Supporting Information

Synthesis of Aromatic Esters via Pd-catalyzed Decarboxylative Coupling of Potassium Oxalate Monoesters with Aryl Bromides and Chlorides

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1. General Information……………………………………………….................................

a. Materials

All reactions were carried out in oven-dried Schlenk tubes under Argon atmosphere (purity ≥99.999%). The NMP solvent was bought from Alfa Aesar (Sealed under argon) without further purification. All aryl halides were purchased from Alfa Aesar or Acros and used directly. All phosphine ligands were bought from Sigma-Aldrich, Strem, or Alfa Aesar and sealed under Argon. All the other reagents and solvents were bought from Sinopharm Chemical Reagent Co. Ltd or Alfa Aesar and were purified when necessary.

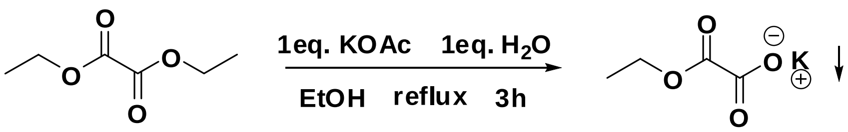
b. Methods

^{1}H-NMR, ^{13}C-NMR spectra were recorded on a Bruker Advance 400 spectrometer at ambient temperature in $CDCl_3$ unless otherwise noted. Data for ^{1}H-NMR are reported as follows: chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz). Data for ^{13}C-NMR are reported in terms of chemical shift (δ ppm). Gas chromatographic (GC) analysis was acquired on a Shimadzu GC-2014 Series GC System equipped with a flame-ionization detector. GC-MS analysis was performed on Thermo Scientific AS 3000 Series GC-MS System. MS analysis was performed on Finnigan LCQ advantage Max Series MS System. Elementary Analysis was carried out on Elementar Vario EL III elemental analyzer. Organic solutions were concentrated under reduced pressure on a Buchi rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

2. Experimental Section…………………………………………………………………

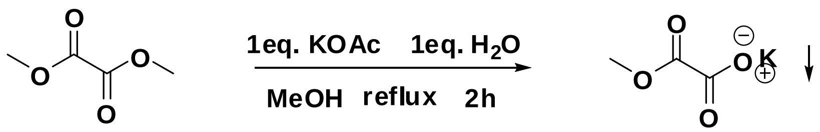
a. Synthesis of Potassium Oxalate monoesters: [1]

Synthesis of ethyl potassium oxalate: [2]



According to the literature procedure, a 100 ml flask was charged with diethyl oxalate (13.5ml, 0.1mol), potassium acetate (9.8g, 0.1mol), and ethanol (20ml) as solvent. Subsequently water (1.8ml, 0.1mol) was added via syringe. The mixture was stirred under reflux condition (90°C oil bath) for 3 h, and a lot of white crystal solid was obtained. The mixture was allowed to cool to room temperature and 20ml diethyl ether was added. The white crystal was filtrate, washed with ethanol and diethyl ether, and dried under vacuum at 30°C for 2 h. {Anal. Calcd for $C_4H_5O_4K$: C/H=9.53(w/w), Found: C/H=9.46(w/w)}

Synthesis of methyl potassium oxalate: [3]



According to the literature procedure, a 100 ml flask was charged with dimethyl oxalate (11.8g, 0.1mol), potassium acetate (9.8g, 0.1mol), and methanol (20ml) as solvent. Subsequently water (1.8ml, 0.1mol) was added via syringe. The mixture was stirred under reflux condition (90°C oil bath) for 2 h, and cooled to room temperature. After addition of 20ml diethyl ether, a lot of white crystal solid was obtained. The white crystal was filtrated, washed with methanol and diethyl ether, and dried under vacuum at 30°C for 2 h. {Anal. Calcd for $C_3H_3O_4K$: C/H=11.91(w/w), Found: C/H=11.88(w/w)}

b. Preparation of the catalyst:

Preparation of palladium (II) trifluoroacetate.
A 50 ml oven-dried flask was charged with $Pd(OAc)_2$ (0.3g, 1.33mmol) and 15ml trifluoroacetatic acid was added. The mixture was stirred in oil bath until $Pd(OAc)_2$ was dissolved. Trifluoroacetatic acid was removed via rotary vapor. Then another 7ml trifluoroacetatic acid was added and was evaporated again. The residue was dried under vacuum at 40°C for 1 h offering a brownish powder.

c. Optimization of the reaction conditions:

General Procedure:
A 10ml oven-dried Schlenk-tube was charged with Pd source (See STable 1), ligand (See STable 1), and ethyl potassium oxalate (0.75mmol). The tube was evacuated and backfilled with argon (this procedure was repeated three times). Bromobenzene (0.5mmol), NMP (1.0 ml) were added by syringe under a counter flow of argon at room temperature. The tube was then sealed and the mixture was allowed to stir under 1atm of argon (The tube was connected to the Schlenk line which was full with argon so that CO_2 can be released to air) at the appointed temperature (150±5°C) for 24 h. Upon completion of the reaction, the mixture was cooled to room temperature and diluted with ethyl acetate, and analyzed by gas chromatography.

STable 1

Various conditions towards the decarboxylative cross-coupling between phenyl halide and ethyl potassium oxalate [a]

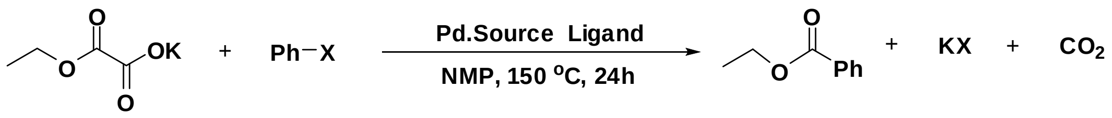


Table 1

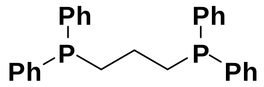
Entry	X	Pd Source	Ligand	Yield [%]
1	Br	$Pd(OAc)_2$	-----	<5
2	Br	$Pd(OAc)_2$	PPh_3	27
3	Br	$Pd(OAc)_2$	$P(o\text{-}Tol)_3$	51
4	Br	$Pd(OAc)_2$	$P(o\text{-}MeOPh)_3$	62
5	Br	$Pd(OAc)_2$	$P(Cy)_3$	9
6	Br	$Pd(OAc)_2$	dppf	23
7	Br	$Pd(OAc)_2$	dppp	81
8	Br	$Pd(OAc)_2$	dppe	68
9	Br	$Pd(OAc)_2$	dppm	21
10	Br	$Pd(OAc)_2$	S-BINAP	36
11	Br	$Pd(OAc)_2$	X-Phos	61
12	Br	$Pd(OAc)_2$	JohnPhos	56
13	Br	$PdCl_2$	dppp	80
14	Br	$Pd(TFA)_2$	dppp	**85**
15	Br	$Pd(acac)_2$	dppp	75
16[c]	Br	$Pd_2(dba)_3$	dppp	81
17	Br	$Pd(dppf)Cl_2$	dppp	79
18	Br	$Pd(PPh_3)_2Cl_2$	dppp	80
19	Br	$Pd(PPh_3)_4$	dppp	77
20	I	$Pd(TFA)_2$	dppp	83
21[b]	Br	$Pd(TFA)_2$	dppp	31
22	Cl	$Pd(TFA)_2$	dppp	<5

[a]Condition for this transformation: 0.5 mmol of aryl halide, 0.75 mmol of ethyl potassium oxalate, 1% mol of catalyst and 3% mol of ligand (If bidentate ligand 1.5%mol), 1ml of NMP, 150°C, 24h. GC yields were determined with the use of naphthalene as an internal standard. Yields were based on aryl halide. [b]Carried out at 140°C. [c]0.5% mmol of $Pd_2(dba)_3$ was used.

In table, acac = acetylacetonate. Cy = cyclohexyl. TFA = trifluoroacetate.

dba= dibenzylideneacetone, NMP = N-methyl-2-pyrrolidone.

Structures of the ligands mentioned in Table 1



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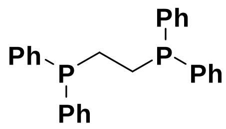
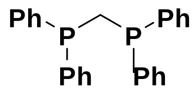
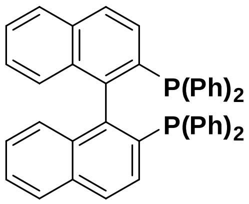


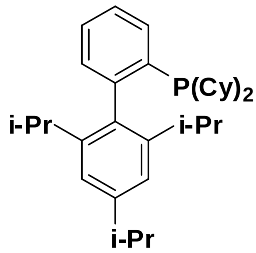
DPPE



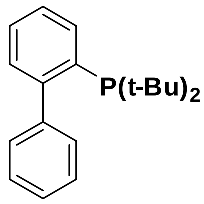
DPPM



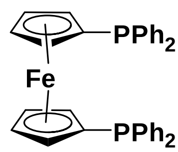
S-BINAP



X-Phos



John-Phos



DPPF

d. General Procedure for the synthesis of aromatic esters from aryl bromides:

General procedure **A**:

Palladium(II) trifluoroacetate (0.01 mmol), 1,3-bis(diphenylphosphino)-propane (0.015 mmol), appointed amount of ethyl (or methyl) potassium oxalate (1.1-1.5 mmol, see Page S8-16 for detailed quantities) and the aryl bromide (1.00 mmol) (if solid) were placed in an oven-dried 20 ml Schlenk-tube. The reaction vessel was evacuated and filled with argon for three times. Then aryl bromide (1.00 mmol) (if liquid) and NMP (2 ml) were added with a syringe under a counter flow of argon. The vessel was sealed, connected to the Schlenk line which was full with argon and stirred at 150±5°C for the appointed time. Upon completion of the reaction, the mixture was cooled to room temperature and diluted with diethyl ether (20ml). It was then filtered through a short silica column to remove the deposition. The organic layers were washed with water (20ml×3), and then with brine, dried over Na_2SO_4, and filtered. The solvents were removed. Purification of the residue by column chromatography (silica gel, ethyl acetate/hexane gradient) yielded the corresponding aryl ester.

e. Optimization of the reaction conditions and general procedures for the synthesis of aromatic esters from aryl chlorides[a]

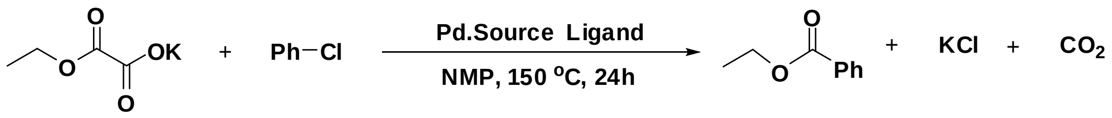
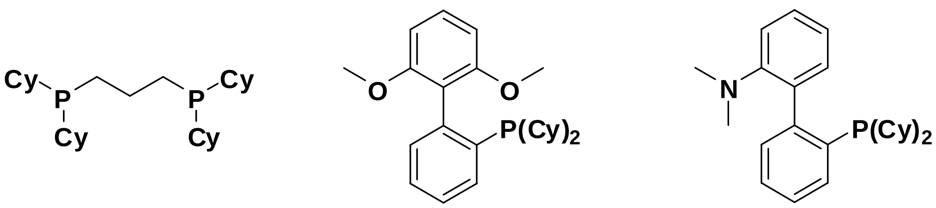


Table 2

Entry	Pd.Source	Ligand	Yield(%)[a]
1	$Pd(TFA)_2$ (1%)	dppp (1.5%)	N.R.
2	$Pd(TFA)_2$ (1%)	$P(o\text{-}MeOPh)_3$ (1.5%)	N.R.
3	$Pd(TFA)_2$ (1%)	John-Phos (3%)	N.R.
4	$Pd(TFA)_2$ (1%)	S-Phos (3%)	trace
5	$Pd(TFA)_2$ (1%)	Dave-Phos (3%)	trace
6	$Pd(TFA)_2$ (1%)	X-Phos (3%)	27%
7	$Pd(TFA)_2$ (2%)	X-Phos (6%)	34%
8	$Pd(TFA)_2$ (5%)	X-Phos (15%)	39%
9	$Pd(TFA)_2$ (1%)	dCypp (1.5%)	42%
10	$Pd(TFA)_2$ (1%)	dCypp (2%)	51%
11	$Pd(TFA)_2$ (3%)	dCypp (6%)	71%

[a]Condition for this transformation: 0.5 mmol of aryl chloride, 0.75 mmol of ethyl potassium oxalate, appointed amount of catalysts and the ligands, 1ml of NMP, 150 °C, 24h. GC yields were determined with the use of naphthalene as an internal standard. Yields were based on aryl chloride.

Structures of the ligands mentioned in Table 2



dCypp S-Phos Dave-Phos

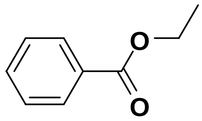
General Procedure for the synthesis of aromatic esters from aryl chlorides:

General procedure **B:**

Palladium(II) trifluoroacetate (0.03 mmol), appointed amount of ethyl potassium oxalate and the aryl chloride (1.00 mmol)(if solid) were placed in an oven-dried 20 ml Schlenk-tube. The reaction vessel was evacuated and filled with argon for three times. Aryl chloride (1.00 mmol) (if liquid), 1,3-bis(dicyclohexylphosphino)propane (0.06 mmol, 108μl*) (as a solution, 250mg in 2ml NMP) and NMP (2 mL) were added with a syringe under a counter flow of argon, the vessel was sealed, connected to the Schlenk line which was full with argon and stirred at 150±5°C for the appointed time. Upon completion of the reaction, the mixture was cooled to room temperature, diluted with diethyl ether (20ml) and filtered through a short silica column to remove the deposition. The organic layers were washed with water (20ml×3) and then with brine, dried over Na_2SO_4, and filtered. The solvents were removed. Purification of the residue by column chromatography (silica gel, ethyl acetate/hexane gradient) yielded the corresponding aryl ester.

* 1, 3-bis(dicyclohexylphosphino)propane was bought from Sigma-Aldrich as a colorless oil (250mg Package), and 2ml NMP was directly added to the bottle to dissolve it before use.

3. Characterization of the Products……………………………………………….

1. 

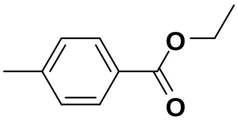
benzoic acid ethyl ester

Prepared according to General Procedure A**:**

Bromobenzene (1.0mmol) was allowed to react with potassium ethyl oxalate (1.5mmol) for 24 h. The product was isolated as a colorless liquid (125mg, 83% yield).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.40 (t, 3H, ***J***=7.2Hz), 4.38 (q, 2H, ***J***=7.1Hz), 7.41-7.46 (m, 2H), 7.52-7.57 (m, 1H), 8.03-8.06 (m, 2H),

^{13}C-NMR (100MHz, $CDCl_3$, δ ppm): 14.3, 60.9, 128.3, 129.5, 130.6, 132.8, 166.6.

2. 

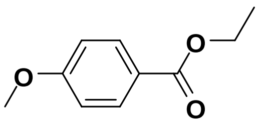
4-methylbenzoic acid ethyl ester

Prepared according to General Procedure A:

4-bromotoluene (1.0mmol) was allowed to react with potassium ethyl oxalate (1.5mmol) for 24 h. The product was isolated as a colorless liquid (157mg, 96% yield).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.38 (t, 3H, ***J***=7.2Hz), 2.39 (s, 3H), 4.36 (q, 2H, ***J***=7.1Hz), 7.22 (d, 2H, ***J***=8.4Hz), 7.93 (d, 2H, ***J***=8.4Hz)

^{13}C-NMR (100MHz, $CDCl_3$, δ ppm): 14.4, 21.7, 60.8, 127.9, 129.1, 129.6, 143.4, 166.7.

3. 

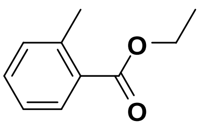
4-methoxybenzoic acid ethyl ester

Prepared according to General Procedure A**:**

4-bromoanisole (1.0mmol) was allowed to react with potassium ethyl oxalate (1.5mmol) for 24 h. The product was isolated as a colorless liquid (171mg, 95% yield).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.37 (t, 3H, ***J***=7.2Hz), 3.83 (s, 3H), 4.34 (q, 2H, ***J***=7.1Hz), 6.90 (d, 2H, ***J***=8.8Hz), 7.99 (d, 2H, ***J***=8.8Hz)

^{13}C-NMR (100MHz, $CDCl_3$, δ ppm): 14.4, 55.4, 60.6, 113.6, 123.0, 131.5, 163.3, 166.4.

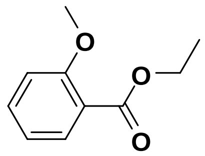
4. 

2-methylbenzoic acid ethyl ester

Prepared according to General Procedure A**:**

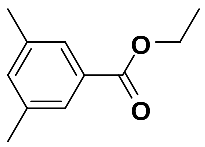
2-bromotoluene (1.0mmol) was allowed to react with potassium ethyl oxalate (1.5mmol) for 24 h.

The product was isolated as a colorless liquid (149mg, 91% yield).
^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.38 (t, 3H, ***J***=7.0Hz), 2.59 (s, 3H), 4.35 (q, 2H, ***J***=7.2Hz), 7.22 (t, 2H, ***J***=7.6Hz), 7.37 (t, 1H, ***J***=7.6Hz), 7.90 (d, 1H, ***J***=8.0Hz)
^{13}C-NMR (100MHz, $CDCl_3$, δ ppm): 14.4, 21.7, 60.7, 125.7, 130.0, 130.5, 131.7, 131.8, 140.0, 167.7.

5. 

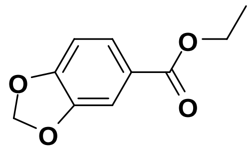
2-methoxybenzoic acid ethyl ester

Prepared according to General Procedure A**:**
2-bromoanisole (1.0mmol) was allowed to react with potassium ethyl oxalate (1.5mmol) for 24 h. The product was isolated as a colorless liquid (142mg, 79% yield).
^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.38 (t, 3H, ***J***=7.0Hz), 3.90 (s, 3H), 4.36 (q, 2H, ***J***=7.2Hz), 6.95-6.99 (m, 2H), 7.43-7.48 (m, 1H), 7.77-7.79 (m, 1H).
^{13}C-NMR (100MHz, $CDCl_3$, δ ppm): 14.3, 56.0, 60.8, 112.1, 120.1, 120.6, 131.5, 133.3, 159.2, 166.2.

6. 

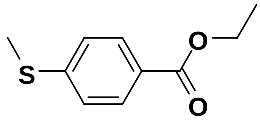
3, 5-dimethyl-benzoic acid ethyl ester

Prepared according to General Procedure A**:**
5-bromo-***m***-xylene (1.0mmol) was allowed to react with potassium ethyl oxalate (1.5mmol) for 24 h. The product was isolated as a yellow liquid (160mg, 90% yield).
^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.38 (t, 3H, ***J***=7.0Hz), 2.34 (s, 6H), 4.35 (q, 2H, ***J***=7.1Hz), 7.15 (d, 1H, ***J***=0.8Hz), 7.65-7.66 (m, 2H).
^{13}C-NMR (100MHz, $CDCl_3$, δ ppm): 14.4, 21.1, 60.8, 127.3, 130.4, 134.4, 137.9, 166.9.

7. 

Benzo[1,3]dioxole-5-carboxylic acid ethyl ester

Prepared according to General Procedure A**:**
4-Bromo-1,2-(methylenedioxy)benzene (1.0mmol) was allowed to react with potassium ethyl oxalate (1.5mmol) for 24 h.. The product was isolated as a yellow liquid (173mg, 89% yield). Spectral data matched literature description.[4]
^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.37 (t, 3H, ***J***=7.0Hz), 4.33 (q, 2H, ***J***=7.2Hz), 6.02 (s, 2H), 6.82 (d, 1H, ***J***=8.4Hz), 7.46 (d, 1H, ***J***=1.6Hz), 7.65 (dd, 1H, J_1=1.6Hz, J_2=8.0Hz).
^{13}C-NMR (100MHz, $CDCl_3$, δ ppm): 14.4, 60.9, 101.8, 107.9, 109.5, 124.6, 125.3, 147.7, 151.5, 166.0.

8. 

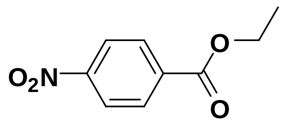
4-methylthiobenzoic acid ethyl ester

Prepared according to General Procedure A:

4-bromothioanisole (1.0mmol) was allowed to react with potassium ethyl oxalate (1.5mmol) for 24 h. The product was isolated as a yellow acicular solid (147mg, 75% yield). Spectral data matched literature description.[11]

^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.38 (t, 3H, ***J***=7.2Hz), 2.51 (s, 3H), 4.35 (q, 2H, ***J***=7.1Hz), 7.24 (d, 2H, ***J***=8.40Hz), 7.93 (d, 2H, ***J***=8.8Hz).

^{13}C-NMR (100MHz, $CDCl_3$, δ ppm): 14.4, 14.9, 60.9, 125.0, 126.7, 129.9, 145.3, 166.6.

9. 

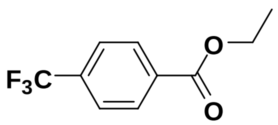
4-nitrobenzoic acid ethyl ester

Prepared according to General Procedure A**:**

4-bromonitrobenzene (1.0mmol) was allowed to react with potassium ethyl oxalate (1.1mmol) for 16 h. The product was isolated as a yellow solid (159mg, 82% yield).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.44 (t, 3H, ***J***=7.0Hz), 4.44 (q, 2H, ***J***=7.2), 8.20-8.23 (m, 2H), 8.27-8.30 (m, 2H).

^{13}C-NMR (100MHz, $CDCl_3$, δ ppm): 14.3, 62.0, 123.5, 130.7, 135.9, 150.6, 164.7.

10. 

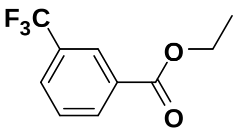
4-(trifluoromethyl)benzoic acid ethyl ester

Prepared according to General Procedure A**:**

4-bromo(trifluoromethyl)benzene (1.0mmol) was allowed to react with potassium ethyl oxalate (1.1mmol) for 16 h.. The product was isolated as a colorless liquid (175mg, 80% yield). Spectral data matched literature description.[5]

^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.42 (t, 3H, ***J***=7.2Hz), 4.41 (q, 2H, ***J***=7.1Hz), 7.69 (d, 2H, ***J***=8.4Hz), 8.15 (dd, 2H, J_1=0.4Hz, J_2=8.8Hz).

^{13}C-NMR (100MHz, $CDCl_3$, δ ppm): 14.3, 61.6, 123.8 (q, ***J***=271Hz), 125.4 (q, ***J***=3.5Hz), 130.0, 133.8, 134.4 (q, ***J***=32.4Hz), 165.4.

11. 

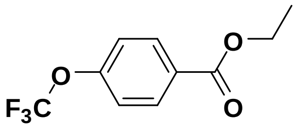
3-(trifluoromethyl)benzoic acid ethyl ester

Prepared according to General Procedure A:

3-bromo(trifluoromethyl)benzene (1.0mmol) was allowed to react with potassium ethyl oxalate (1.1mmol) for 16 h.. The product was isolated as a colorless liquid (205mg, 94% yield). Spectral data matched literature description.[6]

^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.42 (t, 3H, ***J***=7.2Hz), 4.42 (q, 2H, ***J***=7.2Hz), 7.58 (t, 1H, ***J***=7.8Hz), 7.80 (d, 1H, ***J***=7.6Hz), 8.23 (d, 1H, ***J***=7.6Hz), 8.31 (s, 1H).

^{13}C-NMR (100MHz, $CDCl_3$, δ ppm): 14.3, 61.6, 123.8 (q, ***J***=271Hz), 126.5 (q, ***J***=3.8Hz), 129.1, 129.4 (q, ***J***=3.8Hz), 131.1 (q, ***J***=32.8Hz), 131.5, 132.8, 165.3.

12. 

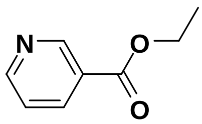
4-trifluoromethoxy-benzoic acid ethyl ester

Prepared according to General Procedure A**:**

4-bromo(trifluoromethoxyl)benzene (1.0mmol) was allowed to react with potassium ethyl oxalate (1.1mmol) for 16 h.. The product was isolated as a colorless liquid (187mg, 80% yield).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.40 (t, 3H, ***J***=7.2Hz), 4.39 (q, 2H, ***J***=7.1Hz), 7.26 (d, 2H, ***J***=8.8Hz), 8.09 (d, 2H, ***J***=8.4Hz).

^{13}C-NMR (100MHz, $CDCl_3$, δ ppm): 14.3, 61.4, 120.4 (q, ***J***=257), 120.3, 129.0, 131.6, 152.6, 165.5.

13. 

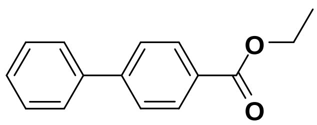
3-pyridinecarboxylic acid ethyl ester

Prepared according to General Procedure A**:**

3-bromopyridine (1.0mmol) was allowed to react with potassium ethyl oxalate (1.1mmol) for 16 h. The product was isolated as a colorless liquid (124mg, 82% yield).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.42 (t, 3H, ***J***=7.0Hz), 4.42 (q, 2H, ***J***=7.1Hz), 7.39 (m, 1H), 8.31 (m, 1H), 8.78 (m, 1H), 9.23 (d, 1H, ***J***=2.0Hz).

^{13}C-NMR (100MHz, $CDCl_3$, δ ppm): 14.2, 61.3, 123.2, 126.3, 136.9, 150.8, 153.2, 165.1.

14. 

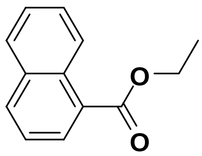
Biphenyl-4-carboxylic acid ethyl ester

Prepared according to General Procedure A**:**

4-Bromobiphenyl (1.0mmol) was allowed to react with Potassium Ethyl Oxalate (1.5mmol) for 24 h. The product was isolated as a yellow solid (183mg, 81% yield). Spectral data matched literature description. [9]

^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.41 (t, 3H, ***J***=7.2Hz), 4.40 (q, 2H, ***J***=7.2Hz), 7.38 (m, 1H), 7.46 (m, 2H), 7.63 (m, 4H), 8.11 (m, 2H).

^{13}C-NMR (100MHz, $CDCl_3$, δ ppm): 14.4, 61.0, 127.1, 127.3, 128.2, 129.0, 129.3, 130.1, 140.1, 145.6, 166.6.

15. 

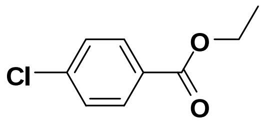
naphthalene-1-carboxylic acid ethyl ester

Prepared according to General Procedure A**:**

1-Bromonaphthalene (1.0mmol) was allowed to react with potassium ethyl oxalate (1.5mmol) for 24 h. The product was isolated as a yellow liquid (124mg, 62% yield).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.44 (t, 3H, ***J***=7.2Hz), 4.46 (q, 2H, ***J***=7.2Hz), 7.44-7.52 (m, 2H),

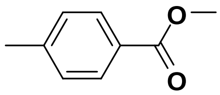
7.57-7,61 (m, 1H), 7.83-7.87 (d, 1H, ***J***=8.4Hz), 7.96-7.98 (d, 1H, ***J***=8.4Hz), 8.16-8.18 (dd, 1H, $\boldsymbol{J_1}$=7.2Hz, $\boldsymbol{J_2}$=1.2Hz), 8.91-8.93 (d, 1H, ***J***=8.4Hz).
^{13}C-NMR (100MHz, $CDCl_3$, δ ppm): 14.4, 61.1, 124.5, 125.9, 126.2, 127.6, 127.7, 128.6, 130.1, 131.4, 133.2, 133.9, 167.6.

16. 

4-chlorobenzoic acid ethyl ester

Prepared according to General Procedure A:

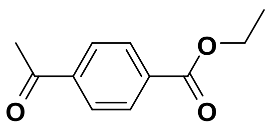
4-chlorobromobenzene (1.0mmol) was allowed to react with potassium ethyl oxalate (1.5mmol) for 24 h. The product was isolated as a colorless liquid (174mg, 94% yield).
^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.39 (t, 3H, ***J***=7.0Hz), 4.37 (q, 2H, ***J***=7.1Hz), 7.38-7.42 (m, 2H), 7.96-7.99 (m, 2H).
^{13}C-NMR (100MHz, $CDCl_3$, δ ppm): 14.4, 61.3, 128.7, 129.0, 131.0, 139.3, 165.8.

17. 

4-methylbenzoic acid methyl ester

Prepared according to General Procedure A**:**

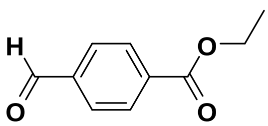
4-bromotoluene (1.0mmol) was allowed to react with potassium methyl oxalate (1.5mmol) for 24 h. The product was isolated as a yellow solid (78mg, 52% yield).
^{1}H-NMR (400 MHz, $CDCl_3$): δ 2.40 (s, 3H), 3.89 (s, 3H), 7.21-7.23 (m, 2H), 7.91-7.94 (m, 2H).
^{13}C-NMR (100MHz, $CDCl_3$, δ ppm): 21.7, 52.0, 127.5, 129.1, 129.7, 143.6, 167.2.

18. 

4-acetylbenzoic acid ethyl ester

Prepared according to General Procedure A**:**

4-bromoacetophenone (1.0mmol) was allowed to react with potassium ethyl oxalate (1.1mmol) for 16 h. The product was isolated as a white solid (123mg, 64% yield). Spectral data matched literature description. [10]
^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.42 (t, 3H, ***J***=7.0Hz), 2.64 (s, 3H), 4.41 (q, 2H, ***J***=7.0Hz), 8.01 (m, 2H), 8.12 (m, 2H).
^{13}C-NMR (100MHz, $CDCl_3$, δ ppm): 14.4, 26.9, 61.5, 128.2, 129.8, 134.4, 140.2, 165.8, 197.6.

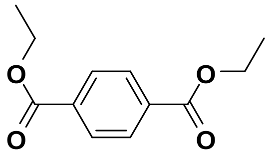
19. 

4-formylbenzoic acid ethyl ester

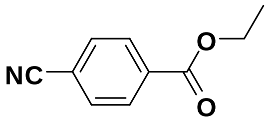
Prepared according to General Procedure A:

4-Bromobenzaldehyde (1.0mmol) was allowed to react with potassium ethyl oxalate (1.1mmol) for 16 h. The product was isolated as a colorless liquid (119mg, 67% yield).
^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.42 (t, 3H, ***J***=7.2Hz), 4.42 (q, 2H, ***J***=7.1Hz), 7.94-7.96 (m, 2H),

8.19-8.22 (m, 2H), 10.10 (s, 1H).
^{13}C-NMR (100MHz, $CDCl_3$, δ ppm): 14.3, 61.6, 129.5, 130.2, 135.5, 139.1, 165.6, 191.7.

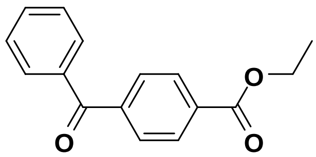
20.


1,4-benzenedicarboxylic acid diethyl ester
Prepared according to General Procedure A:
4-bromobenzoic acid ethyl ester (1.0mmol) was allowed to react with potassium ethyl oxalate (1.1mmol) for 16 h. The product was isolated as a white solid (173mg, 78% yield).
^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.41 (t, 6H, ***J***=7.2Hz), 4.40 (q, 4H, ***J***=7.2Hz), 8.10 (s, 4H).
^{13}C-NMR (100MHz, $CDCl_3$, δ ppm): 14.3, 61.4, 129.5, 134.2, 165.8.

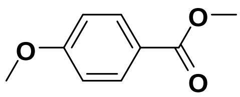
21.


4-cyano-benzoic acid ethyl ester
Prepared according to General Procedure A:
4-bromobenzonitrile (1.0mmol) was allowed to react with potassium ethyl oxalate (1.1mmol) for 16 h. The product was isolated as a yellow solid (150mg, 86% yield).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.42 (t, 3H, ***J***=7.2Hz), 4.42 (q, 2H, ***J***=7.2Hz), 7.74 (d, 2H, ***J***=8.0Hz), 8.14 (d, 2H, ***J***=8.0Hz).
^{13}C-NMR (100MHz, $CDCl_3$, δ ppm): 14.3, 61.9, 116.4, 118.0, 130.1, 132.2, 134.4, 165.0.

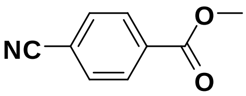
22.


4-ethoxycarbonylbenzophenone
Prepared according to General Procedure A:
4-bromobenzophenone (1.0mmol) was allowed to react with Potassium Ethyl Oxalate (1.1mmol) for 16 h. The product was isolated as a yellow oil (249mg, 98% yield). Spectral data matched literature description. [8]
^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.42 (t, 3H, ***J***=7.2Hz), 4.42 (q, 2H, ***J***=7.2Hz), 7.48-7.52 (m, 2H), 7.59-7.64 (m, 1H), 7.79-7.85 (m, 4H), 8.14-8.17 (m, 2H).
^{13}C-NMR (100MHz, $CDCl_3$, δ ppm): 14.4, 61.5, 128.5, 129.5, 129.8, 130.2, 133.0, 133.7, 137.1, 141.3, 165.9, 196.1.

23.


4-methoxybenzoic acid methyl ester
Prepared according to General Procedure A:
4-bromoanisole (1.0mmol) was allowed to react with potassium methyl oxalate (1.5mmol) for 24 h. The product was isolated as a white solid (91mg, 55% yield).
^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.85 (s, 3H), 3.88 (s, 3H), 6.89-6.93 (m, 2H), 7.97-8.01 (m, 2H).

^{13}C-NMR (100MHz, $CDCl_3$, δ ppm): 51.9, 55.5, 113.7, 122.7, 131.6, 163.4, 166.9.



24.

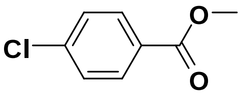
4-cyano-benzoic acid methyl ester

Prepared according to General Procedure A:

4-bromobenzonitrile (1.0mmol) was allowed to react with potassium methyl oxalate (1.5mmol) for 16 h. The product was isolated as a white solid (113mg, 70% yield).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.96 (s, 3H), 7.74-7.76 (m, 2H), 8.13-8.16 (m, 2H).

^{13}C-NMR (100MHz, $CDCl_3$, δ ppm): 52.8, 116.5, 118.0, 130.2, 132.3, 134.0, 165.5.



25.

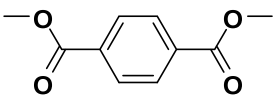
4-chloro-benzoic acid methyl ester

Prepared according to General Procedure A:

4-chlorobromobenzene (1.0mmol) was allowed to react with potassium methyl oxalate (1.5mmol) for 24 h. The product was isolated as a white solid (131mg, 77% yield).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.92 (s, 3H), 7.39-4.43 (m, 2H), 7.96-7.99 (m, 2H).

^{13}C-NMR (100MHz, $CDCl_3$, δ ppm): 52.3, 128.7, 128.8, 131.1, 139.4, 166.3.



26.

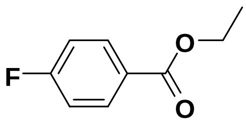
1,4-benzenedicarboxylic acid dimethyl ester

Prepared according to General Procedure A:

4-bromobenzoic acid methyl ester (1.0mmol) was allowed to react with potassium methyl oxalate (1.5mmol) for 24 h. The product was isolated as a white crystal solid (157mg, 81% yield).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.95 (s, 6H), 8.10 (s, 4H).

^{13}C-NMR (100MHz, $CDCl_3$, δ ppm): 52.5, 129.6, 134.0, 166.3.



27.

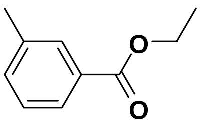
4-fluorobenzoic acid ethyl ester

Prepared according to General Procedure A:

4-bromofluorobenzene (1.0mmol) was allowed to react with potassium ethyl oxalate (1.1mmol) for 16 h. The product was isolated as a colorless liquid (136mg, 81% yield). Spectral data matched literature description. [10]

^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.39 (t, 3H, ***J***=7.0Hz), 4.37 (q, 2H, ***J***=7.0Hz), 7.07-7.13 (m, 2H), 8.03-8.08 (m, 2H).

^{13}C-NMR (100MHz, $CDCl_3$, δ ppm): 14.4, 61.1, 115.5 (d, ***J***=21.8Hz), 126.8, 132.1 (d, ***J***=9.2Hz), 165.1 (d, ***J***=119.6), 167.0.



28.

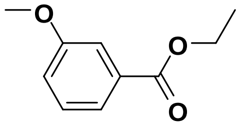
3-methylbenzoic acid ethyl ester

Prepared according to General Procedure B:

3-bromotoluene (1.0mmol) was allowed to react with potassium ethyl oxalate (1.5mmol) for 24 h. The product was isolated as a colorless liquid (120mg, 73% yield).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.39 (t, 3H, ***J***=7.2Hz), 2.40 (s, 3H), 4.37 (q, 2H, ***J***=7.2Hz), 7.29-7.37 (m, 2H), 7.83-7.87 (m, 2H).

^{13}C-NMR (100MHz, $CDCl_3$, δ ppm): 14.4, 21.3, 61.0, 126.8, 128.3, 130.2, 130.5, 133.6, 138.2, 166.9.

29. 

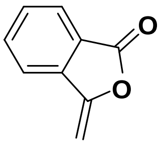
3-methoxybenzoic acid ethyl ester

Prepared according to General Procedure B:

3-bromoanisole (1.0mmol) was allowed to react with potassium ethyl oxalate (1.5mmol) for 24 h. The product was isolated as a colorless liquid (166mg, 92% yield).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.39 (t, 3H, ***J***=7.2Hz), 3.85 (s, 3H), 4.37 (q, 2H, ***J***=7.2Hz), 7.07-7.10 (m, 1H), 7.31-7.35 (m, 1H), 7.56-7.57 (m, 1H), 7.63-7.65 (m, 1H).

^{13}C-NMR (100MHz, $CDCl_3$, δ ppm): 14.4, 55.5, 61.1, 114.1, 119.4, 122.0, 129.4, 131.9, 159.6, 166.5.

30. 

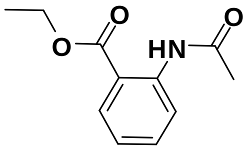
3-methylidene-3H-isobenzofuran-1-one

Prepared according to General Procedure A:

2-bromoacetophenone (1.0mmol) was allowed to react with potassium ethyl oxalate (1.1mmol) for 16 h. The product was isolated as a white solid (45mg, 31% yield). Spectral data matched literature description. [7]

^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.23 (dd, 2H, J_1=3.2Hz, J_2=4.0), 7.55-7.62 (m, 1H), 7.72-7.73 (m, 2H), 7.90-7.92 (m, 1H).

^{13}C-NMR (100MHz, $CDCl_3$, δ ppm): 91.3, 120.7, 125.2, 125.4, 130.5, 134.5, 139.1, 151.9, 166.9.

31. 

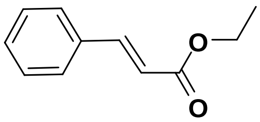
2-acetylamino benzoic acid ethyl ester

Prepared according to General Procedure A:

2-bromo, N-acetyl aniline (1.0mmol) was allowed to react with potassium ethyl oxalate (1.5mmol) for 24 h. The product was isolated as a pale yellow solid (108mg, 52% yield).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.42 (t, 3H, ***J***=7.0Hz), 2.24 (s, 3H), 4.38 (q, 2H, ***J***=7.2Hz), 7.05-7.09 (m, 1H), 7.51-7.56 (m, 1H), 8.03-8.05 (m, 1H), 8.69-8.71 (m, 1H), 11.09 (s, br, 1H).

^{13}C-NMR (100MHz, $CDCl_3$, δ ppm): 14.3, 25.6, 61.5, 115.2, 120.4, 122.4, 130.8, 134.6, 141.7, 168.4, 169.1.

32. 

(E)-ethyl-3-phenylpropenoate

Prepared according to General Procedure A:

β-Bromostyrene (1.0mmol) was allowed to react with potassium ethyl oxalate (1.1mmol) for 10h. The product was isolated as a yellow liquid (156mg, 89% yield). Spectral data matched literature description. [12]

^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.34 (t, 3H, ***J***=7.1Hz), 4.26 (q, 2H, ***J***=7.1Hz), 6.44 (d, 2H, ***J***=16.0Hz), 7.38 (m, 3H), 7.52 (m, 2H), 7.68 (d, 2H, ***J***=16.0Hz).

^{13}C-NMR (100MHz, $CDCl_3$, δ ppm): 14.4, 60.6, 118.4, 128.1, 129.0, 130.3, 134.6, 144.6, 167.1.

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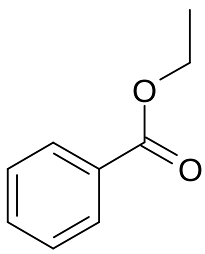

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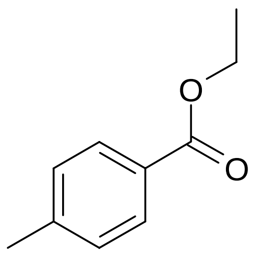

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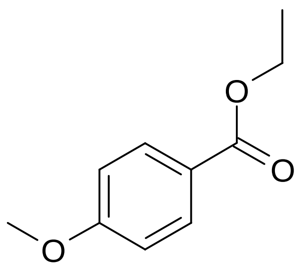

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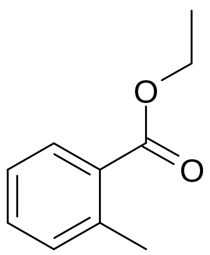

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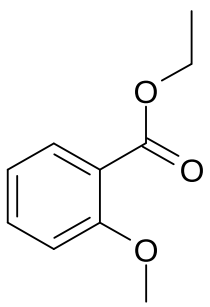

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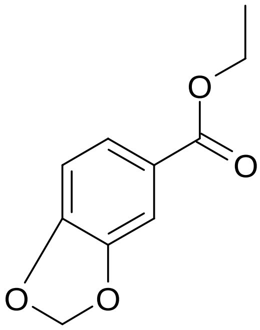

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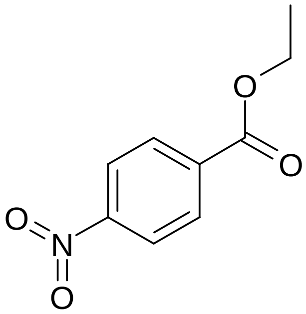

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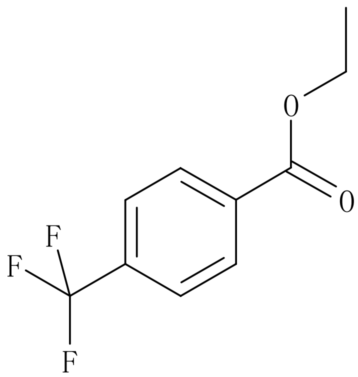

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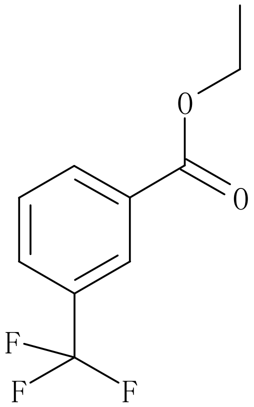

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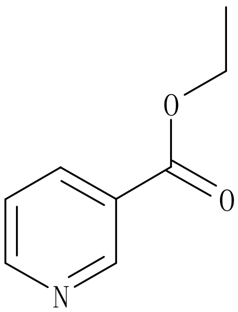

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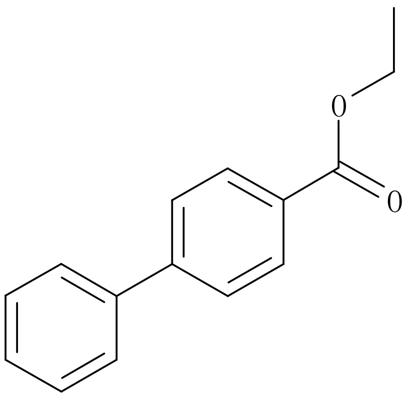

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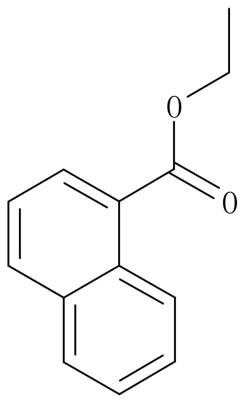

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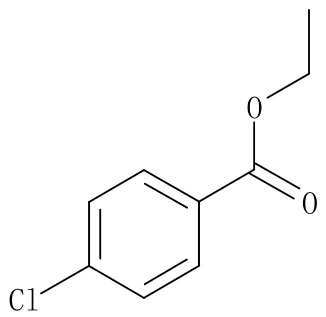

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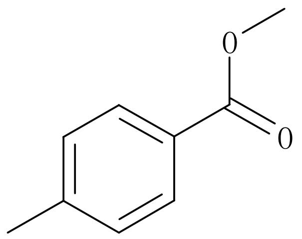

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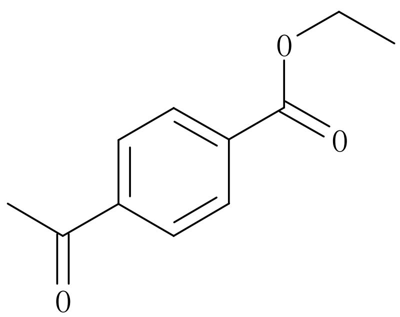

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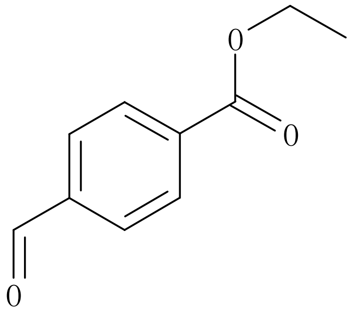

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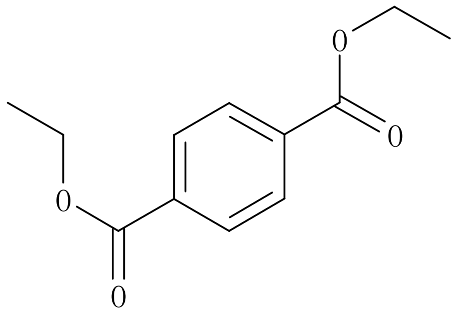

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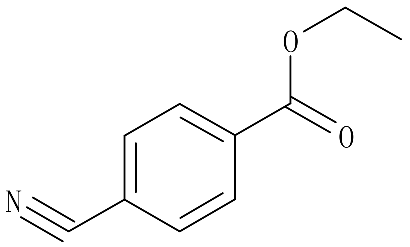

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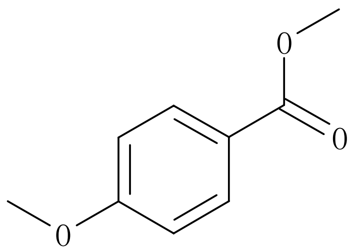

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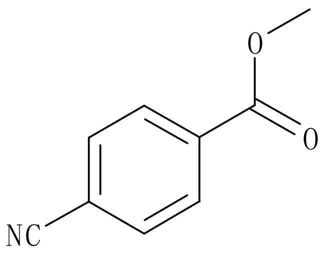

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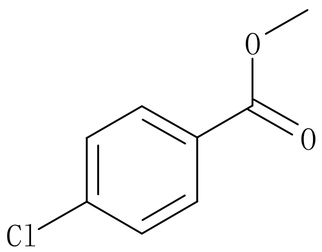

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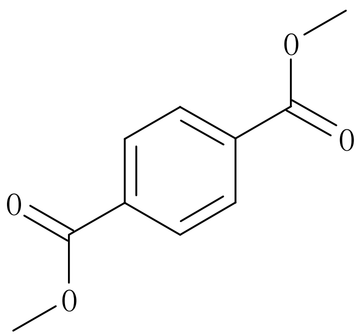

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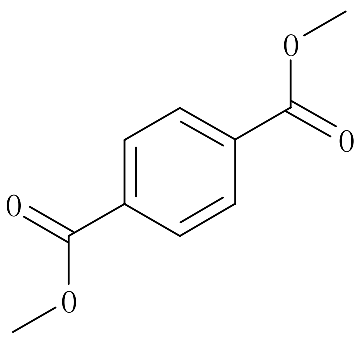

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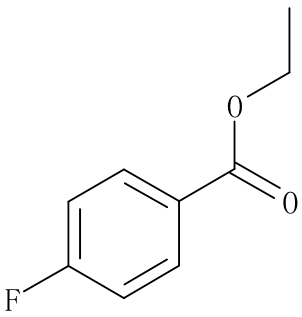

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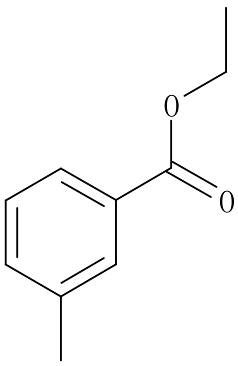

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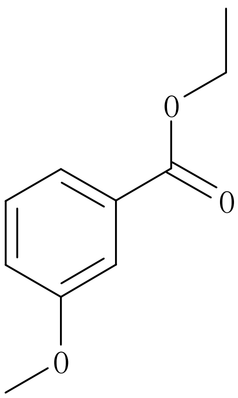

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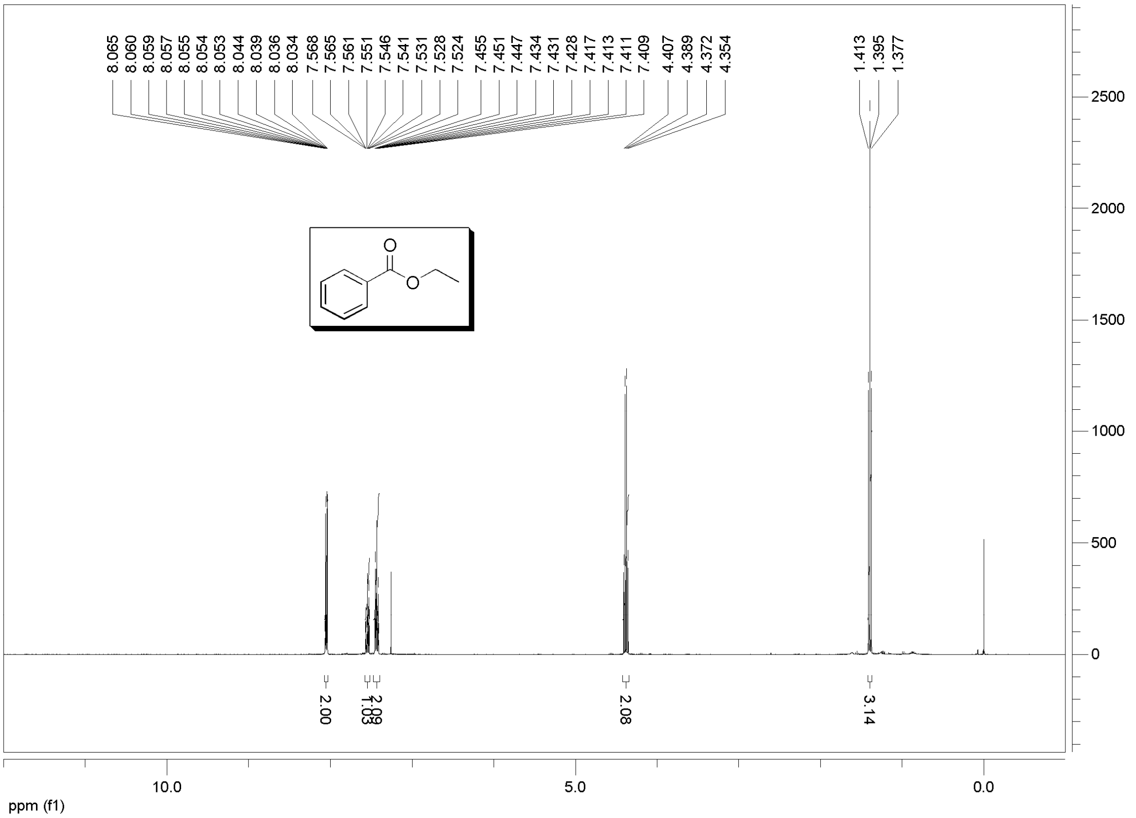
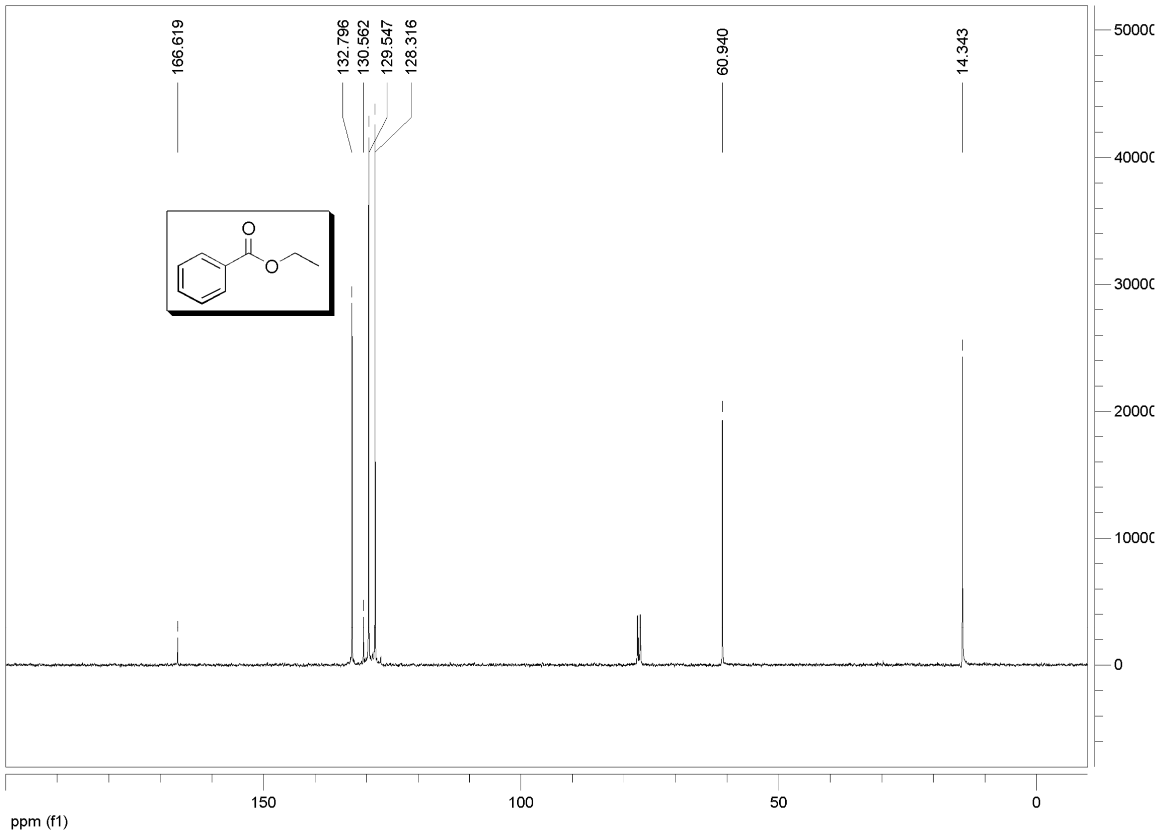
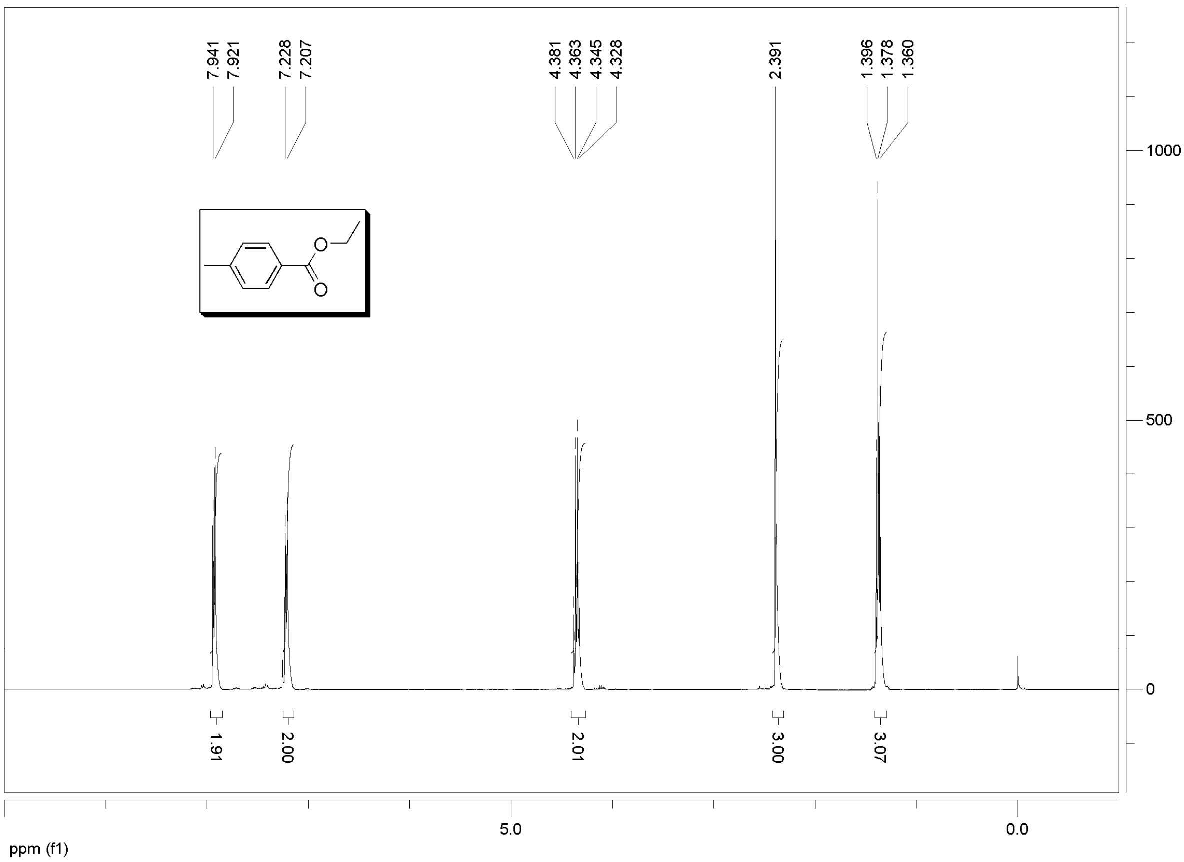
Spectra Data (^{1}H,^{13}C) of all products

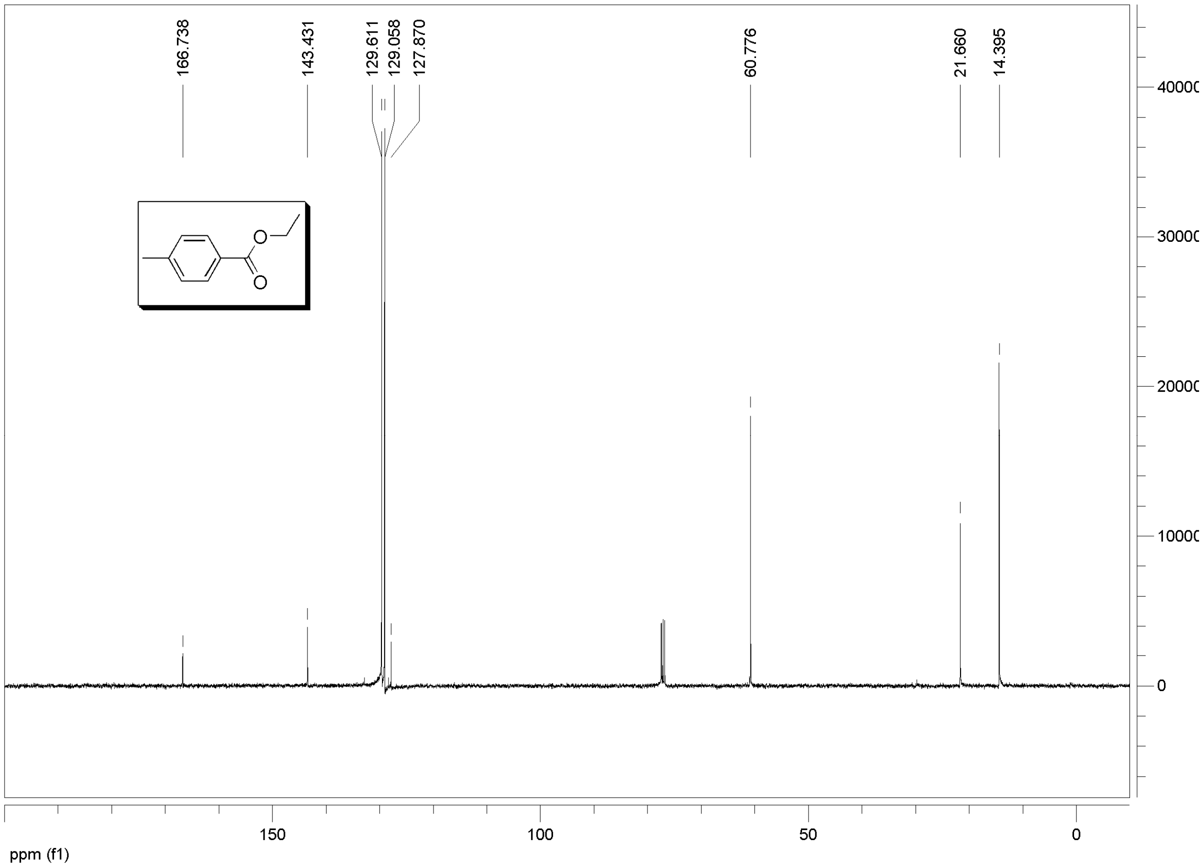
Benzoic acid ethyl ester (1)



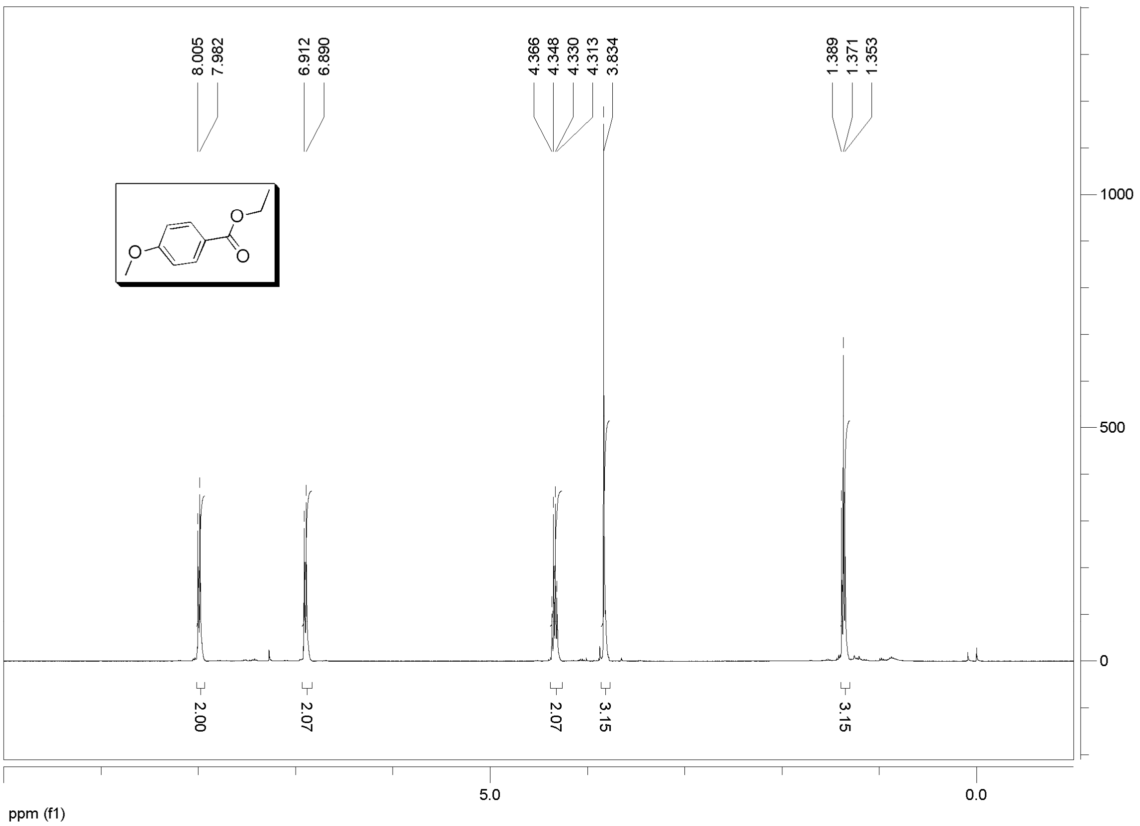


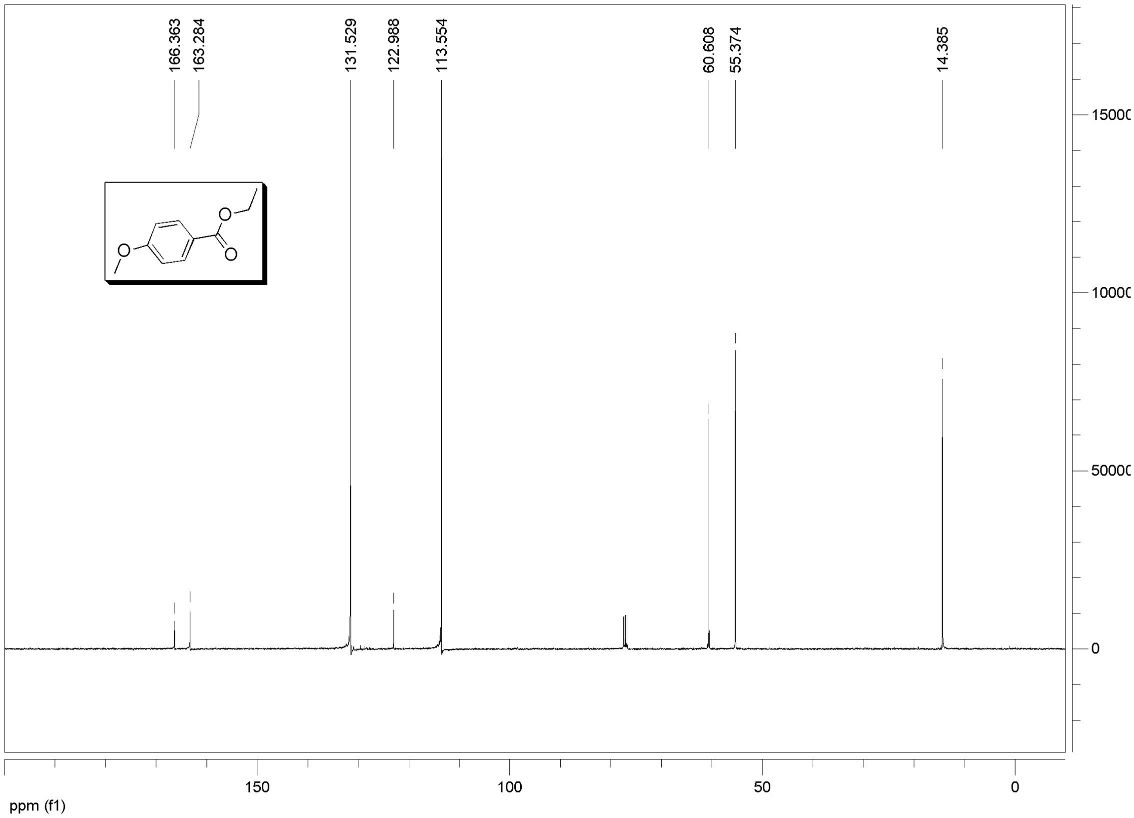
4-methylbenzoic acid ethyl ester (2)





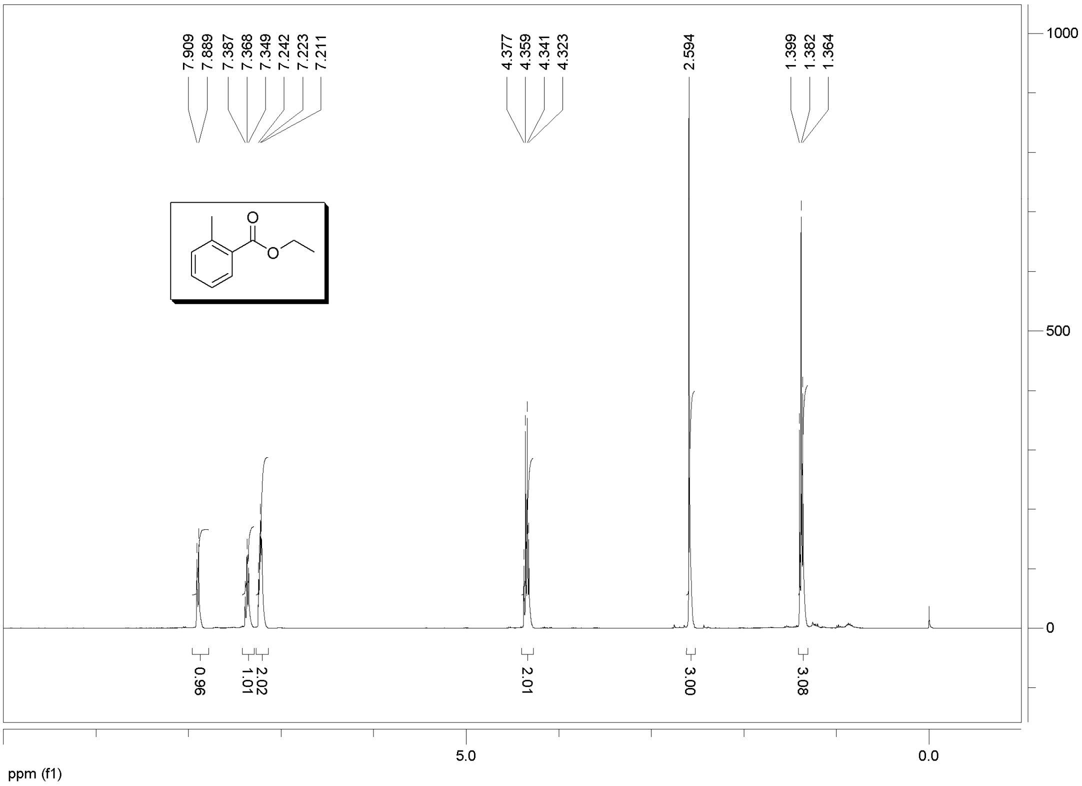
4-methoxybenzoic acid ethyl ester (3)

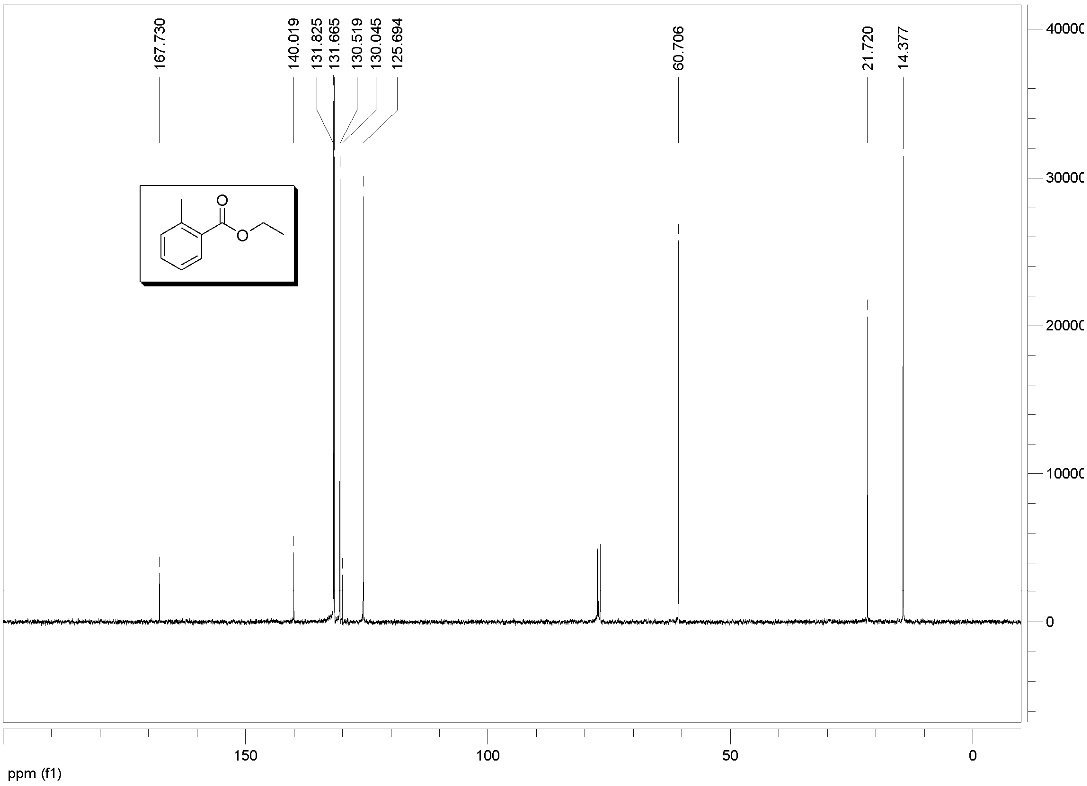




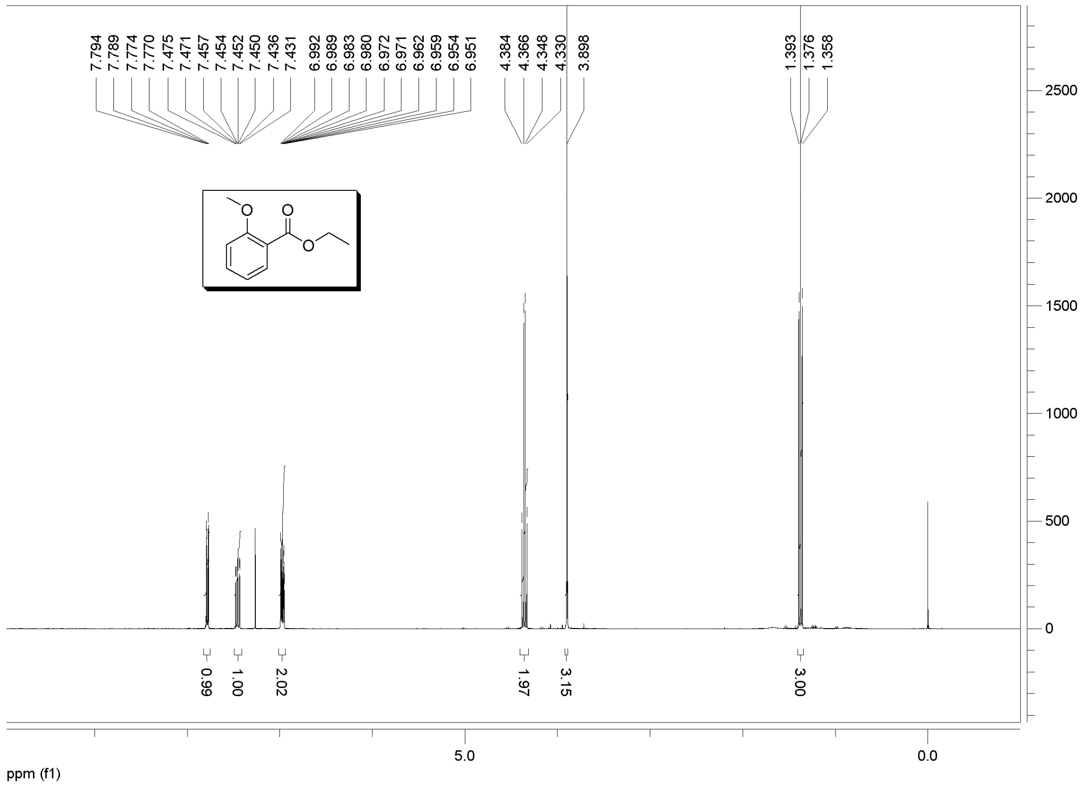
166.363
163.284
131.529
122.988
113.554
60.608
55.374
14.385
15000
10000
50000
0
150
100
50
0
ppm (f1)

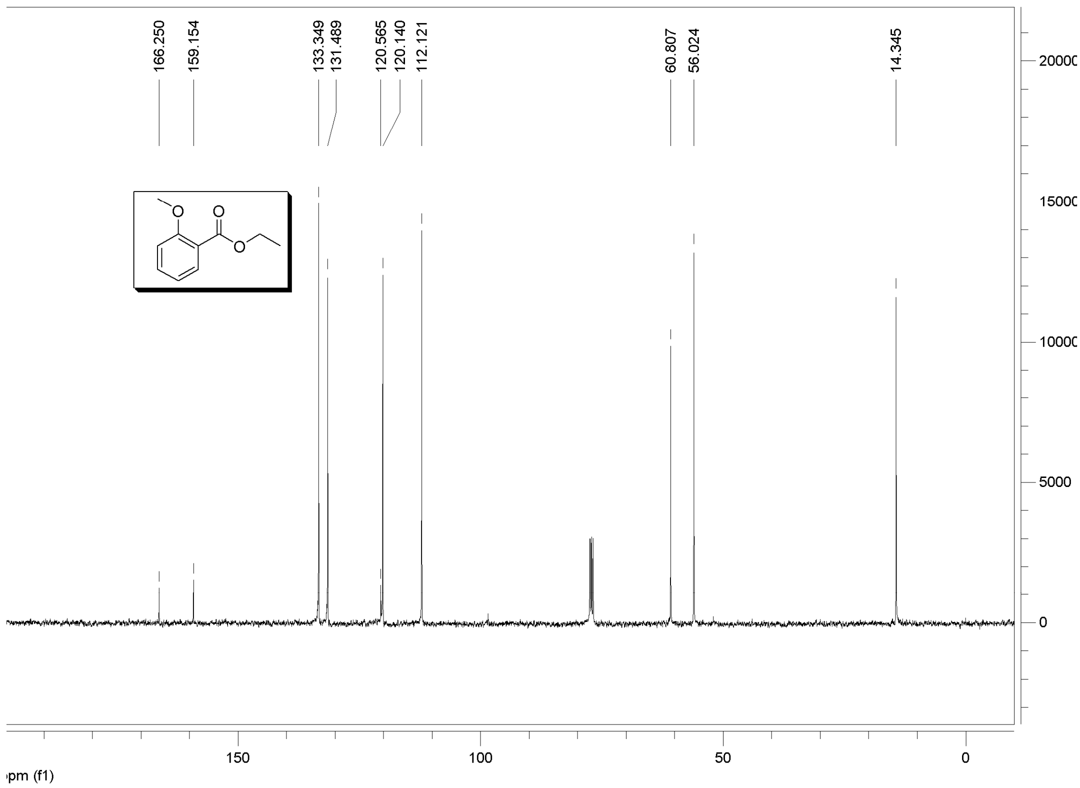
2-methylbenzoic acid ethyl ester (4)



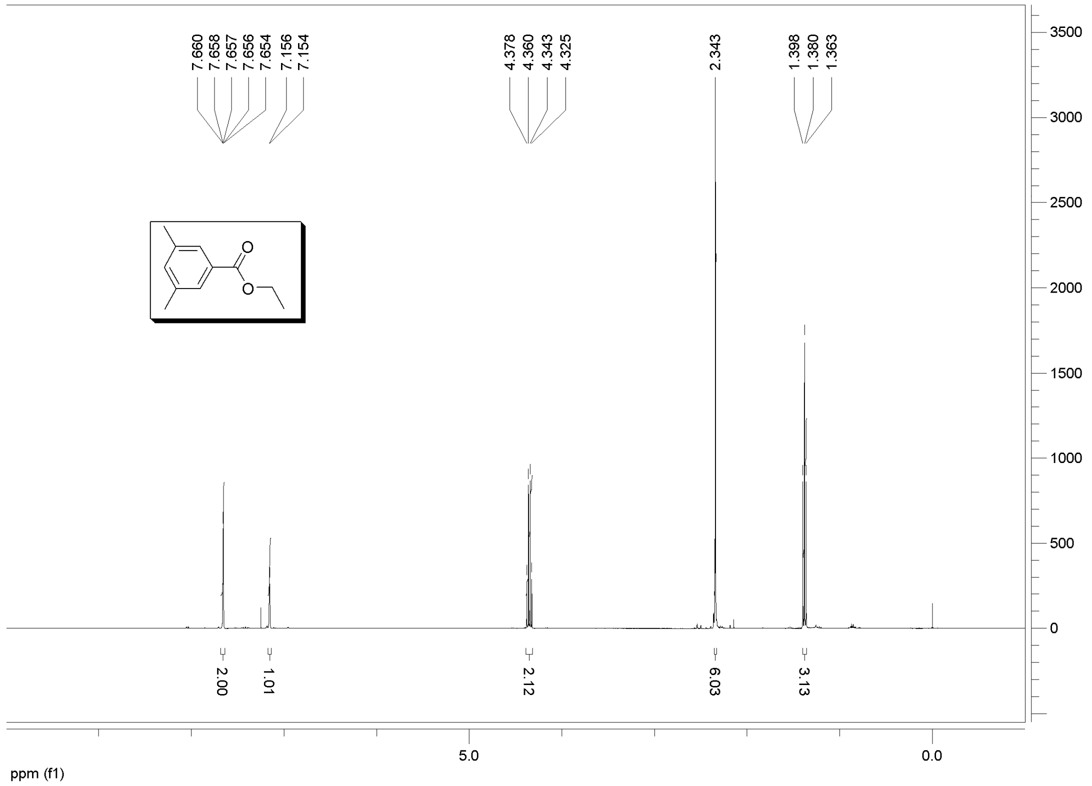


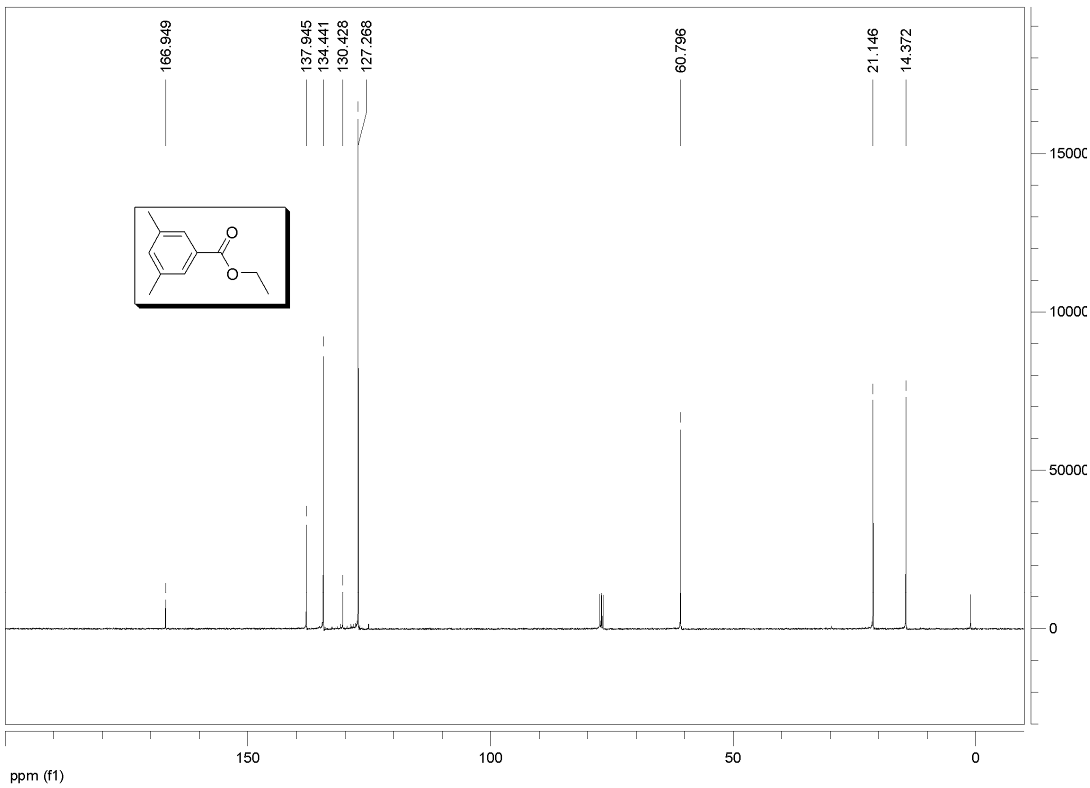
2-methoxybenzoic acid ethyl ester (5)



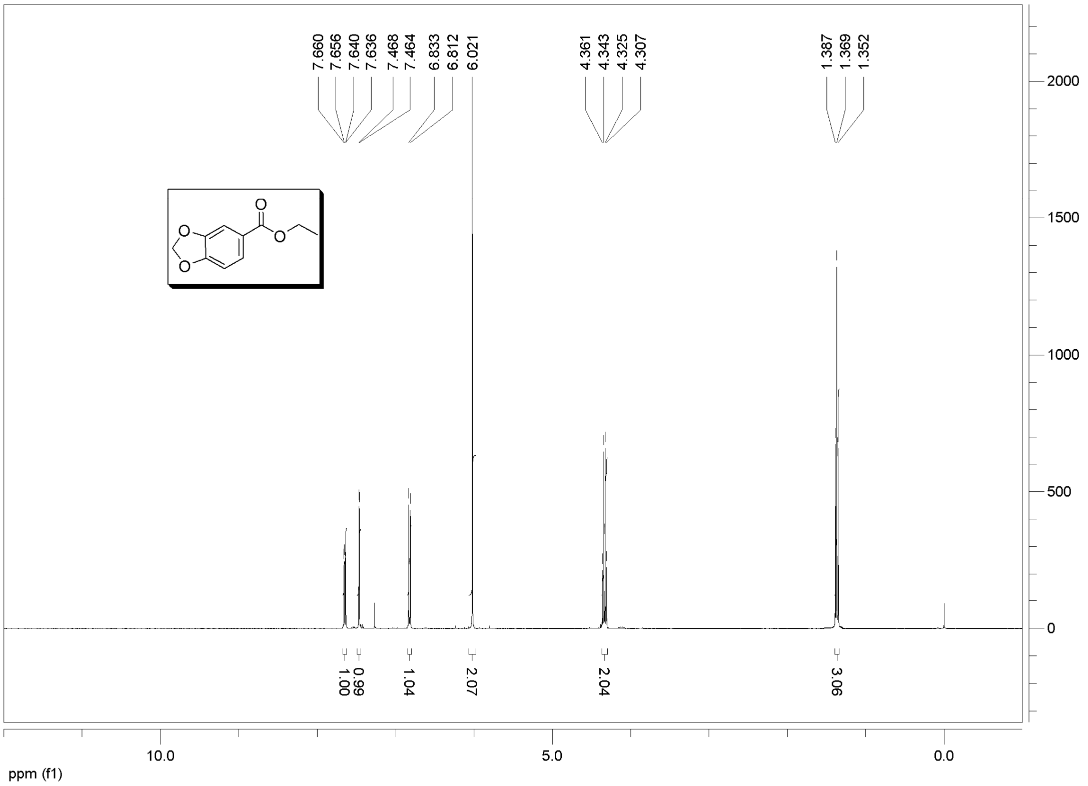


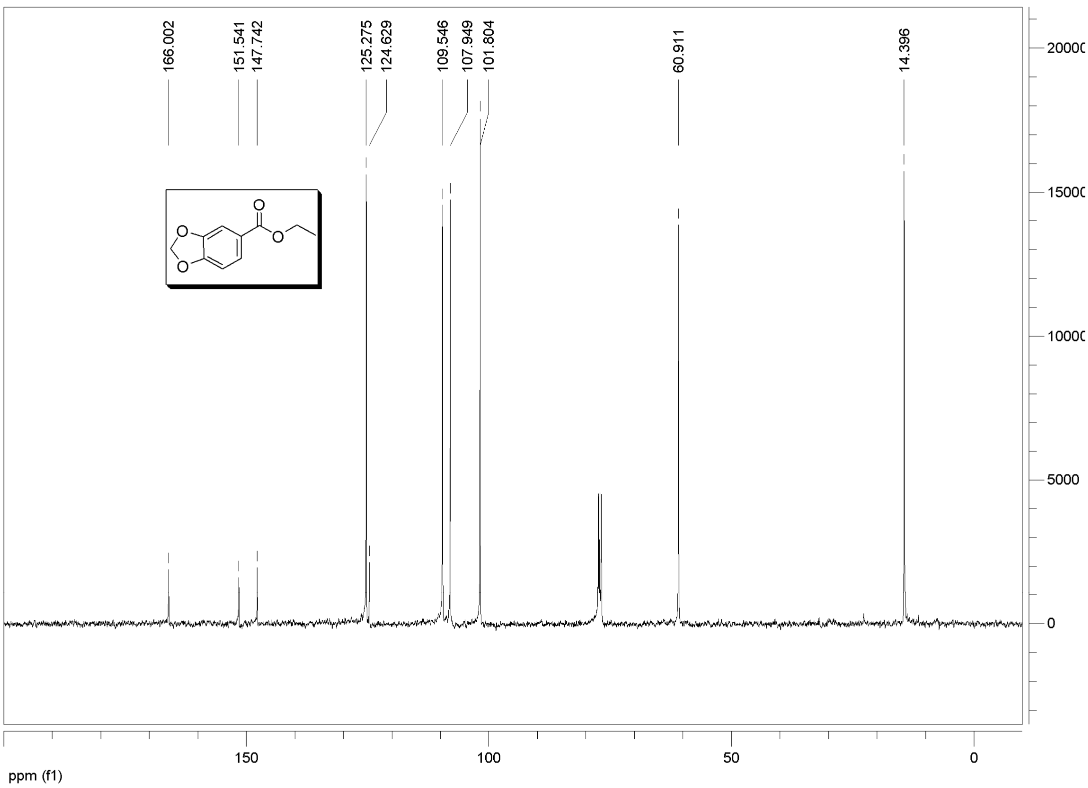
3,5-dimethyl-benzoic acid ethyl ester (6)



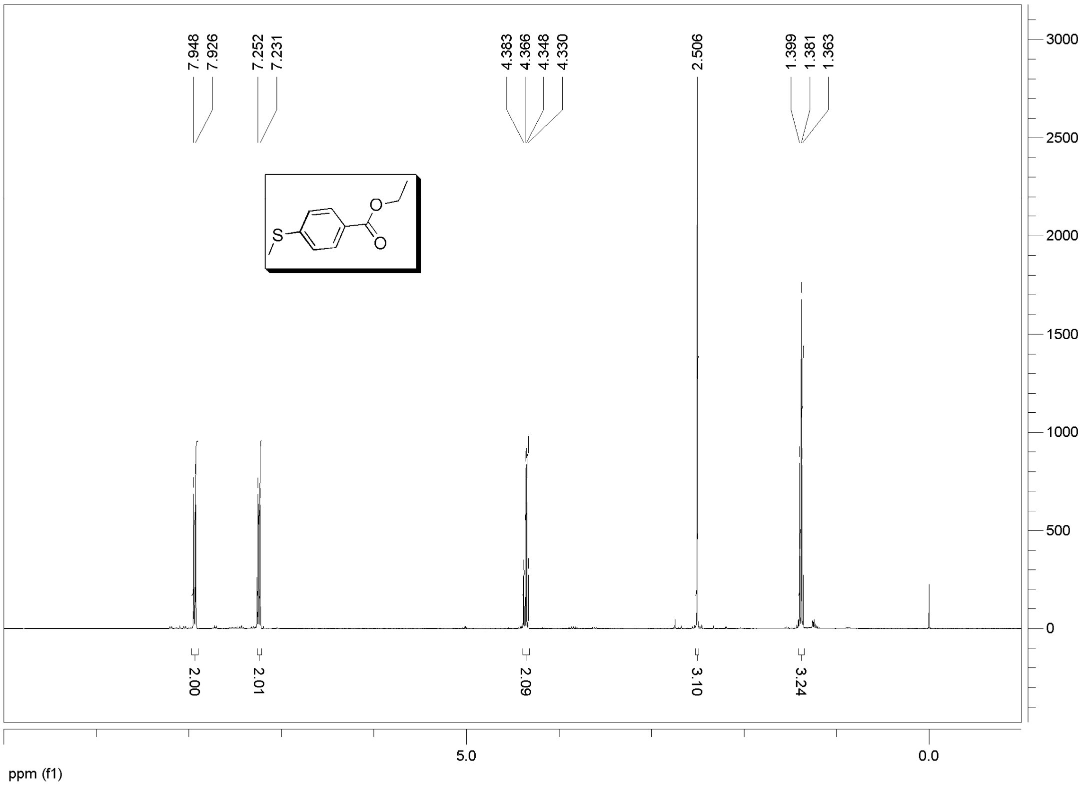


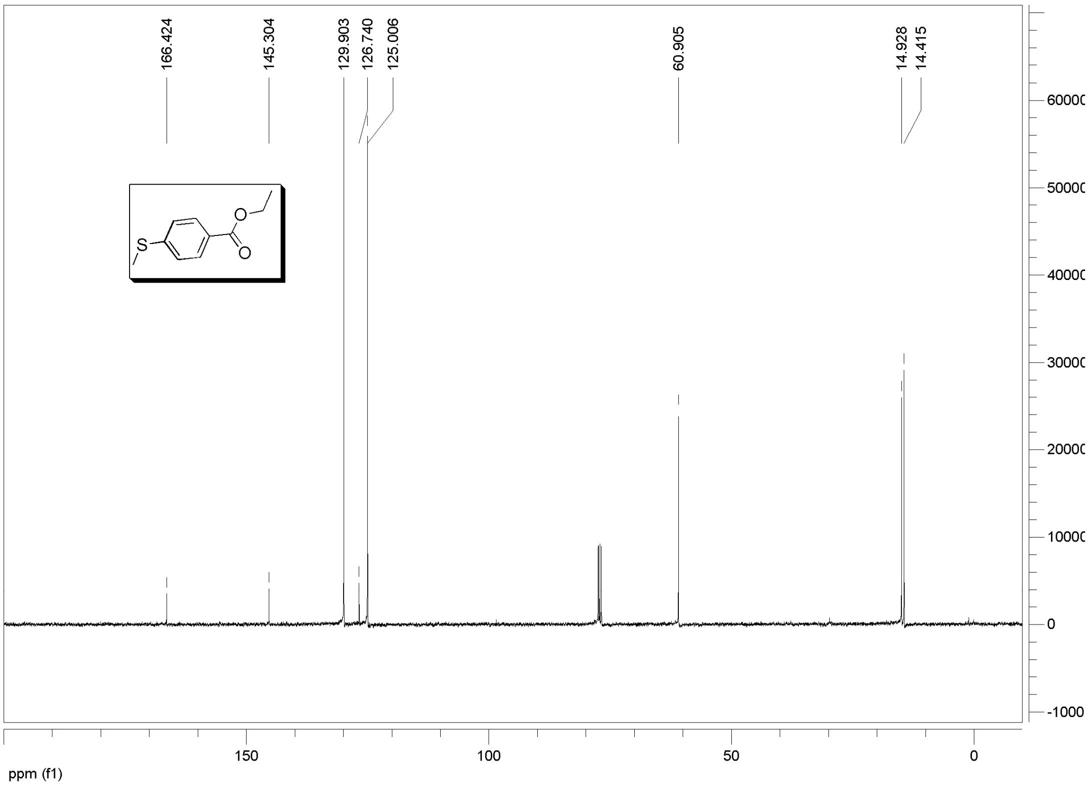
Benzo[1,3]dioxole-5-carboxylic acid ethyl ester (7)



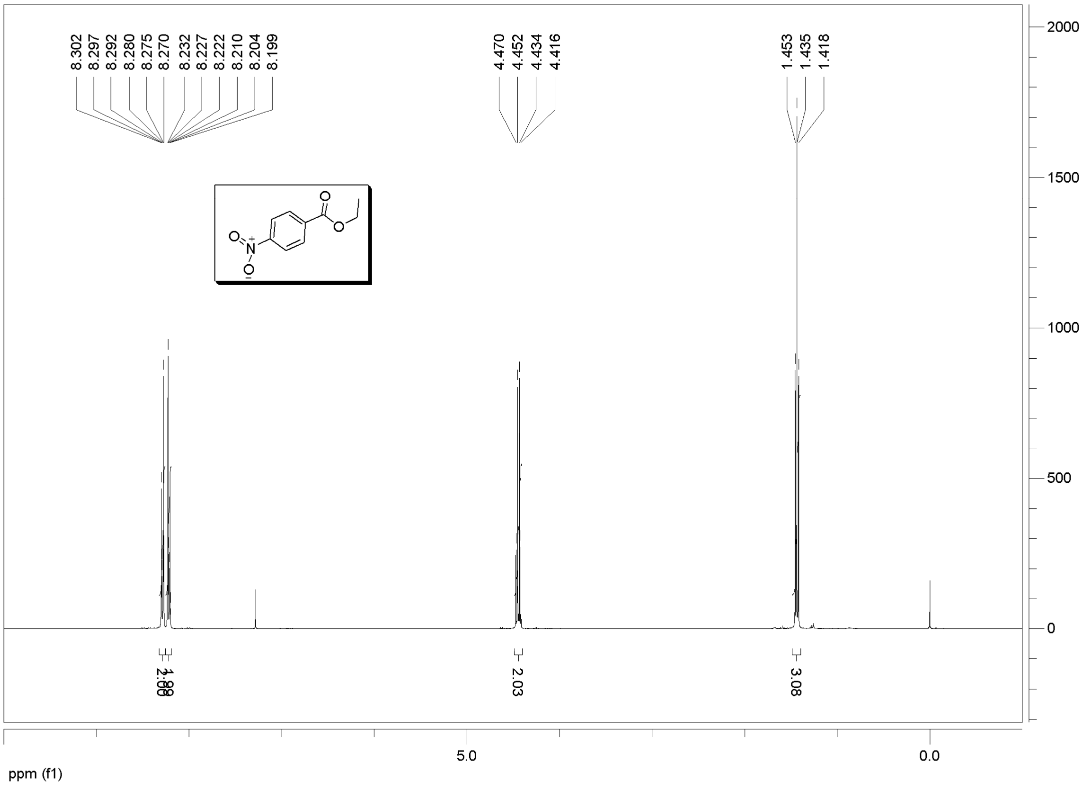


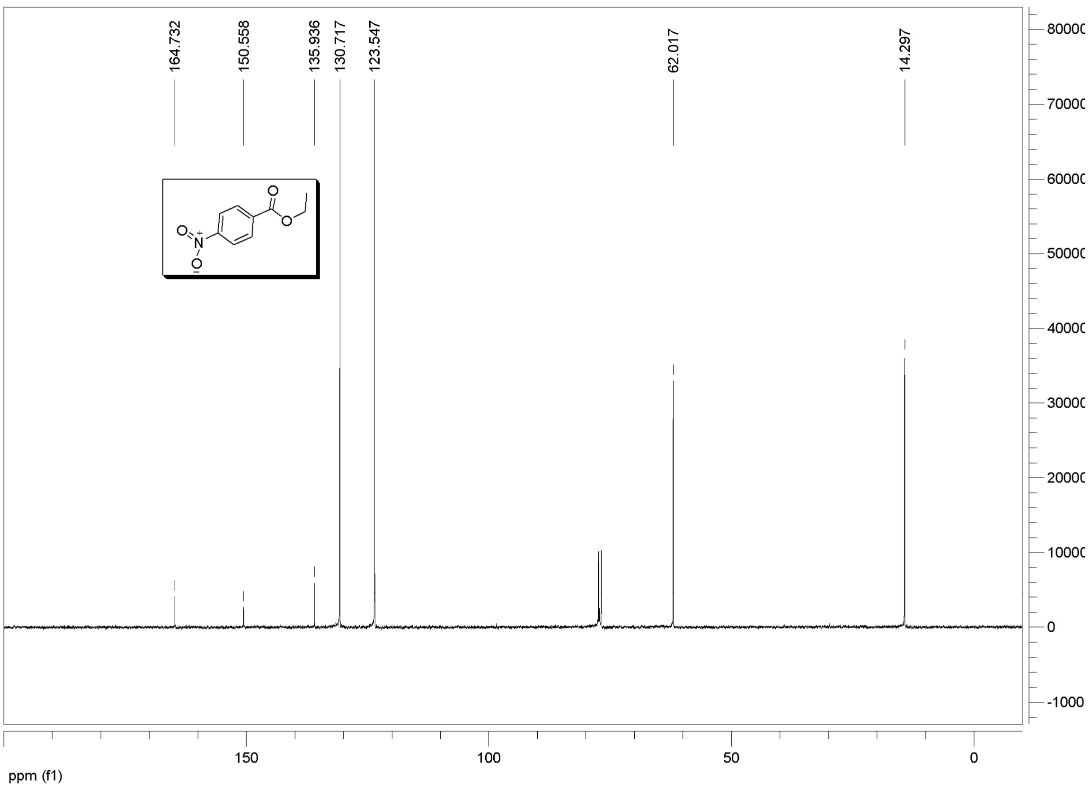
4-methylthiobenzoic acid ethyl ester (8)



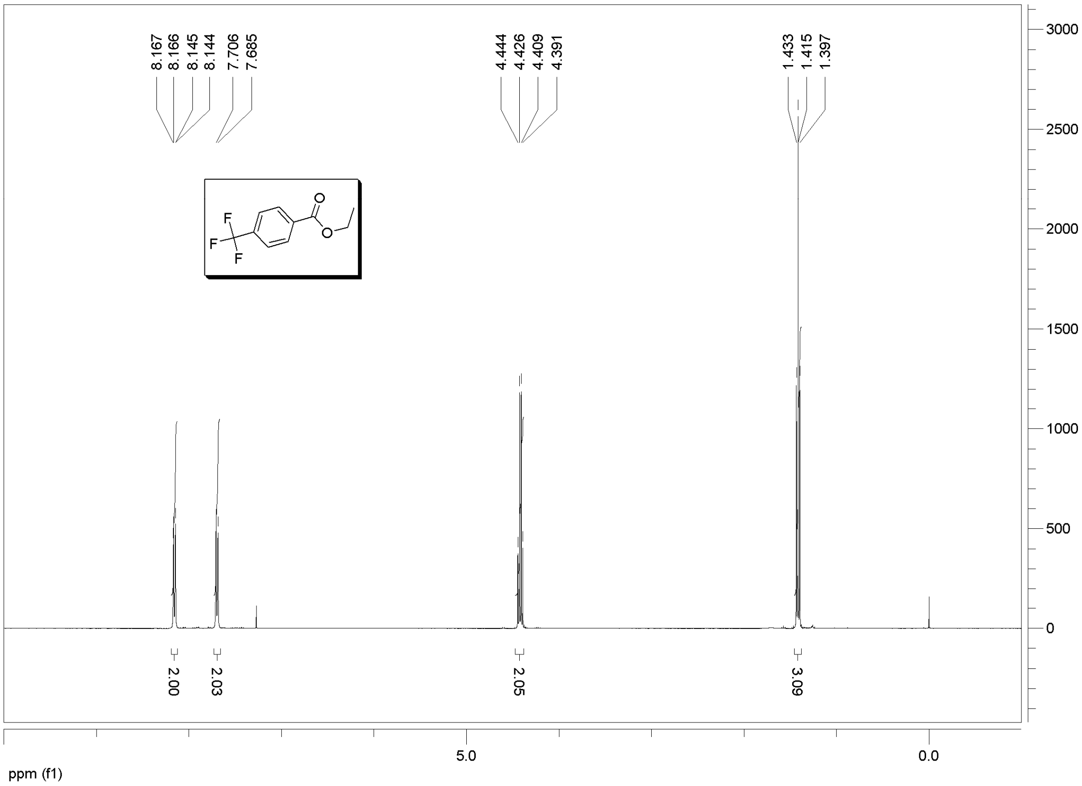


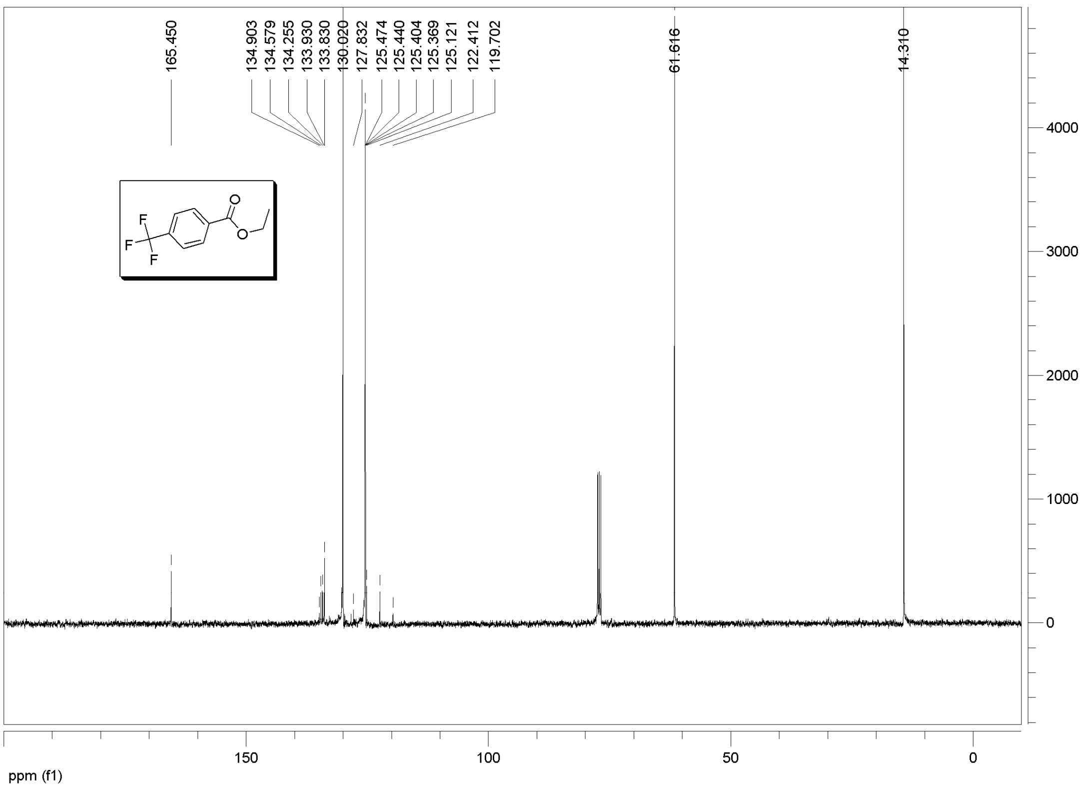
4-nitrobenzoic acid ethyl ester (9)



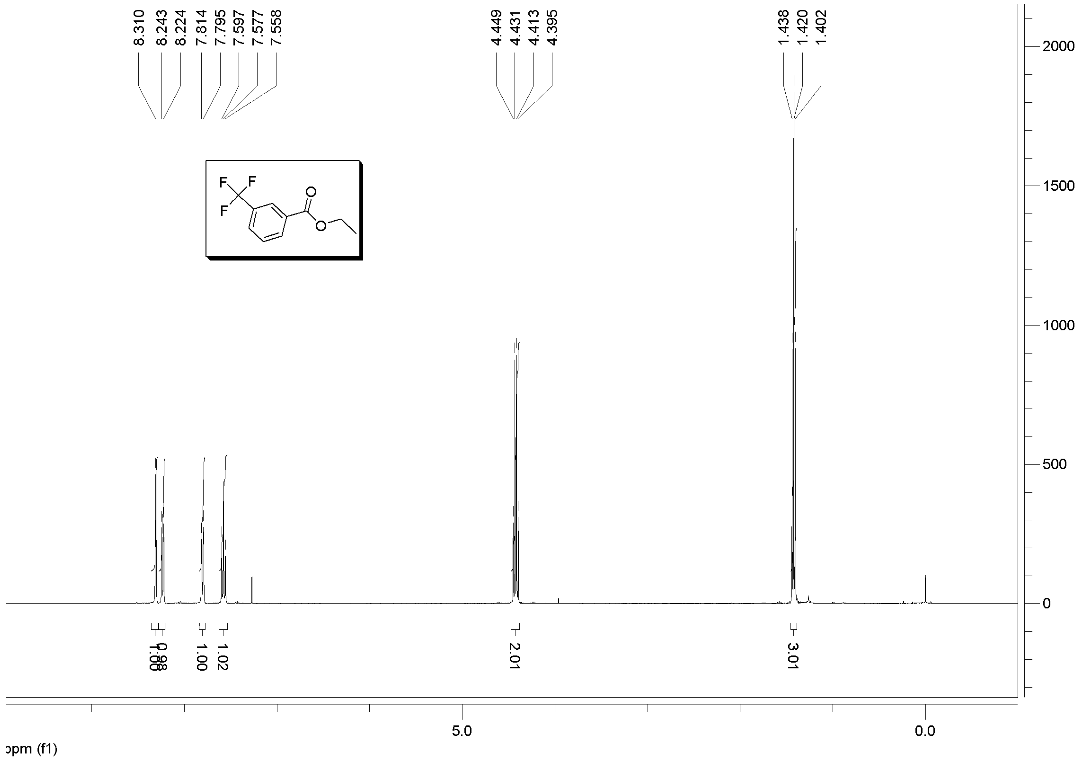


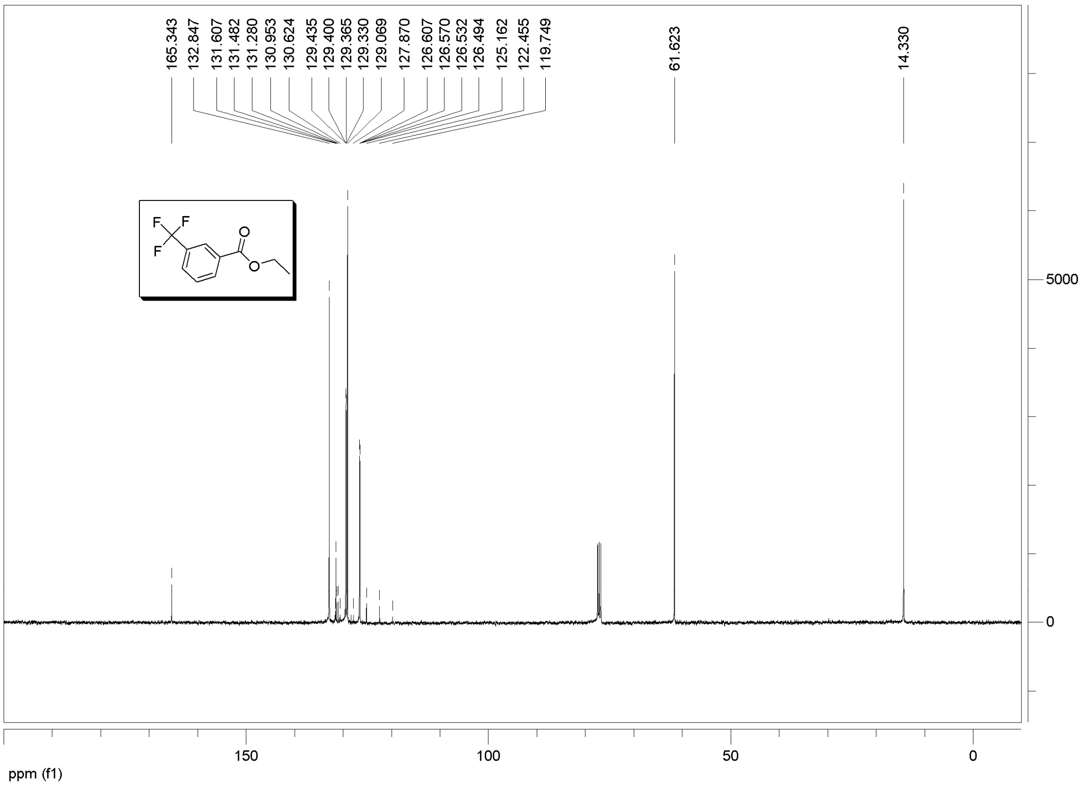
4-(trifluoromethyl)benzoic acid ethyl ester (10)



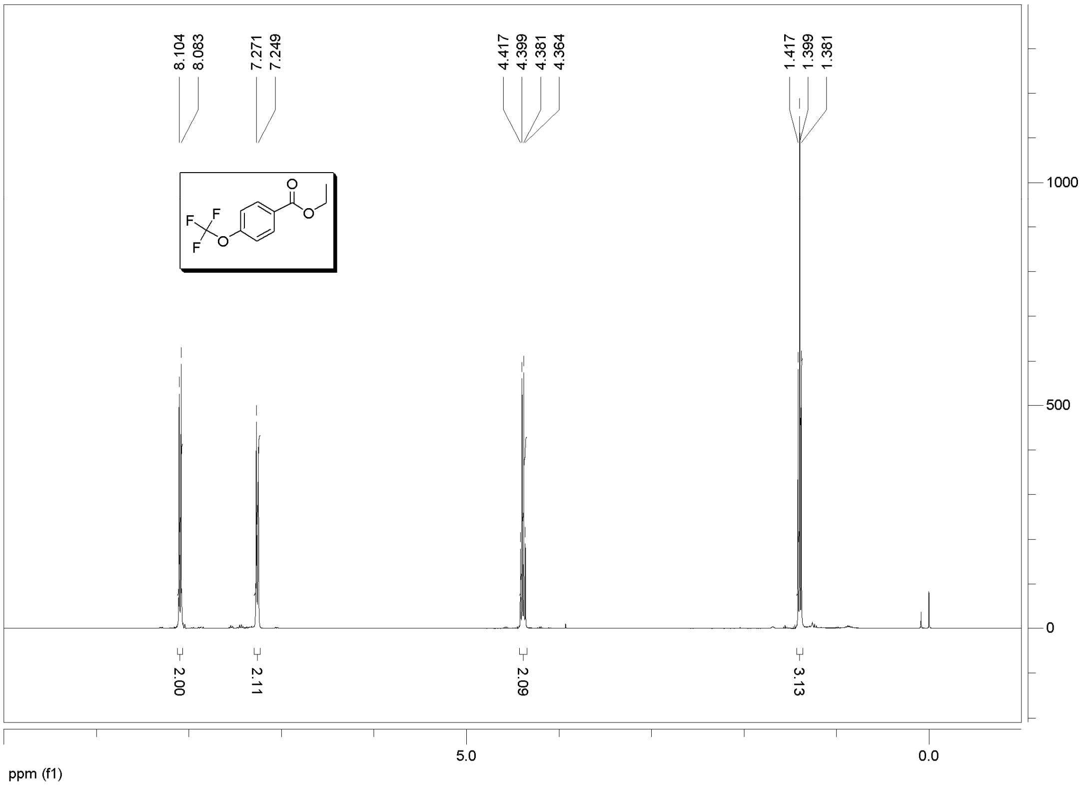


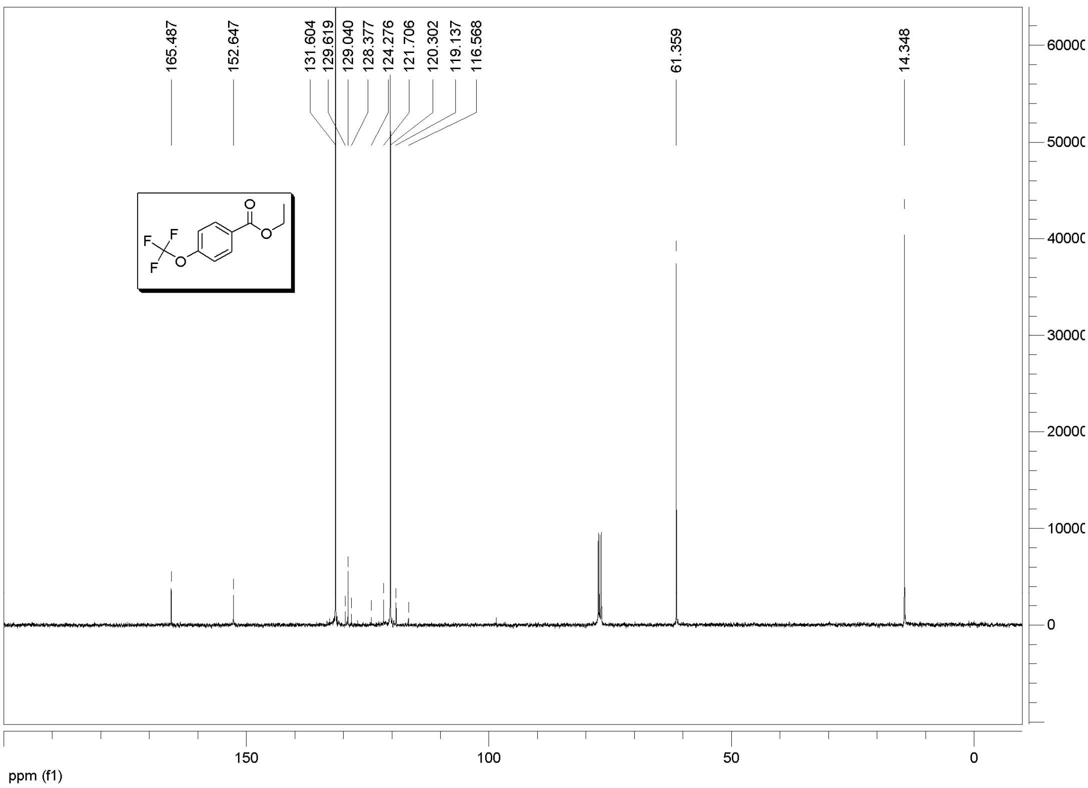
3-(trifluoromethyl)benzoic acid ethyl ester (11)



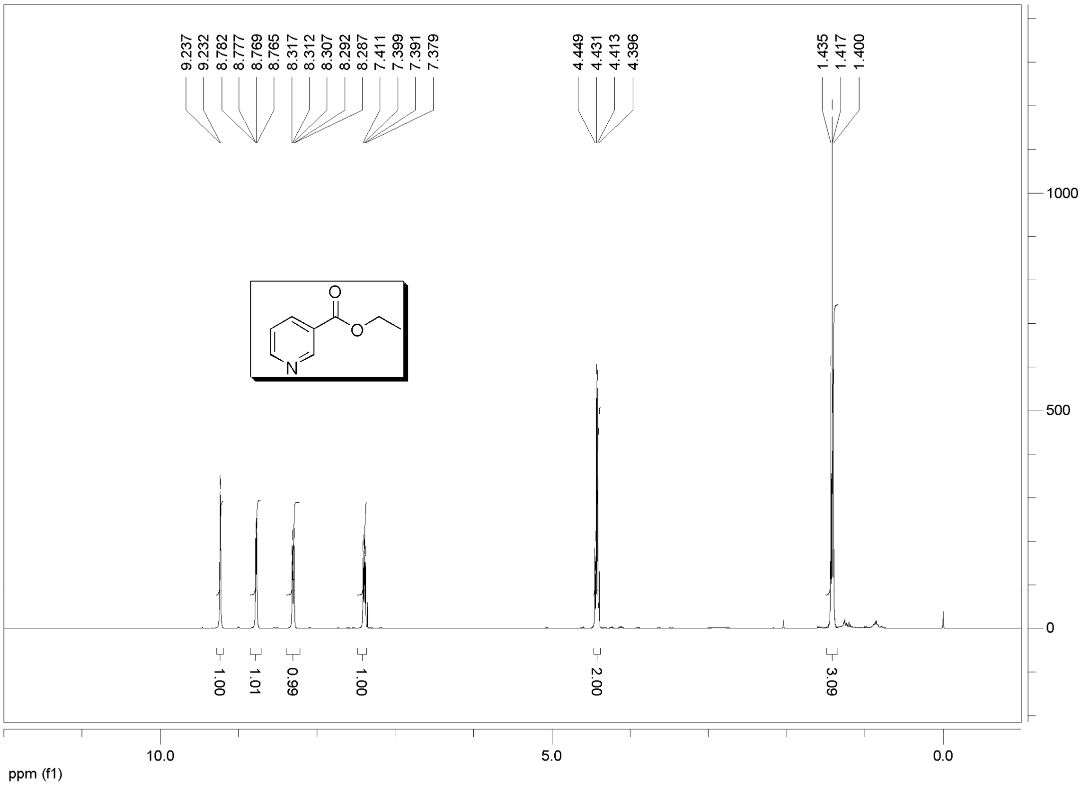


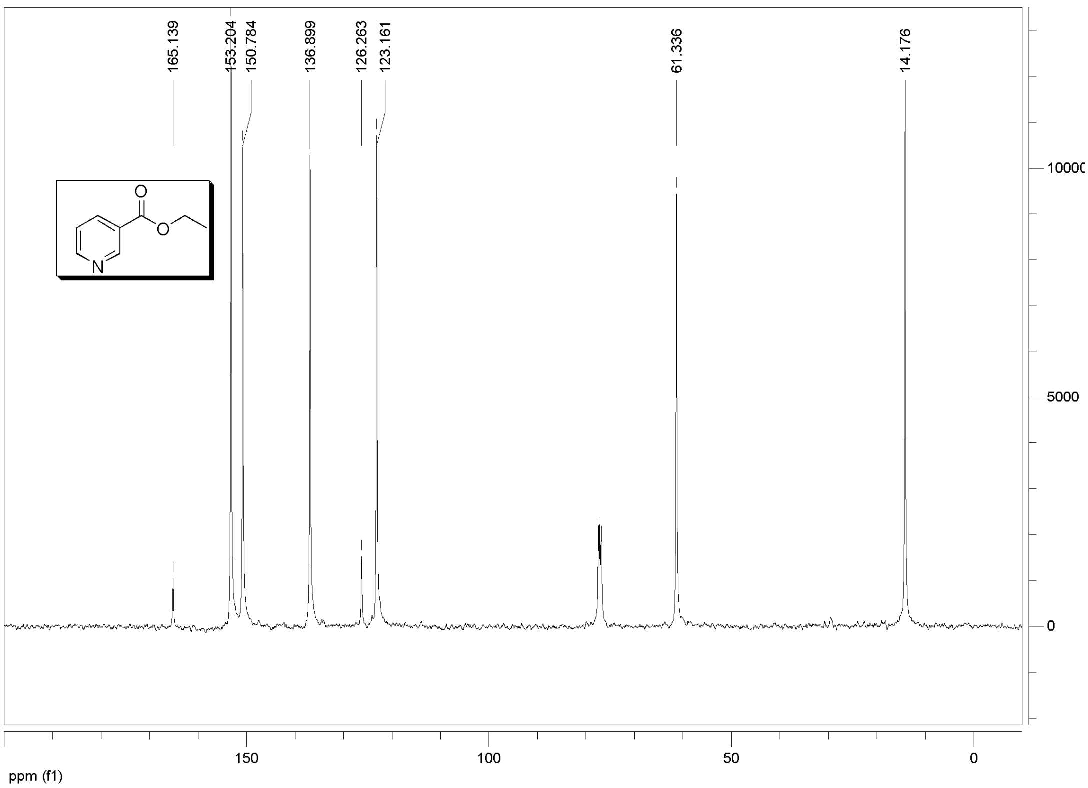
4-trifluoromethoxy-benzoic acid ethyl ester (12)



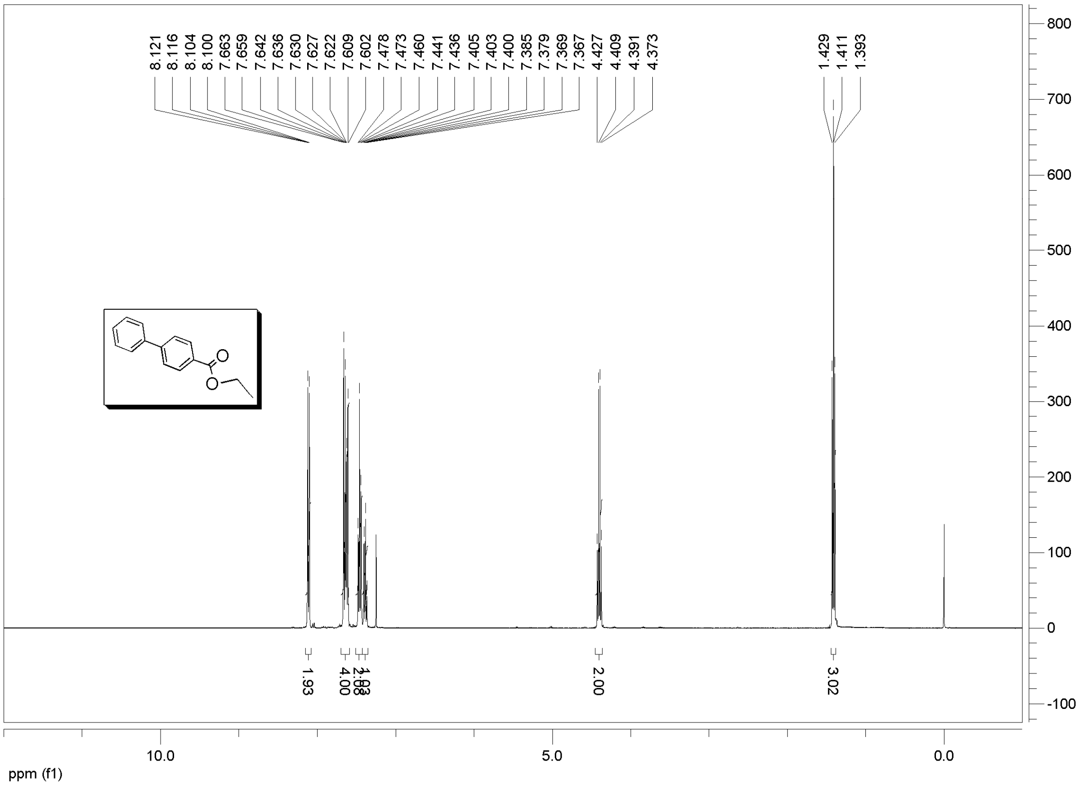


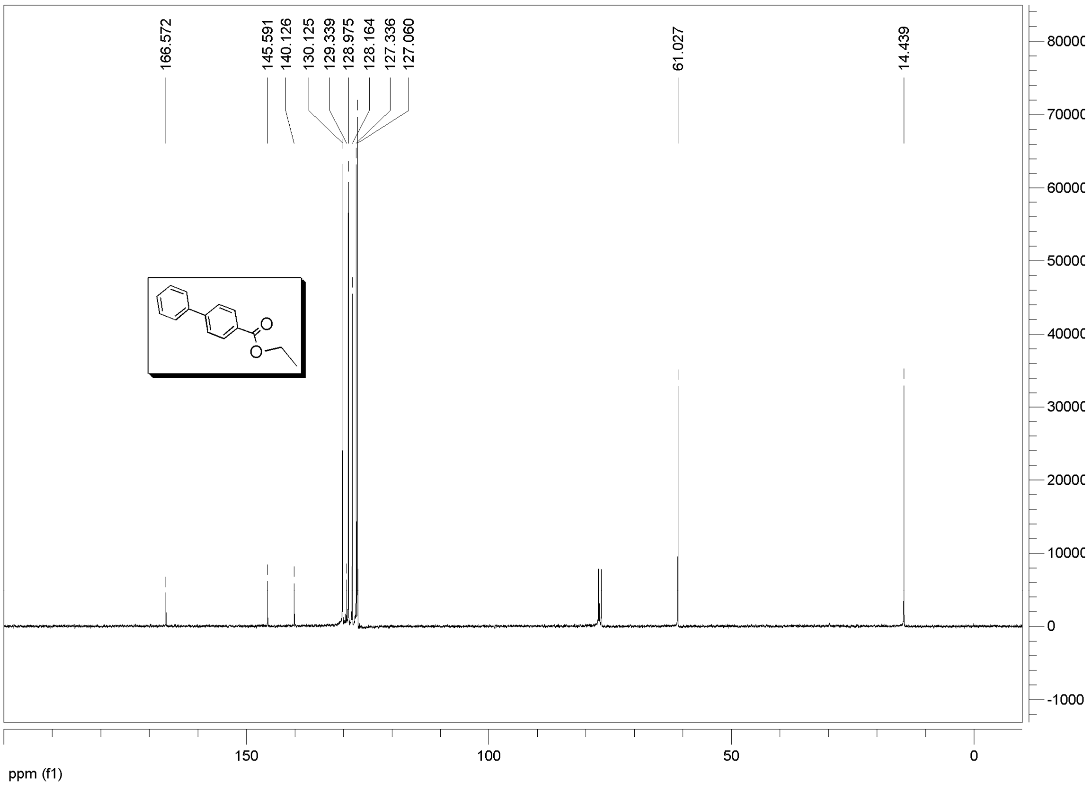
3-pyridinecarboxylic acid ethyl ester (13)



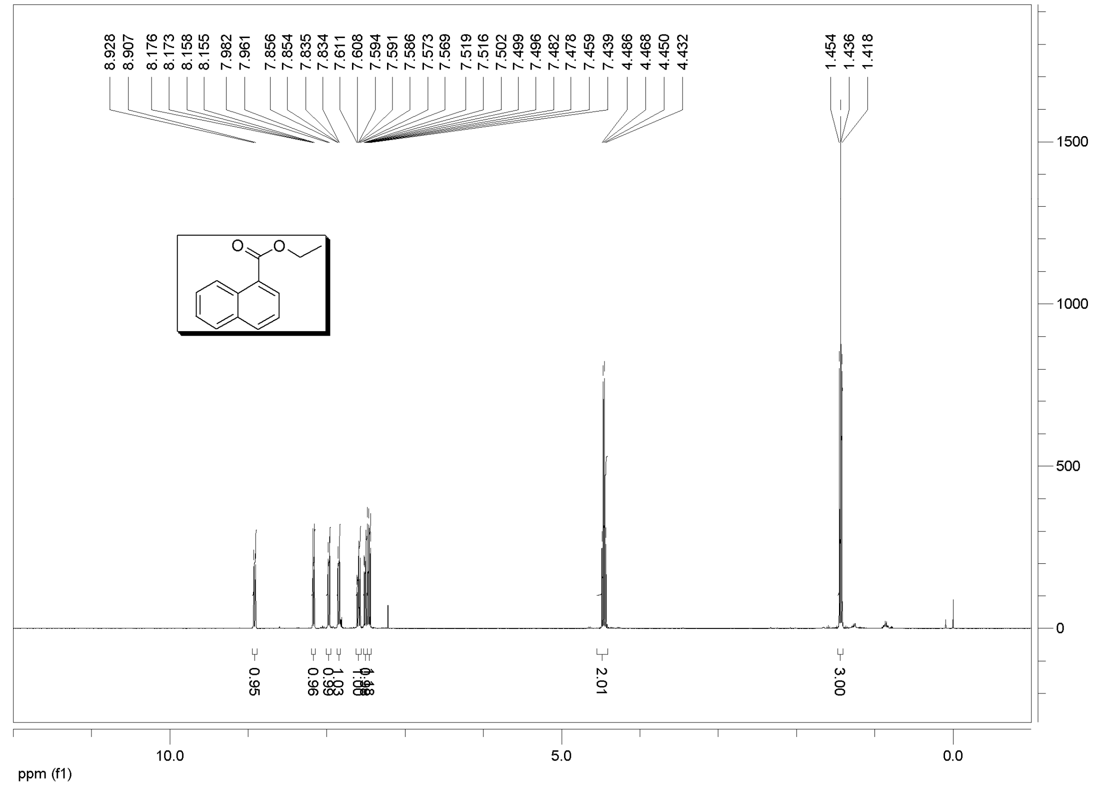


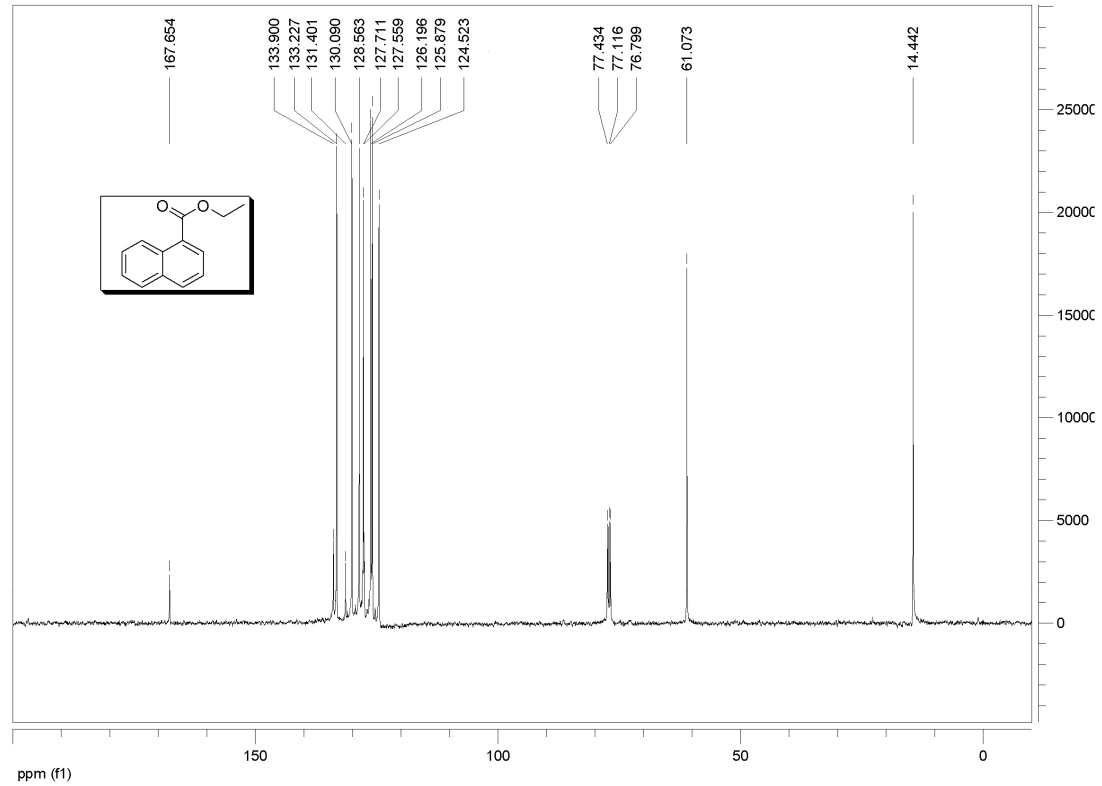
Biphenyl-4-carboxylic acid ethyl ester (14)



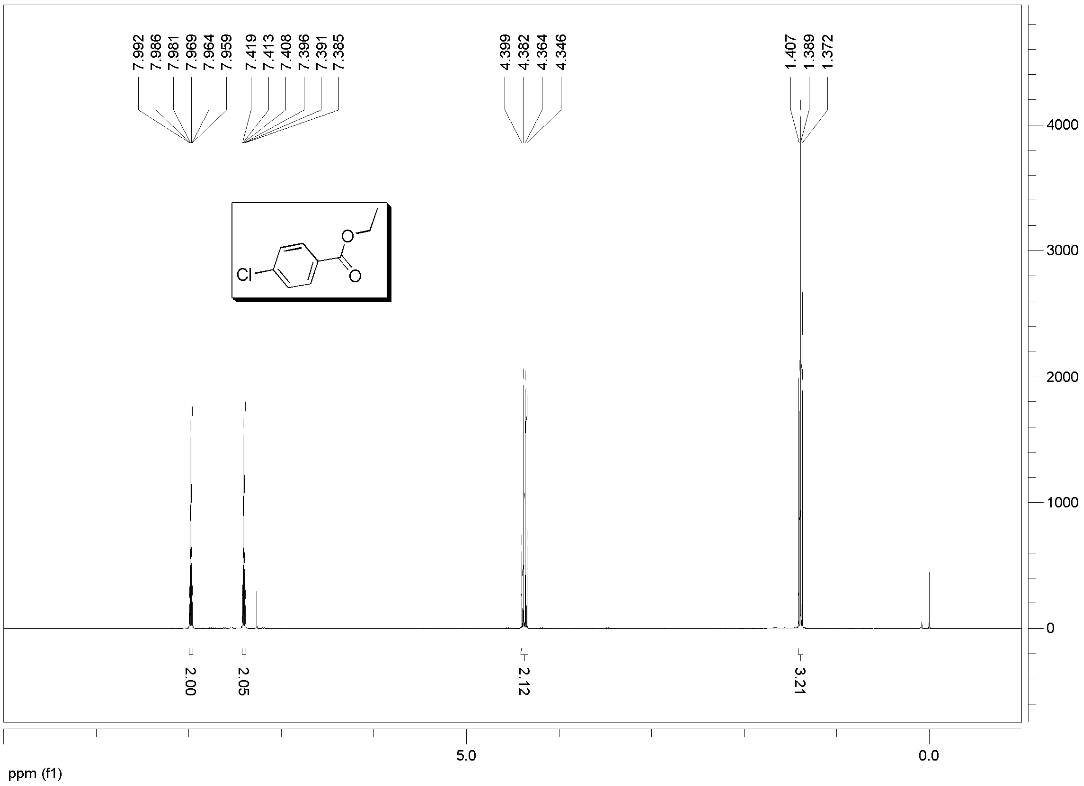


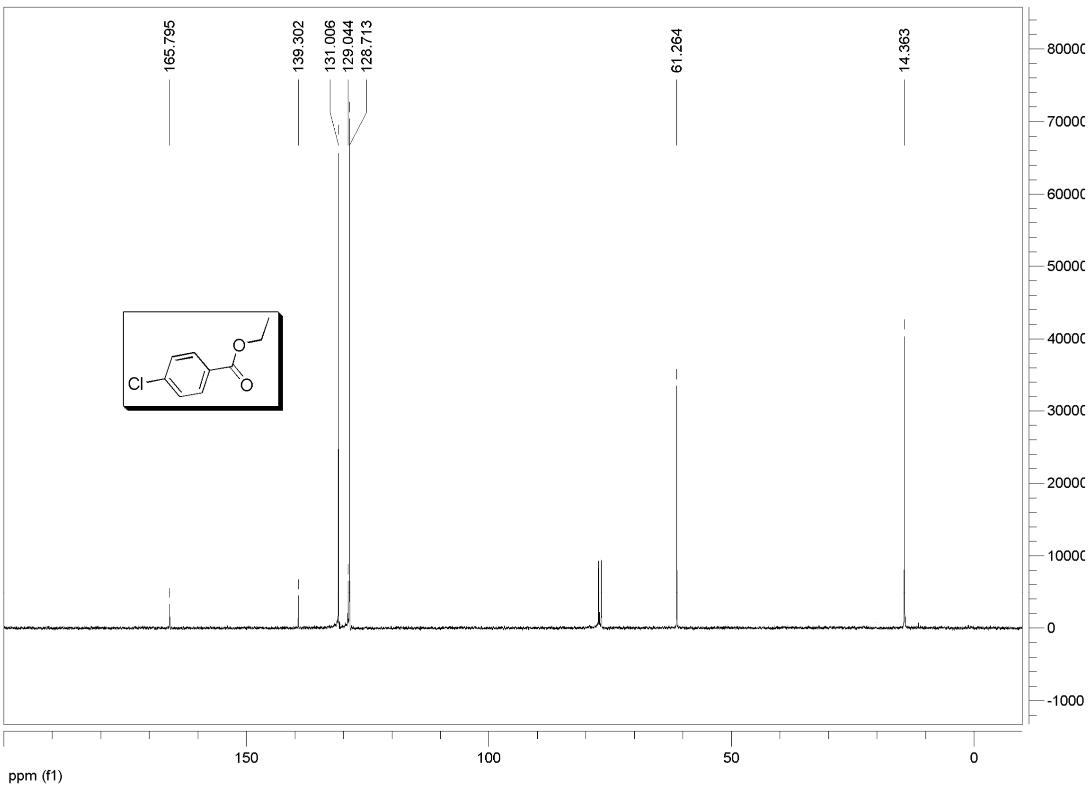
Naphthalene-1-carboxylic acid ethyl ester (15)



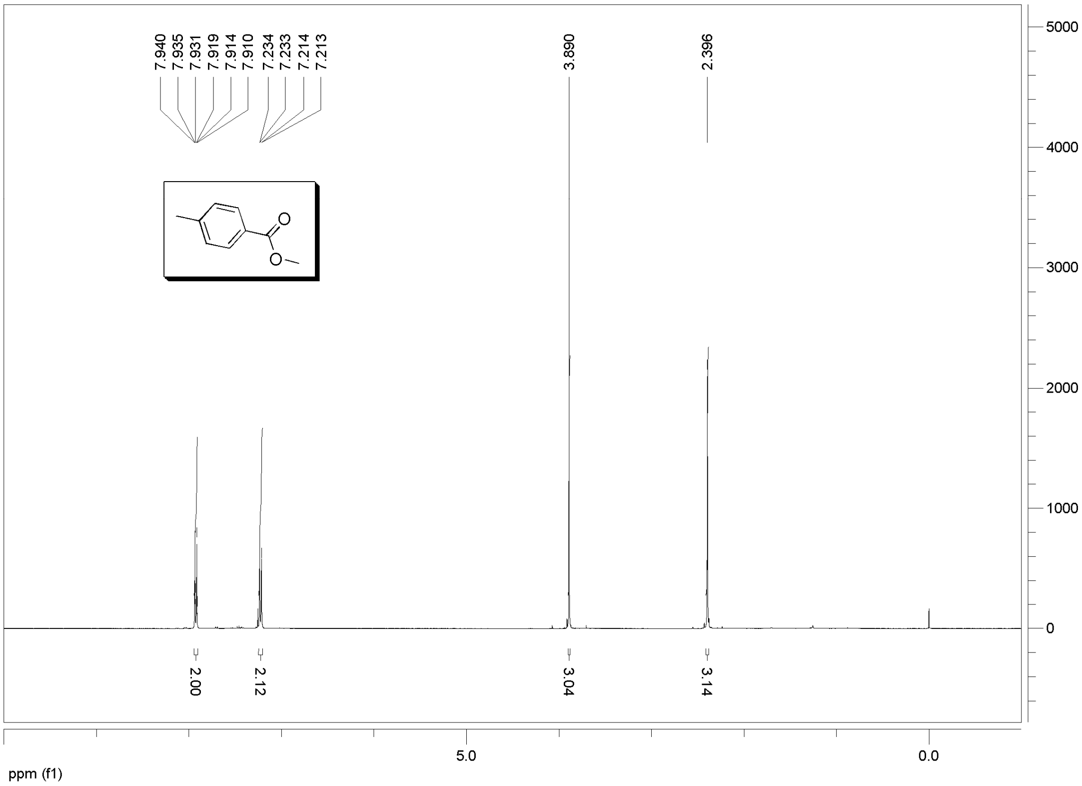


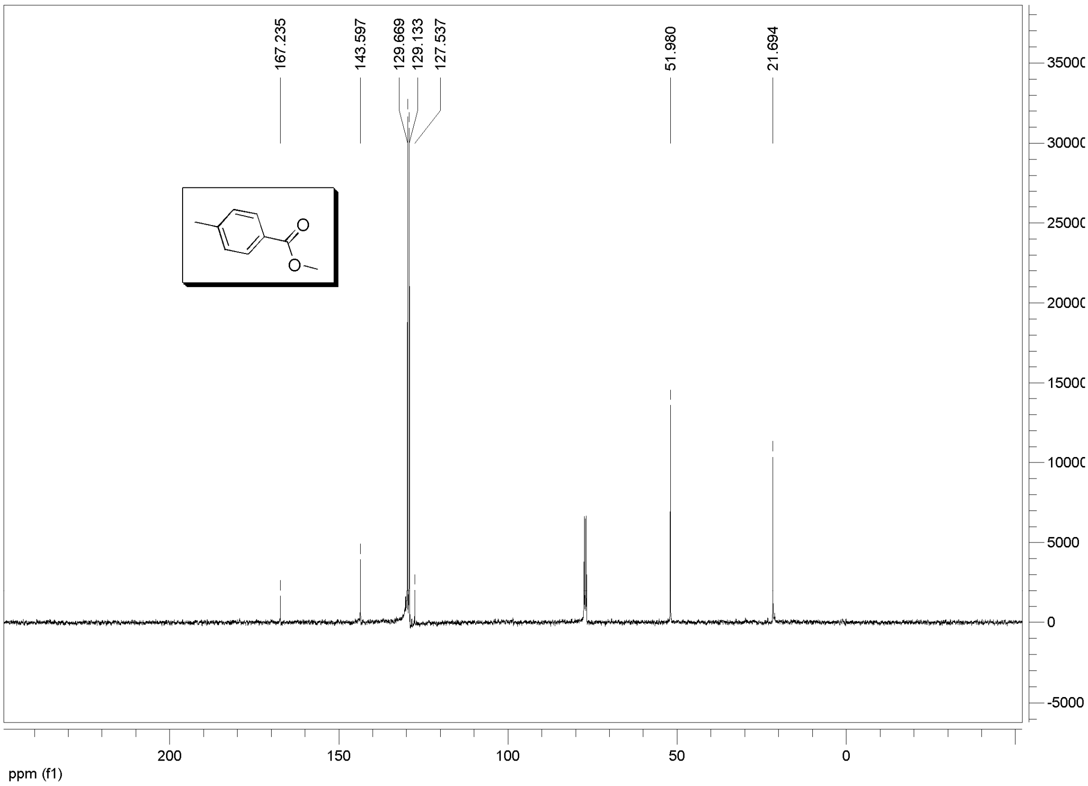
4-chlorobenzoic acid ethyl ester (16)



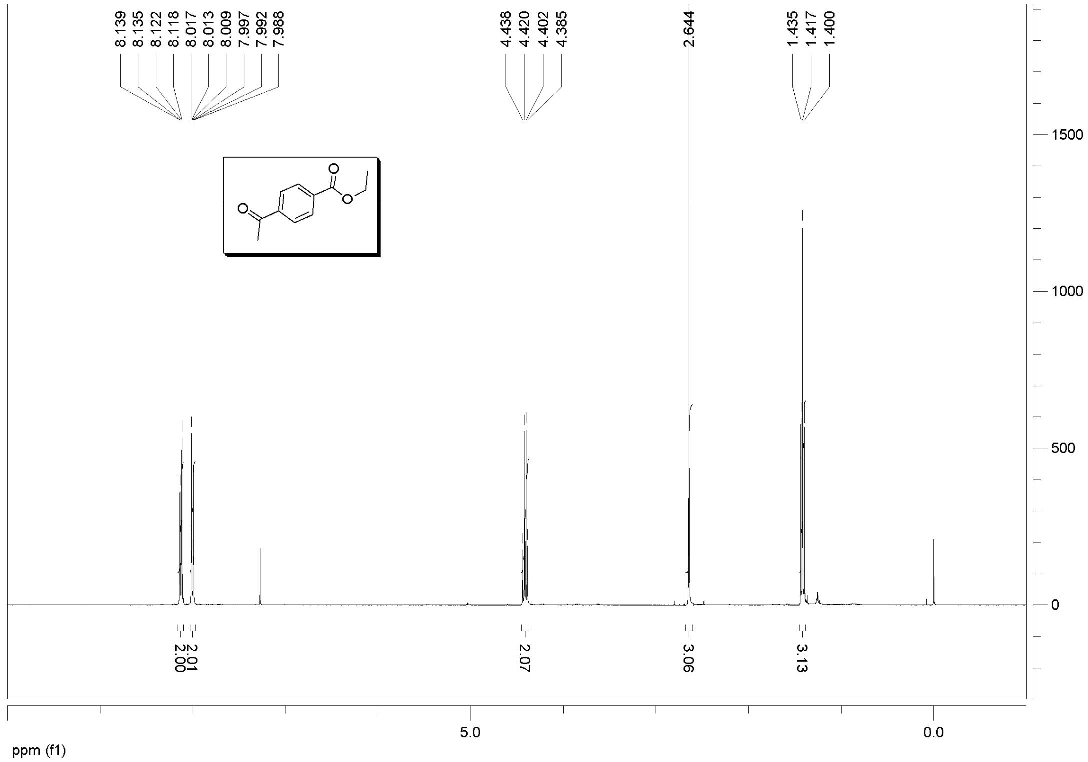


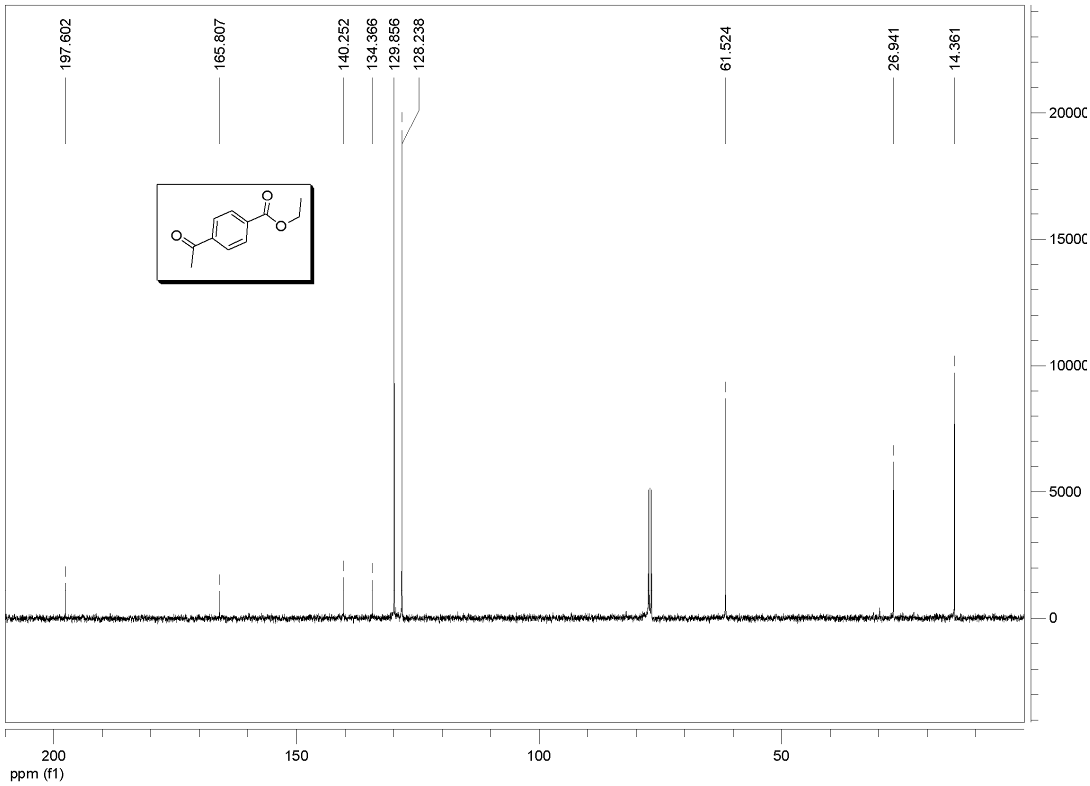
4-methylbenzoic acid methyl ester (17)



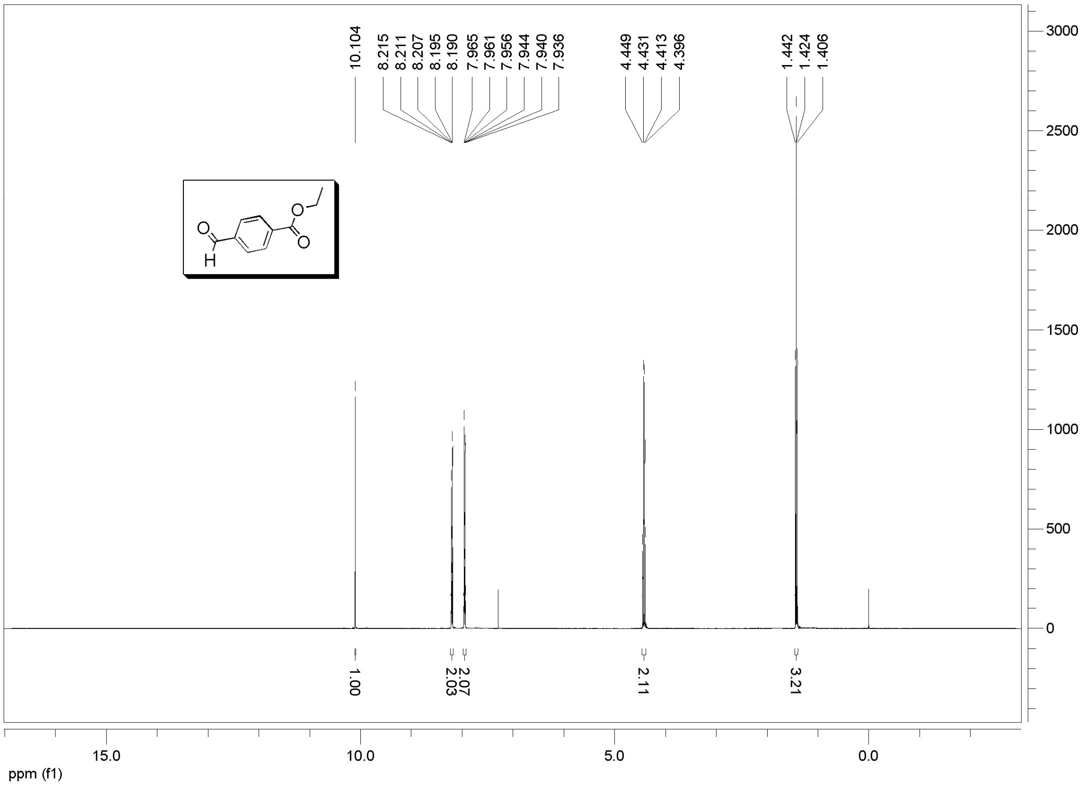


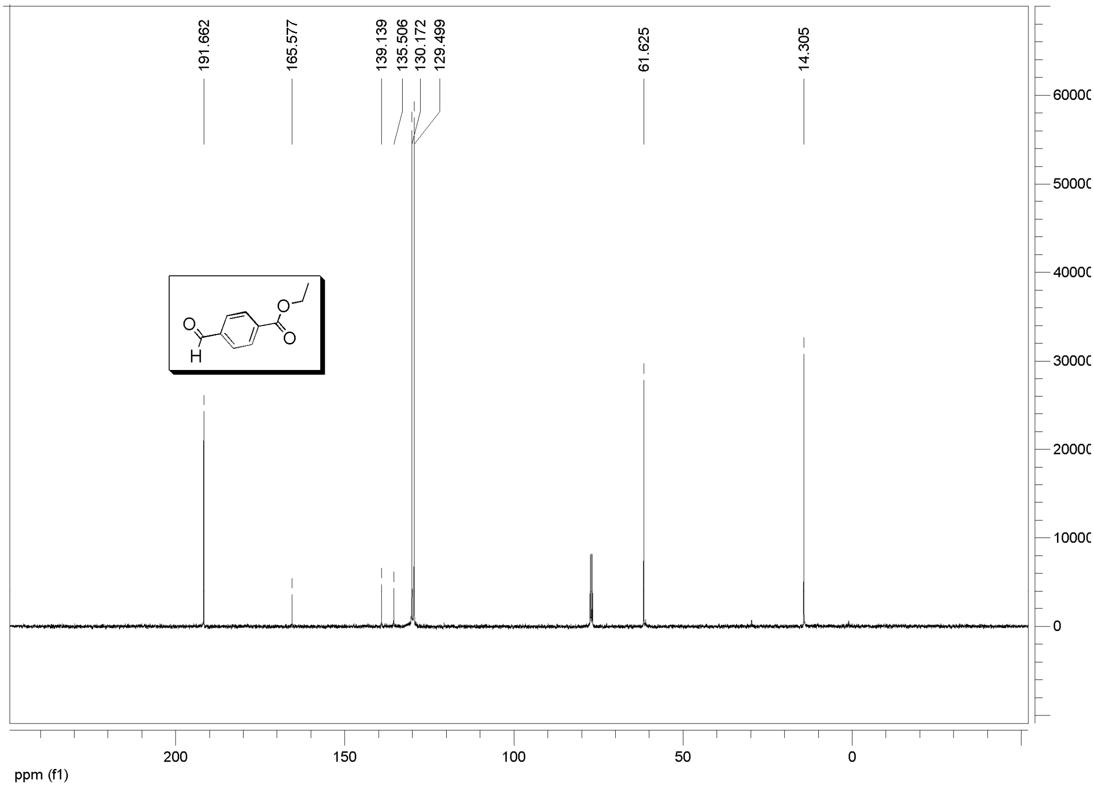
4-acetylbenzoic acid ethyl ester (18)



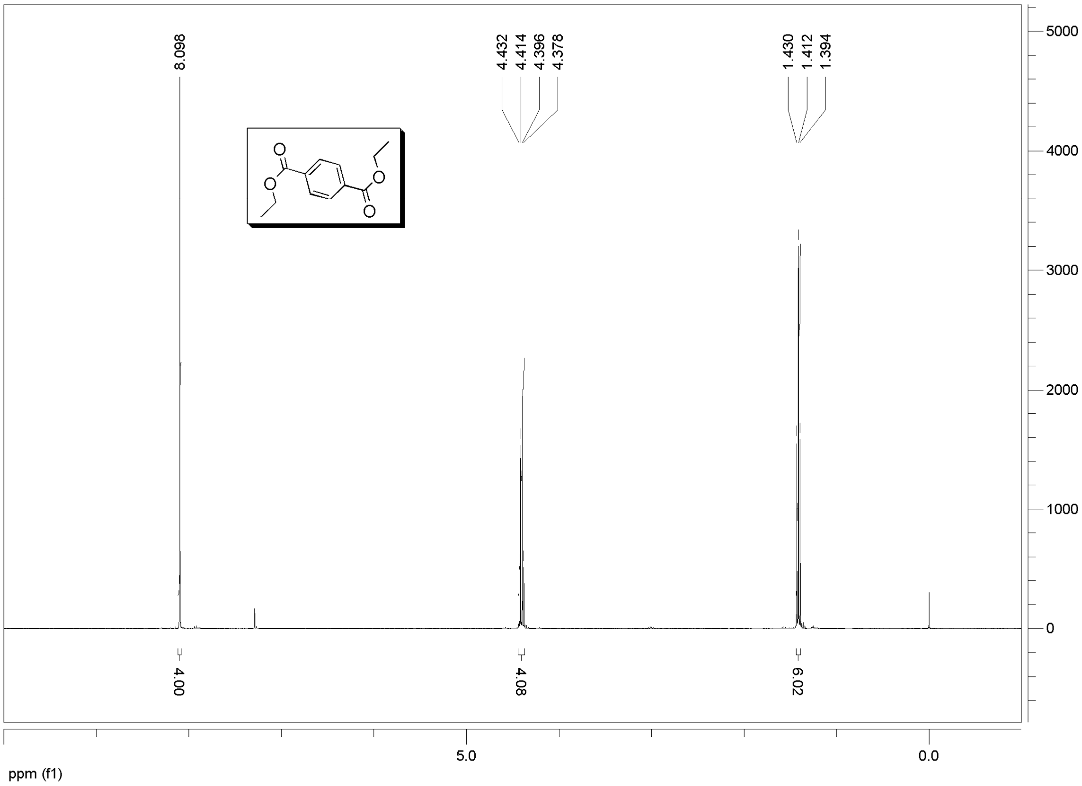


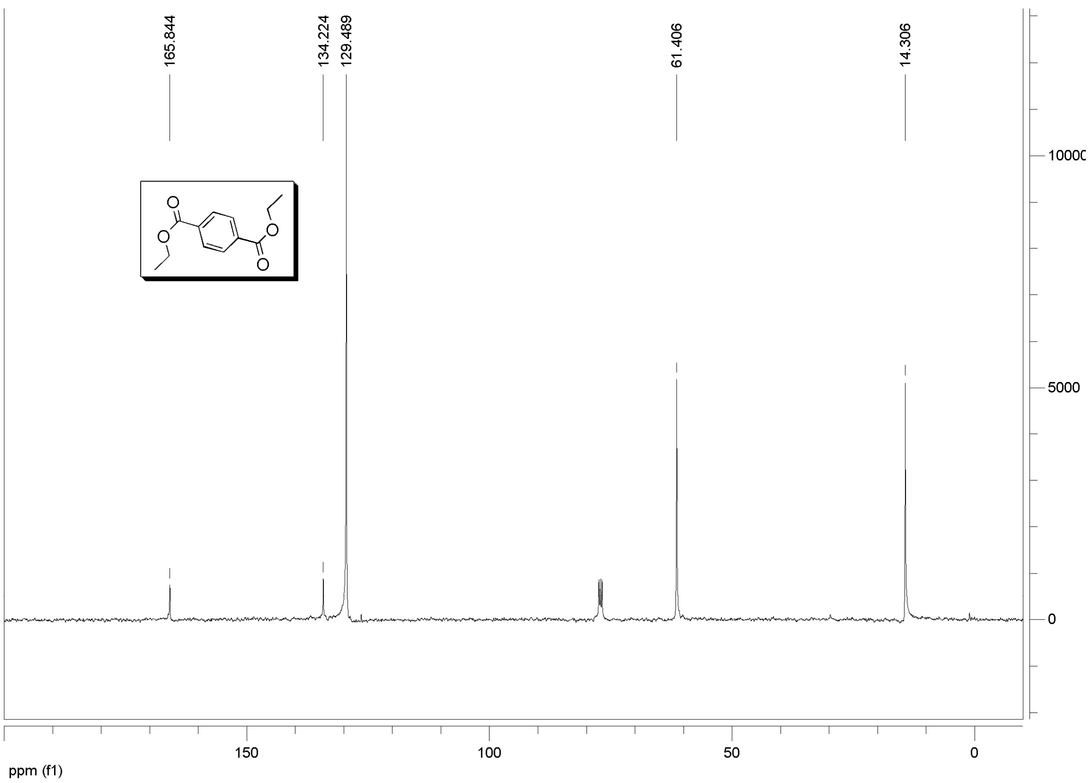
4-formylbenzoic acid ethyl ester (19)



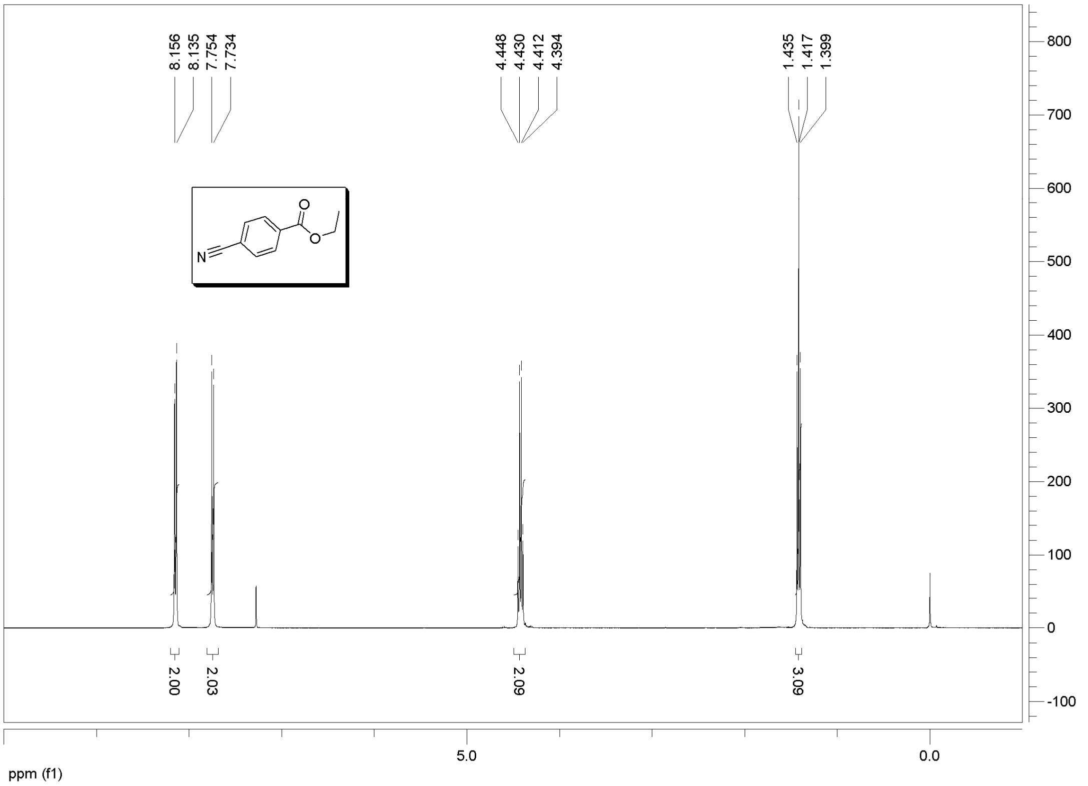


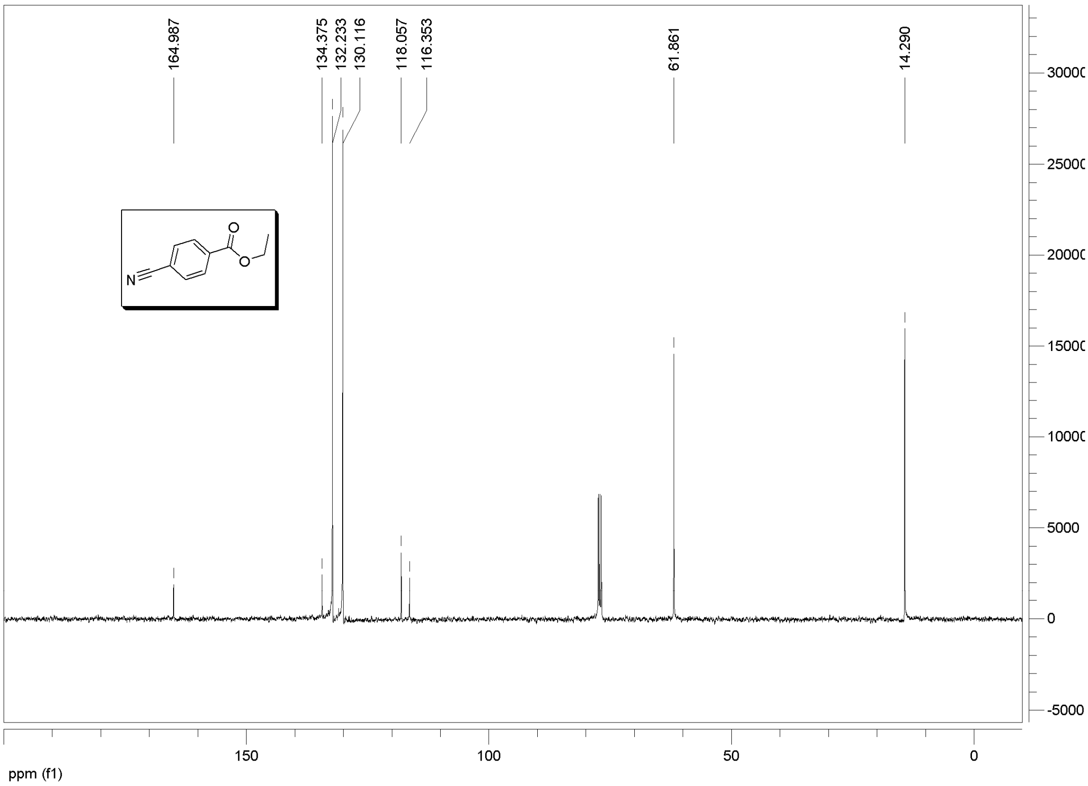
1,4-benzenedicarboxylic acid diethyl ester (20)



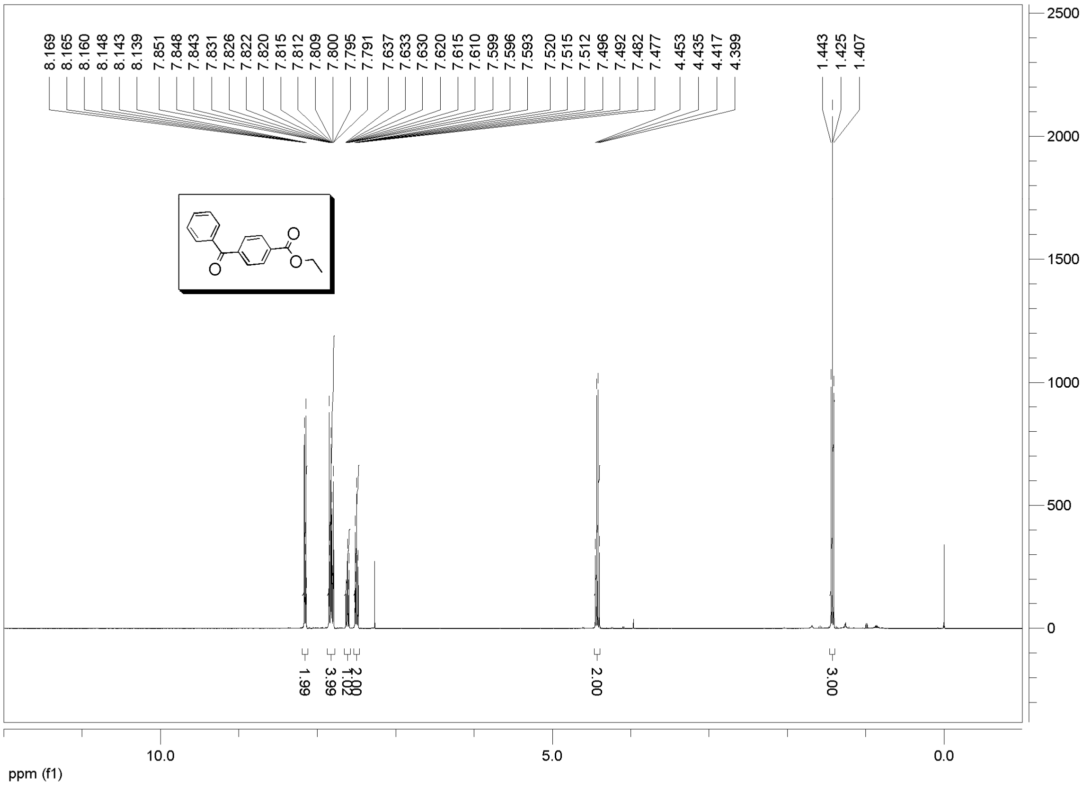


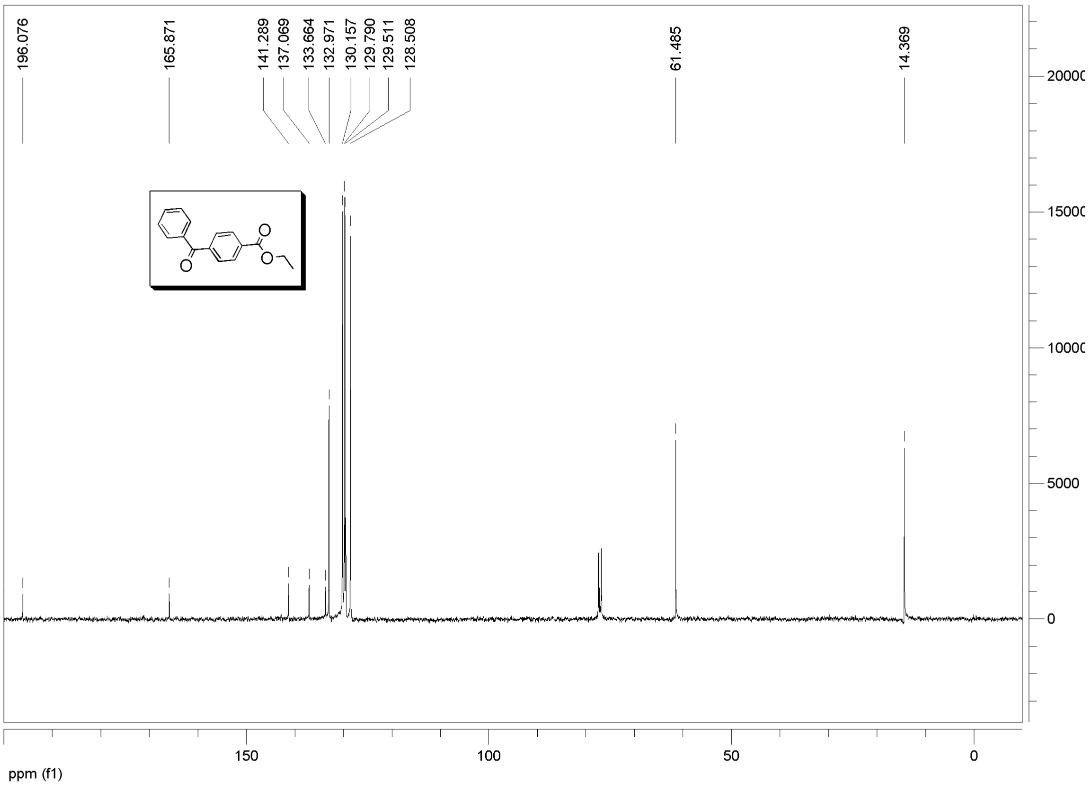
4-Cyano-benzoic acid ethyl ester (21)



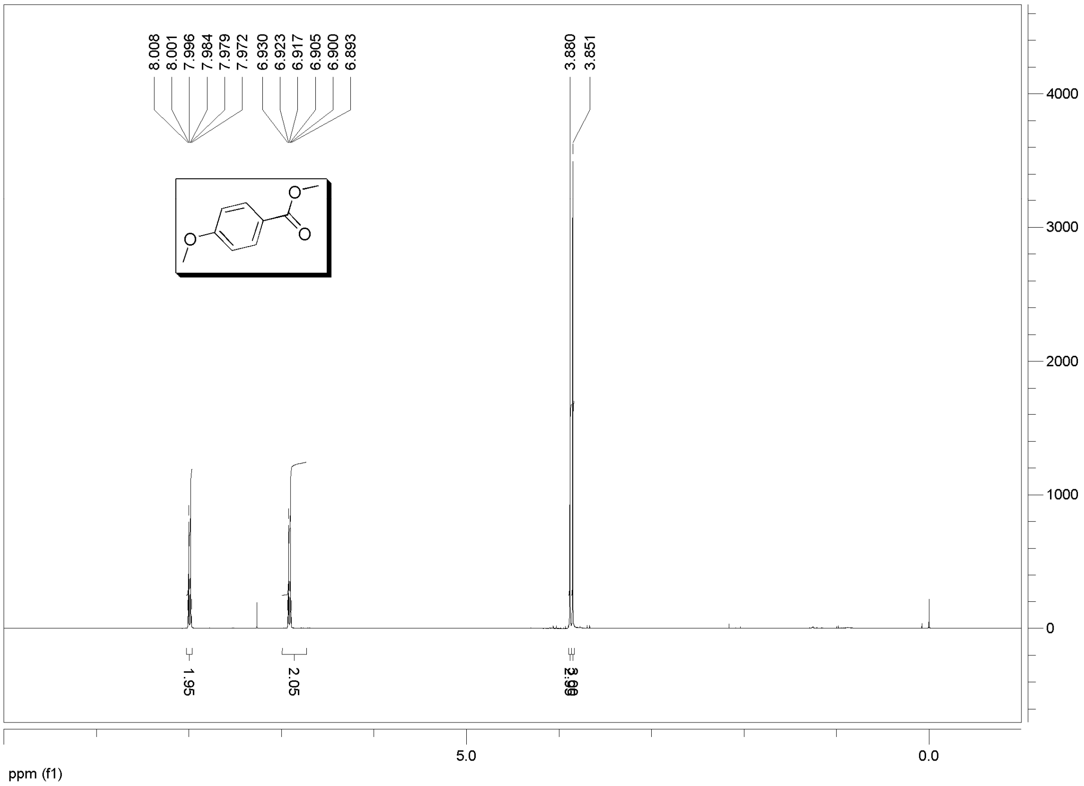


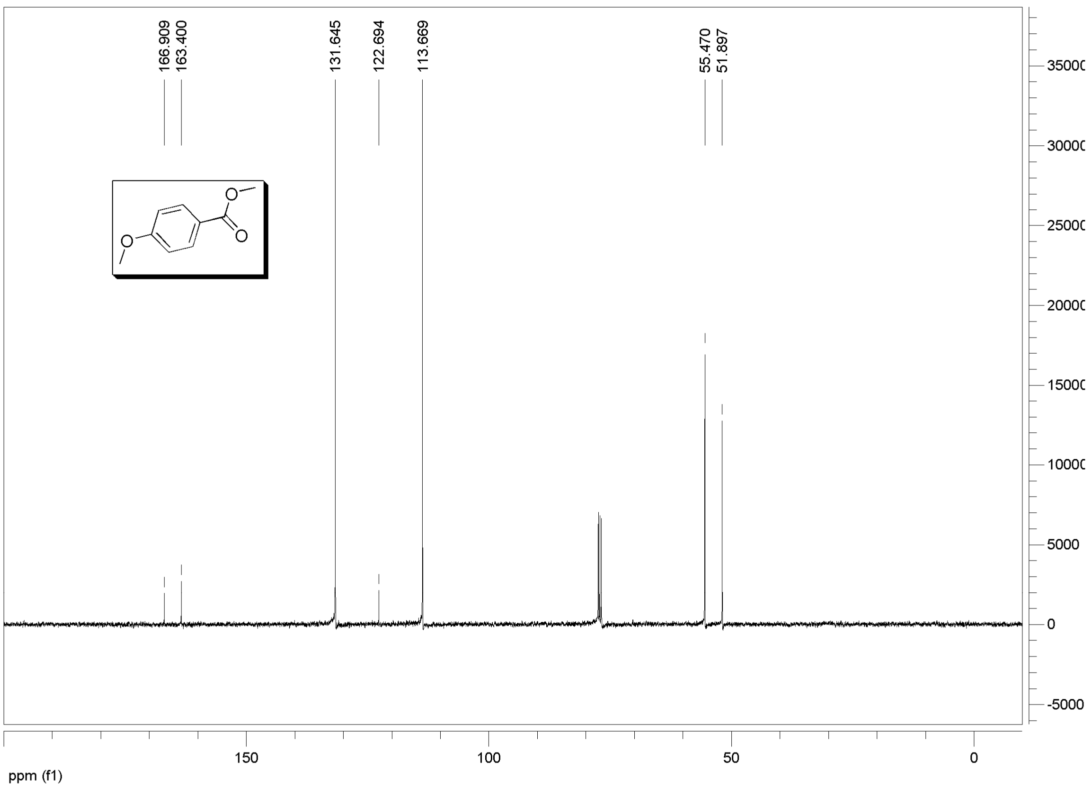
4-ethoxycarbonylbenzophenone (22)



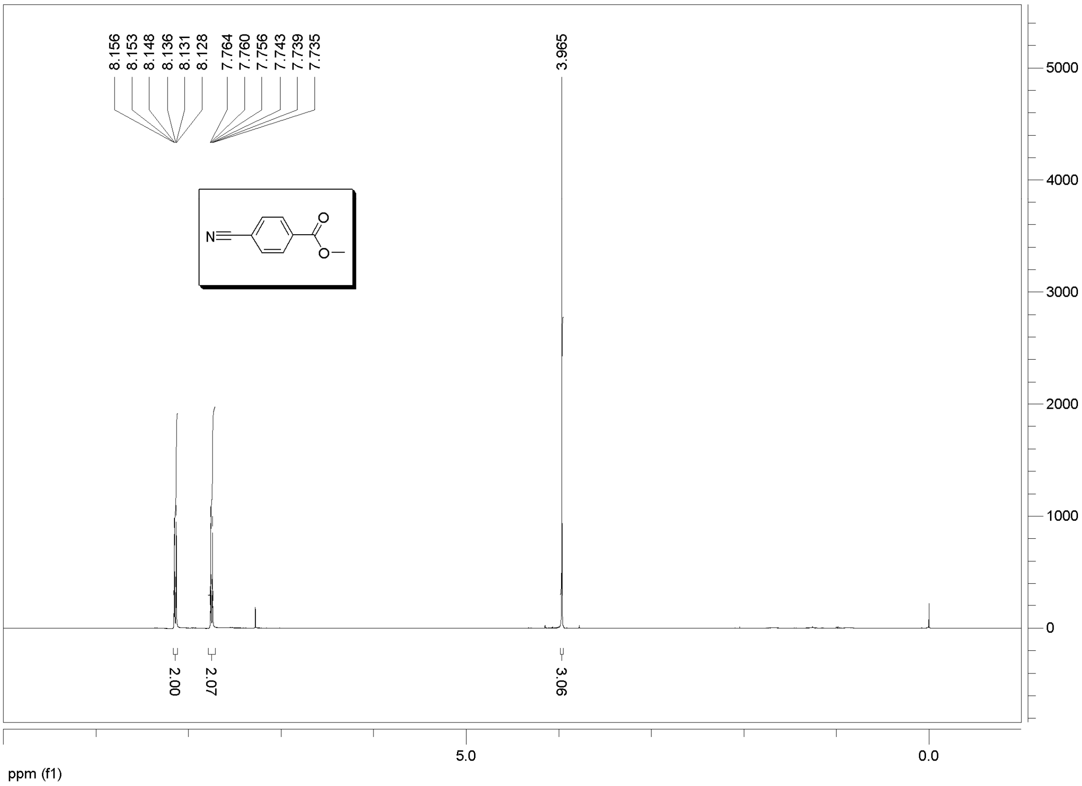


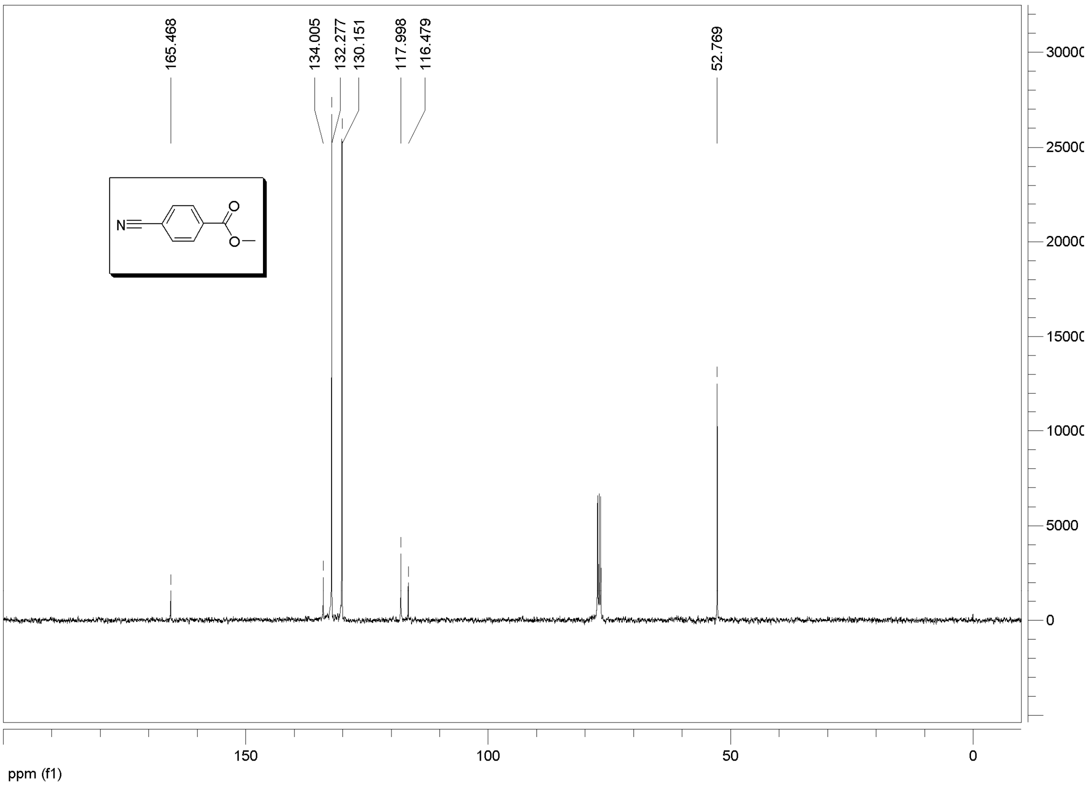
4-methoxybenzoic acid methyl ester (23)



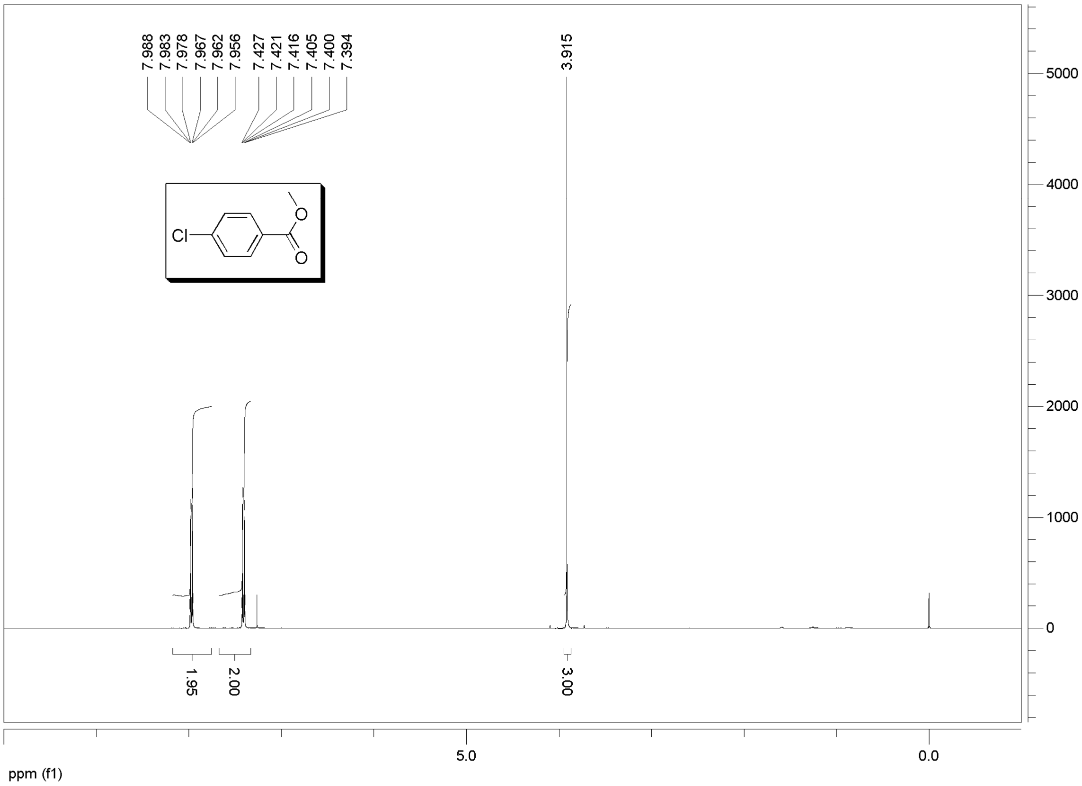


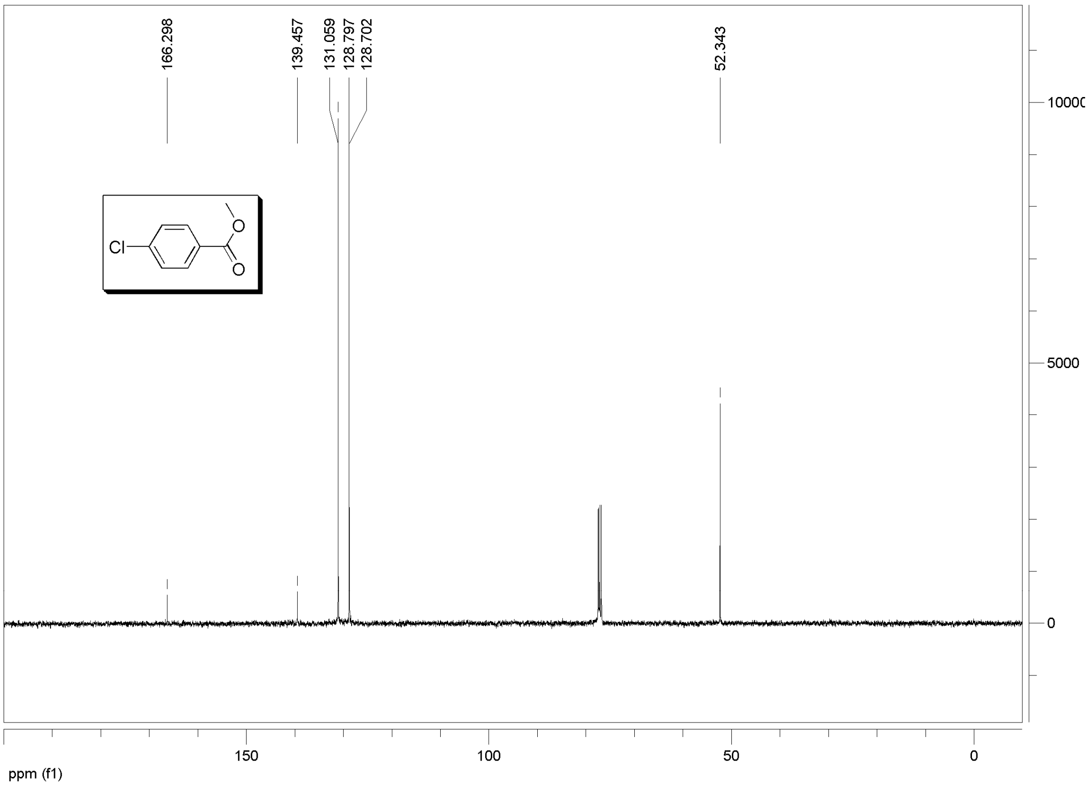
4-cyano-benzoic acid methyl ester (24)



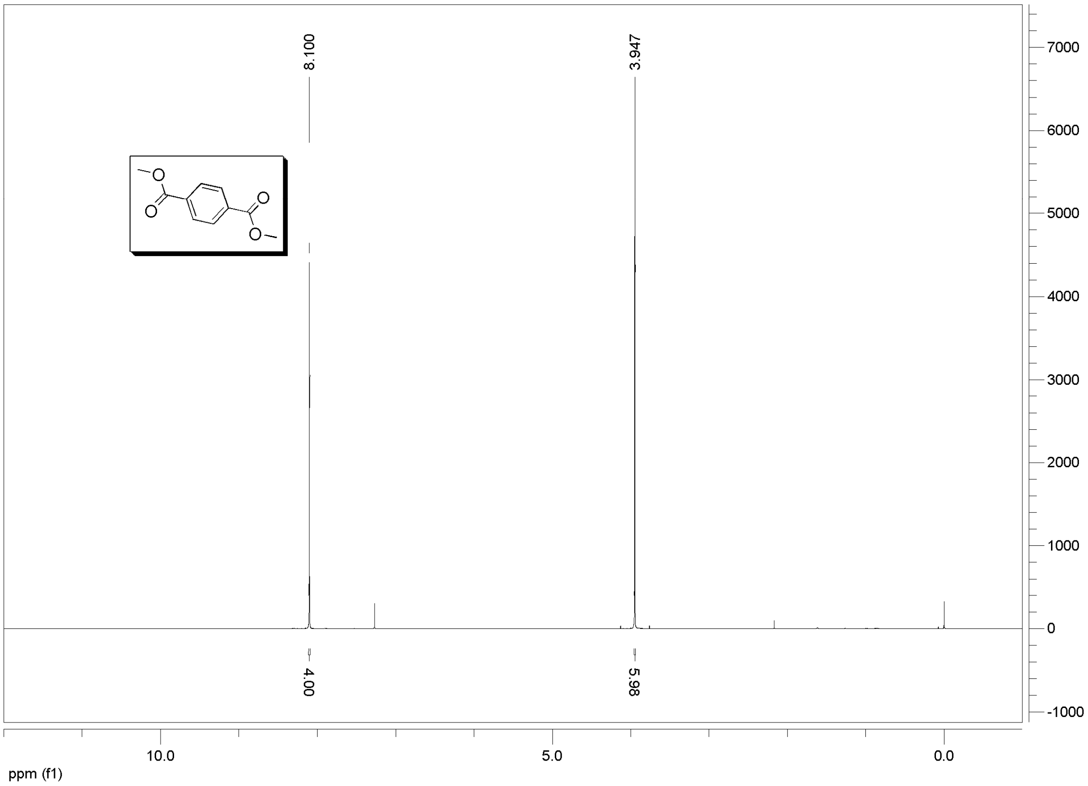


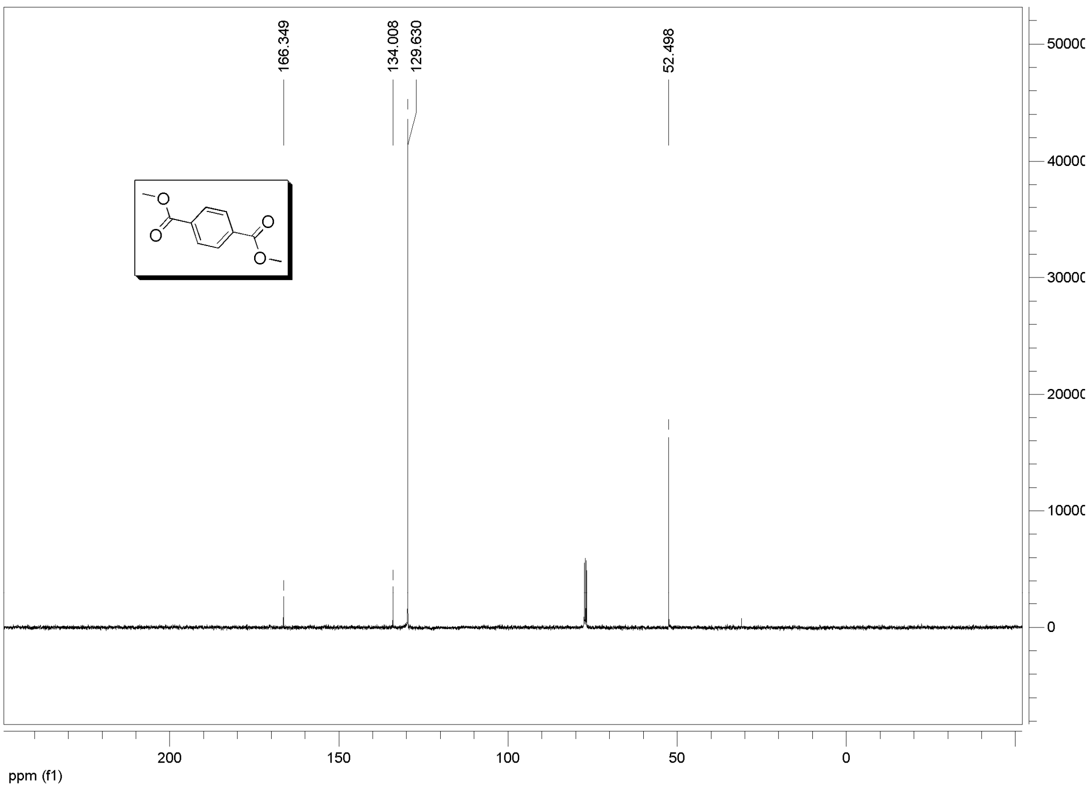
4-chloro-benzoic acid methyl ester (25)



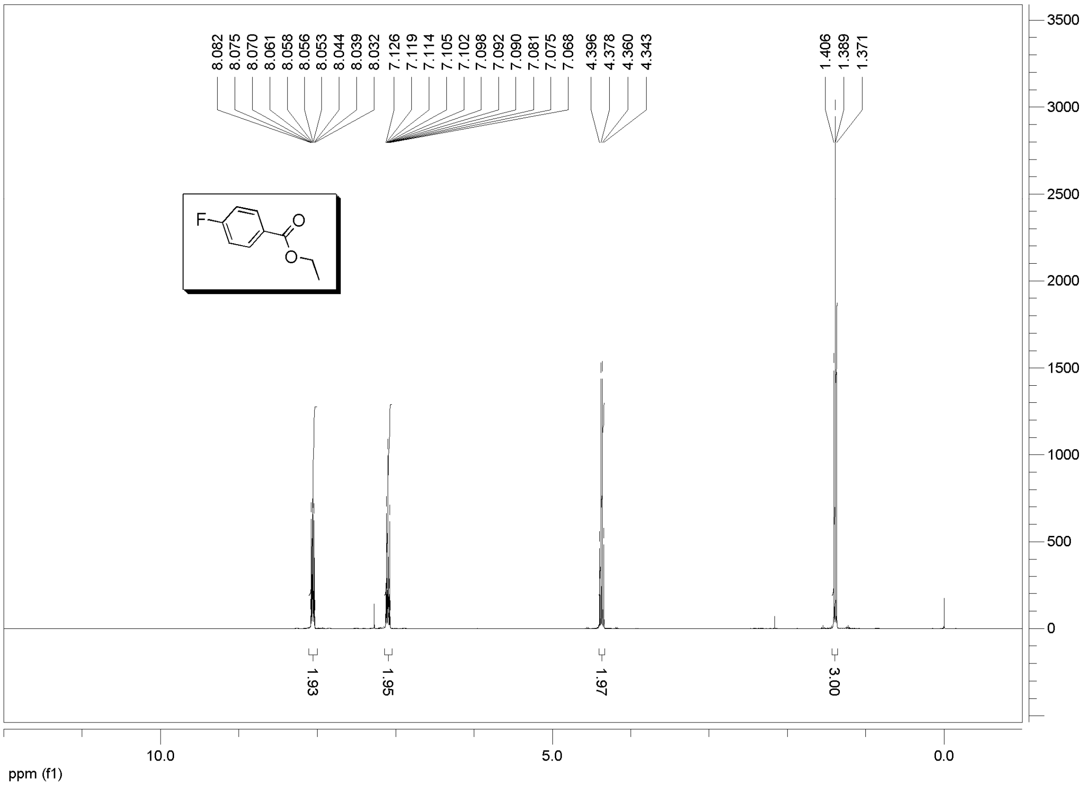


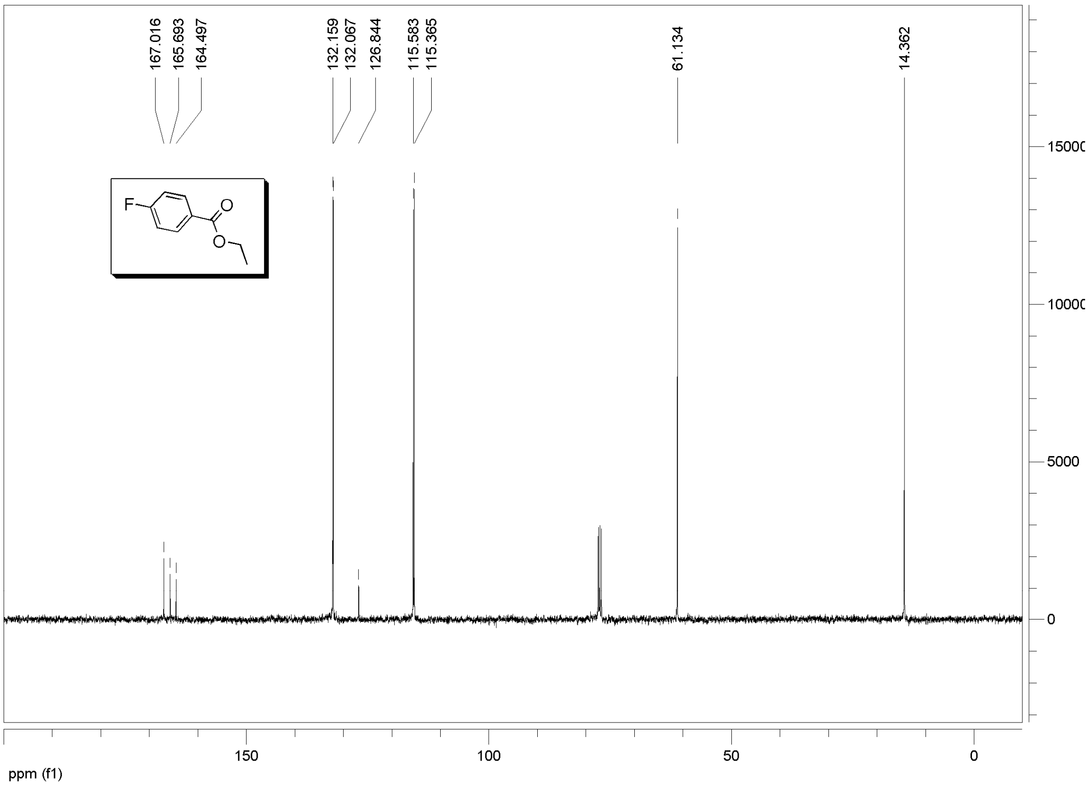
1,4-benzenedicarboxylic acid dimethyl ester (26)



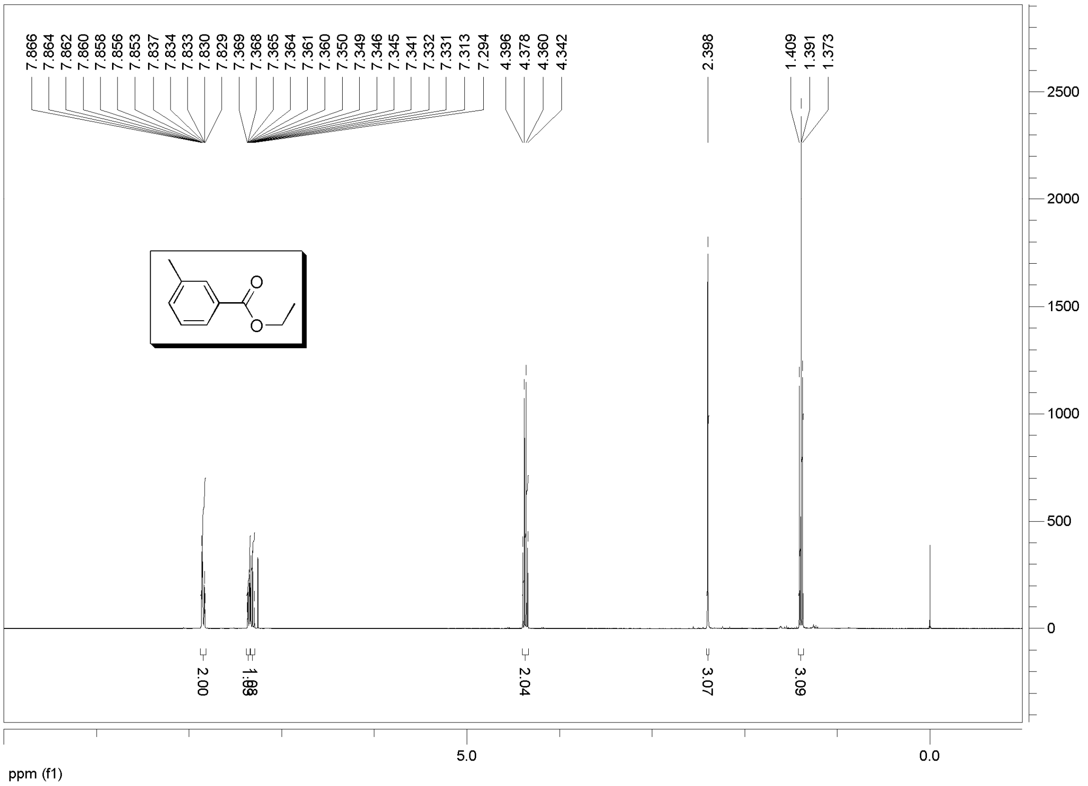


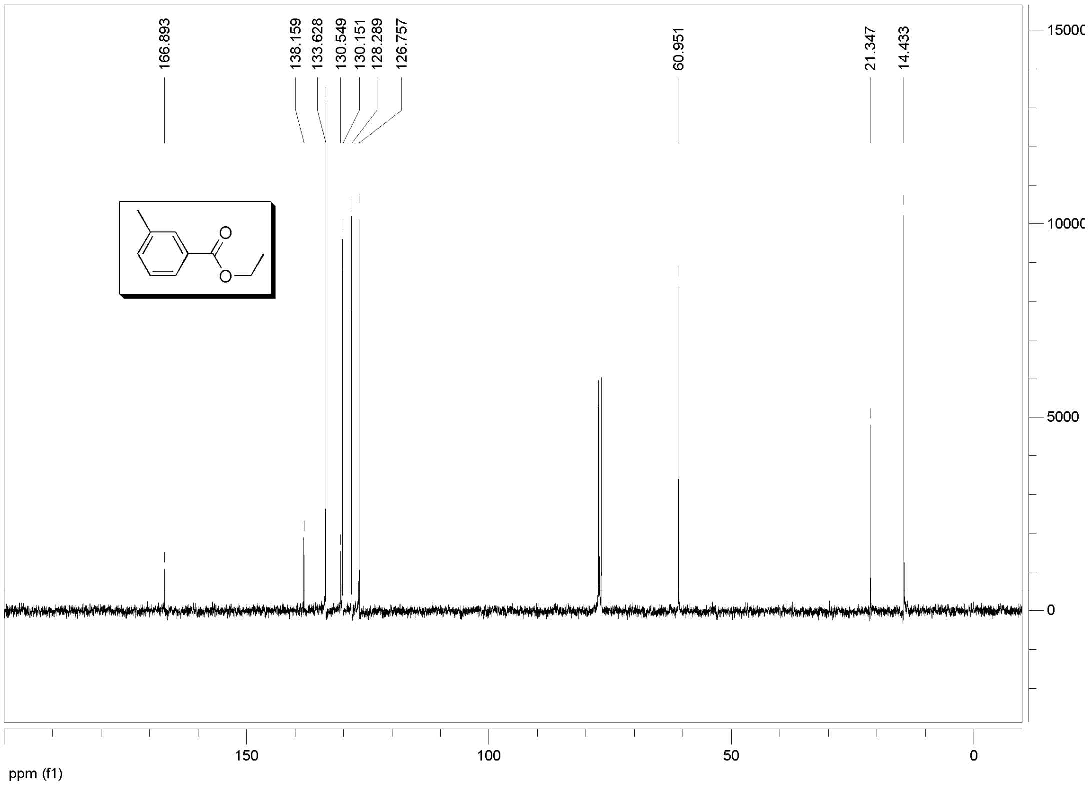
4-fluorobenzoic acid ethyl ester (27)



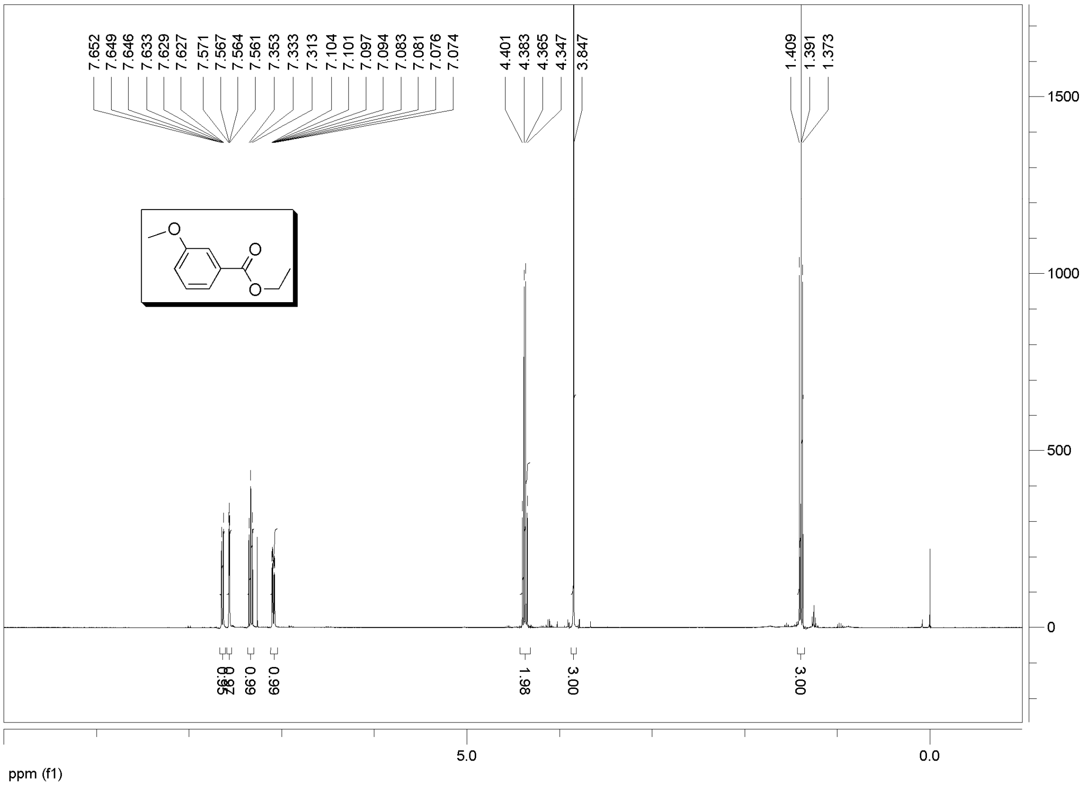


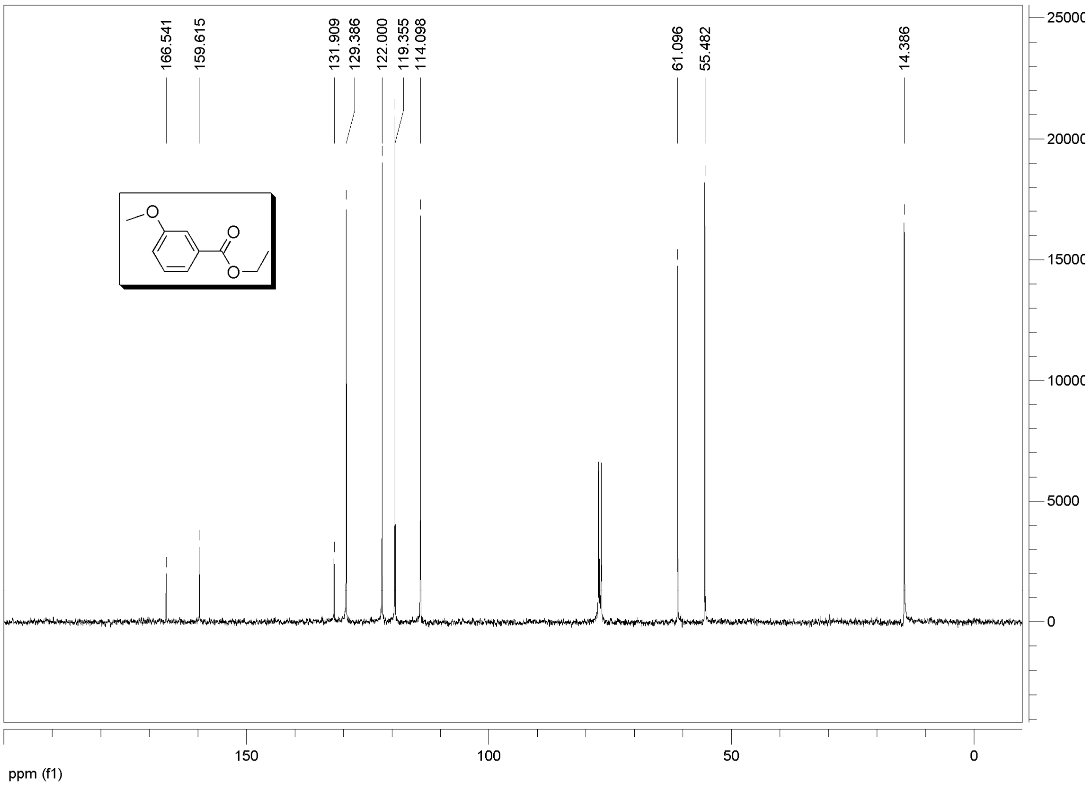
3-methylbenzoic acid ethyl ester (28)



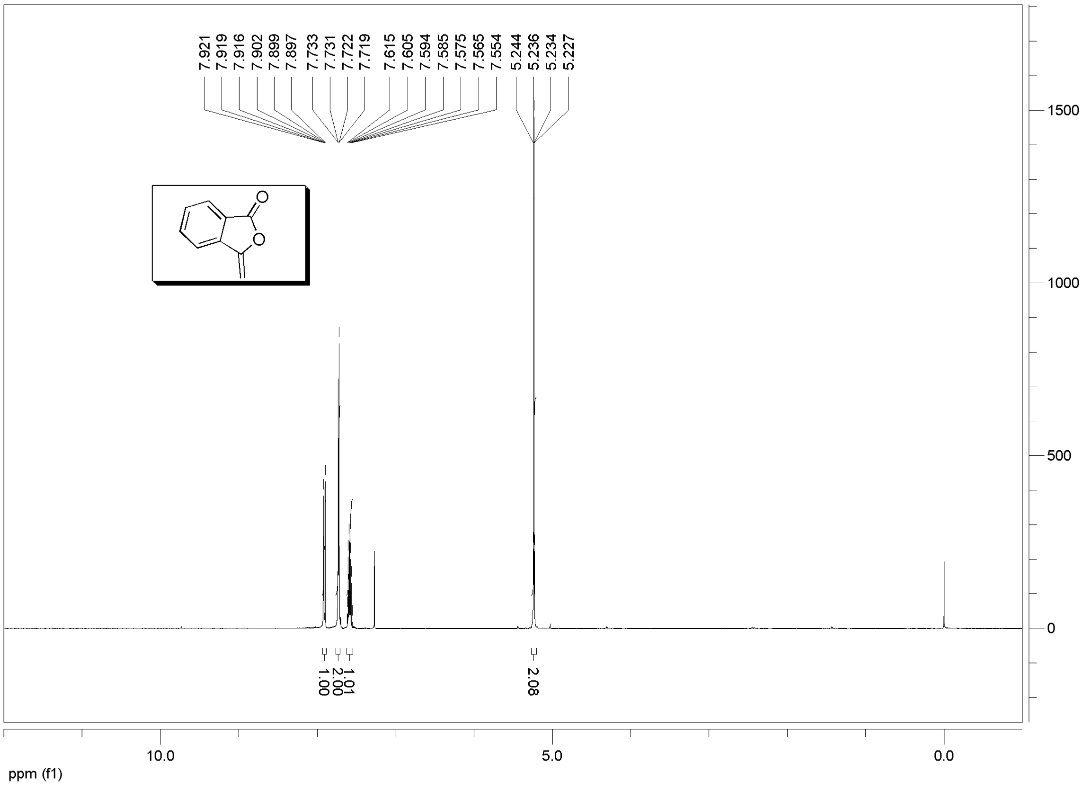


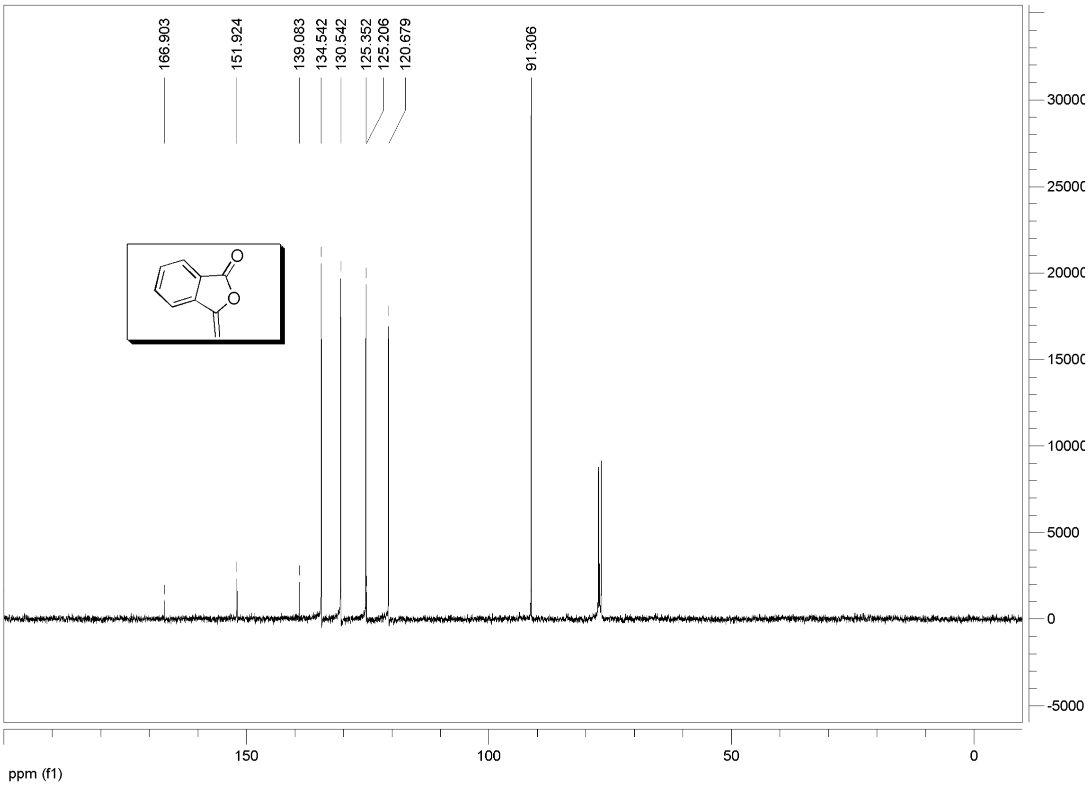
3-methoxybenzoic acid ethyl ester (29)



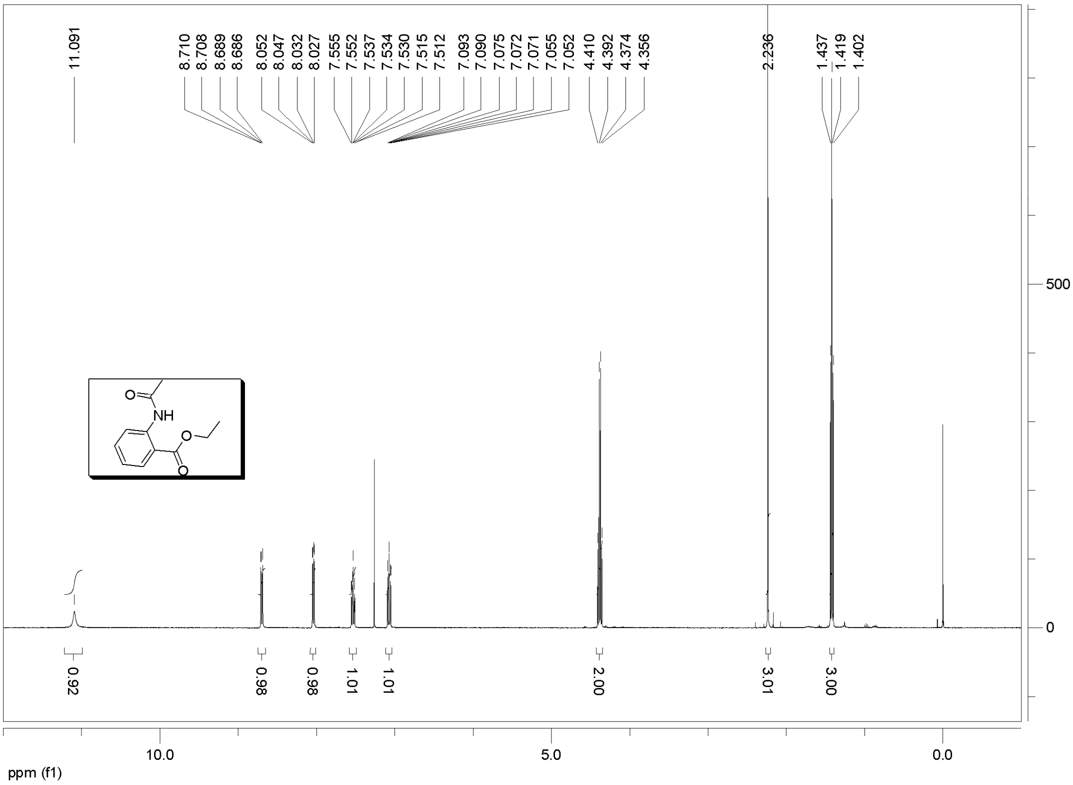


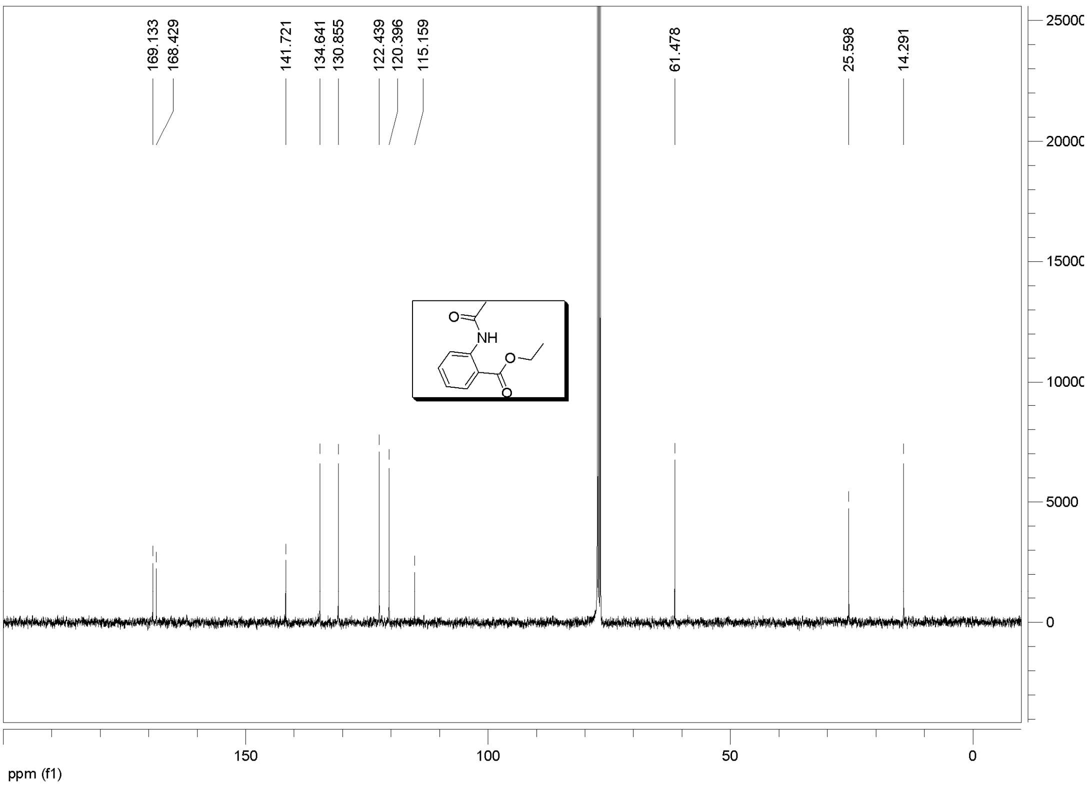
3-methylidene-3H-isobenzofuran-1-one (30)



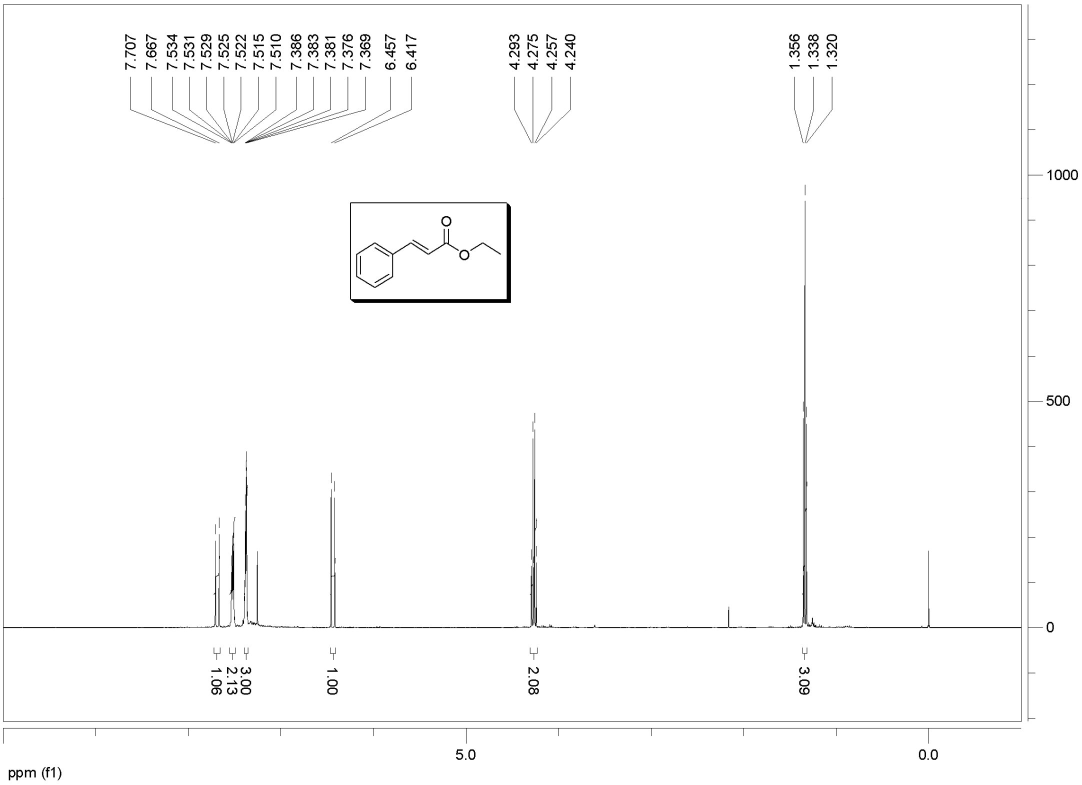


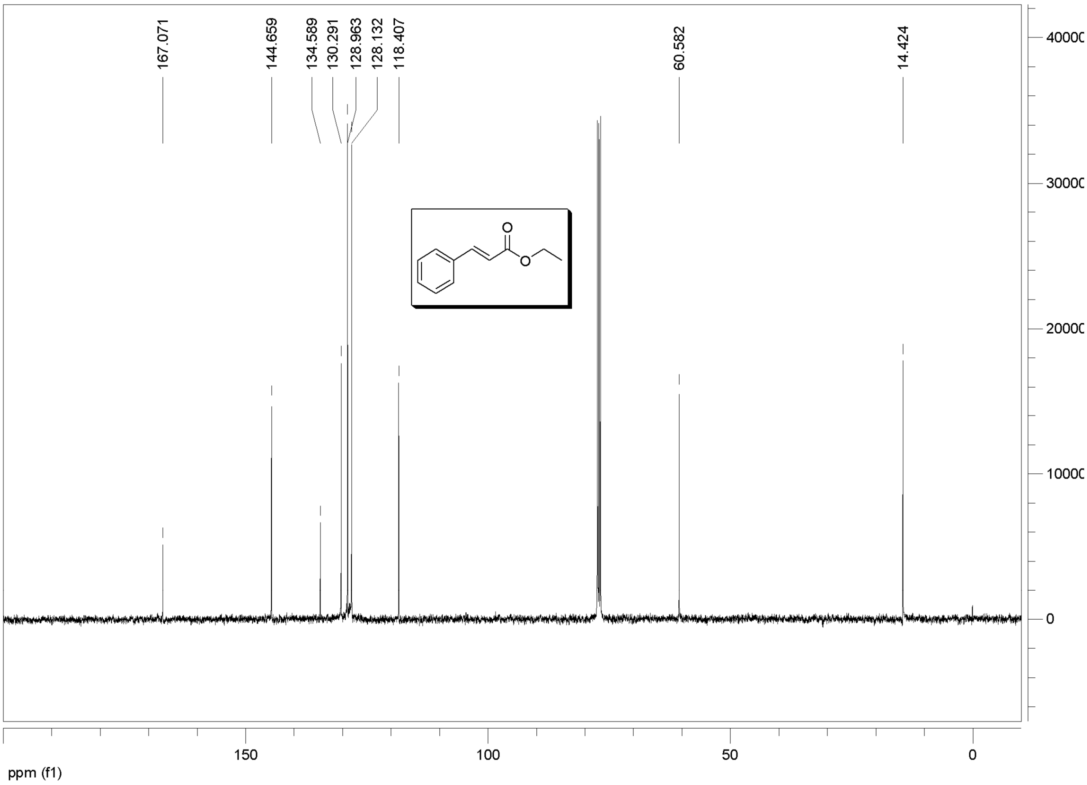
2-acetylamino benzoic acid ethyl ester (31)

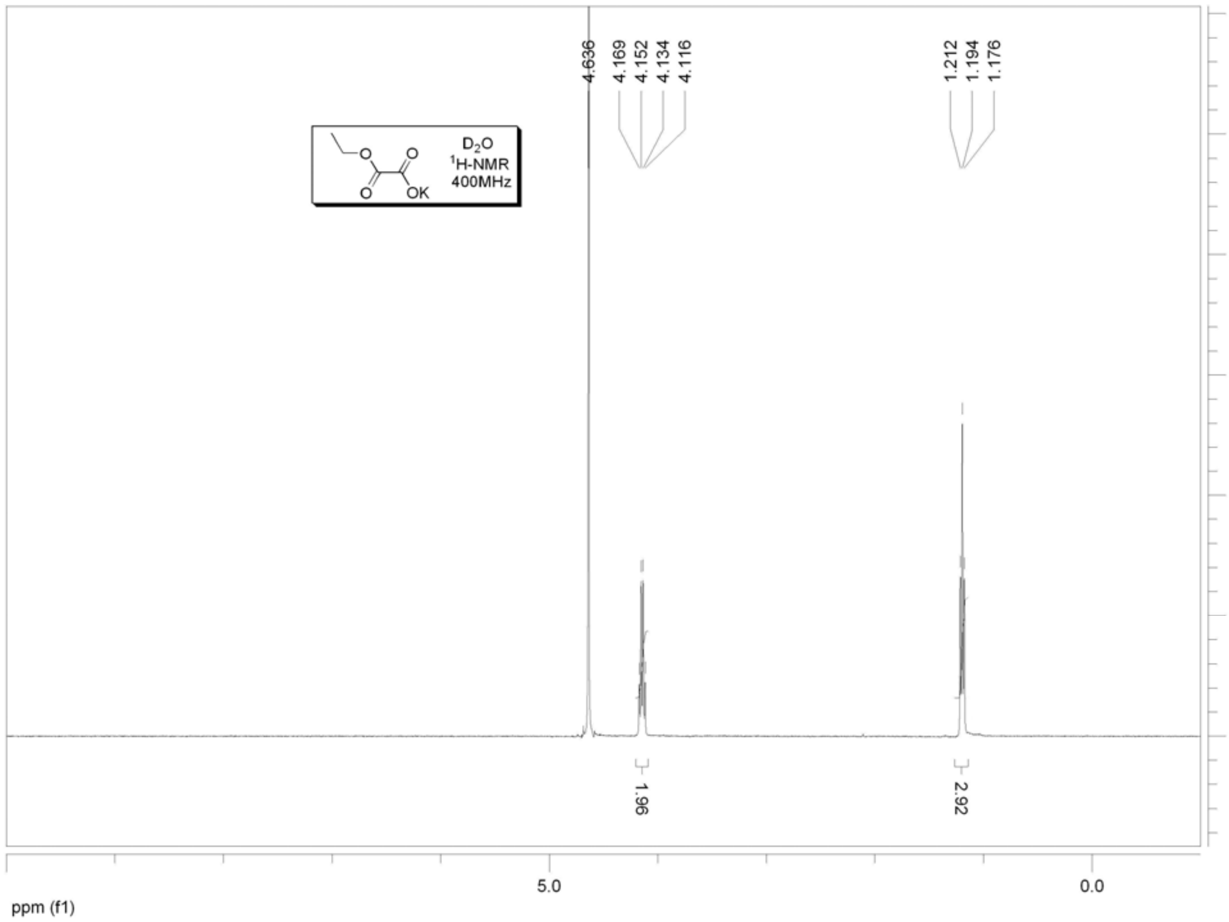




(E)-ethyl-3-phenylpropenoate (32)






D2O
1H-NMR
400MHz
OK
4.636
4.169
4.152
4.134
4.116
1.212
1.194
1.176
1.96
2.92
250
200
150
100
50
0
5.0
0.0
ppm (f1)

Computational method. All calculations were performed using Gaussian03 suite of program.[1] Density functional theory method was used, employing B3LYP hybrid functional.[2] Geometry optimization was done using a combined basis set where LANL2DZ[3] was used for Pd and P atom and 6-31G(d) for the rest. Frequency calculation was done at the same level of theory as geometry optimization, to confirm the stationary points to be minima or saddle points. For saddle points, intrinsic reaction coordinate analysis (IRC)[4] was done to verify that they connect the right reactants and products on the potential energy surface. Single point energy calculations were done using B3LYP method at a larger basis set, that is, LANL2DZ was used for Pd and P, and 6-311+G(d, p) was used for the rest. Solvent effect was accounted for using self-consistent reaction field (SCRF) method, using CPCM model and UAHF radii.[5] THF was used as the solvent.

Reference:

1. Frisch, M. J.; *Gaussian 03, revision D. 01*; Gaussian, Inc.: Wallingford, CT, **2004**.

2. (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.

3. Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 299–310.

4. (a) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363–368. (b) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154–2161. (c) Gonzalez, C.; Schlegel, H. B, *J. Phys. Chem.* **1990**, *94*, 5523–5527.

5. (a) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995–2001. (b) M Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. *J. Comput. Chem.***2003**, *24*, 669–681.

Optimized structures in Figure 1

Pd(PH2(CH2)3PH2)

Pd	-0.027773	-1.213801	-0.027234
P	-1.951577	0.164034	0.070785
C	-1.274863	1.929723	-0.298347
C	0.052887	2.301571	0.395700
C	1.361689	1.869325	-0.299186
P	1.956968	0.074937	0.071154
H	-2.582546	0.444120	1.340157
H	-3.167881	0.266022	-0.712088
H	-2.050044	2.649006	-0.014257
H	-1.160505	1.990721	-1.386297

H	0.078066	3.398770	0.443087
H	0.045748	1.963968	1.441025
H	1.249255	1.934577	-1.387143
H	2.169051	2.552829	-0.016427
H	3.175843	0.119968	-0.713046
H	2.601408	0.326596	1.339694

PhBr

C	0.000000	0.000000	-0.103289
Br	0.000000	0.000000	1.810794
C	0.000000	1.215464	-0.785259
C	0.000000	1.207481	-2.181110
C	0.000000	0.000000	-2.881677
C	0.000000	-1.207481	-2.181110
C	0.000000	-1.215464	-0.785259
H	0.000000	2.149447	-0.233738
H	0.000000	2.151919	-2.718157
H	0.000000	0.000000	-3.967792
H	0.000000	-2.151919	-2.718157
H	0.000000	-2.149447	-0.233738

IN1

Pd	0.234834	0.312933	-0.091114
P	2.231736	1.433873	-1.002775
C	3.859559	0.423385	-0.906824
C	4.150624	-0.205279	0.467920
C	3.367407	-1.484880	0.813088
P	1.554755	-1.195798	1.370942
H	2.394138	1.938893	-2.347681
H	2.696457	2.630072	-0.340881
H	3.785339	-0.359294	-1.670474
H	4.686433	1.080063	-1.194747
H	5.216913	-0.468596	0.479886
H	4.025740	0.543796	1.262937
H	3.887579	-2.031910	1.605490
H	3.321738	-2.145551	-0.060173
H	1.828256	-0.774298	2.724914
H	1.228946	-2.563855	1.702855
C	-1.929258	-0.019167	0.041944
C	-1.764323	1.105952	-0.823590
C	-2.102084	2.394619	-0.316451
C	-2.573350	2.554298	0.970349
C	-2.748009	1.426209	1.808338
C	-2.456507	0.156653	1.353523
H	-1.664562	0.963966	-1.894764

H	-2.016254	3.250716	-0.981496
H	-2.835687	3.542957	1.336861
H	-3.130258	1.556435	2.817549
H	-2.627608	-0.715235	1.976689
Br	-2.149179	-1.786427	-0.777085

TS1

Pd	-0.238034	-0.281205	0.104545
P	-2.311881	-1.183962	1.130848
C	-3.946010	-0.554384	0.347050
C	-4.031490	0.971201	0.158143
C	-3.305957	1.548318	-1.070723
P	-1.402017	1.710770	-0.885887
H	-2.663102	-2.581091	1.229325
H	-2.608427	-0.857580	2.505543
H	-4.039748	-1.060714	-0.620302
H	-4.775821	-0.896203	0.973175
H	-5.095519	1.220156	0.046867
H	-3.704818	1.488615	1.071372
H	-3.713749	2.536145	-1.306470
H	-3.480017	0.909689	-1.944174
H	-1.379652	2.929662	-0.111511
H	-1.134829	2.350041	-2.157073
C	1.872019	0.130218	0.008966
C	2.164586	0.236485	1.381569
C	2.829051	1.379351	1.846598
C	3.261297	2.361249	0.958661
C	3.028300	2.203227	-0.417165
C	2.360139	1.086708	-0.903879
H	1.886059	-0.559448	2.063977
H	3.031579	1.476715	2.910592
H	3.796681	3.233028	1.323793
H	3.376071	2.960054	-1.116570
H	2.183768	0.959273	-1.966772
Br	1.702513	-1.864265	-0.721160

IN2

Pd	-0.156266	0.164814	-0.029457
P	-2.498531	1.055181	-0.044730
C	-3.967856	-0.132445	0.254313
C	-3.784556	-1.528953	-0.365390
C	-2.771234	-2.444480	0.347415
P	-0.940343	-2.097726	-0.058071
H	-2.818080	2.116807	0.859158
H	-2.906463	1.688303	-1.264926

H	-4.087355	-0.220279	1.340155
H	-4.880666	0.329981	-0.132922
H	-4.758359	-2.033674	-0.324062
H	-3.540367	-1.445330	-1.433441
H	-2.968331	-3.490429	0.092912
H	-2.873463	-2.350672	1.434372
H	-0.802818	-2.793323	-1.304955
H	-0.283318	-3.047111	0.788159
C	1.749062	-0.529952	-0.007491
C	2.430679	-0.761633	-1.207510
C	3.736818	-1.263014	-1.190620
C	4.372138	-1.533265	0.022261
C	3.696181	-1.296217	1.220457
C	2.389842	-0.796011	1.207761
H	1.957064	-0.535636	-2.159577
H	4.258390	-1.433506	-2.130010
H	5.388305	-1.919314	0.034012
H	4.186337	-1.492621	2.171641
H	1.884144	-0.597700	2.149471
Br	0.683140	2.485630	0.031140

MeOOCCOOK

O	-1.829824	1.341183	0.589224
C	-1.318401	0.339268	0.137297
O	-2.026393	-0.721208	-0.321056
C	-3.451683	-0.577560	-0.239360
H	-3.769739	-0.463410	0.801055
H	-3.787363	0.295048	-0.807149
H	-3.864814	-1.493011	-0.665543
C	0.193032	0.095240	0.018395
O	0.779592	0.695491	-0.920814
O	0.702958	-0.650677	0.897167
Ca	3.045977	-0.147296	-0.041186

KBr

K	0.000000	0.000000	-1.872986
Br	0.000000	0.000000	1.016764

IN3

Pd	-0.410093	-0.289603	-0.511484
O	0.330839	2.018734	1.122067
C	1.341918	2.226758	0.470698
C	1.483361	2.007272	-1.062344
O	0.812222	1.021452	-1.562975
O	2.165208	2.805968	-1.686968

O	2.460352	2.739967	0.996736
C	2.411567	3.030361	2.401252
H	1.645218	3.781703	2.611960
H	2.191382	2.125636	2.975089
H	3.400791	3.412778	2.653645
C	1.204190	-1.459216	-0.156271
C	1.603933	-1.810616	1.138903
C	2.765082	-2.566162	1.342202
C	3.528704	-2.984949	0.252907
C	3.134623	-2.633270	-1.040078
C	1.982525	-1.868428	-1.245901
H	1.026781	-1.487493	2.002888
H	3.068817	-2.823951	2.354658
H	4.428479	-3.574507	0.409458
H	3.731476	-2.943619	-1.894779
H	1.709053	-1.569909	-2.253657
P	-1.822187	-1.908235	0.472104
C	-3.394480	-1.296254	1.356599
C	-4.295933	-0.353867	0.538695
C	-3.782208	1.086235	0.359923
P	-2.361933	1.247795	-0.900875
H	-1.260183	-2.778500	1.458132
H	-2.370359	-2.890068	-0.416867
H	-3.057237	-0.797683	2.272019
H	-3.962010	-2.182720	1.657552
H	-5.254144	-0.294858	1.070918
H	-4.529226	-0.801712	-0.437421
H	-4.605468	1.737424	0.051738
H	-2.079064	2.646936	-0.828429
H	-3.396789	1.472553	1.309782
H	-3.110114	1.240161	-2.127276

TS2

Pd	0.158226	-0.312281	-0.322156
O	-0.982974	1.280944	-1.027581
C	-0.690966	2.393023	-0.472260
C	0.098306	2.928687	2.013155
O	0.552399	1.869169	2.266366
O	-0.285260	4.036223	2.022428
O	-1.409597	3.428510	-0.958470
C	-2.396746	3.187394	-1.988482
H	-1.930518	2.785219	-2.892752
H	-3.157156	2.482215	-1.642150
H	-2.846067	4.160378	-2.195385
C	-1.574260	-1.304648	0.020992

C	-2.049944	-2.291638	-0.849538
C	-3.287504	-2.902786	-0.615625
C	-4.051370	-2.540493	0.494456
C	-3.576359	-1.559474	1.367415
C	-2.343809	-0.941517	1.132475
H	-1.470426	-2.583605	-1.722741
H	-3.651535	-3.661654	-1.305055
H	-5.011200	-3.017056	0.677162
H	-4.167251	-1.267264	2.232775
H	-1.993443	-0.167748	1.811147
P	1.322685	-2.213024	0.482341
C	3.168853	-2.413177	0.057164
C	4.046161	-1.172967	0.308539
C	3.938286	-0.052322	-0.741095
P	2.312945	0.945830	-0.647876
H	0.809015	-3.503466	0.139381
H	1.343526	-2.345049	1.907969
H	3.213437	-2.701882	-0.999061
H	3.543590	-3.259654	0.641268
H	5.088345	-1.517415	0.312680
H	3.863354	-0.773191	1.315385
H	4.782150	0.635948	-0.632842
H	2.469936	1.813932	-1.775721
H	3.995866	-0.477046	-1.749947
H	2.625101	1.870923	0.394998

IN4

Pd	-0.164959	0.170011	-0.155470
P	-1.301759	-2.057538	-0.156001
P	-2.397273	1.256471	-0.284569
C	-3.098535	-2.180574	0.486411
C	-4.061171	-1.129283	-0.093942
C	-3.892773	0.307075	0.433915
H	-3.762078	0.298049	1.521893
H	-4.795397	0.887422	0.220140
H	-5.079350	-1.449102	0.163993
H	-4.020175	-1.139409	-1.192167
H	-3.474847	-3.185419	0.271768
H	-3.046363	-2.080197	1.576492
H	-2.923208	1.583336	-1.582062
H	-2.601089	2.535524	0.332575
H	-1.447108	-2.726096	-1.420152
H	-0.696537	-3.138787	0.566545
C	1.712098	-0.660575	-0.008431
C	2.625176	-0.588987	-1.070788

C	3.848742	-1.264523	-1.013606
C	4.193103	-2.007933	0.116774
C	3.304238	-2.068977	1.191298
C	2.075930	-1.402155	1.127358
H	2.392312	0.020419	-1.939830
H	4.539250	-1.198549	-1.852253
H	5.147377	-2.527354	0.163473
H	3.565232	-2.634748	2.083850
H	1.401685	-1.463926	1.979668
C	0.857416	1.913763	-0.226665
O	1.349504	2.410765	-1.217074
O	0.878958	2.547542	0.984218
C	1.572410	3.811087	1.002271
H	1.516813	4.161574	2.034165
H	2.614900	3.683293	0.698278
H	1.094660	4.529507	0.329054

TS3

Pd	-0.241029	0.140376	-0.194244
P	-1.573896	-2.014445	-0.075822
P	-2.347980	1.421887	-0.321144
C	-3.330996	-1.887254	0.678370
C	-4.214044	-0.789749	0.058436
C	-3.904984	0.654950	0.489303
H	-3.744405	0.699204	1.572483
H	-4.759702	1.299117	0.260943
H	-5.249083	-0.999737	0.359543
H	-4.206032	-0.868951	-1.037909
H	-3.823575	-2.859020	0.577107
H	-3.196084	-1.701121	1.749971
H	-2.890878	1.698549	-1.626084
H	-2.465344	2.759616	0.197160
H	-1.915417	-2.706078	-1.294580
H	-1.110765	-3.174856	0.642180
C	1.824695	-0.358719	-0.040580
C	2.446053	-0.883032	-1.186071
C	3.486301	-1.805775	-1.071288
C	3.938602	-2.200687	0.191129
C	3.352441	-1.657446	1.336849
C	2.309187	-0.735494	1.223325
H	2.128800	-0.537002	-2.165944
H	3.954404	-2.207500	-1.967279
H	4.756344	-2.911588	0.280587
H	3.714617	-1.944684	2.321699
H	1.878074	-0.294420	2.117118

C	1.280414	1.513833	-0.289034
O	1.608264	2.040266	-1.335881
O	1.441864	2.134164	0.926694
C	2.092105	3.413394	0.870256
H	2.167625	3.751133	1.905449
H	3.088281	3.322030	0.426556
H	1.508977	4.126830	0.280017

PhCOOMe

C	-0.912860	-0.919134	0.000000
C	0.000000	0.259010	0.000000
C	1.395876	0.129423	0.000000
C	2.198888	1.268604	0.000000
C	1.615793	2.538203	0.000000
C	0.224596	2.669876	0.000000
C	-0.581435	1.534286	0.000000
H	1.841393	-0.859035	0.000000
H	3.280669	1.166429	0.000000
H	2.245370	3.424172	0.000000
H	-0.229728	3.656820	0.000000
H	-1.663808	1.611176	0.000000
O	-2.126458	-0.851308	0.000000
O	-0.241432	-2.095120	0.000000
C	-1.066146	-3.268707	0.000000
H	-0.374997	-4.112186	0.000000
H	-1.702022	-3.292657	0.889197
H	-1.702022	-3.292657	-0.889197