Visible Light Photoredox Catalyzed Thiophosphate Synthesis Using Methylene Blue as Promoter

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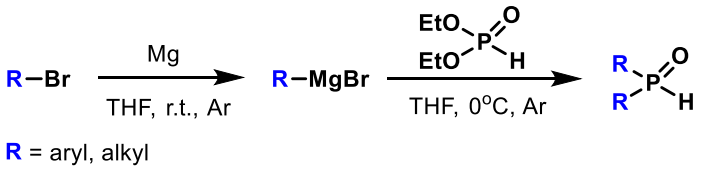
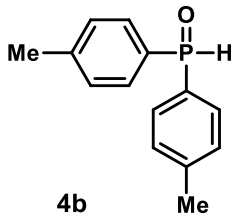
1 Preparation of Substrates

1) Preparation of the phosphine oxides

The secondary phosphines were prepared by a procedure analogous to the one reported by Gessner et al. in 2014.[1]



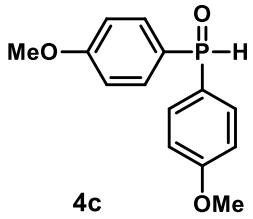
Di-p-tolylphosphine oxide (4b)



4b

1.3g. 39% yield. colourless solid, m.p. 98-99°C. **^{1}H NMR (400 MHz, $CDCl_3$, ppm)**: δ 8.03 (d, *J* = 478.0 Hz, 1H), 7.60-7.54 (m, 4H), 7.30-7.26 (m, 4H), 2.40 (s, 6H). The data matched the reported. [2]

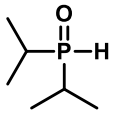
Bis(4-methoxyphenyl)phosphine oxide (4c)



4c

2.8g. 85% yield. colourless solid, m.p. 146-148°C. **^{1}H NMR (400 MHz, $CDCl_3$, ppm)**: δ 8.04 (d, *J* = 481.2 Hz, 1H), 7.62-7.57 (m, 4H), 6.99-6.97 (m, 4H), 3.83 (s, 6H). The data matched the reported. [2]

Diisopropylphosphine oxide (4d)

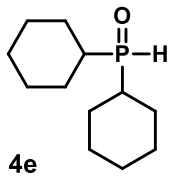


4d

1.7g. 65% yield. colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$, ppm)**: δ 6.36 (d, *J* = 8.1

Hz, 2H), 2.06-2.00 (m, 2H), 1.249-1.19 (m, 12H). The data matched the reported. [3]

Dicyclohexylphosphine oxide (4e)

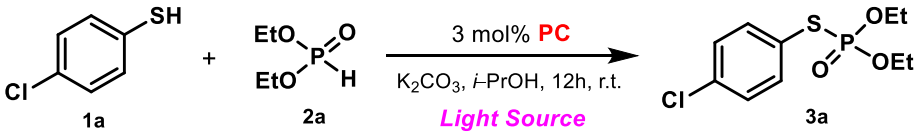


4e

2.8g. 80% yield. colourless solid, m.p. 71-73°C. **^{1}H NMR (400 MHz, $CDCl_3$, ppm)**: δ 6.29 (d, *J* = 434.3 Hz, 1H), 2.00-1.21 (m, 22H). The data matched the reported. [4]

2 Photoredox Dehydrogenative Coupling Reaction

2.1 Optimization of the Photocatalyst and Light Source

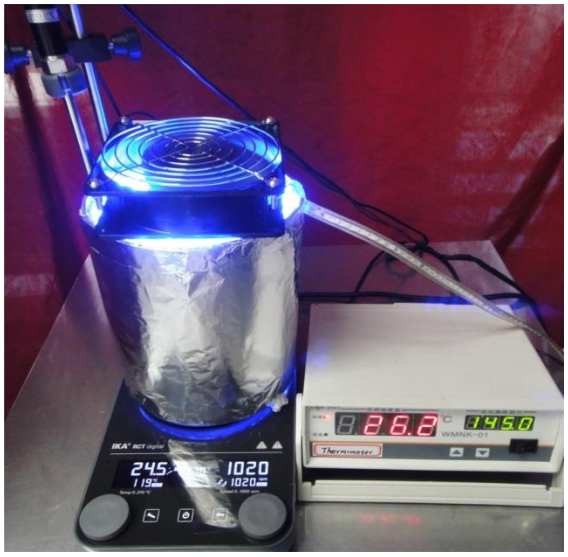


A dry tube equipped with a stirring bar was charged with 4-chlorothiophenol (**1a**) (72.3 mg, 0.5 mmol, 1.0 equiv.) and diethyl phosphonate (**2a**) (207.15 mg, 1.5 mmol, 3.0 equiv.), the photocatalyst (PC) (3.0 mol%) and K_2CO_3 (1.0 equiv.). The solvent ^{i}-PrOH (1.0 mL) were added, the tube was sealed and the mixture was stirred under irradiation for 24 hour in front of the appropriate light source. H_2O (2 mL) and EtOAc (4 mL) were added. The layers were separated and the aqueous layer was extracted with EtOAc (2 x 2 mL). The combined organic layers were dried with $MgSO_4$, filtered and evaporated. Triphenylphosphine (65.6 mg, 0.25 mmol, 0.5 equiv.) and $CDCl_3$ (0.5 mL) were added and the mixture was analysed by ^{31}P NMR spectroscopy to determine the NMR yield.

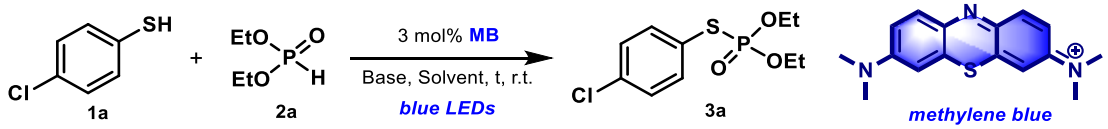
Entry	Photocatalyst	Light Source	λ (nm)	Yield[a] (%)
1	**PC 1**	**blue LEDs**	**455**	**95**
2	PC 2	blue LEDs	455	75
3	PC 3	blue LEDs	455	51
4	PC 4	blue LEDs	455	33
5	PC 5	blue LEDs	455	40
6	PC 6	blue LEDs	455	35
7	PC 7	blue LEDs	455	50
8	PC 8	blue LEDs	455	n.r.
9	PC 9	blue LEDs	455	80
10[b]	PC 1	green LEDs	530	n.r.
11[b]	PC 1	white LEDs	/	20
12[c]	PC 1	UV	310	n.r.
13[d]	PC 1	none	/	n.r.
14	none	blue LED	455	n.r.

[a] ^{31}P NMR yield using triphenylphosphine as an internal standard. [b] The reaction mixture was irradiated with 15 W green LEDs or 15 W white LEDs. [c] The reaction mixture in a common glass flask was irradiated with 1000 W UV light (λ = 310 nm). [d] The reaction was in dark. PC = photocatalyst, LED = light-emitting diode, n.r. = no reaction.

2.2 Picture of Reaction Set-Up



2.3 Optimization of Reaction Conditions

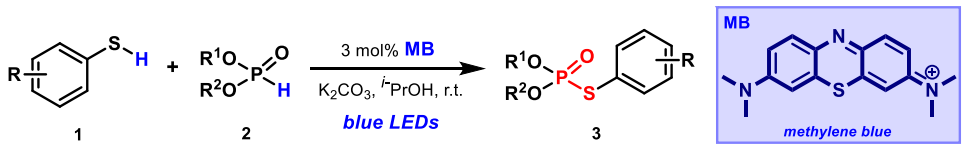


A dry tube equipped with a stirring bar was charged with 4-chlorothiophenol (**1a**) (72.3 mg, 0.5 mmol, 1.0 equiv.) and diethyl phosphonate (**2a**) (207.15 mg, 1.5 mmol, 3.0 equiv.), the methylene blue (MB) (3.0 mol%) and the base (1.0 equiv.). The solvent (1.0 mL) were added, the tube was sealed and the mixture was stirred under irradiation for 12-48 hours in front of the appropriate light source. H_2O (2 mL) and EtOAc (4 mL) were added. The layers were separated and the aqueous layer was extracted with EtOAc (2×2 mL). The combined organic layers were dried with $MgSO_4$, filtered and evaporated.

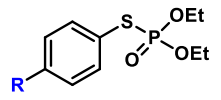
Entry	Base (equiv)	Solvent	t (h)	Yield[a] (%)
1	K_2CO_3	^{i}PrOH	12	60
2	**K_2CO_3**	**^{i}PrOH**	**24**	**95**
3	K_2CO_3	^{i}PrOH	48	90
4	KOAc	^{i}PrOH	24	89
5	Na_2CO_3	^{i}PrOH	24	49
6	$KHCO_3$	^{i}PrOH	24	80
7	CsOAc	^{i}PrOH	24	28
8	^{t}BuOK	^{i}PrOH	36	15
9	Cs_2CO_3	^{i}PrOH	48	N.R.
10	Li_2CO_3	^{i}PrOH	36	trace
11	DBU	^{i}PrOH	36	trace
12	TMEDA	^{i}PrOH	48	N.R.
13	K_2CO_3	MeCN	24	61
14	K_2CO_3	^{i}PrOH: MeCN (4:1)	24	91
15	K_2CO_3	NMP	24	40
16	K_2CO_3	THF	48	N.R.
17	K_2CO_3	DMA	24	35
18	K_2CO_3	MeOH	36	trace
19	K_2CO_3	Dioxane	24	53

2.4 Substrate Scope.

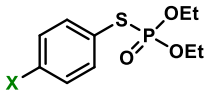
2.4.1 Substrate Scope A:



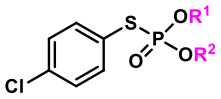
1 2 3



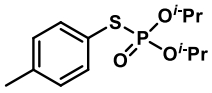
3b, **R = H**, 87%, 24h
3c, **R = Me**, 92%, 24h
3d, **R = OMe**, 66%, 24h
3e, **R = ^{t}Bu**, 61%, 24h



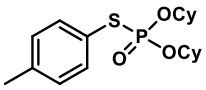
3a, **X = Cl**, 95%, 24h
3f, **X = Br**, 92%, 24h
3g, **X= F**, 64%, 24h



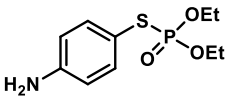
3h, **R^{1} = R^{2} = Me**, 20%, 72h
3i, **R^{1} = R^{2} = ^{i}Pr**, 60%, 24h
3j, **R^{1} = R^{2} = ^{t}Bu**, 37%, 48h



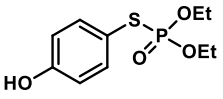
3k, 71%, 24h



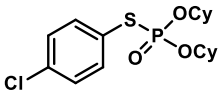
3l, 85%, 24h



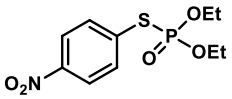
3m, 67%, 24h



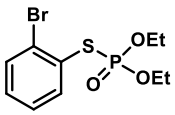
3n, 73%, 24h



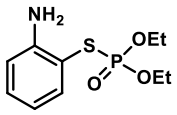
3o, 85%, 24h



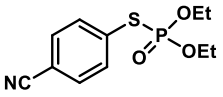
3p, 42%, 48h



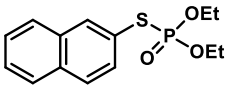
3q, 54%, 48h



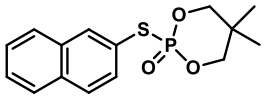
3r, 43%, 48h



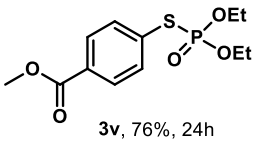
3s, 45%, 48h



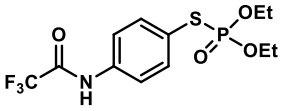
3t, 67%, 24h



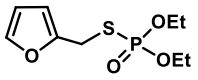
3u, 83%, 24h



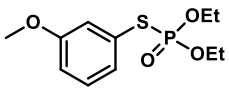
3v, 76%, 24h



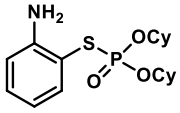
3w, 55%, 36h



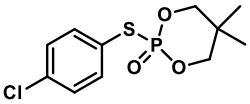
3x, 64%, 24h



3y, 45%, 48h

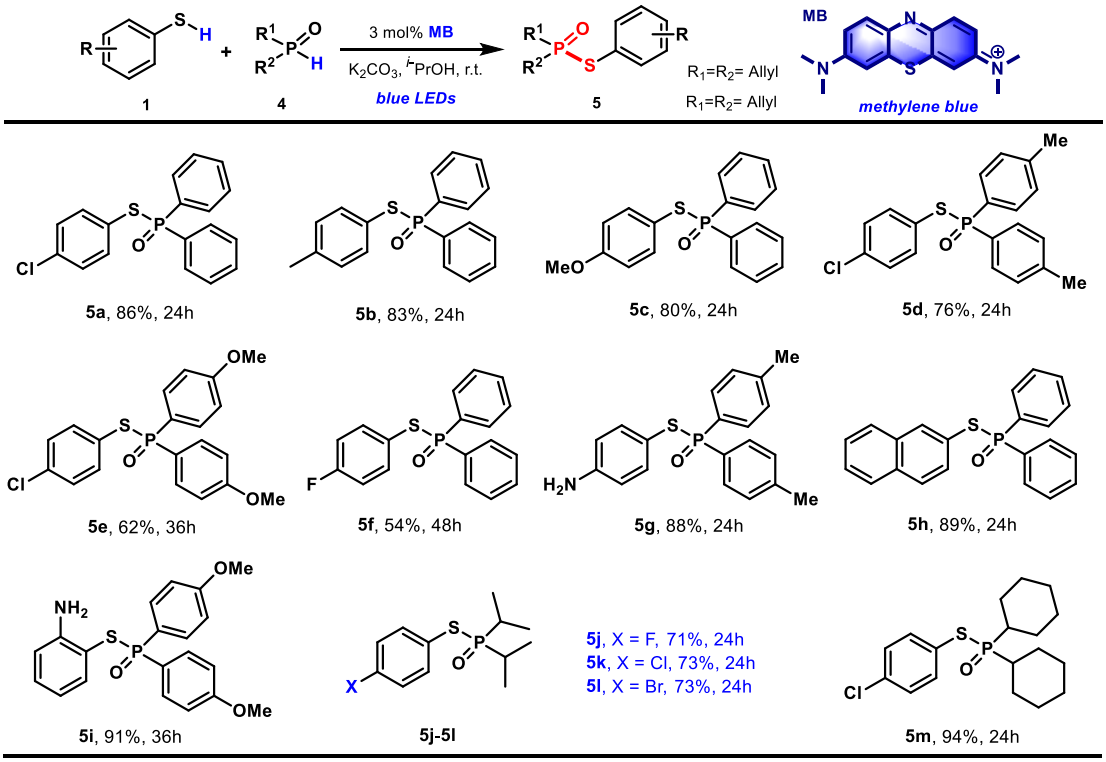


3z, 93%, 24h



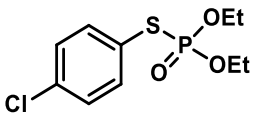
3aa, 80%, 24h

2.4.2 Substrate Scope B:



2.4.3 The Characterization Data of the Products

***S*-(4-chlorophenyl) *O*, *O*-diethyl phosphorothioate (3a)**[5]



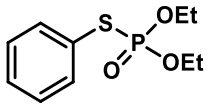
3a

Prepared according to general procedure, the reaction of 4-chlorobenzenethiol **1a** (0.5 mmol), diethyl phosphonate **2a** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}-PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 133.3 mg (95%) of **3a** as colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 7.50-7.49 (m, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 4.24-4.12 (m, 4H), 1.32 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$, ppm):** δ 135.8 (d, *J* = 5.3 Hz), 135.5 (d, *J* = 3.6 Hz), 129.6 (d, *J* = 2.2 Hz), 125.2 (d, *J* =7.1 Hz), 64.3 (d, *J* = 6.1 Hz), 16.1 (d, *J* = 7.1 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 22.1.

HR-MS (ESI): *m/z* calculated for $C_{10}H_{14}ClO_3PS$ $[M+Na]^+$: 302.9987, found: 302.9987.

***O*, *O*-diethyl *S*-phenyl phosphorothioate (3b)**[6]

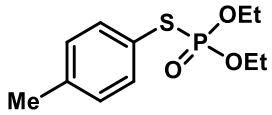


3b

Prepared according to general procedure, the reaction of benzenethiol **1b** (0.5 mmol), diethyl phosphonate **2a** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}-PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 107.1 mg (87%) of **3b** as yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$, ppm)**: δ7.58-7.56 (m, 2 H), 7.35 (d, *J* = 5.2 Hz, 3H), 4.25-4.14 (m, 4 H), 1.31 (t, *J* = 6.9 Hz, 6H). **^{13}C NMR (150 MHz, $CDCl_3$, ppm):** δ 134.6 (d, *J* = 5.3 Hz), 129.4 (d, *J* = 2.2 Hz), 129.0 (d, *J* = 2.8 Hz), 126.6 (d, *J* =7.1 Hz), 64.1 (d, *J* = 5.8 Hz), 16.1 (d, *J* = 7.1 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 22.9.

HR-MS (ESI): *m/z* calculated for $C_{10}H_{15}O_3PS$ $[M+Na]^+$: 269.0377, found: 269.0382.

***O, O*-diethyl *S*-(p-tolyl) phosphorothioate (3c)**[5]



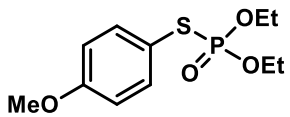
3c

Prepared according to general procedure, the reaction of 4-methylbenzenethiol **1c** (0.5 mmol), diethyl phosphonate **2a** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}-PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 119.7 mg (92%) of **3c** as colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 7.44-7.41 (m, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 4.23-4.14 (m, 4H), 2.34 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$, ppm):** δ 139.3 (d, *J* = 3.1 Hz), 134.6 (d, *J* = 5.3 Hz), 130.2 (d, *J* = 2.5 Hz), 122.8 (d, *J* =7.2 Hz), 64.0 (d, *J* = 5.0 Hz), 21.2, 16.1 (d, *J* = 7.2 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 23.3.

HR-MS (ESI): *m/z* calculated for $C_{11}H_{17}O_3PS$ $[M+Na]^+$: 283.0534, found: 283.0531.

***O, O*-diethyl *S*-(4-methoxyphenyl) phosphorothioate (3d)**[7]



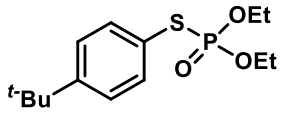
3d

Prepared according to general procedure, the reaction of 4-methoxybenzenethiol **1d** (0.5 mmol), diethyl phosphonate **2a** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}-PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 91.1 mg (66%) of **3d** as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.46 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.24-4.10 (m, 4H), 3.80 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR (150 MHz, $CDCl_3$, ppm):** δ 160.4 (d, *J* = 2.0 Hz), 136.3 (d, *J* = 4.7 Hz), 116.6 (d, *J* = 7.2 Hz), 114.9 (d, *J* = 2.3 Hz), 63.9 (d, *J* = 6.2 Hz), 55.3, 16.0 (d, *J* = 7.0 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 23.5.

HR-MS (ESI): *m/z* calculated for $C_{11}H_{17}O_4PS$ $[M+Na]^+$: 299.0483, found: 299.0479.

_S_-(4-(tert-butyl)phenyl) _O_, _O_-diethyl phosphorothioate (3e)[5]



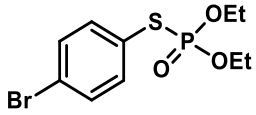
3e

Prepared according to general procedure, the reaction of 4-(tert-butyl)benzenethiol **1e** (0.5 mmol), diethyl phosphonate **2a** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 92.2 mg (61%) of **3e** as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.48 (dd, *J* = 8.5 Hz, *J* = 2.1 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 4.26-4.14 (m, 4H), 1.31-1.29 (m, 15H). **^{13}C NMR (100 MHz, $CDCl_3$, ppm):** δ 152.3 (d, *J* = 3.1 Hz), 134.3 (d, *J* = 5.2 Hz), 126.4 (d, *J* = 2.3 Hz), 122.8 (d, *J* = 7.2 Hz), 63.9 (d, *J* = 6.0 Hz), 34.6, 31.1, 16.0 (d, *J* = 7.1 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 23.3.

HR-MS (ESI): *m/z* calculated for $C_{14}H_{23}O_3PS$ $[M+Na]^+$: 325.1003, found: 325.1002.

_S_-(4-bromophenyl) _O_, _O_-diethyl phosphorothioate (3f)[7]



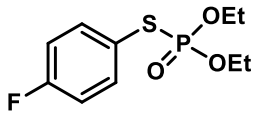
3f

Prepared according to general procedure, the reaction of 4-bromobenzenethiol **1f** (0.5 mmol), diethyl phosphonate **2a** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 149.7 mg (92%) of **3f** as colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 7.48-7.42 (m, 4H), 4.24-4.14 (m, 4H), 1.32 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$, ppm):** δ 136.1 (d, *J* = 5.1 Hz), 132.6 (d, *J* = 2.1 Hz), 126.0 (d, *J* = 7.0 Hz), 123.7 (d, *J* =3.6 Hz), 64.4 (d, *J* = 6.4 Hz), 16.1 (d, *J* = 7.2 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 21.9.

HR-MS (ESI): *m/z* calculated for $C_{10}H_{14}BrO_3PS$ $[M+Na]^+$: 346.9482, found: 346.9480.

***O, O*-diethyl *S*-(4-fluorophenyl) phosphorothioate (3g)**[5]



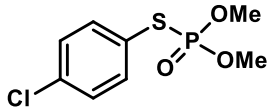
3g

Prepared according to general procedure, the reaction of 4-fluorobenzenethiol **1g** (0.5 mmol), diethyl phosphonate **2a** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 84.5 mg (64%) of **3g** as colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 7.58-7.50 (m, 2H), 7.05 (t, *J* = 8.4 Hz, 2H), 4.26-4.10 (m, 4H), 1.31 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$, ppm):** δ 163.3 (dd, *J* = 248.3 Hz, *J* = 3.1 Hz), 136.7 (dd, *J* = 8.4 Hz, *J* = 4.9 Hz), 121.7 (dd, *J* = 7.1 Hz, *J* = 3.4 Hz), 116.6 (dd, *J* = 22.0 Hz, *J* = 2.1 Hz), 64.2 (d, *J* = 6.1 Hz), 16.1 (d, *J* = 7.1 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 22.6 (d, *J* = 5.0 Hz).

HR-MS (ESI): *m/z* calculated for $C_{10}H_{14}FO_3PS$ $[M+Na]^+$: 287.0283, found: 287.0287.

***S*-(4-chlorophenyl) *O, O*-dimethyl phosphorothioate (3h)**[8]



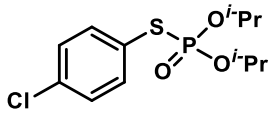
3h

Prepared according to general procedure, the reaction of 4-chlorobenzenethiol **1a** (0.5 mmol), dimethyl phosphonate **2b** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 72h, afforded 25.2 mg (20%) of **3h** as colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 7.50 (dd, *J* = 8.6 Hz, *J* = 2.1 Hz, 2H), 7.38-7.31 (m, 2H), 3.83 (s, 3H), 3.81 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$, ppm):** δ 135.7 (d, *J* = 5.2 Hz), 135.6 (d, *J* = 1.9 Hz), 129.6 (d, *J* = 2.3 Hz), 124.5 (d, *J* =7.0 Hz), 54.3 (d, *J* = 6.4 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 25.4.

HR-MS (ESI): *m/z* calculated for $C_8H_{10}ClO_3PS$ $[M+Na]^+$: 274.9674, found: 274.9673.

***S*-(4-chlorophenyl) *O, O*-diisopropyl phosphorothioate (3i)**[7]



3i

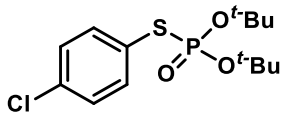
Prepared according to general procedure, the reaction of 4-chlorobenzenethiol **1a** (0.5

mmol), diisopropyl phosphonate **2c** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 92.6 mg (60%) of **3i** as colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 7.7 Hz, 2H), 4.81-4.71 (m, 2H), 1.33 (d, *J* = 6.2 Hz, 6H), 1.27 (d, *J* = 6.2 Hz, 6H). **^{13}C NMR (150 MHz, $CDCl_3$, ppm):** δ 135.4 (d, *J* = 5.4 Hz), 135.1 (d, *J* = 3.4 Hz), 129.3 (d, *J* = 2.0 Hz), 125.9 (d, *J* = 6.9 Hz), 73.5 (d, *J* = 6.8 Hz), 23.8 (d, *J* = 4.1 Hz), 23.5 (d, *J* = 5.6 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 19.6.

HR-MS (ESI): *m/z* calculated for $C_{12}H_{18}ClO_3PS$ $[M+Na]^+$: 331.0300, found: 331.0301.

***O, O*-di-tert-butyl *S*-(4-chlorophenyl) phosphorothioate (3j)**



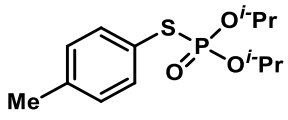
3j

Prepared according to general procedure, the reaction of 4-chlorobenzenethiol **1a** (0.5 mmol), di-tert-butyl phosphonate **2d** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 48h, afforded 62.3 mg (37%) of **3j** as colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 7.53 (d, *J* = 6.9 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 1.47 (s, 18H). **^{13}C NMR (150 MHz, $CDCl_3$, ppm):** δ 135.7 (d, *J* = 5.4 Hz), 134.8 (d, *J* = 3.4 Hz), 129.0 (d, *J* = 1.9 Hz), 127.4 (d, *J* = 7.8 Hz), 85.4 (d, *J* = 9.5 Hz), 30.1 (d, *J* = 4.3 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 12.1.

HR-MS (ESI): *m/z* calculated for $C_{14}H_{22}ClO_3PS$ $[M+Na]^+$: 359.0613, found: 359.0608.

***O, O*-diisopropyl *S*-(p-tolyl) phosphorothioate (3k)**[9]



3k

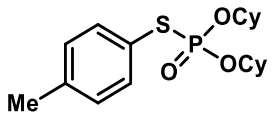
Prepared according to general procedure, the reaction of 4-methylbenzenethiol **1c** (0.5 mmol), diisopropyl phosphonate **2c** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 102.3 mg (71%) of **3k** as colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 7.47 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 4.79-4.73 (m, 2H), 2.34 (s, 3H), 1.30 (dd, *J* = 39.3 Hz, *J* = 6.3 Hz, 12H). **^{13}C NMR (150 MHz, $CDCl_3$, ppm):** δ 138.8 (d, *J* = 3.0 Hz), 134.3 (d, *J* = 5.4 Hz), 129.9

(d, *J* = 2.3 Hz), 123.5 (d, *J* = 7.3 Hz), 73.2 (d, *J* = 6.6 Hz), 23.8 (d, *J* = 4.1 Hz), 23.5 (d, *J* = 5.7 Hz), 21.2. **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 20.8.

HR-MS (ESI): *m/z* calculated for $C_{13}H_{21}O_3PS$ $[M+Na]^+$: 311.0847, found: 311.0854.

***O, O*-dicyclohexyl *S*-(p-tolyl) phosphorothioate (3l)**



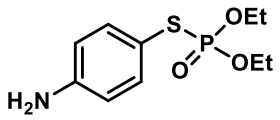
3l

Prepared according to general procedure, the reaction of 4-methylbenzenethiol **1c** (0.5 mmol), dicyclohexyl phosphonate **2e** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 156.6 mg (85%) of **3l** as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.48-7.45 (m, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 4.52-4.43 (m, 2H), 2.33 (s, 3H), 1.93-1.82 (m, 4H), 1.73-1.67 (m, 4H), 1.57-1.42 (m, 6H), 1.36-1.18 (m, 6H). **^{13}C NMR (100 MHz, $CDCl_3$, ppm):** δ 138.8 (d, *J* = 2.9 Hz), 134.4 (d, *J* = 5.2 Hz), 130.0 (d, *J* = 2.2 Hz), 123.7 (d, *J* = 7.0 Hz), 77.9 (d, *J* = 7.0 Hz), 33.4 (dd, *J* = 30.0 Hz, *J* = 4.3 Hz), 25.1, 23.6 (d, *J* = 1.3 Hz), 21.2. **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 20.8.

HR-MS (ESI): *m/z* calculated for $C_{19}H_{29}O_3PS$ $[M+Na]^+$: 391.1473, found: 391.1475.

***S*-(4-aminophenyl) *O, O*-diethyl phosphorothioate (3m)**[7]



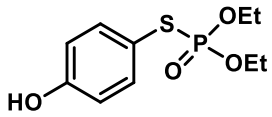
3m

Prepared according to general procedure, the reaction of 4-aminobenzenethiol **1m** (0.5 mmol), diethyl phosphonate **2a** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 87.5 mg (67%) of **3m** as colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 7.30 (d, *J* = 7.8 Hz, 2H), 6.63 (d, *J* = 8.1 Hz, 2H), 4.22-4.11 (m, 4H), 3.76 (br s, 2H), 1.31 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR (150 MHz, $CDCl_3$, ppm):** *δ* 147.7 (d, *J* =2.3 Hz), 136.4 (d, *J* = 4.5 Hz), 115.8 (d, *J* = 2.2 Hz), 113.0 (d, *J* = 7.3 Hz), 63.9 (d, *J* = 6.2 Hz), 16.2 (d, *J* = 7.2 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 23.8.

HR-MS (ESI): *m/z* calculated for $C_{10}H_{16}NO_3PS$ $[M+Na]^+$: 284.0486, found: 284.0504.

***O, O*-diethyl *S*-(4-hydroxyphenyl) phosphorothioate (3n)**[7]



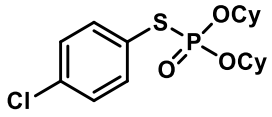
3n

Prepared according to general procedure, the reaction of 4-mercaptophenol **1n** (0.5 mmol), diethyl phosphonate **2a** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}-PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 95.7 mg (73%) of **3n** as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.61 (s, 1H), 7.32-7.27 (m, 2H), 6.62 (d, *J* = 8.4 Hz, 2H), 4.27-4.13 (m, 4H), 1.35 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$, ppm):** δ 158.6 (d, *J* = 3.1 Hz), 136.8 (d, *J* = 4.8 Hz), 117.2 (d, *J* = 2.7 Hz), 113.2 (d, *J* = 7.1 Hz), 64.7 (d, *J* = 6.8 Hz), 16.2 (d, *J* = 6.9 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 25.1.

HR-MS (ESI): *m/z* calculated for $C_{10}H_{15}O_4PS$ $[M+Na]^+$: 285.0326, found: 285.0327.

***S*-(4-chlorophenyl) *O, O*-dicyclohexyl phosphorothioate (3o)**



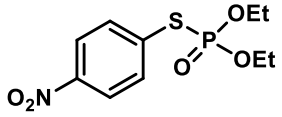
3o

Prepared according to general procedure, the reaction of 4-chlorobenzenethiol **1a** (0.5 mmol), dicyclohexyl phosphonate **2e** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}-PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 165.2 mg (85%) of **3o** as colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 4.49 (m, 2H), 1.93-1.82 (m, 4H), 1.72-1.68 (m, 4H), 1.54-1.47 (m, 6H), 1.32-1.22 (m, 6H). **^{13}C NMR (100 MHz, $CDCl_3$, ppm):** δ 135.4 (d, *J* = 5.4 Hz), 135.0 (d, *J* = 3.1 Hz), 129.3 (d, *J* = 2.0 Hz), 126.0 (d, *J* = 7.0 Hz), 78.2 (d, *J* = 6.8 Hz), 33.3 (dd, *J* = 27.4 Hz, *J* = 4.1 Hz), 25.0, 23.4 (d, *J* = 1.2 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 19.6.

HR-MS (ESI): *m/z* calculated for $C_{18}H_{26}ClO_3PS$ $[M+Na]^+$: 411.0926, found: 411.0929.

***O, O*-diethyl *S*-(4-nitrophenyl) phosphorothioate (3p)**[7]



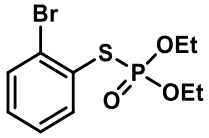
3p

Prepared according to general procedure, the reaction of 4-nitrobenzenethiol **1p** (0.5 mmol), diethyl phosphonate **2a** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}-PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 48h, afforded 61.1 mg (42%) of **3p** as colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 8.20 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.3 Hz, 2H), 4.32-4.16 (m, 4H), 1.35 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$, ppm):** δ 147.8 (d, *J* = 2.1 Hz), 136.2 (d, *J* = 6.5 Hz), 134.1 (d, *J* = 5.9 Hz), 124.1 (d, *J* = 1.5 Hz), 64.7 (d, *J* = 6.4 Hz), 16.0 (d, *J* = 7.0 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 20.1.

HR-MS (ESI): *m/z* calculated for $C_{10}H_{14}NO_5PS$ $[M+Na]^+$: 314.0228, found: 314.0246.

_S_-(2-bromophenyl) _O_, _O_-diethyl phosphorothioate (3q)



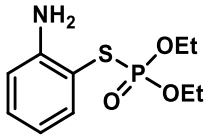
3q

Prepared according to general procedure, the reaction of 2-bromobenzenethiol **1q** (0.5 mmol), diethyl phosphonate **2a** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}-PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 48h, afforded 87.7 mg (54%) of **3q** as colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 7.79 (d, *J* = 7.9 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 7.7 Hz, 1H), 4.28-4.17 (m, 4H), 1.32 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$, ppm):** δ 136.5 (d, *J* = 4.1 Hz), 133.6 (d, *J* = 1.9 Hz), 130.3 (d, *J* = 2.5 Hz), 128.7 (d, *J* =6.1 Hz), 128.5 (d, *J* =7.4 Hz), 128.2 (d, *J* =2.2 Hz), 64.5 (d, *J* = 6.2 Hz), 16.1 (d, *J* = 7.2 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 21.2.

HR-MS (ESI): *m/z* calculated for $C_{10}H_{14}BrO_3PS$ $[M+Na]^+$: 346.9482, found: 346.9481.

_S_-(2-aminophenyl) _O_, _O_-diethyl phosphorothioate (3r)[10]



3r

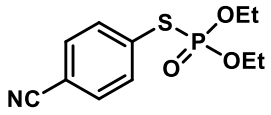
Prepared according to general procedure, the reaction of 2-aminobenzenethiol **1r** (0.5 mmol), diethyl phosphonate **2a** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in

^{i}-PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 48h, afforded 56.1 mg (43%) of **3r** as colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 7.38 (d, *J* = 7.8 Hz, 1H), 7.17 (t, *J* = 7.8 Hz, 1H), 6.74 (d, *J* = 8.1 Hz, 1H), 6.70 (t, *J* = 7.6 Hz, 1H), 4.58-3.79 (br s, 2H), 4.21-4.12 (m, 4H), 1.30 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$, ppm):** δ 149.4 (d, *J* = 4.3 Hz), 137.3 (d, *J* = 4.3 Hz), 131.0 (d, *J* = 3.2 Hz), 118.6 (d, *J* =2.7 Hz), 115.8 (d, *J* =2.8 Hz), 108.0 (d, *J* =7.3 Hz), 64.4 (d, *J* = 6.8 Hz), 16.0 (d, *J* = 6.8 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 22.8.

HR-MS (ESI): *m/z* calculated for $C_{10}H_{16}NO_3PS$ $[M+Na]^+$: 284.0486, found: 284.0486.

***S*-(4-cyanophenyl) *O, O*-diethyl phosphorothioate (3s)**[6]



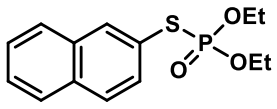
3s

Prepared according to general procedure, the reaction of methyl 4-mercaptobenzonitrile **1s** (0.5 mmol), diethyl phosphonate **2a** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}-PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 48h, afforded 61.0 mg (45%) of **3s** as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.61 (d, *J* = 8.1 Hz, 2H), 4.26-4.13 (m, 4H), 1.31 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$, ppm):** δ 134.3 (d, *J* = 5.8 Hz), 134.0 (d, *J* = 6.7 Hz), 132.7 (d, *J* = 1.7 Hz), 118.1 (d, *J* = 1.5 Hz), 112.5 (d, *J* = 2.2 Hz), 64.7 (d, *J* = 6.4 Hz), 16.1 (d, *J* = 6.9 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 20.4.

HR-MS (ESI): *m/z* calculated for $C_{11}H_{14}NO_3PS$ $[M+Na]^+$: 294.0330, found: 294.0333.

***O, O*-diethyl *S*-(naphthalen-2-yl) phosphorothioate (3t)**[5]



3t

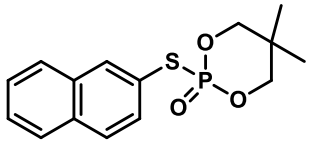
Prepared according to general procedure, the reaction of naphthalene-2-thiol **1t** (0.5 mmol), diethyl phosphonate **2a** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}-PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 99.2 mg (67%) of **3t** as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.09 (s, 1H), 7.85-7.77 (m, 3H), 7.61 (d, *J* = 8.6 Hz, 1H), 7.55-7.47 (m, 2H), 4.29-4.15 (m, 4H), 1.31 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR**

(100 MHz, $CDCl_3$, ppm): δ 134.3 (d, *J* = 6.8 Hz), 133.5 (d, *J* = 2.1 Hz), 133.0 (d, *J* = 1.5 Hz), 130.9 (d, *J* =4.0 Hz), 128.9 (d, *J* = 1.7 Hz), 127.7 (d, *J* =1.2 Hz), 127.6 (d, *J* = 0.9 Hz), 127.0 (d, *J* =1.4 Hz), 126.7 (d, *J* = 0.8 Hz), 123.7 (d, *J* =7.5 Hz), 64.1 (d, *J* = 5.8 Hz), 16.0 (d, *J* = 7.2 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 22.8.

HR-MS (ESI): *m/z* calculated for $C_{14}H_{17}O_3PS$ $[M+Na]^+$: 319.0534, found: 319.0535.

5,5-dimethyl-2-(naphthalen-2-ylthio)-1,3,2-dioxaphosphinane 2-oxide (3u)



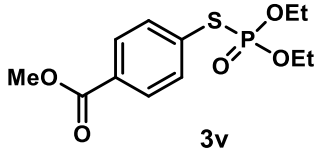
3u

Prepared according to general procedure, the reaction of naphthalene-2-thiol **1t** (0.5 mmol), 5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide **2f** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 127.9 mg (83%) of **3u** as white solid, m.p. 100-102°C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.15 (s, 1H), 7.83-7.80 (m, 3H), 7.68 (d, *J* = 8.6 Hz, 1H), 7.52-7.49 (m, 2H), 4.26-4.23 (m, 2H), 3.99-3.89 (m, 2H), 1.28 (s, 3H), 0.87 (s, 3H). **^{13}C NMR (150 MHz, $CDCl_3$, ppm):** δ 134.6 (d, *J* = 6.7 Hz), 133.7 (d, *J* = 2.3 Hz), 133.72 (d, *J* = 2.0 Hz), 130.9 (d, *J* =4.0 Hz), 129.3 (d, *J* = 1.7 Hz), 127.83 (d, *J* =1.5 Hz), 127.81 (d, *J* = 1.4 Hz), 127.2 (d, *J* = 1.4 Hz), 126.8 (d, *J* = 0.8 Hz), 122.1 (d, *J* =6.8 Hz), 78.4 (d, *J* = 7.3 Hz), 32.6 (d, *J* = 6.7 Hz), 21.2 (d, *J* = 241.0 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 14.6.

HR-MS (ESI): *m/z* calculated for $C_{15}H_{17}O_3PS$ $[M+Na]^+$: 331.3215, found: 331.0550.

Methyl 4-((diethoxyphosphoryl)thio)benzoate (3v)[6]



3v

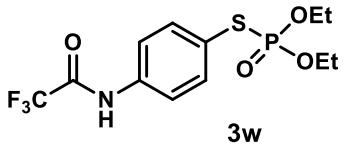
Prepared according to general procedure, the reaction of methyl 4-mercaptobenzoate **1v** (0.5 mmol), diethyl phosphonate **2a** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 115.6 mg (76%) of **3v** as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.00 (d, *J* = 8.2 Hz, 2H), 7.66-7.63 (m, 2H), 4.24-4.16 (m, 4H), 3.92 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR (150 MHz, $CDCl_3$, ppm):** δ 166.4 (s), 133.8 (d, *J* = 5.6 Hz), 133.0 (d, *J* = 6.8 Hz), 130.4 (d, *J* = 2.5 Hz), 130.3 (d, *J* = 1.9 Hz), 64.4 (d, *J* = 6.2 Hz), 52.4 (s), 16.1 (d, *J* = 7.1 Hz). **^{31}P**

NMR (162 MHz, $CDCl_3$, ppm): δ 21.3.

HR-MS (ESI): *m/z* calculated for $C_{12}H_{17}O_5PS$ $[M+Na]^+$: 327.0432, found: 327.0435.

***O, O*-diethyl S-(4-(2,2,2-trifluoroacetamido)phenyl) phosphorothioate (3w)**



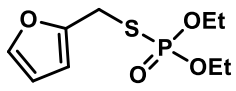
3w

Prepared according to general procedure, the reaction of 2,2,2-trifluoro-*N*-(4-mercaptophenyl)acetamide **1w** (0.5 mmol), diethyl phosphonate **2a** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 36h, afforded 98.2 mg (55%) of **3w** as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.97 (s, 1H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.47 (dd, *J* = 8.7 Hz, *J* = 2.2 Hz, 2H), 4.28-4.11 (m, 4H), 1.40-1.31 (m, 6H). **^{13}C NMR (100 MHz, $CDCl_3$, ppm):** δ 155.2 (d, *J* = 3.8 Hz), 137.6 (d, *J* = 3.1 Hz), 135.5 (d, *J* = 5.1 Hz), 122.1 (d, *J* = 6.8 Hz), 121.7 (d, *J* = 1.6 Hz), 117.5.9 (d, *J* = 286.3 Hz), 64.7 (dd, *J* = 10.5 Hz, *J* = 3.6 Hz), 16.2 (dd, *J* = 30.1 Hz, *J* = 6.7 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 22.7.

HR-MS(ESI): *m/z* calculated for $C_{12}H_{15}F_3NO_4PS$ $[M+Na]^+$: 380.0309, found: 38 0.0319.

***O, O*-diethyl *S*-(furan-2-ylmethyl) phosphorothioate (3x)**[7]



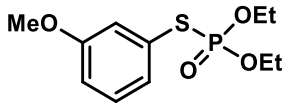
3x

Prepared according to general procedure, the reaction of furan-2-ylmethanethiol **1x** (0.5 mmol), diethyl phosphonate **2a** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 80.0 mg (64%) of **3x** as colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 7.37 (s, 1H), 6.36-6.25 (m, 2H), 4.19-4.04 (m, 6H), 1.33 (t, *J* = 7.0 Hz, 6H). **^{13}C NMR (150 MHz, $CDCl_3$, ppm):** δ 150.2 (d, *J* = 4.6 Hz), 142.5, 110.6, 108.4, 63.6 (d, *J* = 5.6 Hz), 27.2 (d, *J* = 3.8 Hz), 15.9 (d, *J* = 7.2 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 26.2.

HR-MS (ESI): *m/z* calculated for $C_9H_{15}O_4PS$ $[M+Na]^+$: 273.0326, found: 273.0325.

***O, O*-diethyl *S*-(3-methoxyphenyl) phosphorothioate (3y)**[7]



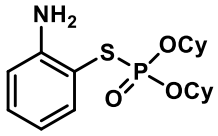
3y

Prepared according to general procedure, the reaction of 3-methoxybenzenethiol **1y** (0.5 mmol), diethyl phosphonate **2a** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 48h, afforded 62.1 mg (45%) of **3y** as colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 7.25 (d, *J* = 8.0 Hz, 1H), 7.18-7.10 (m, 2H), 6.90 (d, *J* = 8.3 Hz, 1H), 4.24-4.15 (m, 4H), 3.81 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$, ppm):** δ 159.9 (d, *J* = 1.6 Hz), 130.1 (d, *J* = 2.2 Hz), 127.6 (d, *J* = 7.0 Hz), 126.7 (d, *J* = 5.4 Hz), 119.7 (d, *J* = 5.3 Hz), 115.1 (d, *J* = 2.7 Hz), 64.2 (d, *J* = 5.6 Hz), 55.4, 16.1 (d, *J* = 7.2 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 22.7.

HR-MS (ESI): *m/z* calculated for $C_{11}H_{17}O_4PS$ $[M+Na]^+$: 299.0483, found: 299.0483.

_S_-(2-aminophenyl) _O_, _O_-dicyclohexyl phosphorothioate (3z)



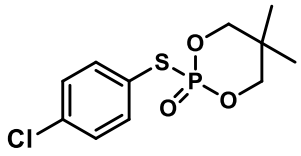
3z

Prepared according to general procedure, the reaction of 2-aminobenzenethiol **1r** (0.5 mmol), dicyclohexyl phosphonate **2e** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 171.7 mg (93%) of **3z** as pale yellow solid, m.p. 90-92°C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.43 (d, *J* = 7.8 Hz, 1H), 7.17 (t, *J* = 7.8 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.73 (t, *J* = 7.5 Hz, 1H), 4.59 (br s, 2H), 4.52-4.42 (m, 2H), 1.92-1.78 (m, 4H), 1.76-1.61 (m, 4H), 1.56-1.46 (m, 6H), 1.35-1.18 (m, 6H). **^{13}C NMR (100 MHz, $CDCl_3$, ppm):** δ 148.6 (d, *J* = 3.8 Hz), 137.6 (d, *J* = 4.2 Hz), 131.1 (d, *J* = 3.0 Hz), 119.5 (d, *J* =2.2 Hz), 116.8 (d, *J* =2.3 Hz), 110.0 (d, *J* =7.9 Hz), 78.5 (d, *J* = 7.7 Hz), 33.4 (dd, *J* = 31.1 Hz, *J* = 4.2 Hz), 25.1, 23.6 (d, *J* = 0.8 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 20.9.

HR-MS (ESI): *m/z* calculated for $C_{18}H_{28}NO_3PS$ $[M+Na]^+$: 392.1425, found: 392.1430.

2-((4-chlorophenyl)thio)-5, 5-dimethyl-1, 3, 2-dioxaphosphinane 2-oxide (3aa)



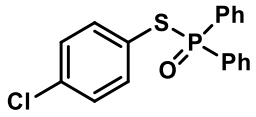
3aa

Prepared according to general procedure, the reaction of 4-chlorobenzenethiol **1a** (0.5 mmol), 5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide **2f** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 117.0 mg (80%) of **3aa** as white solid, m.p. 130-132°C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.57 (dd, *J* = 8.4 Hz, *J* = 1.7 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 4.21 (dd, *J* = 10.8 Hz, *J* = 3.6 Hz, 2H), 4.00-3.89 (m, 2H), 1.29 (s, 3H), 0.89 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$, ppm):** δ 136.0 (d, *J* = 5.0 Hz), 135.8 (d, *J* = 3.2 Hz), 129.8 (d, *J* = 2.1 Hz), 123.4 (d, *J* = 6.4 Hz), 78.4 (d, *J* = 7.1 Hz), 32.6 (d, *J* = 6.9 Hz), 21.2 (d, *J* = 158.6 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 14.1.

HR-MS (ESI): *m/z* calculated for $C_{11}H_{14}ClO_3PS$ $[M+Na]^+$: 314.9987, found: 314.9990.

_S_-(4-chlorophenyl) diphenylphosphinothioate (5a)[6]



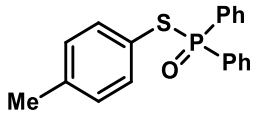
5a

Prepared according to general procedure, the reaction of 4-chlorobenzenethiol **1a** (0.5 mmol), diphenylphosphine oxide **4a** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 148.2 mg (86%) of **5a** as white solid, m.p. 95-97°C.

^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 7.85-7.82 (m, 4H), 7.54-7.52 (m, 2H), 7.47-7.44 (m, 4H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H). **^{13}C NMR (150 MHz, $CDCl_3$, ppm):** δ 136.6 (d, *J* = 3.8 Hz), 135.6 (d, *J* = 2.5 Hz), 132.6 (d, *J* = 2.3 Hz), 132.3 (d, *J* = 106.5 Hz), 131.7 (d, *J* = 10.2 Hz), 129.4 (d, *J* = 1.8 Hz), 128.7 (d, *J* = 13.2 Hz), 124.8 (d, *J* = 5.0 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 41.5.

HR-MS (ESI): *m/z* calculated for $C_{18}H_{14}ClOPS$ $[M+Na]^+$: 367.0089, found: 367.0097.

_S_-(p-tolyl) diphenylphosphinothioate (5b)[11]



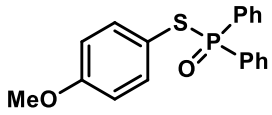
5b

Prepared according to general procedure, the reaction of 4-methylbenzenethiol **1c** (0.5 mmol), diphenylphosphine oxide **4a** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 134.6 mg (83%) of **5b** as white solid, m.p. 112-114 °C.

^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 7.86-7.83 (m, 4H), 7.52-7.49 (m, 2H), 7.45-7.42 (m, 4H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 7.8 Hz, 2H), 2.25 (s, 3H). **^{13}C NMR (150 MHz, $CDCl_3$, ppm):** δ 139.2 (d, *J* = 2.4 Hz), 135.4 (d, *J* = 3.7 Hz), 132.7 (d, *J* = 105.9 Hz), 132.3 (d, *J* = 3.0 Hz), 131.7 (d, *J* = 10.1 Hz), 130.0 (d, *J* = 1.8 Hz), 128.6 (d, *J* = 13.0 Hz), 122.3 (d, *J* = 5.1 Hz), 21.2. **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 41.2.

HR-MS (ESI): *m/z* calculated for $C_{19}H_{17}OPS$ $[M+Na]^+$: 347.0635, found: 347.0634.

_S_-(4-methoxyphenyl) diphenylphosphinothioate (5c)[12]



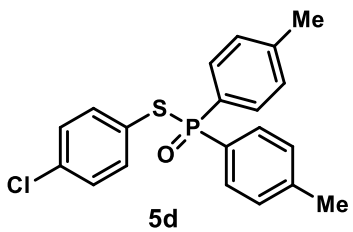
5c

Prepared according to general procedure, the reaction of 4-methoxybenzenethiol **1d** (0.5 mmol), diphenylphosphine oxide **4a** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 136.1 mg (80%) of **5c** as white solid, m.p. 150-152°C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.86-7.81 (m, 4H), 7.53-7.48 (m, 2H), 7.46-7.41 (m, 4H), 7.34-7.31 (m, 2H), 6.74-6.71 (m, 2H), 3.73 (s, 3H). **^{13}C NMR (150 MHz, $CDCl_3$, ppm):** δ 160.5 (d, *J* = 2.3 Hz), 137.1 (d, *J* = 3.5 Hz), 132.7 (d, *J* = 105.6 Hz), 132.3 (d, *J* = 3.0 Hz), 131.7 (d, *J* = 10.1 Hz), 128.6 (d, *J* = 13.0 Hz), 116.1 (d, *J* = 5.0 Hz), 114.8 (d, *J* = 1.9 Hz), 55.3. **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 41.3.

HR-MS (ESI): *m/z* calculated for $C_{19}H_{17}O_2PS$ $[M+Na]^+$: 363.0585, found: 363.0599.

_S_-(4-chlorophenyl) di-p-tolylphosphinothioate (5d)



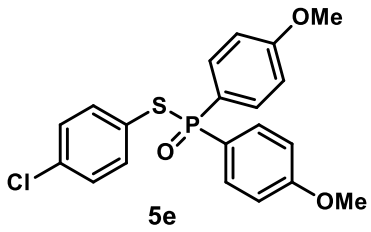
5d

Prepared according to general procedure, the reaction of 4-chlorobenzenethiol **1a** (0.5 mmol), di-p-tolylphosphine oxide **4b** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}-PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 141.6 mg (76%) of **5d** as pale yellow solid, m.p. 119-121°C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.71 (dd, *J* = 12.7 Hz, *J* = 8.0 Hz, 4H), 7.38 (dd, *J* = 8.4 Hz, *J* = 1.3 Hz, 2H), 7.25-7.23 (m, 4H), 7.17 (d, *J* = 8.5 Hz, 2H), 2.39 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$, ppm):** δ 143.1 (d, *J* = 2.9 Hz), 136.4 (d, *J* = 3.9 Hz), 135.3 (d, *J* = 2.4 Hz), 131.7 (d, *J* =10.5 Hz), 129.8 (d, *J* =1.5 Hz), 129.4 (d, *J* =13.6 Hz), 128.7 (d, *J* = 1.3 Hz), 125.3 (d, *J* = 5.0 Hz), 21.6. **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 42.0.

HR-MS (ESI): *m/z* calculated for $C_{20}H_{18}ClOPS$ $[M+Na]^+$: 395.0402, found: 395.0403.

_S_-(4-chlorophenyl) bis(4-methoxyphenyl)phosphinothioate (5e)



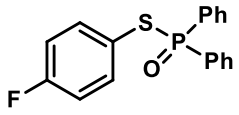
5e

Prepared according to general procedure, the reaction of 4-chlorobenzenethiol **1a** (0.5 mmol), bis(4-methoxyphenyl)phosphine oxide **4c** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}-PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 36h, afforded 125.5 mg (62%) of **5e** as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.77-7.71 (m, 4H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.95-6.92 (m, 4H), 3.84 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$, ppm):** δ 162.9 (d, *J* = 3.0 Hz), 136.4 (d, *J* = 3.8 Hz), 135.3 (d, *J* = 2.3 Hz), 133.7 (d, *J* =11.7 Hz), 129.3 (d, *J* =1.3 Hz), 125.6 (d, *J* =5.2 Hz), 123.6 (d, *J* = 114.4 Hz), 114.3 (d, *J* = 14.4 Hz), 55.5 (d, *J* = 3.4 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 41.6.

HR-MS (ESI): *m/z* calculated for $C_{20}H_{18}ClO_3PS$ $[M+Na]^+$: 427.0300, found: 427.0311.

_S_-(4-fluorophenyl) diphenylphosphinothioate (5f)[11]



5f

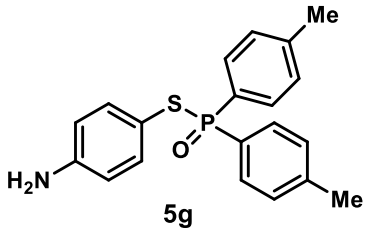
Prepared according to general procedure, the reaction of 4-fluorobenzenethiol **1g** (0.5

mmol), diphenylphosphine oxide **4a** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 48h, afforded 88.6 mg (54%) of **5f** as white solid, m.p. 93-95°C.

^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 7.85-7.81 (m, 4H), 7.53-7.39 (m, 8H), 6.91-6.88 (m, 2H). **^{13}C NMR (150 MHz, $CDCl_3$, ppm):** δ 163.3 (dd, *J* = 248.4 Hz, *J* = 2.3 Hz), 137.3(dd, *J* = 8.2 Hz, *J* = 3.1 Hz), 132.3 (d, *J* = 2.6 Hz), 132.1 (d, *J* = 106.2 Hz), 131.5 (d, *J* = 9.9Hz), 128.5 (d, *J* = 13.1 Hz), 121.0 (dd, *J* = 5.2 Hz, *J* = 3.3 Hz), 116.2 (dd, *J* = 21.8 Hz, *J* = 1.7 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 41.7.

HR-MS (ESI): *m/z* calculated for $C_{18}H_{14}FOPS$ $[M+Na]^+$: 351.0385, found: 351.0396.

_S_-(4-aminophenyl) di-p-tolylphosphinothioate (5g)



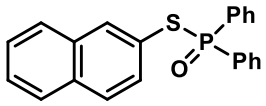
5g

Prepared according to general procedure, the reaction of 4-aminobenzenethiol **1m** (0.5 mmol), di-p-tolylphosphine oxide **4b** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 155.5 mg (88%) of **5g** as yellow oil.

^{1}H NMR (400 MHz, DMSO, ppm): δ 7.68-7.63 (m, 4H), 7.35-7.26 (m, 7H), 6.84 (d, *J* = 7.9 Hz, 1H), 3.91 (br s, 2H), 2.35 (s, 6H). **^{13}C NMR (150 MHz, $CDCl_3$, ppm):** δ 147.2 (d, *J* = 2.2 Hz), 142.6 (d, *J* = 2.8 Hz), 136.8 (d, *J* = 3.3 Hz), 131.6 (d, *J* =10.3 Hz), 130.0 (d, *J* =1.4 Hz), 129.2 (d, *J* =13.3 Hz), 116.0 (d, *J* = 1.8 Hz), 112.6 (d, *J* = 5.1 Hz), 21.6. **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 42.6.

HR-MS (ESI): *m/z* calculated for $C_{20}H_{20}NOPS$ $[M+Na]^+$: 376.4095, found: 376.0906.

_S_-(naphthalen-2-yl) diphenylphosphinothioate (5h)[11]



5h

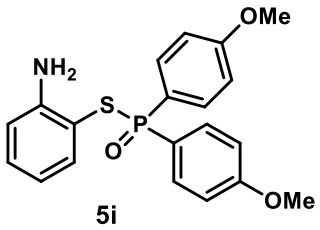
Prepared according to general procedure, the reaction of naphthalene-2-thiol **1t** (0.5 mmol), diphenylphosphine oxide **4a** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 160.3 mg (89%) of **5h** as white solid, m.p. 108-110°C.

^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 7.99 (s, 1H), 7.90-7.86 (m, 4H), 7.75-7.70 (m,

2H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.51-7.42 (m, 9H). **^{13}C NMR (100 MHz, $CDCl_3$, ppm):** δ 135.3 (d, *J* = 4.8Hz), 133.4 (d, *J* = 1.9 Hz), 132.9 (d, *J* = 1.5 Hz), 132.5 (d, *J* = 106.3 Hz), 132.2 (d, *J*= 2.8 Hz), 131.6 (d, *J* = 10.2 Hz), 131.4 (d, *J* = 3.1 Hz), 128.6 (d, *J* = 1.4 Hz), 128.5 (d, *J* = 13.1 Hz), 127.7, 127.5, 126.7, 126.3, 123.4 (d, *J* = 5.2 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 41.5.

HR-MS (ESI): *m/z* calculated for $C_{22}H_{17}OPS$ $[M+Na]^+$: 383.4005, found: 383.0658.

***S*-(2-aminophenyl) bis(4-methoxyphenyl)phosphinothioate (5i)**



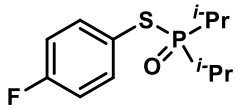
5i

Prepared according to general procedure, the reaction of 2-aminobenzenethiol **1r** (0.5 mmol), bis(4-methoxyphenyl)phosphine oxide **4c** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 36h, afforded 175.3 mg (91%) of **5i** as white solid, m.p. 114-117°C.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.78-7.29 (m, 4H), 7.05-7.02 (m, 2H), 6.95-6.92 (m, 4H), 6.68-6.66 (m, 1H), 6.50-6.46 (m, 1H), 3.83 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$, ppm):** δ 162.8 (d, *J* = 3.1 Hz), 150.5 (d, *J* = 2.8 Hz), 137.6 (d, *J* = 3.2 Hz), 133.5 (d, *J* = 11.7 Hz), 130.7 (d, *J* = 2.4 Hz), 124.3 (d, *J* = 112.2 Hz), 118.5 (d, *J* = 1.3 Hz), 116.2 (d, *J* = 2.0 Hz), 114.1 (d, *J* = 14.1 Hz), 109.4 (d, *J* = 5.1 Hz), 55.4 (d, *J* = 3.5 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 43.8.

HR-MS (ESI): *m/z* calculated for $C_{20}H_{20}NO_3PS$ $[M+Na]^+$: 408.0799, found: 408.0828.

***S*-(4-fluorophenyl) diisopropylphosphinothioate (5j)**



5j

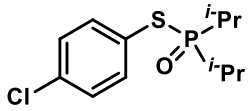
Prepared according to general procedure, the reaction of 4-fluorobenzenethiol **1g** (0.5 mmol), diisopropylphosphine oxide **4d** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 92.4 mg (71%) of **5j** as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.61-7.57 (m, 2H), 7.04-7.00 (m, 2H), 2.26-2.17 (m, 2H), 1.28-1.19 (m, 12H). **^{13}C NMR (100 MHz, $CDCl_3$, ppm):** δ 163.3 (dd, *J* = 247.5 Hz, *J* = 1.7 Hz), 137.4 (dd, *J* = 8.2 Hz, *J* = 3.1 Hz), 121.7 (dd, *J* = 7.8

Hz, *J* = 4.0 Hz), 116.4 (dd, *J* = 21.9 Hz, *J* = 1.3 Hz), 30.4 (d, *J* = 62.6 Hz), 16.4 (d, *J* = 2.9 Hz), 16.1 (d, *J* = 3.1 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 73.4.

HR-MS (ESI): *m/z* calculated for $C_{12}H_{18}FOPS$ $[M+Na]^+$: 283.0698, found: 283.0696.

***S*-(4-chlorophenyl) diisopropylphosphinothioate (5k)**



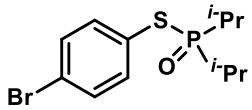
5k

Prepared according to general procedure, the reaction of 4-chlorobenzenethiol **1a** (0.5 mmol), diisopropylphosphine oxide **4d** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 101.0 mg (73%) of **5k** as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.56 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 2.27-2.16 (m, 2H), 1.28-1.19 (m, 12H). **^{13}C NMR (100 MHz, $CDCl_3$, ppm):** δ 136.4 (d, *J* = 3.1 Hz), 134.9 (d, *J* = 2.0 Hz), 129.1 (d, *J* = 1.3 Hz), 125.3 (d, *J* = 4.7 Hz), 30.4 (d, *J* = 62.7 Hz), 16.3 (d, *J* = 3.0 Hz), 16.0 (d, *J* = 3.2 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 74.5.

HR-MS (ESI): *m/z* calculated for $C_{12}H_{18}ClOPS$ $[M+Na]^+$: 299.0402, found: 299.0417.

***S*-(4-bromophenyl) diisopropylphosphinothioate (5l)**



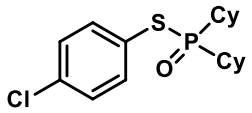
5l

Prepared according to general procedure, the reaction of 4-bromobenzenethiol **1f** (0.5 mmol), diisopropylphosphine oxide **4d** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in ^{i}PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 117.2 mg (73%) of **5l** as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.50-7.43 (m, 4H), 2.27-2.16 (m, 2H), 1.28-1.19 (m, 12H). **^{13}C NMR (100 MHz, $CDCl_3$, ppm):** δ 136.9 (d, *J* = 3.1 Hz), 132.3 (d, *J* = 1.3 Hz), 126.1 (d, *J* = 4.9 Hz), 123.3 (d, *J* = 1.9 Hz), 30.6 (d, *J* = 62.8 Hz), 16.5 (d, *J* = 2.9 Hz), 16.2 (d, *J* = 3.2 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 73.8.

HR-MS (ESI): *m/z* calculated for $C_{12}H_{18}BrOPS$ $[M+Na]^+$: 342.9897, found: 342.9899.

***S*-(4-chlorophenyl) dicyclohexylphosphinothioate (5m)**



5m

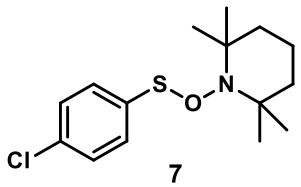
Prepared according to general procedure, the reaction of 4-chlorobenzenethiol **1a** (0.5 mmol), dicyclohexylphosphine oxide **4e** (1.5 mmol), MB (3 mol%) and K_2CO_3 (0.5 mmol) in $^{i-}$PrOH (1.0 mL) at room temperature under the irradiation of 15 W blue LEDs for 24h, afforded 167.7 mg (94%) of **5m** as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 2.02-1.70 (m, 12H), 1.47-1.39 (m, 4H), 1.25-1.18 (m, 6H). **^{13}C NMR (150 MHz, $CDCl_3$, ppm):** δ 136.6 (d, *J* = 3.1 Hz), 135.0 (d, *J* = 3.1 Hz), 129.3 (d, *J* = 0.8 Hz), 125.8 (d, *J* = 4.5 Hz), 40.5 (d, *J* = 6.8 Hz), 26.6 (d, *J* = 5.2 Hz) 26.5 (d, *J* = 5.3 Hz), 26.3 (d, *J* = 3.3 Hz), 26.0 (d, *J* = 3.3 Hz), 25.9 (d, *J* = 1.9 Hz). **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 67.9.

HR-MS (ESI): *m/z* calculated for $C_{18}H_{26}ClOPS$ $[M+Na]^+$: 379.1028, found: 379.1051.

TEMPO adduct

1-(((4-chlorophenyl)thio)oxy)-2,2,6,6-tetramethylpiperidine (7)

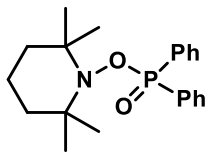


7

Colorless oil. **^{1}H NMR (600 MHz, $CDCl_3$, ppm)**: δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 1.67-1.49 (m, 15H), 0.91 (s, 3H). **^{13}C NMR (150 MHz, $CDCl_3$, ppm):** δ 149.07, 135.80, 128.84, 127.60, 61.61, 59.11, 43.60, 41.49, 35.52, 32.85, 28.86, 28.06, 17.35.

HR-MS (ESI): *m/z* calculated for $C_{15}H_{22}ClNOS$ $[M+Na]^+$: 322.1008, found:322.1010.

2,2,6,6-tetramethylpiperidin-1-yl diphenylphosphinate (8)



8

White solid, m.p. 115-117°C. **^{1}H NMR (600 MHz, $CDCl_3$, ppm)**: δ 7.87-7.83 (m, 4H), 7.48-7.39 (m, 6H), 1.36-0.94 (m, 18H). **^{13}C NMR (100 MHz, $CDCl_3$, ppm):** δ

134.04 (d, *J* = 134.2 Hz), 131.83 (d, *J* = 10.0 Hz), 131.66 (d, *J* = 2.7 Hz), 128.44 (d, *J* = 12.7 Hz), 61.72 (d, *J* = 2.7 Hz), 40.23, 32.62, 17.03. **^{31}P NMR (162 MHz, $CDCl_3$, ppm):** δ 33.4.

HR-MS (ESI): *m/z* calculated for $C_{21}H_{28}NO_2P$ $[M+Na]^+$: 380.1750, found:380.1753.

2.5 The fluorescence emission spectrum of the methylene blue

The fluorescence emission spectrum of the methylene blue showed a peak at 690 nm when excited at 664 nm (Figure S1). The fluorescence emission spectra of methylene blue at different excitation wavelength was tested and the highest emission peak was obtained under the excitation at 664 nm (Figure S2).

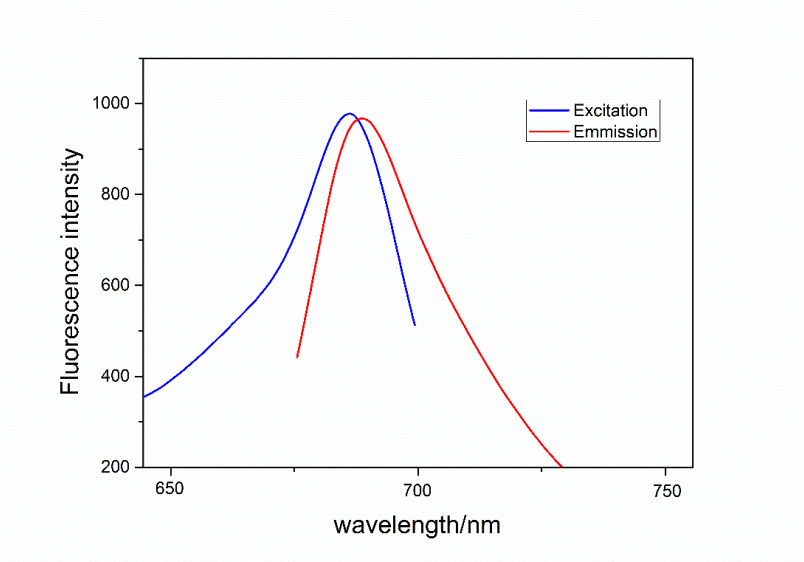


Fig. S1 Fluorescence excitation and emission spectra

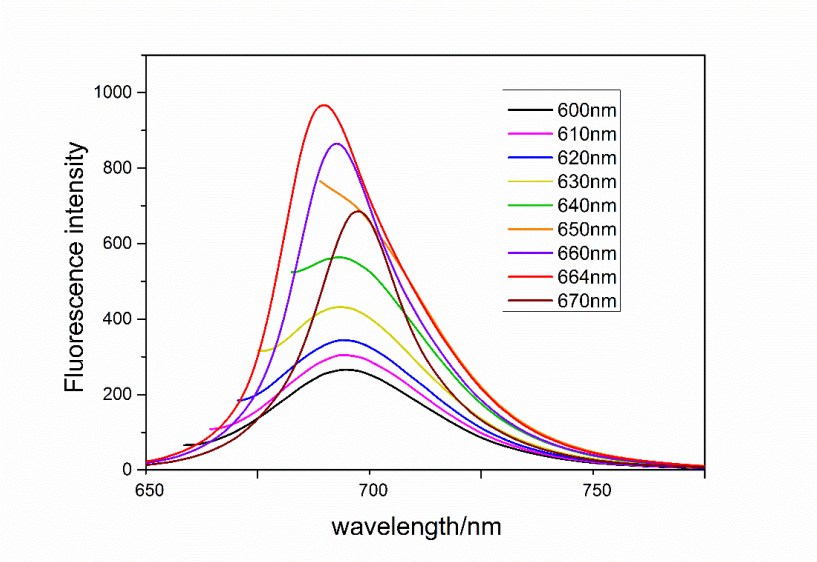
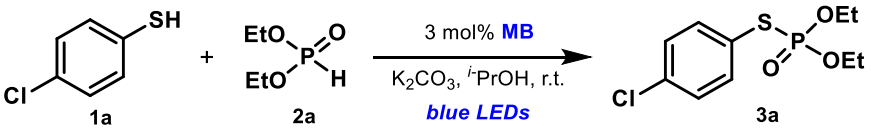


Fig. S2 Fluorescence emission spectra of the methylene blue at different excitation wavelengths

2.6 Determination of quantum yield



The quantum yield of phosphorothioate (**3a**) formation was determined with a potassium ferrioxalate actinometer.[13] The quantum yield (Φ_P) of this reaction was about 3.5%. This low value is consistent with the long reaction times needed for most substrates.

The process are as follows:

A solution of $K_2Fe(C_2O_4)_3$ (0.15 M, 2 mL) was transferred into a fused silica cuvette and irradiated for 60 s under blue LEDs (10W). After a illumination period of 60s, 100 μL were transferred to a 10 mL volumetric flask, and 4 mL of a phenanthroline solution (20 mg of 1,10-phenanthroline in 10 mL of H_2O) and 500 μL of a buffer solution (1.8 g of NaOAc and 1 mL of HOAc in H_2O up to 100 mL) were added prior to adding water up to 10 mL.

The moles of Fe^{2+} generated was measured by determining the absorbance of the Fe(II)-*o*-phenanthroline complex at 510 nm. A blank sample was prepared following the same procedure. Note that the procedure was done under subdued red light illumination conditions.

The moles of Fe^{2+} was calculated according to the follow equation:

$$mmol\mathrm{Fe}^{2+} = \frac{A}{\varepsilon \times d} \times \frac{10mL \times 2mL}{0.1mL} \qquad (1)$$

A is the absorbance and n is the refractive index. ε is the extinction coefficient of the complex at 510 nm (ε=1.11·104 $L \cdot mol^{-1} \cdot cm^{-1}$),[13a] d is the light path length of the cuvette (d = 1 cm).

The photon flux was calculated using the following formulas:

$$\text{photon flux} = \frac{mmol\mathrm{Fe}^{2+}}{t \times \Phi_{450nm} \times f} \times \frac{10^3 mol}{mmol} \qquad (2)$$

Where t is illumination time in 60s, the quantum yield of the photolysis of potassium ferrioxalate ($\Phi_{450nm} = 1$)[13b], total light absorption (f = 1).

Finally, the quantum yield (Φ_P) is given by:

$$\Phi_P = \frac{mol\ \mathbf{3a}}{t_1 \times \text{photon flux}} \times 100 \qquad (3)$$

Where mol **3a** represents the amount of product generated (1.6×10^{-5} mol) and t_1 is the reaction time in 18000s.

3 References

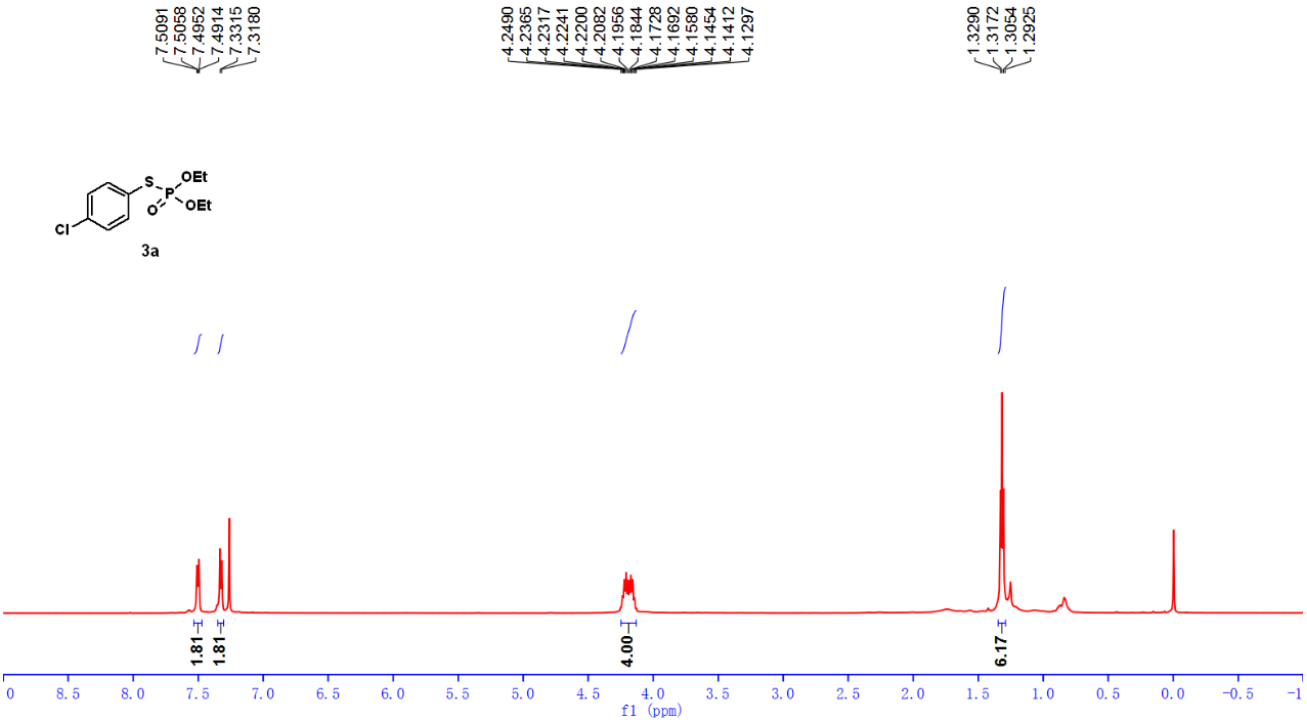
1 S. Molitor, J. Becker and V. H. Gessner, *J. Am. Chem. Soc.*, 2014, **136**, 15517.

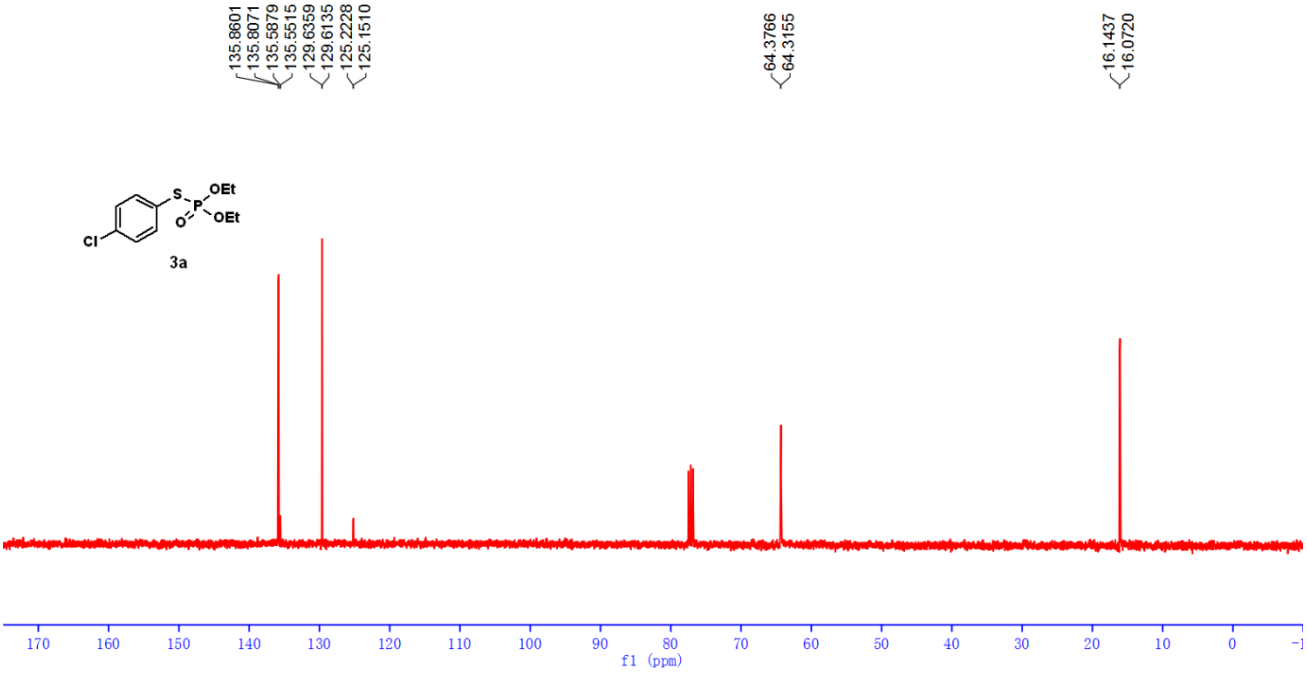
2 R. Shen, B. Luo, J. Yang, L. Zhang and L.-B. Han, *Chem. Commun.*, 2016, **52**, 6451.

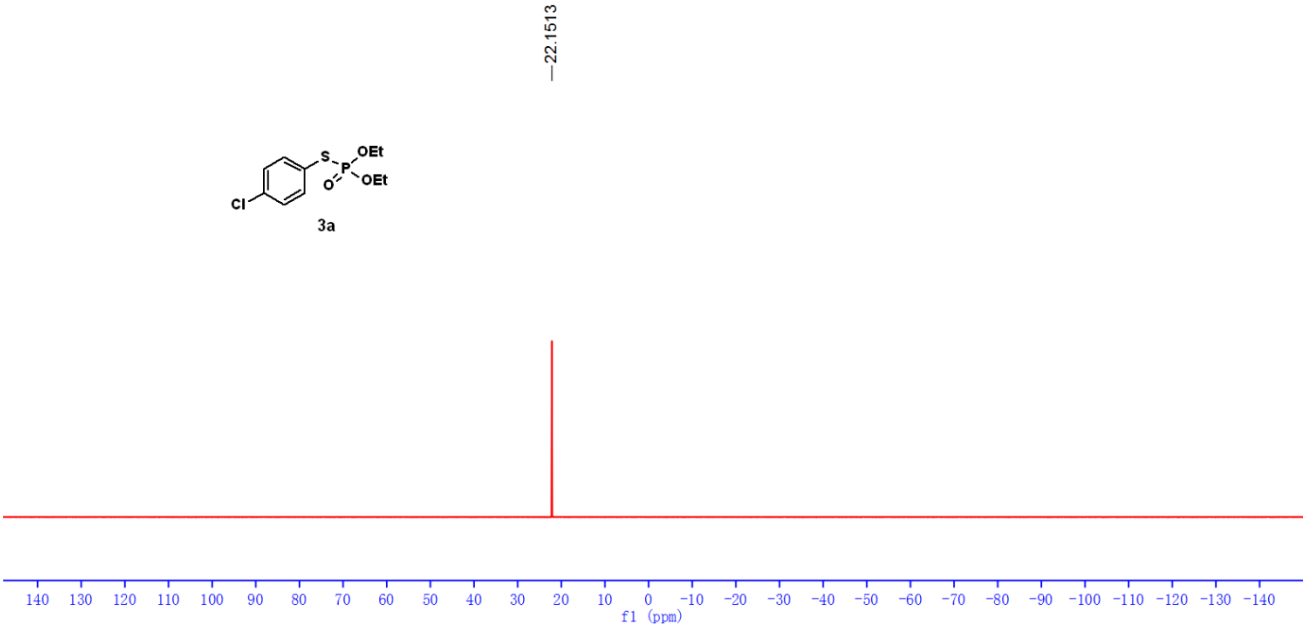
3 N. Qi, N. Zhang, S. R. Allu, J. Gao, J. Guo and Y. He, *Org. Lett.*, 2016, **18**, 6204.

4 C. A. Busacca, J. C. Lorenz, N. Grinberg, N. Haddad, M. Hrapchak, B. Latli, H. Lee, P. Sabila, A. Saha, M. Sarvestani, S. Shen, R. Varsolona, X. Wei and C. H. Senanayake, *Org. Lett.*, 2005, **7**, 4277.
5 Y. Zhu, T. Chen, S. Li, S. Shimada and L.-B. Han, *J. Am. Chem. Soc.*, 2016, **138**, 5825.
6 J. Xu, L. Zhang, X. Li, Y. Gao, G. Tang and Y. Zhao, *Org. Lett.*, 2016, **18**, 1266.
7 S. Song, Y. Zhang, A. Yeerlan, B. Zhu, J. Liu and N. Jiao, *Angew. Chem. Int. Ed.*, 2017, **56**, 2487.
8 J. Bai, X. Cui, H. Wang and Y. Wu, *Chem. Commun.*, 2014, **50**, 8860.
9 G. Kumaraswamy and R. Raju, *Adv. Synth. Catal.*, 2014, **356**, 2591.
10 J. Wang, X. Huang, Z. Ni, S. Wang, Y. Pan and J. Wu, *Tetrahedron*, 2015, **71**, 7853.
11 J.-B Sun, W.-Z Weng, P. Li and B. Zhang, *Green Chem.*, 2017, **19**, 1128.
12 Y. Moon, Y. Moon, H. Choi and S. Hong, *Green Chem.*, 2017, **19**, 1005.
13 (a) J. N. Demas, W. D. Bowman, E. F. Zalewski and R. A. Velapoldi, J. Phys. Chem., 1981, 85, 2766; (b) J. C. Gonzalez-Gomez, N. P. Ramirez, T. Lana-Villarreal and P. Bonete, Org. Biomol. Chem., 2017,15, 9680.

4 ^{1}H NMR, ^{13}C NMR, ^{31}P NMR of Compounds



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OEt
S
P
O
Cl
3a
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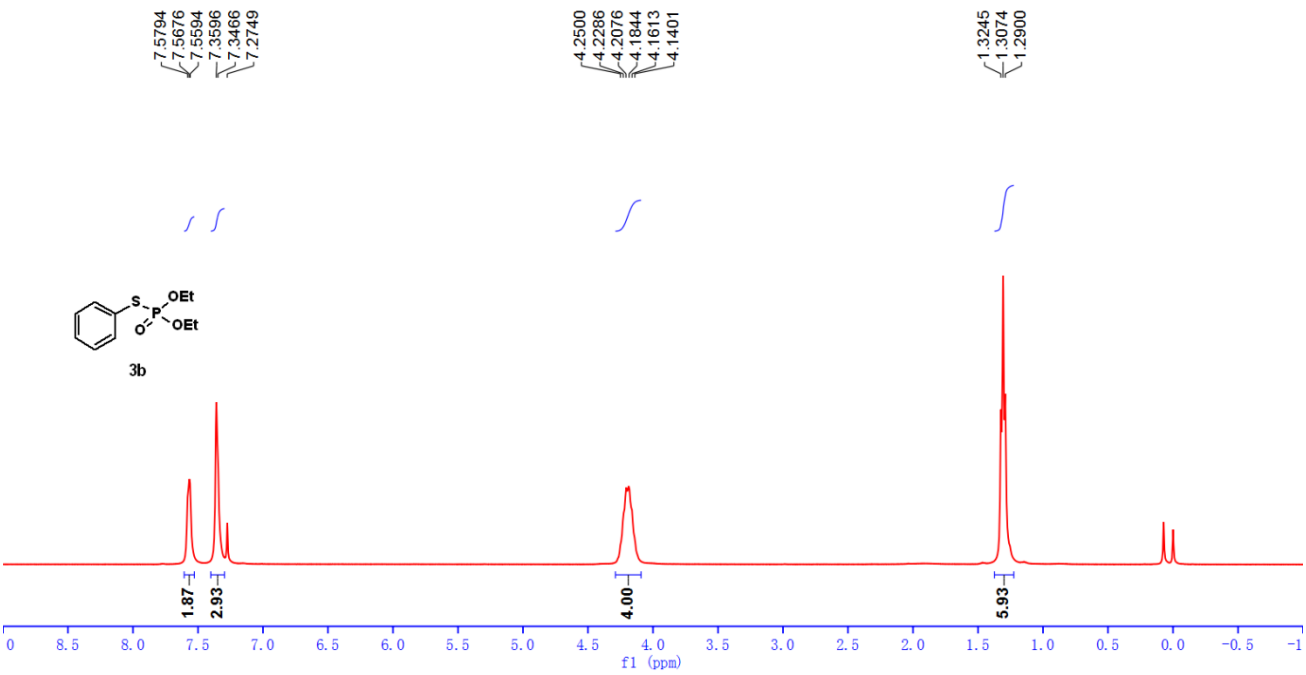
f1 (ppm)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4.1613
4.1401
1.3245
1.3074
1.2900
OEt
OEt
S
P
O
3b
1.87
2.93
4.00
5.93
0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
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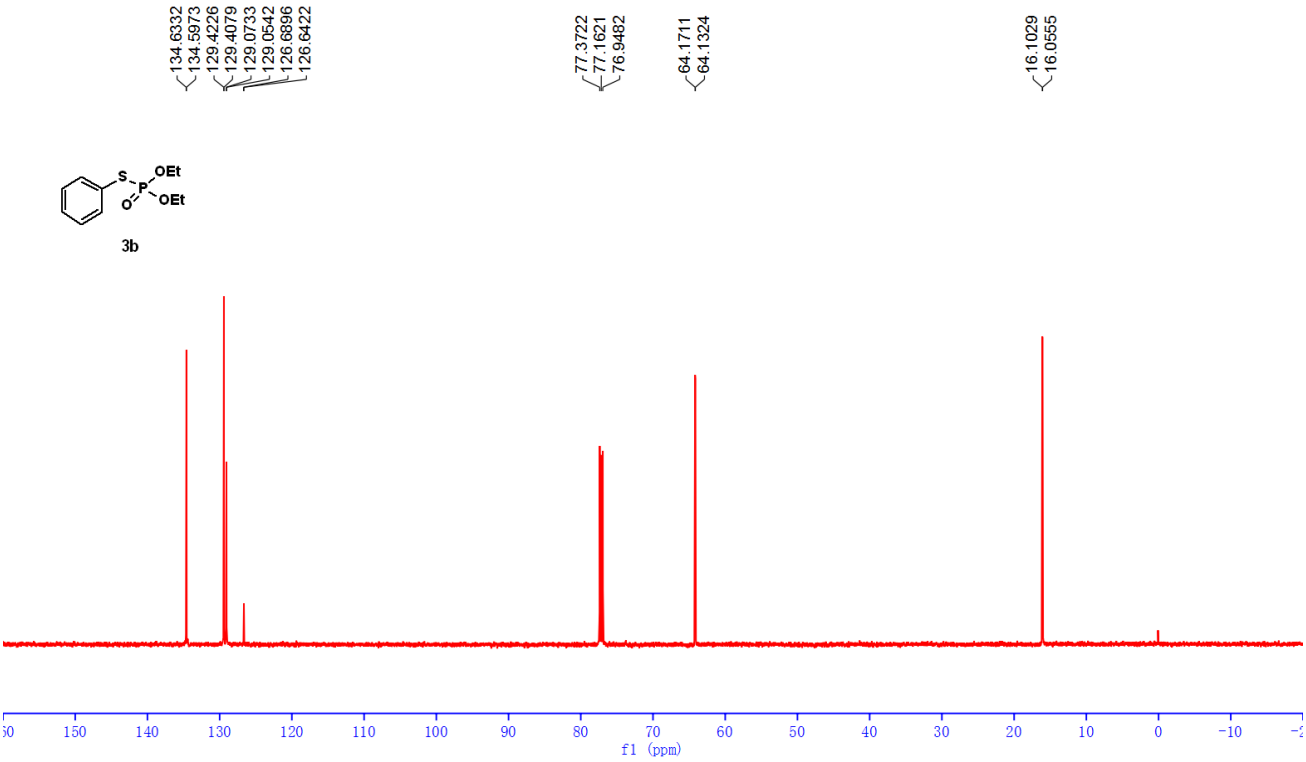
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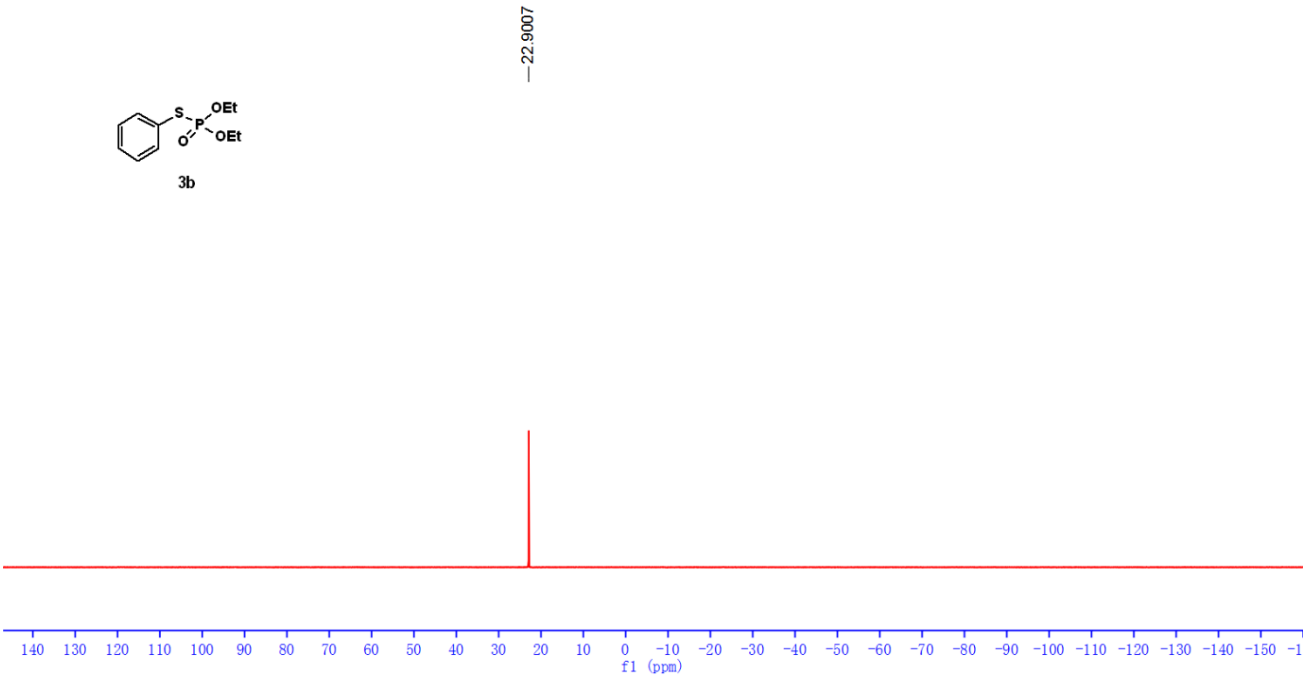
76.9482
64.1711
64.1324
16.1029
16.0555
OEt
OEt
3b
f1 (ppm)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OEt
3b
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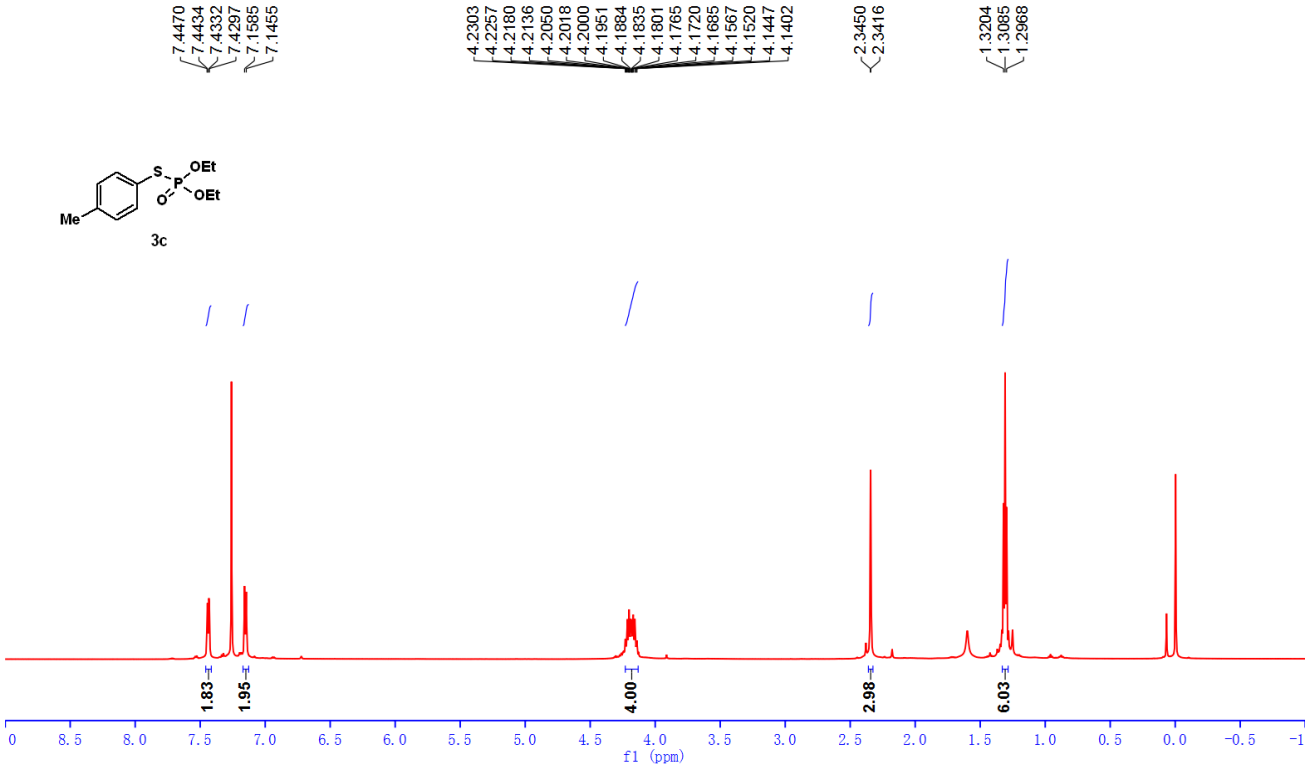
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7.1455
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4.2180
4.2136
4.2050
4.2018
4.2000
4.1951
4.1884
4.1835
4.1801
4.1765
4.1720
4.1685
4.1567
4.1520
4.1447
4.1402
2.3450
2.3416
1.3204
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OEt
OEt
Me
3c
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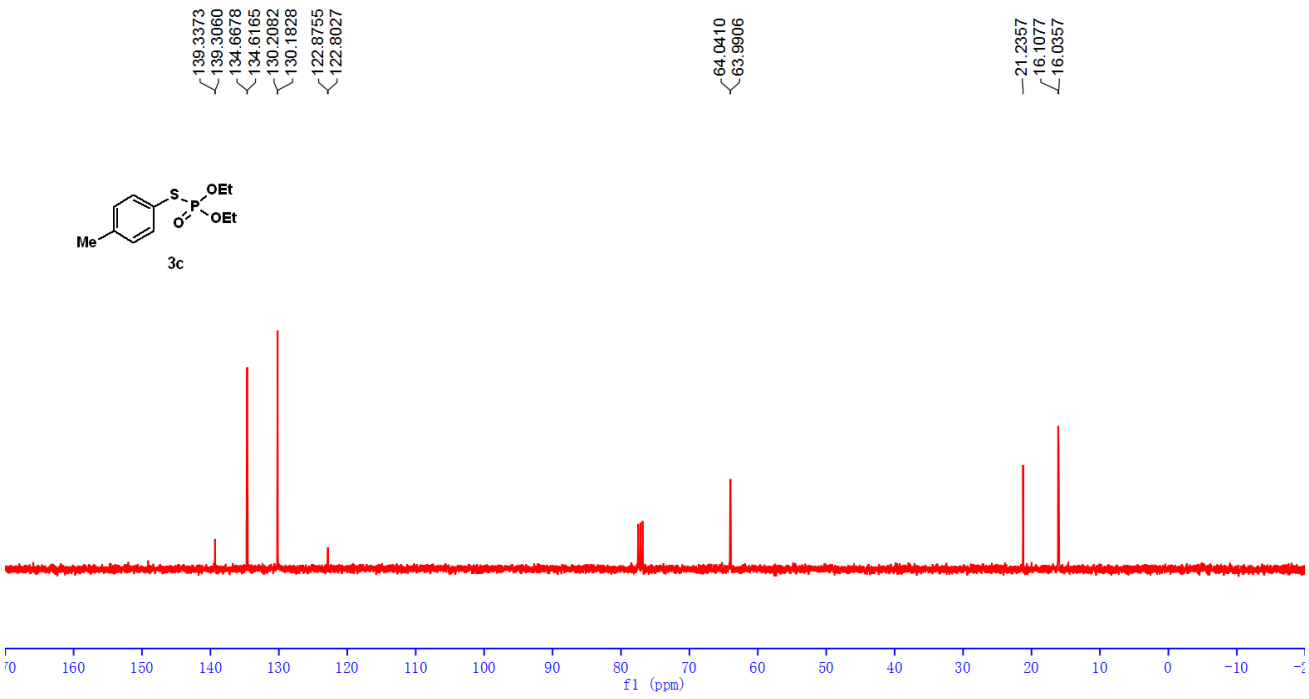
1.95
4.00
2.98
6.03
f1 (ppm)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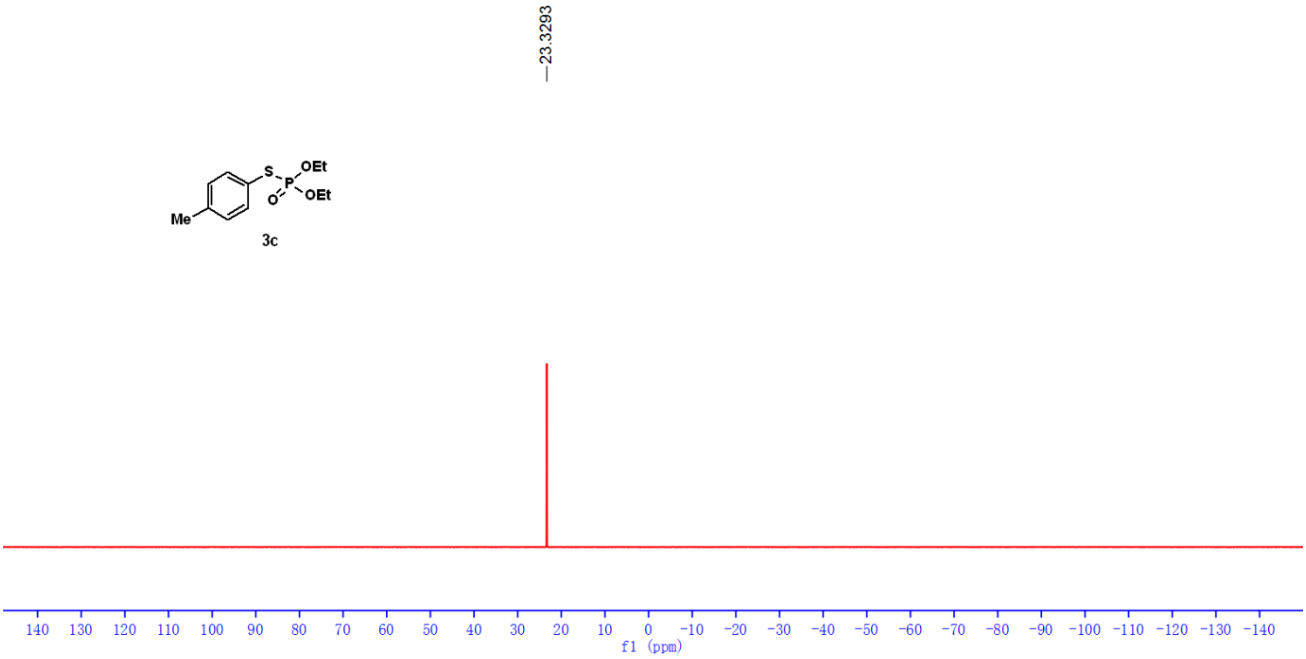
OEt
Me
3c
f1 (ppm)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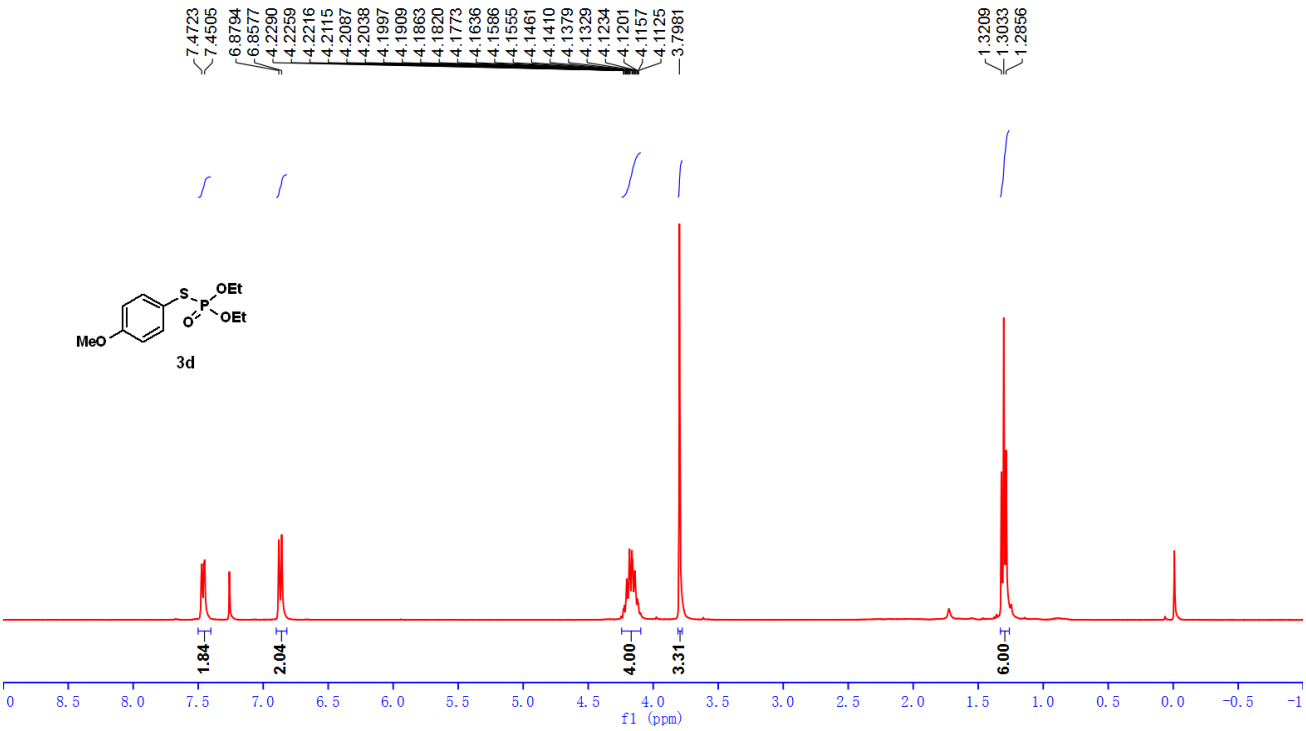
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6.8577
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4.2259
4.2216
4.2115
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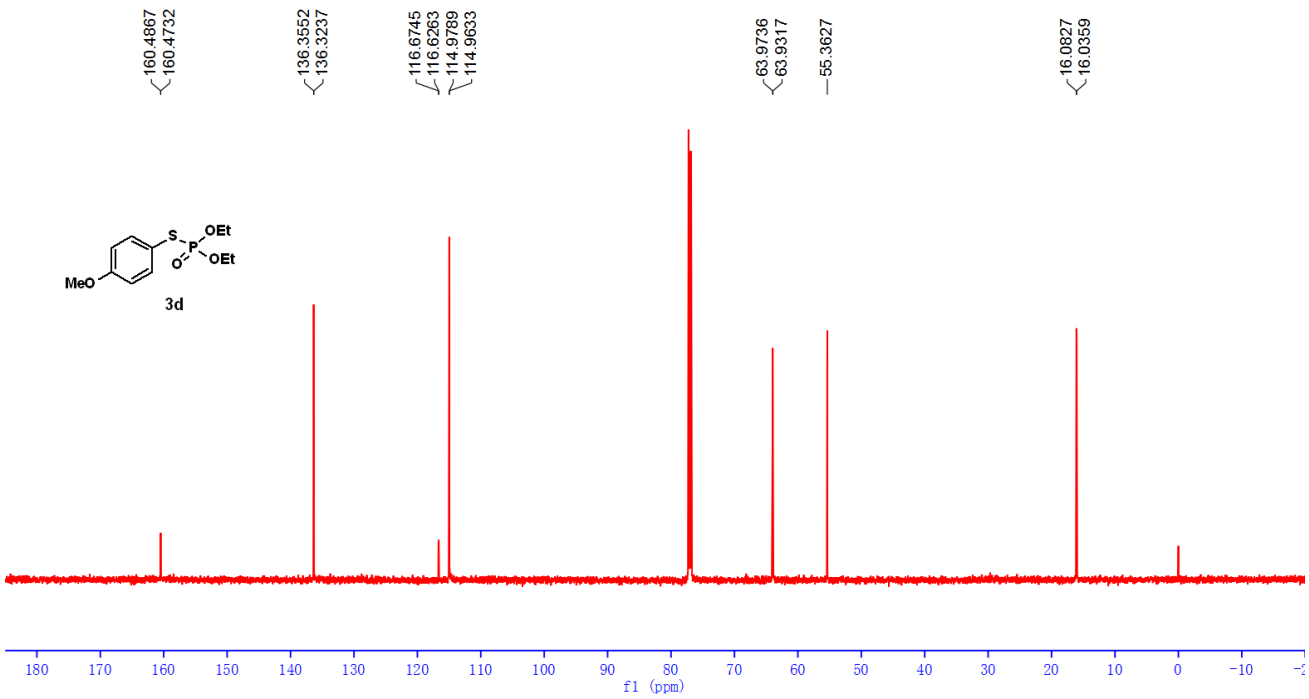
4.2038
4.1997
4.1909
4.1863
4.1820
4.1773
4.1636
4.1586
4.1555
4.1461
4.1410
4.1379
4.1329
4.1234
4.1201
4.1157
4.1125
3.7981
1.3209
1.3033
1.2856
MeO
OEt
OEt
3d
1.84
2.04
4.00
3.31
6.00
0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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OEt
MeO
3d
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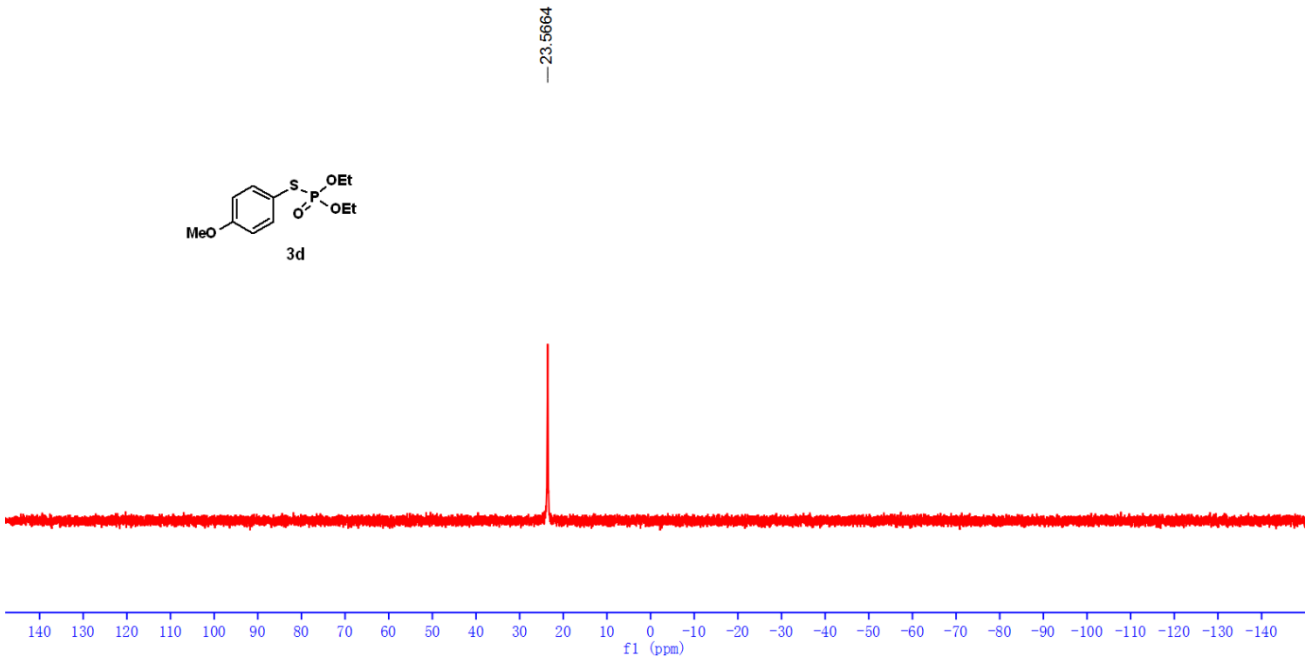
f1 (ppm)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OEt
MeO
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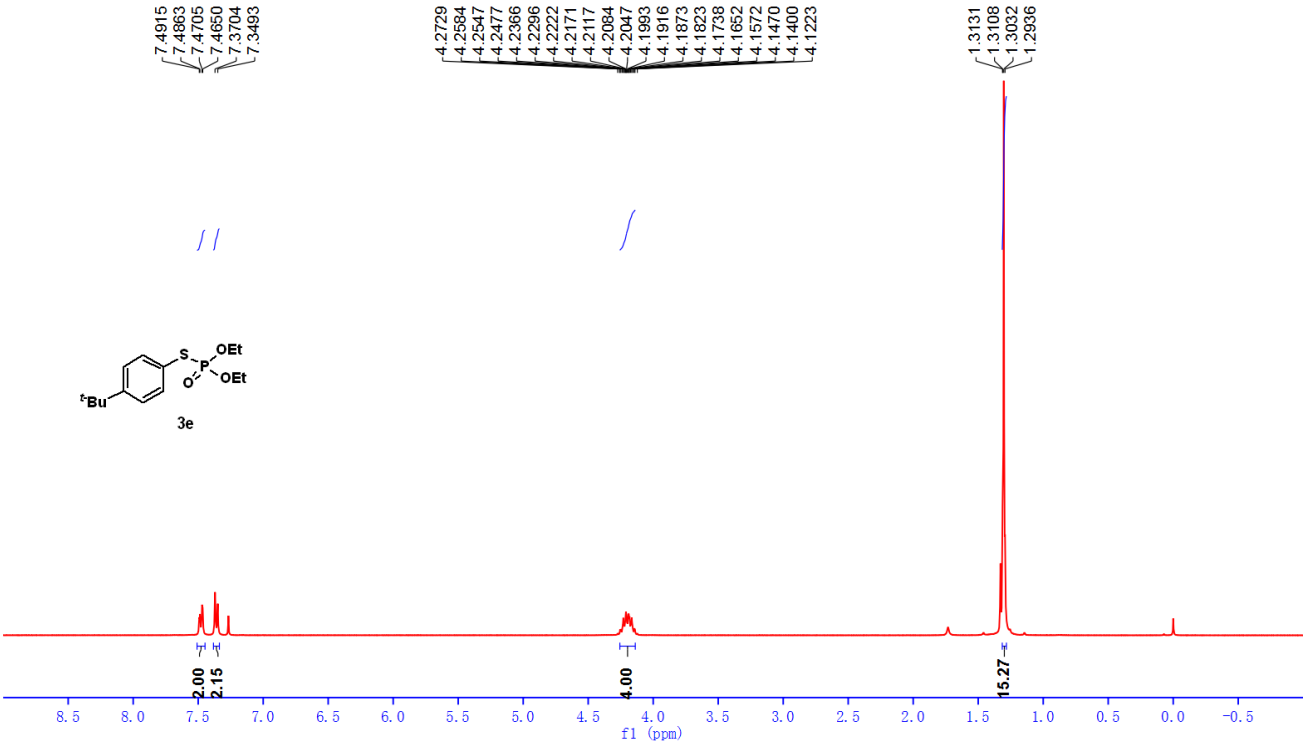
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4.2366
4.2296
4.2222
4.2171
4.2117
4.2084
4.2047
4.1993
4.1916
4.1873
4.1823
4.1738
4.1652
4.1572
4.1470
4.1400
4.1223
1.3131
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OEt
tBu
3e
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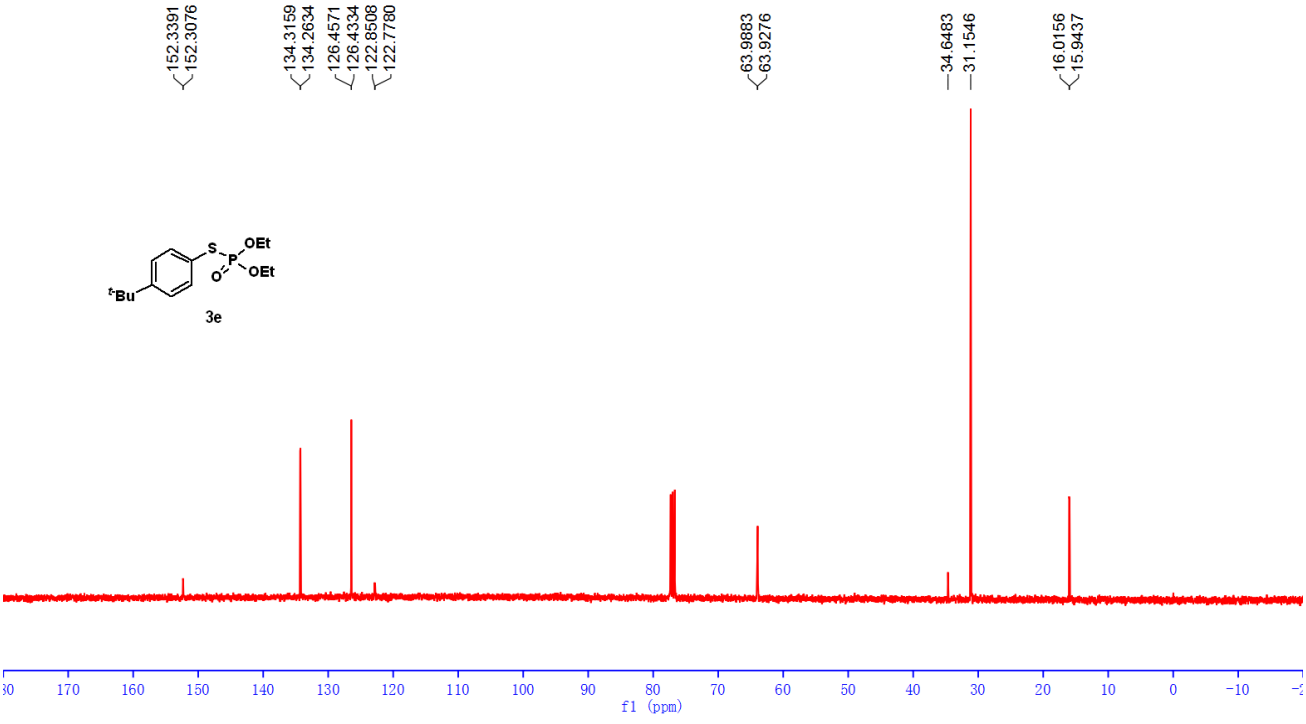
4.00
15.27
f1 (ppm)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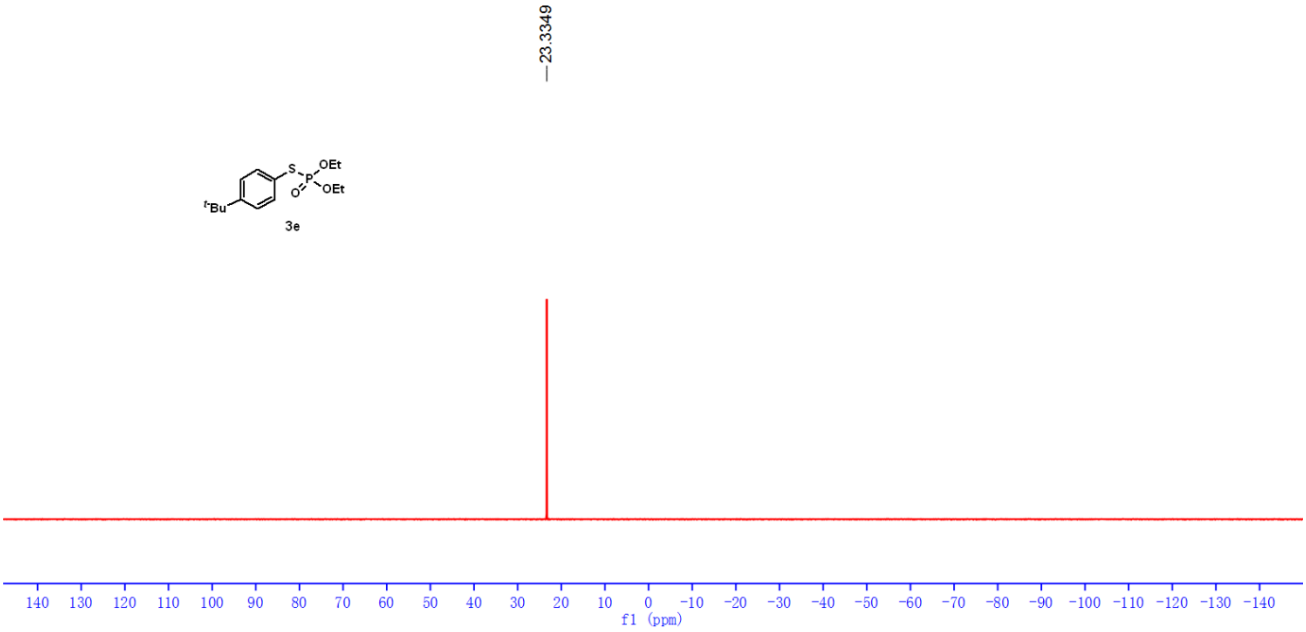
16.0156
15.9437
OEt
OEt
tBu
3e
f1 (ppm)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OEt
S
P
O
tBu
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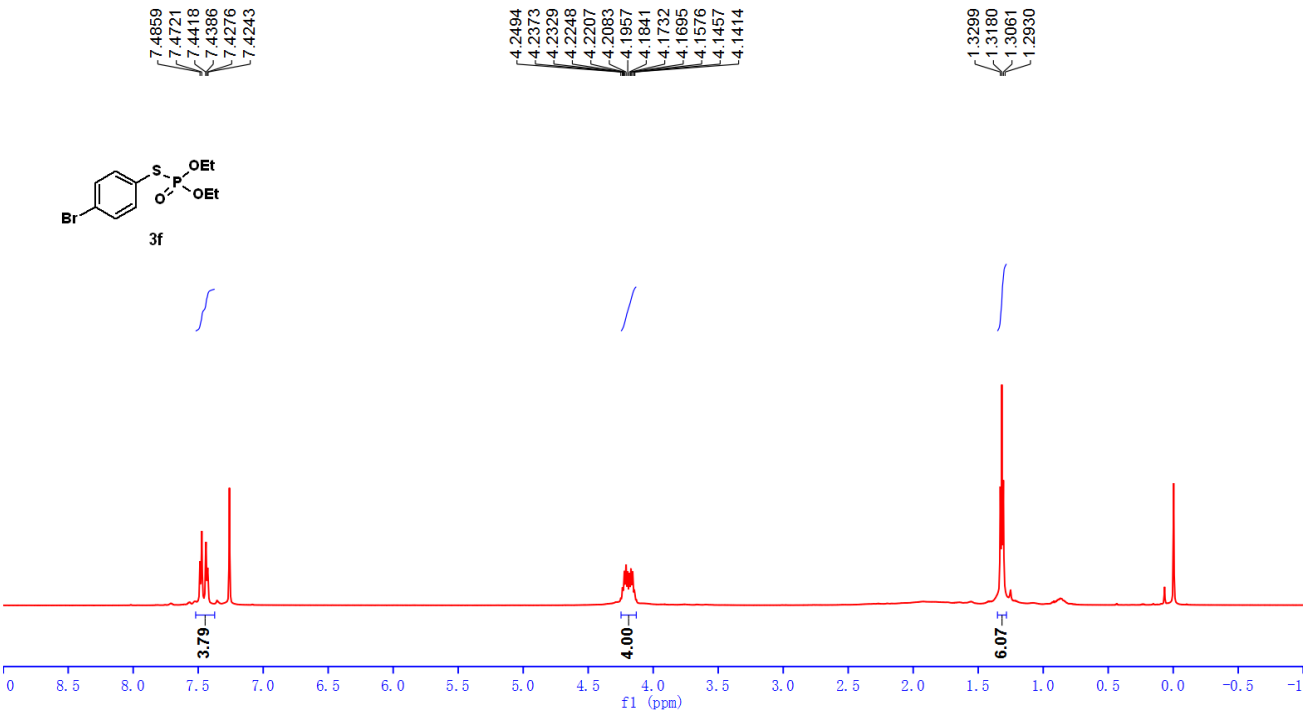
f1 (ppm)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4.1957
4.1841
4.1732
4.1695
4.1576
4.1457
4.1414
1.3299
1.3180
1.3061
1.2930
OEt
OEt
S
P
O
Br
3f
3.79
4.00
6.07
0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
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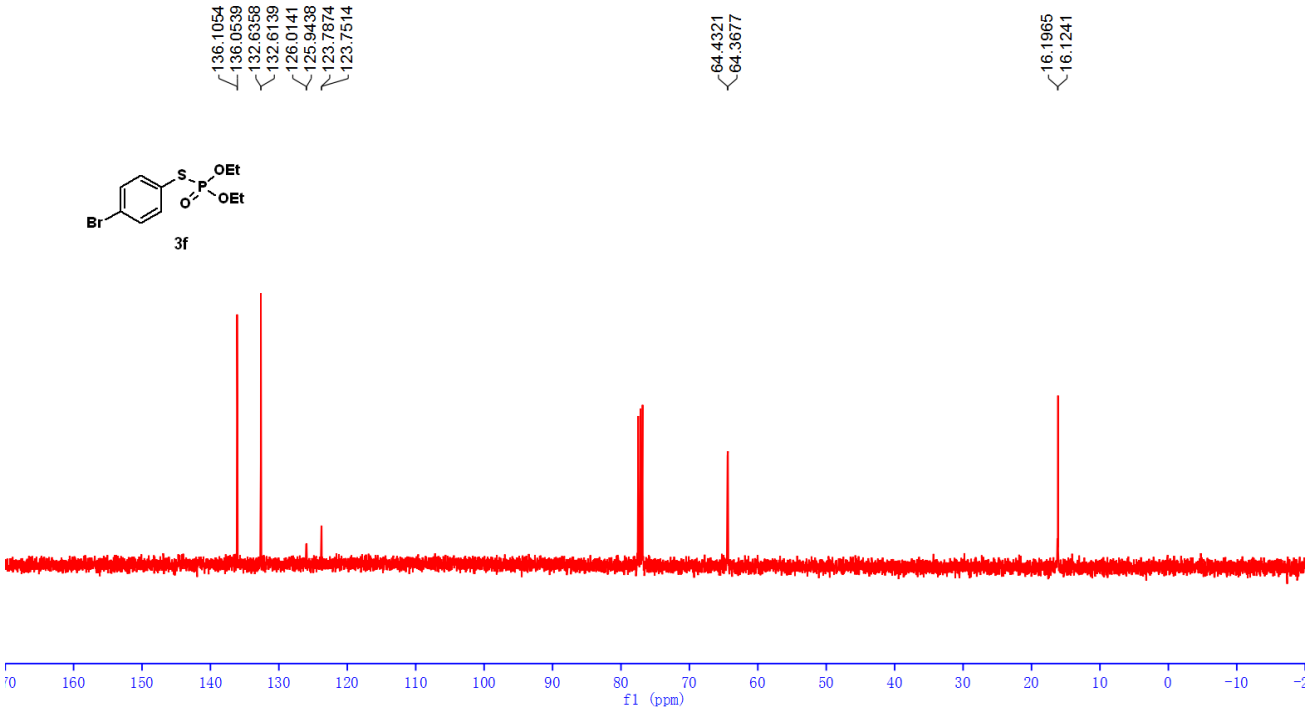
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OEt
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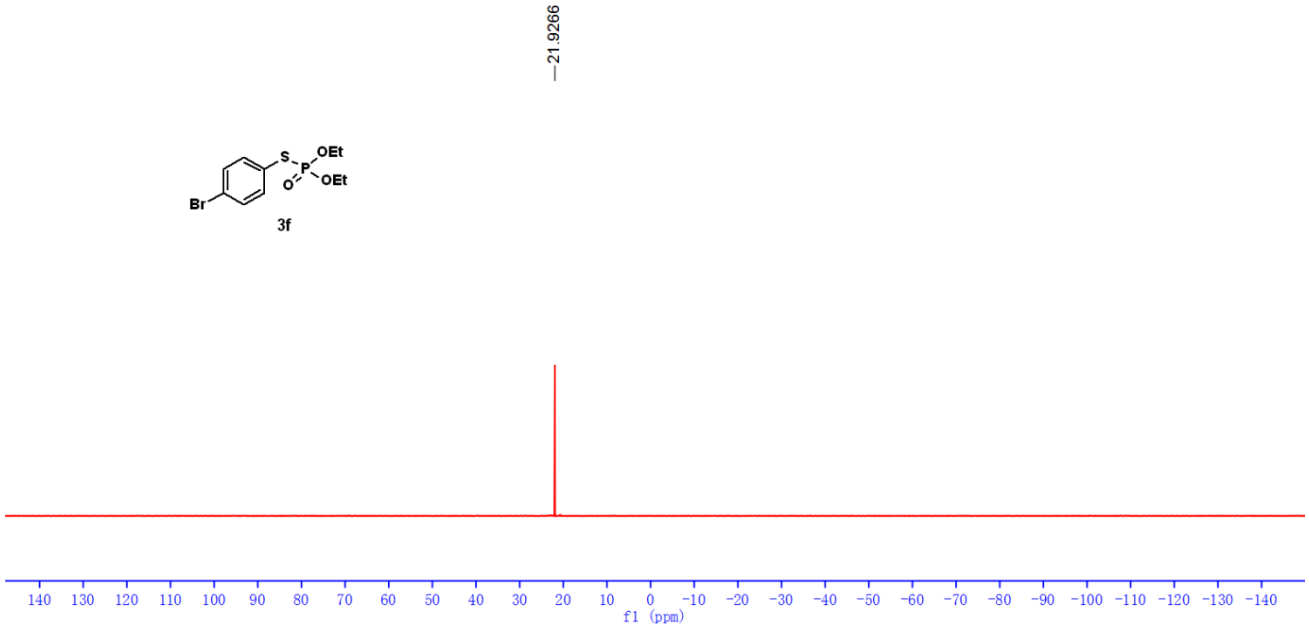
S
P
O
Br
3f
f1 (ppm)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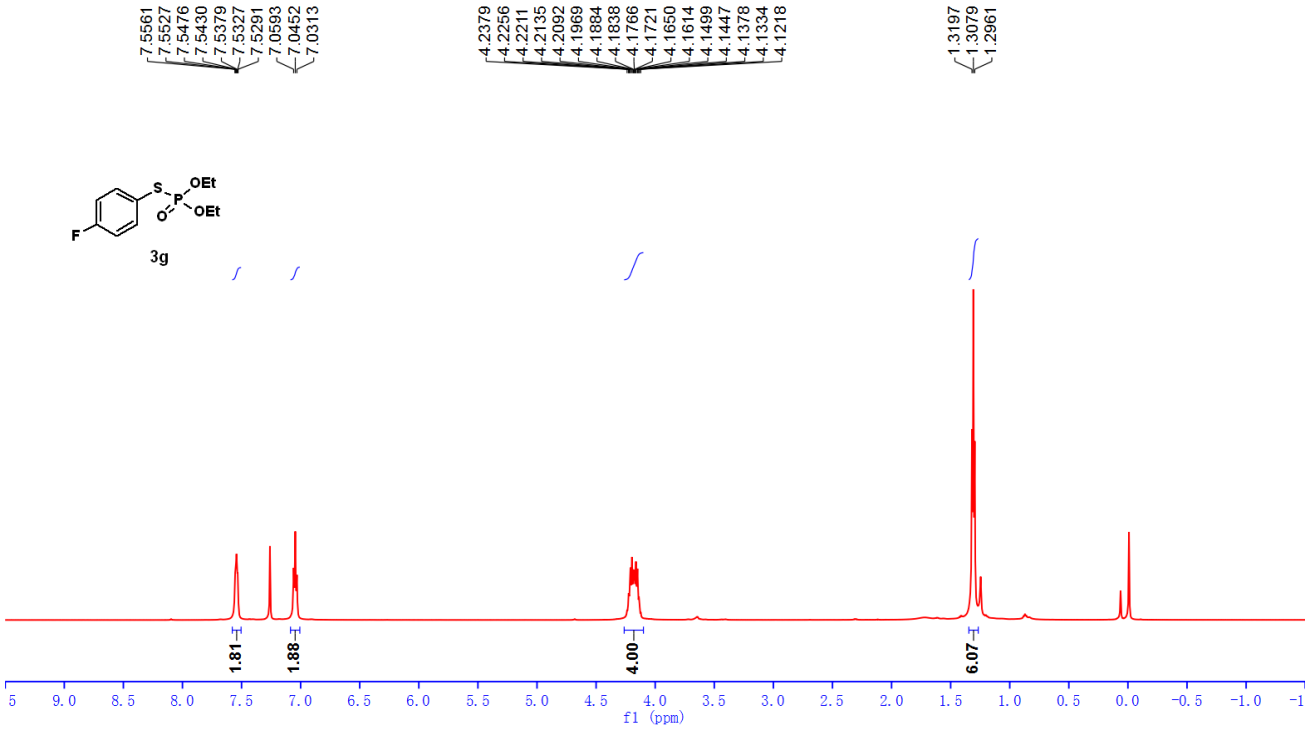
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4.1614
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4.1447
4.1378
4.1334
4.1218
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OEt
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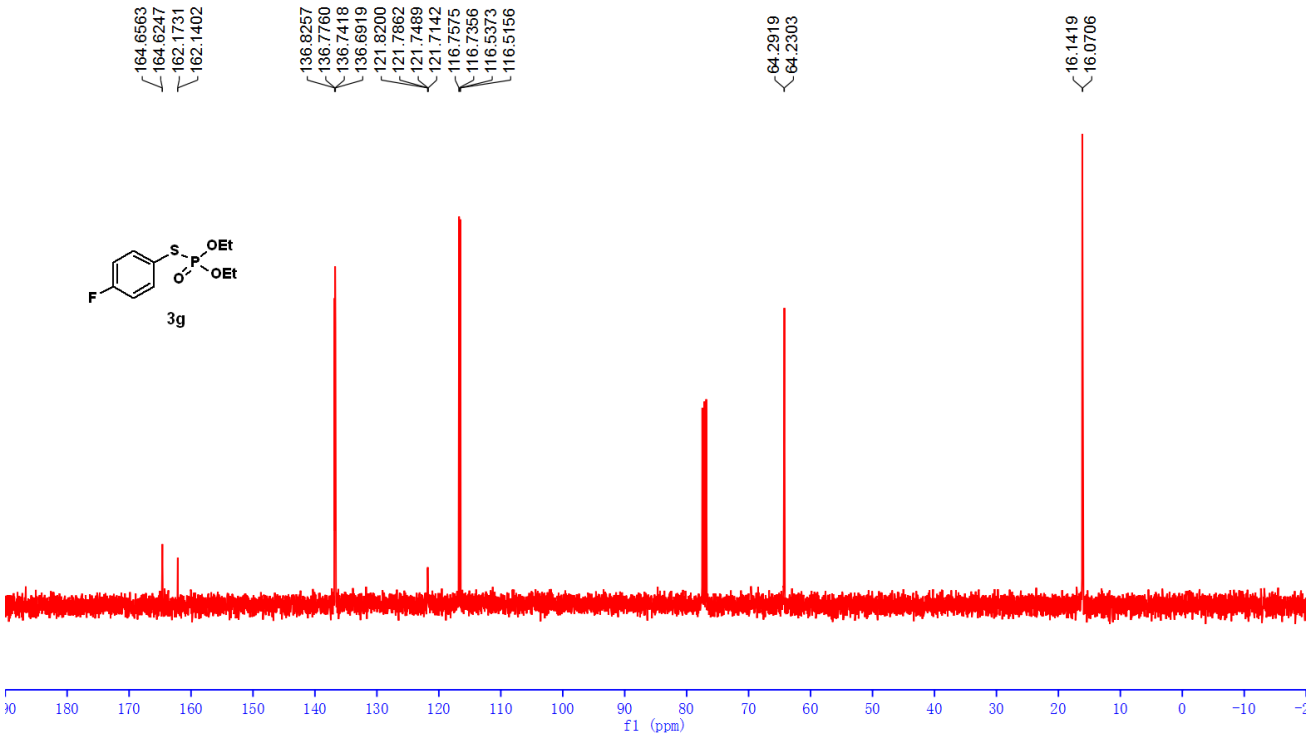
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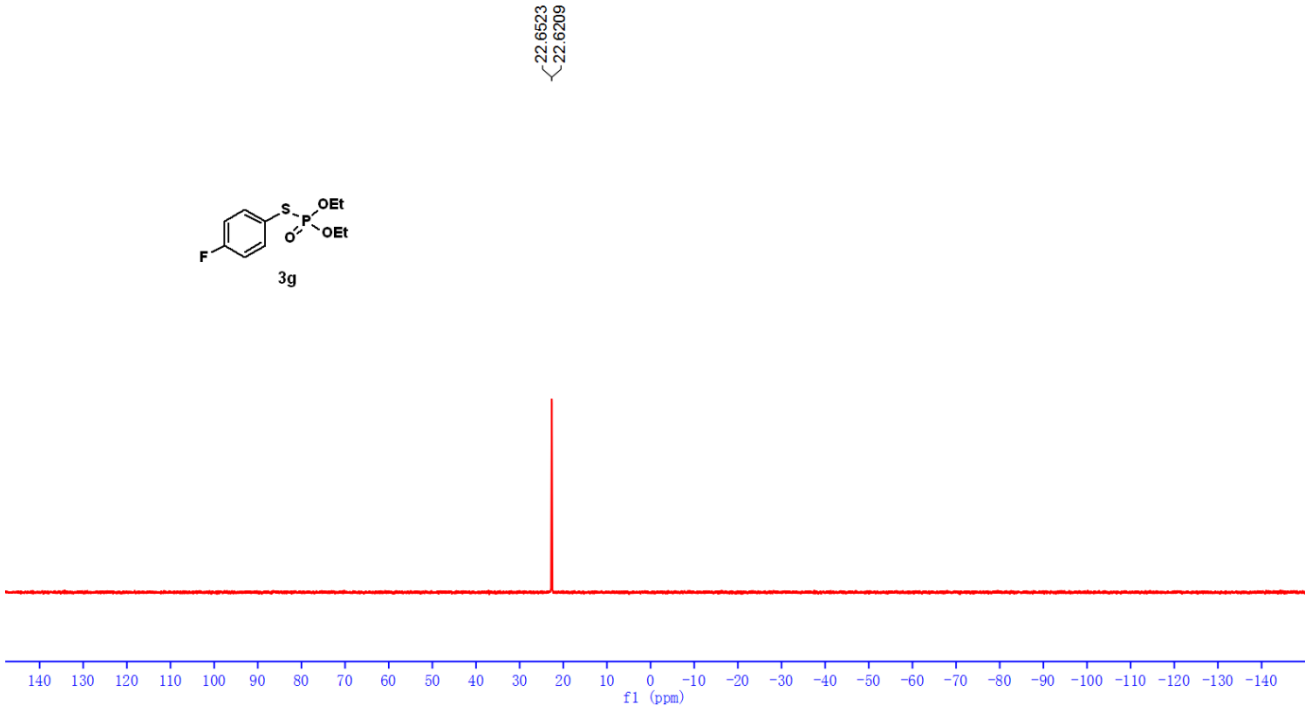
OEt
S
P
O
F
3g
f1 (ppm)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OEt
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P
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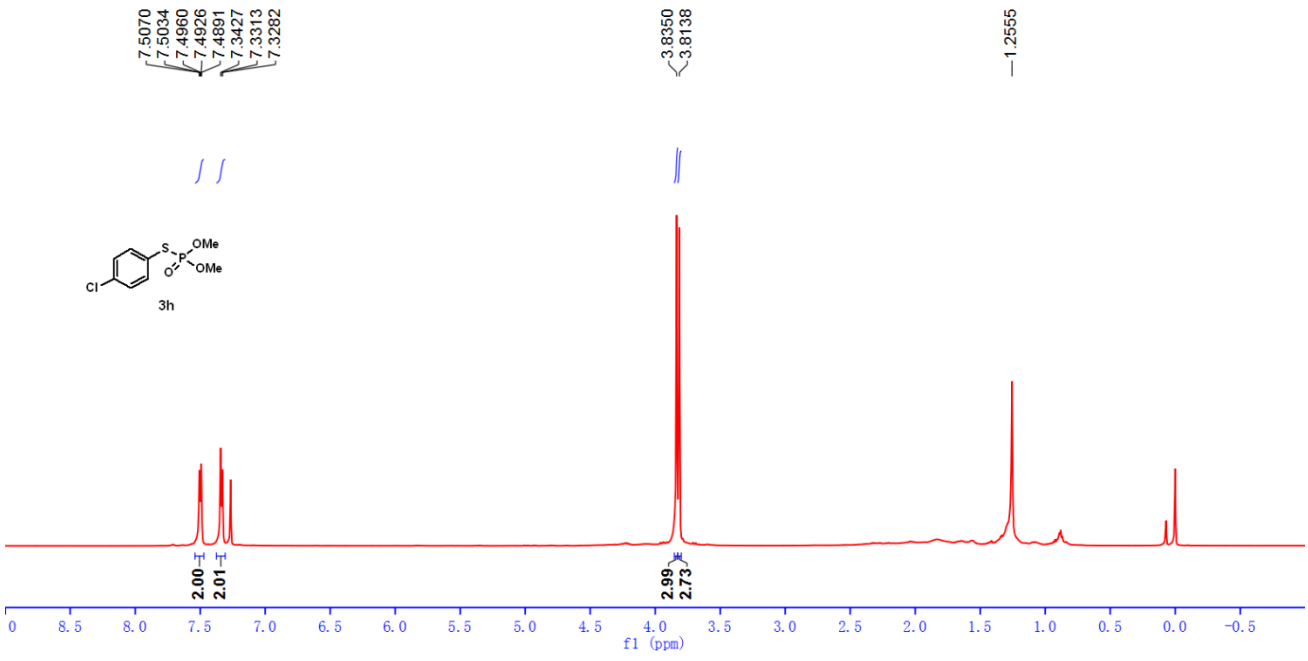
f1 (ppm)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3.8350
3.8138
1.2555
OMe
OMe
S
P
O
Cl
3h
2.00
2.01
2.99
2.73
0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
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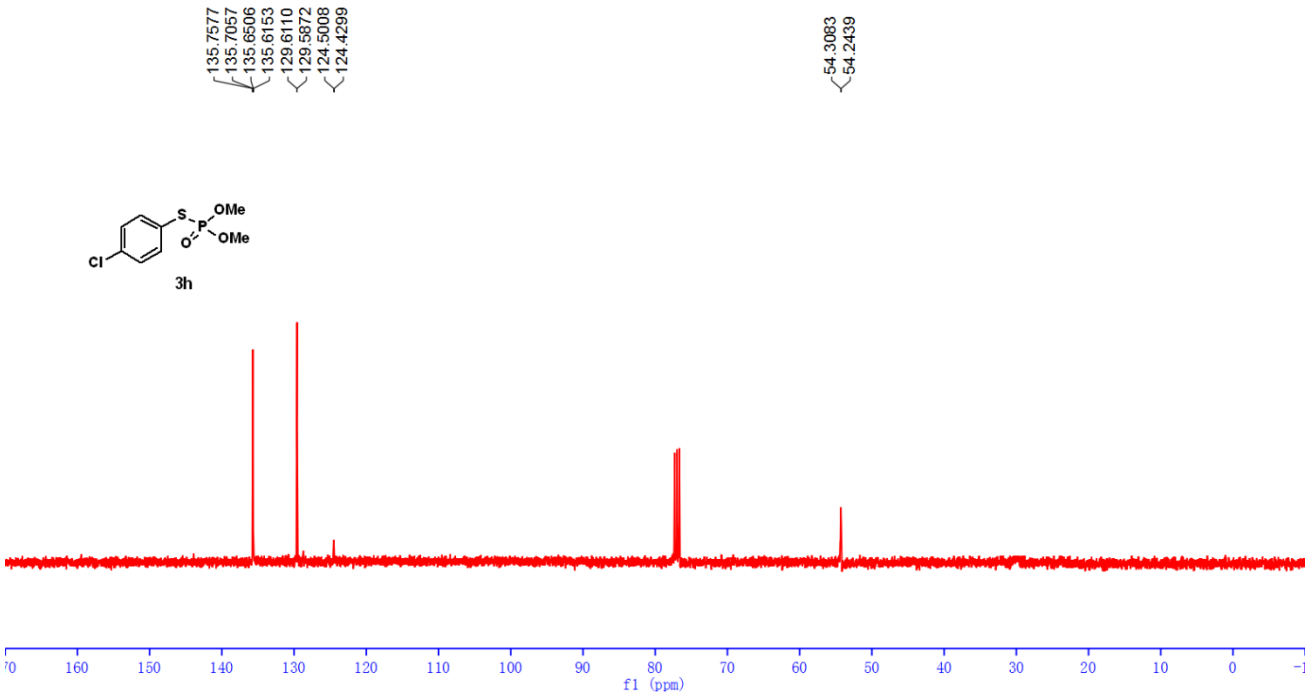
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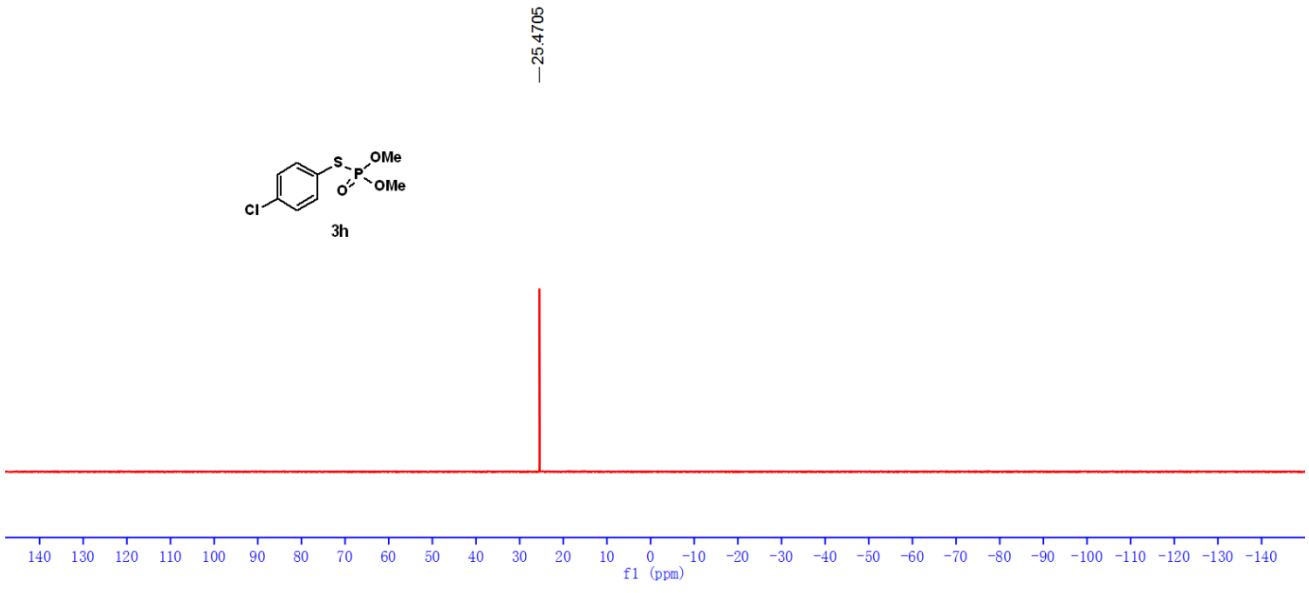
OMe
S
P
O
Cl
3h
f1 (ppm)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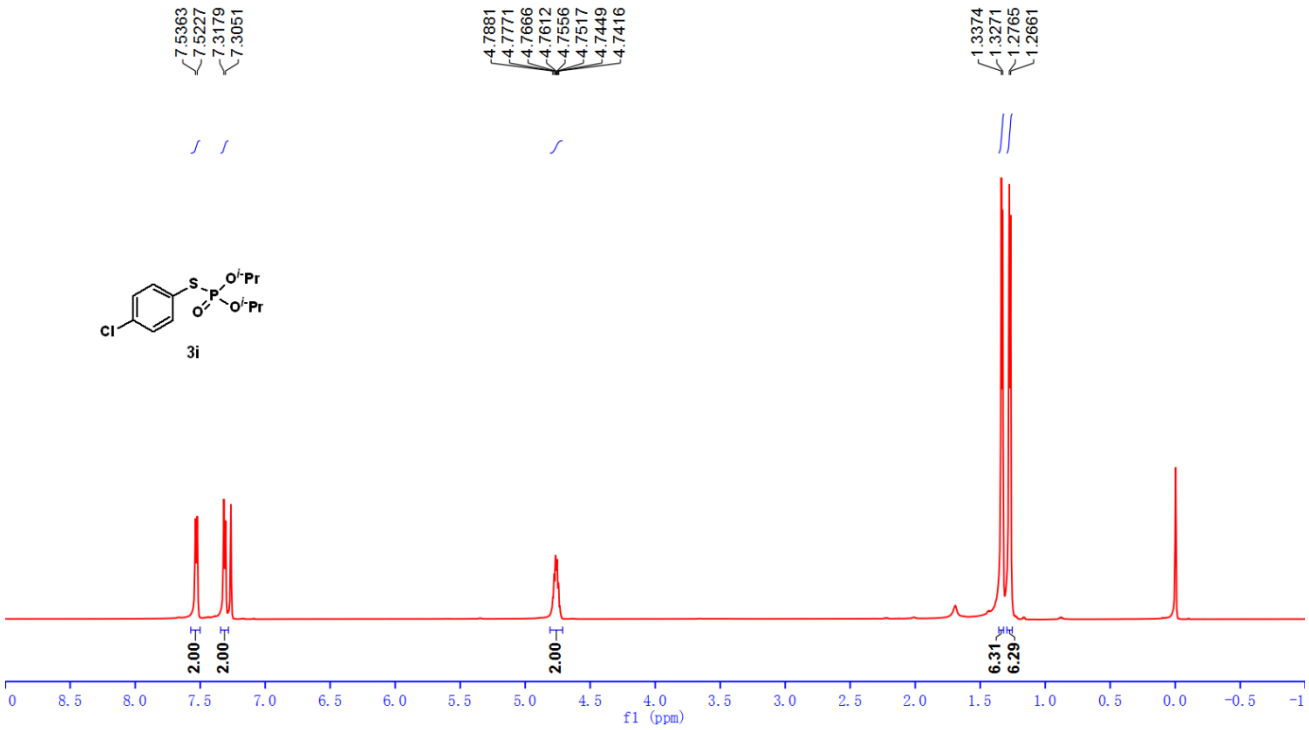
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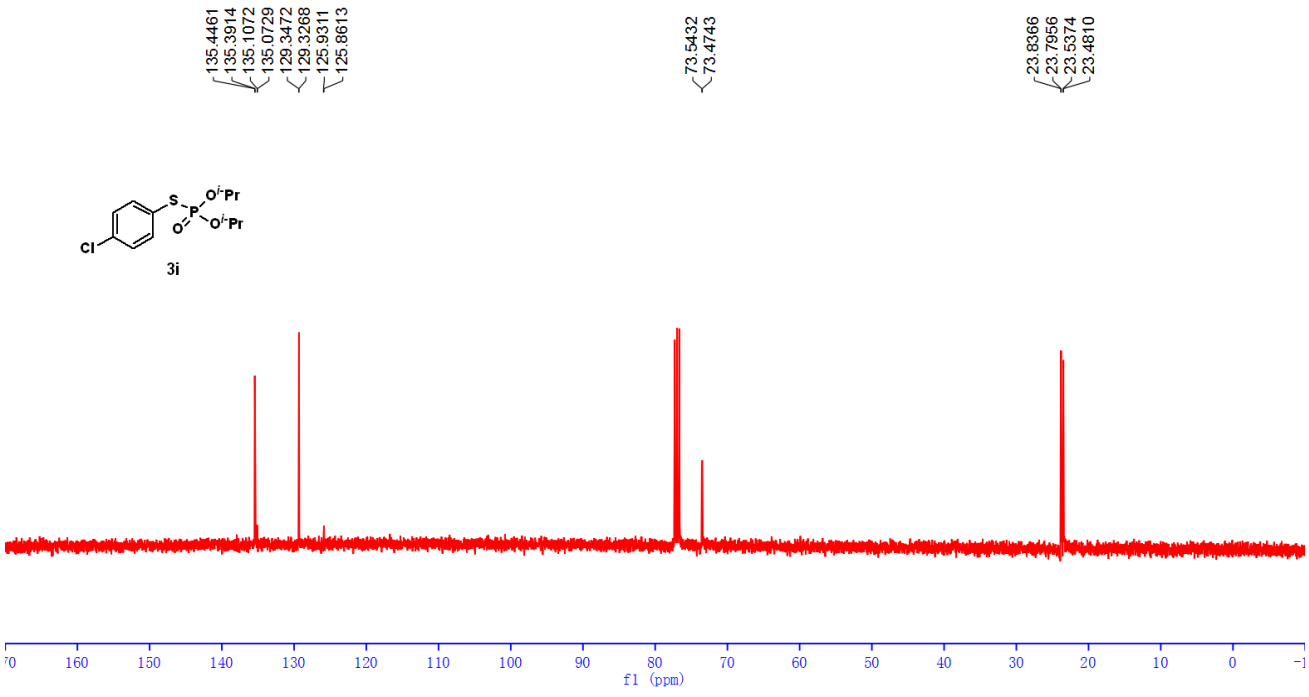
f1 (ppm)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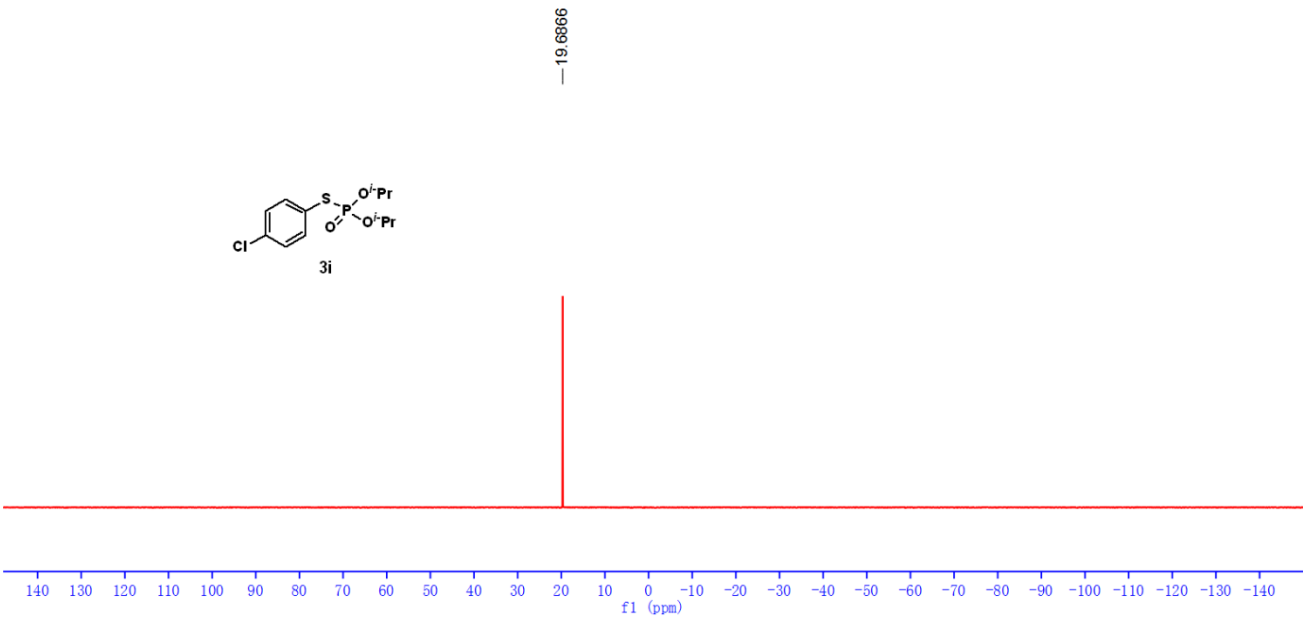
f1 (ppm)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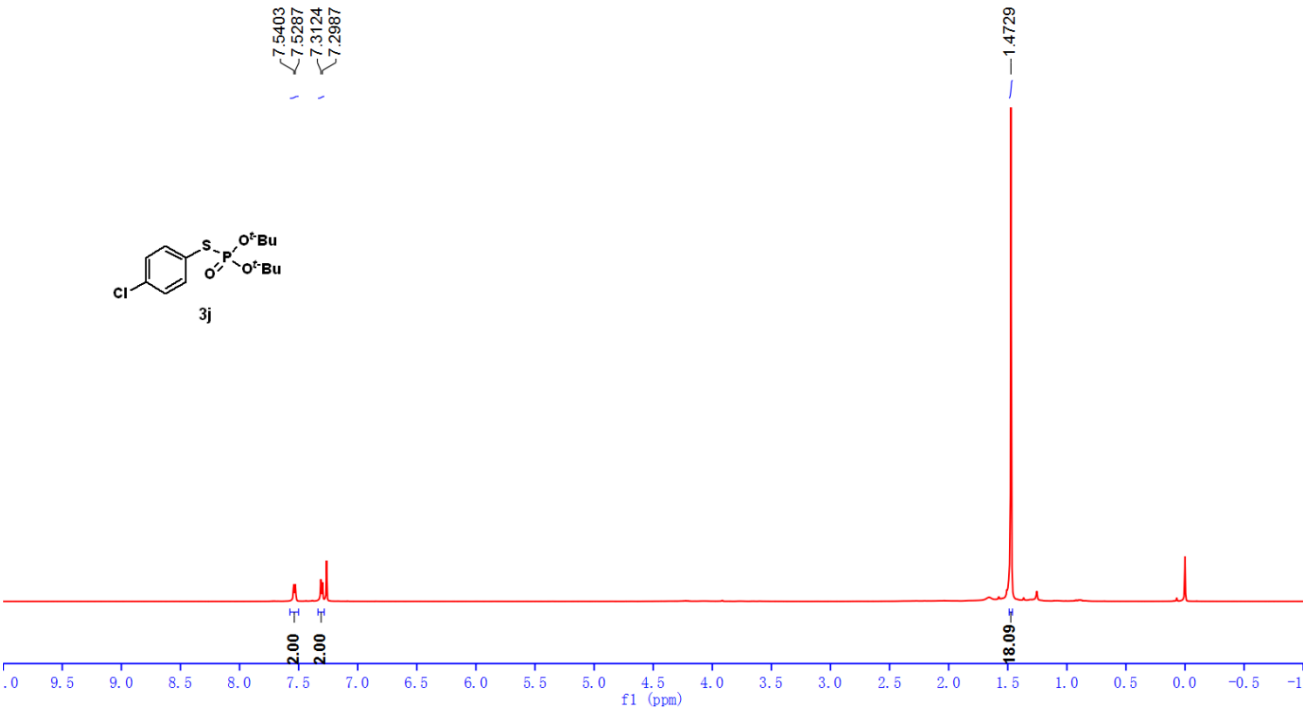
f1 (ppm)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7.3124
7.2987
1.4729
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2.00
18.09
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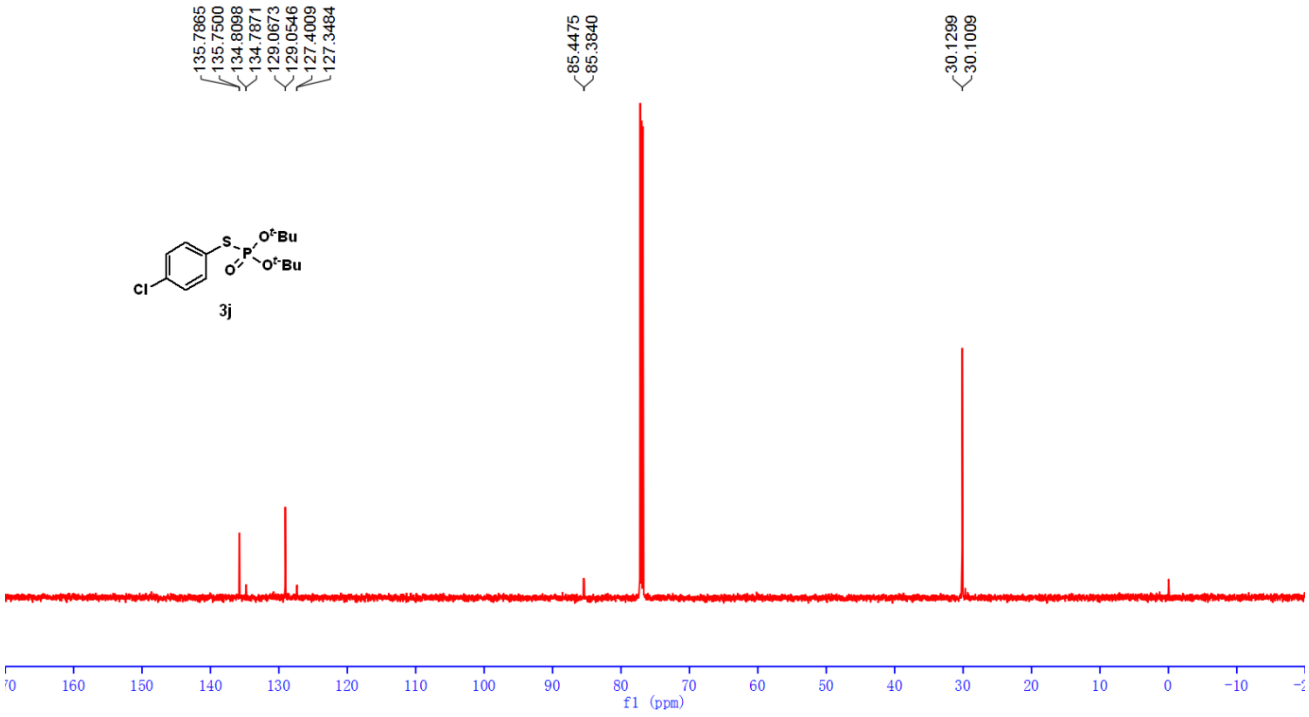
f1 (ppm)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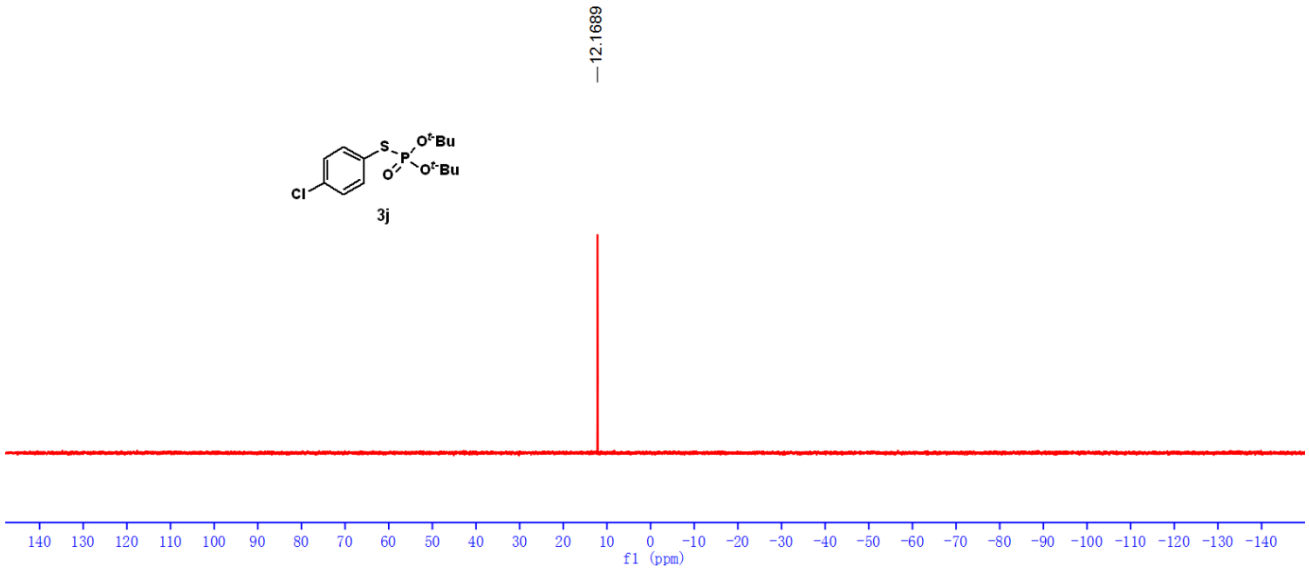
S
P
O
O
O
3j
f1 (ppm)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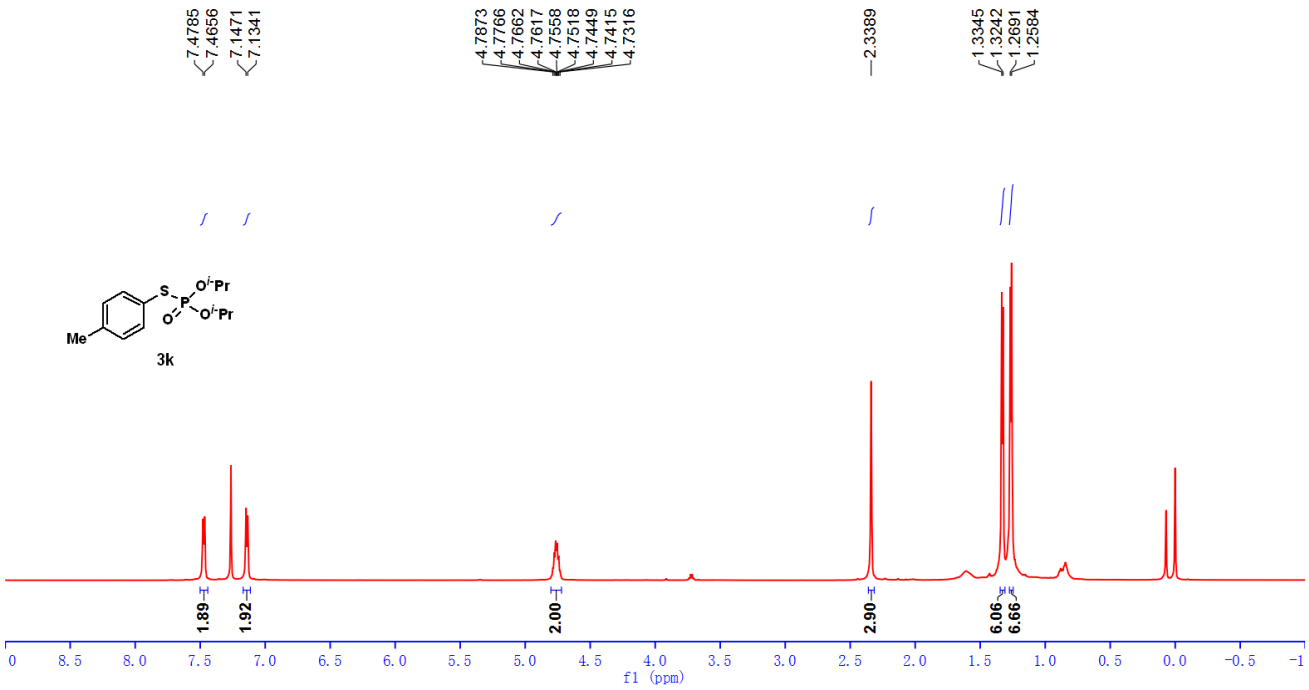
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4.7316
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1.3345
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Me
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2.90
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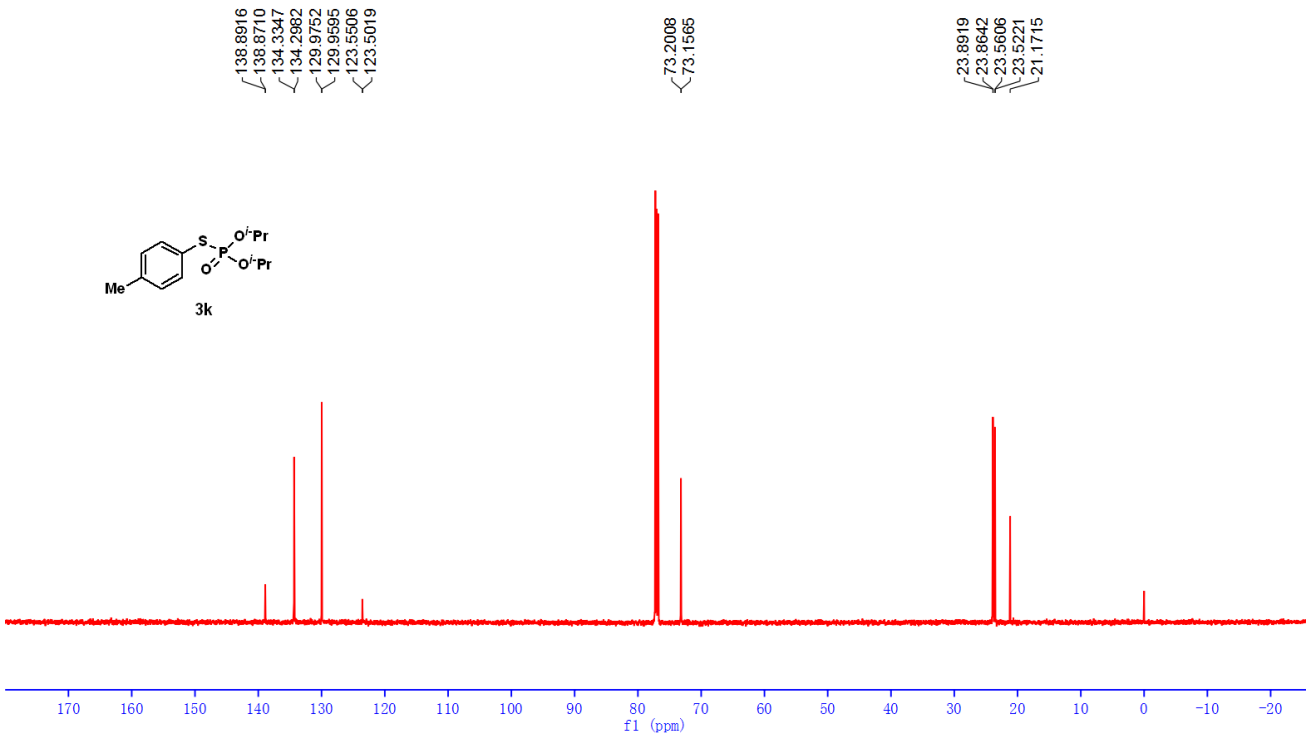
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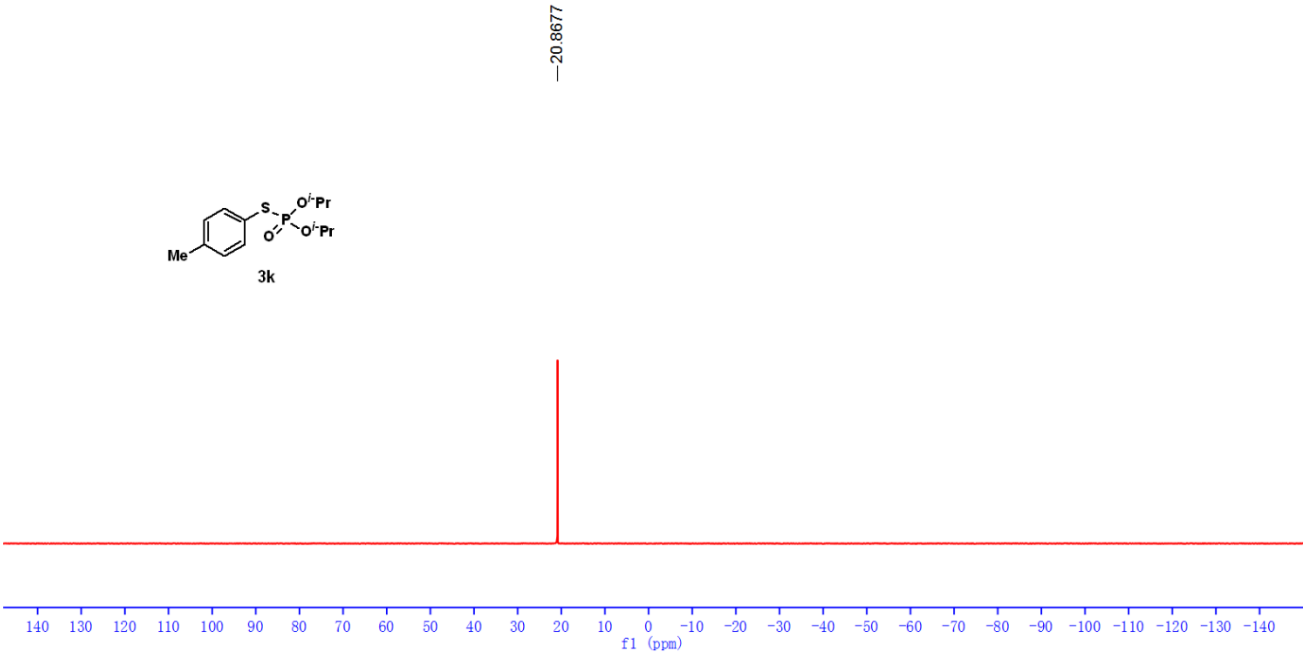
23.8642
23.5606
23.5221
21.1715
Me
3k
f1 (ppm)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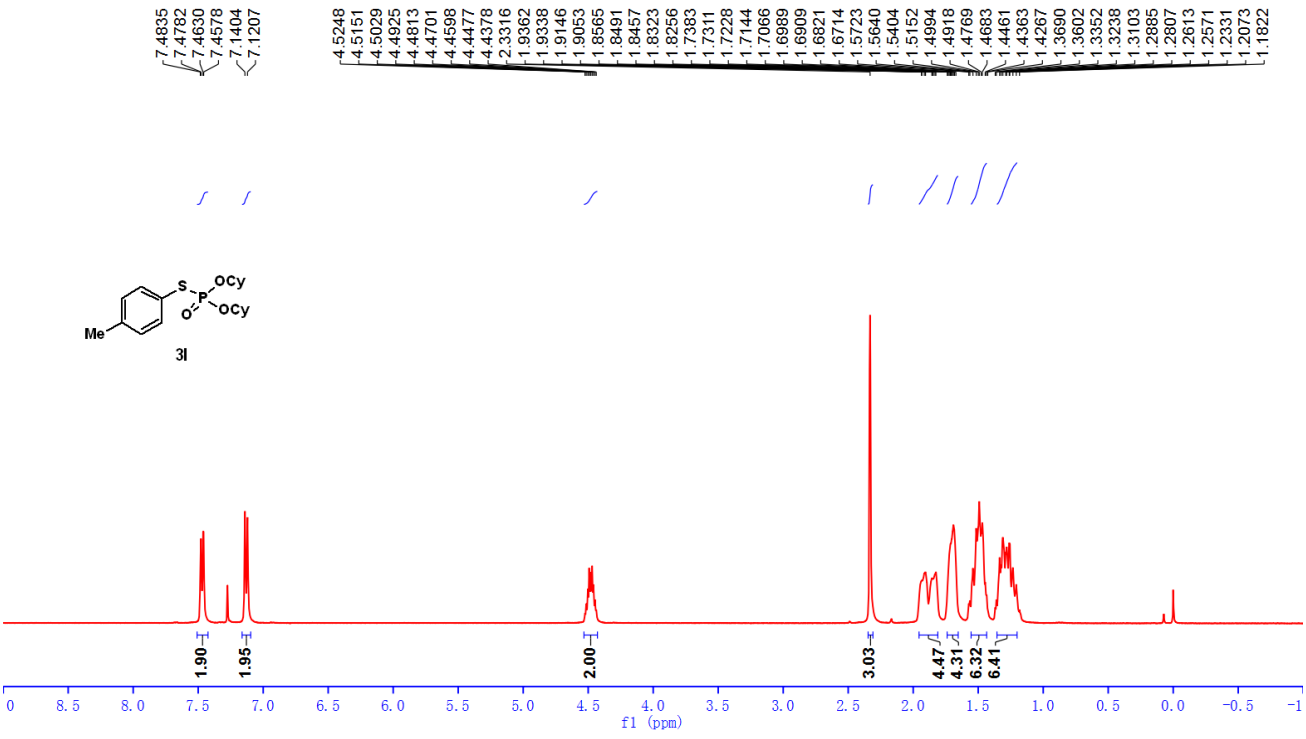
Me
S
P
O
O
O-iPr
O-iPr
3k
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
f1 (ppm)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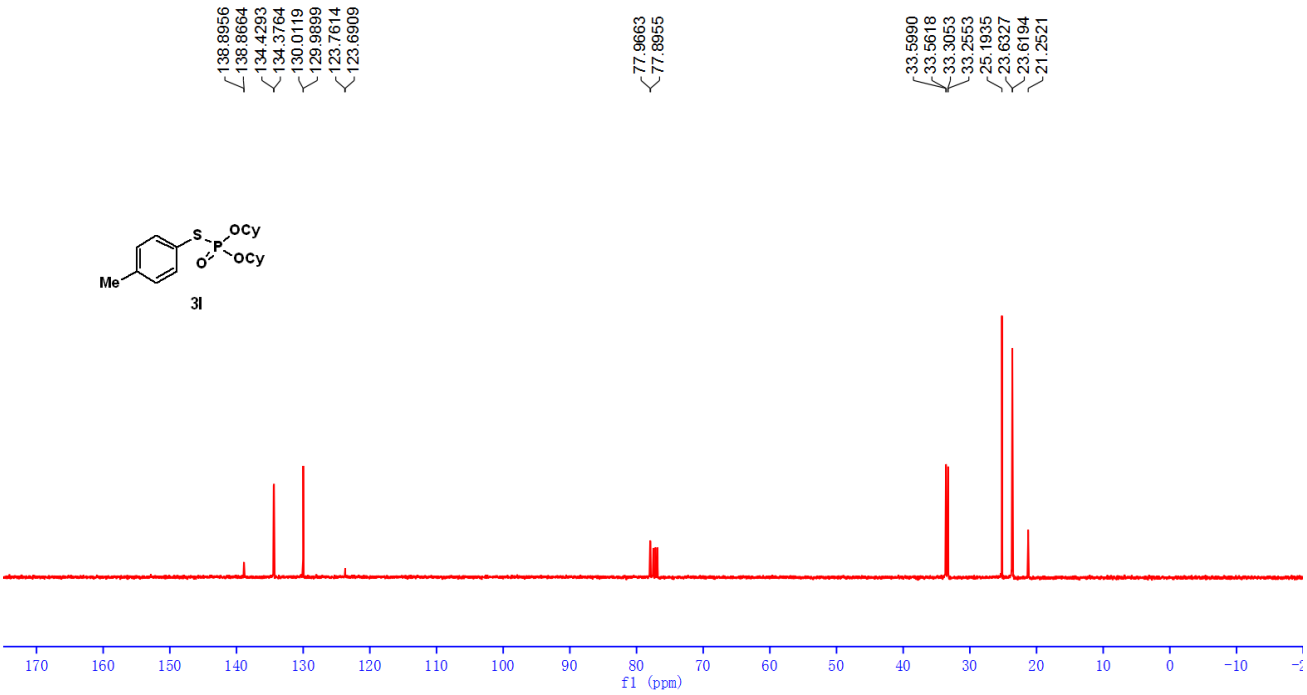
7.1404
7.1207
4.5248
4.5151
4.5029
4.4925
4.4813
4.4701
4.4598
4.4477
4.4378
2.3316
1.9362
1.9338
1.9146
1.9053
1.8565
1.8491
1.8457
1.8323
1.8256
1.7383
1.7311
1.7228
1.7144
1.7066
1.6989
1.6909
1.6821
1.6714
1.5723
1.5640
1.5404
1.5152
1.4994
1.4918
1.4769
1.4683
1.4461
1.4363
1.4267
1.3690
1.3602
1.3352
1.3238
1.3103
1.2885
1.2807
1.2613
1.2571
1.2331
1.2073
1.1822
Me
S
P
O
OCy
OCy
3l
1.90
1.95
2.00
3.03
4.47
4.31
6.32
6.41
0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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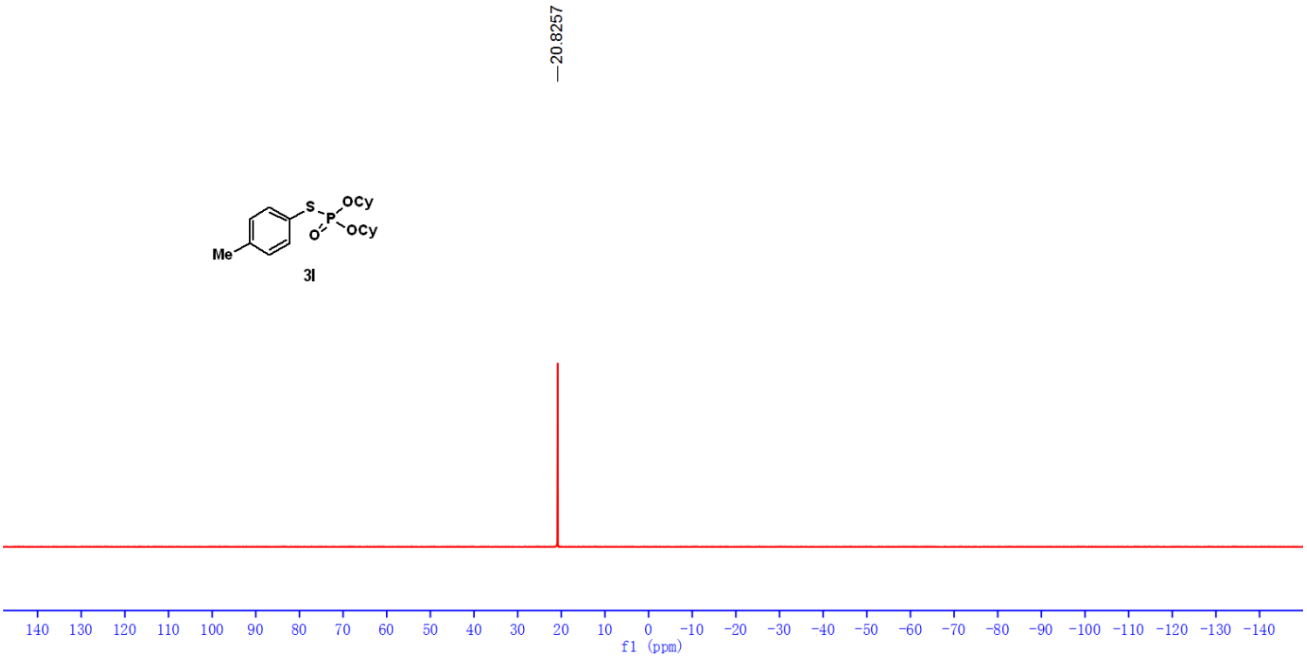
134.4293
134.3764
130.0119
129.9899
123.7614
123.6909
77.9663
77.8955
33.5990
33.5618
33.3053
33.2553
25.1935
23.6327
23.6194
21.2521
Me
3l
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


20.8257
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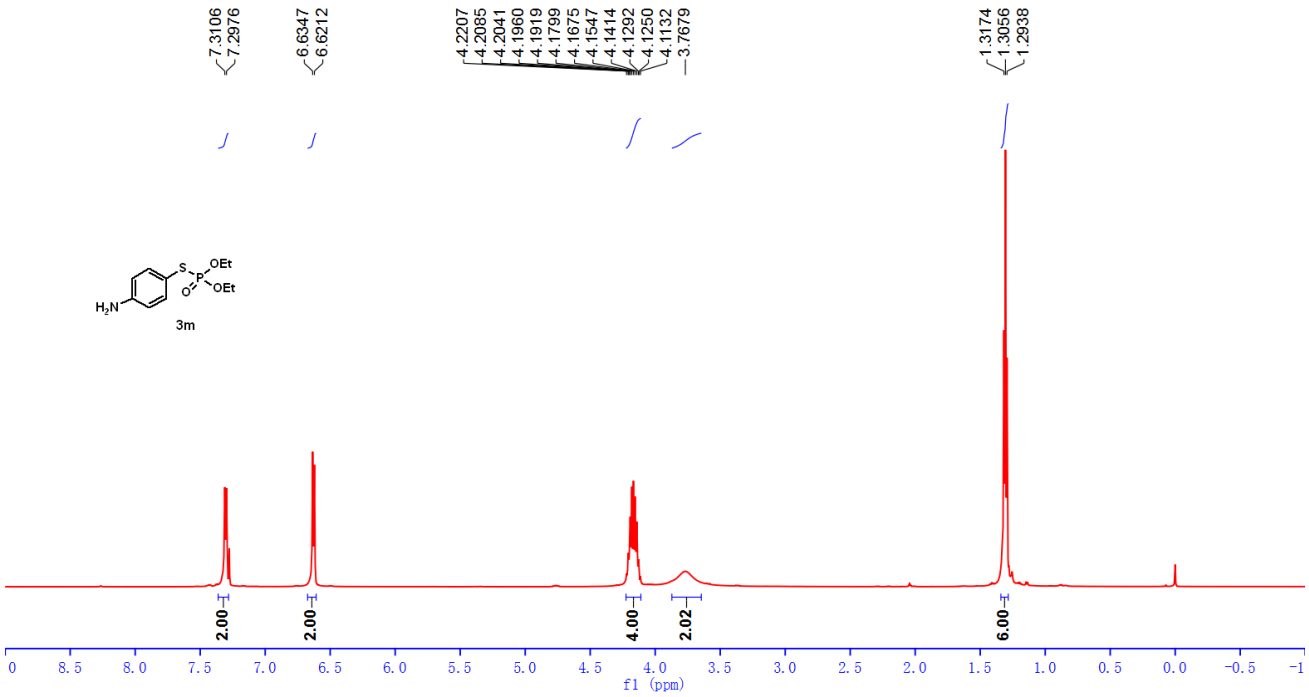
f1 (ppm)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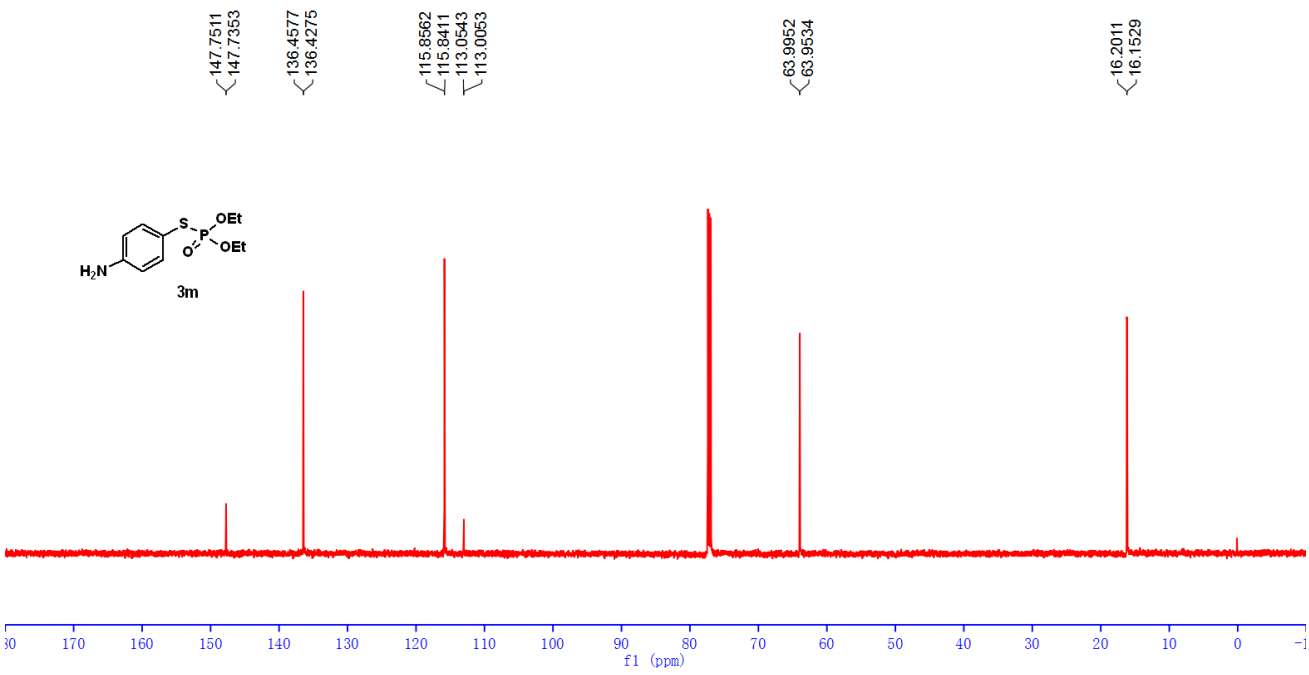
7.2976
6.6347
6.6212
4.2207
4.2085
4.2041
4.1960
4.1919
4.1799
4.1675
4.1547
4.1414
4.1292
4.1250
4.1132
3.7679
1.3174
1.3056
1.2938
3m
2.00
2.00
4.00
2.02
6.00
f1 (ppm)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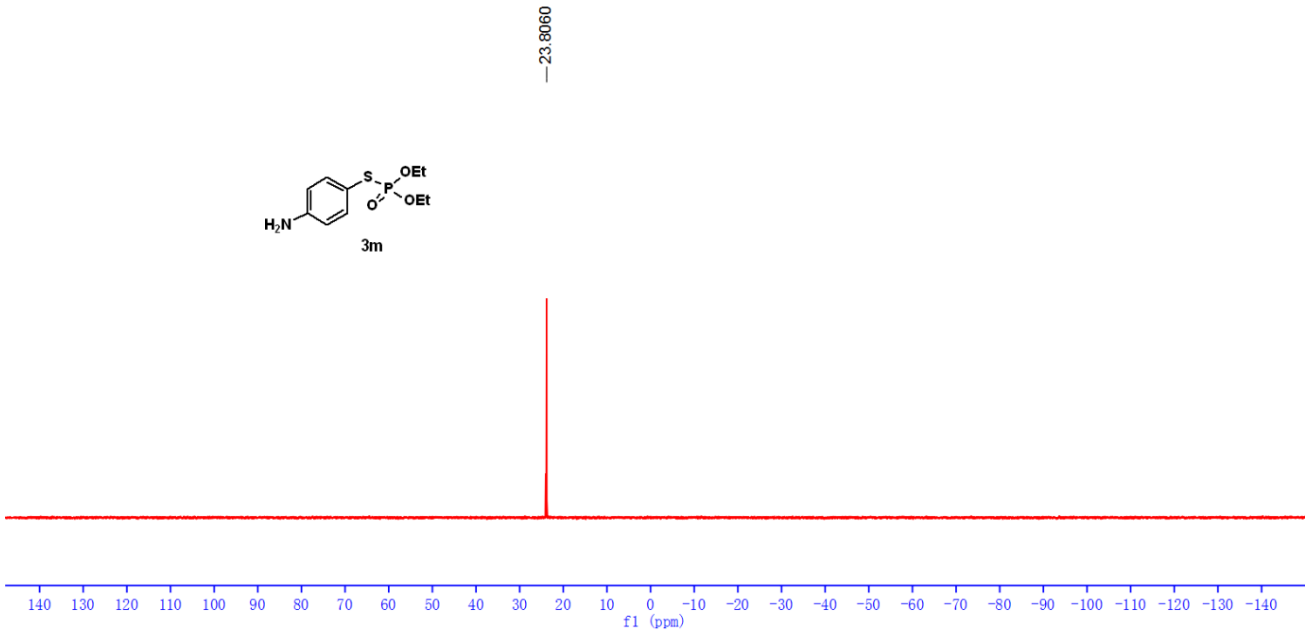
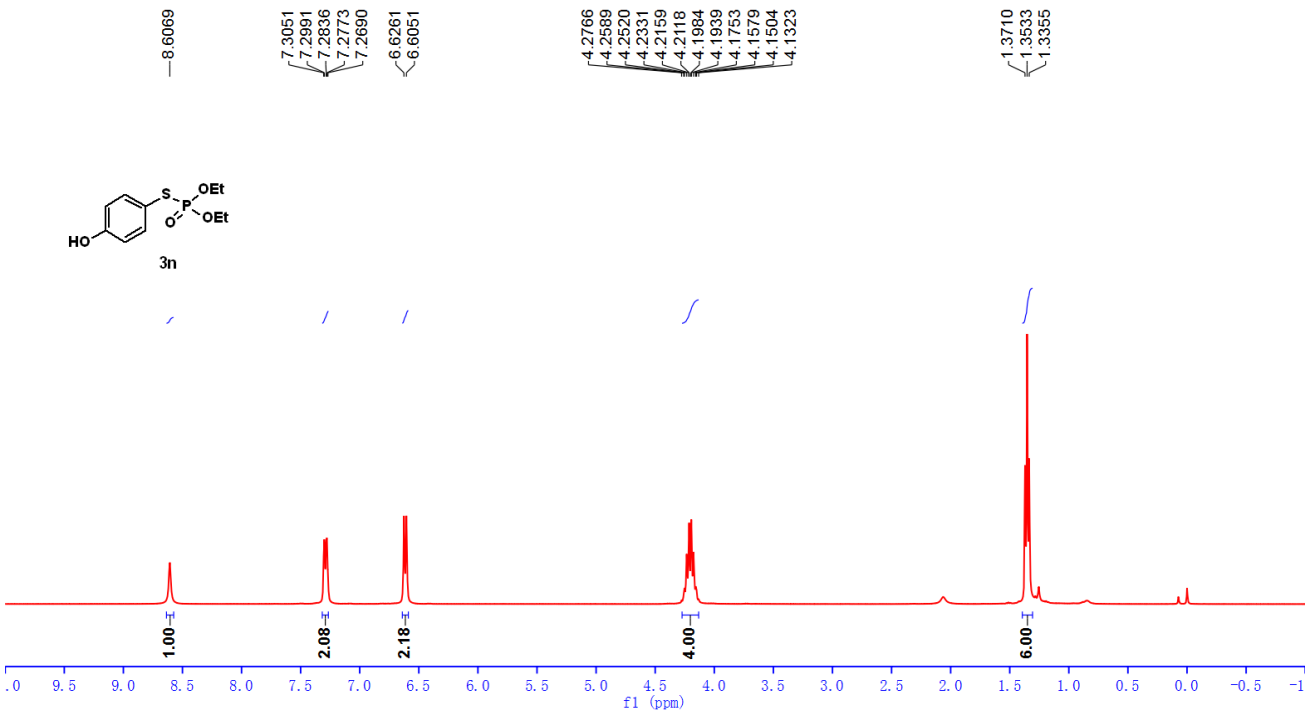
147.7353
136.4577
136.4275
115.8562
115.8411
113.0543
113.0053
63.9952
63.9534
16.2011
16.1529
3m
f1 (ppm)


23.8060
OEt
OEt
S
P
O
H2N
3m
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
f1 (ppm)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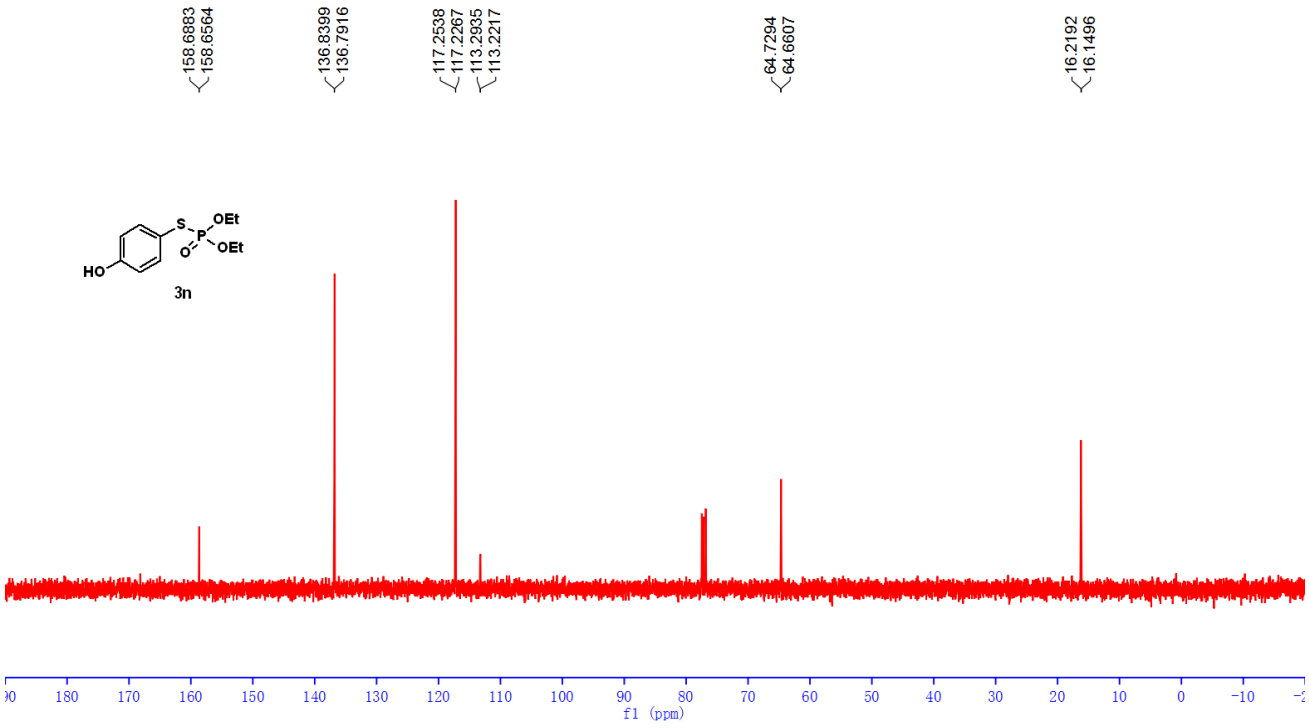
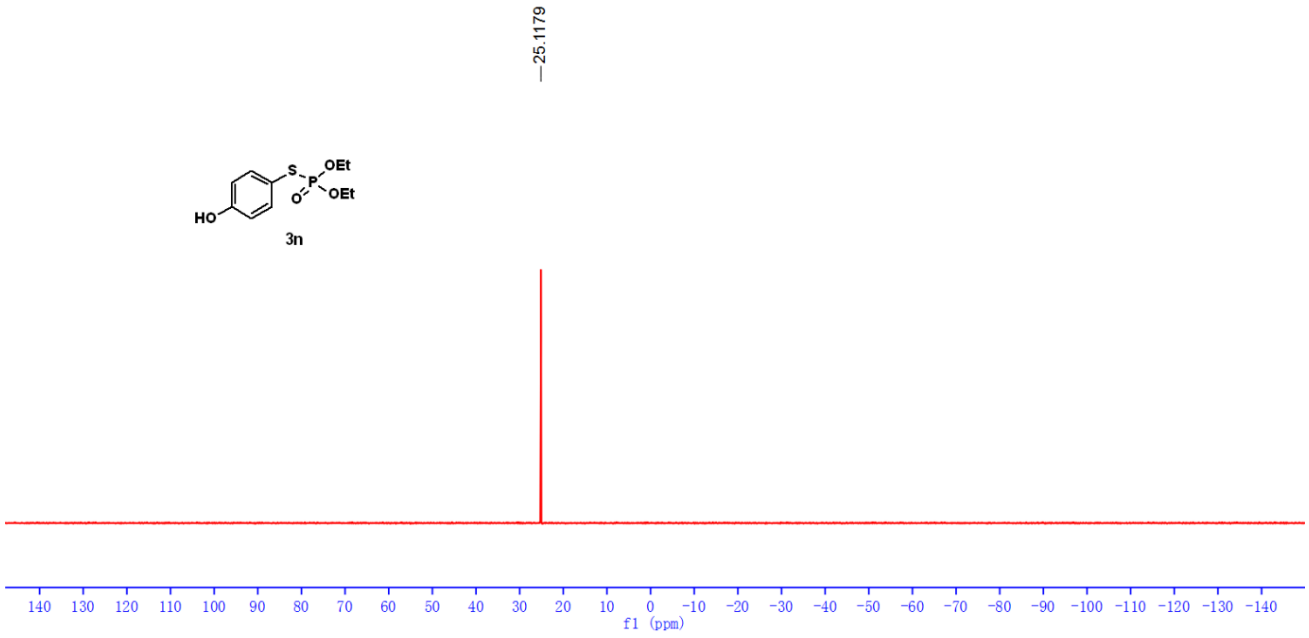
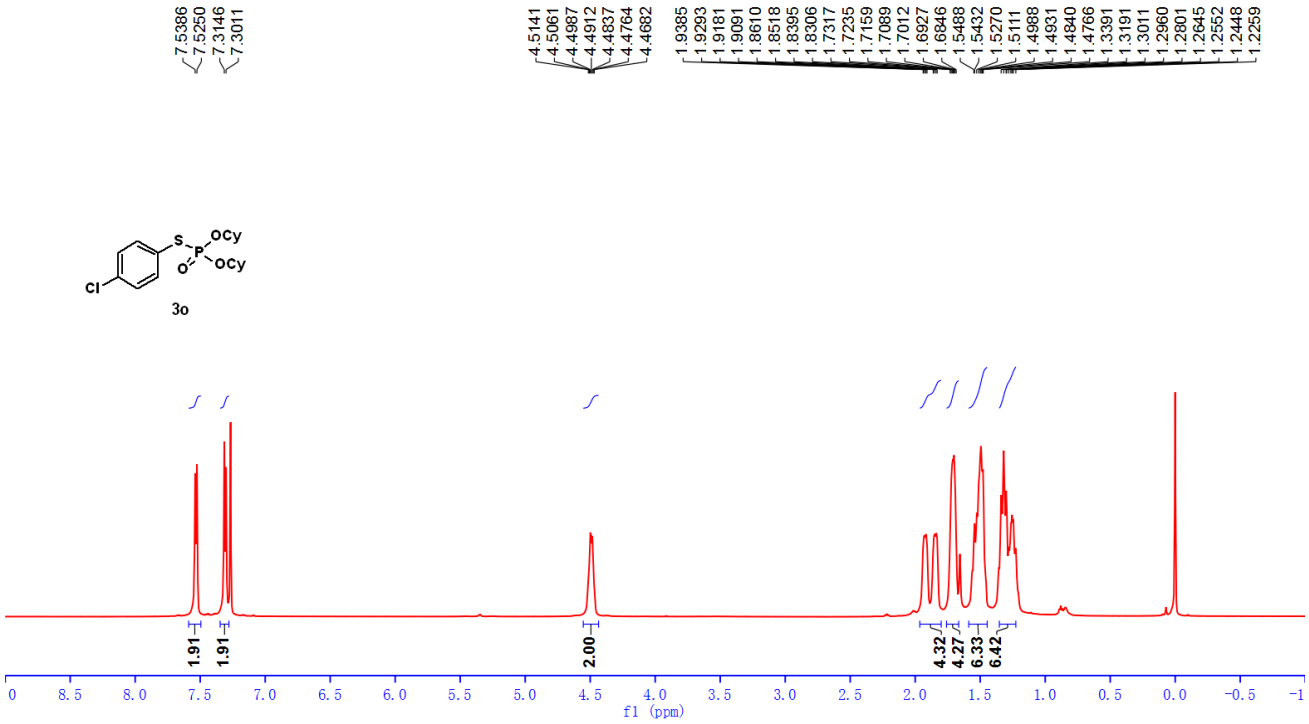
7.3051
7.2991
7.2836
7.2773
7.2690
6.6261
6.6051
4.2766
4.2589
4.2520
4.2331
4.2159
4.2118
4.1984
4.1939
4.1753
4.1579
4.1504
4.1323
1.3710
1.3533
1.3355
OEt
OEt
S
P
O
HO
3n
1.00
2.08
2.18
4.00
6.00
f1 (ppm)


158.6883
158.6564
136.8399
136.7916
117.2538
117.2267
113.2935
113.2217
64.7294
64.6607
16.2192
16.1496
OEt
OEt
HO
3n
f1 (ppm)


25.1179
OEt
OEt
HO
3n
f1 (ppm)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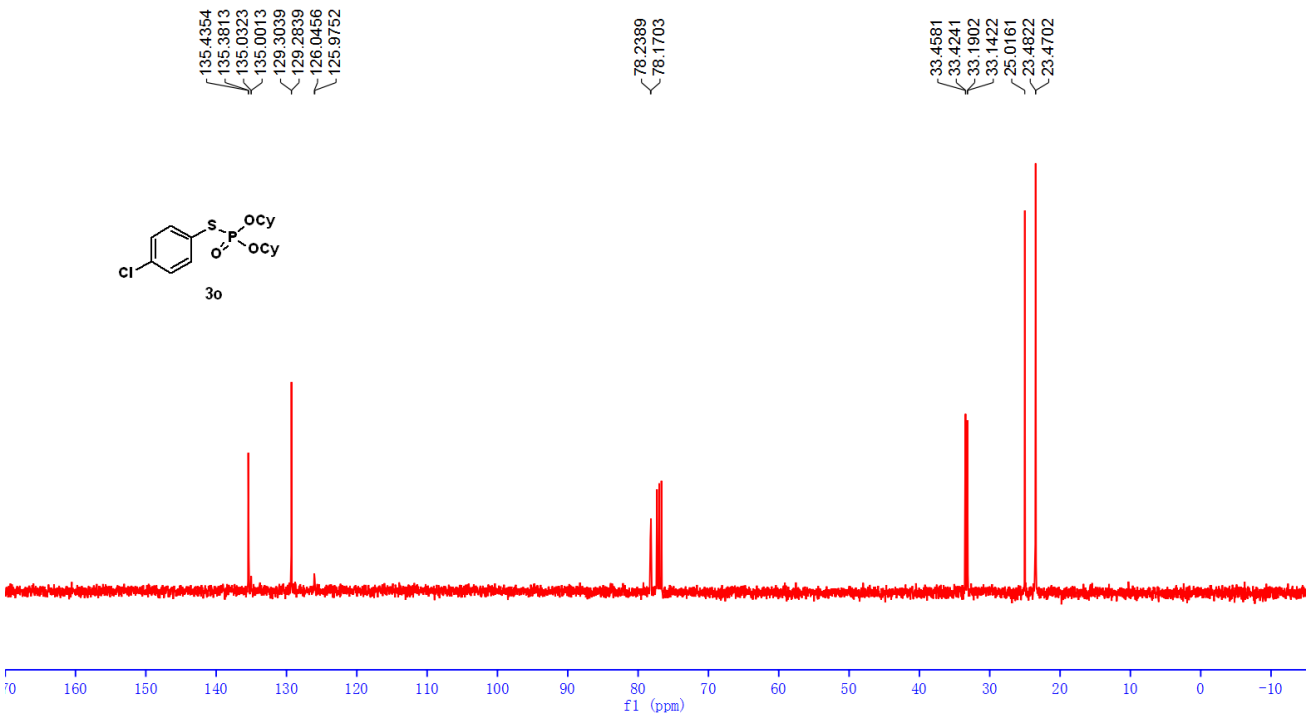
7.5250
7.3146
7.3011
4.5141
4.5061
4.4987
4.4912
4.4837
4.4764
4.4682
1.9385
1.9293
1.9181
1.9091
1.8610
1.8518
1.8395
1.8306
1.7317
1.7235
1.7159
1.7069
1.7012
1.6927
1.6846
1.5488
1.5432
1.5270
1.5111
1.4988
1.4931
1.4840
1.4766
1.3391
1.3191
1.3011
1.2960
1.2801
1.2645
1.2552
1.2448
1.2259
S
P
O
OCy
OCy
Cl
3o
1.91
1.91
2.00
4.32
4.27
6.33
6.42
f1 (ppm)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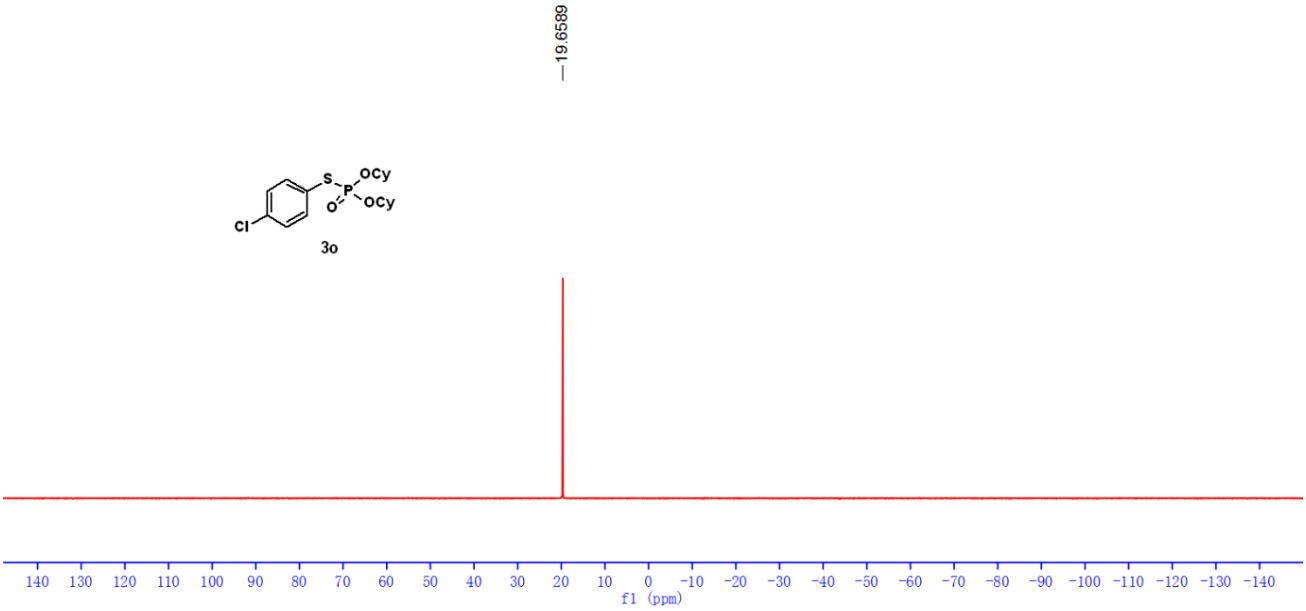
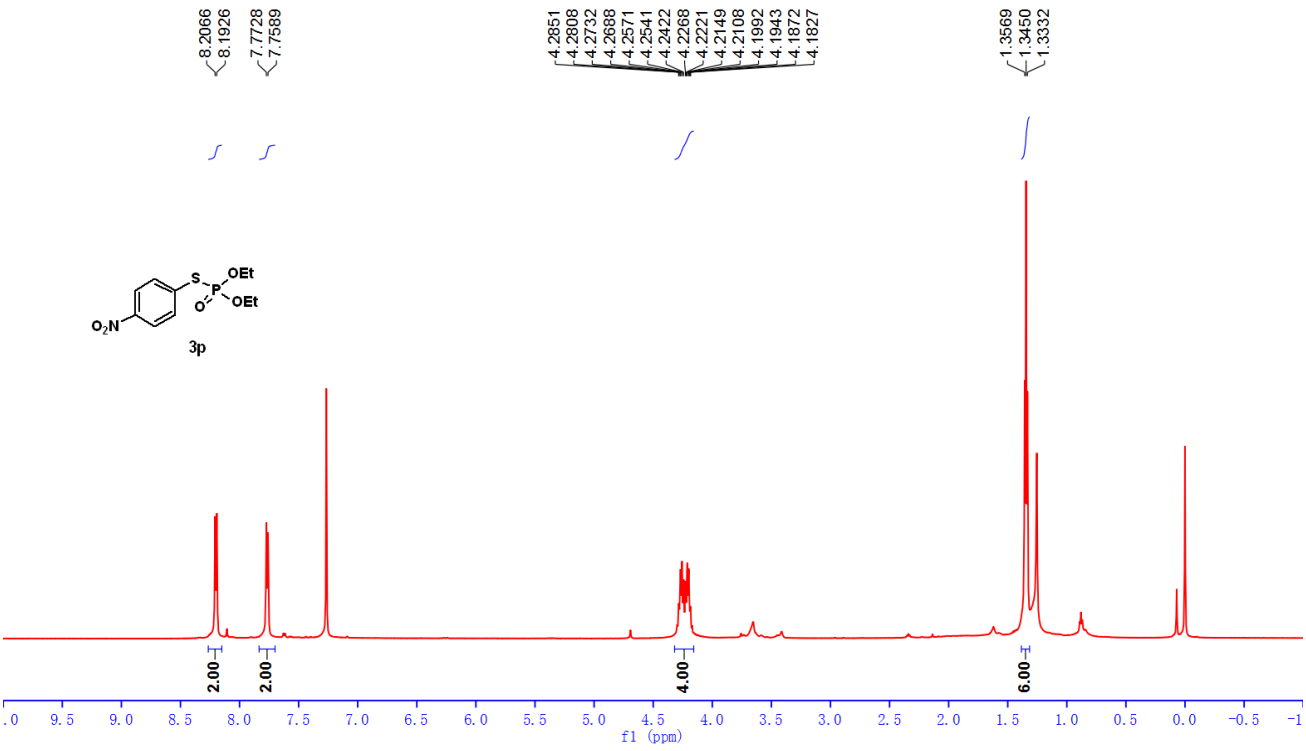
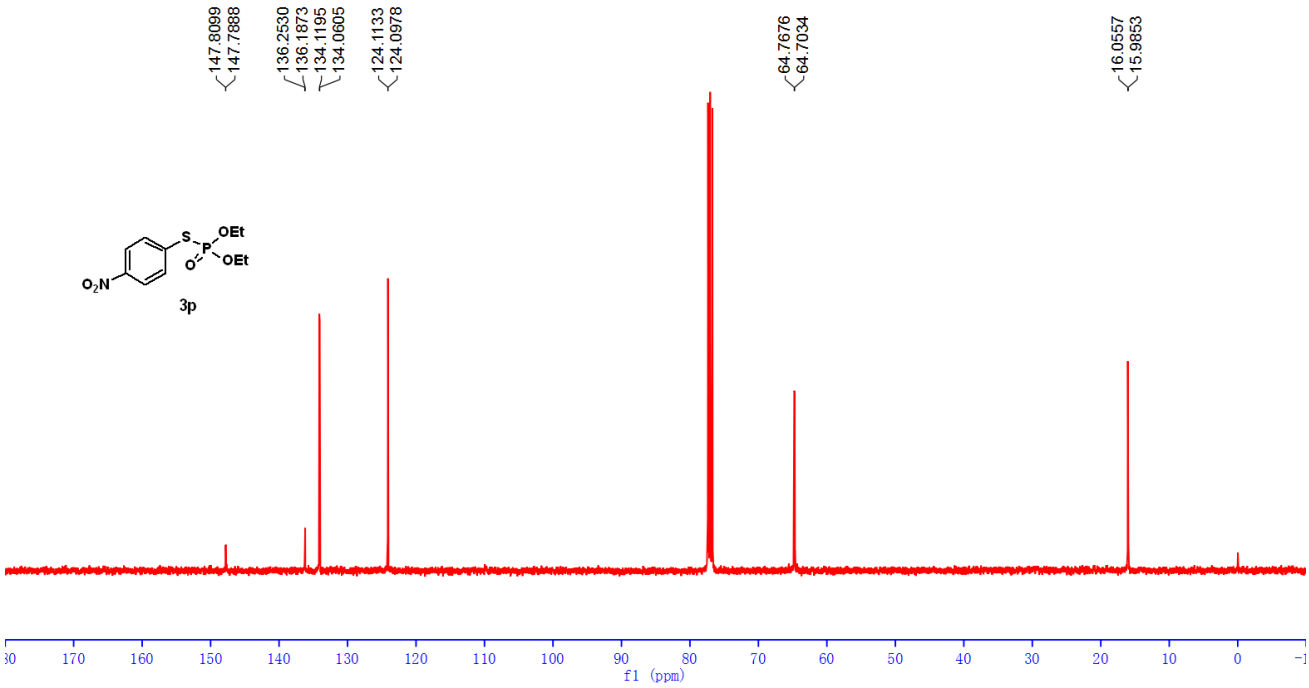
135.3813
135.0323
135.0013
129.3039
129.2839
126.0456
125.9752
78.2389
78.1703
33.4581
33.4241
33.1902
33.1422
25.0161
23.4822
23.4702
S
P
O
OCy
OCy
Cl
3o
f1 (ppm)


19.6589
OCy
OCy
S
P
O
Cl
3o
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
f1 (ppm)


8.2066
8.1926
7.7728
7.7589
4.2851
4.2808
4.2732
4.2688
4.2571
4.2541
4.2422
4.2268
4.2221
4.2149
4.2108
4.1992
4.1943
4.1872
4.1827
1.3569
1.3450
1.3332
OEt
OEt
S
P
O
O2N
3p
2.00
2.00
4.00
6.00
f1 (ppm)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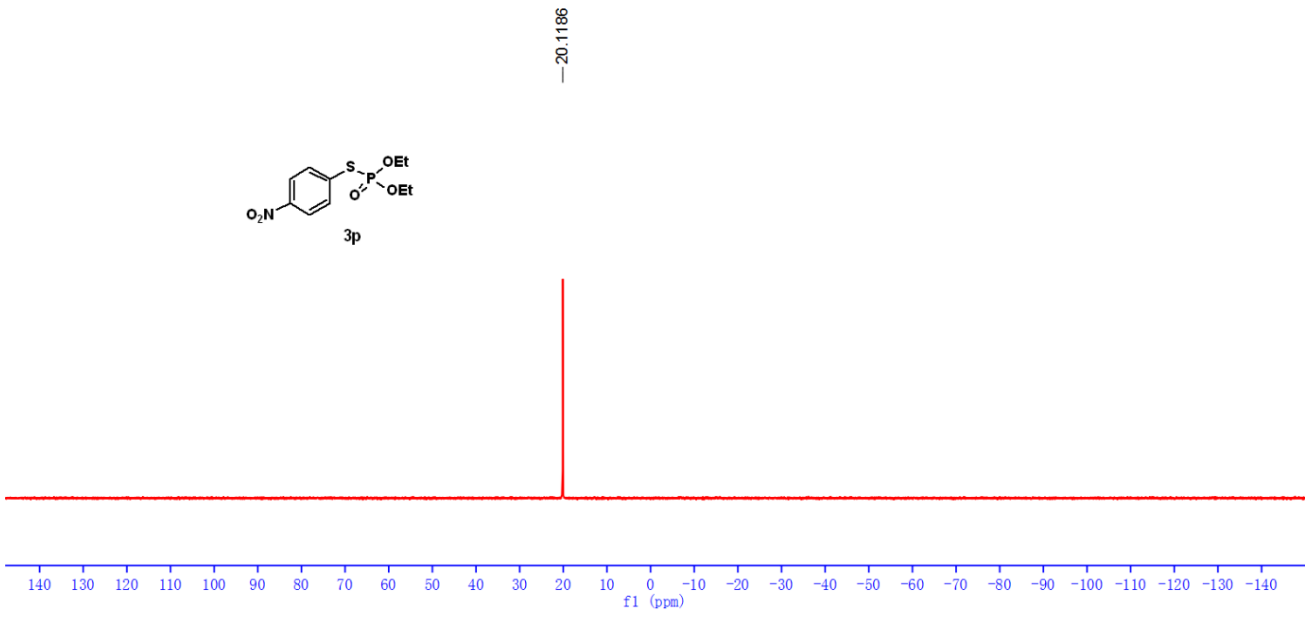
147.7888
136.2530
136.1873
134.1195
134.0605
124.1133
124.0978
64.7676
64.7034
16.0557
15.9853
OEt
OEt
S
P
O
O2N
3p
f1 (ppm)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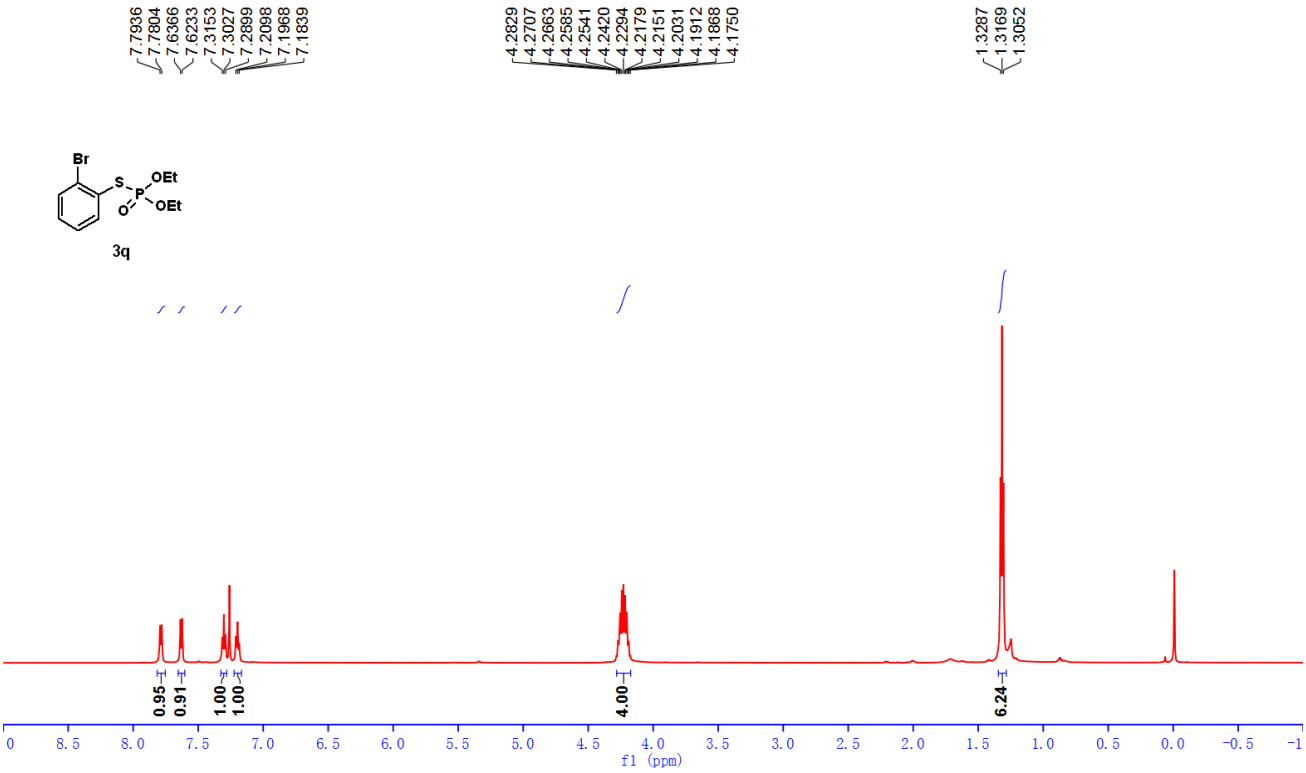
OEt
OEt
S
P
O
O2N
3p
f1 (ppm)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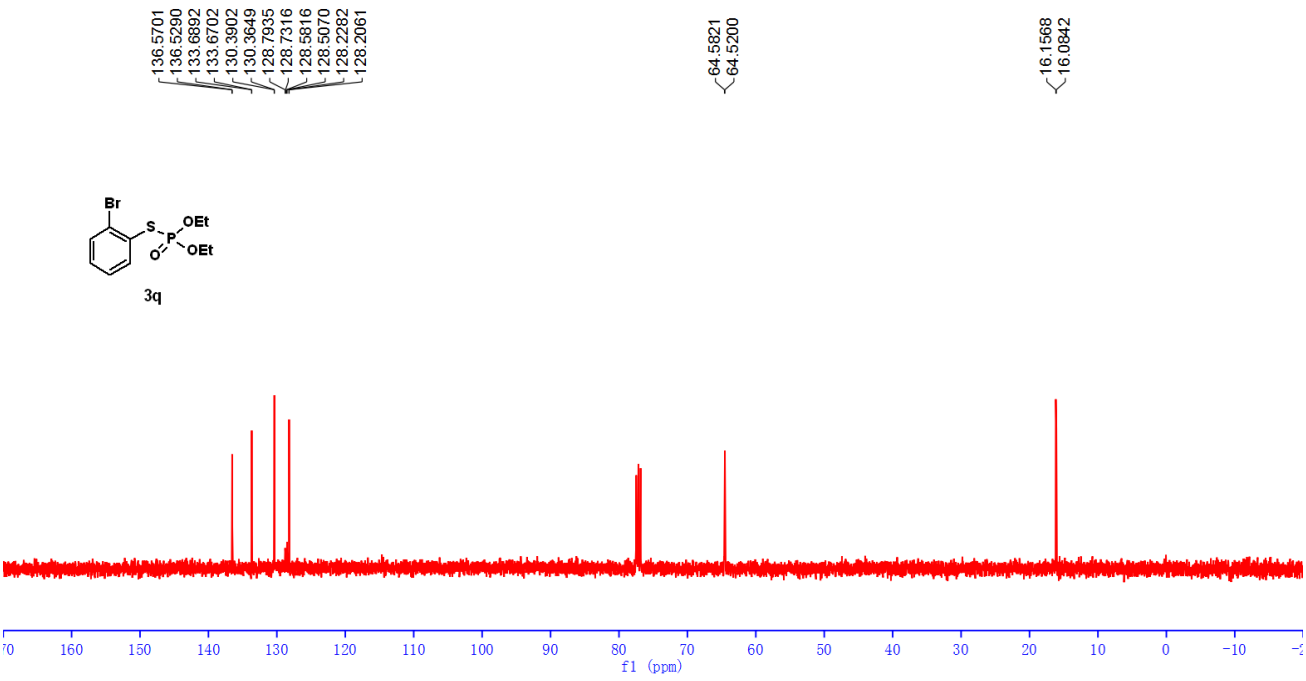
7.7804
7.6366
7.6233
7.3153
7.3027
7.2899
7.2098
7.1968
7.1839
4.2829
4.2707
4.2663
4.2585
4.2541
4.2420
4.2294
4.2179
4.2151
4.2031
4.1912
4.1868
4.1750
1.3287
1.3169
1.3052
Br
S
P
OEt
OEt
O
3q
0.95
0.91
1.00
1.00
4.00
6.24
f1 (ppm)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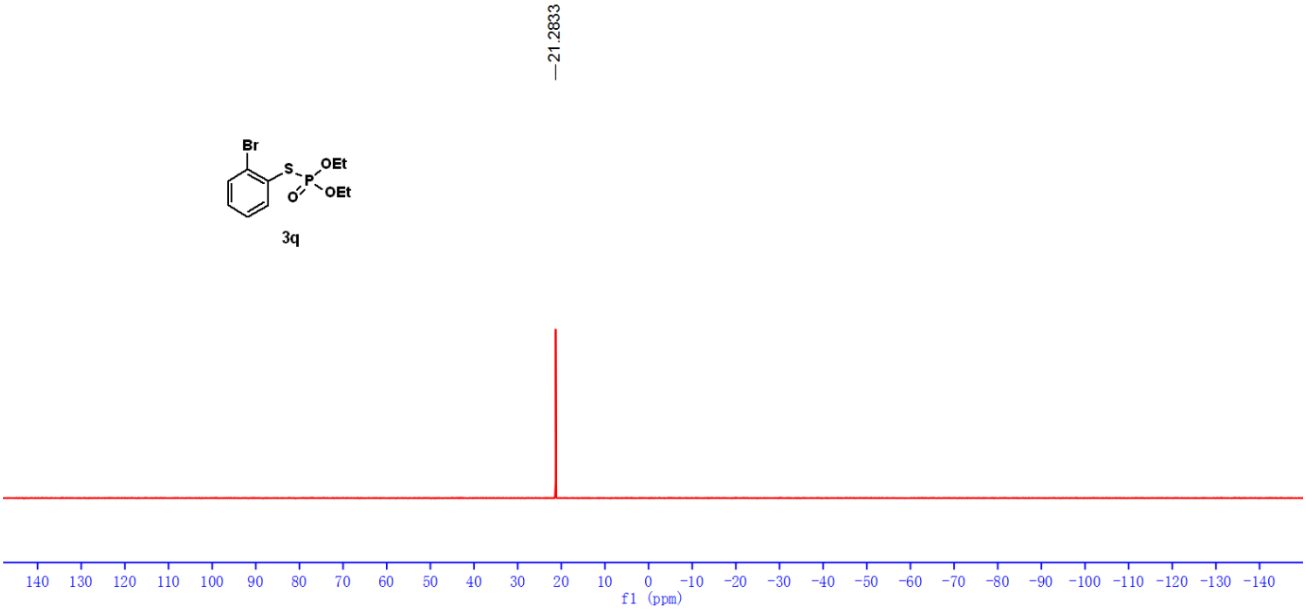
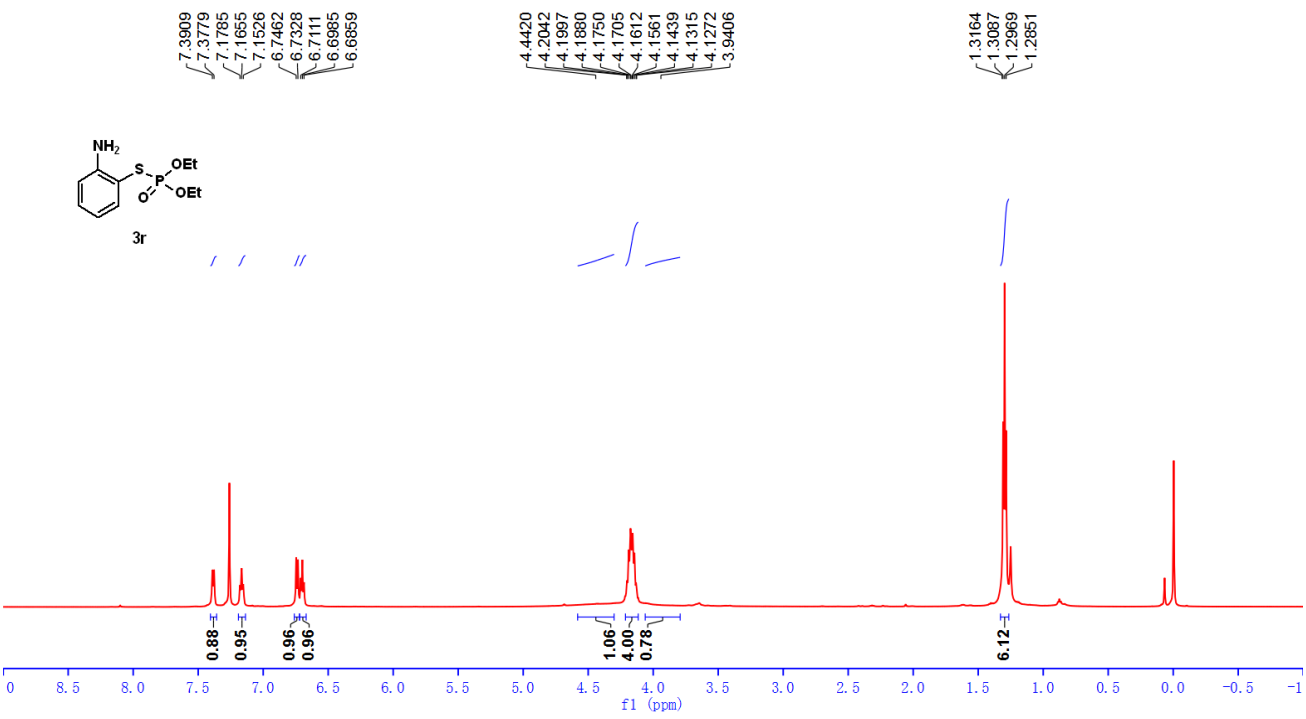
128.7935
128.7316
128.5816
128.5070
128.2282
128.2061
64.5821
64.5200
16.1568
16.0842
Br
S
P
OEt
OEt
O
3q
f1 (ppm)


21.2833
Br
S
P
OEt
OEt
O
3q
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
f1 (ppm)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7.1526
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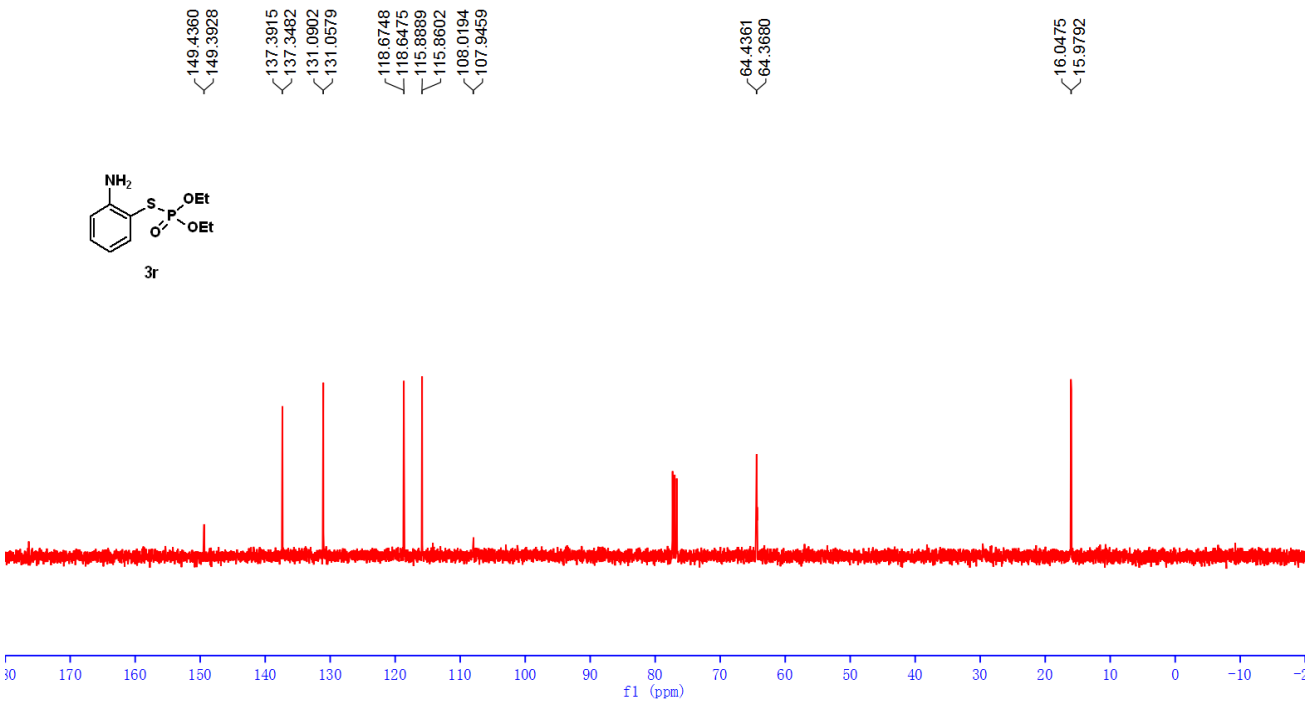
6.7328
6.7111
6.6985
6.6859
4.4420
4.2042
4.1997
4.1880
4.1750
4.1705
4.1612
4.1561
4.1439
4.1315
4.1272
3.9406
1.3164
1.3087
1.2969
1.2851
NH2
S
P
OEt
OEt
O
3r
0.88
0.95
0.96
0.96
1.06
4.00
0.78
6.12
0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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137.3482
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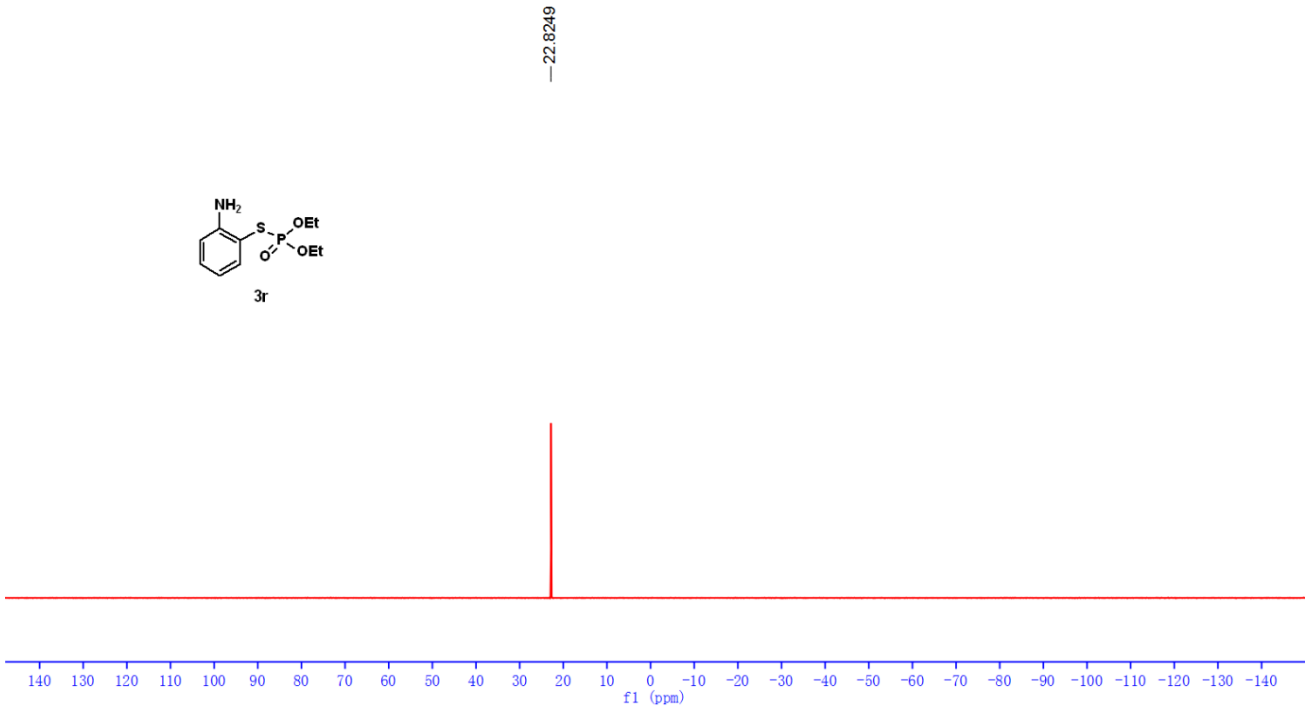
115.8889
115.8602
108.0194
107.9459
64.4361
64.3680
16.0475
15.9792
NH2
S
P
O
OEt
OEt
3r
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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OEt
3r
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120
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80
70
60
50
40
30
20
10
0
-10
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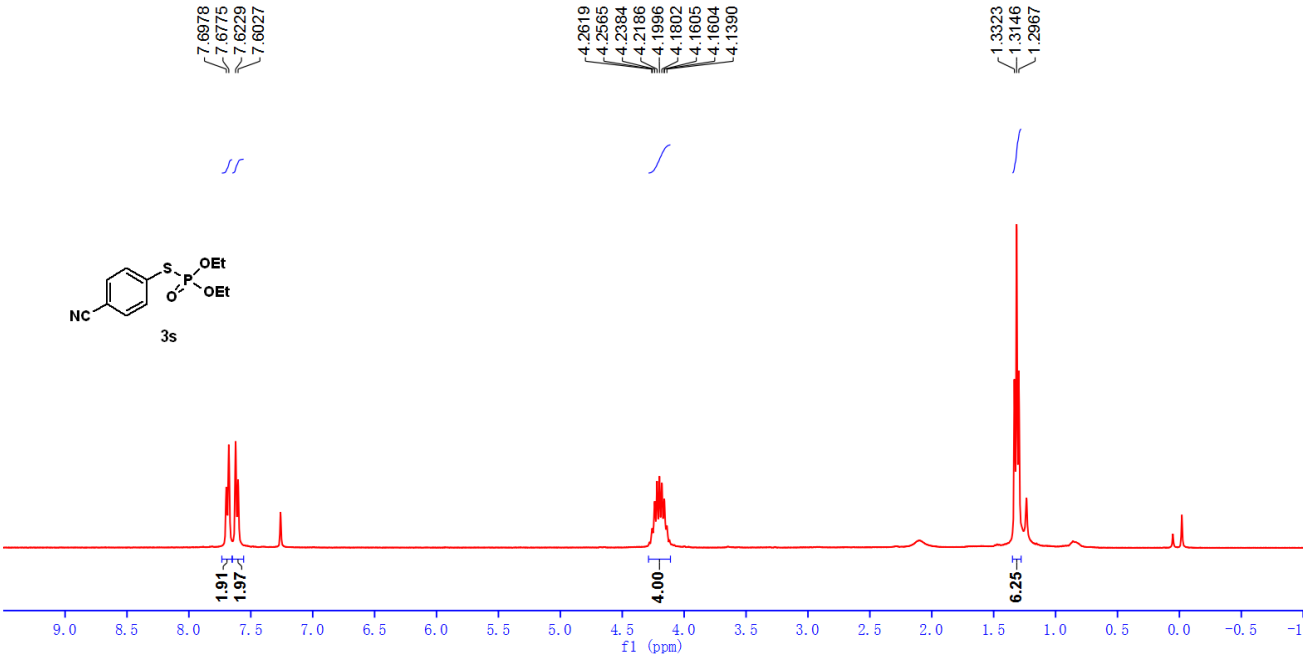
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
f1 (ppm)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7.6027
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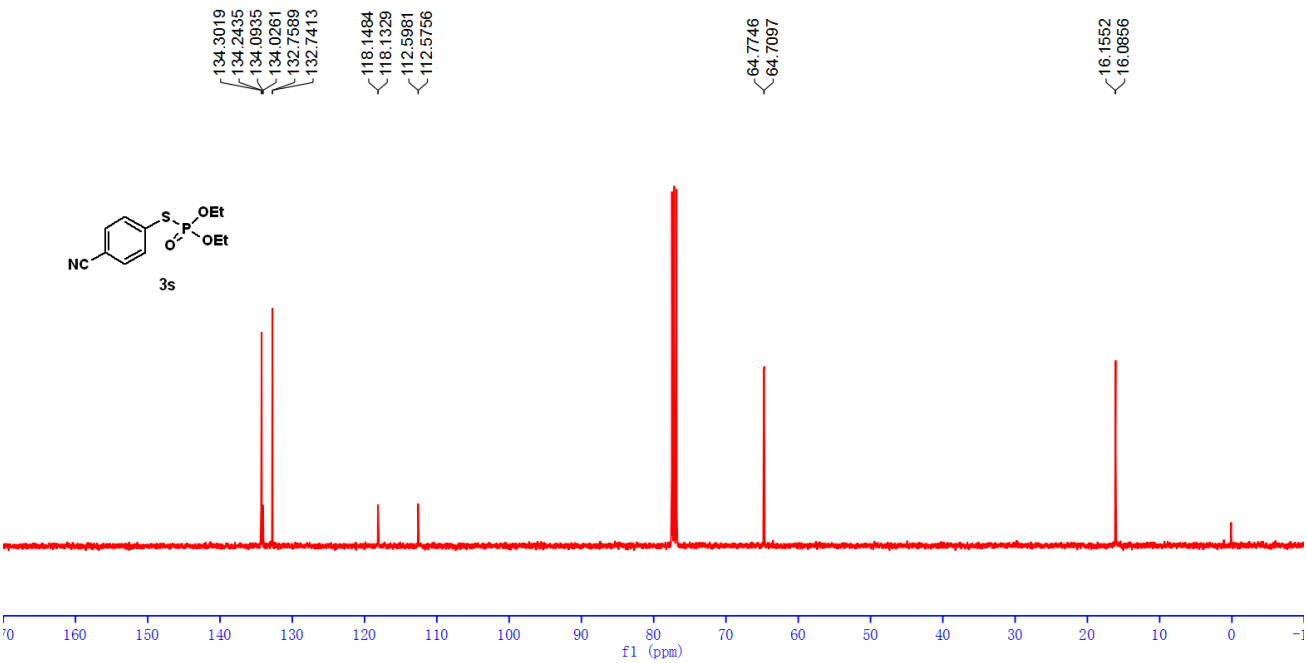
4.2384
4.2186
4.1996
4.1802
4.1605
4.1604
4.1390
1.3323
1.3146
1.2967
OEt
OEt
S
P
O
NC
3s
1.91
1.97
4.00
6.25
f1 (ppm)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112.5981
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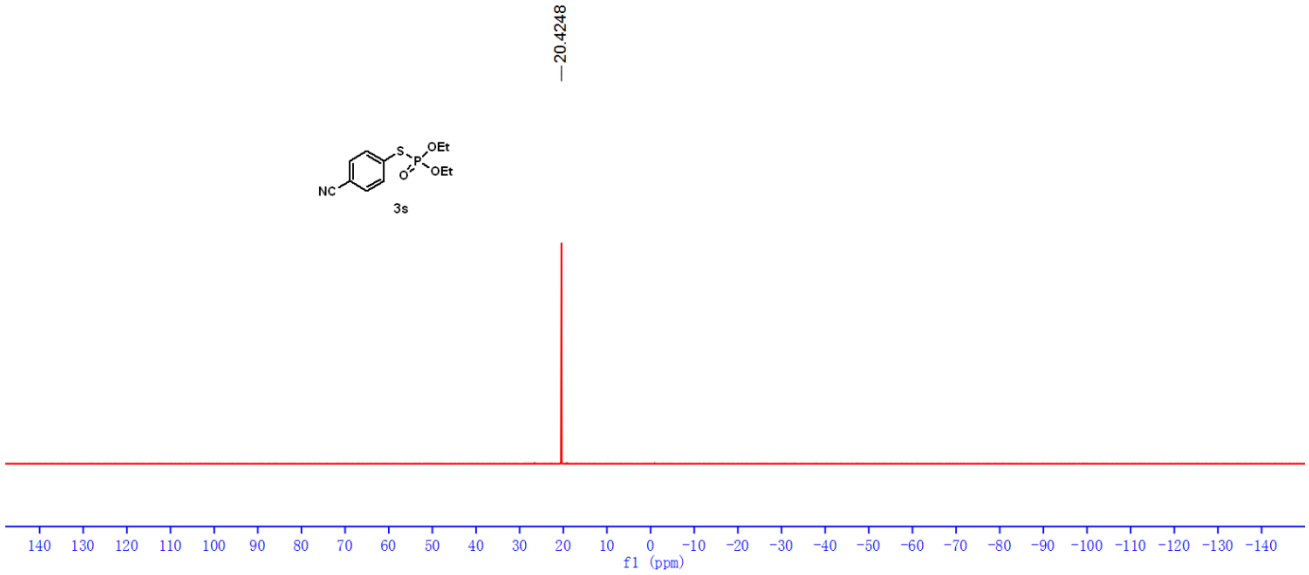
64.7097
16.1552
16.0856
OEt
OEt
S
P
O
NC
3s
f1 (ppm)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NC
S
P
OEt
OEt
O
3s
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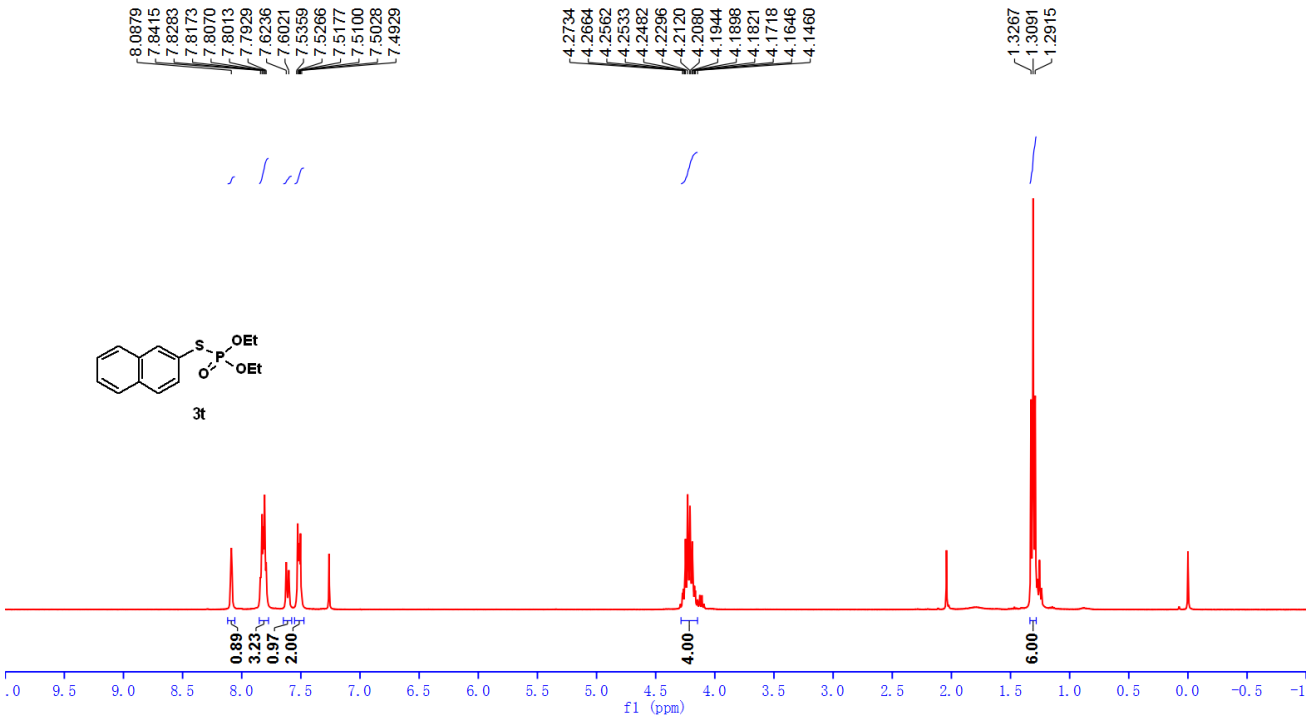
f1 (ppm)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4.2533
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4.2296
4.2120
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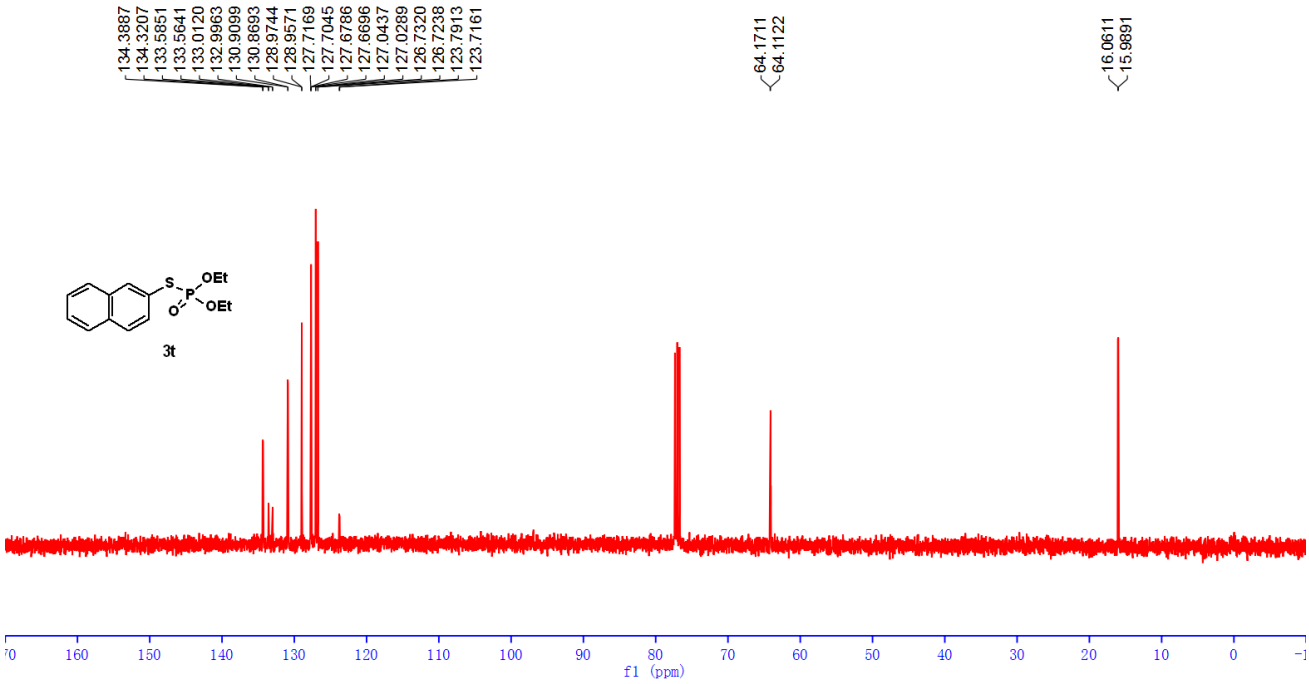
4.1944
4.1898
4.1821
4.1718
4.1646
4.1460
1.3267
1.3091
1.2915
S
P
OEt
OEt
O
3t
0.89
3.23
0.97
2.00
4.00
6.00
.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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127.0437
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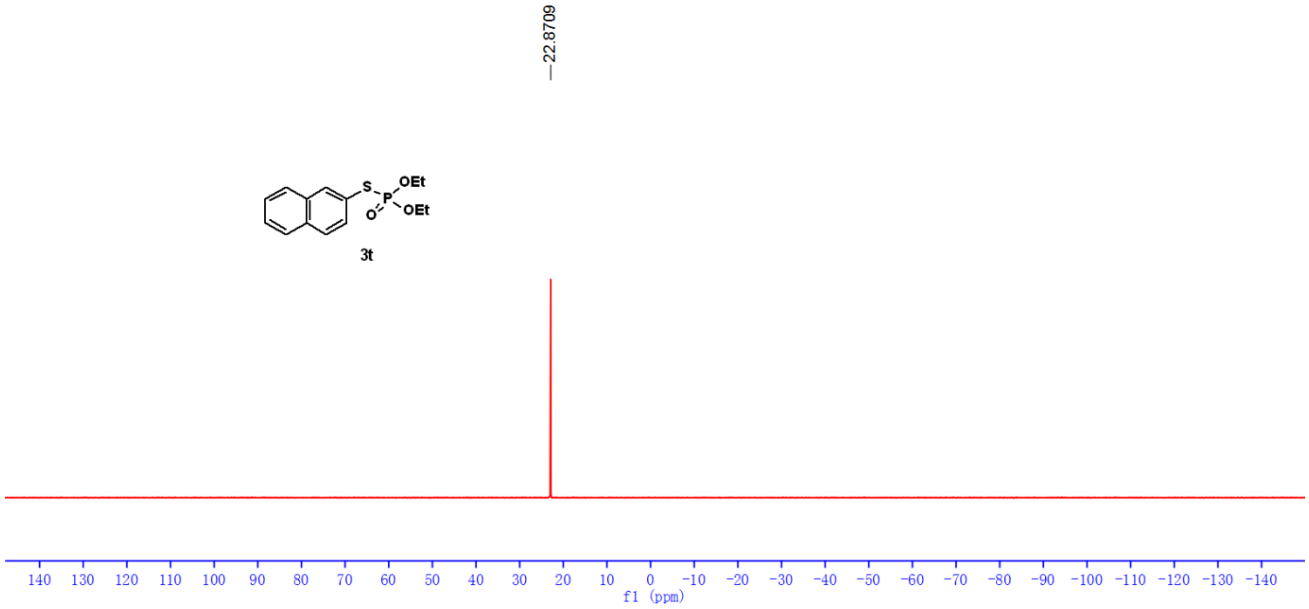
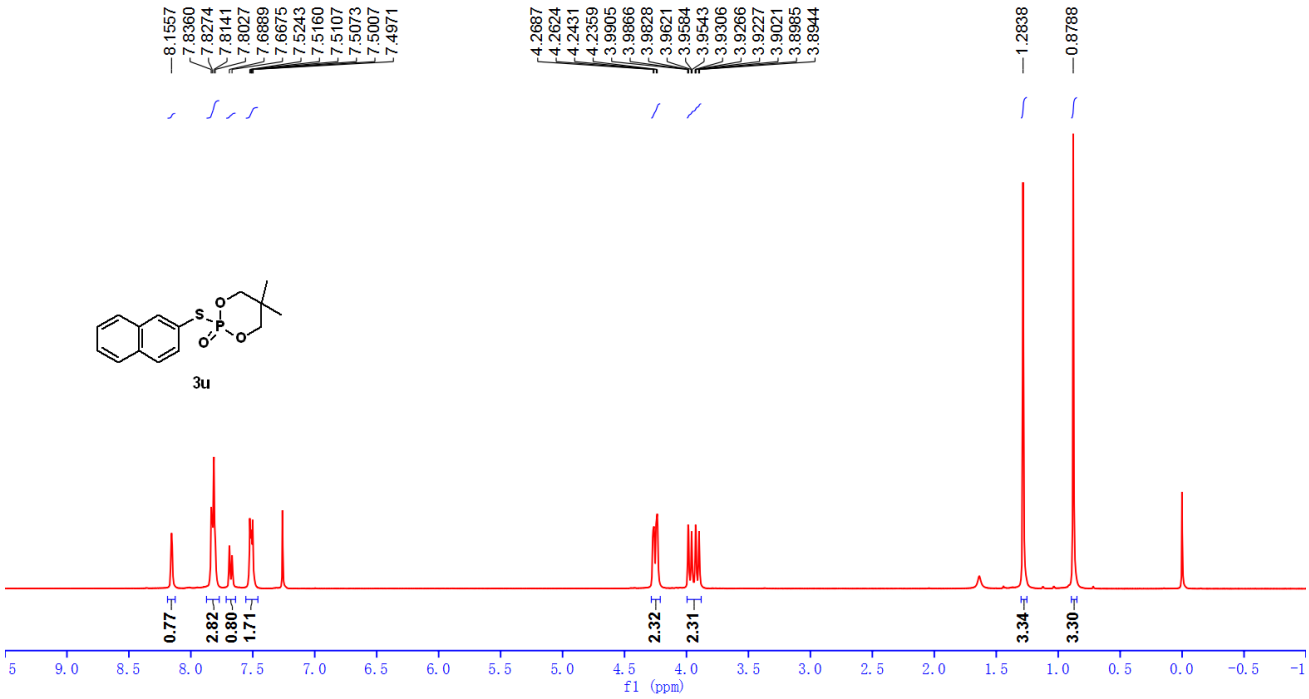
OEt
OEt
3t
f1 (ppm)


22.8709
OEt
OEt
3t
f1 (ppm)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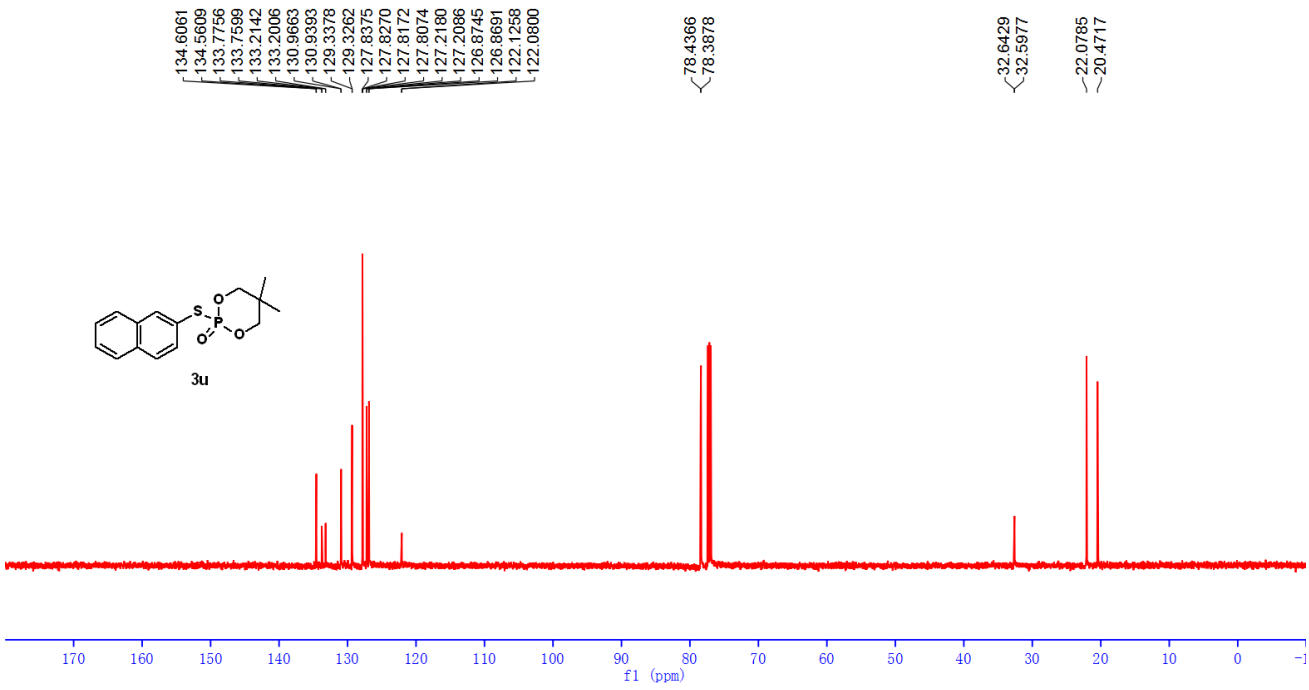
0.77
2.82
0.80
1.71
2.32
2.31
3.34
3.30
f1 (ppm)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133.7756
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133.2142
133.2006
130.9663
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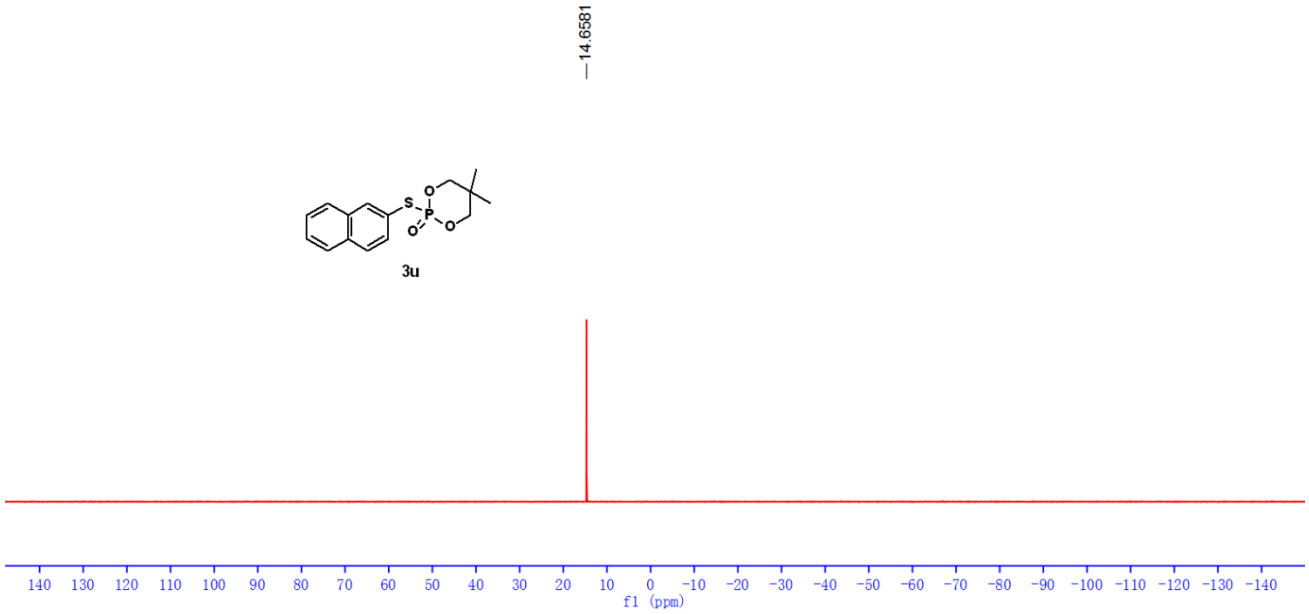
129.3262
127.8375
127.8270
127.8172
127.8074
127.2180
127.2086
126.8745
126.8691
122.1258
122.0800
78.4366
78.3878
32.6429
32.5977
22.0785
20.4717
3u
f1 (ppm)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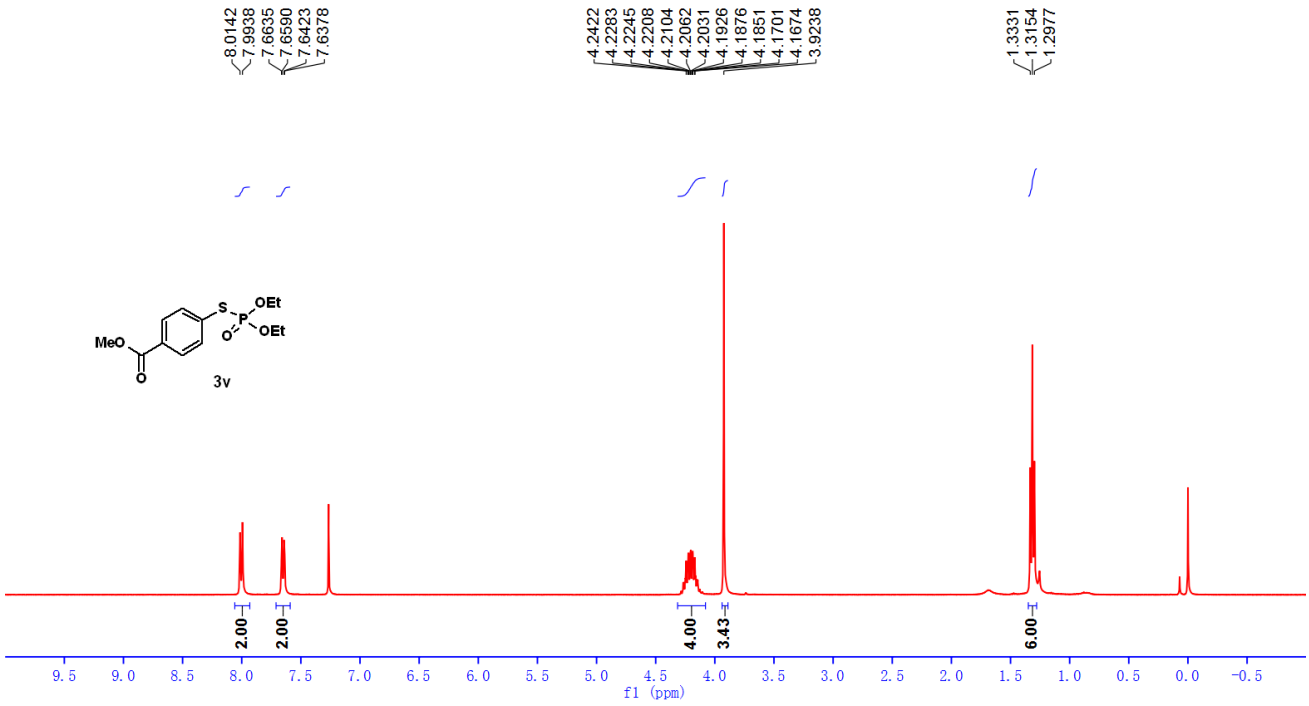
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7.6635
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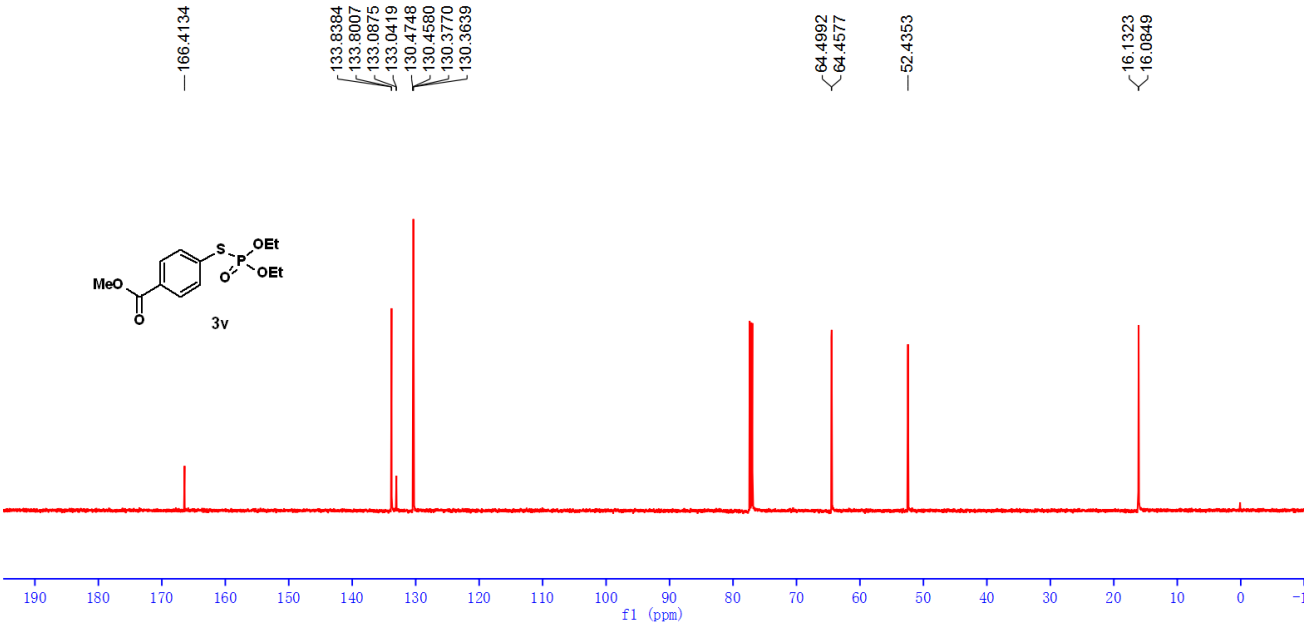
7.6423
7.6378
4.2422
4.2283
4.2245
4.2208
4.2104
4.2062
4.2031
4.1926
4.1876
4.1851
4.1701
4.1674
3.9238
1.3331
1.3154
1.2977
MeO
OEt
OEt
3v
2.00
2.00
4.00
3.43
6.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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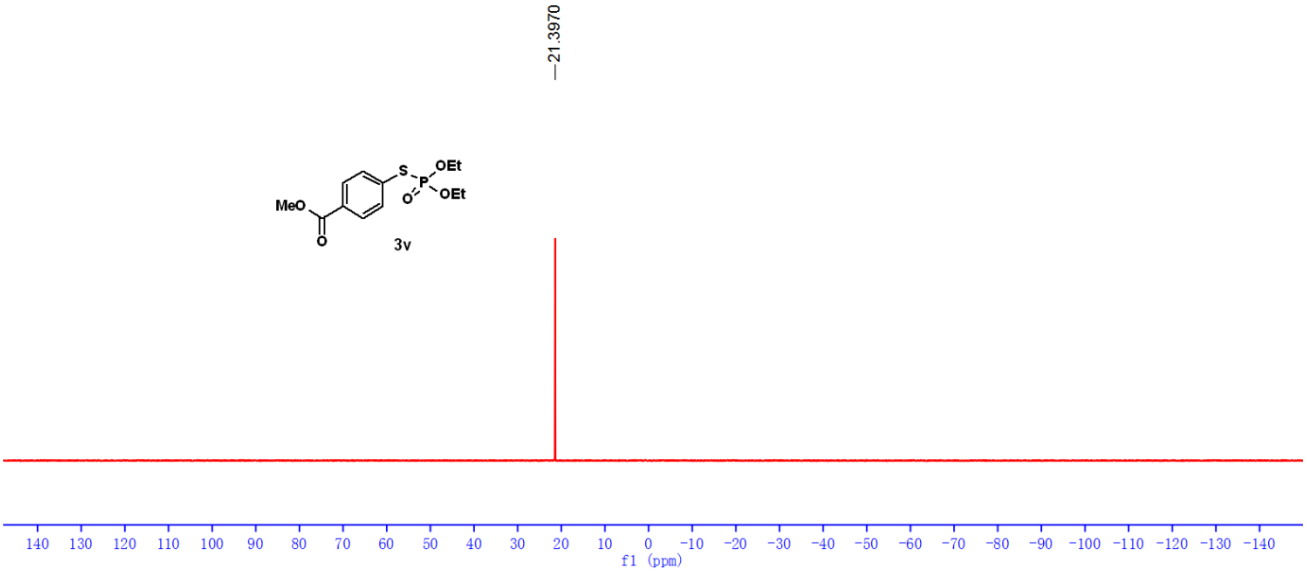
133.8384
133.8007
133.0875
133.0419
130.4748
130.4580
130.3770
130.3639
64.4992
64.4577
52.4353
16.1323
16.0849
MeO
O
S
O
P
OEt
OEt
3v
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


21.3970
MeO
O
S
O
P
OEt
OEt
3v
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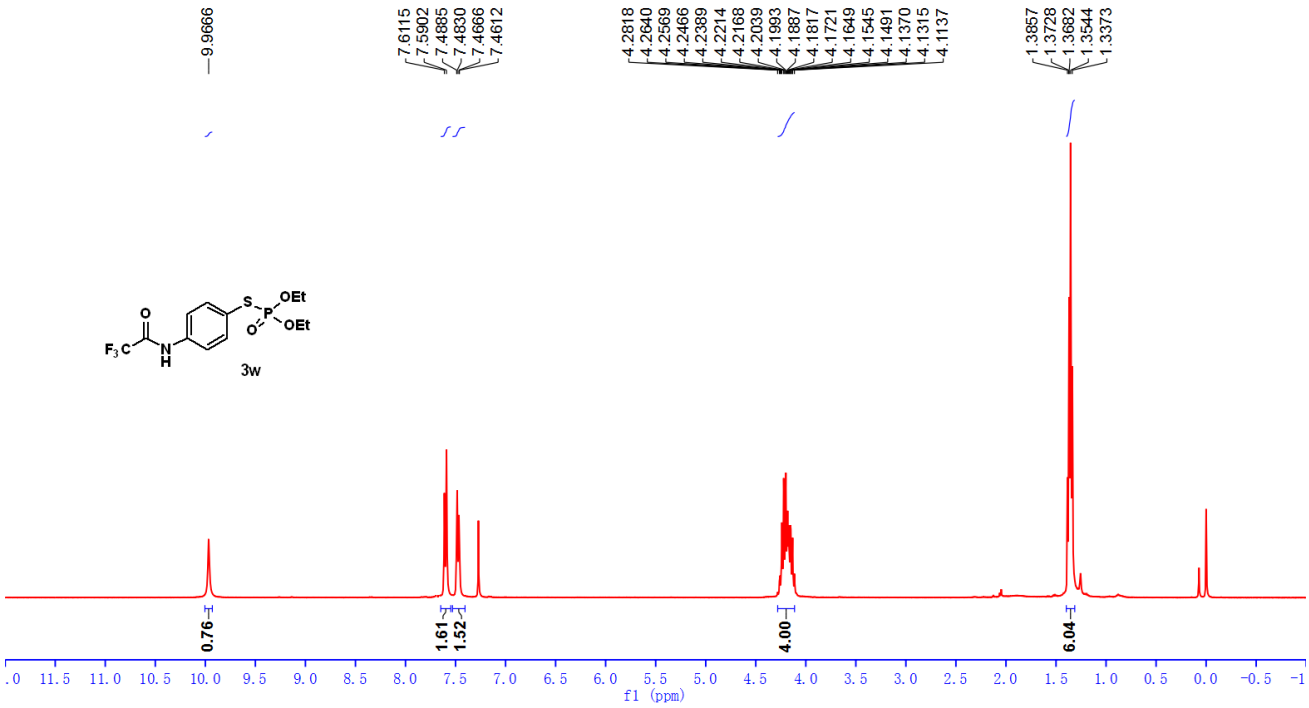
f1 (ppm)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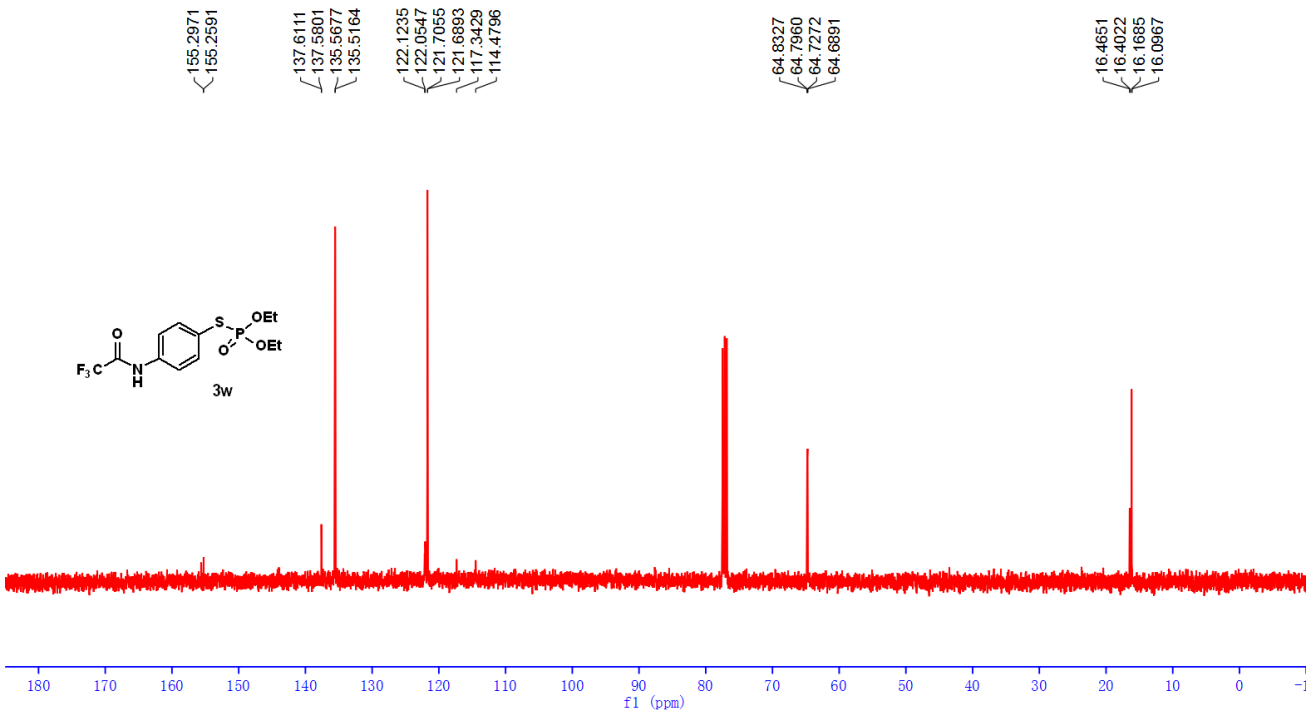
7.5902
7.4885
7.4830
7.4666
7.4612
4.2818
4.2640
4.2569
4.2466
4.2389
4.2214
4.2168
4.2039
4.1993
4.1887
4.1817
4.1721
4.1649
4.1545
4.1491
4.1370
4.1315
4.1137
1.3857
1.3728
1.3682
1.3544
1.3373
0.76
1.61
1.52
4.00
6.04
f1 (ppm)
3w


155.2971
155.2591
137.6111
137.5801
135.5677
135.5164
122.1235
122.0547
121.7055
121.6893
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114.4796
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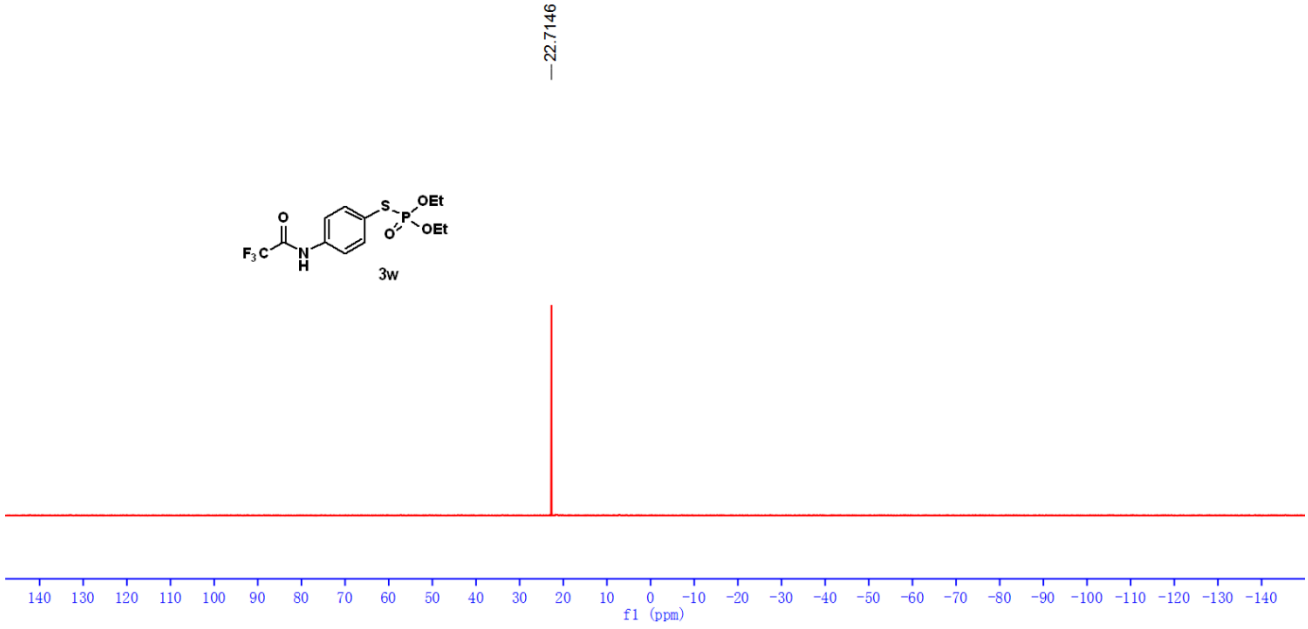
64.7272
64.6891
16.4651
16.4022
16.1685
16.0967
f1 (ppm)
3w


22.7146
3w
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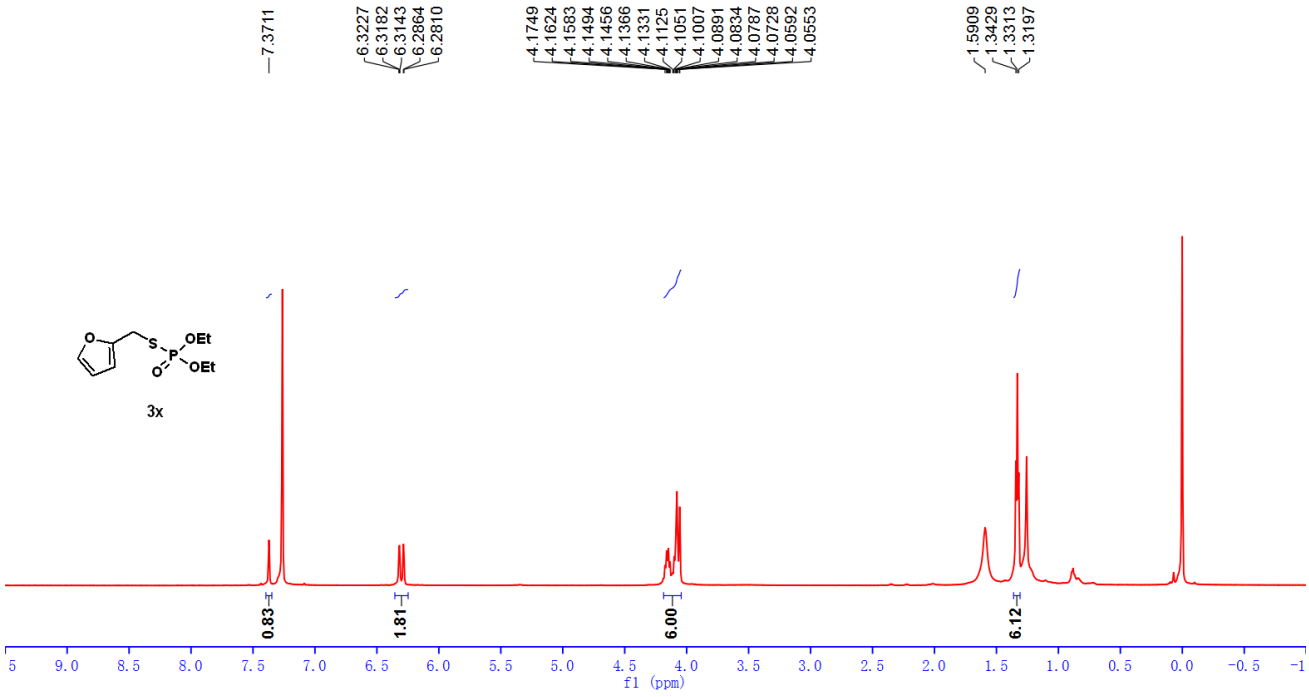
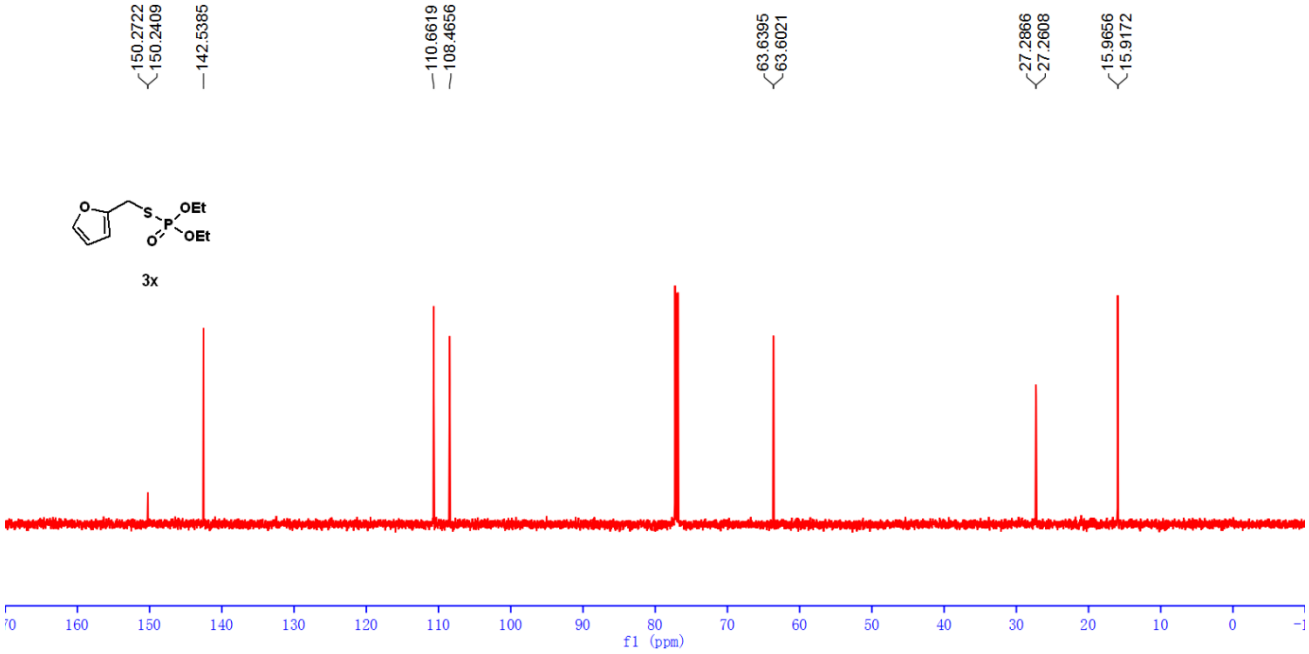
f1 (ppm)


7.3711
6.3227
6.3182
6.3143
6.2864
6.2810
4.1749
4.1624
4.1583
4.1494
4.1456
4.1366
4.1331
4.1125
4.1051
4.1007
4.0891
4.0834
4.0787
4.0728
4.0592
4.0553
1.5909
1.3429
1.3313
1.3197
3x
0.83
1.81
6.00
6.12
5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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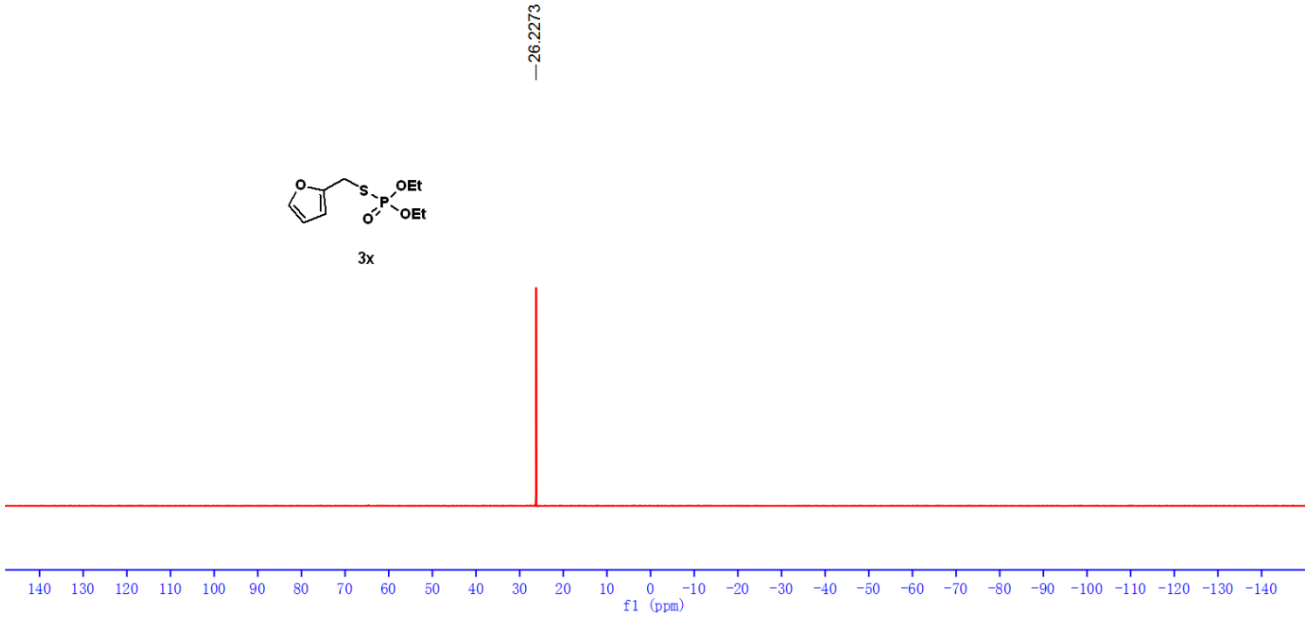
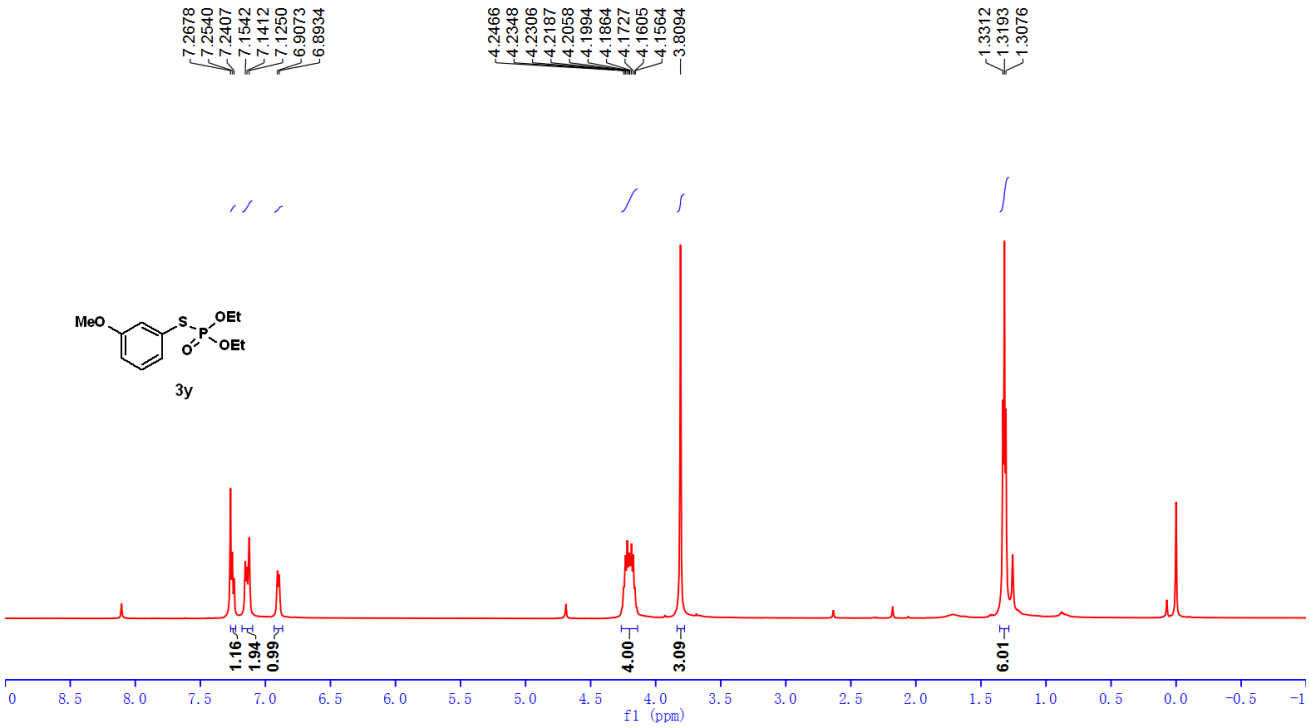
150.2409
142.5385
110.6619
108.4656
63.6395
63.6021
27.2866
27.2608
15.9656
15.9172
OEt
OEt
3x
f1 (ppm)


26.2273
OEt
OEt
3x
f1 (ppm)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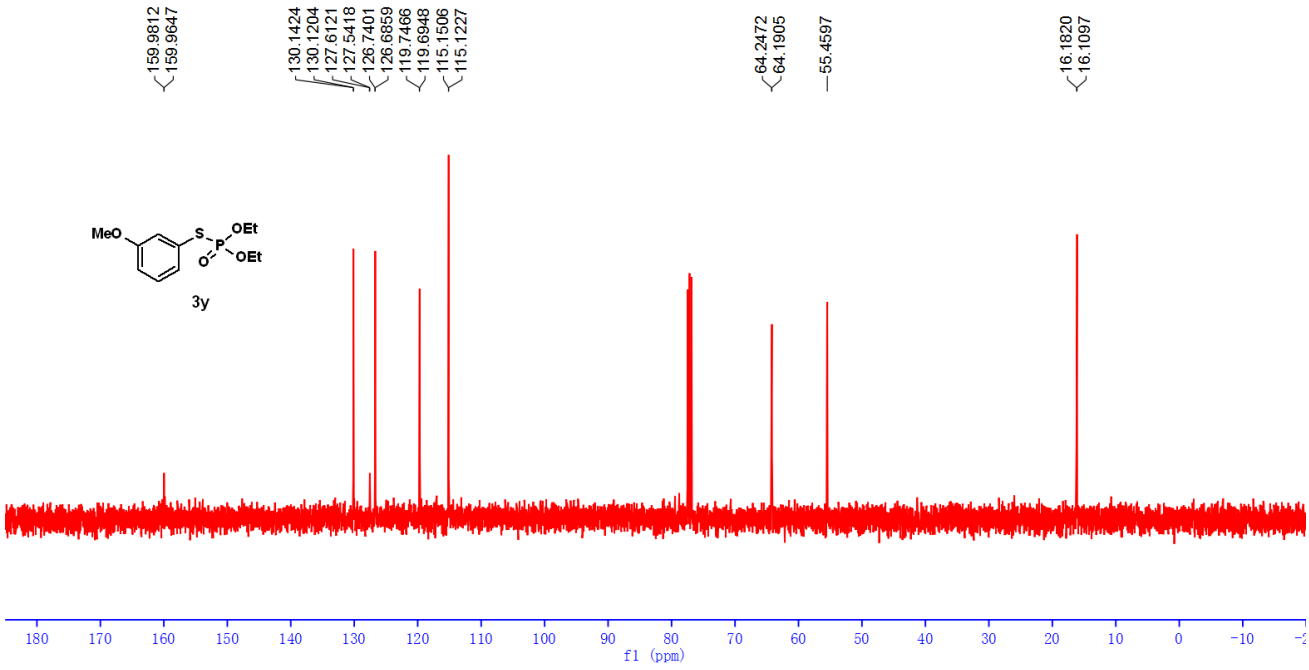
7.2540
7.2407
7.1542
7.1412
7.1250
6.9073
6.8934
4.2466
4.2348
4.2306
4.2187
4.2058
4.1994
4.1864
4.1727
4.1605
4.1564
3.8094
1.3312
1.3193
1.3076
MeO
S
OEt
O
P
OEt
3y
1.16
1.94
0.99
4.00
3.09
6.01
f1 (ppm)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130.1204
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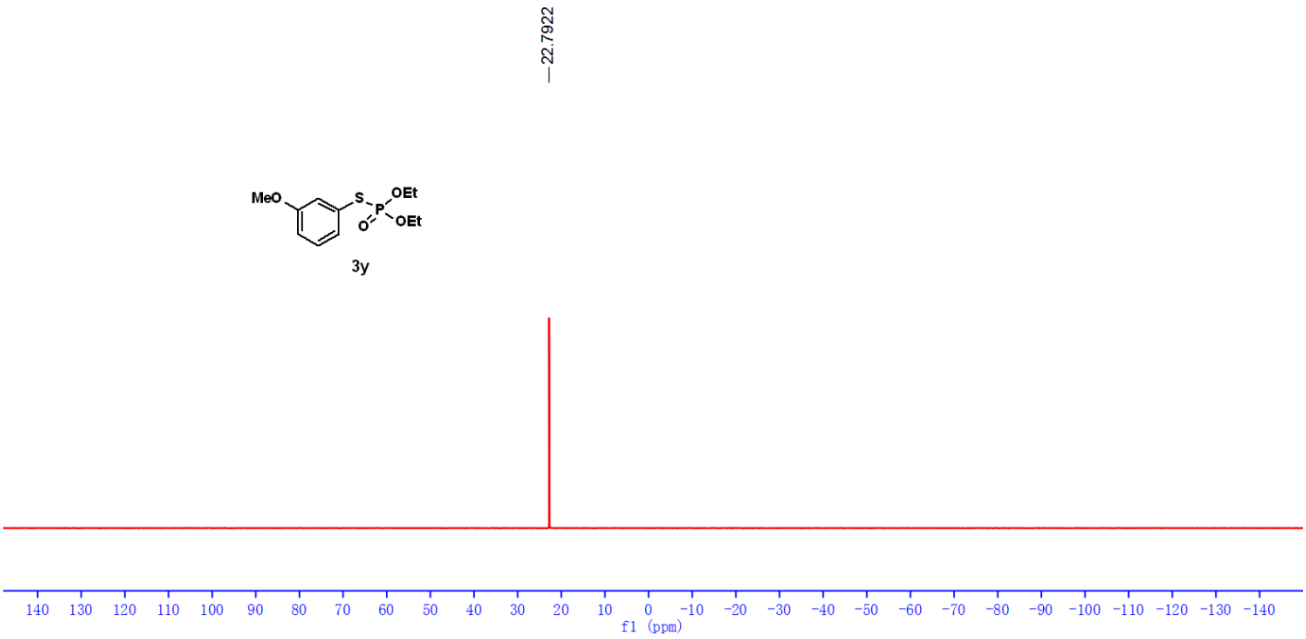
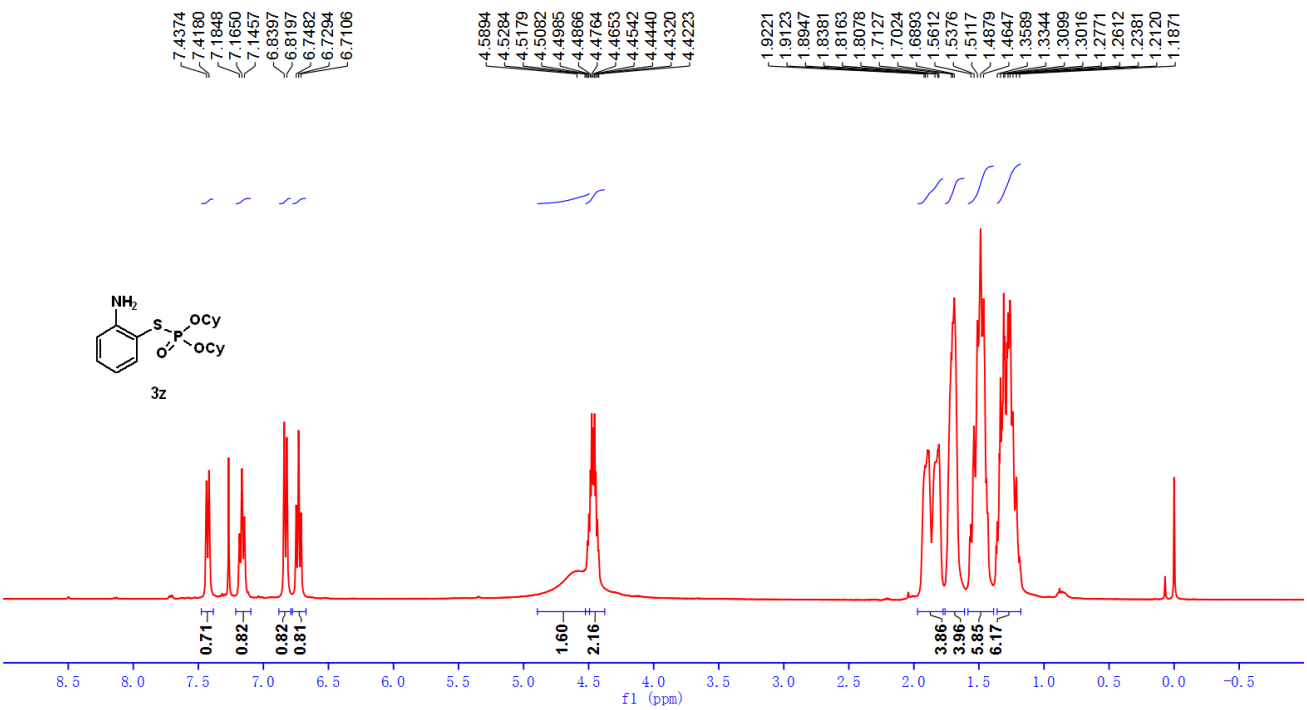
127.5418
126.7401
126.6859
119.7466
119.6948
115.1506
115.1227
64.2472
64.1905
55.4597
16.1820
16.1097
MeO
S
OEt
O
P
OEt
3y
f1 (ppm)


22.7922
MeO
S
P
OEt
OEt
O
3y
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
f1 (ppm)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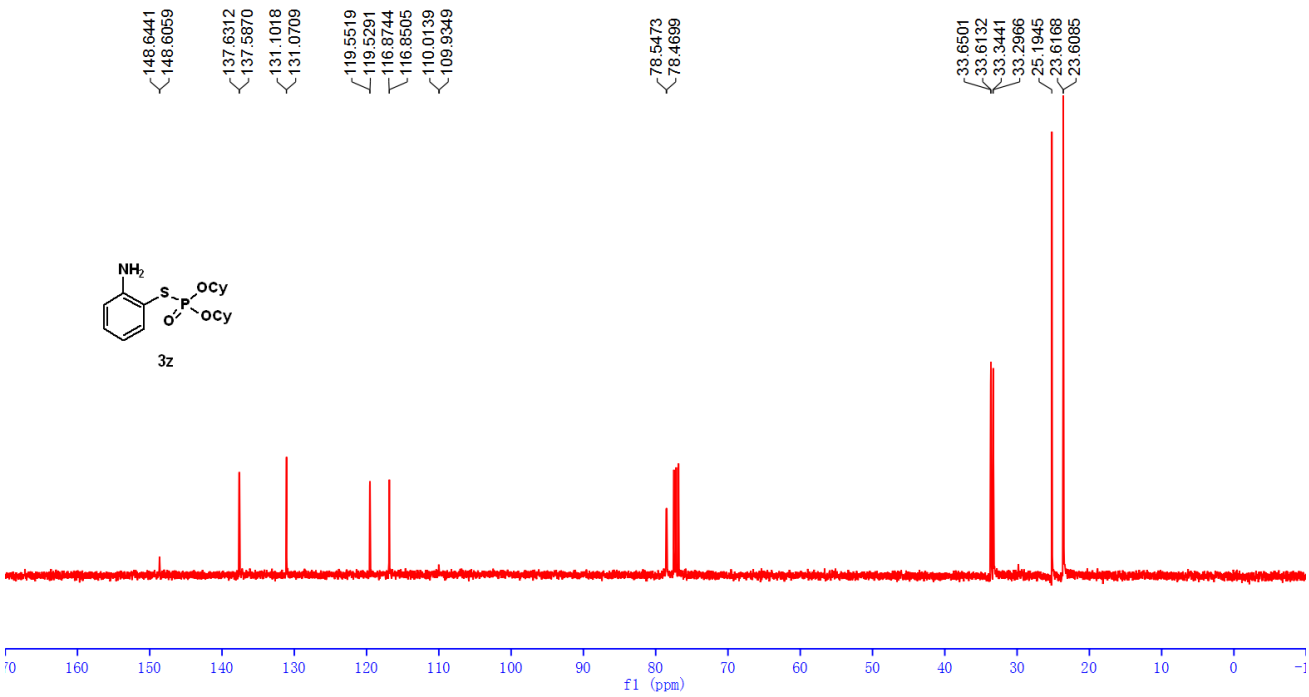
7.1848
7.1650
7.1457
6.8397
6.8197
6.7482
6.7294
6.7106
4.5894
4.5284
4.5179
4.5082
4.4985
4.4866
4.4764
4.4653
4.4542
4.4440
4.4320
4.4223
1.9221
1.9123
1.8947
1.8381
1.8163
1.8078
1.7127
1.7024
1.6893
1.5612
1.5376
1.5117
1.4879
1.4647
1.3589
1.3344
1.3099
1.3016
1.2771
1.2612
1.2381
1.2120
1.1871
NH2
S
P
OCy
OCy
O
3z
0.71
0.82
0.82
0.81
1.60
2.16
3.86
3.96
5.85
6.17
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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137.5870
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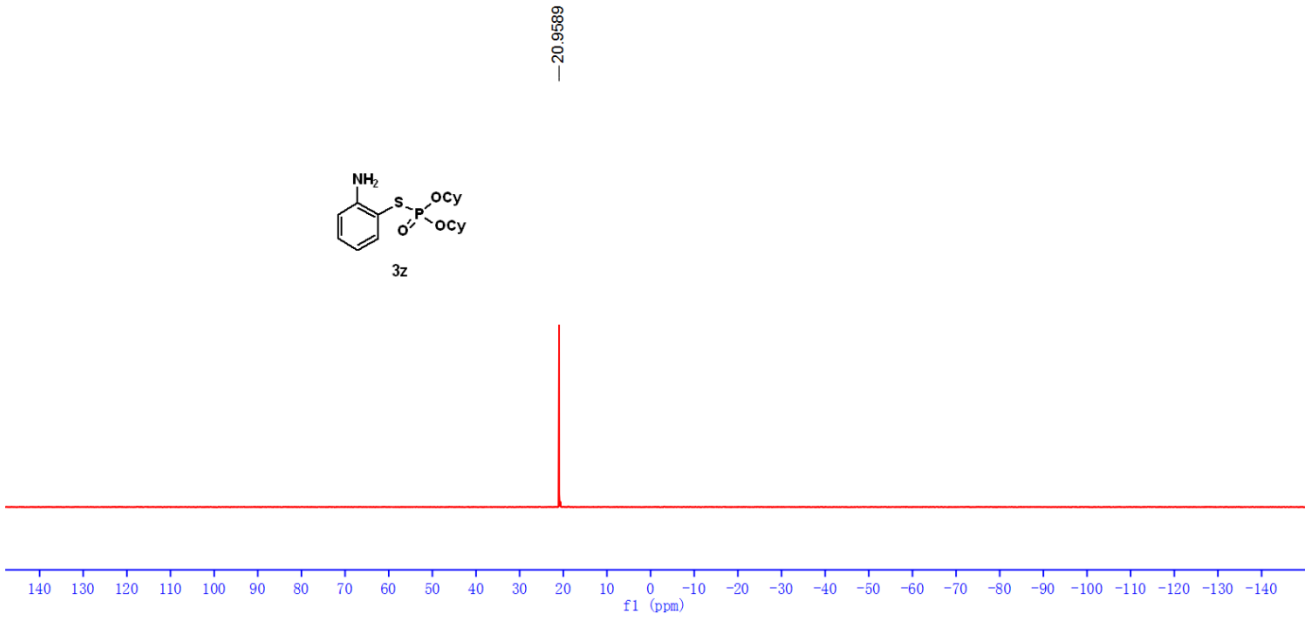
131.0709
119.5519
119.5291
116.8744
116.8505
110.0139
109.9349
78.5473
78.4699
33.6501
33.6132
33.3441
33.2966
25.1945
23.6168
23.6085
NH2
S
P
O
OCy
OCy
3z
f1 (ppm)


20.9589
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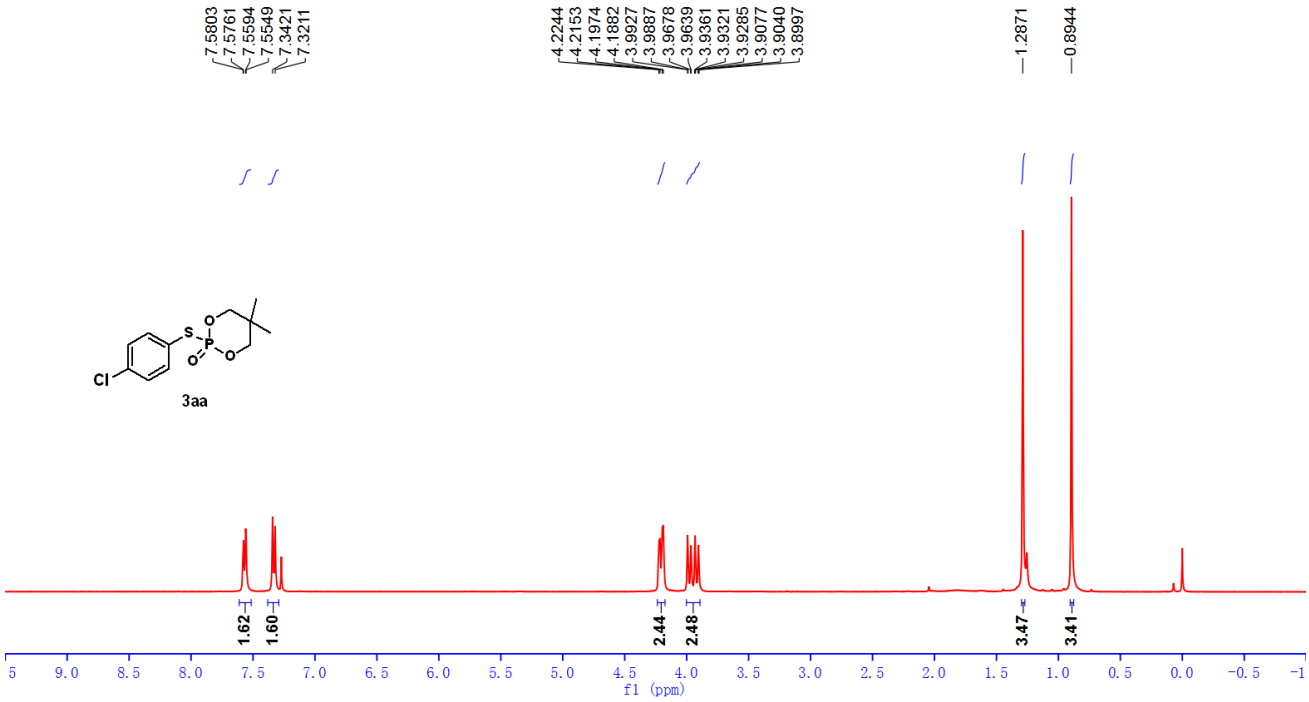
S
P
O
OCy
OCy
3z
f1 (ppm)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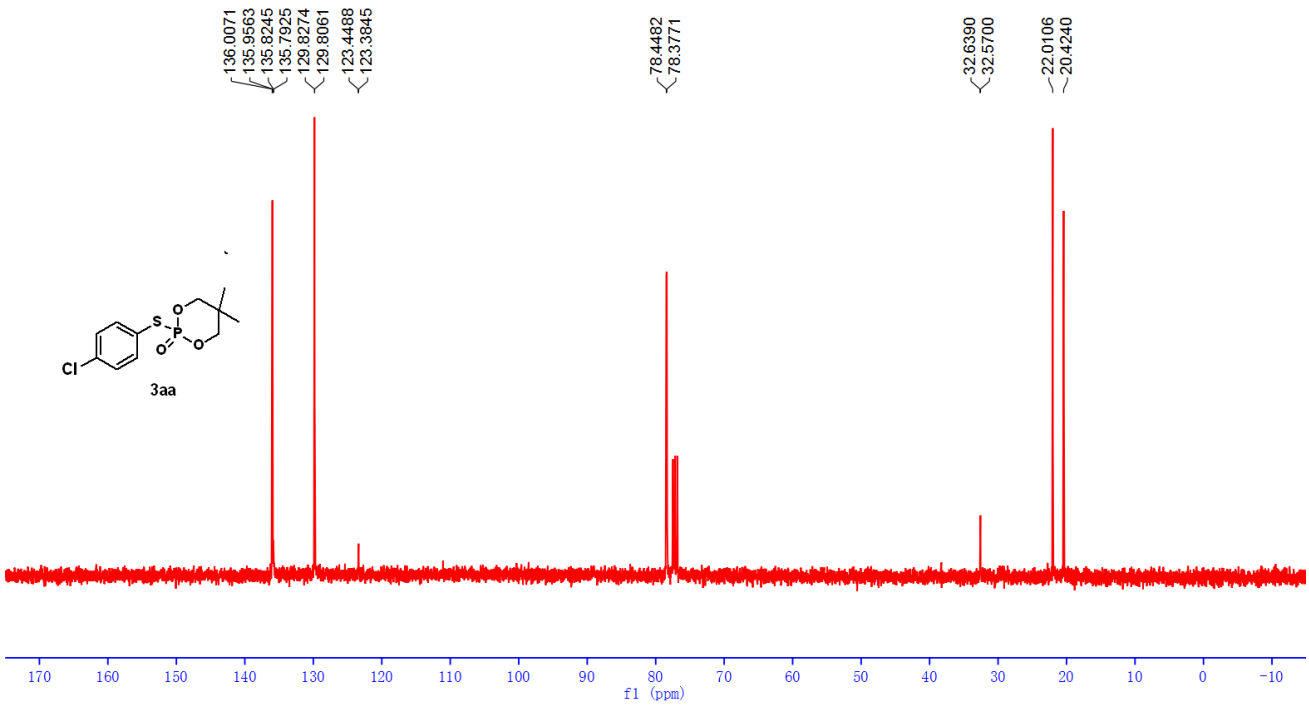
7.5594
7.5549
7.3421
7.3211
4.2244
4.2153
4.1974
4.1882
3.9927
3.9887
3.9678
3.9639
3.9361
3.9321
3.9285
3.9077
3.9040
3.8997
1.2871
0.8944
Cl
3aa
1.62
1.60
2.44
2.48
3.47
3.41
f1 (ppm)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135.7925
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78.3771
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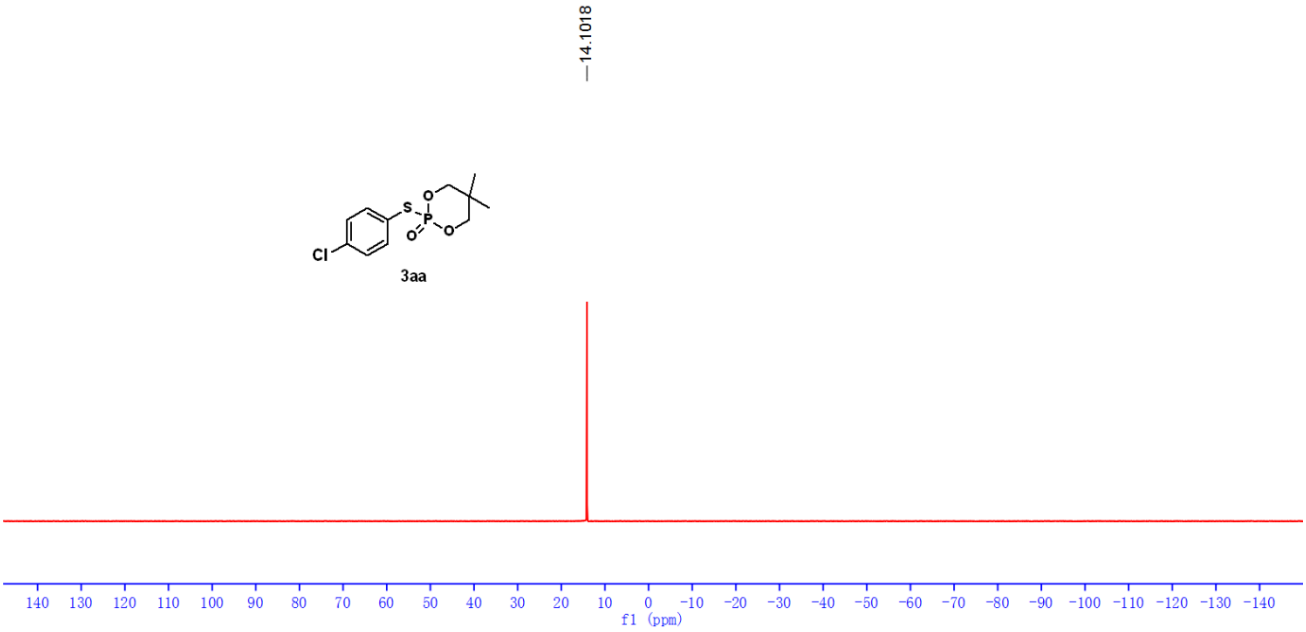
22.0106
20.4240
Cl
3aa
f1 (ppm)


14.1018
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S
O
P
O
O
3aa
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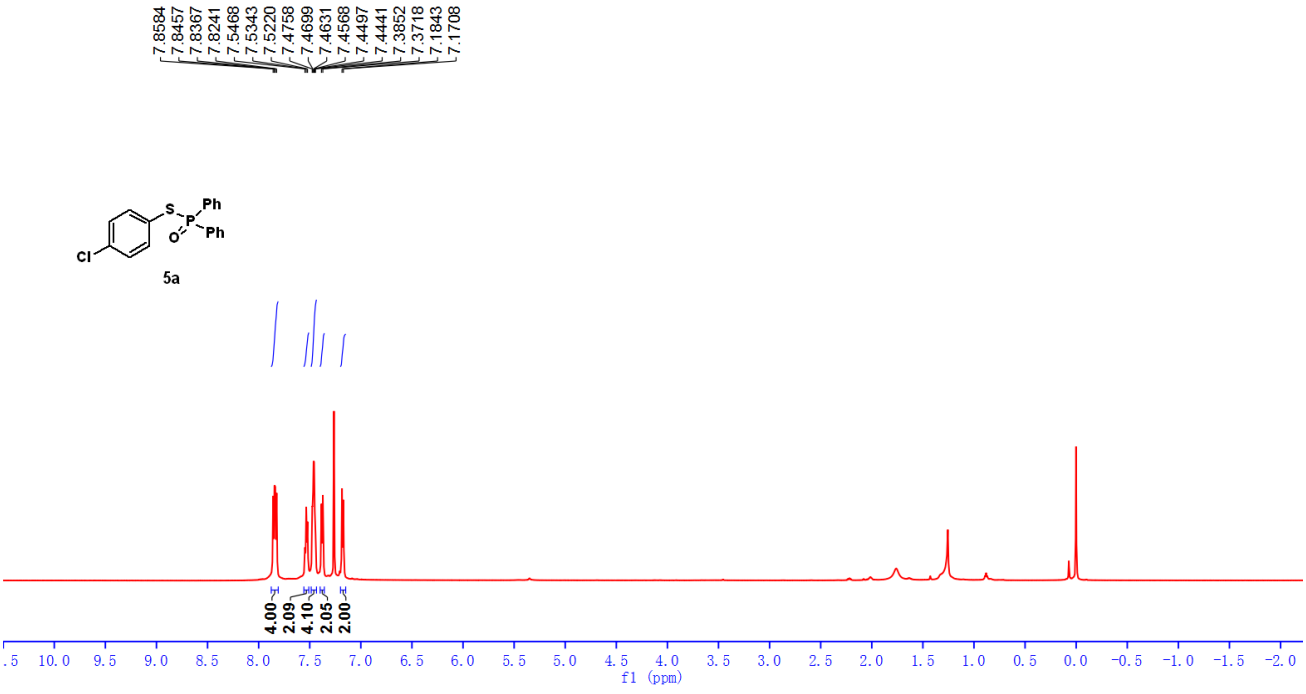
f1 (ppm)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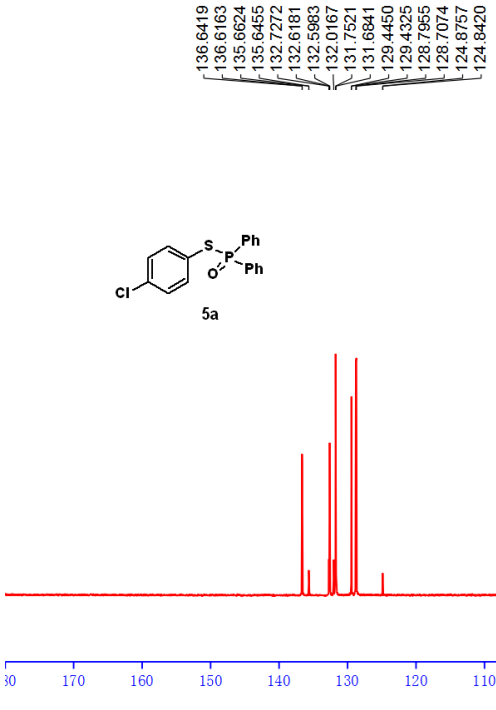
7.8367
7.8241
7.5468
7.5343
7.5220
7.4758
7.4699
7.4631
7.4568
7.4497
7.4441
7.3852
7.3718
7.1843
7.1708
Cl
S
O
P
Ph
Ph
5a
4.00
2.09
4.10
2.05
2.00
.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)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135.6624
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132.5983
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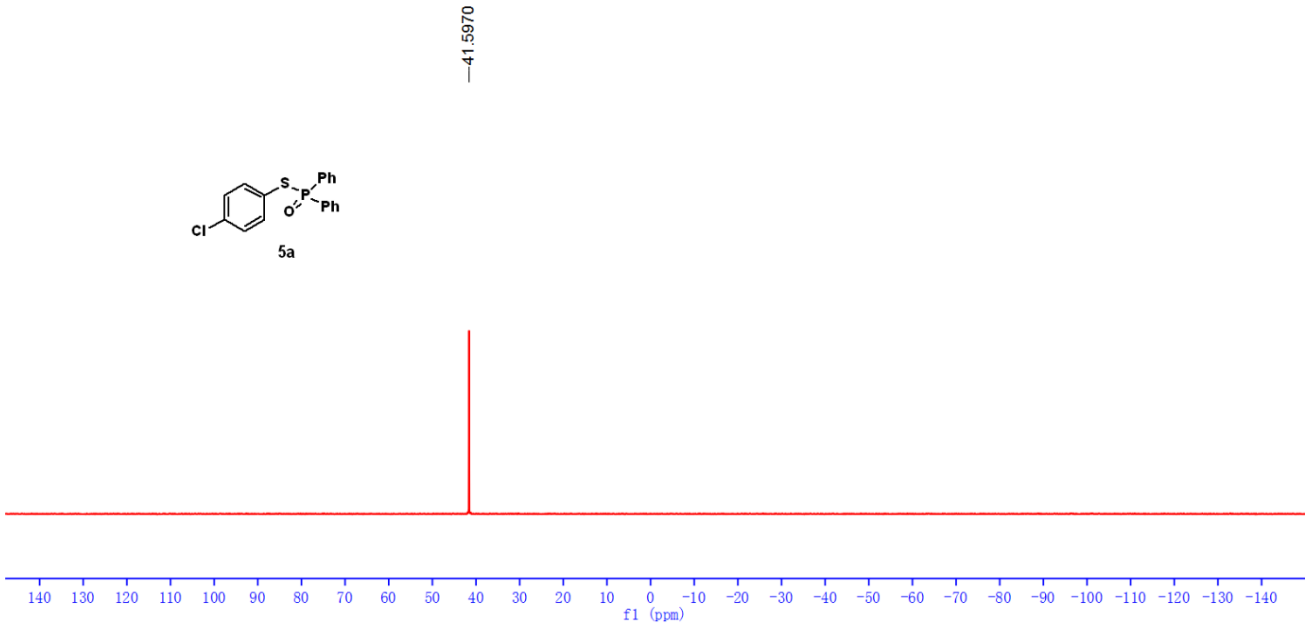
131.7521
131.6841
129.4450
129.4325
128.7955
128.7074
124.8757
124.8420
S
P
O
Ph
Ph
Cl
5a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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Ph
Ph
Cl
5a
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130
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110
100
90
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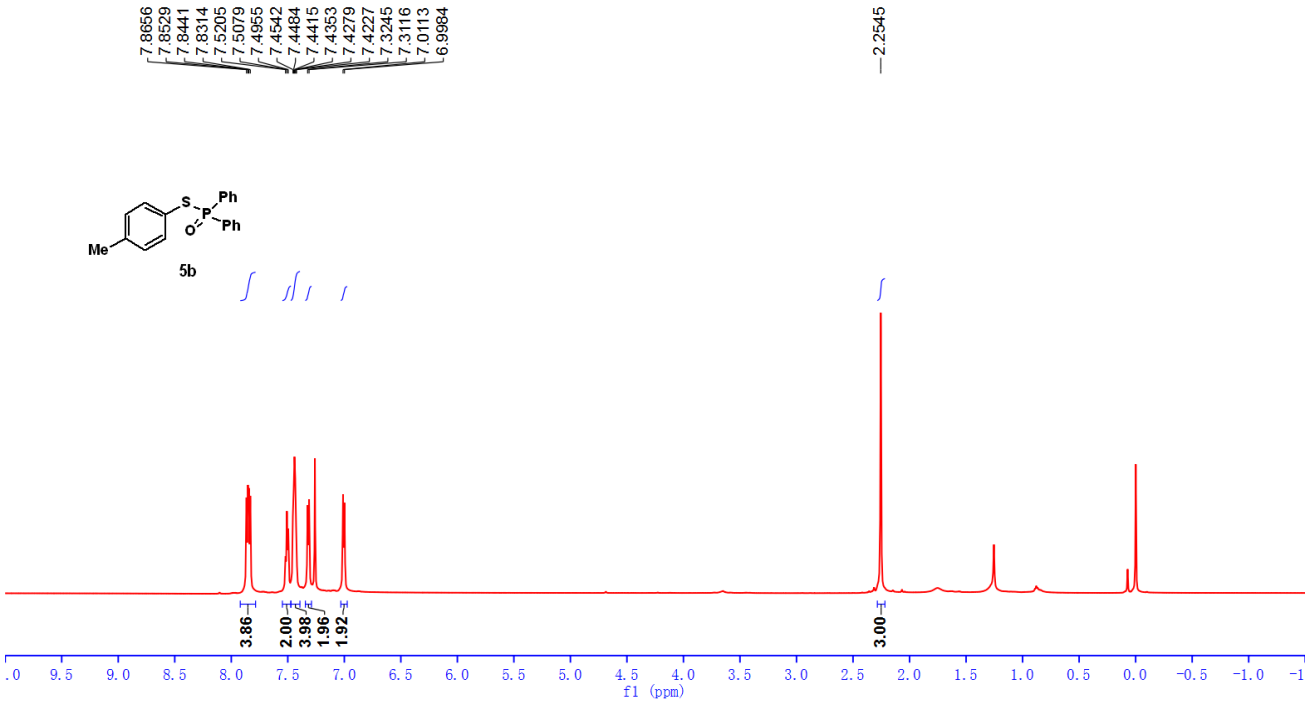
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
f1 (ppm)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7.8314
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7.5079
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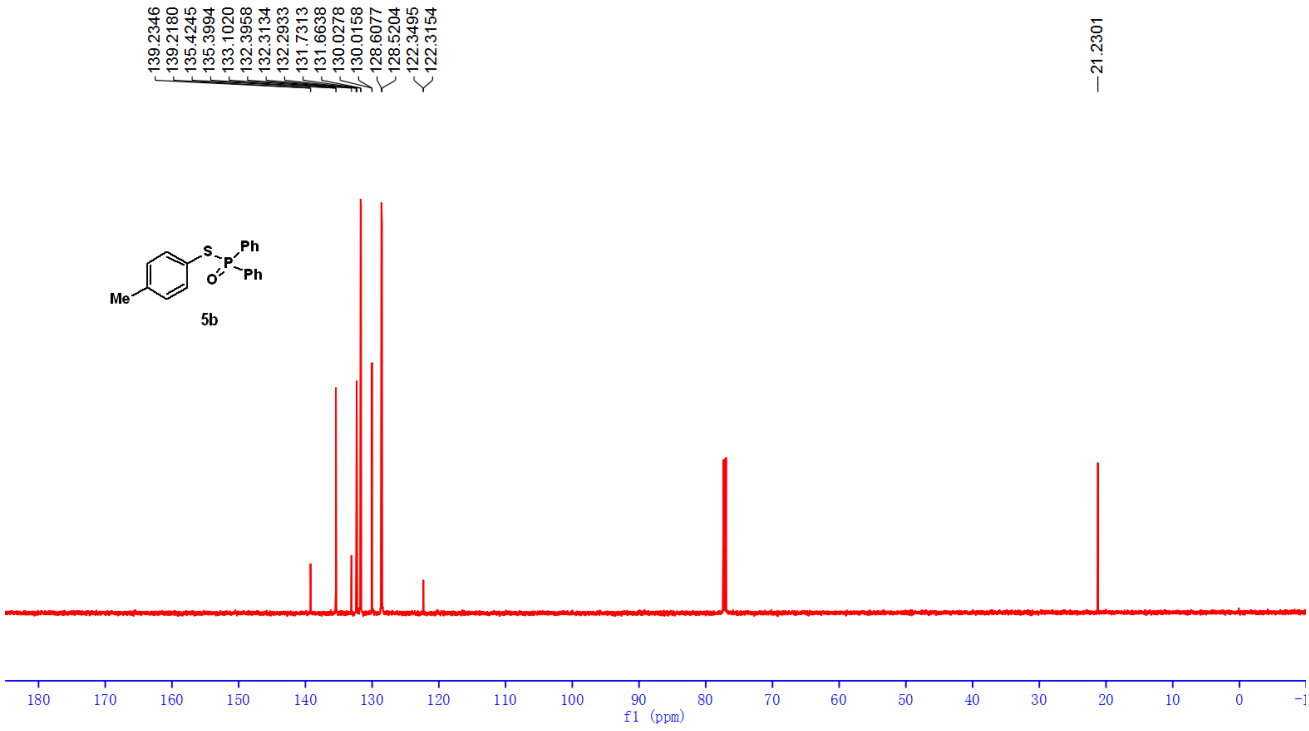
7.4542
7.4484
7.4415
7.4353
7.4279
7.4227
7.3245
7.3116
7.0113
6.9984
2.2545
Ph
S
P
O
Ph
Me
5b
3.86
2.00
3.98
1.96
1.92
3.00
f1 (ppm)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130.0278
130.0158
128.6077
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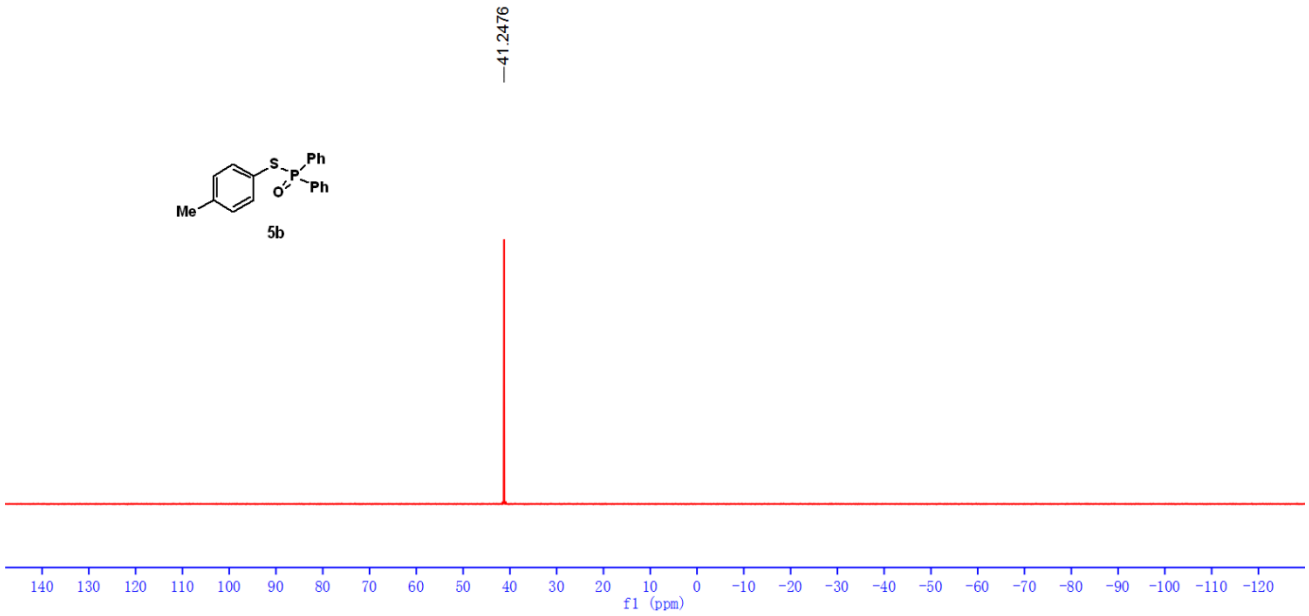
122.3495
122.3154
21.2301
Ph
S
P
O
Ph
Me
5b
f1 (ppm)


41.2476
Me
S
P
O
Ph
Ph
5b
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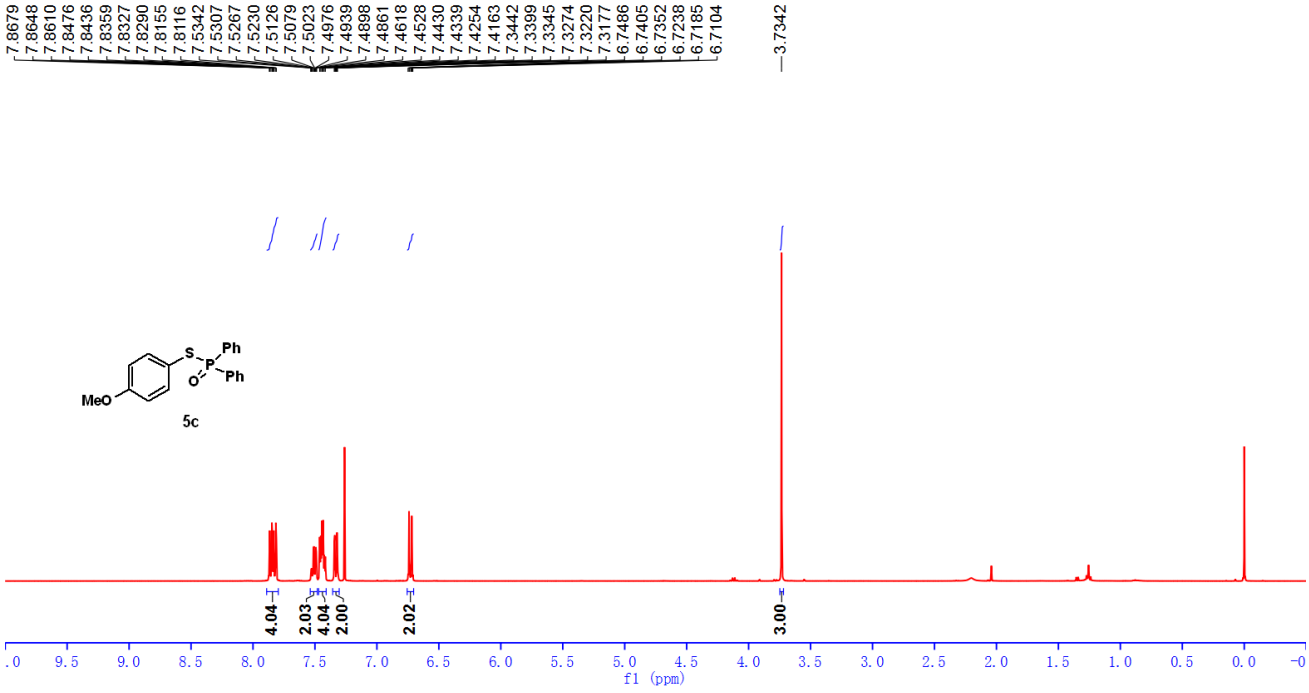
f1 (ppm)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7.5307
7.5267
7.5230
7.5126
7.5079
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7.4618
7.4528
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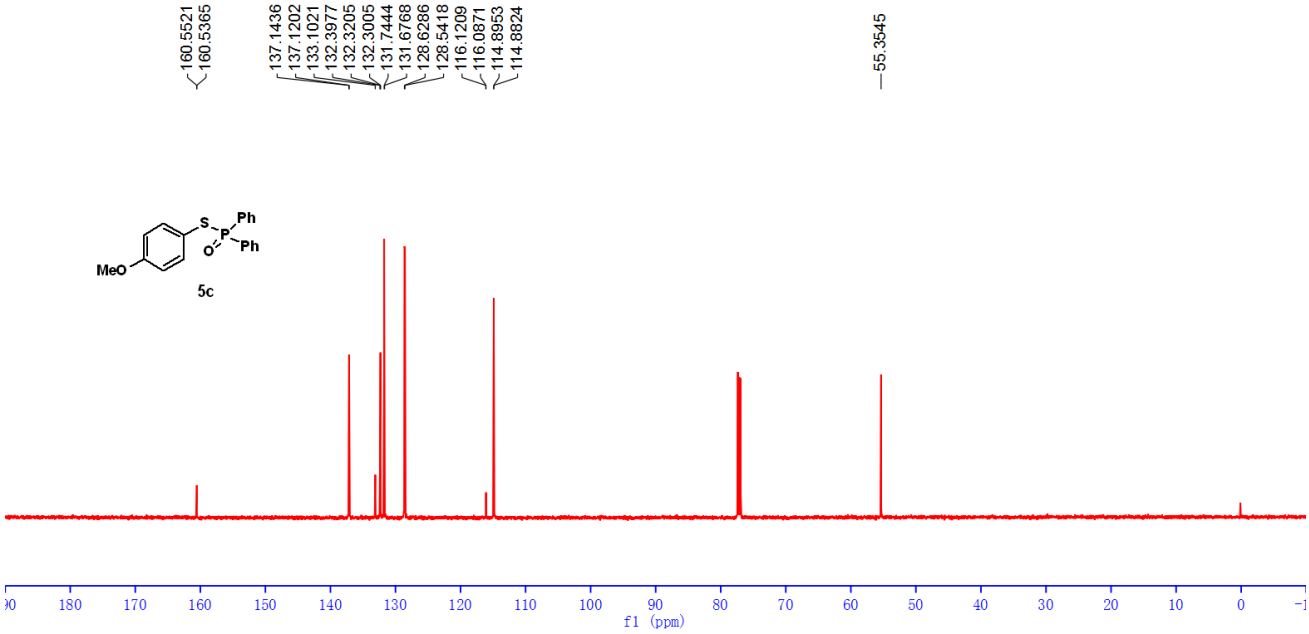
7.4254
7.4163
7.3442
7.3399
7.3345
7.3274
7.3220
7.3177
6.7486
6.7405
6.7352
6.7238
6.7185
6.7104
3.7342
MeO
S
P
O
Ph
Ph
5c
4.04
2.03
4.04
2.00
2.02
3.00
.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)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131.7444
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128.6286
128.5418
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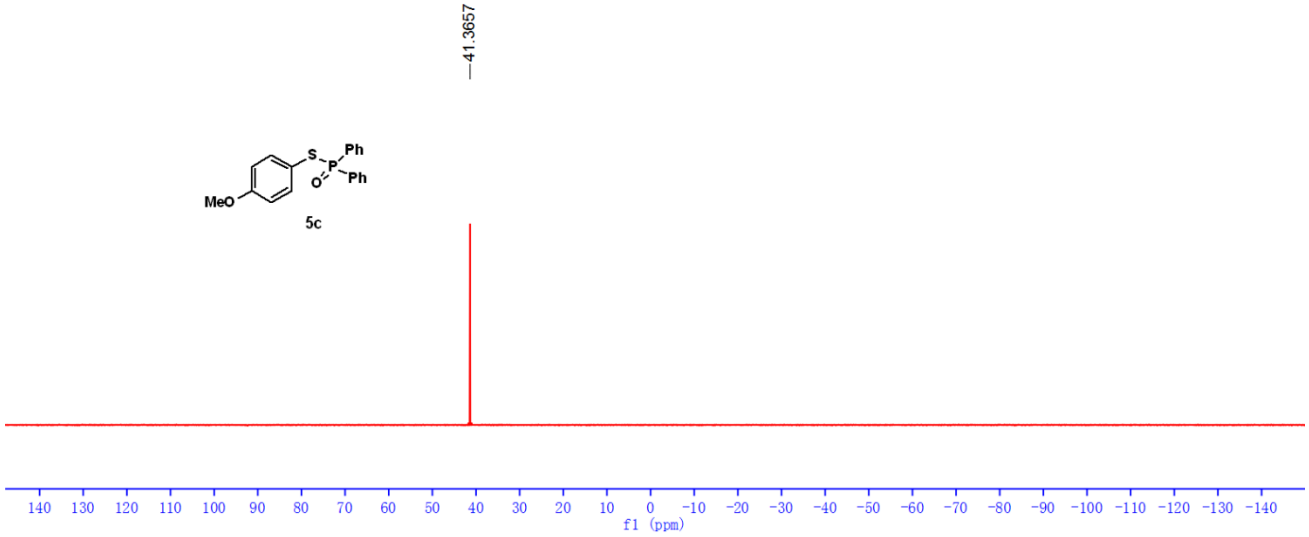
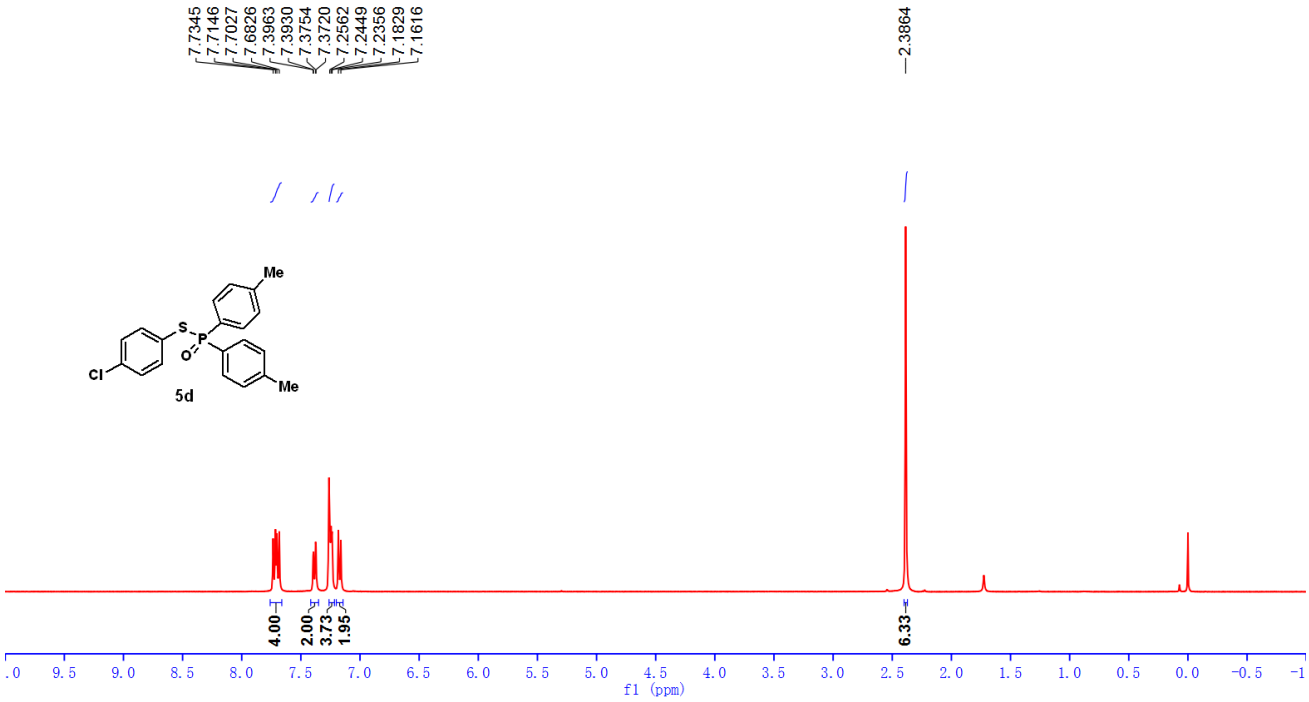
MeO
S
P
O
Ph
Ph
5c
f1 (ppm)


41.3657
MeO
S
P
O
Ph
Ph
5c
f1 (ppm)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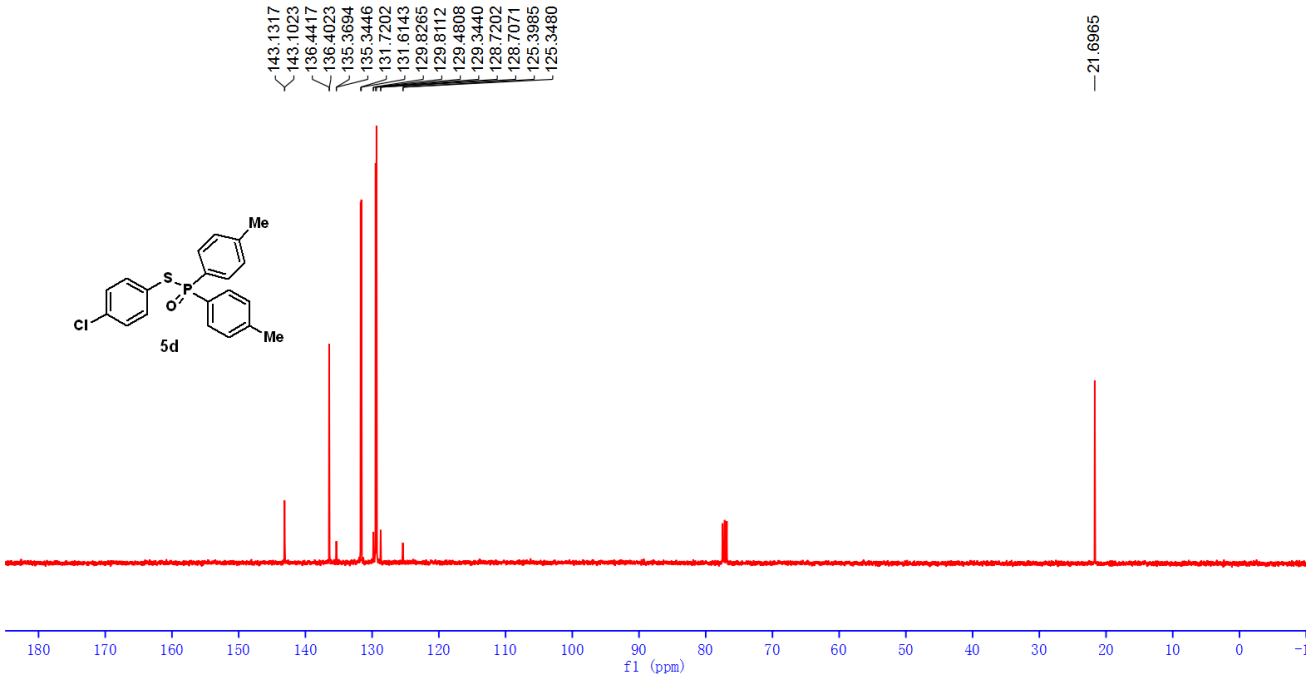
7.7146
7.7027
7.6826
7.3963
7.3930
7.3754
7.3720
7.2562
7.2449
7.2356
7.1829
7.1616
2.3864
Me
S
P
O
Cl
Me
5d
4.00
2.00
3.73
1.95
6.33
f1 (ppm)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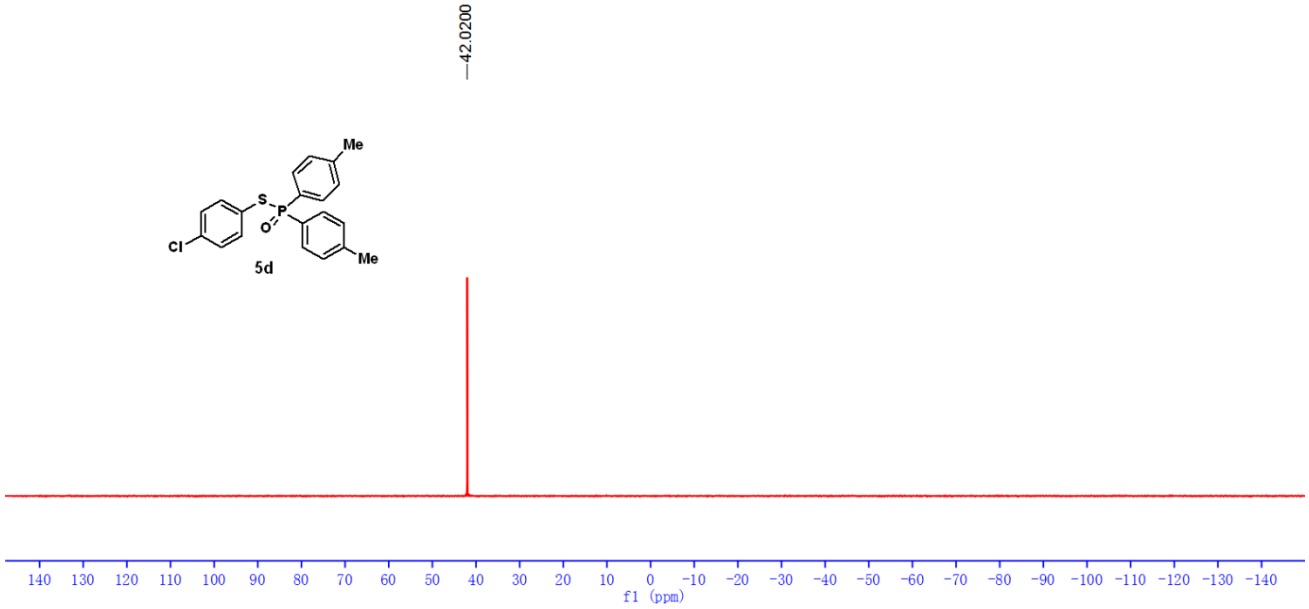
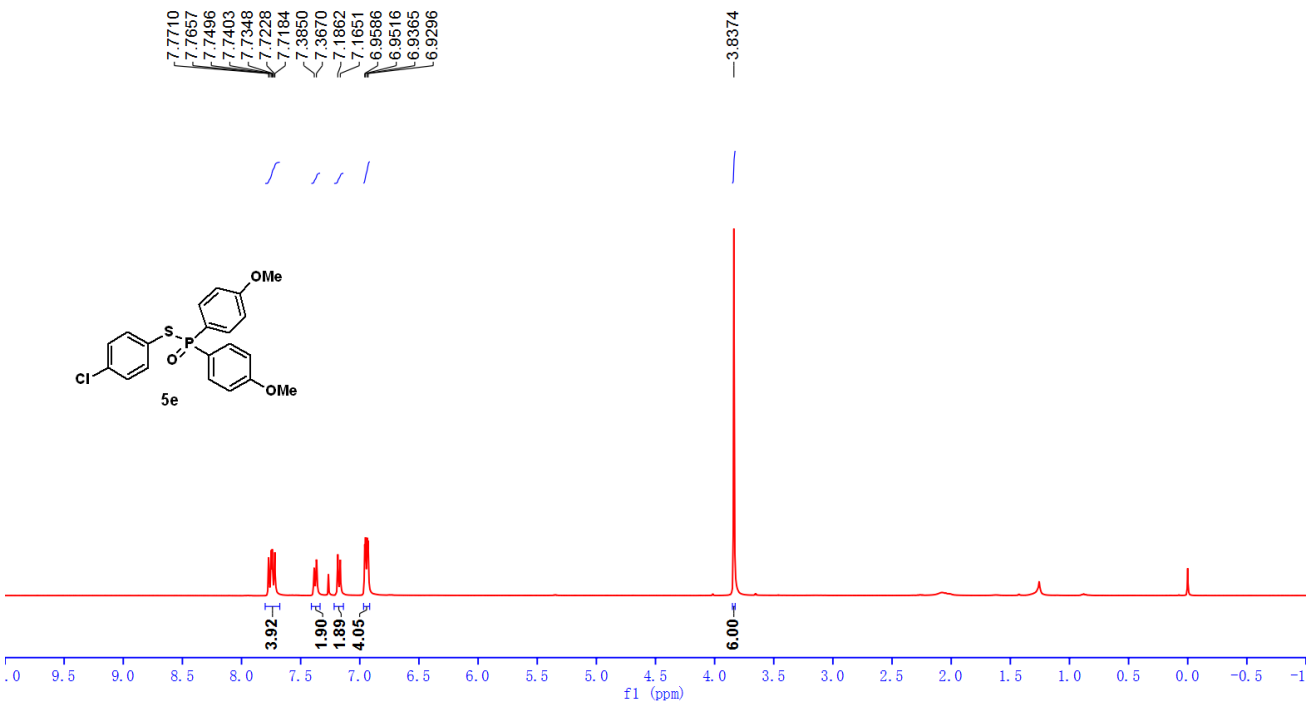
143.1023
136.4417
136.4023
135.3694
135.3446
131.7202
131.6143
129.8265
129.8112
129.4808
129.3440
128.7202
128.7071
125.3985
125.3480
21.6965
Me
S
P
O
Cl
Me
5d
f1 (ppm)


42.0200
Me
S
P
O
Cl
Me
5d
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
f1 (ppm)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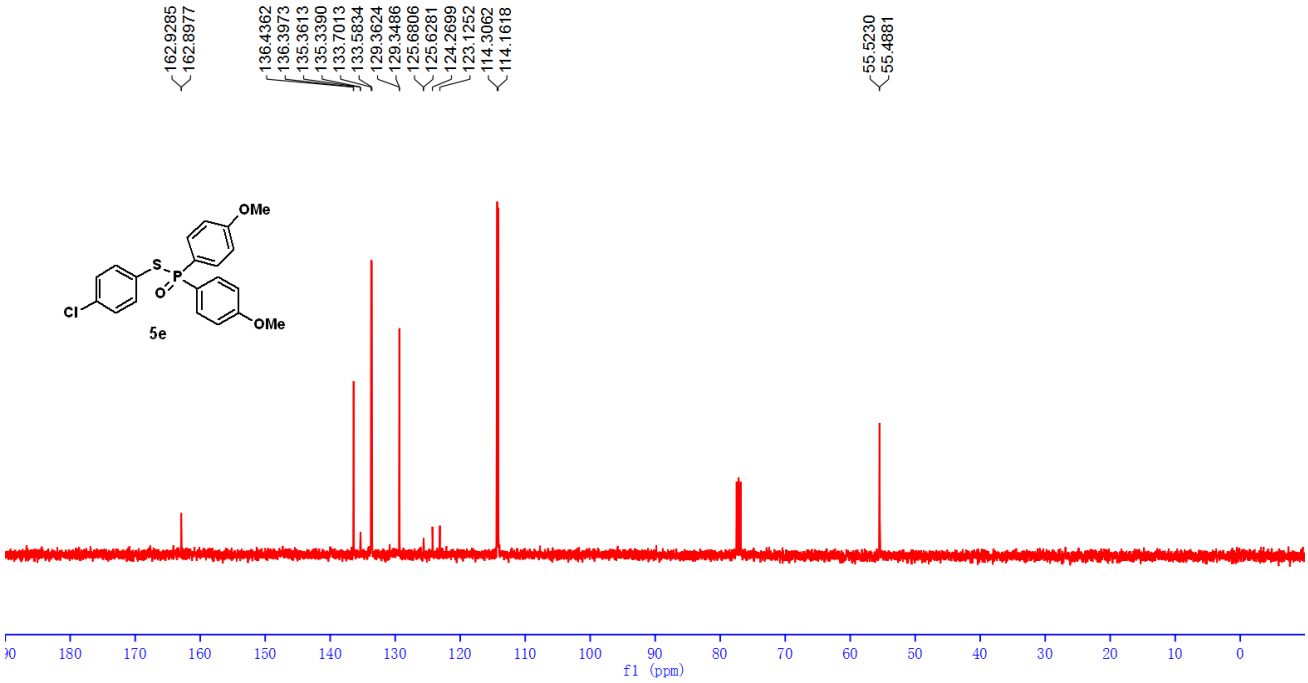
7.7496
7.7403
7.7348
7.7228
7.7184
7.3850
7.3670
7.1862
7.1651
6.9586
6.9516
6.9365
6.9296
3.8374
OMe
S
P
O
Cl
OMe
5e
3.92
1.90
1.89
4.05
6.00
.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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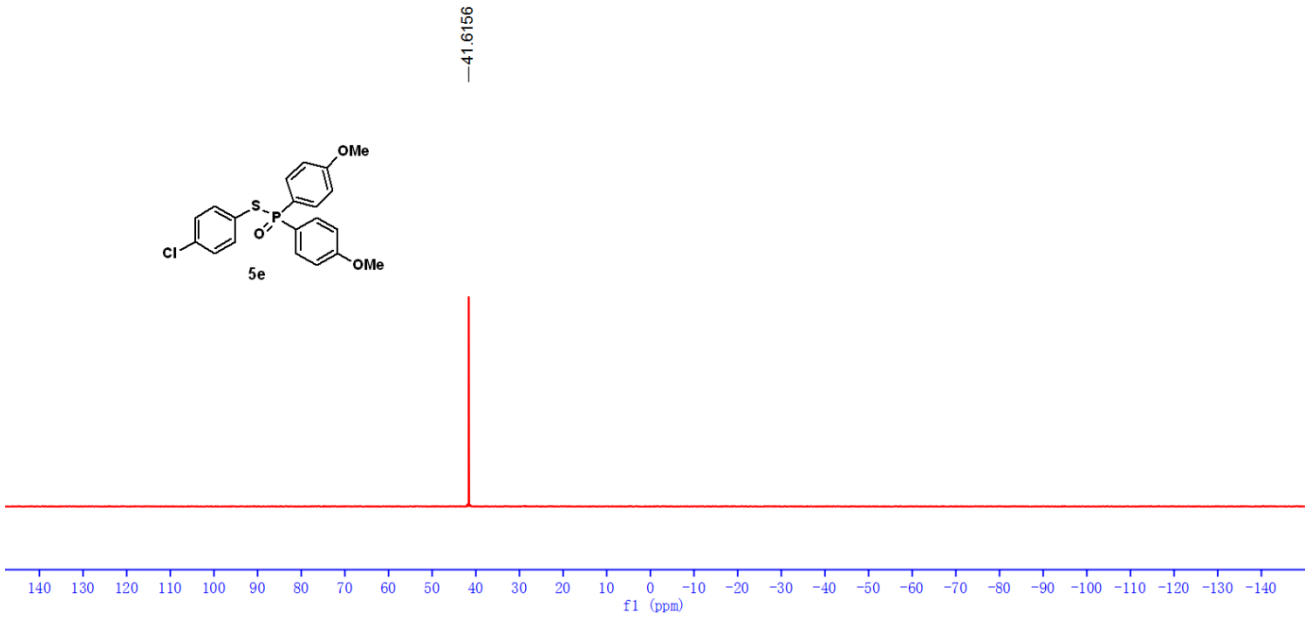
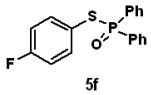
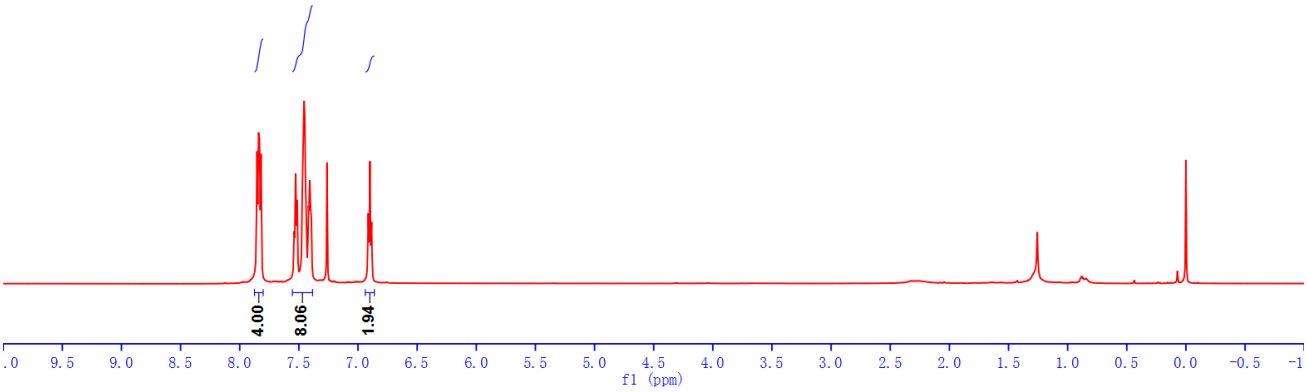
135.3613
135.3390
133.7013
133.5834
129.3624
129.3486
125.6806
125.6281
124.2699
123.1252
114.3062
114.1618
55.5230
55.4881
OMe
S
P
O
Cl
OMe
5e
f1 (ppm)

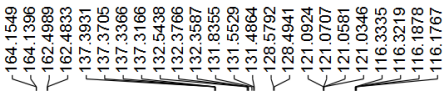

41.6156
OMe
S
P
O
Cl
OMe
5e
f1 (ppm)


7.8539
7.8411
7.8323
7.8197
7.5394
7.5270
7.5146
7.4695
7.4640
7.4568
7.4510
7.4432
7.4380
7.4187
7.4093
7.4047
7.3960
6.9132
6.8891
6.8851


S
Ph
P
O
Ph
F

5f


4.00
8.06
1.94
f1 (ppm)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164.1396
162.4989
162.4833
137.3931
137.3705
137.3366
137.3166
132.5438
132.3766
132.3587
131.8355
131.5529
131.4864
128.5792
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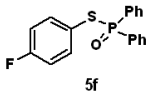
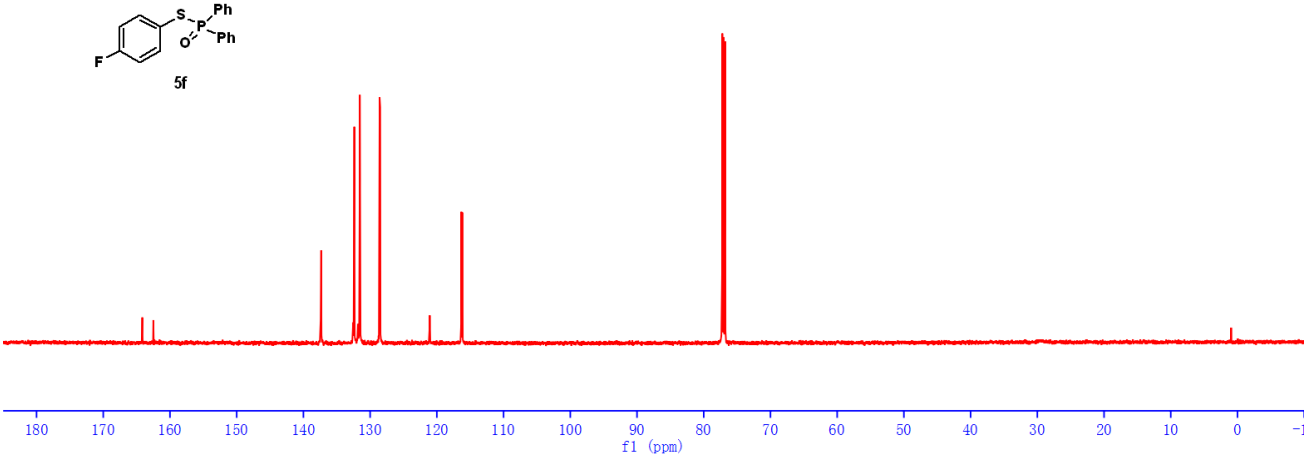
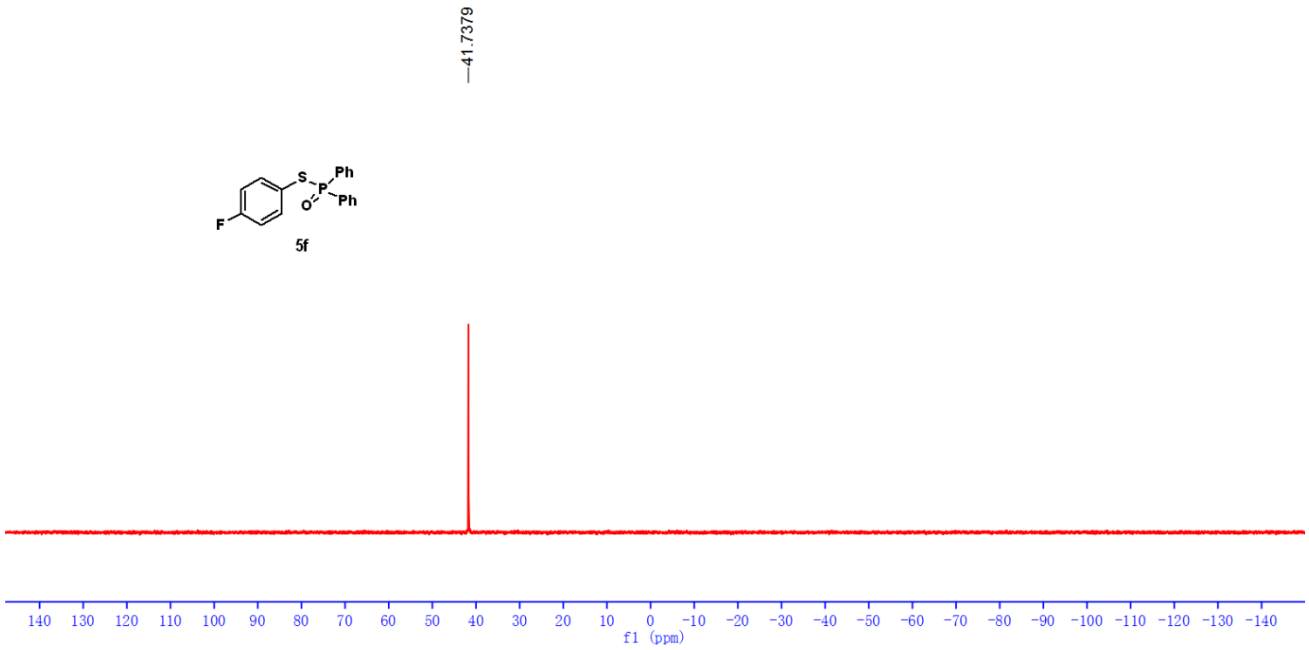
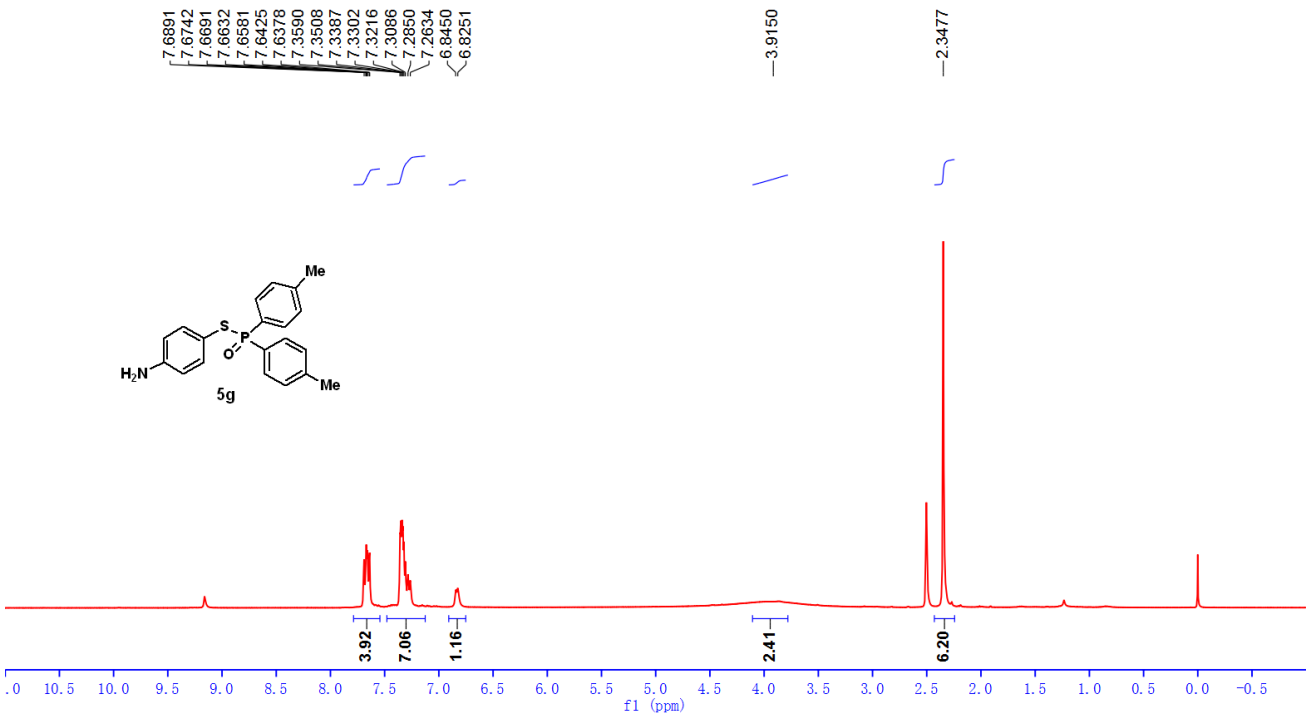
121.0924
121.0707
121.0581
121.0346
116.3335
116.3219
116.1878
116.1767

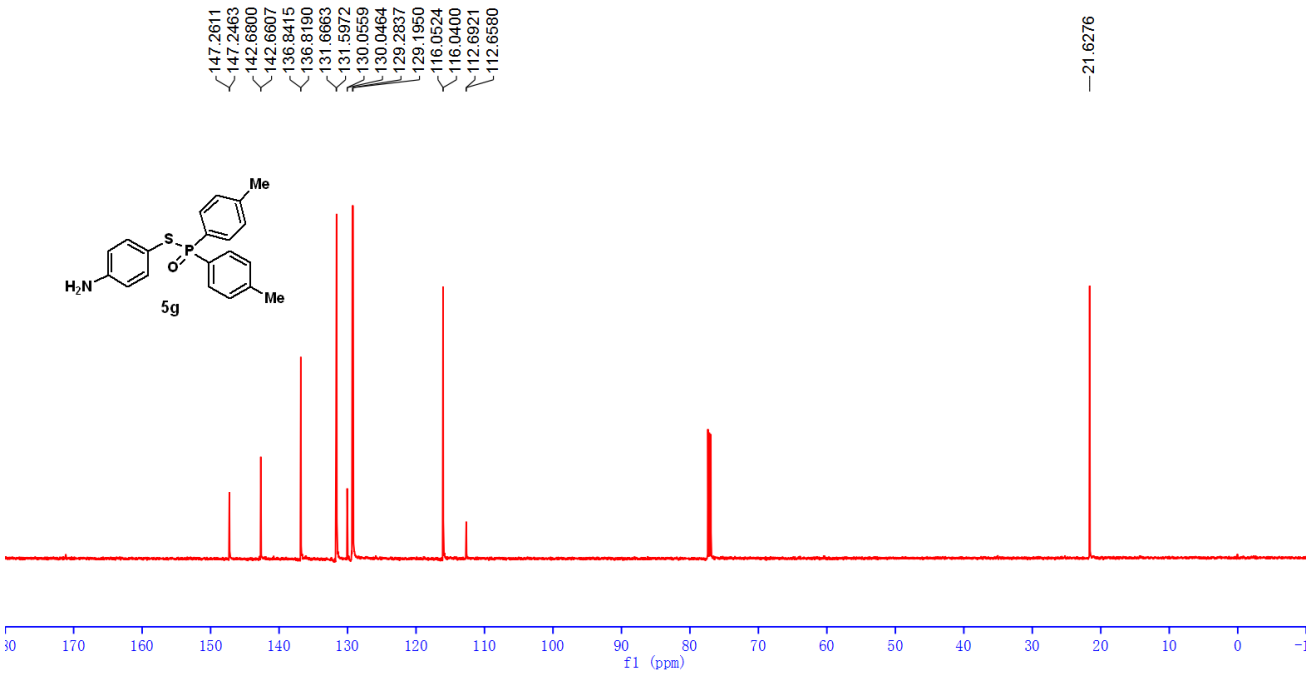

S
Ph
P
O
Ph
F

5f


f1 (ppm)


41.7379
Ph
Ph
S
P
O
F
5f
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
f1 (ppm)


7.6891
7.6742
7.6691
7.6632
7.6581
7.6425
7.6378
7.3590
7.3508
7.3387
7.3302
7.3216
7.3086
7.2850
7.2634
6.8450
6.8251
3.9150
2.3477
Me
S
P
O
H2N
Me
5g
3.92
7.06
1.16
2.41
6.20
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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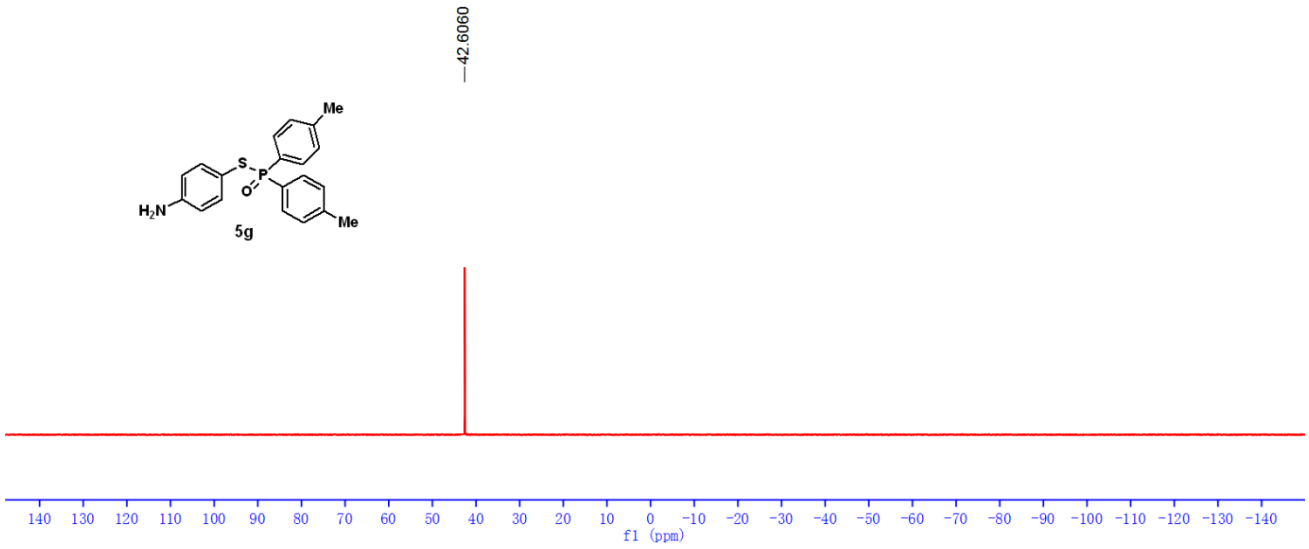
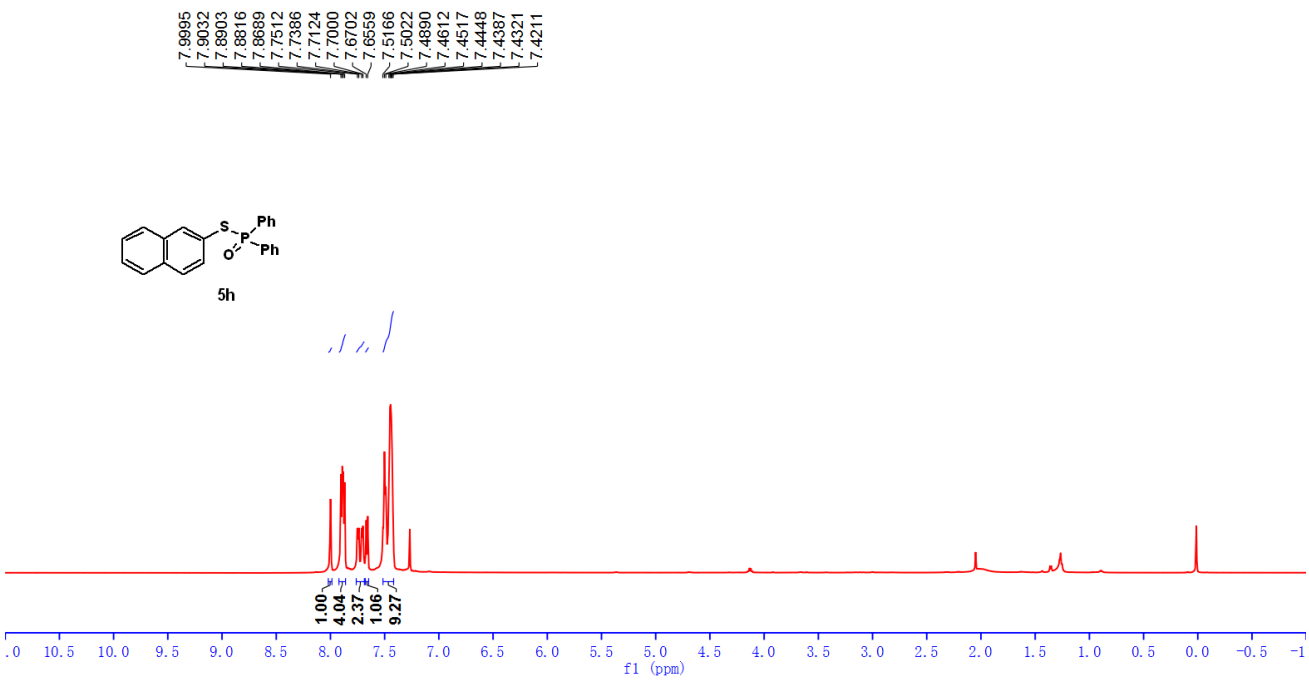
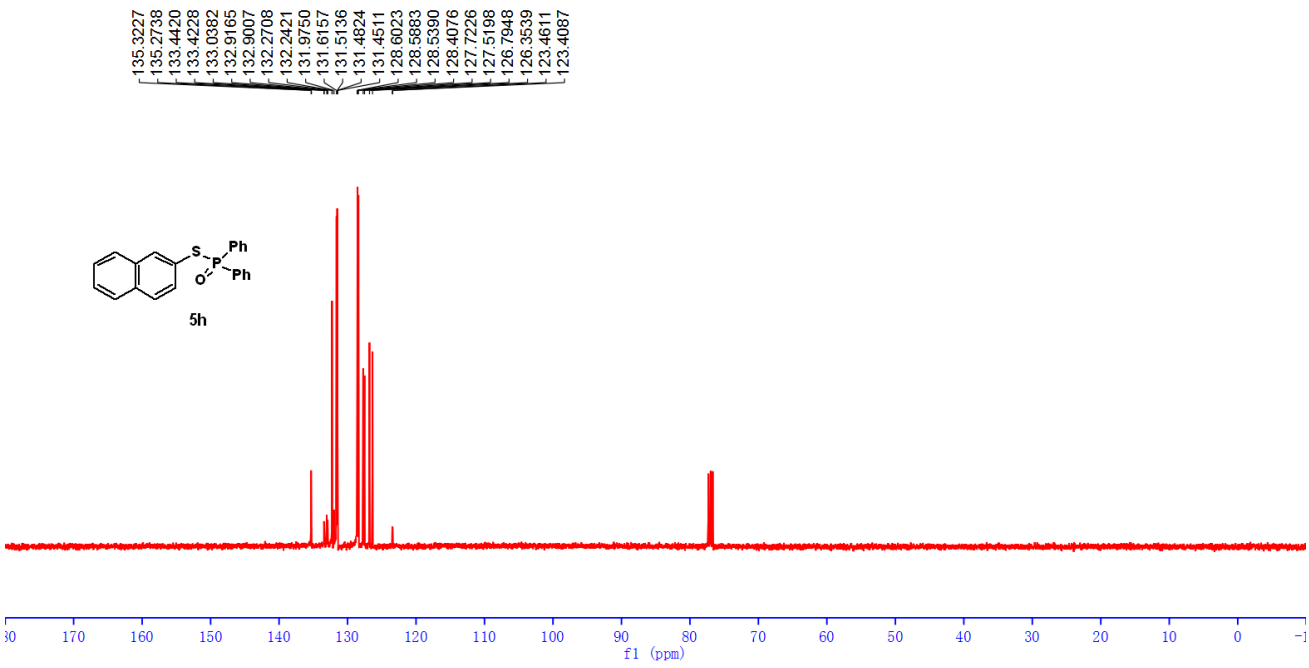
147.2463
142.6800
142.6607
136.8415
136.8190
131.6663
131.5972
130.0559
130.0464
129.2837
129.1950
116.0524
116.0400
112.6921
112.6580
21.6276
Me
S
P
O
H2N
Me
5g
f1 (ppm)


42.6060
Me
S
P
O
H2N
Me
5g
f1 (ppm)


7.9995
7.9032
7.8903
7.8816
7.8689
7.7512
7.7386
7.7124
7.7000
7.6702
7.6559
7.5166
7.5022
7.4890
7.4612
7.4517
7.4448
7.4387
7.4321
7.4211
S
P
O
Ph
Ph
5h
1.00
4.04
2.37
1.06
9.27
f1 (ppm)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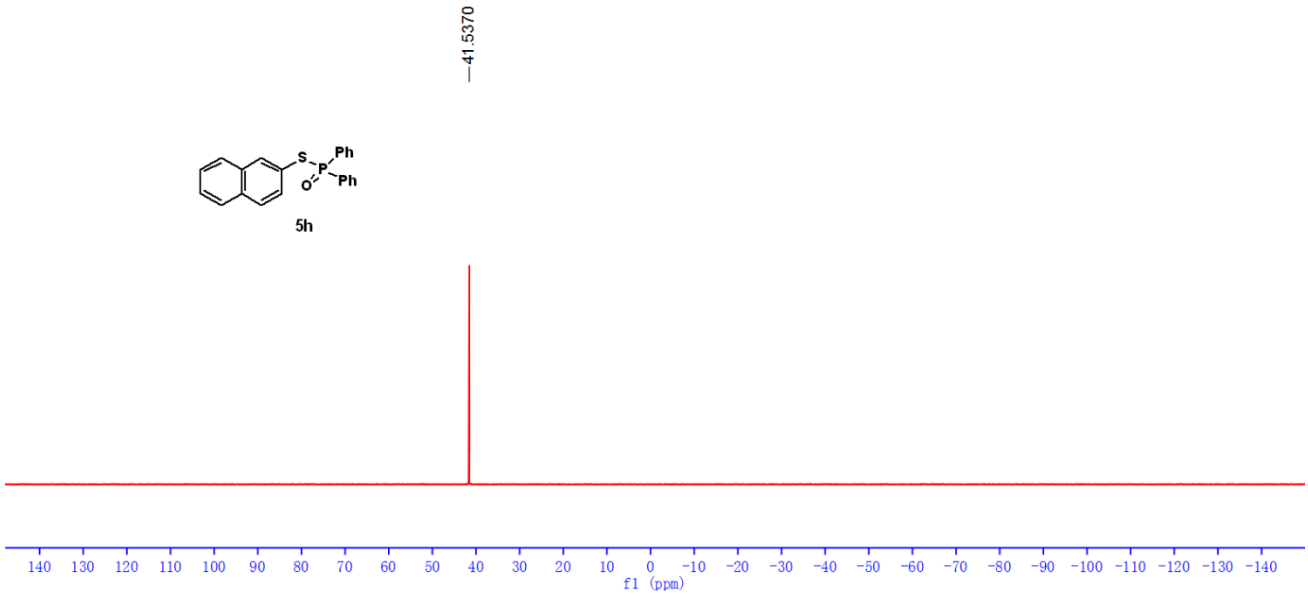
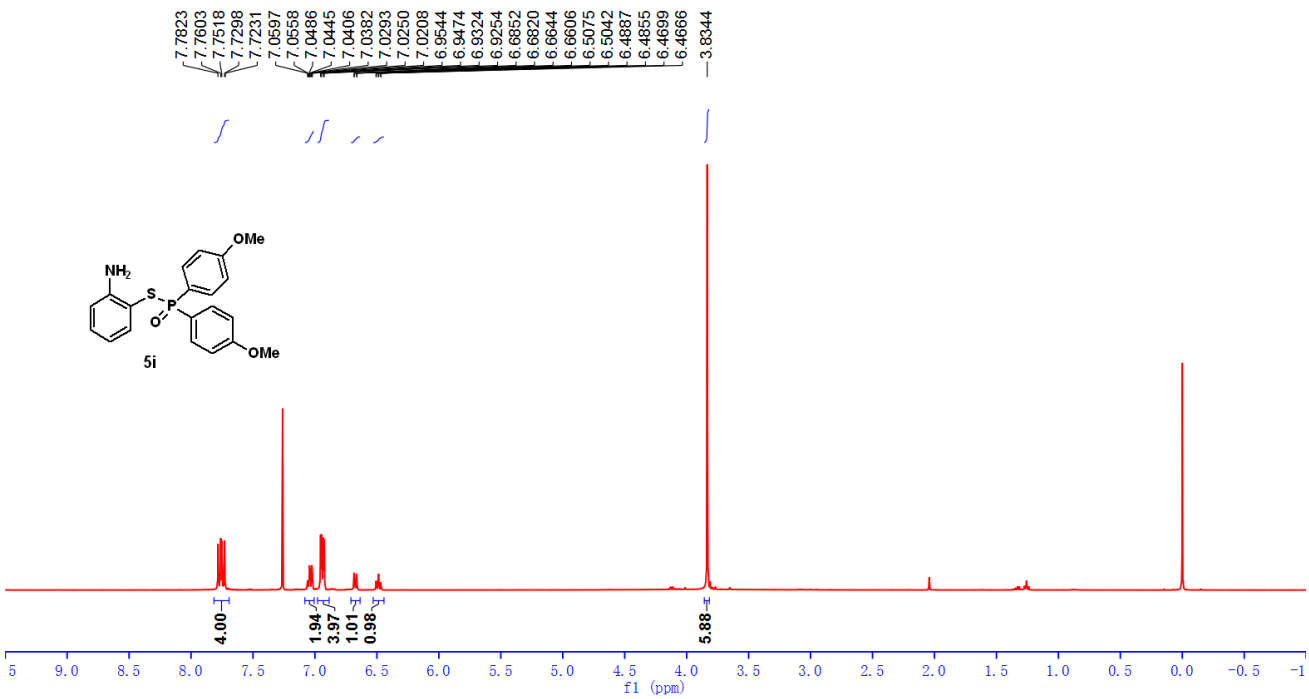
135.2738
133.4420
133.4228
133.0382
132.9165
132.9007
132.2708
132.2421
131.9750
131.6157
131.5136
131.4824
131.4511
128.6023
128.5883
128.5390
128.4076
127.7226
127.5198
126.7948
126.3539
123.4611
123.4087
S
P
O
Ph
Ph
5h
f1 (ppm)


41.5370
Ph
Ph
S
P
O
5h
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
f1 (ppm)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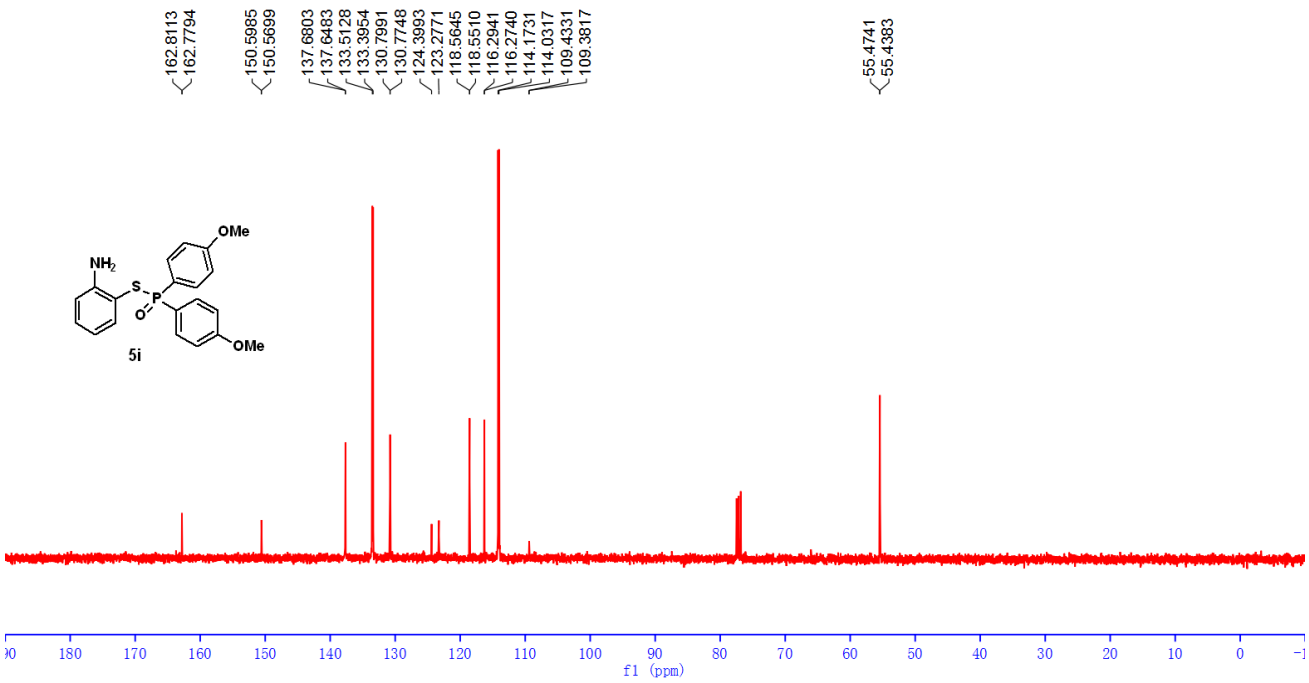
7.7298
7.7231
7.0597
7.0558
7.0486
7.0445
7.0406
7.0382
7.0293
7.0250
7.0208
6.9544
6.9474
6.9324
6.9254
6.6852
6.6820
6.6644
6.6606
6.5075
6.5042
6.4887
6.4855
6.4699
6.4666
3.8344
NH2
S
P
O
OMe
OMe
5i
4.00
1.94
3.97
1.01
0.98
5.88
5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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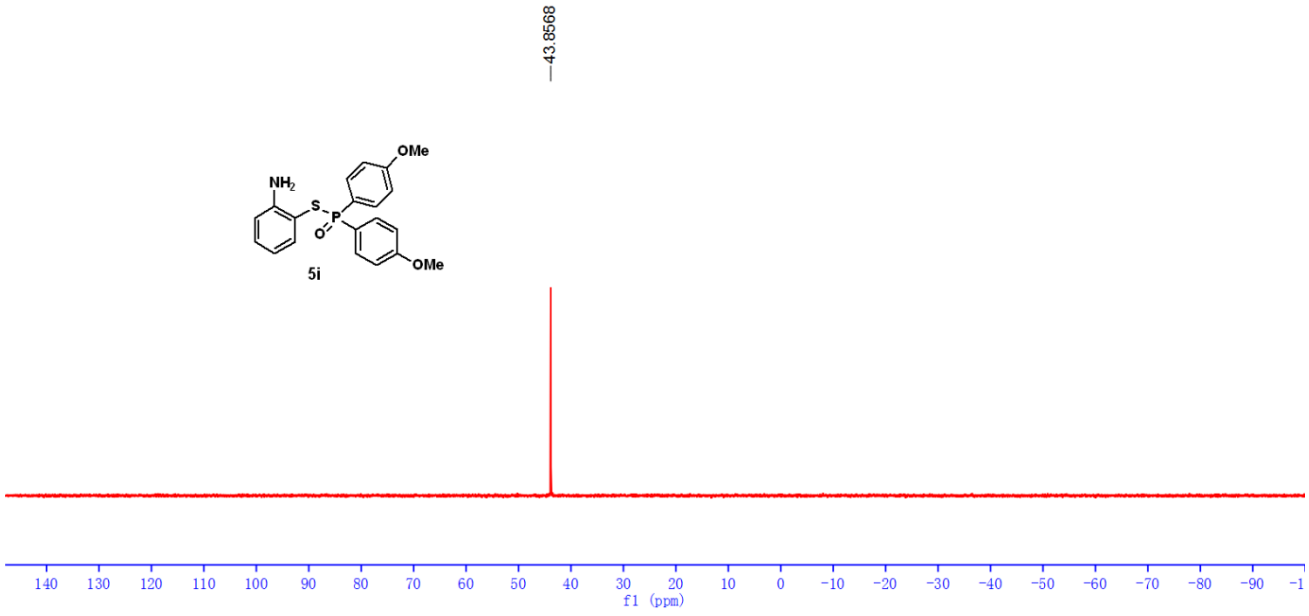
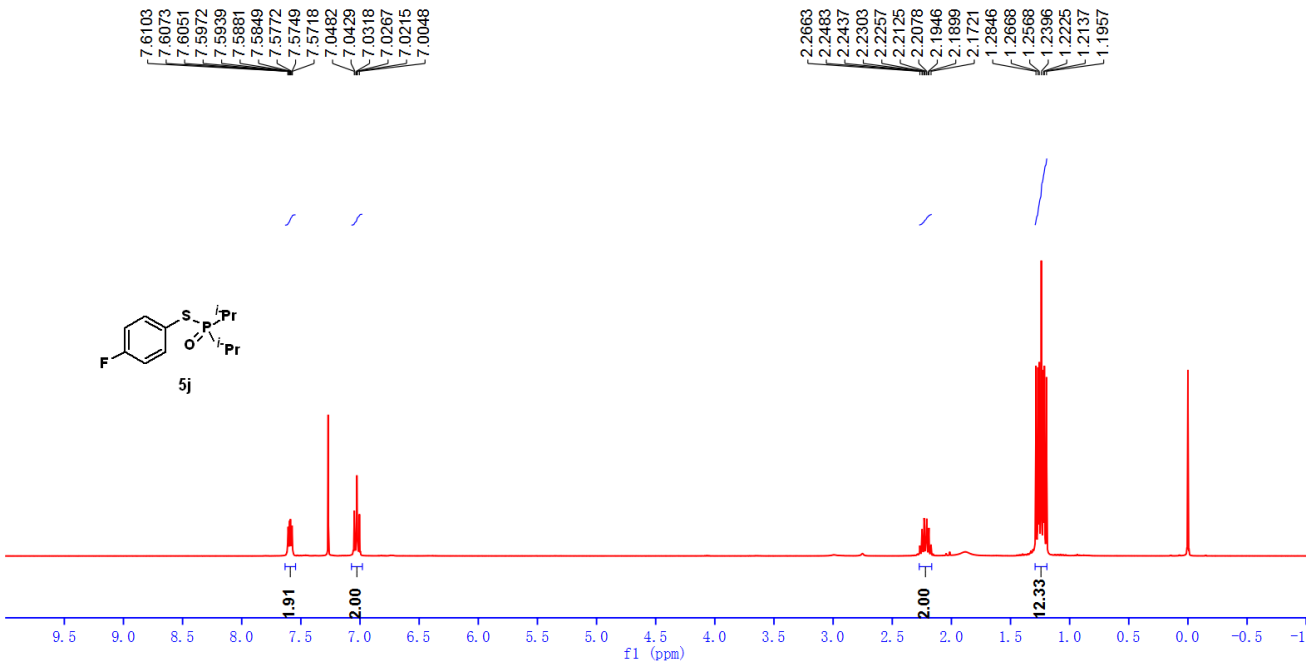
133.5128
133.3954
130.7991
130.7748
124.3993
123.2771
118.5645
118.5510
116.2941
116.2740
114.1731
114.0317
109.4331
109.3817
55.4741
55.4383
NH2
S
P
O
OMe
OMe
5i
f1 (ppm)


43.8568
NH2
S
P
O
OMe
OMe
5i
f1 (ppm)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7.6051
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7.5939
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7.5849
7.5772
7.5749
7.5718
7.0482
7.0429
7.0318
7.0267
7.0215
7.0048
2.2663
2.2483
2.2437
2.2303
2.2257
2.2125
2.2078
2.1946
2.1899
2.1721
1.2846
1.2668
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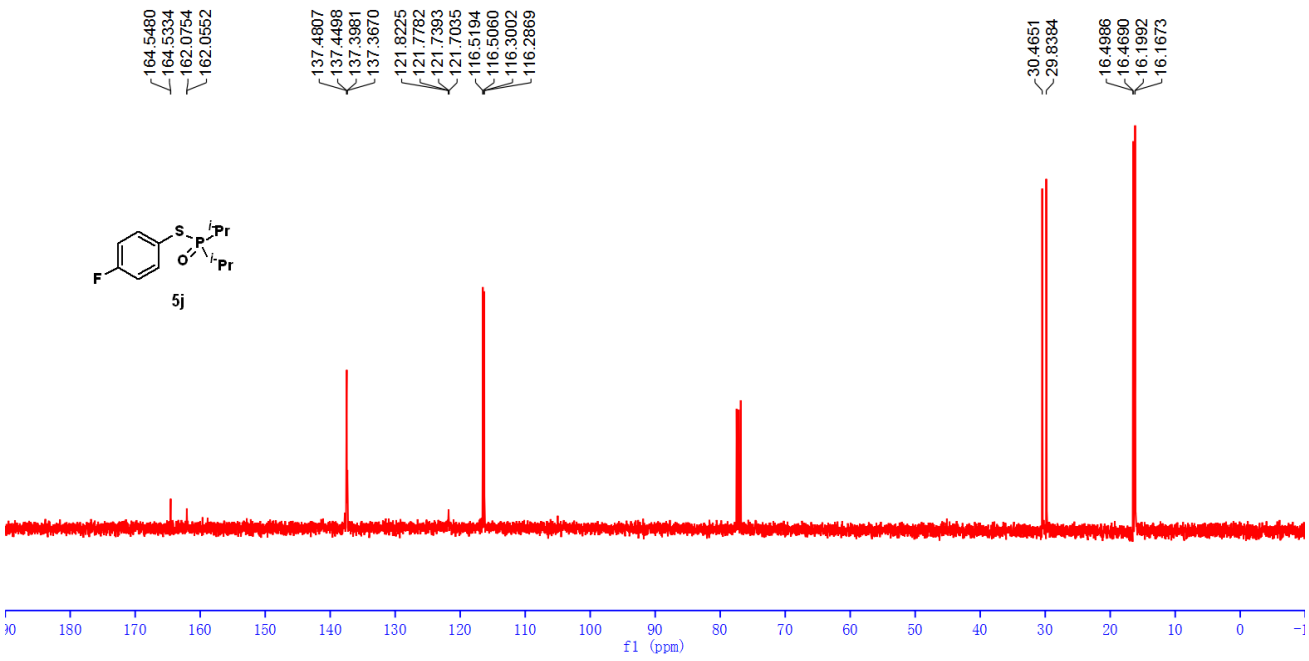
1.2396
1.2225
1.2137
1.1957
5j
1.91
2.00
2.00
12.33
f1 (ppm)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137.3981
137.3670
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121.7782
121.7393
121.7035
116.5194
116.5060
116.3002
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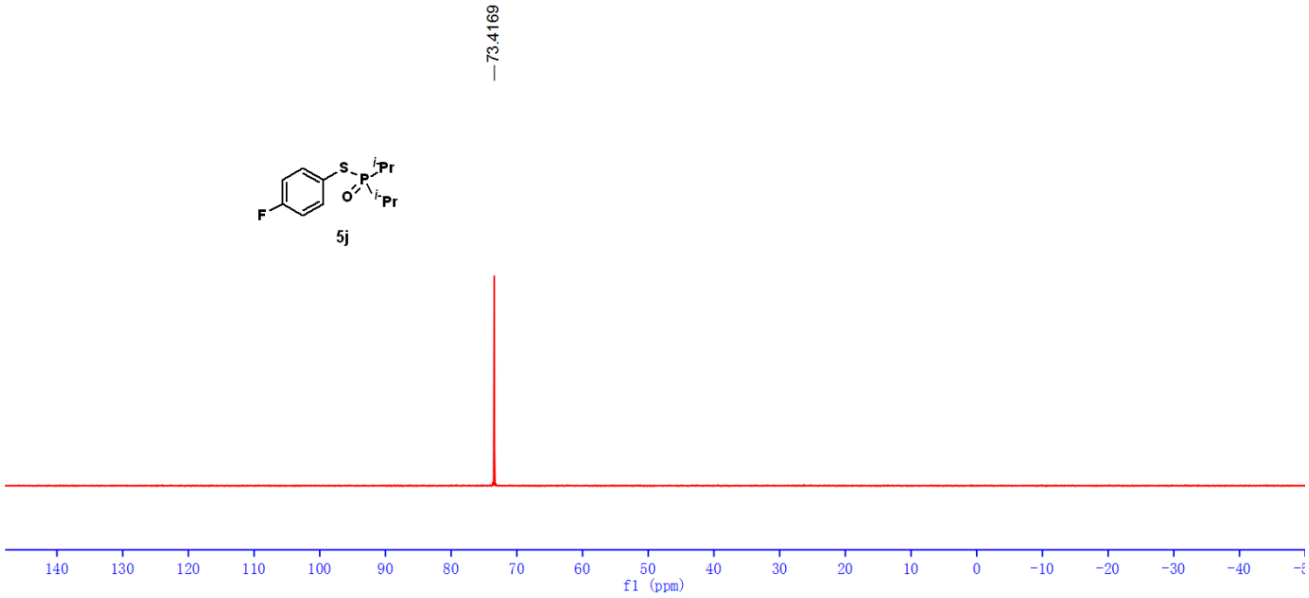
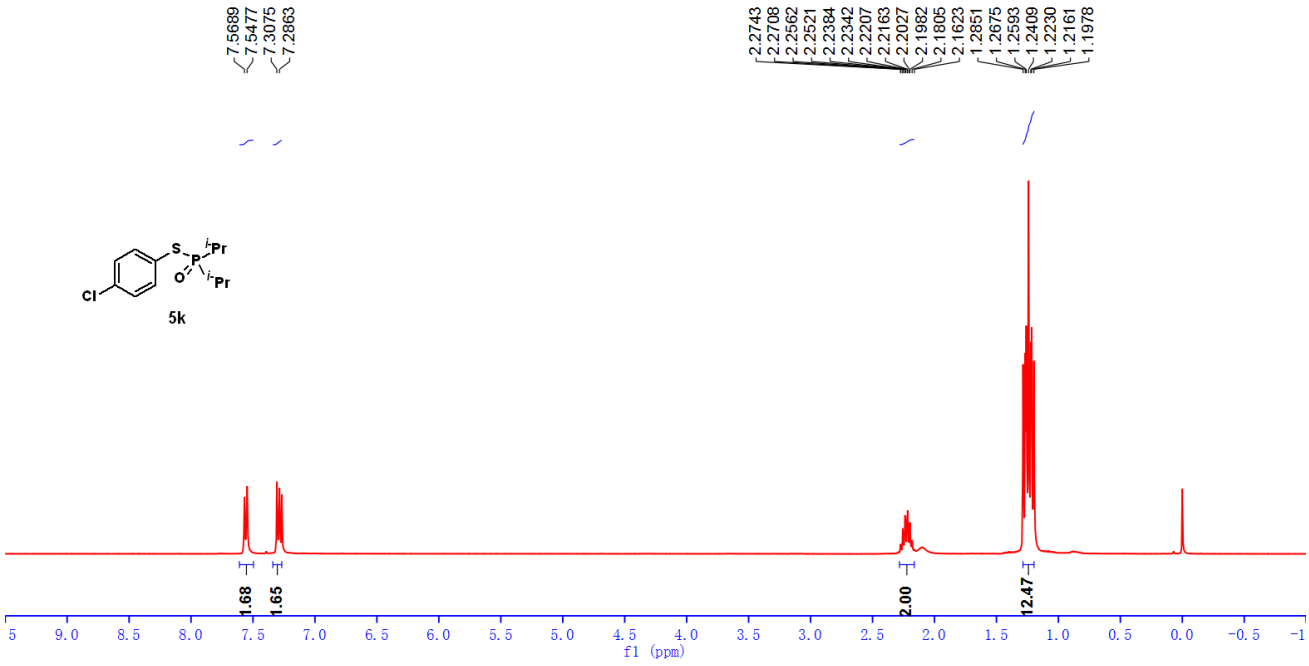
30.4651
29.8384
16.4986
16.4690
16.1992
16.1673
5j
f1 (ppm)


73.4169
F
5j
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)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7.3075
7.2863
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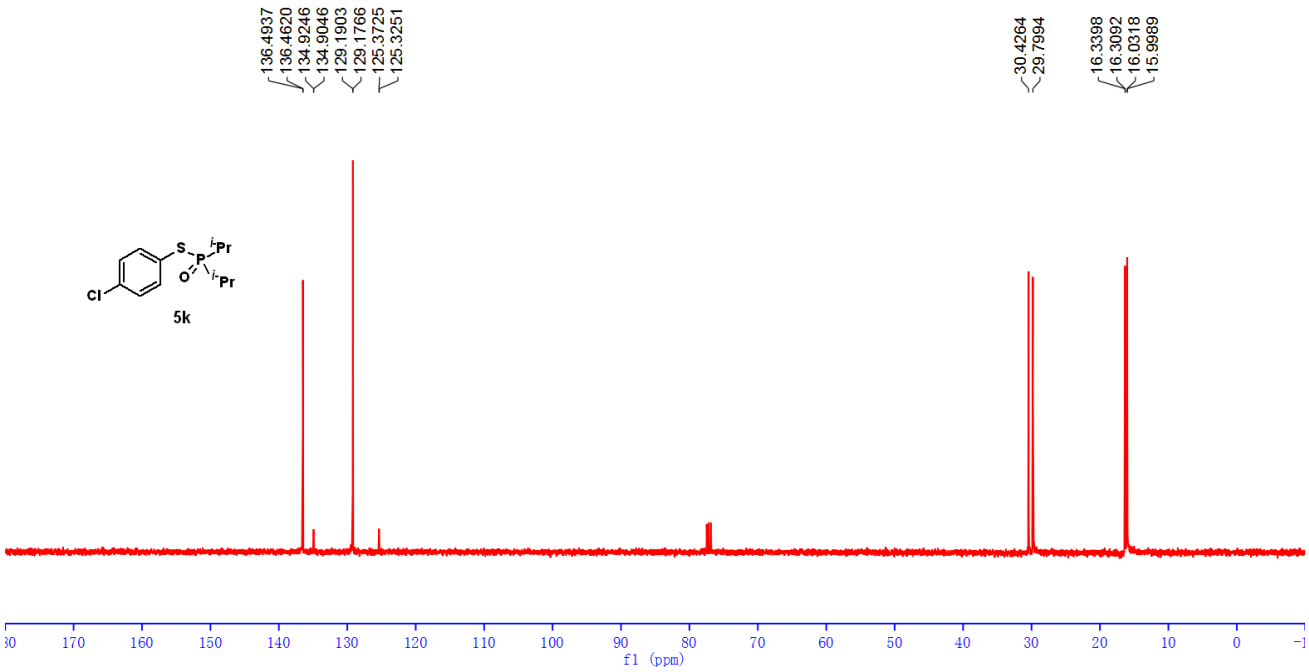
2.2708
2.2562
2.2521
2.2384
2.2342
2.2207
2.2163
2.2027
2.1982
2.1805
2.1623
1.2851
1.2675
1.2593
1.2409
1.2230
1.2161
1.1978
Cl
5k
1.68
1.65
2.00
12.47
5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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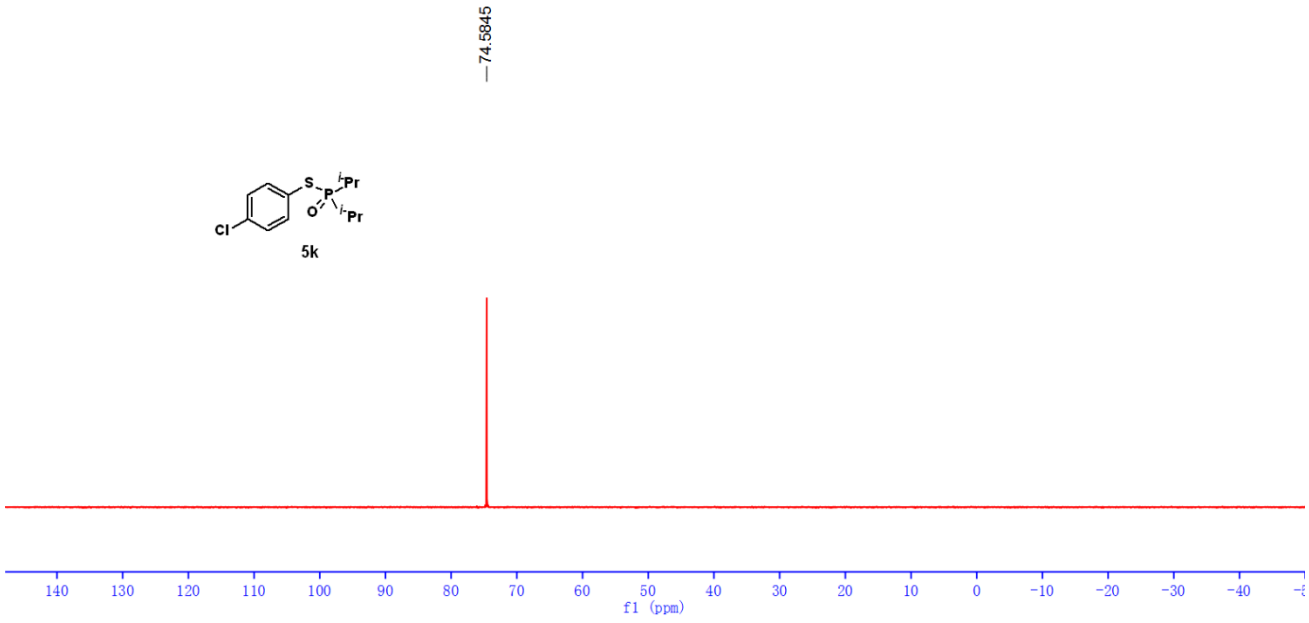
134.9246
134.9046
129.1903
129.1766
125.3725
125.3251
30.4264
29.7994
16.3398
16.3092
16.0318
15.9989
Cl
S
P
O
iPr
iPr
5k
f1 (ppm)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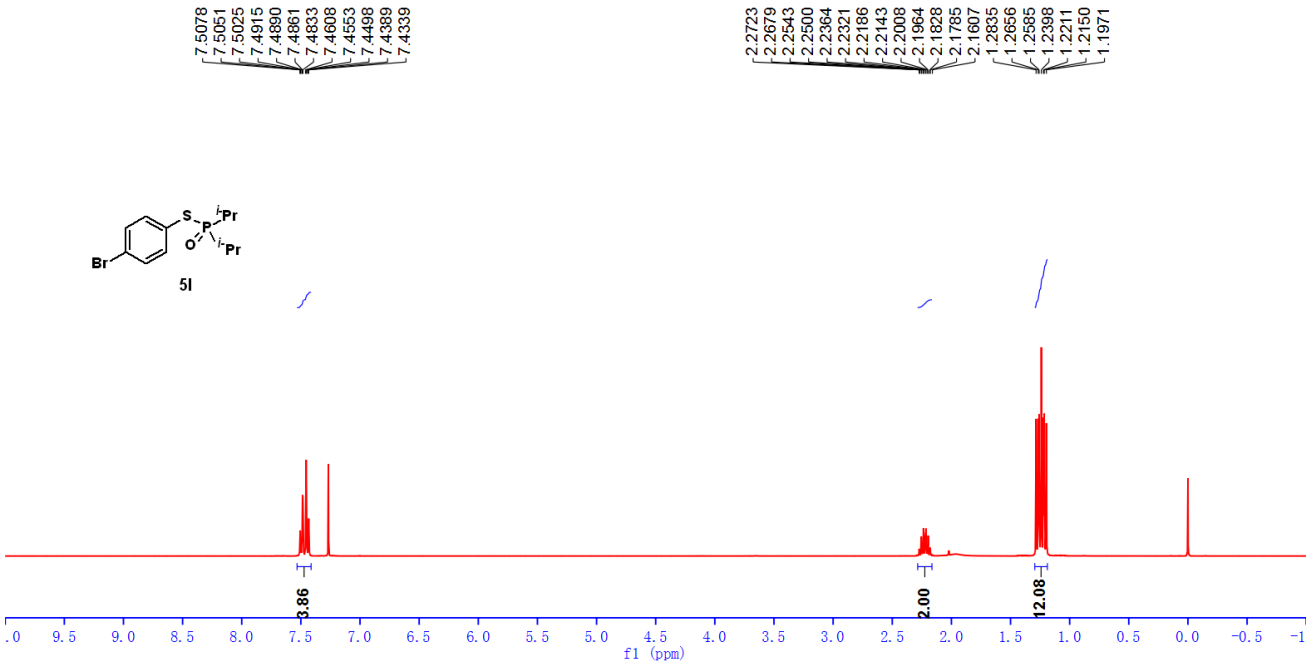
P
O
iPr
iPr
5k
f1 (ppm)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7.5025
7.4915
7.4890
7.4861
7.4833
7.4608
7.4553
7.4498
7.4389
7.4339
2.2723
2.2679
2.2543
2.2500
2.2364
2.2321
2.2186
2.2143
2.2008
2.1964
2.1828
2.1785
2.1607
1.2835
1.2656
1.2585
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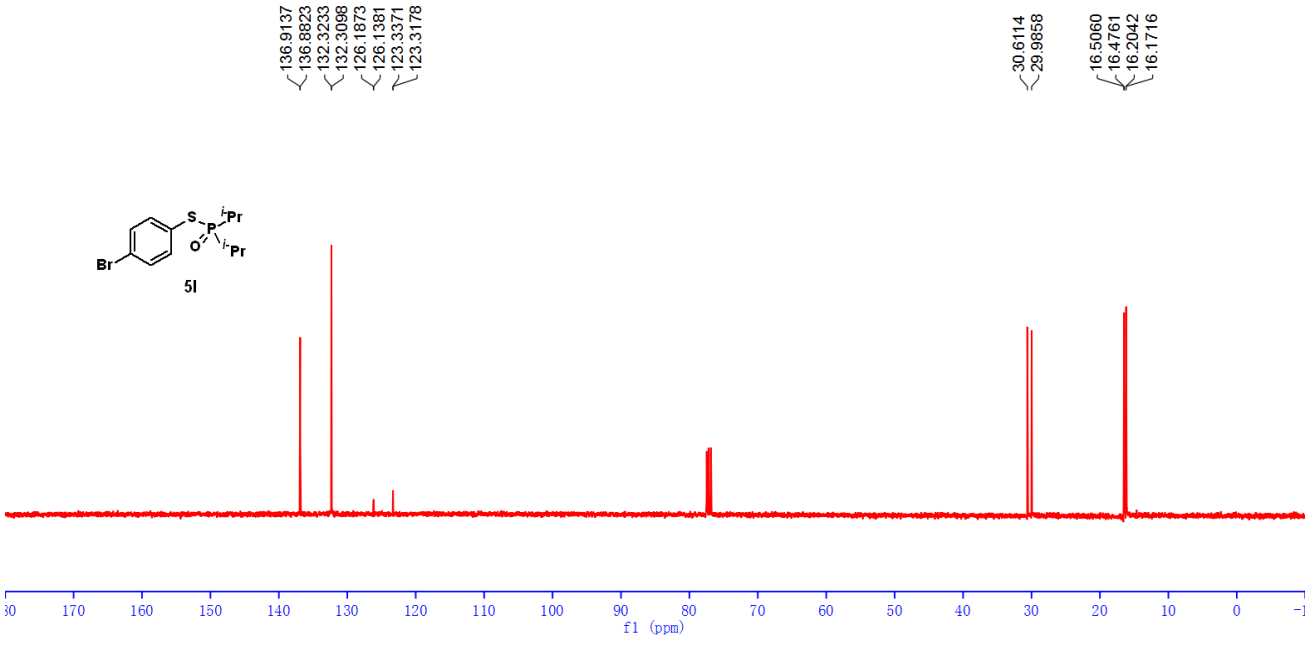
1.2211
1.2150
1.1971
Br
5l
3.86
2.00
12.08
f1 (ppm)


136.9137
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132.3098
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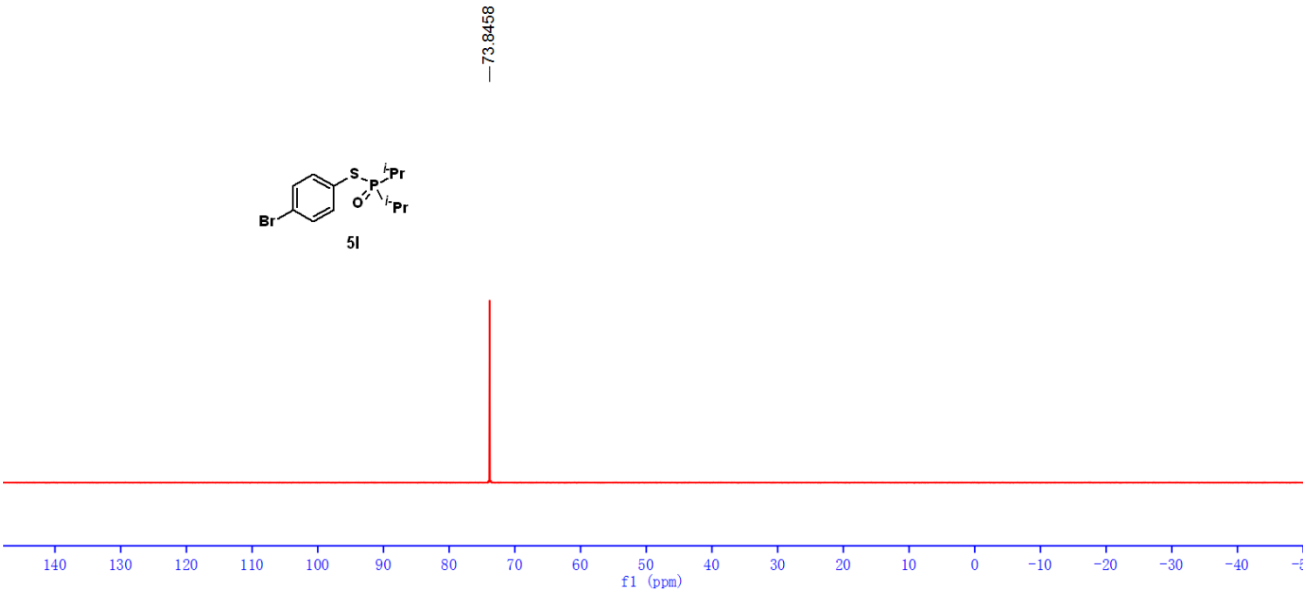
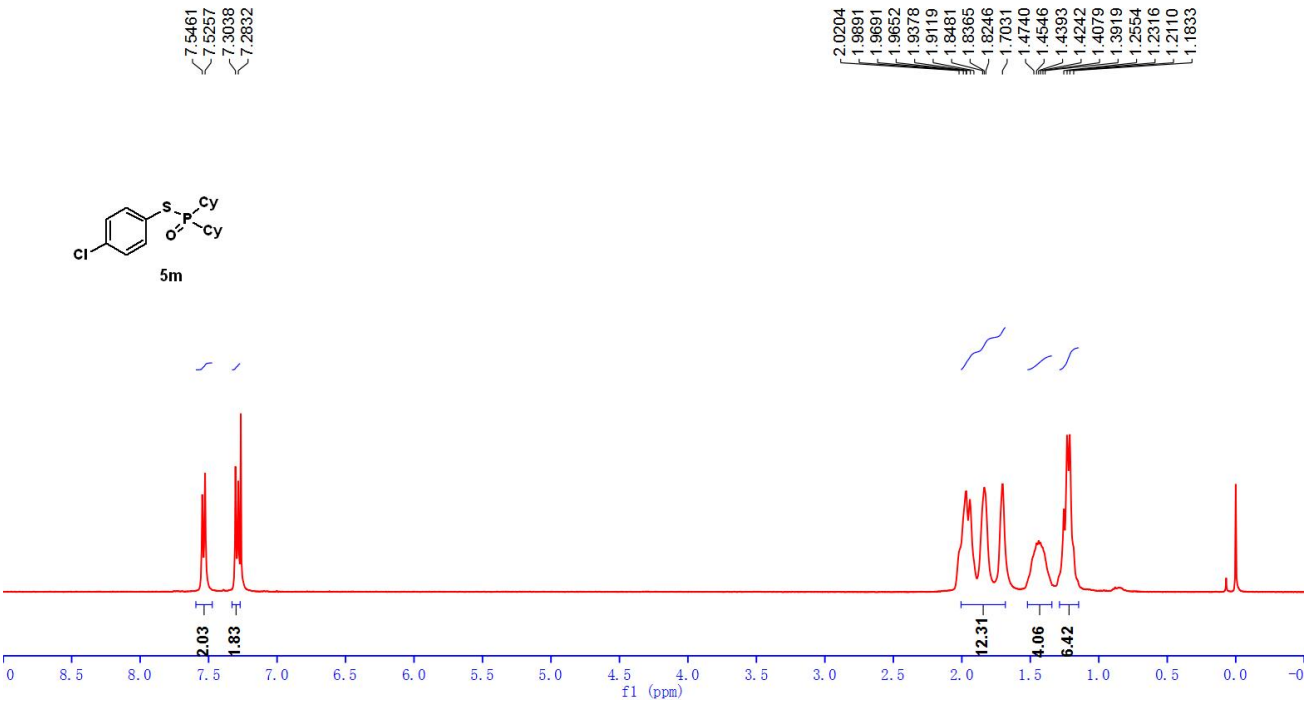
126.1381
123.3371
123.3178
30.6114
29.9858
16.5060
16.4761
16.2042
16.1716
Br
5l
f1 (ppm)


73.8458
Br
S
P
O
iPr
iPr
5l
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)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1.9119
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1.8365
1.8246
1.7031
1.4740
1.4546
1.4393
1.4242
1.4079
1.3919
1.2554
1.2316
1.2110
1.1833
Cl
S
P
O
Cy
Cy
5m
2.03
1.83
12.31
4.06
6.42
0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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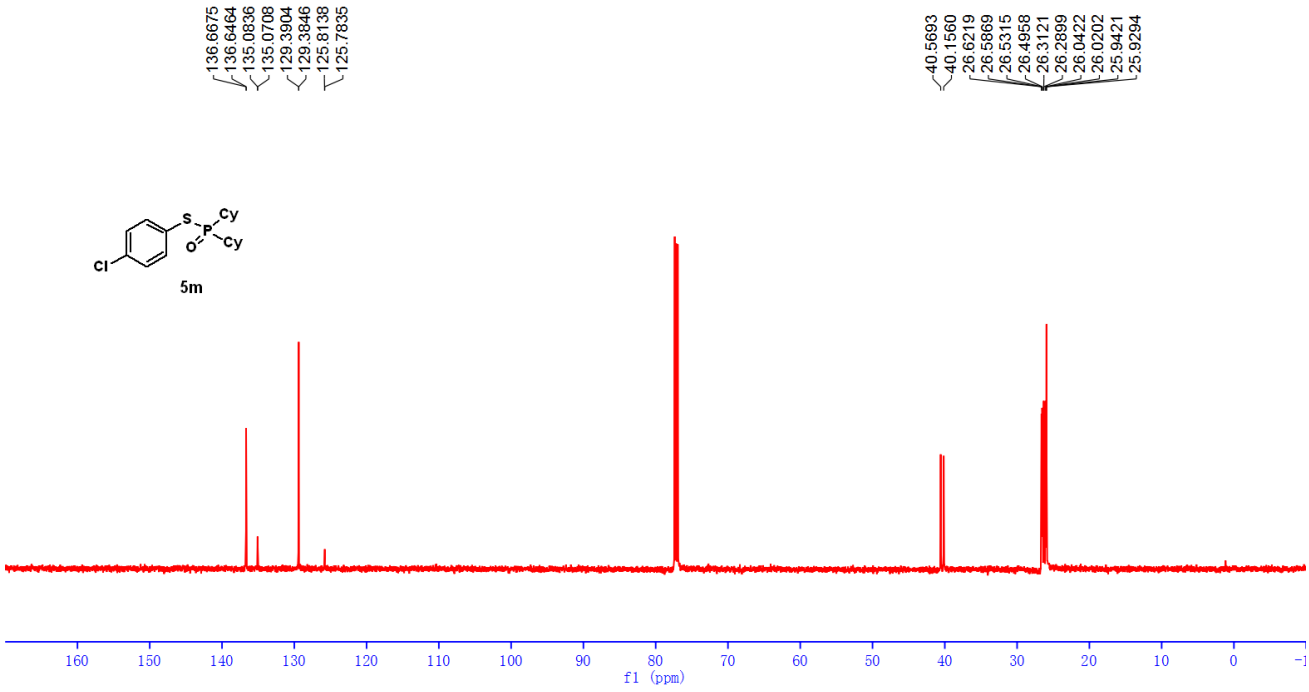
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125.8138
125.7835
40.5693
40.1560
26.6219
26.5869
26.5315
26.4958
26.3121
26.2899
26.0422
26.0202
25.9421
25.9294
Cl
S
P
O
Cy
Cy
5m
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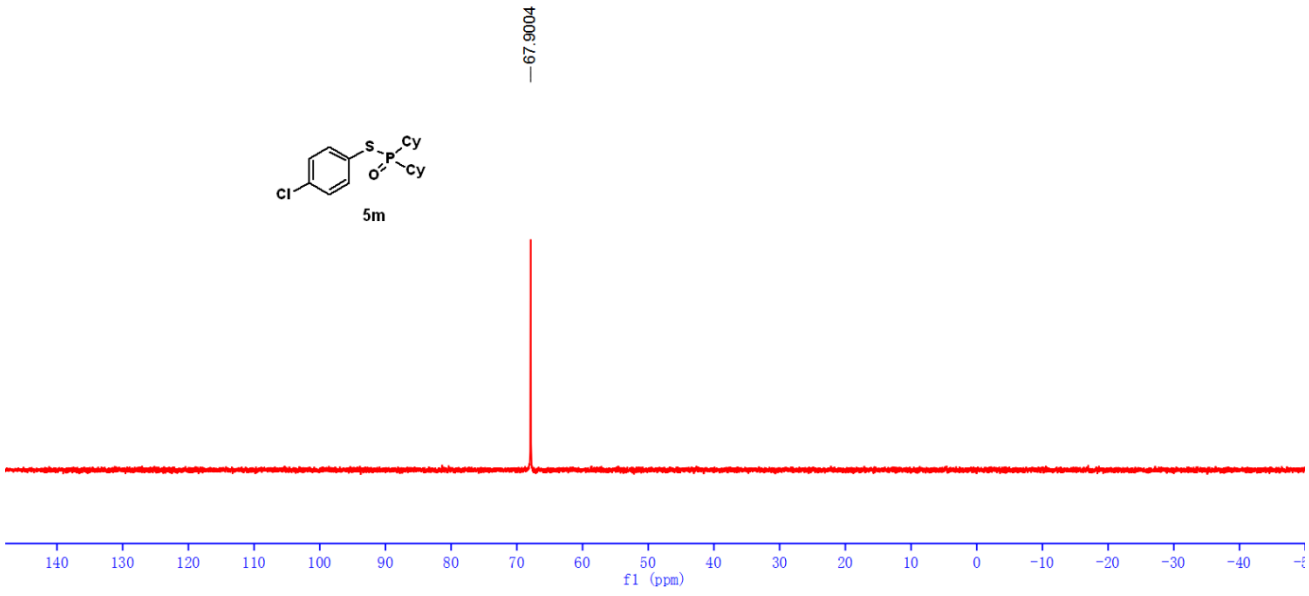
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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P
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Cy
Cy
5m
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130
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-20
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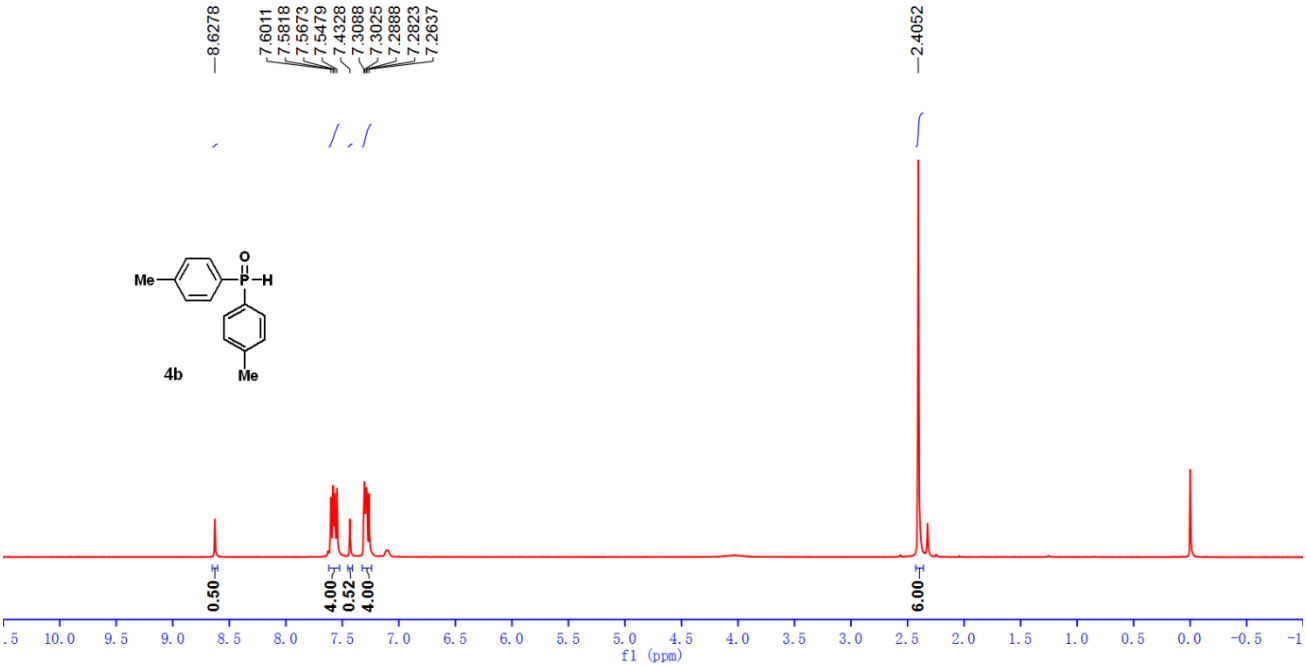
-40
f1 (ppm)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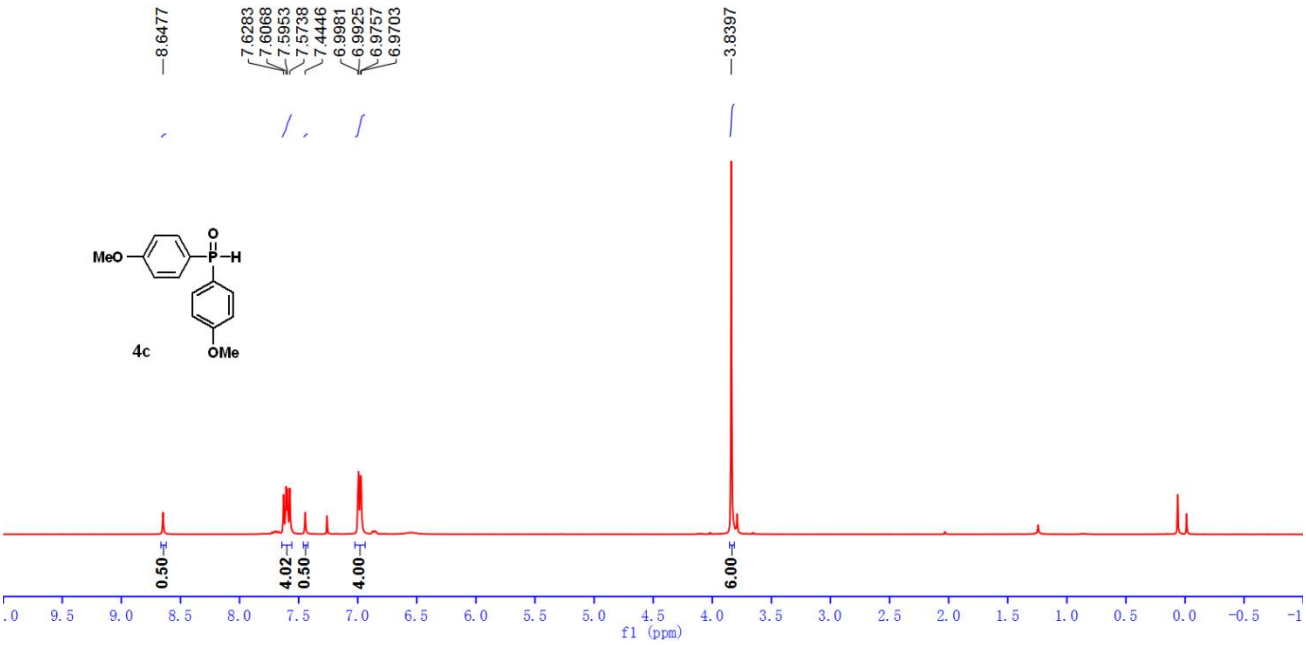
7.6011
7.5818
7.5673
7.5479
7.4328
7.3088
7.3025
7.2888
7.2823
7.2637
2.4052
Me
O
P
H
Me
4b
0.50
4.00
0.52
4.00
6.00
f1 (ppm)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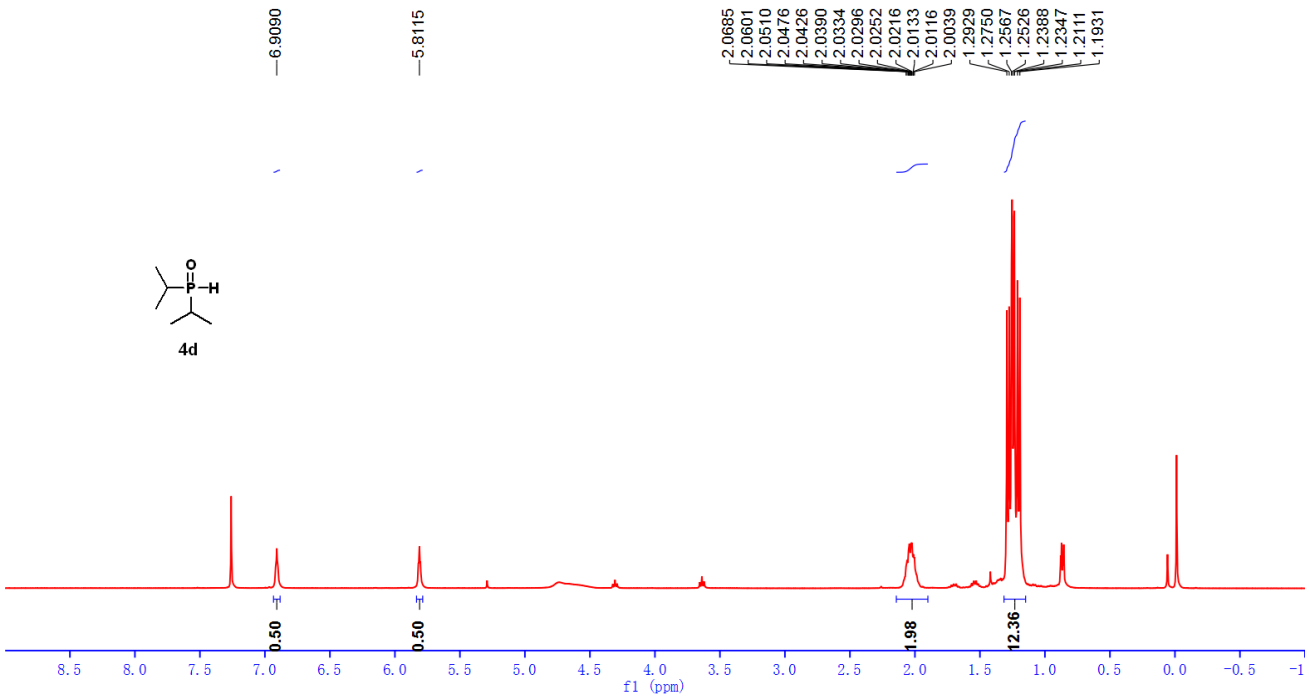
7.6283
7.6068
7.5953
7.5738
7.4446
6.9981
6.9925
6.9757
6.9703
3.8397
MeO
O
P
H
OMe
4c
0.50
4.02
0.50
4.00
6.00
f1 (ppm)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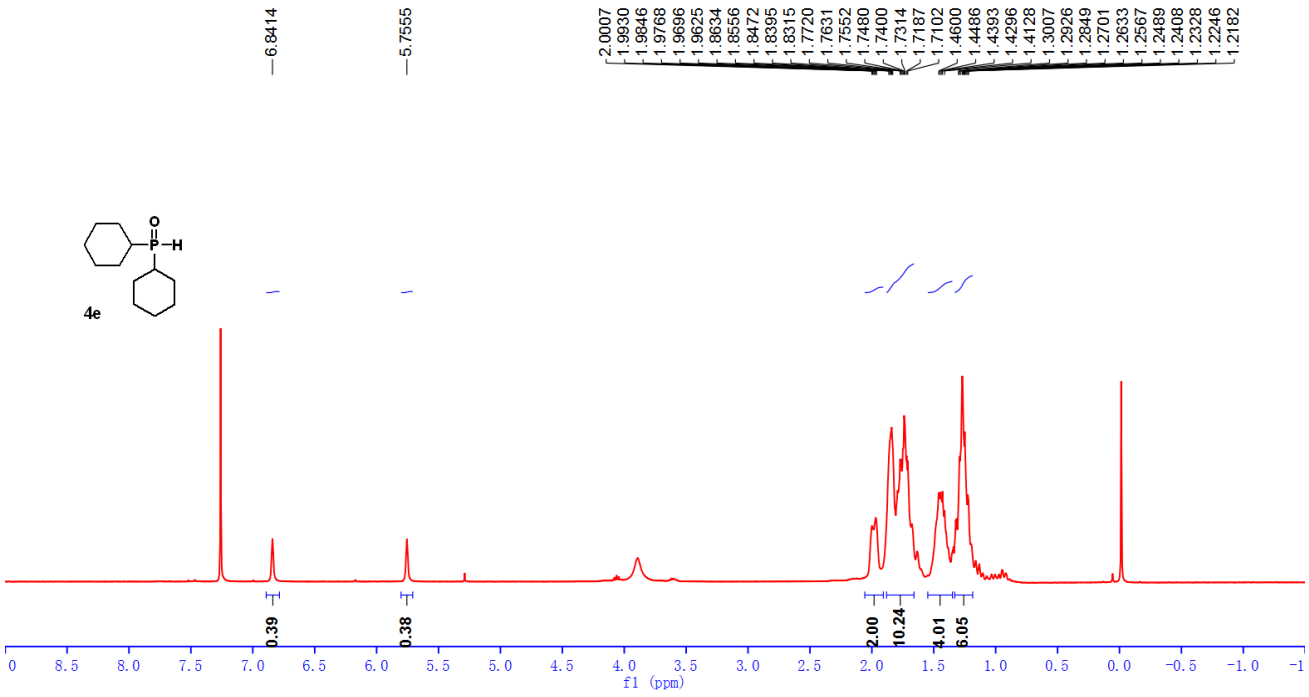
5.8115
2.0685
2.0601
2.0510
2.0476
2.0426
2.0390
2.0334
2.0296
2.0252
2.0216
2.0133
2.0116
2.0039
1.2929
1.2750
1.2567
1.2526
1.2388
1.2347
1.2111
1.1931
4d
0.50
0.50
1.98
12.36
f1 (ppm)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5.7555
2.0007
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1.8634
1.8556
1.8472
1.8395
1.8315
1.7720
1.7631
1.7552
1.7480
1.7400
1.7314
1.7187
1.7102
1.4600
1.4486
1.4393
1.4296
1.4128
1.3007
1.2926
1.2849
1.2701
1.2633
1.2567
1.2489
1.2408
1.2328
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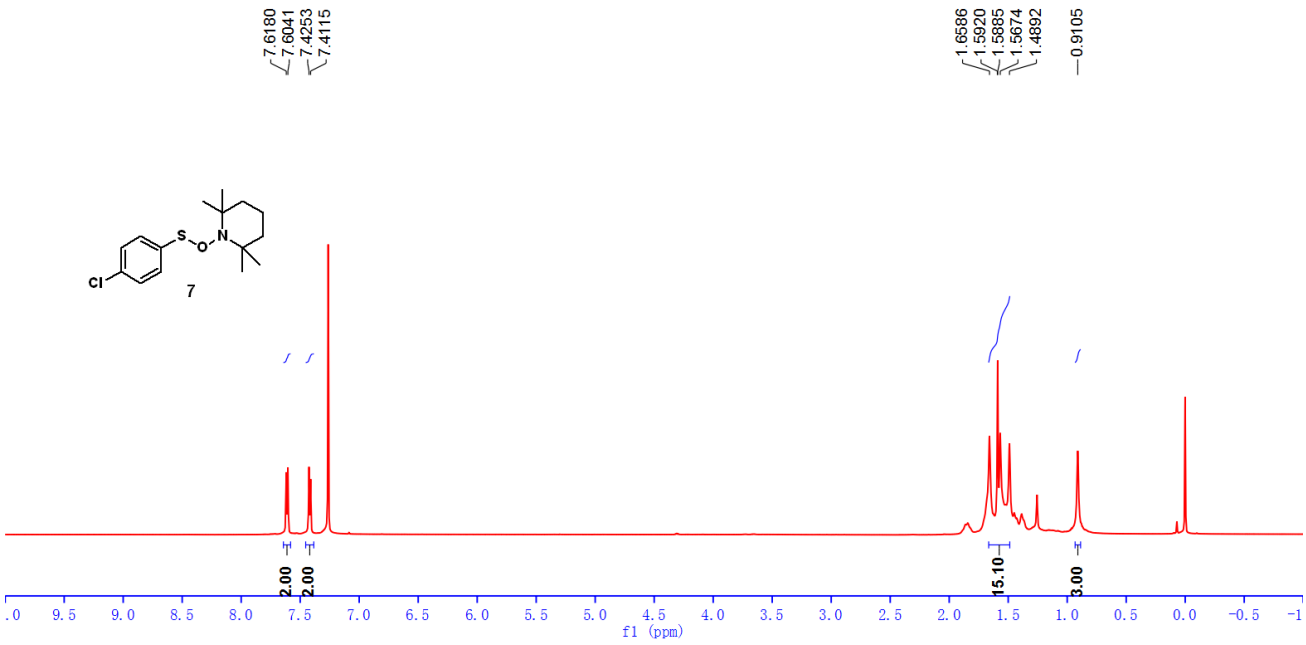
1.2182
4e
0.39
0.38
2.00
10.24
4.01
6.05
f1 (ppm)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7.6041
7.4253
7.4115
1.6586
1.5920
1.5885
1.5674
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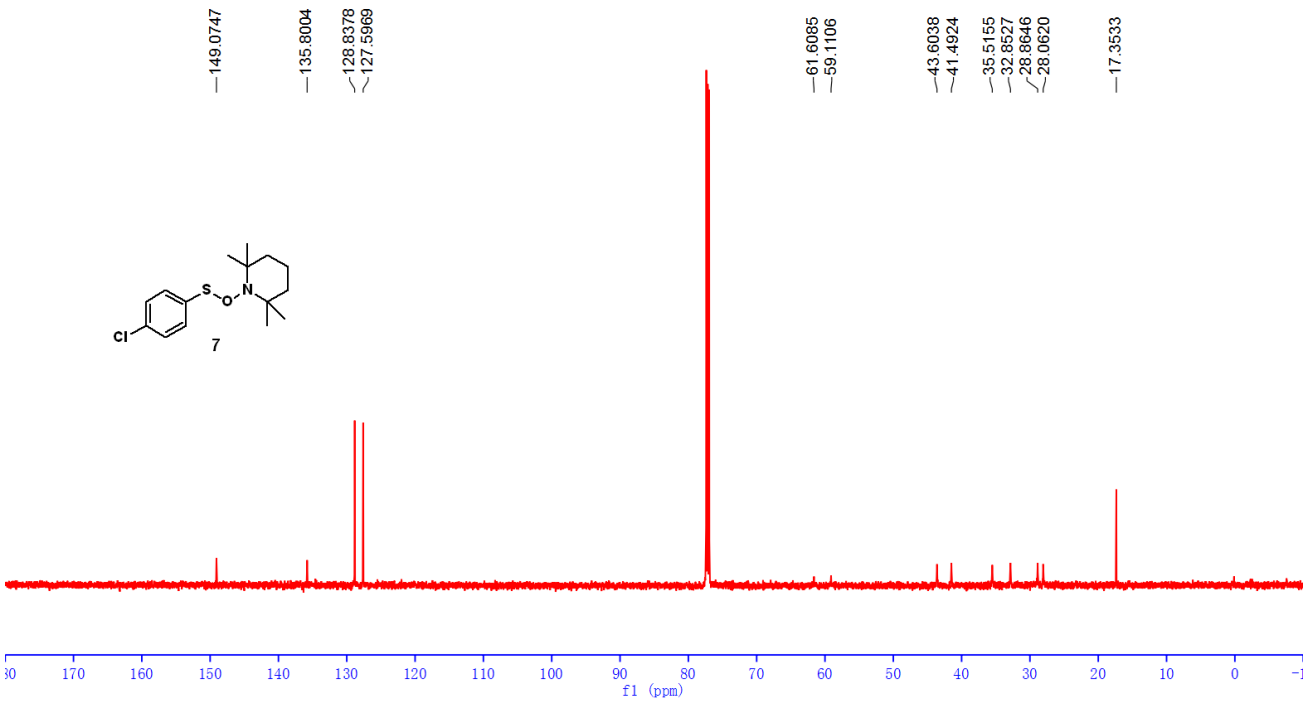
0.9105
Cl
S
O
N
7
2.00
2.00
15.10
3.00
f1 (ppm)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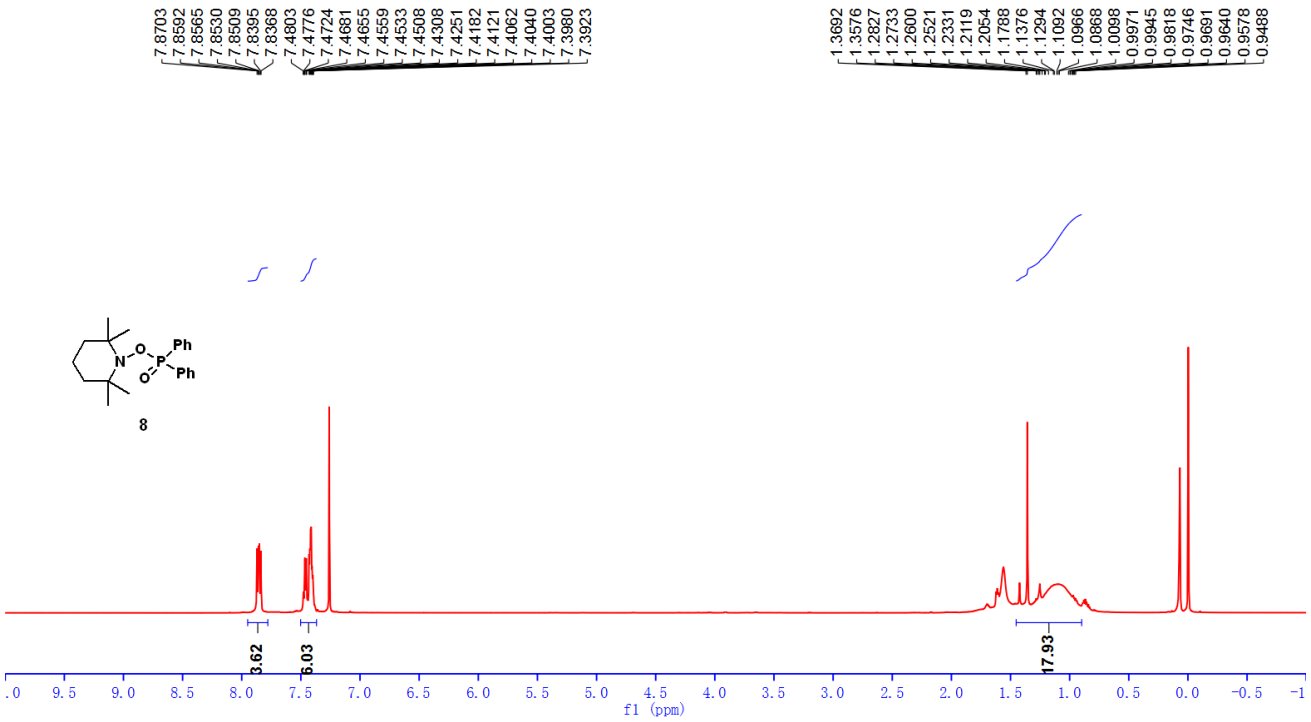
135.8004
128.8378
127.5969
61.6085
59.1106
43.6038
41.4924
35.5155
32.8527
28.8646
28.0620
17.3533
Cl
S
O
N
7
f1 (ppm)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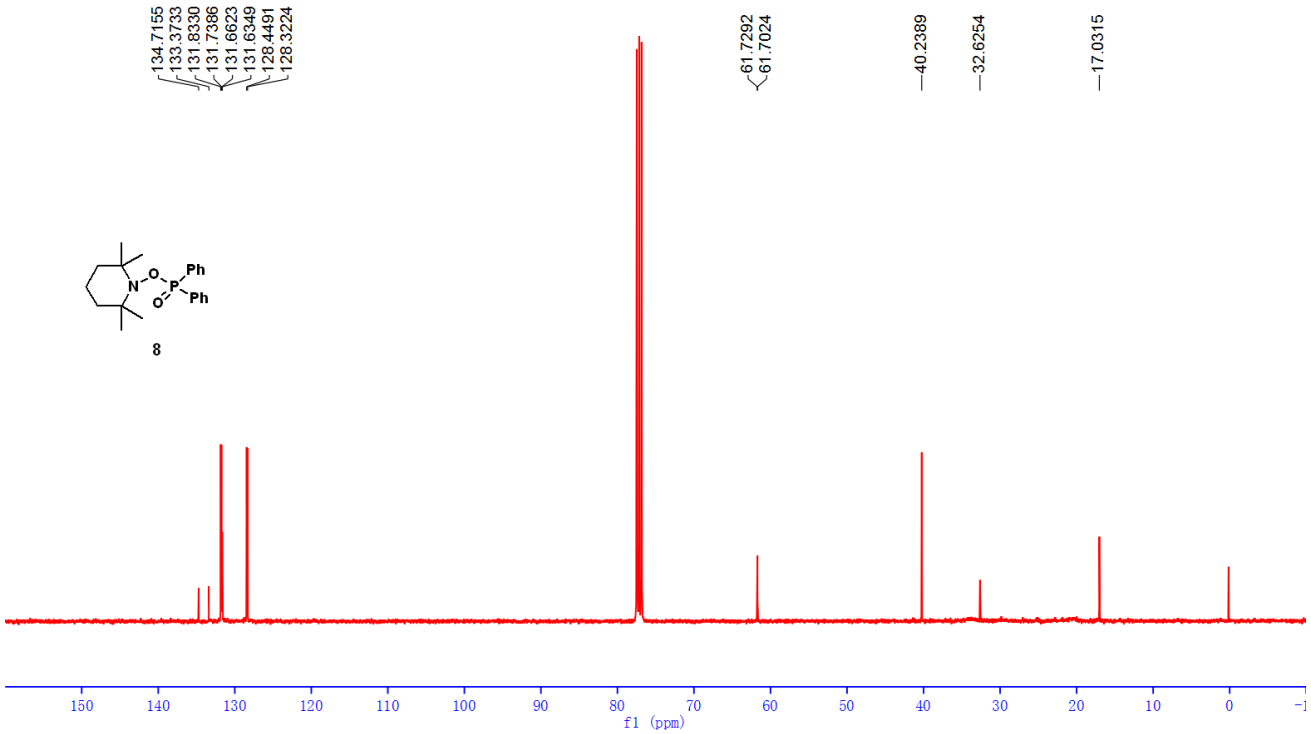
7.8592
7.8565
7.8530
7.8509
7.8395
7.8368
7.4803
7.4776
7.4724
7.4681
7.4655
7.4559
7.4533
7.4508
7.4308
7.4251
7.4182
7.4121
7.4062
7.4040
7.4003
7.3980
7.3923
1.3692
1.3576
1.2827
1.2733
1.2600
1.2521
1.2331
1.2119
1.2054
1.1788
1.1376
1.1294
1.1092
1.0966
1.0868
1.0098
0.9971
0.9945
0.9818
0.9746
0.9691
0.9640
0.9578
0.9488
Ph
Ph
O
P
N
O
8
3.62
6.03
17.93
f1 (ppm)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133.3733
131.8330
131.7386
131.6623
131.6349
128.4491
128.3224
61.7292
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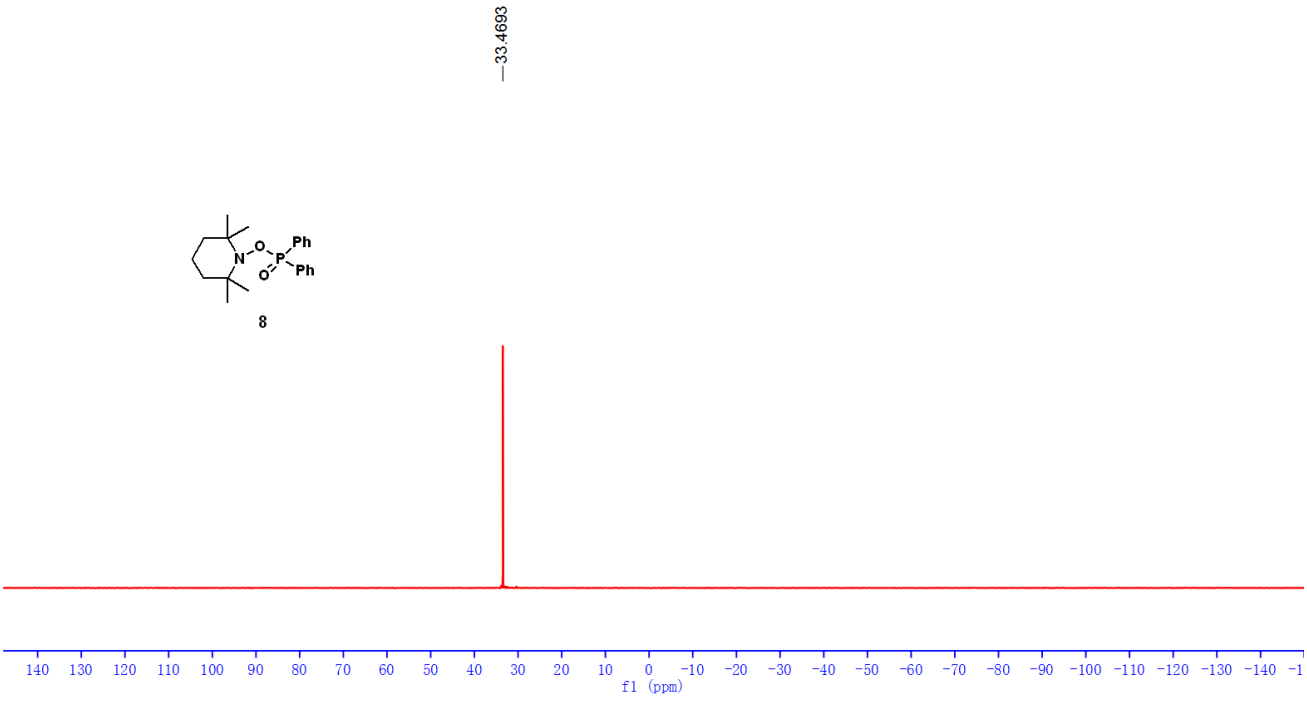
40.2389
32.6254
17.0315
Ph
Ph
O
P
N
O
8
f1 (ppm)


33.4693
Ph
Ph
O
N
O
P
O
8
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -1
f1 (ppm)