

# Regioselective transformation of 3-phosphoryl benzyne intermediates to diverse phosphorus-substituted arenes

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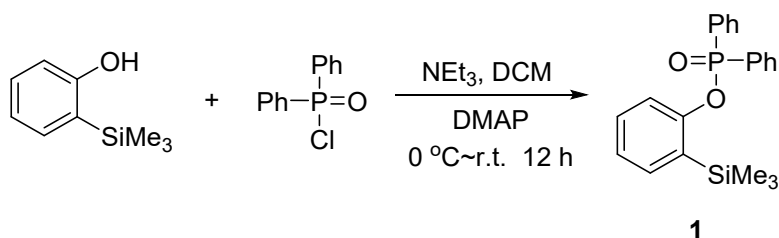
# SUPPORTING INFORMATION

## 1. General

All reactions were performed using standard Schlenk and glovebox (Vigor) techniques under argon atmosphere. All chemicals were purchased from Energy Chemical Inc. THF and toluene are distilled from sodium/benzophenone before use, and acetonitrile and dichloromethane are distilled from calcium hydride before use. Other chemicals are used as commercial products without further purification. Deionized water was purged with Ar overnight before use. Use Bruker 400 MHz or JOEL 400 MHz NMR spectrometer to collect NMR spectra. The external reference for  $^{31}\text{P}$  NMR is 85%  $\text{H}_3\text{PO}_4$  aqueous solution and the external reference for  $^{19}\text{F}$  NMR is  $\text{CF}_3\text{COOH}$  in  $\text{CDCl}_3$ . The NMR multiplicity is abbreviated as follows: s = single peak, d = doublet, t = triplet, m = multiple, br = broad. Chemical shifts ( $\delta$ ) are reported in ppm downfield from  $\text{Me}_4\text{Si}$  ( $\delta$  0.00 for  $^1\text{H}$  NMR in  $\text{CDCl}_3$ ) or the solvent peak ( $\delta$  7.26 for  $^1\text{H}$  NMR in  $\text{CDCl}_3$ ,  $\delta$  2.50 for  $^1\text{H}$  NMR in  $\text{DMSO-d}_6$ ,  $\delta$  77.16 for  $^{13}\text{C}$  NMR in  $\text{CDCl}_3$ , and  $\delta$  39.52 for  $^{13}\text{C}$  NMR in  $\text{DMSO-d}_6$ ) as an internal reference with coupling constants ( $J$ ) in hertz (Hz). High-resolution mass spectra (HRMS) were collected in ESI positive mode on a Bruker maxis UHR-TOF mass spectrometer. The melting point was measured with Hanon MP-300.

## 2. Synthesis of aryne precursor 5 and 6

Synthesis of 1



To a dichloromethane (45.0 mL) solution of 2-(trimethylsilyl)phenol<sup>[1]</sup> (7.5 g, 45.0 mmol, 1.0 eq.) was added triethylamine (12.5 mL, 90.1 mmol, 1.2 eq.) and DMAP (0.3 g, 2.3 mmol, 0.05 eq.). Then diphenyl phosphinic chloride (12.8 g, 54.0 mmol, 1.2 eq.) was added dropwise at 0 °C. The resulting suspension was stirred at room temperature for 8.0 hours. After that, the resulting reaction mixture was poured into a brine solution (20.0 mL) and subsequently extracted three times by ethyl acetate (50.0 mL). The combined organic phases were dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was purified through chromatography on a silica gel plug (eluent: petrol ether/ethyl acetate = 5/1) giving **1** as a white solid (12.0 g, 73% yield).

**M.p. (°C):** 56.9 – 57.5.

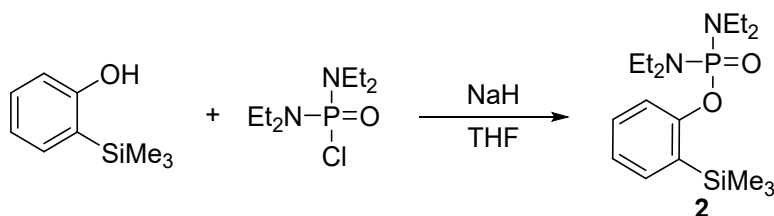
**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (dd,  $J$  = 12.8, 7.2 Hz, 4H, CH-Ar), 7.55 (t,  $J$  = 7.6 Hz, 2H, CH-Ar), 7.50 – 7.49 (m, 4H, CH-Ar), 7.41 (d,  $J$  = 7.2 Hz, 1H, CH-Ar), 7.28 (t,  $J$  = 8.4 Hz, 1H, CH-Ar), 7.19 – 7.15 (m, 1H, CH-Ar), 7.04 (t,  $J$  = 7.2 Hz, 1H, CH-Ar), 0.21 (s, 9H,  $\text{CH}_3$ ).

**$^{13}\text{C}\{\text{H}\}$  NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.77 (d,  $J$  = 8.0 Hz), 135.65, 132.61 (d,  $J$  = 2.8 Hz), 131.87 (d,  $J$  = 10.5 Hz), 130.84, 130.52, 129.87 (d,  $J$  = 8.4 Hz), 128.85 (d,  $J$  = 13.4 Hz), 123.70, 118.43 (d,  $J$  = 4.6 Hz), -0.82.

**$^{31}\text{P}$  NMR** (162 MHz,  $\text{CDCl}_3$ )  $\delta$  30.00.

**HRMS (ESI<sup>+</sup>):**  $m/z$  calcd for  $\text{C}_{21}\text{H}_{23}\text{O}_2\text{PSi}^+$ ,  $[\text{M}+\text{H}]^+$ : 367.1278, found: 367.1272.

Synthesis of 2



2-(trimethylsilyl)phenol (4.6 g, 27.5 mmol, 1.2 eq.) was dissolved in anhydrous tetrahydrofuran (45.0 mL) and sodium hydride (60%, 1.2 g, 30.3 mmol, 1.3 eq.) was added at 0 °C. The resulting suspension was stirred at room temperature for 1.0 hour. bis(diethylamino)phosphoryl chloride<sup>[2]</sup> (6.1 g, 23.0 mmol, 1 eq.) was added at 0 °C and the resulting suspension was stirred at room temperature for 8.0 hours. After that, the resulting reaction mixture was poured into a brine solution (20.0 mL) and subsequently extracted three times with ethyl acetate (50.0 mL). The combined organic phases were dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was purified through chromatography on a silica gel plug (eluent: petrol ether/ethyl acetate = 5/1) giving **2** as a pale yellow oil (7.0 g, 85% yield).

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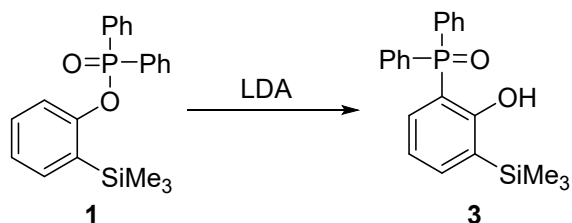
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.62 (d, *J* = 8.4 Hz, 1H, *CH*-Ar), 7.36 (dt, *J* = 7.2, 1.6 Hz, 1H, *CH*-Ar), 7.28 – 7.23 (m, 1H, *CH*-Ar), 6.99 (td, *J* = 7.6, 1.2 Hz, 1H, *CH*-Ar), 3.23 – 3.00 (m, 8H, CH<sub>2</sub>), 1.04 (t, *J* = 7.2 Hz, 12H, CH<sub>3</sub>), 0.26 (s, 9H, CH<sub>3</sub>).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 157.55 (d, *J* = 5.9 Hz), 135.22, 130.73, 128.49 (d, *J* = 10.7 Hz), 122.79, 117.81 (d, *J* = 3.0 Hz), 39.32 (d, *J* = 4.6 Hz), 13.84 (d, *J* = 2.3 Hz), -0.66.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 14.57.

**HRMS (ESI<sup>+</sup>):** *m/z* calcd for C<sub>17</sub>H<sub>34</sub>N<sub>2</sub>O<sub>2</sub>PSi<sup>+</sup>, [M+H]<sup>+</sup>: 357.2122, found: 357.2116.

### Synthesis of 3



To a solution of **1** (7.2 g, 19.6 mmol, 1.0 eq.) in anhydrous tetrahydrofuran (40.0 mL) was added LDA (lithium diisopropylamide, 21.6 mmol, 1.1 eq.) at -80 °C. The mixture was stirred at room temperature for 10 hours. Then the reaction was quenched with aqueous sodium bicarbonate. After that, the resulting reaction mixture was poured into a brine solution (20.0 mL) and extracted three times with ethyl acetate (50.0 mL). The combined organic phases were dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was purified through chromatography on a silica gel plug (eluent: petrol ether/ethyl acetate = 10/1), giving **3** as a white solid (5.7 g, 80% yield).

**M.p. (°C):** 58.8 – 59.4.

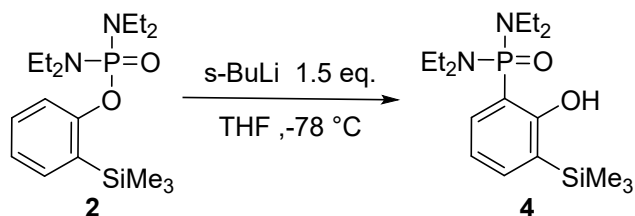
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 11.22 (s, 1H, OH), 7.72 – 7.67 (m, 4H, *CH*-Ar), 7.60 – 7.56 (m, 2H, *CH*-Ar), 7.53 – 7.46 (m, 5H, *CH*-Ar), 7.03 – 6.97 (m, 1H, *CH*-Ar), 6.84 – 6.80 (m, 1H, *CH*-Ar), 0.31 (s, 9H, CH<sub>3</sub>-Si(CH<sub>3</sub>)<sub>3</sub>).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 168.62 (d, *J* = 2.1 Hz), 140.02, 133.34 (d, *J* = 10.5 Hz), 132.54 (d, *J* = 2.1 Hz), 132.16 (d, *J* = 10.3 Hz), 131.56, 129.44 (d, *J* = 4.8 Hz), 128.82 (d, *J* = 12.3 Hz), 118.71 (d, *J* = 11.7 Hz), 110.09 (d, *J* = 102.3 Hz), -0.97.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 40.39.

**HRMS (ESI<sup>+</sup>):** *m/z* calcd for C<sub>21</sub>H<sub>24</sub>O<sub>2</sub>PSi<sup>+</sup>, [M+H]<sup>+</sup>: 367.1278, found: 367.1278.

### Synthesis of 4



To a solution of **2** (2.3 g, 6.5 mmol, 1.0 eq.) in anhydrous tetrahydrofuran (22.0 mL) was dropwise added *s*-BuLi (7.5 mL, 9.7 mmol, 1.5 eq.) at -78 °C. The resulting suspension was stirred at room temperature for 2.0 hours. The reaction was quenched with an aqueous sodium bicarbonate solution. After that, the resulting reaction mixture was poured into a brine solution (20.0 mL) and subsequently extracted three times with ethyl acetate (50.0 mL). The combined organic phases were dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was purified through chromatography on a silica gel plug (eluent: petrol ether/ethyl acetate = 10/1) giving **4** as colorless oil (1.7 g, 74% yield).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.44 – 7.40 (dt, *J* = 7.2, 0.4 Hz, 1H, *CH*-Ar), 7.25 – 7.19 (m, 1H, *CH*-Ar), 6.79 – 6.75 (m, 1H, *CH*-Ar), 3.16 – 3.00 (m, 8H, CH<sub>2</sub>-Et), 1.04 (t, *J* = 7.2 Hz, 12H, CH<sub>3</sub>-Et), 0.26 (t, *J* = 3.6 Hz, 9H, CH<sub>3</sub>-Si(CH<sub>3</sub>)<sub>3</sub>).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 167.23 (d, *J* = 5.5 Hz), 139.10, 132.30 (d, *J* = 6.6 Hz), 128.13 (d, *J* = 6.9 Hz), 118.09 (d, *J* = 11.6 Hz), 112.57 (d, *J* = 6.6 Hz), 111.09, 38.51 (d, *J* = 147.7 Hz), 13.61 (d, *J* = 2.9 Hz), -1.04.

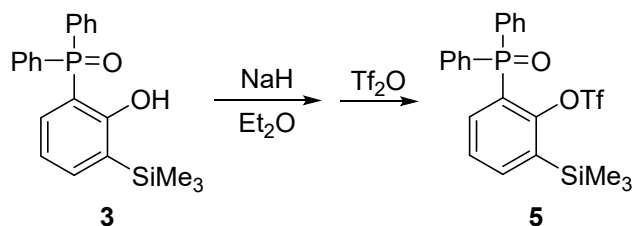
**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 35.71.

**HRMS (ESI<sup>+</sup>):** *m/z* calcd for C<sub>17</sub>H<sub>34</sub>N<sub>2</sub>O<sub>2</sub>PSi<sup>+</sup>, [M+H]<sup>+</sup>: 357.2122, found: 357.2116.



## SUPPORTING INFORMATION

### Synthesis of **5**



To a solution of **3** (1.3 g, 3.6 mmol, 1.0 eq.) in anhydrous tetrahydrofuran (30.0 mL) was added sodium hydride (60.0%, 171.8 mg, 4.29 mmol, 1.2 eq.) at 0 °C. The resulting suspension was stirred at room temperature for 0.5 hours. Then trifluoromethanesulfonic anhydride (0.8 mL, 4.7 mmol, 2.0 eq.) was slowly added at 0 °C and the resulting suspension was stirred at room temperature for 2.0 hours. The reaction was quenched with an aqueous sodium bicarbonate solution. After that, the resulting reaction mixture was poured into a brine solution (20.0 mL) and subsequently extracted three times with ethyl acetate (50.0 mL). The combined organic phases were dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was purified through chromatography on a silica gel plug (eluent: petrol ether/ethyl acetate = 5/1) giving **5** as a white solid (1.3 g, 73% yield).

**M.p. (°C):** 127.5 – 128.6.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.78 – 7.75 (m, 1H, *CH*-Ar), 7.67 – 7.62 (m, 4H, *CH*-Ar), 7.54 (td, *J* = 7.2, 1.6 Hz, 2H, *CH*-Ar), 7.47 – 7.43 (m, 4H, *CH*-Ar), 7.34 (td, *J* = 7.2, 1.6 Hz, 1H, *CH*-Ar), 7.26 – 7.21 (m, 1H, *CH*-Ar), 0.40 (s, 9H, CH<sub>3</sub>).

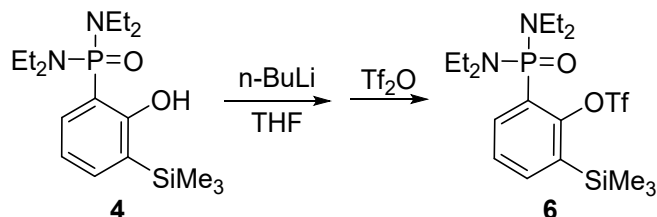
**<sup>13</sup>C{<sup>1</sup>H} NMR** (400 MHz, CDCl<sub>3</sub>) δ 153.16, 140.87 (d, *J* = 1.7 Hz), 137.82 (d, *J* = 3.3 Hz), 136.91 (d, *J* = 9.8 Hz), 133.43, 132.36, 131.85 (d, *J* = 2.8 Hz), 131.75 (d, *J* = 9.9 Hz), 128.27 (d, *J* = 12.5 Hz), 127.14, 126.81 (d, *J* = 11.0 Hz), 126.18, 119.80, 116.61, 0.27.

**<sup>31</sup>P NMR** (400 MHz, CDCl<sub>3</sub>) δ 27.97.

**<sup>19</sup>F NMR** (400 MHz, CDCl<sub>3</sub>) δ 70.96.

**HRMS (ESI<sup>+</sup>):** *m/z* calcd for C<sub>22</sub>H<sub>23</sub>F<sub>3</sub>O<sub>4</sub>PSSi<sup>+</sup>, [M+H]<sup>+</sup>: 499.0771, found: 499.0765.

### Synthesis of **6**



To a solution of **4** (2.5 g, 7.0 mmol, 1.0 eq.) in anhydrous tetrahydrofuran (30.0 mL) was added *n*-BuLi (5.3 mL, 8.4 mmol, 1.2 eq.) at -78 °C. The resulting suspension was stirred at room temperature for 0.5 hours. Then trifluoromethane sulfonic anhydride (1.8 mL, 10.5 mmol, 1.5 eq.) was slowly added at 0 °C and the resulting suspension was stirred at room temperature for 2.0 hours. The reaction was quenched with an aqueous sodium bicarbonate solution. After that, the resulting reaction mixture was poured into a brine solution (20.0 mL) and subsequently extracted three times with ethyl acetate (50.0 mL). The combined organic phases were dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was purified through chromatography on a silica gel plug (eluent: petrol ether/ethyl acetate = 5/1) giving **6** as pale yellow oil (2.4 g, 72% yield).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.69 – 7.63 (m, 2H, *CH*-Ar), 7.37 (td, *J* = 7.6, 2.0 Hz, 1H, *CH*-Ar), 3.17 – 2.95 (m, 8H, CH<sub>2</sub>), 1.02 (t, *J* = 7.2 Hz, 12H, CH<sub>3</sub>), 0.37 (t, *J* = 3.2 Hz, 9H, CH<sub>3</sub>).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 152.99, 139.96, 137.24 (d, *J* = 4.6 Hz), 135.76 (d, *J* = 4.9 Hz), 128.44, 127.03 (d, *J* = 10.4 Hz), 123.28 (q, *J*<sub>C-F</sub> = 319.2 Hz), 38.05 (d, *J* = 4.2 Hz), 13.11 (d, *J* = 2.4 Hz), 0.47.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 24.42.

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ 70.88.

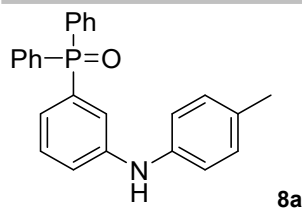
**HRMS (ESI<sup>+</sup>):** *m/z* calcd for C<sub>18</sub>H<sub>33</sub>F<sub>3</sub>N<sub>2</sub>O<sub>4</sub>PSSi<sup>+</sup>, [M+H]<sup>+</sup>: 489.1615, found: 489.1606.

### 3. The reactions of arylene precursor **5** and **6** with various trapping agents.

#### General synthetic procedure:

3-phosphoryl benzyne precursor (**5** or **6**) (0.1 mmol), cesium fluoride (0.3 mmol, 3.0 eq.) and trapping agent (**7a** – **7j**, 0.2 mmol, 2.0 eq.) were placed in a dried Schlenk flask. Then 1 mL of acetonitrile (0.1 M) was added with a syringe under nitrogen gas. The resulting mixture was stirred at room temperature for 12 hours. After that, the volatile was removed under vacuum, and the residue was purified by column chromatography on silica gel to afford the pure product.

## SUPPORTING INFORMATION



According to the general synthetic procedure, **8a** was obtained as a white solid (25.6 mg, 67% yield).

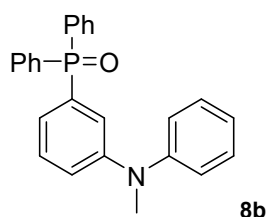
**M.p.** (°C): 97.4 – 98.0.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.70 – 7.66 (m, 4H, CH-Ar), 7.54 – 7.52 (m, 2H, CH-Ar), 7.47 – 7.44 (m, 4H, CH-Ar), 7.31 – 7.25 (m, 2H, CH-Ar), 7.16 (d, *J* = 8.0 Hz, 1H, CH-Ar), 7.06 – 7.01 (m, 3H, CH-Ar), 6.94 (d, *J* = 8.4 Hz, 2H, CH-Ar), 5.84 (s, 1H, NH), 2.29 (s, 3H, CH<sub>3</sub>).

**<sup>13</sup>C{H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 143.53 (d, *J* = 14.1 Hz), 138.08, 132.89, 132.05, 131.86, 131.12 (d, *J* = 9.9 Hz), 130.86 (d, *J* = 2.2 Hz), 130.80, 128.89, 128.46 (d, *J* = 13.9 Hz), 127.49 (d, *J* = 12.1 Hz), 122.15 (d, *J* = 9.8 Hz), 118.56, 117.81 (d, *J* = 2.0 Hz), 19.70.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 29.56.

**HRMS (ESI<sup>+</sup>):** *m/z* calcd for C<sub>25</sub>H<sub>23</sub>NOP<sup>+</sup>, [M+H]<sup>+</sup>: 384.1512, found: 384.1512.



According to the general synthetic procedure, **8b** was obtained as a white solid (26.8 mg, 70% yield).

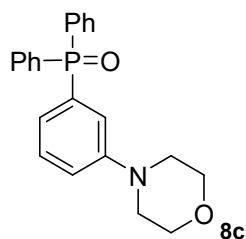
**M.p.** (°C): 121.7 – 123.2.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.70 – 7.64 (m, 4H, CH-Ar), 7.55 – 7.50 (m, 2H, CH-Ar), 7.46 – 7.42 (m, 4H, CH-Ar), 7.32 – 7.23 (m, 4H, CH-Ar), 7.07 – 6.99 (m, 5H, CH-Ar), 3.28 (s, 3H, CH<sub>3</sub>).

**<sup>13</sup>C{H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 149.23 (d, *J* = 13.8 Hz), 148.23, 133.68, 133.22, 132.65, 132.21 (d, *J* = 9.7 Hz), 131.94 (d, *J* = 2.5 Hz), 129.58, 129.18 (d, *J* = 14.0 Hz), 128.57 (d, *J* = 12.0 Hz), 123.45 (d, *J* = 25.7 Hz), 123.15 (d, *J* = 10.5 Hz), 121.21 (d, *J* = 2.4 Hz), 120.56 (d, *J* = 11.0 Hz), 40.27.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 30.51.

**HRMS (ESI<sup>+</sup>):** *m/z* calcd for C<sub>25</sub>H<sub>23</sub>NOP<sup>+</sup>, [M+H]<sup>+</sup>: 384.1512, found: 384.1516.



According to the general synthetic procedure, **8c** was obtained as a yellow oil (22.1 mg, 61% yield).

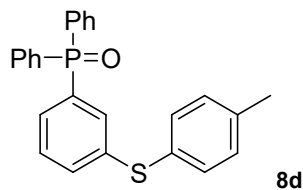
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.67 – 7.62 (m, 4H, CH-Ar), 7.54 – 7.50 (m, 2H, CH-Ar), 7.46 – 7.42 (m, 4H, CH-Ar), 7.39 – 7.36 (m, 1H, CH-Ar), 7.32 – 7.27 (m, 1H, CH-Ar), 7.05 (dd, *J* = 8.0, 2.4 Hz, 1H, CH-Ar), 6.95 – 6.90 (m, 1H, CH-Ar), 3.81 – 3.79 (m, 2H, CH<sub>2</sub>), 3.16 – 3.13 (m, 2H, CH<sub>2</sub>).

**<sup>13</sup>C{H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 151.34 (d, *J* = 13.2 Hz), 133.70, 133.21, 132.66, 132.19 (d, *J* = 9.9 Hz), 131.99 (d, *J* = 2.3 Hz), 129.33 (d, *J* = 14.1 Hz), 128.59 (d, *J* = 12.1 Hz), 123.19 (d, *J* = 10.5 Hz), 118.69, 66.79, 48.77.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 30.44.

**HRMS (ESI<sup>+</sup>):** *m/z* calcd for C<sub>22</sub>H<sub>23</sub>NO<sub>2</sub>P<sup>+</sup>, [M+H]<sup>+</sup>: 364.1461, found: 364.1462.

## SUPPORTING INFORMATION



According to the general synthetic procedure on 0.1 mmol, **8d** was obtained as a white solid (32.1 mg, 80% yield).

Synthetic procedure on 1.0 mmol scale:

Cesium fluoride (4 mmol, 4.0 eq., 0.63 g), *p*-toluenethiol (2 mmol, 2.0 eq., 0.25 g), and dry acetonitrile (8 mL, 0.1 M) were placed in a dried Schlenk flask (50 mL) under nitrogen gas. The mixture was stirred at room temperature for 0.5 hours under nitrogen gas. Then 3-phosphoryl benzyne precursor **5** (1 mmol, 0.50 g) in 2 mL of acetonitrile was added with a syringe. The resulting mixture was stirred at room temperature for 18 hours. After that, the volatile was removed under vacuum, and the residue was purified by column chromatography on silica gel to afford the pure product **8d** (0.74 mmol, 0.28 g) in 74% isolated yield.

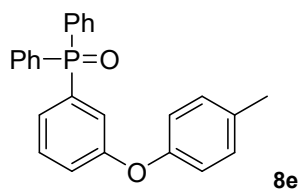
**M.p.** (°C): 113.3 – 115.9.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.62 – 7.56 (m, 4H, *CH*-Ar), 7.51 – 7.37 (m, 8H, *CH*-Ar), 7.29 – 7.28 (m, 2H, *CH*-Ar), 7.25 – 7.23 (m, 2H, *CH*-Ar), 7.07 (d, *J* = 8.2 Hz, 2H, *CH*-Ar), 2.30 (s, 3H, CH<sub>3</sub>).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 139.48 (d, *J* = 13.2 Hz), 138.61, 133.68 (d, *J* = 101.5 Hz), 132.84 (d, *J* = 141.4 Hz), 132.72, 132.03, 131.67, 131.64 (d, *J* = 2.2 Hz), 131.51, 130.42, 129.45 (d, *J* = 9.6 Hz), 129.24 (d, *J* = 2.3 Hz), 129.13, 128.59 (d, *J* = 12.2 Hz), 21.32.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 29.50.

**HRMS (ESI<sup>+</sup>):** *m/z* calcd for C<sub>25</sub>H<sub>22</sub>OPS<sup>+</sup>: [M+H]<sup>+</sup>: 401.1123, found: 401.1121.



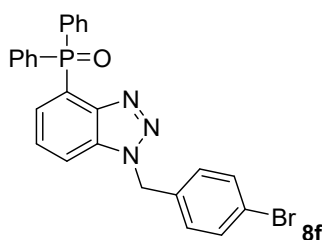
According to the general synthetic procedure, **8e** was obtained as light yellow oil (22.3 mg, 58% yield).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.68 – 7.63 (m, 5H, *CH*-Ar), 7.56 – 7.52 (m, 2H, *CH*-Ar), 7.50 – 7.44 (m, 5H, *CH*-Ar), 7.38 – 7.35 (m, 1H, *CH*-Ar), 7.33 – 7.30 (m, 1H, *CH*-Ar), 7.11 (d, *J* = 8.4 Hz, 2H, *CH*-Ar), 6.87 (d, *J* = 8.4 Hz, 2H, *CH*-Ar), 2.32 (s, 3H, CH<sub>3</sub>).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 158.27 (d, *J* = 15.1 Hz), 153.86, 133.77, 132.85 (d, *J* = 9.8 Hz), 130.54, 130.15 (d, *J* = 14.0 Hz), 128.84, 128.71 (d, *J* = 11.3 Hz), 126.37 (d, *J* = 9.8 Hz), 121.67 (d, *J* = 11.0 Hz), 121.39, 119.49, 20.87.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 29.57.

**HRMS (ESI<sup>+</sup>):** *m/z* calcd for C<sub>25</sub>H<sub>22</sub>O<sub>2</sub>P<sup>+</sup>, [M+H]<sup>+</sup>, 385.1352, found: 385.1357.



According to the general synthetic procedure, **8f** was obtained as a white solid (24.4 mg, 50% yield).

**M.p.** (°C): 58.8 – 59.2.

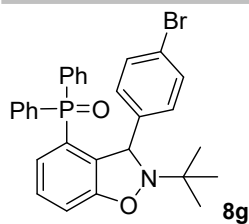
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.18 – 8.13 (m, 1H, *CH*-Ar), 7.95 – 7.90 (m, 4H, *CH*-Ar), 7.54 – 7.38 (m, 10H, *CH*-Ar), 7.14 (d, *J* = 8.4 Hz, 2H, *CH*-Ar), 5.74 (s, 2H, CH<sub>2</sub>).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 145.33 (d, *J* = 9.0 Hz), 133.18, 132.79 (d, *J* = 2.0), 132.70, 132.29 (d, *J* = 2.2 Hz), 132.17, 132.10 (d, *J* = 2.8 Hz), 131.71, 130.66 (d, *J* = 5.8 Hz), 129.50, 128.39 (d, *J* = 12.7 Hz), 127.29 (d, *J* = 11.1 Hz), 125.34, 124.35, 122.86, 113.89 (d, *J* = 2.8 Hz), 51.84.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 24.88.

**HRMS (ESI<sup>+</sup>):** *m/z* calcd for C<sub>25</sub>H<sub>20</sub>BrN<sub>3</sub>OP<sup>+</sup>, [M(<sup>79</sup>Br)+H]<sup>+</sup>: 488.0522, found: 488.0519, [M(<sup>81</sup>Br)+H]<sup>+</sup>: 490.0502, found 490.0496.

## SUPPORTING INFORMATION



According to the general synthetic procedure, **8g** was obtained as a white solid (29.3 mg, 55% yield).

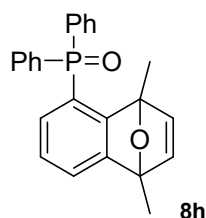
**M.p. (°C):** 81.7 – 82.6.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.54 – 7.47 (m, 3H, CH-Ar), 7.44 – 7.39 (m, 3H, CH-Ar), 7.21 – 7.04 (m, 6H, CH-Ar), 6.94 – 6.88 (m, 4H, CH-Ar), 6.59 (ddd, *J* = 12.8, 8.4, 0.8 Hz, 1H, CH-Ar), 6.28 (d, *J* = 1.6 Hz, 1H, CH), 1.18 (s, 9H, CH<sub>3</sub>).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 158.40 (d, *J* = 12.3 Hz), 141.25, 133.76 (d, *J* = 7.5 Hz), 132.98 (d, *J* = 104.3 Hz), 132.08 (d, *J* = 10.0 Hz), 131.97 (d, *J* = 2.7 Hz), 131.08 (d, *J* = 2.3 Hz), 130.45 (d, *J* = 104.0 Hz), 130.27 (d, *J* = 104.0 Hz), 128.65 (d, *J* = 13.1 Hz), 128.45 (d, *J* = 12.2 Hz), 128.12 (d, *J* = 12.4 Hz), 127.34, 125.23 (d, *J* = 11.4 Hz), 121.34, 110.61 (d, *J* = 2.6 Hz), 65.36 (d, *J* = 1.4 Hz), 61.88, 25.33.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 29.90.

**HRMS (ESI<sup>+</sup>):** *m/z* calcd for C<sub>29</sub>H<sub>28</sub>BrNO<sub>2</sub>P<sup>+</sup>, [M(<sup>79</sup>Br)+H]<sup>+</sup>: 532.1036, found: 532.1034, [M(<sup>81</sup>Br)+H]<sup>+</sup>: 534.1016, found 534.1010.



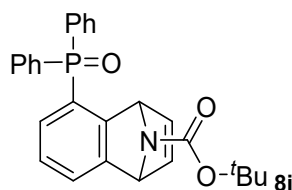
According to the general synthetic procedure, **8h** was obtained as colorless oil. (28.1 mg, 76% yield).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.71 – 7.66 (m, 2H, CH-Ar), 7.58 – 7.53 (m, 4H, CH-Ar), 7.50 – 7.43 (m, 4H, CH-Ar), 7.26 – 7.23 (m, 1H, CH-Ar), 6.89 (td, *J* = 8.0, 2.0 Hz, 1H, CH-Ar), 6.82 (d, *J* = 5.6 Hz, 1H, CH-Ar), 6.72 (d, *J* = 5.2 Hz, 1H, CH-Ar), 6.55 (ddd, *J* = 12.8, 8, 0.8 Hz, 1H, CH-Ar), 1.90 (s, 3H, CH<sub>3</sub>), 1.79 (s, 3H, CH<sub>3</sub>).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 158.84 (d, *J* = 8.1 Hz), 155.24 (d, *J* = 9.3 Hz), 147.57, 146.73, 133.98 (d, *J* = 22.2 Hz), 132.94 (d, *J* = 23.4 Hz), 132.28 (d, *J* = 9.7 Hz), 128.56, 128.80 (d, *J* = 10.1 Hz), 128.63, 126.57 (d, *J* = 102.5 Hz), 124.32 (d, *J* = 11.1 Hz), 121.27 (d, *J* = 2.0 Hz), 91.78 (d, *J* = 1.3 Hz), 87.60, 18.17, 15.21.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 30.84.

**HRMS (ESI<sup>+</sup>):** *m/z* calcd for C<sub>24</sub>H<sub>22</sub>O<sub>2</sub>P<sup>+</sup>, [M+H]<sup>+</sup>: 373.1352, found: 373.1350.



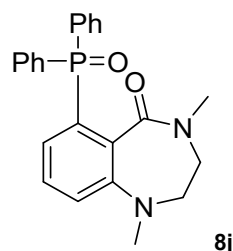
According to the general synthetic procedure, **8i** was obtained as colorless oil (23.0 mg, 52% yield).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.70 – 7.65 (m, 4H, CH-Ar), 7.59 – 7.54 (m, 2H, CH-Ar), 7.50 – 7.45 (m, 4H, CH-Ar), 7.39 (d, *J* = 6.8 Hz, 1H, CH), 7.0 – 6.73 (br, 4H, CH), 6.91 (br, 2H), 1.25 (s, 9H, CH<sub>3</sub>).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 154.70, 150.01 (br), 143.60 (br), 132.15 (br), 142.94 (br), 132.22, 132.15, 132.05, 128.87, 128.77, 128.75, 128.65, 127.73 (d, *J* = 11.0 Hz), 124.91 (d, *J* = 11.0 Hz), 123.96, 80.79, 66.27 (br), 65.31 (br), 28.12.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 28.75.

**HRMS (ESI<sup>+</sup>):** *m/z* calcd for C<sub>27</sub>H<sub>29</sub>NO<sub>3</sub>P<sup>+</sup>, [M+H]<sup>+</sup>: 446.1880, found: 446.1877.



According to the general synthetic procedure, **8j** was obtained as a yellow solid (17.6 mg, 45.0% yield).

## SUPPORTING INFORMATION

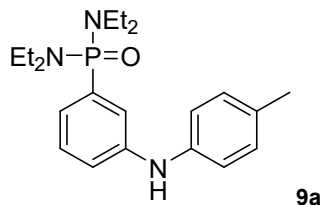
**M.p. (°C):** 92.9 – 93.8.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.75 – 7.73 (5H, CH-Ar), 7.50 – 7.45 (m, 3H, CH-Ar), 7.44 – 7.38 (m, 4H, CH-Ar), 7.09 (d, *J* = 8.0 Hz, 1H, CH-Ar), 3.12 – 3.09 (m, 4H, CH<sub>2</sub>), 2.80 (s, 3H, CH<sub>3</sub>), 2.58 (s, 3H, CH<sub>3</sub>).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 167.98 (d, *J* = 4.0 Hz), 146.43 (d, *J* = 11.7 Hz), 133.62, 132.76 (d, *J* = 10.4 Hz), 132.59 (d, *J* = 7.5 Hz), 131.50 (d, *J* = 2.3 Hz), 130.55 (d, *J* = 13.3 Hz), 128.24 (d, *J* = 8.4 Hz), 127.91 (d, *J* = 12.6 Hz), 121.62, 57.30, 47.69, 40.27, 33.20.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 33.87.

**HRMS (ESI<sup>+</sup>):** *m/z* calcd for C<sub>23</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>P<sup>+</sup>, [M+H]<sup>+</sup>: 391.1570, found 391.1565.



According to the general synthetic procedure, **9a** was obtained as colorless oil (22.2 mg, 60% yield).

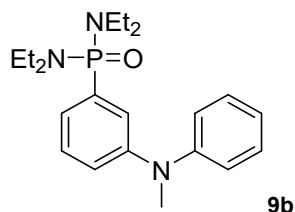
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.39 (d, *J* = 13.6 Hz, 1H, CH-Ar), 7.24 – 7.06 (m, 5H, CH-Ar), 6.99 (d, *J* = 8.4 Hz, 2H, CH-Ar), 5.83 (s br, 1H, NH), 3.10 – 3.02 (m, 8H, CH<sub>2</sub>), 2.29 (s, 3H, CH<sub>3</sub>), 1.03 (t, *J* = 7.2 Hz, 12H, CH<sub>3</sub>).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 144.28 (d, *J* = 15.3 Hz), 139.89, 134.33 (d, *J* = 153.0 Hz), 131.43, 129.96, 129.17 (d, *J* = 14.8 Hz), 129.17 (d, *J* = 14.8 Hz), 123.07 (d, *J* = 8.3 Hz), 120.42 (d, *J* = 10.3 Hz), 119.34, 118.39 (d, *J* = 1.9), 38.42 (d, *J* = 4.0 Hz), 20.80, 13.78 (d, *J* = 2.6 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 29.10.

**HRMS (ESI<sup>+</sup>):** *m/z* calcd for C<sub>21</sub>H<sub>33</sub>N<sub>3</sub>OP<sup>+</sup>, [M+H]<sup>+</sup>: 374.236, found: 374.239.

According to the general synthetic procedure, **9b** and **9b'** were isolated in 53% (19.8 mg, light yellow oil) and 33% (12.3mg, light yellow oil), respectively.

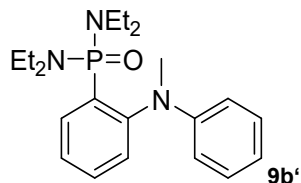


**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.33 (d, *J* = 14.3 Hz, 1H, CH-Ar), 7.31 – 7.25 (m, 4H, CH-Ar), 7.14 – 6.93 (m, 4H, CH-Ar), 3.32 (s, 3H, CH<sub>3</sub>), 3.05 (dq, *J* = 14.6, 7.3 Hz, 8H), 1.02 (t, *J* = 7.1 Hz, 12H).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 149.05 (d, *J* = 15.2 Hz), 148.80, 134.06 (d, *J* = 152.9 Hz), 129.44, 129.11 (d, *J* = 14.9 Hz), 123.91 (d, *J* = 8.6 Hz), 122.46, 122.25 (d, *J* = 10.5 Hz), 121.92, 121.78 (d, *J* = 1.8 Hz), 40.37, 38.43 (d, *J* = 4.2 Hz), 13.78 (d, *J* = 2.4 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 29.57.

**HRMS (ESI<sup>+</sup>):** *m/z* calcd for C<sub>21</sub>H<sub>33</sub>N<sub>3</sub>OP<sup>+</sup>, [M+H]<sup>+</sup>: 374.2356, found: 374.2354.



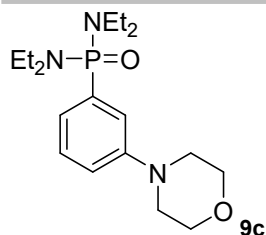
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.75 (ddd, *J* = 13.1, 7.7, 1.6 Hz, 1H, CH-Ar), 7.52 – 7.43 (m, 1H, CH-Ar), 7.33 – 7.25 (m, 2H, CH-Ar), 7.15 – 7.07 (m, 2H), 6.67 (t, *J* = 7.3 Hz, 1H, CH-Ar), 6.54 (d, *J* = 7.9 Hz, 2H, CH-Ar), 3.28 (s, 3H, CH<sub>3</sub>), 3.12 – 2.80 (m, 8H, CH<sub>2</sub>), 1.00 (t, *J* = 7.1 Hz, 12H, CH<sub>3</sub>).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 152.94 (d, *J* = 4.7 Hz), 150.24, 135.08 (d, *J* = 7.2 Hz), 132.84, 131.57 (d, *J* = 9.3 Hz), 130.06, 128.59, 126.16 (d, *J* = 22.1 Hz), 116.77, 113.88, 41.49, 38.84 (d, *J* = 4.0 Hz), 14.04.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 27.88.

**HRMS (ESI<sup>+</sup>):** *m/z* calcd for C<sub>21</sub>H<sub>33</sub>N<sub>3</sub>OP<sup>+</sup>, [M+H]<sup>+</sup>: 374.2356, found: 374.2351.

## SUPPORTING INFORMATION



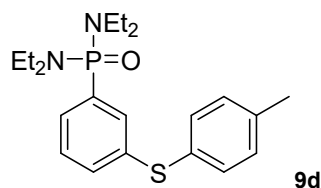
According to the general synthetic procedure, **9c** was obtained as light yellow oil (25.4 mg, 72% yield).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.37 (dd, *J* = 13.6, 1.2 Hz, 1H, *CH*-Ar), 7.29 – 7.24 (m, 1H, *CH*-Ar), 7.14 (dd, *J* = 11.2, 7.6 Hz, 1H, *CH*-Ar), 6.95 (dd, *J* = 8.0, 2.4 Hz, 1H, *CH*-Ar), 3.82 (t, *J* = 4.8 Hz, 4H, CH<sub>2</sub>), 3.16 (t, *J* = 4.8 Hz, 4H, CH<sub>2</sub>), 3.08 – 3.00 (m, 8H, CH<sub>2</sub>-Et), 1.01 (t, *J* = 7.2 Hz, 12H, CH<sub>3</sub>-Et).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 151.18 (d, *J* = 14.7 Hz), 134.15 (d, *J* = 152.1 Hz), 128.98 (d, *J* = 14.7 Hz), 122.72 (d, *J* = 8.4 Hz), 119.33 (d, *J* = 10.6 Hz), 117.90 (d, *J* = 2.3 Hz), 66.91, 49.12, 38.39 (d, *J* = 4.2 Hz), 13.77 (d, *J* = 2.7 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 29.36.

**HRMS (ESI<sup>+</sup>):** *m/z* calcd for C<sub>18</sub>H<sub>33</sub>N<sub>3</sub>O<sub>2</sub>P<sup>+</sup>, [M+H]<sup>+</sup>: 354.2305, found: 354.2301.



According to the general synthetic procedure, **9d** was obtained as a white solid (35.9 mg, 90% yield).

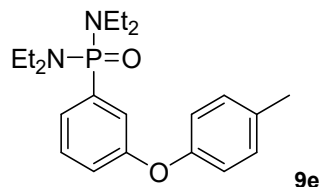
**M.p. (°C):** 74.3 – 75.6.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.63 – 7.57 (m, 1H, *CH*-Ar), 7.49 (dd, *J* = 12.4, 1.2 Hz, 1H, *CH*-Ar), 7.31 – 7.29 (m, 4H, *CH*-Ar), 7.13 (d, *J* = 8.0 Hz, 2H, *CH*-Ar), 3.02 – 2.94 (m, 8H, CH<sub>2</sub>-Et), 2.33 (s, 3H, CH<sub>3</sub>), 0.97 (t, *J* = 7.2 Hz, 12H, CH<sub>3</sub>-Et).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 138.29, 138.18 (d, *J* = 14.5 Hz), 134.41 (d, *J* = 152.0 Hz), 133.17, 131.91 (d, *J* = 9.7 Hz), 131.48 (d, *J* = 2.4 Hz), 130.36, 130.27, 129.98 (d, *J* = 8.8 Hz), 129.11 (d, *J* = 13.7 Hz), 38.36 (d, *J* = 4.1 Hz), 21.23, 13.65 (*J* = 2.6).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 28.22.

**HRMS (ESI<sup>+</sup>):** *m/z* calcd for C<sub>21</sub>H<sub>32</sub>N<sub>2</sub>O<sub>2</sub>P<sup>+</sup>, [M+H]<sup>+</sup>: 391.1967, found: 391.1969.



According to the general synthetic procedure, **9e** was obtained as colorless oil (21.3 mg, 57% yield).

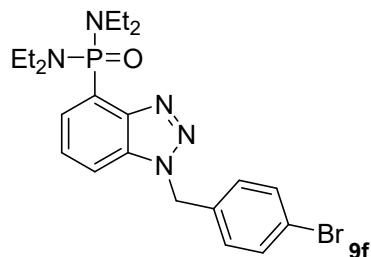
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.51 – 7.46 (m, 1H, CH<sub>3</sub>-Ar), 7.36 – 7.03 (m, 2H, CH<sub>3</sub>-Ar), 7.11 (d, *J* = 8.3 Hz, 2H, CH<sub>3</sub>-Ar), 7.04 (d, *J* = 8.2 Hz, 2H, CH<sub>3</sub>-Ar), 6.87 (d, *J* = 8.5 Hz, 2H, CH<sub>3</sub>-Ar), 3.13 – 2.94 (m, 8H, CH<sub>2</sub>), 2.31 (s, 3H, CH<sub>3</sub>), 1.01 – 0.98 (m, 12H, CH<sub>3</sub>).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 157.77 (d, *J* = 16.7 Hz), 154.54, 135.54 (d, *J* = 153.2 Hz), 133.30, 130.42, 129.81 (d, *J* = 14.9 Hz), 126.55 (d, *J* = 8.5 Hz), 121.47 (d, *J* = 9.7 Hz), 120.92, 119.19, 38.37 (d, *J* = 3.9 Hz), 20.83, 13.73 (d, *J* = 2.7 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 28.02.

**HRMS (ESI<sup>+</sup>):** *m/z* calcd for C<sub>21</sub>H<sub>32</sub>N<sub>2</sub>O<sub>2</sub>P<sup>+</sup>, [M+H]<sup>+</sup>: 375.2196, found: 375.2198.

According to the general synthetic procedure, **9f** and **9f'** were isolated in 58% (27.7 mg, colorless solid) and 10% (5.0 mg, light yellow oil), respectively.



## SUPPORTING INFORMATION

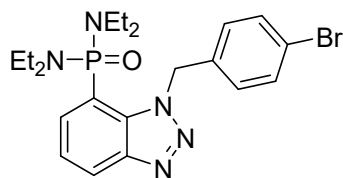
**M.p. (°C):** 43.0 – 43.4.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.10 (ddd, *J* = 13.6, 6.0, 2.0 Hz, 1H, *CH*-Ar), 7.48 – 7.44 (m, 4H, *CH*-Ar), 7.13 (d, *J* = 8.4 Hz, 2H, *CH*-Ar), 5.78 (s, 2H, *CH*<sub>2</sub>), 3.28 – 3.11 (m, 8H, *CH*<sub>2</sub>-Et), 0.99 (t, *J* = 7.2 Hz, 12H, *CH*<sub>3</sub>-Et).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 145.46 (d, *J* = 7.4 Hz), 133.62, 132.57 (d, *J* = 10.8 Hz), 132.36, 131.67 (d, *J* = 6.9 Hz), 129.36, 127.57 (d, *J* = 12.7 Hz), 126.57 (d, *J* = 150.0 Hz), 122.81, 112.53 (d, *J* = 2.6 Hz), 51.75, 38.34 (d, *J* = 5.2 Hz), 13.69 (d, *J* = 2.5 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 23.69.

**HRMS (ESI<sup>+</sup>):** *m/z* calcd for C<sub>21</sub>H<sub>30</sub>BrN<sub>5</sub>OP<sup>+</sup>, [M(<sup>79</sup>Br)+H]<sup>+</sup>: 478.1366, found: 478.1362. [M(<sup>81</sup>Br)+H]<sup>+</sup>: 480.1346, found 480.1348.

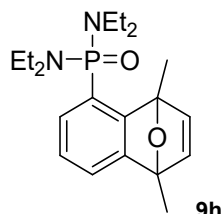


**9f**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.26 – 8.23 (m, 1H, *CH*-Ar), 7.70 – 7.64 (m, 1H, *CH*-Ar), 7.42 – 7.38 (m, 3H, *CH*-Ar), 7.16 (d, *J* = 8.4 Hz, 2H, *CH*-Ar), 6.58 (s, 2H, *CH*<sub>2</sub>), 3.11 – 2.96 (m, 8H, *CH*<sub>2</sub>-Et), 1.02 (t, *J* = 7.2 Hz, 12H, *CH*<sub>3</sub>-Et).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 146.86, 136.19, 133.32 (d, *J* = 8.0 Hz), 131.54, 129.56, 124.24 (d, *J* = 2.7 Hz), 123.08, 122.95, 121.56, 117.61 (d, *J* = 157.0 Hz), 53.46 (d, *J* = 63.7 Hz), 39.22 (d, *J* = 4.8 Hz), 13.94 (d, *J* = 2.0 Hz).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 27.35.



**9h**

According to the general synthetic procedure, **9h** was obtained as a white solid (22.8 mg, 63% yield).

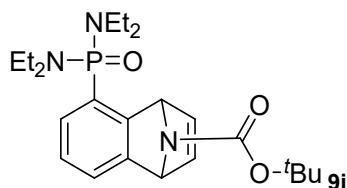
**M.p. (°C):** 83.8 – 84.3.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.17 – 7.14 (m, 1H, *CH*-Ar), 7.06 – 7.00 (m, 1H, *CH*-Ar), 6.97 – 6.92 (m, 2H, *CH*-C=C), 6.66 (d, *J* = 5.2 Hz, 1H, *CH*-Ar), 3.15 – 2.99 (m, 8H, *CH*<sub>2</sub>-Et), 2.20 (s, 3H, *CH*<sub>3</sub>), 1.86 (s, 3H, *CH*<sub>3</sub>), 1.06 (dt, *J* = 36.0, 7.2 Hz, 12H, *CH*<sub>3</sub>-Et).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 158.47 (d, *J* = 10.2 Hz), 154.82 (d, *J* = 11.0 Hz), 147.80, 146.39, 127.70 (d, *J* = 10.5 Hz), 126.41 (d, *J* = 156.9 Hz), 124.07 (d, *J* = 11.5 Hz), 120.33 (d, *J* = 2.4 Hz), 92.06, 87.24, 39.19 (d, *J* = 4.4 Hz), 38.86 (d, *J* = 5.3 Hz), 17.68, 15.25, 14.16, 13.57.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 28.45.

**HRMS (ESI<sup>+</sup>):** *m/z* calcd for C<sub>20</sub>H<sub>32</sub>N<sub>2</sub>O<sub>2</sub>P<sup>+</sup>: [M+H]<sup>+</sup>, 363.2196, found: 363.2191.



According to the general synthetic procedure, **9i** was obtained as light yellow oil (23.4 mg, 54% yield).

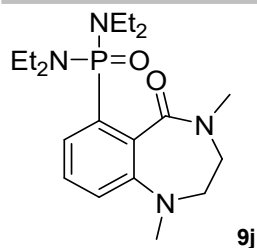
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.29 (d, *J* = 6.8 Hz, 1H, *CH*-Ar), 6.96 – 6.92 (m, 2H, *CH*-Ar), 6.26 (s, 1H, *CH*-C=C), 5.49 (s, 1H, *CH*-C=C), 3.11 – 3.01 (m, 8H, *CH*<sub>2</sub>-Et), 2.03 (s, 2H, *CH*), 1.36 (s, 9H, *CH*<sub>3</sub>-*t*Bu), 1.04 (t, *J* = 7.2 Hz, 12H, *CH*<sub>3</sub>-Et).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 154.76, 154.22 (d, *J* = 9.9 Hz), 149.51 (d, *J* = 10.9 Hz), 143.83, 143.18, 131.02, 128.91, 126.93, 124.37 (d, *J* = 10.9 Hz), 122.92, 80.54, 66.77, 65.47, 38.47, 28.26, 13.90.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 27.58.

**HRMS (ESI<sup>+</sup>):** *m/z* calcd for C<sub>23</sub>H<sub>37</sub>N<sub>3</sub>O<sub>3</sub>P<sup>+</sup>, [M+H]<sup>+</sup>: 434.2567, found: 434.2570.

## SUPPORTING INFORMATION



According to the general synthetic procedure, **9j** was obtained as yellow oil (28.4 mg, 75% yield).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.37 – 7.28 (m, 2H, *CH*-Ar), 6.98 (d, *J* = 7.6 Hz, 2H, *CH*-Ar), 3.16 – 3.07 (m, 13H, *CH*<sub>2</sub> and *N-CH*<sub>3</sub>), 2.81 – 2.77 (m, 5H, *CH*<sub>2</sub> and *CH*<sub>3</sub>), 1.04 (d, *J* = 6.5 Hz, 12H, *CH*<sub>3</sub>).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 169.74, 146.38 (d, *J* = 13.2 Hz), 135.21 (d, *J* = 9.1 Hz), 134.24 (d, *J* = 151.1 Hz), 129.52, 126.98, 120.52 (d, *J* = 54.3 Hz), 56.81, 47.88, 38.82, 33.69, 29.83, 13.85.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 29.30.

**HRMS (ESI<sup>+</sup>):** *m/z* calcd for C<sub>19</sub>H<sub>34</sub>N<sub>4</sub>O<sub>2</sub>P<sup>+</sup>, [M+H]<sup>+</sup> 381.2414, found: 381.2411.

After 5 days in the solvent of CDCl<sub>3</sub> under air

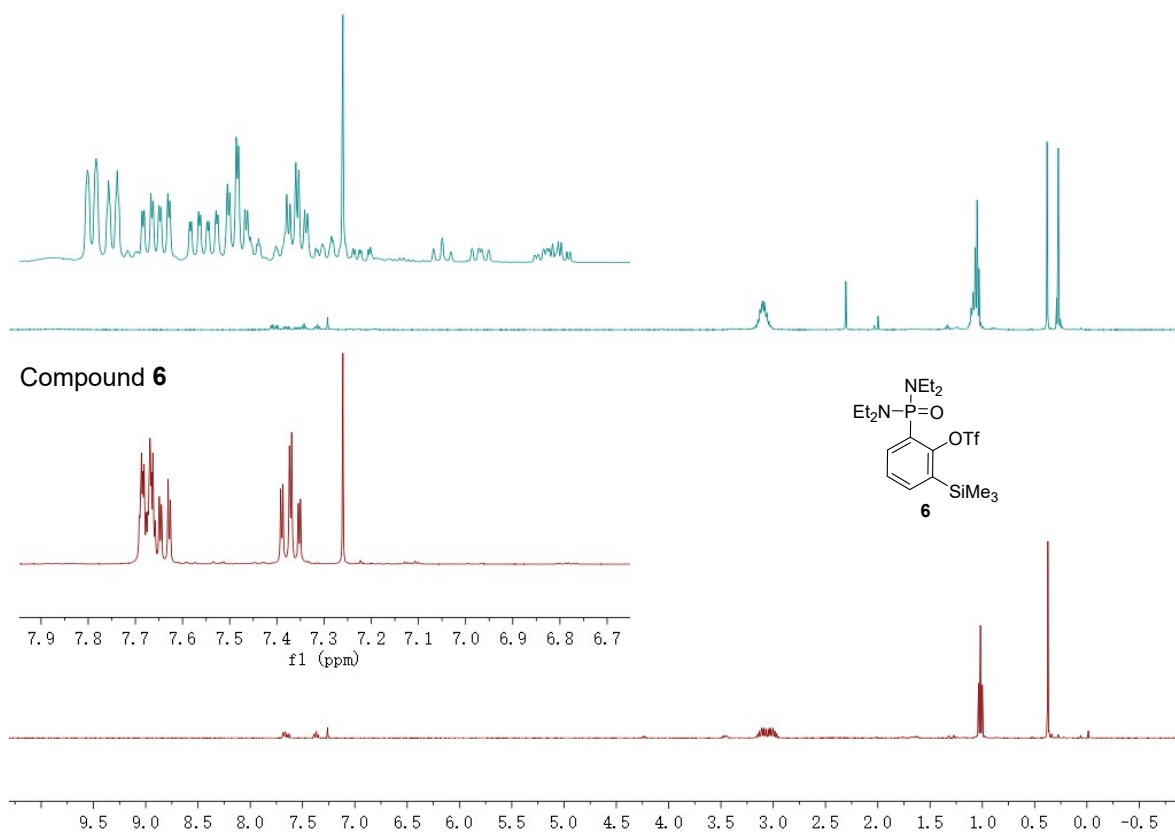
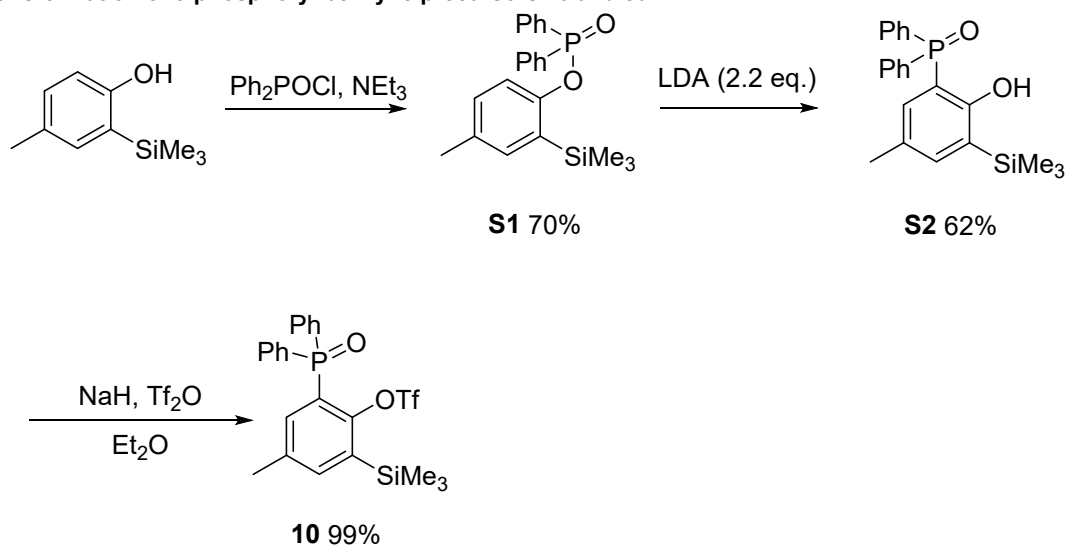


Figure S1, Stacked <sup>1</sup>H NMR spectra of compound **6** in CDCl<sub>3</sub>.

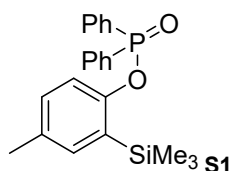


## SUPPORTING INFORMATION

### 4. Further transformation of 3-phosphoryl benzyne precursors **10** and **8d**



Scheme S1, Synthesis of 3-phosphoryl benzyne precursor **10**.



To a dichloromethane (15.0 mL) solution of 4-methyl-2-(trimethylsilyl)phenol (2.70 g, 15.0 mmol, 1.0 eq.) was added triethylamine (4.2 mL, 30.0 mmol, 2.0 eq.) and DMAP (0.37 g, 0.3 mmol, 0.2 eq.). Then diphenyl phosphinic chloride (3.97 g, 18.0 mmol, 1.2 eq.) was added dropwise at 0 °C. The resulting suspension was stirred at room temperature for 8.0 hours. After that, the resulting reaction mixture was poured into a brine solution (20.0 mL) and subsequently extracted three times by ethyl acetate (30.0 mL). The combined organic phases were dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was purified through chromatography on a silica gel plug (eluent: petrol ether/ethyl acetate = 5/1), giving **S1** as a white solid (4.0 g, 70% yield).

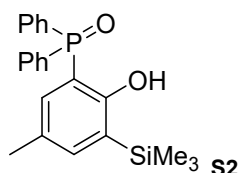
**M.p. (°C):** 56.2 – 56.1

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.93 – 7.84 (m, 4H, Ar-CH), 7.58 – 7.52 (m, 2H, Ar-CH), 7.49 – 7.44 (m, 4H, Ar-CH), 7.17 (d, *J* = 9.0 Hz, 2H, Ar-CH), 6.96 (dd, *J* = 8.4, 2.0 Hz, 2H, Ar-CH), 2.25 (s, 3H, CH<sub>3</sub>), 0.20 (s, 9H, Si-CH<sub>3</sub>).

**<sup>13</sup>C{H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 154.61 (d, *J* = 8.2 Hz), 136.11, 132.51 (d, *J* = 2.3 Hz), 132.41 (d, *J* = 88.7 Hz), 131.81 (d, *J* = 10.5 Hz), 131.23, 130.62, 129.45 (d, *J* = 8.6 Hz), 128.73 (d, *J* = 13.5 Hz), 118.11 (d, *J* = 4.4 Hz), 20.76, -0.77.

**<sup>31</sup>P NMR** (162 MHz, ) δ 30.38.

**HRMS (ESI<sup>+</sup>):** *m/z* calcd for C<sub>22</sub>H<sub>25</sub>O<sub>2</sub>PSi<sup>+</sup>, [M+H]<sup>+</sup>: 380.1361, found: 380.1360.



To a solution of **S1** (2.28 g, 6.0 mmol, 1.0 eq.) in anhydrous tetrahydrofuran (30.0 mL) was added LDA (lithium diisopropylamide, 7.2 mmol, 1.2 eq.) at -80 °C. The mixture was stirred at room temperature for 10 hours. Then the reaction was quenched with aqueous sodium bicarbonate. After that, the resulting reaction mixture was poured into a brine solution (20.0 mL) and extracted three times with ethyl acetate (20.0 mL). The combined organic phases were dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was purified through chromatography on a silica gel plug (eluent: petrol ether/ethyl acetate = 10/1), giving **S2** as an orange-red solid (1.42 g, 62% yield).

**M.p. (°C):** 58.6 – 59.8.

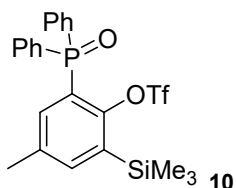
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 11.11 (s, 1H, OH), 7.77 – 7.68 (m, 4H, Ar-CH), 7.59 – 7.53 (m, 4H, Ar-CH), 7.50 – 7.45 (m, 4H, Ar-CH), 7.35 (d, *J* = 1.7 Hz, 1H, Ar-CH), 6.81 (dd, *J* = 13.5, 1.7 Hz, 1H, Ar-CH), 2.20 (s, 3H, CH<sub>3</sub>), 0.34 (s, 9H, CH<sub>3</sub>).

**<sup>13</sup>C{H} NMR** (101 MHz, CDCl<sub>3</sub>) δ 166.63 (d, *J* = 1.6 Hz), 141.09, 132.97 (d, *J* = 10.5 Hz), 132.70, 132.55 (d, *J* = 1.6 Hz), 132.13 (d, *J* = 10.3 Hz), 131.66, 129.25 (d, *J* = 5.1 Hz), 128.79 (d, *J* = 12.2 Hz), 127.53 (d, *J* = 11.9 Hz), 109.16 (d, *J* = 102.6 Hz), 20.74, -0.85.

## SUPPORTING INFORMATION

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 40.40.

**HRMS (ESI<sup>+</sup>)**: *m/z* calcd for C<sub>22</sub>H<sub>25</sub>O<sub>2</sub>PSi, [M+H]<sup>+</sup>: 478.1366, found: 478.1365.



To a solution of **S2** (0.76 g, 2.0 mmol, 1.0 eq.) in anhydrous ether (15.0 mL) was added sodium hydride (60.0%, 96.0 mg, 2.4 mmol, 1.2 eq.) at 0 °C. The resulting suspension was stirred at room temperature for 0.5 hours. Then trifluoromethanesulfonic anhydride (0.4 mL, 2.4 mmol, 1.2 eq.) was slowly added at 0 °C and the resulting suspension was stirred at room temperature for 2.0 hours. The reaction was quenched with an aqueous sodium bicarbonate solution. After that, the resulting reaction mixture was poured into a brine solution (20.0 mL) and subsequently extracted three times with ethyl acetate (20.0 mL). The combined organic phases were dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was purified through chromatography on a silica gel plug (eluent: petrol ether/ethyl acetate = 5/1) giving **10** as a white solid (1.02 g, 99.92% yield).

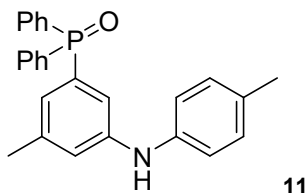
**M.p.** (°C): 126.7 – 128.3.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.65 – 7.60 (m, 4H, CH-Ar), 7.50 – 7.46 (m, 3H, CH-Ar), 7.43 – 7.38 (m, 3H, CH-Ar), 6.98 (dd, *J* = 14.1, 2.2 Hz, 1H, CH-Ar), 2.23 (s, 3H, CH<sub>3</sub>), 0.36 (s, 9H, CH<sub>3</sub>).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 151.35, 141.62, 137.50, 137.40, 136.98 (d, *J* = 10.8 Hz), 133.10 (d, *J* = 107.5 Hz), 132.02 (d, *J* = 2.5 Hz), 131.92 (d, *J* = 9.9 Hz), 128.44 (d, *J* = 12.4 Hz), 126.30 (d, *J* = 96.3 Hz), 120.00, 116.81, 20.94, 0.47.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 28.62.

**HRMS (ESI<sup>+</sup>)**: *m/z* calcd for C<sub>23</sub>H<sub>24</sub>F<sub>3</sub>O<sub>4</sub>PSSi, [M+H]<sup>+</sup>: 512.0854, found: 512.0850.



According to the general synthetic procedure on 0.1 mmol scale, **11** was obtained as a white solid (36.4 mg, 92% yield).

**M.p.** (°C): 96.8 – 97.7.

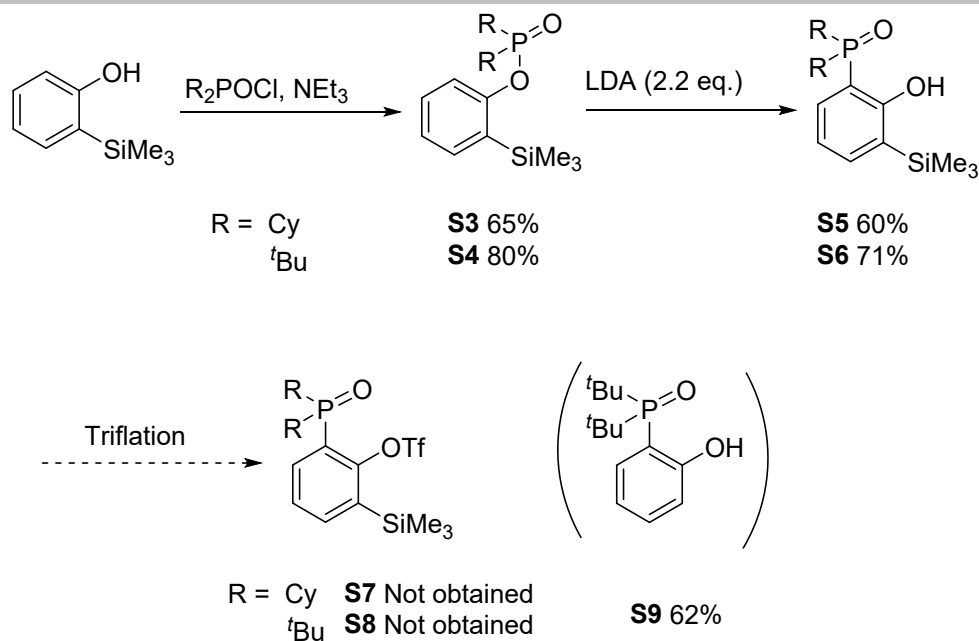
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.72 – 7.63 (m, 4H, CH-Ar), 7.55 – 7.51 (m, 2H, CH-Ar), 7.47 – 7.42 (m, 4H, CH-Ar), 7.04 – 6.91 (m, 7H, CH-Ar), 2.28 (s, 3H, CH<sub>3</sub>), 2.26 (s, 3H, CH<sub>3</sub>).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 144.37 (d, *J* = 15.3 Hz), 139.73 (d, *J* = 13.7 Hz), 139.38, 133.71, 133.25, 132.19 (d, *J* = 9.8 Hz), 131.92 (d, *J* = 1.7 Hz), 131.70, 129.97, 128.52 (d, *J* = 12.0 Hz), 124.03 (d, *J* = 9.6 Hz), 119.84, 119.57, 117.14 (d, *J* = 11.5 Hz), 21.65, 20.81.

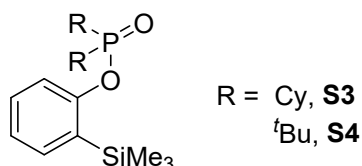
**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 30.44.

**HRMS (ESI<sup>+</sup>)**: *m/z* calcd for C<sub>26</sub>H<sub>25</sub>NOP<sup>+</sup>, [M+H]<sup>+</sup>: 398.1669, found: 398.1665.

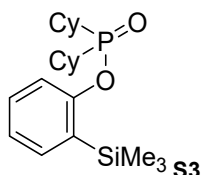
## SUPPORTING INFORMATION



Scheme S2, Attempt to synthesize 3-phosphorus functionalized benzyne precursor **S7** and **S8**.



To a dichloromethane (15.0 mL) solution of 2-(trimethylsilyl)phenol (2.49 g, 15.0 mmol, 1.0 eq.) was added triethylamine (2.5 mL, 30.0 mmol, 1.2 eq.) and DMAP (0.37 g, 0.3 mmol, 0.2 eq.). Then  $\text{R}_2\text{POCl}$  ( $\text{R} = \text{Cy}; \text{tBu}$ ) (18.0 mmol, 1.2 eq.) was added dropwise at 0 °C. The resulting suspension was stirred at room temperature for 8.0 hours. After that, the resulting reaction mixture was poured into brine solution (20.0 mL) and subsequently extracted three times by ethyl acetate (30.0 mL). The combined organic phases were dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was purified through chromatography on a silica gel plug (eluent: petrol ether/ethyl acetate = 5/1), giving **S3** (colorless oil, 3.69 g, 65% yield) and **S4** (colorless oil, 3.92 g, 65% yield) respectively.

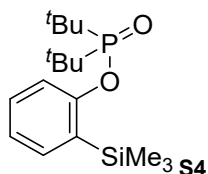


**$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (d,  $J = 8.4$  Hz, 1H, CH-Ar), 7.37 – 7.32 (m, 1H, CH-Ar), 7.27 – 7.23 (m, 1H, CH-Ar), 7.02 (td,  $J = 7.3, 0.8$  Hz, 1H, CH-Ar), 2.04 – 1.77 (m, 9H, Cy-H), 1.68 (s, 2H, Cy-H), 1.55 – 1.43 (m, 4H, Cy-H), 1.22 – 1.17 (m, 6H, Cy-H), 1.06 (t,  $J = 7.1$  Hz, 1H, Cy-H), 0.29 (s, 9H,  $\text{CH}_3$ ).

**$^{13}\text{C}\{\text{H}\}$  NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.31 (d,  $J = 9.6$  Hz), 135.42, 131.00, 128.24 (d,  $J = 7.7$  Hz), 123.04, 118.67 (d,  $J = 2.4$  Hz), 39.36 (d,  $J = 4.6$  Hz), 37.55, 36.68, 26.35 (d,  $J = 14.0$  Hz), 25.73 (d,  $J = 30.1$  Hz), 25.55, 25.51, 13.87 (d,  $J = 2.2$  Hz), -0.32.

**$^{31}\text{P NMR}$**  (162 MHz,  $\text{CDCl}_3$ )  $\delta$  60.32.

**HRMS (ESI $^+$ )**:  $m/z$  calcd for  $\text{C}_{21}\text{H}_{35}\text{O}_2\text{PSi}^+$ ,  $[\text{M}+\text{H}]^+$ : 378.2144, found: 378.2147.



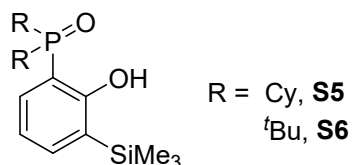
**$^1\text{H NMR}$**  (400 MHz, )  $\delta$  8.22 (d,  $J = 8.5$  Hz, 1H, Ar-CH), 7.37 (dd,  $J = 7.8, 2.2$  Hz, 1H, Ar-CH), 7.24 (ddd,  $J = 8.9, 5.1, 1.9$  Hz, 1H, Ar-CH), 6.99 (td,  $J = 7.3, 0.9$  Hz, 1H, Ar-CH), 1.32 (d,  $J = 14.8$  Hz, 18H,  $\text{CH}_3$ ), 0.32 (s, Si- $\text{CH}_3$ ).

**$^{13}\text{C}\{\text{H}\}$  NMR** (100 MHz, )  $\delta$  160.78 (d,  $J = 9.5$  Hz), 135.58, 131.00, 127.65 (d,  $J = 7.5$  Hz), 122.78, 119.36, 37.91 (d,  $J = 80.5$  Hz), 26.88, 0.27.

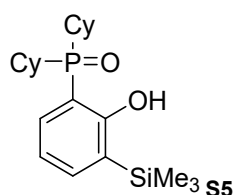
**$^{31}\text{P NMR}$**  (162 MHz, )  $\delta$  69.43.

**HRMS (ESI $^+$ )**:  $m/z$  calcd for  $\text{C}_{17}\text{H}_{32}\text{OPSi}^+$ ,  $[\text{M}+\text{H}]^+$ : 327.1904, found: 327.1914.

## SUPPORTING INFORMATION



To a solution of **S3** or **S4** (3.0 mmol, 1.0 eq.) in anhydrous tetrahydrofuran (10.0 mL) was added LDA (lithium diisopropylamide, 6.6 mmol, 2.2 eq.) at -80 °C. The mixture was stirred at room temperature for 10 hours. Then the reaction was quenched with aqueous sodium bicarbonate. After that, the resulting reaction mixture was poured into brine solution (10.0 mL) and extracted three times with ethyl acetate (30.0 mL). The combined organic phases were dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was purified through chromatography on a silica gel plug (eluent: petrol ether/ethyl acetate = 10/1), giving **S5** (white solid, 0.68 g, 60% yield) and **S6** (white solid, 0.70 g, 71% yield) respectively..



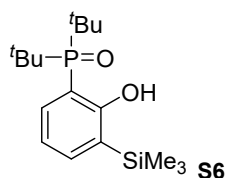
**M.p. (°C):** 53.6 – 54.8.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 11.45 (s, 1H, OH), 7.48 – 7.46 (m, 1H, CH-Ar), 7.00 – 6.95 (m, 1H, CH-Ar), 6.82 (td, *J* = 7.4, 2.5 Hz, 1H, CH-Ar), 2.06 – 1.97 (m, 4H, Cy-H), 1.86 – 1.77 (m, 4H, Cy-H), 1.69 (d, *J* = 10.8, 4H, Cy-H), 1.41 – 1.11 (m, 10H, Cy-H), 0.28 (s, 9H, CH<sub>3</sub>).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 170.05, 139.27, 130.85 (d, *J* = 9.5 Hz), 128.85 (d, *J* = 3.8 Hz), 118.14 (d, *J* = 10.4 Hz), 106.90 (d, *J* = 85.2 Hz), 36.12, 35.46, 26.47, 26.36 (d, *J* = 1.4 Hz), 26.24, 25.81, 25.33 (d, *J* = 1.4 Hz), 24.13 (d, *J* = 2.7 Hz), -1.06.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 61.07.

**HRMS (ESI<sup>+</sup>):** *m/z* calcd for C<sub>21</sub>H<sub>36</sub>O<sub>2</sub>PSi<sup>+</sup>, [M+H]<sup>+</sup>: 379.2217, found: 379.2213.



**M.p. (°C):** 55.7 – 56.1.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 12.22 (s, 1H, OH), 7.44 (dt, *J* = 7.2, 1.6 Hz, 1H, CH-Ar), 7.27 – 7.22 (m, 1H, CH-Ar), 6.77 (td, *J* = 7.2, 2.8 Hz, 1H, CH-Ar), 1.31 (d, *J* = 14.0 Hz, 18H, CH<sub>3</sub>), 0.26 (s, 9H, CH<sub>3</sub>).

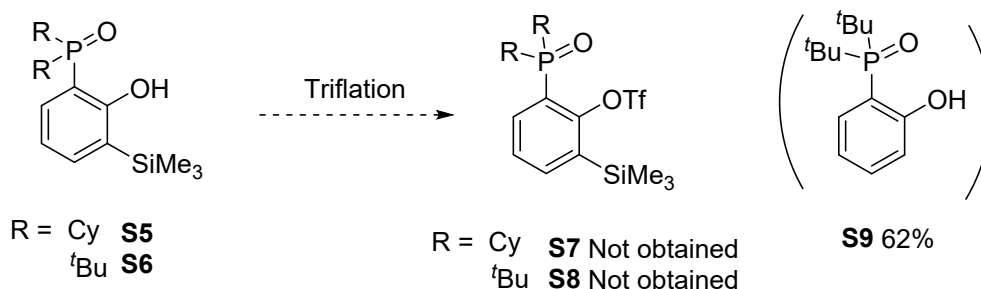
**<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 170.13, 138.97, 131.88 (d, *J* = 9.5 Hz), 129.04 (d, *J* = 3.8 Hz), 117.24 (d, *J* = 10.3 Hz), 107.87 (d, *J* = 79.2 Hz), 37.11 (d, *J* = 58.1 Hz), 26.75 (s), -1.03 (s).

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 68.625.

**HRMS (ESI<sup>+</sup>):** *m/z* calcd for C<sub>17</sub>H<sub>32</sub>O<sub>2</sub>PSi<sup>+</sup>, [M+H]<sup>+</sup>: 327.1904, found: 327.1908.

Various methods had been tried to get triflation products **S7** and **S8** from substrates **S5** and **S6** respectively (Table S1), no desired products were obtained for the potentially high steric-hindrance environment around the OH group. In different reaction conditions starting materials **S5** and **S6** were always detected, and sometimes unknown compounds were generated. Meanwhile, unexpected compound **9** was isolated in entries 4 and 5, because the brook rearrangement reaction probably occurred.

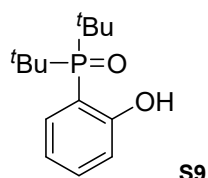
Table S1, Screening reaction conditions to synthesize **S7** and **S8**.



## SUPPORTING INFORMATION

Entry	Reaction condition	Reference	Results
1	Pyridine, Tf <sub>2</sub> O, DCM	<i>J. Am. Chem. Soc.</i> <b>2021</b> , <i>143</i> , 513–523	<b>S5</b> and <b>S6</b> were intact. No <b>S7</b> and <b>S8</b> were obtained.
2	NEt <sub>3</sub> , Tf <sub>2</sub> O, DCM	<i>Org. Lett.</i> <b>2002</b> , <i>4</i> , 4717–4718	<b>S5</b> and <b>S6</b> were intact. No <b>S7</b> and <b>S8</b> were obtained.
3	NEt <sub>3</sub> , Tf <sub>2</sub> O, CH <sub>3</sub> CN	<i>Angew. Chem. Int. Ed.</i> <b>2018</b> , <i>57</i> , 2605–2610	<b>S5</b> and <b>S6</b> were intact. No <b>S7</b> and <b>S8</b> were obtained.
4	NaH, Tf <sub>2</sub> O, Et <sub>2</sub> O	<i>RSC Adv.</i> , <b>2013</b> , <i>3</i> , 21331-21334	Less than 20% <b>S5</b> and <b>S6</b> were observed. No <b>S7</b> and <b>S8</b> were obtained. <b>S9</b> was isolated in 62%.
5	n-BuLi, Tf <sub>2</sub> O, Et <sub>2</sub> O	<i>Synlett</i> , <b>2014</b> ; <i>25</i> , 2488-2492	Less than 20% <b>S5</b> and <b>S6</b> were observed. No <b>S7</b> and <b>S8</b> were obtained. <b>S9</b> was isolated in 62%.
6	NEt <sub>3</sub> , CF <sub>3</sub> SO <sub>2</sub> Cl, DCM	<i>Chem. Commun.</i> , <b>2017</b> , <i>53</i> , 11584-11587	<b>S5</b> and <b>S6</b> were intact. No <b>S7</b> and <b>S8</b> were obtained.
7	n-BuLi, CF <sub>3</sub> SO <sub>2</sub> Cl, Et <sub>2</sub> O	<i>Chem. Commun.</i> , <b>2017</b> , <i>53</i> , 11584-11587	<b>S5</b> and <b>S6</b> were intact. No <b>S7</b> and <b>S8</b> were obtained.
8	DIPEA, PhNTf <sub>2</sub>	<i>Org. Lett.</i> <b>2000</b> , <i>2</i> , 477-480.	<b>S5</b> and <b>S6</b> were intact. No <b>S7</b> and <b>S8</b> were obtained.

## SUPPORTING INFORMATION



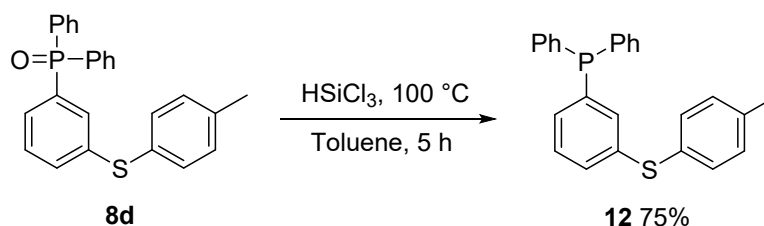
Colorless oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 12.33 (br, 1H, OH), 7.41 – 7.31 (m, 1H, CH-Ar), 7.29 – 7.21 (m, 1H, CH-Ar), 6.88 (ddd, *J* = 8.4, 3.6, 0.8 Hz, 1H, CH-Ar), 6.83 – 6.76 (m, 1H, CH-Ar), 1.34 (d, *J* = 12 Hz, 18H, CH<sub>3</sub>).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 165.53, 133.58 (d, *J* = 1.4 Hz), 130.69 (d, *J* = 9.0 Hz), 118.81 (d, *J* = 6.3 Hz), 117.87 (d, *J* = 10.7 Hz), 109.33 (d, *J* = 80.1 Hz), 37.18 (d, *J* = 58.0 Hz), 26.67.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 69.03.

**HRMS (ESI<sup>+</sup>):** *m/z* calcd for C<sub>14</sub>H<sub>24</sub>O<sub>2</sub>P<sup>+</sup>, [M+H]<sup>+</sup>: 255.1509, found: 255.1504.



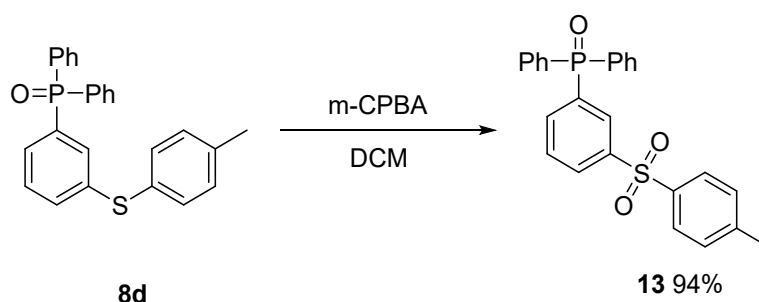
According to the literature,<sup>[3]</sup> a modified method was carried out. In a high-pressure reaction vessel, **8d** (95.3 mg, 0.238 mmol, 1.0 eq.) was dispersed in toluene (dry, 3 mL) and trichlorosilane (0.18 mL, 1.78 mmol, 7.5 eq.) was added. The vessel was sealed and upon heating to 100 °C and the solid was dissolved completely. The reaction was carried out at 100 °C for 5 hours until judged complete by TLC analysis. The solvent and residual reagents were removed under reduced pressure. The residue was purified through chromatography on a silica gel plug (CH<sub>2</sub>Cl<sub>2</sub>). Removal of the solvent in vacuum afforded target compound **12** (68.7 mg, 75%) as light yellow oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.37 – 7.27 (m, 12H, CH-Ar), 7.24 – 7.18 (m, 3H, CH-Ar), 7.17 – 7.09 (m, 3H, CH-Ar), 2.37 (s, 3H, CH<sub>3</sub>).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 138.61 (d, *J* = 13.2 Hz), 138.32 (d, *J* = 6.5 Hz), 138.02, 136.80 (d, *J* = 10.8 Hz), 133.95, 133.76, 132.97, 131.59, 131.39, 130.27, 129.27, 129.12 (d, *J* = 7.0 Hz), 128.92, 128.64 (d, *J* = 7.0 Hz), 21.34.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ -4.45.

**HRMS (ESI<sup>+</sup>):** *m/z* calcd for C<sub>25</sub>H<sub>22</sub>PS<sup>+</sup>, [M+H]<sup>+</sup>: 385.1175, found: 385.1179.



According to the literature,<sup>[4]</sup> a modified method was carried out. To a solution of **8d** (48.1 mg, 0.12 mmol, 1 eq.) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (2.0 mL) was slowly added *m*-chloroperbenzoic acid (72.48 mg, 0.252 mmol, 2.1 eq.) at 0 °C. After stirring for 1 hour at the same temperature, the mixture was allowed to warm to room temperature, and to this was added aqueous saturated solution of sodium bicarbonate (1 mL) and an aqueous saturated solution of sodium sulfite (1 mL). The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and the combined organic extract was washed with brine (5 mL), dried (Na<sub>2</sub>SO<sub>4</sub>), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified through chromatography on a silica gel plug (n-hexane/EtOAc = 2/1) to give **13** (49.0 mg, 94%) as light yellow oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.16 (d, *J* = 11.6 Hz, 1H, CH-Ar), 8.05 (dd, *J* = 8.0, 1.2 Hz, 1H, CH-Ar), 7.85 (dd, *J* = 11.2, 7.6 Hz, 1H, CH-Ar), 7.71 (d, *J* = 8.4 Hz, 2H, CH-Ar), 7.63 – 7.53 (m, 7H, CH-Ar), 7.47 – 7.43 (m, 4H, CH-Ar), 7.24 (d, *J* = 8.4 Hz, 2H, CH-Ar), 2.36 (s, 3H, CH<sub>3</sub>).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 144.76, 142.86 (d, *J* = 12.0 Hz), 137.82, 136.40 (d, *J* = 9.7 Hz), 134.99 (d, *J* = 100.9 Hz), 132.61 (d, *J* = 2.4 Hz), 132.10 (d, *J* = 10.0 Hz), 131.71, 130.93 (d, *J* = 11.3 Hz), 130.73 (d, *J* = 1.8 Hz), 130.66, 130.17, 129.70 (d, *J* = 11.5 Hz), 128.88 (d, *J* = 12.4 Hz), 127.93, 21.70.

**<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 28.97.

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**HRMS (ESI<sup>+</sup>):** *m/z* calcd for C<sub>25</sub>H<sub>22</sub>O<sub>3</sub>PS<sup>+</sup>, [M+H]<sup>+</sup>: 433.1022, found: 433.1028.

### 5. Crystallographic data:

X-ray data collection and structural refinement. Intensity data for compounds **5**, **8a** and **9f** were collected using a Bruker APEX II diffractometer. The crystals were measured at 150 K. The structure was solved by direct phase determination (SHELX-2013) and refined for all data by full-matrix least squares methods on *F*<sup>2</sup>. All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride in their respective parent atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations. CCDC; 2155866-2155868 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallography Data Center via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Table S2.** X-ray data.

Compound Formula	<b>5</b> C <sub>22</sub> H <sub>22</sub> F <sub>3</sub> O <sub>4</sub> PSSi <sub>2</sub>	<b>8a</b> C <sub>25</sub> H <sub>22</sub> NOP	<b>9f</b> C <sub>21</sub> H <sub>31</sub> BrN <sub>5</sub> O <sub>2</sub> P
CCDC	2155867	2155866	2155868
Fw	498.51	383.40	496.38
Cryst syst	monoclinic	monoclinic	monoclinic
Space size	P 21/n	P 21/n	P 21/n
Size (mm <sup>3</sup> )	0.070 x 0.070 x 0.090	0.080x0.07x0.05	0.120x0.100x0.070
T, K	150	302	150
<i>a</i> , Å	12.443(3)	12.647(11)	16.2044(5)
<i>b</i> , Å	11.957(2)	b=12.361(9)	28.6736(9)
<i>c</i> , Å	17.315(4)	c=13.858(11)	21.3349(7)
$\alpha$ , deg	90	90	90
$\beta$ , deg	109.966(1)	107.269(3)	107.471(1)
$\gamma$ , deg	90	90	90
V, Å <sup>3</sup>	2421.1(9)	2068.8(3)	9455.7(5)
Z	4	4	4
$d_{\text{calcd}}$ g.cm <sup>-3</sup>	1.368	1.231	1.395
$\mu$ , mm <sup>-1</sup>	0.298	0.148	3.225
Refl collected	47013	20127	140593
T <sub>min</sub> /T <sub>max</sub>	0.974/0.979	0.982/0.997	0.713/0.798
N <sub>measd</sub>	4026	2746	16716
[R <sub>int</sub> ]	0.0551	0.1048	0.0616
R [ <i>I</i> >2 $\sigma$ ( <i>I</i> )]	0.0412	0.0556	0.0308( 16716)
R <sub>w</sub> [ <i>I</i> >2 $\sigma$ ( <i>I</i> )]	0.1169	0.1198	0.0802( 18651)
GOF	1.052	1.034	1.037
Largest diff peak/hole[e.Å <sup>-3</sup> ]	0.286/-0.314	0.223/-0.238	0.86/1-1.081

## SUPPORTING INFORMATION

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### 6. Theoretical study

All the computational calculations reported in this work were performed using the Gaussian 09 code.<sup>[5-6]</sup> The geometries for the ground state of these compounds were optimized at the B3LYP hybrid functional and 6-311G\* basis set for all atoms. The frequency calculations confirmed the nature of all revealed equilibrium geometries: there were no imaginary frequencies.

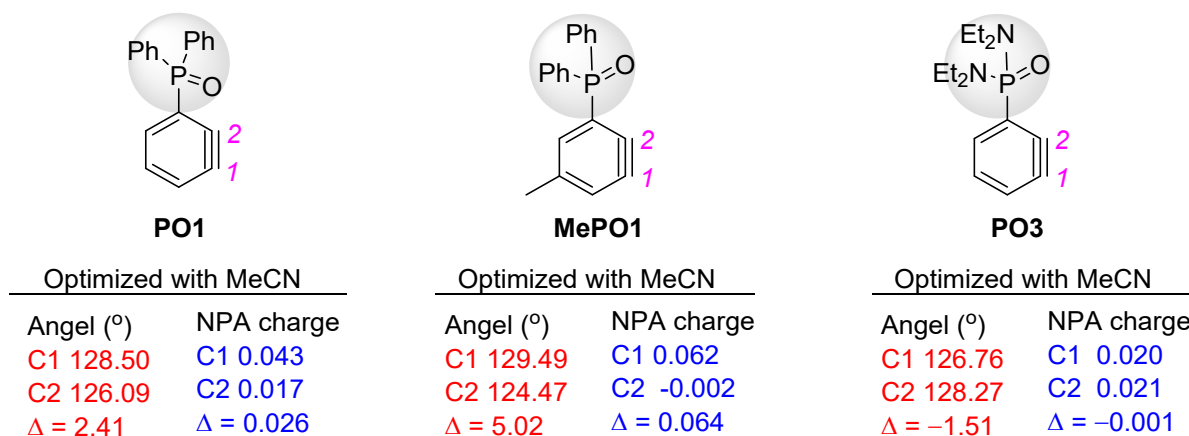
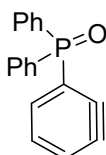


Figure S2. Distortion angle and NPA charges of optimized structures for **PO1** **MePO1** and **PO2** in the solvent of acetonitrile via DFT calculation at B3LYP/6-311G\*level of theory ( $\Delta = C1-C2$ ).



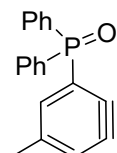
#### PO1 (In MeCN):

Zero-point correction=	0.252072 (Hartree/Particle)
Thermal correction to Energy=	0.269093
Thermal correction to Enthalpy=	0.270038
Thermal correction to Gibbs Free Energy=	0.204132
Sum of electronic and zero-point Energies=	-1110.165447
Sum of electronic and thermal Energies=	-1110.148426
Sum of electronic and thermal Enthalpies=	-1110.147481
Sum of electronic and thermal Free Energies=	-1110.213387

C	3.04454	2.80011	0.52326
C	3.40353	2.83975	-0.84028
C	2.62851	1.95617	-1.56821
C	1.73308	1.20956	-1.13611
C	1.29389	1.09386	0.17389
C	2.0318	1.96153	1.01365
P	0.00452	0.00856	0.88821
O	0.04971	0.00167	2.38583
C	-1.59714	0.59201	0.22082
C	0.31375	-1.64315	0.16367
C	-1.75189	1.20215	-1.02947
C	-3.0143	1.60472	-1.45977
C	-4.1271	1.40723	-0.6448
C	-3.97644	0.81214	0.60642
C	-2.71725	0.40776	1.04098
C	0.84833	-2.61651	1.01457
C	1.12962	-3.89084	0.52722
C	0.87946	-4.19944	-0.80806
C	0.34051	-3.23411	-1.65767
C	0.05457	-1.96024	-1.17466
H	3.57733	3.44106	1.21958
H	4.18699	3.48544	-1.21756

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H	1.79917	1.95449	2.07403
H	-0.89138	1.38472	-1.6641
H	-3.12603	2.08134	-2.42834
H	-5.10895	1.725	-0.98087
H	-4.83926	0.66866	1.24878
H	-2.59014	-0.03514	2.02265
H	1.02918	-2.36775	2.05444
H	1.54172	-4.64309	1.1921
H	1.09849	-5.19279	-1.18666
H	0.13622	-3.47533	-2.69588
H	-0.38361	-1.22464	-1.84066

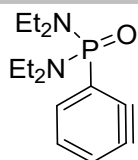


### MePO1 (In MeCN):

Zero-point correction=	0.279551 (Hartree/Particle)
Thermal correction to Energy=	0.298403
Thermal correction to Enthalpy=	0.299347
Thermal correction to Gibbs Free Energy=	0.229525
Sum of electronic and zero-point Energies=	-1149.462935
Sum of electronic and thermal Energies=	-1149.444083
Sum of electronic and thermal Enthalpies=	-1149.443139
Sum of electronic and thermal Free Energies=	-1149.512961

C	1.41548	-0.09475	-0.05604
C	2.61684	0.06769	0.66532
C	3.89512	0.00059	0.07116
C	4.03217	-0.24118	-1.31598
C	2.80168	-0.38841	-1.92482
C	1.677	-0.3322	-1.40011
P	-0.18868	-0.00832	0.82064
C	5.12995	0.18189	0.92627
O	-0.01804	-0.03174	2.3094
C	-1.15963	-1.42998	0.20002
C	-1.40818	-2.46894	1.10315
C	-2.12892	-3.58972	0.69643
C	-2.60318	-3.67935	-0.61021
C	-2.36192	-2.64352	-1.51205
C	-1.64565	-1.52	-1.1094
C	-1.02933	1.50508	0.22326
C	-1.88453	2.14149	1.13144
C	-2.57653	3.28919	0.75469
C	-2.41726	3.8132	-0.52681
C	-1.55748	3.19189	-1.43035
C	-0.86232	2.0434	-1.05811
H	2.53491	0.24098	1.7347
H	5.0037	-0.29961	-1.79275
H	5.13218	1.15855	1.41834
H	5.183	-0.57716	1.71182
H	6.04212	0.10792	0.33109
H	-1.04125	-2.38374	2.12002
H	-2.32158	-4.39154	1.402
H	-3.16489	-4.55277	-0.92601
H	-2.73701	-2.70794	-2.52839
H	-1.48047	-0.71343	-1.8156
H	-1.98791	1.74097	2.13388
H	-3.23573	3.77786	1.4649
H	-2.95538	4.70952	-0.81847
H	-1.4197	3.60586	-2.42408
H	-0.17741	1.58514	-1.76339

## SUPPORTING INFORMATION



### PO2 (In MeCN):

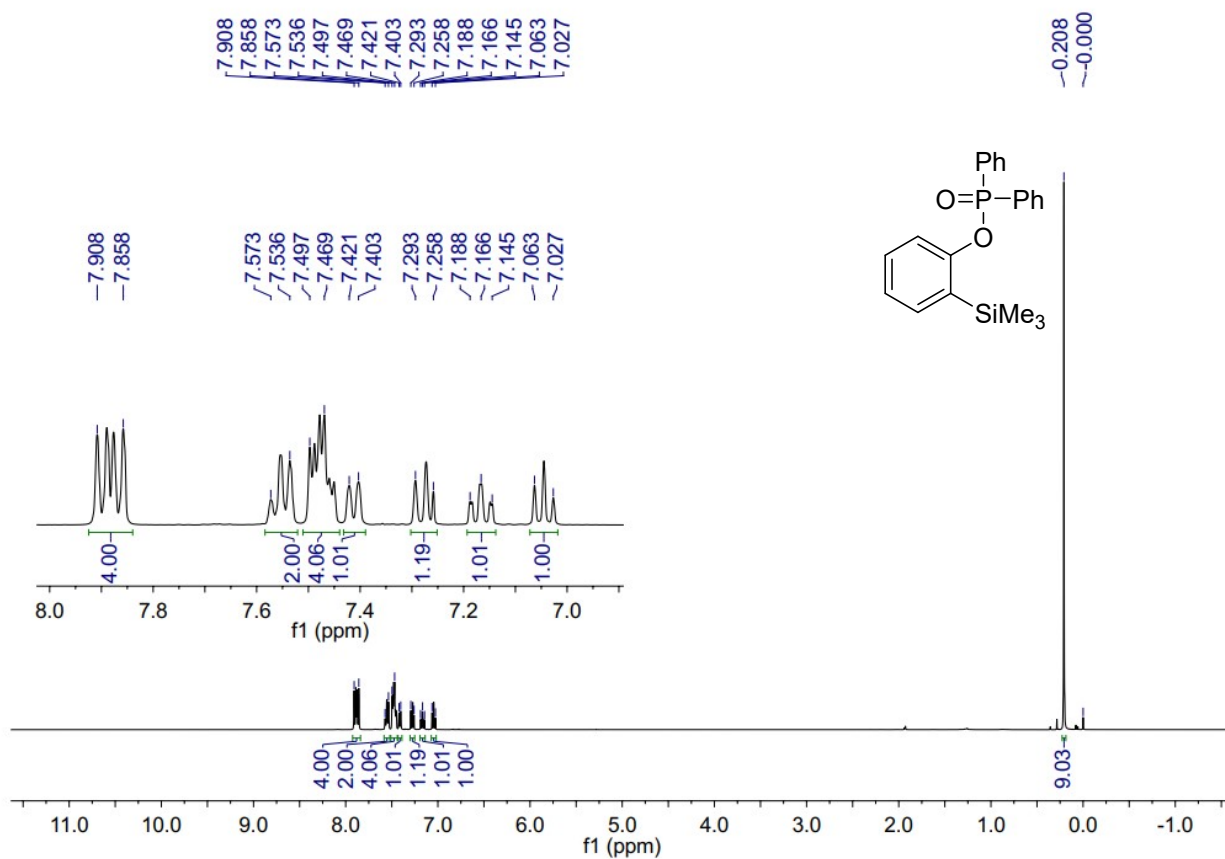
Zero-point correction=	0.350627 (Hartree/Particle)
Thermal correction to Energy=	0.371902
Thermal correction to Enthalpy=	0.372846
Thermal correction to Gibbs Free Energy=	0.299868
Sum of electronic and zero-point Energies=	-1073.180473
Sum of electronic and thermal Energies=	-1073.159198
Sum of electronic and thermal Enthalpies=	-1073.158254
Sum of electronic and thermal Free Energies=	-1073.231232

C	1.9473	0.45509	1.09911
C	3.14627	0.70484	1.31255
C	4.09495	1.01972	0.35331
C	3.51918	1.0286	-0.93346
C	2.1612	0.7496	-1.15604
C	1.2635	0.43637	-0.10604
P	-0.47163	-0.01262	-0.47139
O	-0.7244	0.07133	-1.94145
N	-0.7378	-1.57284	0.09237
N	-1.35823	0.96887	0.57357
C	-2.78793	0.66405	0.7616
C	-0.93547	2.34771	0.88938
C	-3.7542	1.35099	-0.2084
C	-0.87514	3.33401	-0.28227
C	-1.03421	-2.64584	-0.87501
C	-0.67298	-1.92872	1.5137
C	0.18601	-3.26051	-1.56448
C	0.47196	-2.86711	1.90389
H	5.14245	1.23825	0.52266
H	4.15151	1.26309	-1.78494
H	1.76112	0.76811	-2.16503
H	-2.90536	-0.41778	0.67775
H	-3.04707	0.92339	1.79511
H	-1.63509	2.71463	1.64661
H	0.04153	2.31113	1.37706
H	-4.77284	0.98862	-0.03664
H	-3.76842	2.43521	-0.07464
H	-3.48247	1.13694	-1.24394
H	-0.58689	4.32464	0.0842
H	-0.13639	3.02644	-1.02489
H	-1.83493	3.42543	-0.79245
H	-1.59158	-3.41552	-0.32972
H	-1.70561	-2.24833	-1.63729
H	-0.59705	-1.00184	2.08499
H	-1.62923	-2.38732	1.80325
H	-0.12839	-4.06772	-2.23421
H	0.69936	-2.51015	-2.16852
H	0.90029	-3.67327	-0.84937
H	0.46645	-3.02756	2.98653
H	0.37648	-3.84622	1.42895
H	1.44117	-2.44646	1.62839

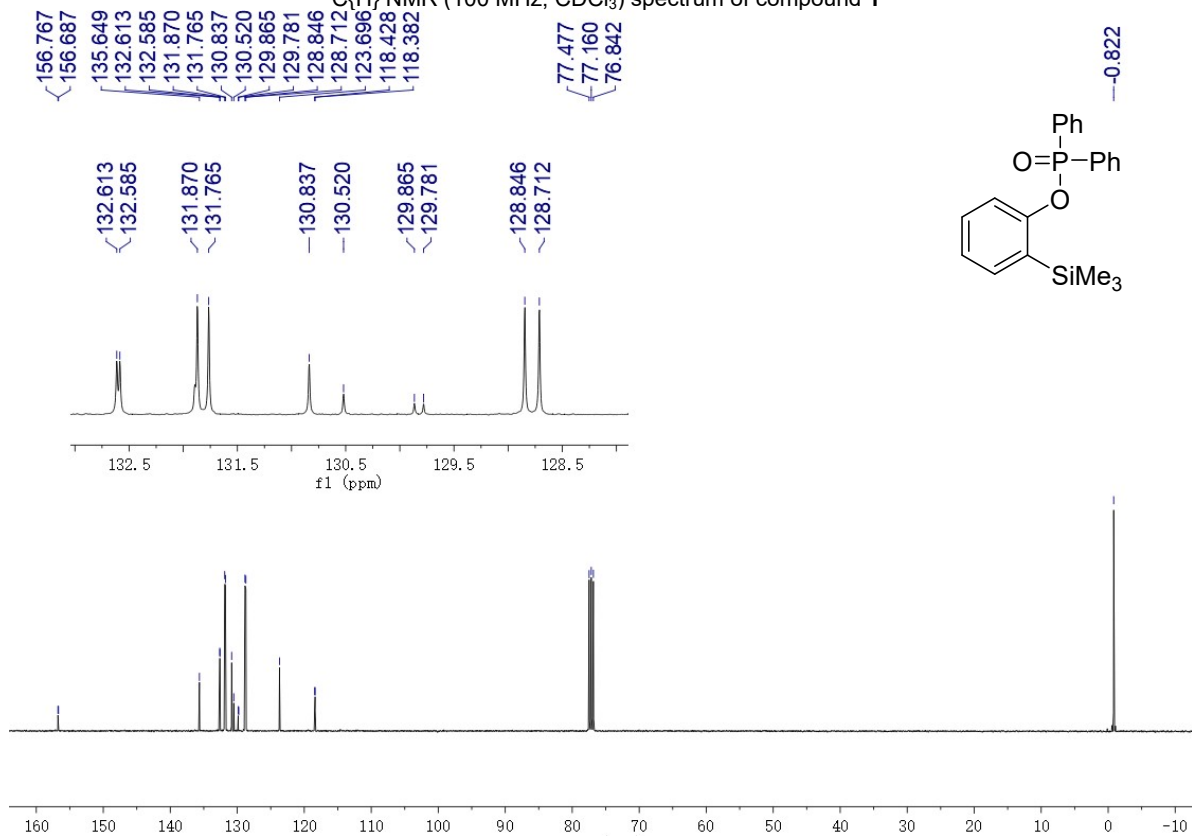
# SUPPORTING INFORMATION

## 7. NMR Spectra

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 1

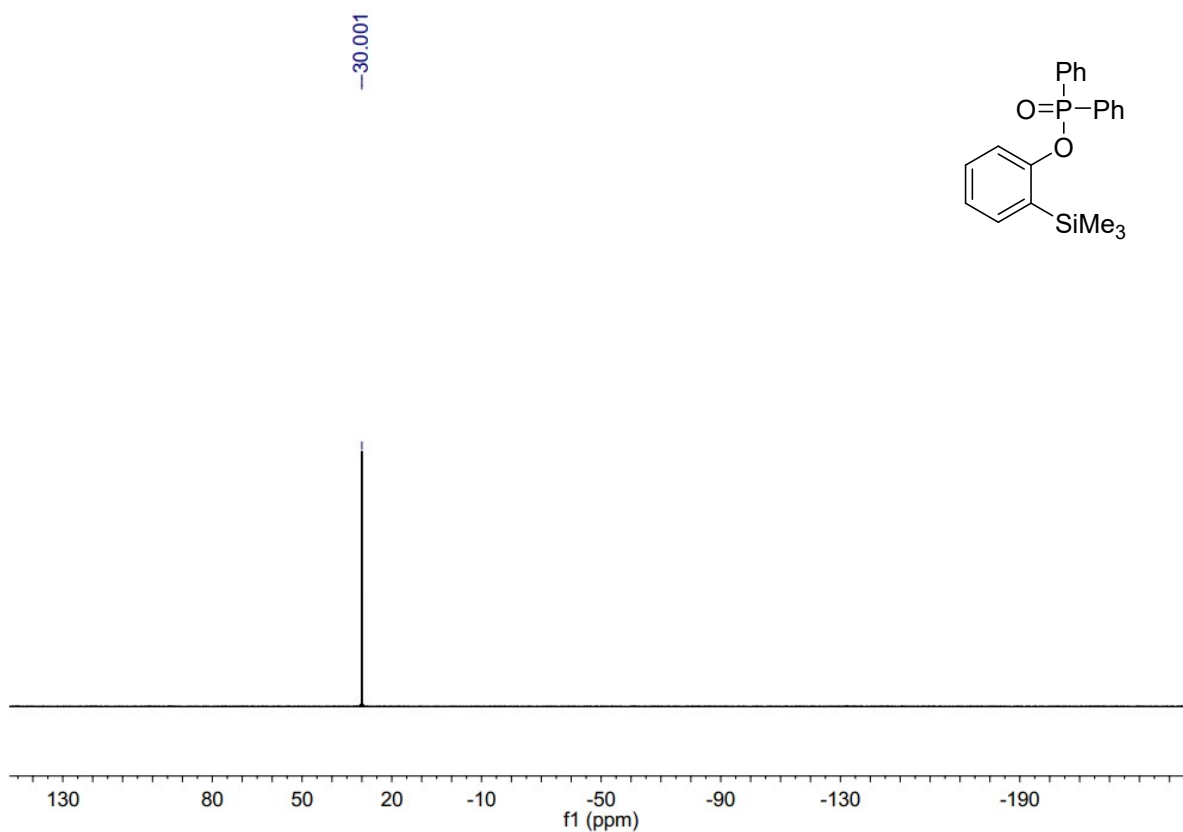


<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) spectrum of compound 1

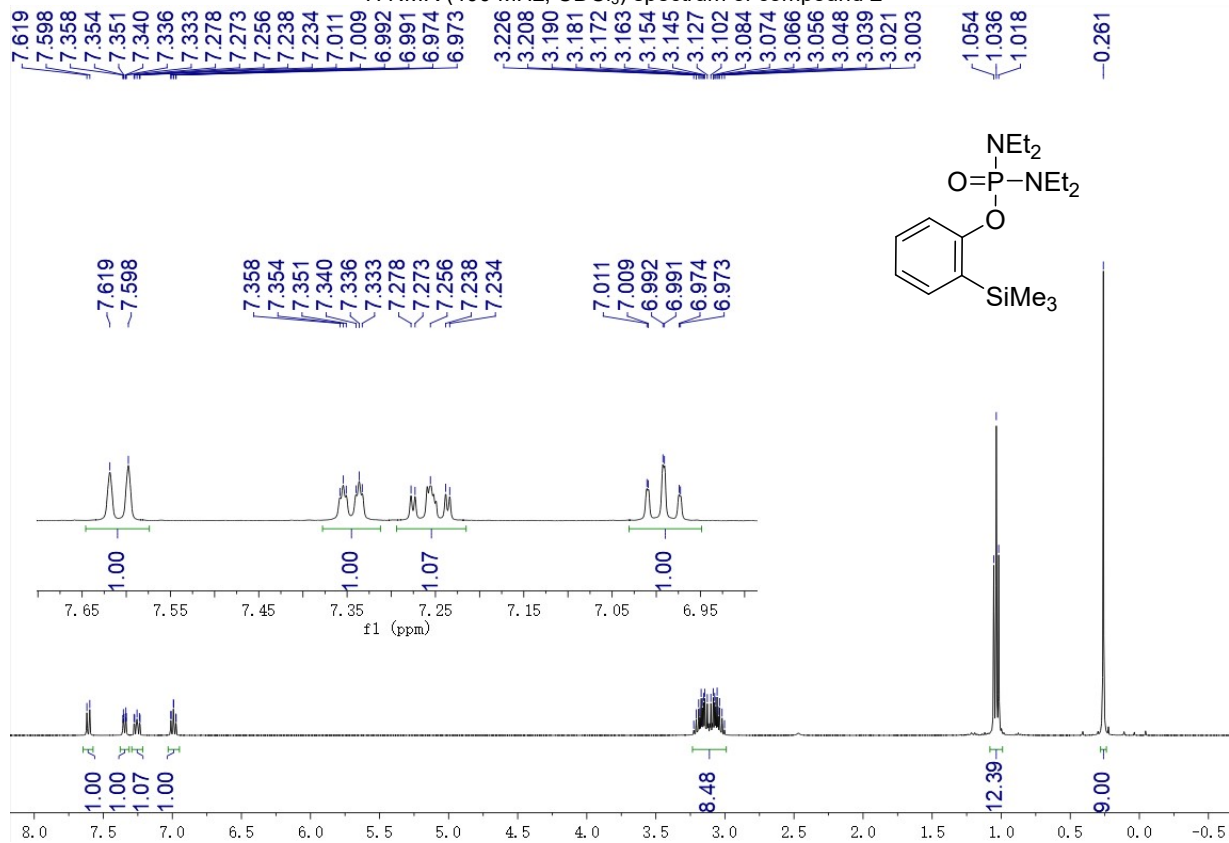


# SUPPORTING INFORMATION

<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) spectrum of compound 1

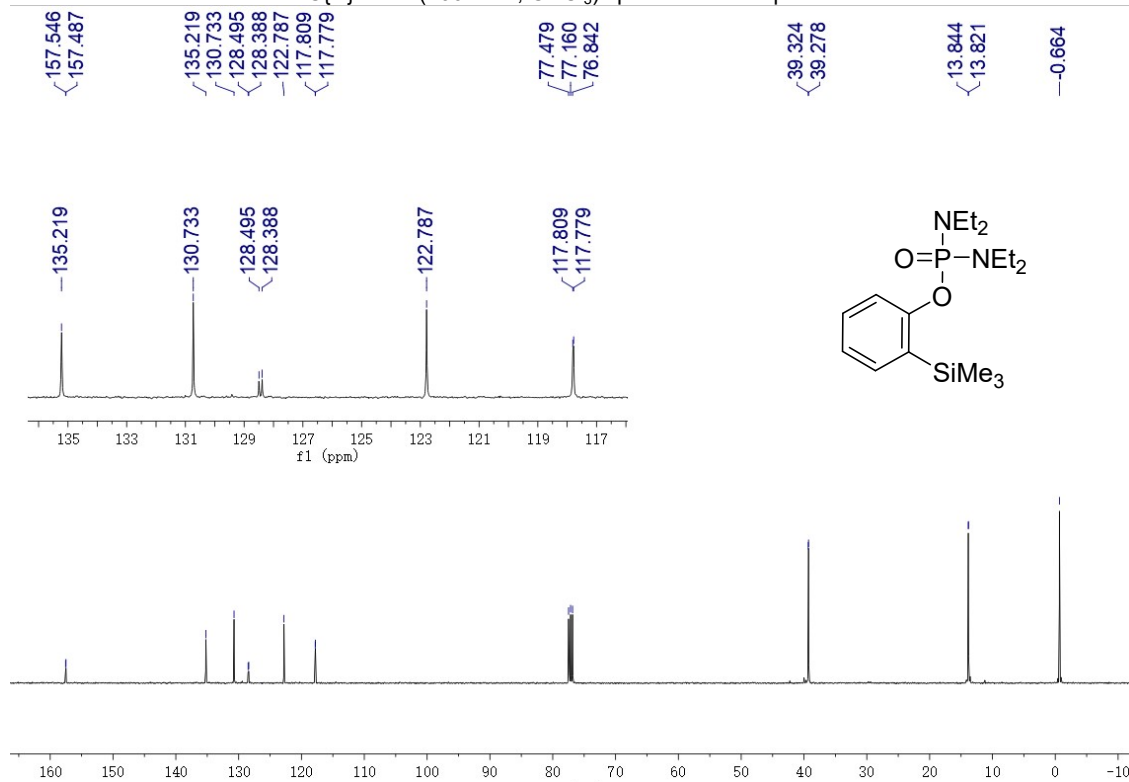


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 2

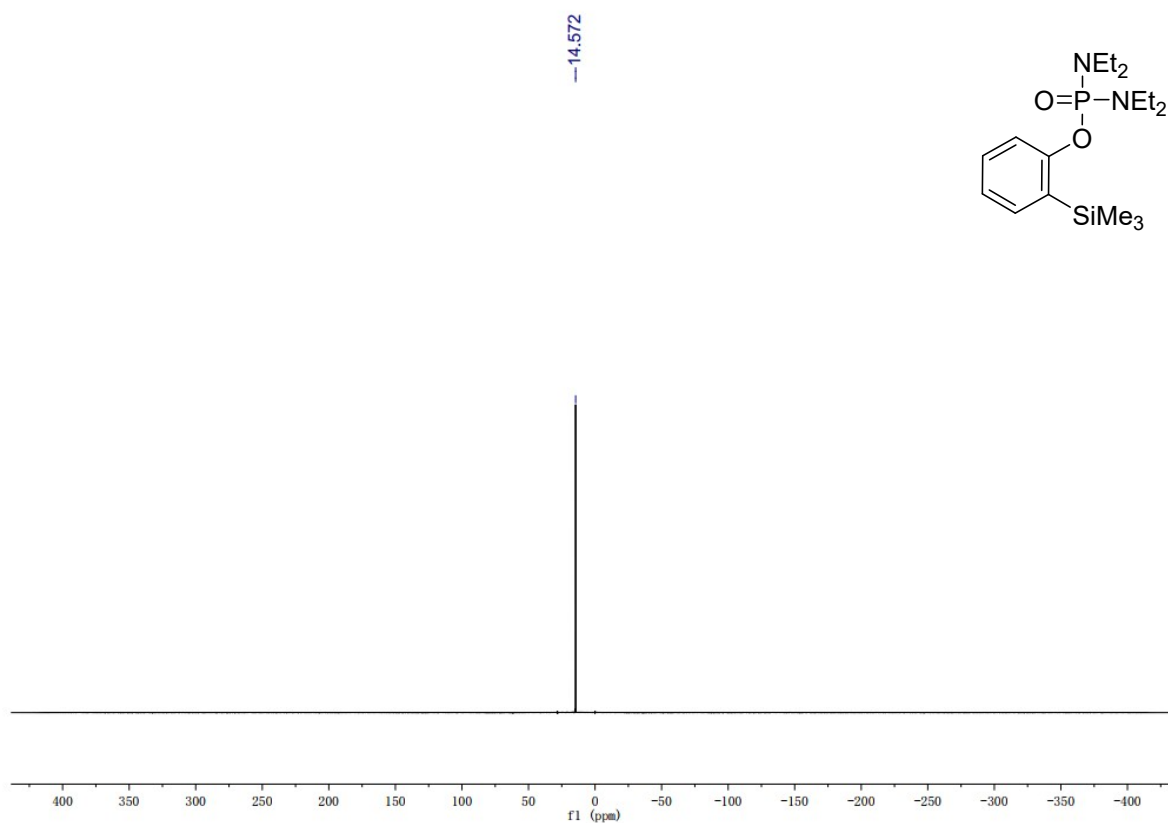


# SUPPORTING INFORMATION

$^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of compound **2**

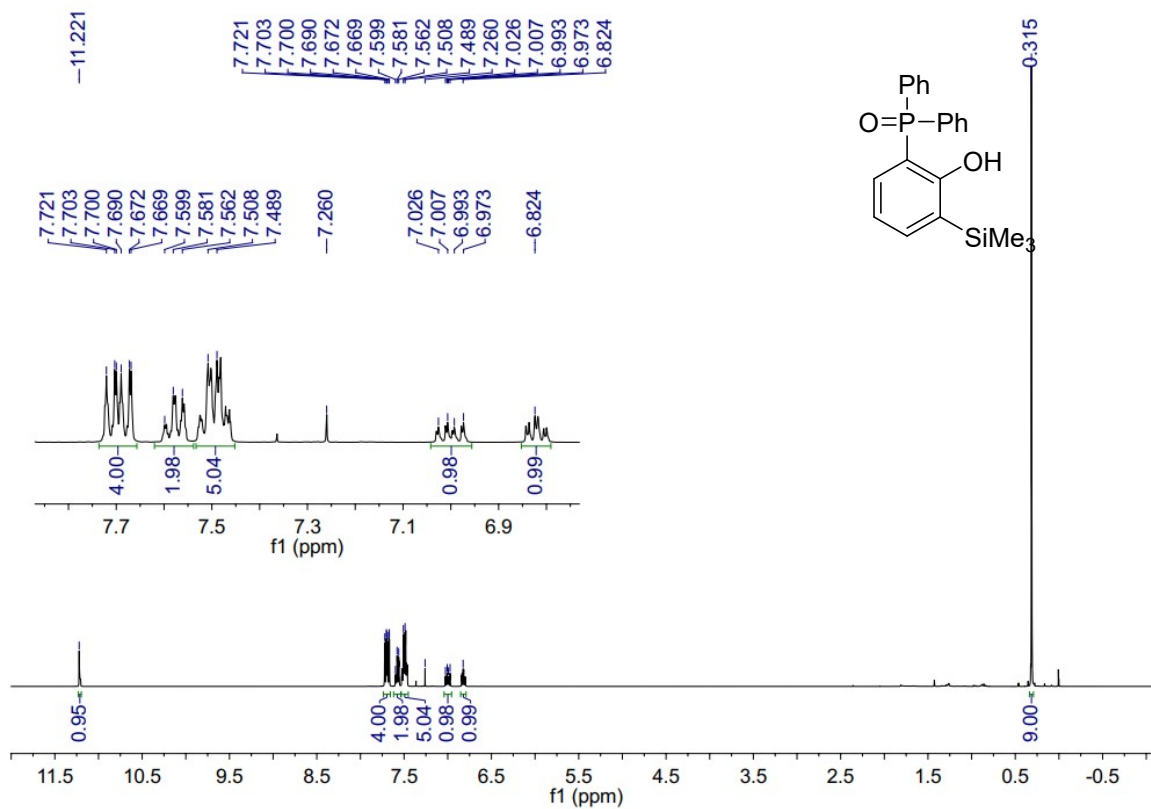


$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of compound **2**

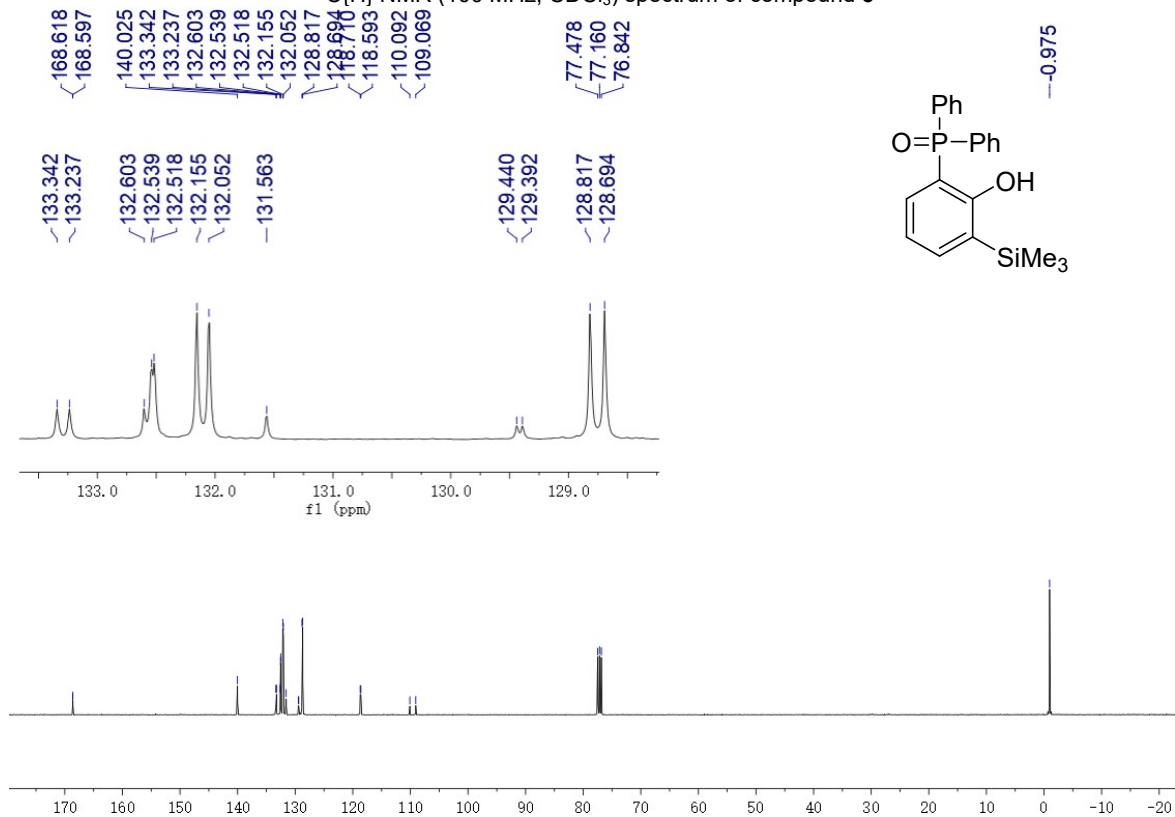


# SUPPORTING INFORMATION

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound **3**

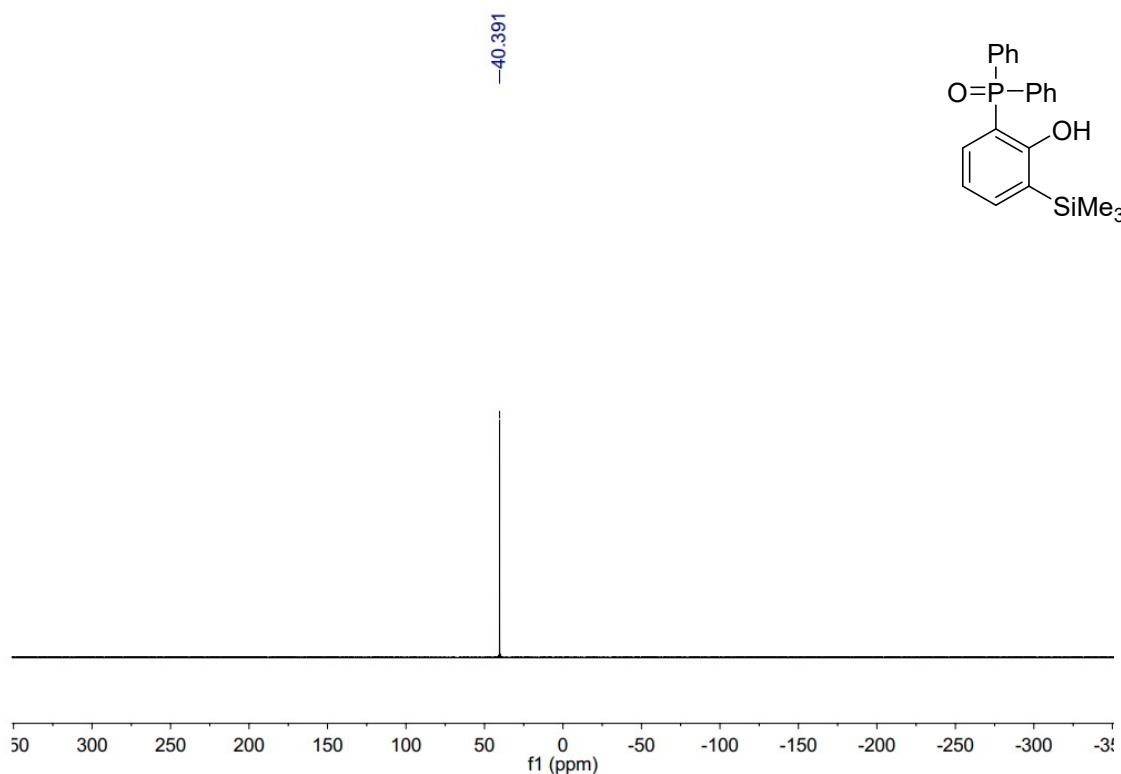


<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) spectrum of compound **3**

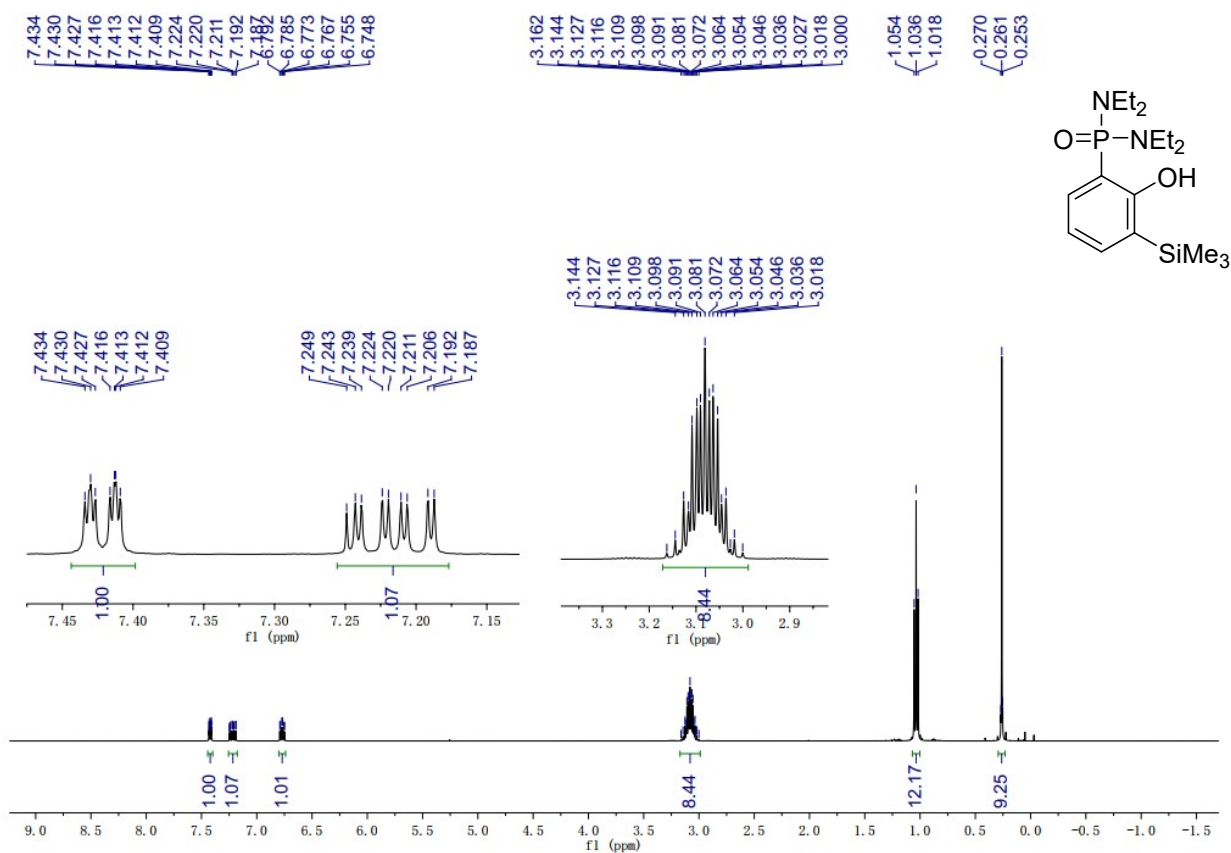


# SUPPORTING INFORMATION

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of compound **3**



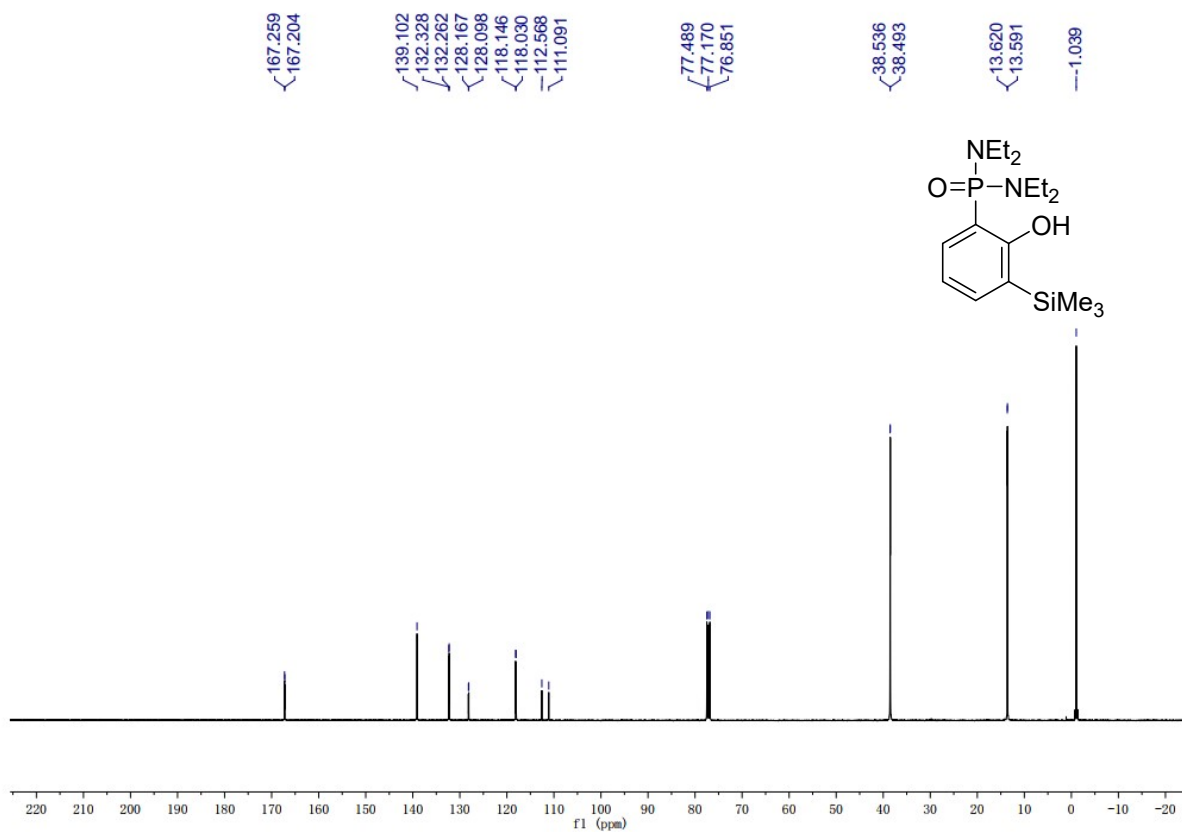
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of compound **4**



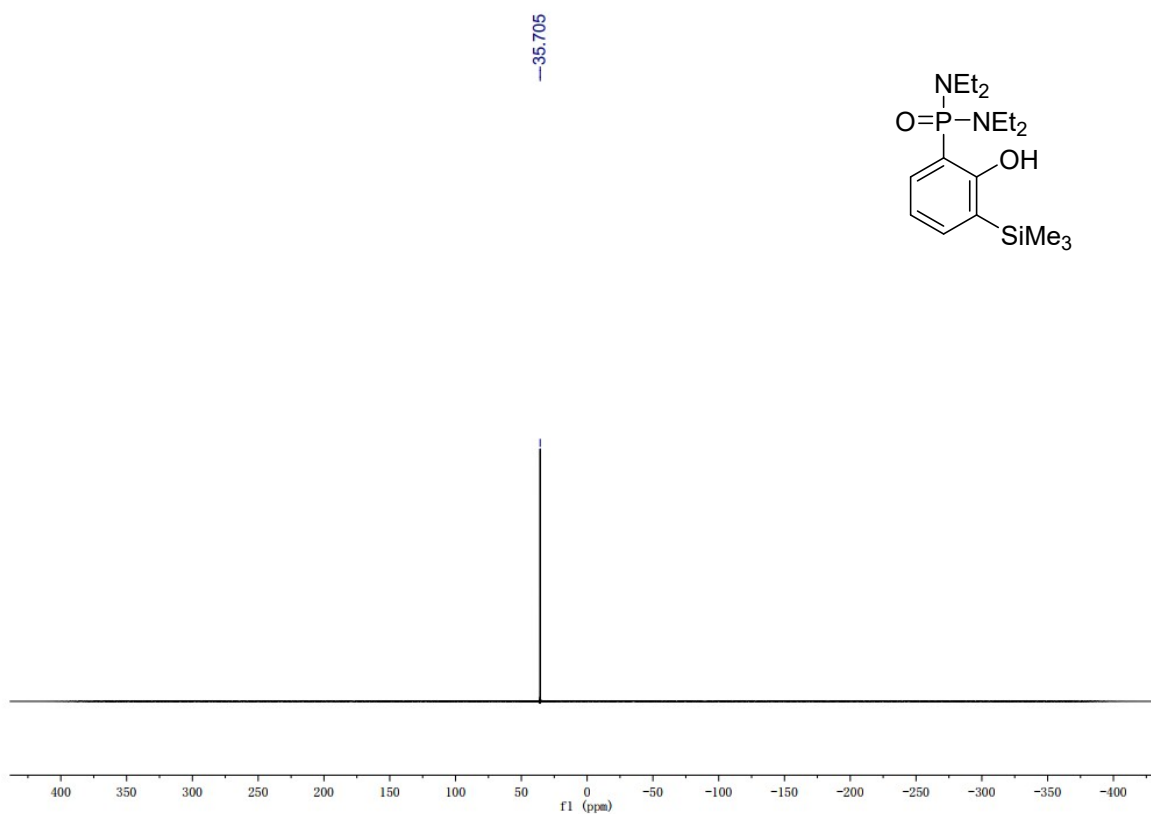


# SUPPORTING INFORMATION

$^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of compound **4**

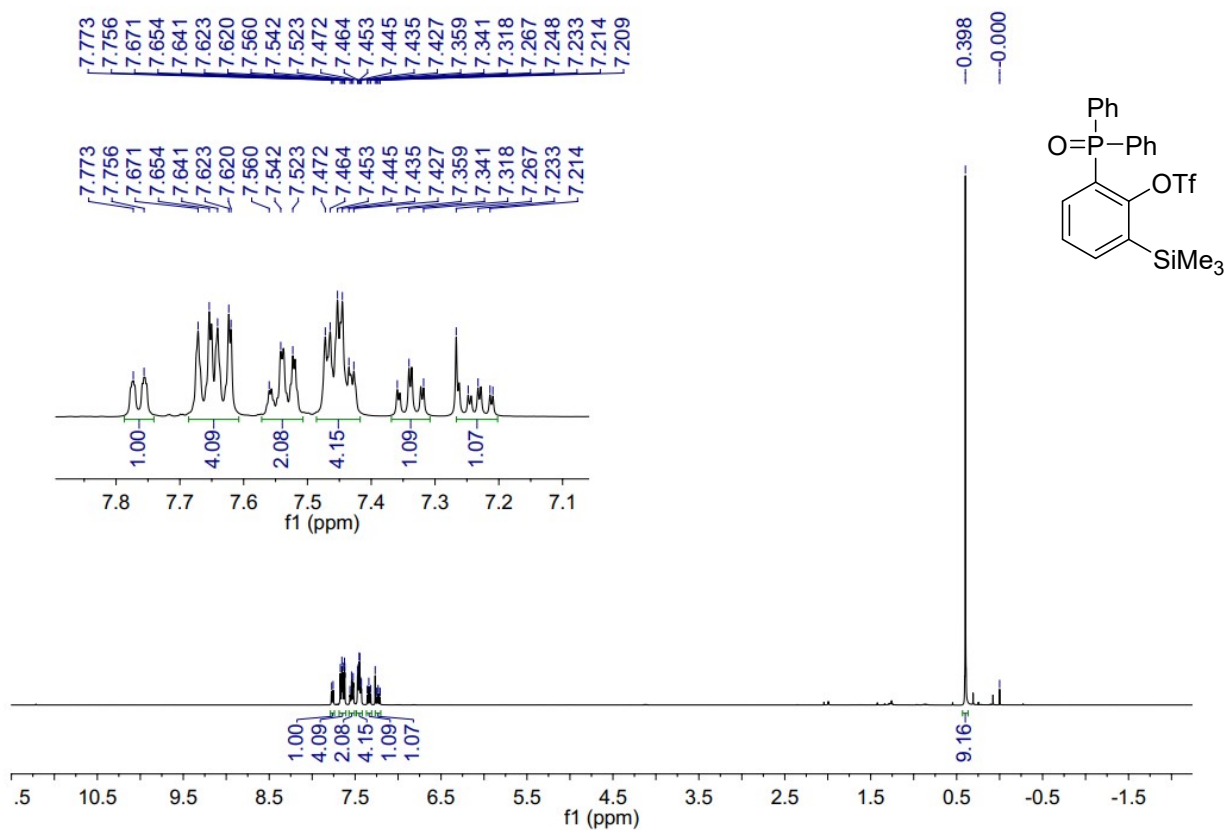


$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of compound **4**

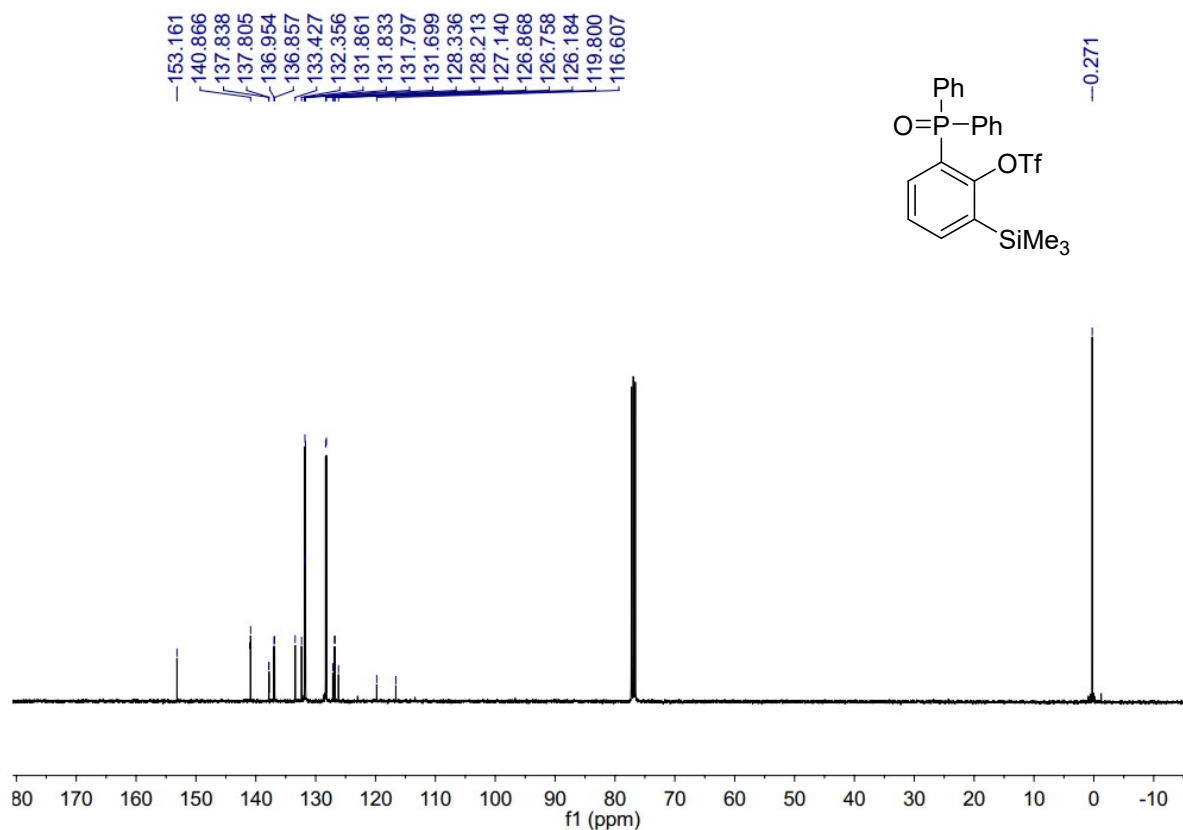


# SUPPORTING INFORMATION

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound **5**

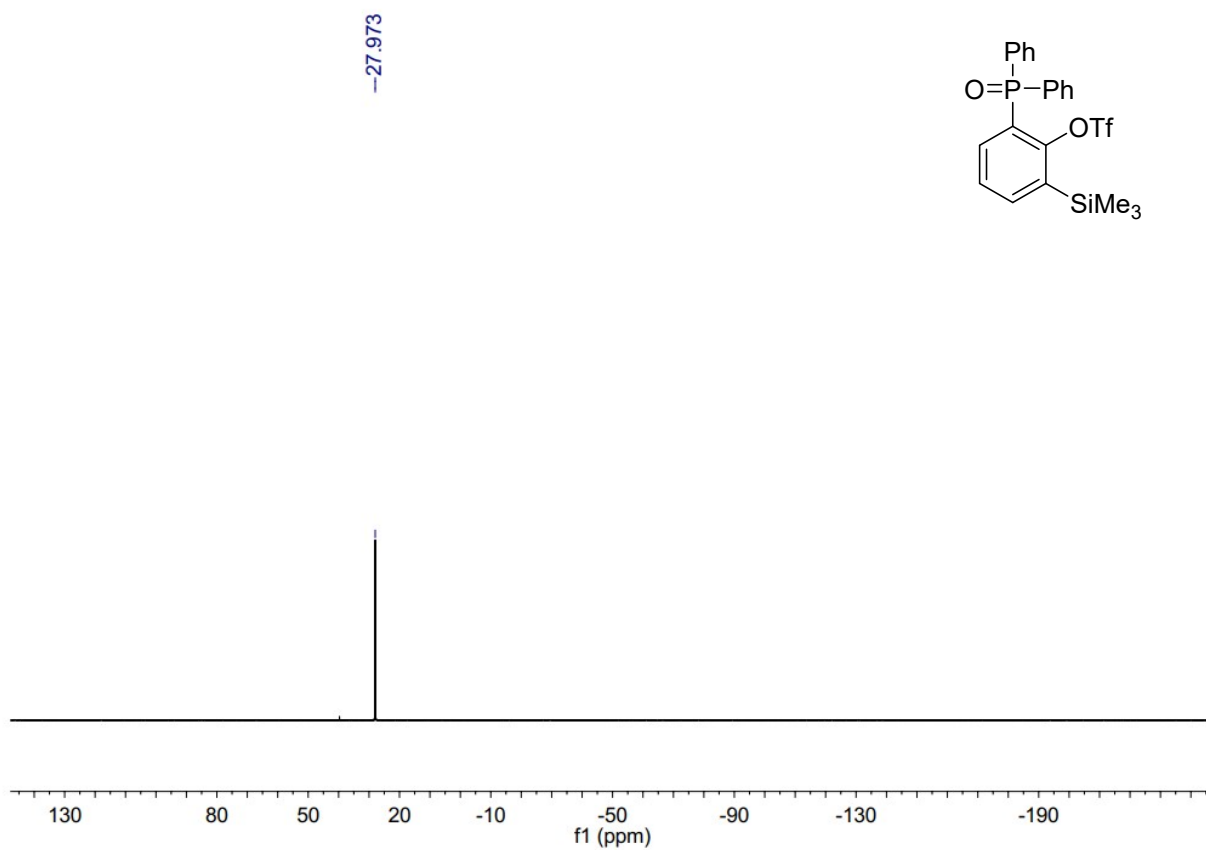


<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) spectrum of compound **5**

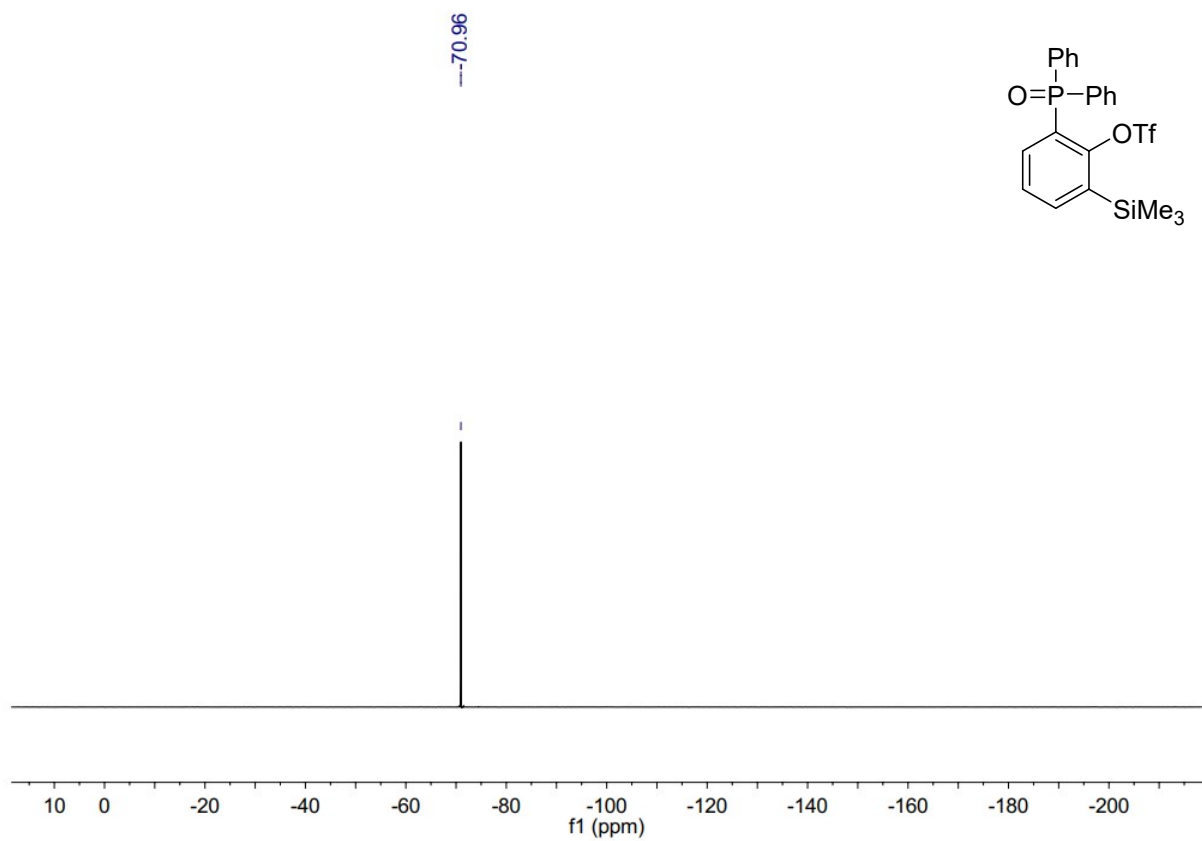


# SUPPORTING INFORMATION

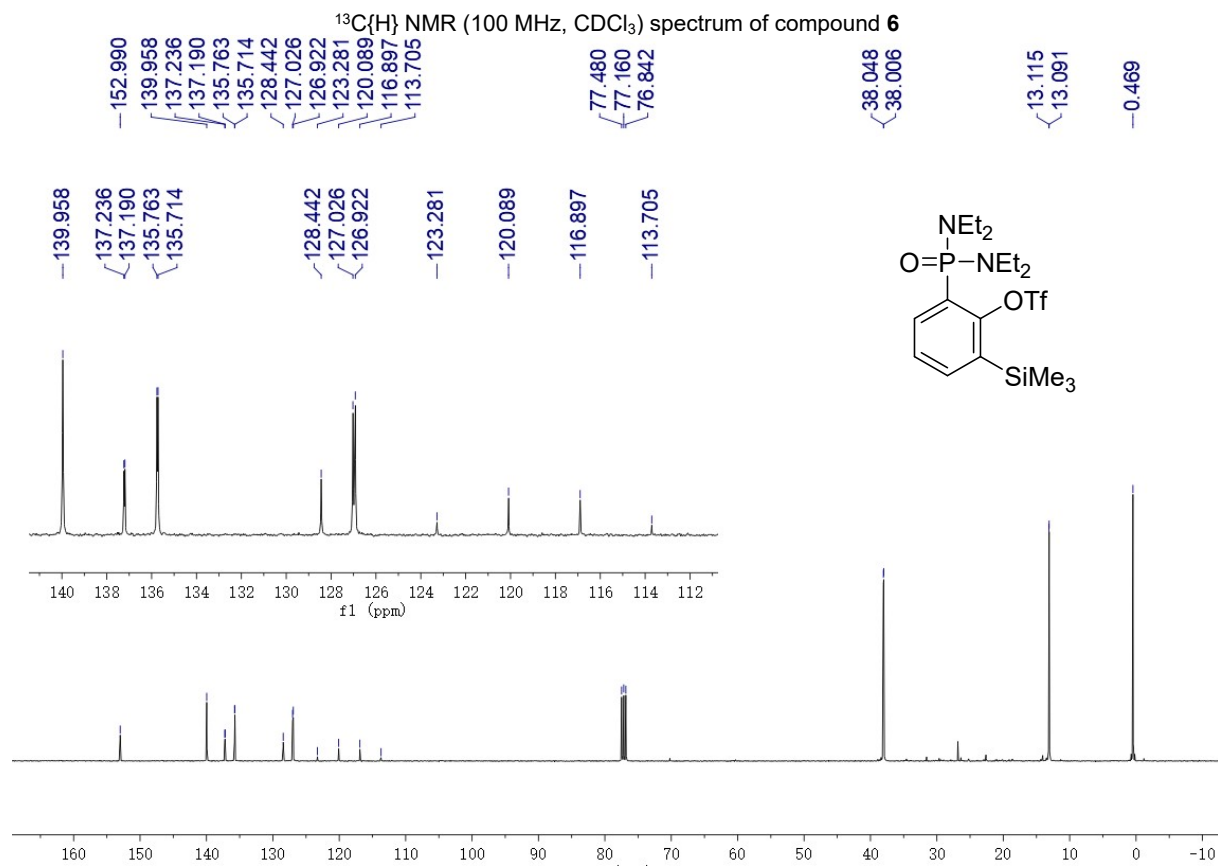
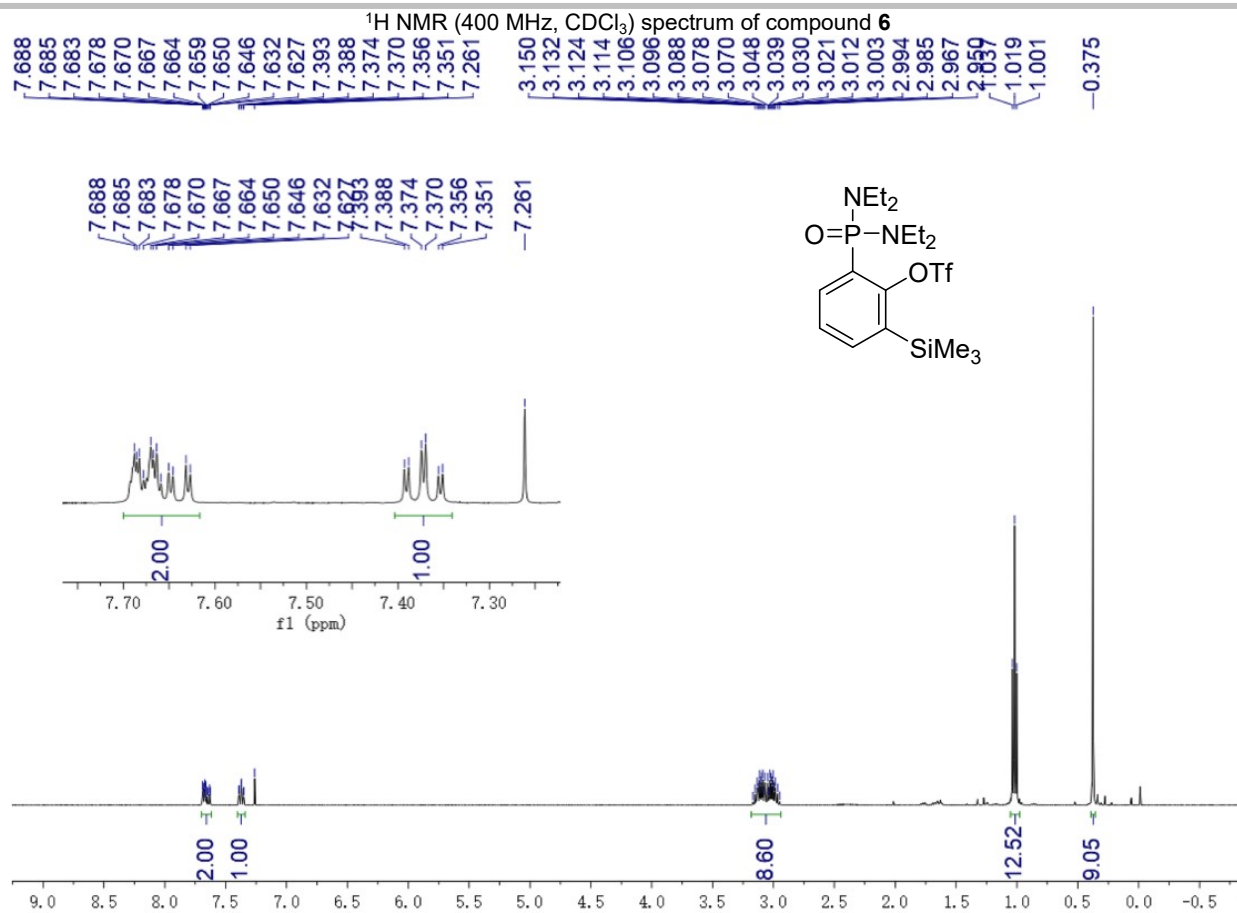
$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of compound **5**



$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) spectrum of compound **5**

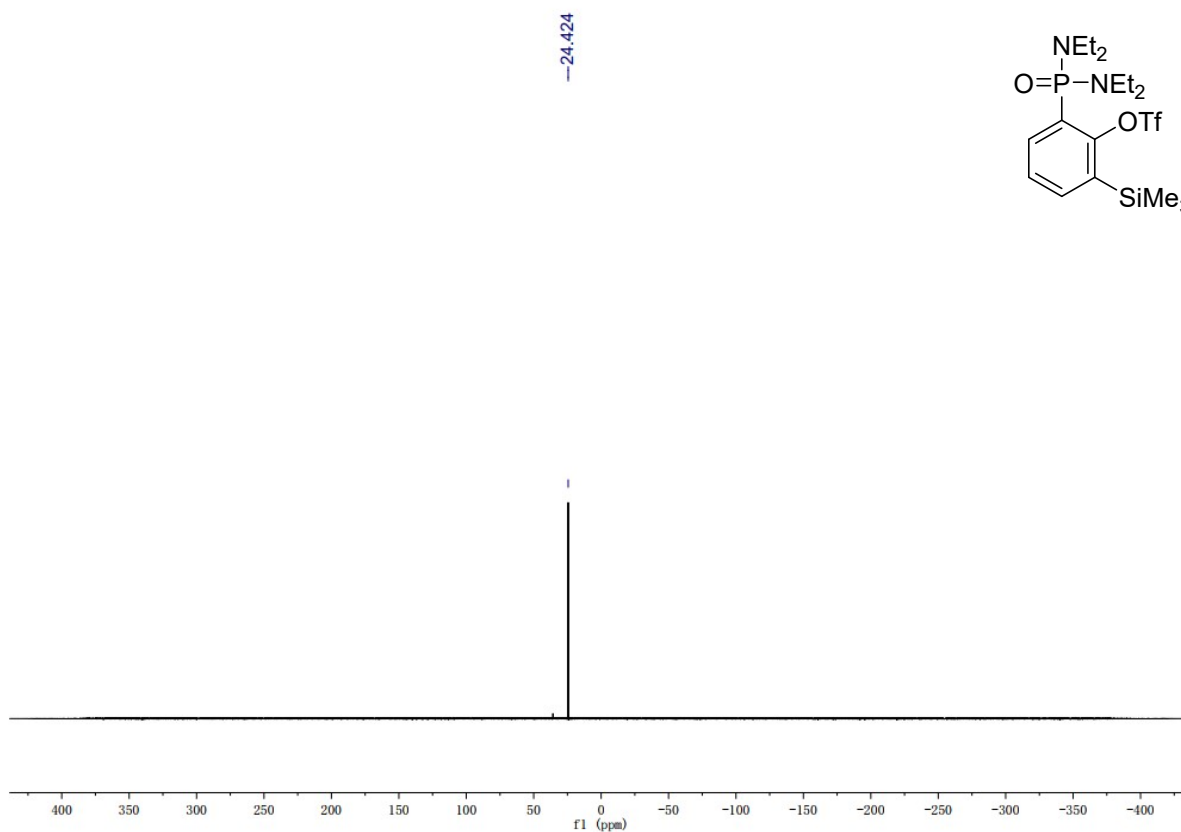


# SUPPORTING INFORMATION

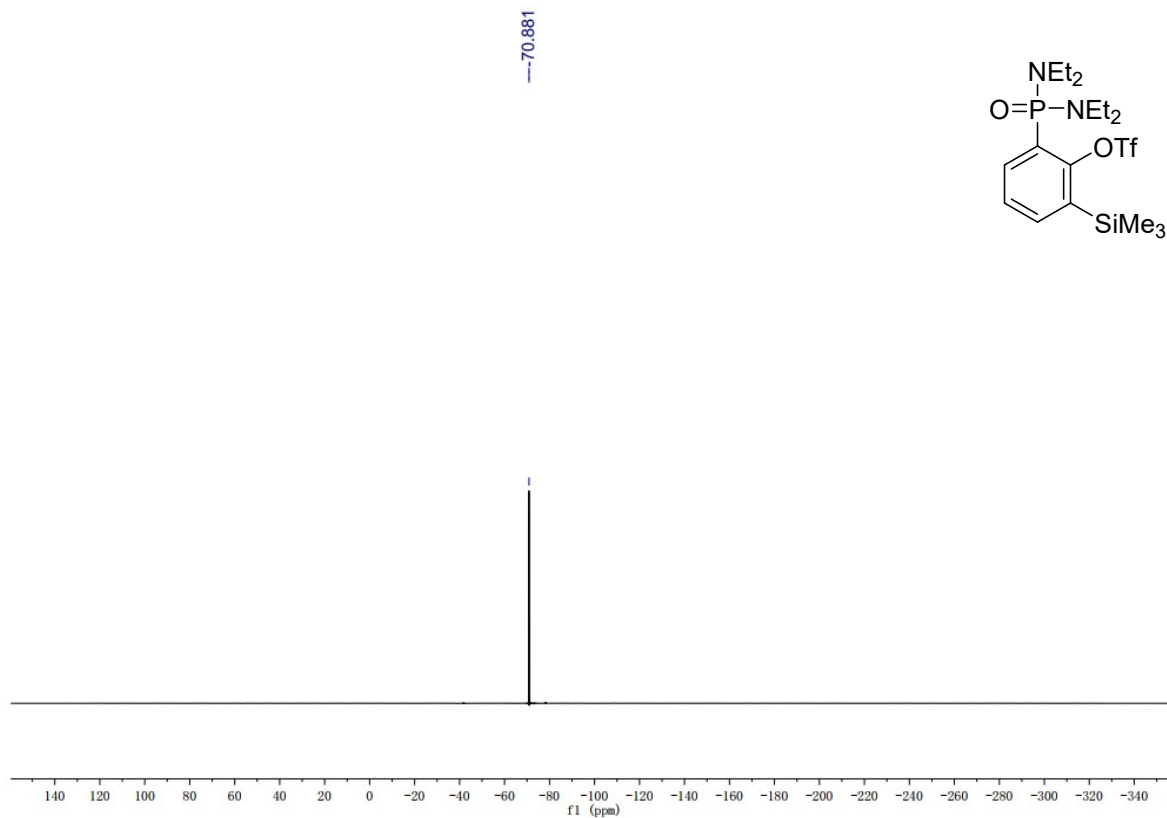


# SUPPORTING INFORMATION

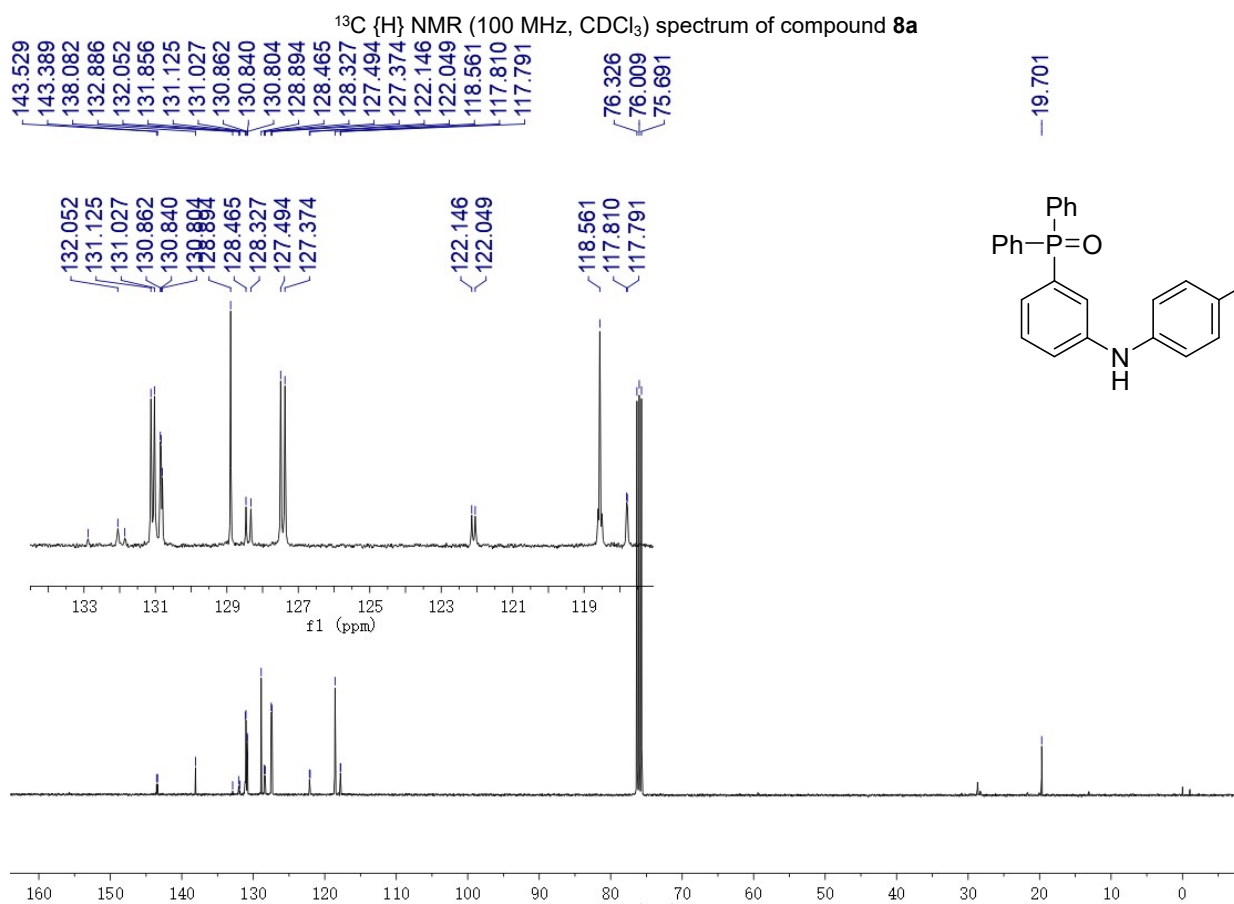
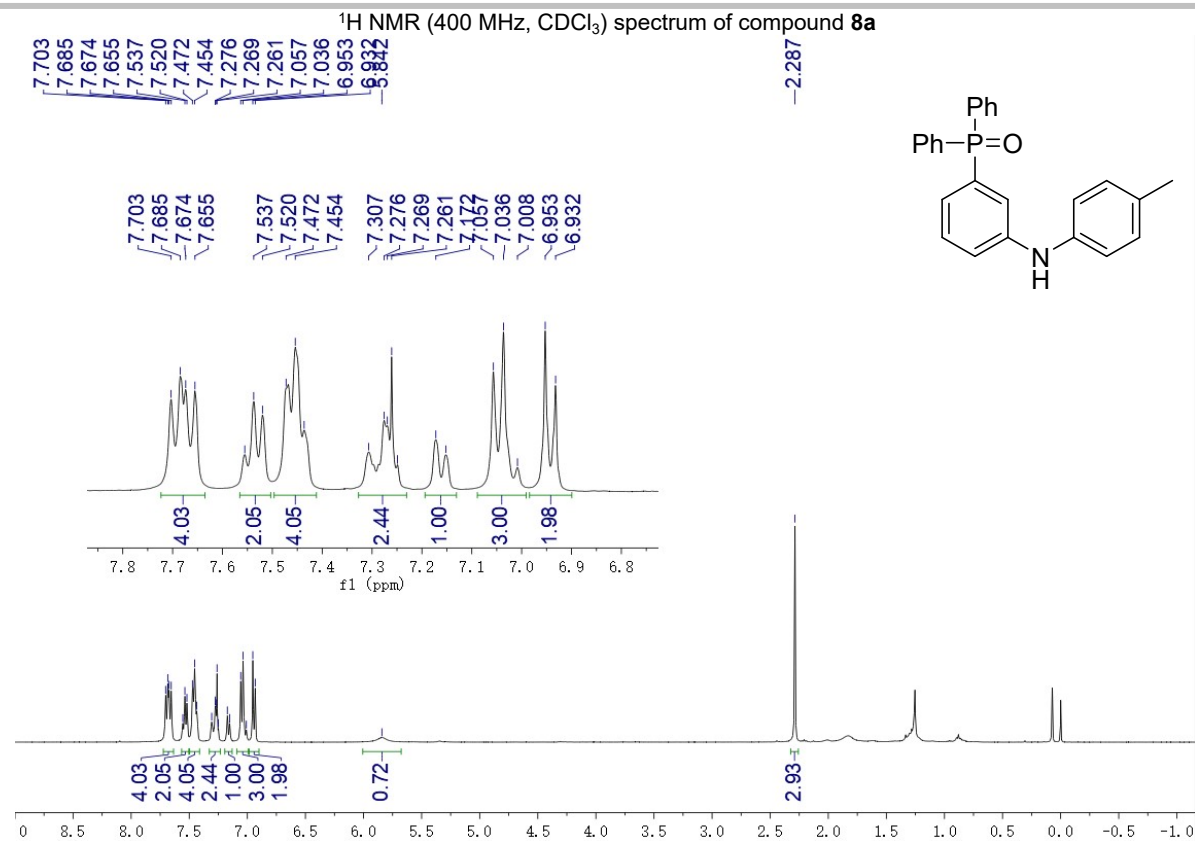
$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of compound **6**



$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) spectrum of compound **6**

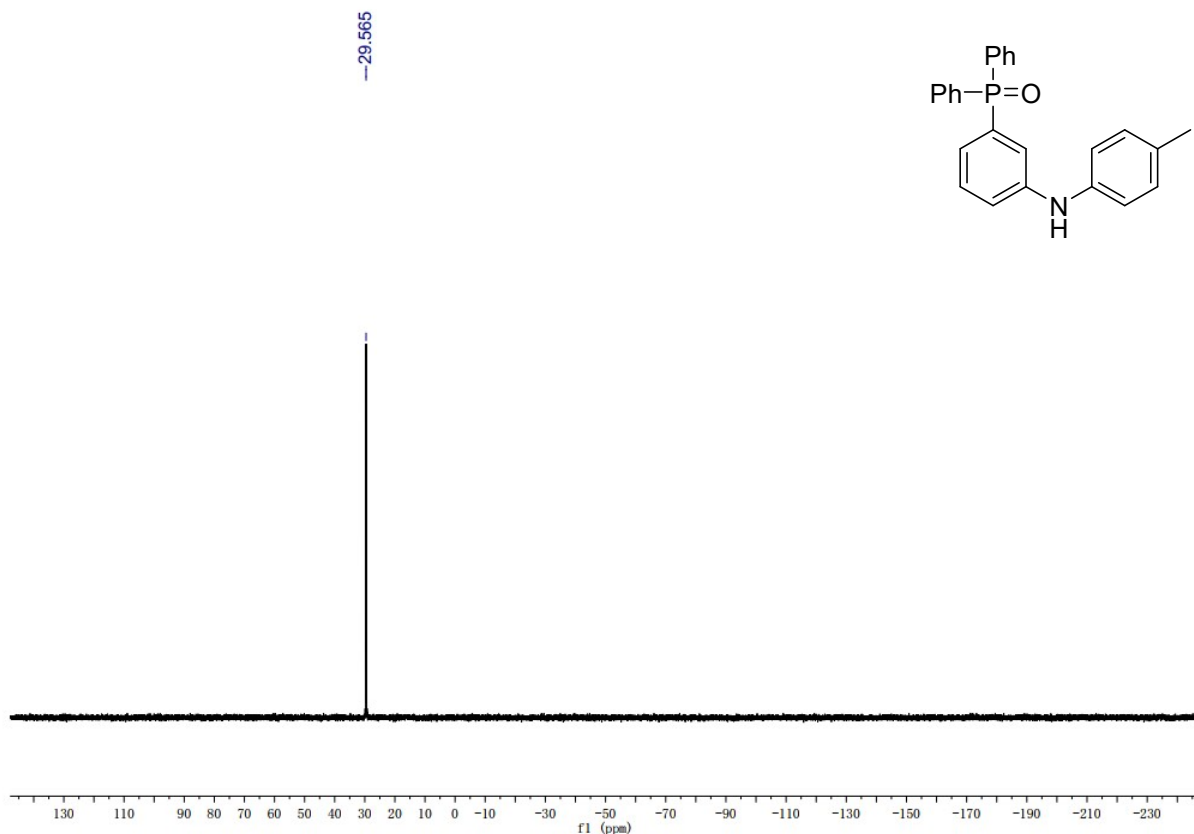


# SUPPORTING INFORMATION

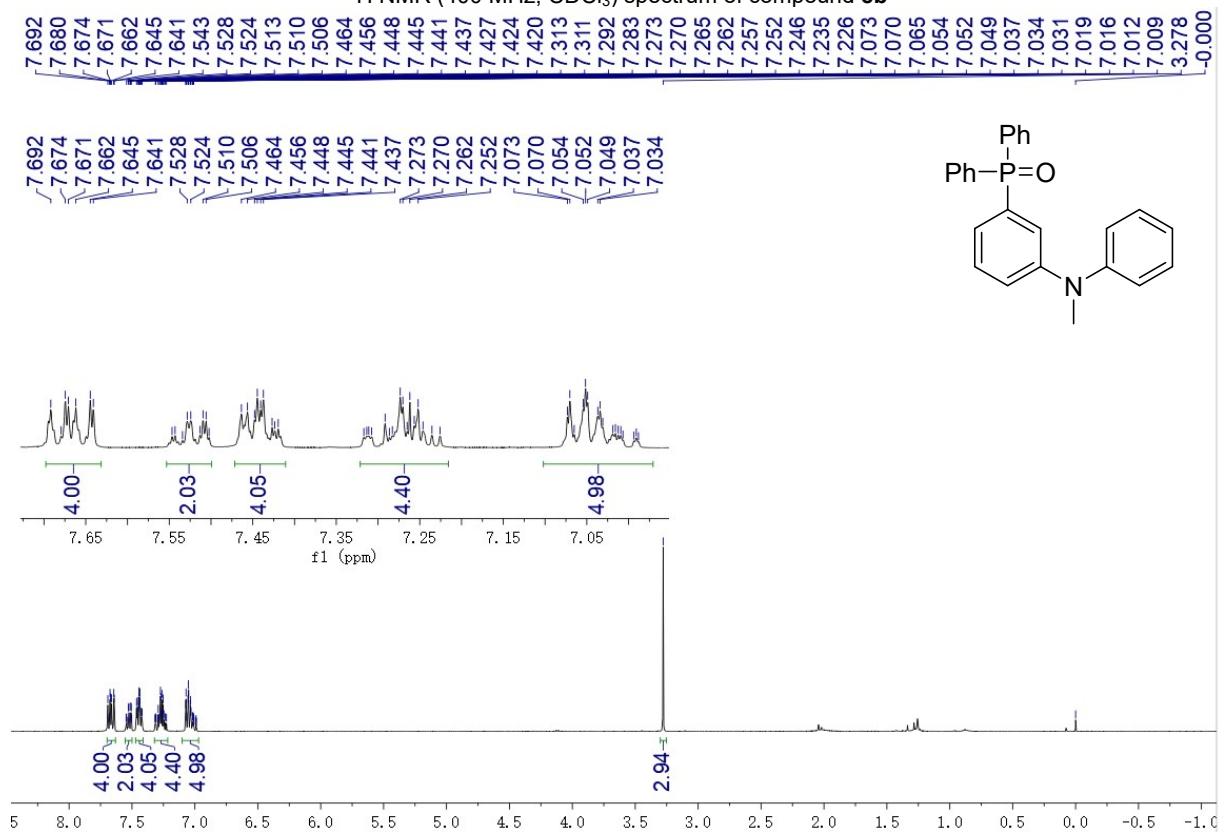


# SUPPORTING INFORMATION

<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) spectrum of compound **8a**

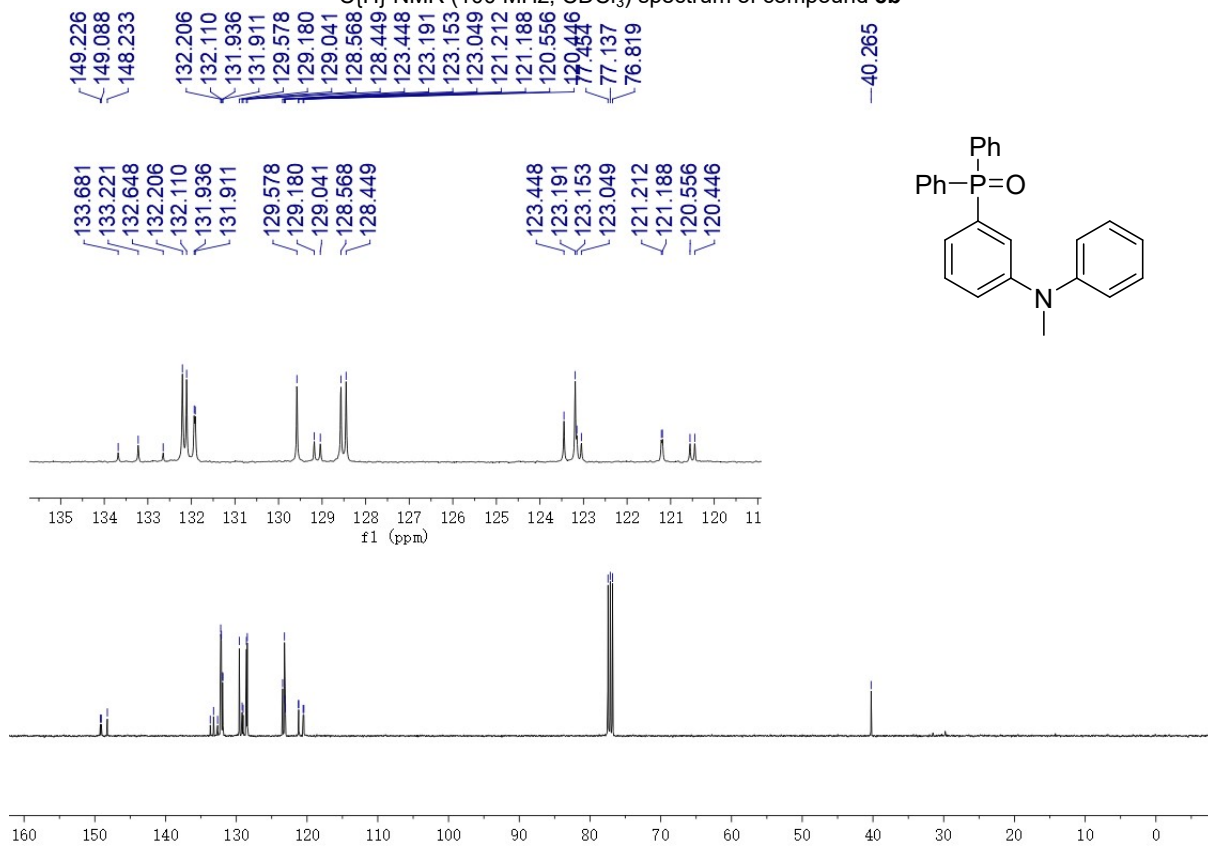


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound **8b**

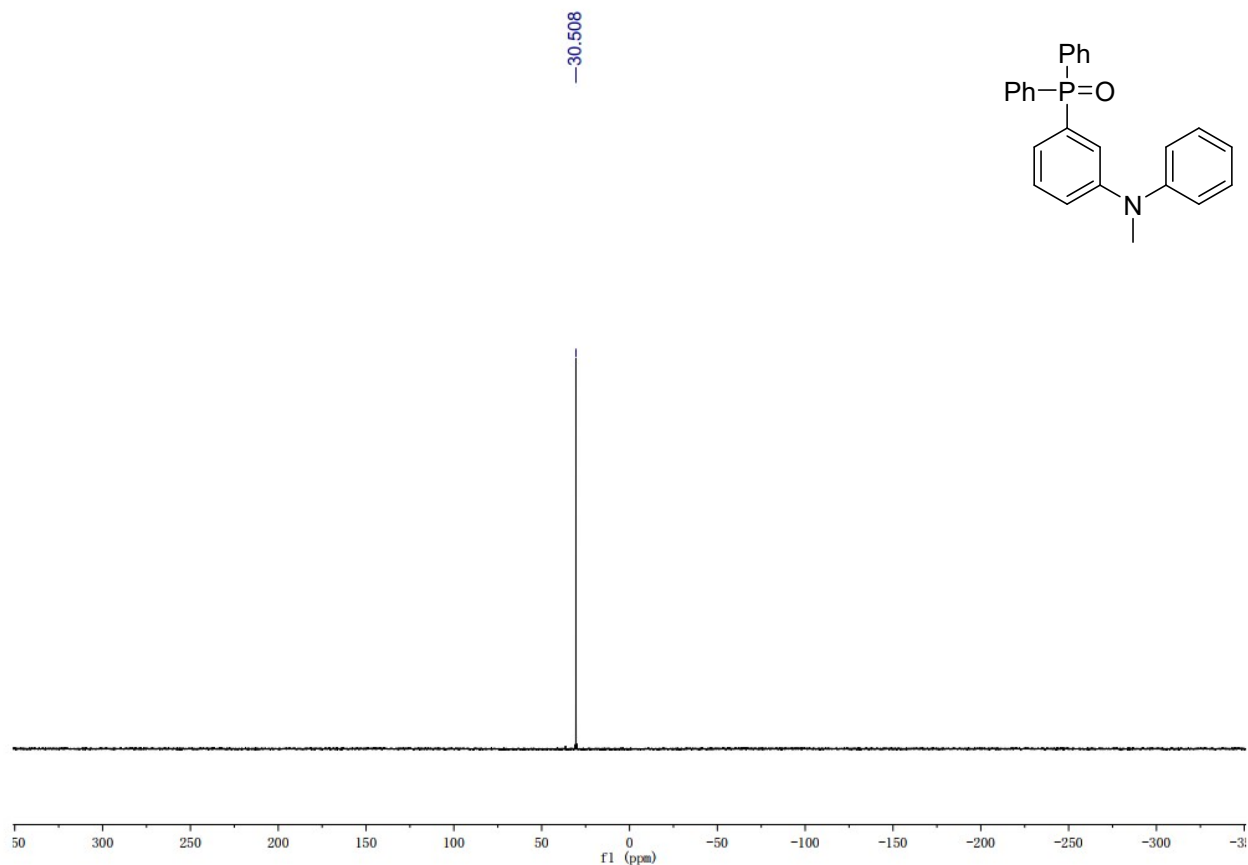


# SUPPORTING INFORMATION

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of compound **8b**

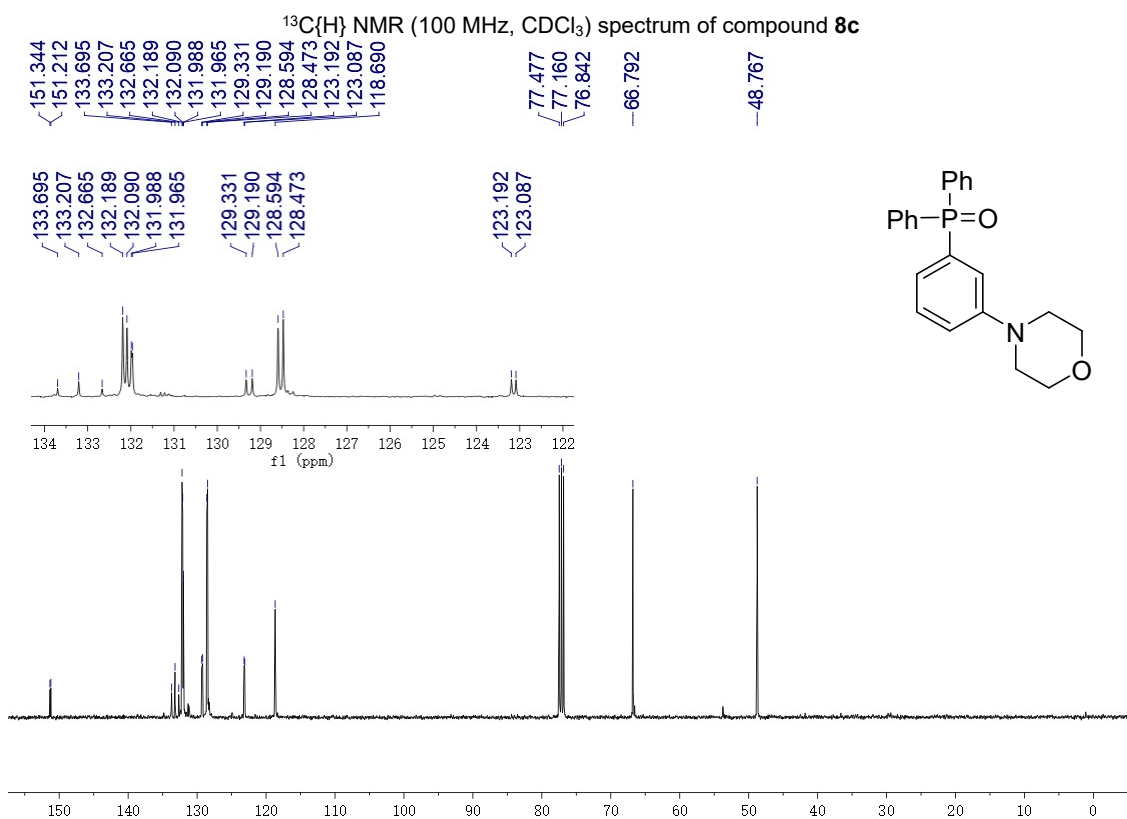
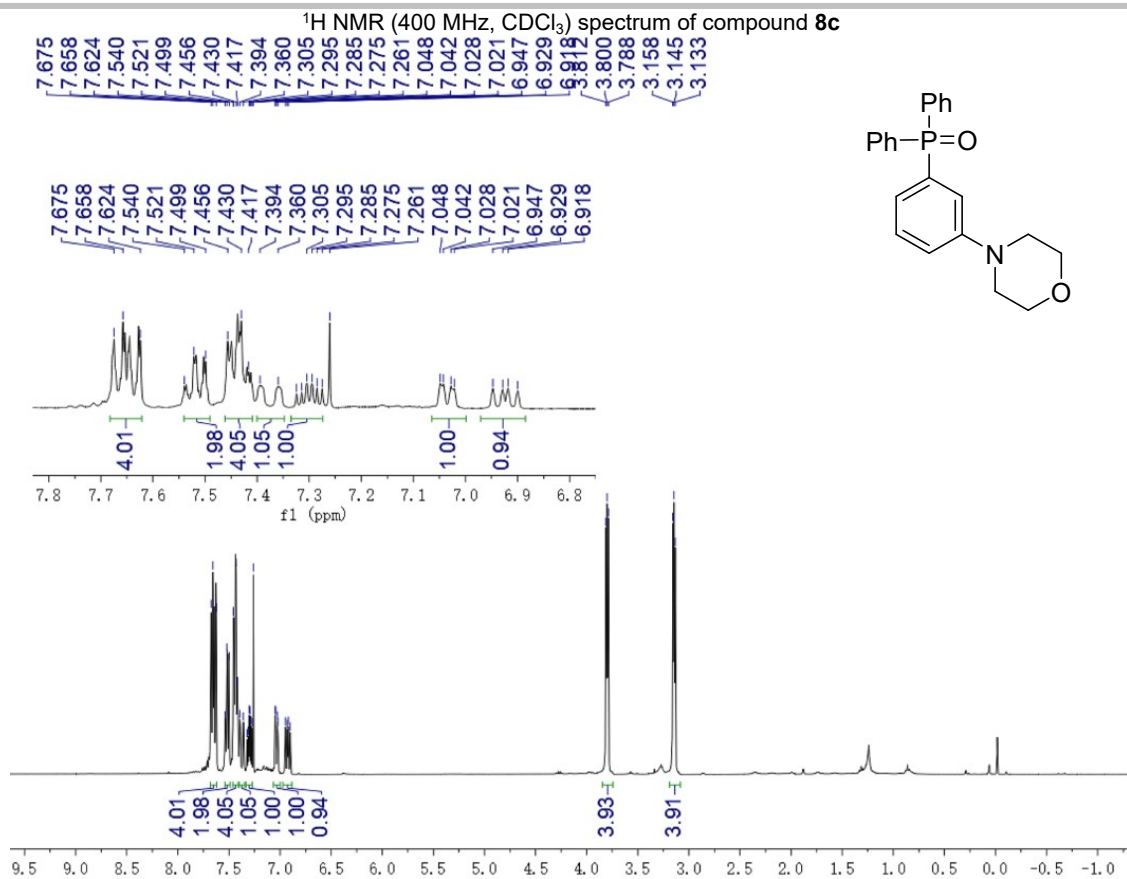


$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of compound **8b**



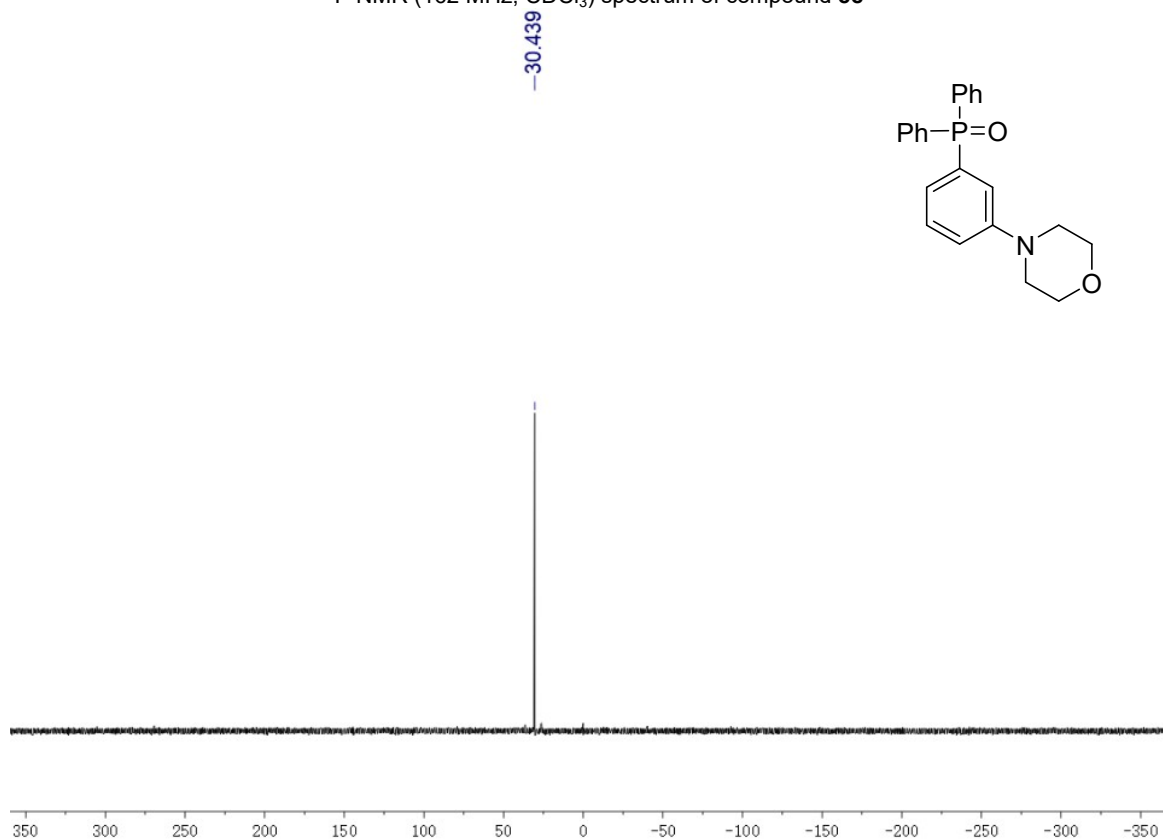


# SUPPORTING INFORMATION

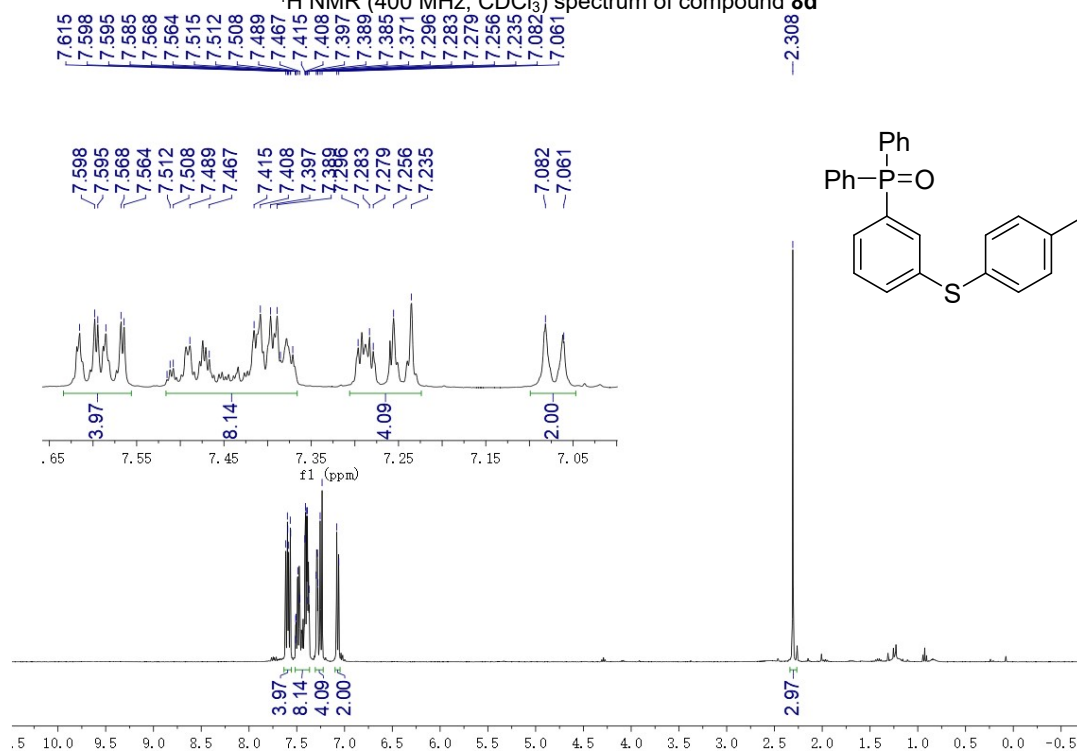


# SUPPORTING INFORMATION

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of compound **8c**

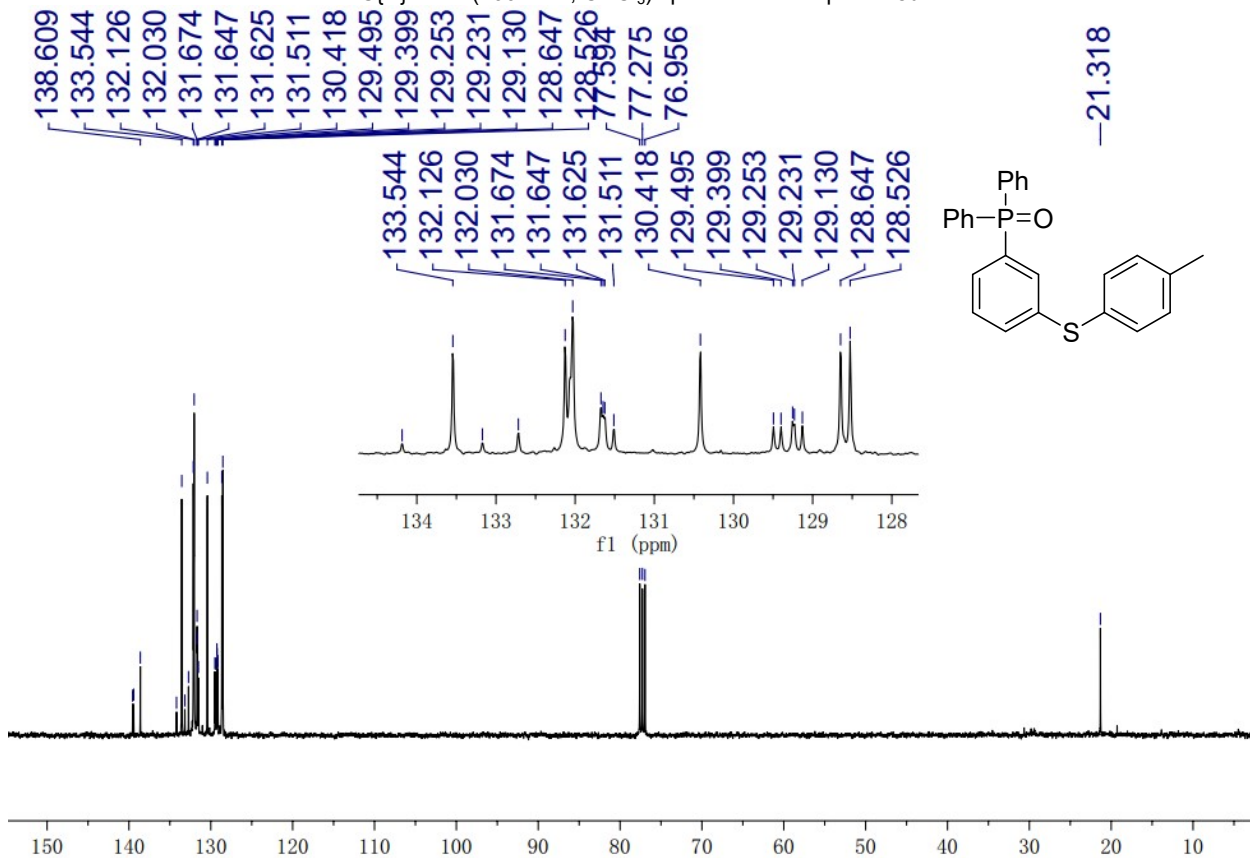


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of compound **8d**

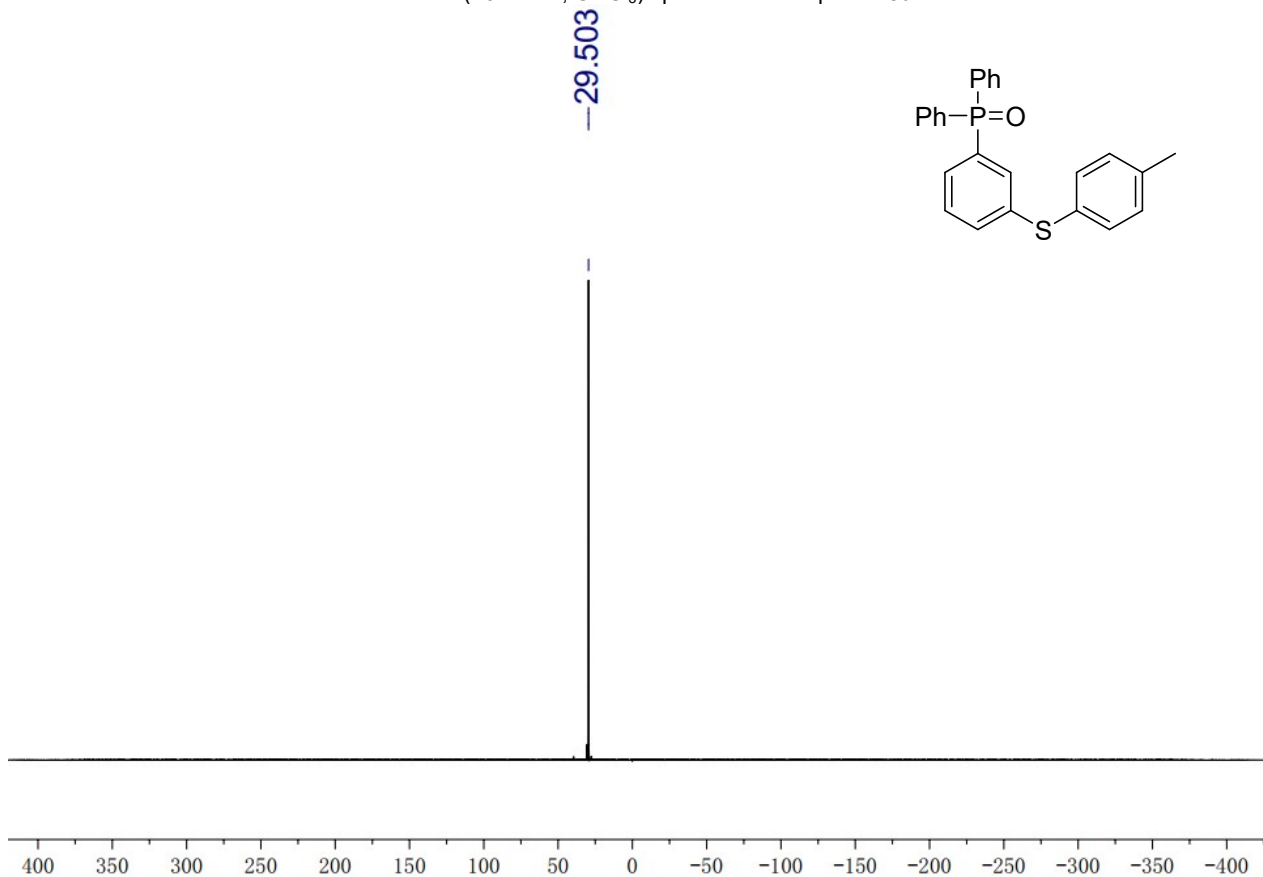


# SUPPORTING INFORMATION

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of compound **8d**

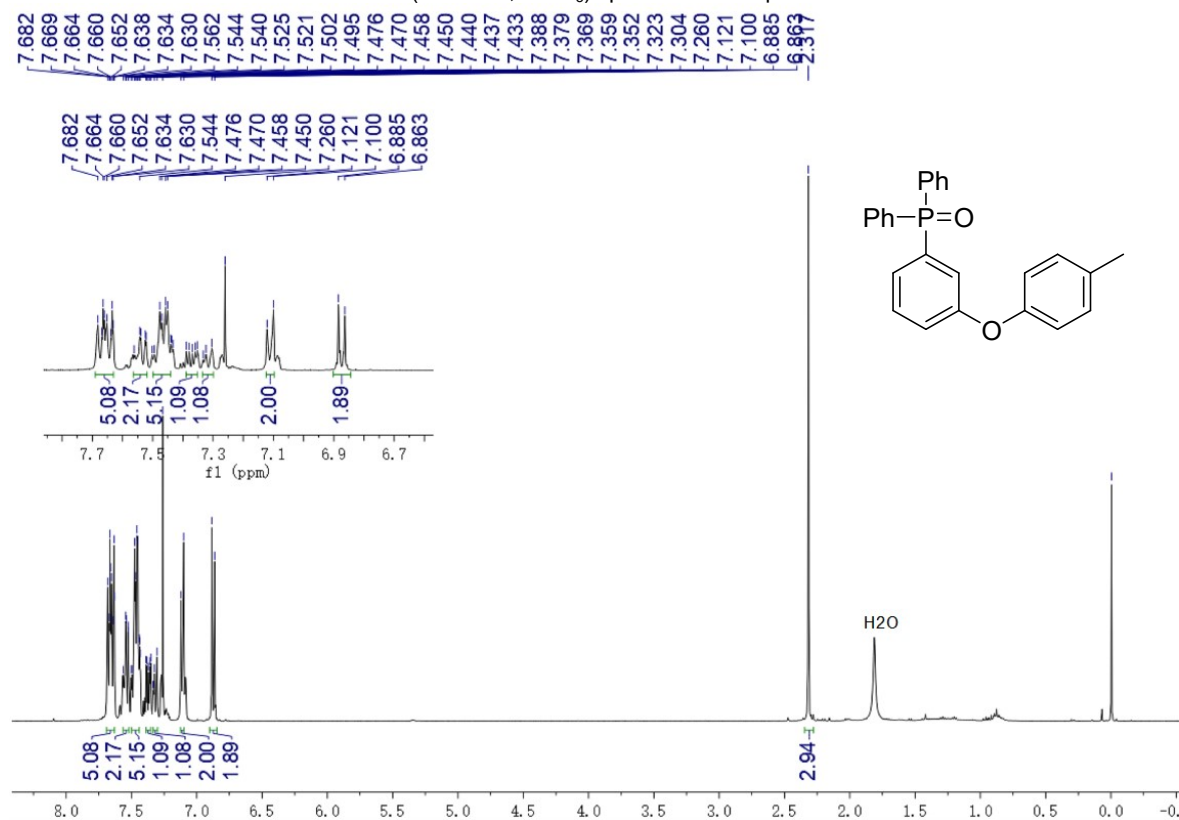


$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of compound **8d**

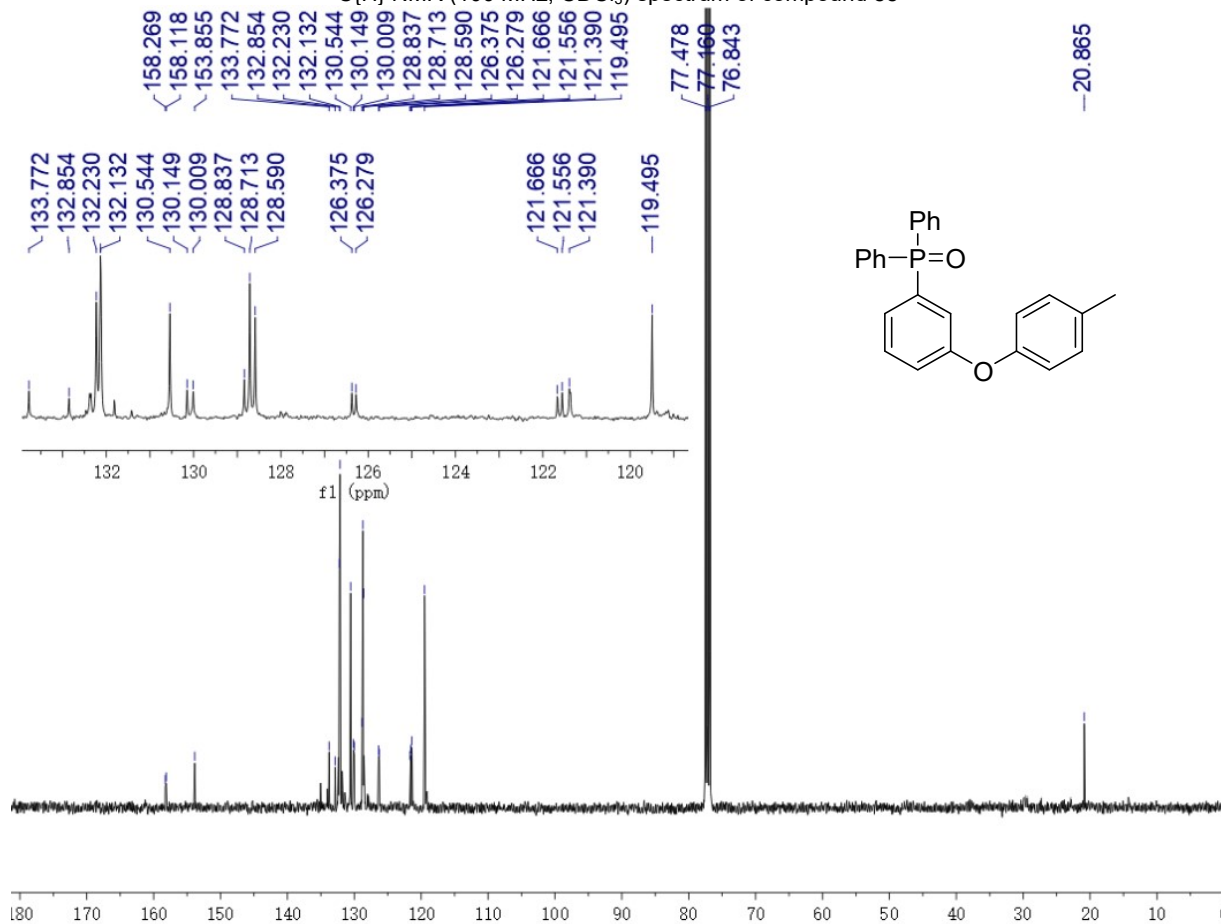


# SUPPORTING INFORMATION

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound **8e**



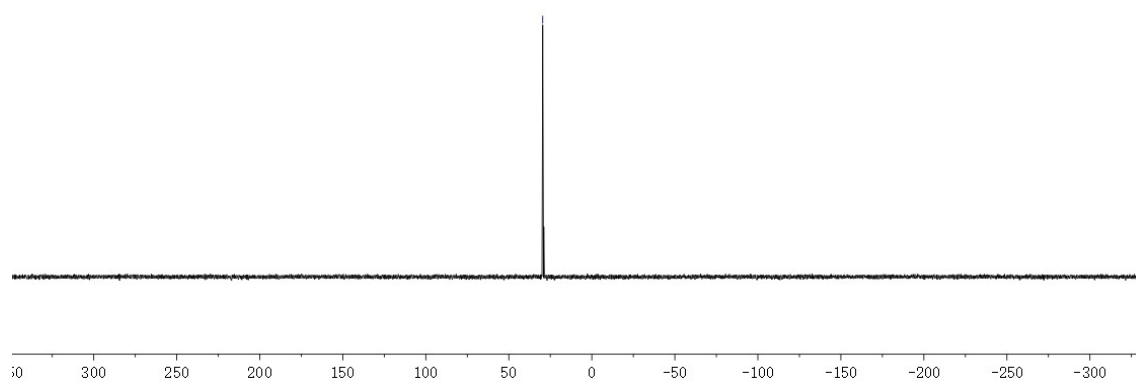
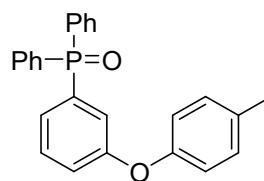
<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) spectrum of compound **8e**



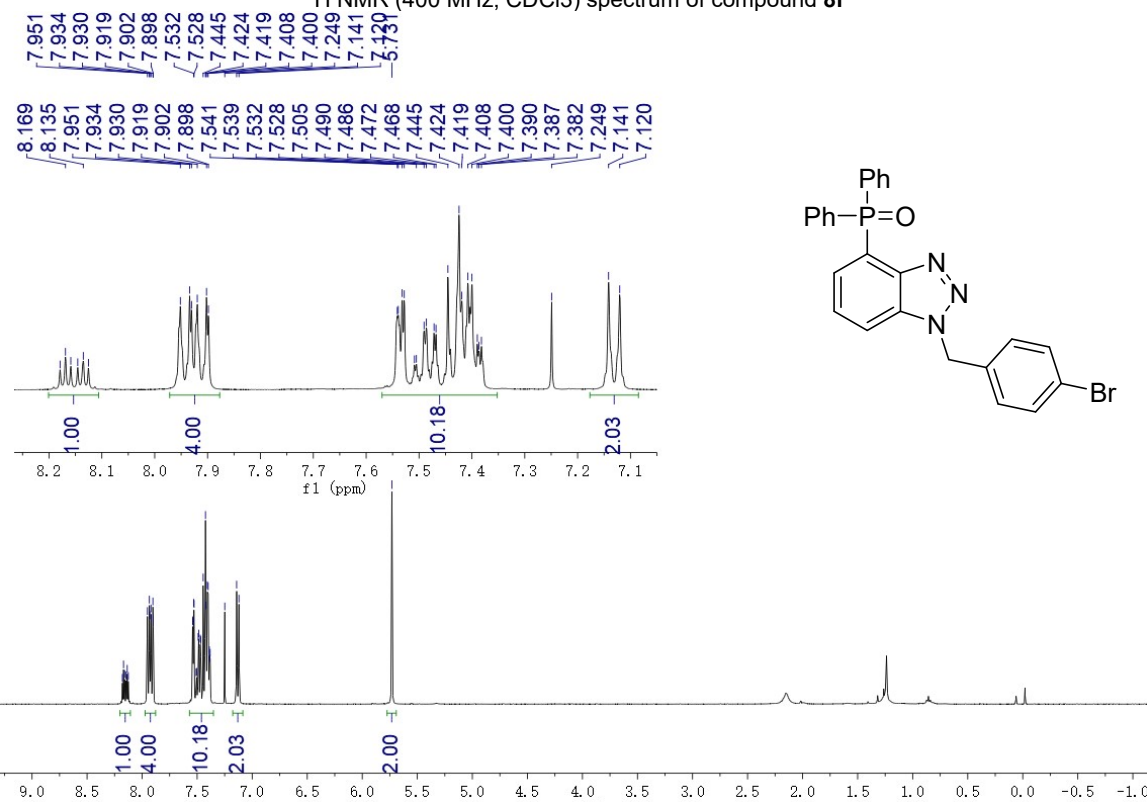
# SUPPORTING INFORMATION

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of compound **8e**

-29.571

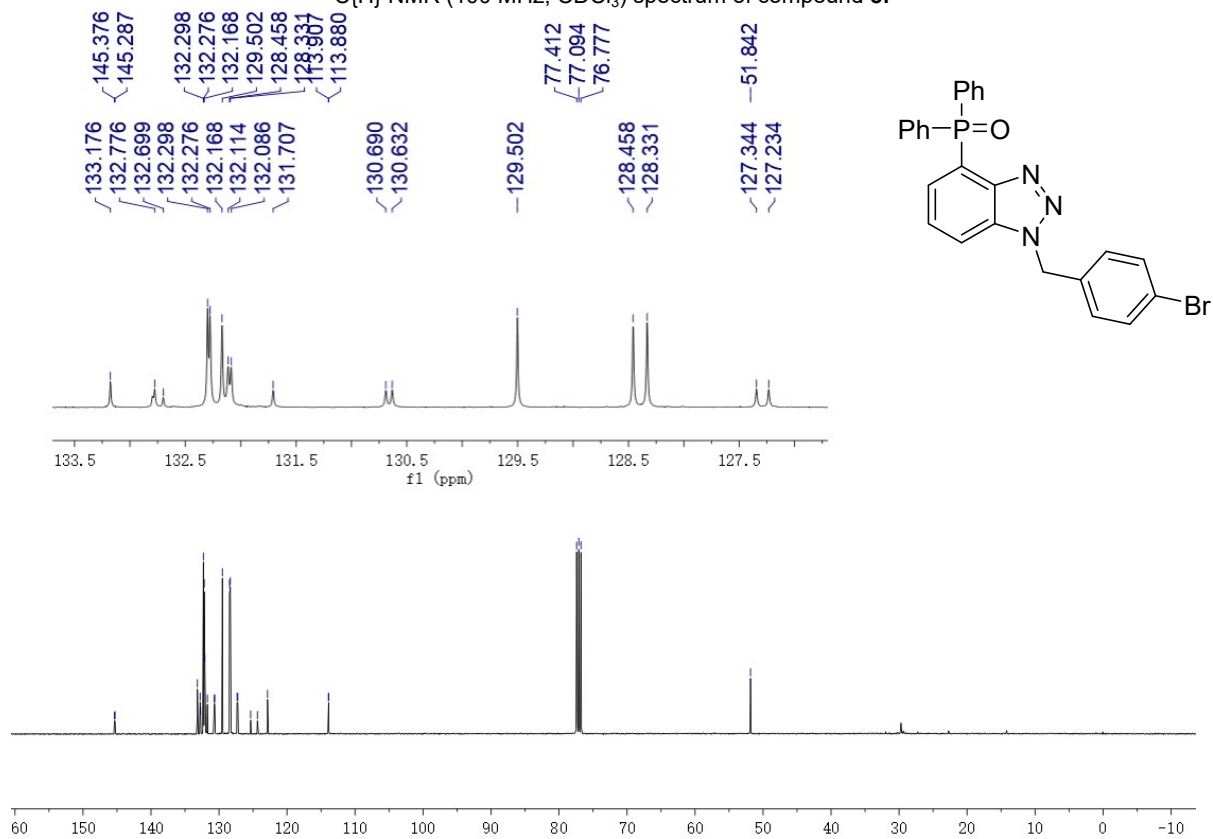


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of compound **8f**

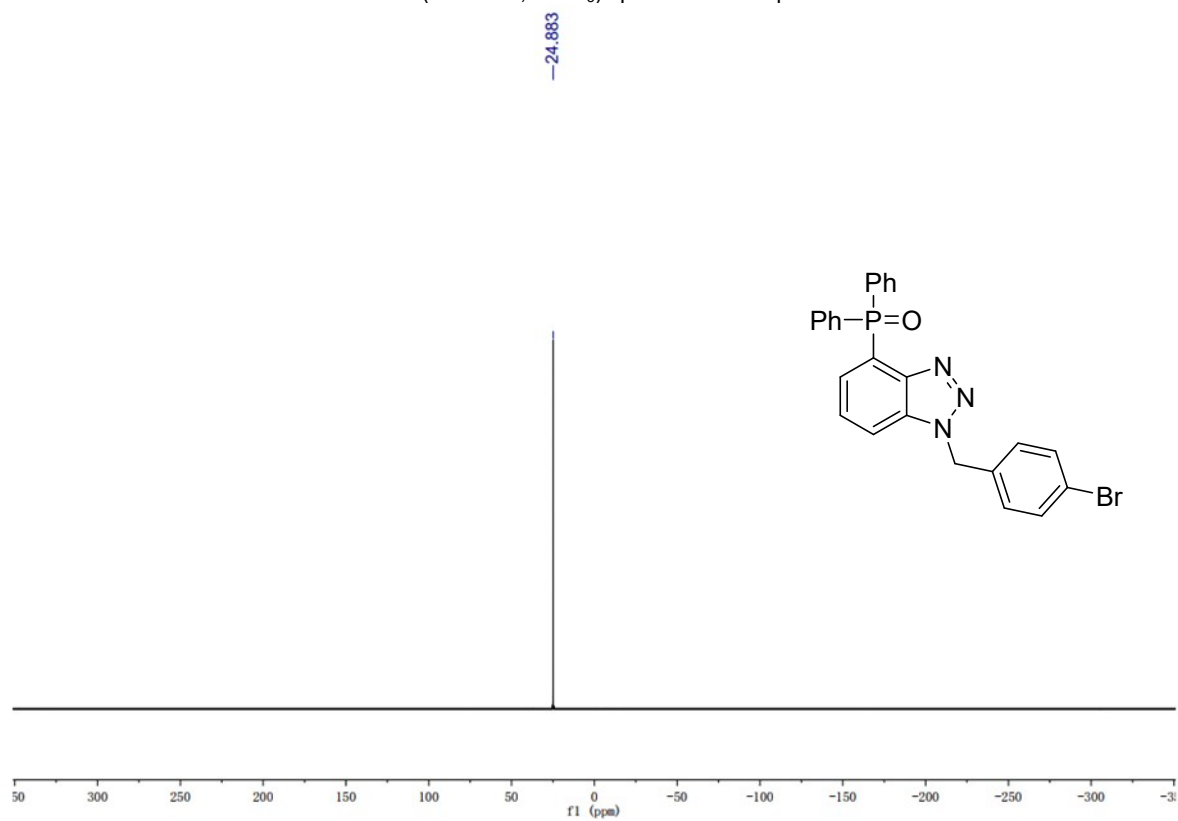


# SUPPORTING INFORMATION

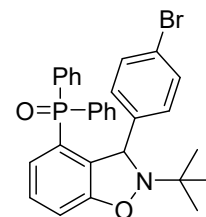
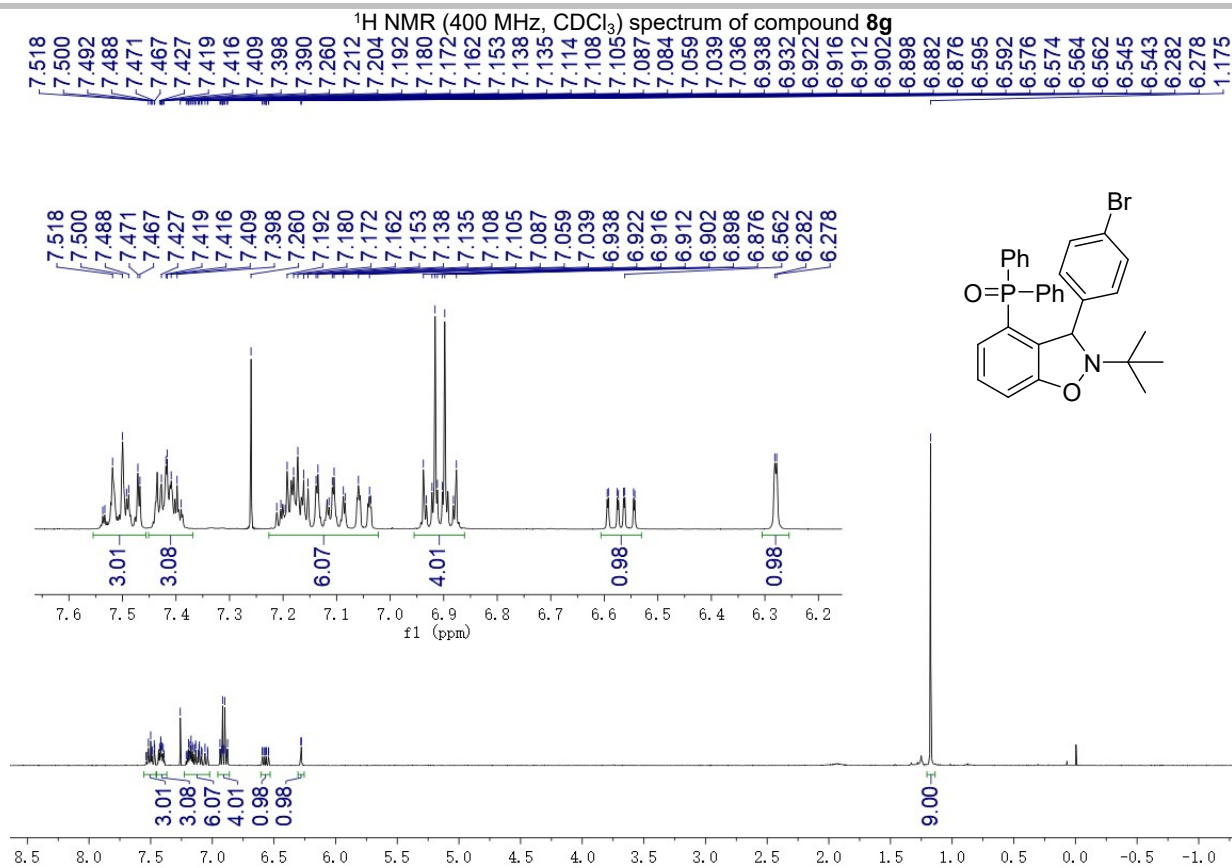
$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of compound **8f**



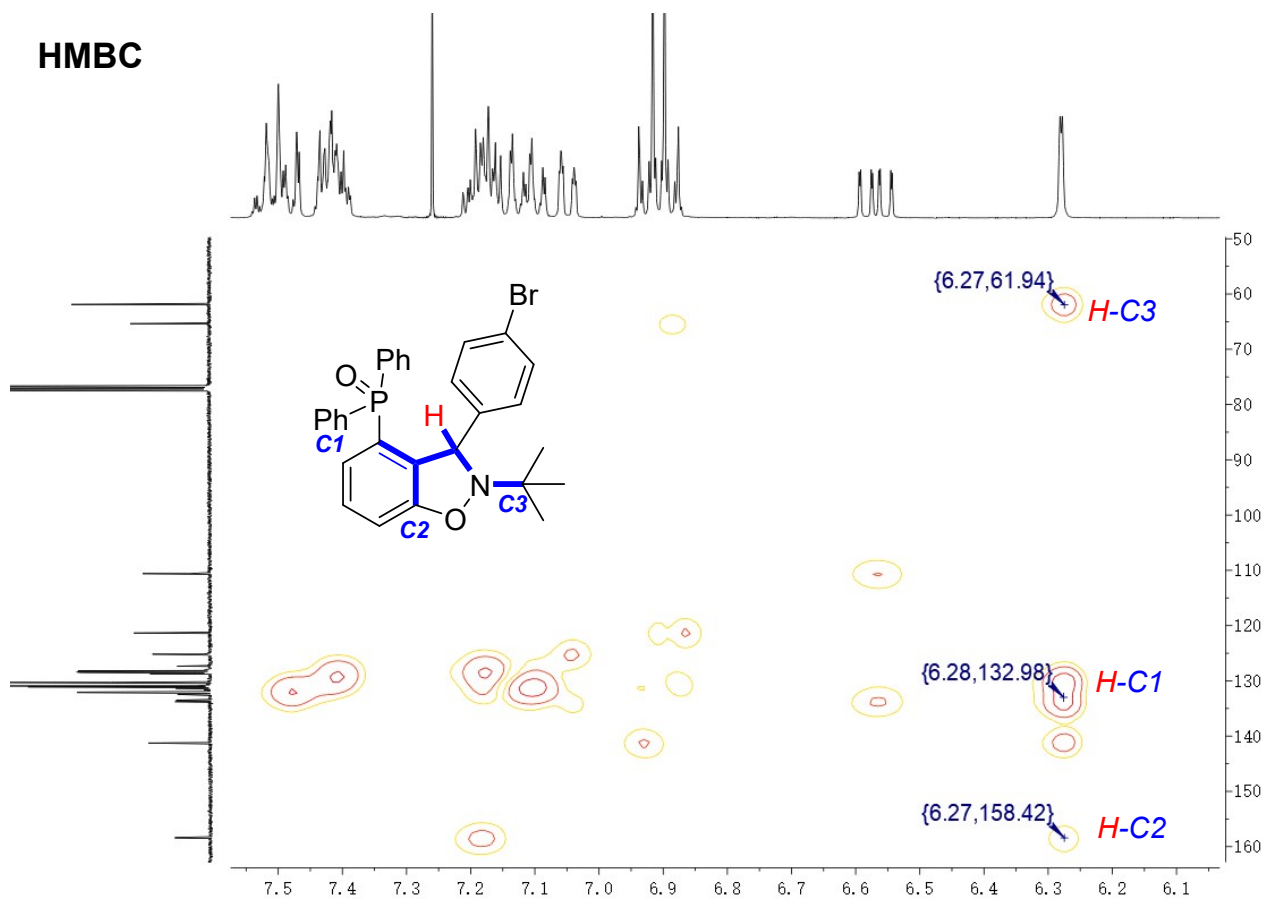
$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of compound **8f**



# SUPPORTING INFORMATION



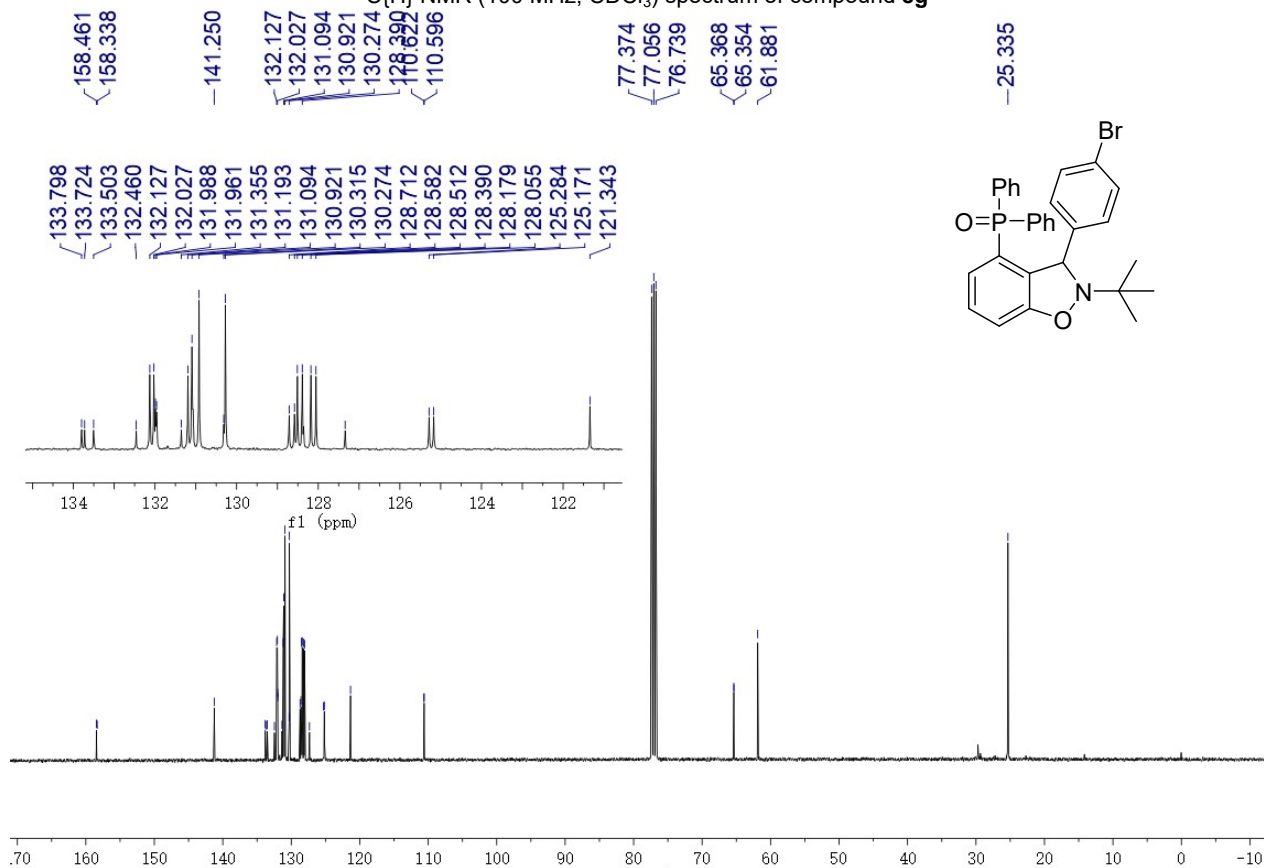
## HMBC



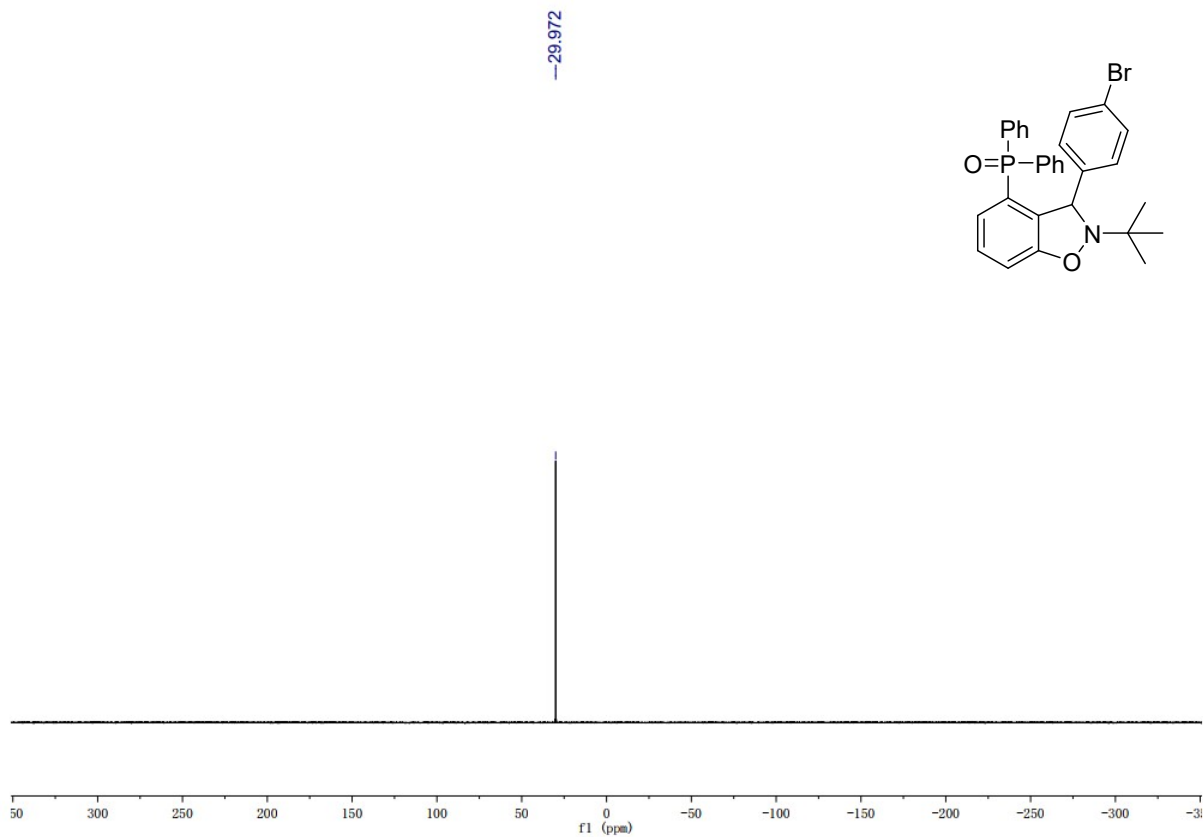


# SUPPORTING INFORMATION

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of compound **8g**

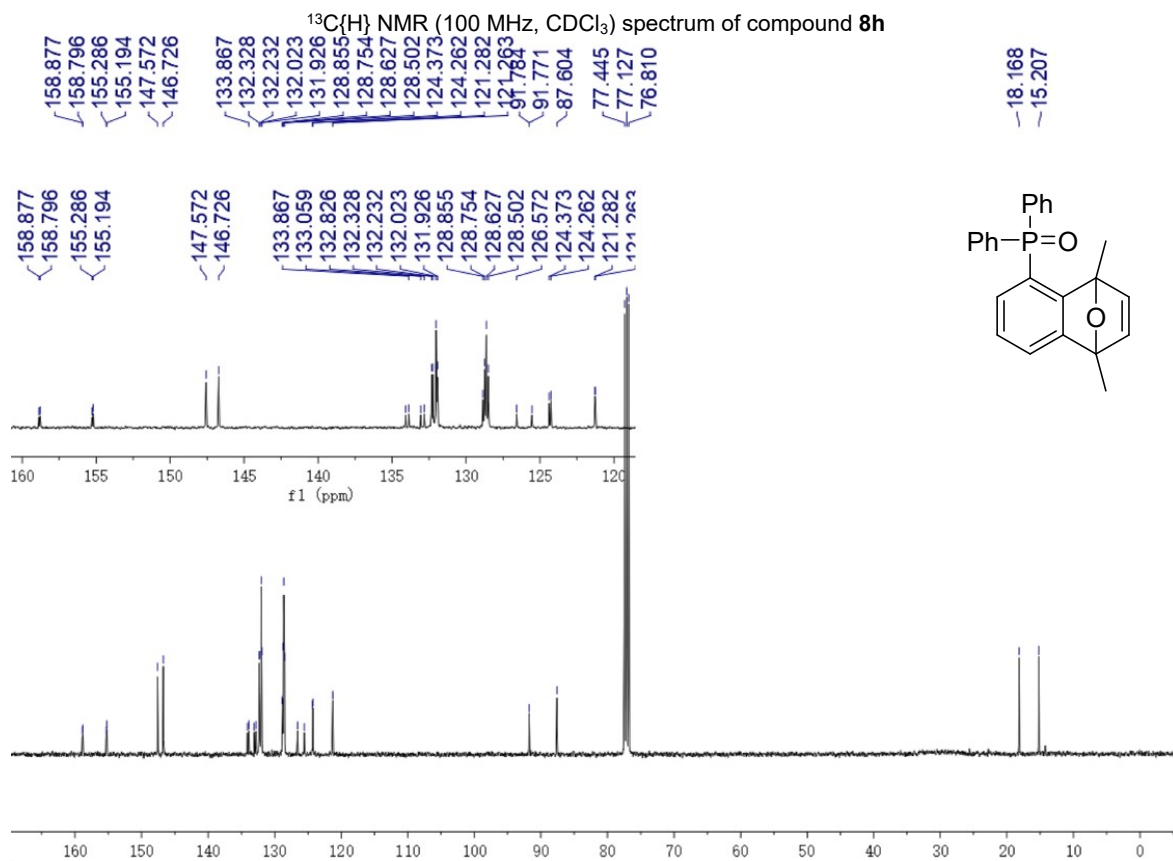
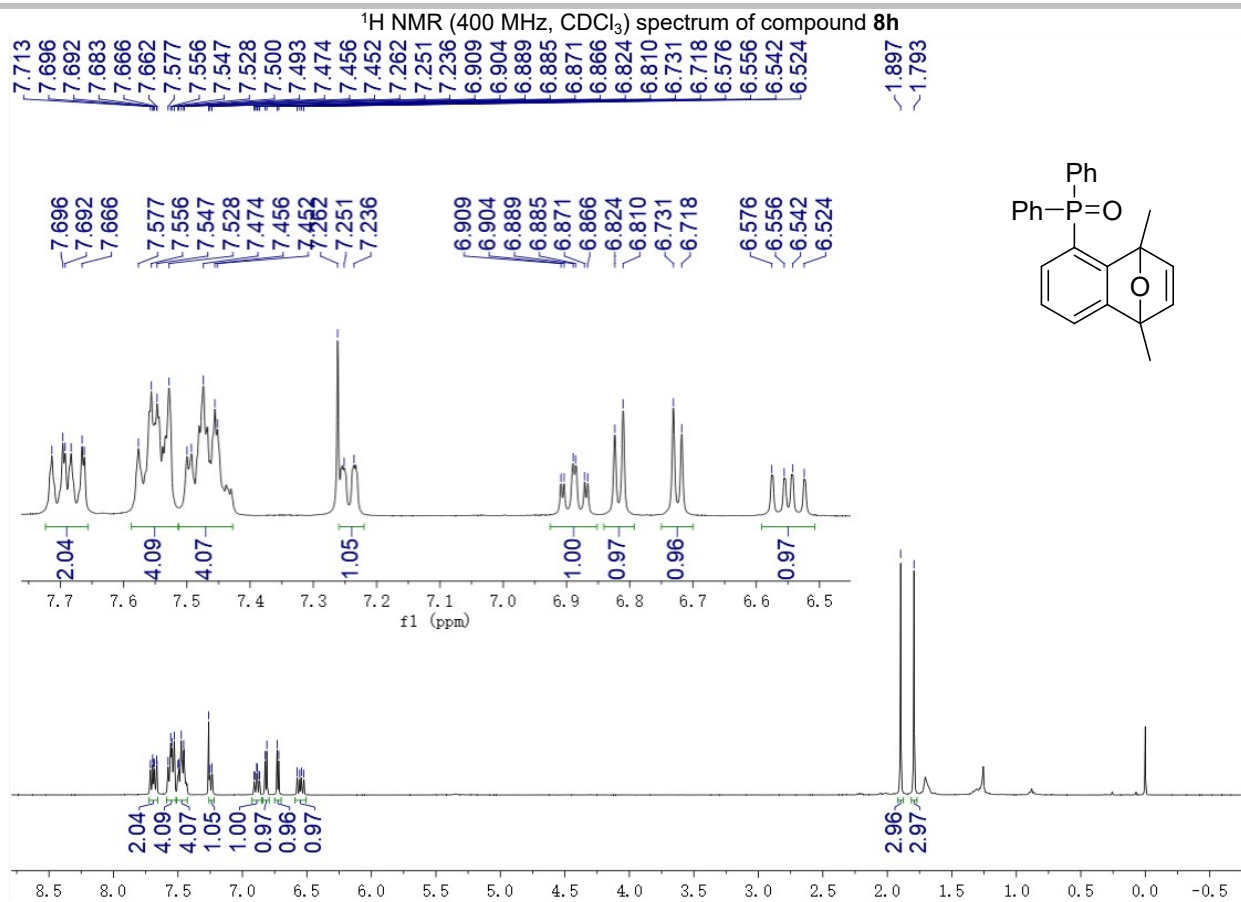


$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of compound **8g**



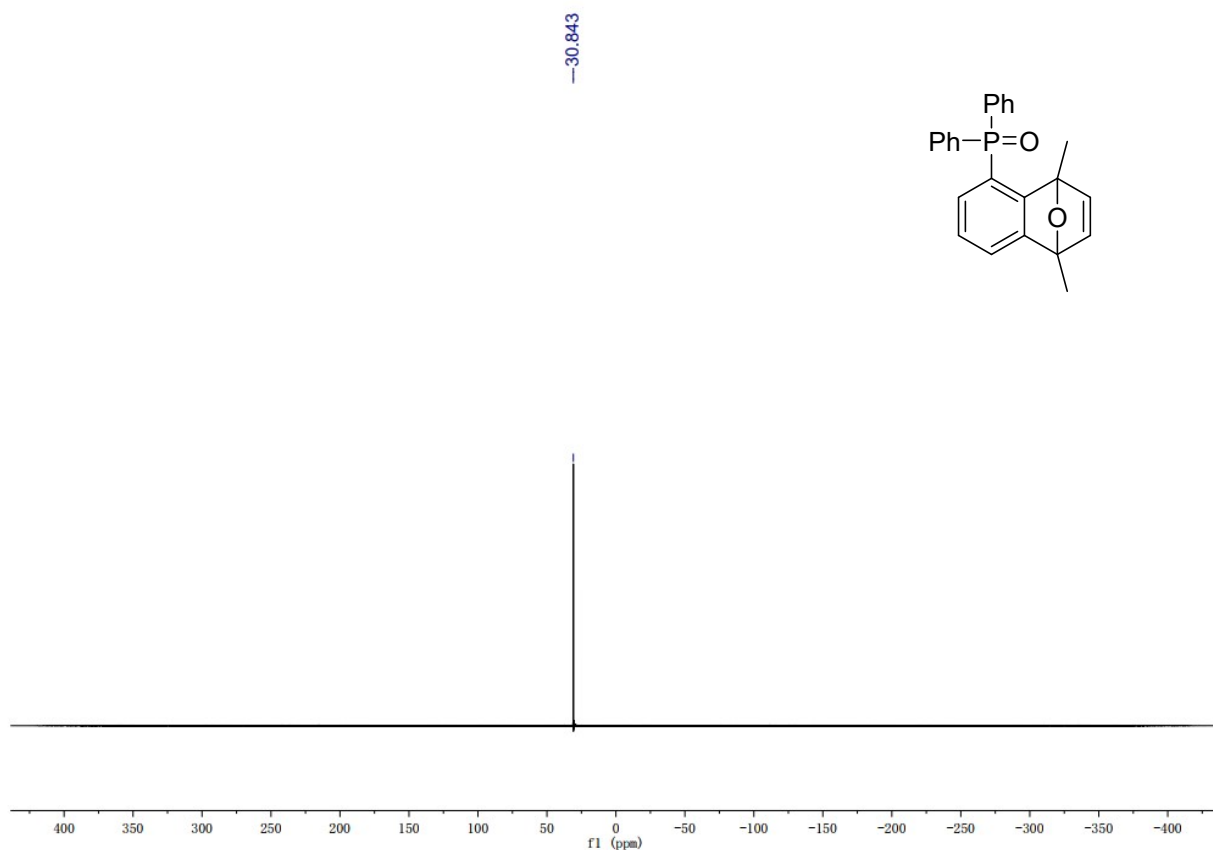


# SUPPORTING INFORMATION

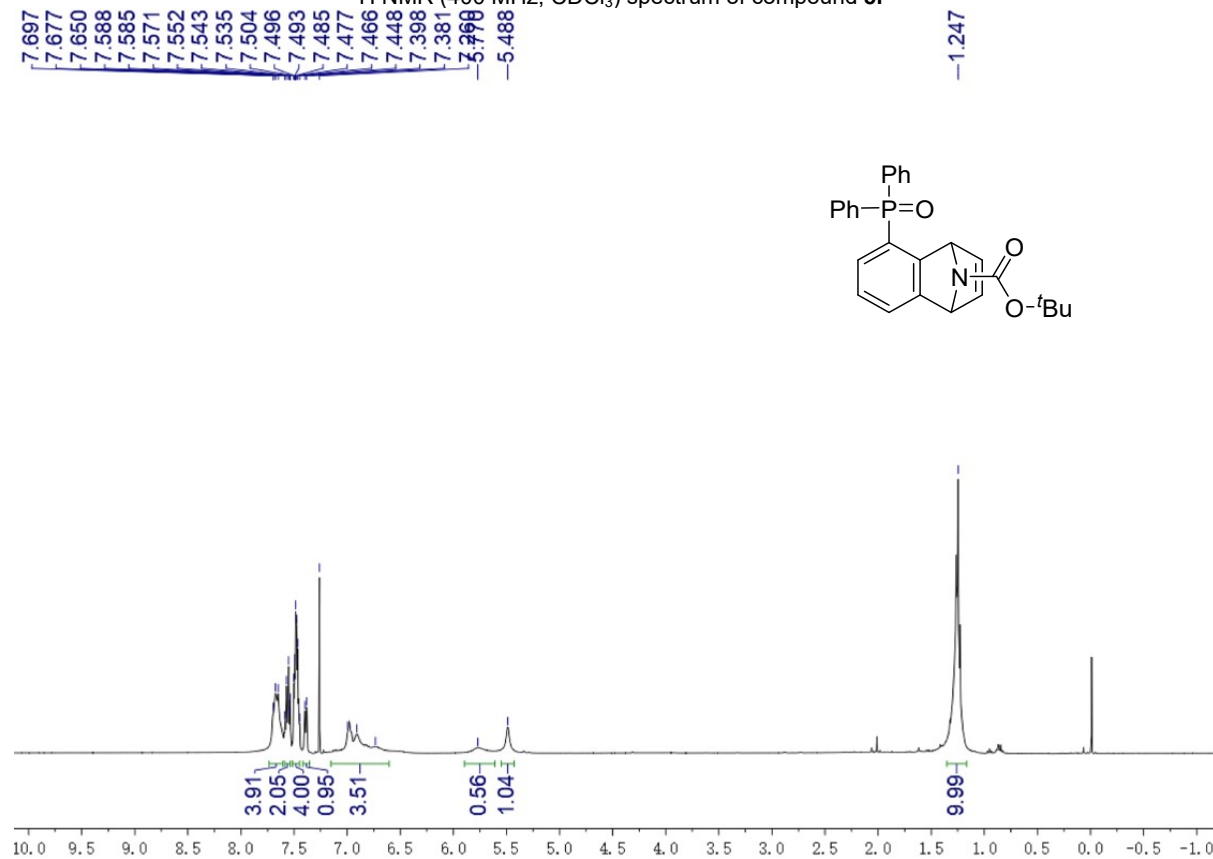


# SUPPORTING INFORMATION

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of compound **8h**

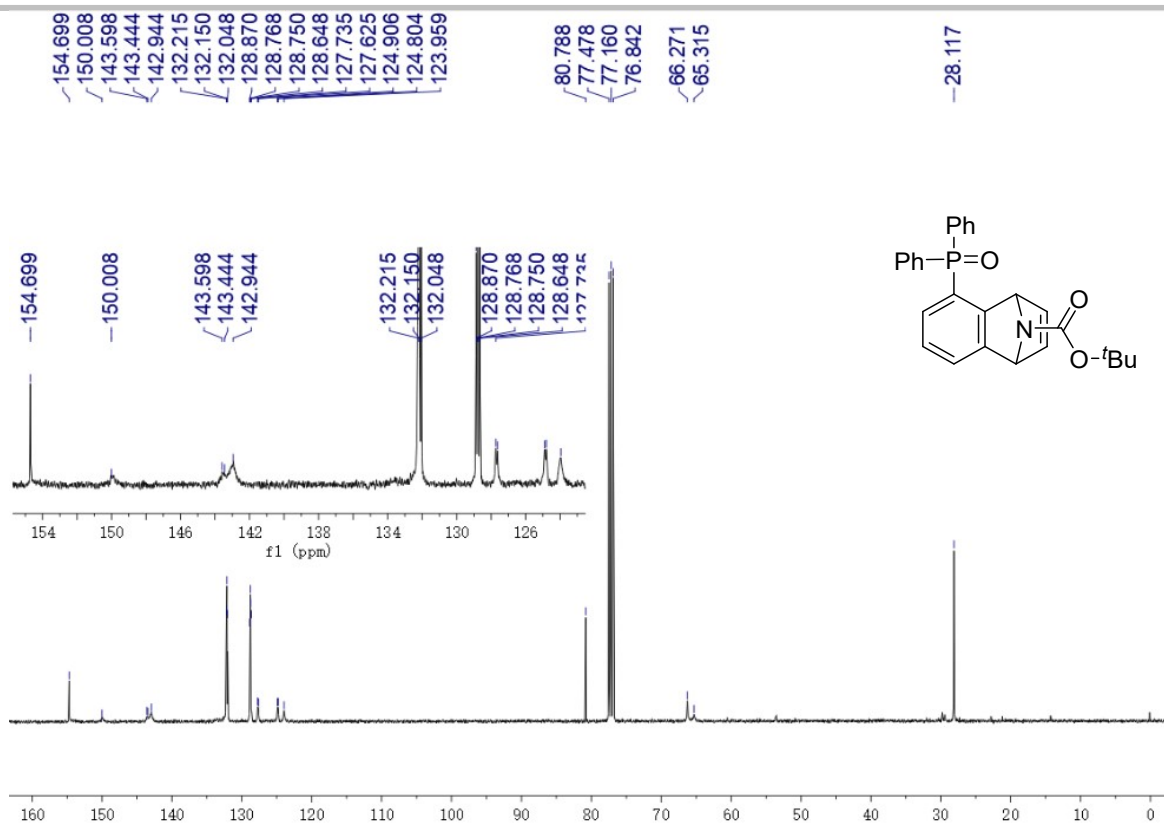


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of compound **8i**

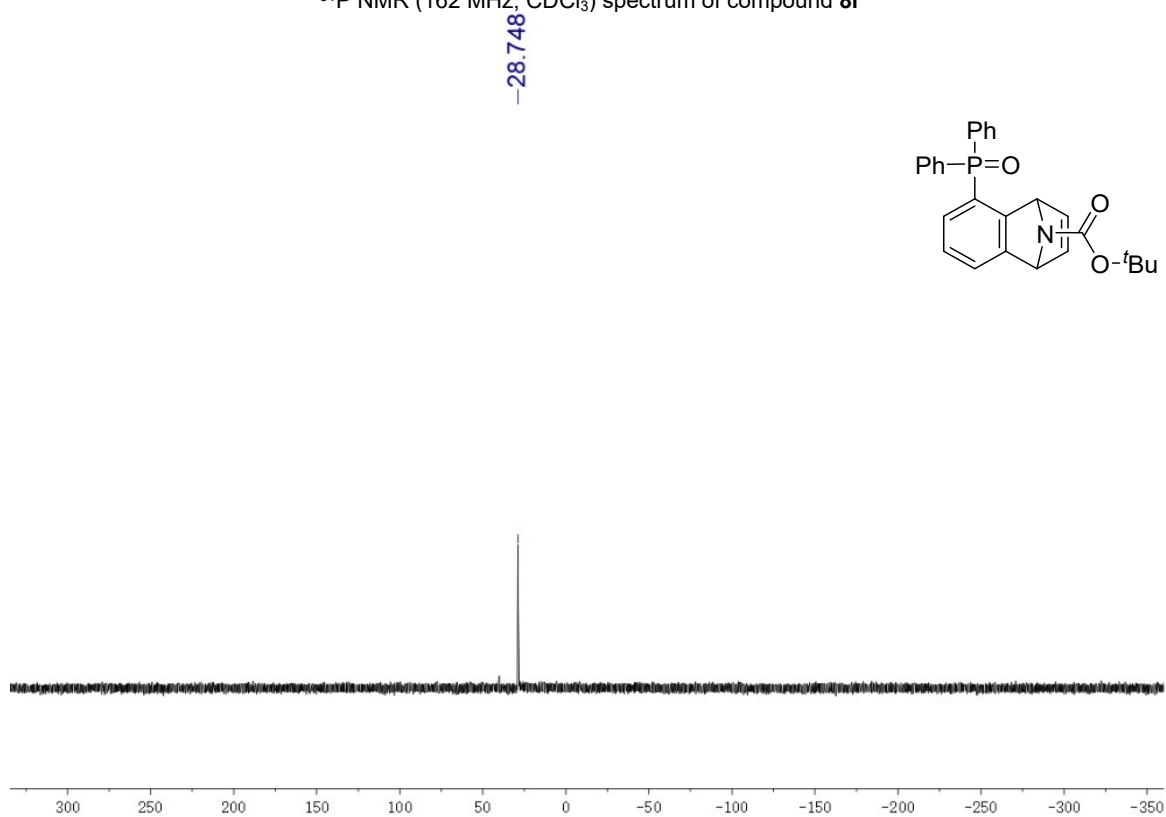


$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of compound **8i**

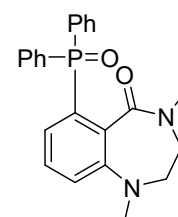
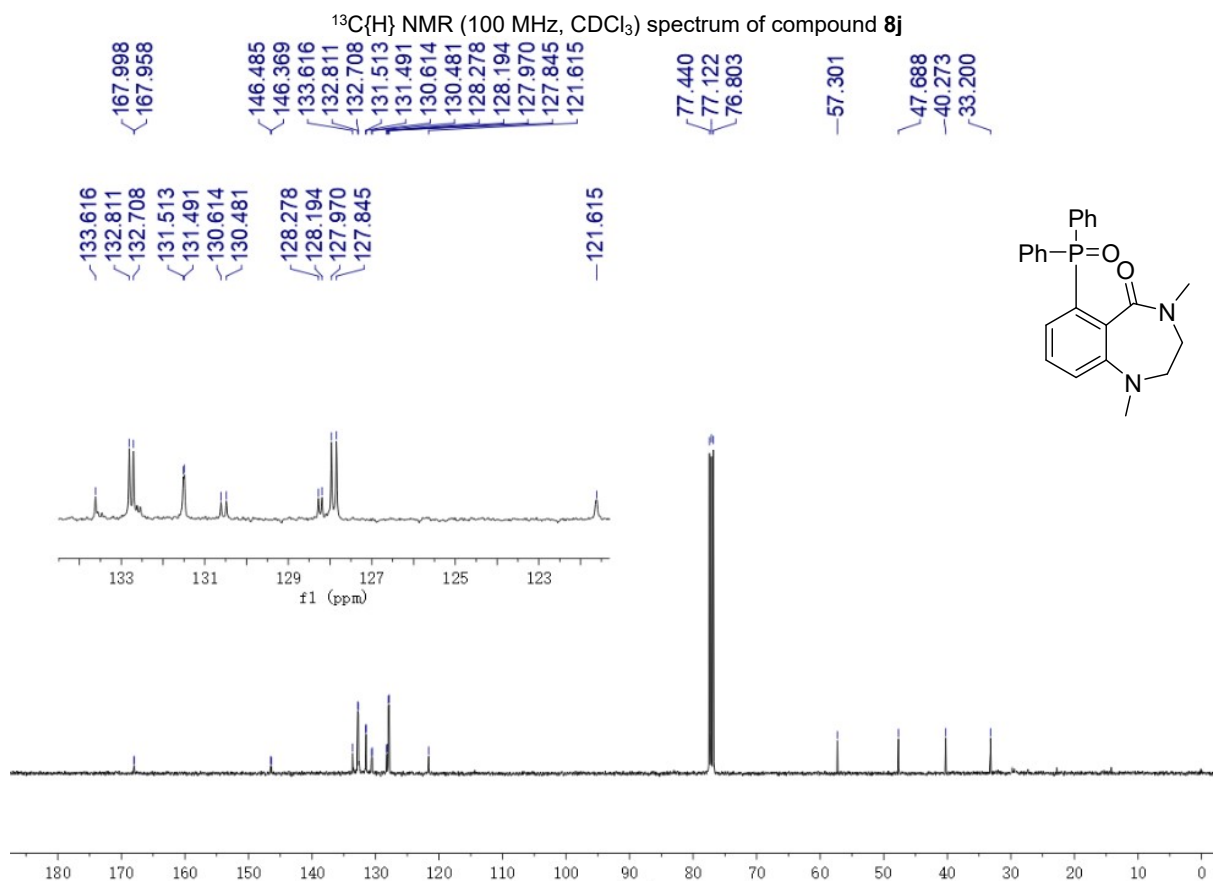
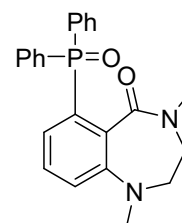
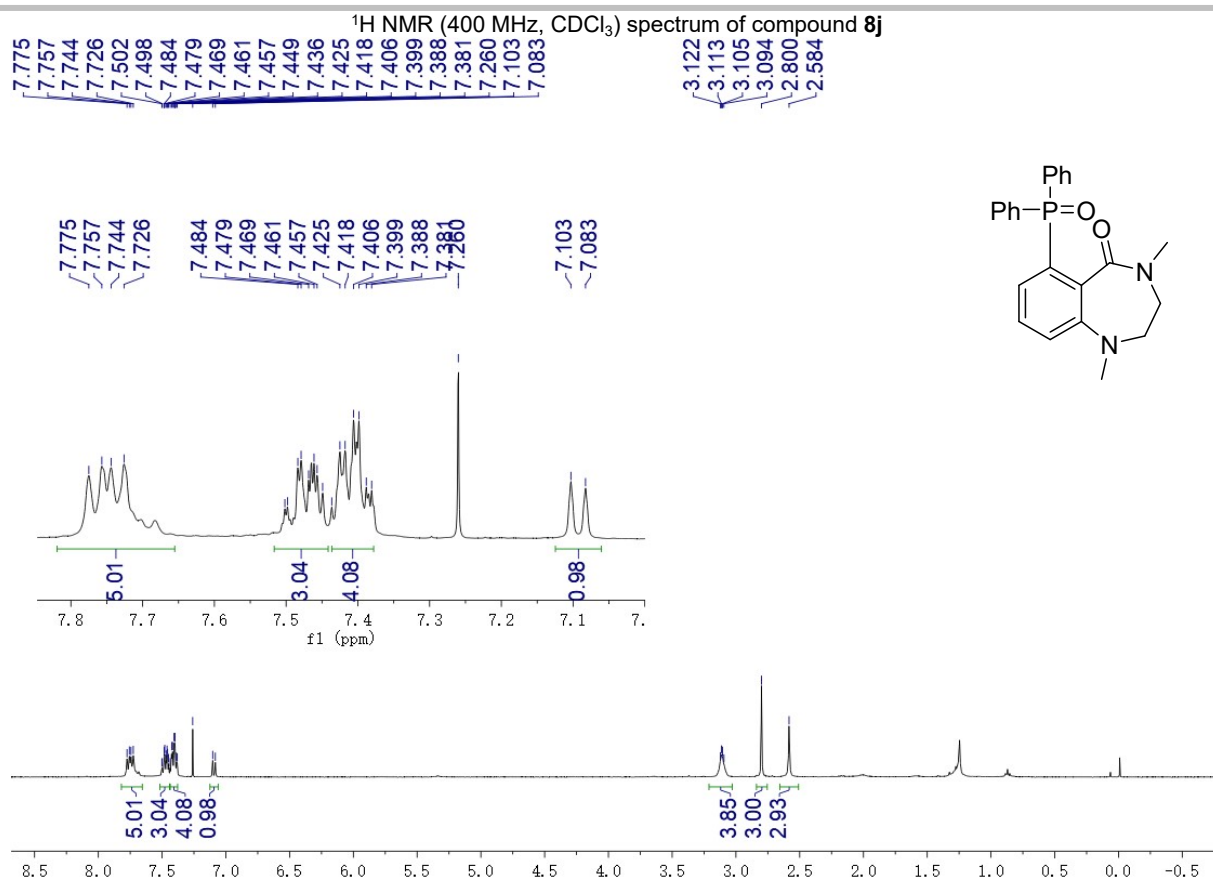
# SUPPORTING INFORMATION



<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) spectrum of compound **8i**

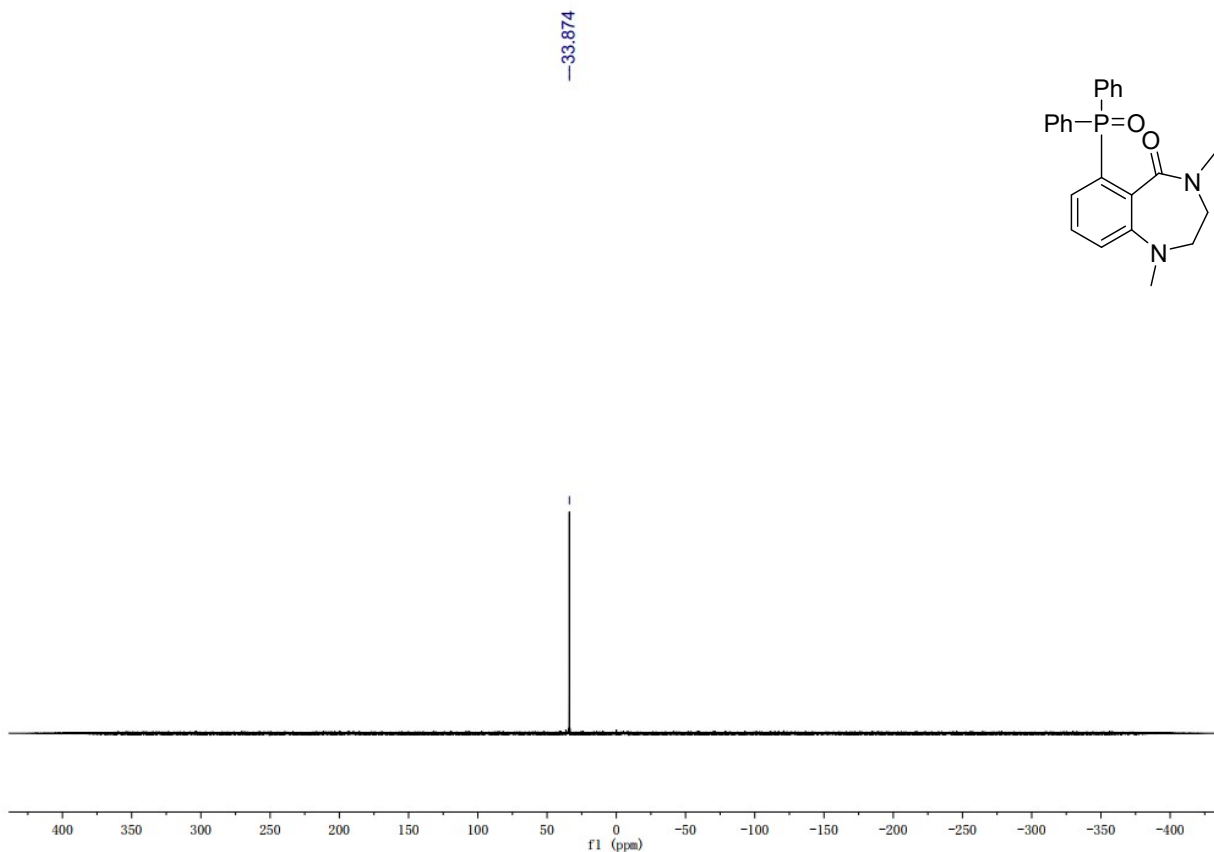


# SUPPORTING INFORMATION

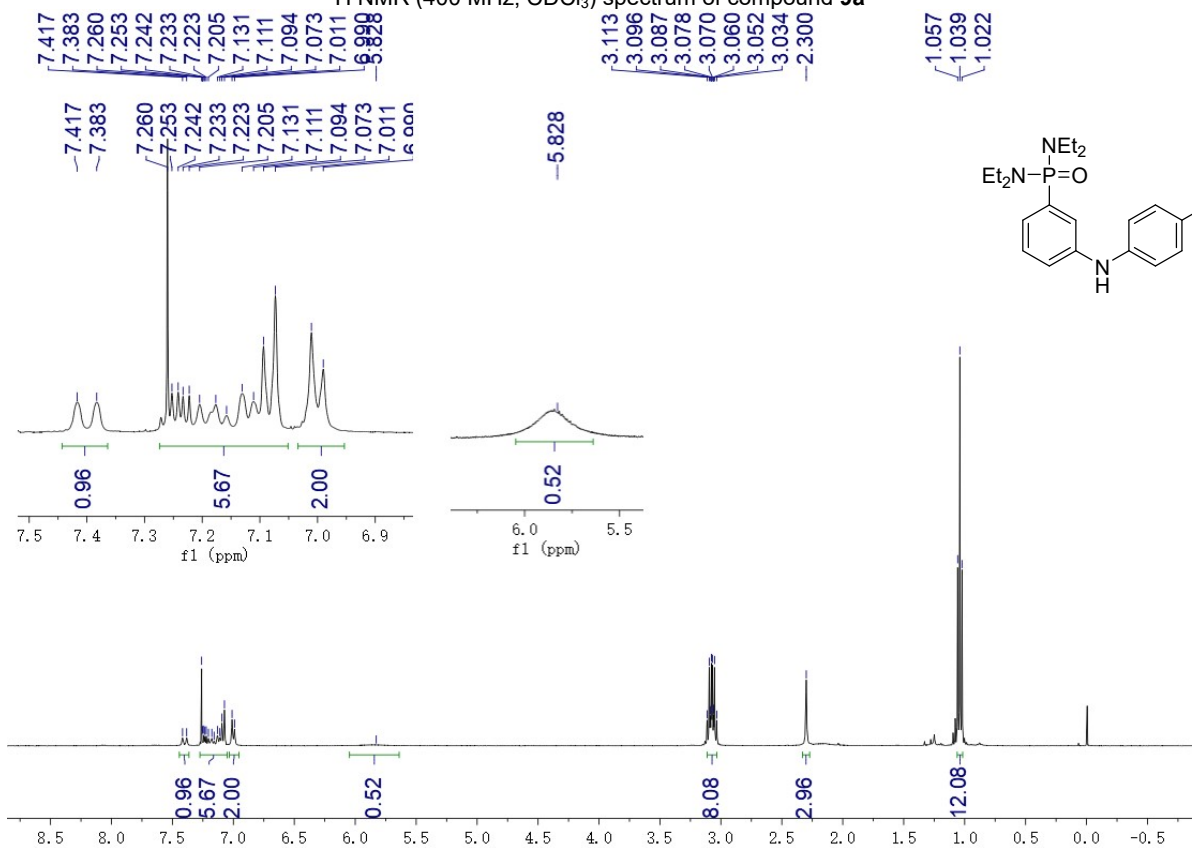


# SUPPORTING INFORMATION

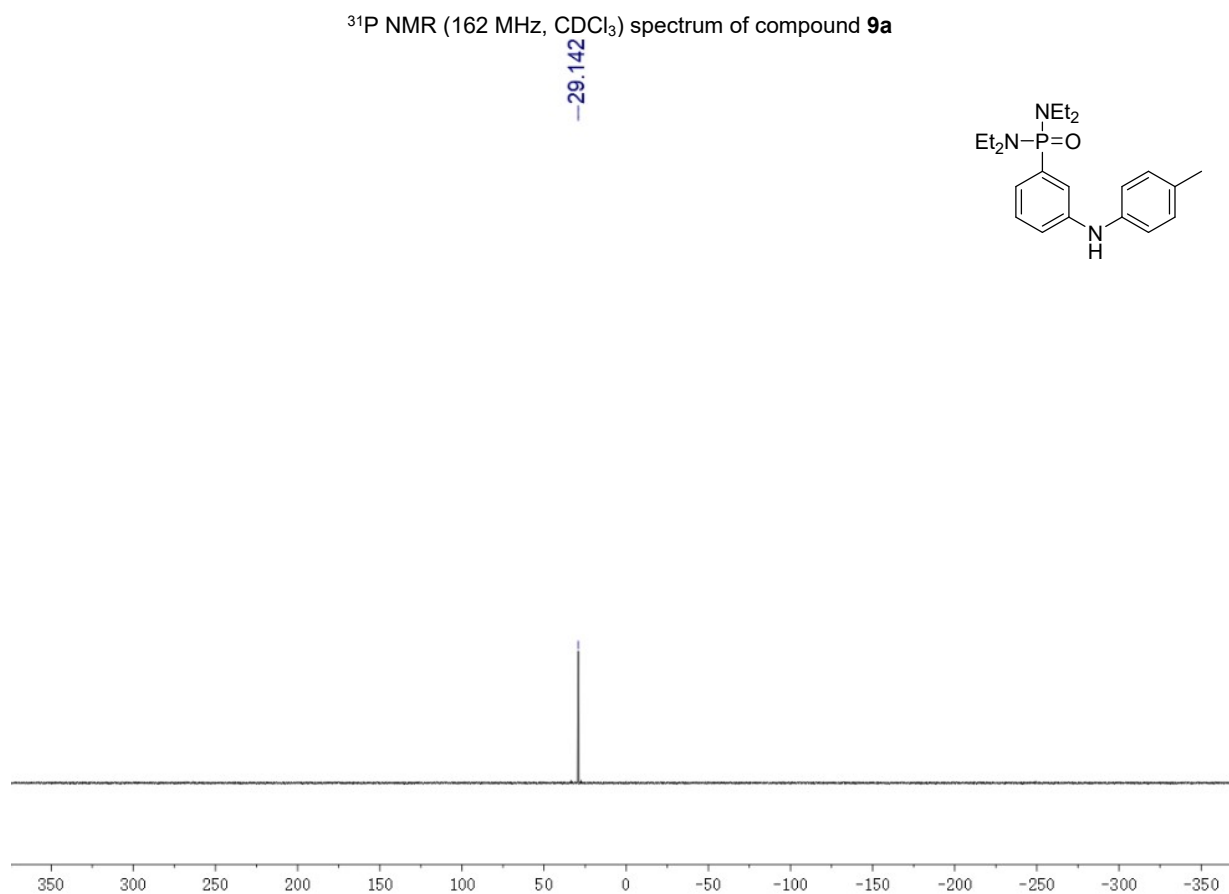
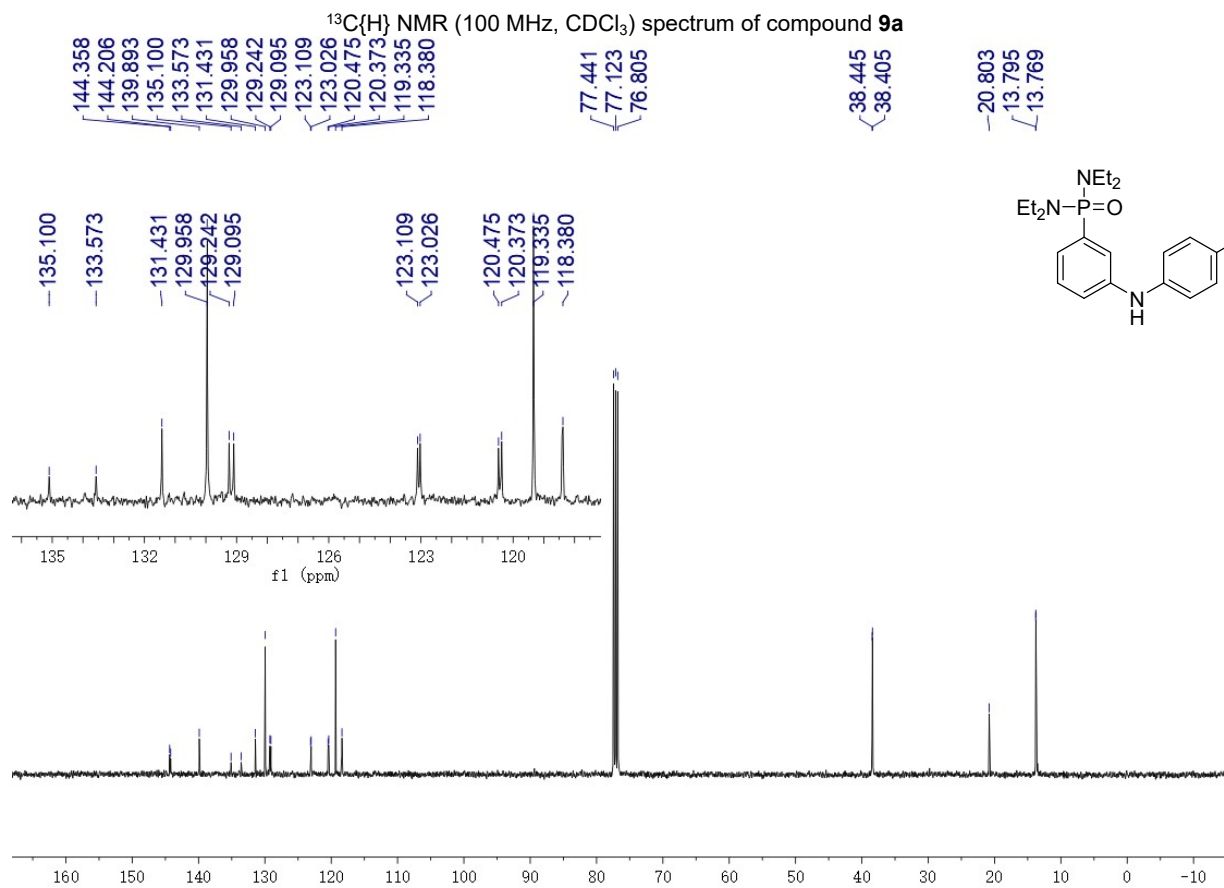
<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) spectrum of compound **8j**



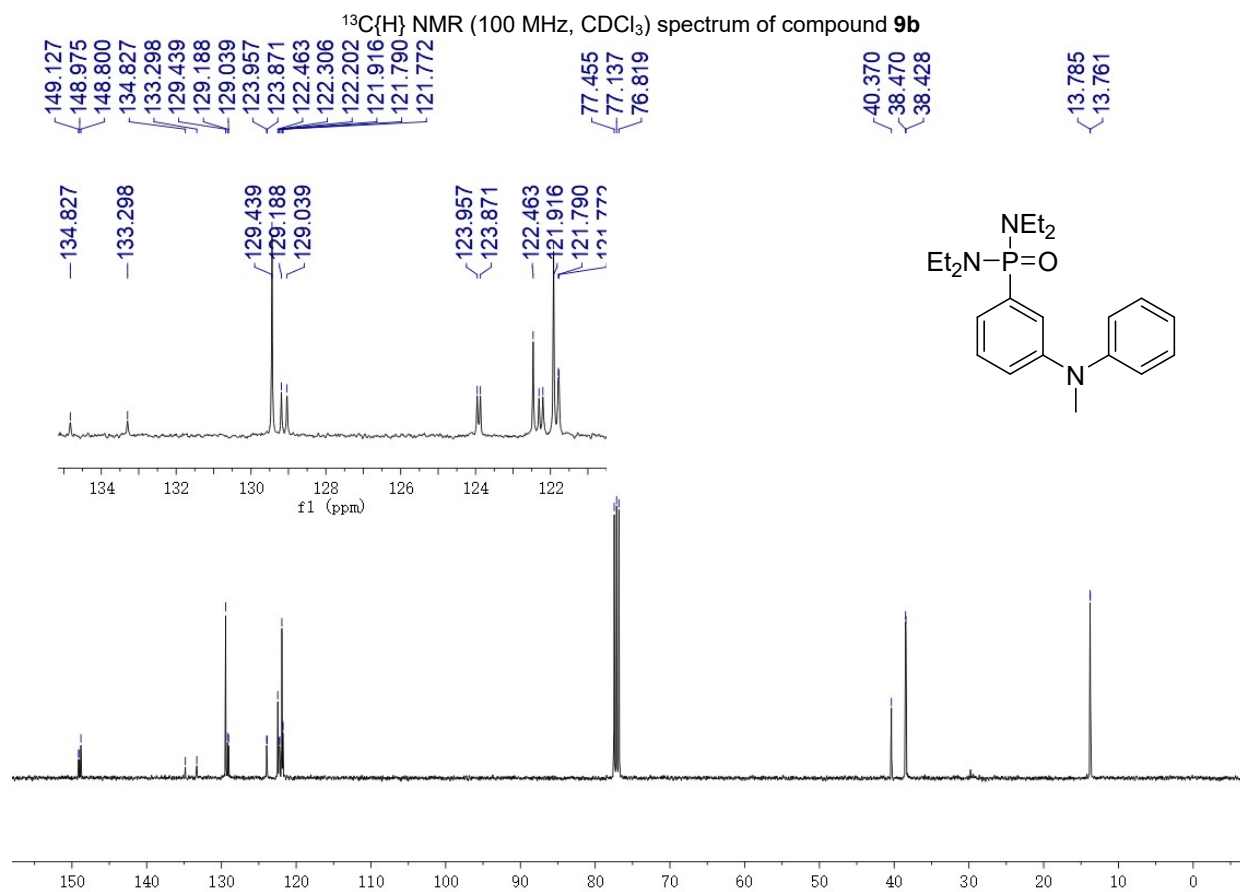
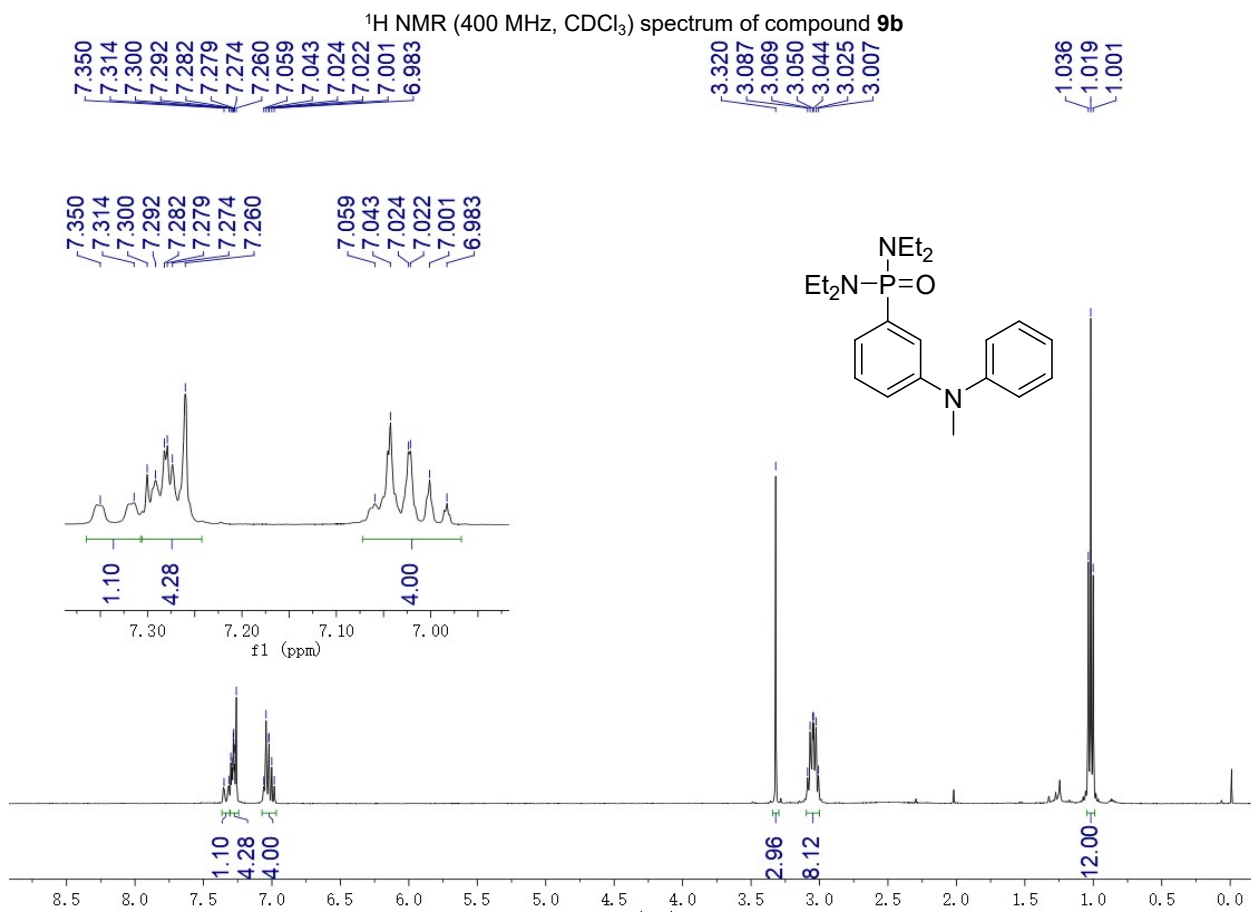
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound **9a**



# SUPPORTING INFORMATION



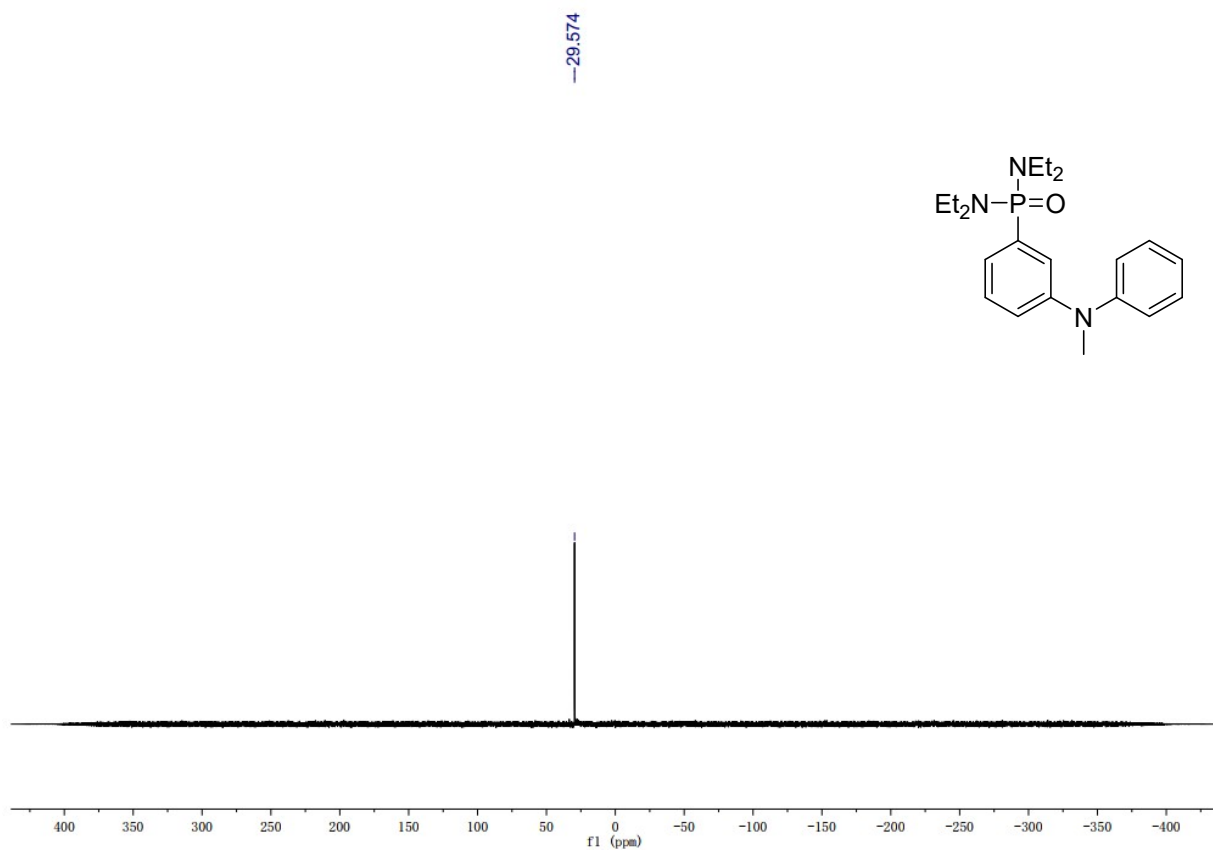
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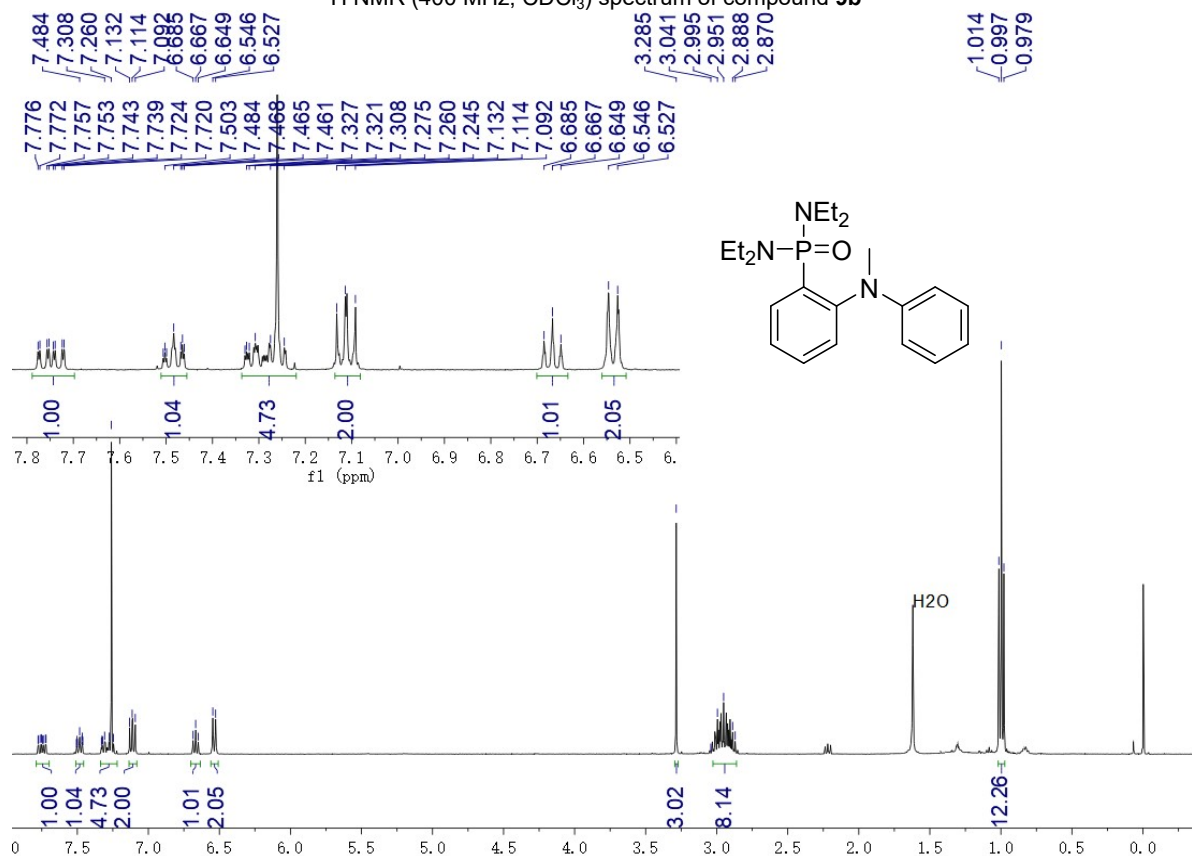


# SUPPORTING INFORMATION

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of compound **9b**

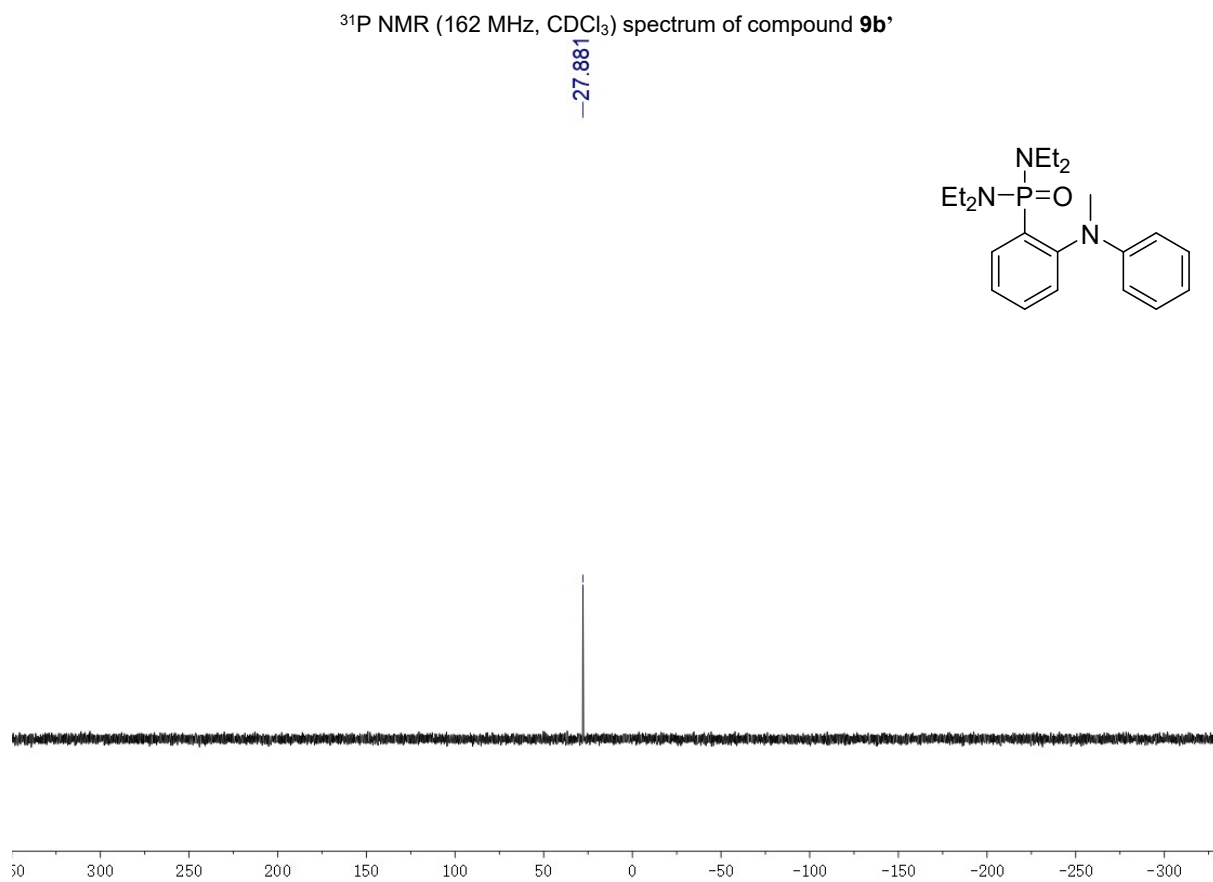
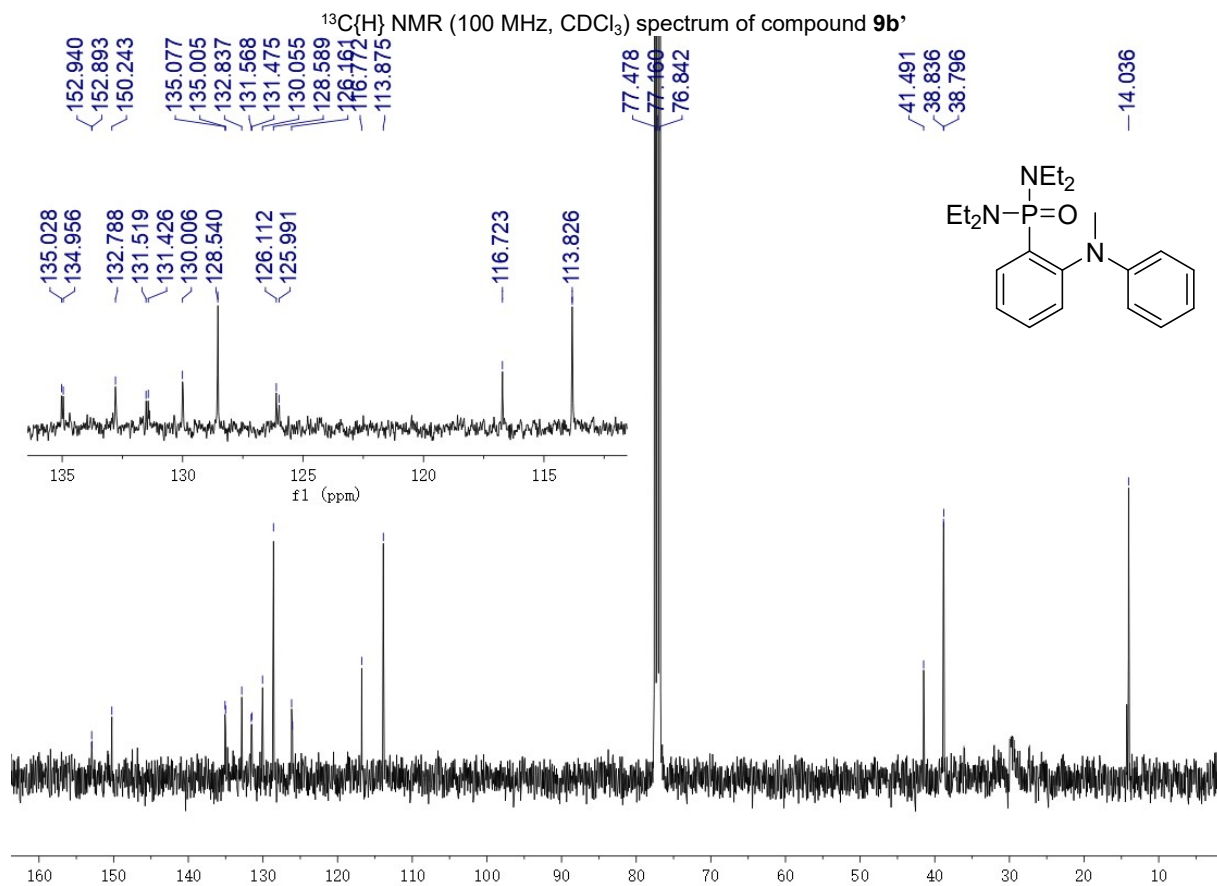


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of compound **9b'**

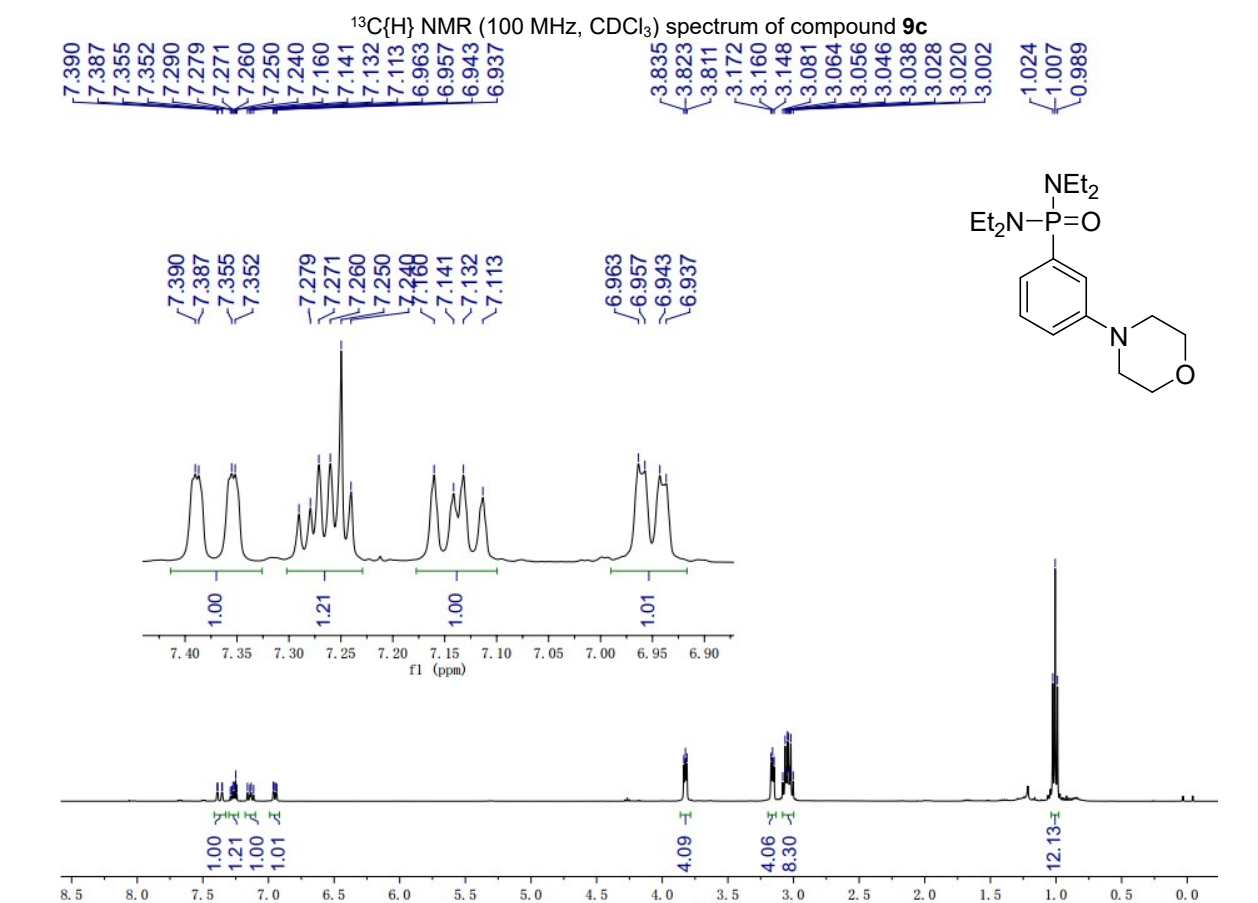
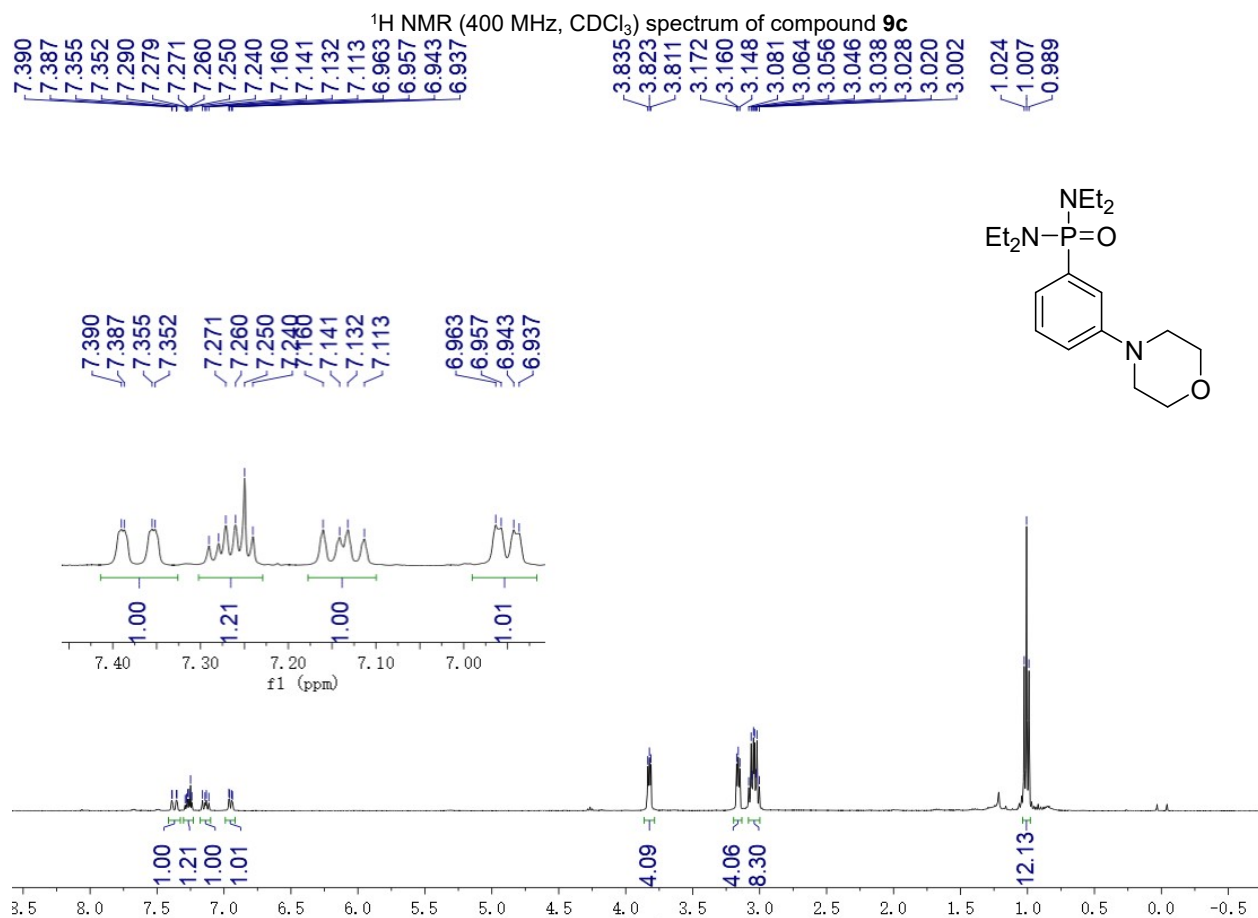




# SUPPORTING INFORMATION

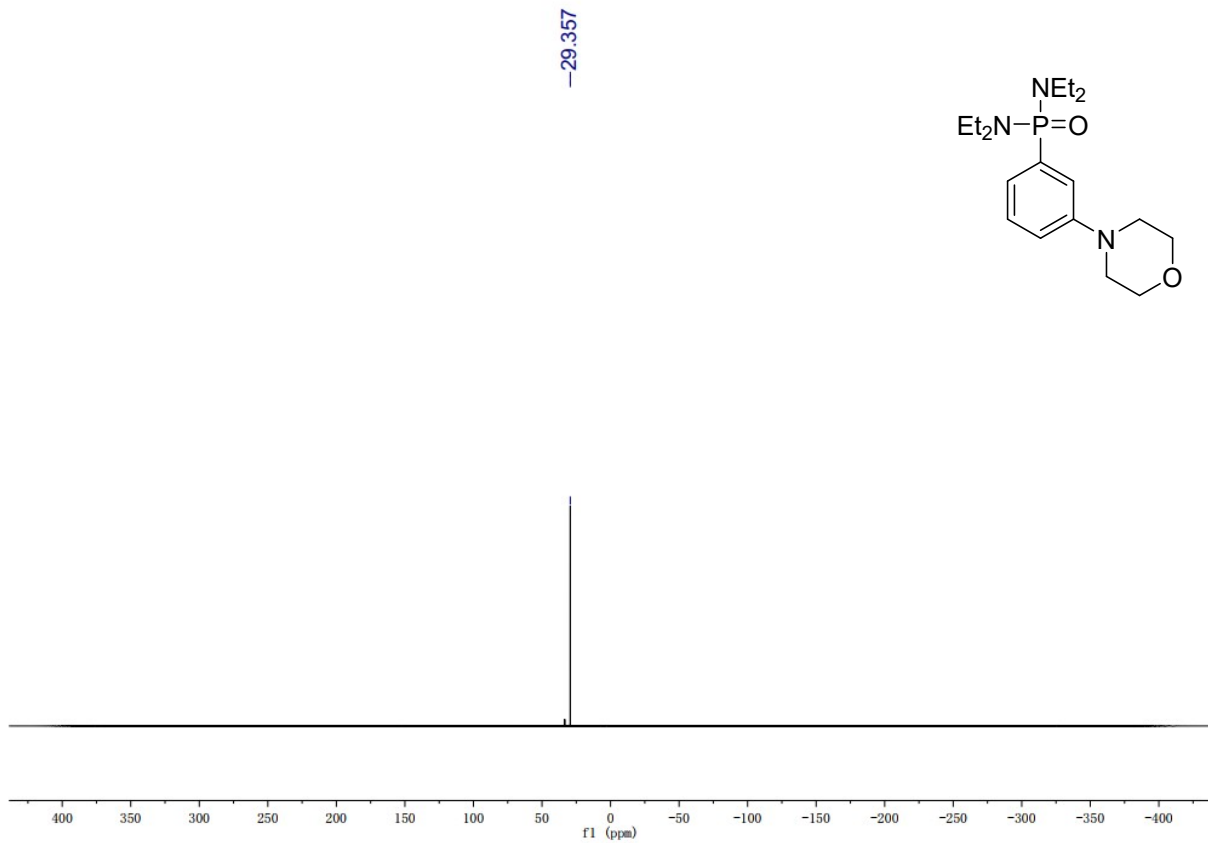


# SUPPORTING INFORMATION

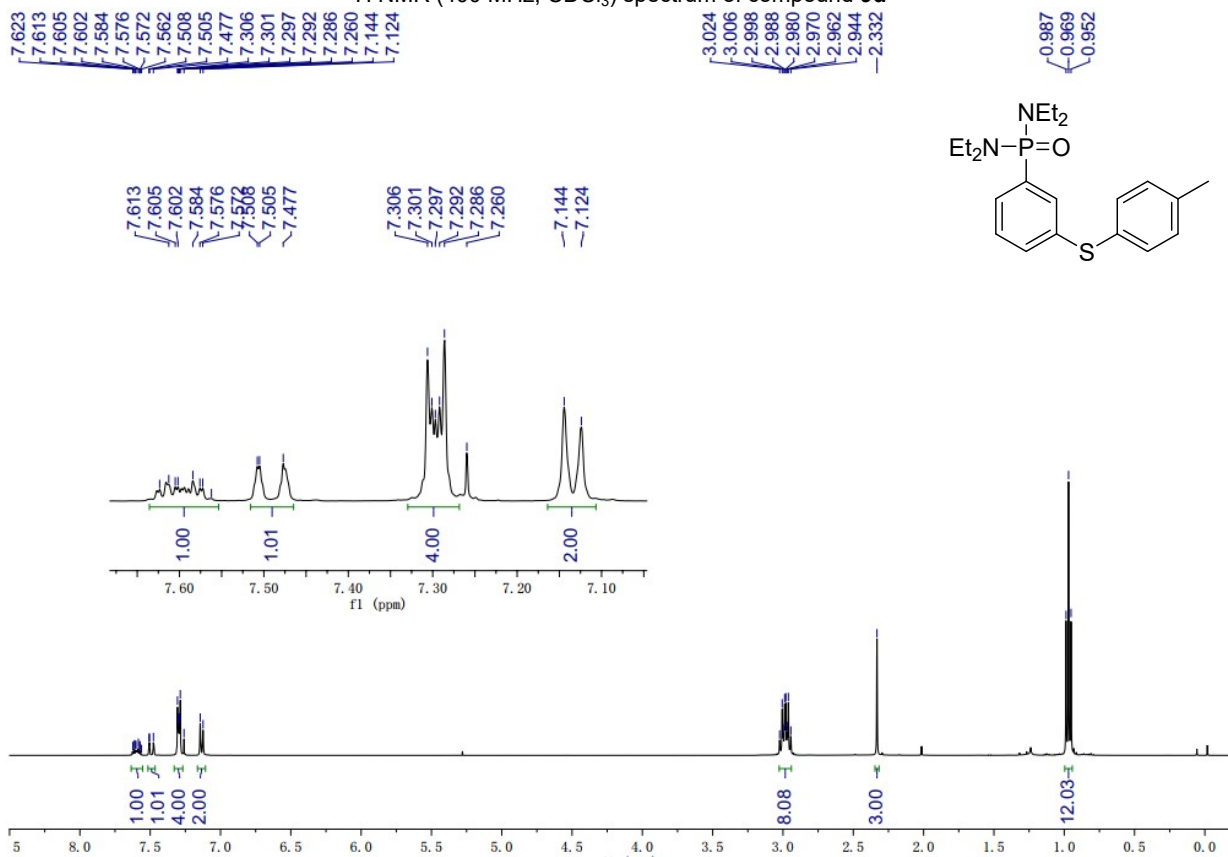


# SUPPORTING INFORMATION

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of compound **9c**

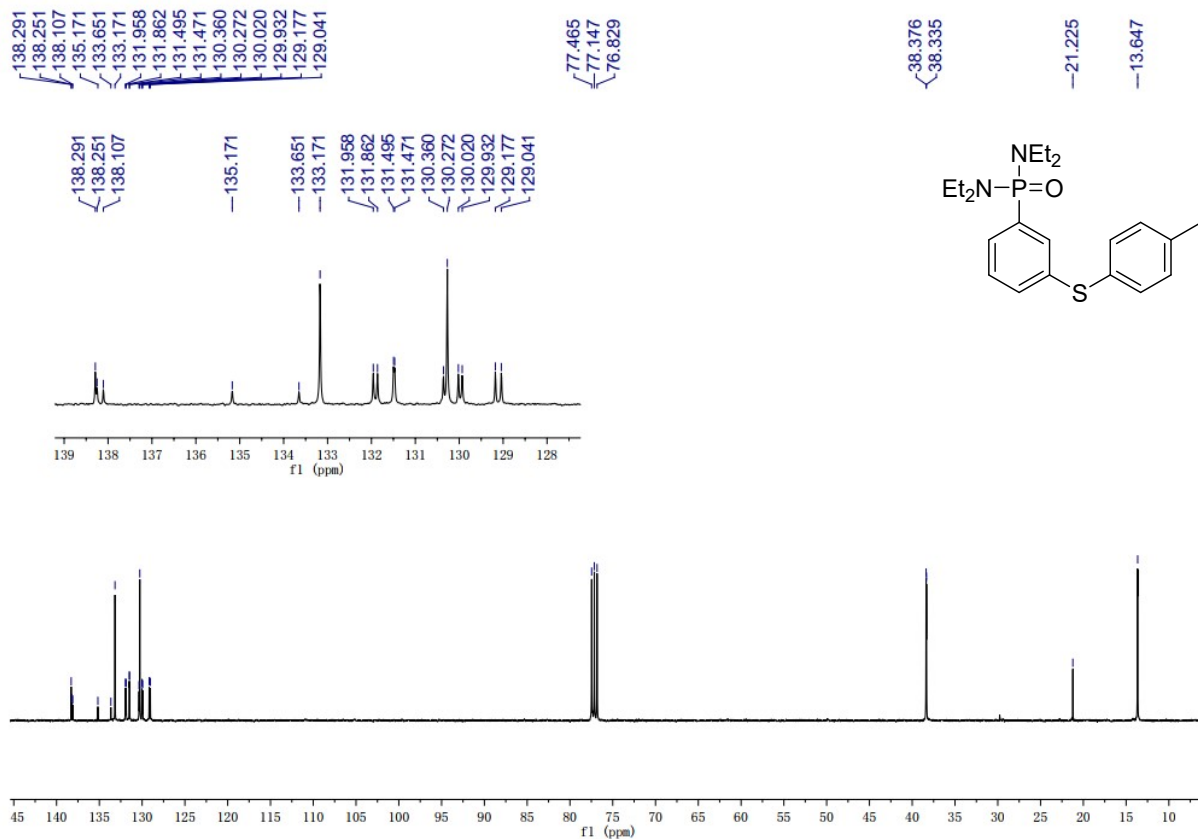


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of compound **9d**

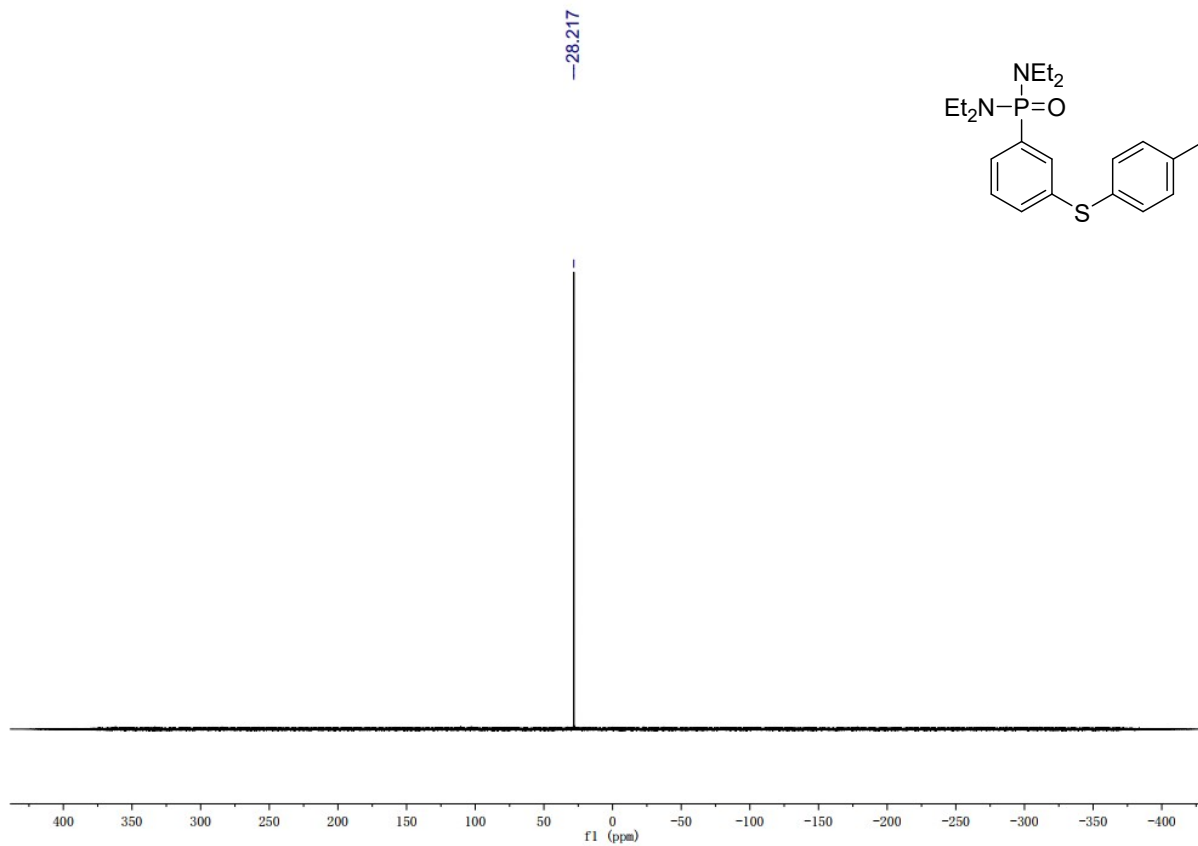


# SUPPORTING INFORMATION

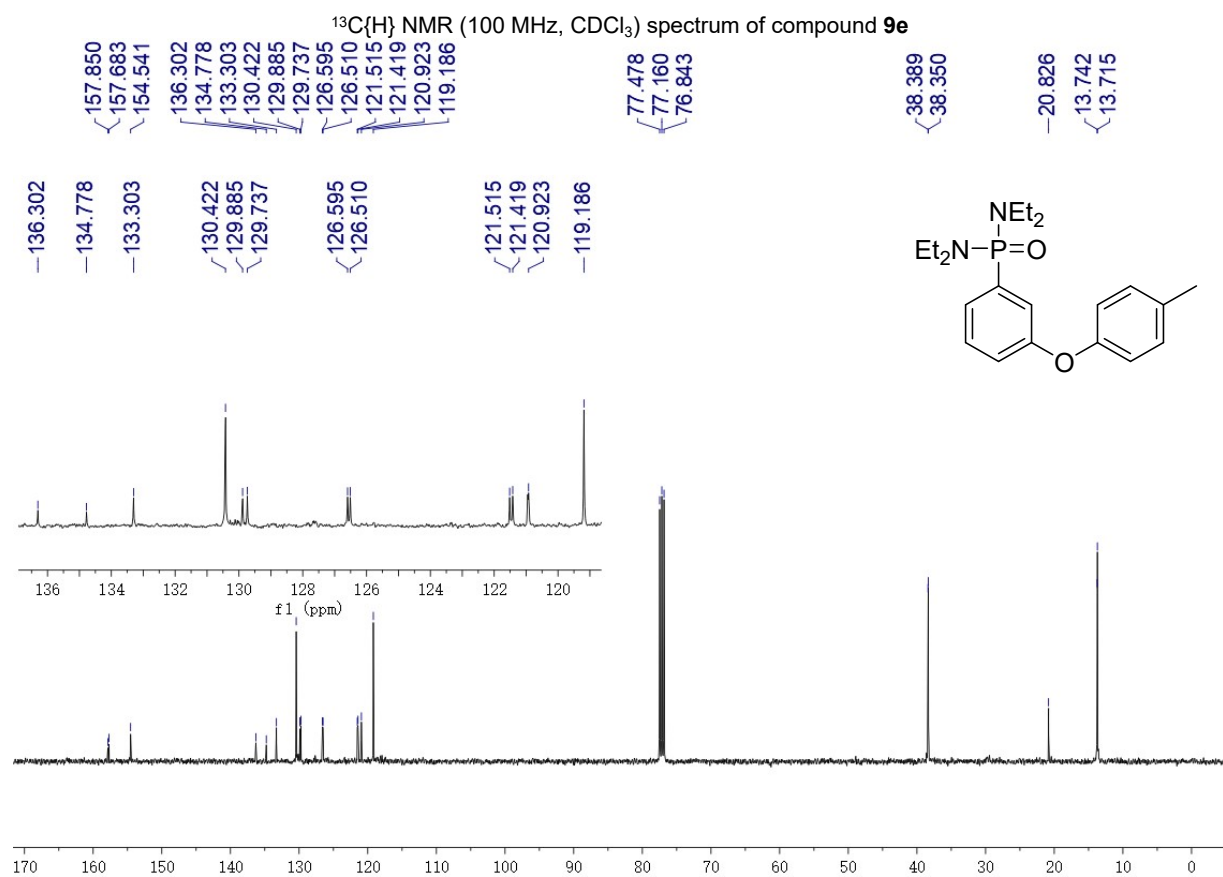
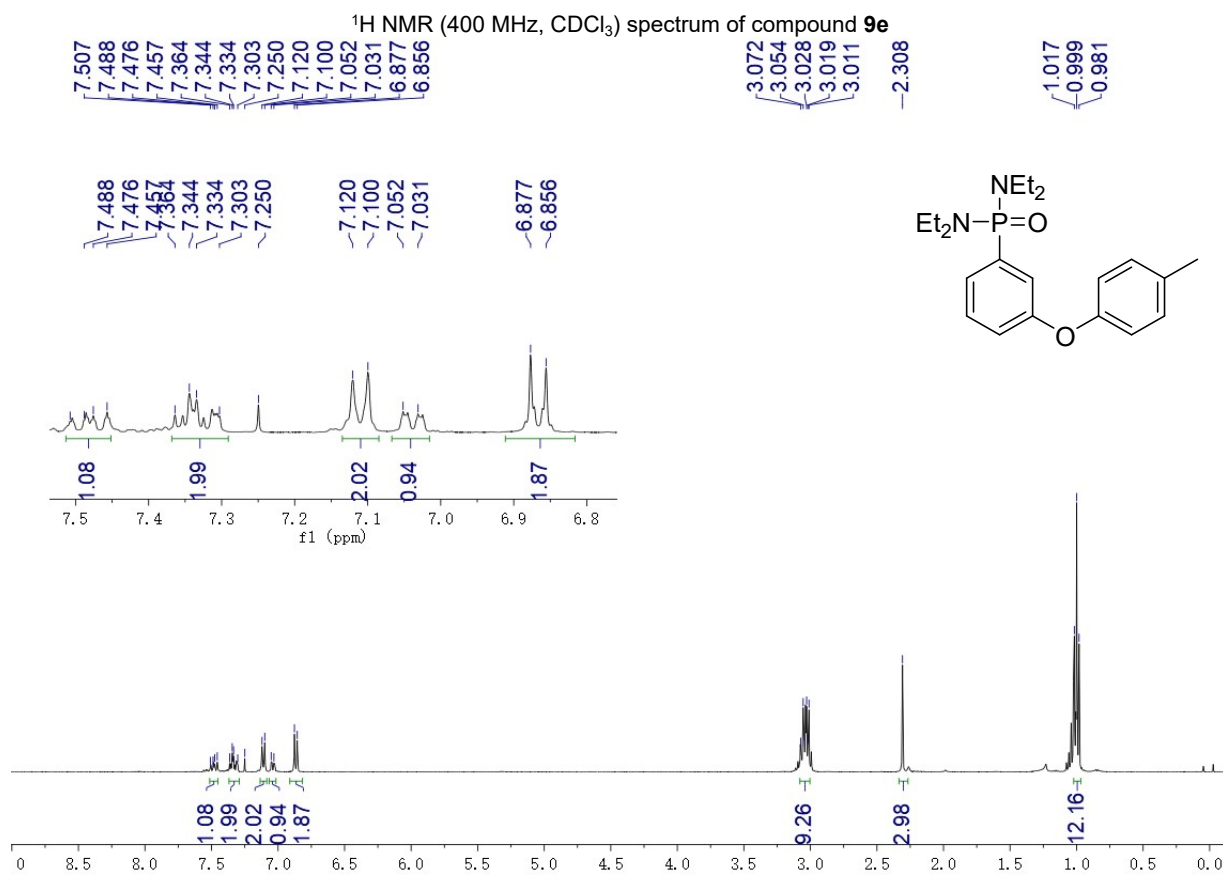
$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of compound **9d**



$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of compound **9d**

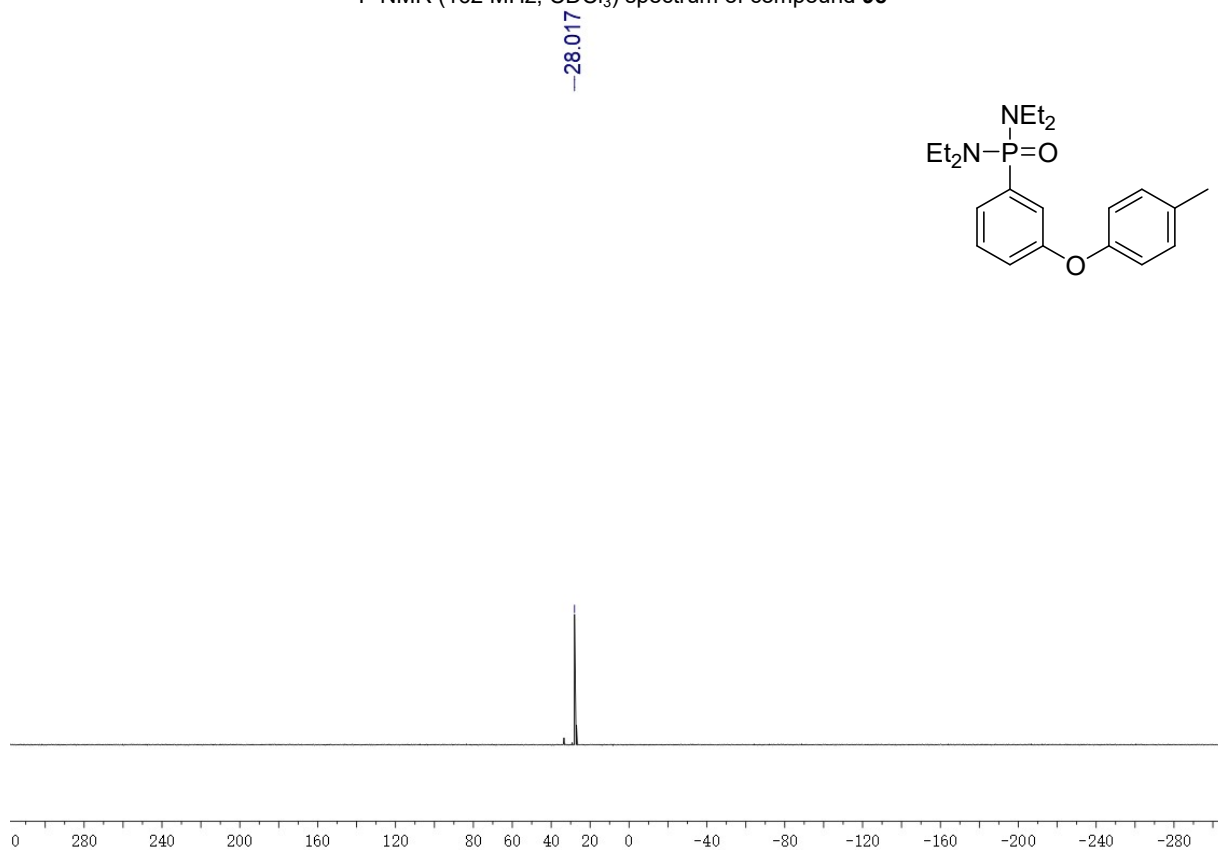


# SUPPORTING INFORMATION

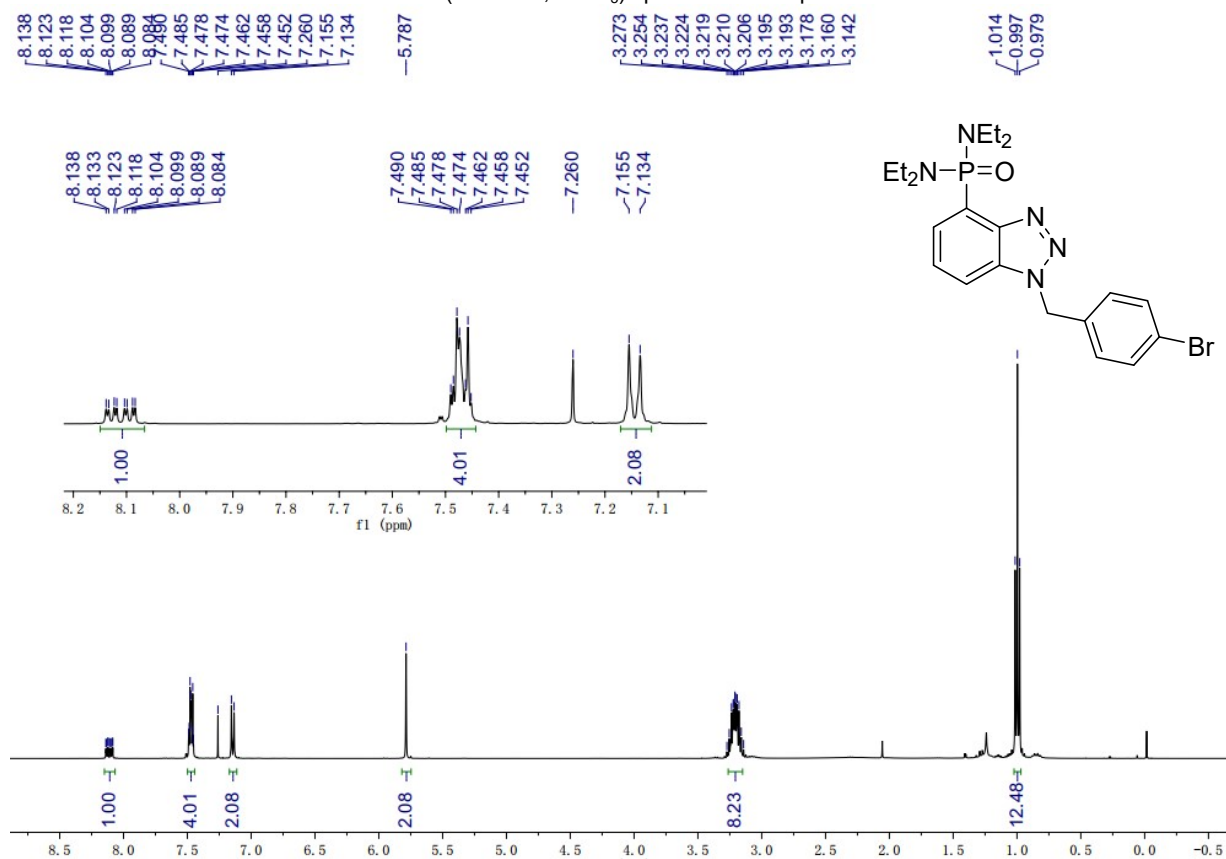


# SUPPORTING INFORMATION

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of compound **9e**

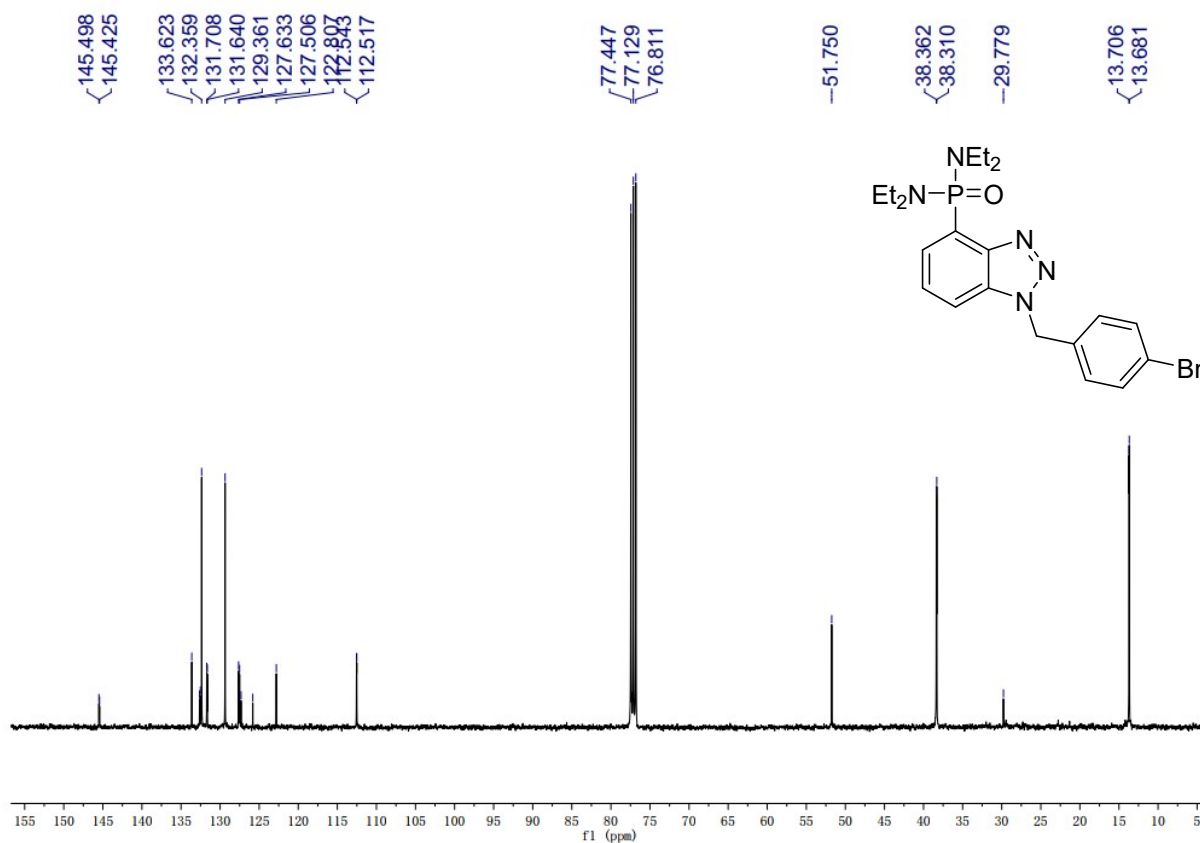


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of compound **9f**

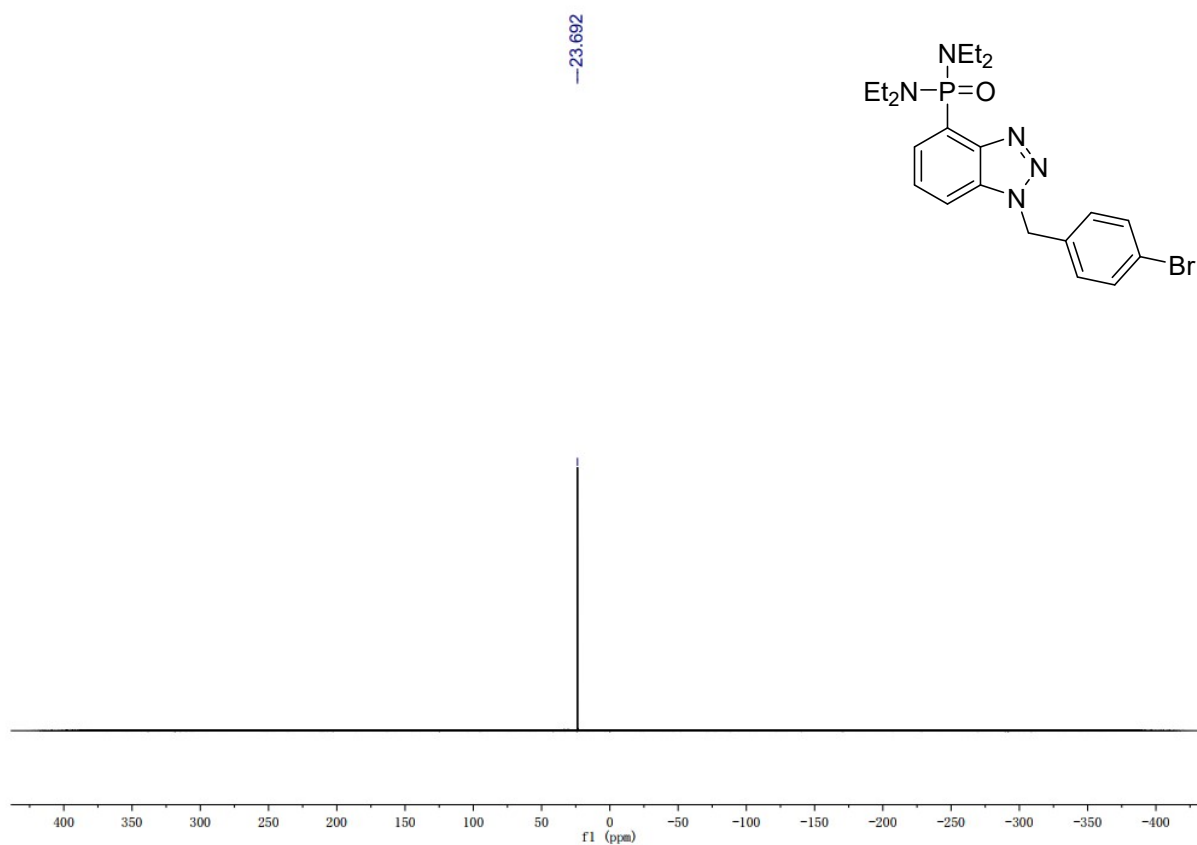


# SUPPORTING INFORMATION

$^{13}\text{C}\{\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of compound **9f**

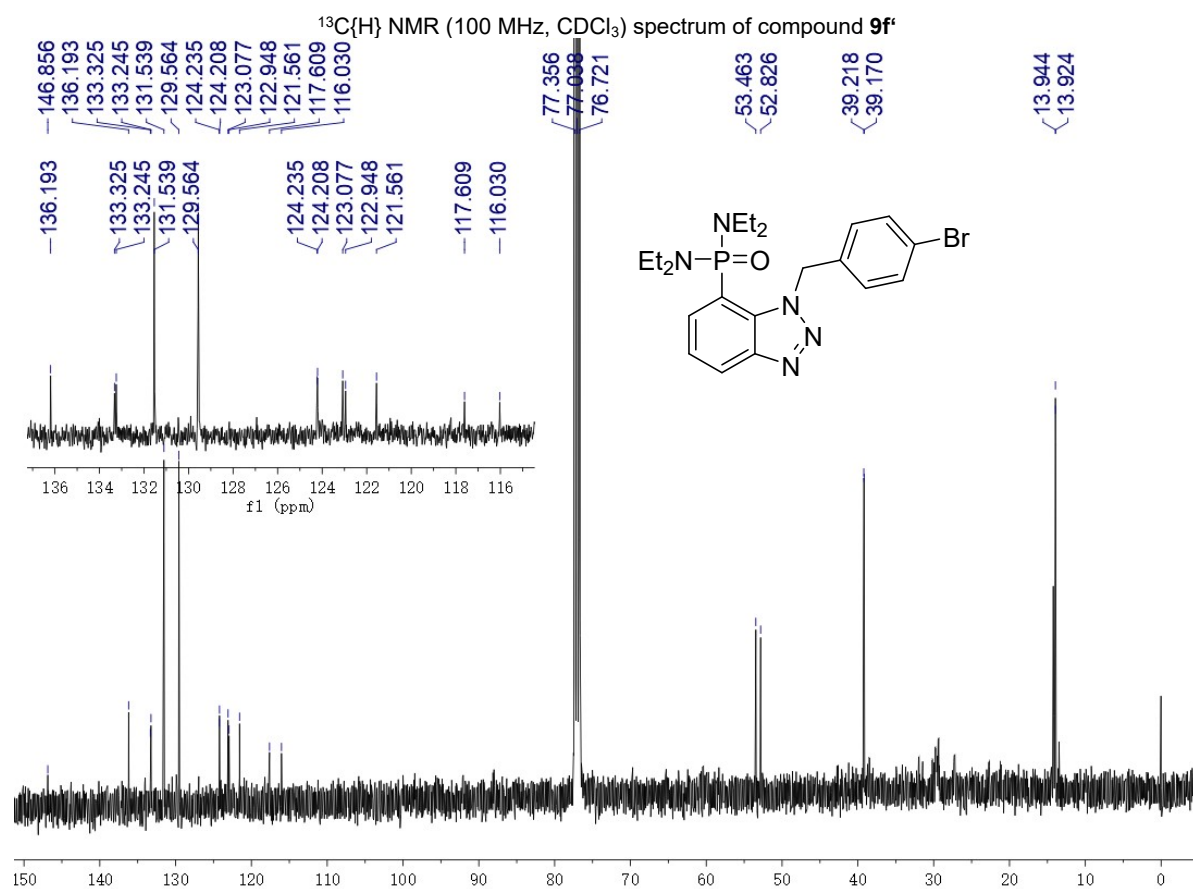
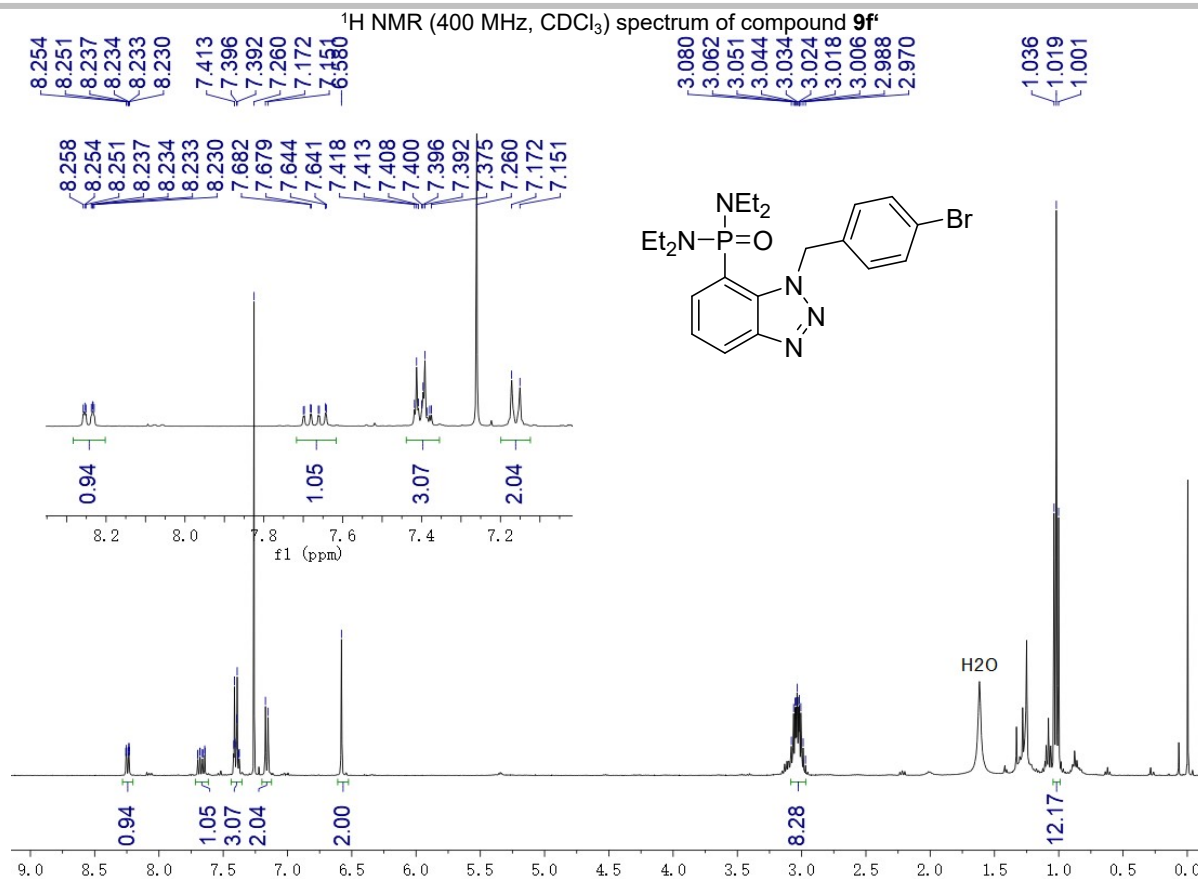


$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of compound **9f**





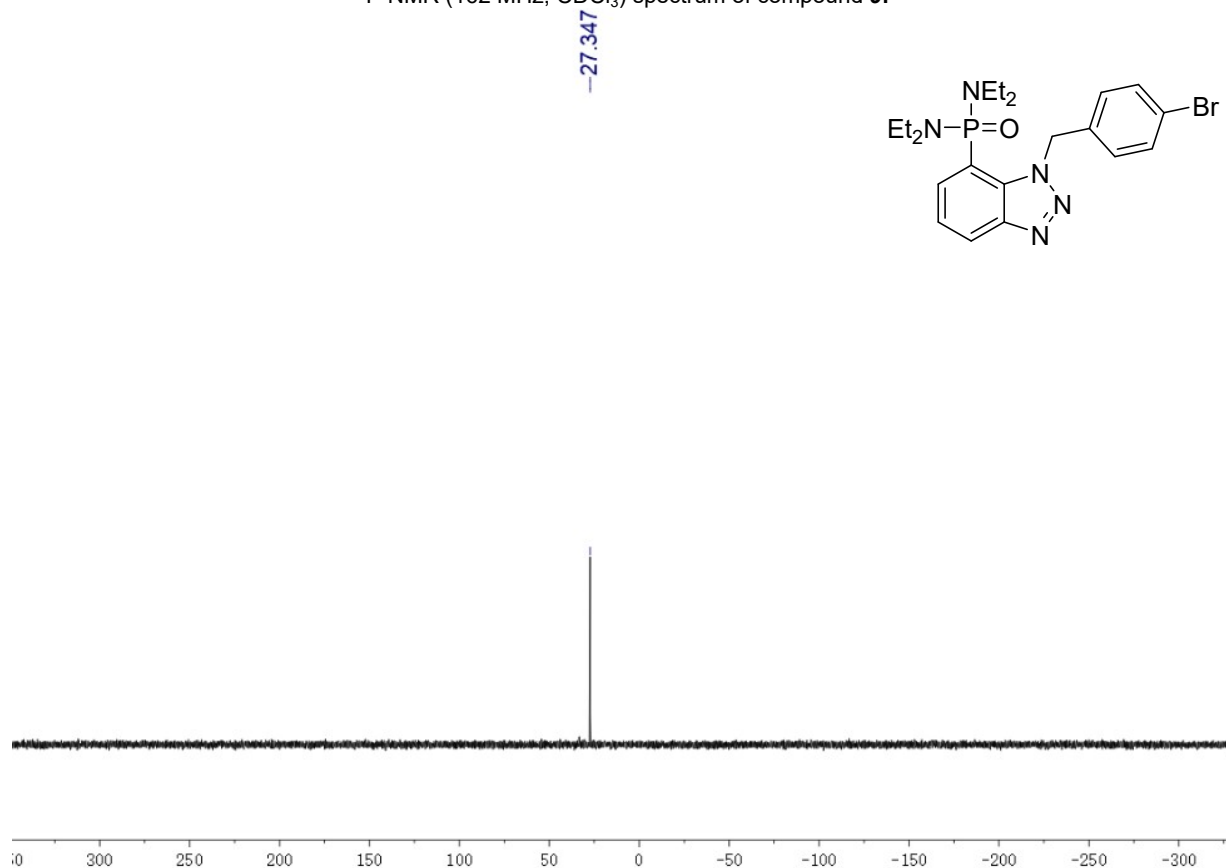
# SUPPORTING INFORMATION



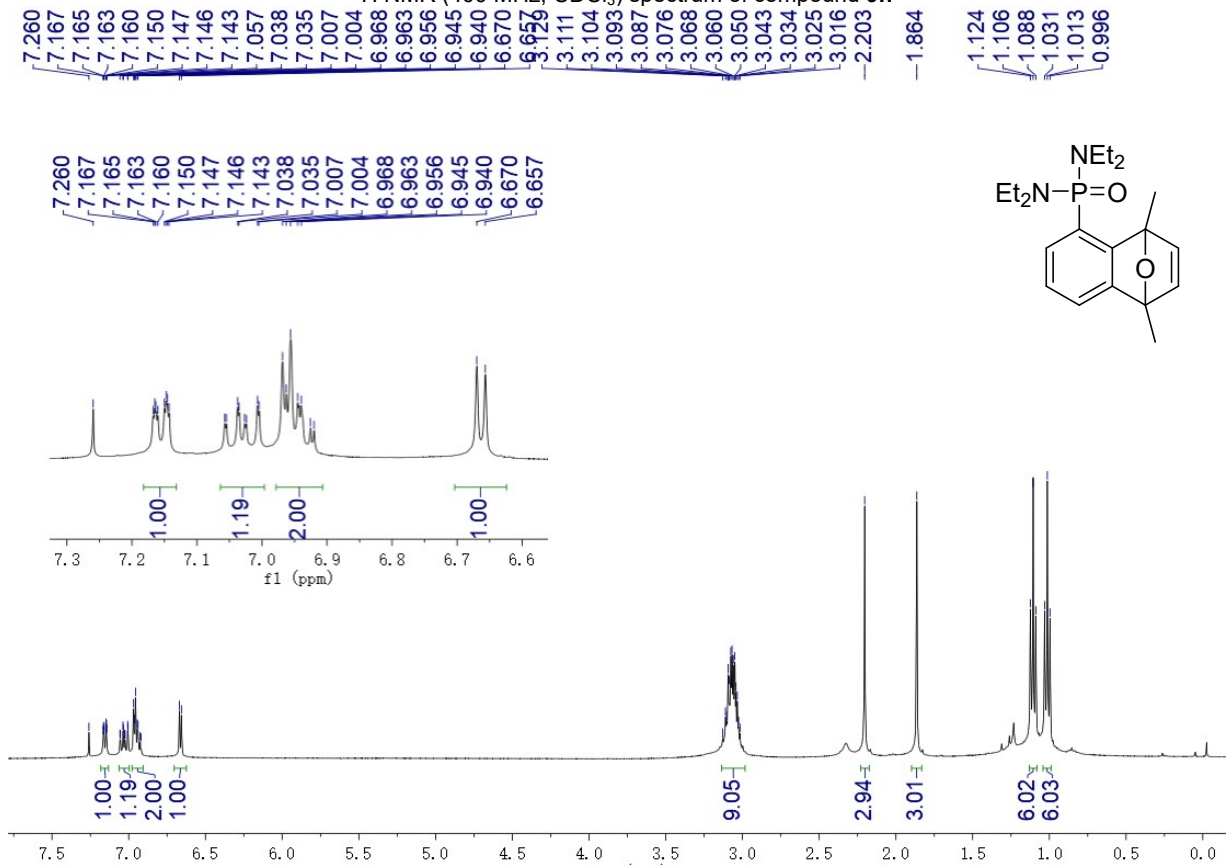


# SUPPORTING INFORMATION

<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) spectrum of compound **9f**

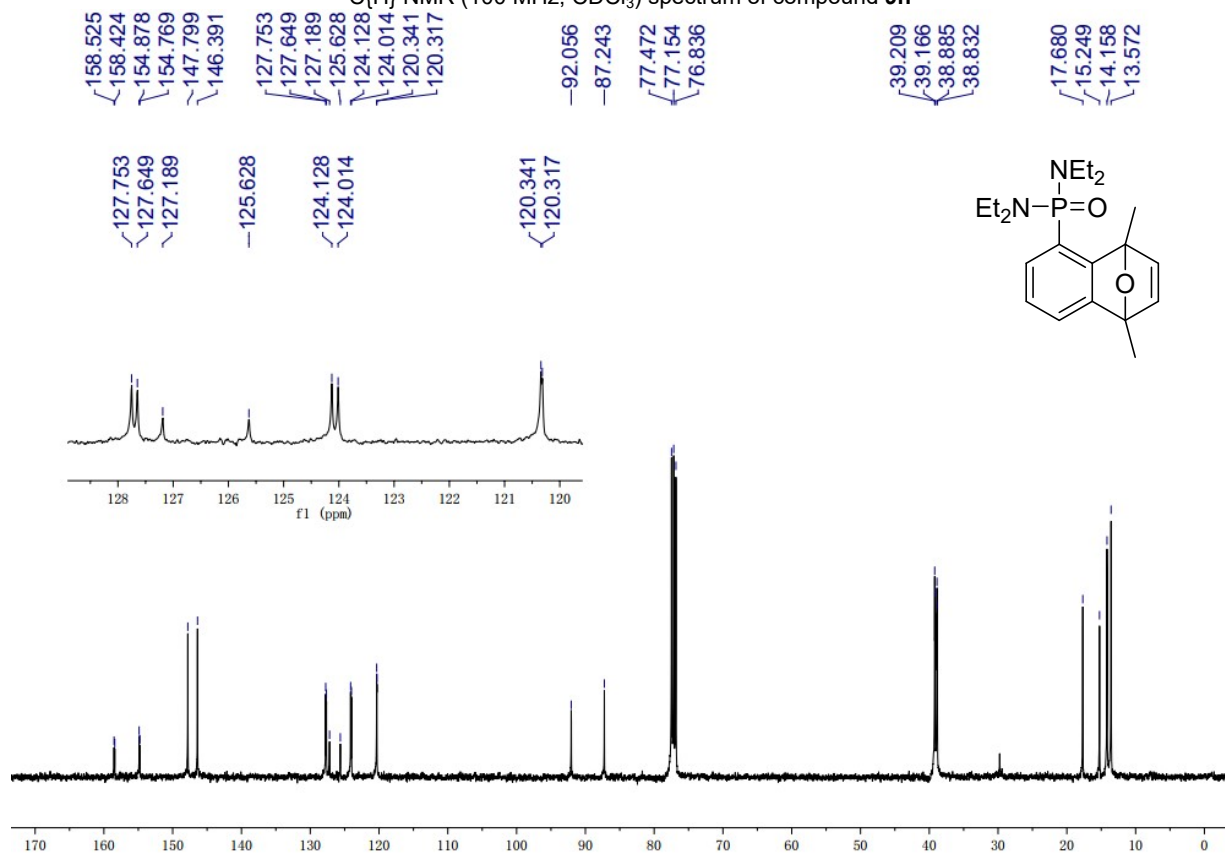


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound **9h**

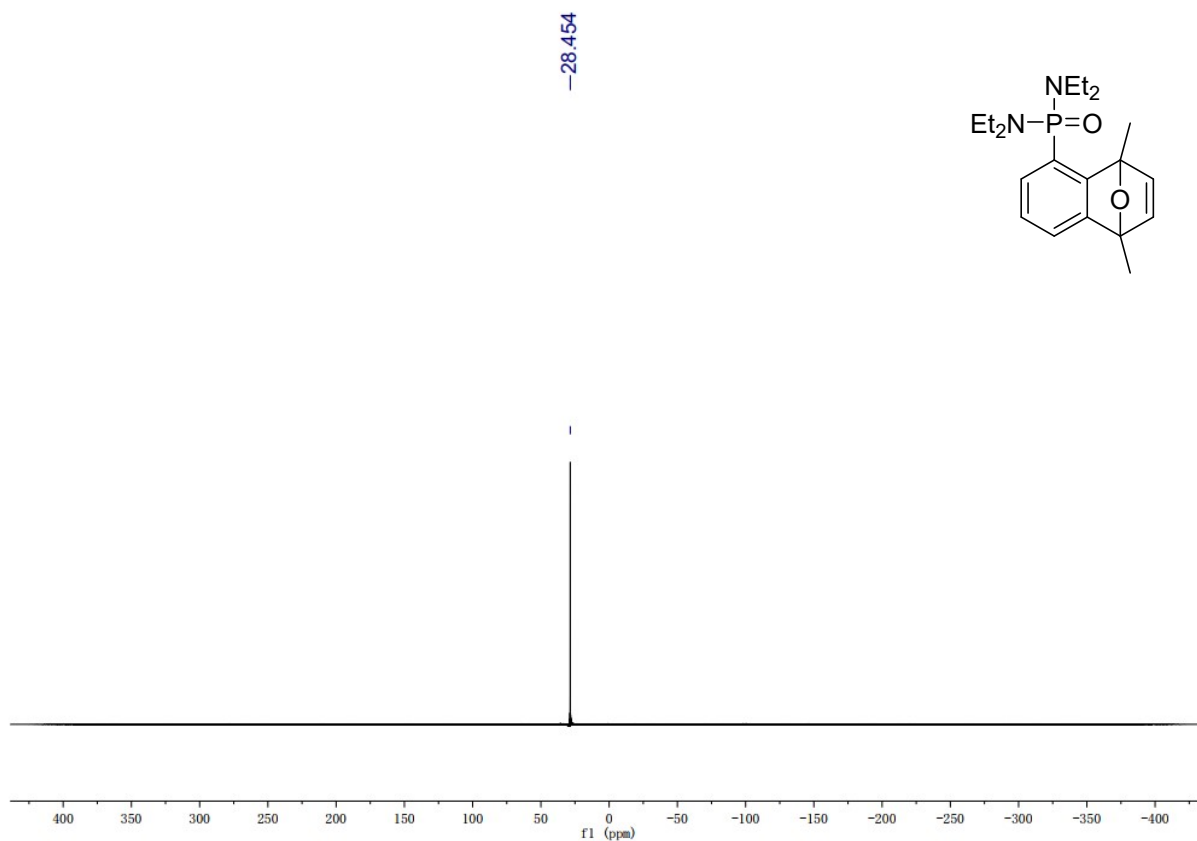


# SUPPORTING INFORMATION

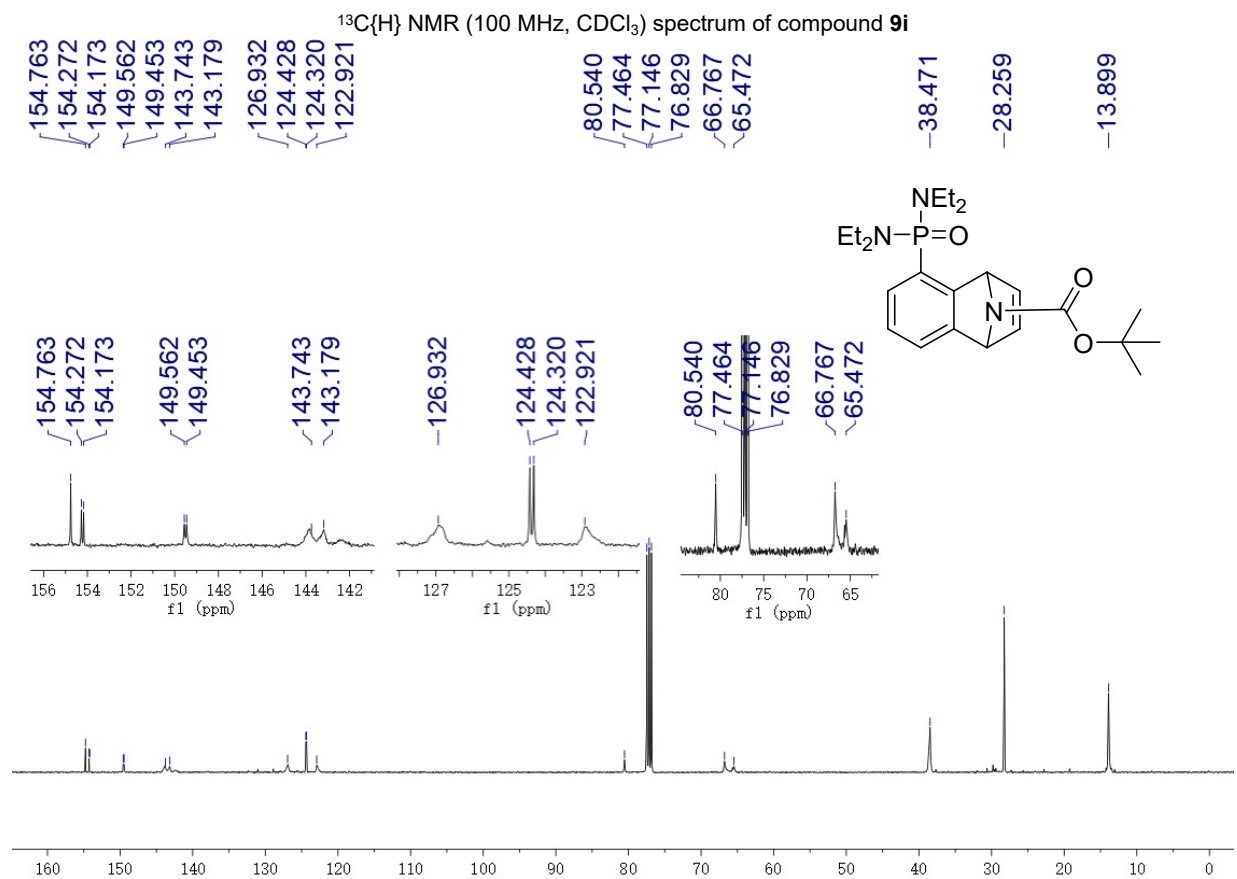
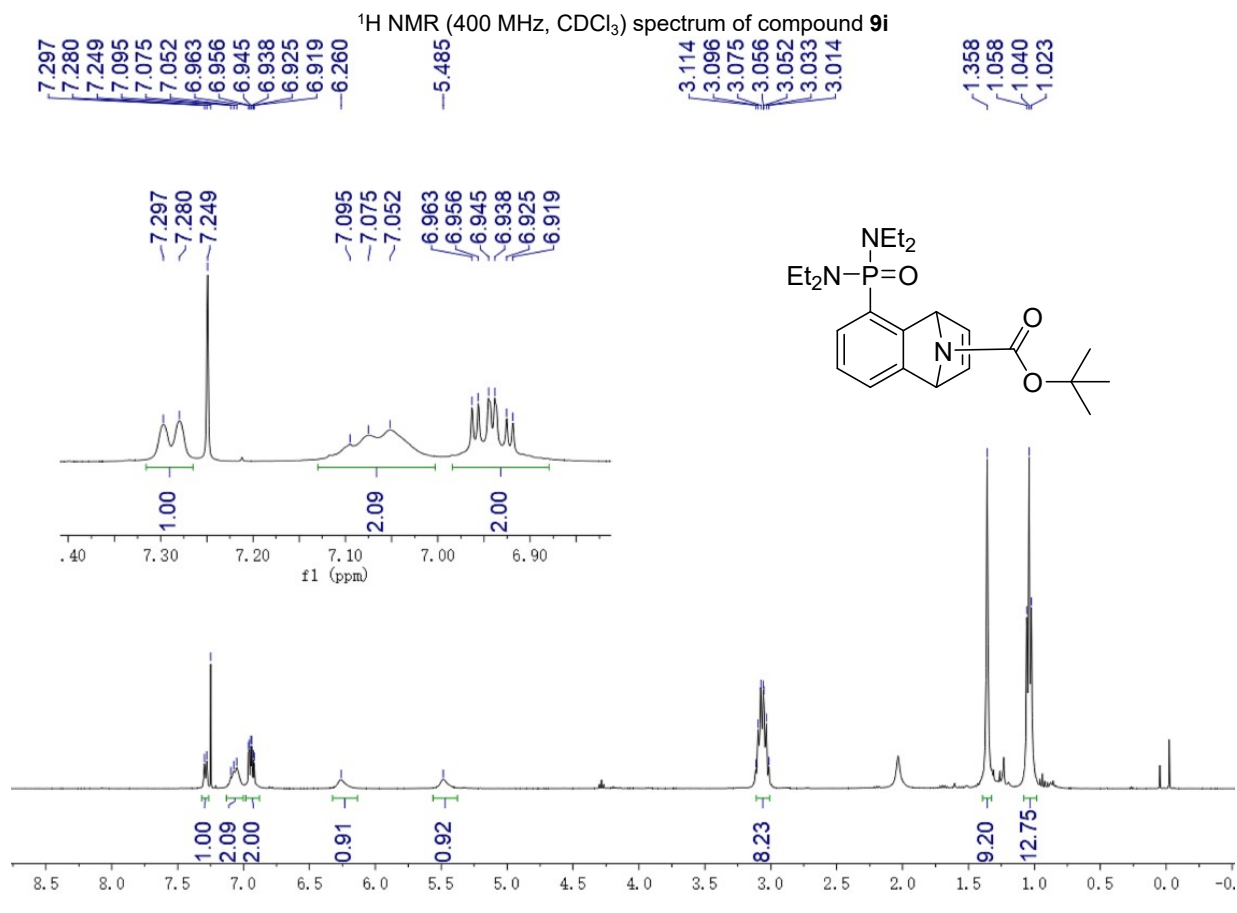
$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of compound **9h**



$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of compound **9h**

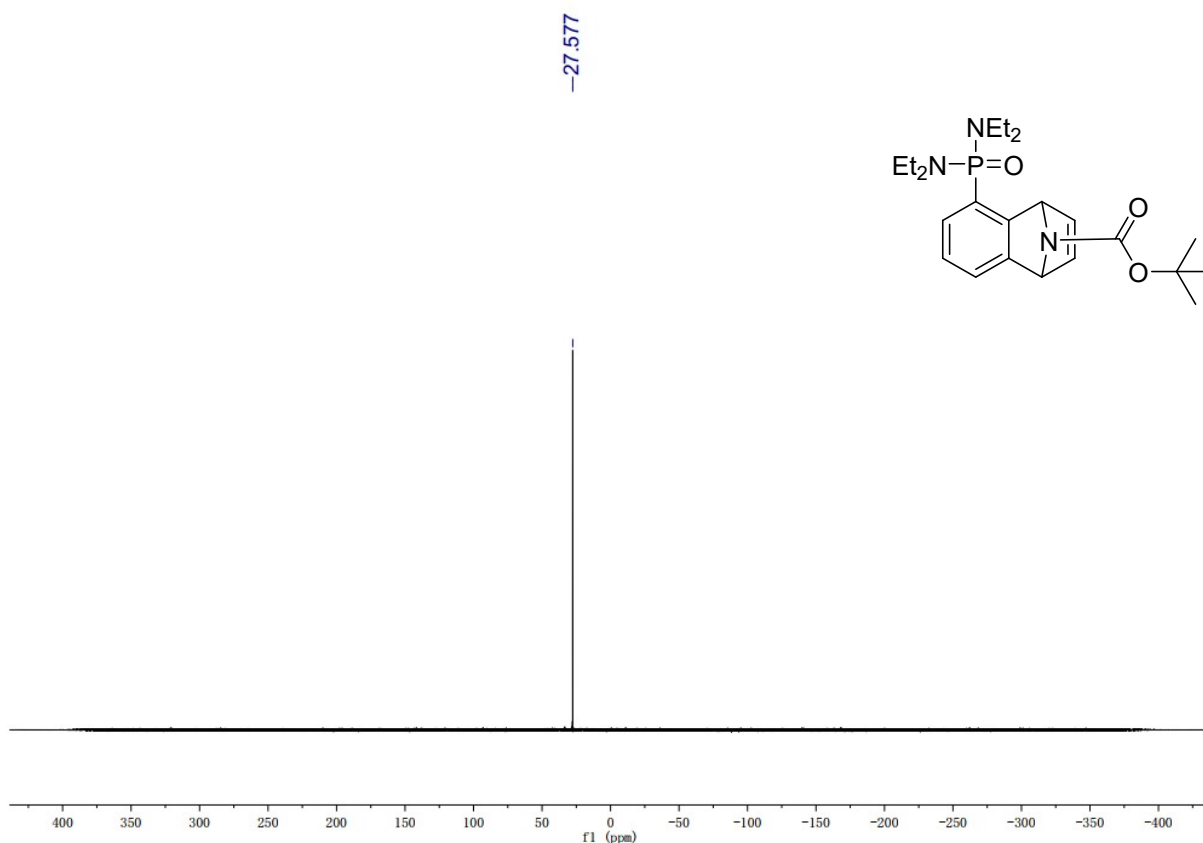


# SUPPORTING INFORMATION

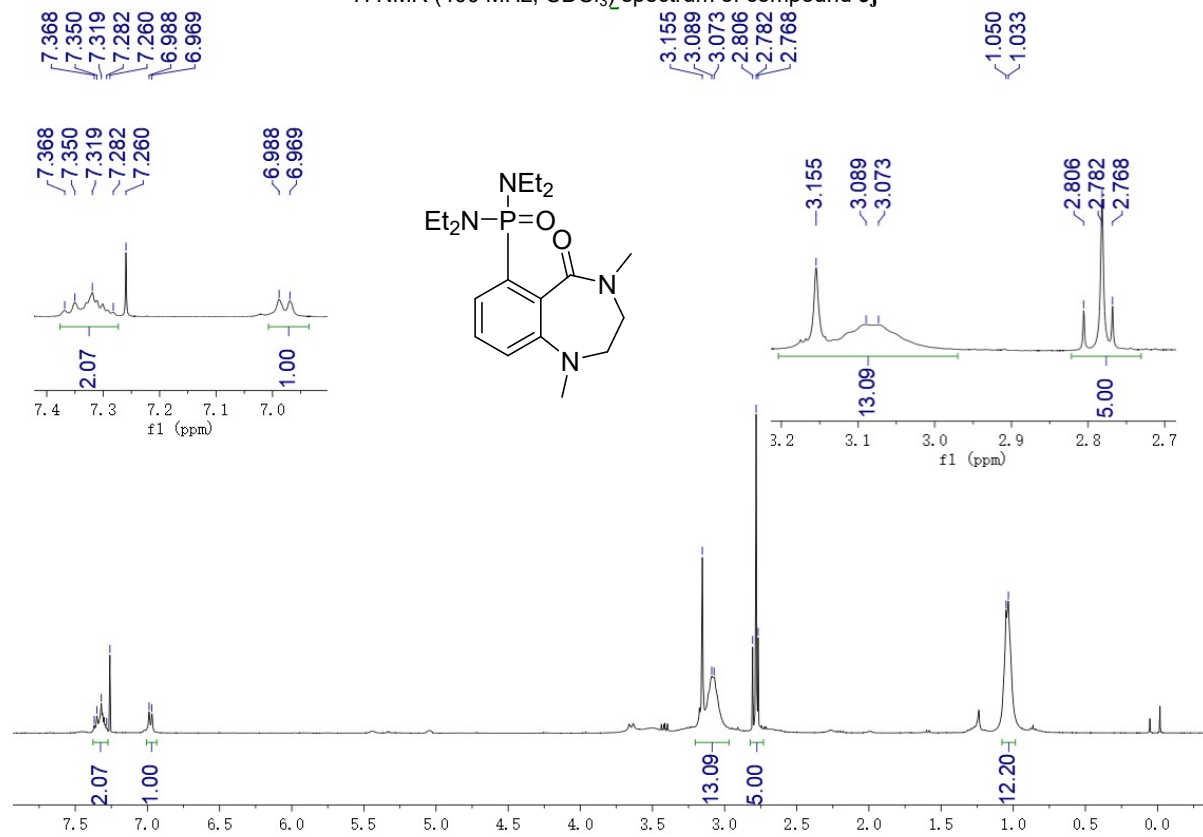


# SUPPORTING INFORMATION

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of compound **9i**

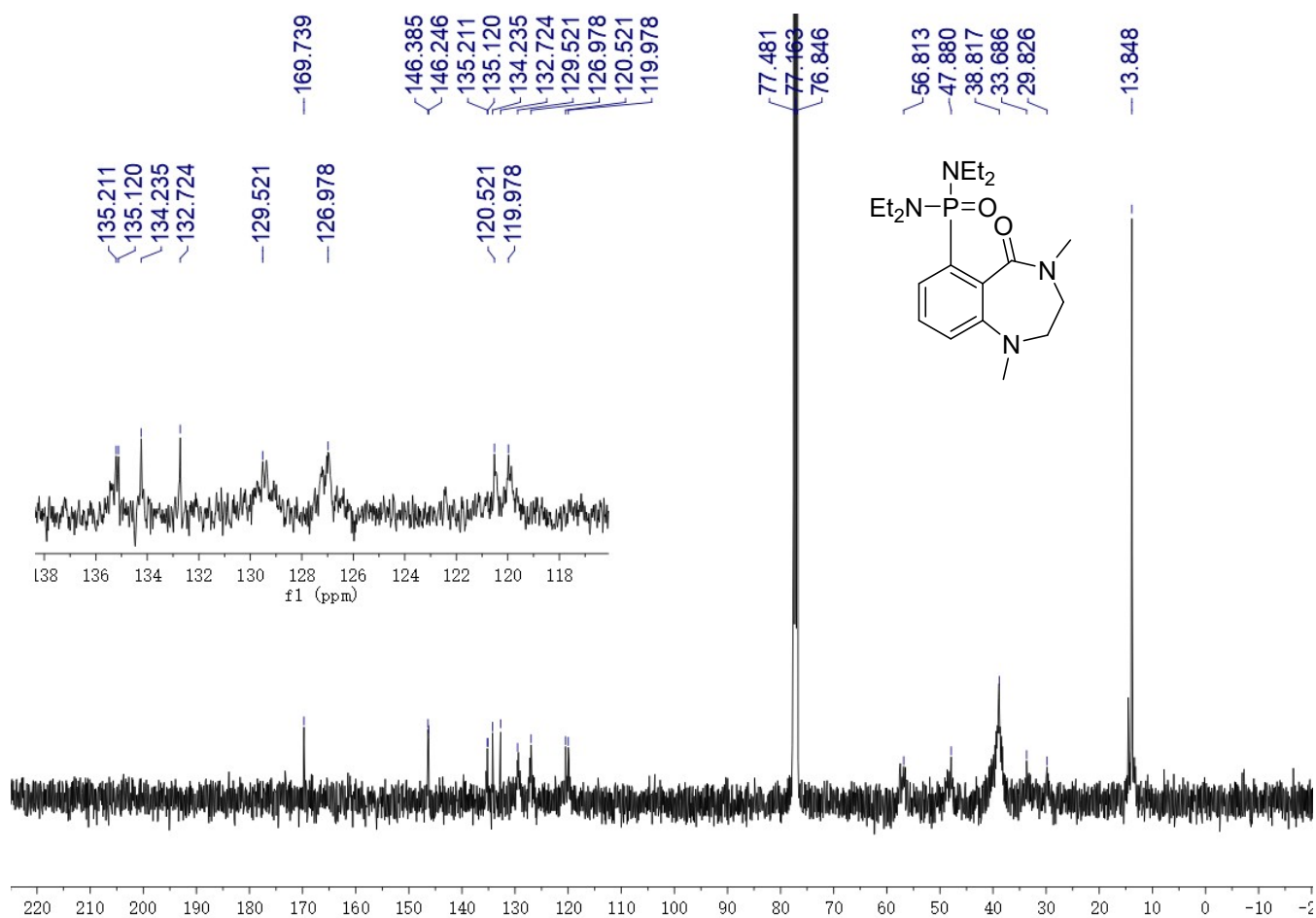


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of compound **9j**

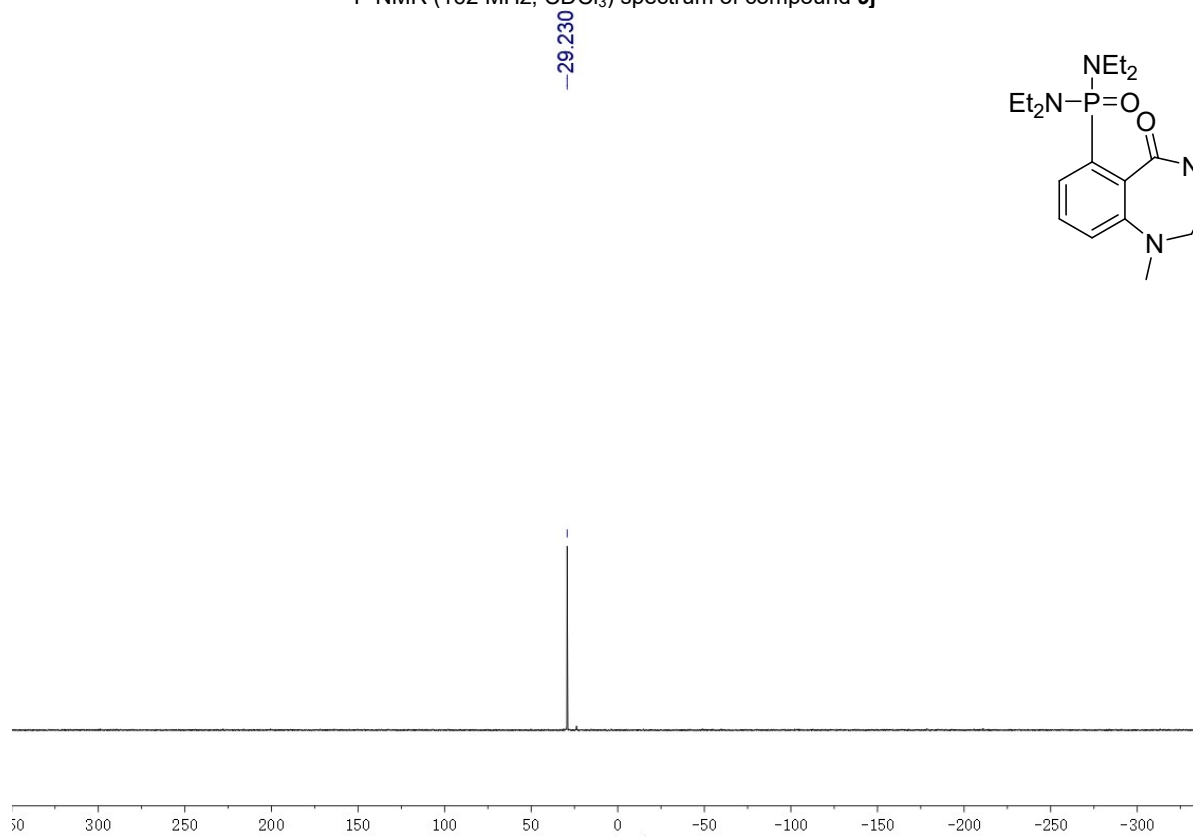


# SUPPORTING INFORMATION

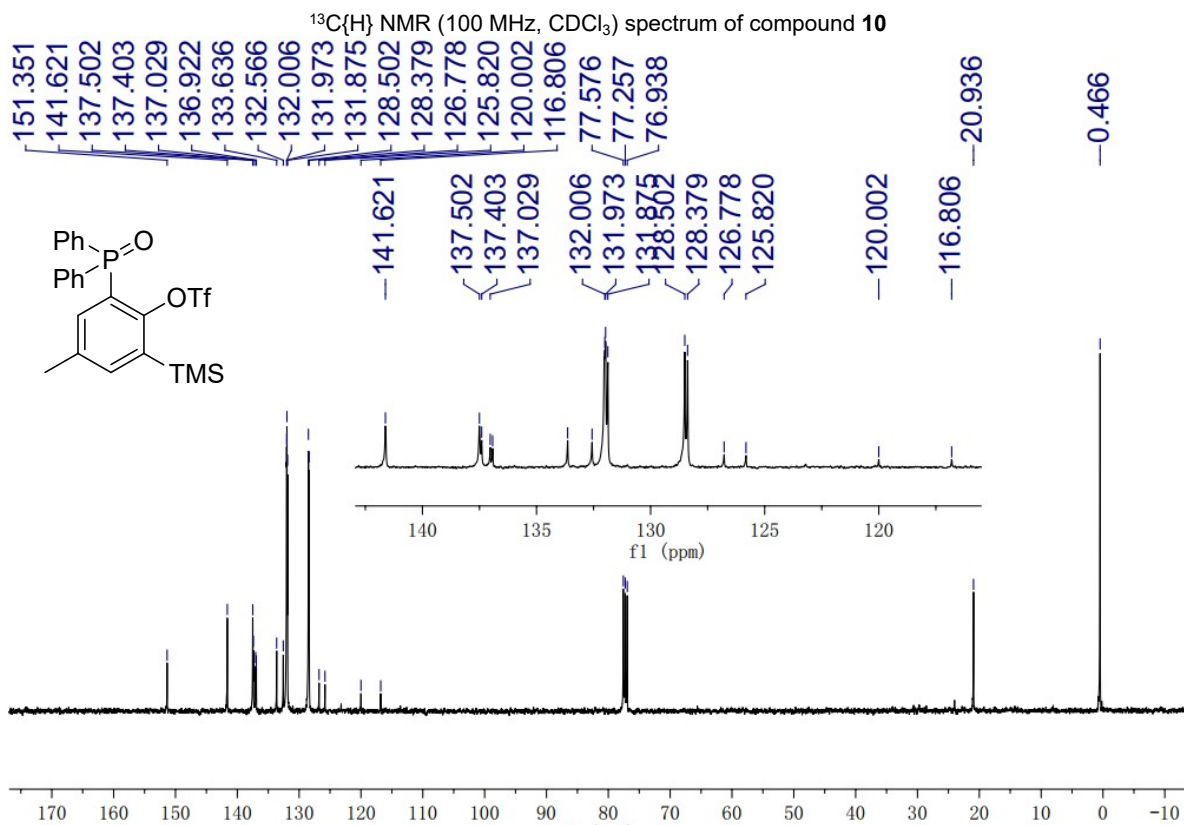
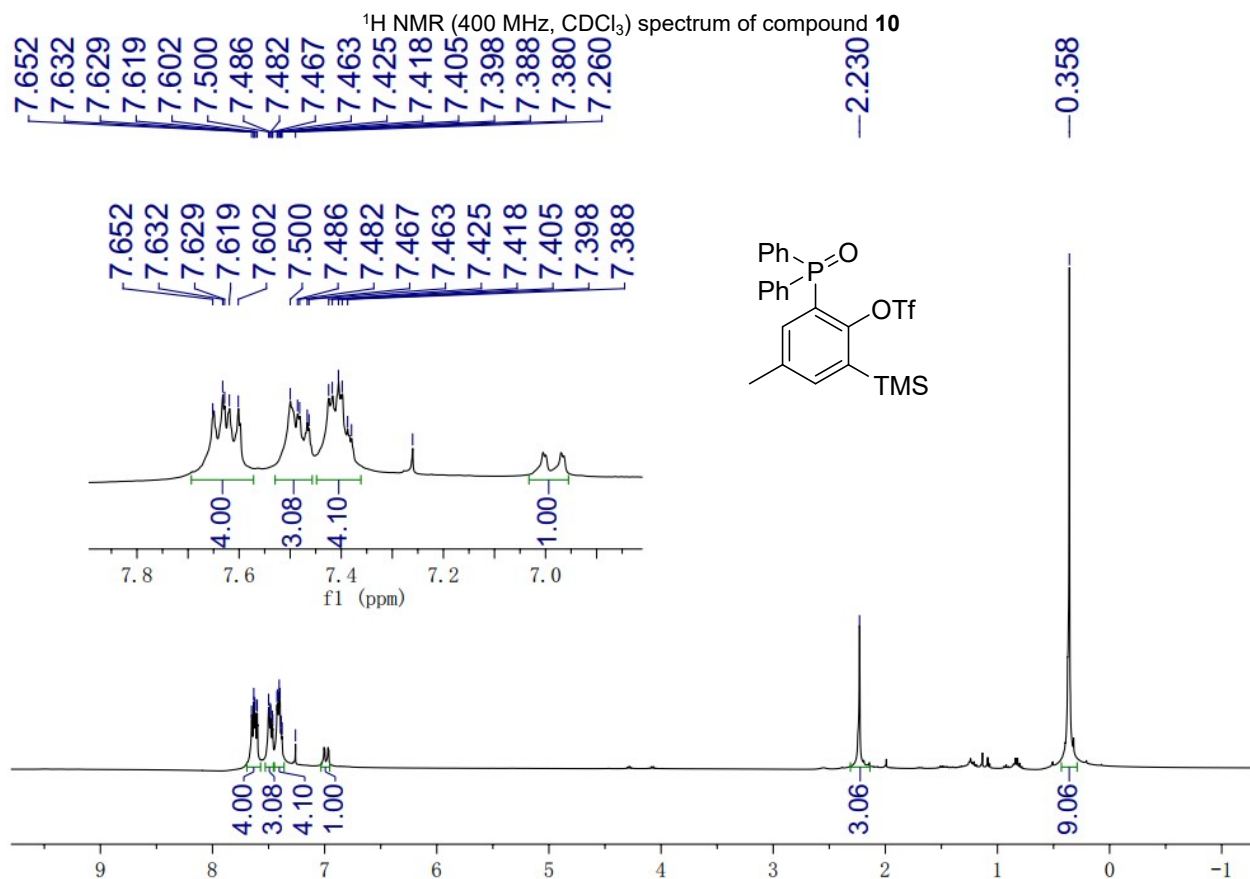
$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of compound **9j**



$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of compound **9j**

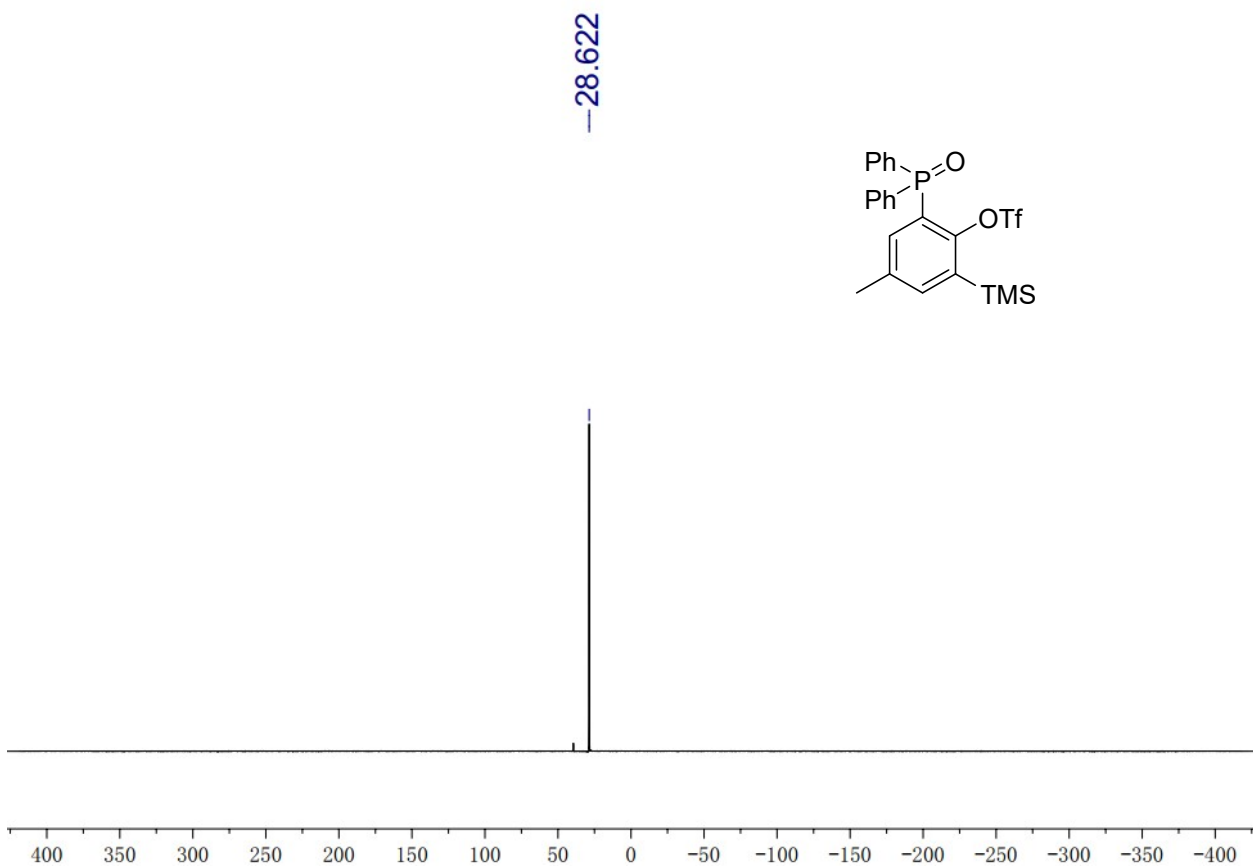


# SUPPORTING INFORMATION

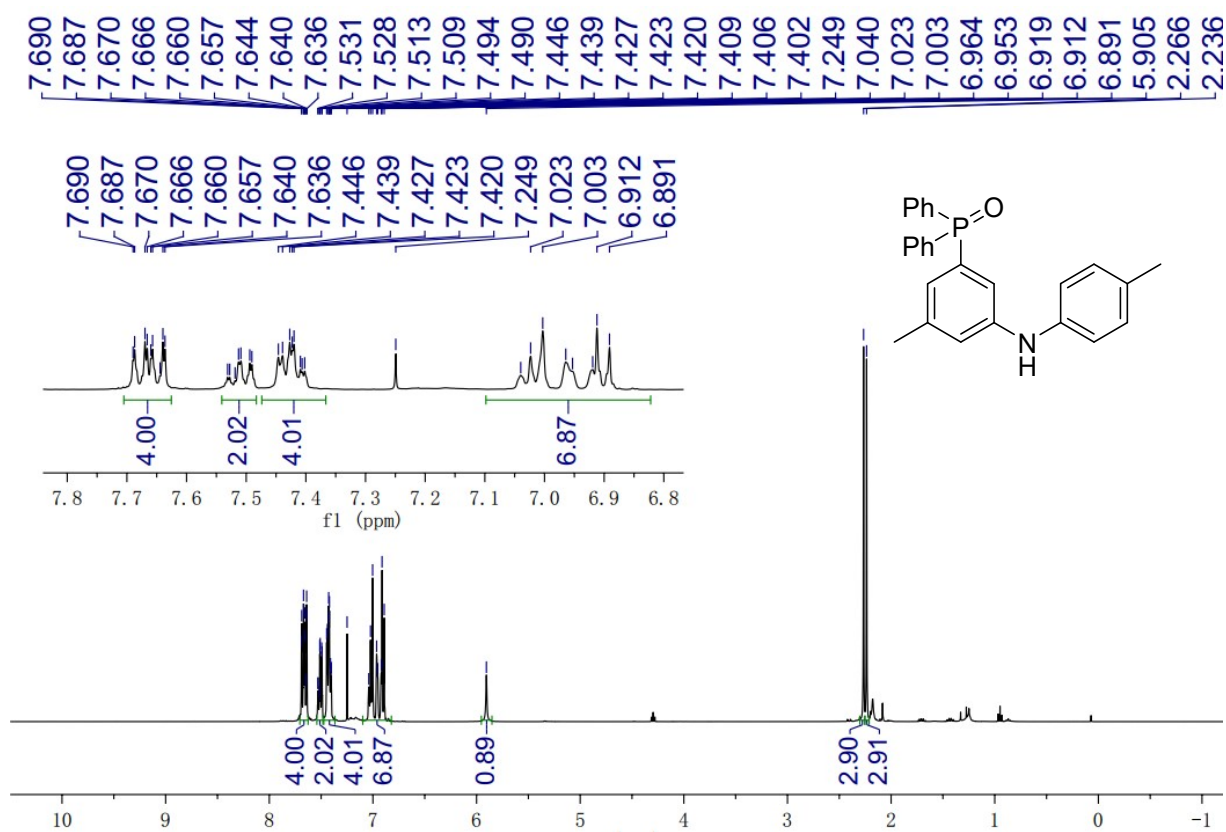


# SUPPORTING INFORMATION

<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) spectrum of compound **10**



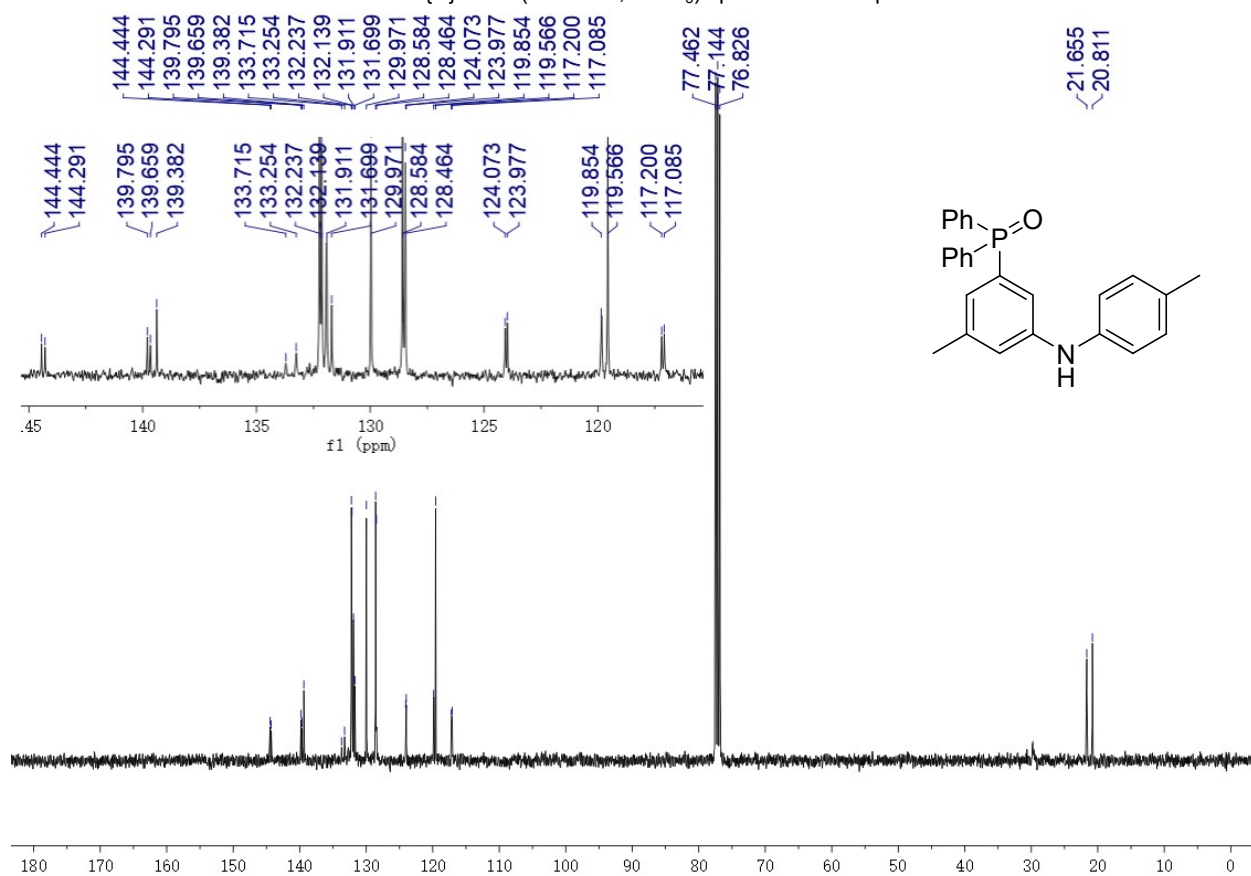
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound **11**



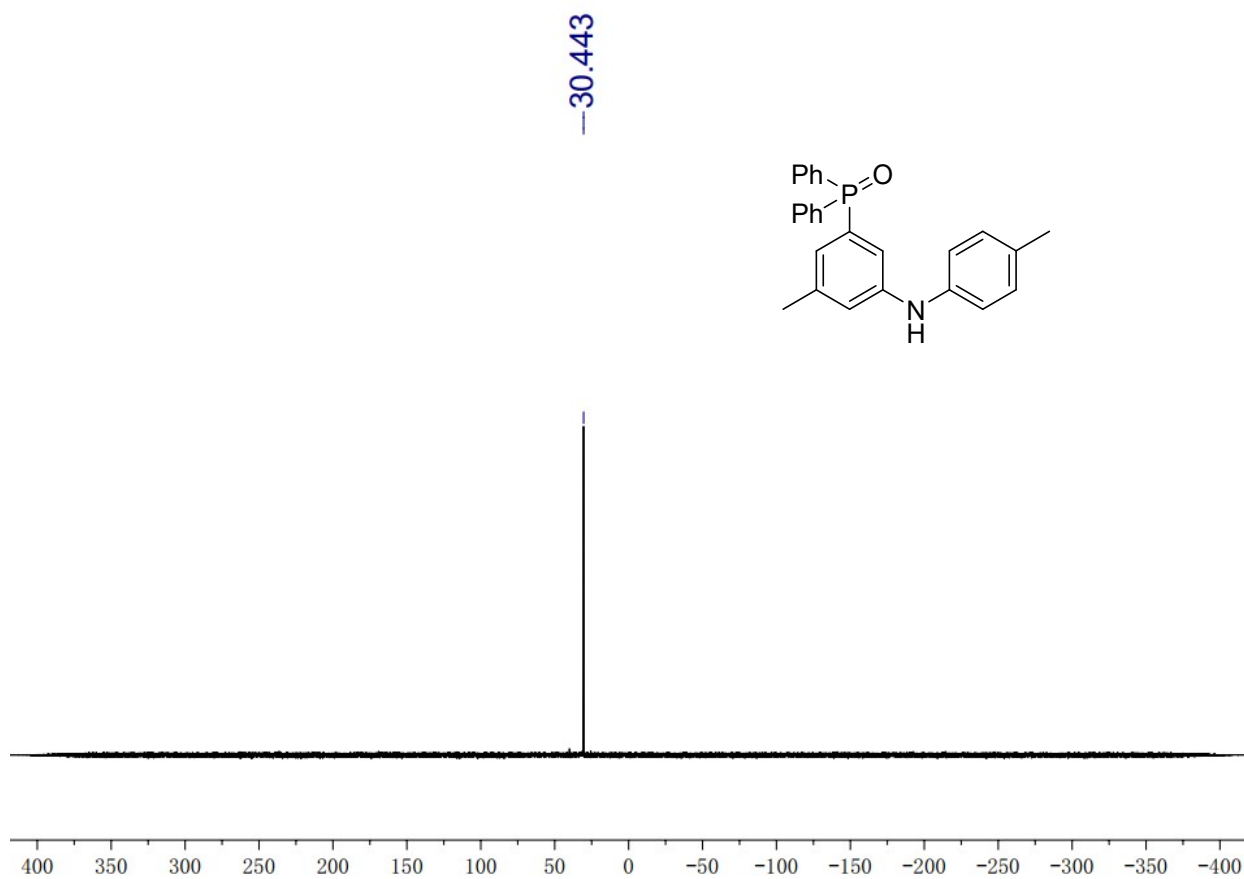


# SUPPORTING INFORMATION

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of compound **11**



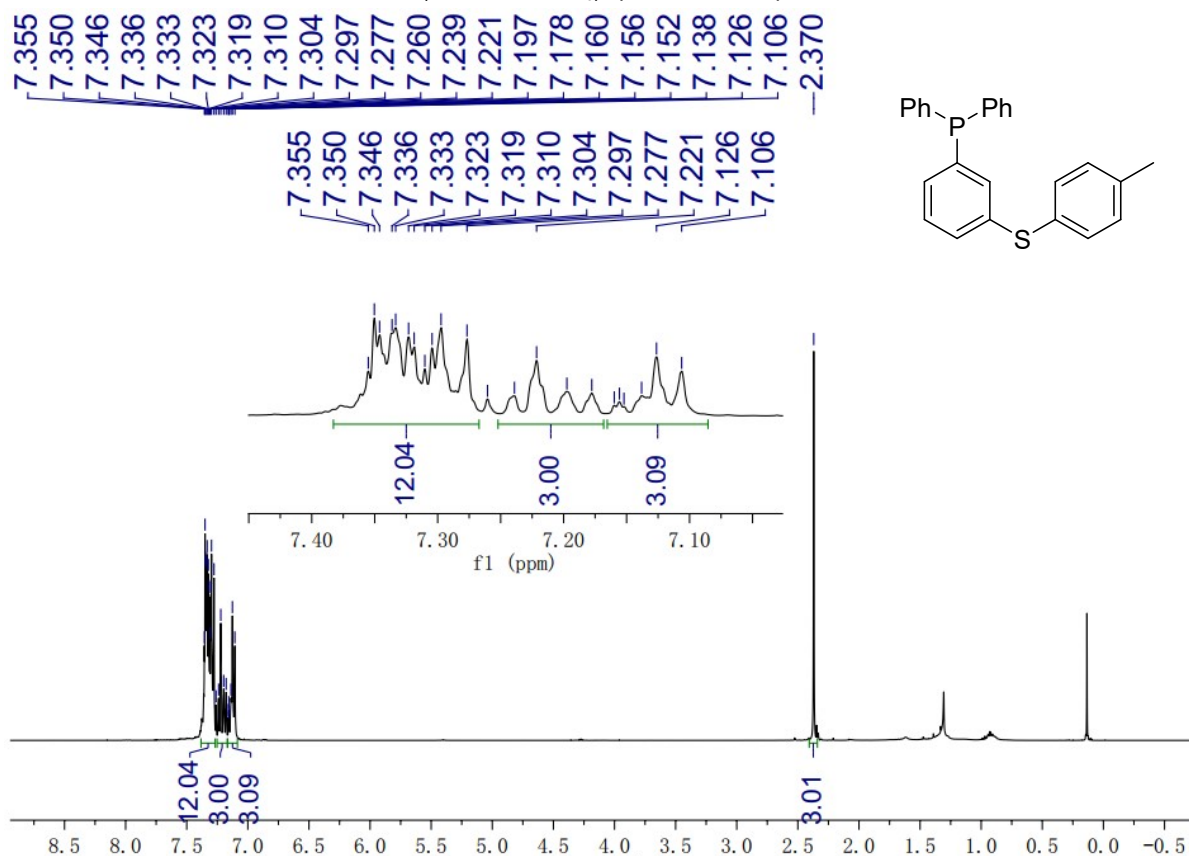
$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of compound **11**



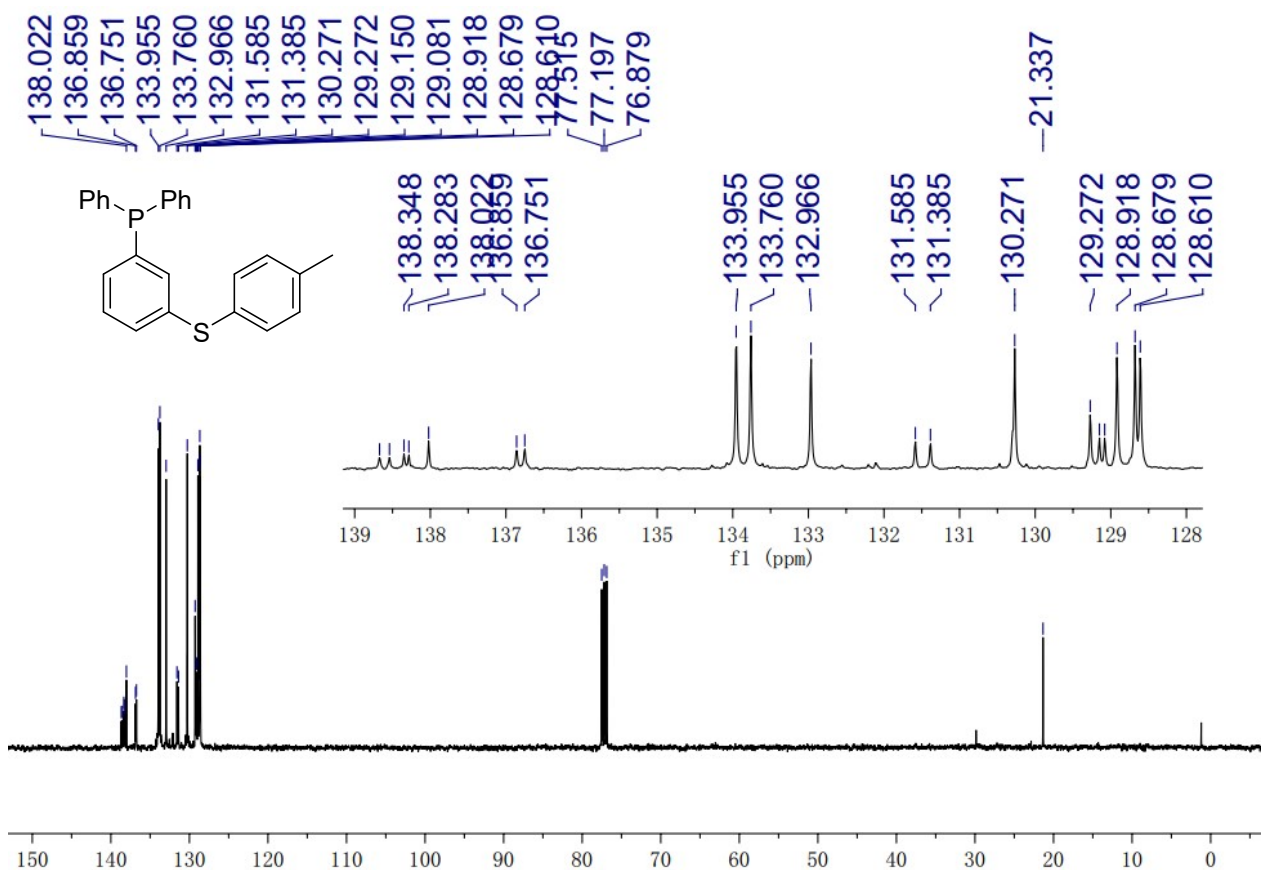


# SUPPORTING INFORMATION

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound **12**

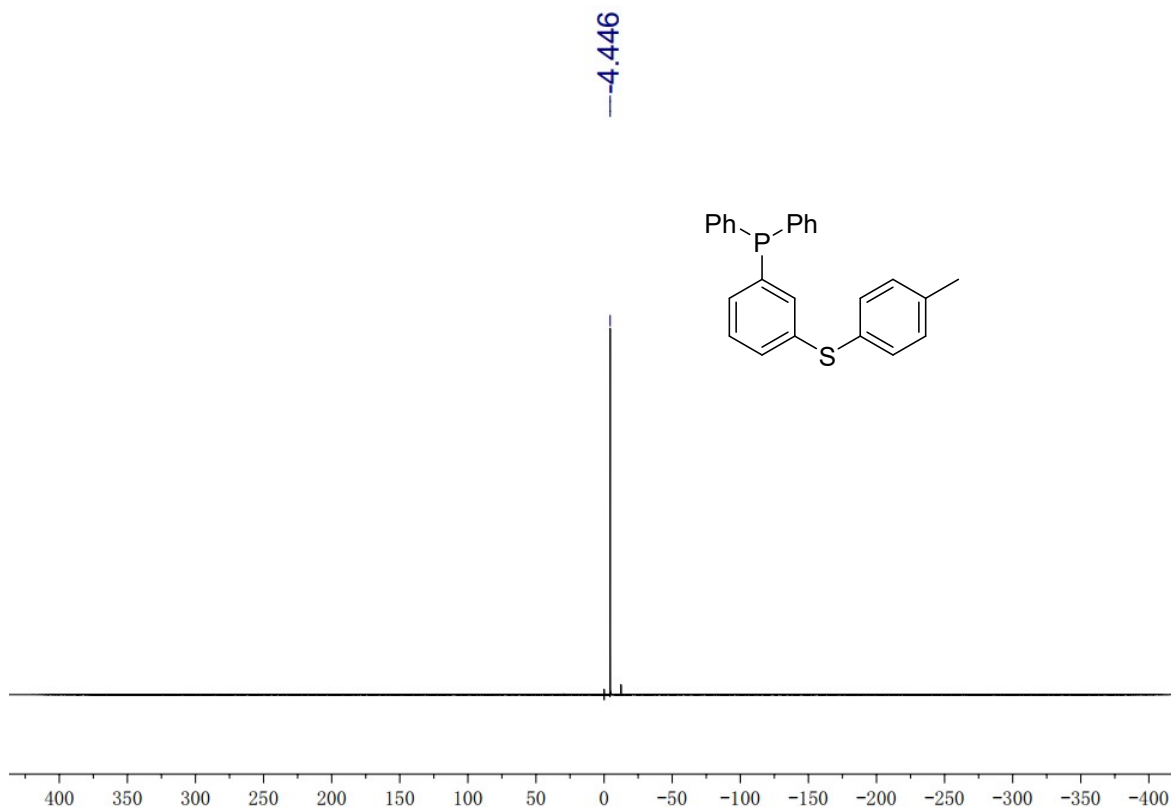


<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) spectrum of compound **12**

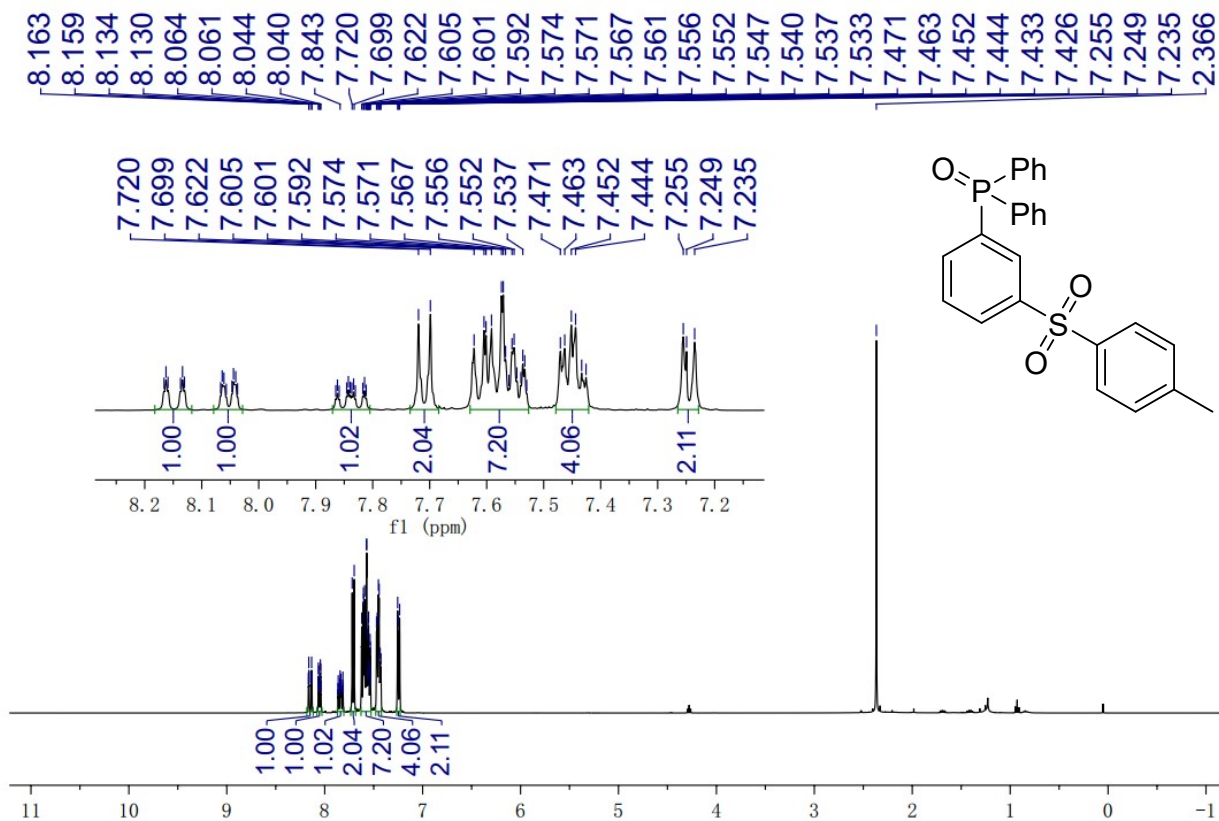


# SUPPORTING INFORMATION

<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) spectrum of compound **12**

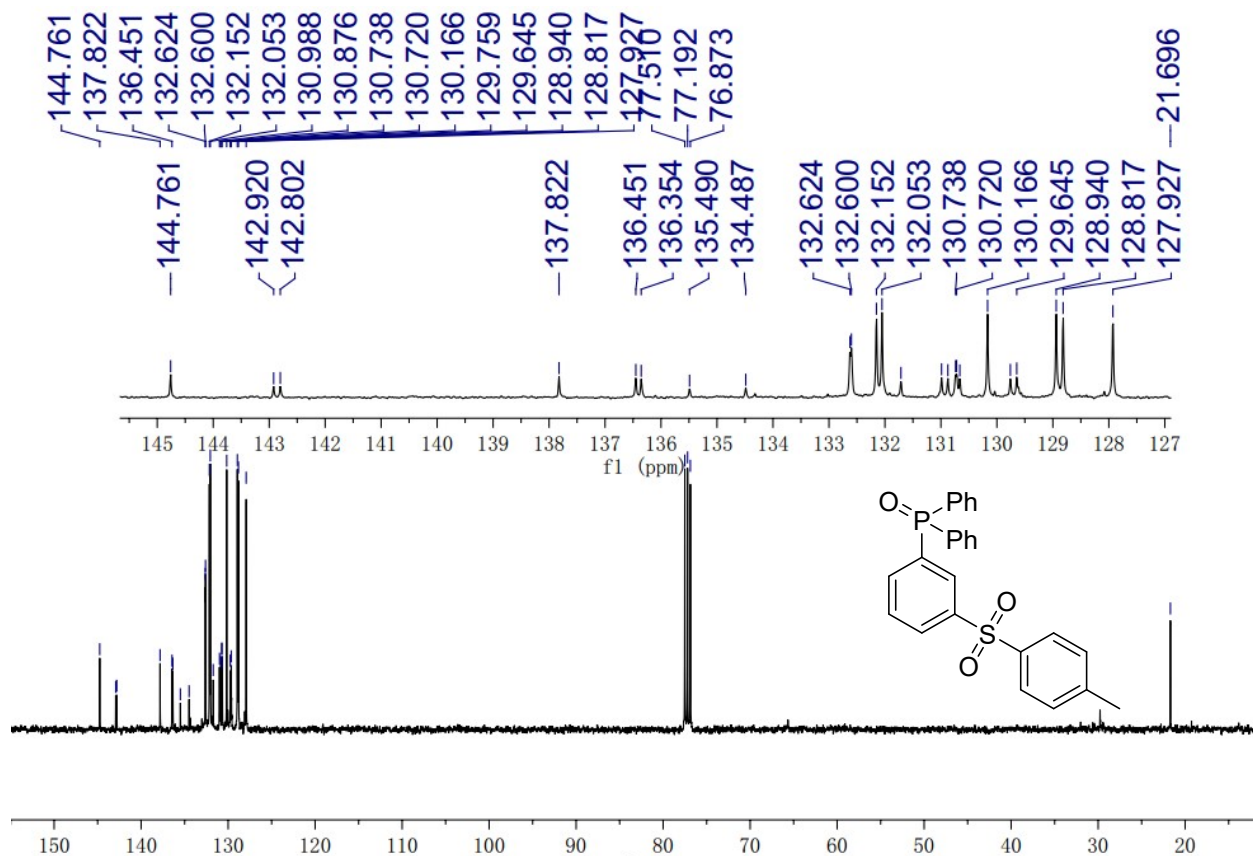


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound **13**

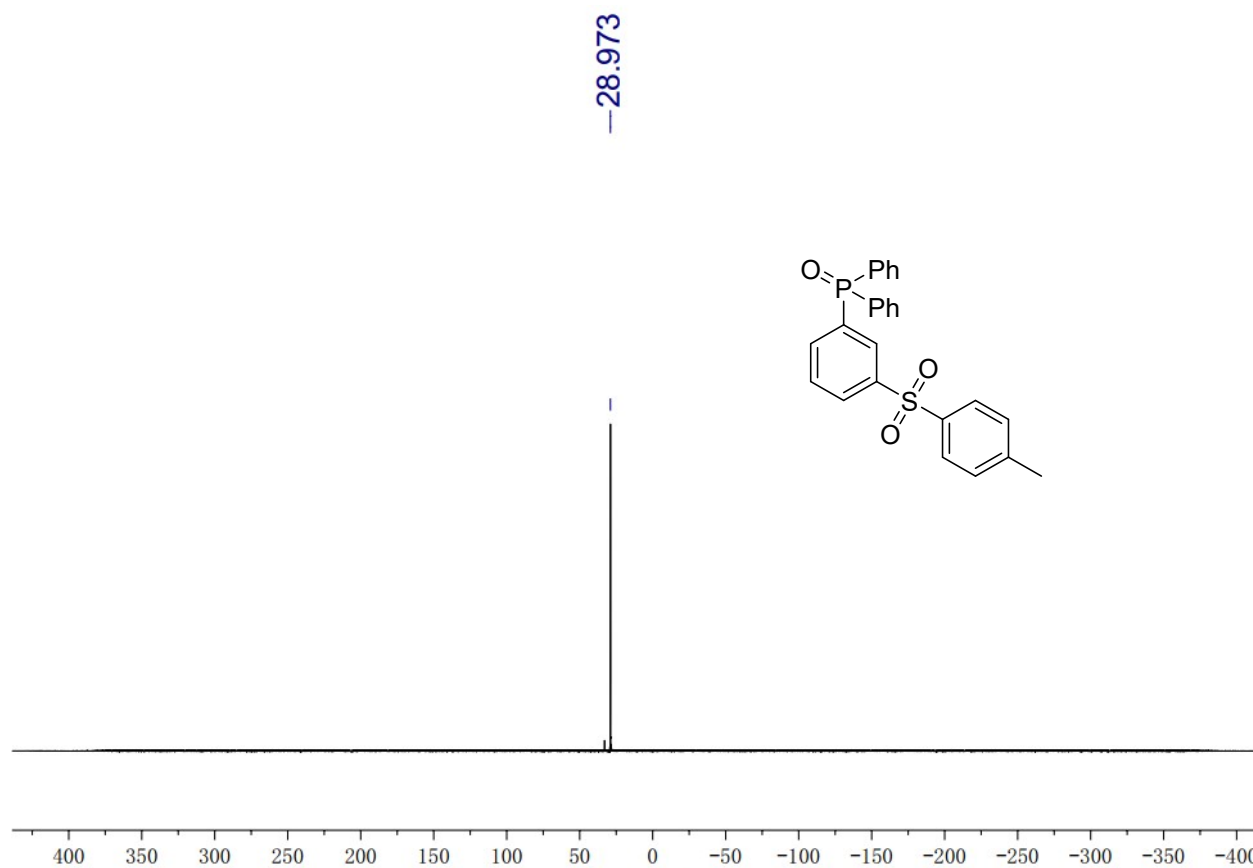


# SUPPORTING INFORMATION

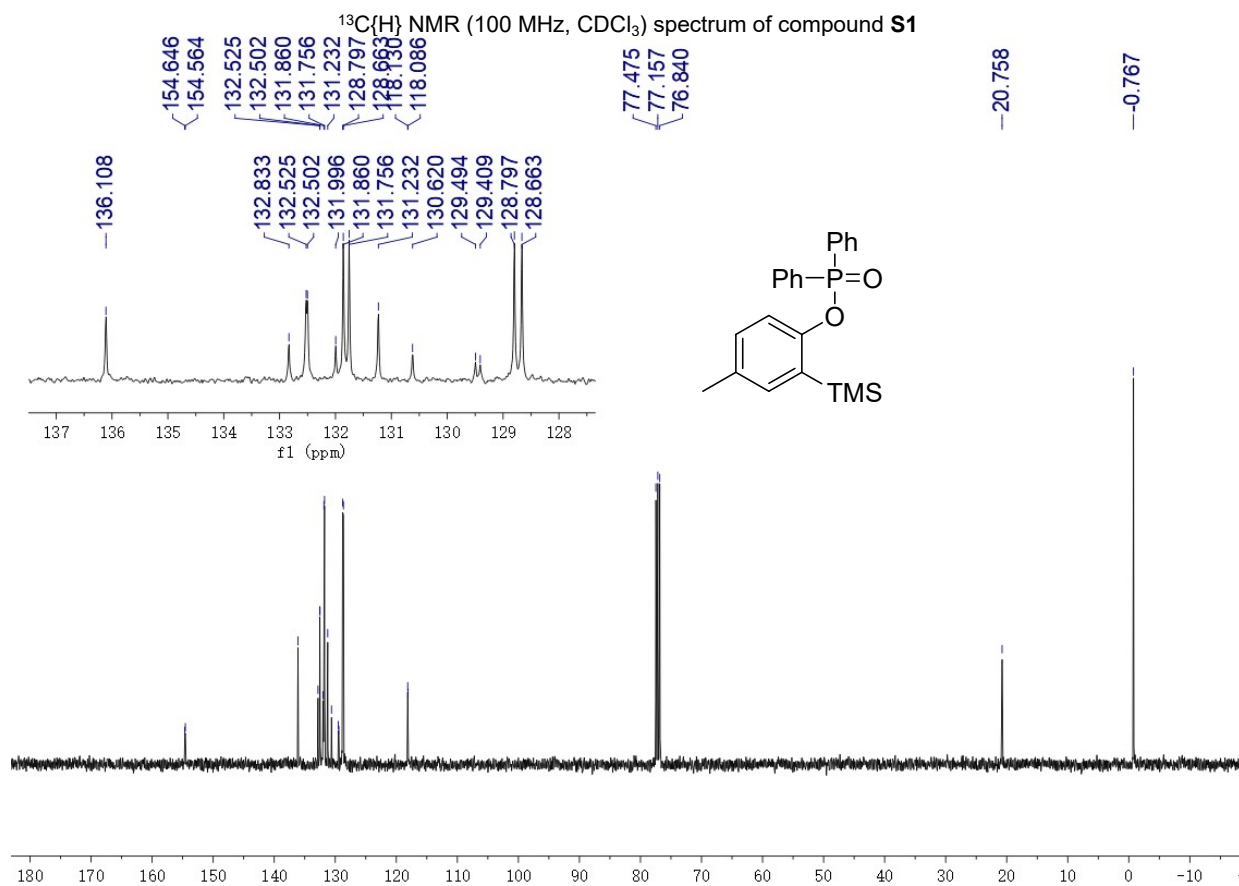
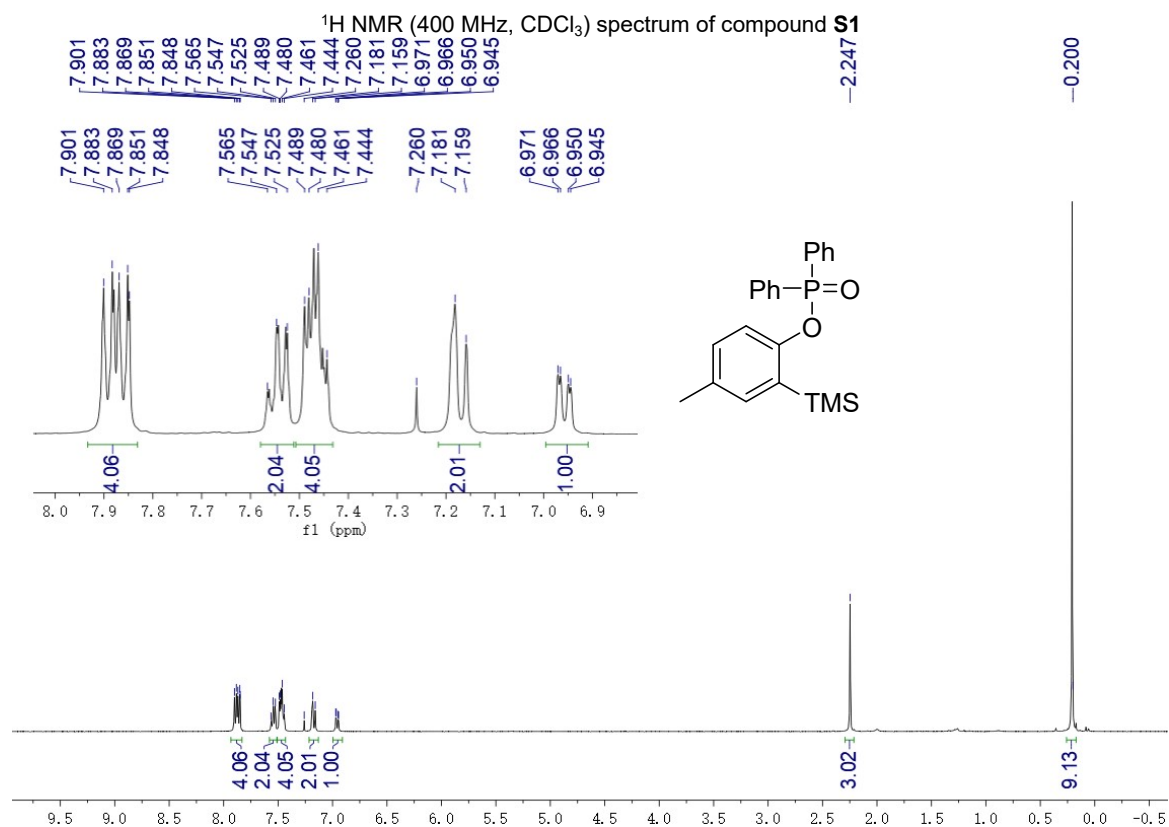
$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of compound **13**



$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of compound **13**

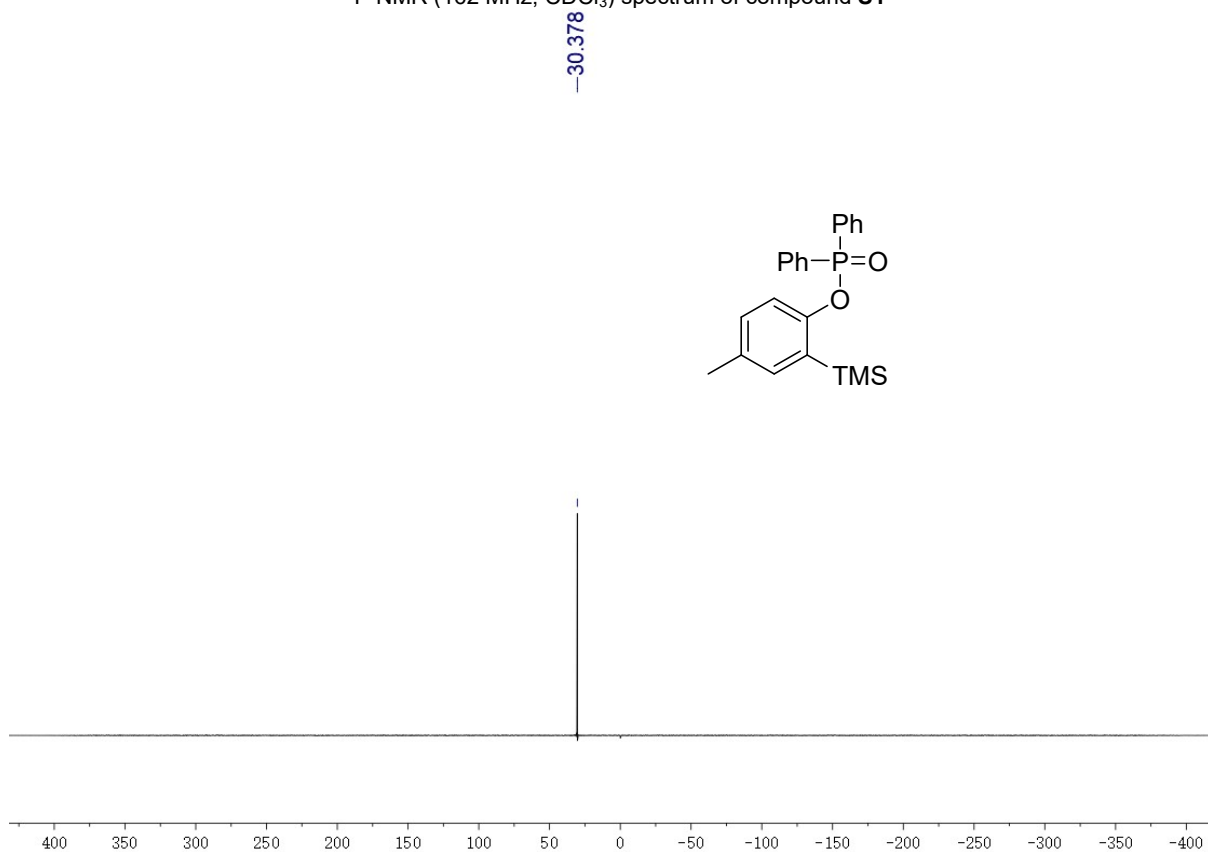


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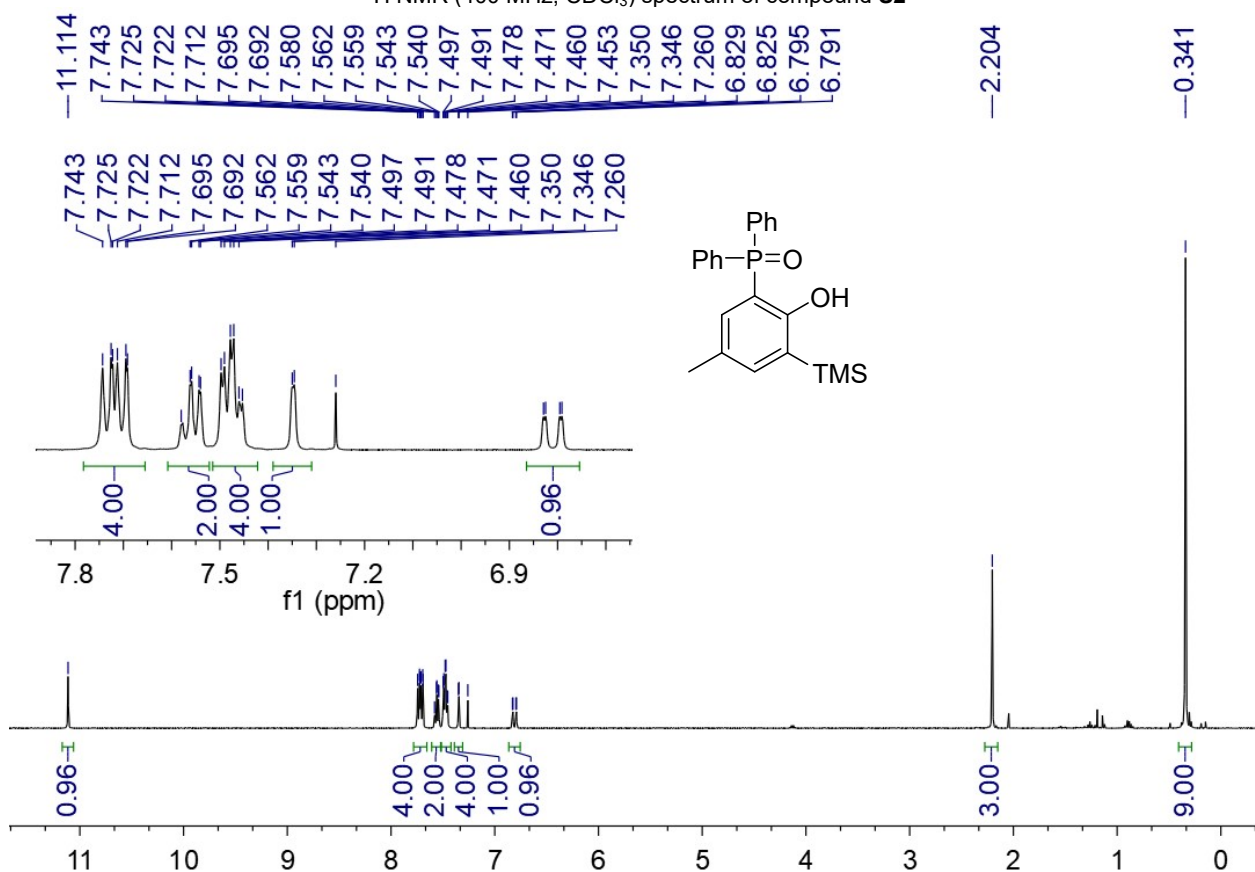


# SUPPORTING INFORMATION

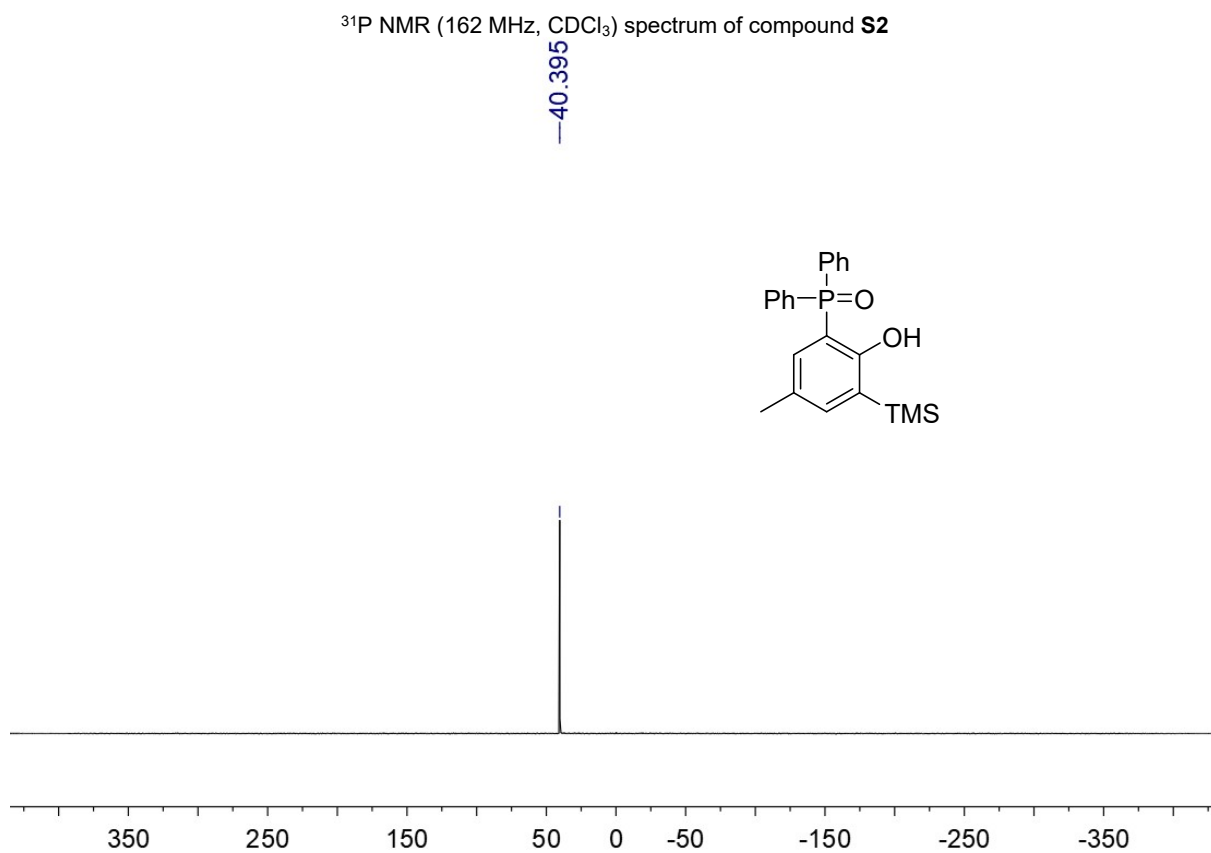
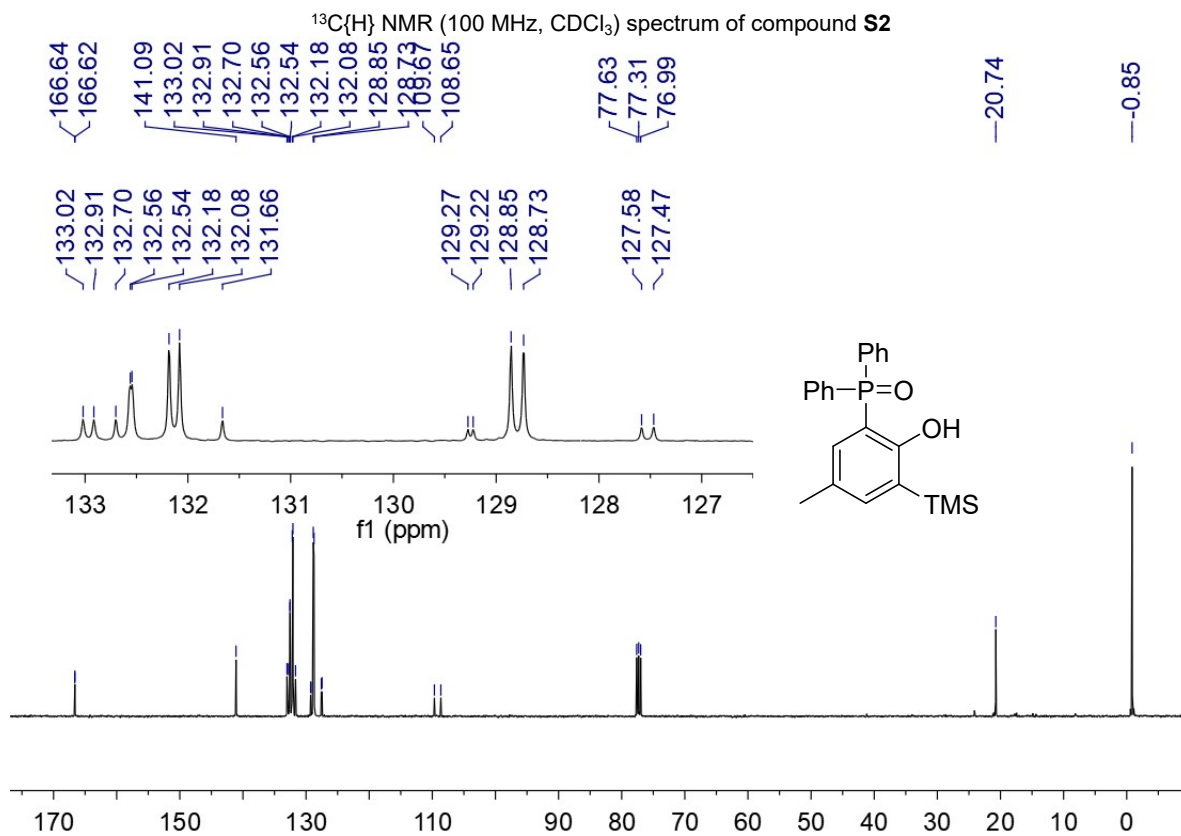
<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) spectrum of compound **S1**



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound **S2**



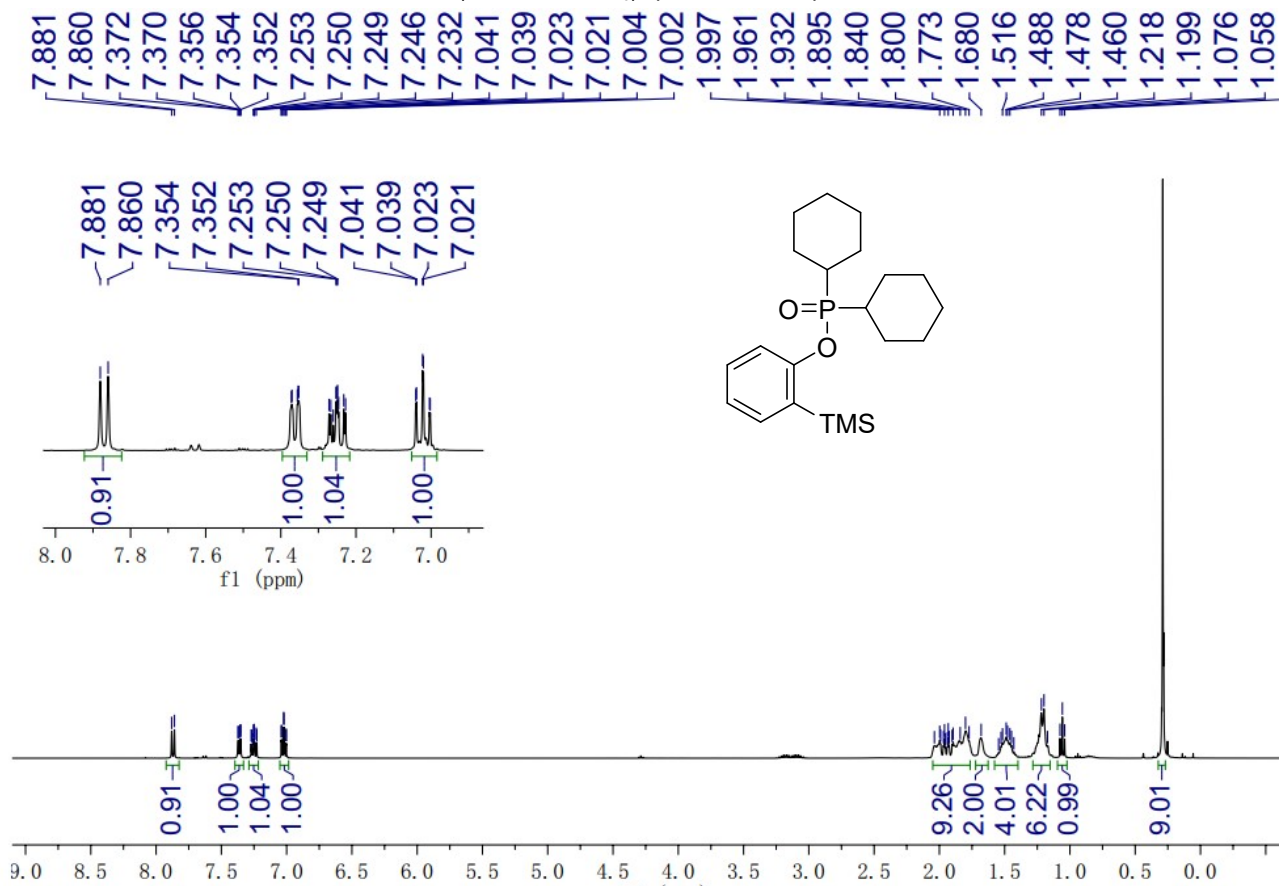
# SUPPORTING INFORMATION



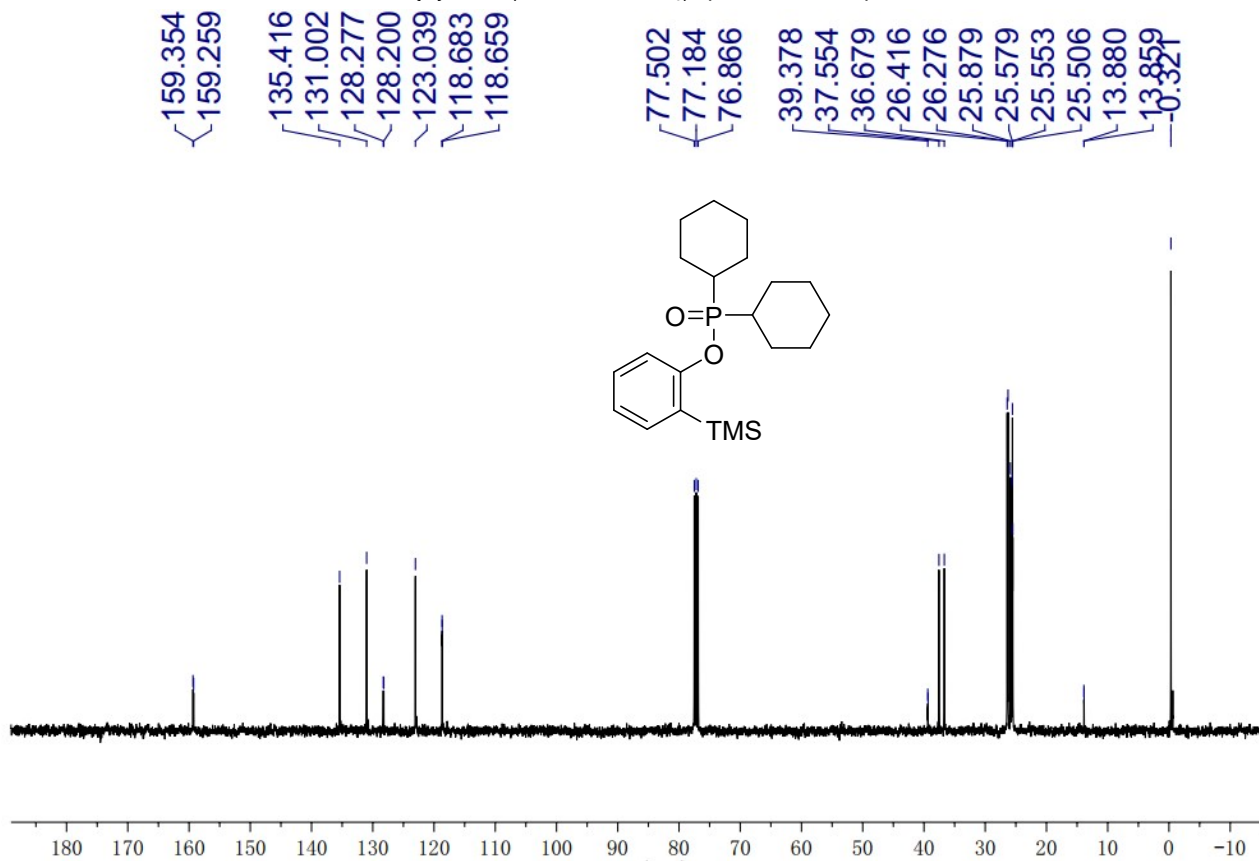


# SUPPORTING INFORMATION

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound **S3**

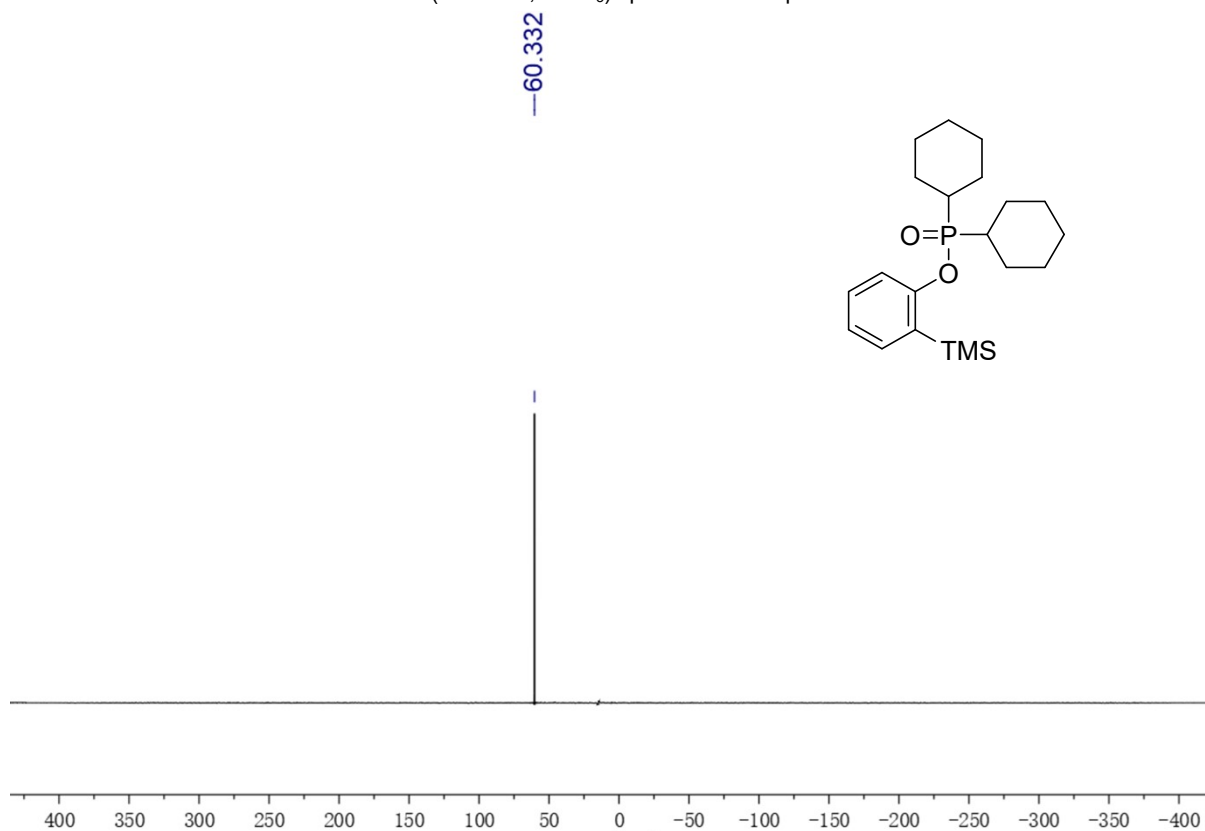


<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) spectrum of compound **S3**

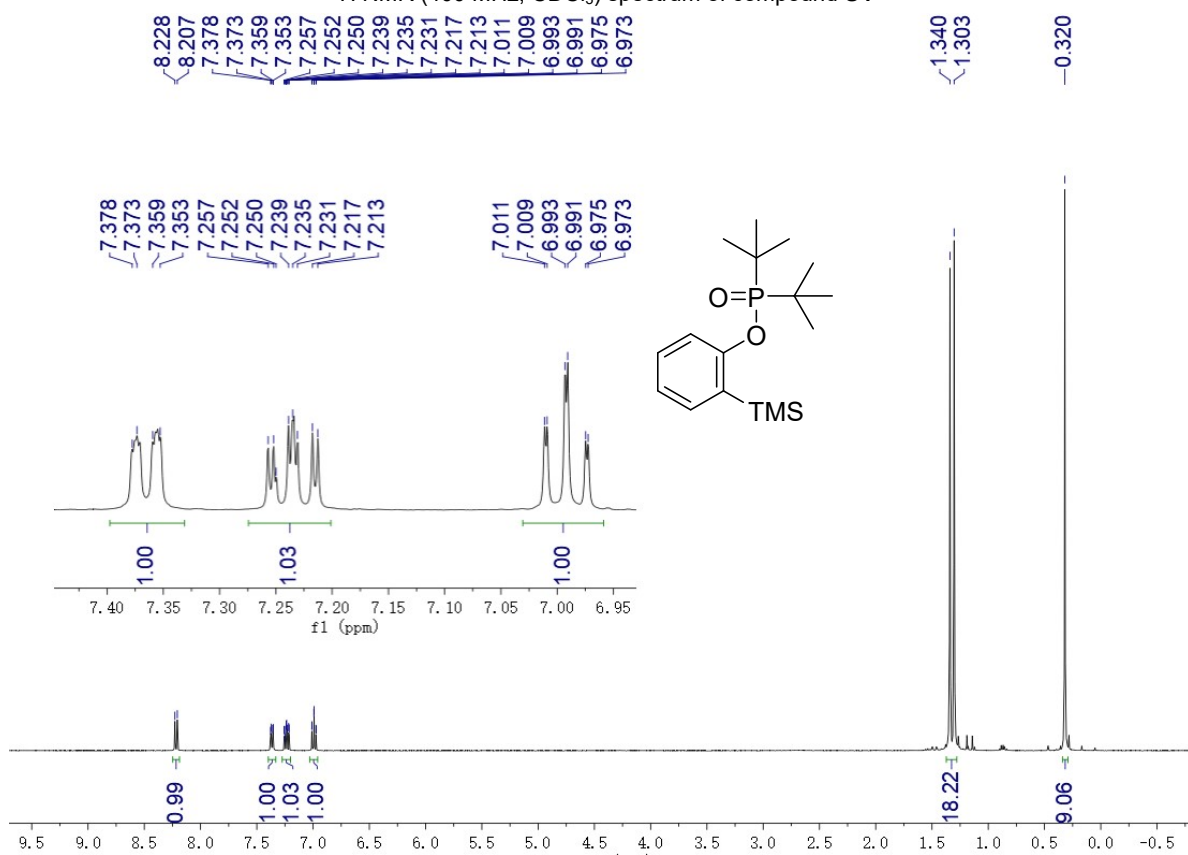


# SUPPORTING INFORMATION

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of compound **S3**



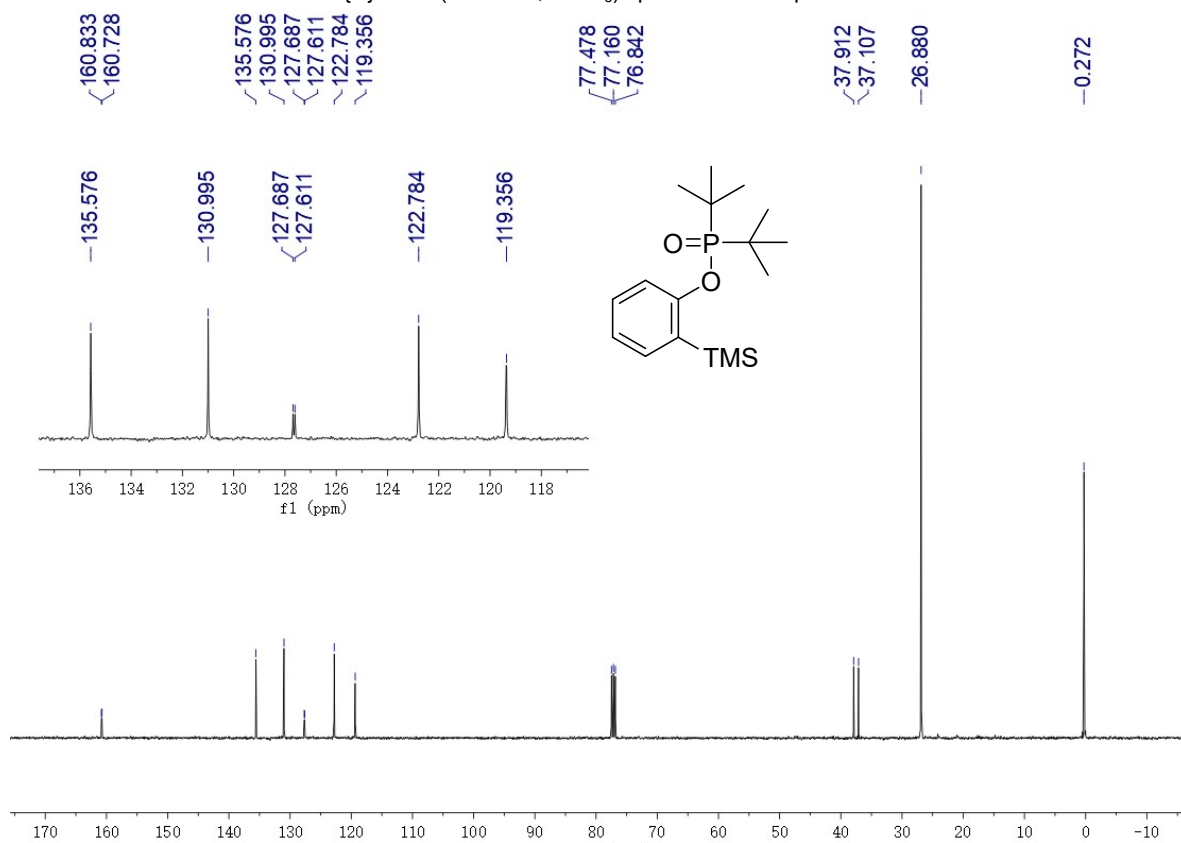
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of compound **S4**



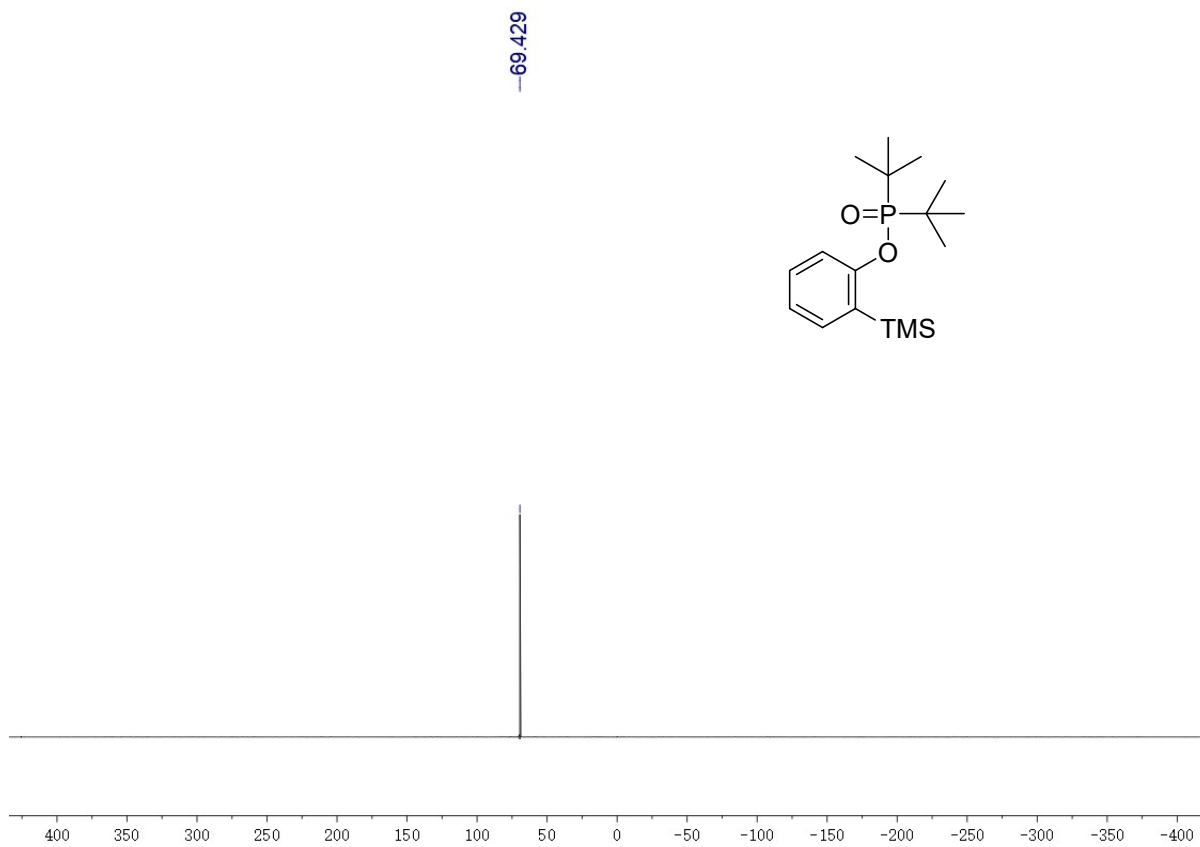


# SUPPORTING INFORMATION

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of compound **S4**

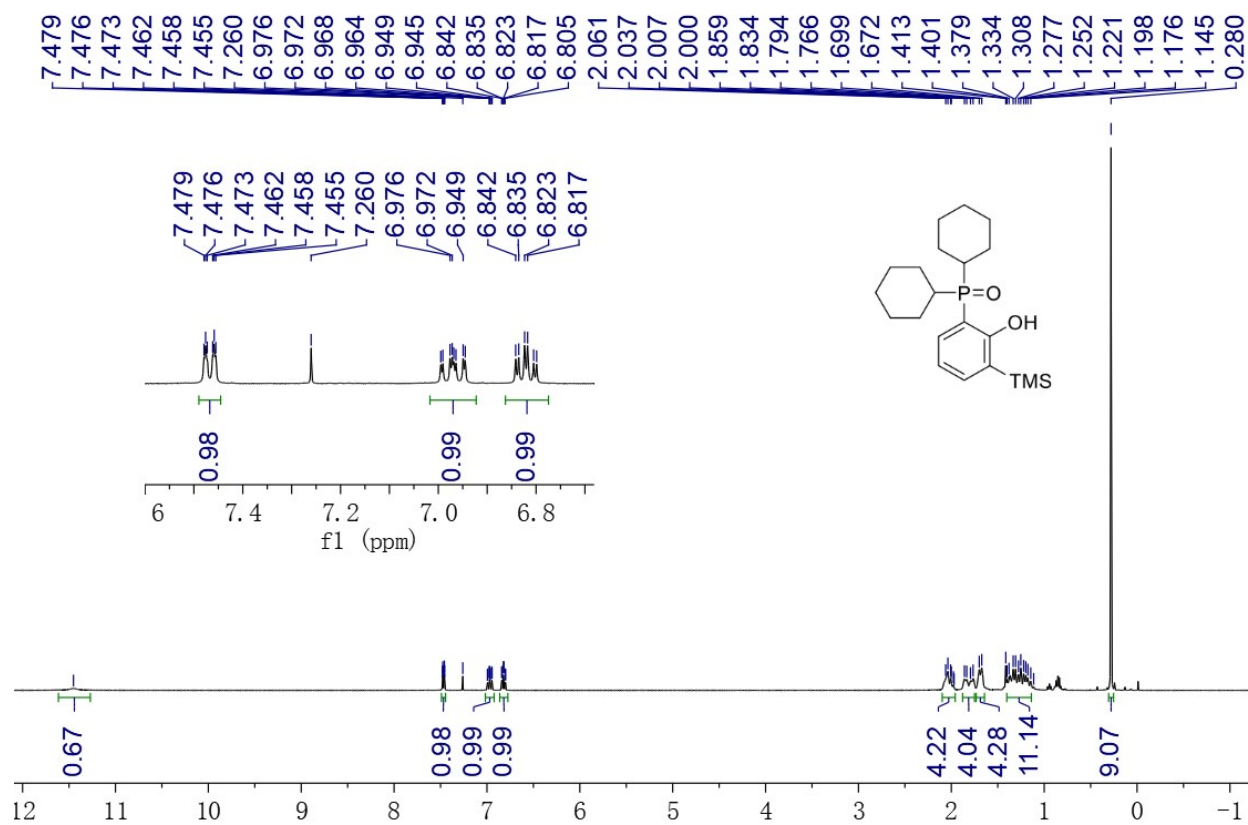


$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of compound **S4**

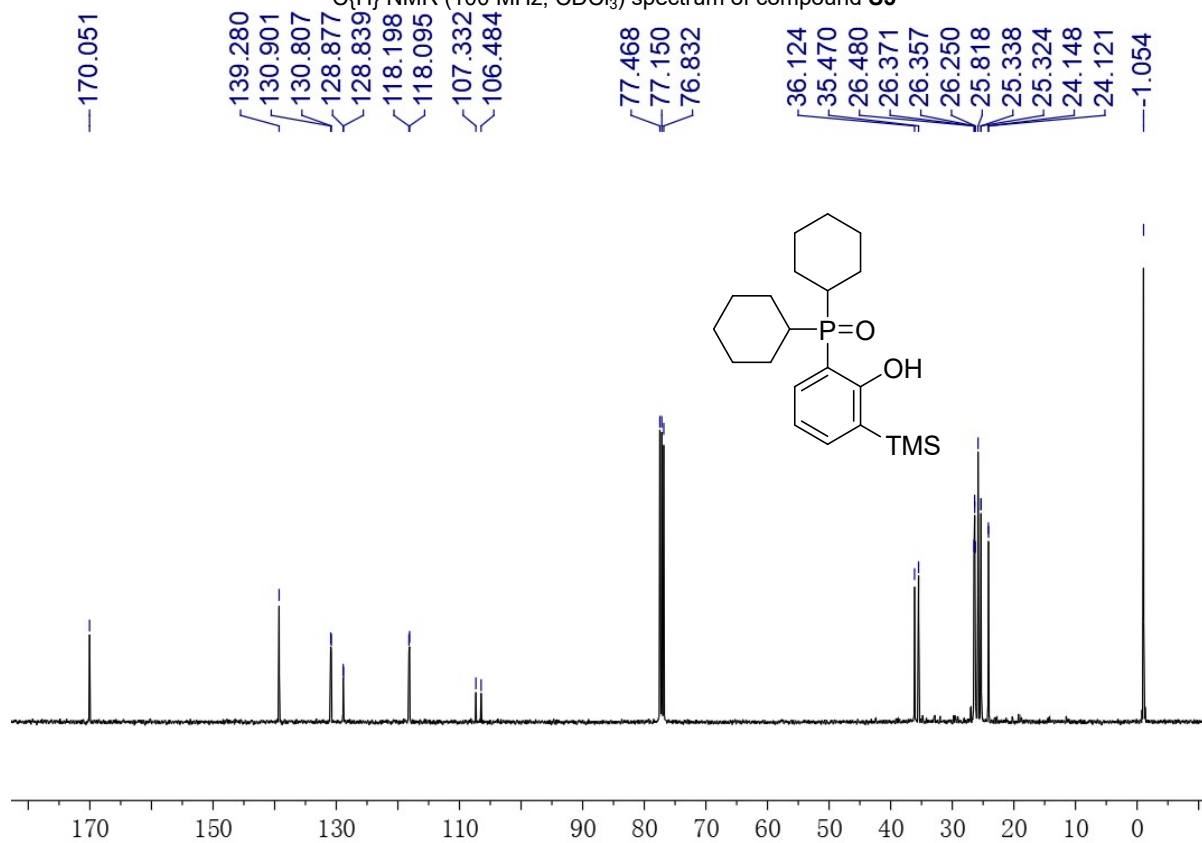


# SUPPORTING INFORMATION

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound **S5**

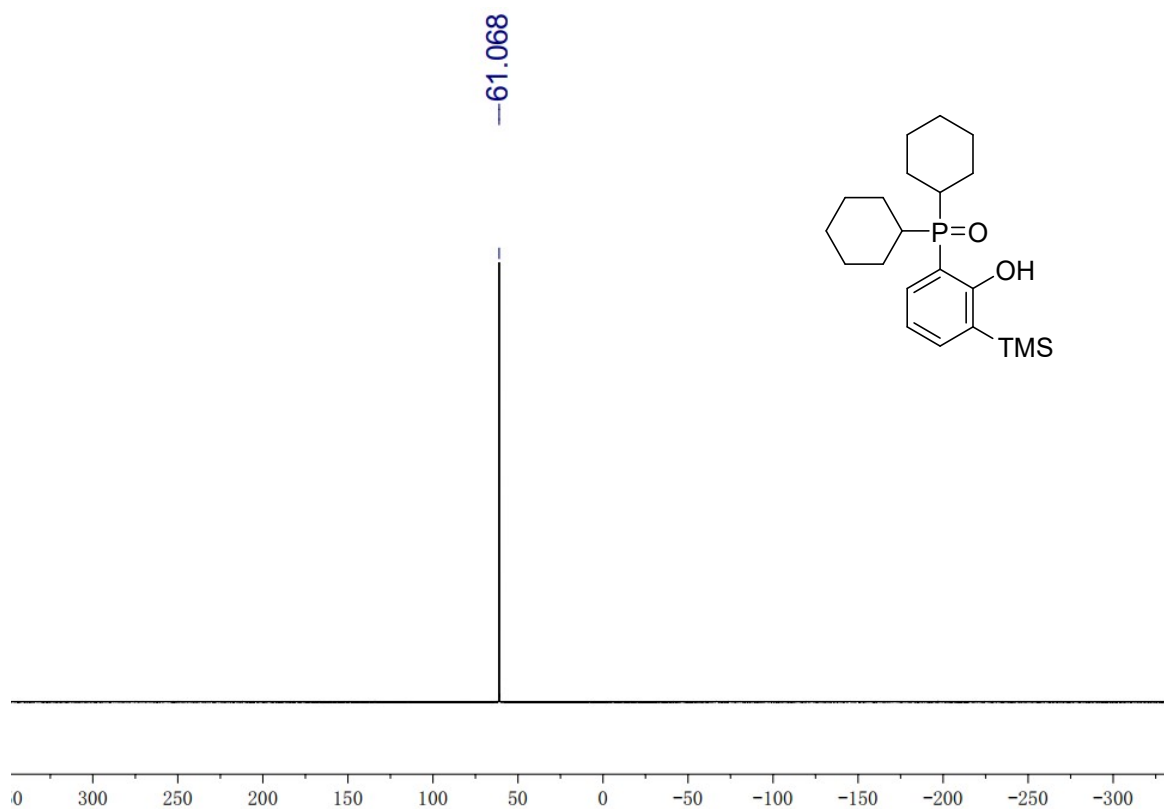


<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) spectrum of compound **S5**

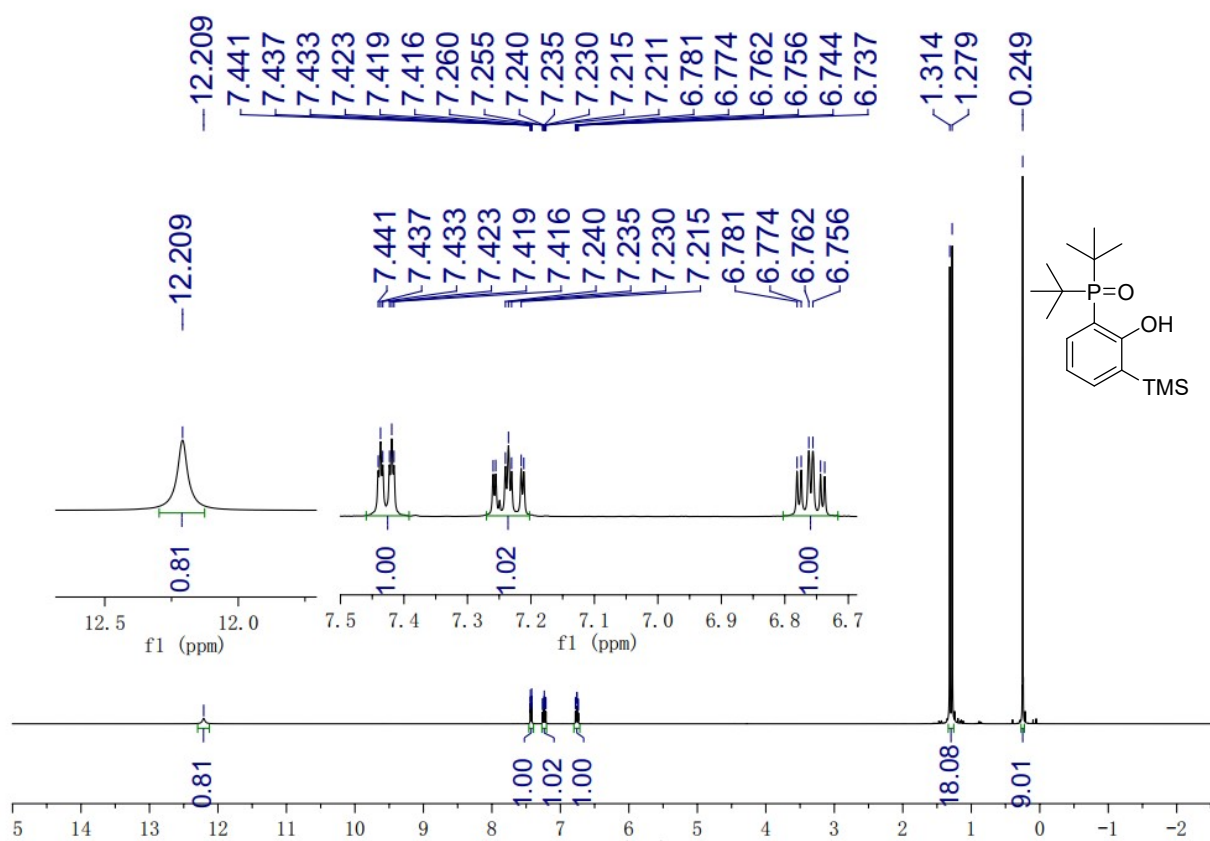


# SUPPORTING INFORMATION

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of compound **S5**

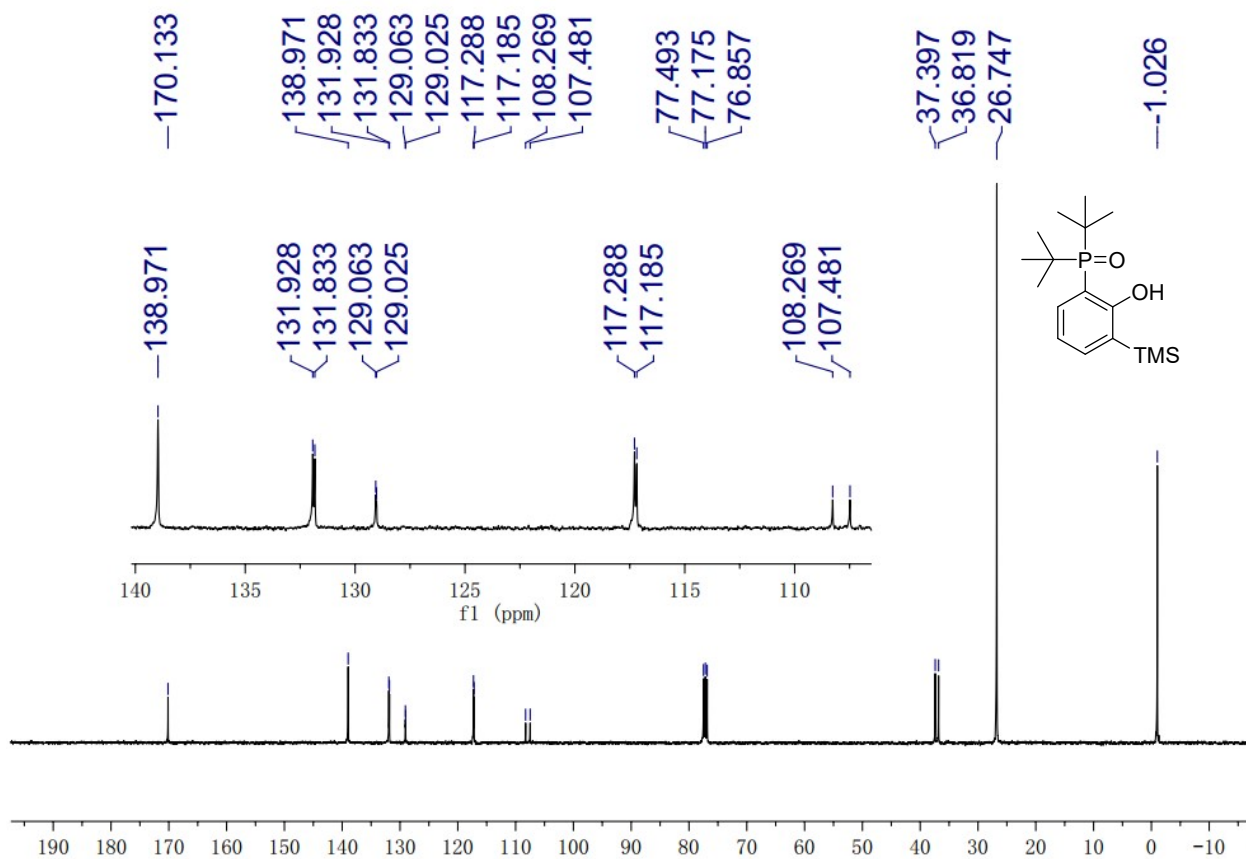


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of compound **S6**

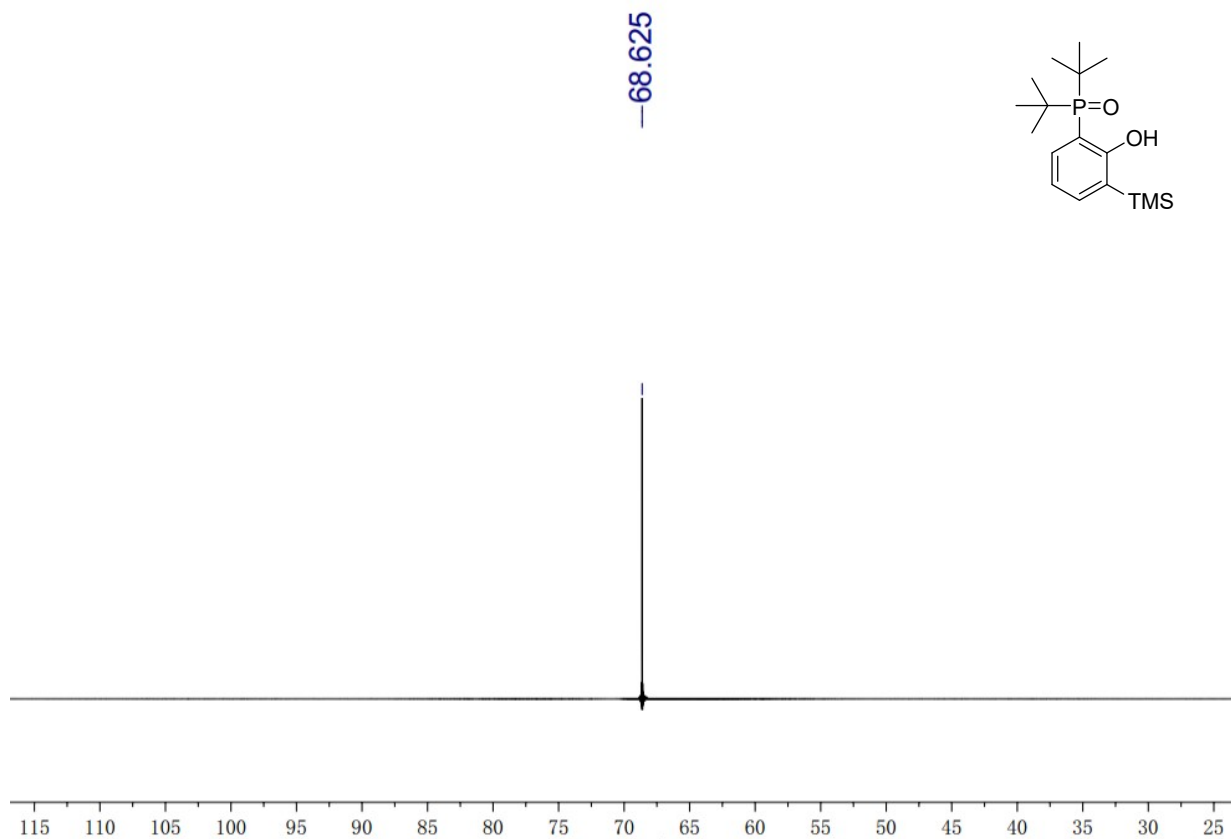


# SUPPORTING INFORMATION

$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of compound **S6**

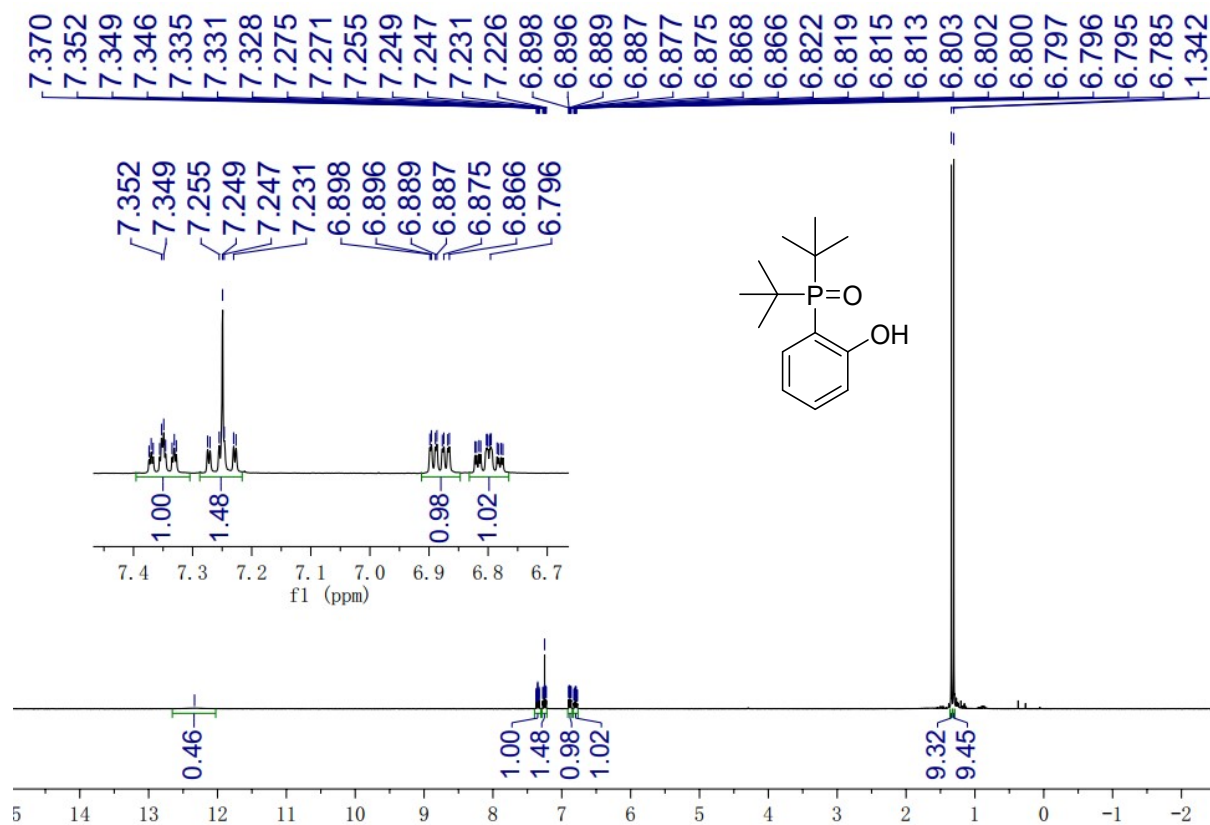


$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of compound **S6**

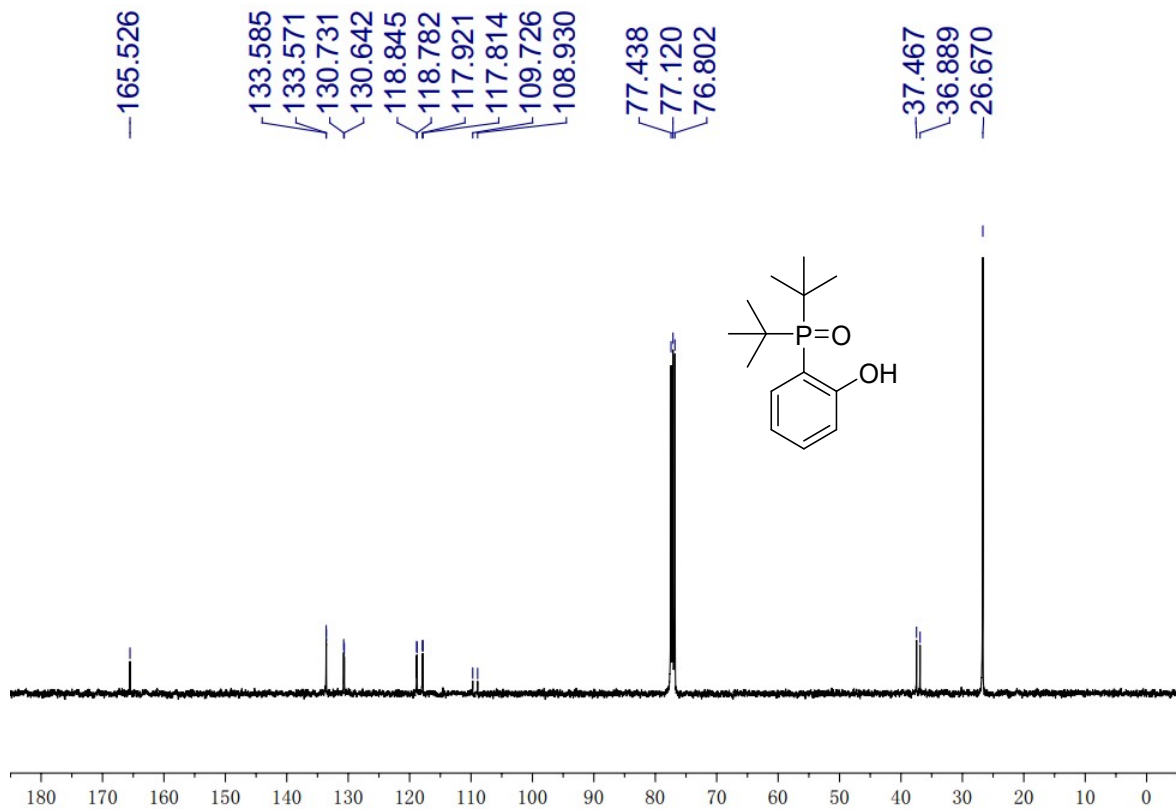


# SUPPORTING INFORMATION

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound **S9**

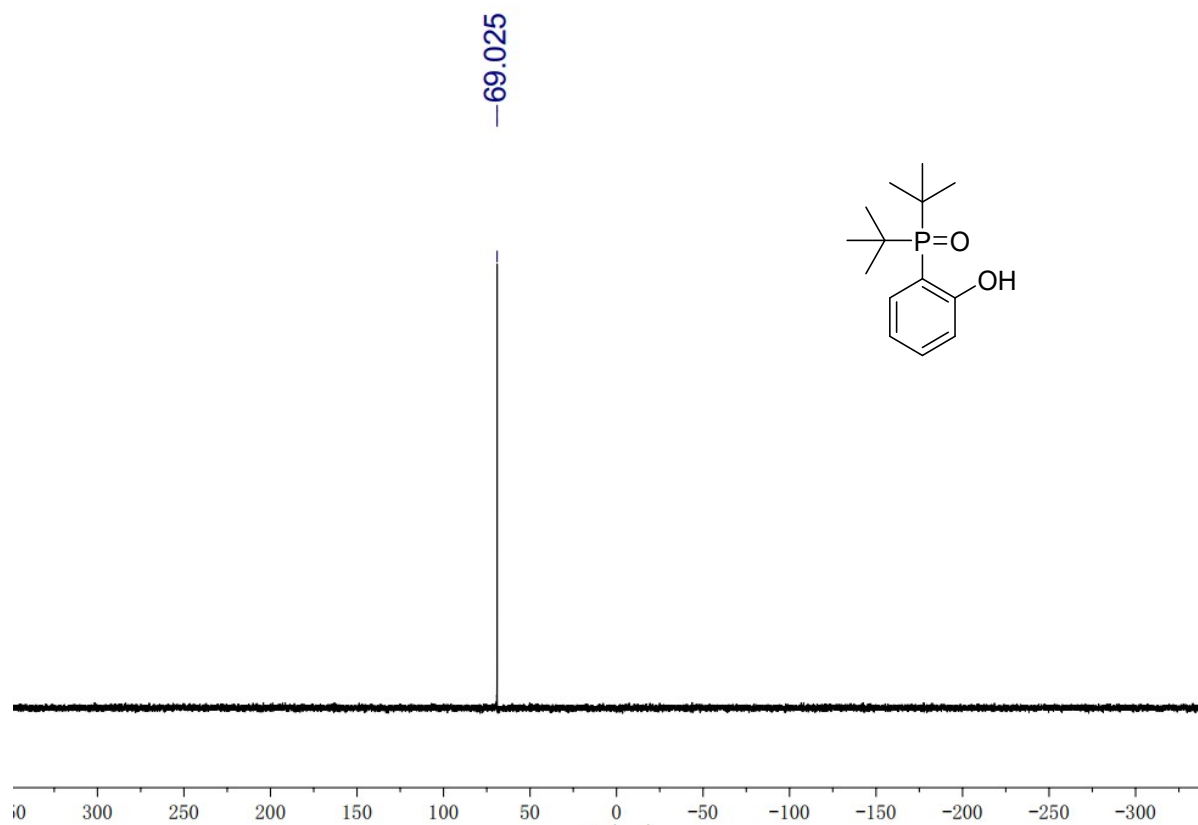


<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) spectrum of compound **S9**



# SUPPORTING INFORMATION

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ) spectrum of compound **S9**



## SUPPORTING INFORMATION

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