

Supporting Information

A Mechanochemical Construction of C-P Bonds through Radical- Radical Coupling

Ruizhi Sun ^a, Juxin Jiang ^a, Wenhao Li ^a, Zengdian Zhao ^a, Dong Liu, ^{b*} Hui Liu, ^{a*} and Lizhi Zhang ^{a *}

^a School of Chemistry and Chemical Engineering, Shandong University of Technology, Zibo, Shandong, 255000, P. R. China. E-mail: lizhizhangsdut@foxmail.com, zhanglizhi@sdut.edu.cn.

^b School of Science, China Pharmaceutical University, Nanjing, Jiangsu, 210009, P. R. China.

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1 General Information.

^1H NMR (400 MHz), ^{13}C NMR (100 MHz) were measured on a Bruker Avance 400 MHz spectrometer. Chemical shifts are reported in parts per million (ppm, δ) downfield from residual solvents peaks and coupling constants are reported as Hz. Splitting patterns are designated as singlet (s), doublet (d), triplet (t), splitting patterns that could not be interpreted or easily visualized are designated as multiplet (m). Electrospray mass spectra were obtained using an ESI/TOF Mariner Mass Spectrometer. Unless otherwise noted, all other commercially available reagents and solvents were used without further purification. Solvents were purchased from commercial suppliers. Purifications of reactions products were carried out by flash chromatography using silica gel (200–300 mesh). All electro-magnetic mill (EMM) reactions were carried out using grinding vessels in an energy field-coupled reactor (EFCR001) which was designed by Prof. Zengdian Zhao from Shandong University of Technology. The commercialized energy field-coupled reactor was purchased from Shandong Xinding Nano Technology Co., Ltd. The schematic diagram of the reactor is shown in Figure S1. The grinding medium used is SUS304 customized steel stainless rods (5.0 x 1.0 mm). The reaction bottle used is a customized 35 mL sealed tube (160 x 30 mm), with a TFE stopper, as shown in Figure S2. The control experiment with ball-milling conditions was conducted in a planetary ball mill equipment (YXQM-0.4 L, purchased from MITR, Changsha, Hunan province, China) equipped with a 50 mL stainless-steel grinding vessel with agate ball as grinding media.

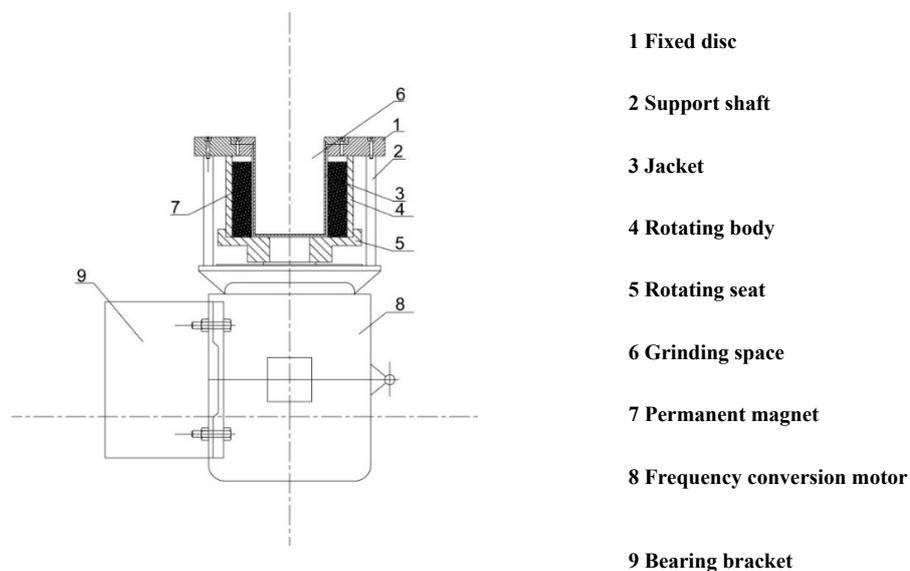


Fig. S1 Schematic Diagram of the Reactor

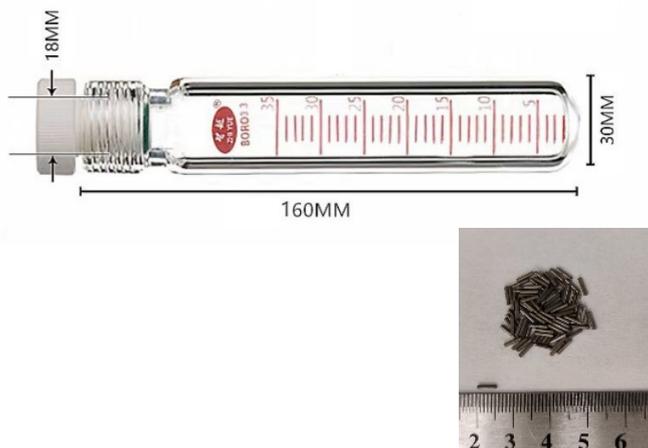
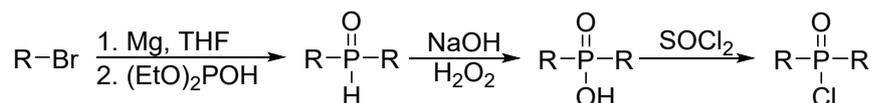


Fig. S2 the sealed tube and SUS 304 rods for the EMM reaction

2 The Synthesis of Starting Materials

1. Preparation of phosphonic chloride:

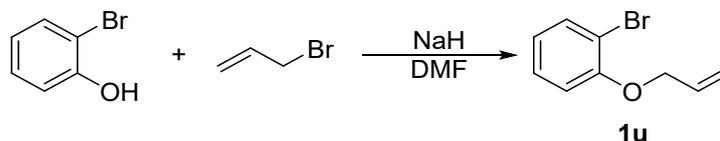


Step 1: Under argon, aryl bromide (20 mmol) in THF (15 mL) was added slowly to a stirred THF (20 mL) solution of I_2 (0.05 g, 0.2 mmol) containing magnesium turnings (0.48 g, 20 mmol), and heated to initiate the reaction. When the color of I_2 faded, the remainder of aryl bromide (10 mmol) was added dropwise over the course of 15 min. After magnesium turnings was consumed up, diethyl phosphate (1.38 g, 10 mmol) was added slowly into the reaction mixture, then stirred for 2 h. Then hydrochloric acid (20 mL, 6M) was added slowly upon stirring. The solution was evaporated under reduced pressure. The residue was extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo to give crude product.

Step 2: Hydrogen peroxide (30%, 10 mL) was added dropwise to a suspension of crude product in aqueous NaOH (5M, 10 mL) at room temperature, and the mixture was stirred for 1 h. Then hydrochloric acid (conc.) was added dropwise until no white solid was precipitated out. Then, DCM (20 mL) was added into the mixture, the organic layer was separated and dried over anhydrous Na_2SO_4 and concentrated in vacuo to give crude phosphinic acid which was used directly without purification.

Step 3: Solution of phenylphosphinic acid in toluene (20 mL) and SOCl_2 (5 mL) was refluxed for 1 h, then cooled to room temperature and evaporated to dryness to afford the crude aryl phosphinic chloride.

2. Preparation of 1-(allyloxy)-2-bromobenzene (**1u**):



To a 100 mL round-bottom flask containing 15 mL of DMF was added NaH (60% dispersion in mineral oil, 15 mmol), and the mixture was stirred at room temperature for 15 minutes. A solution of 2-bromophenol (10 mmol) in 5 mL of DMF was then slowly added dropwise to the reaction system. After stirring for 30 minutes, allyl bromide (12 mmol) was introduced, and the reaction was allowed to proceed overnight at room temperature. Upon completion, the reaction was quenched by the addition of 20 mL of water. The aqueous layer was extracted with ethyl acetate (3×15 mL). The combined organic layers were washed with saturated brine (3×10 mL), dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude residue was purified by column chromatography to afford the desired product.

3 General Procedure

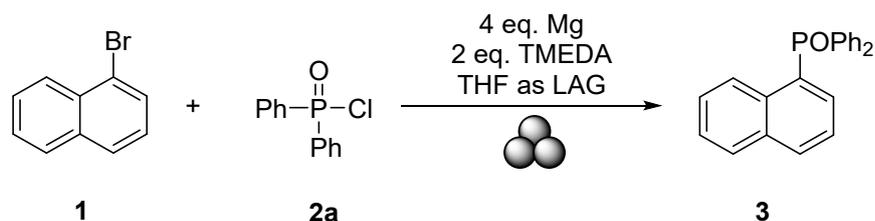
The procedure is illustrated in four steps:

- 1. Steel rods and sealed tube**: A glass test tube is shown with two steel rods inserted through the stopper. A small amount of dark, crystalline solid is visible on the surface of the test tube.
- 2. Reactants and steel rods were added**: The test tube is shown tilted, with a dark, viscous liquid coating the inner surface of the glass.
- 3. Place the sealed tube in the reactor.**: The test tube is shown inserted into a circular opening of a metal reactor. The reactor has a blue surface and a central black well.
- 4. Reaction finished**: The test tube is shown upright, containing a dark, viscous liquid.

Fig. S3 the description of general procedure in picture.

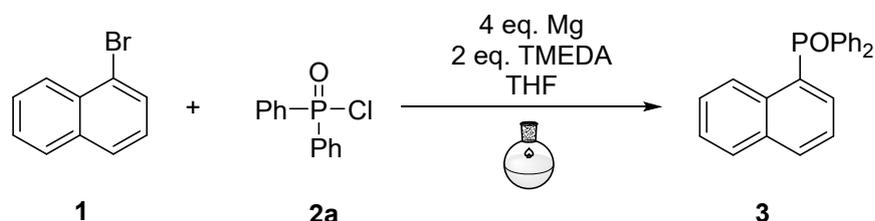
3.1 Control experiments

1. Ball-milling conditions



A stainless-steel vessel (50 mL) was loaded under air with 2-bromonaphthalene (1.5 eq, 7.5 mmol), **2a** (1 eq, 5 mmol), Mg powder (4 eq, 20 mmol), TMEDA (2.0 equiv, 10 mmol), and THF (1 mL). Then two stainless-steel balls (diameter: 10 mm) were added as mill media, and the reaction was carried at planetary ball mill for 180 minutes. After completion of the reaction, the mixture was filtered through silica gel and eluted with EtOAc. The resulting filtrate was concentrated under reduced pressure to remove the solvent. The product was purified by column chromatography on silica gel.

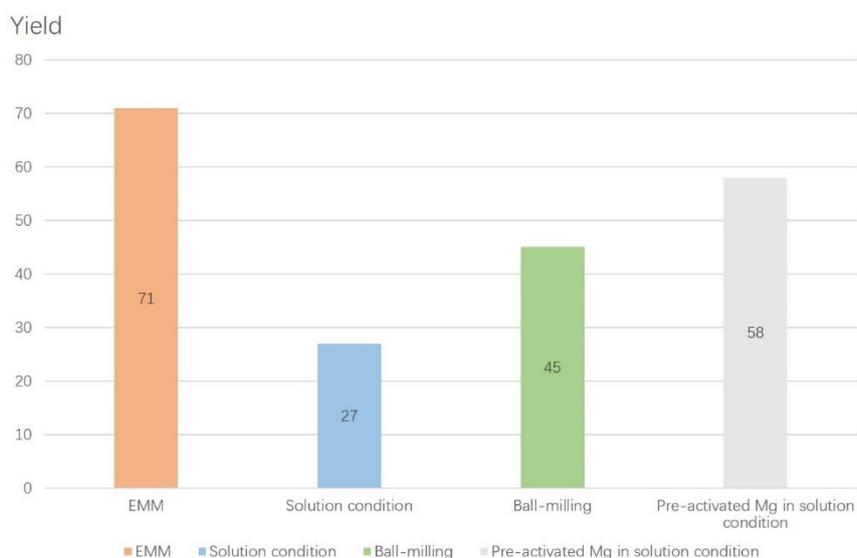
2. Solution conditions



A 35 mL reaction tube was loaded under air with 2-bromonaphthalene (0.75 mmol, 1.5 eq.), **2a** (0.5 mmol, 1.0 eq.), Mg powder (2 mmol, 4 eq.), TMEDA (1 mmol, 2 eq.), and THF (0.1 mL). Then the mixture was stirred for 3h under room temperature, after completion of the reaction, the mixture was filtered through silica gel and eluted with EtOAc, and the resulting filtrate was concentrated under reduced pressure to remove the solvent. The product was purified by column chromatography on silica gel.

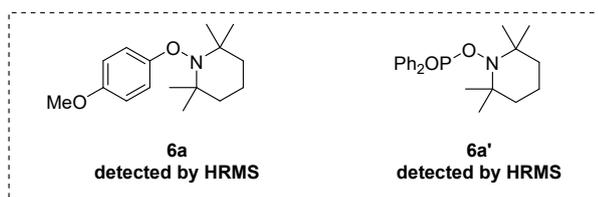
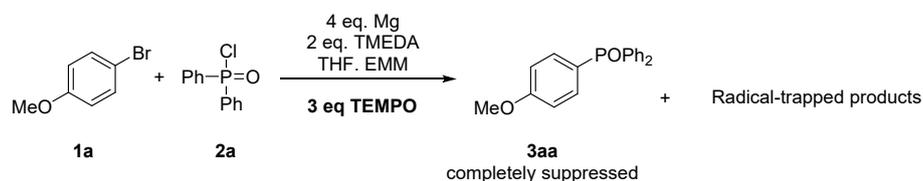
3. The reactivity of EMM-pre-activated Mg powder under solution-phase conditions.

A 35 mL reaction tube was loaded under air with Mg powder (2 mmol, 4 eq.) and THF (0.1 mL). Then ferromagnetic rods (5 g, 1.0 mm*5.0 mm) were added as mill media, and the reaction was carried at 2240 RPM for 40 minutes, then 2-bromonaphthalene (0.75 mmol, 1.5 eq.), **2a** (0.5 mmol, 1.0 eq.), TMEDA (1 mmol, 2 eq.) were added. Then the mixture was allowed to stirred for 3h under room temperature, after completion of the reaction, the mixture was filtered through silica gel and eluted with EtOAc, and the resulting filtrate was concentrated under reduced pressure to remove the solvent. The product was purified by column chromatography on silica gel.



4 Mechanism Verification Experiment.

4.1 Radical Trapping experiment with TEMPO



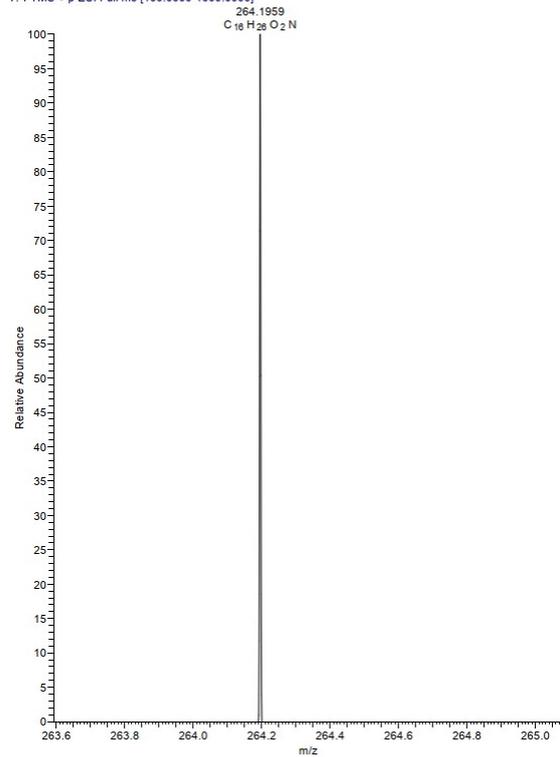
A 35 mL reaction tube was loaded under air with **1a** (0.75 mmol, 1.5 eq.), **2a** (0.5 mmol, 1.0 eq.), Mg powder (2 mmol, 4 eq.), TMEDA (1 mmol, 2 eq.), TEMPO (3 eq.) and THF (0.1 mL). Then ferromagnetic rods (5 g, 1.0 mm*5.0 mm) were added as mill media, and the reaction was carried at 2240 RPM for 180 minutes. After completion of the reaction, the mixture was filtered through silica gel and eluted with EtOAc. The resulting filtrate was concentrated under reduced pressure to remove the solvent. And the mixture was analyzed by HRMS.

HRMS of **6a** and **6a'**:

HRMS (ESI, m/z): Calculated for C₁₆H₂₆NO₂; (M+H) 264.1958, found 264.1959.

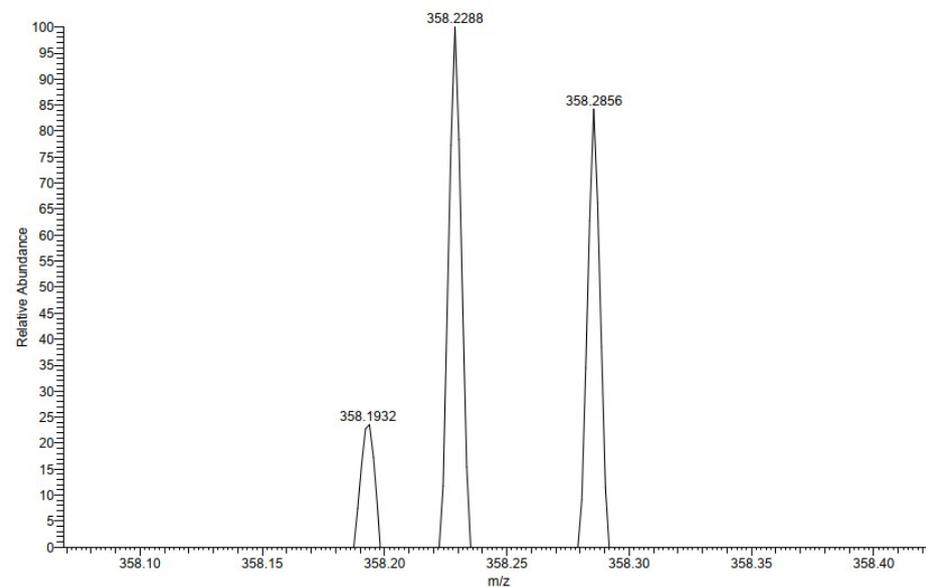
HRMS (ESI, m/z): Calculated for C₂₁H₂₉NO₂P (M+H) 358.1930, found 358.1932.

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zhao-549 #17 RT: 0.08 AV: 1 NL: 1.60E7
T: FTMS + p ESI Full ms [100.0000-1000.0000]

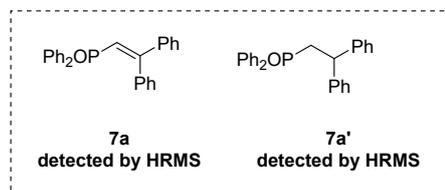
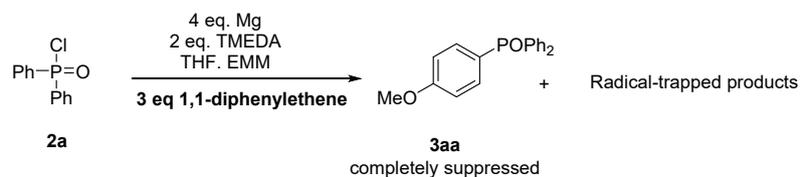


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zhao-549 #17 RT: 0.08 AV: 1 NL: 1.15E7
T: FTMS + p ESI Full ms [100.0000-1000.0000]



4.3 Radical Trapping experiment with 1,1-Diphenylethylene

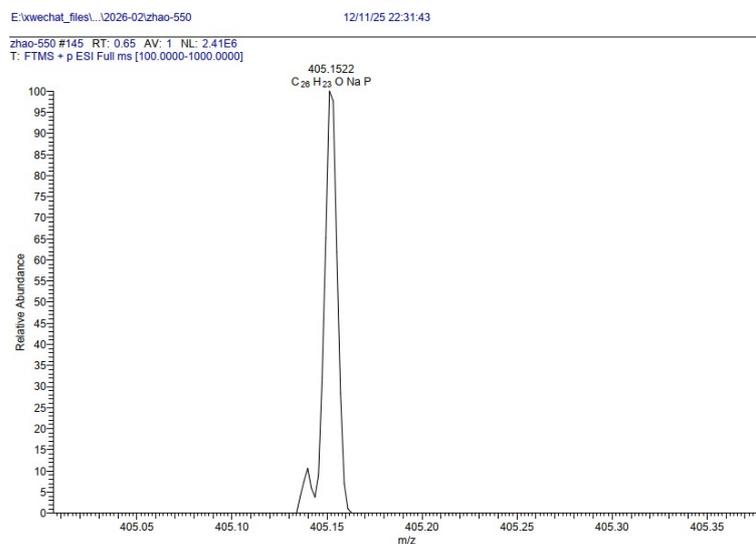
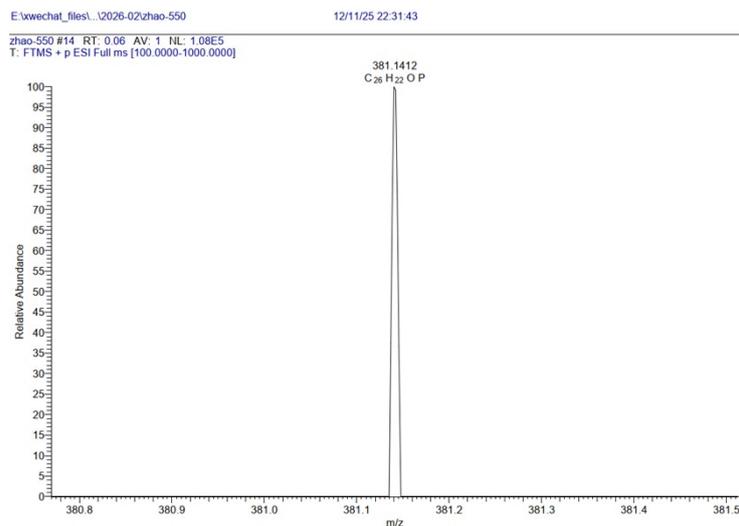


A 35 mL reaction tube was loaded under air with **2a** (0.5 mmol, 1.0 eq.), Mg powder (2 mmol, 4 eq.), TMEDA (1 mmol, 2 eq.), 1,1-diphenylethene (3 eq.) and THF (0.1 mL). Then ferromagnetic rods (5 g, 1.0 mm*5.0 mm) were added as mill media, and the reaction was carried at 2240 RPM for 180 minutes. After completion of the reaction, the mixture was filtered through silica gel and eluted with EtOAc. The resulting filtrate was concentrated under reduced pressure to remove the solvent. And the mixture was analyzed by HRMS.

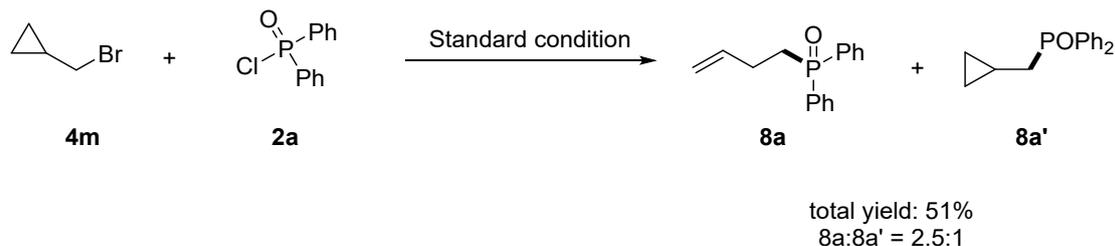
HRMS of **7a** and **7a'**:

HRMS (ESI, m/z): Calculated for C₂₆H₂₂OP; (M+H) 381.1403, found 381.1412.

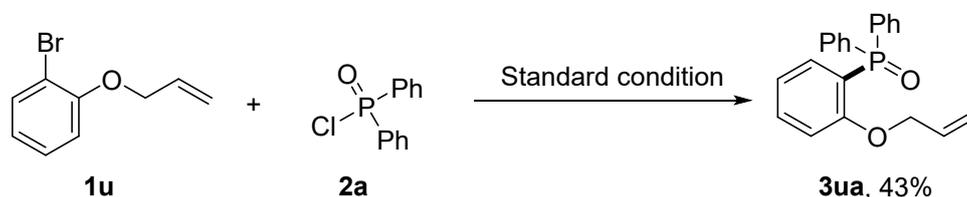
HRMS (ESI, m/z): Calculated for C₂₆H₂₃OPNa (M+Na) 405.1378, found 405.1522.



4.4 Radical Trapping experiment with Radical clock.



A 35 mL reaction tube was loaded under air with **4m** (0.75 mmol, 1.5 eq.) **2a** (0.5 mmol, 1.0 eq.), Mg powder (2 mmol, 4 eq.), TMEDA (1 mmol, 2 eq.), and THF (0.1 mL). Then ferromagnetic rods (5 g, 1.0 mm*5.0 mm) were added as mill media, and the reaction was carried at 2240 RPM for 180 minutes. After completion of the reaction, the mixture was filtered through silica gel and eluted with EtOAc, the resulting filtrate was concentrated under reduced pressure to remove the solvent. The product was purified by column chromatography on silica gel (EtOAc) to give mixture of **9a** and **9a'** (yield 51 %, 8a : 8a' = 2.5 : 1).



A 35 mL reaction tube was loaded under air with **1u** (0.75 mmol, 1.5 eq.) **2a** (0.5 mmol, 1.0 eq.), Mg powder (2 mmol, 4 eq.), TMEDA (1 mmol, 2 eq.), and THF (0.1 mL). Then ferromagnetic rods (5 g, 1.0 mm*5.0 mm) were added as mill media, and the reaction was carried at 2240 RPM for 180 minutes. After completion of the reaction, the mixture was filtered through silica gel and eluted with EtOAc, the resulting filtrate was concentrated under reduced pressure to remove the solvent. The product was purified by column chromatography on silica gel (EtOAc) to give **3ua** (43%).

4.5 Temperature detection of the reaction system.

We conducted two parallel reactions and monitored the temperature changes of the reaction systems as follows. The monitoring results indicated that the two reactions exhibit a nearly consistent variation trend, with the temperature difference well controlled within 10 °C.

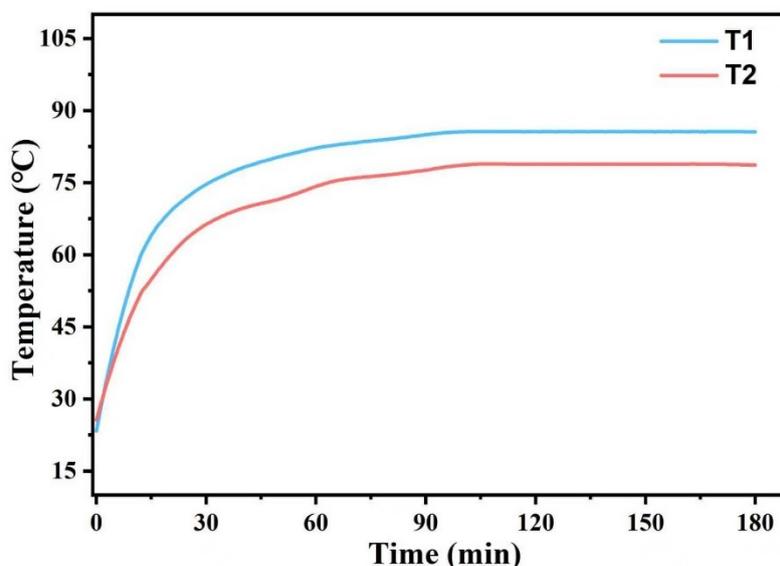


Fig S4. reaction temperature detection

4.6 SEM images of Mg powder before and after milling.

Before milling, the particles state of magnesium was observed by SEM, and the SEM images were shown in Fig S5.

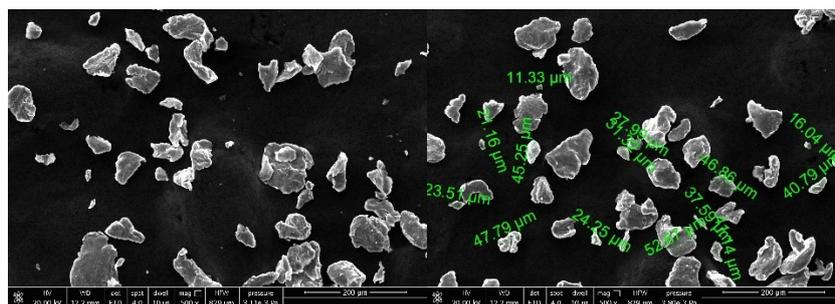


Fig S5. SEM images of Mg powder before milling

A 35 mL reaction tube was loaded under air with Mg powder (150 mg), THF (1.0 mL). Then ferromagnetic rods (5g, 1.0 mm*5.0 mm) were added as milling media, and the mixture was milled at 50 Hz for 10 minutes, the powder attached to the surface of ferromagnetic rods is tested by SEM, and the SEM images were shown in Fig S6.

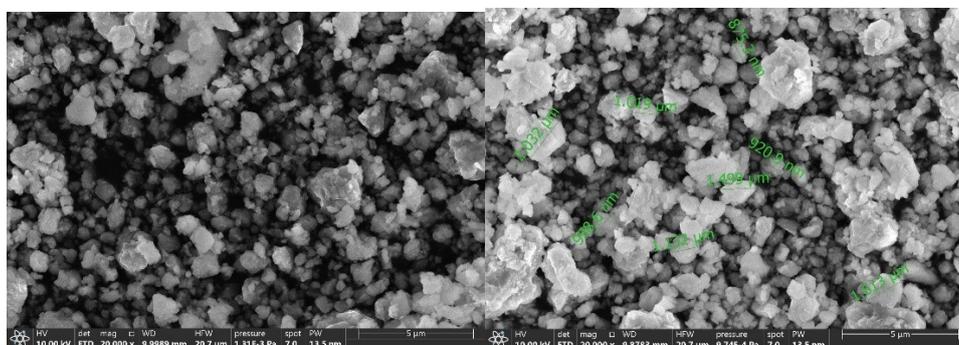
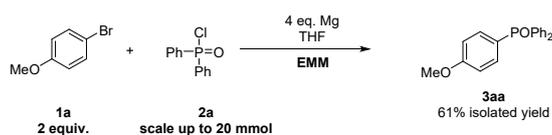


Fig S6. SEM images of Mg powder after milling

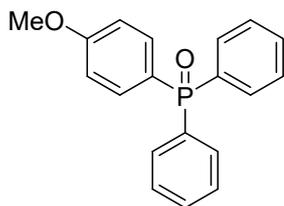
5 Scale-up experiment.



A sealed tube was loaded under air with **1a** (30 mmol, 1.5 eq.) **2a** (20 mmol, 1.0 eq.), Mg powder (80 mmol, 4 eq.), TMEDA (40 mmol, 2 eq.), and THF (4 mL). Then ferromagnetic rods (20g, 1.0 mm*5.0 mm) were added as milling media, and the reaction was carried at 2240 RPM for 180 min with a 10 min break every 50 min. After completion, the crude mixture was diluted with EtOAc and filtered through a pad of silica gel to remove the insoluble materials. The filtrate was concentrated under reduced pressure. The resulting solid was recrystallized from PE/EA to afford the product **3aa** (yield: 61%).

6 Physical Data for the Product

1. (4-methoxyphenyl)diphenylphosphine oxide (3aa)^[1]



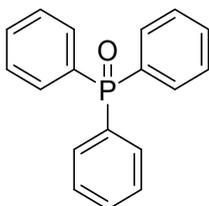
A white solid, the compound was prepared according to the general procedure. Yield: 96 mg, 66%.

¹H NMR (400 MHz, Chloroform-d): δ 7.57 (dd, J = 12.0, 6.9 Hz, 1H), 7.49 (dd, J = 11.5, 8.4 Hz, 1H), 7.42 (d, J = 5.9 Hz, 0H), 7.35 (td, J = 7.7, 2.7 Hz, 1H), 6.87 (dd, J = 8.8, 2.3 Hz, 1H), 3.73 (s, 1H).

¹³C NMR (101 MHz, Chloroform-d): δ 162.51 (d, J = 2.7 Hz), 133.97 (d, J = 11.3 Hz), 133.40, 132.36, 132.04 (d, J = 9.9 Hz), 131.86 (d, J = 2.8 Hz), 123.45 (d, J = 110.5 Hz), 114.11 (d, J = 13.2 Hz), 55.37.

³¹P NMR (162 MHz, Chloroform-d): δ 29.28.

2. triphenylphosphine oxide (3ba) ^[1]



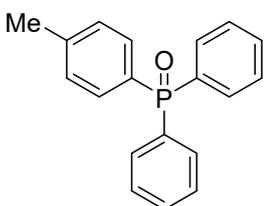
A white solid, the compound was prepared according to the general procedure. Yield: 103 mg, 74%.

¹H NMR (400 MHz, Chloroform-d): δ 7.72 – 7.63 (m, 6H), 7.54 (td, J = 7.3, 1.6 Hz, 3H), 7.45 (td, J = 7.5, 2.9 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-d): δ 133.00, 132.08 (d, J = 9.9 Hz), 131.97 (d, J = 2.7 Hz), 128.52 (d, J = 12.1 Hz).

³¹P NMR (162 MHz, Chloroform-d): δ 29.24.

3. diphenyl(p-tolyl)phosphine oxide (3ca) ^[2]



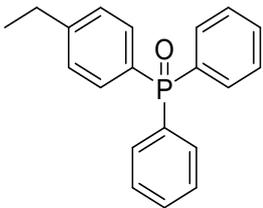
A white solid, the compound was prepared according to the general procedure. Yield: 86 mg, 59%.

¹H NMR (400 MHz, Chloroform-d): δ 7.71 – 7.62 (m, 4H), 7.59 – 7.50 (m, 4H), 7.49 – 7.41 (m, 4H), 7.27 (dd, J = 8.5, 2.4 Hz, 2H), 2.40 (s, 3H).

¹³C NMR (101 MHz, Chloroform-d): δ 142.38 (d, J = 2.8 Hz), 133.17, 132.14, 132.02 (d, J = 10.2 Hz), 131.95 (d, J = 9.9 Hz), 131.75 (d, J = 2.9 Hz), 129.51, 129.17 (d, J = 12.5 Hz), 128.36 (d, J = 12.1 Hz), 21.53 (d, J = 1.3 Hz).

³¹P NMR (162 MHz, Chloroform-d): δ 29.35.

4. (4-ethylphenyl)diphenylphosphine oxide (3da) ^[3]



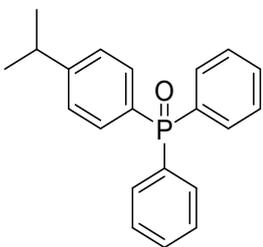
A white solid, the compound was prepared according to the general procedure. Yield: 102 mg, 66%.

¹H NMR (400 MHz, Chloroform-d): δ 7.72 – 7.63 (m, 4H), 7.62 – 7.51 (m, 4H), 7.45 (td, J = 7.4, 2.9 Hz, 4H), 7.29 (dd, J = 8.2, 2.7 Hz, 2H), 2.70 (q, J = 7.6 Hz, 2H), 1.25 (t, J = 7.6 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-d): δ 148.64 (d, J = 2.9 Hz), 133.32, 132.28, 132.18, 132.10 (d, J = 9.8 Hz), 131.85 (d, J = 2.8 Hz), 129.32 (d, J = 106.6 Hz), 128.47 (d, J = 12.0 Hz), 28.92, 15.21.

³¹P NMR (162 MHz, Chloroform-d): δ 29.29.

5. (4-isopropylphenyl)diphenylphosphine oxide (3ea)



A white solid, the compound was prepared according to the general procedure. Yield: 75 mg, 47%.

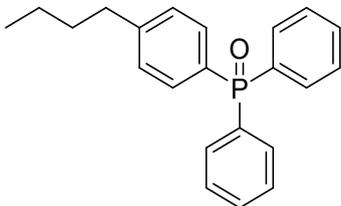
¹H NMR (400 MHz, Chloroform-d): δ 7.68 (dd, J = 12.0, 6.8 Hz, 4H), 7.62 – 7.50 (m, 4H), 7.45 (td, J = 7.6, 2.8 Hz, 4H), 7.31 (dd, J = 8.2, 2.7 Hz, 2H), 2.94 (p, J = 6.9 Hz, 1H), 1.25 (d, J = 6.9 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-d): δ 152.44 (d, J = 2.5 Hz), 134.15, 133.48 (d, J = 11.3 Hz), 133.11, 132.08 (d, J = 9.9 Hz), 131.53 (d, J = 2.7 Hz), 128.32 (d, J = 12.0 Hz), 116.57 (d, J = 115.8 Hz), 111.23 (d, J = 12.9 Hz), 80.71 – 65.96 (m), 39.97.

³¹P NMR (162 MHz, Chloroform-d): δ 29.83.

HRMS (APCI, m/z): Calculated for C₂₁H₂₁O₁P₁; (M+H)321.1403, found 321.1419.

6. (4-butylphenyl)diphenylphosphine oxide (3fa)



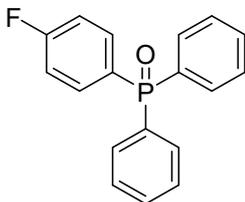
A white solid, the compound was prepared according to the general procedure. Yield: 71 mg, 43%.

¹H NMR (400 MHz, Chloroform-d): δ 7.64 – 7.54 (m, 4H), 7.52 – 7.41 (m, 4H), 7.36 (td, J = 7.3, 2.9 Hz, 4H), 7.18 (dd, J = 8.1, 2.7 Hz, 2H), 2.56 (t, J = 7.8 Hz, 2H), 1.51 (p, J = 7.6 Hz, 2H), 1.26 (h, J = 7.3 Hz, 2H), 0.83 (t, J = 7.3 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-d): δ 147.42 (d, *J* = 2.8 Hz), 133.21, 132.12 (d, *J* = 10.4 Hz), 132.07 (d, *J* = 9.9 Hz), 131.88 (d, *J* = 2.9 Hz), 128.66 (d, *J* = 12.6 Hz), 128.47 (d, *J* = 12.1 Hz), 35.67 (d, *J* = 1.2 Hz), 33.26, 22.33, 13.93.

³¹P NMR (162 MHz, Chloroform-d): δ 29.52.

7. (4-fluorophenyl)diphenylphosphine oxide (3ga) [1]



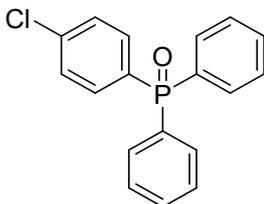
A white solid, the compound was prepared according to the general procedure. Yield: 90 mg, 61%.

¹H NMR (400 MHz, Chloroform-d): δ 7.71 – 7.63 (m, 6H), 7.55 (td, *J* = 7.2, 1.5 Hz, 2H), 7.50 – 7.44 (m, 3H), 7.15 (td, *J* = 8.7, 2.1 Hz, 2H).

¹³C NMR (101 MHz, Chloroform-d): δ 166.31 (d, *J* = 3.2 Hz), 163.79 (d, *J* = 3.2 Hz), 134.58 (dd, *J* = 11.4, 8.8 Hz), 132.76, 132.14 (d, *J* = 2.8 Hz), 132.01 (d, *J* = 10.0 Hz), 131.72, 129.05 (d, *J* = 3.5 Hz), 128.62 (d, *J* = 12.2 Hz), 127.99 (d, *J* = 3.5 Hz), 115.93 (dd, *J* = 21.3, 13.2 Hz).

¹⁹F NMR (377 MHz, Chloroform-d): δ -106.53 – -106.66 (m).

8. (4-chlorophenyl)diphenylphosphine oxide (3ha) [4]



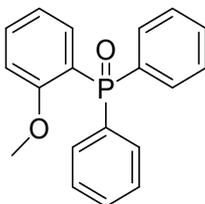
A white solid, the compound was prepared according to the general procedure. Yield: 96 mg, 66%.

¹H NMR (400 MHz, Chloroform-d): δ 7.72 – 7.58 (m, 6H), 7.58 – 7.40 (m, 8H).

¹³C NMR (101 MHz, Chloroform-d): δ 138.59 (d, *J* = 3.3 Hz), 133.49 (d, *J* = 10.7 Hz), 132.54, 132.21 (d, *J* = 2.7 Hz), 132.01 (d, *J* = 9.9 Hz), 131.50, 130.62, 128.96, 128.71.

³¹P NMR (162 MHz, Chloroform-d): δ 28.52.

9. (2-methoxyphenyl)diphenylphosphine oxide (3ia) [8]



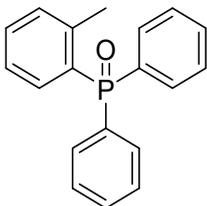
A white solid, the compound was prepared according to the general procedure. Yield: 111 mg, 72%.

¹H NMR (400 MHz, Chloroform-d): δ 7.82 – 7.74 (m, 1H), 7.73 – 7.67 (m, 4H), 7.57 – 7.47 (m, 3H), 7.42 (td, *J* = 7.5, 3.0 Hz, 4H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.92 (dd, *J* = 8.3, 5.3 Hz, 1H), 3.55 (s, 3H).

¹³C NMR (101 MHz, Chloroform-d): δ 160.87 (d, $J = 3.3$ Hz), 134.97 (d, $J = 7.1$ Hz), 134.32 (d, $J = 2.1$ Hz), 133.71, 132.64, 131.82 (d, $J = 10.3$ Hz), 131.48 (d, $J = 2.7$ Hz), 128.13 (d, $J = 12.5$ Hz), 120.96 (d, $J = 11.6$ Hz), 120.73, 119.70, 111.42 (d, $J = 6.5$ Hz), 55.27.

³¹P NMR (162 MHz, Chloroform-d): δ 27.49 (d, $J = 13.8$ Hz).

10. diphenyl(o-tolyl)phosphine oxide (3ja) ^[3]



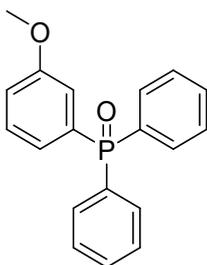
A white solid, the compound was prepared according to the general procedure. Yield: 71 mg, 61%.

¹H NMR (400 MHz, Chloroform-d): δ 7.61 – 7.53 (m, 4H), 7.45 (td, $J = 7.3, 1.6$ Hz, 2H), 7.40 – 7.30 (m, 5H), 7.19 (dd, $J = 8.1, 3.8$ Hz, 1H), 7.03 (dd, $J = 7.8, 2.7$ Hz, 1H), 6.94 (dd, $J = 14.8, 8.4$ Hz, 1H), 2.37 (s, 3H).

¹³C NMR (101 MHz, Chloroform-d): δ 143.26 (d, $J = 8.1$ Hz), 133.49 (d, $J = 12.9$ Hz), 133.14, 132.16 (d, $J = 2.6$ Hz), 132.11, 131.97, 131.89 (d, $J = 9.4$ Hz), 131.20, 130.17, 128.59 (d, $J = 12.0$ Hz), 125.22 (d, $J = 12.9$ Hz).

³¹P NMR (162 MHz, Chloroform-d): δ 31.92 (d, $J = 13.0$ Hz).

11. (3-methoxyphenyl)diphenylphosphine oxide (3ka) ^[7]



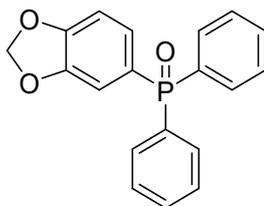
A white solid, the compound was prepared according to the general procedure. Yield: 97 mg, 63%.

¹H NMR (400 MHz, Chloroform-d): δ 7.72 – 7.63 (m, 4H), 7.54 (td, $J = 7.3, 1.5$ Hz, 2H), 7.45 (td, $J = 7.4, 2.9$ Hz, 4H), 7.36 (td, $J = 7.9, 3.8$ Hz, 1H), 7.29 (ddd, $J = 13.3, 2.7, 1.3$ Hz, 1H), 7.14 (dd, $J = 11.7, 7.5$ Hz, 1H), 7.06 (dd, $J = 8.3, 2.7$ Hz, 1H), 3.78 (s, 3H).

¹³C NMR (101 MHz, Chloroform-d): δ 159.56 (d, $J = 14.8$ Hz), 134.30, 133.28, 132.92, 132.06 (d, $J = 9.8$ Hz), 131.93 (d, $J = 10.4$ Hz), 129.69 (d, $J = 14.3$ Hz), 128.52 (d, $J = 12.1$ Hz), 124.33 (d, $J = 10.1$ Hz), 118.15 (d, $J = 2.6$ Hz), 116.78 (d, $J = 10.7$ Hz), 55.42.

³¹P NMR (162 MHz, Chloroform-d): δ 29.46.

12. benzo[d][1,3]dioxol-5-ylidiphenylphosphine oxide (3la) ^[3]



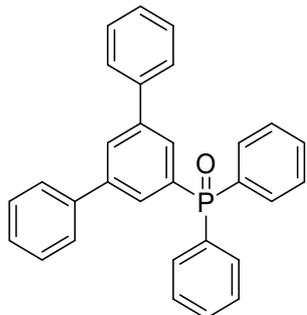
A white solid, the compound was prepared according to the general procedure. Yield: 98 mg, 61%.

¹H NMR (400 MHz, Chloroform-d): δ 7.70 – 7.62 (m, 4H), 7.53 (td, *J* = 7.2, 1.5 Hz, 2H), 7.45 (td, *J* = 7.5, 3.0 Hz, 4H), 7.18 (ddd, *J* = 12.6, 8.0, 1.5 Hz, 1H), 7.08 (dd, *J* = 11.3, 1.5 Hz, 1H), 6.87 (dd, *J* = 7.9, 2.4 Hz, 1H), 5.99 (s, 2H).

¹³C NMR (101 MHz, Chloroform-d): δ 150.85 (d, *J* = 2.8 Hz), 147.98 (d, *J* = 18.1 Hz), 133.11, 131.99 (d, *J* = 9.9 Hz), 128.49 (d, *J* = 12.2 Hz), 127.53 (d, *J* = 11.0 Hz), 126.03, 124.96, 111.46 (d, *J* = 12.7 Hz), 108.63 (d, *J* = 15.1 Hz), 101.65.

³¹P NMR (162 MHz, Chloroform-d): δ 29.31.

13. [1,1':3',1''-terphenyl]-5'-yldiphenylphosphine oxide (3ma) ^[6]



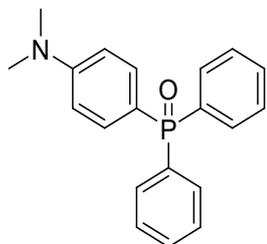
A white solid, the compound was prepared according to the general procedure. Yield: 92 mg, 43%.

¹H NMR (400 MHz, Chloroform-d): δ 7.87 (s, 1H), 7.79 (d, *J* = 12.2 Hz, 2H), 7.66 (dd, *J* = 12.2, 7.7 Hz, 4H), 7.46 (dd, *J* = 19.2, 7.6 Hz, 6H), 7.40 – 7.28 (m, 8H), 7.24 (t, *J* = 7.4 Hz, 2H).

¹³C NMR (101 MHz, Chloroform-d): δ 144.74 (d, *J* = 2.9 Hz), 139.90, 133.09, 132.63 (d, *J* = 10.2 Hz), 132.13 (d, *J* = 9.9 Hz), 132.05, 132.01 (d, *J* = 2.8 Hz), 131.60, 130.56, 128.99, 128.57 (d, *J* = 12.1 Hz), 128.20, 127.28 (d, *J* = 1.9 Hz), 127.15.

³¹P NMR (162 MHz, Chloroform-d): δ 29.40.

14. (4-(dimethylamino)phenyl)diphenylphosphine oxide (3na) ^[8]



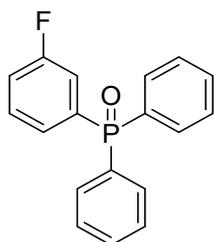
A white solid, the compound was prepared according to the general procedure. Yield: 98 mg, 61%.

¹H NMR (400 MHz, Chloroform-d): δ 7.71 – 7.64 (m, 4H), 7.61 – 7.51 (m, 4H), 7.49 – 7.43 (m, 4H), 7.31 (dd, *J* = 8.1, 2.8 Hz, 2H), 1.26 (d, *J* = 7.0 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-d): δ 153.22 (d, *J* = 2.8 Hz), 133.23, 132.28, 132.19, 132.13, 132.04, 131.87 (d, *J* = 2.8 Hz), 129.91, 128.47 (d, *J* = 12.1 Hz), 126.74 (d, *J* = 12.5 Hz), 23.71.

³¹P NMR (162 MHz, Chloroform-d): δ 29.39.

15. (3-fluorophenyl)diphenylphosphine oxide (3oa) ^[6]



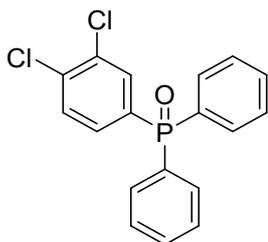
A white solid, the compound was prepared according to the general procedure. Yield: 106.5 mg, 72%.

¹H NMR (400 MHz, Chloroform-d): δ 7.64 – 7.55 (m, 4H), 7.53 – 7.47 (m, 2H), 7.45 – 7.35 (m, 6H), 7.32 – 7.26 (m, 1H), 7.7.19 – 7.14 (m, 1H).

¹³C NMR (101 MHz, Chloroform-d): δ 163.74 (d, J = 16.8 Hz), 161.25 (d, J = 16.8 Hz), 135.89 (d, J = 5.6 Hz), 134.87 (d, J = 5.4 Hz), 132.32, 132.27 (d, J = 2.9 Hz), 132.05 (d, J = 9.9 Hz), 131.28, 130.54 (dd, J = 13.9, 7.4 Hz), 128.67 (d, J = 12.3 Hz), 127.84 (dd, J = 9.2, 3.3 Hz), 119.28 (d, J = 2.6 Hz), 119.07 (dd, J = 6.7, 4.2 Hz), 118.84 (d, J = 10.7 Hz).

³¹P NMR (162 MHz, Chloroform-d): δ 28.37.

16. (3,4-dichlorophenyl)diphenylphosphine oxide (3pa)



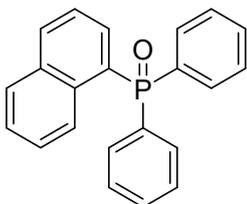
A white solid, the compound was prepared according to the general procedure. Yield: 112.8 mg, 65%

¹H NMR (400 MHz, Chloroform-d): δ 7.79 (dd, J = 11.7, 1.7 Hz, 1H), 7.71 – 7.62 (m, 4H), 7.60 – 7.54 (m, 3H), 7.53 – 7.44 (m, 6H).

¹³C NMR (101 MHz, Chloroform-d): δ 136.79 (d, J = 3.1 Hz), 133.80, 133.79 (d, J = 11.1 Hz), 133.55, 133.39, 132.79, 132.47 (d, J = 2.9 Hz), 131.98 (d, J = 10.0 Hz), 131.09, 130.99, 130.86 (d, J = 3.8 Hz), 130.72, 128.79 (d, J = 12.4 Hz), 85.21 – 65.27 (m).

³¹P NMR (162 MHz, Chloroform-d): δ 27.46.

17. naphthalen-1-ylidiphenylphosphine oxide (3qa)^[1]



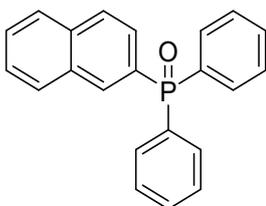
A white solid, the compound was prepared according to the general procedure. Yield: 116 mg, 71%.

¹H NMR (400 MHz, Chloroform-d): δ 8.29 (d, J = 13.8, 1.5 Hz, 1H), 7.89 (, J = 11.6, 8.1, 2.2 Hz, 3H), 7.76 – 7.68 (m, 4H), 7.67 – 7.60 (m, 1H), 7.61 – 7.51 (m, 4H), 7.49 – 7.44 (m, 4H).

¹³C NMR (101 MHz, Chloroform-d): δ 134.73 (d, J = 2.4 Hz), 134.05 (d, J = 9.2 Hz), 133.04, 132.49, 132.36, 132.17 (d, J = 10.0 Hz), 132.06 (d, J = 2.8 Hz), 132.00, 130.05, 129.00, 128.60 (d, J = 12.1 Hz), 128.31, 127.87, 127.01, 126.86 (d, J = 10.7 Hz).

³¹P NMR (162 MHz, Chloroform-d): δ 32.47.

18. naphthalen-2-ylidiphenylphosphine oxide (3ra)^[1]



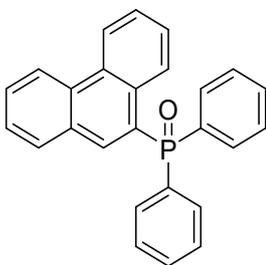
A white solid, the compound was prepared according to the general procedure. Yield: 129.6 mg, 79%

¹H NMR (400 MHz, Chloroform-d): δ 8.29 (d, J = 15.3 Hz, 1H), 7.915 - 7.858 (m, 3H), 7.76 - 7.68 (m, 4H), 7.67 - 7.62 (m, 1H), 7.60 - 7.50 (m, 4H), 7.489 - 7.441 (m, 4H).

¹³C NMR (101 MHz, Chloroform-d): δ 134.73 (d, J = 2.4 Hz), 134.05 (d, J = 9.2 Hz), 133.04, 132.49, 132.36, 132.17 (d, J = 10.0 Hz), 132.06 (d, J = 2.8 Hz), 132.00, 130.05, 129.00, 128.60 (d, J = 12.1 Hz), 128.42, 128.31, 127.87, 127.01, 126.86 (d, J = 10.7 Hz).

³¹P NMR (162 MHz, Chloroform-d): δ 32.47.

19. phenanthren-9-ylidiphenylphosphine oxide (3sa) ^[5]



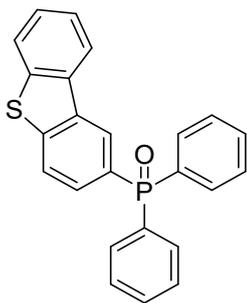
A white solid, the compound was prepared according to the general procedure. Yield: 98 mg, 61%.

¹H NMR (400 MHz, Chloroform-d): δ 8.67 (td, J = 11.8, 8.3 Hz, 3H), 7.78 - 7.67 (m, 6H), 7.66 - 7.59 (m, 2H), 7.55 (td, J = 7.9, 7.3, 2.2 Hz, 3H), 7.46 (td, J = 7.6, 2.8 Hz, 5H).

¹³C NMR (101 MHz, Chloroform-d): δ 136.91 (d, J = 11.3 Hz), 133.12, 132.18, 132.17 (d, J = 9.8 Hz), 132.07, 132.04, 130.85 (dd, J = 19.3, 8.4 Hz), 130.09, 129.76, 129.61, 129.18, 128.70, 128.34, 127.33, 127.24 (d, J = 7.4 Hz), 127.07, 125.85, 123.08, 122.67.

³¹P NMR (162 MHz, Chloroform-d): δ 32.78 (d, J = 14.1 Hz).

20. dibenzo[b,d]thiophen-2-ylidiphenylphosphine oxide (3ta) ^[16]



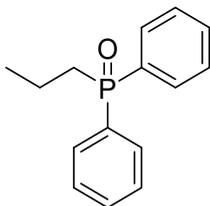
A white solid, the compound was prepared according to the general procedure. Yield: 132.5 mg, 69%.

¹H NMR (400 MHz, Chloroform-d): δ 8.62 (dd, J = 12.6, 1.5 Hz, 1H), 8.16 - 8.09 (m, 1H), 7.91 (dd, J = 8.2, 2.5 Hz, 1H), 7.87 - 7.82 (m, 1H), 7.73 (ddd, J = 12.0, 8.3, 1.4 Hz, 4H), 7.62 - 7.54 (m, 3H), 7.51 - 7.43 (m, 6H).

¹³C NMR (101 MHz, Chloroform-d): δ 143.52 (d, *J* = 2.7 Hz), 139.51, 135.67 (d, *J* = 13.2 Hz), 134.80, 133.16, 132.17 (d, *J* = 9.9 Hz), 129.25 (d, *J* = 11.8 Hz), 128.66, 128.64 (d, *J* = 12.1 Hz), 127.61, 127.52, 125.82 (d, *J* = 10.1 Hz), 124.93, 122.98, 122.86 (d, *J* = 2.3 Hz), 122.09.

³¹P NMR (162 MHz, Chloroform-d): δ 29.90.

21. diphenyl(propyl)phosphine oxide (4aa) ^[13]



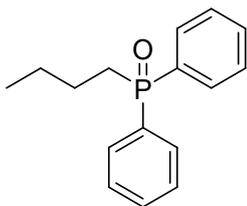
A white solid, the compound was prepared according to the general procedure. Yield: 81 mg, 67%.

¹H NMR (400 MHz, Chloroform-d): δ 7.79 – 7.70 (m, 4H), 7.53 – 7. (m, 6H), 2.31 – 2.20 (m, 2H), 1.73 – 1.60 (m, 2H), 1.03 (td, *J* = 7.4, 1.1 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-d): δ 133.67, 132.70, 131.64 (d, *J* = 2.8 Hz), 130.78 (d, *J* = 9.2 Hz), 128.62 (d, *J* = 11.5 Hz), 32.21, 31.50, 15.71 (d, *J* = 15.5 Hz), 15.28 (d, *J* = 3.9 Hz).

³¹P NMR (162 MHz, Chloroform-d): δ 32.43.

22. butyldiphenylphosphine oxide (4ba) ^[3]



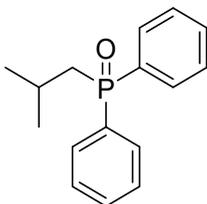
A white solid, the compound was prepared according to the general procedure. Yield: 80 mg, 65%.

¹H NMR (400 MHz, Chloroform-d): δ 7.74 (ddd, *J* = 11.4, 8.1, 1.6 Hz, 4H), 7.53f – 7.44 (m, 6H), 2.33 – 2.21 (m, 2H), 1.60 (dq, *J* = 16.3, 8.3, 7.7 Hz, 2H), 1.42 (h, *J* = 7.3 Hz, 2H), 0.88 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-d): δ 133.65, 132.67, 131.64 (d, *J* = 2.8 Hz), 130.77 (d, *J* = 9.2 Hz), 128.62 (d, *J* = 11.5 Hz), 29.83, 29.11, 24.12 (d, *J* = 15.1 Hz), 23.47 (d, *J* = 4.0 Hz), 13.62.

³¹P NMR (162 MHz, Chloroform-d): δ 32.65 (t, *J* = 9.9 Hz).

23. isobutyldiphenylphosphine oxide(4ca) ^[10]



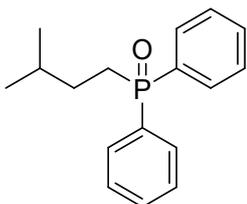
A white solid, the compound was prepared according to the general procedure. Yield: 65 mg, 51%.

¹H NMR (400 MHz, Chloroform-d): δ 7.81 – 7.70 (m, 4H), 7.53 – 7.42 (m, 6H), 2.27 – 2.10 (m, 3H), 1.01 (d, *J* = 6.3 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-d): δ 134.41, 133.44, 131.52 (d, *J* = 2.6 Hz), 130.68 (d, *J* = 9.1 Hz), 128.60 (d, *J* = 11.4 Hz), 38.70, 38.00, 24.70 (d, *J* = 9.0 Hz), 23.65 (d, *J* = 3.8 Hz).

³¹P NMR (162 MHz, Chloroform-d): δ 29.39.

24. isopentyldiphenylphosphine oxide (4da) ^[11]



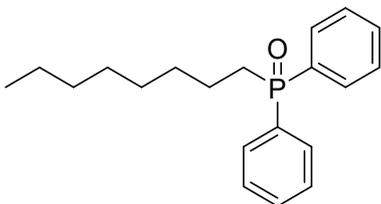
A white solid, the compound was prepared according to the general procedure. Yield: 70 mg, 51%.

¹H NMR (400 MHz, Chloroform-d): δ 7.74 (ddd, $J = 11.4, 8.1, 1.6$ Hz, 4H), 7.53 – 7.44 (m, 6H), 2.31 – 2.20 (m, 2H), 1.65 – 1.57 (m, 1H), 1.55 – 1.49 (m, 2H), 0.89 (d, $J = 6.5$ Hz, 6H).

¹³C NMR (101 MHz, Chloroform-d): δ 133.58, 132.61, 131.65 (d, $J = 2.6$ Hz), 130.77 (d, $J = 9.2$ Hz), 128.63 (d, $J = 11.4$ Hz), 29.91 (d, $J = 3.9$ Hz), 29.12 (d, $J = 14.6$ Hz), 27.98, 27.26, 22.03.

³¹P NMR (162 MHz, Chloroform-d): δ 33.12.

25. octyldiphenylphosphine oxide(4ea) ^[9]



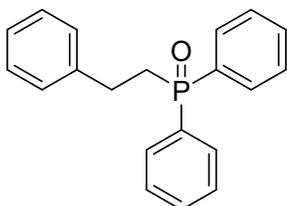
A white solid, the compound was prepared according to the general procedure. Yield: 101 mg, 64%.

¹H NMR (400 MHz, Chloroform-d): δ 7.78 – 7.69 (m, 4H), 7.52 – 7.43 (m, 6H), 2.30 – 2.21 (m, 2H), 1.67– 1.57 (m, 2H), 1.39 (p, $J = 6.8$ Hz, 2H), 1.26 – 1.22 (m, 9H), 0.85 (t, $J = 6.8$ Hz, 3H).

¹³C NMR (101 MHz, Chloroform-d): δ 133.69, 132.72, 131.60 (d, $J = 2.7$ Hz), 130.76 (d, $J = 9.2$ Hz), 128.60 (d, $J = 11.6$ Hz), 31.74, 30.97 (d, $J = 14.6$ Hz), 30.09, 29.37, 29.01 (d, $J = 1.8$ Hz), 22.59, 21.40 (d, $J = 3.9$ Hz), 14.07.

³¹P NMR (162 MHz, Chloroform-d): δ 32.63.

26. phenethyldiphenylphosphine oxide (4fa) ^[9]



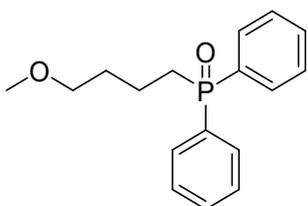
A white solid, the compound was prepared according to the general procedure. Yield: 75 mg, 48%.

¹H NMR (400 MHz, Chloroform-d): δ 7.75 – 7.63 (m, 4H), 7.48 – 7.33 (m, 6H), 7.21 – 7.13 (m, 2H), 7.13 – 7.04 (m, 3H), 2.90 – 2.79 (m, 2H), 2.55 – 2.44 (m, 2H).

¹³C NMR (101 MHz, Chloroform-d): δ 140.17, 140.02, 132.14, 131.16, 130.80, 130.78, 129.77, 129.67, 127.74, 127.63, 127.57, 127.00, 125.29, 31.17, 30.48, 26.49, 26.46.

³¹P NMR (162 MHz, Chloroform-d): δ 31.67.

27. (4-methoxybutyl)diphenylphosphine oxide (4ga)



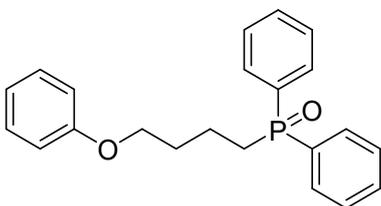
A white solid, the compound was prepared according to the general procedure. Yield: 75 mg, 52%.

¹H NMR (400 MHz, Chloroform-d): δ 7.74 (ddd, J = 11.4, 8.1, 1.6 Hz, 4H), 7.53 – 7.44 (m, 6H), 3.39 – 3.31 (m, 2H), 3.28 (s, 3H), 2.34f – 2.27 (m, 2H), 1.71 – 1.67 (m, 4H).

¹³C NMR (101 MHz, Chloroform-d): δ 133.48, 132.50, 131.70 (d, J = 2.7 Hz), 130.77 (d, J = 9.2 Hz), 128.65 (d, J = 11.6 Hz), 72.08, 58.58, 30.76 (d, J = 14.4 Hz), 29.91, 29.19, 18.52 (d, J = 3.8 Hz).

³¹P NMR (162 MHz, Chloroform-d): δ 32.53.

28. (4-phenoxybutyl)diphenylphosphine oxide (4ha) ^[14]



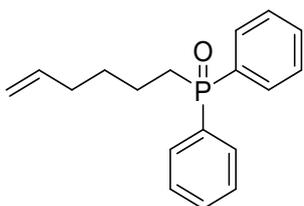
A white solid, the compound was prepared according to the general procedure. Yield: 106.8 mg, 61%.

¹H NMR (400 MHz, Chloroform-d): δ 7.78 – 7.70 (m, 4H), 7.55 – 7.42 (m, 6H), 7.29 – 7.22 (m, 2H), 6.98 – 6.89 (m, 1H), 6.87 – 6.79 (m, 2H), 3.94 (t, J = 5.9 Hz, 2H), 2.40 – 2.28 (m, 2H).

¹³C NMR (101 MHz, Chloroform-d): δ 158.81, 133.45, 132.47, 131.75 (d, J = 2.7 Hz), 130.81 (d, J = 9.2 Hz), 129.45, 128.70 (d, J = 11.5 Hz), 120.67, 114.43, 66.89, 30.29 (d, J = 14.4 Hz), 29.41 (d, J = 72.0 Hz), 18.48 (d, J = 3.7 Hz).

³¹P NMR (162 MHz, Chloroform-d): δ 32.43.

29. hex-5-en-1-ylidiphenylphosphine oxide (4ia)



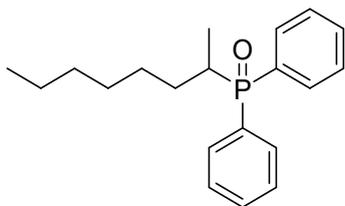
A white solid, the compound was prepared according to the general procedure. Yield: 65 mg, 46%.

¹H NMR (400 MHz, Chloroform-d): δ 7.78 – 7.70 (m, 4H), 7.53 – 7.44 (m, 6H), 5.79 – 5.68 (m, 1H), 5.02 – 4.87 (m, 2H), 2.32 – 2.21 (m, 2H), 2.03 (q, J = 7.5 Hz, 2H), 1.71 – 1.59 (m, 2H), 1.50 (p, J = 7.4 Hz, 2H).

¹³C NMR (101 MHz, Chloroform-d): δ 138.16, 133.57, 132.59, 131.68 (d, J = 2.7 Hz), 130.72, 128.64 (d, J = 11.5 Hz), 114.82, 33.19, 30.24, 30.09, 29.95, 29.23, 20.98 (d, J = 3.9 Hz).

³¹P NMR (162 MHz, Chloroform-d): δ 32.55.

30. octan-2-ylidiphenylphosphine oxide (4ja) ^[12]



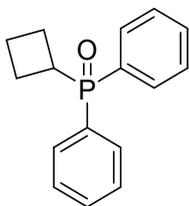
A white solid, the compound was prepared according to the general procedure. Yield: 105 mg, 67%.

¹H NMR (400 MHz, Chloroform-d): δ 7.78 – 7.70 (m, 4H), 7.53 – 7.43 (m, 6H), 5.78 – 5.68f (m, 1H), 5.02 – 4.87 (m, 2H), 2.46 – 2.20 (m, 2H), 2.03 (q, J = 7.2 Hz, 2H), 1.82 – 1.57 (m, 3H), 1.50 (p, J = 7.4 Hz, 2H).

¹³C NMR (101 MHz, Chloroform-d): δ 131.42 (d, J = 1.9 Hz), 131.04 (d, J = 8.6 Hz), 128.59 (d, J = 2.7 Hz), 128.48 (d, J = 2.9 Hz), 32.34, 31.59 (d, J = 5.8 Hz), 28.92, 28.72, 27.38 (d, J = 12.4 Hz), 22.52, 14.01, 12.04 (d, J = 2.6 Hz).

³¹P NMR (162 MHz, Chloroform-d): δ 32.63.

31. cyclobutyldiphenylphosphine oxide (4ka) ^[17]



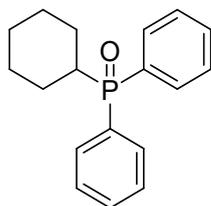
A white solid, the compound was prepared according to the general procedure. Yield: 102 mg, 80%.

¹H NMR (400 MHz, Chloroform-d): δ 7.73 – 7.62 (m, 4H), 7.55 – 7.39 (m, 6H), 3.35 (m, 1H), 2.59 – 2.46 (m, 2H), 2.24 – 2.09 (m, 3H), 2.07 – 1.95 (m, 1H).

¹³C NMR (101 MHz, Chloroform-d): δ 132.93, 131.97, 131.62 (d, J = 2.8 Hz), 130.98 (d, J = 9.3 Hz), 128.55 (d, J = 11.4 Hz), 32.97, 32.24, 21.29 (d, J = 5.3 Hz), 20.18 (d, J = 15.4 Hz).

³¹P NMR (162 MHz, Chloroform-d): δ 32.34.

32. cyclohexyldiphenylphosphine oxide (4la) ^[9]



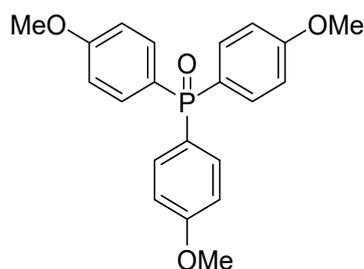
A white solid, the compound was prepared according to the general procedure. Yield: 85.2 mg, 60%.

¹H NMR (400 MHz, Chloroform-d): δ 7.85 – 7.70 (m, 4H), 7.53 – 7.39 (m, 6H), 2.24 (dtd, J = 12.5, 6.2, 3.1 Hz, 1H), 1.90 – 1.65 (m, 5H), 1.58 – 1.49 (m, 2H), 1.24 (q, J = 11.2, 10.7 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-d): δ 166.75, 153.30, 135.23, 126.07, 124.25, 121.52, 120.99, 84.26, 82.62, 33.02, 29.53, 29.33, 25.39, 25.35.

³¹P NMR (162 MHz, Chloroform-d): δ 35.42.

33. tris(4-methoxyphenyl)phosphine oxide (5aa) ^[8]



A colourless liquid, the compound was prepared according to the general procedure.

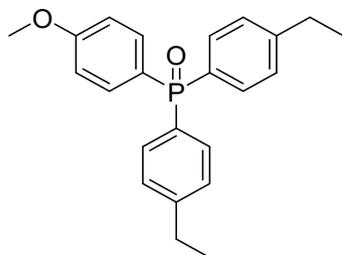
Yield: 125 mg, 68%

¹H NMR (400 MHz, Chloroform-d): δ 7.56 (dd, *J* = 11.5, 8.8 Hz, 6H), 6.95 (dd, *J* = 8.8, 2.2 Hz, 6H), 3.83 (d, *J* = 1.0 Hz, 9H).

¹³C NMR (101 MHz, Chloroform-d): δ 162.32 (d, *J* = 2.8 Hz), 133.85 (d, *J* = 11.3 Hz), 124.31 (d, *J* = 111.2 Hz), 113.98 (d, *J* = 13.1 Hz), 55.33.

³¹P NMR (162 MHz, Chloroform-d): δ 29.44 – 28.92 (m).

34. bis(4-ethylphenyl)(4-methoxyphenyl)phosphine oxide (5ab)



A colourless liquid, the compound was prepared according to the general procedure.

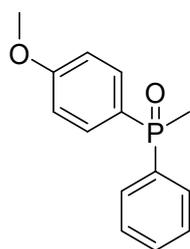
Yield: 95 mg, 52%.

¹H NMR (400 MHz, Chloroform-d): δ 7.55 – 7.61 (m, 6H), 7.27 (dd, *J* = 8.2, 2.6 Hz, 4H), 6.95 (dd, *J* = 8.8, 2.2 Hz, 2H), 3.82 (s, 3H), 2.68 (q, *J* = 7.6 Hz, 4H), 1.23 (t, *J* = 7.6 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-d): δ 162.33 (d, *J* = 2.8 Hz), 148.31 (d, *J* = 2.8 Hz), 133.92 (d, *J* = 11.3 Hz), 132.14 (d, *J* = 10.2 Hz), 130.66, 129.60, 127.98 (d, *J* = 12.4 Hz), 124.22 (d, *J* = 110.0 Hz), 113.96 (d, *J* = 13.2 Hz), 55.32, 28.88 (d, *J* = 1.4 Hz), 15.22.

³¹P NMR (162 MHz, Chloroform-d): δ 29.03.

35. (4-methoxyphenyl)(methyl)(phenyl)phosphine oxide (5ac) ^[15]



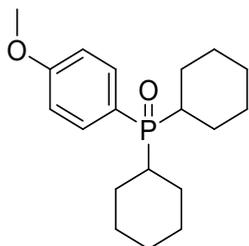
A colourless liquid, the compound was prepared according to the general procedure.

Yield: 61 mg, 50%.

¹H NMR (400 MHz, Chloroform-d): δ 7.68 – 7.52 (m, 4H), 7.45 – 7.33 (m, 3H), 6.90 (dd, *J* = 8.7, 2.2 Hz, 2H), 3.76 (s, 3H), 1.91 (d, *J* = 13.1 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-d): δ 162.34 (d, *J* = 2.9 Hz), 134.98, 133.97, 132.40 (d, *J* = 11.1 Hz), 131.63 (d, *J* = 2.8 Hz), 130.46 (d, *J* = 9.8 Hz), 128.61 (d, *J* = 11.8 Hz), 125.58, 124.51, 114.21 (d, *J* = 13.0 Hz), 55.36, 16.78 (d, *J* = 74.1 Hz).

36. dicyclohexyl(4-methoxyphenyl)phosphine oxide(5ad)



A colourless liquid, the compound was prepared according to the general procedure.
Yield: 81.6 mg, 51%.

¹H NMR (400 MHz, Chloroform-d): δ 7.58 (t, $J = 9.0$ Hz, 2H), 6.99 (dd, $J = 8.8, 2.1$ Hz, 2H), 3.86 (s, 3H), 2.04 – 1.96 (m, 4H), 1.86 – 1.73 (m, 4H), 1.65 (dd, $J = 23.6, 15.0$ Hz, 4H), 1.30 – 1.12 (m, 10H).

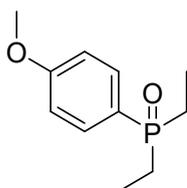
¹³C NMR (101 MHz, Chloroform-d): δ 133.18 (d, $J = 8.8$ Hz), 113.89 (d, $J = 11.4$ Hz), 55.27, 35.50, 34.83, 26.55, 26.42, 26.30, 25.89, 25.51 (d, $J = 2.5$ Hz), 24.58 (d, $J = 3.3$ Hz).

³¹P NMR (162 MHz, Chloroform-d): δ 45.48.

³¹P NMR (162 MHz, Chloroform-d): δ 29.96 (q, $J = 12.2$ Hz).

HRMS (APCI, m/z): Calculated for C₁₉H₂₉O₂P₁; (M+H) 321.1978, found 321.1974.

37. diethyl(4-methoxyphenyl)phosphine oxide (5ae)



A colourless liquid, the compound was prepared according to the general procedure.
Yield: 70 mg, 66%.

¹H NMR (400 MHz, Chloroform-d): δ 7.68 – 7.58 (m, 2H), 7.01 (dd, $J = 8.8, 2.1$ Hz, 2H), 3.86 (s, 3H), 2.08 – 1.97 (m, 2H), 1.86 (ddd, $J = 15.1, 9.8, 7.6$ Hz, 2H), 1.11 (dt, $J = 16.9, 7.7$ Hz, 6H).

¹³C NMR (101 MHz, Chloroform-d): δ 162.20 (d, $J = 2.9$ Hz), 132.31 (d, $J = 9.9$ Hz), 122.34 (d, $J = 98.0$ Hz), 114.21 (d, $J = 12.0$ Hz), 55.29, 22.32 (d, $J = 69.7$ Hz), 5.53 (d, $J = 5.1$ Hz).

³¹P NMR (162 MHz, Chloroform-d): δ 44.51.

HRMS (APCI, m/z): Calculated for C₁₁H₁₇O₂P₁; (M+H) 213.1039, found 213.1044.

38. (4-methoxyphenyl)dioctylphosphine oxide(5af)



A colourless liquid, the compound was prepared according to the general procedure.
Yield: 96 mg, 51%.

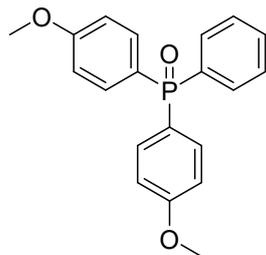
¹H NMR (400 MHz, Chloroform-d): δ 7.66 – 7.58 (m, 2H), 7.02 – 6.97 (m, 2H), 3.85 (s, 3H), 1.98 – 1.89 (m, 2H), 1.86 – 1.76 (m, 2H), 1.60 (td, $J = 12.3, 11.5, 5.9$ Hz, 2H), 1.47 – 1.37 (m, 2H), 1.36 – 1.29 (m, 4H), 1.23 (d, $J = 5.9$ Hz, 16H), 0.86 (t, $J = 6.9$ Hz, 6H).

¹³C NMR (101 MHz, Chloroform-d): δ 162.06 (d, $J = 2.5$ Hz), 132.14 (d, $J = 9.9$ Hz), 114.13 (d, $J = 11.8$ Hz), 55.25, 31.74, 30.99 (d, $J = 14.1$ Hz), 30.46, 29.78, 29.00, 22.58, 21.44 (d, $J = 3.9$ Hz), 14.05.

³¹P NMR (162 MHz, Chloroform-d): δ 40.63.

HRMS (APCI, m/z): Calculated for C₂₃H₄₁O₁P₁; (M+H) 381.2917, found 381.2926.

39. bis(4-methoxyphenyl)(phenyl)phosphine oxide(5ag) ^[1]



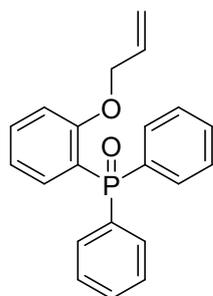
A colourless liquid, the compound was prepared according to the general procedure. Yield: 86.2 mg, 52%.

¹H NMR (400 MHz, Chloroform-d): δ 7.69 – 7.62 (m, 2H), 7.57 (dd, J = 11.5, 8.7 Hz, 4H), 7.53 – 7.49 (m, 1H), 7.45 (dt, J = 7.6, 3.7 Hz, 2H), 6.96 (dd, J = 8.8, 2.3 Hz, 4H), 3.84 (s, 6H).

¹³C NMR (101 MHz, Chloroform-d): δ 162.41 (d, J = 2.8 Hz), 133.93 (d, J = 11.2 Hz), 132.01 (d, J = 9.9 Hz), 131.70 (d, J = 2.8 Hz), 128.41 (d, J = 12.1 Hz), 124.00 (d, J = 110.7 Hz), 114.04 (d, J = 13.2 Hz), 55.36.

³¹P NMR (162 MHz, Chloroform-d): δ 29.01 (d, J = 12.0 Hz).

40. (2-(allyloxy)phenyl)diphenylphosphine oxide(3ta)



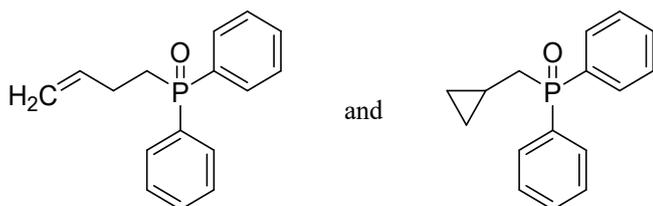
A colourless liquid, the compound was prepared according to the general procedure. Yield: 71 mg, 43%.

¹H NMR (400 MHz, Chloroform-d): δ 7.89 (ddd, J = 13.4, 7.6, 1.8 Hz, 1H), 7.78 – 7.70 (m, 4H), 7.51 – 7.47 (m, 3H), 7.43 – 7.38 (m, 4H), 7.08 (td, J = 7.4, 1.9 Hz, 1H), 6.88 (dd, J = 8.3, 5.3 Hz, 1H), 5.51 – 5.42 (m, 1H), 5.09 – 4.92 (m, 2H), 4.32 (d, J = 5.3 Hz, 2H).

¹³C NMR (101 MHz, Chloroform-d): δ 159.60 (d, J = 3.4 Hz), 135.02 (d, J = 6.9 Hz), 134.17 (d, J = 2.1 Hz), 133.72, 132.65, 131.98, 131.86 (d, J = 10.3 Hz), 131.47 (d, J = 2.7 Hz), 128.10 (d, J = 12.5 Hz), 121.04 (d, J = 11.7 Hz), 119.95, 117.91, 112.29 (d, J = 6.5 Hz), 69.05.

³¹P NMR (162 MHz, Chloroform-d): δ 26.79 (d, J = 13.8 Hz).

41. but-3-en-1-ylidiphenylphosphine oxide (8a and 8a')



A white solid, the compound was prepared according to the general procedure. Yield: 65 mg, 51%, **8a** : **8a'** = 2.5:1.

¹H NMR (400 MHz, Chloroform-d): δ 7.68 – 7.59 (m, 6H), 7.46 – 7.31 (m, 9H), 5.81 – 5.67 (m, 1H), 4.98 – 4.82 (m, 2H), 2.32 – 2.19 (m, 5H), 2.14 (dd, *J* = 11.0, 6.9 Hz, 1H), 0.42 – 0.33 (m, 1H), -0.01 (q, *J* = 5.3 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-d): δ 137.34 (d, *J* = 15.9 Hz), 133.67, 133.30, 132.71, 132.32, 131.79 (d, *J* = 2.9 Hz), 131.67 (d, *J* = 2.7 Hz), 130.94 (d, *J* = 9.2 Hz), 130.79 (d, *J* = 9.2 Hz), 128.70 (d, *J* = 11.6 Hz), 128.54 (d, *J* = 11.4 Hz), 115.22, 35.04 (d, *J* = 71.7 Hz), 29.35, 28.64, 25.52 (d, *J* = 3.2 Hz), 5.39 (d, *J* = 7.8 Hz), 3.91 (d, *J* = 3.8 Hz).

³¹P NMR (162 MHz, Chloroform-d): δ 32.10.

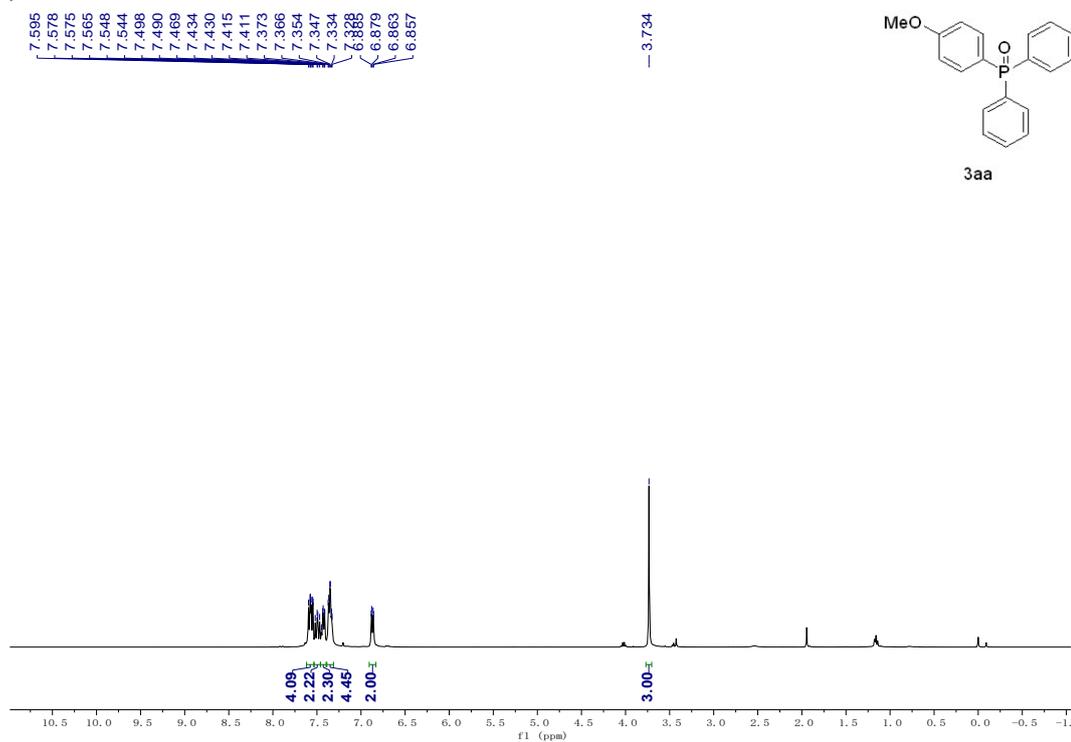
HRMS (APCI, m/z): Calculated for C₂₁H₂₁O₁P₁; (M+H) 279.0909, found 279.0908.

7 Reference

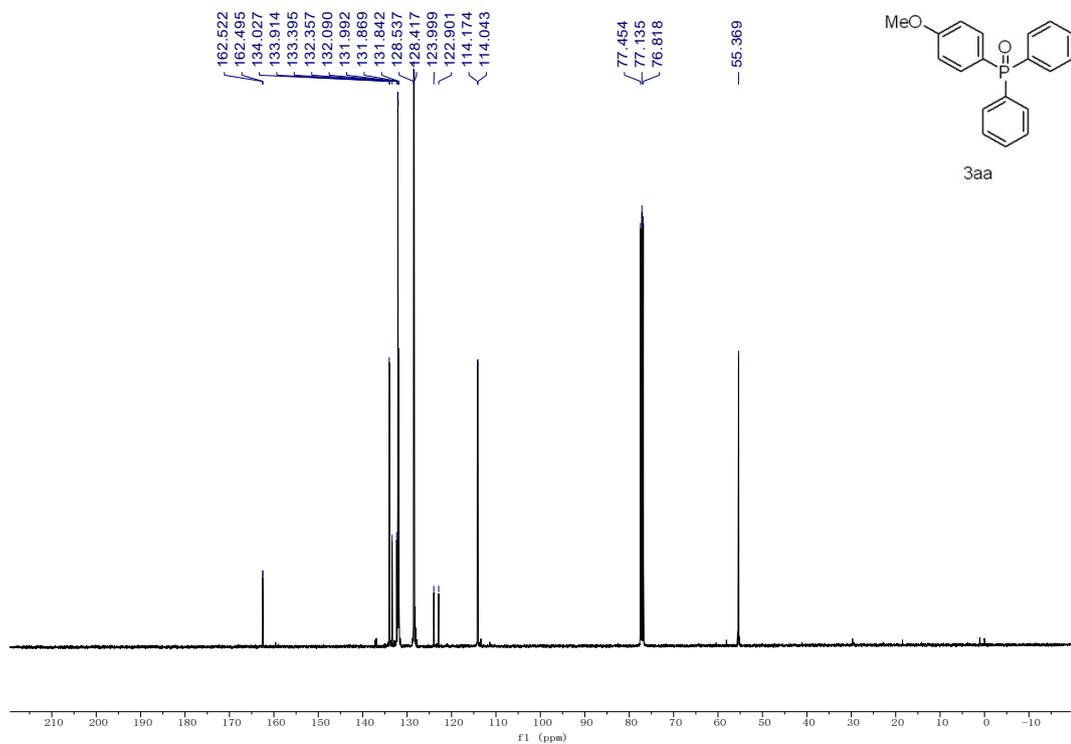
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8. Copies of the NMR spectra.

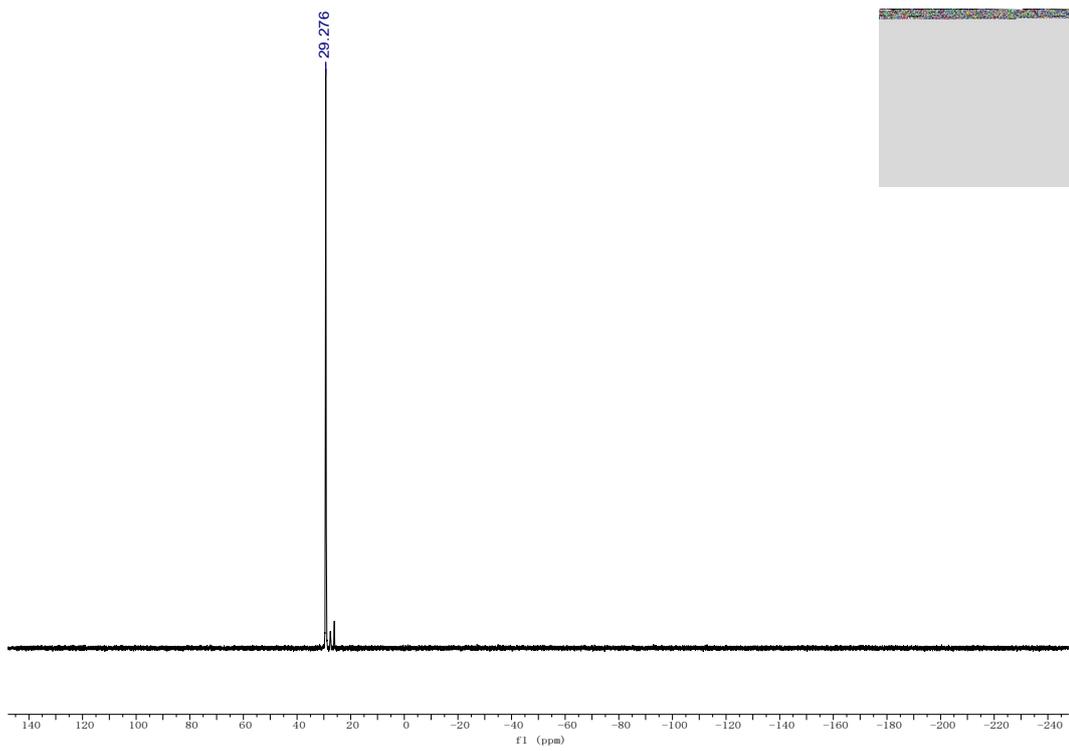
(3aa) ¹H NMR



¹³C NMR

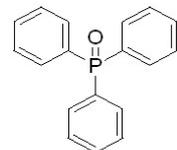


³¹P NMR

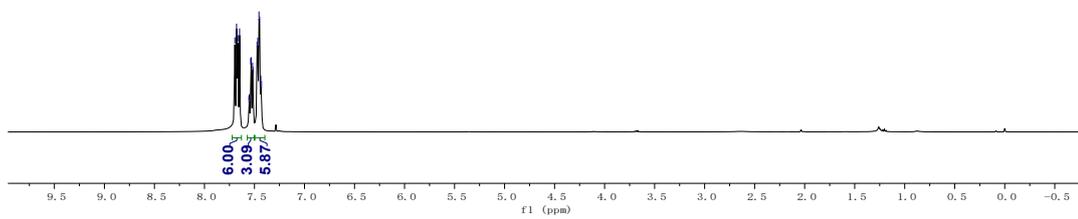


(3ba)

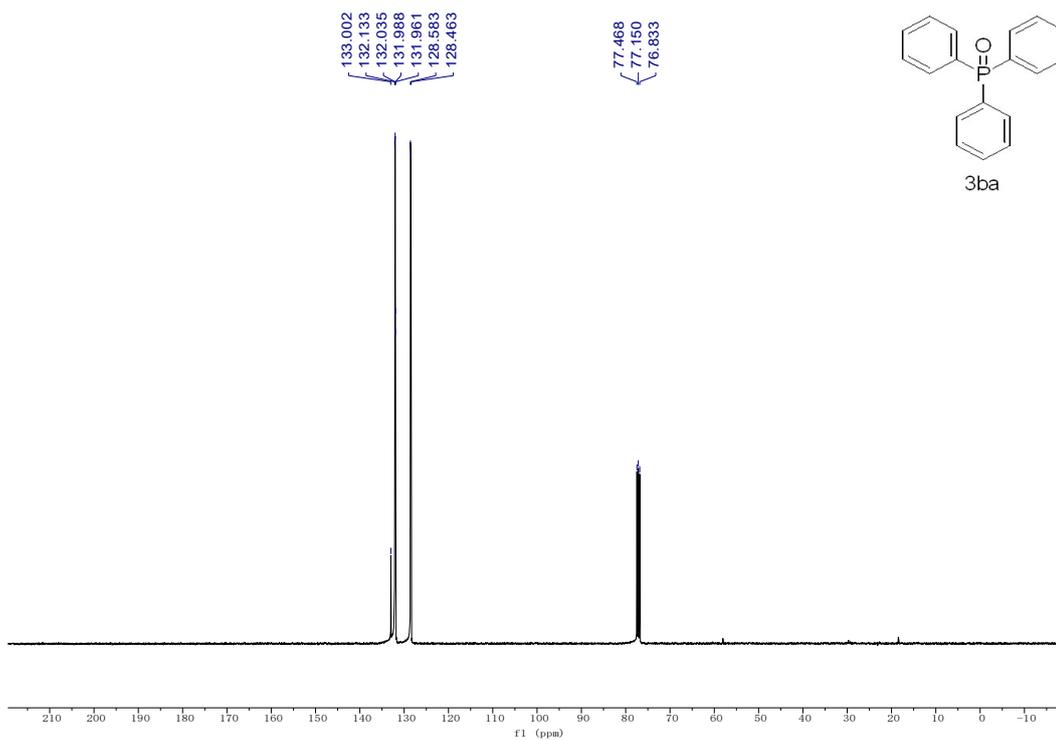
¹H NMR



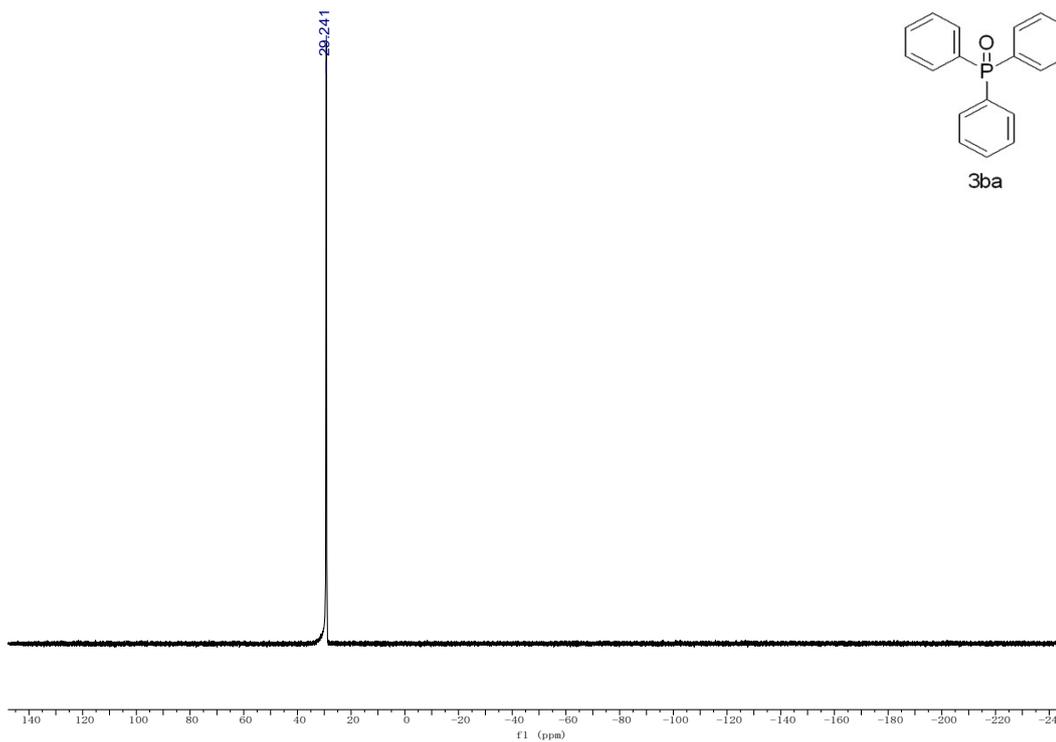
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¹³C NMR

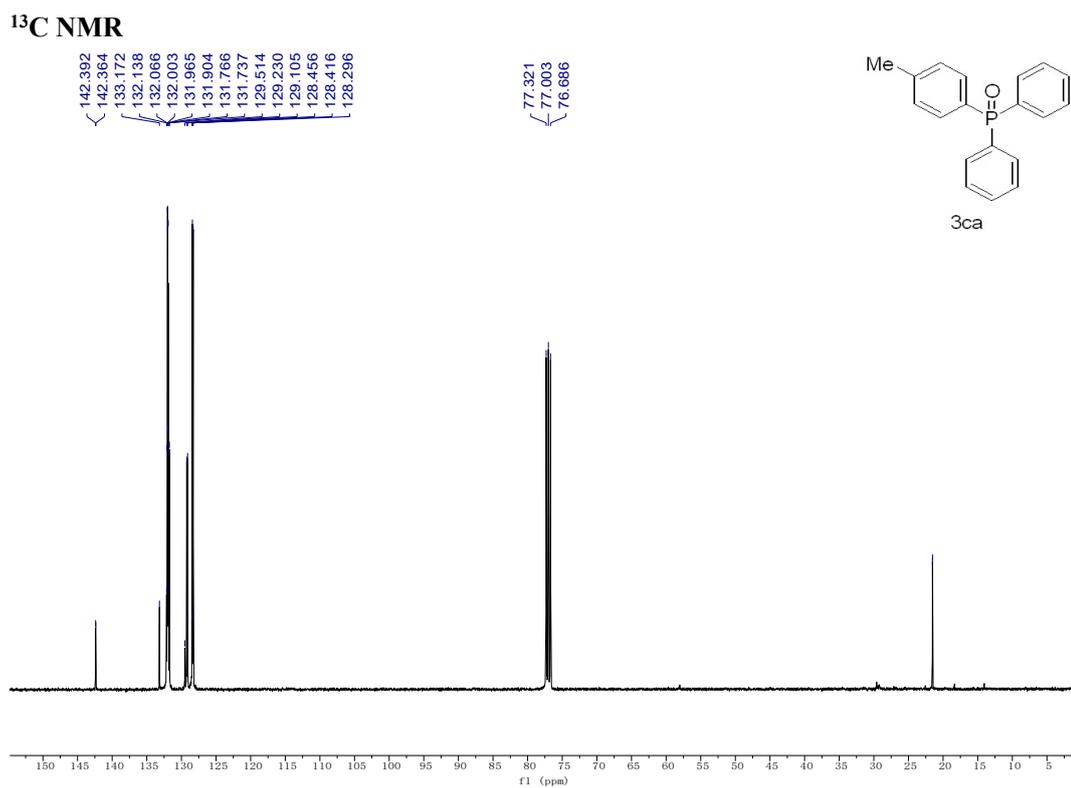
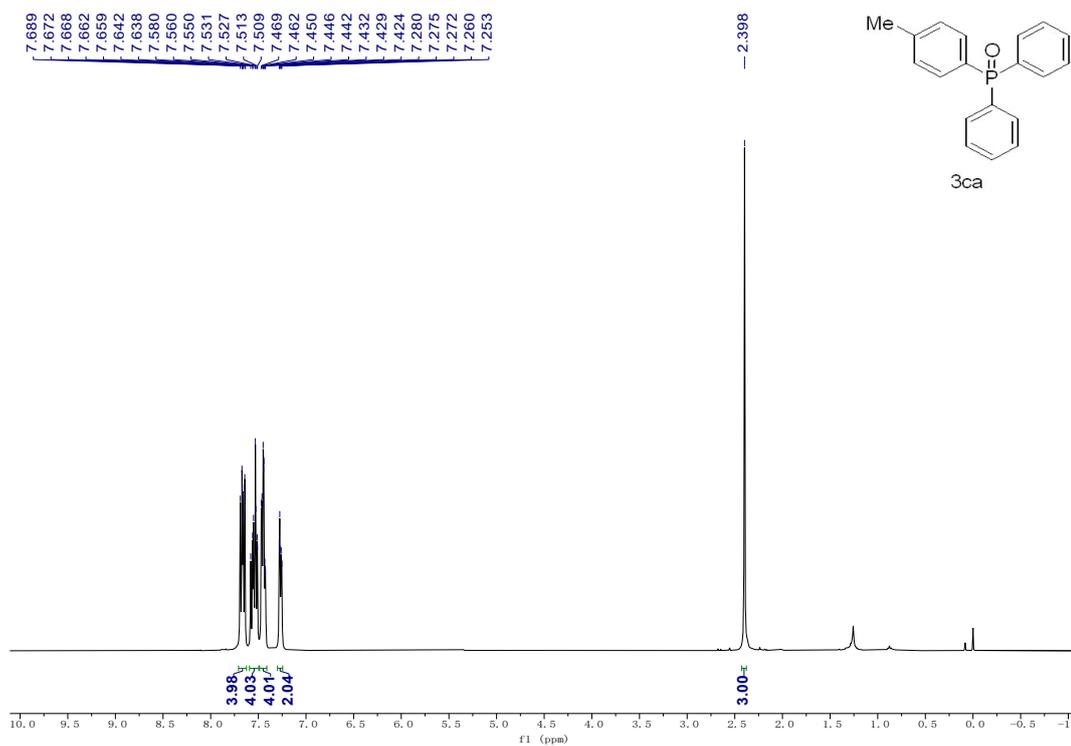


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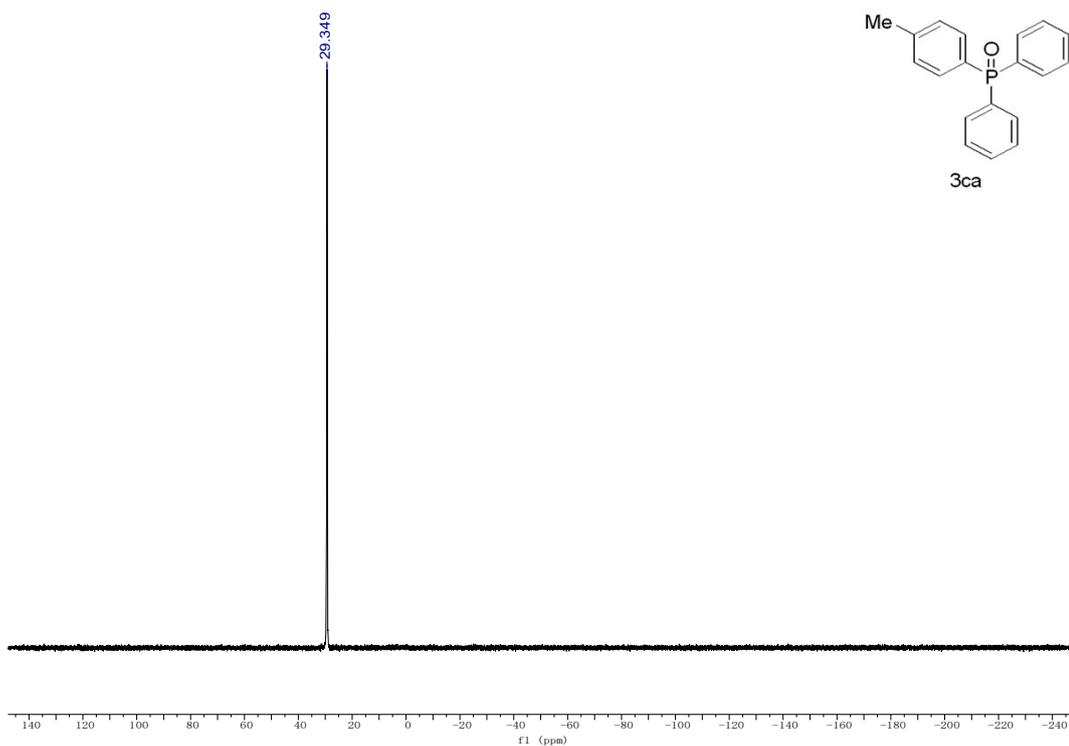


(3ca)

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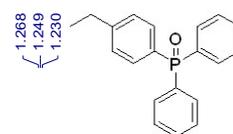


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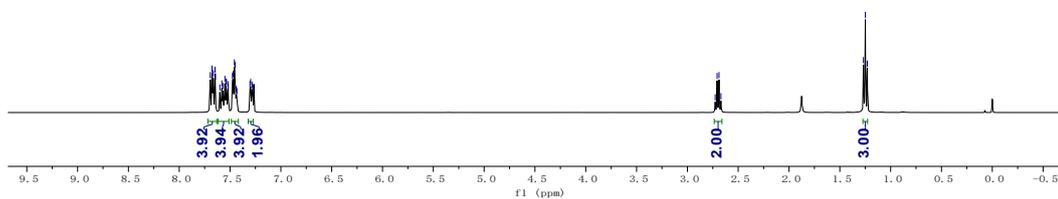


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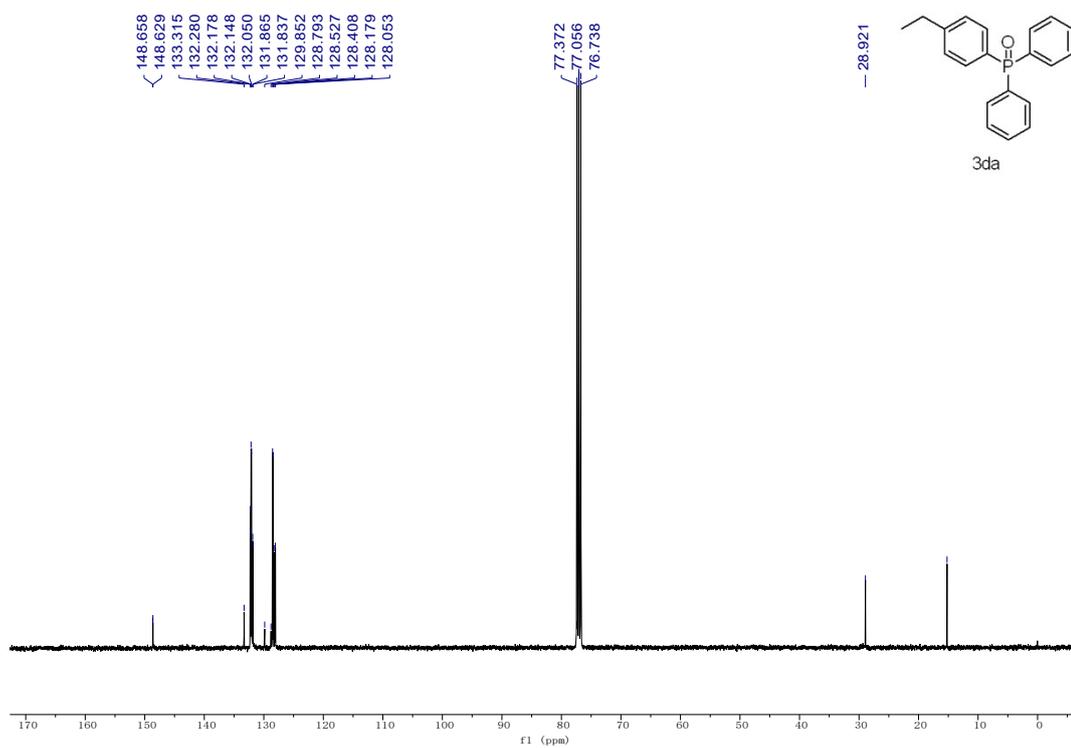
¹H NMR



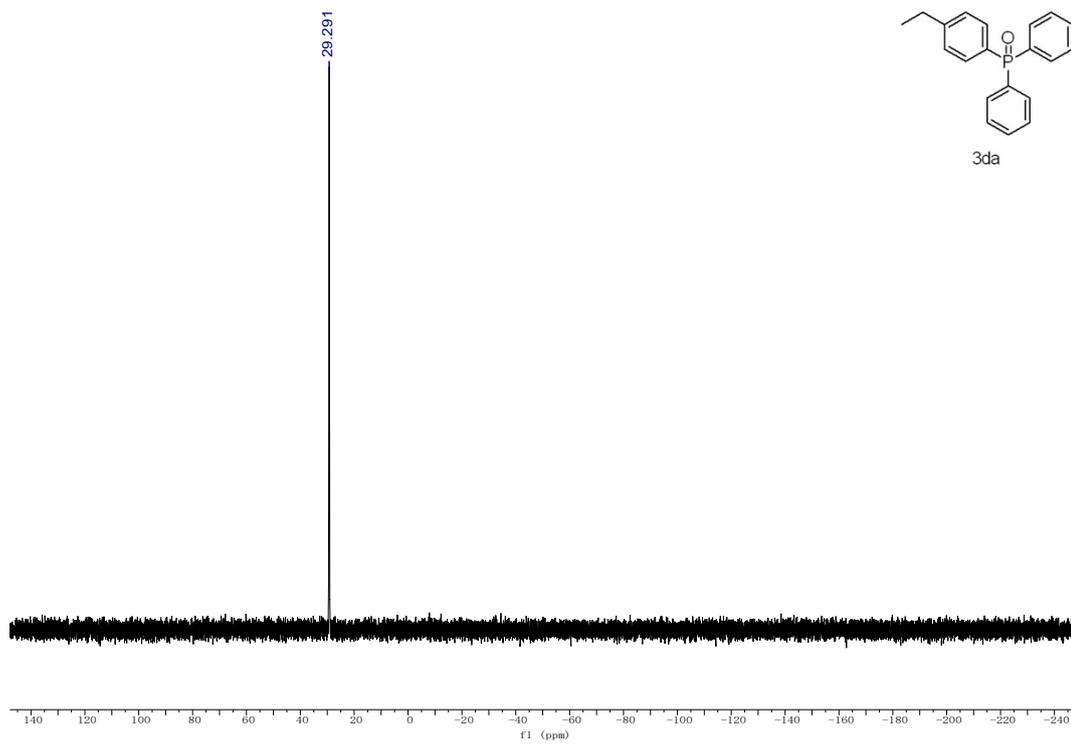
3da



¹³C NMR

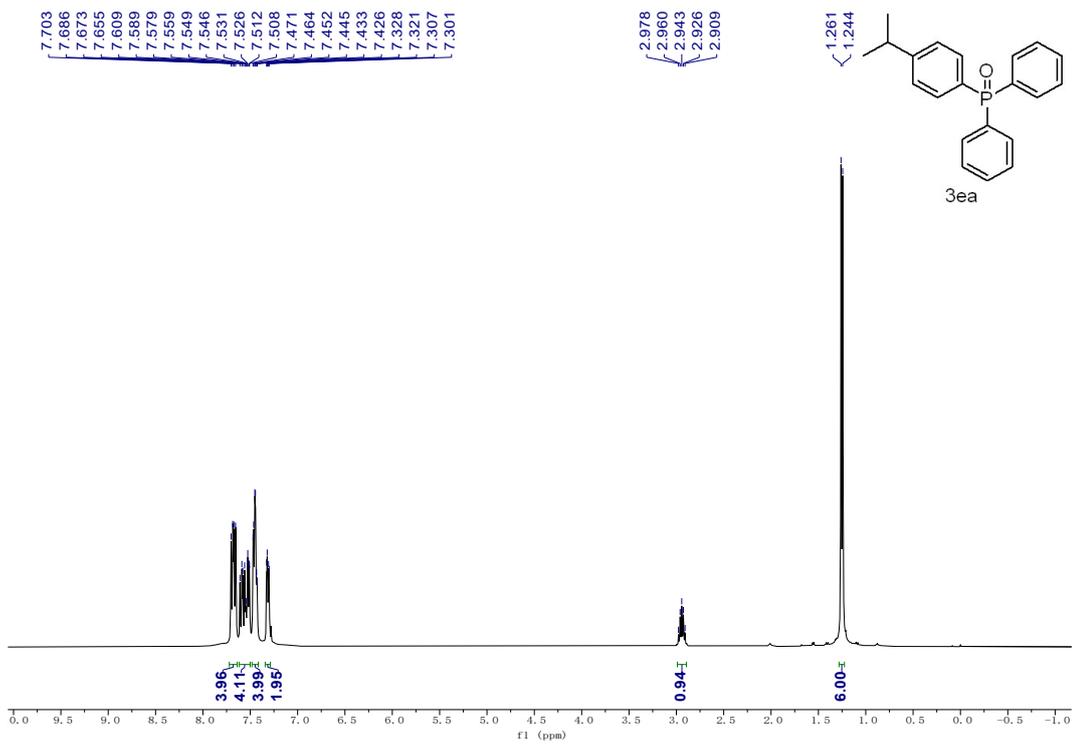


³¹P NMR

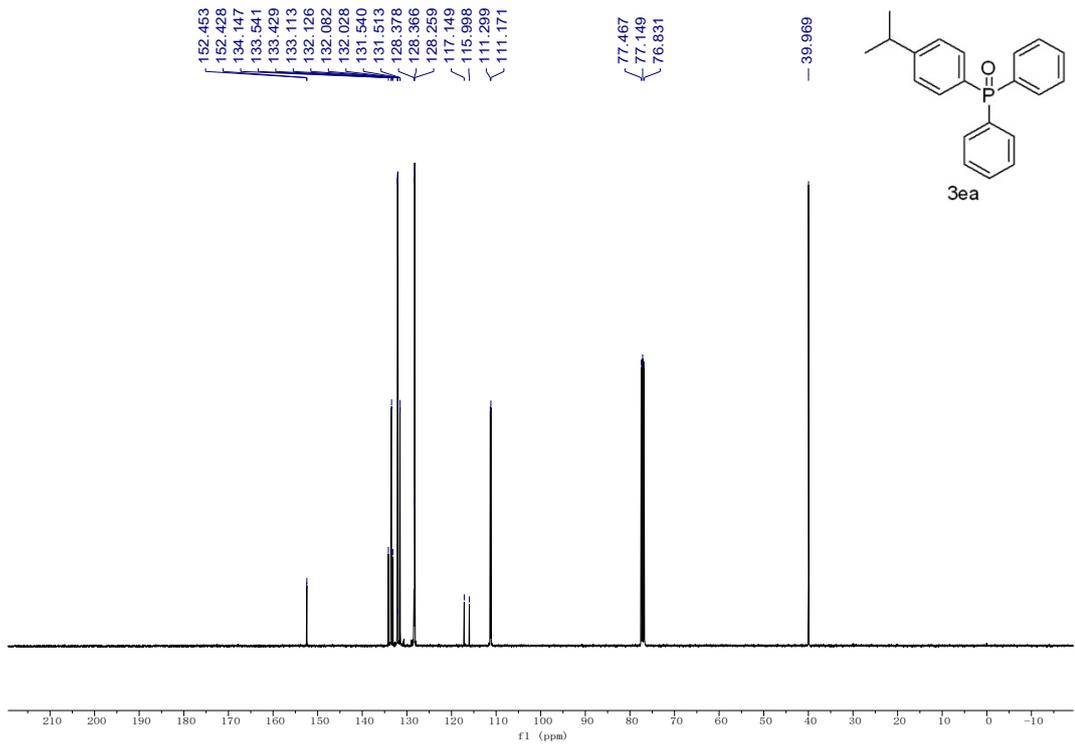


(3ea)

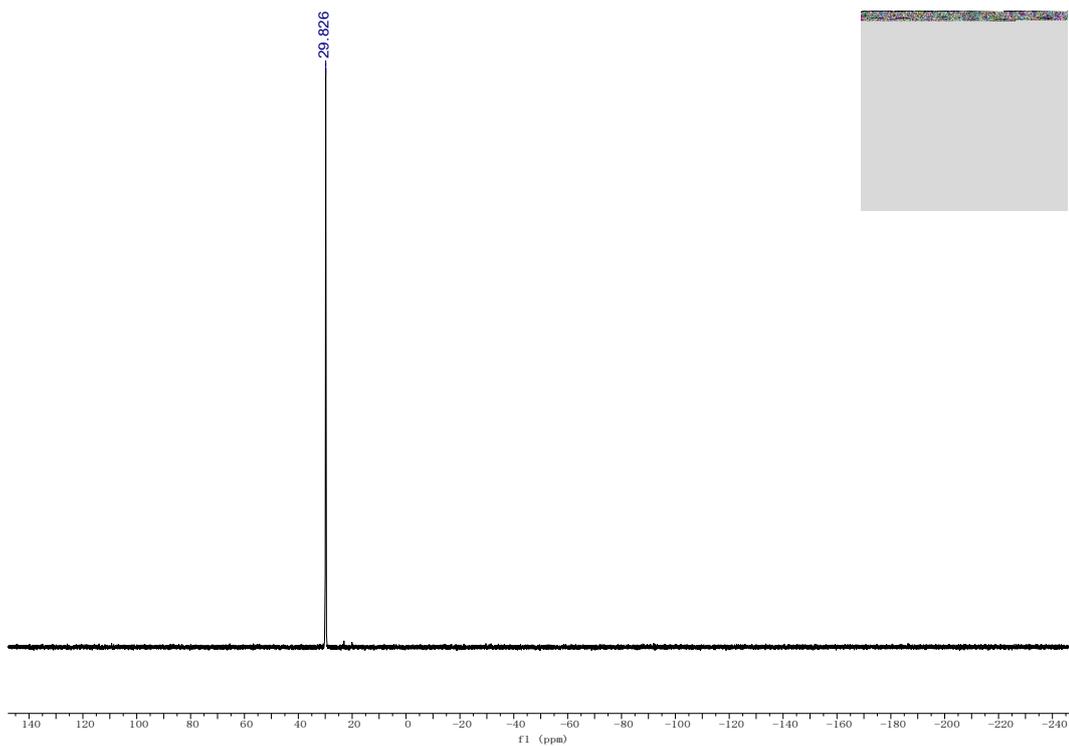
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¹³C NMR

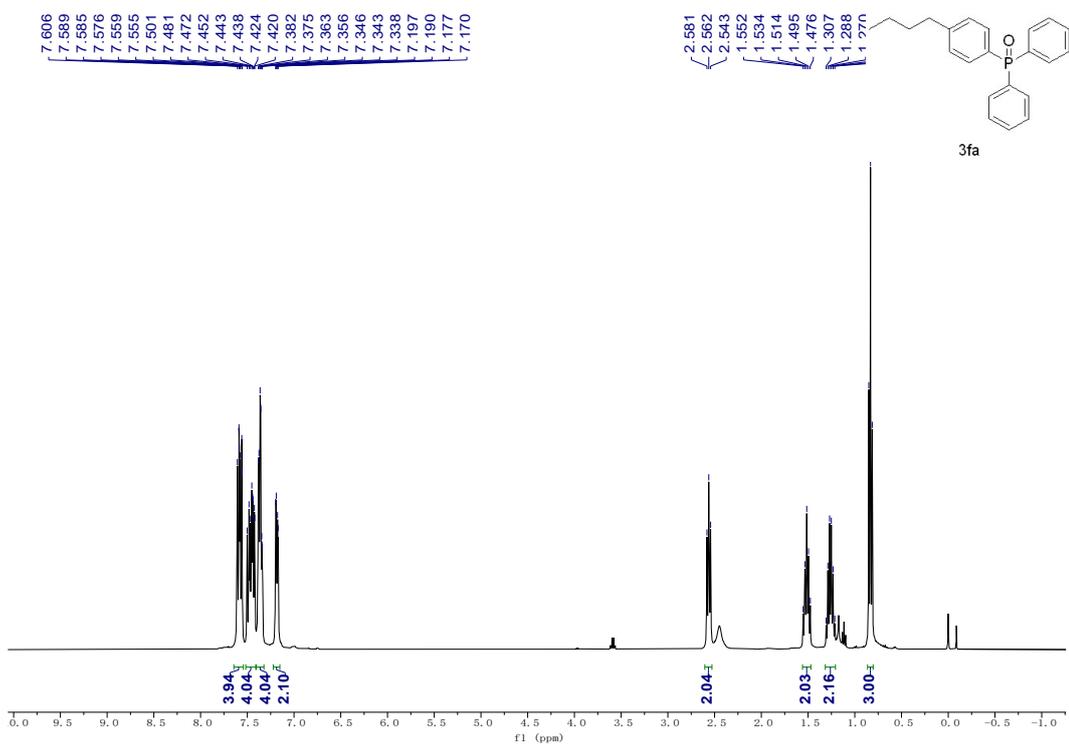


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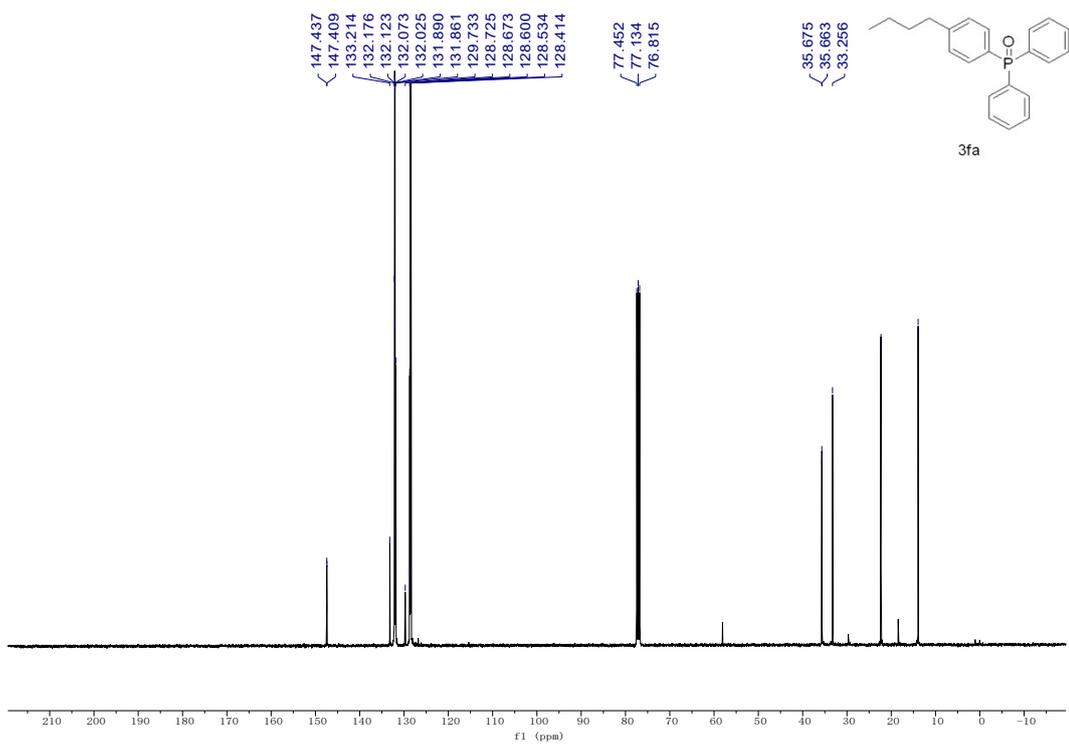


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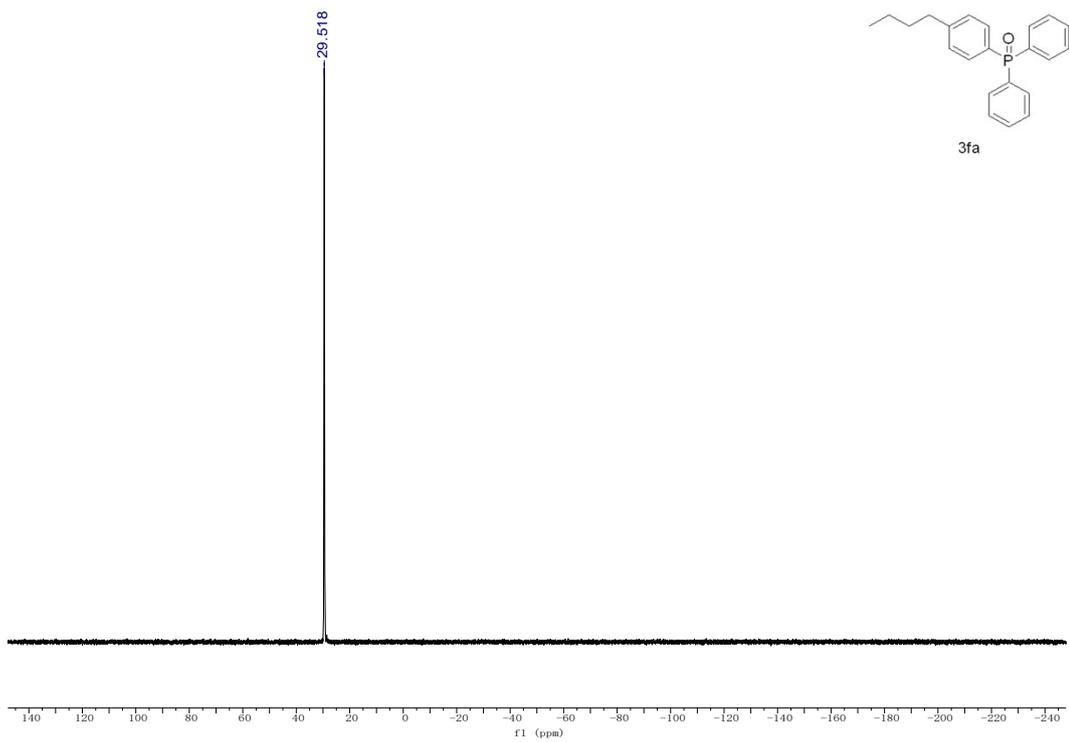
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¹³C NMR

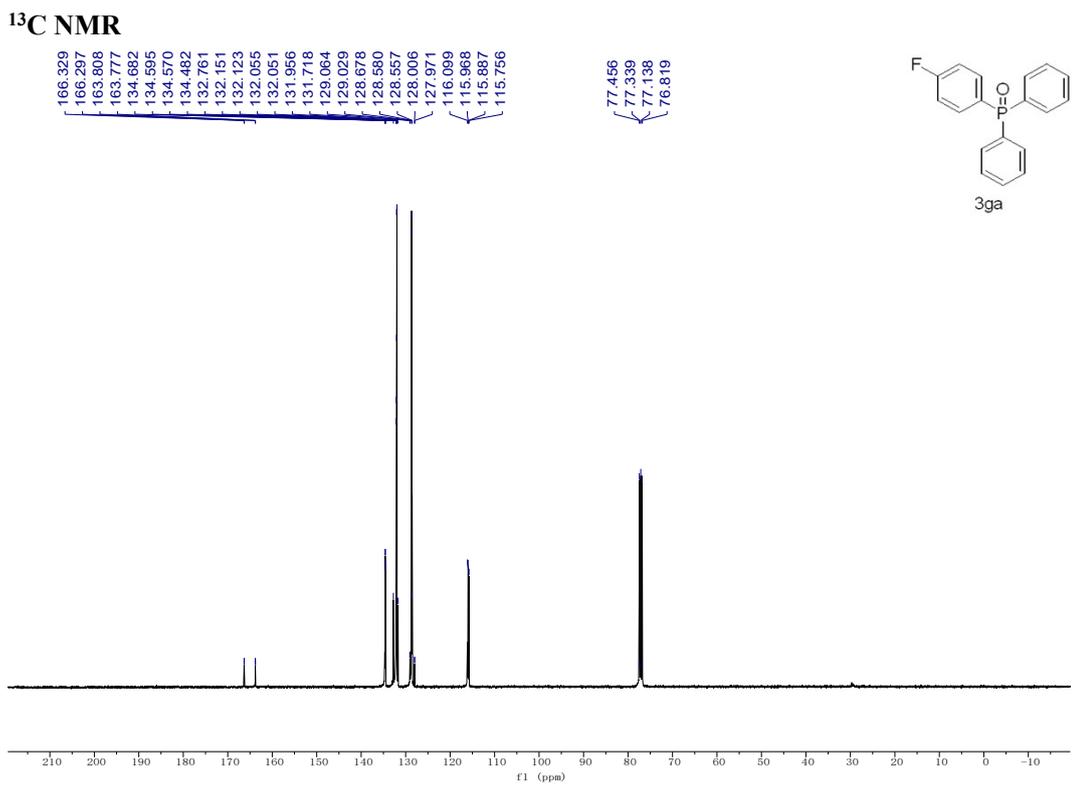
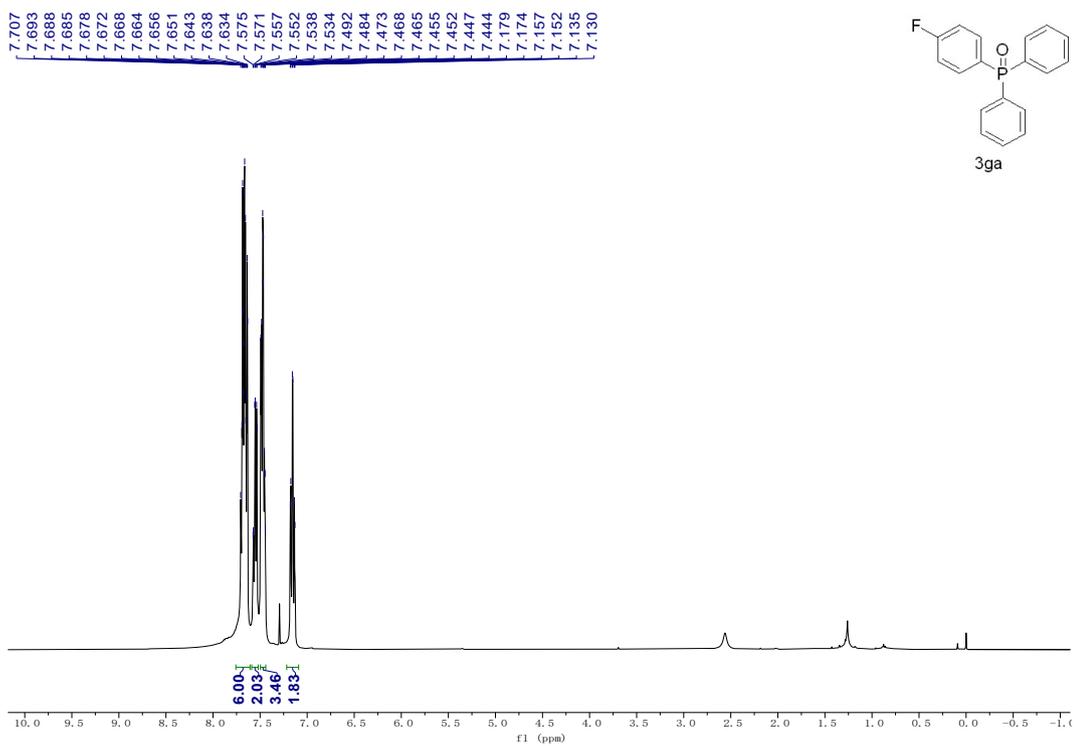


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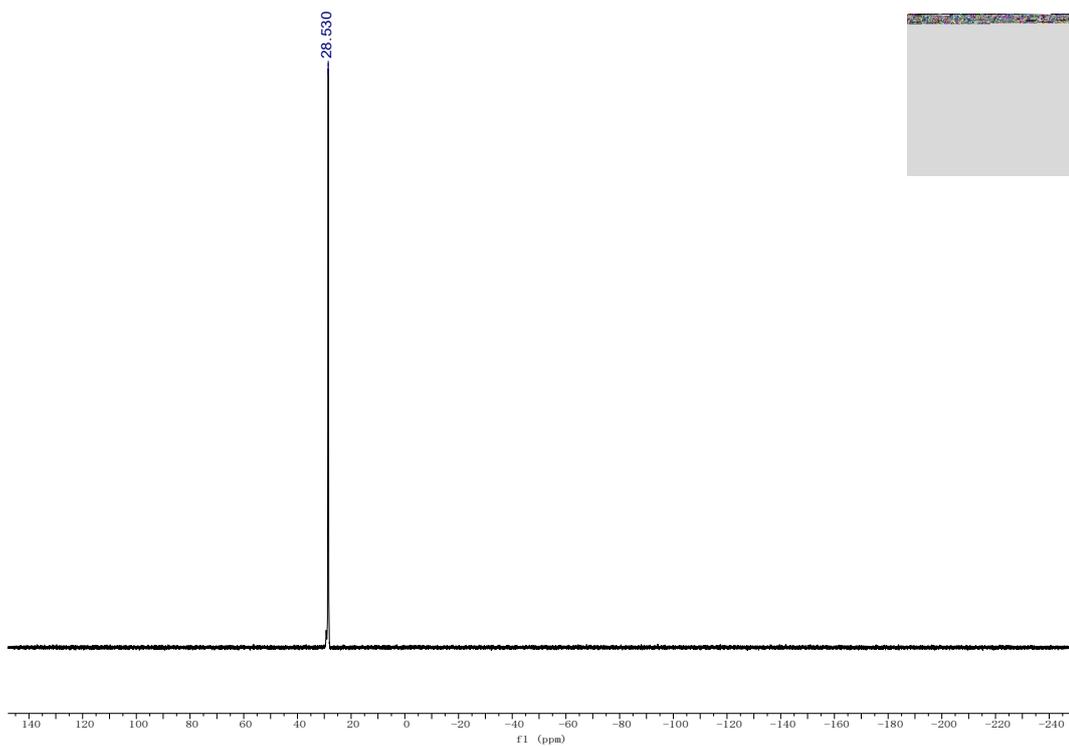


(3ga)

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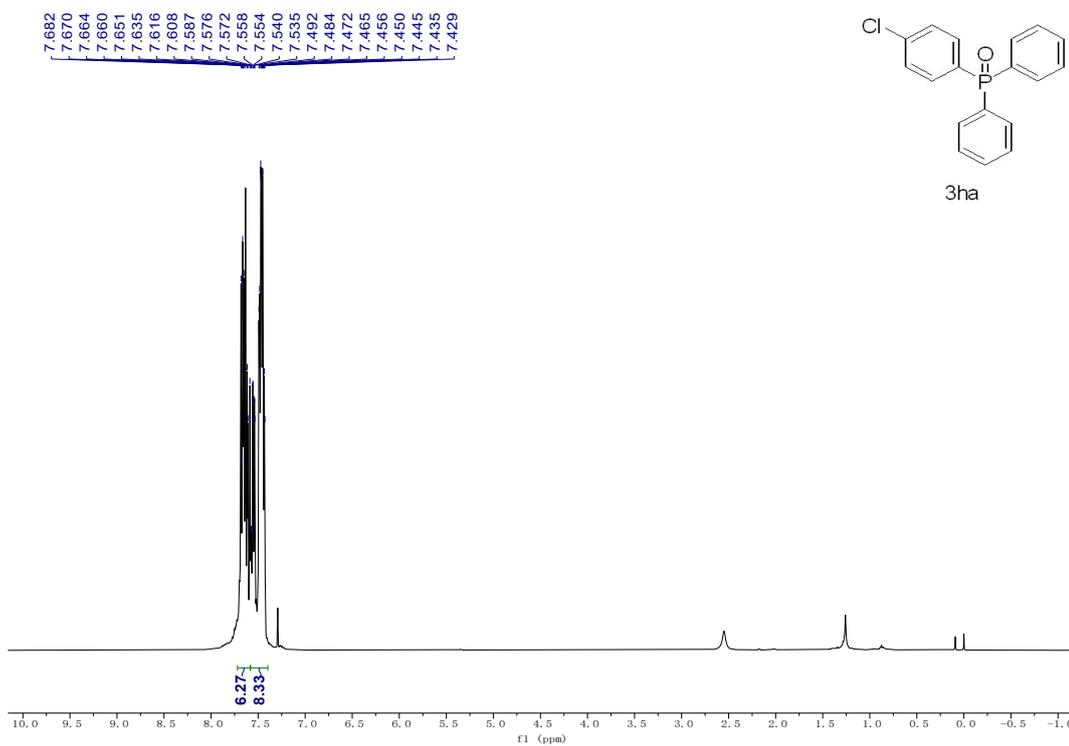


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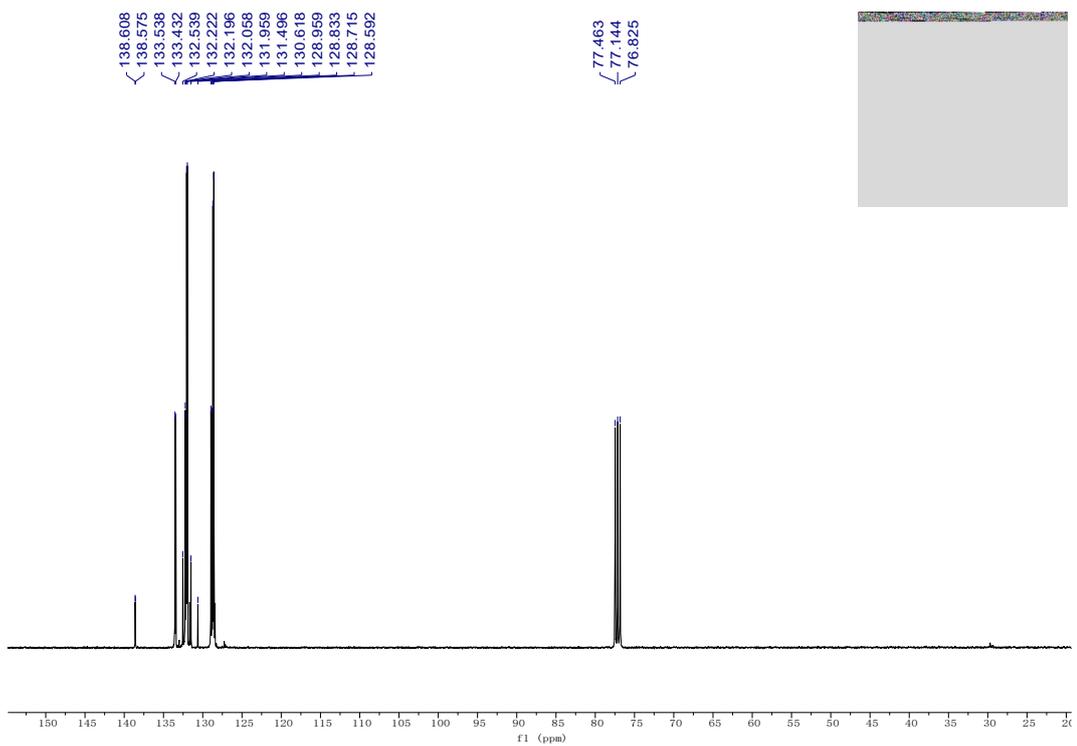


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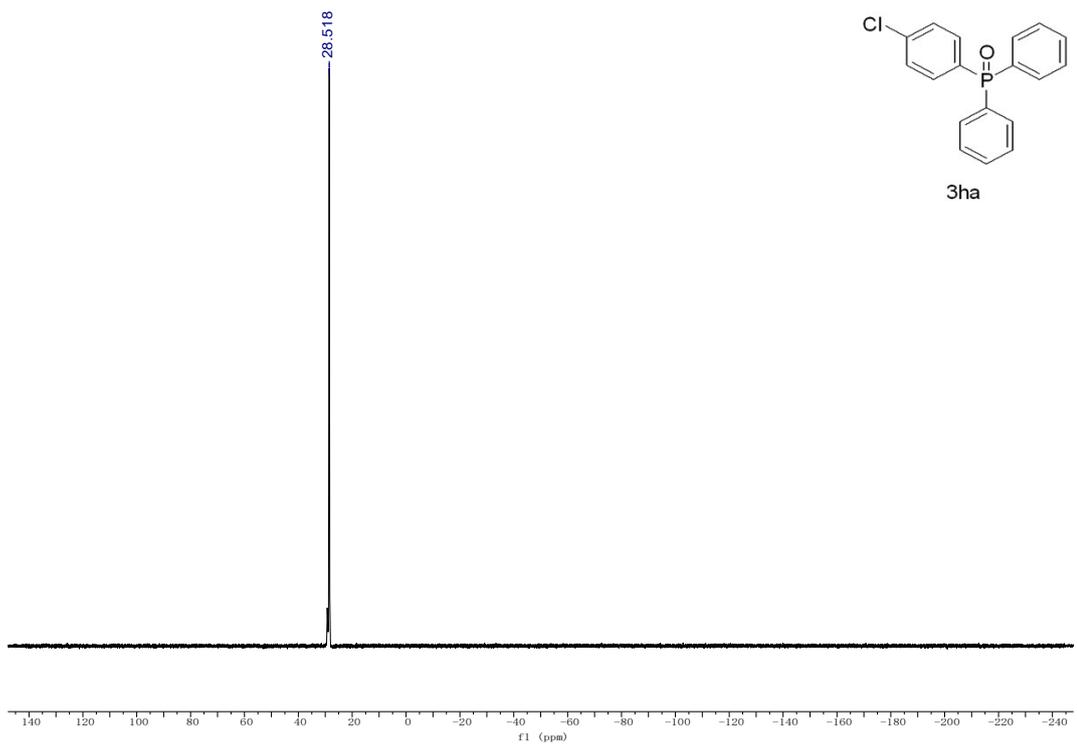
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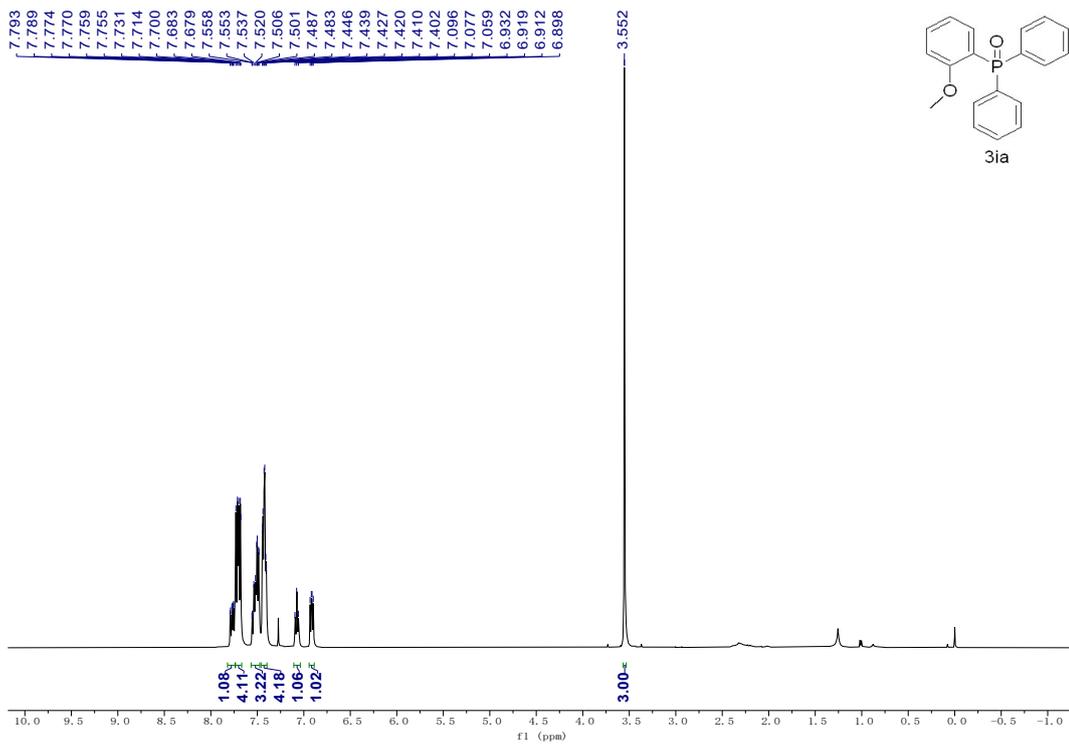


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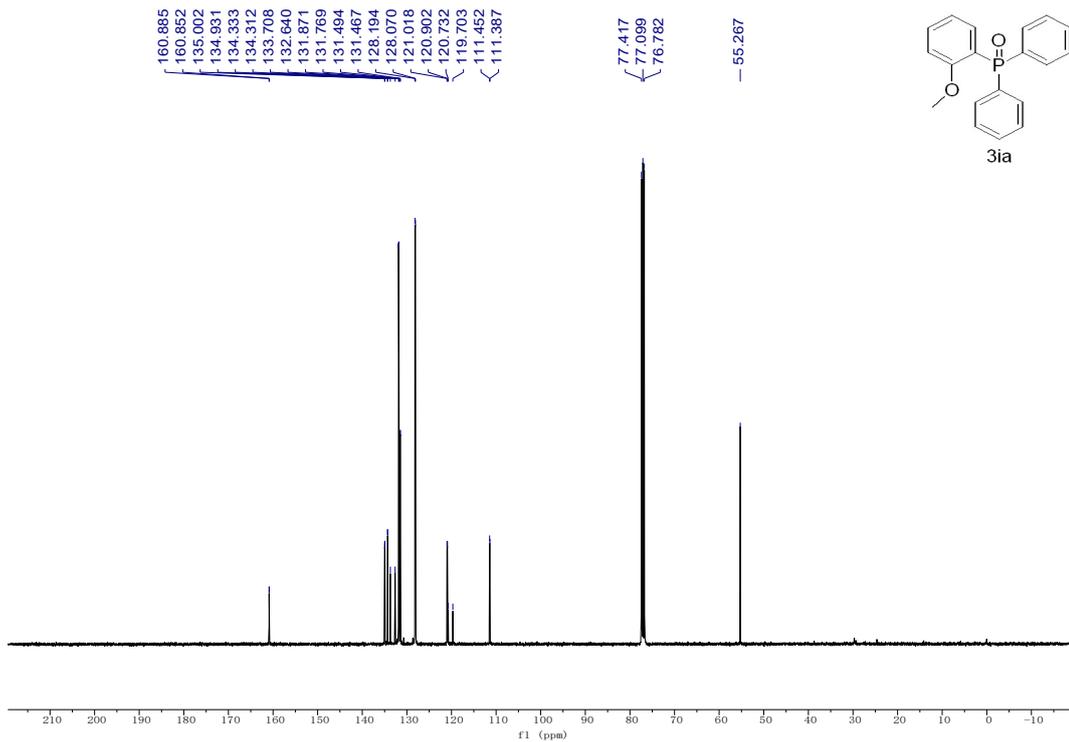


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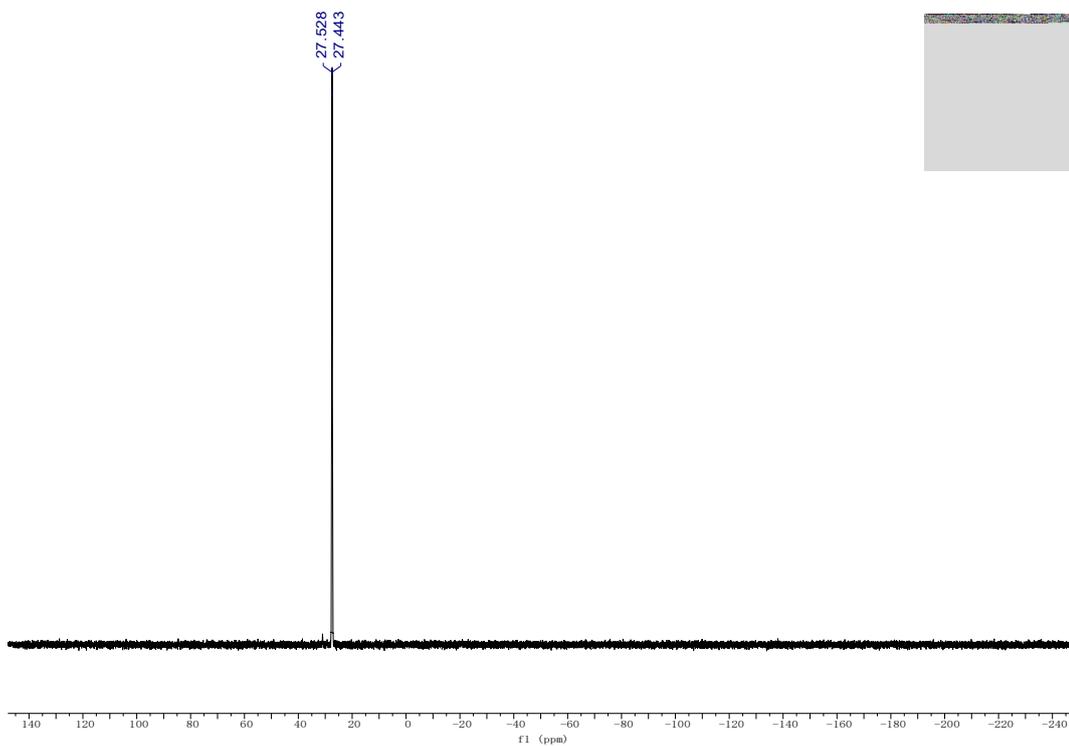
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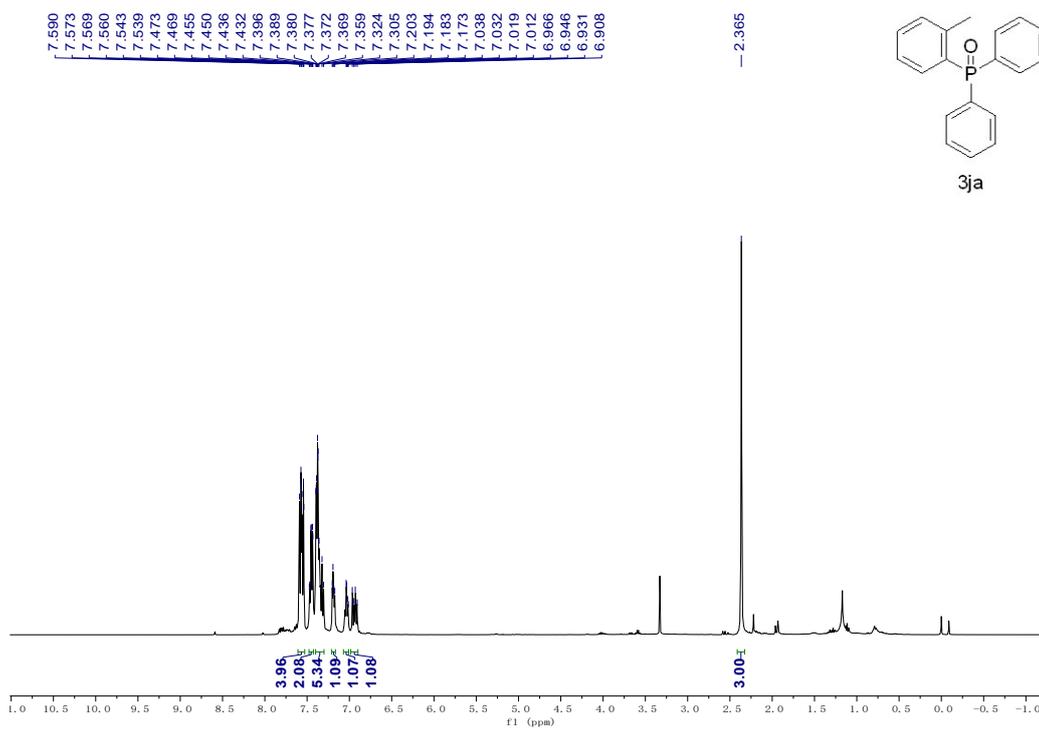


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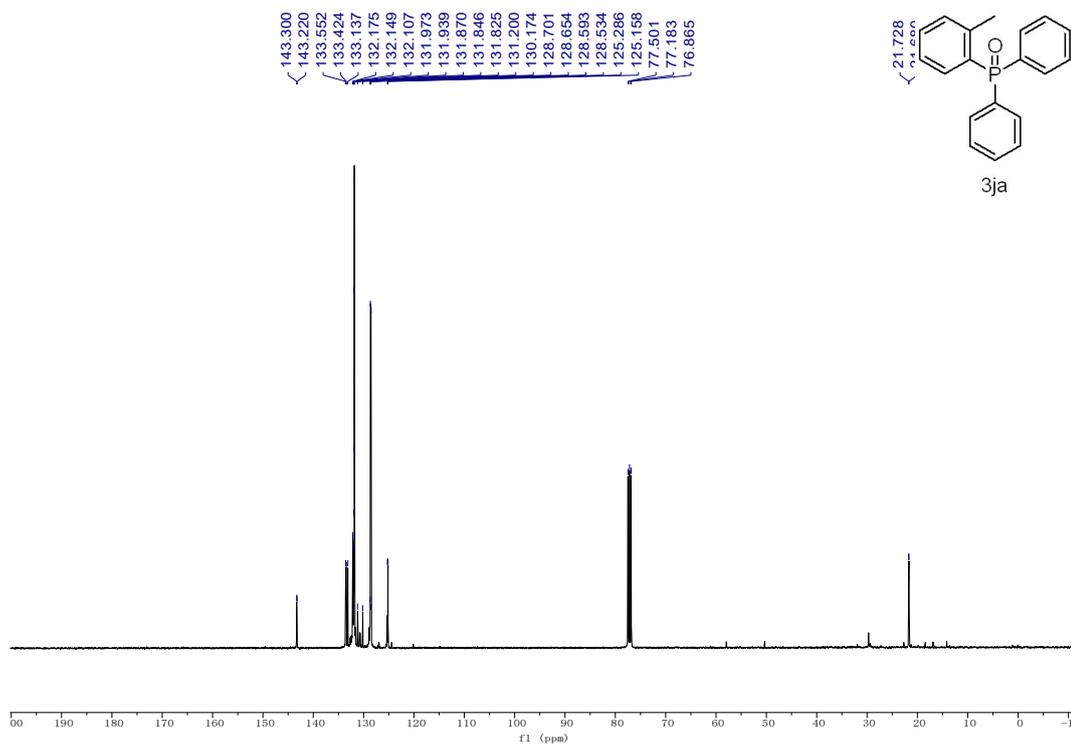


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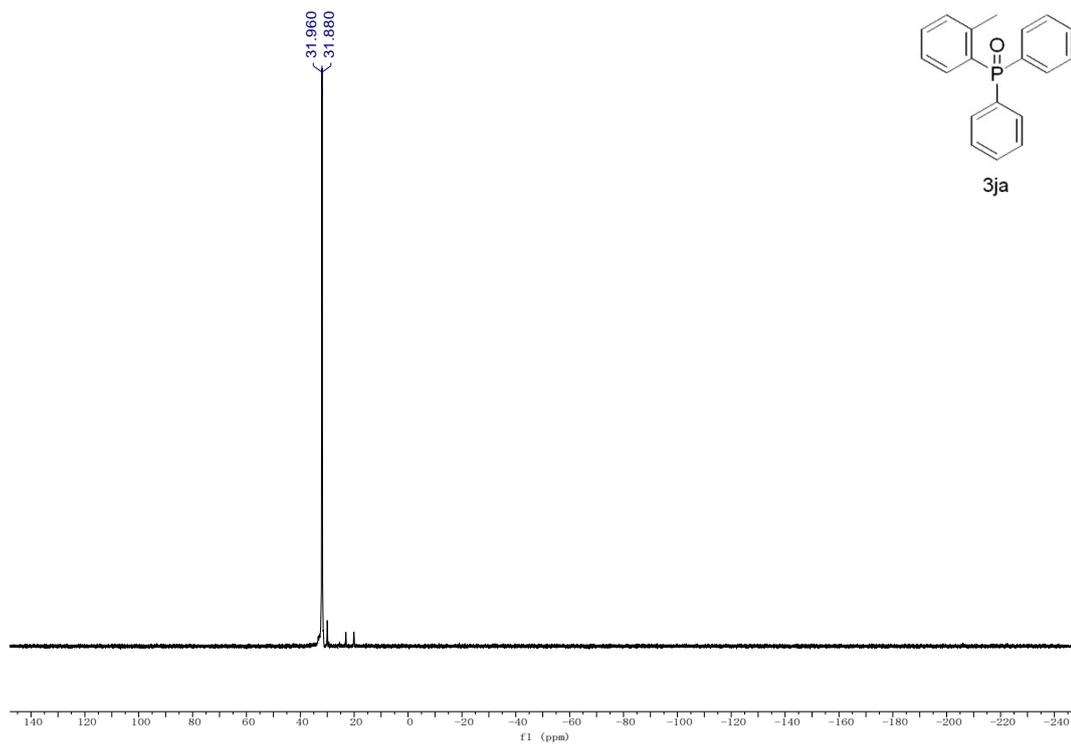
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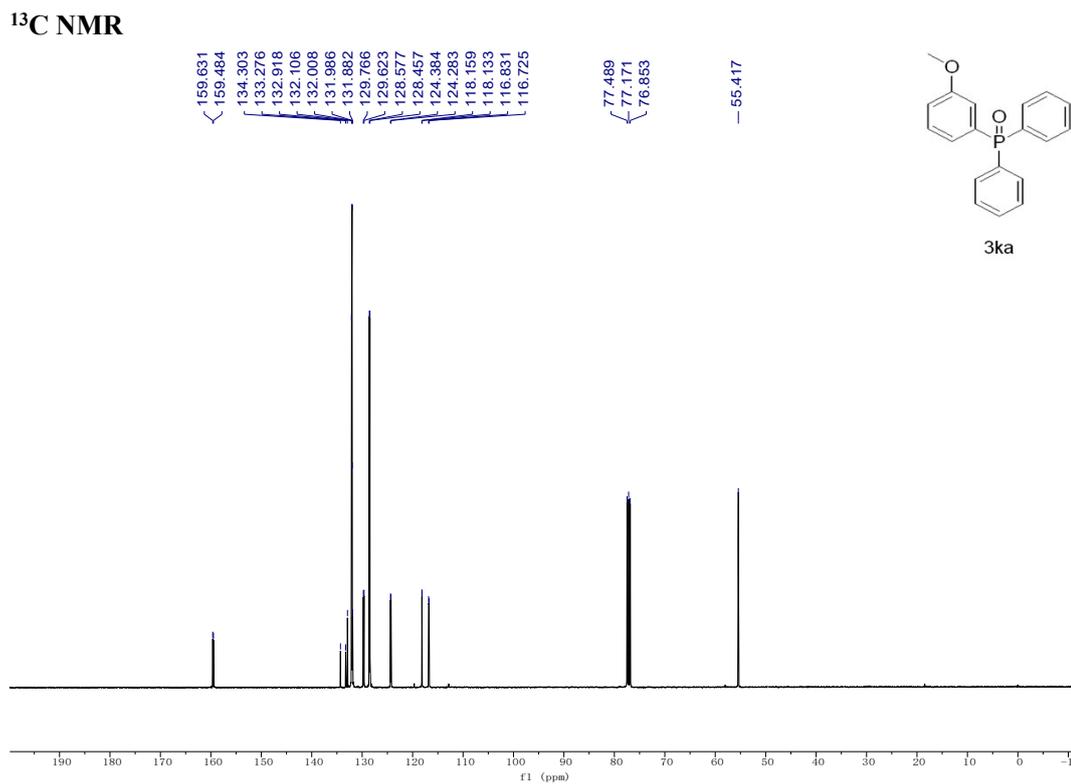
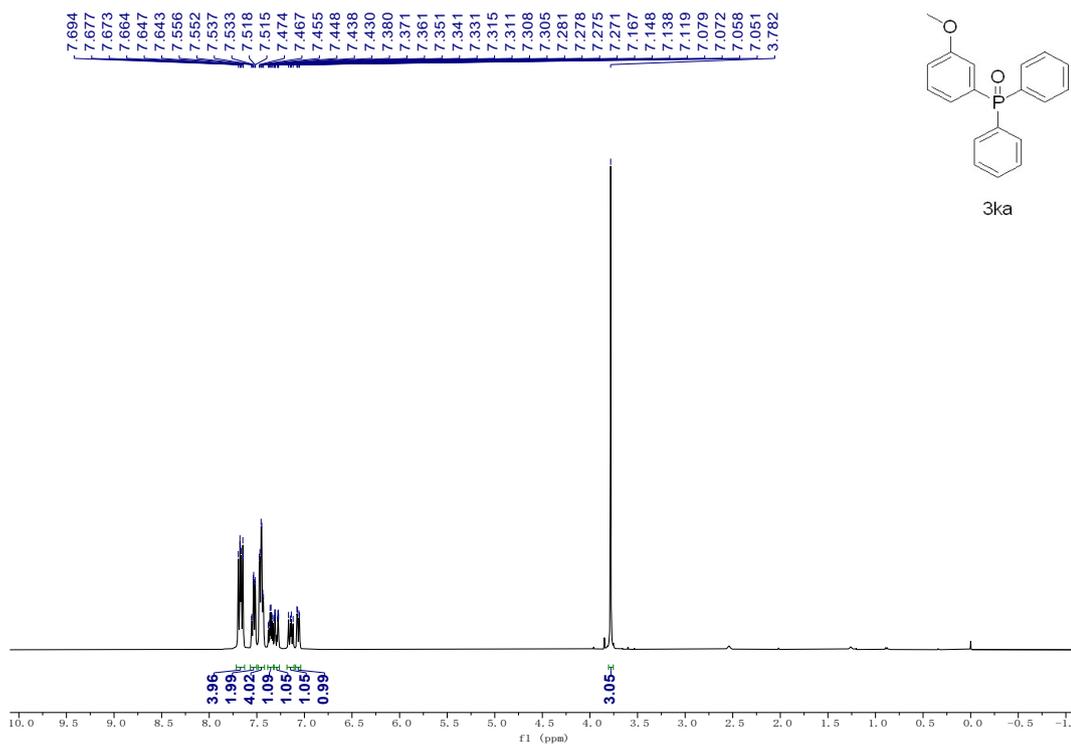


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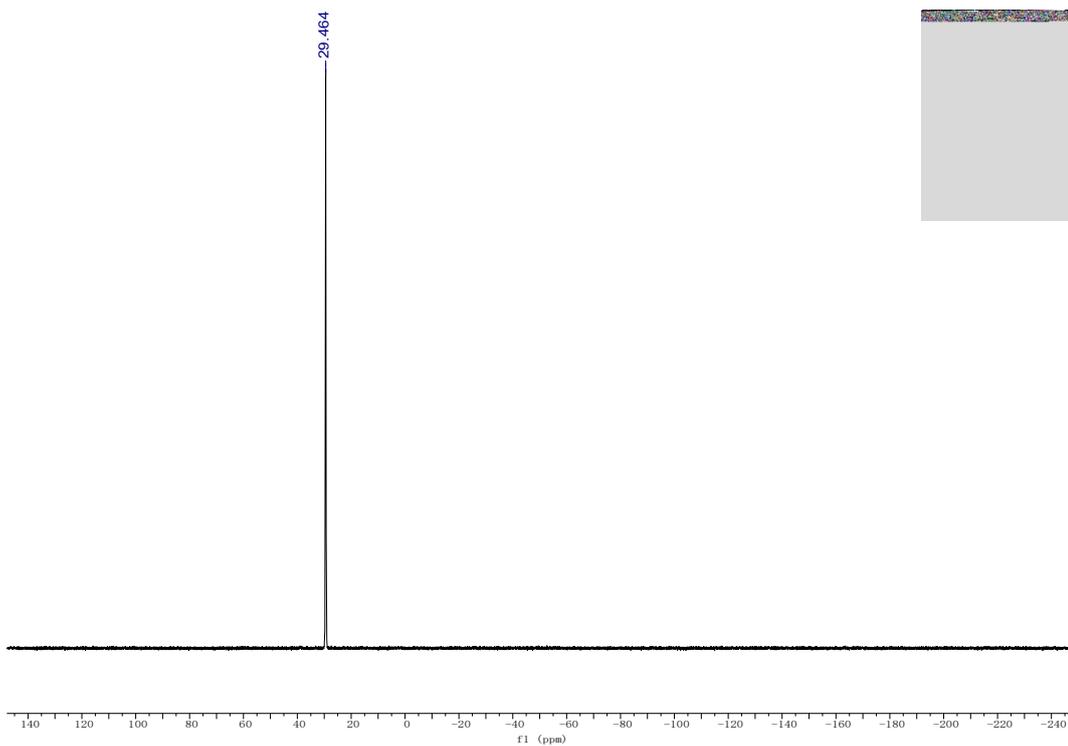


(3ka)

¹H NMR

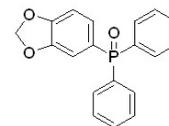
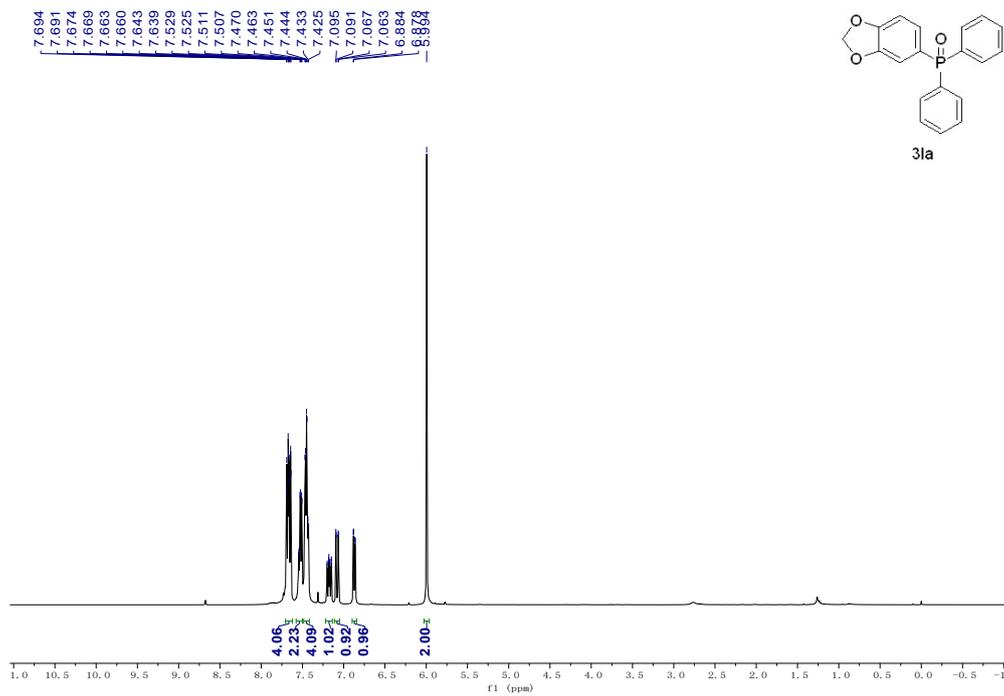


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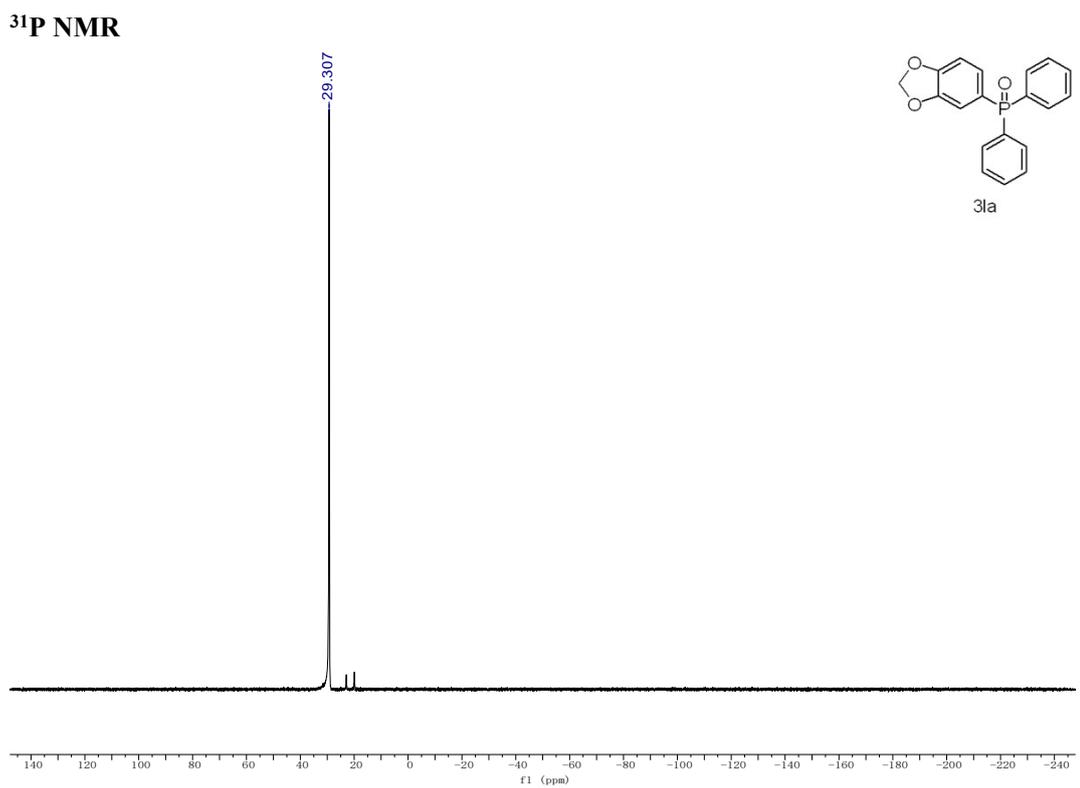
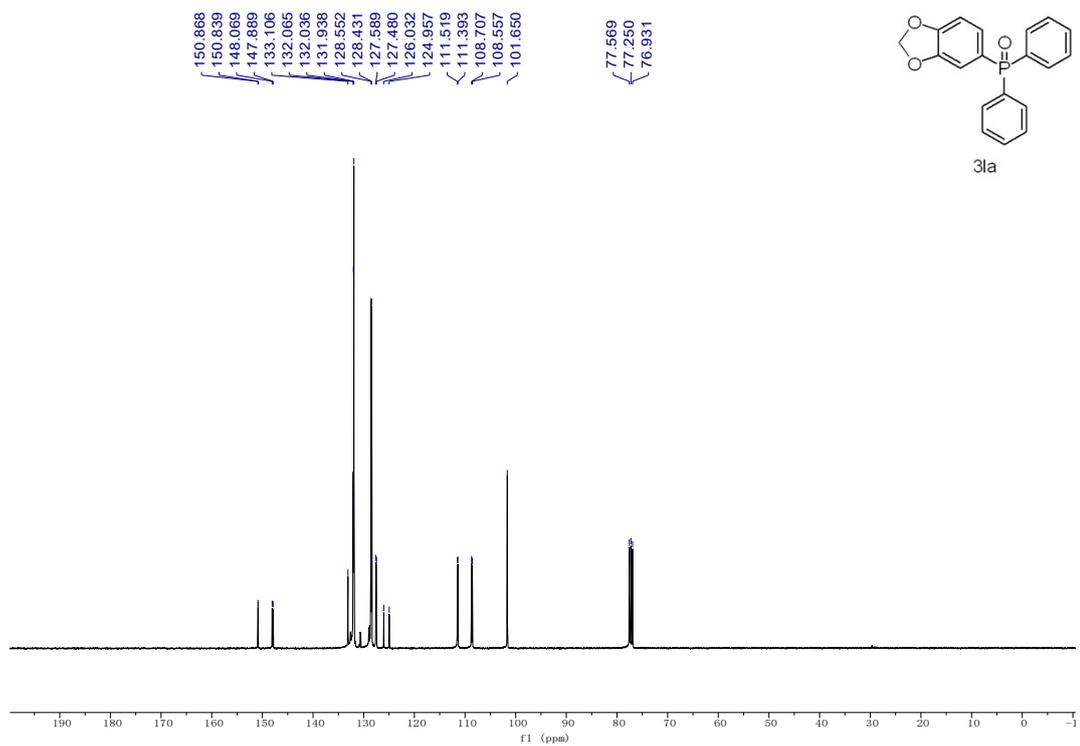
(3la)

¹H NMR

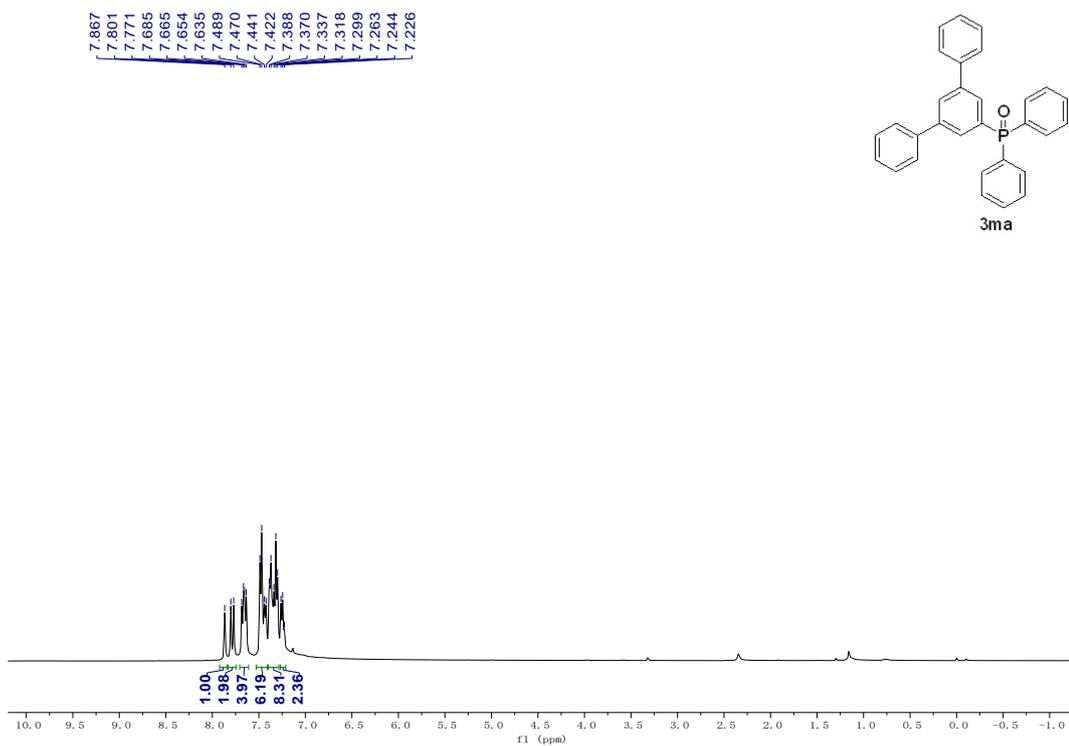


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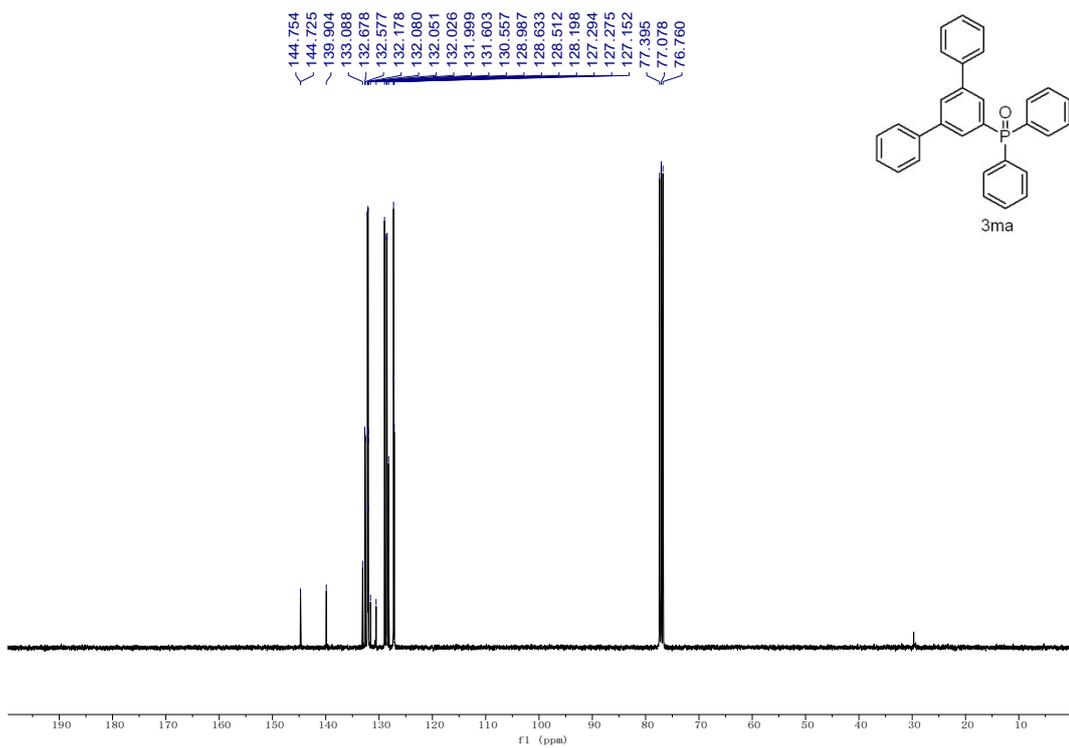
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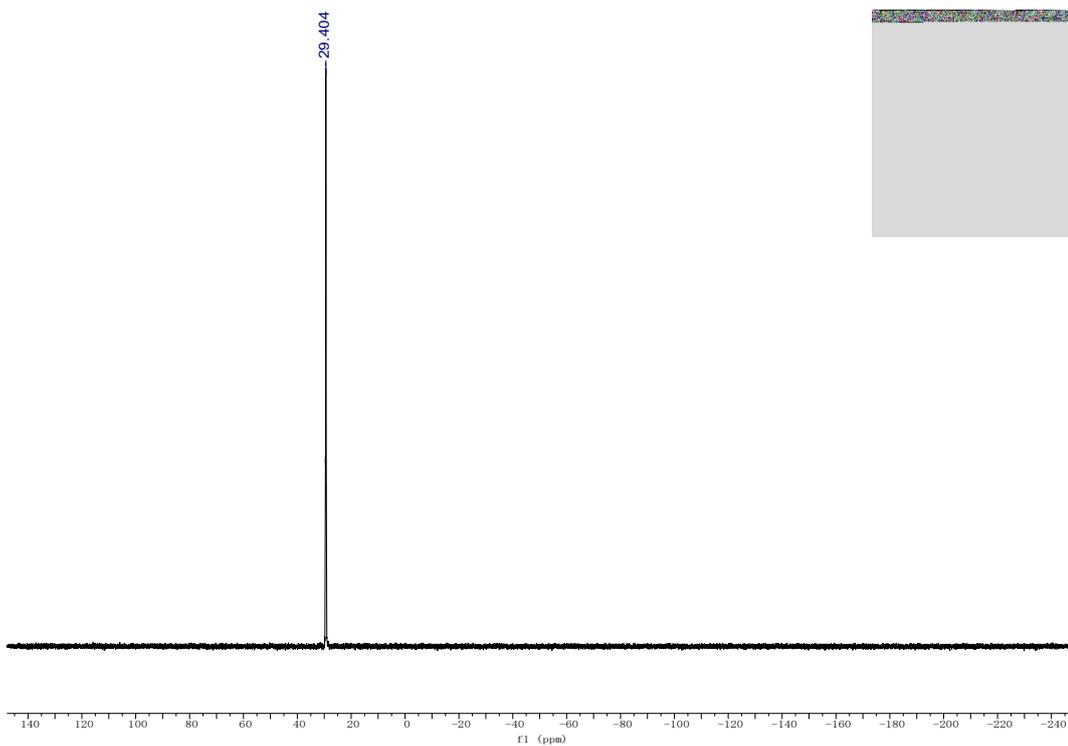
(3ma)
¹H NMR



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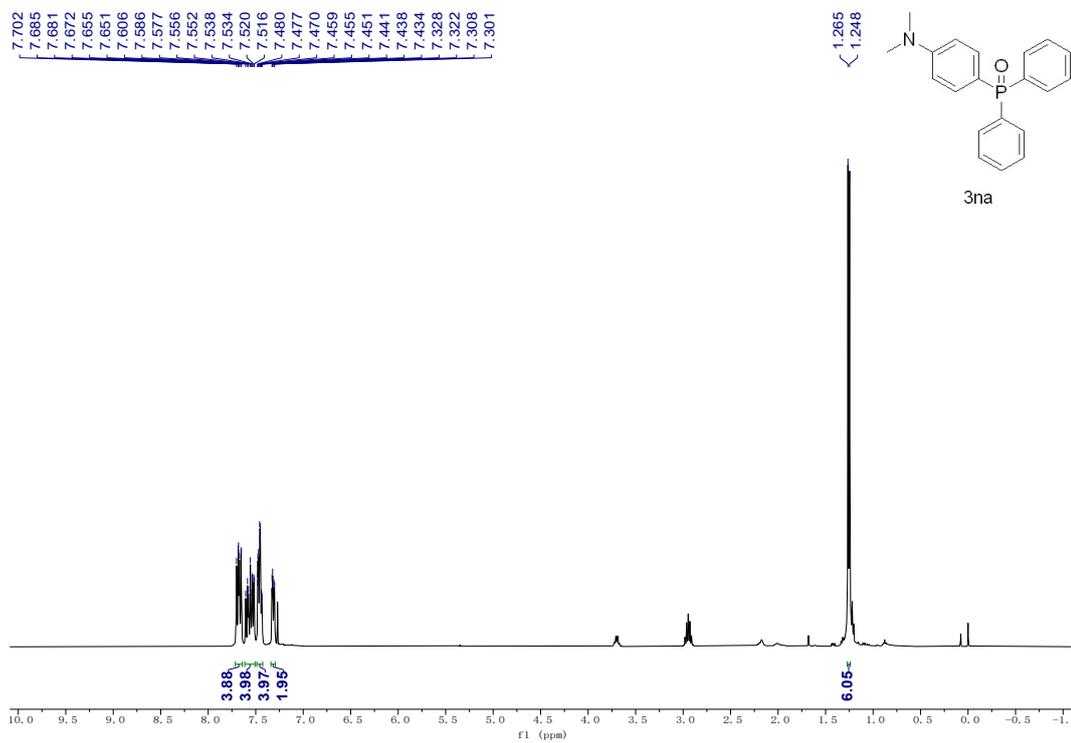


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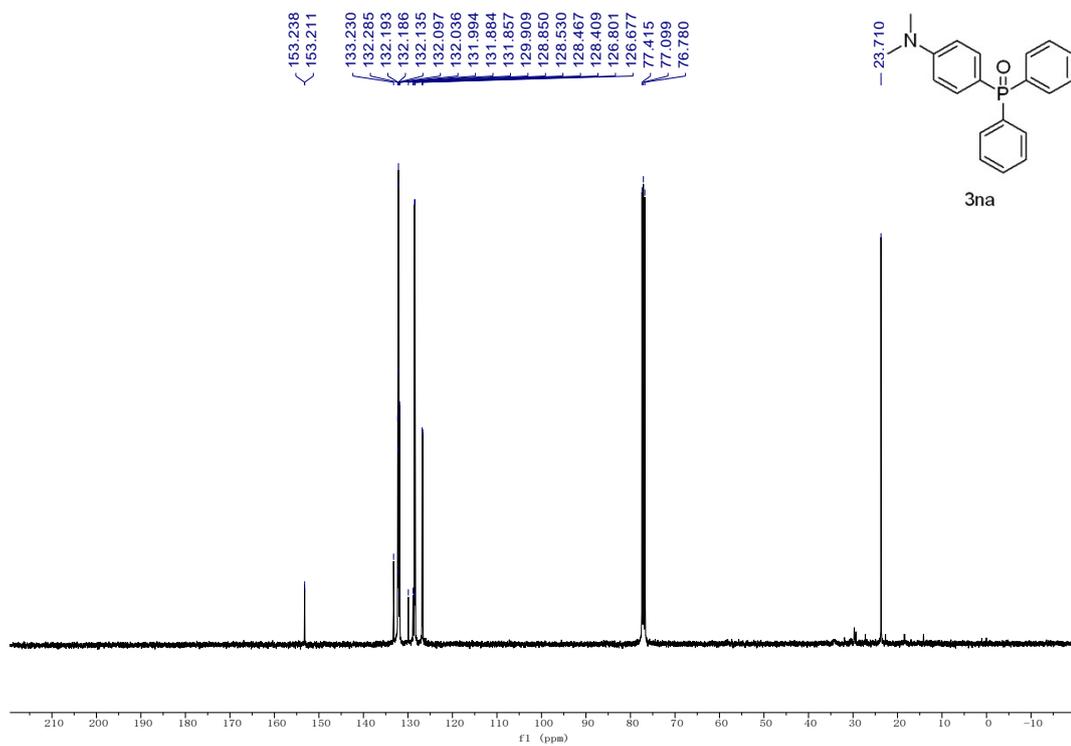


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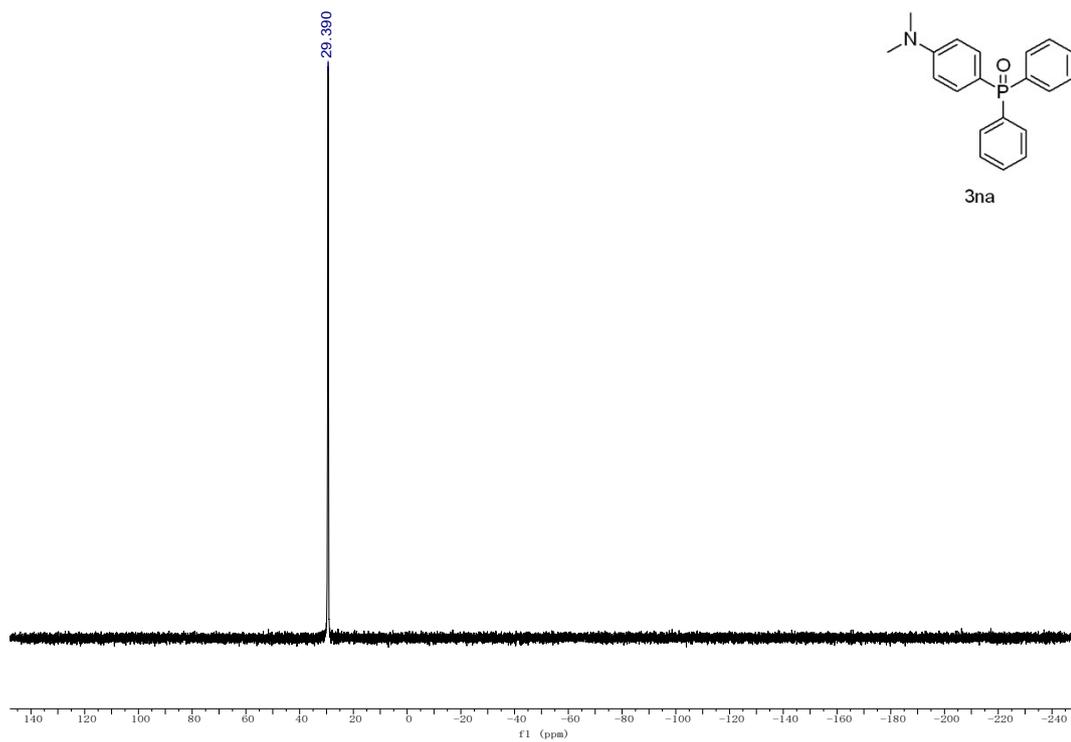
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¹³C NMR

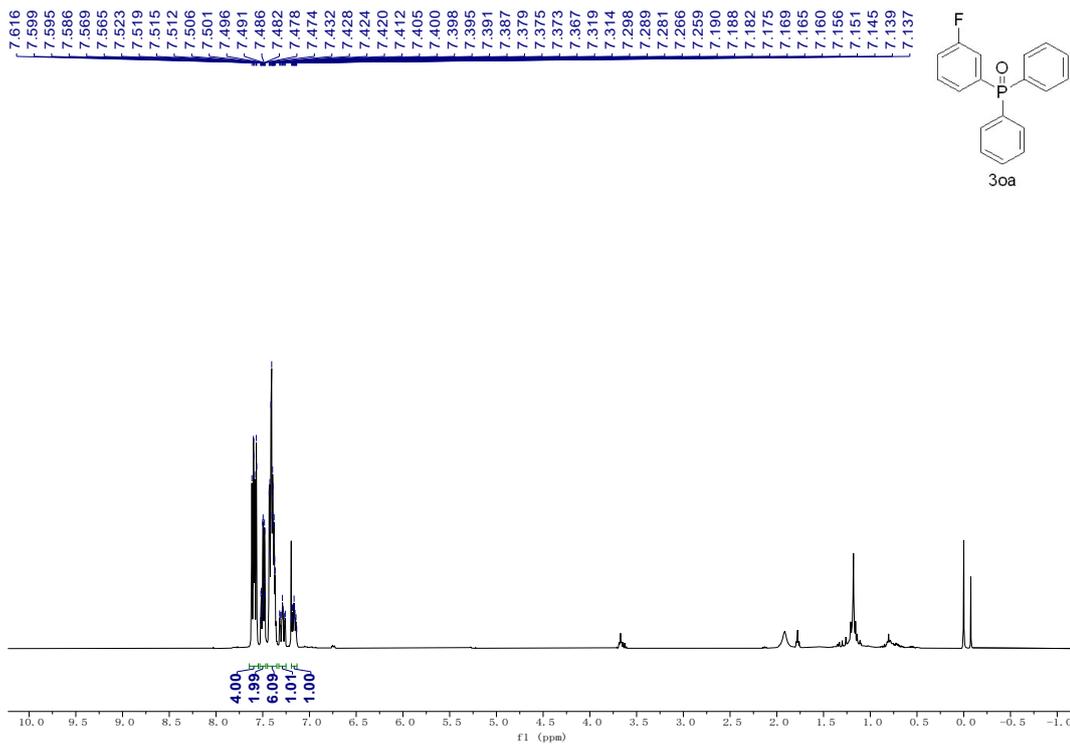


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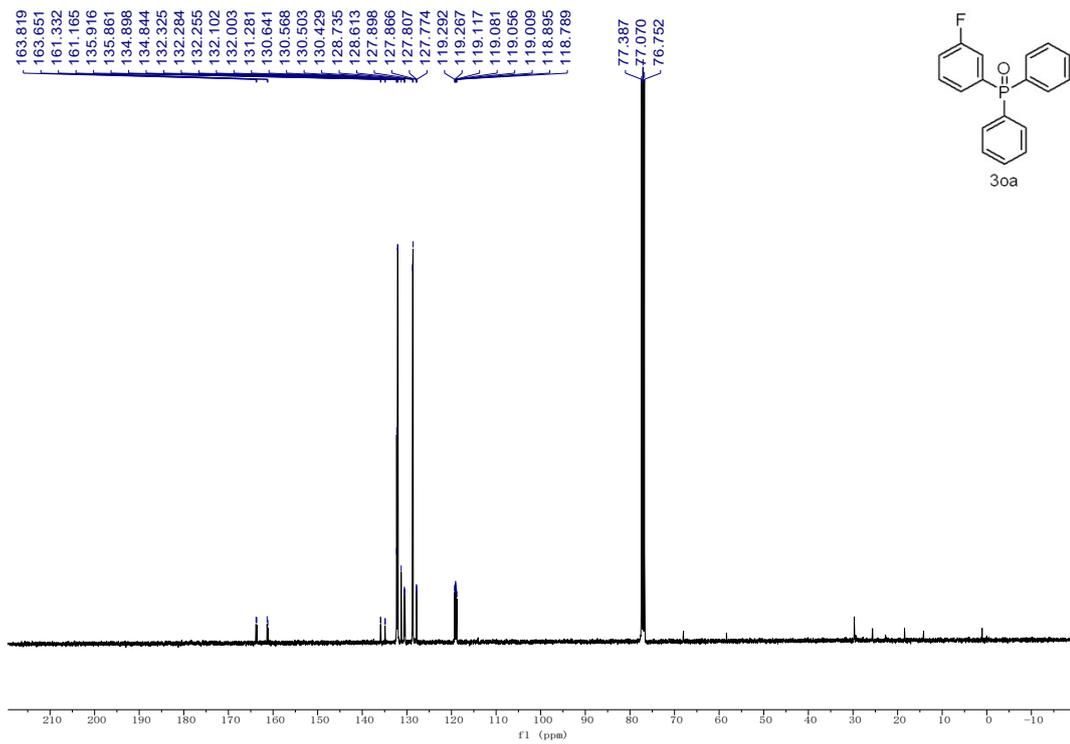


(30a)

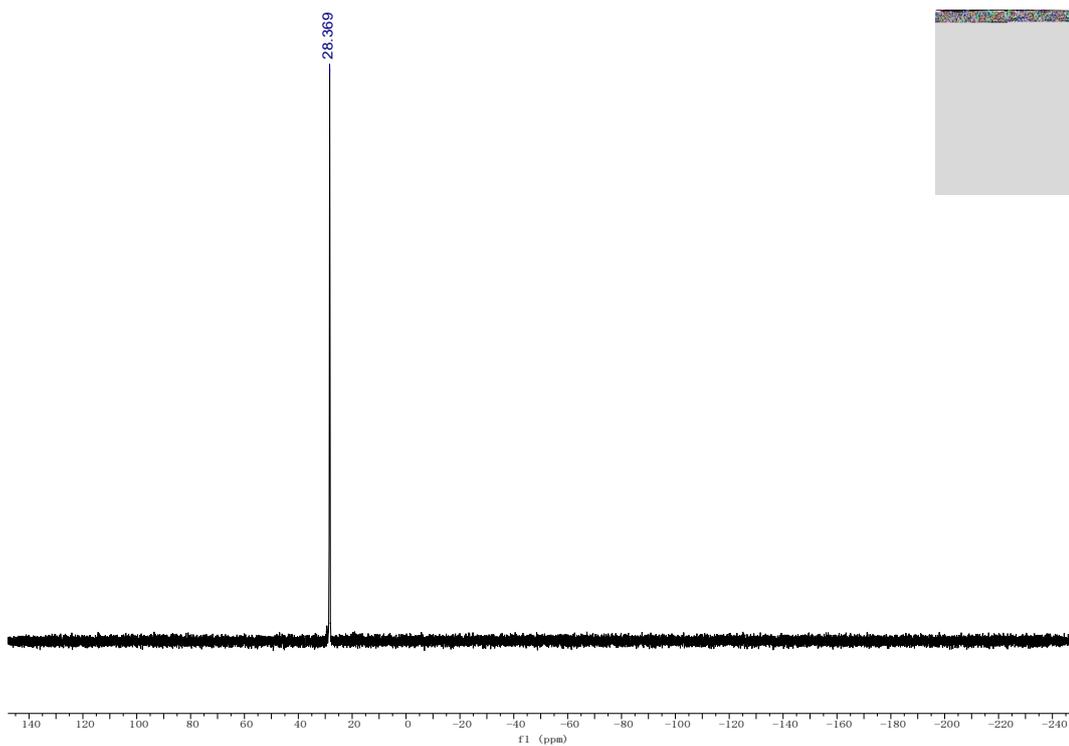
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¹³C NMR

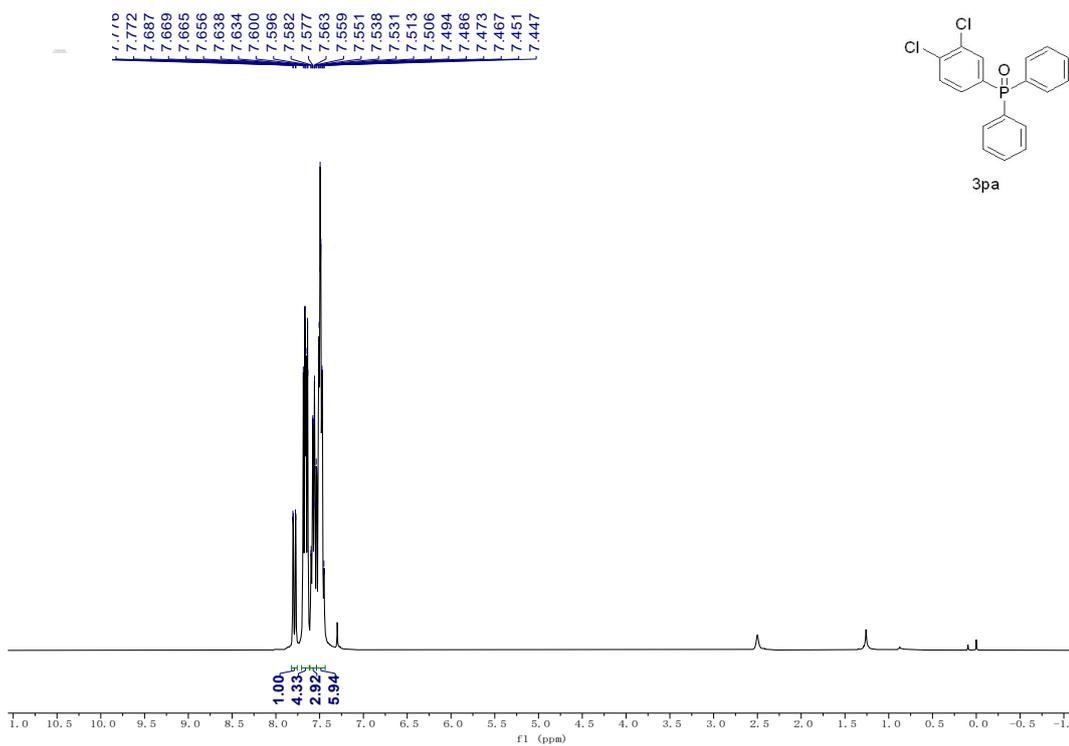


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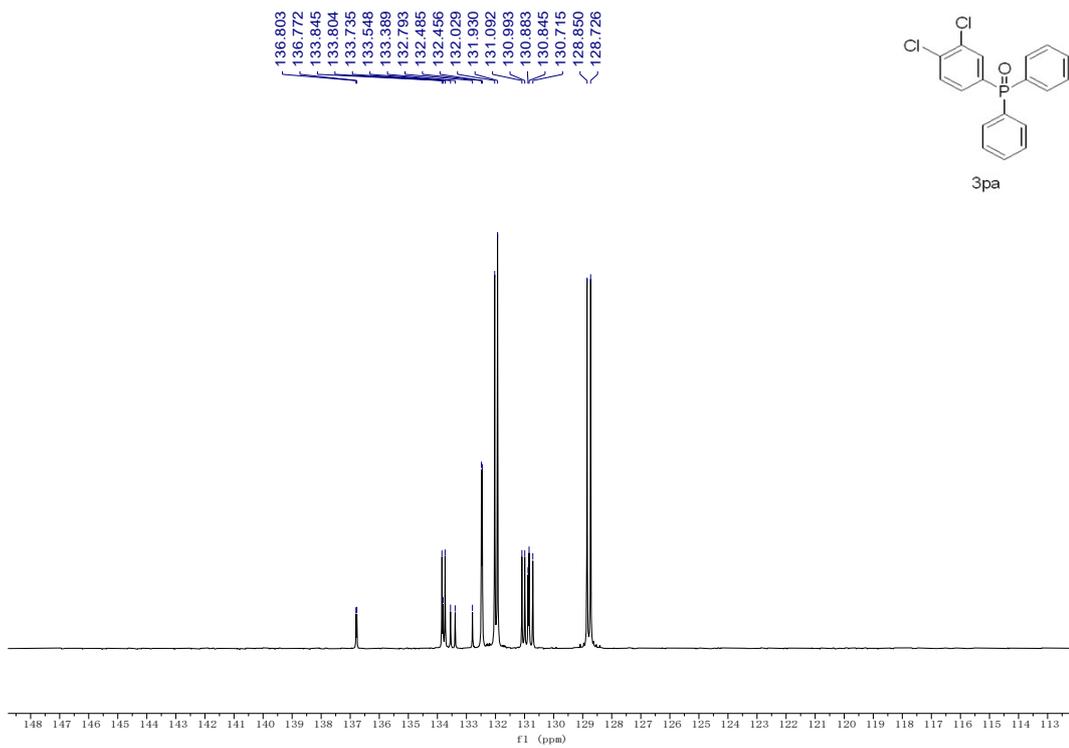


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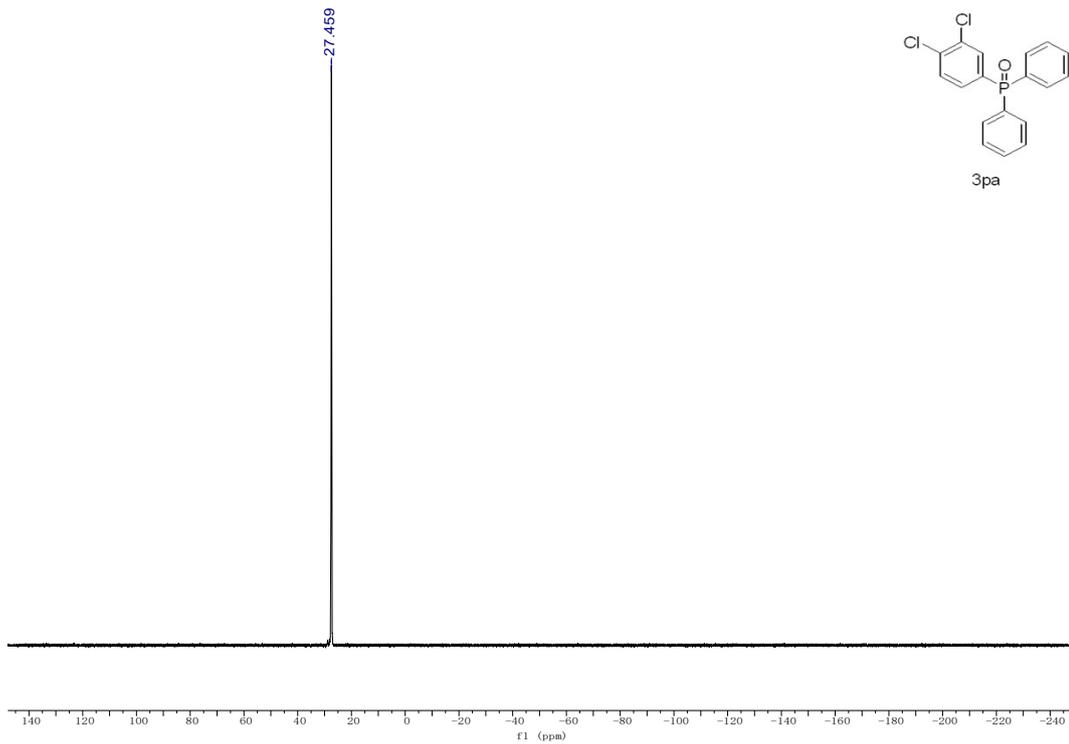
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¹³C NMR

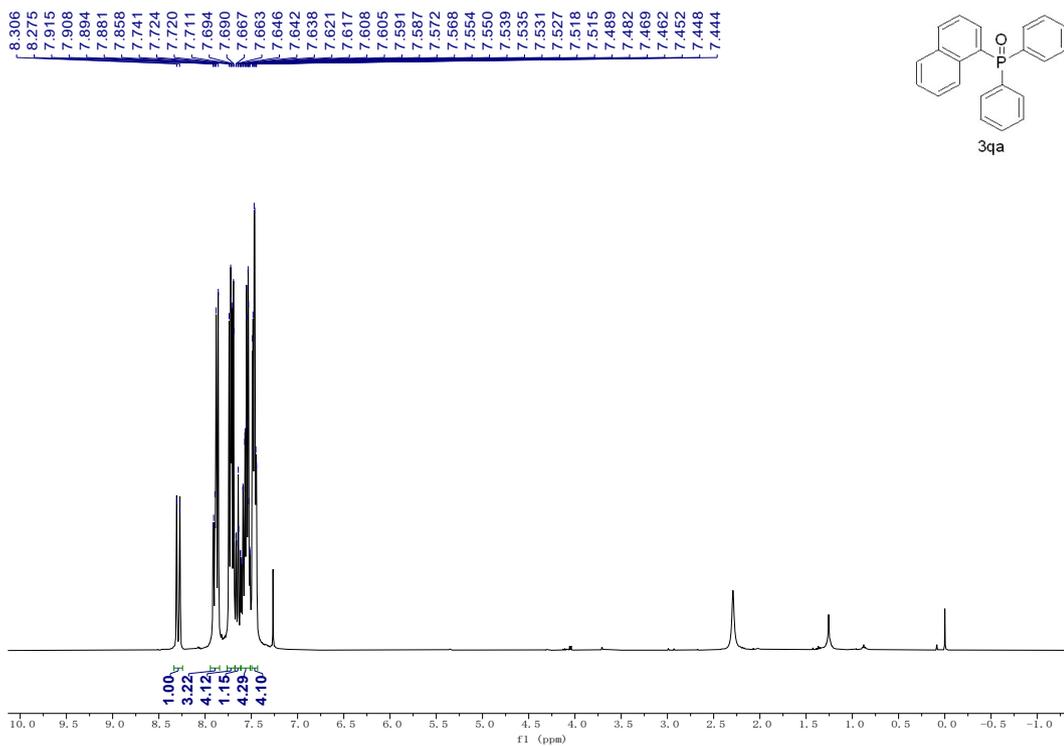


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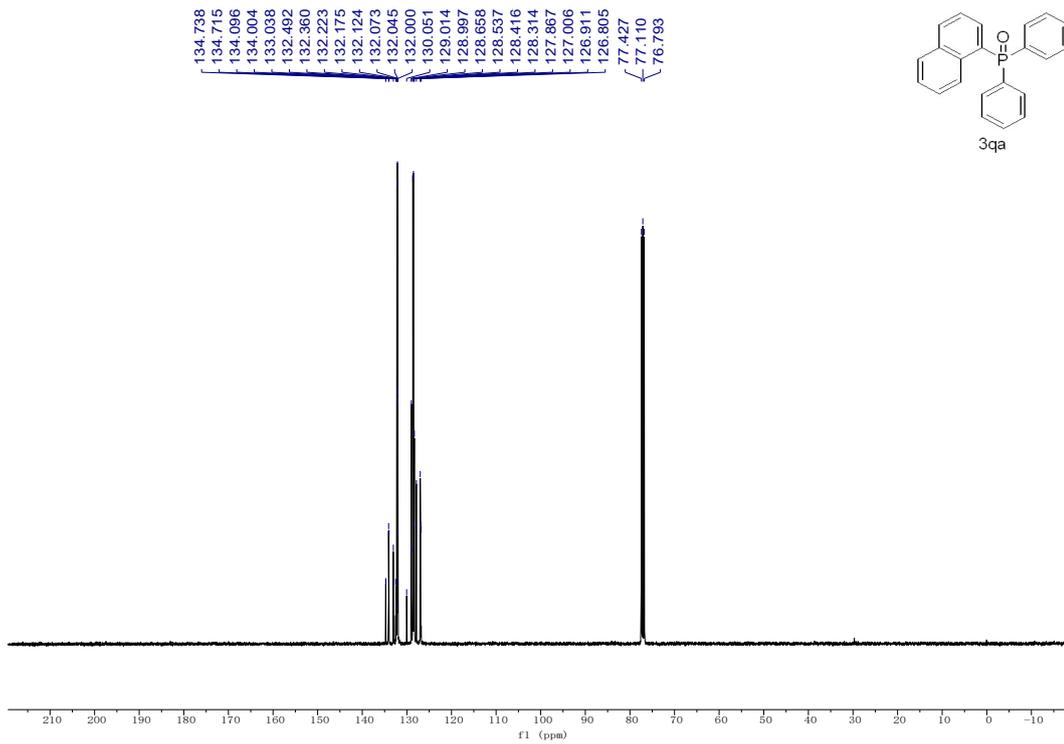


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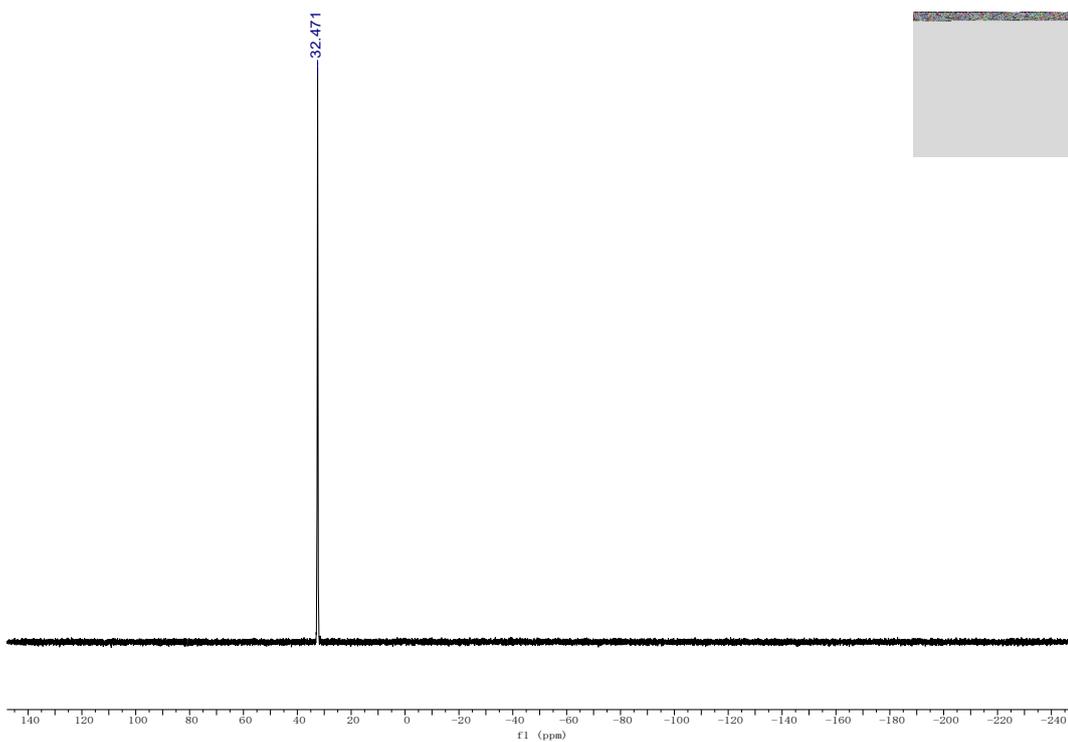
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¹³C NMR

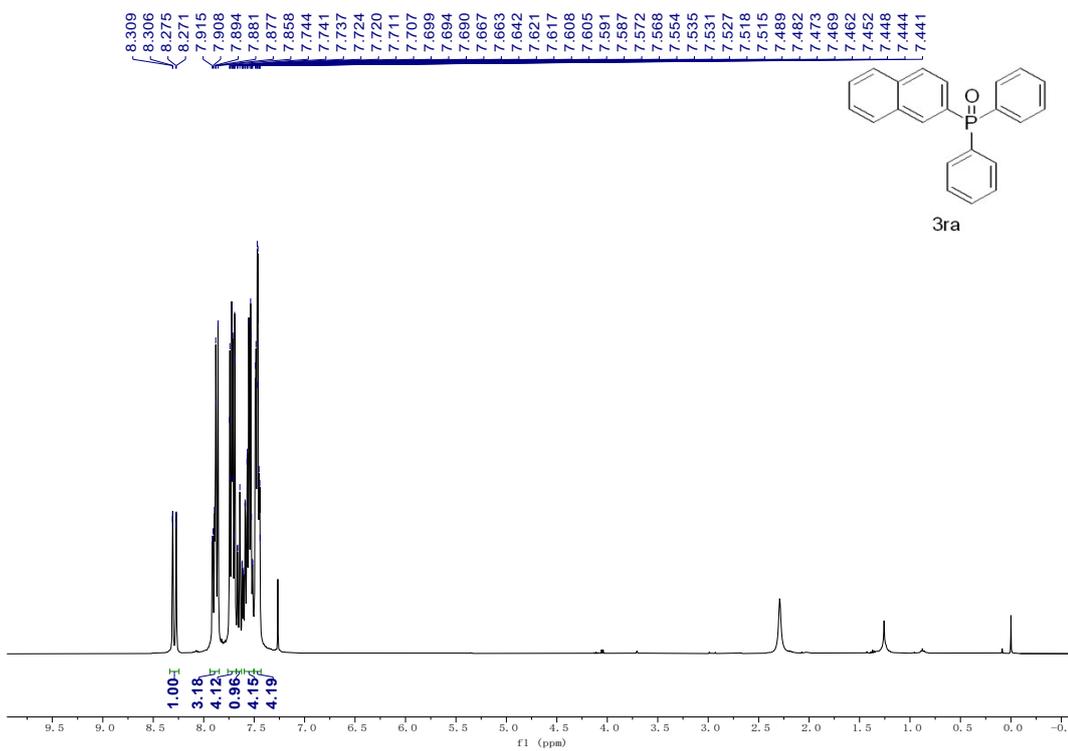


³¹P NMR

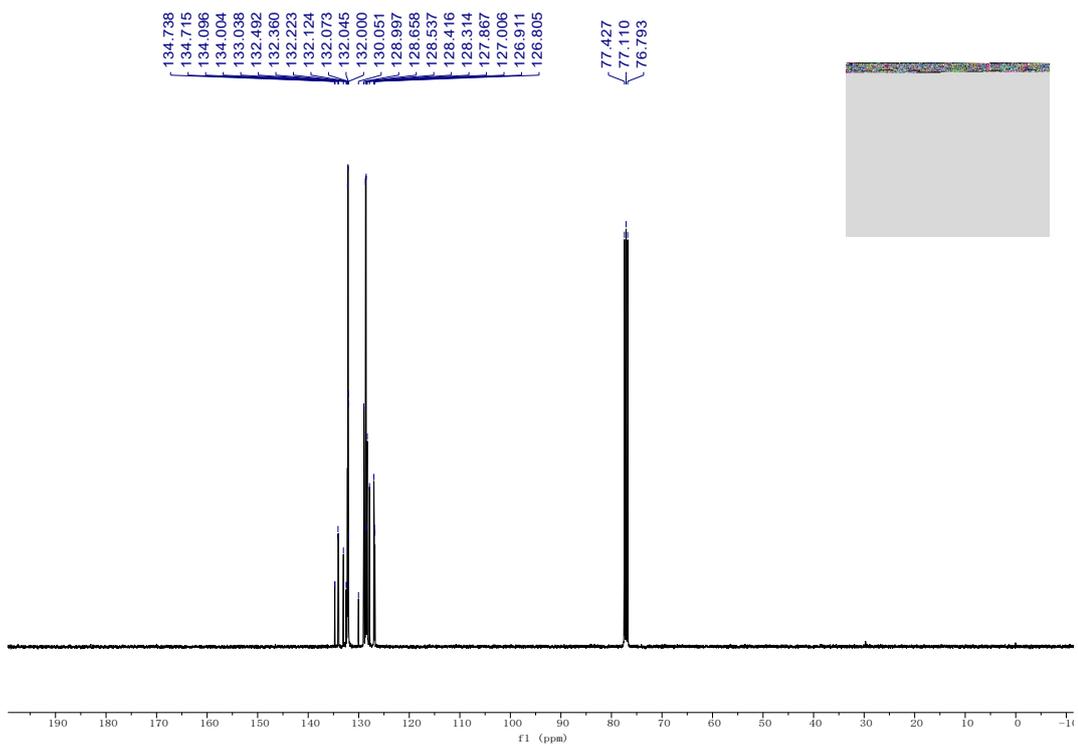


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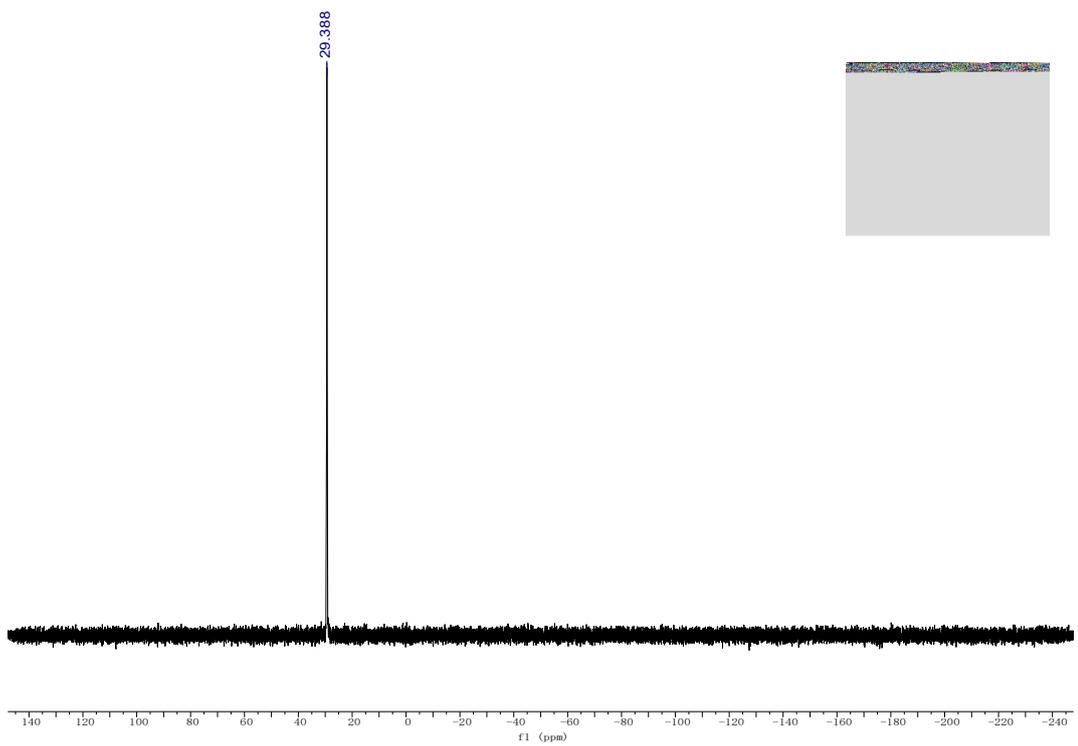
¹H NMR



¹³C NMR

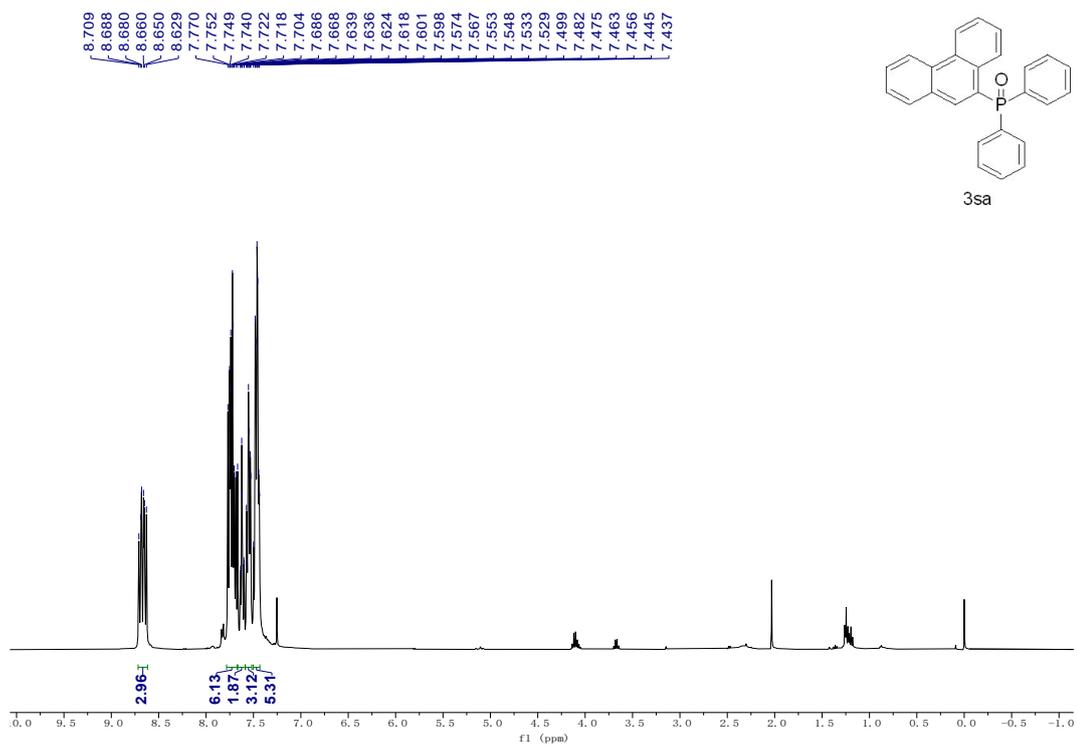


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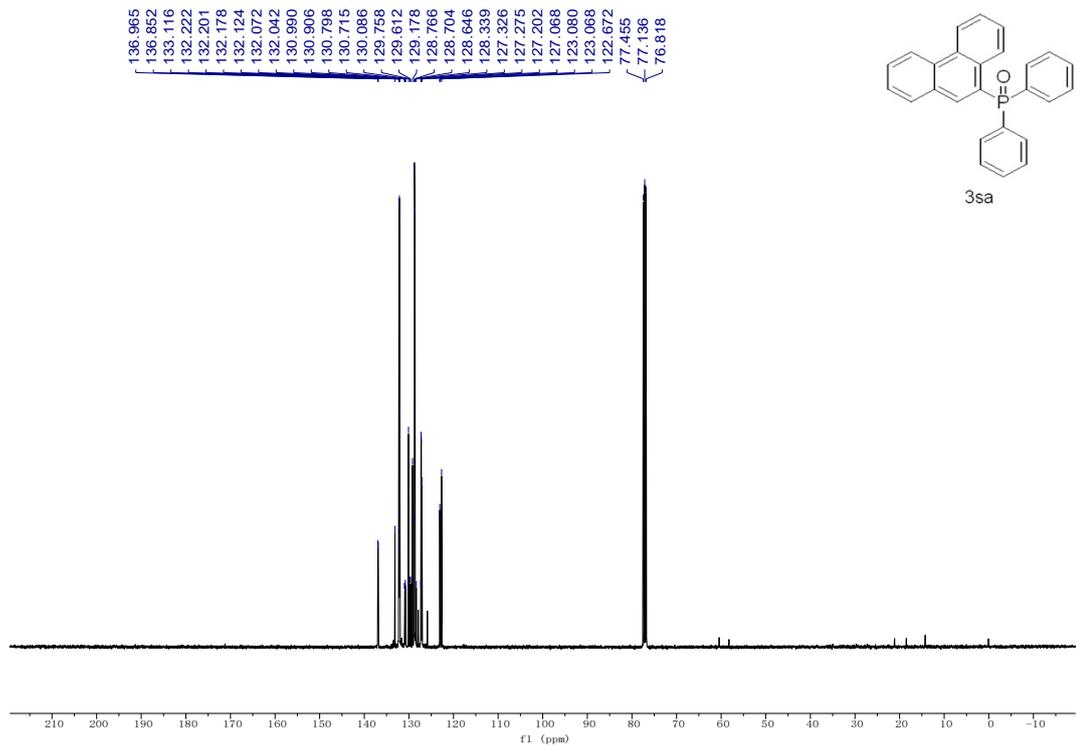


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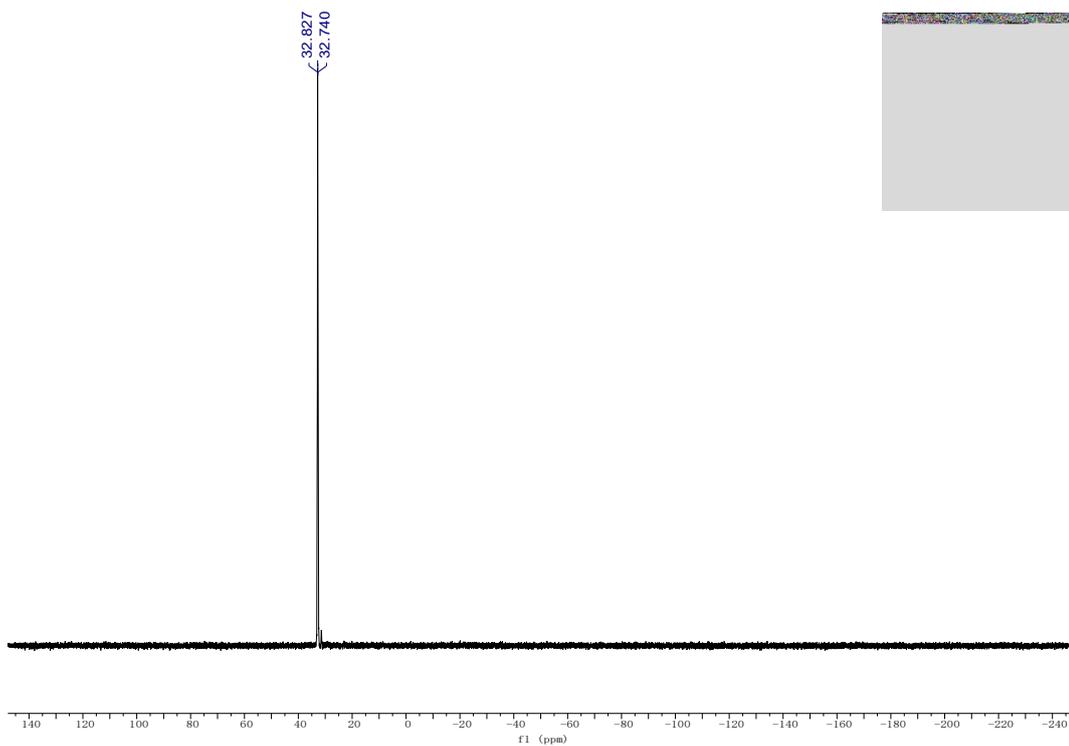
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¹³C NMR

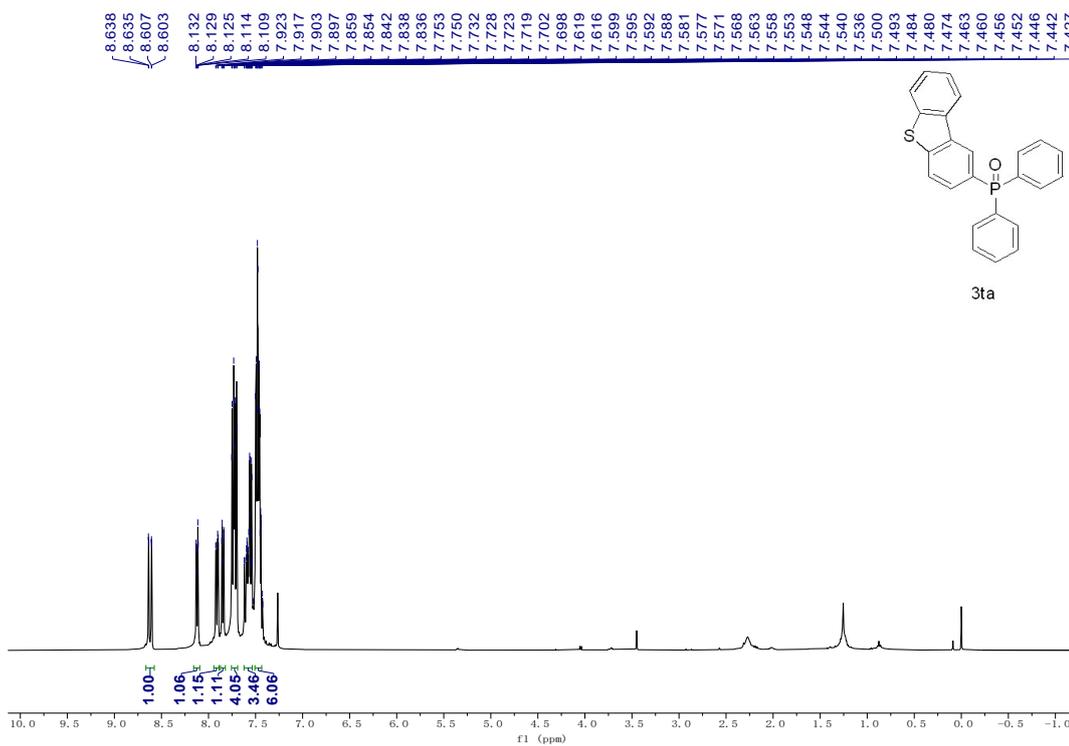


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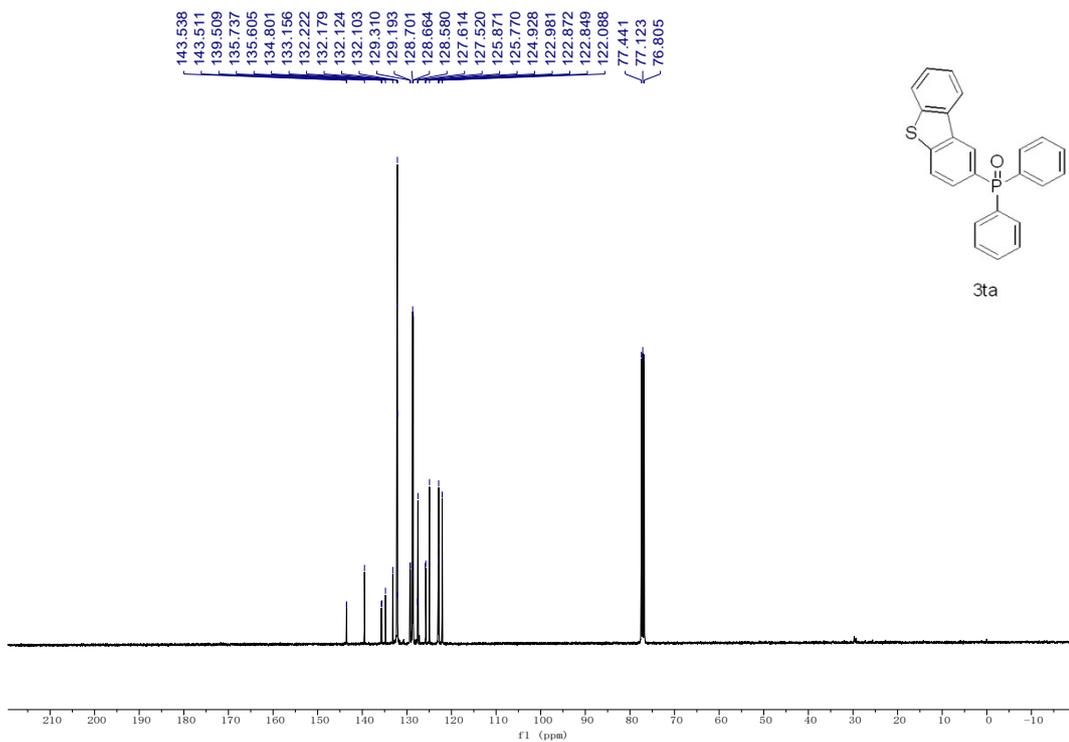


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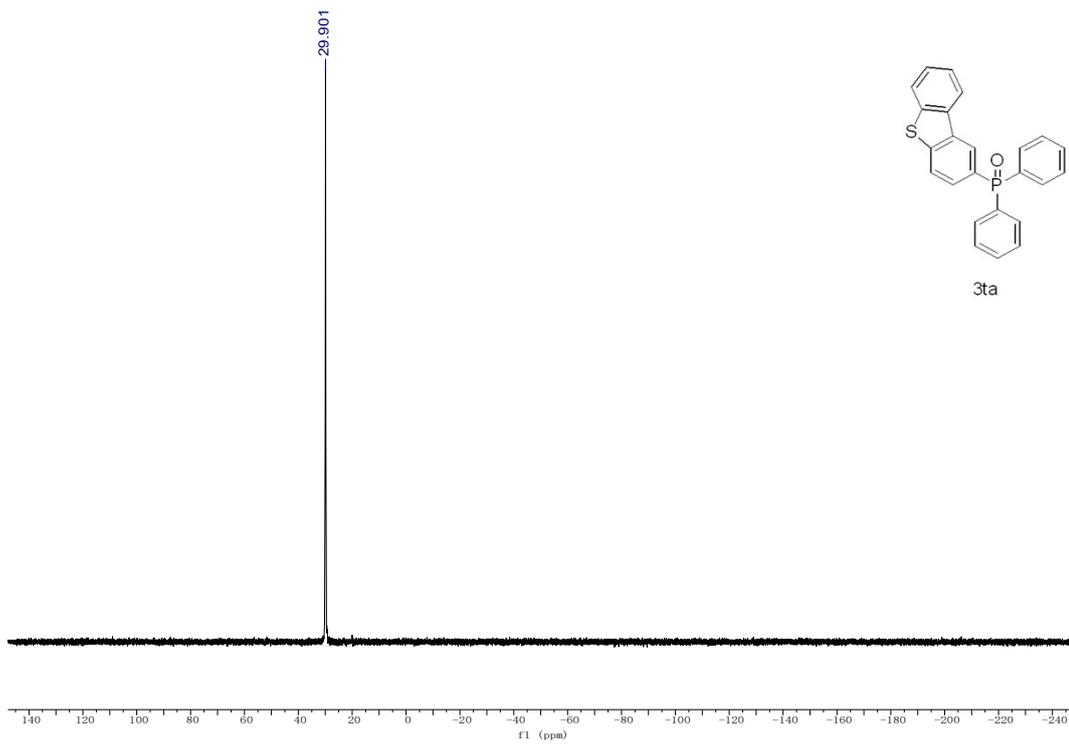
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¹³C NMR

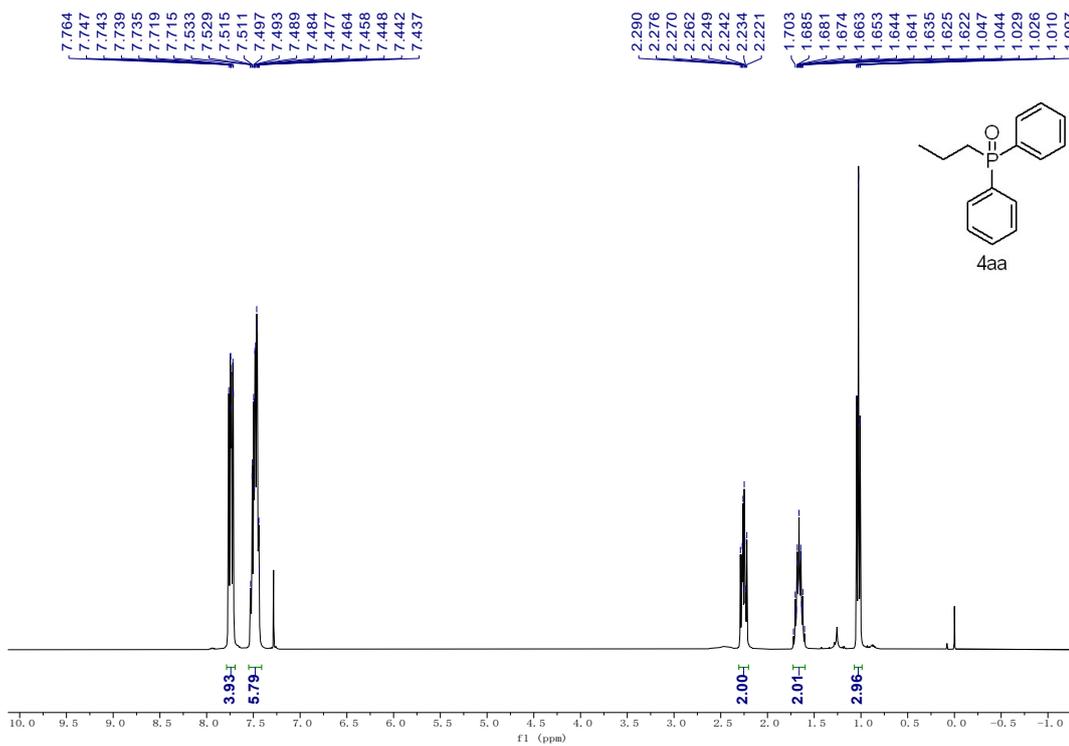


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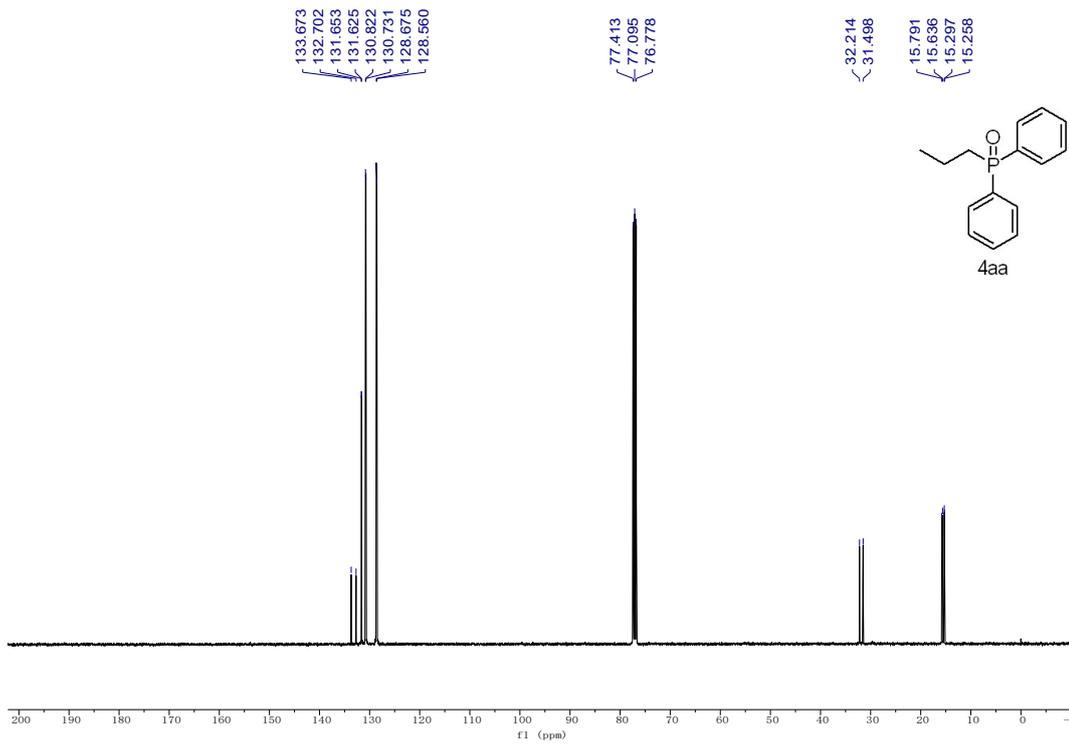


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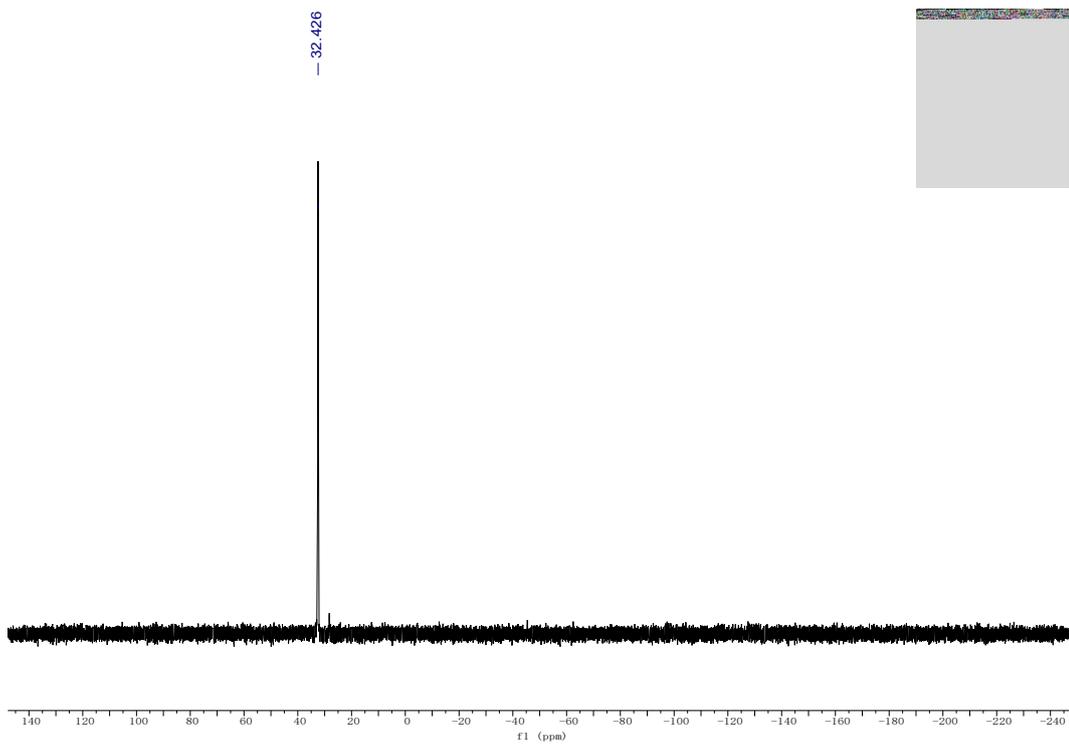
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¹³C NMR

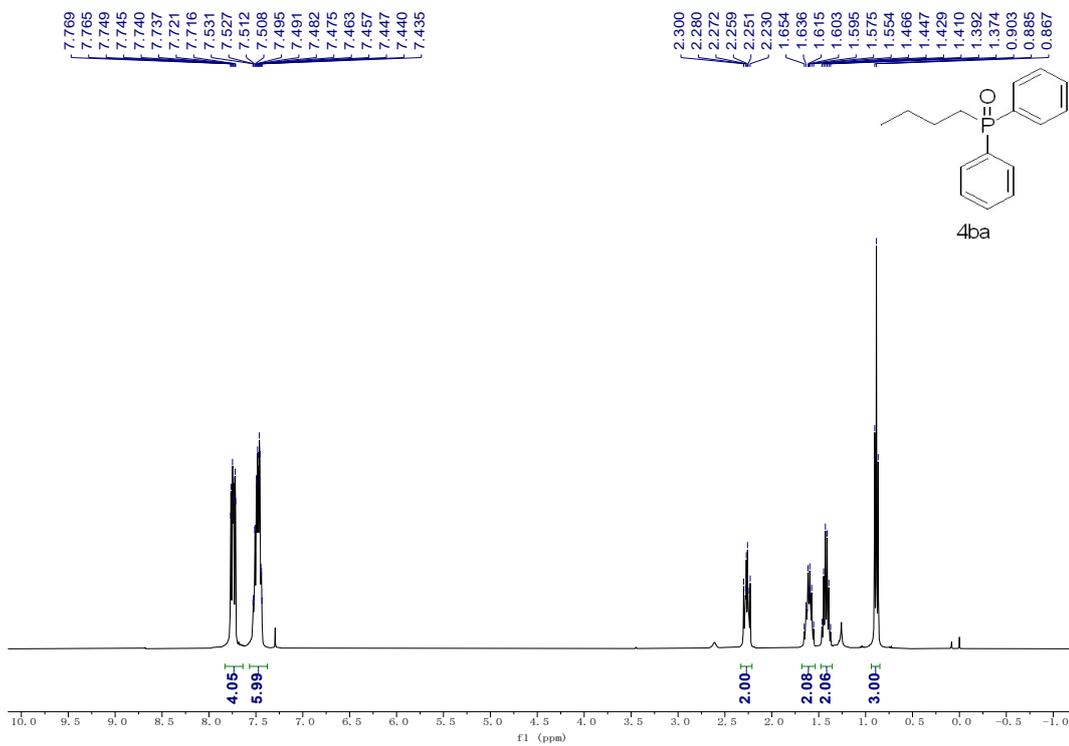


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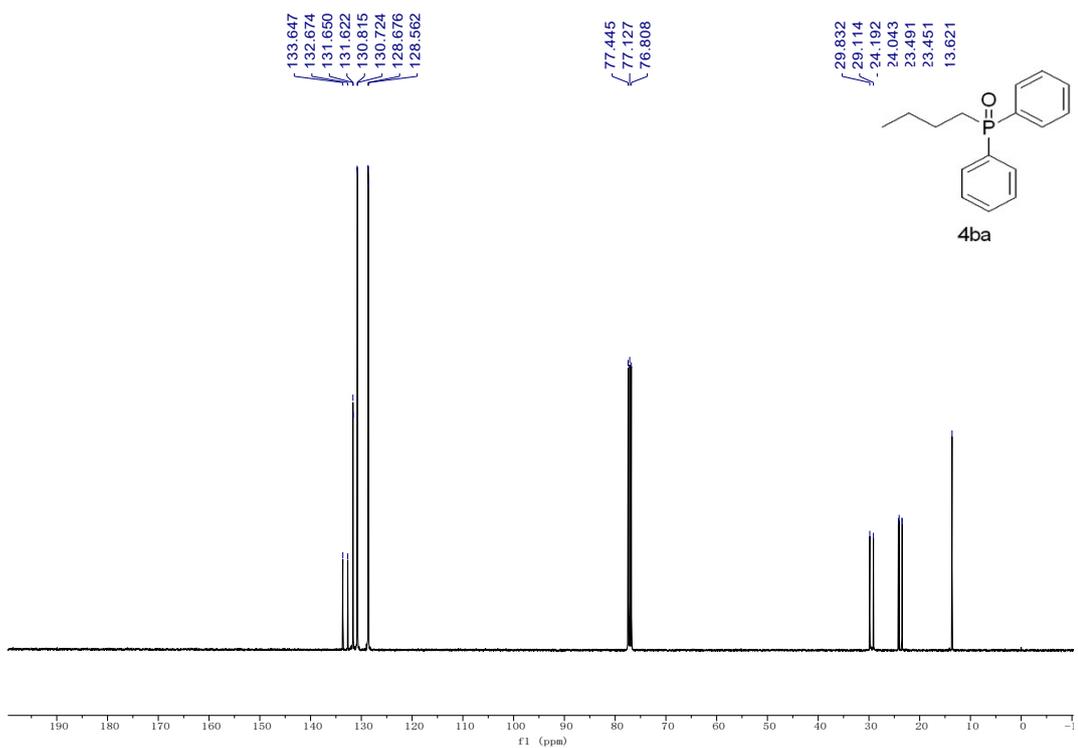


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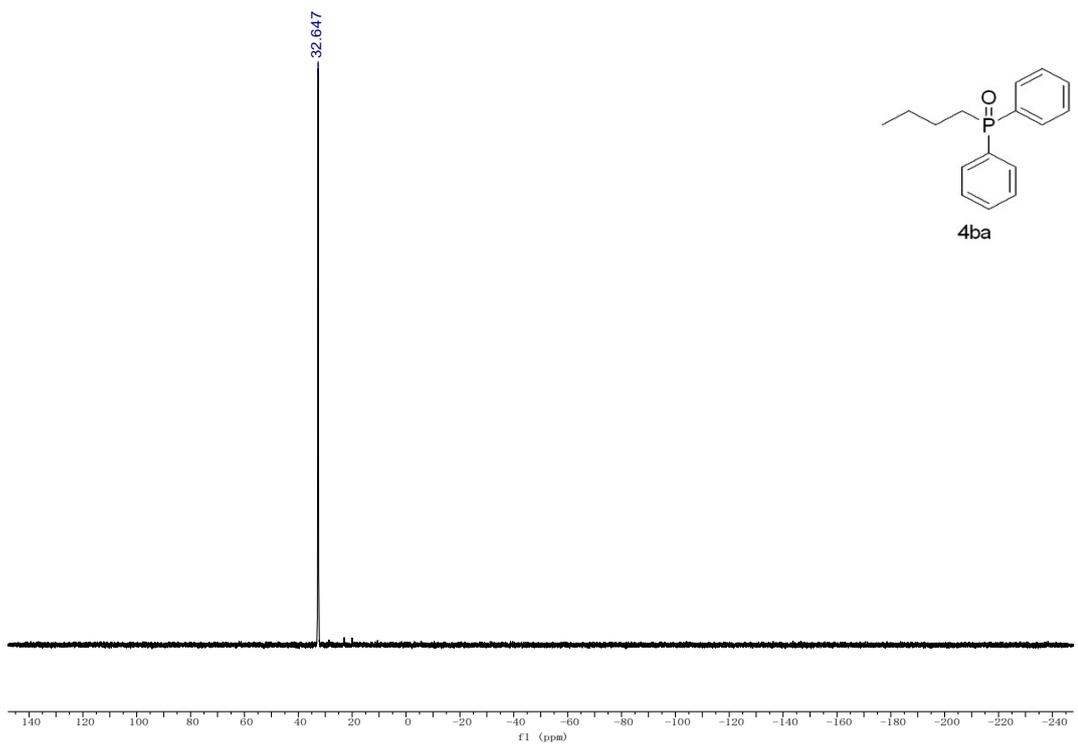
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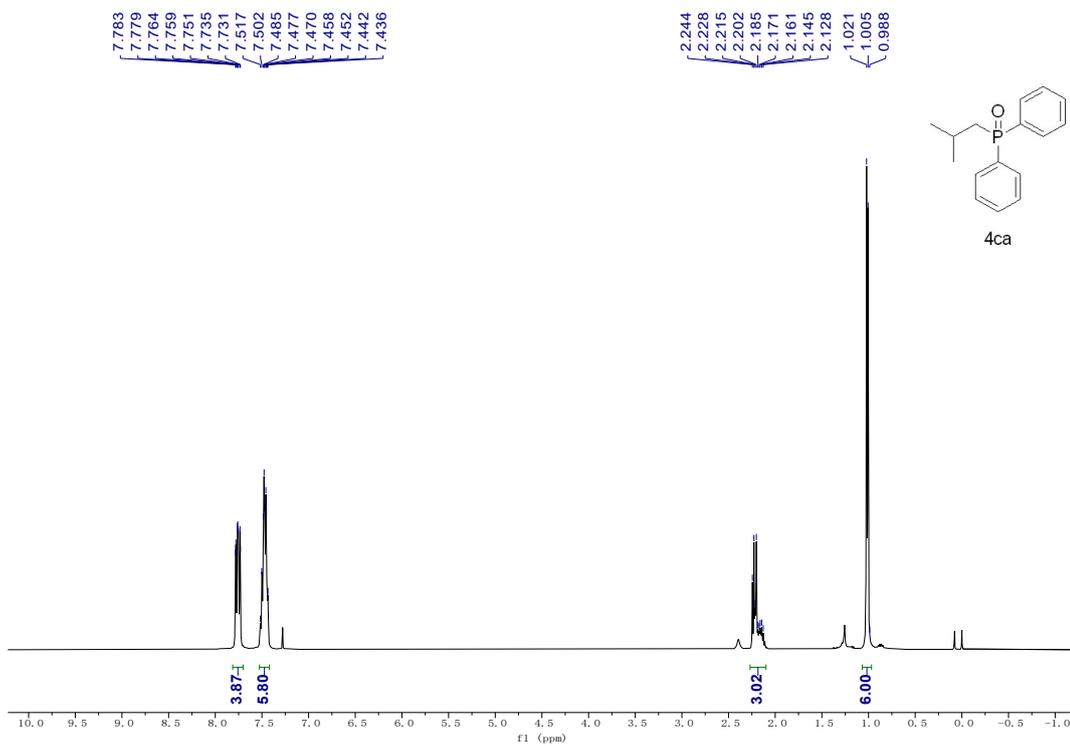


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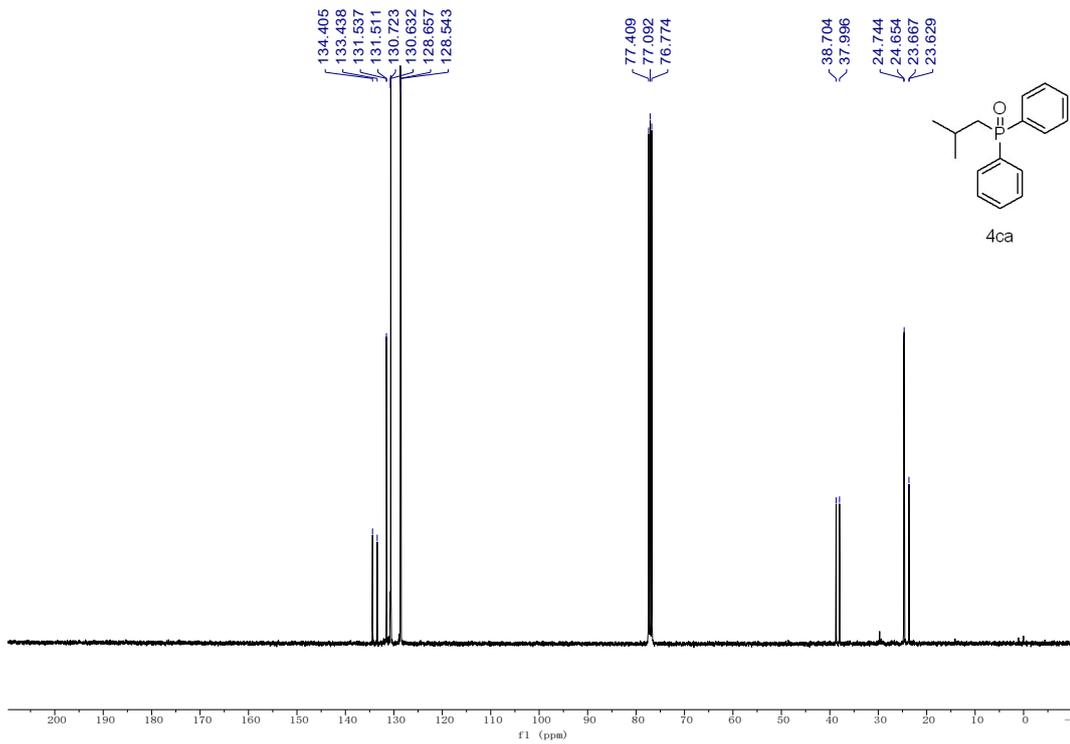


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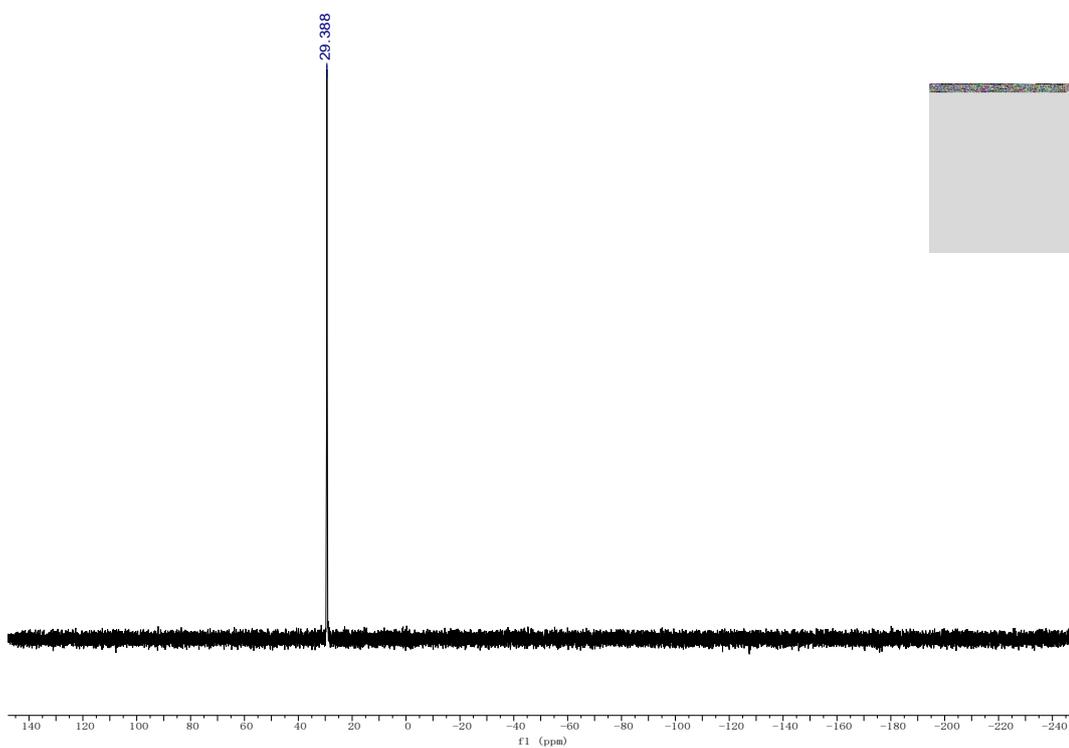
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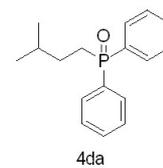
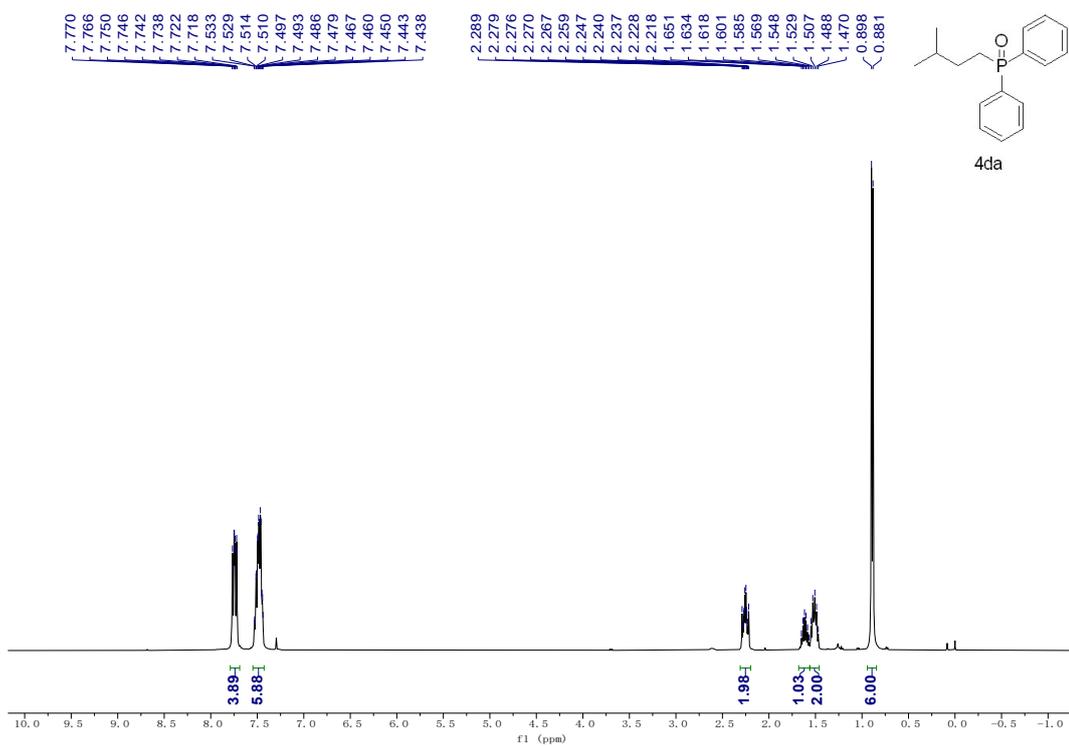


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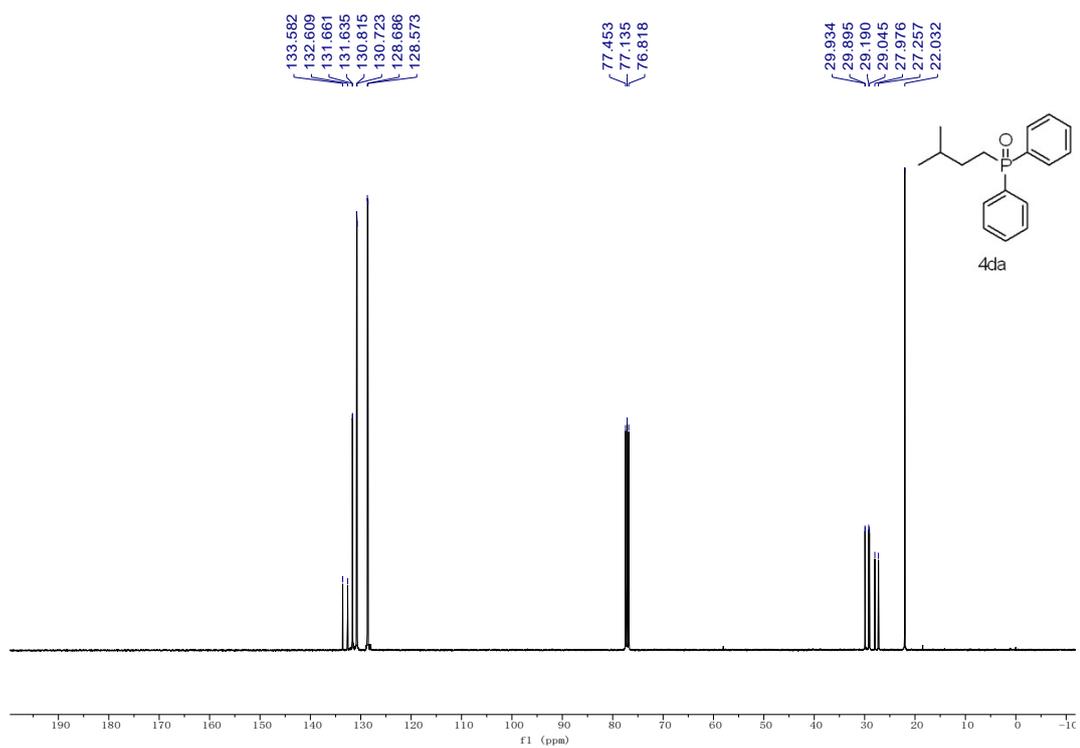


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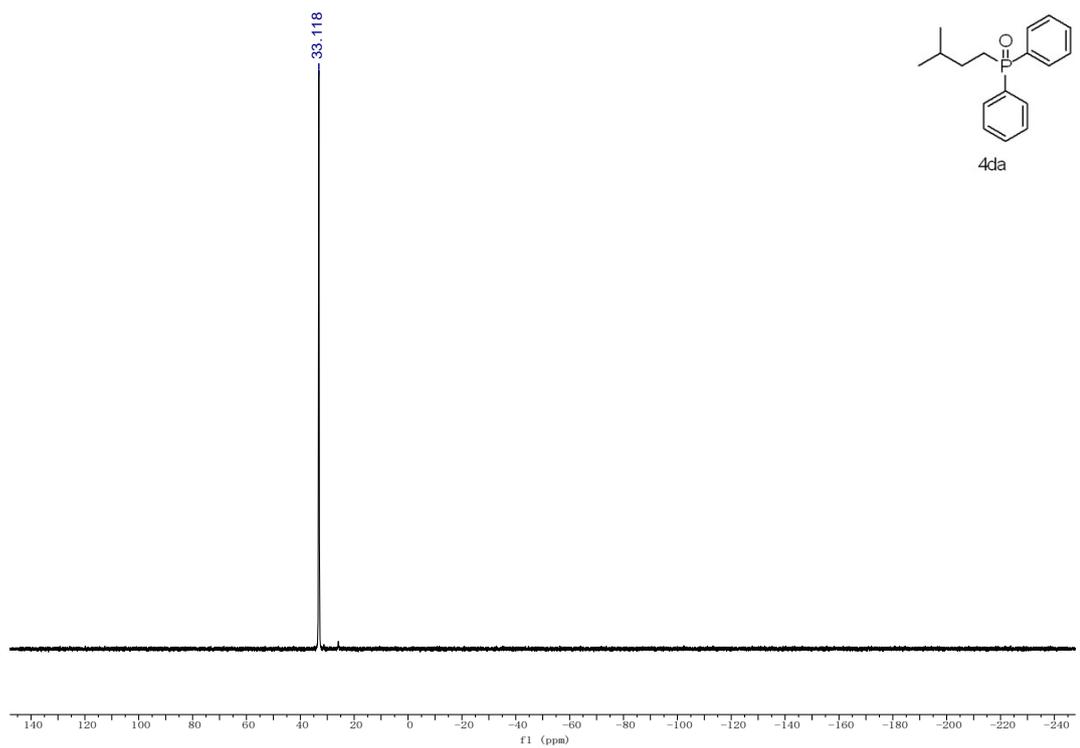
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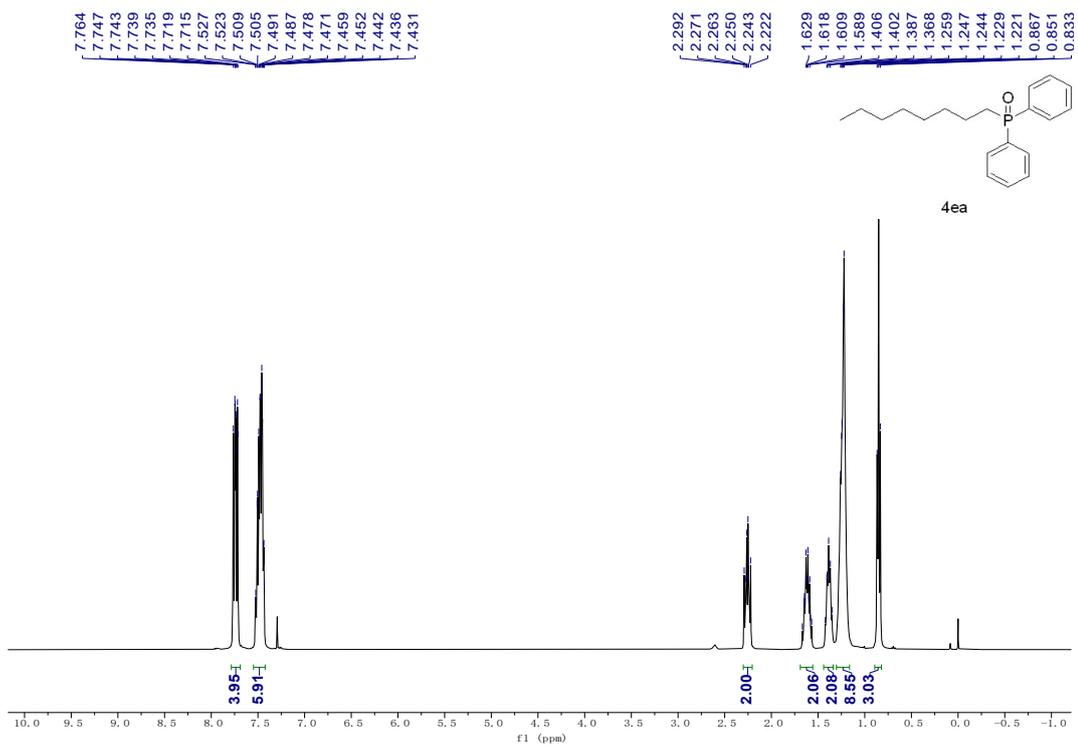


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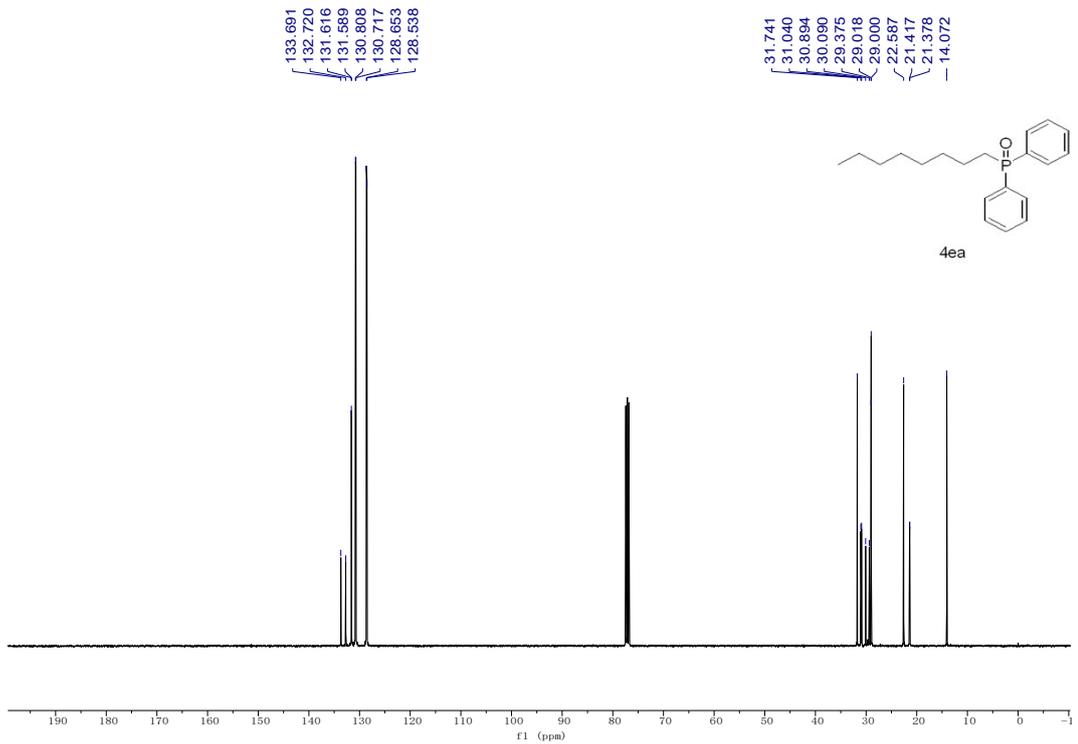


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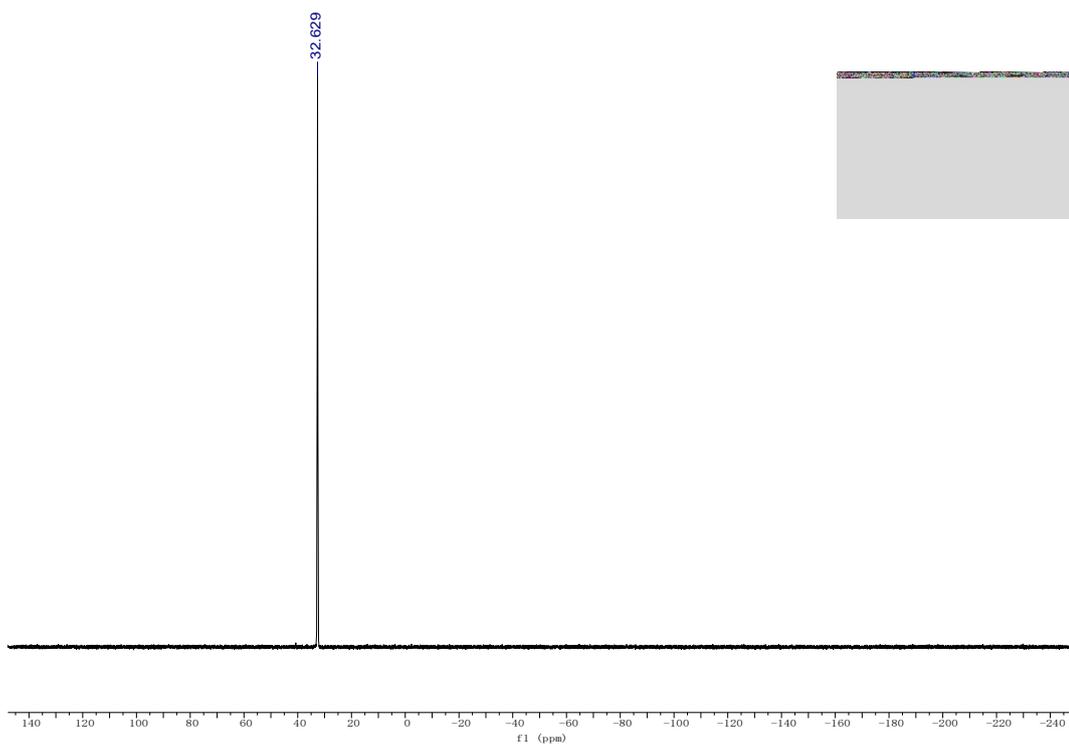
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¹³C NMR

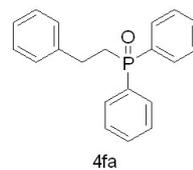
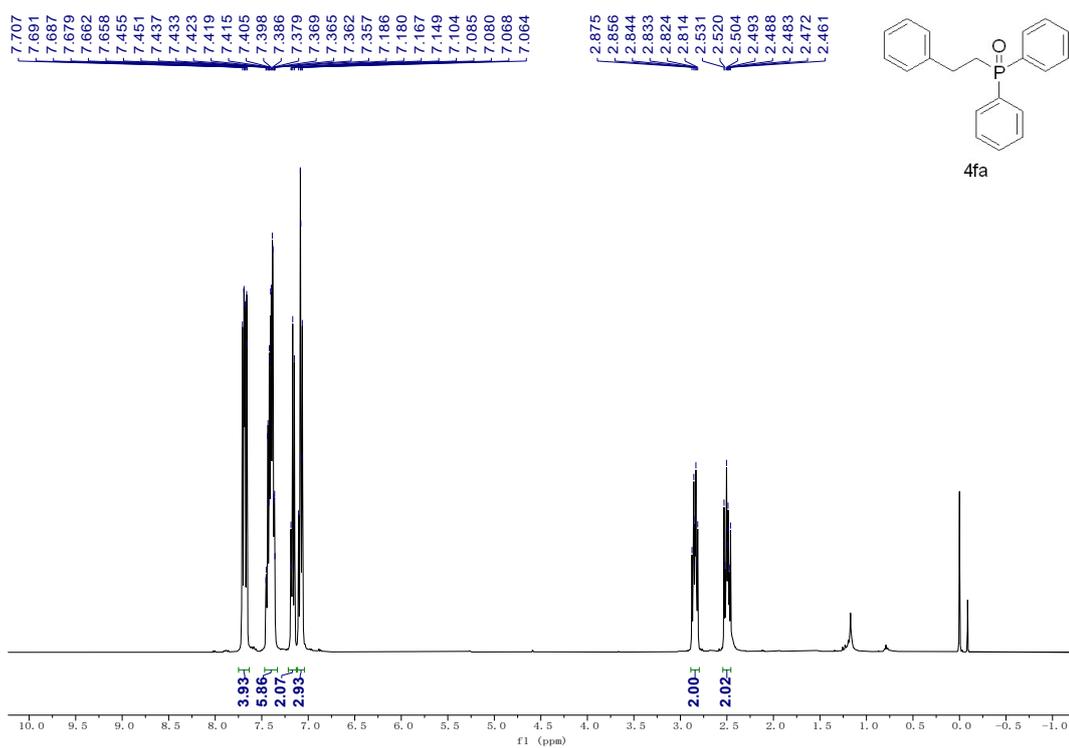


³¹P NMR

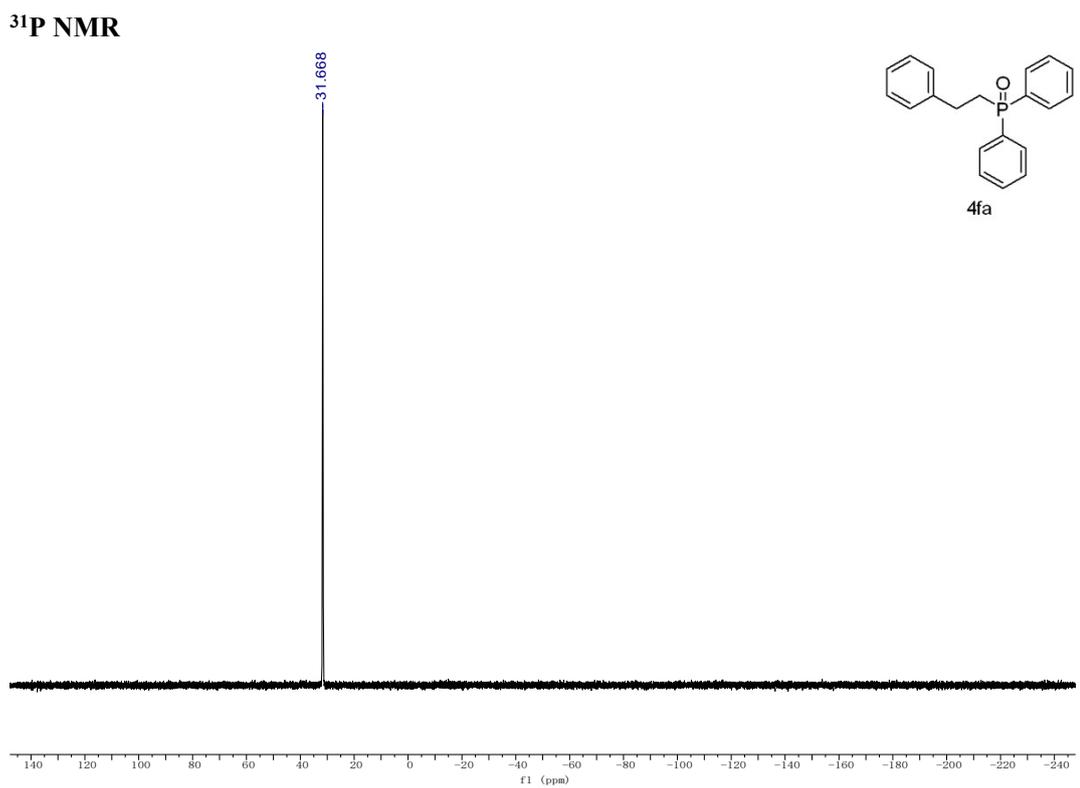
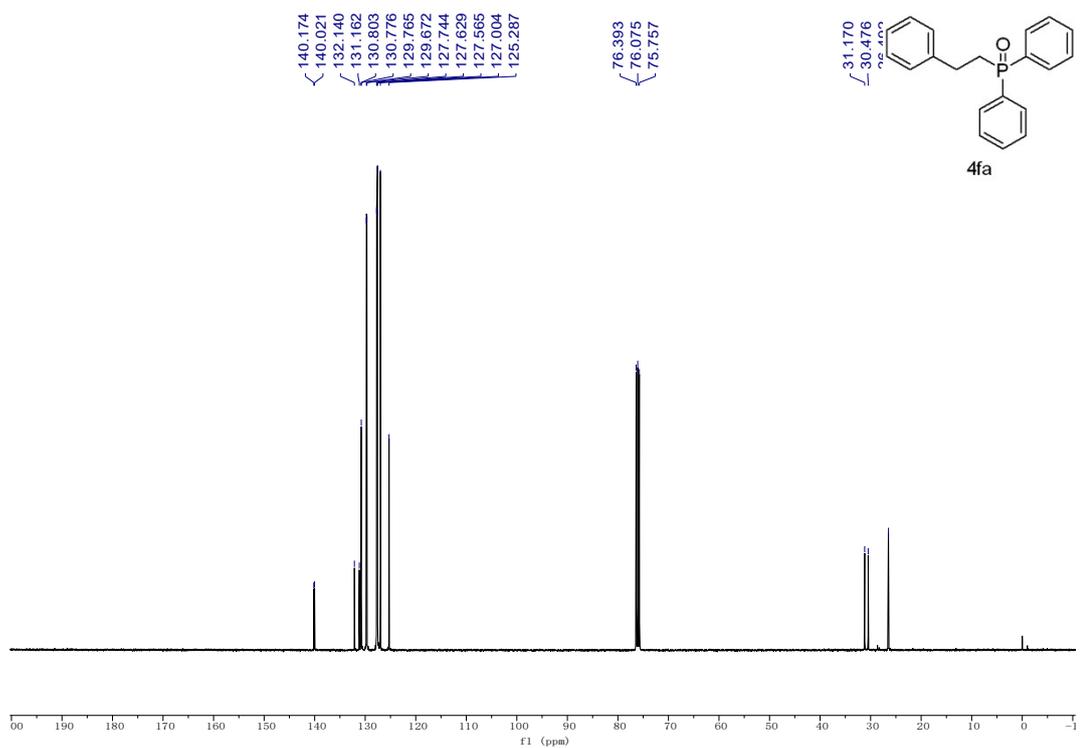


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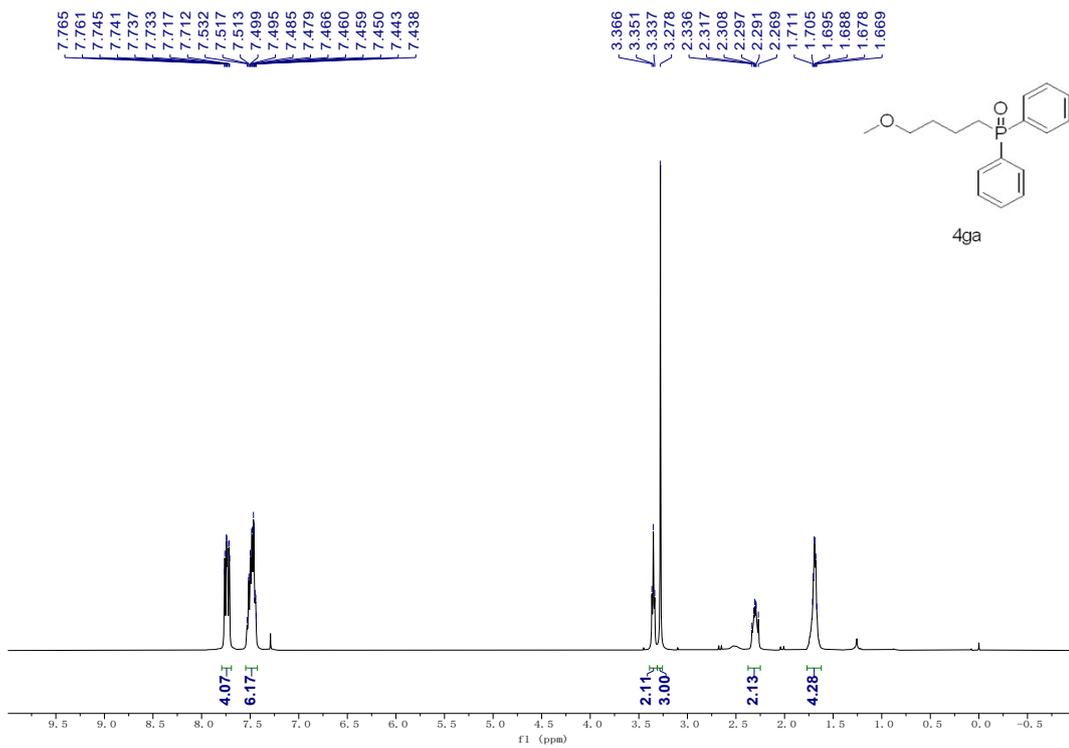
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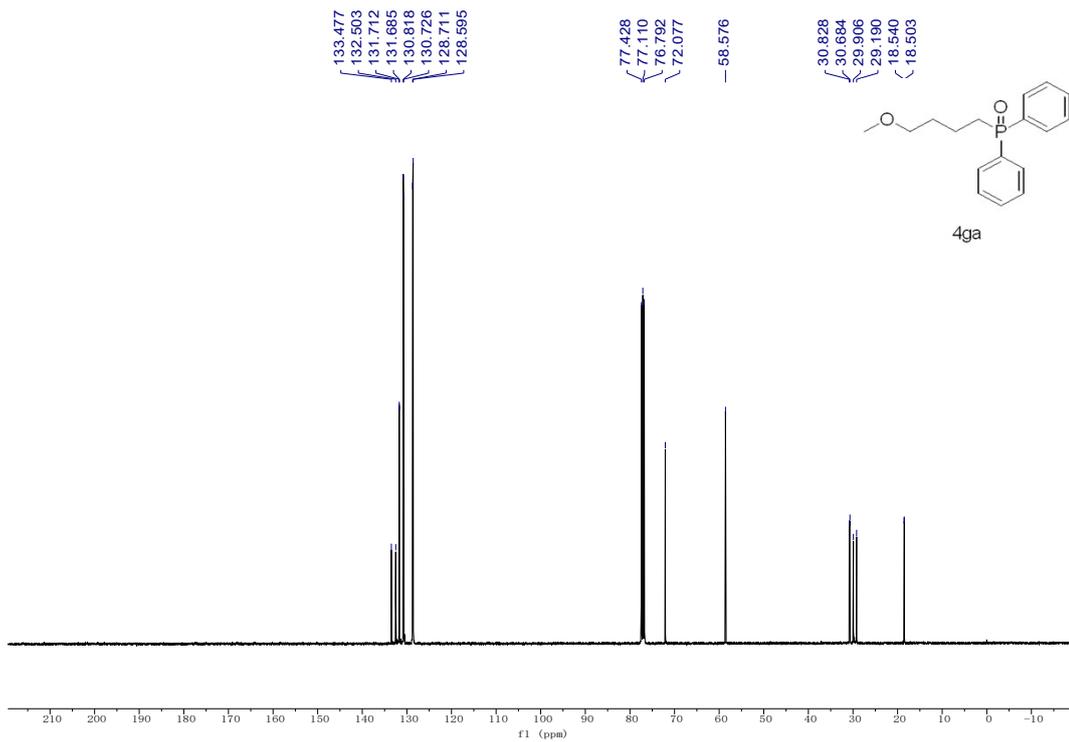
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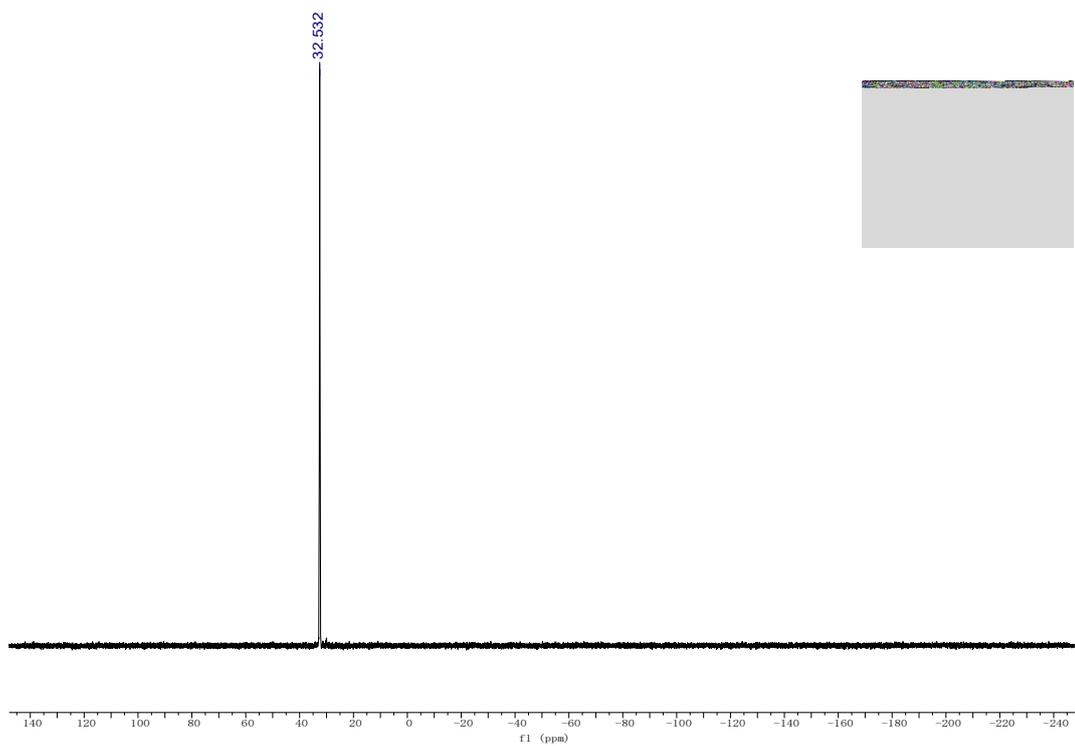
(4ga)
¹H NMR



¹³C NMR

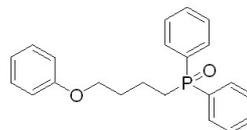
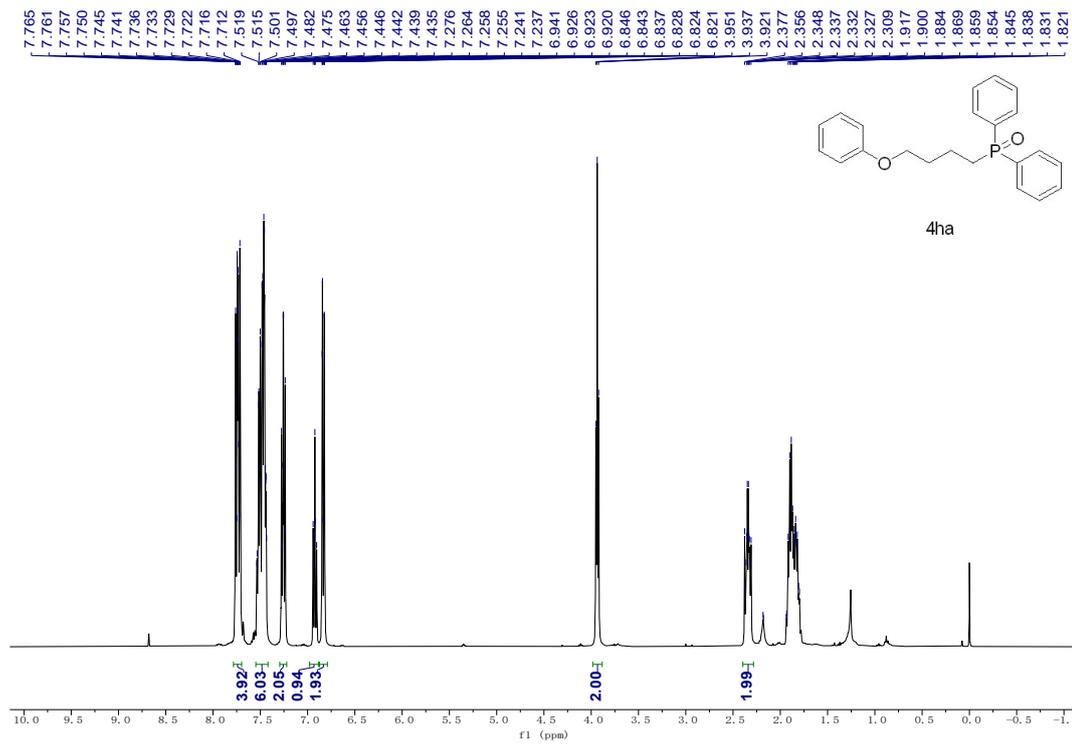


³¹P NMR



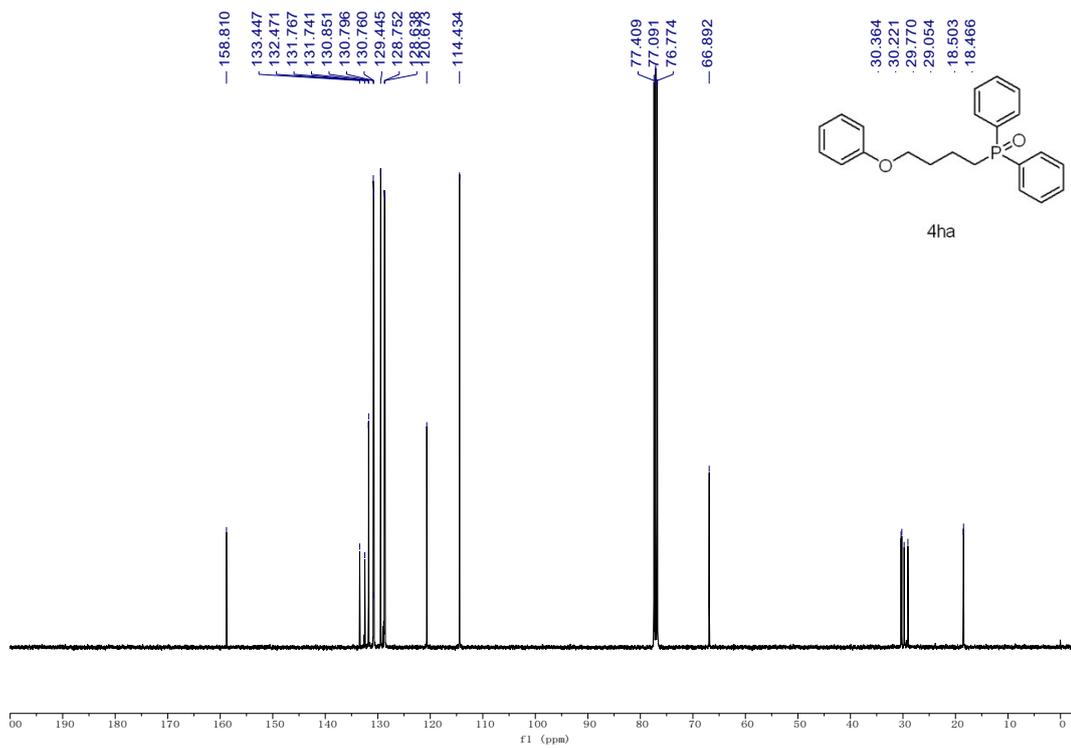
(4ha)

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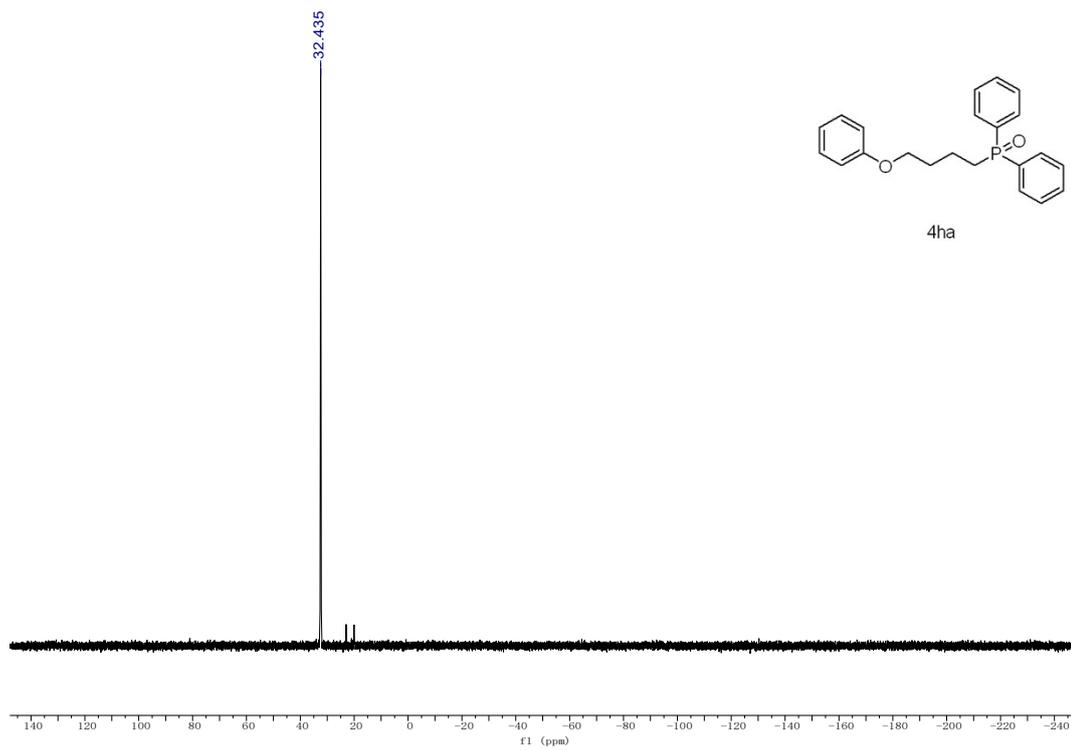


4ha

¹³C NMR

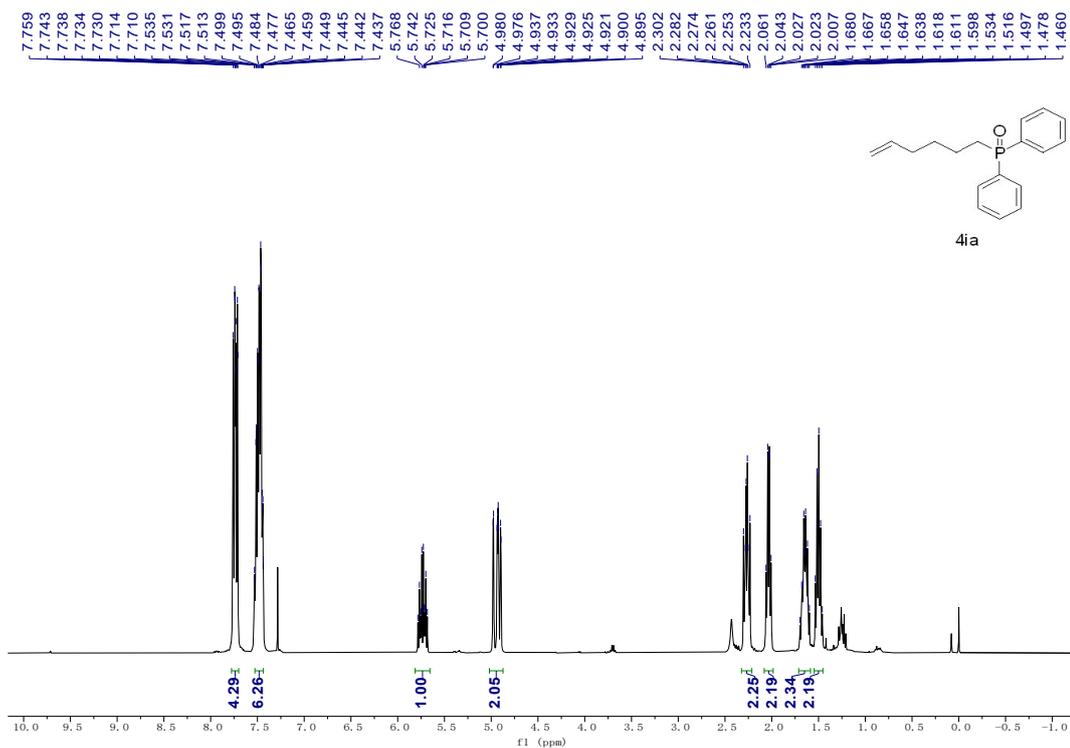


³¹P NMR

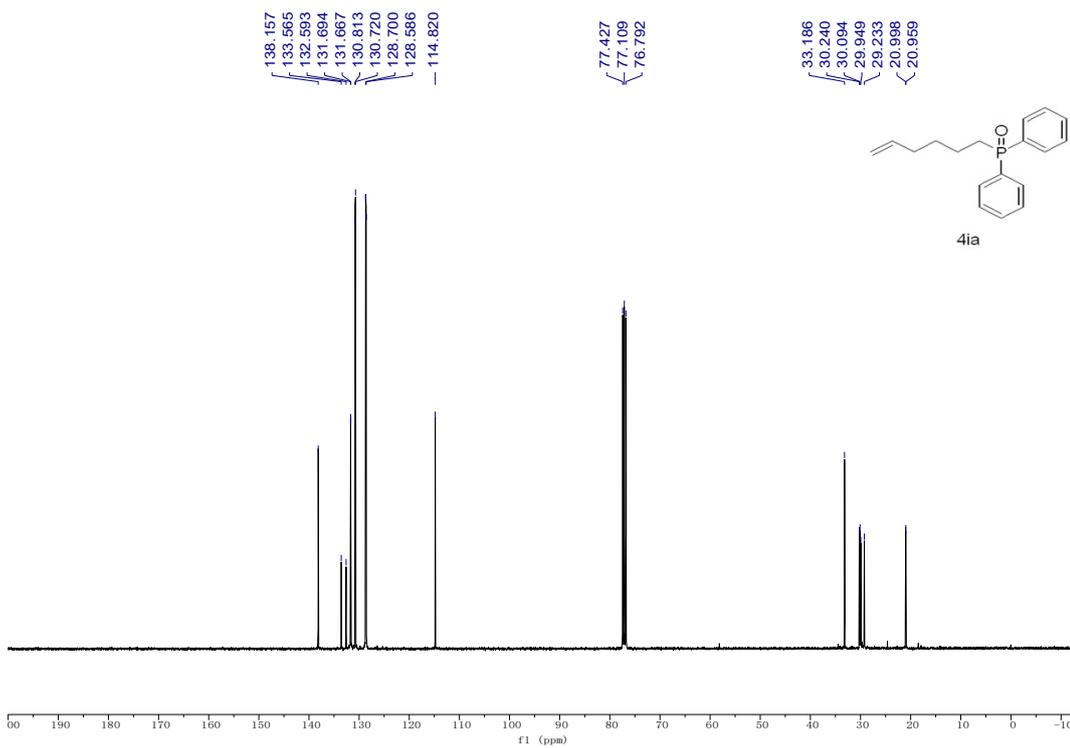


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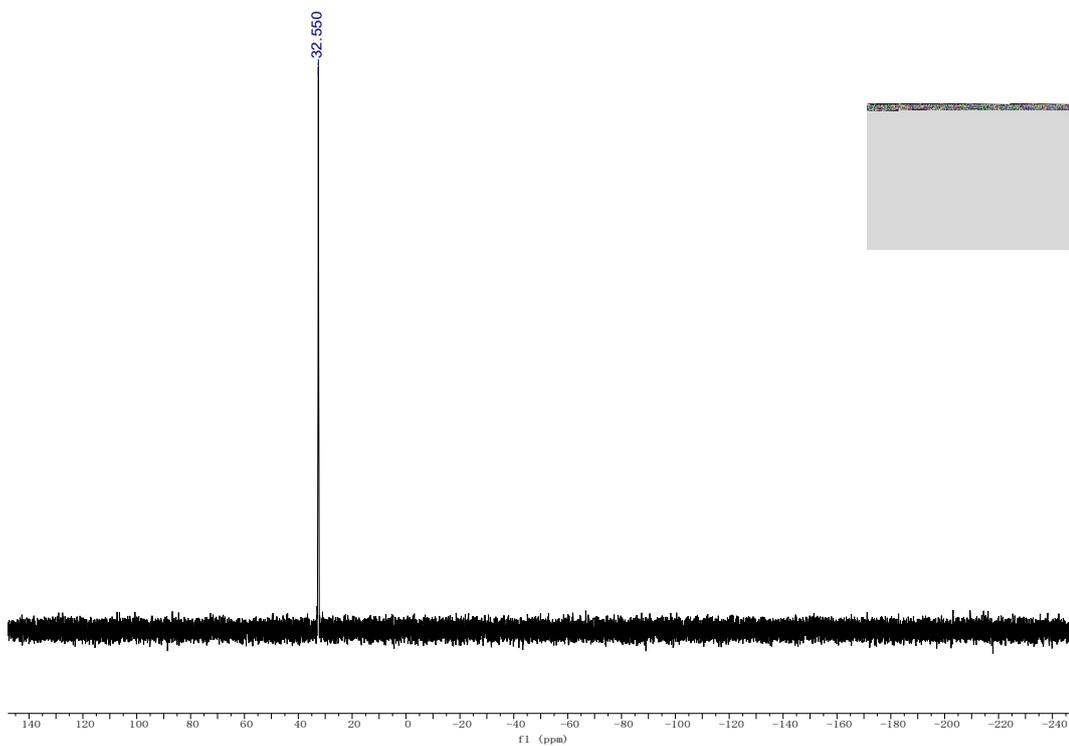
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¹³C NMR

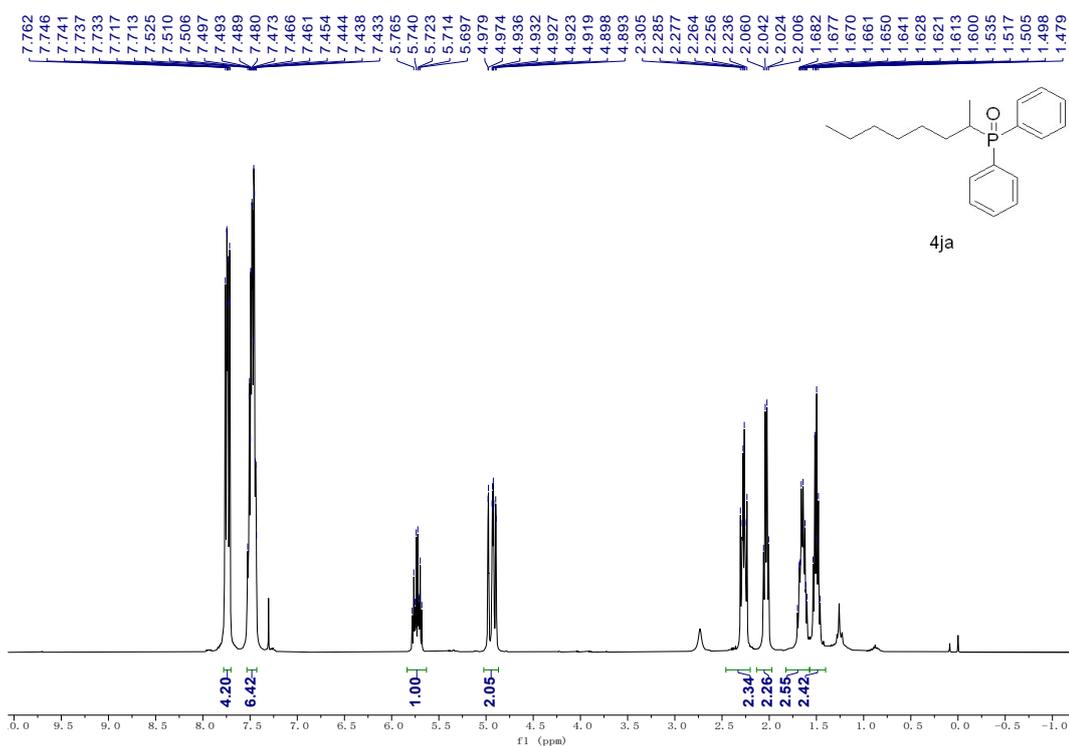


³¹P NMR

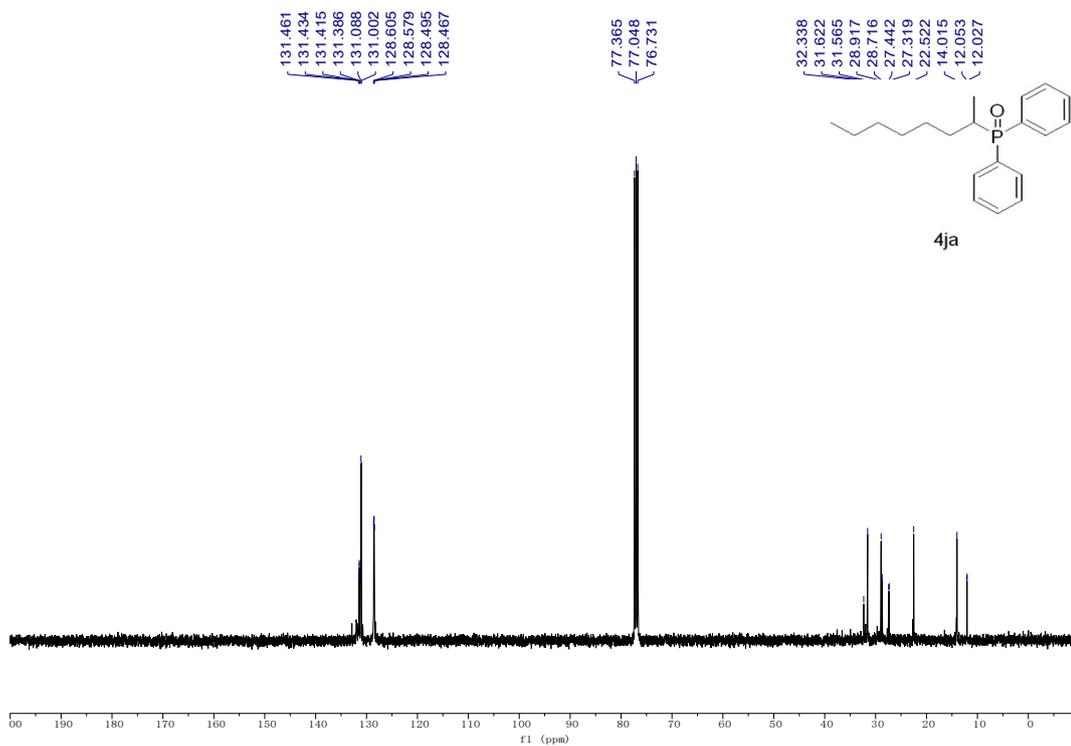


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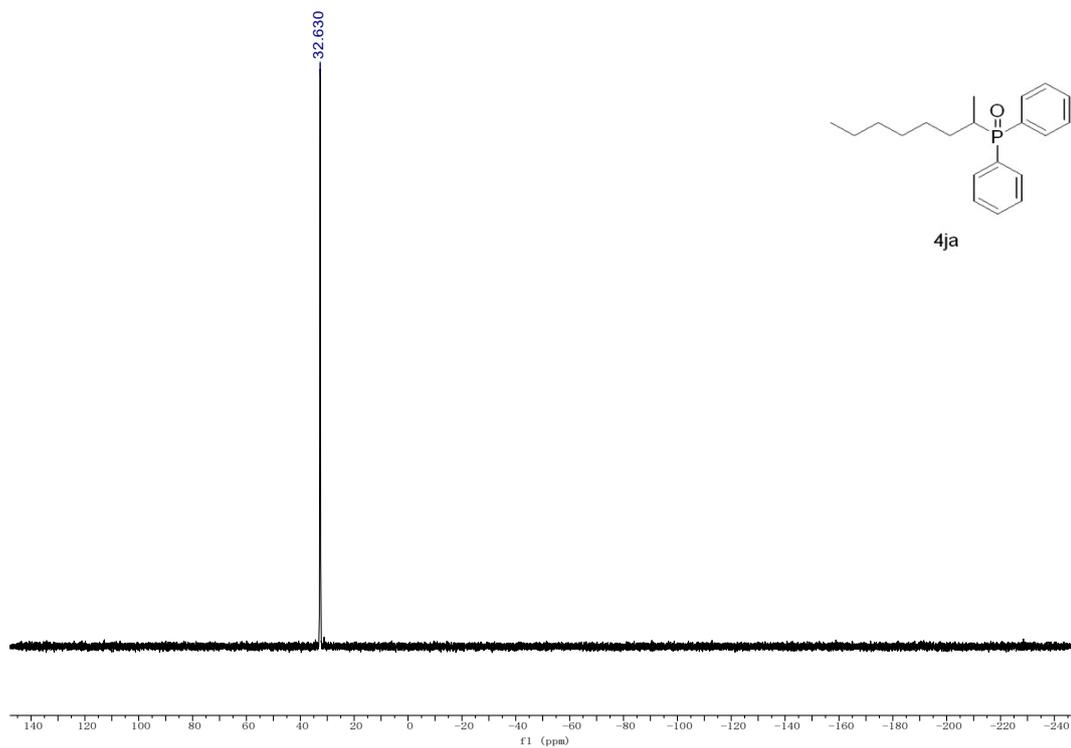
¹H NMR



¹³C NMR

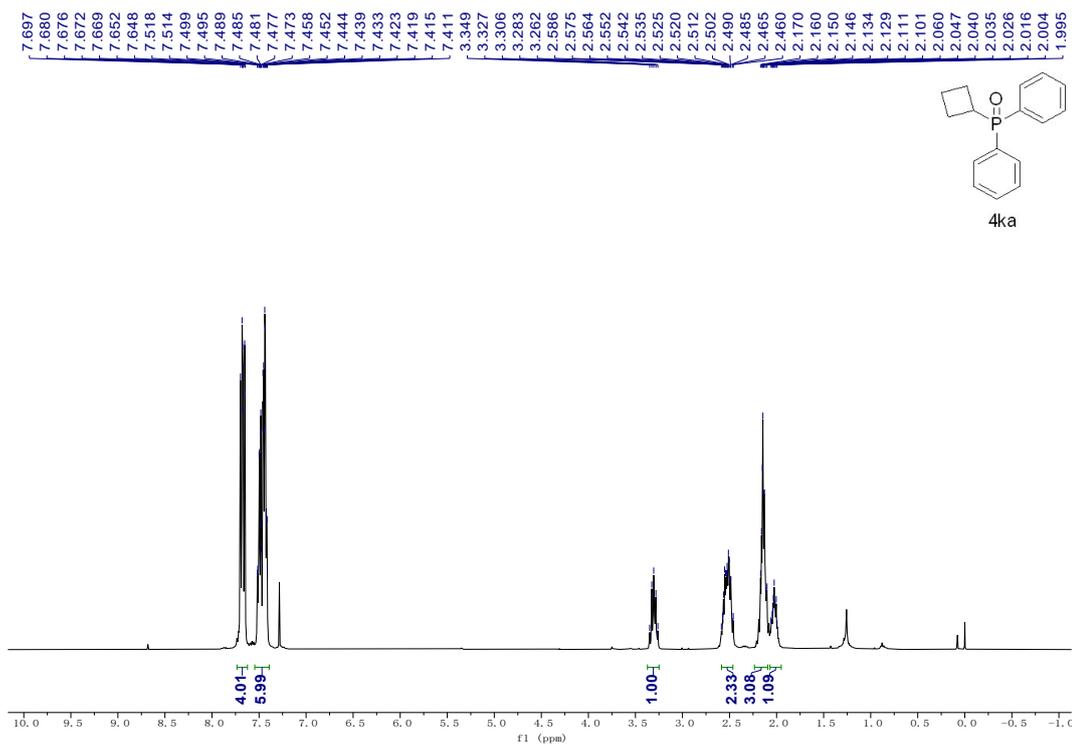


³¹P NMR

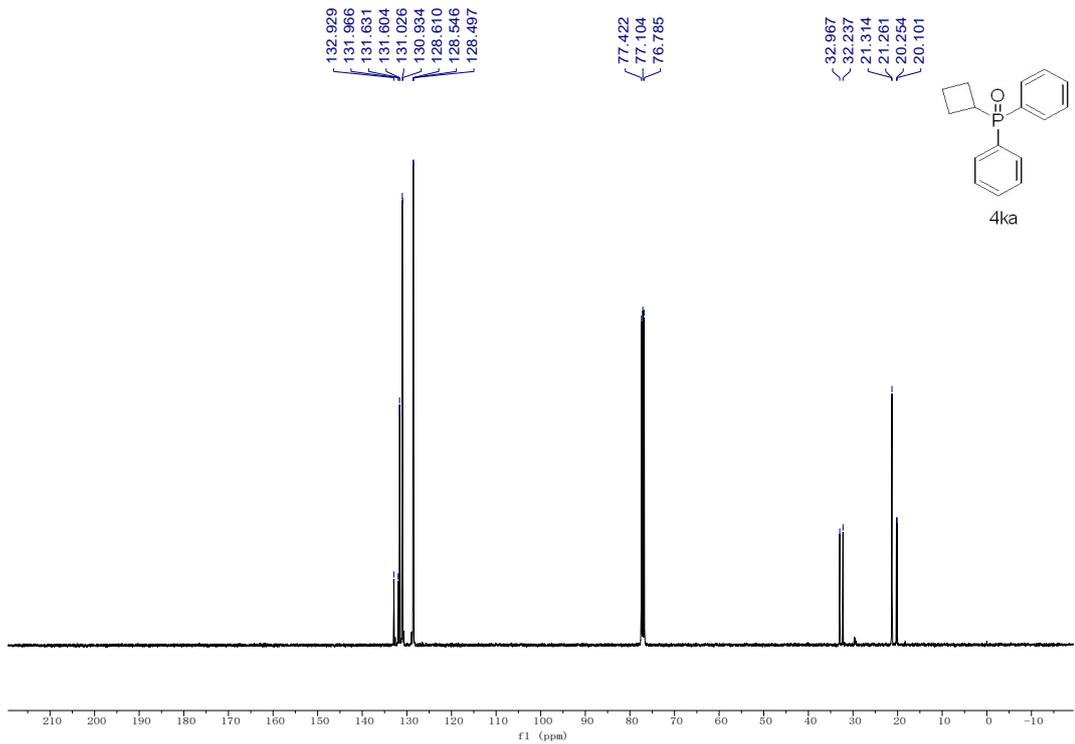


(4ka)

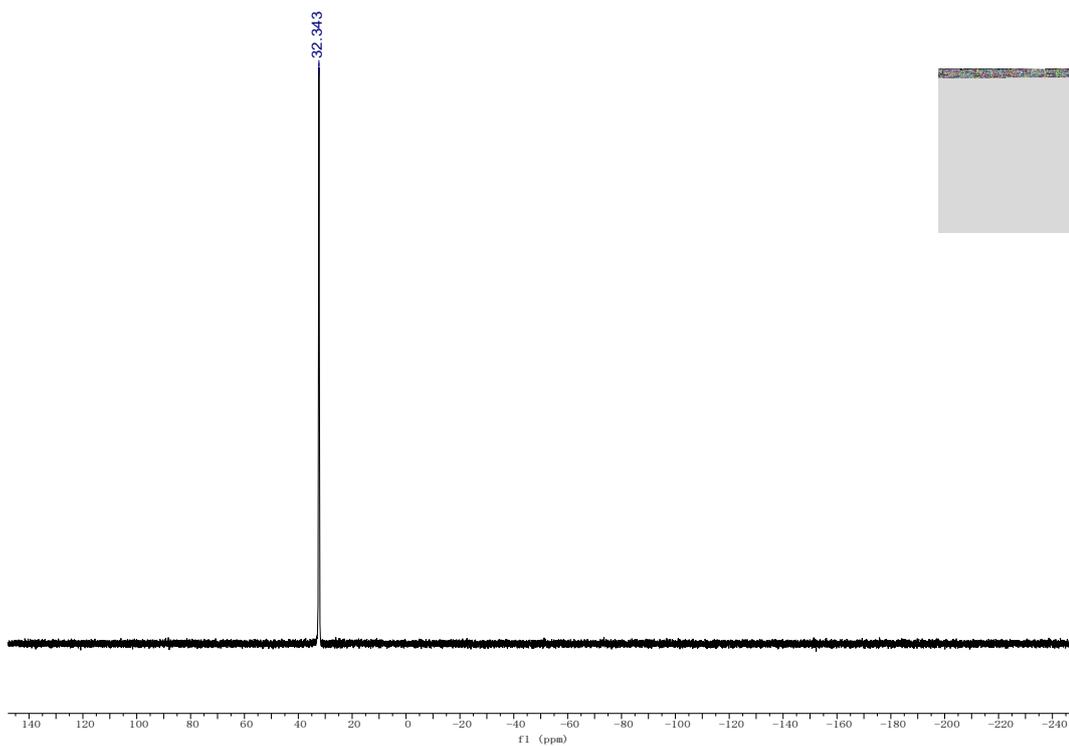
¹H NMR



¹³C NMR

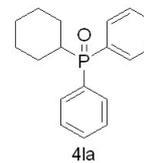
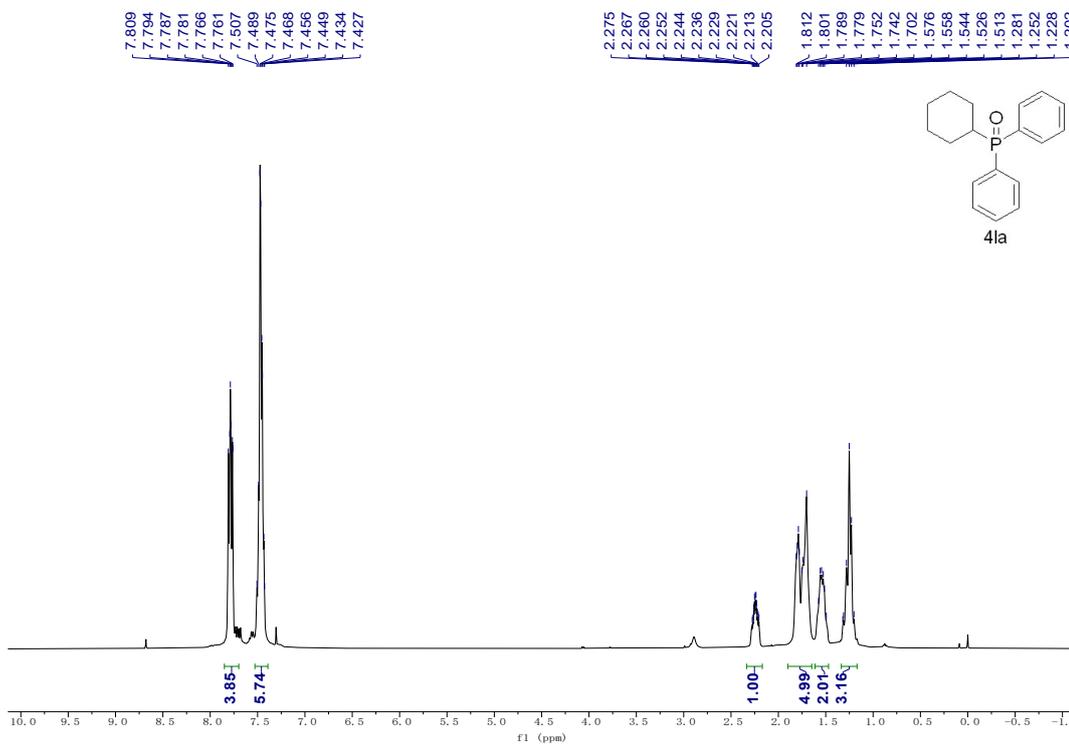


³¹P NMR

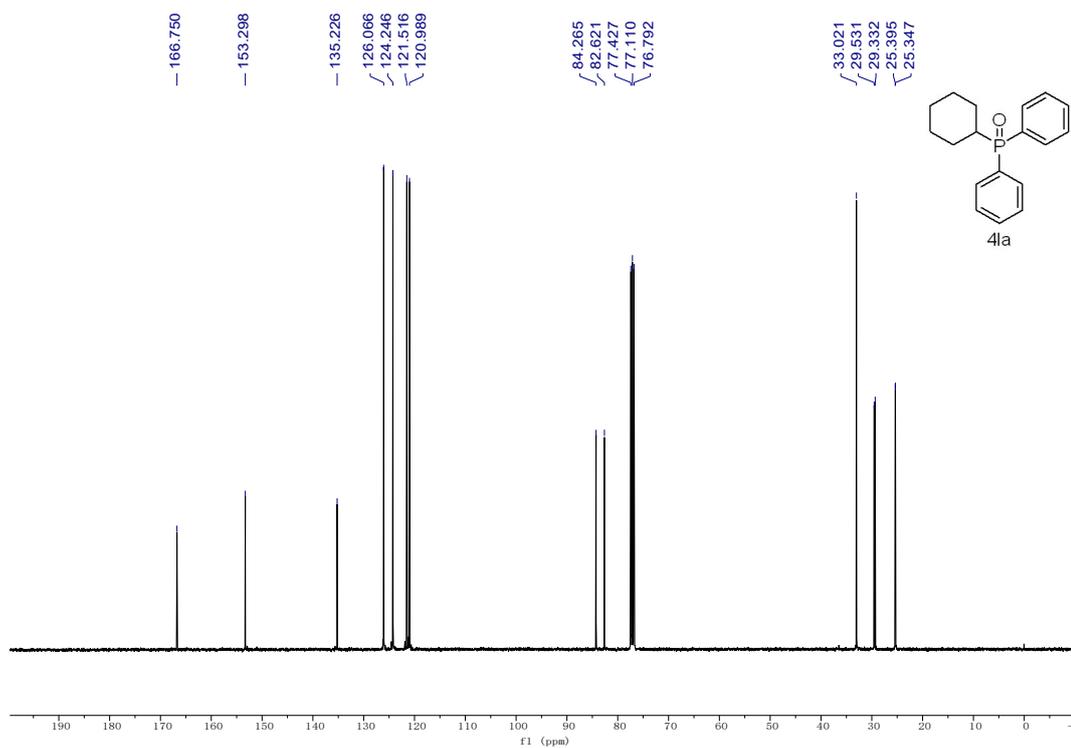


(41a)

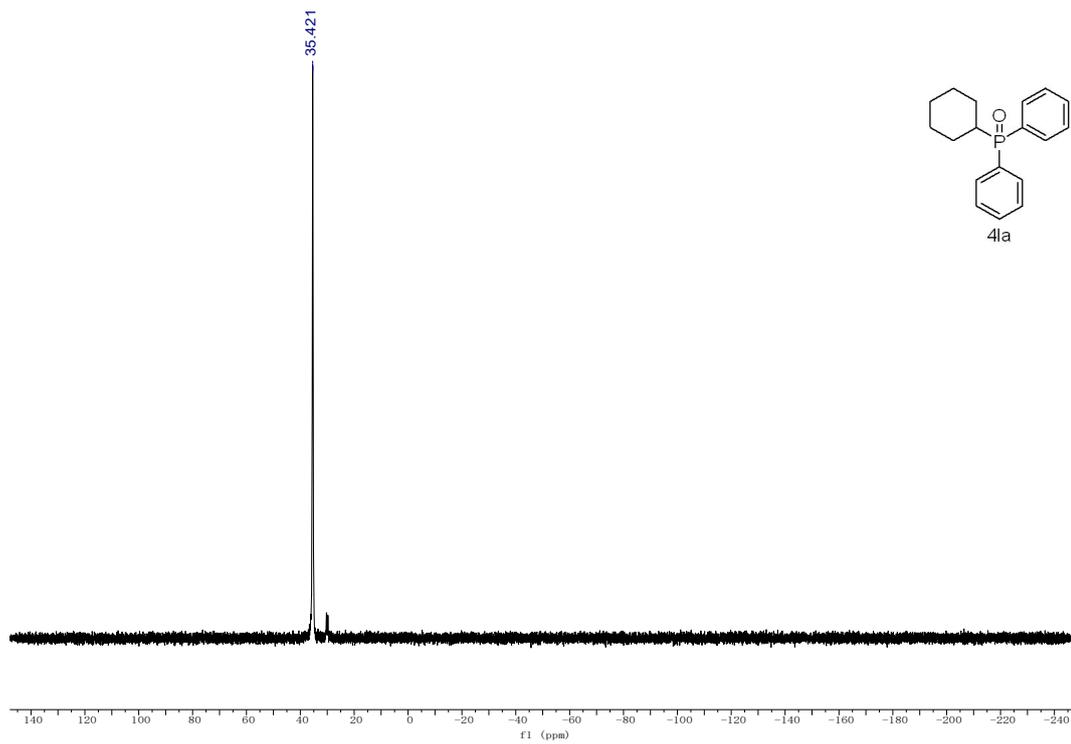
¹H NMR



¹³C NMR

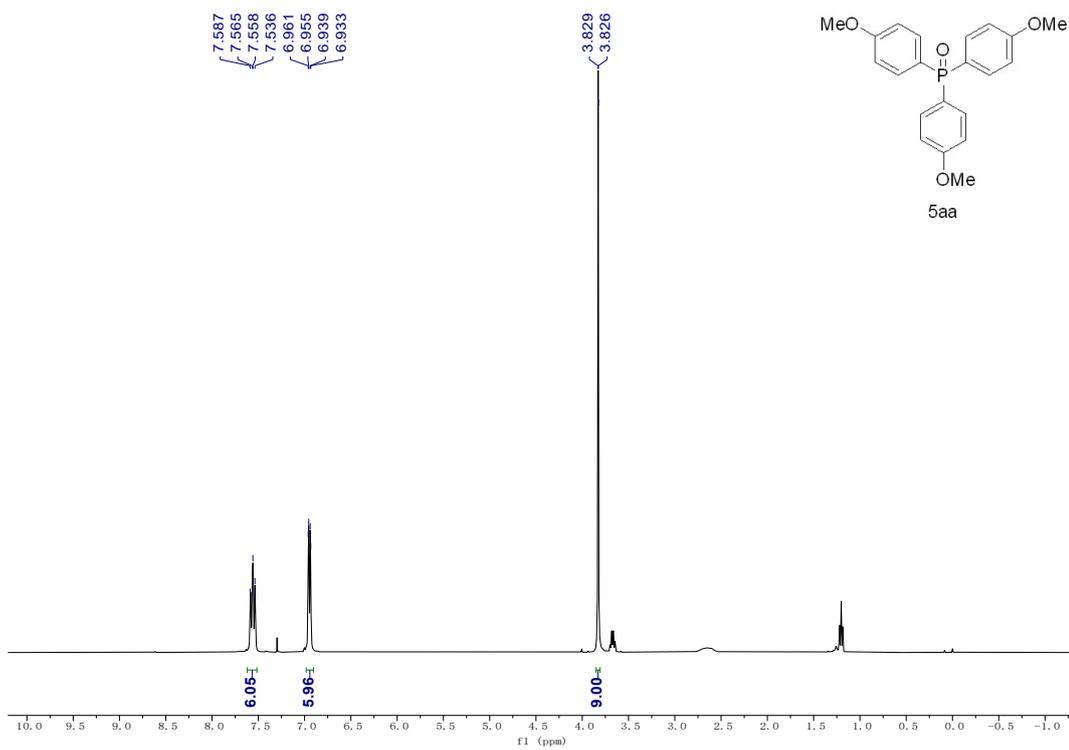


³¹P NMR

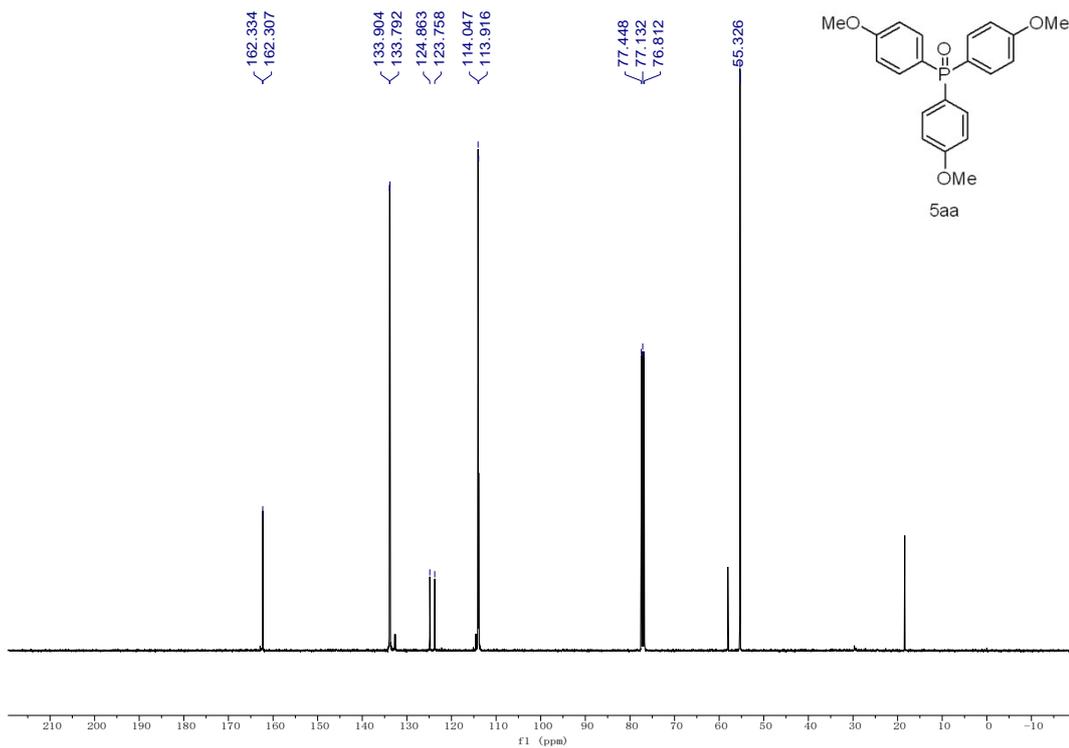


(5aa)

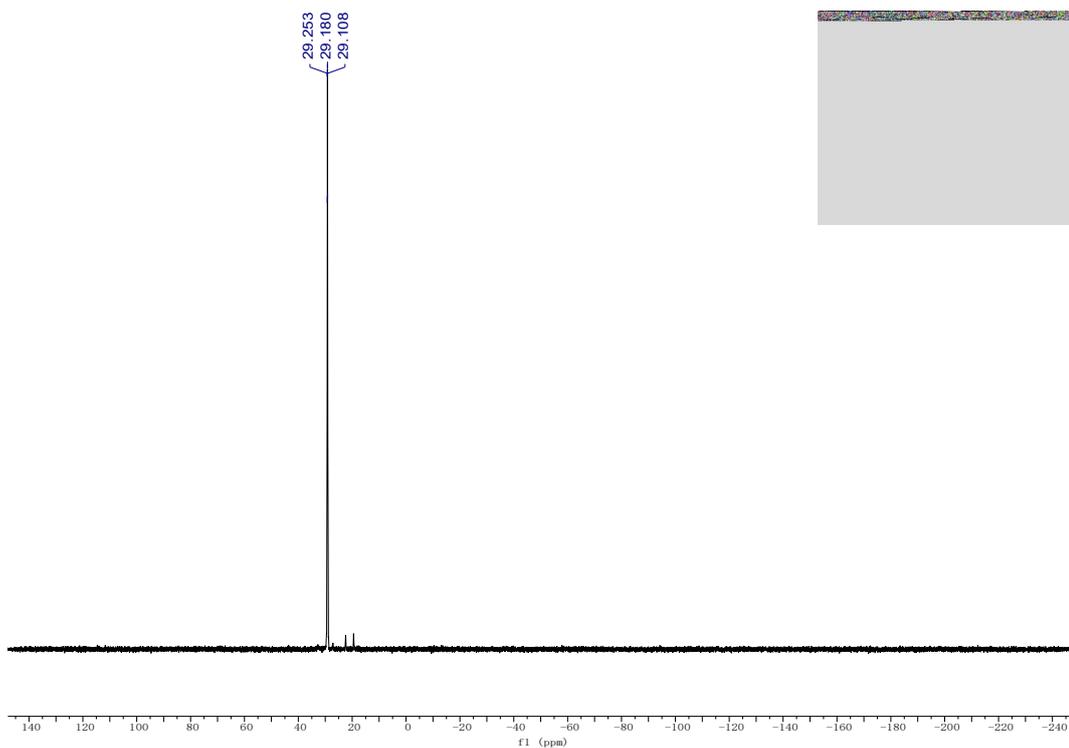
¹H NMR



¹³C NMR

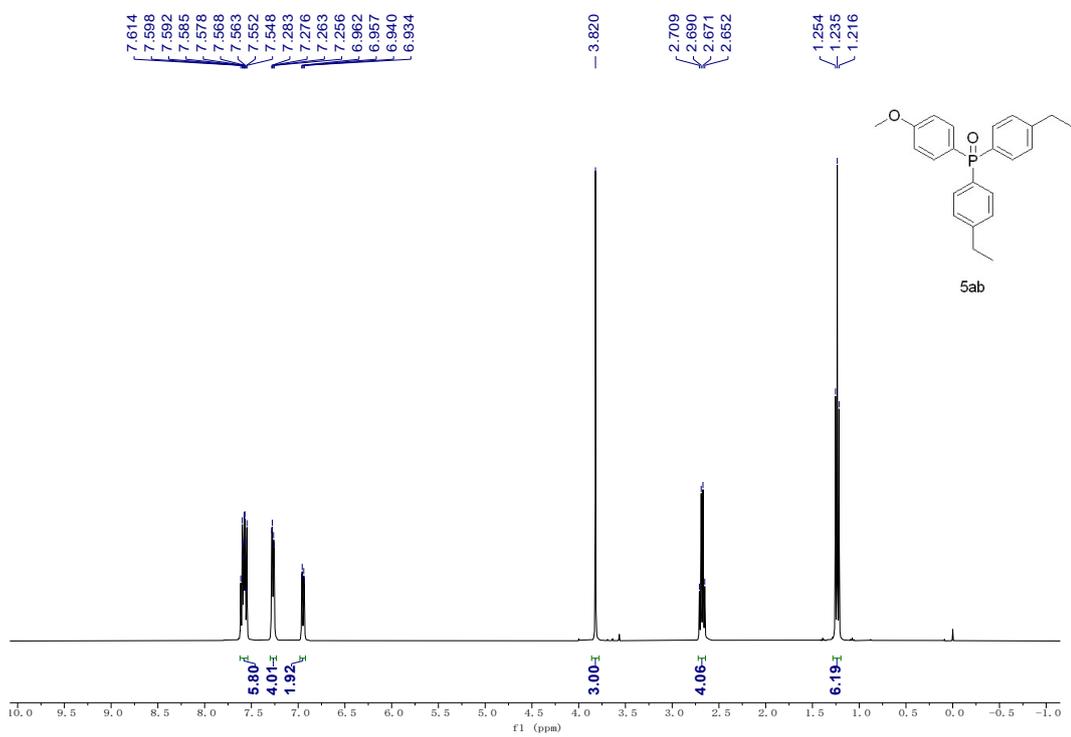


³¹P NMR

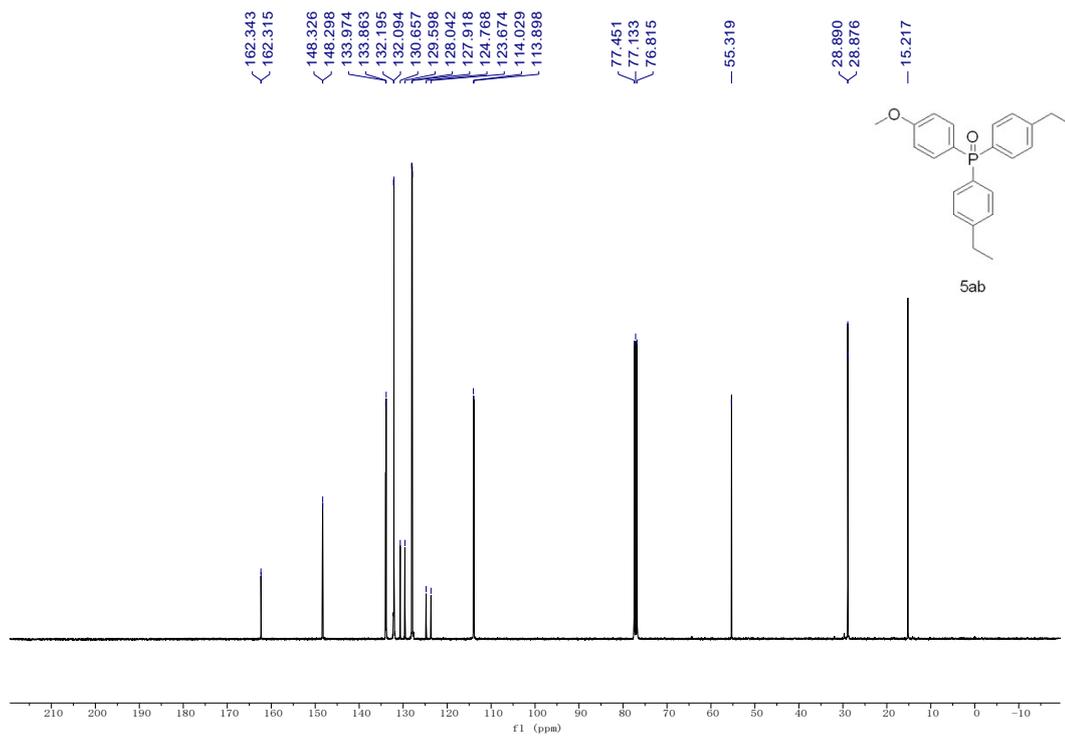


(5ab)

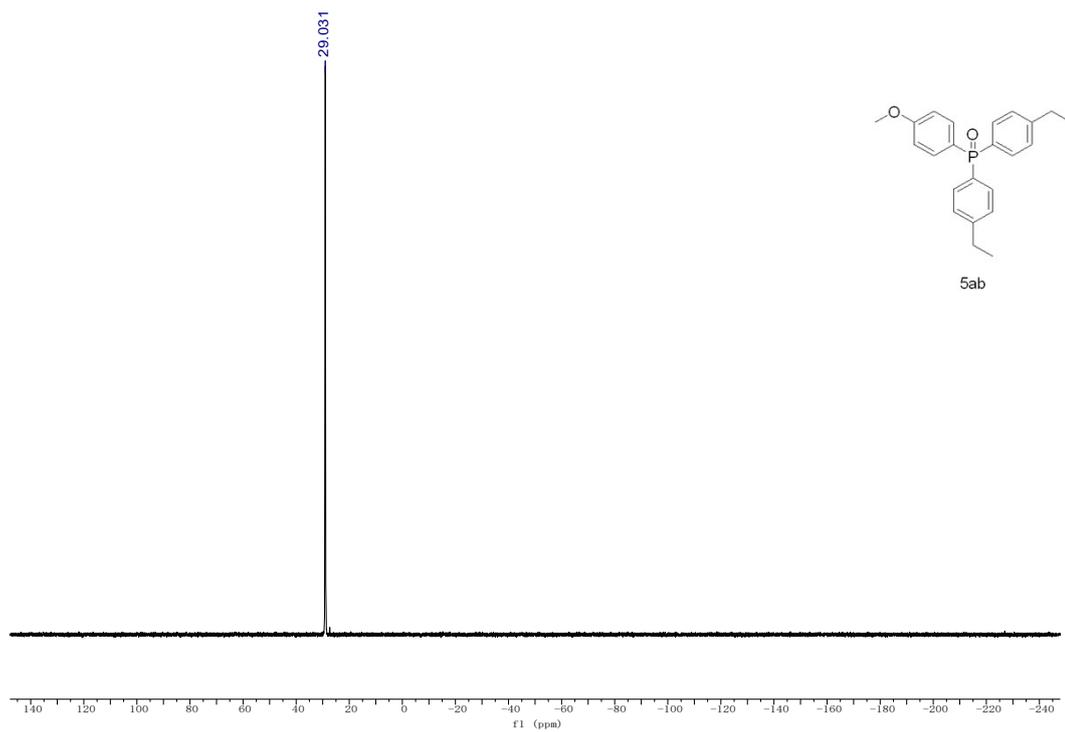
¹H NMR



¹³C NMR

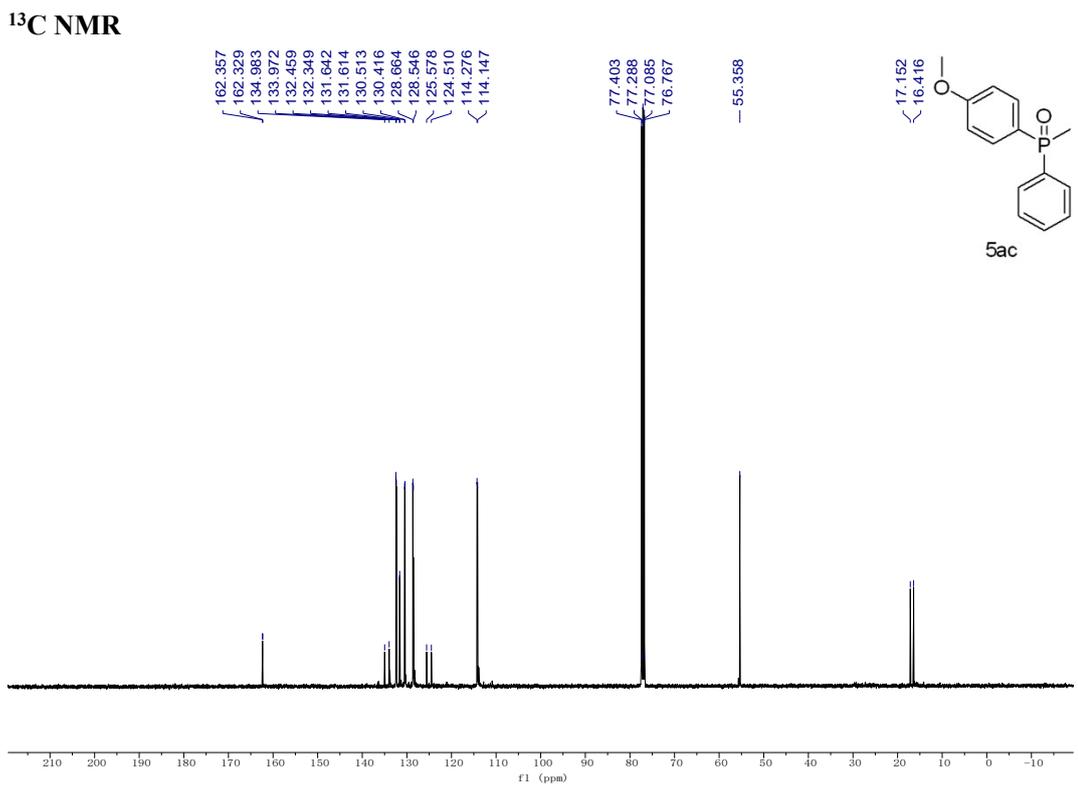
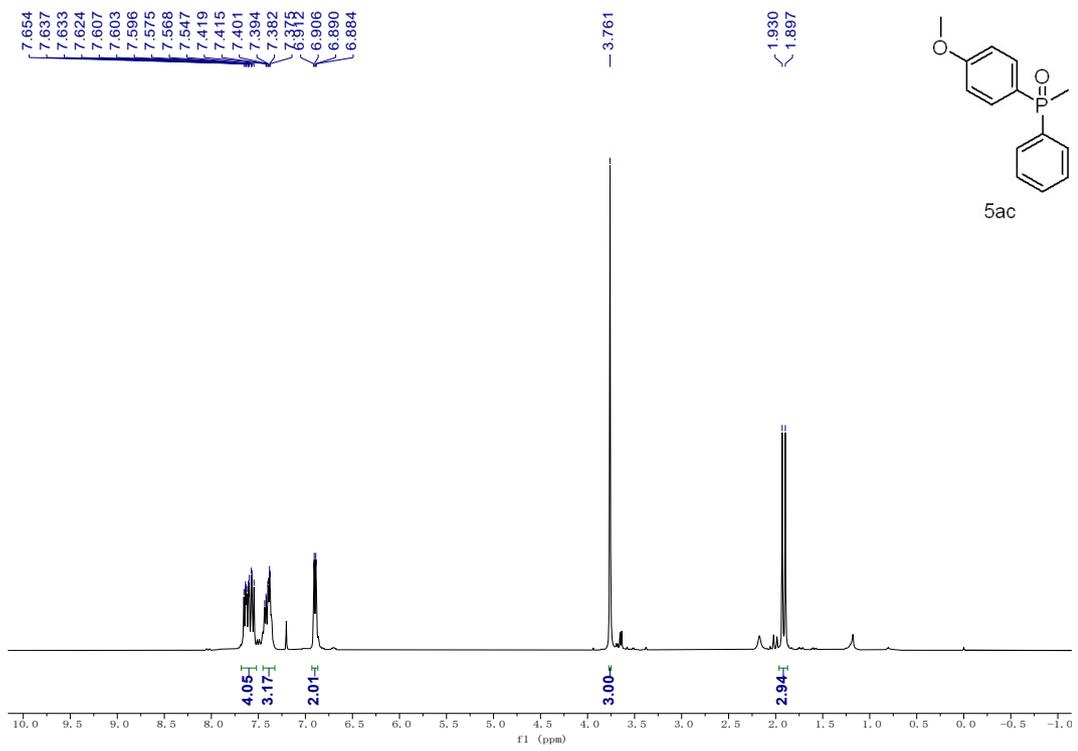


³¹P NMR

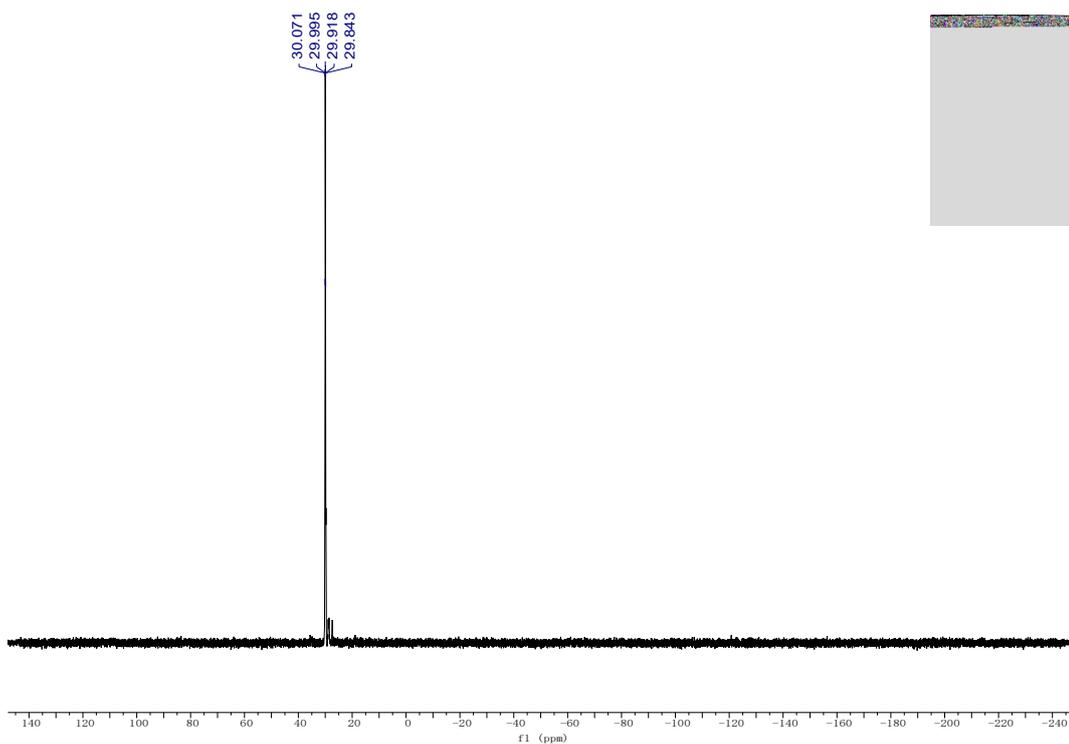


(5ac)

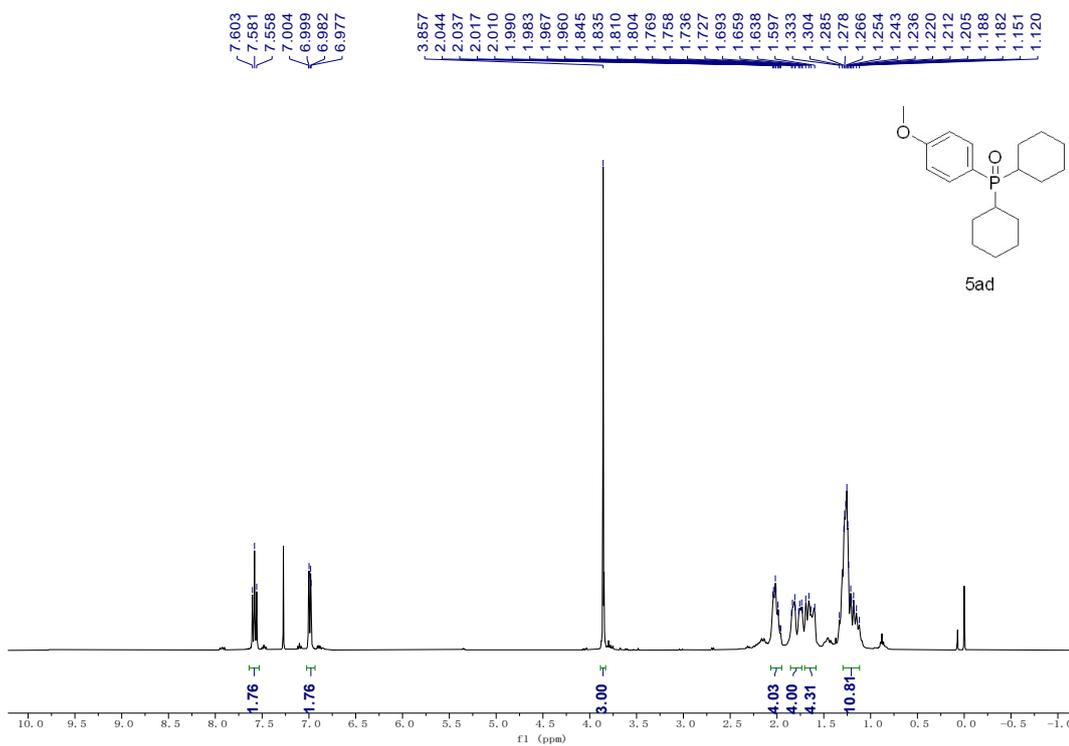
¹H NMR



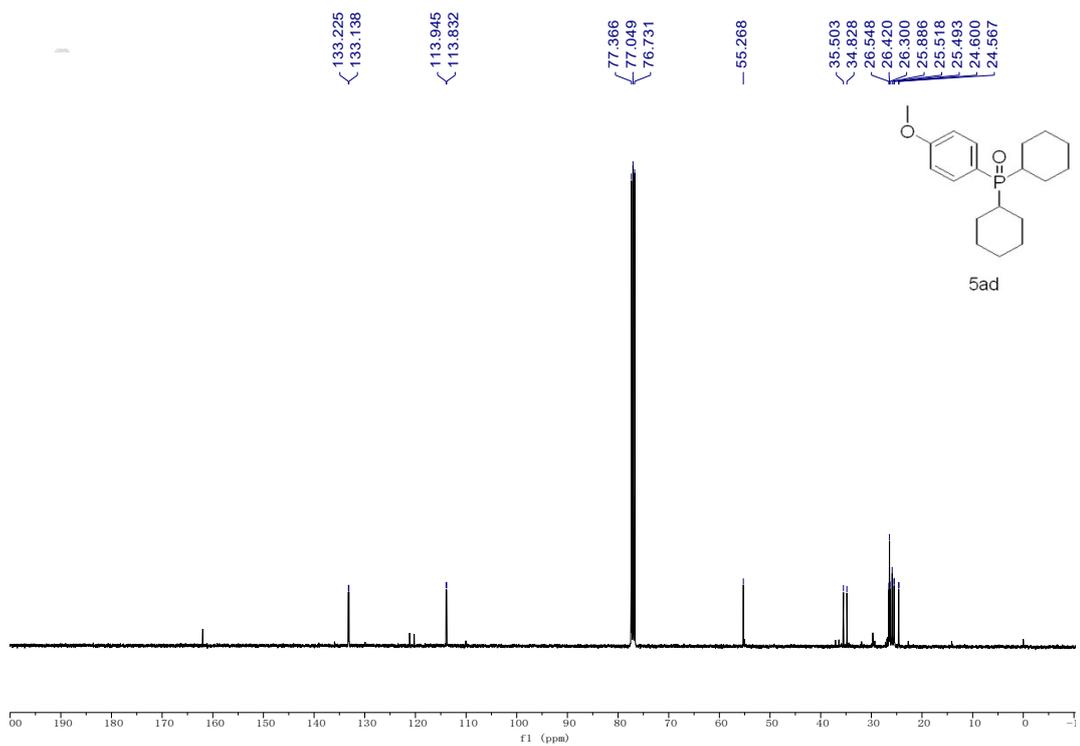
³¹P NMR



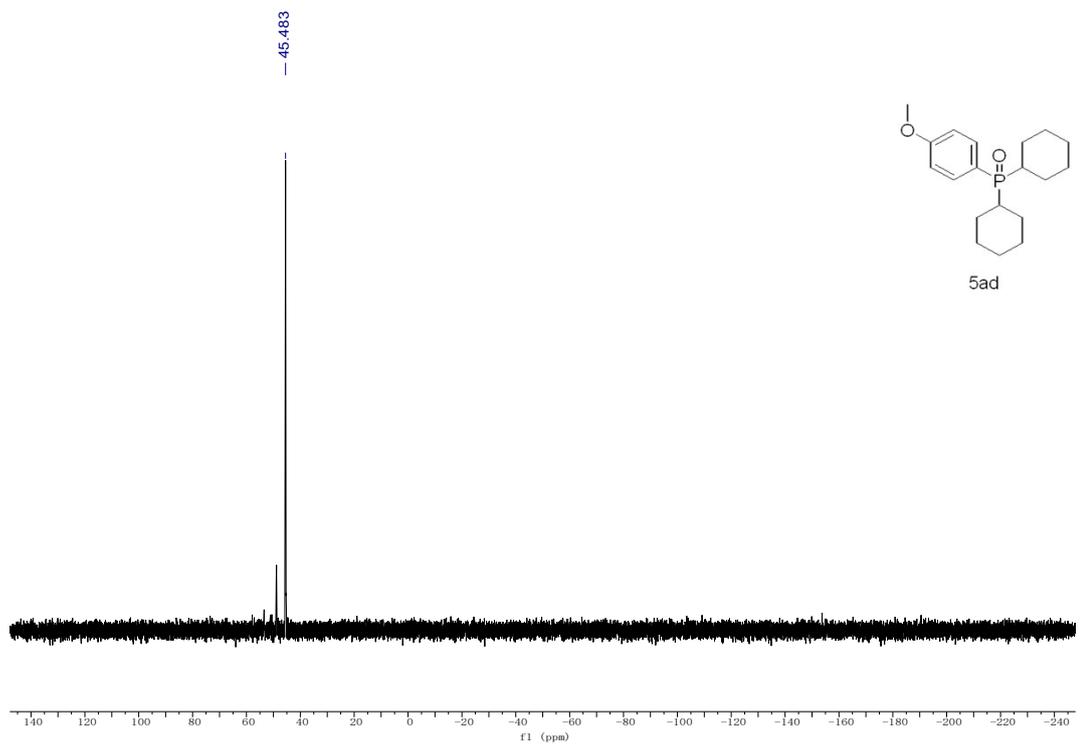
(5ad)
¹H NMR



¹³C NMR

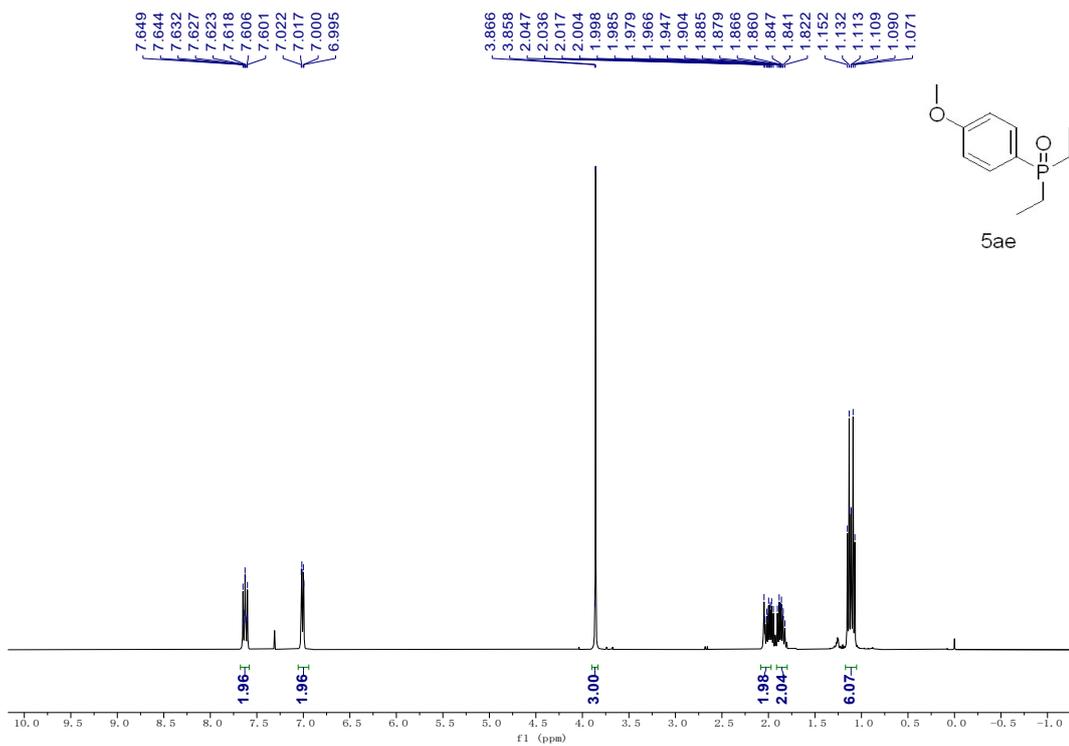


³¹P NMR

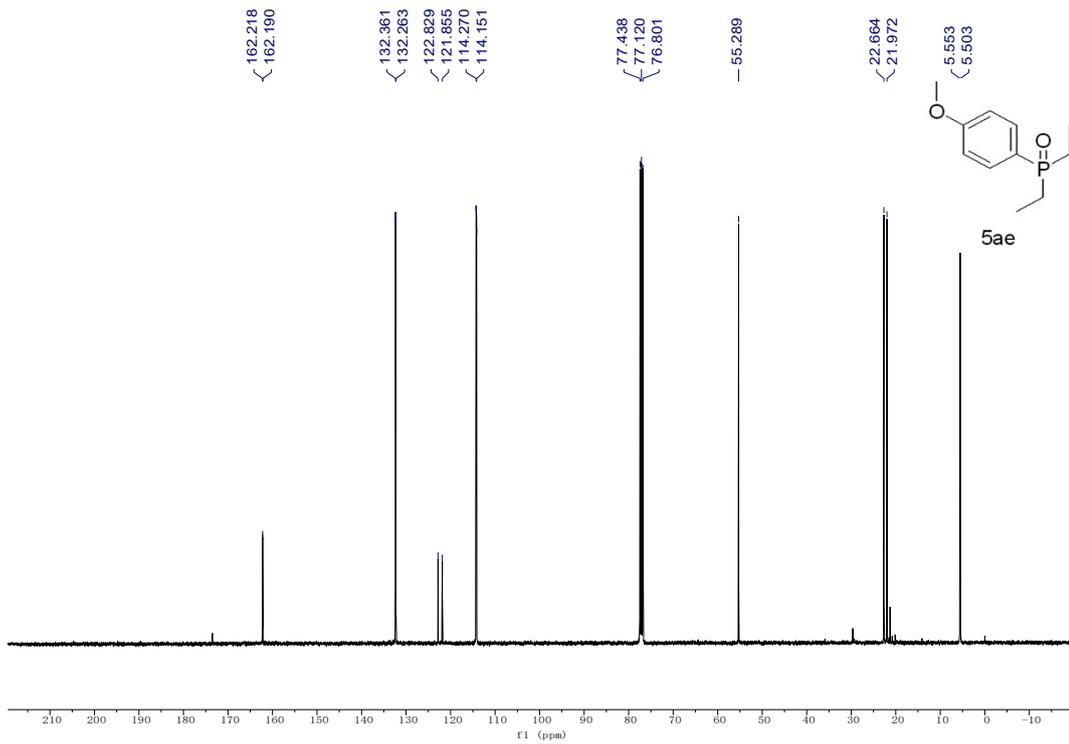


(5ae)

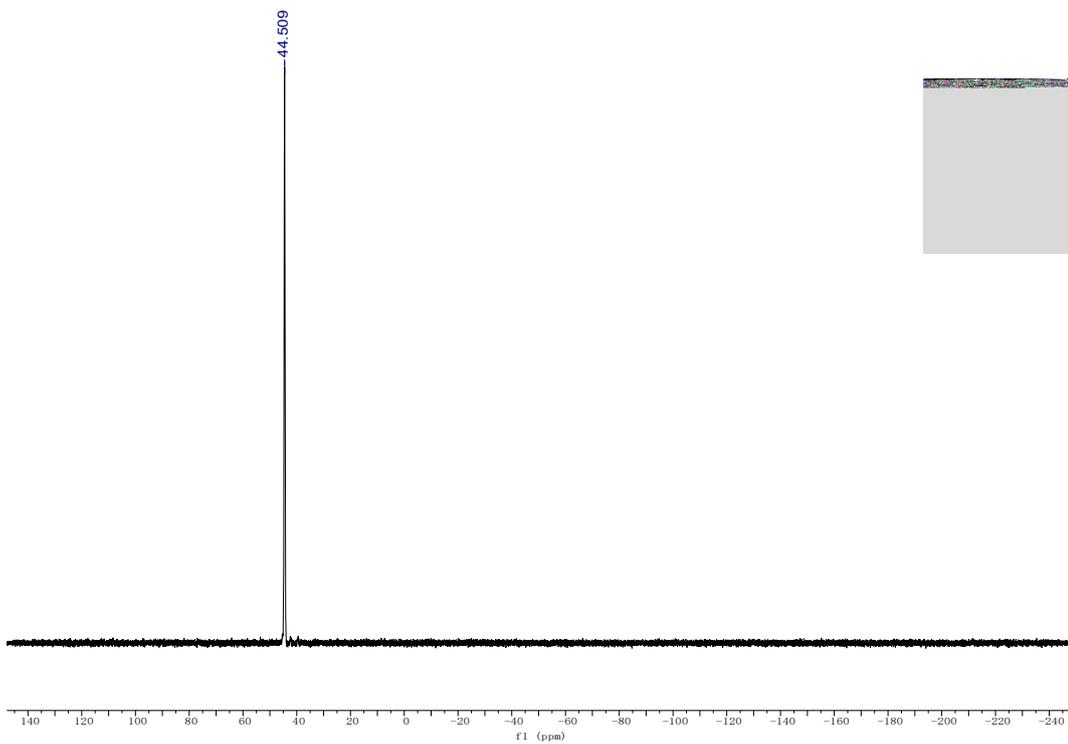
¹H NMR



¹³C NMR

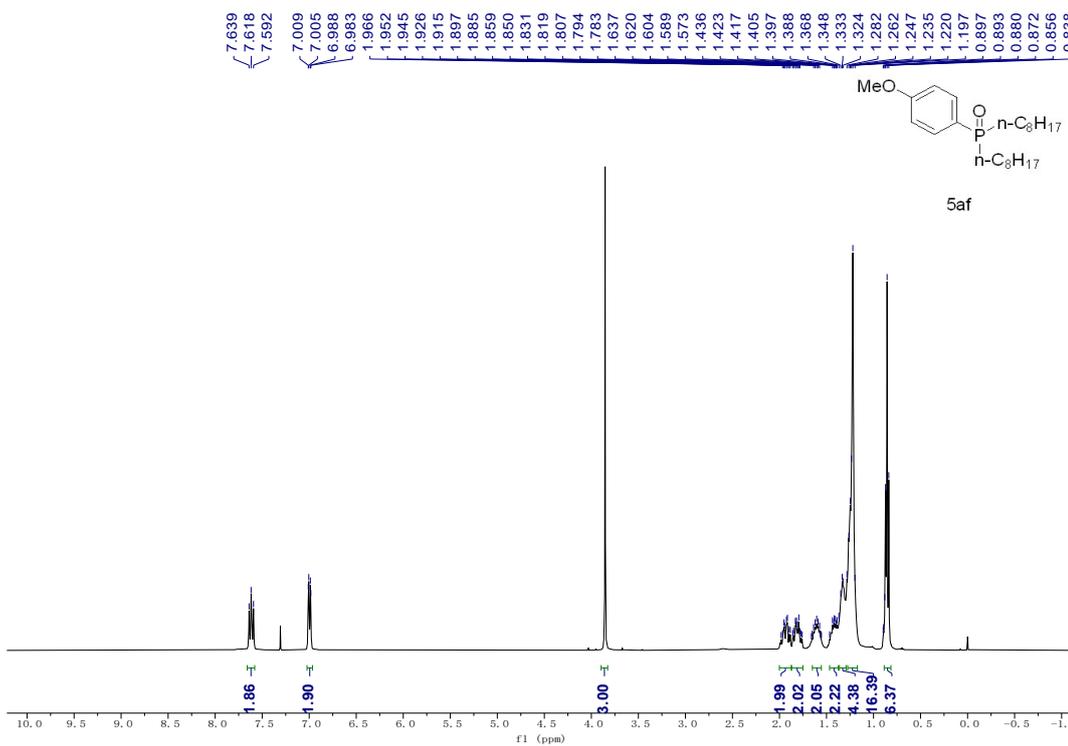


³¹P NMR

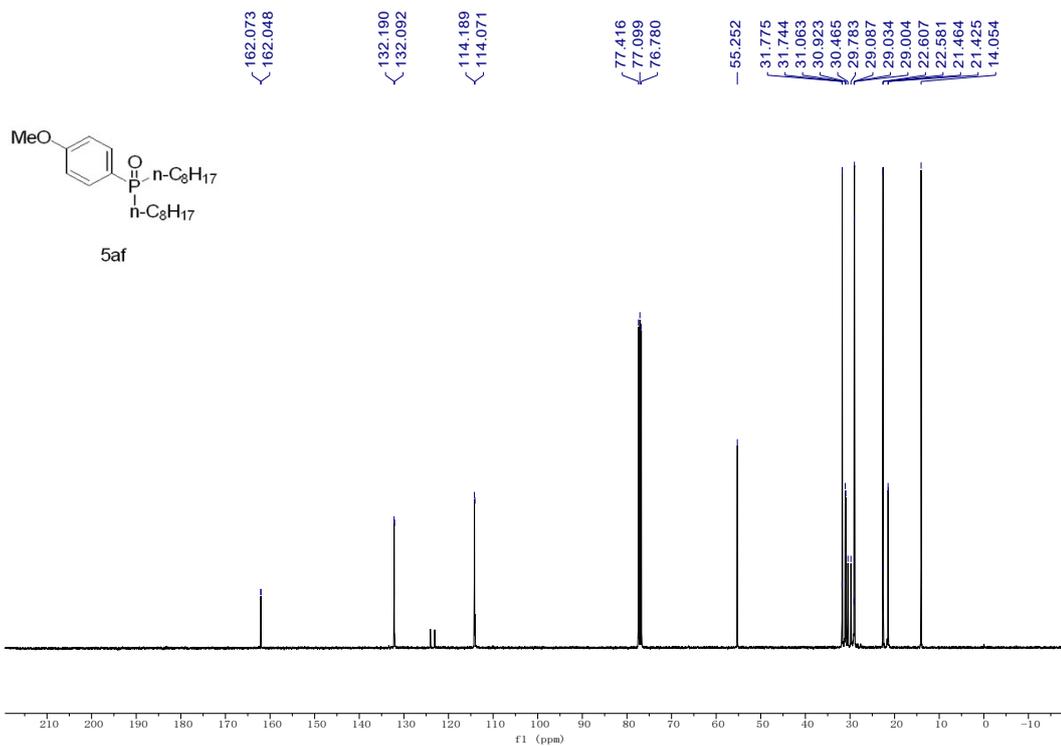


(5af)

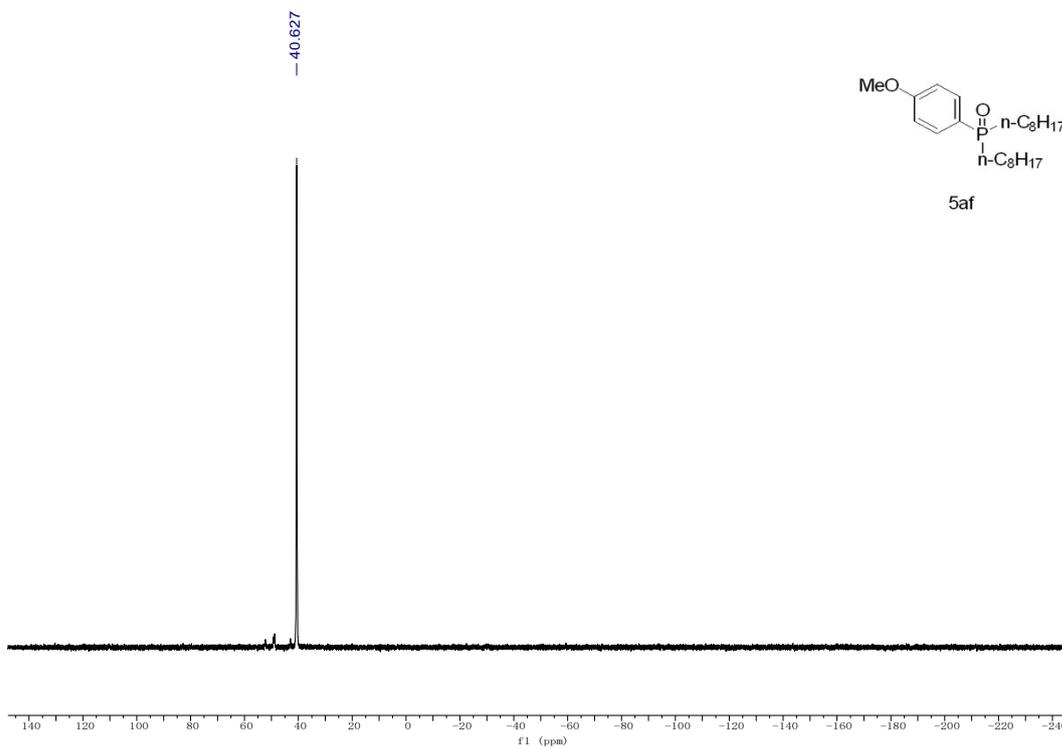
¹H NMR



¹³C NMR

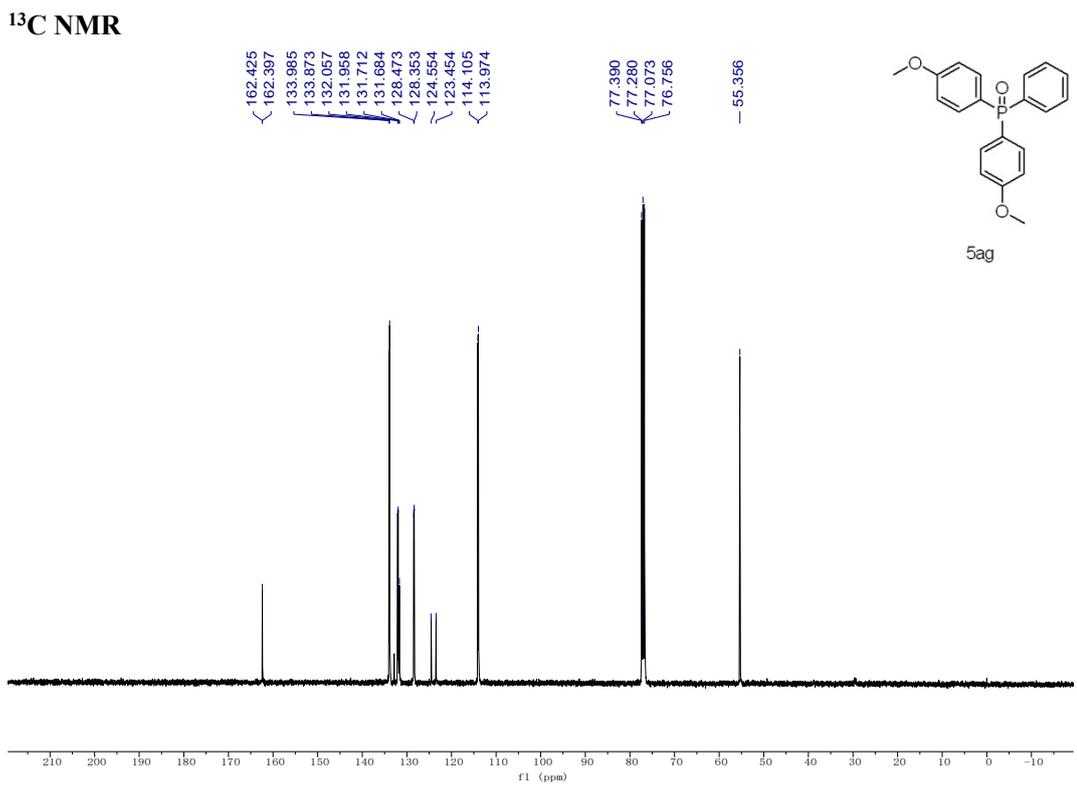
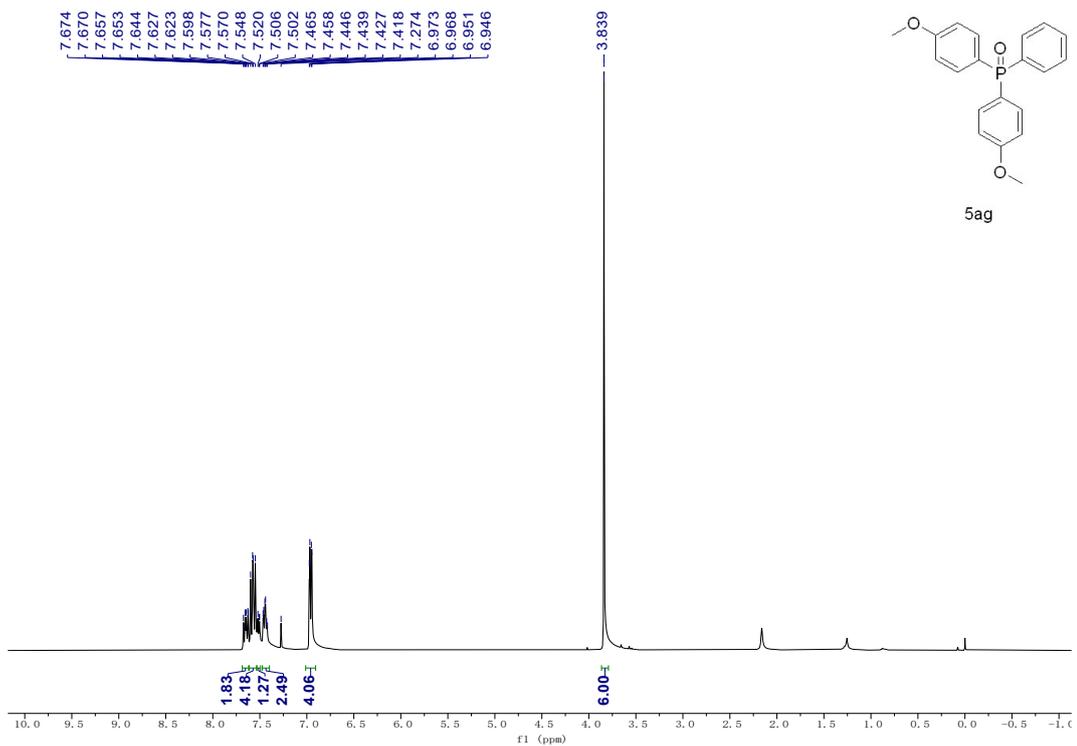


³¹P NMR

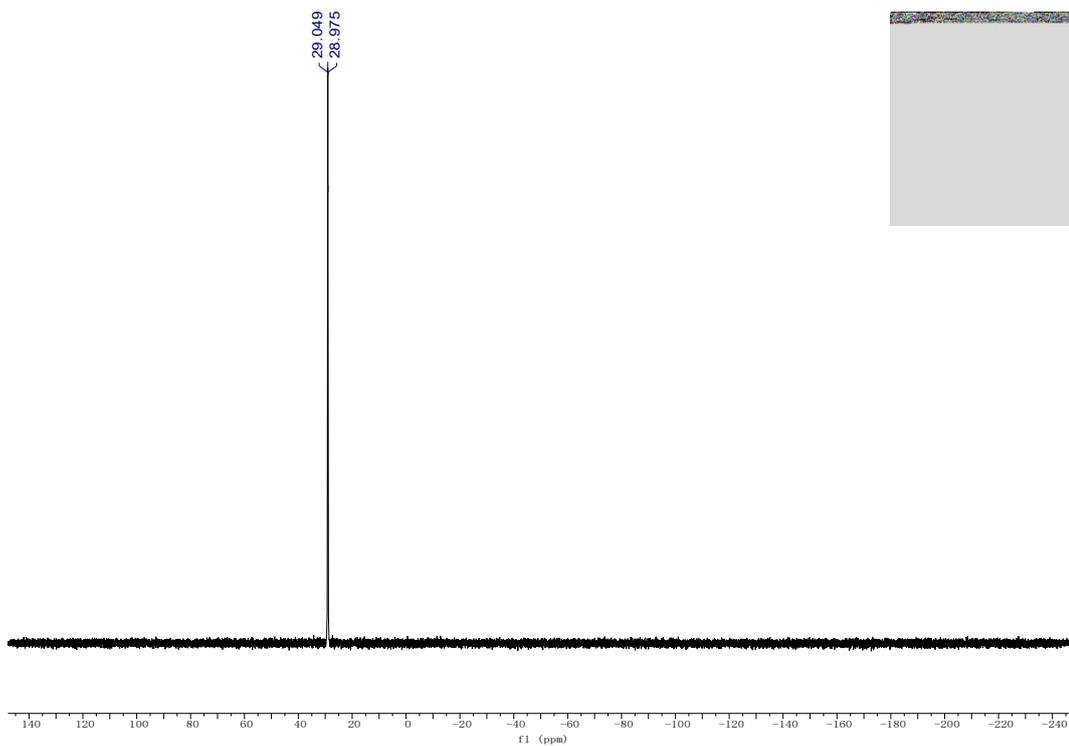


(5ag)

¹H NMR

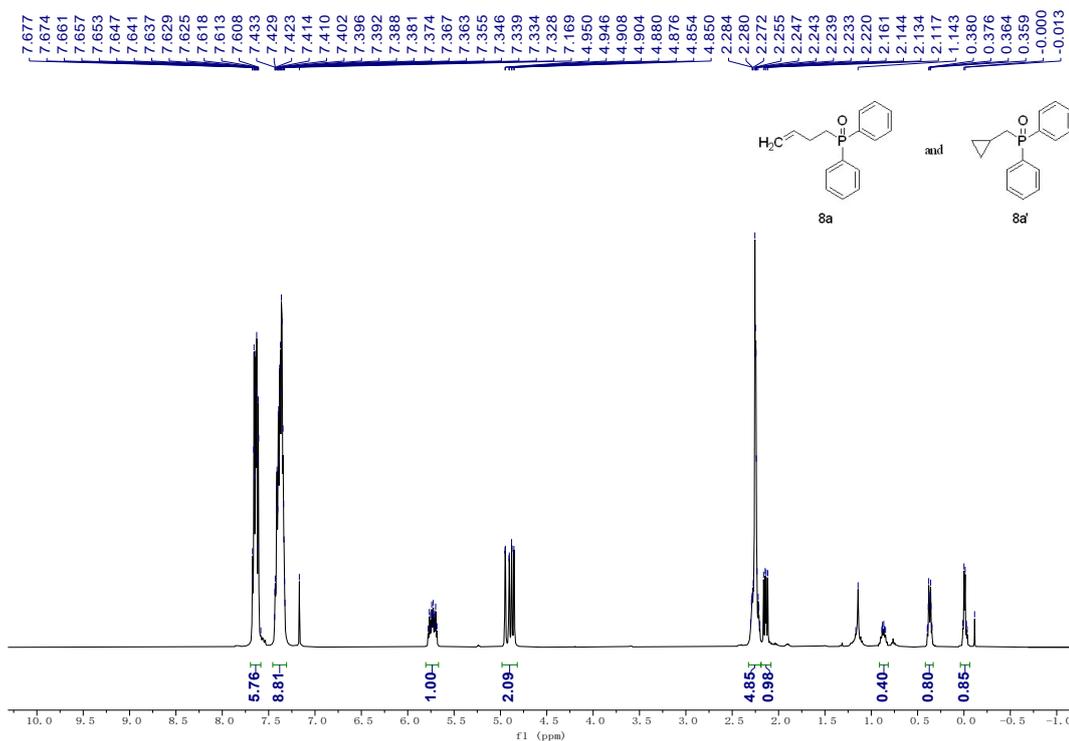


³¹P NMR

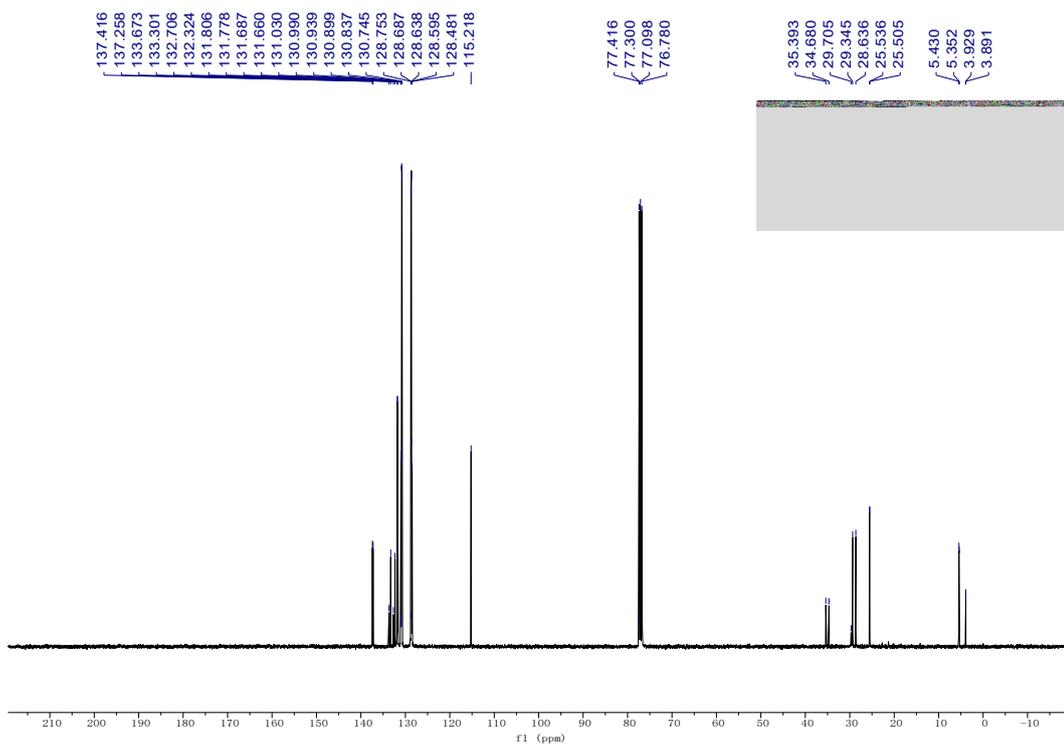


(8a and 8a')

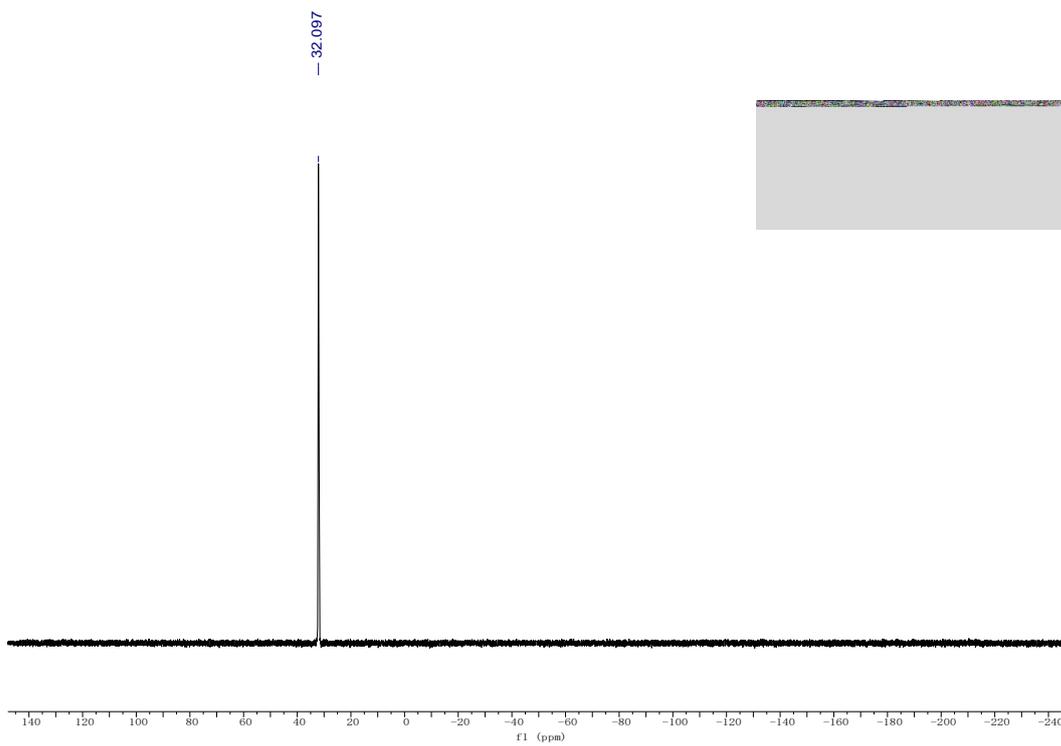
¹H NMR



¹³C NMR

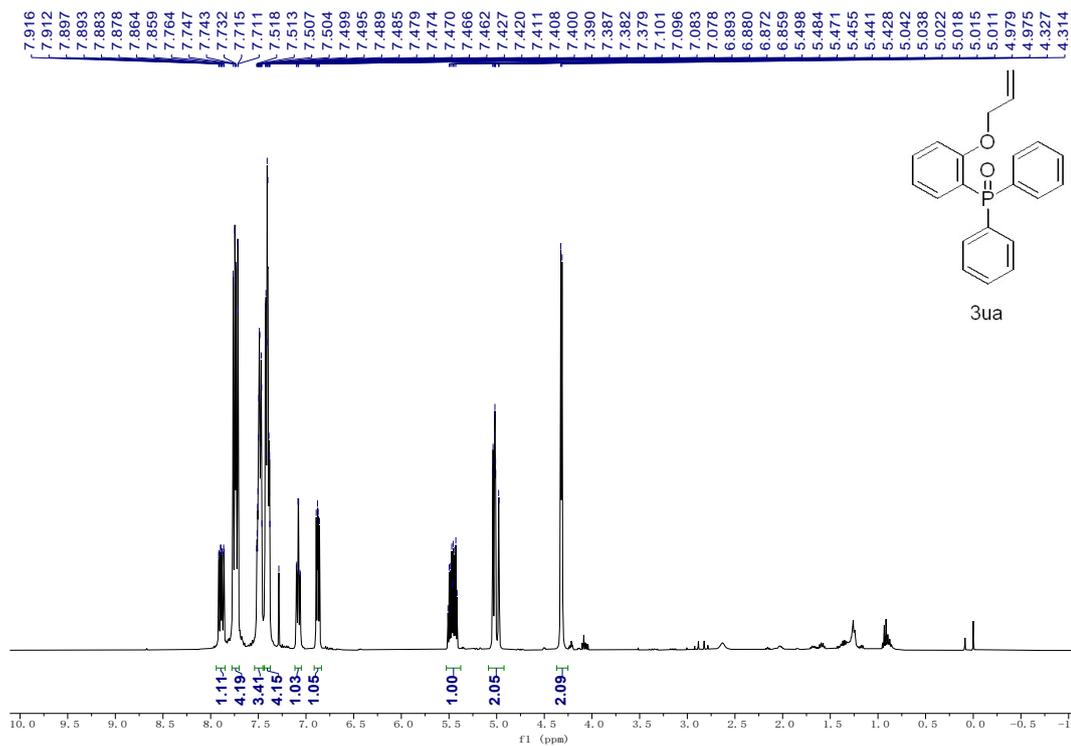


³¹P NMR

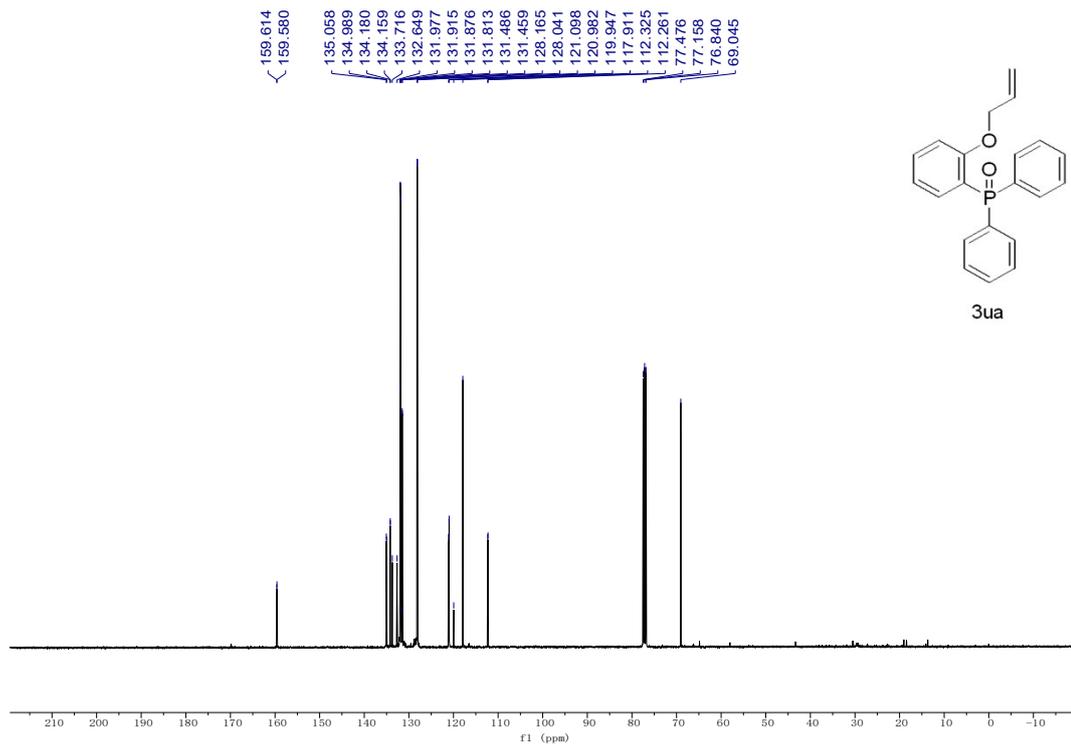


(3ua)

¹H NMR



¹³C NMR



³¹P NMR

