# Electronic Supplementary Information

## Photoinduced synthesis of C2-linked phosphine oxides via radical difunctionalization of acetylene

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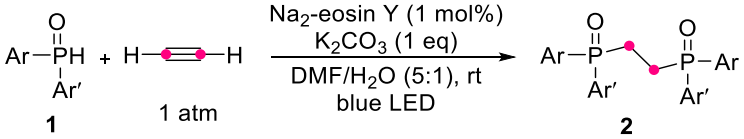
# 1. General information

Unless stated otherwise, all reactions were carried out under 1 atm acetylene. NMR spectra were recorded on Bruker AMX 500 spectrometer at 500 MHz for $^{1}H$ NMR, 125 MHz for $^{13}C$ NMR, 202 MHz for $^{31}P$ NMR, 470 MHz for $^{19}F$ NMR. The $^{1}H$ NMR chemical shifts were measured relative to $CDCl_3$ with trimethylbenzene as internal standard. Melting points were measured on X-4 melting point apparatus and uncorrected. High resolution mass spectra (HRMS) were performed on a VG Autospec-3000 spectrometer. Column chromatography was performed with silica gel (300-400 mesh) with petroleum ether and ethyl acetate as eluents. Commercially available reagents and catalysts were purchased from Energy Chemical Ltd. or Bide Pharmatech Ltd., and were used without further purification unless indicated otherwise. The light source conditions: 10 W blue LED (460-470 nm, WP-TEC-1020HSL, made in WATTCAS, China), and maintaining a relatively constant temperature close to room temperature by regulating the condensed water.

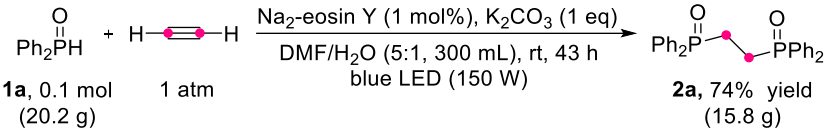
# 2. General procedure

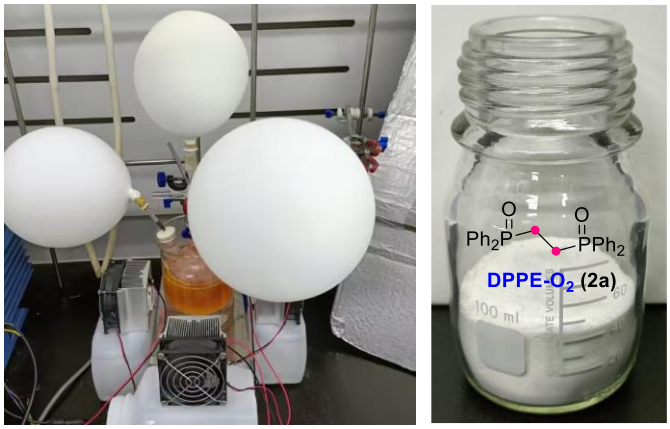
## 2.1 General procedure for the synthesis of product 2



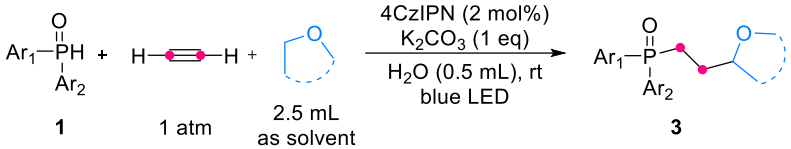

$Na_2$-eosin Y (2.1 mg, 0.003 mmol, 1 mol%), $K_2CO_3$ (41.5 mg, 0.3 mmol, 1 eq) and phosphine oxides (0.3 mmol, 1 eq) were added sequentially to a 10 mL Schlenk tube equipped with a magnetic stir bar. This resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with acetylene for three times. Then, DMF (2.5 mL) and $H_2O$ (0.5 mL) were subsequently added in this order. The reaction was stirred under 10 W blue LED irradiation at room temperature. The mixture was extracted with ethyl acetate and the organic phase was dried over $Na_2SO_4$. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/petroleum ether to give products **2** (DPPE-dioxide analogues), and the solvents is recycled. The yield of products was recorded in isolated yield.

**100 mmol scale-up experiment:** $Na_2$-eosin Y (692 mg, 1 mmol, 1 mol%), $K_2CO_3$ (13.82 g, 100 mmol, 1 eq) and phosphine oxides (100 mmol, 20.2 g, 1 eq) were added sequentially to a 500 mL three-necked reaction flask was equipped with a magnetic stir bar. This resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with acetylene for three times. Then, DMF (250 mL) and $H_2O$ (50 mL) were subsequently added in this order. The reaction was stirred under blue LED (50 W * 3) irradiation at room temperature. The mixture was extracted with ethyl acetate, and washed with water, then the organic phase was dried over $Na_2SO_4$. The resulting solution was quickly filtered through silica gel to remove the pigment and was concentrated in vacuum. The crude product **2a** was purified by recrystallization with dichloromethane/petroleum ether (15.8 g, 74% yield).



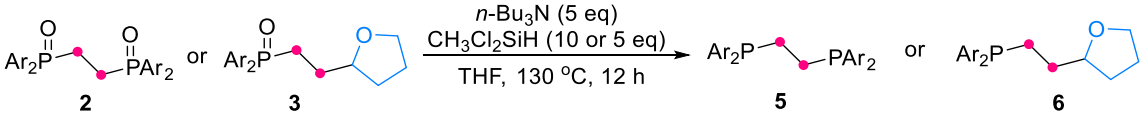




## 2.2 General procedure for the synthesis of product 3




4CzIPN (4.7 mg, 0.006 mmol, 2 mol%), $K_2CO_3$ (41.5 mg, 0.3 mmol, 1 eq) and phosphine oxides (0.3 mmol, 1 eq) were added sequentially to a 10 mL Schlenk tube equipped with a magnetic stir bar. This resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with acetylene for three times. Then, solvent (2.5 mL) and $H_2O$ (0.5 mL) were subsequently added in this order. For phosphine oxides, 0.08, 0.08, 0.07, 0.06 mmol were added in batches every 7 hours. The reaction was stirred under 10 W blue LED irradiation at room temperature. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/petroleum ether to give products **3** (C2-linked oxacyclic diarylalkylphosphine oxides), and was recorded in isolated yield.

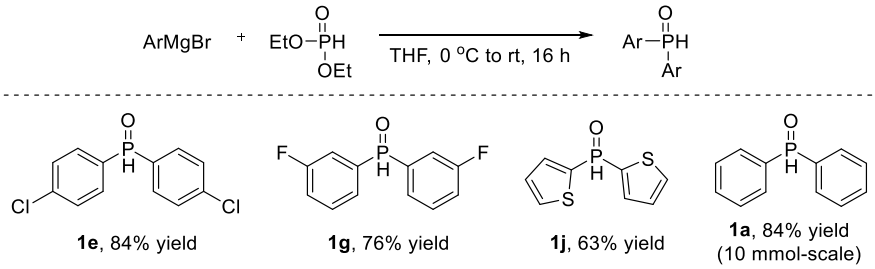
## 2.3 Reduction to phosphine ligands



The 10 mL flask was pumped with nitrogen for three times, **2** or **3** (0.1-0.3 mmol, 1 eq) dissolved in 1mL dry THF was added into the tube, then *n*-$Bu_3N$ (0.5-1.5 mmol, 5 eq) and $CH_3Cl_2SiH$ (0.5-3 mmol, 10 or 5 eq) were added, and the reaction was carried out at 130 °C for 12 h. The reaction mixture was then diluted with EtOAc and filtered through a short pad of silica using EtOAc. The filtrate was concentrated in vacuo before it was purified by flash chromatography (PE/EA = 20:1) on silica gel to afford products **5** or **6**.

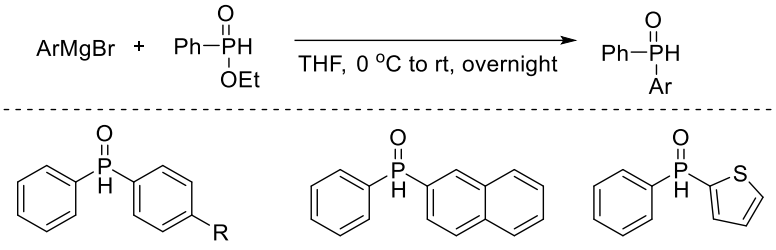
## 2.4 Preparation of substrates

### a) Synthesis of phosphine oxides 1a, 1e, 1g and 1j[1]




A 50 mL two-necked reaction flask was equipped with a magnetic stir bar and flushed with nitrogen. Diethylphosphite (0.78 mL, 6 mmol) was added dropwise at 0 °C to a solution of phenylmagnesium bromide in THF (19.2 mmol ArMgBr). The mixture was stirred for 15-30 minutes at 0 °C, then stirred at room temperature for 16 hours. After that it was cooled again to 0 °C, and $NH_4Cl$ aqueous was then added slowly. The mixture was extracted with EtOAc and the organic phase was washed with $NaHCO_3$ aqueous and brine, then it was dried over $Na_2SO_4$. After the solvent had been completely removed, the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate = 1/1 as eluent to give the phosphine oxide substrates, and the solvents is recycled. The other symmetric phosphine oxides are commercially available. Notes: the sources of **1a** include commercial purchase and preparation through the above methods; the Grignard reagents were purchased from Energy Chemical Ltd.

### b) Synthesis of phosphine oxides 1k-p[2]

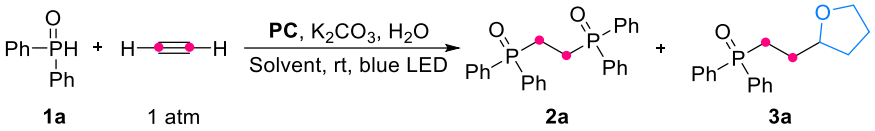



A 50 mL two-necked reaction flask was equipped with a magnetic stir bar and flushed with nitrogen. Ethyl phenylphosphinate (1.02 g, 6 mmol) was added dropwise at 0 °C to a solution of phenylmagnesium bromide in THF (9.6 mmol ArMgBr). The mixture was stirred for 15-30 minutes at 0 °C, then stirred at room temperature overnight. After that it was cooled again to 0 °C, the resulting mixture was quenched with 1 M HCl and extracted with EtOAc. The combined organic layer was dried over $Na_2SO_4$ and evaporated in vacuo. After the solvent had been completely removed, the residue was purified by column chromatography on silica gel using petroleum

ether/ethyl acetate = 1/1 as eluent to give the phosphine oxides **1k-p**, and the solvents is recycled. Notes: the Grignard reagents were purchased from Energy Chemical Ltd.

## 3. Reaction optimization

**Table S1. Conditions optimization[a]**

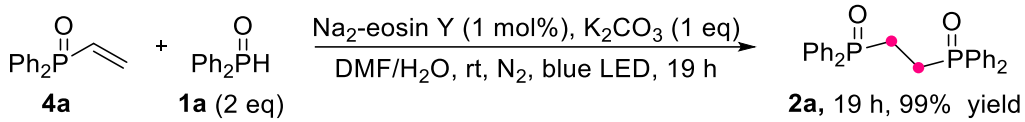



| Entry | **PC** (2 mol%) | Base (1 eq) | Solvent (2.5 mL) | $H_2O$ (mL) | Time (h) | Yield (%)[b] | |
|---|---|---|---|---|---|---|---|
| | | | | | | **2a** | **3a** |
| 1 | $Na_2$-eosin Y | $K_2CO_3$ | THF | 0.5 | 22 | 48 | 45 |
| 2 | 4CzIPN | $K_2CO_3$ | THF | 0.5 | 20 | 29 | 53 |
| 3 | $Ir(ppy)_3$ | $K_2CO_3$ | THF | 0.5 | 36 | 11 | 16 |
| 4 | Tetrabromofluorescein | $K_2CO_3$ | THF | 0.5 | 28 | 22 | 35 |
| 5 | Rose Bengal | $K_2CO_3$ | THF | 0.5 | 28 | 17 | 19 |
| 6 | $Na_2$-eosin Y | $K_2CO_3$ | $CH_3CN$ | 0.5 | 48 | 22 | - |
| 7 | $Na_2$-eosin Y | $K_2CO_3$ | DMF | 0.5 | 11 | 72 | - |
| 8 | $Na_2$-eosin Y | $K_2CO_3$ | DMF | 0.5 | 15 | 80 | - |
| 9 | $Na_2$-eosin Y | $K_2CO_3$ | DMSO | 0.5 | 45 | 76 | - |
| 10 | $Na_2$-eosin Y | $K_2CO_3$ | Toluene | 0.5 | 48 | 13 | - |
| 11 | $Na_2$-eosin Y | - | DMF | 0.5 | 36 | trace | - |
| 12 | $Na_2$-eosin Y | $Et_3N$ | DMF | 0.5 | 36 | trace | - |
| 13 | $Na_2$-eosin Y | $K_2CO_3$ | DMF | 1.0 | 18 | 74 | - |
| 14 | $Na_2$-eosin Y | $K_2CO_3$ | DMF | 0.25 | 18 | 69 | - |
| 15 | $Na_2$-eosin Y (1 mol%) | $K_2CO_3$ | DMF | 0.5 | 15 | 78 | - |
| 16 | - | $K_2CO_3$ | DMF | 0.5 | 24 | trace | - |
| 17[c] | $Na_2$-eosin Y (1 mol%) | $K_2CO_3$ | DMF | 0.5 | 17 | 69 | - |
| 18[d] | $Na_2$-eosin Y | $K_2CO_3$ | THF | 0.5 | 24 | 28 | 60 |
| 19[e] | $Na_2$-eosin Y | $K_2CO_3$ | THF | 0.5 | 26 | 21 | 64 |
| 20[f] | $Na_2$-eosin Y | $K_2CO_3$ | THF | 0.5 | 30 | 10 | 66 |
| 21[f] | $Na_2$-eosin Y (3 mol%) | $K_2CO_3$ | THF | 0.5 | 32 | 11 | 67 |
| 22[f] | 4CzIPN | $K_2CO_3$ | THF | 0.5 | 28 | 7 | 71 |
| 23[g] | $Na_2$-eosin Y (1 mol%) | $K_2CO_3$ | DMF | 0.5 | 15 | trace | - |

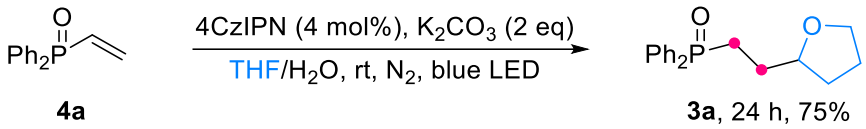
[a]Reaction condition: under acetylene atmosphere (1 atm), **1a** (0.3 mmol), **PC** (0.006 mmol), base (0.3 mmol), and $H_2O$ (0.5 mL) in solvent (2.5 mL) were irradiated by blue LED (460-470 nm) at room temperature. [b]Isolated yield. [c]green LED (535-540 nm). [d]0.15, 0.15 mmol of **1a** were added in batches every 10 hours. [e]0.1, 0.1, 0.1 mmol of **1a** were added in batches every 8 hours. [f]0.08, 0.08, 0.07, 0.06 mmol 0f **1a** were added in batches every 7 hours. [g]No light.

## 4. Control experiments

### a) Control experiments with phosphinoyl ethylene

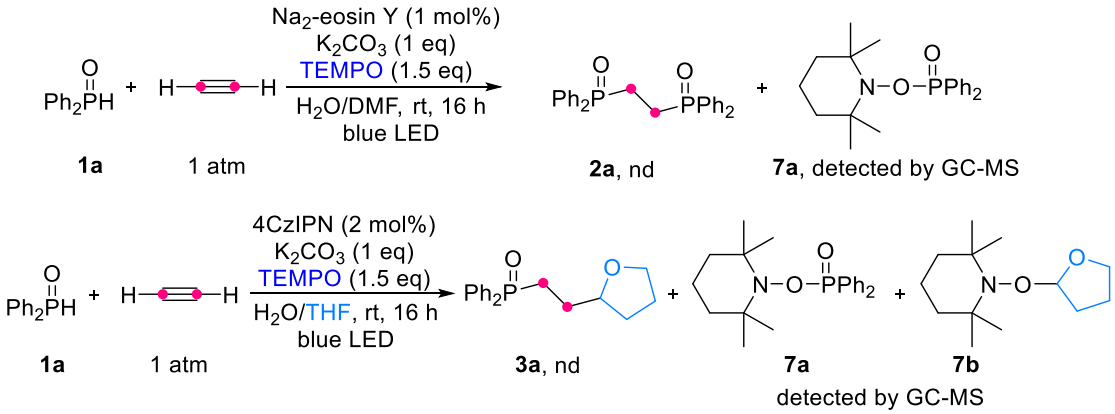



$Na_2$-eosin Y (1.5 mg, 0.003 mmol, 1 mol%), $K_2CO_3$ (27.7 mg, 0.2 mmol, 1 eq) phosphine oxides (0.24 mmol, 1.2 eq) and phosphinoyl ethylene (0.2 mmol, 1 eq) were added sequentially to a 10 mL Schlenk tube equipped with a magnetic stir bar. This resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then, DMF (1.5 mL) and $H_2O$ (0.3 mL) were subsequently added in this order. The reaction was stirred under 10 W blue LED irradiation at room temperature. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/petroleum ether to give the product **2a** in 99% isolated yield.



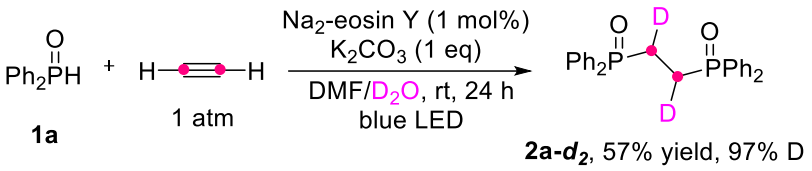

4CzIPN (4.7 mg, 0.003 mmol, 4 mol%), $K_2CO_3$ (41.5 mg, 0.3 mmol, 2 eq) and phosphinoyl ethylene (0.15 mmol, 1 eq) were added sequentially to a 10 mL Schlenk tube equipped with a magnetic stir bar. This resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with nitrogen for three times. Then, THF (2.5 mL) and $H_2O$ (0.5 mL) were subsequently added in this order. The reaction was stirred under 10 W blue LED irradiation at room temperature. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/petroleum ether to give the product **3a** in 75% isolated yield.

### b) Radical capture experiments with TEMPO

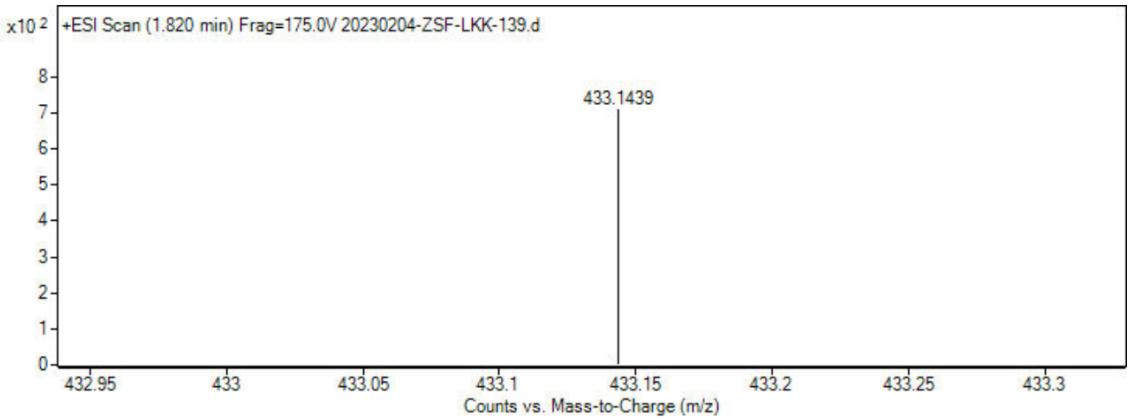



According to the general procedure 2, the above radical capture experiments with TEMPO (1.5 eq) were carried out, the related radical capture products **7a** and **7b** were detected by GC-MS. **7a**, m/z 357.07 (M); **7b**, m/z 228.18 ($M+H^+$).

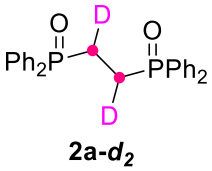
### c) Deuterium-labelling experiments

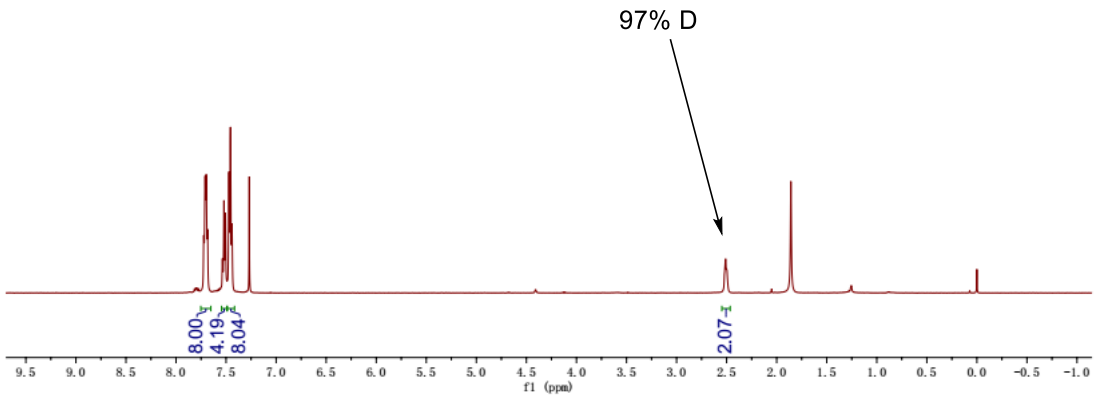



According to the general procedure 2.1, $D_2O$ was used instead of $H_2O$, the deuterium-labelling product **2a**-$d_2$ was obtained in 57% isolated yield. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.70 (dd, J = 11.9, 6.6 Hz, 8H), 7.52 (t, J = 7.3 Hz, 4H), 7.46 (t, J = 7.3 Hz, 8H), 2.51 (d, J = 4.1 Hz, 2H). **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{26}H_{23}D_2O_2P_2^+$ 433.1450; found 433.1439.

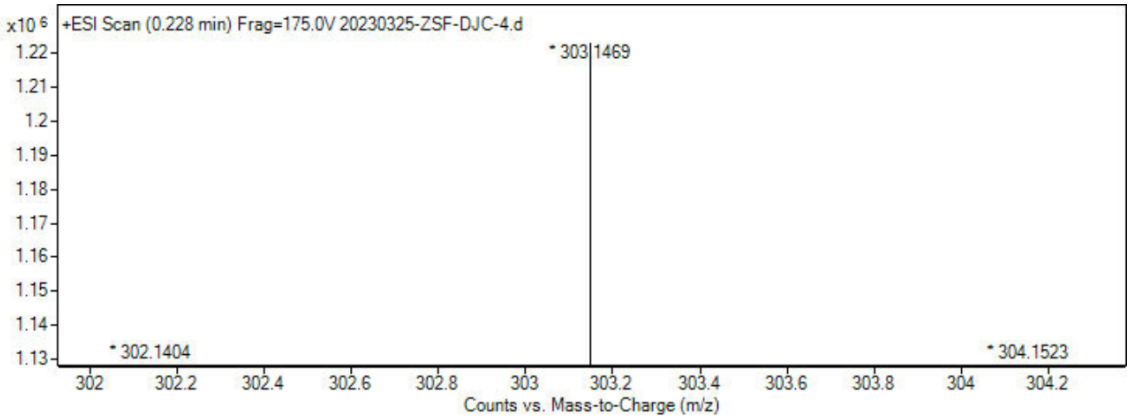


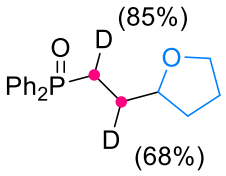




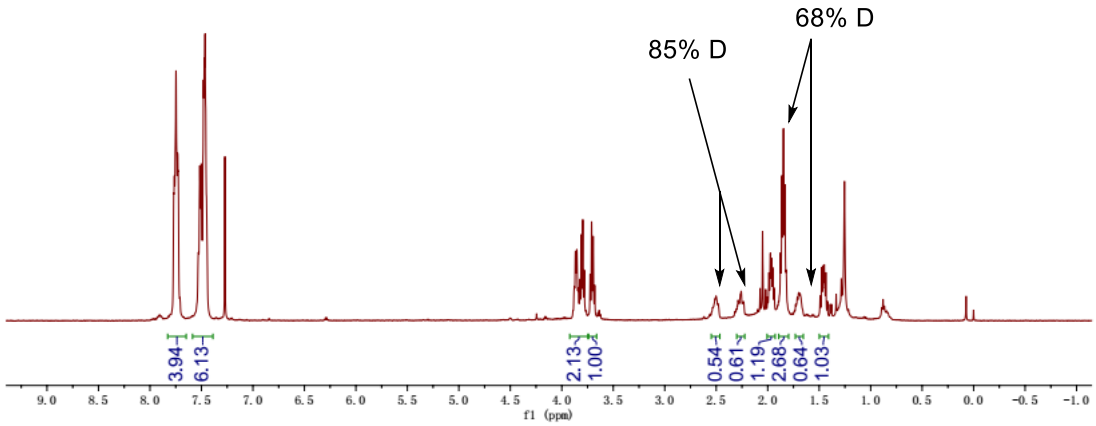




According to the general procedure 2.2, $D_2O$ was used instead of $H_2O$, the deuterium-labelling product **3a-*d*$_2$** was obtained in 21% isolated yield. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.83 – 7.65 (m, 4H), 7.59 – 7.39 (m, 6H), 3.83 (ddd, *J* = 21.7, 13.3, 6.1 Hz, 2H), 3.70 (dd, *J* = 14.8, 7.3 Hz, 1H), 2.51 (t, *J* = 12.7 Hz, 1H), 2.26 (dd, *J* = 17.5, 9.5 Hz, 1H), 1.97 (dt, *J* = 12.5, 6.6 Hz, 1H), 1.89 – 1.80 (m, 3H), 1.71 (dd, *J* = 14.0, 7.2 Hz, 1H), 1.46 (td, *J* = 15.6, 7.7 Hz, 1H). **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{20}D_2O_2P^+$ 303.1477; found 303.1469.

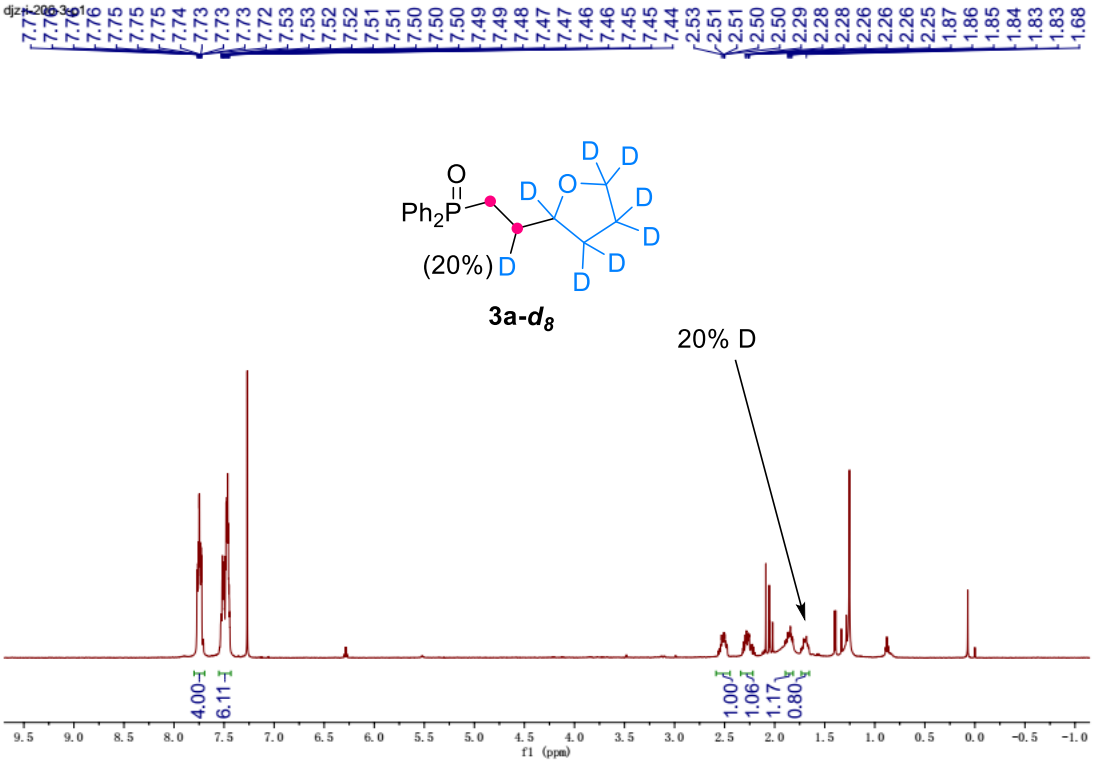



**3a-*d*$_2$**

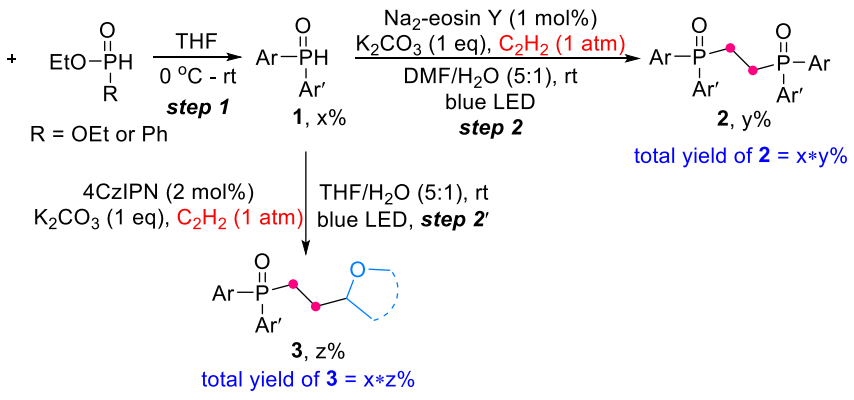



According to the general procedure 2.2, THF-$d_8$ was used instead of THF, the deuterium-labelling product **3a-*d*$_8$** was obtained in 52% isolated yield. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.80 – 7.69 (m, 4H), 7.55 – 7.43 (m, 6H), 2.59 – 2.45 (m, 1H), 2.34 – 2.22 (m, 1H), 1.89 – 1.81 (m, 1H), 1.69 (ddd, *J* = 18.4, 8.0, 4.0 Hz, 0.8H). **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{14}D_8O_2P^+$ 309.1854; found 309.1845.




## 5. Calculation of total yield and sustainability metrics

### a) Total yield[a]



| Entry | Product | step 1 (%) | Step 2 or step 2' (%) | Total yield (%) |
|---|---|---|---|---|
| 1 | **2e** | 84 | 63 | 53 |
| 2 | **2g** | 76 | 56 | 43 |
| 3 | **2j** | 63 | 30 | 19 |
| 4 | **2k** | 77 | 42 | 32 |
| 5 | **2l** | 79 | 52 | 41 |
| 6 | **2m** | 72 | 58 | 42 |
| 7 | **2n** | 85 | 55 | 47 |
| 8 | **2o** | 65 | 64 | 42 |
| 9 | **3e** | 84 | 54 | 45 |
| 10 | **3h** | 76 | 50 | 38 |
| 11 | **3k** | 63 | 22 | 14 |
| 12 | **3l** | 74 | 41 | 30 |
| 13 | **3m** | 77 | 42 | 32 |
| 14 | **3n** | 79 | 49 | 39 |
| 15 | **3o** | 72 | 45 | 32 |
| 16 | **3p** | 85 | 50 | 43 |

[a]Only for the substrates that need to be prepared.

## b) Atom economy (atom utilisation)

$$\textbf{Atom economy} = \frac{\textit{FW (g/mol) product}}{\textit{FW of all reactants}} * 100\% \begin{cases} = \frac{430}{202*2+26} * 100\% = 100\% & \text{(example 1, for } \textbf{2a}\text{)} \\ = \frac{300}{202+26+72} * 100\% = 100\% & \text{(example 2, for } \textbf{3a}\text{)} \end{cases}$$

## c) Process mass intensity (PMI)

$$\textbf{PMI}_{\textbf{(reaction)}} = \frac{\textit{total input mass to reaction (g)}}{\textit{mass of product (g)}}$$

i) For the 0.3 mmol-scale reaction of **1a** to **2a**

$$\textbf{PMI} = \frac{\textit{60.6 mg (}\textbf{1a}\textit{) + 255 mg (}C_2H_2\textit{)}^a \textit{ + 2.1 mg (}Na_2\textit{-eosin Y) + 41.5 mg (}K_2CO_3\textit{) + 2370 mg (DMF) + 500 mg (}H_2O\textit{)}}{\textit{50.5 mg (}\textbf{2a}\textit{)}}$$

$$= \frac{3229.2}{50.5} = \textbf{63.9}$$

ii) For the 0.3 mmol-scale reaction of **1a** to **3a**

$$\textbf{PMI} = \frac{\textit{60.6 mg (}\textbf{1a}\textit{) + 255 mg (}C_2H_2\textit{)}^a \textit{ + 4.7 (4CzIPN) + 41.5 mg (}K_2CO_3\textit{) + 2225 mg (THF) + 500 mg (}H_2O\textit{)}}{\textit{63.6 mg (}\textbf{3a}\textit{)}}$$

$$= \frac{3086.8}{63.6} = \textbf{48.5}$$

iii) For the 100 mmol-scale reaction of **1a** to **2a**

$$\textbf{PMI} = \frac{\textit{20.2 g (}\textbf{1a}\textit{) + 5.4 g (}C_2H_2\textit{)}^a \textit{ + 0.7 g (}Na_2\textit{-eosin Y) + 13.8 g (}K_2CO_3\textit{) + 237 g (DMF) + 50 g (}H_2O\textit{)}}{\textit{15.8 g (}\textbf{2a}\textit{)}}$$

$$= \frac{327.1}{15.8} = \textbf{20.7}$$

[a]Based on the volume change of the acetylene balloon.

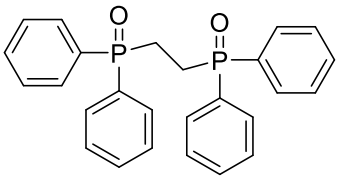
### d) EcoScale of 100 mmol 1a scale-up reaction

| Parameter | Penalty |
|---|---|
| 1. Yield: 74% | 13 |
| 2. Price of reaction[a]: < $10 | 0 |
| 3. Safety[b]: DMF (T) | 5 |
| $Na_2$-eosin Y (F, T) | 10 |
| acetylene ($F^+$) | 10 |
| 4. rt, 43 h | 2 |
| 5. 1 atm | 0 |
| 6. Extraction with EtOAc | 3 |
| 7. Drying over $Na_2SO_4$ | 0 |
| 8. Crystallization and filtration | 1 |
| *Penalty points total* | *44* |
| **EcoScale** = *100 - Penalty points total* = ***56*** | |

[a]Price of reaction components (to obtain 10 mmol of end product). [b]Based on the hazard warning symbols.

## 6. Characterization data of products

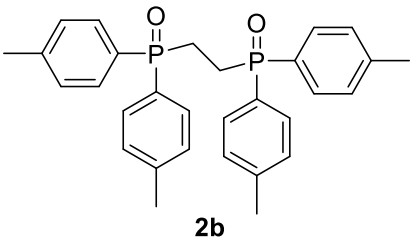
**ethane-1,2-diylbis(diphenylphosphine oxide)[3]**



**2a**

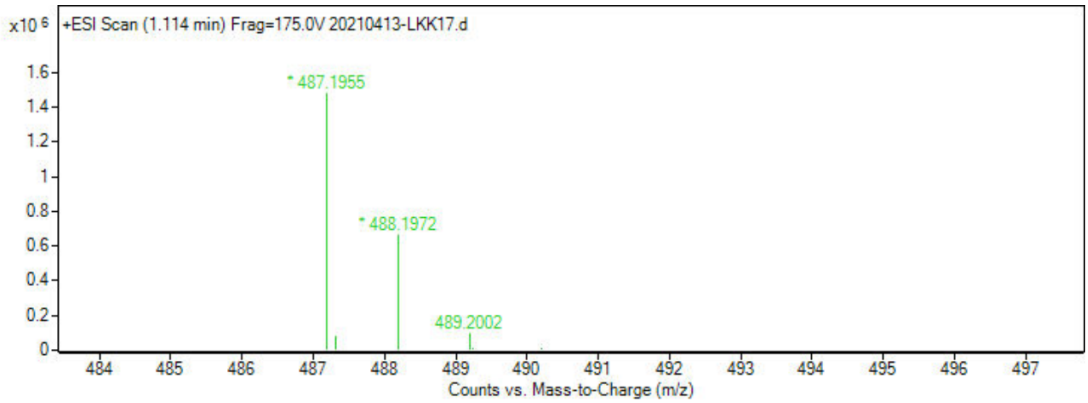
White solid, 50.5 mg, 78% yield. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.71 (s, 8H), 7.48 (d, *J* = 28.7 Hz, 12H), 2.53 (s, 4H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 132.05, 131.88 (d, *J* = 99.6 Hz), 130.74 (t, *J* = 4.5 Hz), 128.82 (t, *J* = 5.8 Hz), δ 22.05 – 21.29 (m). **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 32.60.

**ethane-1,2-diylbis(di-p-tolylphosphine oxide)**

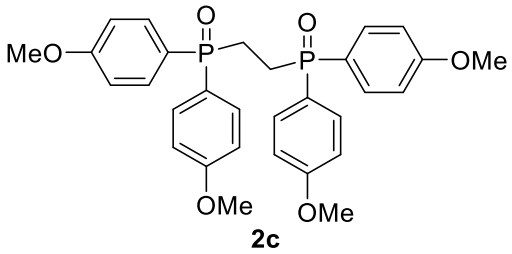


**2b**

White solid,41.3 mg, 57% yield, m.p. 225-227 °C. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 11.6, 6.9 Hz, 8H), 7.24 (d, *J* = 7.6 Hz, 8H), 2.46 (s, 4H), 2.36 (s, 12H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 142.45, 130.80 (t, *J* = 4.7 Hz), 129.52 (t, *J* = 6.0 Hz), 128.81 (d, *J* = 103.0 Hz), 22.19 – 21.54 (m), 21.56. **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 33.20. **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{30}H_{33}O_2P_2^+$ 487.1950; found 487.1955.

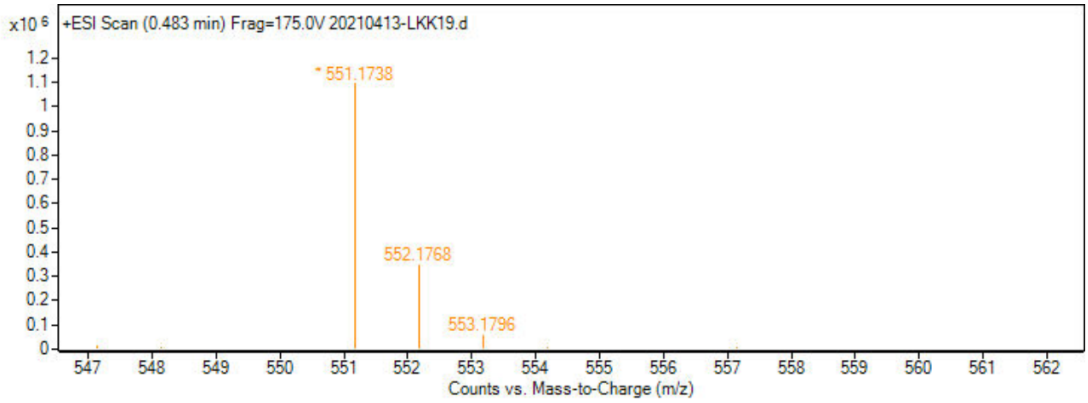



**ethane-1,2-diylbis(bis(4-methoxyphenyl)phosphine oxide)**

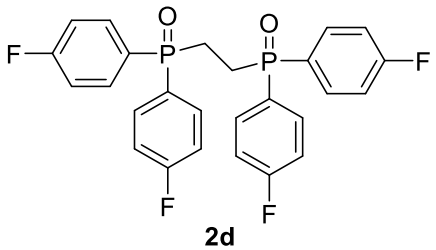



**2c**

White solid, 28.9 mg, 35% yield, m.p. 149-151 °C. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.60 (td, *J* = 8.5, 6.4 Hz, 8H), 6.94 (d, *J* = 8.3 Hz, 8H), 3.82 (s, 12H), 2.43 (d, *J* = 1.7 Hz, 4H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 162.44, 132.63 (t, *J* = 5.4 Hz), 123.96 – 122.78 (m), 114.35 (t, *J* = 6.4 Hz), 55.33, 22.64 – 21.61 (m). **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 33.04. **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{30}H_{33}O_6P_2^+$ 551.1747; found 551.1738.



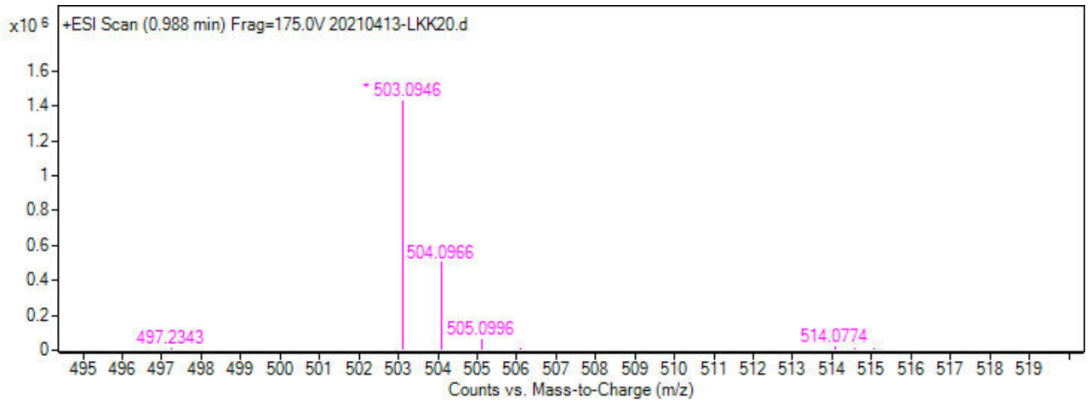

**ethane-1,2-diylbis(bis(4-fluorophenyl)phosphine oxide)**



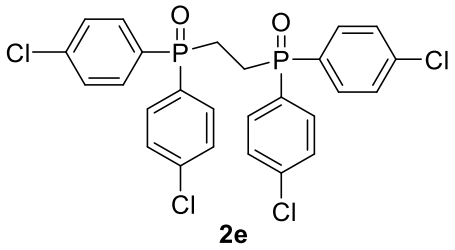

**2d**

White solid, 43.7 mg, 58% yield, m.p. 211-213 °C. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.78 – 7.61 (m, 8H), 7.17 (t, *J* = 8.4 Hz, 8H), 2.47 (s, 4H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 165.22 (d, *J* = 254.6 Hz), 133.23 (dt, *J* = 9.0, 5.5 Hz), 127.45 (d, *J* = 103.9 Hz), 116.47 (dt, *J* = 21.3, 6.4 Hz), 22.41 – 21.27 (m). **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 31.41. **$^{19}$F NMR** (471 MHz, $CDCl_3$) δ -105.64. **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{26}H_{21}F_4O_2P_2^+$

503.0947; found 503.0946.

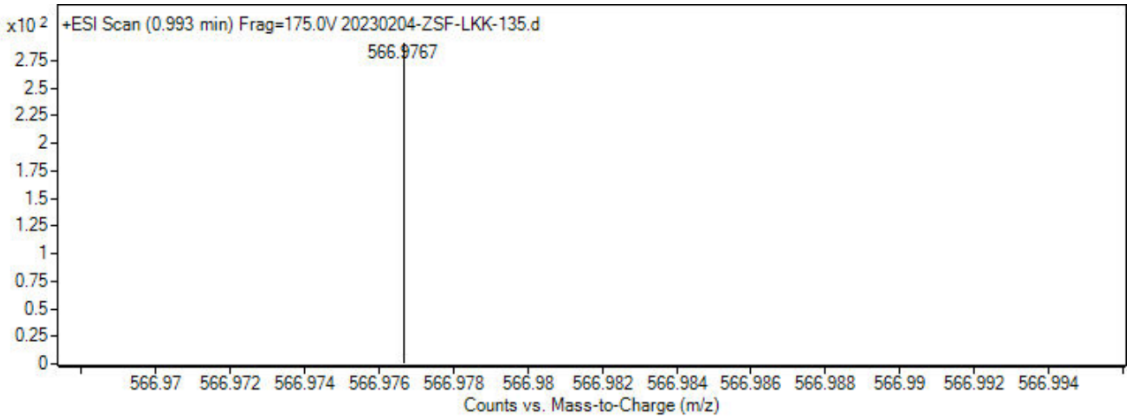



**ethane-1,2-diylbis(bis(4-chlorophenyl)phosphine oxide)**

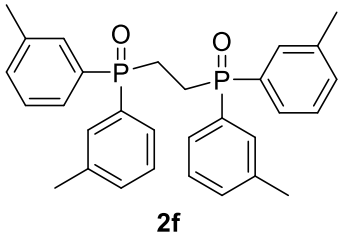



**2e**

White solid, 53.5 mg, 63% yield, m.p. 228-231 °C. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.62 (td, *J* = 8.3, 6.1 Hz, 8H), 7.45 (d, *J* = 8.1 Hz, 8H), 2.46 (s, 4H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 139.14, 132.05 (t, *J* = 5.2 Hz), 129.81 (d, *J* = 100.8 Hz), 129.41 (t, *J* = 6.2 Hz), 24.04 – 20.36 (m). **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 31.29. **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{26}H_{21}Cl_4O_2P_2^+$ 566.9765; found 566.9767.



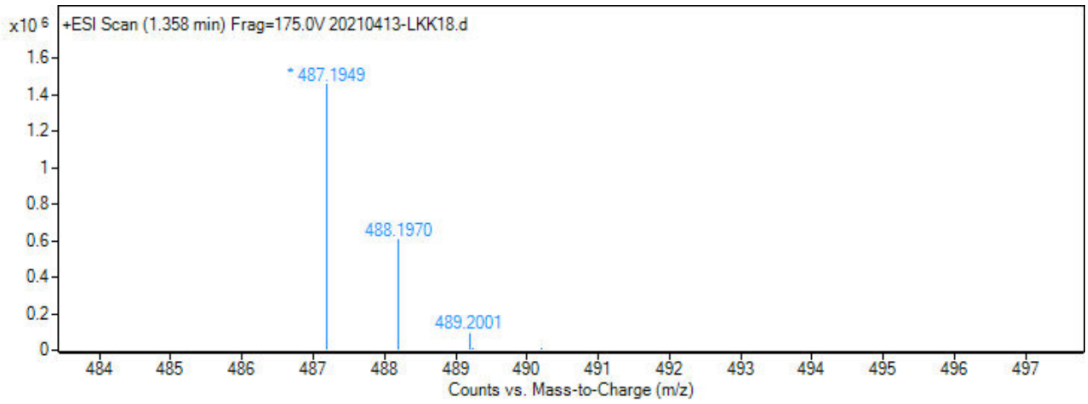

**ethane-1,2-diylbis(di-m-tolylphosphine oxide)**



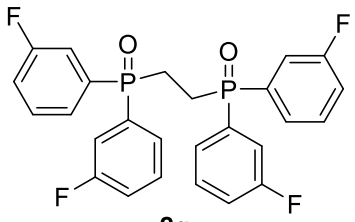

**2f**

White solid, 35.4 mg, 49% yield, m.p. 150-152 °C. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.56 (s, 4H), 7.46 (s, 4H), 7.32 (q, *J* = 7.8 Hz, 8H), 2.50 (s, 4H), 2.36 (s, 12H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 138.75 (t, *J* = 5.1 Hz), 132.81, 131.89 (d, *J* = 99.7 Hz), 131.27, 128.67 (t, *J* = 5.4 Hz), 127.72, 21.65 (d, *J* = 62.1 Hz), 21.40. **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 33.06. **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{30}H_{33}O_2P_2^+$ 487.1950; found

487.1949.

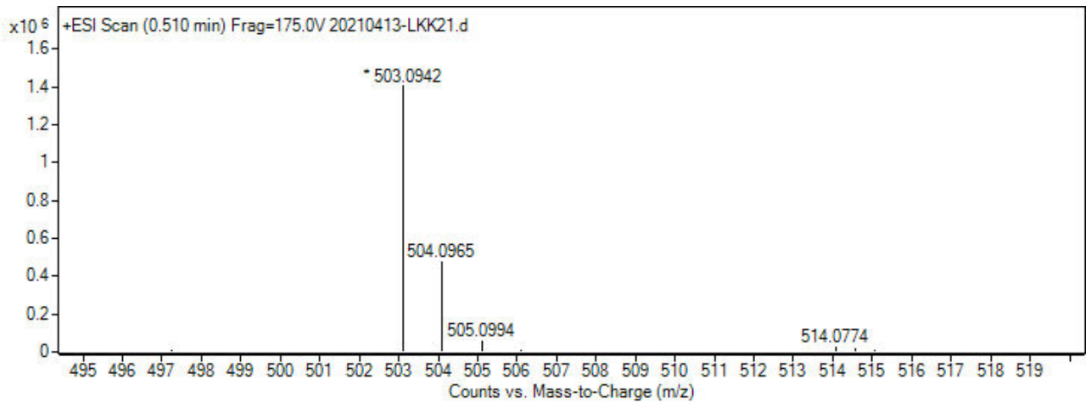



**ethane-1,2-diylbis(bis(3-fluorophenyl)phosphine oxide)**

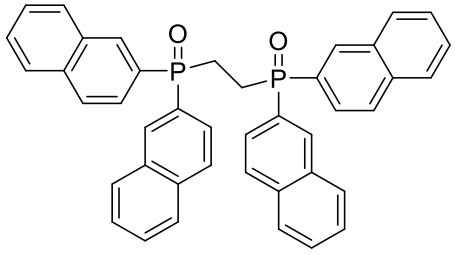


**2g**

White solid, 42.1 mg, 56% yield. m.p. 150-152 °C. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 15.6, 13.5 Hz, 12H), 7.27 – 7.18 (m, 4H), 2.51 (s, 4H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 162.76 (dt, *J* = 252, 7.6 Hz), 133.78 (dd, *J* = 100.1, 5.4 Hz), 131.16 (dd, *J* = 14.0, 7.2 Hz), 126.27 (dd, *J* = 8.1, 4.2 Hz), 119.79 (d, *J* = 21.1 Hz), 117.84 (dt, *J* = 22.3, 4.9 Hz), 22.03 – 20.92 (m). **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 30.67. **$^{19}$F NMR** (471 MHz, $CDCl_3$) δ -109.79. **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{26}H_{21}F_4O_2P_2^+$ 503.0947; found 503.0942.



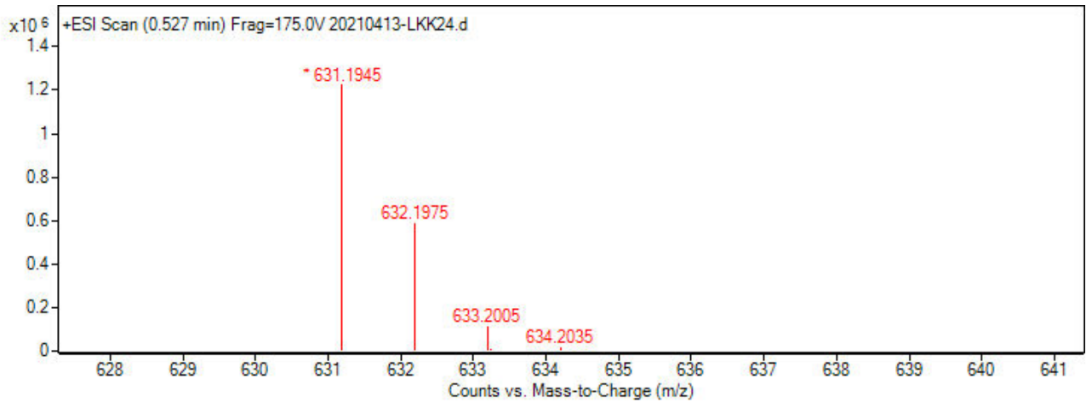

**ethane-1,2-diylbis(di(naphthalen-2-yl)phosphine oxide)**



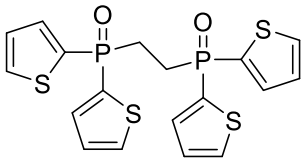
**2i**

White solid, 50.9 mg, 54% yield, m.p. 155-157 °C **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 8.47 – 8.32 (m, 4H), 7.94 – 7.77 (m, 12H), 7.65 (s, 4H), 7.55 (dt, *J* = 14.6, 7.0 Hz, 8H), 2.80 (s, 4H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ

134.75, 132.90, 132.54 (t, $J$ = 6.3 Hz), 128.95 (d, $J$ = 99.9 Hz), 128.93, 128.83 (t, $J$ = 5.6 Hz), 128.31, 127.83, 127.07, 125.46 (t, $J$ = 4.8 Hz), 22.09 – 20.99 (m). **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 33.09. **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{42}H_{33}O_2P_2^+$ 631.1950; found 631.1945.

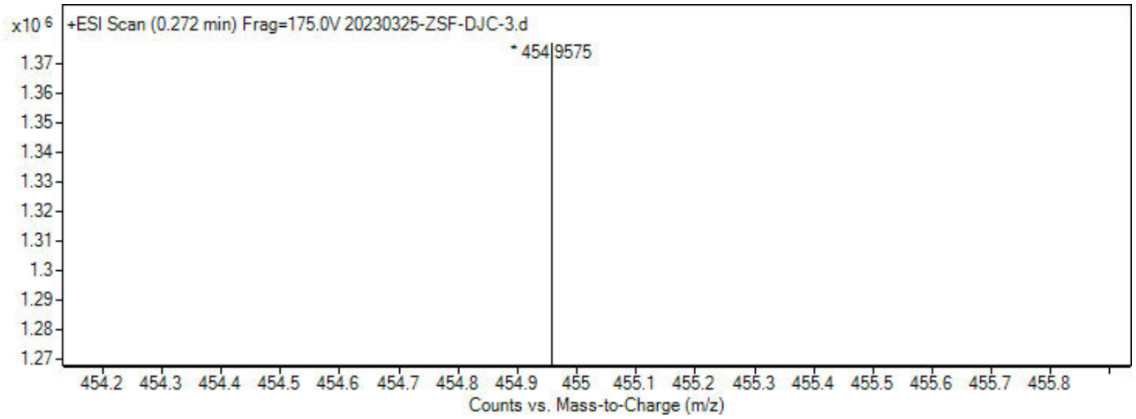



**ethane-1,2-diylbis(di(thiophen-2-yl)phosphine oxide)**

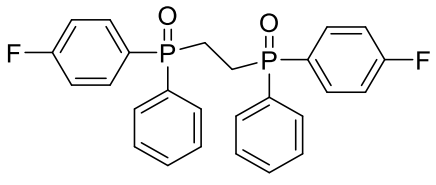


**2j**

White solid, 81.4 mg, 30% yield, m.p. 124-126 °C. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.78 – 7.69 (m, 4H), 7.58 (dd, $J$ = 6.5, 3.3 Hz, 4H), 7.19 (t, $J$ = 4.1 Hz, 4H), 2.61 (d, $J$ = 2.2 Hz, 4H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 135.75 (t, $J$ = 5.2 Hz), 133.94 (d, $J$ = 2.4 Hz), 133.29 – 131.94 (m), 128.61 (t, $J$ = 7.2 Hz), 26.73 – 25.54 (m). $^{31}$P NMR (202 MHz, $CDCl_3$) δ 21.85. **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{17}O_2P_2S_4^+$ 454.9581; found 454.9575.



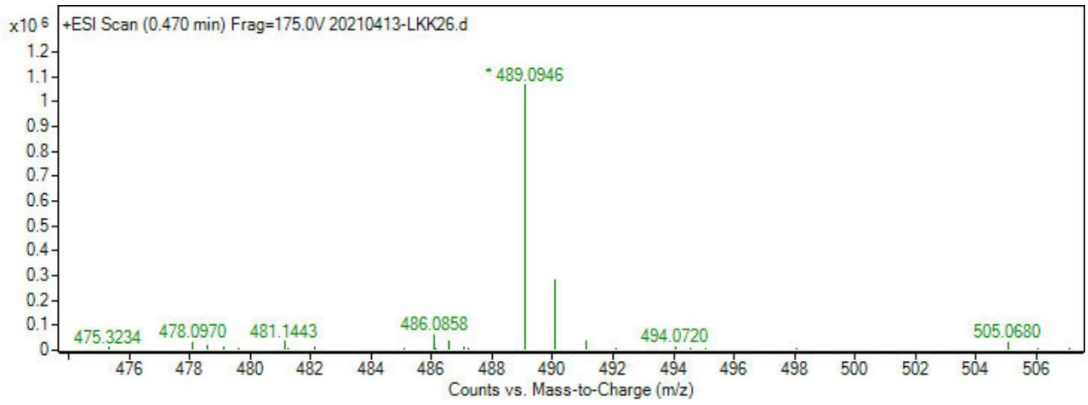

**ethane-1,2-diylbis((4-fluorophenyl)(phenyl)phosphine oxide)**



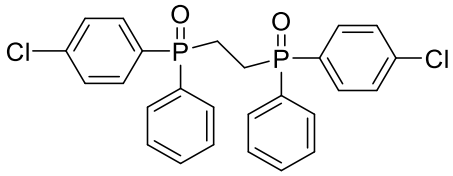
**2k**

White solid, 31.2 mg, 42% yield, m.p. 130-133 °C. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.70 (s, 8H), 7.54 (t, $J$ = 7.2 Hz, 2H), 7.47 (t, $J$ = 7.1 Hz, 4H), 7.15 (t, $J$ = 7.5 Hz, 4H), 2.51 (s, 4H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ

165.13 (d, *J* = 253.7 Hz), 133.38 – 133.22 (m), 132.28, 132.02 – 131.17 (m), 130.70 (t, *J* = 4.7 Hz), 128.98 (t, *J* = 5.9 Hz), 128.24 – 127.35 (m), 116.31 (dt, *J* = 21.3, 6.4 Hz), 22.27 – 21.25 (m). **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 32.18. **$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -106.13. **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{26}H_{22}F_2NaO_2P_2^+$ 489.0955; found 489.0946.

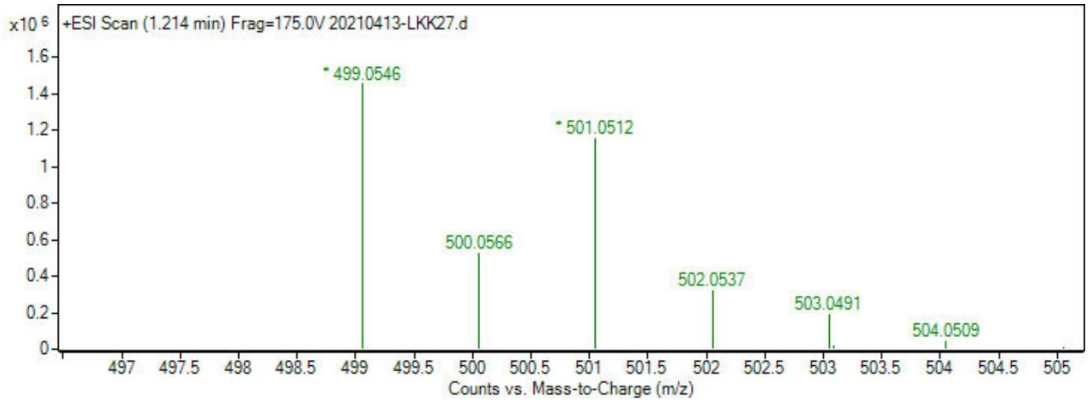



**ethane-1,2-diylbis((4-chlorophenyl)(phenyl)phosphine oxide)**

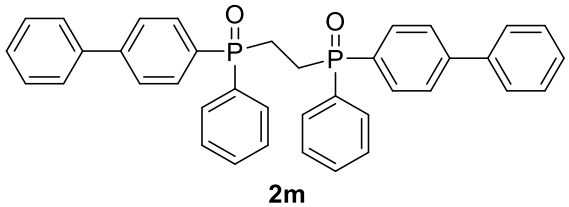



**2l**

White solid, 38.4 mg, 52% yield, m.p. 221-223 °C. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.77 – 7.58 (m, 8H), 7.54 (t, *J* = 7.2 Hz, 2H), 7.46 (dd, *J* = 18.6, 7.7 Hz, 8H), 2.49 (s, 4H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 138.83, 132.38, 132.20, 131.39 (d, *J* = 100.0 Hz), 130.69, 129.27 (t, *J* = 5.7 Hz), 129.03 (t, *J* = 5.4 Hz), 22.21 – 20.81 (m). **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 32.00. **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{26}H_{23}Cl_2O_2P_2^+$ 499.0545; found 499.0546.

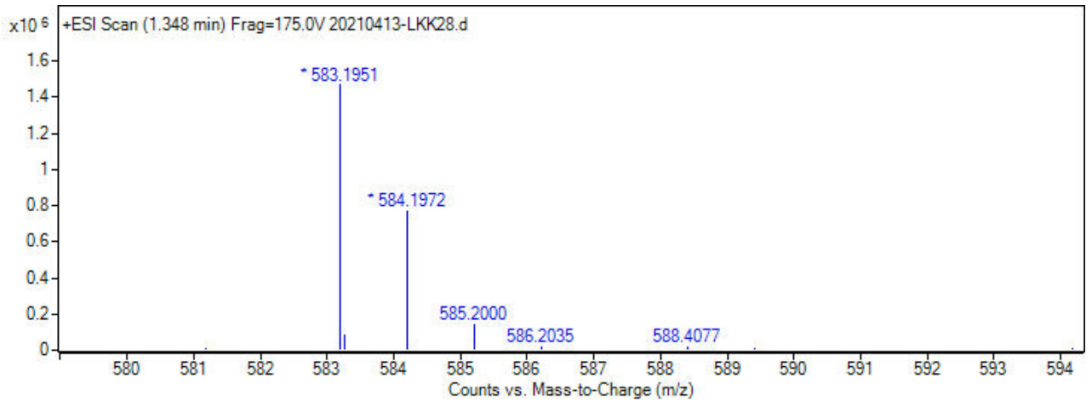



**ethane-1,2-diylbis([1,1'-biphenyl]-4-yl(phenyl)phosphine oxide)**

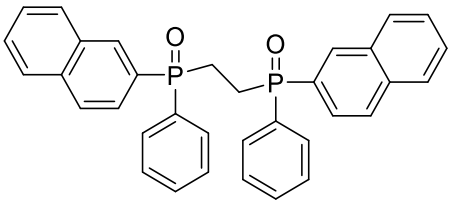



**2m**

White solid, 50.3 mg, 58%, m.p. 115-116 °C. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.77 (dt, *J* = 13.0, 7.3 Hz, 8H), 7.66 (d, *J* = 7.3 Hz, 4H), 7.59 – 7.50 (m, 6H), 7.45 (dt, *J* = 14.6, 7.4 Hz, 8H), 7.37 (dd, *J* = 8.9, 5.6 Hz, 2H), 2.59 (s, 4H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 144.92, 139.74, 132.12, 132.03 (d, *J* = 100.3 Hz), 131.34 (t, *J* = 4.8 Hz), 130.81 (t, *J* = 4.7 Hz), 130.37 (d, *J* = 99.6 Hz), 129.07 – 128.77 (m), 128.23, 127.53 (t, *J* = 6.0 Hz), 127.25, 22.31 – 21.29 (m). **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 32.76. **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{38}H_{33}O_2P_2^+$ 583.1950; found 583.1951.

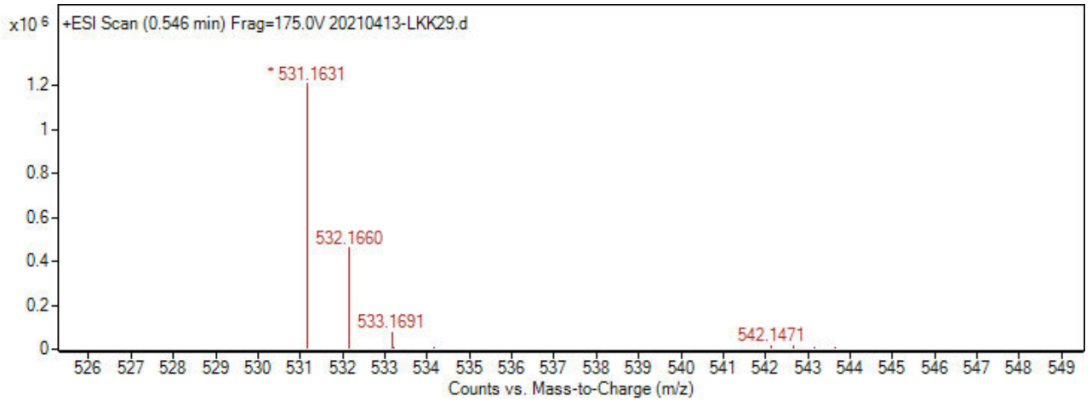



**ethane-1,2-diylbis(naphthalen-2-yl(phenyl)phosphine oxide)**

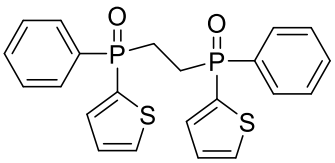


**2n**

White solid, 43.5 mg, 55% yield, m.p. 148-150 °C. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 8.37 (d, *J* = 12.3 Hz, 2H), 7.87 (ddd, *J* = 21.5, 14.9, 7.9 Hz, 6H), 7.74 (s, 4H), 7.66 – 7.38 (m, 12H), 2.68 (d, *J* = 13.4 Hz, 4H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 134.74 (d, *J* = 3.8 Hz), 132.95 (t, *J* = 4.1 Hz), 132.60 – 132.44 (m), 132.13 (d, *J* = 2.5 Hz), 131.67 (d, *J* = 7.7 Hz), 130.83 – 130.74 (m), 129.09 (d, *J* = 10.2 Hz), 128.95 – 128.75 (m), 128.34 (d, *J* = 3.6 Hz), 127.84 (d, *J* = 3.0 Hz), 127.10 (d, *J* = 3.3 Hz), 125.41 (q, *J* = 5.5 Hz), 22.15 – 21.14 (m). **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 33.06. **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{34}H_{29}O_2P_2^+$ 531.1637; found 531.1631.

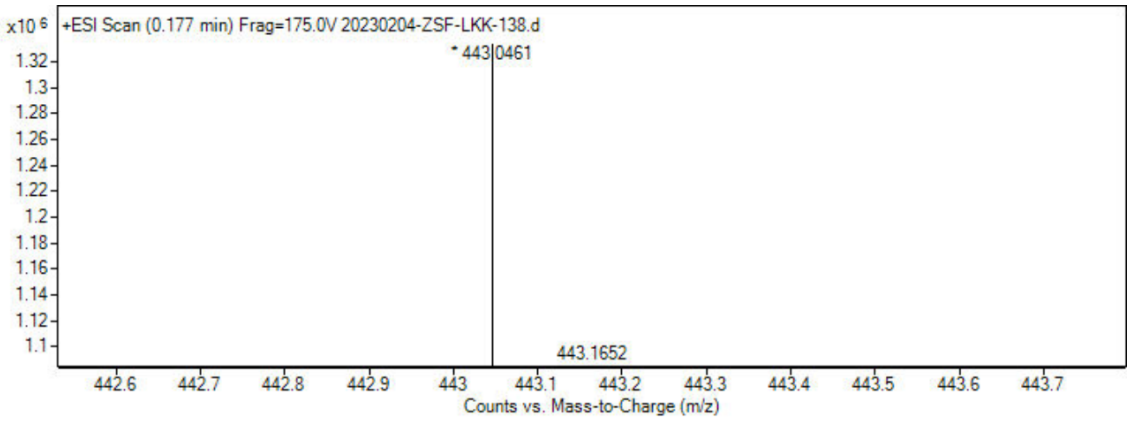



**ethane-1,2-diylbis(phenyl(thiophen-2-yl)phosphine oxide)**

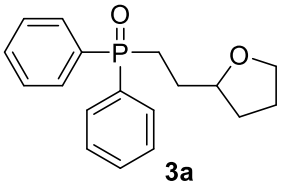


**2o**

White solid, 42.3 mg, 64% yield, m.p. 147-150 °C. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.82 – 7.66 (m, 6H), 7.61 – 7.41 (m, 8H), 7.18 (dt, *J* = 11.4, 4.0 Hz, 2H), 2.70 – 2.41 (m, 4H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 135.54 (q, *J* = 4.8 Hz), 133.63 (t, *J* = 1.9 Hz), 132.71 (d, *J* = 107.8 Hz), 132.43 (d, *J* = 3.5 Hz), 131.66 (d, *J* = 106.4 Hz), 130.68 (dd, *J* = 9.1, 4.7 Hz), 128.91 (dd, *J* = 9.9, 6.1 Hz), 128.55 (td, *J* = 6.8, 3.2 Hz), 24.56 – 23.40 (m). **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 27.56. **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{21}O_2P_2S_2^+$ 443.0453; found 443.0461.

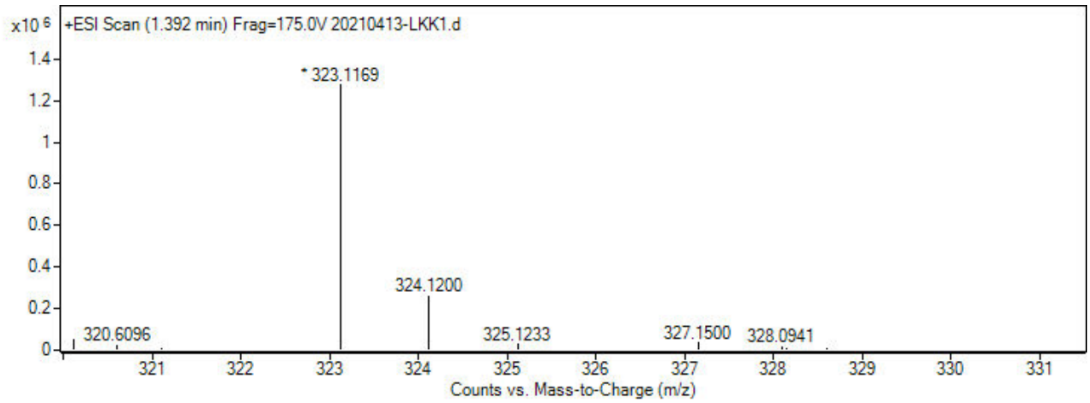



**diphenyl(2-(tetrahydrofuran-2-yl)ethyl)phosphine oxide**

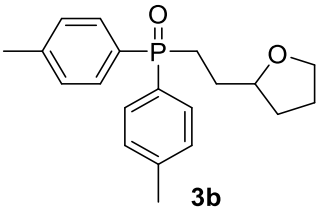


**3a**

White solid, 63.6 mg, 71% yield, m.p. 93-95 °C. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 12.8, 4.7 Hz, 4H), 7.54 – 7.39 (m, 6H), 3.86 (td, *J* = 11.7, 7.2 Hz, 1H), 3.80 (dd, *J* = 14.8, 7.0 Hz, 1H), 3.70 (dd, *J* = 14.7, 7.4 Hz, 1H), 2.52 (td, *J* = 15.0, 4.3 Hz, 1H), 2.28 (qd, *J* = 12.4, 4.2 Hz, 1H), 1.96 (dt, *J* = 12.4, 6.5 Hz, 1H), 1.91 – 1.79 (m, 3H), 1.77 – 1.66 (m, 1H), 1.50 – 1.38 (m, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 132.96 (dd, *J* = 98.4, 46.8 Hz), 131.68 (d, *J* = 2.3 Hz), 130.77 (dd, *J* = 14.1, 9.2 Hz), 128.63 (d, *J* = 12.2 Hz), 79.15 (d, *J* = 14.8 Hz), 67.69, 31.01, 27.31 (d, *J* = 3.3 Hz), 26.51 (d, *J* = 72.9 Hz), 25.64. **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 33.02. **HRMS** (ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{21}NaO_2P^+$ 323.1171; found 323.1169.

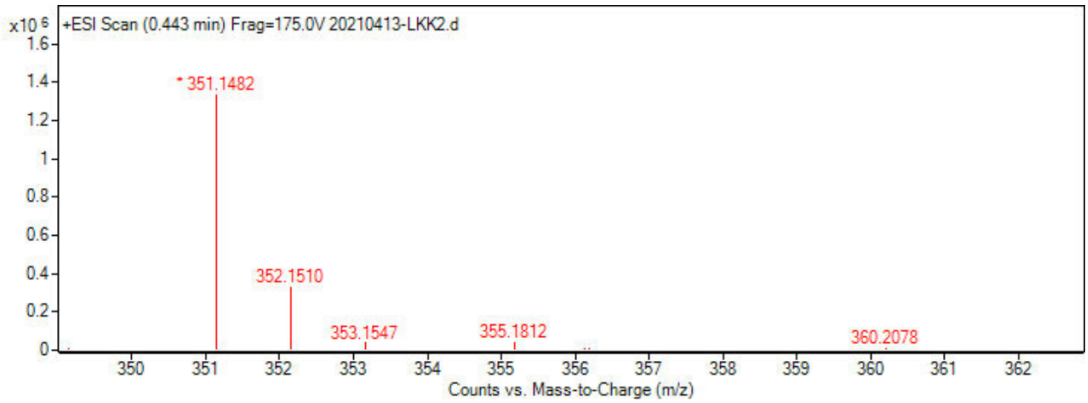


**(2-(tetrahydrofuran-2-yl)ethyl)di-p-tolylphosphine oxide**

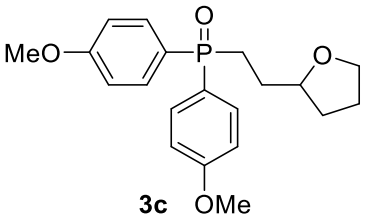


**3b**

Colorless liquid, 55.0 mg, 56% yield. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.62 (t, *J* = 8.2 Hz, 4H), 7.26 (t, *J* = 8.4 Hz, 4H), 3.79 (ddq, *J* = 51.3, 22.0, 7.3 Hz, 3H), 2.47 (td, *J* = 14.9, 4.4 Hz, 1H), 2.38 (s, 6H), 2.29 – 2.16 (m, 1H), 1.96 (dt, *J* = 12.4, 6.6 Hz, 1H), 1.91 – 1.76 (m, 3H), 1.75 – 1.63 (m, 1H), 1.45 (td, *J* = 15.6, 7.7 Hz, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 141.99 (d, *J* = 2.6 Hz), 130.78 (dd, *J* = 14.4, 9.6 Hz), 130.25 (dd, *J* = 99.8, 49.7 Hz), 129.32 (dd, *J* = 12.0, 2.2 Hz), 79.27 (d, *J* = 14.9 Hz), 67.70, 31.03, 27.40 (d, *J* = 3.5 Hz), 26.67 (d, *J* = 73.1 Hz), 25.66, 21.54. **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 33.08. **HRMS** (ESI) m/z: $[M + Na]^+$ calcd for $C_{20}H_{25}NaO_2P^+$ 351.1484; found 531.1482.

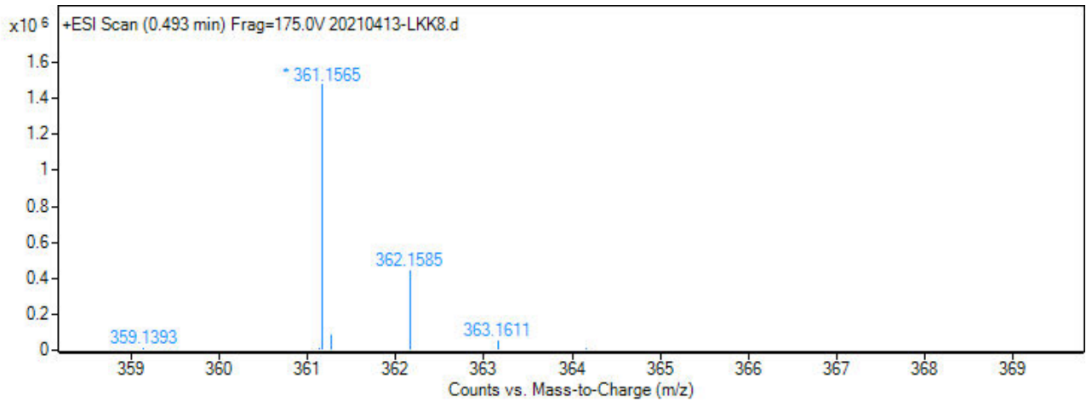



**bis(4-methoxyphenyl)(2-(tetrahydrofuran-2-yl)ethyl)phosphine oxide**

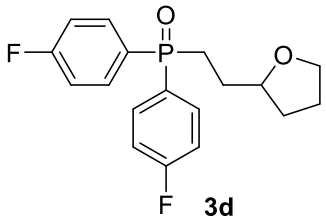


**3c**

Colorless liquid, 47.8 mg, 44% yield. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.76 – 7.55 (m, 4H), 6.96 (ddd, *J* = 8.8, 3.1, 2.3 Hz, 4H), 3.88 – 3.77 (m, 8H), 3.70 (dd, *J* = 15.0, 7.1 Hz, 1H), 2.44 (dddd, *J* = 15.0, 12.3, 10.7, 4.5 Hz, 1H), 2.27 – 2.15 (m, 1H), 1.96 (ddd, *J* = 12.1, 10.2, 6.3 Hz, 1H), 1.90 – 1.78 (m, 3H), 1.75 – 1.64 (m, 1H), 1.45 (ddd, *J* = 15.6, 12.1, 7.5 Hz, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 162.18 (d, *J* = 2.8 Hz), 132.58 (dd, *J* = 14.3, 10.6 Hz), 124.41 (dd, *J* = 104.9, 51.2 Hz), 114.14 (dd, *J* = 12.6, 2.3 Hz), 79.24 (d, *J* = 15.0 Hz), 67.68, 55.29, 31.02, 27.47 (d, *J* = 3.5 Hz), 26.92 (d, *J* = 73.8 Hz), 25.65. **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 32.88. **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{26}O_4P^+$ 361.1563; found 561.1565.

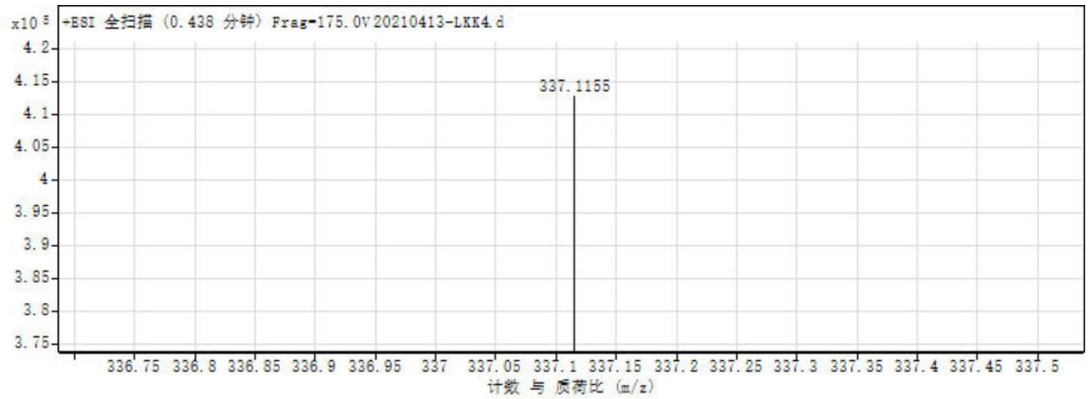



**bis(4-fluorophenyl)(2-(tetrahydrofuran-2-yl)ethyl)phosphine oxide**

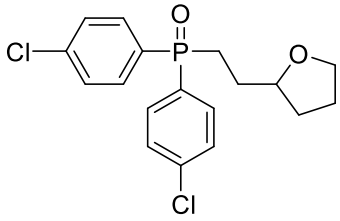


**3d**

Colorless liquid, 44.1 mg, 44% yield. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.82 – 7.63 (m, 4H), 7.17 (tdd, *J* = 8.6, 3.6, 2.0 Hz, 4H), 3.91 – 3.76 (m, 2H), 3.70 (dd, *J* = 15.1, 7.1 Hz, 1H), 2.55 – 2.45 (m, 1H), 2.26 (dtd, *J* = 16.5, 12.2, 4.4 Hz, 1H), 1.98 (dt, *J* = 12.4, 6.5 Hz, 1H), 1.91 – 1.80 (m, 3H), 1.67 (tdd, *J* = 13.7, 8.4, 4.2 Hz, 1H), 1.45 (ddd, *J* = 15.5, 12.2, 7.7 Hz, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 164.98 (d, *J* = 250.3 Hz), 133.36 – 133.07 (m) 128.69 (ddd, *J* = 101.7, 53.9, 3.4 Hz), 116.14 (ddd, *J* = 21.3, 12.8, 2.7 Hz), 79.01 (d, *J* = 14.8 Hz), 67.75, 31.06, 27.29 (d, *J* = 3.6 Hz), 26.72 (d, *J* = 73.8 Hz), 25.67. **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 31.89. **$^{19}$F NMR** (471 MHz, $CDCl_3$) δ -106.66. **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{20}F_2O_2P^+$ 337.1163; found 337.1155.



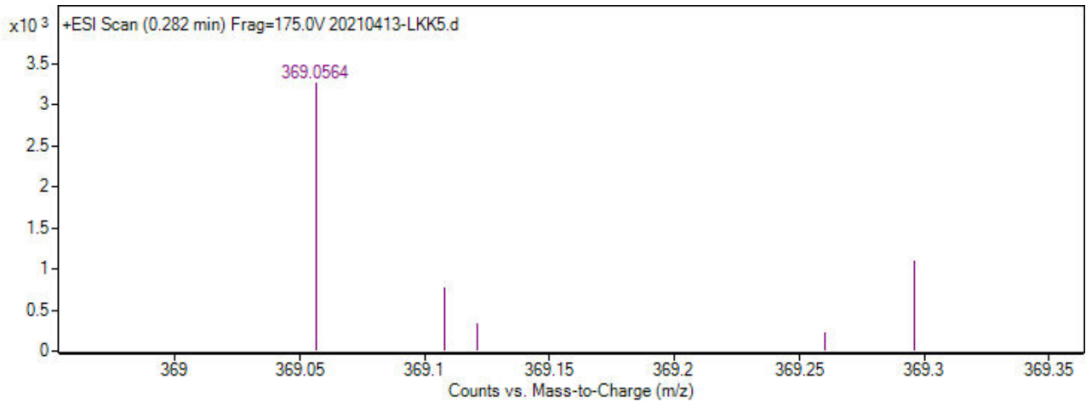

**bis(4-chlorophenyl)(2-(tetrahydrofuran-2-yl)ethyl)phosphine oxide**



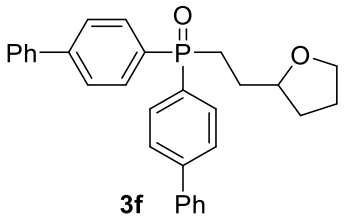
**3e**

Colorless liquid, 59.7 mg, 54% yield. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.71 – 7.61 (m, 4H), 7.46 (ddd, *J* = 8.3,

3.6, 2.2 Hz, 4H), 3.85 (ddd, *J* = 10.9, 7.1, 3.7 Hz, 1H), 3.80 (dd, *J* = 15.1, 6.9 Hz, 1H), 3.70 (dd, *J* = 15.1, 7.1 Hz, 1H), 2.54 – 2.46 (m, 1H), 2.33 – 2.19 (m, 1H), 1.97 (dt, *J* = 12.4, 6.5 Hz, 1H), 1.90 – 1.81 (m, 3H), 1.66 (dddd, *J* = 21.6, 12.9, 8.5, 4.4 Hz, 1H), 1.45 (ddd, *J* = 15.5, 12.2, 7.7 Hz, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 138.59 (d, *J* = 3.4 Hz), 132.12 (dd, *J* = 15.2, 10.2 Hz), 131.02 (dd, *J* = 99.8, 50.2 Hz), 129.15 (dd, *J* = 12.1, 2.7 Hz), 78.93 (d, *J* = 14.7 Hz), 67.75, 31.06, 27.21 (d, *J* = 3.6 Hz), 26.37 (d, *J* = 73.7 Hz), 25.66. **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 32.17. **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{20}Cl_2O_2P^+$ 369.0572; found 369.0564.

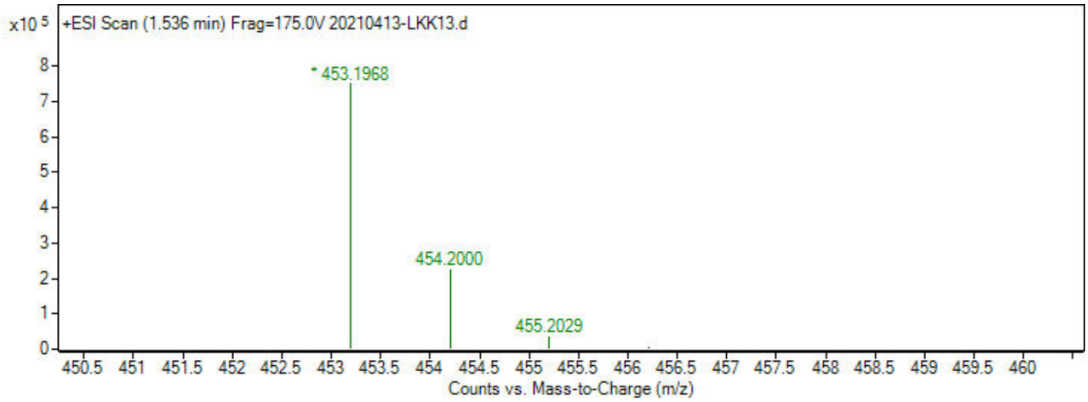



**di([1,1'-biphenyl]-4-yl)(2-(tetrahydrofuran-2-yl)ethyl)phosphine oxide**

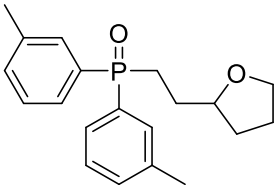



**3f**

White solid, 57.6 mg, 43% yield, m.p. 168-170 ºC. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.85 (ddd, *J* = 11.0, 8.3, 2.7 Hz, 4H), 7.69 (dt, *J* = 8.0, 2.7 Hz, 4H), 7.59 (dd, *J* = 7.4, 1.6 Hz, 4H), 7.45 (t, *J* = 7.6 Hz, 4H), 7.38 (t, *J* = 7.2 Hz, 2H), 3.90 (td, *J* = 11.5, 7.3 Hz, 1H), 3.83 (dd, *J* = 14.9, 6.9 Hz, 1H), 3.71 (dd, *J* = 14.8, 7.4 Hz, 1H), 2.66 – 2.52 (m, 1H), 2.40 – 2.29 (m, 1H), 2.02 – 1.74 (m, 5H), 1.48 (ddd, *J* = 15.7, 12.2, 7.6 Hz, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 144.52 (d, *J* = 2.1 Hz), 139.94, 131.66 (dd, *J* = 99.7, 48.2 Hz), 131.33 (dd, *J* = 14.4, 9.6 Hz), 128.94, 128.12, 127.37 (dd, *J* = 11.9, 1.8 Hz), 127.25, 79.25 (d, *J* = 14.9 Hz), 67.77, 31.09, 27.44 (d, *J* = 3.5 Hz), 26.73 (d, *J* = 73.2 Hz), 25.71. **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 32.66. **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{30}H_{30}O_2P^+$ 453.1978; found 453.1968.

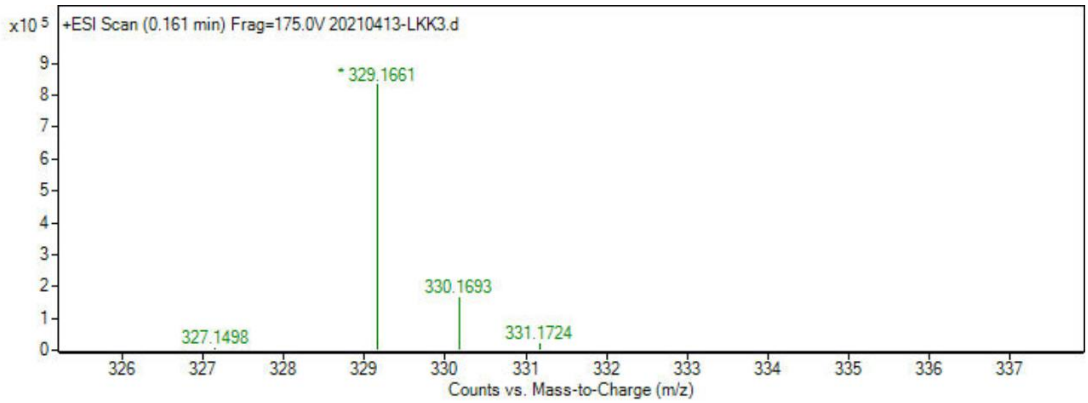



**(2-(tetrahydrofuran-2-yl)ethyl)di-m-tolylphosphine oxide**

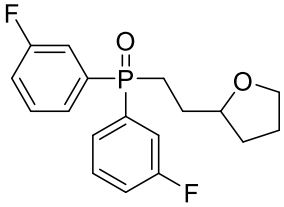


**3g**

Colorless liquid, 59.3 mg, 60% yield. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 9.9 Hz, 2H), 7.54 – 7.42 (m, 2H), 7.38 – 7.27 (m, 4H), 3.94 – 3.62 (m, 3H), 2.50 (ddd, *J* = 22.0, 15.0, 4.3 Hz, 1H), 2.37 (s, 6H), 2.25 (td, *J* = 15.9, 4.0 Hz, 1H), 1.97 (dt, *J* = 12.4, 6.6 Hz, 1H), 1.92 – 1.77 (m, 3H), 1.71 (dq, *J* = 12.8, 8.1 Hz, 1H), 1.46 (td, *J* = 15.5, 7.6 Hz, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 138.48 (dd, *J* = 11.5, 2.2 Hz), 132.84 (dd, *J* = 98.0, 50.4 Hz), 132.43 (d, *J* = 2.7 Hz), 131.33 (dd, *J* = 16.4, 8.9 Hz), 128.45 (dd, *J* = 12.3, 1.4 Hz), 127.67 (dd, *J* = 13.4, 9.6 Hz), 79.26 (d, *J* = 14.9 Hz), 67.69, 31.04, 27.33 (d, *J* = 3.5 Hz), 26.53 (d, *J* = 72.7 Hz), 25.65, 21.41. **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 32.99. **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{26}O_2P^+$ 329.1665; found 329.1661.

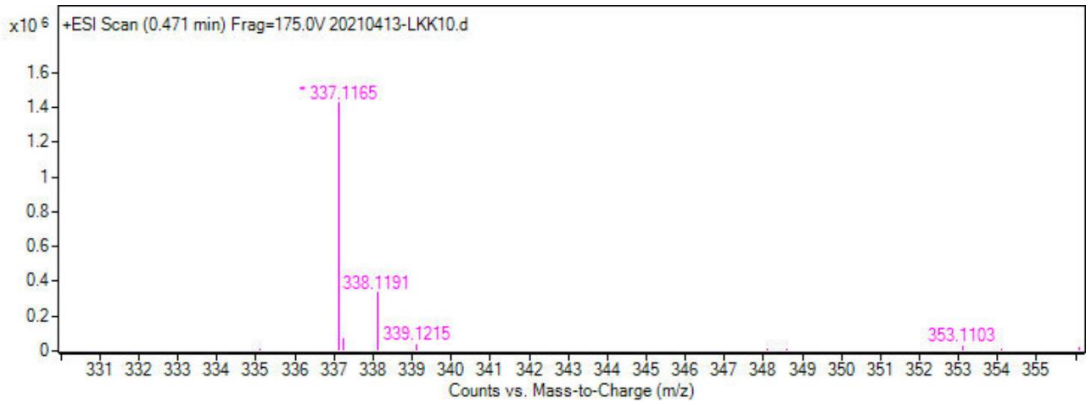



**bis(3-fluorophenyl)(2-(tetrahydrofuran-2-yl)ethyl)phosphine oxide**

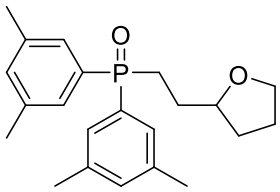


**3h**

Colorless liquid, 50.2 mg, 50% yield. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.56 – 7.40 (m, 6H), 7.22 (t, *J* = 8.3 Hz, 2H), 3.91 – 3.77 (m, 2H), 3.71 (dd, *J* = 15.1, 7.1 Hz, 1H), 2.58 – 2.47 (m, 1H), 2.28 (dtd, *J* = 16.5, 12.2, 4.5 Hz, 1H), 1.99 (dt, *J* = 12.4, 6.5 Hz, 1H), 1.93 – 1.82 (m, 3H), 1.75 – 1.64 (m, 1H), 1.46 (ddd, *J* = 15.5, 12.2, 7.7 Hz, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 162.69 (ddd, *J* = 250.9, 16.4, 3.0 Hz), 135.22 (ddd, *J* = 97.5, 46.8, 5.5 Hz), 130.80 (ddd, *J* = 13.7, 7.4, 1.7 Hz), 126.36 (ddd, *J* = 14.7, 8.9, 3.1 Hz), 119.16 (dd, *J* = 21.1, 2.0 Hz), 117.73 (ddd, *J* = 22.5, 15.0, 10.1 Hz), 78.92 (d, *J* = 14.8 Hz), 67.75, 31.06, 27.18 (d, *J* = 3.7 Hz), 26.32 (d, *J* = 73.7 Hz), 25.66. **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 31.19. **$^{19}$F NMR** (471 MHz, $CDCl_3$) δ -110.57 (d, *J* = 4.8 Hz). **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{20}F_2O_2P^+$ 337.1163; found 337.1165.

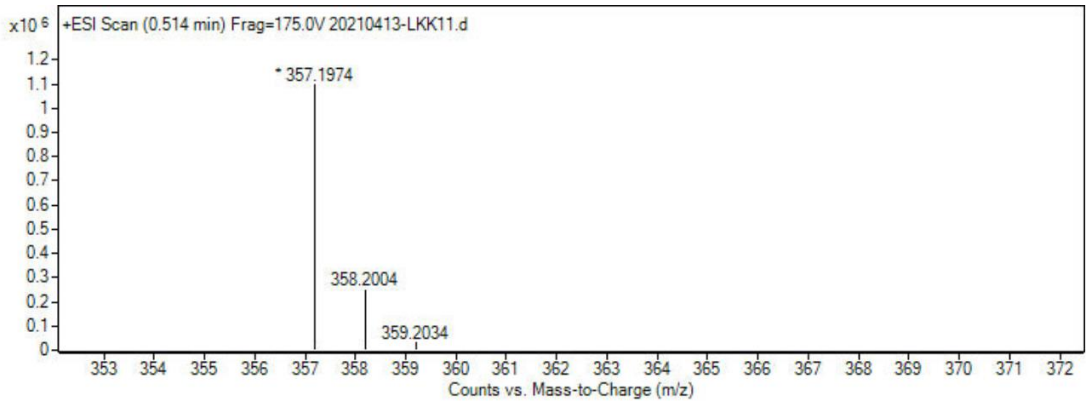



**bis(3,5-dimethylphenyl)(2-(tetrahydrofuran-2-yl)ethyl)phosphine oxide**

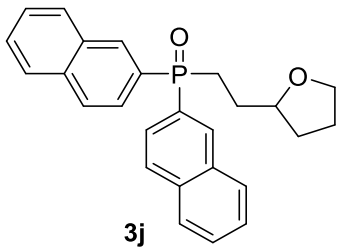


**3i**

White solid, 39.3 mg, 37% yield, m.p. 70-73 ºC. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 11.7 Hz, 4H), 7.11 (s, 2H), 3.87 (td, *J* = 11.5, 7.1 Hz, 1H), 3.81 (dd, *J* = 15.0, 6.9 Hz, 1H), 3.71 (dd, *J* = 14.6, 7.5 Hz, 1H), 2.48 (dddd, *J* = 14.8, 12.3, 10.5, 4.4 Hz, 1H), 2.33 (d, *J* = 1.9 Hz, 12H), 2.26 – 2.17 (m, 1H), 1.97 (ddd, *J* = 12.2, 10.2, 6.4 Hz, 1H), 1.90 – 1.79 (m, 3H), 1.75 – 1.64 (m, 1H), 1.46 (ddd, *J* = 15.6, 12.2, 7.5 Hz, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 138.24 (dd, *J* = 12.2, 1.3 Hz), 133.32 (d, *J* = 1.8 Hz), 132.89 (dd, *J* = 97.6, 57.4 Hz), 128.29 (dd, *J* = 16.3, 9.3 Hz), 79.36 (d, *J* = 14.9 Hz), 67.66, 31.07, 27.35 (d, *J* = 3.5 Hz), 26.53 (d, *J* = 72.5 Hz), 25.65, 21.29. **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 32.96. **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{30}O_2P^+$ 357.1978; found 357.1974.

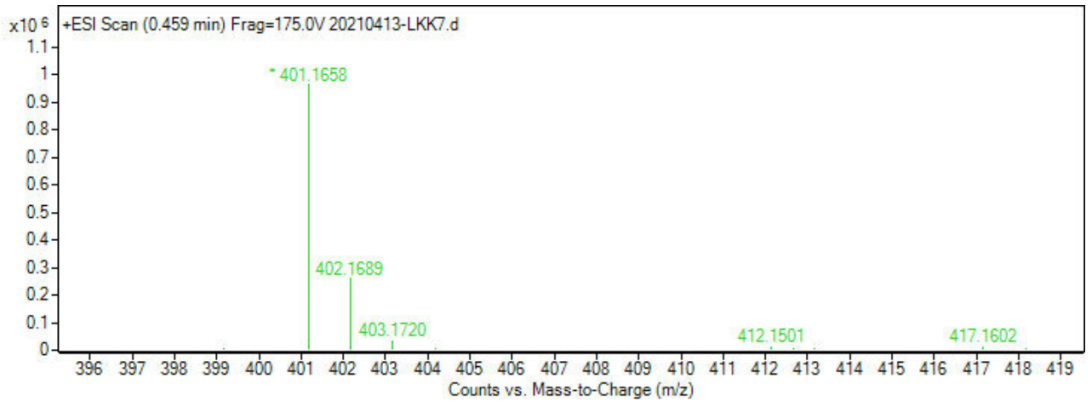



**di(naphthalen-2-yl)(2-(tetrahydrofuran-2-yl)ethyl)phosphine oxide**

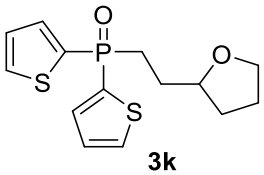


**3j**

Colorless liquid, 46.7 mg, 46% yield. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 8.44 (dd, *J* = 13.2, 7.3 Hz, 2H), 7.98 – 7.80 (m, 6H), 7.71 (t, *J* = 8.6 Hz, 2H), 7.57 (td, *J* = 14.8, 7.1 Hz, 4H), 3.91 (td, *J* = 11.1, 7.2 Hz, 1H), 3.81 (dd, *J* = 15.0, 6.9 Hz, 1H), 3.72 (dd, *J* = 15.0, 7.1 Hz, 1H), 2.85 – 2.63 (m, 1H), 2.54 – 2.39 (m, 1H), 1.96 (tt, *J* = 8.4, 5.4 Hz, 2H), 1.84 (dt, *J* = 13.6, 6.9 Hz, 3H), 1.46 (ddd, *J* = 15.4, 12.3, 7.7 Hz, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ134.65 (d, *J* = 2.3 Hz), 132.78 (dd, *J* = 24.1, 8.5 Hz), 132.56 (d, *J* = 2.3 Hz), 130.04 (dd, *J* = 99.0, 49.7 Hz), 128.91, 128.58 (dd, *J* = 11.4, 2.4 Hz), 128.13, 127.83, 126.97, 125.71 (dd, *J* = 10.2, 8.8 Hz), 79.26 (d, *J* = 14.8 Hz), 67.75, 31.13, 27.48 (d, *J* = 3.4 Hz), 26.42 (d, *J* = 73.2 Hz), 25.68. **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 33.19. **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{26}H_{26}O_2P^+$ 401.1665; found 401.1658.

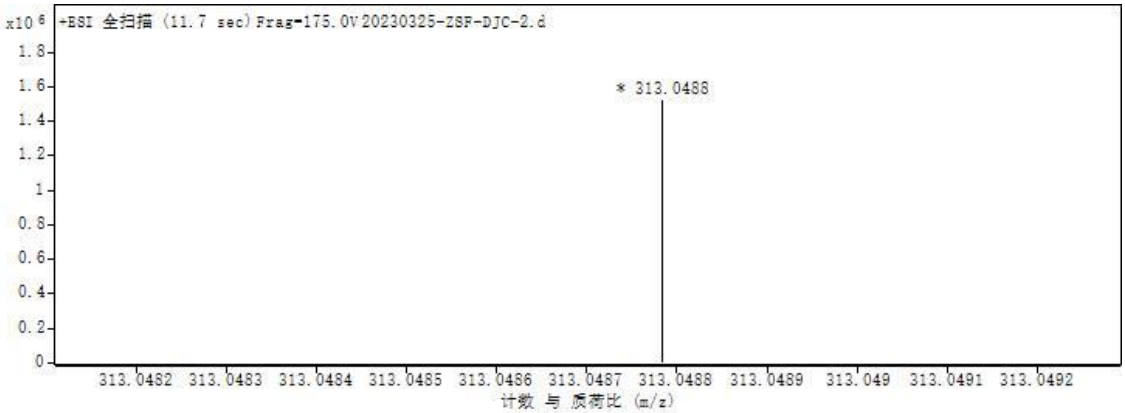



**(2-(tetrahydrofuran-2-yl)ethyl)di(thiophen-2-yl)phosphine oxide**

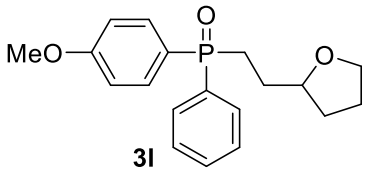


**3k**

Colorless liquid, 41.4 mg, 22% yield. **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.72 (t, *J* = 4.4 Hz, 2H), 7.61 (dd, *J* = 7.2, 3.6 Hz, 2H), 7.20 (td, *J* = 3.5, 1.8 Hz, 2H), 3.93 – 3.77 (m, 2H), 3.71 (dd, *J* = 14.6, 7.5 Hz, 1H), 2.52 (dtd, *J* = 16.5, 11.9, 4.7 Hz, 1H), 2.39 – 2.21 (m, 1H), 2.02 – 1.93 (m, 1H), 1.92 – 1.78 (m, 4H), 1.48 (ddd, *J* = 15.3, 12.0, 7.5 Hz, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 135.42 (t, *J* = 9.9 Hz), 134.1 (dd, *J* = 113.4, 32.8 Hz), 133.29 (t, J = 6.3 Hz), 128.37 (d, *J* = 13.9 Hz), 78.97 (d, *J* = 16.2 Hz), 67.78, 31.07 (d, *J* = 3.3 Hz), 30.77 (d, *J* = 80.7 Hz), 27.54 (d, *J* = 3.7 Hz), 25.67. $^{31}$P NMR (202 MHz, $CDCl_3$) δ 22.71. **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{18}O_2PS_2^+$ 313.0480; found 313.0488.

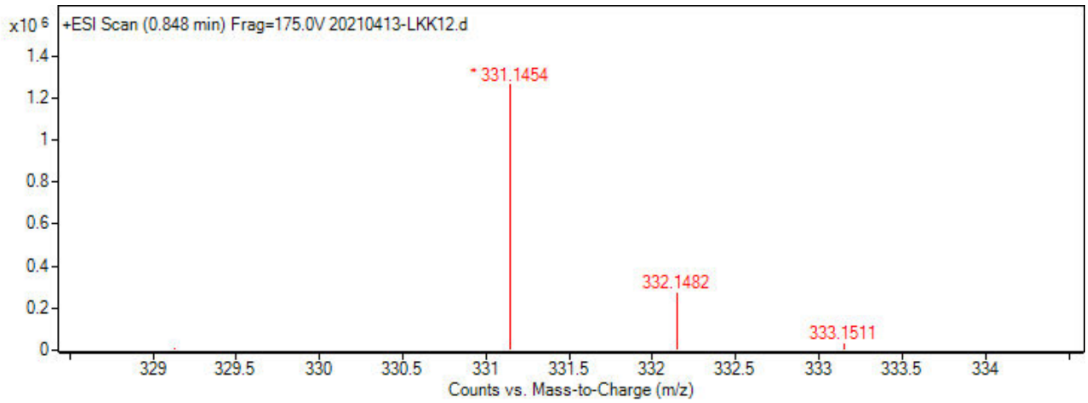



**(4-methoxyphenyl)(phenyl)(2-(tetrahydrofuran-2-yl)ethyl)phosphine oxide**

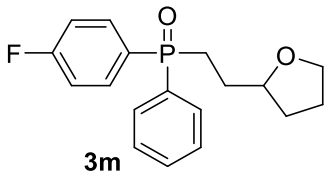



**3l**

Colorless liquid, 40.6 mg, 41% yield. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.70 (dddd, *J* = 22.7, 11.7, 5.8, 2.4 Hz, 4H), 7.47 (tt, *J* = 8.2, 7.1 Hz, 3H), 7.04 – 6.91 (m, 2H), 3.90 – 3.77 (m, 5H), 3.70 (dd, *J* = 14.7, 7.4 Hz, 1H), 2.48 (ddd, *J* = 15.0, 13.6, 4.4 Hz, 1H), 2.24 (ddd, *J* = 27.3, 12.4, 4.3 Hz, 1H), 2.01 – 1.92 (m, 1H), 1.84 (dt, *J* = 12.3, 6.0 Hz, 3H), 1.71 (ttd, *J* = 11.9, 8.0, 4.0 Hz, 1H), 1.51 – 1.39 (m, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 162.32, 133.44 (dd, *J* = 99.0, 47.4 Hz), 132.66 (dd, *J* = 14.5, 10.6 Hz), 131.54 (d, *J* = 2.6 Hz), 130.73 (dd, *J* = 14.6, 9.3 Hz), 128.57 (d, *J* = 10.7 Hz), 123.90 (dd, *J* = 104.4, 52.1 Hz), 114.24 (dd, *J* = 12.7, 2.5 Hz), 79.22 (dd, *J* = 14.8, 2.2 Hz), 67.70, 55.31, 31.03 (d, *J* = 3.0 Hz), 27.39 (t, *J* = 2.7 Hz), 26.71 (dd, *J* = 73.4, 5.6 Hz), 25.65. **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 32.96 (d, *J* = 4.4 Hz). **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{24}O_3P^+$ 331.1458; found 331.1454.

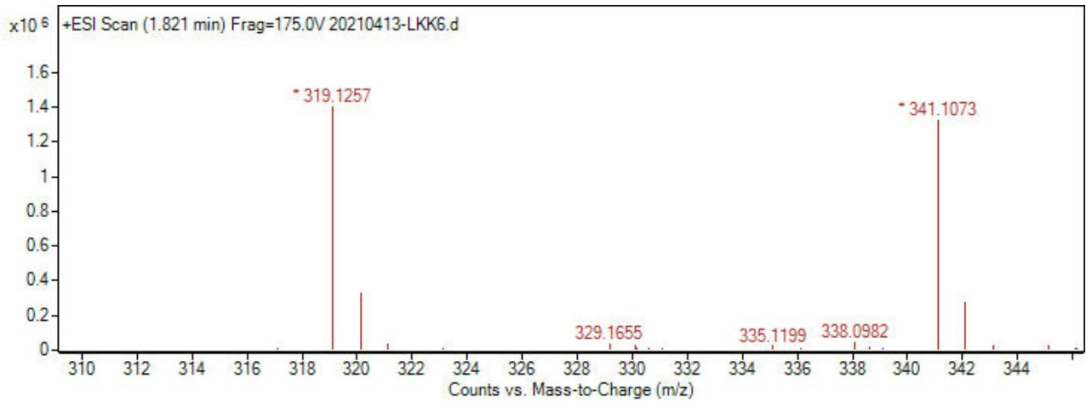



**(4-fluorophenyl)(phenyl)(2-(tetrahydrofuran-2-yl)ethyl)phosphine oxide**

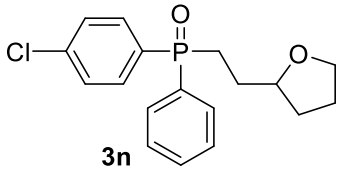



**3m**

Colorless liquid, 40.4 mg, 42% yield. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.80 – 7.69 (m, 4H), 7.56 – 7.50 (m, 1H), 7.50 – 7.45 (m, 2H), 7.16 (tdd, *J* = 8.5, 3.5, 1.9 Hz, 2H), 3.91 – 3.75 (m, 2H), 3.70 (dd, *J* = 15.0, 7.1 Hz, 1H), 2.61 – 2.43 (m, 1H), 2.32 – 2.21 (m, 1H), 1.97 (dt, *J* = 12.5, 6.6 Hz, 1H), 1.92 – 1.79 (m, 3H), 1.76 – 1.62 (m, 1H), 1.45 (ddd, *J* = 15.5, 12.3, 7.6 Hz, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 164.90 (d, *J* = 253.0 Hz), 133.25 (ddd, *J* = 15.2, 10.6, 8.7 Hz), 132.42 (dd, *J* = 83.4, 49.3 Hz), 131.83 (d, *J* = 2.6 Hz), 130.70 (dd, *J* = 14.9, 9.3 Hz), 128.93 (dd, *J* = 102.3, 50.1 Hz), 128.72 (dd, *J* = 11.7, 1.9 Hz), 115.99 (ddd, *J* = 21.4, 12.7, 2.4 Hz), 79.08 (dd, *J* = 14.8, 3.0 Hz), 67.72, 31.04 (d, *J* = 3.9 Hz), 27.31 (dd, *J* = 3.3, 2.4 Hz), 26.62 (dd, *J* = 73.4, 3.9 Hz), 25.66. **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 32.30. **$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -107.08 (d, *J* = 5.5 Hz). **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{21}FO_2P^+$ 319.1258; found 319.1257.

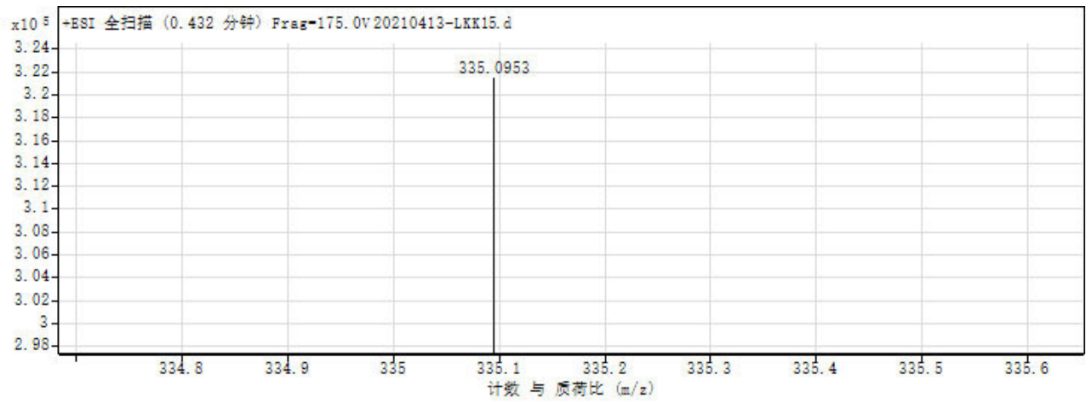



**(4-chlorophenyl)(phenyl)(2-(tetrahydrofuran-2-yl)ethyl)phosphine oxide**

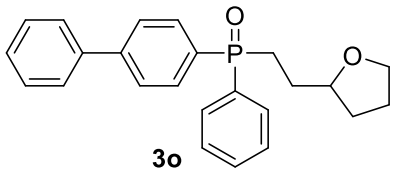



**3n**

Colorless liquid, 49.2 mg, 49% yield. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.79 – 7.62 (m, 4H), 7.57 – 7.41 (m, 5H), 3.92 – 3.75 (m, 2H), 3.74 – 3.66 (m, 1H), 2.58 – 2.44 (m, 1H), 2.26 (dddd, *J* = 23.0, 15.0, 12.1, 4.4 Hz, 1H), 1.97 (dt, *J* = 12.3, 6.6 Hz, 1H), 1.91 – 1.79 (m, 3H), 1.76 – 1.63 (m, 1H), 1.45 (ddd, *J* = 15.5, 12.1, 7.6 Hz, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 138.26 (d, *J* = 3.3 Hz), 132.97 (d, *J* = 47.9 Hz), 132.23 (dd, *J* = 15.3, 10.0 Hz), 131.91 (d, *J* = 2.7 Hz), 131.22 (d, *J* = 49.7 Hz), 130.69 (dd, *J* = 14.6, 9.3 Hz), 128.99 (dd, *J* = 12.1, 2.4 Hz), 128.76 (dd, *J* = 11.7, 2.1 Hz), 79.06 (dd, *J* = 14.8, 4.5 Hz), 67.73, 31.05 (d, *J* = 4.2 Hz), 27.29 (t, *J* = 3.8 Hz), 26.47 (dd, *J* = 73.3, 5.5 Hz), 25.66. **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 32.30. **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{21}ClO_2P^+$ 335.0962; found 335.0953.



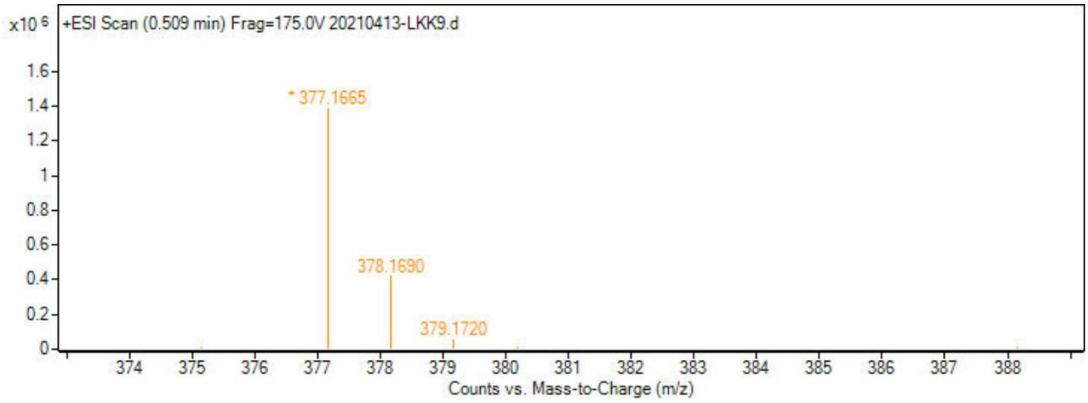

**[1,1'-biphenyl]-4-yl(phenyl)(2-(tetrahydrofuran-2-yl)ethyl)phosphine oxide**



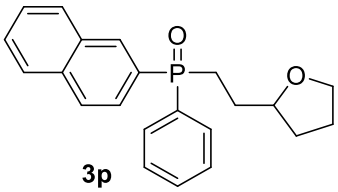

**3o**

White solid, 51.3 mg, 45% yield, m.p. 131-134 °C. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.87 – 7.75 (m, 4H), 7.68 (dd, *J* = 5.2, 2.9 Hz, 2H), 7.62 – 7.56 (m, 2H), 7.53 – 7.42 (m, 5H), 7.37 (t, *J* = 7.3 Hz, 1H), 3.84 (ddd, *J* = 21.7, 10.8, 5.6 Hz, 2H), 3.70 (dd, *J* = 14.9, 7.3 Hz, 1H), 2.63 – 2.49 (m, 1H), 2.36 – 2.24 (m, 1H), 2.01 – 1.80 (m, 4H), 1.74 (dtd, *J* = 16.5, 8.2, 4.1 Hz, 1H), 1.47 (ddd, *J* = 15.4, 12.3, 7.6 Hz, 1H). **$^{13}$C NMR** (126 MHz,

$CDCl_3$) δ 144.49 (d, *J* = 2.5 Hz), 139.94, 133.10 (dd, *J* = 98.6, 47.2 Hz), 131.72 (d, *J* = 2.6 Hz), 131.58 (dd, *J* = 99.5, 48.7 Hz), 131.33 (dd, *J* = 14.6, 9.5 Hz), 130.81 (dd, *J* = 14.5, 9.3 Hz), 128.94, 128.69 (dd, *J* = 11.6, 1.7 Hz), 128.11, 127.33 (dd, *J* = 11.9, 1.8 Hz), 127.25, 79.22 (dd, *J* = 14.9, 2.5 Hz), 67.74, 31.07 (d, *J* = 0.9 Hz), 27.41 – 27.37 (m), 26.64 (dd, *J* = 73.1, 3.5 Hz), 25.69. **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 32.72. **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{26}O_2P^+$ 377.1665; found 377.1665.

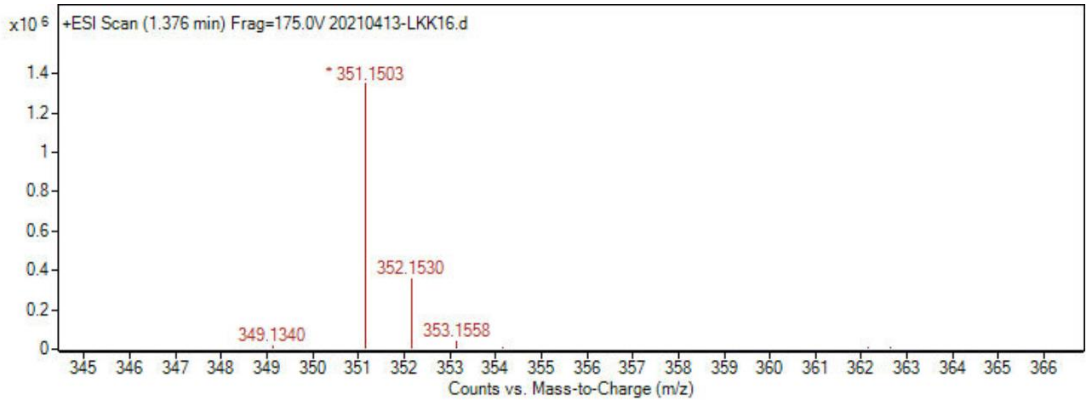



**naphthalen-2-yl(phenyl)(2-(tetrahydrofuran-2-yl)ethyl)phosphine oxide**

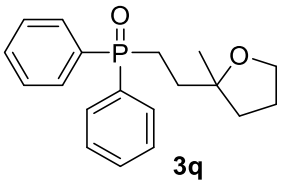



**3p**

Colorless liquid, 52.1 mg, 50% yield. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 8.41 (dd, *J* = 13.1, 6.3 Hz, 1H), 7.96 – 7.84 (m, 3H), 7.83 – 7.74 (m, 2H), 7.67 (t, *J* = 8.9 Hz, 1H), 7.61 – 7.42 (m, 5H), 3.88 (dq, *J* = 13.8, 6.9 Hz, 1H), 3.84 – 3.76 (m, 1H), 3.70 (dd, *J* = 14.8, 7.3 Hz, 1H), 2.70 – 2.55 (m, 1H), 2.45 – 2.30 (m, 1H), 2.01 – 1.66 (m, 5H), 1.50 – 1.40 (m, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 134.61 (d, *J* = 2.2 Hz), 133.03 (dd, *J* = 98.8, 45.5 Hz), 132.80 (dd, *J* = 23.6, 8.4 Hz), 132.57 (dd, *J* = 12.7, 2.6 Hz), 131.77 (d, *J* = 2.5 Hz), 130.79 (dd, *J* = 14.1, 9.5 Hz), 129.80 (dd, *J* = 98.8, 50.0 Hz), 128.87, 128.70 (dd, *J* = 11.9, 1.4 Hz), 128.53 (dd, *J* = 11.5, 2.0 Hz), 128.12, 127.81, 126.96, 125.63 (dd, *J* = 10.3, 9.2 Hz), 79.19 (dd, *J* = 14.7, 4.5 Hz), 67.72 (d, *J* = 2.0 Hz), 31.06, 27.37 (t, *J* = 4.0 Hz), 26.41 (dd, *J* = 72.9, 4.3 Hz), 25.65. **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 33.29. **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{24}O_2P^+$ 351.1508; found 351.1503.

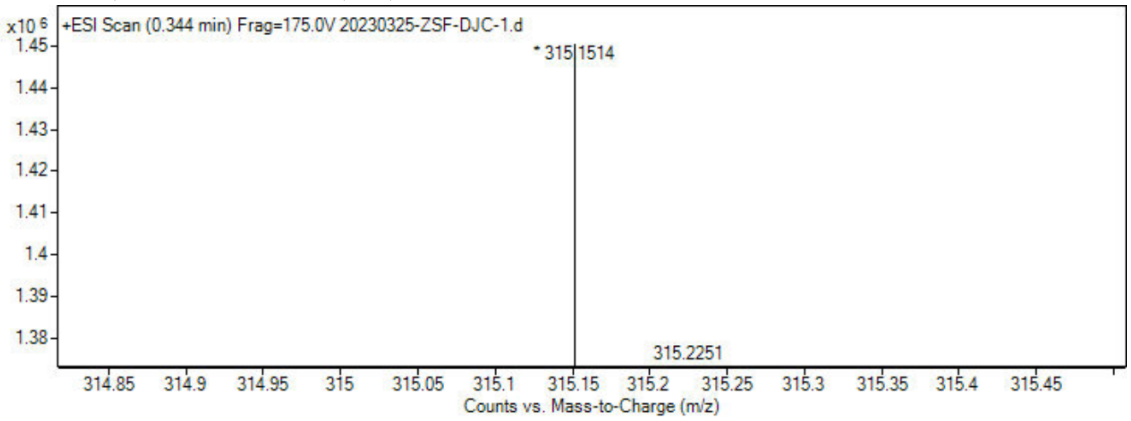



**(2-(2-methyltetrahydrofuran-2-yl)ethyl)diphenylphosphine oxide**

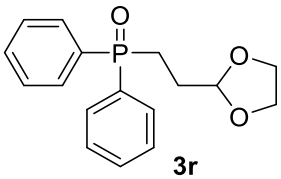


**3q**

Colorless liquid, 45.0 mg, 48% yield (**3q**/**3q'** = 2.3:1). **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.81 – 7.67 (m, 4H), 7.56 – 7.42 (m, 6H), 4.01 (dd, *J* = 12.7, 6.1 Hz, 1H), 3.97 – 3.85 (m, 1H), 3.82 (dd, *J* = 14.1, 7.5 Hz, 1H), 3.70 (dd, *J* = 14.7, 7.3 Hz, 1H), 2.46 – 2.22 (m, 2H), 2.00 – 1.58 (m, 6H), 1.19 (s, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 131.89 (d, *J* = 98.9 Hz), 130.71 (d, *J* = 2.3 Hz), 129.78 (t, *J* = 9.5 Hz), 127.65 (dd, *J* = 11.7, 2.5 Hz), 80.85 (d, *J* = 14.0 Hz), 66.32, 36.00, 31.77 (d, *J* = 224.3 Hz), 30.82 (d, *J* = 3.3 Hz), 24.96, 24.40. **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 34.12. **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{24}O_2P^+$ 351.1508; found 315.1514.

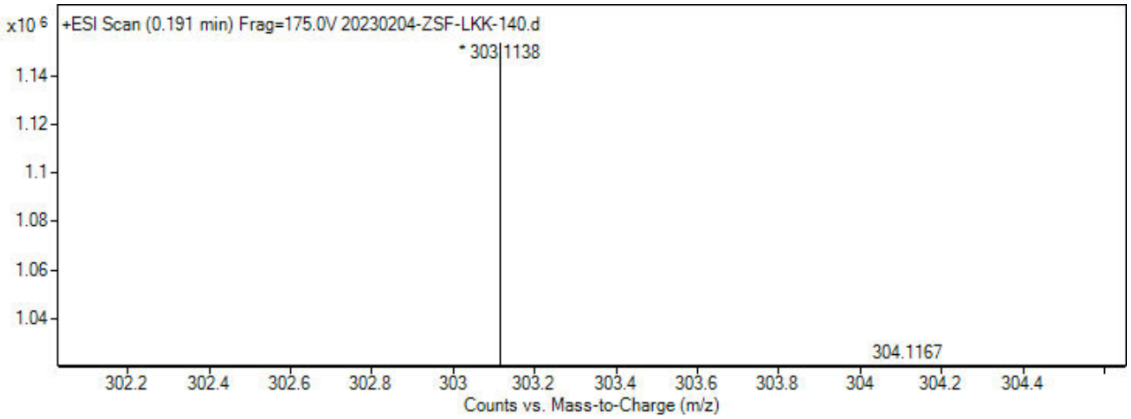



**(2-(1,3-dioxolan-2-yl)ethyl)diphenylphosphine oxide**

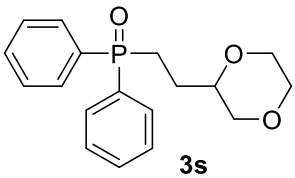


**3r**

Colorless liquid, 30.5 mg (**3r**/**3r'** = 5.5:1), 34% yield. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 11.2, 7.3 Hz, 4H), 7.56 – 7.42 (m, 6H), 4.96 (t, *J* = 4.1 Hz, 1H), 3.99 – 3.78 (m, 4H), 2.47 – 2.31 (m, 2H), 1.97 (ddd, *J* = 16.5, 8.1, 4.2 Hz, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 132.62 (d, *J* = 99.2 Hz), 31.82 (d, *J* = 2.5 Hz), 130.84 (d, *J* = 9.3 Hz), 128.71 (d, *J* = 11.5 Hz), 103.51 (d, *J* = 16.3 Hz), 65.08, 25.82 (d, *J* = 2.7 Hz), δ 23.46 (d, *J* = 73.9 Hz). **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 32.96. **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{20}O_3P^+$ 303.1145; found 303.1138.

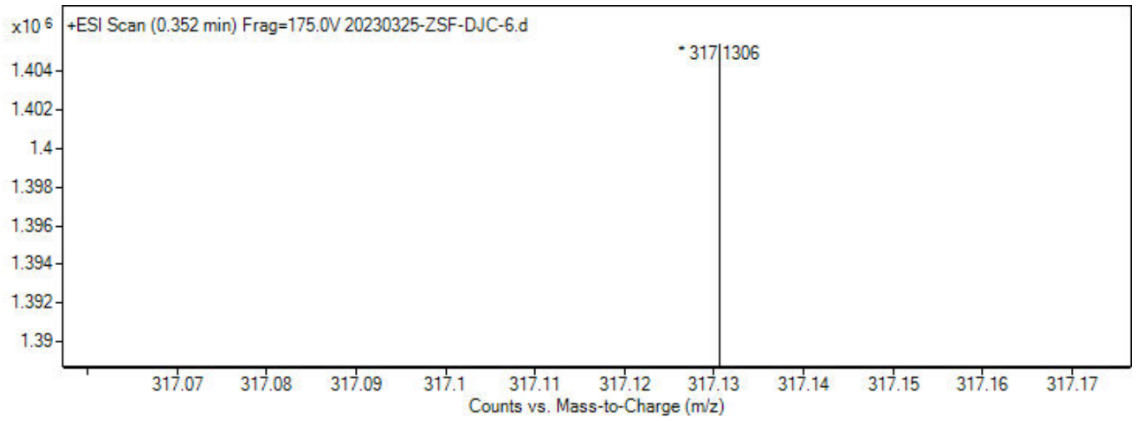



**(2-(1,4-dioxan-2-yl)ethyl)diphenylphosphine oxide**

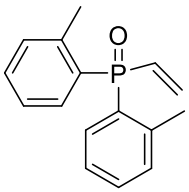


**3s**

Colorless liquid, 36.1 mg, 38% yield. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.88 – 7.63 (m, 4H), 7.50 (dd, *J* = 19.8, 6.7 Hz, 6H), 3.76 – 3.49 (m, 6H), 3.22 (t, *J* = 10.6 Hz, 1H), 2.62 – 2.49 (m, 1H), 2.37 – 2.19 (m, 1H), 1.75 (s, 1H), 1.67 – 1.54 (m, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 132.50 (dd, *J* = 98.9, 67.5 Hz),131.90 (d, *J* = 2.4 Hz), 130.77 (dd, *J* = 15.3, 9.4 Hz), 128.76 (dd, *J* = 11.8, 5.5 Hz), 75.11 (d, *J* = 13.5 Hz), 70.87, 66.73, 66.40, 25.28 (d, *J* = 72.9 Hz), 23.41 (d, *J* = 3.4 Hz). $^{31}$P NMR (202 MHz, $CDCl_3$) δ 35.46. **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{22}O_3P^+$ 317.1301; found 317.1306.

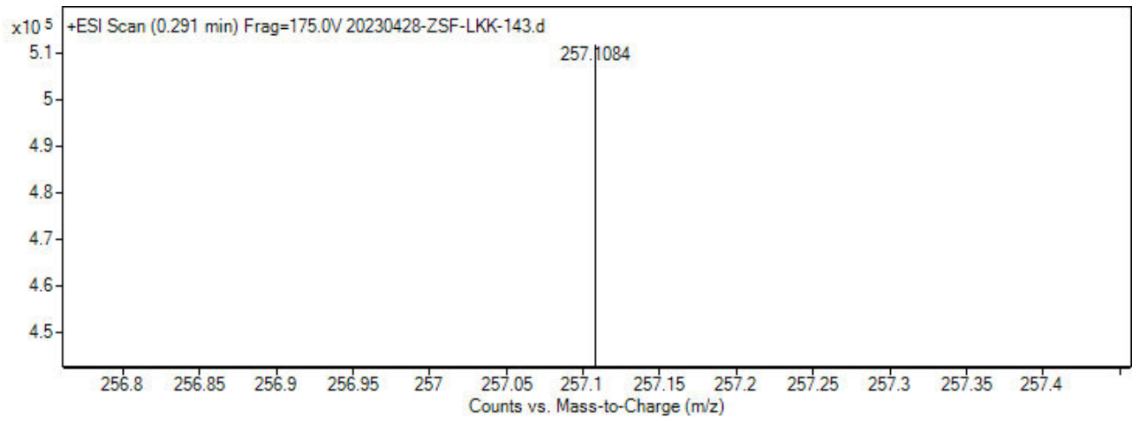



**di-o-tolyl(vinyl)phosphine oxide**

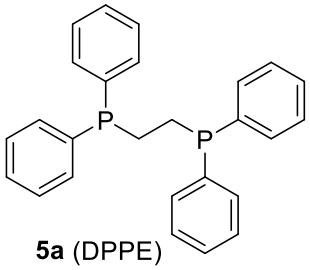


**4h**

Colorless liquid, 15.8 mg, 21% yield. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 13.8, 7.7 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.29 – 7.18 (m, 4H), 6.75 (ddd, *J* = 24.7, 18.5, 12.6 Hz, 1H), 6.40 – 6.24 (m, 2H), 2.39 (s, 6H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 142.06 (d, *J* = 8.5 Hz), 134.61, 132.38 (d, *J* = 11.9 Hz), 131.94 (d, *J* = 2.2 Hz), 131.76 (d, *J* = 10.8 Hz), 131.17 (d, *J* = 97.4 Hz), 130.91 (d, *J* = 102.5 Hz), 125.70 (d, *J* = 12.5 Hz), 21.40 (d, *J* = 4.2 Hz). **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ 26.52. **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{18}OP^+$ 257.1090; found 257.1084.



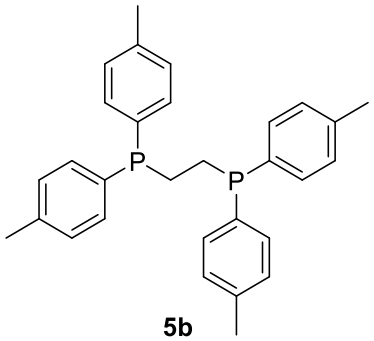
**1,2-bis(diphenylphosphanyl)ethane (DPPE)[4]**




**5a** (DPPE)

White solid, 101.7 mg, 85% yield. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.18 (m, 20H), 2.15 – 2.03 (m, 4H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 138.19 (dd, *J* = 7.4, 5.9 Hz), 132.82 (t, *J* = 9.4 Hz), 128.75, 128.54 (t, *J* = 3.1 Hz), 23.95 (d, *J* = 2.3 Hz). **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ -12.62.

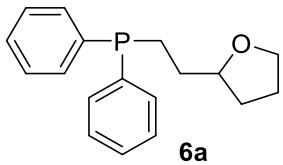
**1,2-bis(di-p-tolylphosphanyl)ethane[5]**




**5b**

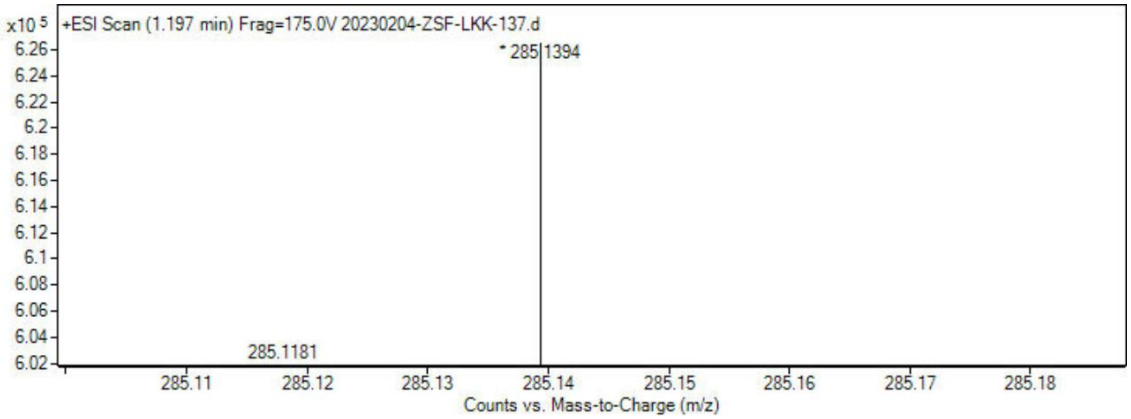
White solid, 25.9 mg, 57% yield. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 7.1 Hz, 8H), 7.10 (d, *J* = 7.7 Hz, 8H), 2.32 (s, 12H), 2.04 (s, 4H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 138.49, 134.89 (t, *J* = 6.0 Hz), 132.70 (t, *J* = 9.6 Hz), 129.21 (t, *J* = 3.2 Hz), 24.04 (d, *J* = 2.8 Hz), 21.27. **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ -14.32.

**diphenyl(2-(tetrahydrofuran-2-yl)ethyl)phosphane**

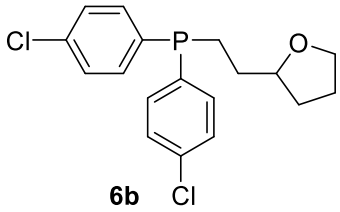



**6a**

Colorless liquid, 23.5 mg, 83% yield. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.42 (t, *J* = 6.7 Hz, 4H), 7.30 (t, *J* = 8.4 Hz, 6H), 3.86 (dq, *J* = 14.3, 6.8 Hz, 2H), 3.71 (dd, *J* = 14.7, 7.4 Hz, 1H), 2.20 (td, *J* = 12.6, 4.8 Hz, 1H), 2.09 – 1.92 (m, 2H), 1.90 – 1.79 (m, 2H), 1.72 – 1.62 (m, 1H), 1.56 (ddd, *J* = 18.7, 12.9, 5.3 Hz, 1H), 1.47 – 1.38 (m, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 138.70 (dd, *J* = 12.8, 6.8 Hz), 132.74 (dd, *J* = 18.5, 6.1 Hz), 128.52 (d, *J* = 4.0 Hz), 128.39 (d, *J* = 6.8 Hz), 79.83 (d, *J* = 13.9 Hz), 67.69, 31.89 (d, *J* = 16.1 Hz), 31.15, 25.70, 24.53 (d, *J* = 11.3 Hz). **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ -15.54. **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{22}OP^+$ 285.1403; found 351.1503.

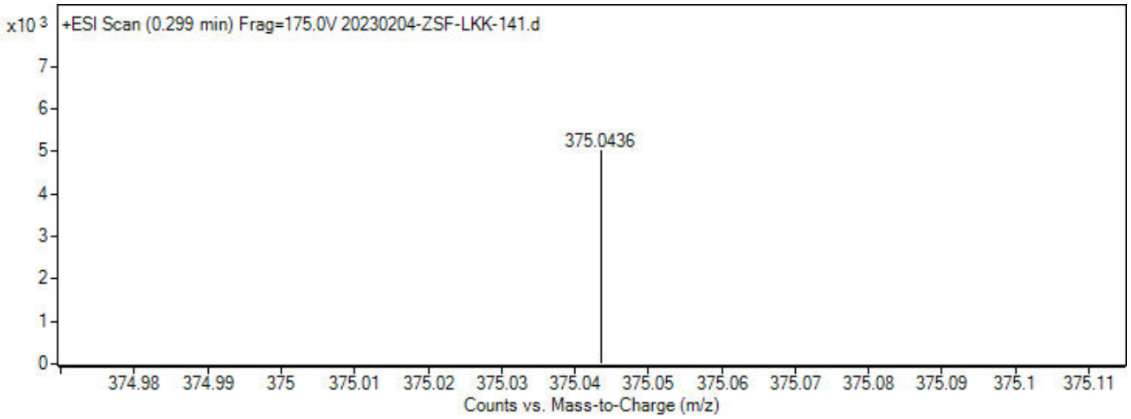



**bis(4-chlorophenyl)(2-(tetrahydrofuran-2-yl)ethyl)phosphane**

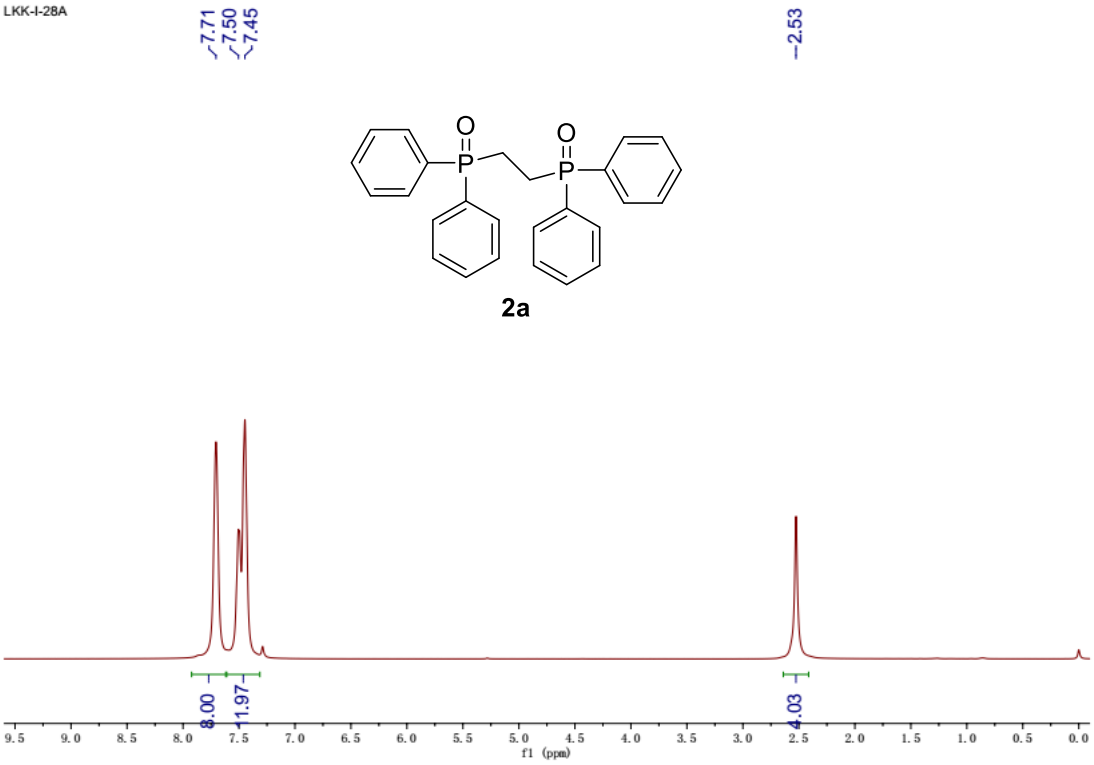


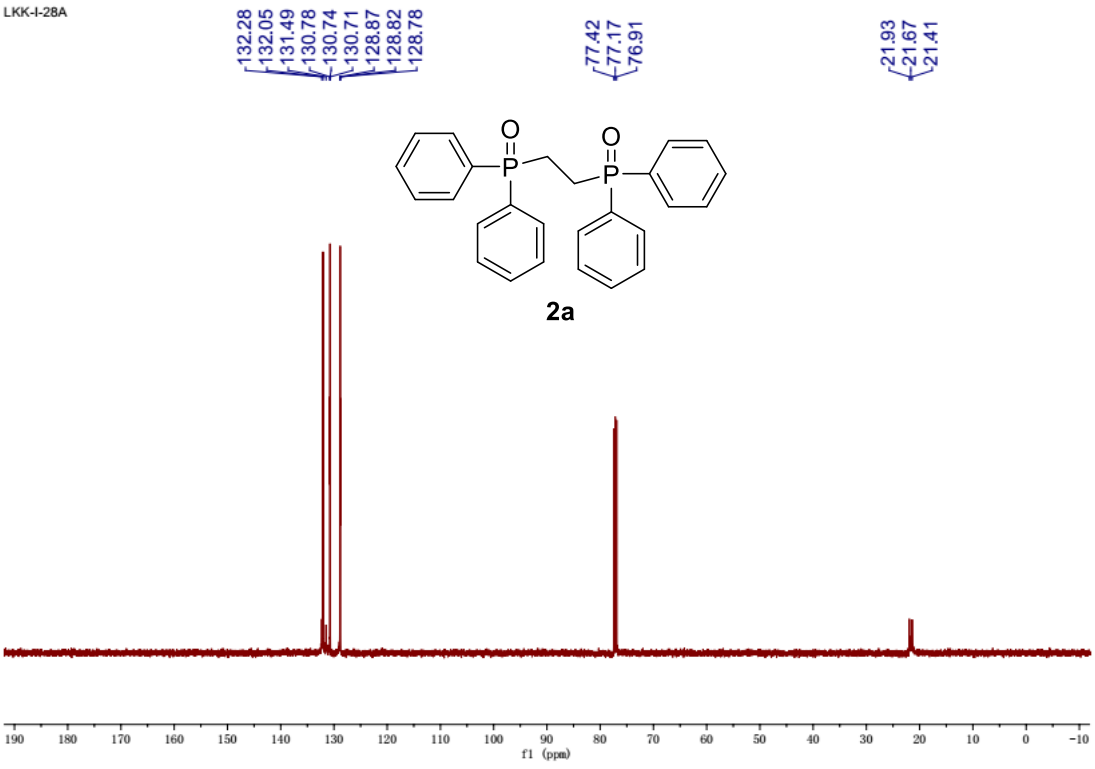

**6b**

Colorless liquid, 28.7 mg, 81% yield. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 8H), 3.92 – 3.77 (m, 2H), 3.71 (dd, *J* = 14.8, 7.4 Hz, 1H), 2.23 – 2.11 (m, 1H), 1.98 (ddd, *J* = 24.5, 11.6, 5.7 Hz, 2H), 1.90 – 1.81 (m, 2H), 1.65 – 1.60 (m, 1H), 1.57 – 1.48 (m, 1H), 1.45 – 1.39 (m, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 136.84 (dd, *J* = 14.2, 12.4 Hz), 135.02 (d, *J* = 2.2 Hz), 133.96 (dd, *J* = 19.2, 3.0 Hz), 128.76 (d, *J* = 6.7 Hz), 79.62 (d, *J* = 13.9 Hz), 67.73, 31.71 (d, *J* = 15.7 Hz), 31.19, 25.70, 24.60 (d, *J* = 11.6 Hz). **$^{31}$P NMR** (202 MHz, $CDCl_3$) δ -17.20. **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{19}C_{l2}NaOP^+$ 375.0443; found 375.0436.

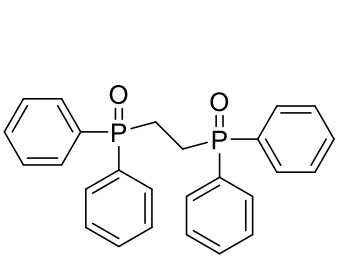


## 7. NMR spectra



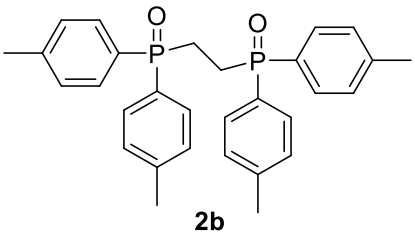
LKK-I-28A



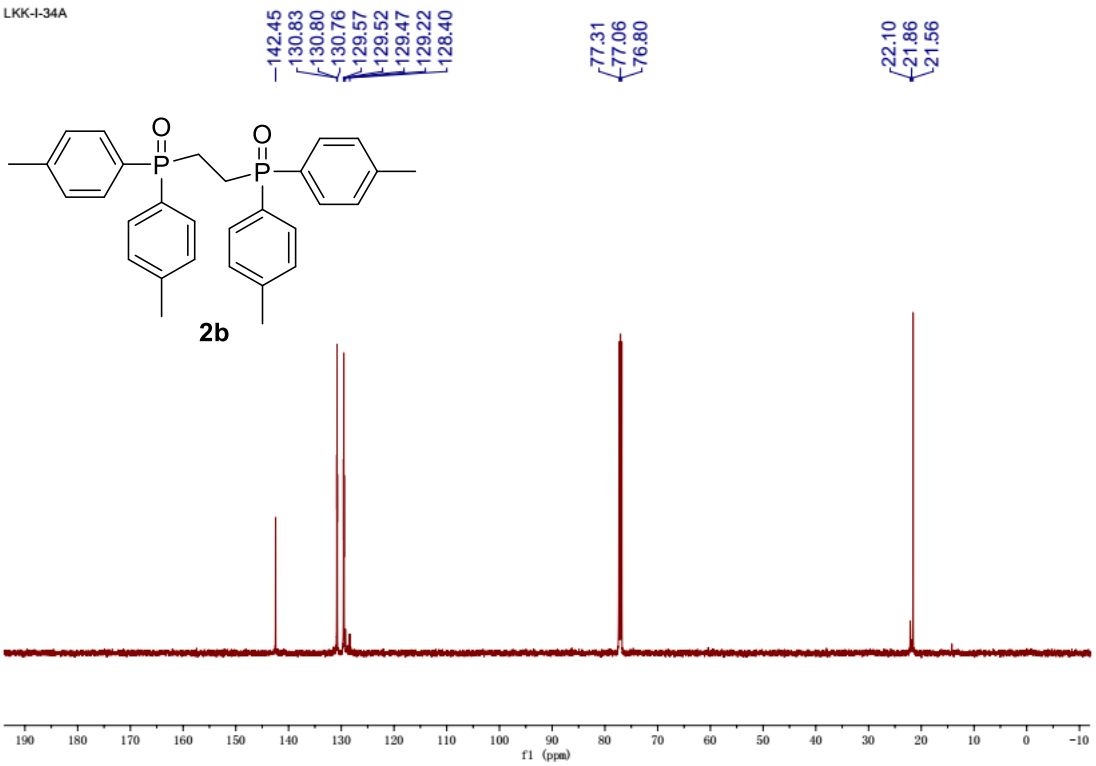
2a

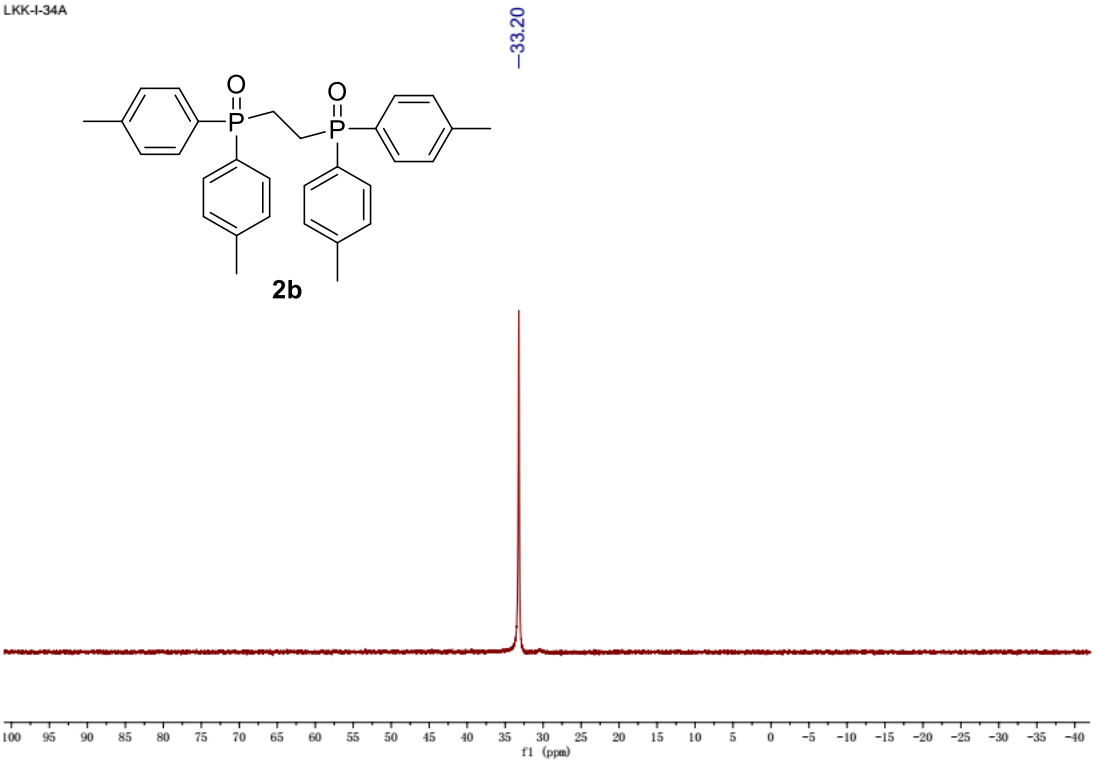


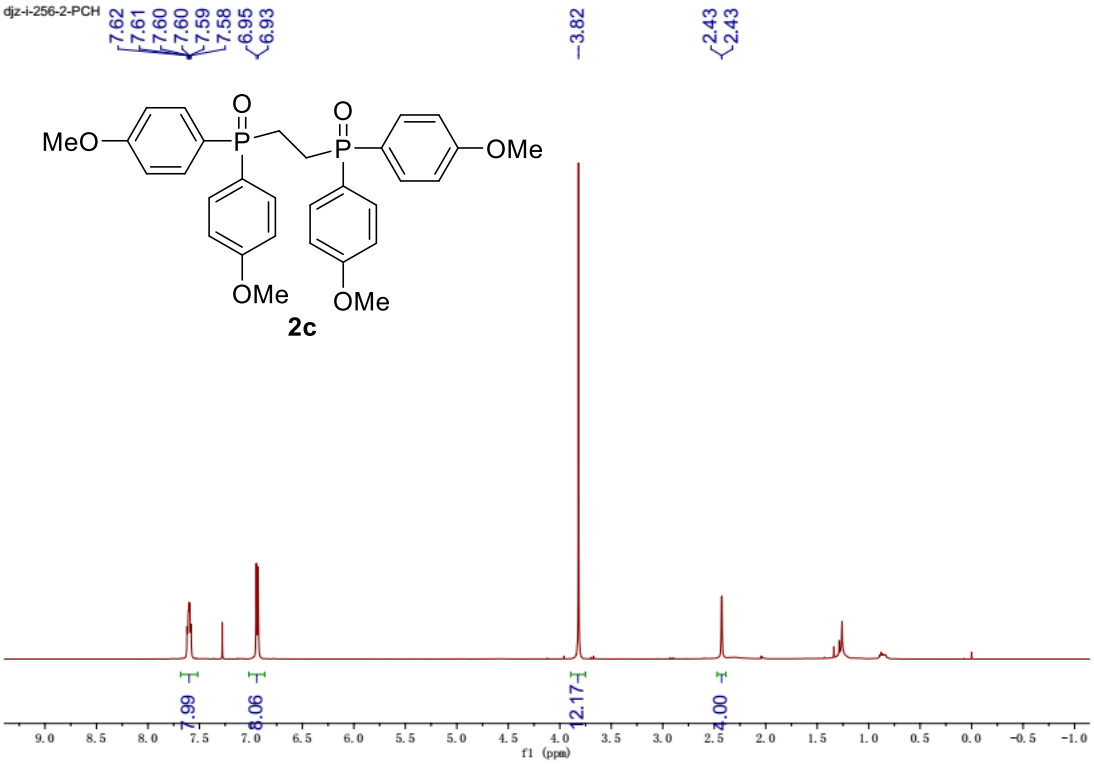

LKK-I-34A

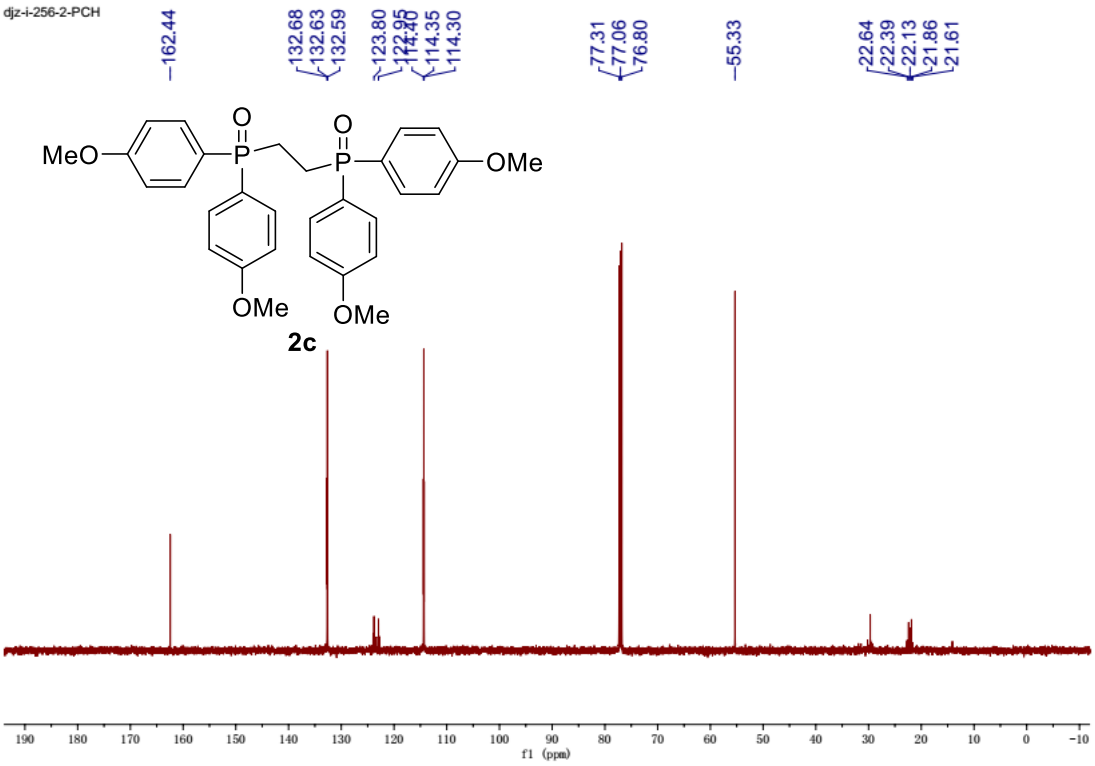


2b

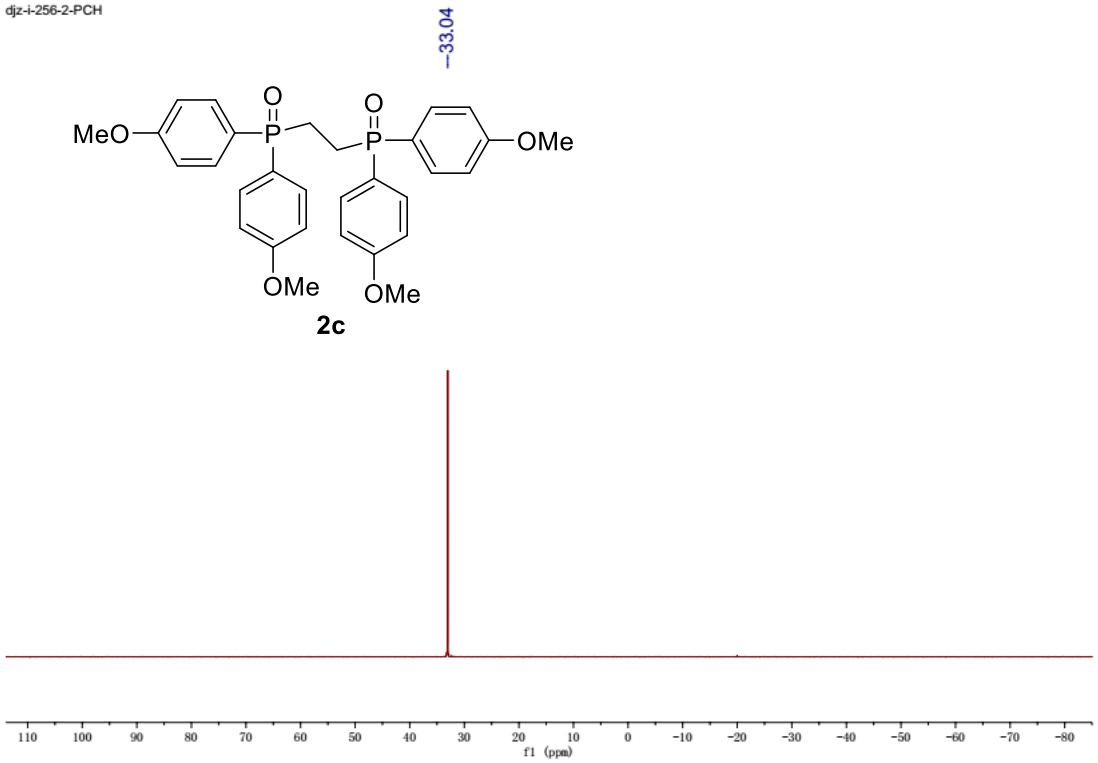

LKK-I-34A
142.45
130.83
130.80
130.76
129.57
129.52
129.47
129.22
128.40
77.31
77.06
76.80
22.10
21.86
21.56
2b
f1 (ppm)


LKK-I-34A
33.20
2b
f1 (ppm)

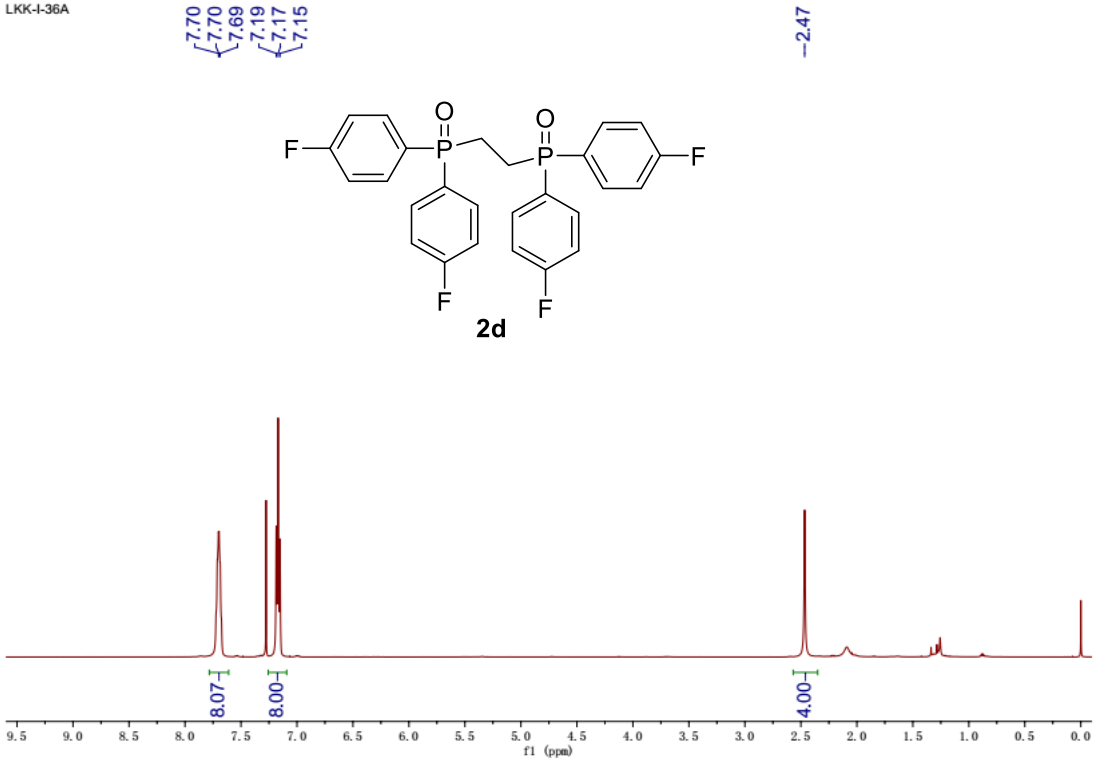

djz-i-256-2-PCH
7.62
7.61
7.60
7.60
7.59
7.58
6.95
6.93
3.82
2.43
2.43
MeO
OMe
OMe
OMe
2c
7.99
8.06
12.17
4.00
f1 (ppm)

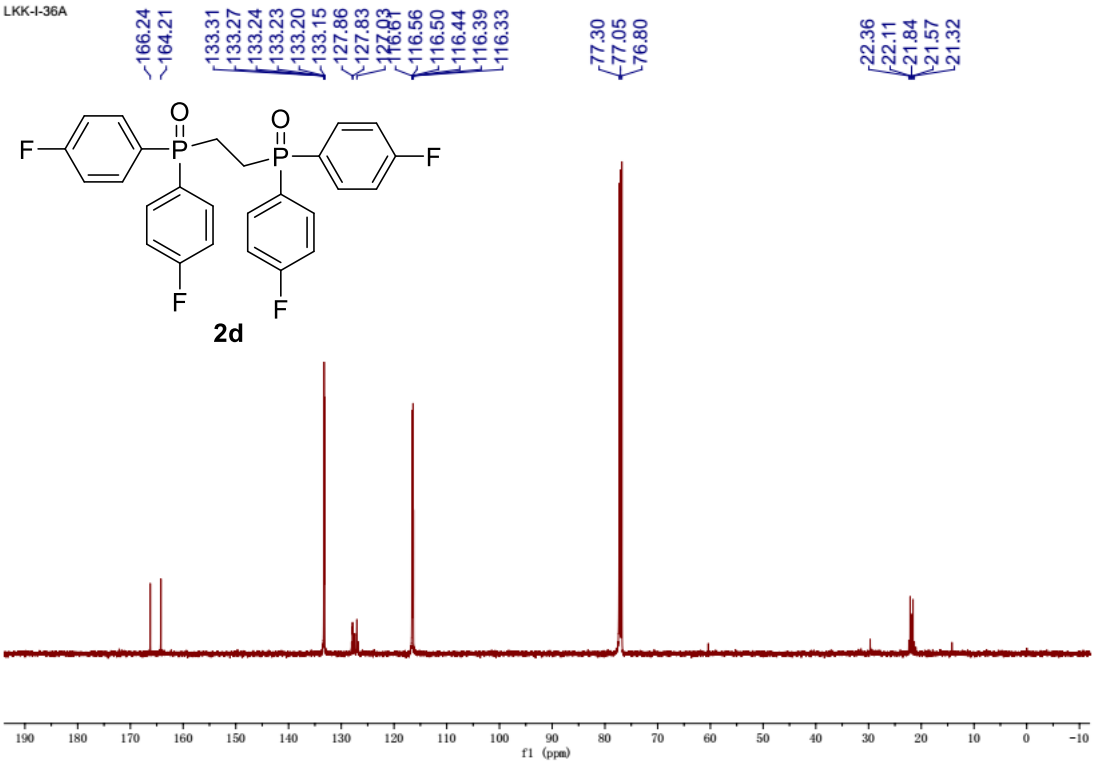

djz-i-256-2-PCH
162.44
132.68
132.63
132.59
123.80
114.35
114.30
77.31
77.06
76.80
55.33
22.64
22.39
22.13
21.86
21.61
MeO
OMe
OMe
OMe
2c
f1 (ppm)

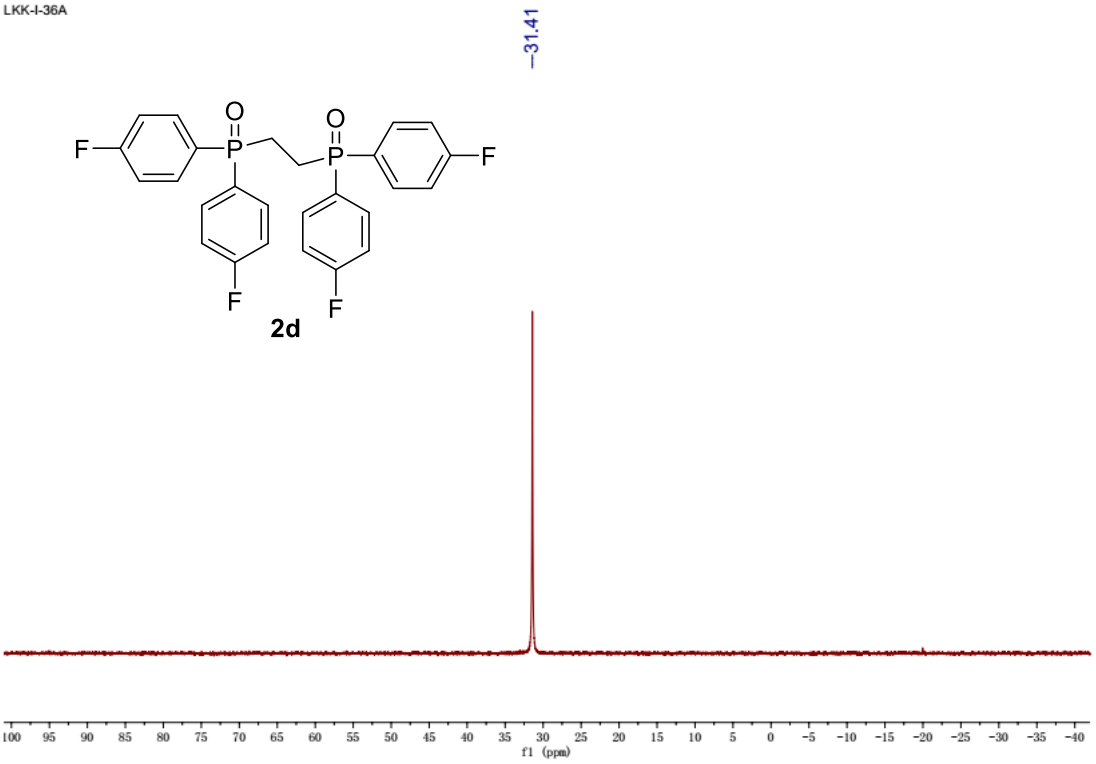
djz-i-256-2-PCH



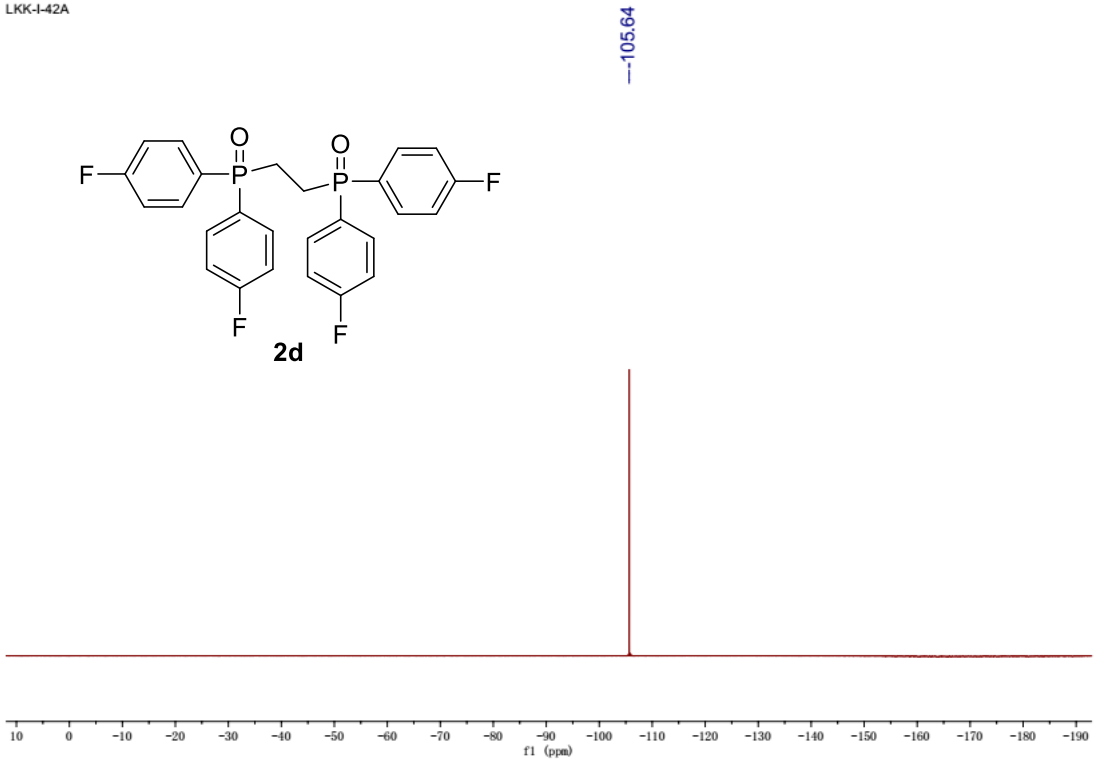

LKK-I-36A



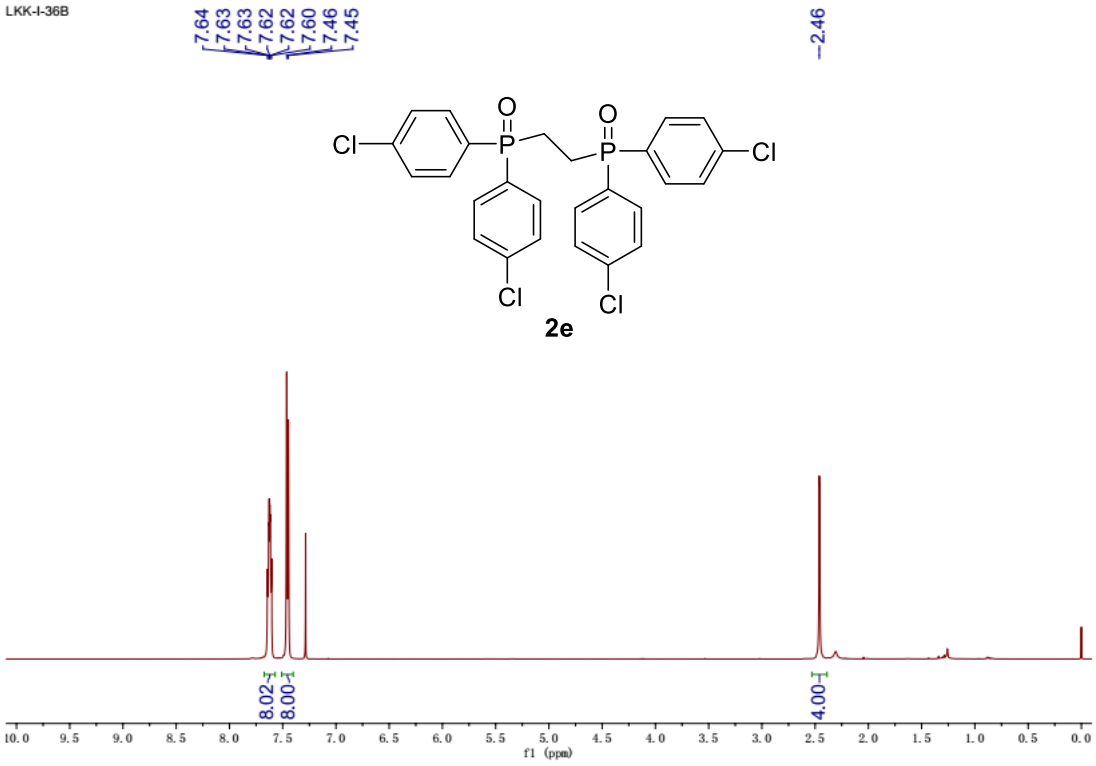

LKK-I-36A
166.24
164.21
133.31
133.27
133.24
133.23
133.20
133.15
127.86
127.83
127.03
116.61
116.56
116.50
116.44
116.39
116.33
77.30
77.05
76.80
22.36
22.11
21.84
21.57
21.32
F
O
P
O
P
F
F
F
2d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

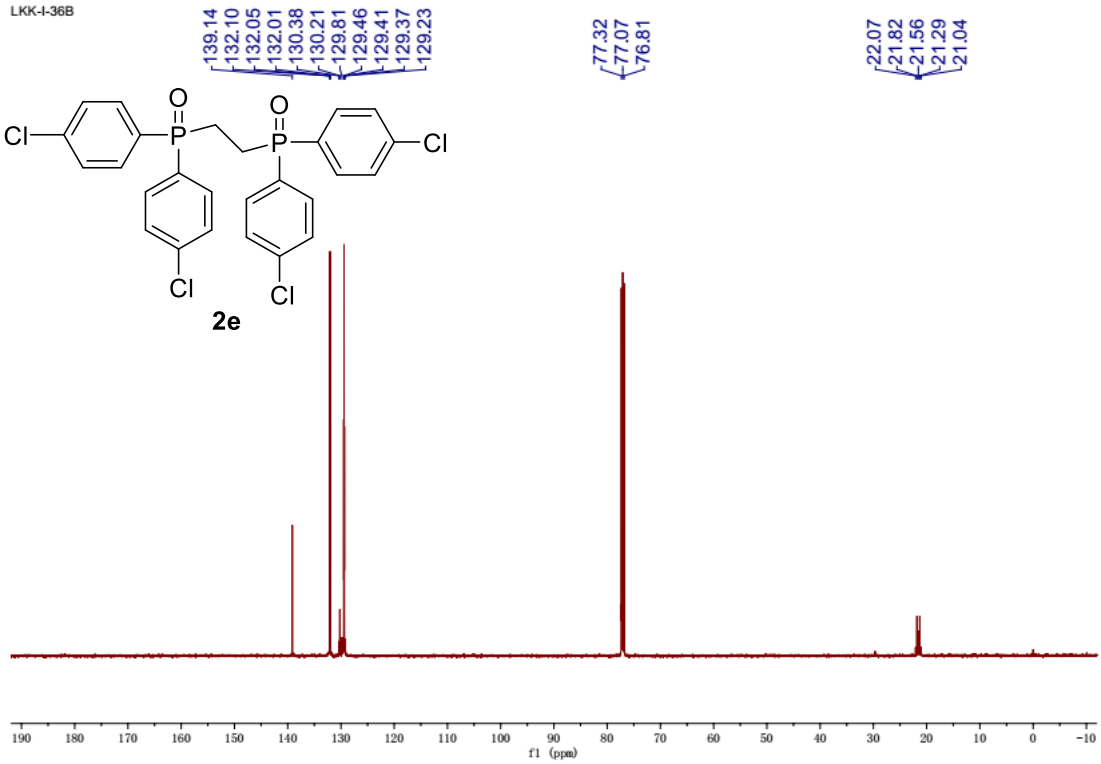

LKK-I-36A
31.41
F
O
P
O
P
F
F
F
2d
100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40
f1 (ppm)

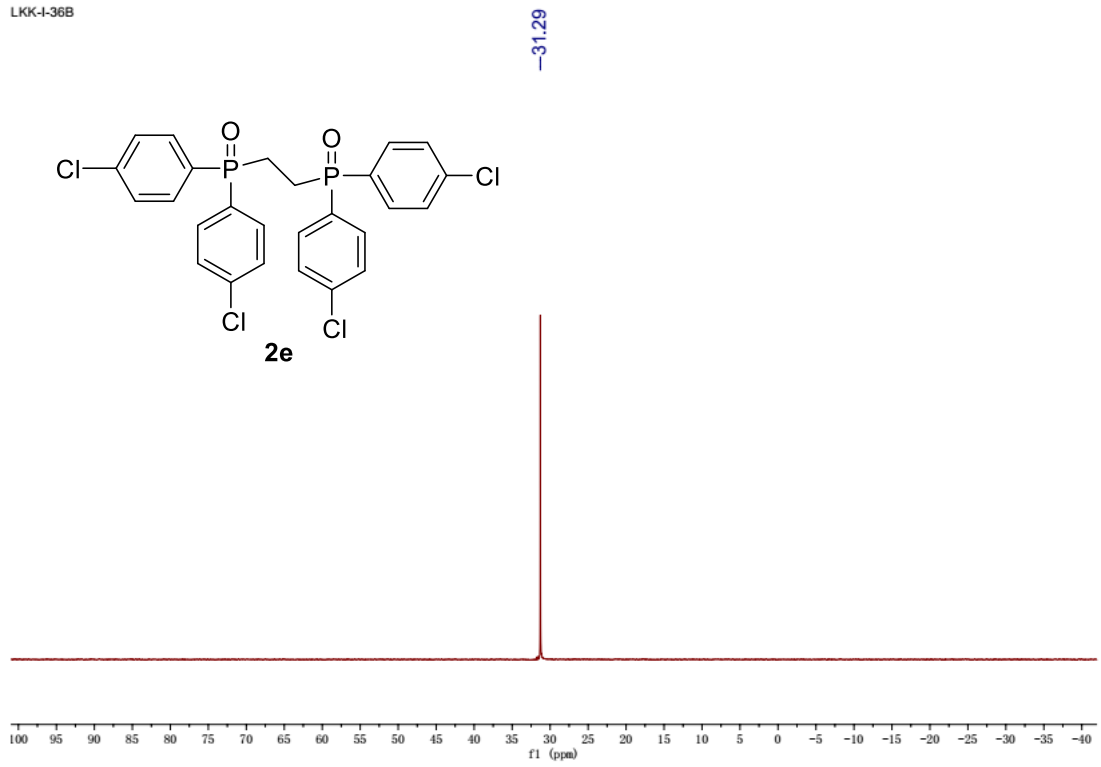
LKK-I-42A

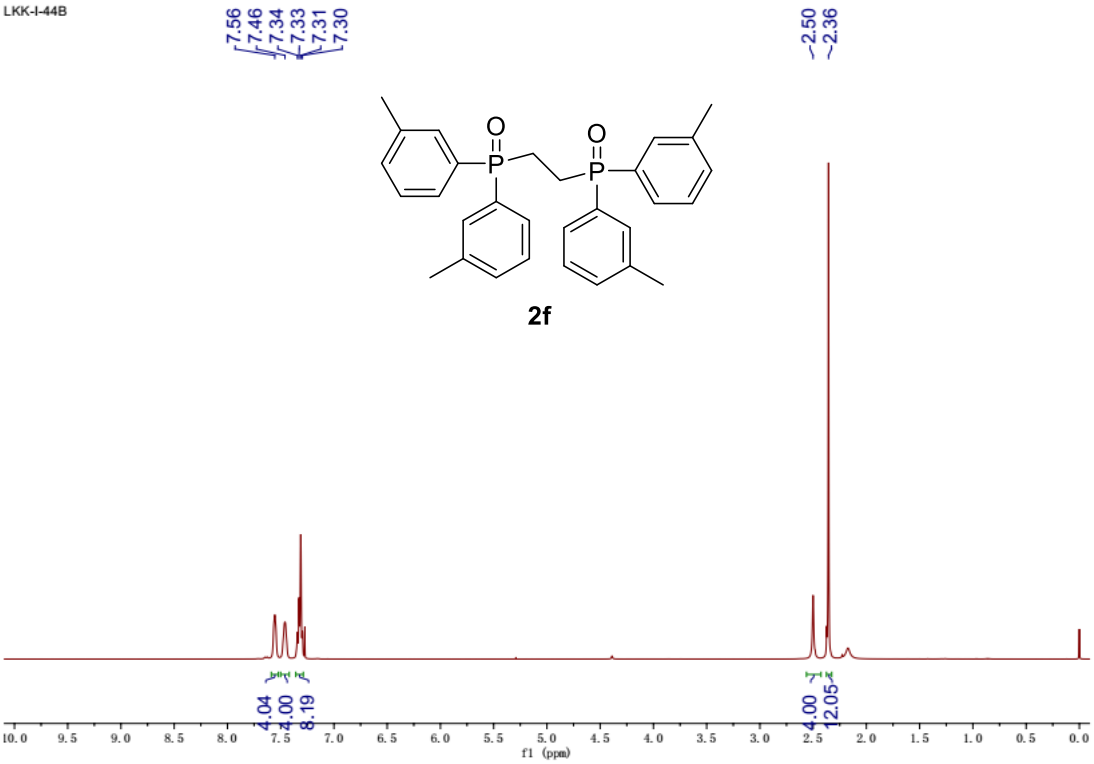


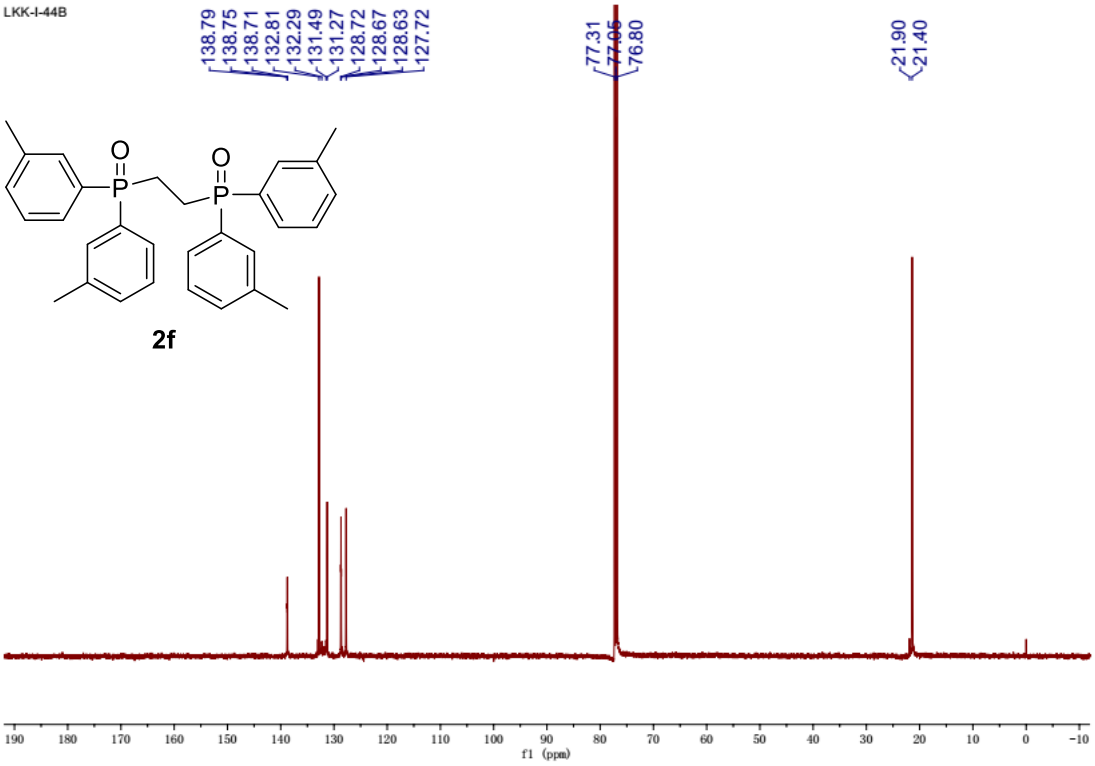

LKK-I-36B



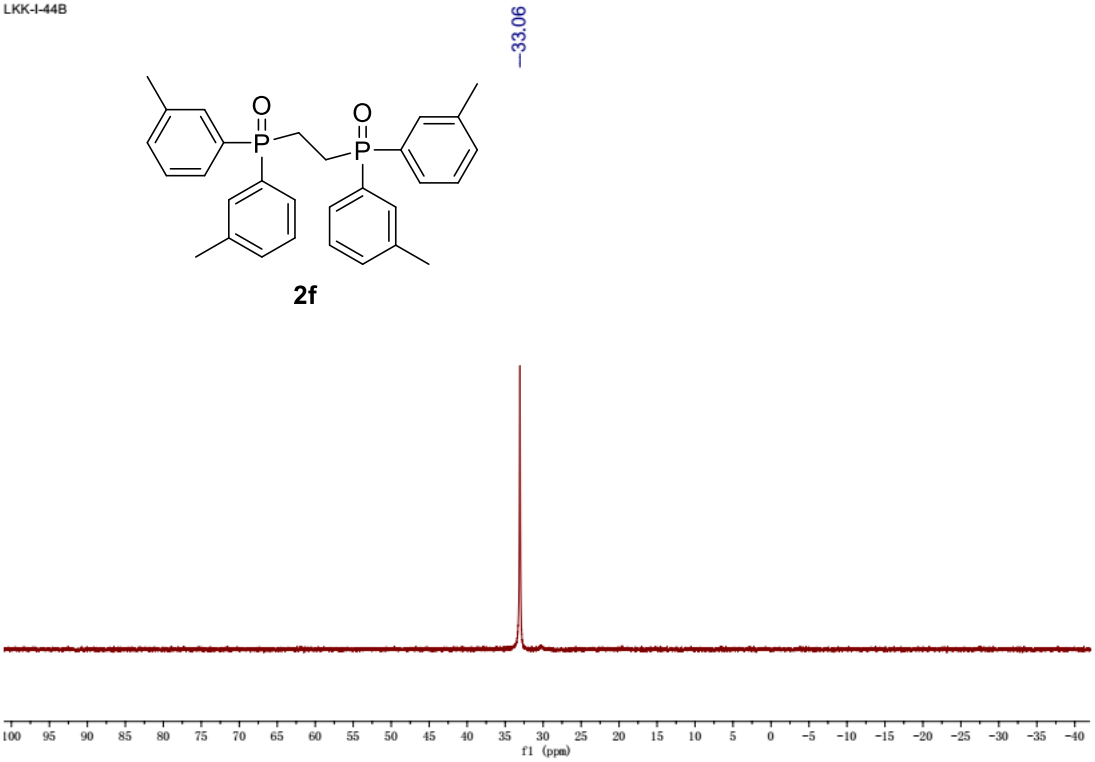

LKK-I-36B
139.14
132.10
132.05
132.01
130.38
130.21
129.81
129.46
129.41
129.37
129.23
77.32
77.07
76.81
22.07
21.82
21.56
21.29
21.04
Cl
Cl
Cl
Cl
2e
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


LKK-I-36B
31.29
Cl
Cl
Cl
Cl
2e
100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40
f1 (ppm)


LKK-I-44B
7.56
7.46
7.34
7.33
7.31
7.30
2.50
2.36
2f
4.04
4.00
8.19
4.00
12.05
f1 (ppm)

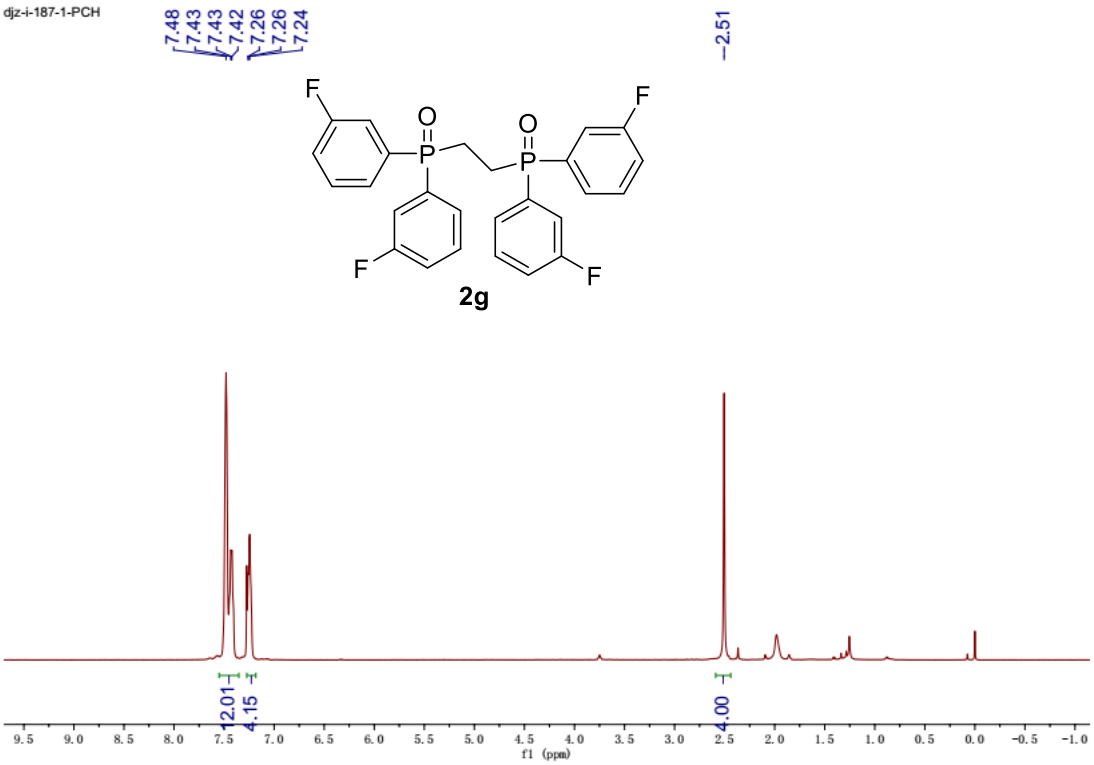

LKK-I-44B
138.79
138.75
138.71
132.81
132.29
131.49
131.27
128.72
128.67
128.63
127.72
77.31
77.06
76.80
21.90
21.40
2f
f1 (ppm)

LKK-I-44B

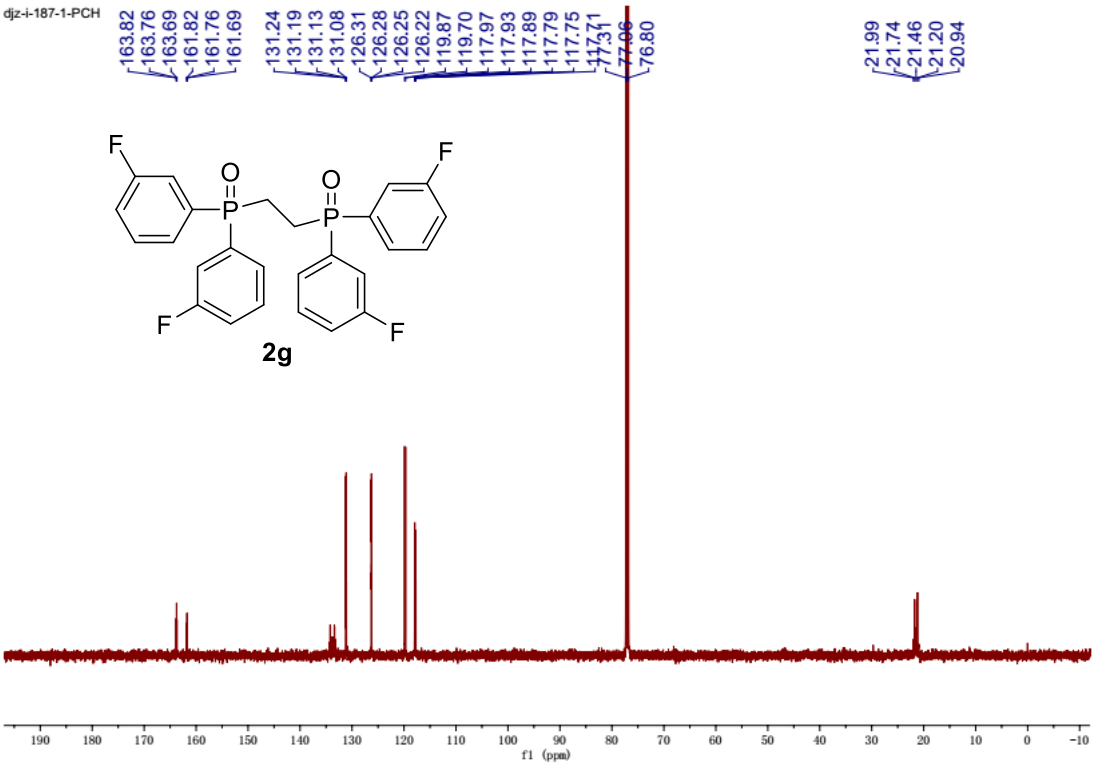


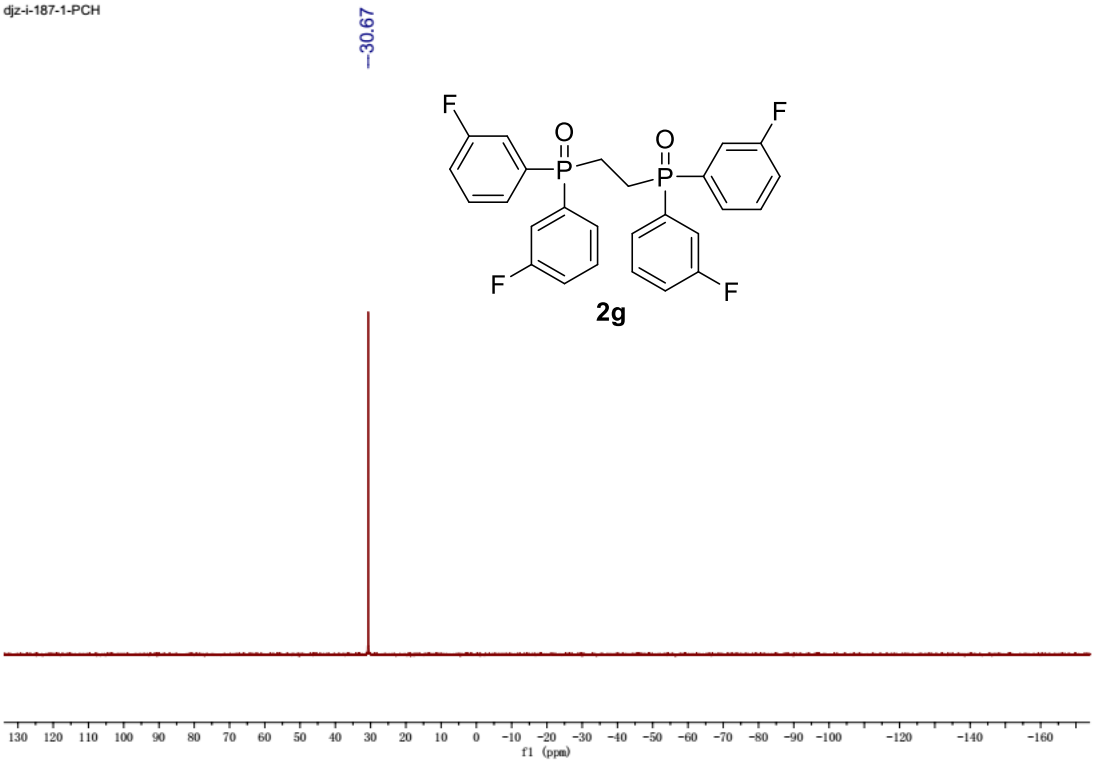

**2f**

djz-i-187-1-PCH

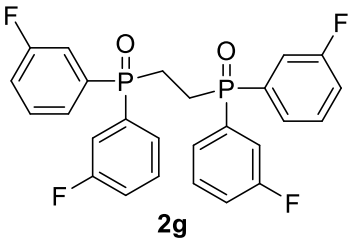



**2g**


djz-i-187-1-PCH
163.82
163.76
163.69
161.82
161.76
161.69
131.24
131.19
131.13
131.08
126.31
126.28
126.25
126.22
119.87
119.70
117.97
117.93
117.89
117.79
117.75
117.71
77.06
76.80
21.99
21.74
21.46
21.20
20.94
F
O
P
O
P
F
F
F
2g
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


djz-i-187-1-PCH
-30.67
F
O
P
O
P
F
F
F
2g
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160
f1 (ppm)

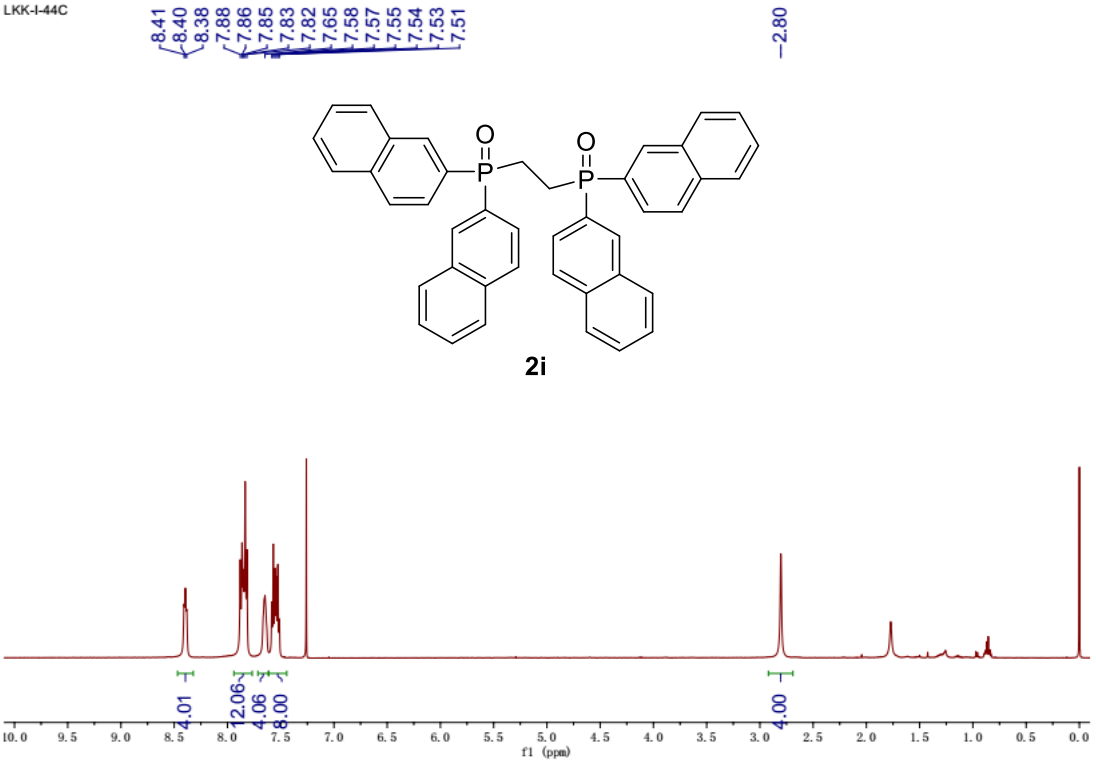
djz-i-187-1-PCH



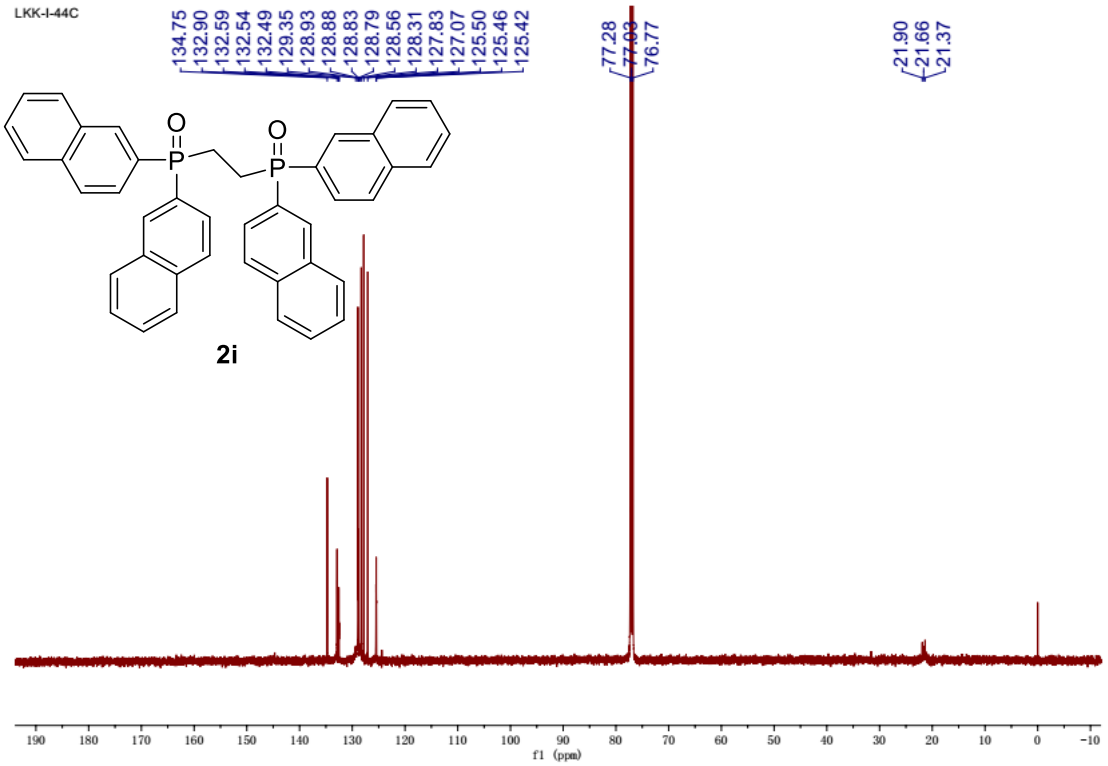

2g

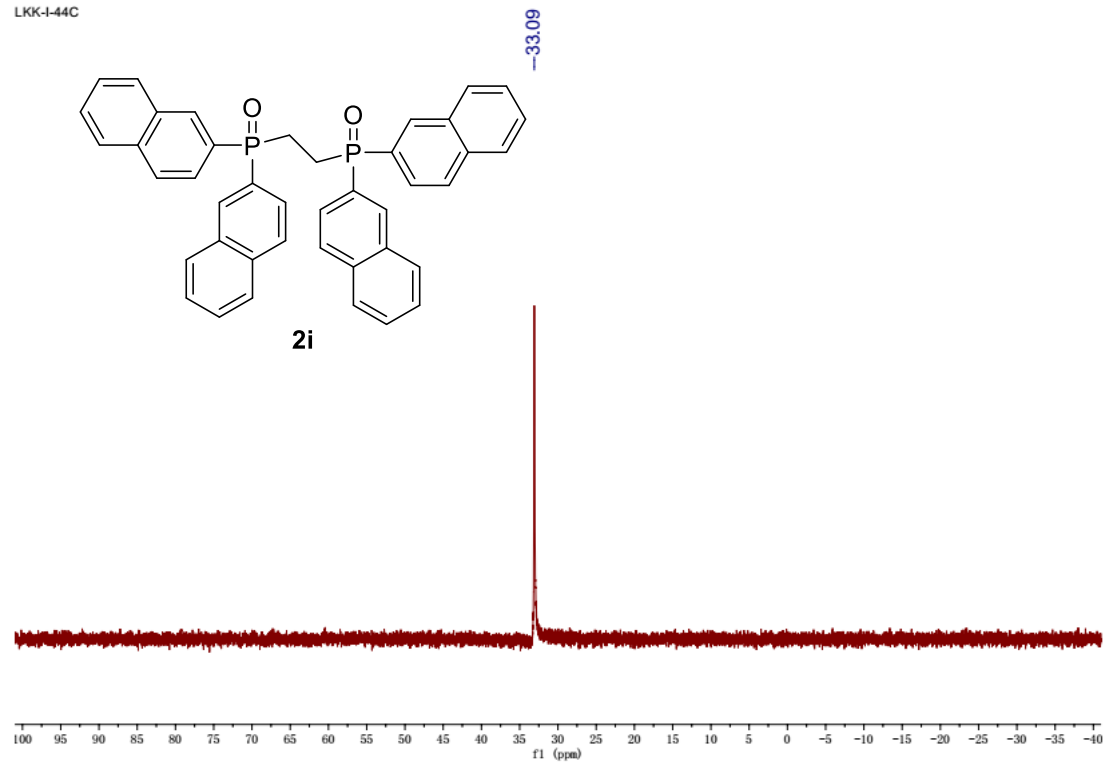



LKK-I-44C

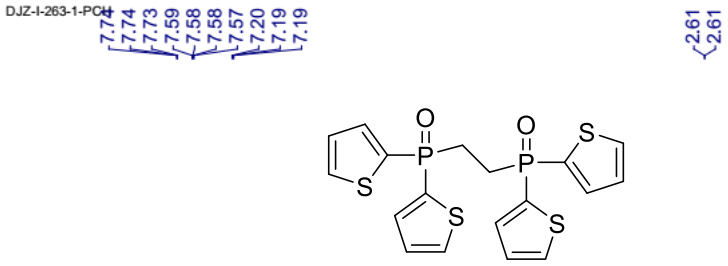



2i


LKK-I-44C
134.75
132.90
132.59
132.54
132.49
129.35
128.93
128.88
128.83
128.79
128.56
128.31
127.83
127.07
125.50
125.46
125.42
77.28
77.03
76.77
21.90
21.66
21.37
2i
f1 (ppm)

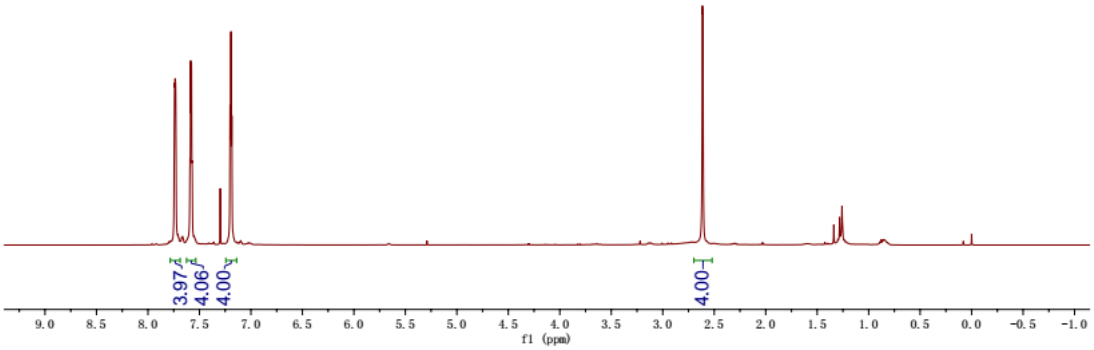

LKK-I-44C
33.09
2i
f1 (ppm)

DJZ-I-263-1-PCH

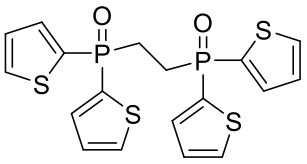




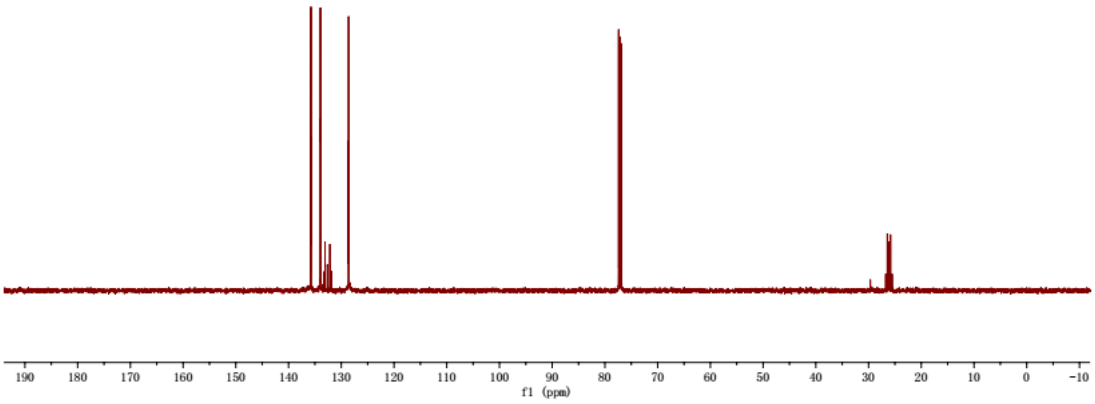

**2j**



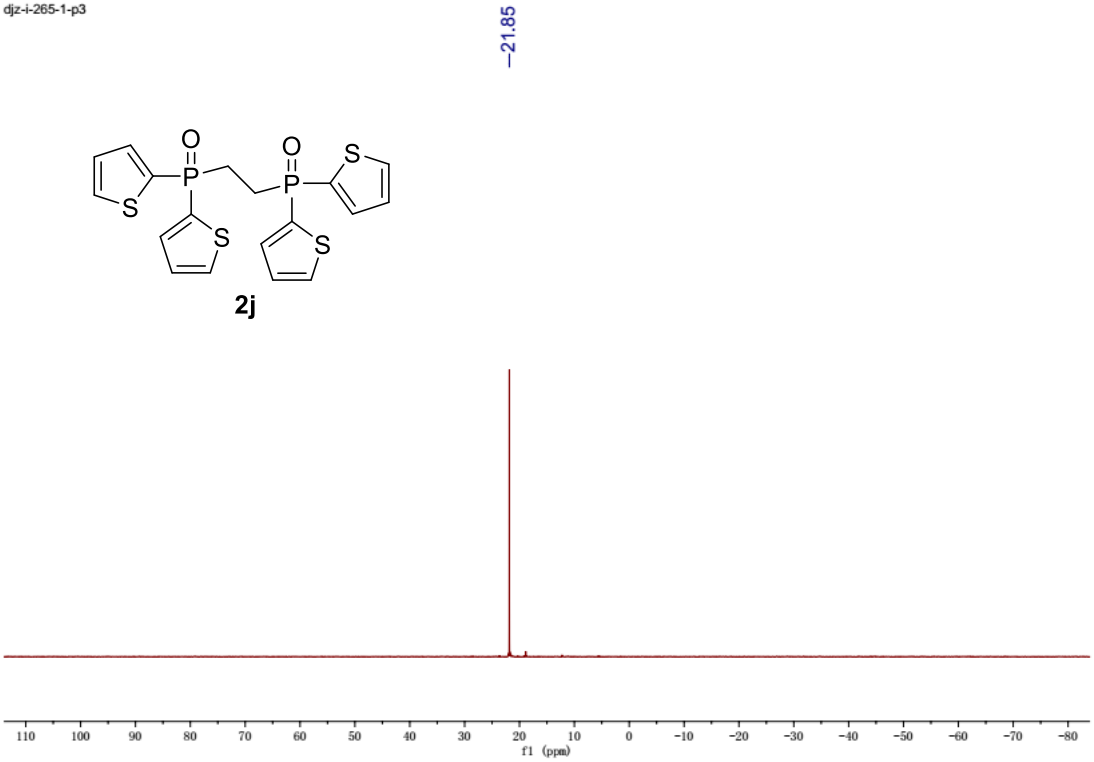

djz-i-265-1-p3

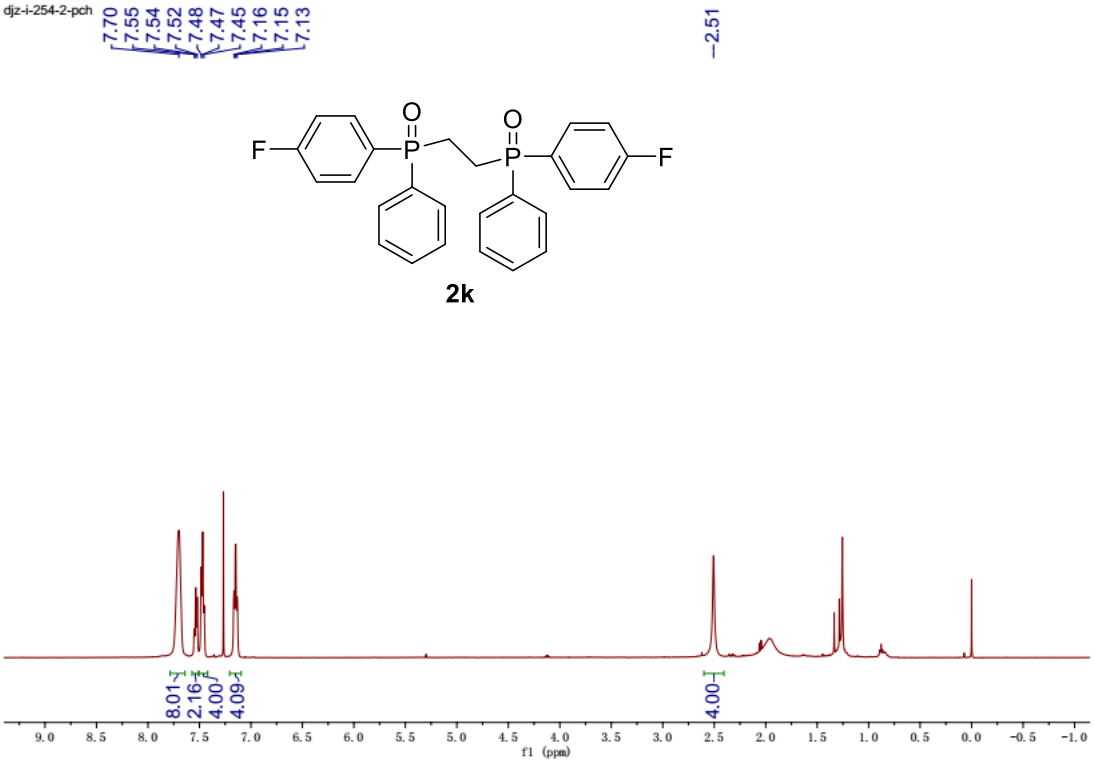
**2j**

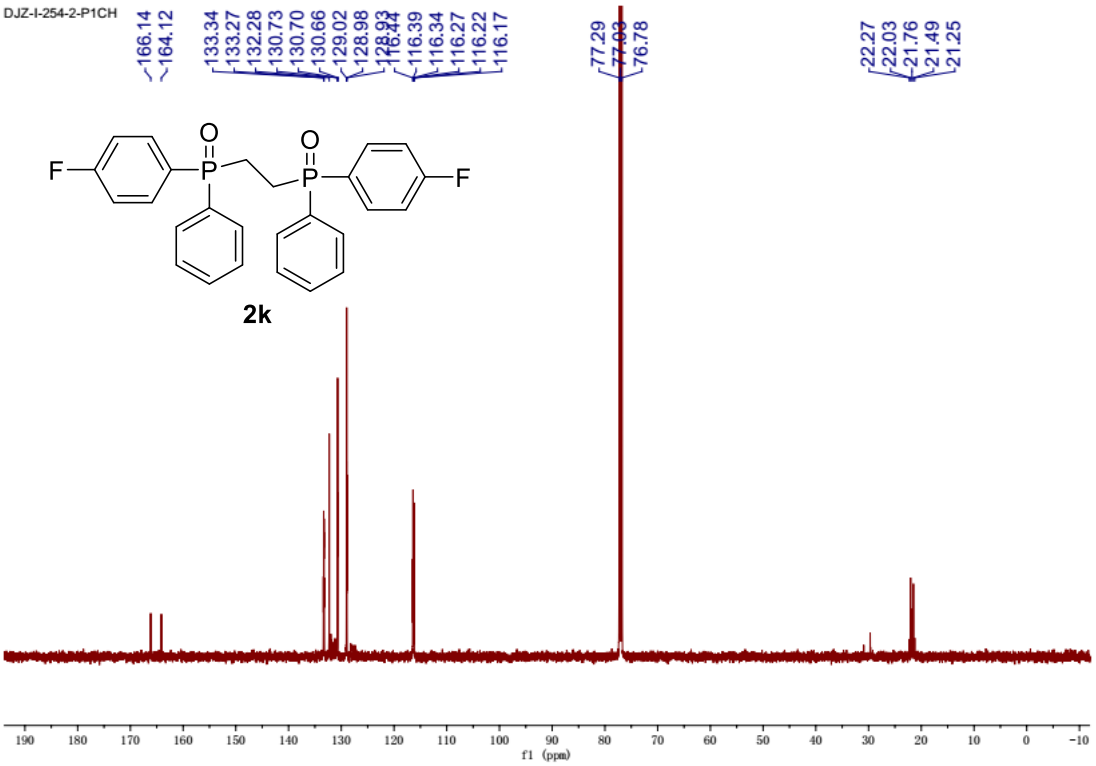


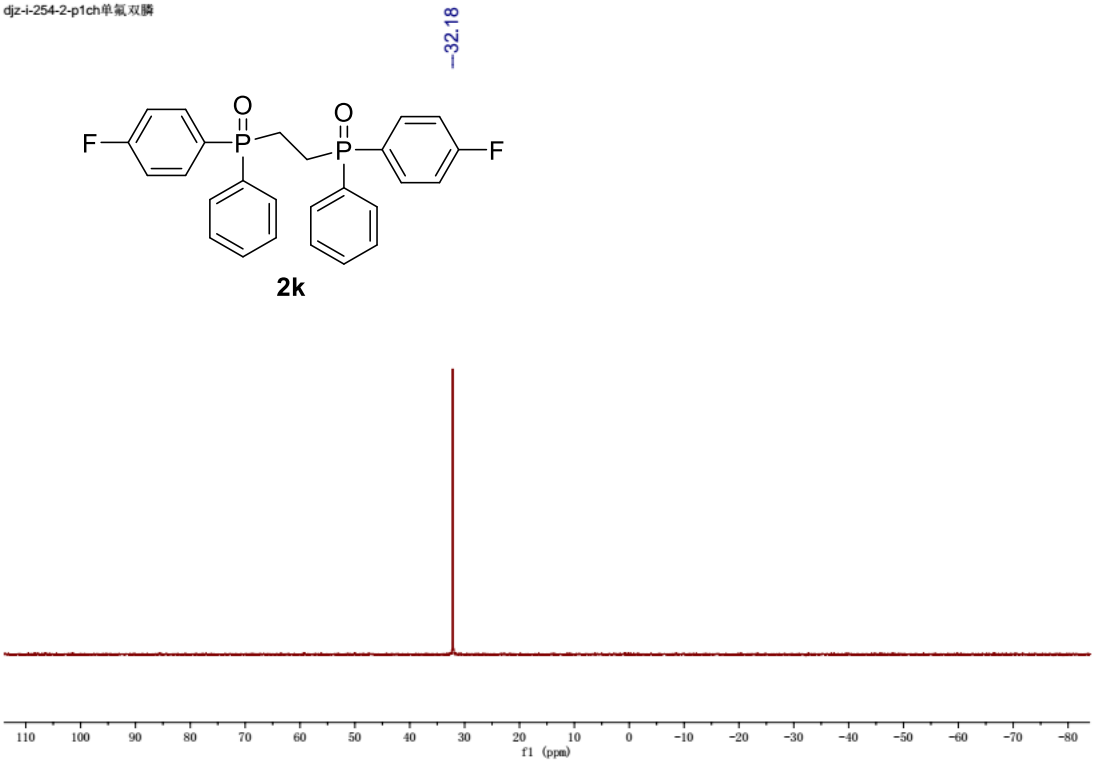
djz-i-265-1-p3



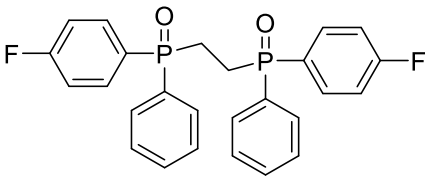

djz-i-254-2-pch




DJZ-I-254-2-P1CH
166.14
164.12
133.34
133.27
132.28
130.73
130.70
130.66
129.02
128.98
128.93
116.44
116.39
116.34
116.27
116.22
116.17
77.29
77.03
76.78
22.27
22.03
21.76
21.49
21.25
F
O
P
O
P
F
2k
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


djz-i-254-2-p1ch单氟双膦
32.18
F
O
P
O
P
F
2k
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
f1 (ppm)

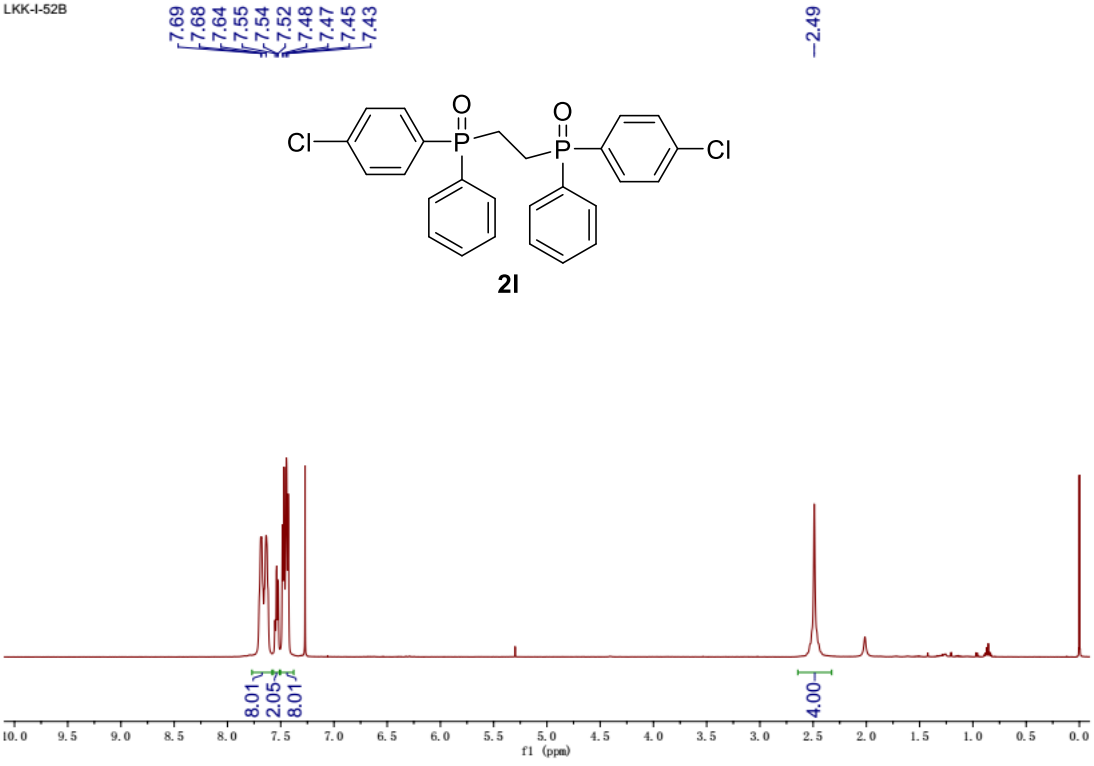
LKK-I-51B




2k



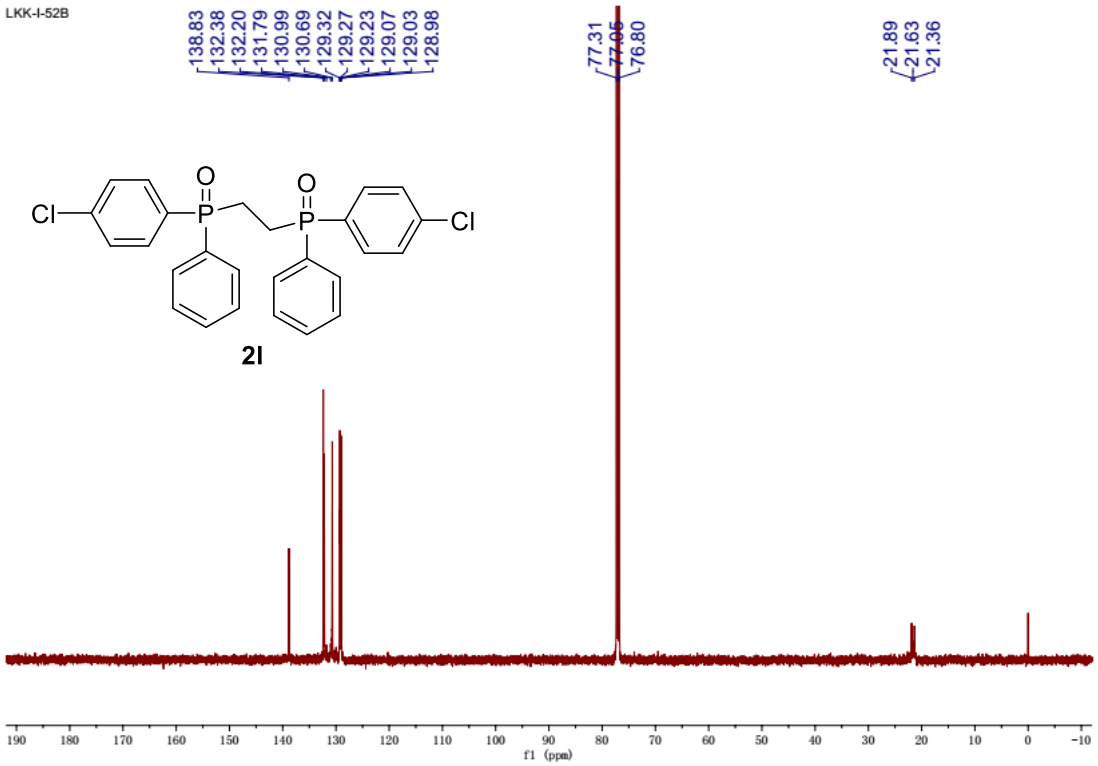

LKK-I-52B

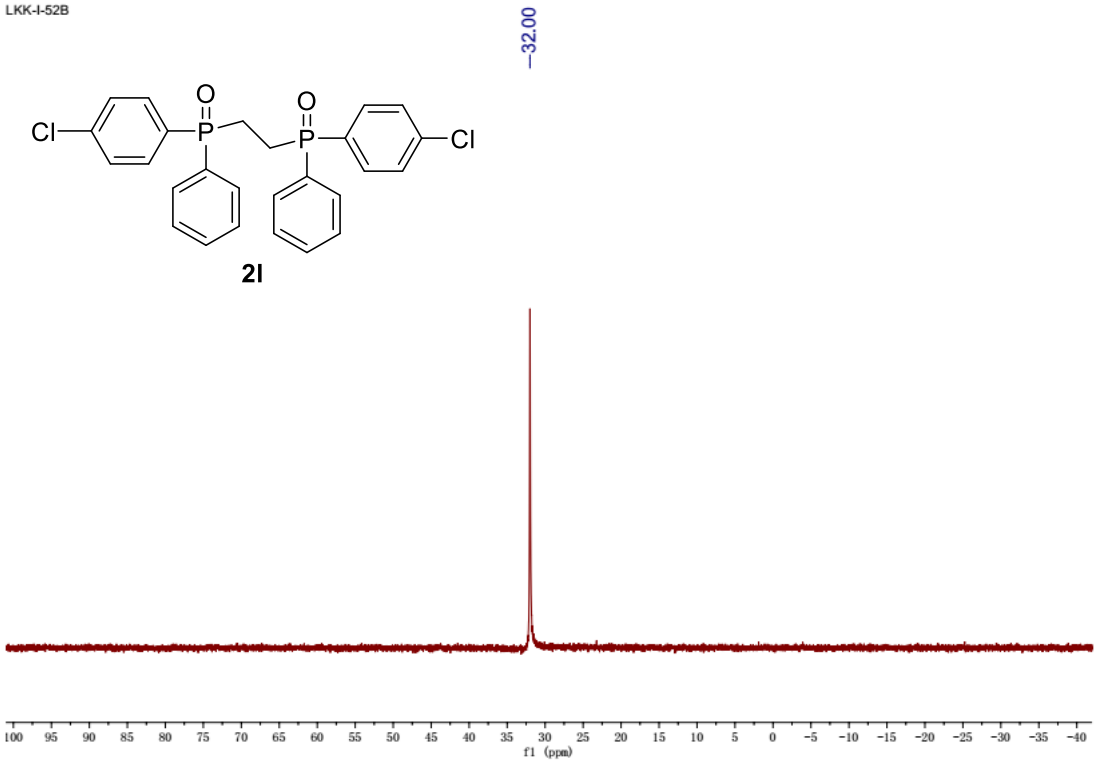




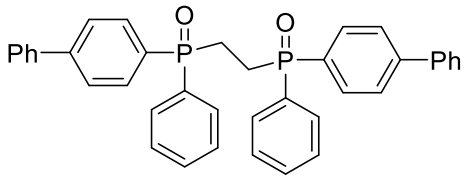


2l

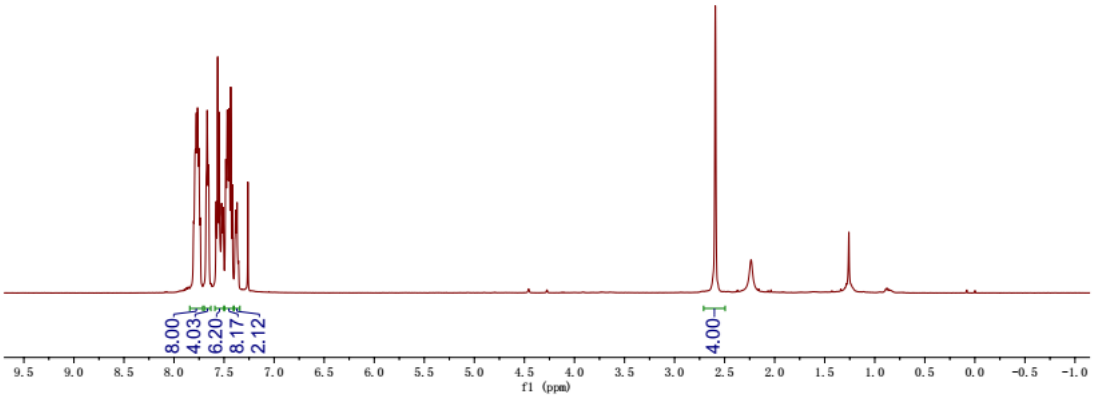

LKK-I-52B
138.83
132.38
132.20
131.79
130.99
130.69
129.32
129.27
129.23
129.07
129.03
128.98
77.31
77.06
76.80
21.89
21.63
21.36
Cl
O
P
O
P
Cl
2l
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


LKK-I-52B
−32.00
Cl
O
P
O
P
Cl
2l
100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 −5 −10 −15 −20 −25 −30 −35 −40
f1 (ppm)

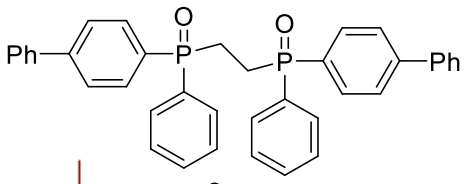

7.86
7.77
7.76
7.75
7.74
7.73
7.72
7.71
7.70
7.69
7.68
7.67
7.66
7.65
7.64
7.63
7.62
7.61
7.60
7.59
7.58
7.56
7.55
7.52
7.51
7.48
7.47
7.45
7.43
7.42
7.38
7.38
7.37
7.36
2.59


Ph
O
P
O
P
Ph

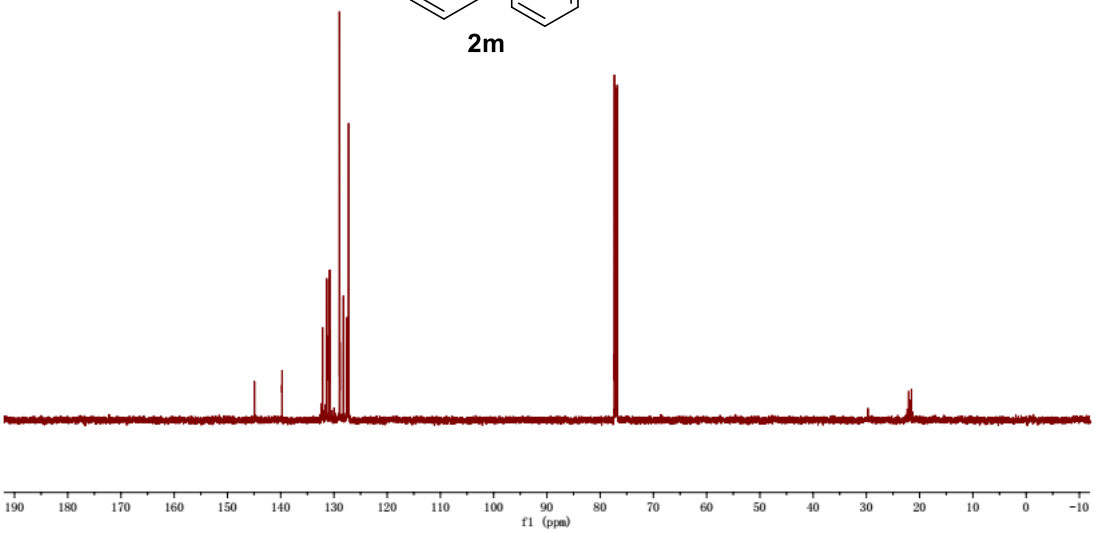
**2m**


8.00
4.03
6.20
8.17
2.12
4.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

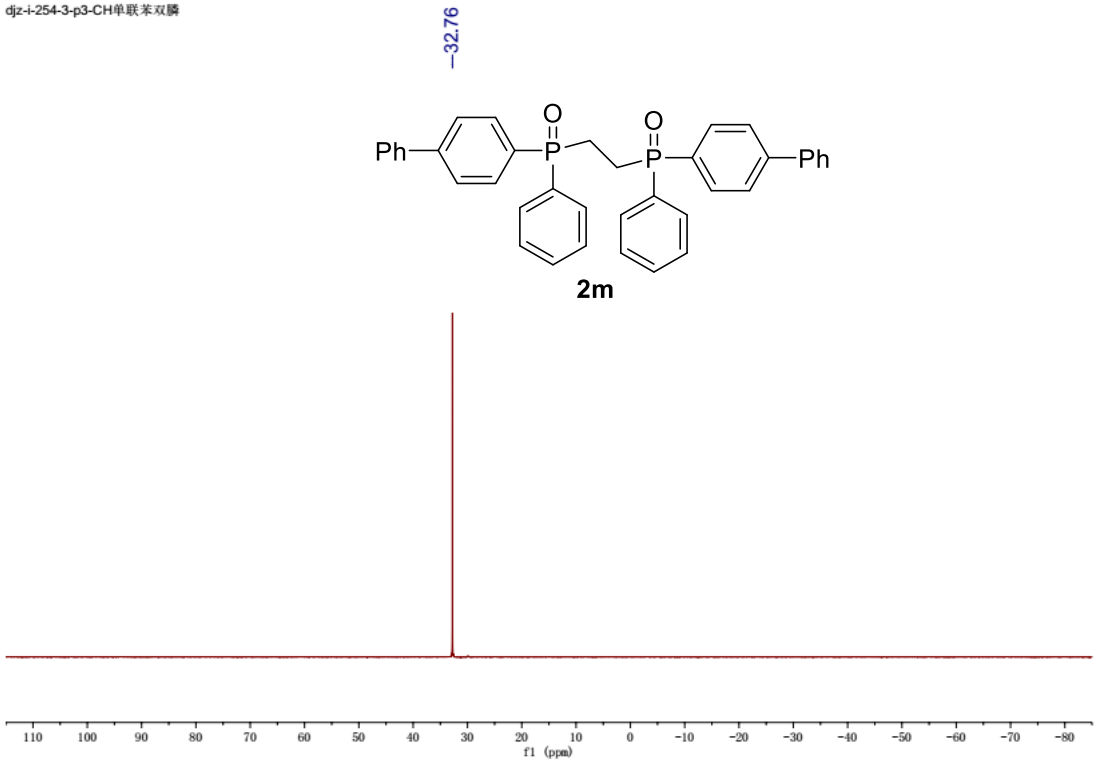

144.91
139.74
132.44
132.14
131.63
131.38
131.34
131.30
130.84
130.81
130.77
129.98
128.97
128.91
128.87
128.23
127.58
127.53
127.48
127.25
77.32
77.07
76.82
22.31
22.06
21.80
21.54
21.29


Ph
O
P
O
P
Ph

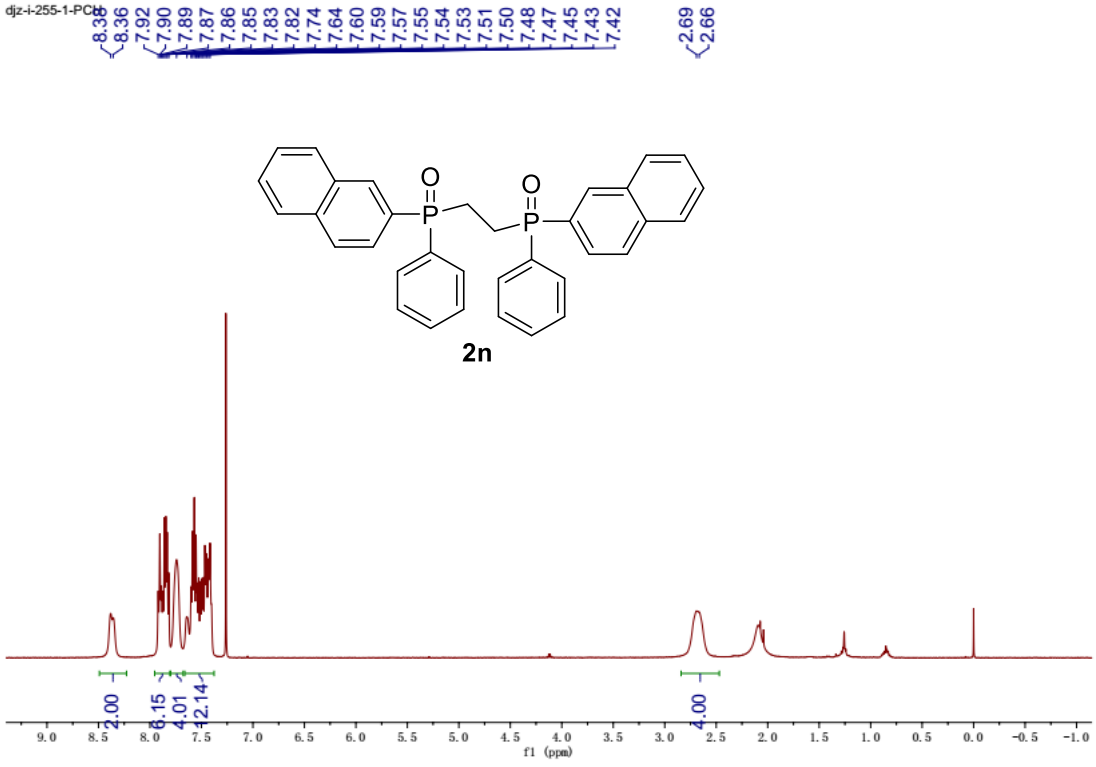
**2m**

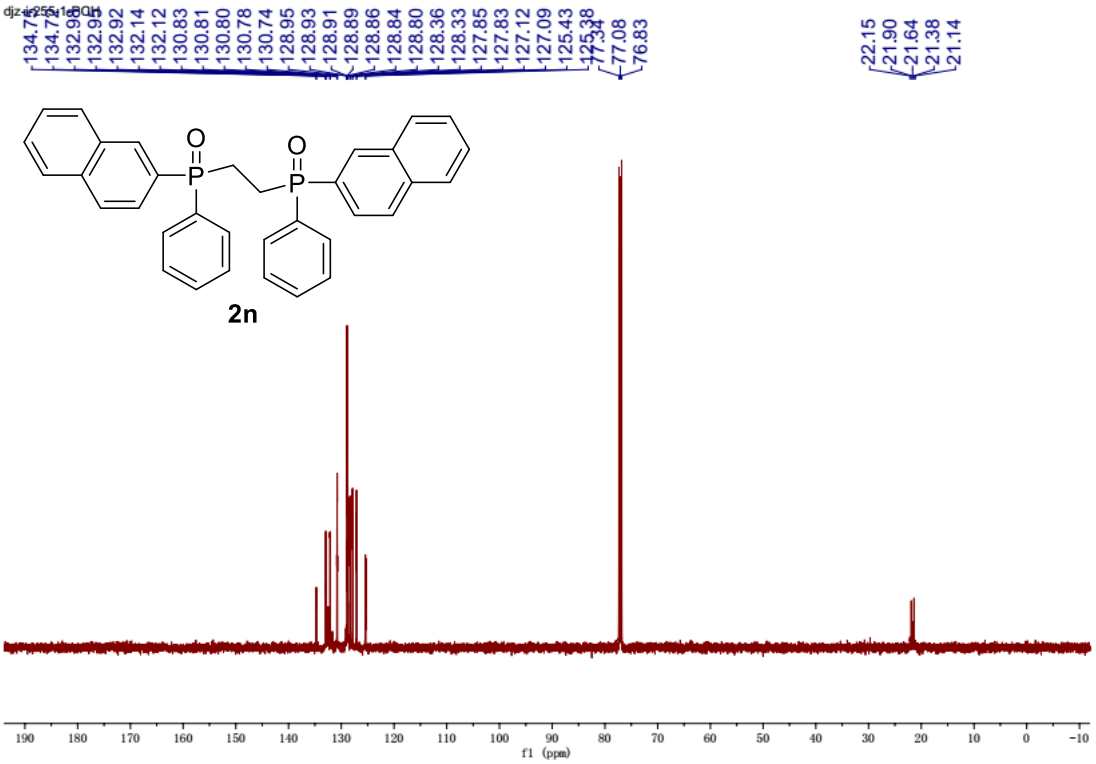

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

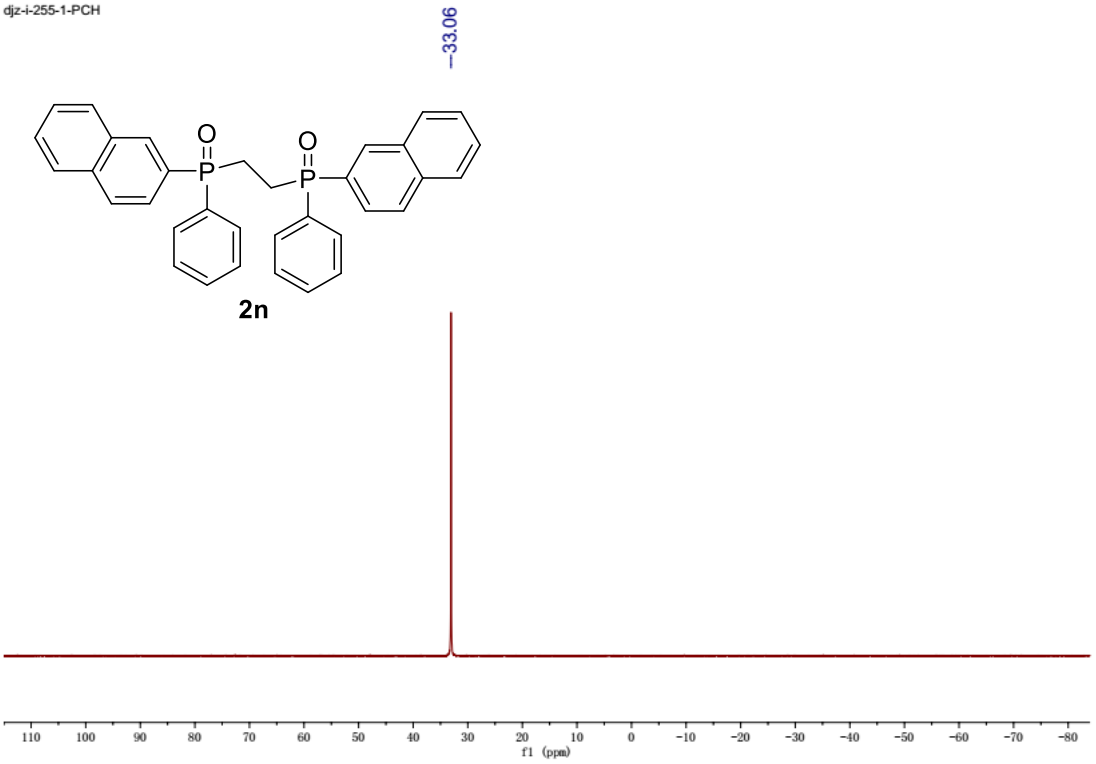
djz-i-254-3-p3-CH单联苯双膦

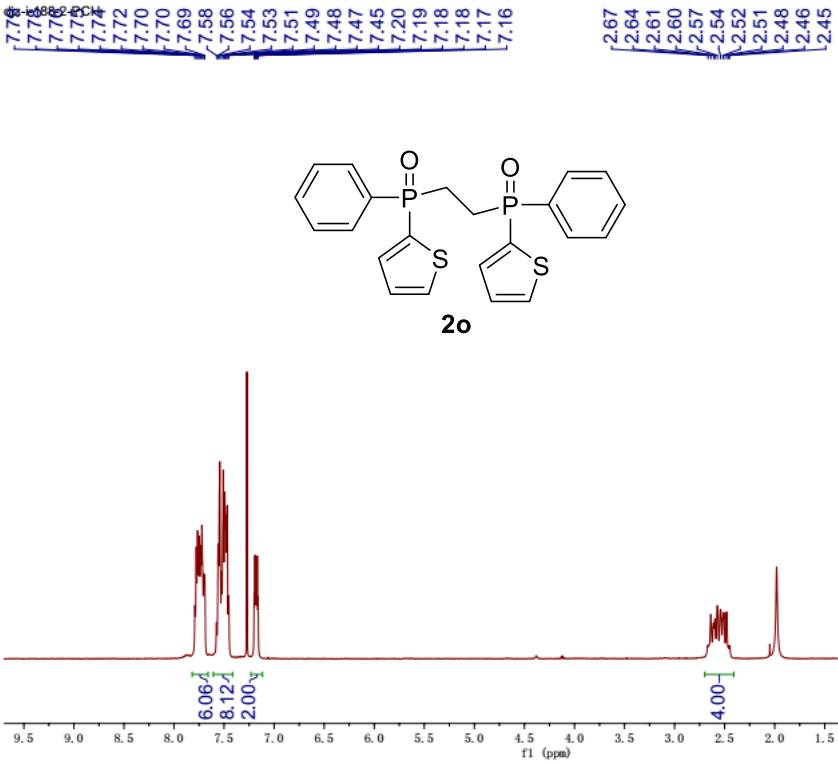


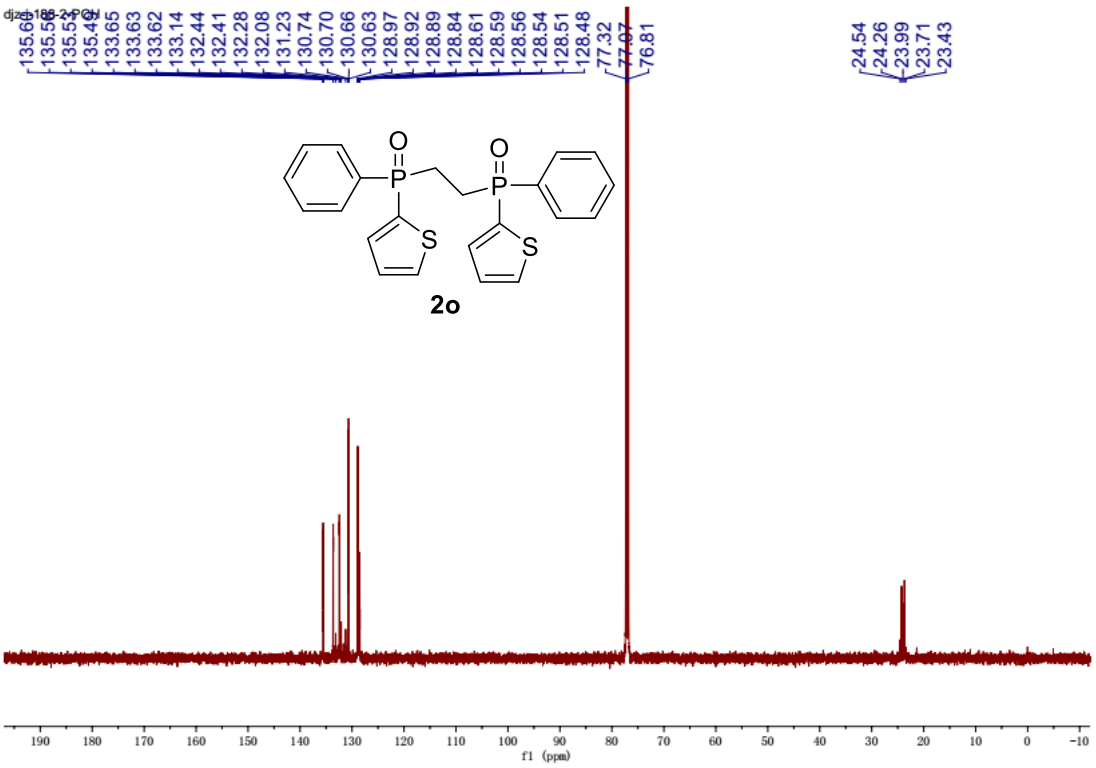

djz-i-255-1-PCB



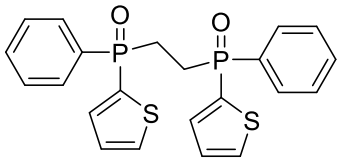

134.75
134.72
132.96
132.95
132.92
132.14
132.12
130.83
130.81
130.80
130.78
130.74
128.95
128.93
128.91
128.89
128.86
128.84
128.80
128.36
128.33
127.85
127.83
127.12
127.09
125.43
125.38
77.34
77.08
76.83
22.15
21.90
21.64
21.38
21.14
O
P
O
P
2n
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


djz-i-255-1-PCH
33.06
O
P
O
P
2n
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
f1 (ppm)


7.78
7.77
7.76
7.75
7.74
7.72
7.70
7.70
7.69
7.58
7.56
7.54
7.53
7.51
7.49
7.48
7.47
7.45
7.20
7.19
7.18
7.17
7.16
2.67
2.64
2.61
2.60
2.57
2.54
2.52
2.51
2.48
2.46
2.45
O
P
O
P
S
S
2o
6.06
8.12
2.00
4.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


135.60
135.55
135.51
135.46
133.65
133.63
133.62
133.14
132.44
132.41
132.28
132.08
131.23
130.74
130.70
130.66
130.63
128.97
128.92
128.89
128.84
128.61
128.59
128.56
128.54
128.51
128.48
77.32
77.07
76.81
24.54
24.26
23.99
23.71
23.43
O
P
O
P
S
S
2o
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

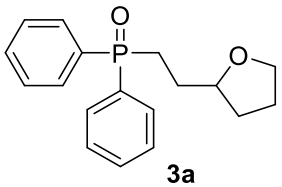
djz-i-188-2-PCH



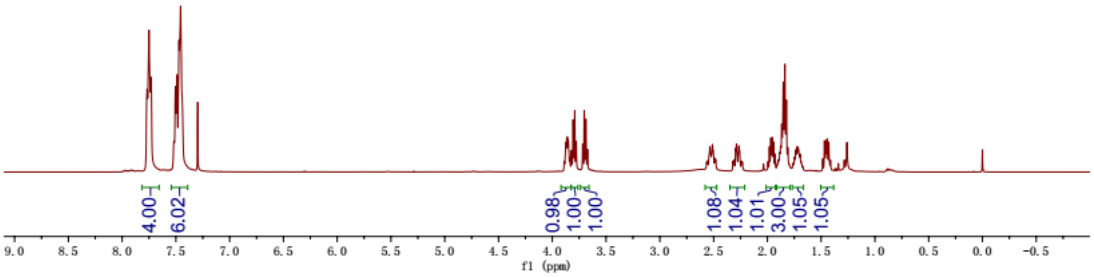
**2o**





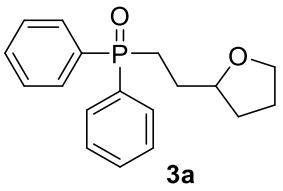


**3a**

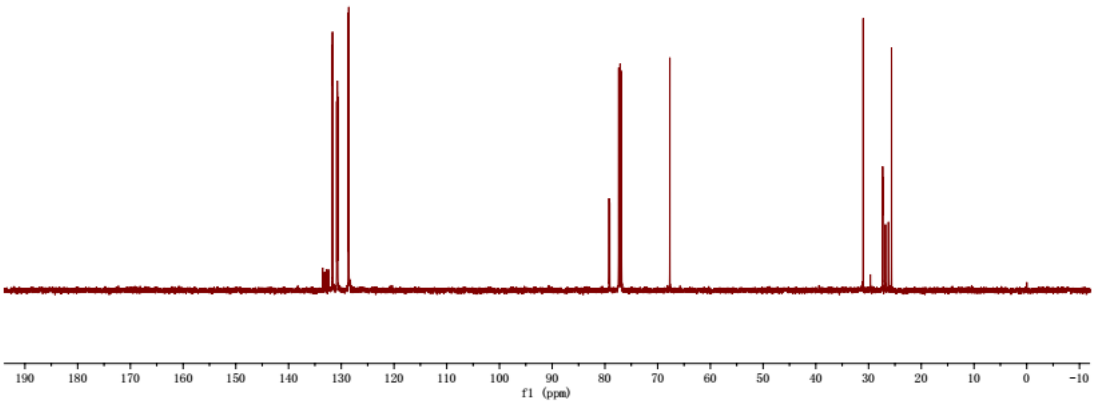


LKK-I-22A-1

133.53
133.17
132.76
132.38
131.69
131.67
130.86
130.79
130.75
130.68
128.68
128.58
79.21
79.09
77.37
77.12
76.86
67.69
31.01
27.32
27.30
26.80
26.22
25.64

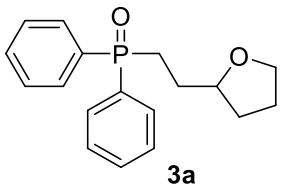


3a

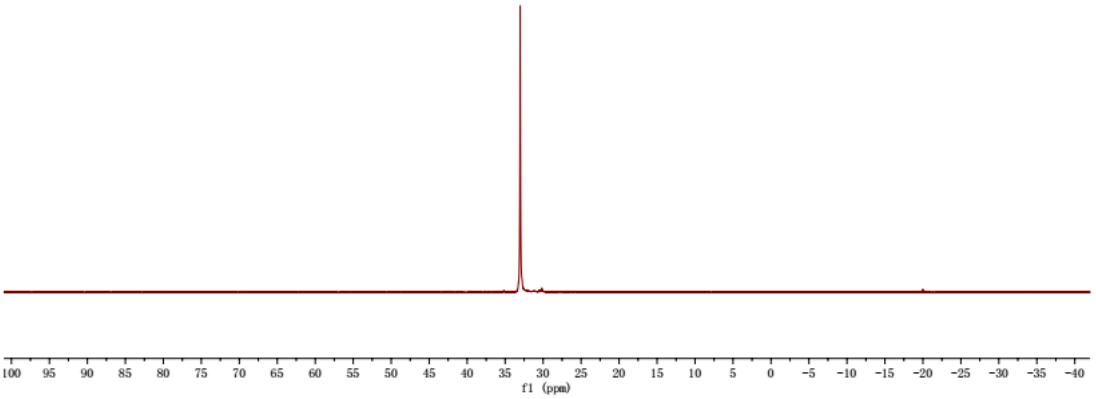


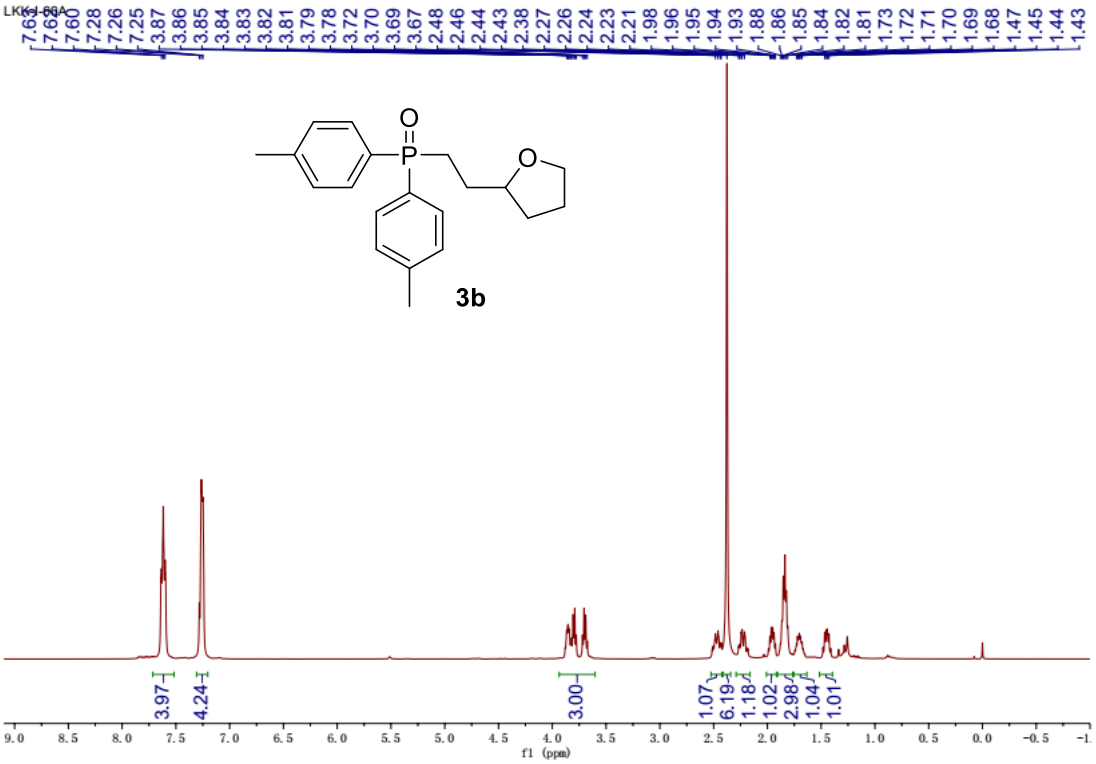

LKK-I-22A-1

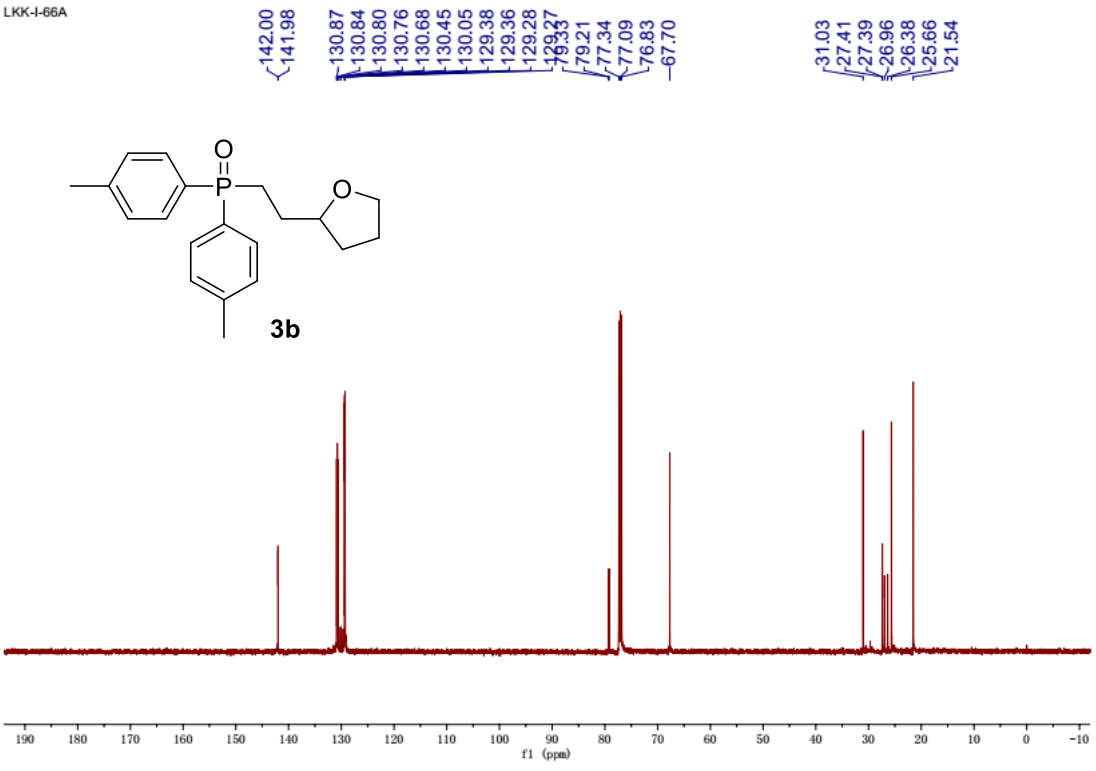
33.02



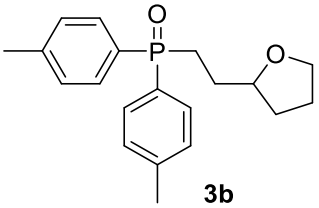
3a




LKK-I-66A
7.63
7.62
7.60
7.28
7.26
7.25
3.87
3.86
3.85
3.84
3.83
3.82
3.81
3.79
3.78
3.72
3.70
3.69
3.67
2.48
2.46
2.44
2.43
2.38
2.27
2.26
2.24
2.23
2.21
1.98
1.96
1.95
1.94
1.93
1.88
1.86
1.85
1.84
1.82
1.81
1.73
1.72
1.71
1.70
1.69
1.68
1.47
1.45
1.44
1.43
3b
3.97
4.24
3.00
1.07
6.19
1.18
1.02
2.98
1.04
1.01
f1 (ppm)


LKK-I-66A
142.00
141.98
130.87
130.84
130.80
130.76
130.68
130.45
130.05
129.38
129.36
129.28
79.21
77.34
77.09
76.83
67.70
31.03
27.41
27.39
26.96
26.38
25.66
21.54
3b
f1 (ppm)

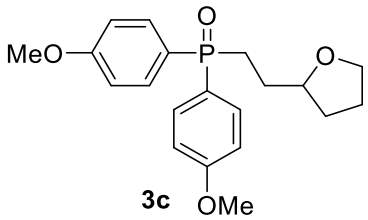
LKK-I-66A



3b

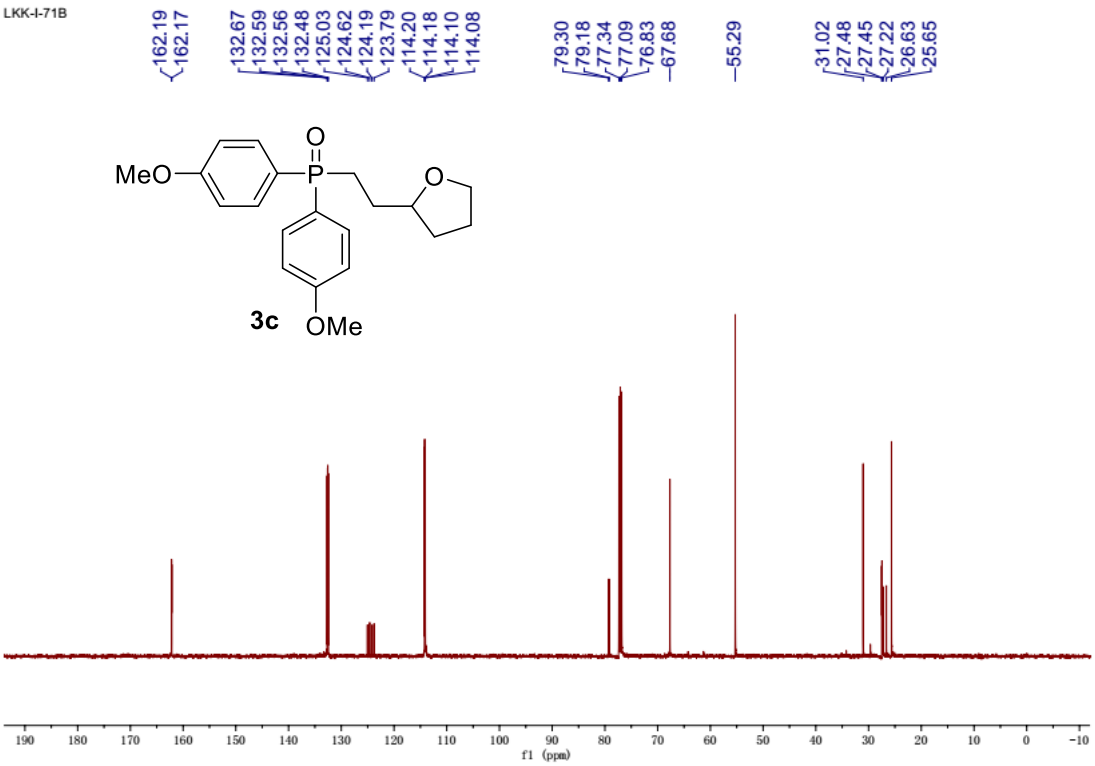



LKK-I-71B

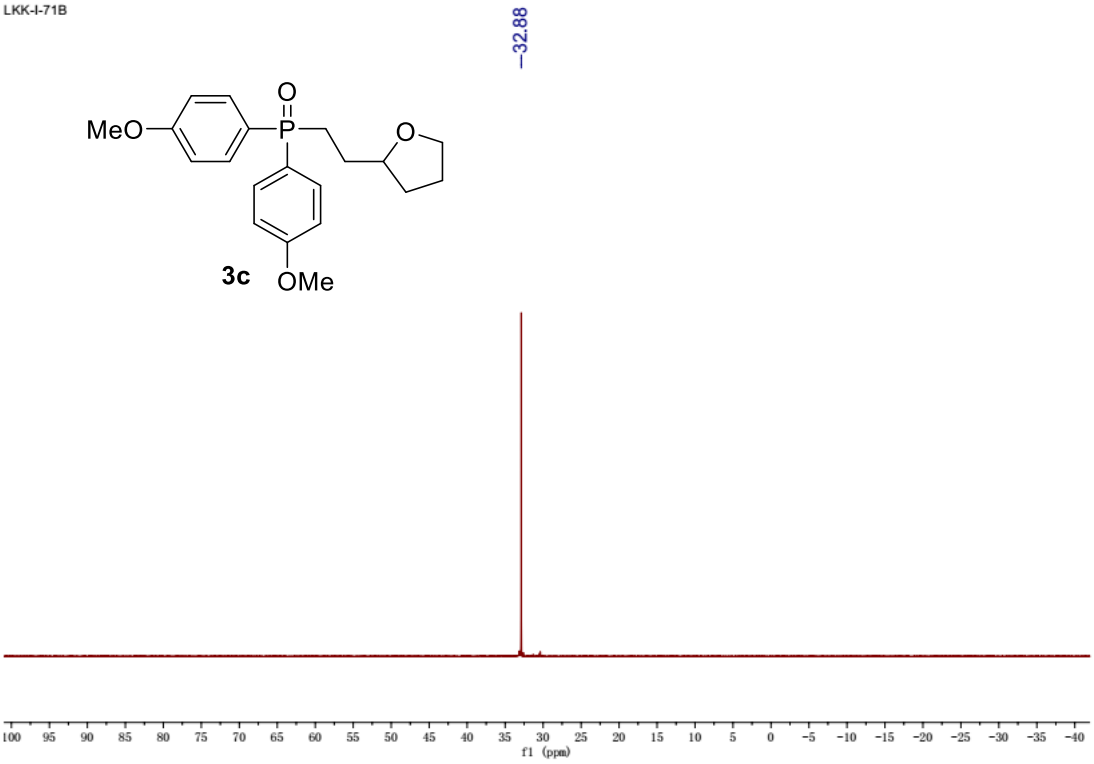


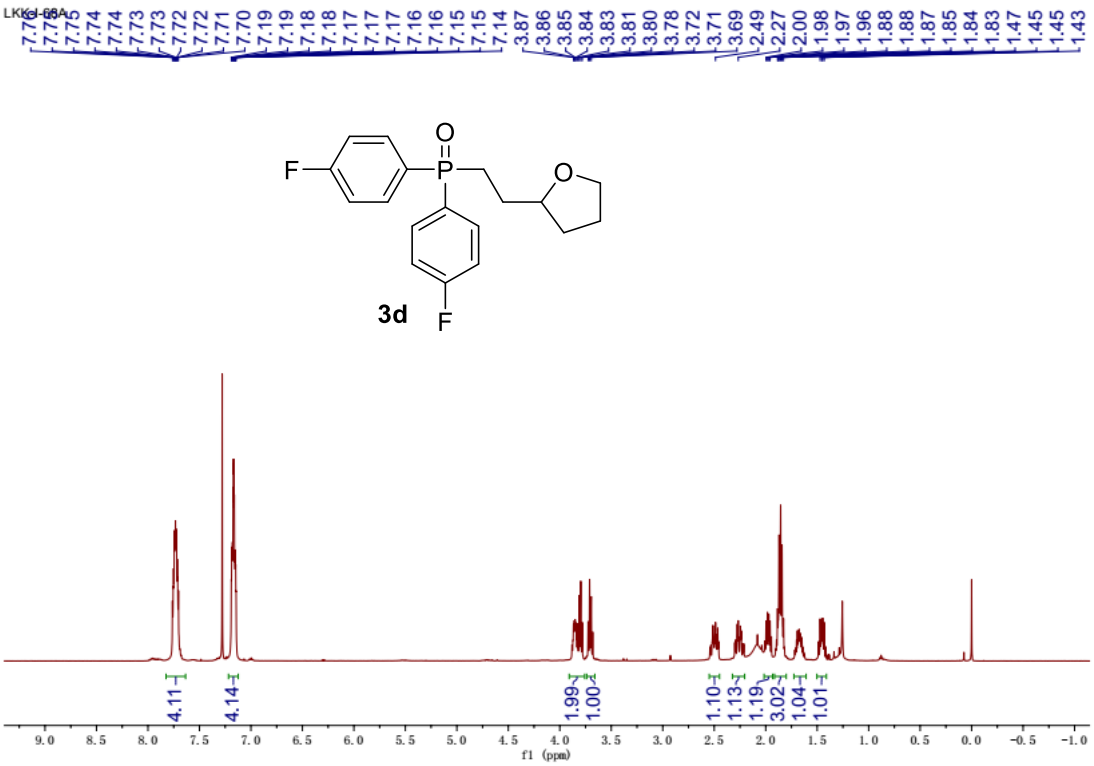
3c

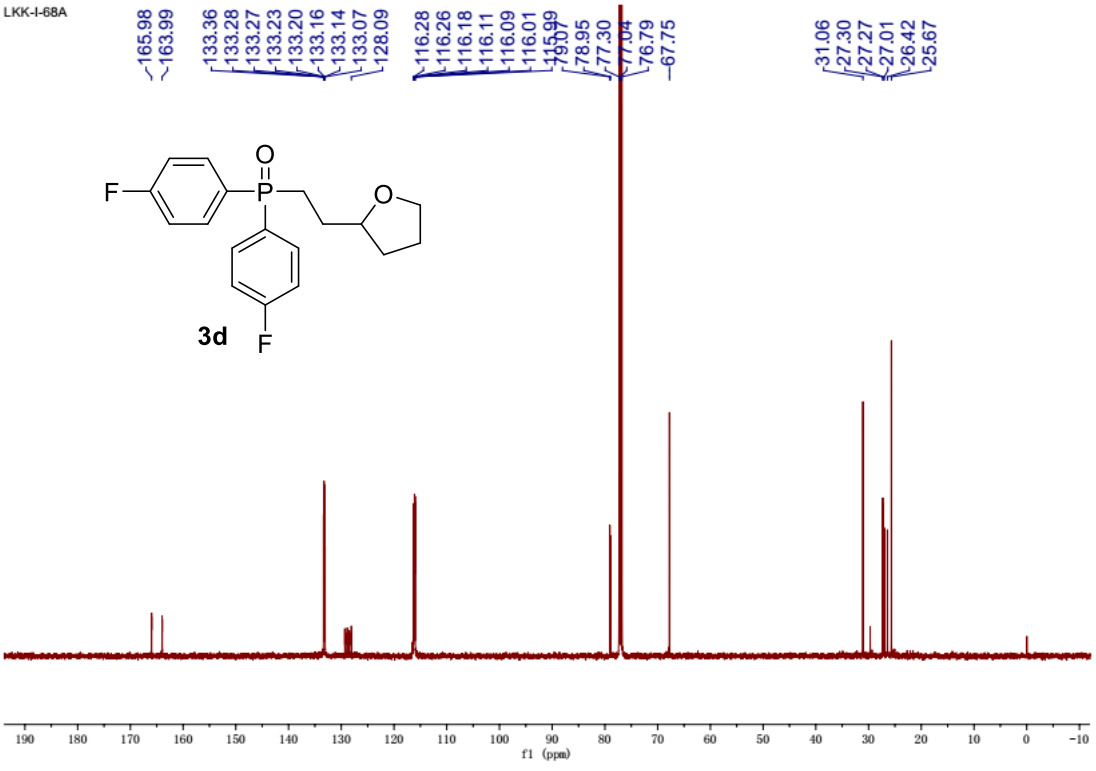
LKK-I-71B



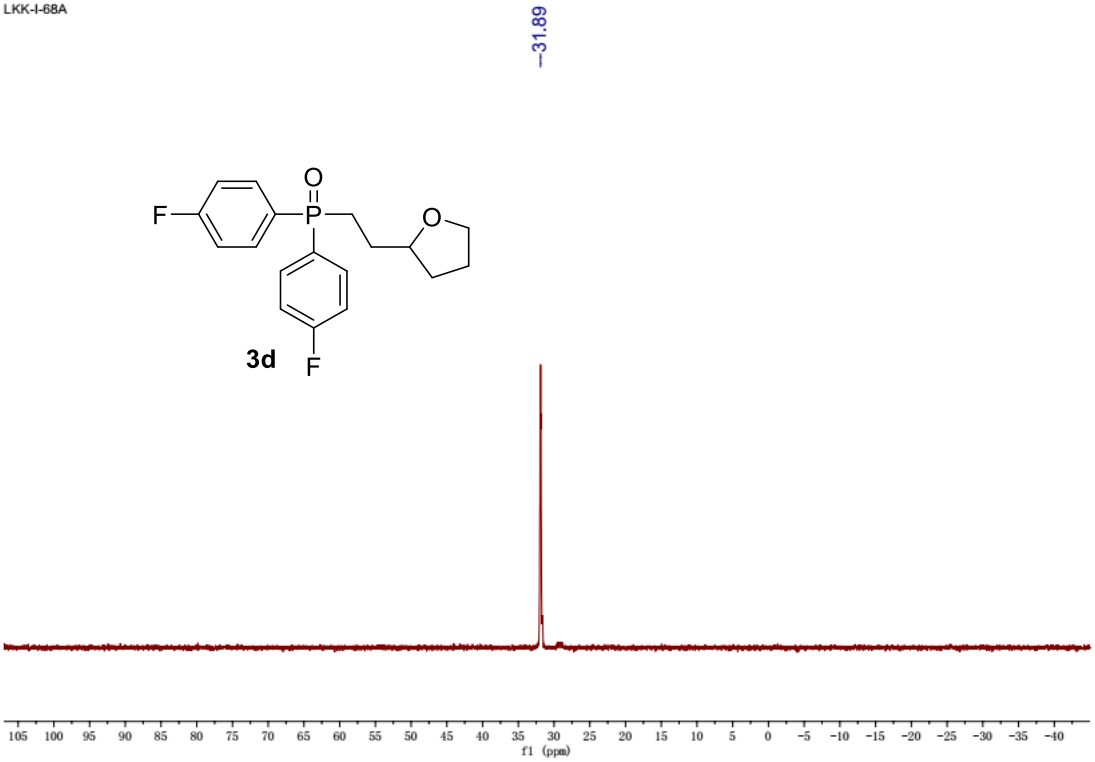

LKK-I-71B



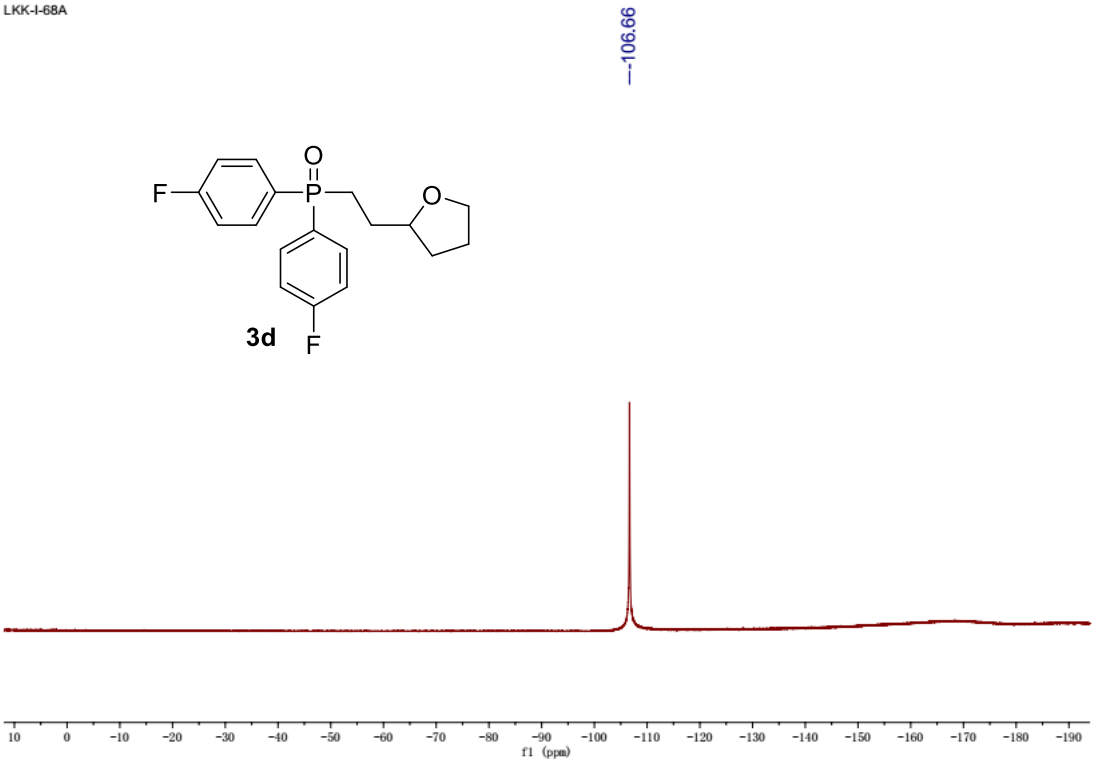

LKK-I-68A
7.76 7.75 7.75 7.74 7.74 7.73 7.73 7.72 7.72 7.71 7.70 7.19 7.19 7.18 7.18 7.17 7.17 7.17 7.16 7.16 7.15 7.15 7.14
3.87 3.86 3.85 3.84 3.83 3.81 3.80 3.78 3.72 3.71 3.69 2.49 2.27 2.00 1.98 1.97 1.96 1.88 1.88 1.87 1.85 1.84 1.83 1.47 1.45 1.45 1.43
O
P
F
O
3d
F
4.11
4.14
1.99
1.00
1.10
1.13
1.19
3.02
1.04
1.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


LKK-I-68A
165.98 163.99
133.36 133.28 133.27 133.23 133.20 133.16 133.14 133.07 128.09
116.28 116.26 116.18 116.11 116.09 116.01 115.99 79.07 78.95 77.30 77.04 76.79 67.75
31.06 27.30 27.27 27.01 26.42 25.67
O
P
F
O
3d
F
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

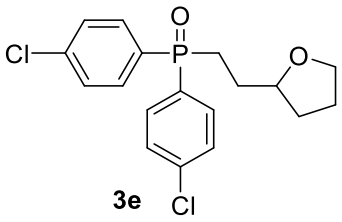
LKK-I-68A

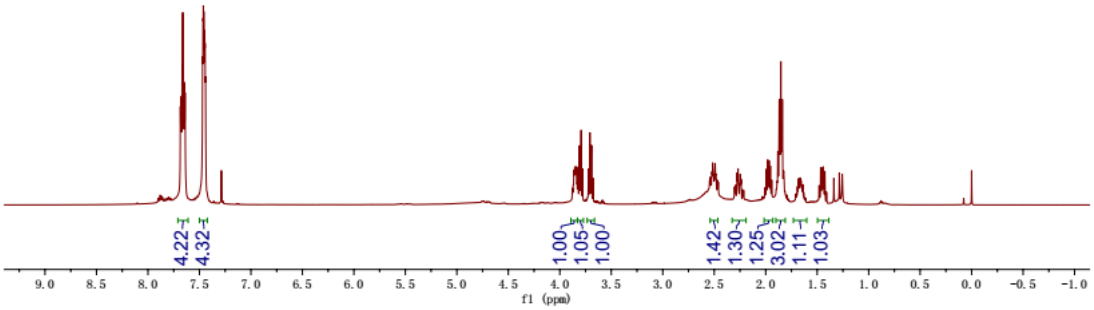



LKK-I-68A

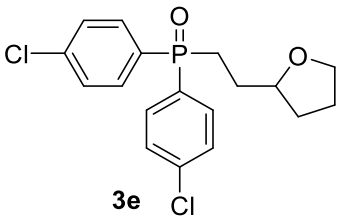


LKK-I-66B

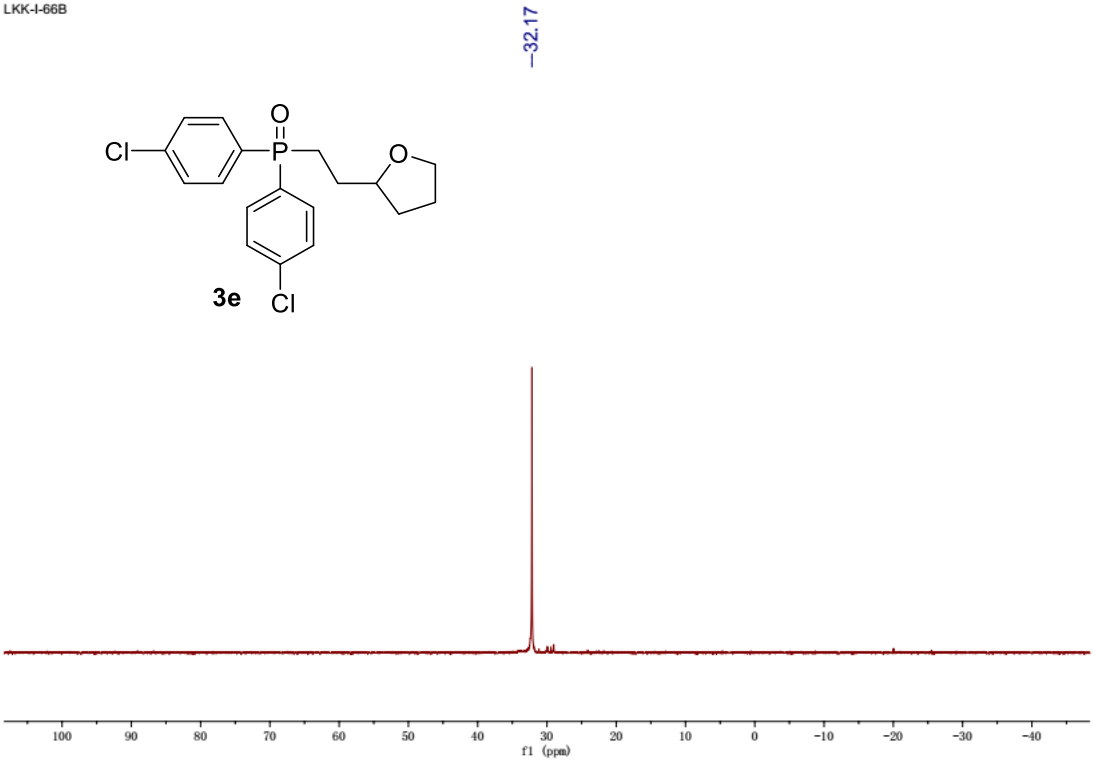


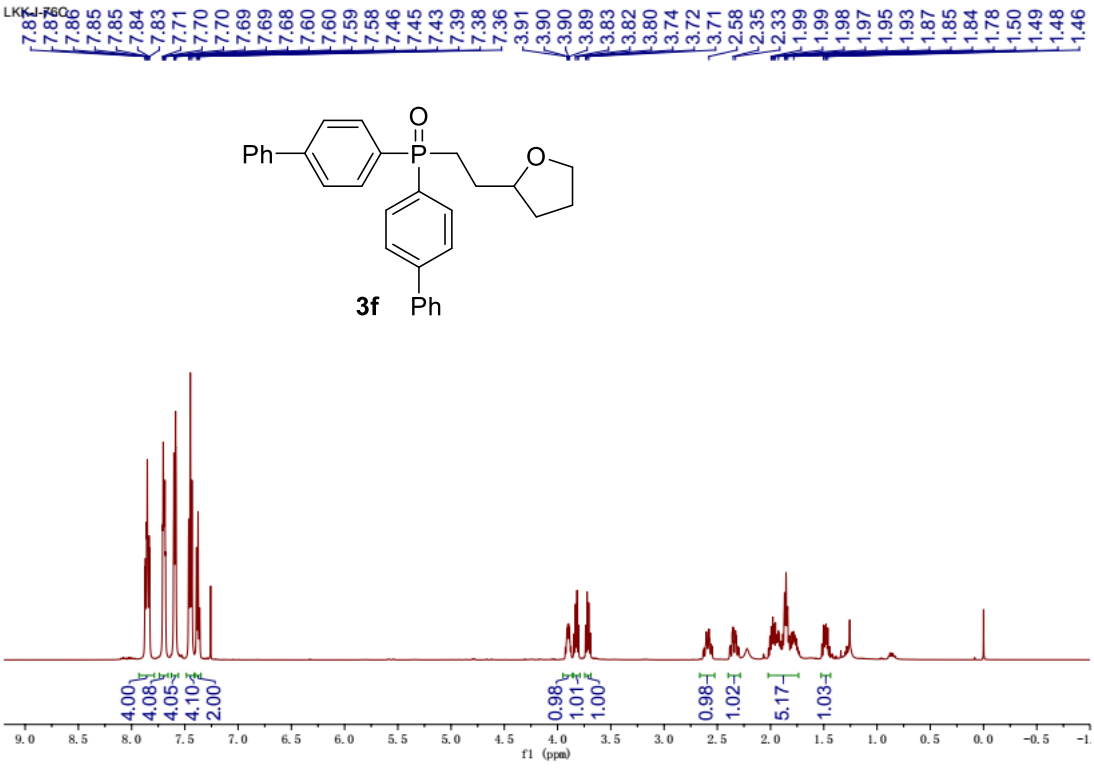

LKK-I-66B

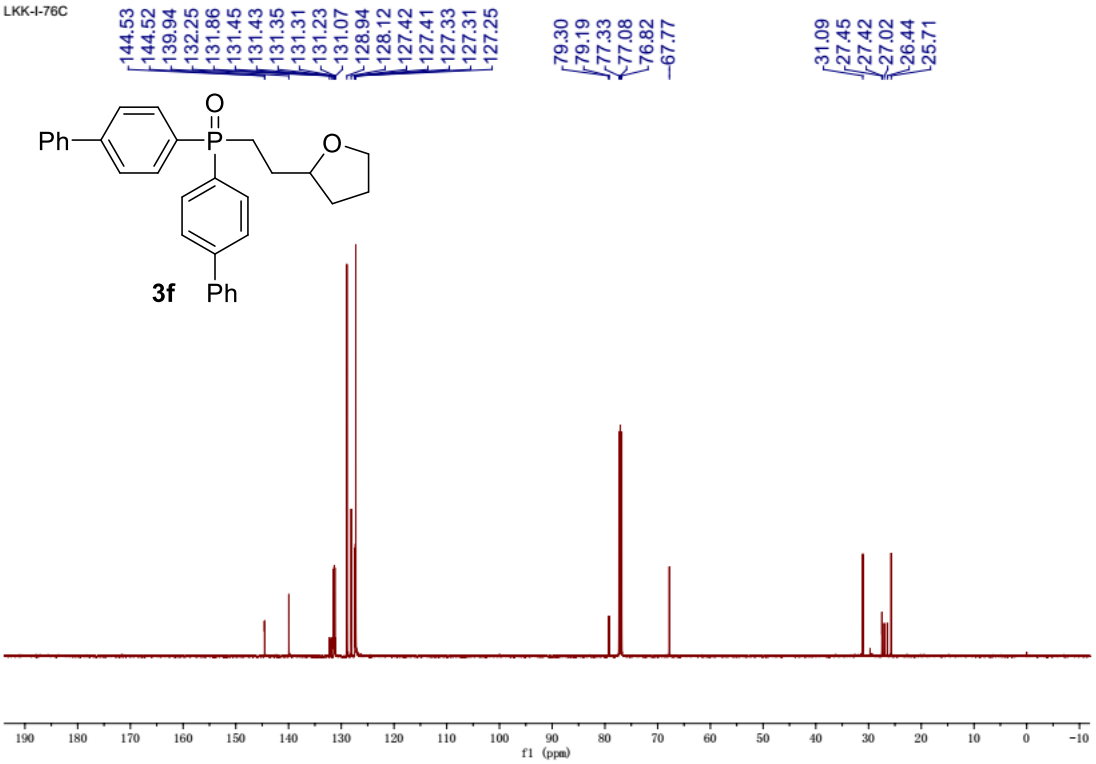


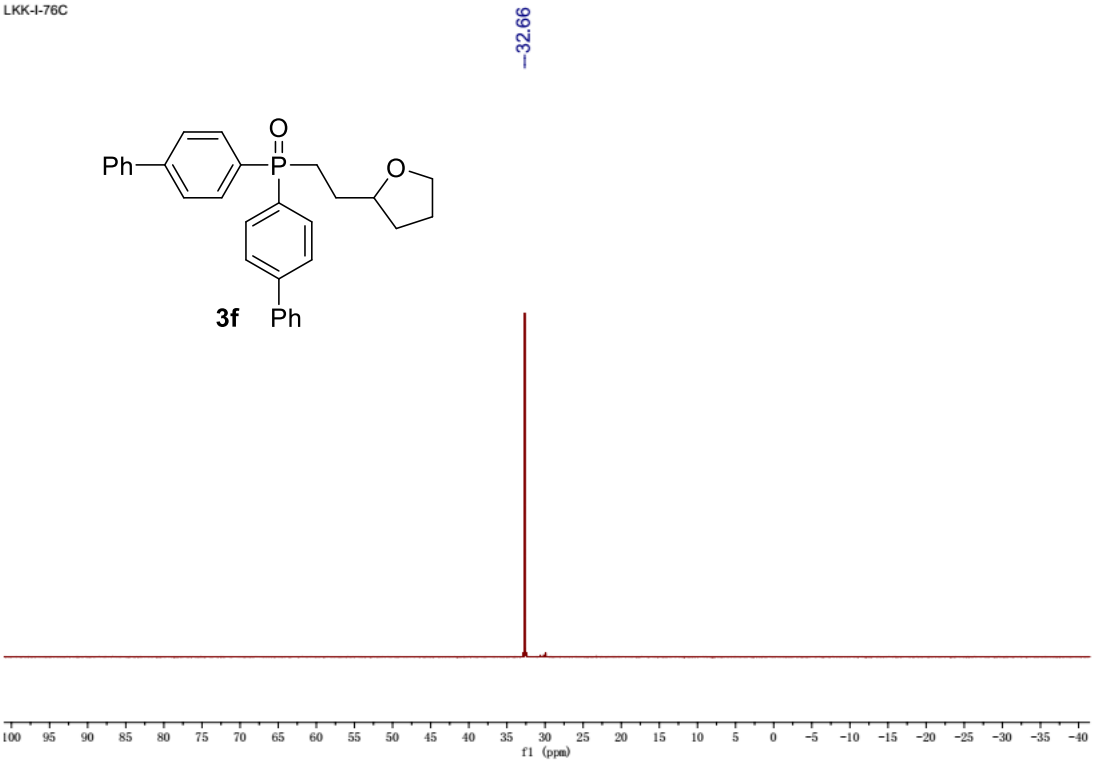
LKK-I-66B

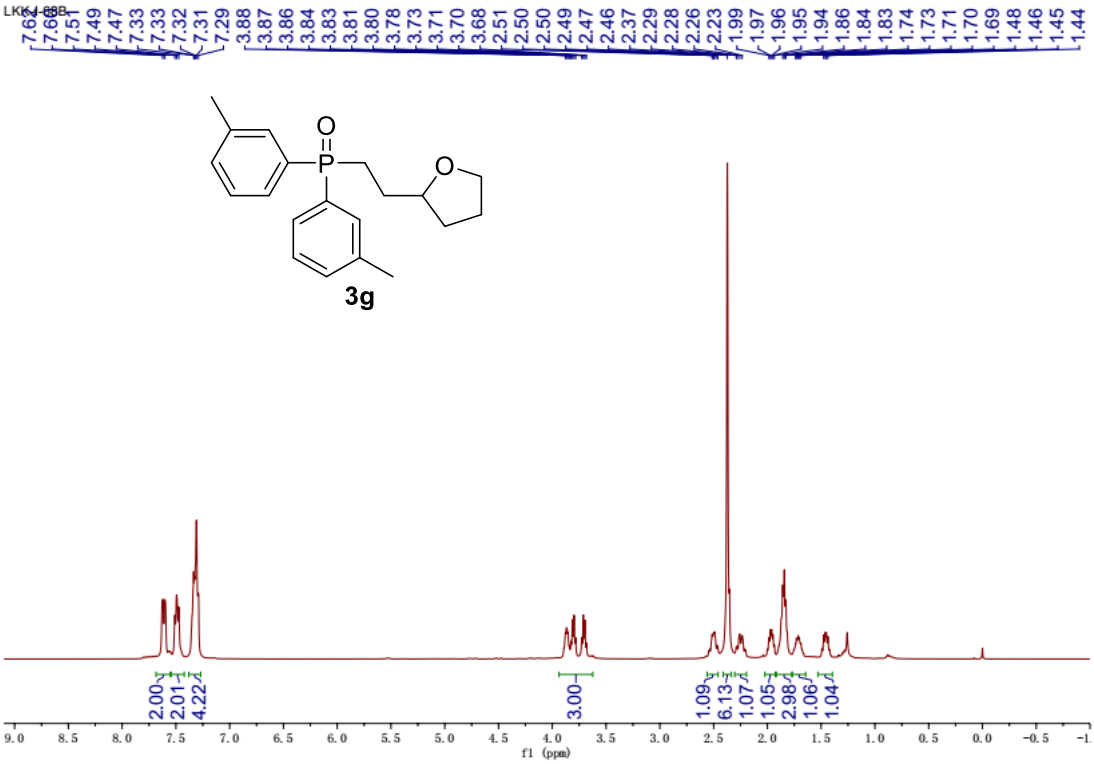


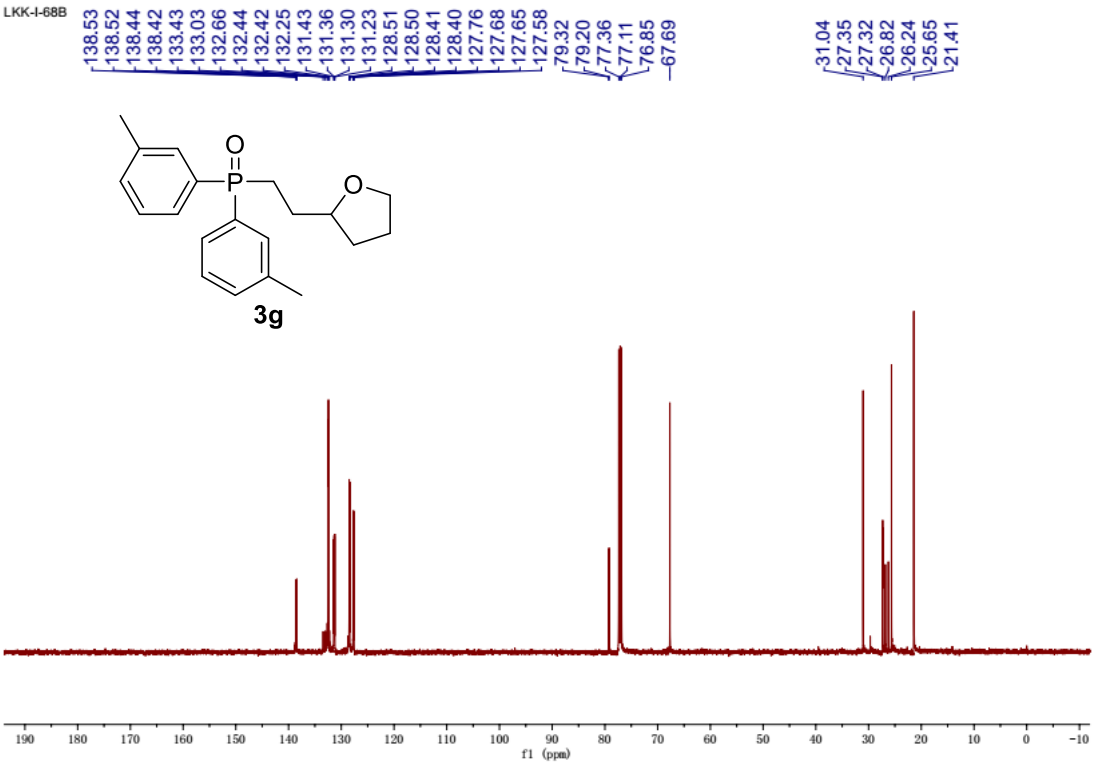

LKK-I-76C



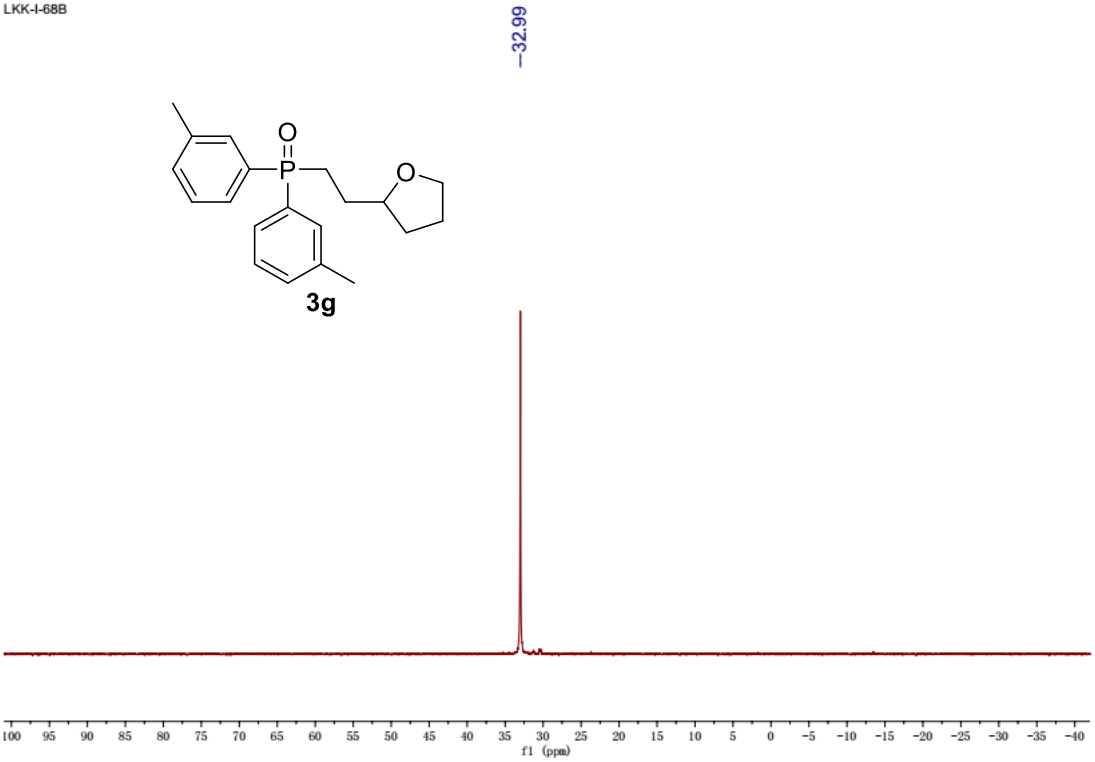

LKK-I-76C
144.53
144.52
139.94
132.25
131.86
131.45
131.43
131.35
131.31
131.23
131.07
128.94
128.12
127.42
127.41
127.33
127.31
127.25
79.30
79.19
77.33
77.08
76.82
67.77
31.09
27.45
27.42
27.02
26.44
25.71
Ph
O
P
O
3f
Ph
f1 (ppm)


LKK-I-76C
32.66
Ph
O
P
O
3f
Ph
f1 (ppm)

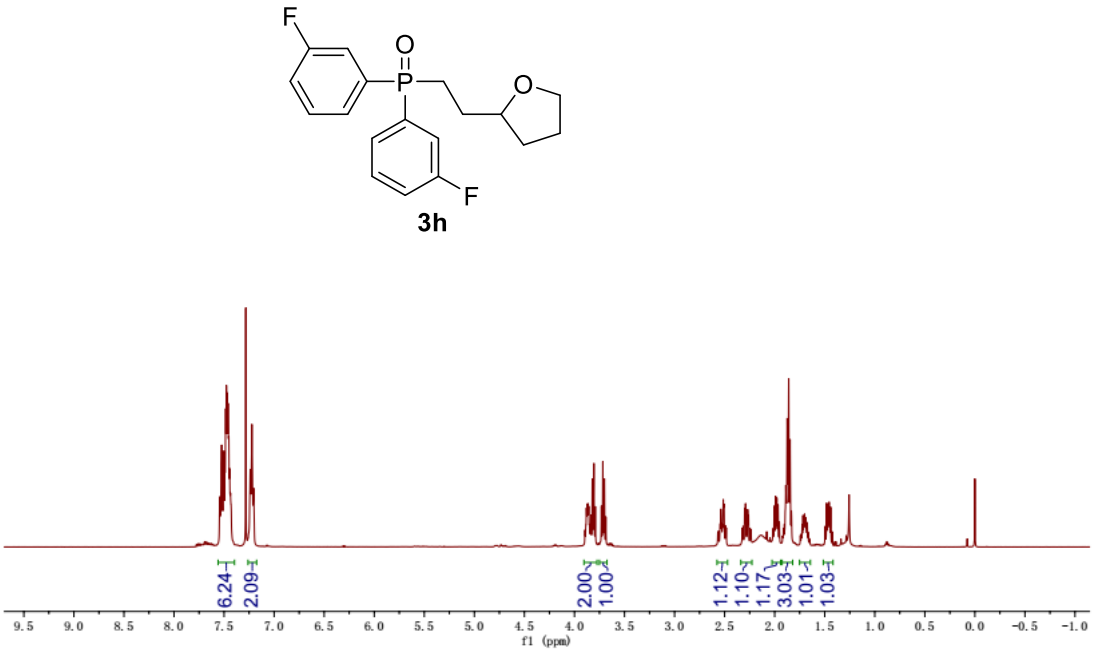

LKK-I-68B
7.62
7.60
7.51
7.49
7.47
7.33
7.32
7.31
7.29
3.88
3.87
3.86
3.84
3.83
3.81
3.80
3.78
3.73
3.71
3.70
3.68
2.51
2.50
2.49
2.47
2.46
2.37
2.29
2.28
2.26
2.23
1.99
1.97
1.96
1.95
1.94
1.86
1.84
1.83
1.74
1.73
1.71
1.70
1.69
1.48
1.46
1.45
1.44
O
P
O
3g
2.00
2.01
4.22
3.00
1.09
6.13
1.07
1.05
2.98
1.06
1.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


LKK-I-68B
138.53
138.52
138.44
138.42
133.43
133.03
132.66
132.44
132.42
132.25
131.43
131.36
131.30
131.23
128.51
128.50
128.41
128.40
127.76
127.68
127.65
127.58
79.32
79.20
77.36
77.11
76.85
67.69
31.04
27.35
27.32
26.82
26.24
25.65
21.41
O
P
O
3g
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

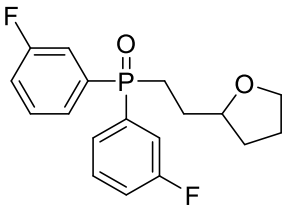
LKK-I-68B


32.99
O
P
O
3g
100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40
f1 (ppm)


7.54
7.52
7.50
7.50
7.49
7.48
7.48
7.47
7.46
7.45
7.44
7.44
7.24
7.22
7.21
3.88
3.87
3.86
3.86
3.84
3.82
3.81
3.79
3.73
3.72
3.70
3.69
2.54
2.51
2.51
2.30
2.29
2.27
2.26
2.00
1.99
1.98
1.97
1.89
1.88
1.86
1.85
1.83
1.72
1.70
1.48
1.46
1.46
1.44


F
O
P
O
F
3h
6.24
2.09
2.00
1.00
1.12
1.10
1.17
3.03
1.01
1.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

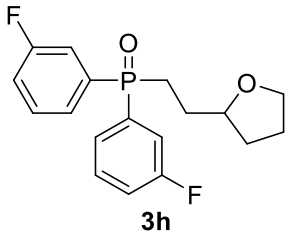
LKK-I-72D

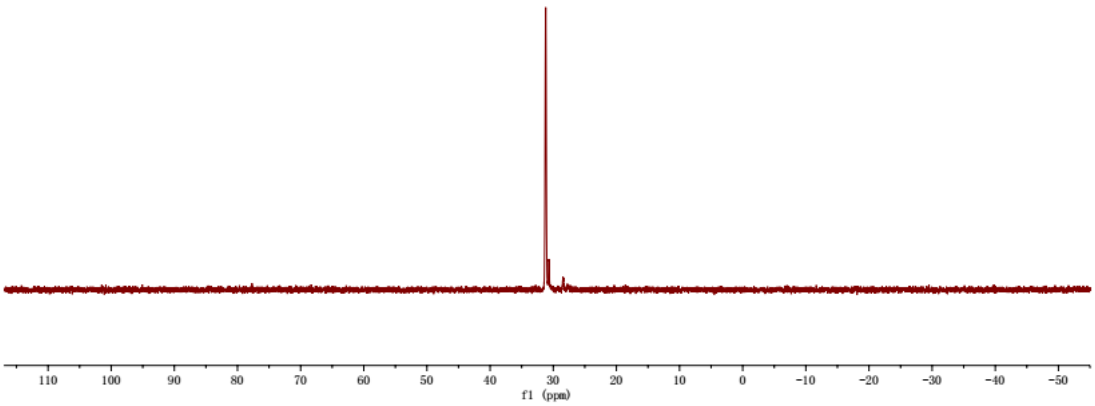

**3h**



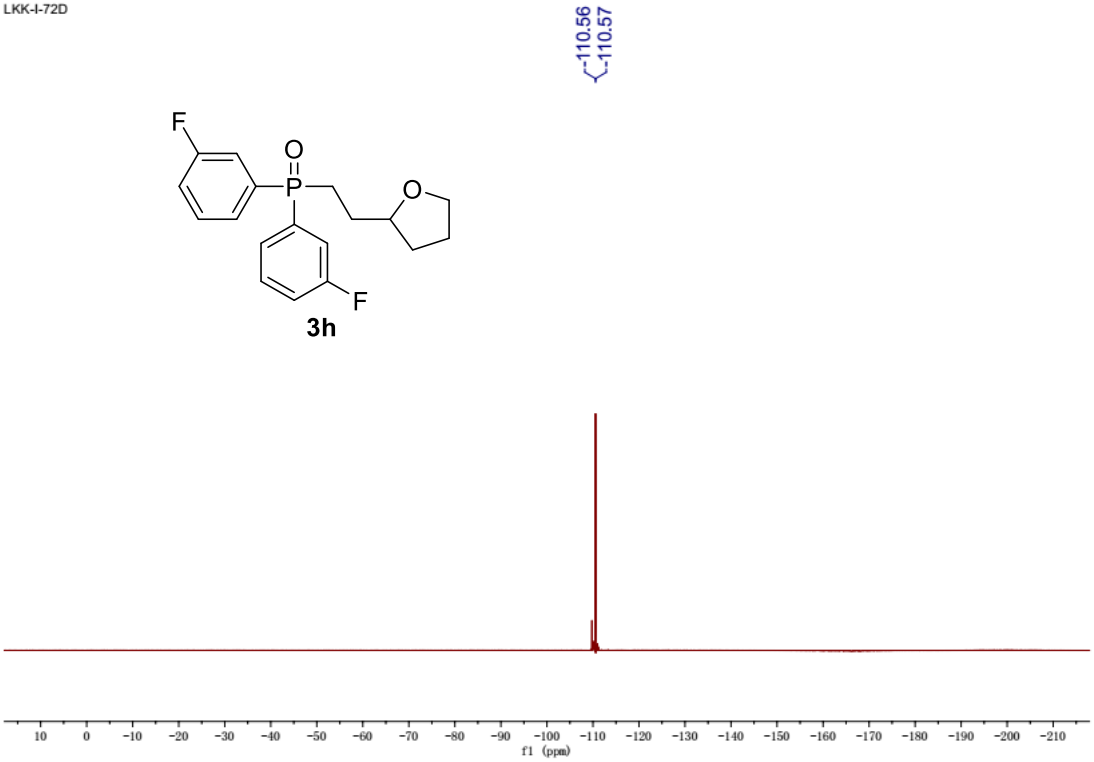

LKK-I-72D

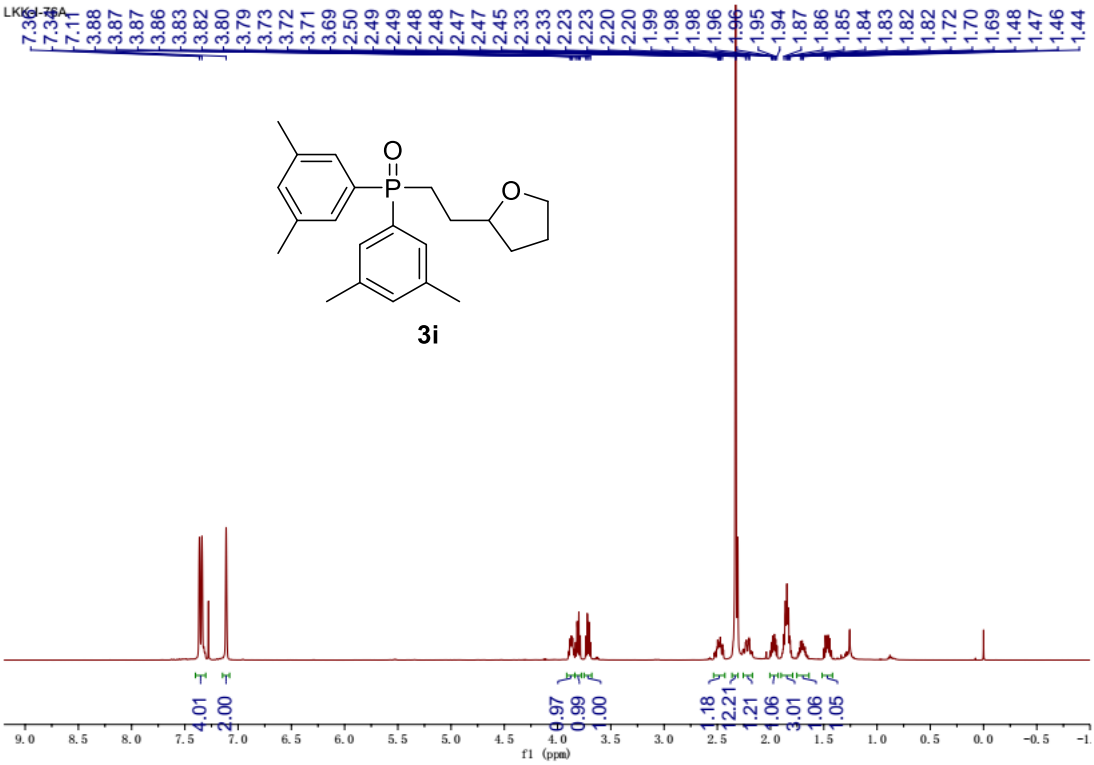

**3h**



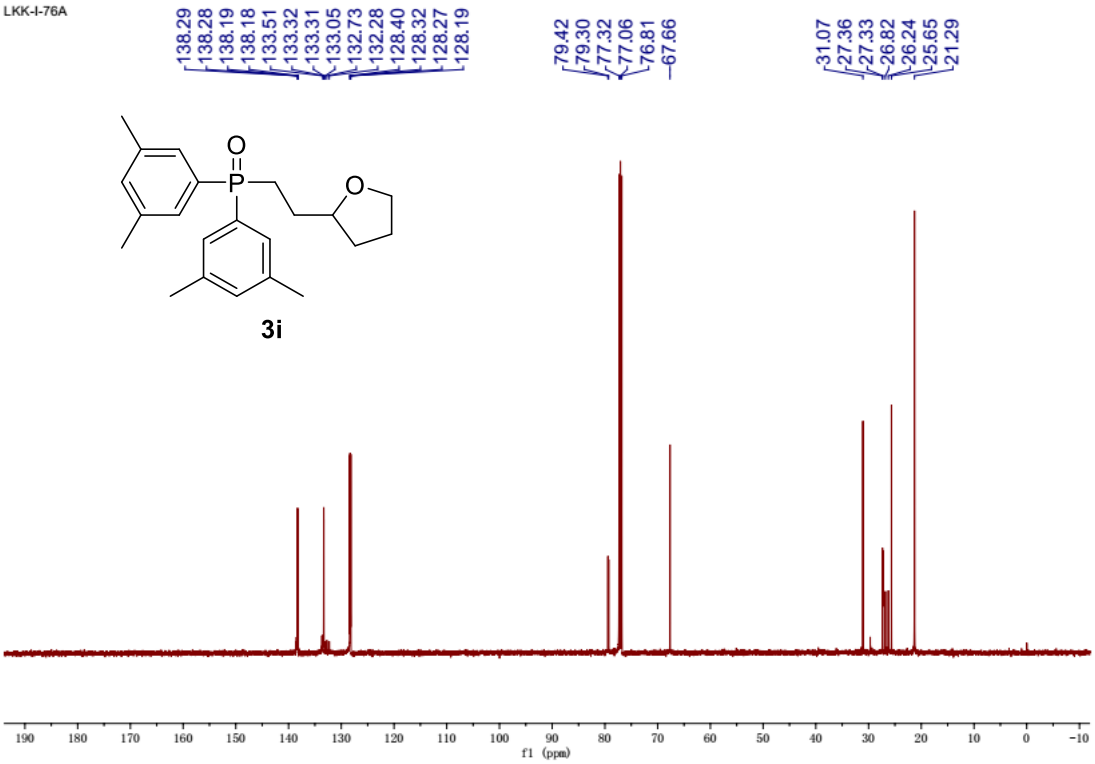
LKK-I-72D



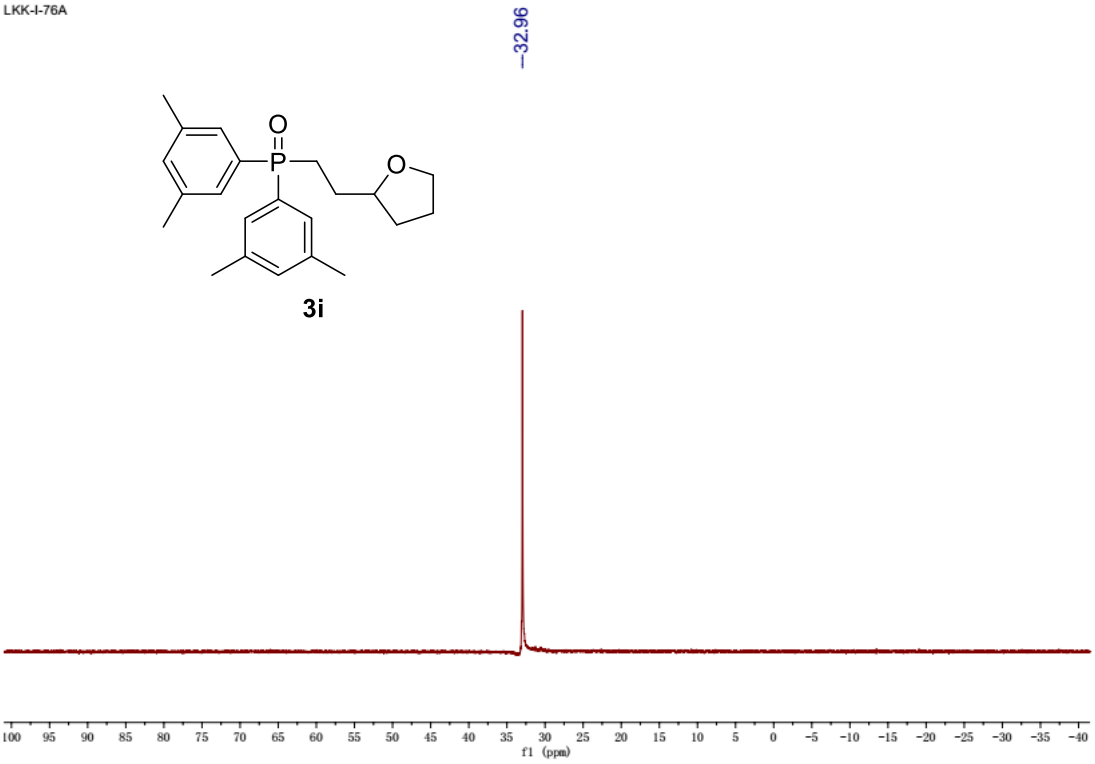

LKK-I-76A

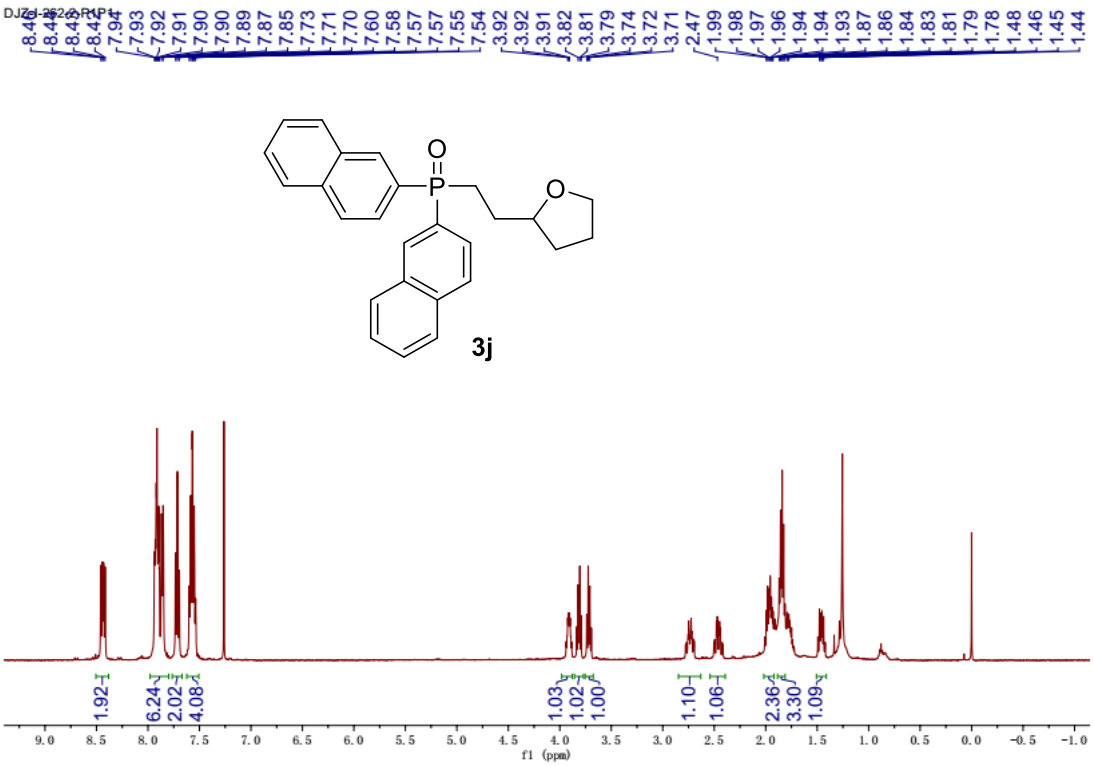


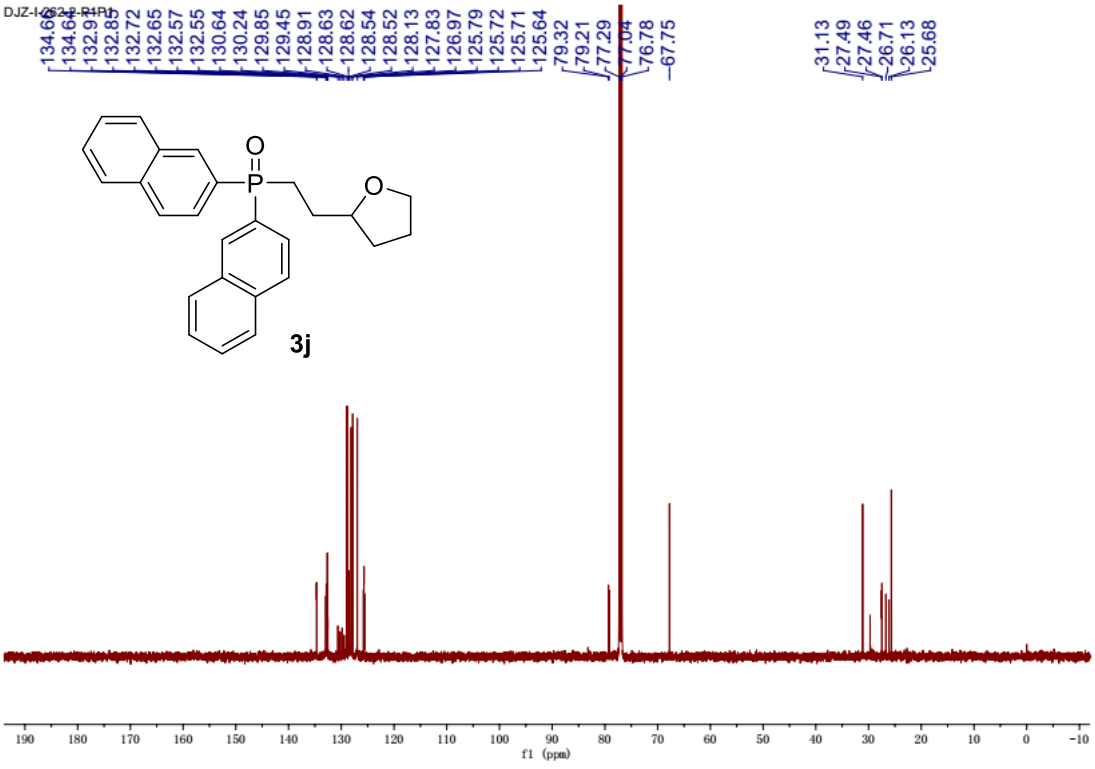
LKK-I-76A



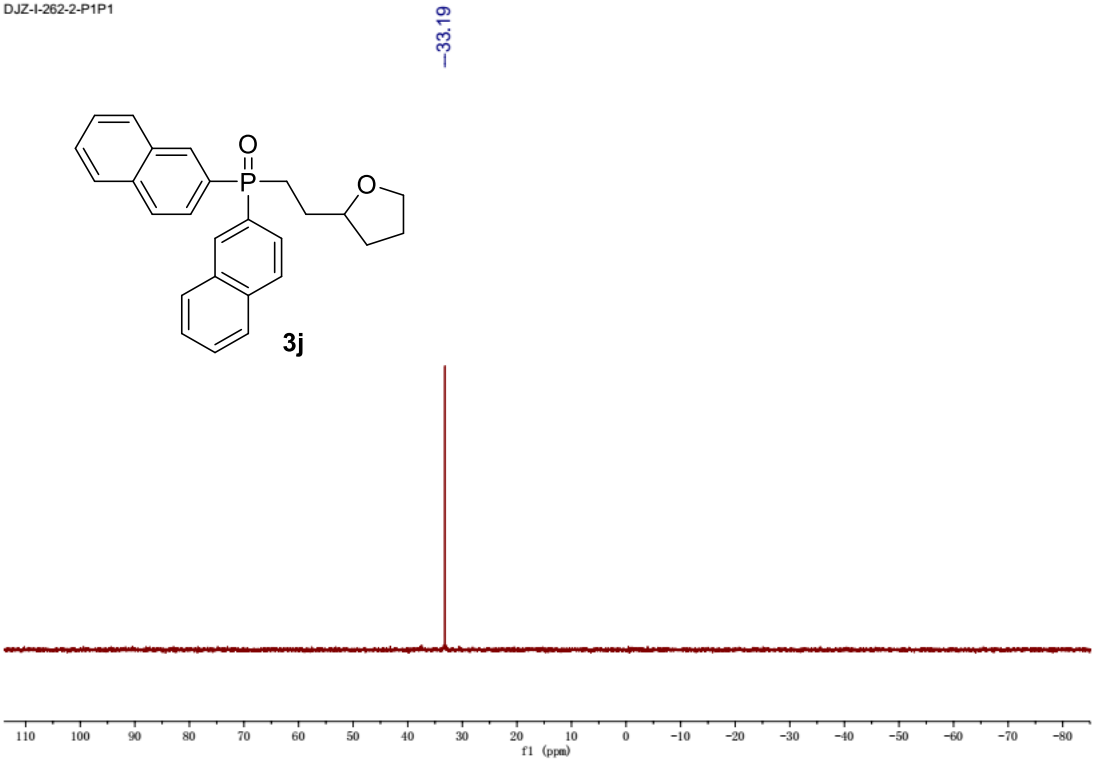

LKK-I-76A



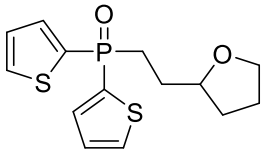

8.46
8.45
8.43
8.42
7.94
7.93
7.92
7.91
7.90
7.90
7.89
7.87
7.85
7.73
7.71
7.70
7.60
7.58
7.57
7.57
7.55
7.54
3.92
3.92
3.91
3.82
3.81
3.79
3.74
3.72
3.71
2.47
1.99
1.98
1.97
1.96
1.94
1.94
1.93
1.87
1.86
1.84
1.83
1.81
1.79
1.78
1.48
1.46
1.45
1.44
O
P
O
3j
1.92
6.24
2.02
4.08
1.03
1.02
1.00
1.10
1.06
2.36
3.30
1.09
f1 (ppm)


134.66
134.64
132.91
132.85
132.72
132.65
132.57
132.55
130.64
130.24
129.85
129.45
128.91
128.63
128.62
128.54
128.52
128.13
127.83
126.97
125.79
125.72
125.71
125.64
79.32
79.21
77.29
77.04
76.78
67.75
31.13
27.49
27.46
26.71
26.13
25.68
O
P
O
3j
f1 (ppm)

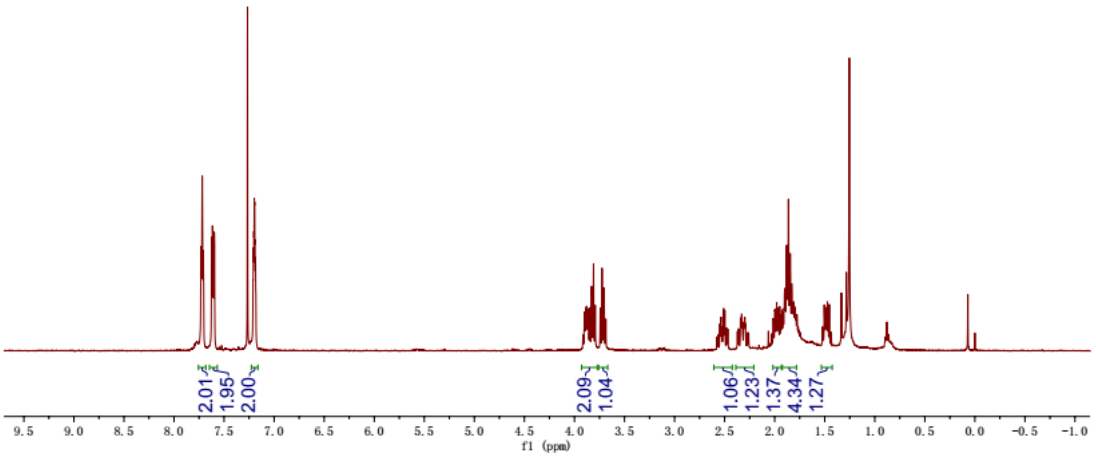
DJZ-I-262-2-P1P1

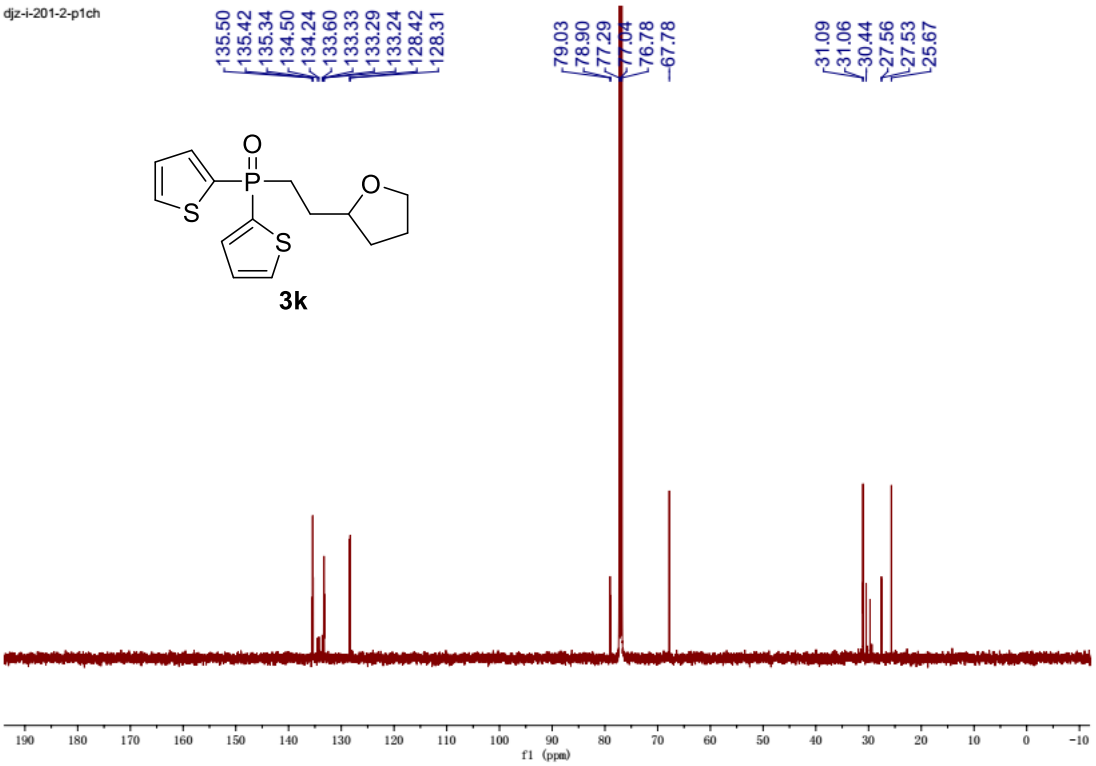


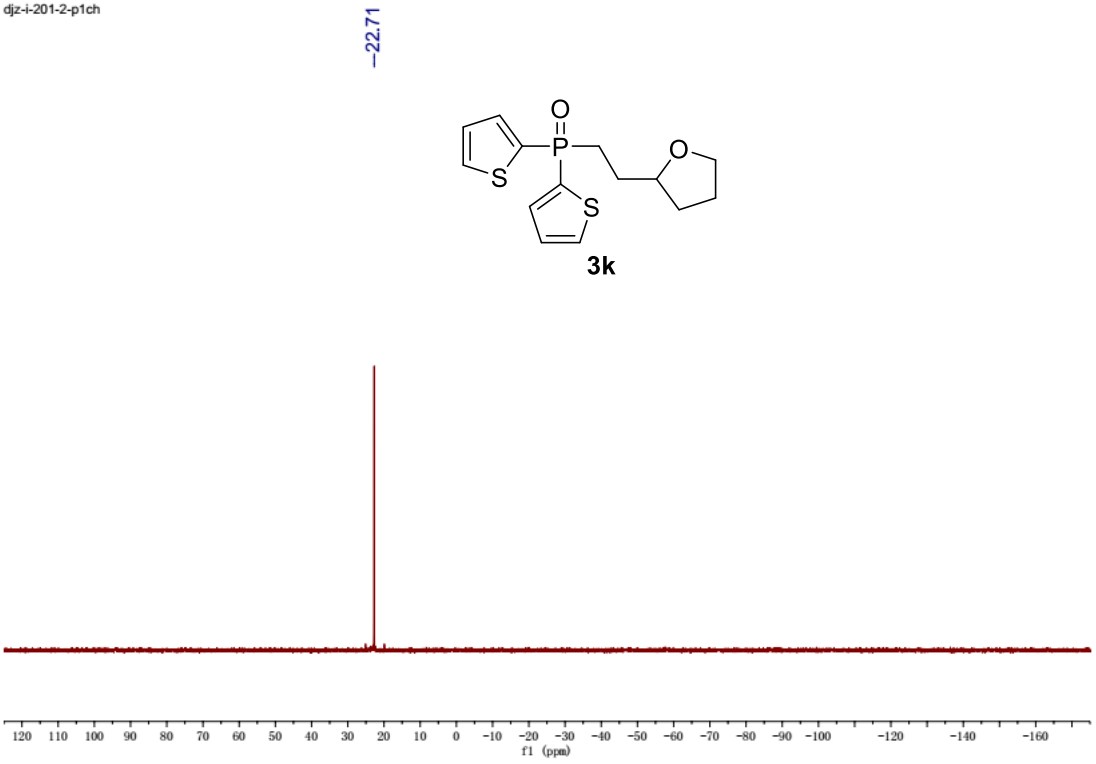

3j

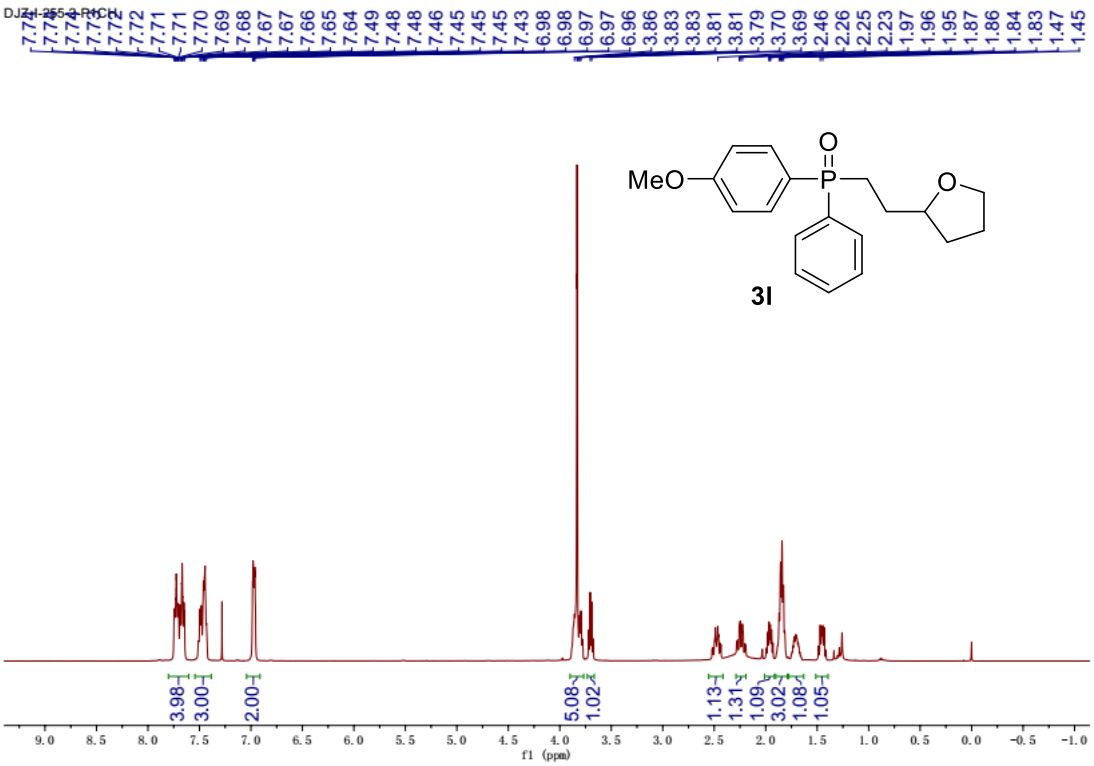


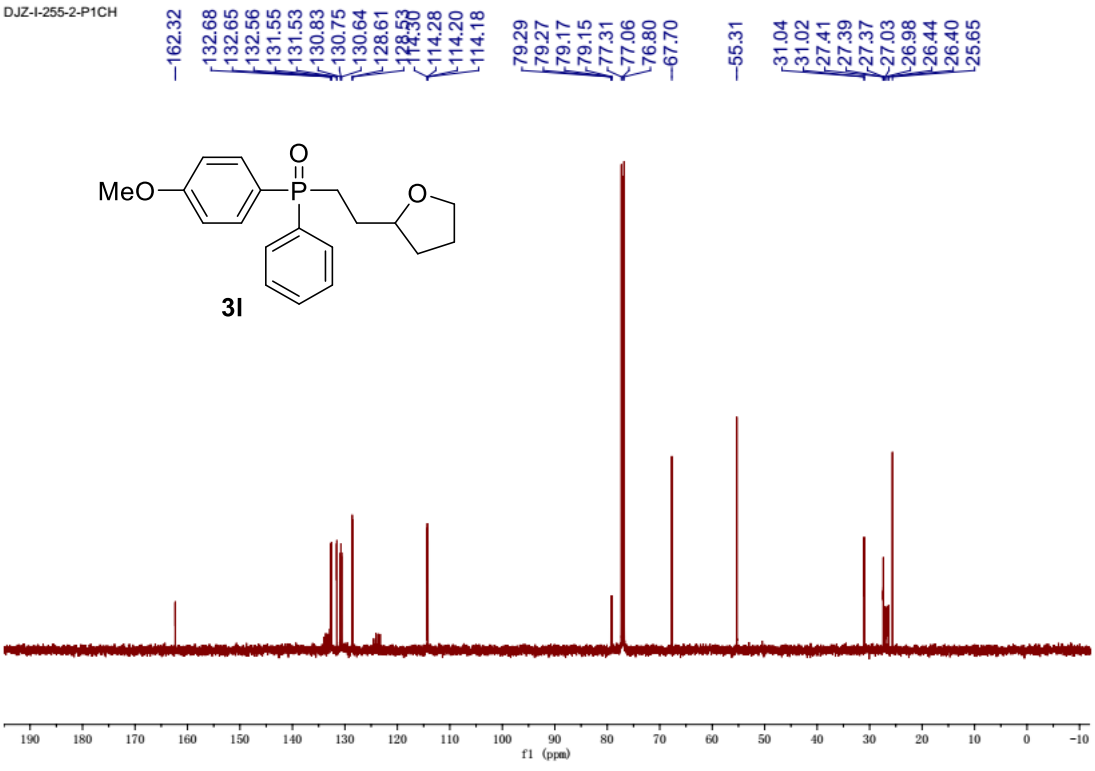

3k



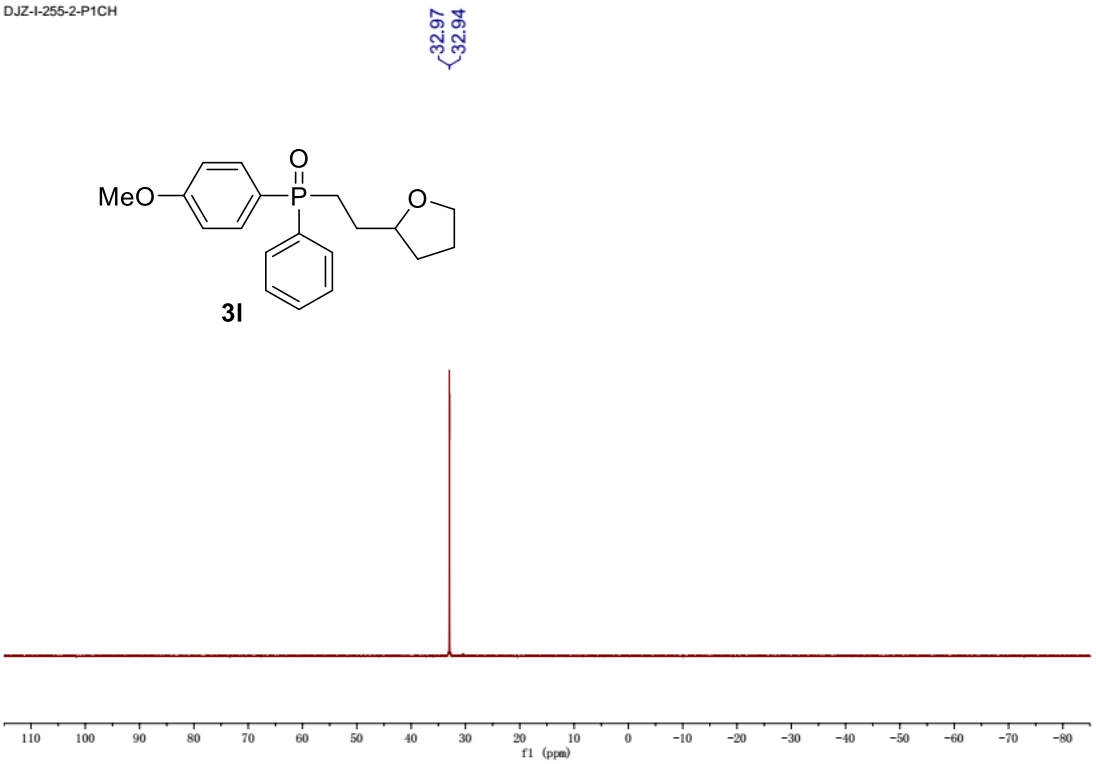

djz-i-201-2-p1ch
135.50
135.42
135.34
134.50
134.24
133.60
133.33
133.29
133.24
128.42
128.31
79.03
78.90
77.29
77.04
76.78
67.78
31.09
31.06
30.44
27.56
27.53
25.67
O
P
S
S
O
3k
f1 (ppm)


djz-i-201-2-p1ch
22.71
O
P
S
S
O
3k
f1 (ppm)

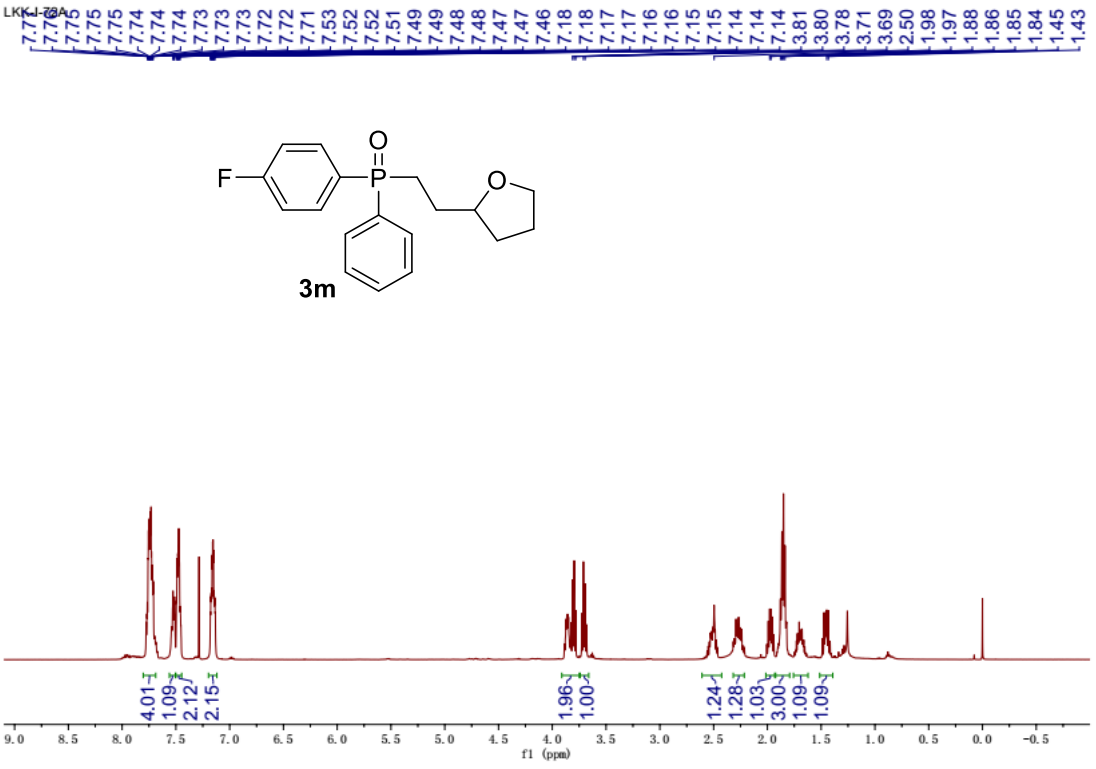

DJZ-I-255-2-P1CH
MeO
O
P
O
3l
3.98
3.00
2.00
5.08
1.02
1.13
1.31
1.09
3.02
1.08
1.05
f1 (ppm)

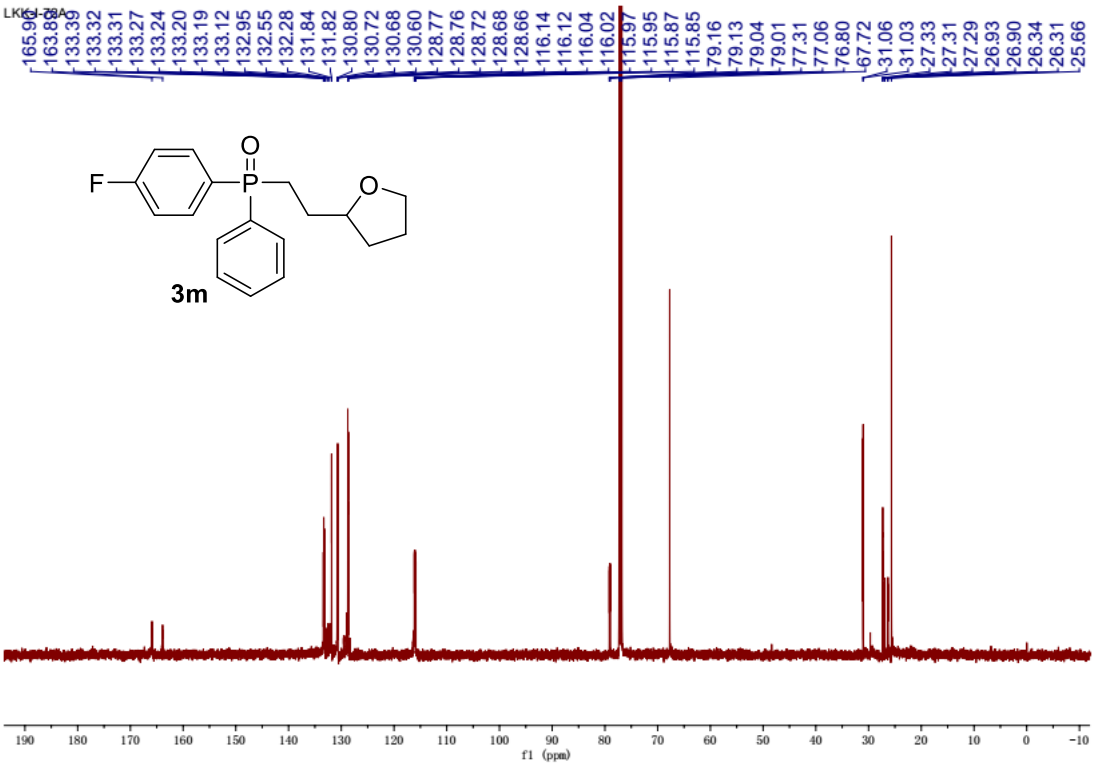

DJZ-I-255-2-P1CH
MeO
O
P
O
3l
f1 (ppm)

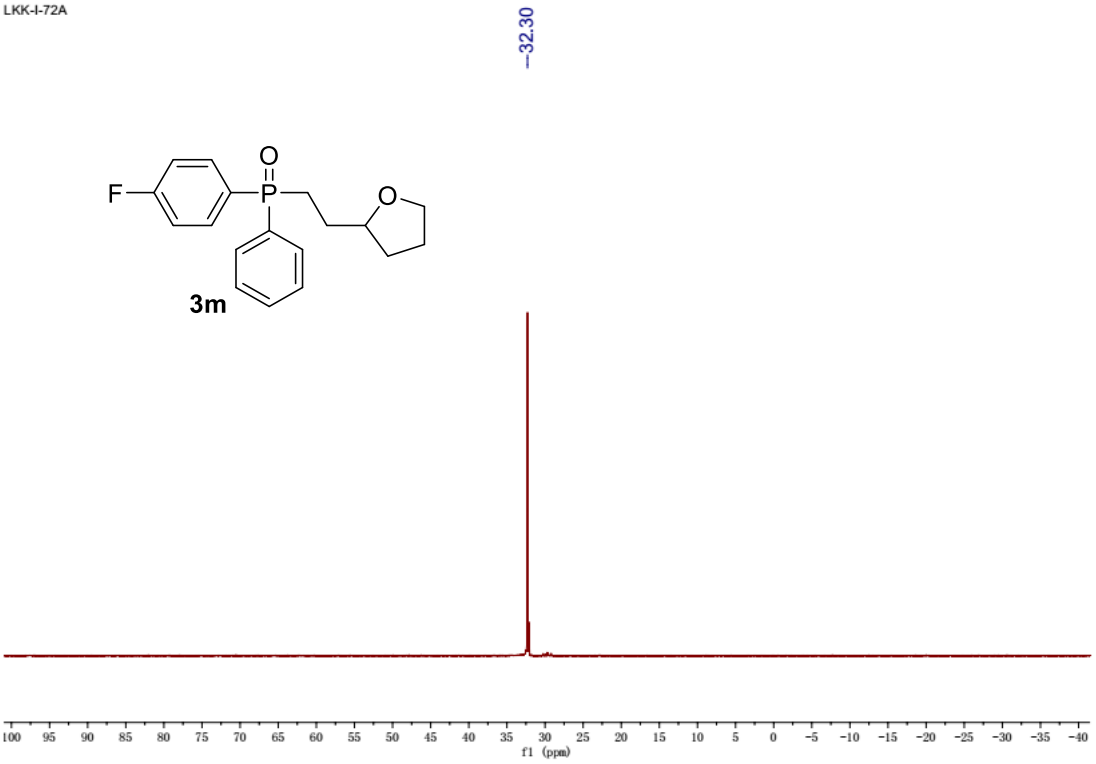
DJZ-I-255-2-P1CH



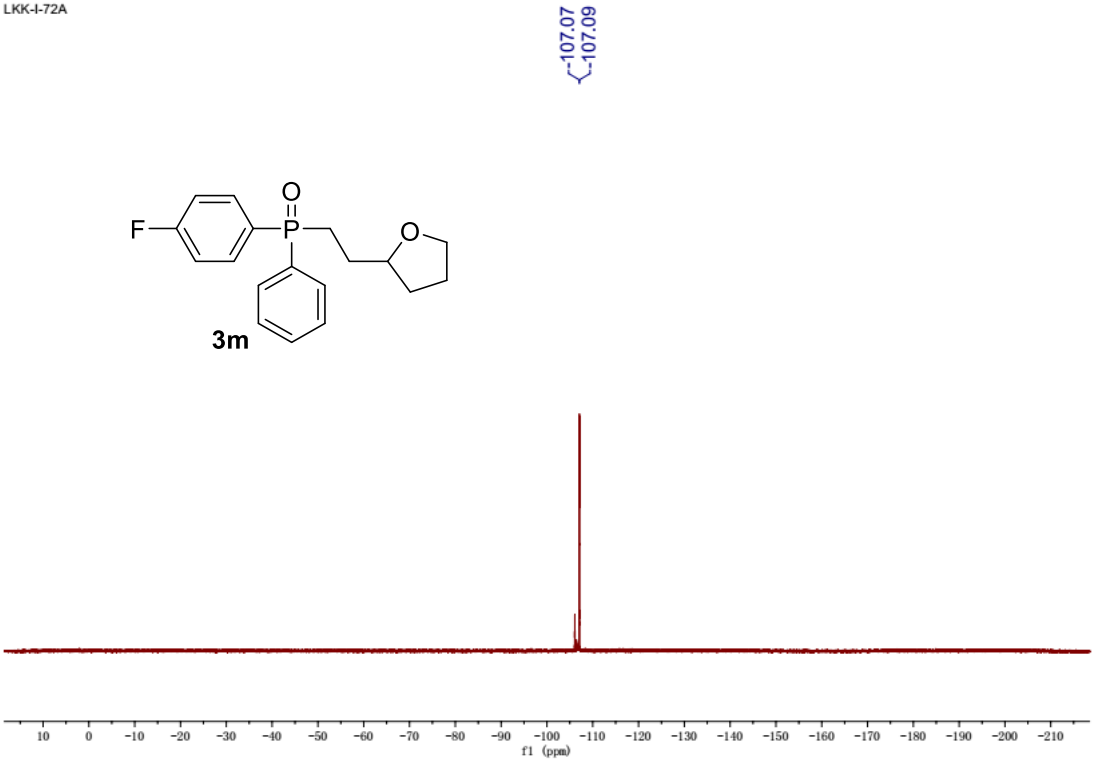

LKKJ-ZSA



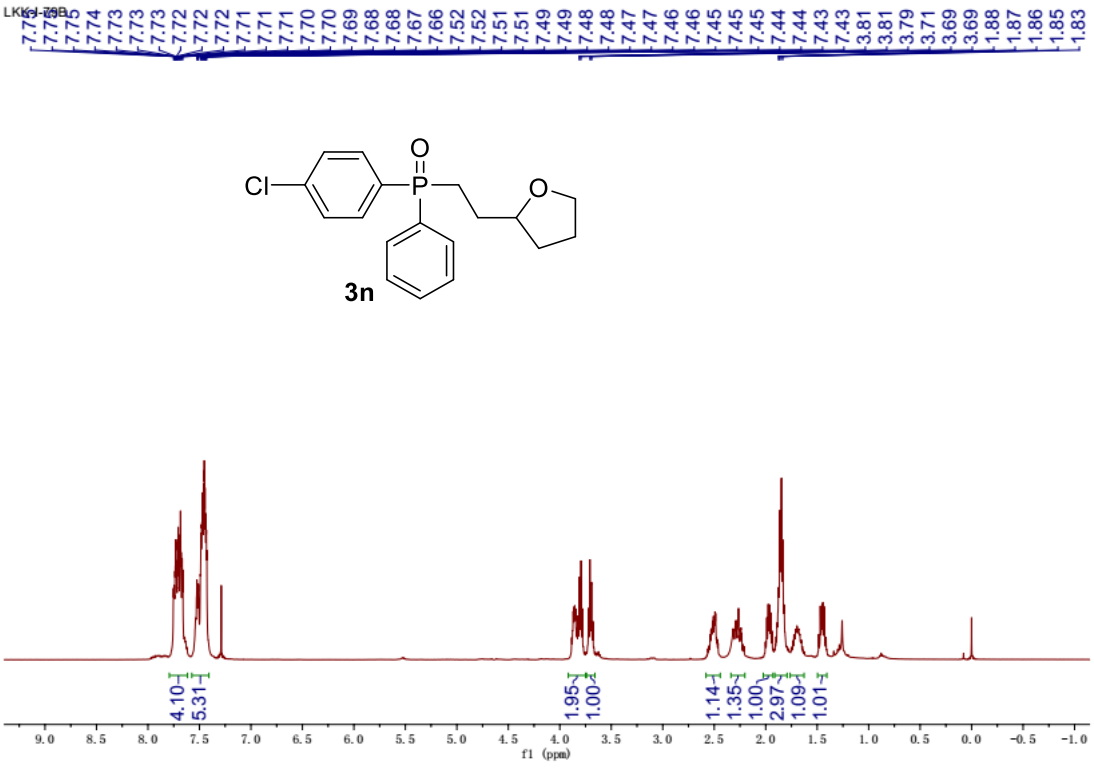

LKK-I-72A
165.96
163.88
133.39
133.32
133.31
133.27
133.24
133.20
133.19
133.12
132.95
132.55
132.28
131.84
131.82
130.80
130.72
130.68
130.60
128.77
128.76
128.72
128.68
128.66
116.14
116.12
116.04
116.02
115.97
115.95
115.87
115.85
79.16
79.13
79.04
79.01
77.31
77.06
76.80
67.72
31.06
31.03
27.33
27.31
27.29
26.93
26.90
26.34
26.31
25.66
F
O
P
O
3m
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

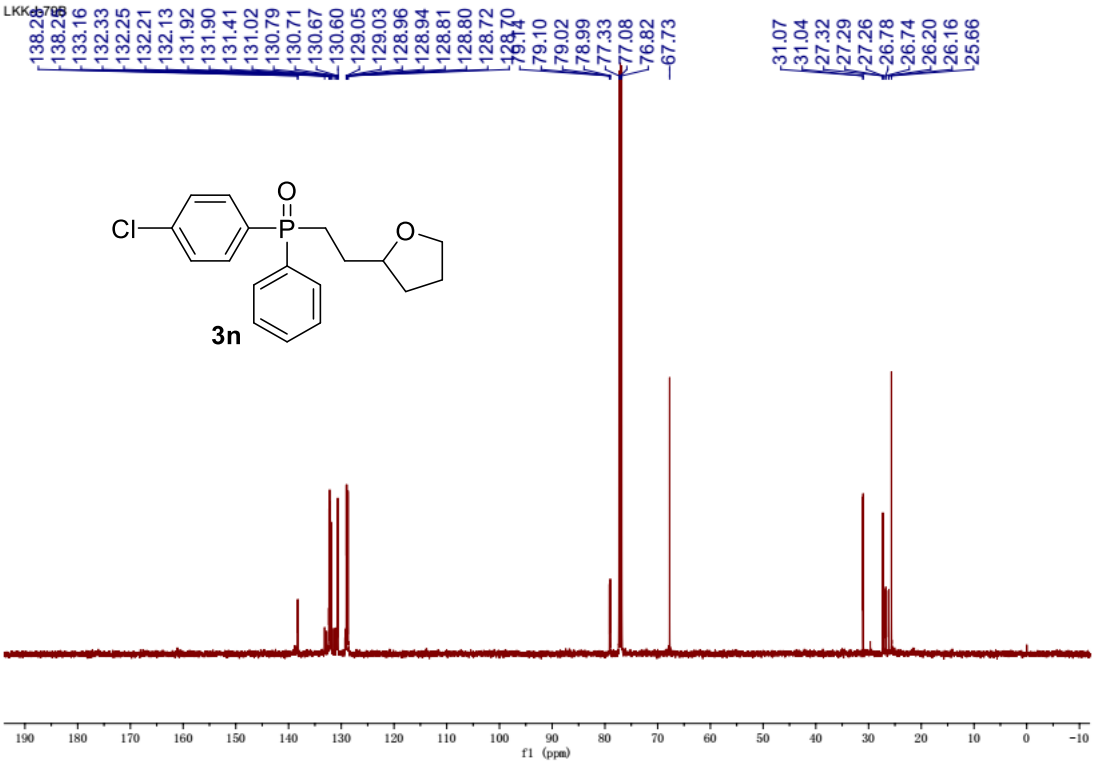

LKK-I-72A
32.30
F
O
P
O
3m
100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 −5 −10 −15 −20 −25 −30 −35 −40
f1 (ppm)

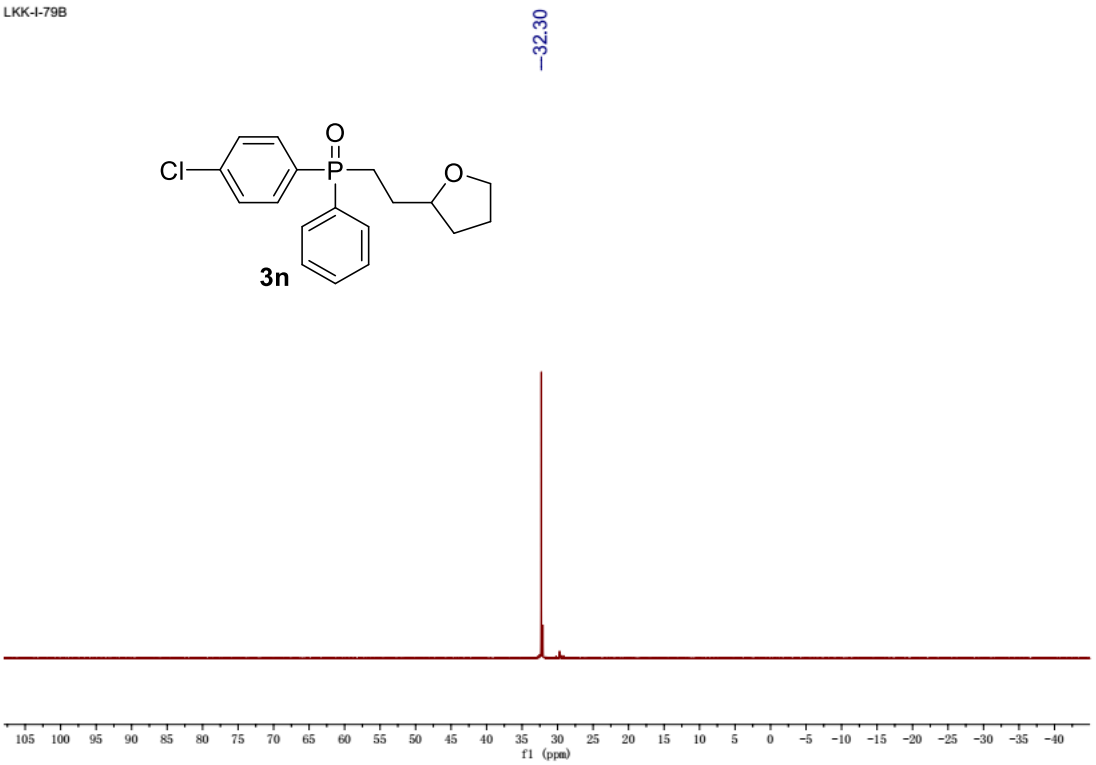
LKK-I-72A

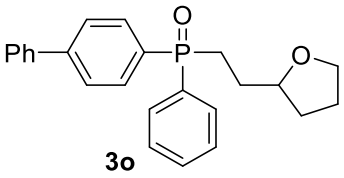



LKK-I-73B

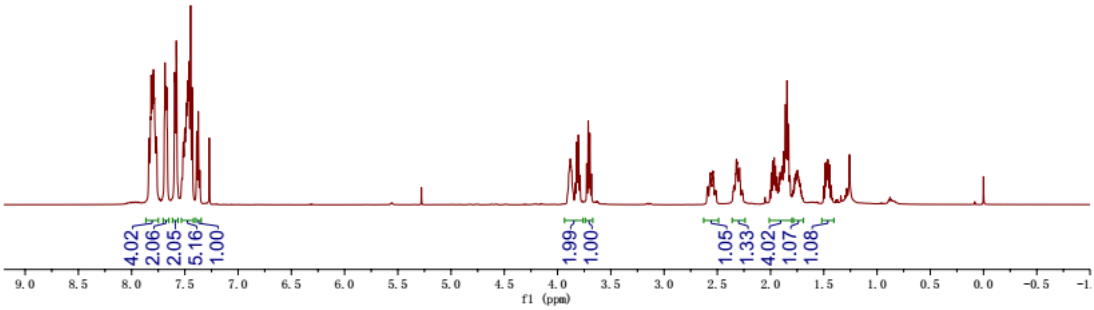


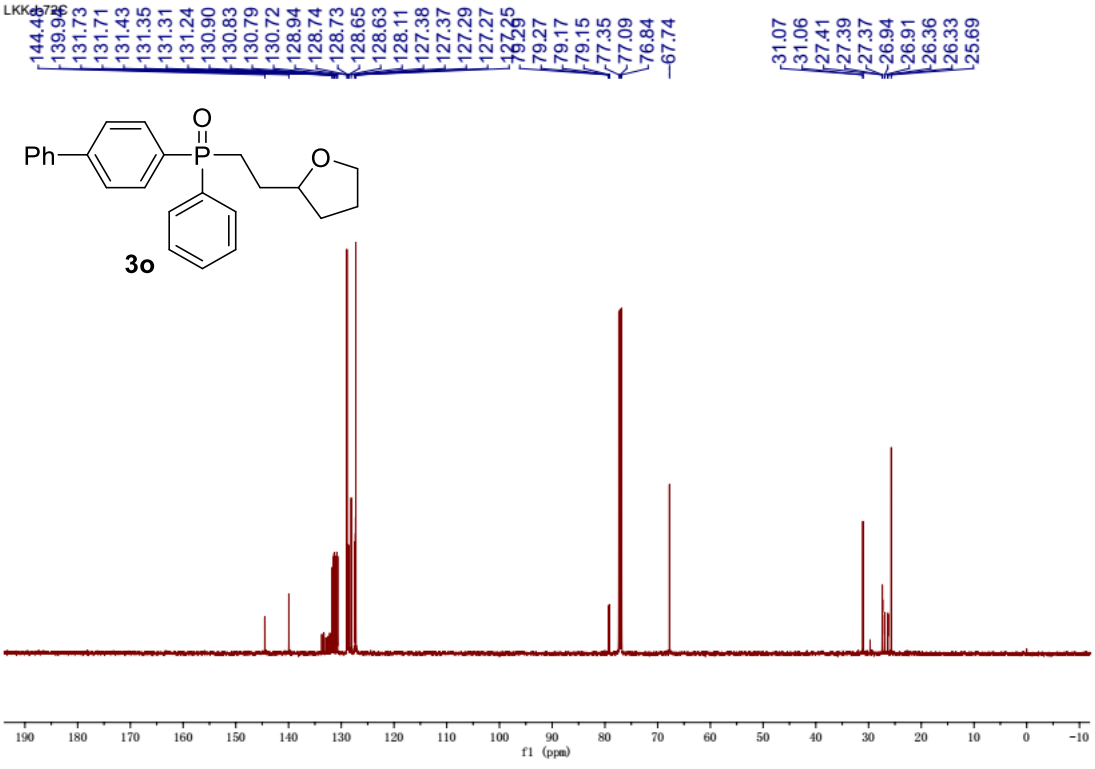

LKK-I-79B
138.29
138.26
133.16
132.33
132.25
132.21
132.13
131.92
131.90
131.41
131.02
130.79
130.71
130.67
130.60
129.05
129.03
128.96
128.94
128.81
128.80
128.72
128.70
79.14
79.10
79.02
78.99
77.33
77.08
76.82
67.73
31.07
31.04
27.32
27.29
27.26
26.78
26.74
26.20
26.16
25.66
Cl
O
P
O
3n
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


LKK-I-79B
32.30
Cl
O
P
O
3n
105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40
f1 (ppm)


O
Ph
P
O

3o

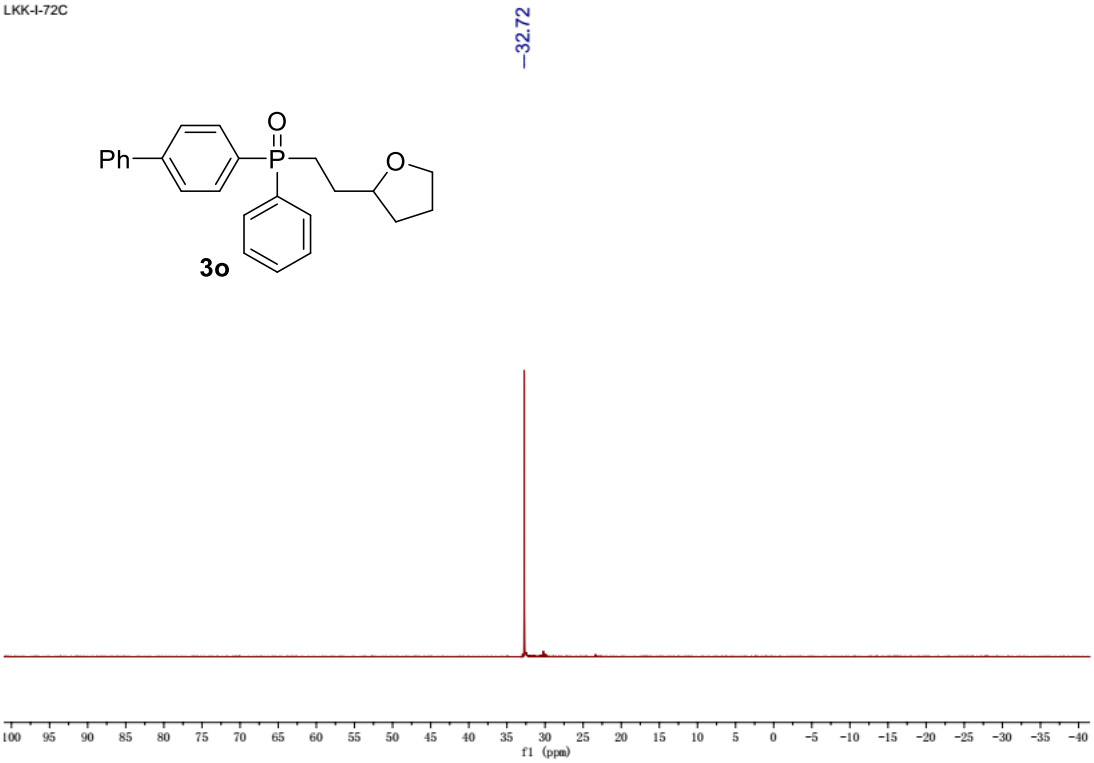

4.02
2.06
2.05
5.16
1.00
1.99
1.00
1.05
1.33
4.02
1.07
1.08
f1 (ppm)


144.46
139.96
131.73
131.71
131.43
131.35
131.31
131.24
130.90
130.83
130.79
130.72
128.94
128.74
128.73
128.65
128.63
128.11
127.38
127.37
127.29
127.27
79.27
79.17
79.15
77.35
77.09
76.84
67.74
31.07
31.06
27.41
27.39
27.37
26.94
26.91
26.36
26.33
25.69
f1 (ppm)

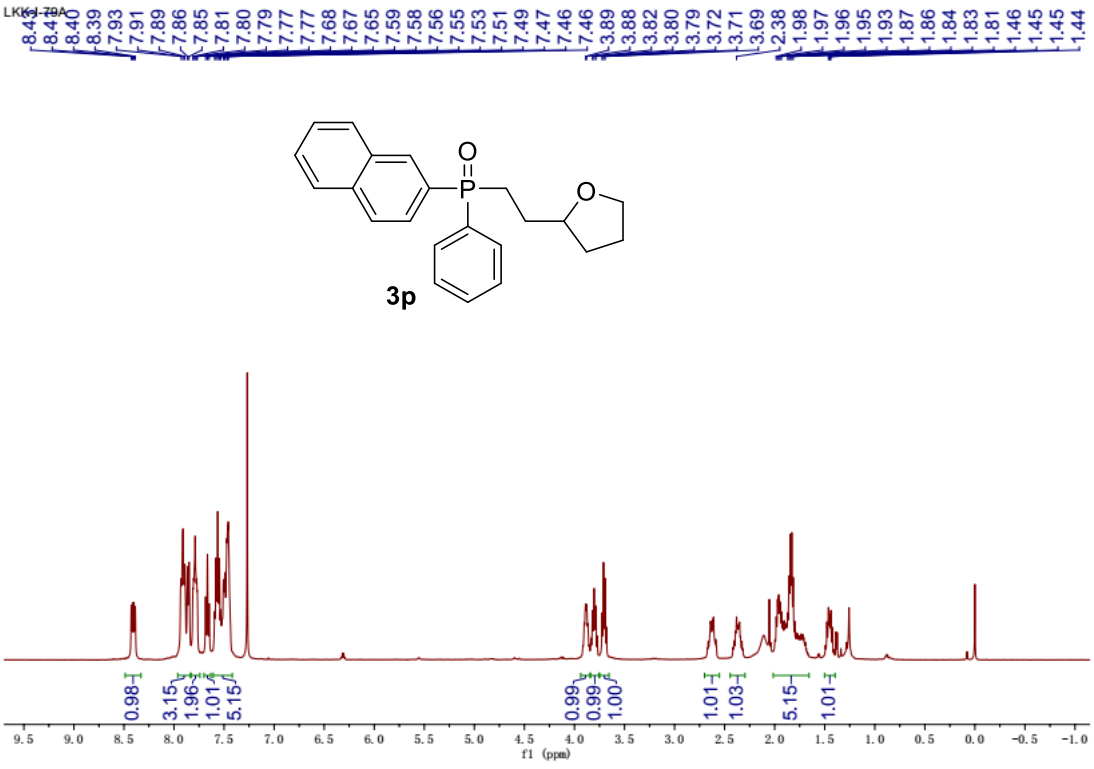

O
Ph
P
O

3o

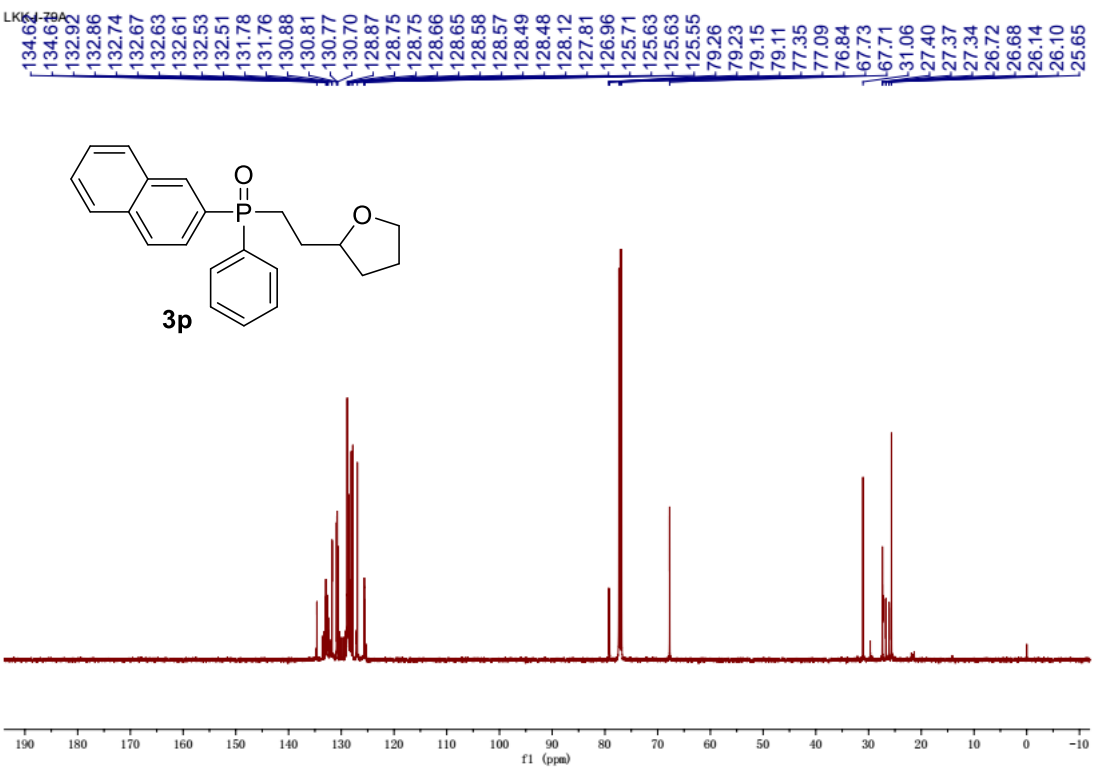
LKK-I-72C



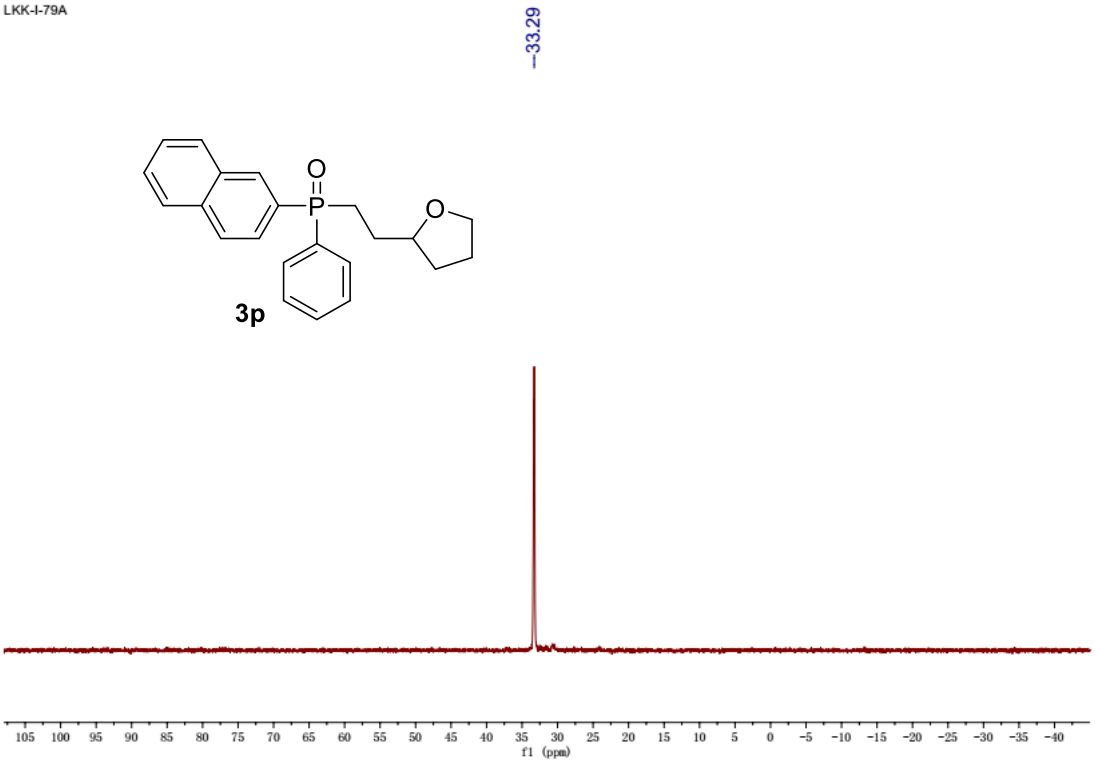

LKK-I-79A

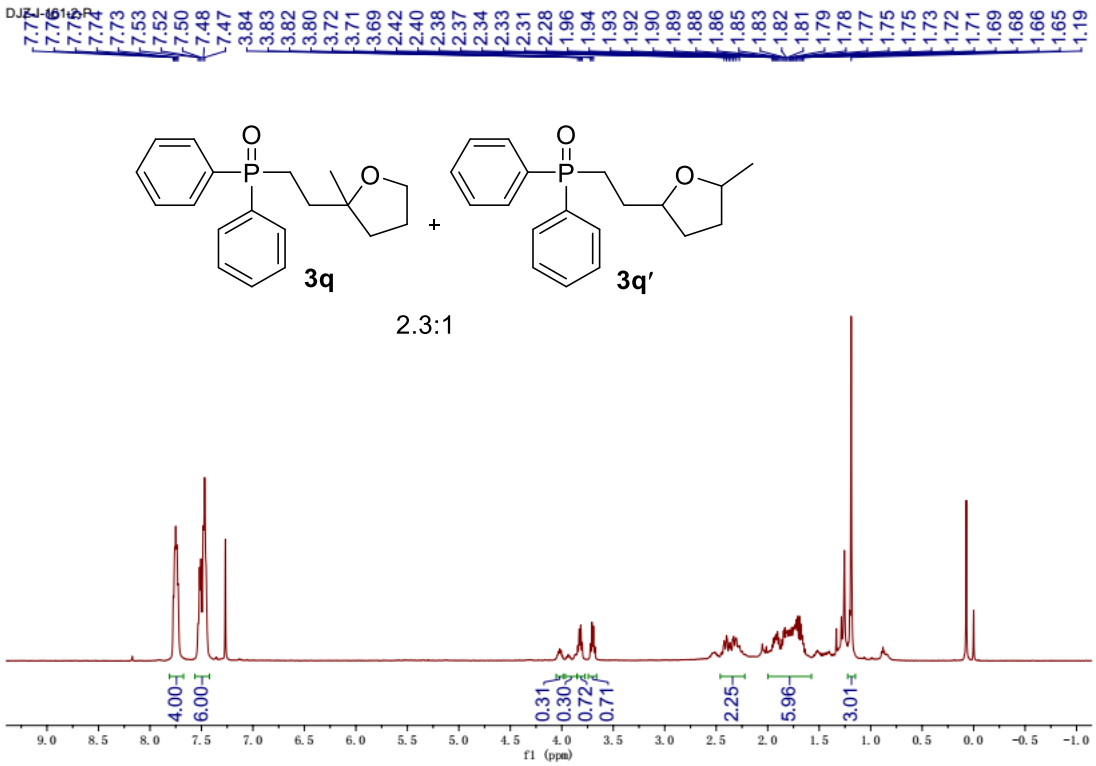


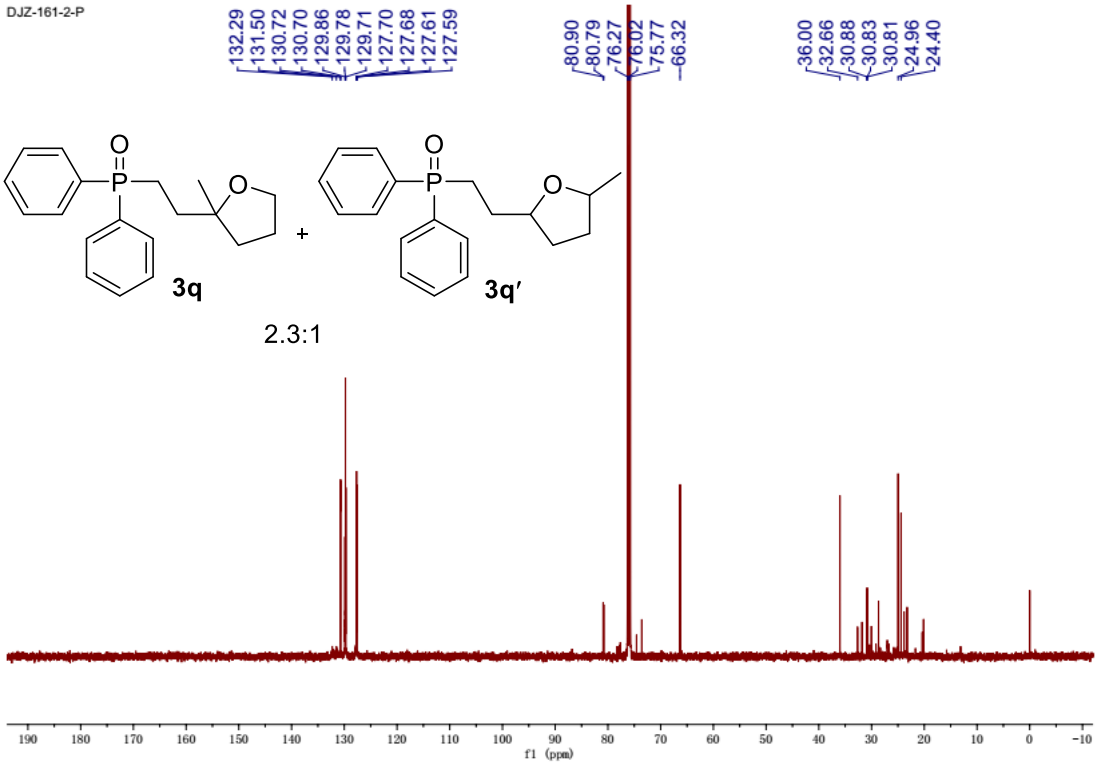
LKK-I-79A



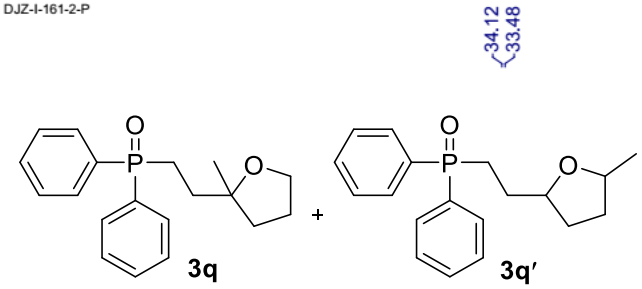

LKK-I-79A




DJZ-161-2P
7.77 7.76 7.75 7.74 7.73 7.53 7.52 7.50 7.48 7.47 3.84 3.83 3.82 3.80 3.72 3.71 3.69 2.42 2.40 2.38 2.37 2.34 2.33 2.31 2.28 1.96 1.94 1.93 1.92 1.90 1.89 1.88 1.86 1.85 1.83 1.82 1.81 1.79 1.78 1.77 1.75 1.75 1.73 1.72 1.71 1.69 1.68 1.66 1.65 1.19
3q
3q′
2.3:1
4.00 6.00 0.31 0.30 0.72 0.71 2.25 5.96 3.01
f1 (ppm)


DJZ-161-2-P
132.29 131.50 130.72 130.70 129.86 129.78 129.71 127.70 127.68 127.61 127.59 80.90 80.79 76.27 76.02 75.77 66.32 36.00 32.66 30.88 30.83 30.81 24.96 24.40
3q
3q′
2.3:1
f1 (ppm)

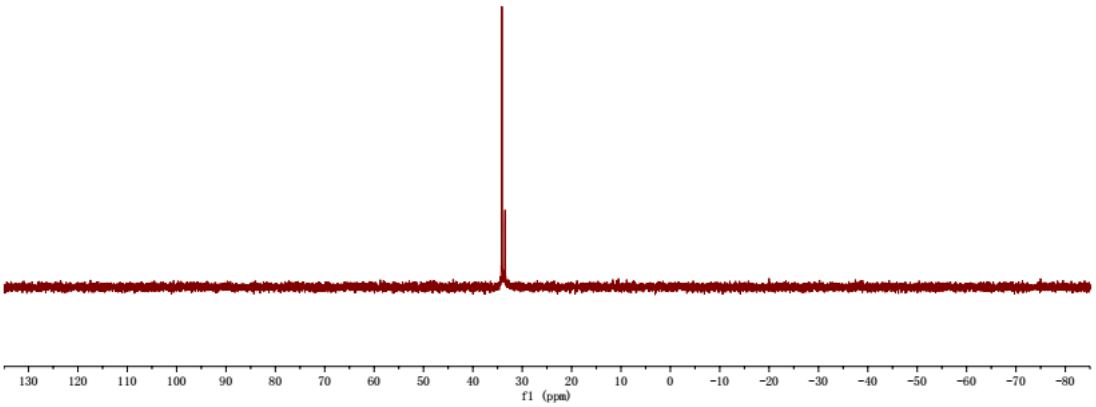
DJZ-I-161-2-P



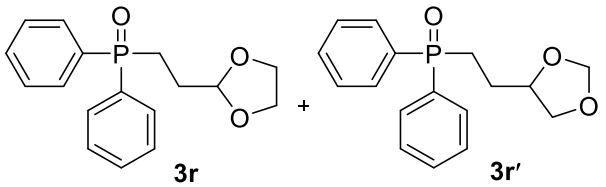



**3q** + **3q′**

2.3:1

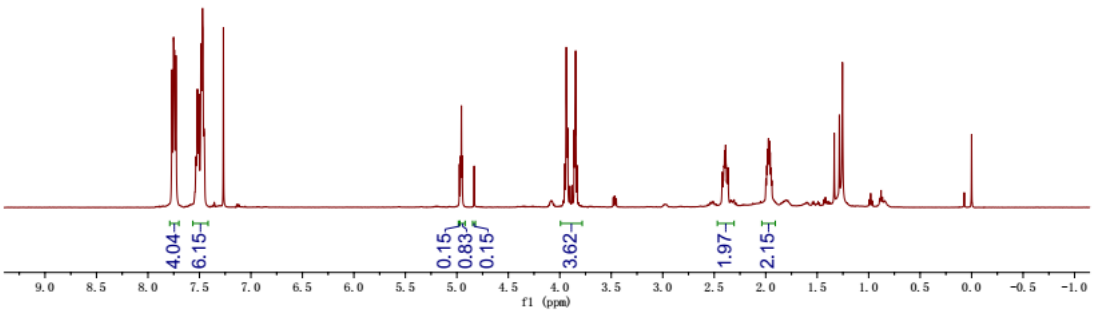


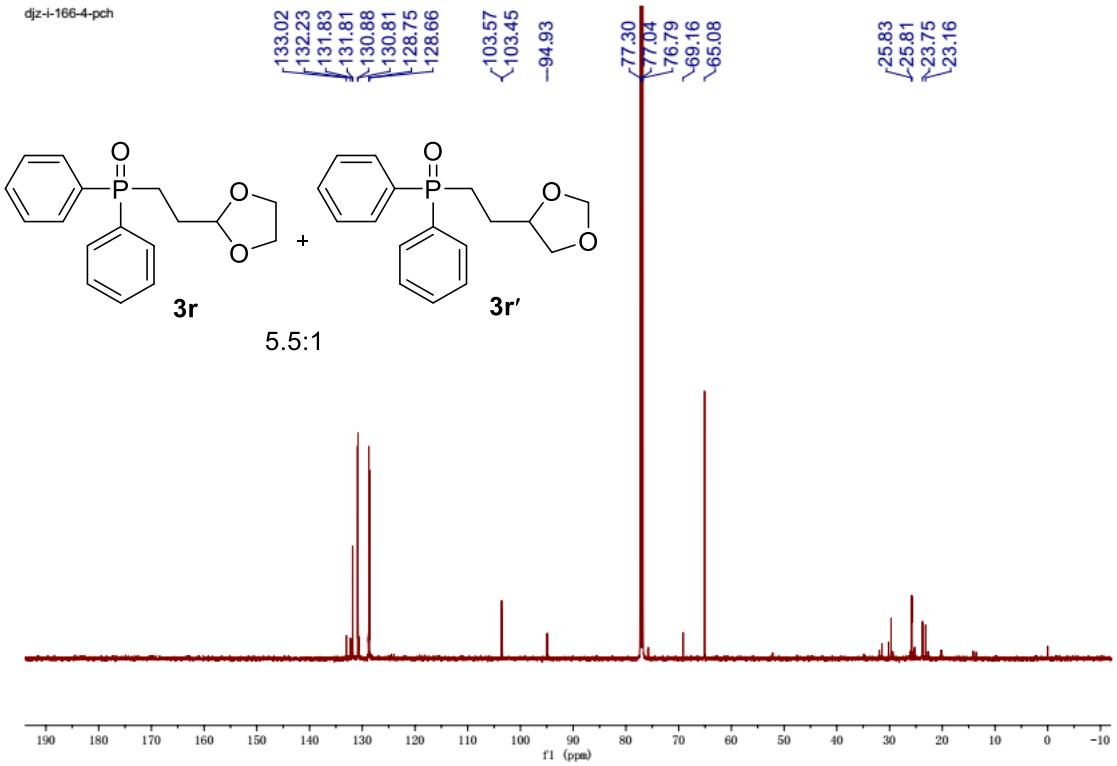

djz-i-166-4-pch

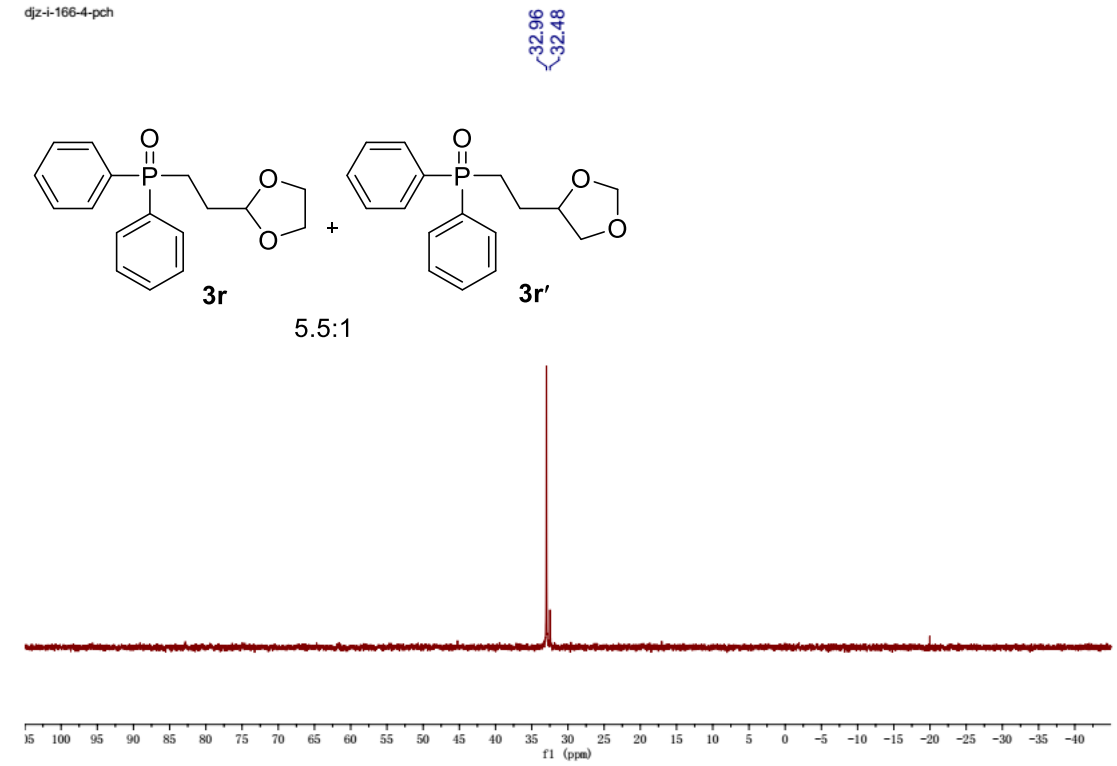



**3r** + **3r′**

5.5:1




djz-i-166-4-pch
133.02
132.23
131.83
131.81
130.88
130.81
128.75
128.66
103.57
103.45
94.93
77.30
77.04
76.79
69.16
65.08
25.83
25.81
23.75
23.16
3r
3r′
5.5:1
f1 (ppm)

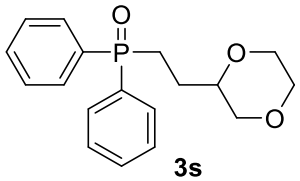

djz-i-166-4-pch
32.96
32.48
3r
3r′
5.5:1
f1 (ppm)

djz-i-211-2-p2

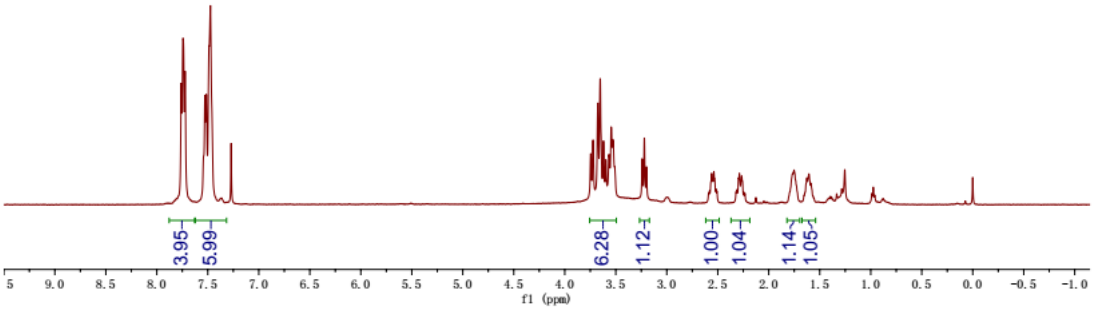
7.76 7.74 7.72 7.53 7.51 7.49 7.47

3.75 3.72 3.68 3.65 3.62 3.60 3.57 3.55 3.53 3.51 3.24 3.22 3.20

2.56 2.54 2.29 2.27 1.75 1.63 1.61 1.59



**3s**

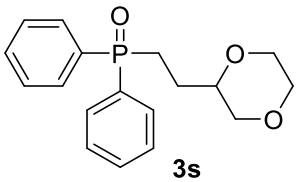



djz-i-211-2-p2

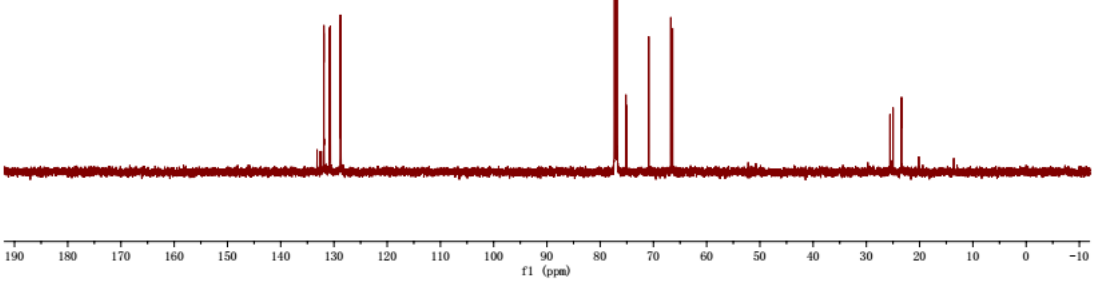
133.17 132.63 132.38 131.91 131.89 131.84 130.87 130.80 130.75 130.67 128.82 128.78 128.73 128.69

77.31 77.06 76.80 75.17 75.06 70.87 66.73 66.40

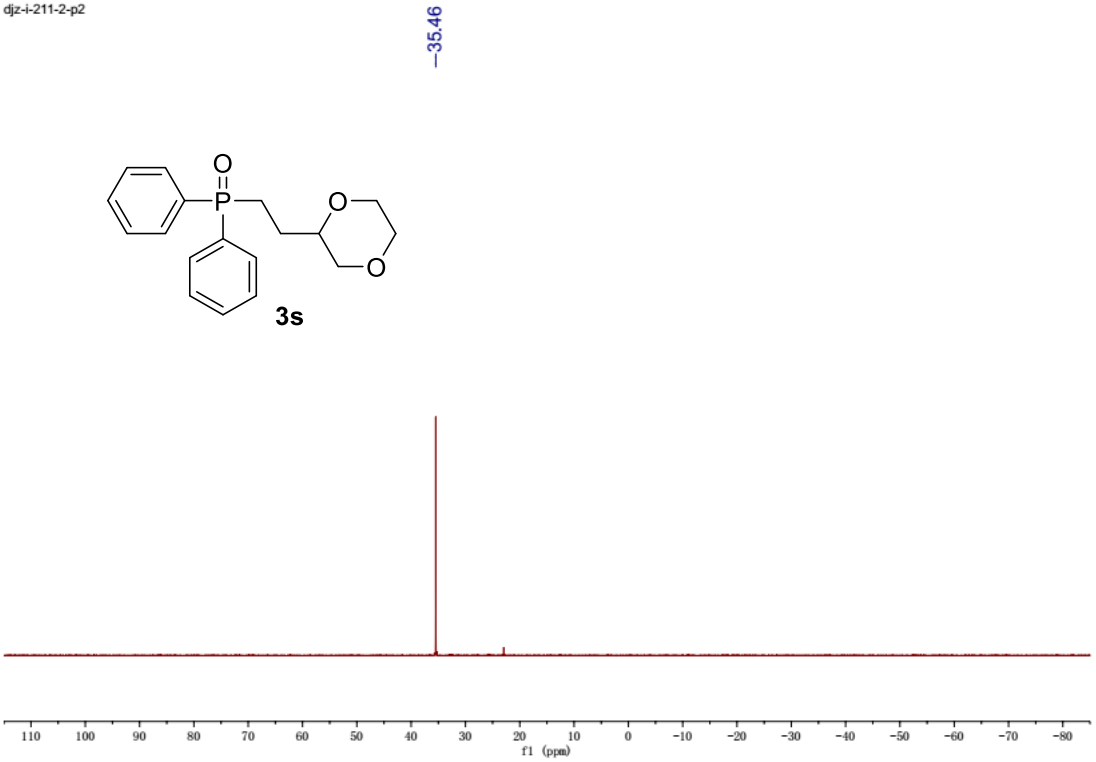
25.57 24.99 23.43 23.40



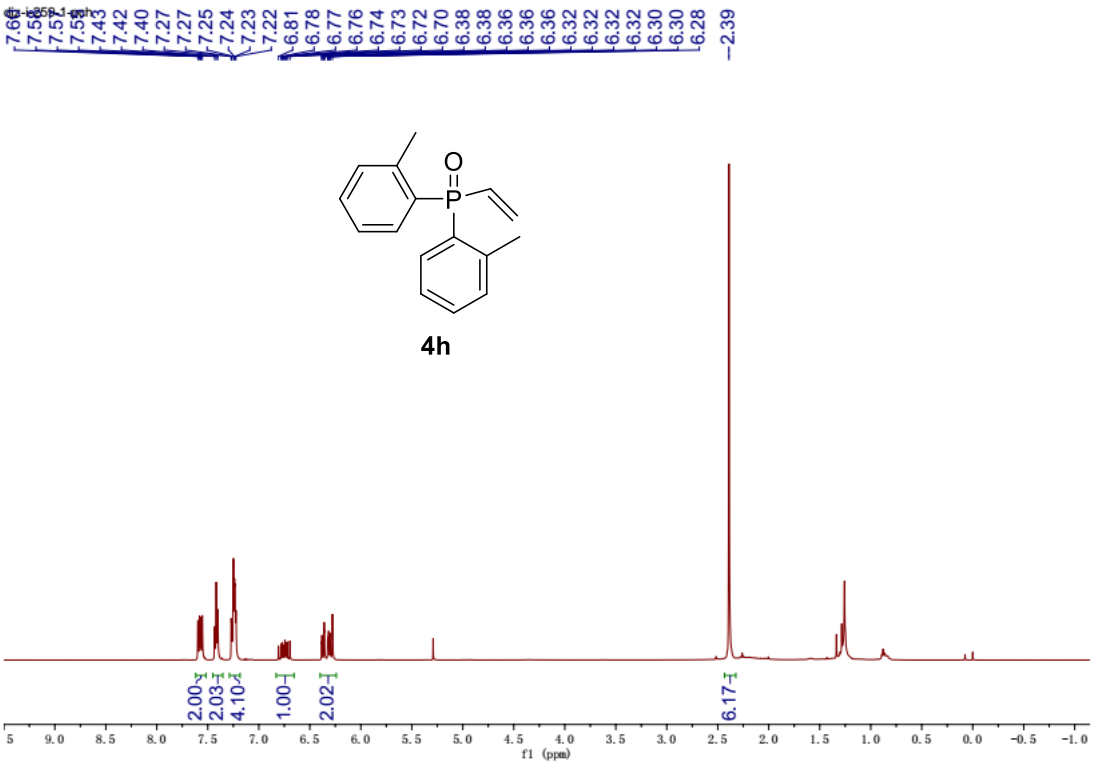
**3s**



djz-i-211-2-p2

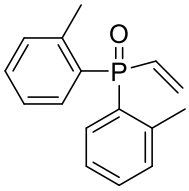



djz-i-259-1-prh

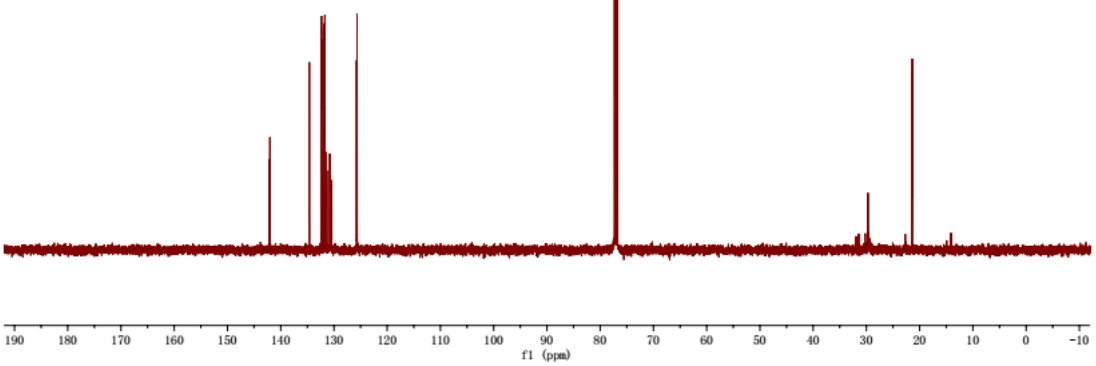


djz-i-259-1-pch

142.09
142.02
134.61
132.43
132.33
131.95
131.94
131.81
131.72
131.56
131.32
130.78
130.50
125.75
125.65
77.30
77.05
76.80
21.41
21.38

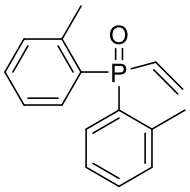


**4h**

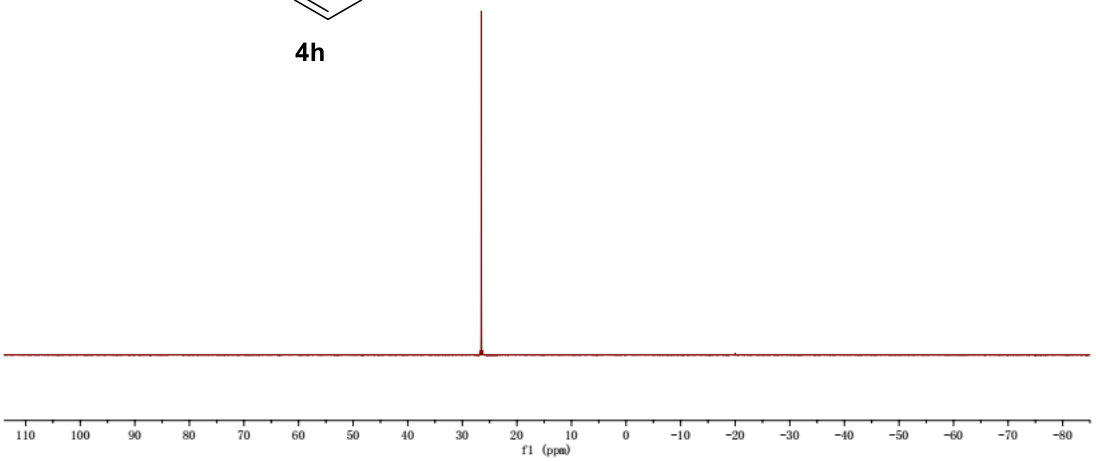


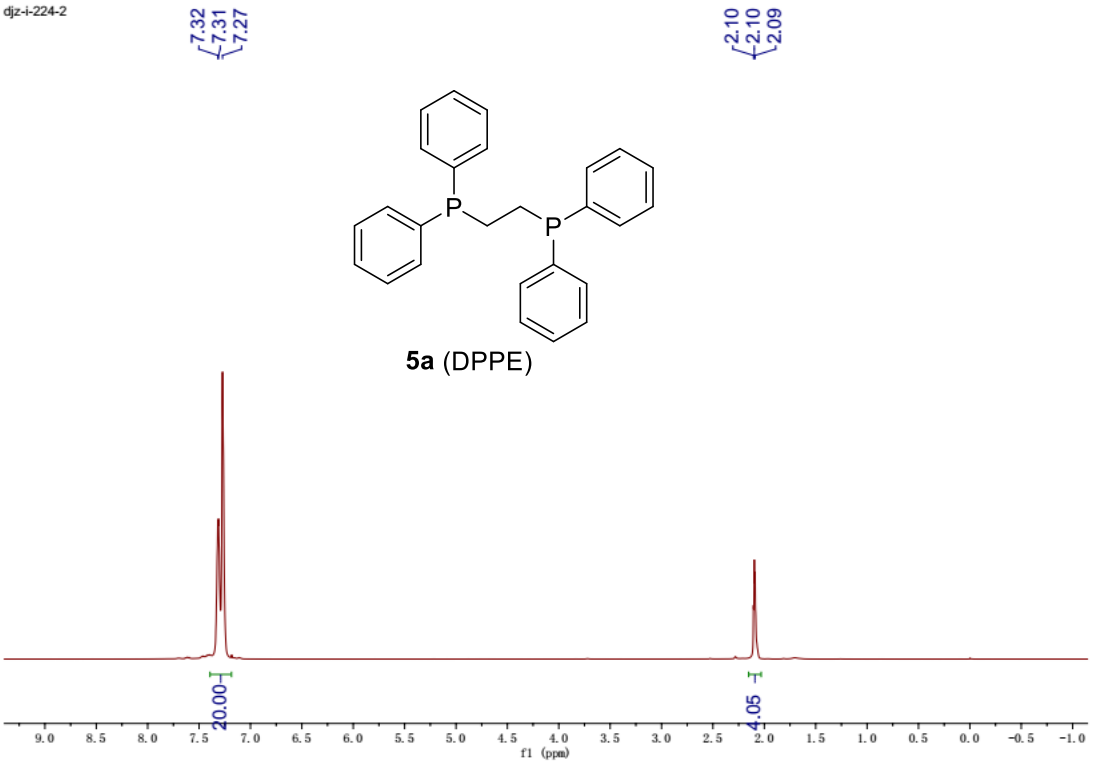

djz-i-259-1-pch

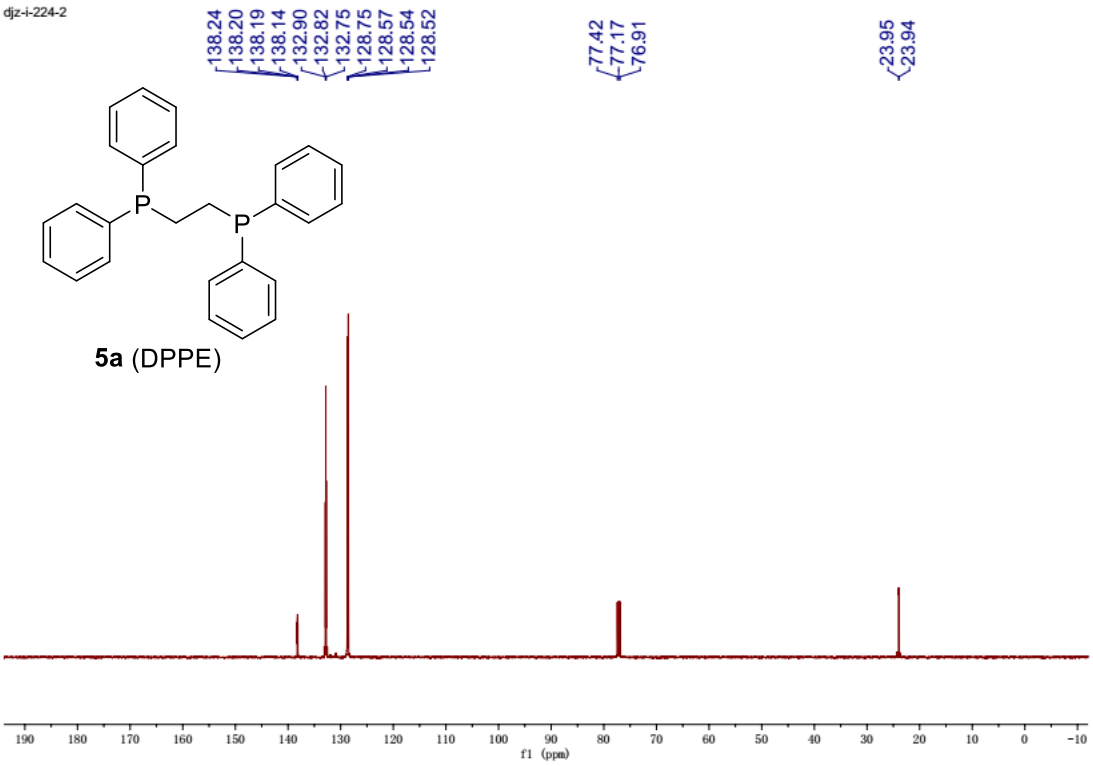
−26.52



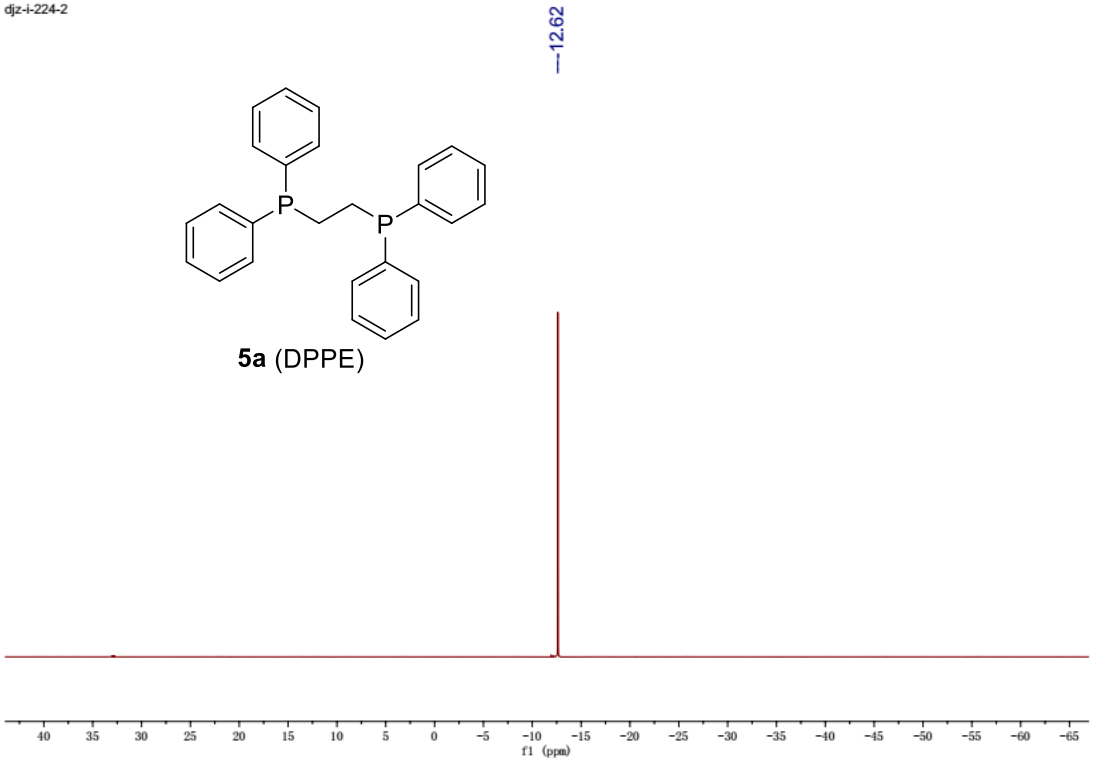
**4h**




djz-i-224-2
7.32
7.31
7.27
2.10
2.10
2.09
P
P
5a (DPPE)
20.00
4.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

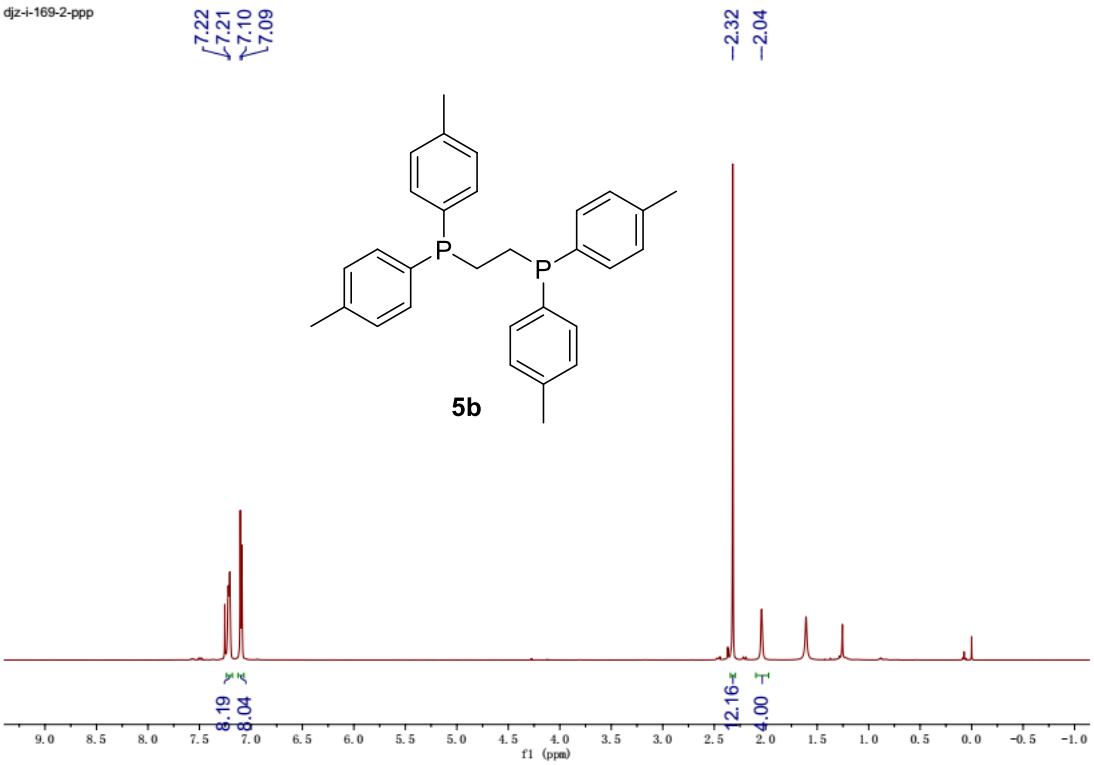

djz-i-224-2
138.24
138.20
138.19
138.14
132.90
132.82
132.75
128.75
128.57
128.54
128.52
77.42
77.17
76.91
23.95
23.94
P
P
5a (DPPE)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

djz-i-224-2



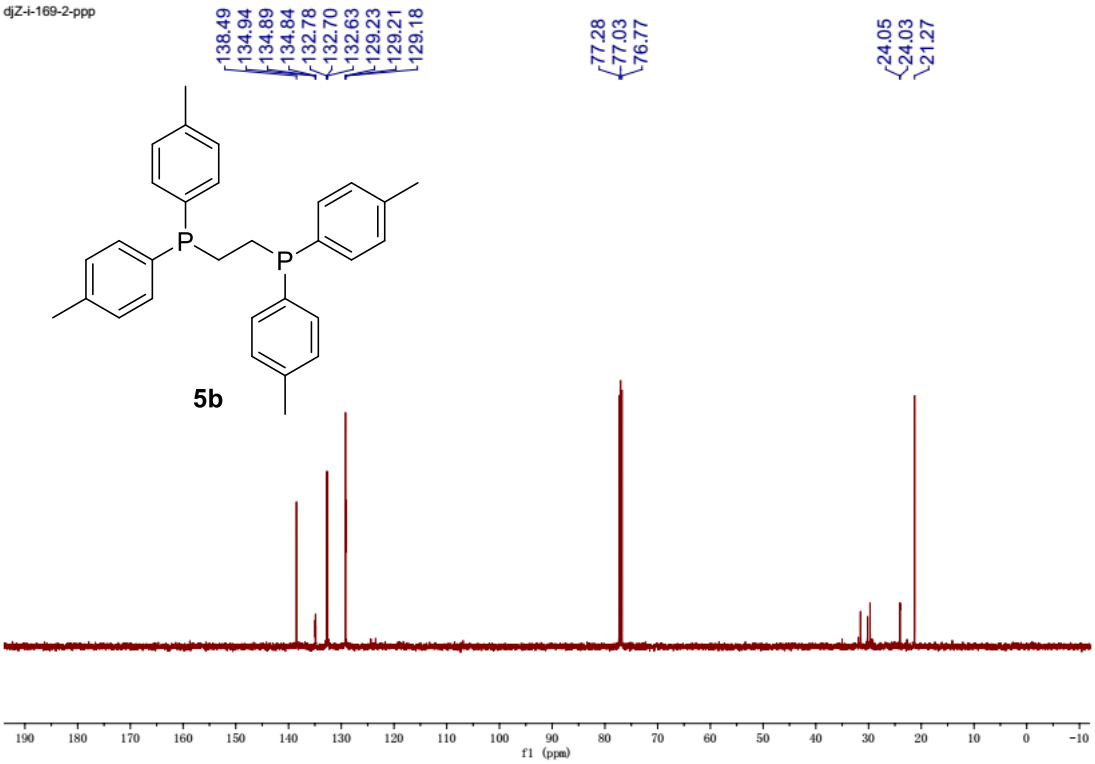

**5a** (DPPE)

djz-i-169-2-ppp

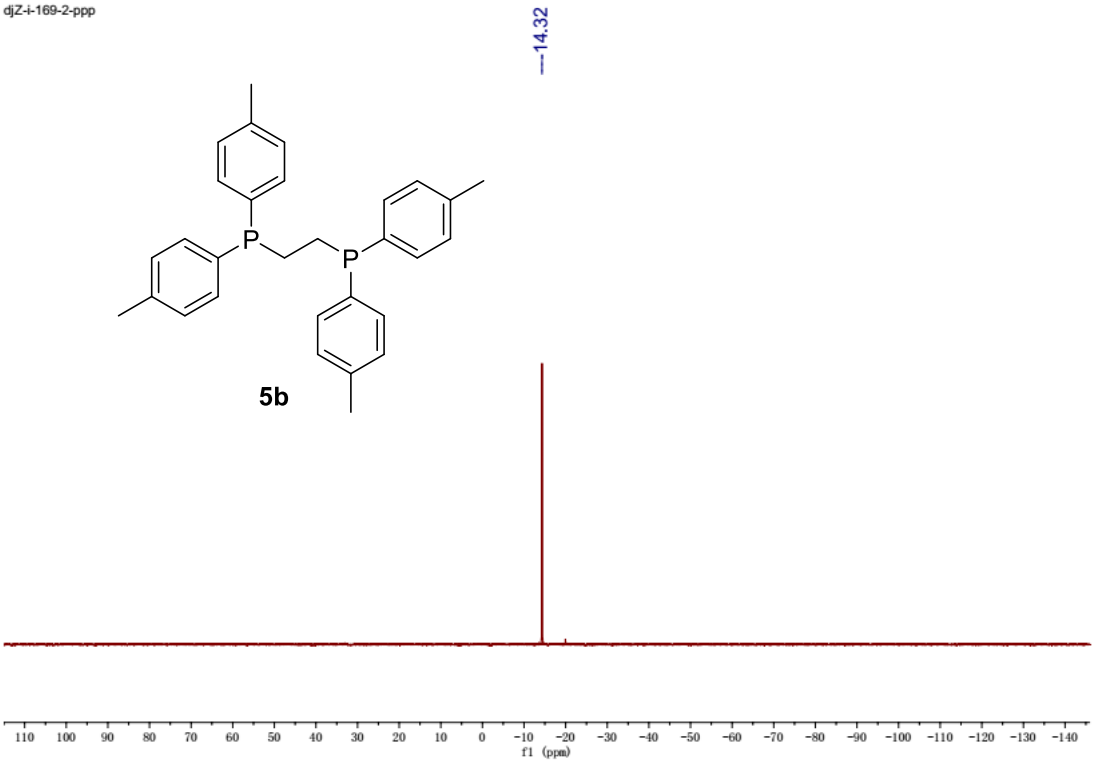


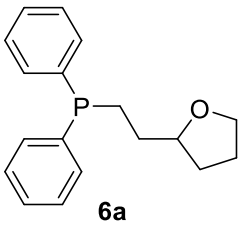

**5b**

djZ-i-169-2-ppp

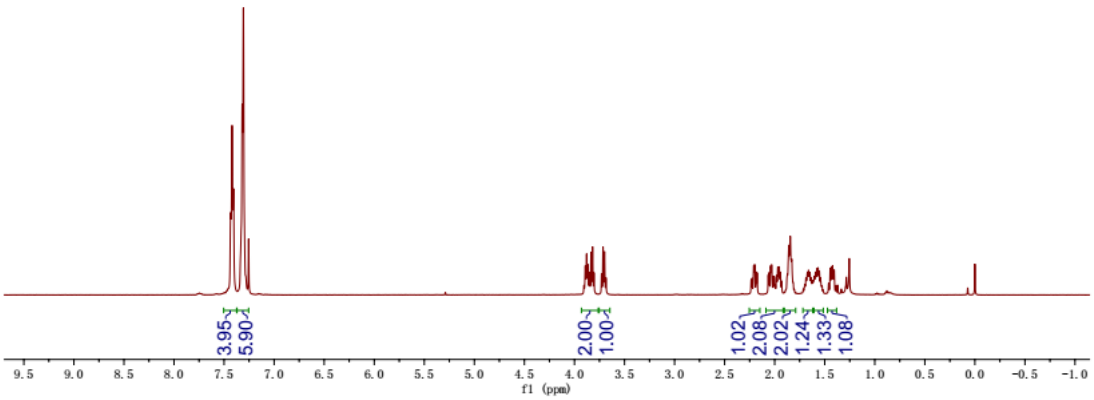


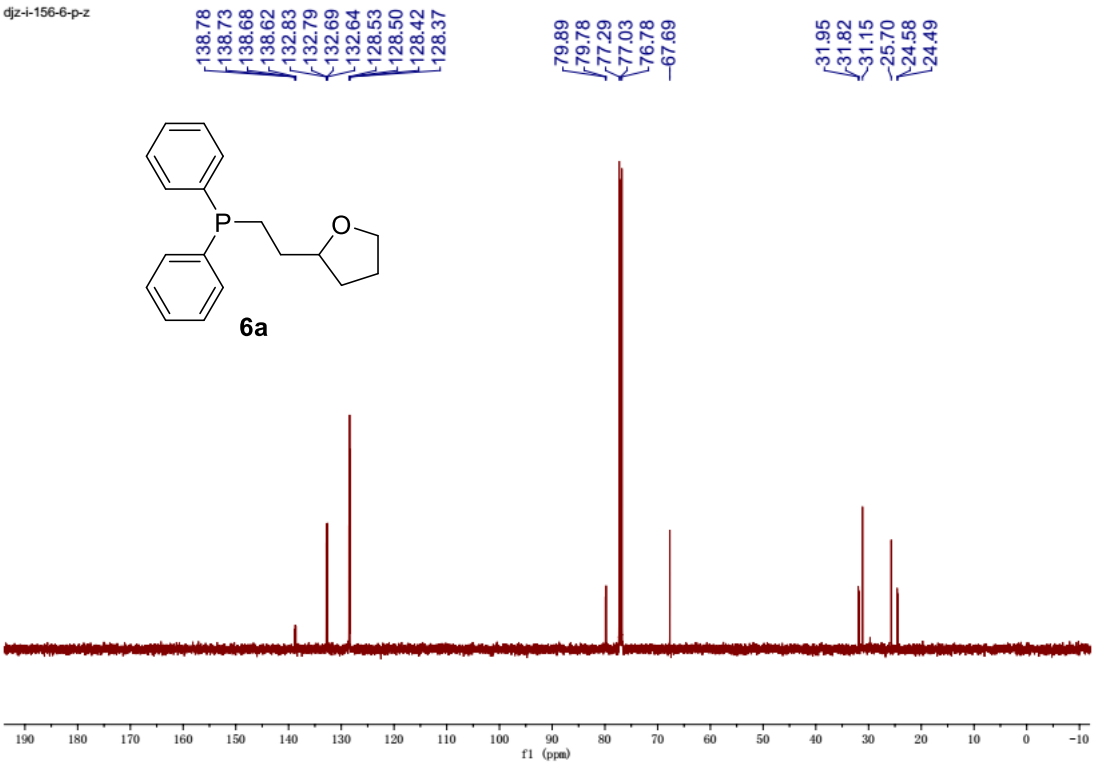

djZ-i-169-2-ppp





6a

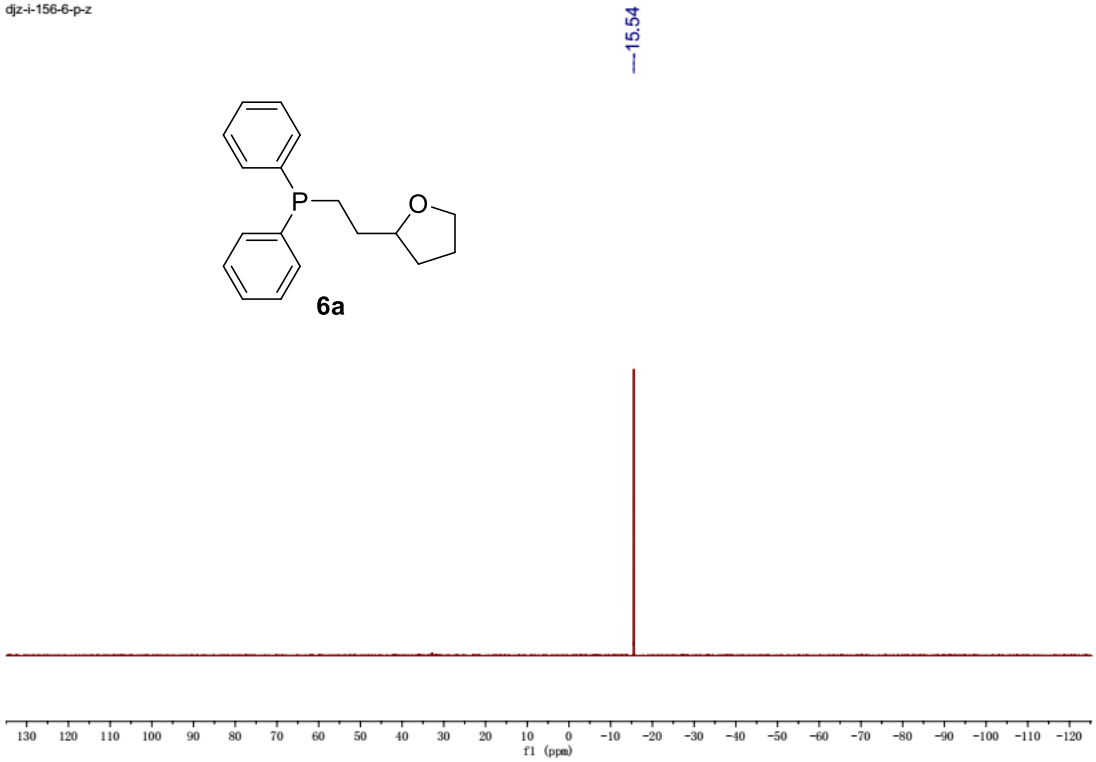


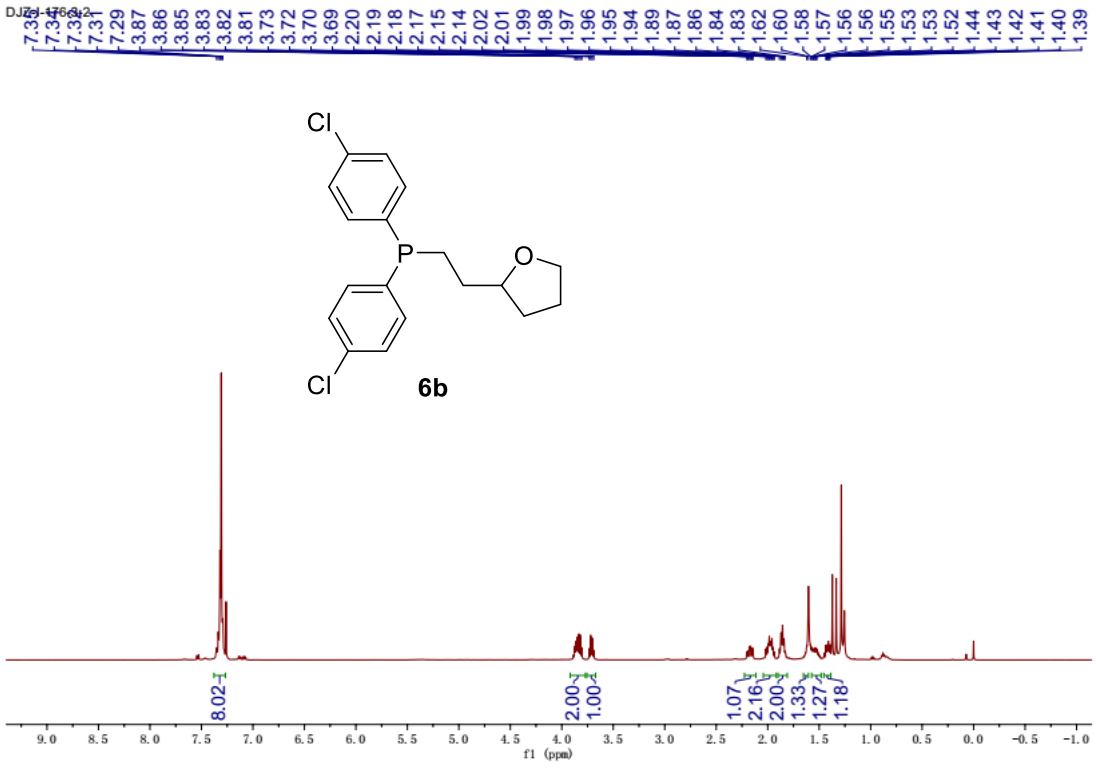


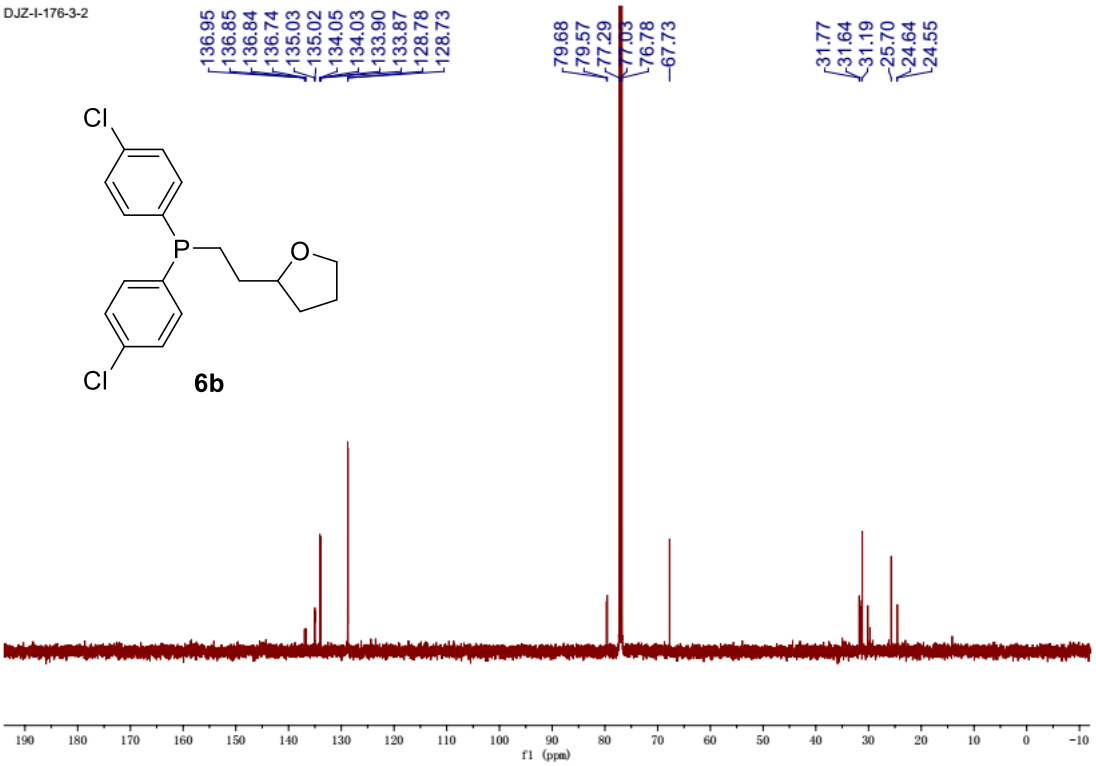


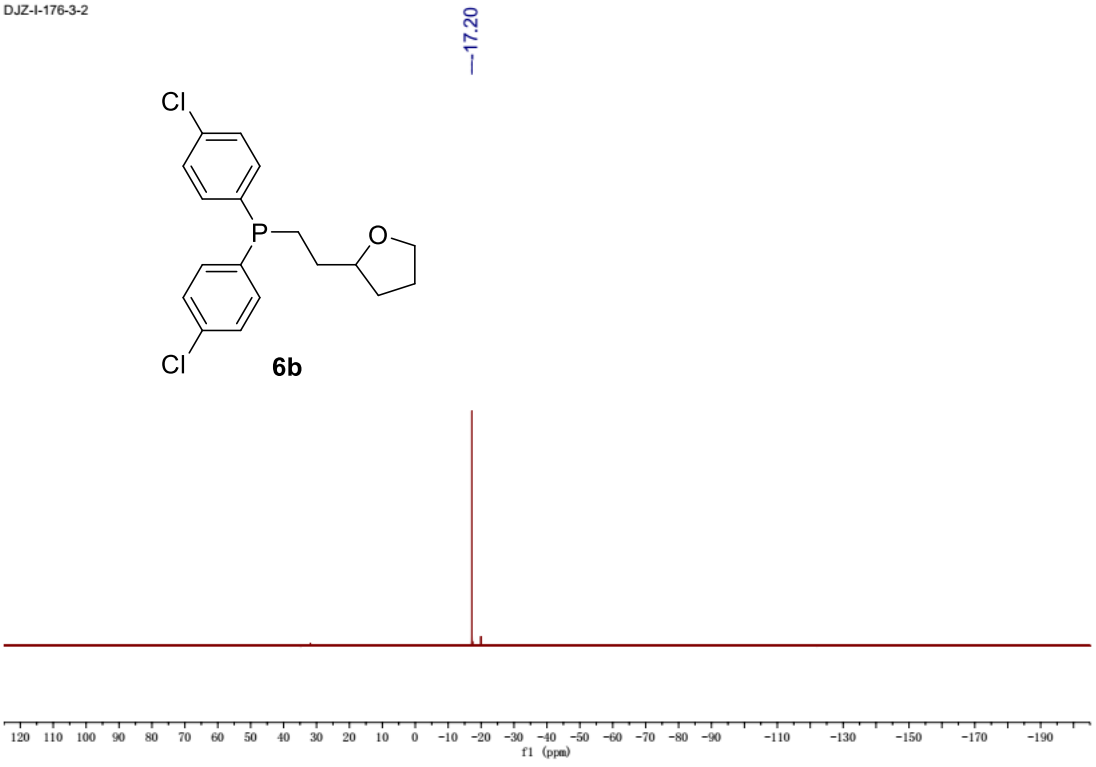
6a

djz-i-156-6-p-z


15.54
P
O
6a
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120
f1 (ppm)


7.35 7.34 7.33 7.31 7.29 3.87 3.86 3.85 3.83 3.82 3.81 3.73 3.72 3.70 3.69 2.20 2.19 2.18 2.17 2.15 2.14 2.02 2.01 1.99 1.98 1.97 1.96 1.95 1.94 1.89 1.87 1.86 1.84 1.83 1.62 1.60 1.58 1.57 1.56 1.56 1.55 1.53 1.53 1.52 1.44 1.43 1.42 1.41 1.40 1.39
Cl
P
O
Cl
6b
8.02
2.00
1.00
1.07
2.16
2.00
1.33
1.27
1.18
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


DJZ-I-176-3-2
136.95
136.85
136.84
136.74
135.03
135.02
134.05
134.03
133.90
133.87
128.78
128.73
79.68
79.57
77.29
77.03
76.78
67.73
31.77
31.64
31.19
25.70
24.64
24.55
Cl
P
O
Cl
6b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


DJZ-I-176-3-2
17.20
Cl
P
O
Cl
6b
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190
f1 (ppm)

## 8. References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2. Y. Okugawa, Y. Hayashi, S. Kawauchi, K. Hirano and M. Miura, *Org. Lett.*, 2018, **20**, 3670-3673.
3. A. Yoshimura, Y. Saga, Y. Sato, A. Ogawa, T. Chen and L.-B. Han, *Tetrahedron Lett.*, 2016, **57**, 3382-3384.
4. C. Laye, J. Lusseau, F. Robert and Y. Landais, *Adv. Synth. Catal.*, 2021, **363**, 3035-3043.
5. K. Kim, A. M. P. Moeljadi, H. Hirao and S. H. Hong, *Adv. Synth. Catal.*, 2017, **359**, 3292-3298.