1.Analytical Methods

NMR spectra were recorded on Bruker Avance 300 (300 MHz) and Bruker Avance 400(400 MHz) NMR spectrometers. Chemical shifts δ (ppm) were given relative to solvent: references for CDCl3 were 7.26 ppm (^{1}H-NMR) and 77.16 ppm (^{13}C-NMR). ^{13}C-NMR spectra were acquired on a broad band decoupled mode. Multiplets were assigned as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), m (multiplet) and br. s (broad singlet). All measurements were carried out at room temperature unless otherwise stated. For GC analyses, HP 6890 chromatograph with a 29 m HP5 column was used. The products were isolated from the mixture by following column chromatography on silica gel 60, 0.064-0.2 mm, 70-230 mesh (Merk).

2.Materials and Methods

All commercial reagents were ordered from Acros Organics, Alfa Aesar, Aldrich or Strem. Dry solvents were prepared according to standard procedures.[1] Air- and moisture-sensitive syntheses were performed under argon atmosphere in glassware after heat gun-dried under vacuum. Analytical data of literature known compounds were in accord with reported data.

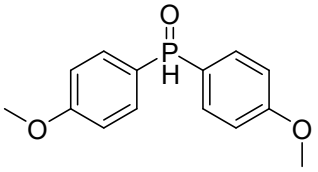
3.General Procedure for the Alkoxycarbonylation of Olefins

Alkoxycarbonylation experiments were carried out in a 300 mL autoclave which can be placed with six 4 mL vials or five 12 mL vials. Generally, exact amount of cobalt precursor, secondary phosphine oxide or other additives were weighed and added into the vials with a small stirring bar. Methanol solvent and olefin were added by syringe under argon atmosphere. The autoclave was flushed by nitrogen gas three times and then twice with carbon monoxide. 40 bar of carbon monoxide was pressurized at room temperature then the autoclave was heated to 120 ℃ for 20 hours with 600 rpm stirring speed. To terminate the reaction, the autoclave was cooled by 0 ℃ ice water. Isooctane (57 mg, 0.5 mmol) was added to each as internal standard. The solution was analyzed by gas chromatography.

4. Synthesis and Characterization of SPOs

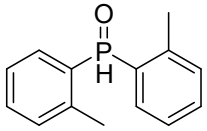
The secondary phosphine oxides were synthesized following the literature.[2]

Bis(4-methoxyphenyl) phosphine oxide (SPO1):



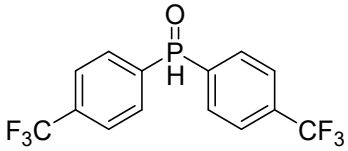
A round-bottom flask with a stirring bar was prepared and filled with argon. Mg (450 mg, 18 mmol) was added into the flask then dry THF (20 mL) was added in the flask under argon. 4-methoxyphenyl bromide (1.88 mL, 15 mmol) was added to the flask slowly and stirred at room temperature for overnight. The mixture was cooled by ice bath, then of diethylphosphite (0.64 mL, 5 mmol) was added dropwise. Let the mixture warm up to room temperature and stir for overnight. The mixture was quenched by saturated NH_4Cl aqueous solution (20 mL) and extracted by EtOAc (10 mL each, 3 times). The organic layer was separated and dried by anhydrous $MgSO_4$, and the solvent was removed under vacuum. Basically pure product was obtained after chromatography using silica gel (70-230 mesh) (DCM:MeOH = 80:1 or 40:1) with 67 % yield (878 mg). NMR characterization data: ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 8.02 (d, J = 478.1 Hz 1H), 7.60 (dd, J = 13.1, 8.8 Hz, 4H), 6.98 (dd, J = 8.8, 2.2 Hz, 4H), 3.83 (s, 6H); ^{31}P{^{1}H} NMR (162 MHz, CDCl3) δ/ppm: 20.8; ^{13}C NMR (75 MHz, CDCl3) δ/ppm: 163.00, 132.70, 122.93, 114.53, 55.47.

Di-o-tolylphosphine oxide (SPO2):



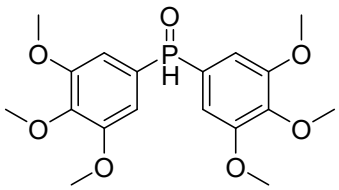
A round-bottom flask with a stirring bar was prepared and filled with argon. Mg (450 mg, 18 mmol) was added into the flask then dry THF (20 mL) was added in the flask under argon. 2-methylphenyl bromide (1.80 mL, 15 mmol) was added to the flask slowly and stirred at room temperature for overnight. The mixture was cooled by ice bath, then of diethylphosphite (0.64 mL, 5 mmol) was added dropwise. Let the mixture warm up to room temperature and stir for overnight. The mixture was quenched by saturated NH_4Cl aqueous solution (20 mL) and extracted by EtOAc (10 mL each, 3 times). The organic layer was separated and dried by anhydrous $MgSO_4$, and the solvent was removed under vacuum. Basically pure product was obtained after chromatography using silica gel (70-230 mesh) (DCM:MeOH = 80:1 or 40:1) with 45 % yield (518 mg). NMR characterization data: ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 8.20 (d, J = 477.4 Hz, 1H), 7.70 (dd, J = 15.23, 7.5 Hz, 2H), 7.44 (t, J = 7.3 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.24 (t, J = 6.2 Hz, 2H), 2.37 (s, 6H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ/ppm: 17.8. ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 141.27, 132.64, 132.47, 131.39, 129.25, 126.24, 20.21.

Bis(4-(trifluoromethyl)phenyl)phosphine oxide (SPO3)



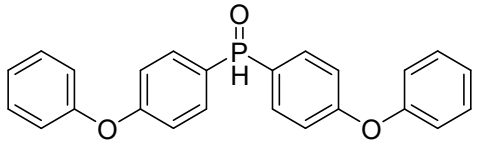
A round-bottom flask with a stirring bar was prepared and filled with argon. Mg (450 mg, 18 mmol) was added into the flask then dry THF (20 mL) was added in the flask under argon. *p*-trifluoromethylphenyl bromide (2.10 mL, 15 mmol) was added to the flask slowly and stirred at room temperature for overnight. The mixture was cooled by ice bath, then of diethylphosphite (0.64 mL, 5 mmol) was added dropwise. Let the mixture warm up to room temperature and stir for overnight. The mixture was quenched by saturated NH_4Cl aqueous solution (20 mL) and extracted by EtOAc (10 mL each, 3 times). The organic layer was separated and dried by anhydrous $MgSO_4$, and the solvent was removed under vacuum. Basically pure product was obtained after chromatography using silica gel (70-230 mesh) (DCM:MeOH = 80:1 or 40:1) with 28 % yield (472.9 mg). NMR characterization data: ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 8.12 (d, J = 493.9 Hz ,1H), 7.78 (dd, J = 13.3, 7.9 Hz, 4H), 7.67 (dd, J = 8.6, 1.9 Hz, 4H); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ/ppm: 17.7; ^{19}F NMR (282 MHz, $CDCl_3$) δ/ppm: -63.56; ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 135.56, 134.80, 134.34, 131.10, 125.90.

Bis(3,4,5-trimethoxyphenyl)phosphine oxide (SPO4)



A round-bottom flask with a stirring bar was prepared and filled with argon. Mg (450 mg, 18 mmol) was added into the flask then dry THF (20 mL) was added in the flask under argon. 1-bromo-3,4,5-trimethoxybenzene (3.71 g, 15 mmol) was added to the flask slowly and stirred at room temperature for overnight. The mixture was cooled by ice bath, then of diethylphosphite (0.64 mL, 5 mmol) was added dropwise. Let the mixture warm up to room temperature and stir for overnight. The mixture was quenched by saturated NH_4Cl aqueous solution (20 mL) and extracted by EtOAc (10 mL each, 3 times). The organic layer was separated and dried by anhydrous $MgSO_4$, and the solvent was removed under vacuum. Basically pure product was obtained after chromatography using silica gel (70-230 mesh) (DCM:MeOH = 80:1 or 40:1) with 56 % yield (1070.1 mg). NMR characterization data: ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 7.86 (d, J = 484.3 Hz, 1H), 6.79 (d, J = 7.5 Hz, 4H), 3.76 (s, 6H), 3.74 (s, 12H); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ/ppm: 22.1; ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 153.72, 141.51, 126.27, 107.46, 60.68, 56.19.

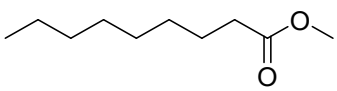
Bis(4-phenoxyphenyl)phosphine oxide (SPO5)



A round-bottom flask with a stirring bar was prepared and filled with argon. Mg (450 mg, 18 mmol) was added into the flask then dry THF (20 mL) was added in the flask under argon. 4-Bromodiphenyl ether (2.63 mL, 15 mmol) was added to the flask slowly and stirred at room temperature for overnight. The mixture was cooled by ice bath, then of diethylphosphite (0.64 mL, 5 mmol) was added dropwise. Let the mixture warm up to room temperature and stir for overnight. The mixture was quenched by saturated NH_4Cl aqueous solution (20 mL) and extracted by EtOAc (10 mL each, 3 times). The organic layer was separated and dried by anhydrous $MgSO_4$, and the solvent was removed under vacuum. Basically pure product was obtained after chromatography using silica gel (70-230 mesh) (DCM:MeOH = 80:1 or 40:1) with 62 % yield (1195.5 mg). NMR characterization data: ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 8.12 (d, J = 449.2 Hz, 1H), 7.65 (dd, J = 13.2, 8.8 Hz, 4H), 7.39 (t, J = 7.6 Hz, 4H), 7.19 (t, J = 7.4 Hz, 2H), 7.06 (dt, J = 8.7, 1.9 Hz, 8H); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ/ppm: 20.3; ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 161.78, 155.43, 133.00, 130.21, 129.83, 125.54, 120.29, 118.20.

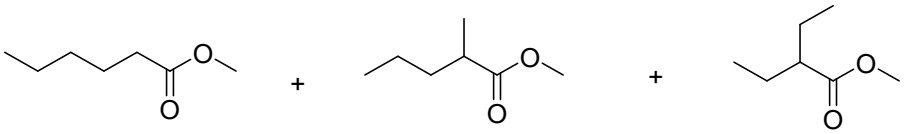
5. NMR data of ester products

Methyl nonanoate (**2**)



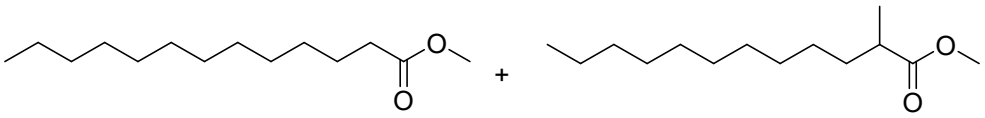
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 3.65 (s, 3H), 2.29 (t, *J* = 7.5 Hz, 2 H), 1.60 (m, 2H), 1.27 (m, 10H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 174.49, 51.56, 34.26, 31.94, 29.35, 29.29, 29.25, 25.10, 22.78, 14.22.

Methyl hexanoate (**2a**), methyl 2-methylpentanoate (**2a'**) & methyl 2-ethylbutanoate (**2a''**)



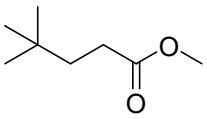
(**2a**) ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 3.58 (s, 3H), 2.22 (t, *J* = 7.6 Hz, 2 H), 1.62 (m, 2H), 1.27 (m, 4H), 0.86 (m, 3H); (**2a**) ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 174.20, 51.32, 34.03, 31.34, 24.65, 22.32, 13.84.

Methyl tridecanoate (**2b**) & methyl 2-methyldodecanoate (**2b'**)



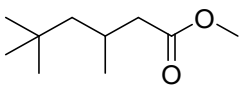
(**2b**) ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 3.65 (s, 3H), 2.28 (t, *J* = 7.5 Hz, 2 H), 1.60 (m, 2H), 1.24 (m, 18H), 0.84 (t, *J* = 6.7 Hz, 3H); (**2b**) ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 174.43, 51.52, 34.24, 32.05, 29.78, 29.76, 29.73, 29.58, 29.49, 29.40, 29.30, 25.10, 22.81, 14.22.

Methyl 4,4-dimethylpentanoate (**2c**)



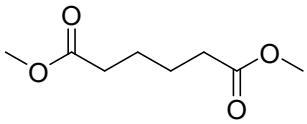
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 3.66 (s, 3H), 2.27 (t, *J* = 8.4 Hz, 2 H), 1.54 (t, *J* = 8.4 Hz, 2H), 0.89 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 175.04, 51.67, 38.74, 30.18, 30.04, 29.11.

Methyl 3,5,5-trimethylhexanoate (**2d**)



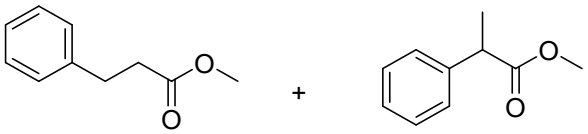
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 3.63 (s, 3H), 2.28 (m, 1H), 2.06 (m, 1H), 1.21 (m, 1H), 1.09 (m, 1H), 0.94 (d, *J* = 6.5 Hz, 3H), 0.88 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 173.67, 51.37, 50.63, 43.92, 31.15, 30.01, 27.10, 22.81.

Dimethyl adipate (**2e**)



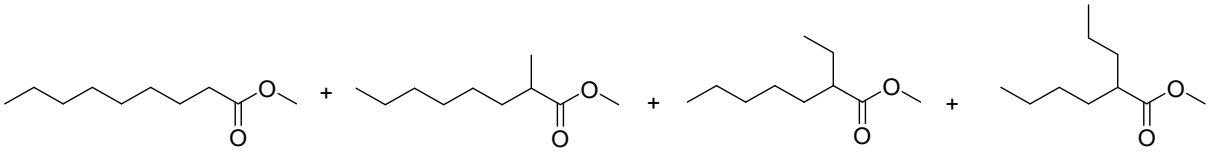
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 3.64 (s, 6H), 2.30 (m, 4H), 1.64 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 173.83, 51.62, 33.76, 24.47.

Methyl 3-phenylpropanoate (**2f**) & methyl 2-phenylpropanoate (**2f'**)



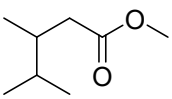
(**2f**) ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 7.31-7.18 (m, 5H), 3.67 (s, 3H), 2.96 (t, J = 7.8 Hz, 2H), 2.64 (t, J = 7.8 Hz, 4H); (**2f**) ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 173.40, 140.59, 128.59, 128.35, 126.35, 51.67, 35.77, 31.02.

Methyl nonanoate (**2g**), methyl 2-methyloctanoate (**2g'**), methyl 2-ethylheptanoate (**2g''**) & methyl 2-propylhexanoate (**2g'''**)



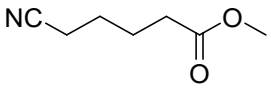
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 3.66 (s, 3H), 2.91 (t, J = 7.5 Hz, 2H), 1.62 (m, 2H), 1.27 (m, 10H), 0.86 (m, 3H). *Mixture of linear and branched products; ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 173.50, 177.02, 174.42, 51.50, 51.34, 47.40, 39.56, 34.21, 33.93, 31.90, 31.79, 29.31, 29.25, 29.21, 27.92, 27.22, 25.57, 25.06, 22.73, 22.68, 22.58, 17.15, 14.16, 14.13, 14.08, 11.94.

Methyl 3,4-dimethylpentanoate (**2h**)



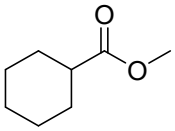
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 3.64 (s, 3H), 2.36 (dd, J = 14.6, 5.2 Hz, 1H), 2.03 (m, 1H), 1.83 (m, 1H), 1.66 (m, 1H), 0.83 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 174.29, 51.47, 39.09, 36.00, 32.17, 19.90, 18.35, 15.93.

Methyl 5-cyanopentanoate (**2i**)



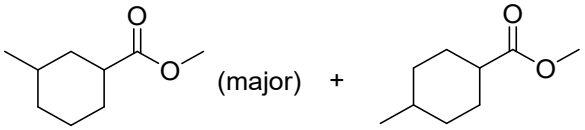
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 3.63 (s, 3H), 2.35 (td, J = 6.9, 2.3 Hz, 4H), 1.69 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 173.18, 119.36, 51.65, 33.00, 24.78, 23.85, 16.94.

Methyl cyclohexanecarboxylate (**2j**)



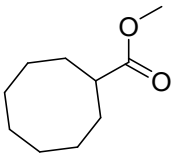
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 3.65 (s, 3H), 2.33 (s, 1H), 1.90-1.24 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 176.68, 51.53, 43.22, 29.12, 25.85, 25.55.

Methyl 3-methylcyclohexane-1-carboxylate (**2k**) & methyl 4-methylcyclohexane-1-carboxylate (**2k'**)



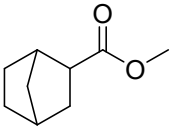
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 3.69 (s, 3H), 2.33-2.15 (m, 1H), 1.92-1.23 (m, 9H), 0.88 (m, 3H); (**2k**) ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 176.66, 51.55, 43.51, 37.55, 34.46, 32.18, 28.74, 25.60, 22.70.

Methyl cyclooctanecarboxylate (**2l**)



^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 3.64 (s, 3H), 2.51 (s, 1H), 1.86-1.52 (m, 14H); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 177.92, 51.62, 43.62, 28.87, 26.89, 26.25, 25.36.

Methyl bicyclo[2.2.1]heptane-2-carboxylate (**2m**)

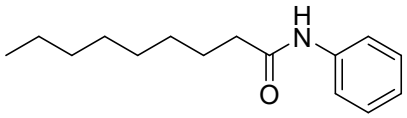


^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 3.64 (s, 3H), 2.48 (m, 1H), 2.32 (m, 2H), 1.81(m, 1H), 1.52-1.40 (m, 4H), 1.28-1.17 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 176.59, 51.60, 46.36, 40.90, 36.47, 36.02, 34.16, 29.47, 28.63.

Nonanoic acid and isomerization mixture

(Nonanoic acid) ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 11.51 (br. s, 1H), 2.34 (t, *J* = 7.5 Hz, 2H), 1.63 (m, 2H), 1.30 (m, 10H), 0.87 (m, 3H); (Nonanoic acid) ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 180.80, 34.28, 31.94, 29.34, 29.23, 29.20, 24.80, 22.77, 14.20.

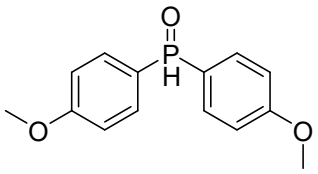
N-phenylnonanamide

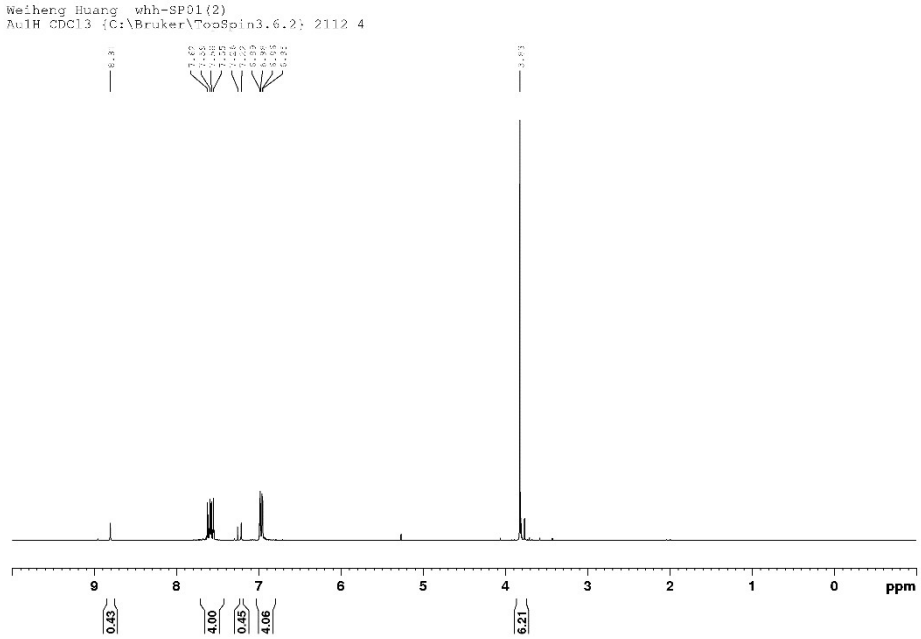


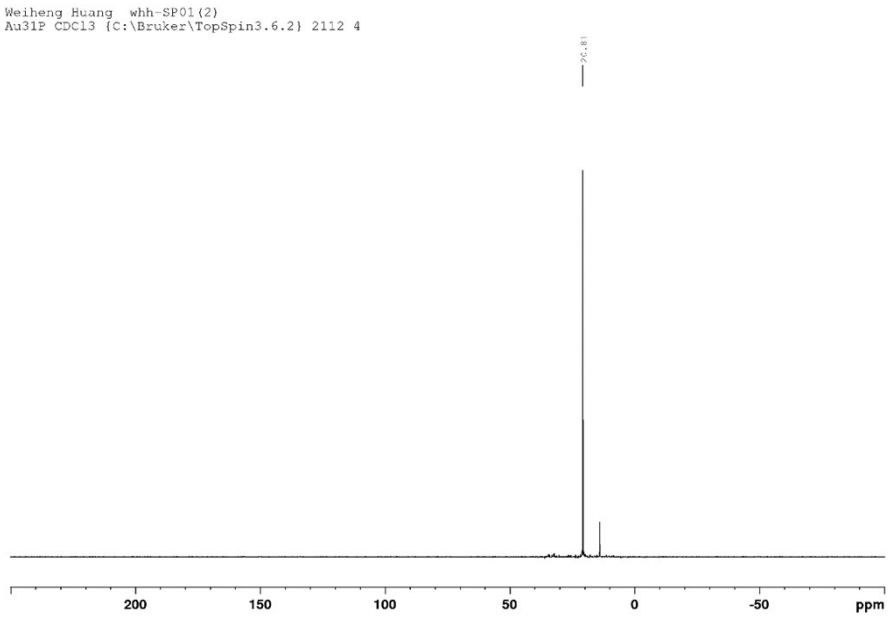
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 7.81 (br. s, 1H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 2.45 (t, *J* = 7.6 Hz, 2H), 1.81 (m, 2H), 1.38 (m 10H), 0.97 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 171.95, 138.17, 129.00, 124.22, 120.06, 37.85, 31.91, 29.45, 29.39, 29.25, 25.81, 22.73, 14.18.

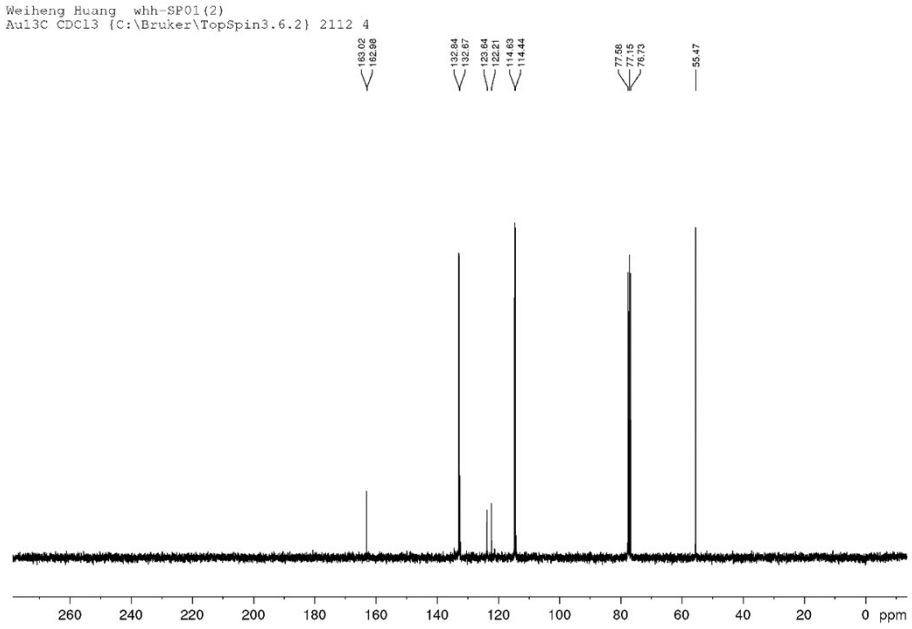
6.NMR spectra

Bis(4-methoxyphenyl) phosphine oxide (SPO1):

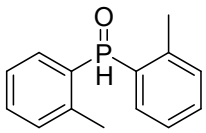


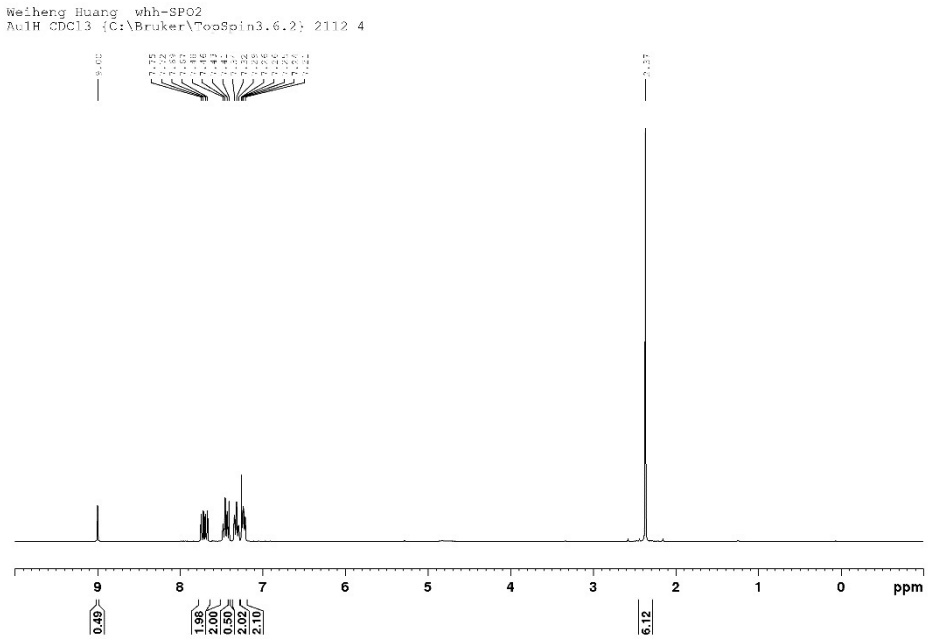




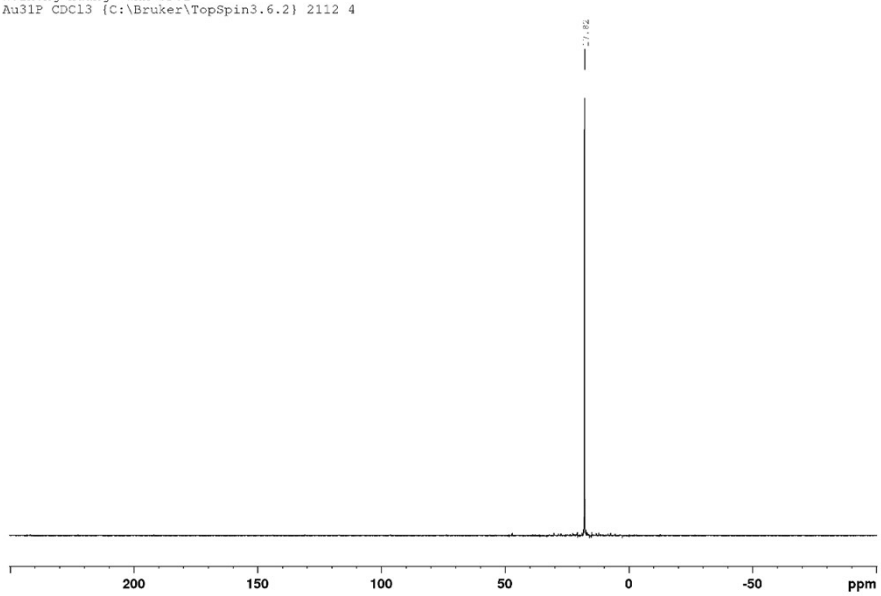


Di-o-tolylphosphine oxide (SPO2):

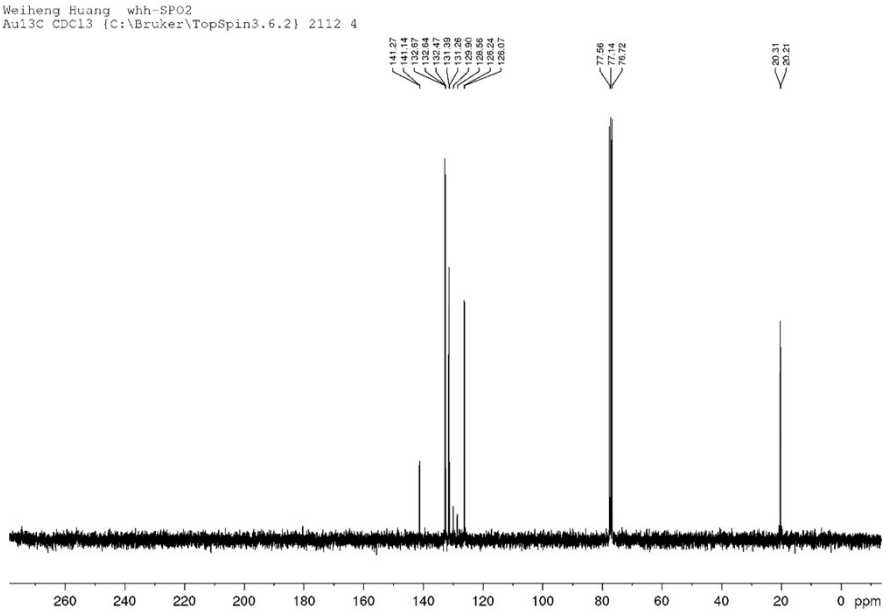




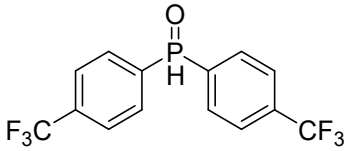
Weiheng Huang whh-SPO2
Au31P CDCl3 {C:\Bruker\TopSpin3.6.2} 2112 4

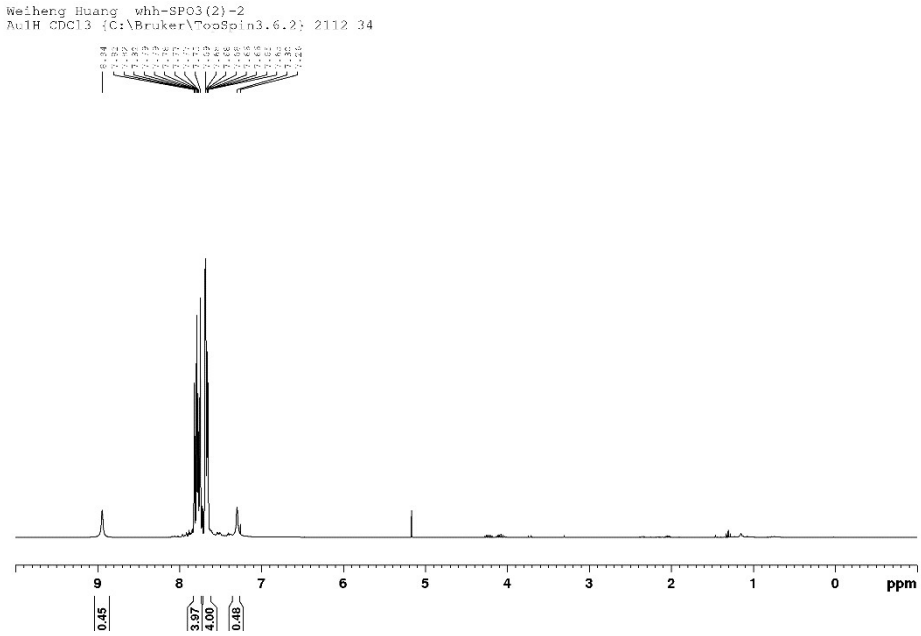


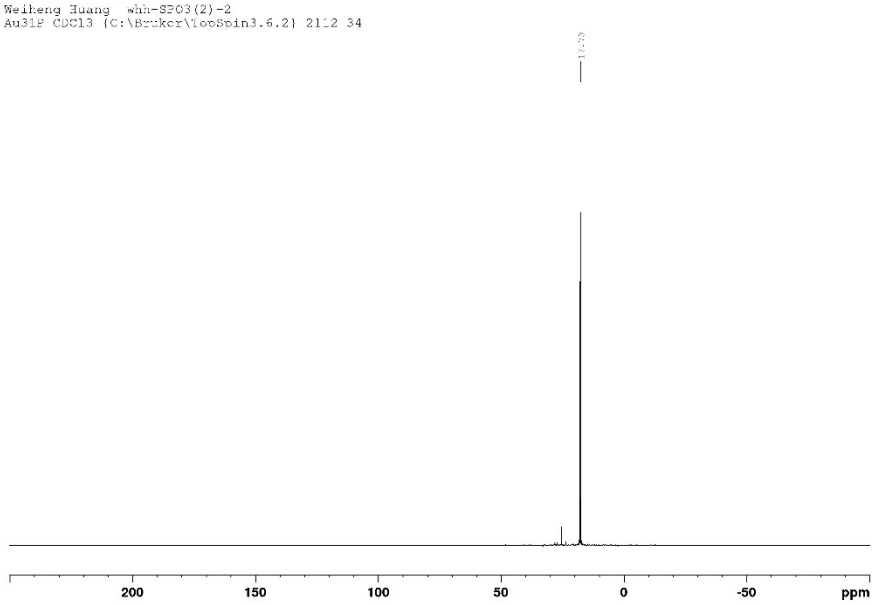
Weiheng Huang whh-SPO2
Au13C CDCl3 {C:\Bruker\TopSpin3.6.2} 2112 4

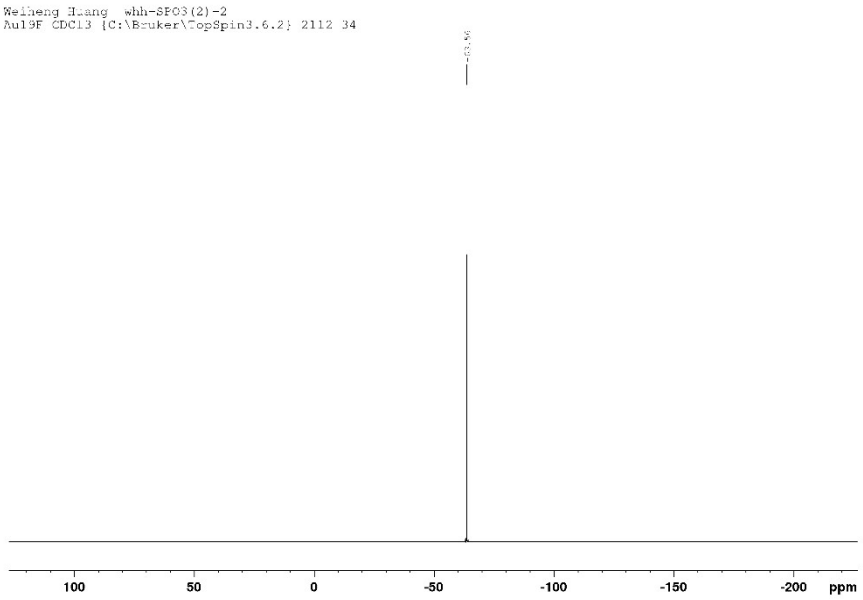


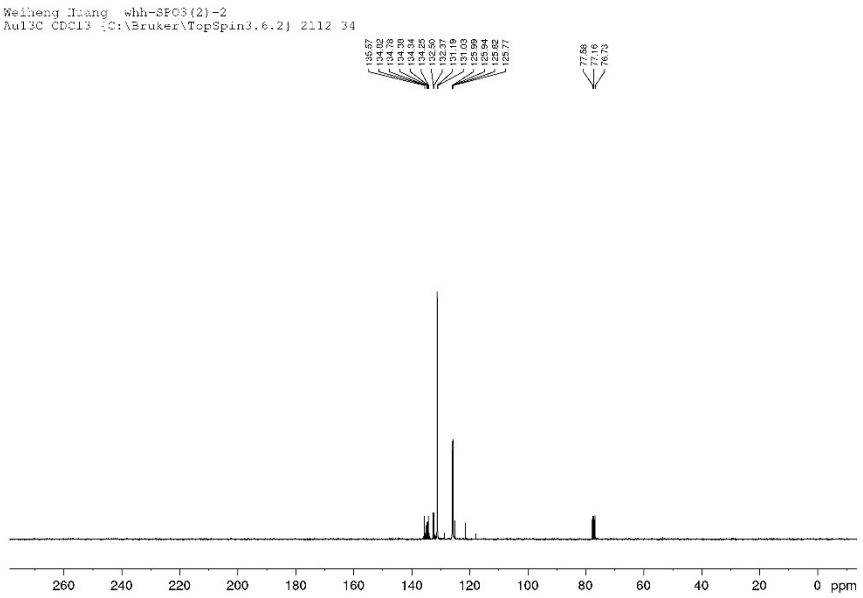
Bis(4-(trifluoromethyl)phenyl)phosphine oxide (SPO3)



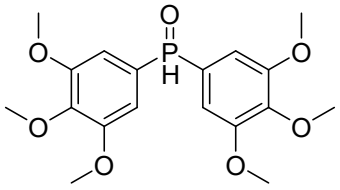


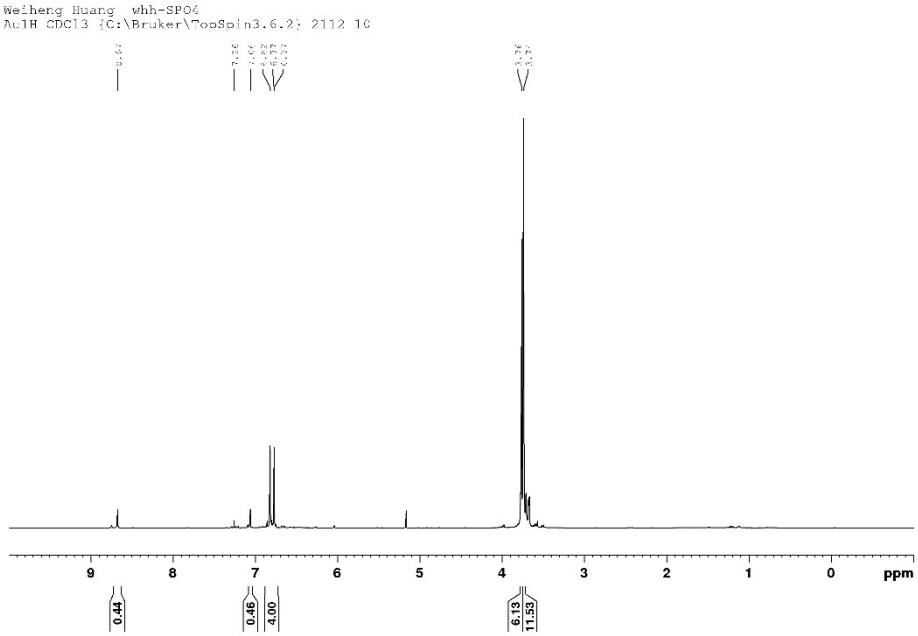


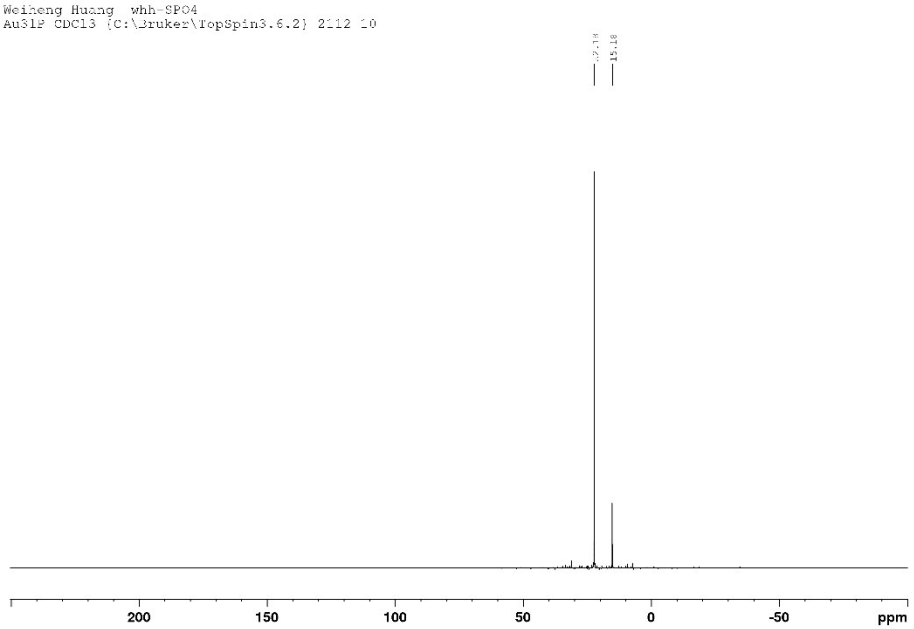

Weiheng Huang whh-8PO3(2)-2
Au19F CDCl3 {C:\Bruker\TopSpin3.6.2} 2112 34
-63.56
100
50
0
-50
-100
-150
-200
ppm

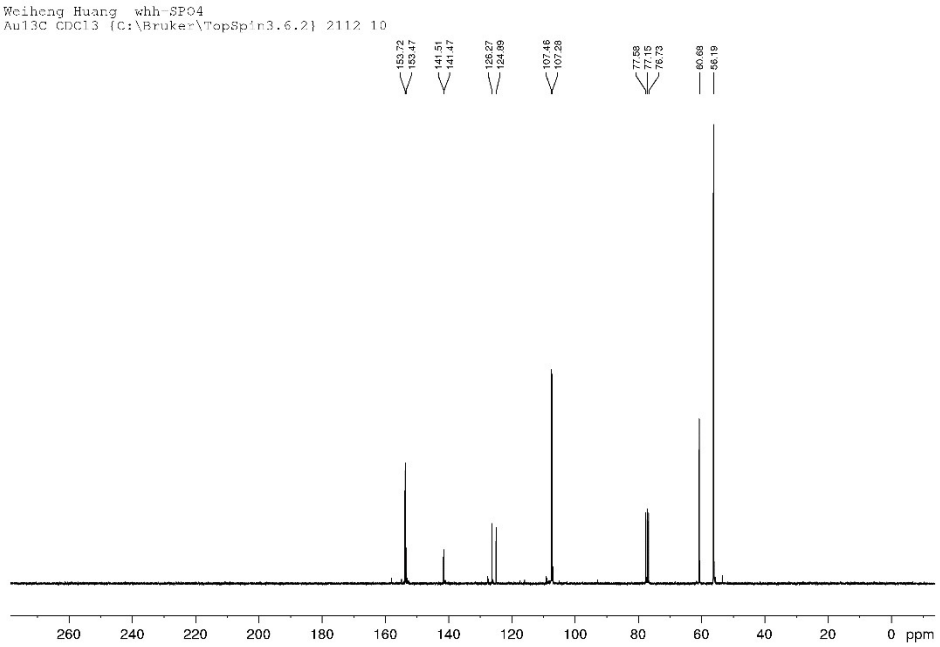

Weiheng Huang whh-8PO3(2)-2
Au13C CDCl3 {C:\Bruker\TopSpin3.6.2} 2112 34
135.57
134.92
134.78
134.30
134.14
134.05
132.50
132.37
131.19
131.03
125.99
125.84
125.62
125.27
77.68
77.16
76.63
260
240
220
200
180
160
140
120
100
80
60
40
20
0 ppm

Bis(3,4,5-trimethoxyphenyl)phosphine oxide (SPO4)

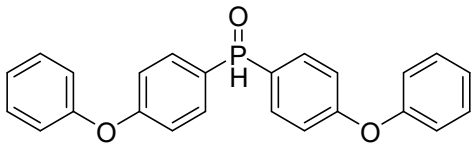




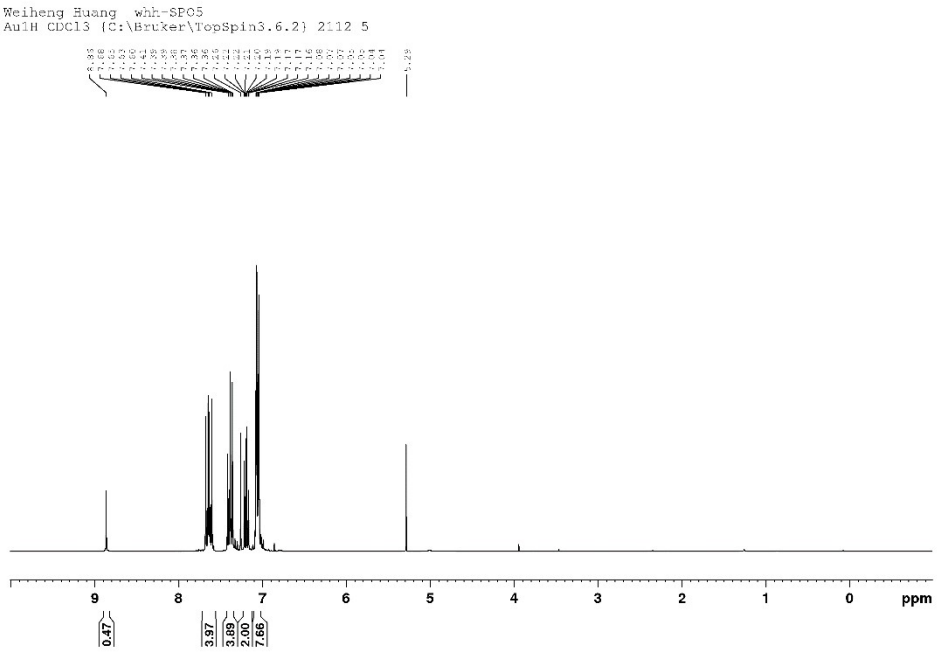




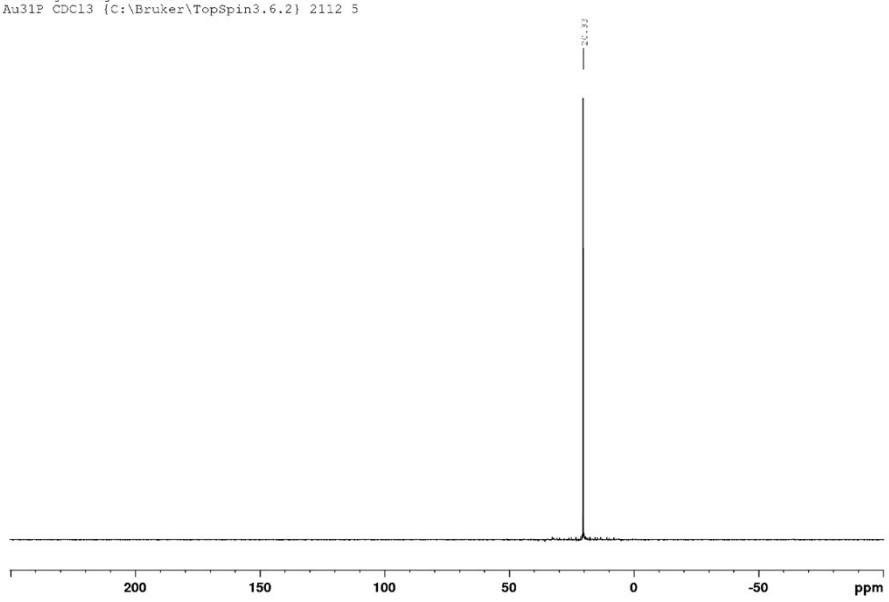
Bis(4-phenoxyphenyl)phosphine oxide (SPO5)



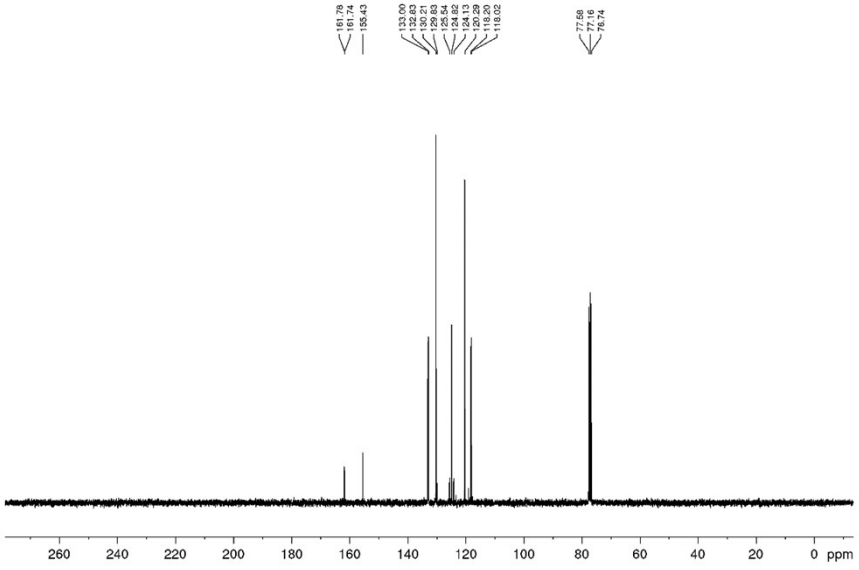
(DCM: 5.29)



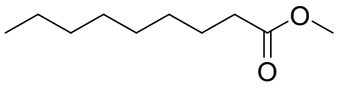
Weiheng Huang whh-SPO5
Au31P CDCl3 {C:\Bruker\TopSpin3.6.2} 2112 5



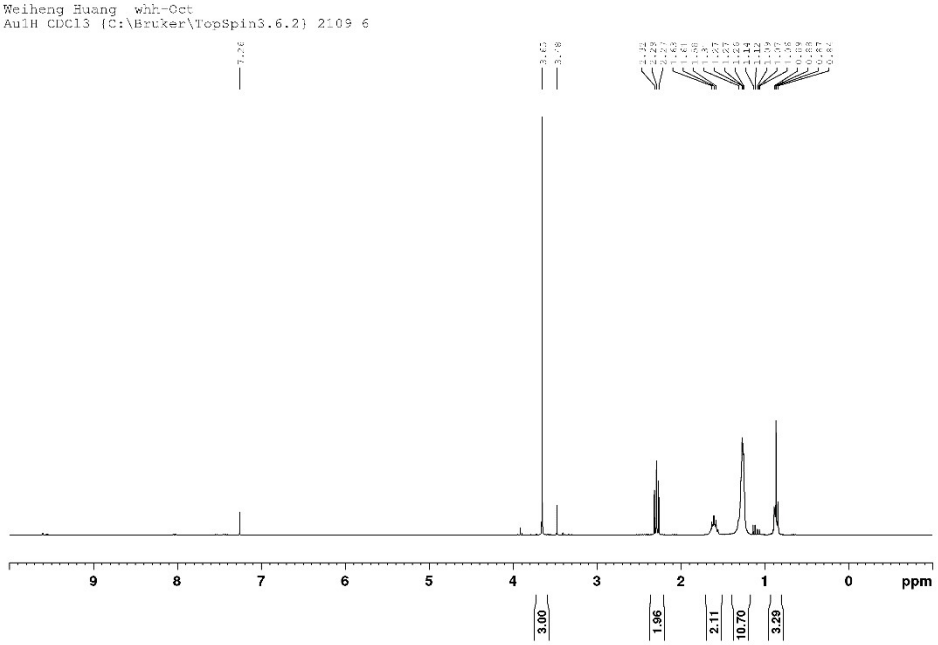
Weiheng Huang whh-SPO5
Au13C CDCl3 {C:\Bruker\TopSpin3.6.2} 2112 5



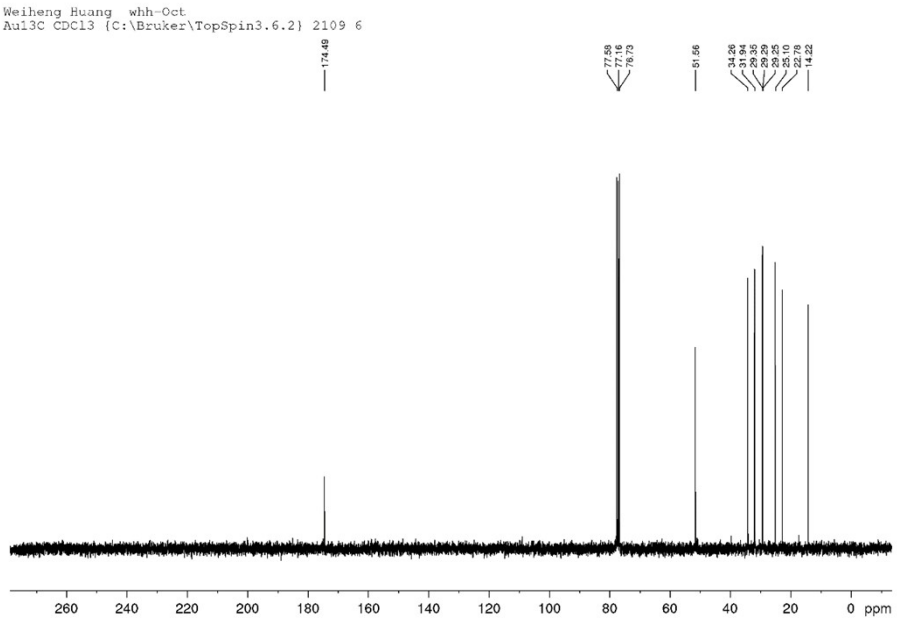
Methyl nonanoate (**2**)



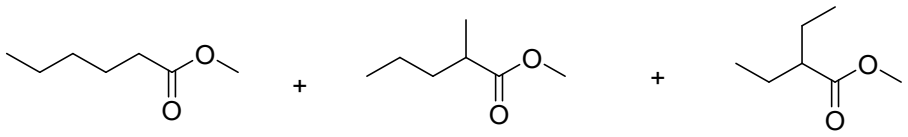
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 3.65 (s, 3H), 2.29 (t, J = 7.5 Hz, 2 H), 1.60 (m, 2H), 1.27 (m, 10H), 0.87 (t, J = 6.8 Hz, 3H). *MeOH: 3.48.



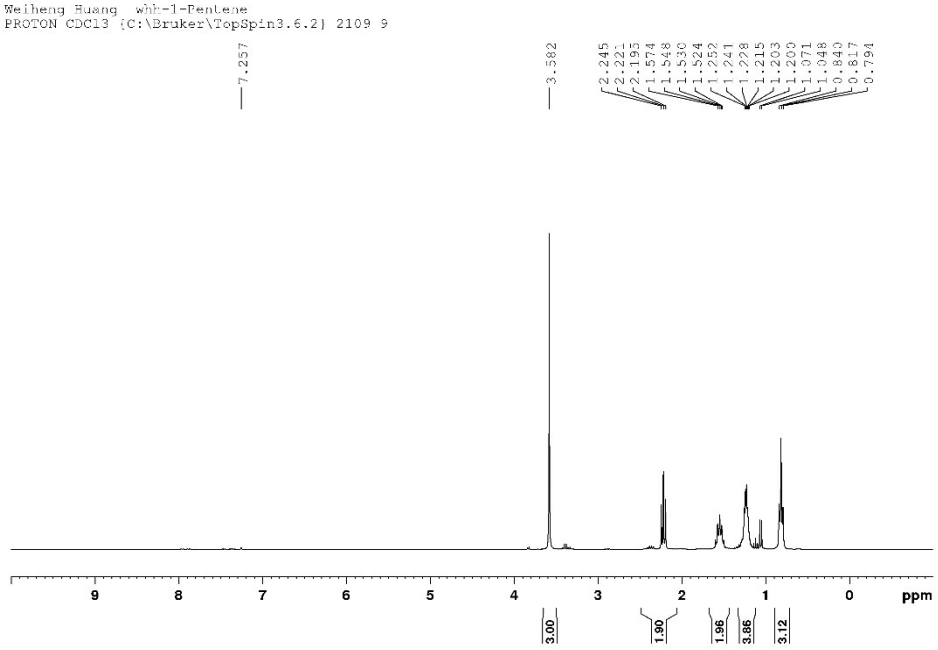
^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 174.49, 51.56, 34.26, 31.94, 29.35, 29.29, 29.25, 25.10, 22.78, 14.22.



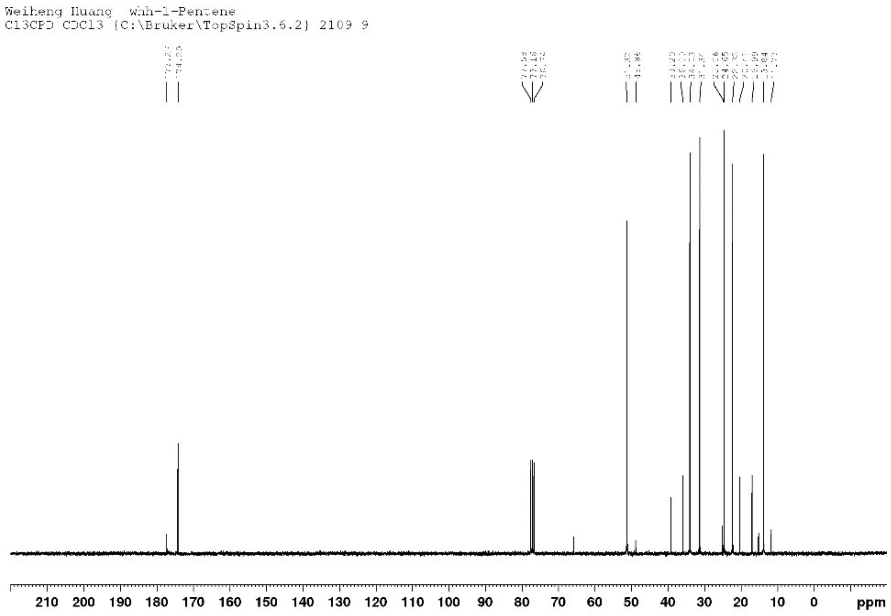
Methyl hexanoate (**2a**), methyl 2-methylpentanoate (**2a'**) & methyl 2-ethylbutanoate (**2a''**)



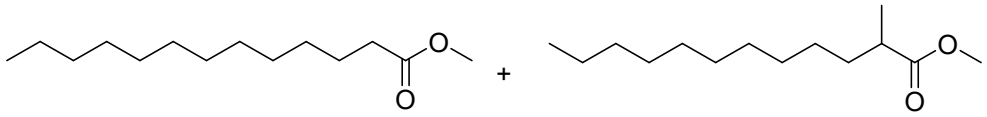
(**2a**) ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 3.58 (s, 3H), 2.22 (t, J = 7.6 Hz, 2 H), 1.62 (m, 2H), 1.27 (m, 4H), 0.86 (m, 3H).



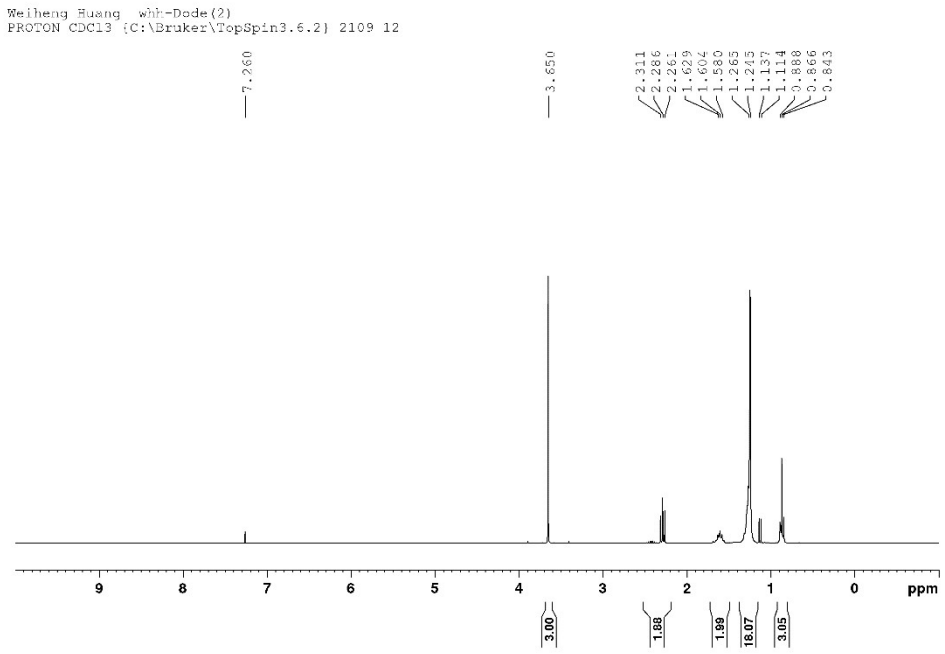
(**2a**) ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 174.20, 51.32, 34.03, 31.34, 24.65, 22.32, 13.84.



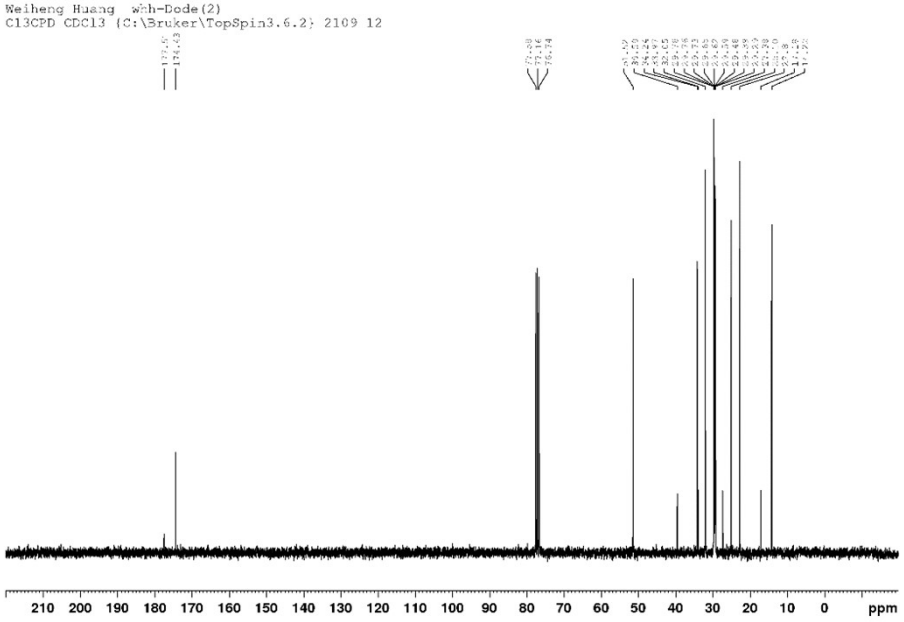
Methyl tridecanoate (**2b**) & methyl 2-methyldodecanoate (**2b'**)



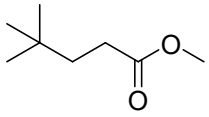
(**2b**) ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 3.65 (s, 3H), 2.28 (t, J = 7.5 Hz, 2 H), 1.60 (m, 2H), 1.24 (m, 18H), 0.84 (t, J = 6.7 Hz, 3H).



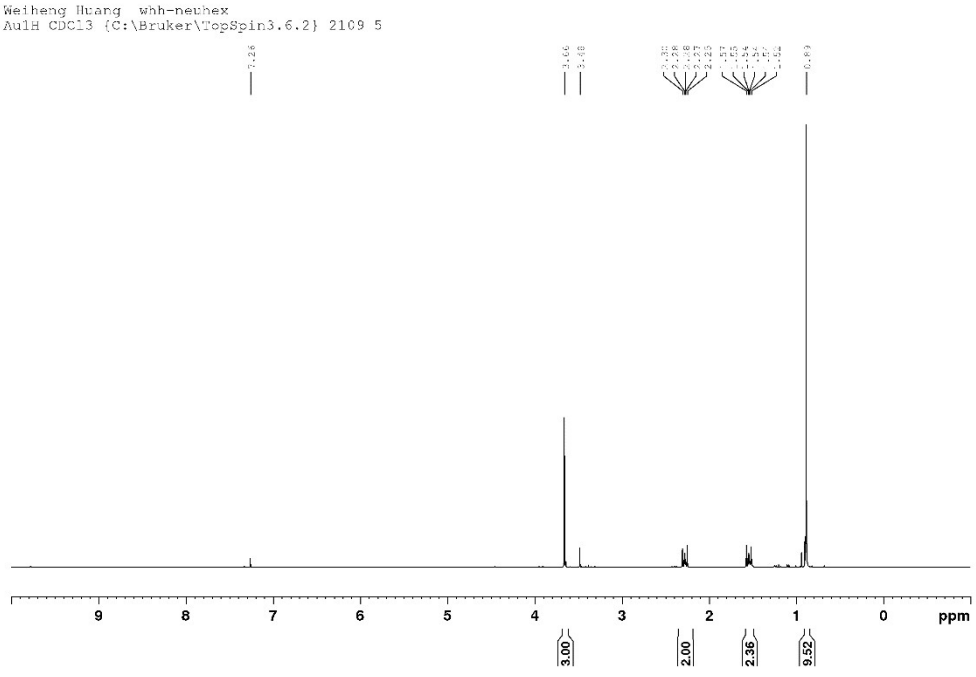
(**2b**) ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 174.43, 51.52, 34.24, 32.05, 29.78, 29.76, 29.73, 29.58, 29.49, 29.40, 29.30, 25.10, 22.81, 14.22.



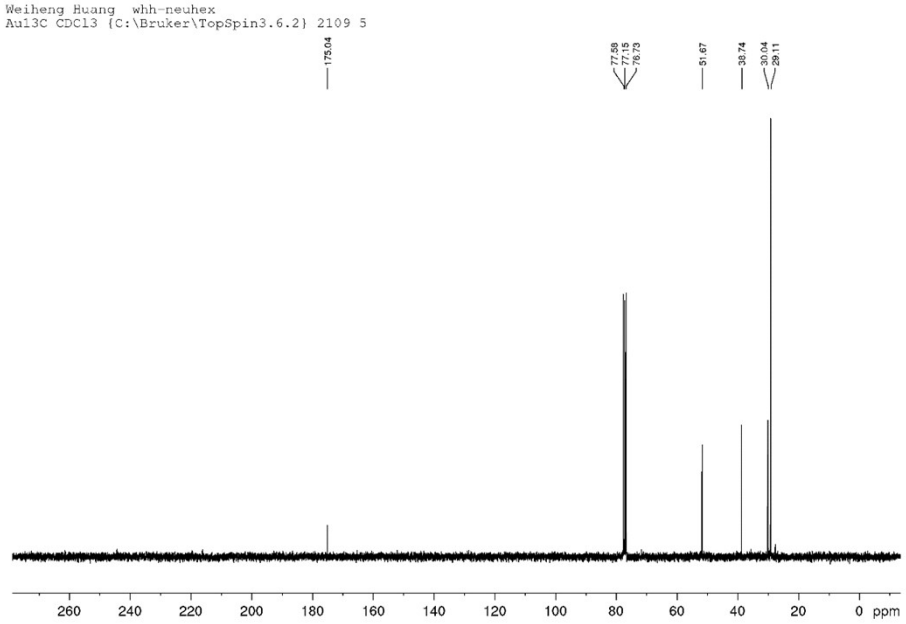
Methyl 4,4-dimethylpentanoate (**2c**)



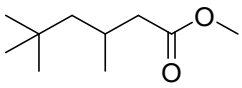
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 3.66 (s, 3H), 2.27 (t, *J* = 8.4 Hz, 2 H), 1.54 (t, *J* = 8.4 Hz, 2H), 0.89 (s, 9H). *MeOH: 3.48.



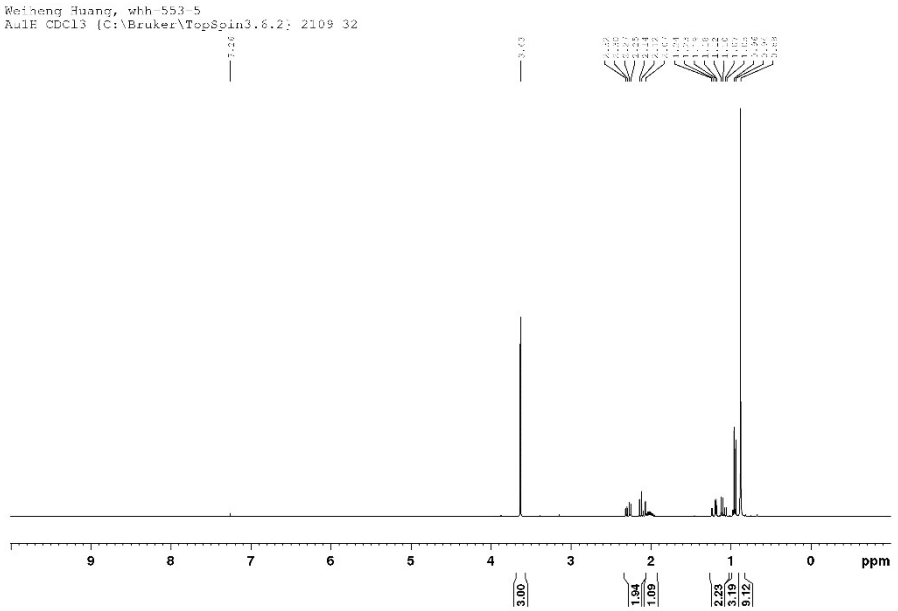
^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 175.04, 51.67, 38.74, 30.18, 30.04, 29.11.



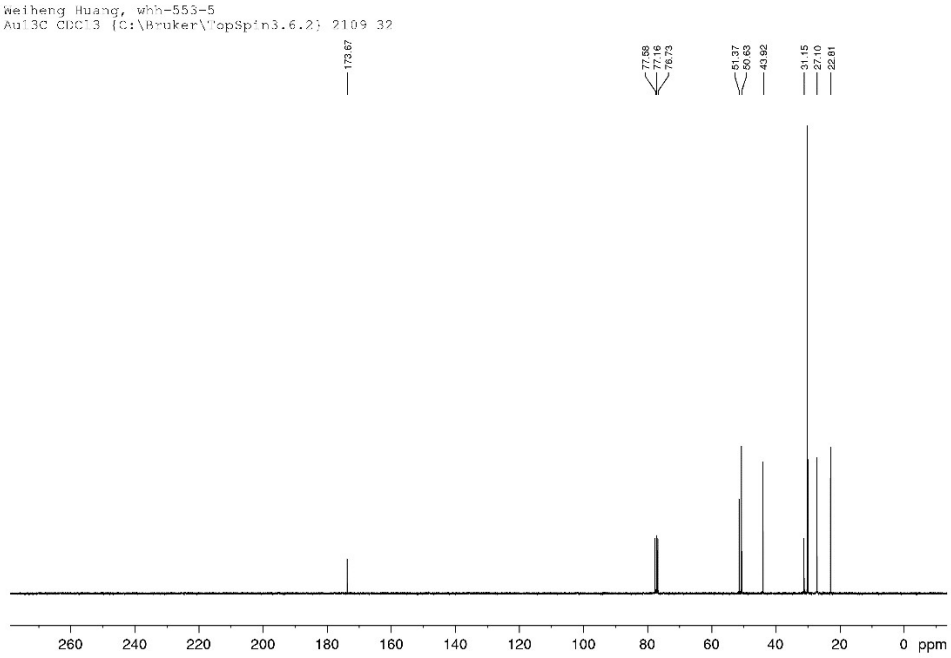
Methyl 3,5,5-trimethylhexanoate (**2d**)



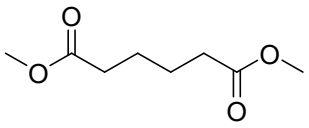
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 3.63 (s, 3H), 2.28 (m, 1H), 2.06 (m, 1H), 1.21 (m, 1H), 1.09 (m, 1H), 0.94 (d, J = 6.5 Hz, 3H), 0.88 (s, 9H).



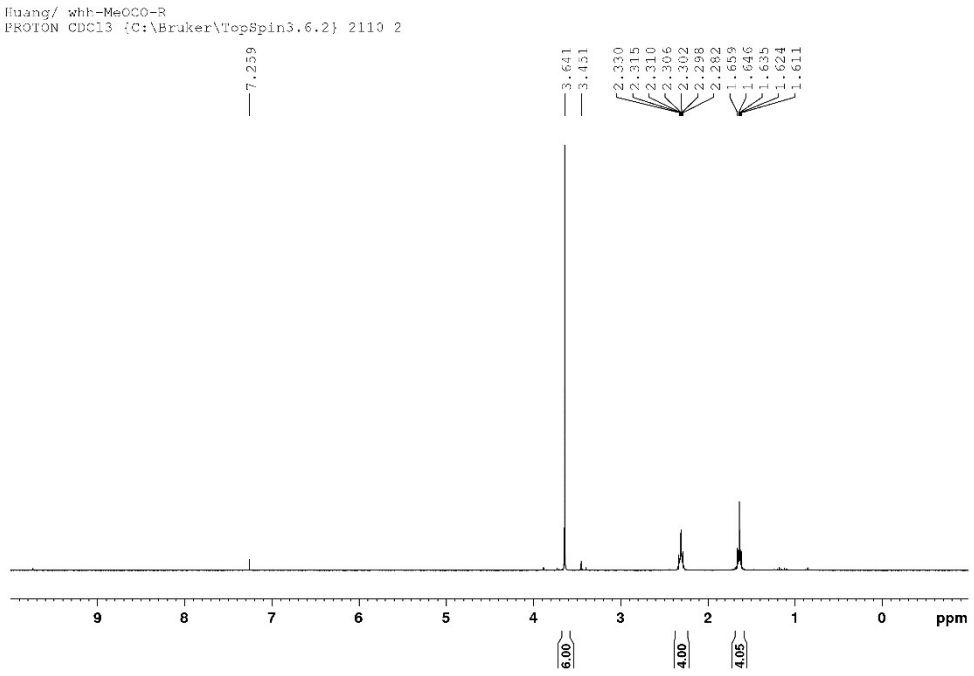
^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 173.67, 51.37, 50.63, 43.92, 31.15, 30.01, 27.10, 22.81.



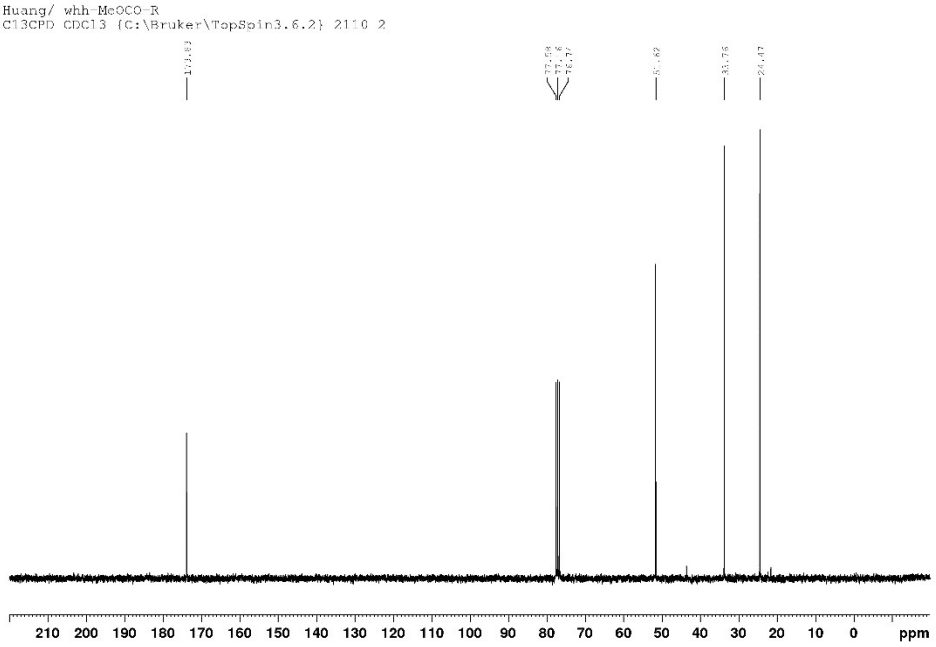
Dimethyl adipate (**2e**)



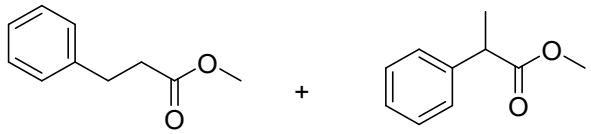
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 3.64 (s, 6H), 2.30 (m, 4H), 1.64 (m, 4H).



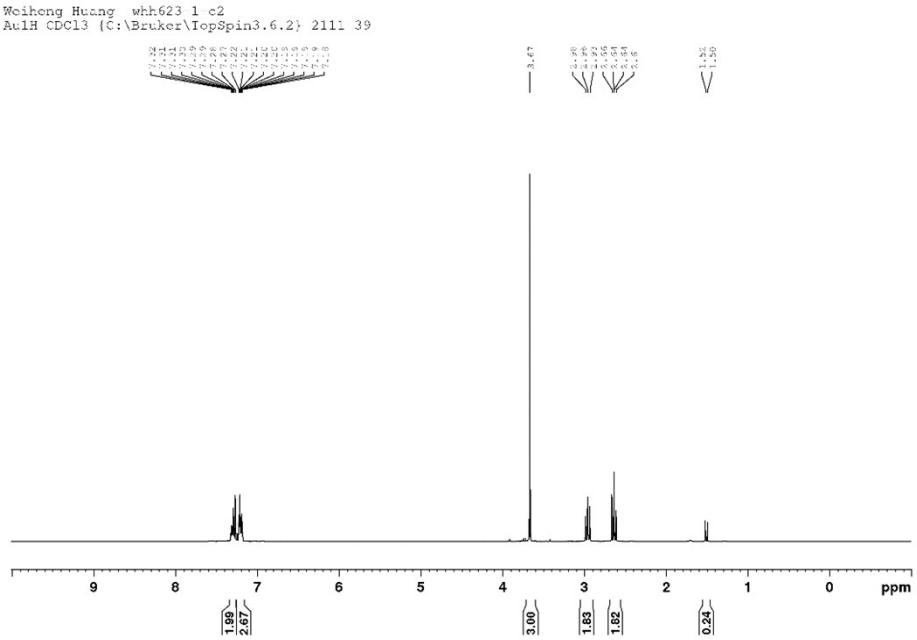
^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 173.83, 51.62, 33.76, 24.47.



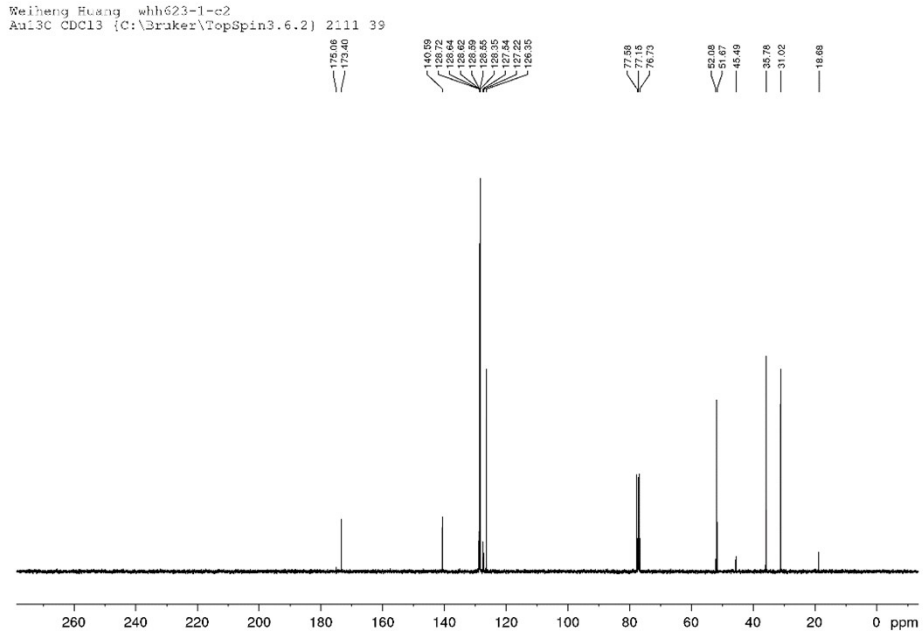
Methyl 3-phenylpropanoate (**2f**) & methyl 2-phenylpropanoate (**2f'**)



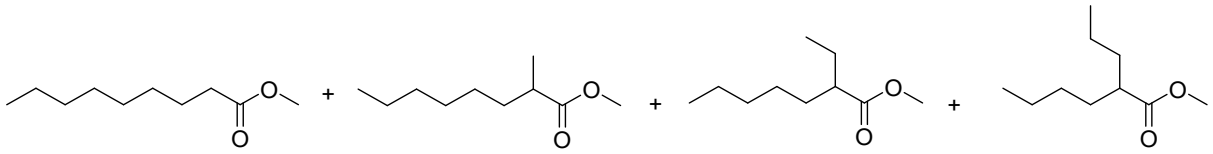
(**2f**) ^1H NMR (300 MHz, $CDCl_3$) δ/ppm: 7.31-7.18 (m, 5H), 3.67 (s, 3H), 2.96 (t, J = 7.8 Hz, 2H), 2.64 (t, J = 7.8 Hz, 4H).



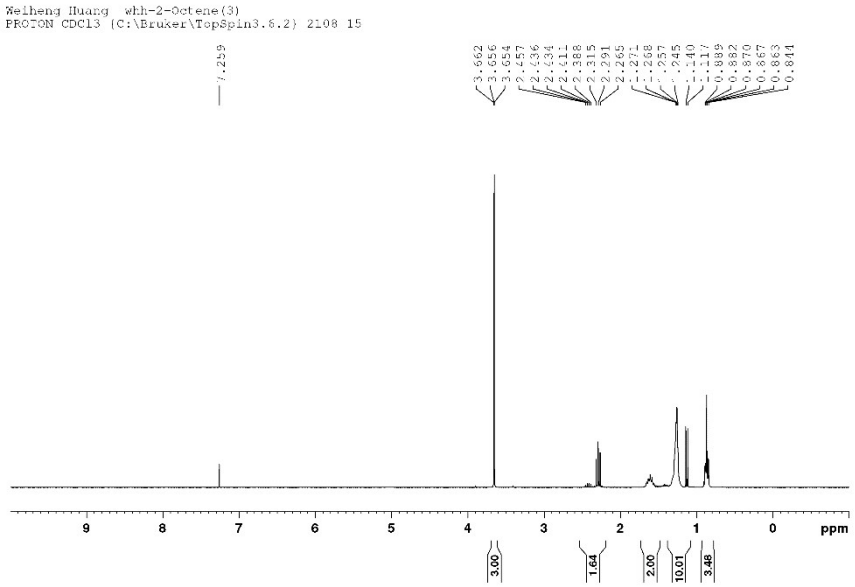
(**2f**) ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 173.40, 140.59, 128.59, 128.35, 126.35, 51.67, 35.77, 31.02.



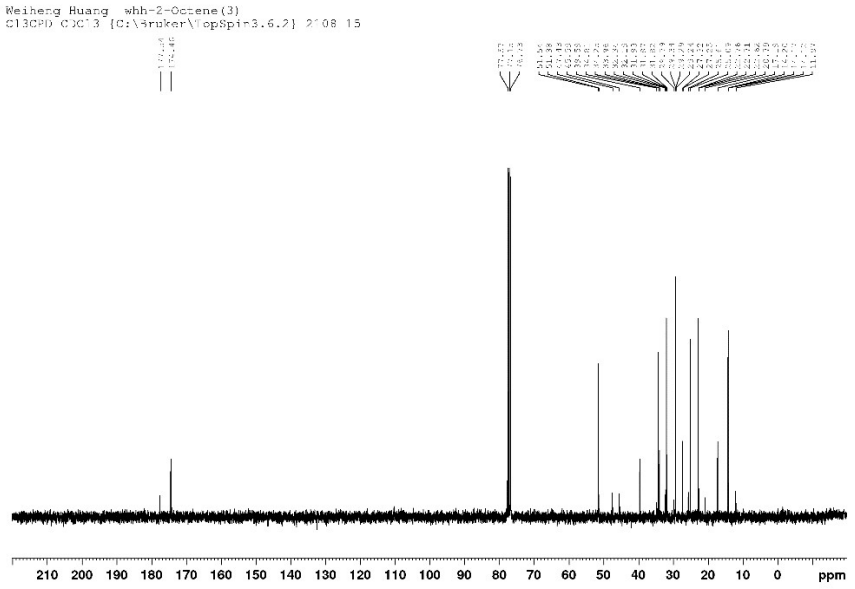
Methyl nonanoate (**2g**), methyl 2-methyloctanoate (**2g'**), methyl 2-ethylheptanoate (**2g''**) & methyl 2-propylhexanoate (**2g'''**)



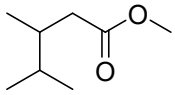
^1H NMR (300 MHz, $CDCl_3$) δ/ppm: 3.66 (s, 3H), 2.91 (t, J = 7.5 Hz, 2H), 1.62 (m, 2H), 1.27 (m, 10H), 0.86 (m, 3H). *Mixture of linear and branched products.



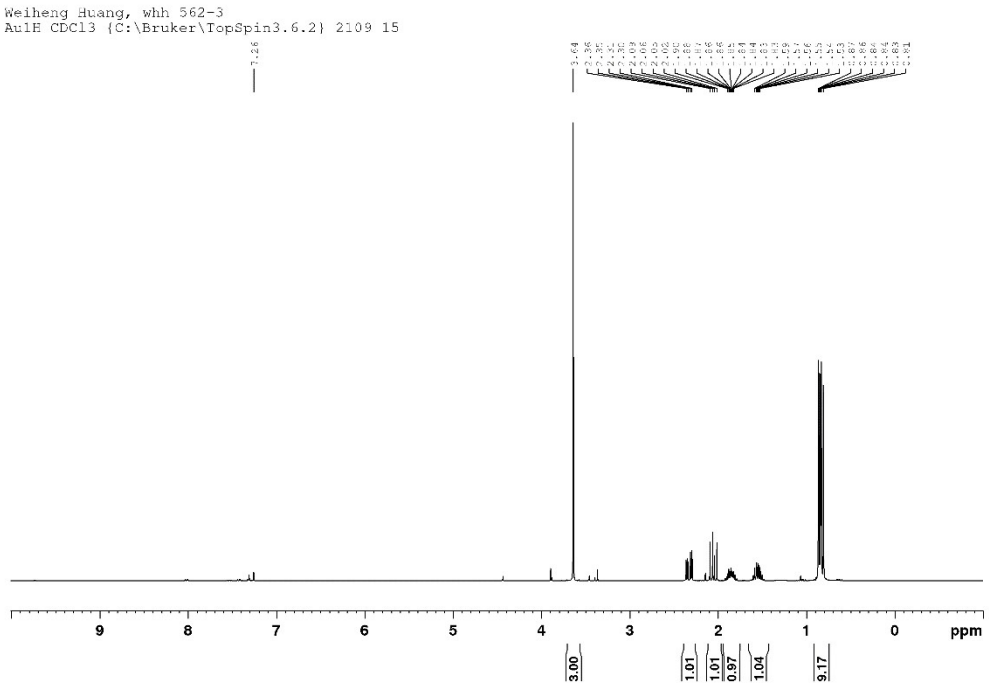
^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 173.50, 177.02, 174.42, 51.50, 51.34, 47.40, 39.56, 34.21, 33.93, 31.90, 31.79, 29.31, 29.25, 29.21, 27.92, 27.22, 25.57, 25.06, 22.73, 22.68, 22.58, 17.15, 14.16, 14.13, 14.08, 11.94.



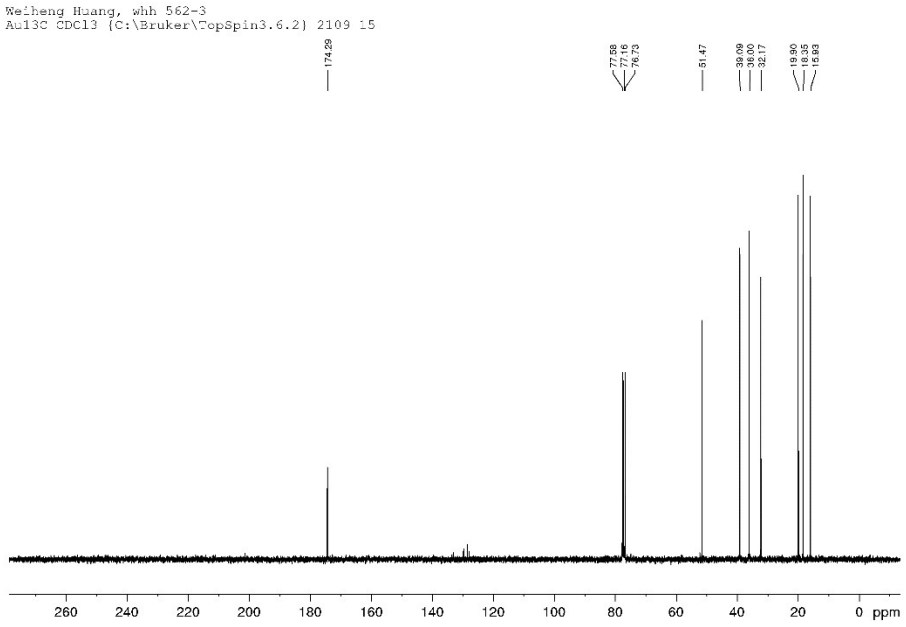
Methyl 3,4-dimethylpentanoate (**2h**)



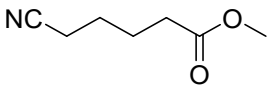
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 3.64 (s, 3H), 2.36 (dd, *J* = 14.6, 5.2 Hz, 1H), 2.03 (m, 1H), 1.83 (m, 1H), 1.66 (m, 1H), 0.83 (m, 9H).



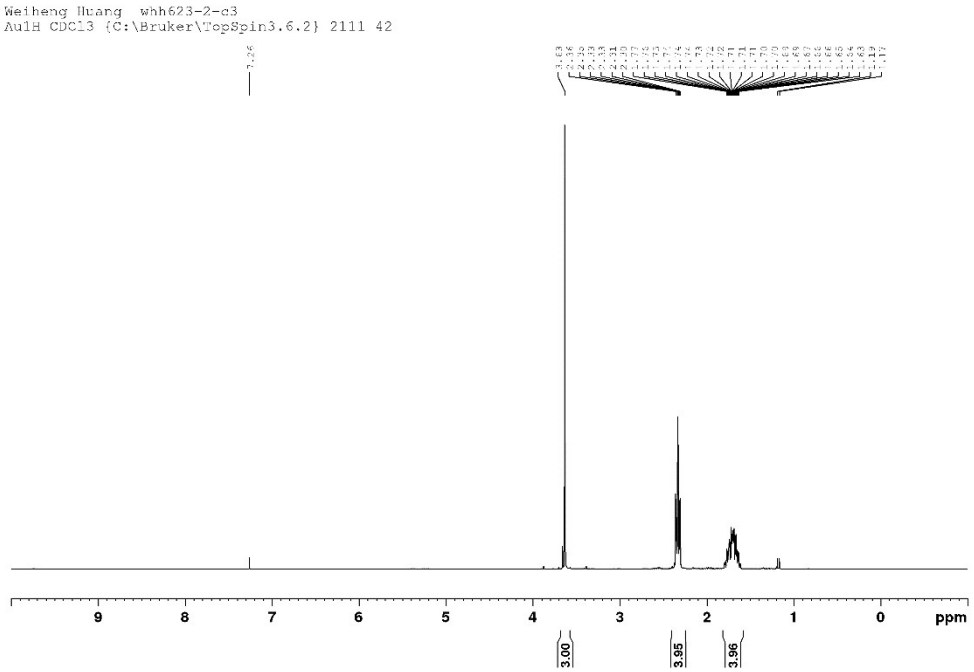
^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 174.29, 51.47, 39.09, 36.00, 32.17, 19.90, 18.35, 15.93.



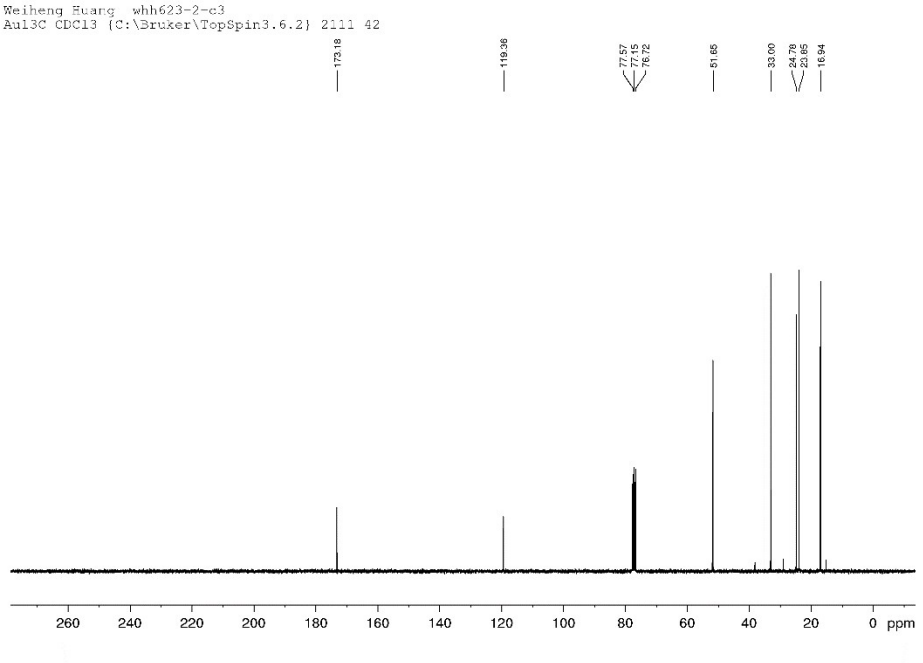
Methyl 5-cyanopentanoate (**2i**)



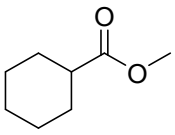
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 3.63 (s, 3H), 2.35 (td, J = 6.9, 2.3 Hz, 4H), 1.69 (m, 4H).



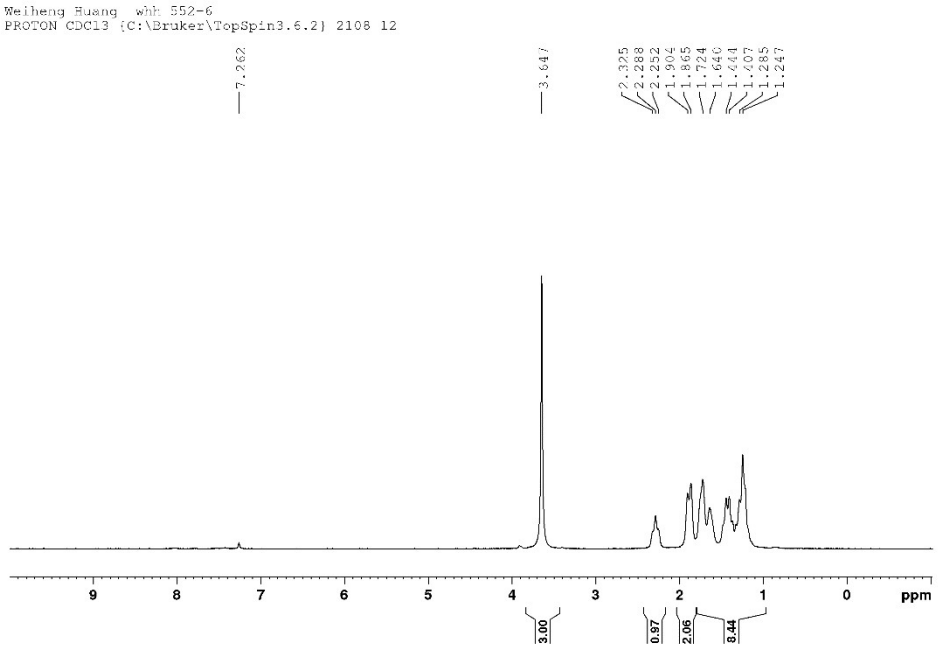
^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 173.18, 119.36, 51.65, 33.00, 24.78, 23.85, 16.94.



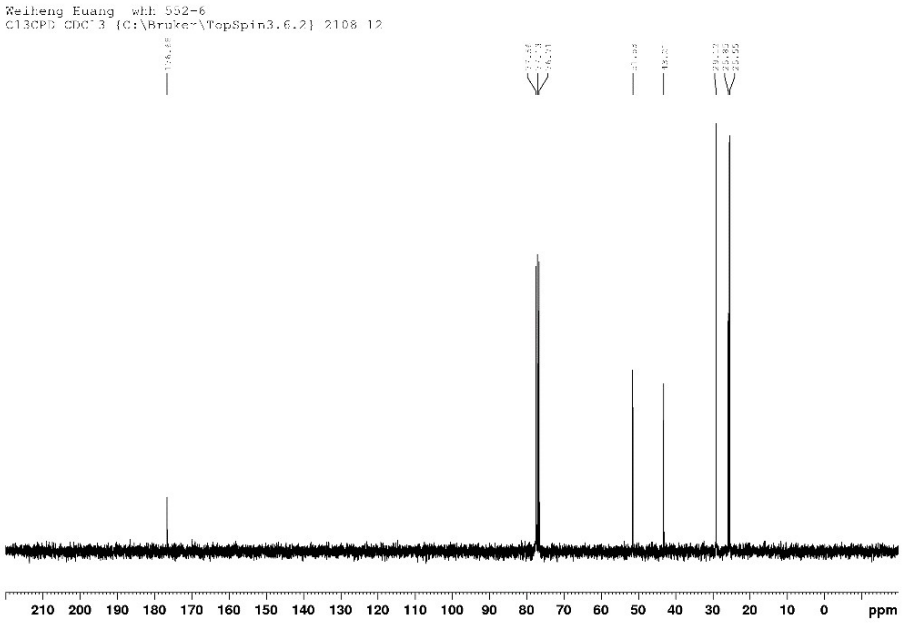
Methyl cyclohexanecarboxylate (**2j**)



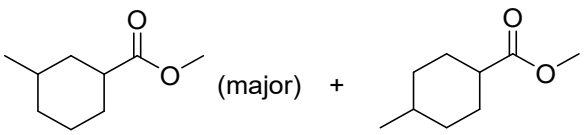
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 3.65 (s, 3H), 2.33 (s, 1H), 1.90-1.24 (m, 10H).



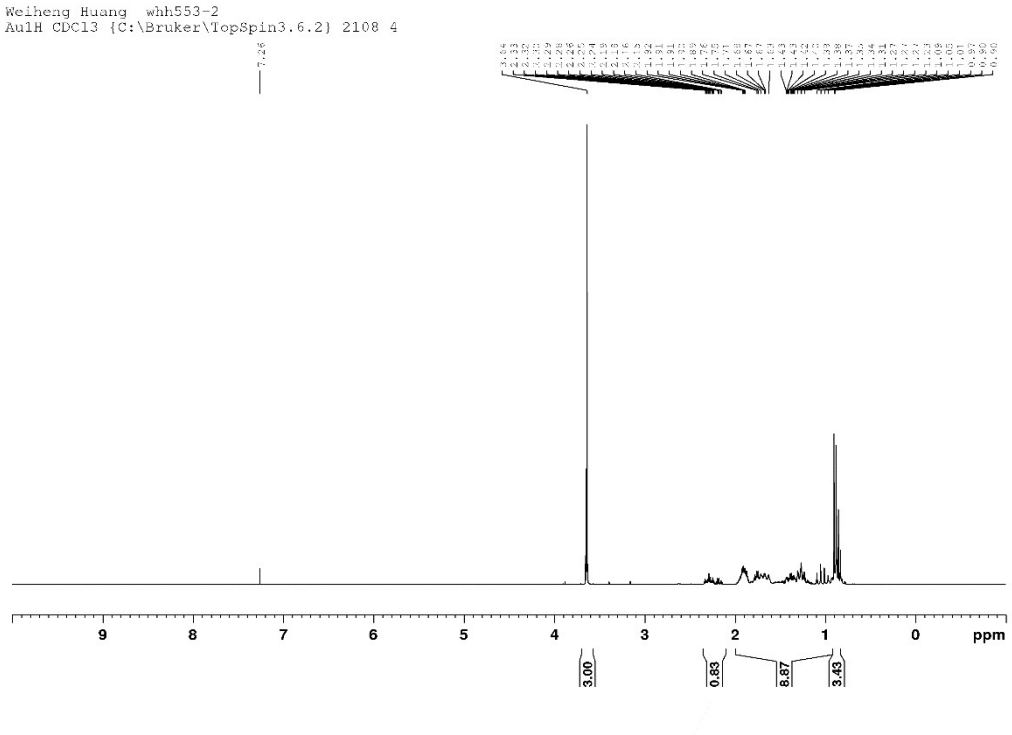
^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 176.68, 51.53, 43.22, 29.12, 25.85, 25.55.



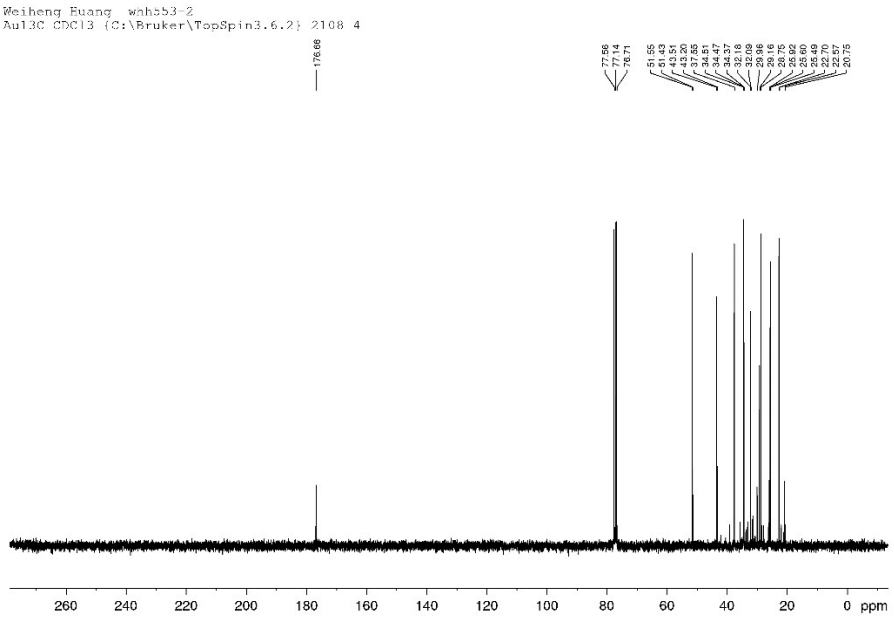
Methyl 3-methylcyclohexane-1-carboxylate (**2k**) & methyl 4-methylcyclohexane-1-carboxylate (**2k'**)



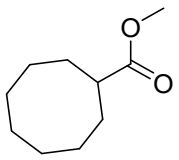
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 3.69 (s, 3H), 2.33-2.15 (m, 1H), 1.92-1.23 (m, 9H), 0.88 (m, 3H).



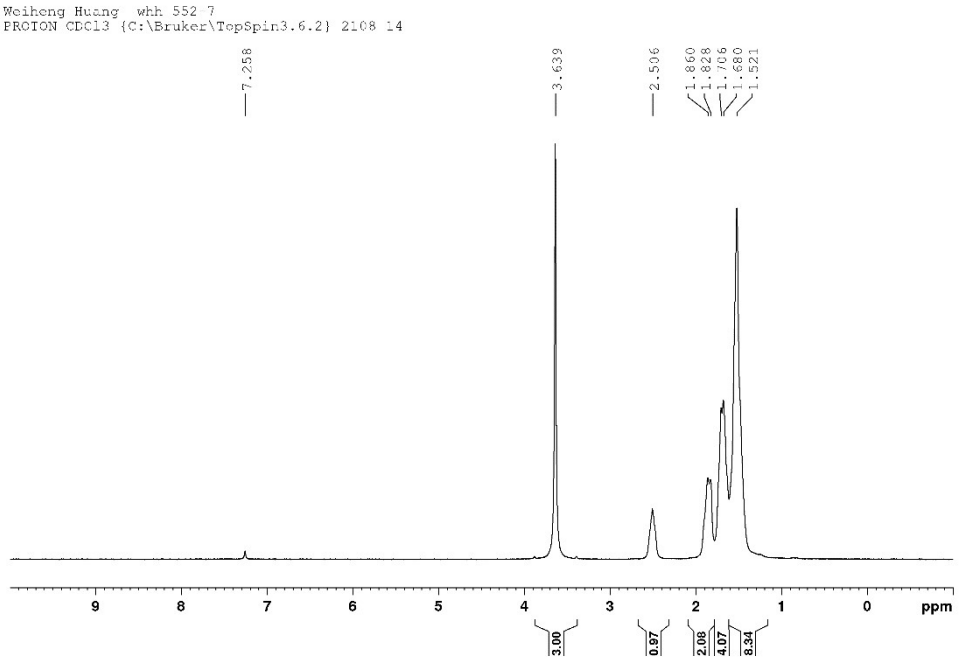
(**2k**) ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 176.66, 51.55, 43.51, 37.55, 34.46, 32.18, 28.74, 25.60, 22.70.



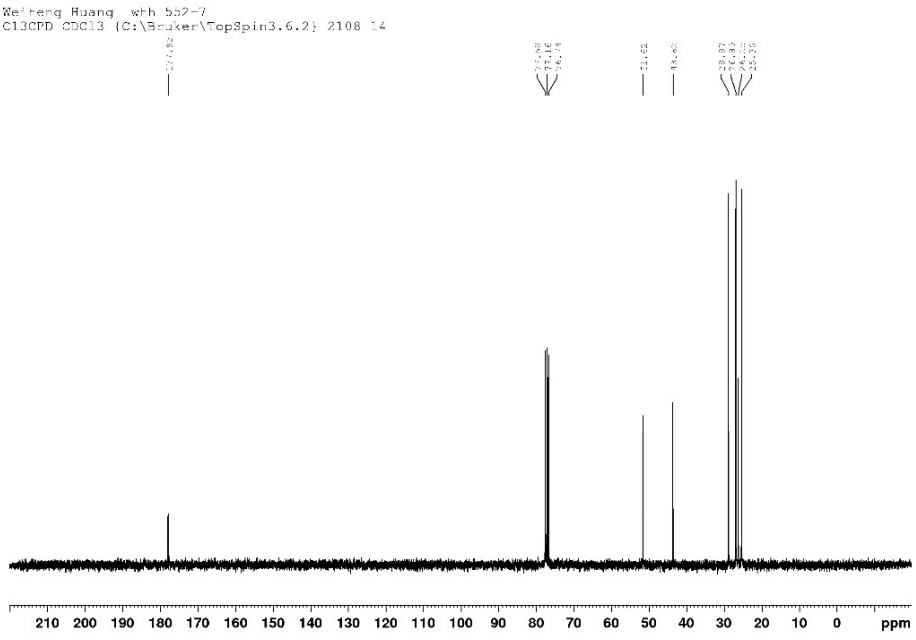
Methyl cyclooctanecarboxylate (**2l**)



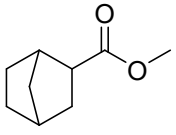
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 3.64 (s, 3H), 2.51 (s, 1H), 1.86-1.52 (m, 14H).



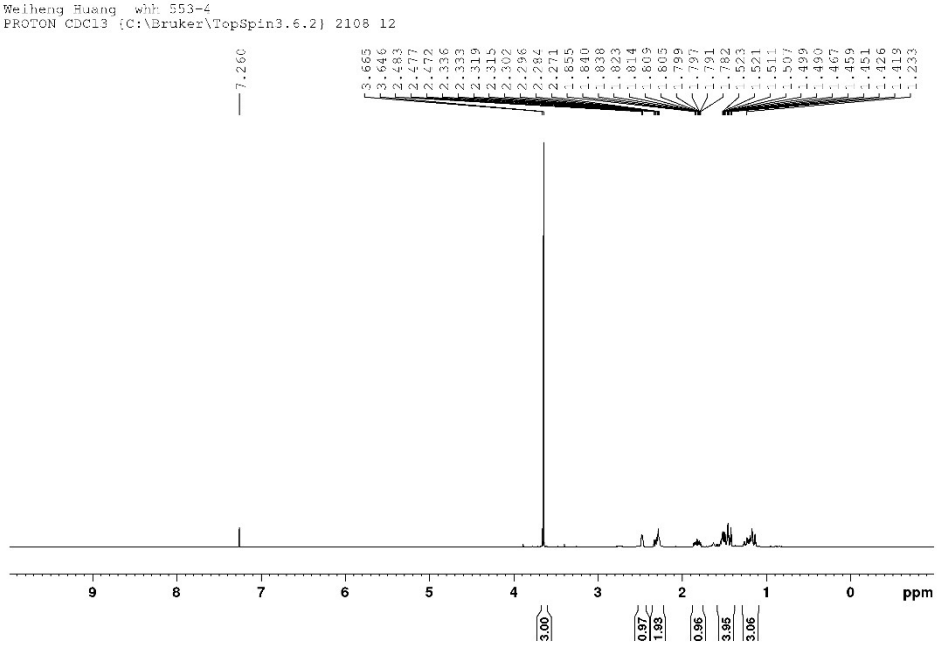
^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 177.92, 51.62, 43.62, 28.87, 26.89, 26.25, 25.36.



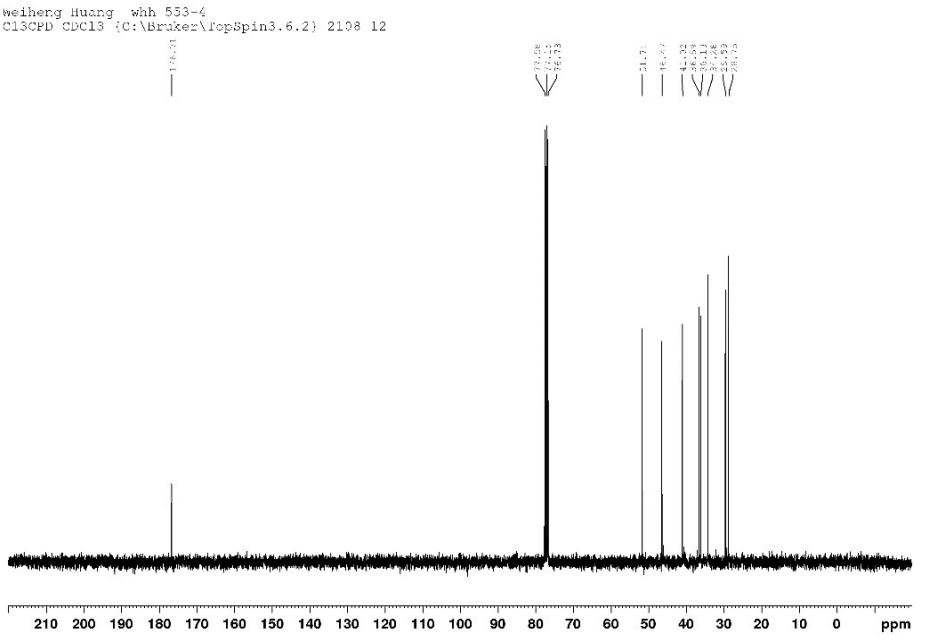
Methyl bicyclo[2.2.1]heptane-2-carboxylate (**2m**)



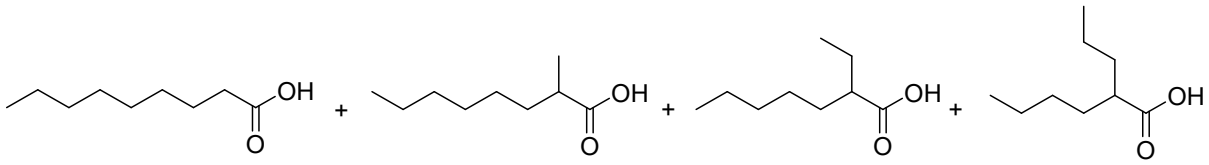
^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 3.64 (s, 3H), 2.48 (m, 1H), 2.32 (m, 2H), 1.81(m, 1H), 1.52-1.40 (m, 4H), 1.28-1.17 (m, 3H).



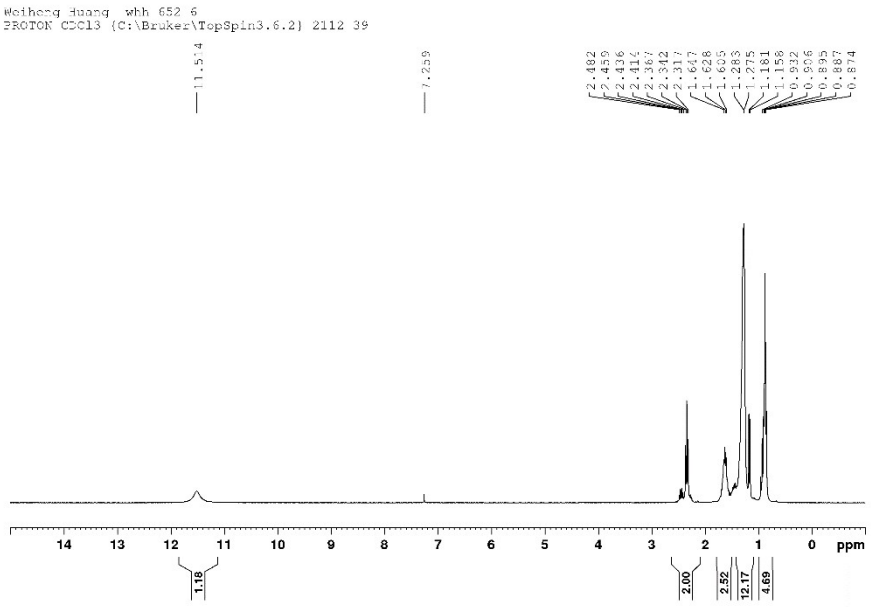
^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 176.59, 51.60, 46.36, 40.90, 36.47, 36.02, 34.16, 29.47, 28.63.



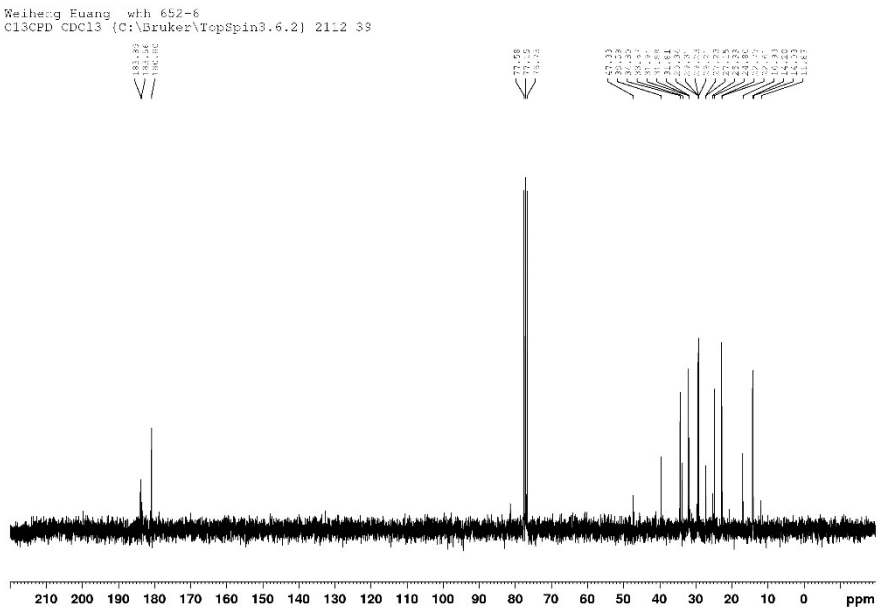
Nonanoic acid and isomerization mixture



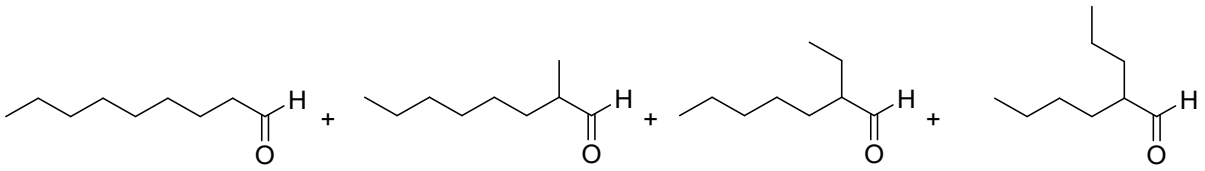
(Nonanoic acid) ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 11.51 (br. s, 1H), 2.34 (t, J = 7.5 Hz, 2H), 1.63 (m, 2H), 1.30 (m, 10H), 0.87 (m, 3H).



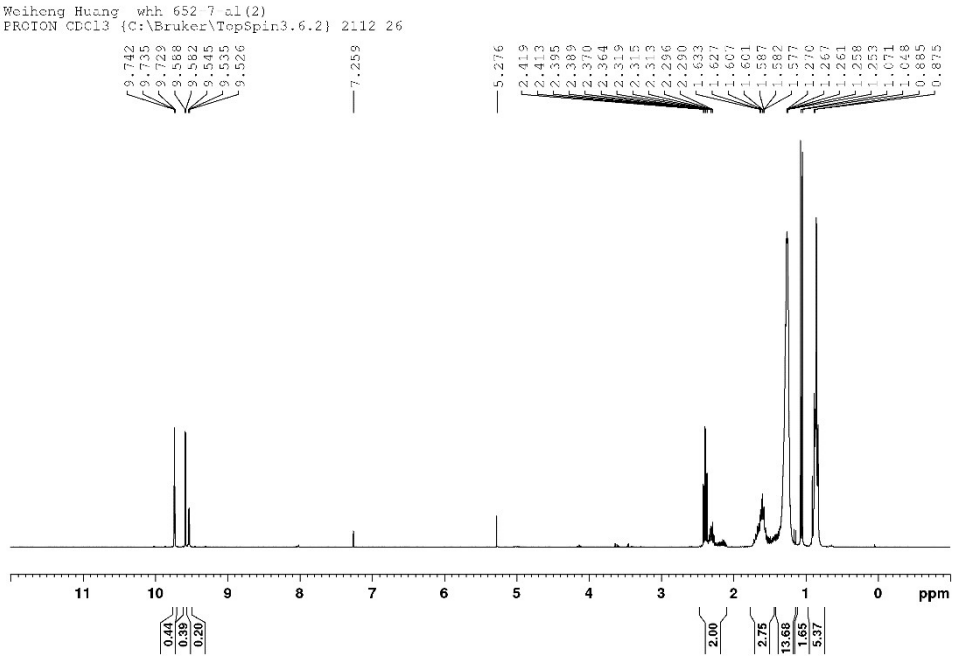
(Nonanoic acid) ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 180.80, 34.28, 31.94, 29.34, 29.23, 29.20, 24.80, 22.77, 14.20.



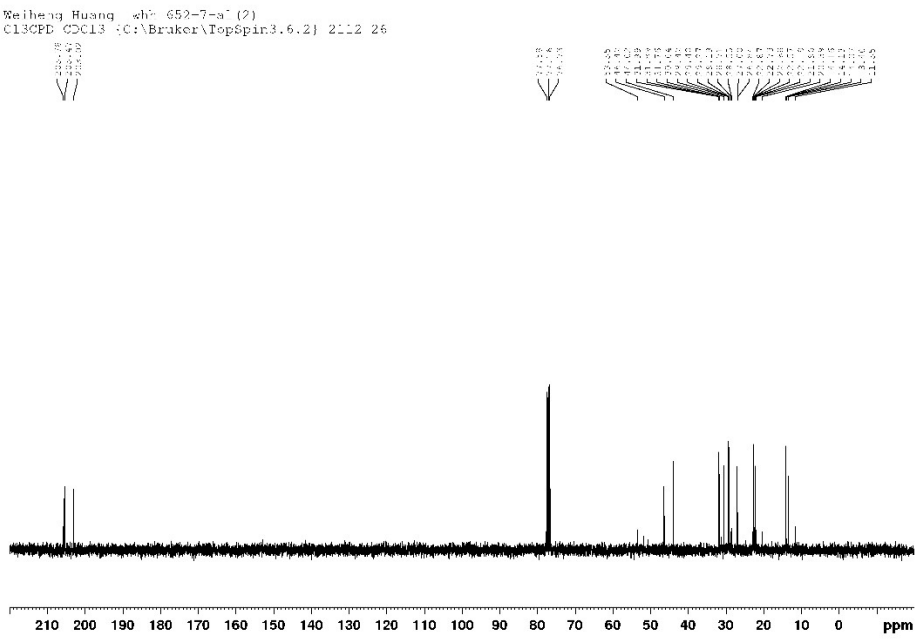
Nonanal, 2-methyloctanal, 2-ethylheptanal and 2-propylhexanal



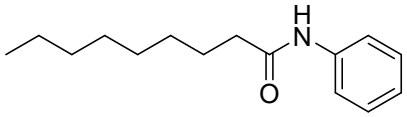
^{1}H NMR shows it is the linear and branched mixture.



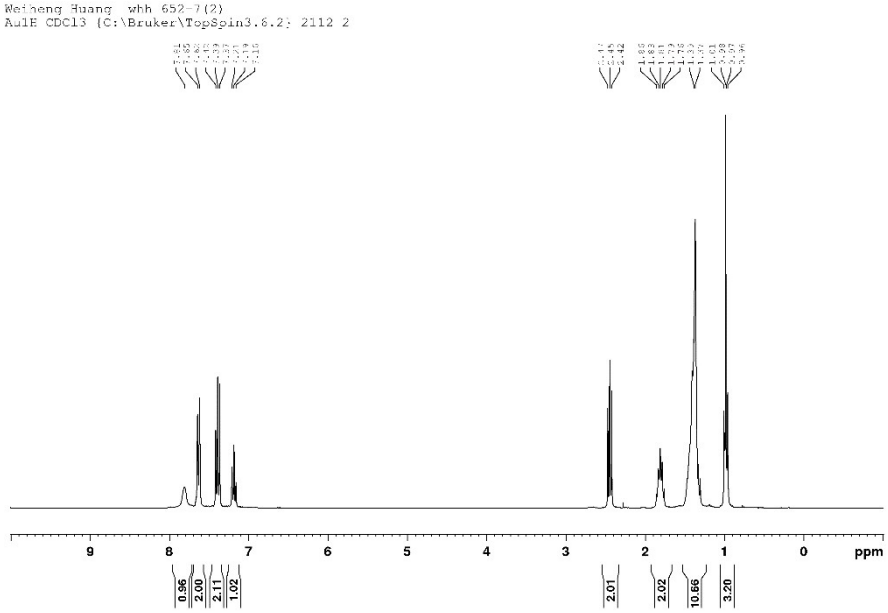
^{13}C NMR shows it is the linear and branched mixture.



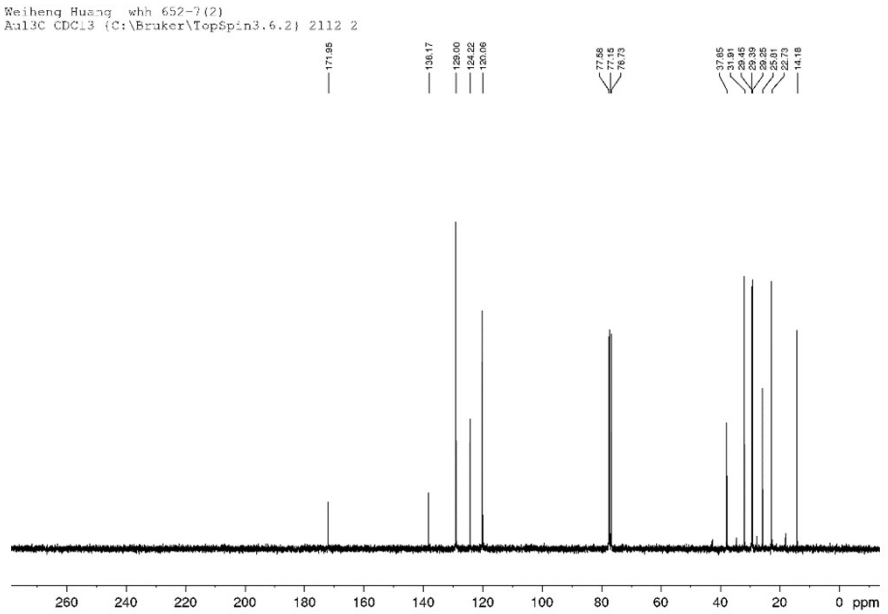
N-phenylnonanamide



^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm: 7.81 (br. s, 1H), 7.65 (d, J = 7.8 Hz, 2H), 7.39 (t, J = 7.8 Hz, 2H), 7.19 (t, J = 7.4 Hz, 1H), 2.45 (t, J = 7.6 Hz, 2H), 1.81 (m, 2H), 1.38 (m 10H), 0.97 (t, J = 6.8 Hz, 3H).



^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 171.95, 138.17, 129.00, 124.22, 120.06, 37.85, 31.91, 29.45, 29.39, 29.25, 25.81, 22.73, 14.18.



7. Crystal from $Co_2(CO)_8$ and Ph_2POH

X-ray crystal structure analysis of **AX2380**:

Data were collected on a Bruker Kappa APEX II Duo diffractometer. The structure was solved by direct methods (SHELXS-97: Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112.) and refined by full-matrix least-squares procedures on F^2 (SHELXL-2018: Sheldrick, G. M. *Acta Cryst.* **2015**, *C71*, 3.). XP (Bruker AXS) was used for graphical representations.

Contributions of disordered solvent were removed from the diffraction data using the SQUEEZE procedure in PLATON (Spek, A. L. *Acta Cryst.* **2009**, *D65*, 148).

Table S1. Crystallographic Details

chemical formula	$C_{27}H_{20}CoO_5P_2$
formula weight	545.30
crystal system	orthorhombic
unit cell dimensions	
a [Å]	41.7016(13)
b [Å]	15.1215(5)
c [Å]	19.8592(5)
a [deg]	90
b [deg]	90
g [deg]	90
V [Å^3]	12523.0(7)
T [K]	150(2)
space group	*Fdd*2
Z	16
m [mm^{-1}]	5.509
density [g/cm^3]	1.157
no. of reflections measured	25253
no. of independent reflections	4985 (R_{int} = 0.0455)
no. of observed reflections ($I > 2\sigma(I)$)	4453
no. of parameters	373
R_1 (I>2s(I))	0.0502
wR_2 (all data)	0.1317
Goodness of fit on F^2	1.018
largest diff. peak and hole [e/Å^3]	1.371 and -0.204

CCDC 2236654 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

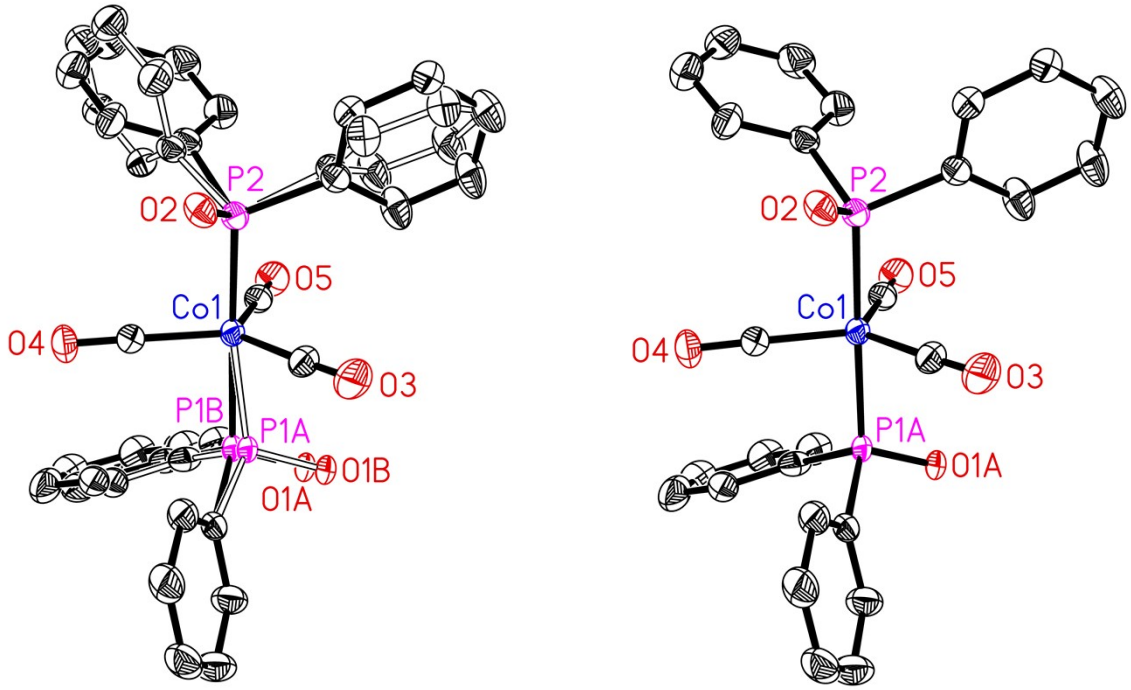


Figure S1. ORTEP representation of **AX2380**. Displacement ellipsoids correspond to 30% probability. Hydrogen atoms are omitted for clarity. The complex molecule is strongly disordered.

Left: The lower occupied parts of the disorder are shown with unfilled bonds.

Right: Disordered parts of the complex is shown in only one orientation.

The presence of hydrogen atoms at O1A/O1B and/or O2 cannot be determined with certainty. Therefore, no hydrogen at these oxygen atoms were included.

8. ^{1}H NMR spectra of Ph_2POD and Ph_2POH with $Co_2(CO)_8$

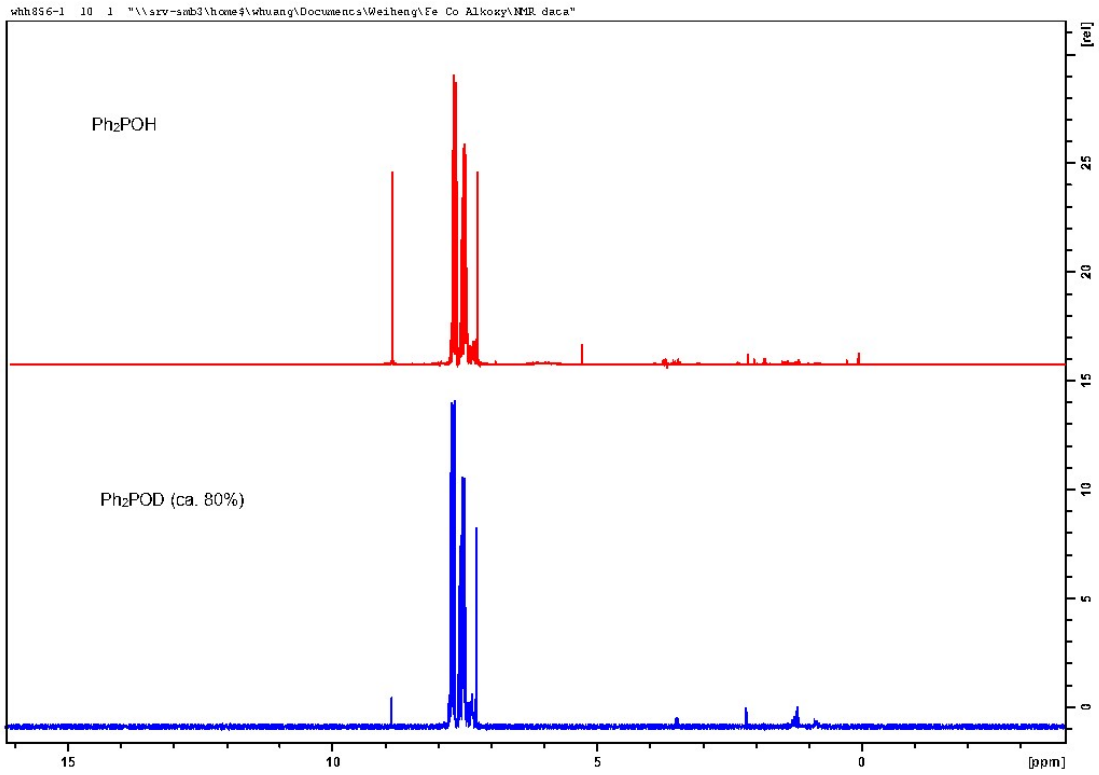


Figure S2. ^{1}H NMR spectra of Ph_2POH and Ph_2POD.

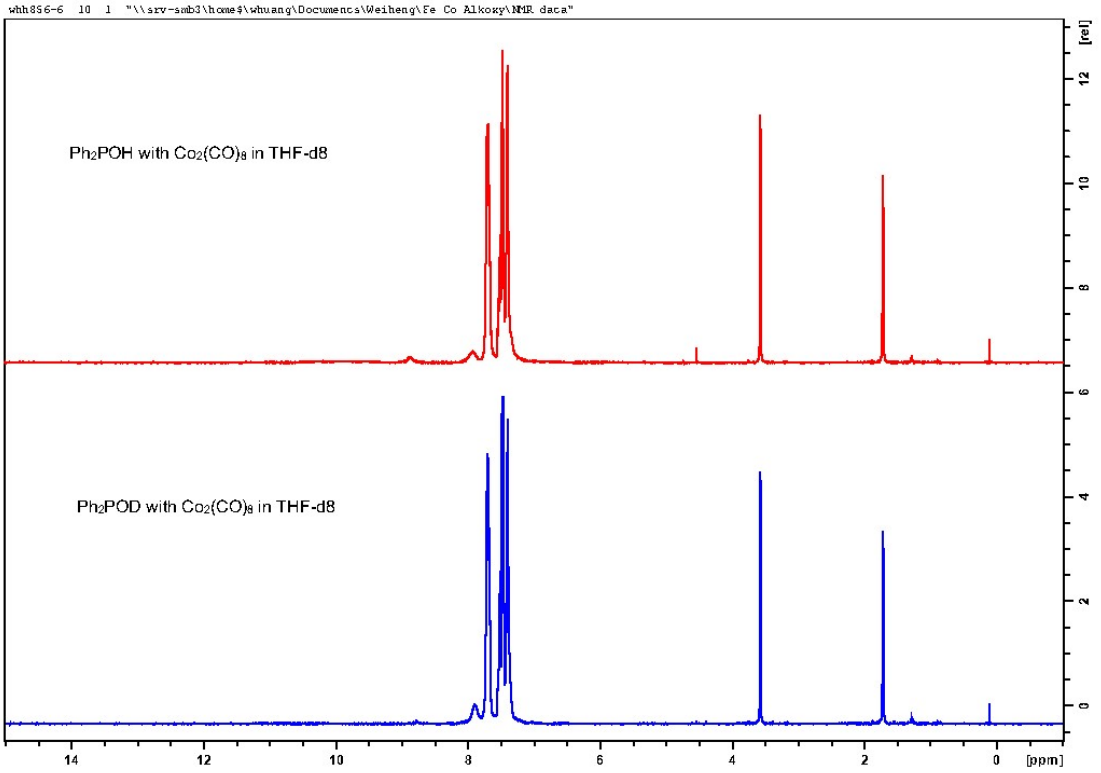


Figure S3. ^{1}H NMR spectra of Ph_2POH and Ph_2POD with $Co_2(CO)_8$ in THF-*d*8.

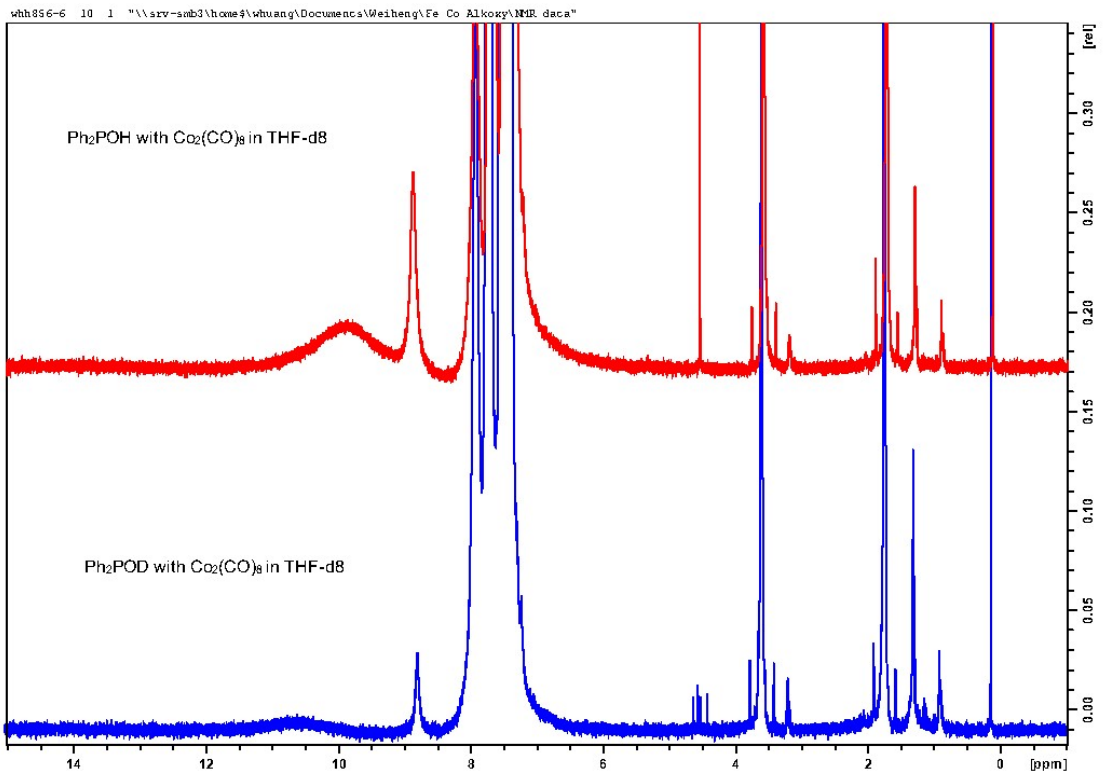


Figure S4. ^{1}H NMR spectra of Ph_2POH and Ph_2POD with $Co_2(CO)_8$ in THF-*d*8 (zooming).

Reference

1 Purification of Laboratory Chemical (Eds: Perrin, D. D.; Armarego, W. L. F.-). Pergamon Press, Oxford, 1988 **3**.
2 R. Shen, B. Luo, J. Yang, L. Zhang, L. B. Han, *Chem. Comm.* 2016, **52**, 6451-6454.