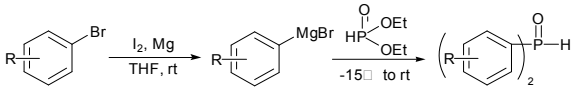
1. General information

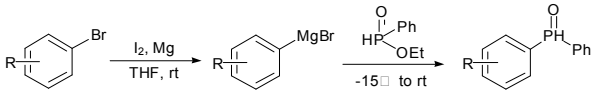
All chemicals were obtained from commercial suppliers or prepared according to the former reference. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded on Bruker ARX-400. Mass spectra were performed on a Bruker Esquire 3000 plus mass spectrometer equipped with ESI interface and ion trap analyzer.

2. Typical procedures for the synthesis of substrates

Substrates H-phosphine oxides **1** can be prepared according to the former reference.[1]
Method 1: Preparation of the symmetric H-phosphine oxides.[1a-1b]



Method 2: Preparation of the unsymmetric H-phosphine oxides.[1c-1d]

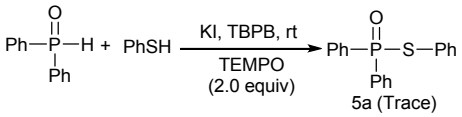


Reference

1 (a) T. L. Emmick and R. L. Letsinger, *J. Am. Chem. Soc.*, 1968, **90**, 3459-3465; (b) H. R. Hays, *J. Org. Chem.*, 1968, **3**, 3690-3694; (c) M. Harger and S. Westlake, *Tetrahedron*, 1982, **38**, 1511-1515; (d) K. Shioji, S. Tsukimoto, H. Tanaka and K. Okuma, *Chem. Lett.*, 2003, **32**, 604-605.

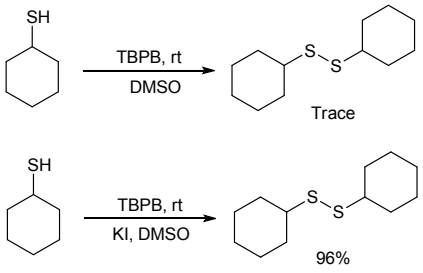
3. Preliminary mechanistic studies

a) Radical trapping experiments using TEMPO

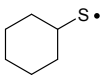


To a round bottomed flask, thiophenol(0.5 mmol), H-phosphine oxides/ H-phosphinate esters (0.75 mmol), TBPB (0.6 mmol), TEMPO (1.0 mmol), KI (0.1 mmol) and 1.5 ml DMSO were added and reacted in at room temperature for 8 hours. And only trace product was obtained.

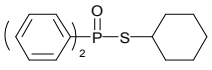
b) Role of KI in catalyzing the oxidation of thiol



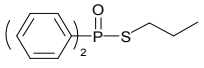
Disulfide product was generate from thiyl radical.



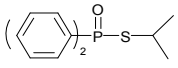
4. Characterization data of products

 **(3a)**

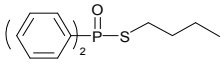
Compound **3a** was obtained in 97% yield according to the general procedure **A** as white solid; **m.p.** 80-81℃; **^{1}H NMR ($CDCl_3$, 400 MHz)**, δ 7.87-7.82 (m, 4H), 7.51-7.48 (m, 2H), 7.46-7.41 (m, 4H), 3.32-3.24 (m, 1H), 1.92-1.89 (m, 2H), 1.64-1.62 (m, 2H), 1.52-1.44 (m, 3H), 1.30-1.22 (m, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 134.5, 133.5, 132.1 (d, *J* = 2.8), 131.52 (d, *J* = 10.3), 128.64 (d, *J* = 12.89), 44.46 (d, *J* = 2.0), 35.59(d, *J* = 3.8), 25.74, 25.30; **^{31}P NMR ($CDCl_3$, 162 MHz):** δ 42.11; **MS (ESI, *m/z*)** $[M+H]^+$ 317.00, $[M+Na]^+$ 338.90.

 **(3b)**

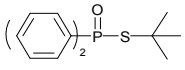
Compound **3b** was obtained in 97% yield according to the general procedure **A** as colorless oil; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.88-7.83 (m, 4H), 7.58-7.49 (m, 2H), 7.47-7.42 (m, 4H), 2.78-2.72 (m, 2H), 1.67-1.58 (m, *J* = 7.3, 2H), 0.93-0.89 (t, *J* = 7.3, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 134.0, 132.9, 132.25 (d, *J* = 2.9), 131.5 (d, *J* = 10.3), 128.71 (d, *J* = 12.9), 31.24 (d, *J* = 2.3), 24.08 (d, *J* = 5.0), 13.28; **^{31}P NMR ($CDCl_3$, 162 MHz):** δ 43.20; **MS (ESI, *m/z*)** $[M+H]^+$ 276.90, $[M+Na]^+$ 298.90.

 **(3c)**

Compound **3c** was obtained in 99% yield according to the general procedure **A** as white solid; **m.p.** 104-106℃; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.88-7.83 (m, 4H), 7.52-7.48 (m, 2H), 7.47-7.42 (m, 4H), 3.45-3.35 (m, *J* = 6.8, 1H), 1.33-1.32 (d, *J* = 6.8, 6H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 134.4, 133.4, 132.1 (d, *J* = 2.9), 131.5 (d, *J* = 10.3), 128.6 (d, *J* = 12.9), 36.9 (d, *J* = 2.2), 25.8 (d, *J* = 4.6); **^{31}P NMR ($CDCl_3$, 162 MHz):** δ 41.6; **MS (ESI, *m/z*)** $[M+H]^+$ 276.90, $[M+Na]^+$ 298.90.

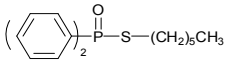
 **(3d)**

Compound **3d** was obtained in 97% yield according to the general procedure **A** as colorless oil; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.88-7.82 (m, 4H), 7.53-7.48 (m, 2H), 7.47-7.42 (m, 4H), 2.80-2.74 (m, 2H), 1.61-1.54 (m, *J* = 7.4), 1.37-1.27 (m, *J* = 7.4), 0.82-0.78 (t, *J* = 7.3); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 133.9, 132.8, 132.2 (d, *J* = 2.9), 131.5 (d, *J* = 10.3), 128.7 (d, *J* = 12.9), 32.6 (d, *J* = 4.9), 29.0 (d, *J* = 2.3), 21.7, 13.4; **^{31}P NMR ($CDCl_3$, 162 MHz):** δ 43.2; **MS (ESI, *m/z*)** $[M+H]^+$ 290.90, $[M+Na]^+$ 312.90.

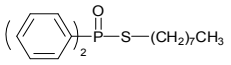
 **(3e)**

Compound **3e** was obtained in 88% yield according to the general procedure **A** as

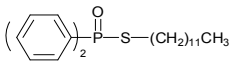
white solid; **m.p.** 126-127℃; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.89-7.83 (m, 4H), 7.50-7.46 (m, 2H), 7.45-7.40 (m, 4H), 1.45 (d, *J* = 0.72, 9H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 135.6, 135.5, 131.9 (d, *J* = 3.0), 131.5 (d, *J* = 10.2), 128.5 (d, *J* = 12.9), 52.4 (d, *J* = 3.5), 33.5 (d, *J* = 4.3); **^{31}P NMR ($CDCl_3$, 162 MHz):** δ 39.1; **MS (ESI, *m/z*)** $[M+H]^+$ 290.90, $[M+Na]^+$ 312.90.


(3f)

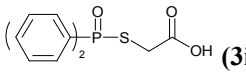
Compound **3f** was obtained in 90% yield according to the general procedure **A** as colorless oil; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.88-7.82 (m, 4H), 7.52-7.48 (m, 2H), 7.47-7.42 (m, 4H), 2.79-2.73 (m, 2H), 1.62-1.54 (m, *J* = 7.2, 2H), 1.32-1.25 (m, 2H), 1.23-1.13 (m, 4H), 0.82-0.79 (t, *J* = 7.2, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 134.0, 132.9, 132.2 (d, *J* = 2.8), 131.5 (d, *J* = 10.2), 128.7 (d, *J* = 13.4), 31.1, 30.5 (d, *J* = 4.7), 29.3 (d, *J* = 2.1), 28.2, 22.4, 13.9; **^{31}P NMR ($CDCl_3$, 162 MHz):** δ 43.1; **MS (ESI, *m/z*)** $[M+H]^+$ 319.00, $[M+Na]^+$ 341.00.


(3g)

Compound **3g** was obtained in 98% yield according to the general procedure **A** as colorless oil; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.88-7.83 (m, 4H), 7.53-7.48 (m, 2H), 7.47-7.42 (m, 4H), 2.73-2.73 (m, 2H), 1.62-1.54 (m, *J* = 7.2, 2H), 1.31-1.16 (m, 10H), 0.85-0.81 (t, *J* = 7.1, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 133.9, 132.9, 132.2 (d, *J* = 2.9), 131.5 (d, *J* = 10.3), 128.7 (d, *J* = 12.9), 31.74, 30.57 (d, *J* = 4.9), 29.3 (d, *J* = 2.3), 29.06, 28.90, 28.59, 22.6, 14.1; **^{31}P NMR ($CDCl_3$, 162 MHz):** δ 43.2; **MS (ESI, *m/z*)** $[M+H]^+$ 347.00, $[M+Na]^+$ 369.00.

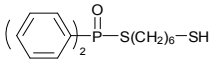

(3h)

Compound **3h** was obtained in 96% yield according to the general procedure **A** as colorless oil; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.88-7.83 (m, 4H), 7.53-7.48 (m, 2H), 7.47-7.42 (m, 4H), 2.80-2.73 (m, 2H), 1.62-1.54 (m, *J* = 7.2, 2H), 1.27-1.17 (m, 18H), 0.87-0.83 (t, *J* = 7.1, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 134.0, 132.9, 132.2 (d, *J* = 3.0), 131.5 (d, *J* = 10.3), 128.7 (d, *J* = 12.9), 31.9, 30.57 (d, *J* = 4.9), 29.6, 29.5, 29.4, 29.3, 29.29 (d, *J* = 2.2), 28.9, 28.6, 22.7, 14.1; **^{31}P NMR ($CDCl_3$, 162 MHz):** δ 43.0; **MS (ESI, *m/z*)** $[M+H]^+$ 403.10, $[M+Na]^+$ 425.10.


(3i)

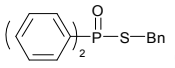
Compound **3i** was obtained in 66% yield according to the general procedure **A** as white solid; **m.p.** 125-127℃; **^{1}H NMR (DMSO-d6, 400 MHz)**: δ 12.9 (br, 1H), 7.83-7.78 (m, 4H), 7.66-7.63 (m, 2H), 7.60-7.55 (m, 4H), 3.52-3.49 (d, *J* = 10.6, 2H); **^{13}C NMR ($CDCl_3$, 100 MHz):** δ 169.4 (d, *J* = 4.7), 133.2, 132.7 (d, *J* = 2.8), 132.2, 131.0

(d, *J* = 10.4), 129.1 (d, *J* = 12.7), 30.2; **^{31}P NMR (DMSO-d6, 162 MHz):** δ 40.7; **MS (ESI, *m/z*)** $[M+H]^+$ 292.90, $[M+Na]^+$ 314.90.



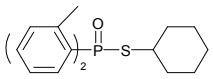
(3j)

Compound **3h** was obtained in 82% yield according to the general procedure **A** as yellow oil; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.87-7.82 (m, 4H), 7.53-7.49 (m, 2H), 7.47-7.43 (m, 4H), 2.80-2.73 (m, 2H), 2.47-2.41 (q, *J* = 7.4, 2H), 1.63-1.56 (m, *J* = 7.4, 2H), 1.54-1.48 (m, 2H), 1.30-1.27 (m, 4H), 1.22 (s, 1H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 133.9, 132.8, 132.3 (d, *J* = 2.9), 131.5 (d, *J* = 10.3), 128.7 (d, *J* = 12.9), 33.7, 30.4 (d, *J* = 4.7), 29.1 (d, *J* = 2.2), 27.9, 27.6, 24.4; **^{31}P NMR ($CDCl_3$, 162 MHz):** δ 43.1; **MS (ESI, *m/z*)** $[M+H]^+$ 351.00, $[M+Na]^+$ 372.90.



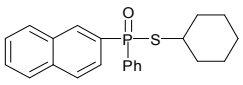
(3k)

Compound **3i** was obtained in 95% yield according to the general procedure **A** as white solid; **m.p.** 76-78℃**; ^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.87-7.81 (m, 4H), 7.53-7.49 (m, 2H), 7.46-7.41 (m, 4H), 7.24-7.15 (m, 5H), 4.01 (d, *J* = 9.1, 2H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 136.8 (d, *J* = 5.4), 133.5, 133.2, 132.3 (d, *J* = 2.9), 131.6 (d, *J* = 10.4), 129.0, 128.7, 128.6 (d, *J* = 2.8), 127.4, 33.2 (d, *J* = 2.1); **^{31}P NMR ($CDCl_3$, 162 MHz):** δ 42.8; **MS (ESI, *m/z*)** $[M+H]^+$ 324.90, $[M+Na]^+$ 346.90.



(3l)

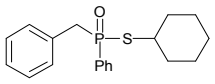
Compound **3i** was obtained in 81% yield according to the general procedure **A** as white solid; **m.p.** 101-103℃; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.87-7.81 (m, 2H), 7.40-7.36 (m, 2H), 7.26-7.23 (m, 2H), 7.20-7.17 (m, 2H), 3.47-3.39 (m, 1H), 2.39 (s, 6H), 2.02-1.98 (m, 2H), 1.70-1.65 (m, 2H), 1.58-1.47 (m, 3H), 1.37-1.23 (m, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 141.8 (d, *J* = 9.7), 133.1, 132.7 (d, *J* = 12.1), 132.0 (d, *J* = 2.9), 131.9 (d, *J* = 11.6), 125.5 (d, *J* = 13.2), 44.3 (d, *J* = 2.1), 35.8 (d, *J* = 3.6), 26.0, 25.4, 21.5 (d, *J* = 4.0); **^{31}P NMR ($CDCl_3$, 162 MHz):** δ 45.1; **MS (ESI, *m/z*)** $[M+H]^+$ 345.00, $[M+Na]^+$ 367.00.



(3m)

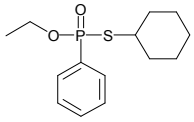
Compound **3m**was obtained in 76% yield according to the general procedure **A** as white solid; **m.p.** 118-120℃; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 8.75-8.73 (m, 1H), 8.04-7.98 (m, 2H), 7.88-7.82 (m, 3H), 7.52-7.41 (m, 6H), 3.51-3.42 (m, 1H), 2.00-1.96 (m, 2H), 1.67-1.63 (m, 2H), 1.57-1.47 (m, 3H), 1.34-1.19 (m, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 133.9, 133.8, 133.5 (d, *J* = 3.1), 133.2 (d, *J* = 11.1), 132.1 (d, *J* = 2.8), 131.6 (d, *J* = 10.7), 128.8, 128.6 (d, *J* = 13.0), 127.2, 127.1 (d, *J* = 4.9), 127.2,

127.1 (d, *J* = 4.96), 126.4, 124.3 (d, *J* = 14.9); 44.8 (d, *J* = 2.0), 35.7 (d, *J* = 11.6), 25.9, 25.3; **^{31}P NMR ($CDCl_3$, 162 MHz):** δ 44.4; **MS (ESI, *m/z*)** $[M+H]^+$ 366.90, $[M+Na]^+$ 388.90.



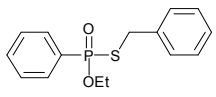
(3n)

Compound **3n** was obtained in 65% yield according to the general procedure **A** as white c solid; **m.p.** 147-149℃**; ^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.70-7.65 (m, 2H), 7.50-7.46 (m, 1H), 7.41-7.37 (m, 2H), 7.19-7.17 (m, 3H), 7.05-7.03 (m, 2H), 7.48-7.47 (m, 2H), 3.20-3.10 (m, 1H), 2.00-1.97 (m, 1H), 1.70-1.62 (m, 2H), 1.57-1.50 (m, 2H), 1.47-1.44(m, 1H), 1.33-1.13 (m, 4H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 132.0 (d, *J* = 4.7), 131.5 (d, *J* = 9.7), 131.0 (d, *J* = 8.4), 130.1 (d, *J* = 5.6), 128.3 (d, *J* = 2.4), 128.2, 127.0 (d, *J* = 3.5), 43.8 (d, *J* = 2.4), 35.8 (d, *J* = 12.1), 25.8 (d, *J* = 8.6), 25.2; **^{31}P NMR ($CDCl_3$, 162 MHz):** δ 47.7; **MS (ESI, *m/z*)** $[M+H]^+$ 331.00, $[M+Na]^+$ 353.00.



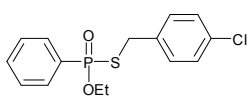
(3o)

Compound **3o** was obtained in 73% yield according to the general procedure **A** as colorless oil; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.88-7.82 (m, 2H), 7.53-7.49 (m, 1H), 7.47-7.42 (m, 2H) , 4.24-4.17 (m, *J* = 7.2, 2H), 3.22-3.14 (m, 1H), 1.98-1.94 (m, 1H), 1.83-1.80 (m, 1H), 1.65-1.59 (m, 2H), 1.50-1.38 (m, 3H), 1.36-1.33 (t, *J* = 7.1, 3H), 1.29-1.16 (m, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 134.3, 133.0, 132.8, 132.3 (d, *J* = 3.1), 131.1 (d, *J* = 10.8), 130.0, 128.5 (d, *J* = 14.6), 128.3, 62.1 (d, *J* = 6.7), 45.1 (d, *J* = 2.4), 35.4 (d, *J* = 14.3), 25.8, 25.2, 16.4 (d, *J* = 6.8); **^{31}P NMR ($CDCl_3$, 162 MHz):** δ 44.2; **MS (ESI, *m/z*)** $[M+H]^+$ 284.90, $[M+Na]^+$ 306.90.



(3p)

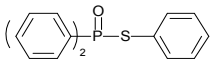
Compound **3p** was obtained in 81% yield according to the general procedure **A** as colorless oil; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.83-7.78 (m, 2H), 7.54-7.50 (m, 1H), 7.45-7.40 (m, 2H), 7.22-7.17 (m, 5H), 4.27-4.06 (m, 2H), 4.00-3.85 (m, *J* = 11.4, 2H), 1.34-1.30 (m, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 137.2 (d, *J* = 5.2), 133.2, 132.5 (d, *J* = 3.16), 131.7, 131.2 (d, *J* = 10.8), 128.8, 128.5(d, *J* = 1.63), 128.4, 127.4, 62.2 (d, *J* = 6.76), 34.5 (d, *J* = 2.6), 16.3 (d, *J* = 6.9); **^{31}P NMR ($CDCl_3$, 162 MHz):** δ 43.6; **MS (ESI, *m/z*)** $[M+Na]^+$ 314.90.



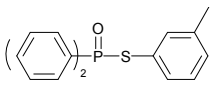
(3q)

Compound **3q** was obtained in 84% yield according to the general procedure **A** as

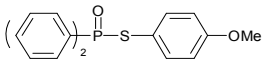
colorless oil; **^{1}H NMR ($CDCl_3$, 400 MHz)**: 7.78-7.73 (m, 2H), 7.53-7.49 (m, 1H), 7.43-7.39 (m, 2H), 7.16-7.10 (m, 4H), 4.26-4.08 (m, 2H), 3.96-3.84 (m, 2H), 1.34-1.31 (m, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 135.9 (d, *J* = 4.7), 133.2 (d, *J* = 7.7), 132.5 (d, *J* = 3.1), 131.6, 131.2 (d, *J* = 10.9), 130.2, 128.6, 128.5 (d, *J* = 14.8), 65.4 (d, *J* = 6.8), 33.8 (d, *J* = 2.5), 16.3 (d, *J* = 6.8); **^{31}P NMR ($CDCl_3$, 162 MHz):** δ 43.4; **MS (ESI, *m/z*)** $[M+Na]^+$ 348.90.


(5a)

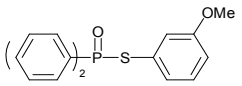
Compound **5a** was obtained in 96% yield according to the general procedure **B** as white solid; **m.p.** 88-89℃; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.84-7.80 (m, 4H), 7.50-7.47 (m, 2H), 7.43-7.39 (m, 6H), 7.23-7.21 (m, 1H), 7.18-7.15 (m, 2H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 135.4 (d, *J* = 3.7), 132.9, 132.3 (d, *J* = 2.8), 132.1, 131.6 (d, *J* = 10.0), 129.1 (d, *J* = 1.5), 128.9 (d, *J* = 2.0), 128.5 (d, *J* = 12.1), 126.2 (d, *J* = 5.0); **^{31}P NMR ($CDCl_3$, 162 MHz):** δ 41.3; **MS (ESI, *m/z*)** $[M+H]^+$ 310.90, $[M+Na]^+$ 332.90.


(5b)

Compound **5b** was obtained in 99% yield according to the general procedure **B** as white solid; **m.p.** 106-107℃; **^{1}H NMR (DMSO-d6, 400 MHz)**: δ 7.84-7.79 (m, 4H), 7.62-7.59 (m, 2H), 7.56-7.52 (m, 4H), 7.23-7.22 (m, 2H), 7.16-7.10 (m, 2H); **^{13}C NMR (DMSO-d6, 100 MHz)**: δ 138.6, 135.2 (d, *J* = 3.7), 132.9, 132.6 (d, *J* = 2.7), 132.0, 131.7 (d, *J* = 3.7), 131.1 (d, *J* = 10.1), 129.7, 129.0, 128.9 (d, *J* = 12.5); **^{31}P NMR (DMSO-d6, 162 MHz):** δ 41.2; **MS (ESI, *m/z*)** $[M+H]^+$ 324.90, $[M+Na]^+$ 346.90.

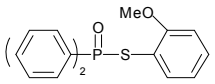

(5c)

Compound **5c** was obtained in 98% yield according to the general procedure **B** as white solid; **m.p.** 140-142℃; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.84-7.79 (m, 4H), 7.50-7.47 (m, 2H), 7.43-7.40 (m, 4H), 7.31-7.30 (m, 2H), 6.71-6.70 (m, 2H), 3.71 (m, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 160.4, 137.0 (d, *J* = 3.4), 133.0, 132.2 (d, *J* = 2.7), 131.6 (d, *J* = 10.1), 128.5 (d, *J* = 12.9), 116.0 (d, *J* = 4.9), 114.8 (d, *J* = 1.6), 55.2; **^{31}P NMR ($CDCl_3$, 162 MHz):** δ 41.3; **MS (ESI, *m/z*)** $[M+H]^+$ 340.90 , $[M+Na]^+$ 362.90.


(5d)

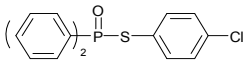
Compound **5d** was obtained in 99% yield according to the general procedure **B** as white solid; **m.p.** 92-93℃; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.85-7.41 (m, 4H), 7.49-

7.47 (m, 2H), 7.43-7.39 (m, 4H), 7.09-7.05 (m, 1H), 7.02-7.00 (m, 1H), 6.95-6.94 (s, 1H), 6.77-6.75 (m, 1H), 3.63 (s, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 159.6, 133.0, 132.3 (d, *J* = 2.9), 132.1, 131.7 (d, *J* = 10.1), 129.8 (d, *J* = 1.5), 128.6 (d, *J* = 13.0), 127.6 (d, *J* = 4.0), 127.1 (d, *J* = 5.0), 119.7 (d, *J* = 3.7), 115.7 (d, *J* = 2.0), 55.2; **^{31}P NMR ($CDCl_3$, 162 MHz):** δ 41.3; **MS (ESI, *m/z*)** $[M+H]^+$ 340.90 , $[M+Na]^+$ 362.90.



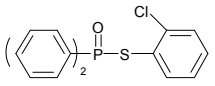
(5e)

Compound **5e**was obtained in 99% yield according to the general procedure **B** as white solid; **m.p.** 66-67℃; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.87-7.83 (m, 4H), 7.68-7.66 (m, 1H), 7.48-7.44 (m, 2H), 7.41-7.37 (m, 4H), 7.21-7.18 (m, 1H), 6.85-6.82 (m, 1H), 6.68-6.67 (m, 1H), 3.60(s, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 159.4 (d, *J* = 3.3), 137.6 (d, *J* = 4.0), 133.4, 132.6, 132.1 (d, *J* = 2.9), 131.7 (d, *J* = 10.3), 130.7, 128.3 (d, *J* = 13.1), 121.2, 111.1, 55.5; **^{31}P NMR ($CDCl_3$, 162 MHz):** δ 41.3; **MS (ESI, *m/z*)** $[M+H]^+$ 340.90 , $[M+Na]^+$ 362.90.



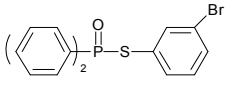
(5f)

Compound **5f**was obtained in 99% yield according to the general procedure **B** as white solid; **m.p.** 103-104℃; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.83-7.79 (m, 4H), 7.52-7.49 (m, 2H), 7.45-7.41 (m, 4H), 7.36-7.34 (m, 2H), 7.16-7.14 (m, 2H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 136.5 (d, *J* = 3.5), 135.5 (d, *J* = 2.4), 132.5 (d, *J* = 2.5), 131.6 (d, *J* = 10.1), 129.3, 128.7 (d, *J* = 13.0), 124.7 (d, *J* = 4.6); **^{31}P NMR ($CDCl_3$, 162 MHz):** δ 41.4; **MS (ESI, *m/z*)** $[M+H]^+$ 344.90, $[M+Na]^+$ 366.80.



(5g)

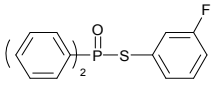
Compound **5g** was obtained in 95% yield according to the general procedure **B** as white solid; **m.p.** 91-92℃; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.88-7.83 (m, 4H), 7.51-7.47 (m, 2H), 7.44-7.39 (m, 4H), 7.27-7.23 (m, 1H), 7.16-7.10 (m, 2H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 137.7 (d, *J* = 4.7), 136.9 (d, *J* = 4.0), 132.8, 132.5 (d, *J* = 2.9), 131.7 (d, *J* = 10.4), 130.0, 128.6 (d, *J* = 13.2), 127.2, 126.6 (d, *J* = 4.8); **^{31}P NMR ($CDCl_3$, 162 MHz):** δ 40.0; **MS (ESI, *m/z*)** $[M+H]^+$ 344.90, $[M+Na]^+$ 366.90.



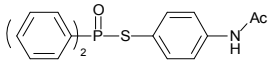
(5h)

Compound **5h** was obtained in 96% yield according to the general procedure **B** as white solid; **m.p.** 151-153℃; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.84-7.80 (m, 4H), 7.53-7.48 (m, 3H), 7.46-7.42 (m, 5H), 7.36-7.34 (m, 1H), 7.07-7.04 (m, 1H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 137.6 (d, *J* = 3.8), 133.9 (d, *J* = 3.6), 132.59 (d, *J* = 2.9),

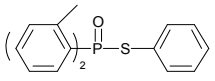
132.51, 132.1 (d, J = 2.0), 131.6 (d, J = 10.2), 130.3, 128.7 (d, J = 13.0), 128.4 (d, J = 5.0), 122.4; **^{31}P NMR ($CDCl_3$, 162 MHz):** δ 41.7; **MS (ESI, *m/z*)** $[M+H]^+$ 388.80, $[M+Na]^+$ 410.60.


(5i)

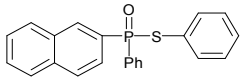
Compound **5i** was obtained in 97% yield according to the general procedure **B** as white solid; **m.p.** 81-82℃; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.83-7.78 (m, 4H), 7.50-7.47 (m, 2H), 7.43-7.40 (m, 4H), 7.22 (s, 1H), 7.15-7.12 (m, 2H), 6.92-6.89 (m, 1H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 158.0, 156.0 (d, J = 1.7), 127.38, 127.30 (d, J = 3.0), 126.5, 126.4 (d, J = 3.0), 125.7, 125.0 (d, J = 6.9), 123.4 (d, J = 13.1), 116.8 (d, J = 22.6), 110.0 (d, J = 4.1); **^{31}P NMR ($CDCl_3$, 162 MHz):** δ 41.5; **MS (ESI, *m/z*)** $[M+H]^+$ 328.90, $[M+Na]^+$ 350.90.


(5j)

Compound **5j** was obtained in 51% yield according to the general procedure **B** as white solid; **m.p.** 156-157℃; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 9.65 (s, 1H), 7.83-7.78 (m, 4H), 7.54-7.51 (m, 2H), 7.46-7.40 (m, 6H), 7.19-7.17 (m, 2H), 2.10 (s, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 169.3, 140.2, 136.3 (d, J = 3.4), 132.68, 132.62 (d, J = 2.8), 131.52 (d, J = 10.2), 128.8 (d, J = 13.0), 120.3; **^{31}P NMR ($CDCl_3$, 162 MHz):** δ 42.5; **MS (ESI, *m/z*)** $[M+H]^+$ 368.00, $[M+Na]^+$ 389.90.

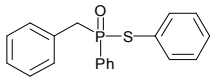

(5k)

Compound **5k** was obtained in 87% yield according to the general procedure **B** as white solid; **m.p.** 86-87℃; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.73-7.68 (m, 2H), 7.39-7.37 (m, 2H), 7.32-7.29 (m, 2H), 7.20-7.17 (m, 2H), 7.14-7.10 (m, 5H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 140.9 (d, J = 9.7), 134.6 (d, J = 3.7), 131.6 (d, J = 11.6), 131.2 (d, J = 2.8), 130.8 (d, J = 12.0), 130.7, 129.9, 127.9 (d, J = 1.5), 127.8 (d, J = 2.0), 125.2 (d, J = 4.9), 124.5 (d, J = 13.3), 20.4 (d, J = 4.0); **^{31}P NMR ($CDCl_3$, 162 MHz):** δ 43.8; **MS (ESI, *m/z*)** $[M+H]^+$ 339.00, $[M+Na]^+$ 360.90.

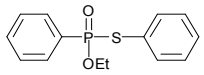

(5l)

Compound **5l** was obtained in 97% yield according to the general procedure **B** as white solid; **m.p.** 101-102℃; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 8.78-8.76 (m, 1H), 8.00-7.96 (m, 2H), 7.87-7.79 (m, 3H), 7.51-7.39 (m, 8H), 7.24-7.20 (m, 1H), 7.17-7.14 (m, 2H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 135.4 (d, J = 3.9), 133.9 (d, J = 10.2),

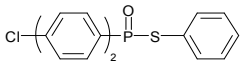
133.8 (d, *J* = 3.1), 133.5 (d, *J* = 11.0), 133.1 (d, *J* = 9.4), 132.6, 132.3 (d, *J* = 2.8), 131.8 (d, *J* = 10.6), 129.0, 128.8, 128.6 (d, *J* = 13.2), 127.8, 127.3, 127.1 (d, *J* = 4.8), 126.5, 14.3 (d, *J* = 15.0); **^{31}P NMR ($CDCl_3$, 162 MHz):** δ 43.3; **MS (ESI, *m/z*)** $[M+H]^+$ 361.00, $[M+Na]^+$ 382.90.


(5m)

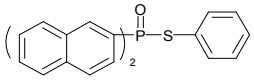
Compound **5m** was obtained in 71% yield according to the general procedure **B** as White solid; **m.p.** 119-121℃; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.63-7.59 (m, 2H), 7.45-7.43 (m, 3H), 7.36-7.33 (m, 2H), 7.27-7.22 (m, 2H), 7.21-7.18 (m, 4H), 7.07-7.05 (m, 2H), 3.57-3.53 (m, 2H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 135.4 (d, *J* = 3.5), 132.2 (d, *J* = 2.9), 131.7 (d, *J* = 9.6), 130.8, 130.7 (d, *J* = 8.3), 130.1 (d, *J* = 5.8), 129.2, 128.9 (d, *J* = 1.8), 128.5 (d, *J* = 3.1), 128.3 (d, *J* = 12.7), 127.1 (d, *J* = 3.6), 125.9 (4.9), 41.6 (d, 66.0); **^{31}P NMR ($CDCl_3$, 162 MHz):** δ 47.0; **MS (ESI, *m/z*)** $[M+H]^+$ 324.90, $[M+Na]^+$ 346.90.


(5n)

Compound **5n** was obtained in 99% yield according to the general procedure **B** as colorless oil; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.65-7.59 (m, 2H), 7.48-7.44(m, 1H), 7.36-7.32 (m, 2H), 7.28-7.24 (m, 3H), 7.20-7.16 (m, 2H), 4.40-4.25 (m, *J* = 7.1, 2H), 1.39-1.36 (t, *J* = 7.0, 3H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 135.5 (d, *J* = 4.2), 132.5 (d, *J* = 3.2), 132.2, 131.5 (d, *J* = 10.5), 130.7, 129.1 (d, *J* = 2.1), 128.9 (d, *J* = 2.6), 128.2 (d, *J* = 14.8), 126.6 (d, *J* = 5.5), 62.5 (d, *J* = 6.9), 16.3 (d, *J* = 6.7); **^{31}P NMR ($CDCl_3$, 162 MHz):** δ 41.7; **MS (ESI, *m/z*)** $[M+H]^+$ 278.90, $[M+Na]^+$ 300.90.

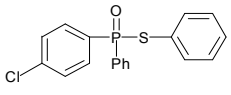

(5o)

Compound **5o** was obtained in 90% yield according to the general procedure **B** as white solid; **m.p.** 46-48℃; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.76-7.69 (m, 4H), 7.41-7.39 (m, 6H), 7.28-7.24 (m, 1H), 7.22-7.318 (m, 2H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 139.2 (d, *J* = 3.7), 135.4 (d, *J* = 3.9), 132.9 (d, *J* = 11.2), 131.2, 130.1, 129.3 (d, *J* = 1.7), 129.3, 129.1 (d, *J* = 13.7), 125.3 (d, *J* = 5.1); **^{31}P NMR ($CDCl_3$, 162 MHz):** δ 39.3; **MS (ESI, *m/z*)** $[M+H]^+$ 378.80, $[M+Na]^+$ 400.20.


(5p)

Compound **5p** was obtained in 99% yield according to the general procedure **B** as white solid; **m.p.** 150-151℃; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 8.78-8.76 (m, 1H), 8.00-7.79 (m, 6H), 7.51-7.39 (m, 9H), 7.23-7.20 (m, 1H), 7.17-7.14 (m, 2H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 135.4 (d, *J* = 3.9), 133.9 (d, *J* = 10.2), 133.8 (d, *J* = 3.1),

133.5 (d, *J* = 11.0), 133.1 (d, *J* = 9.4), 132.6, 132.3 (d, *J* = 2.8), 131.8 (d, *J* = 10.4), 129.0, 128.8, 128.6 (d, *J* = 13.2), 127.8, 127.3, 127.1 (d, *J* = 4.8), 126.5, 124.3 (d, *J* = 15.0); **^{31}P NMR ($CDCl_3$, 162 MHz):** δ 45.3; **MS (ESI, *m/z*)** $[M+H]^+$ 411.00, $[M+Na]^+$ 432.90.

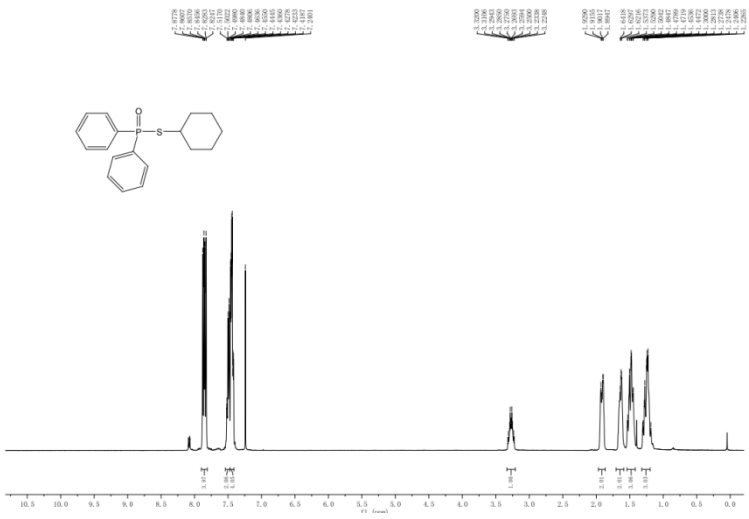


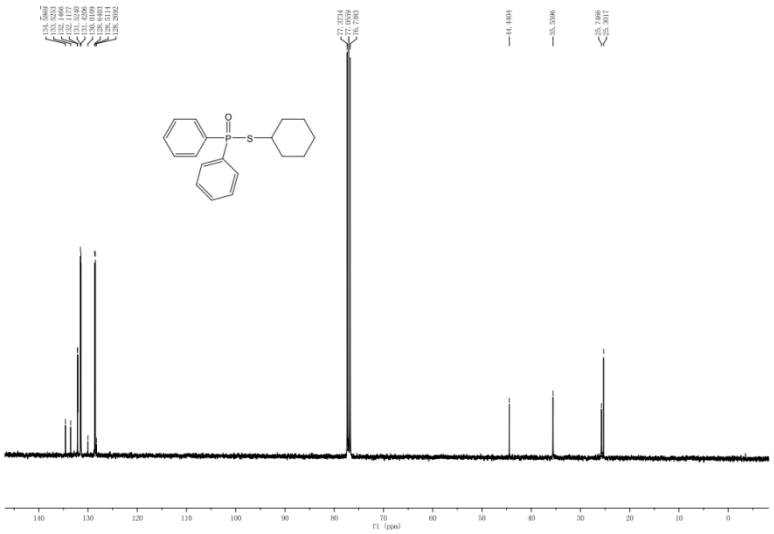
(5q)

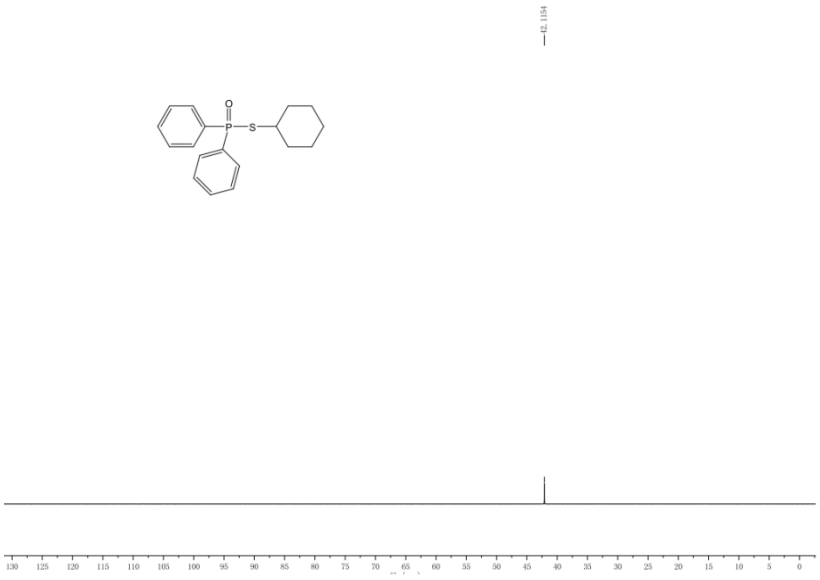
Compound **5q** was obtained in 95% yield according to the general procedure B as white solid; **m.p.** 62-64℃; **^{1}H NMR ($CDCl_3$, 400 MHz)**: δ 7.84-7.79 (m, 4H), 7.51-7.37 (m, 7H), 7.25-7.22 (m, 1H), 7.20-7.17 (m, 2H); **^{13}C NMR ($CDCl_3$, 100 MHz)**: δ 138.9 (d, *J* = 3.5), 135.4 (d, *J* = 3.9), 133.0 (d, *J* = 11.0), 132.5 (d, *J* = 2.9), 132.3 (d, *J* = 2.9), 131.7 (d, *J* = 8.5), 131.59 (d, *J* = 9.9), 131.55 (d, *J* = 10.2), 130.6, 129.2, 129.1, 128.9 (d, *J* = 13.7), 128.7 (d, *J* = 13.1), 128.5 (d, *J* = 13.1), 125.7 (d, *J* = 5.1); **^{31}P NMR ($CDCl_3$, 162 MHz):** δ 40.3; **MS (ESI, *m/z*)** $[M+H]^+$ 344.90, $[M+Na]^+$ 367.10.

5. Copies of NMR spectra for products

3a







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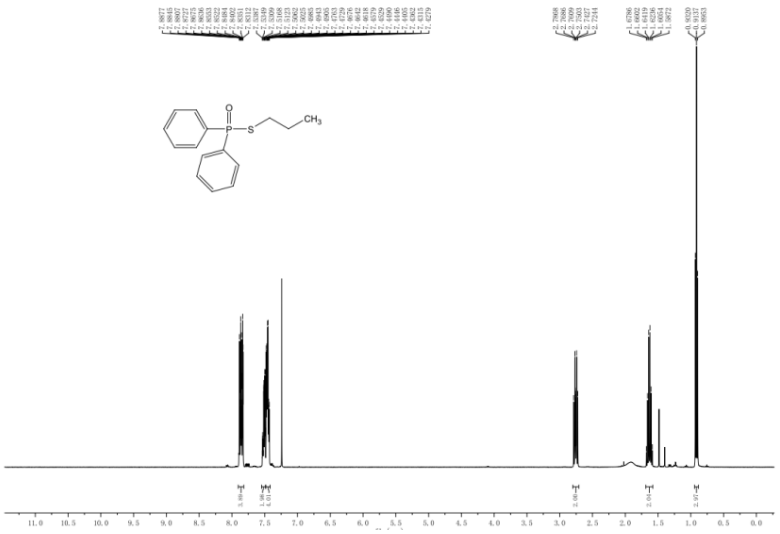

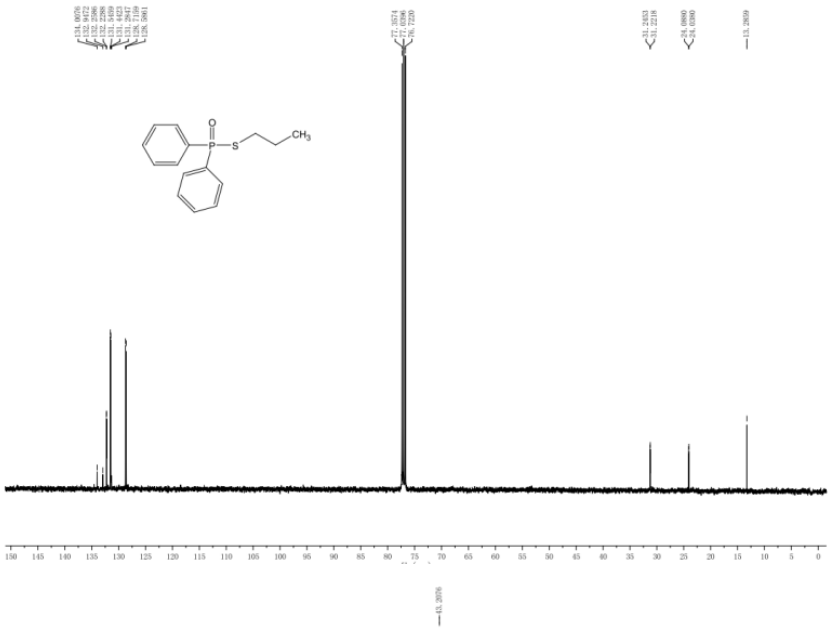

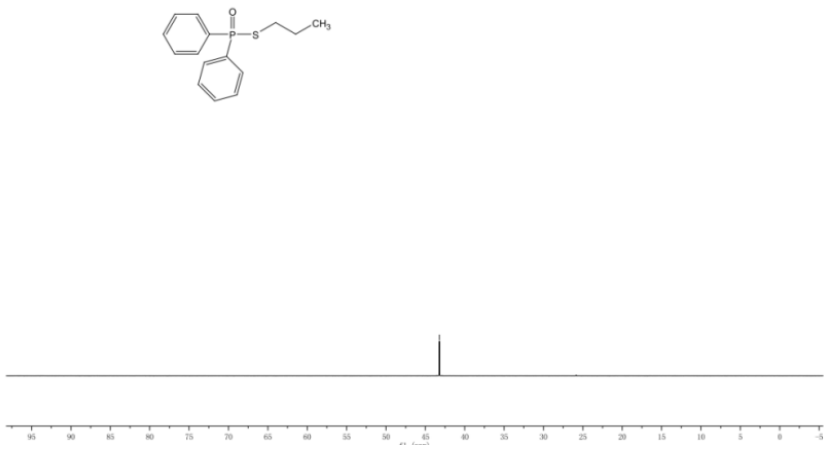

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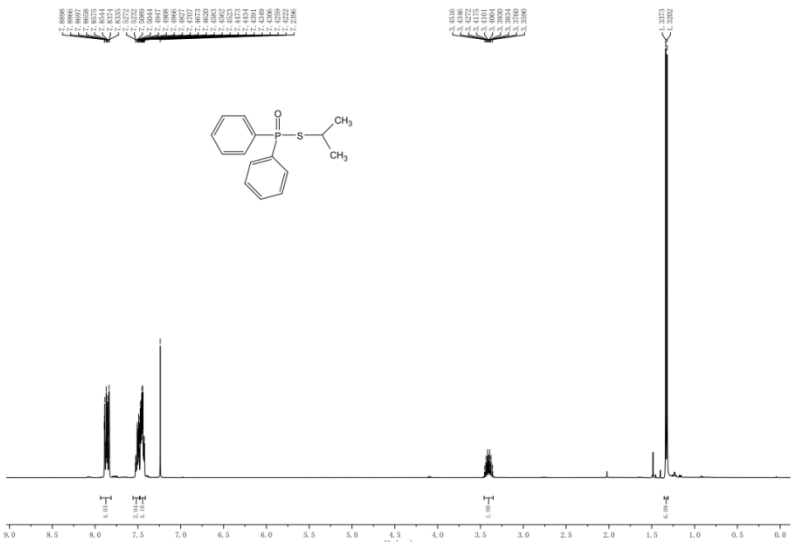

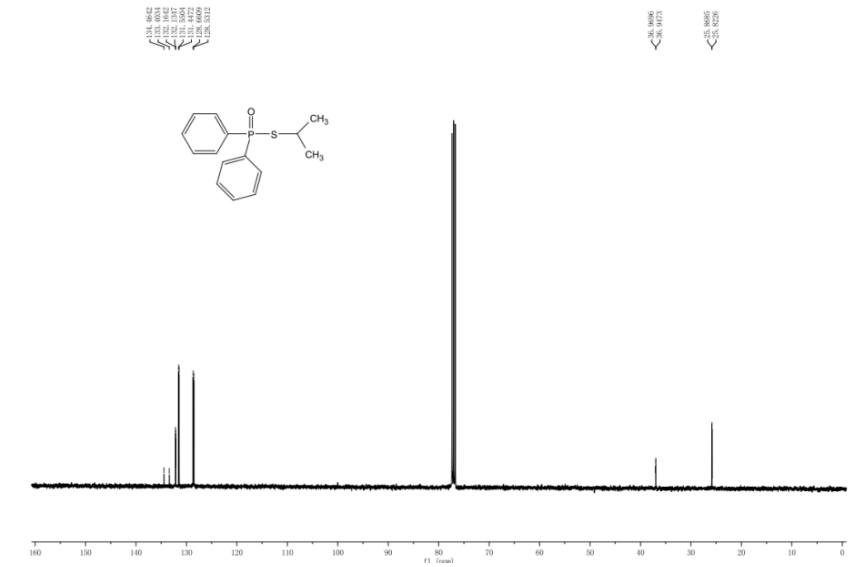

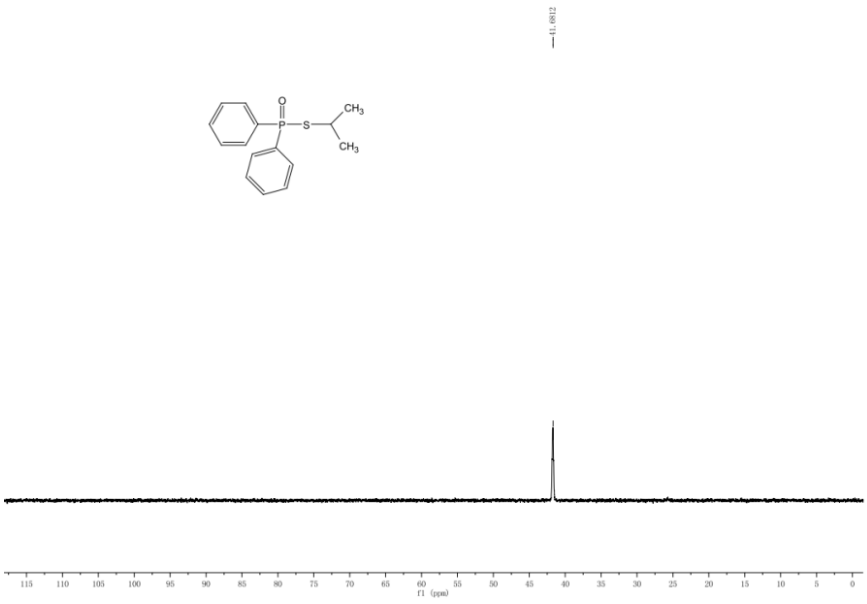

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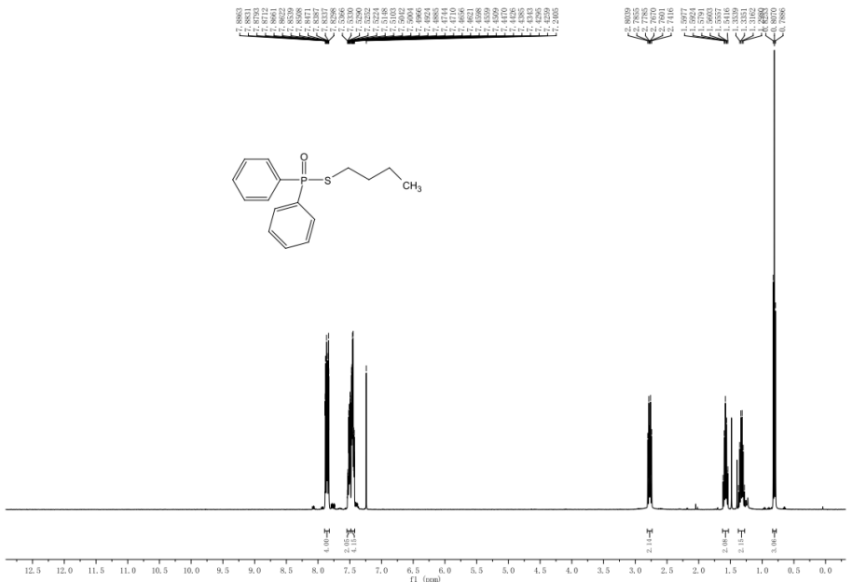

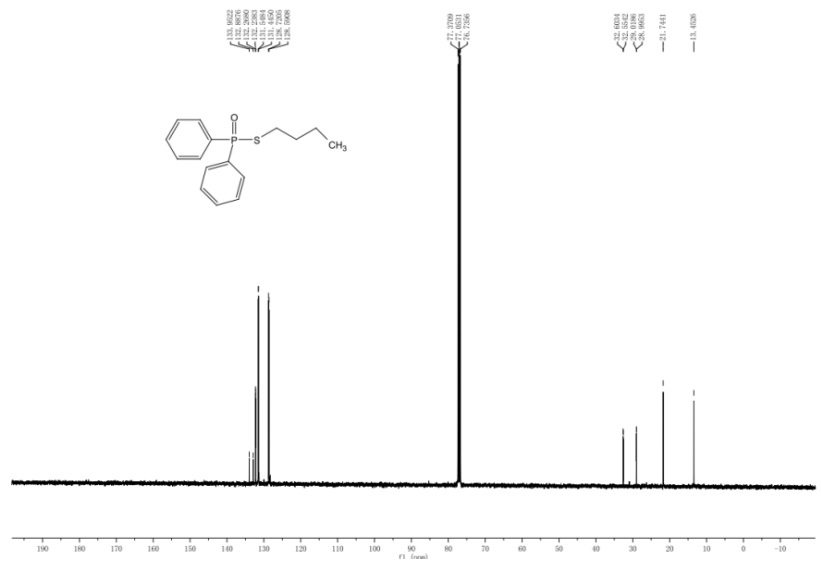

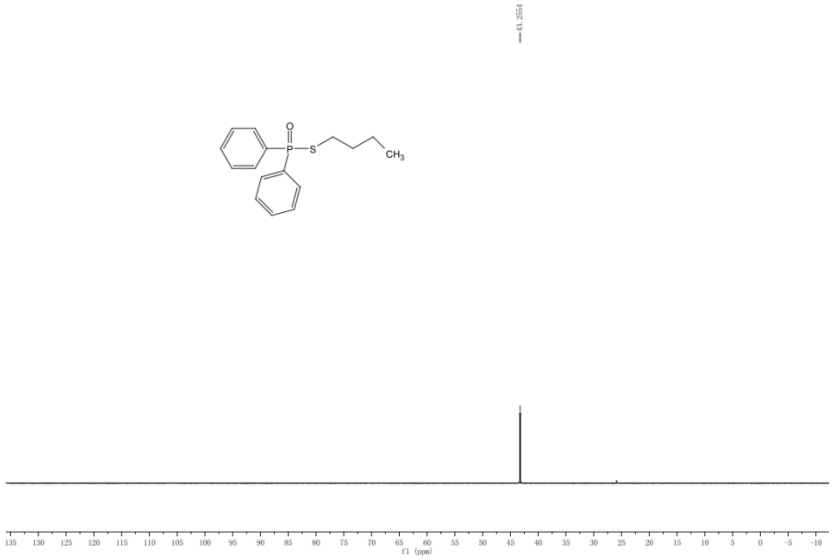

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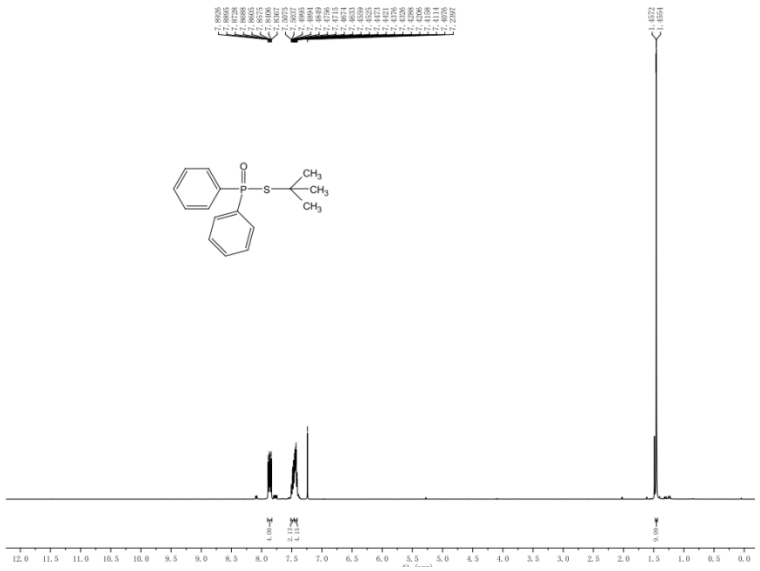

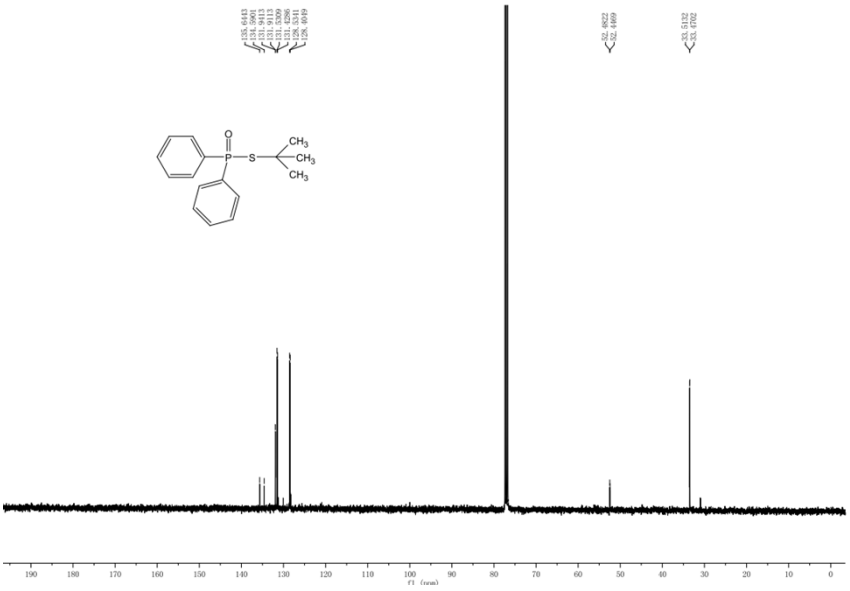
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131.9113
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131.1999
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128.4049
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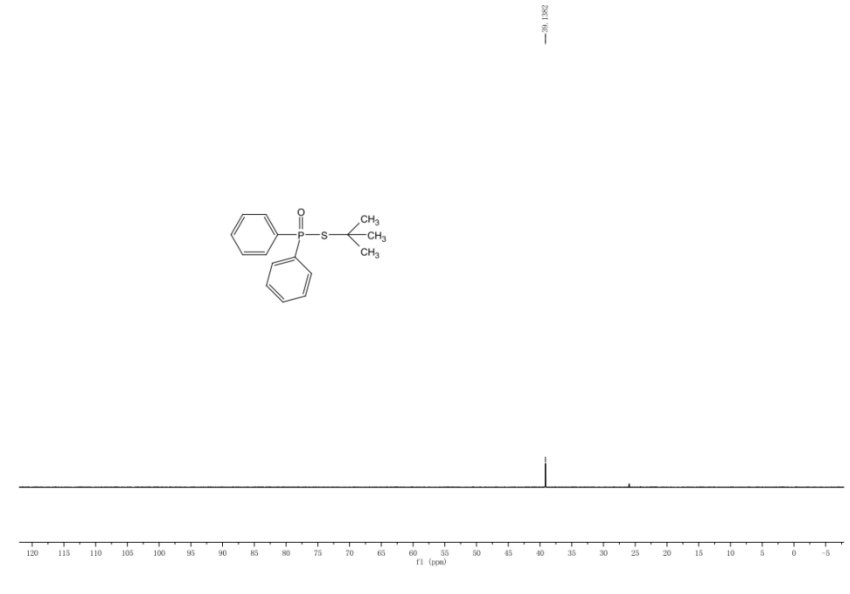
52.4469
43.5132
43.4782
O
P
S
CH3
CH3
CH3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


39.1382
O
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S
CH3
CH3
CH3
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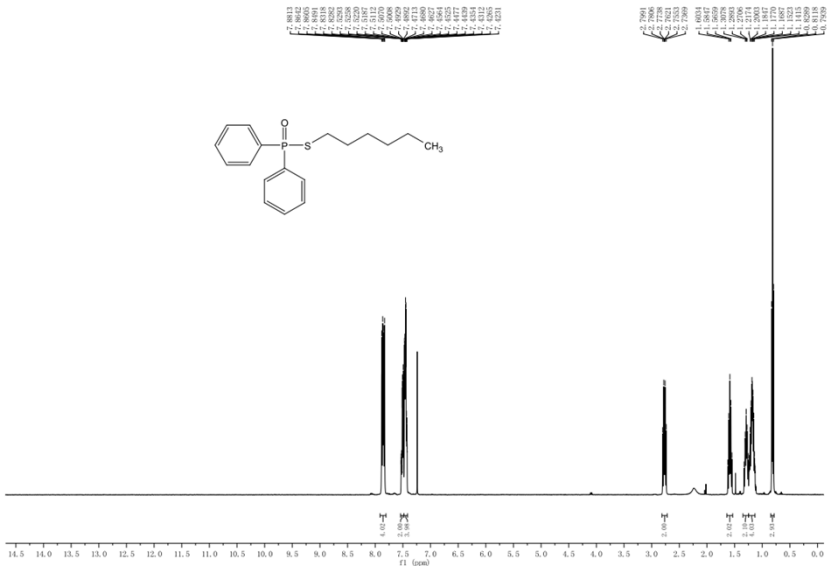
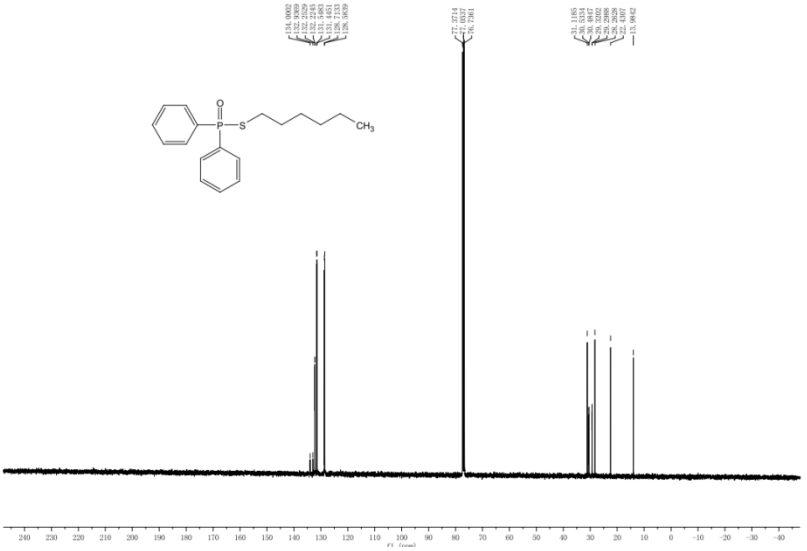
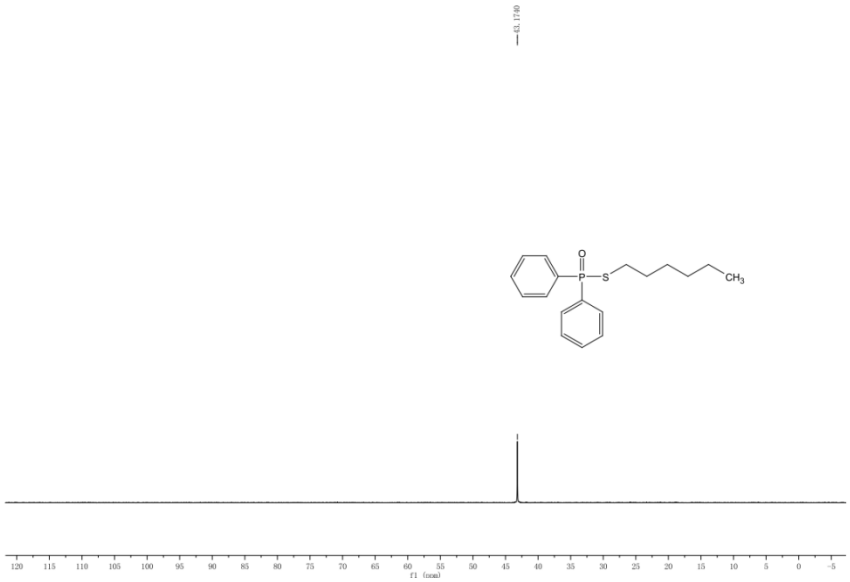
f1 (ppm)

3f







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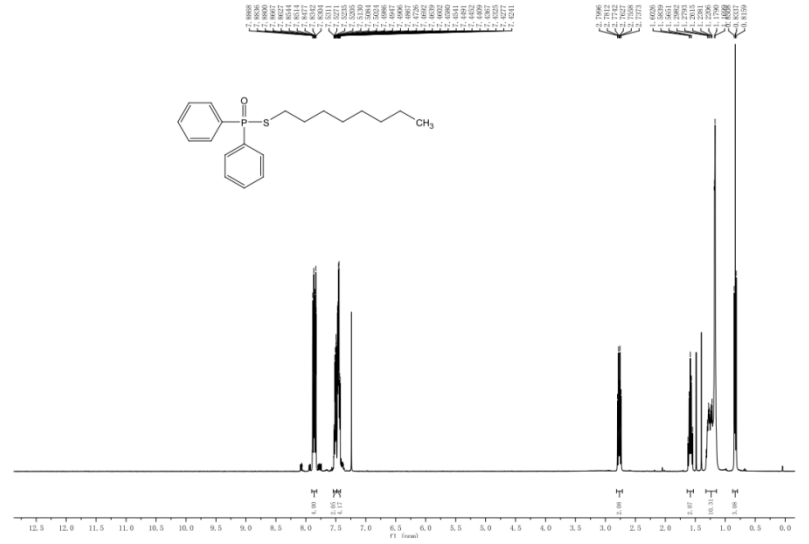
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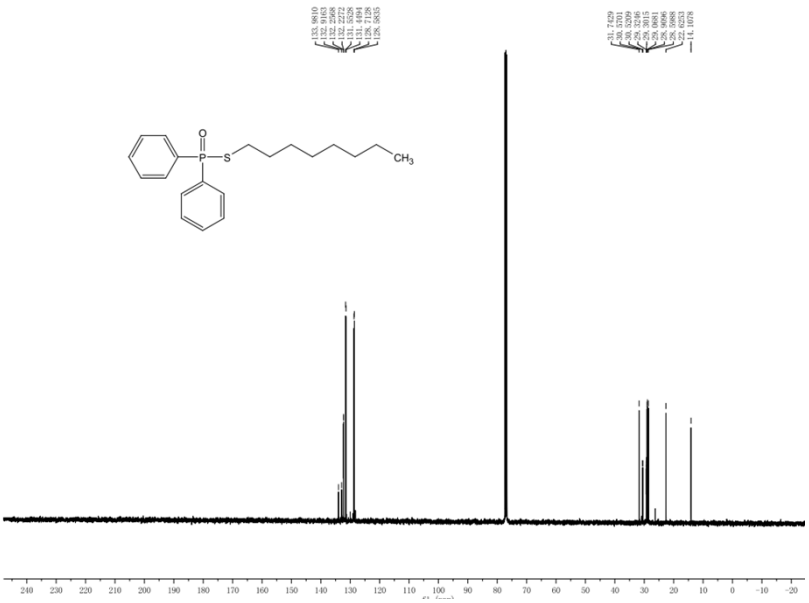
P
S
CH3
f1 (ppm)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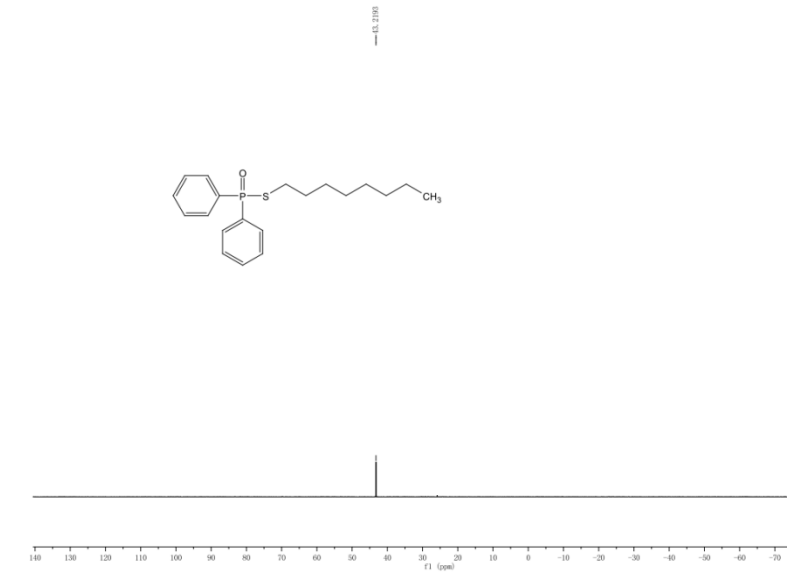
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S
CH3
f1 (ppm)

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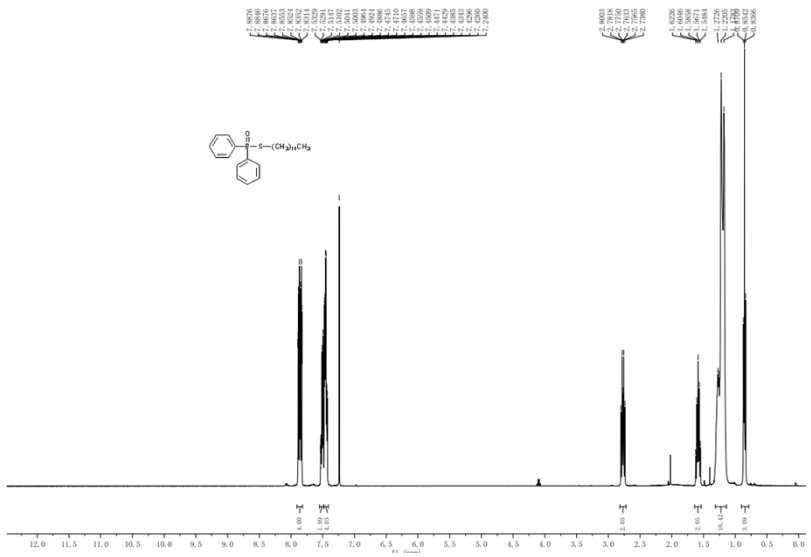

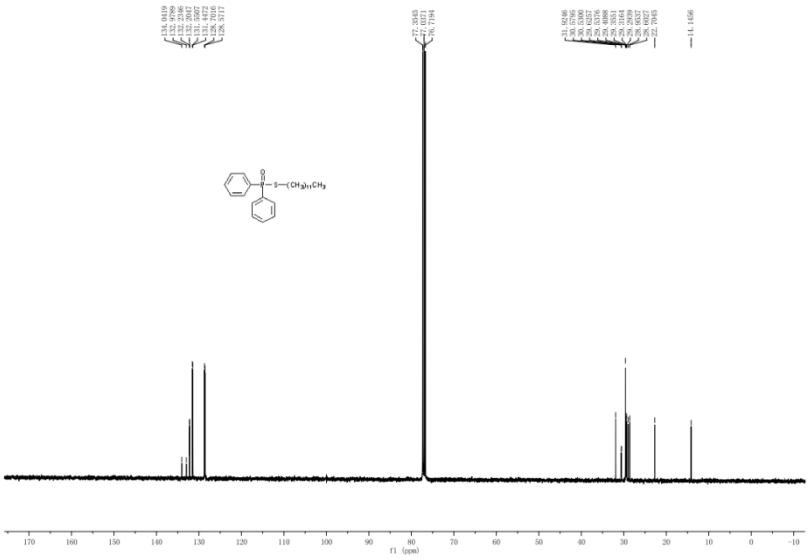

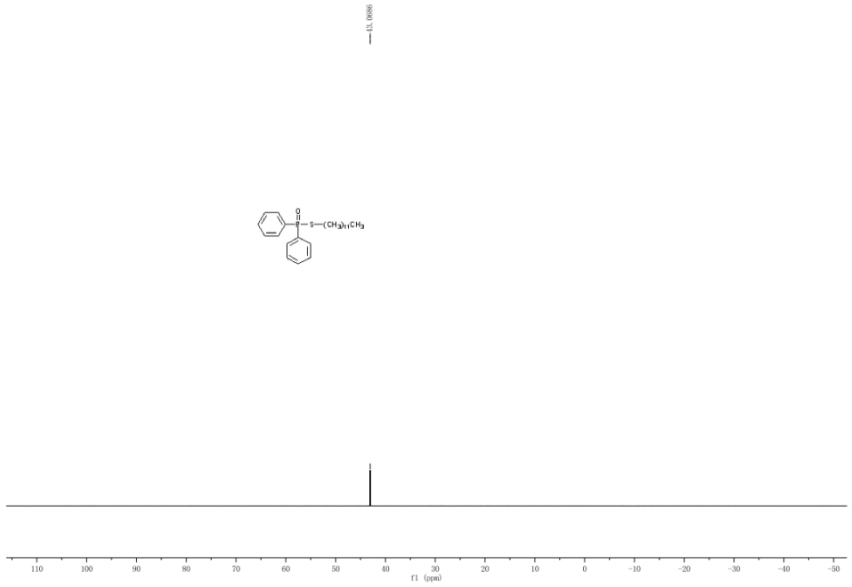

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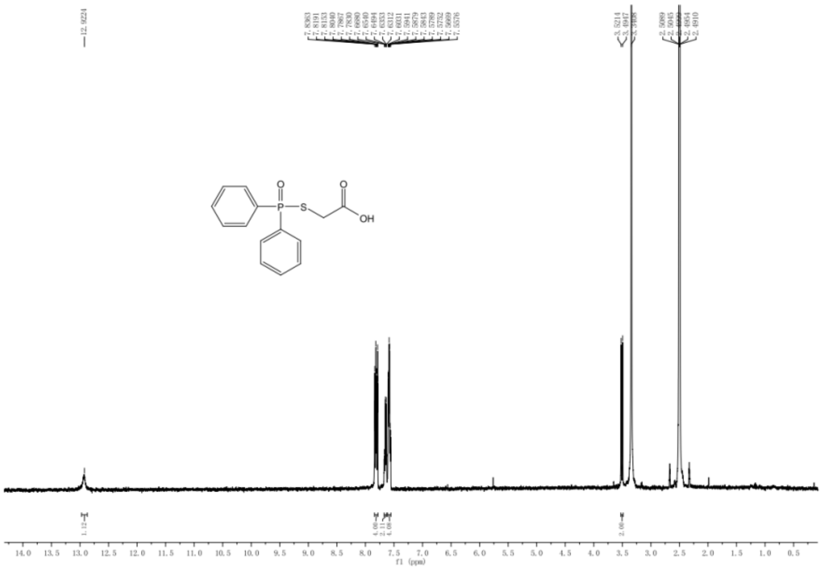

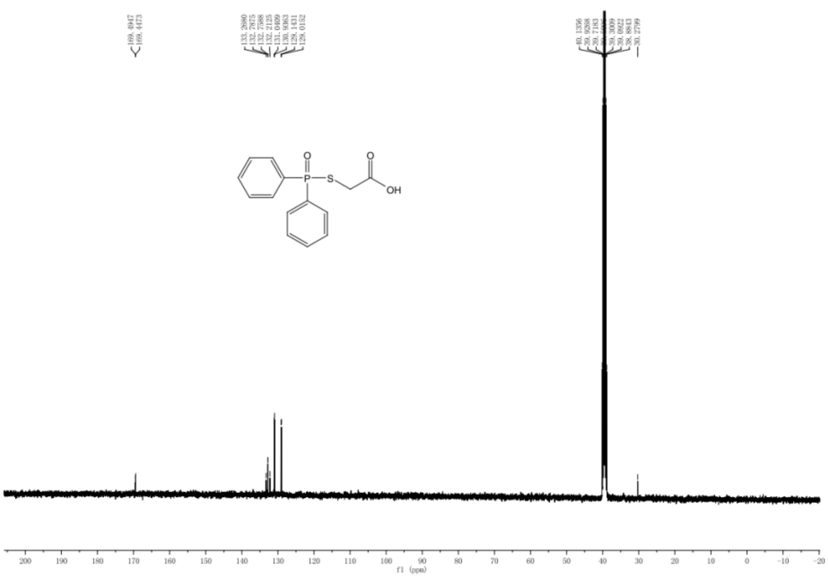

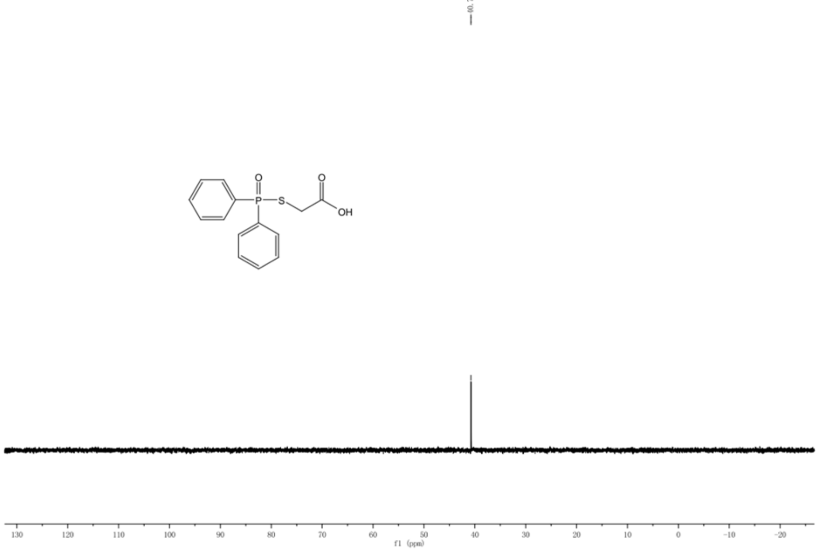

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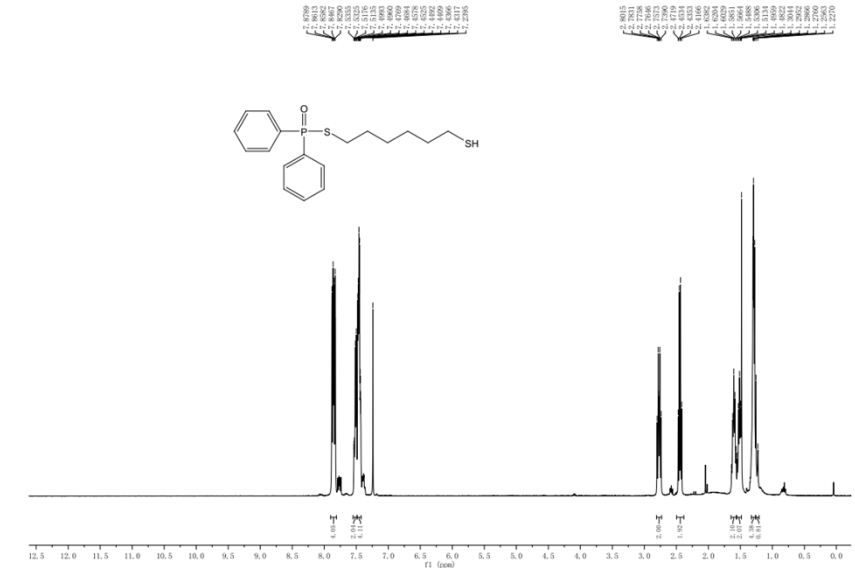

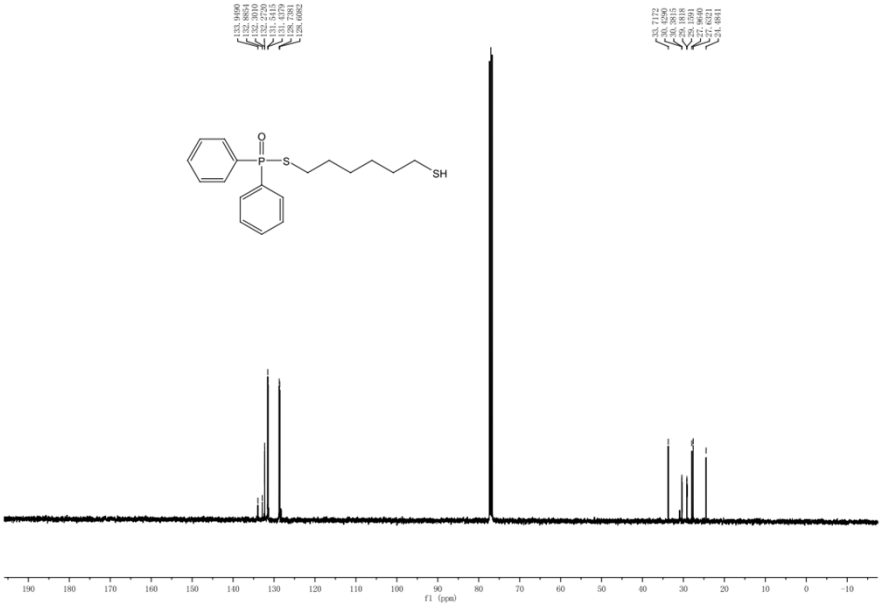

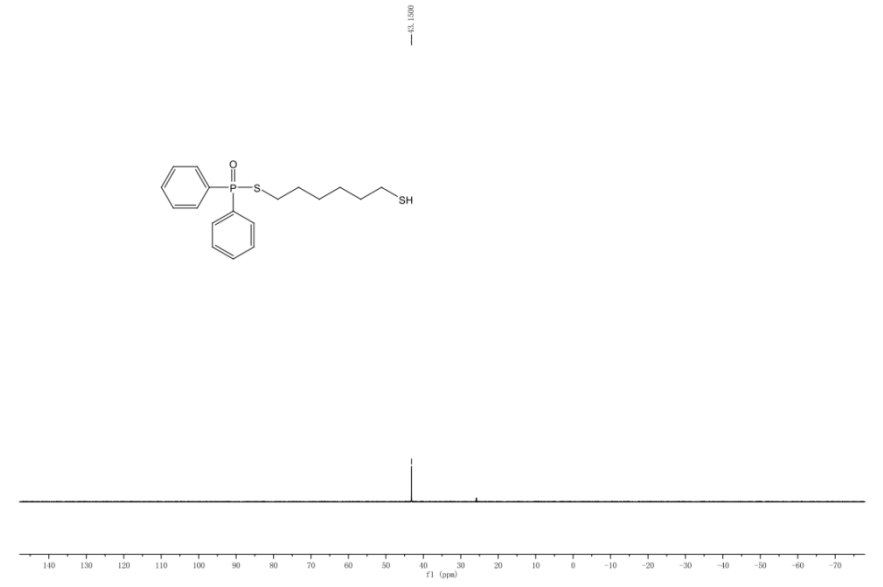

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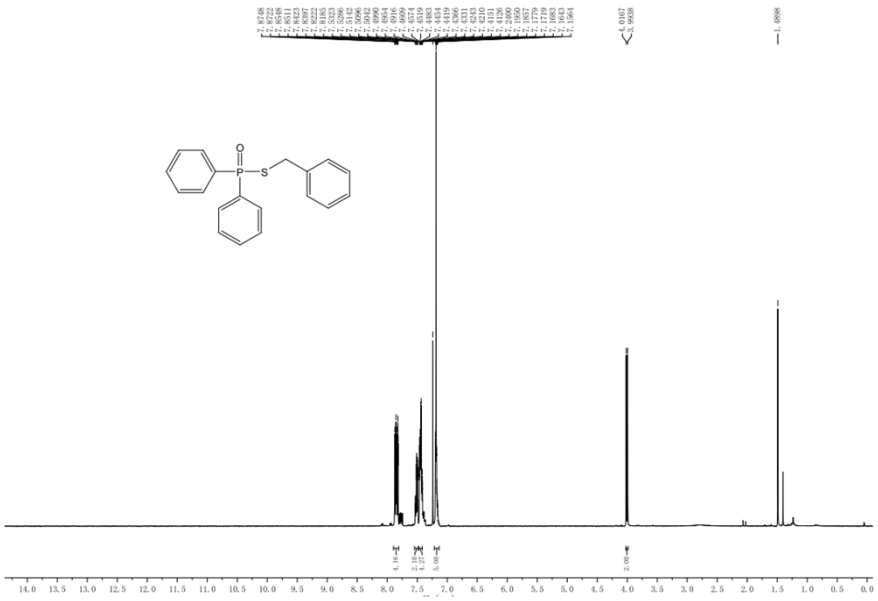

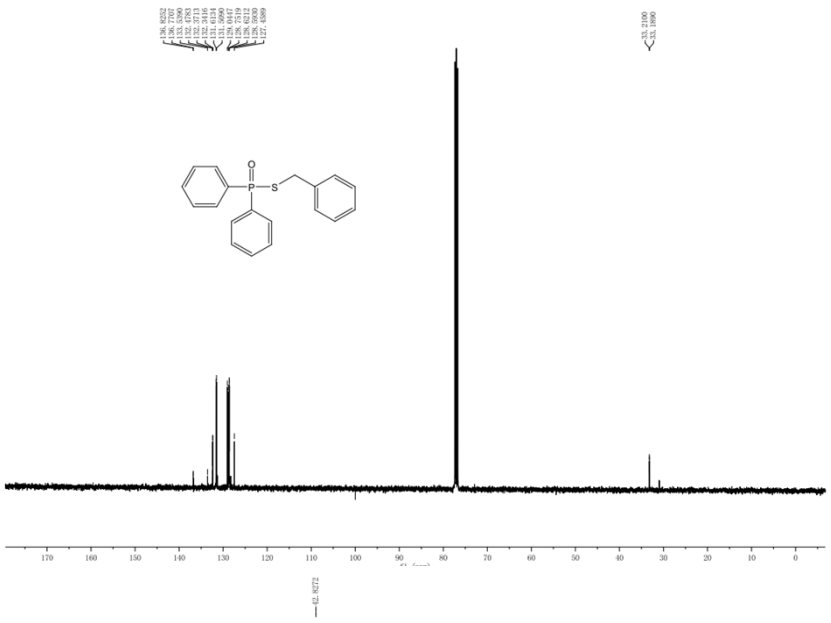

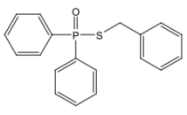

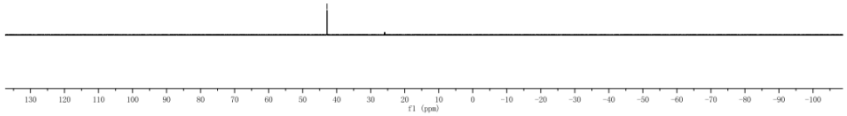

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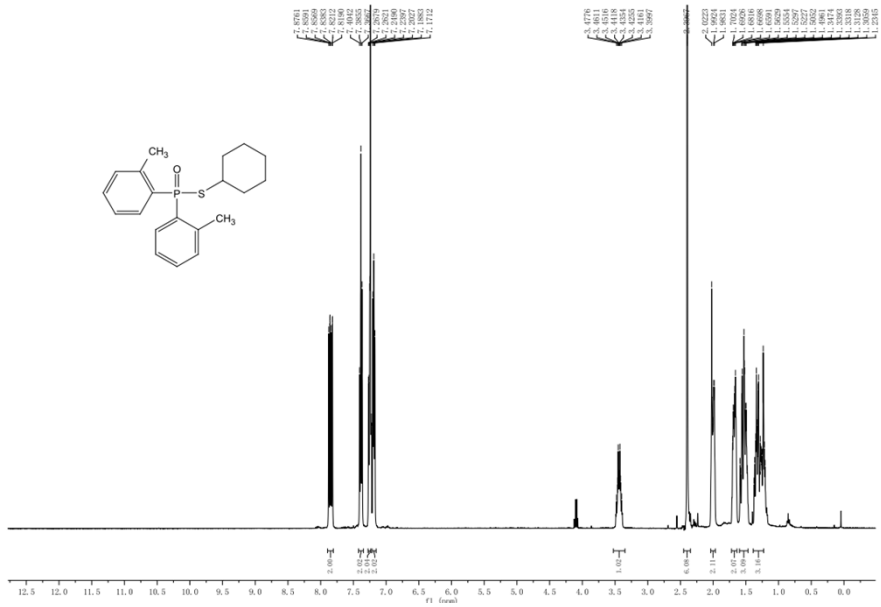

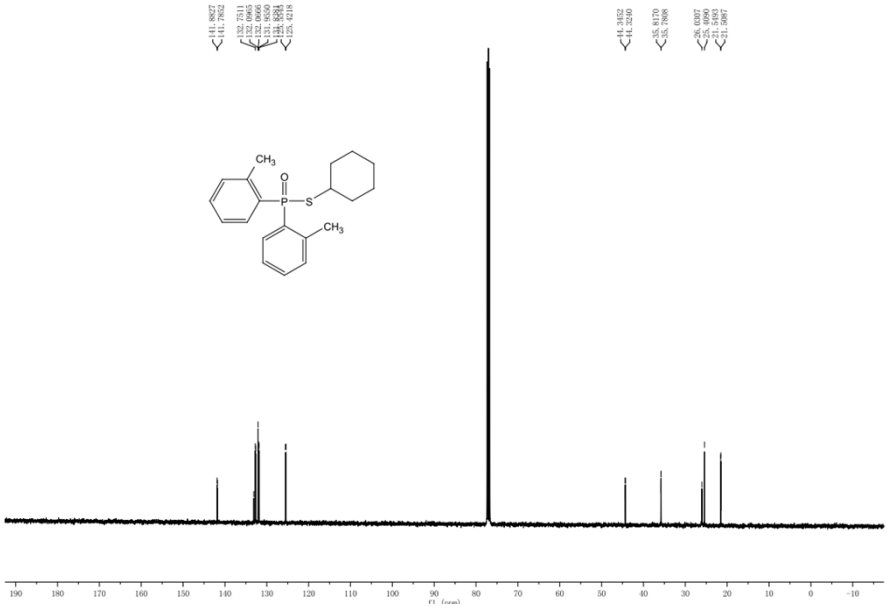

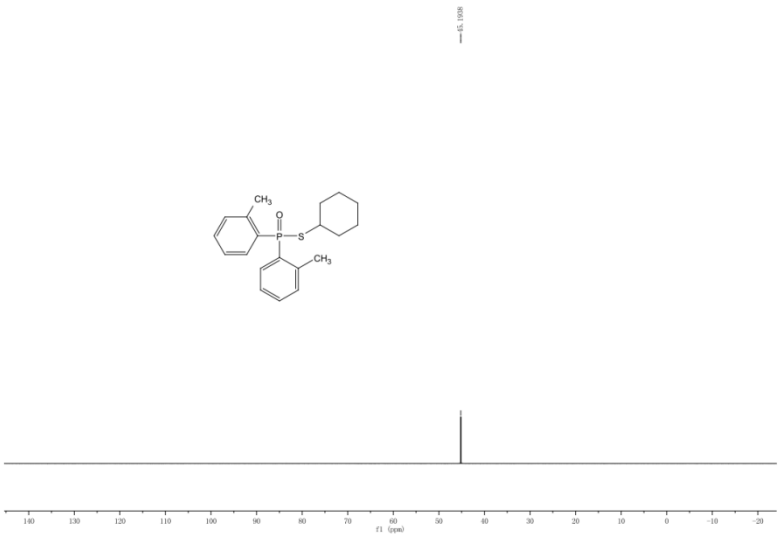

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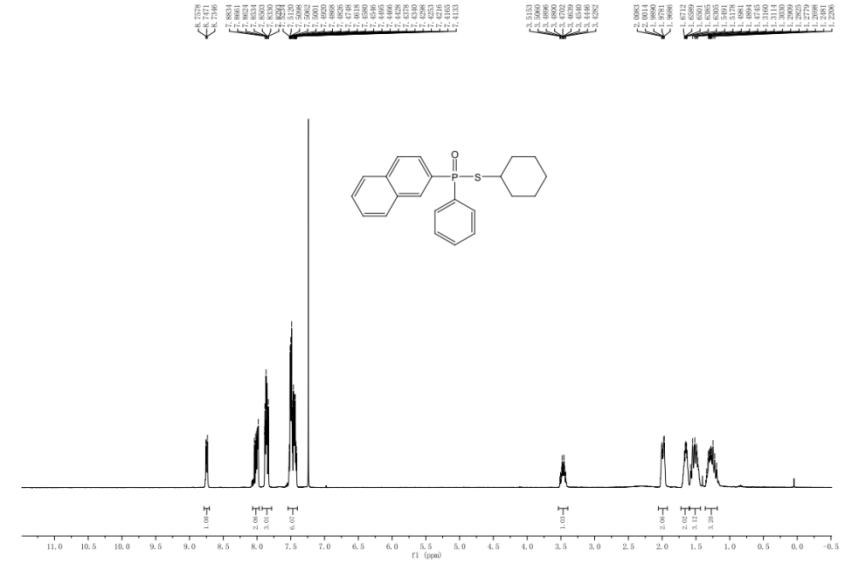

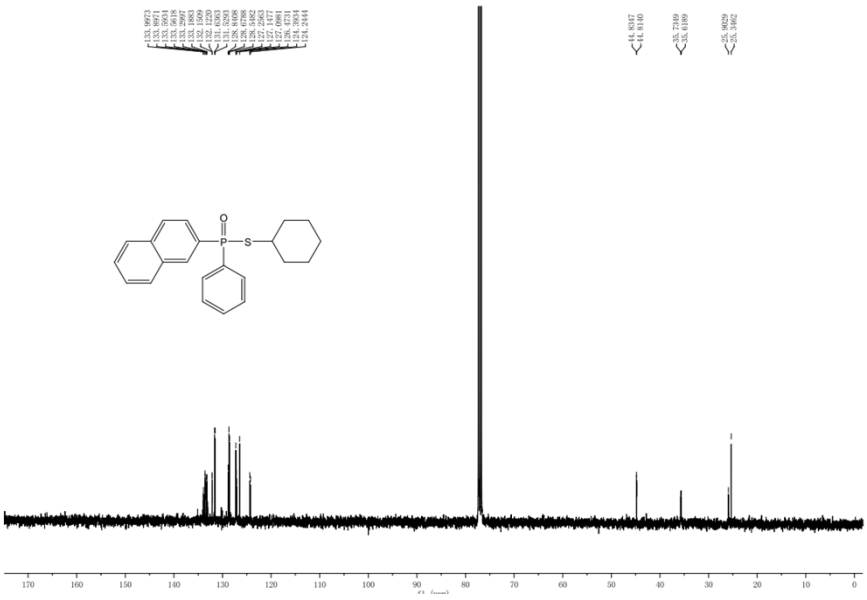

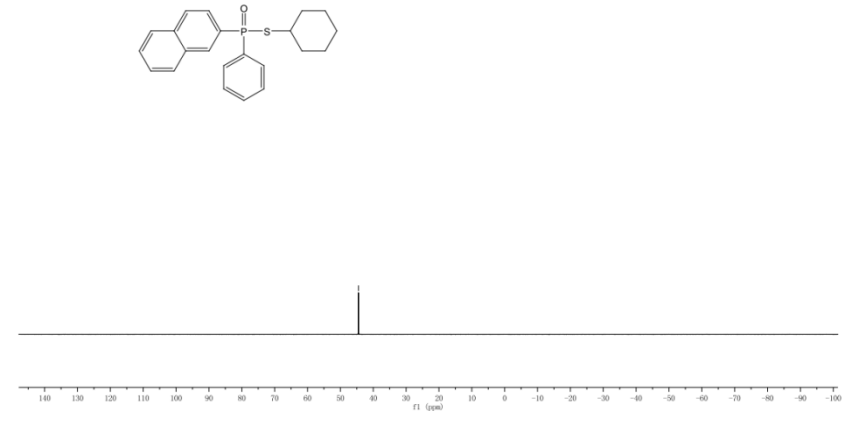

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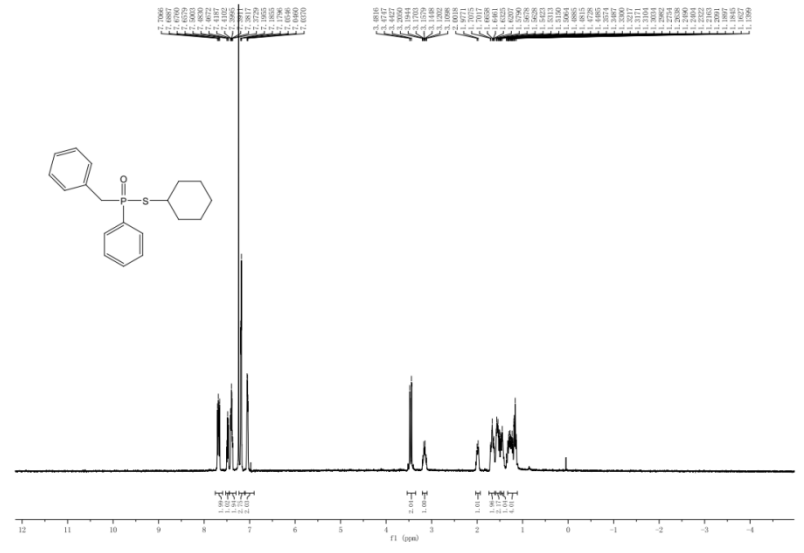

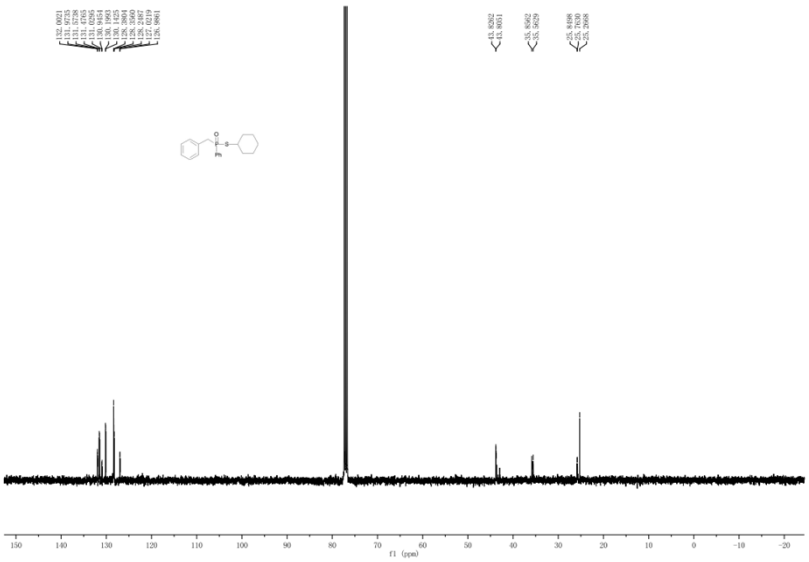

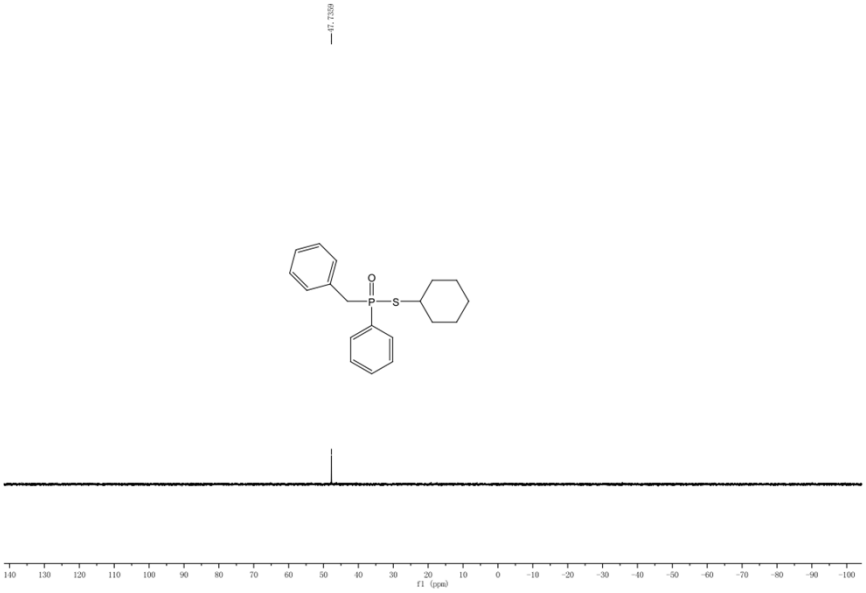

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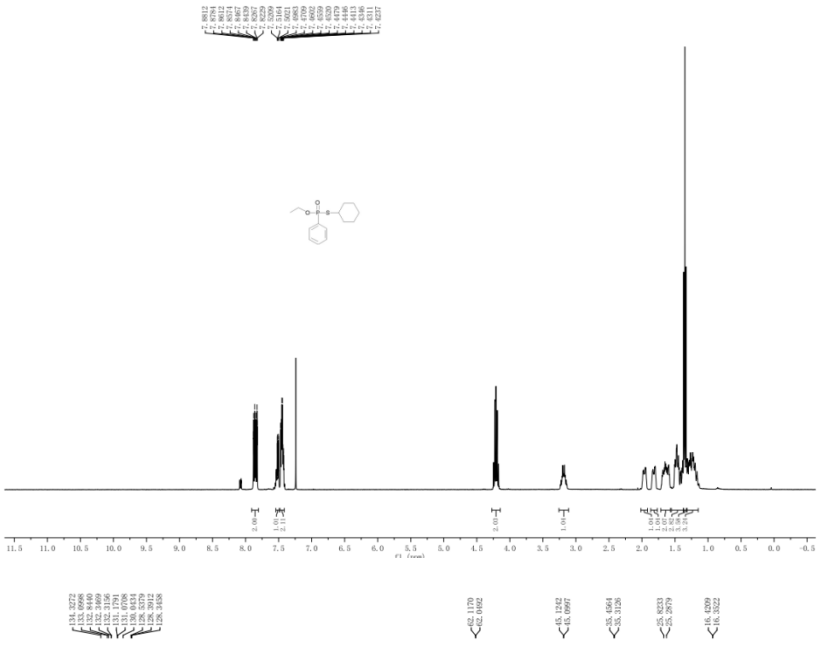

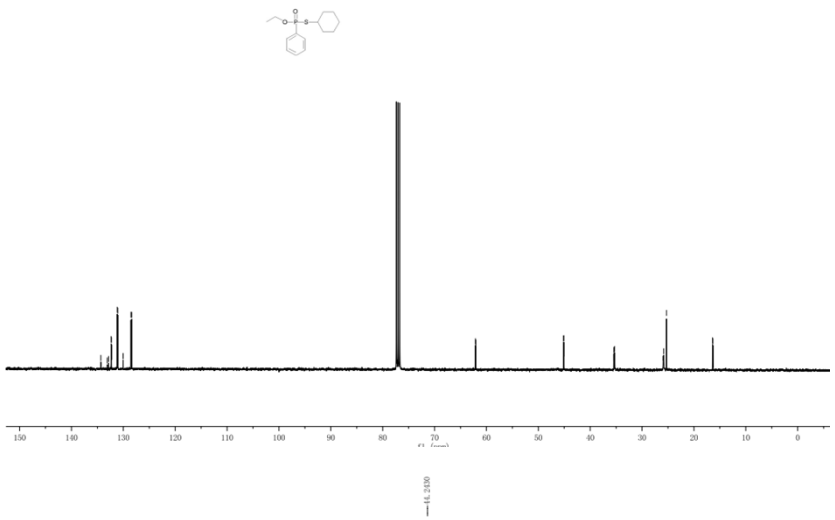

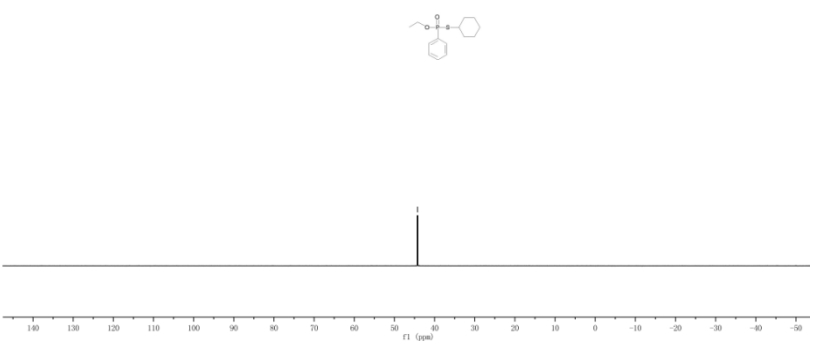

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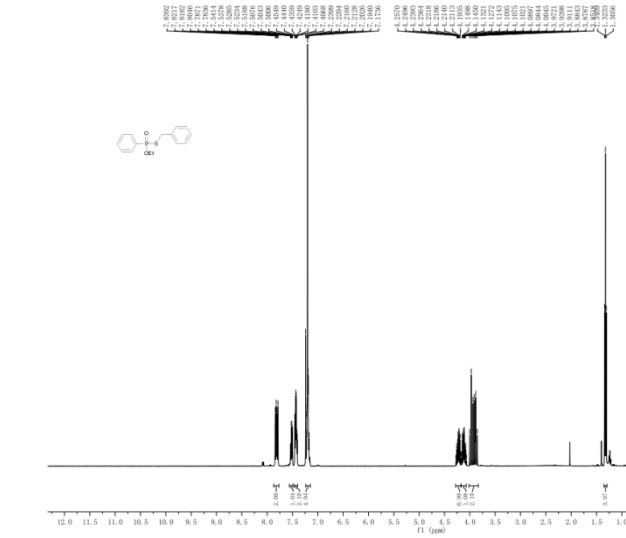

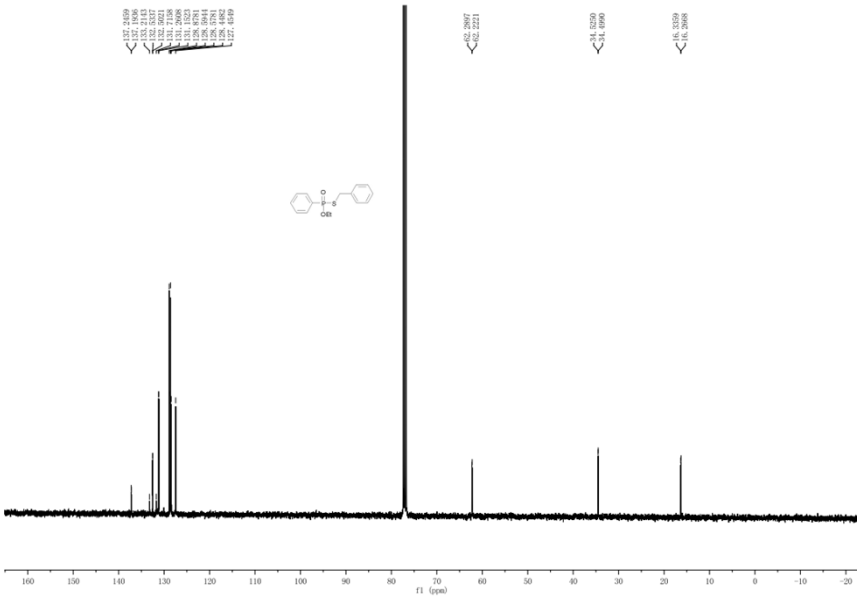

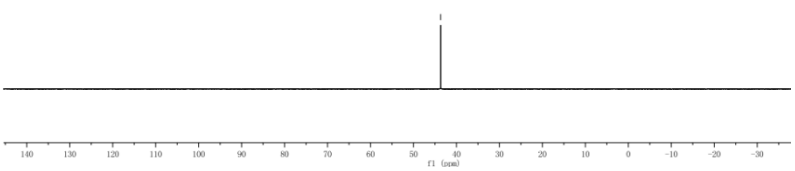

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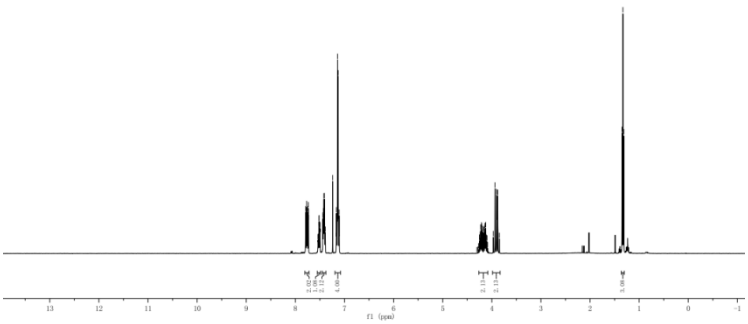

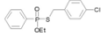

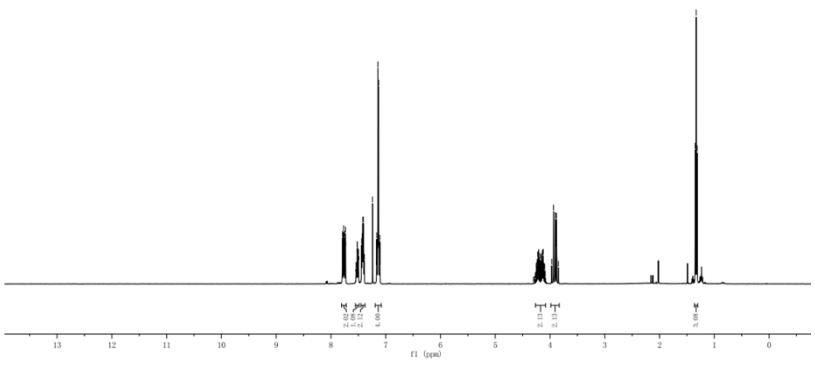

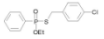

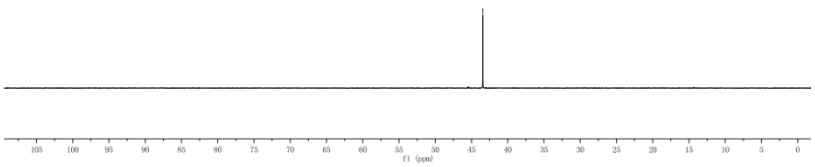

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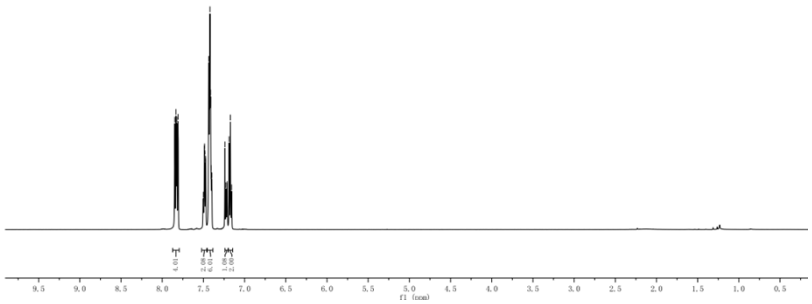

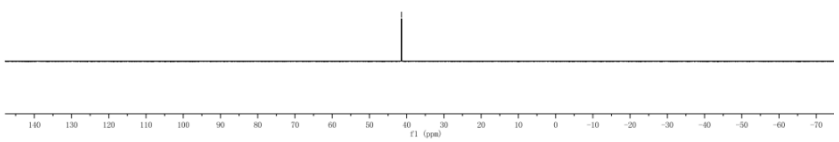

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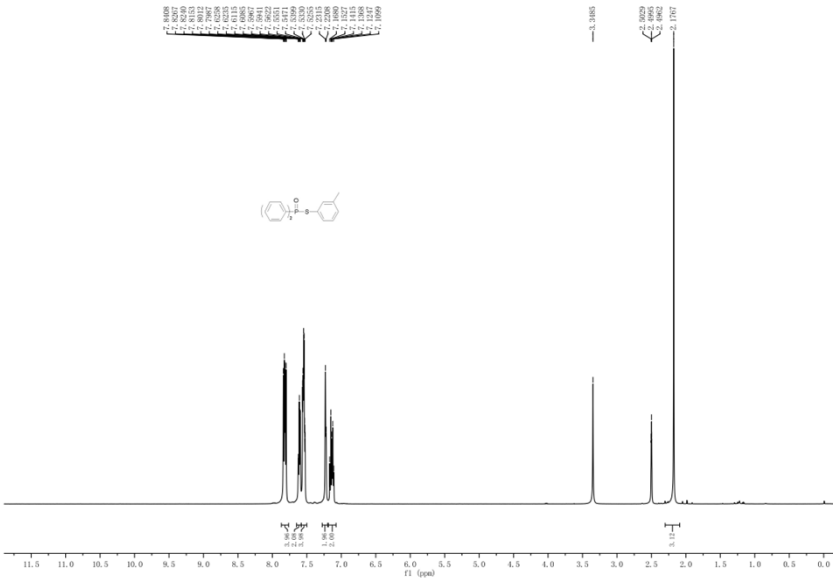

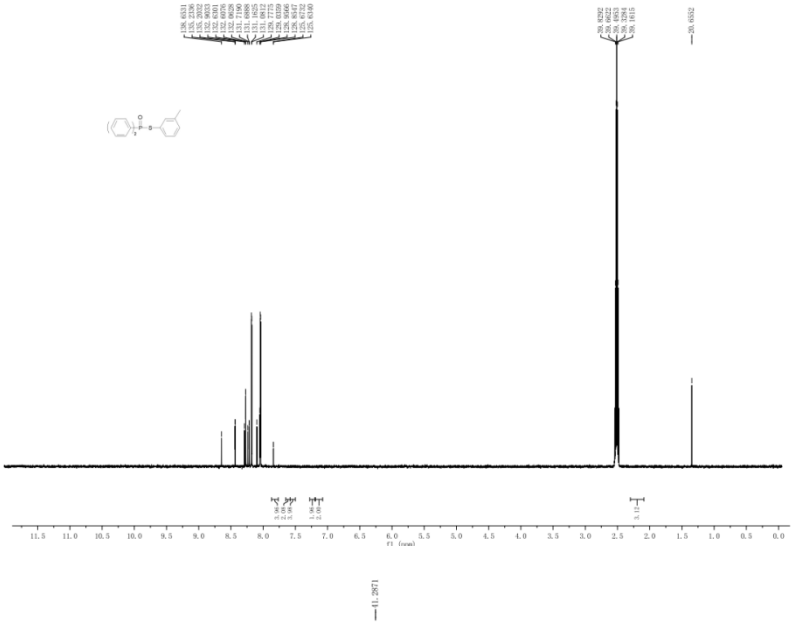

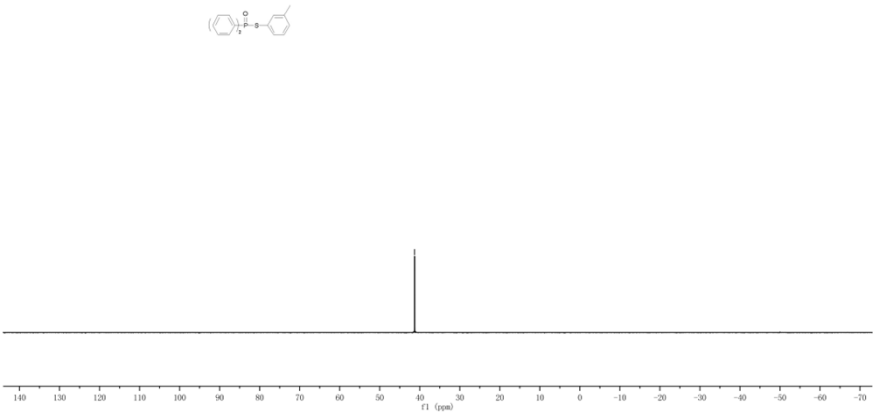

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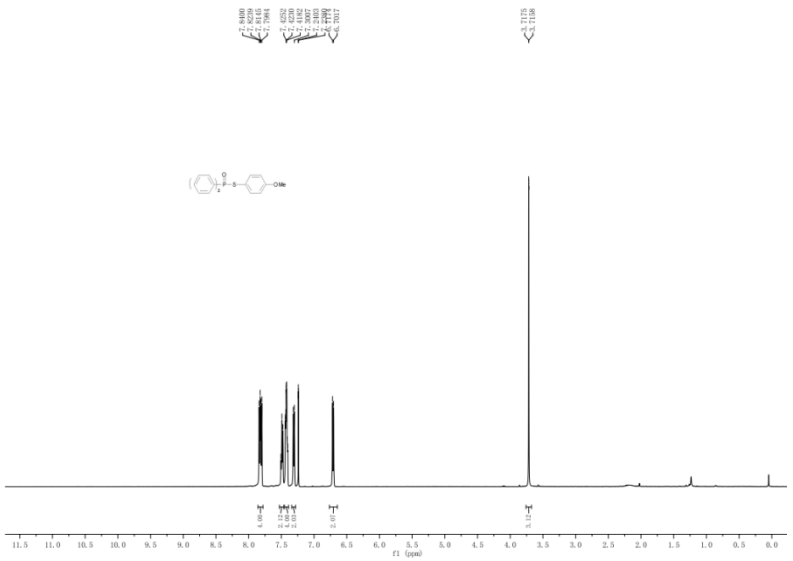

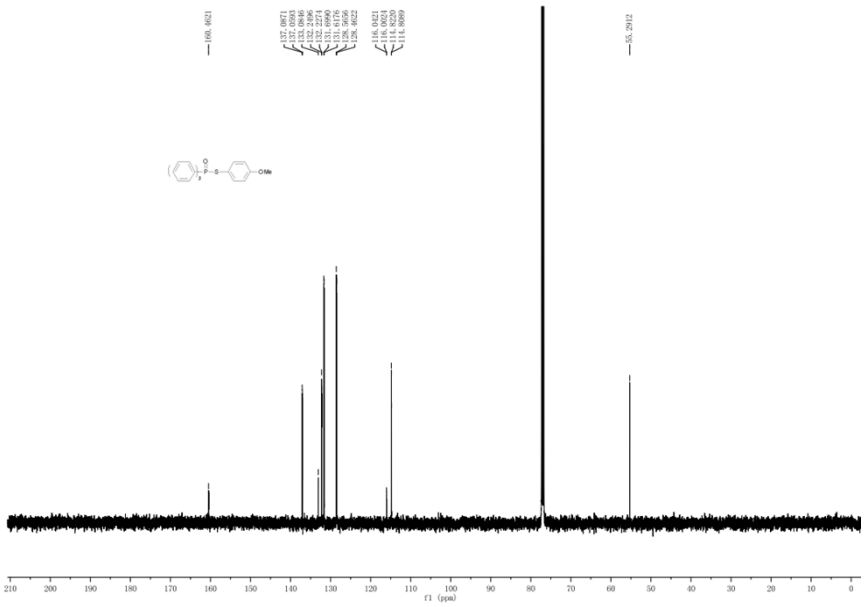

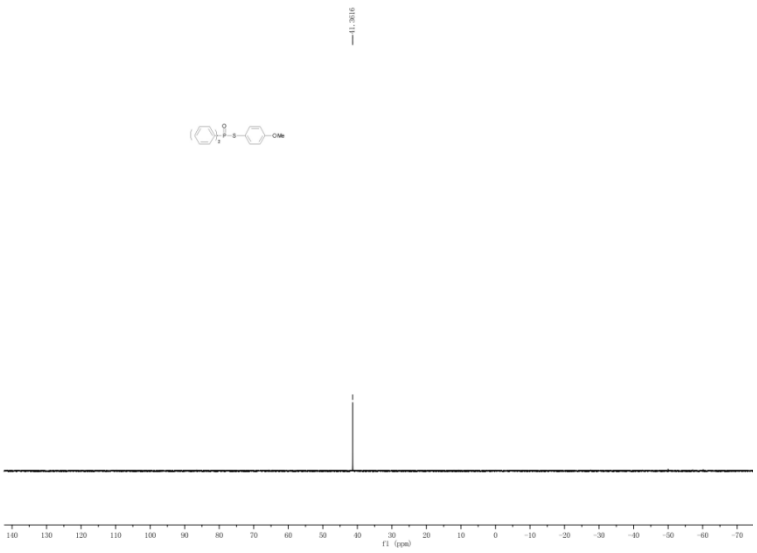

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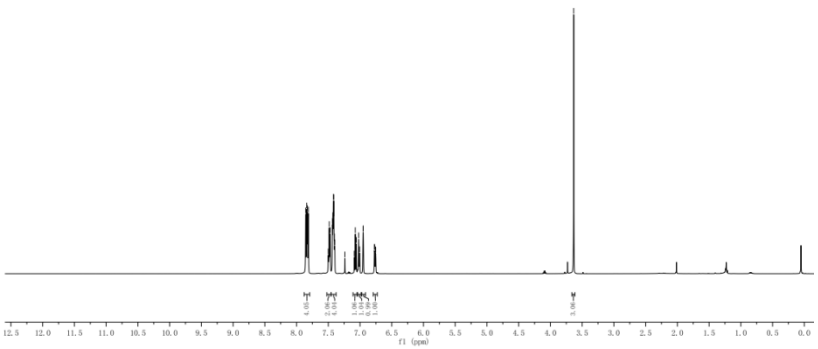

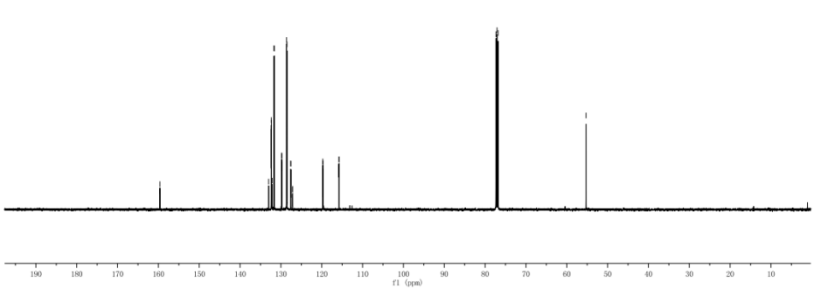

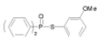

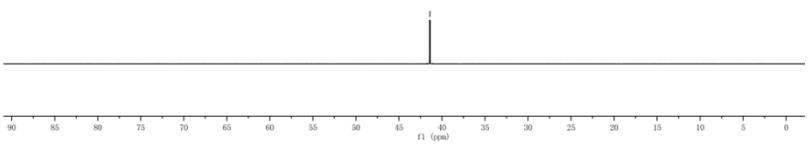

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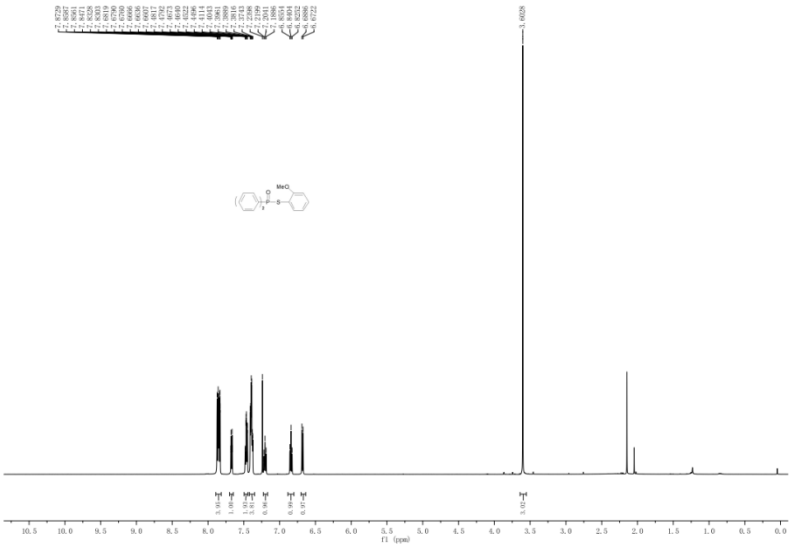

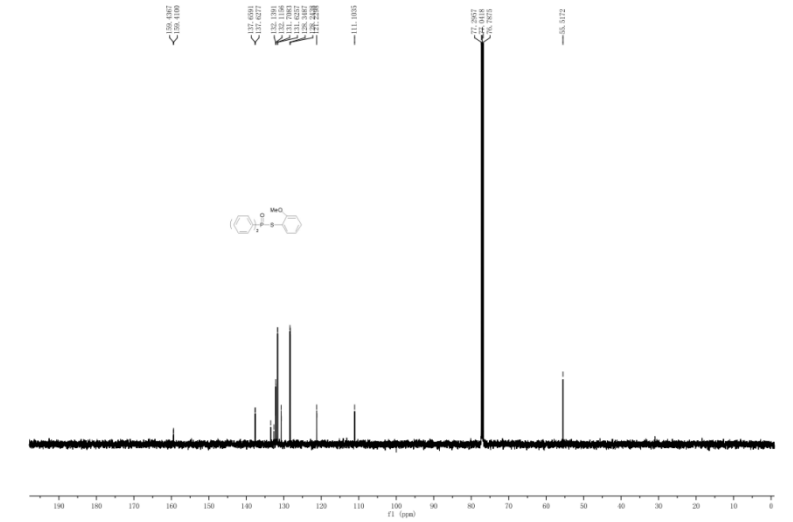

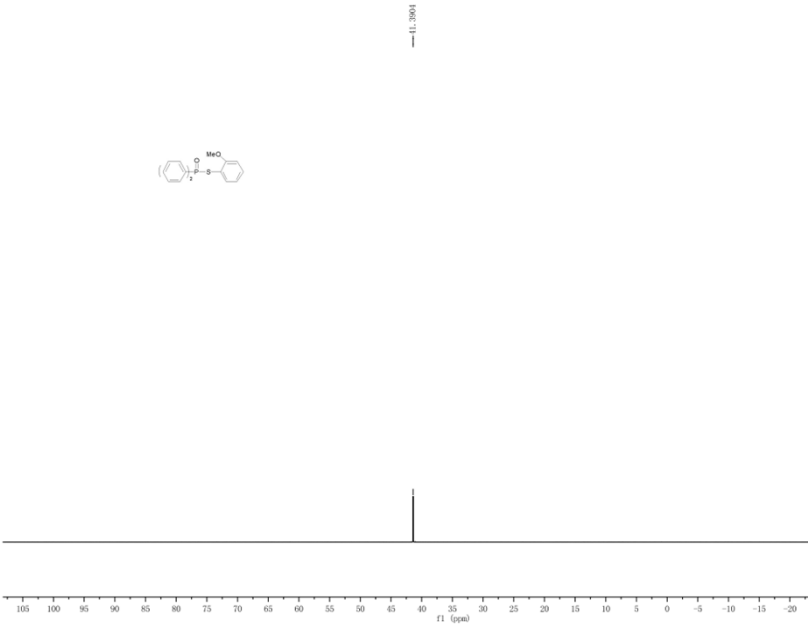

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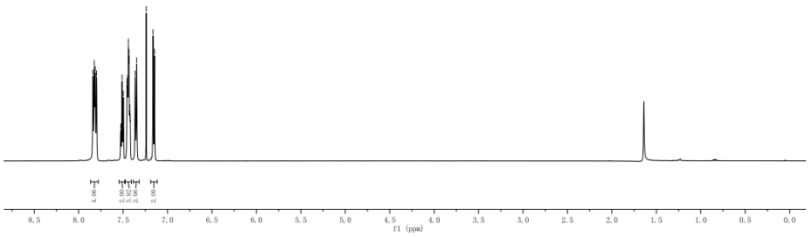

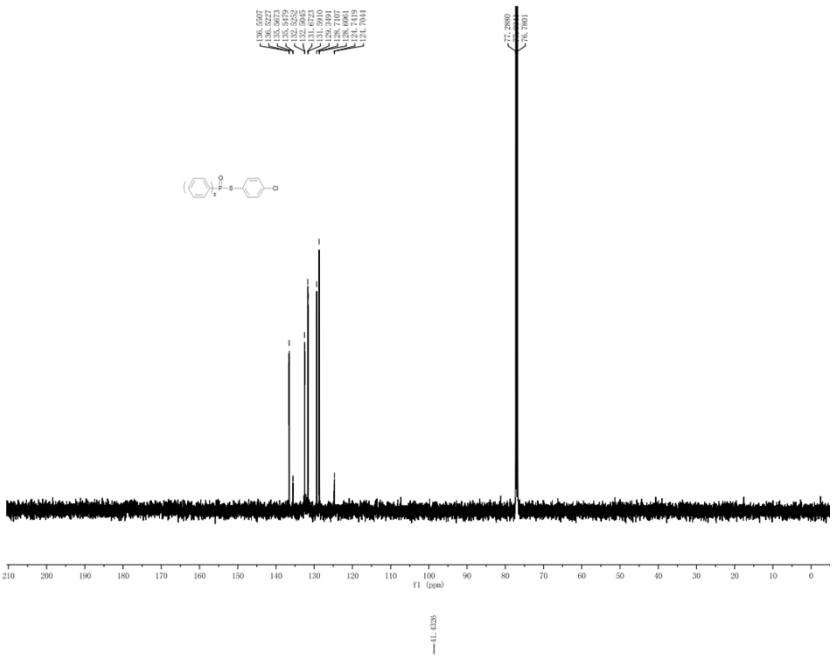

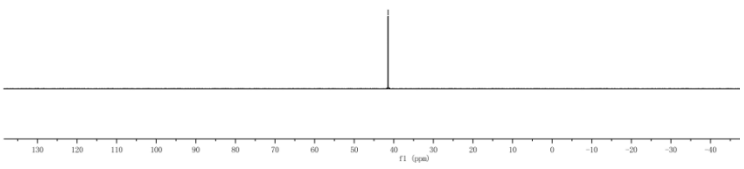

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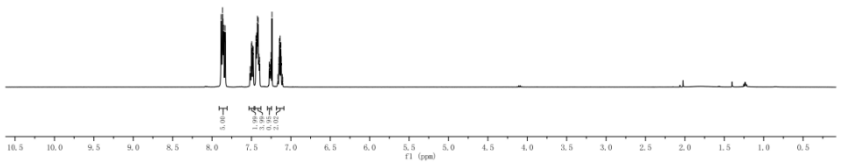

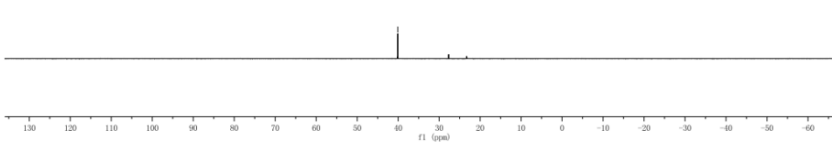

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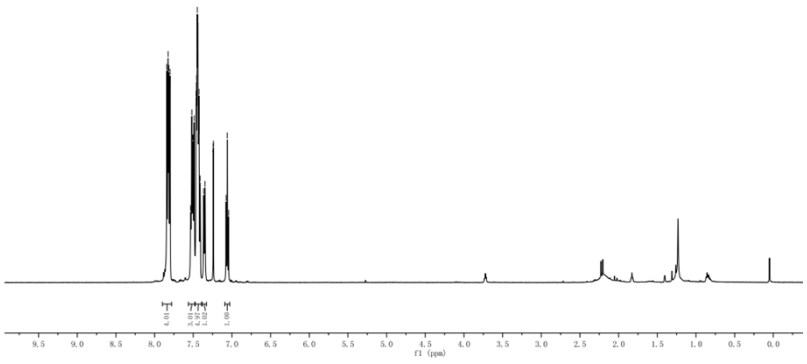

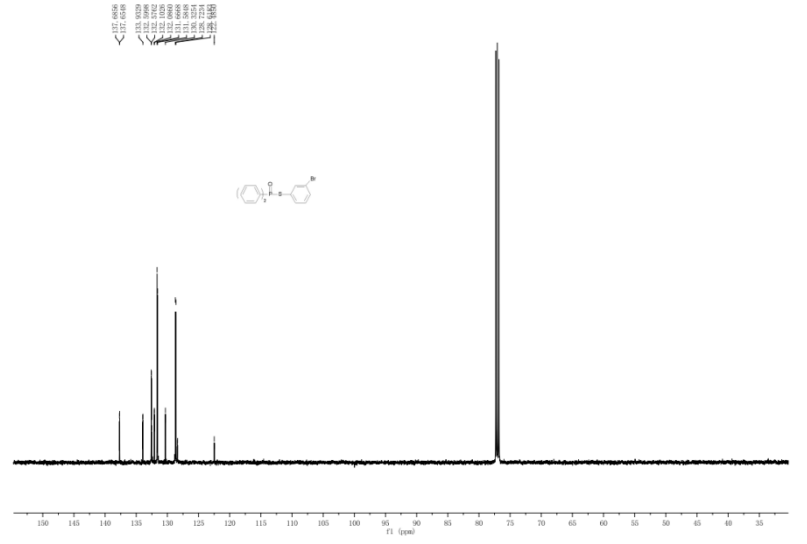

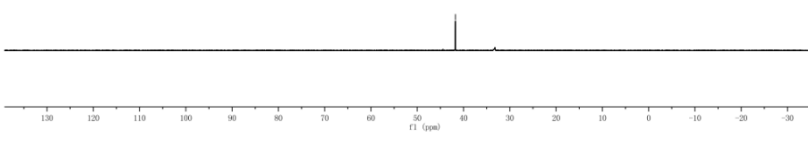

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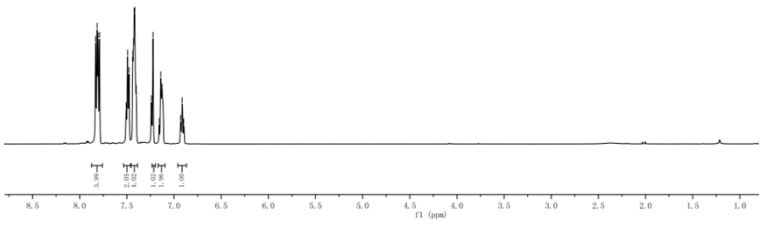

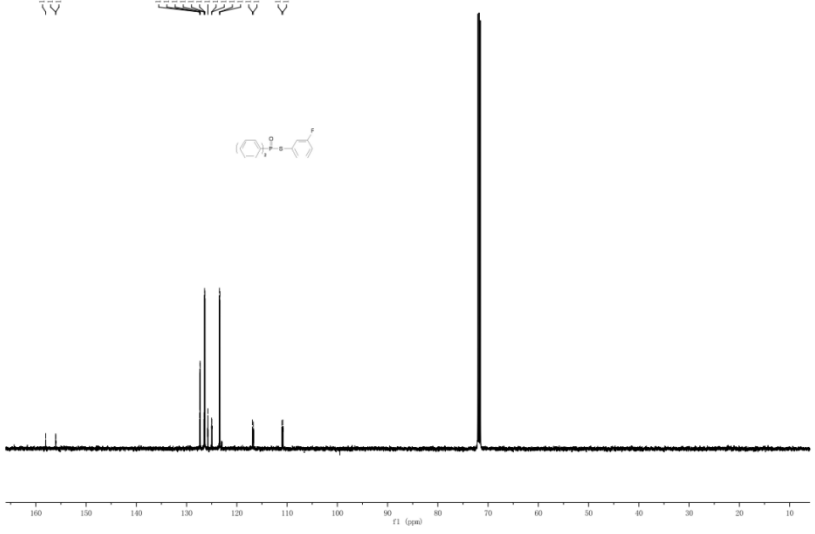

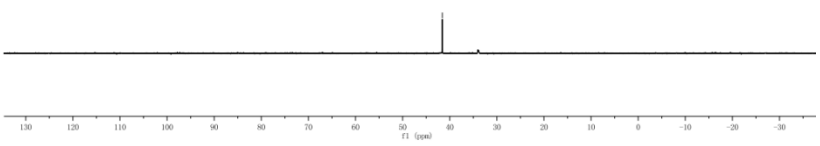

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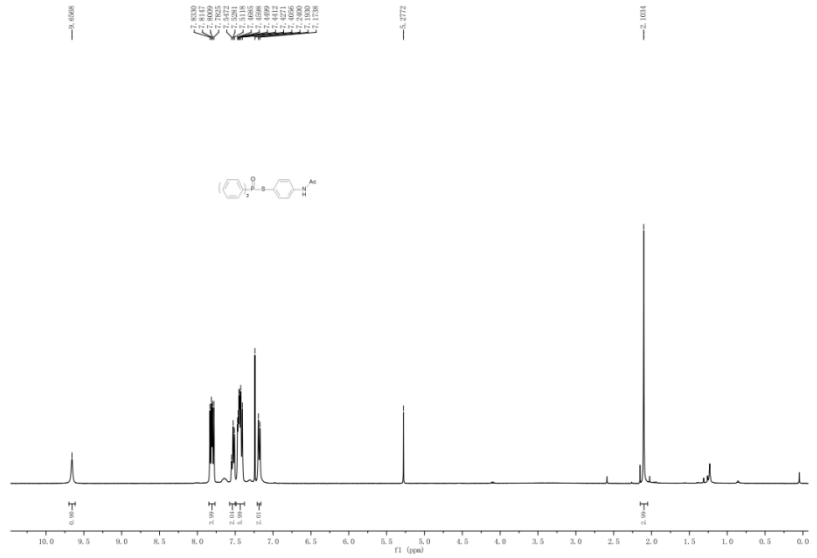

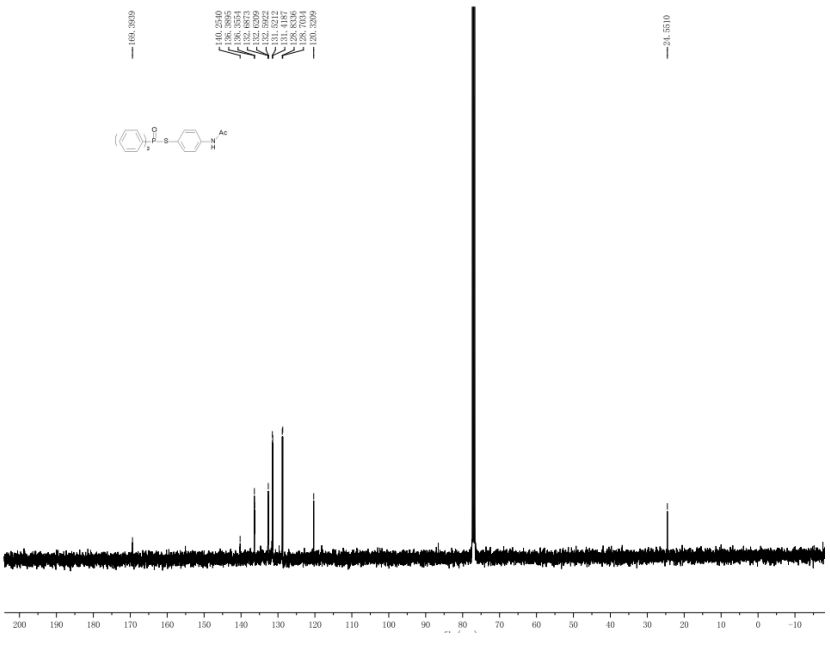

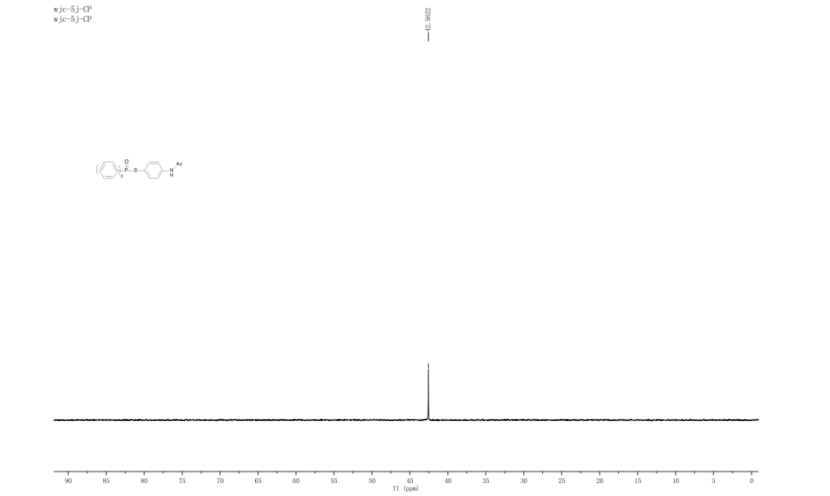

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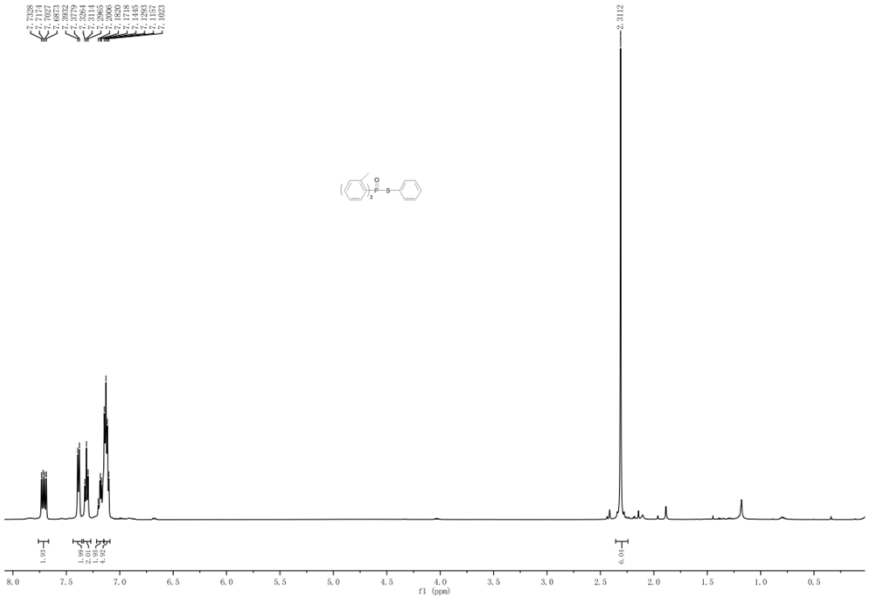

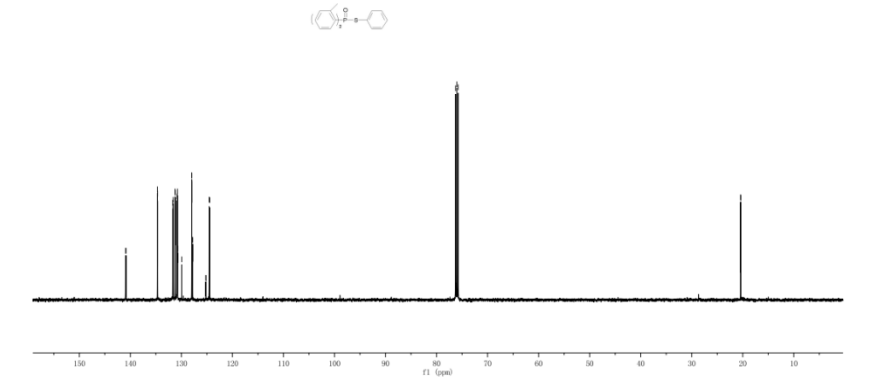

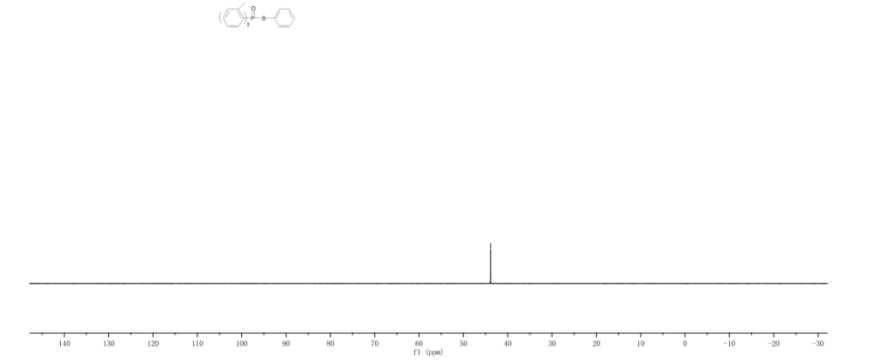

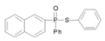

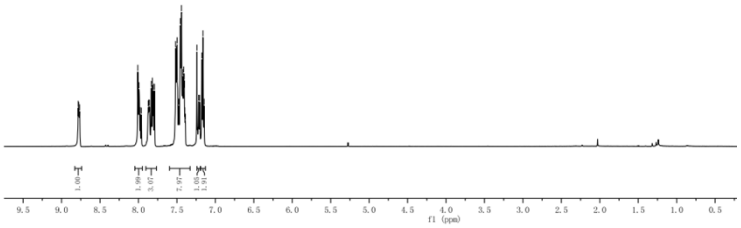
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f1 (ppm)

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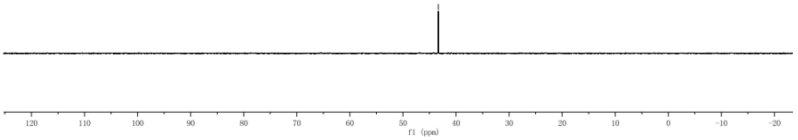
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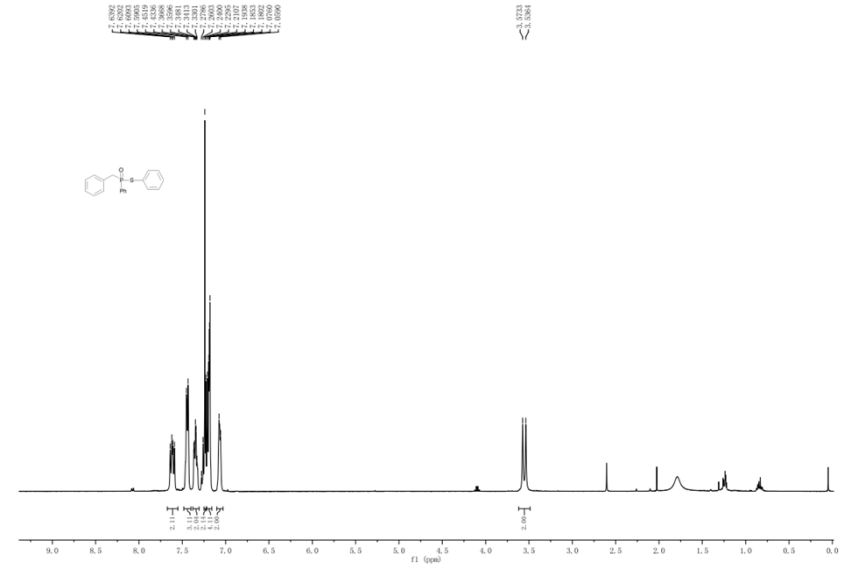

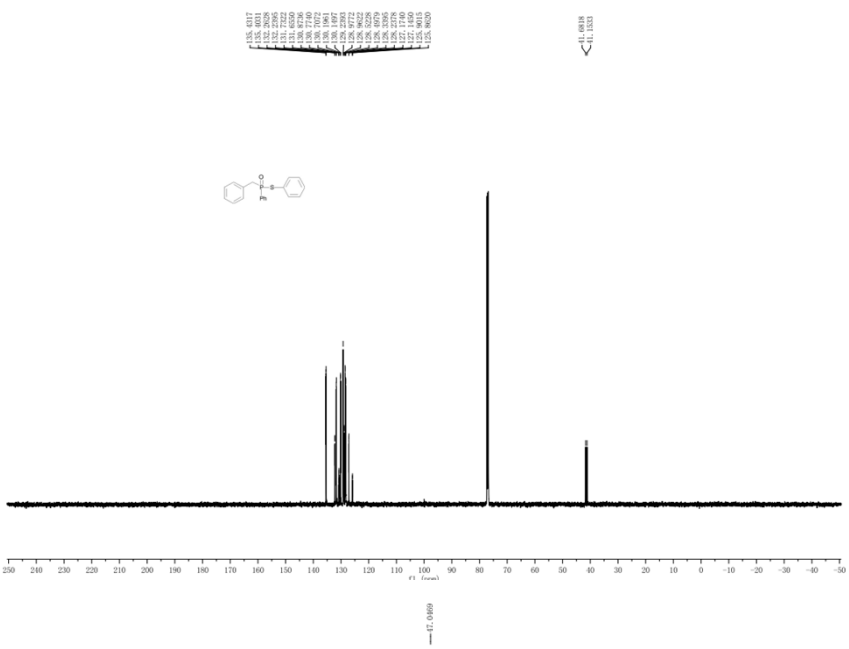

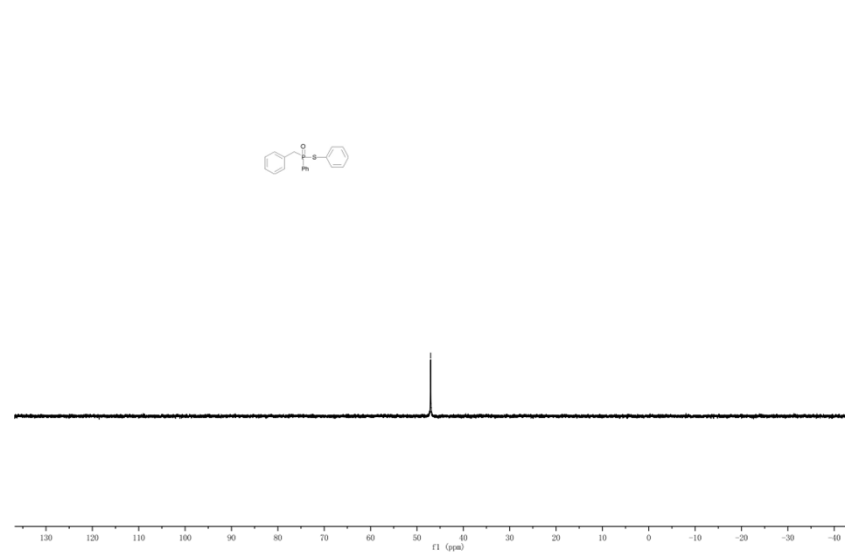

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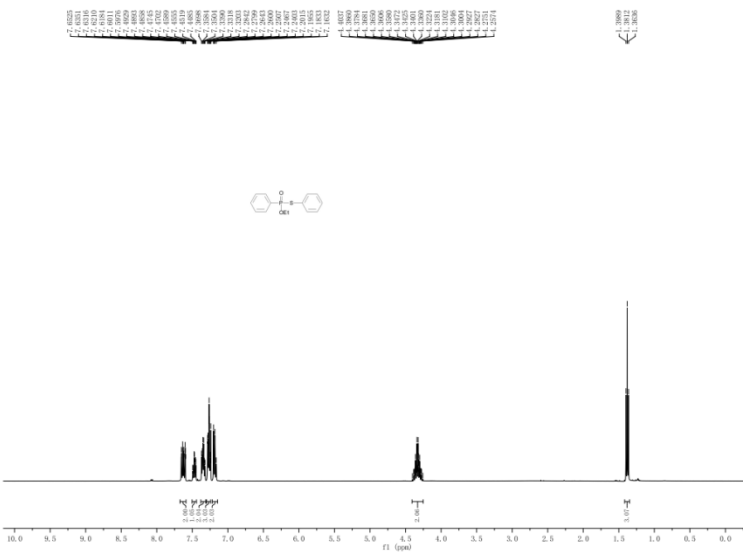

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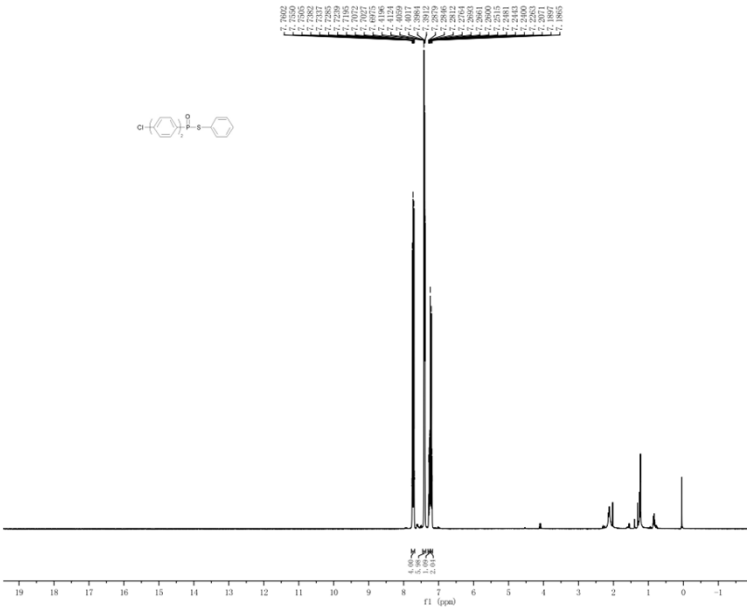

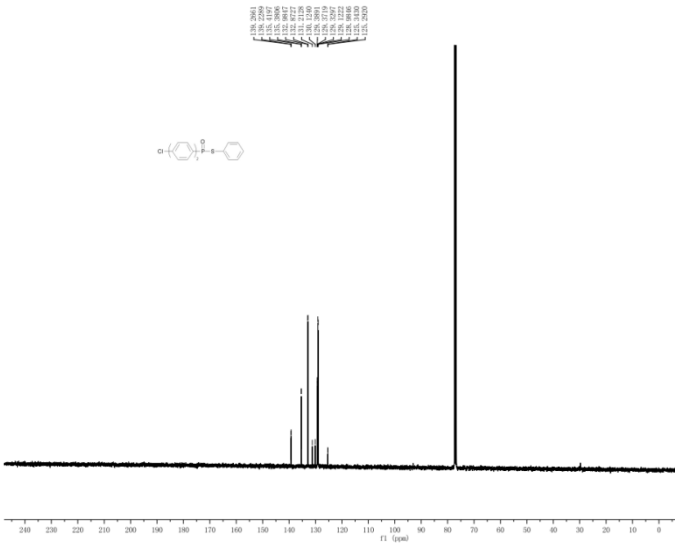

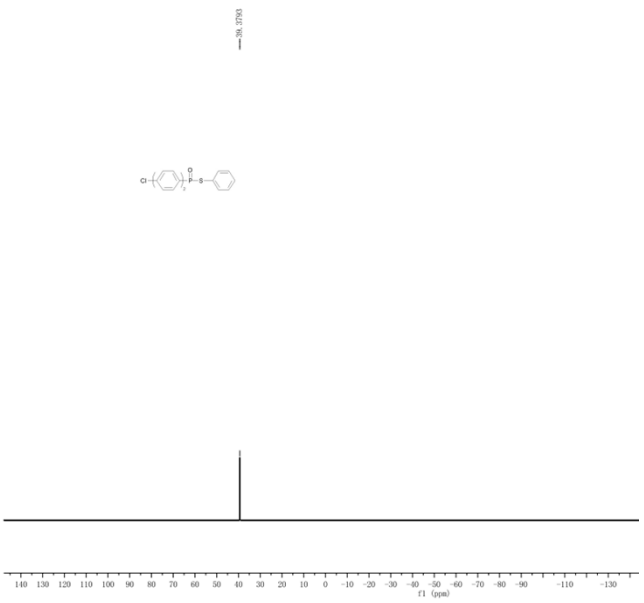

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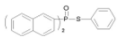

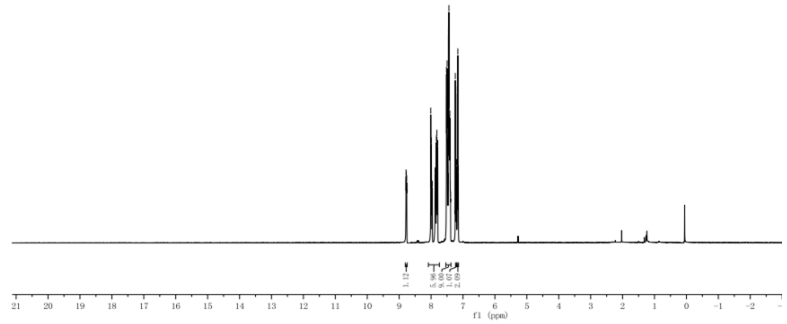

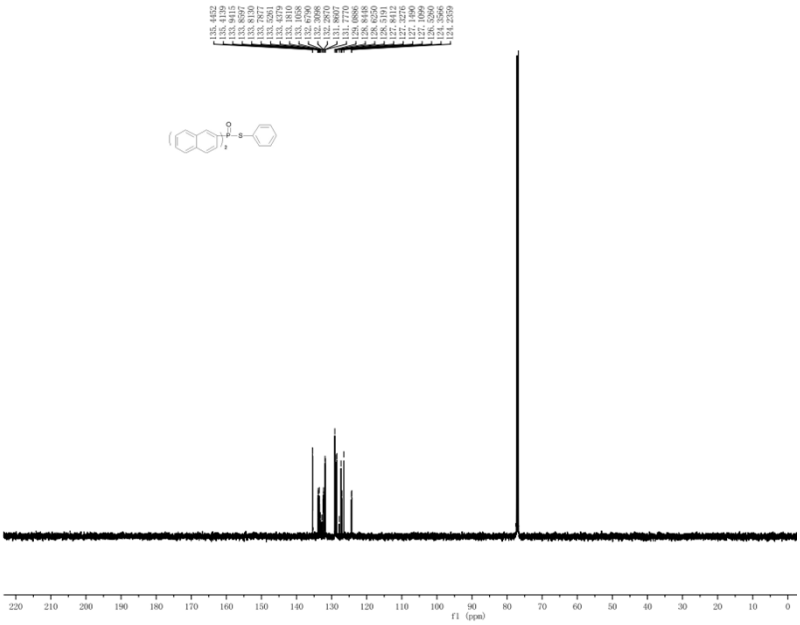

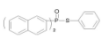

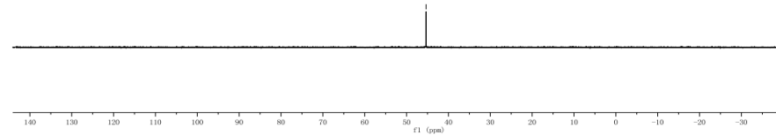

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