

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 ^1H NMR, 125 MHz for ^{13}C NMR, 202 MHz for ^{31}P NMR, 470 MHz for ^{19}F NMR. The ^1H 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.



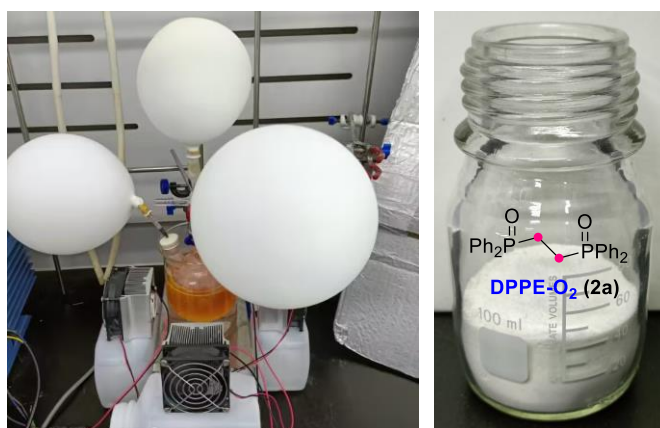
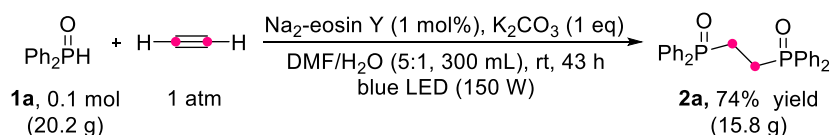
2. General procedure

2.1 General procedure for the synthesis of product 2

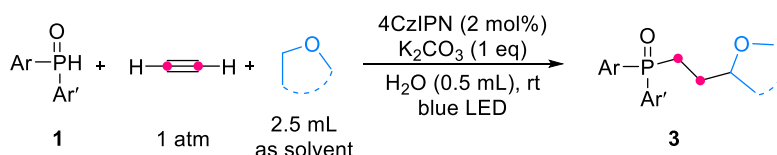


Na_2 -eosin Y (2.1 mg, 0.003 mmol, 1 mol%), K_2CO_3 (41.5 mg, 0.3 mmol, 1 eq) and phosphine oxides **1** (0.3 mmol, 1 eq) were added sequentially to a 10 mL Schlenk tube equipped with a magnetic stir bar. This resulting mixture was sealed and degassed via vacuum evacuation and subsequent backfill with 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: Na₂-eosin Y (692 mg, 1 mmol, 1 mol%), K₂CO₃ (13.82 g, 100 mmol, 1 eq) and **1a** (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 H₂O (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 Na₂SO₄. 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).

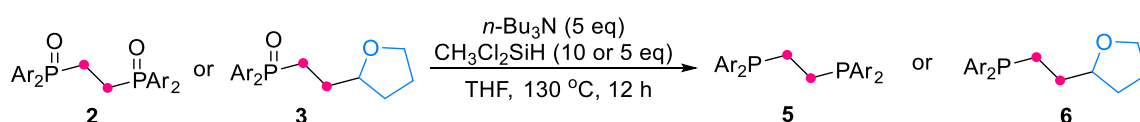


2.2 General procedure for the synthesis of product 3



4CzIPN (4.7 mg, 0.006 mmol, 2 mol%), K₂CO₃ (41.5 mg, 0.3 mmol, 1 eq) and **1** (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 H₂O (0.5 mL) were subsequently added in this order. For phosphine oxides, 0.08 mmol, 0.08 mmol, 0.07 mmol, 0.07 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.

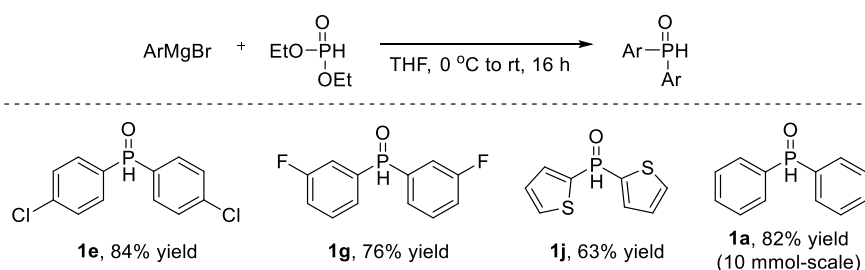
2.3 Reduction to phosphine ligands



The 10 mL flask was pumped with nitrogen for three times, **2** or **3** (0.1-0.3 mmol, 1 eq) dissolved in 1 mL dry THF was added into the tube, then *n*-Bu₃N (0.5-1.5 mmol, 5 eq) and CH₃Cl₂SiH (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**.

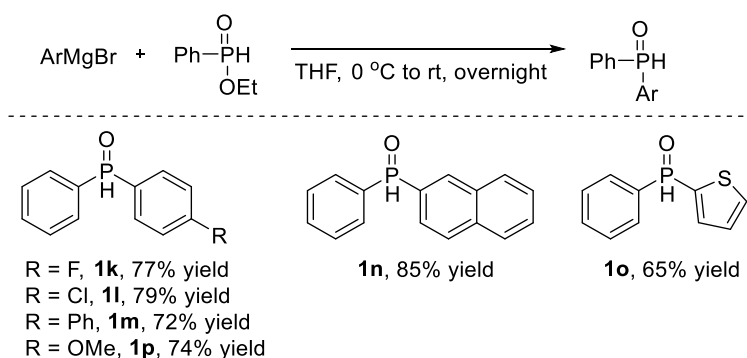
2.4 Preparation of substrates

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 Grignard reagent 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 NH₄Cl aqueous was then added slowly. The mixture was extracted with EtOAc and the organic phase was washed with NaHCO₃ aqueous and brine, then it was dried over Na₂SO₄. 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.

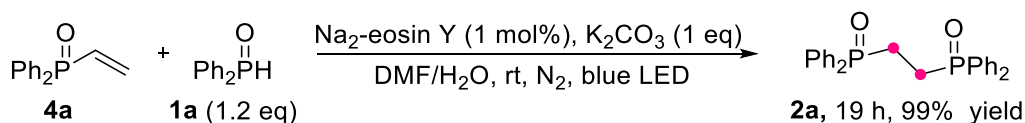
b) Synthesis of phosphine oxides **1k-p**²



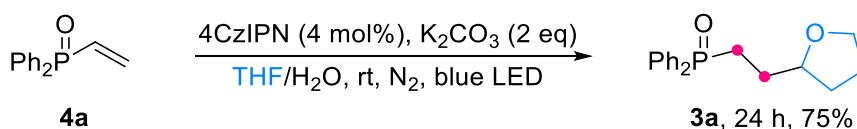
A 50 mL two-necked reaction flask was equipped with a magnetic stir bar and flushed with nitrogen. Ethyl phenylphosphinate (1.02 g, 6 mmol) was added dropwise at 0 °C to a solution of Grignard reagent in THF (9.6 mmol ArMgBr). The mixture was stirred for 15-30 minutes at 0 °C, then stirred at room temperature 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 Na₂SO₄ 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

4. Control experiments

a) Control experiments with phosphinoyl ethylene

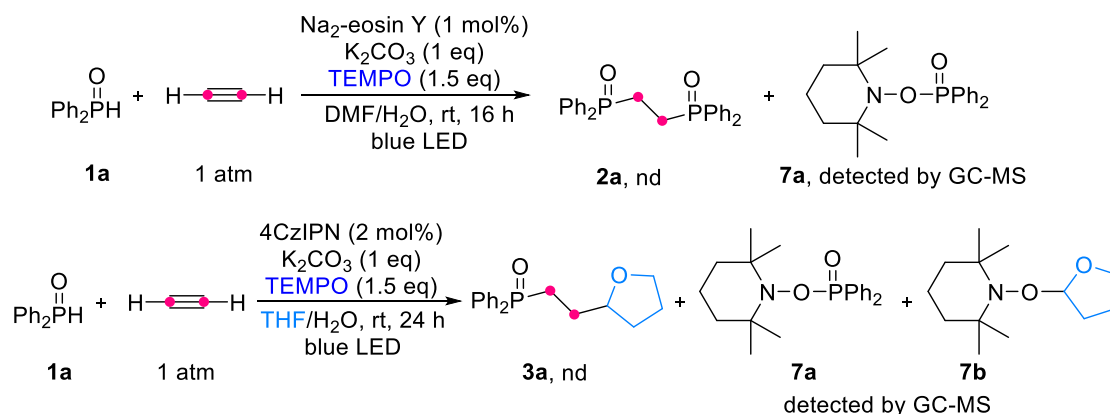


$\text{Na}_2\text{-eosin Y}$ (1.4 mg, 0.002 mmol, 1 mol%), K_2CO_3 (27.7 mg, 0.2 mmol, 1 eq), **1a** (0.24 mmol, 1.2 eq) and phosphinoyl ethylene (**4a**, 0.2 mmol, 1 eq) were added sequentially to a 10 mL Schlenk tube equipped with a magnetic stir bar. This resulting mixture was sealed and degassed 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, 0.006 mmol, 4 mol%), K_2CO_3 (41.5 mg, 0.3 mmol, 2 eq) and phosphinoyl ethylene (**4a**, 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

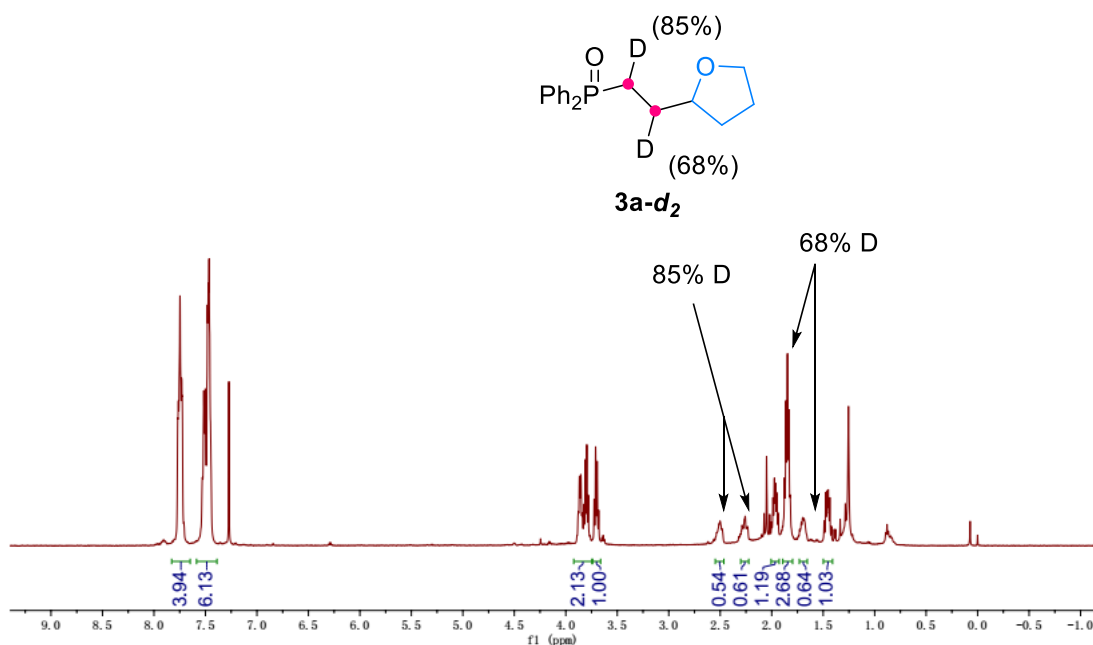
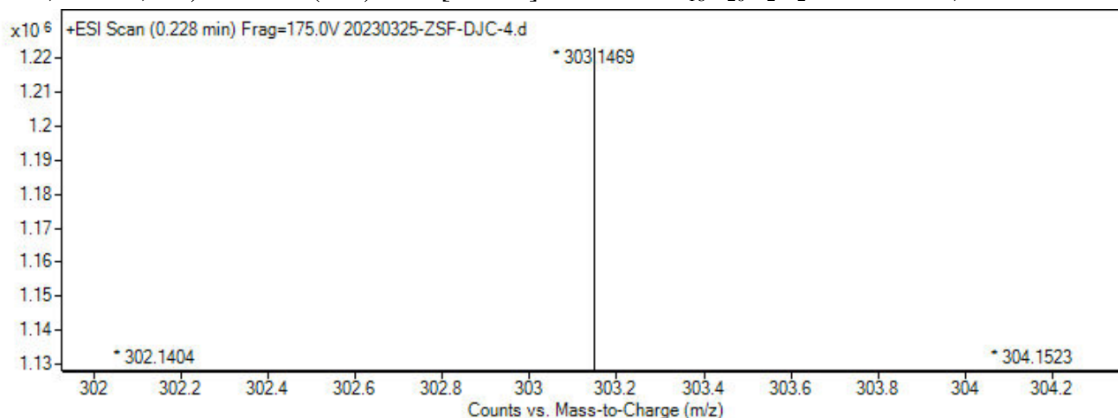


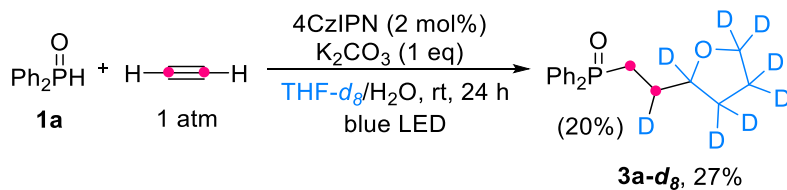
According to the general procedure 2, the above radical capture experiments with TEMPO (1.5 eq) were carried out, the related radical capture products **7a** and **7b** were detected by GC-MS: **7a**, m/z 357.07 (M); **7b**, m/z 228.18 ($\text{M}+\text{H}^+$).

c) Deuterium-labelling experiments

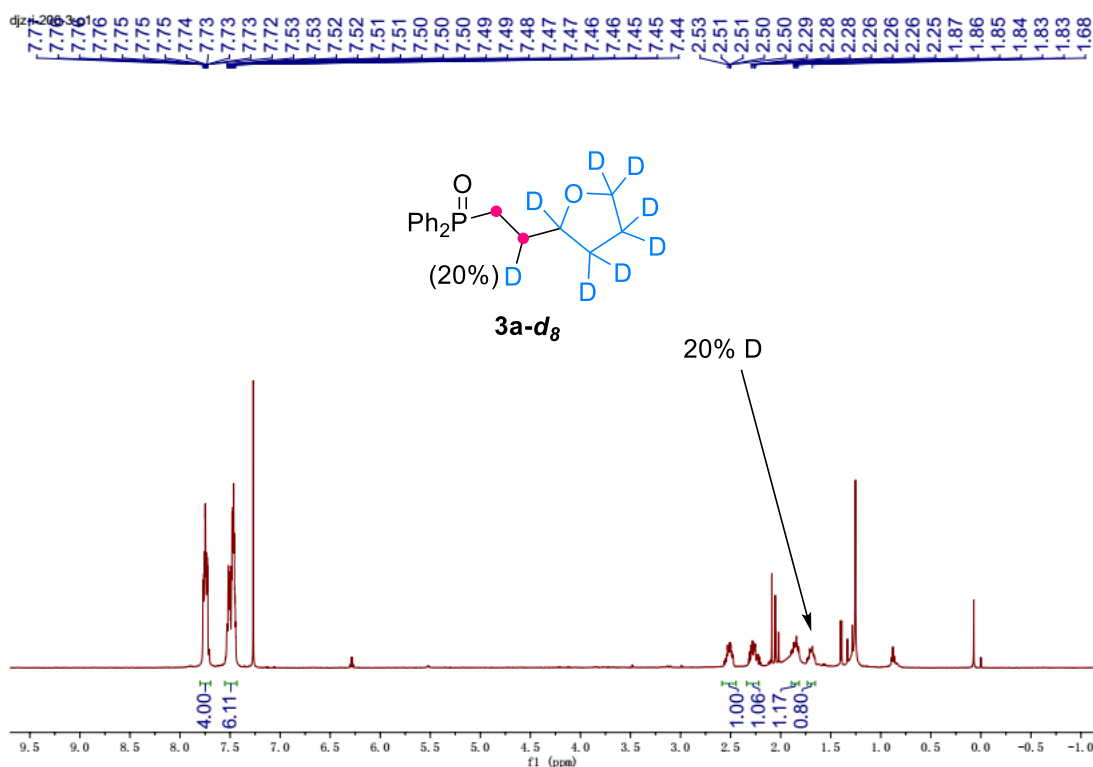


According to the general procedure 2.2, D₂O was used instead of H₂O, the deuterium-labelling product **3a-d₂** was obtained in 21% isolated yield. ¹H NMR (500 MHz, CDCl₃) δ 7.83 – 7.65 (m, 4H), 7.59 – 7.39 (m, 6H), 3.83 (ddd, *J* = 21.7, 13.3, 6.1 Hz, 2H), 3.70 (dd, *J* = 14.8, 7.3 Hz, 1H), 2.51 (t, *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 C₁₈H₂₀D₂O₂P⁺ 303.1477; found 303.1469.



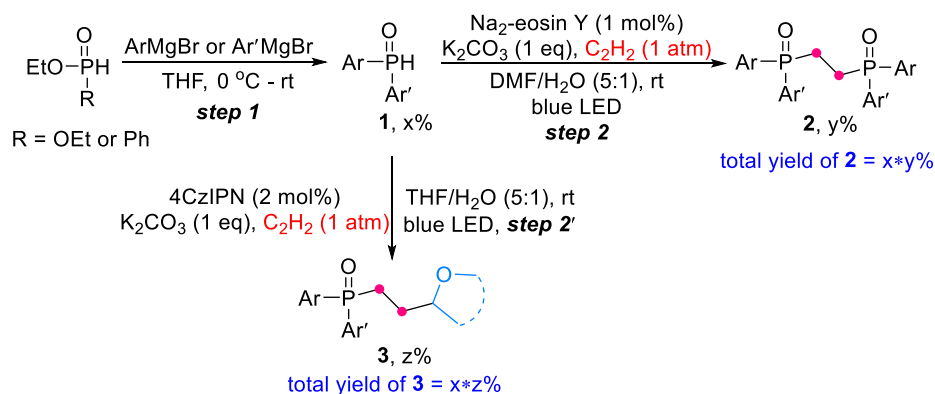


According to the general procedure 2.2, THF- d_8 was used instead of THF, the deuterium-labelling product **3a- d_8** was obtained in 27% isolated yield. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.80 – 7.69 (m, 4H), 7.55 – 7.43 (m, 6H), 2.59 – 2.45 (m, 1H), 2.34 – 2.22 (m, 1H), 1.89 – 1.81 (m, 1H), 1.69 (ddd, $J = 18.4, 8.0, 4.0$ Hz, 0.8H). **HRMS** (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{14}\text{D}_8\text{O}_2\text{P}^+$ 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

^aOnly for the substrates that need to be prepared.

b) Atom economy (atom utilisation)

$$\text{Atom economy} = \frac{\text{FW (g/mol) product}}{\text{FW of all reactants}} * 100\%$$

$$\left. \begin{aligned} &= \frac{430}{202*2+26} * 100\% = 100\% \quad (\text{example 1, for } \mathbf{2a}) \\ &= \frac{300}{202+26+72} * 100\% = 100\% \quad (\text{example 2, for } \mathbf{3a}) \end{aligned} \right\}$$

c) Process mass intensity (PMI)

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

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

$$\text{PMI} = \frac{60.6 \text{ mg (1a)} + 255 \text{ mg (C}_2\text{H}_2\text{)}^a + 2.1 \text{ mg (Na}_2\text{-eosin Y)} + 41.5 \text{ mg (K}_2\text{CO}_3\text{)} + 2370 \text{ mg (DMF)} + 500 \text{ mg (H}_2\text{O)}}{50.5 \text{ mg (2a)}}$$

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

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

$$\text{PMI} = \frac{60.6 \text{ mg (1a)} + 255 \text{ mg (C}_2\text{H}_2\text{)}^a + 4.7 \text{ (4CzIPN)} + 41.5 \text{ mg (K}_2\text{CO}_3\text{)} + 2225 \text{ mg (THF)} + 500 \text{ mg (H}_2\text{O)}}{63.6 \text{ mg (3a)}}$$

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

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

$$\text{PMI} = \frac{20.2 \text{ g (1a)} + 5.4 \text{ g (C}_2\text{H}_2\text{)}^a + 0.7 \text{ g (Na}_2\text{-eosin Y)} + 13.8 \text{ g (K}_2\text{CO}_3\text{)} + 237 \text{ g (DMF)} + 50 \text{ g (H}_2\text{O)}}{15.8 \text{ g (2a)}}$$

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

^aBased on the volume change of the acetylene balloon.

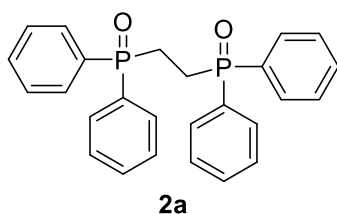
d) EcoScale of 100 mmol 1a scale-up reaction

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 ₂ SO ₄	0
8. Crystallization and filtration	1
<i>Penalty points total</i>	<i>44</i>
<hr/>	
EcoScale = 100 - Penalty points total = 56	

^aPrice of reaction components (to obtain 10 mmol of end product). ^bBased on the hazard warning symbols.

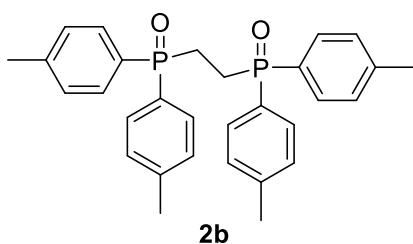
6. Characterization data of products

ethane-1,2-diylbis(diphenylphosphine oxide)³

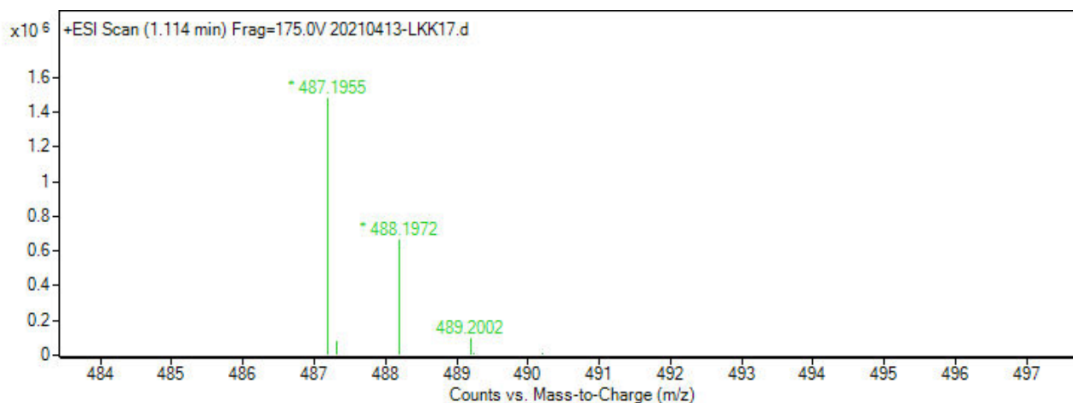


White solid, 50.5 mg, 78% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.71 (s, 8H), 7.48 (d, *J* = 28.7 Hz, 12H), 2.53 (s, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 132.05, 131.88 (d, *J* = 99.6 Hz), 130.74 (t, *J* = 4.5 Hz), 128.82 (t, *J* = 5.8 Hz), δ 22.05 – 21.29 (m). ³¹P NMR (202 MHz, CDCl₃) δ 32.60.

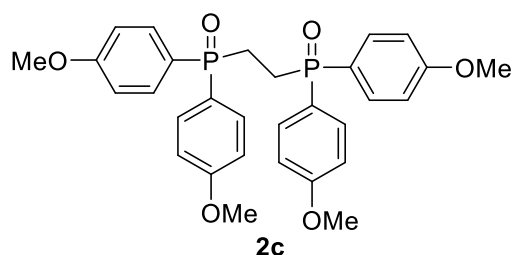
ethane-1,2-diylbis(di-p-tolylphosphine oxide)



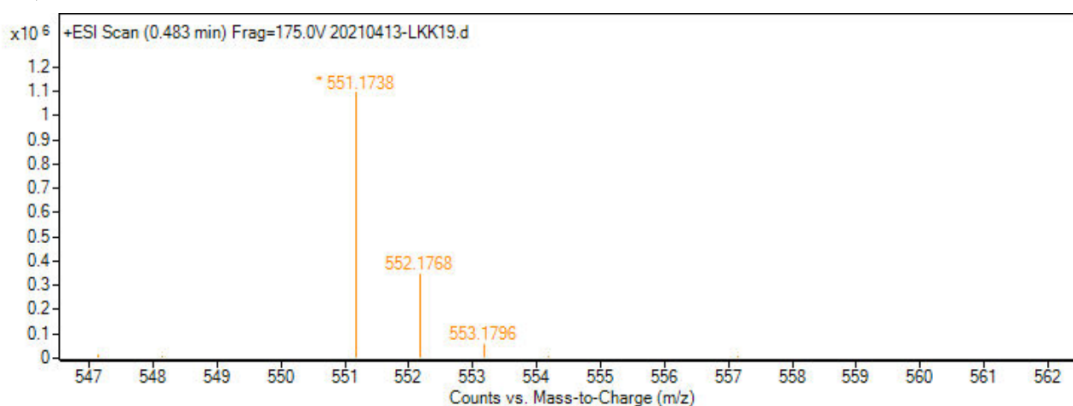
White solid, 41.3 mg, 57% yield, m.p. 225-227 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.57 (dd, *J* = 11.6, 6.9 Hz, 8H), 7.24 (d, *J* = 7.6 Hz, 8H), 2.46 (s, 4H), 2.36 (s, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 142.45, 130.80 (t, *J* = 4.7 Hz), 129.52 (t, *J* = 6.0 Hz), 128.81 (d, *J* = 103.0 Hz), 22.19 – 21.54 (m), 21.56. ³¹P NMR (202 MHz, CDCl₃) δ 33.20. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₃₀H₃₃O₂P₂⁺ 487.1950; found 487.1955.



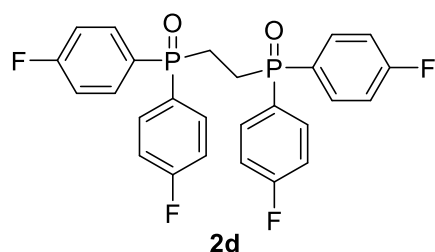
ethane-1,2-diylbis(bis(4-methoxyphenyl)phosphine oxide)



White solid, 28.9 mg, 35% yield, m.p. 149-151 °C. $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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). $^{31}\text{P NMR}$ (202 MHz, CDCl_3) δ 33.04. **HRMS** (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{30}\text{H}_{33}\text{O}_6\text{P}_2^+$ 551.1747; found 551.1738.

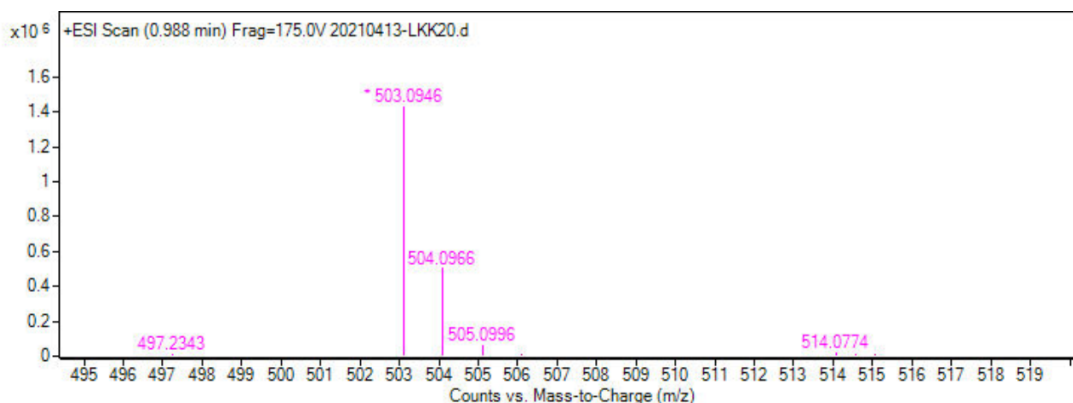


ethane-1,2-diylbis(bis(4-fluorophenyl)phosphine oxide)

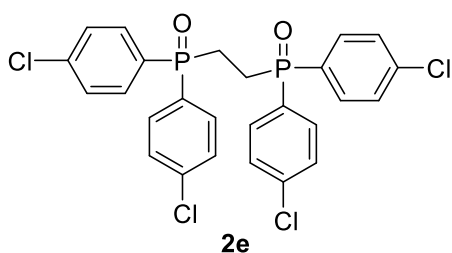


White solid, 43.7 mg, 58% yield, m.p. 211-213 °C. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.78 – 7.61 (m, 8H), 7.17 (t, $J = 8.4$ Hz, 8H), 2.47 (s, 4H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 165.22 (d, $J = 254.6$ Hz), 133.23 (dt, $J = 9.0, 5.5$ Hz), 127.45 (d, $J = 103.9$ Hz), 116.47 (dt, $J = 21.3, 6.4$ Hz), 22.41 – 21.27 (m). $^{31}\text{P NMR}$ (202 MHz, CDCl_3) δ 31.41. $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ -105.64. **HRMS** (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{21}\text{F}_4\text{O}_2\text{P}_2^+$

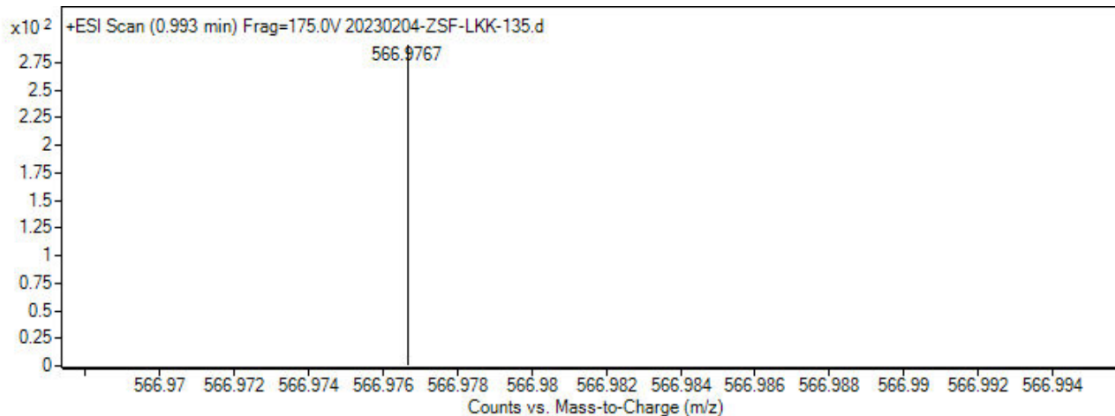
503.0947; found 503.0946.



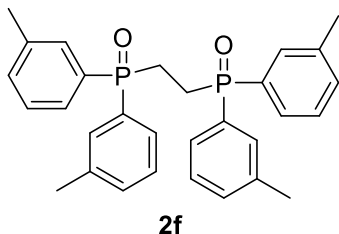
ethane-1,2-diylbis(bis(4-chlorophenyl)phosphine oxide)



White solid, 53.5 mg, 63% yield, m.p. 228-231 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.62 (td, *J* = 8.3, 6.1 Hz, 8H), 7.45 (d, *J* = 8.1 Hz, 8H), 2.46 (s, 4H). ¹³C NMR (126 MHz, CDCl₃) 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). ³¹P NMR (202 MHz, CDCl₃) δ 31.29. HRMS (ESI) m/z: [M + H]⁺ calcd for C₂₆H₂₁Cl₄O₂P₂⁺ 566.9765; found 566.9767.

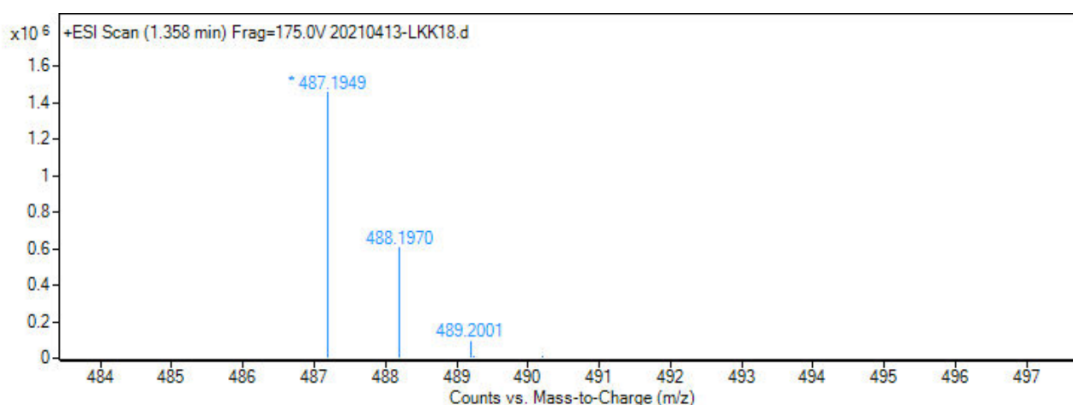


ethane-1,2-diylbis(di-m-tolylphosphine oxide)

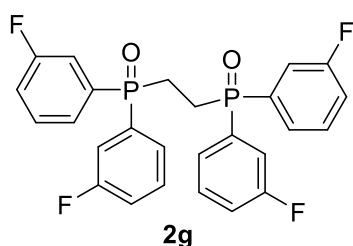


White solid, 35.4 mg, 49% yield, m.p. 150-152 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.56 (s, 4H), 7.46 (s, 4H), 7.32 (q, *J* = 7.8 Hz, 8H), 2.50 (s, 4H), 2.36 (s, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 138.75 (t, *J* = 5.1 Hz), 132.81, 131.89 (d, *J* = 99.7 Hz), 131.27, 128.67 (t, *J* = 5.4 Hz), 127.72, 21.65 (d, *J* = 62.1 Hz), 21.40. ³¹P NMR (202 MHz, CDCl₃) δ 33.06. HRMS (ESI) m/z: [M + H]⁺ calcd for C₃₀H₃₃O₂P₂⁺ 487.1950; found

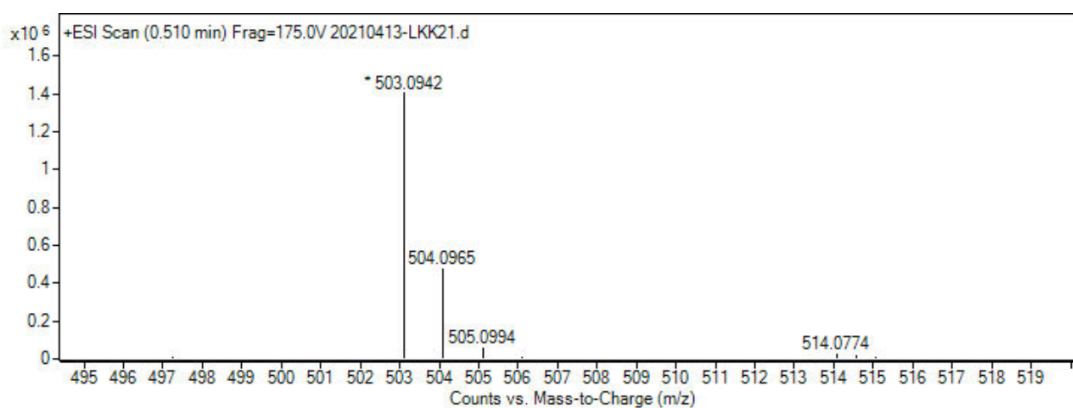
487.1949.



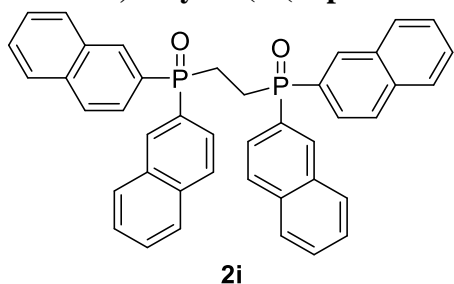
ethane-1,2-diylbis(bis(3-fluorophenyl)phosphine oxide)



White solid, 42.1 mg, 56% yield. m.p. 150-152 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.44 (dd, *J* = 15.6, 13.5 Hz, 12H), 7.27 – 7.18 (m, 4H), 2.51 (s, 4H). ¹³C NMR (126 MHz, CDCl₃) 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). ³¹P NMR (202 MHz, CDCl₃) δ 30.67. ¹⁹F NMR (471 MHz, CDCl₃) δ -109.79. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₆H₂₁F₄O₂P₂⁺ 503.0947; found 503.0942.

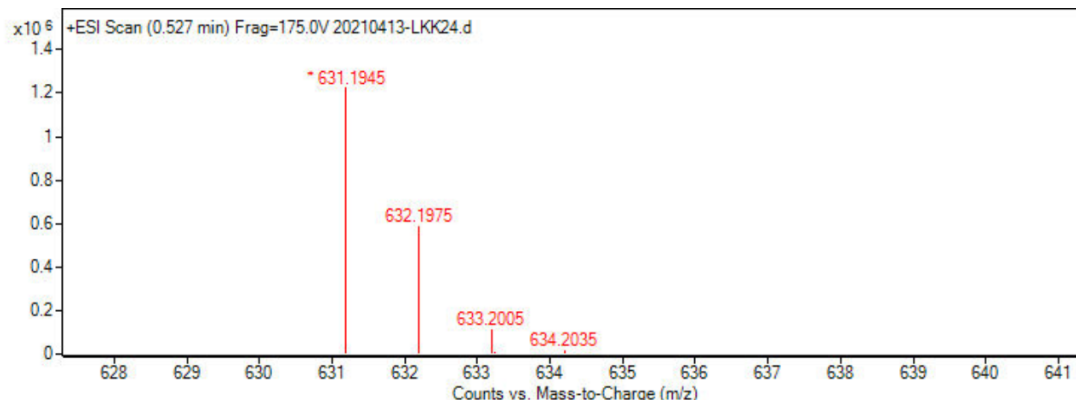


ethane-1,2-diylbis(di(naphthalen-2-yl)phosphine oxide)

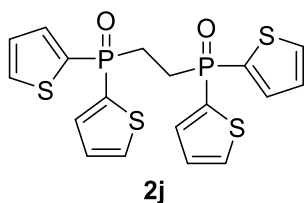


White solid, 50.9 mg, 54% yield, m.p. 155-157 °C ¹H NMR (500 MHz, CDCl₃) δ 8.47 – 8.32 (m, 4H), 7.94 – 7.77 (m, 12H), 7.65 (s, 4H), 7.55 (dt, *J* = 14.6, 7.0 Hz, 8H), 2.80 (s, 4H). ¹³C NMR (126 MHz, CDCl₃) δ

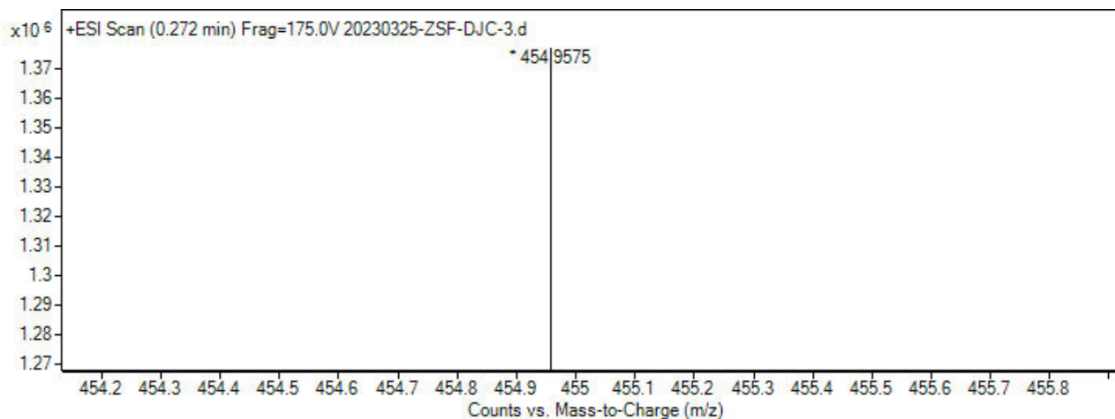
134.75, 132.90, 132.54 (t, $J = 6.3$ Hz), 128.95 (d, $J = 99.9$ Hz), 128.93, 128.83 (t, $J = 5.6$ Hz), 128.31, 127.83, 127.07, 125.46 (t, $J = 4.8$ Hz), 22.09 – 20.99 (m). ^{31}P NMR (202 MHz, CDCl_3) δ 33.09. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{42}\text{H}_{33}\text{O}_2\text{P}_2^+$ 631.1950; found 631.1945.



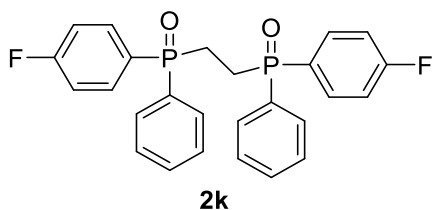
ethane-1,2-diylbis(di(thiophen-2-yl)phosphine oxide)



White solid, 81.4 mg, 30% yield, m.p. 124-126 °C. ^1H 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 : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{17}\text{O}_2\text{P}_2\text{S}_4^+$ 454.9581; found 454.9575.

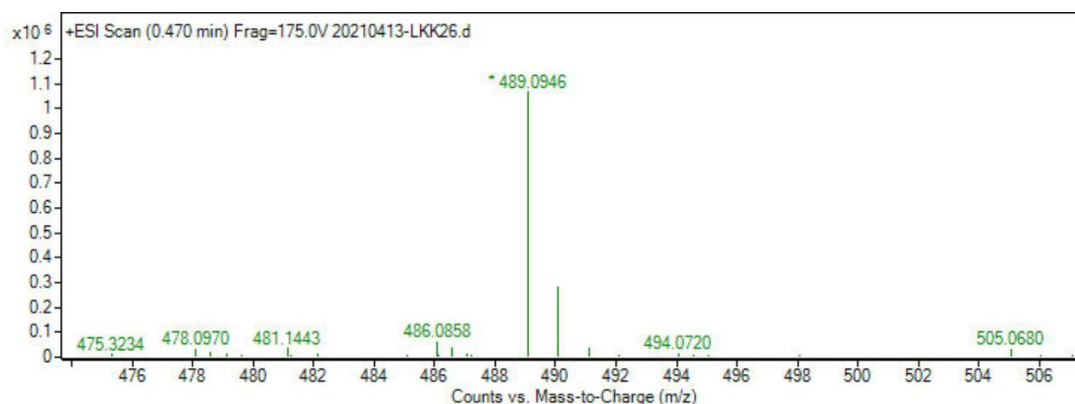


ethane-1,2-diylbis((4-fluorophenyl)(phenyl)phosphine oxide)

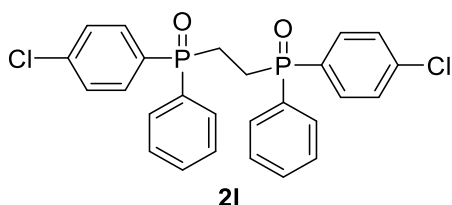


White solid, 31.2 mg, 42% yield, m.p. 130-133 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.70 (s, 8H), 7.54 (t, $J = 7.2$ Hz, 2H), 7.47 (t, $J = 7.1$ Hz, 4H), 7.15 (t, $J = 7.5$ Hz, 4H), 2.51 (s, 4H). ^{13}C NMR (126 MHz, CDCl_3) δ

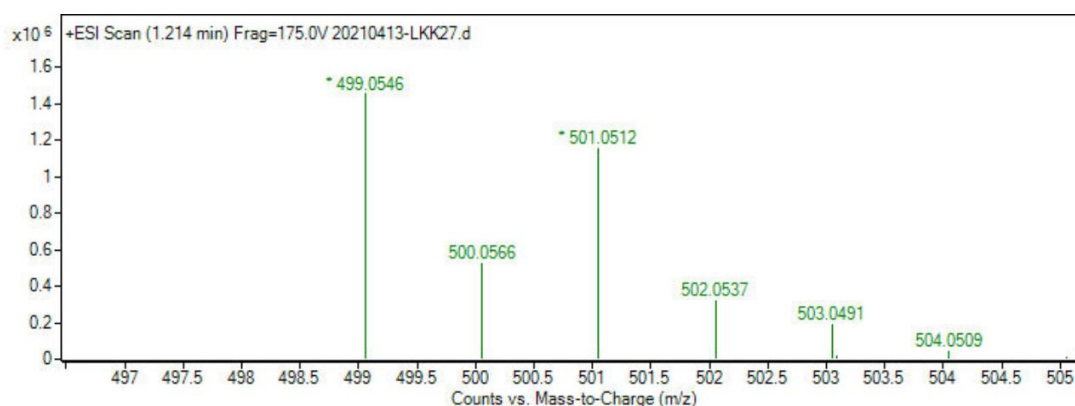
165.13 (d, $J = 253.7$ Hz), 133.38 – 133.22 (m), 132.28, 132.02 – 131.17 (m), 130.70 (t, $J = 4.7$ Hz), 128.98 (t, $J = 5.9$ Hz), 128.24 – 127.35 (m), 116.31 (dt, $J = 21.3, 6.4$ Hz), 22.27 – 21.25 (m). ^{31}P NMR (202 MHz, CDCl_3) δ 32.18. ^{19}F NMR (376 MHz, CDCl_3) δ -106.13. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{22}\text{F}_2\text{NaO}_2\text{P}_2^+$ 489.0955; found 489.0946.



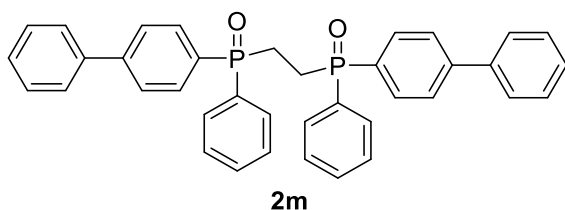
ethane-1,2-diylbis((4-chlorophenyl)(phenyl)phosphine oxide)



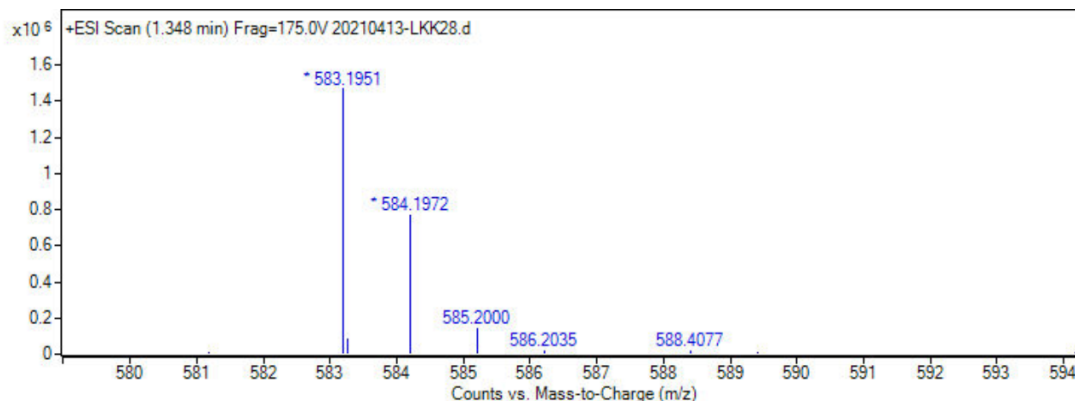
White solid, 38.4 mg, 52% yield, m.p. 221-223 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.77 – 7.58 (m, 8H), 7.54 (t, $J = 7.2$ Hz, 2H), 7.46 (dd, $J = 18.6, 7.7$ Hz, 8H), 2.49 (s, 4H). ^{13}C NMR (126 MHz, CDCl_3) δ 138.83, 132.38, 132.20, 131.39 (d, $J = 100.0$ Hz), 130.69, 129.27 (t, $J = 5.7$ Hz), 129.03 (t, $J = 5.4$ Hz), 22.21 – 20.81 (m). ^{31}P NMR (202 MHz, CDCl_3) δ 32.00. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{23}\text{Cl}_2\text{O}_2\text{P}_2^+$ 499.0545; found 499.0546.



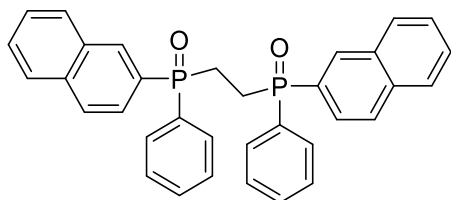
ethane-1,2-diylbis([1,1'-biphenyl]-4-yl(phenyl)phosphine oxide)



White solid, 50.3 mg, 58% yield, m.p. 115-116 °C. $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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). $^{31}\text{P NMR}$ (202 MHz, CDCl_3) δ 32.76. **HRMS** (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{38}\text{H}_{33}\text{O}_2\text{P}_2^+$ 583.1950; found 583.1951.

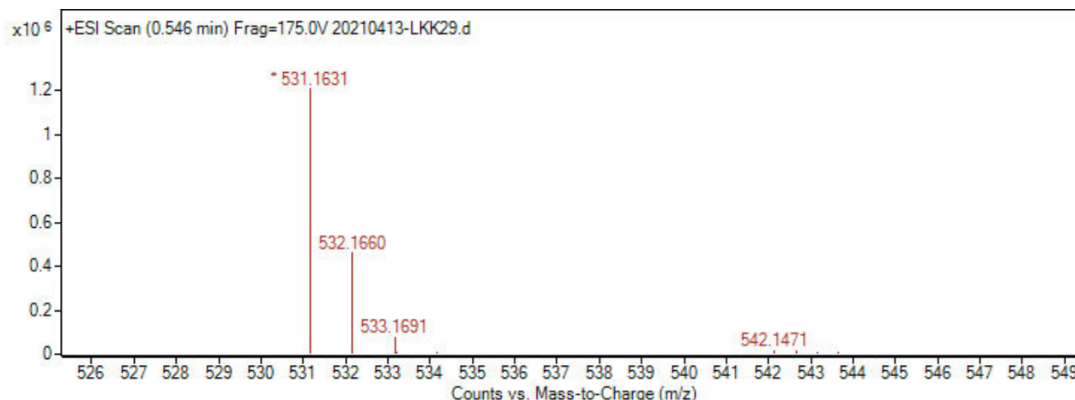


ethane-1,2-diylbis(naphthalen-2-yl(phenyl)phosphine oxide)

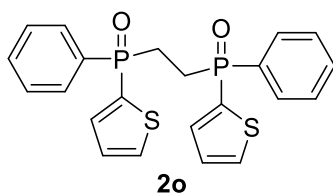


2n

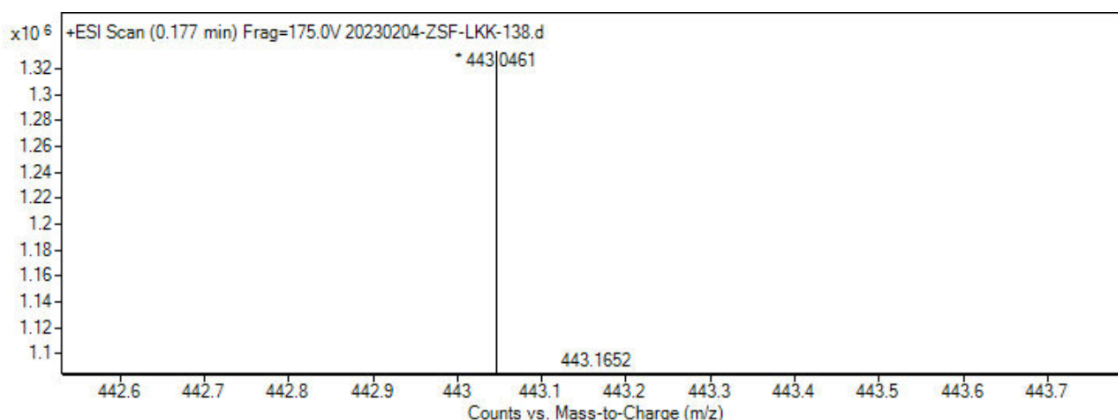
White solid, 43.5 mg, 55% yield, m.p. 148-150 °C. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.37 (d, $J = 12.3$ Hz, 2H), 7.87 (ddd, $J = 21.5, 14.9, 7.9$ Hz, 6H), 7.74 (s, 4H), 7.66 – 7.38 (m, 12H), 2.68 (d, $J = 13.4$ Hz, 4H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 134.74 (d, $J = 3.8$ Hz), 132.95 (t, $J = 4.1$ 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). $^{31}\text{P NMR}$ (202 MHz, CDCl_3) δ 33.06. **HRMS** (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{34}\text{H}_{29}\text{O}_2\text{P}_2^+$ 531.1637; found 531.1631.



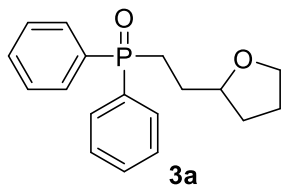
ethane-1,2-diylbis(phenyl(thiophen-2-yl)phosphine oxide)



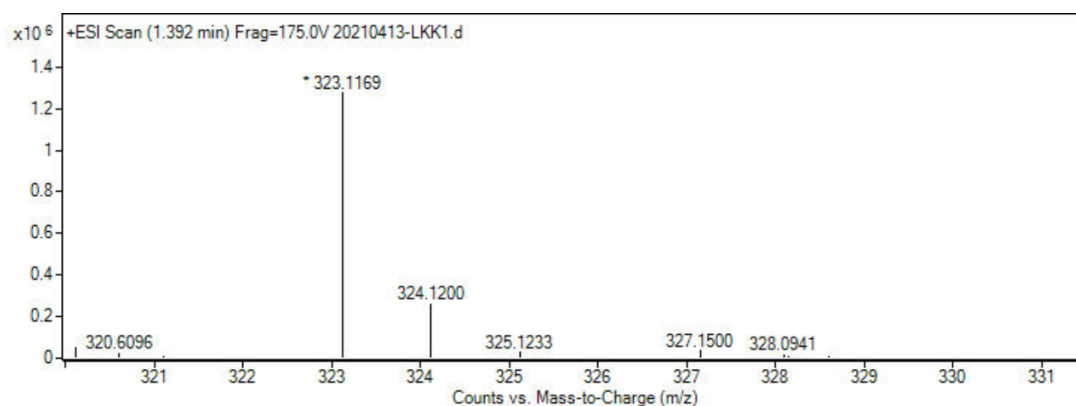
White solid, 42.3 mg, 64% yield, m.p. 147-150 °C. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.82 – 7.66 (m, 6H), 7.61 – 7.41 (m, 8H), 7.18 (dt, $J = 11.4, 4.0$ Hz, 2H), 2.70 – 2.41 (m, 4H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 135.54 (q, $J = 4.8$ Hz), 133.63 (t, $J = 1.9$ Hz), 132.71 (d, $J = 107.8$ Hz), 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). $^{31}\text{P NMR}$ (202 MHz, CDCl_3) δ 27.56. **HRMS** (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{21}\text{O}_2\text{P}_2\text{S}_2^+$ 443.0453; found 443.0461.



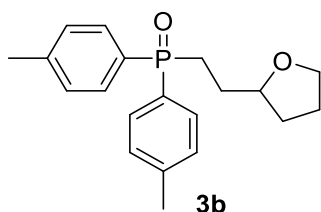
diphenyl(2-(tetrahydrofuran-2-yl)ethyl)phosphine oxide



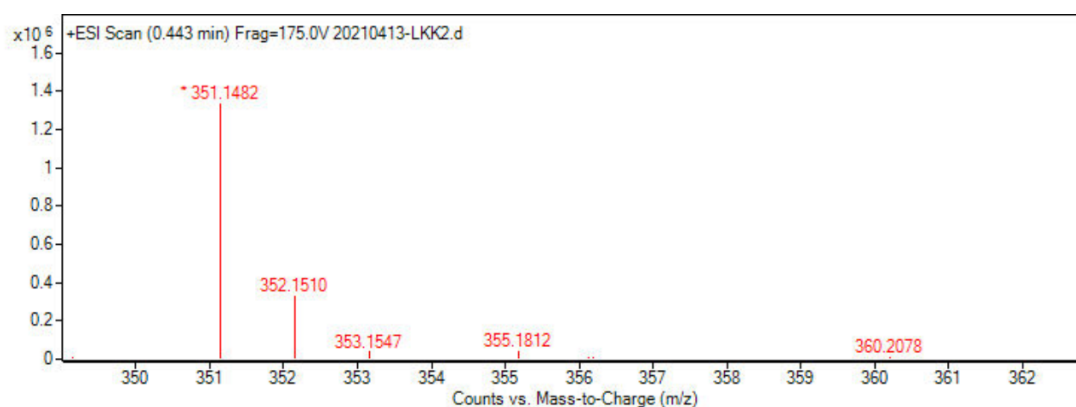
White solid, 63.6 mg, 71% yield, m.p. 93-95 °C. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.75 (dd, $J = 12.8, 4.7$ Hz, 4H), 7.54 – 7.39 (m, 6H), 3.86 (td, $J = 11.7, 7.2$ Hz, 1H), 3.80 (dd, $J = 14.8, 7.0$ Hz, 1H), 3.70 (dd, $J = 14.7, 7.4$ Hz, 1H), 2.52 (td, $J = 15.0, 4.3$ Hz, 1H), 2.28 (qd, $J = 12.4, 4.2$ 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). $^{13}\text{C NMR}$ (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. $^{31}\text{P NMR}$ (202 MHz, CDCl_3) δ 33.02. **HRMS** (ESI) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{18}\text{H}_{21}\text{NaO}_2\text{P}^+$ 323.1171; found 323.1169.



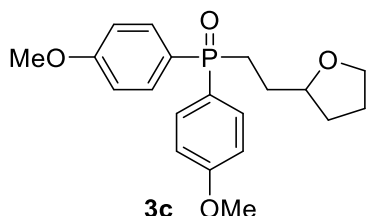
(2-(tetrahydrofuran-2-yl)ethyl)di-p-tolylphosphine oxide



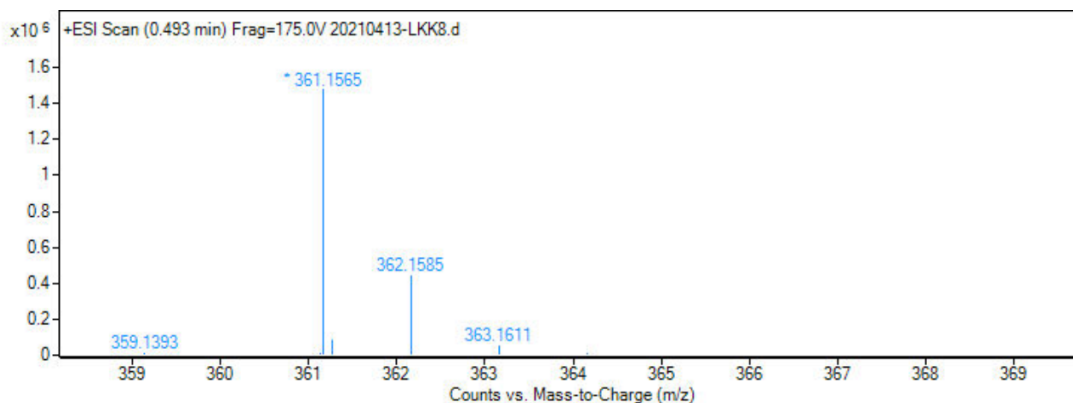
Colorless liquid, 55.0 mg, 56% yield. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.62 (t, $J = 8.2$ Hz, 4H), 7.26 (t, $J = 8.4$ Hz, 4H), 3.79 (ddq, $J = 51.3, 22.0, 7.3$ Hz, 3H), 2.47 (td, $J = 14.9, 4.4$ Hz, 1H), 2.38 (s, 6H), 2.29 – 2.16 (m, 1H), 1.96 (dt, $J = 12.4, 6.6$ Hz, 1H), 1.91 – 1.76 (m, 3H), 1.75 – 1.63 (m, 1H), 1.45 (td, $J = 15.6, 7.7$ Hz, 1H). $^{13}\text{C NMR}$ (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. $^{31}\text{P NMR}$ (202 MHz, CDCl_3) δ 33.08. **HRMS** (ESI) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{25}\text{NaO}_2\text{P}^+$ 351.1484; found 351.1482.



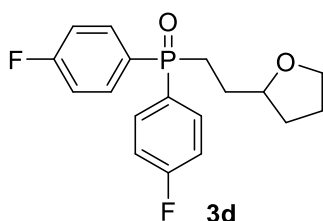
bis(4-methoxyphenyl)(2-(tetrahydrofuran-2-yl)ethyl)phosphine oxide



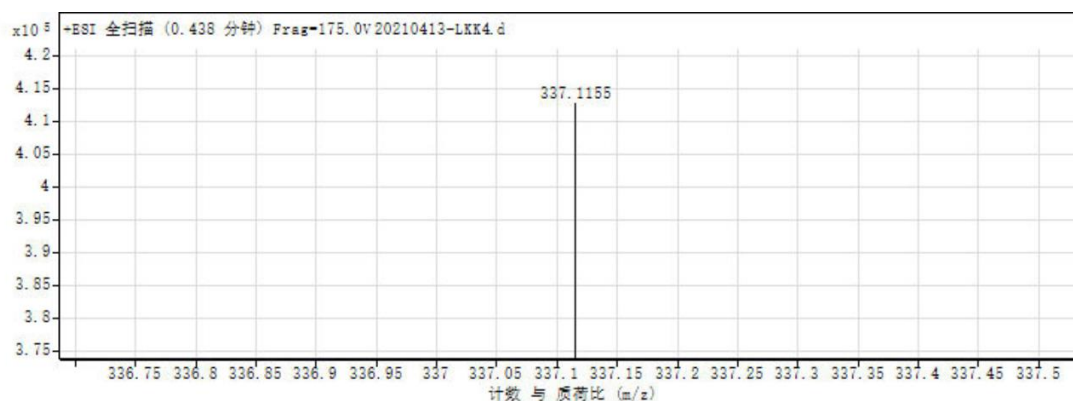
Colorless liquid, 47.8 mg, 44% yield. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.76 – 7.55 (m, 4H), 6.96 (ddd, $J = 8.8, 3.1, 2.3$ Hz, 4H), 3.88 – 3.77 (m, 8H), 3.70 (dd, $J = 15.0, 7.1$ Hz, 1H), 2.44 (dddd, $J = 15.0, 12.3, 10.7, 4.5$ Hz, 1H), 2.27 – 2.15 (m, 1H), 1.96 (ddd, $J = 12.1, 10.2, 6.3$ Hz, 1H), 1.90 – 1.78 (m, 3H), 1.75 – 1.64 (m, 1H), 1.45 (ddd, $J = 15.6, 12.1, 7.5$ Hz, 1H). $^{13}\text{C NMR}$ (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. $^{31}\text{P NMR}$ (202 MHz, CDCl_3) δ 32.88. **HRMS** (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{26}\text{O}_4\text{P}^+$ 361.1563; found 361.1565.



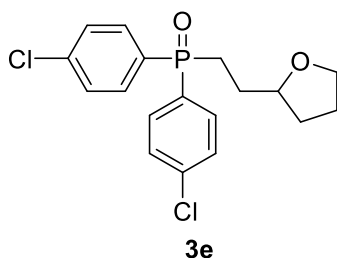
bis(4-fluorophenyl)(2-(tetrahydrofuran-2-yl)ethyl)phosphine oxide



Colorless liquid, 44.1 mg, 44% yield. $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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. $^{31}\text{P NMR}$ (202 MHz, CDCl_3) δ 31.89. $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ -106.66. **HRMS** (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{20}\text{F}_2\text{O}_2\text{P}^+$ 337.1163; found 337.1155.

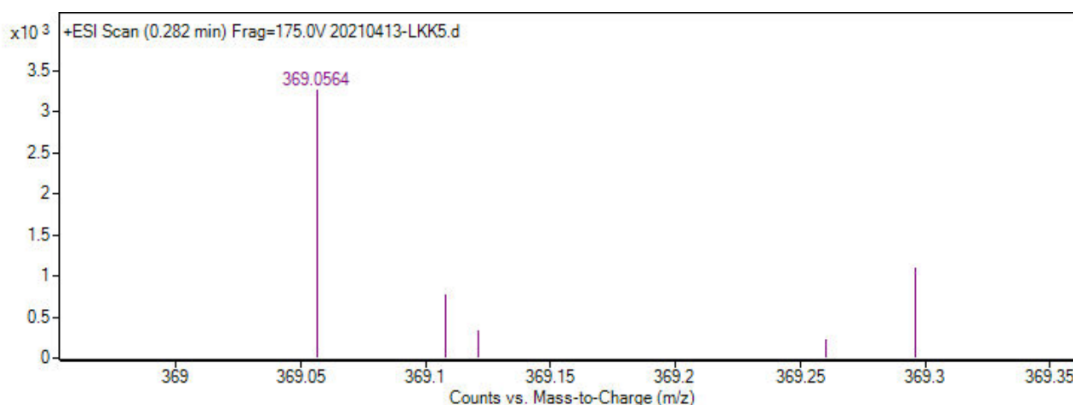


bis(4-chlorophenyl)(2-(tetrahydrofuran-2-yl)ethyl)phosphine oxide

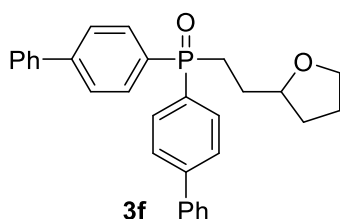


Colorless liquid, 59.7 mg, 54% yield. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.71 – 7.61 (m, 4H), 7.46 (ddd, $J = 8.3,$

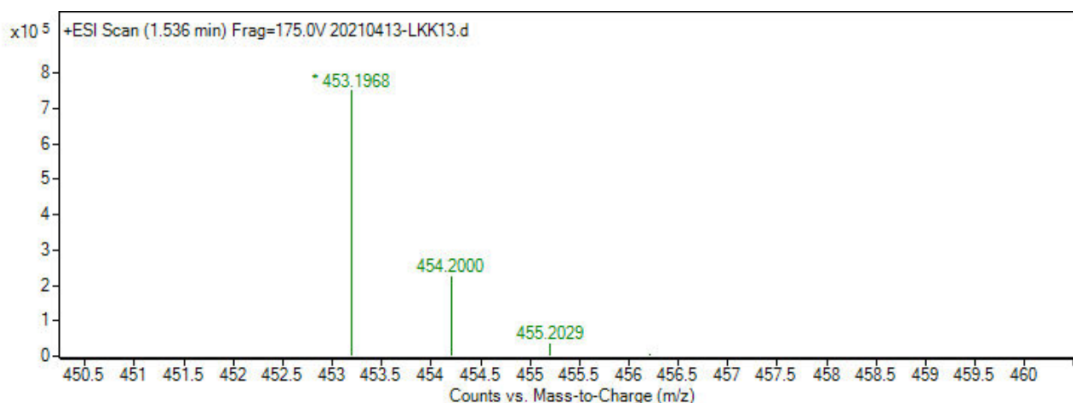
3.6, 2.2 Hz, 4H), 3.85 (ddd, $J = 10.9, 7.1, 3.7$ Hz, 1H), 3.80 (dd, $J = 15.1, 6.9$ Hz, 1H), 3.70 (dd, $J = 15.1, 7.1$ Hz, 1H), 2.54 – 2.46 (m, 1H), 2.33 – 2.19 (m, 1H), 1.97 (dt, $J = 12.4, 6.5$ Hz, 1H), 1.90 – 1.81 (m, 3H), 1.66 (dddd, $J = 21.6, 12.9, 8.5, 4.4$ Hz, 1H), 1.45 (ddd, $J = 15.5, 12.2, 7.7$ 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 : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{20}\text{Cl}_2\text{O}_2\text{P}^+$ 369.0572; found 369.0564.



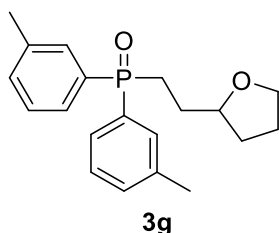
di([1,1'-biphenyl]-4-yl)(2-(tetrahydrofuran-2-yl)ethyl)phosphine oxide



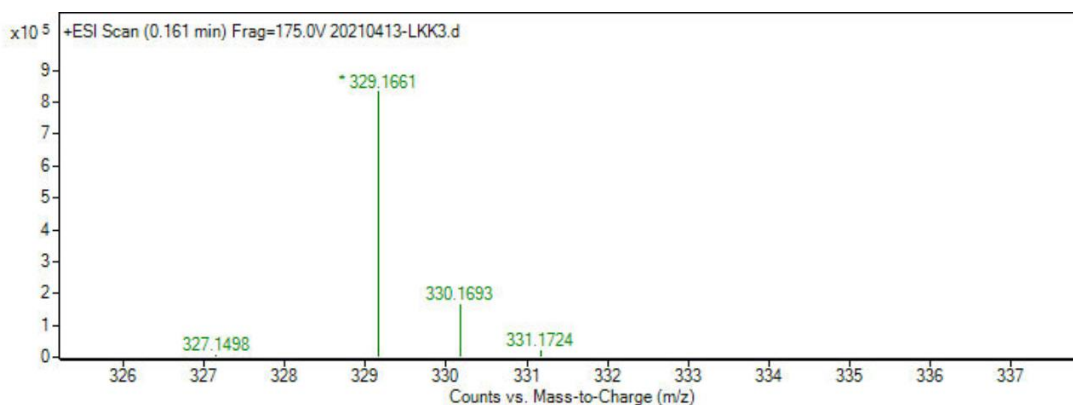
White solid, 57.6 mg, 43% yield, m.p. 168-170 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.85 (ddd, $J = 11.0, 8.3, 2.7$ Hz, 4H), 7.69 (dt, $J = 8.0, 2.7$ Hz, 4H), 7.59 (dd, $J = 7.4, 1.6$ Hz, 4H), 7.45 (t, $J = 7.6$ Hz, 4H), 7.38 (t, $J = 7.2$ Hz, 2H), 3.90 (td, $J = 11.5, 7.3$ Hz, 1H), 3.83 (dd, $J = 14.9, 6.9$ 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 : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{30}\text{H}_{30}\text{O}_2\text{P}^+$ 453.1978; found 453.1968.



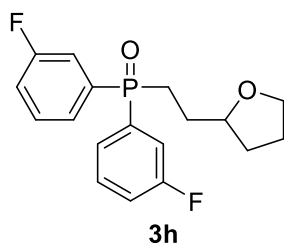
(2-(tetrahydrofuran-2-yl)ethyl)di-m-tolylphosphine oxide



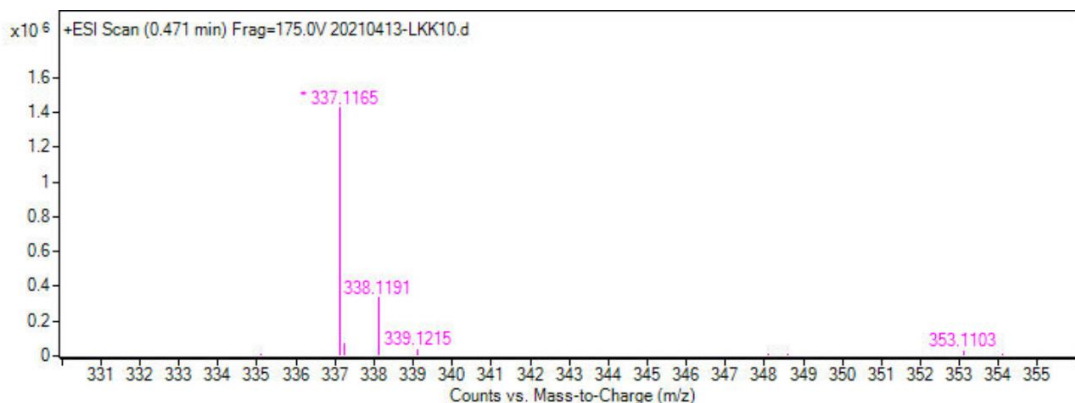
Colorless liquid, 59.3 mg, 60% yield. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.61 (d, $J = 9.9$ Hz, 2H), 7.54 – 7.42 (m, 2H), 7.38 – 7.27 (m, 4H), 3.94 – 3.62 (m, 3H), 2.50 (ddd, $J = 22.0, 15.0, 4.3$ Hz, 1H), 2.37 (s, 6H), 2.25 (td, $J = 15.9, 4.0$ Hz, 1H), 1.97 (dt, $J = 12.4, 6.6$ Hz, 1H), 1.92 – 1.77 (m, 3H), 1.71 (dq, $J = 12.8, 8.1$ Hz, 1H), 1.46 (td, $J = 15.5, 7.6$ Hz, 1H). $^{13}\text{C NMR}$ (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. $^{31}\text{P NMR}$ (202 MHz, CDCl_3) δ 32.99. **HRMS** (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{26}\text{O}_2\text{P}^+$ 329.1665; found 329.1661.



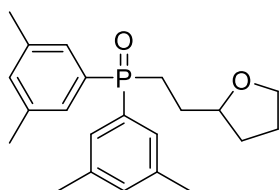
bis(3-fluorophenyl)(2-(tetrahydrofuran-2-yl)ethyl)phosphine oxide



Colorless liquid, 50.2 mg, 50% yield. $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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. $^{31}\text{P NMR}$ (202 MHz, CDCl_3) δ 31.19. $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ -110.57 (d, $J = 4.8$ Hz). **HRMS** (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{20}\text{F}_2\text{O}_2\text{P}^+$ 337.1163; found 337.1165.

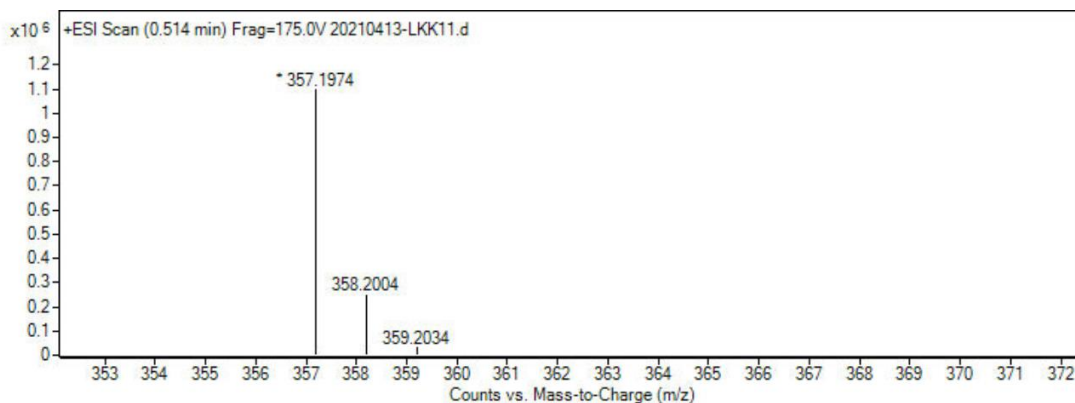


bis(3,5-dimethylphenyl)(2-(tetrahydrofuran-2-yl)ethyl)phosphine oxide

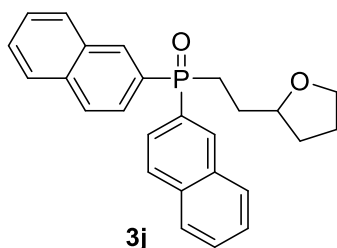


3i

White solid, 39.3 mg, 37% yield, m.p. 70-73 °C. ¹H NMR (500 MHz, CDCl₃) 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). ¹³C NMR (126 MHz, CDCl₃) 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. ³¹P NMR (202 MHz, CDCl₃) δ 32.96. HRMS (ESI) m/z: [M + H]⁺ calcd for C₂₂H₃₀O₂P⁺ 357.1978; found 357.1974.

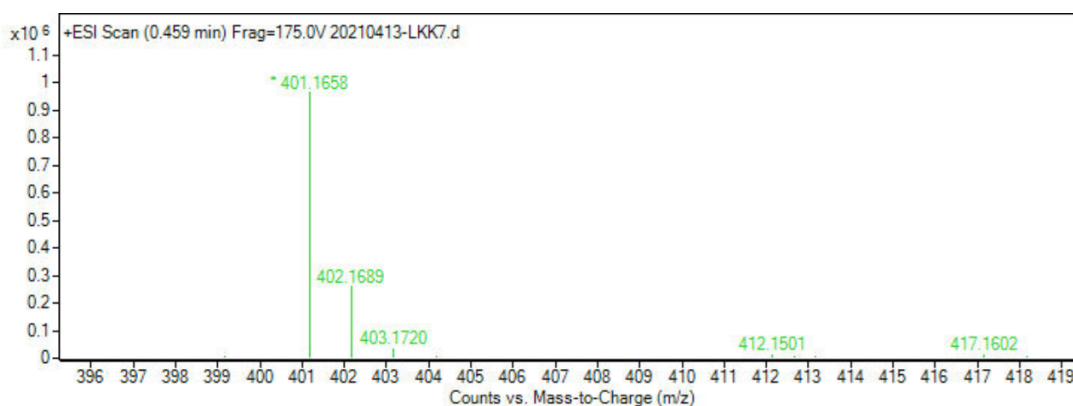


di(naphthalen-2-yl)(2-(tetrahydrofuran-2-yl)ethyl)phosphine oxide

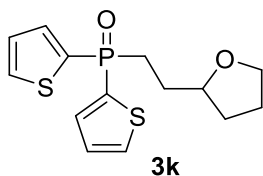


3j

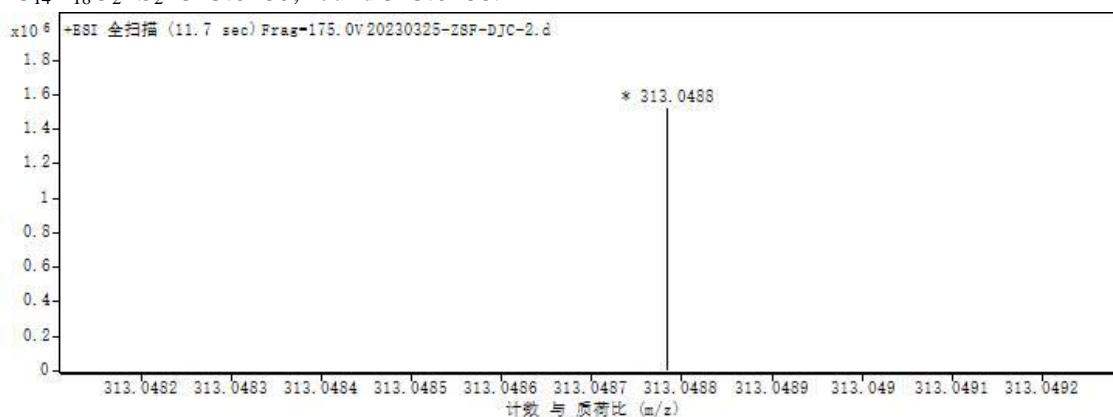
Colorless liquid, 46.7 mg, 46% yield. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.44 (dd, $J = 13.2, 7.3$ Hz, 2H), 7.98 – 7.80 (m, 6H), 7.71 (t, $J = 8.6$ Hz, 2H), 7.57 (td, $J = 14.8, 7.1$ Hz, 4H), 3.91 (td, $J = 11.1, 7.2$ Hz, 1H), 3.81 (dd, $J = 15.0, 6.9$ Hz, 1H), 3.72 (dd, $J = 15.0, 7.1$ Hz, 1H), 2.85 – 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). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 134.65 (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. $^{31}\text{P NMR}$ (202 MHz, CDCl_3) δ 33.19. **HRMS** (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{26}\text{O}_2\text{P}^+$ 401.1665; found 401.1658.



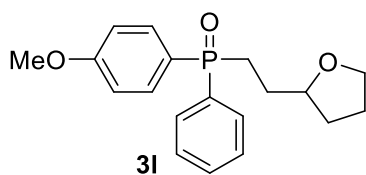
(2-(tetrahydrofuran-2-yl)ethyl)di(thiophen-2-yl)phosphine oxide



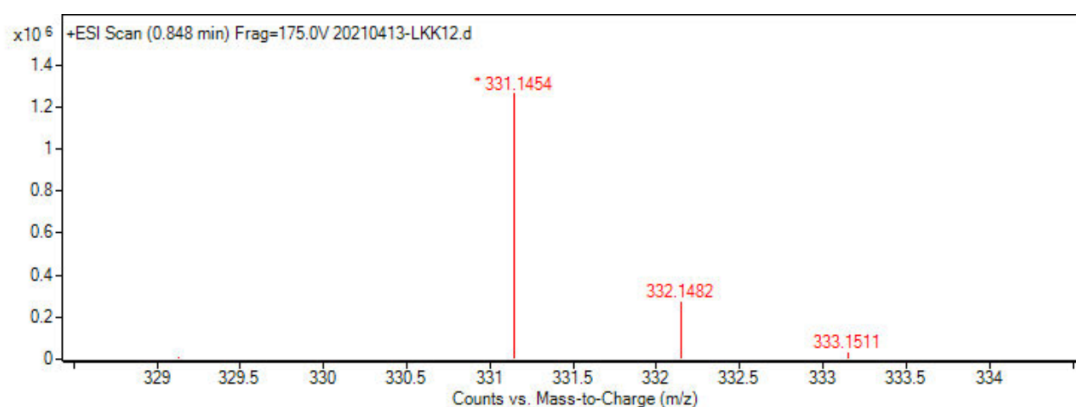
Colorless liquid, 41.4 mg, 22% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.72 (t, $J = 4.4$ Hz, 2H), 7.61 (dd, $J = 7.2, 3.6$ Hz, 2H), 7.20 (td, $J = 3.5, 1.8$ Hz, 2H), 3.93 – 3.77 (m, 2H), 3.71 (dd, $J = 14.6, 7.5$ Hz, 1H), 2.52 (dtd, $J = 16.5, 11.9, 4.7$ Hz, 1H), 2.39 – 2.21 (m, 1H), 2.02 – 1.93 (m, 1H), 1.92 – 1.78 (m, 4H), 1.48 (ddd, $J = 15.3, 12.0, 7.5$ Hz, 1H). $^{13}\text{C NMR}$ (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. $^{31}\text{P NMR}$ (202 MHz, CDCl_3) δ 22.71. **HRMS** (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{18}\text{O}_2\text{PS}_2^+$ 313.0480; found 313.0488.



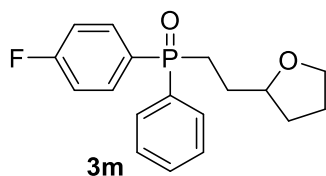
(4-methoxyphenyl)(phenyl)(2-(tetrahydrofuran-2-yl)ethyl)phosphine oxide



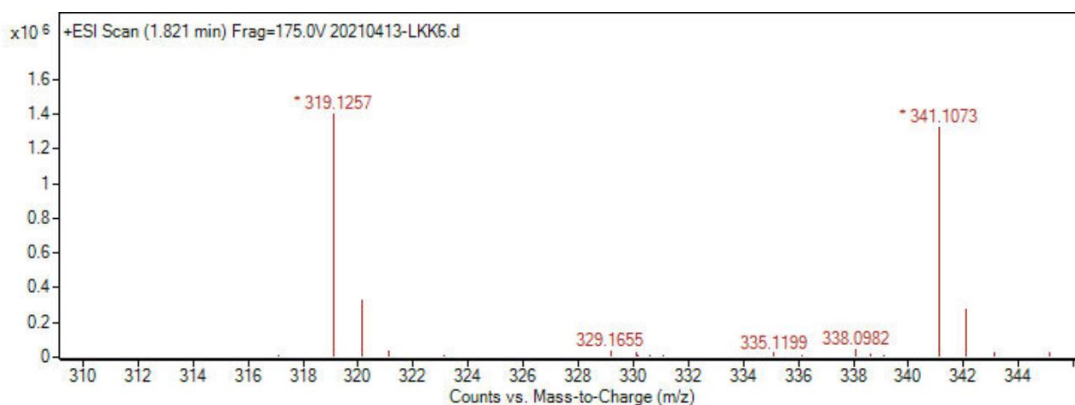
Colorless liquid, 40.6 mg, 41% yield. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.70 (dddd, $J = 22.7, 11.7, 5.8, 2.4$ Hz, 4H), 7.47 (tt, $J = 8.2, 7.1$ Hz, 3H), 7.04 – 6.91 (m, 2H), 3.90 – 3.77 (m, 5H), 3.70 (dd, $J = 14.7, 7.4$ Hz, 1H), 2.48 (ddd, $J = 15.0, 13.6, 4.4$ Hz, 1H), 2.24 (ddd, $J = 27.3, 12.4, 4.3$ Hz, 1H), 2.01 – 1.92 (m, 1H), 1.84 (dt, $J = 12.3, 6.0$ Hz, 3H), 1.71 (tt, $J = 11.9, 8.0, 4.0$ Hz, 1H), 1.51 – 1.39 (m, 1H). $^{13}\text{C NMR}$ (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. $^{31}\text{P NMR}$ (202 MHz, CDCl_3) δ 32.96 (d, $J = 4.4$ Hz). **HRMS** (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{24}\text{O}_3\text{P}^+$ 331.1458; found 331.1454.



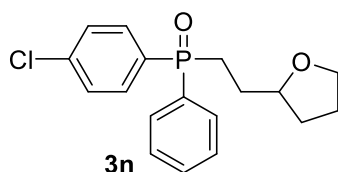
(4-fluorophenyl)(phenyl)(2-(tetrahydrofuran-2-yl)ethyl)phosphine oxide



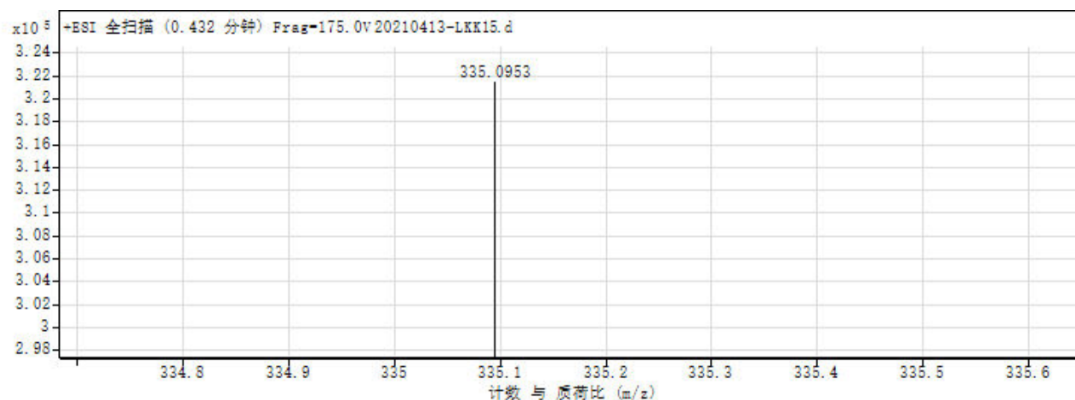
Colorless liquid, 40.4 mg, 42% yield. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.80 – 7.69 (m, 4H), 7.56 – 7.50 (m, 1H), 7.50 – 7.45 (m, 2H), 7.16 (tdd, $J = 8.5, 3.5, 1.9$ Hz, 2H), 3.91 – 3.75 (m, 2H), 3.70 (dd, $J = 15.0, 7.1$ Hz, 1H), 2.61 – 2.43 (m, 1H), 2.32 – 2.21 (m, 1H), 1.97 (dt, $J = 12.5, 6.6$ 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). $^{13}\text{C NMR}$ (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. $^{31}\text{P NMR}$ (202 MHz, CDCl_3) δ 32.30. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -107.08 (d, $J = 5.5$ Hz). **HRMS** (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{21}\text{FO}_2\text{P}^+$ 319.1258; found 319.1257.



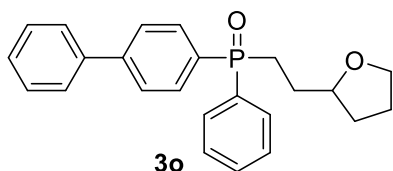
(4-chlorophenyl)(phenyl)(2-(tetrahydrofuran-2-yl)ethyl)phosphine oxide



Colorless liquid, 49.2 mg, 49% yield. $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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. $^{31}\text{P NMR}$ (202 MHz, CDCl_3) δ 32.30. **HRMS** (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{21}\text{ClO}_2\text{P}^+$ 335.0962; found 335.0953.

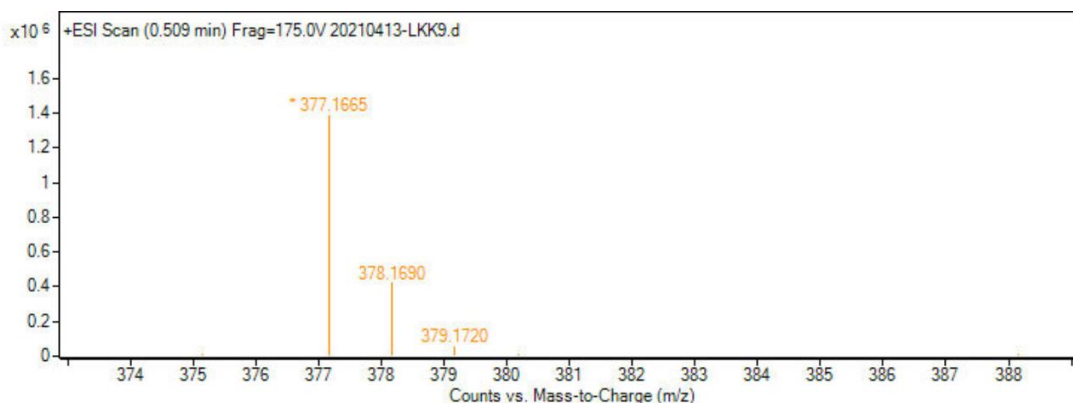


[1,1'-biphenyl]-4-yl(phenyl)(2-(tetrahydrofuran-2-yl)ethyl)phosphine oxide

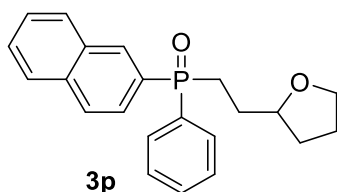


White solid, 51.3 mg, 45% yield, m.p. 131-134 °C. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.87 – 7.75 (m, 4H), 7.68 (dd, $J = 5.2, 2.9$ Hz, 2H), 7.62 – 7.56 (m, 2H), 7.53 – 7.42 (m, 5H), 7.37 (t, $J = 7.3$ Hz, 1H), 3.84 (ddd, $J = 21.7, 10.8, 5.6$ Hz, 2H), 3.70 (dd, $J = 14.9, 7.3$ Hz, 1H), 2.63 – 2.49 (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). $^{13}\text{C NMR}$ (126 MHz,

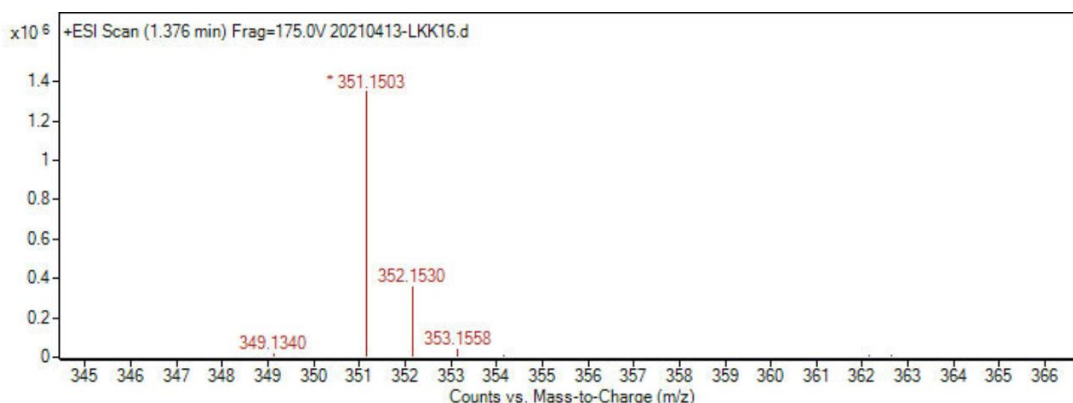
CDCl₃) δ 144.49 (d, *J* = 2.5 Hz), 139.94, 133.10 (dd, *J* = 98.6, 47.2 Hz), 131.72 (d, *J* = 2.6 Hz), 131.58 (dd, *J* = 99.5, 48.7 Hz), 131.33 (dd, *J* = 14.6, 9.5 Hz), 130.81 (dd, *J* = 14.5, 9.3 Hz), 128.94, 128.69 (dd, *J* = 11.6, 1.7 Hz), 128.11, 127.33 (dd, *J* = 11.9, 1.8 Hz), 127.25, 79.22 (dd, *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. ³¹P NMR (202 MHz, CDCl₃) δ 32.72. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₄H₂₆O₂P⁺ 377.1665; found 377.1665.



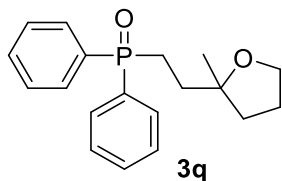
naphthalen-2-yl(phenyl)(2-(tetrahydrofuran-2-yl)ethyl)phosphine oxide



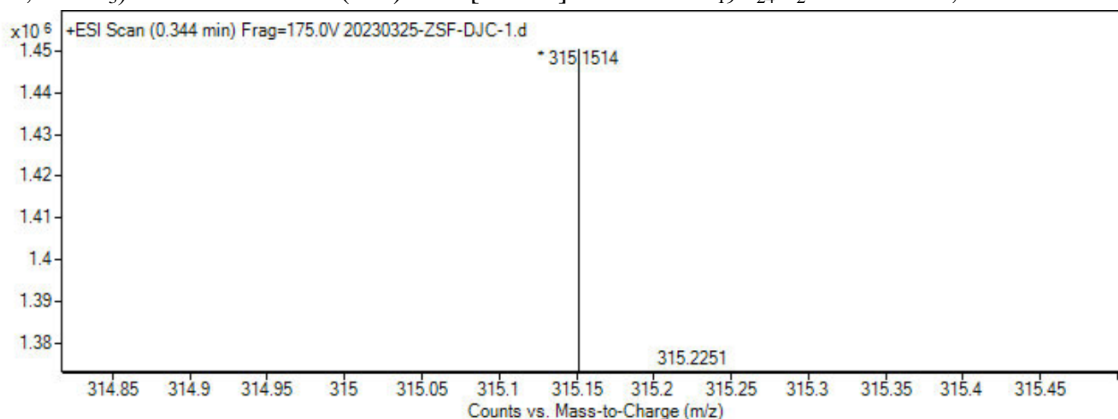
Colorless liquid, 52.1 mg, 50% yield. ¹H NMR (500 MHz, CDCl₃) δ 8.41 (dd, *J* = 13.1, 6.3 Hz, 1H), 7.96 – 7.84 (m, 3H), 7.83 – 7.74 (m, 2H), 7.67 (t, *J* = 8.9 Hz, 1H), 7.61 – 7.42 (m, 5H), 3.88 (dq, *J* = 13.8, 6.9 Hz, 1H), 3.84 – 3.76 (m, 1H), 3.70 (dd, *J* = 14.8, 7.3 Hz, 1H), 2.70 – 2.55 (m, 1H), 2.45 – 2.30 (m, 1H), 2.01 – 1.66 (m, 5H), 1.50 – 1.40 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) 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. ³¹P NMR (202 MHz, CDCl₃) δ 33.29. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₂₂H₂₄O₂P⁺ 351.1508; found 351.1503.



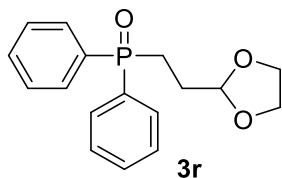
(2-(2-methyltetrahydrofuran-2-yl)ethyl)diphenylphosphine oxide



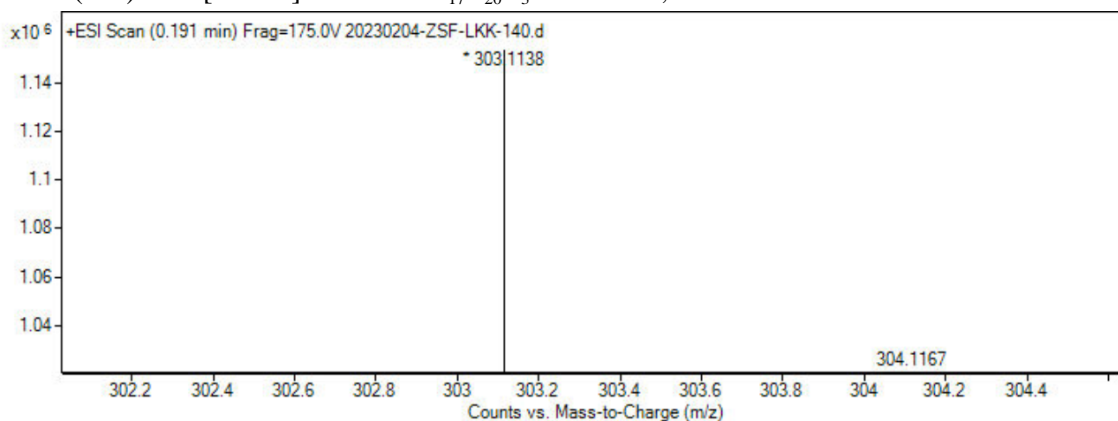
Colorless liquid, 45.0 mg (**3q/3q'** = 2.3:1), 48% yield. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.81 – 7.67 (m, 4H), 7.56 – 7.42 (m, 6H), 4.01 (dd, $J = 12.7, 6.1$ Hz, 1H), 3.97 – 3.85 (m, 1H), 3.82 (dd, $J = 14.1, 7.5$ Hz, 1H), 3.70 (dd, $J = 14.7, 7.3$ Hz, 1H), 2.46 – 2.22 (m, 2H), 2.00 – 1.58 (m, 6H), 1.19 (s, 3H). $^{13}\text{C NMR}$ (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. $^{31}\text{P NMR}$ (202 MHz, CDCl_3) δ 34.12. **HRMS** (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{24}\text{O}_2\text{P}^+$ 351.1508; found 315.1514.



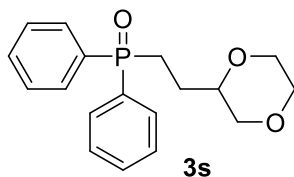
(2-(1,3-dioxolan-2-yl)ethyl)diphenylphosphine oxide



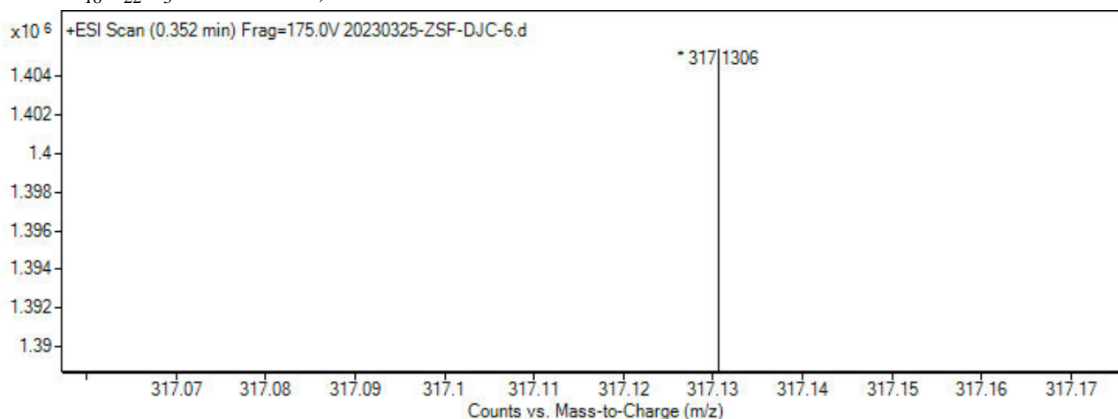
Colorless liquid, 30.5 mg (**3r/3r'** = 5.5:1), 34% yield. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.75 (dd, $J = 11.2, 7.3$ Hz, 4H), 7.56 – 7.42 (m, 6H), 4.96 (t, $J = 4.1$ Hz, 1H), 3.99 – 3.78 (m, 4H), 2.47 – 2.31 (m, 2H), 1.97 (ddd, $J = 16.5, 8.1, 4.2$ Hz, 2H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) 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). $^{31}\text{P NMR}$ (202 MHz, CDCl_3) δ 32.96. **HRMS** (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{20}\text{O}_3\text{P}^+$ 303.1145; found 303.1138.



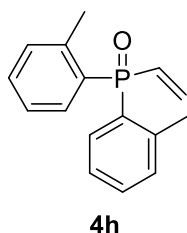
(2-(1,4-dioxan-2-yl)ethyl)diphenylphosphine oxide



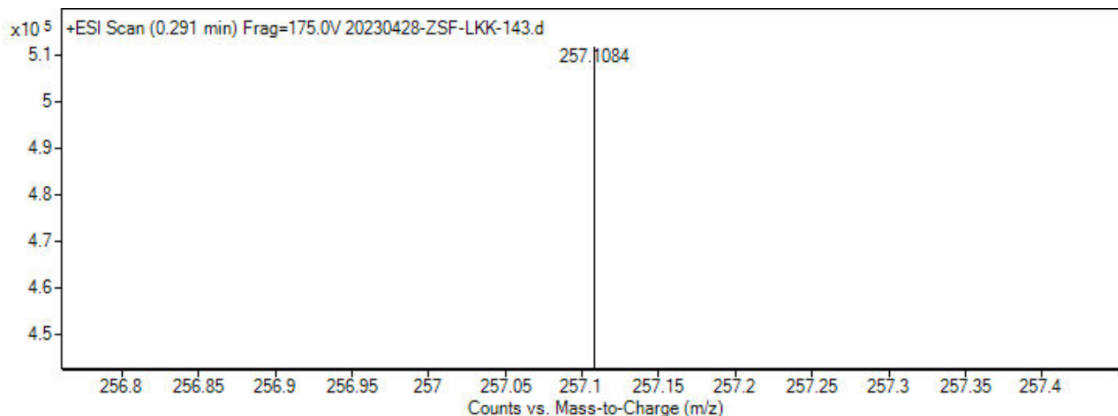
Colorless liquid, 36.1 mg, 38% yield. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.88 – 7.63 (m, 4H), 7.50 (dd, $J = 19.8, 6.7$ Hz, 6H), 3.76 – 3.49 (m, 6H), 3.22 (t, $J = 10.6$ Hz, 1H), 2.62 – 2.49 (m, 1H), 2.37 – 2.19 (m, 1H), 1.75 (s, 1H), 1.67 – 1.54 (m, 1H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 132.50 (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). $^{31}\text{P NMR}$ (202 MHz, CDCl_3) δ 35.46. **HRMS** (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{22}\text{O}_3\text{P}^+$ 317.1301; found 317.1306.



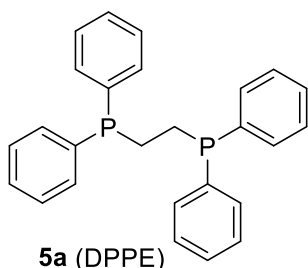
di-*o*-tolyl(vinyl)phosphine oxide



Colorless liquid, 15.8 mg, 21% yield. $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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). $^{31}\text{P NMR}$ (202 MHz, CDCl_3) δ 26.52. **HRMS** (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{18}\text{OP}^+$ 257.1090; found 257.1084.

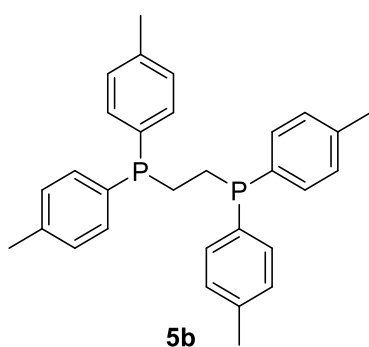


1,2-bis(diphenylphosphanyl)ethane (DPPE)⁴



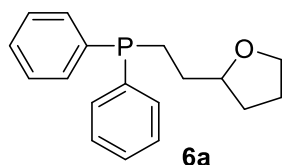
White solid, 101.7 mg, 85% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.39 – 7.18 (m, 20H), 2.15 – 2.03 (m, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 138.19 (dd, *J* = 7.4, 5.9 Hz), 132.82 (t, *J* = 9.4 Hz), 128.75, 128.54 (t, *J* = 3.1 Hz), 23.95 (d, *J* = 2.3 Hz). ³¹P NMR (202 MHz, CDCl₃) δ -12.62.

1,2-bis(di-*p*-tolylphosphanyl)ethane⁵

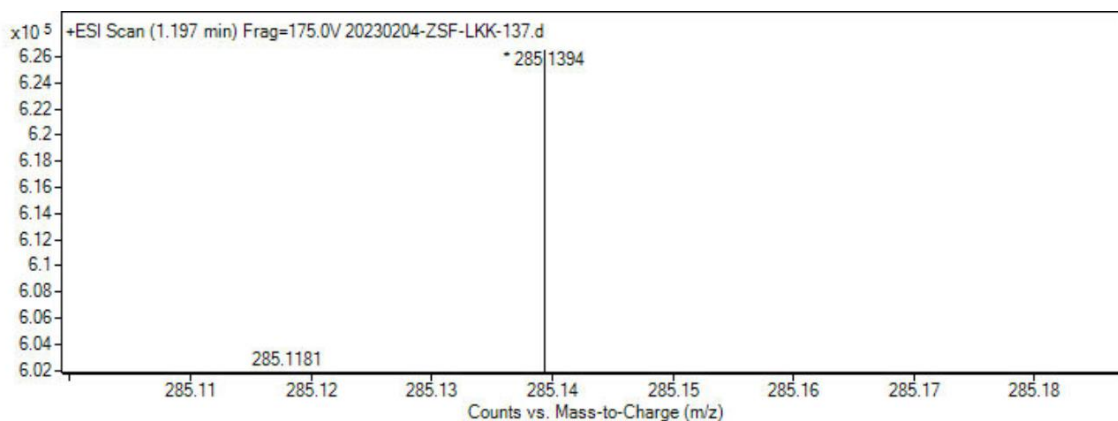


White solid, 27.1 mg, 60% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.21 (d, *J* = 7.1 Hz, 8H), 7.10 (d, *J* = 7.7 Hz, 8H), 2.32 (s, 12H), 2.04 (s, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 138.49, 134.89 (t, *J* = 6.0 Hz), 132.70 (t, *J* = 9.6 Hz), 129.21 (t, *J* = 3.2 Hz), 24.04 (d, *J* = 2.8 Hz), 21.27. ³¹P NMR (202 MHz, CDCl₃) δ -14.32.

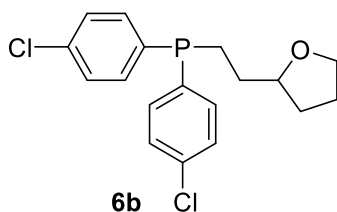
diphenyl(2-(tetrahydrofuran-2-yl)ethyl)phosphane



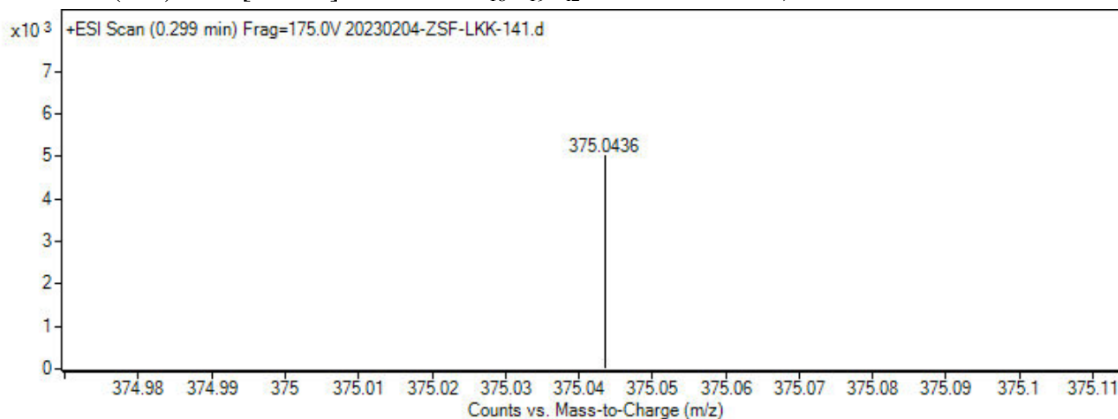
Colorless liquid, 23.5 mg, 83% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.42 (t, *J* = 6.7 Hz, 4H), 7.30 (t, *J* = 8.4 Hz, 6H), 3.86 (dq, *J* = 14.3, 6.8 Hz, 2H), 3.71 (dd, *J* = 14.7, 7.4 Hz, 1H), 2.20 (td, *J* = 12.6, 4.8 Hz, 1H), 2.09 – 1.92 (m, 2H), 1.90 – 1.79 (m, 2H), 1.72 – 1.62 (m, 1H), 1.56 (ddd, *J* = 18.7, 12.9, 5.3 Hz, 1H), 1.47 – 1.38 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) 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). ³¹P NMR (202 MHz, CDCl₃) δ -15.54. HRMS (ESI) *m/z*: [M + H]⁺ calcd for C₁₈H₂₂OP⁺ 285.1403; found 351.1503.



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



Colorless liquid, 28.7 mg, 81% yield. $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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). $^{31}\text{P NMR}$ (202 MHz, CDCl_3) δ -17.20. **HRMS** (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{19}\text{Cl}_2\text{NaOP}^+$ 375.0443; found 375.0436.

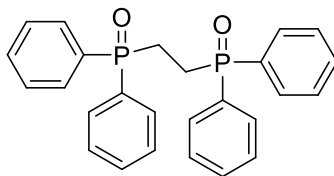


7. NMR spectra

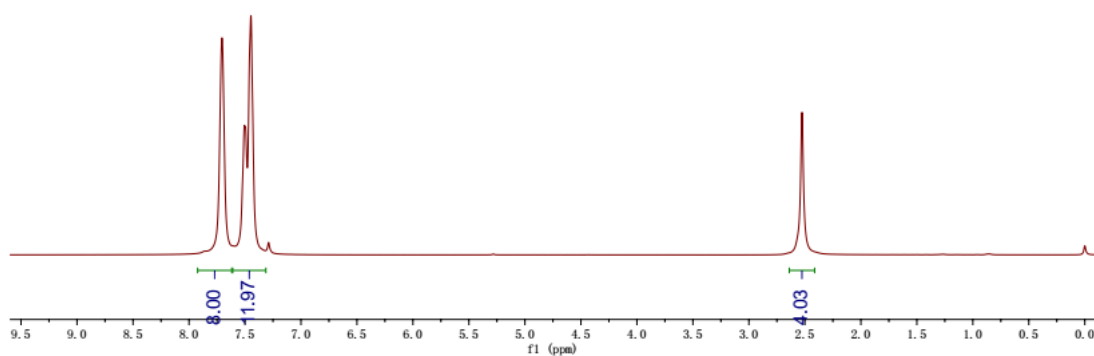
LKK-I-28A

7.71
7.50
7.45

-2.53



2a

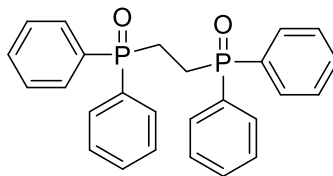


LKK-I-28A

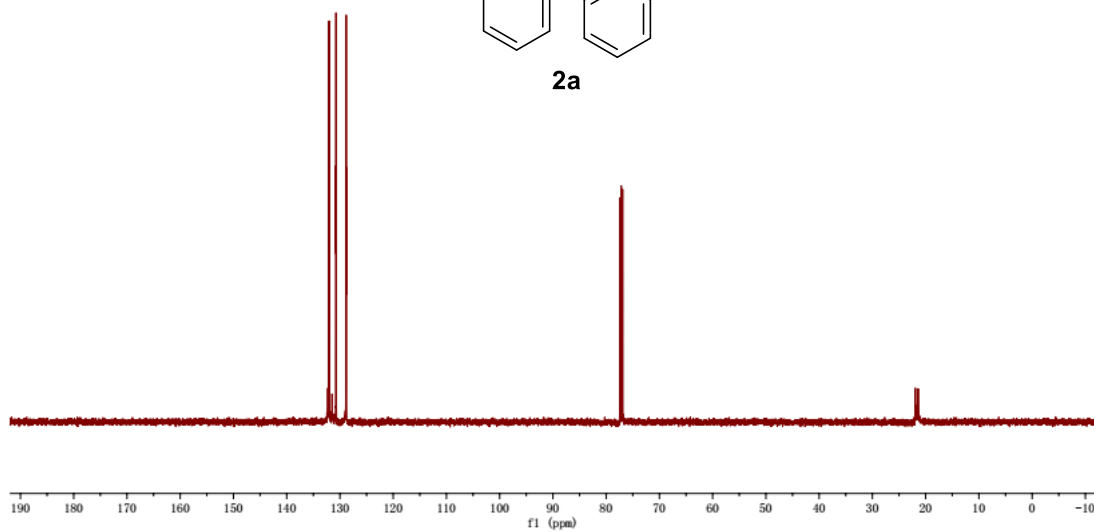
132.28
132.05
131.49
130.78
130.74
130.71
128.87
128.82
128.78

77.42
77.17
76.91

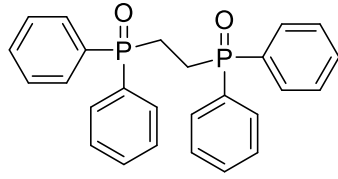
21.93
21.67
21.41



2a

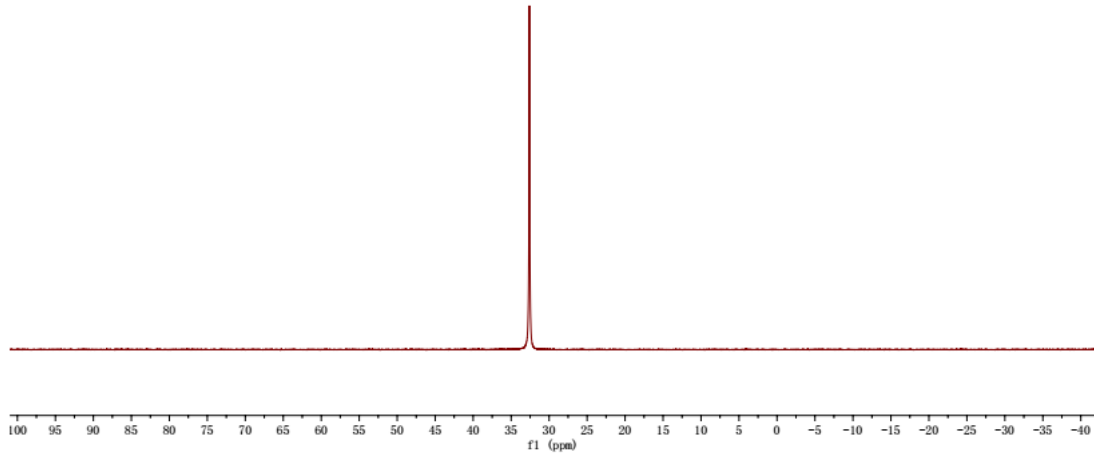


LKK-I-28A



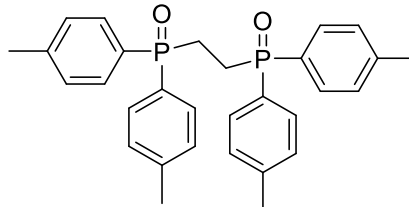
2a

-32.60



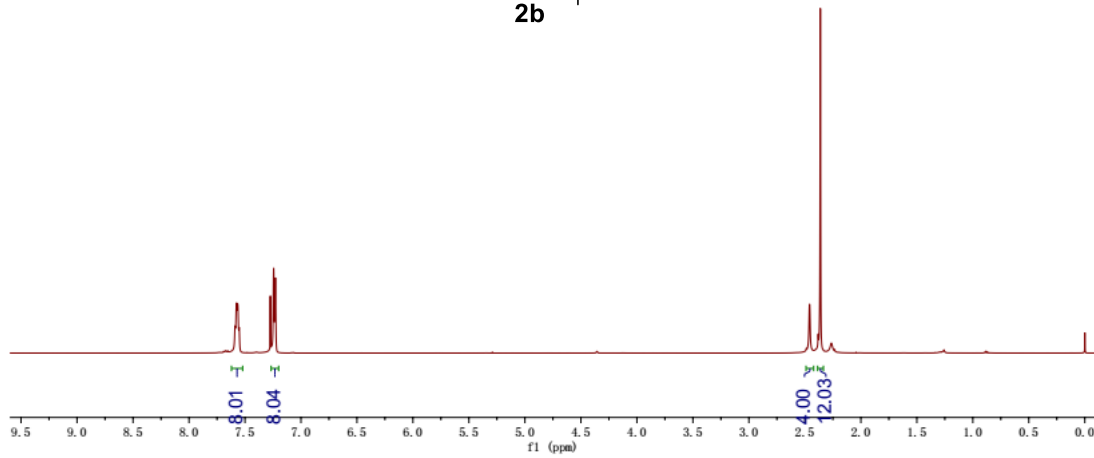
LKK-I-34A

7.59
7.57
7.55
7.24
7.23

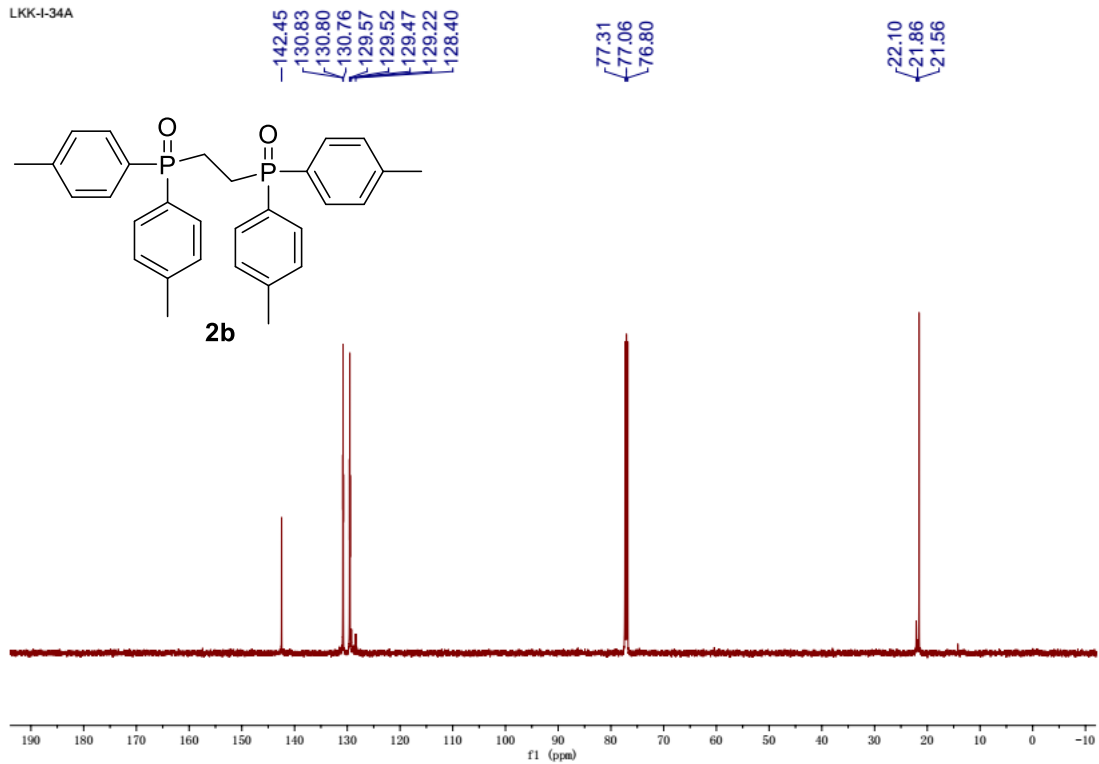


2b

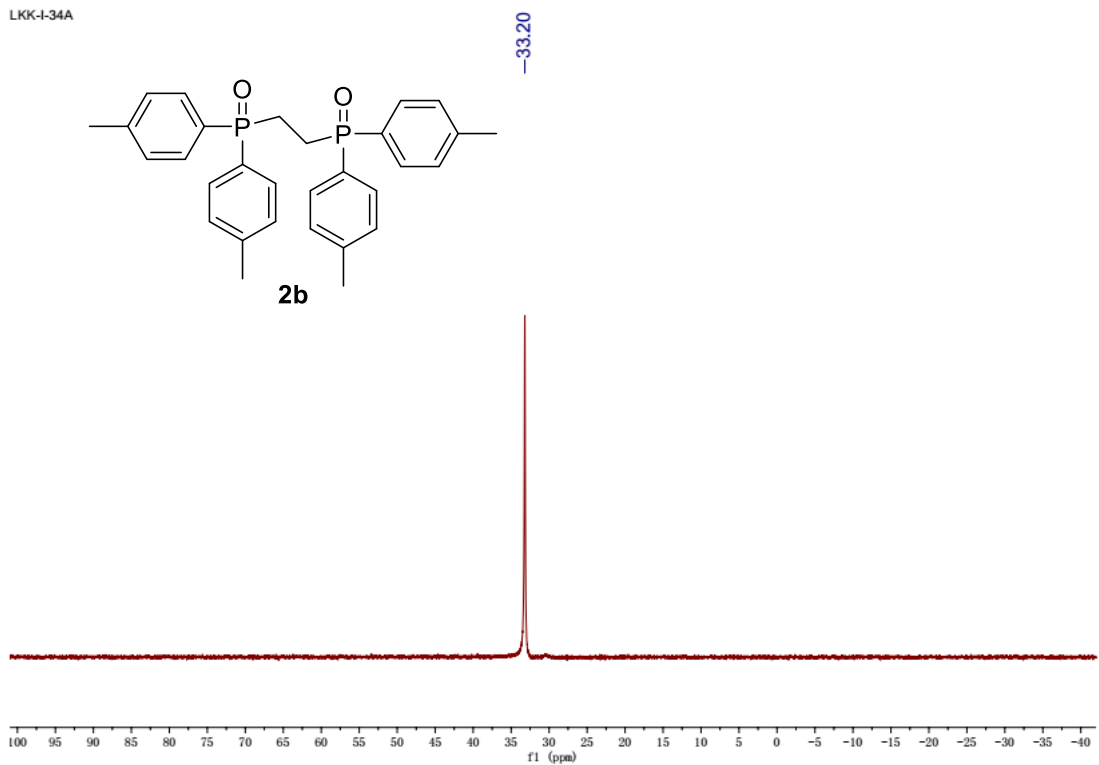
2.46
2.36

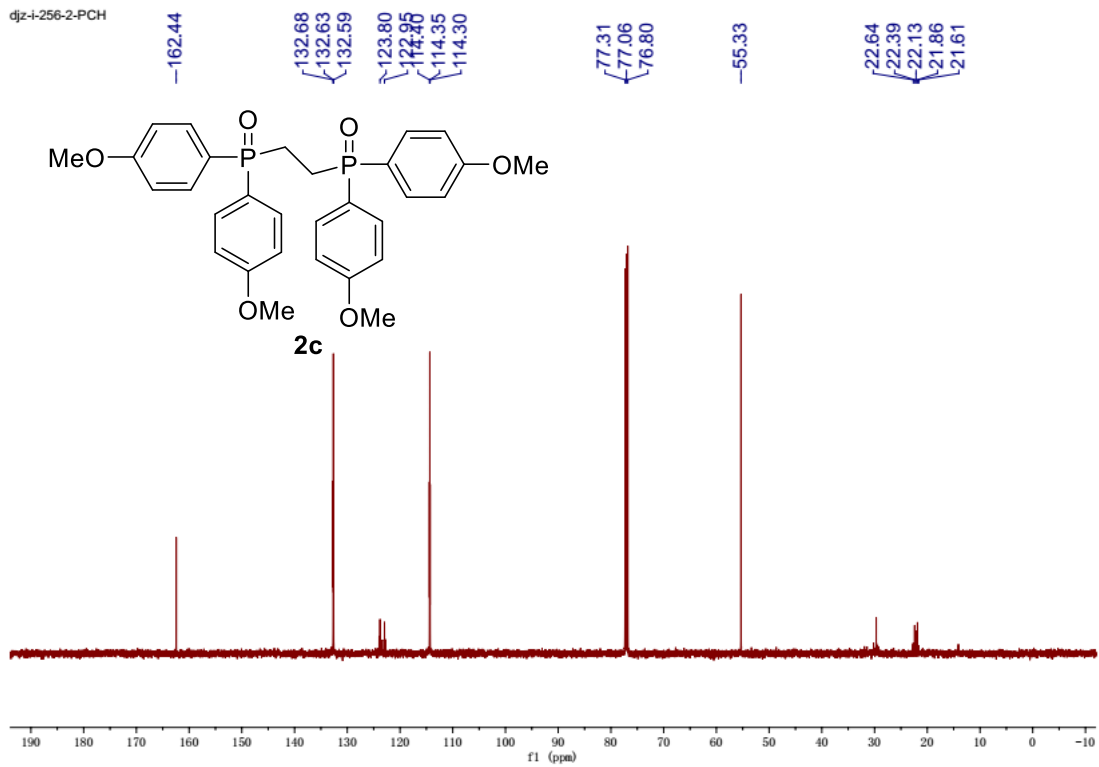
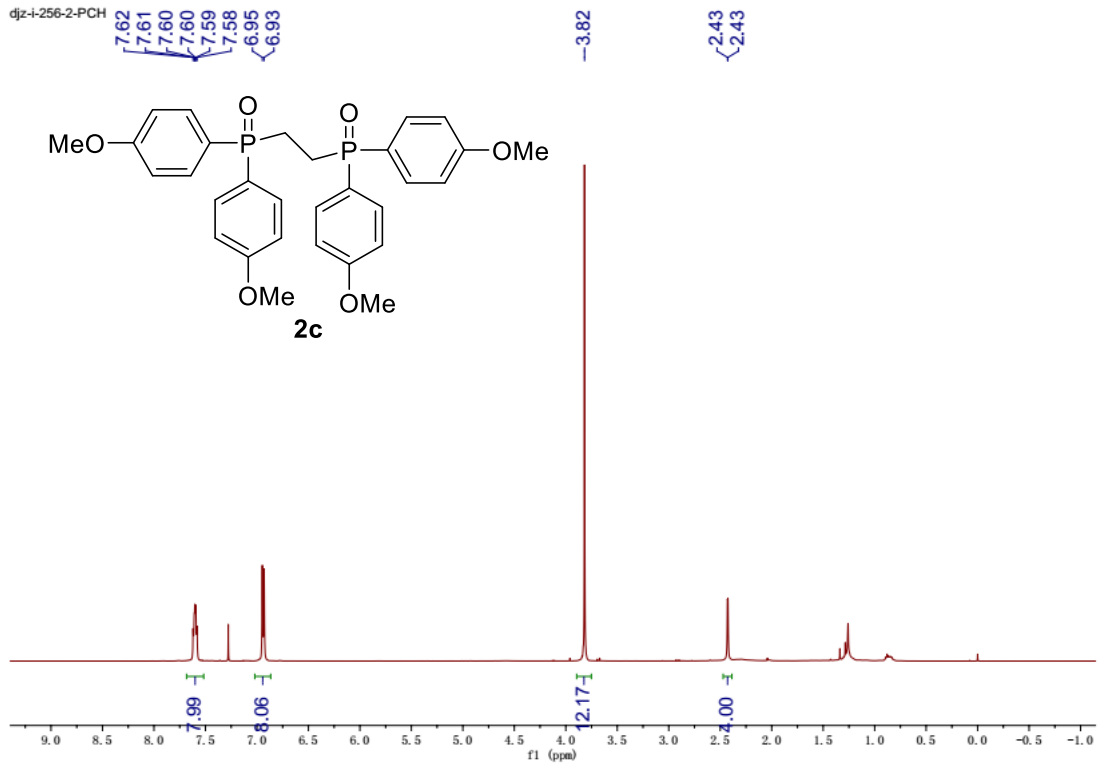


LKK-I-34A

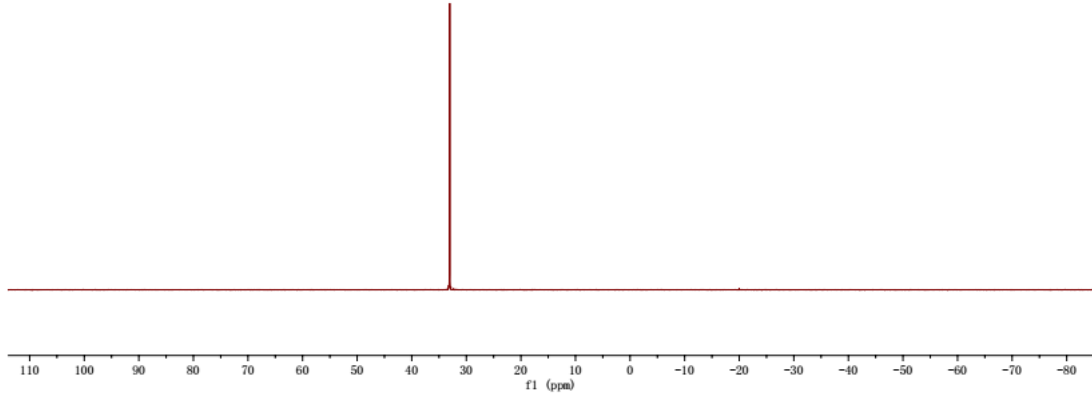
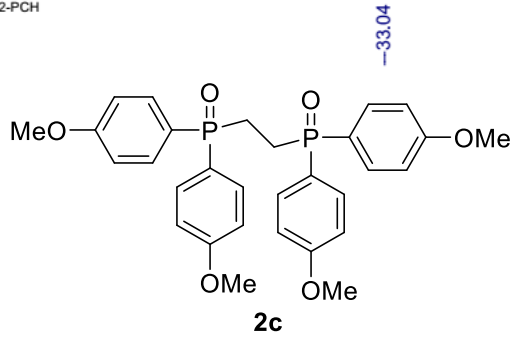


LKK-I-34A



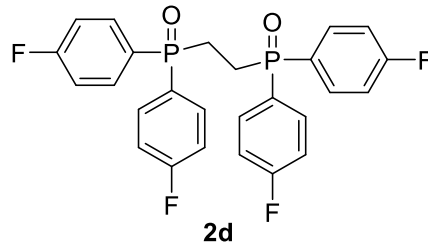


djz-4-256-2-PCH

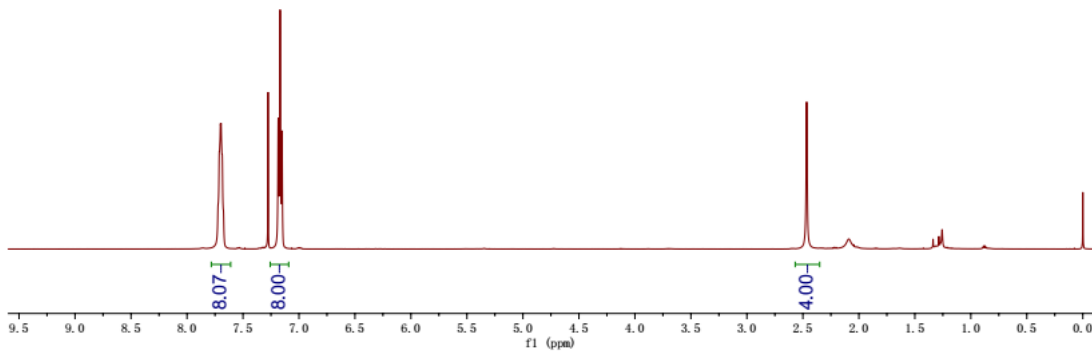


LKK-I-36A

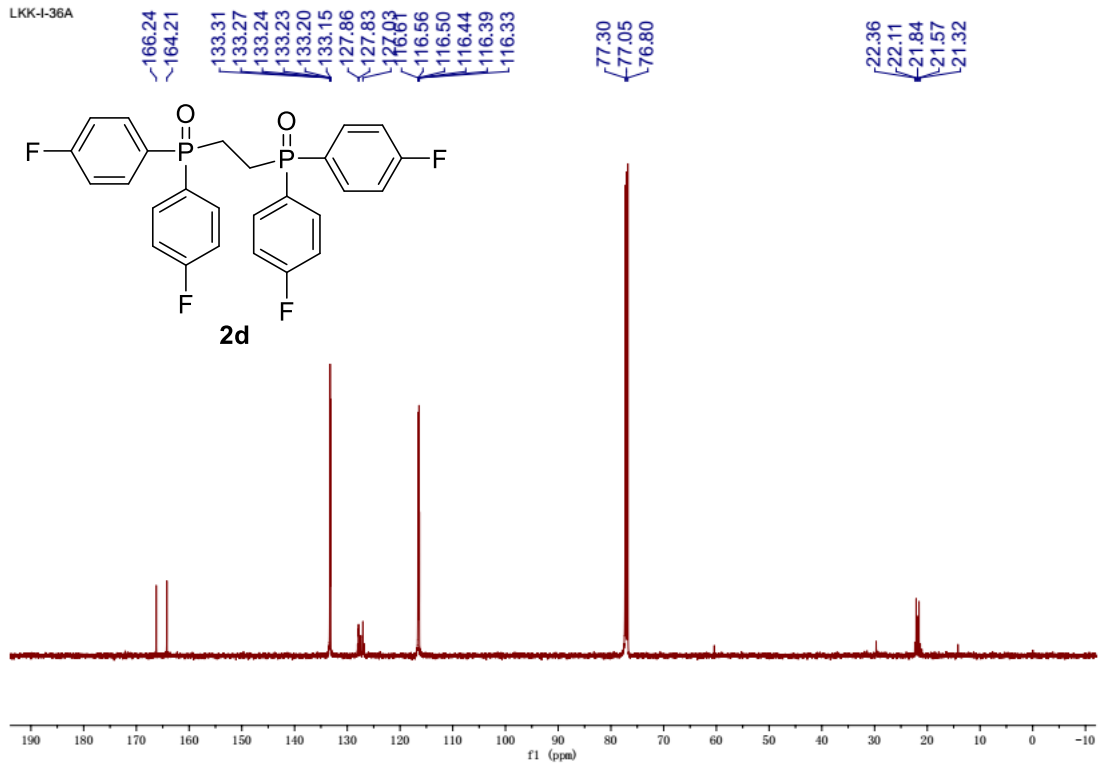
7.70
7.69
7.19
7.17
7.15



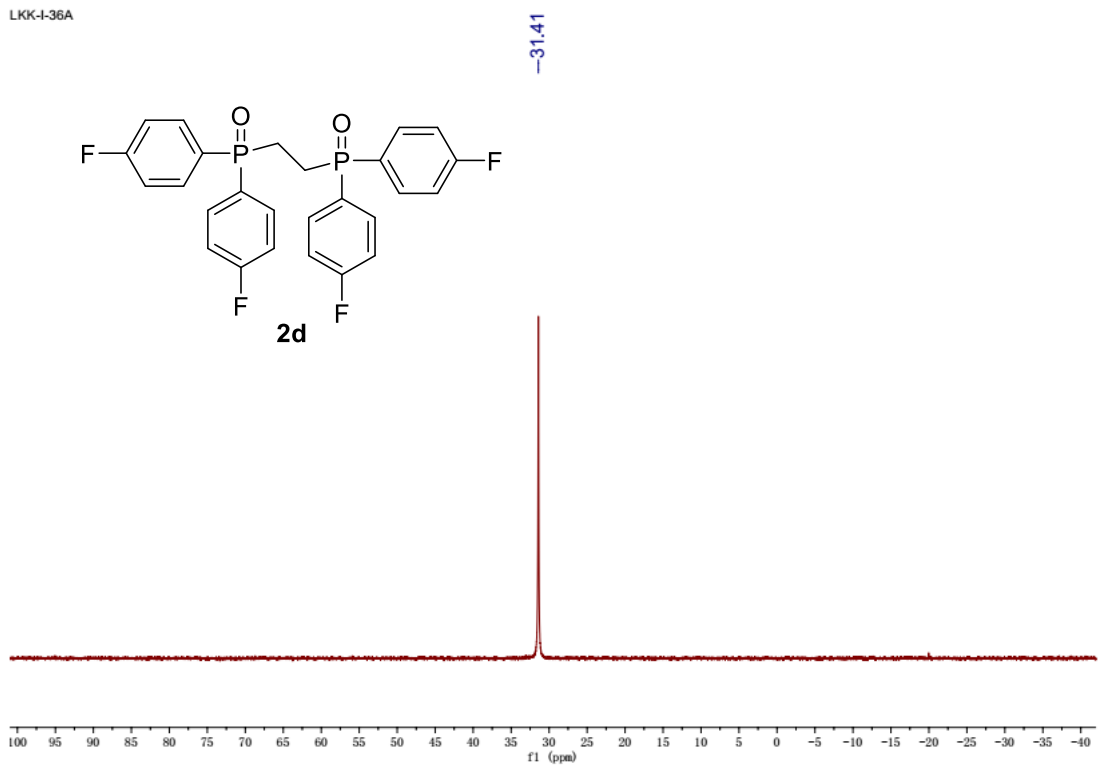
-2.47



LKK-I-36A

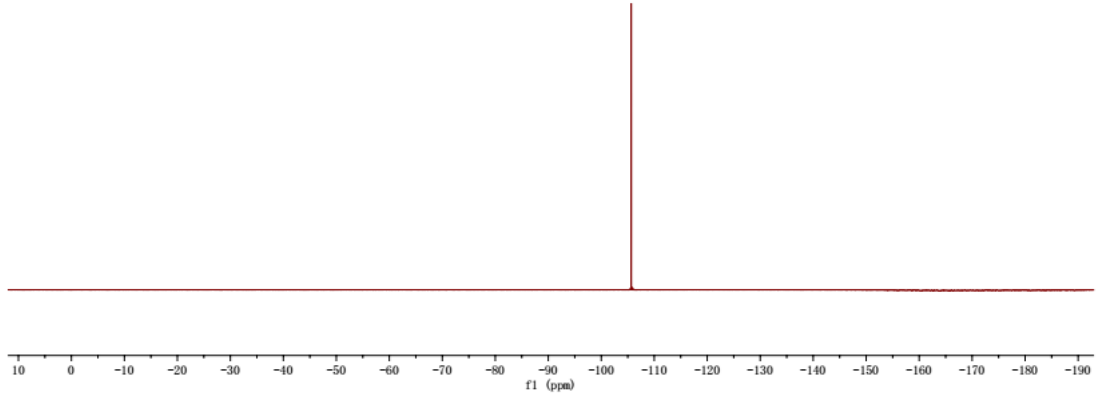
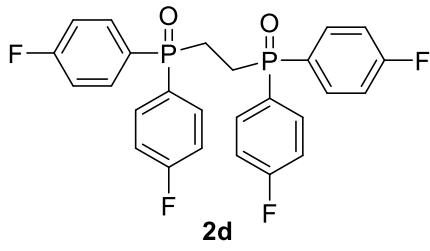


LKK-I-36A



LKK-I-42A

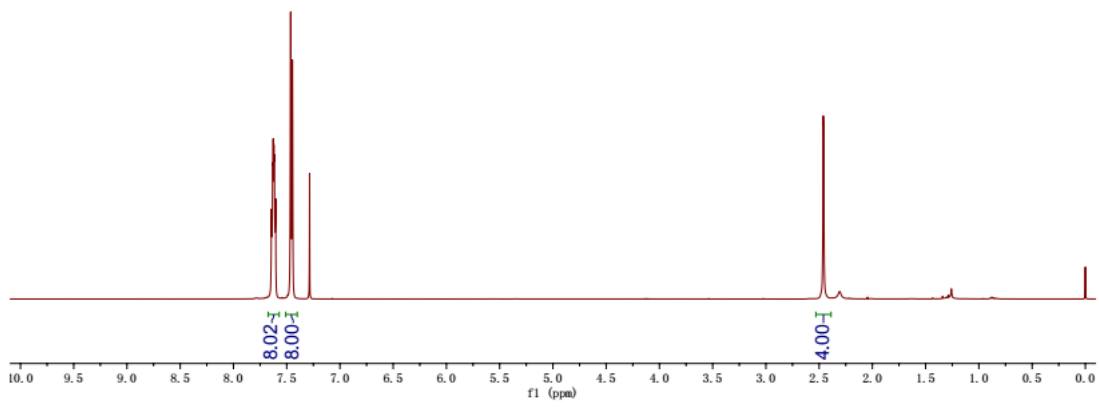
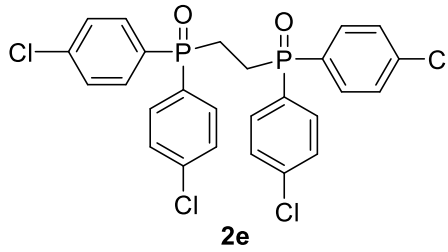
--105.64



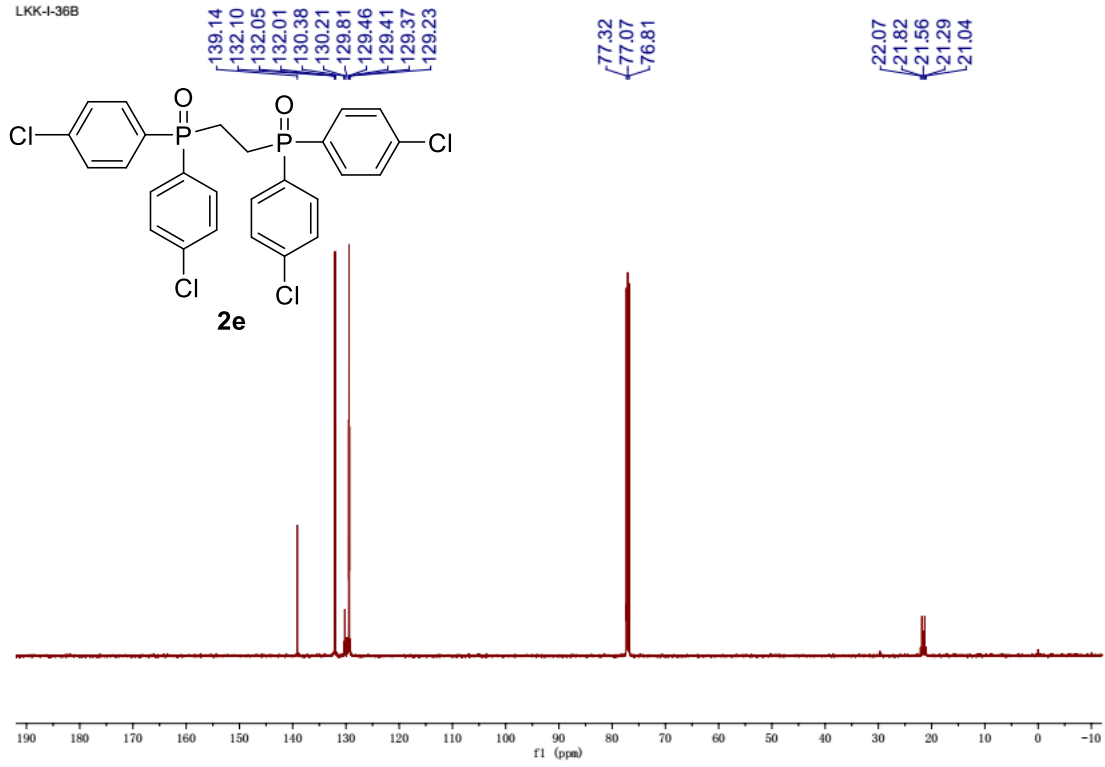
LKK-I-36B

7.64
7.63
7.63
7.62
7.60
7.46
7.45

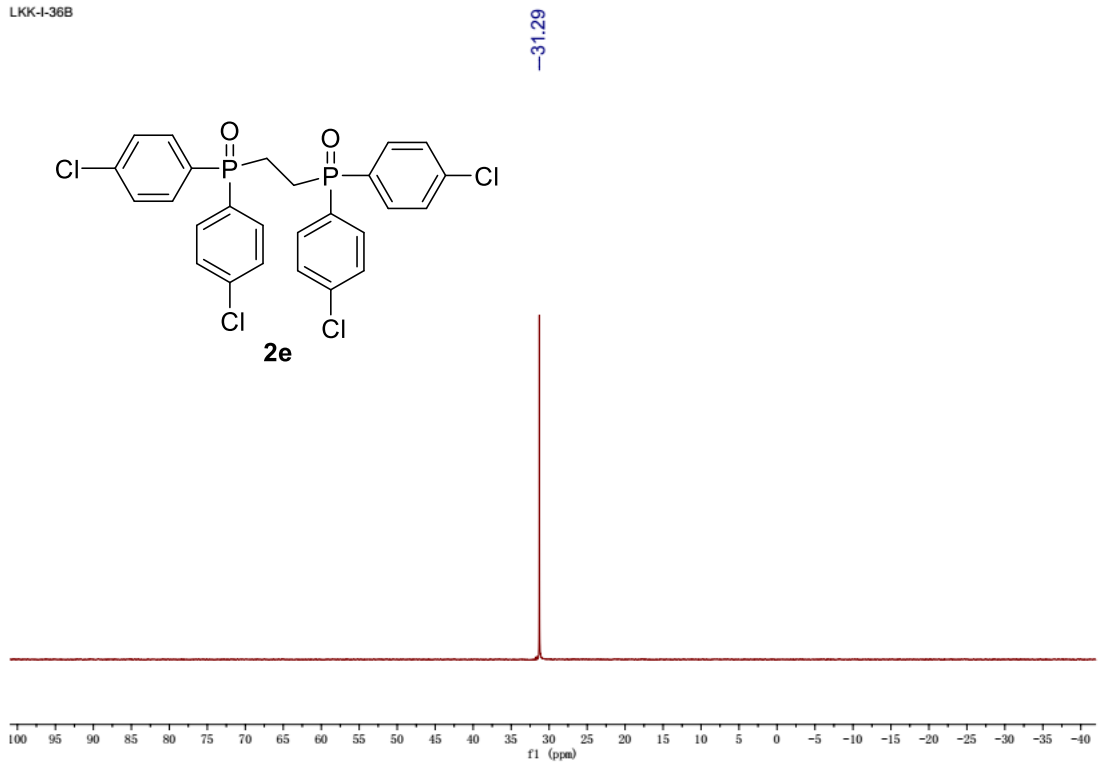
--2.46



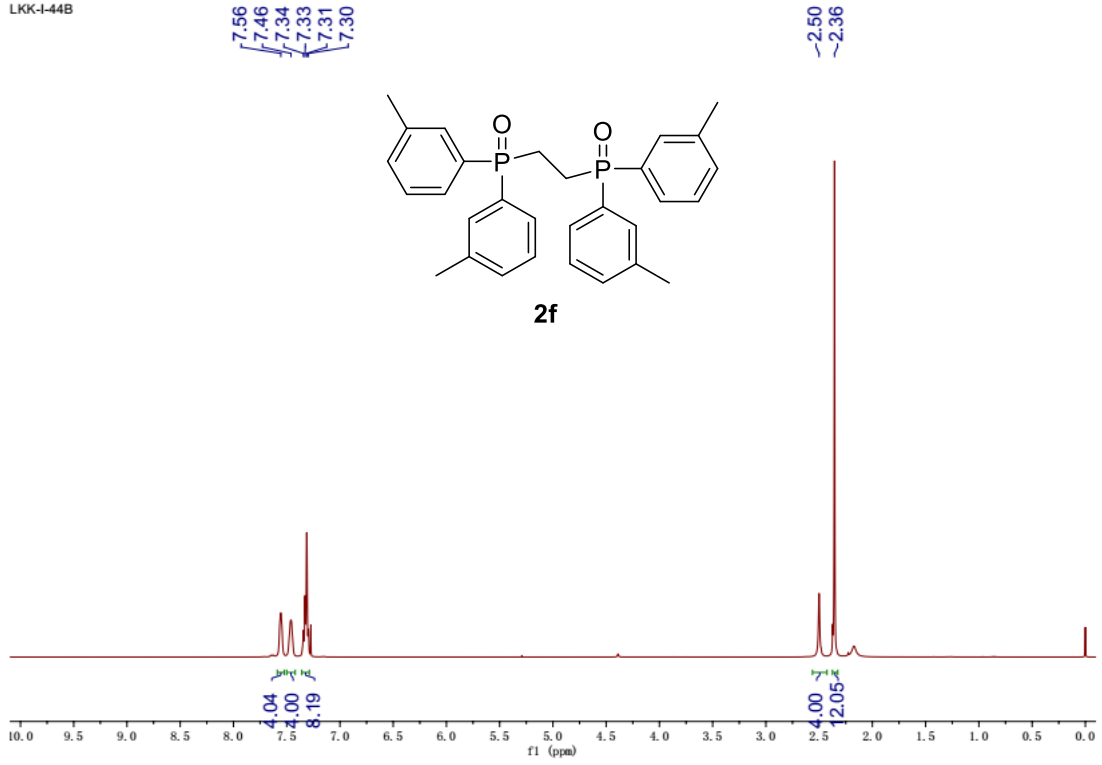
LKK-I-36B



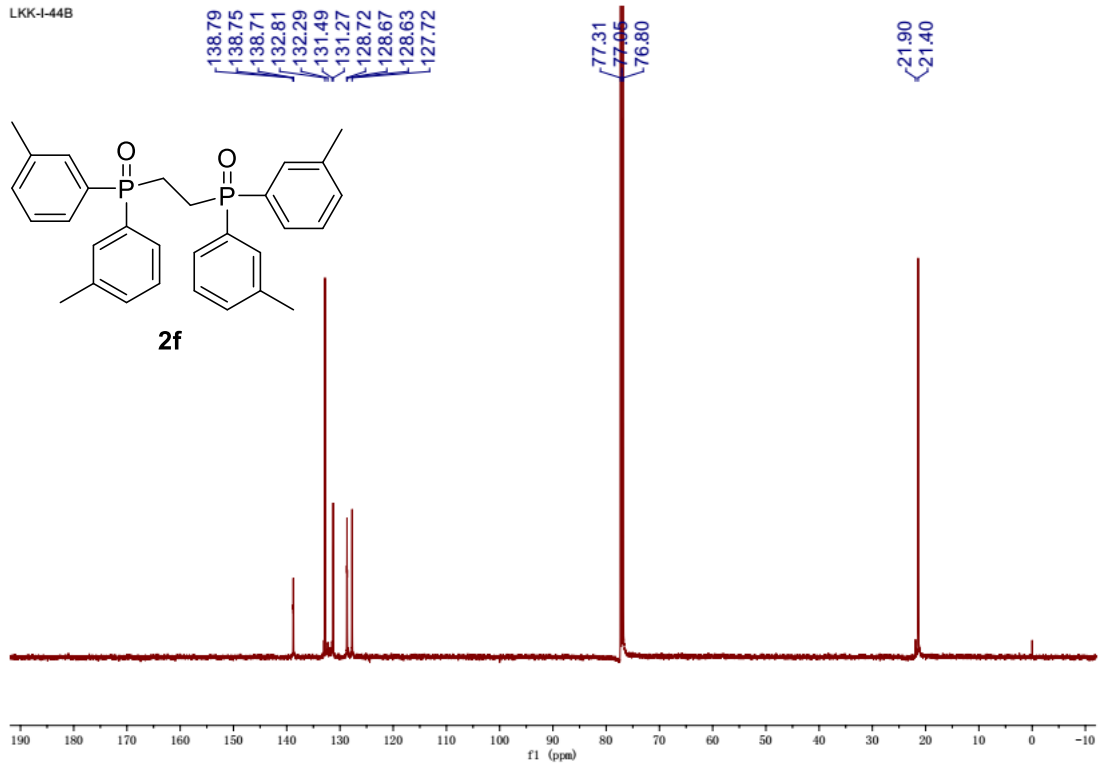
LKK-I-36B



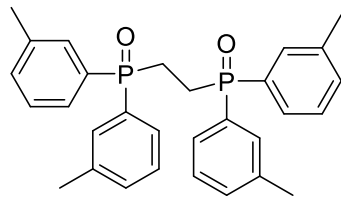
LKK-I-44B



LKK-I-44B

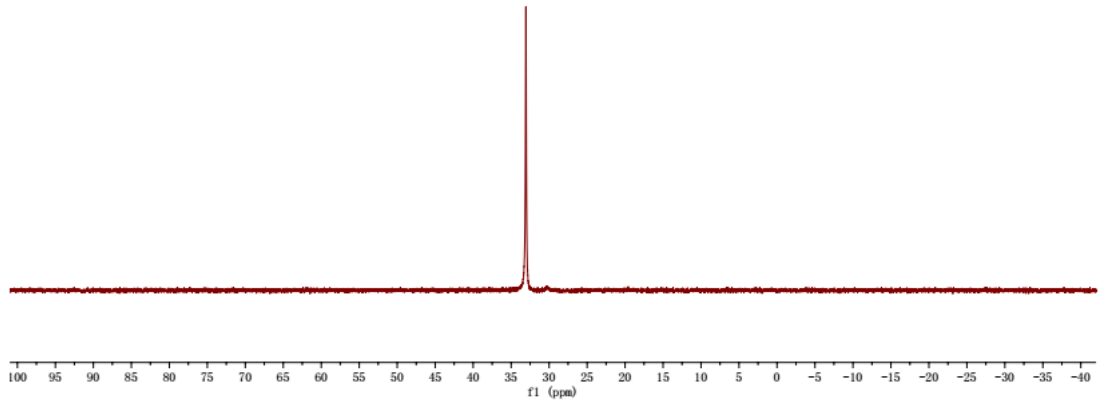


LKK-I-44B



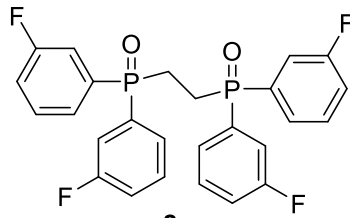
2f

-33.06



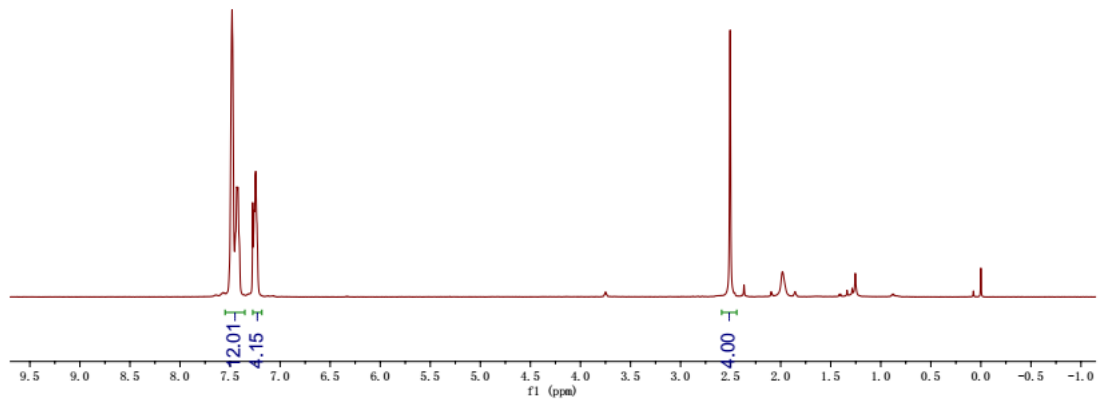
djz-i-187-1-PCH

7.48
7.43
7.43
7.42
7.26
7.24

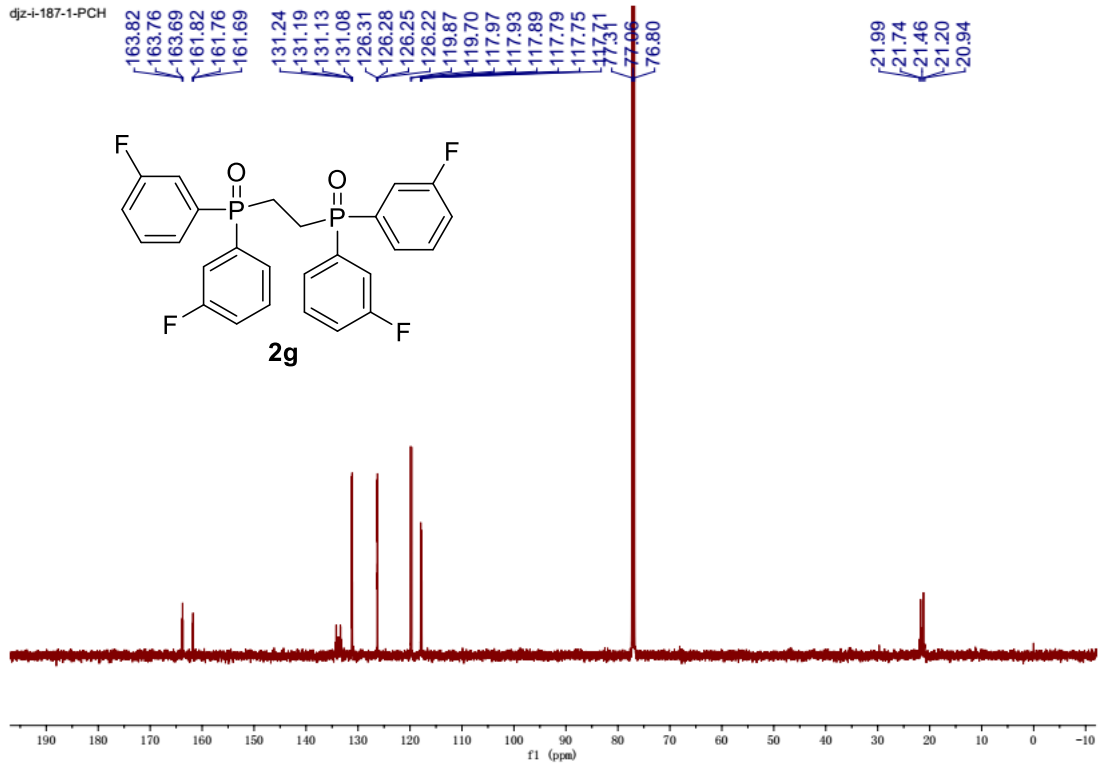


2g

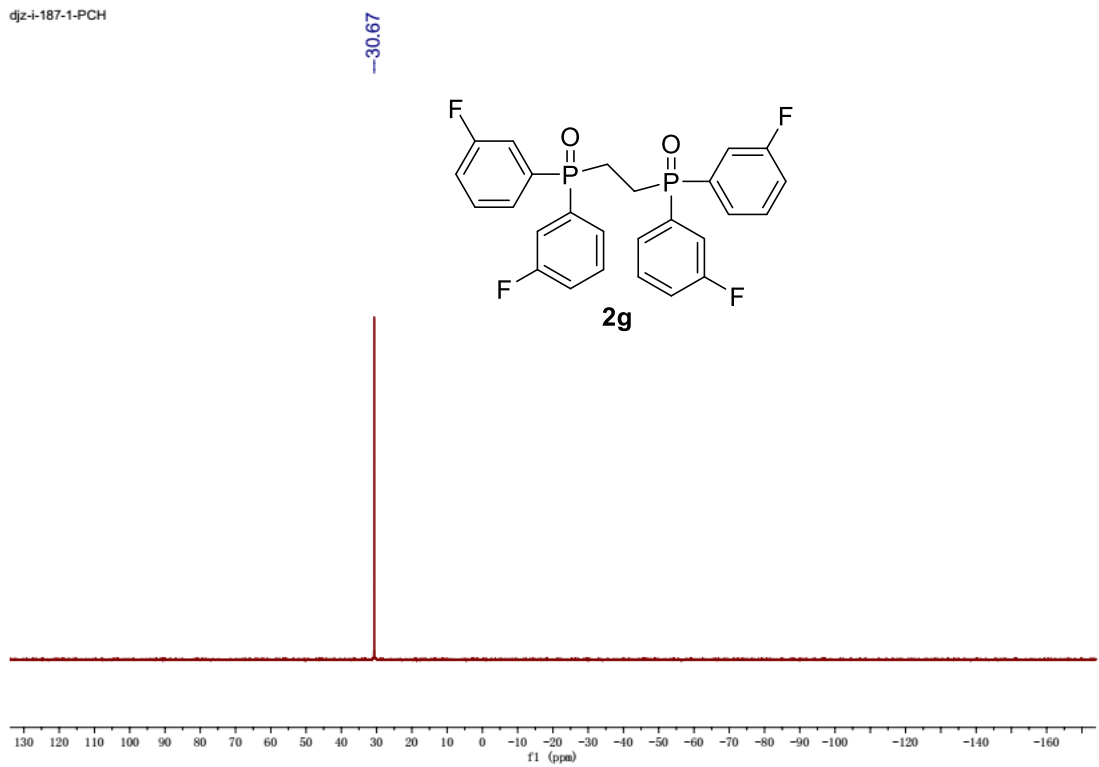
-2.51



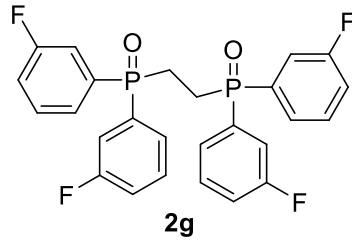
djz-i-187-1-PCH



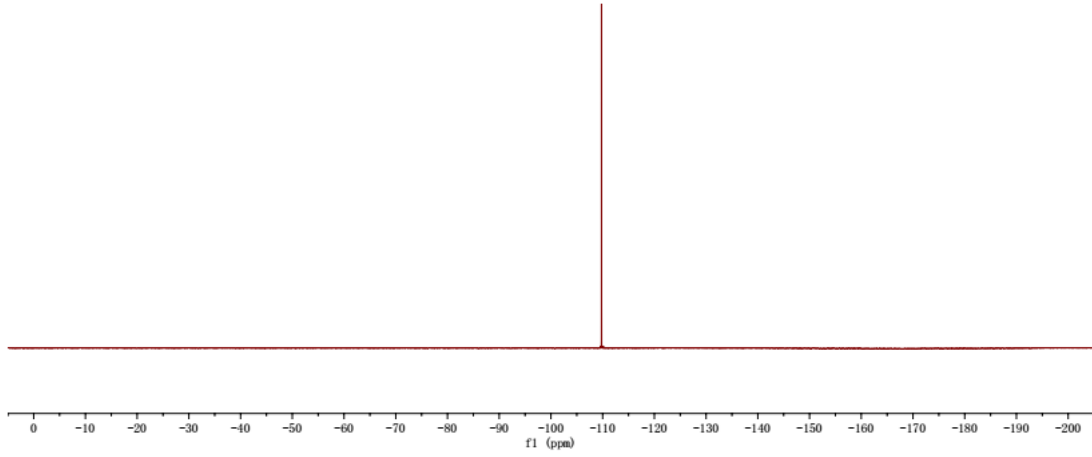
djz-i-187-1-PCH



djz-187-1-PCH



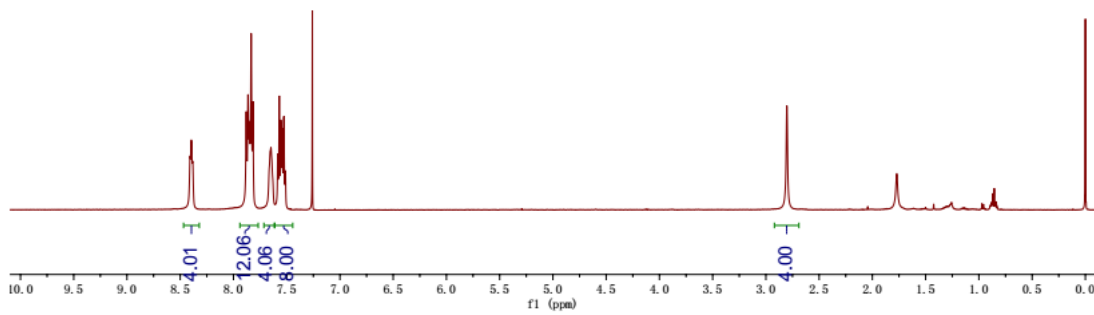
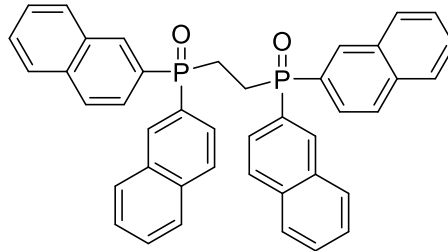
-109.79



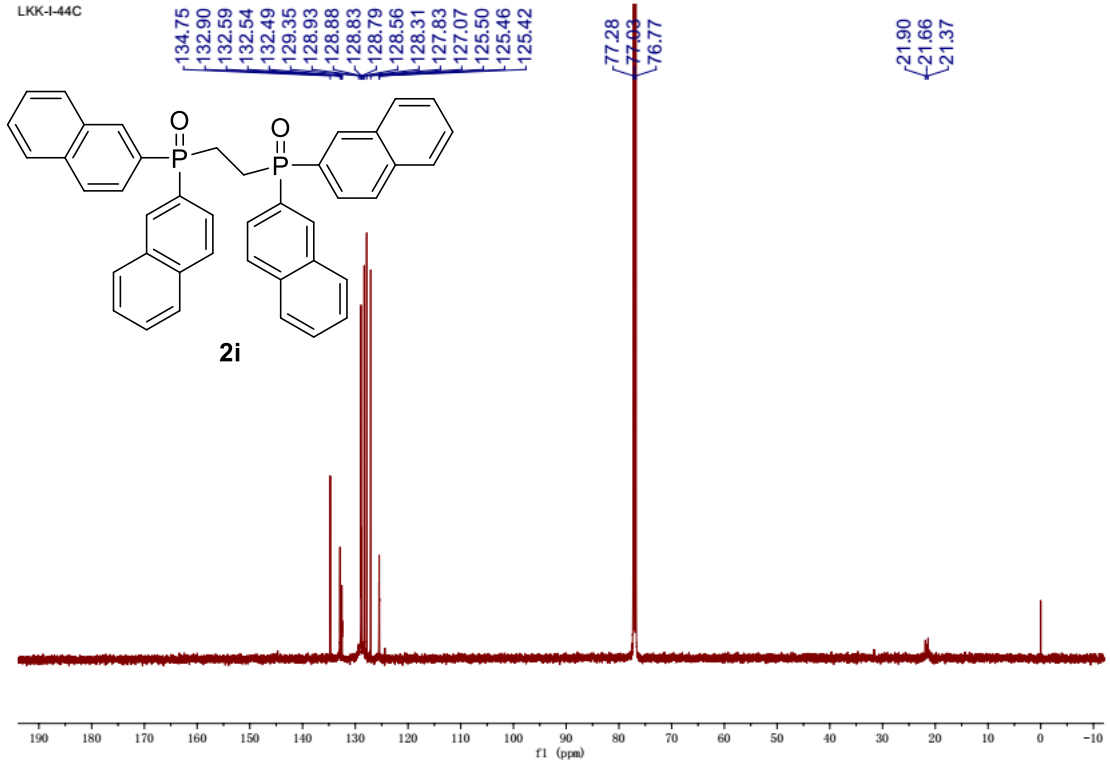
LKK-I-44C

8.41
8.40
8.38
7.86
7.85
7.83
7.82
7.65
7.57
7.55
7.54
7.53
7.51

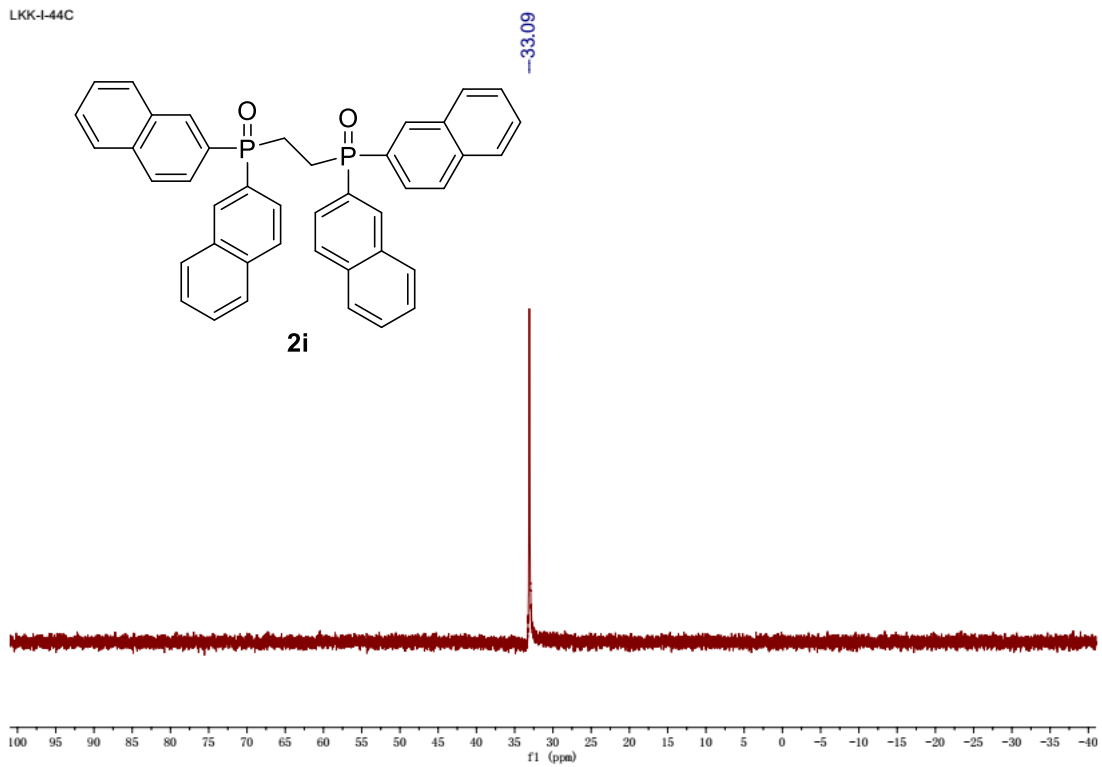
-2.80



LKK-I-44C



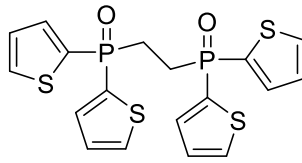
LKK-I-44C



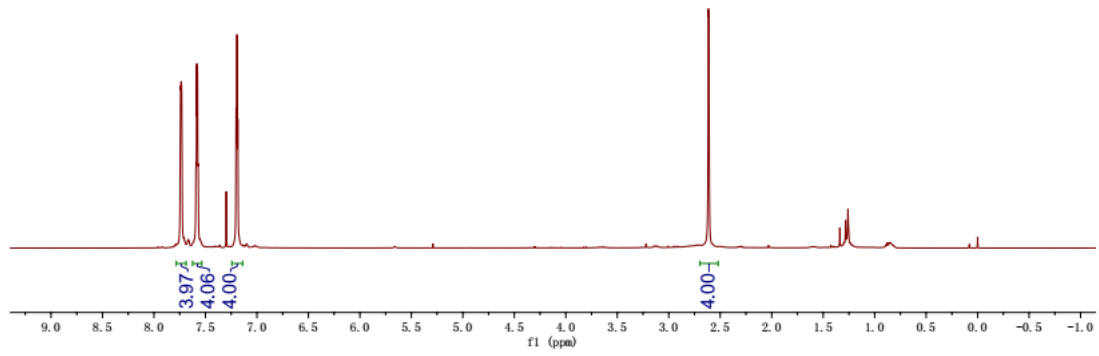
DJZ-I-263-1-PC

7.74
7.74
7.73
7.59
7.58
7.58
7.57
7.20
7.19
7.19

2.61
2.61



2j

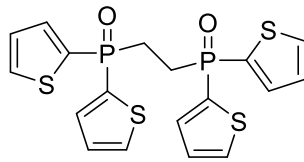


djz-i-265-1-p3

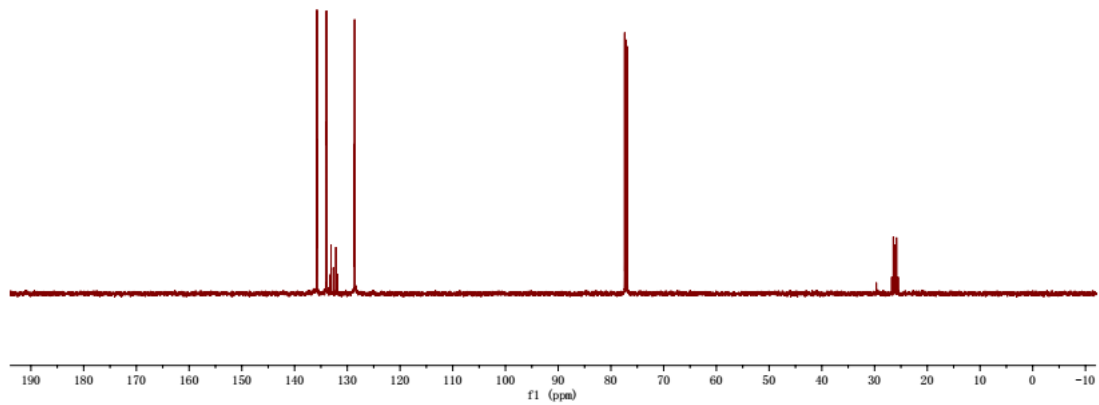
135.80
135.75
135.71
133.95
133.94
133.29
133.08
132.61
132.16
131.94
128.67
128.61
128.56

77.39
77.13
76.88

26.73
26.43
26.14
25.84
25.54

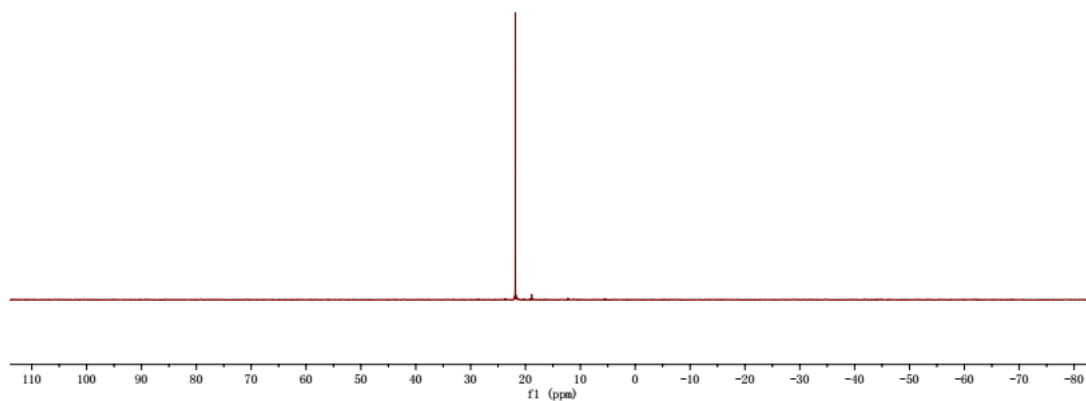
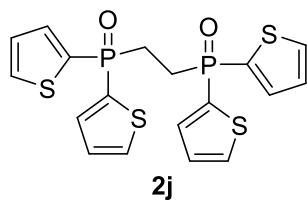


2j



djz-i-265-1-p3

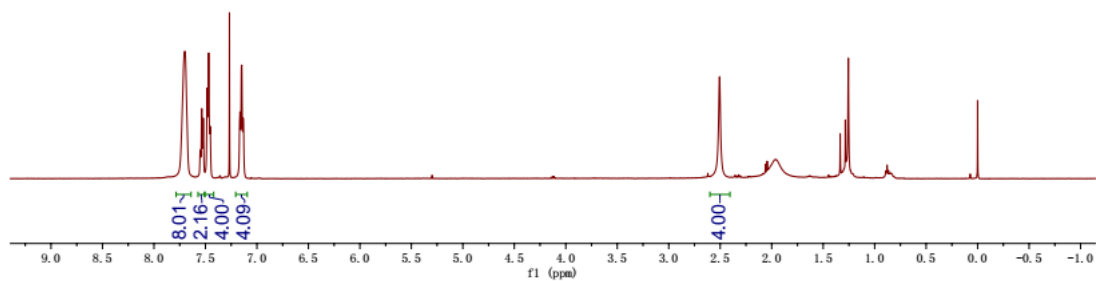
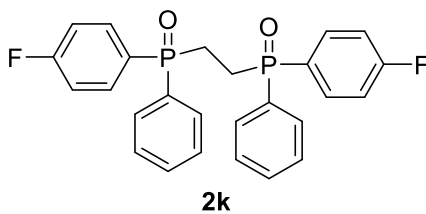
-21.85



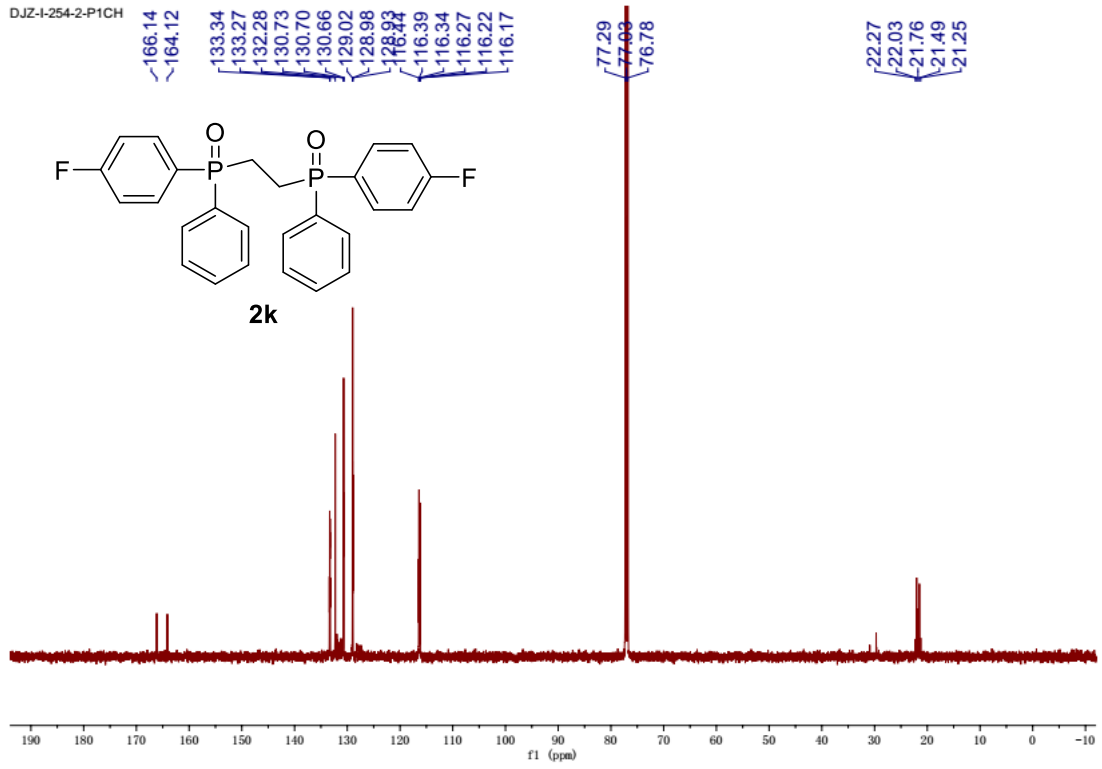
djz-i-254-2-pch

7.70
7.55
7.54
7.52
7.48
7.47
7.45
7.16
7.15
7.13

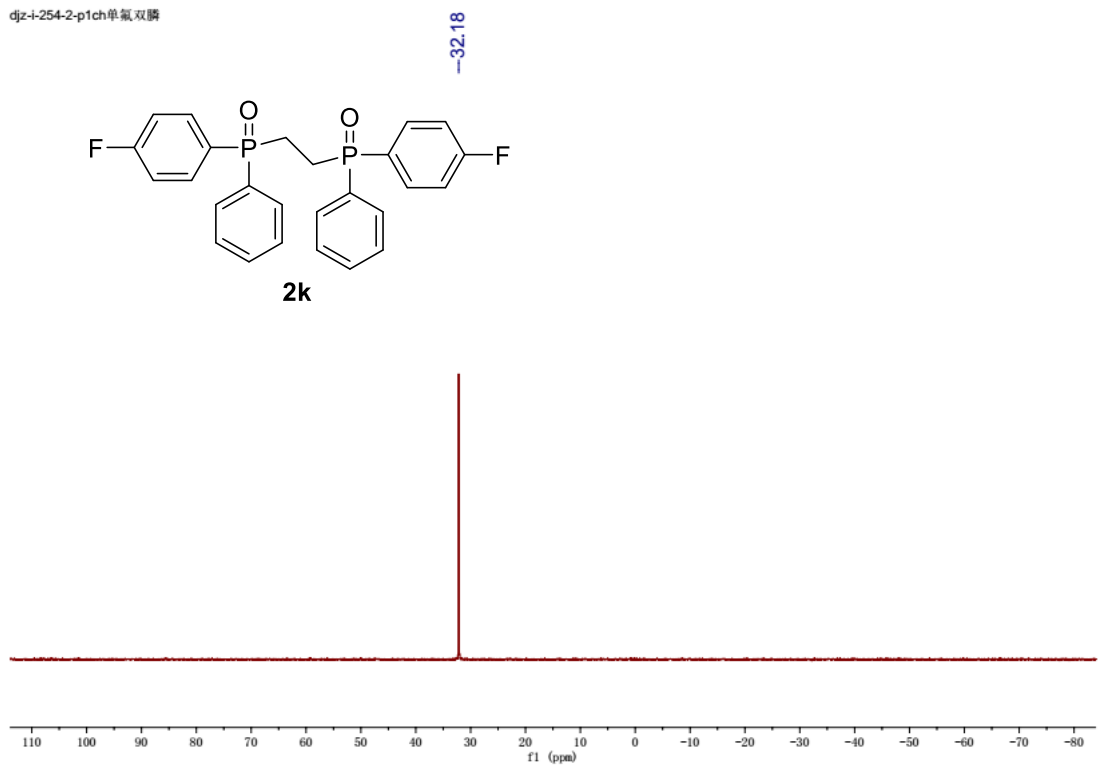
-2.51



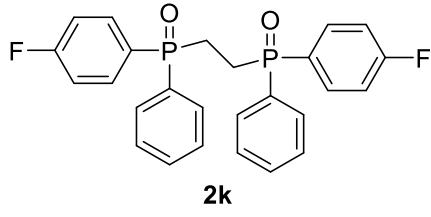
DJZ-I-254-2-P1CH



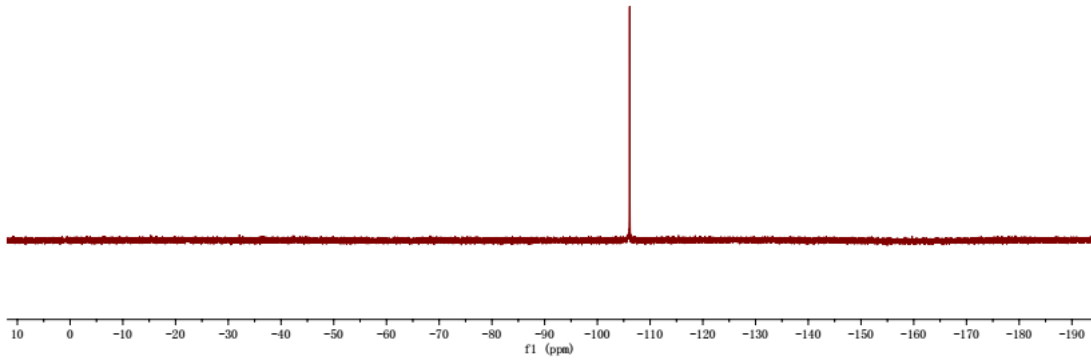
djz-i-254-2-p1ch单氟双膦



LKK-I-51B

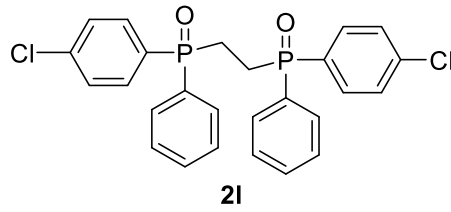


--106.13

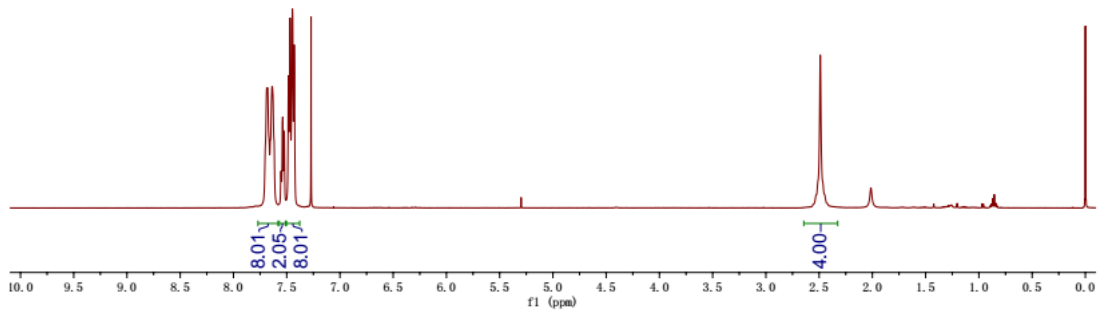


LKK-I-52B

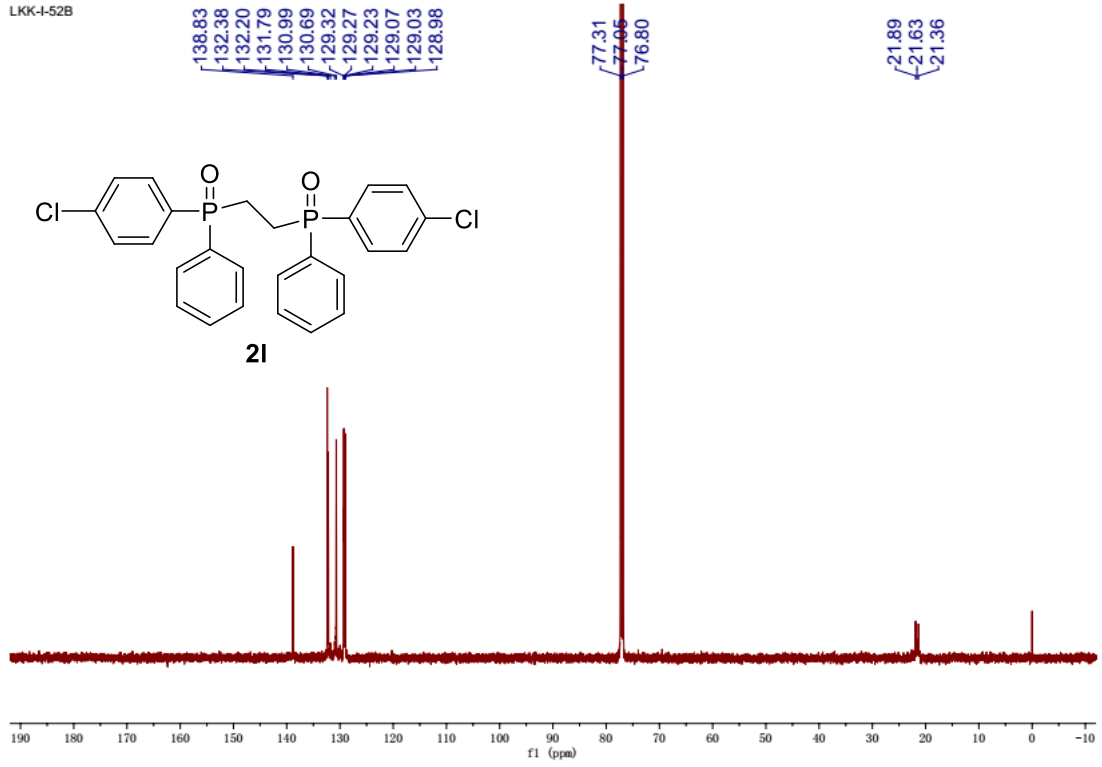
7.69
7.68
7.64
7.55
7.54
7.52
7.48
7.47
7.45
7.43



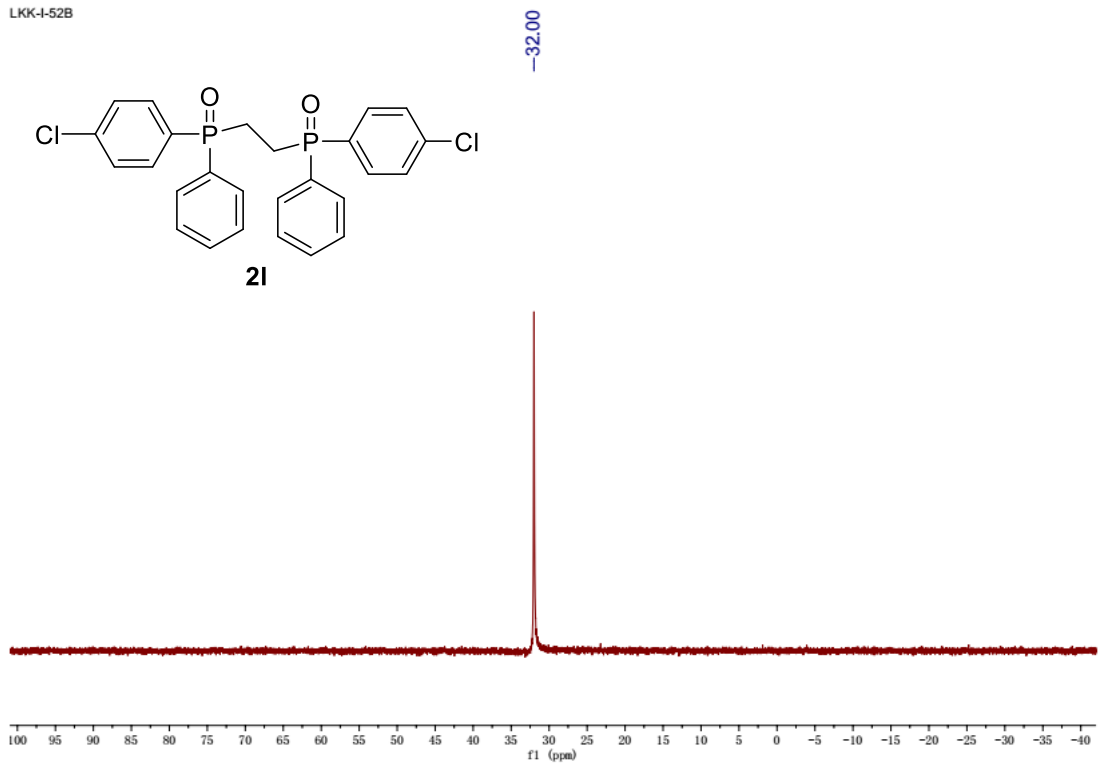
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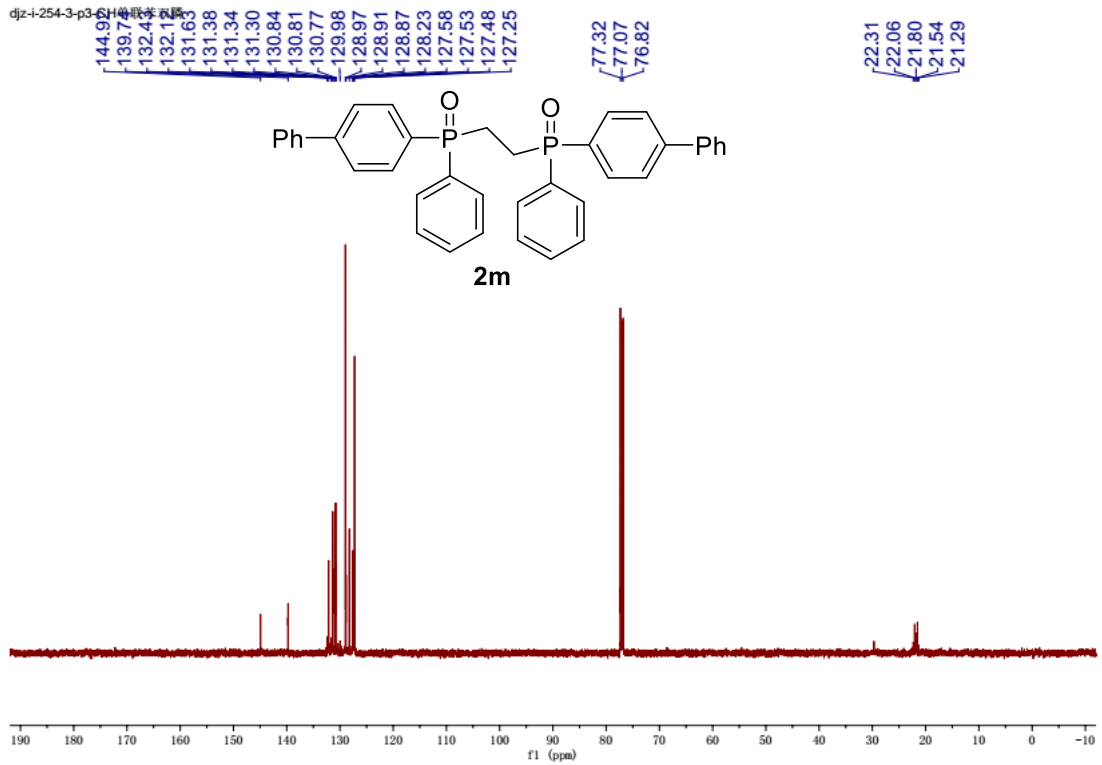
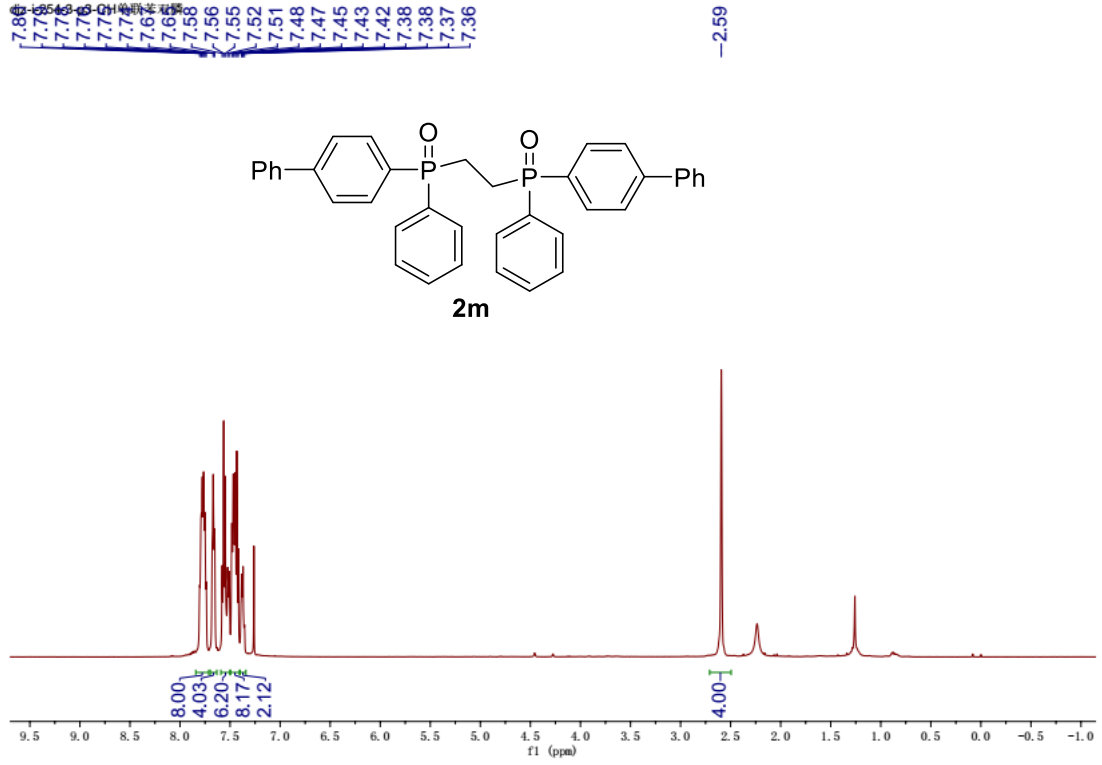


LKK-I-52B

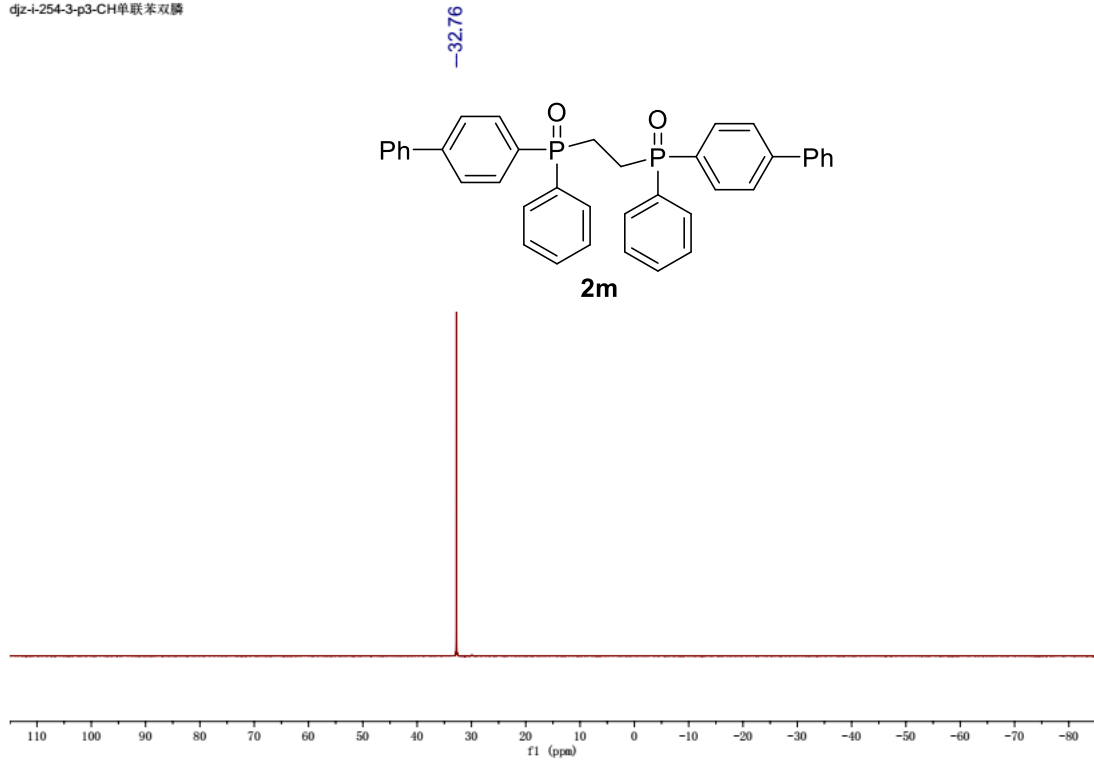


LKK-I-52B

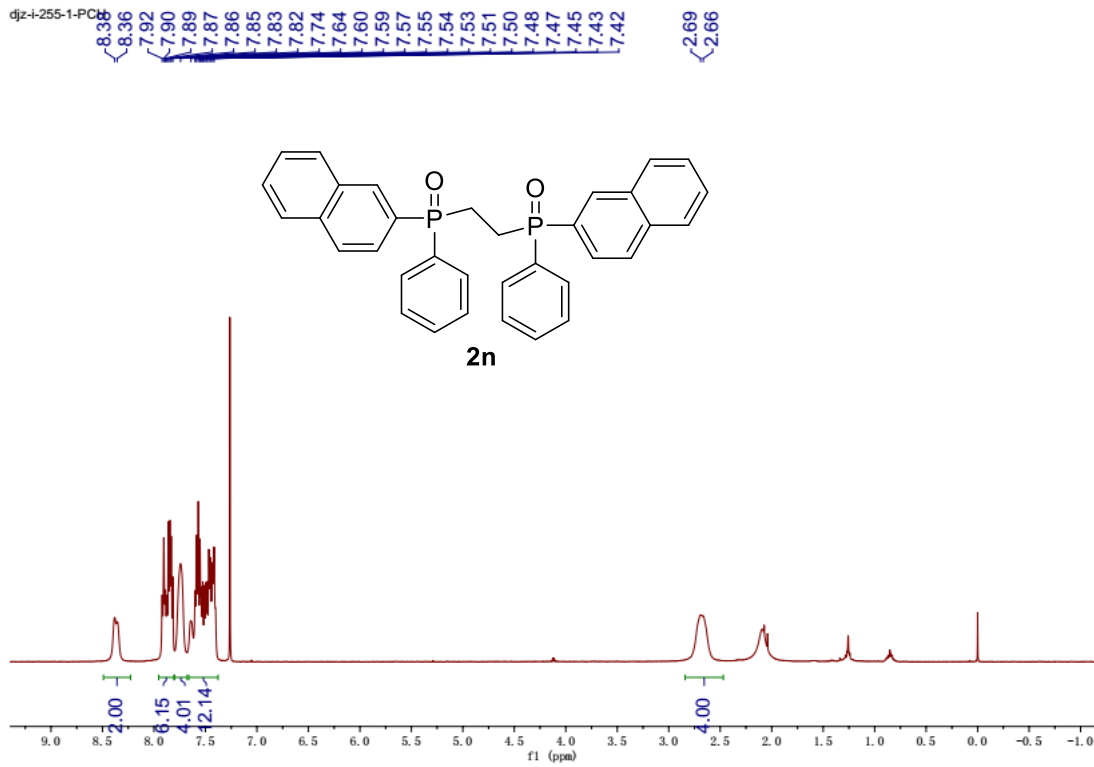


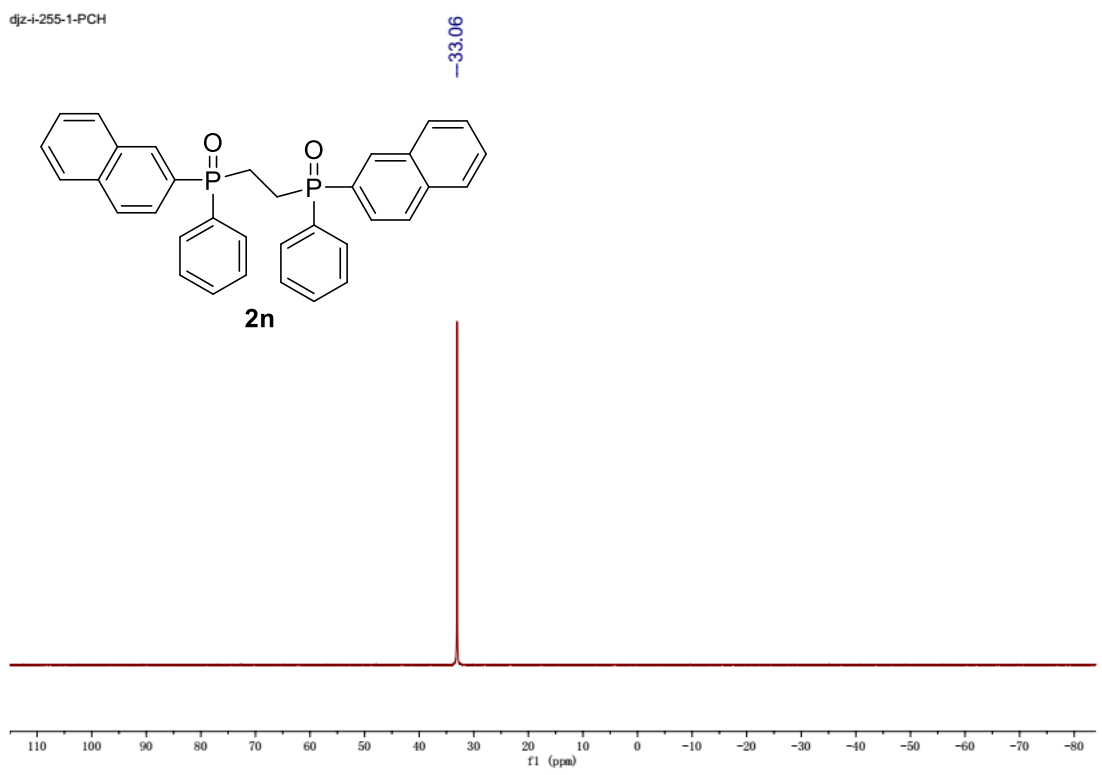
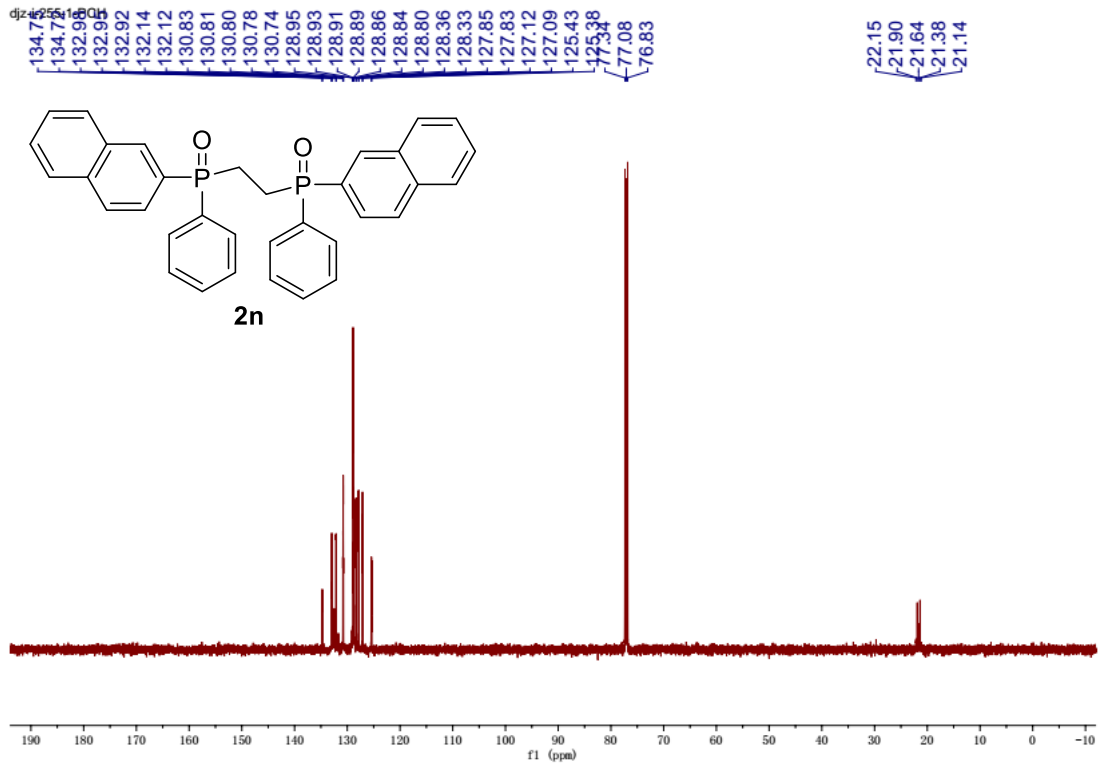


djz-i-254-3-p3-CH单联苯双膦

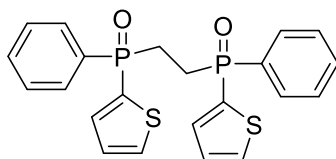


djz-i-255-1-PC

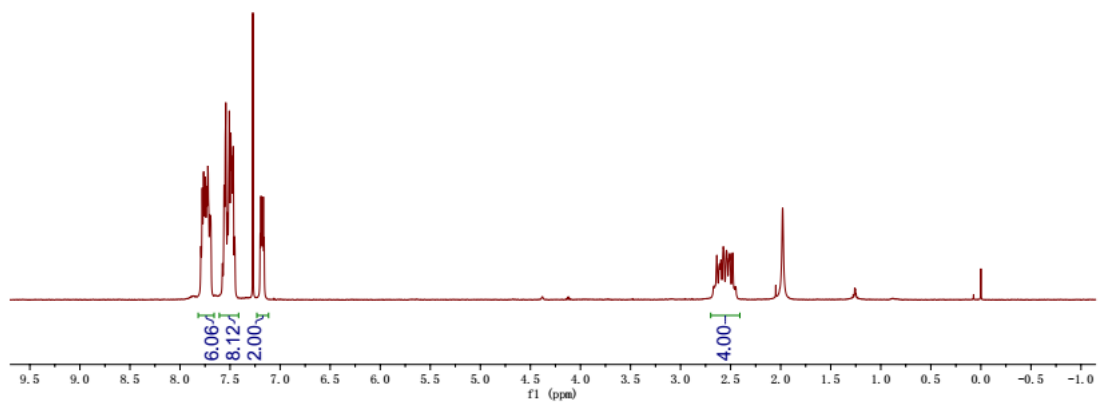




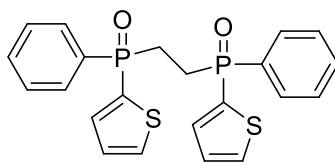
7.78
7.78
7.77
7.77
7.72
7.70
7.69
7.58
7.56
7.54
7.53
7.51
7.49
7.48
7.47
7.45
7.20
7.19
7.18
7.17
7.16
2.67
2.64
2.61
2.60
2.57
2.54
2.52
2.48
2.46
2.45



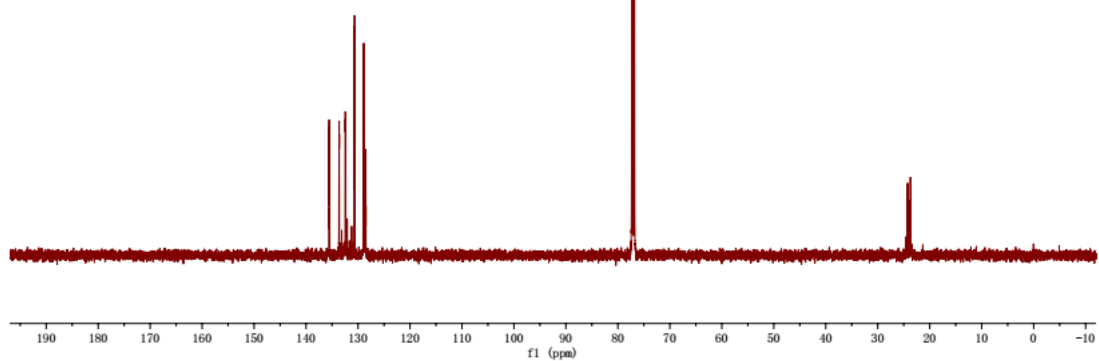
2o



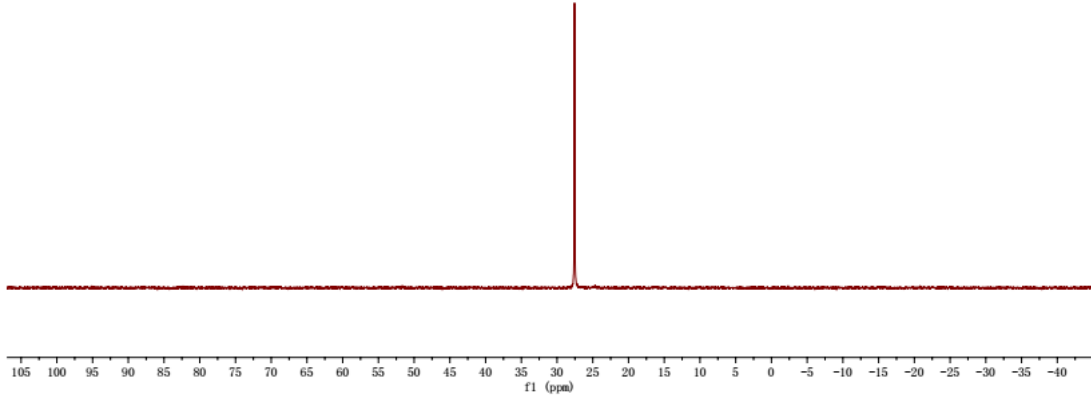
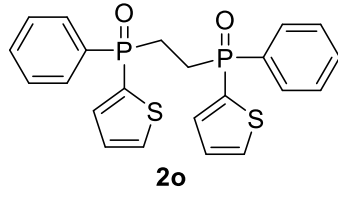
135.61
135.56
135.54
135.49
133.63
133.62
133.14
132.44
132.41
132.28
132.08
131.23
130.74
130.70
130.66
130.63
128.97
128.92
128.89
128.84
128.61
128.59
128.56
128.54
128.51
128.48
77.32
77.07
76.81
24.54
24.26
23.99
23.71
23.43



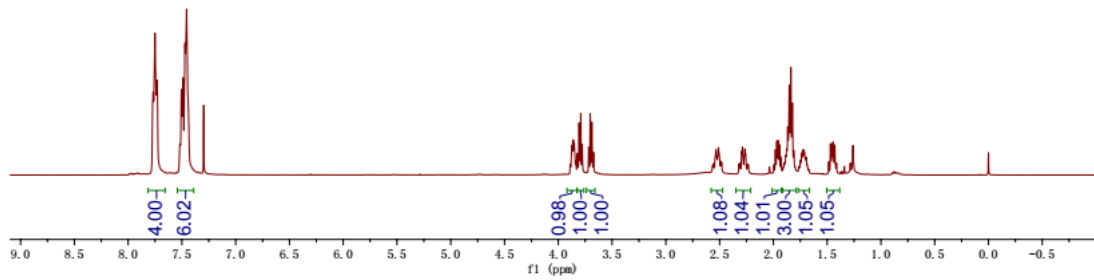
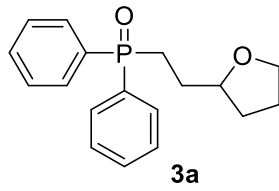
2o



-27.56



LKK-188-2
7.71
7.70
7.70
7.73
7.52
7.50
7.49
7.47
7.46
3.87
3.87
3.86
3.85
3.82
3.81
3.79
3.78
3.72
3.70
3.69
3.67
2.53
2.51
2.29
2.27
2.26
1.98
1.97
1.95
1.94
1.93
1.89
1.88
1.87
1.85
1.84
1.82
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1.73
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1.47
1.46
1.45
1.44
1.43

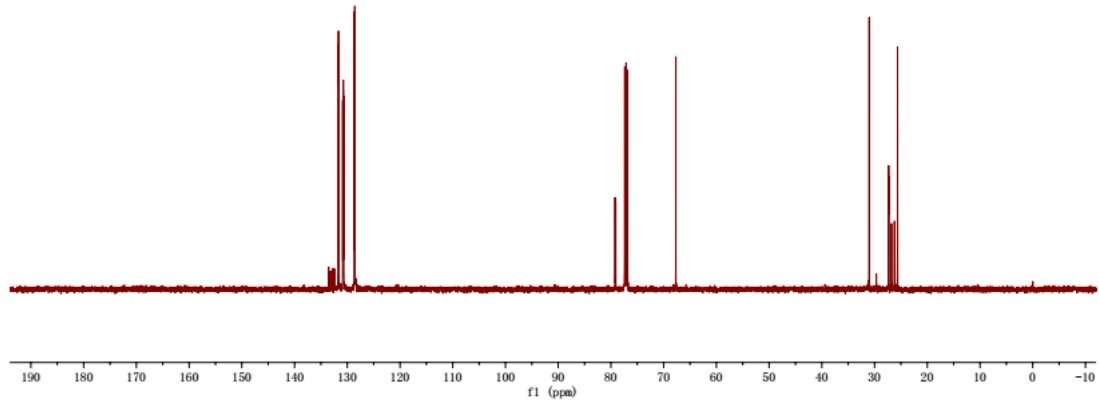
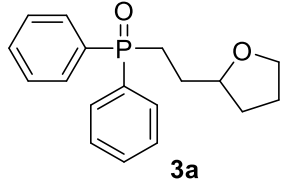


LKK-I-22A-1

133.53
133.17
132.76
132.38
131.69
131.67
130.86
130.79
130.75
130.68
128.68
128.58

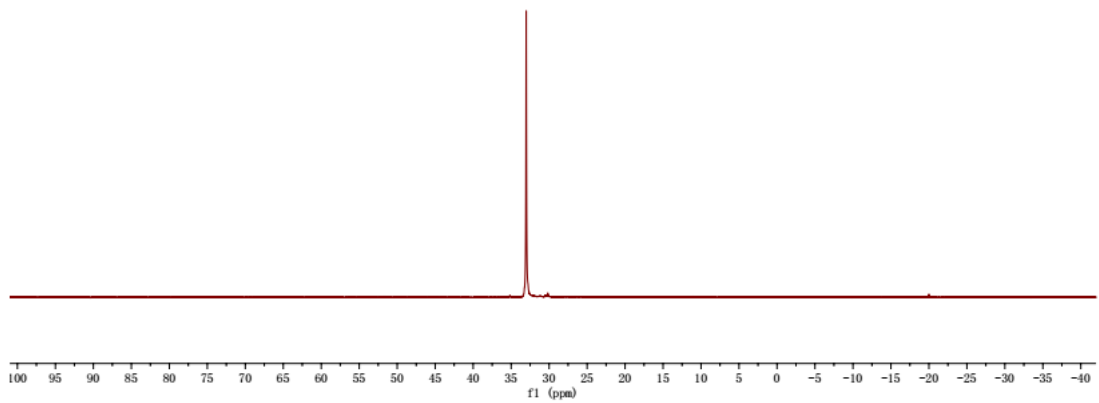
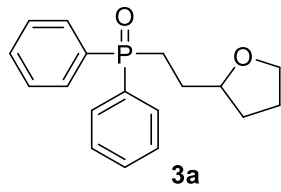
79.21
79.09
77.37
77.12
76.86
67.69

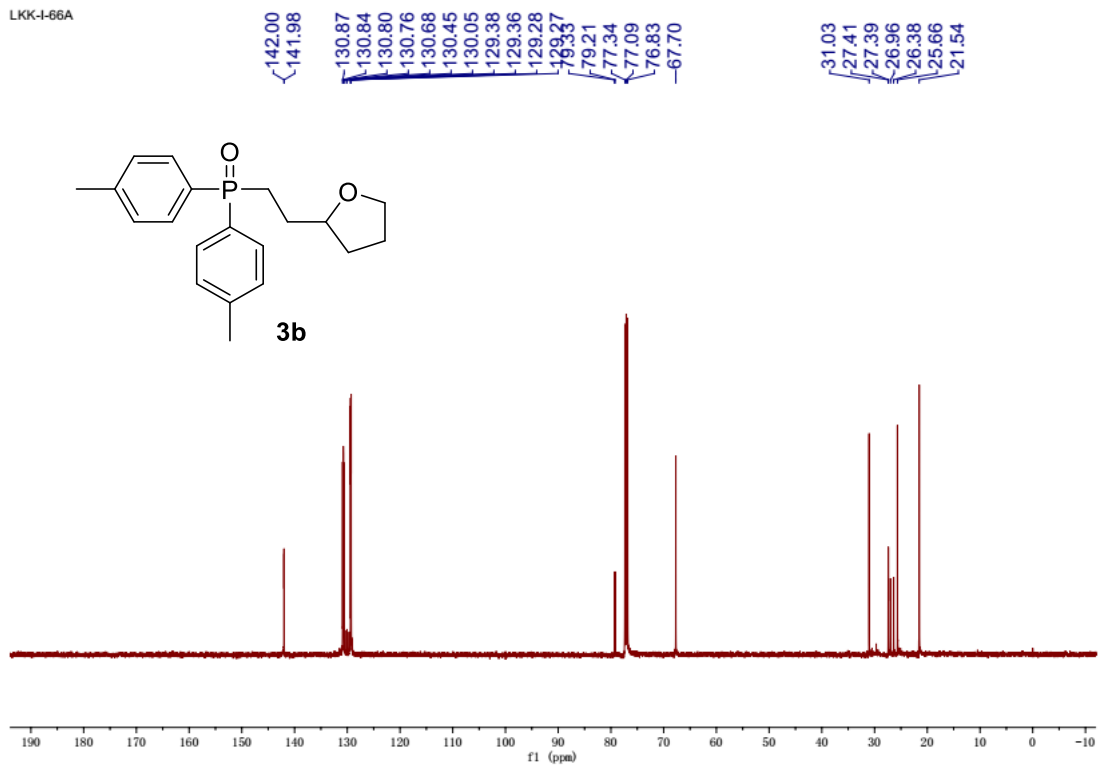
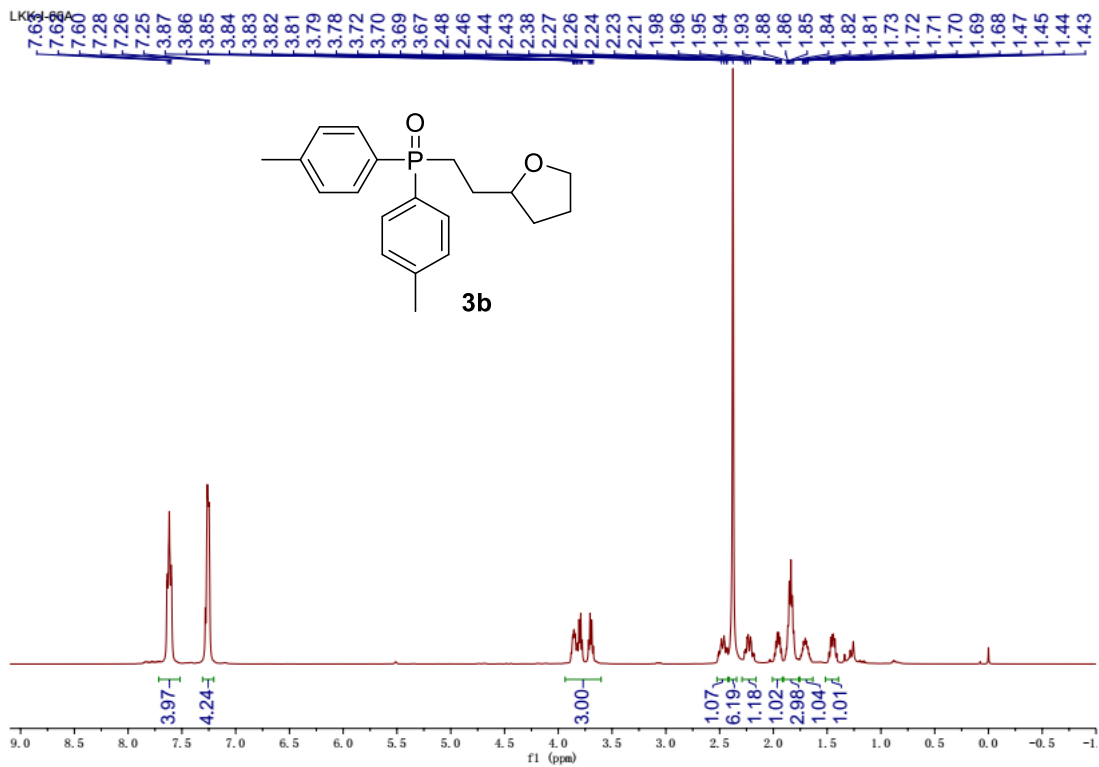
31.01
27.32
27.30
26.80
26.22
25.64



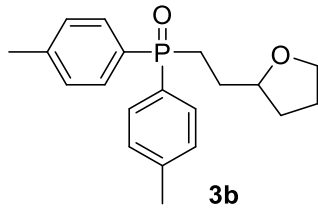
LKK-I-22A-1

-33.02

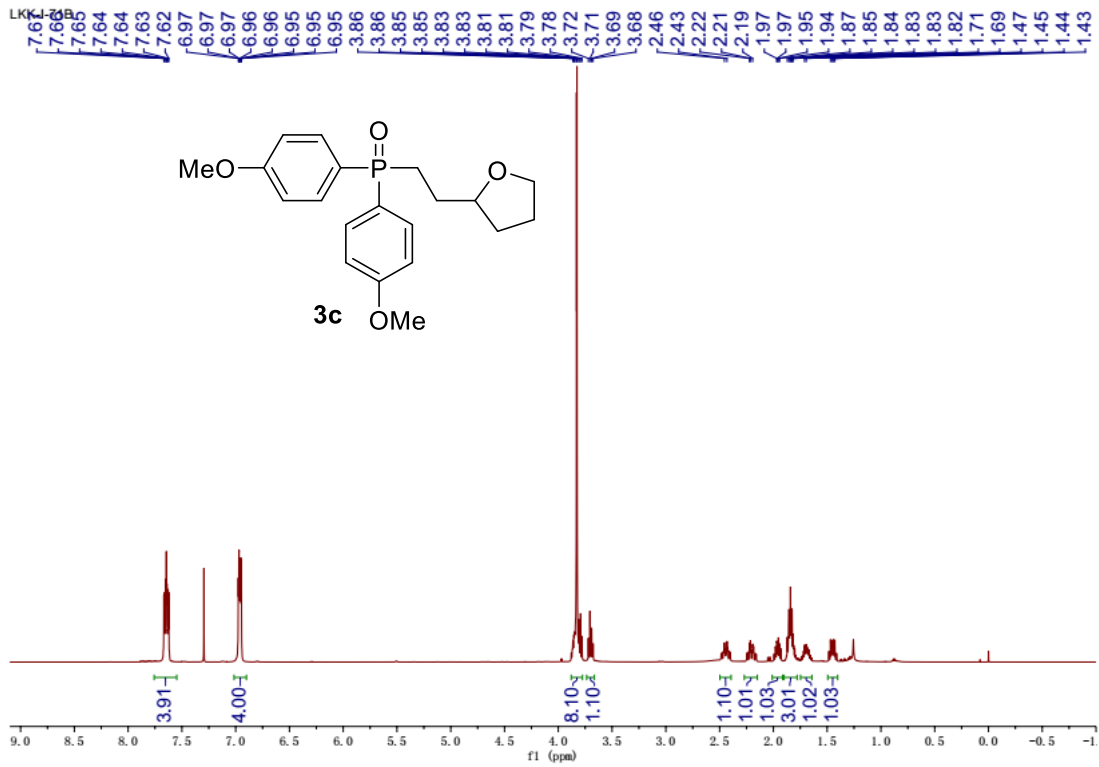
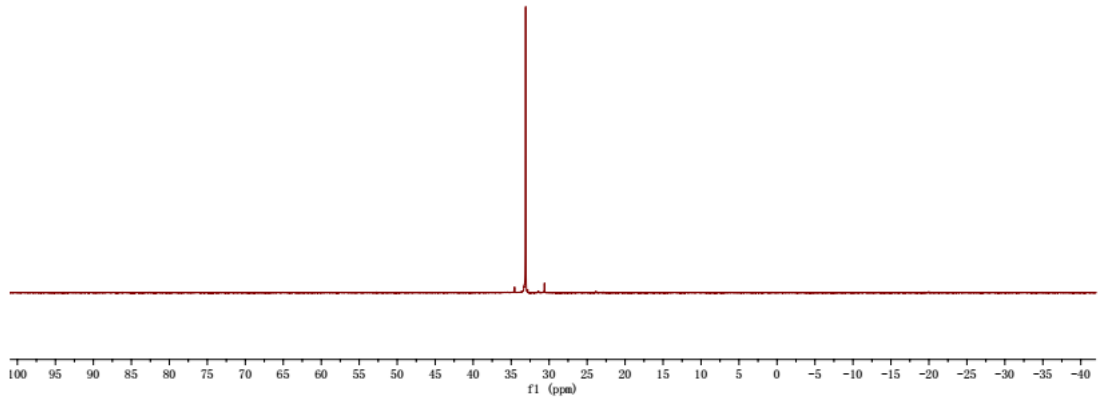




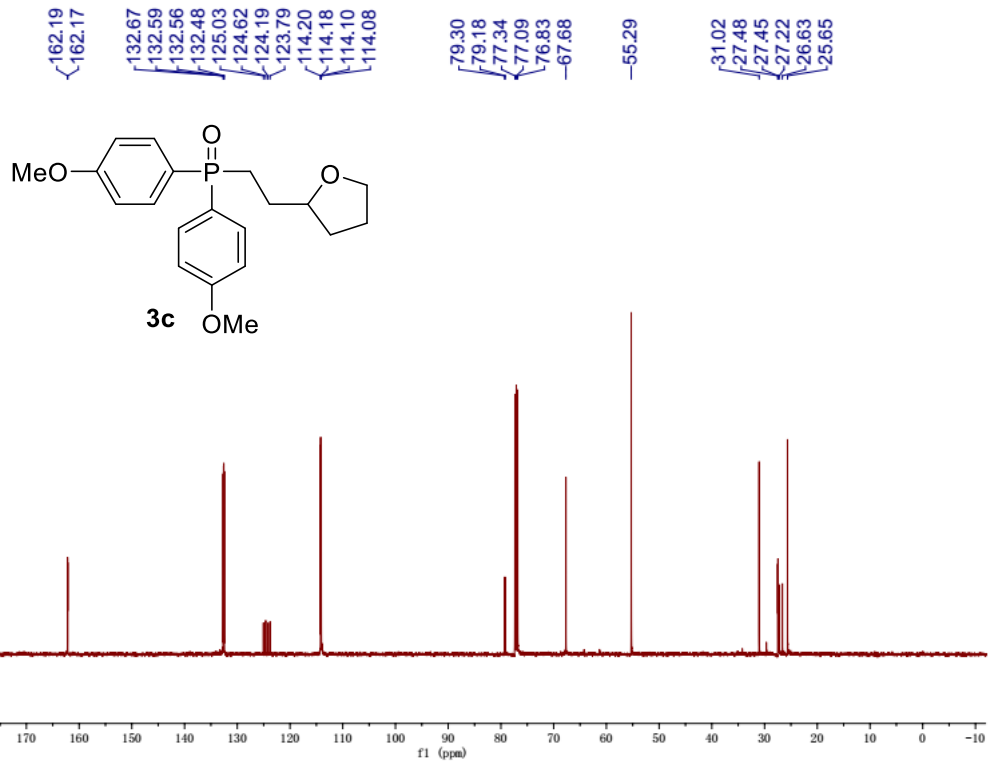
LKK-I-66A



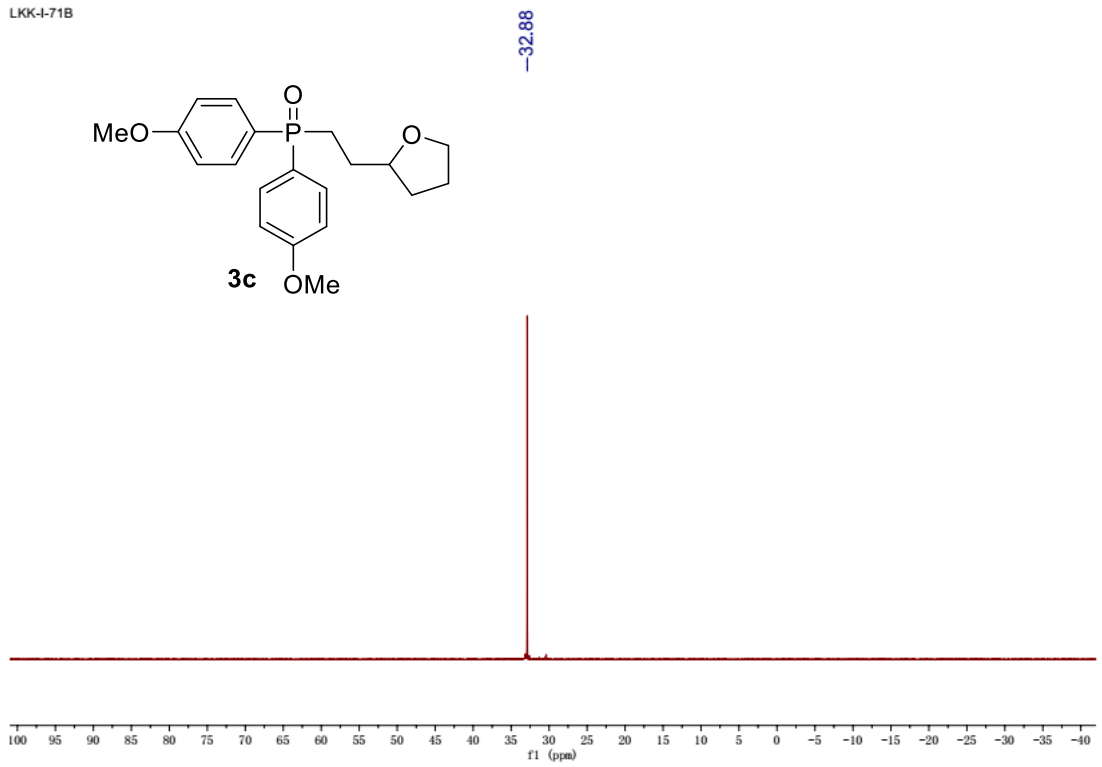
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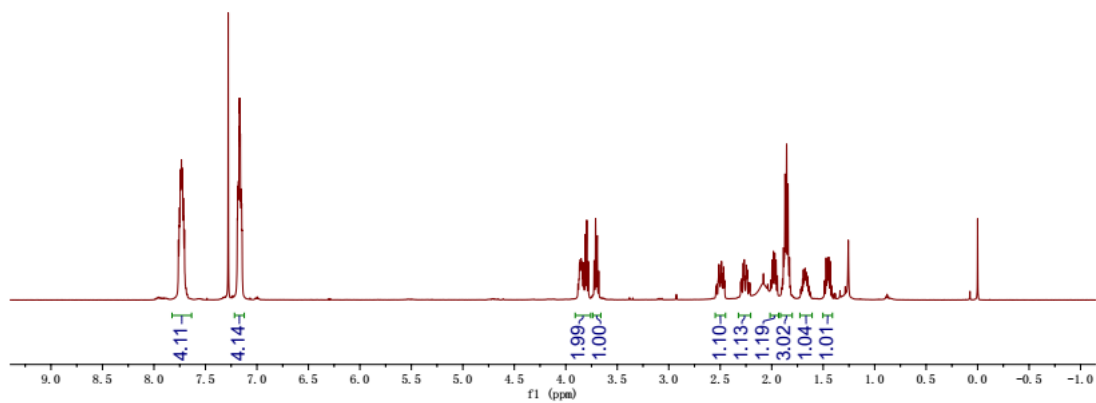
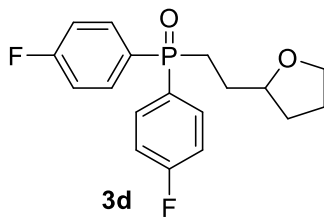
LKK-I-71B



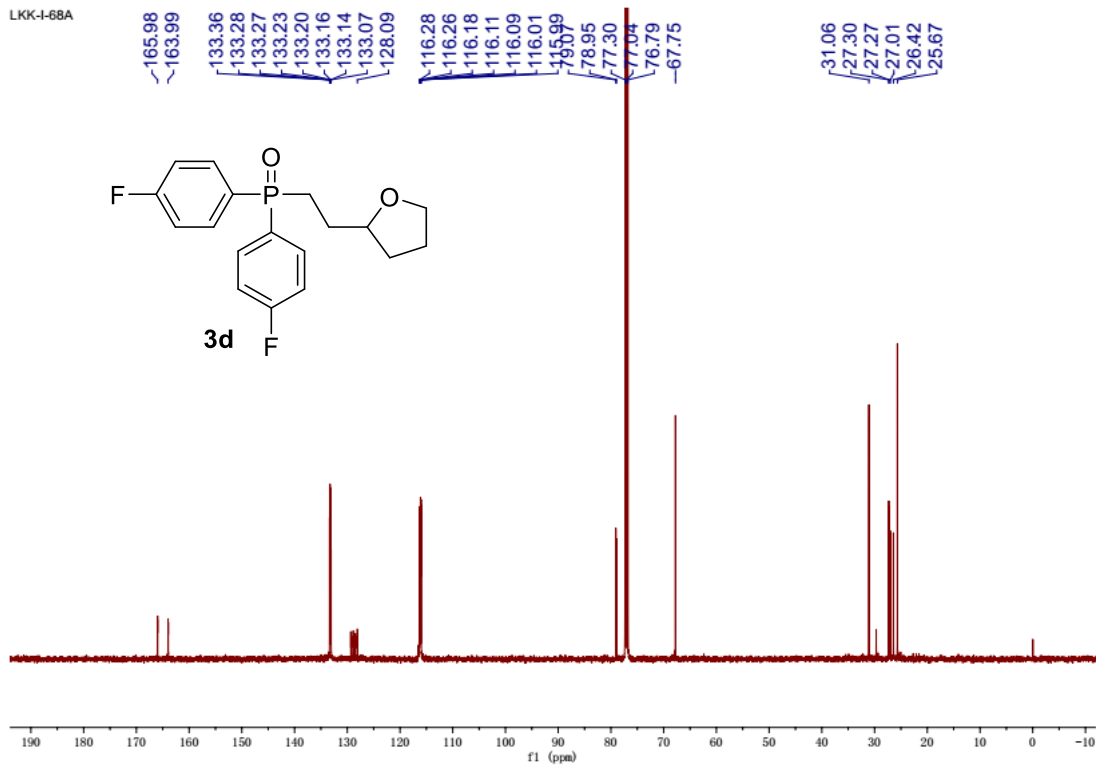
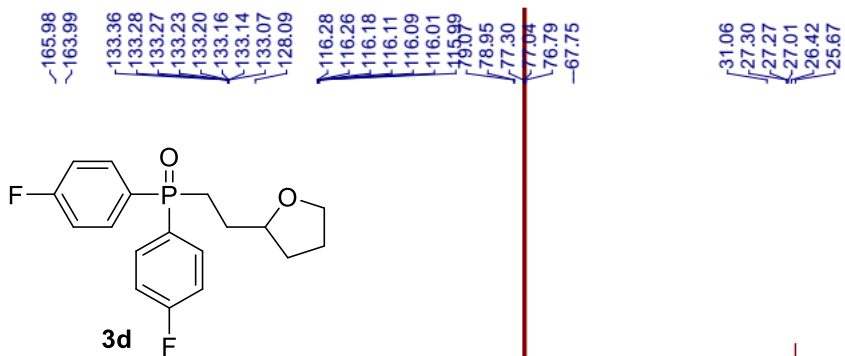
LKK-I-71B



LKK-I-68A
 7.76
7.75
7.74
7.74
7.73
7.72
7.72
7.71
7.70
7.19
7.19
7.18
7.18
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
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1.87
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1.84
1.83
1.47
1.45
1.43

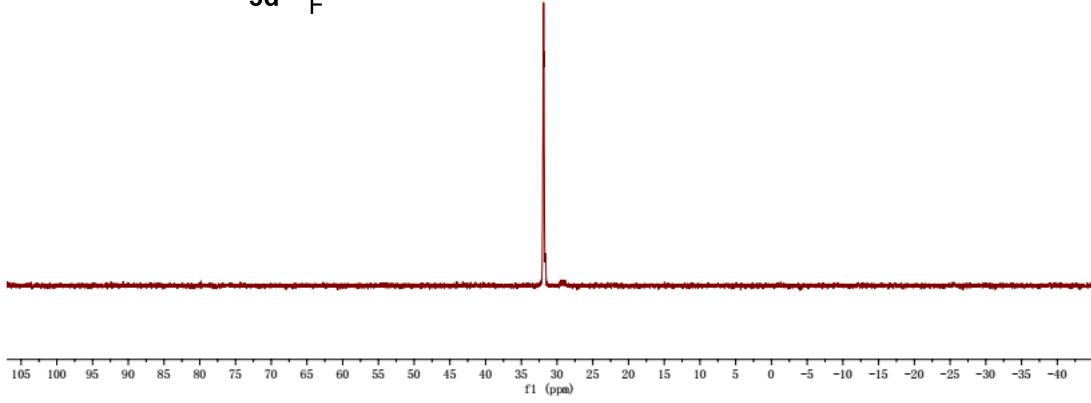
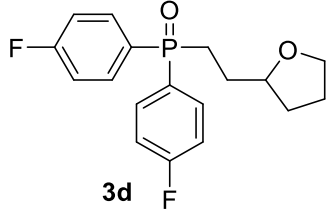


LKK-I-68A



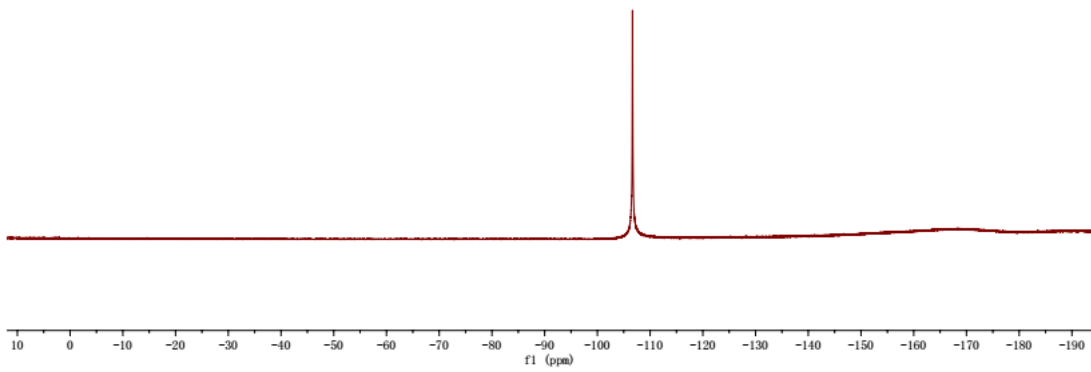
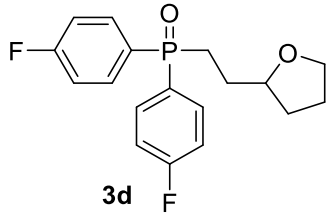
LKK-I-68A

-31.89



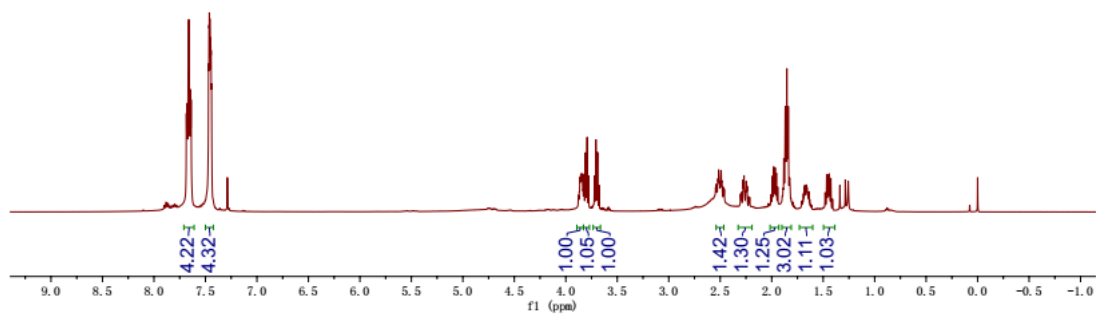
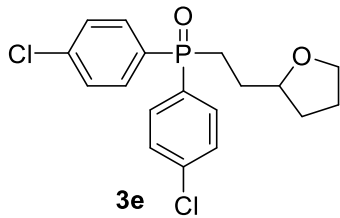
LKK-I-68A

-106.66



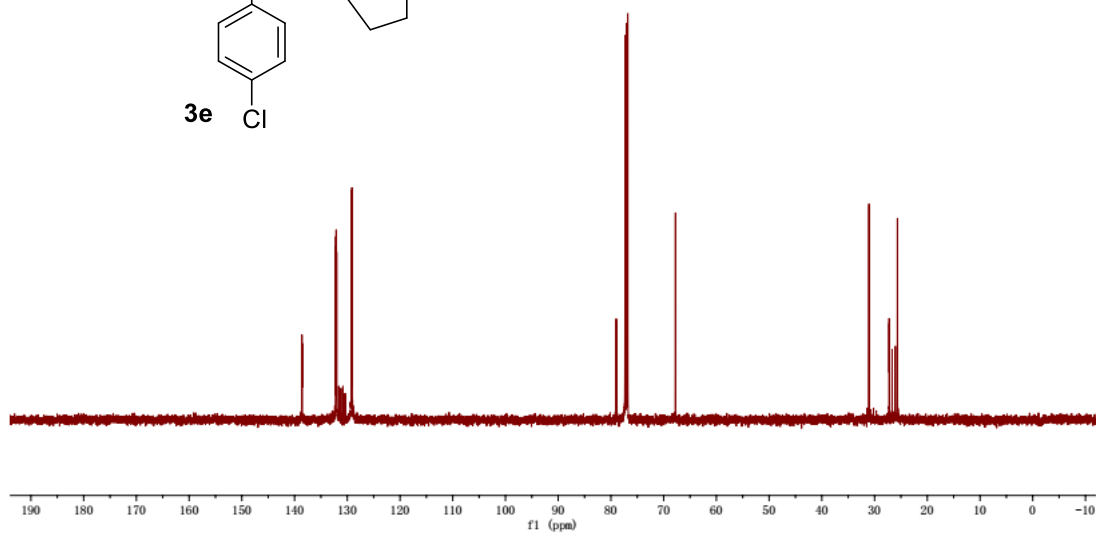
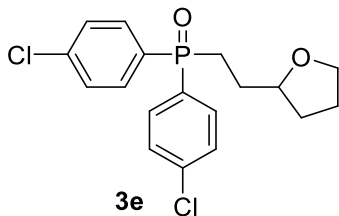
LKK-1-66B

7.66
7.66
7.67
7.66
7.65
7.64
7.47
7.46
7.46
7.46
7.45
7.45
7.44
3.86
3.85
3.84
3.82
3.81
3.79
3.78
3.72
3.71
3.69
2.54
2.52
2.51
2.51
2.50
2.49
2.28
2.27
2.25
1.99
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1.85
1.84
1.83
1.67
1.47
1.44
1.43



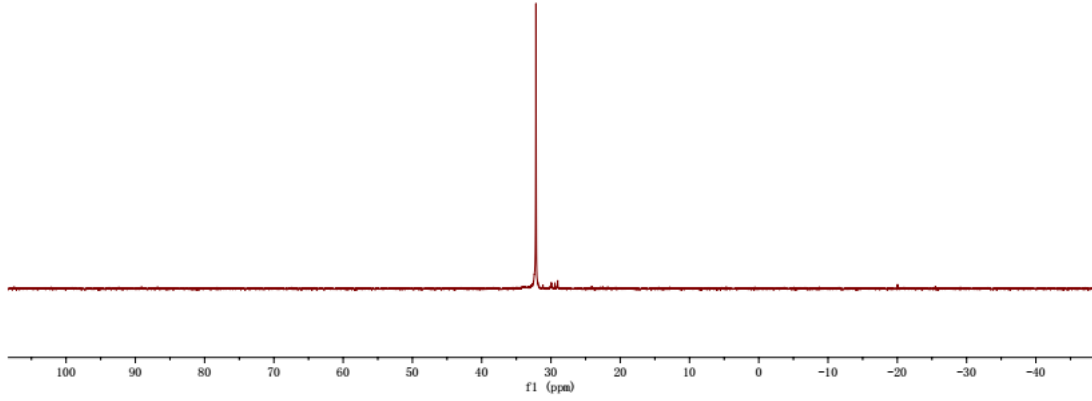
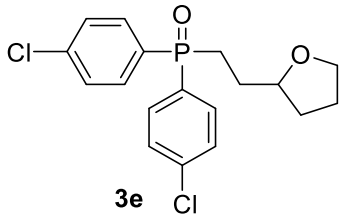
LKK-1-66B

138.60
138.58
132.23
132.14
132.10
132.02
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131.22
130.82
130.42
129.21
129.19
129.12
129.10
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26.08
25.66

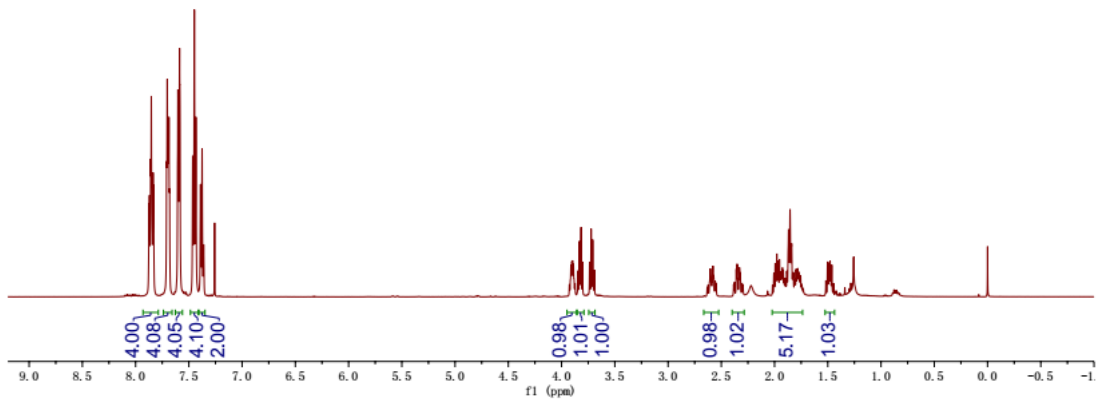
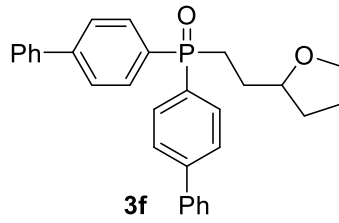


LKK-I-66B

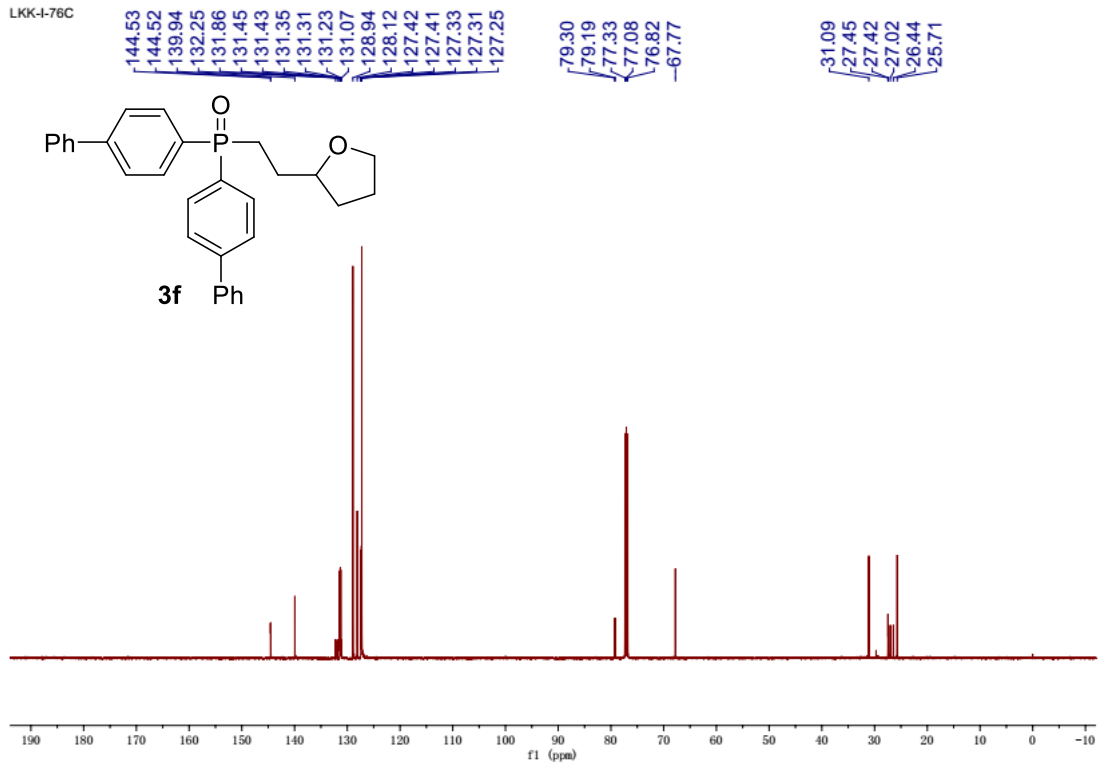
-32.17



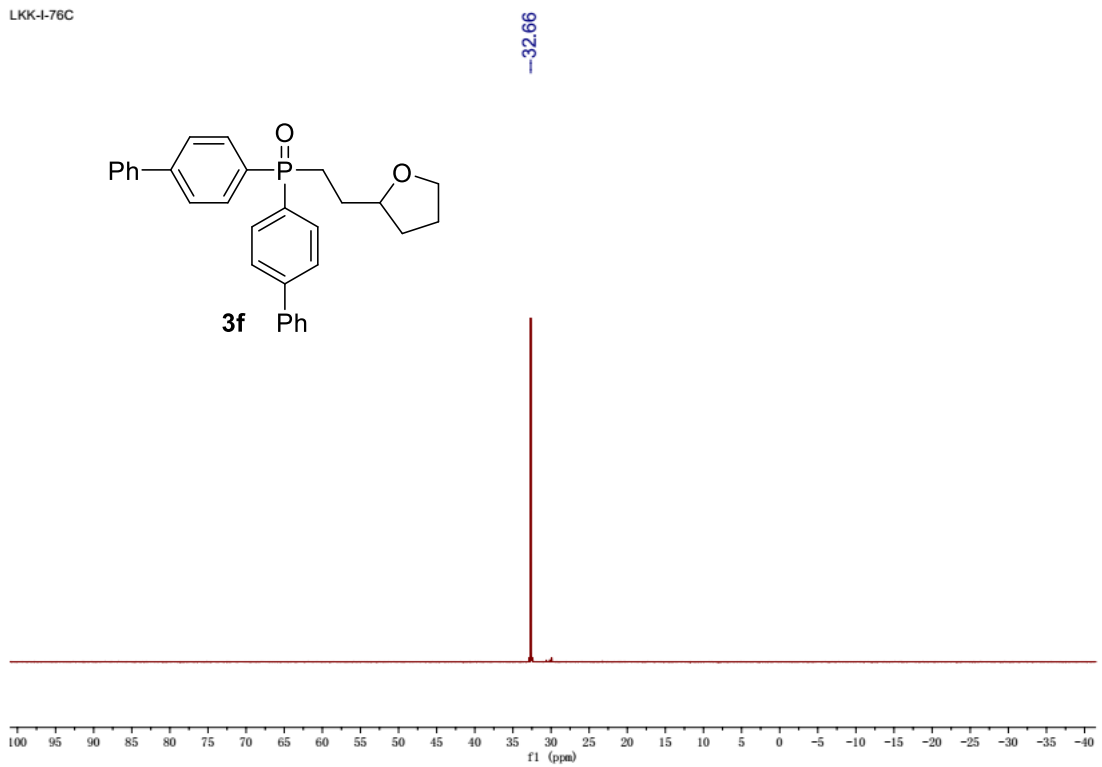
LKK-I-66B
7.84
7.83
7.77
7.70
7.69
7.69
7.68
7.60
7.60
7.59
7.58
7.46
7.45
7.43
7.39
7.38
7.36
3.91
3.90
3.89
3.83
3.82
3.80
3.74
3.72
3.71
2.58
2.35
2.33
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1.85
1.84
1.78
1.50
1.49
1.48

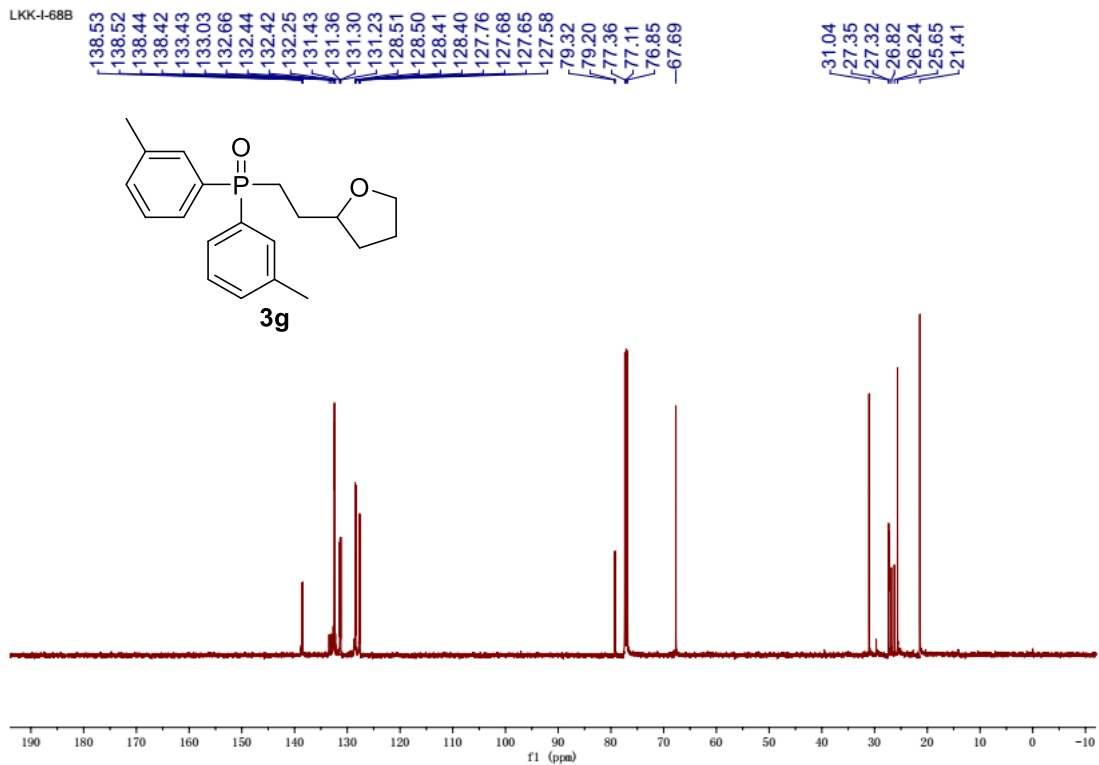
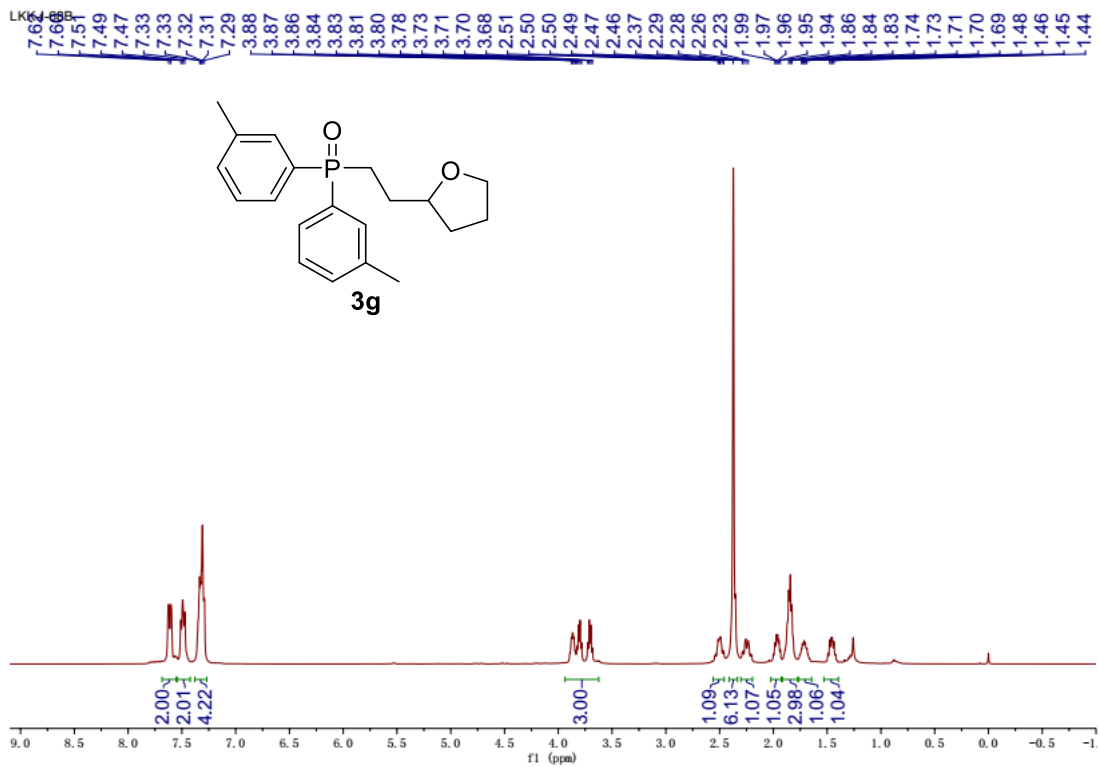


LKK-I-76C

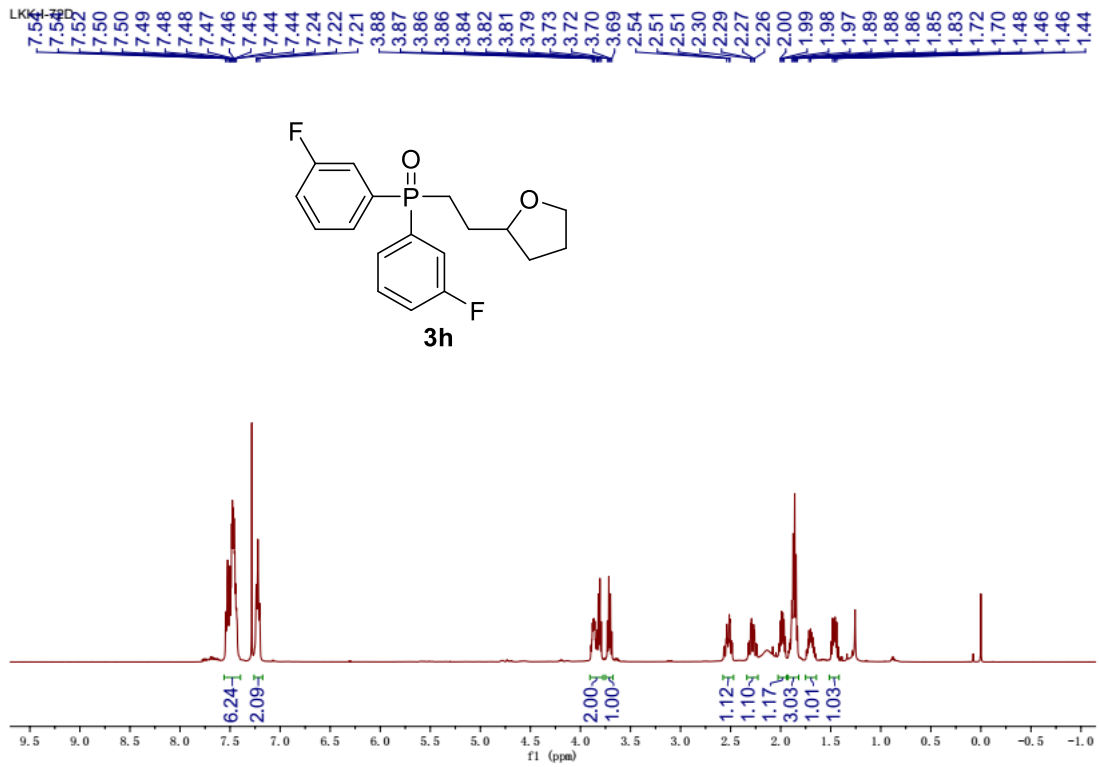
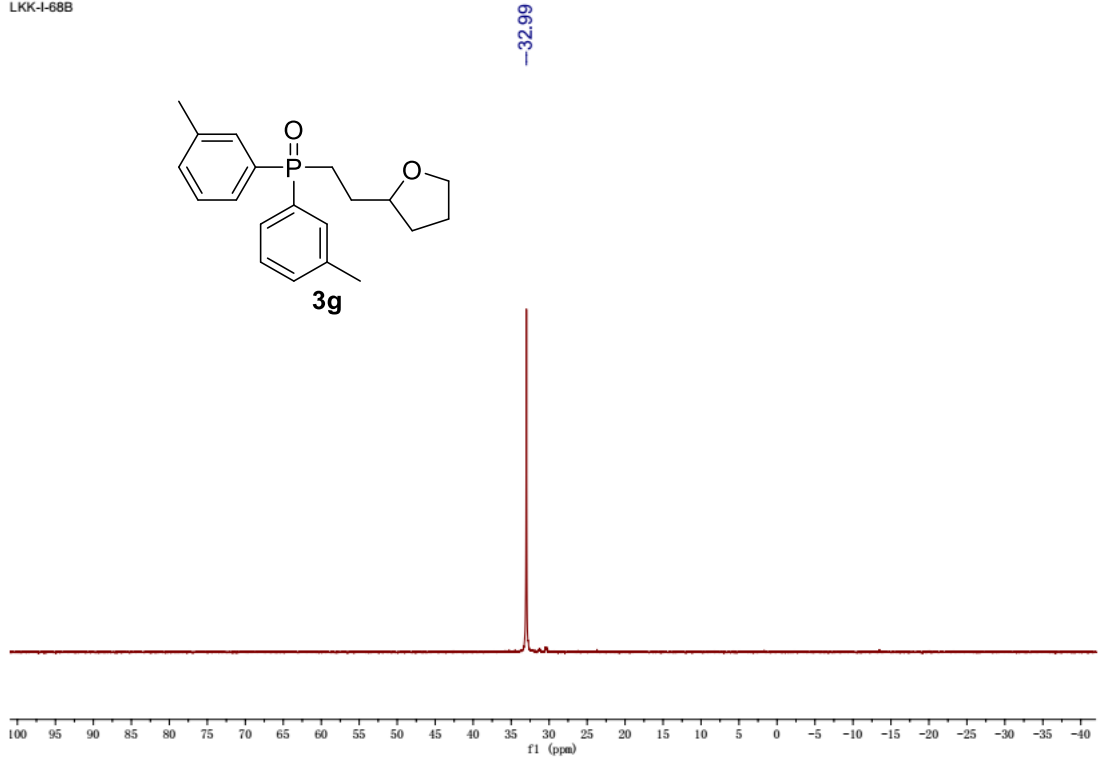


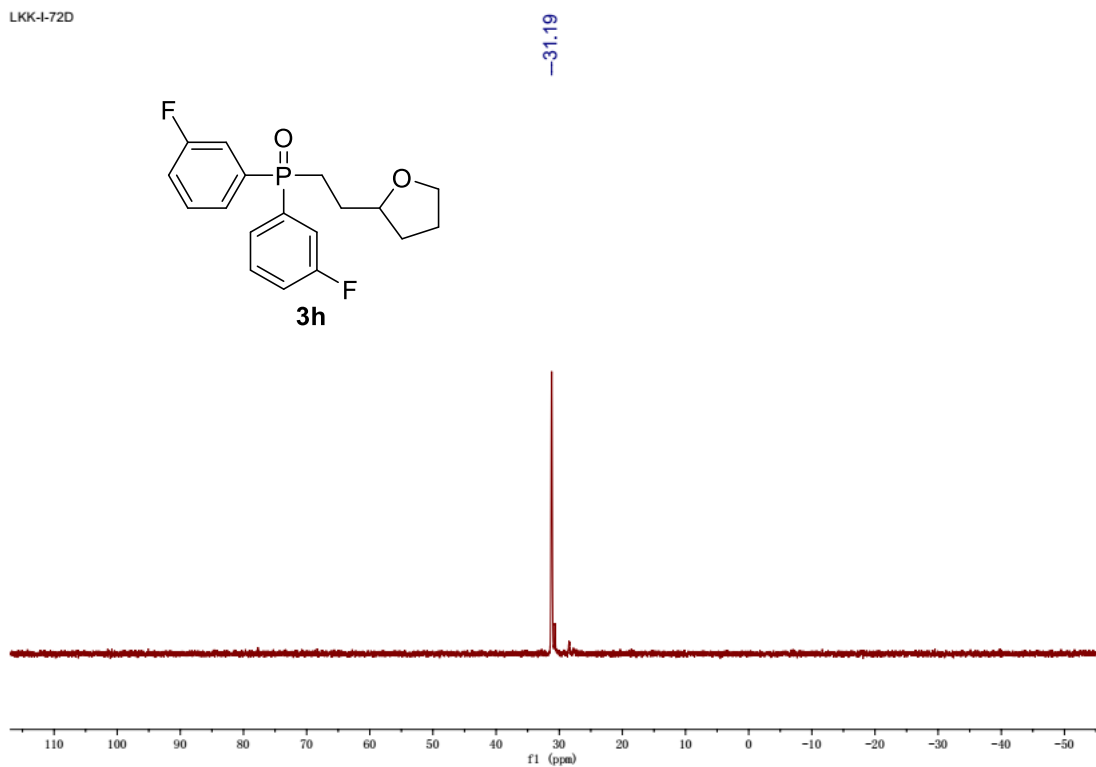
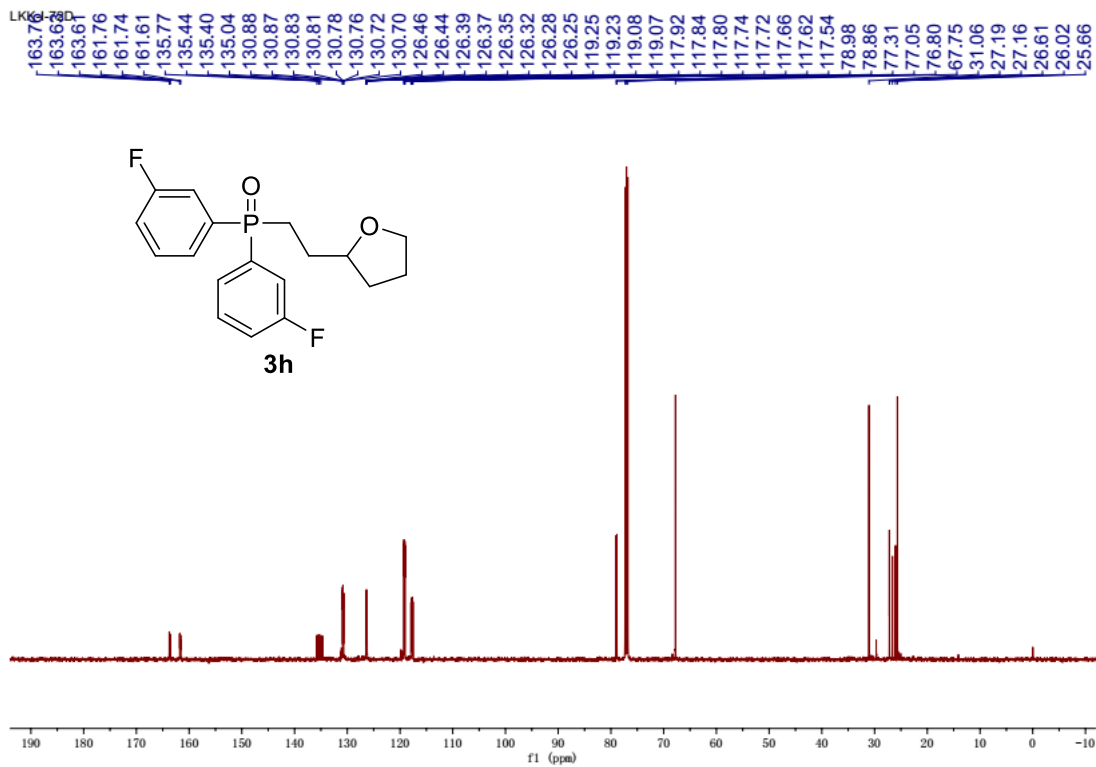
LKK-I-76C





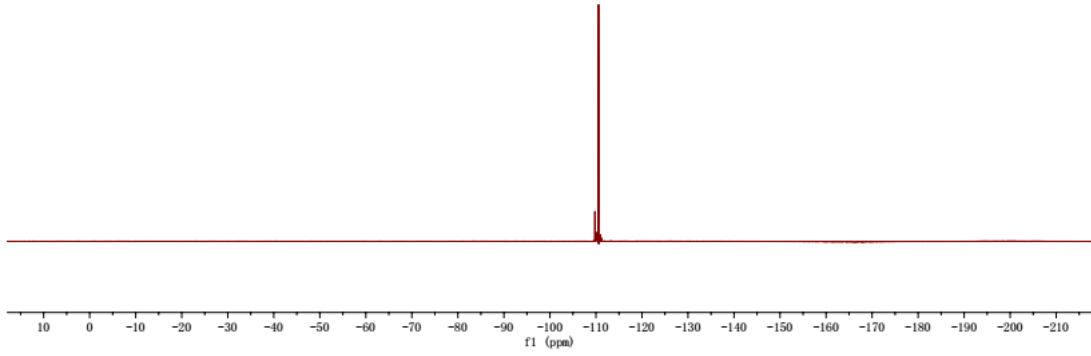
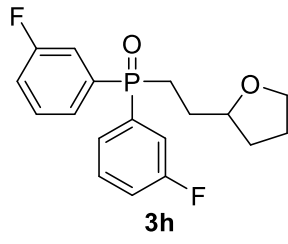
LKK-I-68B



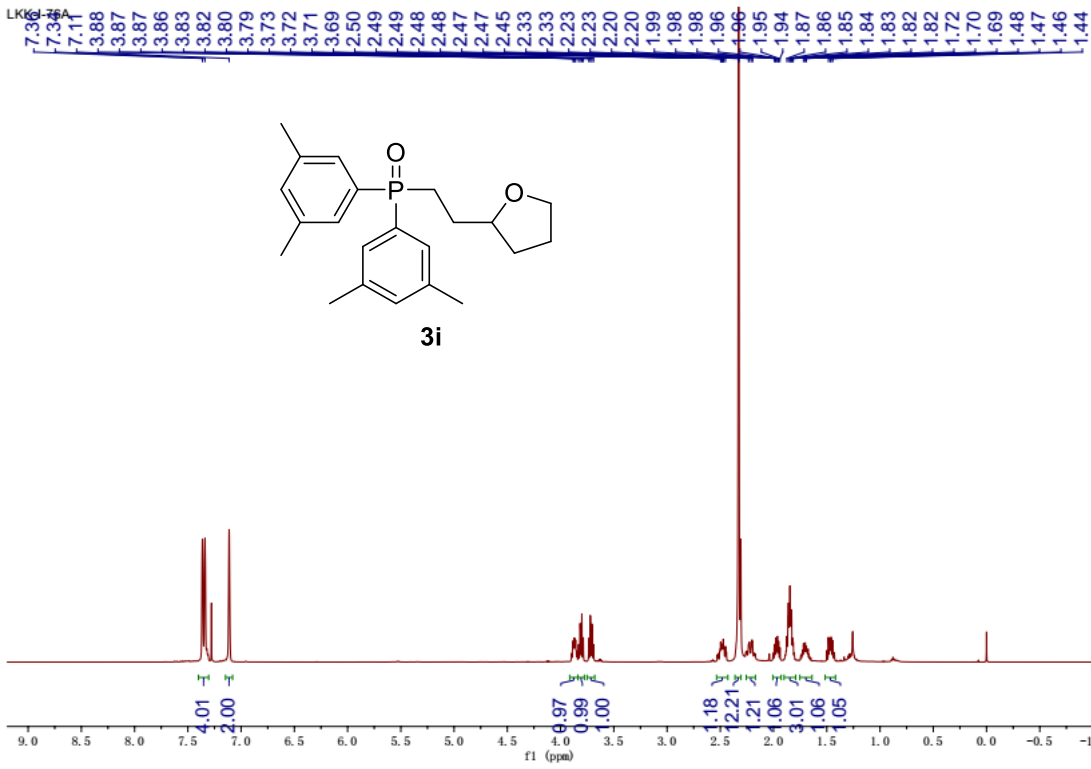
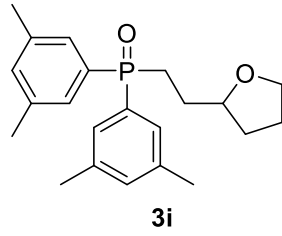


LKK-4-72D

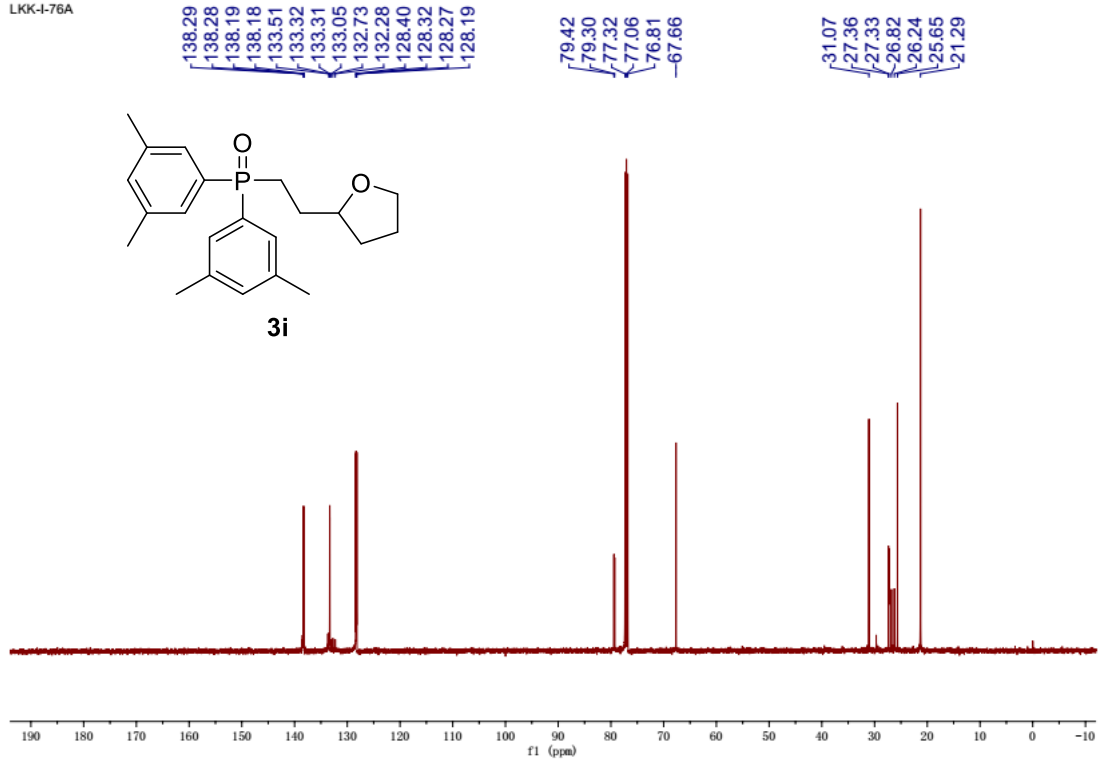
110.56
110.57



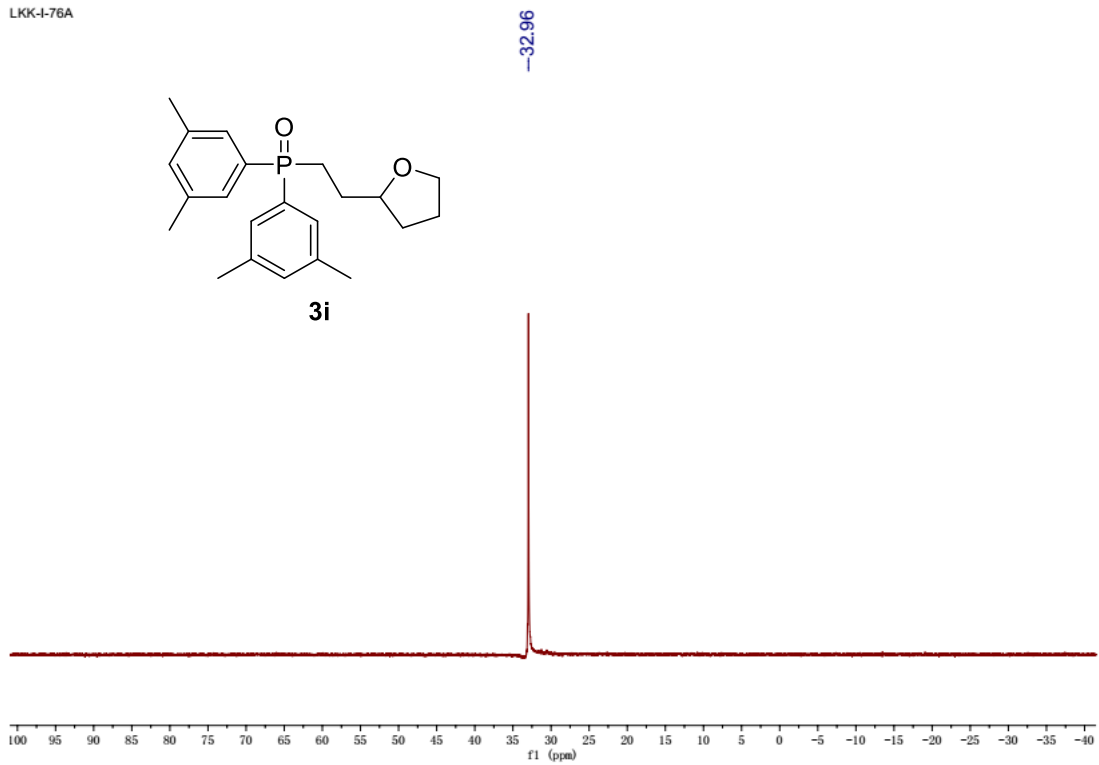
LKK-4-72A

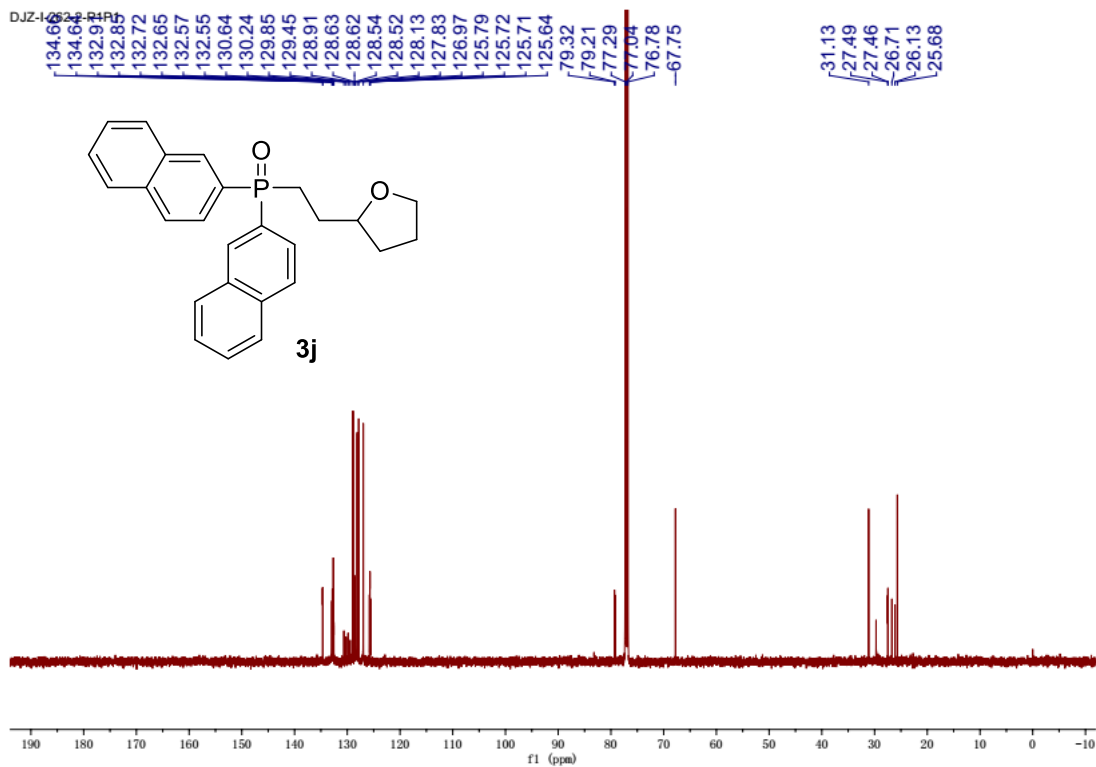
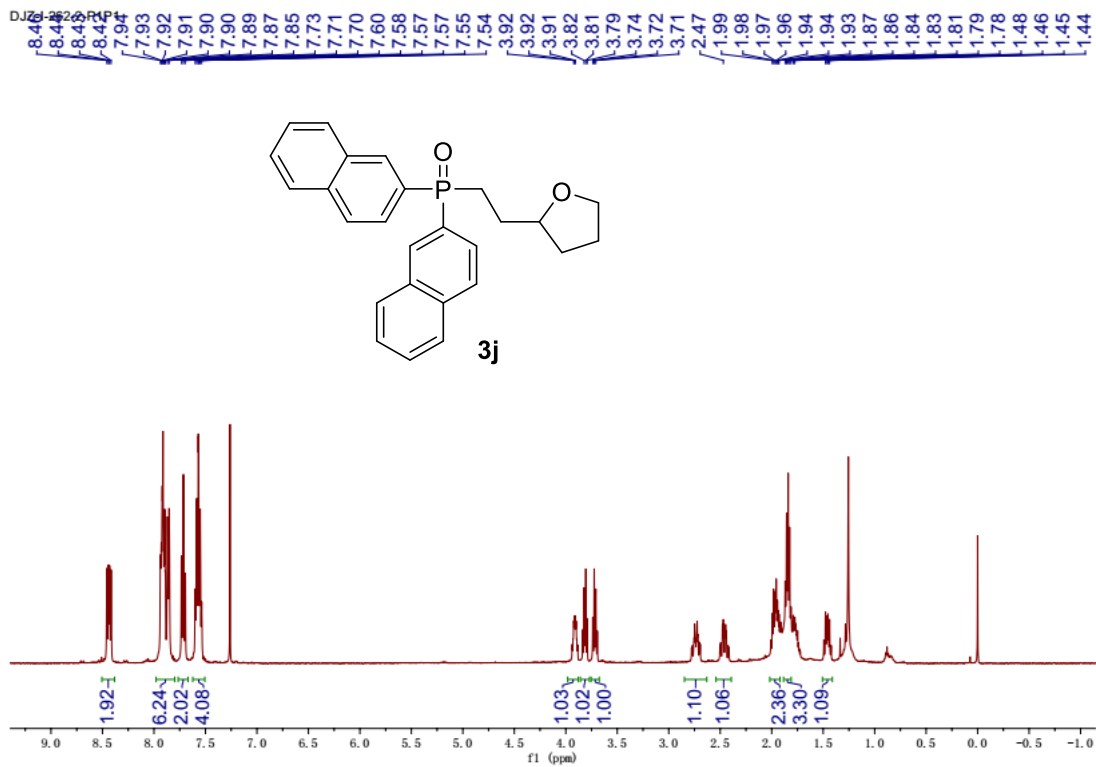


LKK-I-76A

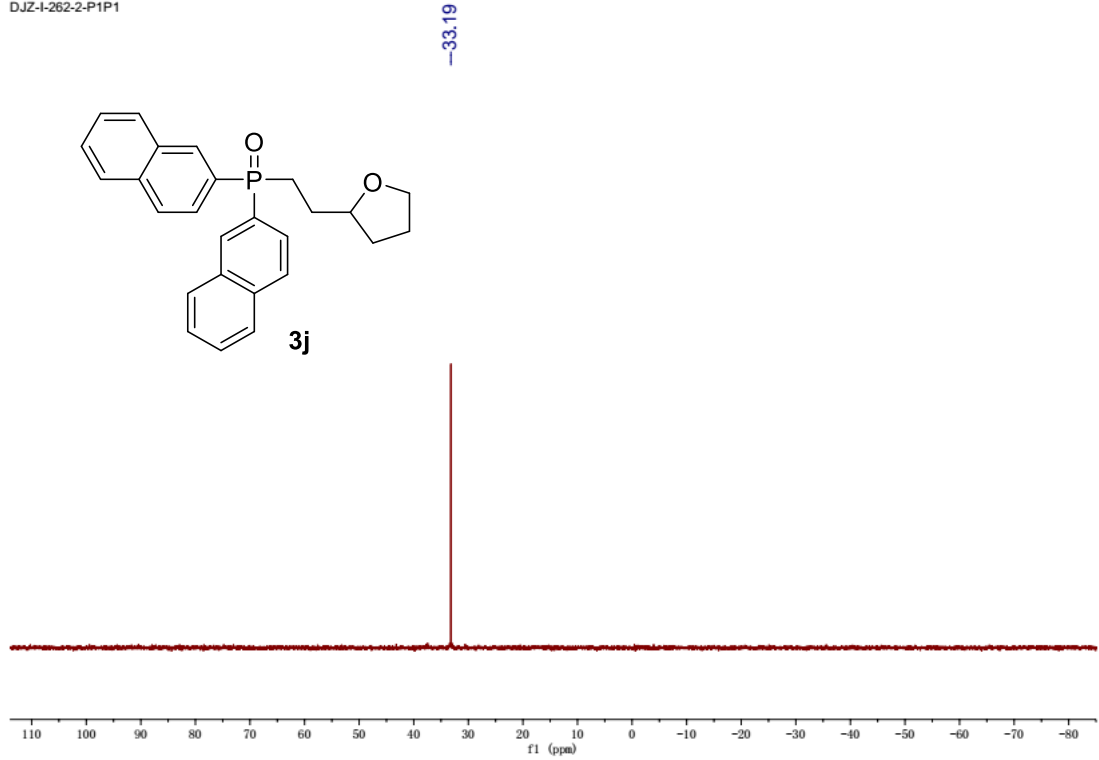


LKK-I-76A



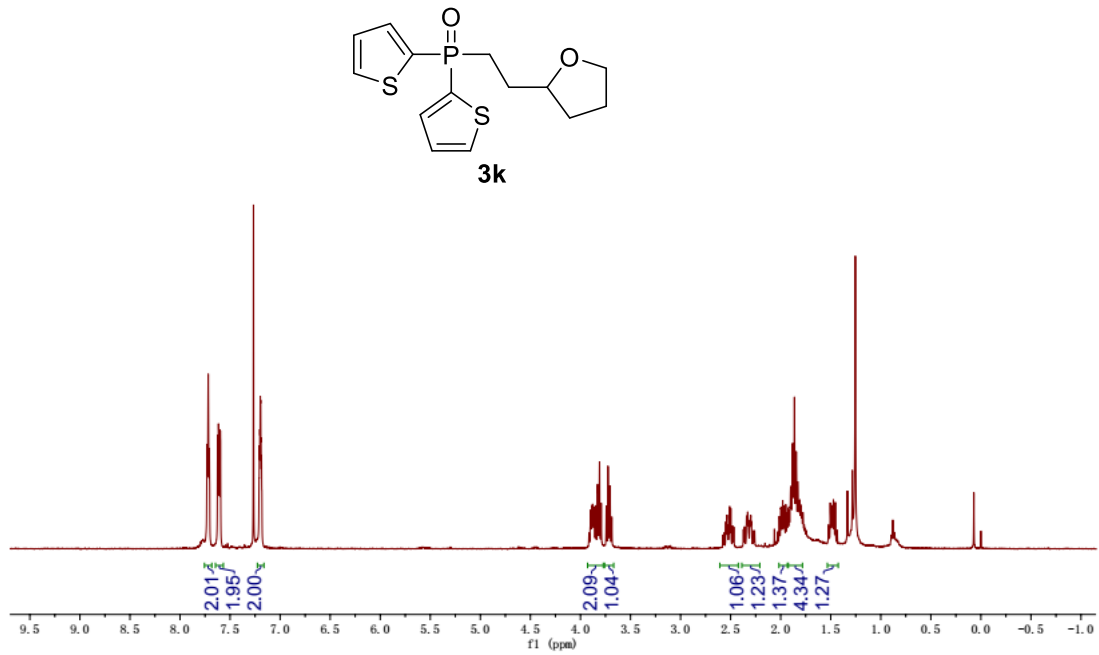


DJZ-1-262-2-P1P1

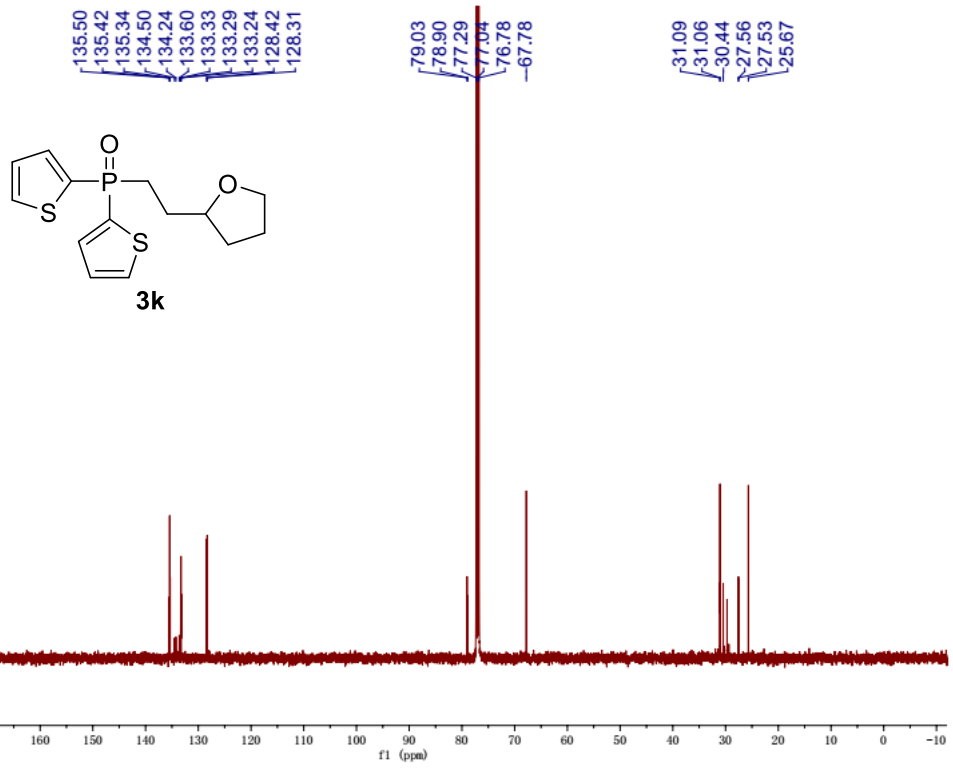


双峰分叠

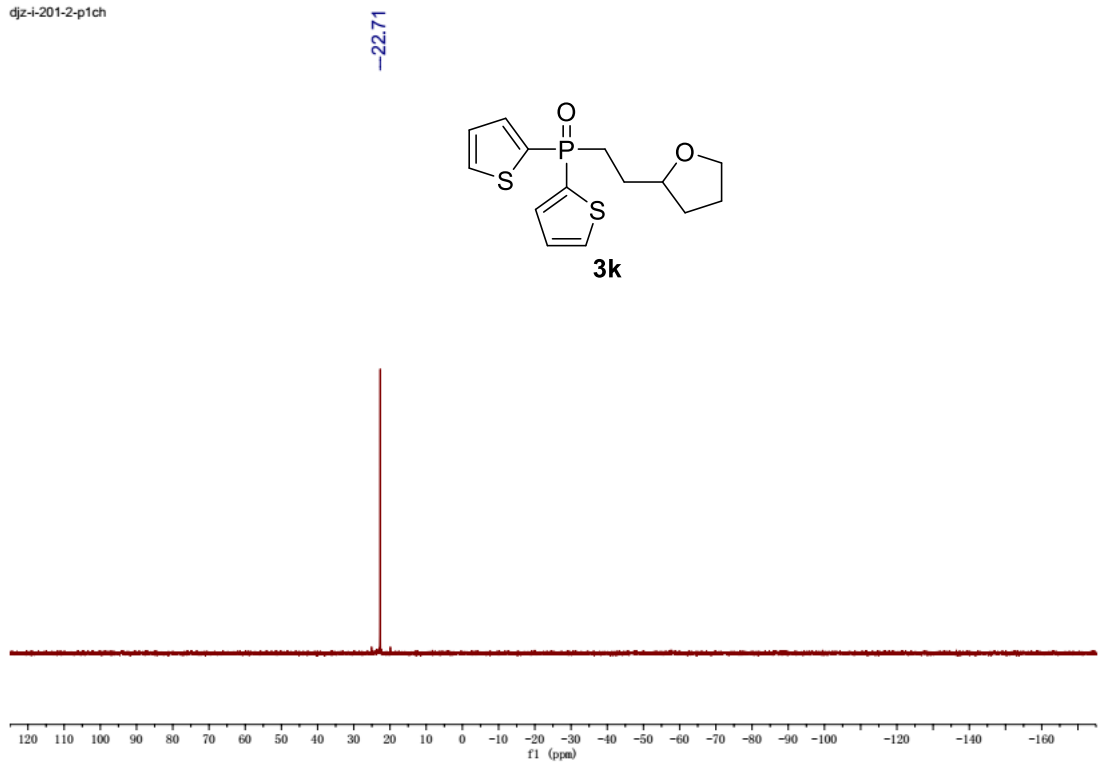
Chemical Shift (ppm)
7.77
7.77
7.77
7.62
7.61
7.60
7.21
7.20
7.19
7.19
3.90
3.89
3.88
3.87
3.85
3.83
3.81
3.79
3.74
3.72
3.71
2.54
2.51
2.50
2.34
2.33
2.30
2.00
1.98
1.97
1.95
1.94
1.93
1.91
1.90
1.88
1.86
1.84
1.83
1.82
1.81
1.80
1.78
1.50
1.48
1.47
1.45

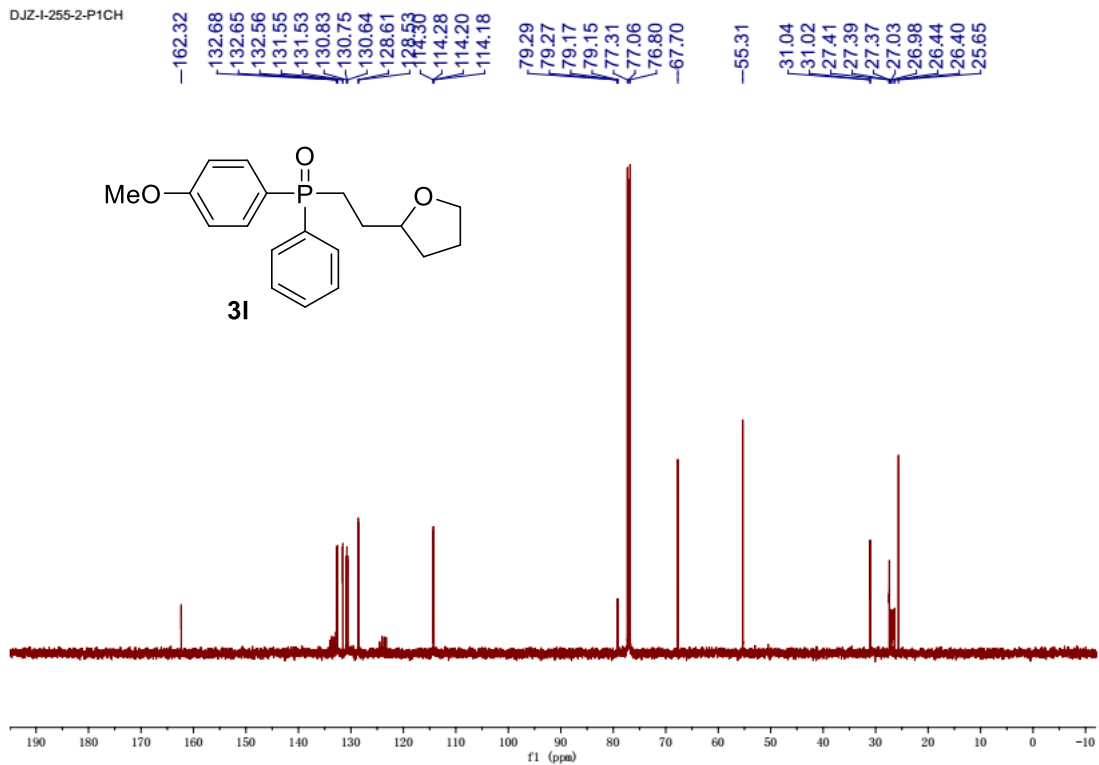
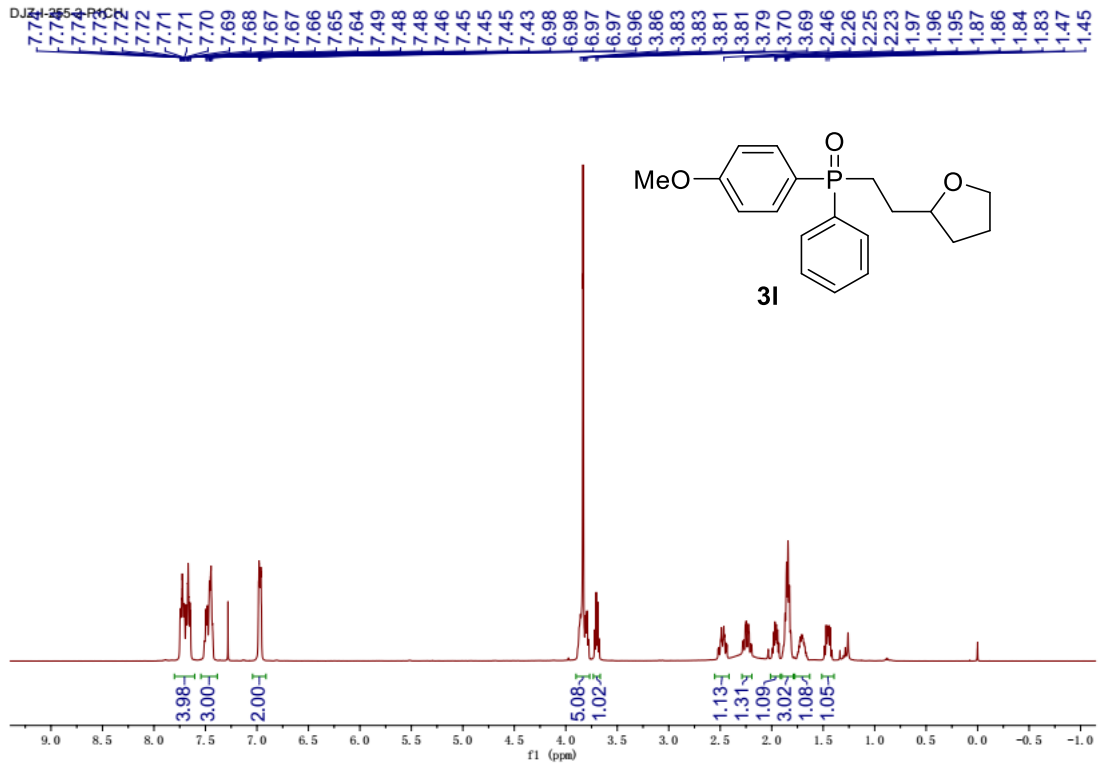


djz-i-201-2-p1ch

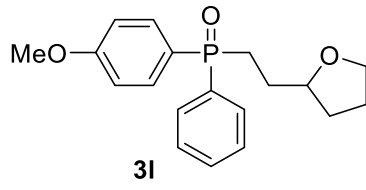


djz-i-201-2-p1ch

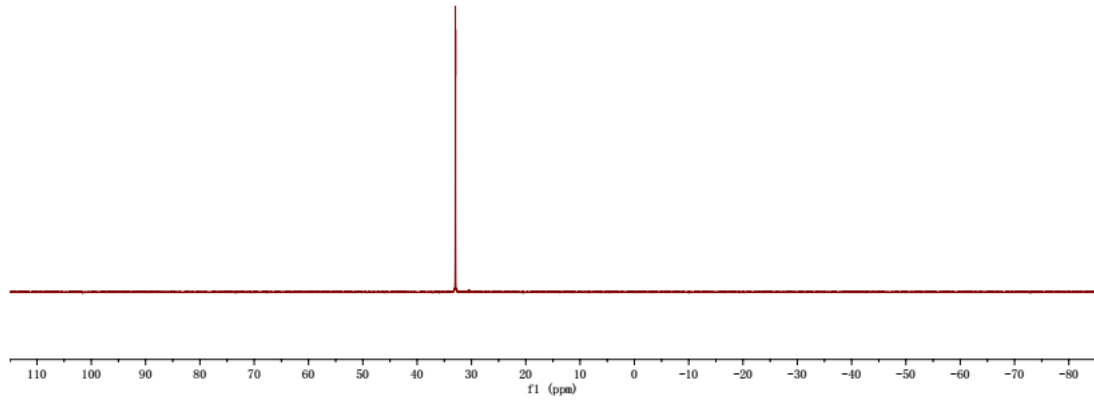




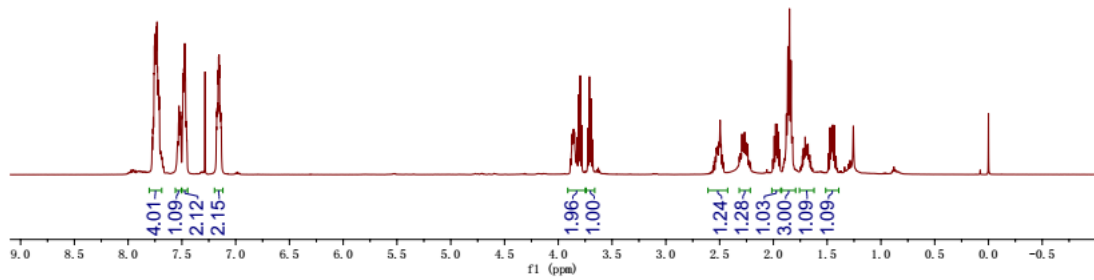
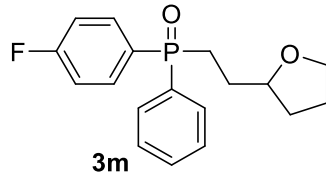
DJZ-1-255-2-P1CH

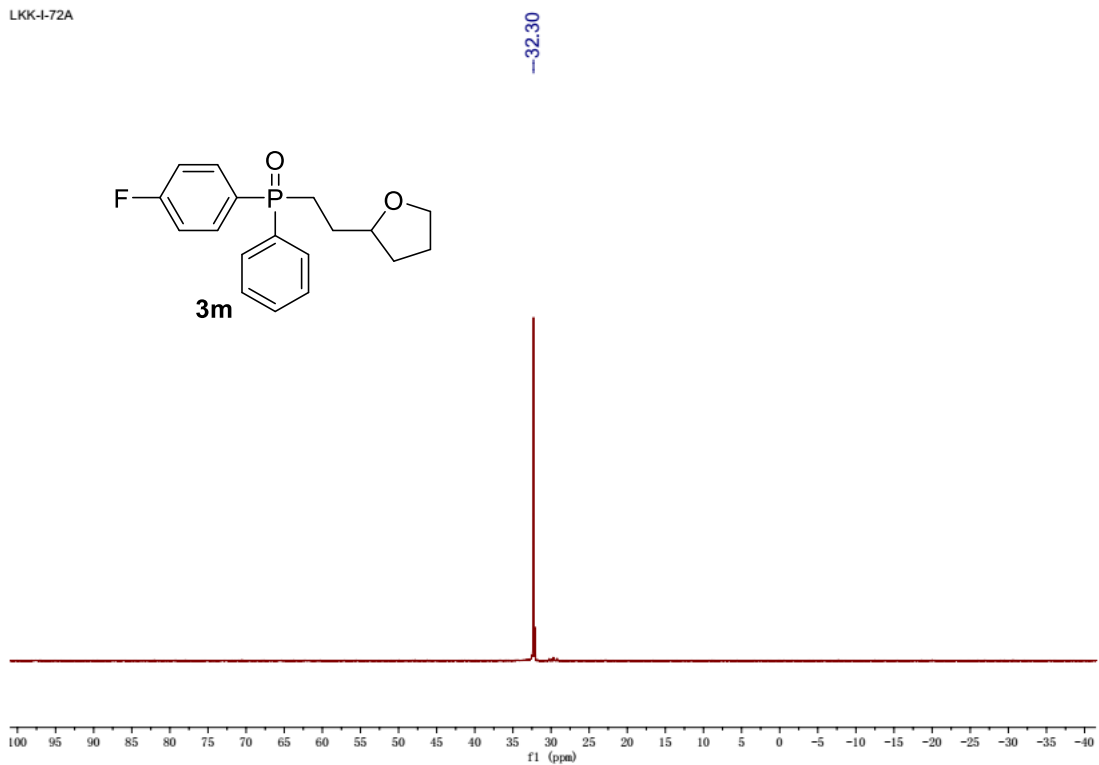
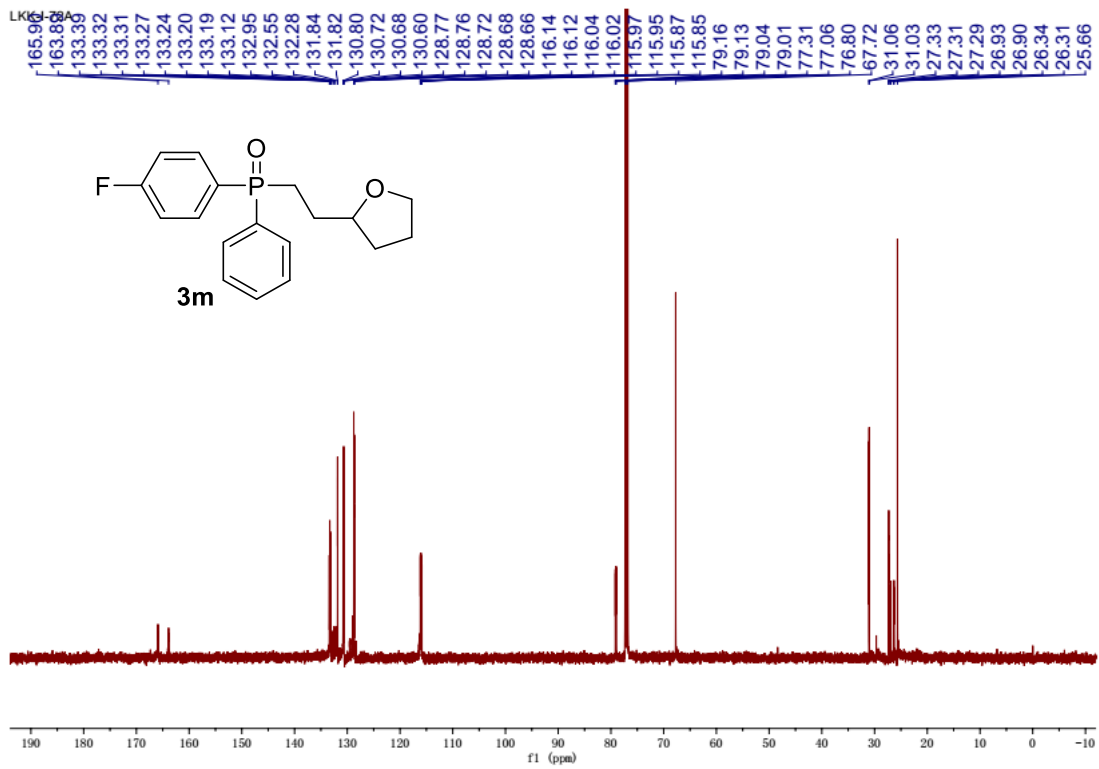


32.97
32.94



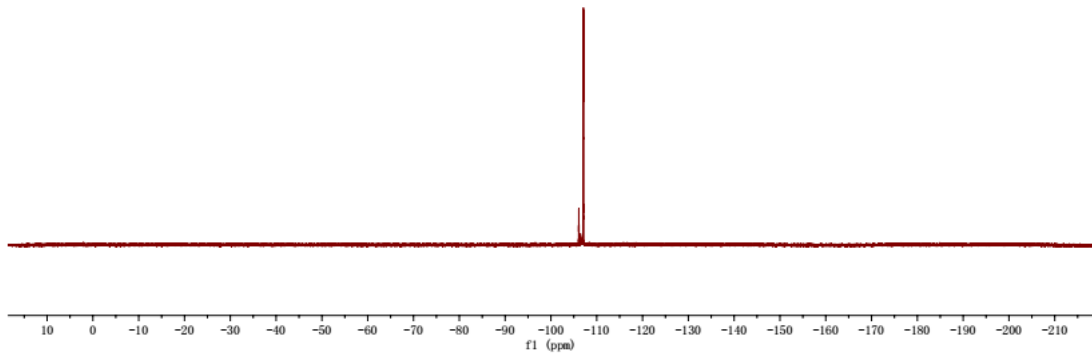
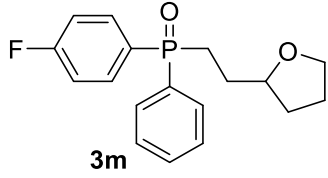
LKK-1-29A
7.71
7.70
7.75
7.75
7.74
7.74
7.74
7.73
7.73
7.72
7.71
7.53
7.52
7.51
7.49
7.49
7.48
7.48
7.47
7.47
7.46
7.18
7.18
7.17
7.17
7.16
7.16
7.15
7.15
7.14
7.14
3.81
3.80
3.78
3.71
3.69
2.50
1.98
1.97
1.88
1.86
1.85
1.84
1.45
1.43



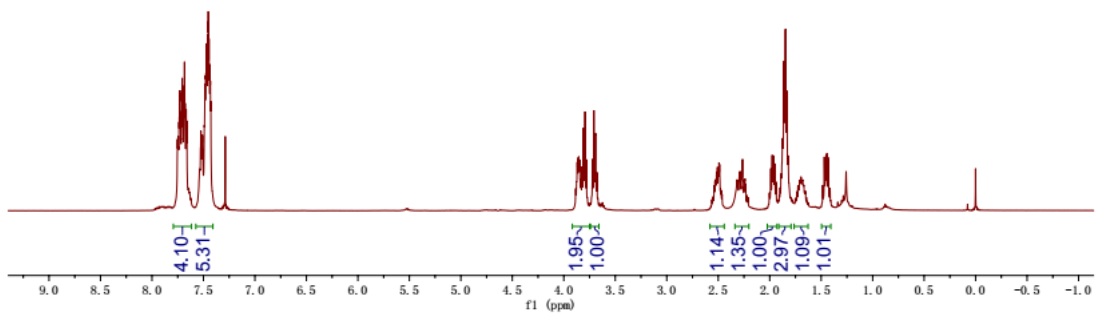
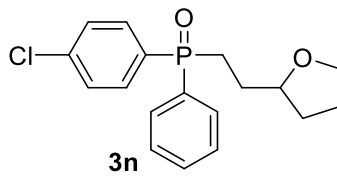


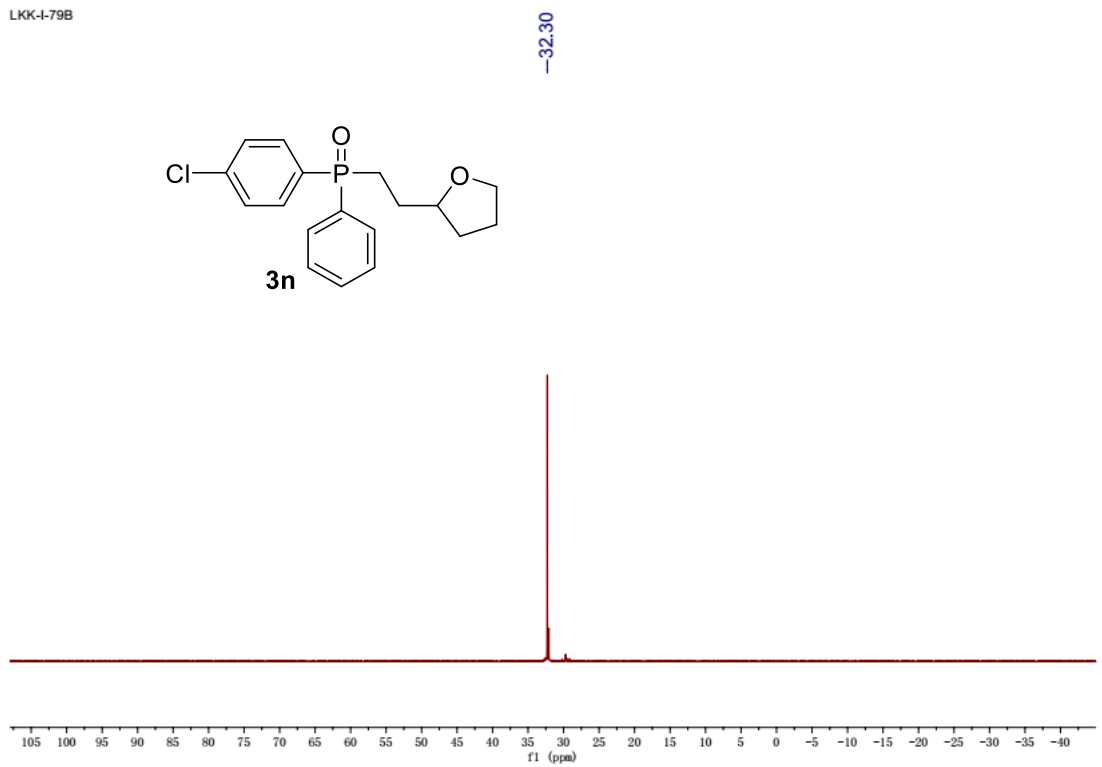
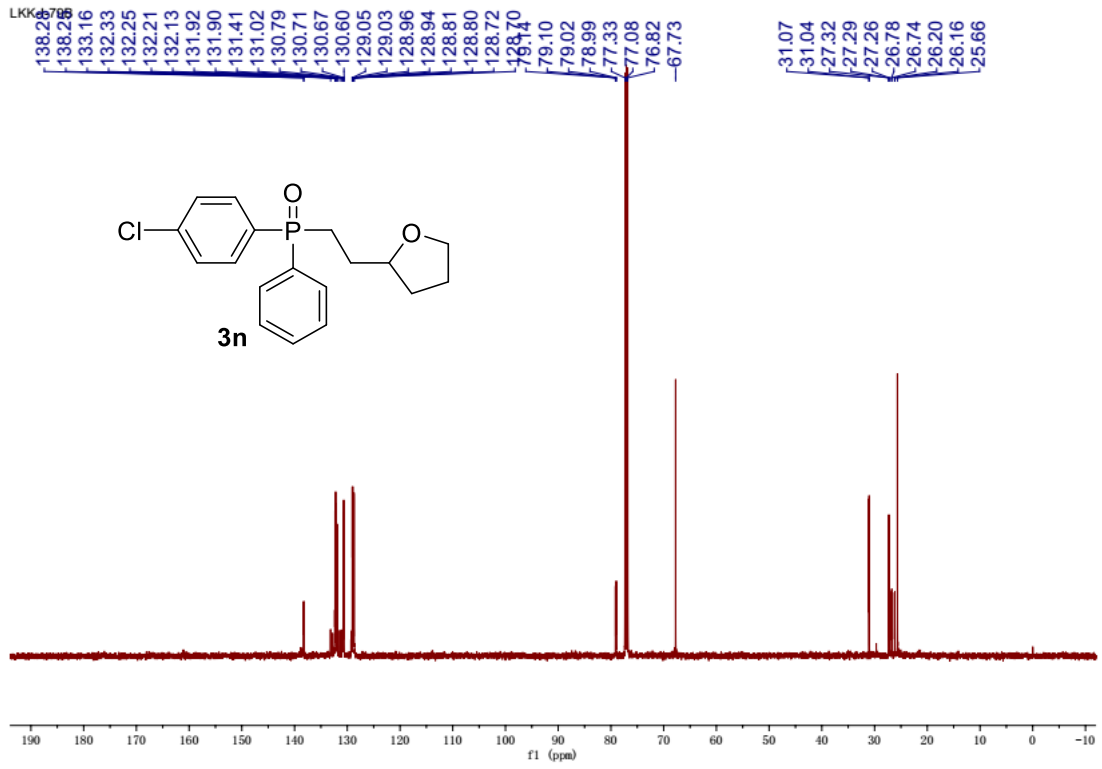
LKK-I-72A

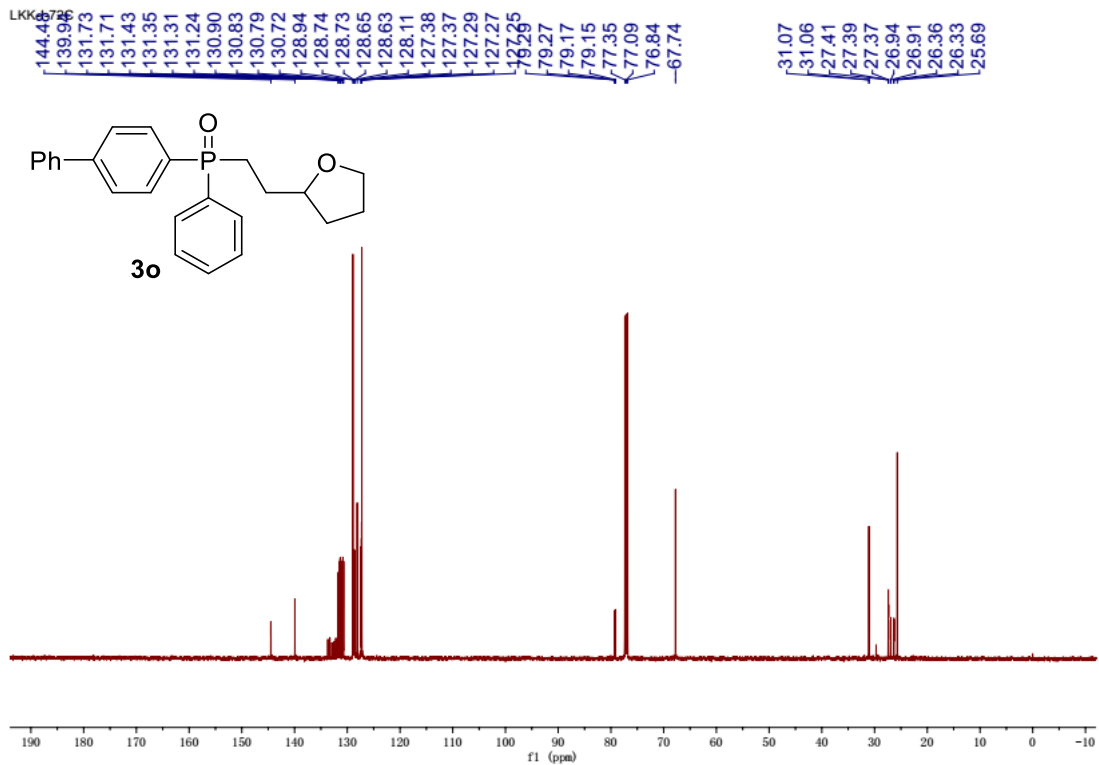
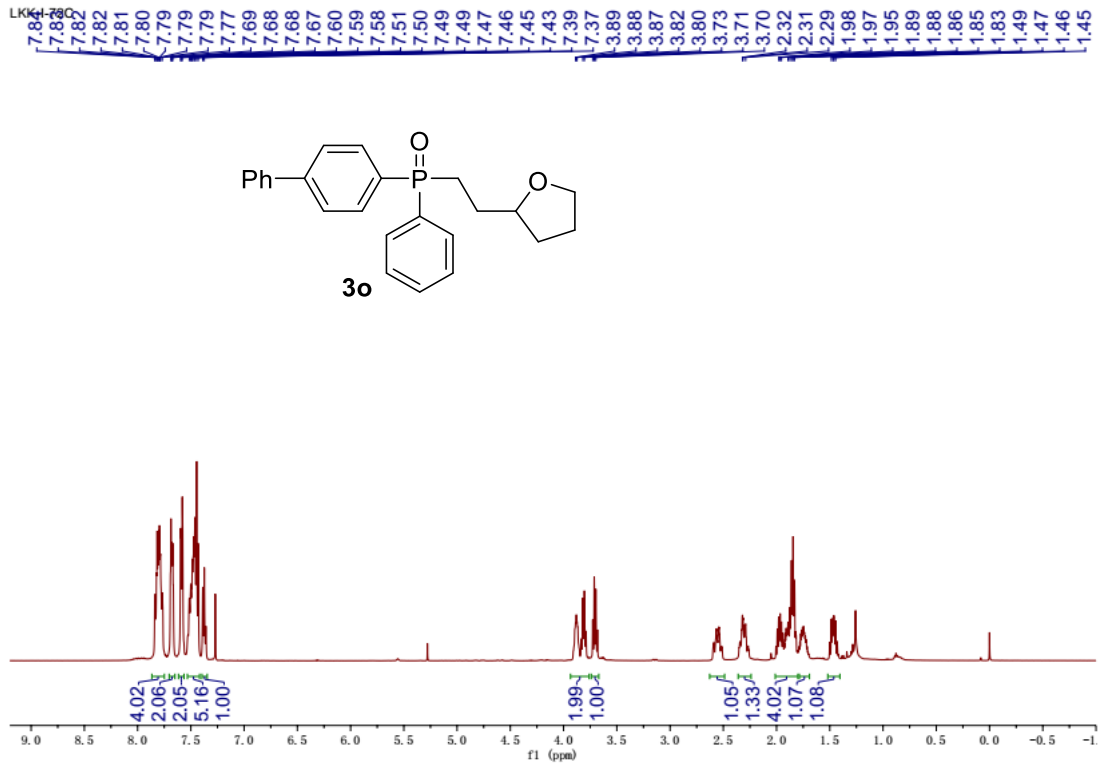
107.07
107.09



LKK-I-72B
7.77
7.77
7.77
7.74
7.73
7.73
7.73
7.72
7.72
7.71
7.71
7.71
7.70
7.70
7.69
7.68
7.68
7.67
7.66
7.52
7.51
7.51
7.49
7.49
7.48
7.48
7.47
7.47
7.46
7.46
7.45
7.45
7.45
7.44
7.44
7.43
7.43
3.81
3.81
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3.69
3.69
1.88
1.87
1.86
1.85
1.83

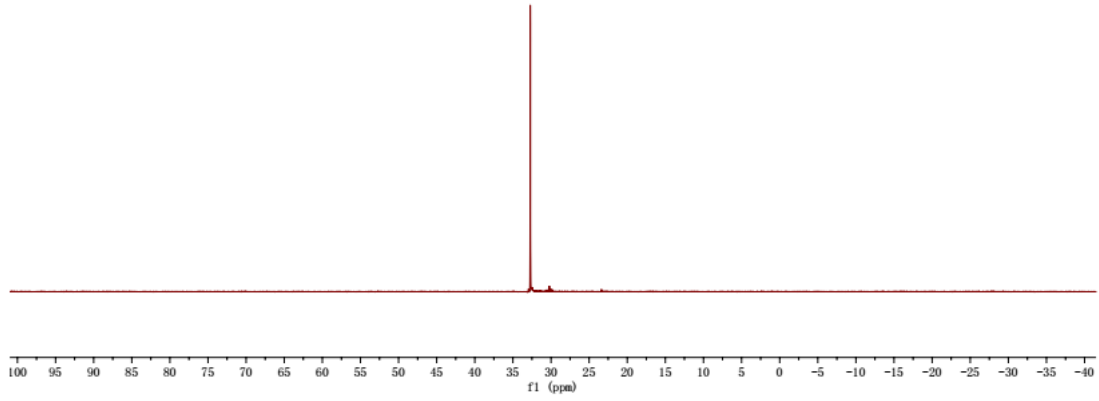
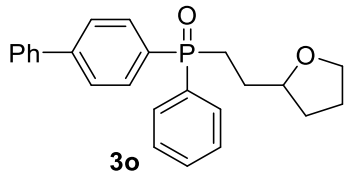




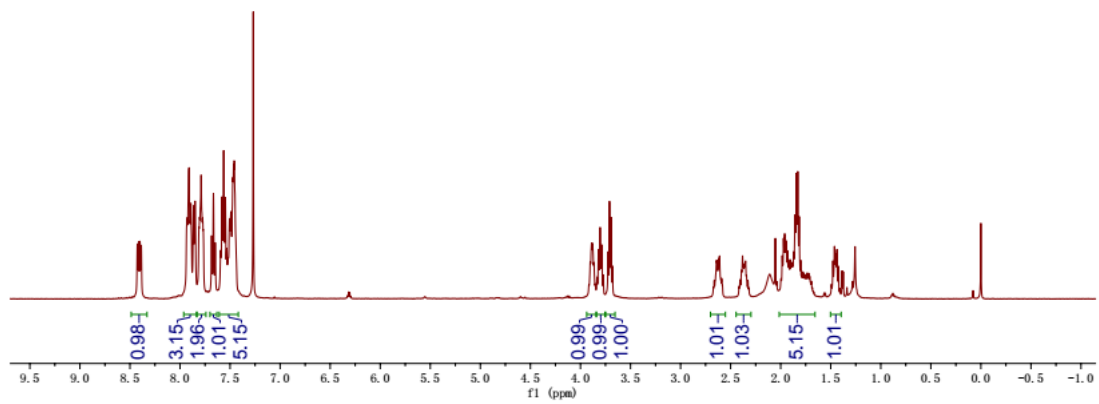
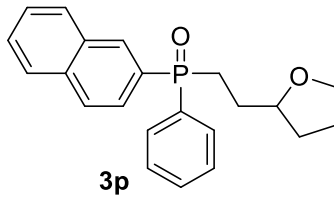


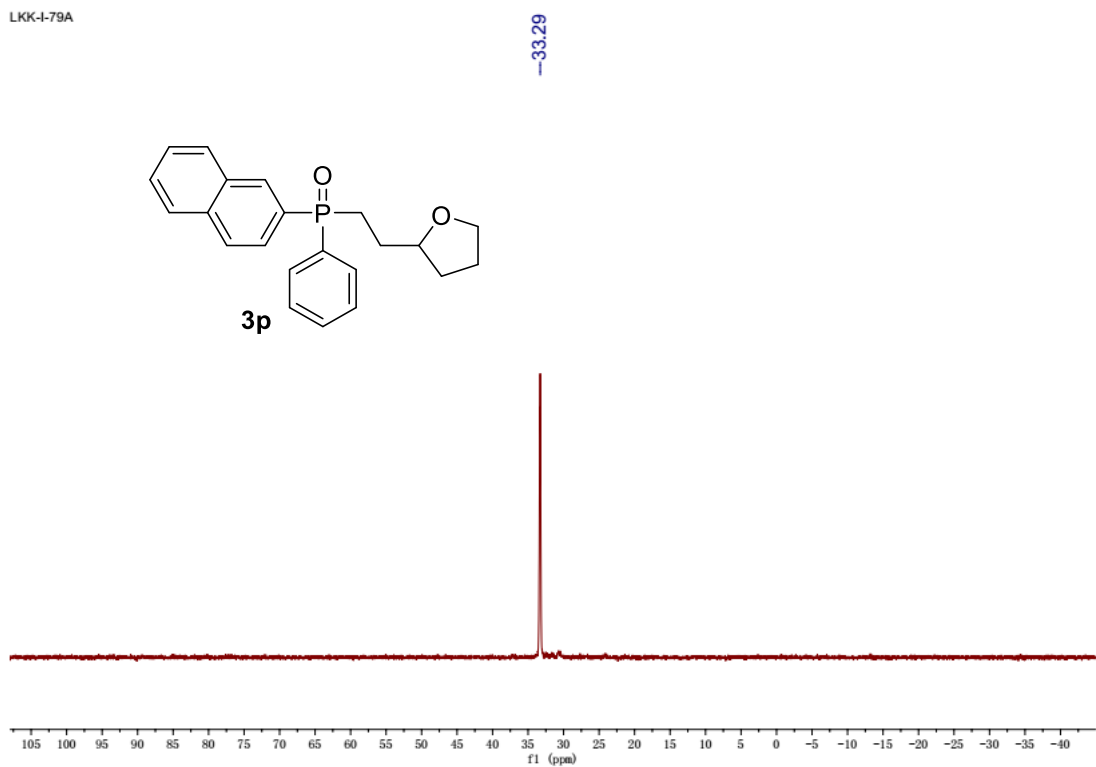
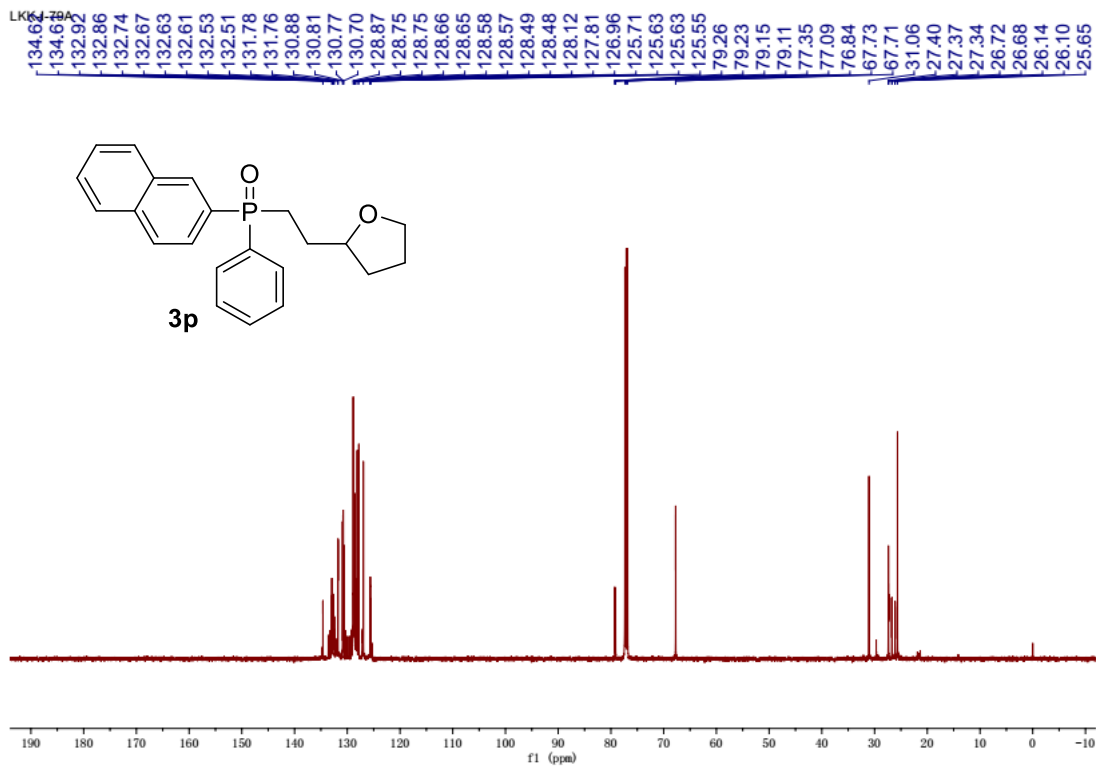
LKK-I-72C

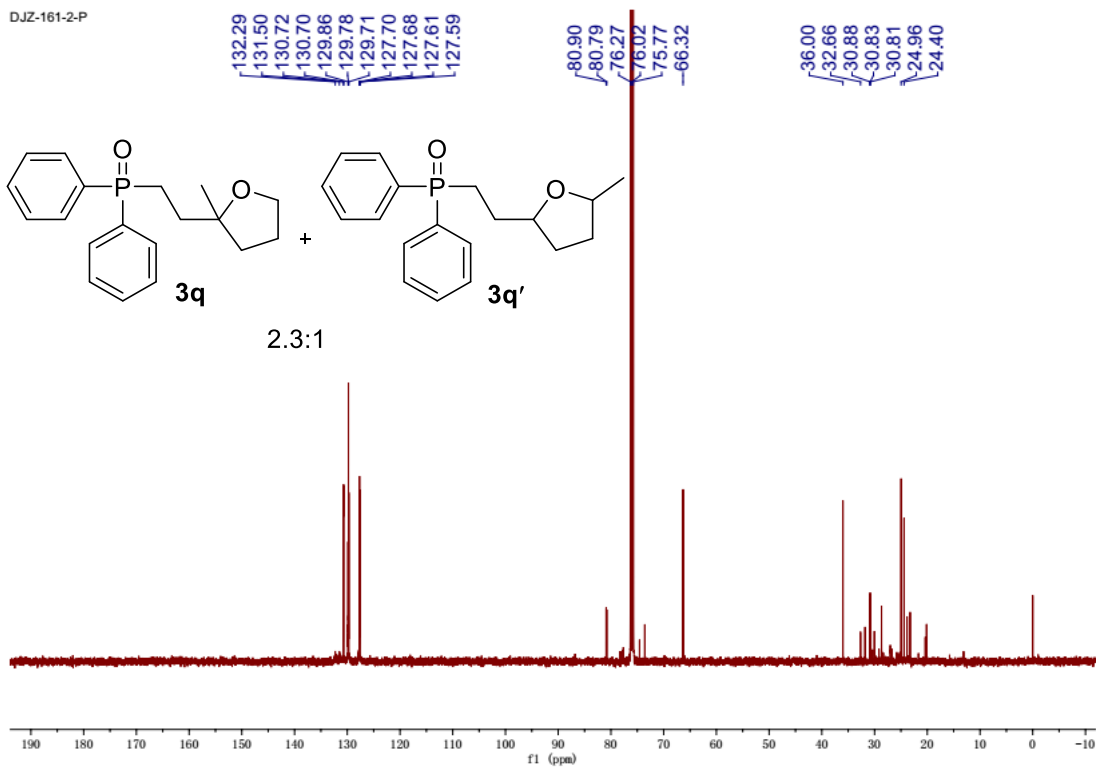
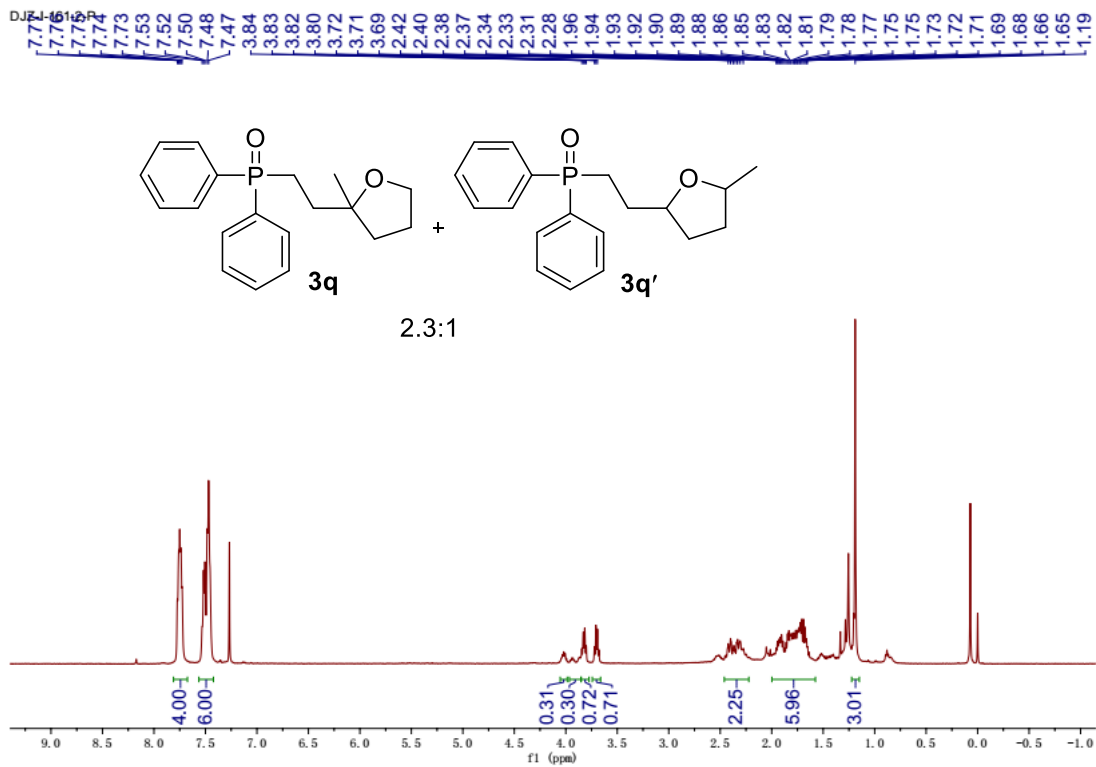
-32.72

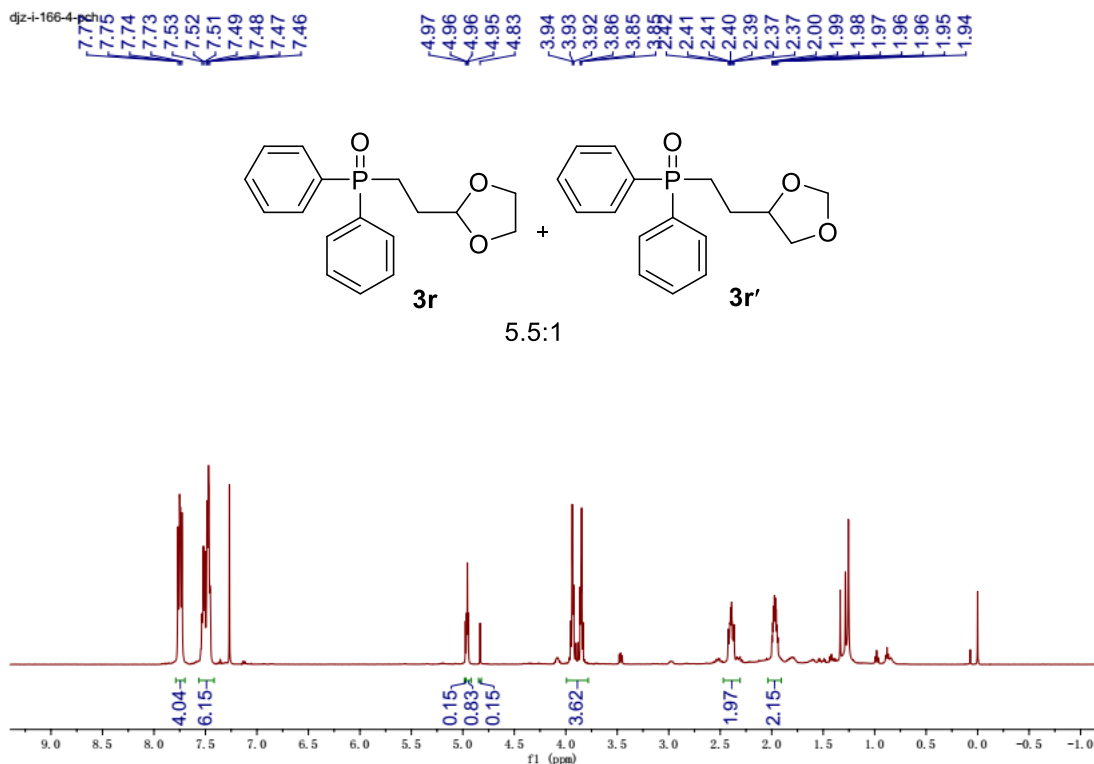
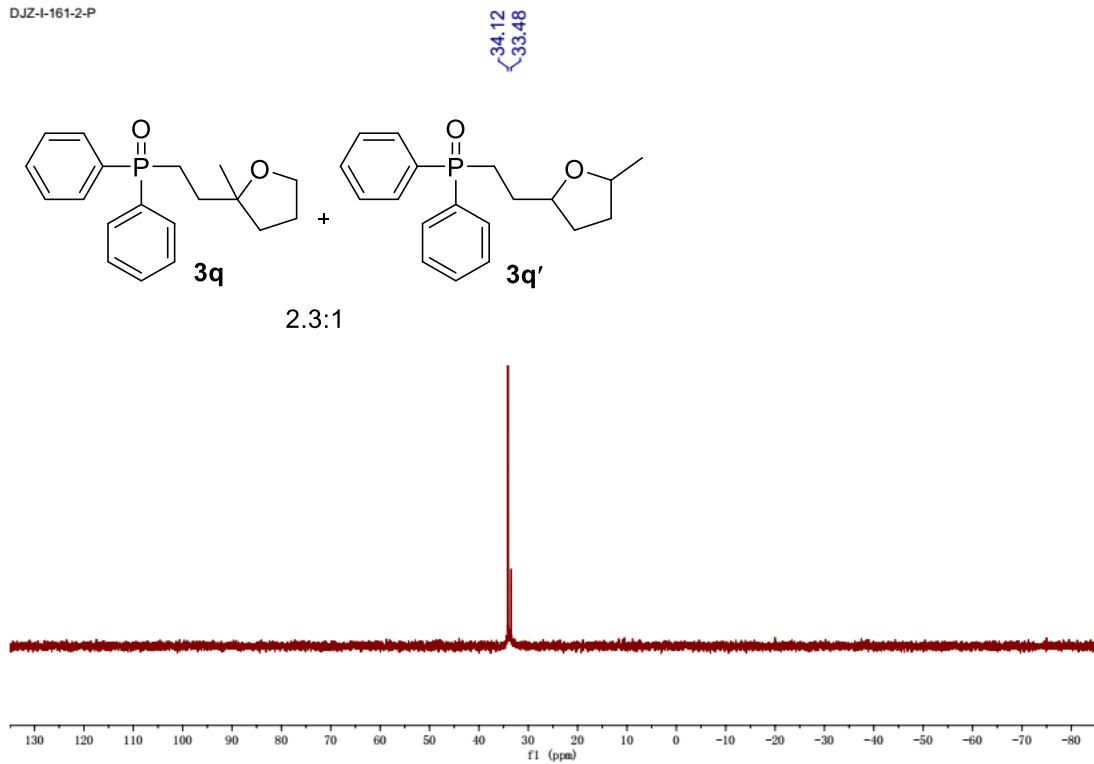


LKK-I-72A
8.43
8.41
8.40
8.39
7.93
7.91
7.89
7.86
7.85
7.81
7.80
7.79
7.77
7.77
7.68
7.67
7.65
7.59
7.58
7.56
7.55
7.53
7.51
7.49
7.47
7.46
7.46
3.89
3.88
3.82
3.80
3.79
3.72
3.71
3.69
2.38
1.98
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1.86
1.84
1.83
1.81
1.46
1.45
1.44

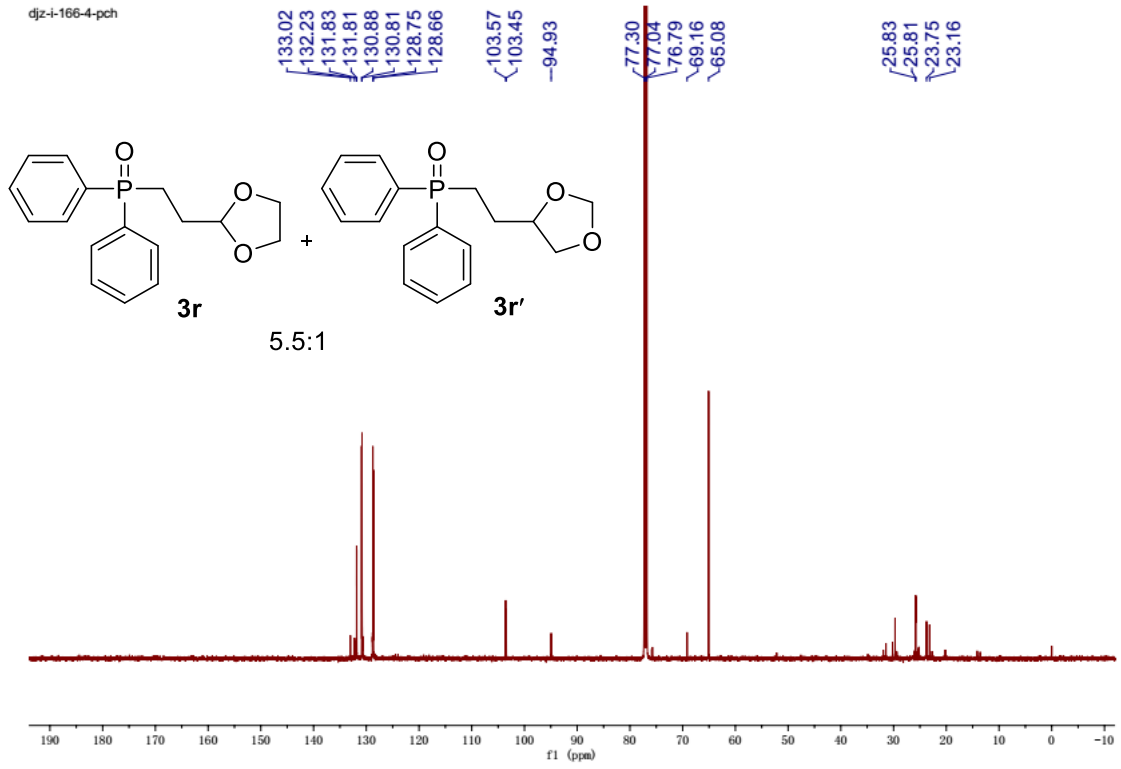




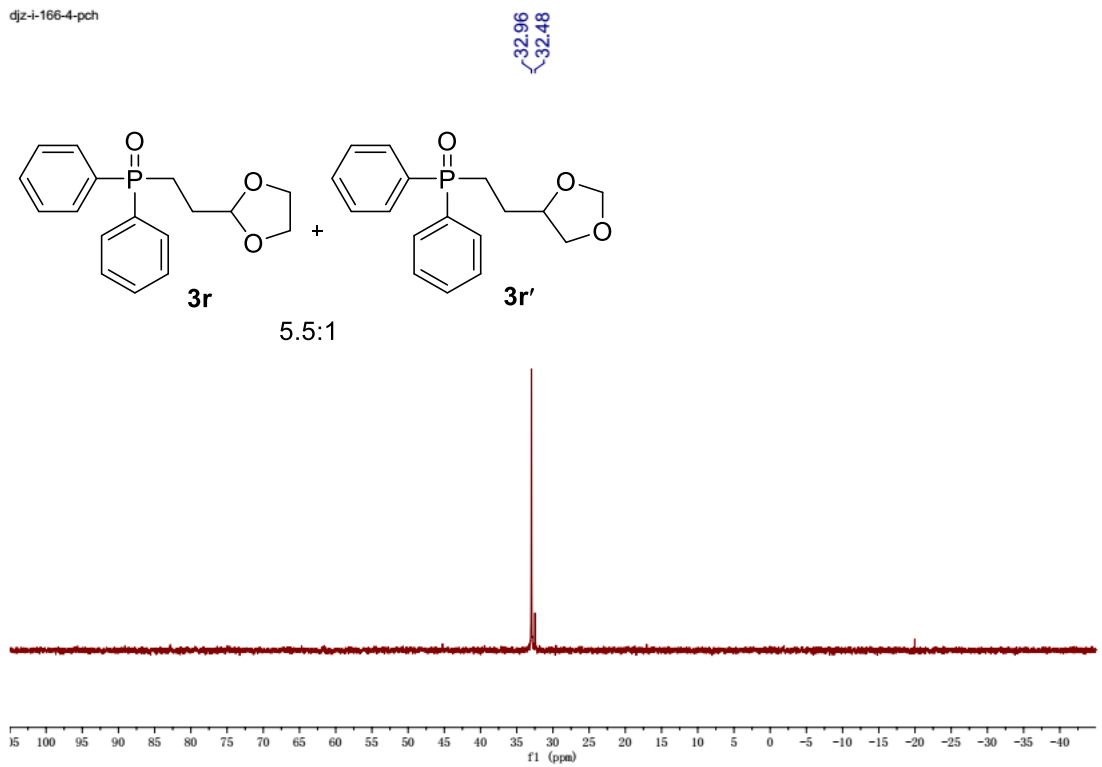




djz-i-166-4-pch



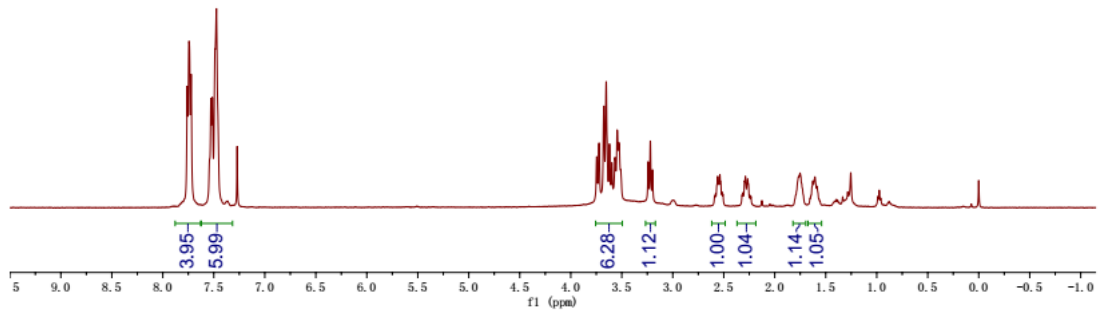
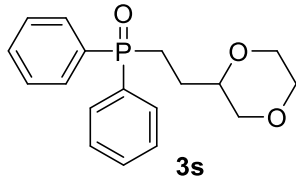
djz-i-166-4-pch



djz-i-211-2-p2

7.76
7.74
7.72
7.53
7.51
7.49
7.47

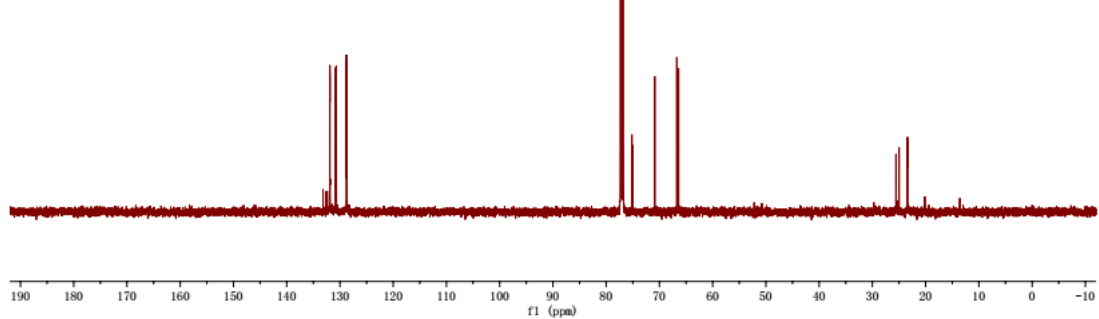
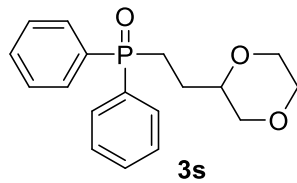
3.75
3.72
3.68
3.65
3.62
3.60
3.57
3.55
3.53
3.51
3.24
3.22
3.20
2.56
2.54
2.29
1.77
1.63
1.61
1.59

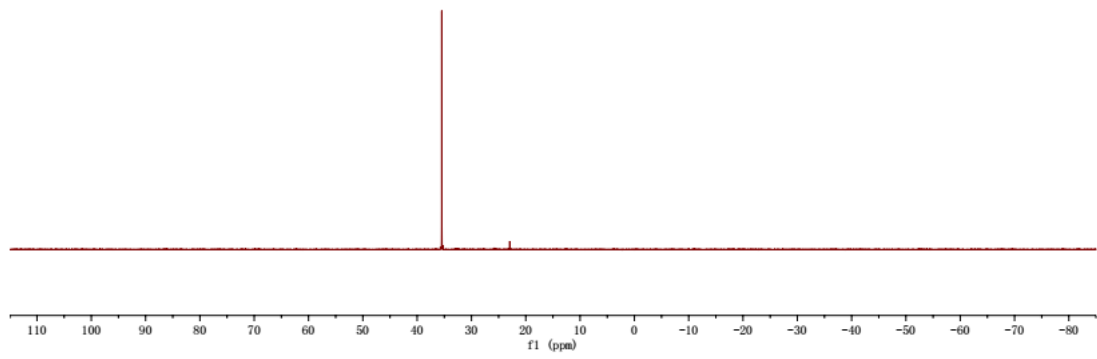
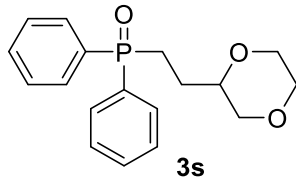


djz-i-211-2-p2

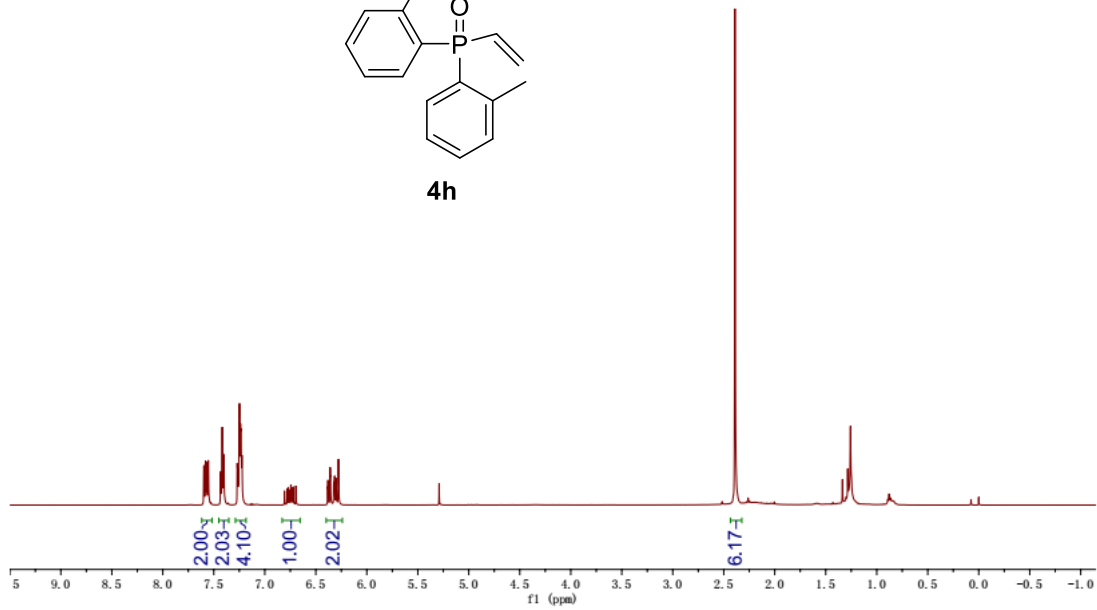
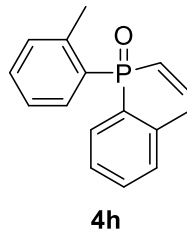
133.17
132.63
132.38
131.91
131.89
131.84
130.87
130.80
130.75
130.67
128.82
128.78
128.73
128.69

77.31
77.06
76.80
75.17
75.06
70.87
66.73
66.40
25.57
24.99
23.43
23.40





7.66
7.58
7.55
7.53
7.43
7.42
7.40
7.27
7.27
7.25
7.24
7.23
7.22
6.81
6.78
6.77
6.76
6.74
6.73
6.72
6.70
6.38
6.38
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6.36
6.32
6.32
6.32
6.30
6.30
6.28
-2.39

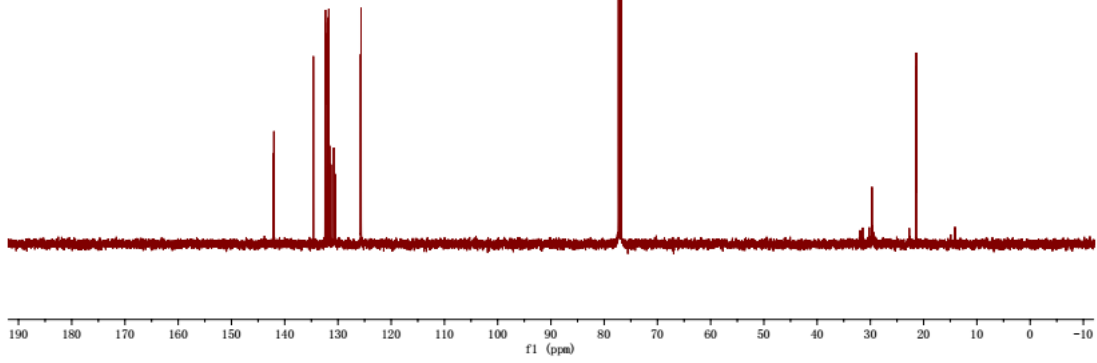
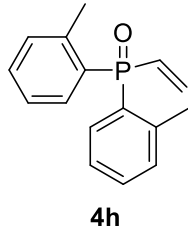


djz-i-259-1-pch

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

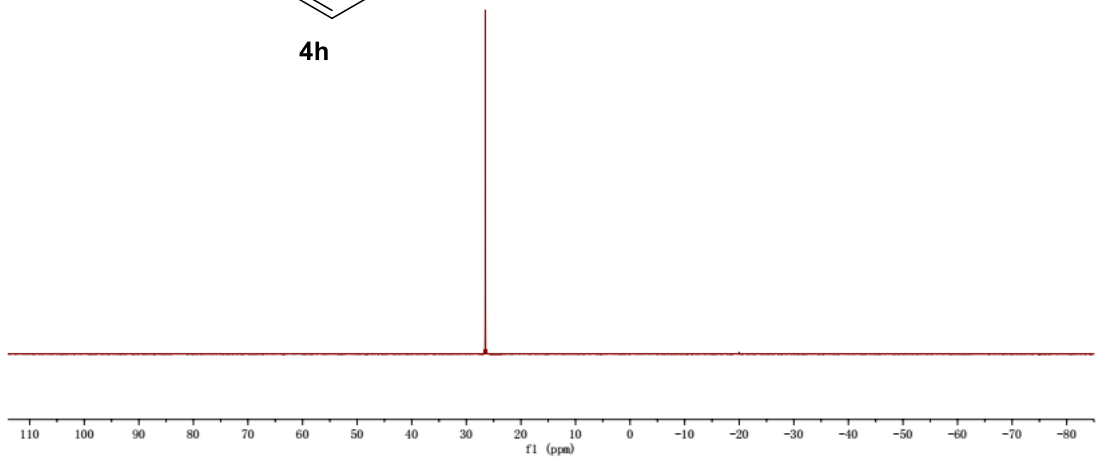
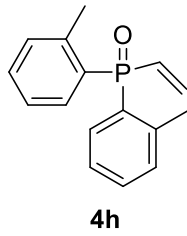
77.30
77.05
76.80

21.41
21.38



djz-i-259-1-pch

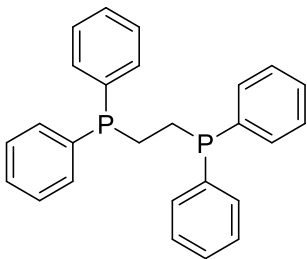
-26.52



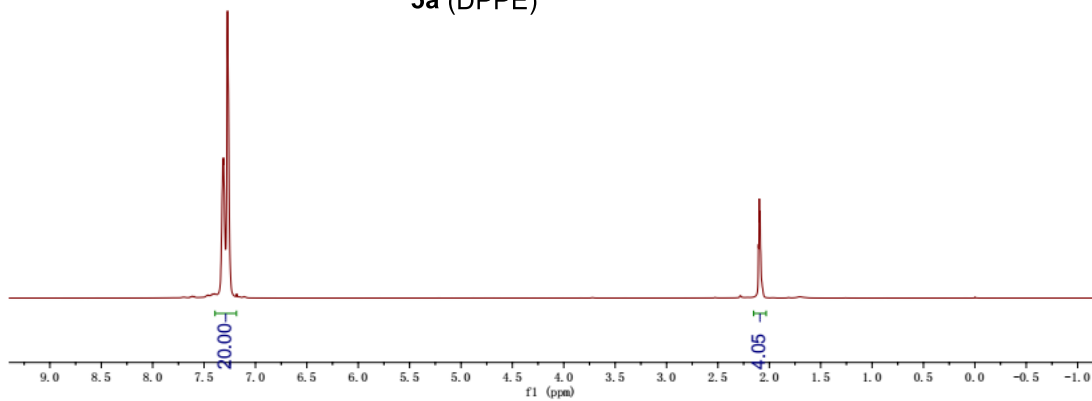
djz-i-224-2

7.32
7.31
7.27

2.10
2.10
2.09



5a (DPPE)

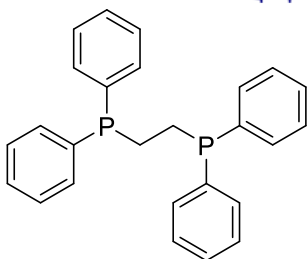


djz-i-224-2

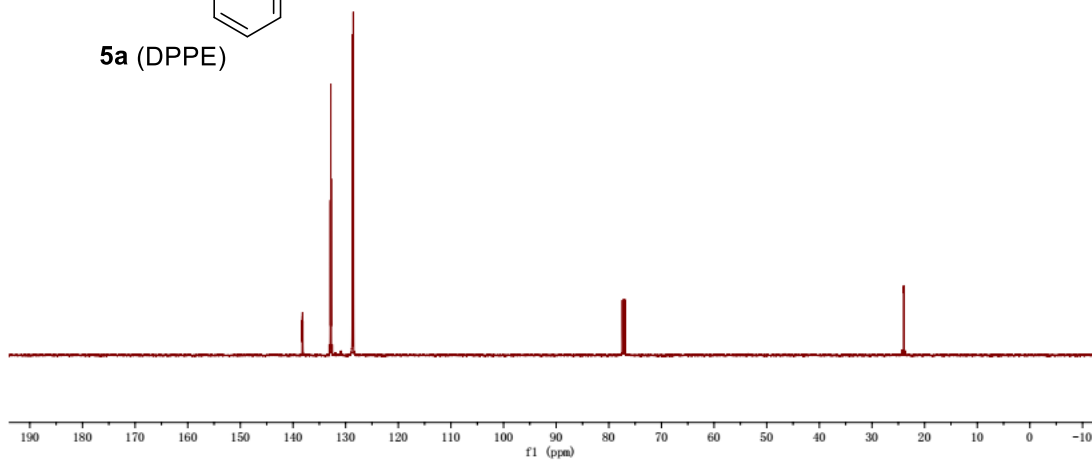
138.24
138.20
138.19
138.14
132.90
132.82
132.75
128.75
128.57
128.54
128.52

77.42
77.17
76.91

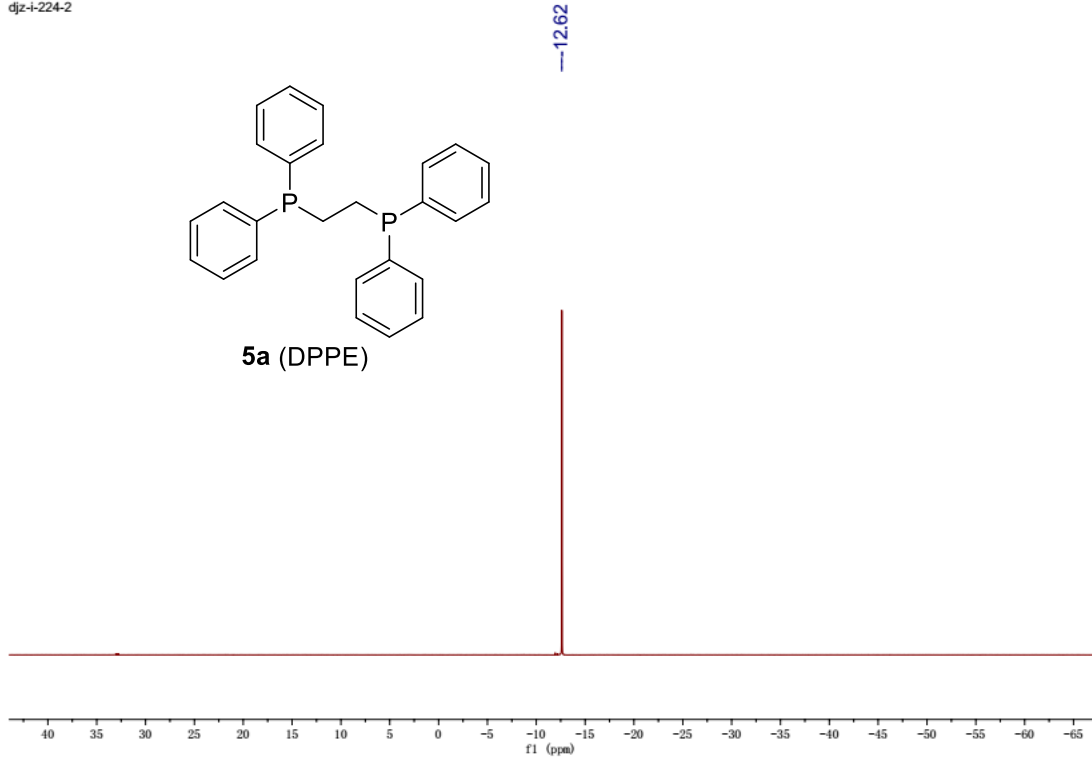
23.95
23.94



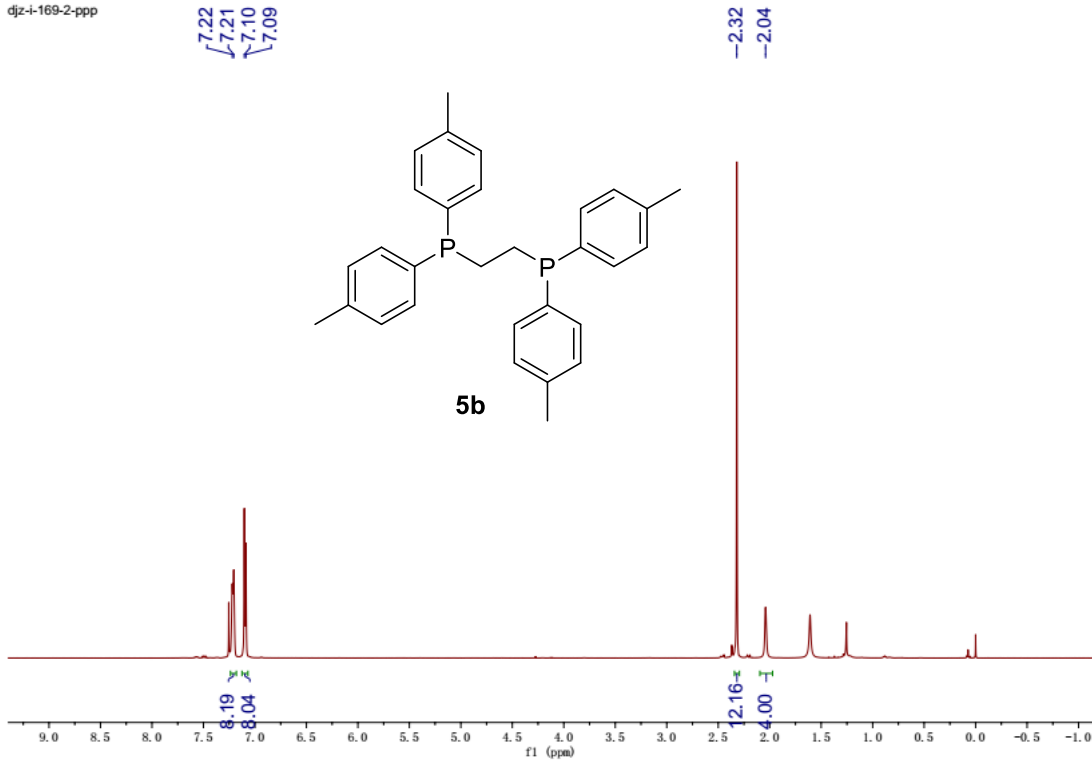
5a (DPPE)



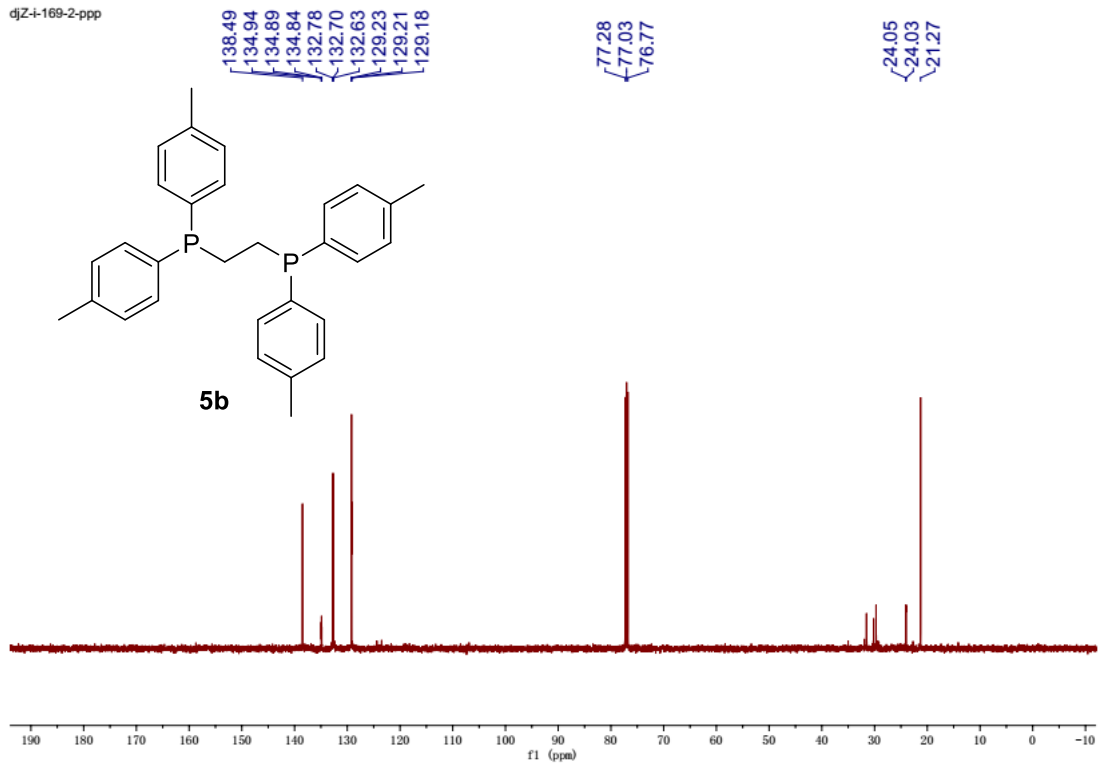
djz-i-224-2



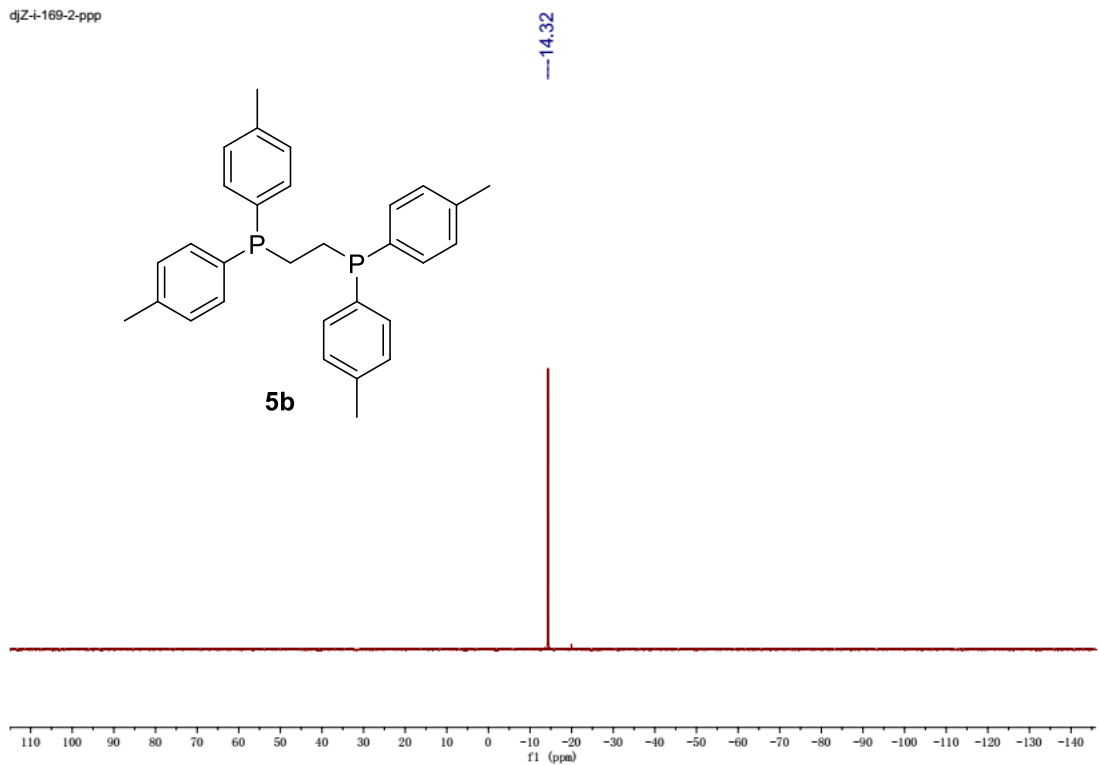
djz-i-169-2-ppp

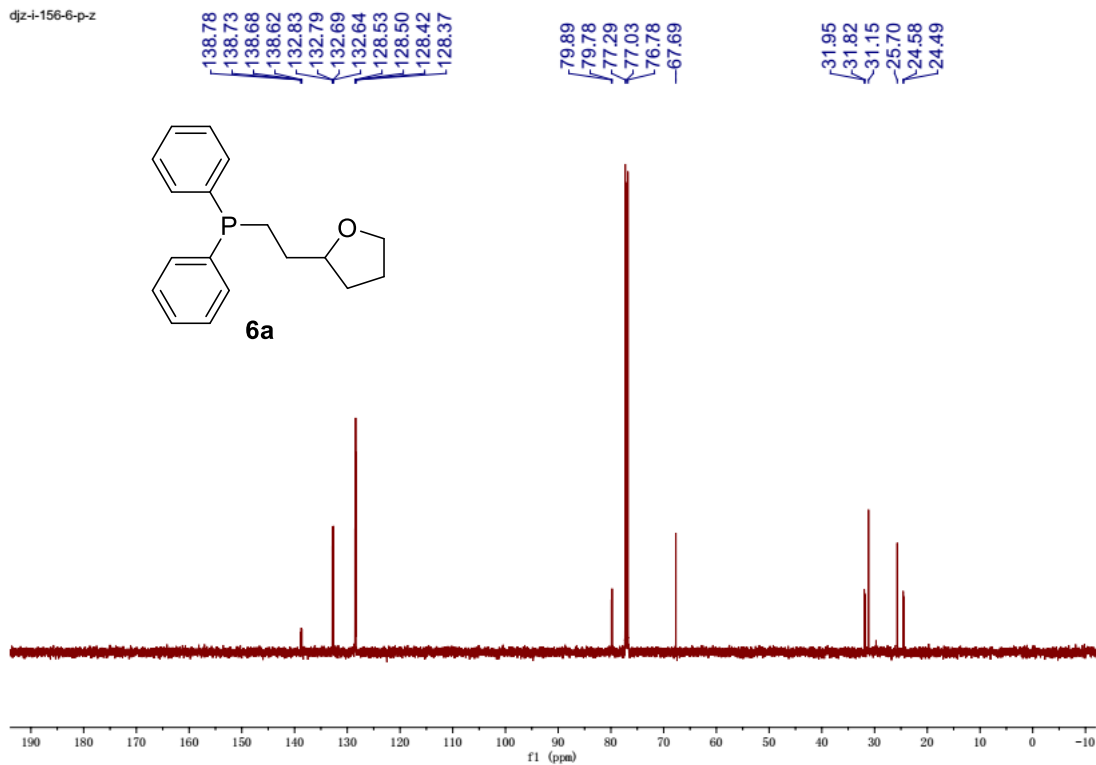
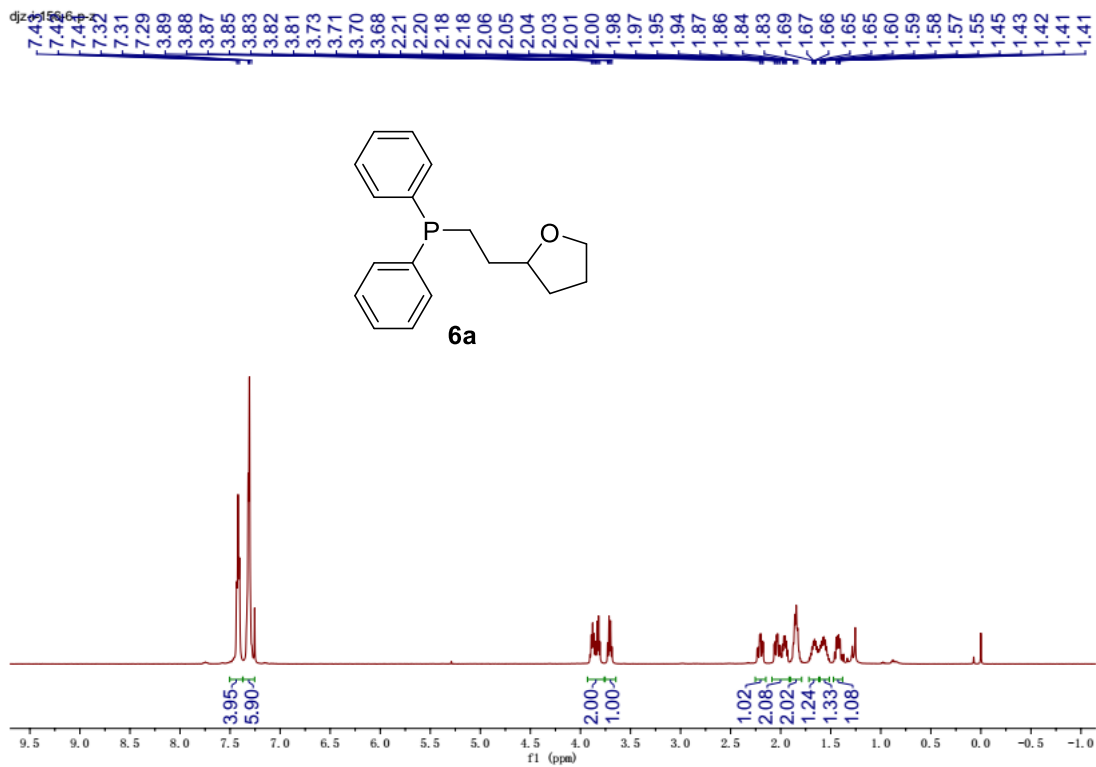


djZ-i-169-2-ppp

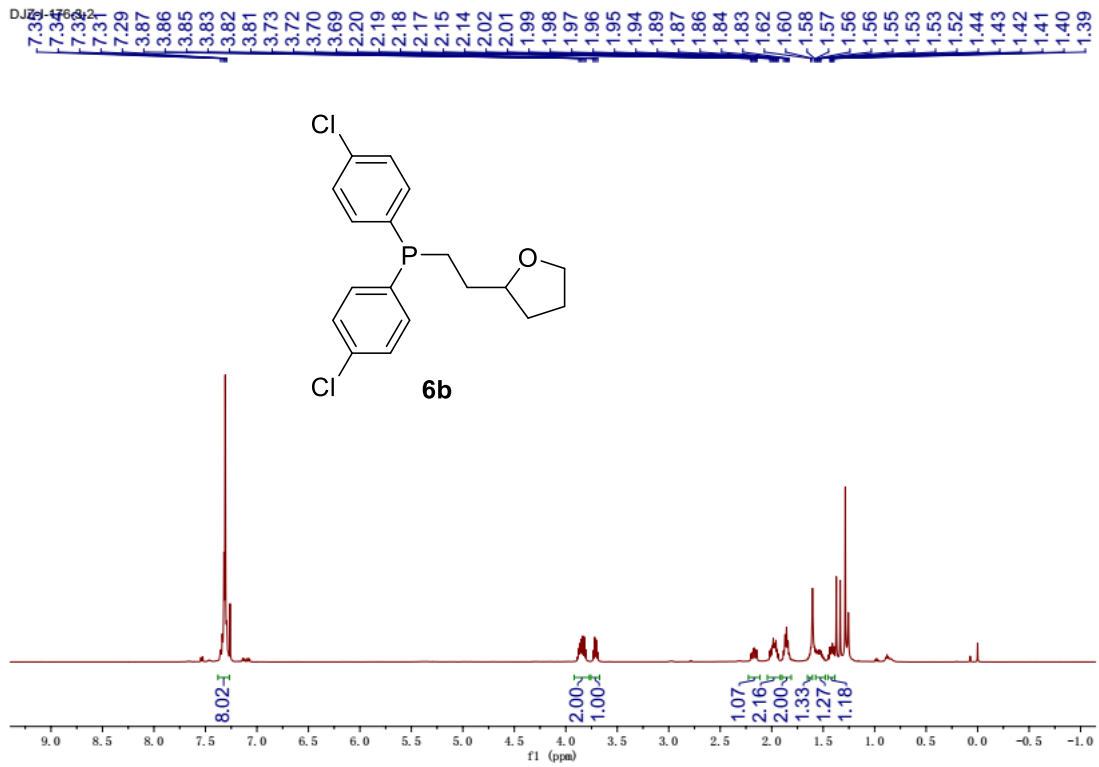
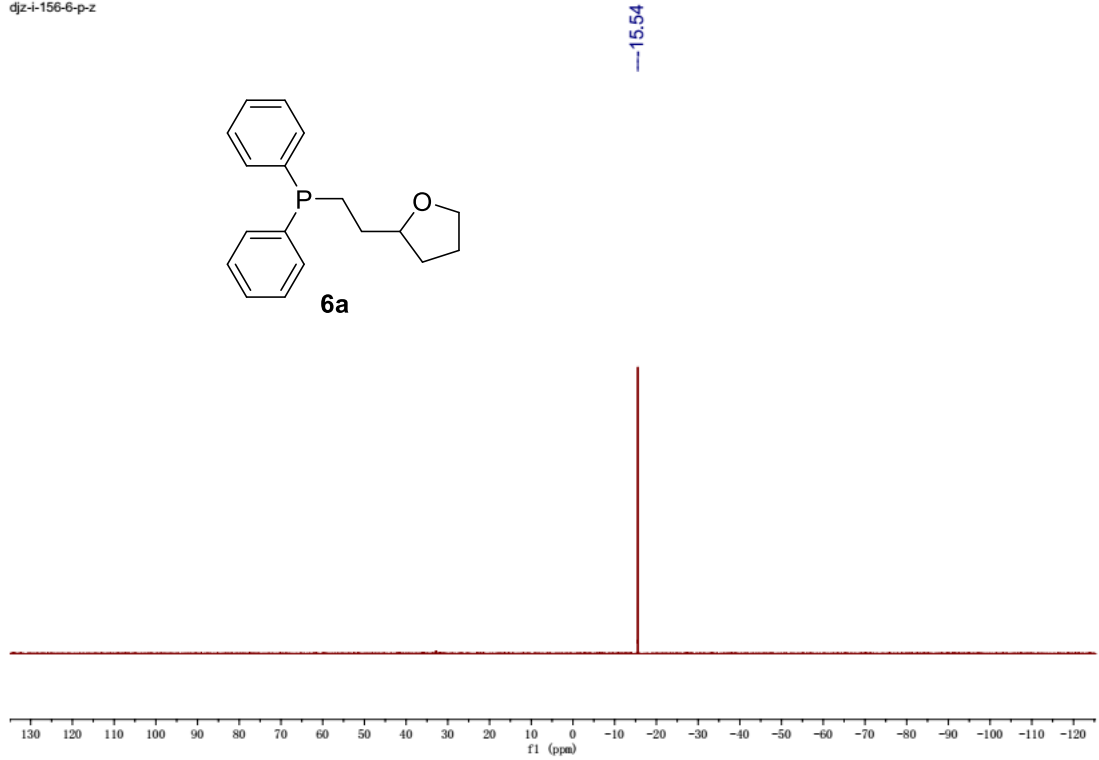


djZ-i-169-2-ppp

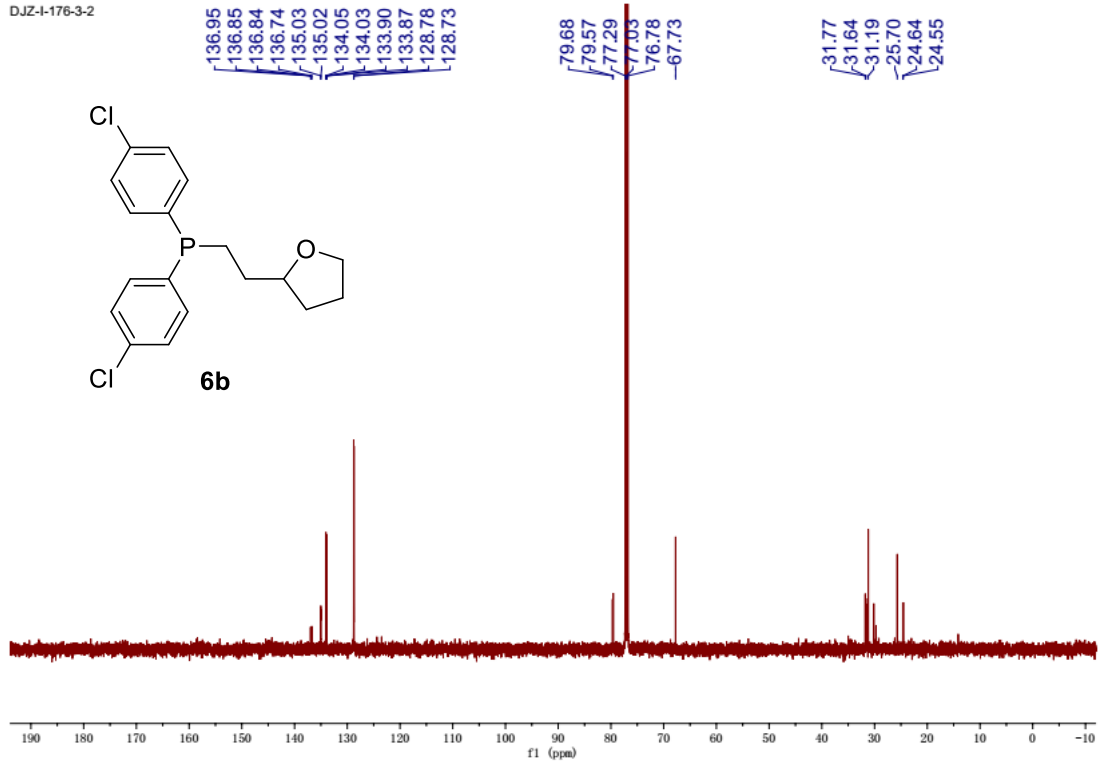




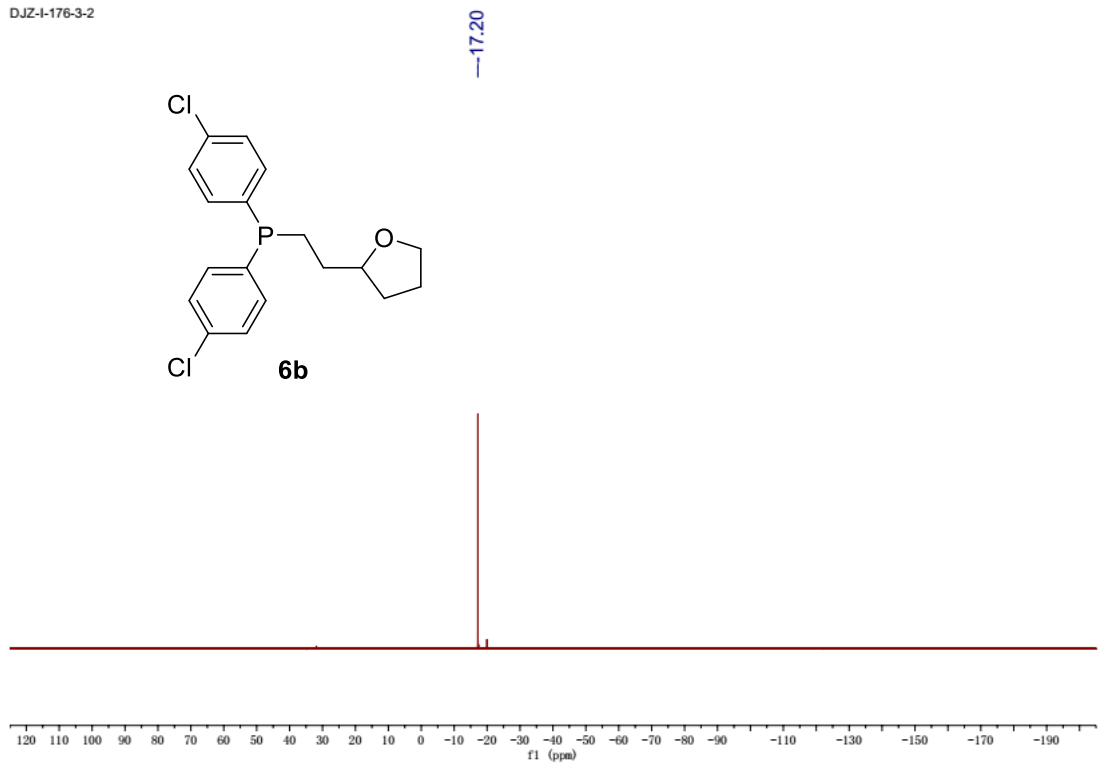
djz-1-156-6-p-z



DJZ-1-176-3-2



DJZ-1-176-3-2



8. References

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2. Y. Okugawa, Y. Hayashi, S. Kawauchi, K. Hirano and M. Miura, *Org. Lett.*, 2018, **20**, 3670-3673.
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