Supporting Information

Base Induced Mechanistic Variation in Palladium Catalyzed Carbonylation of Aryl Iodides

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Analytical Methods: ^{1}H NMR and ^{13}C NMR were recorded on a Varian Mercury 300 MHz NMR spectrometer. Gas chromatographic analyses were preformed on Varian GC 2000 gas chromatography instrument with an FID detector with biphenyl as the internal standard. IR spectra were recorded on a Mettler Toledo React IR™ 4000 spectrometer using a DiCom probe.

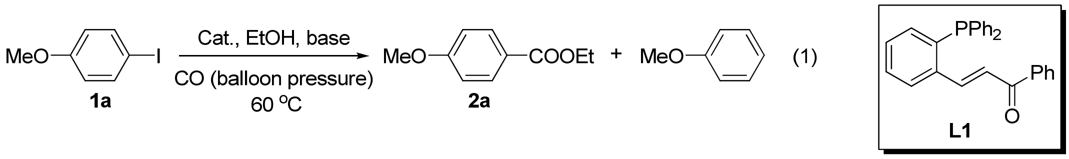
Reagents: All common reagents were prepared in our lab or purchased from commercial suppliers and were purified following established procedures. The complex $Pd(CH_3CN)_2Cl_2$ was prepared via known procedure.[1] The P-olefin ligand **1** was prepared in our lab on a scale of 10 g.[2] All dry solvents were dried according to standard procedures and stored under nitrogen.

Experimental Details

1. Preparation of sodium alkoxide: Under the protection of the nitrogen gas, to 10 mL alcohol (ethanol, isopropanol, n-butanol, benzyl alcohol) was added 230 mg (10 mmol) Na. The resulting solution was stirred until the Na disappeared at 0 ^{o}C. Sodium tert-butoxide was obtained from a commercial supplier.

2. Preparation of sodium alksulfide: Under the protection of the nitrogen gas, to 3 mL thiol was added 138 mg (6 mmol) Na. The resulting solution was stirred until the Na disappeared at 60 °C. Then 18 mL THF was added to the mixture.

3. General procedure for the kinetic experiments in Figure 1 with *in situ* IR



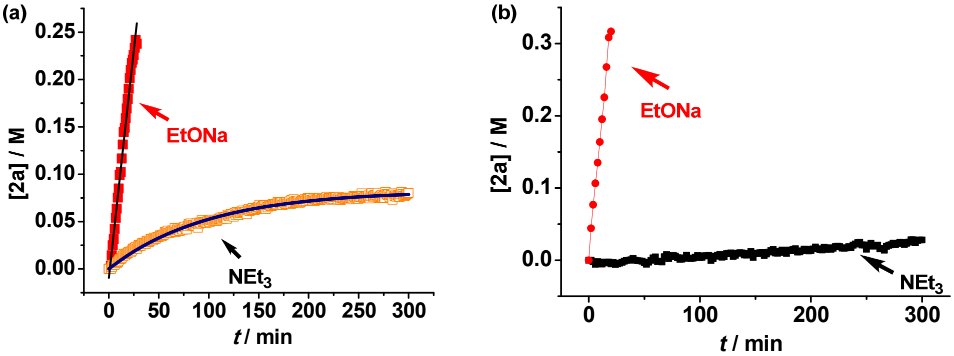
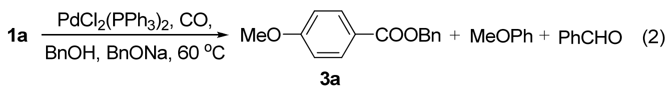


Figure S1. Kinetic plots of carbonylation of **1a** at 60 °C under balloon pressure of CO recorded by *in situ* IR. Reaction conditions: [Cat.] = 0.0067 M, [**1a**] = 0.33 M, [EtONa] = 0.44 M, [NEt_3] = 1.0 M.(a) Cat.= $PdCl_2(MeCN)_2$/**L1**; (b) Cat. = $PdCl_2(PPh_3)_2$.

Under the protection of nitrogen gas, to a Schlenk tube was added the selected Pd catalyst (2 mol %), aryl iodide (1 mmol) and biphenyl as internal standard. The system was charged with CO (balloon) and was degassed 3 times. Then solutions of different bases were added by syringe. Reactions were carried out with [**Cat.**] = 0.0067 M, [**1a**] = 0.33 M, [EtONa] = 0.40 M, [NEt_3] = 1.0 M with continuous stirring at 60 °C. The reaction was monitored by *in situ* IR and GC. Infrared absorbance were converted to the corresponding concentrations.

4. Procedure for the kinetic experiments in Figure 2:



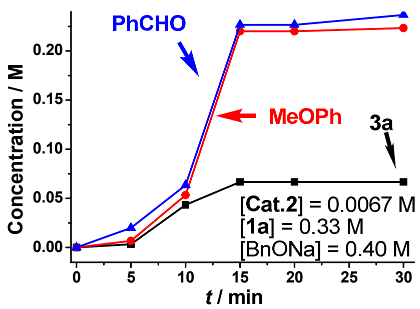


Figure S2. Kinetic plots of benzoxycarbonylation of **1a** at 60 °C under balloon pressure of CO.

Under the protection of the nitrogen gas, to a Schlenk tube was added $Pd(PPh_3)_2Cl_2$ (2 mol%), **1a** (1 mmol) and biphenyl as internal standard. The system was charged with CO (balloon) and was degassed 3 times. Then the solutions of BnONa (1.2 equiv) was added by syringe. The reaction was carried out at 60 °C with continuous stirring. Data was determined by GC via aliquots taken at 5 min intervals.

5. Procedure for the kinetic experiments in Figure 3:

A: Reaction of complex I with EtONa and CO:

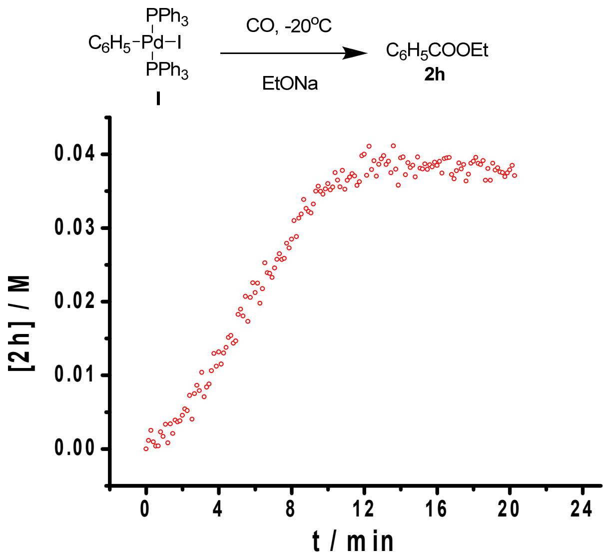


Figure S3. Kinetic plots of complex experiment of complex I with CO.

An oven dried self-prepared three-necked micro reactor with a magnetic stirrer was allowed to be vacuumed and purged with CO for three times. The micro reactor was charged in -20 °C ethanol bath and EtONa (1.2 mmol, 2.4 M in 0.5 mL of THF) was added in via a syringe. Then complex I (100 mg, 0.12 mmol, 0.06 M in 2.0 mL of THF) was charged to the reactor and at the same time the reaction progress was monitored by *in situ* IR. 30 min later, the reaction was quenched by saturated NH_4Cl and the GC yield of ethyl benzoate was 83%. Infrared absorbance were converted to the corresponding concentrations.

B: Reaction of complex I with CO:

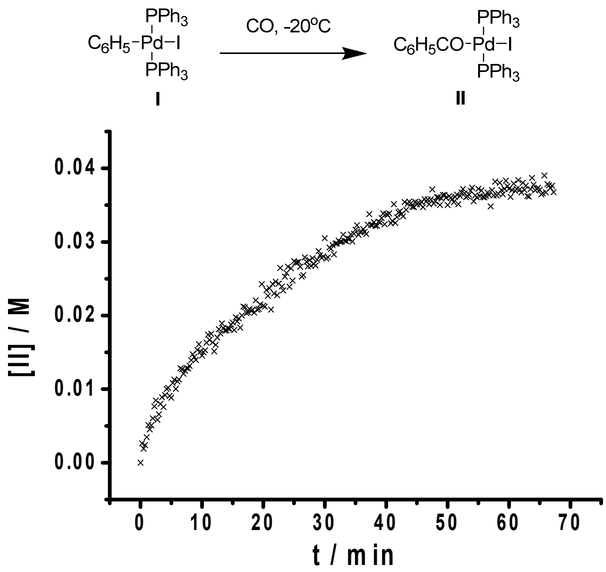


Figure S4. Kinetic plots of complex experiment of complex I with CO and EtONa.

An oven dried self-prepared three-necked micro reactor with a magnetic stirrer was allowed to be vacuumed and purged with CO for three times. The micro reactor was charged in -20 °C ethanol bath. Then complex I (100 mg, 0.12 mmol, 0.048 M in 2.5 mL of THF) was added in via a syringe and at the same time the reaction progress was monitored by *in situ* IR. 1.5 h later, hexane (10 mL) was added to the reactor and the resulted mixture was extracted, yellow solid was obtained with 77% yield.[3] Infrared absorbance were converted to the corresponding concentrations.

6. Procedure for the kinetic experiments in Figure 6, 7 and 8:

A.

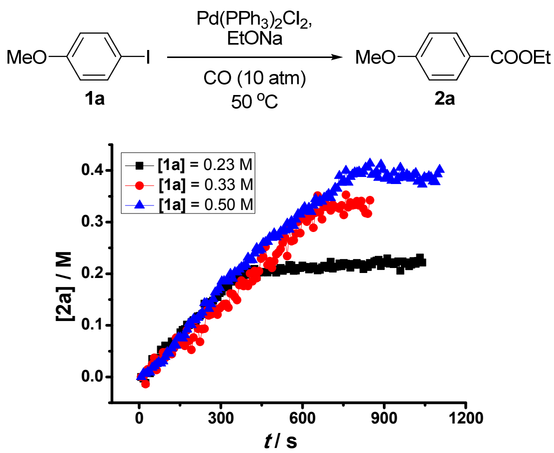
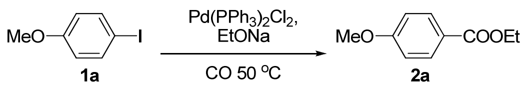


Figure S5. The kinetic plots by variation of the initial concentration of 1a.

To an autoclave was added $Pd(PPh_3)_2Cl_2$, aryl iodides and biphenyl as internal standard. The system was charged with CO (10atm) and was degassed 3 times. The solution of EtONa was added by syringe. Reactions were carried out with [**Cat. 2**] = 0.0033 M, [EtONa] = 0.50 M and different initial concentrations of **1a** at 50 ^{o}C. Data was detected by *in situ* IR and GC. Infrared absorbance were converted to the corresponding concentrations.

B.



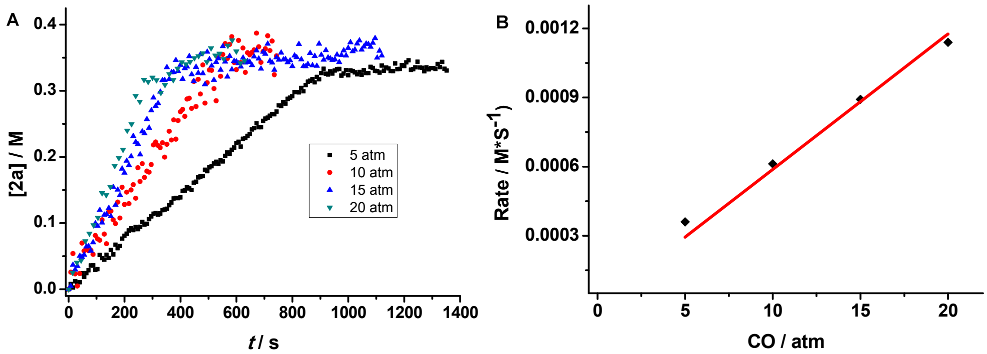
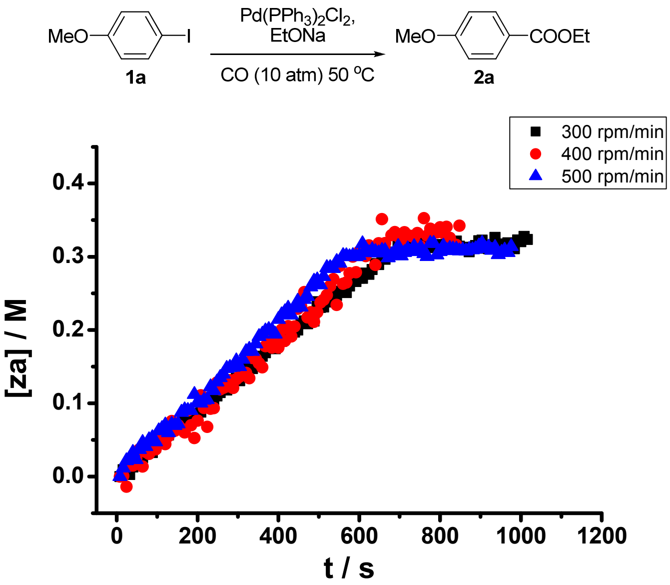


Figure S6. The kinetic plots by variation of the pressure of CO.

To an autoclave was added Pd(PPh$_3$)$_2$Cl$_2$, aryl iodides and biphenyl as internal standard. The system was charged with CO (the pressure of CO ranged from 5 to 20 atm) and was degassed 3 times. The solution of EtONa was added by syringe. Reactions were carried out with [**Cat. 2**] = 0.0033 M, [EtONa] = 0.50 M, [1a]=0.33 M and different pressure of CO at 50 ^{o}C. Date was detected by *in situ* IR and GC. Infrared absorbance were converted to the corresponding concentrations.

C.



A

Figure S7. The kinetic plots by variation of the stirring rate.

To an autoclave was added $Pd(PPh_3)_2Cl_2$, aryl iodides and biphenyl as internal standard. The system was charged with CO (10 atm) and was degassed 3 times. The solution of EtONa was added by syringe. Reactions were carried out with [**Cat. 2**] = 0.0033 M, [EtONa] = 0.50 M and [**1a**]=0.33 M at 50 °C while varying the stirring rate from 300, 400 to 500 rpm/min. Data was detected by *in situ* IR and GC. Infrared absorbance were converted to the corresponding concentrations

D.

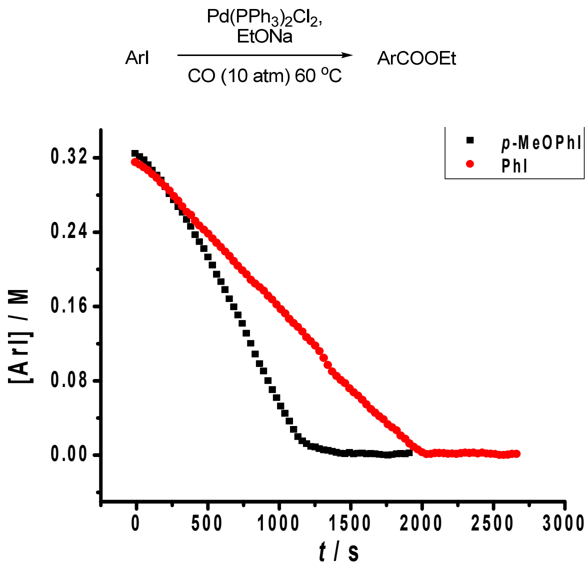


Figure S8. The kinetic plots employing different ArI.

To an autoclave was added aryl iodides and biphenyl as internal standard. The system was allowed to be vacuumed and purged with CO for three times. With a CO balloon, the solution of EtONa was added by syringe. The reaction temperature rised to 60^{o}C. $PdCl_2(PPh_3)_2$ was added by a syringe. Reactions were carried out with [**Cat. 2**] = 0.005 M, [EtONa] = 0.30 M and [**1a**]=0.25 M at 60 ^{o}C. Data was detected by *in situ* IR and GC. Infrared absorbance were converted to the corresponding concentrations

7. Procedure for the carbonylation of aryl iodides of Table 2

General procedure for carbonylation of aryl iodides under balloon pressure: $Pd(PPh_3)_2Cl_2$ (2 mol %) and the selected aryl iodide (1 mmol) were added into a oven-dried Schlenk tube under N_2 atmosphere. Then the system was evacuated and filled with CO (balloon) for 3 times, and corresponding sodium alkoxide (1.2 equiv) and EtOH were added. The reaction mixture was stirred at room temperature for 24 h and quenched NH_4Cl (aq) after dilution with ether (10 mL). The aqueous layer was extracted with ether (3 × 10 mL). The combined organic phase was dried over Na_2SO_4, filtered and concentrated. The residue was purified by a flash chromatography (PE / EtOAc = 30/1) on silica gel to afford the product.

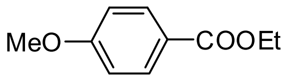
General procedure for carbonylation of aryl iodides under 10 atm CO: Pd catalyst (2 mol %), aryl iodide (1 mmol) and corresponding sodium alkoxide (1.2 equiv) were added together with 3 mL alcohol solvent to an autoclave. The system was evacuated and refilled with CO for 3 times and the system pressure was retained at 10 atm. The reaction mixture was stirred at 80 ^{o}C or 95 ^{o}C or 60^{o}C for 24 h, and the autoclave was cooled to room temperature and depressurized. The reaction mixture was diluted with ether (10 mL) and quenched with NH_4Cl (aq.). The aqueous layer was extracted with ether (3 × 10 mL). The combined organic phase was dried over Na_2SO_4, filtered and concentrated. The residue was purified by a flash chromatography (PE / EtOAc = 30/1) on silica gel to afford the product.

8. Procedure for the thiocarbonylation of aryl iodides of Table 3

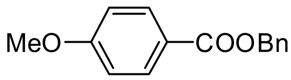
Pd catalyst (2 mol %), aryl iodide (1 mmol) and corresponding sodium alkythiolate (1.2 mmol, 4 mL in THF) were added together to an autoclave. The system was evacuated and refilled with CO for 3 times and the system pressure was retained at 10 atm. The reaction mixture was stirred at 60

^{o}C or 70 ^{o}C for 24 h, and the autoclave was cooled to room temperature and depressurized. The reaction mixture was diluted with ether (10 mL) and quenched with NH_4Cl (aq.). The aqueous layer was extracted with ether (3 × 10 mL). The combined organic phase was dried over Na_2SO_4, filtered and concentrated. The residue was purified by a flash chromatography (PE / EtOAc = 50/1) on silica gel to afford the product.

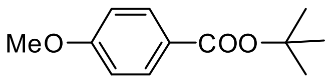
Preparation and NMR data of compounds



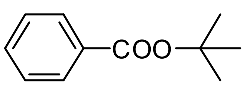
Ethyl 4-methoxybenzoate (2a):[4] 1.0 mmol scale (151 mg, 84% yield) as a colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ =1.30 (t, J = 7.2 Hz, 3H), 3.74 (s, 3H), 4.26 (q, J = 6.3 Hz, 2H), 6.82 (d, J= 8.1 Hz, 2H), 7.92(d, J = 8.1 Hz, 2H); ^{13}C NMR (75MHz, CDCl3): δ = 14.52, 55.46, 60.74, 113.68, 131.66, 163.42, 166.46.



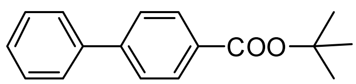
Benzyl 4-methoxybenzoate (3a):[5] 1.0 mmol scale provided (195 mg, 81% yield) as a colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.82 (s, 3H), 5.36 (s, 2H), 6.92 (d, J = 7.5 Hz, 2H), 7.37-7.48 (m, 4H), 8.07 (d, J = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.78, 66.77, 114.01, 122.87, 128.52, 128.98, 132.15, 136.69, 163.82, 166.56.



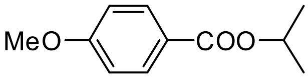
Tert-butyl 4-methoxybenzoate (2p):[6] 1.0 mmol scale provided (181 mg, 87% yield) as a colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.74 (s, 9H), 3.00 (s, 3H), 6.05 (d, J = 8.7 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.48, 55.62, 80.74, 113.58, 124.66, 131.60, 163.15, 165.84.



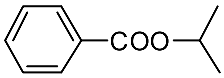
Tert-butyl benzoate (2b):[7] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.42 (s, 9H), 7.20-7.33 (m, 3H), 7.83 (d, J = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.39, 81.11, 128.40, 129.63, 132.19, 132.66, 165.97.



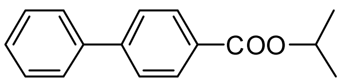
Tert-butyl biphenyl-4-carboxylate (2c):[8] 1.0 mmol scale provided (185 mg, 73% yield) as white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.50 (s, 9H), 7.24 -7.96 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.50, 81.23, 127.15, 127.53, 128.30, 129.18, 130.23, 131.02, 140.40, 145.39, 165.92.



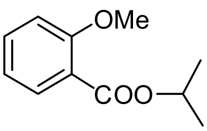
Isopropyl 4-methoxybenzoate (2d):[9] 1.0 mmol scale provided (171 mg, 88% yield) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.34 (s, 3H), 1.36 (s, 3H), 3.84 (s, 3H), 5.22 (m, 1H), 6.90 (d, J = 7.8 Hz, 2H), 7.99 (d, J = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.22, 55.61, 68.15, 113.68, 123.51, 131.71, 163.36, 166.10.



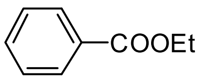
Isopropyl benzoate (2e):[10] 1.0 mmol scale provided (141 mg, 86% yield) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.36 (s, 3H), 1.38 (s, 3H), 5.26 (m, 1H), 7.41 -8.06 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=22.20, 68.58, 128.50, 129.73, 131.09, 132.94, 166.35.



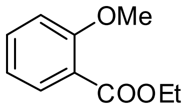
Isopropyl biphenyl-4-carboxylate (2f):[11] 1.0 mmol scale provided (227 mg, 94% yield) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.41 (s, 3H), 1.43 (s, 3H), 5.31 (m, 1H), 7.414-8.16 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.27, 68.63, 127.22, 127.54, 128.35, 129.18, 129.87, 130.30, 140.32, 145.65, 166.25.



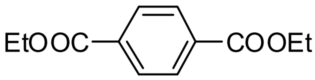
Isopropyl 2-methoxybenzoate (2g):[12] 1.0 mmol scale provided (160 mg, 82% yield) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.32 (s, 3H), 1.34 (s, 3H), 3.85 (s, 3H), 5.22 (m, 1H), 6.91-7.74 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.14, 56.14, 68.27, 112.18, 120.24, 121.00, 131.50, 133.42, 159.25, 165.88



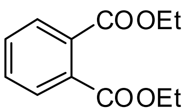
Ethyl benzoate (2h):[13] 1.0 mmol scale provided (126 mg, 84% yield) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.39 (t, J = 6.9 Hz, 3H), 4.38(q, J = 7.2 Hz, 2H), 7.43-7.57 (m, 3H), 8.05(d, J = 6.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.53, 61.13, 128.51, 129.73, 130.72. 132.99, 166.80.



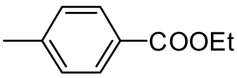
Ethyl 2-methoxybenzoate (2i):[14] 1.0 mmol scale provided (151 mg, 84% yield) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.26 (t, J = 7.2 Hz, 3H), 3.76 (s, 3H), 4.24 (q, J = 6.9 Hz, 2H), 6.83-7.69 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.48, 56.11, 60.91, 112.23, 120.25, 120.64, 131.61, 133.52, 159.27, 166.35.



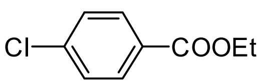
Diethyl terephthalate (2j):[13] 1.0 mmol scale provided (200 mg, 90% yield) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.33 (t, J = 6.9 Hz, 6H), 4.32 (q, J = 6.6 Hz, 4H), 8.00 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.41, 61.50, 129.59, 134.30, 165.86.



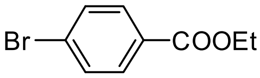
Diethyl phthalate (2k):[13] 1.0 mmol scale provided (200 mg, 90% yield) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.33 (t, J = 6.9 Hz, 6H), 4.33(q, J = 6.9 Hz, 4H), 7.47-7.51 (m, 2H), 7.67-7.70 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.73, 59.24, 126.48, 128.6, 129.86, 165.28.



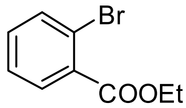
Ethyl 4-methylbenzoate (2l):[9] 1.0 mmol scale provided (120 mg, 73% yield) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.41 (t, J = 7.2 Hz, 3H), 2.41 (s, 3H), 4.39 (q, J = 7.2 Hz, 2H), 7.24 (d, J = 7.8 Hz, 2H), 7.98 (d, J = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.66, 21.89, 61.02, 128.13, 129.33, 129.87, 166.95.



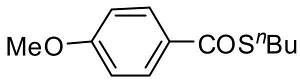
Ethyl 4-chlorobenzoate (2m):[13] 1.0 mmol scale provided (138 mg, 75% yield) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.39 (t, J = 7.8 Hz, 3H), 4.37 (q, J = 7.2 Hz, 2H), 7.40 (d, J = 8.7 Hz, 2H), 7.97 (d, J = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.51, 61.42, 128.85, 129.14, 131.14, 139.44, 165.95.



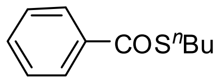
Ethyl 4-bromobenzoate (2n):[13] 1.0 mmol scale provided (183 mg, 80% yield) as a colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.30 (t, J = 7.2 Hz, 3H), 4.28 (q, J = 7.5Hz, 2H), 7.48 (d, J = 8.1 Hz, 2H), 7.81(d, J = 9.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.50, 61.43, 128.10, 129.61, 131.30, 131.85, 166.06.



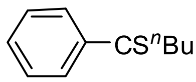
Ethyl 2-bromobenzoate (2o):[15] 1.0 mmol scale provided (185 mg, 81% yield) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.33 (t, J = 7.5 Hz, 3H), 4.33 (q, J = 6.6 Hz, 2H), 7.19-7.71 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.41, 61.78, 121.67, 127.34, 131.35, 132.59, 132.73, 134.40, 166.33.



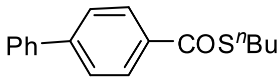
***S*-butyl 4-methoxybenzothioate (4b)**[16]**:** 1.0 mmol scale provided (193 mg, 86% yield) as a yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.94 (t, J = 6.6 Hz, 3H), 1.30-1.55 (m, 2H), 1.55-1.72 (m, 2H), 3.05 (t, J = 6.6 Hz, 2H), 3.85 (s, 3H), 6.91 (d, J = 8.4 Hz, 2H), 7.95 (d, J = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.5, 22.0, 28.5, 31.7, 113.6, 129.2, 130.1, 163.5, 190.6.



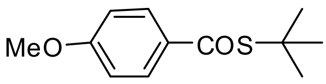
S-butyl benzothioate (4a)[17]**:** 1.0 mmol scale provided (176 mg, 91% yield) as a yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.95 (t, J = 7.2 Hz, 3H), 1.38-1.52 (m, 2H), 1.60-1.75 (m, 2H), 3.08 (t, J = 7.2 Hz, 2H), 7.44 (t, J = 7.8 Hz, 2H), 7.56 (t, J = 7.8 Hz, 1H), 7.97 (d, J = 6.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.5, 22.0, 28.6, 31.6, 127.1, 128.4, 133.1, 137.2, 191.9.



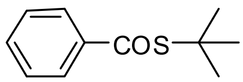
1-phenylpentane-1-thione (4a')[18]**:** 1.0 mmol scale provided (12.5 mg, 7% yield) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 (t, J = 8.8 Hz, 3H), 1.40-1.50 (m, 2H), 1.55-1.70 (m, 2H), 2.91 (t, J = 7.2 Hz, 2H), 7.15 (t, J = 8.0 Hz, 1H), 7.25 (t, J = 7.2 Hz, 2H), 7.32 (d, J = 6.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.6, 21.6, 31.2, 33.2, 125.7, 127.8, 129.0, 137.0.



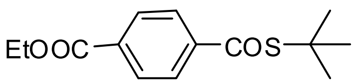
S-butyl biphenyl-4-carbothioate (4c): 1.0 mmol scale provided (211 mg, 78% yield) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, J = 7.2 Hz, 3H), 1.35-1.55 (m, 2H), 1.55-1.75 (m, 2H), 3.09 (t, J = 7.2 Hz, 2H), 7.30-7.50 (m, 3H), 7.50-7.70 (m, 4H), 8.03 (d, J = 8.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.6, 22.0, 28.7, 31.6, 127.1, 127.7, 128.1, 128.9, 135.9, 139.8, 145.9, 191.6. HRMS (APCI) calcd for $C_{17}H_{18}OS$ $[M]^+$: 270.1078; found 270.1080.



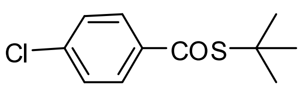
S-tert-butyl 4-methoxybenzothioate (4d)[19]: 1.0 mmol scale provided (166 mg, 74% yield) as a yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.57 (s, 9H), 3.85 (s, 3H), 6.89 (d, J = 7.8 Hz, 2H), 7.90 (d, J = 7.8 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 30.5, 48.3, 55.9, 114.0, 129.5, 131.6, 163.8, 192.0.



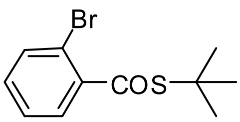
S-tert-butyl benzothioate (4e)[20]: 1.0 mmol scale provided (184 mg, 95% yield) as a yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.58 (s, 9H), 7.40 (t, J = 7.8 Hz, 2H), 7.52 (t, J = 7.5 Hz, 2H), 7.92 (d, J = 7.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.9, 48.0, 126.8, 128.3, 132.8, 138.2, 192.8.



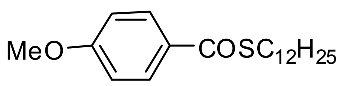
Ethyl 4-(tert-butylthiocarbonyl)benzoate (4f): 1.0 mmol scale provided (133 mg, 50% yield) as a yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.41 (t, J = 6.9 Hz, 3H), 1.59 (s, 9H), 4.38 (q, J = 6.9 Hz, 2H), 7.96 (d, J = 8.4 Hz, 2H), 8.08 (d, J = 8.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5, 30.1, 31.3, 48.9, 61.6, 126.5, 127.1, 129.6, 129.8, 134.3, 137.0, 141.7, 165.9, 192.4. HRMS (APCI) calcd for $C_{14}H_{18}O_3S$ $[M]^+$: 266.0977; found 266.0974.



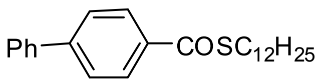
S-tert-butyl 4-chlorobenzothioate(4g): 1.0 mmol scale provided (173 mg, 76% yield) as a yellow liquid. ^{1}H NMR (300 MHz, CDCl3): δ = 1.58 (s, 9H), 7.41 (d, J = 9.0 Hz, 2H), 7.85 (d, J = 8.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.8, 48.4, 128.4, 128.7, 136.5, 139.1, 191.5. HRMS (APCI) calcd for $C_{11}H_{13}OSCl$ $[M]^+$: 228.0376; found 228.0378.



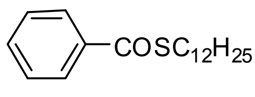
S-tert-butyl 2-bromobenzothioate (4h): 1.0 mmol scale provided (205 mg, 75% yield) as a yellow liquid. ^{1}H NMR (300 MHz, CDCl3): δ = 1.59 (s, 9H), 7.27-7.33 (m, 2H), 7.50 (d, J = 7.5 Hz, 1H), 7.59 (d, J = 7.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.9, 49.8, 118.8, 127.3, 128.9, 131.9, 133.9, 140.8, 194.3. HRMS (APCI) calcd for $C_{11}H_{13}OSBr$ $[M]^+$: 271.9870; found 271.9874



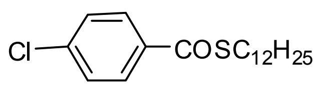
S-dodecyl 4-methoxybenzothioate (4i): 1.0 mmol scale provided (296 mg, 88% yield) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, J = 5.7 Hz, 3H), 1.26-1.44 (m, 18H), 1.60-1.68 (m, 2H), 3.04 (t, J = 7.2 Hz, 2H), 3.86 (s, 3H), 6.92 (d, J = 8.7 Hz, 2H), 7.95 (d, J = 9.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 22.6, 28.8, 28.9, 29.1, 29.3, 29.4, 29.5, 29.6, 31.8, 55.4, 113.6, 129.2, 130.1, 163.5, 190.5. HRMS (APCI) calcd for $C_{20}H_{32}O_2S$ $[M]^+$: 336.2123; found336.2126.



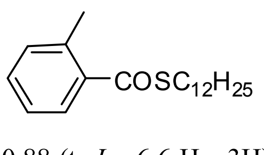
S-dodecyl biphenyl-4-carbothioate (4k): 1.0 mmol scale provided (344 mg, 90% yield) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.9 Hz, 3H), 1.24-1.46 (m, 18H), 1.60-1.71 (m, 2H), 3.09 (t, J = 7.5 Hz, 2H), 7.37-7.50 (m, 5H), 7.61-7.68 (t, 2H), 8.04 (d, J = 8.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1, 22.7, 28.9, 29.0, 29.2, 29.3, 29.6, 31.9, 127.2, 127.7, 128.2, 128.9, 135.9, 139.8, 145.9, 191.6. HRMS (APCI) calcd for $C_{25}H_{34}OS$ $[M]^+$: 382.2330; found 382.2322.



S-dodecyl benzothioate (4j)[21]: 1.0 mmol scale provided (239 mg, 78% yield) as a yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, J = 6.6 Hz, 3H), 1.26-1.44 (m, 18H), 1.61-1.72 (m, 2H), 3.07 (t, J = 7.5 Hz, 2H), 7.44 (t, J = 7.8 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.96 (d, J = 7.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 22.6, 28.9, 29.0, 29.3, 29.4, 29.5, 29.6, 31.8, 127.1, 128.4, 133.1, 137.2, 192.0.



S-dodecyl 4-chlorobenzothioate (4l): 1.0 mmol scale provided (184 mg, 54% yield) as a yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, J = 5.7 Hz, 3H), 1.26-1.42 (m, 18H), 1.61-1.69 (m, 2H), 3.07 (t, J = 7.2 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 7.91 (d, J = 8.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.4, 22.9, 29.2, 29.4, 29.6, 29.7, 29.9, 32.2, 128.8, 129.1, 135.8, 139.8, 191.2. HRMS (APCI) calcd for $C_{19}H_{29}OSCl$ $[M]^+$: 340.1628; found 340.1631.



S-dodecyl 2-methylbenzothioate (4m): 1.0 mmol scale provided (253 mg, 79% yield) as a yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.6 Hz, 3H), 1.26-1.44 (m, 18H), 1.60-1.69 (m, 2H), 2.48 (s, 3H), 3.03 (t, J = 7.5 Hz, 2H), 7.24 (t, J = 7.5 Hz, 2H), 7.33-7.39 (m, 1H), 7.76 (d, J = 7.8 Hz, 1H). ^{13}C NMR (75 MHz,

$CDCl_3$): δ = 14.4, 20.8, 22.9, 29.2, 29.4, 29.6, 29.8, 29.9, 32.2, 125.9, 128.6, 131.7, 136.8, 138.1, 194.9. HRMS (APCI) calcd for $C_{20}H_{32}OS$ $[M]^+$: 320.2174; found 320.2178.

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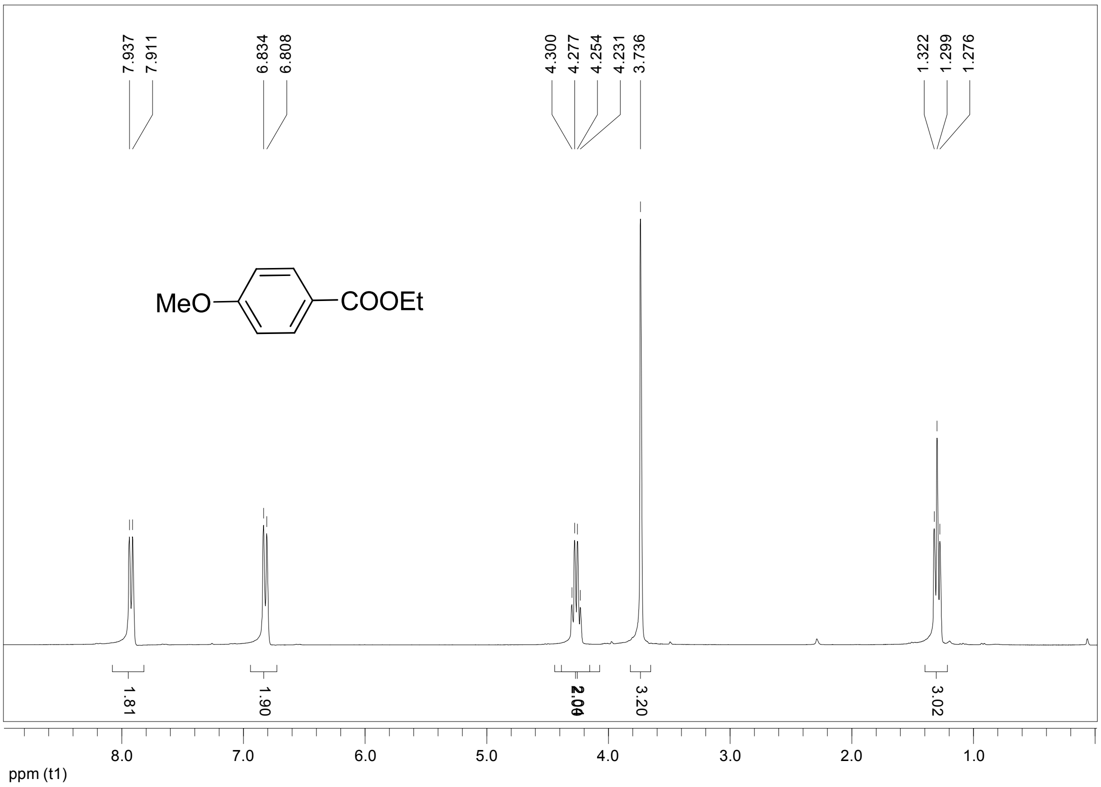
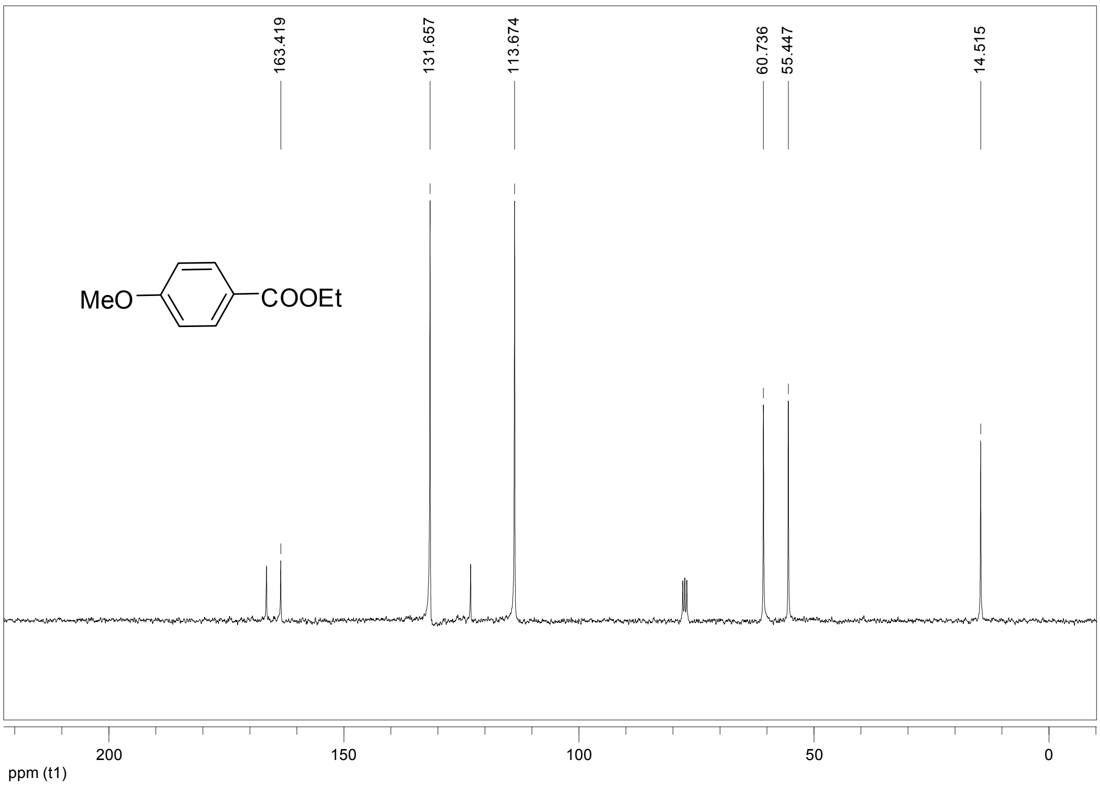
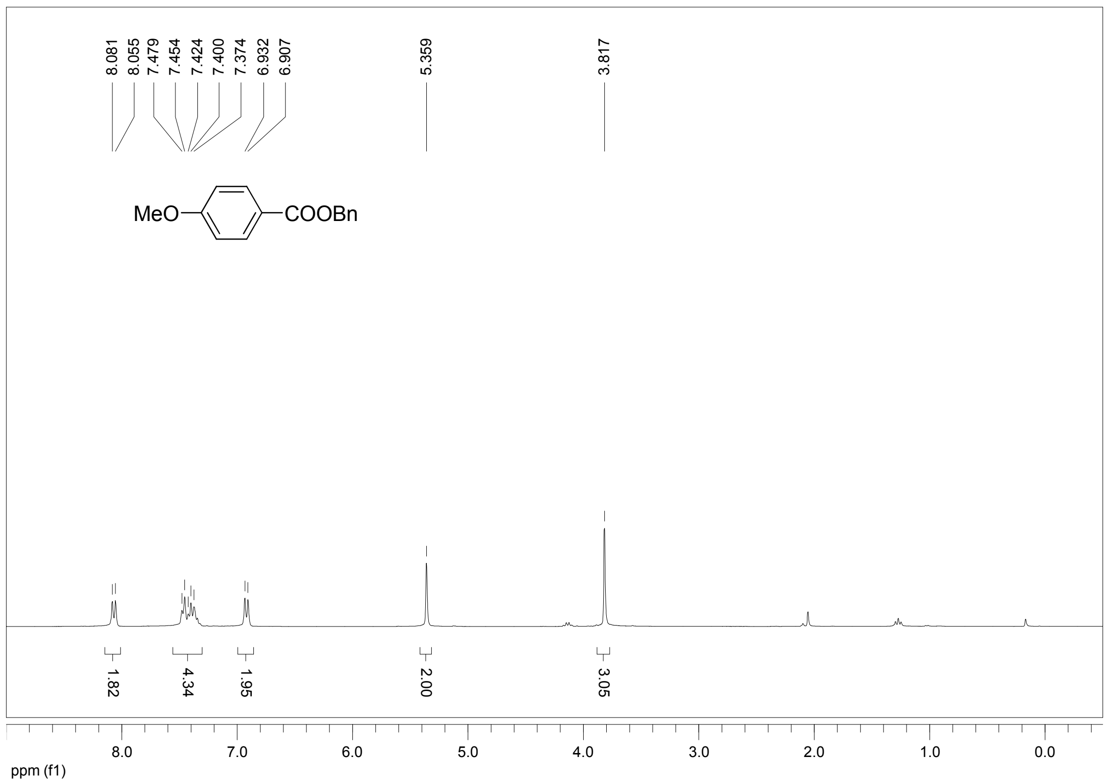
NMR spectra of the products of the reactions in Table 1 and Complexes.



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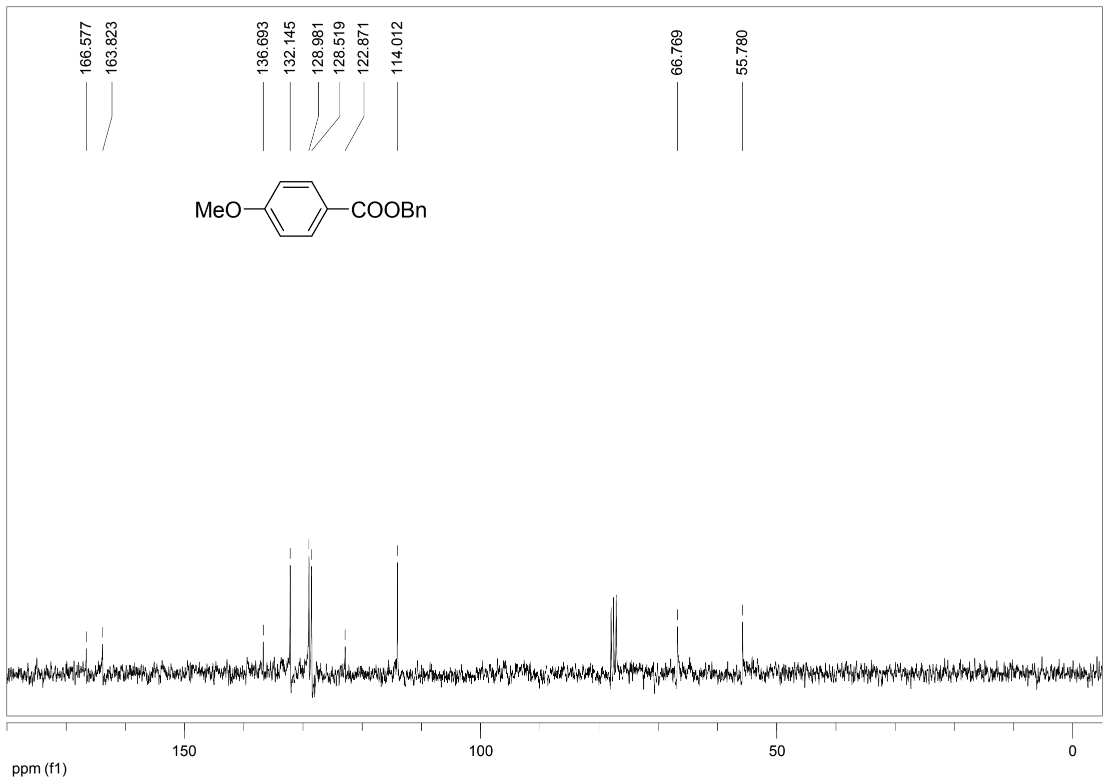
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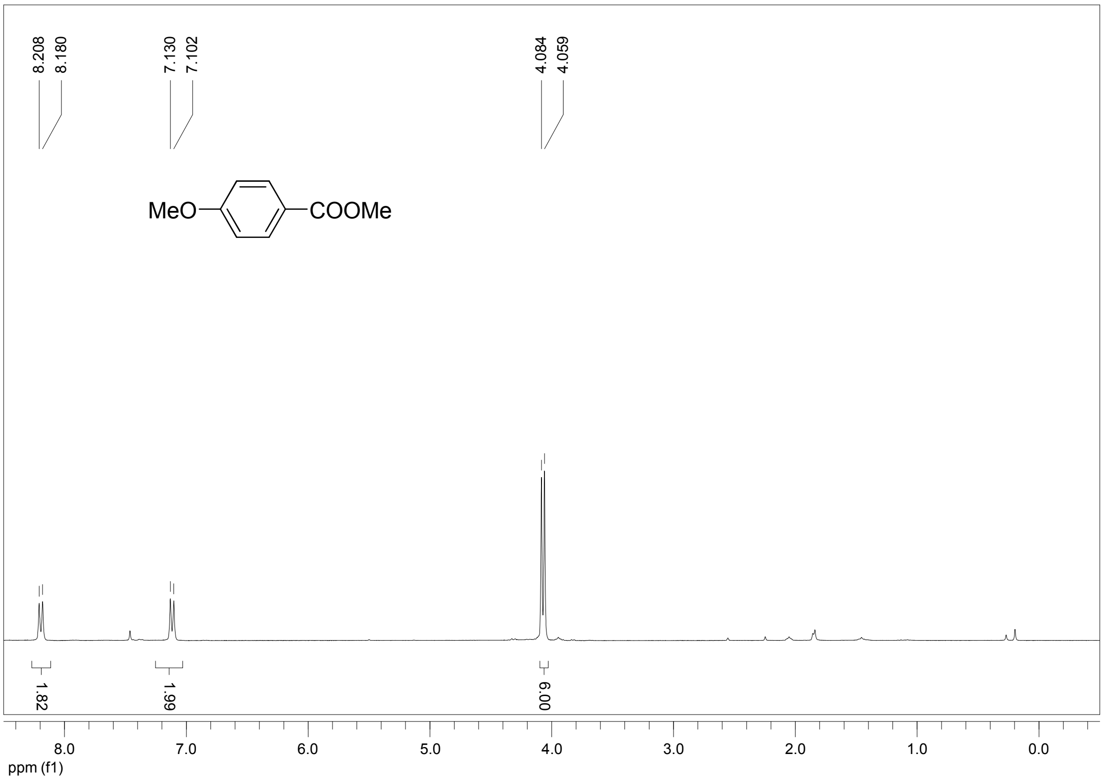
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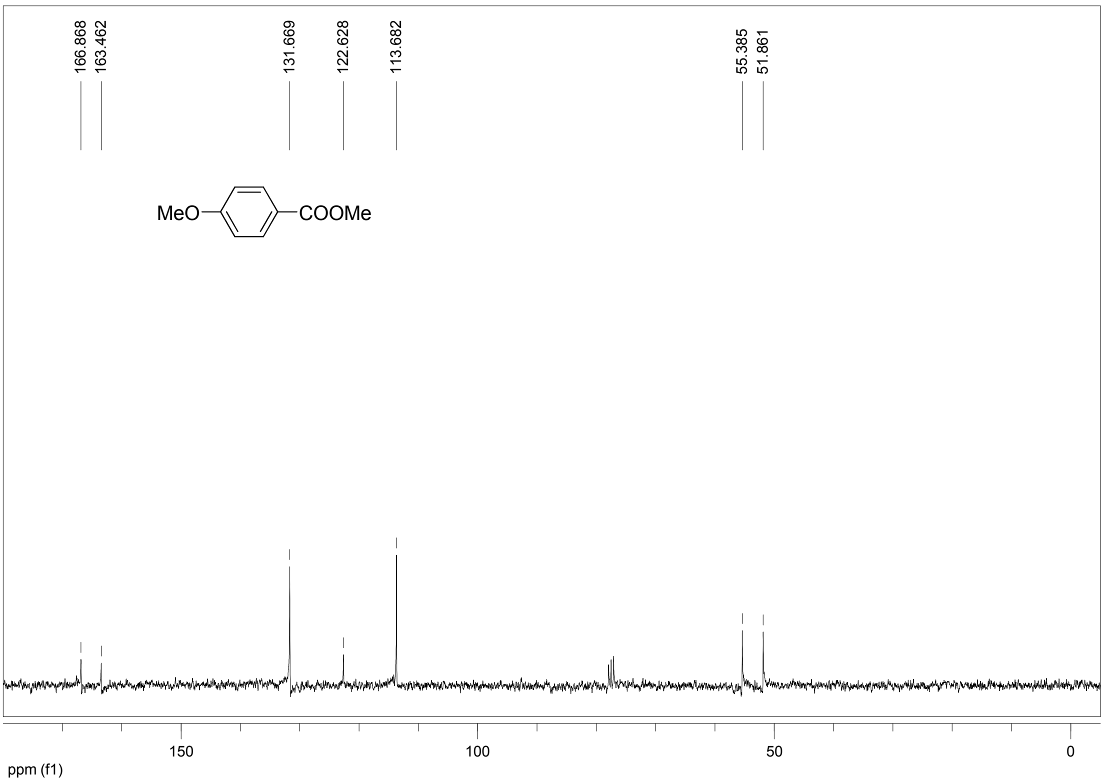
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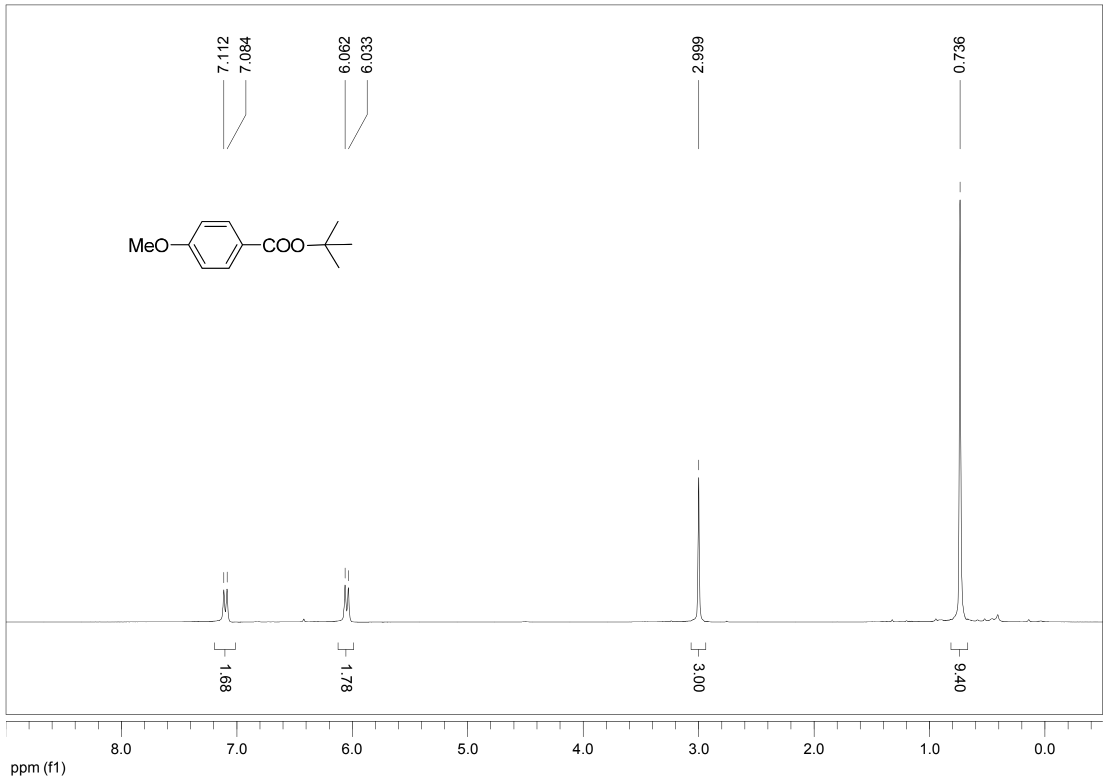
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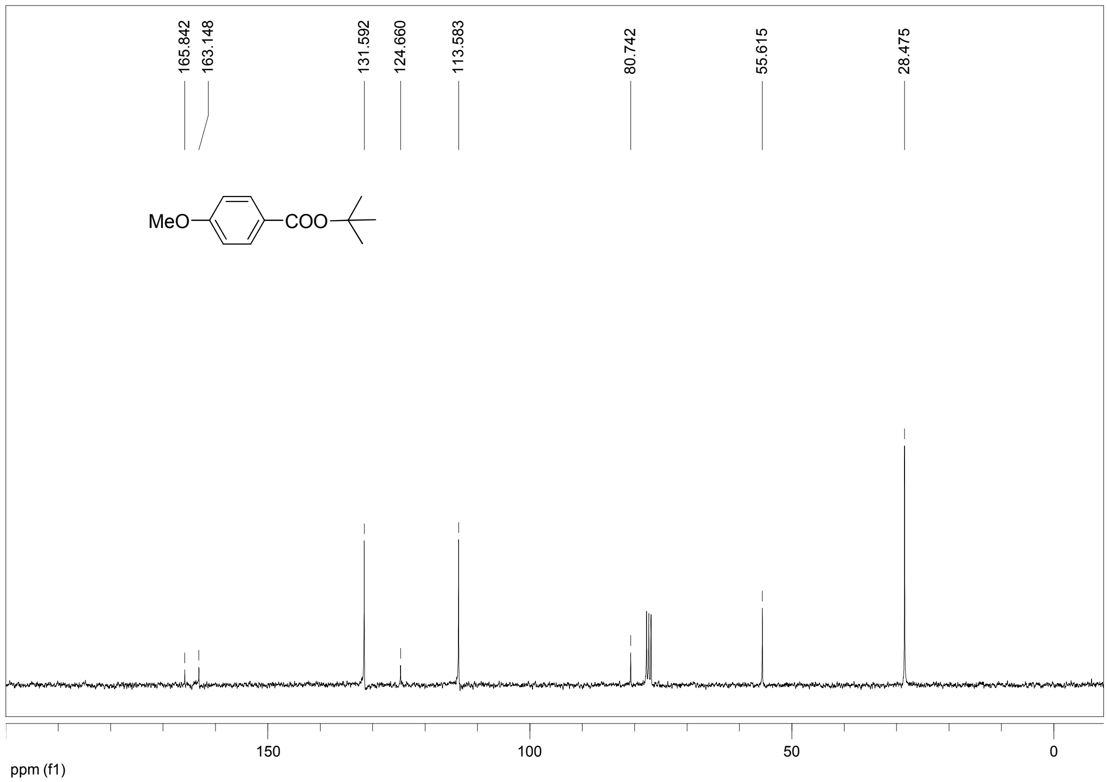
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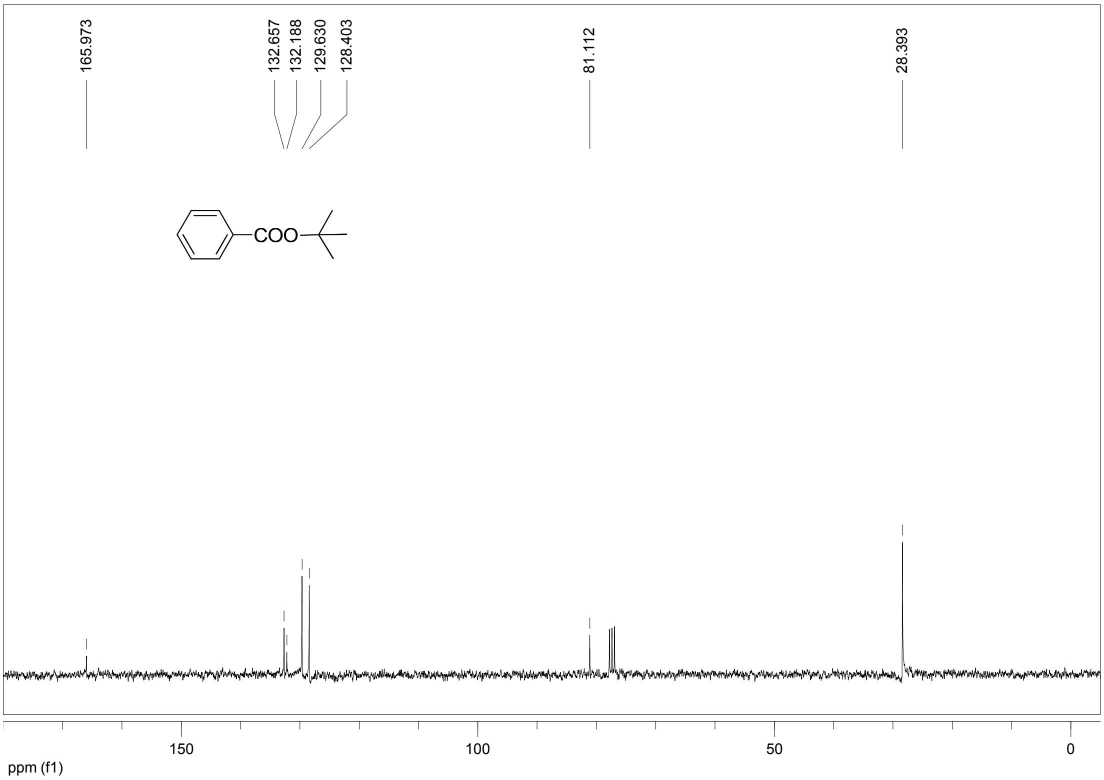
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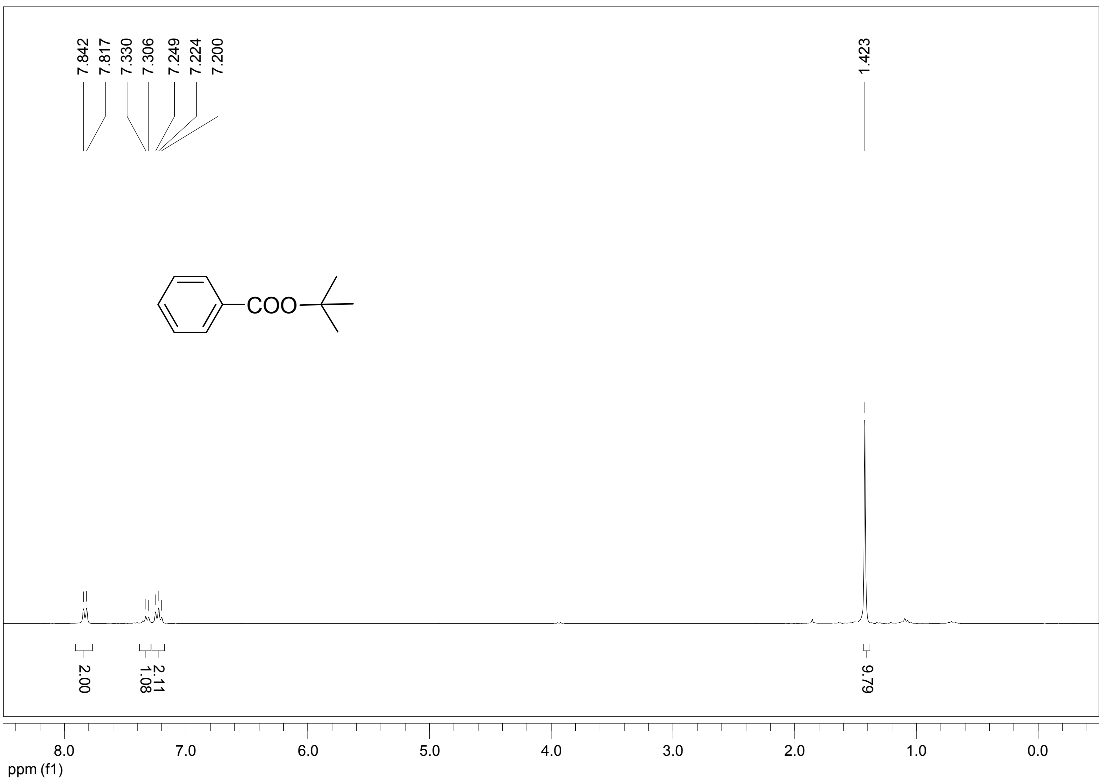
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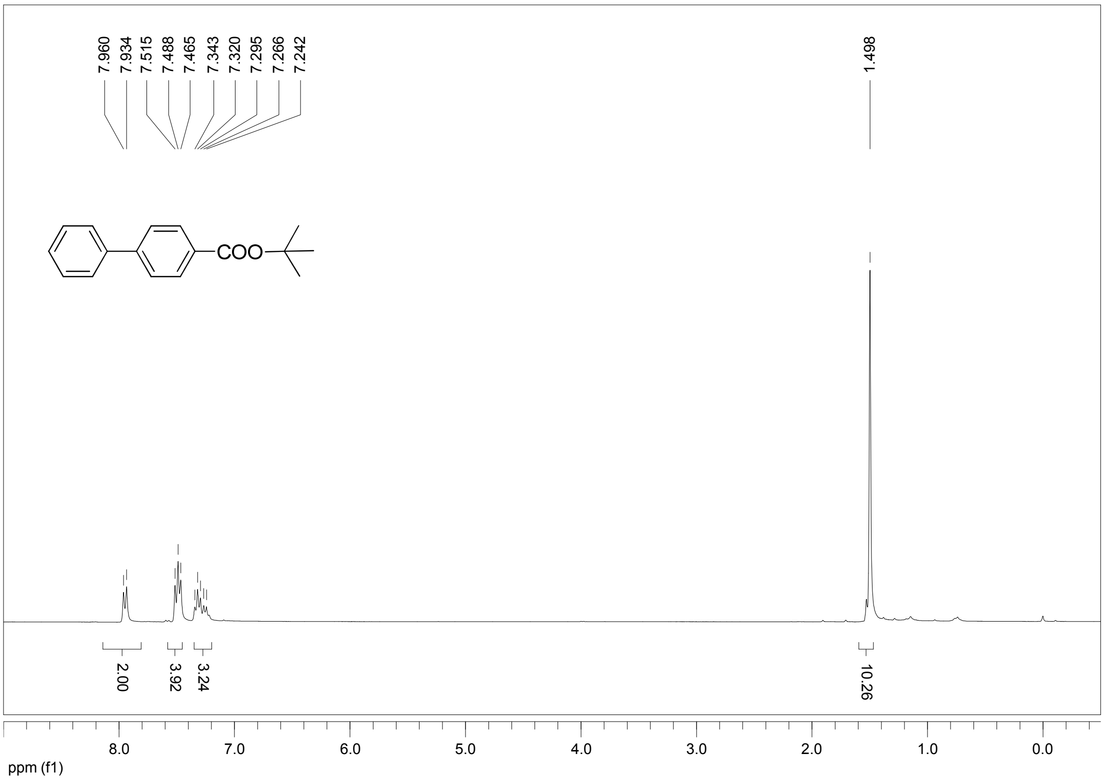
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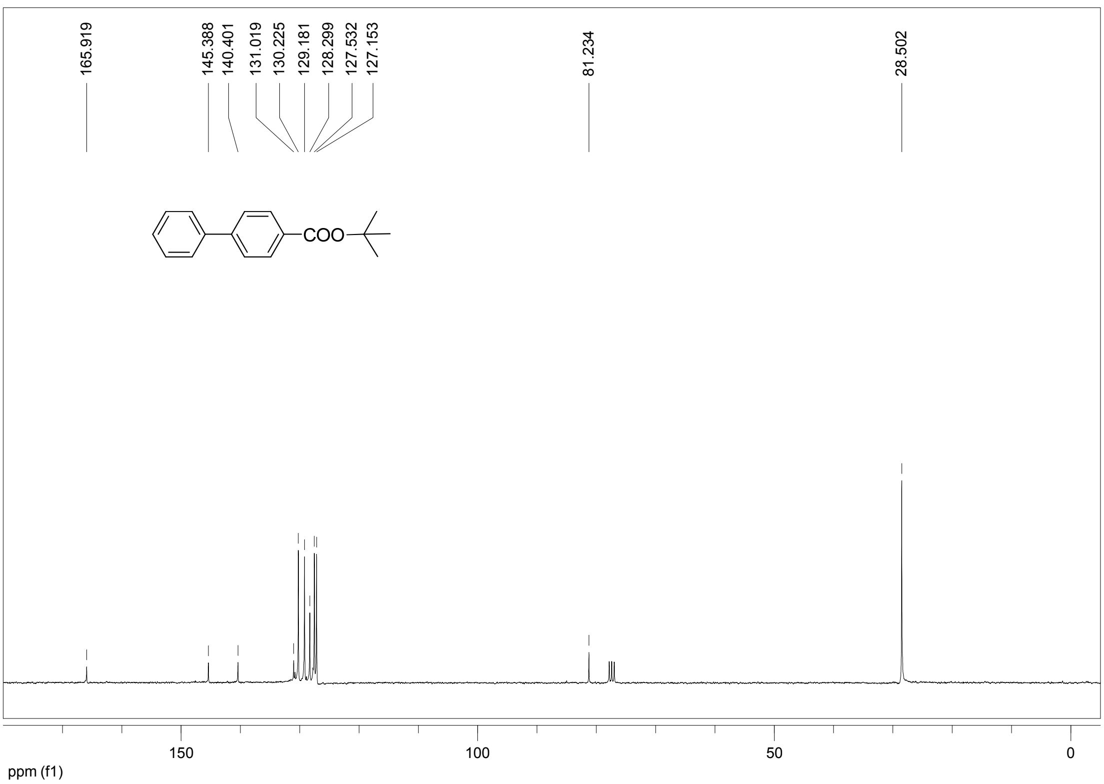
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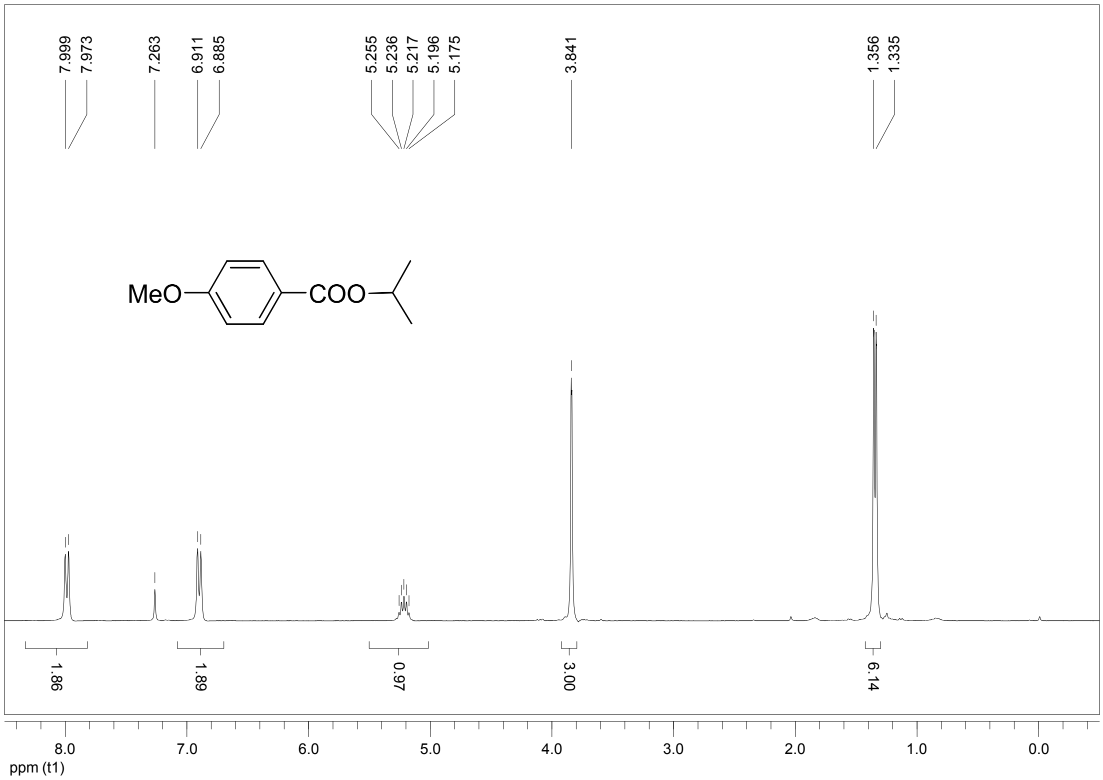
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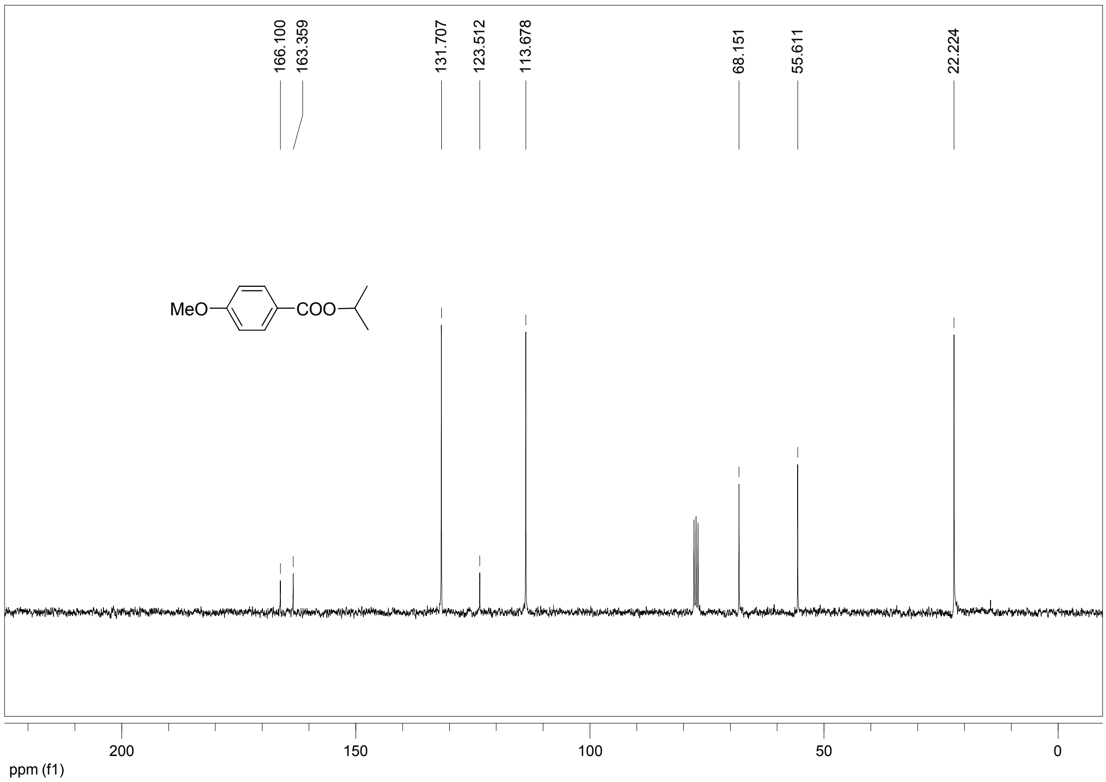
7.973
7.263
6.911
6.885
5.255
5.236
5.217
5.196
5.175
3.841
1.356
1.335
MeO
COO
1.86
1.89
0.97
3.00
6.14
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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163.359
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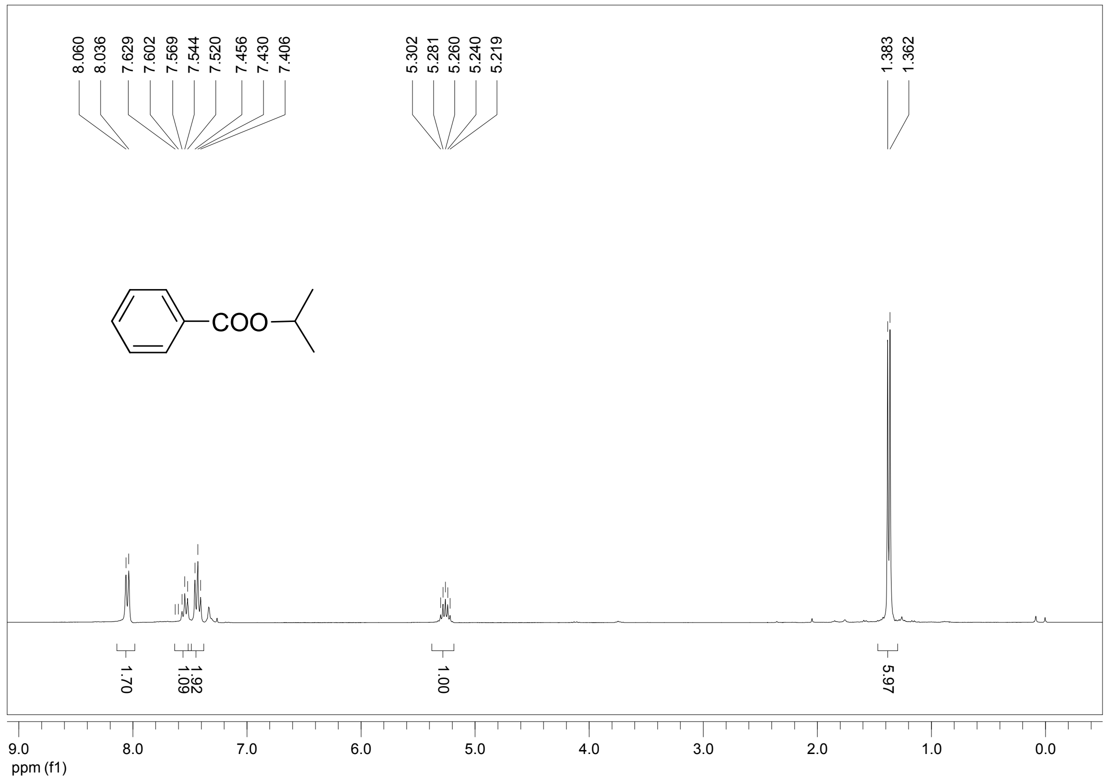
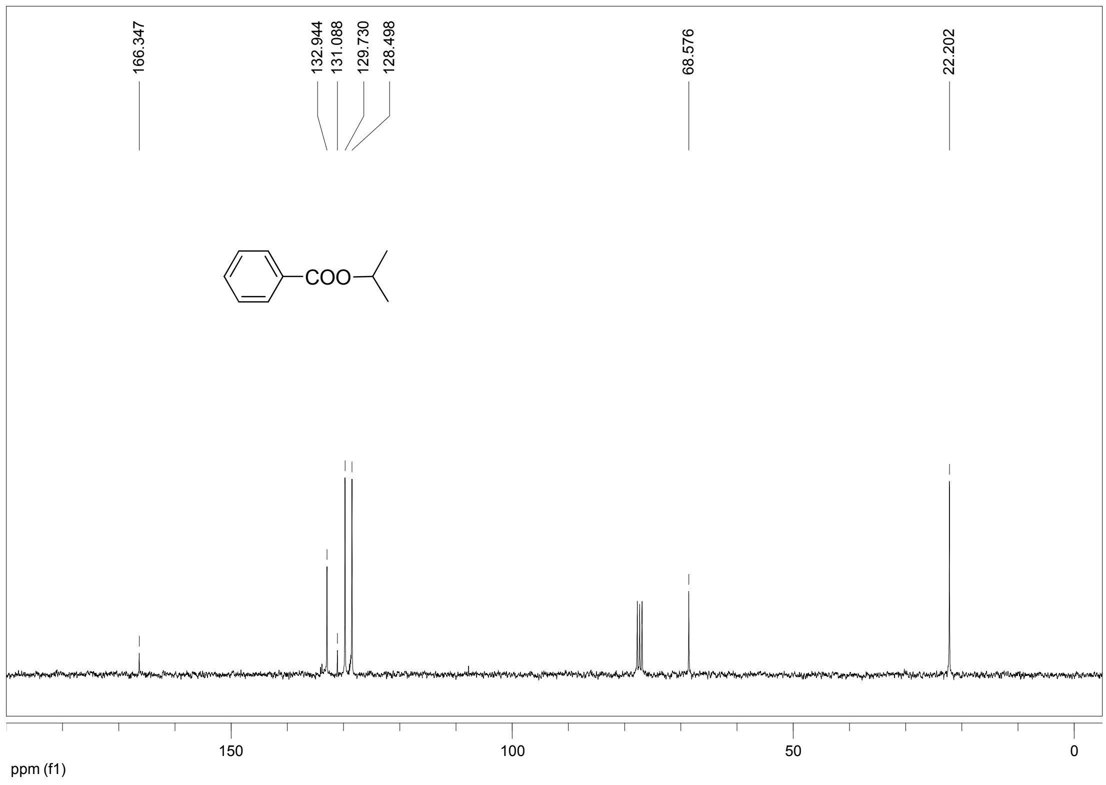
123.512
113.678
68.151
55.611
22.224
MeO
COO
200
150
100
50
0
ppm (f1)


8.060
8.036
7.629
7.602
7.569
7.544
7.520
7.456
7.430
7.406
5.302
5.281
5.260
5.240
5.219
1.383
1.362
COO
1.70
1.09
1.92
1.00
5.97
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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68.576
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COO
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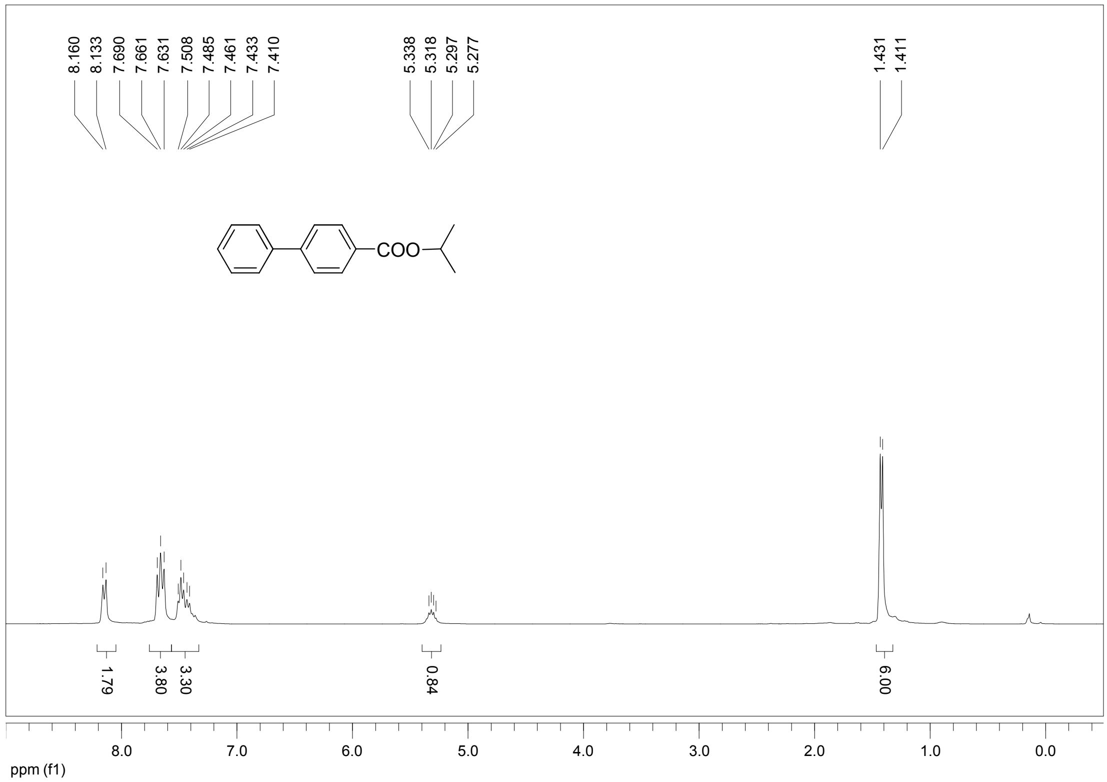
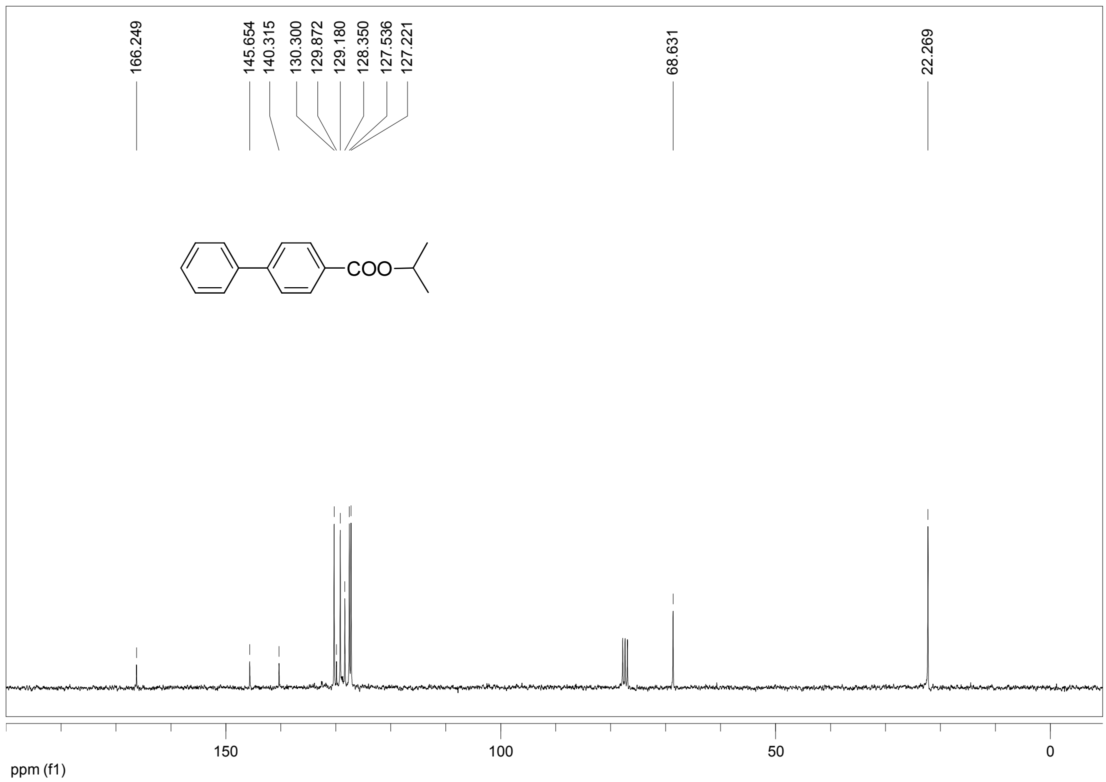
100
50
0
ppm (f1)


8.160
8.133
7.690
7.661
7.631
7.508
7.485
7.461
7.433
7.410
5.338
5.318
5.297
5.277
1.431
1.411
COO
1.79
3.80
3.30
0.84
6.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


166.249
145.654
140.315
130.300
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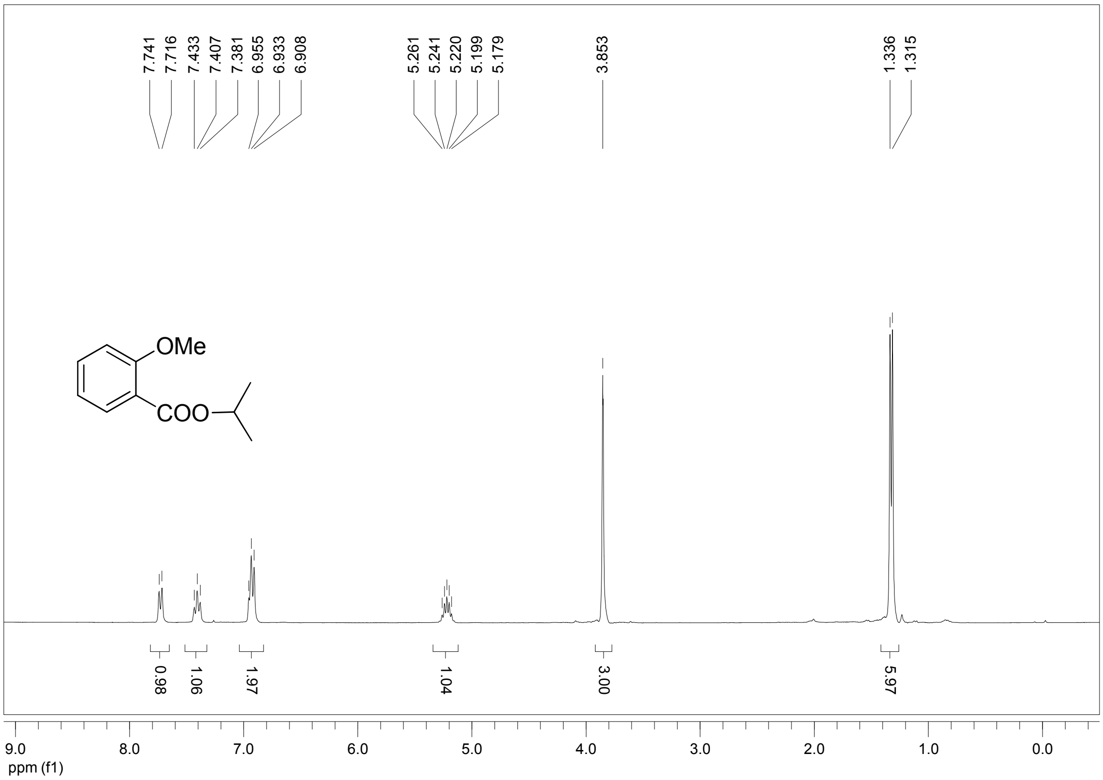
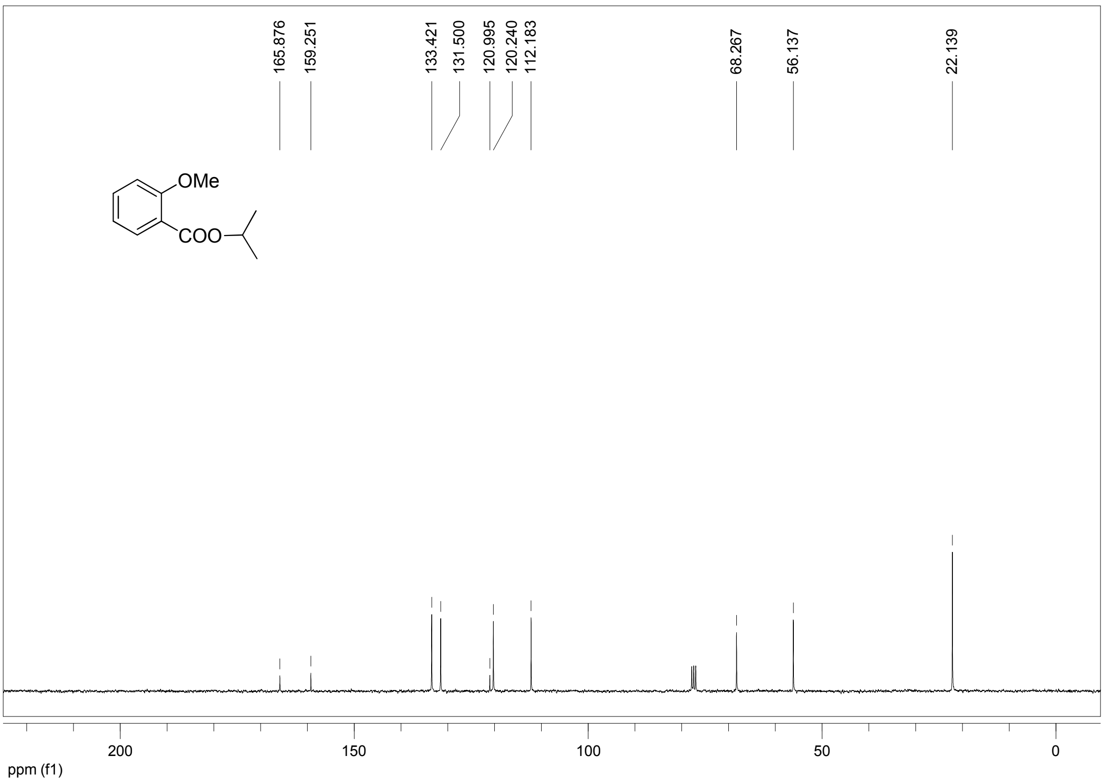
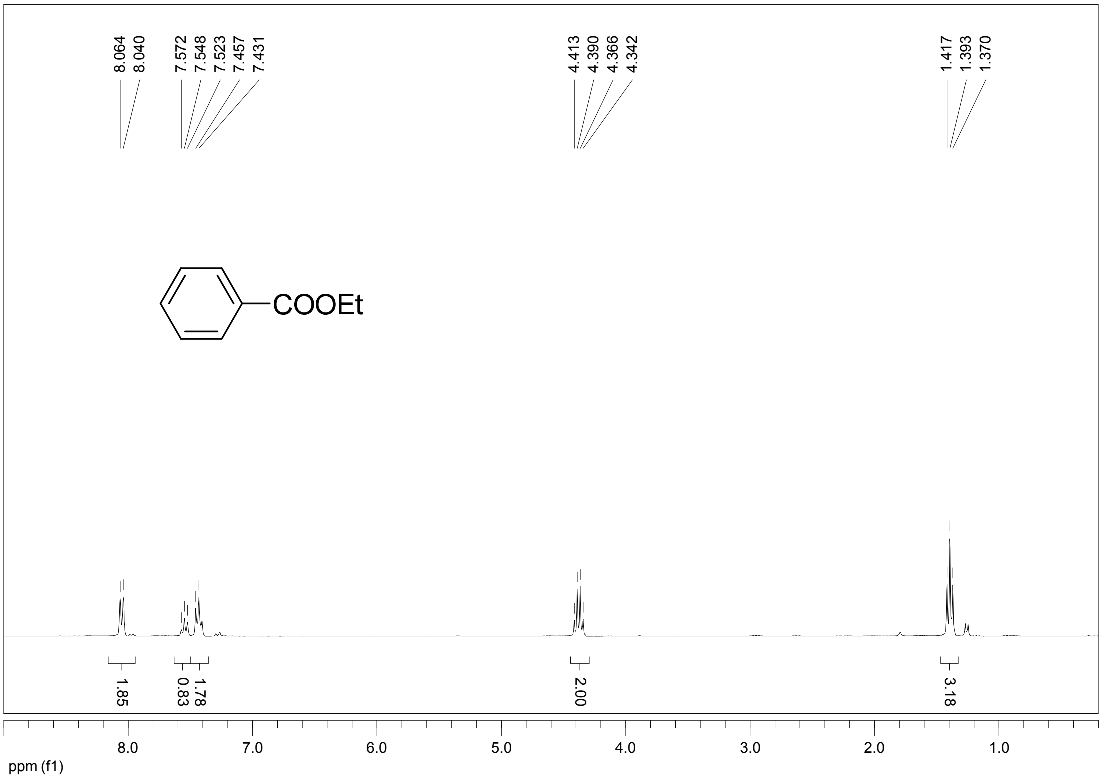
129.180
128.350
127.536
127.221
68.631
22.269
COO
150
100
50
0
ppm (f1)


7.741
7.716
7.433
7.407
7.381
6.955
6.933
6.908
5.261
5.241
5.220
5.199
5.179
3.853
1.336
1.315
OMe
COO
0.98
1.06
1.97
1.04
3.00
5.97
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


165.876
159.251
133.421
131.500
120.995
120.240
112.183
68.267
56.137
22.139
OMe
COO
200
150
100
50
0
ppm (f1)


8.064
8.040
7.572
7.548
7.523
7.457
7.431
4.413
4.390
4.366
4.342
1.417
1.393
1.370
COOEt
1.85
0.83
1.78
2.00
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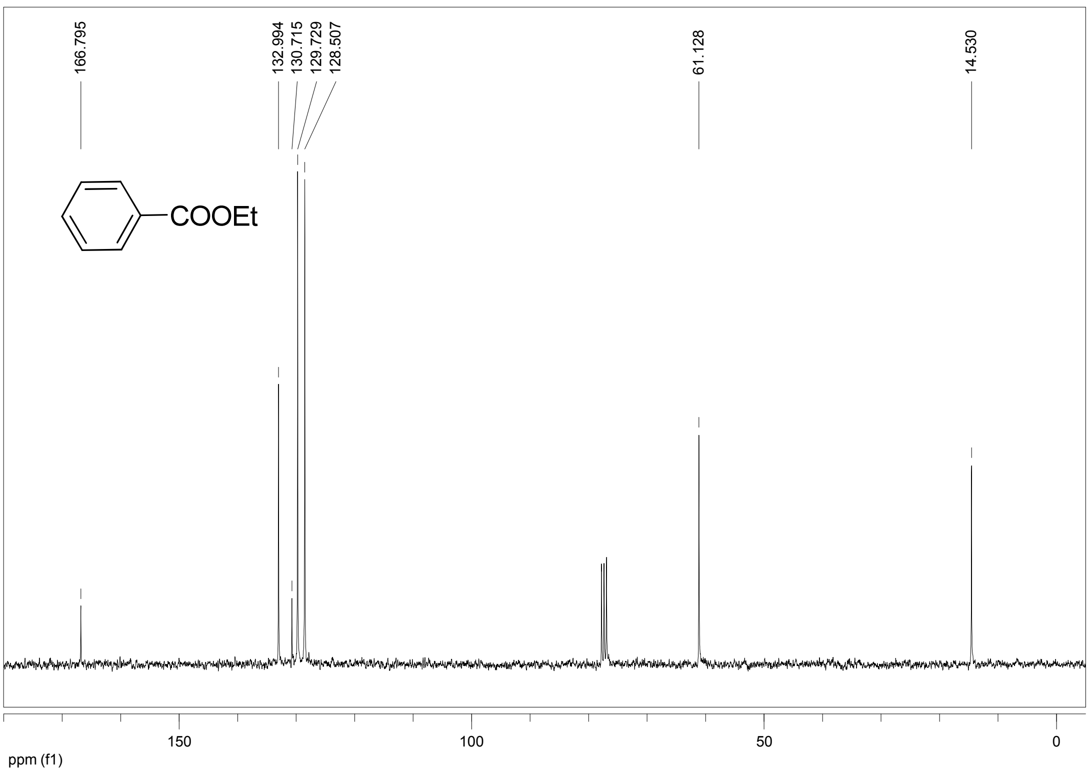
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)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128.507
61.128
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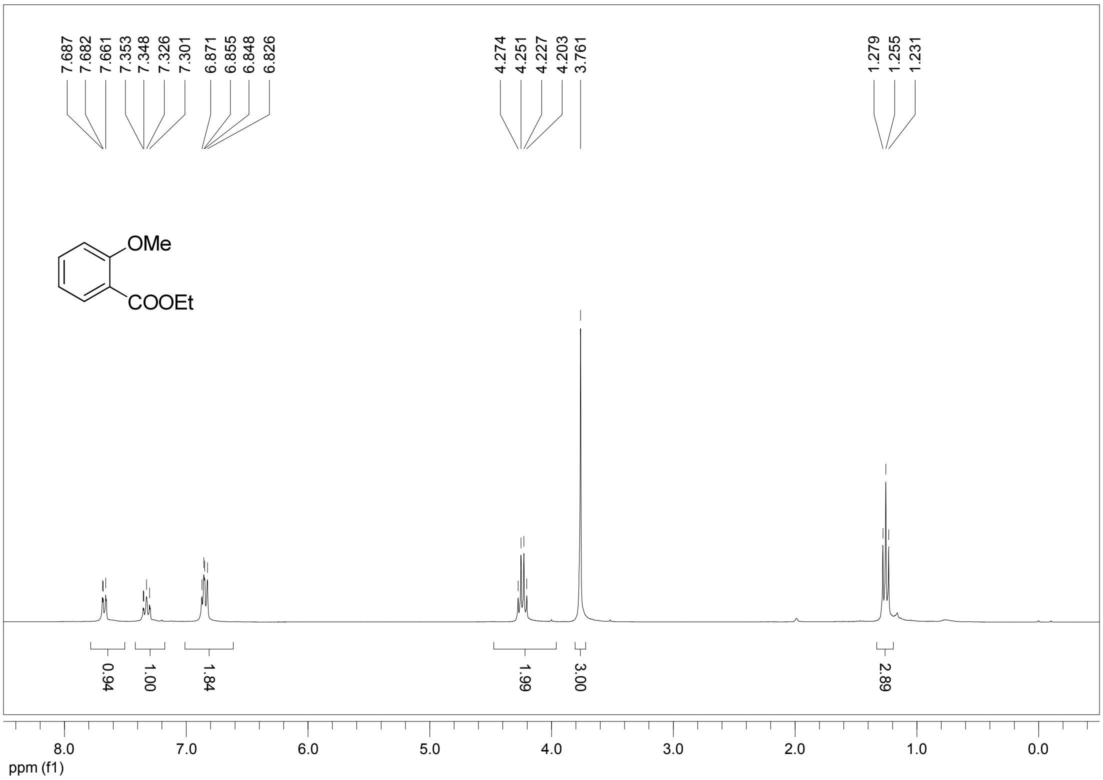
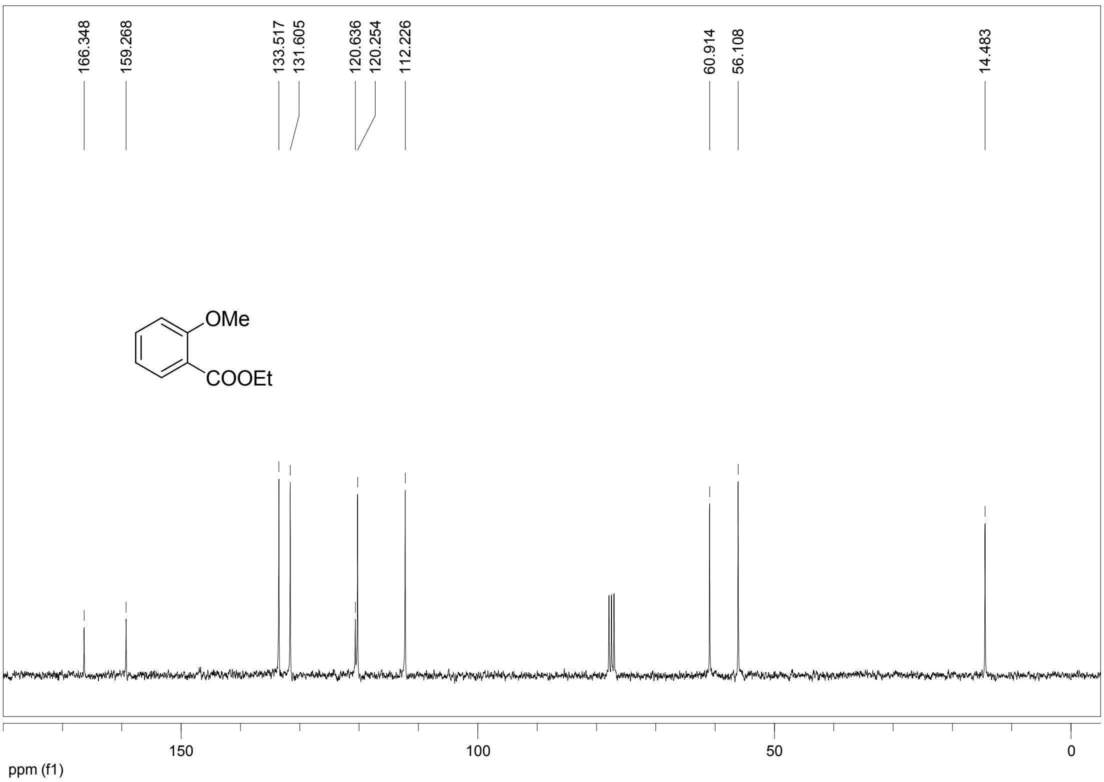
150
100
50
0
ppm (f1)


7.687
7.682
7.661
7.353
7.348
7.326
7.301
6.871
6.855
6.848
6.826
4.274
4.251
4.227
4.203
3.761
1.279
1.255
1.231
OMe
COOEt
0.94
1.00
1.84
1.99
3.00
2.89
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


166.348
159.268
133.517
131.605
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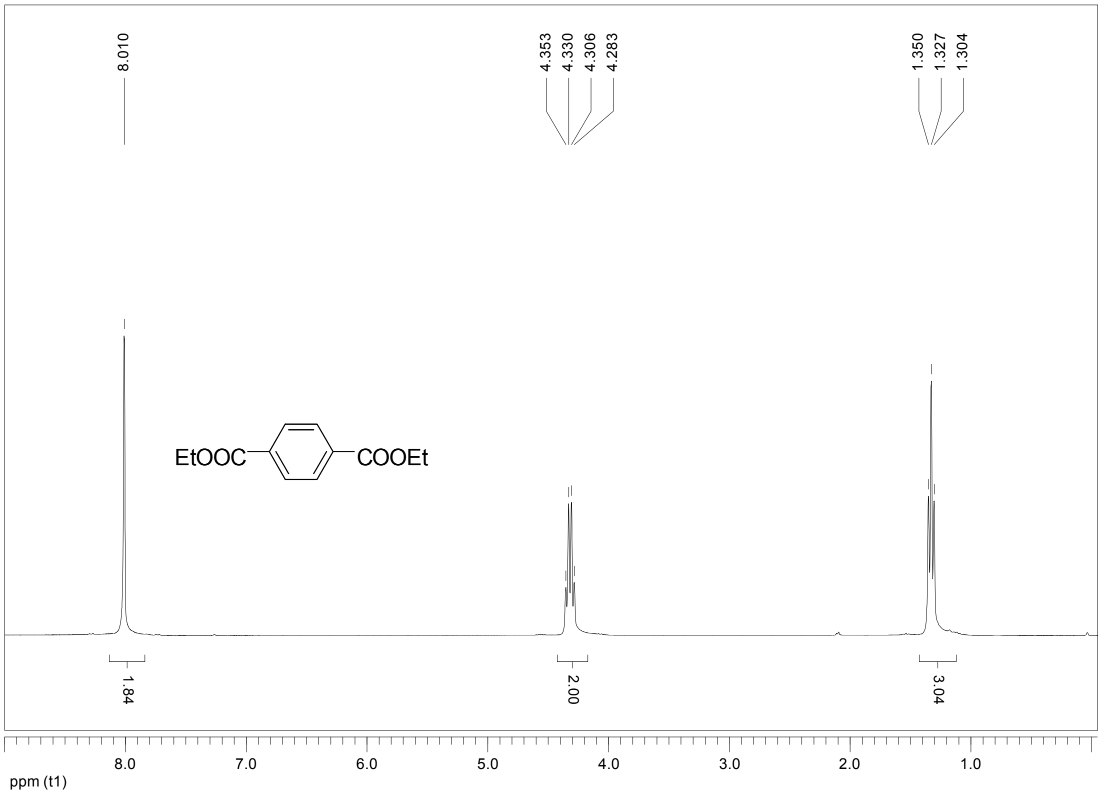
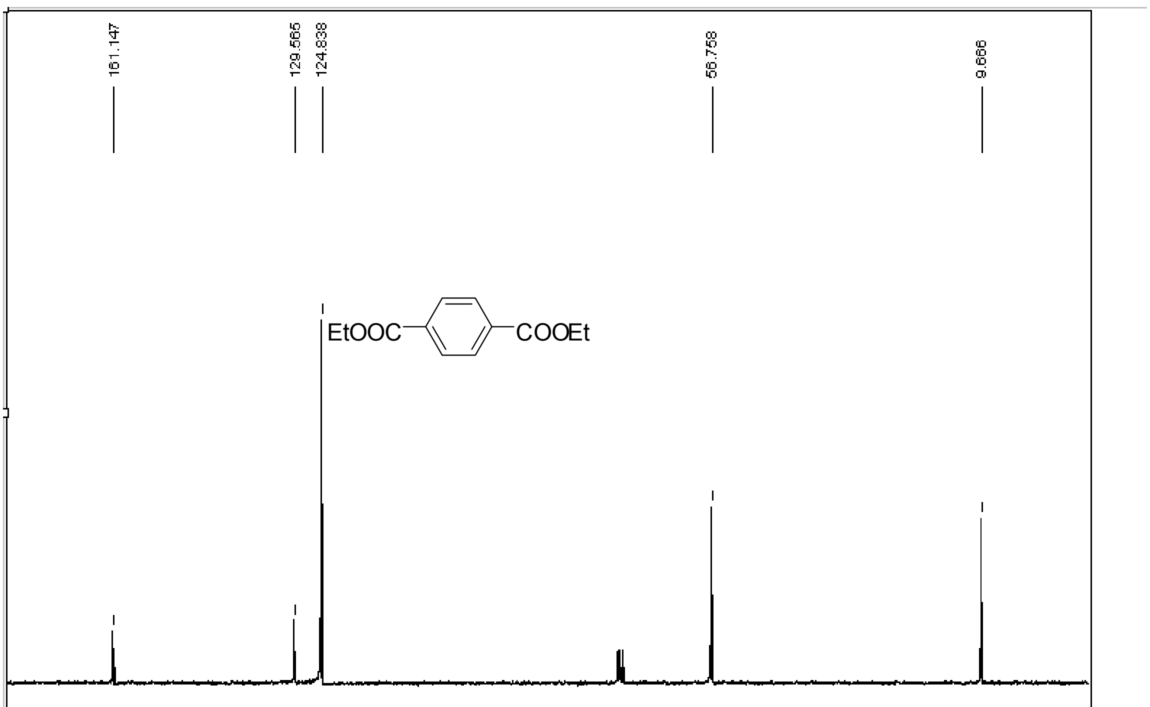
120.254
112.226
60.914
56.108
14.483
OMe
COOEt
150
100
50
0
ppm (f1)


8.010
4.353
4.330
4.306
4.283
1.350
1.327
1.304
EtOOC
COOEt
1.84
2.00
3.04
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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129.565
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9.656
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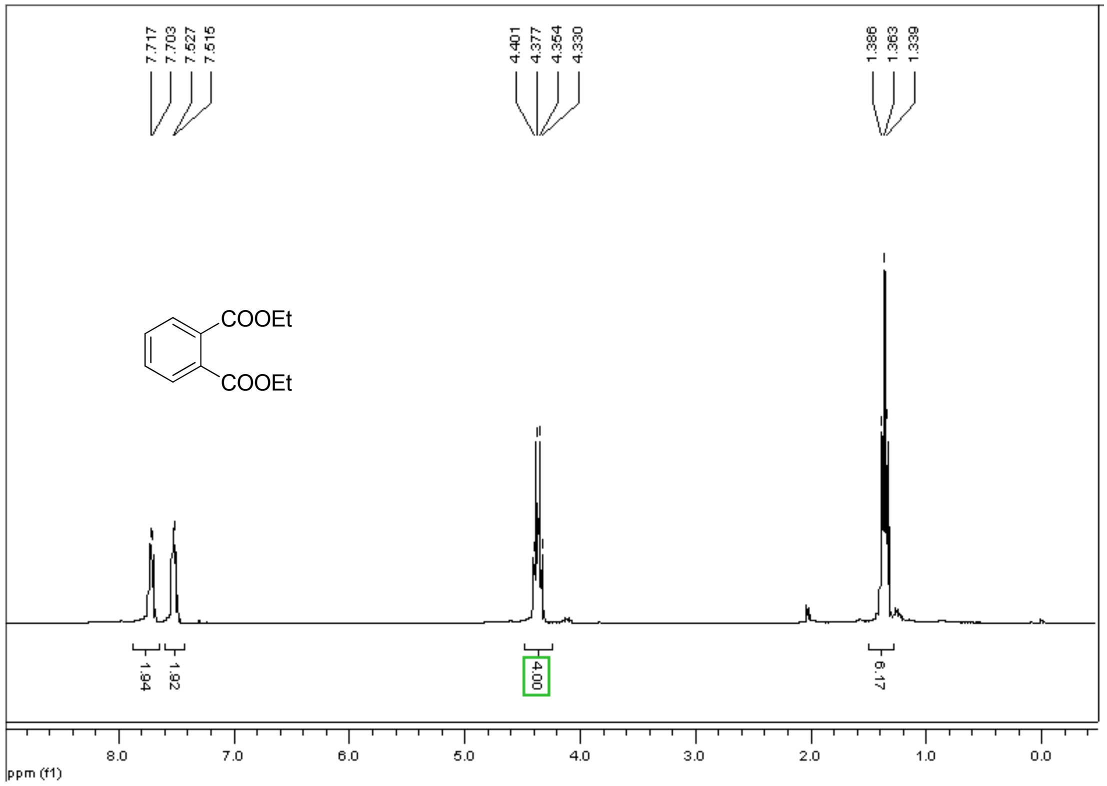
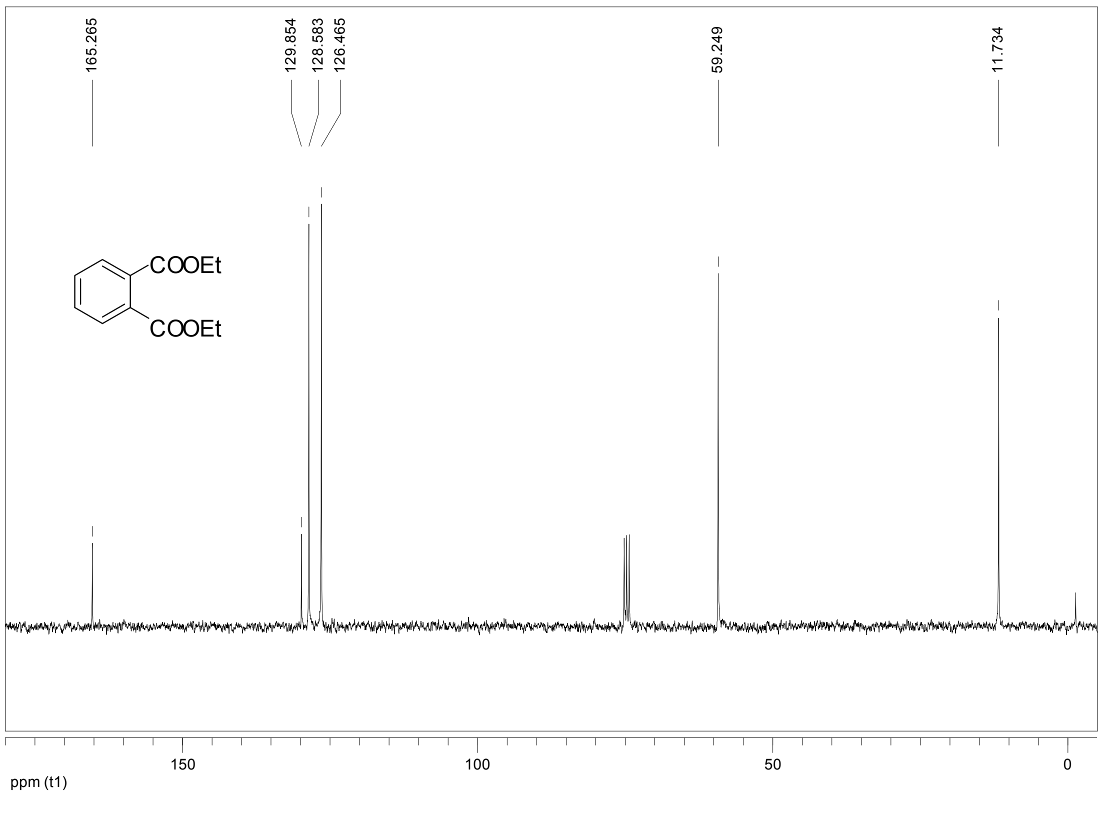
COOEt
150
100
50
0
ppm (f1)


7.717
7.703
7.527
7.515
4.401
4.377
4.354
4.330
1.386
1.363
1.339
COOEt
COOEt
1.94
1.92
4.00
6.17
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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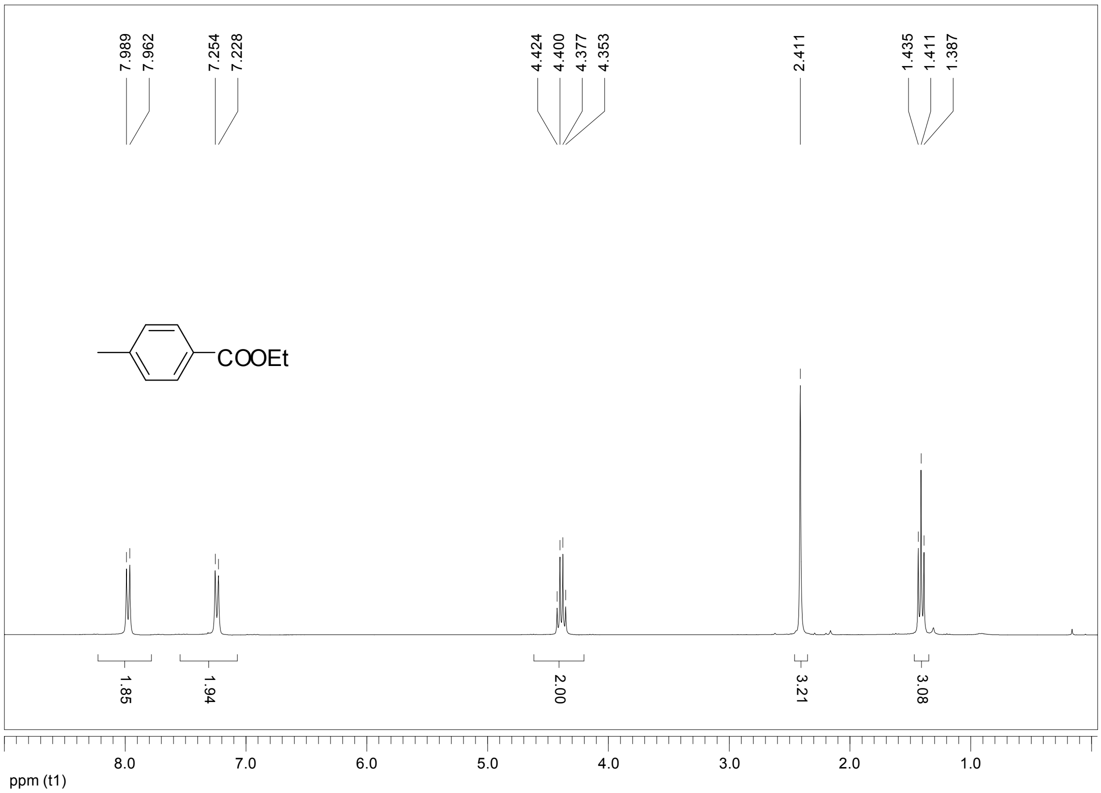
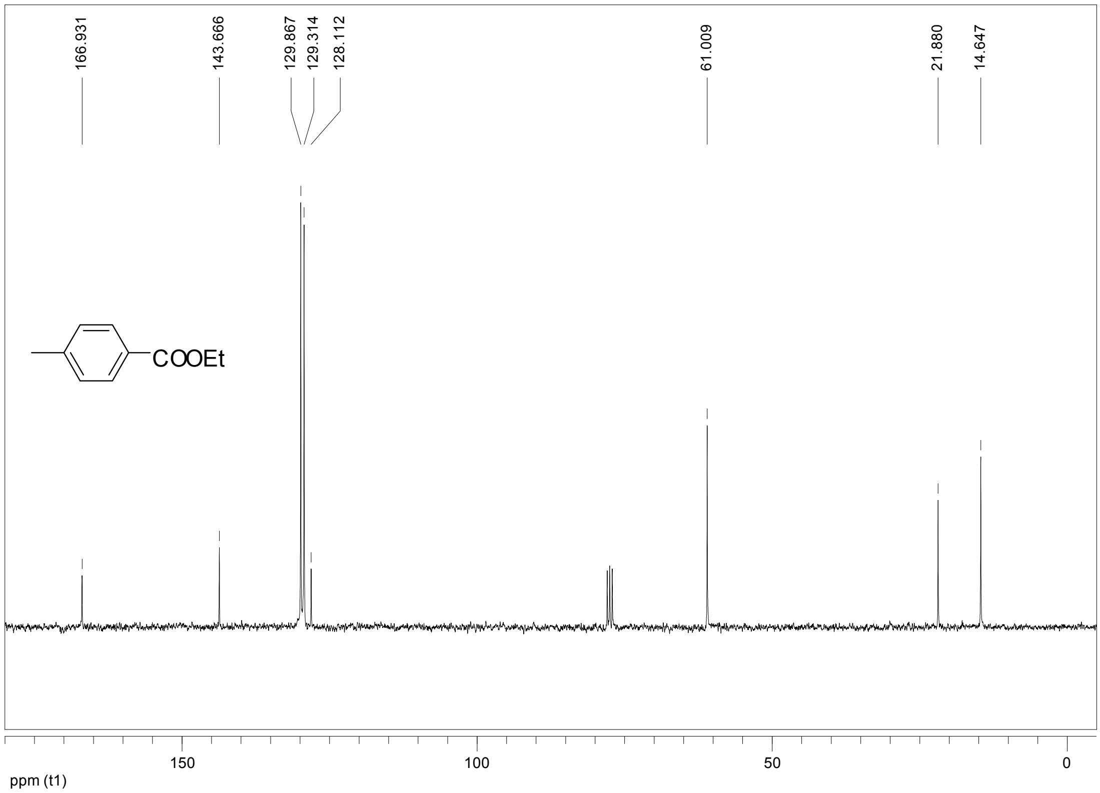
128.583
126.465
59.249
11.734
COOEt
COOEt
150
100
50
0
ppm (t1)


7.989
7.962
7.254
7.228
4.424
4.400
4.377
4.353
2.411
1.435
1.411
1.387
COOEt
1.85
1.94
2.00
3.21
3.08
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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143.666
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129.314
128.112
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21.880
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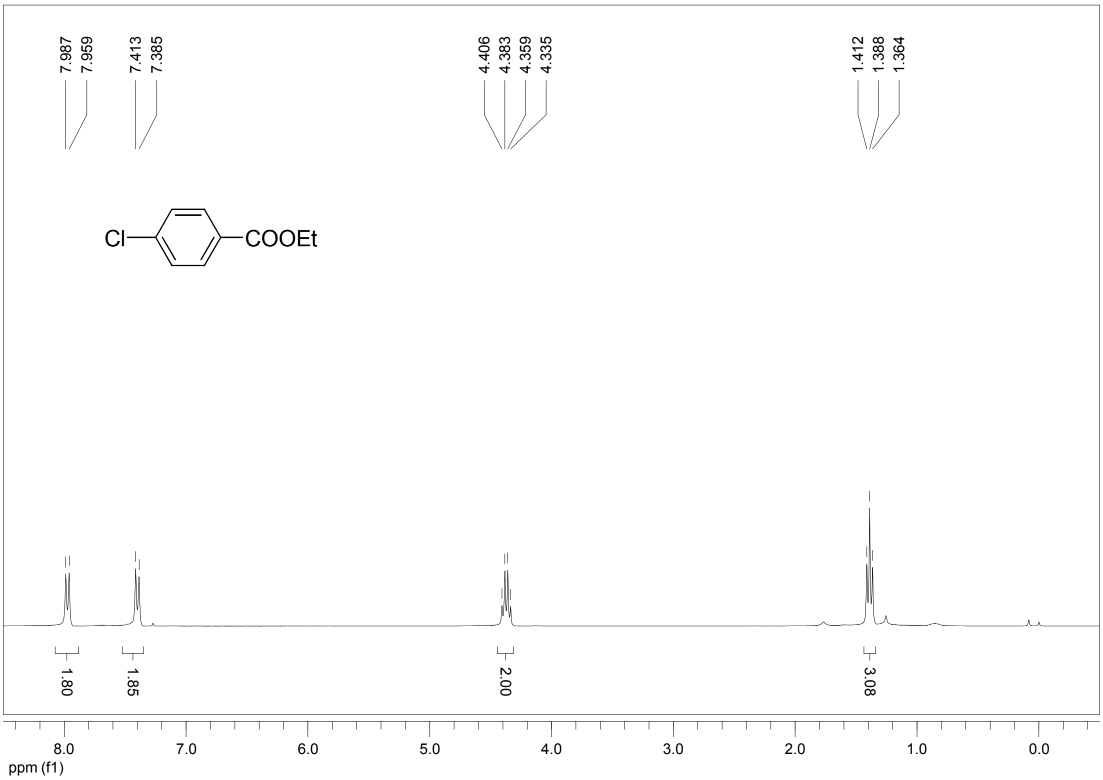
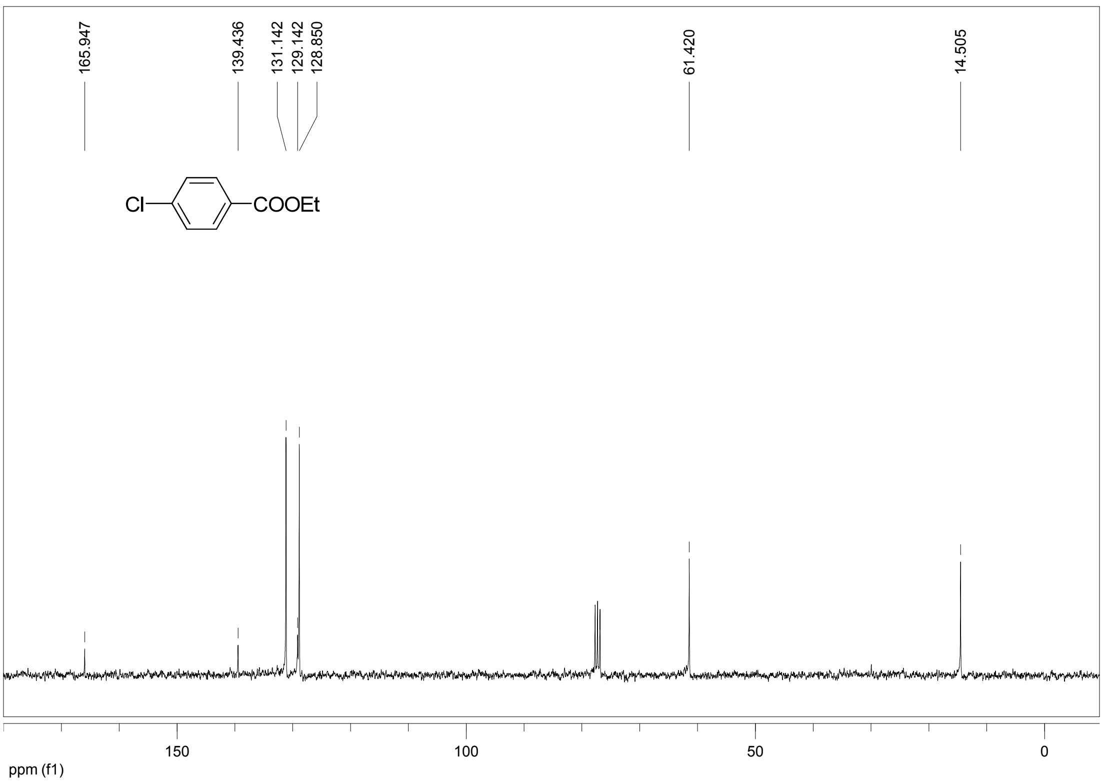
150
100
50
0
ppm (t1)


7.987
7.959
7.413
7.385
4.406
4.383
4.359
4.335
1.412
1.388
1.364
Cl
COOEt
1.80
1.85
2.00
3.08
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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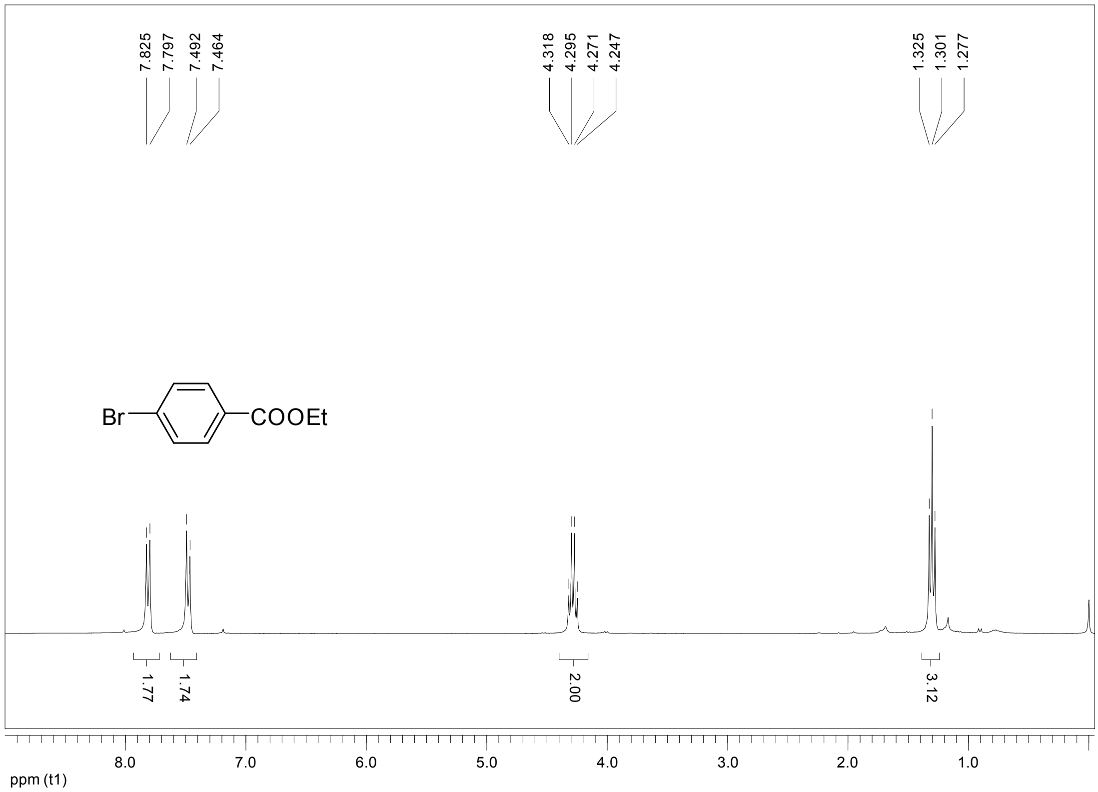
100
50
0
ppm (f1)


7.825
7.797
7.492
7.464
4.318
4.295
4.271
4.247
1.325
1.301
1.277
Br
COOEt
1.77
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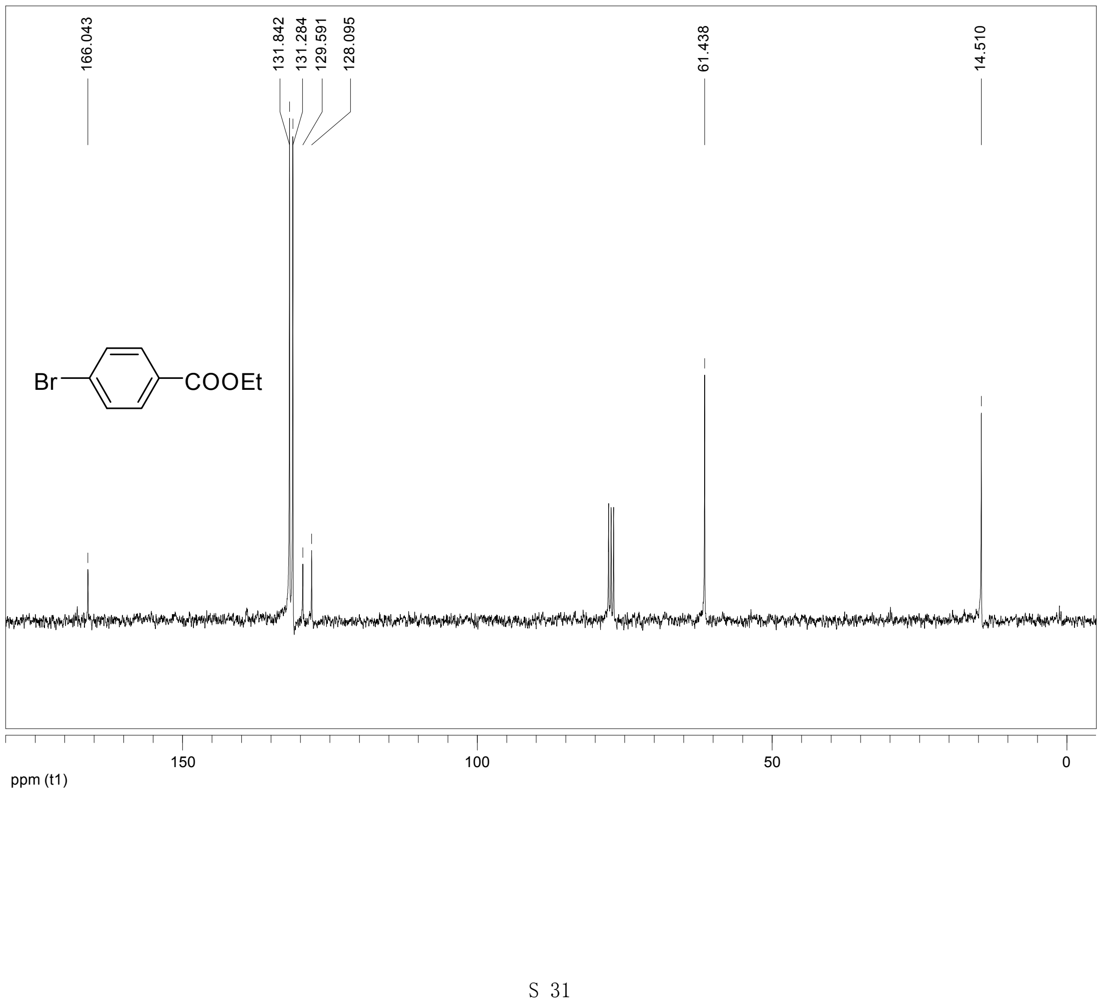
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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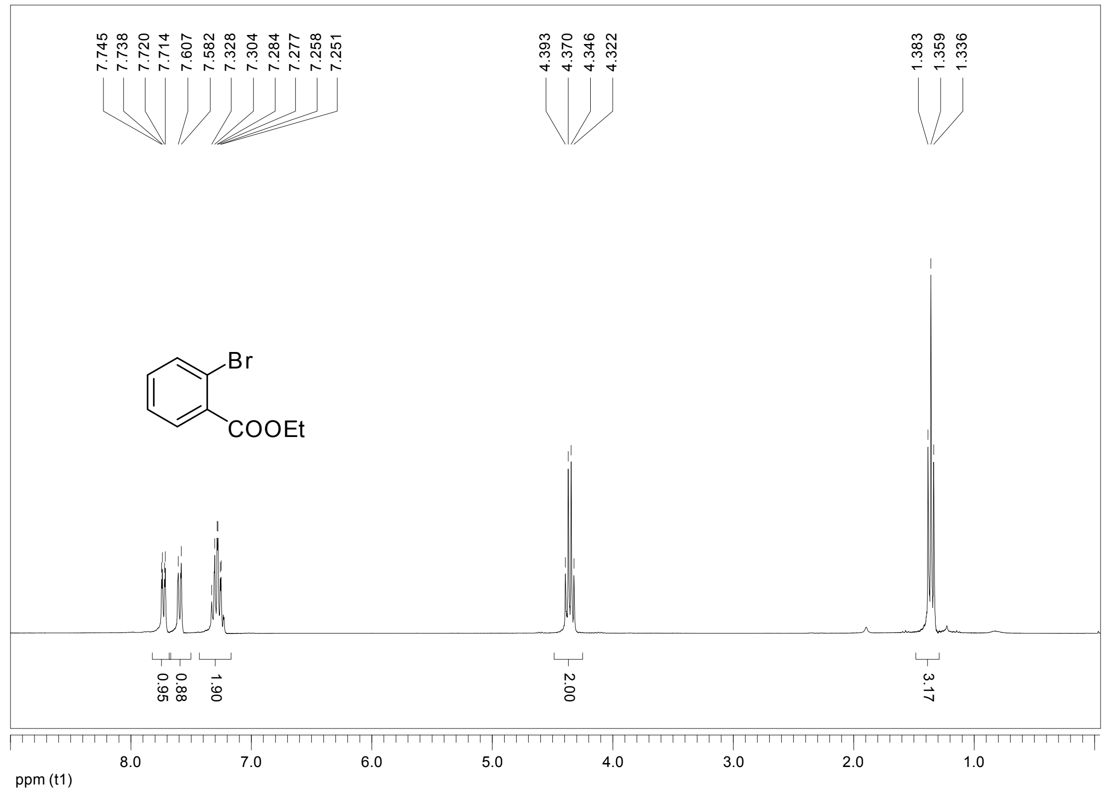
COOEt
150
100
50
0
ppm (t1)


7.745
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7.714
7.607
7.582
7.328
7.304
7.284
7.277
7.258
7.251
4.393
4.370
4.346
4.322
1.383
1.359
1.336
Br
COOEt
0.95
0.88
1.90
2.00
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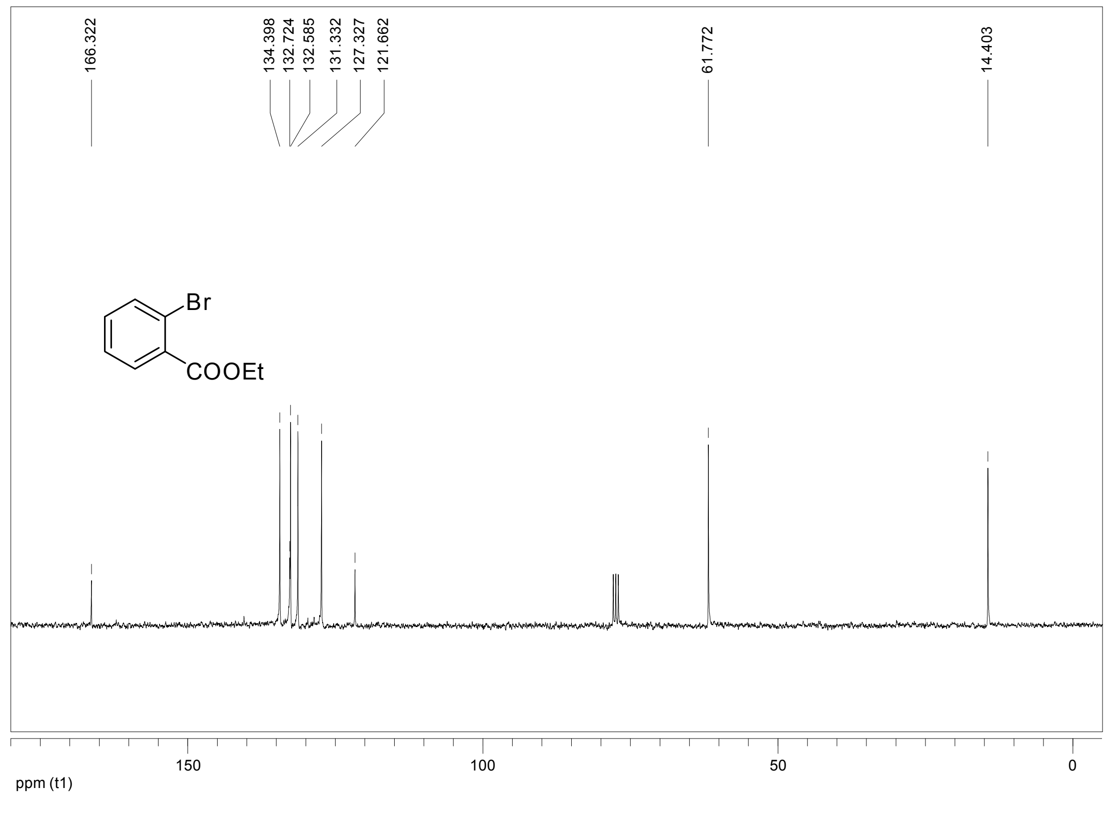
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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61.772
14.403
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COOEt
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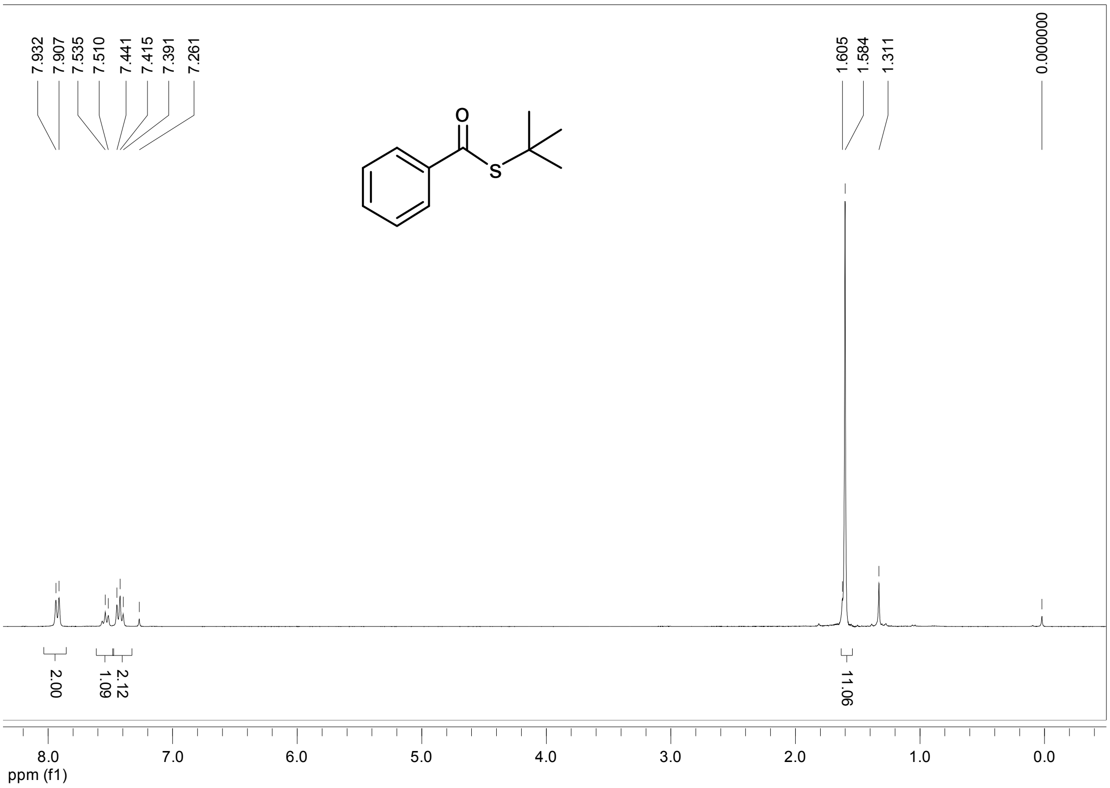
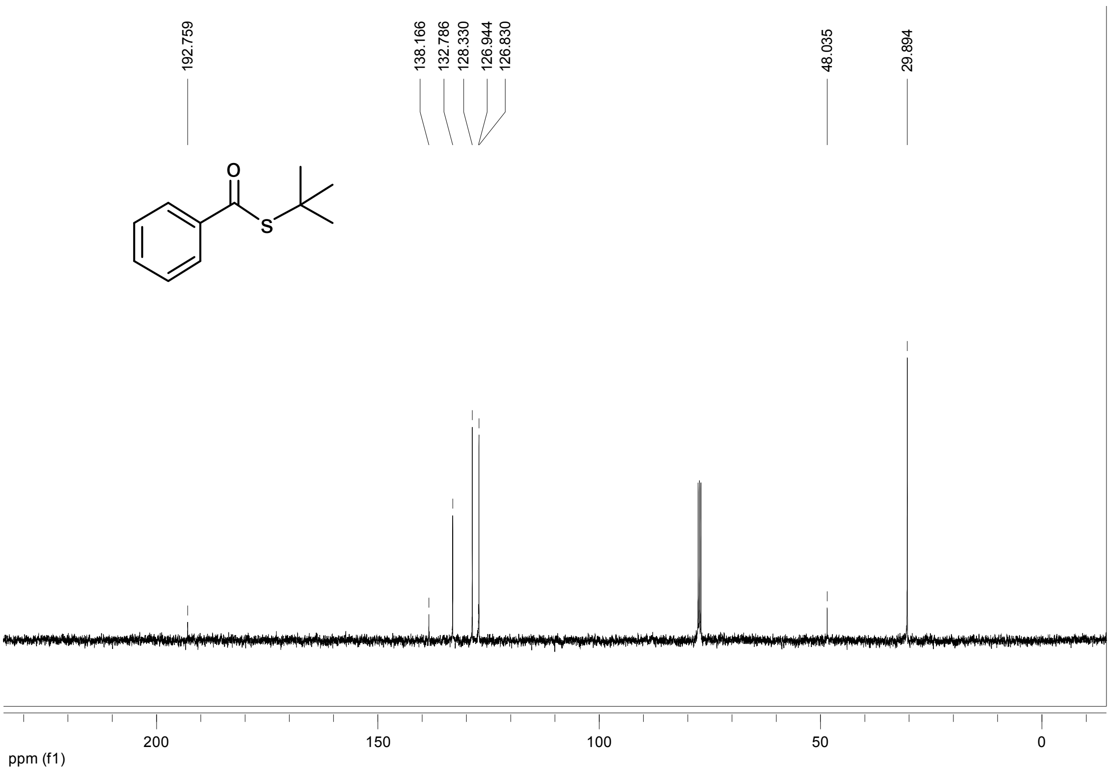
100
50
0
ppm (t1)


7.932
7.907
7.535
7.510
7.441
7.415
7.391
7.261
1.605
1.584
1.311
0.000000
O
S
2.00
1.09
2.12
11.06
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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138.166
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126.944
126.830
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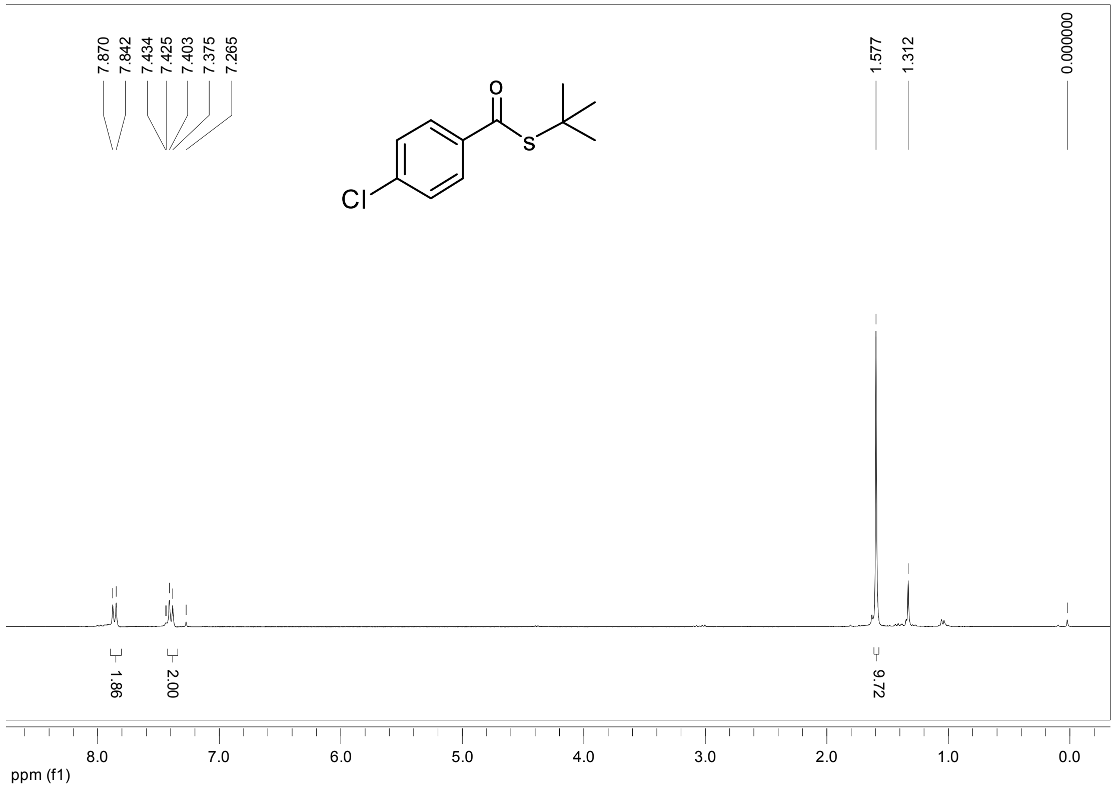
29.894
O
S
200
150
100
50
0
ppm (f1)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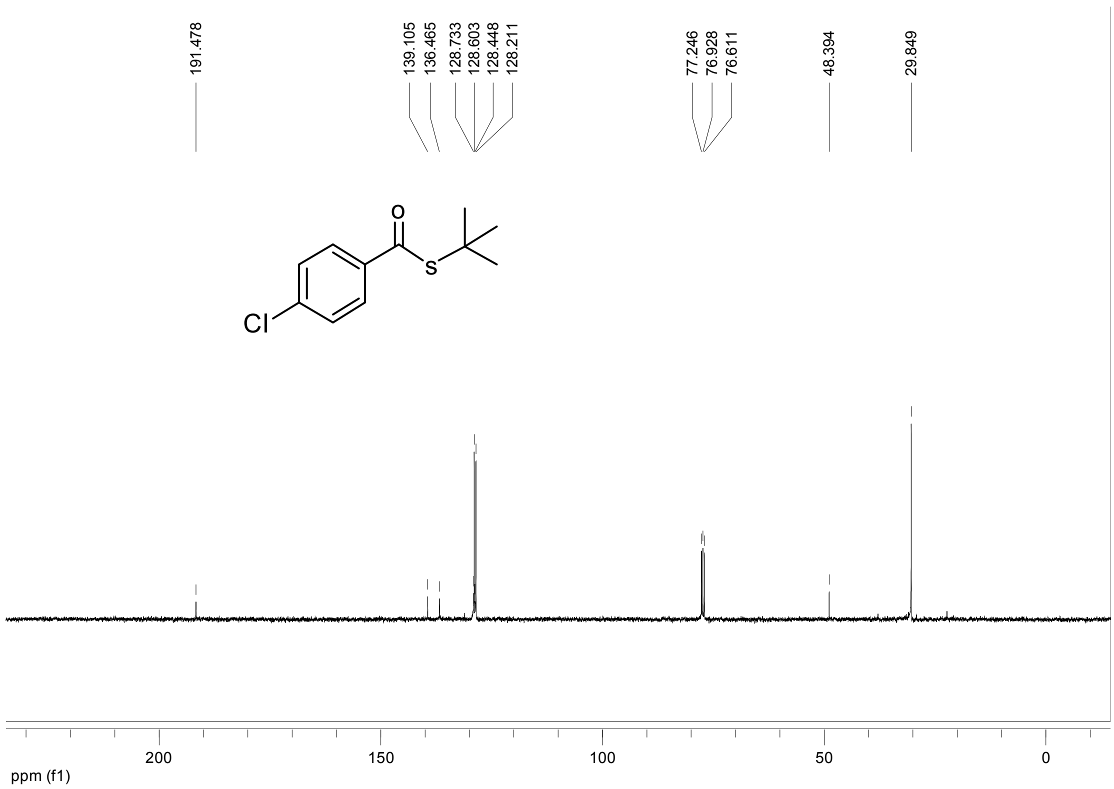
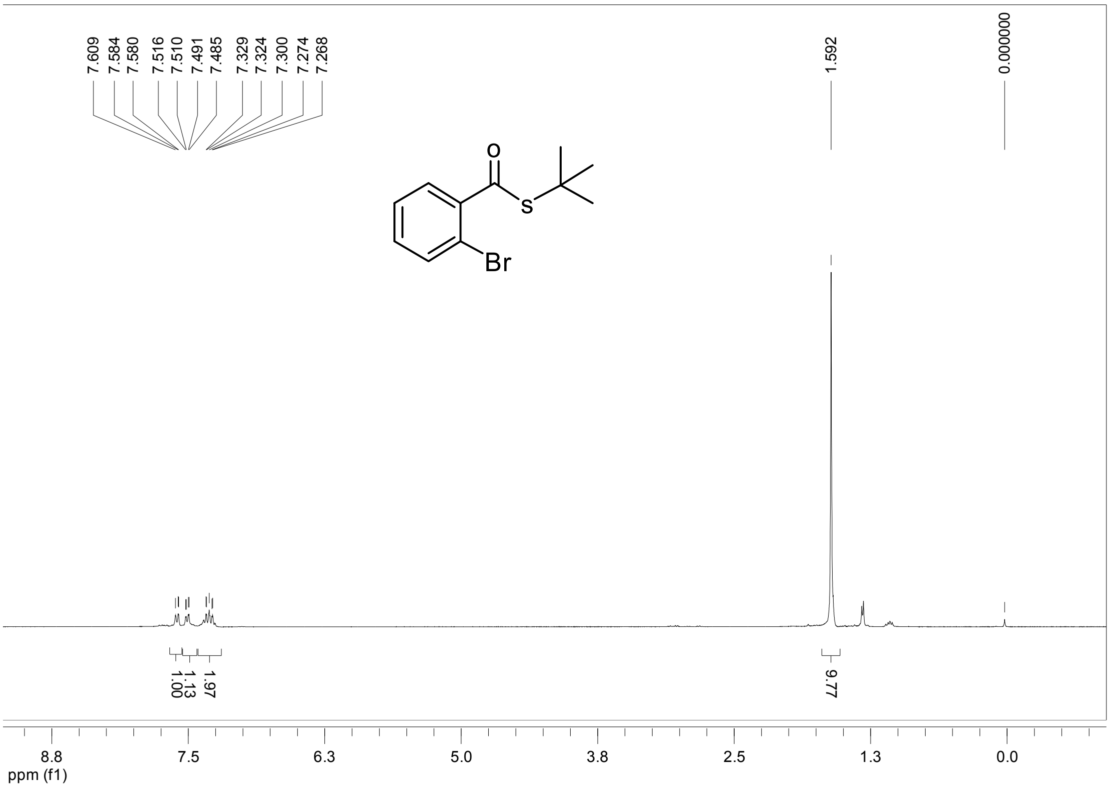
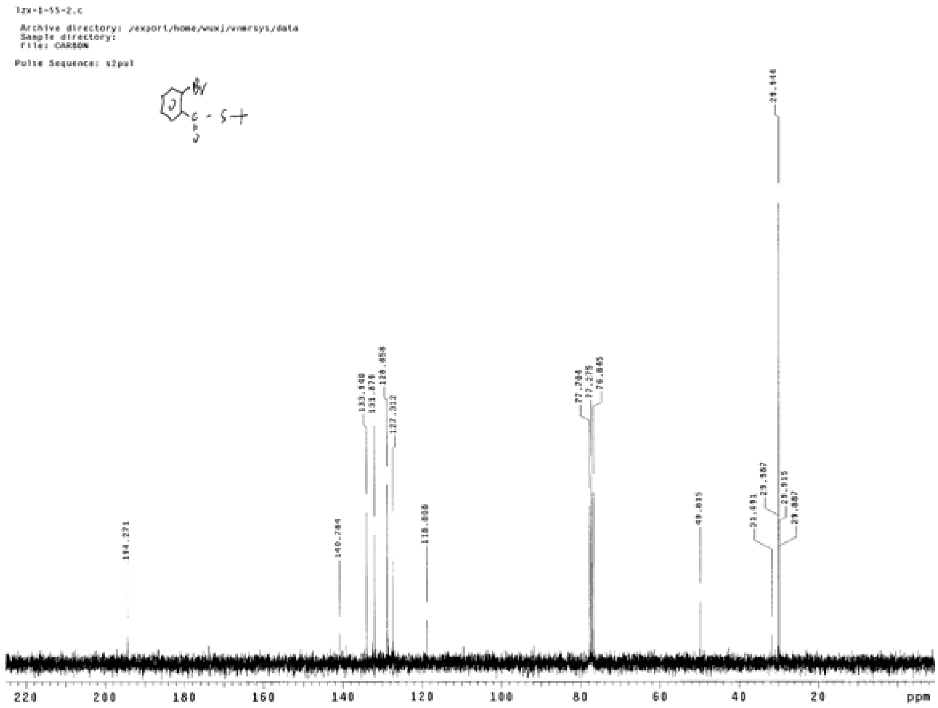
7.842
7.434
7.425
7.403
7.375
7.265
1.577
1.312
0.000000
O
S
Cl
1.86
2.00
9.72
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


191.478
139.105
136.465
128.733
128.603
128.448
128.211
77.246
76.928
76.611
48.394
29.849
O
S
Cl
200
150
100
50
0
ppm (f1)


7.609
7.584
7.580
7.516
7.510
7.491
7.485
7.329
7.324
7.300
7.274
7.268
1.592
0.000000
O
S
Br
1.00
1.13
1.97
9.77
8.8
7.5
6.3
5.0
3.8
2.5
1.3
0.0
ppm (f1)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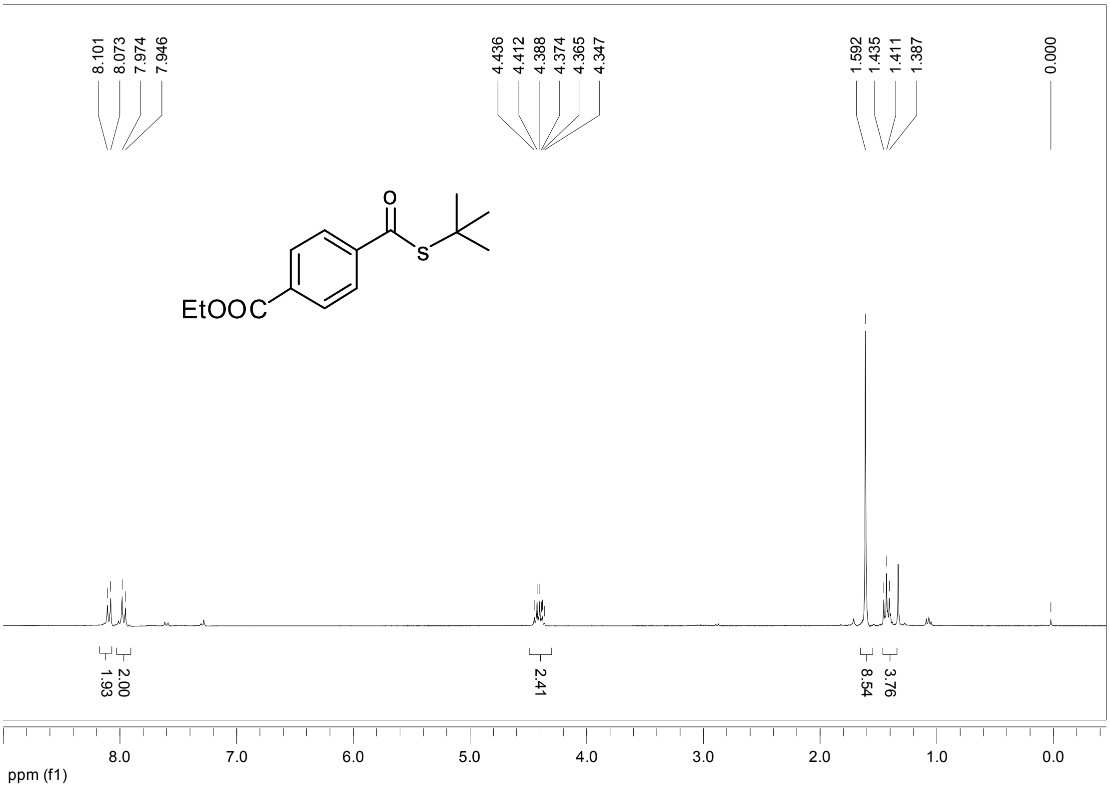
Sample directory:
File: CARBON
Pulse Sequence: s2pul
220
200
180
160
140
120
100
80
60
40
20
ppm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4.412
4.388
4.374
4.365
4.347
1.592
1.435
1.411
1.387
0.000
O
S
EtOOC
1.93
2.00
2.41
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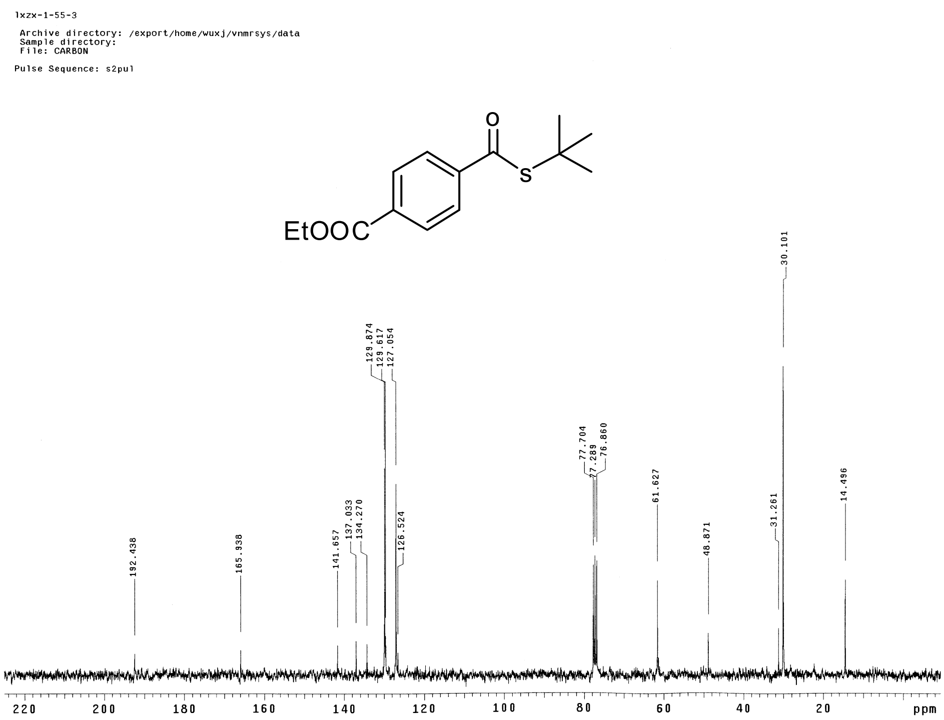
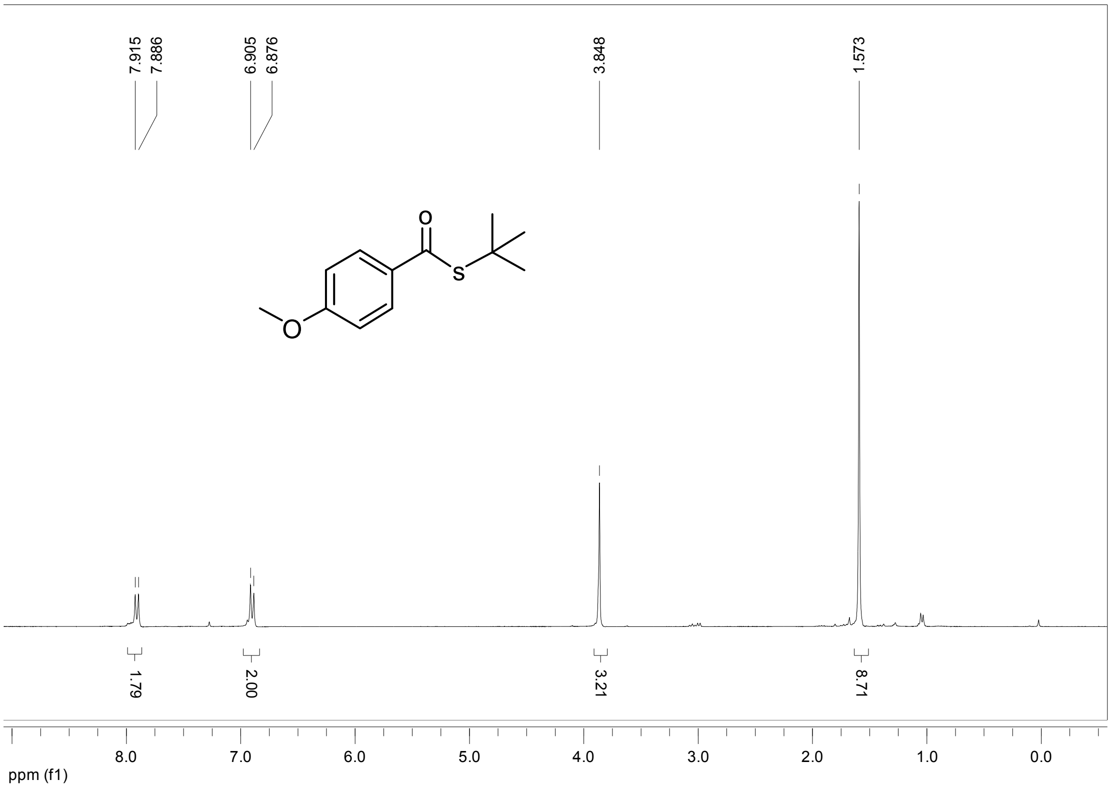
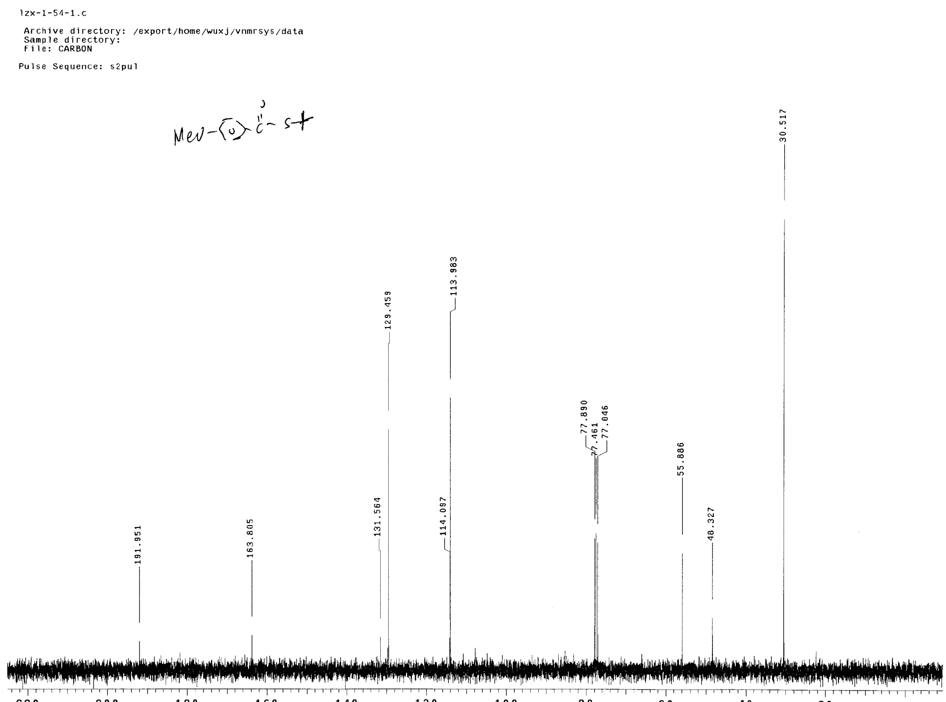
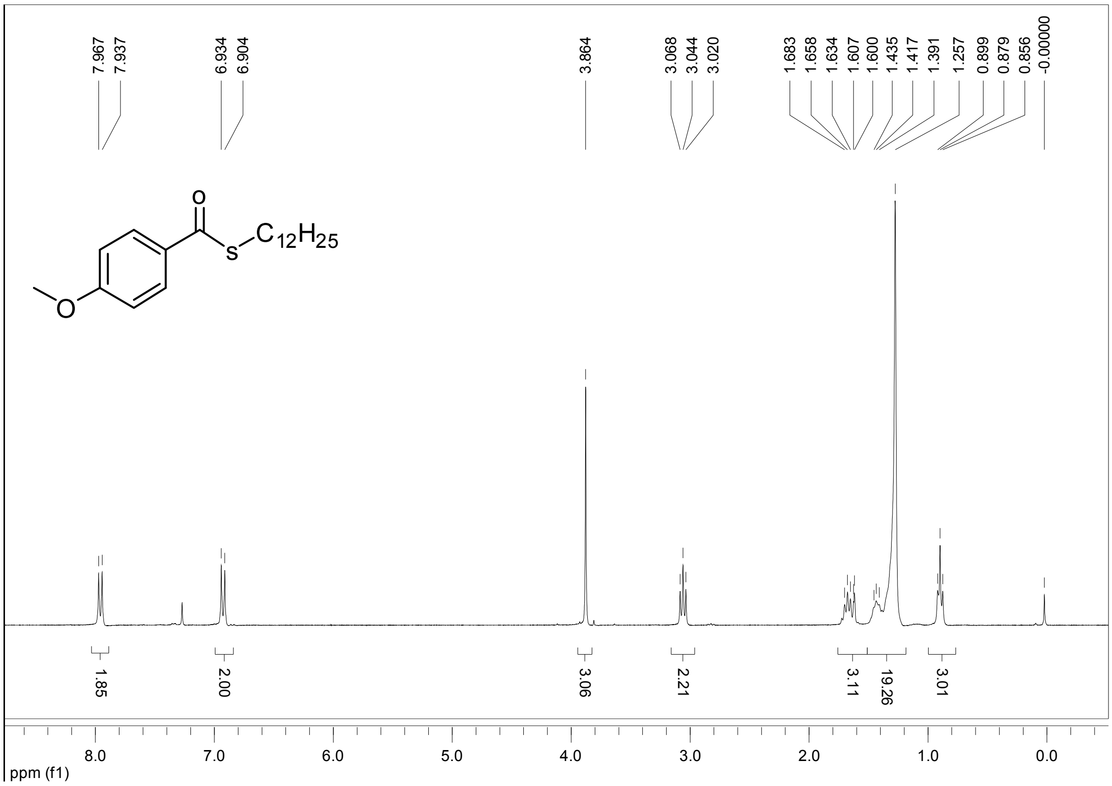
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


lxzx-1-55-3
Archive directory: /export/home/wuxj/vnmrsys/data
Sample directory:
File: CARBON
Pulse Sequence: s2pul
O
S
EtOOC
192.438
165.938
141.657
137.033
134.270
129.874
129.617
127.054
126.524
77.704
77.289
76.860
61.627
48.871
31.261
30.101
14.496
220
200
180
160
140
120
100
80
60
40
20
ppm



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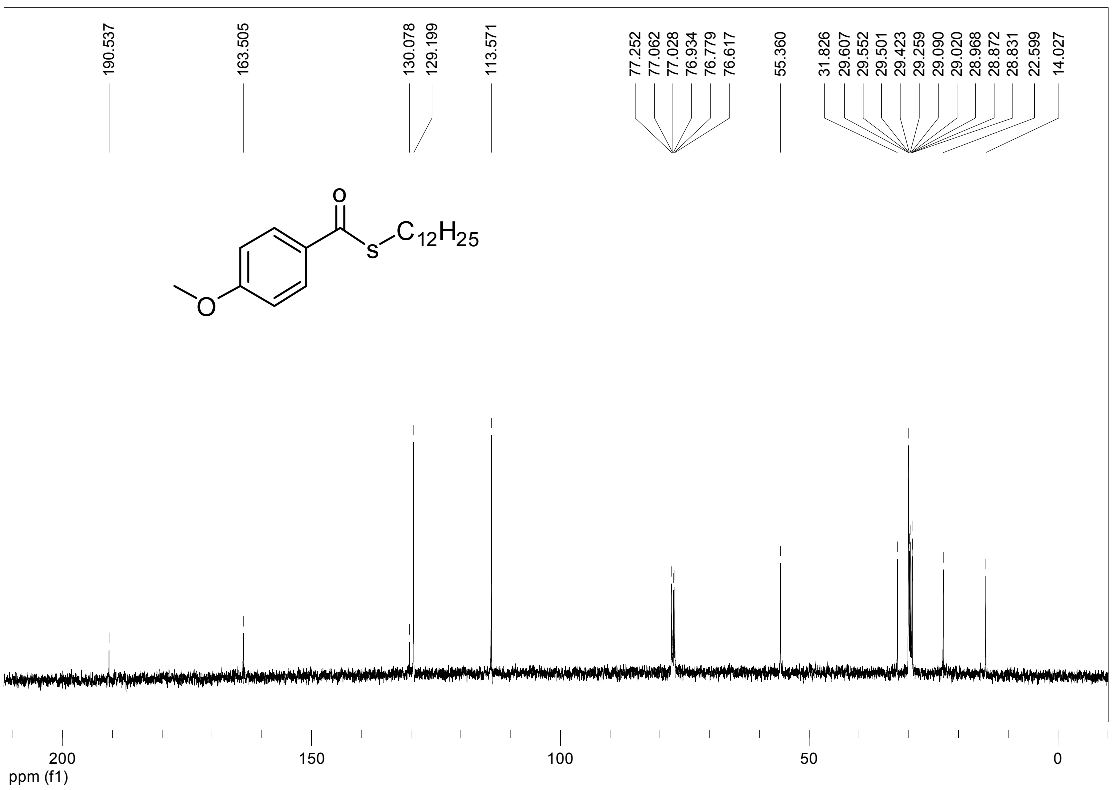
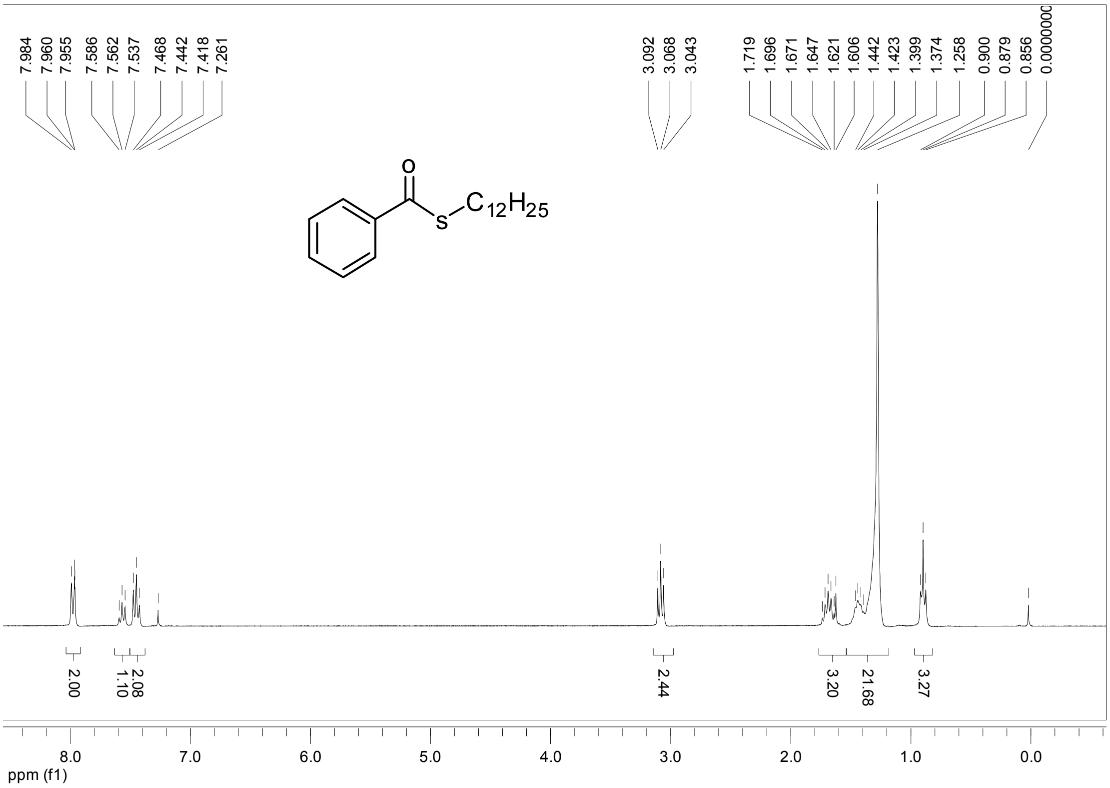
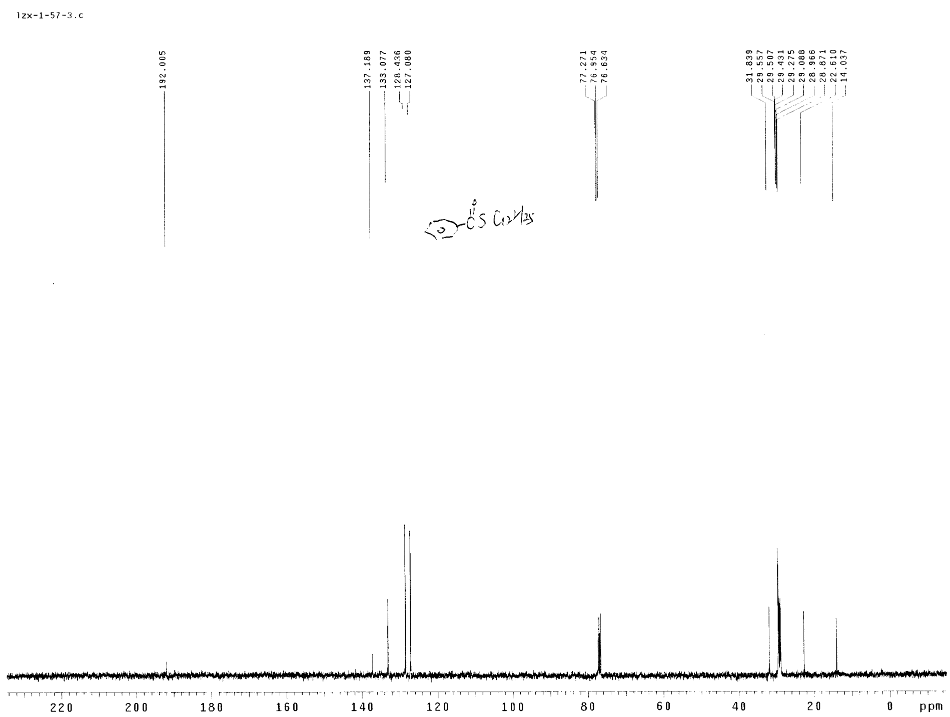
7.937
6.934
6.904
3.864
3.068
3.044
3.020
1.683
1.658
1.634
1.607
1.600
1.435
1.417
1.391
1.257
0.899
0.879
0.856
-0.00000
O
S
$C_{12}H_{25}$
O
1.85
2.00
3.06
2.21
3.11
19.26
3.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

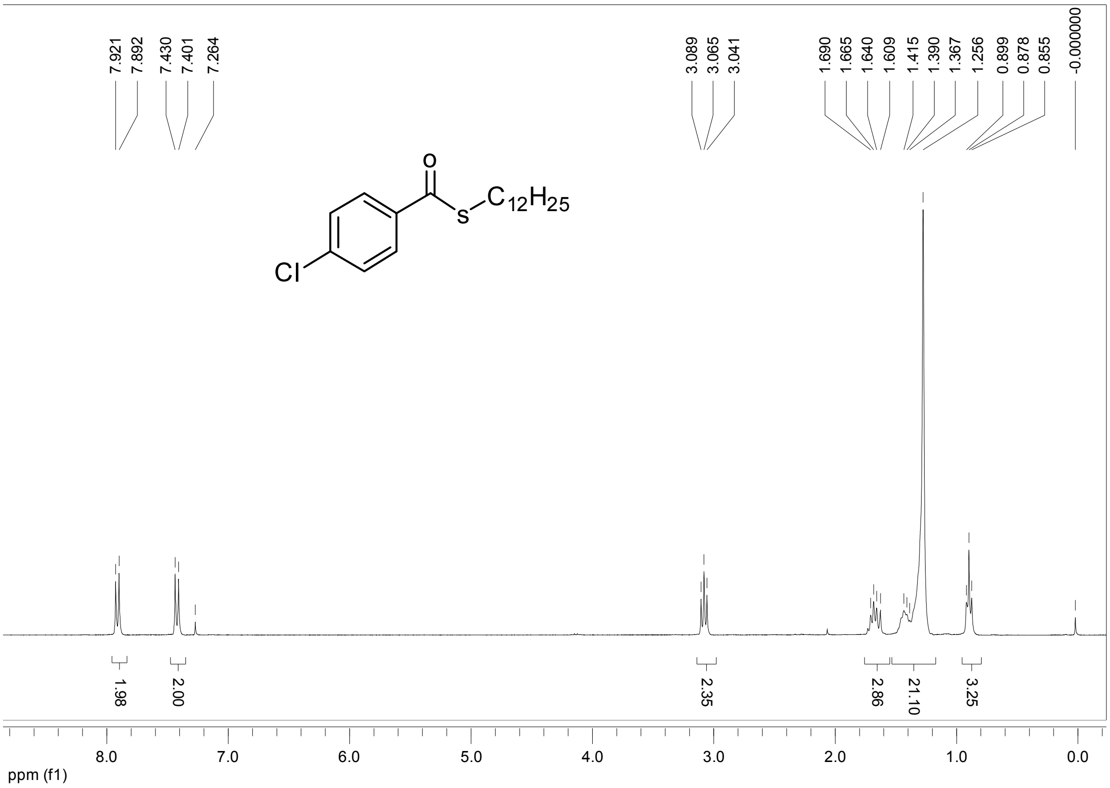

190.537
163.505
130.078
129.199
113.571
77.252
77.062
77.028
76.934
76.779
76.617
55.360
31.826
29.607
29.552
29.501
29.423
29.259
29.090
29.020
28.968
28.872
28.831
22.599
14.027
O
S
$C_{12}H_{25}$
O
200
150
100
50
0
ppm (f1)

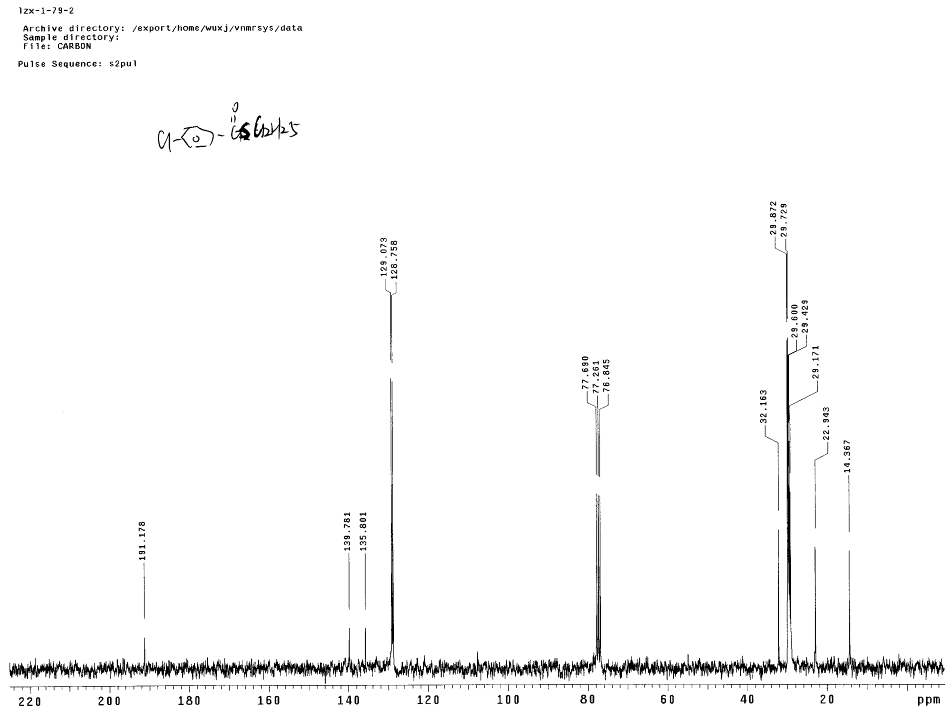


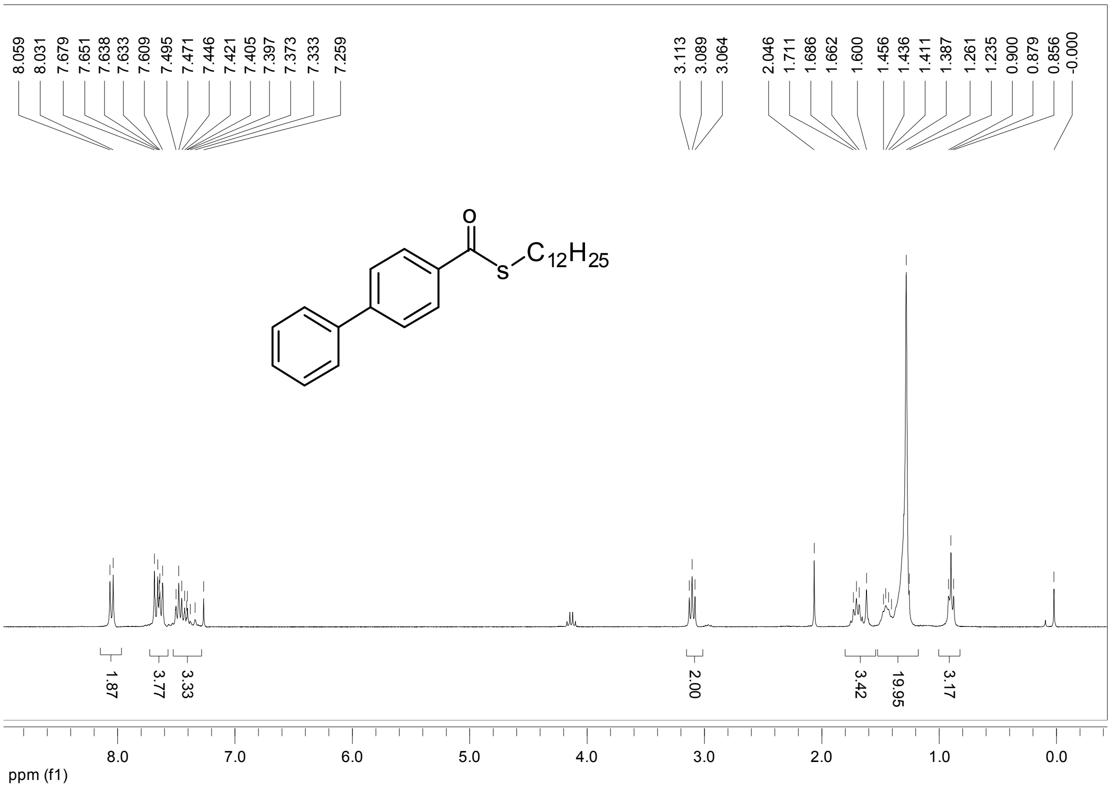
7.984
7.960
7.955
7.586
7.562
7.537
7.468
7.442
7.418
7.261
3.092
3.068
3.043
1.719
1.696
1.671
1.647
1.621
1.606
1.442
1.423
1.399
1.374
1.258
0.900
0.879
0.856
0.0000000
2.00
1.10
2.08
2.44
3.20
21.68
3.27
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)



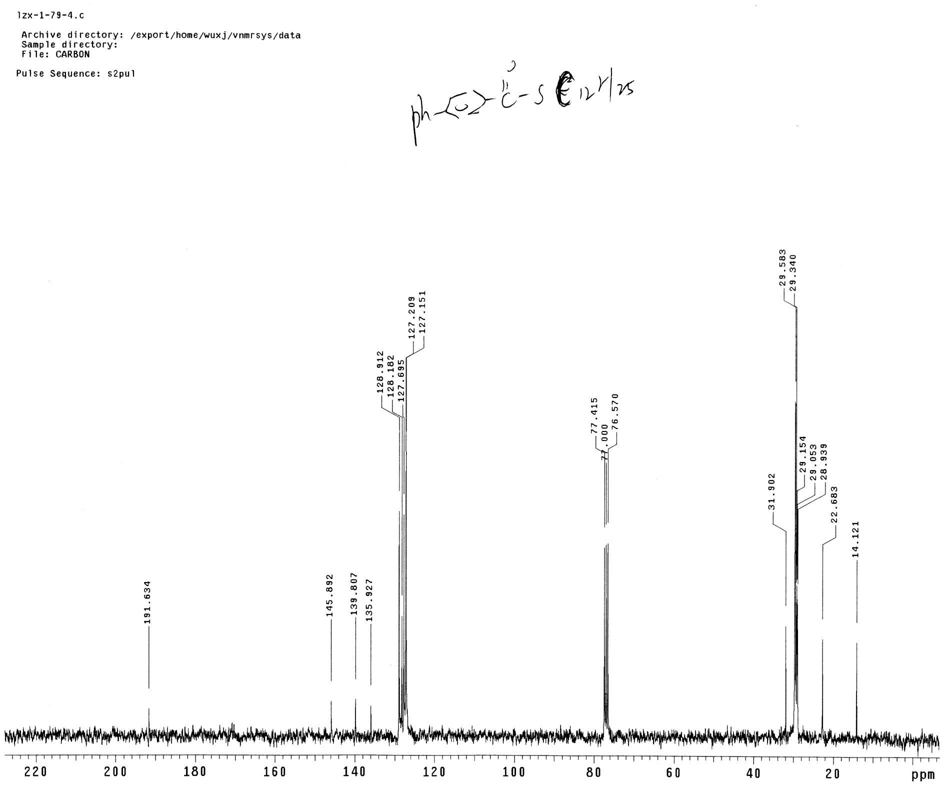
lzx-1-57-3.c
192.005
137.189
133.077
128.436
127.080
77.271
76.954
76.634
31.839
29.557
29.507
29.431
29.275
29.088
28.966
28.871
22.610
14.037
220
200
180
160
140
120
100
80
60
40
20
0
ppm


O
S
C12H25
Cl
7.921
7.892
7.430
7.401
7.264
3.089
3.065
3.041
1.690
1.665
1.640
1.609
1.415
1.390
1.367
1.256
0.899
0.878
0.855
-0.000000
1.98
2.00
2.35
2.86
21.10
3.25
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

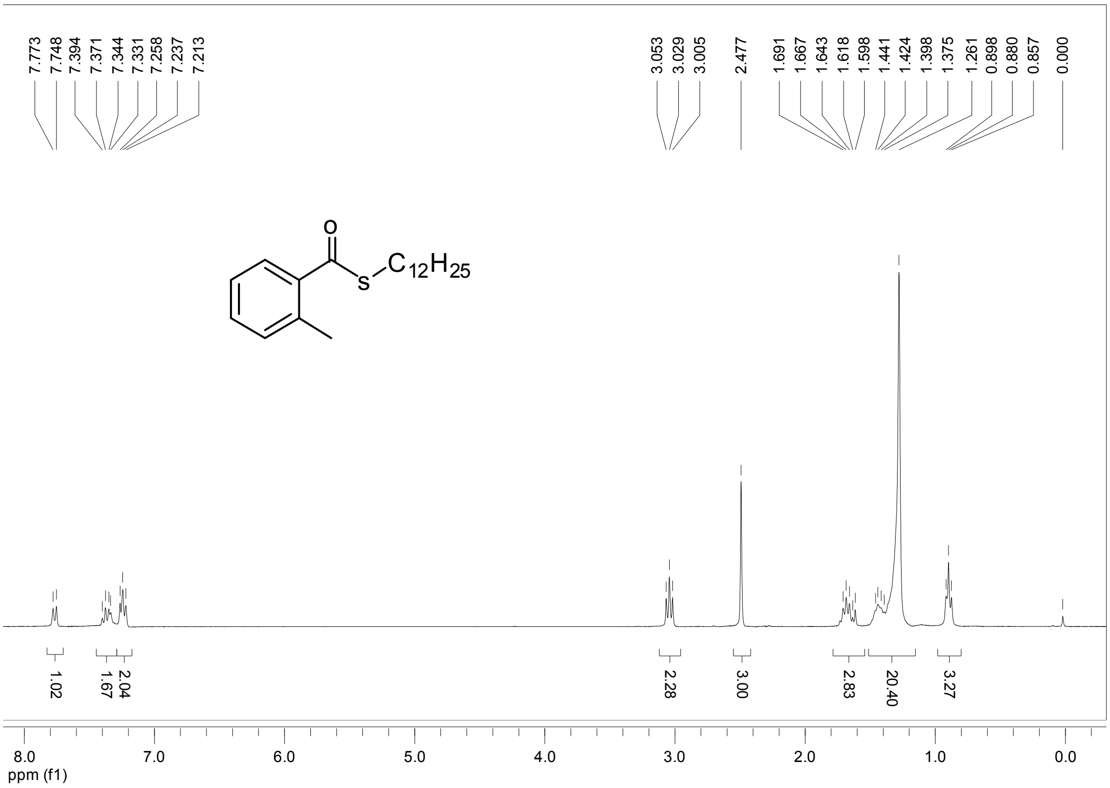

lzx-1-79-2
Archive directory: /export/home/wuxj/vnmrsys/data
Sample directory:
File: CARBON
Pulse Sequence: s2pul
191.178
139.781
135.801
129.073
128.758
77.680
77.261
76.845
32.163
29.872
29.729
29.600
29.429
29.171
22.943
14.367
220
200
180
160
140
120
100
80
60
40
20
ppm



8.059 8.031 7.679 7.651 7.638 7.633 7.609 7.495 7.471 7.446 7.421 7.405 7.397 7.373 7.333 7.259
3.113 3.089 3.064
2.046 1.711 1.686 1.662 1.600 1.456 1.436 1.411 1.387 1.261 1.235 0.900 0.879 0.856 -0.000
O
S
$C_{12}H_{25}$
1.87 3.77 3.33 2.00 3.42 19.95 3.17
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
ppm (f1)



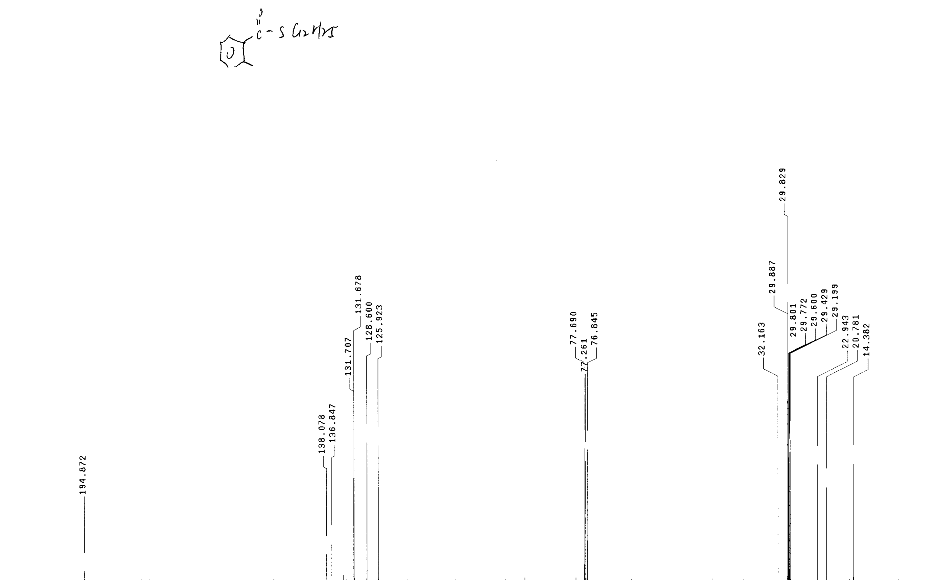
lzx-1-79-4.c
Archive directory: /export/home/wuxj/vnmrsys/data
Sample directory:
File: CARBON
Pulse Sequence: s2pul
191.634
145.892 139.807 135.927
128.912 128.182 127.695 127.209 127.151
77.415 77.000 76.570
31.902 29.583 29.340 29.154 29.053 28.939 22.683 14.121
220 200 180 160 140 120 100 80 60 40 20 ppm

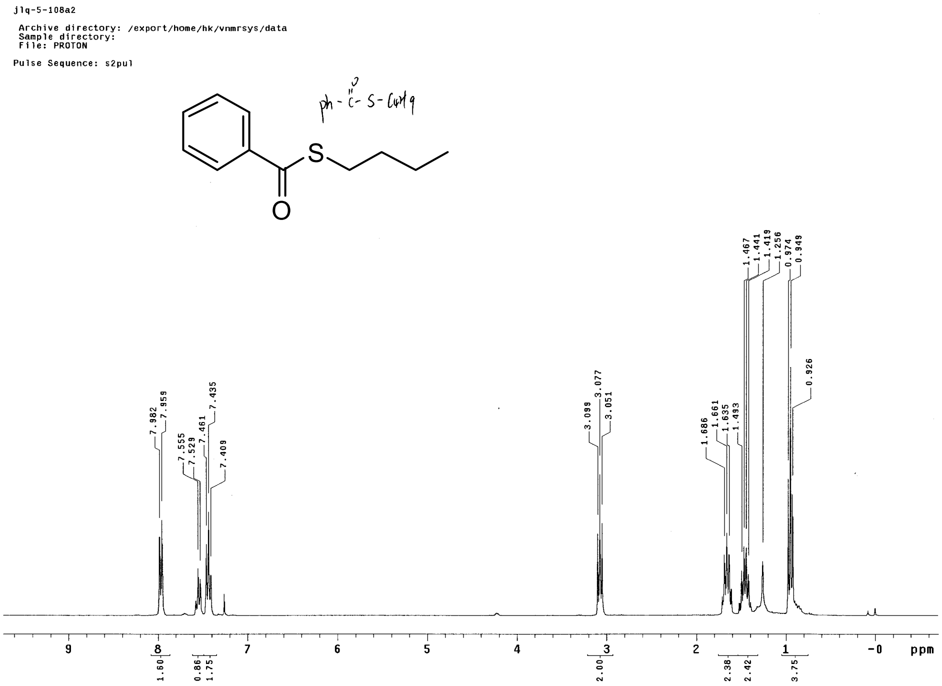


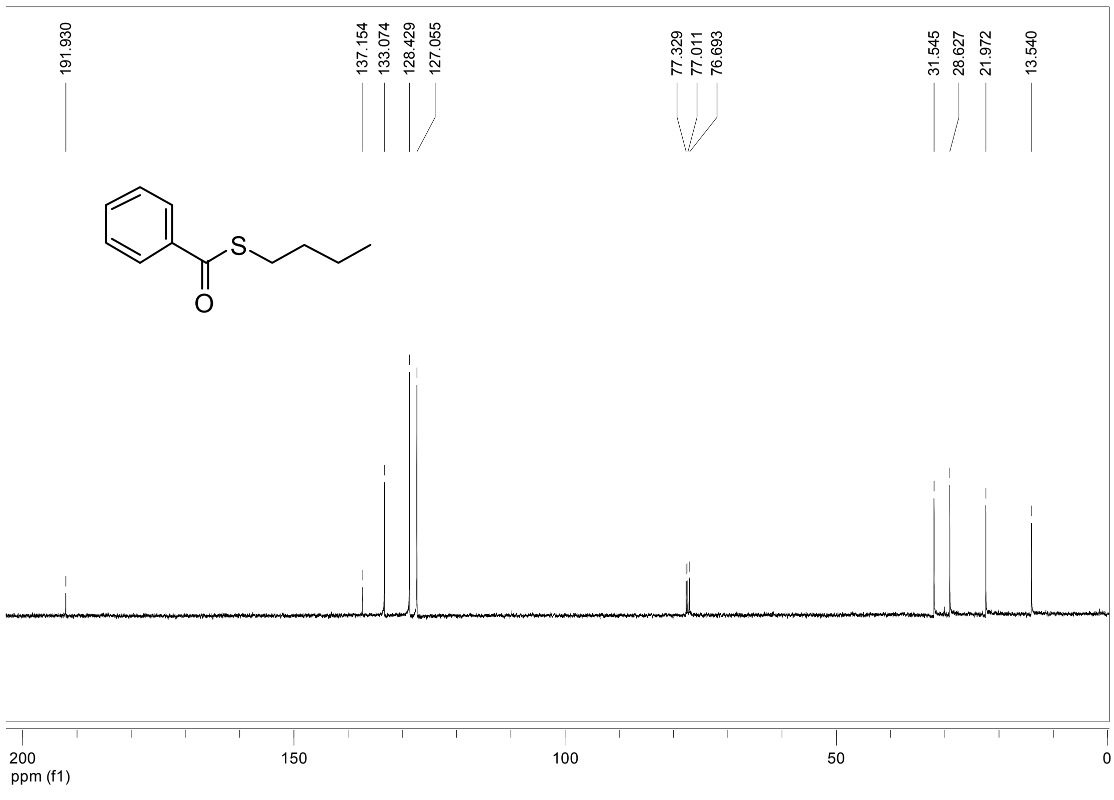
lzx-1-79-1.c

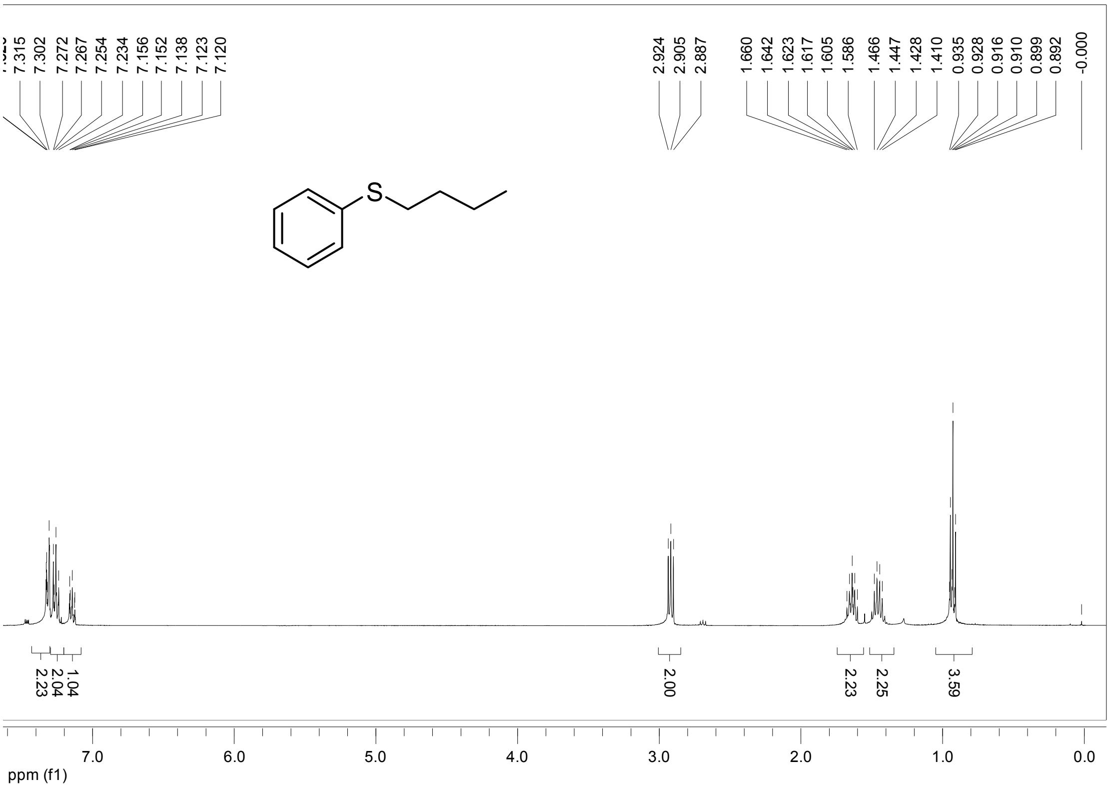
Archive directory: /export/home/wuxj/vnmrsys/data
Sample directory:
File: CARBON

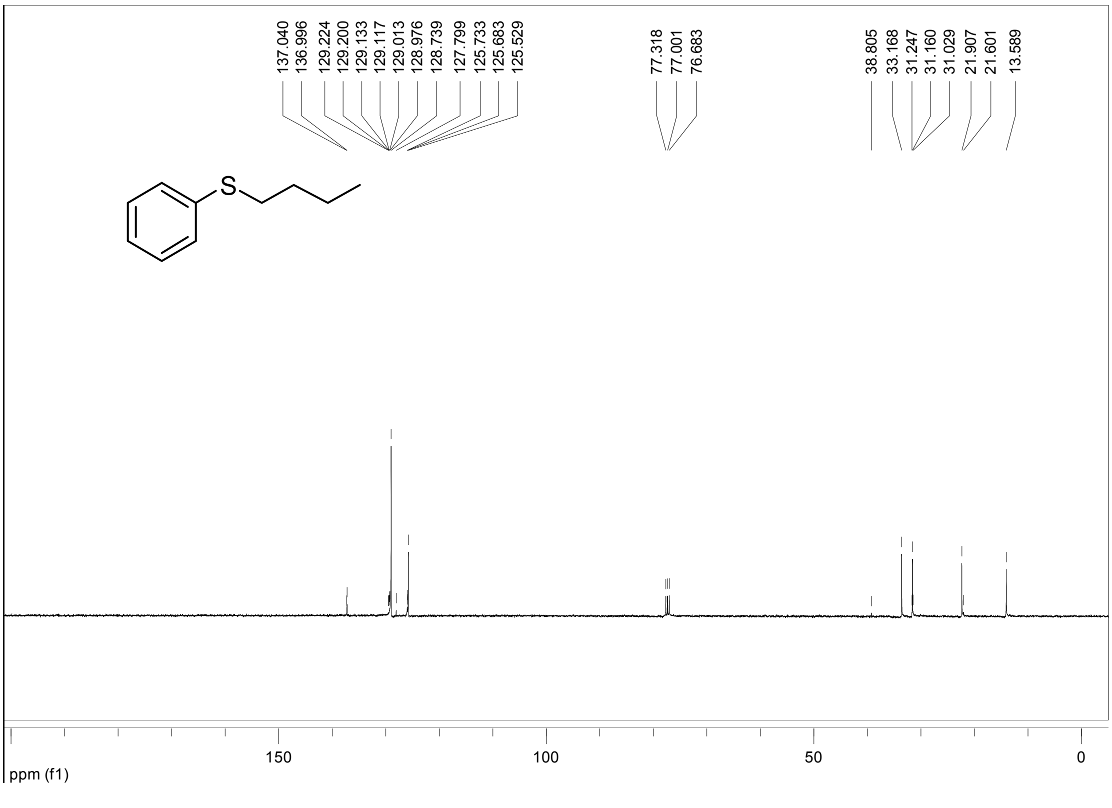
Pulse Sequence: s2pul

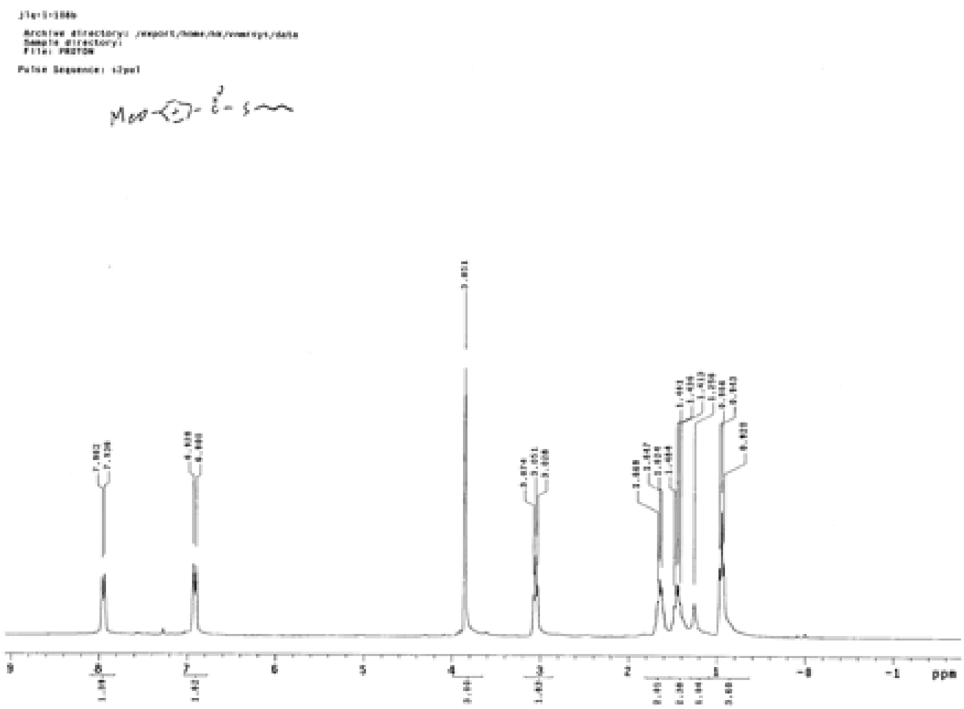


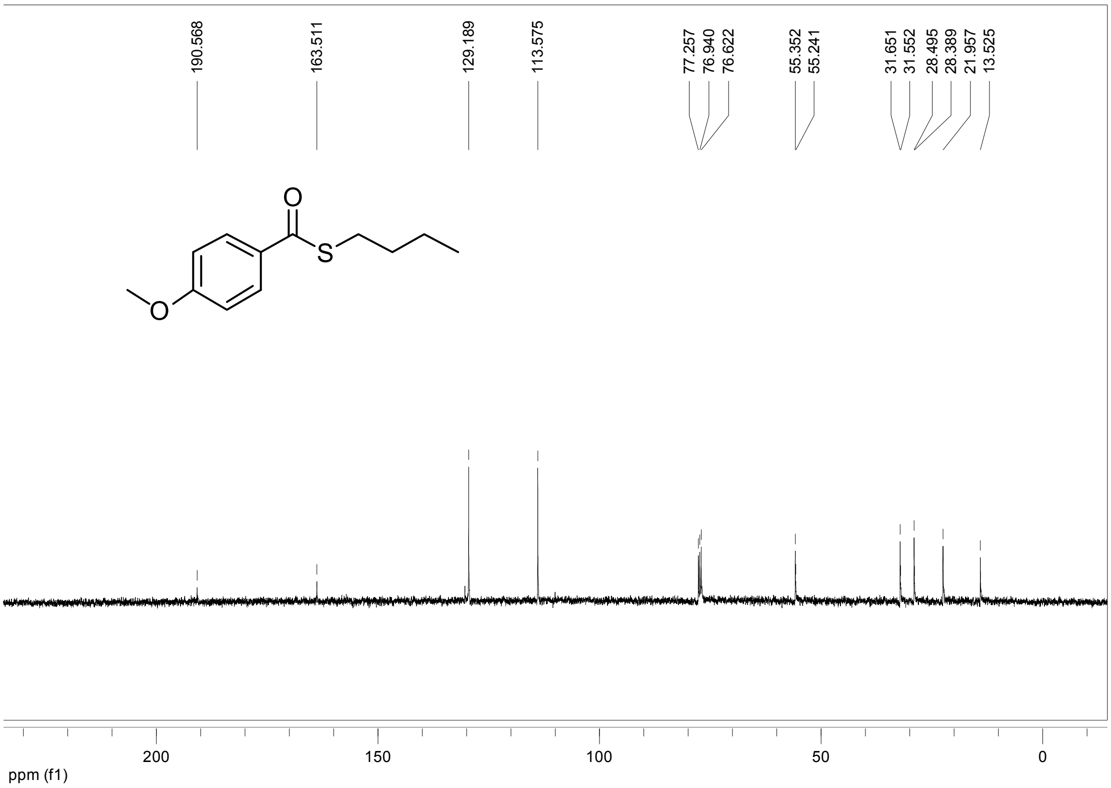

jlq-5-108a2
Archive directory: /export/home/hk/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
7.982
7.959
7.555
7.529
7.461
7.435
7.409
3.099
3.077
3.051
1.686
1.661
1.635
1.493
1.467
1.441
1.419
1.256
0.974
0.949
0.926
ppm
1.60
0.86
1.75
2.00
2.38
2.42
3.75

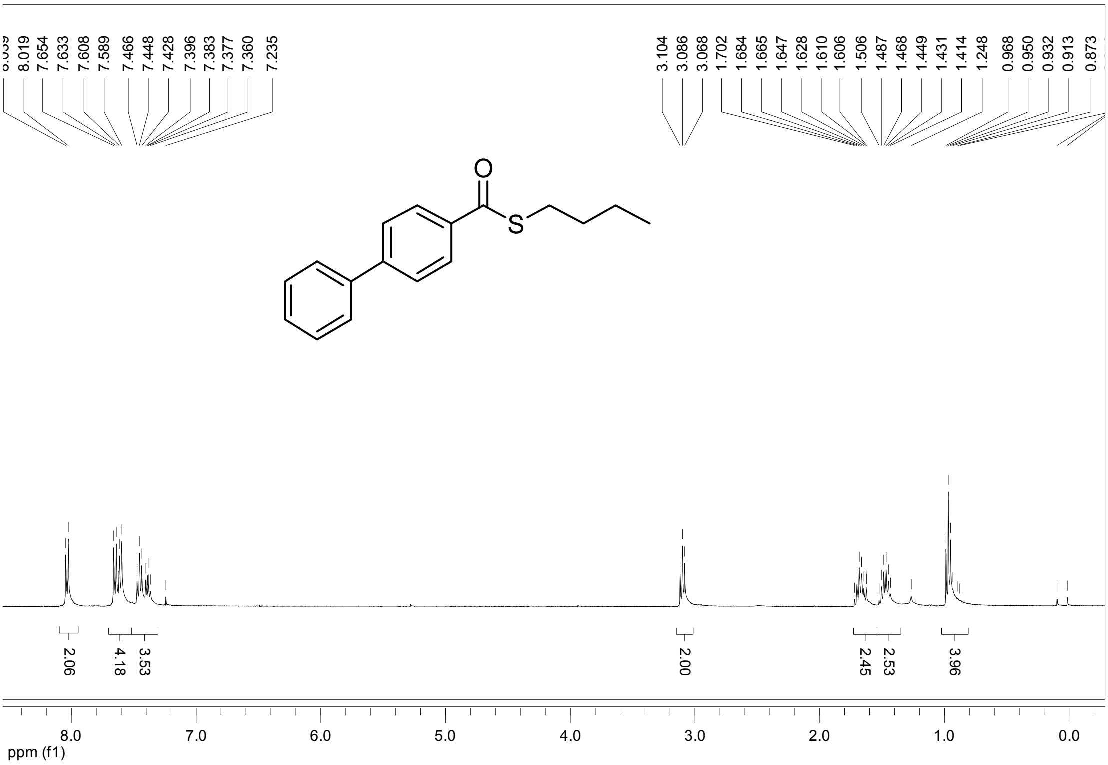

191.930
137.154
133.074
128.429
127.055
77.329
77.011
76.693
31.545
28.627
21.972
13.540
ppm (f1)

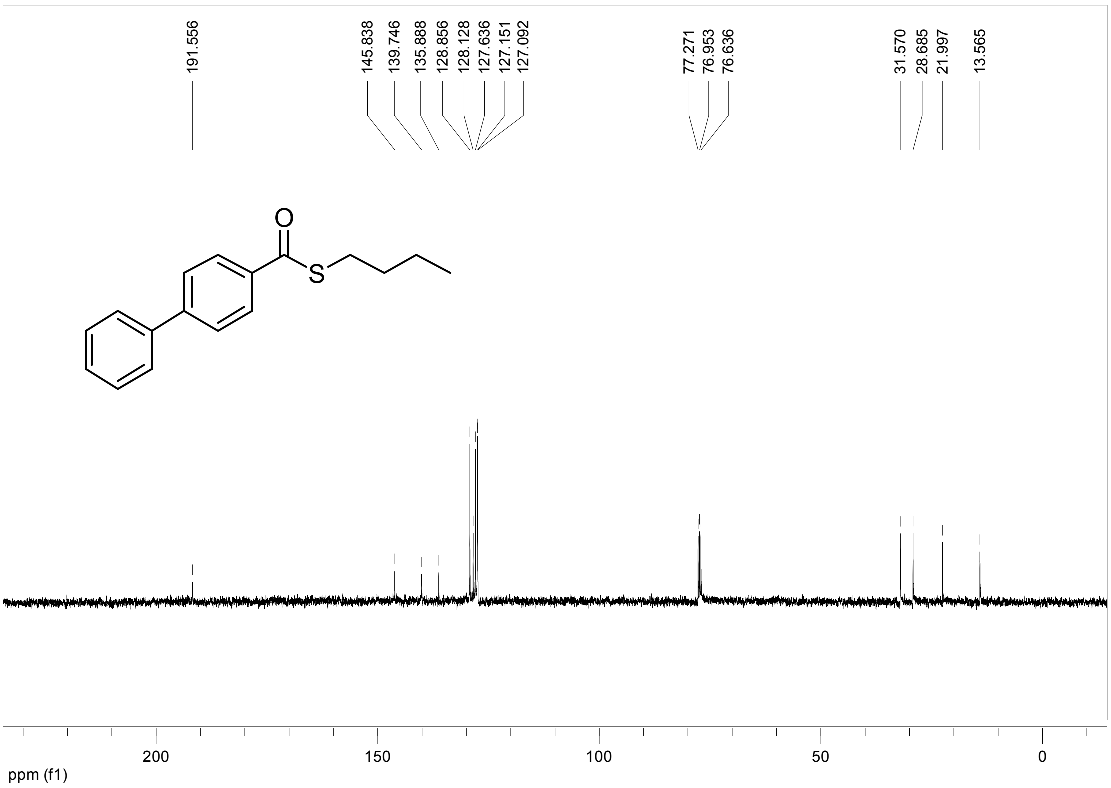


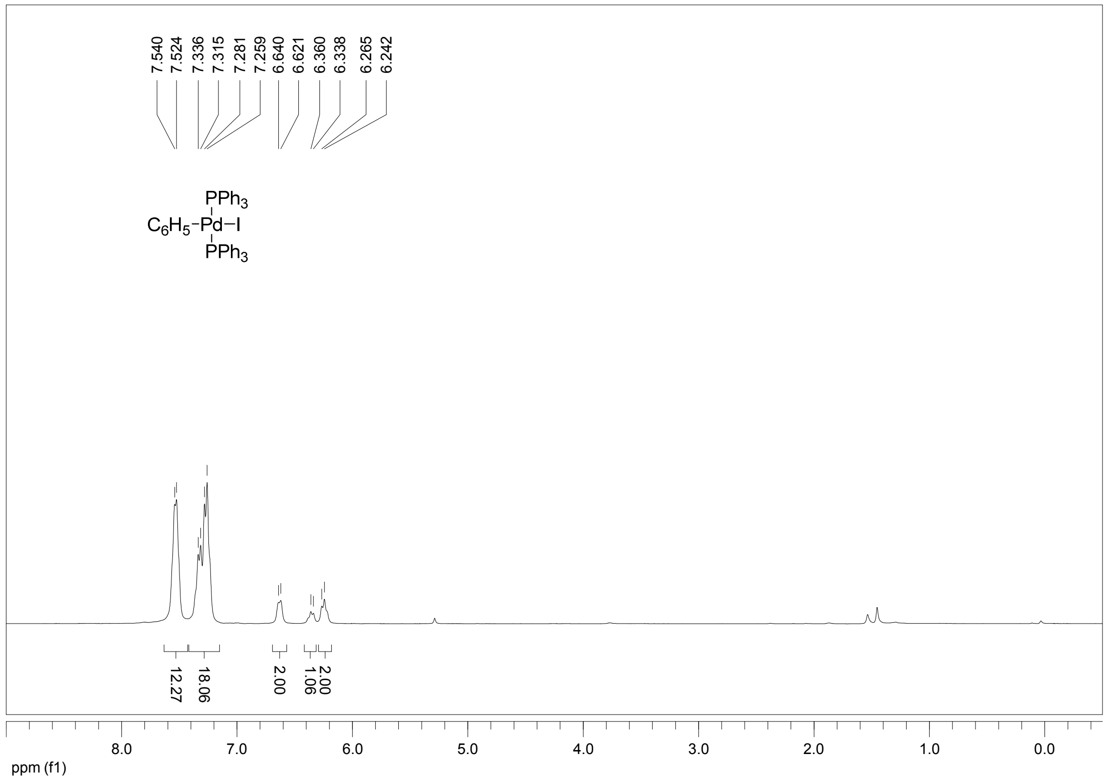


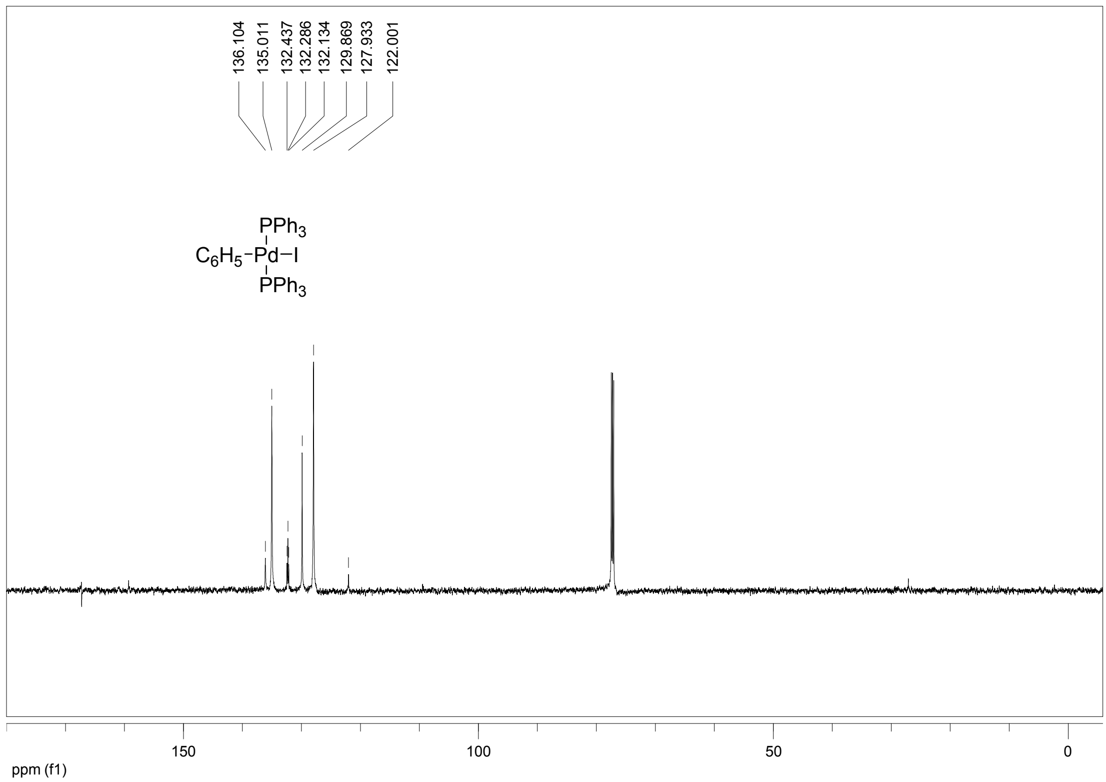



190.568
163.511
129.189
113.575
77.257
76.940
76.622
55.352
55.241
31.651
31.552
28.495
28.389
21.957
13.525
O
S
O
200
150
100
50
0
ppm (f1)


8.039
8.019
7.654
7.633
7.608
7.589
7.466
7.448
7.428
7.396
7.383
7.377
7.360
7.235
3.104
3.086
3.068
1.702
1.684
1.665
1.647
1.628
1.610
1.606
1.506
1.487
1.468
1.449
1.431
1.414
1.248
0.968
0.950
0.932
0.913
0.873
O
S
2.06
4.18
3.53
2.00
2.45
2.53
3.96
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


191.556
145.838
139.746
135.888
128.856
128.128
127.636
127.151
127.092
77.271
76.953
76.636
31.570
28.685
21.997
13.565
O
S
200
150
100
50
0
ppm (f1)


7.540
7.524
7.336
7.315
7.281
7.259
6.640
6.621
6.360
6.338
6.265
6.242
PPh3
C6H5-Pd-I
PPh3
12.27
18.06
2.00
1.06
2.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


136.104
135.011
132.437
132.286
132.134
129.869
127.933
122.001
PPh3
C6H5-Pd-I
PPh3
150
100
50
0
ppm (f1)

Supporting Information of Theoretical part

1. General computational details:

All the geometry calculations were performed using the following Gaussian command line:

```
--------------------------------------------------------
# Opt Freq=noraman RB3LYP/GEN Pseudo=read 5D
……
C H P O 0
6-31+g*
****
Pd    0
SDD
****

Pd    0
SDD
--------------------------------------------------------
```

The calculations were run in Gaussian 03:Rev C.02 mounted in a multiprocessor PC under the Linux operating system. Default SCF convergence criteria were used. Energies are given in Hartrees. Optimization of transition states were performed using the following Gaussian command line:

```
--------------------------------------------------------
#    Opt=(calcfc, ts, nofreeze, noeigen) RB3LYP/GEN Pseudo=read 5D
……
C H P O 0
6-31+g*
****
Pd    0
SDD
```

****

Pd 0

SDD

Single point energies in CH3OH solvent calculations were performed using the following Gaussian command line:

RB3LYP/gen Pseudo=read 5D Scrf(PCM,solvent=CH3OH,read)

……

C H P O 0

6-31g*

****

Pd 0

SDD

****

Pd 0

SDD

radii=UAHF

----

2. R3LYP absolute calculation energies, thermodynamic corrections and number of imaginary frequencies for the optimized geometries and transition states:

	E(elec)	SPE(THF)	Corr.(H)	Corr.(G)
1	−1088.491527	−1088.498238	0.305299	0.229935
2-ts	−1088.473358	−1088.485506	0.304353	0.23064
3	−1088.493319	−1088.50569	0.306847	0.230008
4-ts	−1088.485312	−1088.489607	0.305703	0.233135
5	−1088.531402	−1088.544151	0.308469	0.234105
6-ts	−1088.464682	−1088.475457	0.304302	0.230839
7	−1088.498043	−1088.511543	0.306901	0.232918
8-ts	−1088.488603	−1088.501952	0.305805	0.233897

3. Cartesian coordinates for the optimized geometries and transition states.

1

Pd	0.34619300	-0.48197500	-0.02924600
O	2.40507300	-0.26220800	-0.09041800
C	0.16739900	-2.41393600	-0.04541200
O	0.01978100	-3.54746300	-0.06263000
C	3.26601600	-1.34558400	0.14941000
H	3.10740900	-1.78101500	1.15488800
H	3.09926300	-2.16459800	-0.57777300
P	0.50778400	1.86859500	-0.00941300
C	-1.00220100	2.91781000	-0.09746900
H	-1.65557100	2.70382400	0.75359900
H	-0.73499700	3.98109600	-0.09274100
H	-1.56054800	2.68898200	-1.01006100
C	1.38543700	2.45474700	1.49721300
H	1.58895600	3.53068000	1.44004400
H	0.77979600	2.25196000	2.38637400
H	2.32399900	1.89894900	1.57269000
C	1.56154000	2.44500900	-1.40020900
H	1.04032900	2.29061900	-2.35058800
H	1.80903200	3.50785600	-1.29434100
H	2.46998100	1.83603700	-1.39145200
C	-1.71649600	-0.38996300	0.00539500
C	-2.41950900	-0.36110600	1.22106500
C	-2.45837900	-0.35355600	-1.18679300
C	-3.81863500	-0.28033600	1.24612900
H	-1.87869900	-0.40444000	2.16494600
C	-3.85744800	-0.27313200	-1.16635700
H	-1.94828000	-0.39074600	-2.14787500
C	-4.54325200	-0.23352600	0.05139600

H	-4.34013600	-0.25943200	2.20111500
H	-4.40942800	-0.24685100	-2.10391800
H	-5.62879800	-0.17451100	0.06908300
C	4.72317200	-0.88899200	0.04155100
H	4.93606800	-0.10506000	0.77892300
H	5.41142300	-1.72713200	0.21932100
H	4.92383900	-0.48153500	-0.95685700

2-ts

Pd	-0.38775000	-0.21858600	-0.08905600
O	-2.54429500	-0.59312800	-0.34998600
C	-1.39189000	-1.93052100	-0.13330800
O	-1.82503000	-3.00800400	-0.02253100
C	-3.59246000	-0.54367400	0.61394200
H	-3.43985900	-1.31405700	1.38654200
H	-3.57588900	0.43400800	1.12031600
P	0.19705100	2.05469700	-0.00236200
C	1.03271900	2.62896500	1.53816700
H	1.96431500	2.07182600	1.67454300
H	1.25528800	3.70133500	1.48927000
H	0.38839400	2.43684700	2.40228500
C	1.31962500	2.65456600	-1.33686000
H	1.52636900	3.72543000	-1.22474200
H	2.25947100	2.09593400	-1.29938800
H	0.85708000	2.48042400	-2.31385600
C	-1.26204900	3.17994500	-0.13937500
H	-1.94607100	3.00008900	0.69633100
H	-0.95673200	4.23310100	-0.13125200
H	-1.80269000	2.96904000	-1.06755400
C	1.56275600	-0.71320800	-0.00185000

C	2.29638300	-0.93453100	-1.17956500
C	2.20662000	-0.90837600	1.23122400
C	3.63810500	-1.33480000	-1.12486800
H	1.82339500	-0.81027000	-2.15131500
C	3.54847500	-1.30942700	1.28550400
H	1.66274900	-0.76385700	2.16236800
C	4.27106200	-1.52117200	0.10775600
H	4.18451300	-1.50694700	-2.05012700
H	4.02424700	-1.46178800	2.25231000
H	5.31104400	-1.83539300	0.14959700
C	-4.93980800	-0.76145800	-0.07009300
H	-5.75656500	-0.70547300	0.66253700
H	-5.11001000	0.00079200	-0.83923500
H	-4.97094400	-1.74533400	-0.55054800

3

Pd	-0.17851500	-0.80499900	-0.00186400
C	1.73013900	-1.33425600	-0.00125700
O	1.72387600	-2.56619300	-0.00275700
P	-2.58772300	-0.63334500	0.00059300
C	-3.30209400	0.25973200	1.45228000
H	-2.85693200	1.25745000	1.51773100
H	-4.39149200	0.35404100	1.36873100
H	-3.05986900	-0.28128000	2.37303400
C	-3.30195400	0.29324800	-1.42982600
H	-4.39147300	0.38481900	-1.34527300
H	-2.85700100	1.29241000	-1.47124500
H	-3.05806100	-0.22510800	-2.36310600
C	-3.56471000	-2.20816300	-0.01686500
H	-3.31188900	-2.81205900	0.86111100

H	-4.64351300	-2.01013100	-0.01254400
H	-3.31487700	-2.79025000	-0.91025500
C	0.12882000	1.18076100	-0.00032000
C	0.21805100	1.89075800	-1.20825900
C	0.21162200	1.89159500	1.20747300
C	0.36534700	3.28454100	-1.20649800
H	0.18342100	1.36426200	-2.15877200
C	0.35920800	3.28546900	1.20545800
H	0.17202400	1.36582800	2.15824100
C	0.43259700	3.98860200	-0.00058600
H	0.43431800	3.81655100	-2.15351800
H	0.42349400	3.81817000	2.15242100
H	0.55002400	5.06956500	-0.00070100
O	2.85058200	-0.60413800	0.00136000
C	4.11309000	-1.33163800	0.00266500
H	4.14229900	-1.97465800	0.88837400
H	4.14448100	-1.97404800	-0.88340400
C	5.22940500	-0.30413700	0.00446100
H	5.17275700	0.33532200	0.89198900
H	6.20138700	-0.81252600	0.00605100
H	5.17566300	0.33535800	-0.88321800

4-ts

Pd	0.40000000	-0.59290200	-0.08835900
C	-0.57998300	0.96402700	0.76276200
O	-0.62347700	1.12658100	1.96590300
P	2.74536600	-0.47155400	-0.13730000
C	3.56281700	-0.48170800	1.52303500
H	3.34126300	-1.42388400	2.03482200
H	4.65052900	-0.36598600	1.43821500

H	3.15903200	0.33265700	2.13286200
C	3.68760300	-1.79613300	-1.03137200
H	4.76993900	-1.62547600	-0.97752700
H	3.46141900	-2.77303300	-0.59084100
H	3.38453400	-1.82124900	-2.08346900
C	3.43914600	1.06537400	-0.90097000
H	3.04027200	1.94065400	-0.37865100
H	4.53502100	1.08336800	-0.84951200
H	3.12666200	1.12842500	-1.94831800
C	-1.68177300	-0.62210000	0.02275700
C	-2.39624600	-0.43039600	-1.17249700
C	-2.26114400	-1.37853800	1.05489200
C	-3.64033200	-1.04431100	-1.35596800
H	-1.98402400	0.20137400	-1.95438400
C	-3.50363100	-1.99294500	0.86904900
H	-1.74720100	-1.46538800	2.00878900
C	-4.19245500	-1.83007500	-0.33829500
H	-4.18194800	-0.90219100	-2.28879700
H	-3.94011200	-2.58611300	1.66968100
H	-5.16347100	-2.29912900	-0.47883900
O	-0.74415100	1.97545900	-0.13502600
C	-1.04042500	3.28253600	0.42350700
H	-1.93806700	3.20007700	1.04544400
H	-0.21071300	3.58872000	1.06967200
C	-1.23874800	4.23988600	-0.73778500
H	-2.07111600	3.91894000	-1.37358200
H	-1.46391300	5.24347400	-0.35668900
H	-0.33654900	4.30156200	-1.35659000

5

Pd	-0.53004700	0.11617600	0.09646600
O	2.64080300	-1.05342500	-0.28855900
C	3.37758700	-2.22810800	0.12138100
H	4.30972200	-1.90880900	0.59906400
H	2.78598800	-2.76755900	0.86851100
P	-2.64442400	-0.74919800	0.04103400
C	-3.47198400	-1.10776400	1.66325700
H	-3.54603000	-0.18591800	2.24964200
H	-4.47792700	-1.52309500	1.52010400
H	-2.86890300	-1.82051200	2.23535700
C	-3.94554500	0.27617700	-0.79474800
H	-4.92393100	-0.22177400	-0.78065800
H	-4.02970000	1.24424200	-0.29005700
H	-3.65454000	0.46373700	-1.83350800
C	-2.86097000	-2.37402400	-0.83017900
H	-2.23365300	-3.13298900	-0.35103900
H	-3.90620200	-2.70961900	-0.81137900
H	-2.53477400	-2.27794600	-1.87103200
C	2.32232000	-0.17363700	0.69048800
C	1.54261600	0.99657700	0.17941300
C	1.34313300	2.09634800	1.06232500
C	1.16696900	1.13520300	-1.18856500
C	0.86438400	3.30834100	0.58142100
H	1.62725900	1.97416500	2.10251800
C	0.67972300	2.37772500	-1.65126000
H	1.41729200	0.35507800	-1.89872500
C	0.54777600	3.45621800	-0.78238600
H	0.74322800	4.14722400	1.26162100
H	0.42857100	2.48710000	-2.70311400
H	0.19088500	4.41301900	-1.15494700

O	2.66564300	-0.31796800	1.85103900
C	3.63007600	-3.06627600	-1.11874500
H	4.18769100	-3.97032700	-0.84622800
H	2.68742600	-3.37154600	-1.58607900
H	4.21804900	-2.51013500	-1.85722700

6-ts

Pd	0.30285100	-0.42671800	-0.00021200
O	2.31950800	-0.66064200	0.00012900
C	-0.68811100	-2.03208500	0.00029000
O	-0.97710600	-3.17229700	0.00089900
C	2.87528000	-1.95481200	-0.00021600
H	2.55435800	-2.53124600	0.88589500
H	2.55480300	-2.53058600	-0.88691700
P	0.96156400	1.92340900	-0.00011200
C	-0.27218900	3.30327300	-0.00027500
H	-0.91248900	3.22904100	0.88514500
H	0.22012600	4.28340200	-0.00022400
H	-0.91227400	3.22902700	-0.88585100
C	2.04342900	2.31892000	1.44059100
H	2.48280700	3.32033200	1.35581200
H	1.46707700	2.25838700	2.36995000
H	2.83437900	1.56393400	1.47406900
C	2.04395200	2.31906600	-1.44038200
H	1.46792100	2.25868200	-2.36995000
H	2.48334600	3.32044700	-1.35532200
H	2.83488200	1.56405100	-1.47368400
C	-1.90272100	-0.72998800	0.00008200
C	-2.55261200	-0.44937800	1.21467300
C	-2.55271900	-0.44976400	-1.21453400

C	-3.82620000	0.12380400	1.21364000
H	-2.06344900	-0.68756000	2.15585600
C	-3.82630700	0.12344000	-1.21356800
H	-2.06364600	-0.68824500	-2.15568800
C	-4.46176900	0.41130800	0.00001800
H	-4.32476700	0.34185600	2.15487300
H	-4.32494800	0.34121400	-2.15482500
H	-5.45604900	0.85091400	-0.00000300
C	4.40300300	-1.85172100	0.00020400
H	4.75291000	-1.31196400	0.88871600
H	4.85960200	-2.85126100	0.00000600
H	4.75337300	-1.31139900	-0.88778300

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Pd	0.67663600	0.73689800	-0.13657200
O	-0.59477000	2.25662800	-0.32622400
C	-1.16293000	2.98747600	0.73344600
H	-1.94605200	2.39115200	1.23795400
H	-0.41346600	3.24109500	1.50401300
P	2.49877100	-0.68477100	-0.22977000
C	3.39424100	-0.85211800	1.37255200
H	2.68768700	-1.19357600	2.13479000
H	4.22613100	-1.56218500	1.29381600
H	3.78297500	0.12456600	1.67829400
C	2.21016700	-2.43796500	-0.73296400
H	3.14960400	-3.00297300	-0.75713000
H	1.52766600	-2.91259000	-0.02150000
H	1.74794500	-2.46760200	-1.72484400
C	3.81802100	-0.13619200	-1.40444200
H	4.15560400	0.87118400	-1.13961300

H	4.67781800	-0.81660400	-1.37999500
H	3.41830800	-0.10471800	-2.42327600
C	-0.36673500	-0.61966800	0.86877500
C	-1.69413700	-1.02141900	0.29089600
C	-2.29573200	-2.18899700	0.80014200
C	-2.33493200	-0.29091100	-0.72144900
C	-3.51610000	-2.62621800	0.28953200
H	-1.79581200	-2.73682800	1.59314700
C	-3.56566900	-0.72886100	-1.21783300
H	-1.88488200	0.63346600	-1.07618300
C	-4.15318800	-1.89635500	-0.72224500
H	-3.97374800	-3.53142800	0.68076200
H	-4.06660700	-0.15314000	-1.99179600
H	-5.10724700	-2.23631400	-1.11793400
O	0.06655500	-1.10313100	1.89393500
C	-1.78839400	4.27753100	0.19686800
H	-2.24594600	4.85691600	1.01074800
H	-1.02654000	4.89957800	-0.28810700
H	-2.56219900	4.04844900	-0.54562600

8-ts

Pd	0.87135700	0.50220000	-0.34972200
O	-0.37484300	2.16333800	-0.42484900
C	-0.01952400	3.31207000	0.31189000
H	-0.85669500	4.02477100	0.22446900
H	0.08448100	3.07021800	1.38379300
P	1.91990800	-1.50753300	-0.01645100
C	2.41504200	-1.82920300	1.73508600
H	1.53579800	-1.75608700	2.38276600
H	2.86821800	-2.82181600	1.84755900

H	3.13136300	-1.06747400	2.05920100
C	0.93807800	-3.01708900	-0.43732100
H	1.49638100	-3.93293700	-0.20765100
H	0.00110600	-3.01677100	0.12855600
H	0.68686000	-3.00715200	-1.50274000
C	3.50111200	-1.80363400	-0.93488500
H	4.22848700	-1.02497600	-0.68273800
H	3.92821000	-2.78264000	-0.68502600
H	3.31764400	-1.76125800	-2.01356600
C	-0.72296100	0.51231800	0.89138400
C	-1.97134300	-0.08575900	0.32411200
C	-2.84951300	-0.72079400	1.21812600
C	-2.27353800	-0.05292600	-1.04515900
C	-4.01458800	-1.32665100	0.74309800
H	-2.61225700	-0.72647100	2.27783900
C	-3.44380800	-0.65127600	-1.51250900
H	-1.60563600	0.46695500	-1.72288900
C	-4.31332100	-1.29352700	-0.62256400
H	-4.69017600	-1.81789100	1.43891600
H	-3.68271000	-0.61060000	-2.57215800
H	-5.22274000	-1.76092100	-0.99216800
O	-0.54329500	0.77449300	2.05304600
C	1.26661800	3.97449800	-0.18957700
H	1.47270000	4.89770500	0.37001200
H	2.12551400	3.30170200	-0.06210200
H	1.18398500	4.22662400	-1.25373200

4. full citation of Gaussian 03 program package.

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