

*Electronic Supplementary Information*

*Electronic Supplementary Information for*

**Stereocontrolled C(sp<sup>3</sup>)-P bond formation with non-  
activated alkyl halides and tosylates**

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### **I. General data**

#### **a. Materials**

All the reactions were carried out in oven-dried Schlenk tubes under argon atmosphere (purity  $\geq 99.999\%$ ). Copper(I) iodide was purchased from Sinopharm Chemical Reagent Co., Ltd as a off-white powder and refluxed in THF for further purification. The following Chemicals were purchased and used as received: LiO<sup>t</sup>Bu (99.9%, Alfa-Aesar ), NaO<sup>t</sup>Bu (Acros), LiOMe (99.99%, Acros), Alcohols (Alfa-Aesa or Aldrich), PPh<sub>3</sub> (Aldrich), P(n-Bu)<sub>3</sub> (Aldrich), P(t-Bu)<sub>3</sub> (Aldrich), Diphenylphosphine (Aldrich), Diethyl phosphonate (Aldrich), Diphenylphosphine oxide (Aldrich), N<sup>1</sup>,N<sup>1</sup>,N<sup>2</sup>,N<sup>2</sup>-tetramethylethane-1,2-diamine(Alfa-Aesa), and other alkyl halides were purchased from Aldrich Chemisty or TCI AMERICA.

Anhydrous DMF (Acros) , anhydrous NMP (Acros), anhydrous THF (Acros) were stored over 4 Å molecular sieves under an argon atmosphere in a septum-capped bottle. All the other reagents and solvents mentioned in this text were purchased from commercial sources and used without purification.

#### **b. Analytical Methods**

<sup>1</sup>H-NMR, <sup>13</sup>C-NMR, <sup>31</sup>P-NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature in CDCl<sub>3</sub> unless otherwise noted; Data for <sup>1</sup>H-NMR are reported as follows: chemical shift ( $\delta$  ppm), multiplicity, integration, and coupling constant (Hz). Data for <sup>13</sup>C-NMR are reported in terms of chemical shift ( $\delta$  ppm), multiplicity, and coupling constant (Hz). Gas chromatographic (GC) analysis was acquired on a Shimadzu GC-2014 Series GC System equipped with a flame-ionization detector. GC-MS analysis was performed on Thermo Scientific AS 3000 Series GC-MS System. HRMS analysis was performed on Finnigan LCQ advantage Max Series MS System. HPLC analysis was performed on Waters-Breeze (2487 Dual Absorbance Detector and 1525 Binary HPLC Pump). Chiralpak IC, AD, AS, KM columns were purchased from Daicel Chemical Industries, LTD.. Organic solutions were concentrated under reduced pressure on a Buchi rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

## II. Experimental procedures and characterizations

### Preparation of alkyl tosylates

Alkyl tosylates were prepared according to literature procedure<sup>[1,2]</sup>. *p*-Toluenesulfonyl chloride (22.8 g, 120 mmol) was added over a period of 30 min to a stirred solution of pyridine (50mL) and alcohols (100 mmol) maintained at 0 °C. The reaction mixture was allowed to stir an additional 3 h and then quenched with H<sub>2</sub>O (150 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 \*60 mL), and the combined organic layers were washed with 3 M HCl (3 \*80 mL) followed by 10% NaHCO<sub>3</sub> (1\* 80 mL). The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum and the crude product purified by silica gel chromatography (CH<sub>2</sub>Cl<sub>2</sub>).

### Experimental Procedures for Examples Described in Table 1.

In air, Cu-Cat. ( 0.025 mmol) , bromocyclopentane (1a, 0.25 mmol), diphenylphosphine oxide (2a,0.5mmol), and the base (0.5 mmol ) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). The additives (0.05 mmol), and solvents (0.5 mL) were added in turn under Argon atmosphere at room temperature (if the additive is a solid, it was added along with the Cu-Cat.). The reaction mixture was stirred at the mentioned temperature for the indicated amount of time, then quenched with H<sub>2</sub>O(10 mL). The resulting solution mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 times, 10 mL each), dried over Mg<sub>2</sub>SO<sub>4</sub>, filtered through silica gel with copious washings (CH<sub>2</sub>Cl<sub>2</sub>), benzophenone (45.5mg, 0.25mmol) was added as internal standard. The product was yielded by GC.

**Table S1.** Reaction between **1a** and **2a** under various conditions.

$\text{Cyclopentane-X} + \text{HP(O)Ph}_2 \xrightarrow{\text{conditions}} \text{Cyclopentane-P(O)Ph}_2$

En-try	X	1a 1 equiv		2a 2 equiv		Solvent (0.5 mL)	Temp. (°C)	Yield (%) <sup>a</sup>
		Catalyst (10 mol%)	Additive (20 mol %)	Base (2 equiv.)				
1	Br	CuI	TMEDA	LiOMe		THF	25	48
2	Br	CuI	TMEDA	LiOMe		Toluene	25	12
3	Br	CuI	TMEDA	LiOMe		Dioxane	25	21
4	Br	CuI	TMEDA	LiOMe		DMF	25	68
5	Br	CuI	TMEDA	LiOMe		DMSO	25	65
6	Br	CuI	TMEDA	LiOMe		NMP	25	74
7	Br	CuI	TMEDA	LiOMe		NMP	40	89
<b>8</b>	<b>Br</b>	-	<b>TMEDA</b>	<b>LiOMe</b>		<b>NMP</b>	<b>40</b>	<b>88(85<sup>b</sup>)</b>
9	Br	-	TMEDA	LiO'Bu		NMP	40	78

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10	Br	-	TMEDA	NaO <sup>t</sup> Bu	NMP	40	69
11	Br	-	TMEDA	NaOMe	NMP	40	71
12	Br	-	TMEDA	Cs <sub>2</sub> CO <sub>3</sub>	NMP	40	58
13	Br	-	TMEDA	K <sub>2</sub> CO <sub>3</sub>	NMP	40	16
14	Br	-	TMEDA	LiHMDS	NMP	40	42
15	Br	-	TMEDA	KHMDS	NMP	40	54
16	Br	-	TMEDA	Trimethylamine	NMP	40	5
17	Br	-	TMEDA	DABCO	NMP	40	7
18	Br	-	TMEDA	DBU	NMP	40	11
19	Br	-	TMEDA	DMAP	NMP	40	23
20	Br	-	P <sup>n</sup> Bu <sub>3</sub>	LiOMe	NMP	40	73
21	Br	-	PPh <sub>3</sub>	LiOMe	NMP	40	63
22	Br	-	DMEDA	LiOMe	NMP	40	72
23	Br	-	-	LiOMe	NMP	40	55
<b>24</b>	<b>OTs</b>	<b>-</b>	<b>TMEDA</b>	<b>LiOMe</b>	<b>NMP</b>	<b>40</b>	<b>85(81<sup>b</sup>)</b>
25	I	-	TMEDA	LiOMe	NMP	40	76
26	Cl	-	TMEDA	LiOMe	NMP	40	21

<sup>a</sup> Reaction conditions: R-X (0.25 mmol), HP(O)Ph<sub>2</sub> (0.5 mmol), CuI (10 mol%), additive (20 mol%), Base (0.5 mmol), GC yields after 24 hours (average of two runs). <sup>b</sup> Isolated yields.

### Experimental Procedures for Examples Described in Table 2.

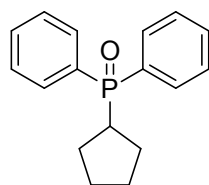
**General Procedure A.** In air, diphenylphosphine oxide (2a, 0.5 mmol), and LiOMe (0.5 mmol) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). The TMEDA (0.05 mmol), NMP (0.5 mL) and the alkyl bromide (0.25 mmol), were added in turn under Argon atmosphere at room temperature (if alkyl bromide is a solid, it was added along with 2a). The reaction mixture was stirred at 40 °C for 24 h, then quenched with H<sub>2</sub>O (10 mL). The resulting solution mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 times, 10 mL each), dried over Mg<sub>2</sub>SO<sub>4</sub>. The resulting solution mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 times, 10 mL each), dried over Mg<sub>2</sub>SO<sub>4</sub>, filtered through silica gel with copious washings (CH<sub>2</sub>Cl<sub>2</sub>), concentrated, and purified by column chromatography.

**General Procedure B.** In air, diphenylphosphine oxide (2a, 0.5 mmol), and LiOMe (0.5 mmol) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). The TMEDA (0.05 mmol), NMP (0.5 mL), and the alkyl tosylate (0.25 mmol) were added in turn under Argon atmosphere at room temperature (if alkyl tosylate is a solid, it was added along with 2a). The reaction mixture was stirred at 40 °C for 24 h, then quenched with H<sub>2</sub>O (10 mL). The resulting solution mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 times, 10 mL each),

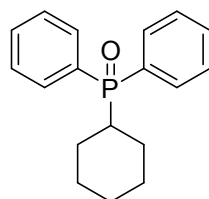
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dried over  $\text{Mg}_2\text{SO}_4$ , The resulting solution mixture was then extracted with  $\text{CH}_2\text{Cl}_2$  (3 times, 10 mL each), dried over  $\text{Mg}_2\text{SO}_4$ , filtered through silica gel with copious washings ( $\text{CH}_2\text{Cl}_2$ ), concentrated, and purified by column chromatography.

**General Procedure C.** In air, diphenylphosphine oxide (2a, 1mmol), and LiOMe (1 mmol) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). The TMEDA (0.05 mmol), NMP (0.5 mL), and 1,3-dibromobutane (0.25 mmol) were added in turn under Argon atmosphere at room temperature. The reaction mixture was stirred at 40 °C for 24 h, then quenched with  $\text{H}_2\text{O}$  (10 mL). The resulting solution mixture was then extracted with  $\text{CH}_2\text{Cl}_2$  (3 times, 10 mL each), dried over  $\text{Mg}_2\text{SO}_4$ , The resulting solution mixture was then extracted with  $\text{CH}_2\text{Cl}_2$  (3 times, 10 mL each), dried over  $\text{Mg}_2\text{SO}_4$ , filtered through silica gel with copious washings ( $\text{CH}_2\text{Cl}_2$ ), concentrated, and purified by column chromatography.

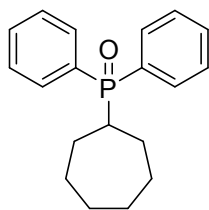


Cyclopentylidiphenylphosphine oxide (3a), following general procedure A, white solid.  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  7.82 (ddd,  $J = 10.8, 7.7, 1.6$  Hz, 4H), 7.62 - 7.28 (m, 6H), 3.20 - 3.04 (m, 1H), 1.78 - 1.42 (m, 8H) ppm.  $^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  134.8 (d,  $J = 94.0$  Hz), 131.8 (d,  $J = 2.4$  Hz), 130.9 (d,  $J = 9.0$  Hz), 1291 (d,  $J = 11.0$  Hz), 35.8 (d,  $J = 75.2$  Hz), 27.0 (d,  $J = 8.2$  Hz), 26.3 ppm. HRMS calcd for  $\text{C}_{17}\text{H}_{19}\text{OP}$  ( $\text{M}^+$ ): 270.1174; found: 270.1176.

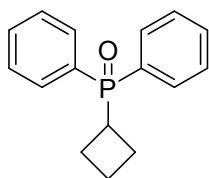


Cyclohexylidiphenylphosphine oxide (3b), following general procedure A, white solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 - 7.70 (m, 4H), 7.55 - 7.41 (m, 6H), 2.32 - 2.16 (m, 1H), 1.90 - 1.62 (m, 5H), 1.61 - 1.43 (m, 2H), 1.32 - 1.19 (m, 3H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  132.0 (d,  $J = 94.3$  Hz), 131.5 (d,  $J = 2.5$  Hz), 131.1 (d,  $J = 8.6$  Hz), 128.6 (d,  $J = 11.1$  Hz), 37.2 (d,  $J = 73.0$  Hz), 26.4 (d,  $J = 13.3$  Hz), 25.8, 24.8 (d,  $J = 2.7$  Hz) ppm.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  34.7 ppm. HRMS calcd for  $\text{C}_{18}\text{H}_{21}\text{OP}$  ( $\text{M}^+$ ): 284.1330; found: 284.1326.

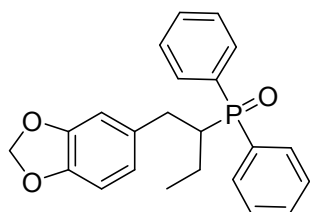
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Cycloheptyldiphenylphosphine oxide (3c), following general procedure A, white solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 – 7.65 (m, 4H), 7.63 – 7.32 (m, 6H), 2.41 (tdd,  $J$  = 13.6, 10.0, 3.5 Hz, 1H), 1.91 – 1.41 (m, 12H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  132.6(d,  $J$  = 94.2 Hz), 131.4 (d,  $J$  = 2.5 Hz), 131.0 (d,  $J$  = 8.6 Hz), 128.6 (d,  $J$  = 11.1 Hz), 37.7 (d,  $J$  = 70.2 Hz), 28.1 (d,  $J$  = 14.7 Hz), 28.0, 26.7 (d,  $J$  = 1.3 Hz) ppm. HRMS calcd for  $\text{C}_{19}\text{H}_{23}\text{OP}(\text{M}^+)$ : 298.1487; found:298.1488.



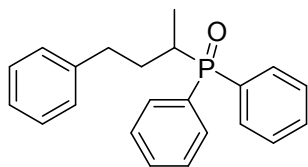
Cyclobutyldiphenylphosphine oxide (3d), following general procedure A, white solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 – 7.62 (m, 4H), 7.53 – 7.41 (m, 6H), 3.47 – 3.16 (m, 1H), 2.63 – 2.39 (m, 2H), 2.20 – 1.98 (m, 4H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  132.5(d,  $J$  = 97.2 Hz), 131.6 (d,  $J$  = 2.2 Hz), 131.0 (d,  $J$  = 9.2 Hz), 128.6 (d,  $J$  = 11.5 Hz), 32.6 (d,  $J$  = 73.2 Hz), 21.3 (d,  $J$  = 5.2 Hz), 20.2(d,  $J$  = 15.2 Hz) ppm.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  32.5 ppm. HRMS calcd for  $\text{C}_{16}\text{H}_{17}\text{OP}(\text{M}^+)$ : 256.1017; found: 256.1017.



(1-(benzo[d][1,3]dioxol-5-yl)butan-2-yl)diphenylphosphine oxide (3e), following general procedure B, white solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 – 7.75 (m, 4H), 7.47 (dd,  $J$  = 12.6, 6.8 Hz, 6H), 6.64 (d,  $J$  = 7.8 Hz, 1H), 6.54 (d,  $J$  = 9.8 Hz, 2H), 5.90 (s, 2H), 2.99 – 2.85 (m, 1H), 2.77 (dt,  $J$  = 14.4, 9.4 Hz, 1H), 2.48 (dd,  $J$  = 13.0, 7.6 Hz, 1H), 1.80 – 1.63 (m, 2H), 0.82 (t,  $J$  = 7.5 Hz, 3H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.5, 145.9, 132.8(d,  $J$  = 95.7 Hz), 131.5 (d,  $J$  = 10.6 Hz), 130.8 (d,  $J$  = 8.6 Hz), 128.6 (d,  $J$  = 11.2 Hz), 121.9, 109.1, 108.1, 100.8, 41.01 (d,  $J$  = 69.0 Hz), 32.9, 20.5, 12.5 (d,  $J$  = 7.3 Hz) ppm.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  35.4 ppm. HRMS calcd for  $\text{C}_{23}\text{H}_{23}\text{O}_3\text{P}(\text{M}^+)$ : 378.1385;

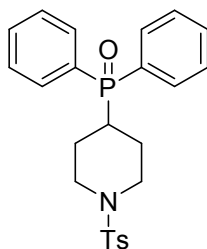
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found: 378.1386.

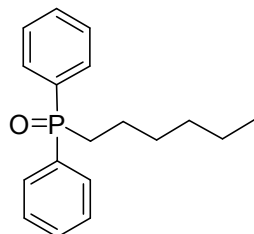


Diphenyl(4-phenylbutan-2-yl)phosphine oxide (3f), following general procedure B, colourless solid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 (ddd,  $J = 19.4, 9.9, 8.4$  Hz, 4H), 7.50 – 7.34 (m, 6H), 7.23 (dt,  $J = 14.1, 7.3$  Hz, 3H), 7.05 (d,  $J = 7.4$  Hz, 2H), 2.90 – 2.80 (m, 1H), 2.63 – 2.47 (m, 1H), 2.42 – 2.24 (m, 1H), 2.03 – 1.89 (m, 1H), 1.79 (qd,  $J = 13.8, 5.1$  Hz, 1H), 1.22 (dd,  $J = 16.7, 7.0$  Hz, 3H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.9, 132.2 (d,  $J = 94.8$  Hz), 131.4 (dd,  $J = 6.2, 2.5$  Hz), 130.91 (dd,  $J = 8.6, 5.0$  Hz), 128.5 (dd,  $J = 11.1, 2.1$  Hz), 128.5, 128.4, 126.0, 33.0 (d,  $J = 12.7$  Hz), 30.5 (d,  $J = 72.5$  Hz), 30.3, 29.6 ppm. HRMS calcd for  $\text{C}_{22}\text{H}_{23}\text{OP}$  ( $\text{M}^+$ ): 334.1487; found: 334.1482.



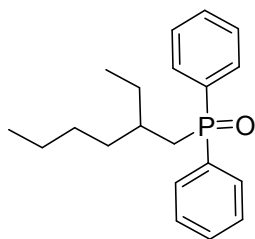
Diphenyl(1-tosylpiperidin-4-yl)phosphine oxide (3g), following general procedure B, white solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77 – 7.68 (m, 4H), 7.61 (d,  $J = 8.1$  Hz, 2H), 7.57 – 7.45 (m, 6H), 7.31 (d,  $J = 8.0$  Hz, 2H), 3.84 (dd,  $J = 11.0, 2.0$  Hz, 2H), 2.43 (s, 3H), 2.36 – 2.25 (m, 2H), 2.24 – 1.77 (m, 5H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  143.7, 132.4 (d,  $J = 99.9$  Hz), 132.1 (d,  $J = 1.9$  Hz), 131.2 (d,  $J = 8.8$  Hz), 129.7, 128.8 (d,  $J = 11.4$  Hz), 128.7, 127.7, 46.1 (d,  $J = 14.0$  Hz), 30.5 (d,  $J = 69.9$  Hz), 24.2 (d,  $J = 1.2$  Hz), 21.6 ppm.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  33.5 ppm. HRMS calcd for  $\text{C}_{24}\text{H}_{26}\text{NO}_3\text{PS}$  ( $\text{M}^+$ ): 439.1371; found: 439.1374.



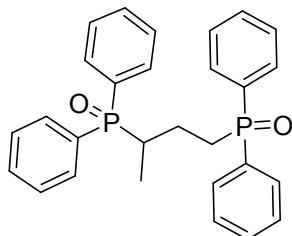
Hexyldiphenylphosphine oxide (3h), following general procedure A, white solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 – 7.61 (m, 4H), 7.60 – 7.35 (m, 6H), 2.34 – 2.13 (m, 2H), 1.72 – 1.52 (m, 2H), 1.47 –

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1.33 (m, 2H), 1.29 – 1.18 (m, 4H), 0.84 (t,  $J = 6.9$  Hz, 3H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  133.5 (d,  $J = 97.7$  Hz), 131.6 (d,  $J = 2.7$  Hz), 130.8 (d,  $J = 9.4$  Hz), 128.6 (d,  $J = 11.5$  Hz), 31.2, 30.6 (d,  $J = 14.6$  Hz), 29.7 (d,  $J = 71.9$  Hz), 22.4, 21.4 (d,  $J = 3.9$  Hz), 14.0 ppm. HRMS calcd for  $\text{C}_{18}\text{H}_{23}\text{OP}$  ( $\text{M}^+$ ): 286.1487; found: 286.1488.



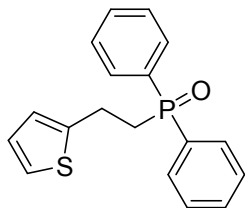
(2-ethylhexyl)diphenylphosphine oxide (3i), following general procedure B, pale yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 – 7.66 (m, 4H), 7.59 – 7.39 (m, 6H), 2.22 (dd,  $J = 11.1, 6.2$  Hz, 2H), 1.86 (dt,  $J = 12.5, 6.2$  Hz, 1H), 1.60 – 1.23 (m, 4H), 1.21 – 1.07 (m, 4H), 0.96 – 0.68 (m, 6H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  134.0 (dd,  $J = 97.3, 19.6$  Hz), 131.5 (d,  $J = 2.5$  Hz), 130.7 (dd,  $J = 9.0, 6.8$  Hz), 128.6 (d,  $J = 11.4$  Hz), 33.7 (d,  $J = 8.0$  Hz), 33.6 (d,  $J = 3.7$  Hz), 33.5 (d,  $J = 71.5$  Hz), 28.2, 27.0 (d,  $J = 7.5$  Hz), 22.7, 14.0, 10.2 ppm.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  31.8 ppm. HRMS calcd for  $\text{C}_{20}\text{H}_{27}\text{OP}$  ( $\text{M}^+$ ): 314.1800; found: 314.1801.



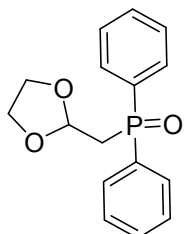
Butane-1,3-diylbis(diphenylphosphine oxide) (3j), following general procedure C, white solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 – 7.56 (m, 8H), 7.55 – 7.32 (m, 12H), 2.86 – 1.77 (m, 5H), 1.19 (dd,  $J = 16.2, 6.1$  Hz, 3H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  133.1 (d,  $J = 98.6$  Hz), , 131.9 (dd,  $J = 95.2, 14.6$  Hz), 131.7 (dd,  $J = 10.3, 2.5$  Hz), 131.6, 130.8 (d,  $J = 10.1$  Hz), 130.6 (d,  $J = 9.4$  Hz), 128.7 (dd,  $J = 11.4, 1.8$  Hz), 128.6 (d,  $J = 11.5$  Hz), 31.7 (dd,  $J = 71.4, 11.0$  Hz), 26.4 (dd,  $J = 71.6, 8.8$  Hz), 22.1 (d,  $J = 1.9$  Hz), 12.1 (d,  $J = 2.0$  Hz) ppm.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  37.1, 33.2 ppm. HRMS calcd for  $\text{C}_{28}\text{H}_{28}\text{O}_2\text{P}_2$  ( $\text{M}^+$ ): 458.1565; found: 458.1566.



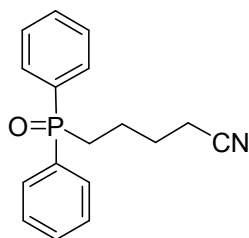
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Diphenyl(2-(thiophen-2-yl)ethyl)phosphine oxide (3k), following general procedure B, pale yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 – 7.71 (m, 4H), 7.60 – 7.43 (m, 6H), 7.23 (dd,  $J = 4.8, 2.9$  Hz, 1H), 7.02 – 6.86 (m, 2H), 3.06 – 2.86 (m, 2H), 2.65 – 2.54 (m, 2H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.3 (d,  $J = 16.0$  Hz), 132.6 (d,  $J = 98.8$  Hz), 131.9 (d,  $J = 2.3$  Hz), 130.8 (d,  $J = 9.4$  Hz), 128.7 (d,  $J = 11.7$  Hz), 127.7, 125.9, 120.5, 30.9 (d,  $J = 70.4$  Hz), 22.2 ppm.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  31.8 ppm. HRMS calcd for  $\text{C}_{18}\text{H}_{17}\text{OSP}$  ( $\text{M}^+$ ): 312.0738; found: 312.0734.



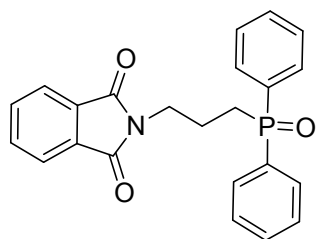
((1,3-dioxolan-2-yl)methyl)diphenylphosphine oxide (3l), following general procedure A, colourless liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 (dd,  $J = 11.9, 7.0$  Hz, 4H), 7.50 (ddd,  $J = 11.6, 10.0, 5.7$  Hz, 6H), 5.31 – 5.16 (m, 1H), 3.92 (t,  $J = 6.9$  Hz, 2H), 3.79 (t,  $J = 6.9$  Hz, 2H), 2.81 (dd,  $J = 11.8, 5.0$  Hz, 2H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  132.2 (d,  $J = 96$  Hz), 131.9 (d,  $J = 2.0$  Hz), 130.9 (d,  $J = 9.6$  Hz), 128.6 (d,  $J = 12.0$  Hz), 99.9, 65.0, 29.7 ppm.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  28.0 ppm. HRMS calcd for  $\text{C}_{16}\text{H}_{17}\text{O}_3\text{P}$  ( $\text{M}^+$ ): 288.0915; found: 288.0918.



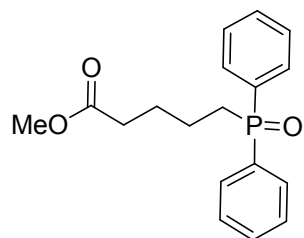
5-(diphenylphosphoryl)pentanenitrile (3m), following general procedure A, white solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 – 7.68 (m, 4H), 7.60 – 7.39 (m, 6H), 2.40 – 2.24 (m, 4H), 1.87 – 1.68 (m, 4H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  132.5 (d,  $J = 98.9$  Hz), 132.0 (d,  $J = 2.7$  Hz), 130.7 (d,  $J = 9.4$  Hz), 128.8 (d,  $J = 11.7$  Hz), 119.2, 29.0 (d,  $J = 71.7$  Hz), 26.4 (d,  $J = 13.8$  Hz), 21.0 (d,  $J = 3.6$  Hz), 16.9 ppm.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  31.9 ppm. HRMS calcd for  $\text{C}_{17}\text{H}_{18}\text{NOP}$  ( $\text{M}^+$ ): 283.1126; found:

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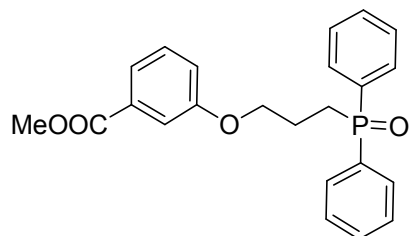
283.1124.



2-(3-(diphenylphosphoryl)propyl)isoindoline-1,3-dione(3n), following general procedure A, white solid.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (dd,  $J = 5.4, 3.0$  Hz, 2H), 7.71 (ddd,  $J = 6.3, 5.0, 3.9$  Hz, 6H), 7.51 (td,  $J = 7.4, 1.3$  Hz, 2H), 7.45 (ddd,  $J = 8.3, 5.2, 2.2$  Hz, 4H), 3.77 (t,  $J = 6.8$  Hz, 2H), 2.33 (ddd,  $J = 11.7, 8.4, 4.9$  Hz, 2H), 2.02 – 1.95 (m, 2H) ppm.  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  167.2, 133.0, 131.4 (d,  $J = 99.4$  Hz), 131.0, 130.9 (d,  $J = 2.8$  Hz), 129.8 (d,  $J = 9.0$  Hz), 127.7 (d,  $J = 11.5$  Hz), 122.3, 37.5 (d,  $J = 17.3$  Hz), 26.4 (d,  $J = 72.4$  Hz), 20.2 (d,  $J = 2.8$  Hz) ppm. HRMS calcd for  $\text{C}_{23}\text{H}_{20}\text{NO}_3\text{P}(\text{M}^+)$ : 389.1181; found: 389.1184.



Methyl 5-(diphenylphosphoryl)pentanoate (3o), following general procedure A, white solid.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 – 7.70 (m, 4H), 7.52 (td,  $J = 7.6, 1.2$  Hz, 2H), 7.47 (ddd,  $J = 8.4, 5.2, 2.0$  Hz, 4H), 3.62 (s, 3H), 2.29 (dt,  $J = 8.0, 5.1$  Hz, 4H), 1.75 (dt,  $J = 14.9, 7.4$  Hz, 2H), 1.66 (ddd,  $J = 8.6, 6.6, 2.7$  Hz, 2H) ppm.  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  173.6, 132.9(d,  $J = 98.2$  Hz), 131.8 (d,  $J = 2.6$  Hz, 2H), 130.8 (d,  $J = 9.0$  Hz), 128.7(d,  $J = 11.8$  Hz), 51.5, 33.5, 29.5(d,  $J = 72.0$  Hz), 26.1(d,  $J = 15.3$  Hz), 21.1(d,  $J = 3.8$  Hz) ppm. HRMS calcd for  $\text{C}_{18}\text{H}_{21}\text{O}_3\text{P}(\text{M}^+)$ : 316.1228; found: 316.1229.



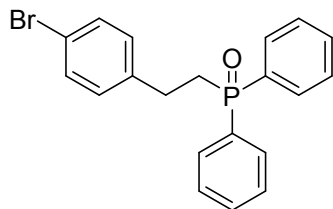
Methyl 3-(3-(diphenylphosphoryl)propoxy)benzoate (3p), following general procedure A, white solid.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (dd,  $J = 10.4, 8.0$  Hz, 4H), 7.62 (d,  $J = 7.8$  Hz, 1H), 7.53 – 7.44 (m, 7H), 7.31 (t,  $J = 8.0$  Hz, 1H), 7.04 (dd,  $J = 8.2, 1.9$  Hz, 1H), 4.05 (t,  $J = 5.8$  Hz, 2H), 3.91 (s,

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3H), 2.45-2.53 (m, 2H), 2.10-2.17 (m, 2H) ppm.  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  166.9, 158.6, 132.8 (d,  $J = 99.0\text{ Hz}$ , 1H), 131.9, 131.8 (d,  $J = 2.8\text{ Hz}$ ), 130.8 (d,  $J = 9.1\text{ Hz}$ ), 129.4, 128.7 (d,  $J = 11.4\text{ Hz}$ ), 122.1, 119.6, 114.8, 67.7 (d,  $J = 14.0\text{ Hz}$ ), 29.8 (d,  $J = 72.2\text{ Hz}$ ), 21.8 (d,  $J = 1.7\text{ Hz}$ ) ppm. HRMS calcd for  $\text{C}_{23}\text{H}_{23}\text{O}_4\text{P}$  ( $\text{M}^+$ ): 394.1334; found: 394.1335.

### Experimental Procedure for Example Described in Scheme 1.

In air, 4-bromophenethyl 4-methylbenzenesulfonate (1b, 0.5 mmol), diphenylphosphine oxide (2a, 0.5 mmol), and LiOMe (0.5 mmol) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). The TMEDA (0.05 mmol), and NMP (0.5 mL) were added in turn under Argon atmosphere at room temperature. The reaction mixture was stirred at 40 °C for 24 h, then quenched with  $\text{H}_2\text{O}$  (10 mL). The resulting solution mixture was then extracted with  $\text{CH}_2\text{Cl}_2$  (3 times, 10 mL each), dried over  $\text{Mg}_2\text{SO}_4$ . The resulting solution mixture was then extracted with  $\text{CH}_2\text{Cl}_2$  (3 times, 10 mL each), dried over  $\text{Mg}_2\text{SO}_4$ , filtered through silica gel with copious washings ( $\text{CH}_2\text{Cl}_2$ ), concentrated, and purified by column chromatography.



(4-bromophenethyl)diphenylphosphine oxide (3n), white solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 – 7.71 (m, 4H), 7.58 – 7.45 (m, 6H), 7.36 (d,  $J = 8.3\text{ Hz}$ , 2H), 7.03 (d,  $J = 8.3\text{ Hz}$ , 2H), 2.99 – 2.78 (m, 2H), 2.66 – 2.41 (m, 2H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.1 (d,  $J = 14.9\text{ Hz}$ ), 132.5 (d,  $J = 98.5\text{ Hz}$ ), 131.9 (d,  $J = 1.6\text{ Hz}$ ), 130.8 (d,  $J = 9.1\text{ Hz}$ ), 131.7, 129.9, 128.8 (d,  $J = 11.5\text{ Hz}$ ), 120.1, 29.7 (d,  $J = 3.7\text{ Hz}$ ), 27.05 (d,  $J = 2.1\text{ Hz}$ ) ppm.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  31.5 ppm. HRMS calcd for  $\text{C}_{20}\text{H}_{18}\text{OPBr}$  ( $\text{M}^+$ ): 384.0279; found: 384.0281.

### Experimental Procedures for Examples Described in Table 3.

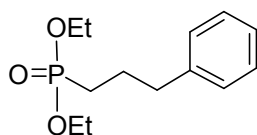
**General Procedure D.** In air,  $\text{Cs}_2\text{CO}_3$  (0.5 mmol) was added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). The TMEDA (0.05

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mmol), NMP (0.5 mL), diethyl phosphonate (4a, 0.5mmol), and the alkyl bromide (0.25 mmol) were added in turn under Argon atmosphere at room temperature. The reaction mixture was stirred at 40 °C for 24 h, then quenched with H<sub>2</sub>O (10 mL). The resulting solution mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub>(3 times, 10 mL each), dried over Mg<sub>2</sub>SO<sub>4</sub>,The resulting solution mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 times, 10 mL each), dried over Mg<sub>2</sub>SO<sub>4</sub>, filtered through silica gel with copious washings (CH<sub>2</sub>Cl<sub>2</sub>), concentrated, and purified by column chromatography.

**General Procedure E.** In air, LiOMe (0.5 mmol ) was added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). The TMEDA (0.05 mmol), NMP (0.5 mL), the alkyl bromide (0.25 mmol), and diphenylphosphine (4b, 0.5mmol) were added in turn under Argon atmosphere at room temperature. The reaction mixture was stirred at 40 °C for 24 h, then quenched with H<sub>2</sub>O (10 mL). The resulting solution mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub>(3 times, 10 mL each), dried over Mg<sub>2</sub>SO<sub>4</sub>,The resulting solution mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 times, 10 mL each), dried over Mg<sub>2</sub>SO<sub>4</sub>, filtered through silica gel with copious washings (CH<sub>2</sub>Cl<sub>2</sub>), concentrated, and purified by column chromatography.

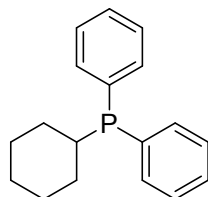
**General Procedure F.** In air, LiOMe (1 mmol ) was added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). The TMEDA (0.05 mmol), NMP (0.5 mL), the alkyl bromide (0.25 mmol), and diphenylphosphine (4b, 1mmol) were added in turn under Argon atmosphere at room temperature. The reaction mixture was stirred at 40 °C for 24 h, then quenched with H<sub>2</sub>O (10 mL). The resulting solution mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub>(3 times, 10 mL each), dried over Mg<sub>2</sub>SO<sub>4</sub>,The resulting solution mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 times, 10 mL each), dried over Mg<sub>2</sub>SO<sub>4</sub>, filtered through silica gel with copious washings (CH<sub>2</sub>Cl<sub>2</sub>), concentrated, and purified by column chromatography.



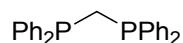
Diethyl 3-phenylpropylphosphonate (5a), following general procedure D, colourless liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.22 (t, *J* = 7.4 Hz, 2H), 7.12 (dd, *J* = 12.5, 7.1 Hz, 3H), 4.11 – 3.91 (m, 4H), 2.63 (t, *J* = 7.5 Hz, 2H), 1.86 (ddd, *J* = 10.8, 8.0, 3.4 Hz, 2H), 1.71 – 1.62 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 6H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 140.0, 127.5, 127.4, 125.1, 60.5 (d, *J* = 6.5 Hz), 35.4 (d, *J* = 17.1 Hz), 24.1 (d, *J* = 141.0 Hz), 23.1 (d, *J* = 4.9 Hz), 15.4 (d, *J* = 5.9 Hz) ppm. HRMS calcd for C<sub>13</sub>H<sub>21</sub>O<sub>3</sub>P

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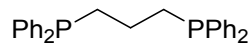
(M<sup>+</sup>): 256.1228; found: 256.1229.



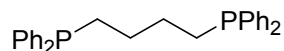
Cyclohexyldiphenylphosphine (5b)<sup>3</sup>, following general procedure E, white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62 – 7.43 (m, 4H), 7.43 – 7.23 (m, 6H), 2.35 – 2.11 (m, 1H), 1.84 – 1.55 (m, 5H), 1.42 – 1.08 (m, 5H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.9 (d, *J* = 13.1 Hz), 133.6 (d, *J* = 19.0 Hz), 128.6, 128.3 (d, *J* = 7.1 Hz), 35.40 (d, *J* = 8.3 Hz), 29.6 (d, *J* = 15.2 Hz), 26.8 (d, *J* = 11.3 Hz), 26.4 ppm. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ -3.6 ppm. HRMS calcd for C<sub>18</sub>H<sub>21</sub>P(M<sup>+</sup>): 268.1381; found: 268.1379.



Bis(diphenylphosphino)methane (5c)<sup>4</sup>, following general procedure F, white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.50 – 7.38 (m, 8H), 7.35 – 7.24 (m, 12H), 2.80 (s, 2H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.6 (t, *J* = 3.3 Hz), 132.8 (t, *J* = 10.3 Hz), 128.7, 128.4 (t, *J* = 3.6 Hz), 27.9 (t, *J* = 22.6 Hz) ppm. HRMS calcd for C<sub>25</sub>H<sub>22</sub>P<sub>2</sub>(M<sup>+</sup>): 384.1197; found: 384.1199.



1,3-bis(diphenylphosphino)propane (5d)<sup>5</sup>, following general procedure F, white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.40 – 7.27 (m, 20H), 2.20 (t, *J* = 7.6 Hz, 4H), 1.69 – 1.53 (m, 2H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.3 (d, *J* = 11.8 Hz), 132.7 (d, *J* = 18.4 Hz), 128.6, 28.4 (d, *J* = 6.8 Hz), 29.6 (t, *J* = 12.1 Hz), 22.3 (t, *J* = 16.8 Hz) ppm. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ -17.4 ppm. HRMS calcd for C<sub>27</sub>H<sub>26</sub>P<sub>2</sub>(M<sup>+</sup>): 412.1510; found: 412.1512.



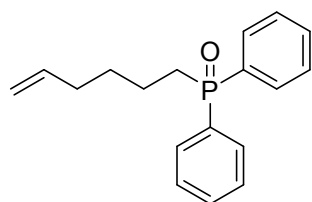
1,4-bis(diphenylphosphino)butane (5e)<sup>4</sup>, following general procedure F, white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.53 – 7.25 (m, 20H), 2.02 (t, *J* = 7.2 Hz, 4H), 1.62 – 1.46 (m, 4H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.5 (d, *J* = 11.9 Hz), 132.7 (d, *J* = 18.4 Hz), 128.5, 128.4 (d, *J* = 6.8 Hz, 1H), 27.6 (dd, *J* = 12.8, 5.2 Hz), 27.4 ppm. HRMS calcd for C<sub>28</sub>H<sub>28</sub>P<sub>2</sub>(M<sup>+</sup>): 426.1666; found: 426.1664.

### Experimental Procedure for Example Described in Scheme 2.

In air, diphenylphosphine oxide (2a, 0.5mmol), and LiOMe(0.5 mmol ) were added to a Schlenk

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tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). The TMEDA (0.05 mmol), 6-bromohex-1-ene (6a, 0.25mmol, and NMP (0.5 mL) were added in turn under Argon atmosphere at room temperature. The reaction mixture was stirred at 40 °C for 24 h, then quenched with H<sub>2</sub>O (10 mL). The resulting solution mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub>(3 times, 10 mL each), dried over Mg<sub>2</sub>SO<sub>4</sub>,The resulting solution mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 times, 10 mL each), dried over Mg<sub>2</sub>SO<sub>4</sub>, filtered through silica gel with copious washings (CH<sub>2</sub>Cl<sub>2</sub>), concentrated, and purified by column chromatography.

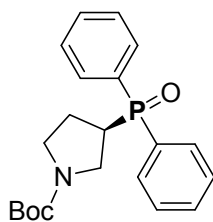


Hex-5-en-1-ylidiphenylphosphine oxide (7), colourless liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.81 – 7.67 (m, 4H), 7.58 – 7.39 (m, 6H), 5.74 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.02 – 4.81 (m, 2H), 2.27 (dd, *J* = 16.3, 11.1 Hz, 2H), 2.04 (dd, *J* = 14.6, 6.9 Hz, 2H), 1.69 – 1.60 (m, 2H), 1.51 (dd, *J* = 14.8, 7.6 Hz, 2H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.1, 131.9 (d, *J* = 2.3 Hz), 130.9 (d, *J* = 9.4 Hz), 128.7 (d, *J* = 11.7 Hz), 114.9, 33.2, 30.1 (d, *J* = 14.7 Hz), 29.7, 21.0 (d, *J* = 3.7 Hz) ppm. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 34.5 ppm. HRMS calcd for C<sub>18</sub>H<sub>21</sub>OP (M<sup>+</sup>):284.1330; found: 284.1333.

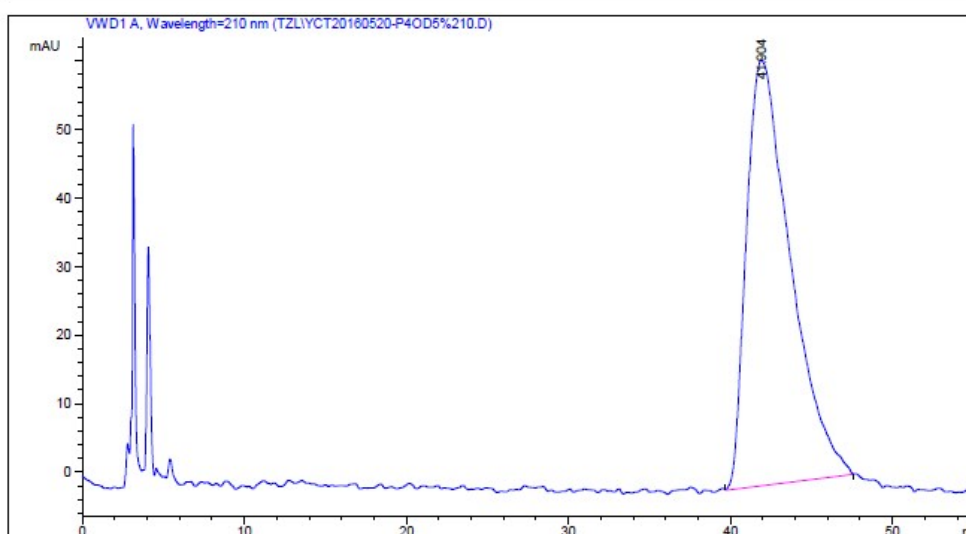
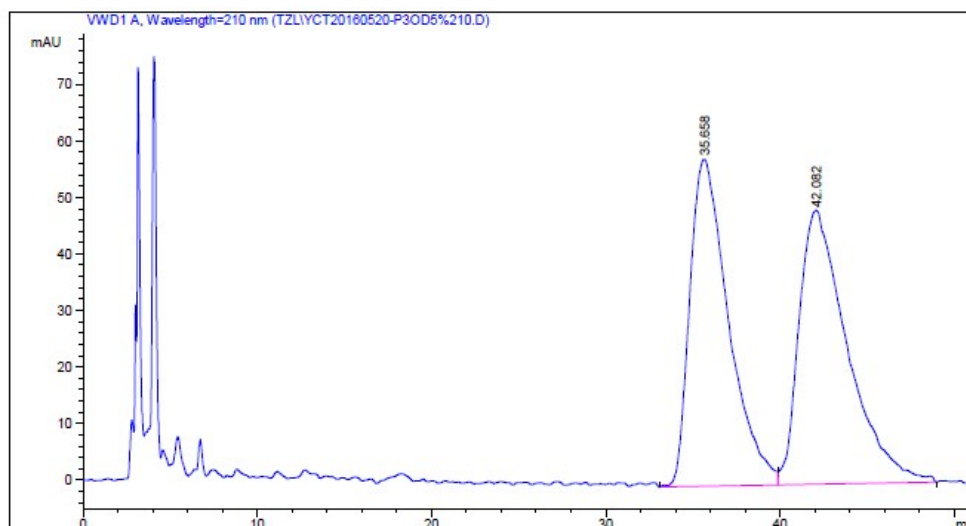
### Experimental Procedures for Examples Described in Table 3.

**General Procedure.** In air, diphenylphosphine oxide (2a, 0.5mmol), and LiOMe(0.5 mmol ) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). The TMEDA (0.05 mmol), NMP (0.5 mL), and the alkyl tosylate (0.25 mmol) were added in turn under Argon atmosphere at room temperature (if alkyl tosylate is a solid, it was added along with 2a). The reaction mixture was stirred at 40 °C for 24 h, then quenched with H<sub>2</sub>O (10 mL). The resulting solution mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub>(3 times, 10 mL each), dried over Mg<sub>2</sub>SO<sub>4</sub>,The resulting solution mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 times, 10 mL each), dried over Mg<sub>2</sub>SO<sub>4</sub>, filtered through silica gel with copious washings (CH<sub>2</sub>Cl<sub>2</sub>), concentrated, and purified by column chromatography.

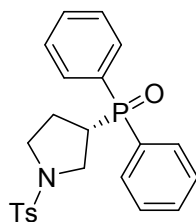
## Electronic Supplementary Information



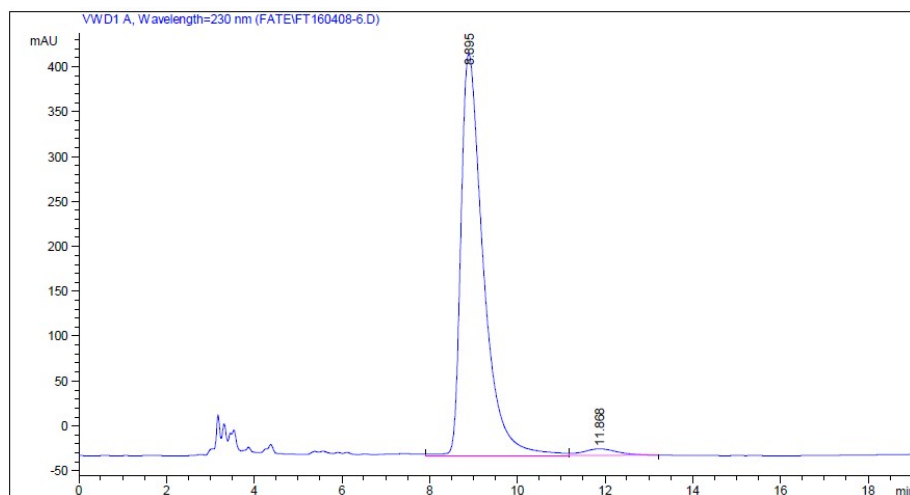
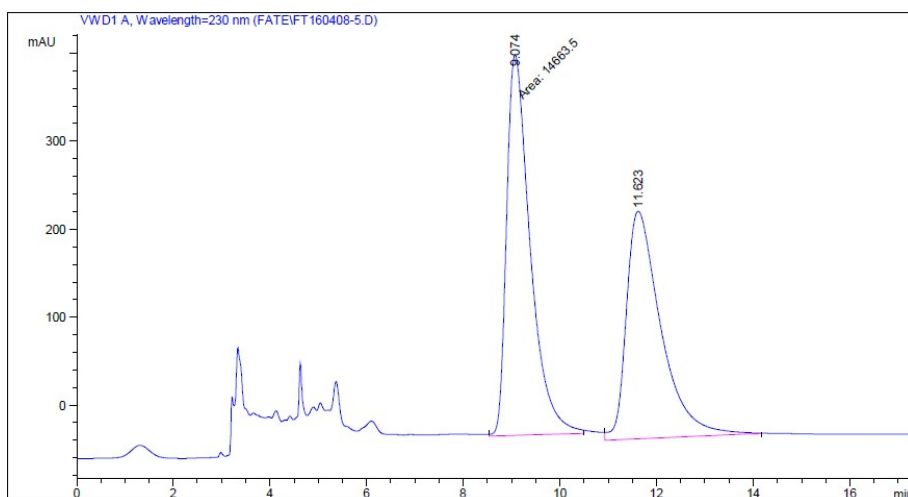
(R)-tert-butyl 3-(diphenylphosphoryl)pyrrolidine-1-carboxylate (9a, 99% ee), colourless solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 – 7.67 (m, 4H), 7.62 – 7.41 (m, 6H), 3.58 (brs, 3H), 3.30 (td,  $J = 10.1$ , 7.1 Hz, 1H), 3.04 (brs, 1H), 2.29 (brs, 1H), 2.07 – 1.83 (m, 1H), 1.42 (s, 9H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  154.2, 132.1 (d,  $J = 6.7$  Hz), 130.9 (d,  $J = 9.0$  Hz), 128.84 (dd,  $J = 11.5$ , 3.4 Hz), 79.6, 46.1 (d,  $J = 8.5$  Hz), 31.9, 29.7, 29.4, 28.4, 22.7 ppm.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  30.6 ppm. HRMS calcd for  $\text{C}_{21}\text{H}_{26}\text{NO}_3\text{P}(\text{M}^+)$ : 371.1650; found: 371.1648. Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel OD column, 1 mL/min, hexane /*i*-PrOH 95:5, retention times (min.): 35.6(minor) and 41.9(major).



## Electronic Supplementary Information

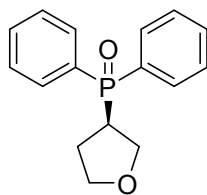


(*S*)-diphenyl(1-tosylpyrrolidin-3-yl)phosphine oxide (9b, 95% ee), white solid  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 – 7.63 (m, 6H), 7.60 – 7.42 (m, 6H), 7.32 (d,  $J = 8.1$  Hz, 2H), 3.64 – 3.55 (m, 1H), 3.40 (dd,  $J = 17.3, 7.7$  Hz, 1H), 3.32 – 3.16 (m, 2H), 3.05 (dd,  $J = 10.1, 8.1$  Hz, 1H), 2.44 (s, 3H), 2.12 (ddd,  $J = 12.5, 10.9, 4.0$  Hz, 1H), 1.96 (ddd,  $J = 12.4, 8.4, 4.5$  Hz, 1H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  143.9, 132.6 (d,  $J = 74.1$  Hz), 132.4 (d,  $J = 2.6$  Hz), 130.8 (d,  $J = 9.5$  Hz), 129.9, 129.0 (d,  $J = 11.6$  Hz), 128.9, 127.6, 47.8, 37.4 (d,  $J = 75.1$  Hz), 29.7, 25.3, 21.6 ppm.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  30.6 ppm. HRMS calcd for  $\text{C}_{23}\text{H}_{24}\text{NO}_3\text{PS}$  ( $\text{M}^+$ ): 425.1215; found: 425.1219. Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel OD column, 1 mL/min, hexane /*i*-PrOH 70:30, retention times (min.): 8.9(major) and 11.9 (minor).

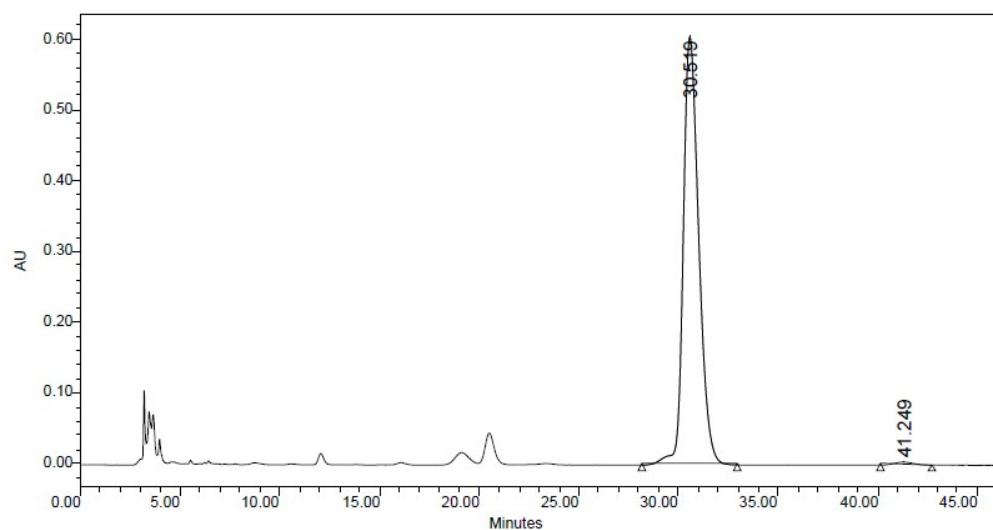
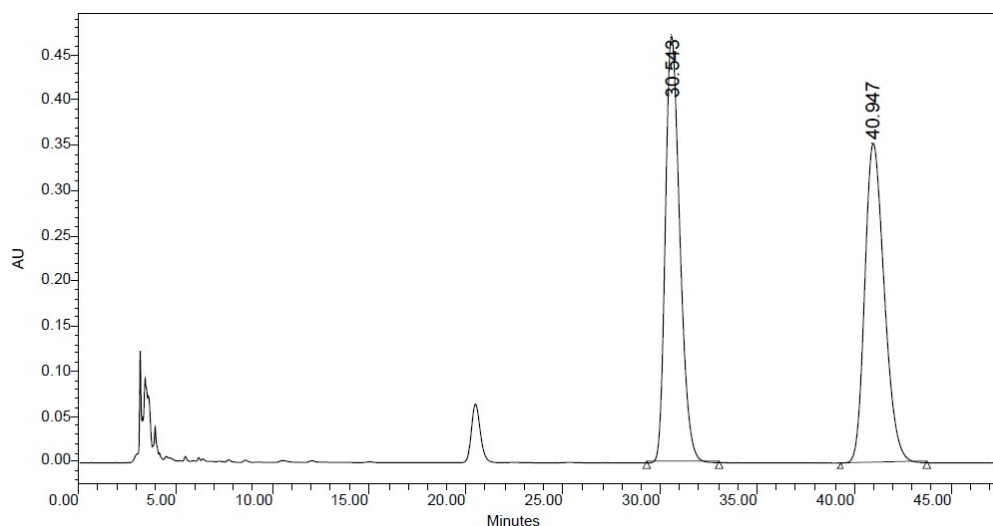




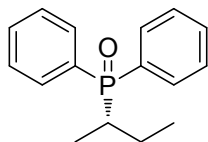
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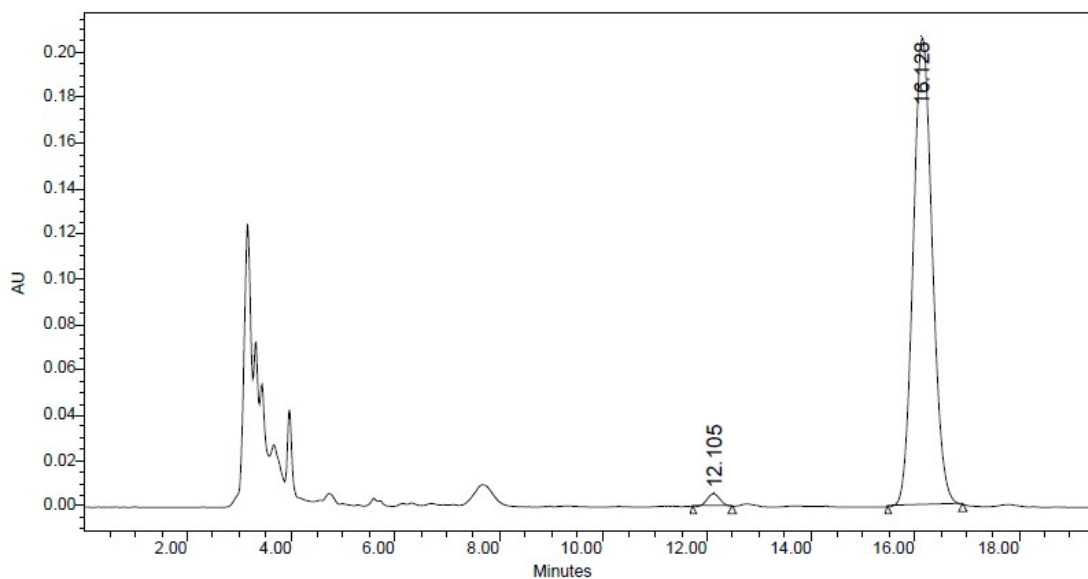
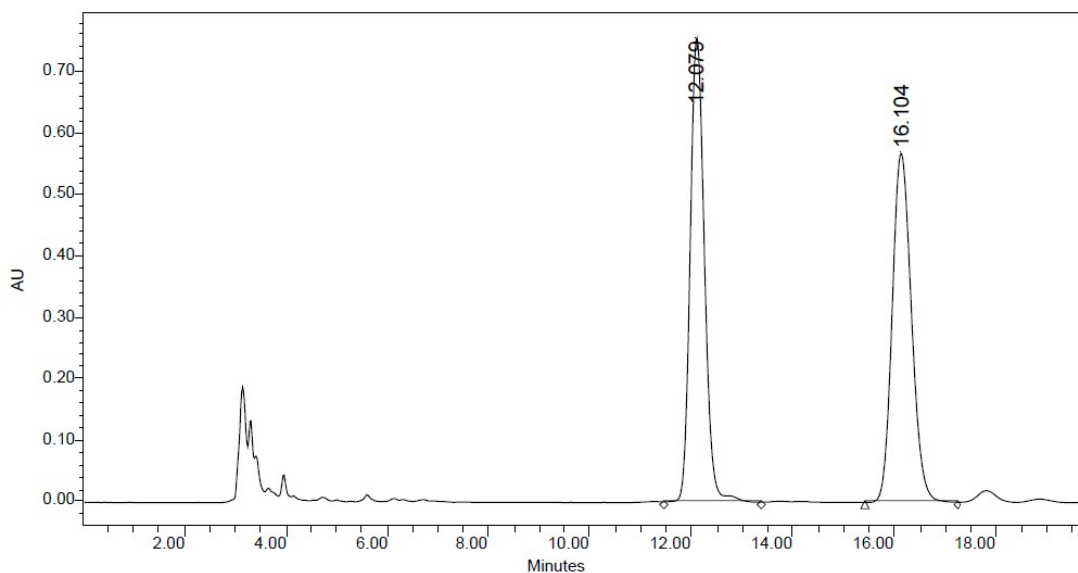
(R)-3- diphenylphosphoryltetrahydrofuran (9c, 98% ee), colourless liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 – 7.72 (m, 4H), 7.56-7.47 (m, 6H), 4.04 – 3.92 (m, 2H), 3.86 (t,  $J = 6.8$  Hz, 2H), 3.16 – 3.04 (m, 1H), 2.32 (ddd,  $J = 16.8, 10.0, 5.7$  Hz, 1H), 2.13 – 2.05 (m, 1H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  132.3 (d,  $J = 98.3$  Hz, 1H), 132.0 (dd,  $J = 6.8, 2.7$  Hz), 130.8 (dd,  $J = 9.2, 3.9$  Hz), 128.8 (dd,  $J = 11.5, 2.9$  Hz), 68.8 (d,  $J = 7.8$  Hz), 67.6 (d,  $J = 2.1$  Hz), 38.1 (d,  $J = 75.2$  Hz), 26.9 (d,  $J = 1.5$  Hz) ppm. HRMS calcd for  $\text{C}_{16}\text{H}_{17}\text{O}_2\text{P}$  ( $\text{M}^+$ ): 272.0966; found: 272.0966. Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel IC column, 1 mL/min, hexane /i-PrOH 70:30 , retention times (min.): 30.5 (major) and 41.2 (minor).



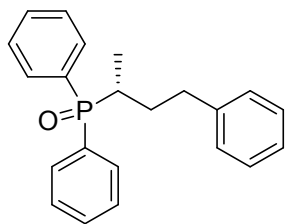
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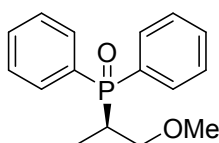
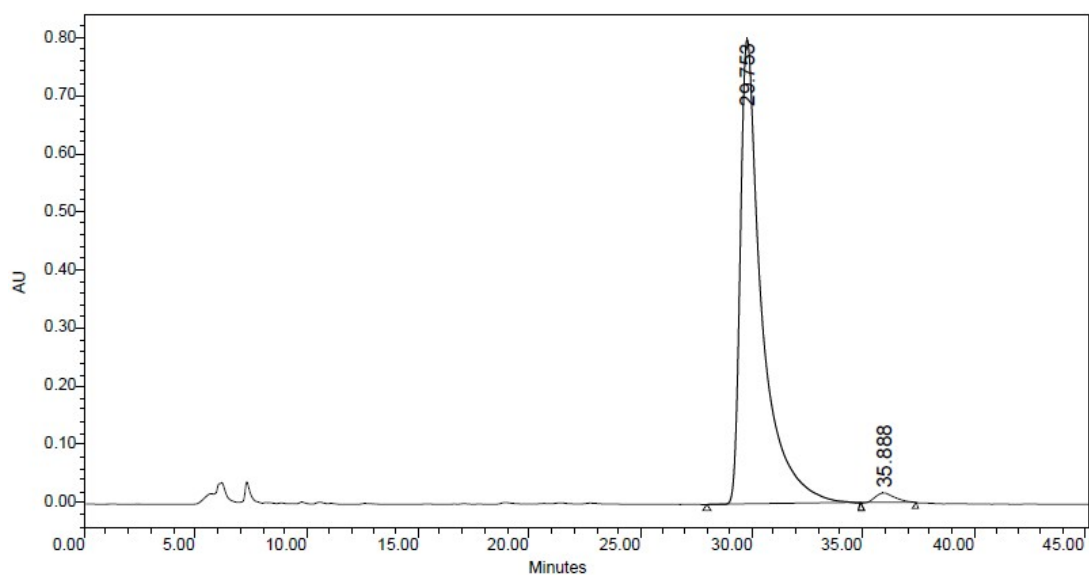
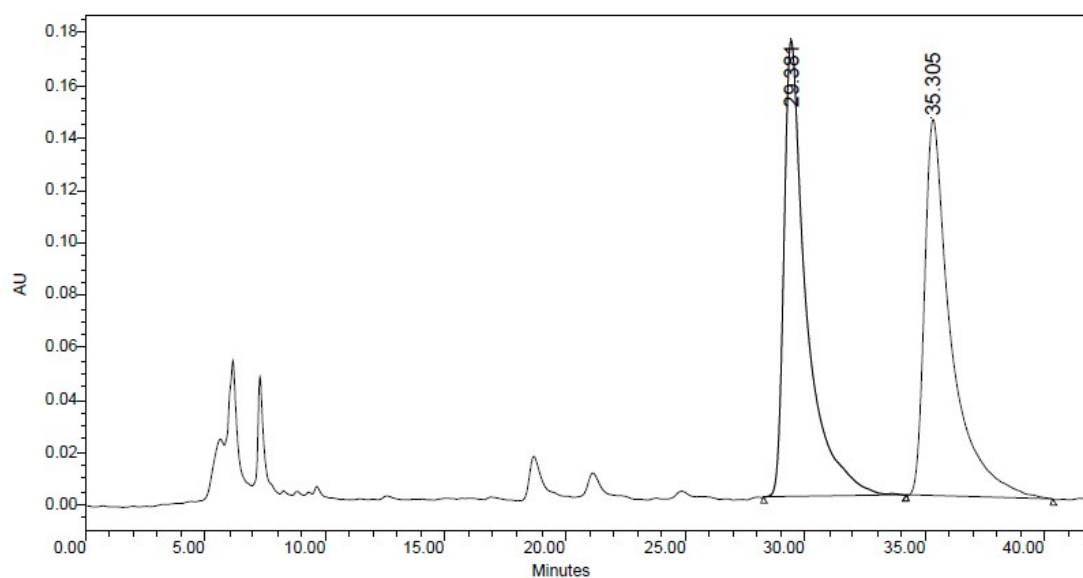
(S)-sec-butylidiphenylphosphine oxide (9d, 96% ee), colourless solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 – 7.70 (m, 4H), 7.56 – 7.37 (m, 6H), 2.34 – 2.23 (m, 1H), 1.81 – 1.67 (m, 1H), 1.52 – 1.39 (m, 1H), 1.17 (dd,  $J = 16.9, 7.1$  Hz, 3H), 0.98 (t,  $J = 7.4$  Hz, 3H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  132.2 (d,  $J = 94.5$  Hz), 131.5 (d,  $J = 2.5$  Hz), 131.1 (d,  $J = 8.6$  Hz), 128.6 (dd,  $J = 11.1, 2.8$  Hz), 33.8 (d,  $J = 72.0$  Hz), 22.1 (d,  $J = 1.2$  Hz), 12.3 (d,  $J = 13.3$  Hz), 11.6 (d,  $J = 2.6$  Hz) ppm.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  37.6 ppm. HRMS calcd for  $\text{C}_{16}\text{H}_{19}\text{OP}$  ( $\text{M}^+$ ): 258.1174; found: 258.1178. Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel IC column, 1 mL/min, hexane /*i*-PrOH 70:30, retention times (min.): 12.1 (minor) and 16.1 (major)



## Electronic Supplementary Information



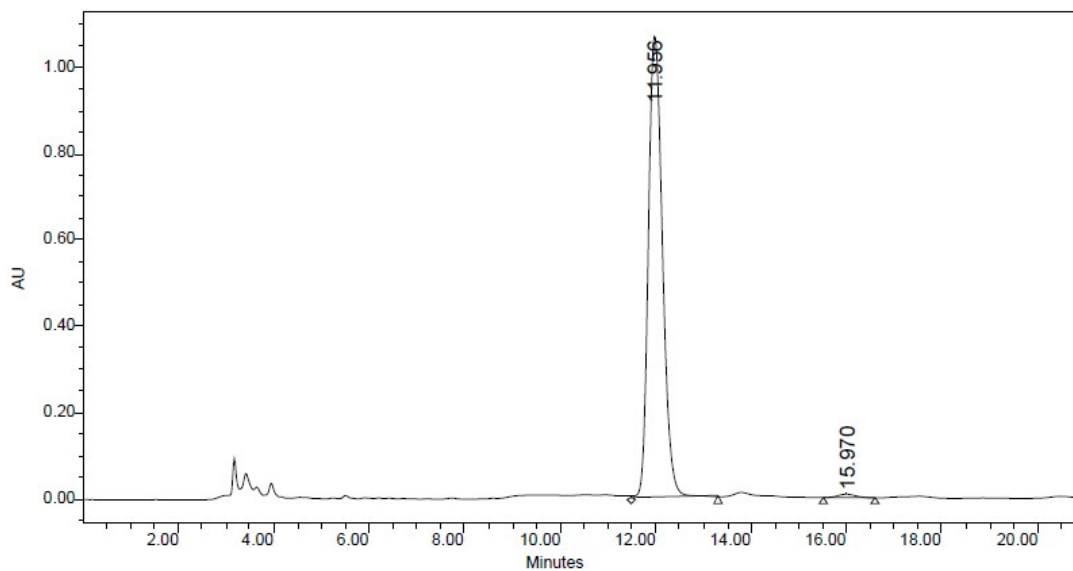
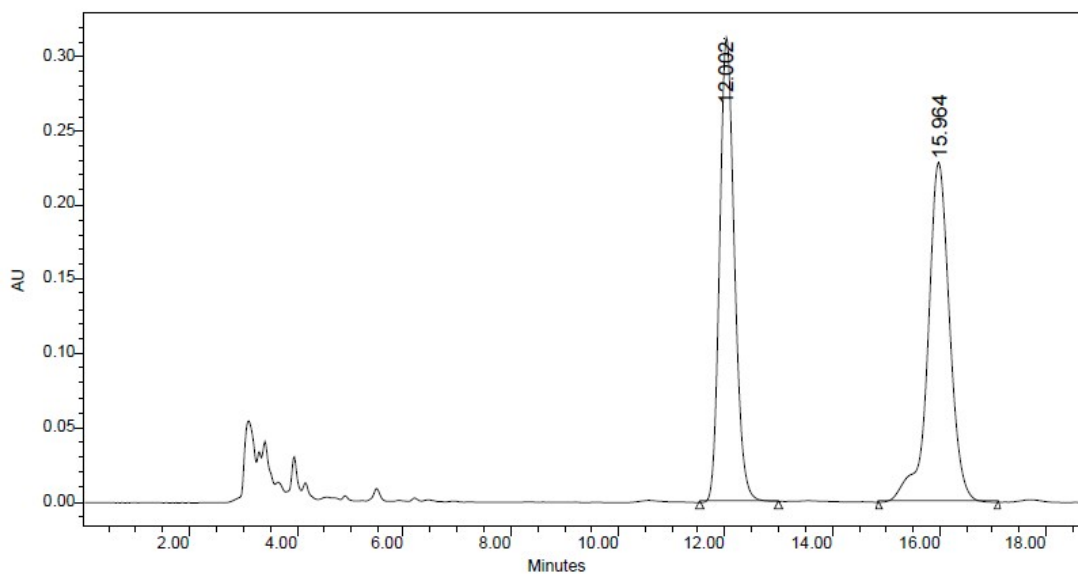
(R)-diphenyl(4-phenylbutan-2-yl)phosphine oxide (9e, 97% ee), colourless solid. Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel AD column, 0.5 mL/min, hexane /i-PrOH 90:10, retention times (min.): 29.8 (major) and 35.9 (minor).



(R)-1-methoxypropan-2-yl)diphenylphosphine oxide (9f, 98% ee), colourless liquid. <sup>1</sup>H NMR (400

### Electronic Supplementary Information

MHz,  $\text{CDCl}_3$ )  $\delta$  7.83-7.75 (m, 4H), 7.53-7.43 (m, 6H), 3.60 (td,  $J = 9.1, 4.3$  Hz, 1H), 3.46 (dd,  $J = 16.7, 9.1$  Hz, 1H), 3.22 (s, 3H), 2.75 (dt,  $J = 11.7, 7.8$  Hz, 1H), 1.23 (dd,  $J = 16.4, 7.1$  Hz, 3H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  132.0(d,  $J = 96.1$  Hz), 131.7 (d,  $J = 2.0$  Hz), 131.0 (d,  $J = 8.9$  Hz), 128.6 (d,  $J = 11.2$  Hz), 72.01 (d,  $J = 3.1$  Hz), 58.8, 33.9 (d,  $J = 71.3$  Hz), 10.9 (d,  $J = 3.2$  Hz) ppm.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  34.3 ppm. HRMS calcd for  $\text{C}_{16}\text{H}_{19}\text{O}_2\text{P}$  ( $\text{M}^+$ ): 274.1123; found: 274.1121. Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel IC column, 0.5 mL/min, hexane /*i*-PrOH 70:30, retention times (min.): 12.0 (major) and 16.0 (minor).



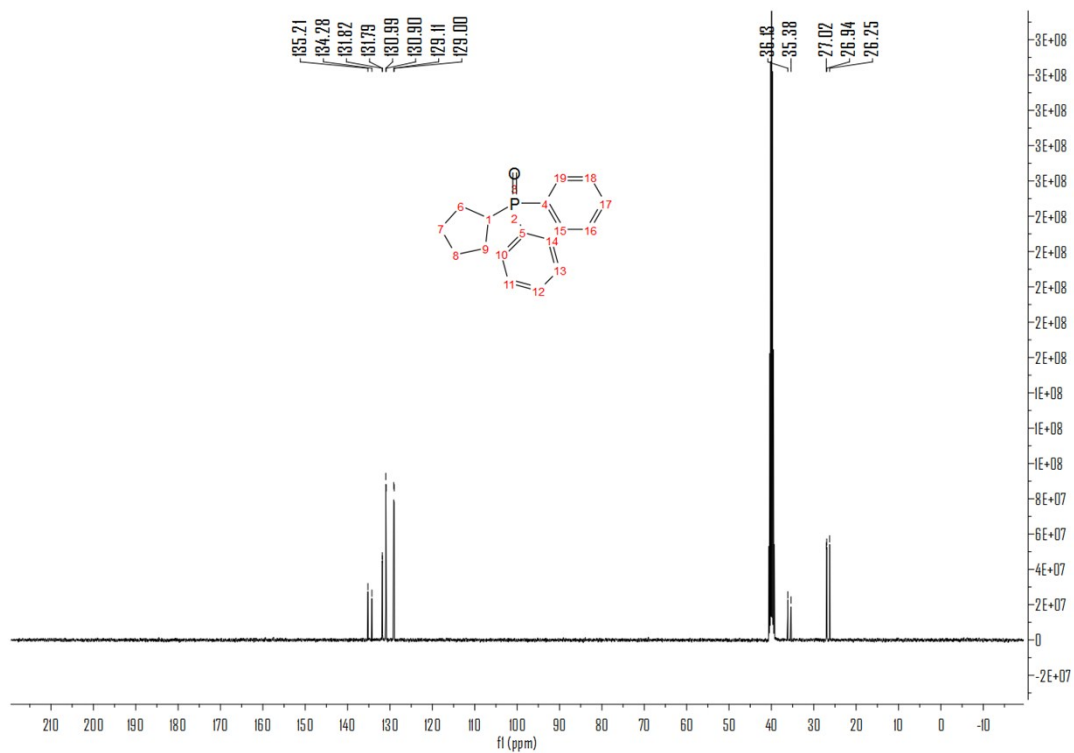
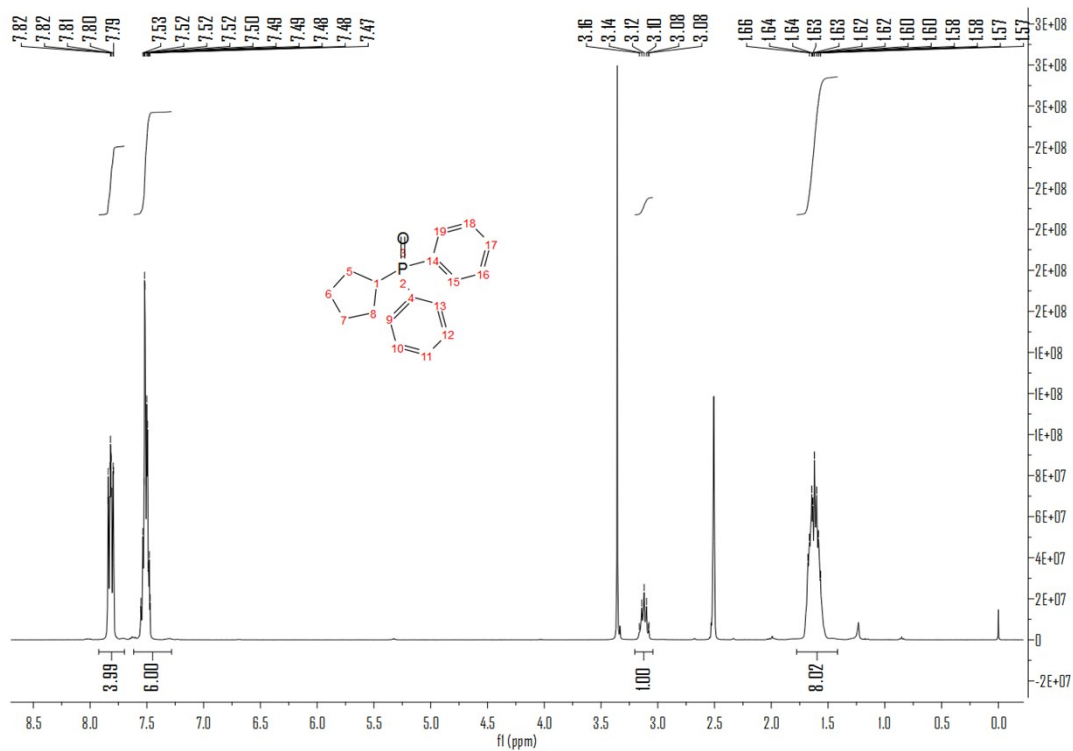
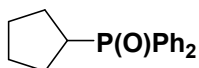
## *Electronic Supplementary Information*

### **III. References**

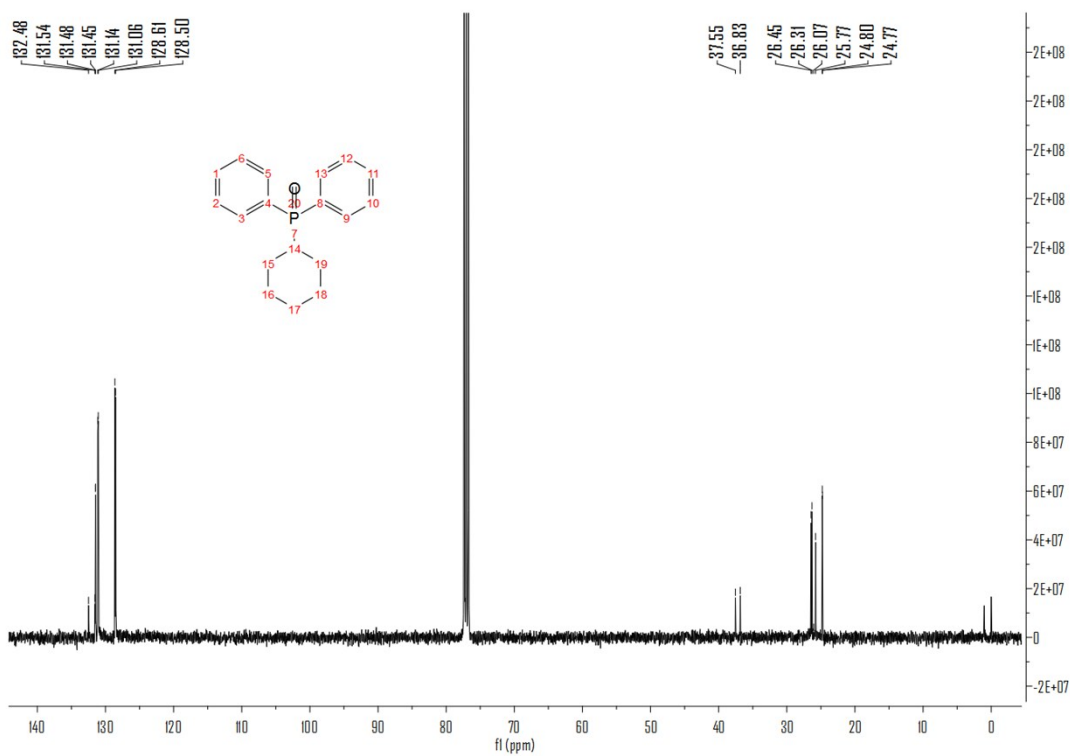
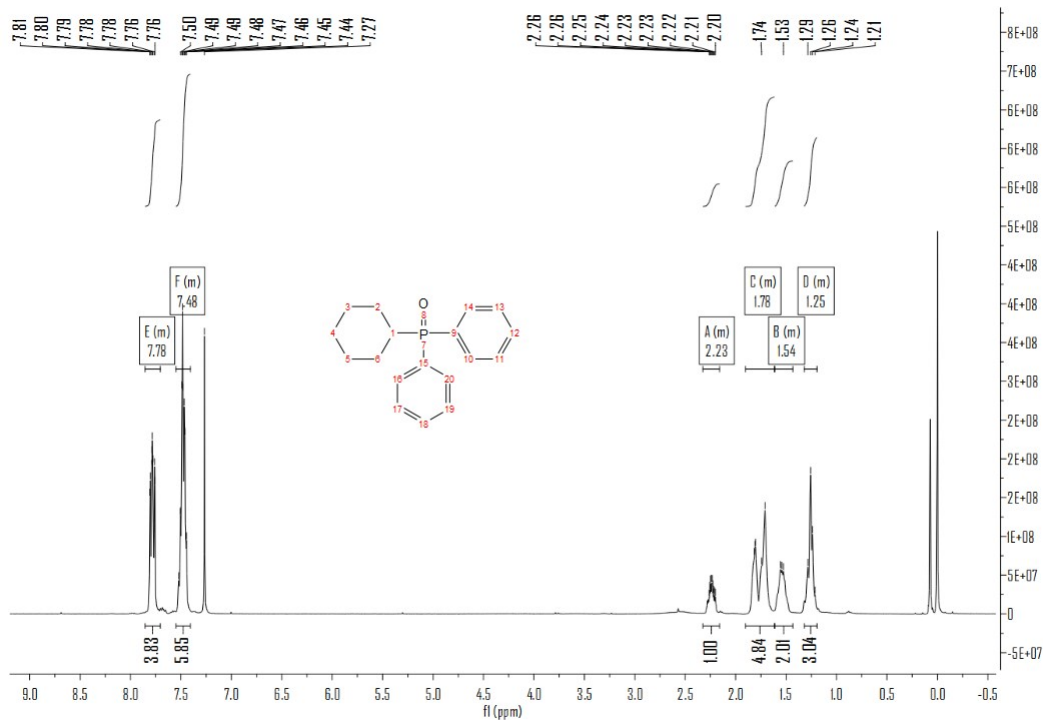
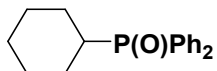
- 1 (a) D. H. Burns, J. D. Miller, H. K. Chan and M. O. Delaney, *J. Am. Chem. Soc.* 1997, **119**, 2125; (b) A. Corruble, J.-Y. Valnot, J. Maddaluno and P. Duhamel, *J. Org. Chem.* 1998, **63**, 8266.
- 2 C.-T. Yang, Z.-Q. Zhang, J. Liang, J.-H. Liu, X.-Y. Lu, H.-H. Chen and L. Liu, *J. Am. Chem. Soc.*, 2012, **134**, 11124.
- 3 S. E. Vaillard, C. Mück-Lichtenfeld, S. Grimme and A. Studer, *Angew. Chem. Int. Ed.* 2007, **46**, 6533.
- 4 M. T. Honaker, B. J. Sandefur, J. L. Hargett, A. L. McDaniel and R. N. Salvatore, *Tetrahedron Lett.* 2003, **44**, 8373.
- 5 Y. Li, S. Das, S. Zhou, K. Junge and M. Beller, *J. Am. Chem. Soc.* 2012, **134**, 9727.

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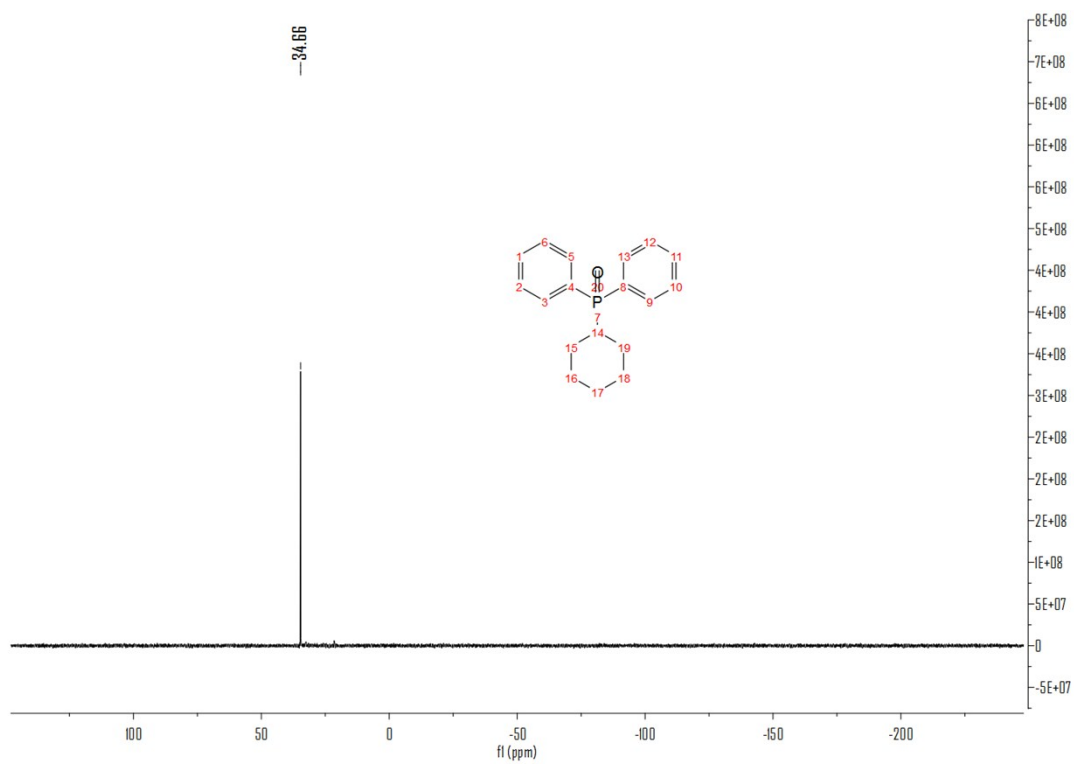
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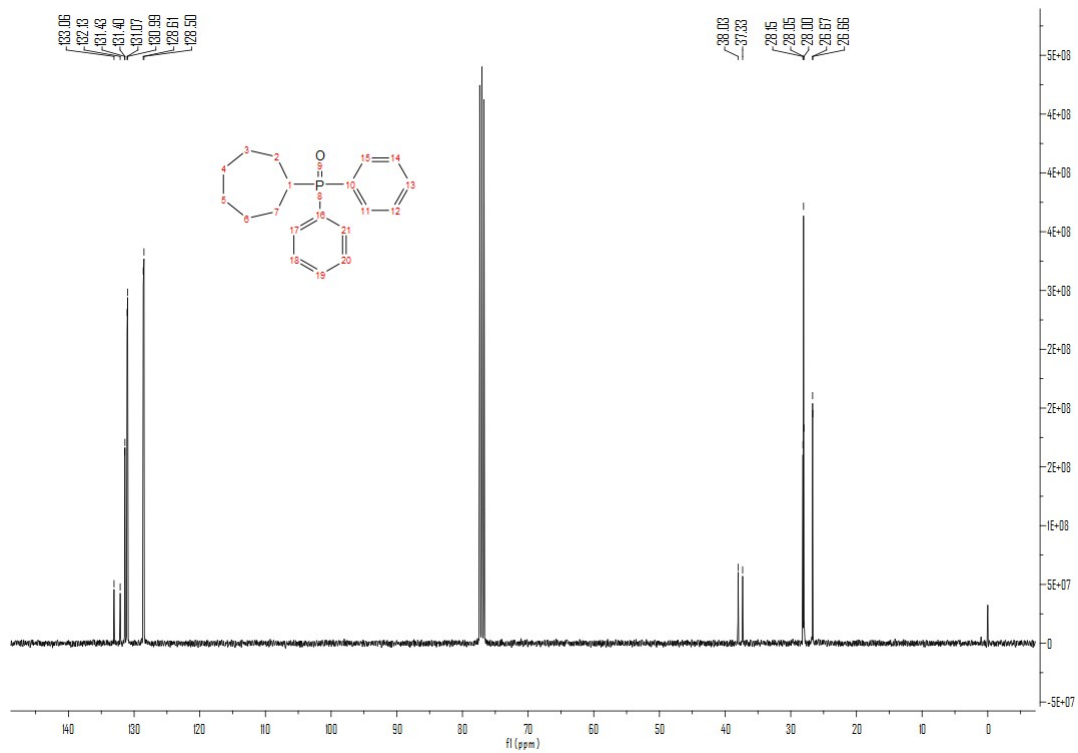
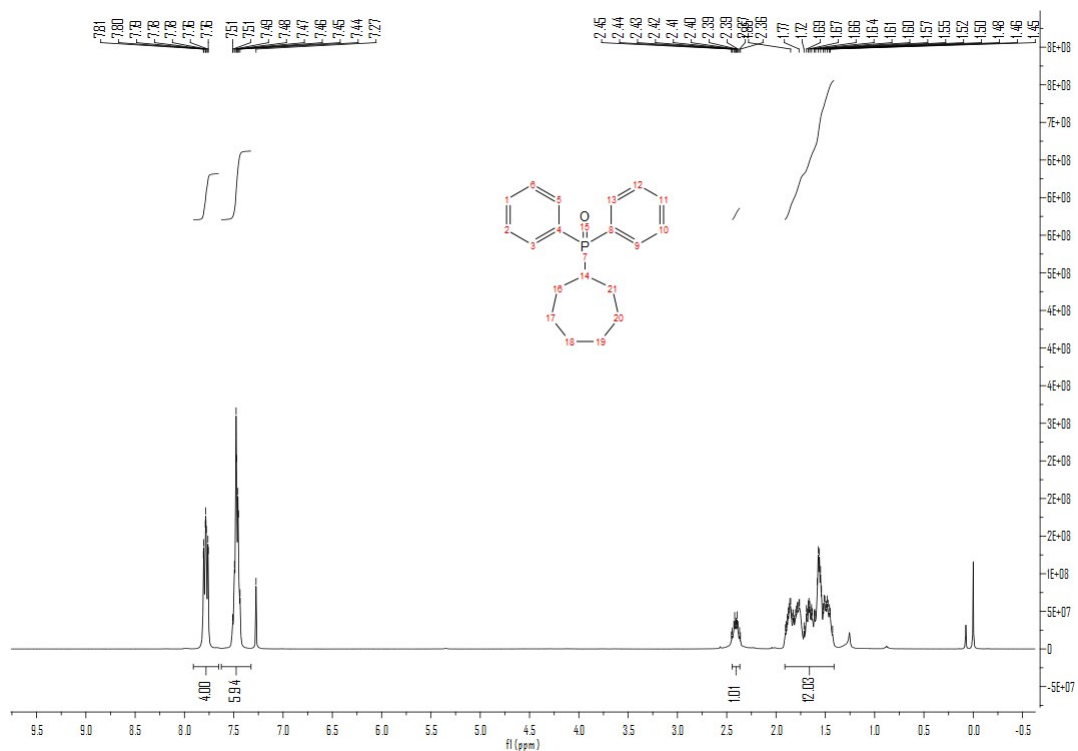
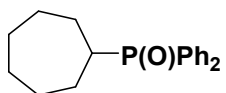


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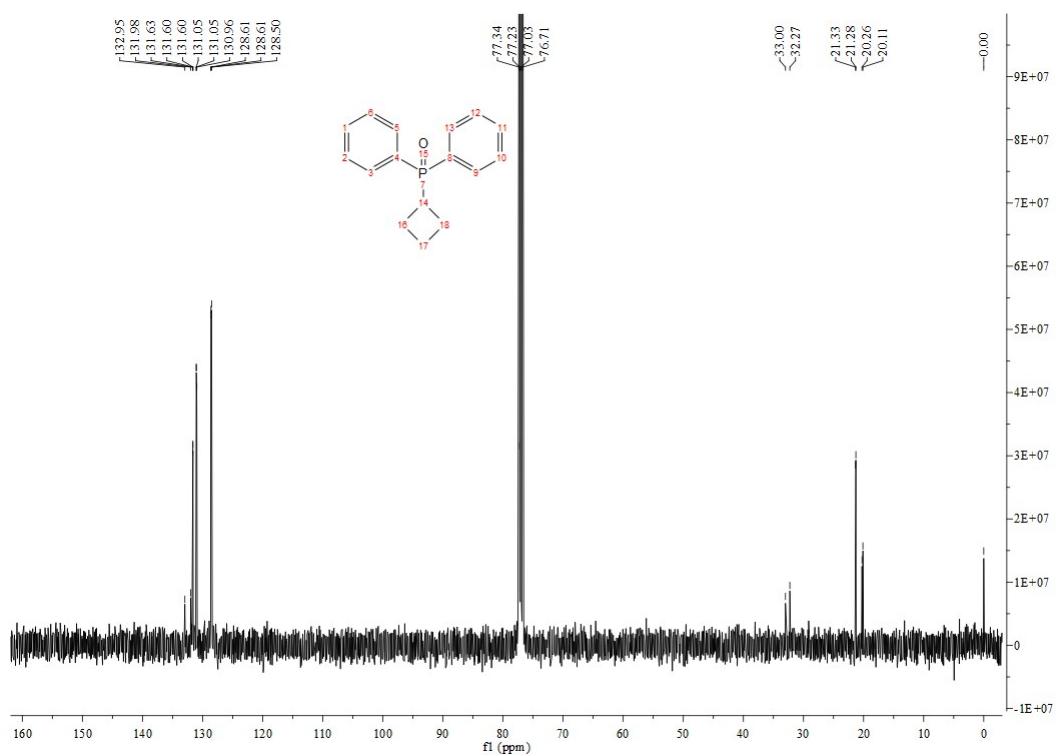
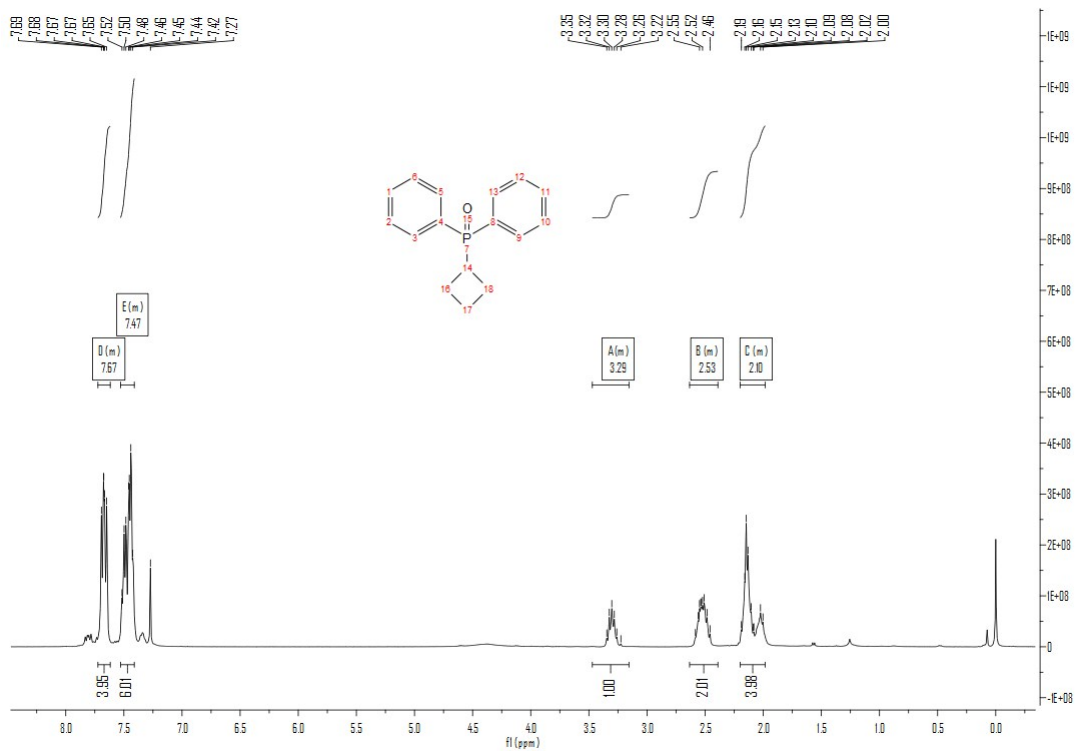
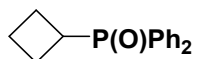




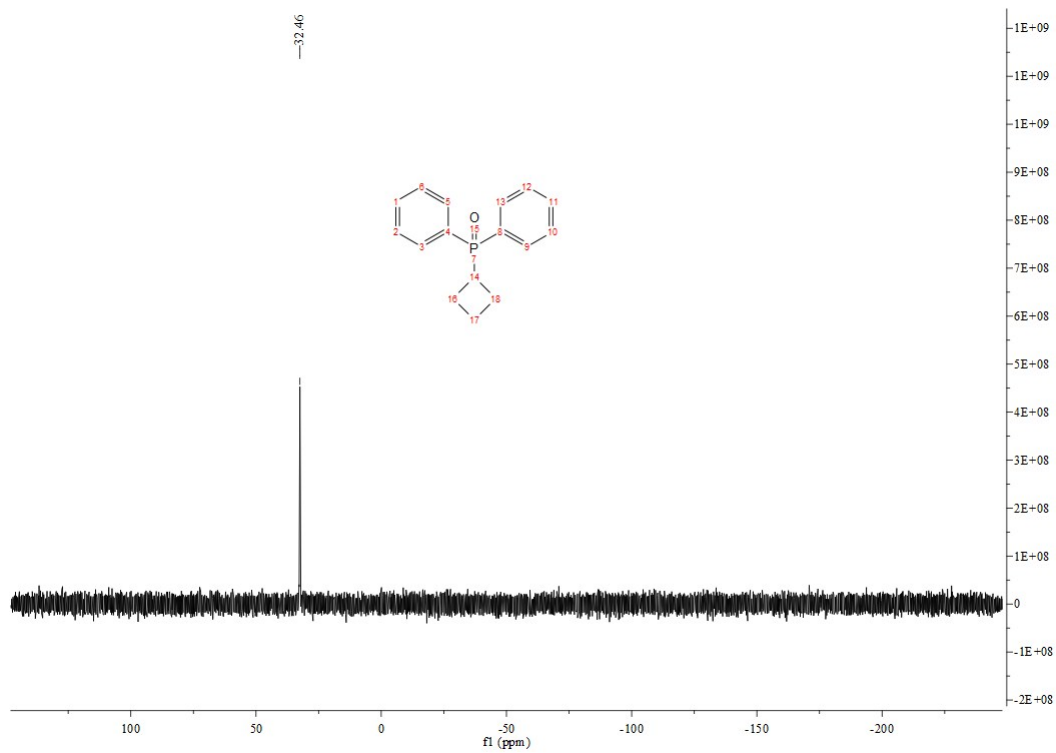
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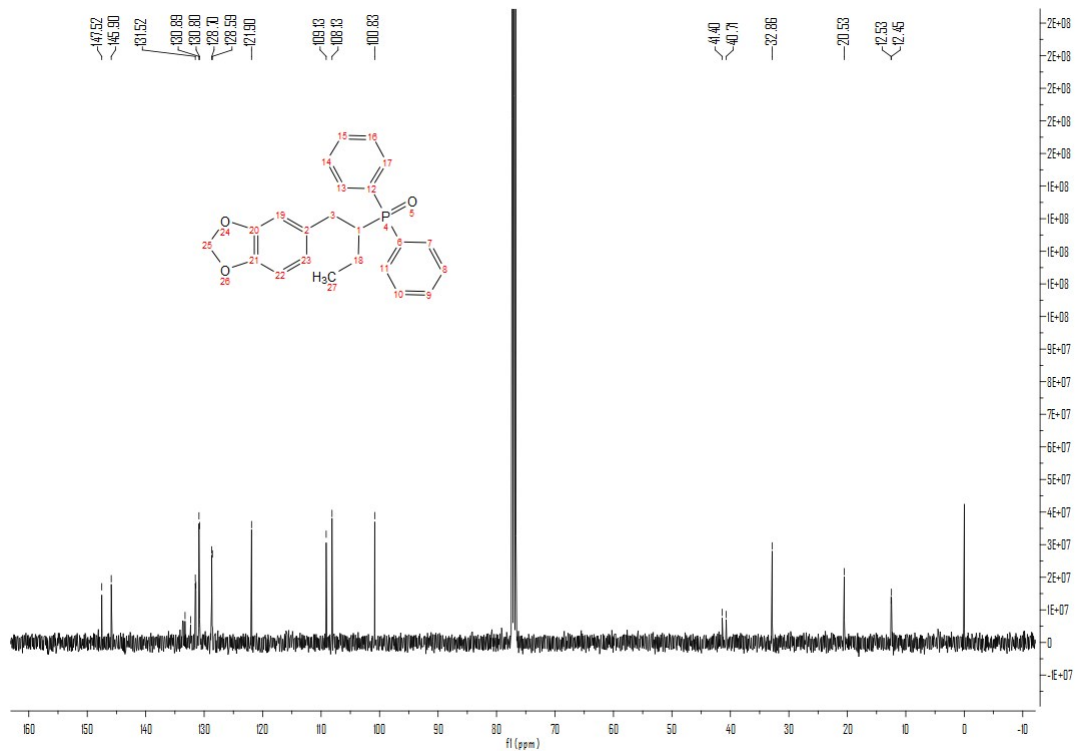
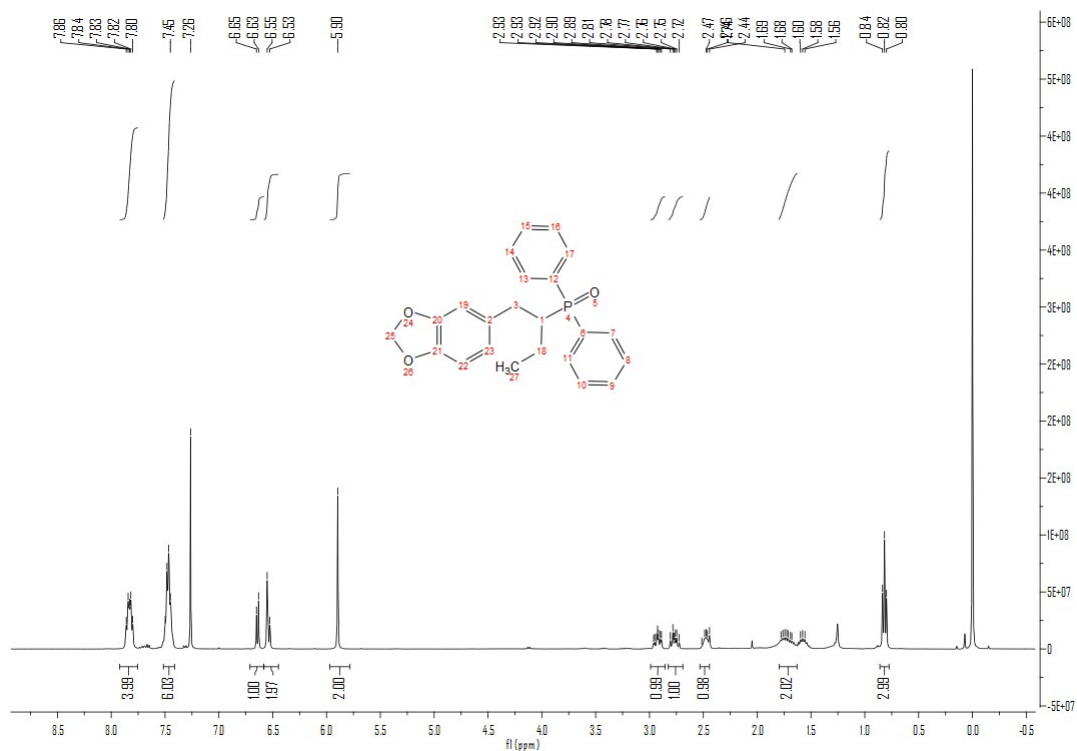
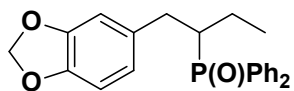
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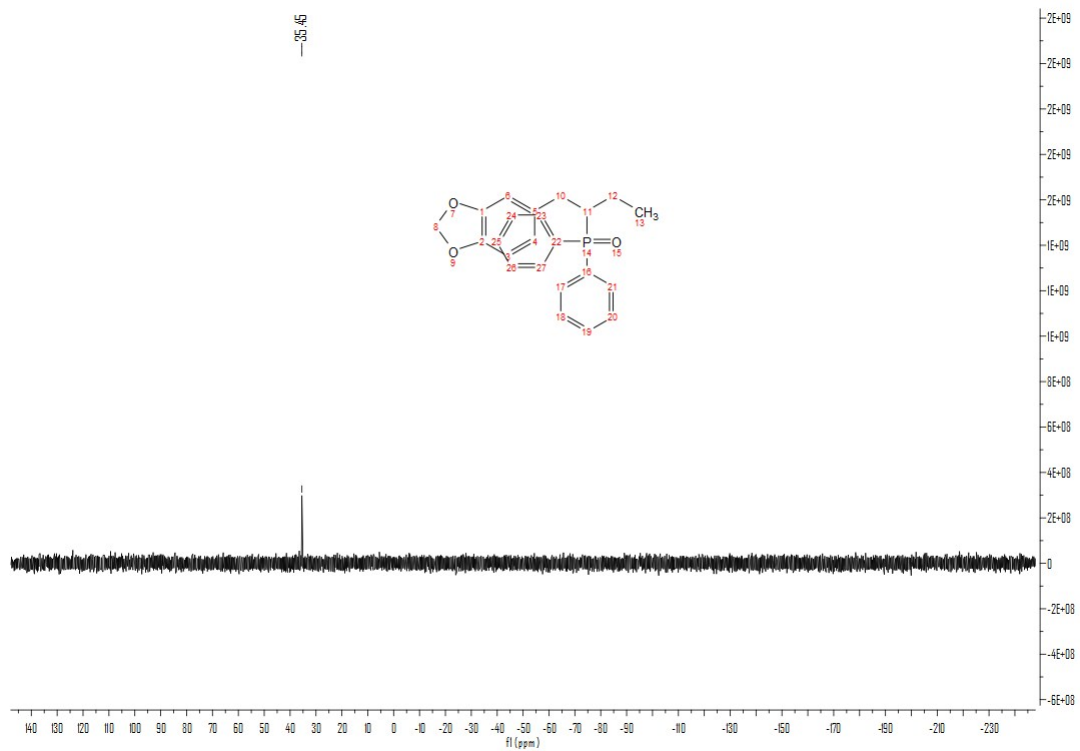
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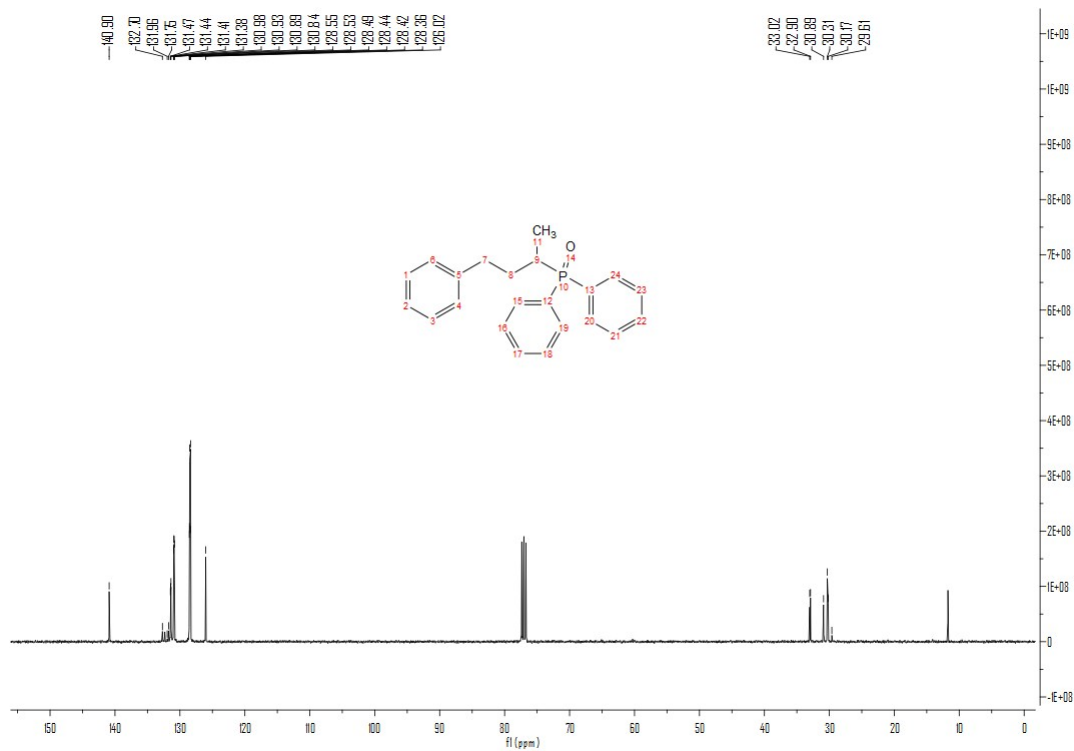
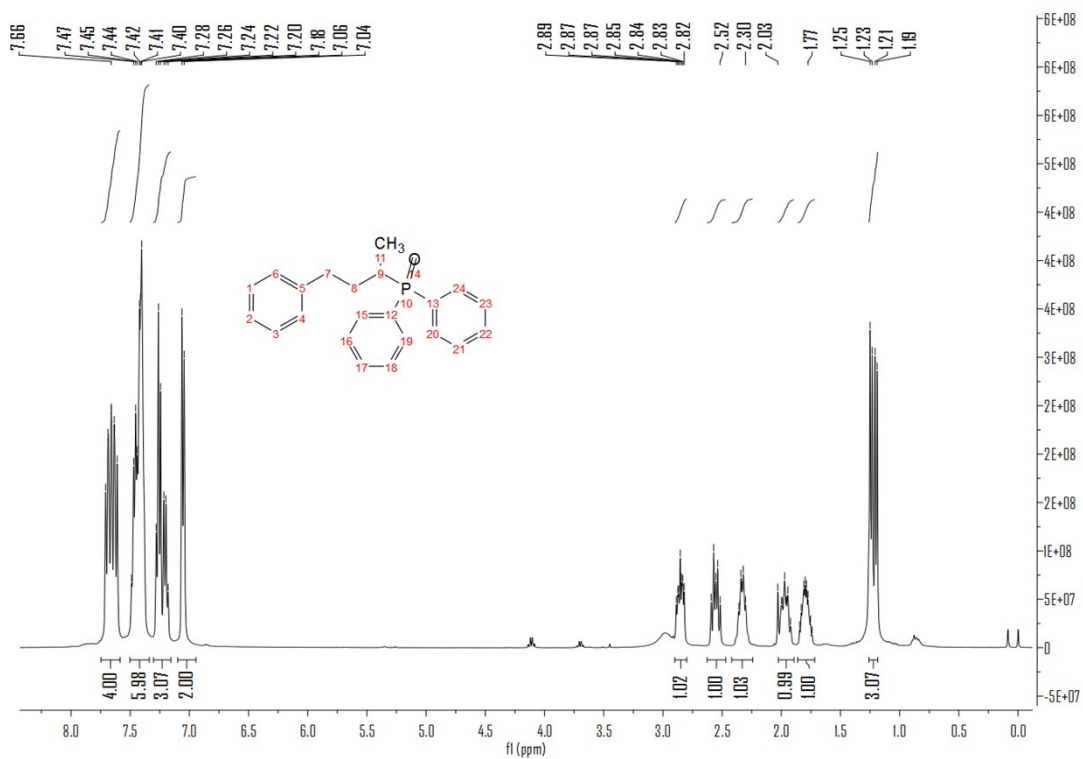
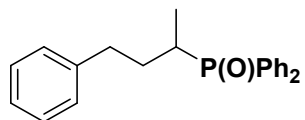
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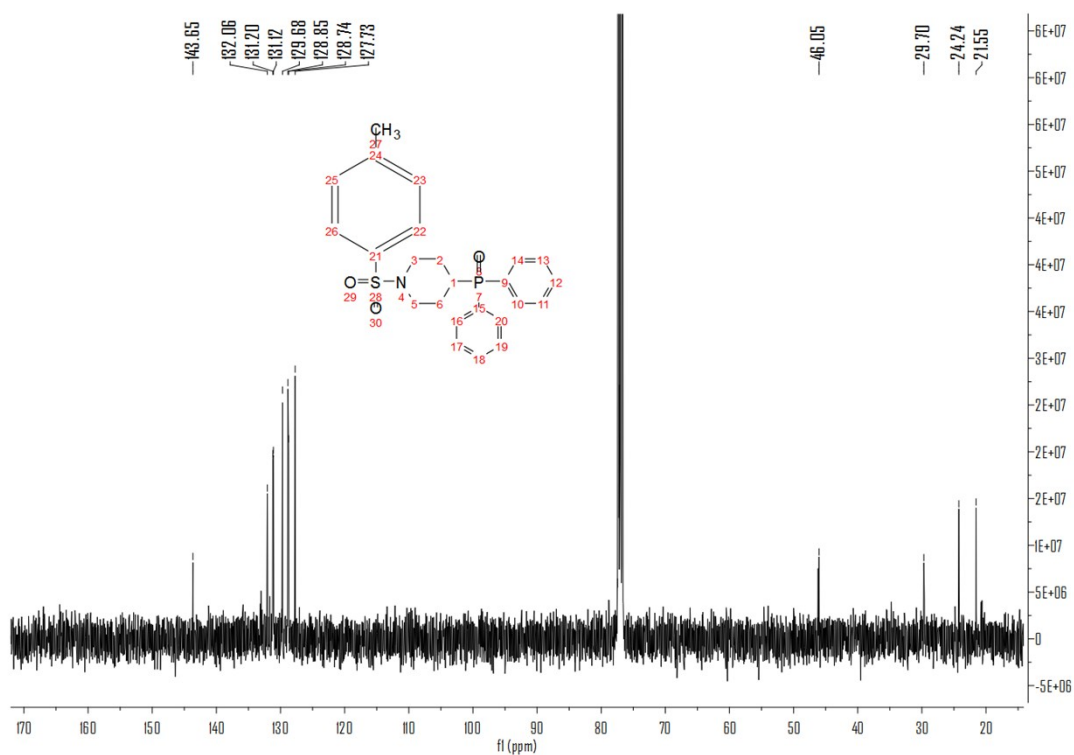
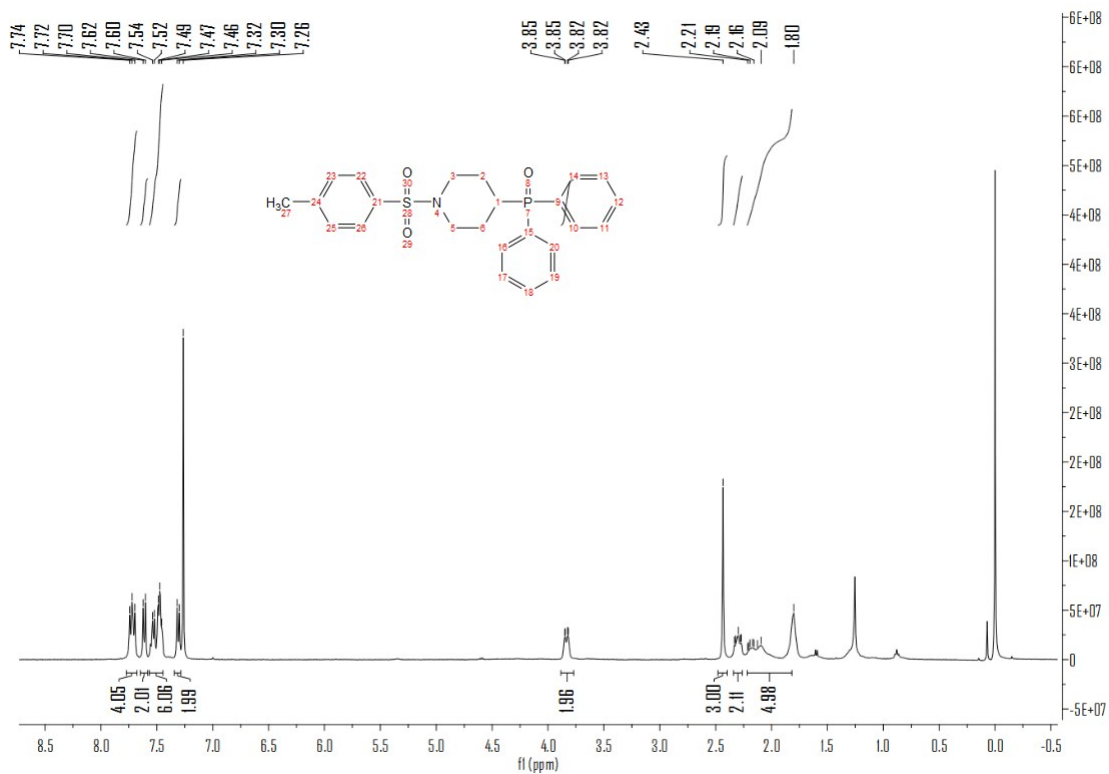
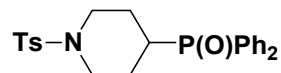
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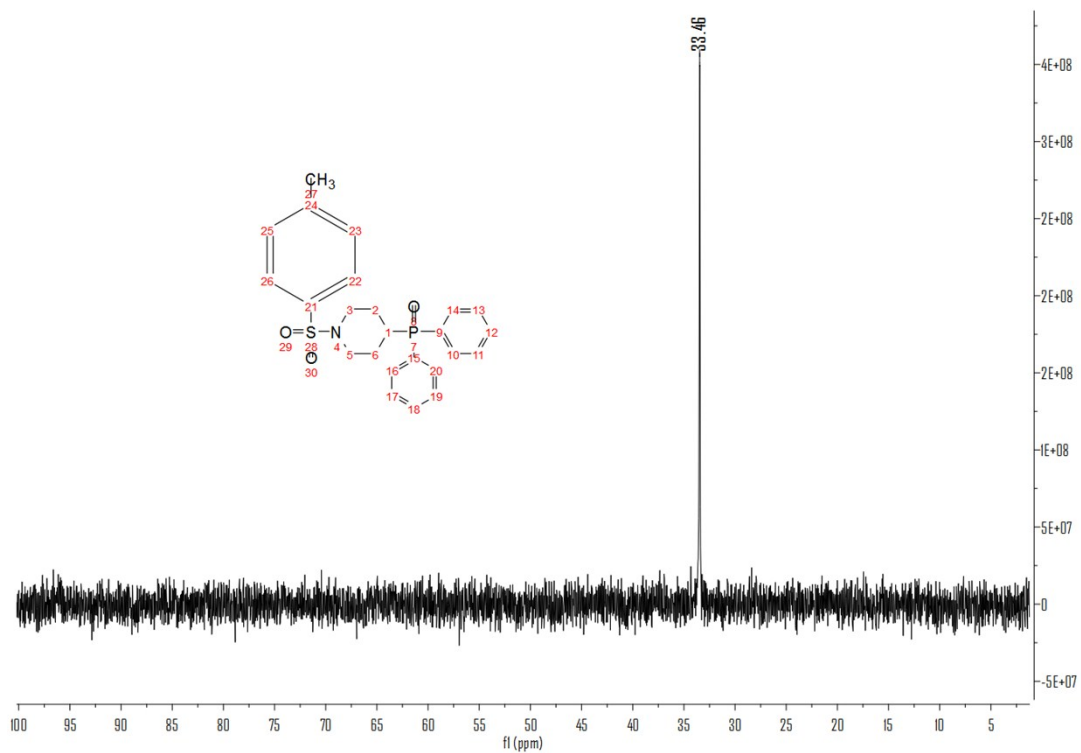
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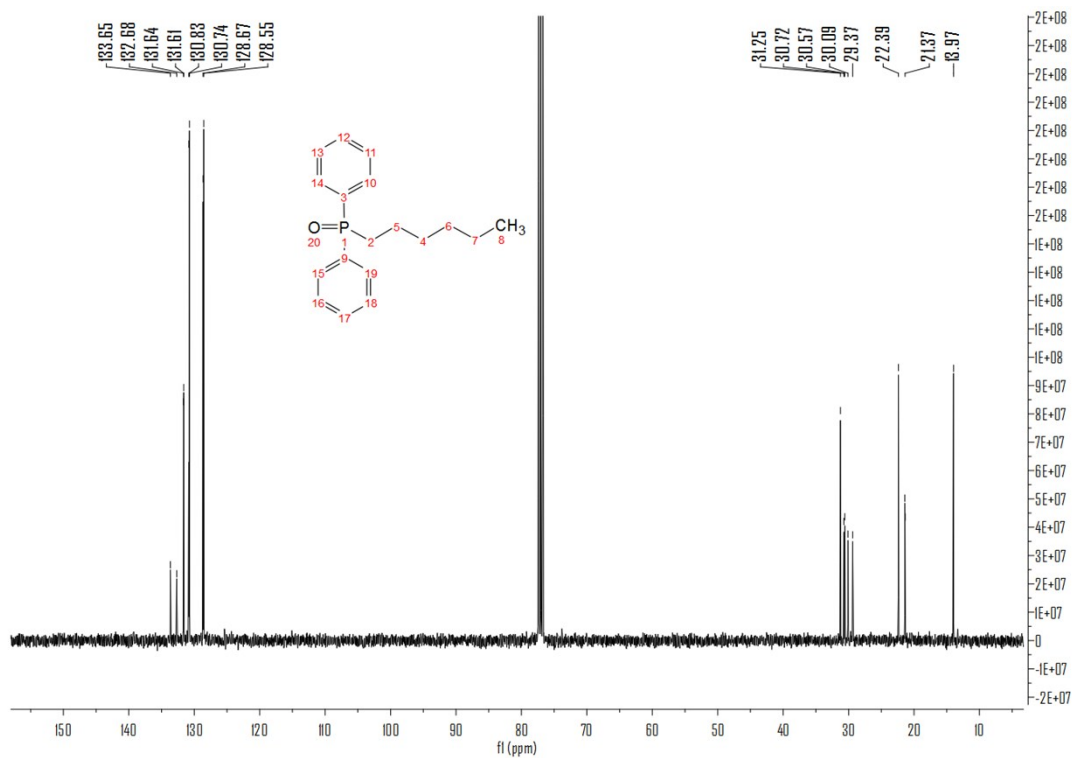
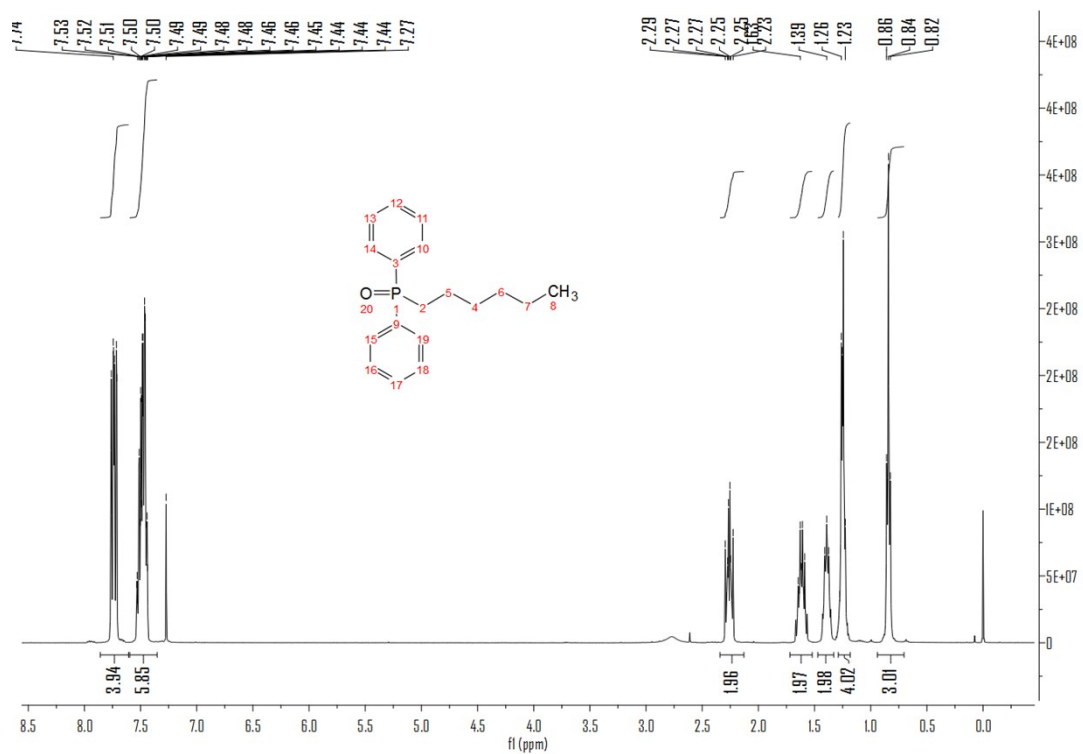
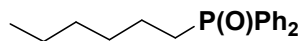


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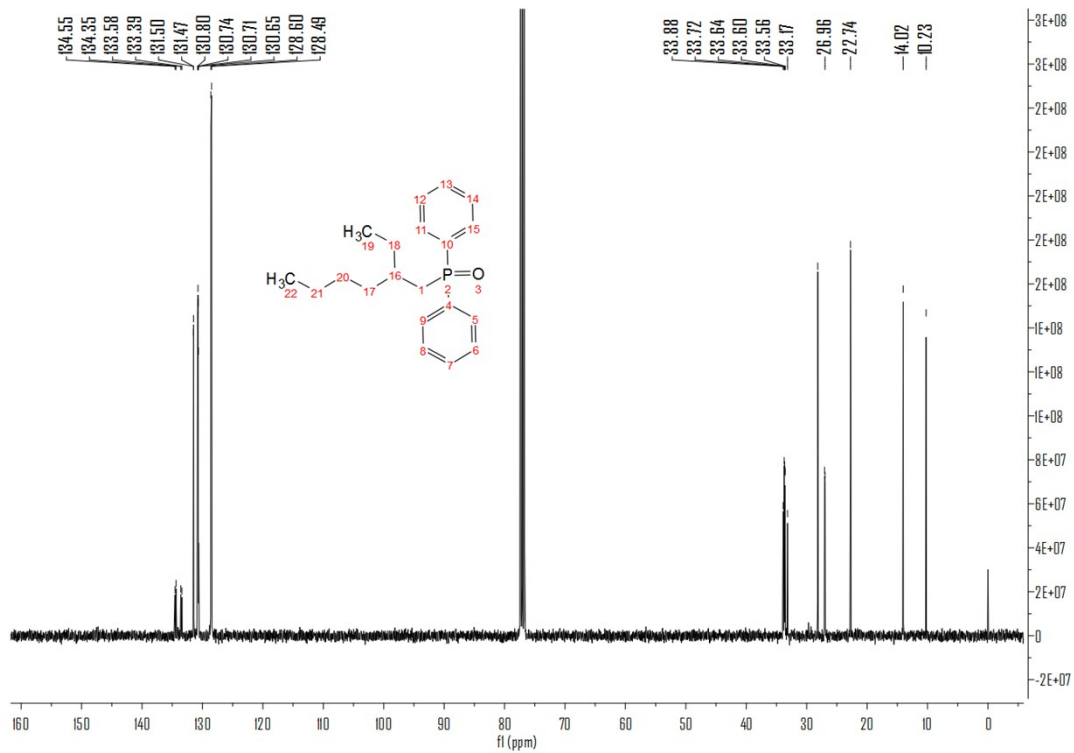
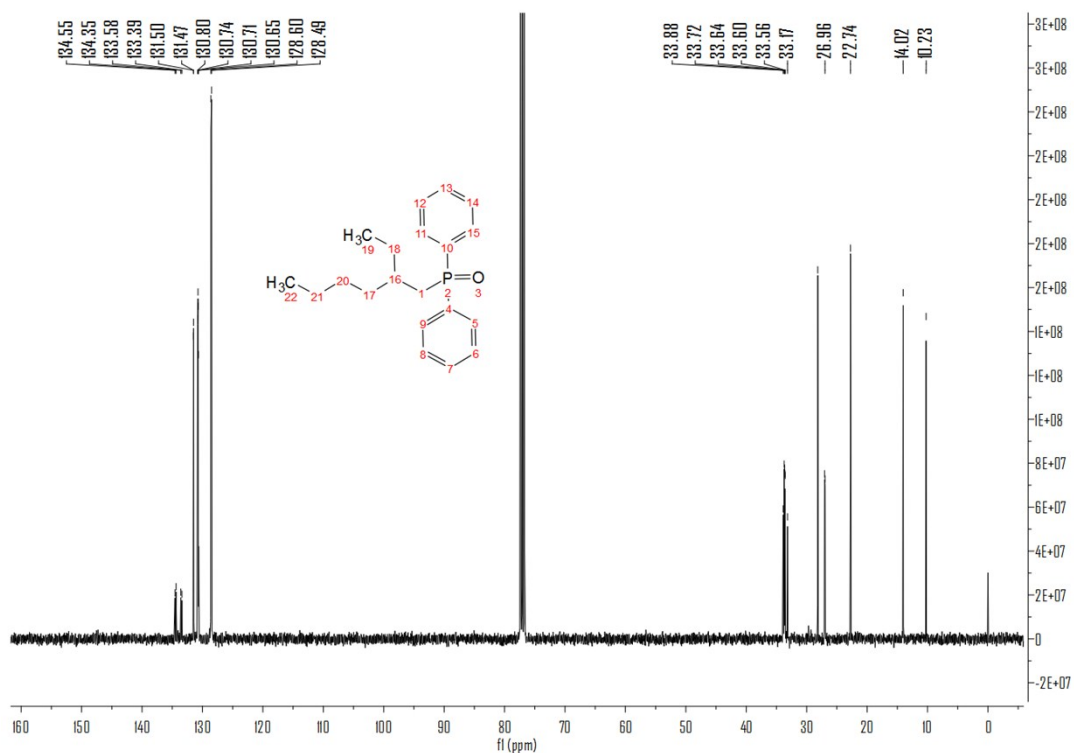
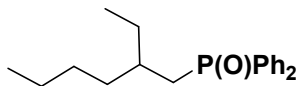




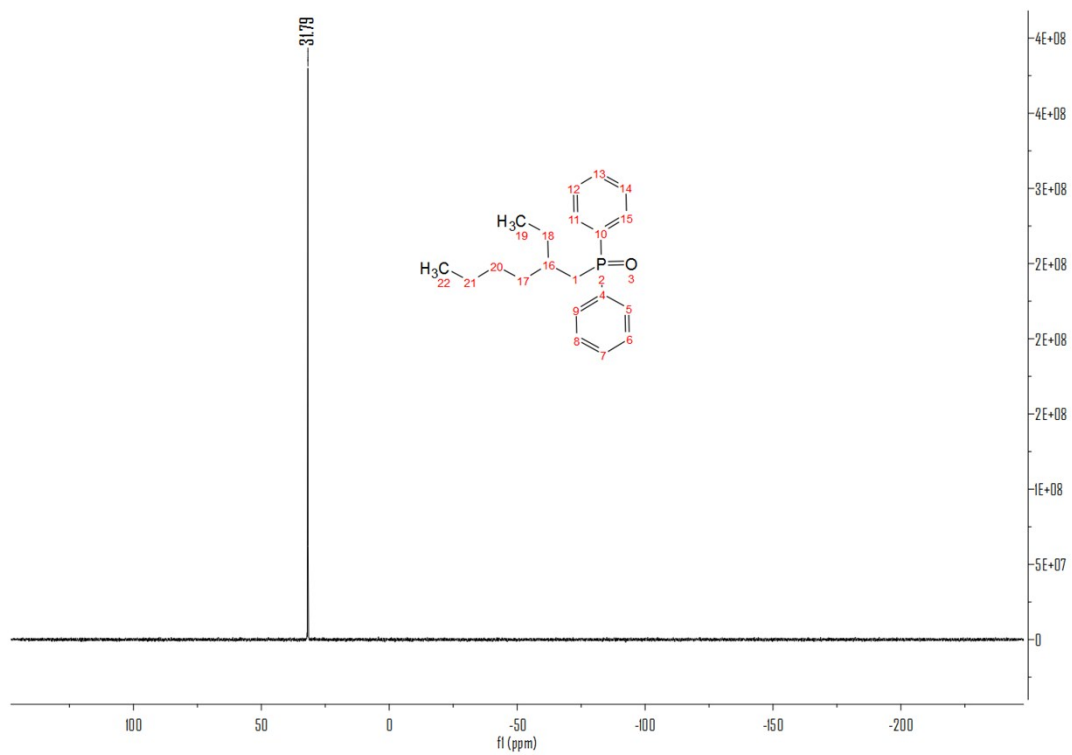
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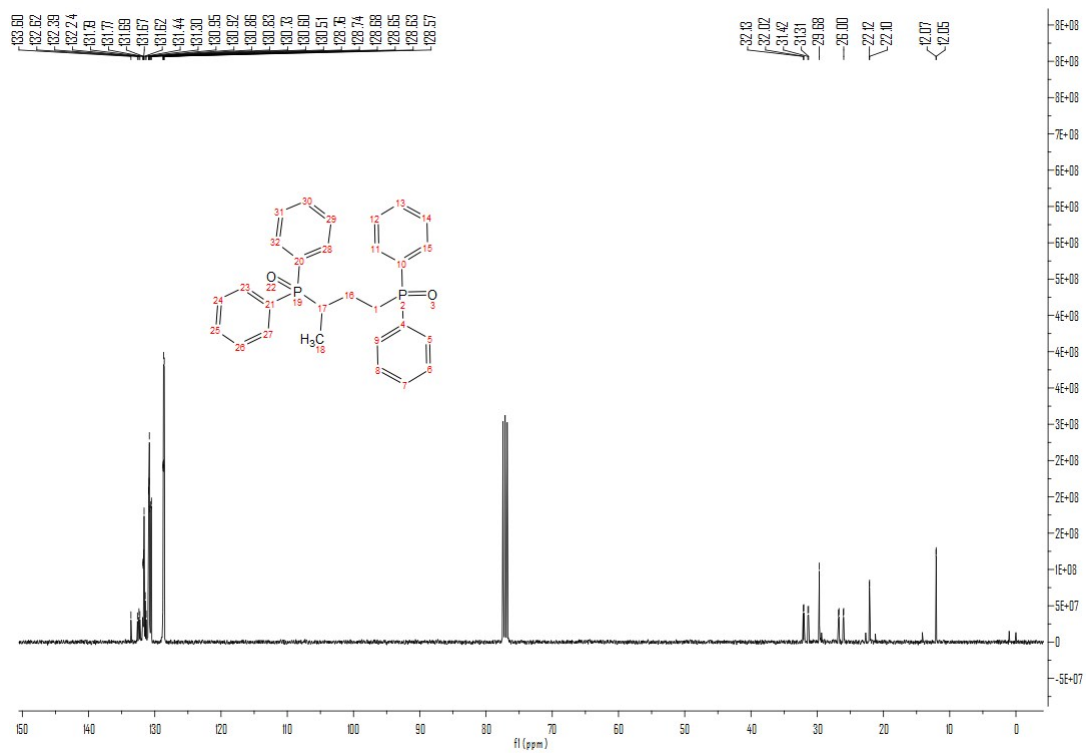
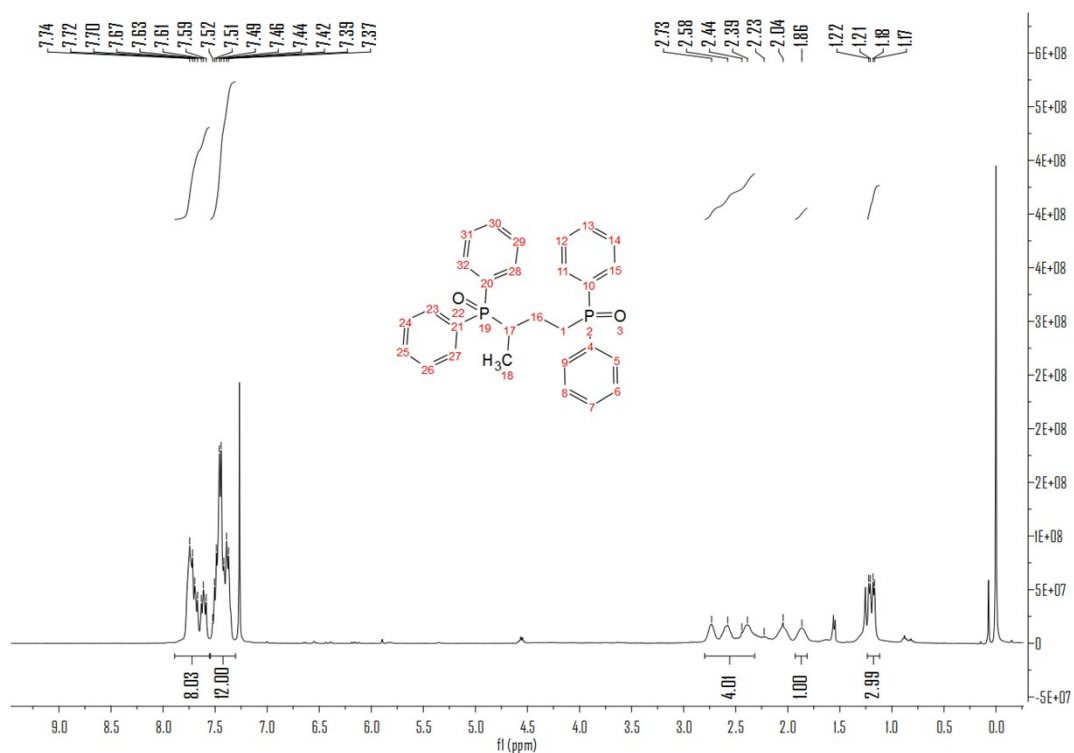
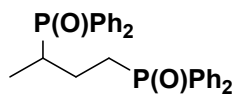
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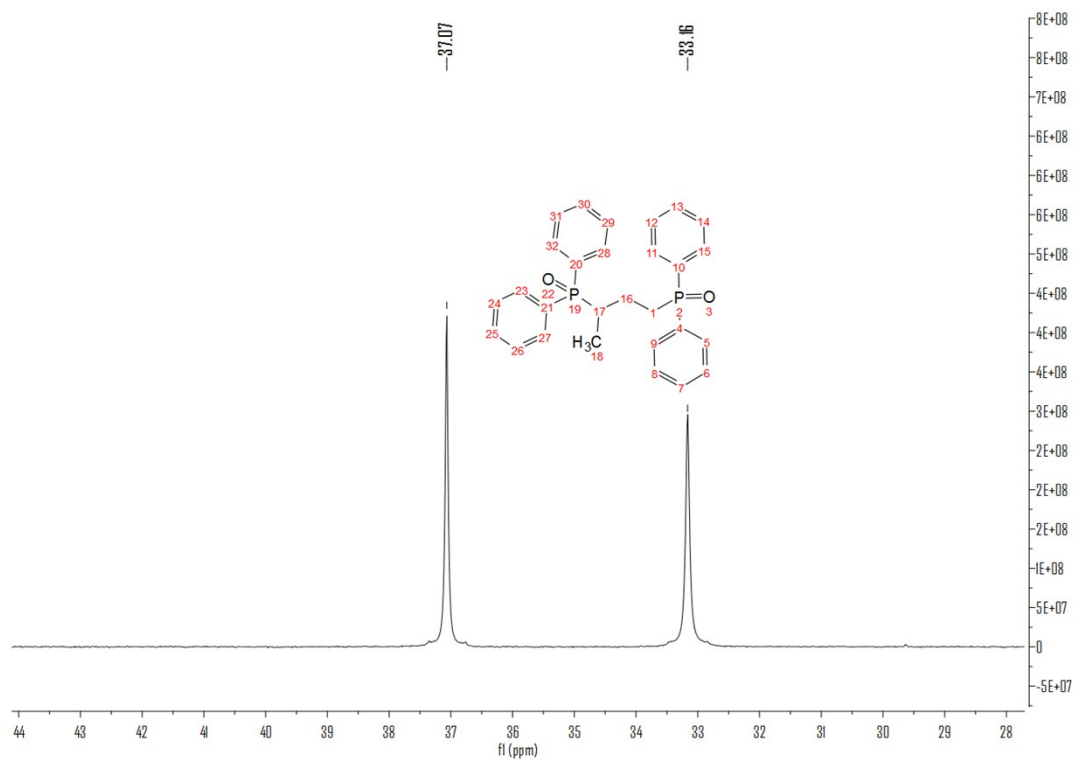
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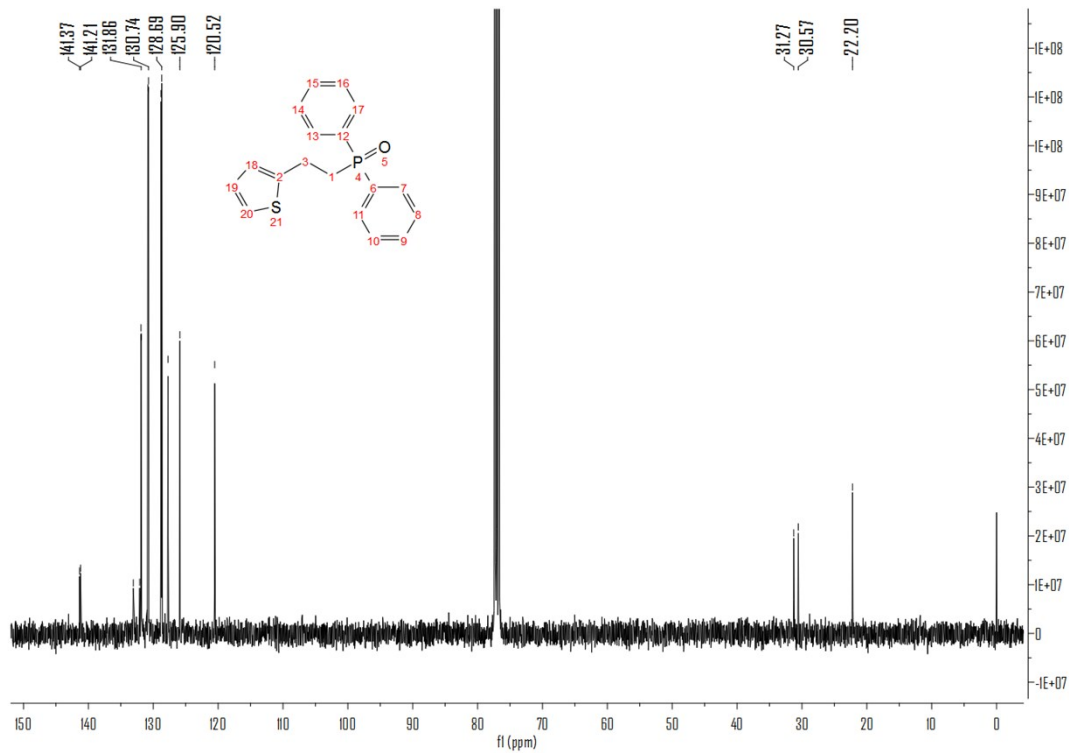
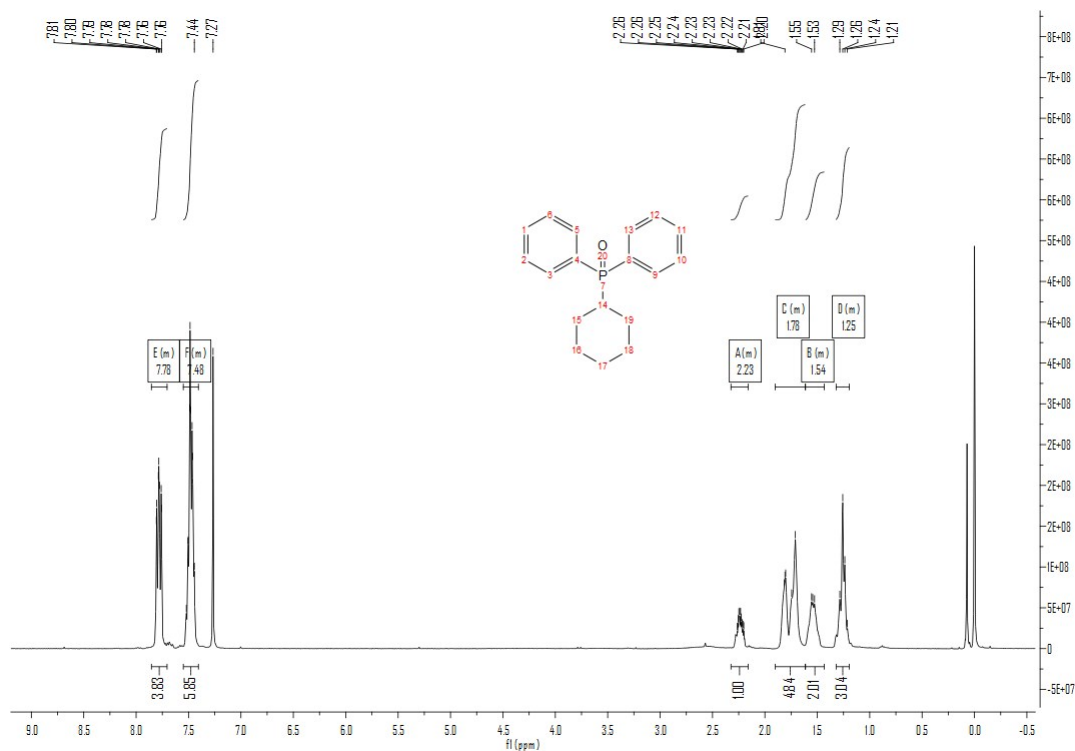
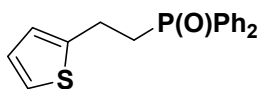
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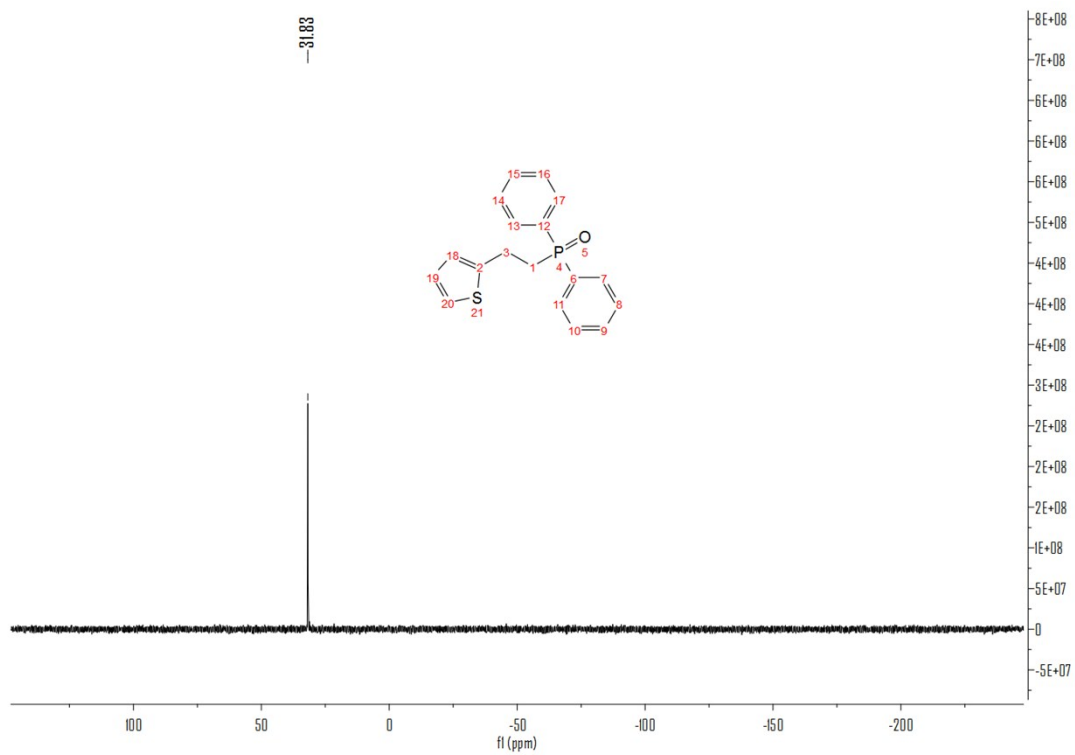
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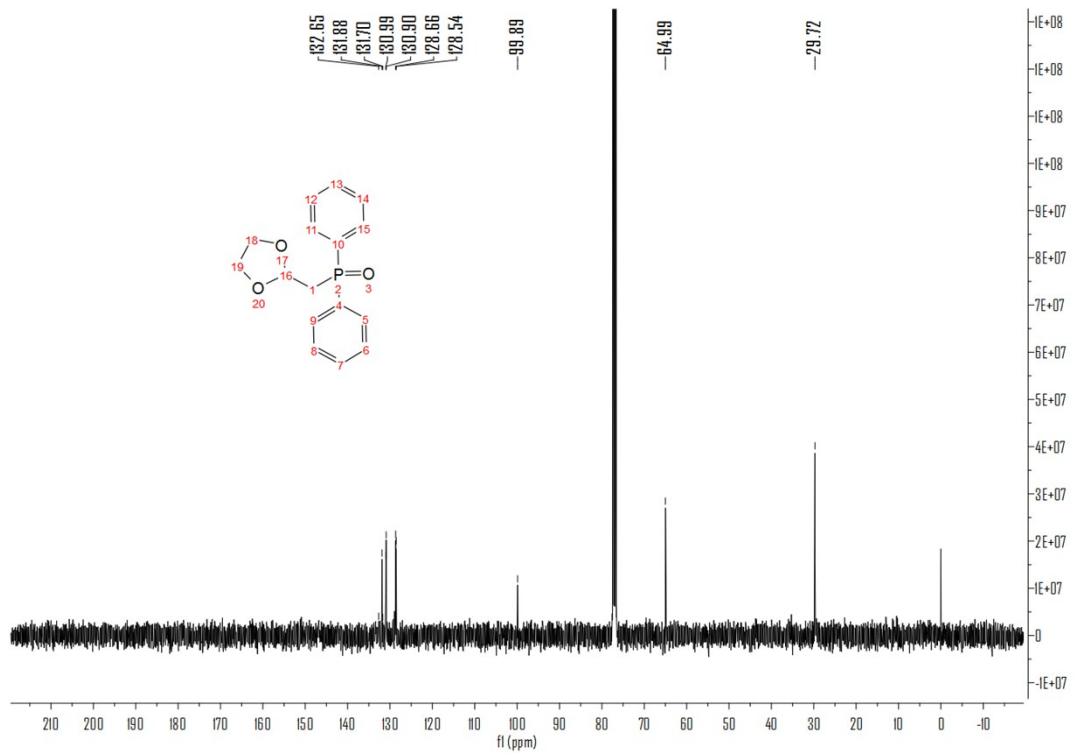
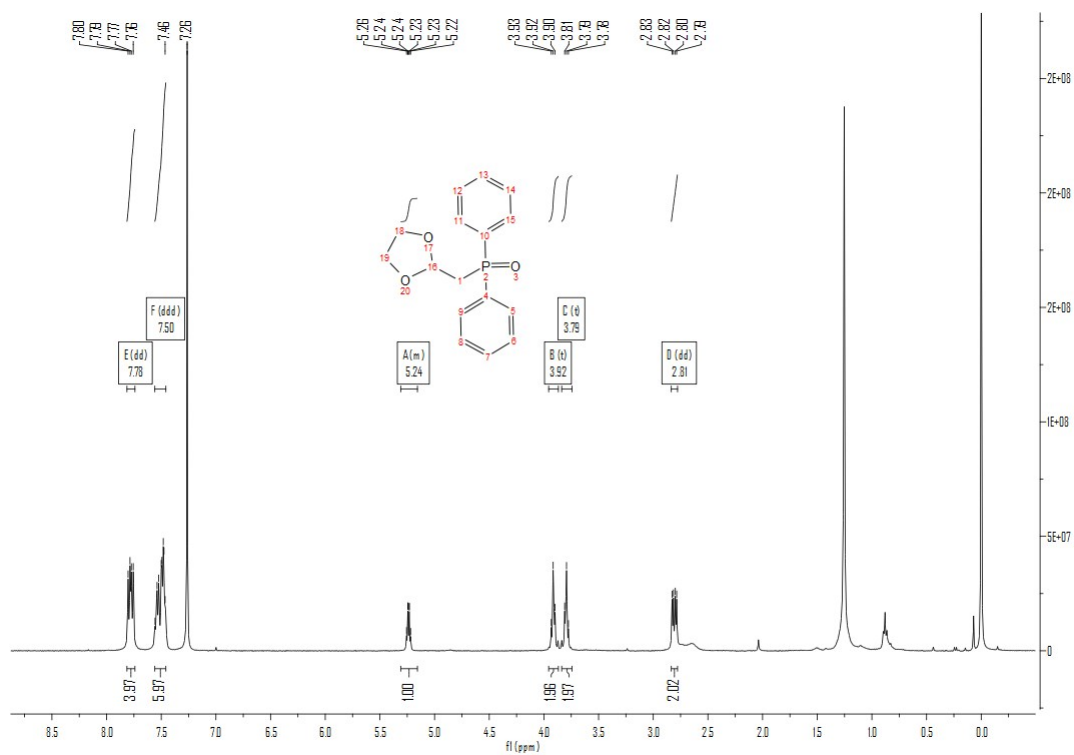
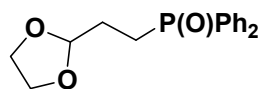
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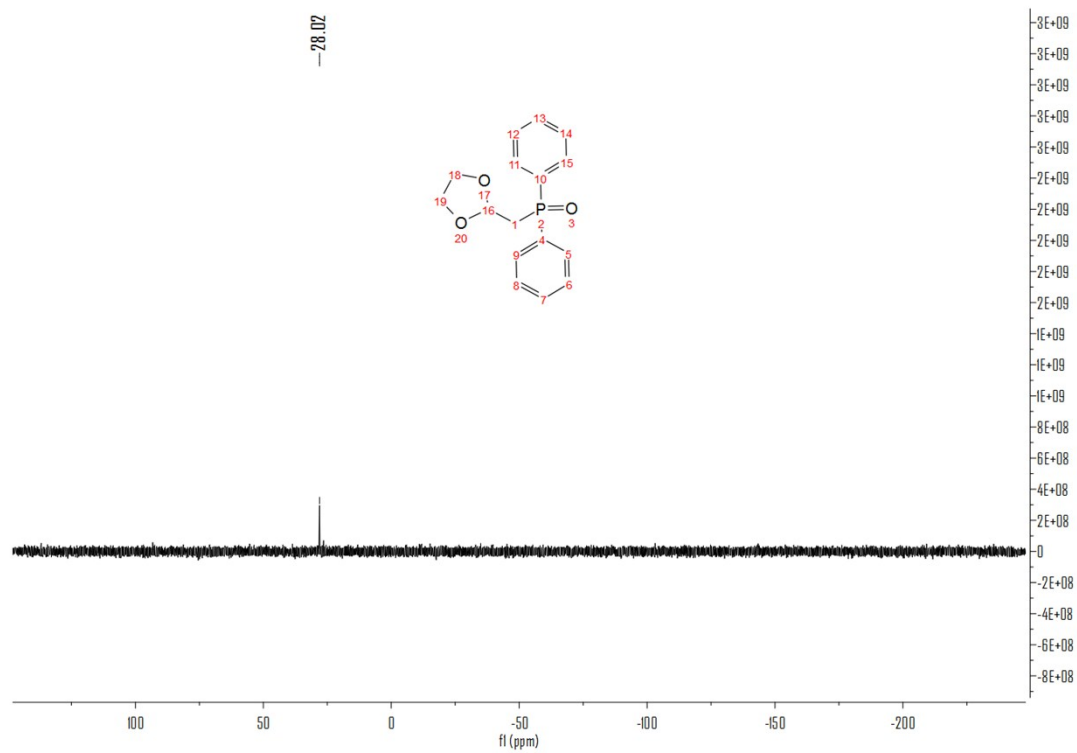


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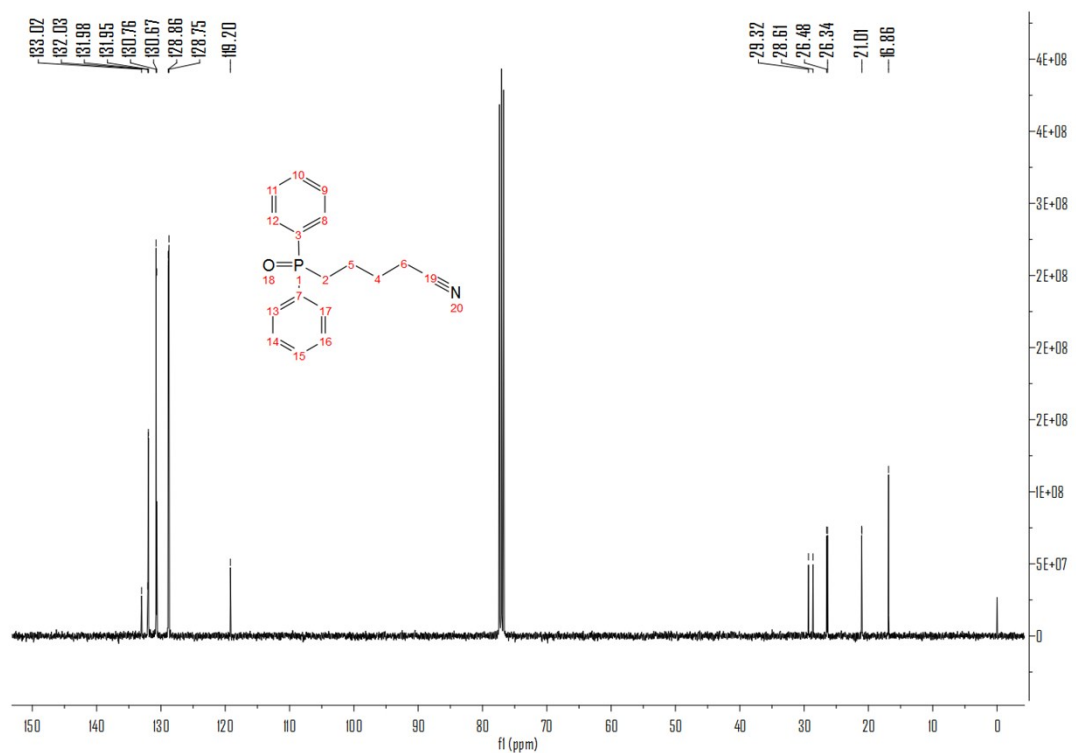
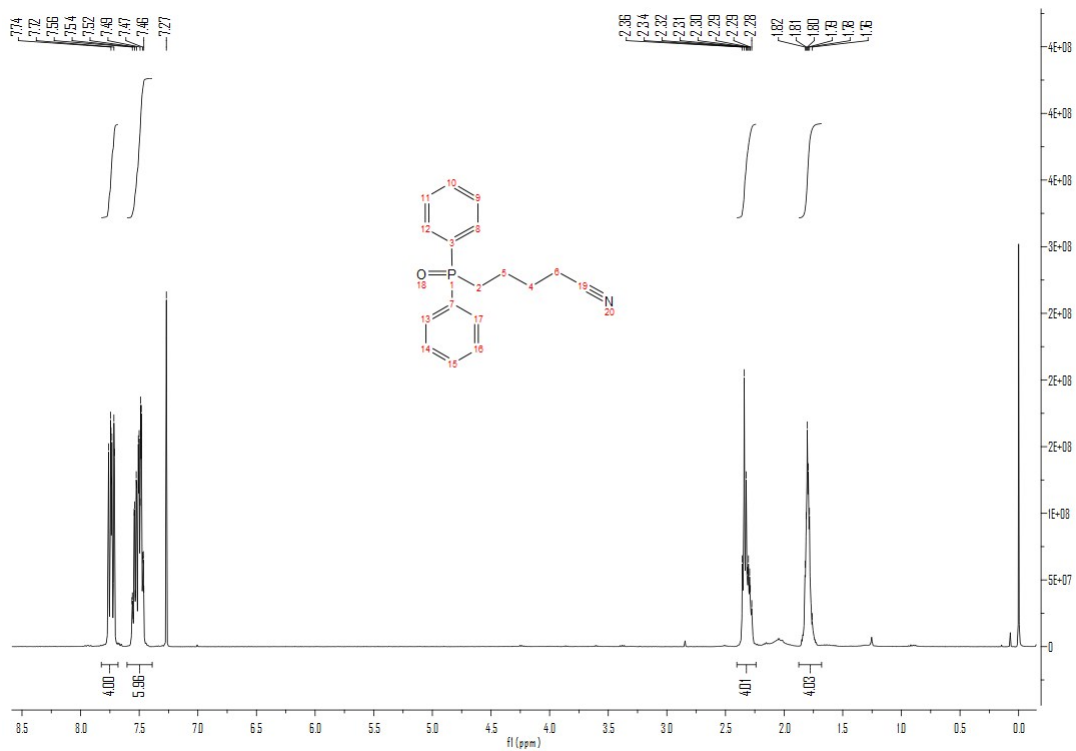
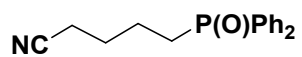




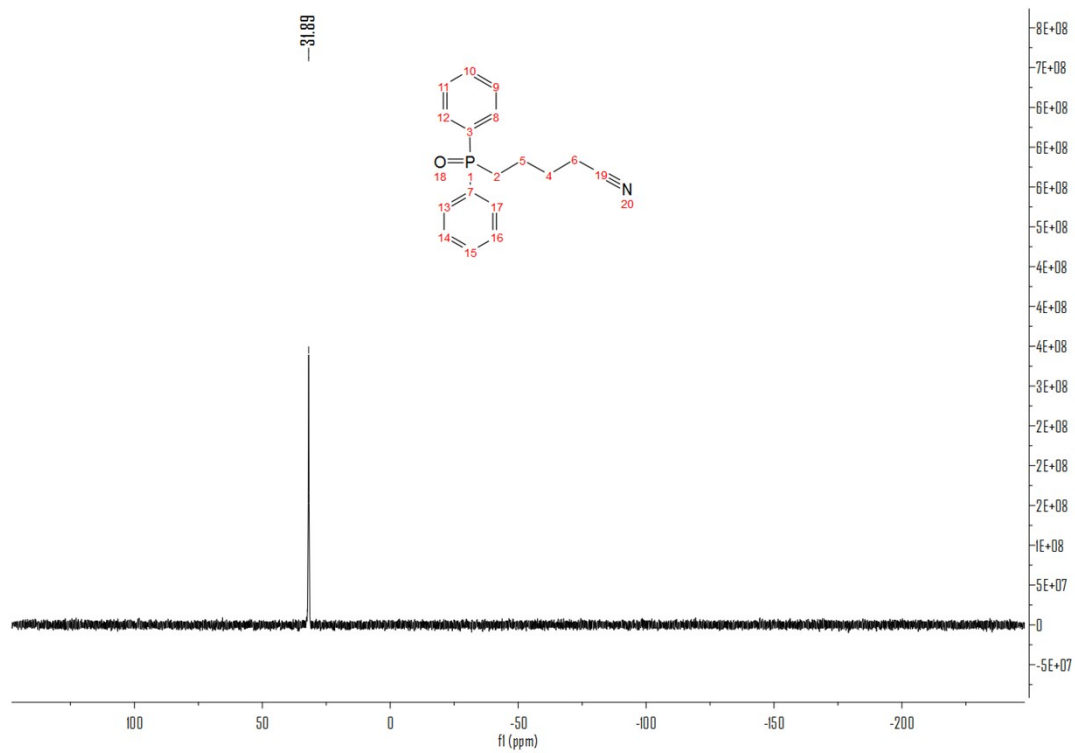
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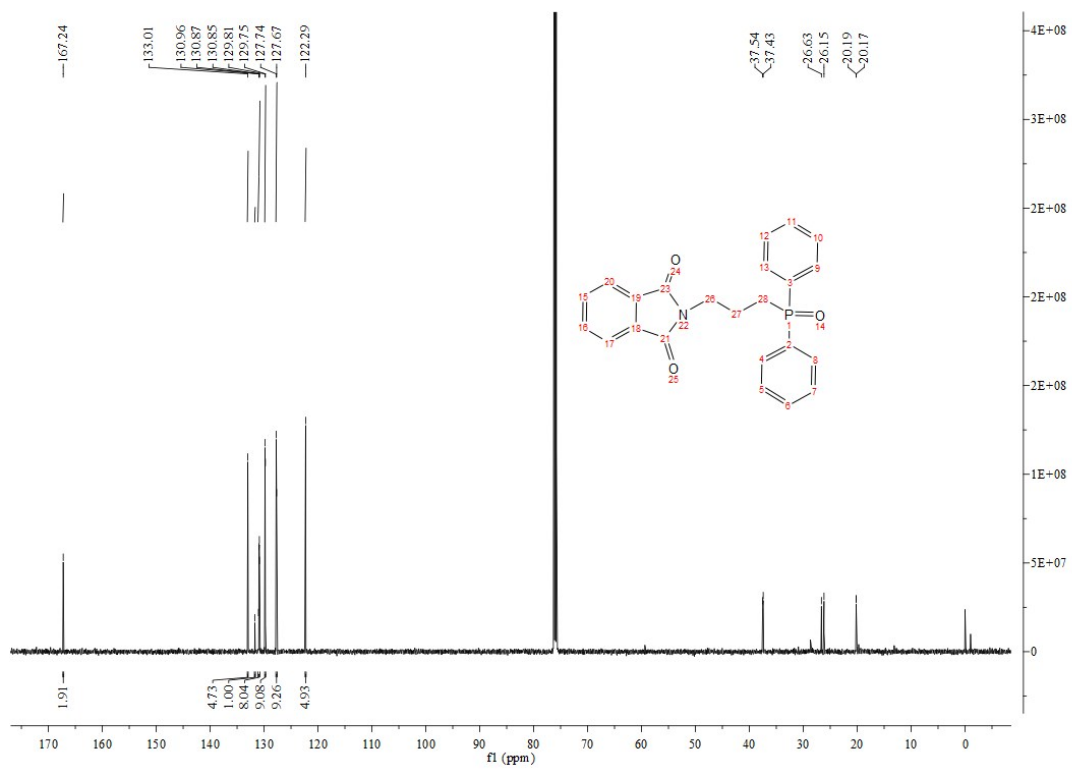
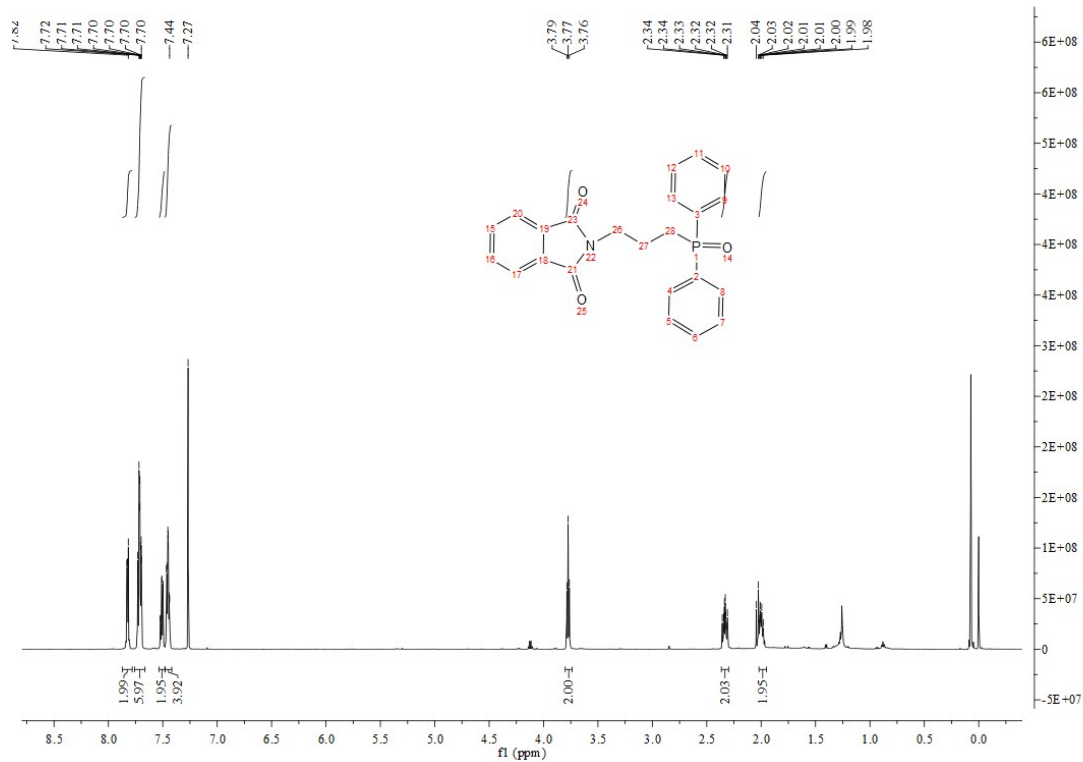
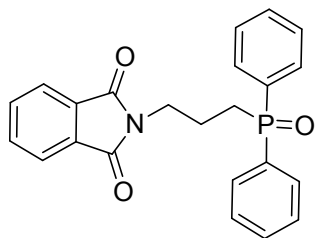
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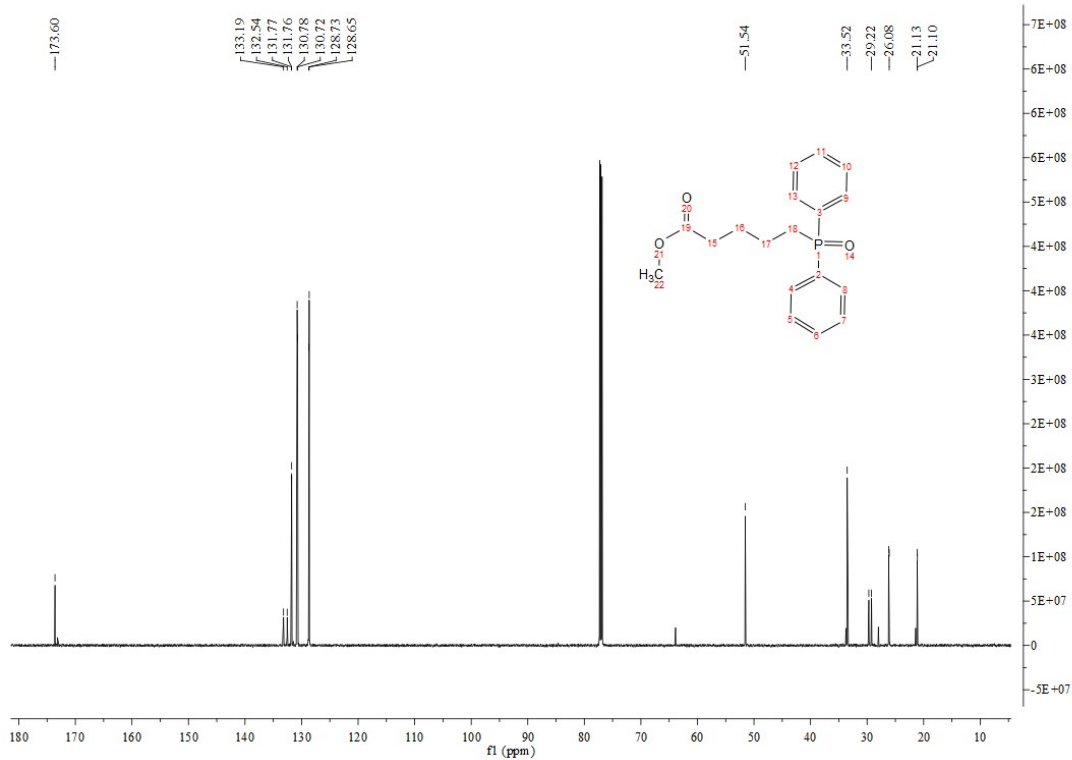
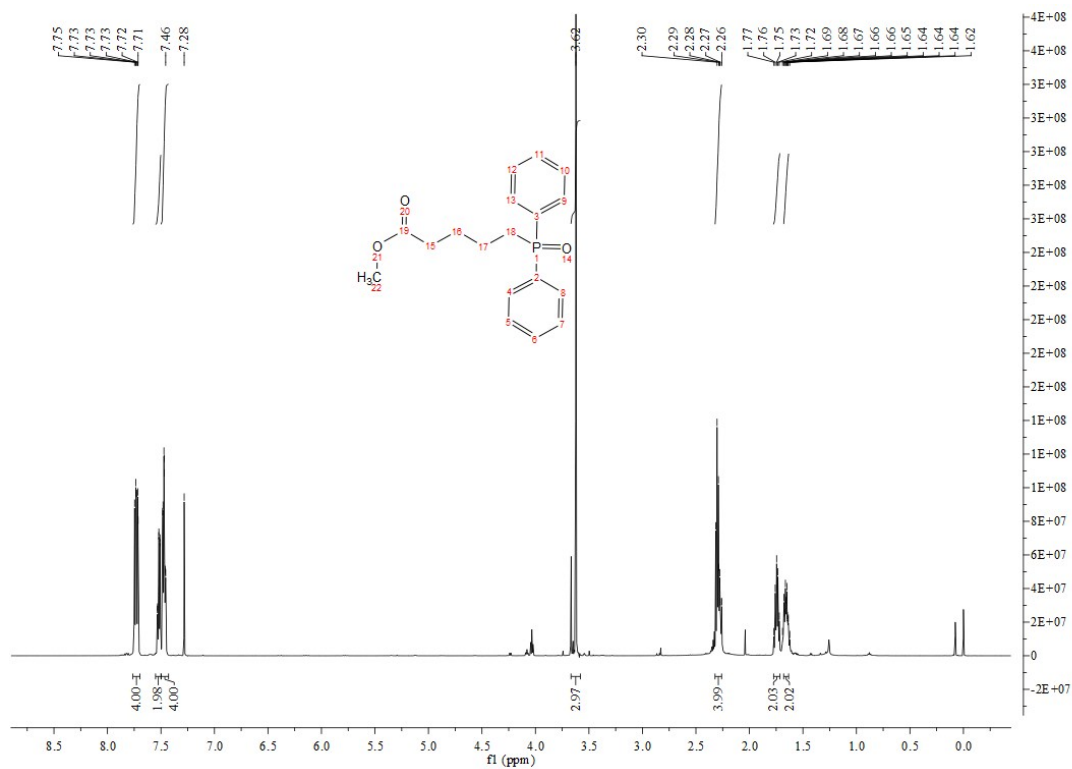
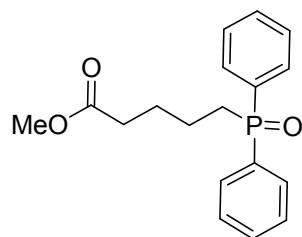
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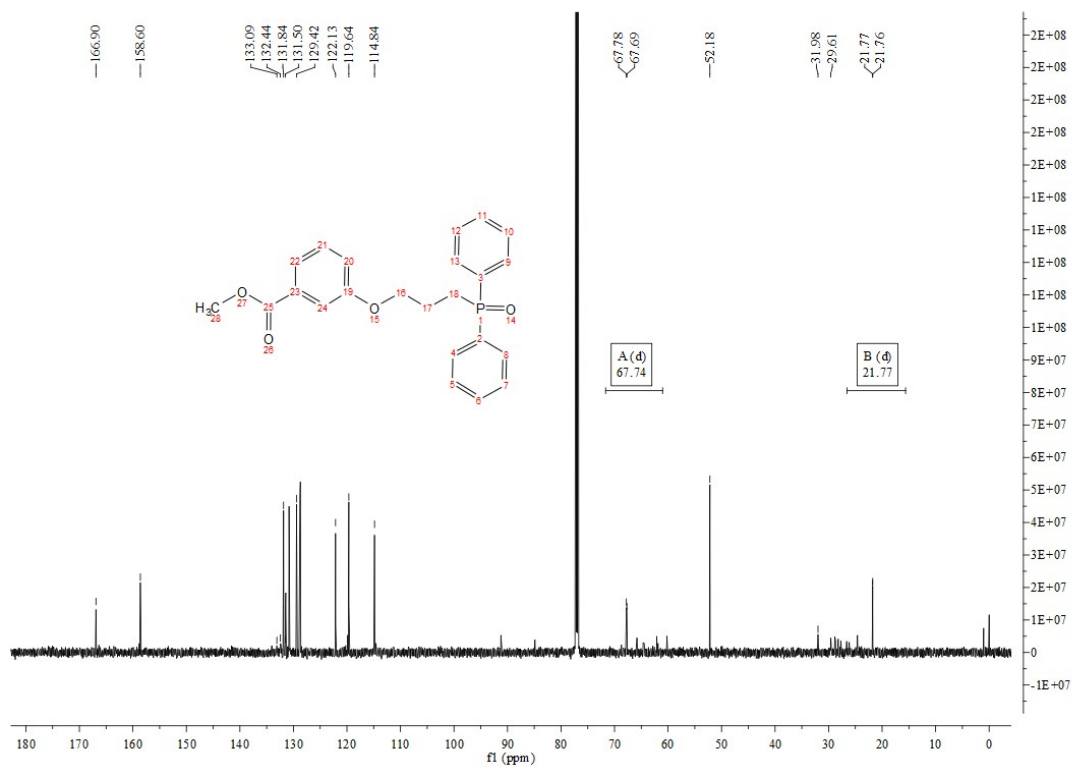
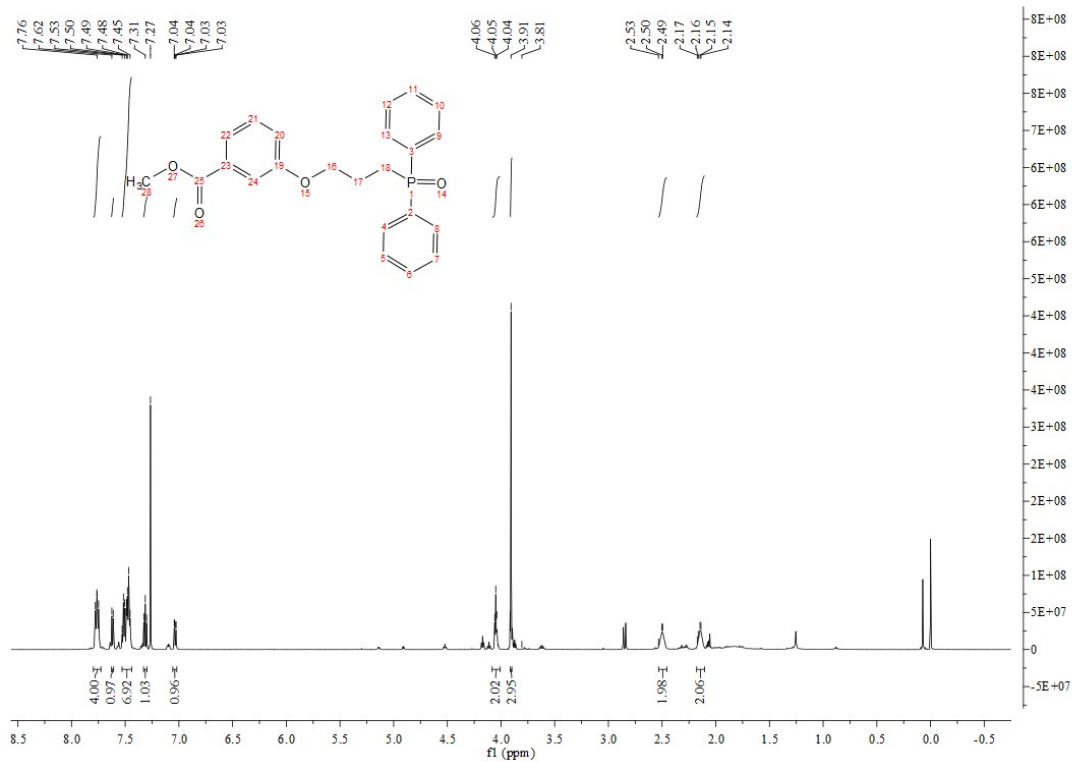
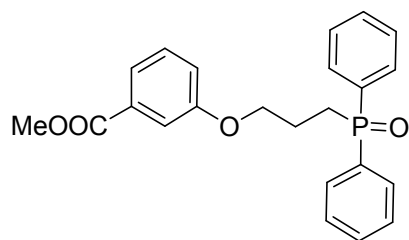
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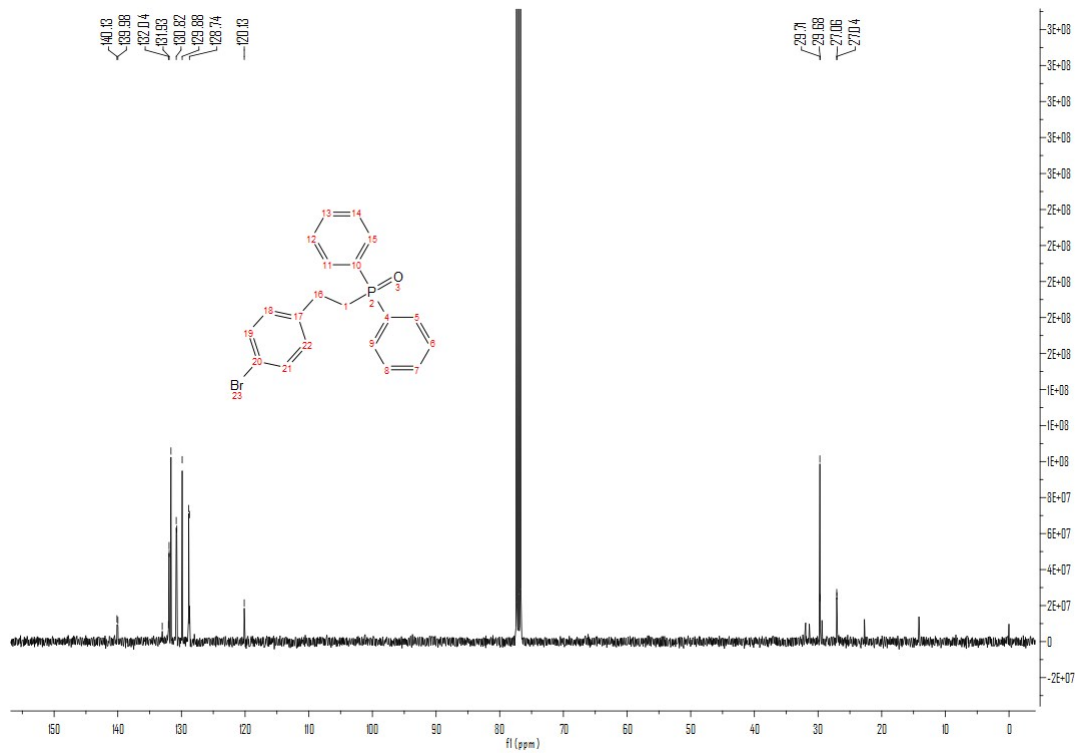
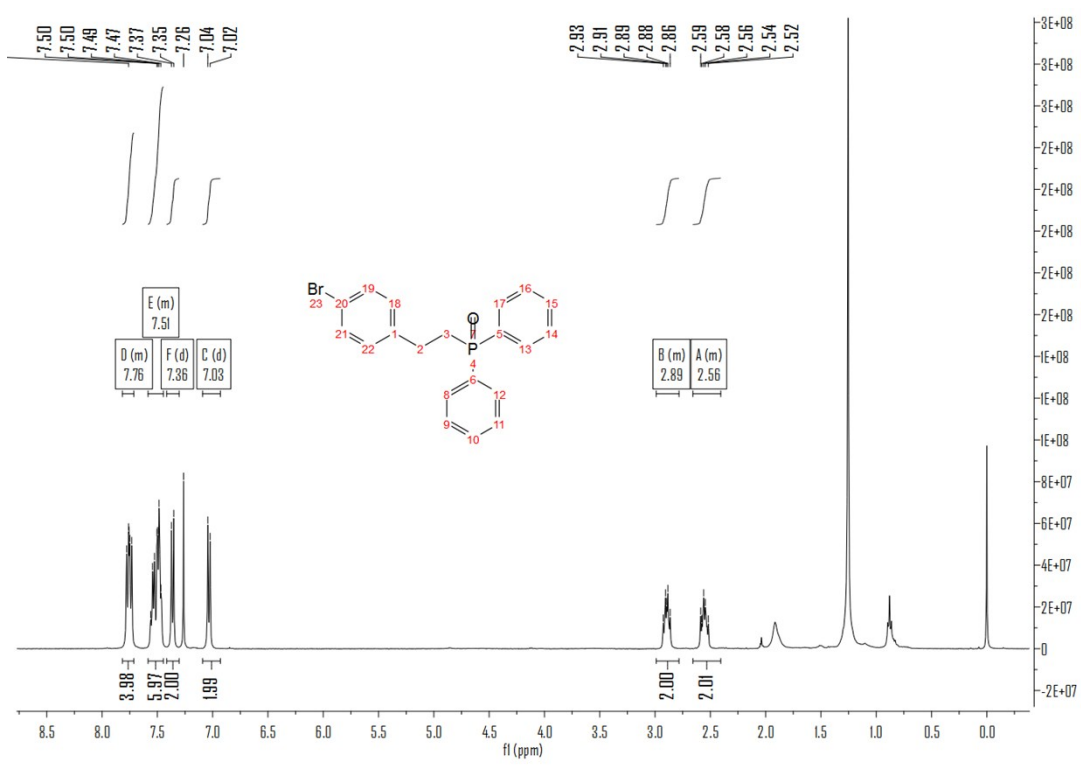
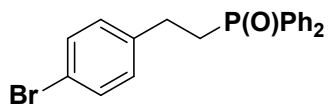
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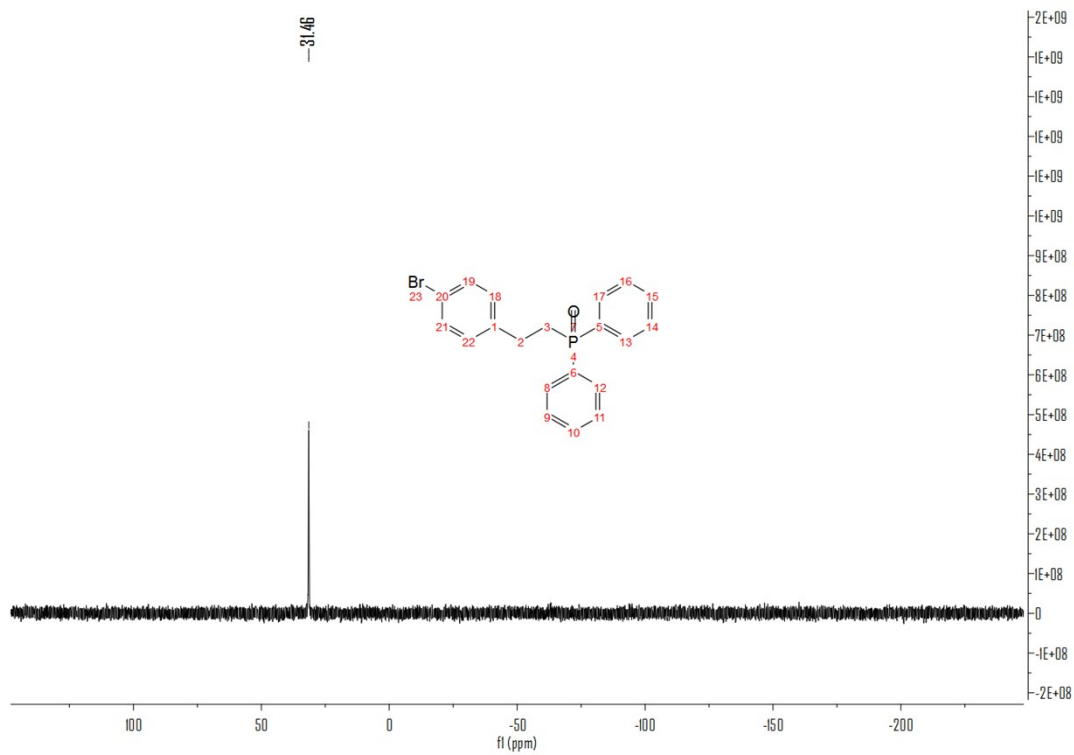
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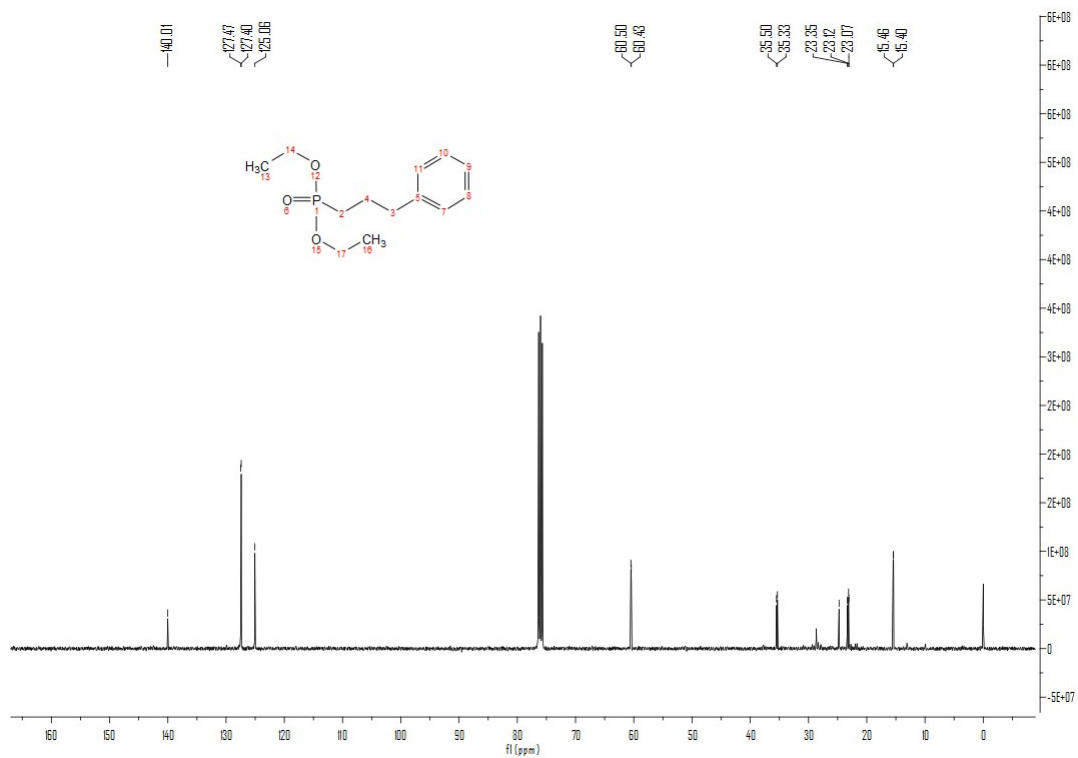
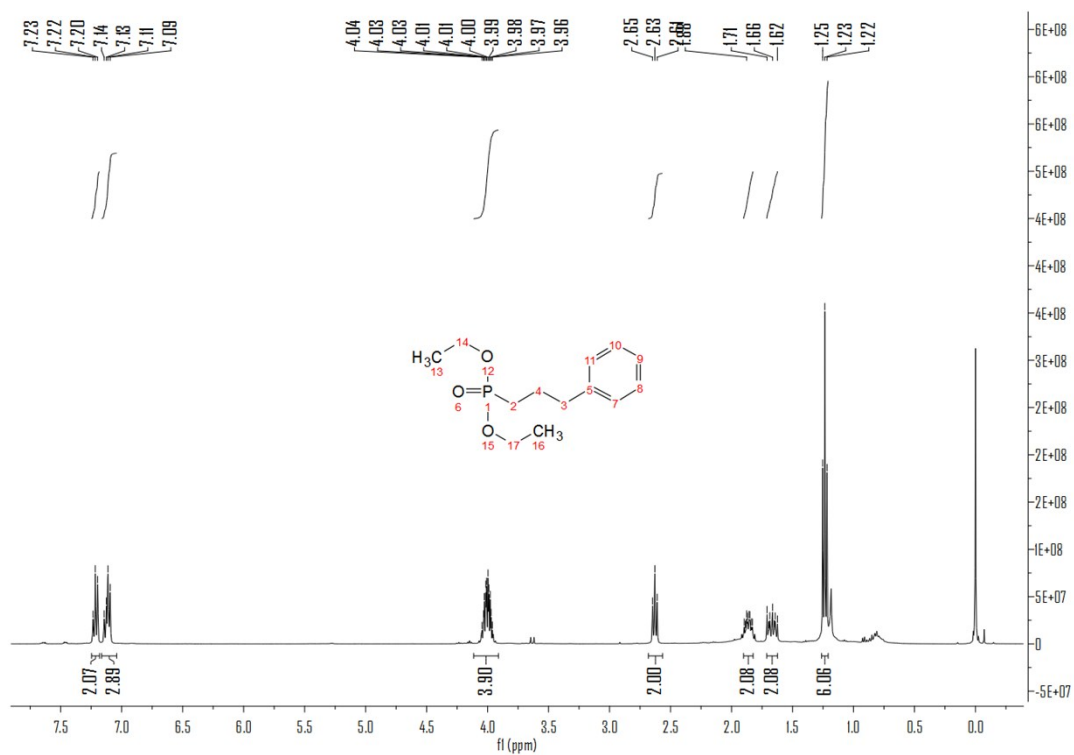
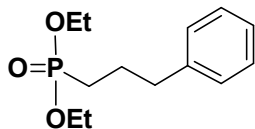


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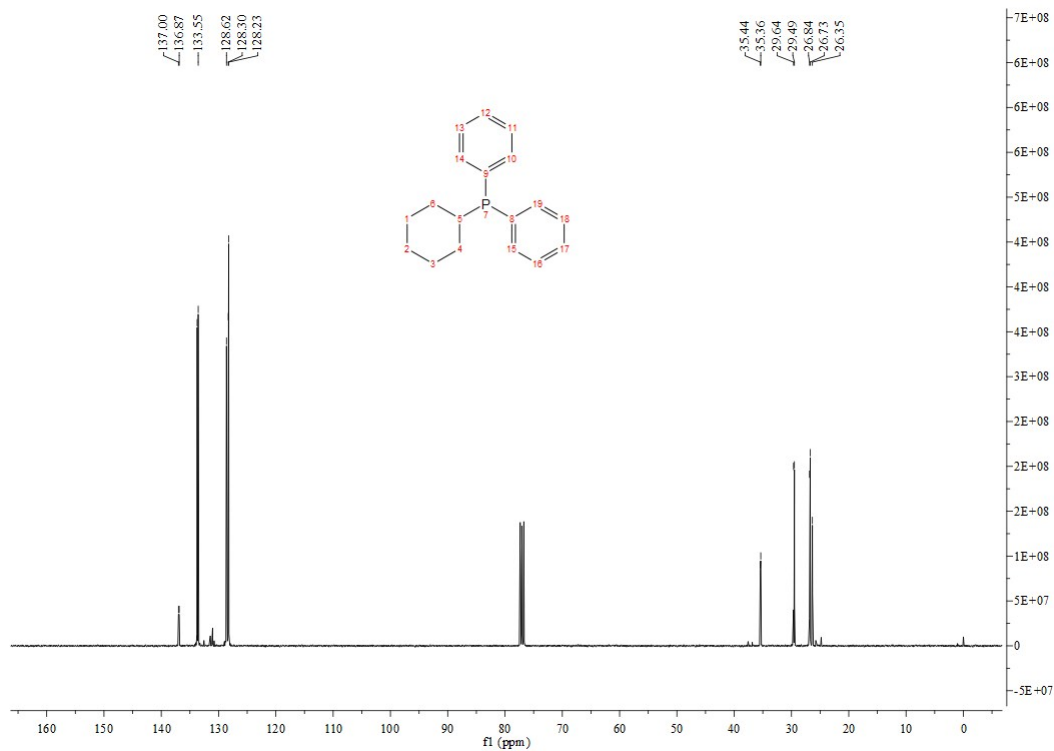
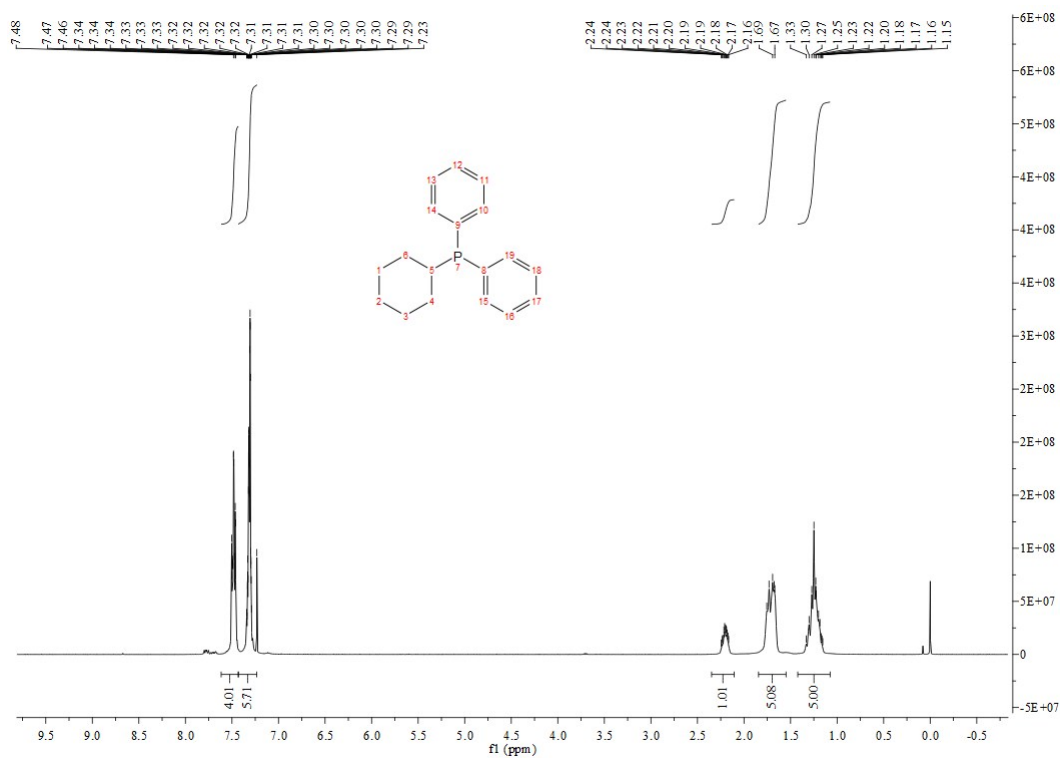


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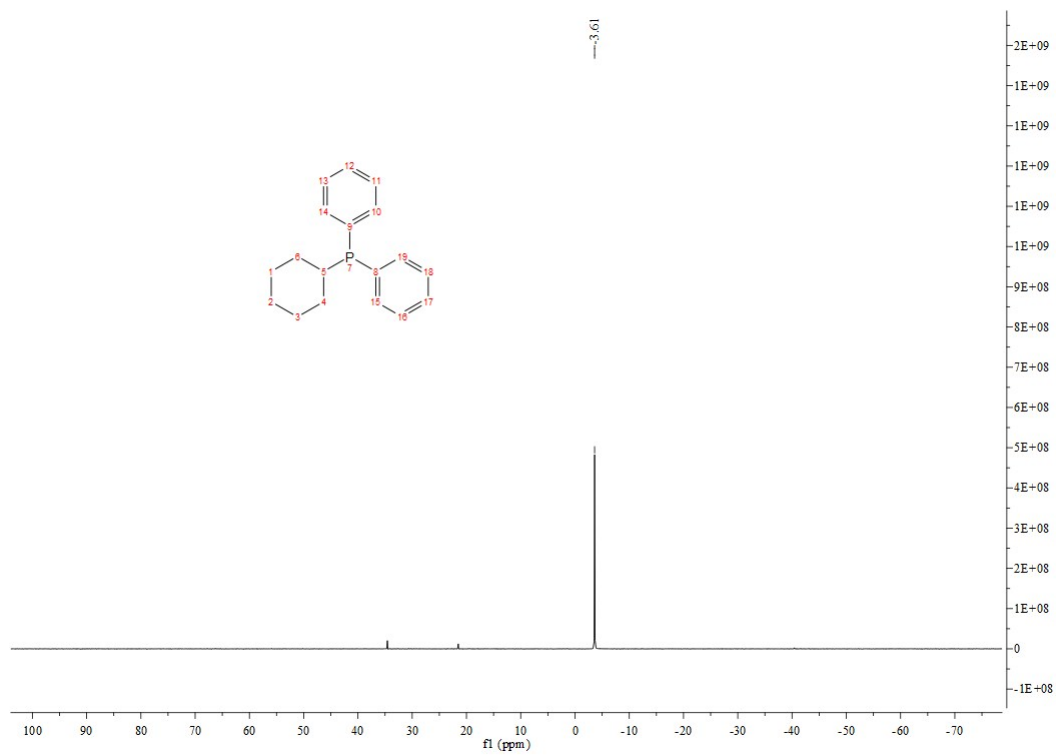


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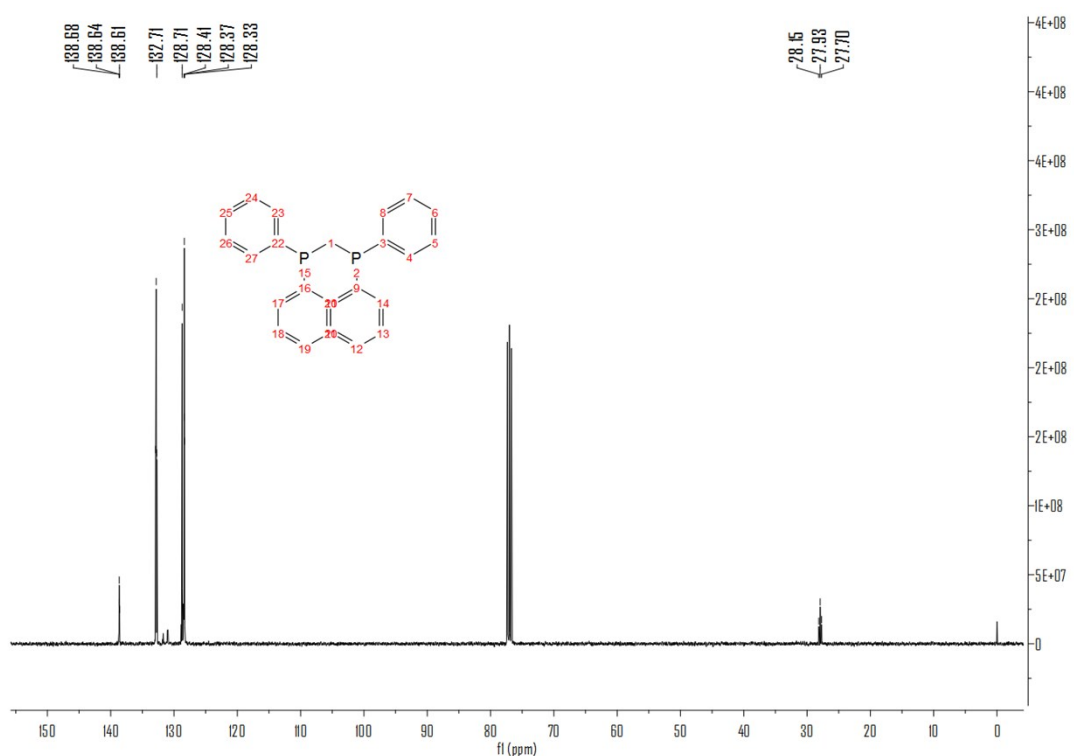
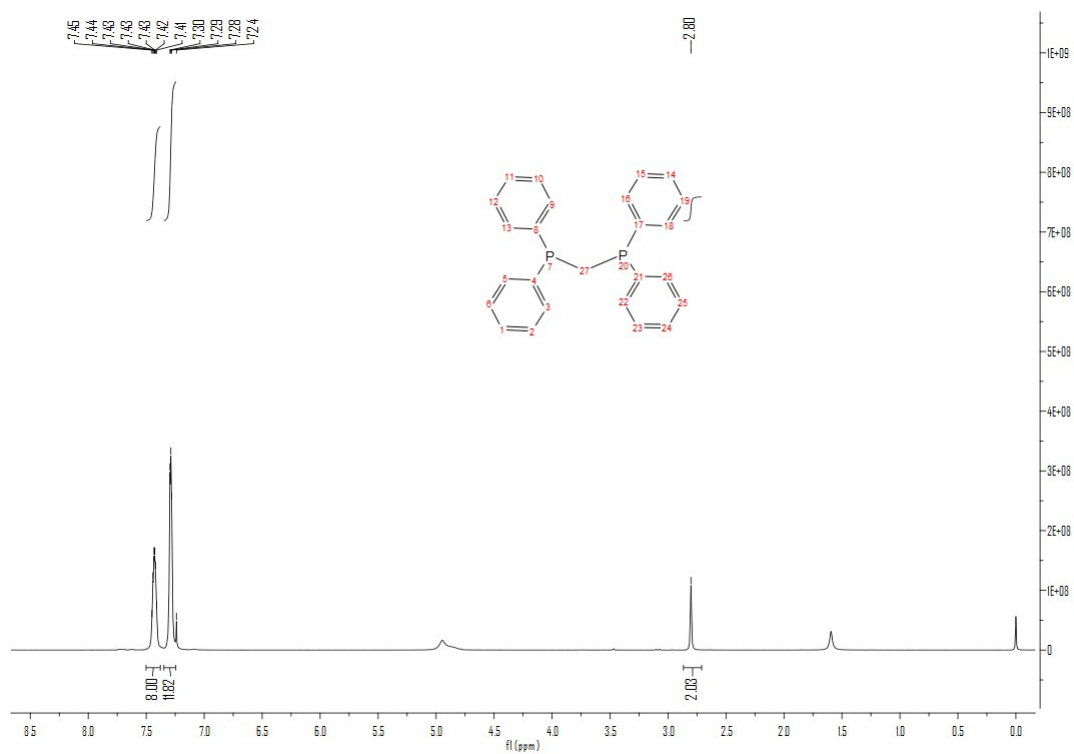
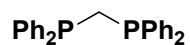
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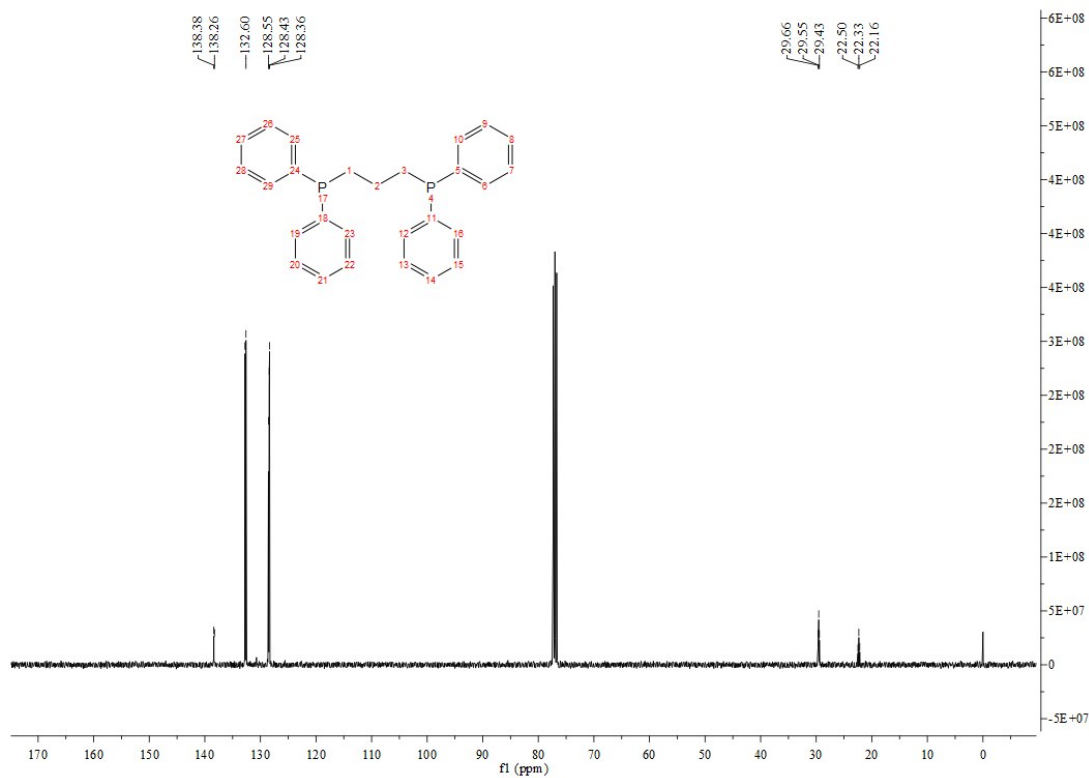
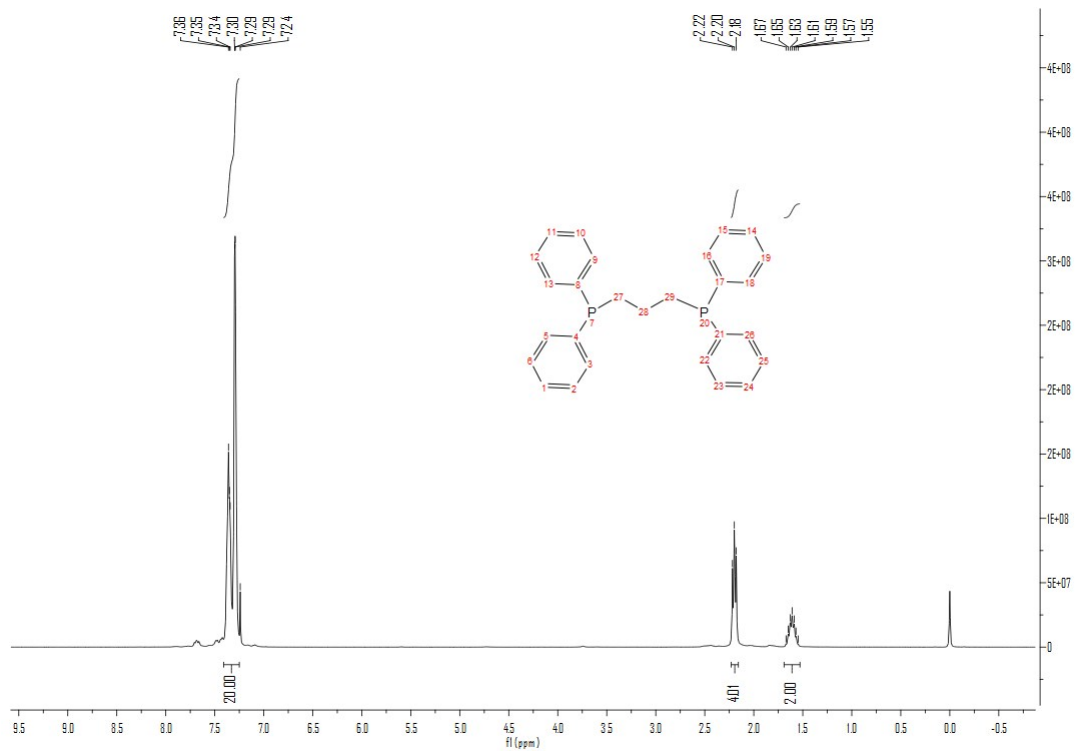
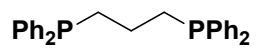
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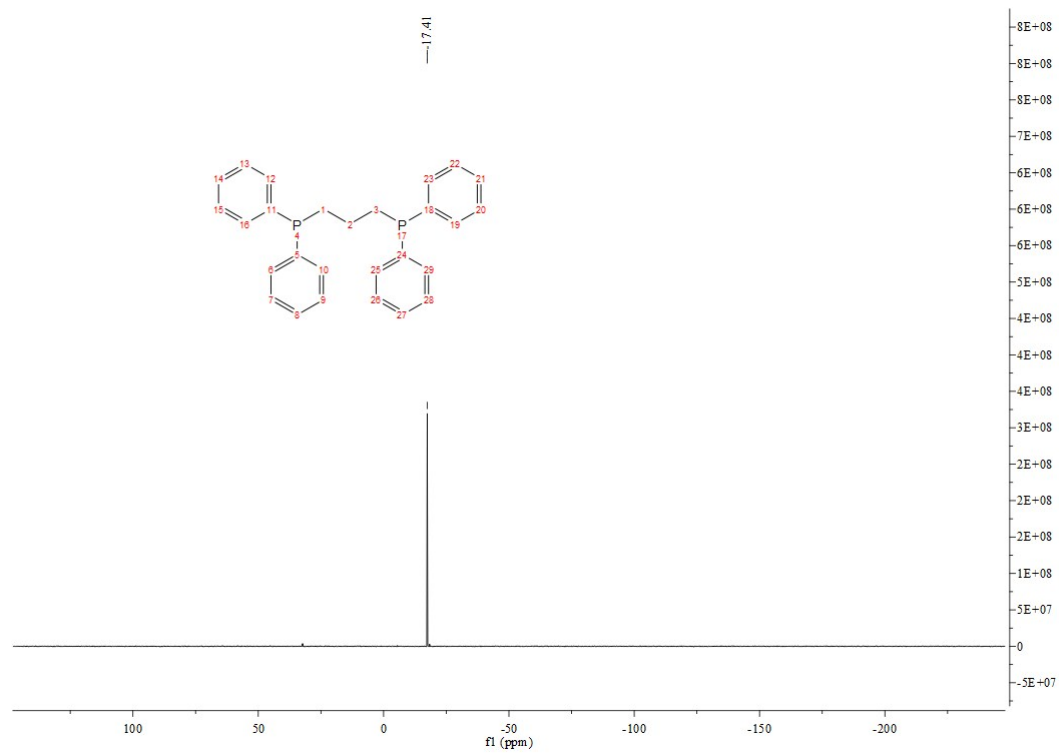
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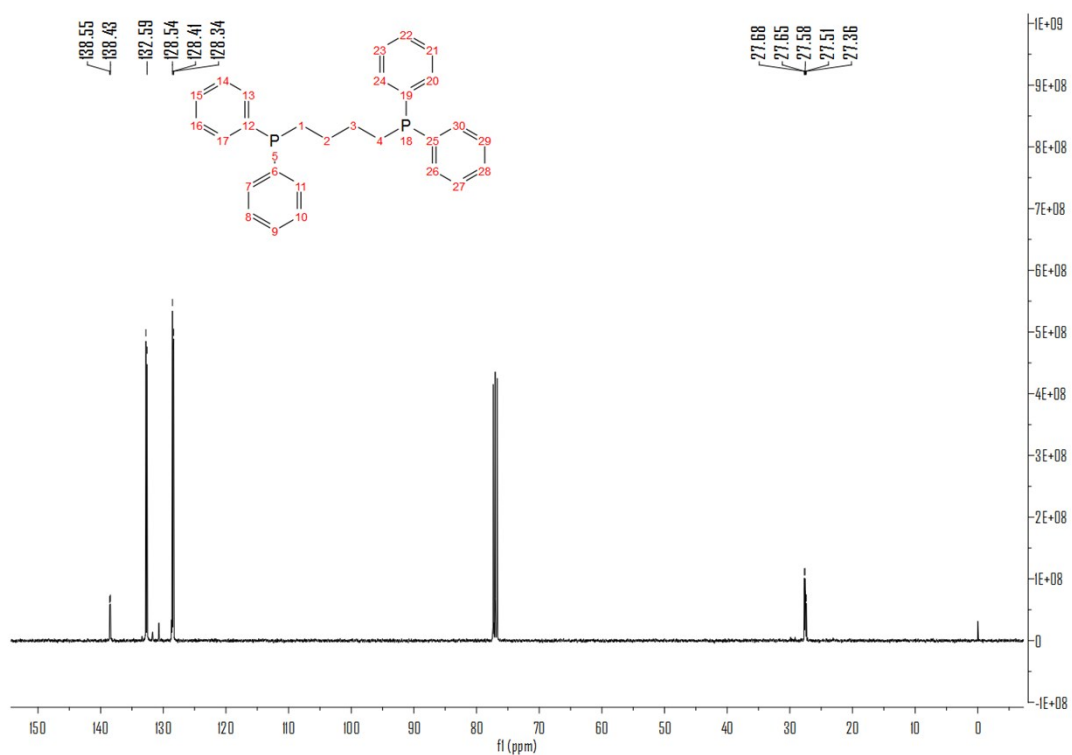
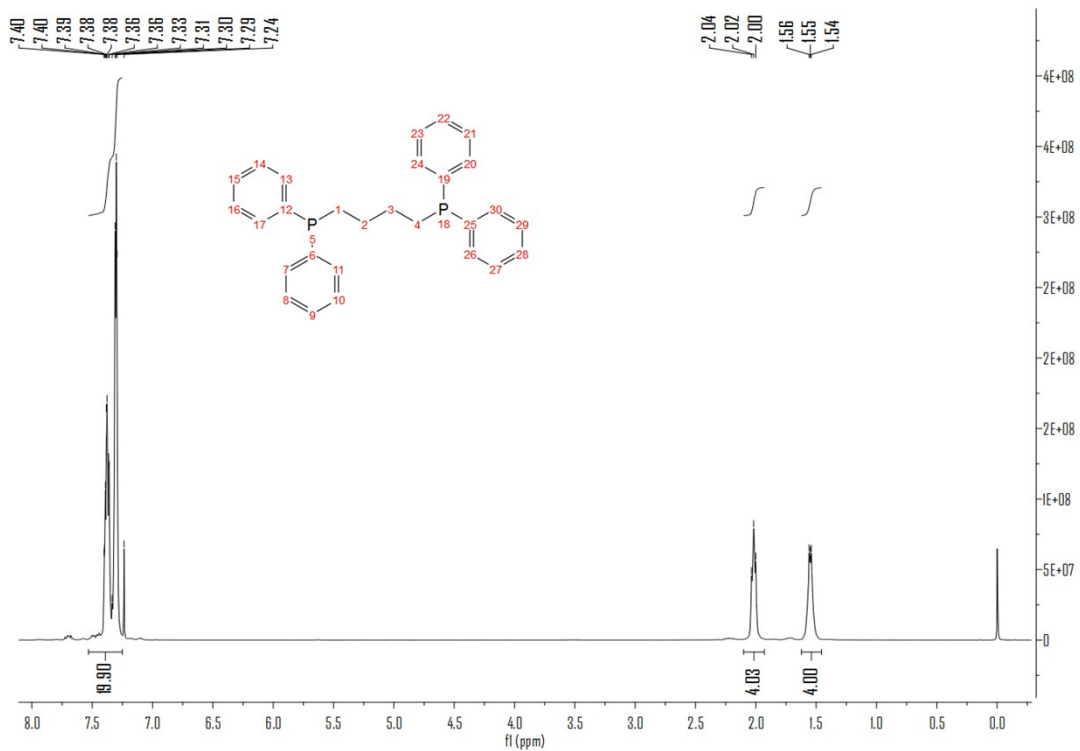
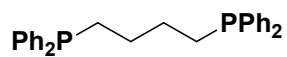
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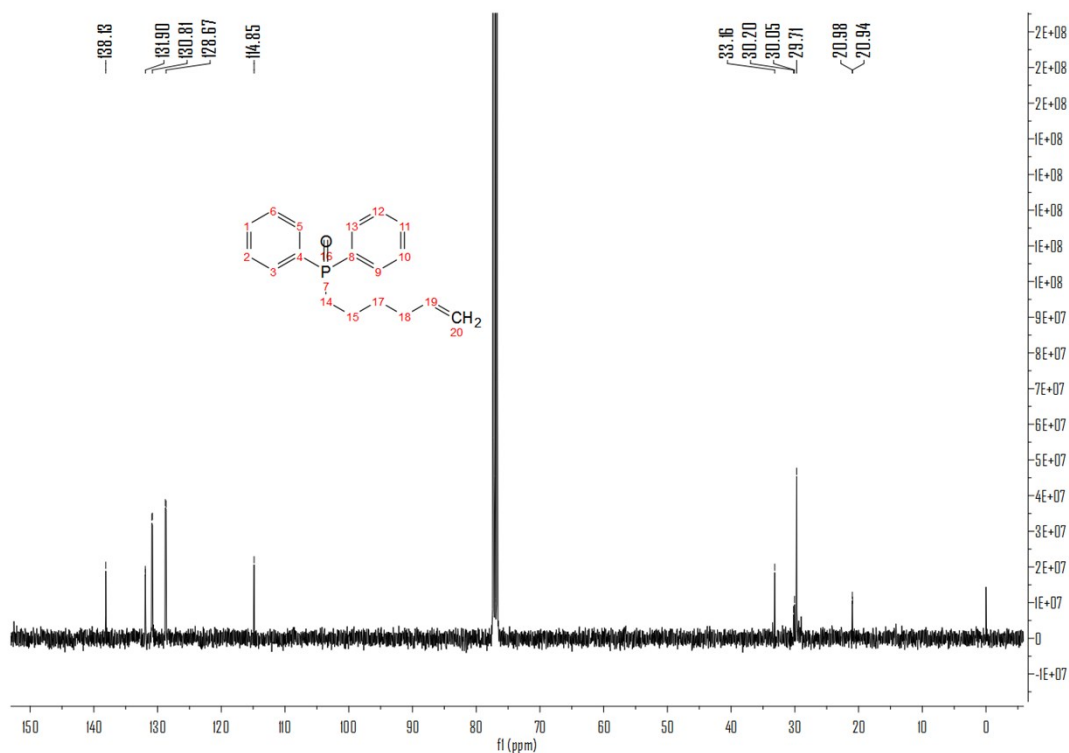
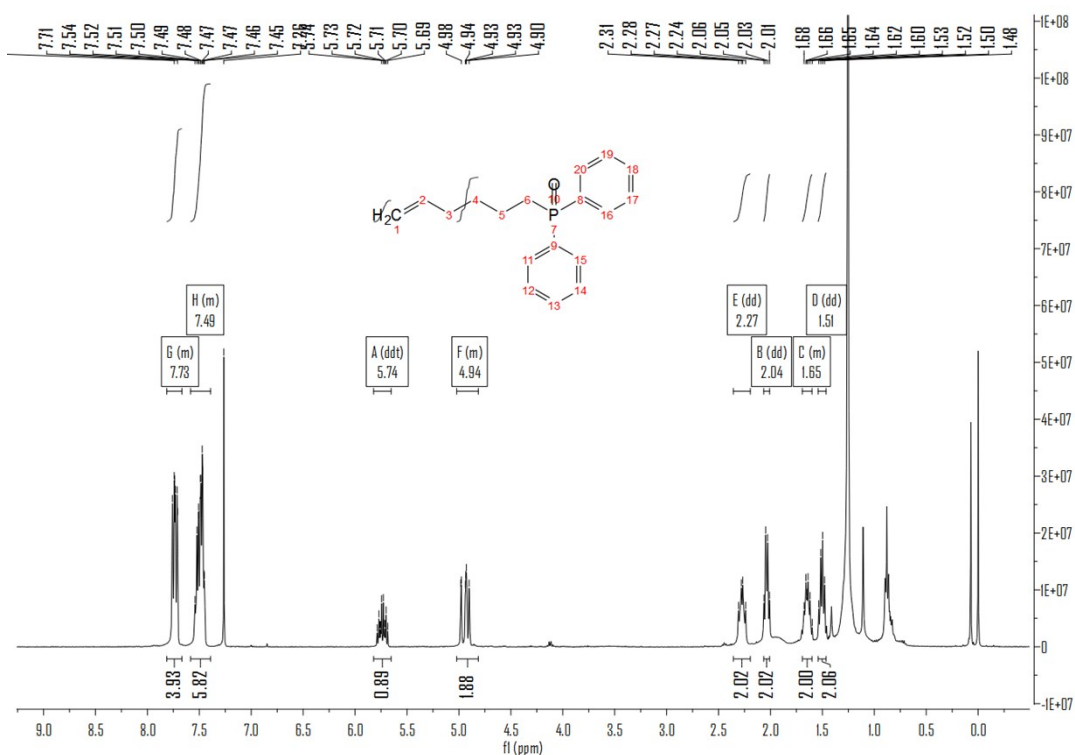
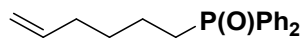
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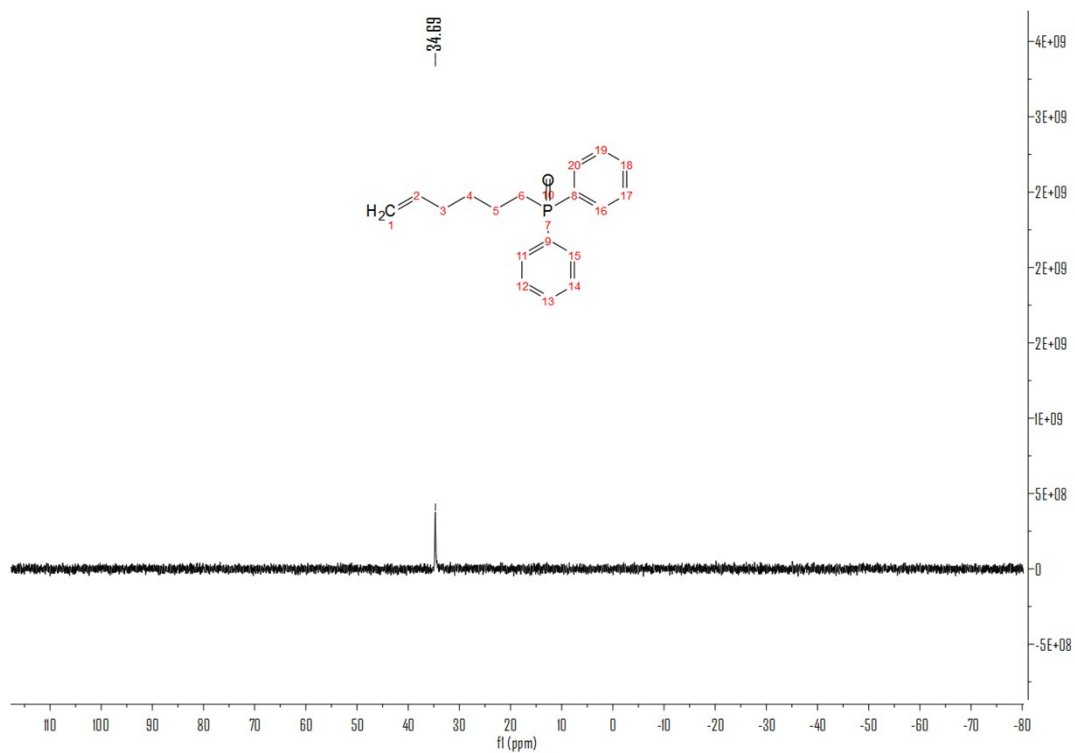


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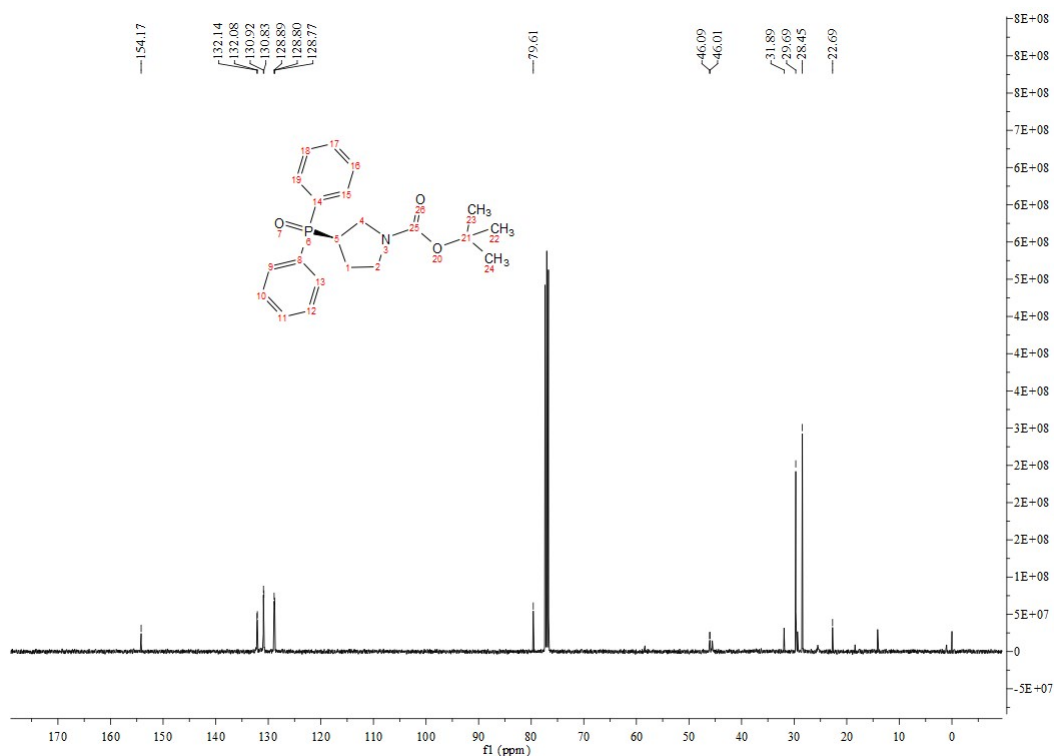
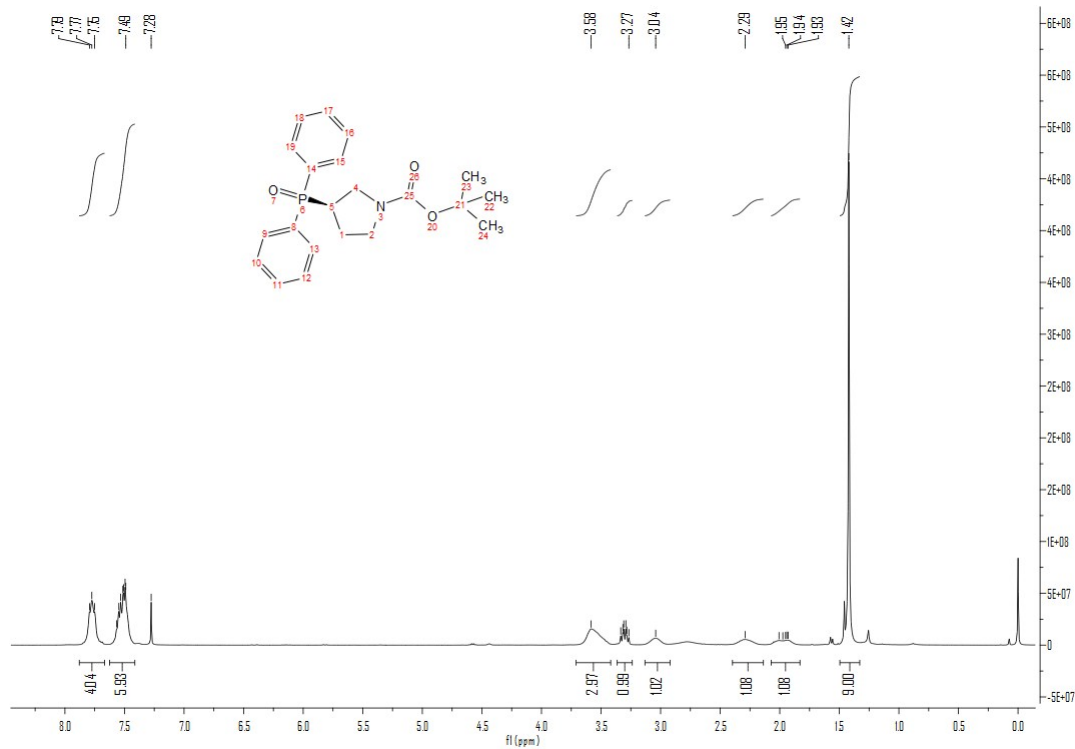
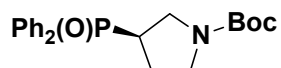




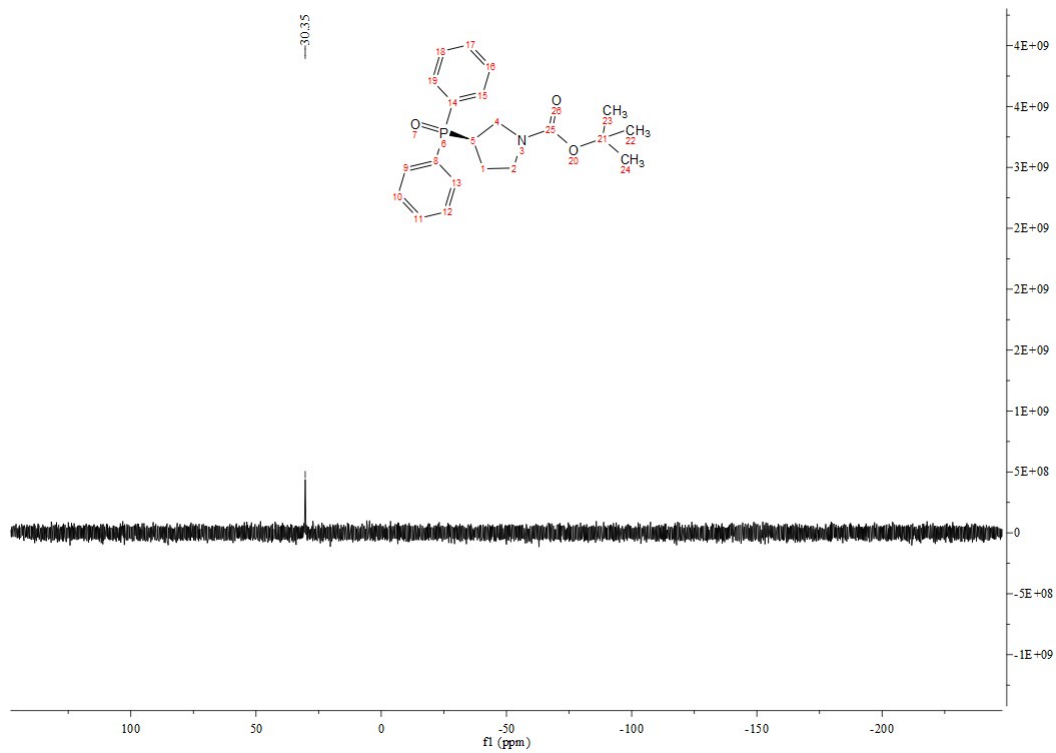
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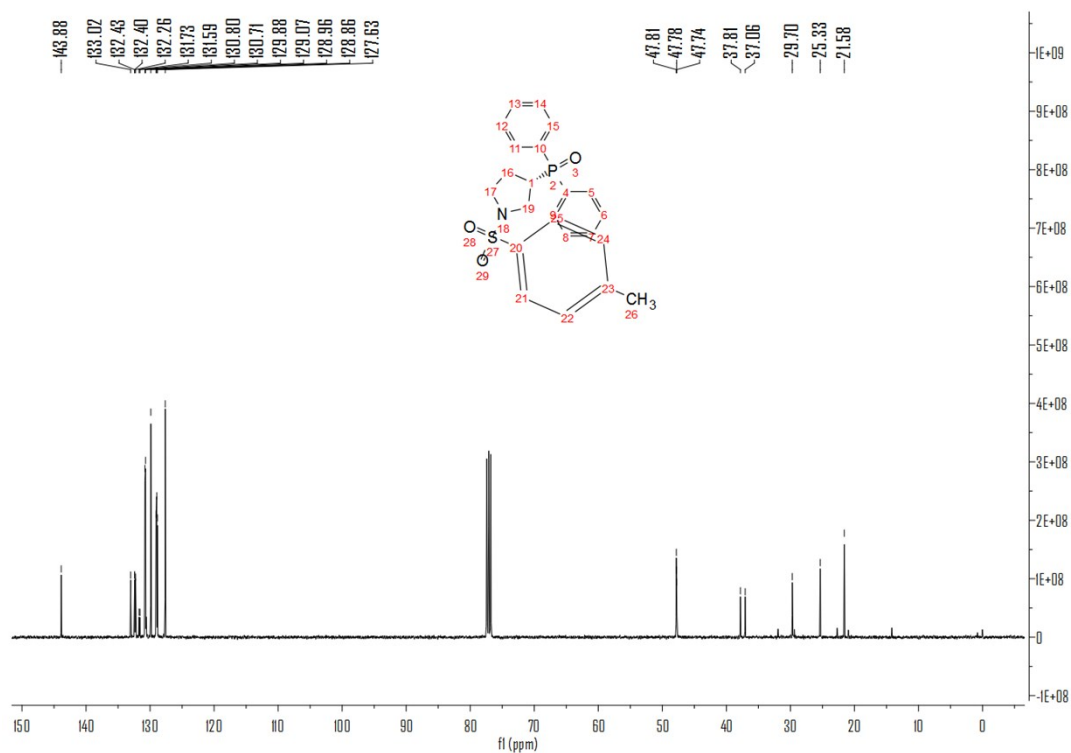
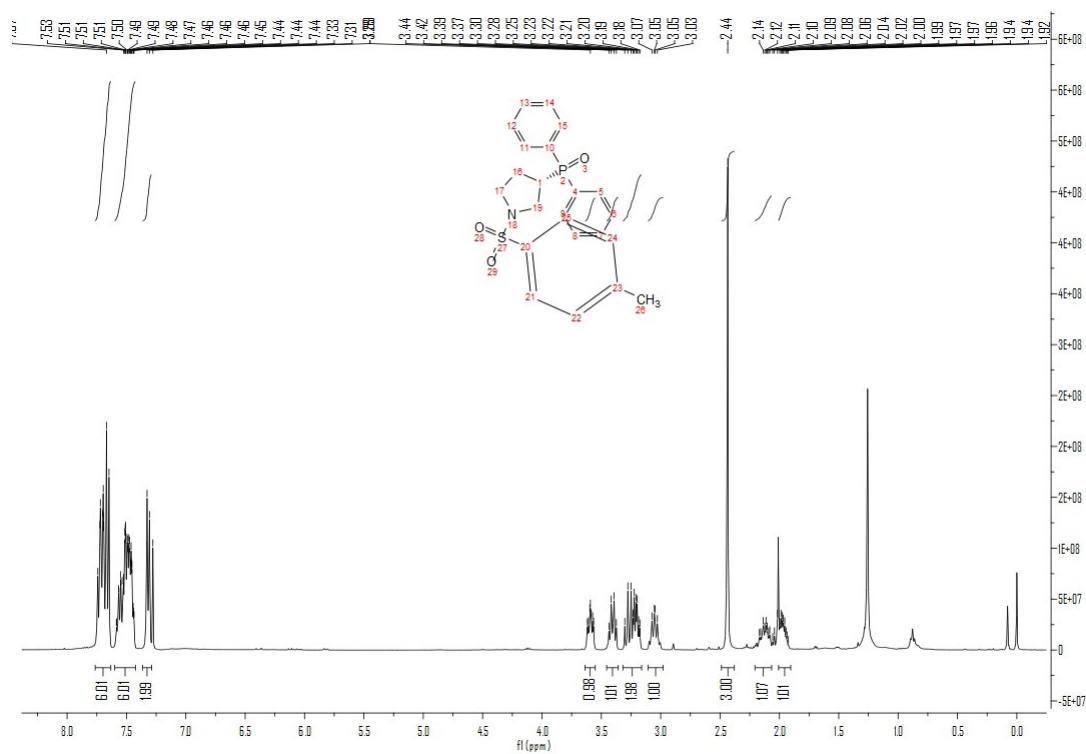
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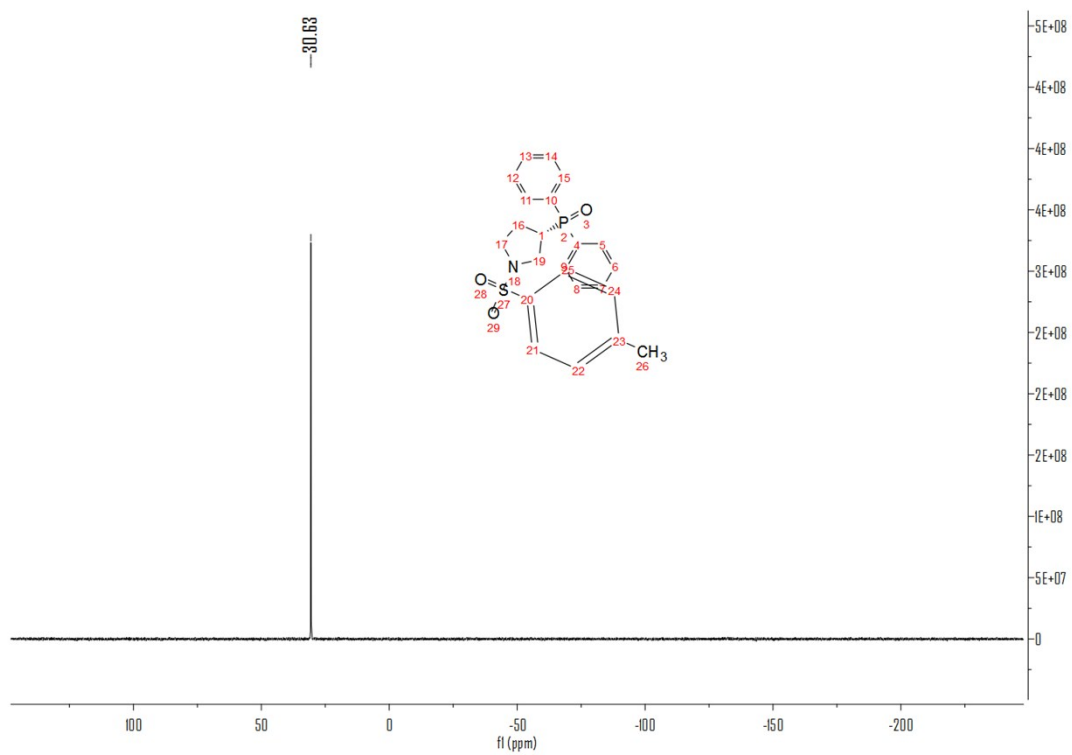
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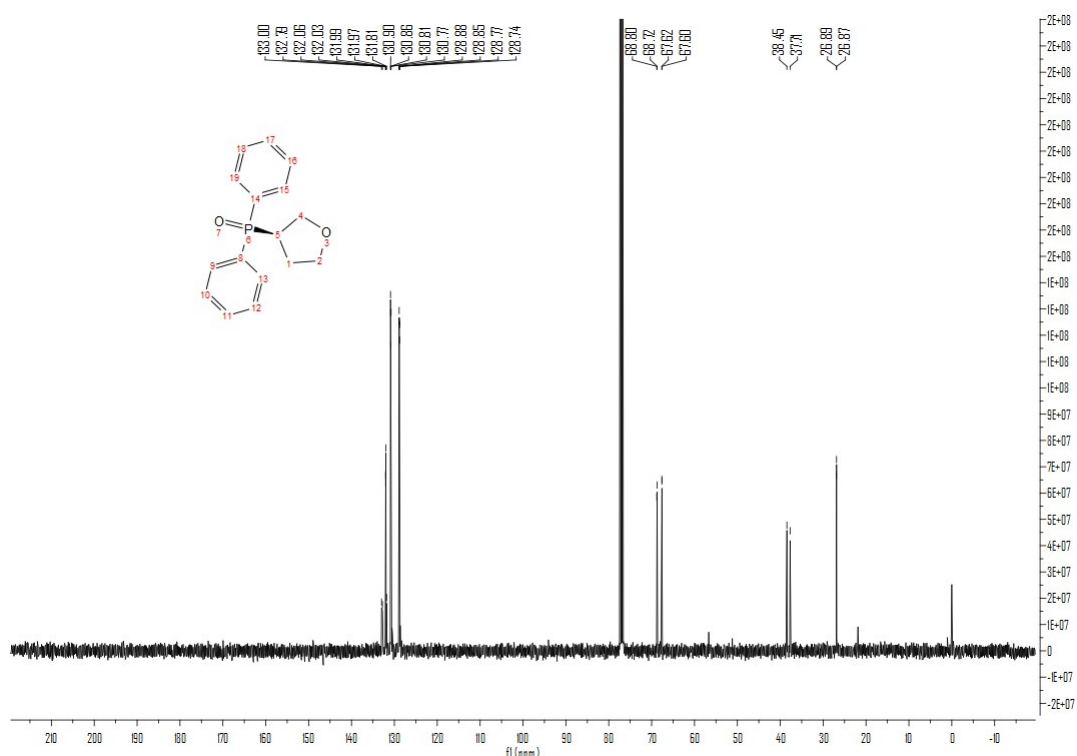
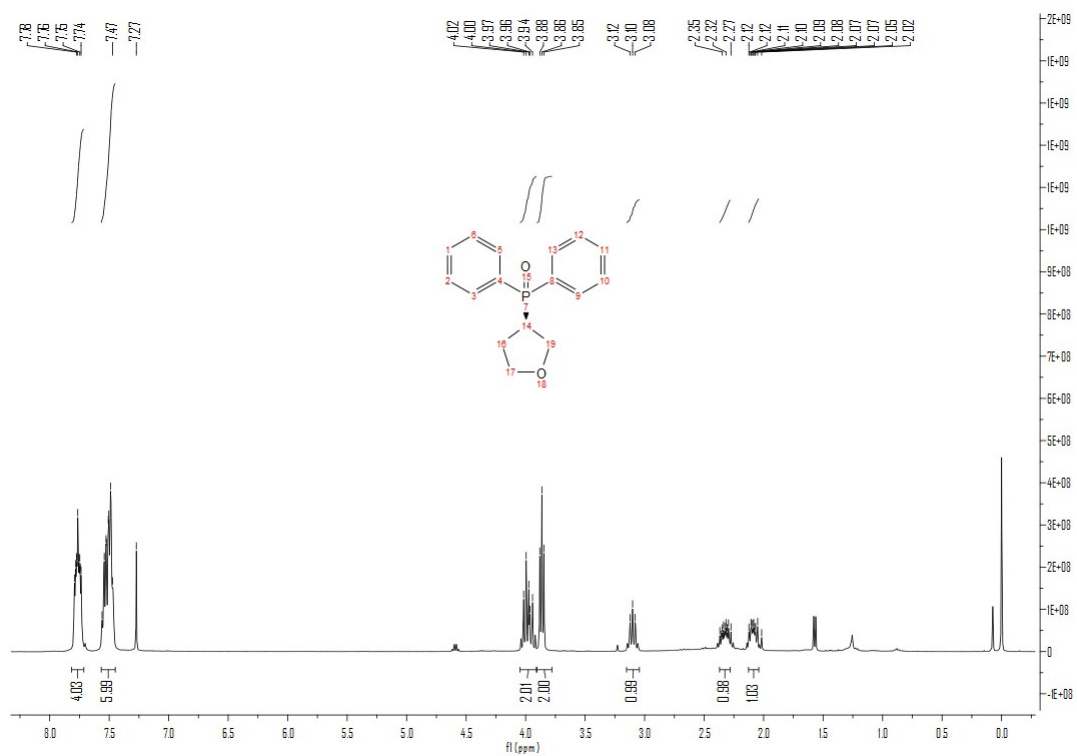
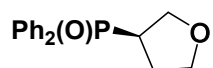
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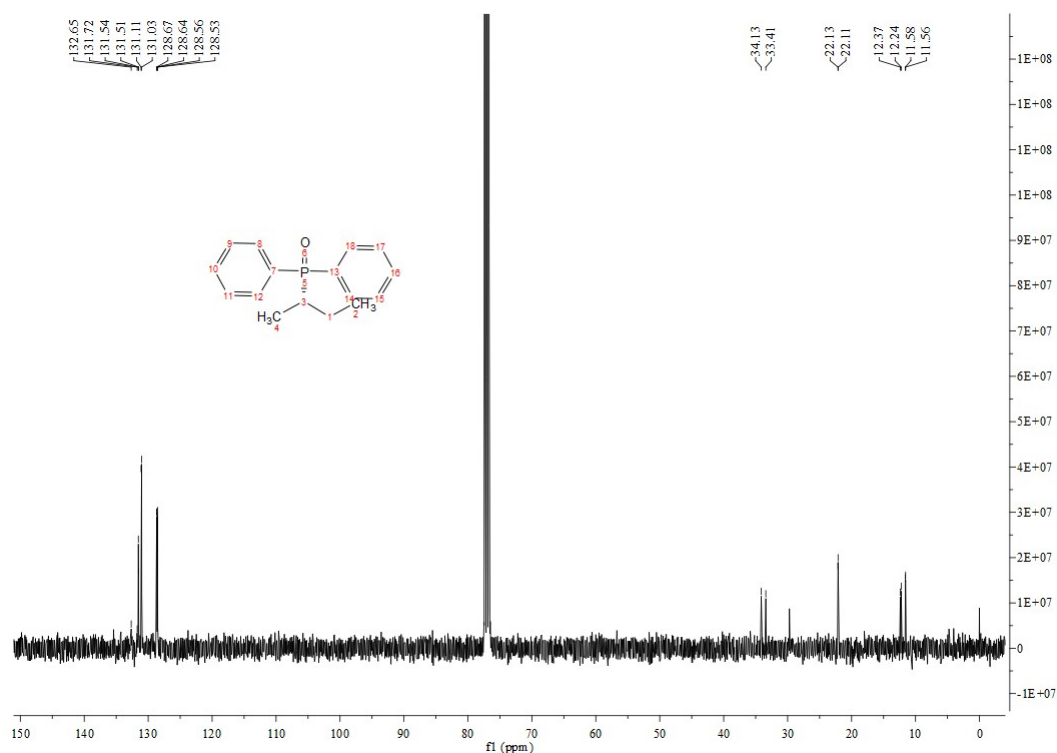
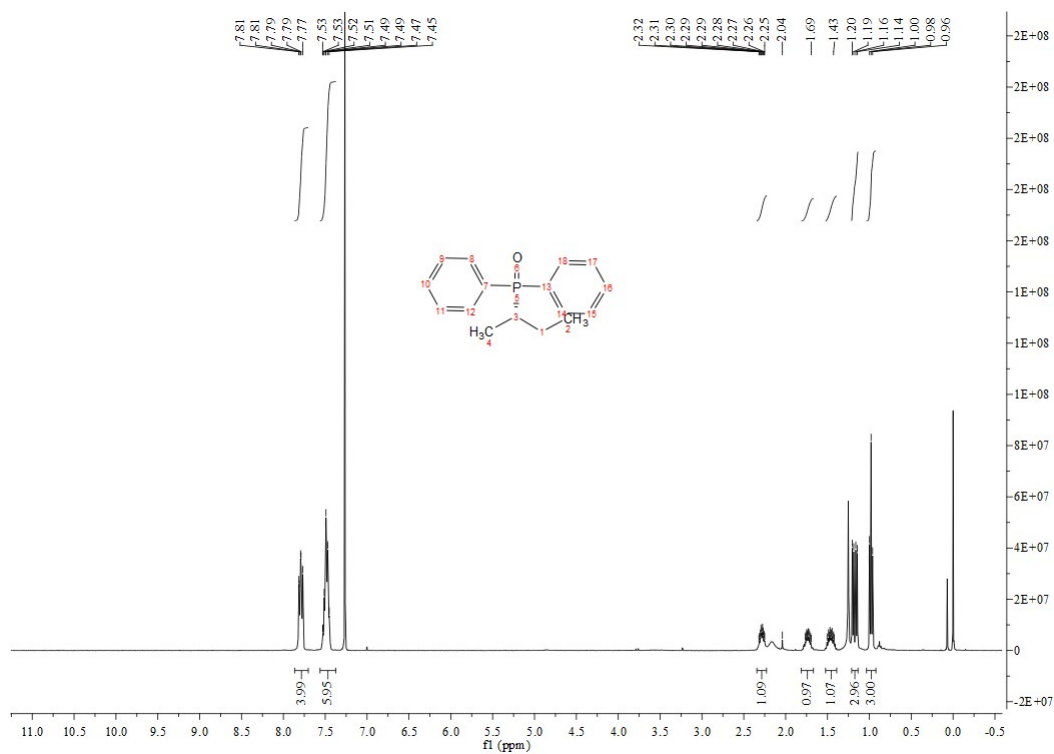
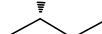


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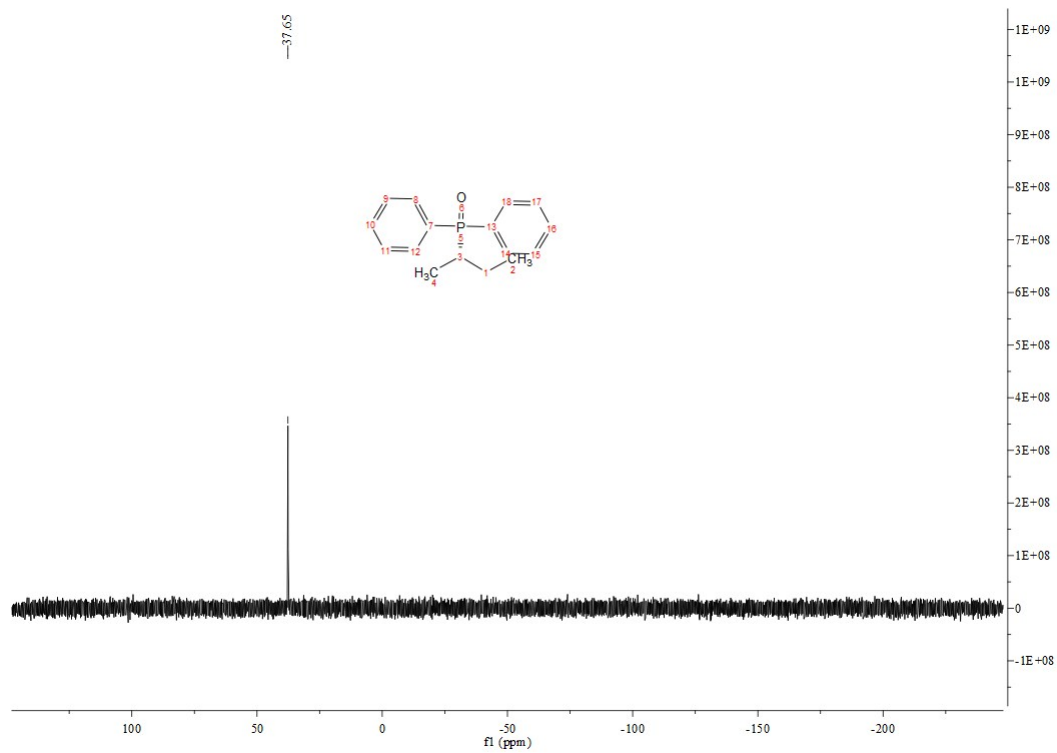


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**P(O)Ph<sub>2</sub>**

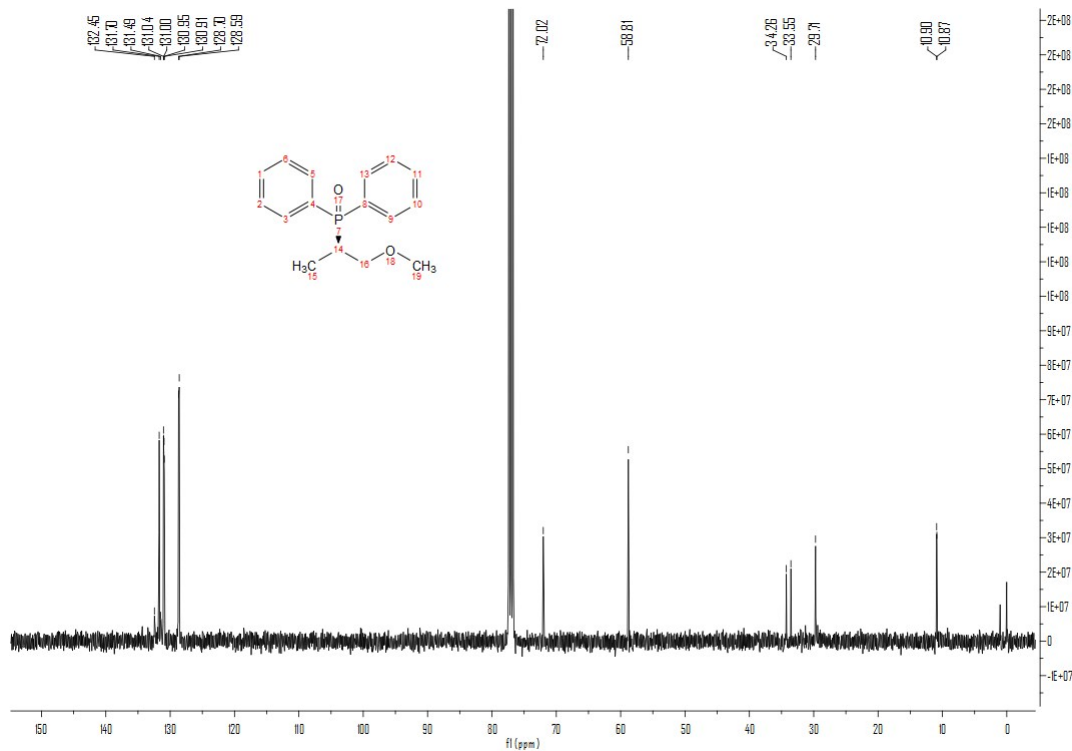
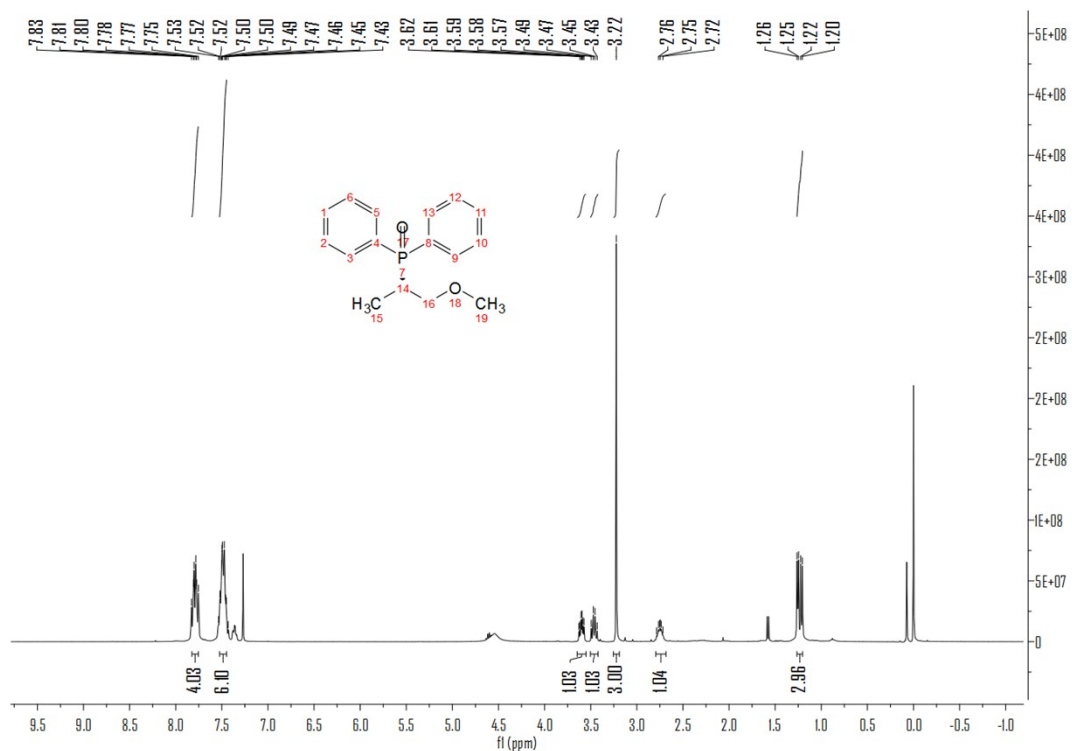
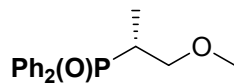


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Electronic Supplementary Information



## Electronic Supplementary Information

