Supporting Information

Environmentally Sustainable Production and Application of Acyl Phosphates

CONTENTS

1. General information

The reagents used for experiments were commercially available and used as received unless otherwise noted. CH_3CN was distilled from CaH_2 under reduced pressure and stored under nitrogen. The instrument for electrolysis is dual display potentiostat (DJS-292B) (made in China). Cyclic voltammograms were obtained on an IVIUMSTAT potentiostat. The amount of electrocatalytic hydrogen evolution was measured on a gas chromatography (kexiao, GC-1690 China) (TCD detector, 13X molecular sieve column, N_2 gas carrier). GC-MS analysis was conducted on a Shimadzu GCMS-QP2010 instrument equipped with a Restec-5HT column (30 m × 0.25 mm, Hewlett-Packard). HRMS were performed by Analysis and Testing Center, Nanchang University. ^1H NMR, ^{13}C NMR and ^{31}P NMR were recorded in $CDCl_3$ on a Bruker Avance III 400 spectrometer with TMS as internal standard (400 MHz ^1H, 101 MHz ^{13}C, 162 MHz ^{31}P) at room temperature. All reactions were carried out at room temperature in air atmosphere. Column chromatography was performed on silica gel (300-400 mesh).

2. General procedure for metal-free electrocatalytic

Phosphates oxide (0.4 mmol), carboxylic acid (0.8 mmol), $^nBu_4NBr$ (0.4 mmol) and CH_3CN (8 mL) were added into oven-dried three-necked flask (25 mL) with a stir bar. The flask was equipped with platinum electrodes (10 × 10 × 0.3mm^3) as the cathode and anode. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA and air atmosphere under room temperature for 6 h. The mixture was ediluted with EtOAc (EA) and filtered through a short plug of silica gel that was then washed with EA. The combined organic phase were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with petroleum ether/ethyl acetate as the eluent (Petroleum ether (PE) /EA = 10:1).

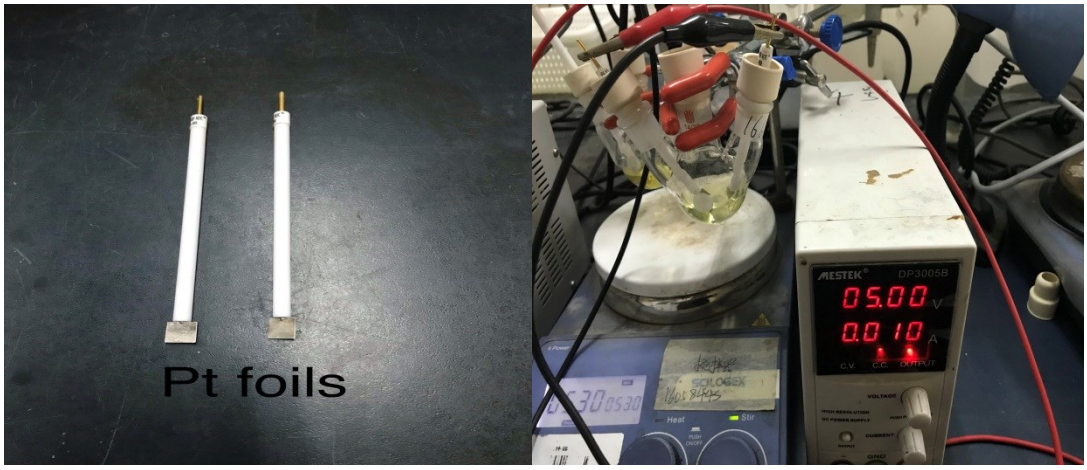
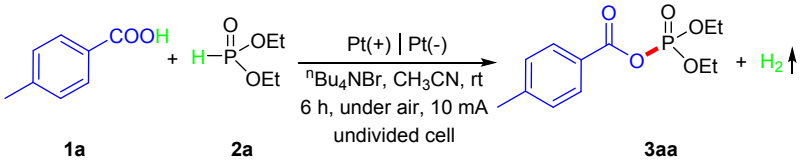


Figure 1

3. Optimization of the Reaction Conditions

Table 1. Screening of amount of electroytes[a]



1a **2a** **3aa**

Entry	$^{n}Bu_4NBr$ (X mol%)	Yield[b] (%)
1	none	-
2	50	61
3	100	84
4	150	81
5	200	78

[a] Reaction conditions: **1a** (0.80 mmol), **2a** (0.40 mmol), solvent (8 mL) in an undivided cell with two Pt foils (each 10 x 10 x 0.3 mm^3) at room temperature for 6 h, air, 10 mA; [b] Isolated yields.

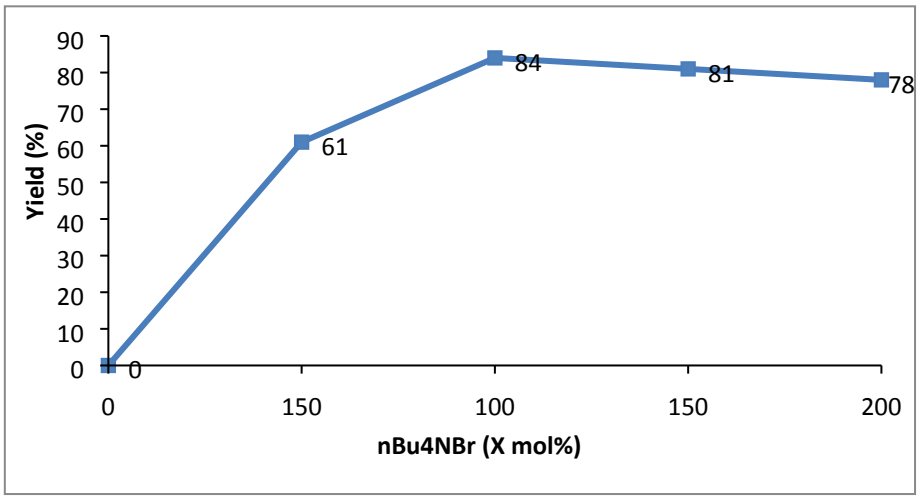
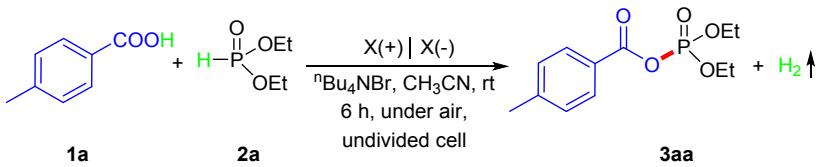


Table 2. Screening of the electrode [a]

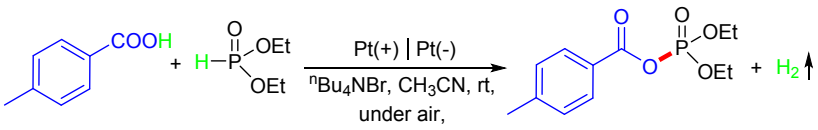


1a **2a** **3aa**

Entry	electrode	Yield[b] (%)
1	Pt(+)/Pt(-)	84
2	C(+)/Pt(-)	72
3	Pt(+)/C(-)	60
4	C(+)/C(-)	27
5	Pt(+)/Glassy C(-)	23
6	Glassy C(+)/Pt(-)	50

[a] Reaction conditions: **1a** (0.80 mmol), **2a** (0.40 mmol), electroyte (0.4 mmol), solvent (8 mL) in an undivided cell at room temperature for 6 h, 10 mA air; [b] Isolated yields.

Table 3. Screening of reaction time [a]

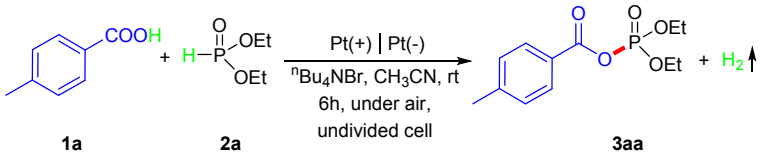


1a **2a** **3aa**

Entry	reaction time (h)	Yield[b] (%)
1	4	77
2	6	84
3	8	69

[a] Reaction conditions: **1a** (0.80 mmol), **2a** (0.40 mmol), electroyte (0.4 mmol), solvent (8 mL) in an undivided cell with two Pt foils (each 10 x 10 x 0.3 mm^3) at room temperature, air;
[b] Isolated yields.

Table 4. Screening of reaction solvents [a]

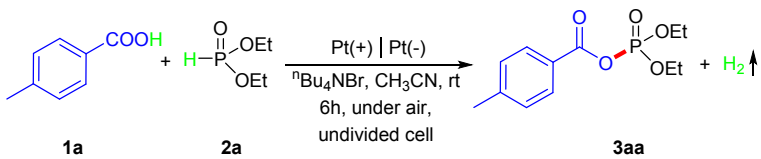


1a **2a** **3aa**

Entry	solvent	Yield[b] (%)
1	CH_3OH	trace
2	CH_3CN	84
3	DCM	30
4	DMF	34
5	DCE	21
6	DMSO	17
7	THF	trace
8	NMP	trace

[a] Reaction conditions: **1a** (0.80 mmol), **2a** (0.40 mmol), electroyte (0.4 mmol), solvent (8 mL) in an undivided cell with two Pt foils (each 10 x 10 x 0.3 mm^3) at room temperature for 6h, air;
[b] Isolated yields.

Table 5. Screening of electrolytes [a]



1a **2a** **3aa**

Entry	electrolyte	Yield[b] (%)
1	$^nBu_4NBr$	84
2	$^nBu_4NCl$	18
3	$^nBu_4NI$	62
4	$^nBu_4NBF_4$	-
5	$LiClO_4$	-
6	NH_4Br	18
7	KBr	30
8	NaBr	32

[a] Reaction conditions: **1a** (0.80 mmol), **2a** (0.40 mmol), electroyte (0.4 mmol), solvent (8 mL) in an undivided cell with two Pt foils (each 10 x 10 x 0.3 mm^3) at room temperature for 6h, air;
[b] Isolated yields.

4. Gram-scale synthesis of 3a

Diethyl phosphite **2a** (4 mmol), 4-Methylbenzoic acid **1a** (8 mmol), $^{n}Bu_4NBr$ (4 mmol) and CH_3CN (80 mL) were added into oven-dried three-necked flask (250 mL) with a stir bar. The flask was equipped with platinum electrodes (10 × 10 × 0.3mm^3) as the cathode and anode. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA and air atmosphere under room temperature for 30 h. The mixture was diluted with EtOAc (EA) and filtered through a short plug of silica gel that was then washed with EA. The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with petroleum ether/ethyl acetate as the eluent (Petroleum ether (PE) /EA = 10:1) to afford 0.849 g (78%) of the product **3a**. The Faradic efficiency of this reaction is 55.75%.

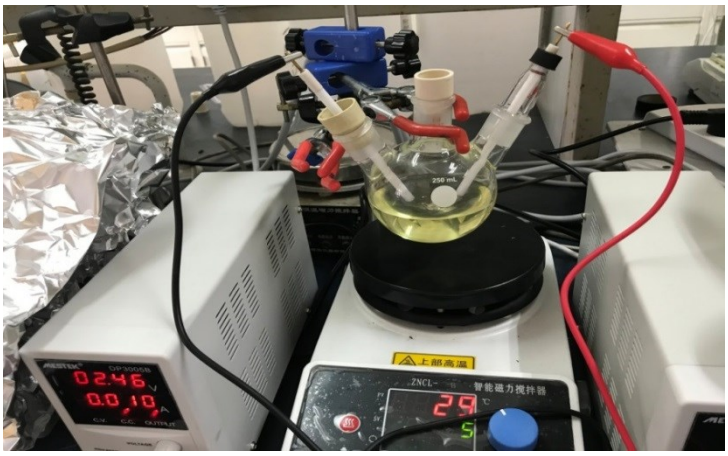


Figure 2

5. Free radical trapping experiment

5.1. radical 1

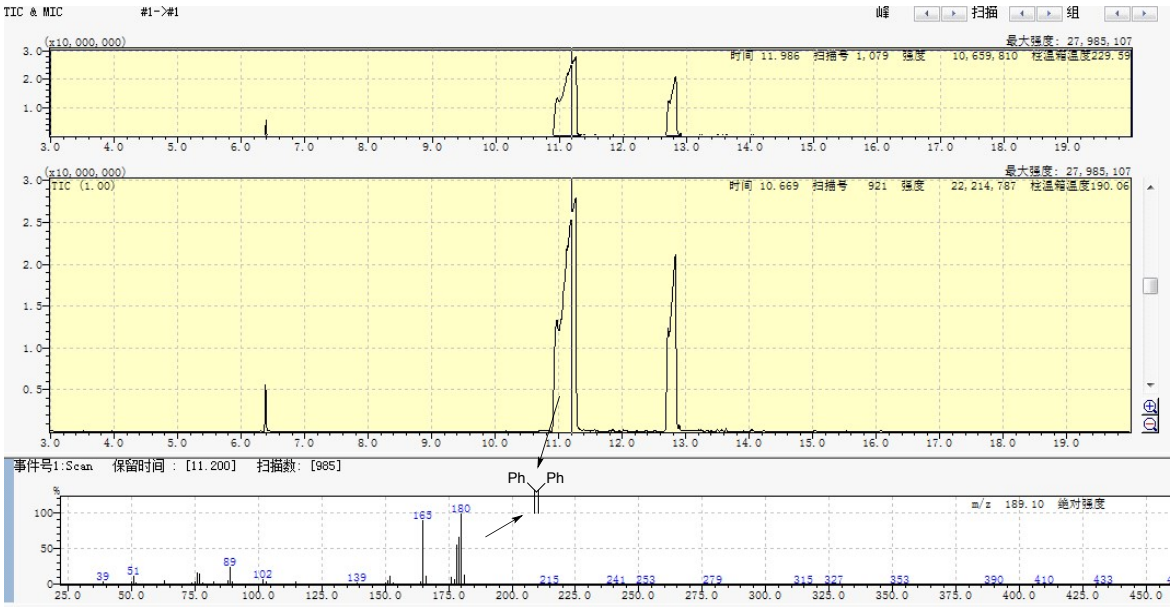


Figure 3

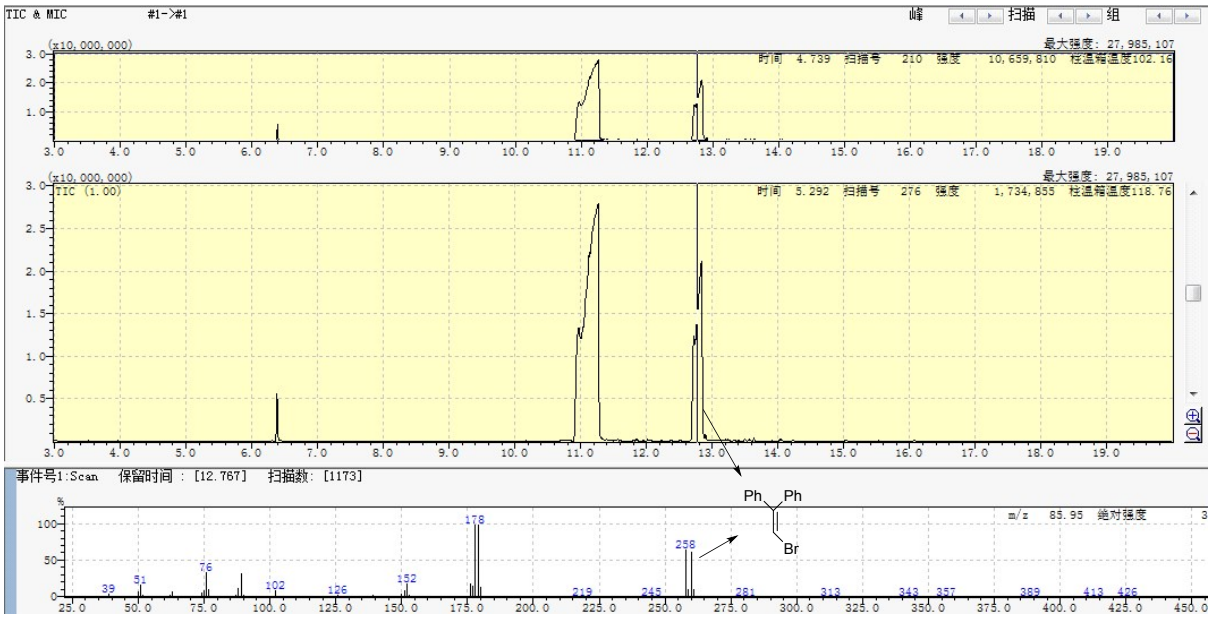


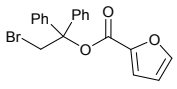
Figure 4

Diethyl phosphite (0.4 mmol), 4-Methylbenzoic acid (0.8 mmol), $^{n}Bu_4NBr$ (0.4 mmol), DPE (0.8 mmol, 2.0 equiv.) and CH_3CN (8 mL) were added into oven-dried three-necked flask (25 mL) with a stir bar. The flask was equipped with platinum electrodes (10 × 10 × 0.3mm^3) as the cathode and anode. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA and air atmosphere under room temperature for 6 h. The result was purified by silica gel column chromatography with petroleum ether as the eluent, but the mixture of DPE and DPE-Br adduct cannot be separated. GC-MS analysis of the products after TCL separation revealed DPE (11.200 min) (mass weight: 180) and DPE-Br adduct (12.767 min) (mass weight: 258). This shows the presence of Br radicals in this system.

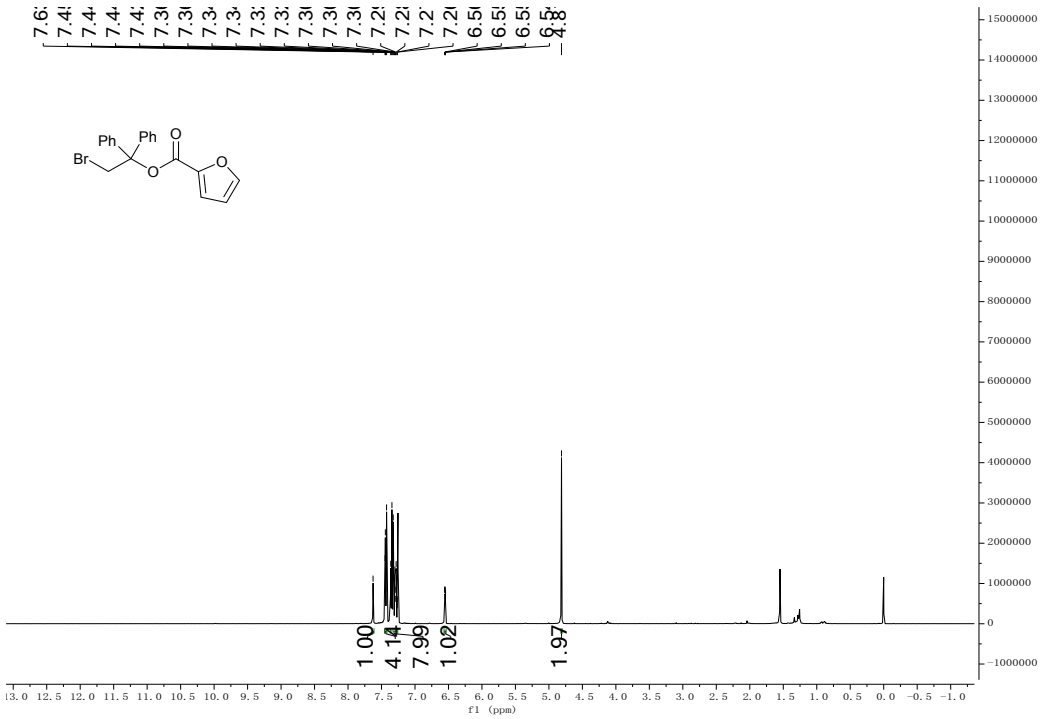
5.2. radical 2

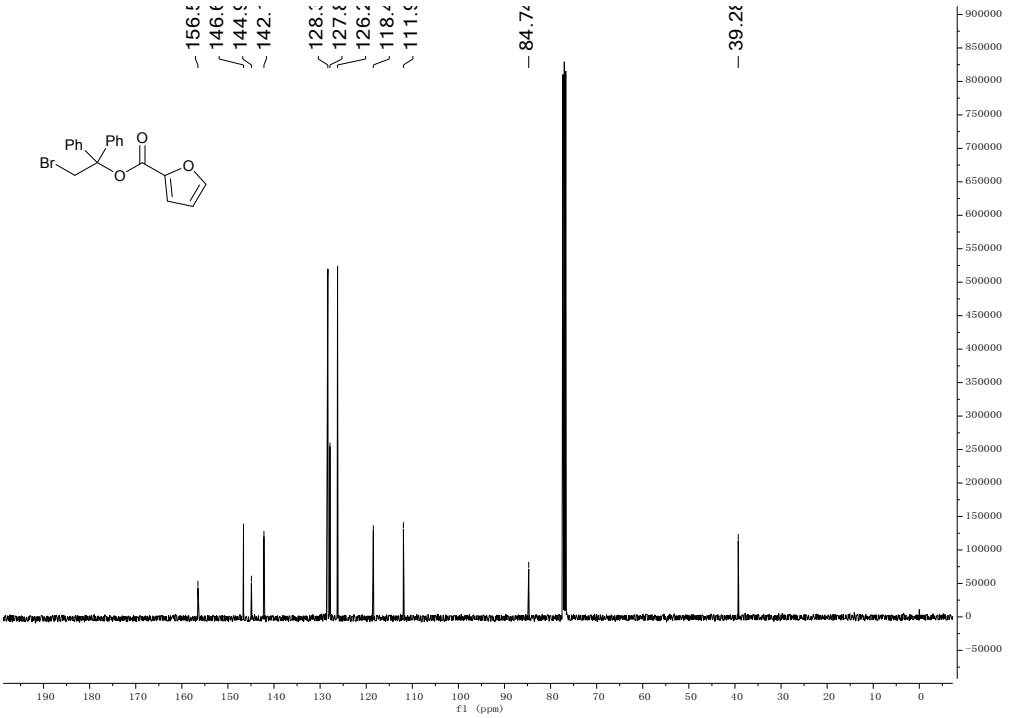
Diethyl phosphite (0.4 mmol), 2-Furoic acid (0.8 mmol), $^{n}Bu_4NBr$ (0.4 mmol), DPE (0.8 mmol, 2.0 equiv.) and CH_3CN (8 mL) were added into oven-dried three-necked flask (25 mL) with a stir bar. The flask was equipped with platinum electrodes (10 × 10 × 0.3mm^3) as the cathode and anode. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA and air atmosphere under room temperature for 6 h.

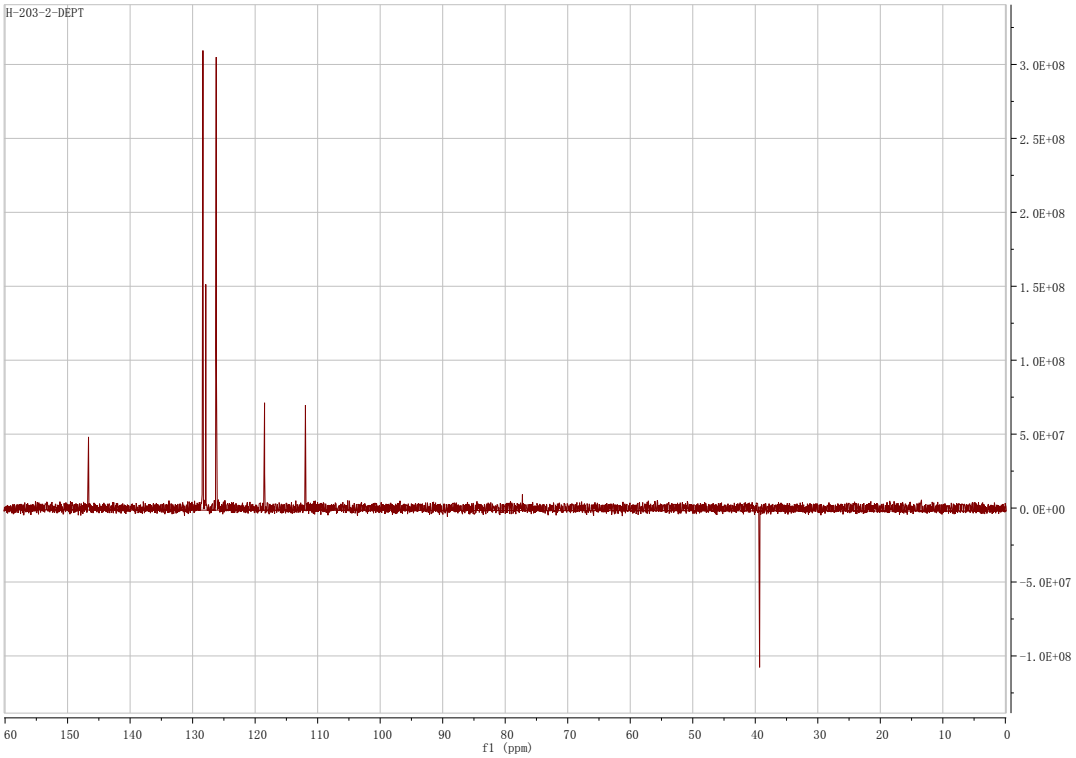
2-bromo-2,2-diphenylethyl furan-2-carboxylate (6): White solid.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.46 – 7.42 (m, 4H), 7.37 – 7.26 (m, 8H), 6.55 (dd, J = 3.5, 1.7 Hz, 1H), 4.81 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.52 (s), 146.64 (s), 144.92 (s), 142.20 (s), 128.34 (s), 127.88 (s), 126.23 (s), 118.47 (s), 111.94 (s), 84.75 (s), 39.28 (s); $C_{19}H_{15}BrO_3$ $[M+H]^+$: 371.0277; found: 371.0287.


Ph
Ph
O
Br
O
O
1.00
4.14
7.99
1.02
1.97
f1 (ppm)


Ph
Ph
O
Br
O
O
84.7
39.2
f1 (ppm)



6. General procedures for cyclic voltammetry (CV).

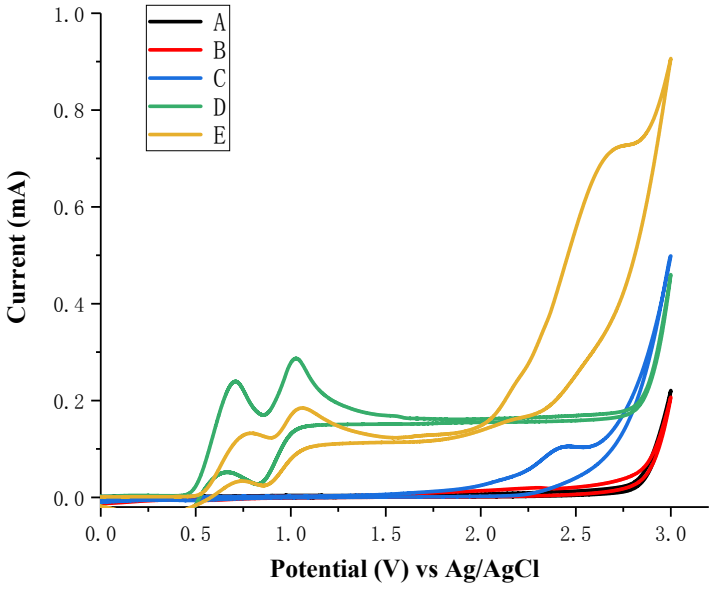


Figure 5

Figure 5. Cyclic voltammograms of reactants and the mixtures in 0.1 M $LiClO_4/CH_3CN$ using a Pt disk working electrode (diameter, 3 mm). Pt wire as counter; Ag/AgCl as reference electrode, at 100 mV/s scan rate: (A) background; (B) **2a** (0.05 M); (C) **1a** (0.05 M); (D) $^nBu_4NBr$ (0.02 M); (E) **1a** (0.05 M), **2a** (0.05 M), $^nBu_4NBr$ (0.02 M).

Pt disk as working electrode

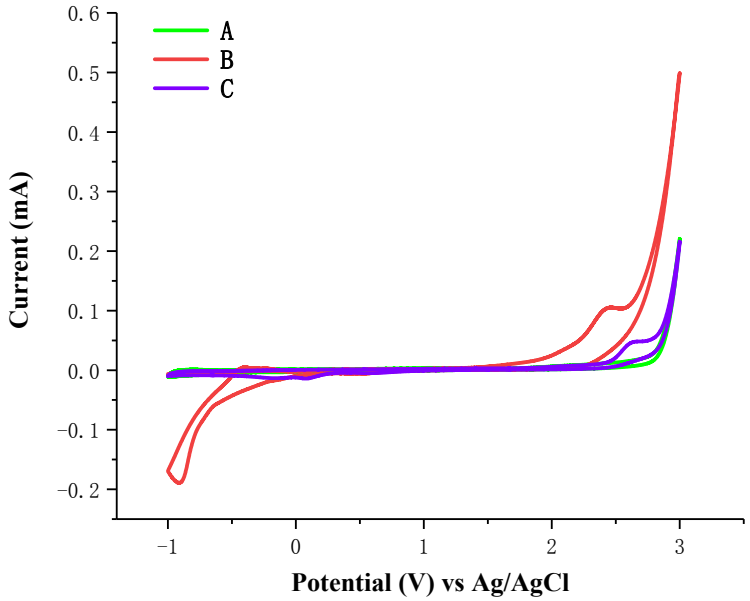


Figure 6

Figure 6. Cyclic voltammograms of reactants and the mixtures in 0.1 M $LiClO_4/CH_3CN$ using a Pt disk working electrode (diameter, 3 mm). Pt wire as counter; Ag/AgCl as reference electrode, at 100 mV/s scan rate: (A) background; (B) **1a** (0.05 M); (C) Sodium benzoate (0.05 M).

CV was performed in a three-electrode cell connected to a Schlenk line under room temperature. platinum disk electrode was used as working electrode, and platinum wire was employed as counter electrode. Ag/AgCl reference electrode was submerged in saturated aqueous KCl solution and separated from reaction by a salt bridge. The CH_3CN (10 mL), containing 0.1 mol/L $LiClO_4$ was poured into the electrochemical cell in all experiments. The scan rate was 100 mV/s ranging from -1.0 V to 3.0 V.

Glassy carbon-disk as working electrode

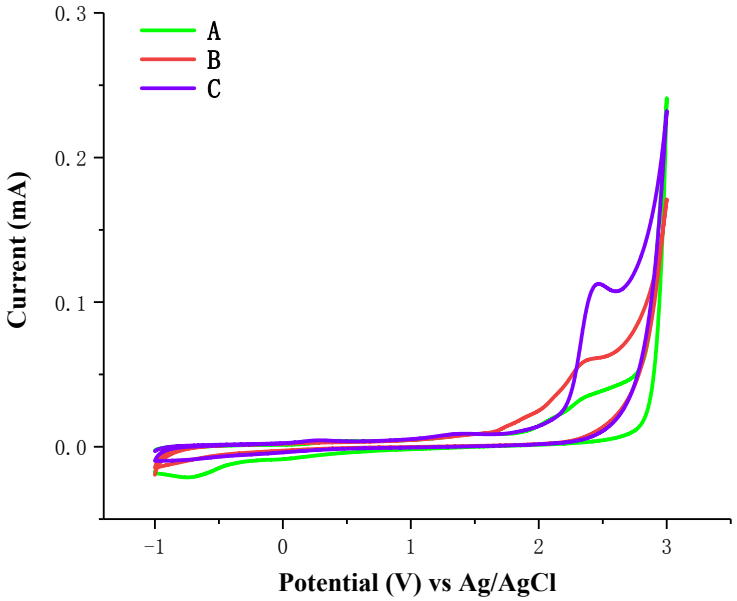


Figure 7

Figure 7. Cyclic voltammograms of reactants and the mixtures in 0.1 M $LiClO_4/CH_3CN$ using a Glassy carbon-disk working electrode (diameter, 3 mm). Pt wire as counter; Ag/AgCl as reference electrode, at 100 mV/s scan rate: (A) background; (B) **1a** (0.05 M); (C) Sodium benzoate (0.05 M).

CV was performed in a three-electrode cell connected to a Schlenk line under room temperature. Glassy carbon-disk electrode was used as working electrode, and platinum wire was employed as counter electrode. Ag/AgCl reference electrode was submerged in saturated aqueous KCl solution and separated from reaction by a salt bridge. The CH_3CN (10 mL), containing 0.1 mol/L $LiClO_4$ was poured into the electrochemical cell in all experiments. The scan rate was 100 mV/s ranging from -1.0 V to 3.0 V.

Glassy carbon-disk or Pt disk as working electrode on **1a**

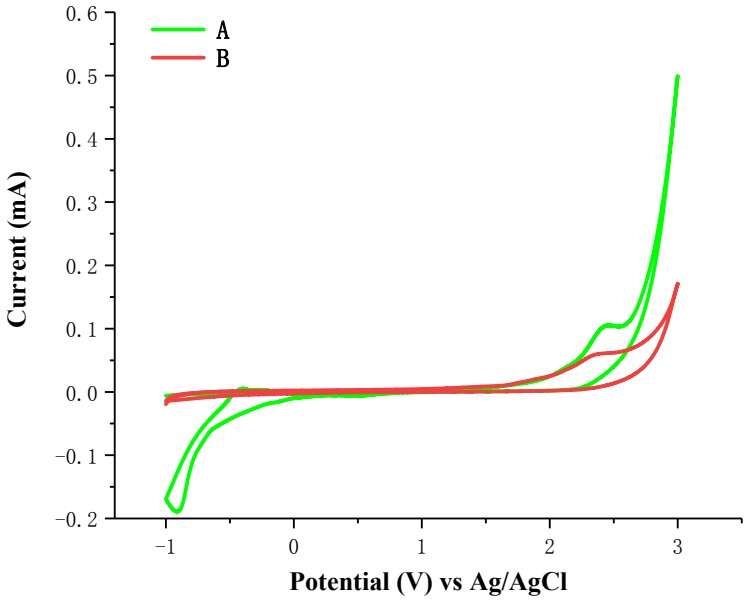


Figure 8

Figure 8. Cyclic voltammograms of reactants and the mixtures in 0.1 M $LiClO_4/CH_3CN$. Pt wire as counter; Ag/AgCl as reference electrode, at 100 mV/s scan rate: (A) **1a** (0.05 M); Pt disk working electrode (diameter, 3 mm); (B) **1a** (0.05 M); Glassy carbon-disk working electrode (diameter, 3 mm).

CV was performed in a three-electrode cell connected to a Schlenk line under room temperature. Platinum disk or glassy carbon-disk electrode was used as working electrode, and platinum wire was employed as counter electrode. Ag/AgCl reference electrode was submerged in saturated aqueous KCl solution and separated from reaction by a salt bridge. The CH_3CN (10 mL), containing 0.1 mol/L $LiClO_4$ was poured into the electrochemical cell in all experiments. The scan rate was 100 mV/s ranging from -1.0 V to 3.0 V.

7. Hydrogen detection experiment

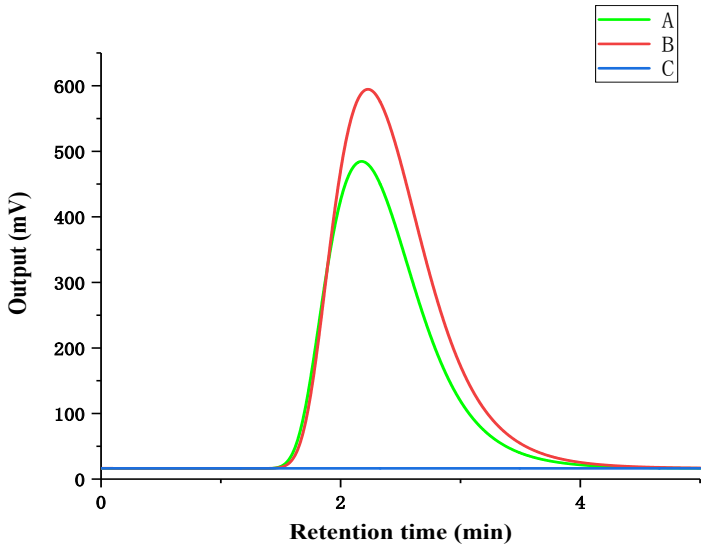


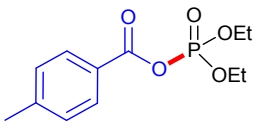
Figure 7

Figure 7. Hydrogen detection experiment of substrates: (A) Diethyl phosphite **2a** (0.4 mmol), 4-Methylbenzoic acid **1a** (0.8 mmol) and $^{n}Bu_4NBr$ (0.4 mmol) in CH_3CN (8 mL) after 3 hours of reaction; (B) Diethyl phosphite **2a** (0.4 mmol), 4-Methylbenzoic acid **1a** (0.8 mmol) and $^{n}Bu_4NBr$ (0.4 mmol) in CH_3CN (8 mL) after 6 hours of reaction; (C) Background (N_2).

Diethyl phosphite (0.4 mmol), 4-Methylbenzoic acid (0.8 mmol), $^{n}Bu_4NBr$ (0.4 mmol) CH_3CN (8 mL) were added into oven-dried three-necked flask (25 mL) with a stir bar. The flask was equipped with platinum electrodes (10 × 10 × 0.3mm^3) as the cathode and anode. Sealed three-necked flask was bubbled with N_2 for 30 min to remove air. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA and closed atmosphere under room temperature for 6h. Next, the amount of electrocatalytic hydrogen evolution was measured on a gas chromatography (kexiao, GC-1690 China) (TCD detector, 13X molecular sieve column, N_2 gas carrier).

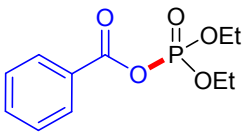
8. Experimental characterization data for products

(diethyl phosphoric) 4-methylbenzoic anhydride (3aa): Colorless liquid; isolated yield = 84%;



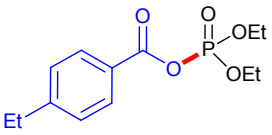
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 7.5 Hz, 2H), 4.29 (p, *J* = 7.2 Hz, 4H), 2.36 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.01 (d, *J* = 8.3 Hz), 145.63 (s), 130.69 (s), 129.45 (s), 125.31 (d, *J* = 8.4 Hz), 65.22 (d, *J* = 5.8 Hz), 21.79 (s), 16.10 (d, *J* = 6.9 Hz). Exhibited spectral data in accordance with previous report.[1]

benzoic (diethyl phosphoric) anhydride (3ba): Colorless liquid; isolated yield = 80%;



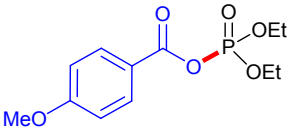
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.4 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 4.29 (p, *J* = 7.3 Hz, 4H), 1.34 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.03 (d, *J* = 8.4 Hz), 134.57 (s), 130.64 (s), 128.78 (s), 128.11 (d, *J* = 8.3 Hz), 65.38 (d, *J* = 5.9 Hz), 16.12 (d, *J* = 6.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -7.77. Exhibited spectral data in accordance with previous report.[1]

(diethyl phosphoric) 4-ethylbenzoic anhydride (3ca): Colorless liquid; isolated yield = 76%;



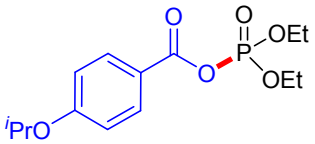
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 4.36 (p, *J* = 7.2 Hz, 4H), 2.73 (q, *J* = 7.7 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 6H), 1.26 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.05 (d, *J* = 8.4 Hz), 151.81 (s), 130.88 (s), 128.33 (s), 125.58 (d, *J* = 8.4 Hz), 65.29 (d, *J* = 5.8 Hz), 29.07 (s), 16.13 (d, *J* = 6.9 Hz), 15.08 (s). ^{31}P NMR (162 MHz, Chloroform-*d*) δ -7.68. For $C_{13}H_{19}O_5P$ $[M+H]^+$: 287.1043; found: 287.1037.

(diethyl phosphoric) 4-methoxybenzoic anhydride (3da): Colorless liquid; isolated yield = 82%;



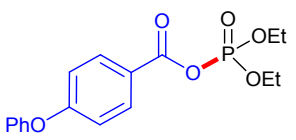
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 2.1 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.10 (dd, *J* = 8.2, 2.7 Hz, 1H), 4.29 (p, *J* = 7.3 Hz, 4H), 3.77 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.95 (d, *J* = 8.5 Hz), 159.74 (s), 129.79 (s), 121.02 (s), 114.96 (s), 65.36 (s), 55.50 (s), 16.15 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ -7.83. For $C_{12}H_{17}O_6P$ $[M+H]^+$: 289.0836; found: 289.0830.

(diethyl phosphoric) 4-isopropoxybenzoic anhydride (3ea): Colorless liquid; isolated yield = 71%;



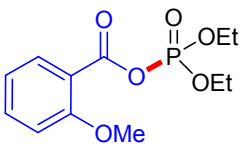
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 4.63 – 4.52 (m, 1H), 4.29 (q, *J* = 7.4 Hz, 4H), 1.36 – 1.28 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.23 (s), 160.66 (d, *J* = 8.3 Hz), 133.02 (s), 119.71 (d, *J* = 8.6 Hz), 115.34 (s), 70.34 (s), 65.18 (d, *J* = 5.8 Hz), 21.85 (s), 16.15 (d, *J* = 7.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -7.58. For $C_{14}H_{21}O_6P$ $[M+H]^+$: 317.1149; found: 317.1141.

(diethyl phosphoric) 4-phenoxybenzoic anhydride (3fa): Colorless liquid; isolated yield = 70%;



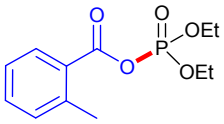
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.8 Hz, 2H), 7.41 (t, *J* = 7.9 Hz, 2H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 4.35 (p, *J* = 7.3 Hz, 4H), 1.41 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.40 (s), 160.49 (d, *J* = 8.1 Hz), 154.97 (s), 133.02 (s), 130.19 (s), 125.05 (s), 122.01 (d, *J* = 8.5 Hz), 120.47 (s), 117.26 (s), 65.31 (d, *J* = 5.8 Hz), 16.16 (d, *J* = 7.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -7.65. For $C_{17}H_{19}O_6P$ $[M+H]^+$: 351.0992; found: 351.0997.

(diethyl phosphoric) 2-methoxybenzoic anhydride (3ga): Colorless liquid; isolated yield = 75%;



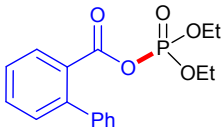
^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.55 (td, *J* = 7.9, 7.5, 1.8 Hz, 1H), 7.02 – 6.96 (m, 2H), 4.34 (p, *J* = 8.3, 7.7 Hz, 4H), 3.90 (s, 3H), 1.39 (t, *J* = 7.5 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.78 (s), 159.40 (d, *J* = 8.1 Hz), 135.67 (s), 133.15 (s), 120.20 (s), 116.99 (d, *J* = 8.4 Hz), 112.25 (s), 65.19 (d, *J* = 5.9 Hz), 55.98 (s), 16.13 (d, *J* = 6.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -8.02. For $C_{12}H_{17}O_6P$ $[M+H]^+$: 289.0836; found: 289.0836.

(diethyl phosphoric) 2-methylbenzoic anhydride (3ha): Colorless liquid; isolated yield = 76%;



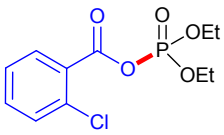
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.88 (m, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.20 (dd, *J* = 8.8, 5.6 Hz, 2H), 4.28 (p, *J* = 7.2 Hz, 4H), 2.56 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.95 (d, *J* = 8.1 Hz), 142.69 (s), 133.80 (s), 132.2 (s), 131.8 (s) 126.68 (d, *J* = 7.9 Hz), 126.07 (s), 65.22 (d, *J* = 5.8 Hz), 22.06 (s), 16.13 (d, *J* = 6.9 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ -7.72. Exhibited spectral data in accordance with previous report.[1]

[1,1'-biphenyl]-2-carboxylic (diethyl phosphoric) anhydride (3ia): Colorless liquid; isolated yield = 81%;



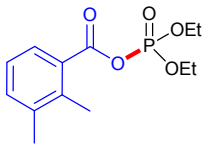
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.7 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.39 (ddd, *J* = 21.6, 13.7, 7.6 Hz, 7H), 3.95 (ddt, *J* = 20.1, 9.2, 5.8 Hz, 4H), 1.23 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.98 (d, *J* = 8.5 Hz), 143.36 (s), 140.66 (s), 132.77 (s), 131.33 (s), 128.61 (s), 128.50 (s), 128.42 (s), 128.39 (s), 127.59 (s), 127.43 (s), 65.01 (d, *J* = 5.9 Hz), 15.99 (d, *J* = 7.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -8.81. For $C_{17}H_{19}O_5P$ $[M+H]^+$: 335.1043; found: 335.1036.

2-chlorobenzoic (diethyl phosphoric) anhydride (3ja): Colorless liquid; isolated yield = 74%;



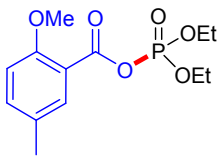
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.6 Hz, 1H), 7.44 (dt, *J* = 7.7, 4.6 Hz, 2H), 7.29 (ddd, *J* = 8.3, 5.5, 3.2 Hz, 1H), 4.31 (p, *J* = 7.1 Hz, 4H), 1.34 (t, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.27 (d, *J* = 8.1 Hz), 135.32 (s), 134.28 (s), 132.81 (s), 131.74 (s), 131.13 (s), 126.88 (s), 65.60 (d, *J* = 5.9 Hz), 16.11 (d, *J* = 7.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -8.35. For $C_{11}H_{14}ClO_5P$ $[M+H]^+$: 351.0781; found: 351.0784.

(diethyl phosphoric) 2,4-dimethylbenzoic anhydride (3ka): Colorless liquid; isolated yield =78;



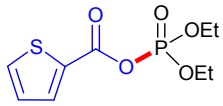
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.76 (m, 1H), 7.38 (d, *J* = 7.4 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 4.35 (p, *J* = 7.2 Hz, 4H), 2.53 (s, 3H), 2.34 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.77 (d, *J* = 8.4 Hz), 140.36 (s), 138.56 (s), 135.12 (s), 129.25 (s), 127.70 (d, *J* = 7.8 Hz), 125.40 (d, *J* = 5.1 Hz), 65.22 (d, *J* = 5.8 Hz), 20.67 (s), 16.77 (s), 16.15 (d, *J* = 7.0 Hz). For $C_{13}H_{19}O_5P$ $[M+H]^+$: 287.1043; found: 287.1047.

(diethyl phosphoric) 2-methoxy-5-methylbenzoic anhydride (3la): Colorless liquid; isolated yield = 58%;



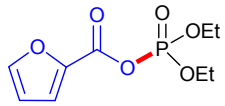
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 2.8 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 1H), 7.04 (dd, *J* = 8.4, 2.8 Hz, 1H), 4.35 (p, *J* = 7.2 Hz, 4H), 3.81 (s, 3H), 2.55 (s, 3H), 1.41 (t, *J* = 7.5 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.90 (d, *J* = 8.3 Hz), 157.50 (s), 134.56 (s), 133.16 (s), 127.39 (d, *J* = 7.9 Hz), 119.90 (s), 116.47 (s), 65.27 (d, *J* = 5.8 Hz), 55.52 (s), 21.14 (s), 16.16 (d, *J* = 6.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -7.71. For $C_{13}H_{19}O_6P$ $[M+H]^+$: 303.0992; found: 303.0992.

(diethyl phosphoric) thiophene-2-carboxylic anhydride (3na): Colorless liquid; isolated yield = 70%;



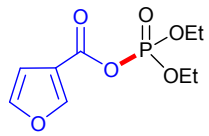
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 3.2 Hz, 1H), 7.64 (d, *J* = 4.7 Hz, 1H), 7.09 (t, *J* = 4.3 Hz, 1H), 4.29 (p, *J* = 7.2 Hz, 4H), 1.35 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.06 (d, *J* = 7.5 Hz), 136.22 (s), 135.32 (s), 131.55 (d, *J* = 10.0 Hz), 128.43 (s), 65.50 (d, *J* = 5.9 Hz), 16.12 (d, *J* = 6.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -8.49. Exhibited spectral data in accordance with previous report.[1]

(diethyl phosphoric) furan-2-carboxylic anhydride (3oa): Yellow liquid; isolated yield = 74%;



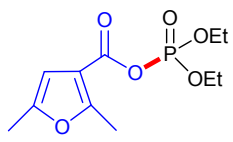
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.34 (d, *J* = 4.2 Hz, 1H), 6.58 (dd, *J* = 3.6, 1.7 Hz, 1H), 4.40 – 4.31 (m, 4H), 1.41 (td, *J* = 7.1, 1.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.04 (d, *J* = 7.0 Hz), 148.41 (s), 142.72 (d, *J* = 11.7 Hz), 121.52 (s), 112.56 (s), 65.51 (d, *J* = 5.9 Hz), 16.06 (d, *J* = 6.7 Hz). For $C_9H_{13}O_6P$ $[M+H]^+$: 249.0523; found: 249.0527.

(diethyl phosphoric) furan-3-carboxylic anhydride (3pa): Yellow liquid; isolated yield = 83%;



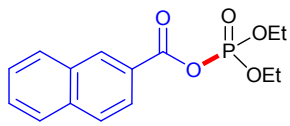
^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (s, 1H), 7.49 (s, 1H), 6.78 (s, 1H), 4.39 – 4.28 (m, 4H), 1.41 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.71 (d, *J* = 7.7 Hz), 149.82 (s), 144.59 (s), 118.01 (d, *J* = 9.8 Hz), 109.96 (s), 65.32 (d, *J* = 5.8 Hz), 16.06 (d, *J* = 6.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -8.36. Exhibited spectral data in accordance with previous report.[1]

(diethyl phosphoric) 2,5-dimethylfuran-3-carboxylic anhydride (3qa): Colorless liquid; isolated yield =60%;



^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.20 (s, 1H), 4.38 – 4.27 (m, 4H), 2.54 (s, 3H), 2.25 (s, 3H), 1.39 (td, *J* = 7.1, 0.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.98 (s), 159.64 (s), 157.90 (s), 150.75 (s), 106.17 (s), 65.07 (d, *J* = 5.8 Hz), 16.11 (d, *J* = 6.8 Hz), 13.89 (s), 13.13 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ -7.94. For $C_{11}H_{17}O_6P$ $[M+H]^+$: 277.0836; found: 277.0838.

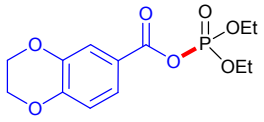
2-naphthoic (diethyl phosphoric) anhydride (3ra): Colorless liquid; isolated yield = 62%;



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.03 (d, *J* = 7.6 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.90 (dd, *J* = 8.4, 4.9 Hz, 2H), 7.68 – 7.62 (m, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 4.41 (p, *J* = 7.3 Hz, 4H), 1.45 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.24 (d, *J* = 8.5 Hz), 136.18 (s), 132.97 (s), 132.35 (s), 129.64 (s), 129.25 (s), 128.88 (s), 128.72 (s), 127.89 (s), 127.12 (s), 125.37 (s), 65.44 (d,

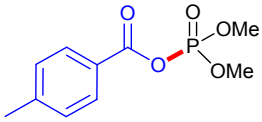
J = 5.8 Hz), 16.18 (d, J = 6.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -7.62. For $C_{15}H_{17}O_5P$ $[M+H]^+$: 309.0886; found: 309.0880.

(diethyl phosphoric) 2,3-dihydrobenzo[b][1,4]dioxine-6-carboxylic anhydride (3sa): Colorless liquid; isolated yield = 80%;



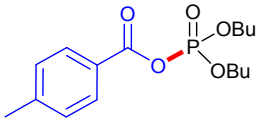
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.4 Hz, 2H), 6.93 – 6.88 (m, 1H), 4.37 – 4.26 (m, 8H), 1.40 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.44 (d, J = 8.1 Hz), 149.28 (s), 143.40 (s), 124.83 (s), 121.09 (d, J = 8.6 Hz), 120.09 (s), 117.58 (s), 65.26 (d, J = 5.8 Hz), 64.74 (s), 64.02 (s), 16.14 (d, J = 6.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -7.73. For $C_{13}H_{17}O_7P$ $[M+H]^+$: 317.0785; found: 317.0788.

(dimethyl phosphoric) 4-methylbenzoic anhydride (3ab): Colorless liquid; isolated yield = 71%;



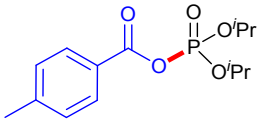
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 3.99 (d, J = 11.7 Hz, 6H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.01 (d, J = 8.2 Hz), 145.90 (s), 130.83 (s), 129.57 (s), 125.11 (d, J = 8.5 Hz), 55.49 (d, J = 5.8 Hz), 21.86 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ -5.01. For $C_{10}H_{13}O_5P$ $[M+H]^+$: 245.0573; found: 245.0571.

(dibutyl phosphoric) 4-methylbenzoic anhydride (3ac): Colorless liquid; isolated yield = 80%;



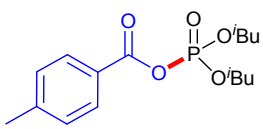
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.88 (m, 2H), 7.22 (s, 2H), 4.30 – 4.22 (m, 3H), 4.08 – 3.98 (m, 1H), 2.40 (d, J = 5.6 Hz, 3H), 1.75 – 1.62 (m, 4H), 1.48 – 1.35 (m, 4H), 0.96 – 0.88 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.05 (d, J = 8.5 Hz), 145.64 (s), 130.76 (s), 129.50 (s), 125.44 (d, J = 8.6 Hz), 68.97 (d, J = 6.3 Hz), 32.24 (d, J = 7.0 Hz), 21.84 (s), 18.64 (s), 13.58 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ -7.38. For $C_{16}H_{25}O_5P$ $[M+H]^+$: 329.1513; found: 329.1512.

(diisopropyl phosphoric) 4-methylbenzoic anhydride (3ad): Colorless liquid; isolated yield = 74%;



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.3 Hz, 2H), 7.22 – 7.17 (m, 2H), 4.86 (dq, J = 12.5, 6.2 Hz, 2H), 2.36 (s, 3H), 1.34 (dd, J = 9.0, 6.2 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.08 (d, J = 8.6 Hz), 145.48 (s), 130.67 (s), 129.48 (s), 125.69 (d, J = 8.2 Hz), 74.28 (d, J = 5.9 Hz), 23.65 (dd, J = 24.0, 5.0 Hz), 21.81 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ -9.68. For $C_{14}H_{21}O_5P$ $[M+H]^+$: 301.1199; found: 301.1199.

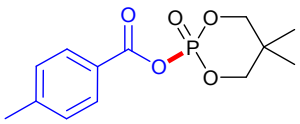
(diisobutyl phosphoric) 4-methylbenzoic anhydride (3ae): Colorless liquid; isolated yield = 66%;



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.2 Hz, 2H), 7.33 – 7.27 (m, 2H), 4.05 (tq, J = 5.7, 3.0 Hz, 4H), 2.43 (s, 3H), 2.03 (dp, J = 13.3, 6.6 Hz, 2H), 0.98 (d, J = 6.7 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.07 (d, J = 8.4 Hz), 145.64 (s), 130.70 (d, J = 9.7 Hz), 129.55 (d, J = 8.0 Hz), 125.46 (d, J

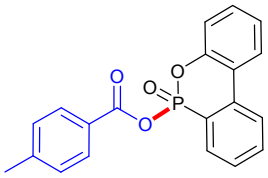
= 8.4 Hz), 74.99 (d, *J* = 6.5 Hz), 29.09 (d, *J* = 7.2 Hz), 21.86 (d, *J* = 2.8 Hz), 18.61 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ -7.47. For $C_{16}H_{25}O_5P$ $[M+H]^+$: 329.1512; found: 329.1514.

5,5-dimethyl-2-oxido-1,3,2-dioxaphosphinan-2-yl 4-methylbenzoate (3af): Colorless liquid; isolated yield = 73%;



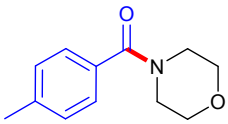
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 4.34 (d, *J* = 10.5 Hz, 2H), 4.05 (dd, *J* = 22.8, 11.0 Hz, 2H), 2.45 (s, 3H), 1.38 (s, 3H), 0.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.86 (d, *J* = 8.7 Hz), 146.08 (s), 130.94 (s), 129.64 (s), 124.96 (d, *J* = 7.7 Hz), 78.93 (d, *J* = 7.2 Hz), 32.31 (d, *J* = 6.7 Hz), 21.90 (d, *J* = 2.9 Hz), 20.20 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ -16.89. For $C_{13}H_{17}O_5P$ $[M+H]^+$: 285.0886; found: 285.0888.

(S)-6-oxidodibenzo[c,e][1,2]oxaphosphinin-6-yl 4-methylbenzoate (3ag): Colorless liquid; isolated yield = 70%;



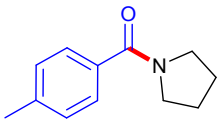
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (dd, *J* = 16.1, 7.1 Hz, 1H), 8.03 – 7.93 (m, 2H), 7.80 – 7.69 (m, 3H), 7.61 – 7.55 (m, 1H), 7.48 – 7.41 (m, 1H), 7.37 – 7.28 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.18 (d, *J* = 7.3 Hz), 149.78 (d, *J* = 8.6 Hz), 145.80 (s), 137.11 (d, *J* = 7.8 Hz), 134.26 (d, *J* = 2.5 Hz), 132.29 (d, *J* = 10.1 Hz), 130.79 (s), 129.41 (s), 128.44 (d, *J* = 16.0 Hz), 125.09 (dd, *J* = 22.3, 5.6 Hz), 123.91 (d, *J* = 12.6 Hz), 122.24 (d, *J* = 12.2 Hz), 121.96 (s), 120.17 (d, *J* = 7.3 Hz), 21.81 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 5.76. For $C_{20}H_{15}O_4P$ $[M+H]^+$: 351.0781; found: 351.0784.

morpholino(p-tolyl)methanone (4a): Colorless liquid; isolated yield = 93%;



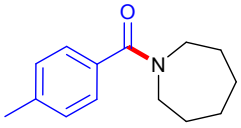
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 3.69 (s, 8H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.70 (s), 140.12 (s), 132.30 (s), 129.16 (s), 127.24 (s), 66.92 (s), 48.25 (s), 42.62 (s), 21.39 (s). Exhibited spectral data in accordance with previous report.[2]

pyrrolidin-1-yl(p-tolyl)methanone (4b): White solid; isolated yield = 83%;



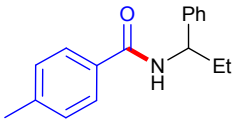
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 3.64 (t, *J* = 6.9 Hz, 2H), 3.44 (t, *J* = 6.6 Hz, 2H), 2.37 (s, 3H), 1.95 (p, *J* = 6.6 Hz, 2H), 1.86 (p, *J* = 6.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.83 (s), 139.87 (s), 134.30 (s), 128.80 (s), 127.20 (s), 49.65 (s), 46.19 (s), 26.40 (s), 24.45 (s), 21.37 (s).

azepan-1-yl(p-tolyl)methanone (4c): Colorless liquid; isolated yield = 62%;



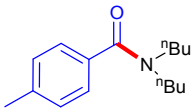
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 3.69 – 3.64 (m, 2H), 3.38 (t, *J* = 5.3 Hz, 2H), 2.36 (s, 3H), 1.87 – 1.79 (m, 2H), 1.66 – 1.55 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.77 (s), 139.00 (s), 134.45 (s), 128.93 (s), 126.52 (s), 49.79 (s), 46.35 (s), 26.47 (s), 21.32 (s).

4-methyl-N-(1-phenylpropyl)benzamide (4d): White solid; isolated yield = 71%;



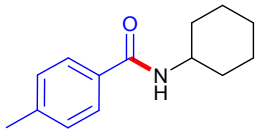
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.33 (q, *J* = 4.9, 4.2 Hz, 4H), 7.27 – 7.22 (m, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.54 (d, *J* = 7.1 Hz, 1H), 5.07 (q, *J* = 7.5 Hz, 1H), 2.36 (s, 3H), 1.91 (tt, *J* = 13.8, 6.8 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.87 (s), 142.32 (s), 141.79 (s), 131.88 (s), 129.18 (s), 128.66 (s), 127.33 (s), 127.00 (s), 126.74 (s), 55.33 (s), 29.21 (s), 21.44 (s), 10.88 (s). Exhibited spectral data in accordance with previous report.[3]

N,N-dibutyl-O-(4-methylbenzoyl)hydroxylamine (4e): Colorless liquid; isolated yield = 77%;



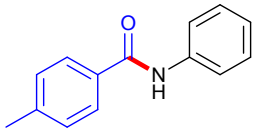
^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 3.47 (s, 2H), 3.20 (s, 2H), 2.36 (s, 3H), 1.67 – 1.35 (m, 6H), 1.14 (s, 2H), 0.97 (s, 3H), 0.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.85, 138.94, 134.40, 128.89, 126.50, 48.81, 44.47, 21.32, 20.28, 19.77, 13.89, 13.68.

N-cyclohexyl-4-methylbenzamide (4f): White solid; isolated yield = 89%;



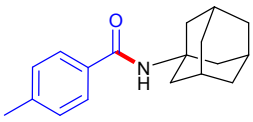
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.07 (s, 1H), 4.01 – 3.89 (m, 1H), 2.38 (s, 3H), 2.01 (dd, *J* = 12.3, 3.3 Hz, 2H), 1.74 (dt, *J* = 13.1, 3.6 Hz, 2H), 1.68 – 1.60 (m, 1H), 1.46 – 1.34 (m, 2H), 1.26 – 1.16 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.66 (s), 141.55 (s), 132.22 (s), 129.12 (s), 126.87 (s), 48.63 (s), 33.23 (s), 25.59 (s), 24.95 (s), 21.40 (s). Exhibited spectral data in accordance with previous report.[3]

4-methyl-N-phenylbenzamide (4g): Colorless liquid; isolated yield = 73%;



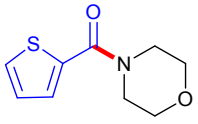
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 9.0 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.93 (s), 142.35 (s), 138.08 (s), 130.22 (s), 129.41 (s), 129.05 (s), 127.12 (s), 124.46 (s), 120.34 (s), 21.50 (s). Exhibited spectral data in accordance with previous report.[4]

N-((3s,5s,7s)-adamantan-1-yl)-4-methylbenzamide (4h): White solid; isolated yield = 66%;



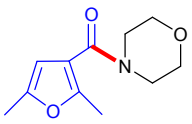
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 5.78 (s, 1H), 2.38 (s, 3H), 2.12 (s, 9H), 1.72 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.63 (s), 141.34 (s), 132.97 (s), 129.09 (s), 126.70 (s), 52.19 (s), 41.74 (s), 36.42 (s), 29.54 (s), 21.38 (s).

morpholino(thiophen-2-yl)methanone (4i): Colorless liquid; isolated yield = 86%;



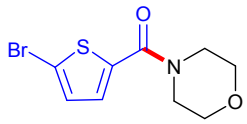
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.29 (dd, *J* = 3.6, 1.0 Hz, 1H), 7.05 (dd, *J* = 5.0, 3.7 Hz, 1H), 3.78 – 3.74 (m, 4H), 3.74 – 3.69 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.63 (s), 136.57 (s), 128.97 (s), 128.88 (s), 126.77 (s), 66.82 (s), 45.86 (s).

morpholino 2,5-dimethylfuran-3-carboxylate (4j): Colorless liquid; isolated yield = 78%;



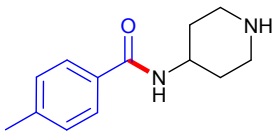
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91 (s, 1H), 3.66 (d, *J* = 19.3 Hz, 8H), 2.34 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.64 (s), 151.77 (s), 150.01 (s), 115.71 (s), 105.80 (s), 66.94 (s), 47.47 (s), 13.20 (s), 12.89 (s).

(5-bromothiophen-2-yl)(morpholino)methanone (4k): White solid; isolated yield = 88%;



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, *J* = 3.9 Hz, 1H), 7.01 (d, *J* = 3.9 Hz, 1H), 3.75 (t, *J* = 4.9 Hz, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.36 (s), 138.21 (s), 129.75 (s), 129.51 (s), 116.89 (s), 66.77 (s), 45.90 (s).

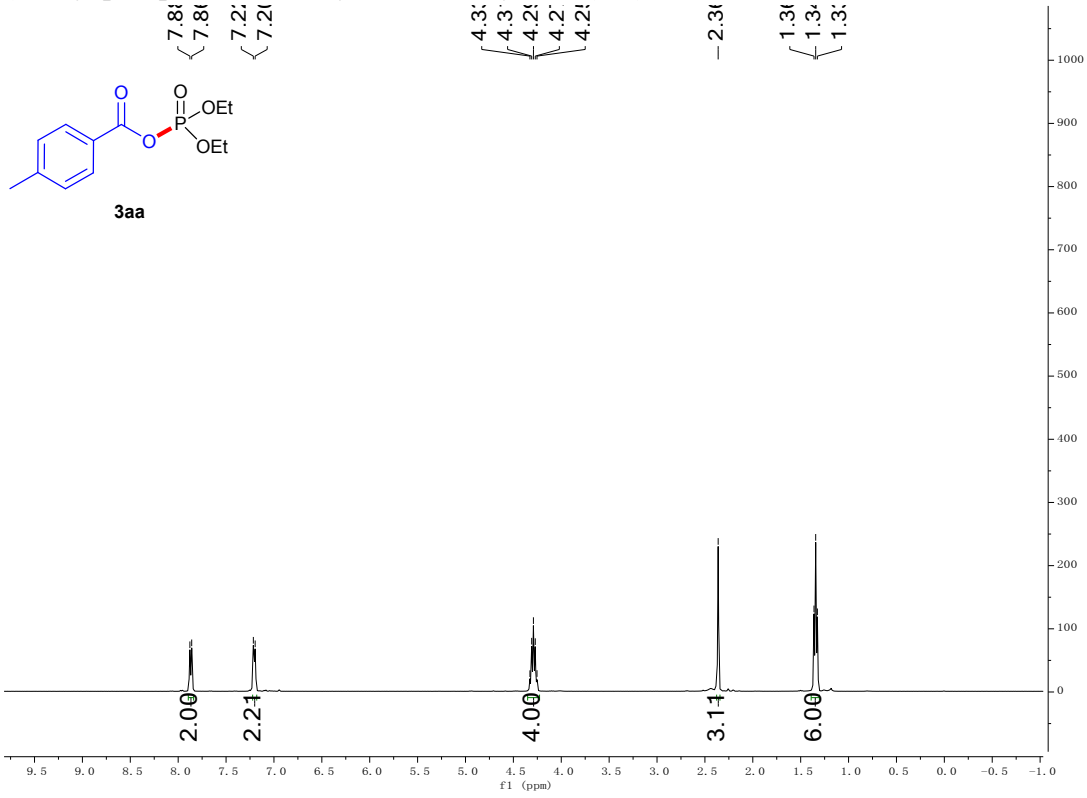
4-methyl-N-(piperidin-4-yl)benzamide (4l): Colorless liquid; isolated yield = 69%;

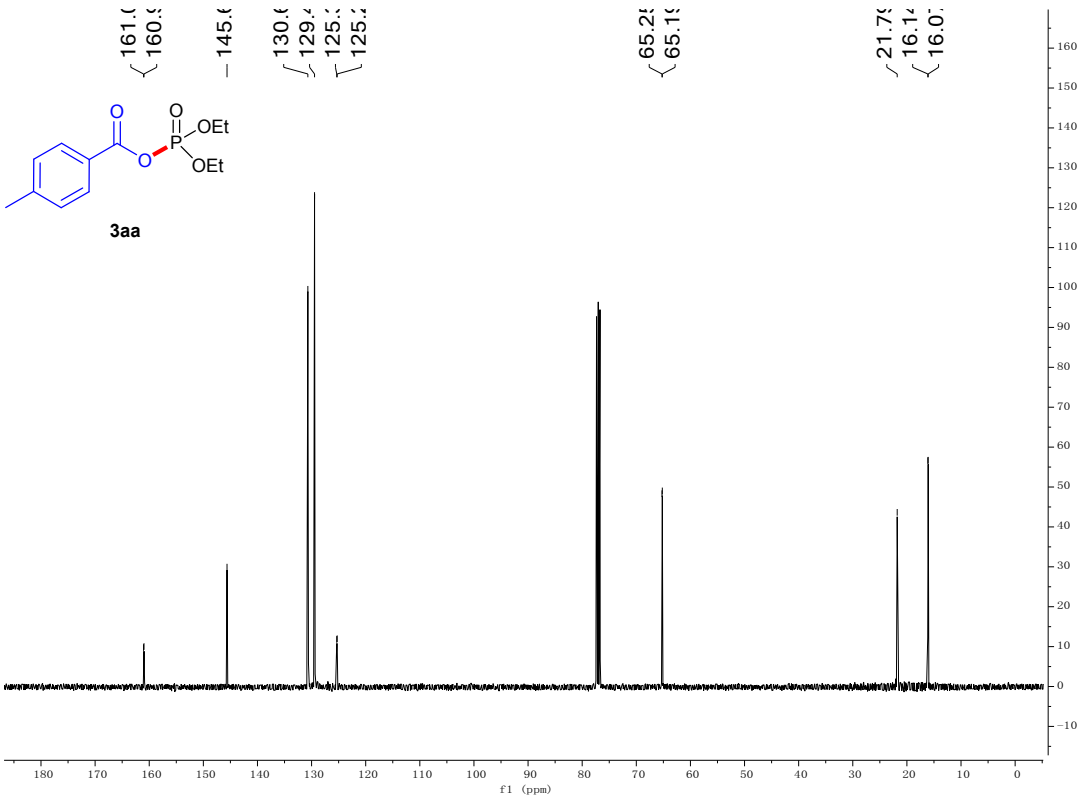


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 4.66 (s, 1H), 3.75 (s, 1H), 2.86 (d, *J* = 80.7 Hz, 2H), 2.36 (s, 3H), 1.69 – 1.52 (m, 2H), 1.31 – 1.09 (m, 2H), 0.97 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.54 (s), δ 139.44 (s), δ 133.50 (s), 128.96 (s), 126.94 (s), 34.31 (d, *J* = 75.7 Hz), 31.19 (s), 21.75 (s), 21.36 (s).

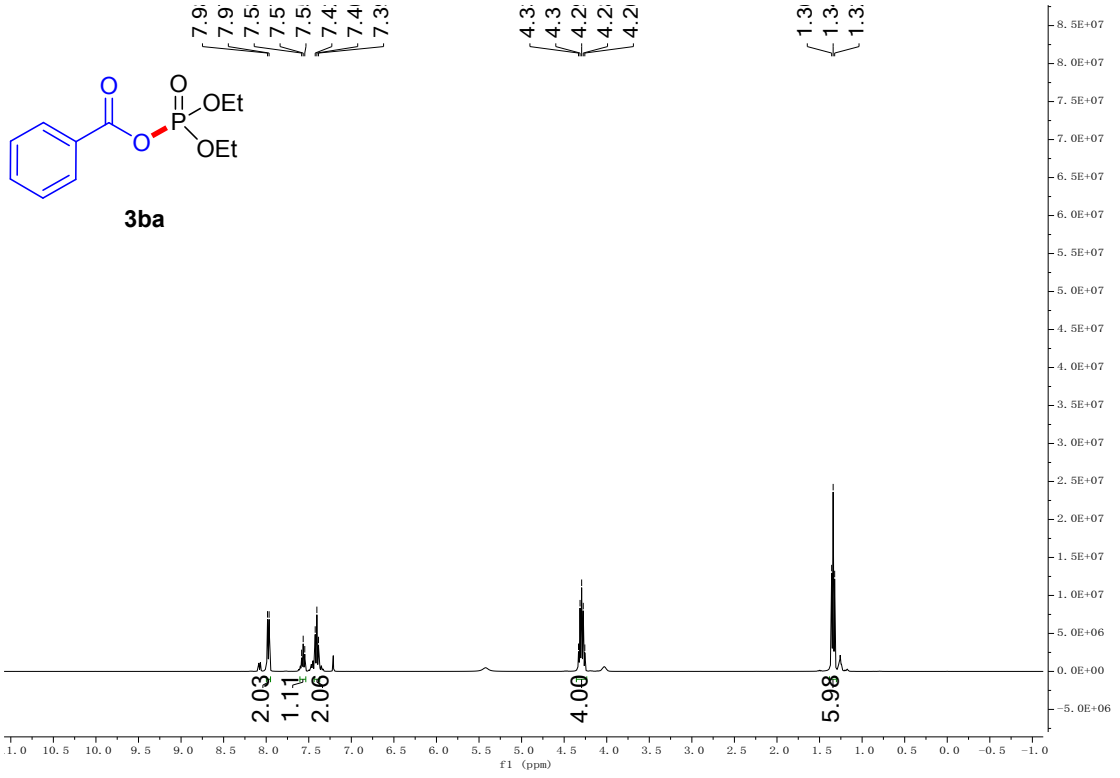
9. Copies of product ^{1}H NMR, ^{13}C NMR and ^{31}P NMR

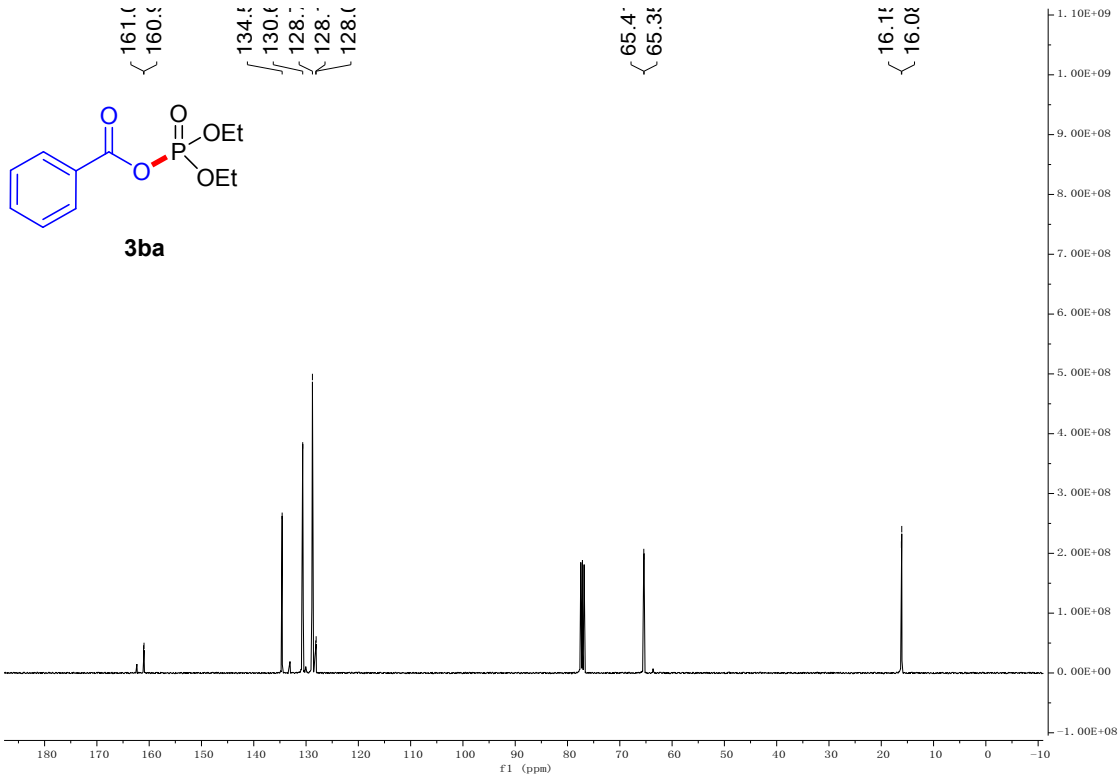
(diethyl phosphoric) 4-methylbenzoic anhydride (3aa)

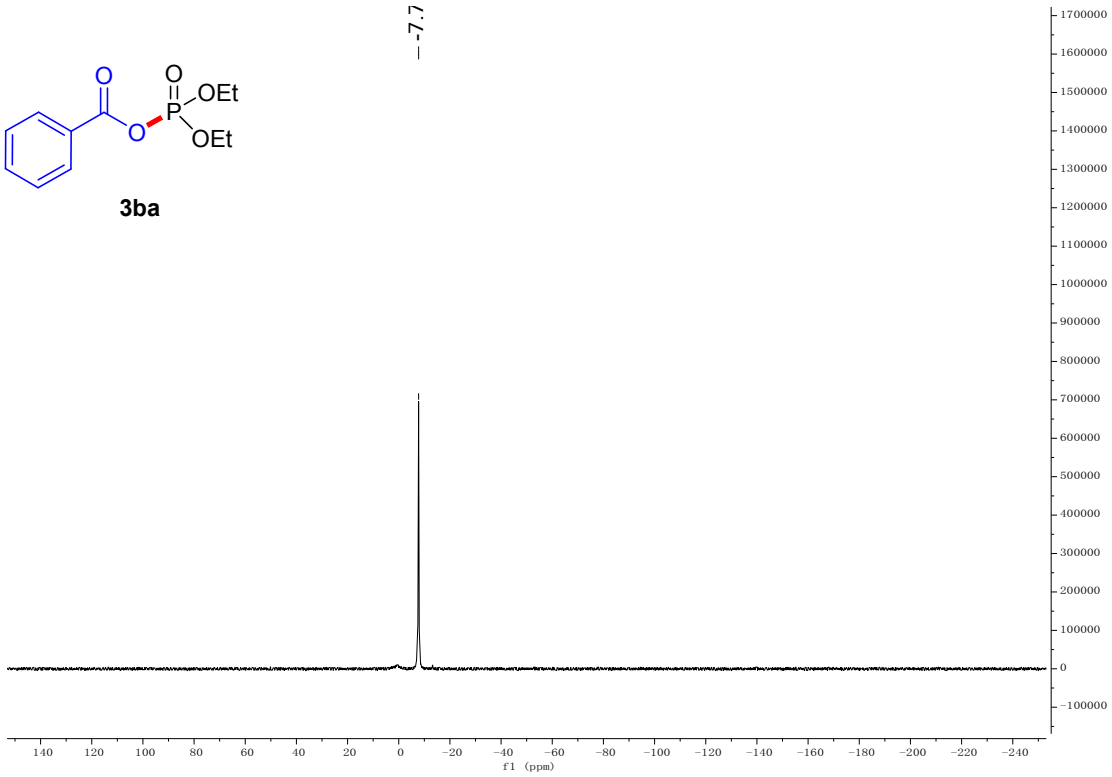




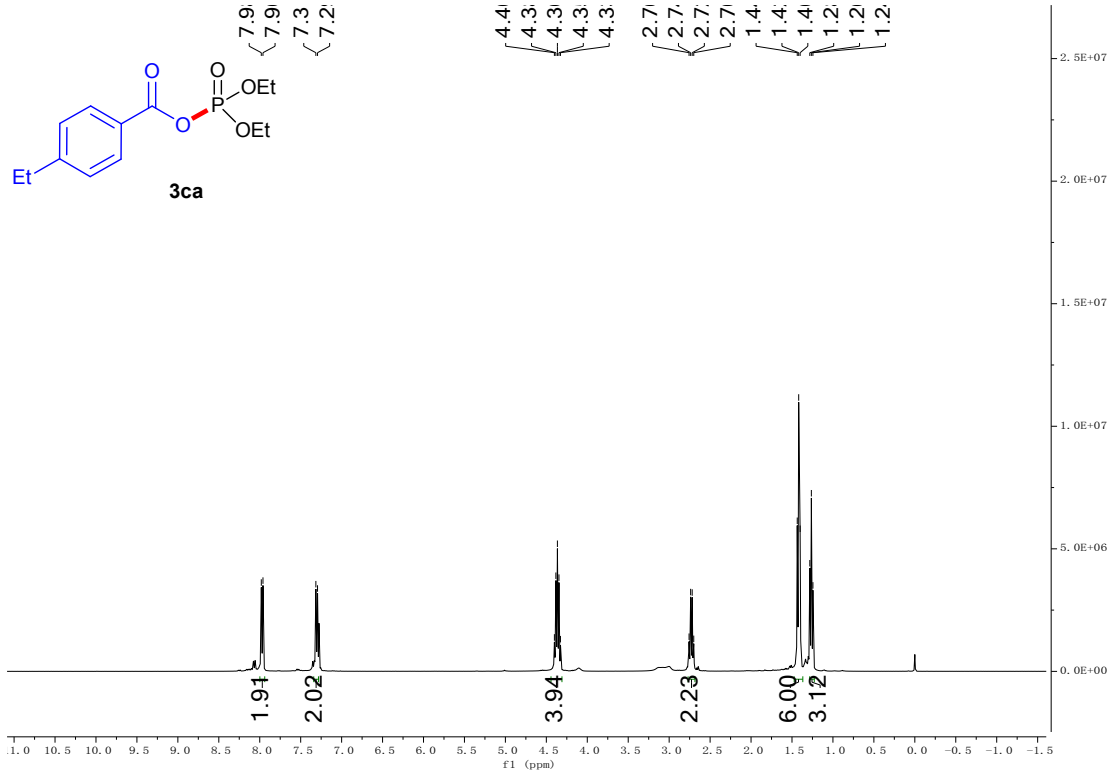
(diethyl phosphoric) 4-methoxybenzoic anhydride (3ba)

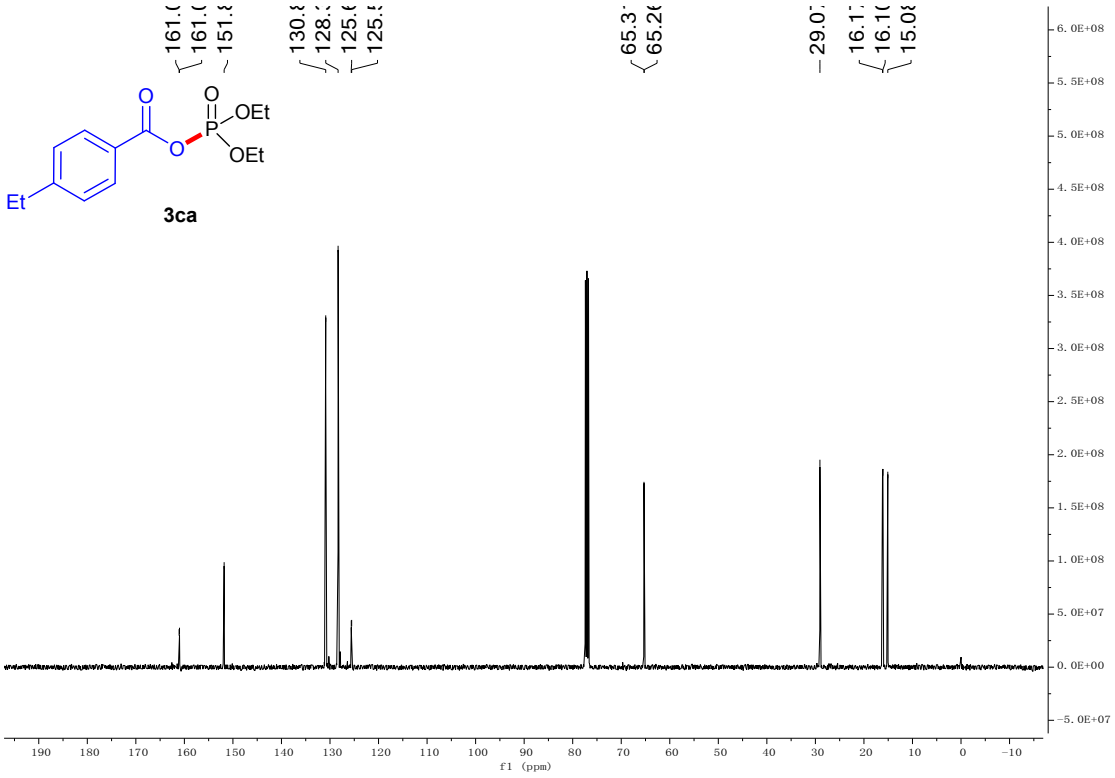






(diethyl phosphoric) 4-ethylbenzoic anhydride (3ca)




161.(
161.(
151.8
130.8
128.(
125.6
125.8
65.3
65.2
29.0
16.1
16.1
15.0
O
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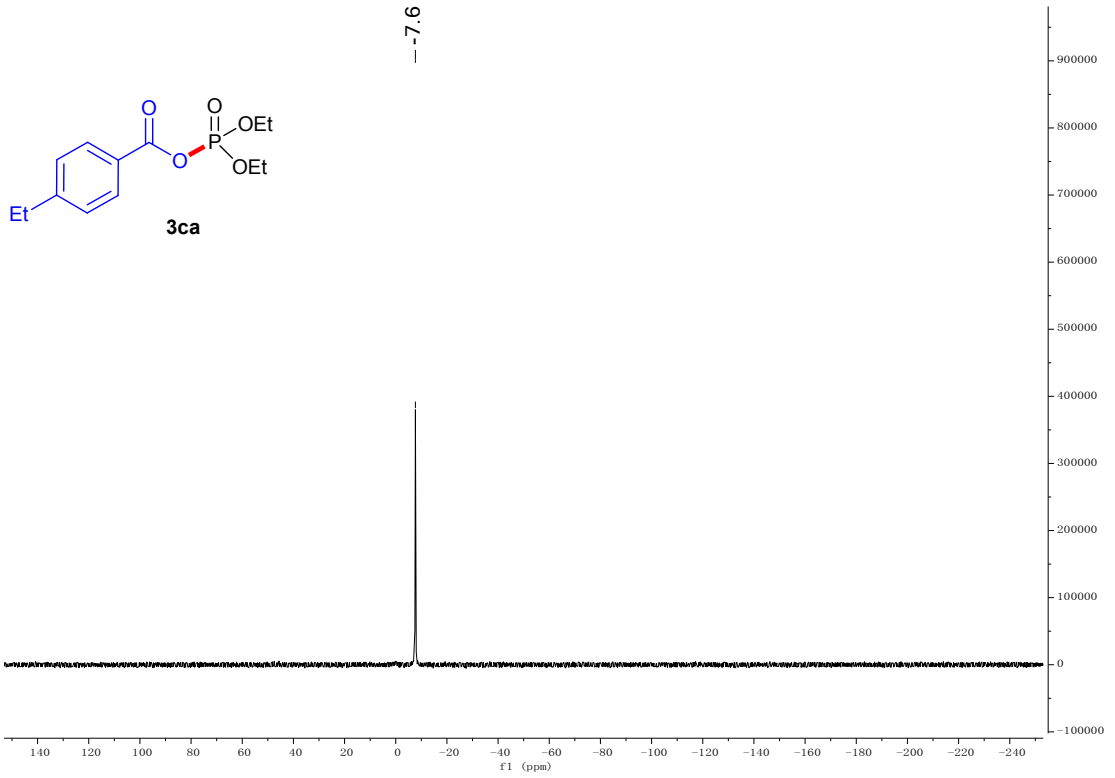
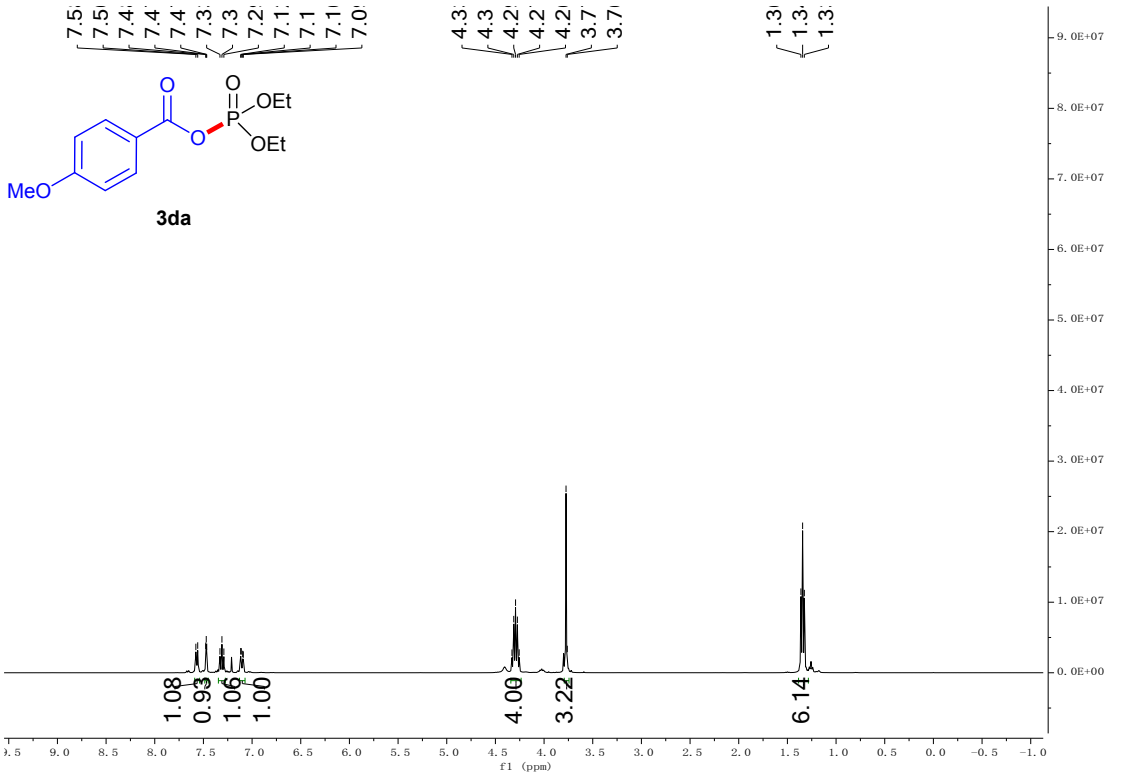
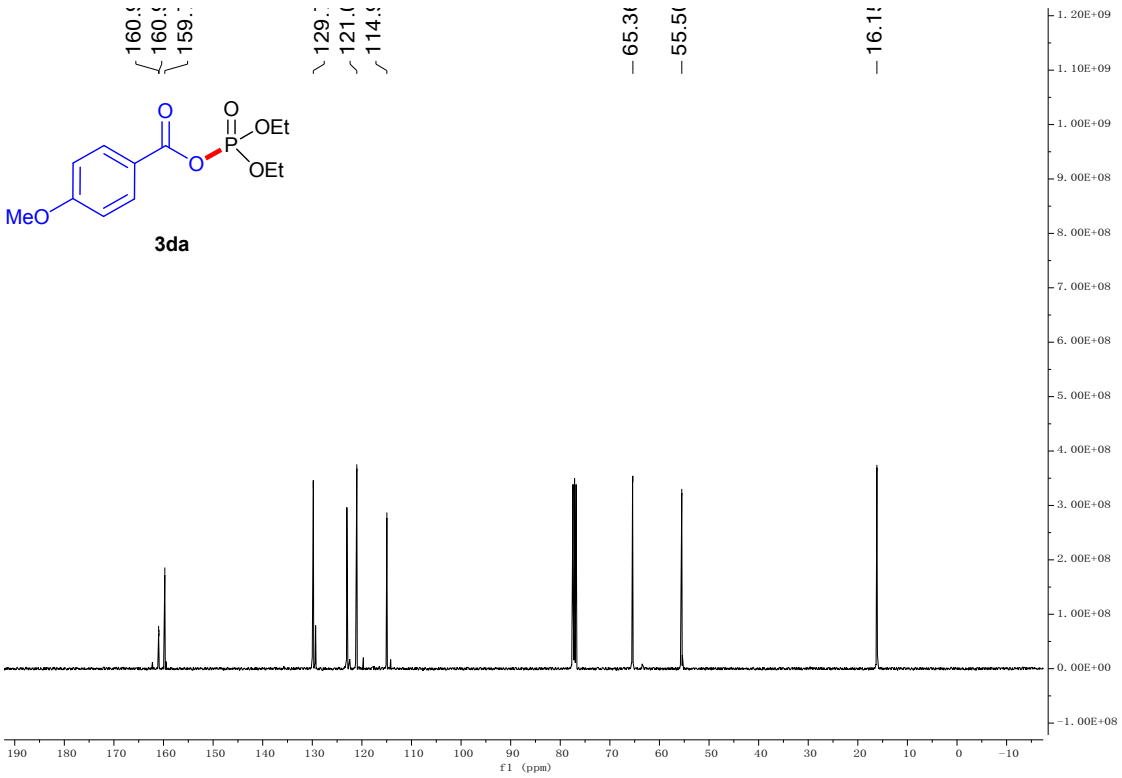
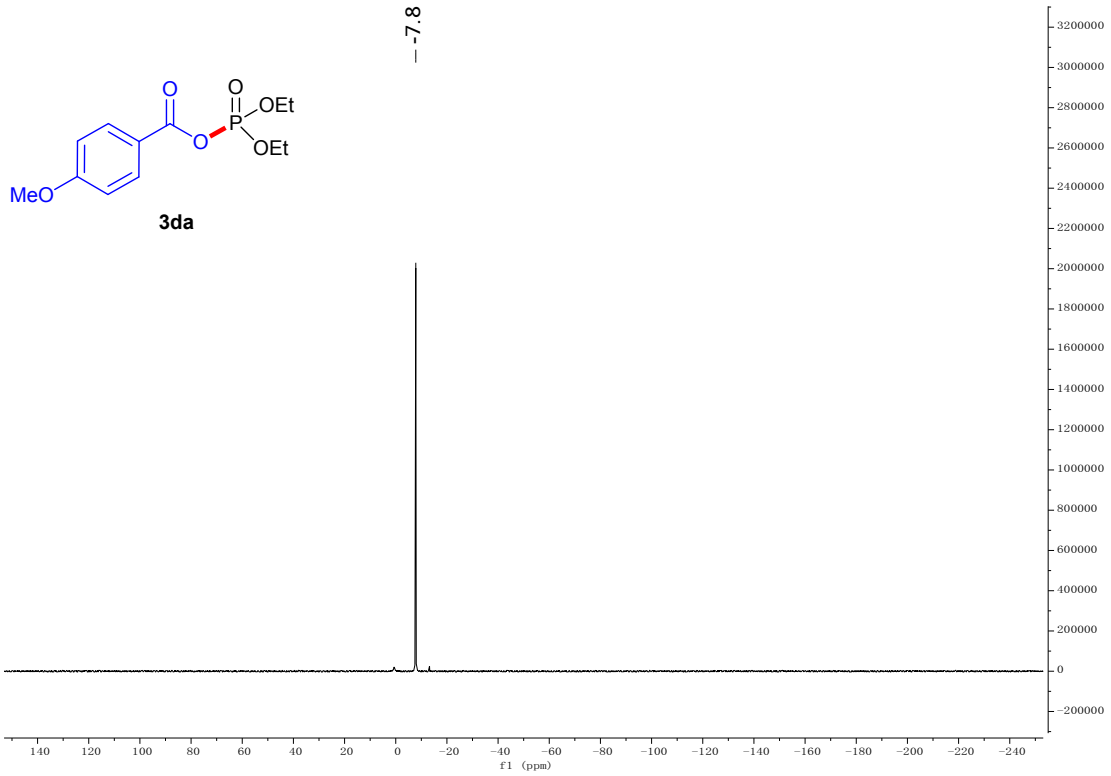
P
OEt
OEt
O
Et
3ca
6. 0E+08
5. 5E+08
5. 0E+08
4. 5E+08
4. 0E+08
3. 5E+08
3. 0E+08
2. 5E+08
2. 0E+08
1. 5E+08
1. 0E+08
5. 0E+07
0. 0E+00
-5. 0E+07
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-7.6
O
O
P
OEt
OEt
O
Et
3ca
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

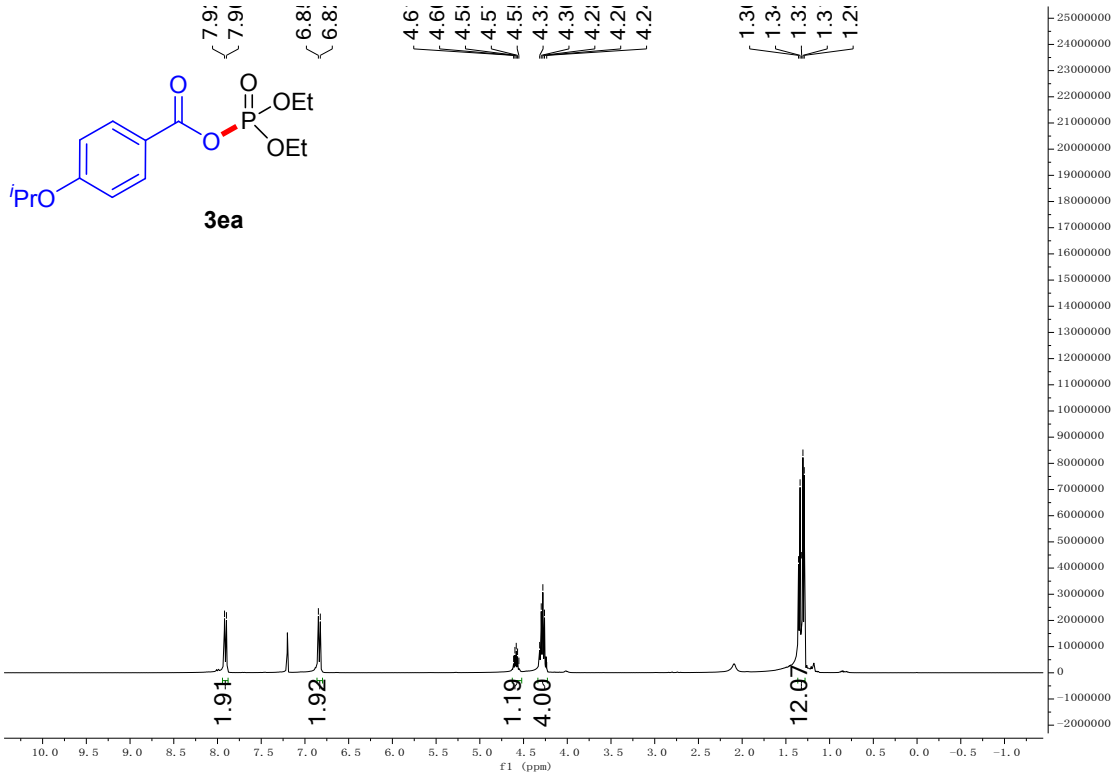
(diethyl phosphoric) 4-methoxybenzoic anhydride (3da)

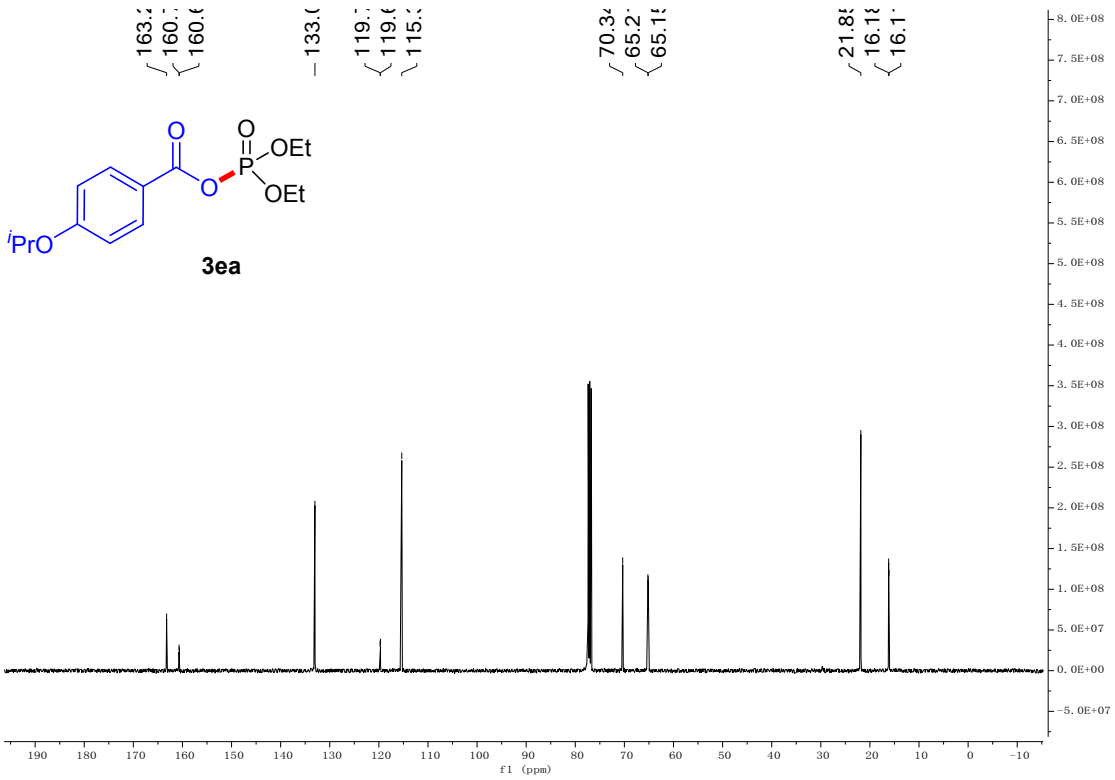


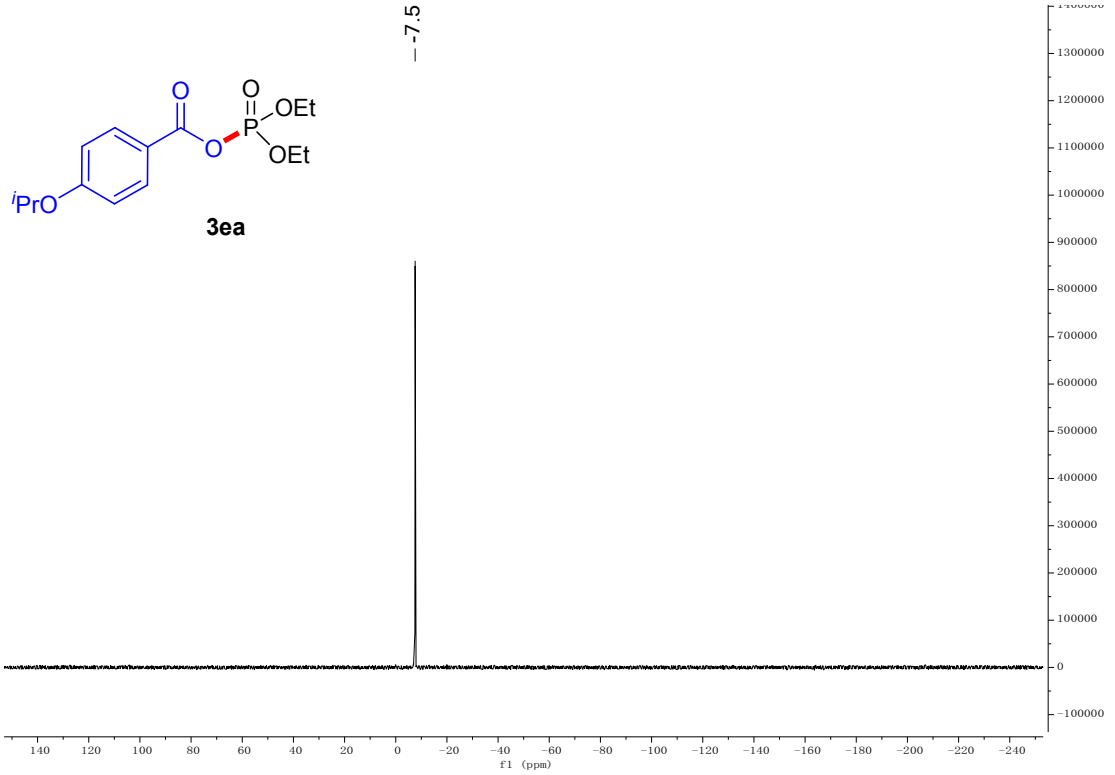




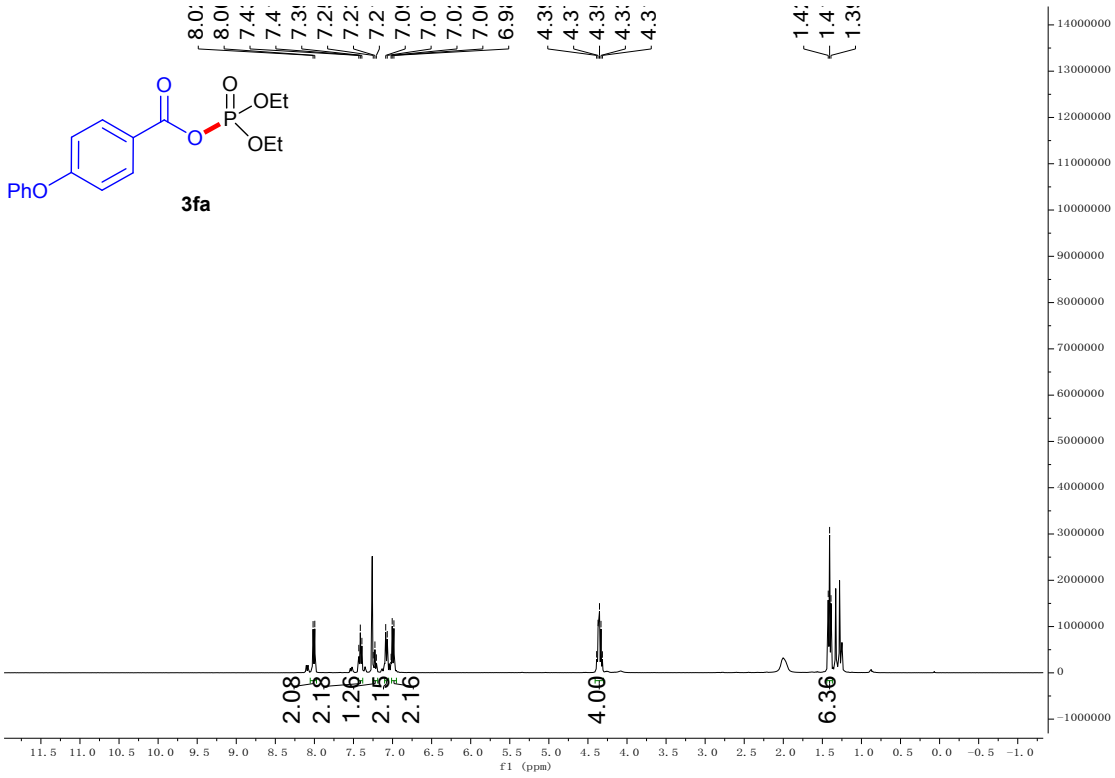
(diethyl phosphoric) 4-isopropoxybenzoic anhydride (3ea)

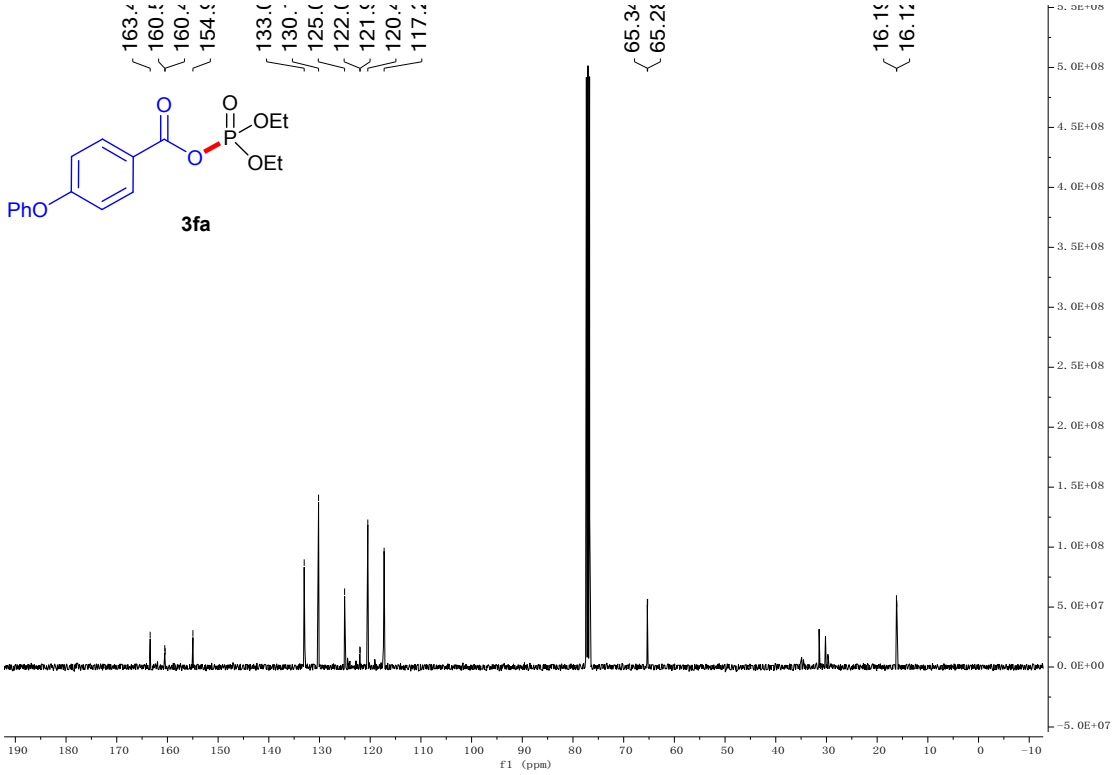


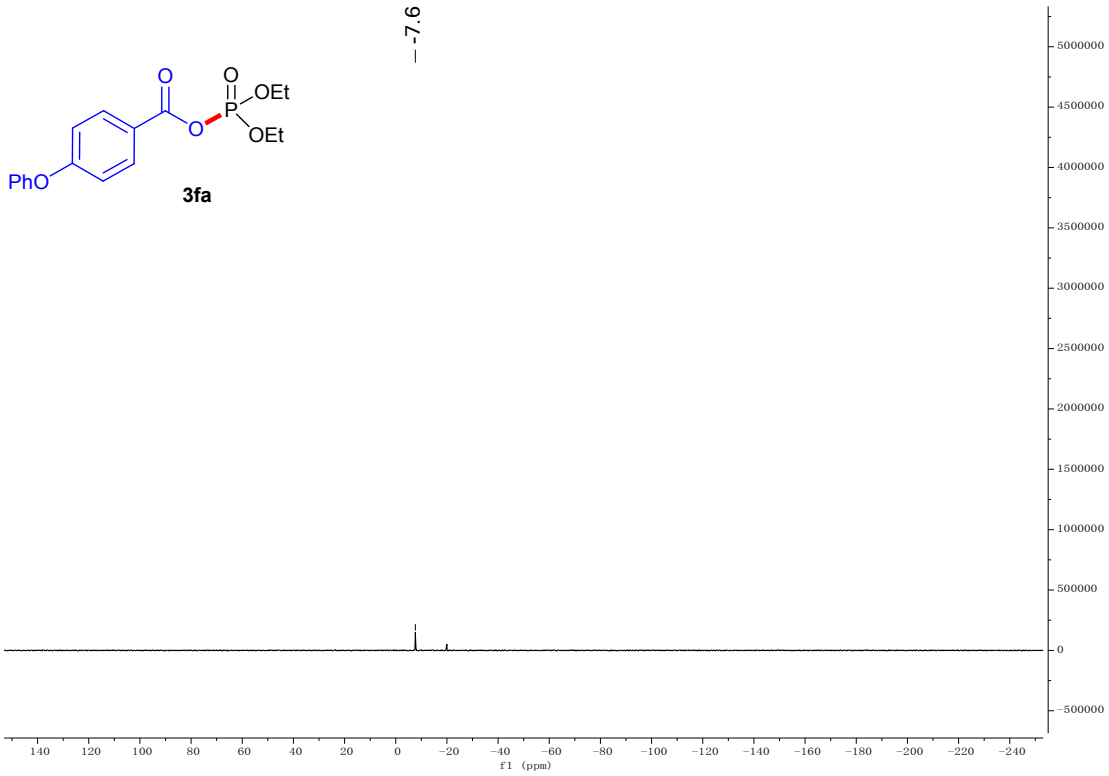

163.
160.
160.
133.
119.
119.
115.
70.3
65.2
65.1
21.8
16.1
16.1
OEt
OEt
iPrO
3ea
f1 (ppm)


-7.5
OEt
OEt
iPrO
3ea
f1 (ppm)

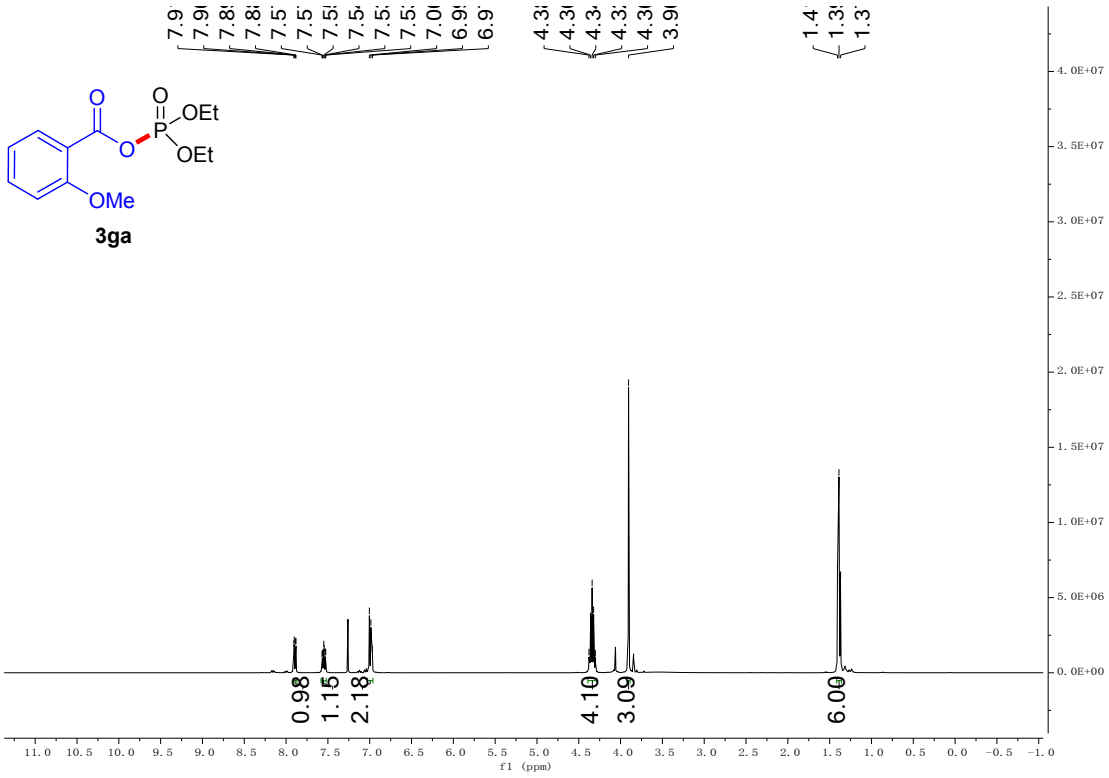
(diethyl phosphoric) 4-phenoxybenzoic anhydride (3fa)

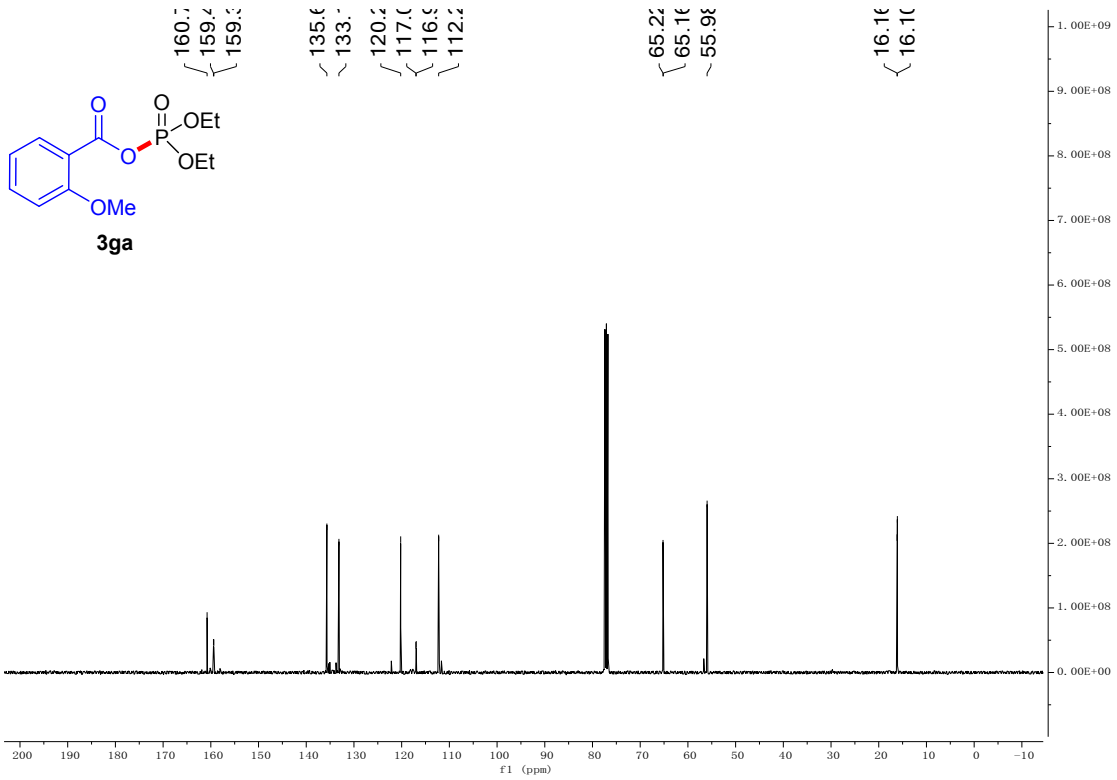


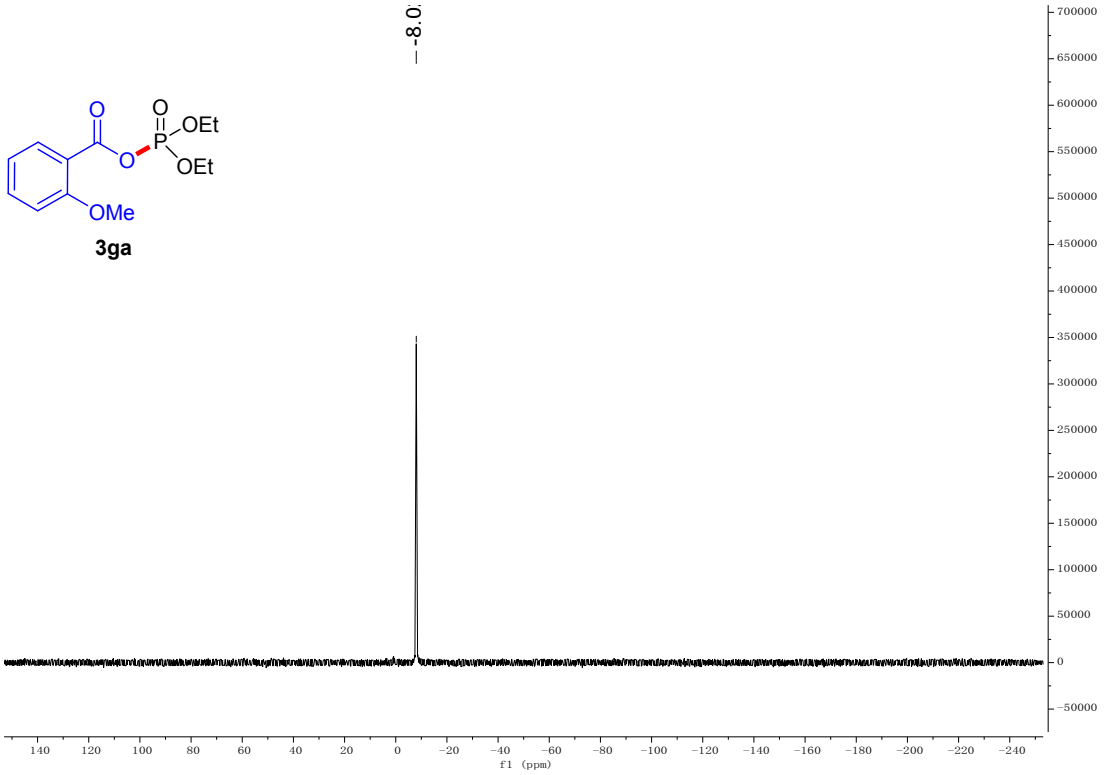




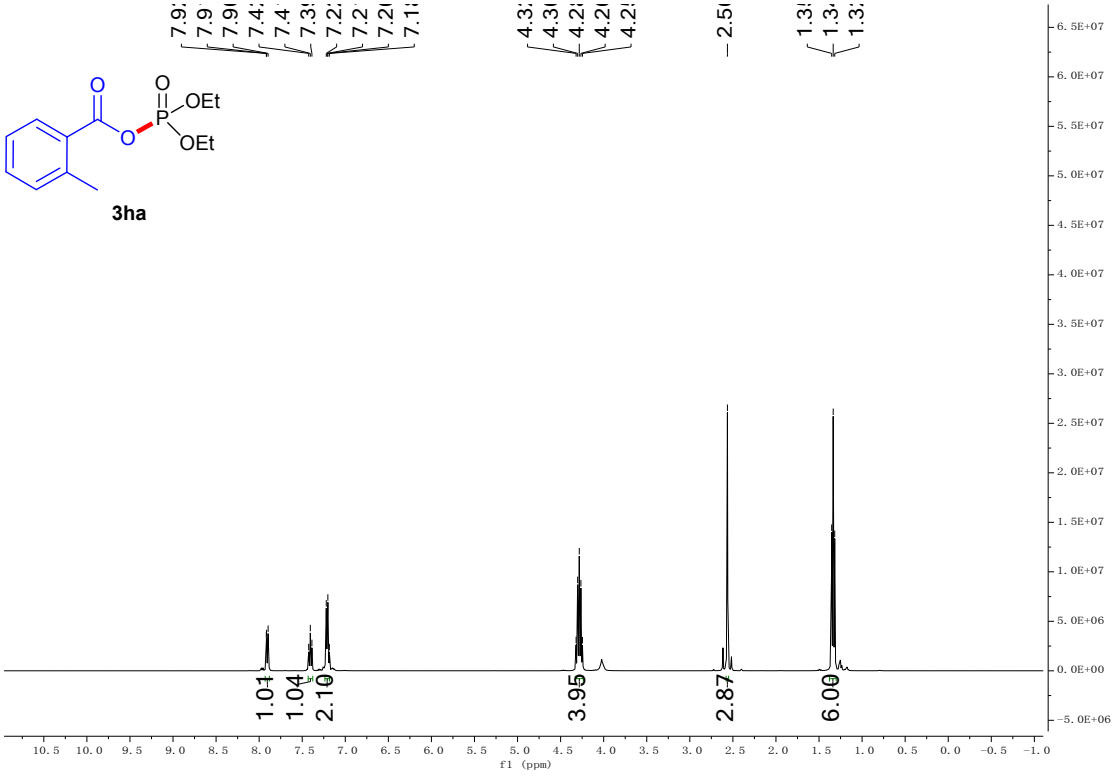
(diethyl phosphoric) 2-methoxybenzoic anhydride (3ga)

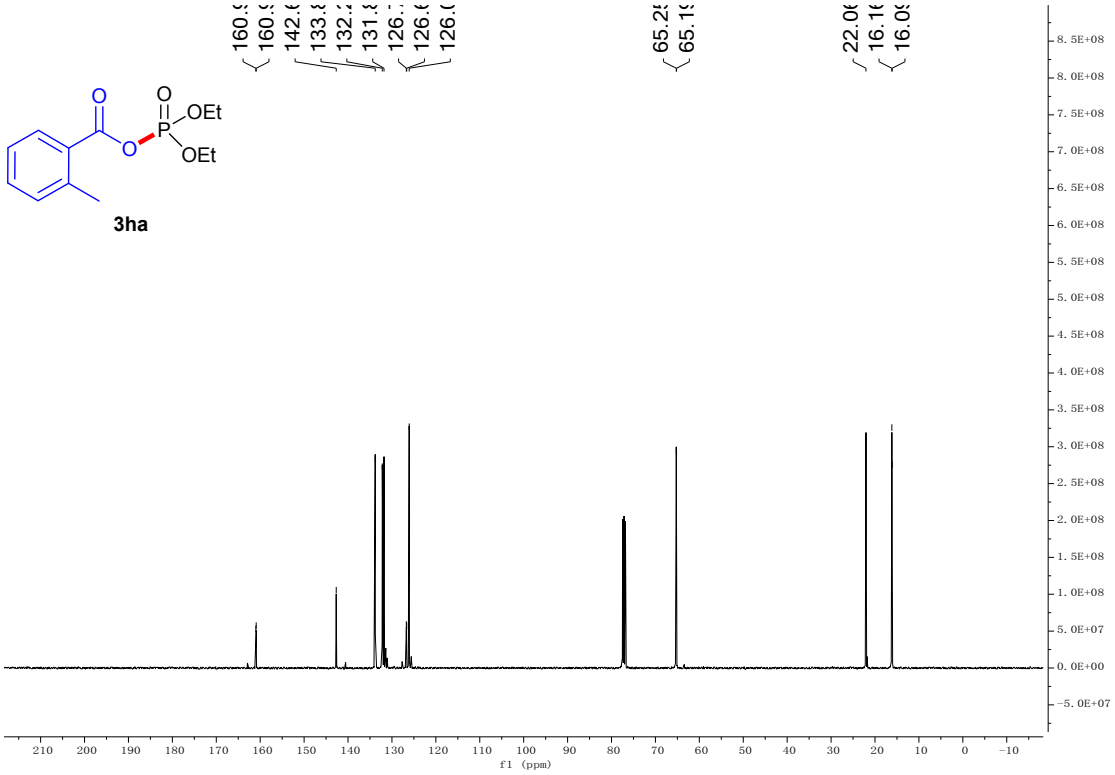


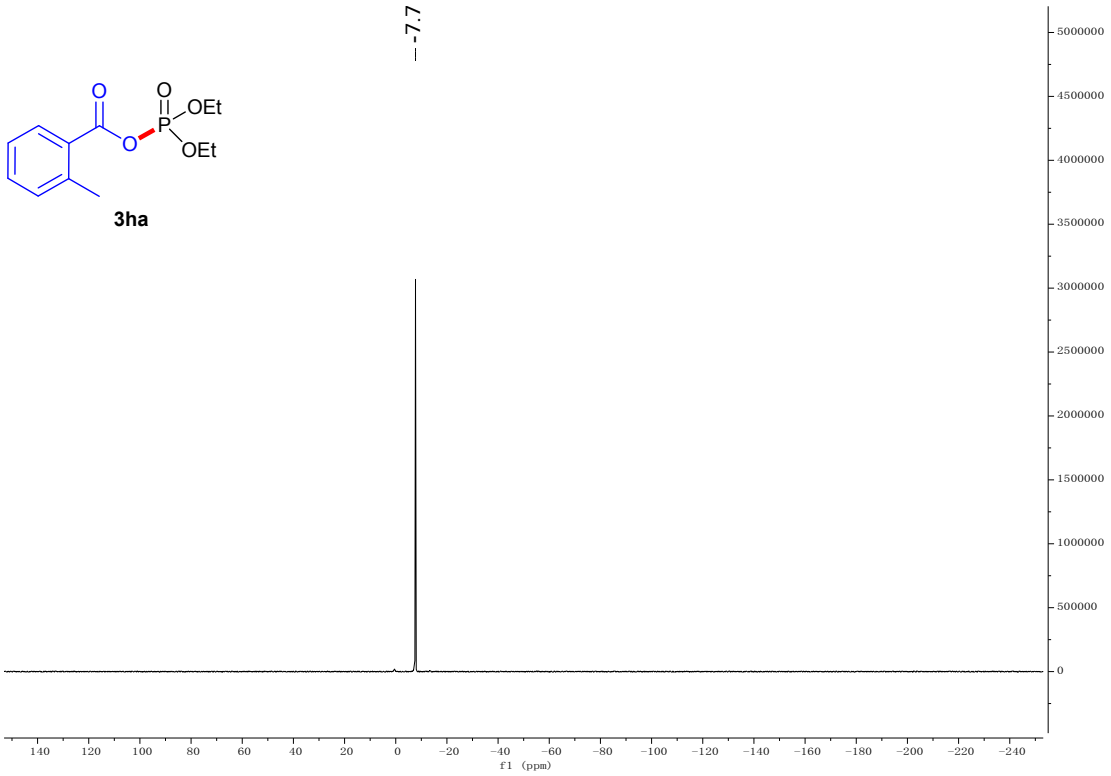

160.7
159.4
159.3
135.6
133.7
120.4
117.0
116.9
112.2
65.22
65.18
55.98
16.18
16.10
OEt
OEt
OMe
3ga
f1 (ppm)


-8.0
OEt
OEt
OMe
3ga
f1 (ppm)

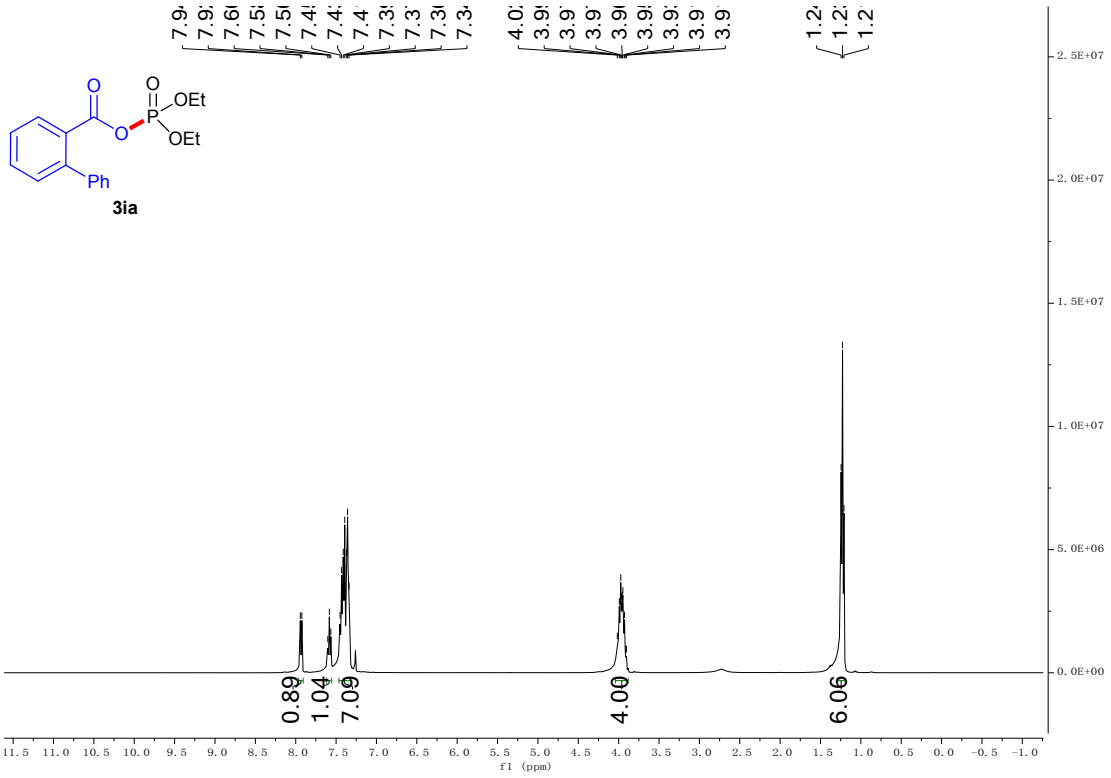
(diethyl phosphoric) 2-methylbenzoic anhydride (3ha)

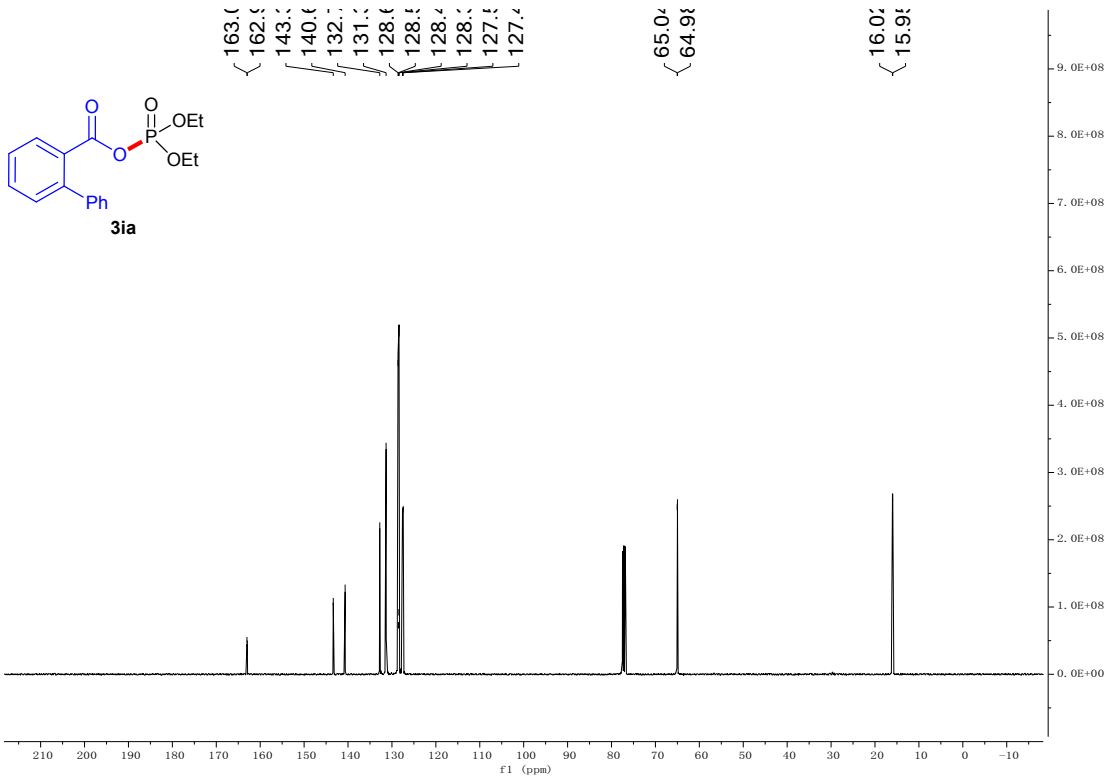


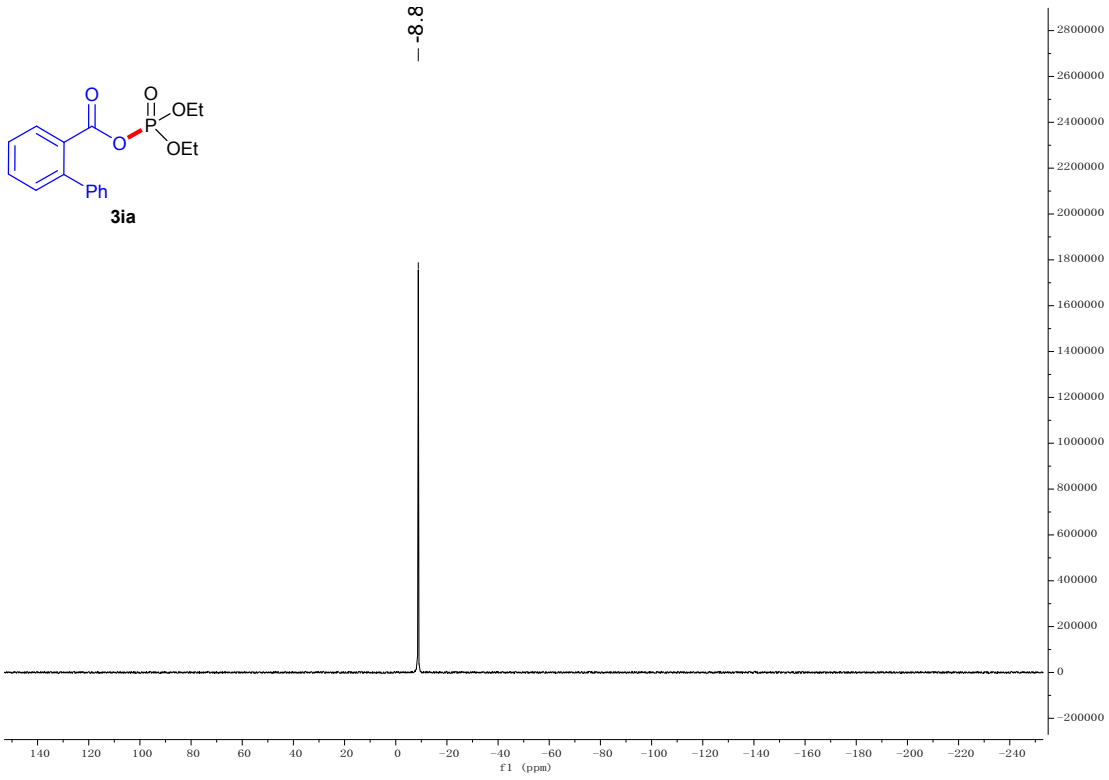




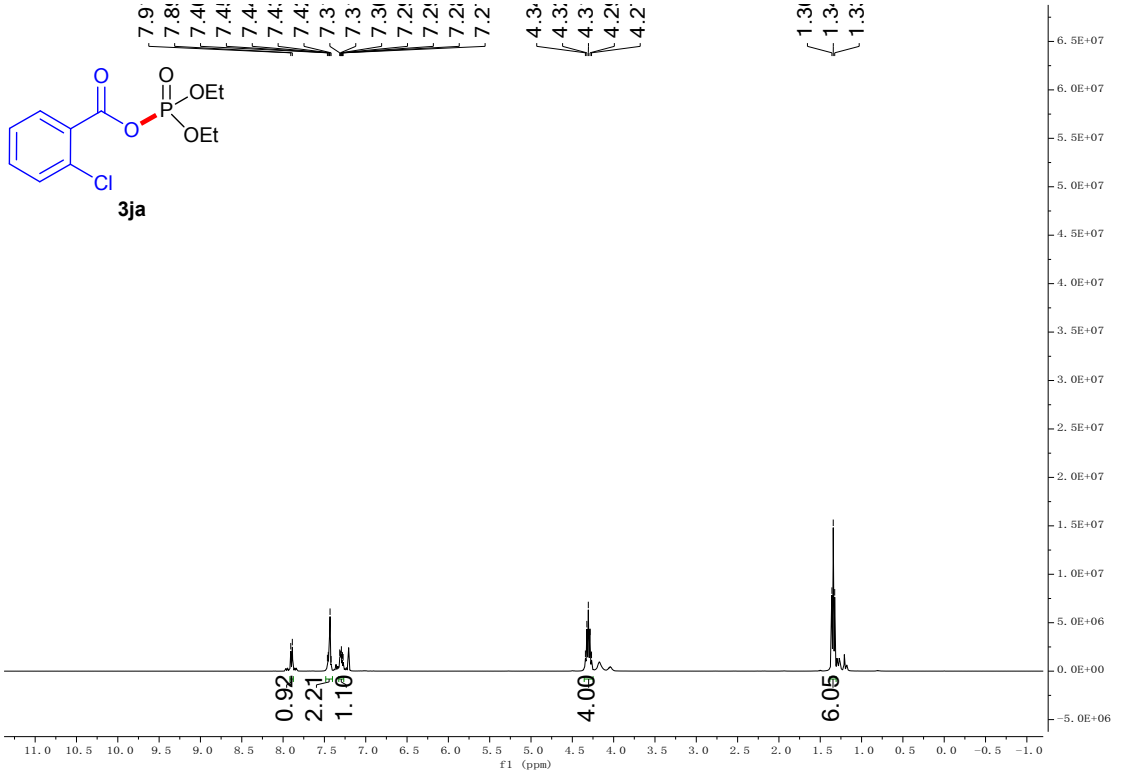
[1,1'-biphenyl]-2-carboxylic (diethyl phosphoric) anhydride (3ia)

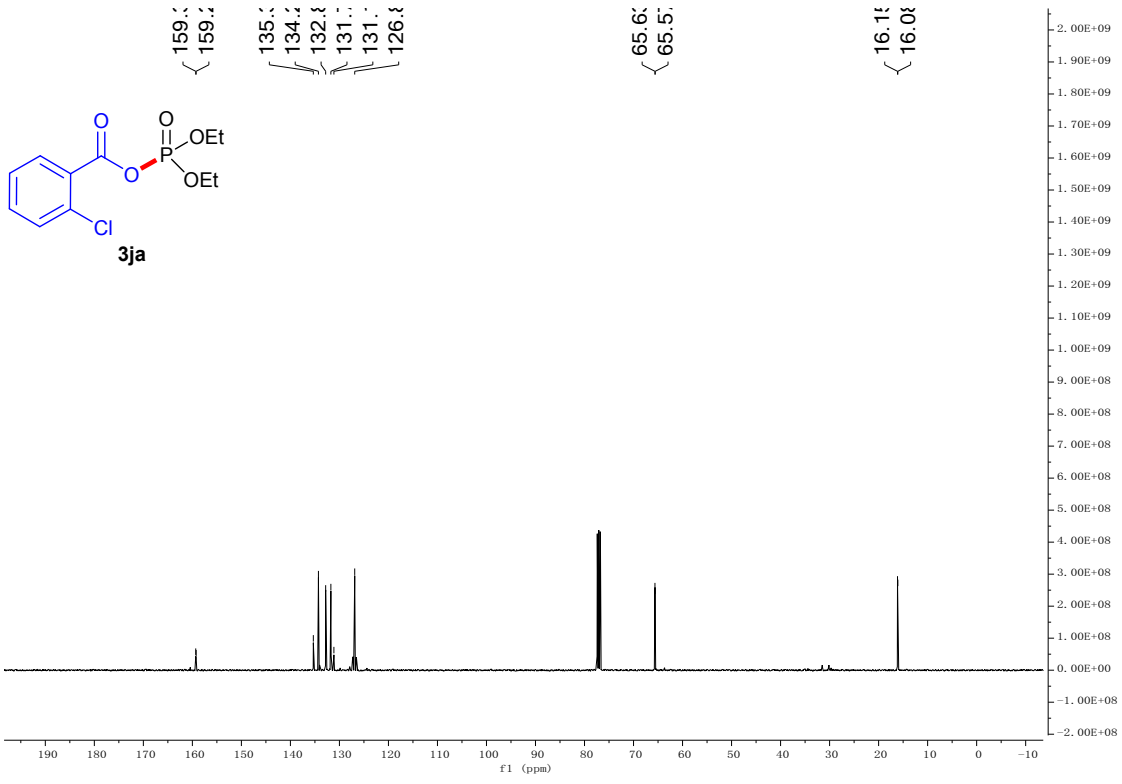


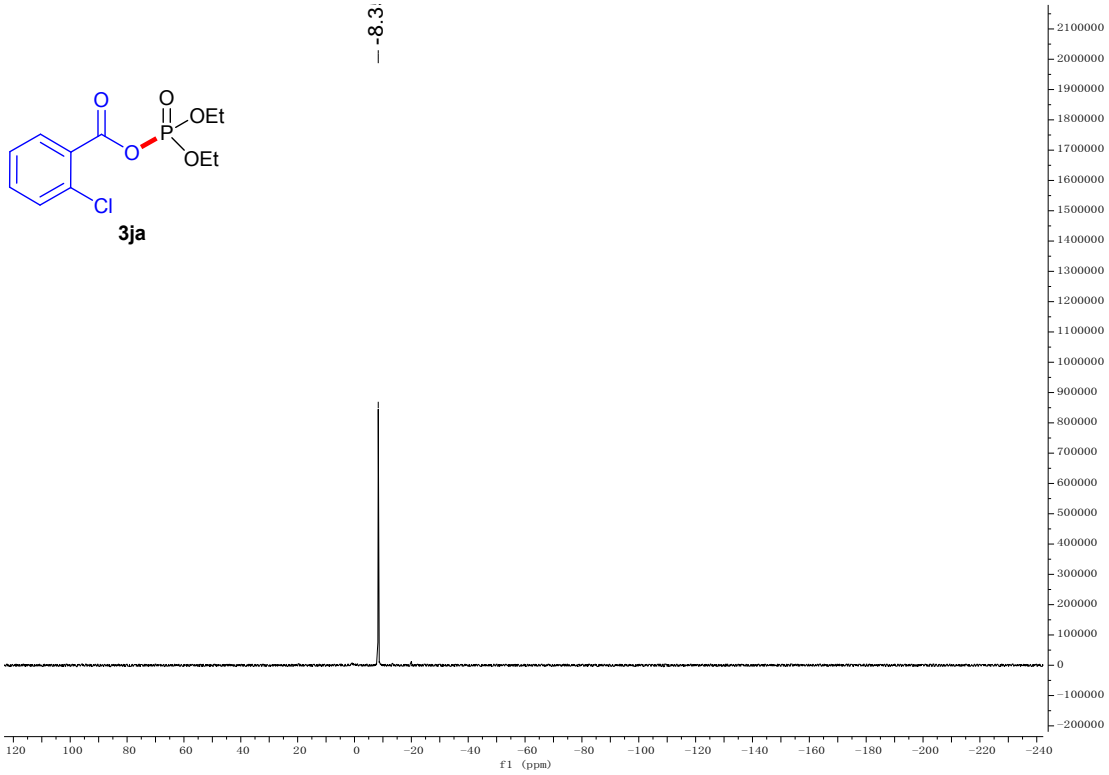

3ia
f1 (ppm)


3ia
f1 (ppm)

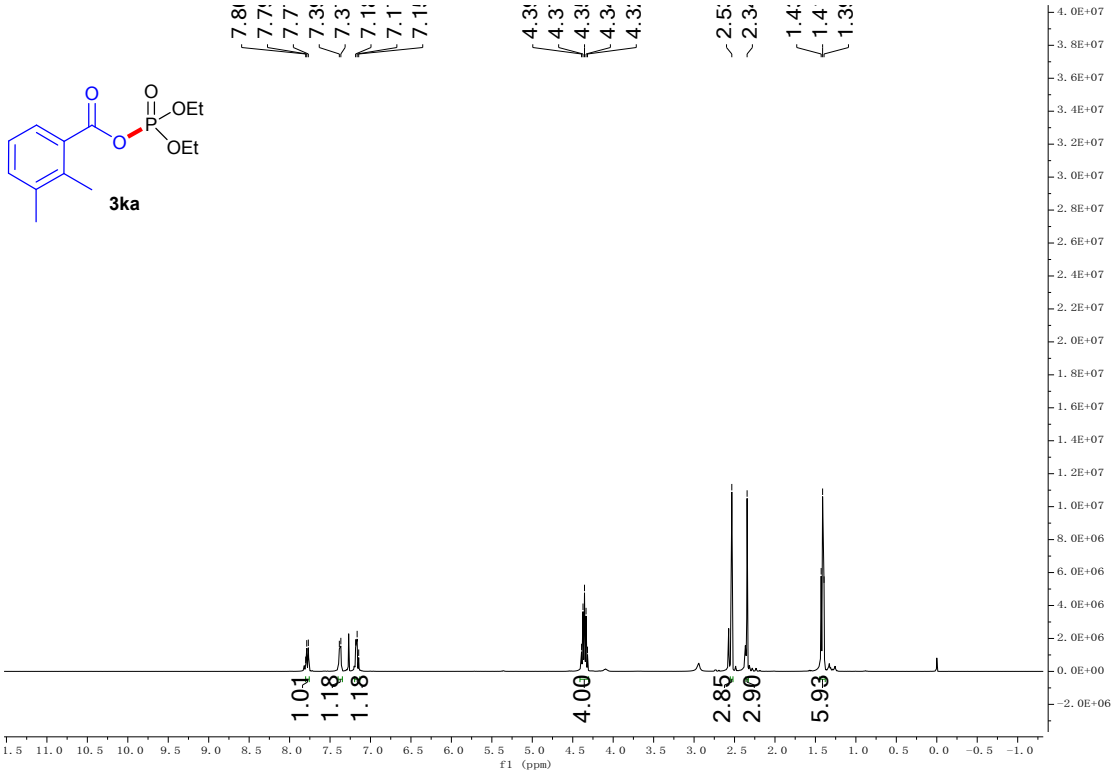
2-chlorobenzoic (diethyl phosphoric) anhydride (3ja)

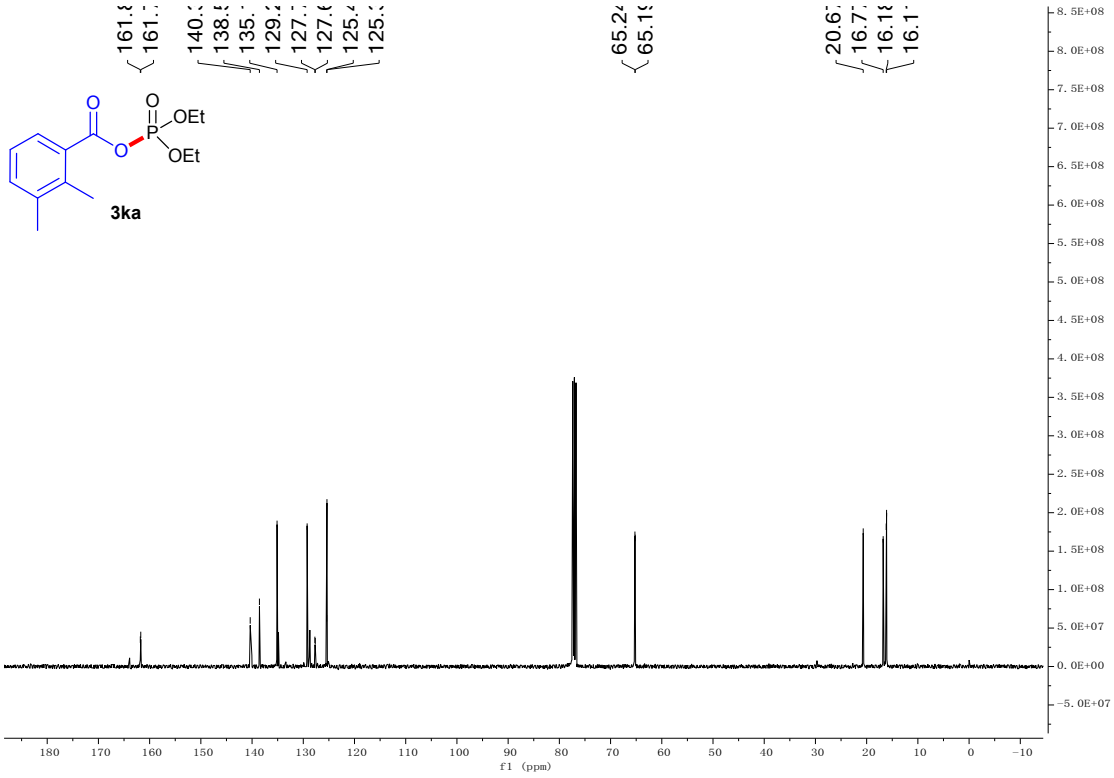




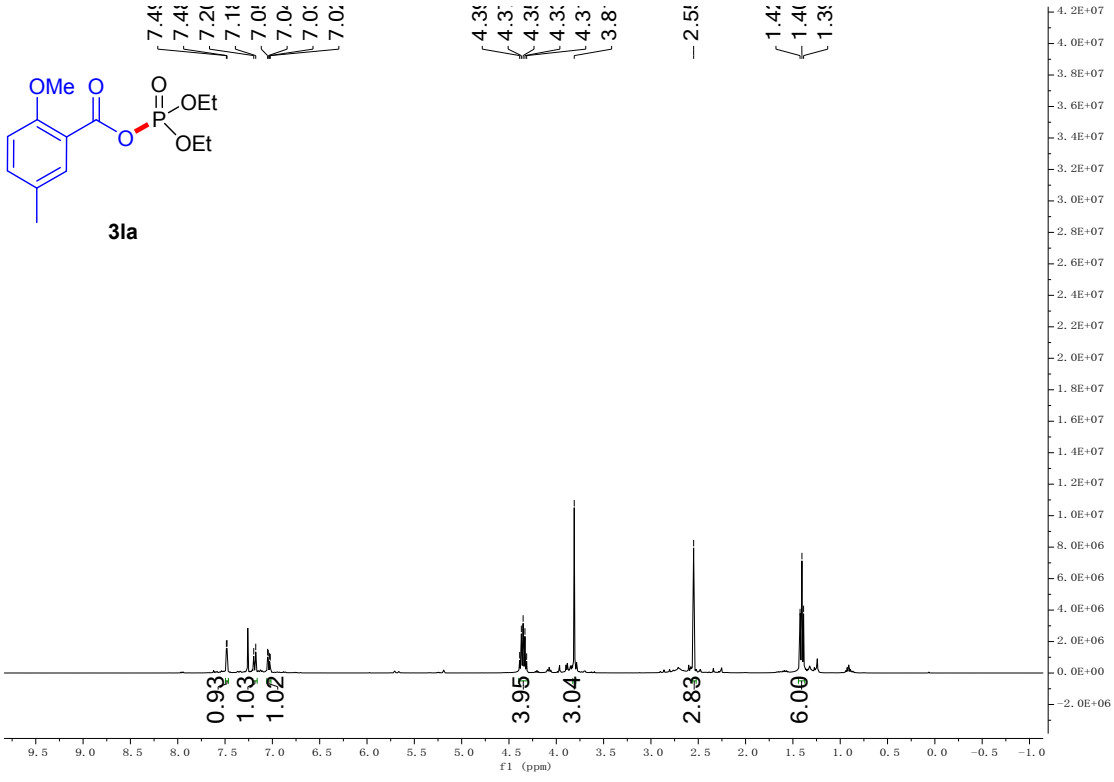


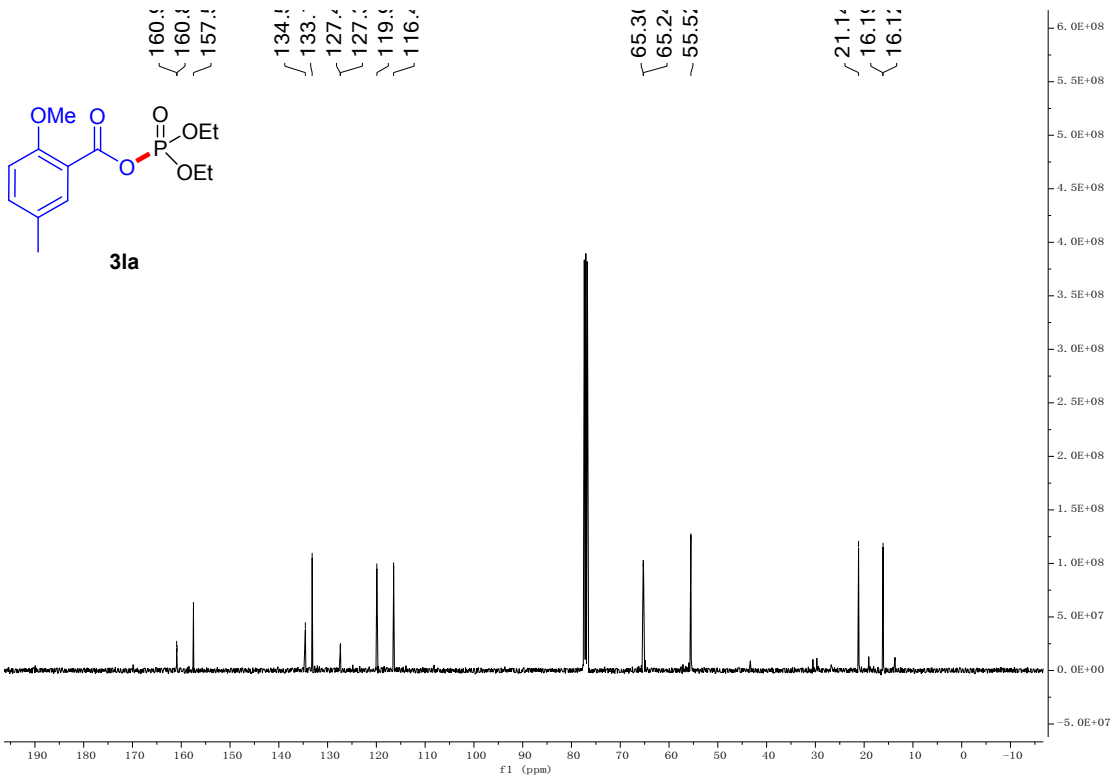
(diethyl phosphoric) 2,4-dimethylbenzoic anhydride (3ka)

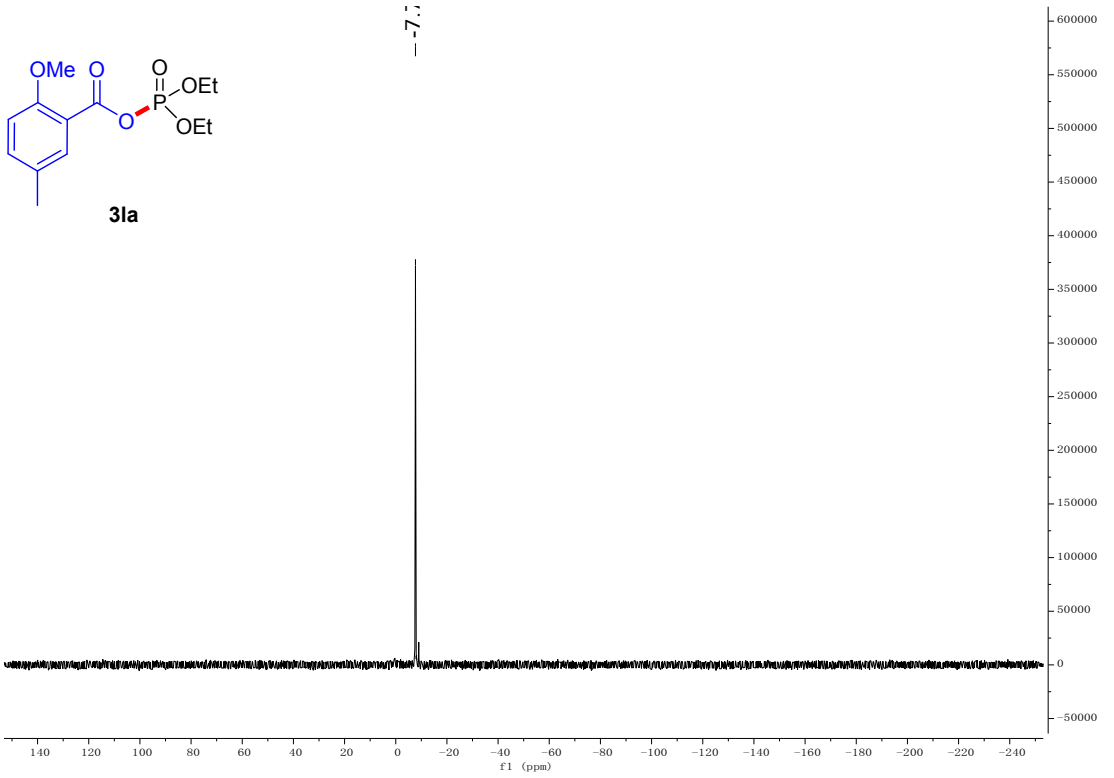




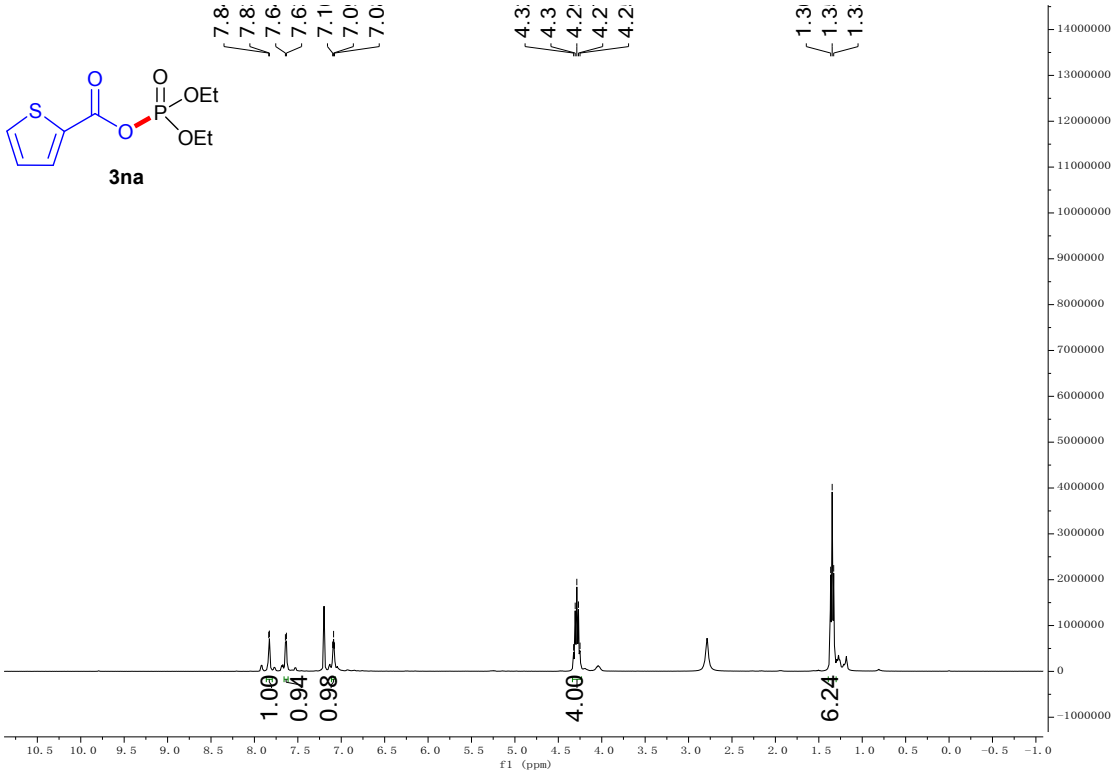
(diethyl phosphoric) 2-methoxy-5-methylbenzoic anhydride (3la)

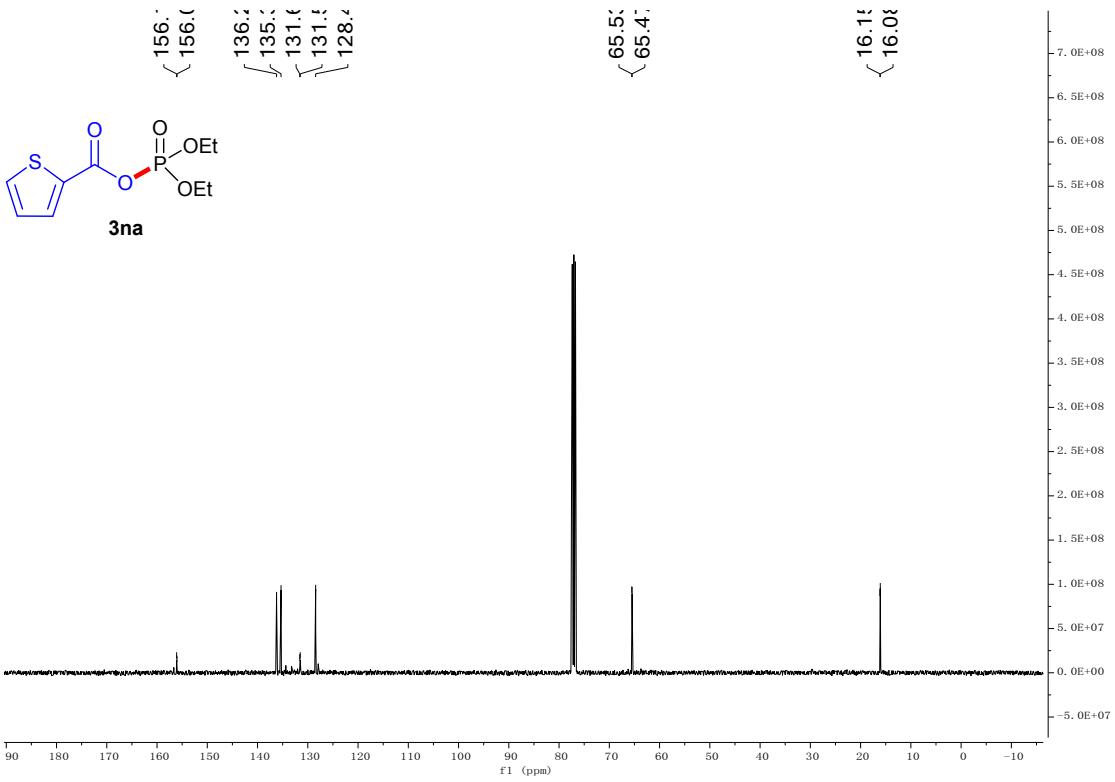


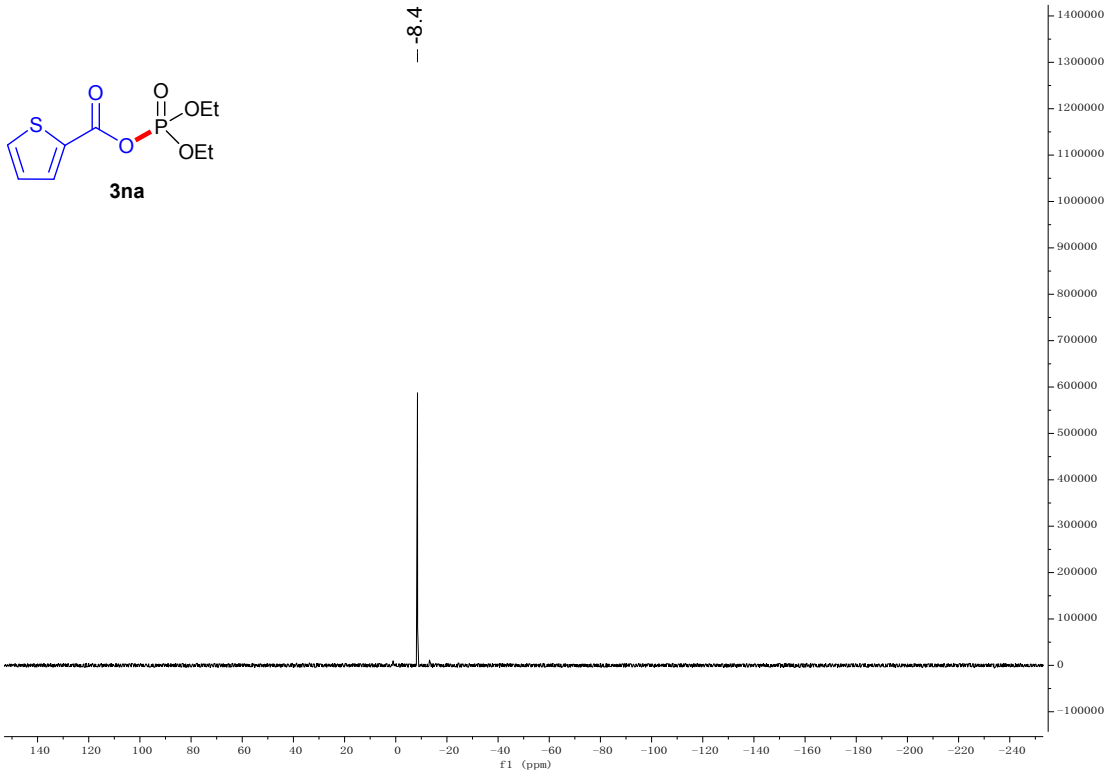

OMe
O
O
O
P
OEt
OEt
3la
160.
160.
157.
134.
133.
127.
127.
119.
116.
65.3
65.2
55.5
21.1
16.1
16.1
6. 0E+08
5. 5E+08
5. 0E+08
4. 5E+08
4. 0E+08
3. 5E+08
3. 0E+08
2. 5E+08
2. 0E+08
1. 5E+08
1. 0E+08
5. 0E+07
0. 0E+00
−5. 0E+07
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


OMe
O
O
O
P
OEt
OEt
3la
-7.
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
−50000
140 120 100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 −220 −240
f1 (ppm)

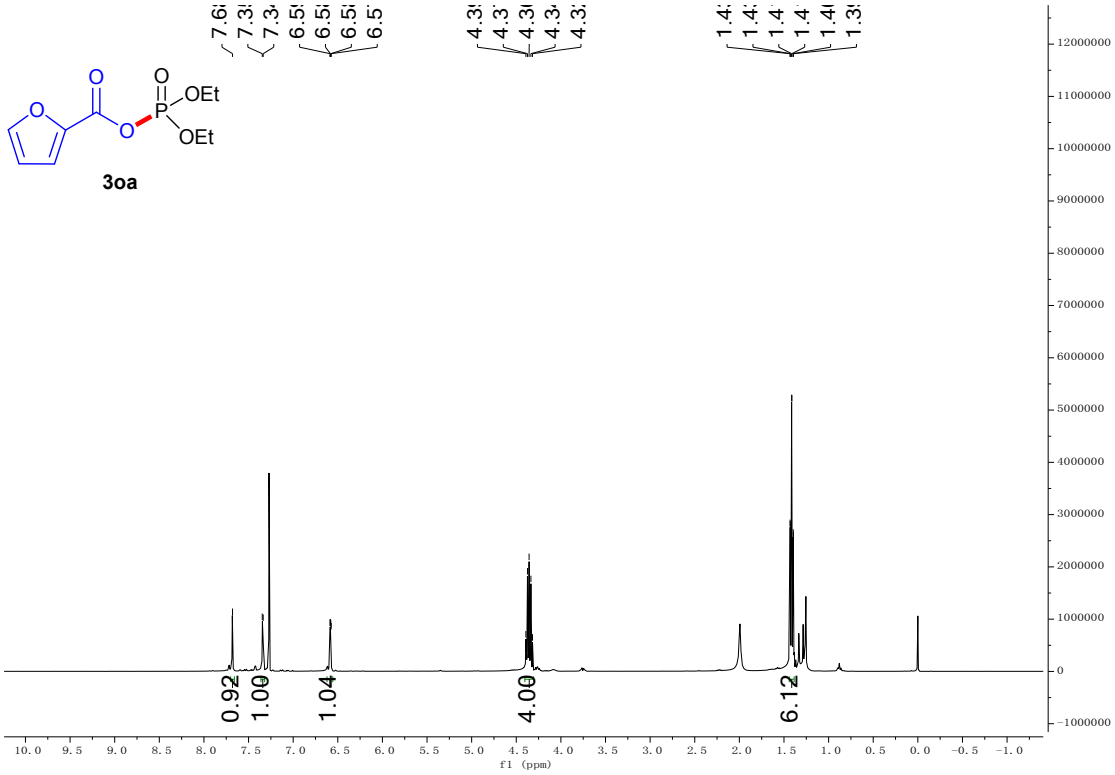
(diethyl phosphoric) thiophene-2-carboxylic anhydride (3na)

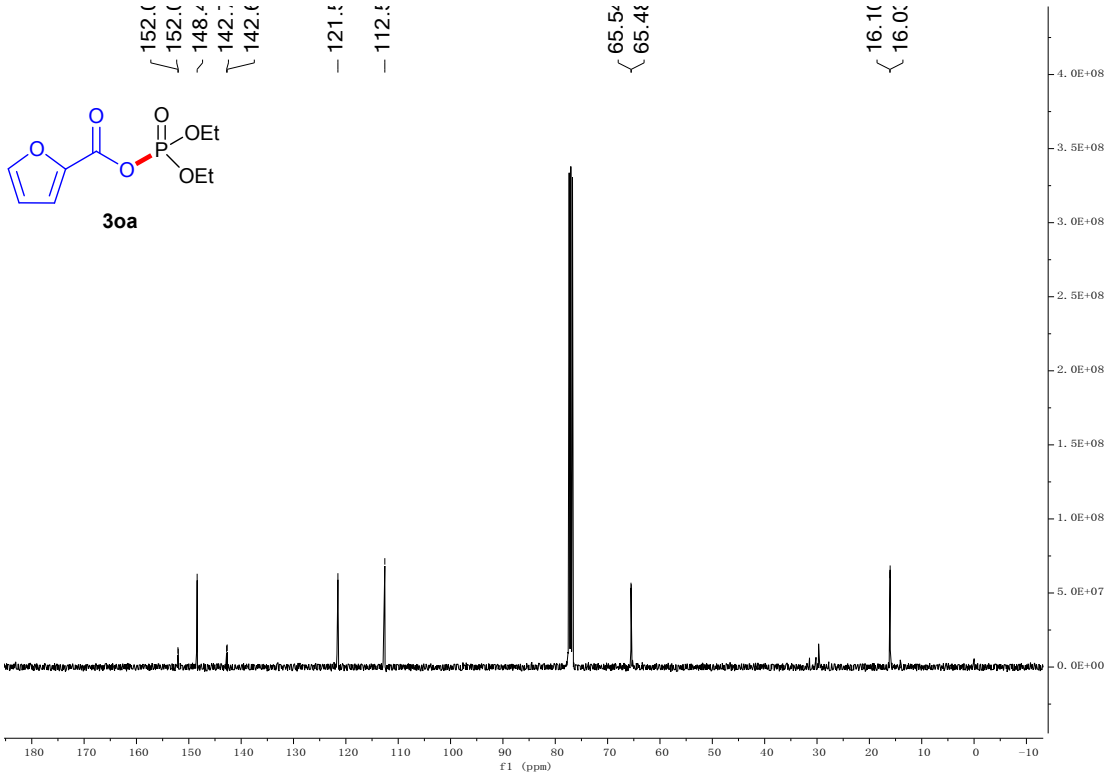




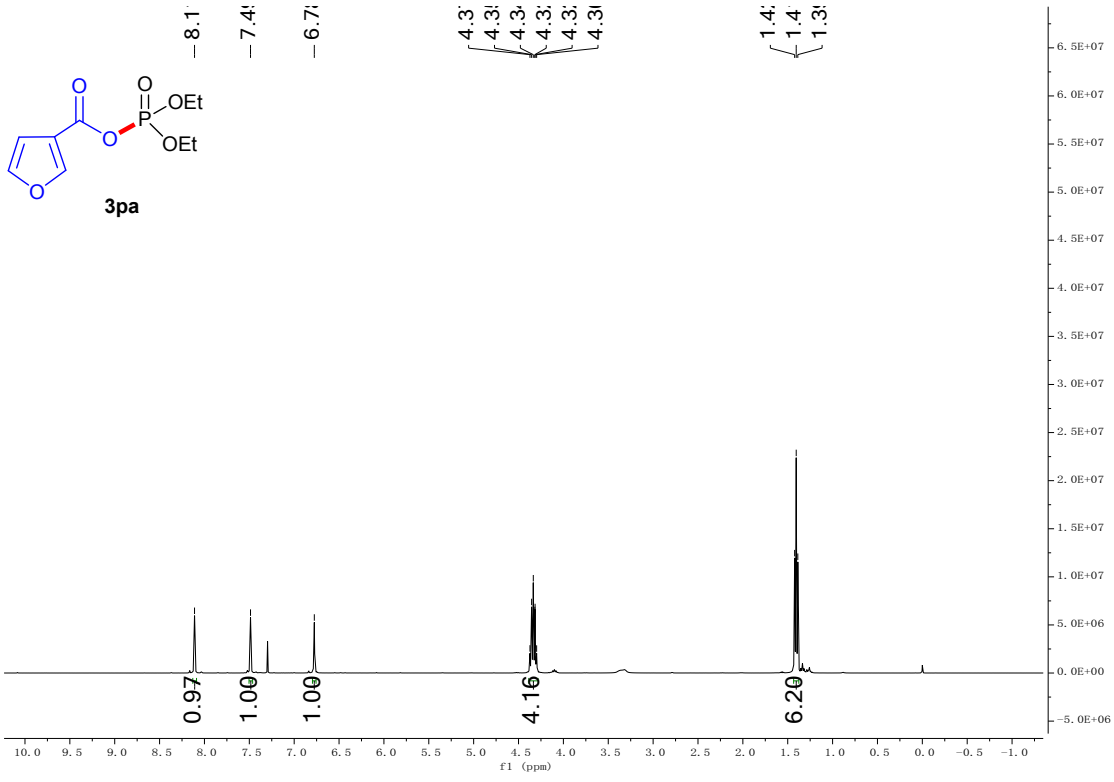


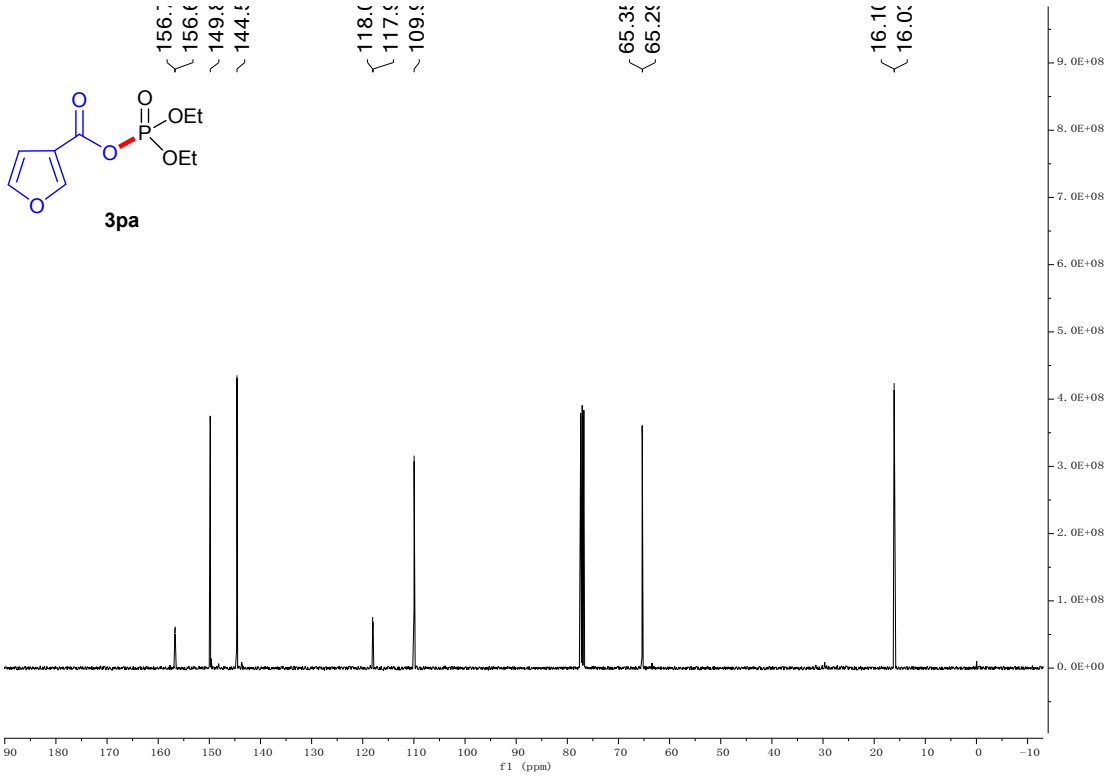
(diethyl phosphoric) 2-methylbenzoic anhydride (3oa)

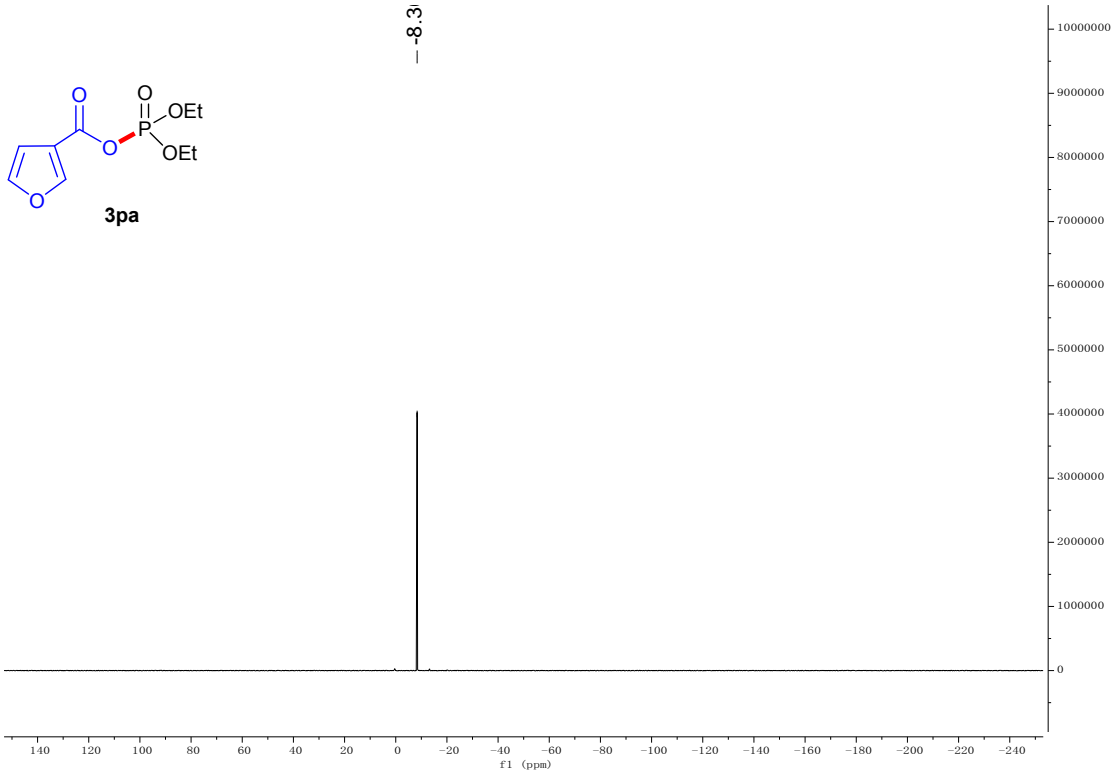




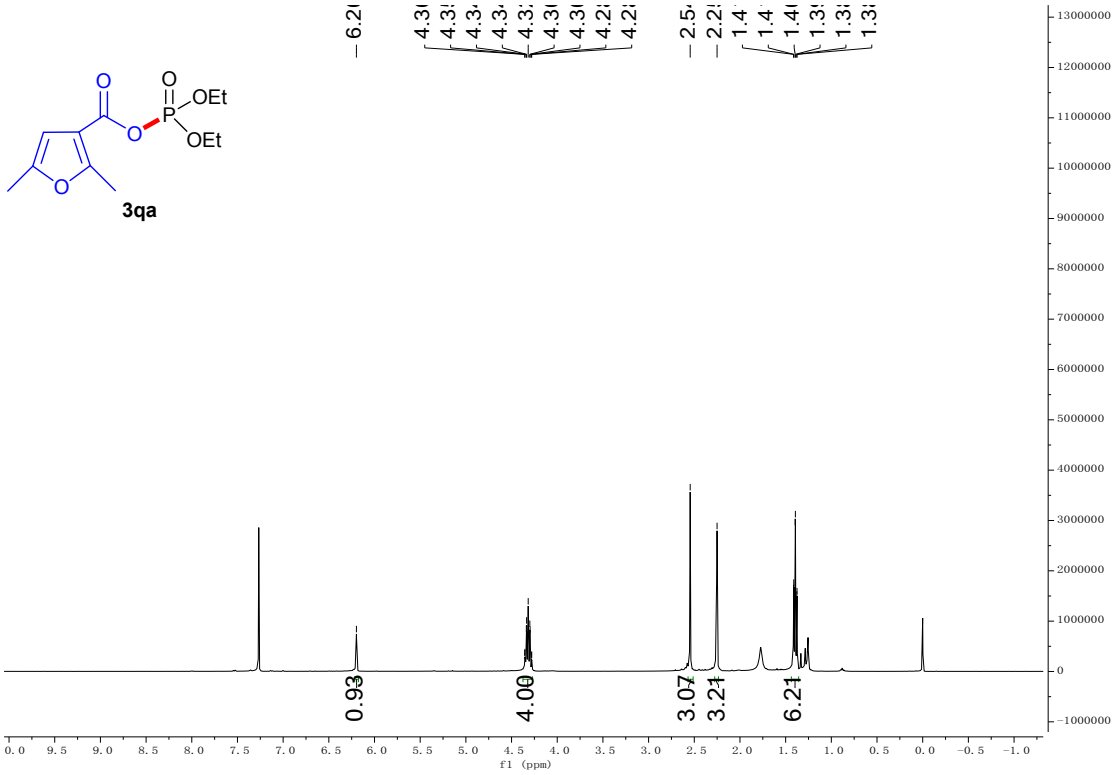
(diethyl phosphoric) furan-3-carboxylic anhydride (3pa)

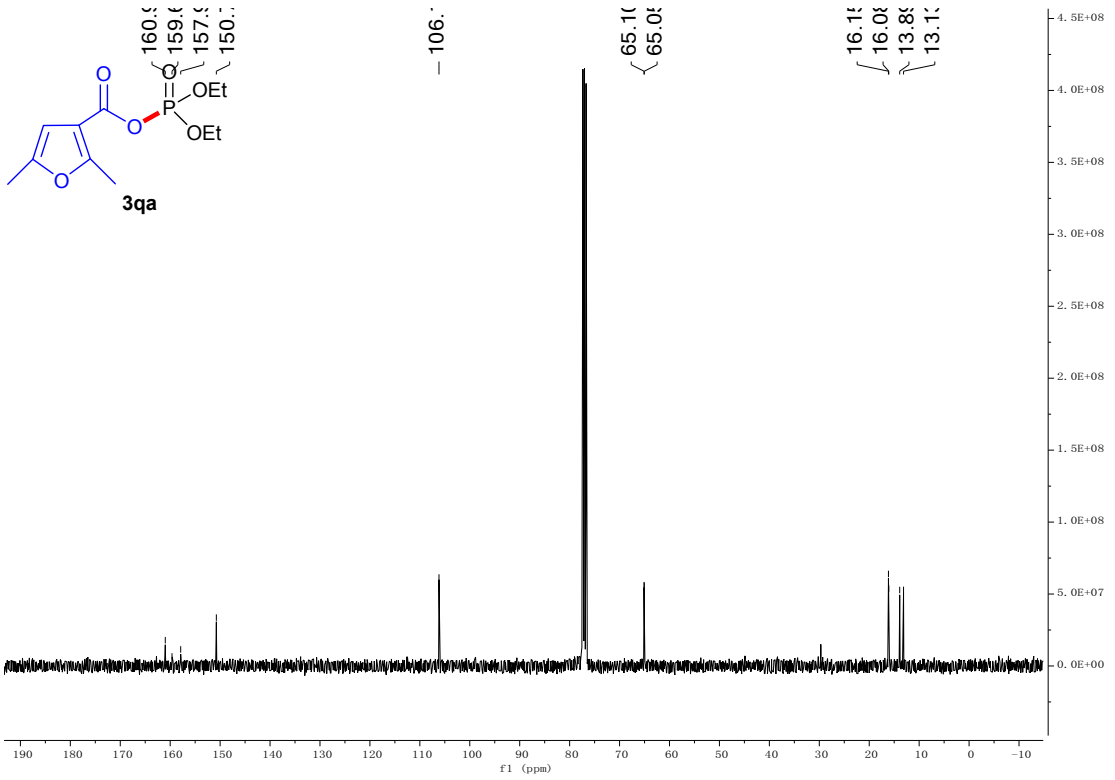


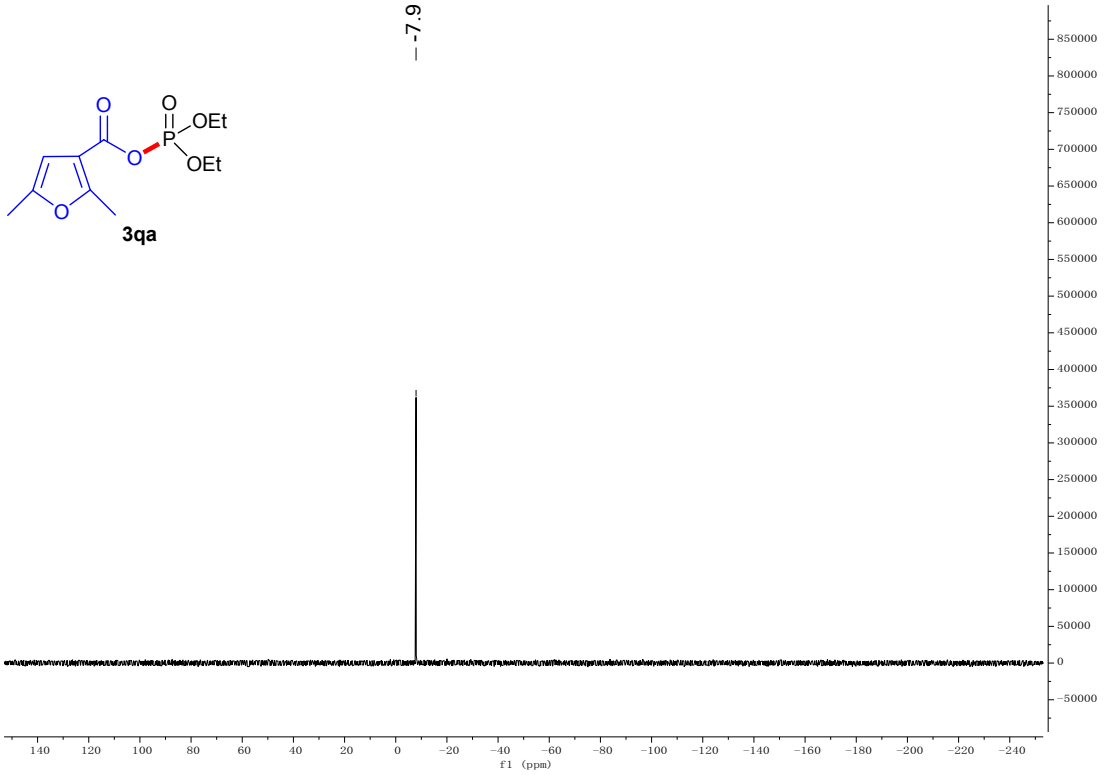

156.
156.
149.
144.
118.
117.
109.
65.3
65.2
16.1
16.0
3pa
9. 0E+08
8. 0E+08
7. 0E+08
6. 0E+08
5. 0E+08
4. 0E+08
3. 0E+08
2. 0E+08
1. 0E+08
0. 0E+00
f1 (ppm)


-8.3
3pa
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
f1 (ppm)

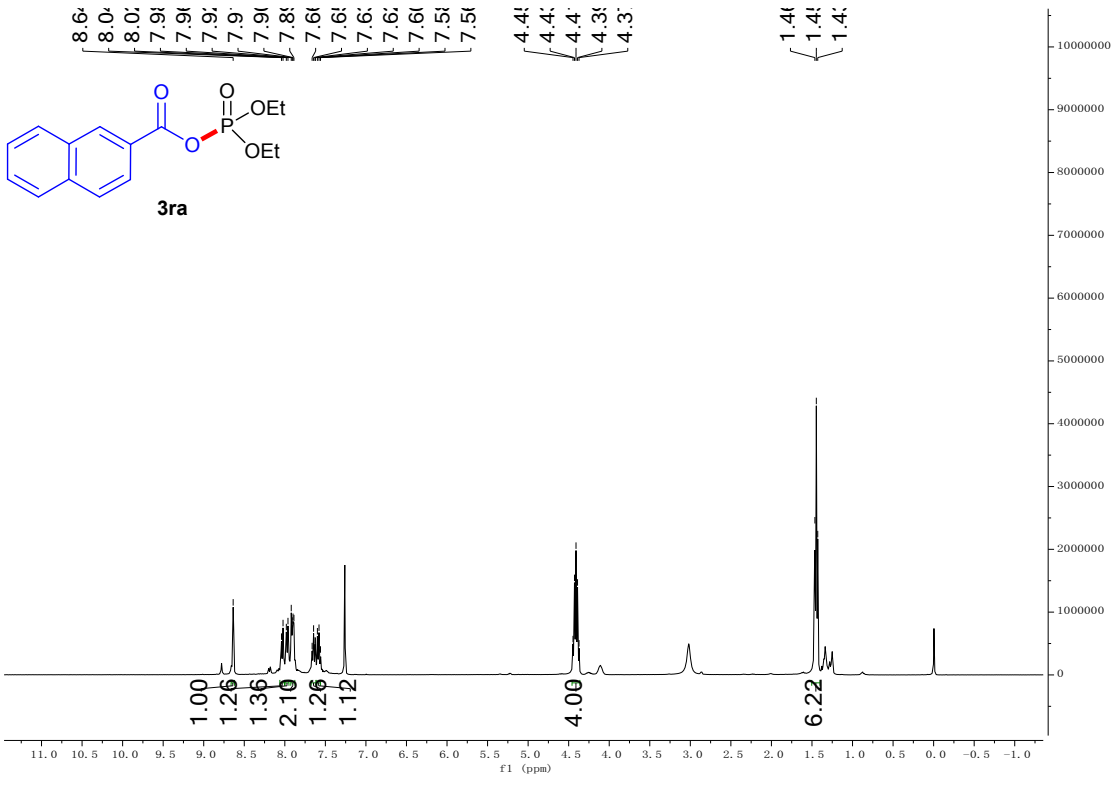
(diethyl phosphoric) 2,5-dimethylfuran-3-carboxylic anhydride (3qa)

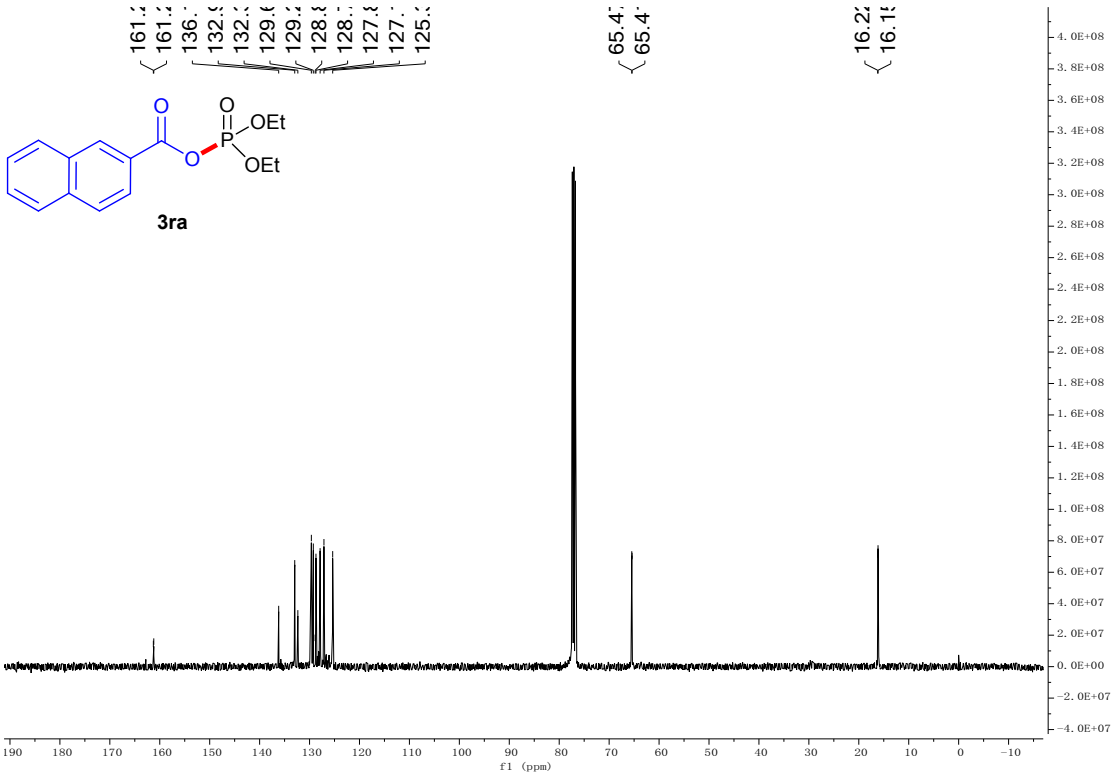


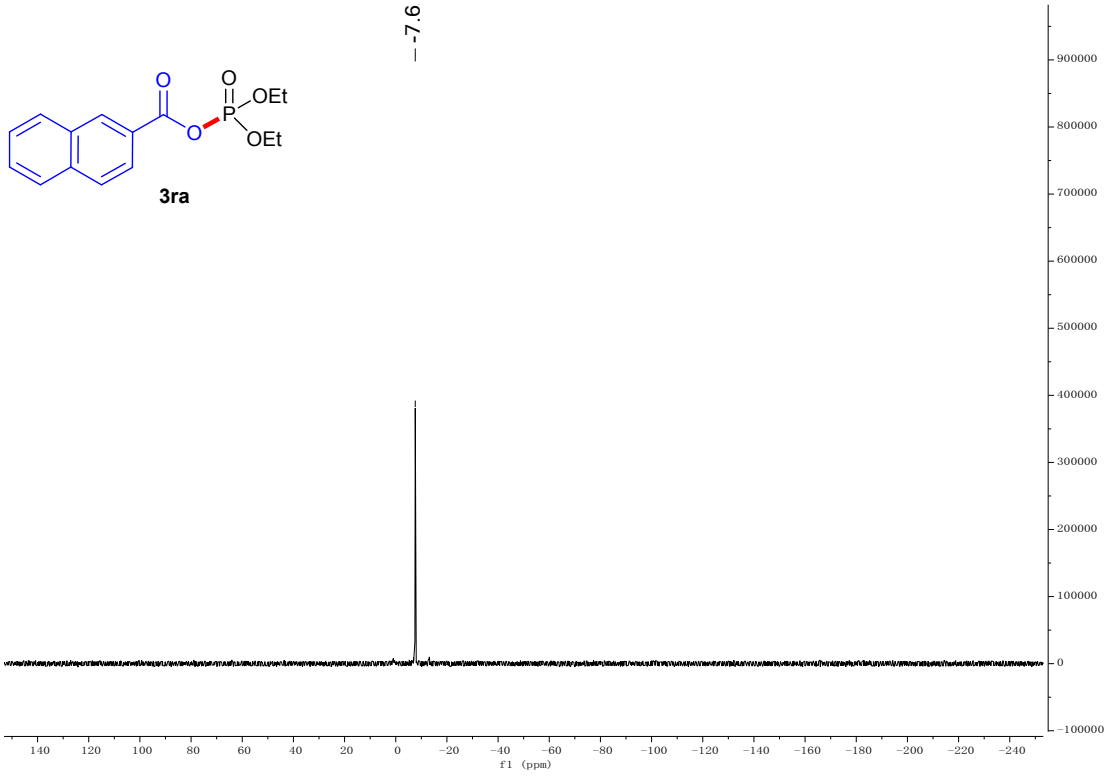




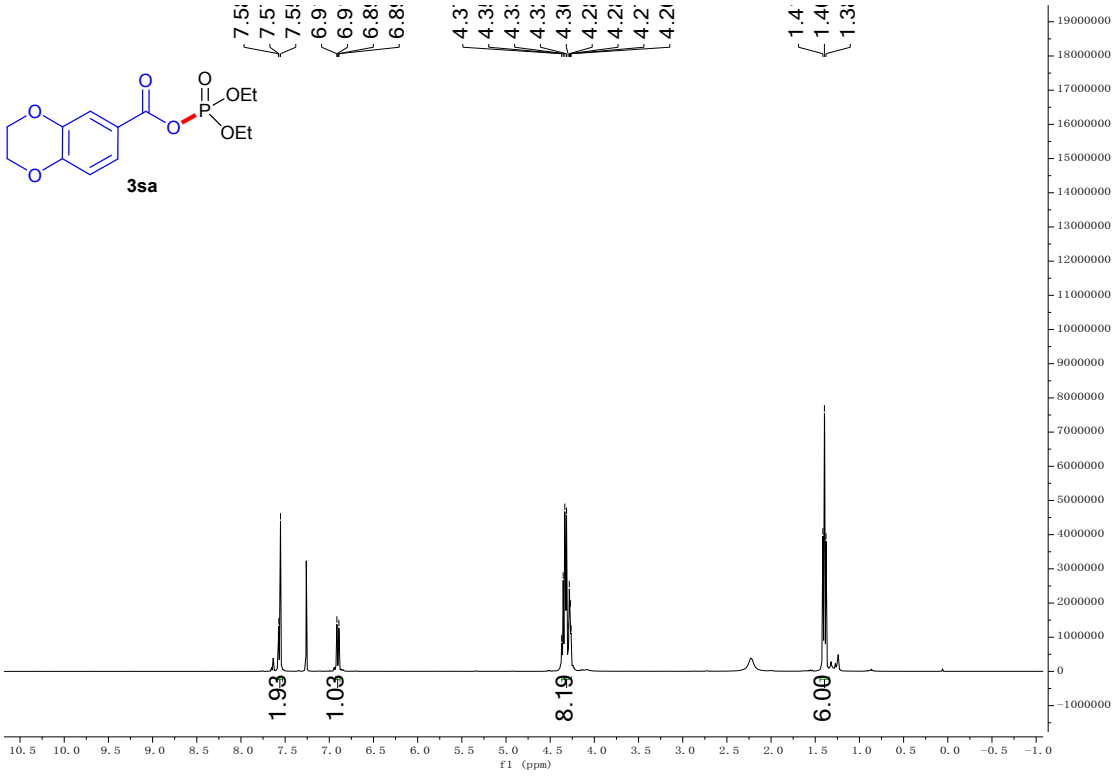
2-naphthoic (diethyl phosphoric) anhydride (3ra)

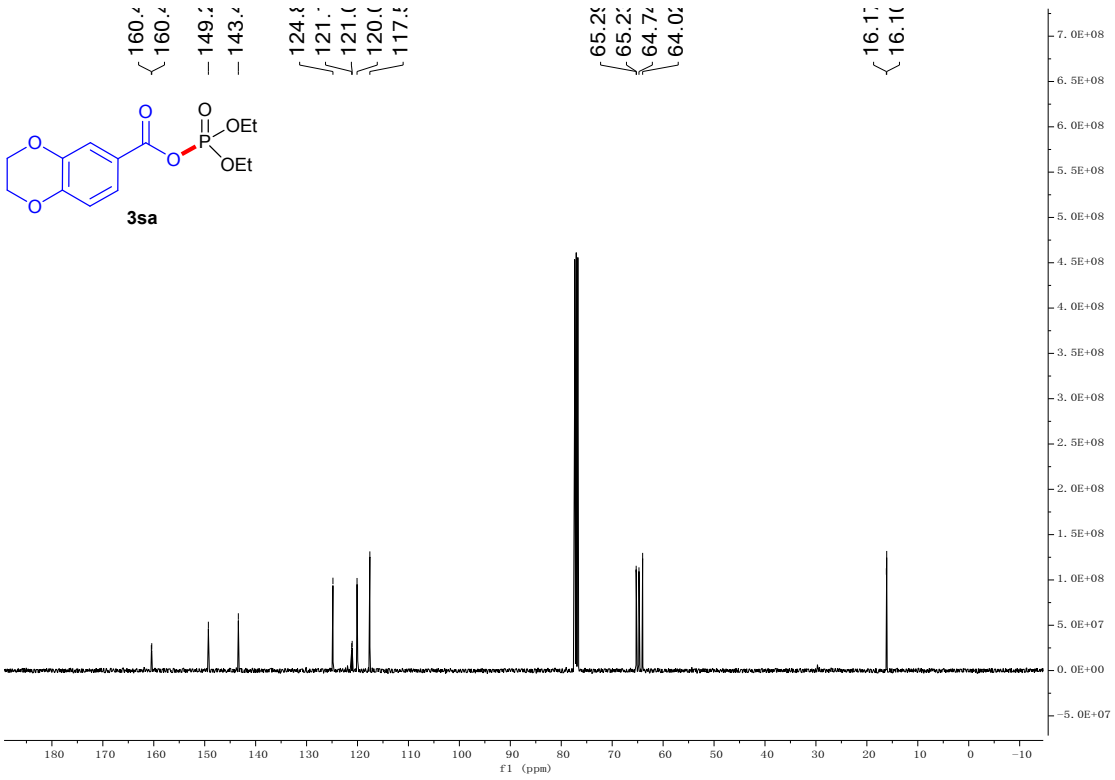


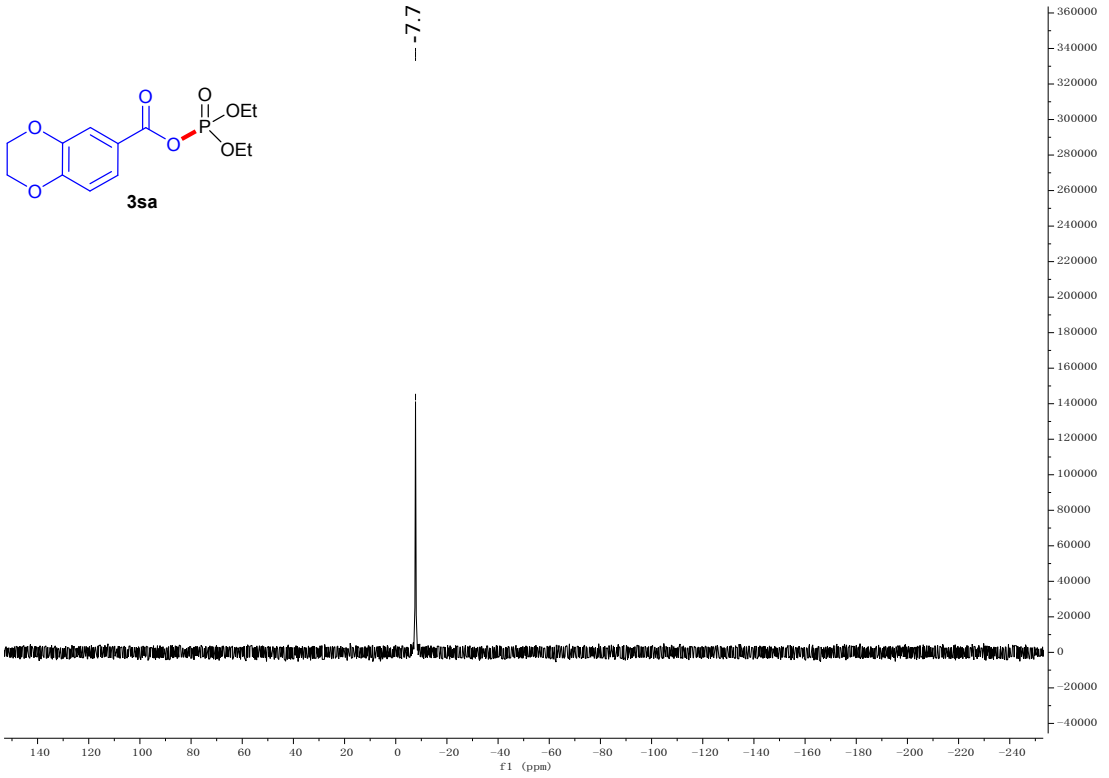

65.4
65.4
16.2
16.1
O
O
OEt
P
O
OEt
3ra
4.0E+08
3.8E+08
3.6E+08
3.4E+08
3.2E+08
3.0E+08
2.8E+08
2.6E+08
2.4E+08
2.2E+08
2.0E+08
1.8E+08
1.6E+08
1.4E+08
1.2E+08
1.0E+08
8.0E+07
6.0E+07
4.0E+07
2.0E+07
0.0E+00
-2.0E+07
-4.0E+07
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-7.6
O
O
OEt
P
O
OEt
3ra
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

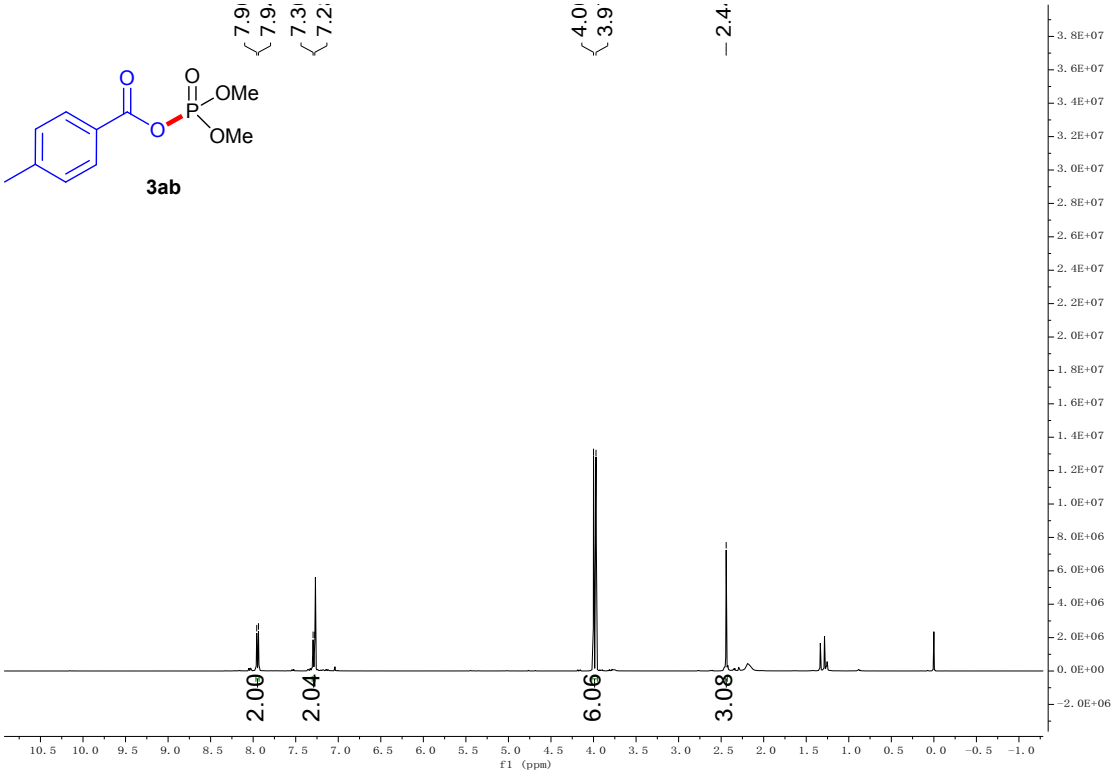
(diethyl phosphoric) 2,3-dihydrobenzo[b][1,4]dioxine-6-carboxylic anhydride (3sa)

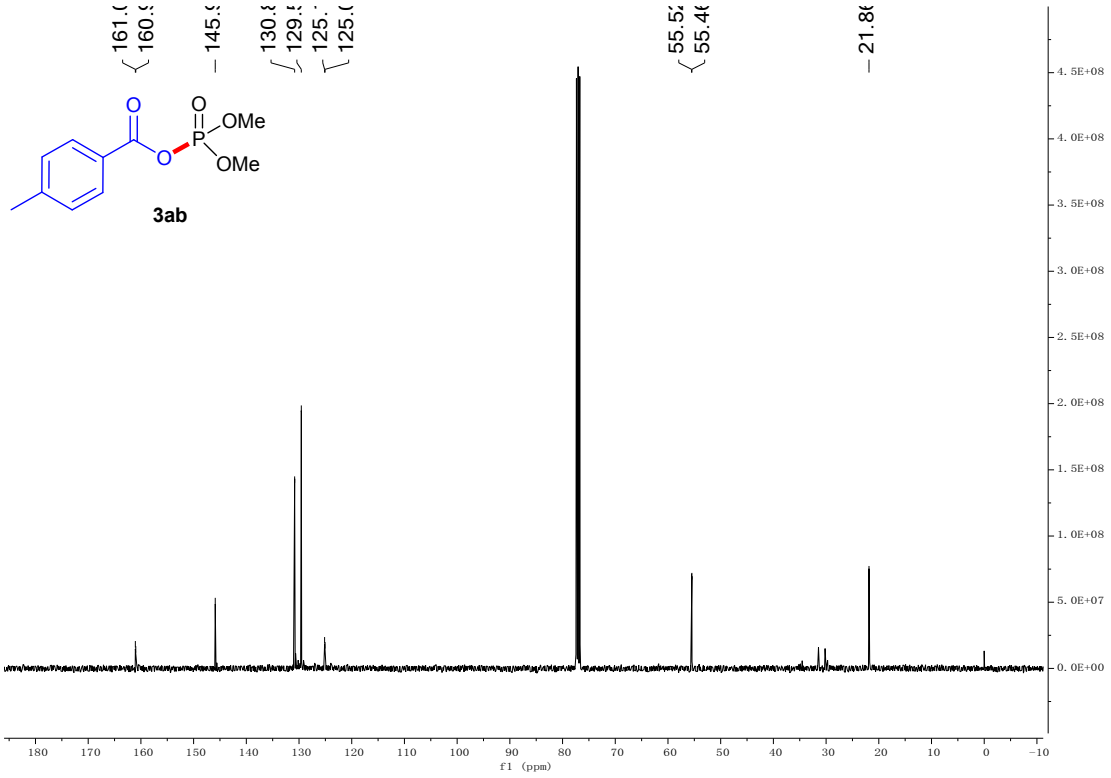


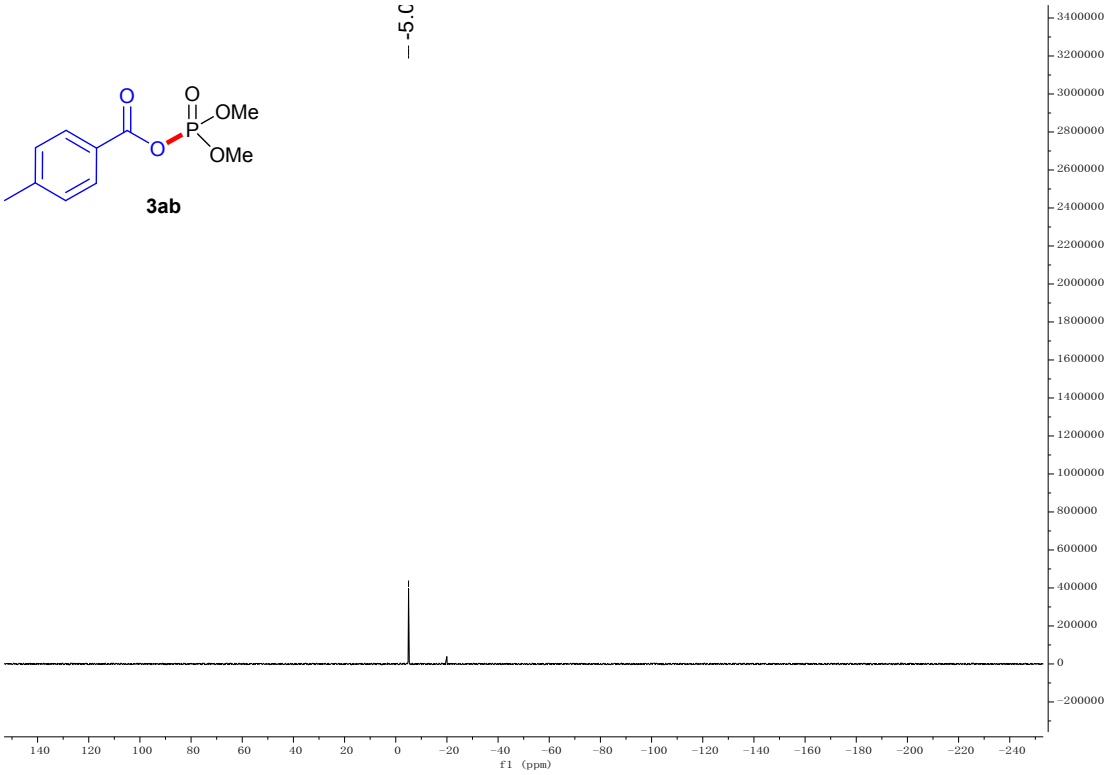




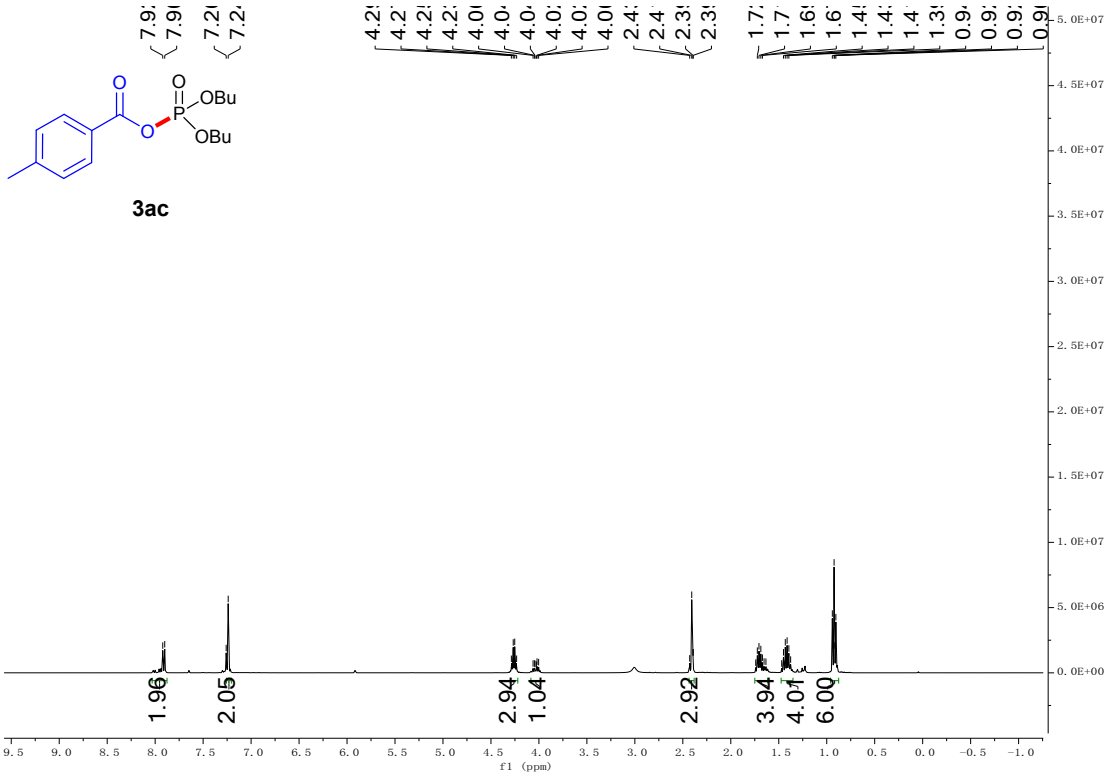
(dimethyl phosphoric) 4-methylbenzoic anhydride (3ab)

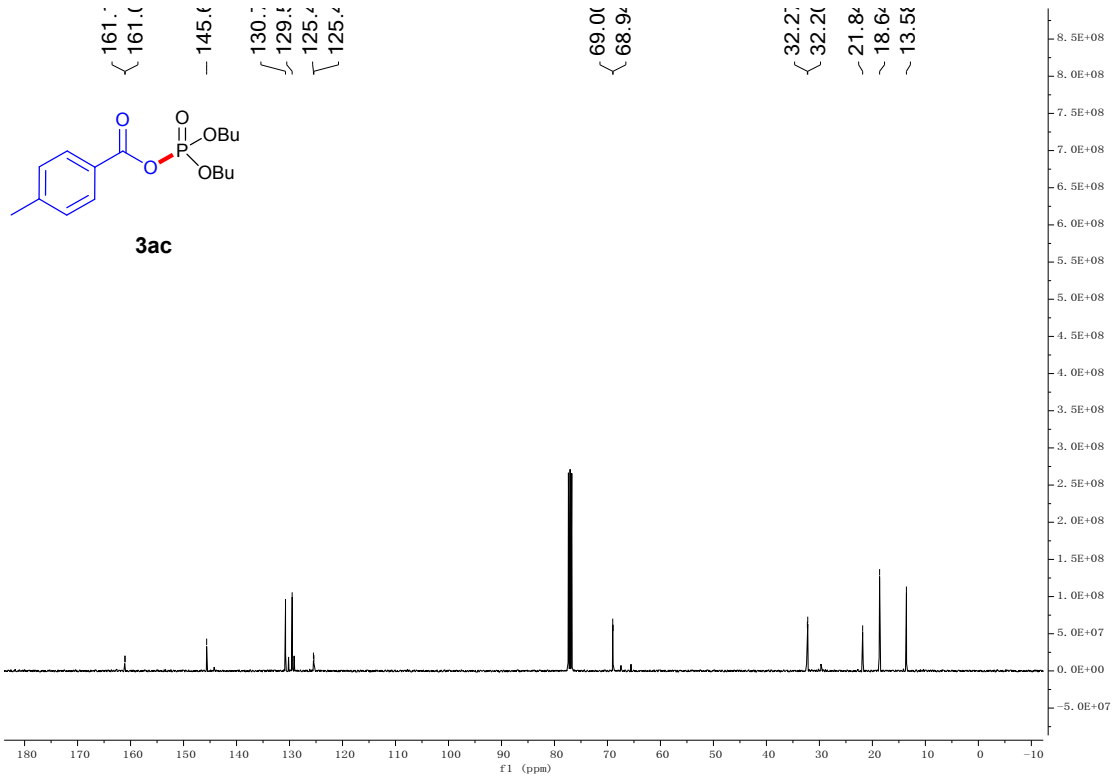


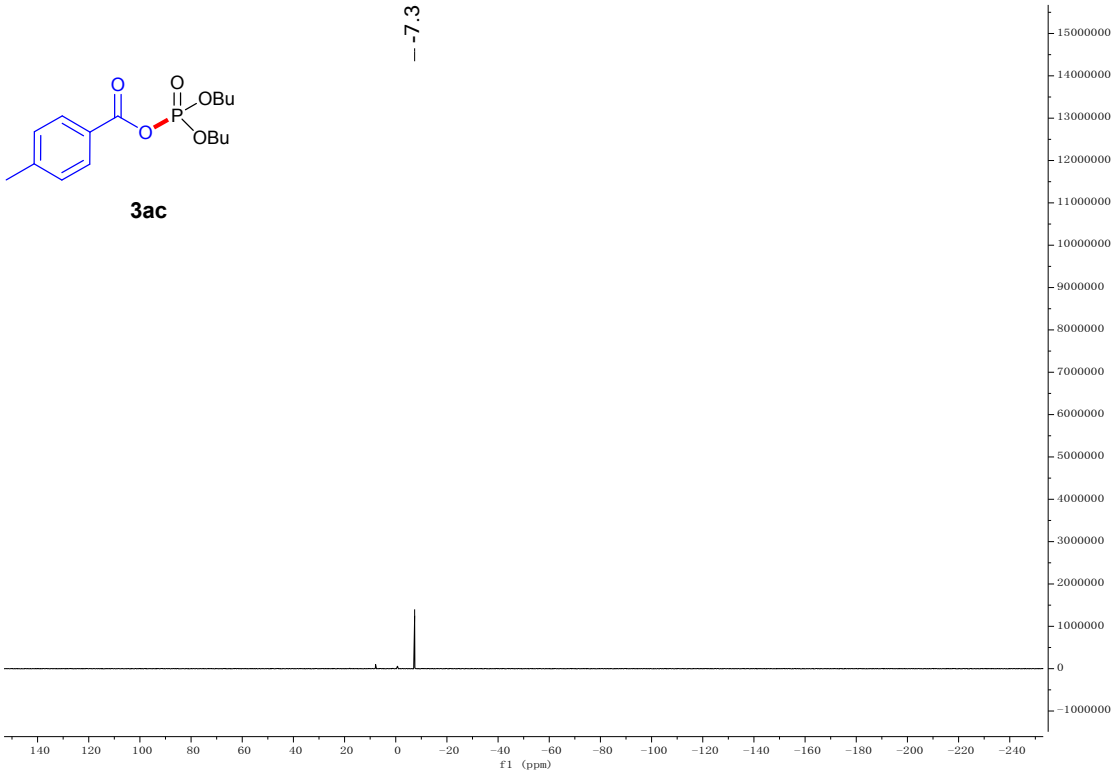

161.(
160.9
145.9
130.8
129.8
125.
125.(
55.5
55.4
21.8
OMe
OMe
3ab
4. 5E+08
4. 0E+08
3. 5E+08
3. 0E+08
2. 5E+08
2. 0E+08
1. 5E+08
1. 0E+08
5. 0E+07
0. 0E+00
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


-5.0
OMe
OMe
3ab
3400000
3200000
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
−200000
140 120 100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 −220 −240
f1 (ppm)

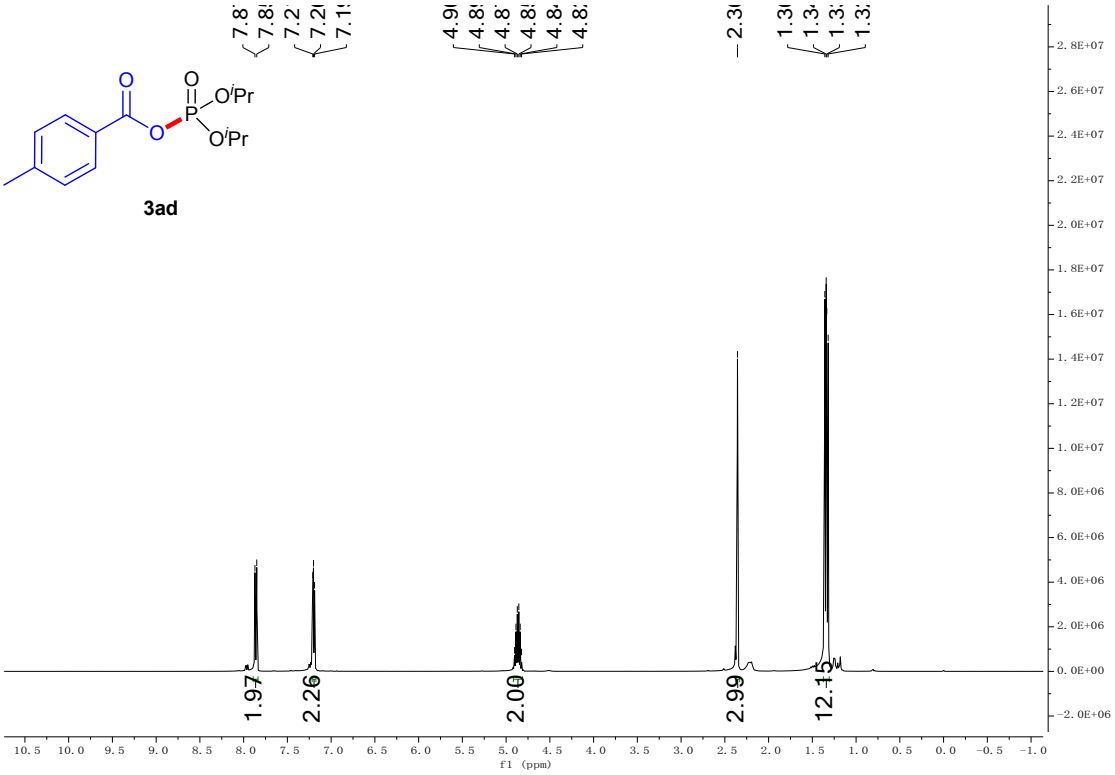
(dibutyl phosphoric) 4-methylbenzoic anhydride (3ac)

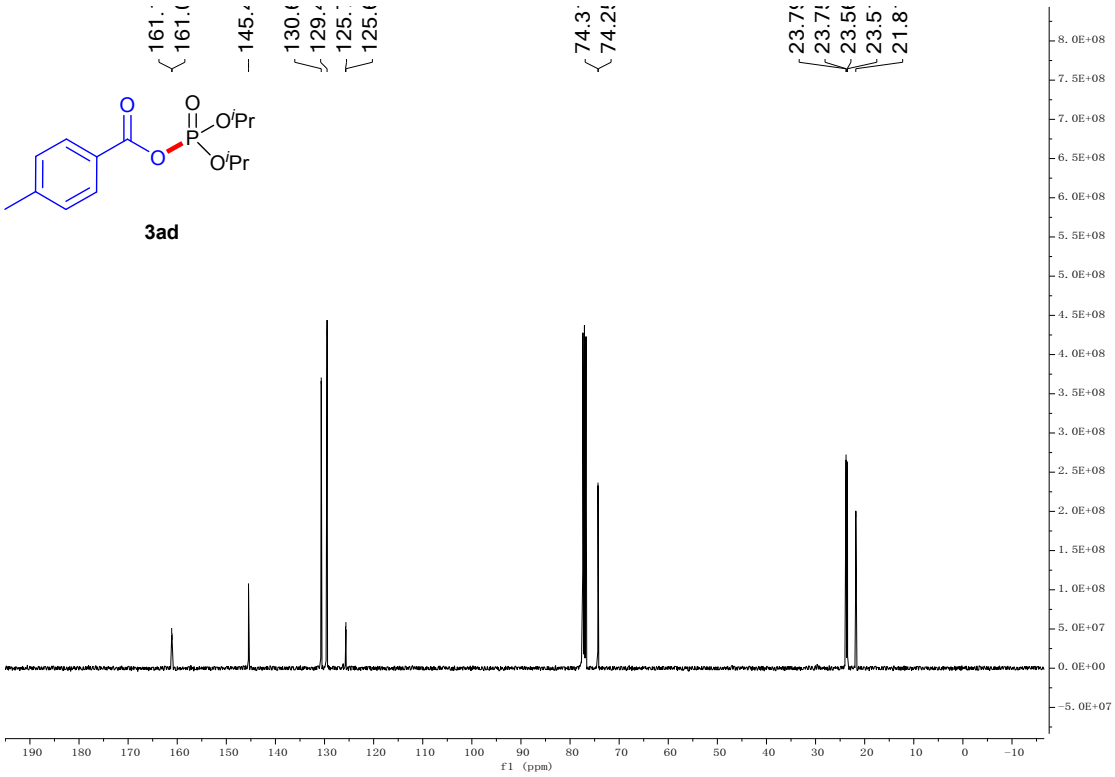


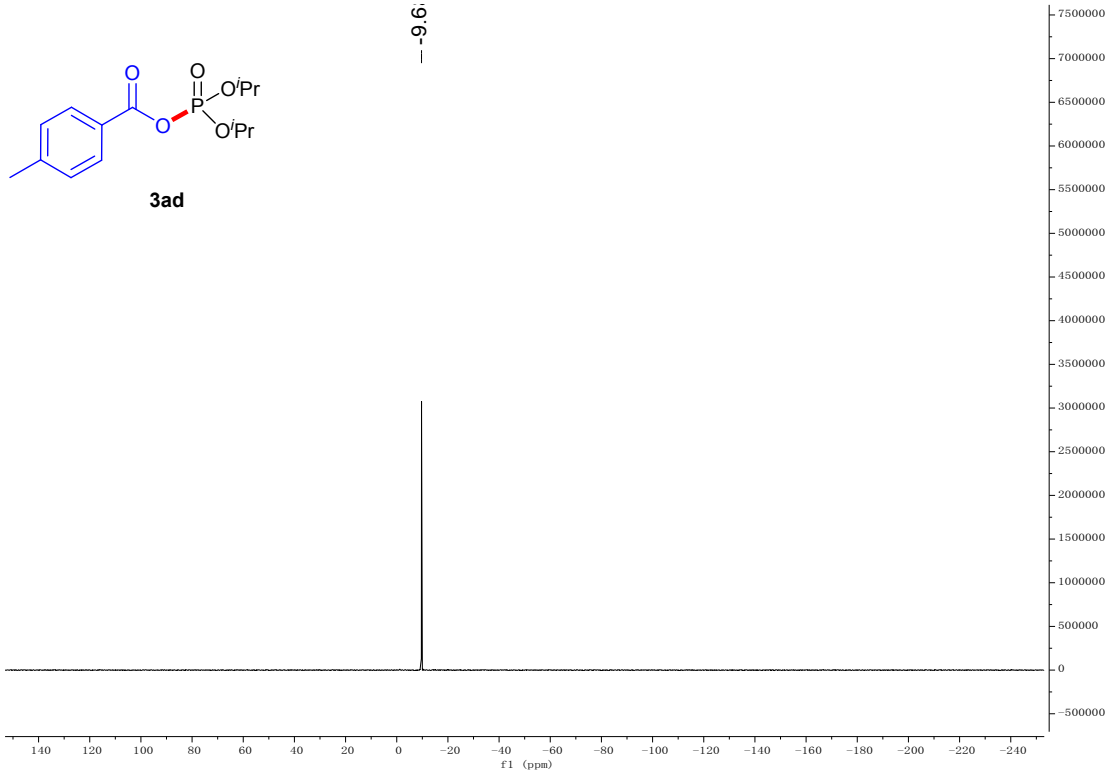




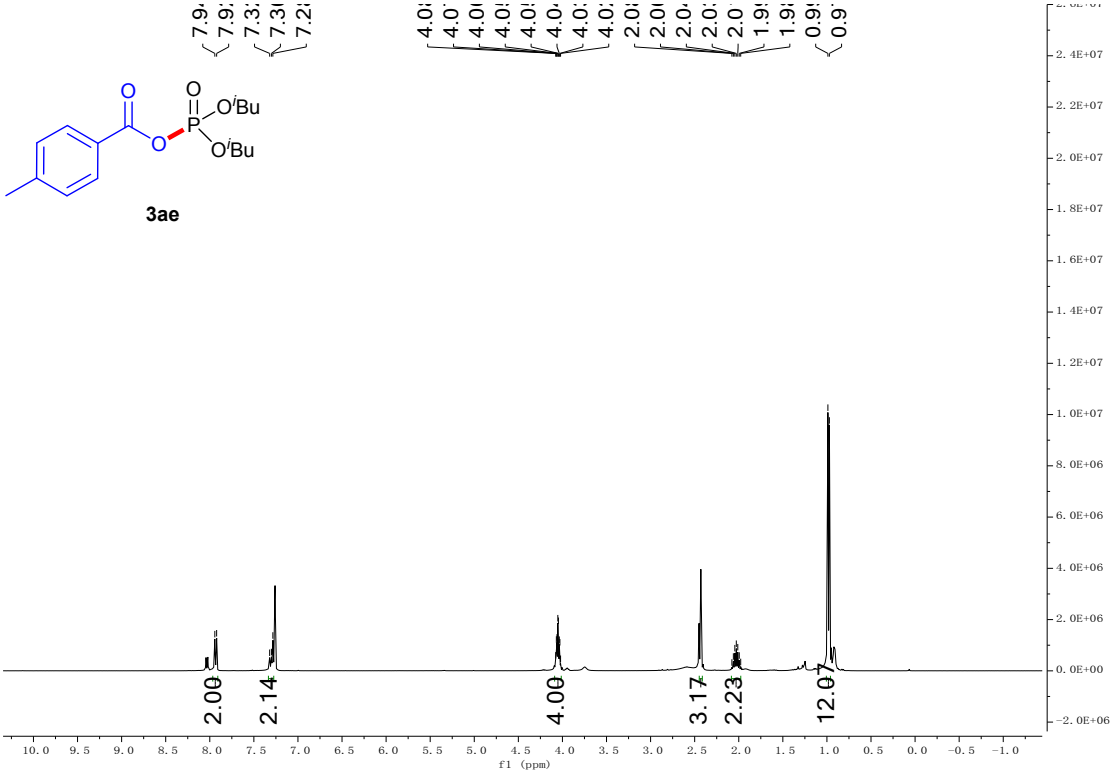
(diisopropyl phosphoric) 4-methylbenzoic anhydride (3ad)

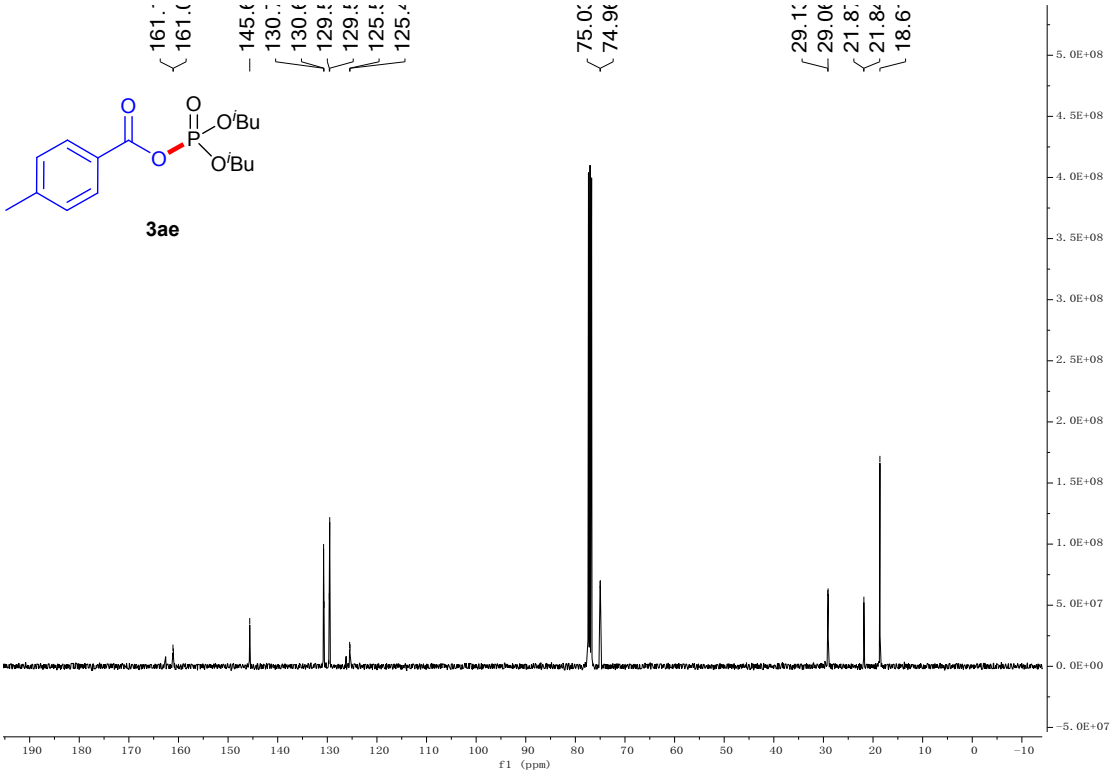


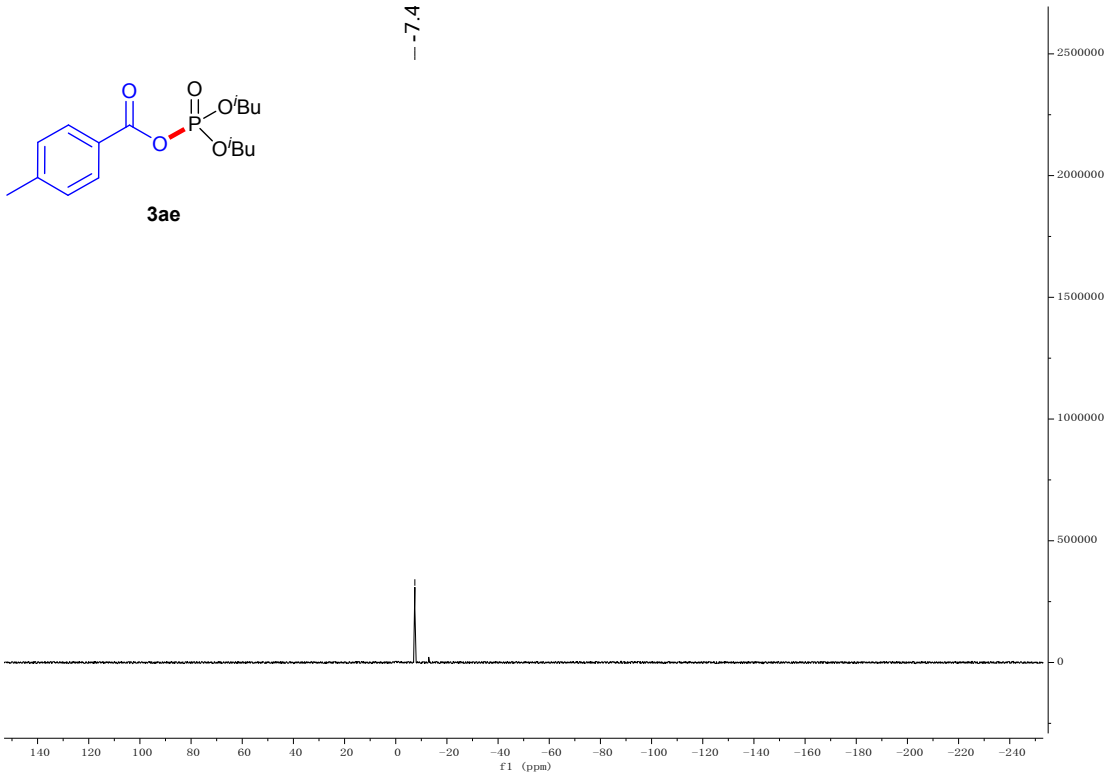

161.
161.
145.
130.
129.
125.
125.
74.3
74.2
23.7
23.7
23.5
23.5
21.8
O
O
P
O
O
O
iPr
iPr
3ad
8.0E+08
7.5E+08
7.0E+08
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-9.6
O
O
P
O
O
O
iPr
iPr
3ad
7500000
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

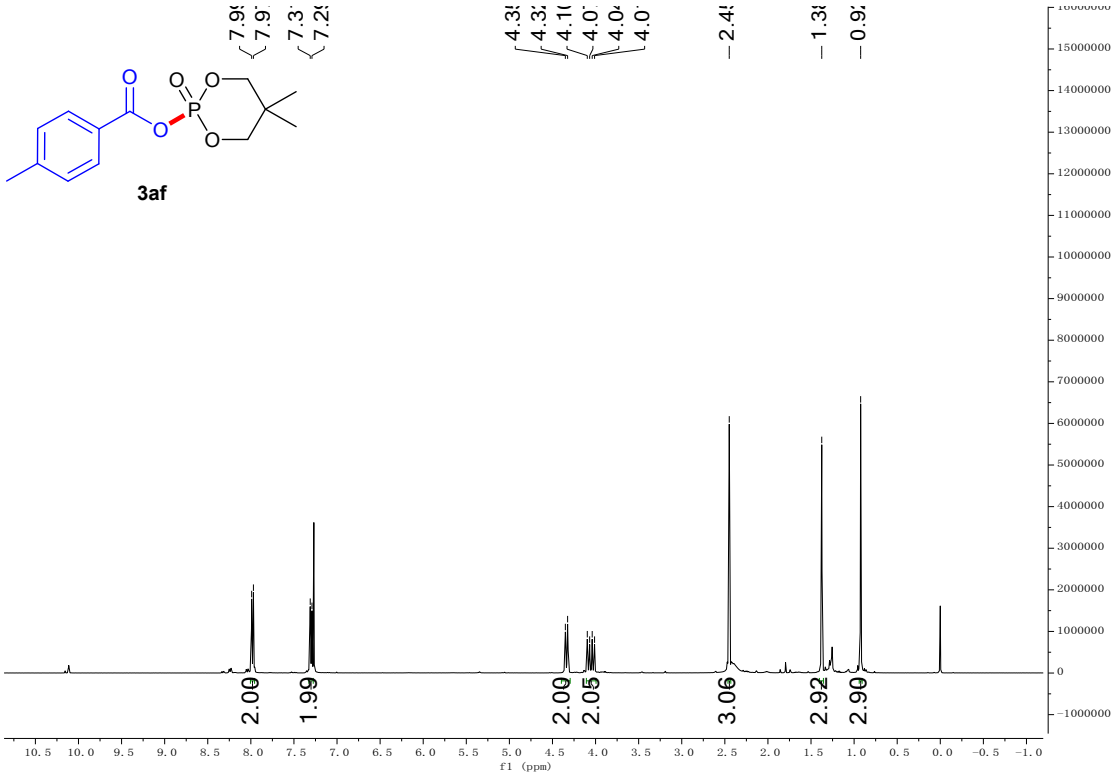
(diisobutyl phosphoric) 4-methylbenzoic anhydride (3ae)

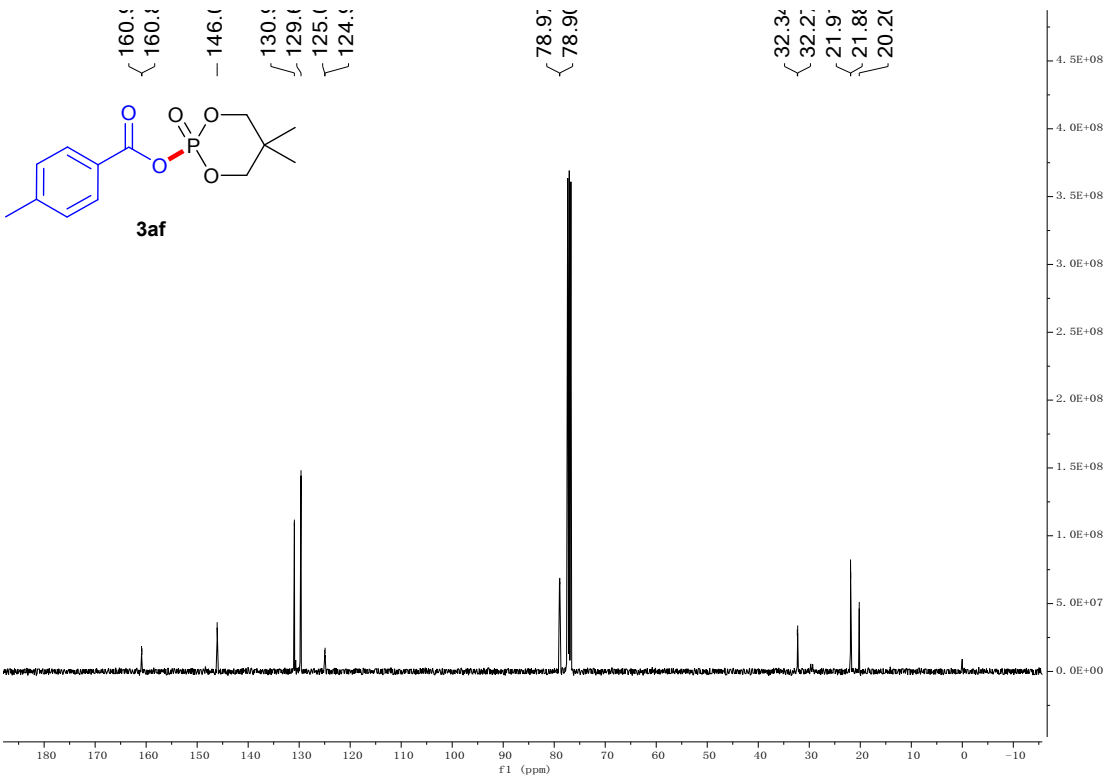


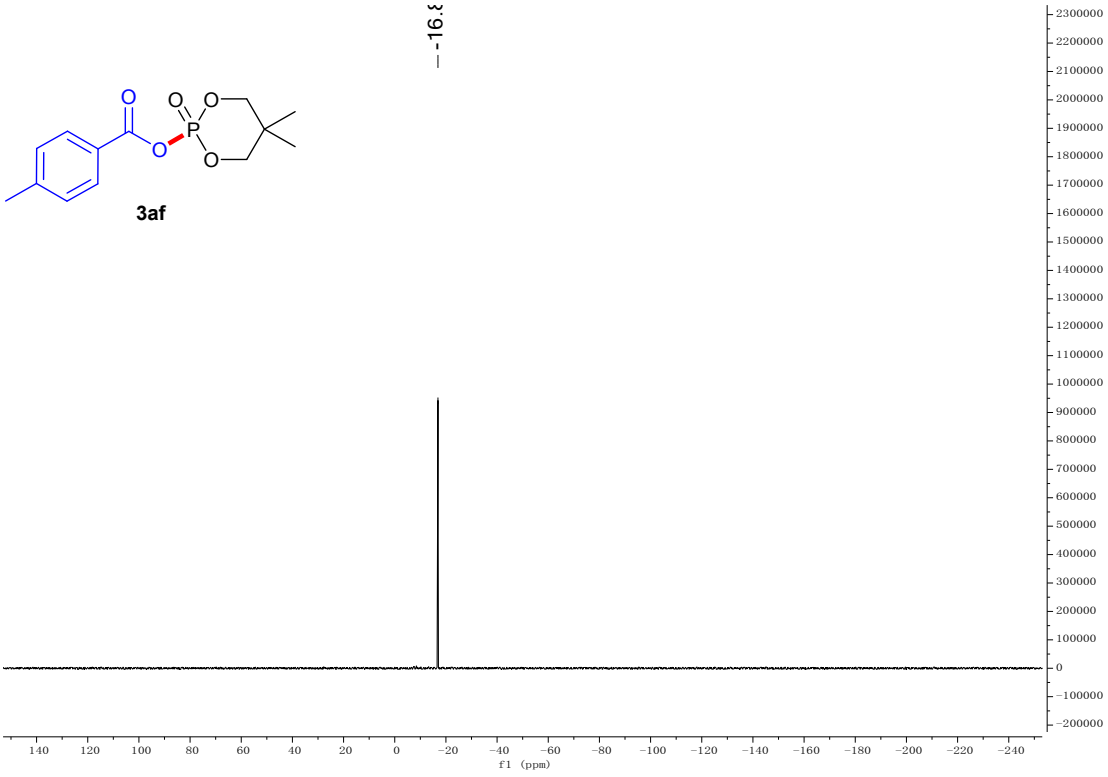




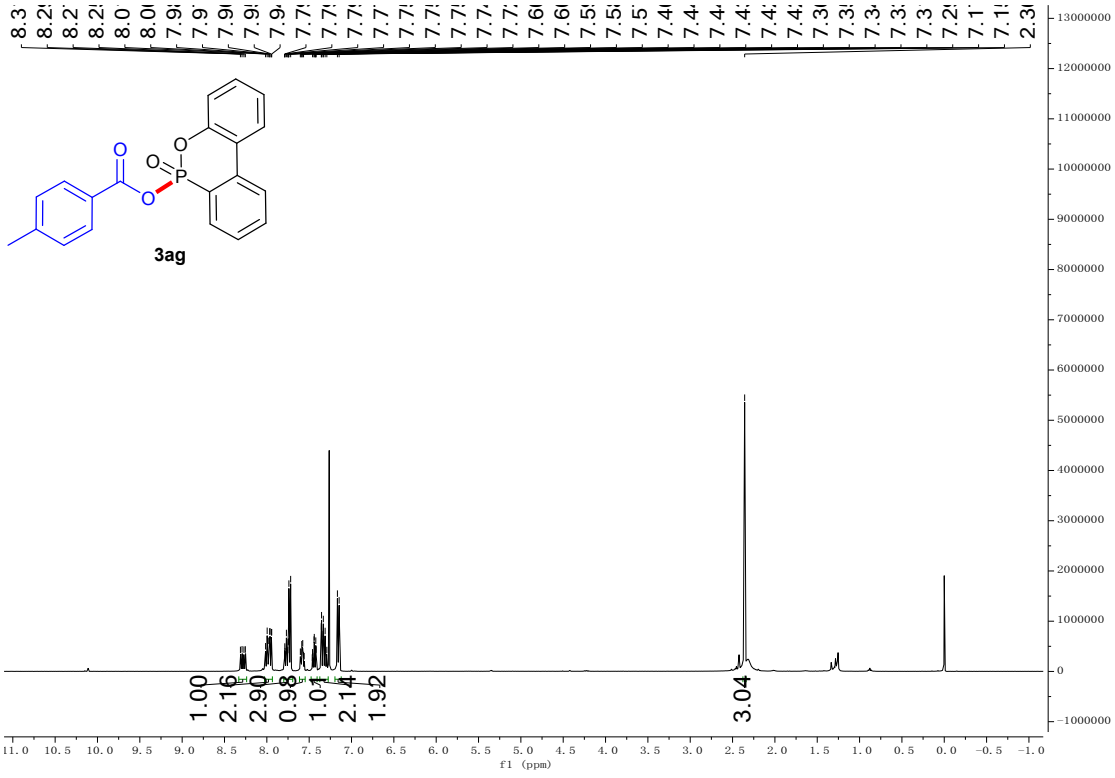
5,5-dimethyl-2-oxido-1,3,2-dioxaphosphinan-2-yl 4-methylbenzoate (3af)

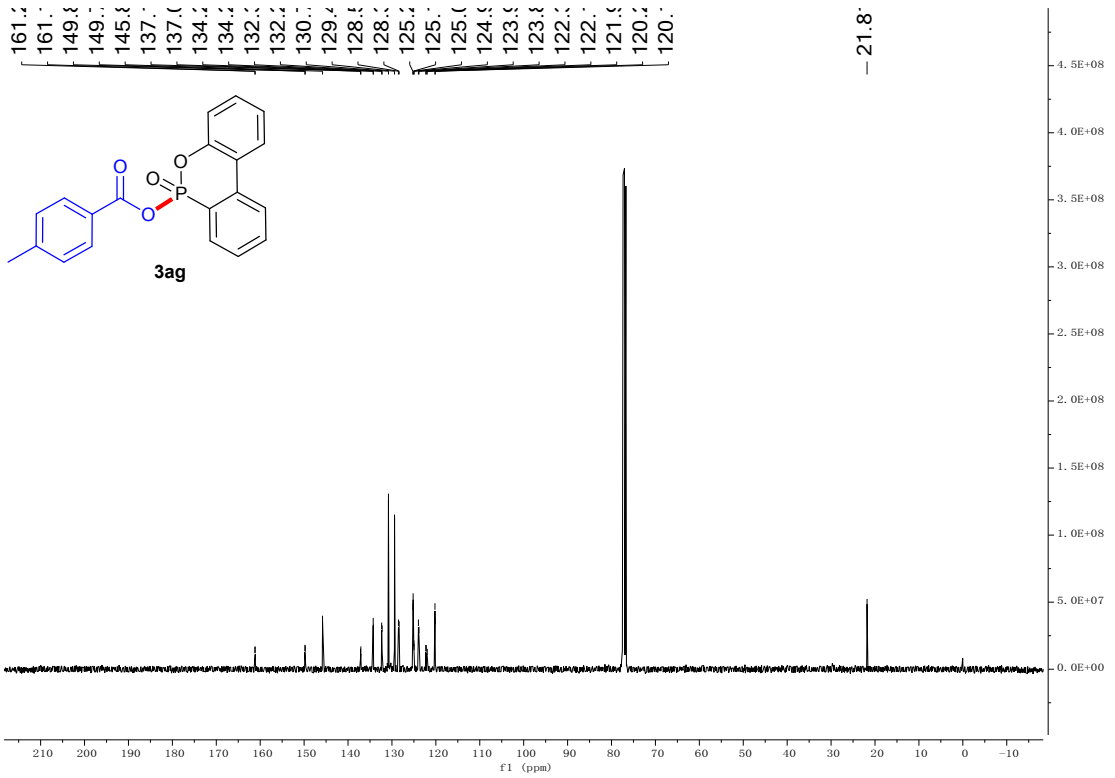


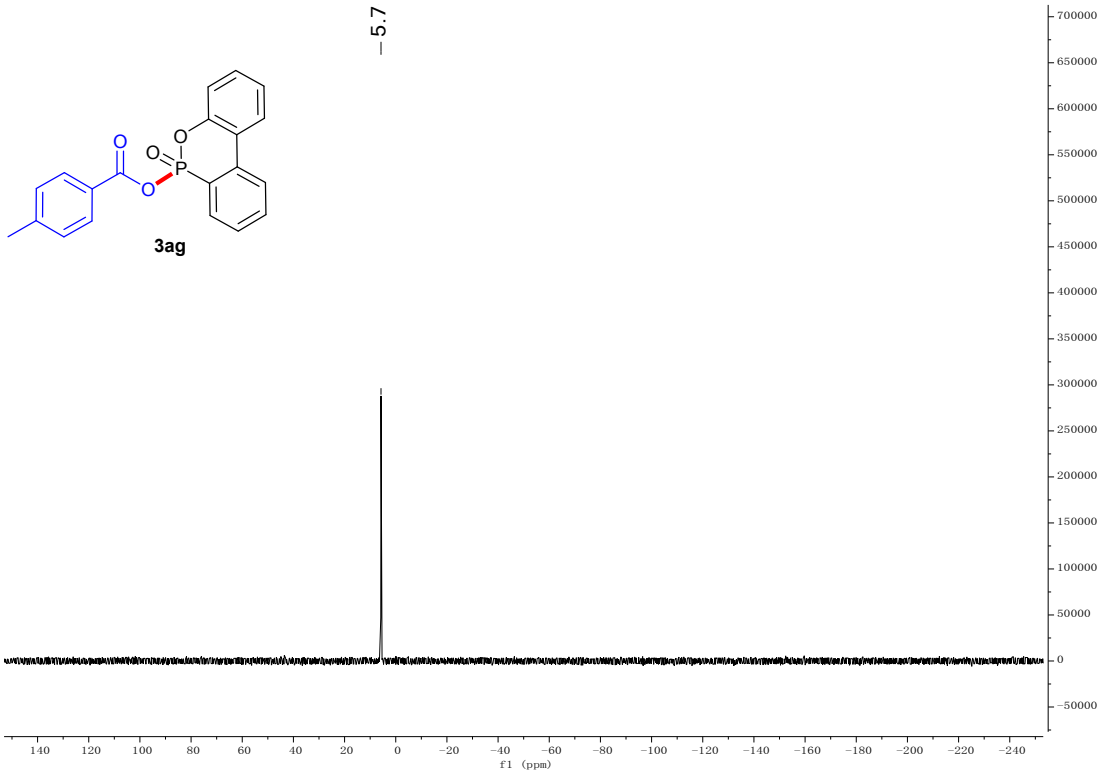

160.
160.
146.
130.
129.
125.
124.
78.9
78.9
32.3
32.2
21.9
21.8
20.2
3af
4. 5E+08
4. 0E+08
3. 5E+08
3. 0E+08
2. 5E+08
2. 0E+08
1. 5E+08
1. 0E+08
5. 0E+07
0. 0E+00
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


−16.
3af
2300000
2200000
2100000
2000000
1900000
1800000
1700000
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
−100000
−200000
140 120 100 80 60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 −220 −240
f1 (ppm)

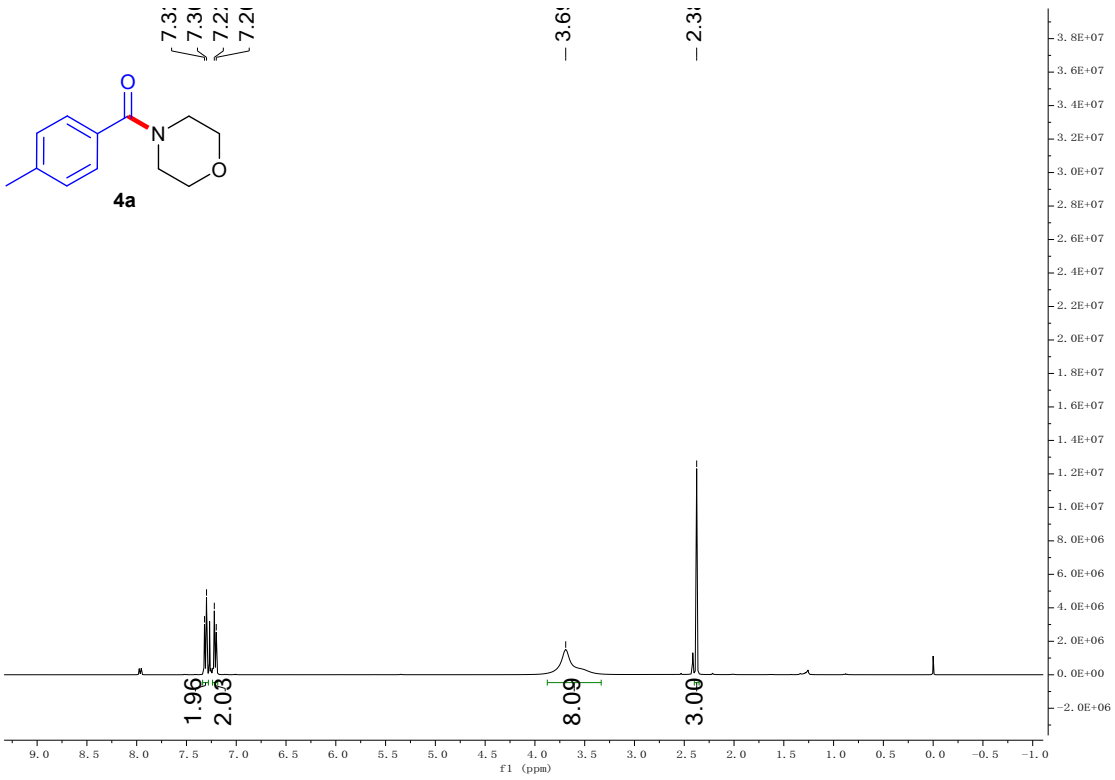
(S)-6-oxidodibenzo[c,e][1,2]oxaphosphinin-6-yl 4-methylbenzoate (3ag)

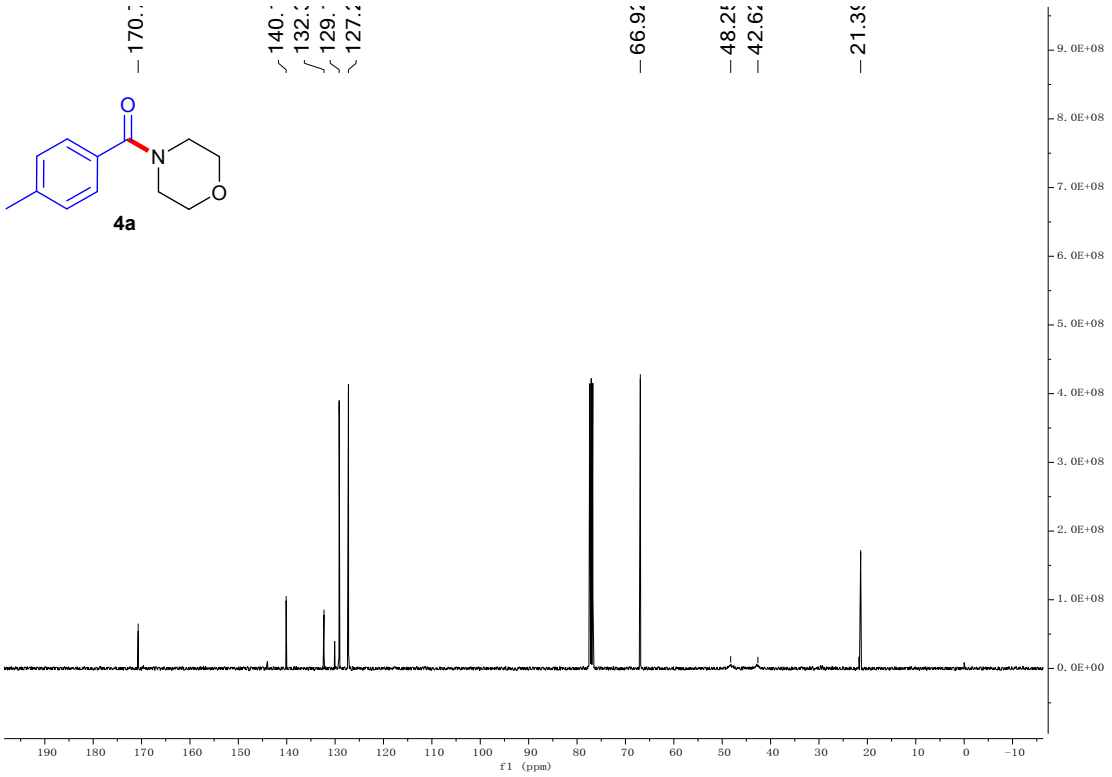




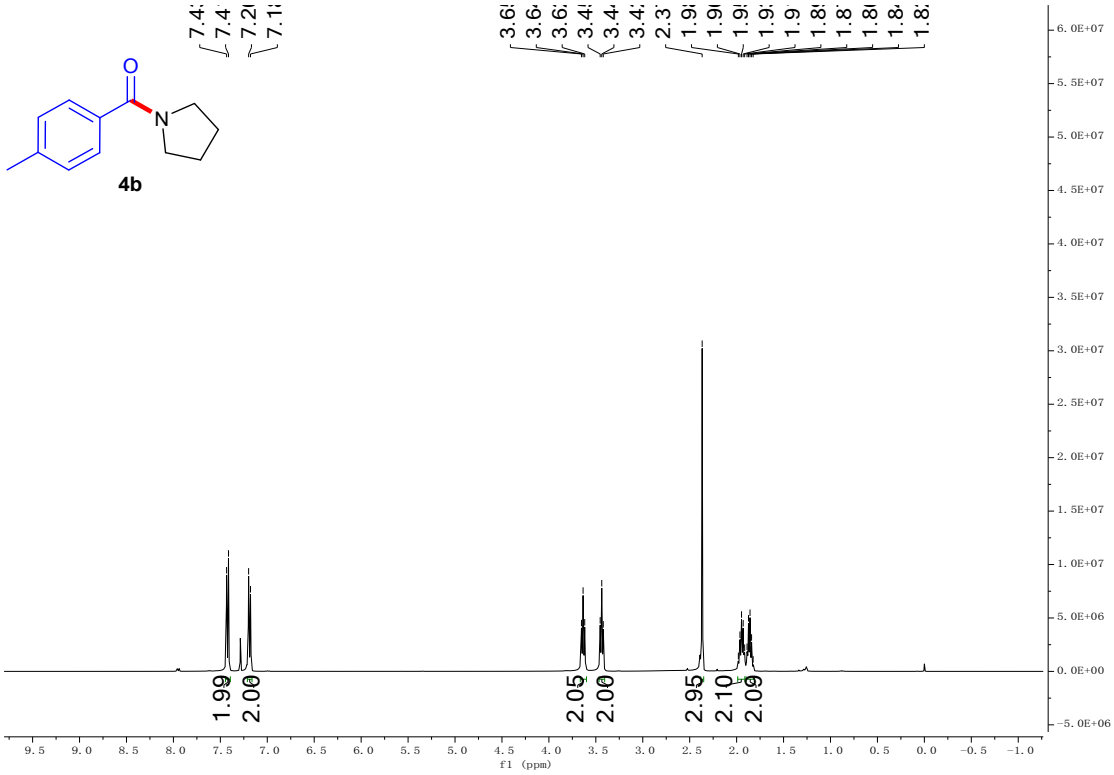


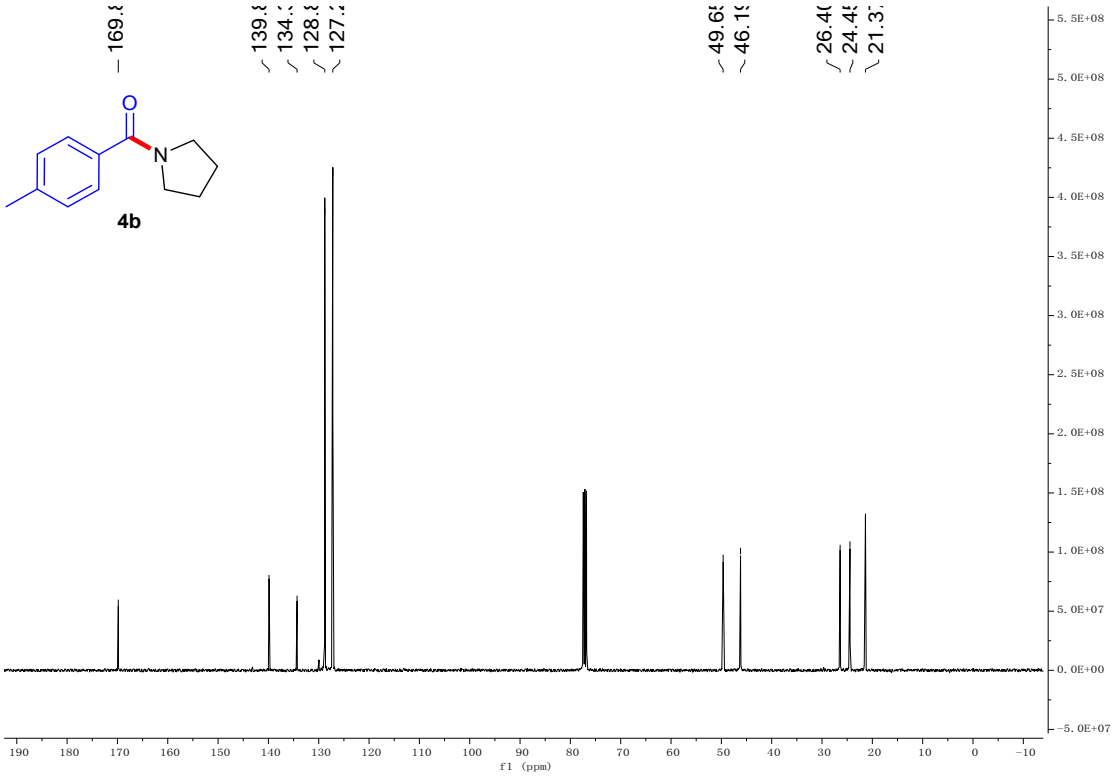
morpholino(p-tolyl)methanone (4a)



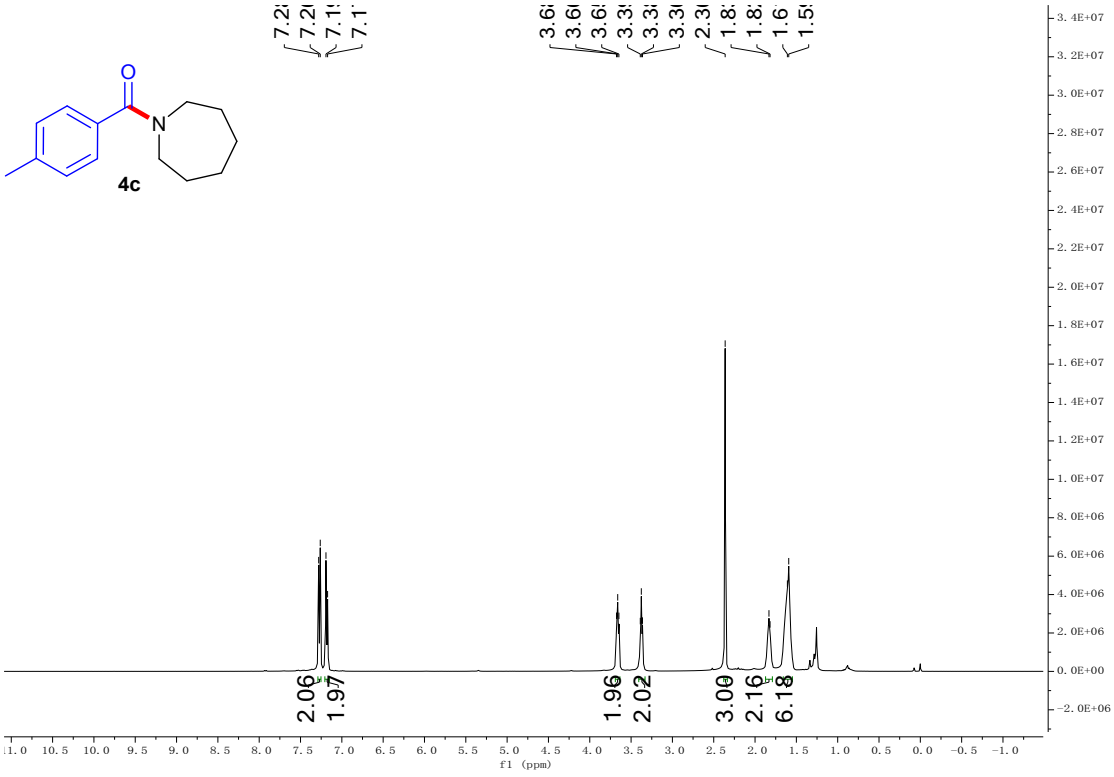


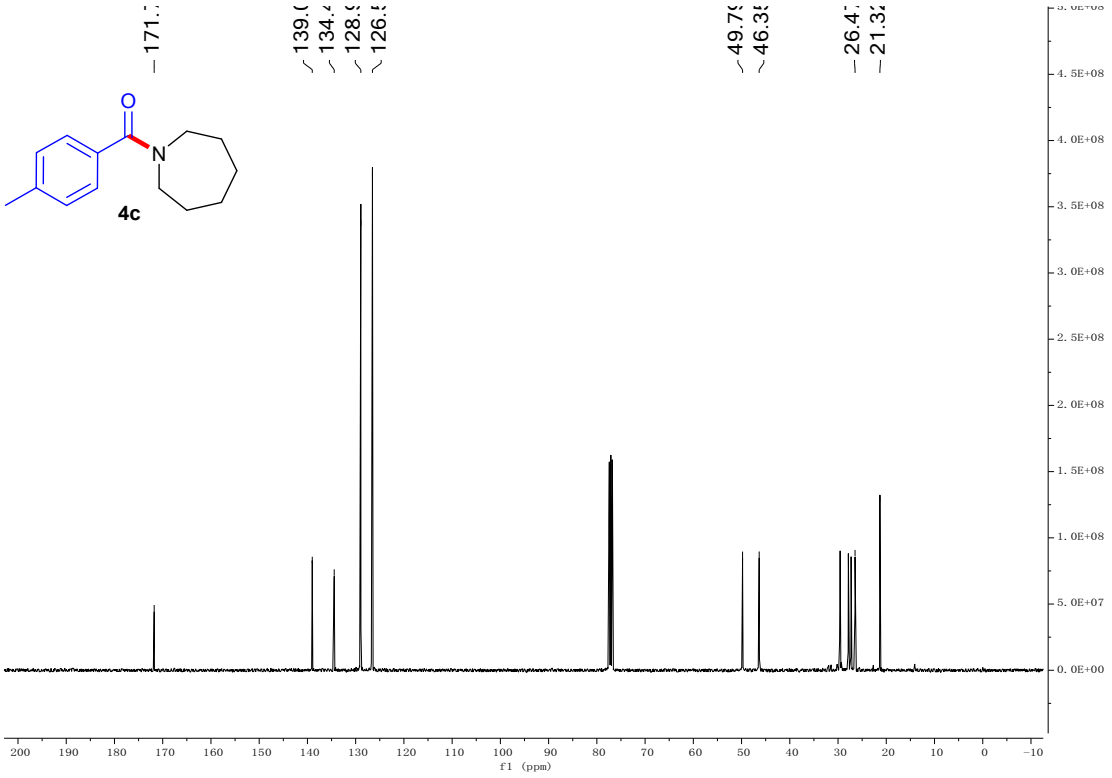
pyrrolidin-1-yl(p-tolyl)methanone (4b)



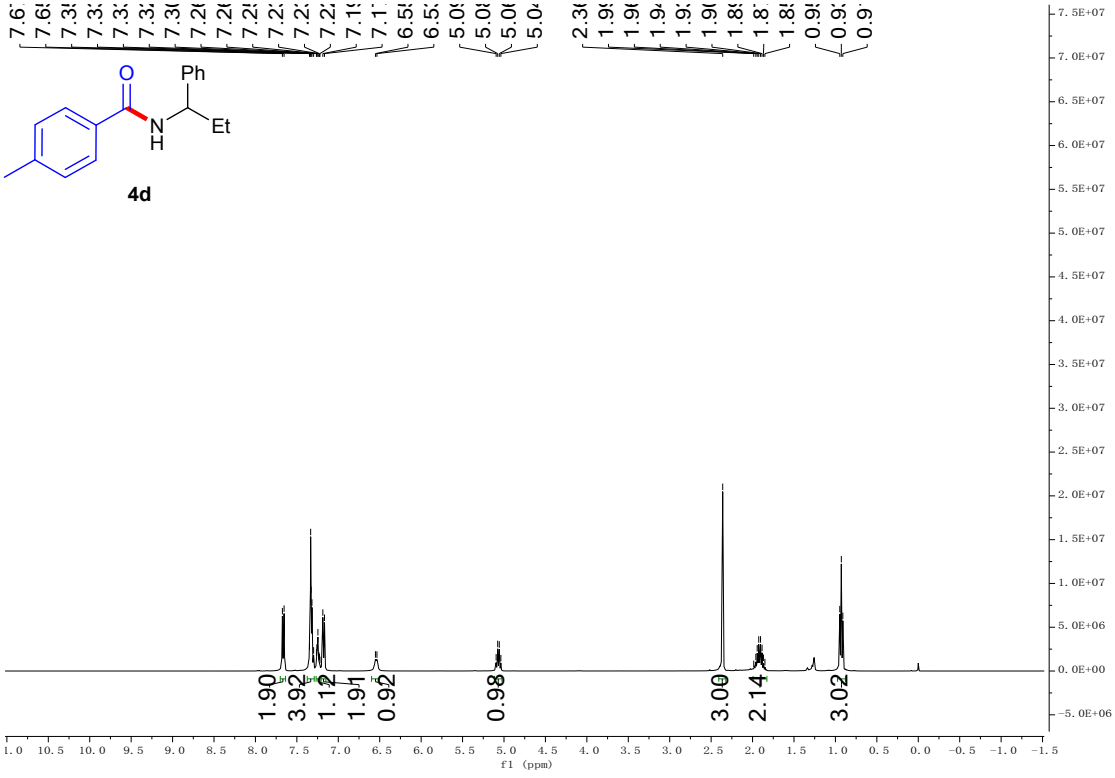


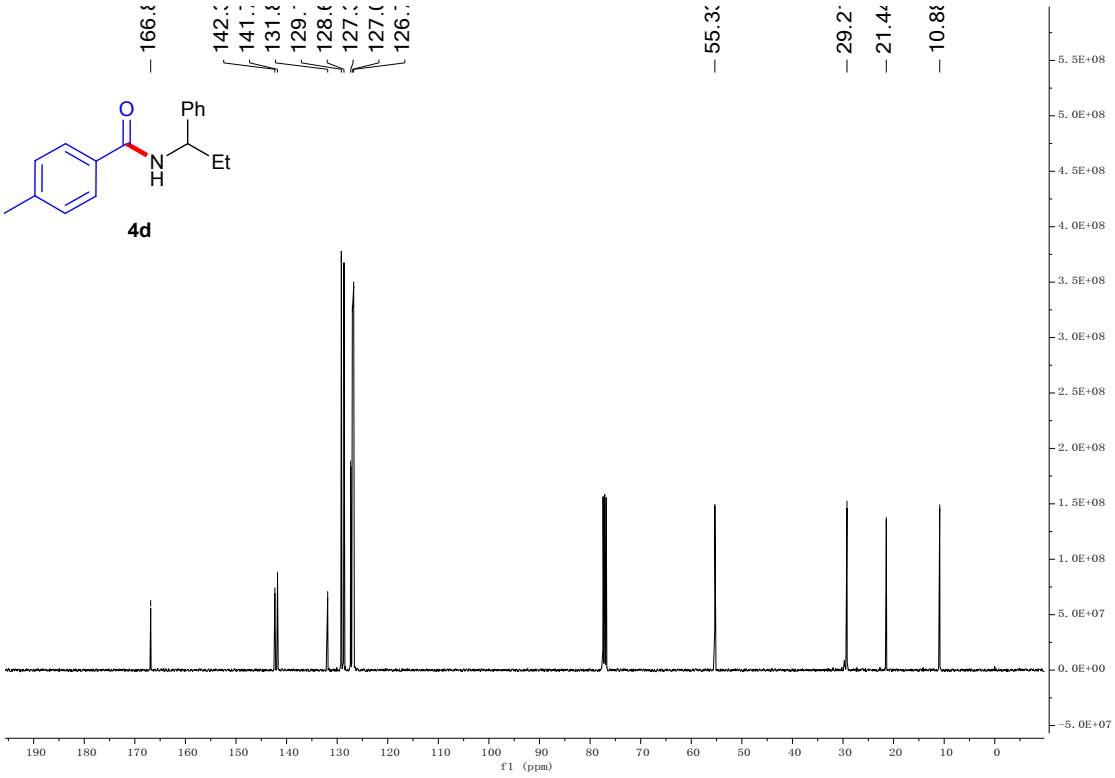
azepan-1-yl(p-tolyl)methanone (4c)



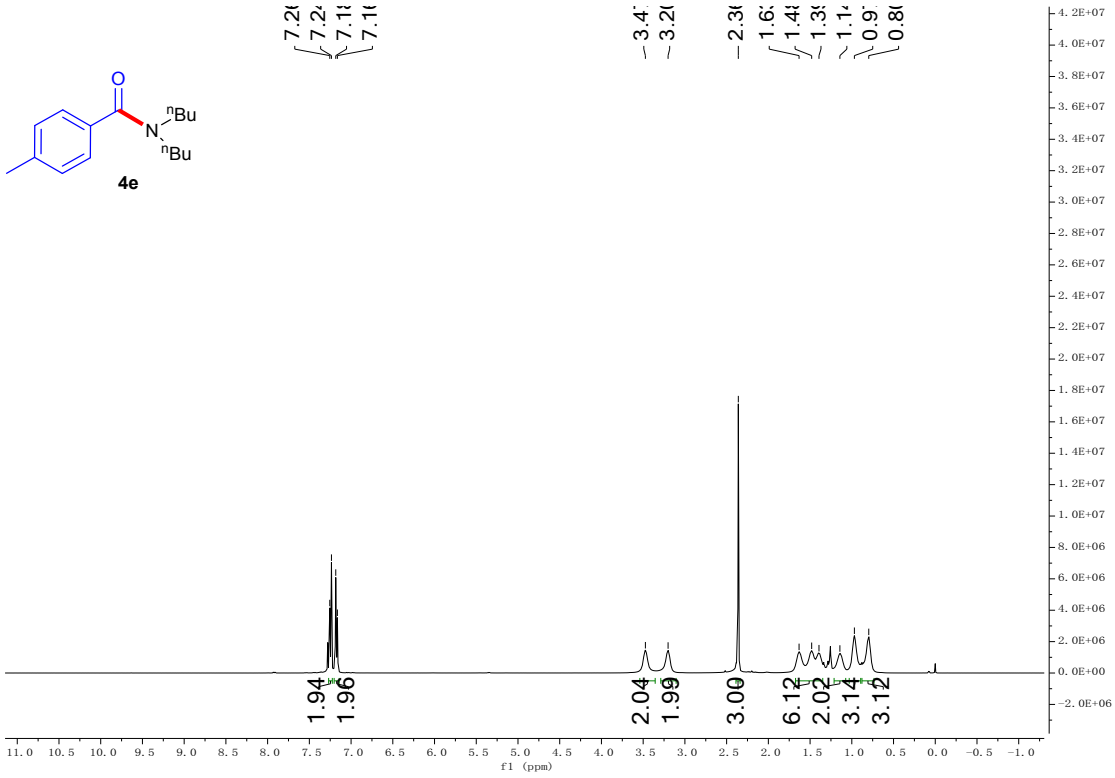


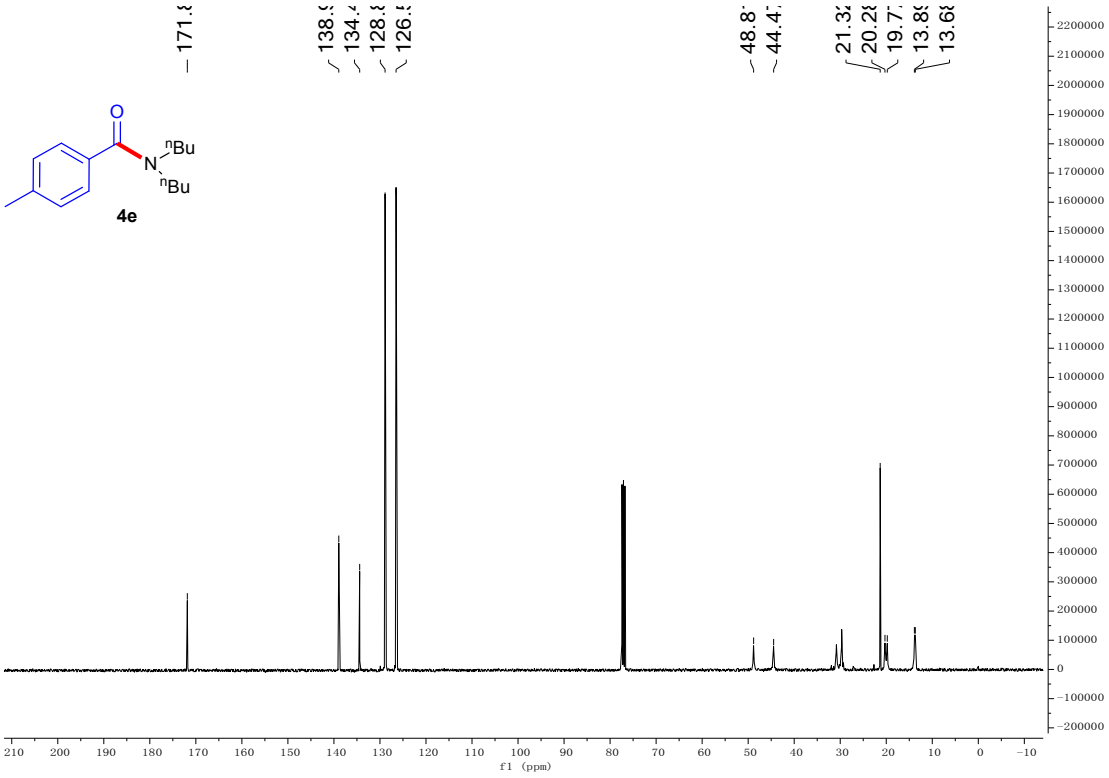
4-methyl-N-(1-phenylpropyl)benzamide (4d)



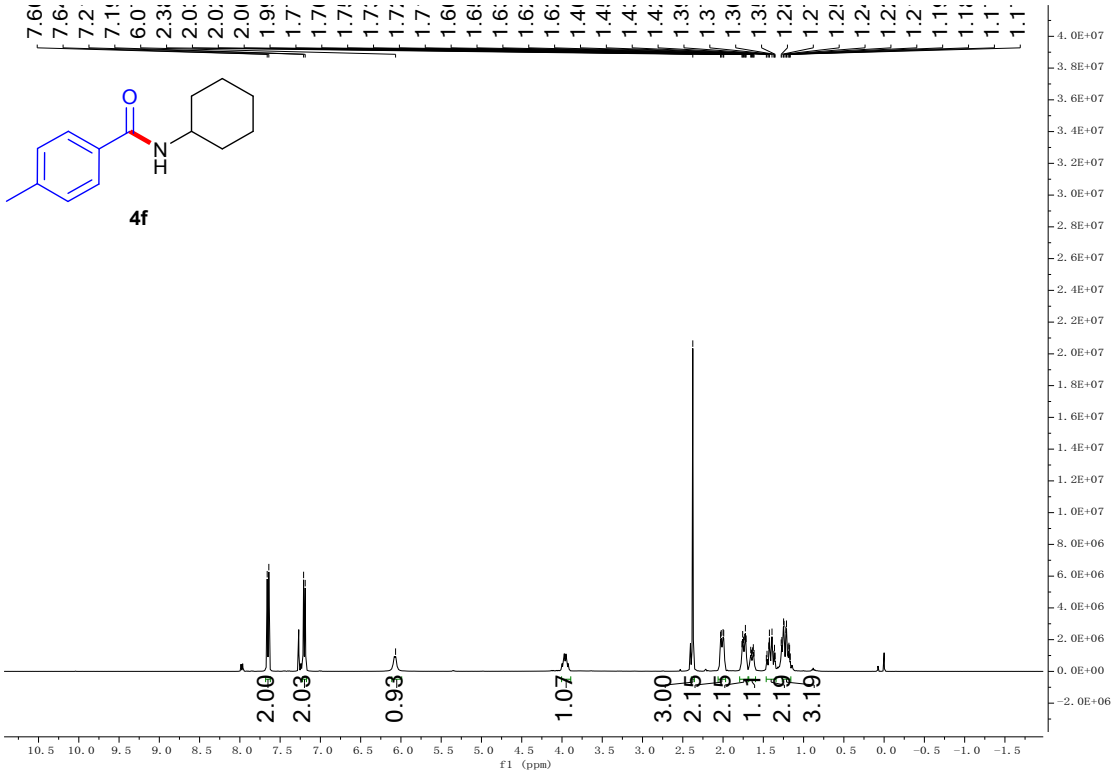


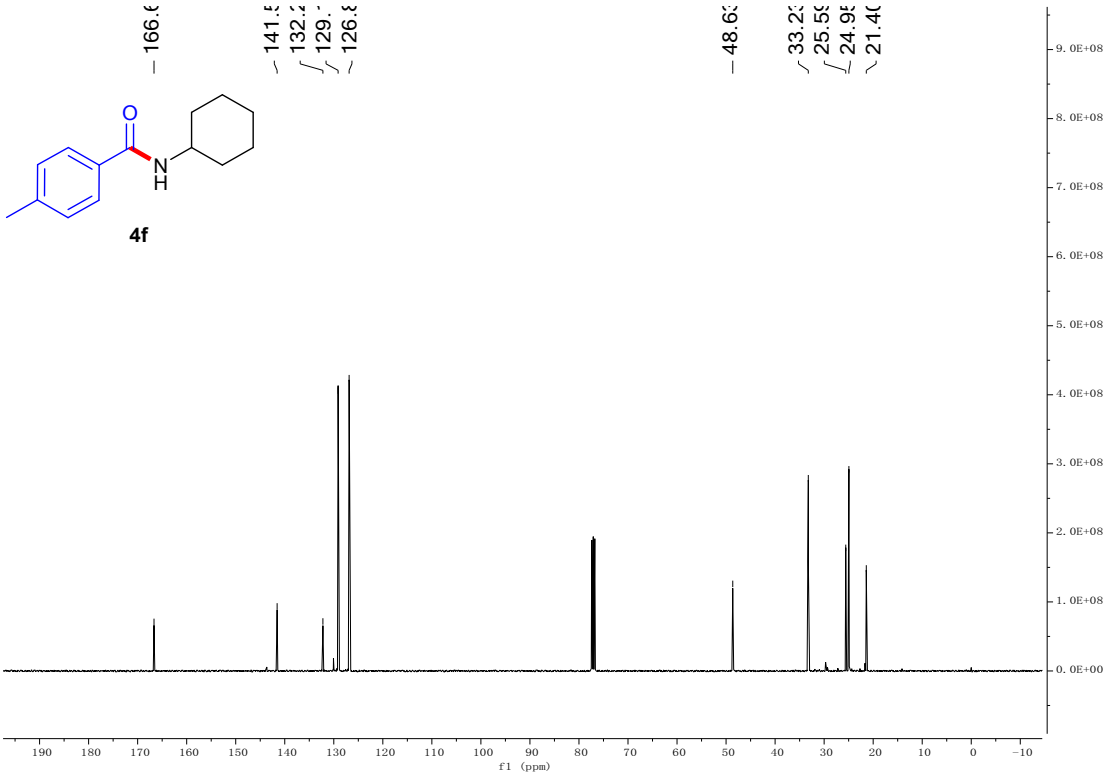
N,N-dibutyl-O-(4-methylbenzoyl)hydroxylamine (4e)



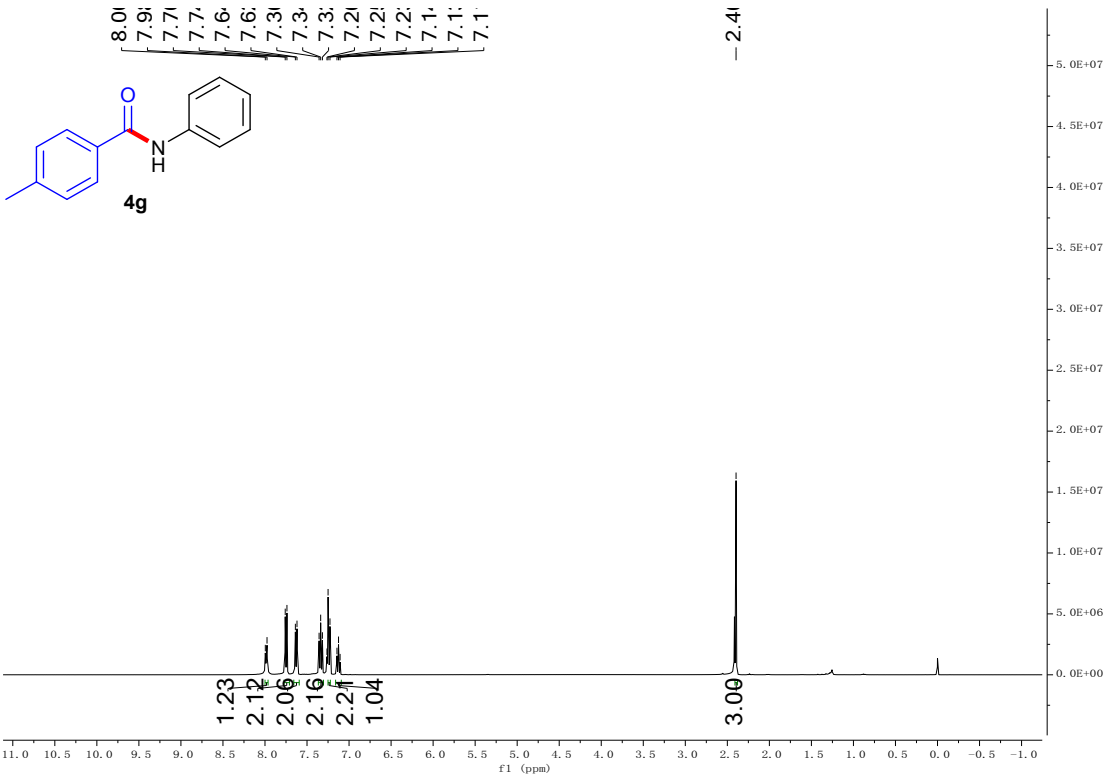


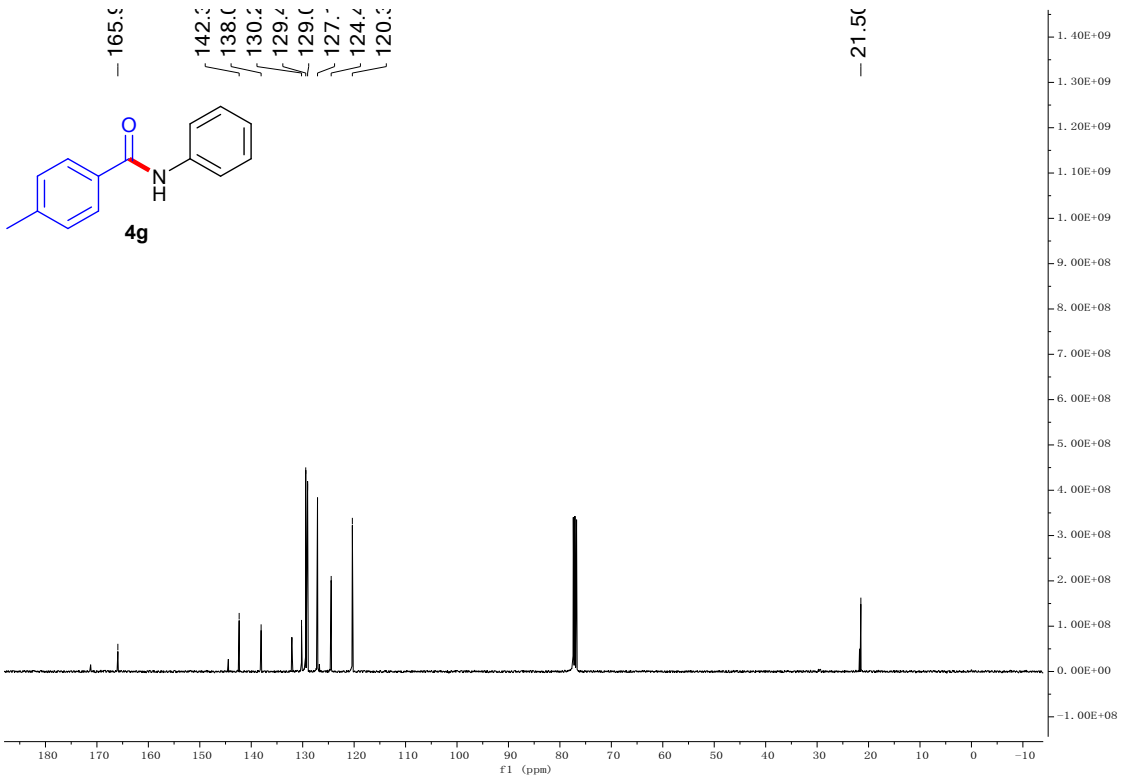
N-cyclohexyl-4-methylbenzamide (4f)



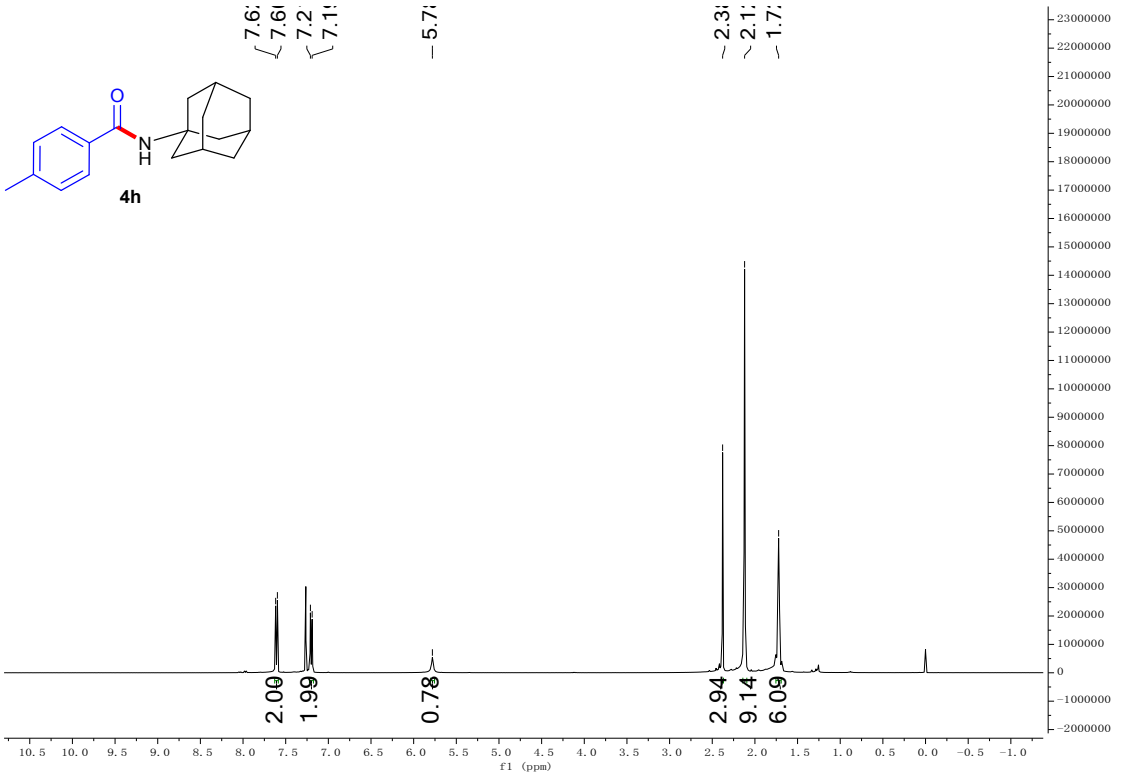


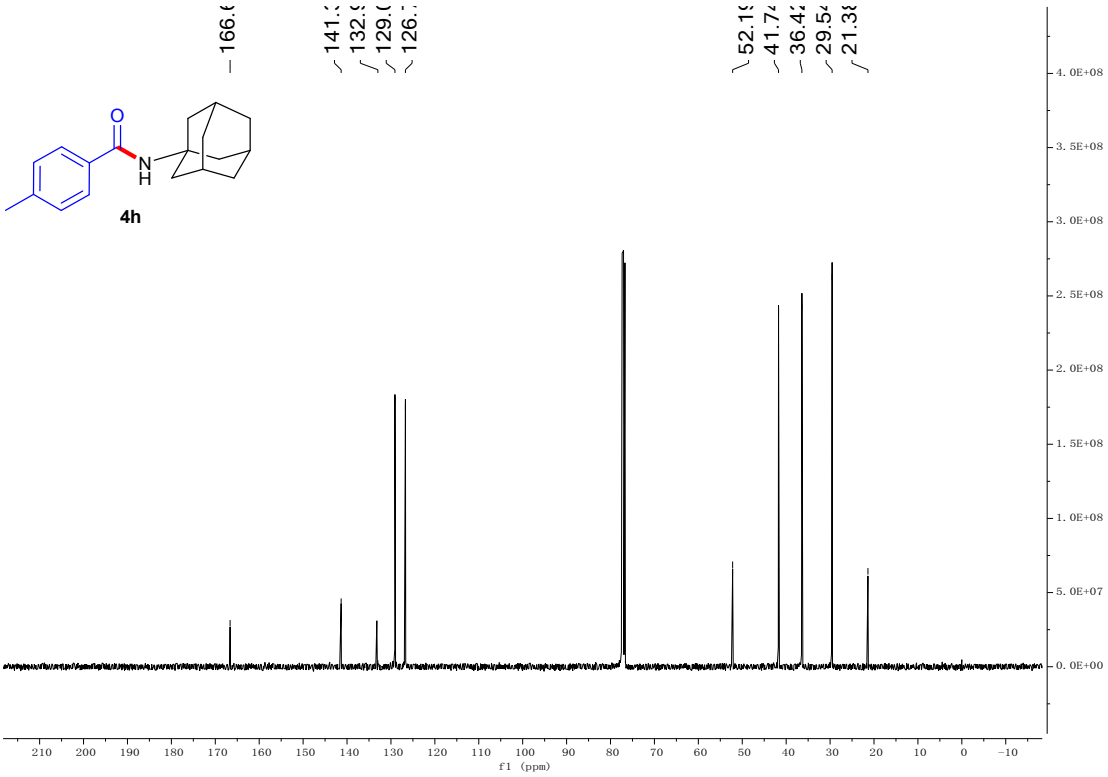
4-methyl-N-phenylbenzamide (4g)



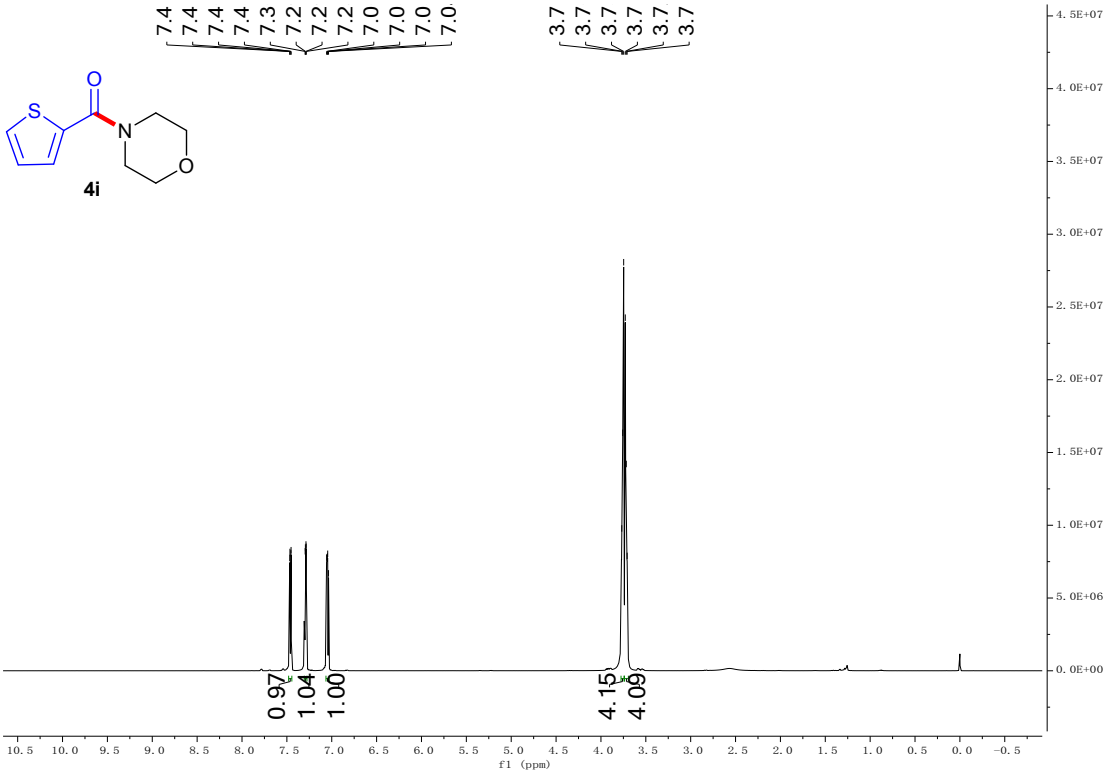


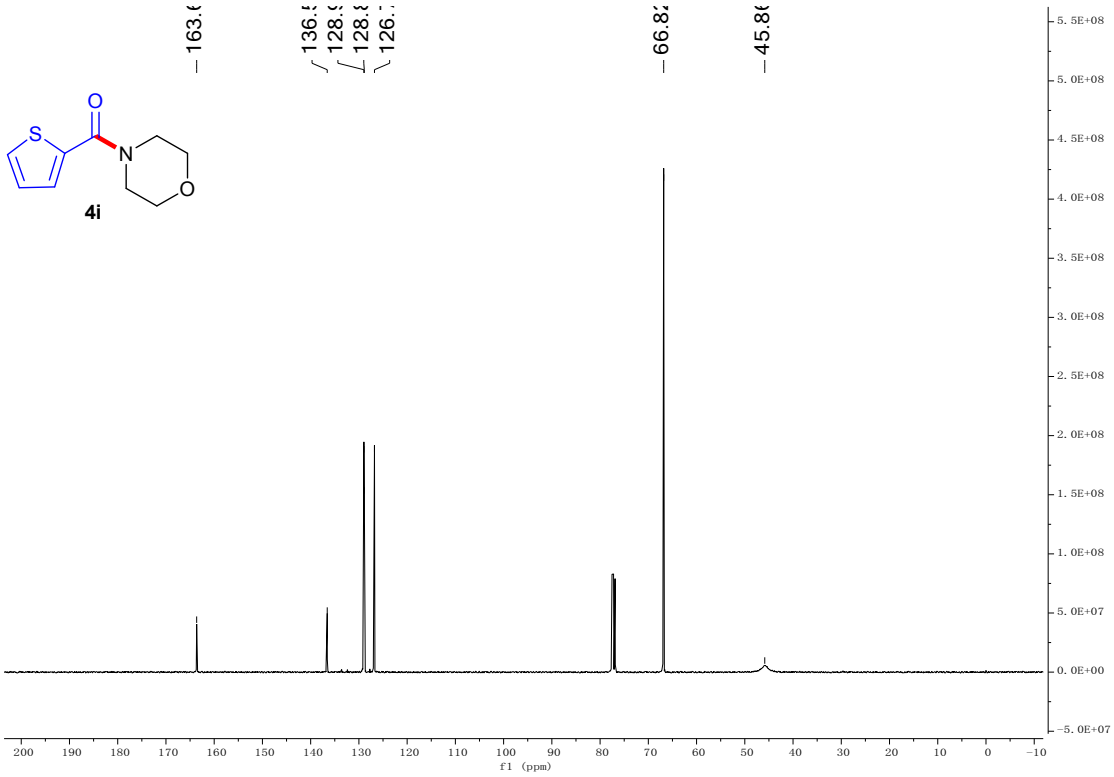
N-((3s,5s,7s)-adamantan-1-yl)-4-methylbenzamide (4h)



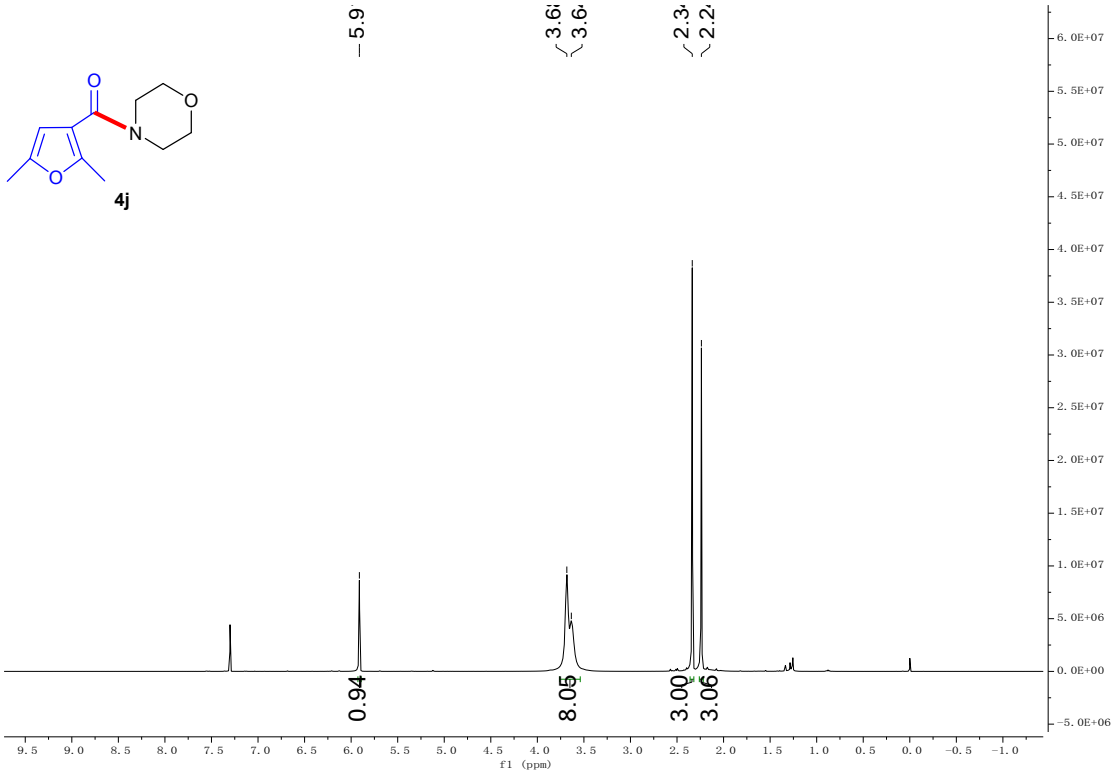


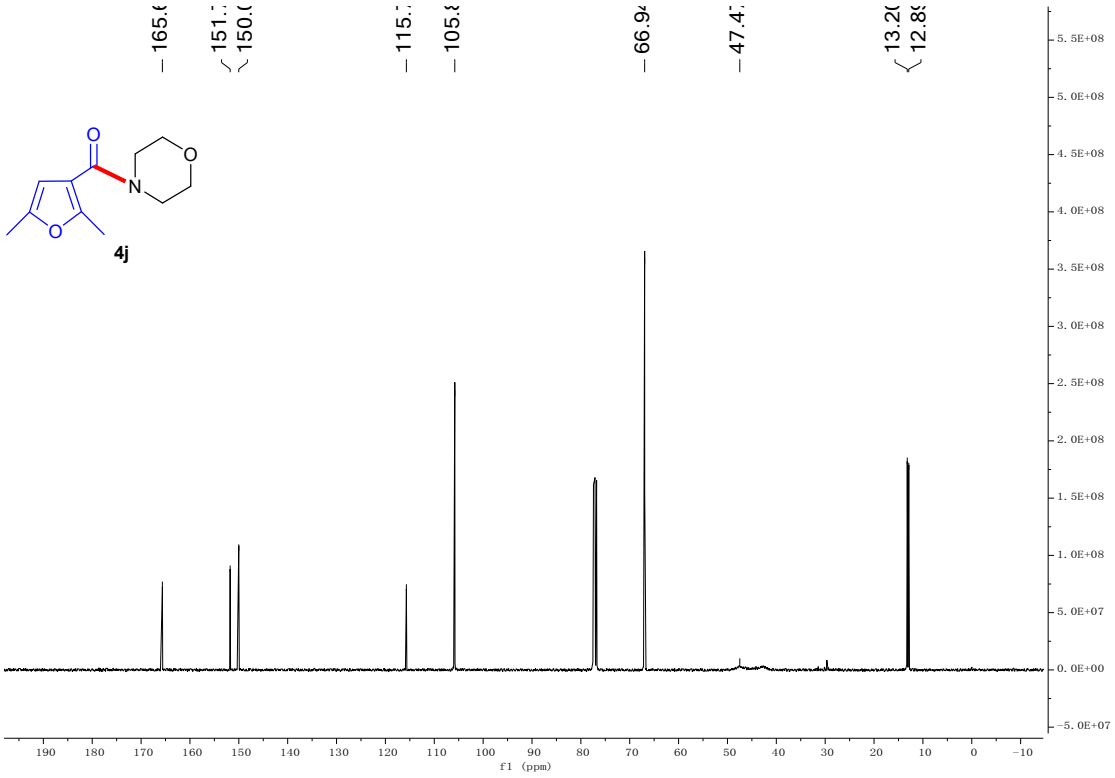
morpholino(thiophen-2-yl)methanone (4i)



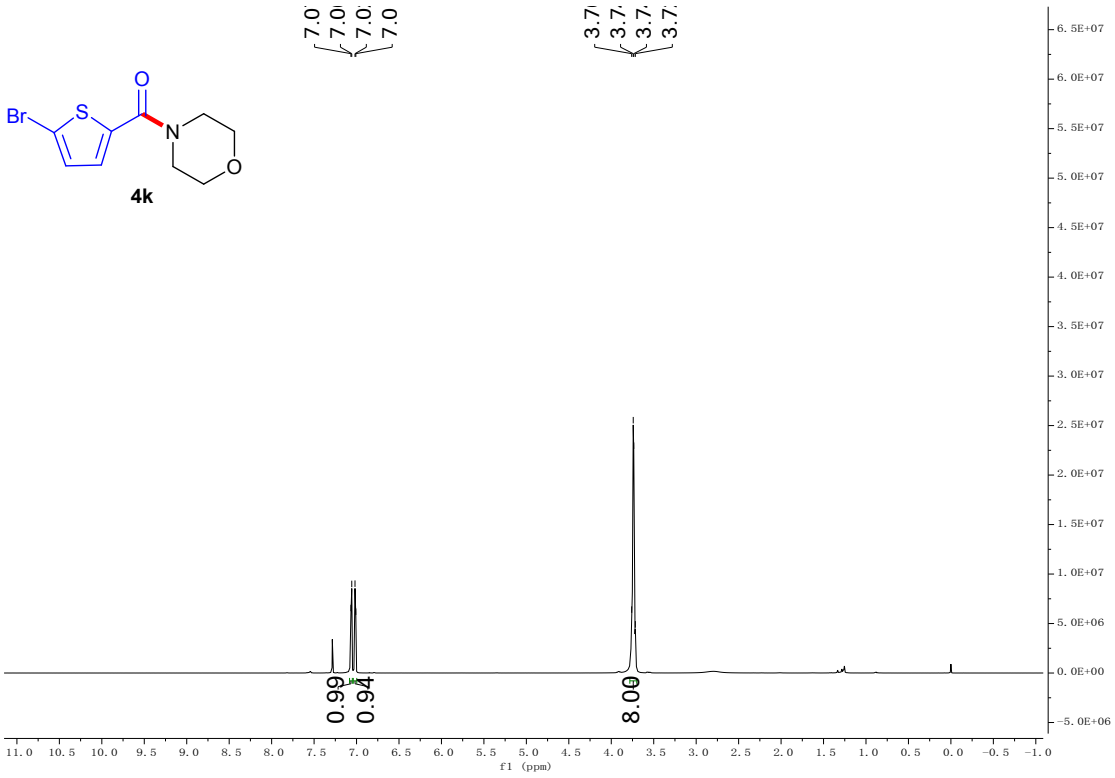


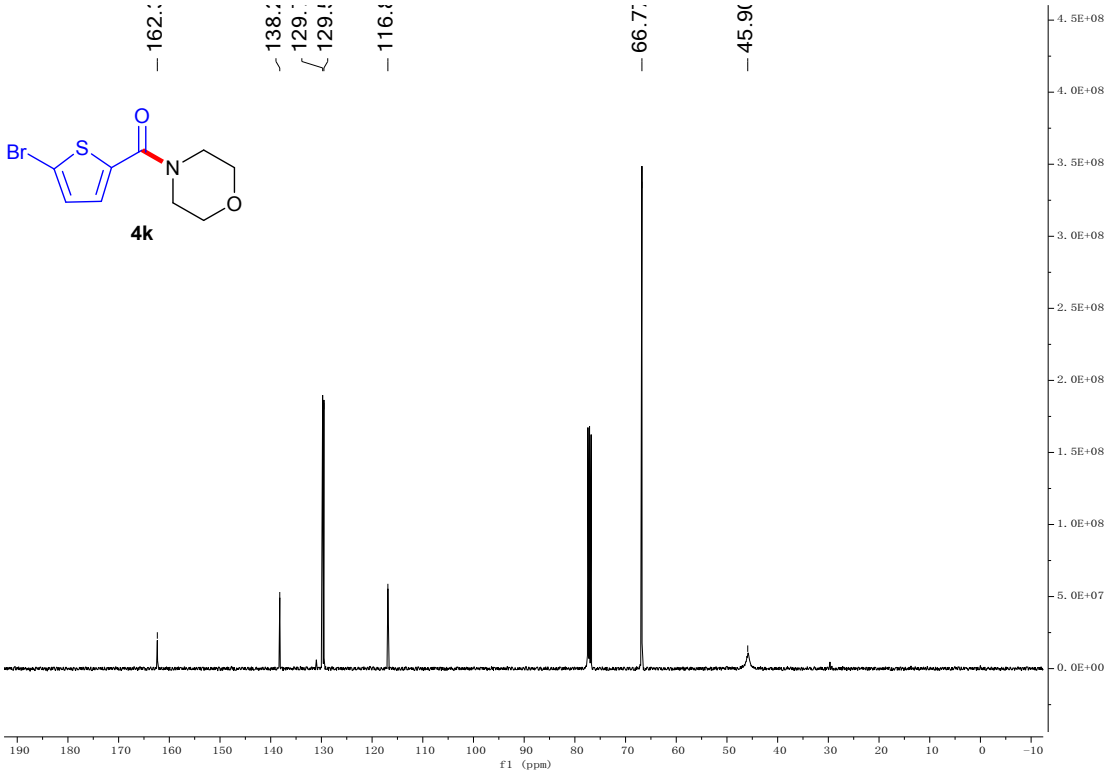
morpholino 2,5-dimethylfuran-3-carboxylate (4j)



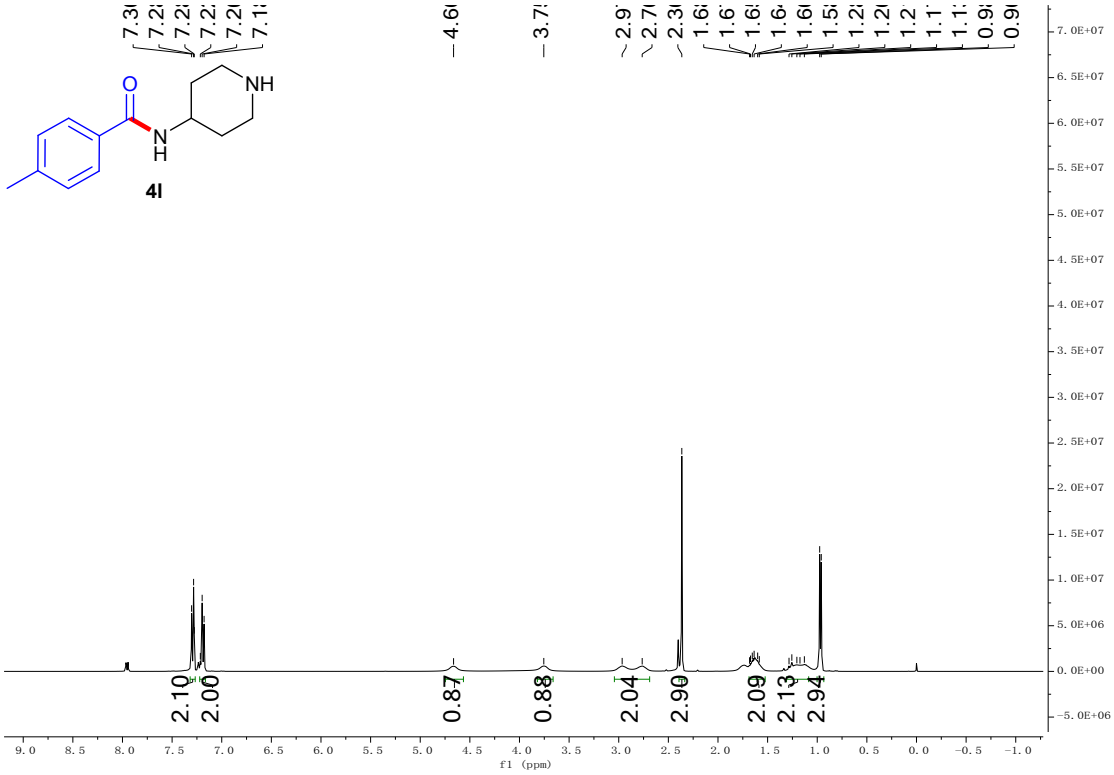


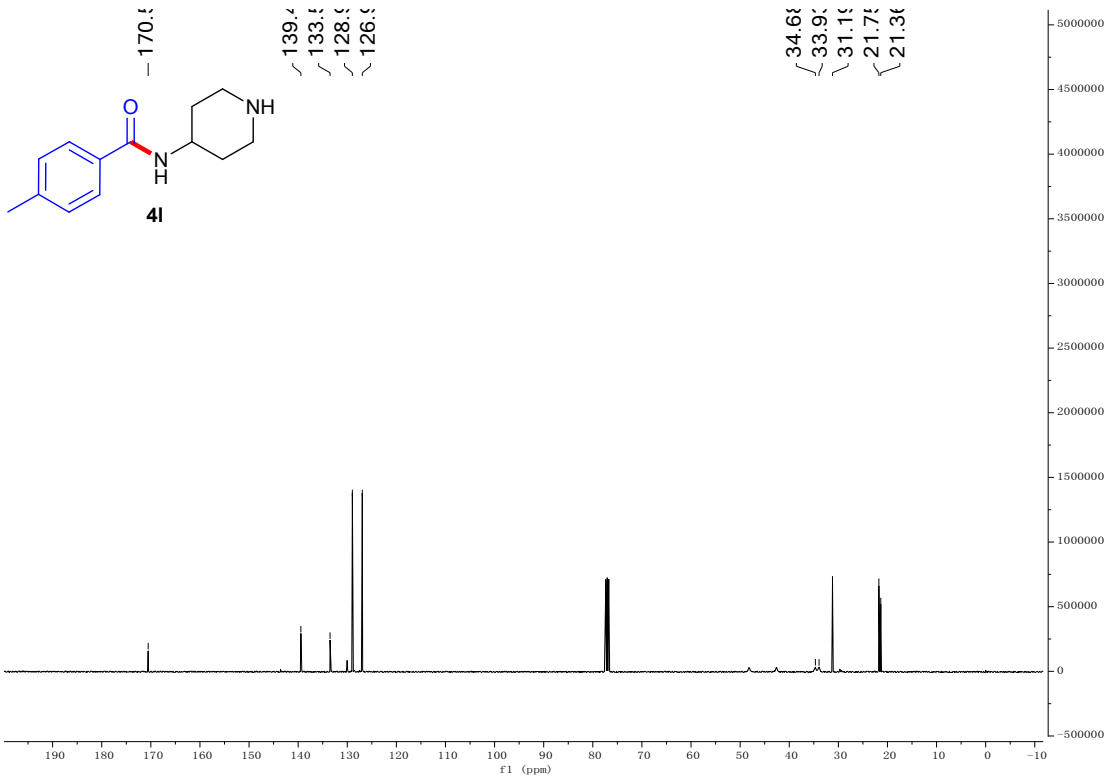
(5-bromothiophen-2-yl)(morpholino)methanone (4k)





4-methyl-N-(piperidin-4-yl)benzamide (4l)





10. References

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2. S. Liu, H. Wang, X. Dai, F. Shi, *Green Chem.,* 2018, **20**, 3457.
3. P. Yu, Y. Wang, Z. Zeng, Y. Chen, *J. Org. Chem.,* 2019, **84**, 14883.
4. S.-M. Wang, C. Zhao, X. Zhang, H.-L. Qin, *Org. Biomol. Chem.,* 2019, **17**, 4087.