General

Chemicals and Solvents. Commercial chemicals (≥98% purity) were used as obtained from Sigma-Aldrich or Fisher. Solvents (anhydrous, ≥99%) were used without further purification. Acetonitrile was stored over molecular sieves (Sigma-Aldrich). Methanol, ethanol, and *iso*-propanol were distilled under an inert atmosphere of nitrogen gas and stored over molecular sieves. Carbon monoxide (4.7) was used.

Analytical thin-layer chromatography. TLC was performed using aluminium plates with silica gel and fluorescent indicator (DC60 F254, Merck). Thin layer chromatography plates were visualized by exposure to UV light.

Column chromatography. Flash column chromatography with silica gel (60 Å, 0.035-0.070 mm) from *Acros Organics*. Pentane or mixtures thereof with ethyl acetate were used as eluents. Product yields were determined as isolated by column chromatography or for optimization and screening purposes by quantitative GC-FID measurements. 1-Dodecanenitrile was used as internal standard; the yield was calculated from a linear calibration curve that was set up from at least five data points of various concentrations of authentic product material.

Gas chromatography with mass-selective detector. *Agilent* 6890N Network GC-System, mass detector 5975 MS. Column: BPX5 (30m x 0.25 mm x 0.25, from *SGE*, carrier gas: H_2. Standard heating procedure: 50°C (2 min), 25°C/min -> 300°C (5 min).

Gas chromatography with FID. *Agilent* 7820A GC-Systems. Column: HP 5 19091J 413 (30 m x 0.32 mm x 0.25 μm) from *Agilent*, carrier gas: N_2. GC-FID was used for reaction optimization screening (Calibration with internal standard 1-dodecanenitrile and analytically pure samples).

NMR. ^{1}H, ^{19}F and ^{13}C nuclear magnetic resonance spectra were recorded on a *Bruker* Avance 300 (300 MHz ^{1}H; 75 MHz ^{13}C; 282 MHz ^{19}F) and *Bruker* Avance 400 (400 MHz ^{1}H, 101 MHz ^{13}C) spectrometers. Chemicals shifts are reported in ppm (δ) relative to solvent residual peak as internal reference. Coupling constants (*J*) are reported in Hertz (Hz). Following abbreviations are used for spin multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sep = septet, m = multiplet, dd = doublet of doublet, dt = doublet of triplet, td = triplet of doublet, tt = triplet of triplet.

High resolution mass spectrometry (HRMS). The spectra were recorded by the Central Analytics Lab at the Department of Chemistry, University of Regensburg, on a MAT SSQ 710 A from *Finnigan*.

General procedure for the synthesis of arenediazonium salts

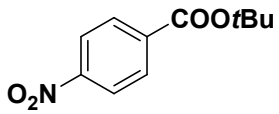
The parent aniline (30 mmol) was dissolved in 32% aqueous tetrafluoroboric acid (12 mL) at room temperature. Afterwards, an aqueous solution of sodium nitrite (30 mmol) in water (4 mL) was added dropwise at 0 °C over 5 min. The resulting mixture was stirred for 40 min and the precipitate was collected by filtration and re-dissolved in minimum amount of acetone. Then, diethyl ether was added until precipitation of diazonium tetrafluoroborate, which is filtered, washed several times with diethyl ether and dried.

General procedure for alkoxycarbonylation

A rolled rim bottle (20 mL) was charged with a magnetic stir bar, the arenediazonium salt (0.9 mmol), sodium formate (0.9 mmol), acetonitrile (1.2 mL for reactions with *t*-BuOH, 9 ml for other alcohols), alcohol (9 mL of *t*-BuOH, 45 mmol of other alcohols) and capped with a snap-on lid. The snap-on lid was punctured with a needle. The reactor was sealed, placed on a magnetic stirrer, and slowly filled with CO (50 bar). After 3 h of stirring, water (5 mL) was added to give an emulsion, which was extracted with ethyl acetate (3 x 5 mL). The organic phases were washed with brine (5 mL) and dried ($MgSO_4$). The solvent was evaporated *in vacuo*; the residue was purified by flash column chromatography (silica gel) using pentane/ethyl acetate mixtures (from 100/0 to 100/20) as eluent to obtain pure product.

Reactions with *tert*-butanol

***Tert*-butyl 4-nitrobenzoate**



$C_{11}H_{13}NO_4$, 223.23 g/mol

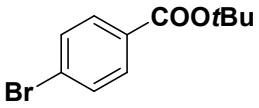
Yield 142.9 mg, 0.64 mmol, 71% (isolated)

^{1}H-NMR (300 MHz, $CDCl_3$): δ_H [ppm] = 8.26 (d, *J* = 8.9 Hz, 2H), 8.14 (d, *J* = 8.9 Hz, 2H), 1.62 (s, 9H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ_C [ppm] = 163.7, 150.2, 137.4, 130.5, 123.3, 82.6, 28.1.

LR MS (EI, 70 eV, m/z): 222.8 [M^+]

***Tert*-butyl 4-bromobenzoate**



$C_{11}H_{13}BrO_2$, 257.13 g/mol

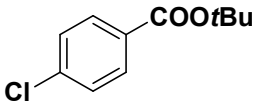
Yield 146.6 mg, 0.57 mmol, 63% (isolated)

^{1}H-NMR (300 MHz, $CDCl_3$): δ_H [ppm] = 7.84 (d, *J* = 8.6 Hz, 2H), 7.54 (d, *J* = 8.6 Hz, 2H), 1.58 (s, 9H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ_C [ppm] = 165.0, 131.4, 131.0, 130.8, 127.4, 81.4, 28.1.

LR MS (EI, 70 eV, m/z): 257.9 [M^+]

***Tert*-butyl 4-chlorobenzoate**



$C_{11}H_{13}ClO_2$, 212.67 g/mol

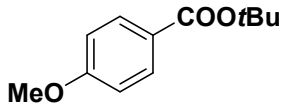
Yield 125.5 mg, 0.59 mmol, 66% (isolated)

^{1}H-NMR (400 MHz, $CDCl_3$): δ_H [ppm] = 7.91 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 1.58 (s, 9H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ_C [ppm] = 164.8, 138.7, 130.8, 130.4, 128.4, 81.4, 28.1.

LR MS (EI, 70 eV, m/z): 212.0 [M^+]

***Tert*-butyl 4-methoxybenzoate**



$C_{12}H_{16}O_3$, 208.26 g/mol

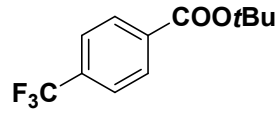
Yield 83.3 mg, 0.40 mmol, 44% (isolated)

^{1}H-NMR (300 MHz, $CDCl_3$): δ_H [ppm] = 7.94 (d, *J* = 9.0 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 3.84 (s, 3H), 1.58 (s, 9H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ_C [ppm] = 165.6, 162.9, 131.3, 124.4, 113.3, 80.5, 55.3, 28.2.

LR MS (EI, 70 eV, m/z): 208.1 [M^+]

***Tert*-butyl 4-(trifluoromethyl)benzoate**



$C_{12}H_{13}F_3O_2$, 246.23 g/mol

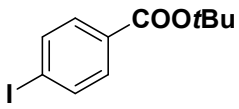
Yield 110.8 mg, 0.45 mmol, 50% (isolated)

^{1}H-NMR (400 MHz, $CDCl_3$): δ_H [ppm] = 8.09 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 1.61 (s, 9H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ_C [ppm] = 164.5, 135.2, 133.9 (q, *J* = 32.5 Hz), 129.8, 125.2 (q, *J* = 3.8 Hz), 122.4, 81.9, 28.1

LR MS (EI, 70 eV, m/z): 246.0 [M^+]

***Tert*-butyl 4-iodobenzoate**



$C_{11}H_{13}IO_2$, 304.13 g/mol

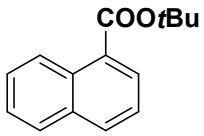
Yield 115.6 mg, 0.38 mmol, 42% (isolated)

^{1}H-NMR (400 MHz, $CDCl_3$): δ_H [ppm] = 7.77 (d, *J* = 8.6 Hz, 2H), 7.68 (d, *J* = 8.6 Hz, 2H), 1.58 (s, 9H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ_C [ppm] = 165.2, 137.5, 131.5, 130.9, 100.0, 81.5, 28.1.

LR MS (EI, 70 eV, m/z): 304.0 [M^+]

***Tert*-butyl 1-naphthoate**



$C_{15}H_{16}O_2$, 228.29 g/mol

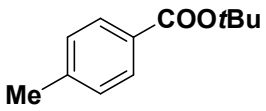
Yield 111.9 mg, 0.49 mmol, 54% (isolated)

^{1}H-NMR (400 MHz, $CDCl_3$): δ_H [ppm] = 8.88 (d, *J* = 8.7 Hz, 1H), 8.10 (dd, *J* = 7.2 Hz, *J* = 1.2 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.64-7.58 (m, 1H), 7.51 (quint, *J* = 7.7 Hz, 2H), 1.70 (s, 9H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ_C [ppm] = 167.1, 133.8, 132.6, 131.2, 129.6, 129.2, 128.4, 127.4, 126.0, 125.8, 124.5, 81.5, 28.3.

LR MS (EI, 70 eV, m/z): 228.1 [M^+]

***Tert*-butyl 4-methylbenzoate**



$C_{12}H_{16}O_2$, 192.26 g/mol

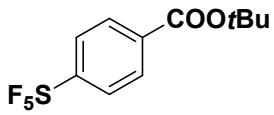
Yield 105.7 mg, 0.55 mmol, 61% (isolated)

^{1}H-NMR (400 MHz, $CDCl_3$): δ_H [ppm] = 7.87 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H), 1.59 (s, 9H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ_C [ppm] = 165.9, 142.9, 129.4, 129.3, 128.9, 80.7, 28.2, 21.6.

LR MS (EI, 70 eV, m/z): 192.1 [M^+]

***Tert*-butyl 4-(pentafluoro-λ^6-sulfanyl)benzoate**



$C_{11}H_{13}F_5O_2S$, 304.28 g/mol

Yield 140.0 mg, 0.46 mmol, 51% (isolated)

^{1}H-NMR (300 MHz, $CDCl_3$): δ_H [ppm] = 8.06 (d, *J* = 8.7 Hz, 2H), 7.79 (d, *J* = 8.9 Hz, 2H), 1.60 (s, 9H).

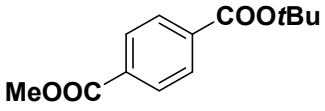
^{13}C-NMR (75 MHz, $CDCl_3$): δ_C [ppm] = 163.9, 156.5 (quint, *J* = 17.6 Hz), 134.8, 129.8, 125.9 (quint, *J* = 4.7 Hz), 82.2, 28.0.

^{19}F-NMR (282 MHz, $CDCl_3$): δ_F [ppm] = 82.7, (quint, *J* = 150.0 Hz, 1F), 61.9 (d, *J* = 150.0 Hz, 4F).

LR MS (EI, 70 eV, m/z): 304.1 [M^+]

HR MS (CI, m/z): found: 305.06080 [MH^+] (calculated: 305.06292)

***Tert*-butyl methyl terephthalate**



$C_{13}H_{16}O_4$, 236.27 g/mol

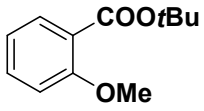
Yield 118.1 mg, 0.50 mmol, 56% (isolated)

^{1}H-NMR (300 MHz, $CDCl_3$): δ_H [ppm] = 8.08-7.99 (m, 4H), 3.92 (s, 3H), 1.58 (s, 9H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ_C [ppm] = 166.3, 164.8, 135.7, 133.3, 129.31, 129.29, 81.6, 52.3, 28.0.

LR MS (EI, 70 eV, m/z): 236.0 [M^+]

***Tert*-butyl 2-methoxybenzoate**



$C_{12}H_{16}O_3$, 208.26 g/mol

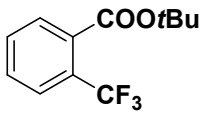
Yield 91.6 mg, 0.44 mmol, 49% (isolated)

^{1}H-NMR (300 MHz, $CDCl_3$): δ_H [ppm] = 7.72 (dd, *J* = 7.9 Hz, *J* = 1.8 Hz, 1H), 7.41 (td, *J* = 7.9 Hz, *J* = 1.8 Hz, 1H), 6.94 (quint, *J* = 3.6 Hz, 2H), 3.87 (s, 3H), 1.57 (s, 9H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ_C [ppm] = 165.3, 159.0, 132.8, 131.3, 121.7, 119.9, 111.9, 80.8, 55.8, 28.2.

LR MS (EI, 70 eV, m/z): 208.1 [M^+]

***Tert*-butyl 2-(trifluoromethyl)benzoate**



$C_{12}H_{13}F_3O_2$, 246.23 g/mol

Yield 101.0 mg, 0.41 mmol, 45% (isolated)

^{1}H-NMR (300 MHz, $CDCl_3$): δ_H [ppm] = 7.74-7.68 (m, 2H), 7.62-7.50 (m, 2H), 1.59 (s, 9H).

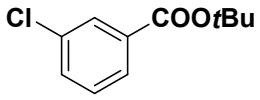
^{13}C-NMR (75 MHz, $CDCl_3$): δ_C [ppm] = 166.3, 133.2 (d, *J* = 2.1 Hz), 131.6, 130.5, 129.9, 128.1 (q, *J* = 32.1 Hz), 126.4 (q, *J* = 5.2 Hz), 123.5 (q, *J* = 273.3 Hz), 82.9, 27.8.

^{19}F-NMR (282 MHz, $CDCl_3$): δ_F [ppm] = -59.4.

LR MS (EI, 70 eV, m/z): 246.2 [M^+]

HR MS (CI, m/z): found: 247.09515 [MH^+] (calculated: 247.09404)

***Tert*-butyl 3-chlorobenzoate**



$C_{11}H_{13}ClO_2$, 212.67 g/mol

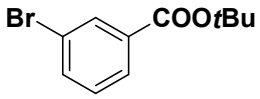
Yield 114.8 mg, 0.54 mmol, 60% (isolated)

^{1}H-NMR (300 MHz, $CDCl_3$): δ_H [ppm] = 7.94 (t, *J* = 1.8 Hz, 1H), 7.86 (dt, *J* = 7.7 Hz, *J* = 1.3 Hz, 1H), 7.48 (dd, *J* = 8.0 Hz, *J* = 1.1 Hz, 1H), 7.34 (t, *J* = 7.9 Hz, 1H), 1.59 (s, 9H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ_C [ppm] = 164.4, 134.2, 133.7, 132.4, 129.4, 127.5, 81.6, 28.1.

LR MS (EI, 70 eV, m/z): 212.0 [M^+]

***Tert*-butyl 3-bromobenzoate**



$C_{11}H_{13}BrO_2$, 257.13 g/mol

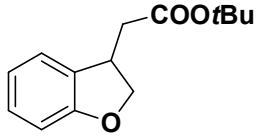
Yield 120.9 mg, 0.47 mmol, 52% (isolated)

^{1}H-NMR (300 MHz, $CDCl_3$): δ_H [ppm] = 8.10 (t, *J* = 1.8 Hz, 1H), 7.91 (dt, *J* = 7.8 Hz, *J* = 1.3 Hz, 1H), 7.64 (dd, *J* = 8.0 Hz, *J* = 1.1 Hz, 1H), 7.28 (t, *J* = 7.9 Hz, 1H), 1.59 (s, 9H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ_C [ppm] = 164.3, 135.3, 133.9, 132.4, 129.7, 128.0, 122.2, 81.7, 28.1.

LR MS (EI, 70 eV, m/z): 258.0 [M^+]

***Tert*-butyl 2-(2,3-dihydrobenzofuran-3-yl)acetate**



$C_{14}H_{18}O_3$, 234.30 g/mol

Yield 46.9 mg, 0.20 mmol, 22% (isolated)

^{1}H-NMR (400 MHz, $CDCl_3$): δ_H [ppm] = 7.14 (q, *J* = 7.6 Hz, 2H), 6.86 (td, *J* = 7.4 Hz, *J* = 0.8 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 4.74 (t, *J* = 9.1 Hz,

1H), 4.26 (dd, *J* = 9.8 Hz, *J* = 6.6 Hz, 1H), 3.89 – 3.79 (m, 1H), 2.71 (dd, *J* = 16.2 Hz, *J* = 5.3 Hz, 1H), 2.51 (dd, *J* = 16.2 Hz, *J* = 9.3 Hz), 1.46 (s, 9H).

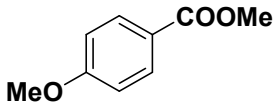
^{13}C-NMR (101 MHz, $CDCl_3$): δ_C [ppm] = 171.1, 159.8, 129.3, 128.5, 124.2, 120.5, 109.6, 81.0, 76.7, 40.7, 38.4, 28.1.

LR MS (EI, 70 eV, m/z): 234.1 [M^+]

HR MS (EI, m/z): found: 234.12516 [M^+] (calculated: 234.12505)

Reactions with other alcohols

Methyl 4-methoxybenzoate



$C_9H_{10}O_3$, 166.18 g/mol

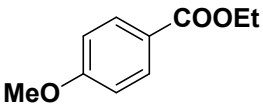
Yield 96.4 mg, 0.58 mmol, 64% (isolated)

^{1}H-NMR (300 MHz, $CDCl_3$): δ_H [ppm] = 7.98 (d, *J* = 9.0 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H), 3.83 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ_C [ppm] = 166.8, 163.2, 131.5, 122.5, 113.5, 55.3, 51.8.

LR MS (EI, 70 eV, m/z): 166.1 [M^+]

Ethyl 4-methoxybenzoate



$C_{10}H_{12}O_3$, 180.20 g/mol

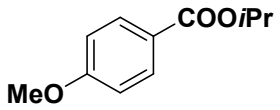
Yield 90.1 mg, 0.50 mmol, 56% (isolated)

^{1}H-NMR (300 MHz, $CDCl_3$): δ_H [ppm] = 7.99 (d, *J* = 9.0 Hz, 2H), 6.90 (d, *J* = 9.0 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 2H) 3.84 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ_C [ppm] = 166.3, 163.2, 131.5, 122.8, 113.5, 60.6, 55.3 14.3.

LR MS (EI, 70 eV, m/z): 180.1 [M^+]

Isopropyl 4-methoxybenzoate



$C_{11}H_{14}O_3$, 194.23 g/mol

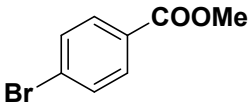
Yield 91.3 mg, 0.47 mmol, 52% (isolated)

^{1}H-NMR (300 MHz, $CDCl_3$): δ_H [ppm] = 7.98 (d, *J* = 8.9 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 5.22 (sep, *J* = 6.3 Hz, 1H) 3.84 (s, 3H), 1.34 (d, *J* = 6.3 Hz, 6H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ_C [ppm] = 165.8, 163.1, 131.4, 123.3, 113.4, 67.9, 55.3 21.9.

LR MS (EI, 70 eV, m/z): 194.1 [M^+]

Methyl 4-bromobenzoate



$C_8H_7BrO_2$, 215.05 g/mol

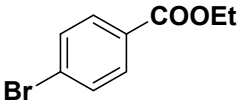
Yield 107.5 mg, 0.50 mmol, 56% (isolated)

^{1}H-NMR (300 MHz, $CDCl_3$): δ_H [ppm] = 7.87 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 2H), 3.89 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ_C [ppm] = 166.3, 131.6, 131.0, 128.9, 128.0, 52.2.

LR MS (EI, 70 eV, m/z): 214.0 [M^+]

Ethyl 4-bromobenzoate



$C_9H_9BrO_2$, 229.07 g/mol

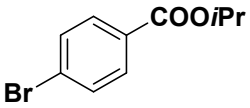
Yield 107.5 mg, 0.50 mmol, 56% (isolated)

^{1}H-NMR (300 MHz, $CDCl_3$): δ_H [ppm] = 7.89 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ_C [ppm] = 165.8, 131.6, 131.0, 129.3, 127.8, 61.2, 14.2.

LR MS (EI, 70 eV, m/z): 230.0 [M^+]

Isopropyl 4-bromobenzoate



$C_{10}H_{11}BrO_2$, 243.10 g/mol

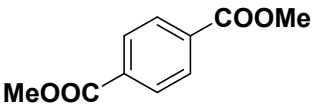
Yield 82.7 mg, 0.34 mmol, 38% (isolated)

^{1}H-NMR (300 MHz, $CDCl_3$): δ_H [ppm] = 7.89 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 5.24 (sep, *J* = 6.3 Hz, 1H), 1.36 (d, *J* = 6.3 Hz, 6H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ_C [ppm] = 165.4, 131.6, 131.0, 129.8, 127.7, 68.7, 21.9.

LR MS (EI, 70 eV, m/z): 241.9 [M^+]

Dimethyl benzene-1,4-dicarboxylate



$C_{10}H_{10}O_4$, 194.19 g/mol

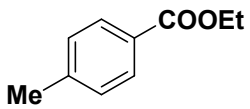
Yield 89.3 mg, 0.46 mmol, 51% (isolated)

^{1}H-NMR (300 MHz, $CDCl_3$): δ_H [ppm] = 8.06 (s, 4H), 3.91 (s, 6H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ_C [ppm] = 166.1, 133.8, 129.4, 52.3.

LR MS (EI, 70 eV, m/z): 194.0 [M^+]

Ethyl 4-methylbenzoate



$C_{10}H_{12}O_2$, 164.20 g/mol

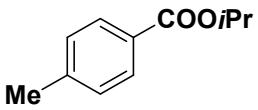
Yield 44.3 mg, 0.27 mmol, 30% (isolated)

^{1}H-NMR (300 MHz, $CDCl_3$): δ_H [ppm] = 7.94 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ_C [ppm] = 166.7, 143.4, 129.5, 129.0, 127.7, 60.7, 21.6, 14.3.

LR MS (EI, 70 eV, m/z): 164.0 [M^+]

Isopropyl 4-methylbenzoate



$C_{11}H_{14}O_2$, 178.23 g/mol

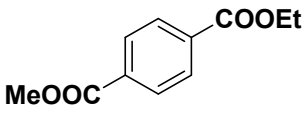
Yield 89.1 mg, 0.50 mmol, 55% (isolated)

^{1}H-NMR (300 MHz, $CDCl_3$): δ_H [ppm] = 7.93 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 5.24 (sep, *J* = 6.3 Hz, 1H), 2.40 (s, 3H), 1.36 (d, *J* = 6.2 Hz, 6H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ_C [ppm] = 166.1, 143.2, 129.5, 128.9, 128.1, 68.0, 21.9, 21.6.

LR MS (EI, 70 eV, m/z): 178.0 [M^+]

Methyl ethyl benzene-1,4-dicarboxylate



$C_{11}H_{12}O_4$, 208.21 g/mol

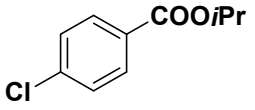
Yield 68.7 mg, 0.33 mmol, 37% (isolated)

^{1}H-NMR (300 MHz, $CDCl_3$): δ_H [ppm] = 8.08 (s, 4H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.93 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ_C [ppm] = 166.2, 165.7, 134.2, 133.7, 129.4, 61.4, 52.4, 14.2.

LR MS (EI, 70 eV, m/z): 208.1 [M^+]

Isopropyl 4-chlorobenzoate



$C_{10}H_{11}ClO_2$, 198.65 g/mol

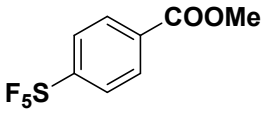
Yield 67.5 mg, 0.34 mmol, 38% (isolated)

^{1}H-NMR (300 MHz, $CDCl_3$): δ_H [ppm] = 7.96 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 8.6 Hz, 2H), 5.23 (sep, *J* = 6.3 Hz, 1H), 1.36 (d, *J* = 6.3 Hz, 6H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ_C [ppm] = 165.2, 139.0, 130.9, 129.3, 128.5, 68.7, 21.9.

LR MS (EI, 70 eV, m/z): 198.0 [M^+]

Methyl 4-(pentafluoro-λ^6-sulfanyl)benzoate



$C_8H_7F_5O_2S$, 262.19 g/mol

Yield 94.4 mg, 0.36 mmol, 40% (isolated)

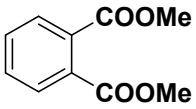
^{1}H-NMR (300 MHz, $CDCl_3$): δ_H [ppm] = 8.13 (d, *J* = 8.9 Hz, 2H), 7.83 (d, *J* = 8.9 Hz, 2H), 3.96 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ_C [ppm] = 165.3, 156.9 (quint, *J* = 17.7 Hz), 133.0, 130.0, 126.2 (quint, *J* = 4.7 Hz), 52.6.

^{19}F-NMR (282 MHz, $CDCl_3$): δ_F [ppm] = 82.4, (quint, *J* = 149.0 Hz, 1F), 61.9 (d, *J* = 149.0 Hz, 4F).

LR MS (EI, 70 eV, m/z): 262.0 [M^+]

Dimethyl benzene-1,2-dicarboxylate



$C_{10}H_{10}O_4$, 194.19 g/mol

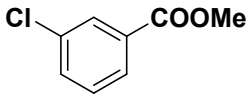
Yield 36.9 mg, 0.19 mmol, 21% (isolated)

^{1}H-NMR (300 MHz, $CDCl_3$): δ_H [ppm] = 7.72 (dd, *J* = 5.7 Hz, *J* = 3.3 Hz, 2H), 7.53 (dd, *J* = 5.7 Hz, *J* = 3.3 Hz, 2H), 3.90 (s, 6H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ_C [ppm] = 168.0, 131.9, 131.1, 128.8, 52.6.

LR MS (EI, 70 eV, m/z): 193.9 [M^+]

Methyl 3-chlorobenzoate



$C_8H_7ClO_2$, 170.59 g/mol

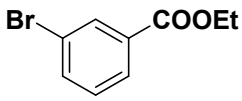
Yield 80.2 mg, 0.47 mmol, 52% (isolated)

^{1}H-NMR (300 MHz, $CDCl_3$): δ_H [ppm] = 8.01 (t, *J* = 1.9 Hz, 1H), 7.91 (dt, *J* = 7.8 Hz, *J* = 1.3 Hz, 1H), 7.51 (dd, *J* = 8.0 Hz, *J* = 1.1 Hz, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 3.91 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ_C [ppm] = 165.8, 134.4, 132.9, 131.8, 129.63, 129.62 127.6, 52.4.

LR MS (EI, 70 eV, m/z): 170.0 [M^+]

Ethyl 3-bromobenzoate



$C_9H_9BrO_2$, 229.07 g/mol

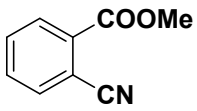
Yield 73.3 mg, 0.32 mmol, 36% (isolated)

^{1}H-NMR (300 MHz, $CDCl_3$): δ_H [ppm] = 8.17 (t, *J* = 1.8 Hz, 1H), 7.97 (dt, *J* = 7.8 Hz, *J* = 1.3 Hz, 1H), 7.66 (dd, *J* = 8.0 Hz, *J* = 1.0 Hz, 1H), 7.31 (t, *J* = 7.9 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ_C [ppm] = 165.2, 135.7, 132.5, 132.3, 129.9, 128.1, 122.4, 61.4, 14.2.

LR MS (EI, 70 eV, m/z): 228.0 [M^+]

Methyl 2-cyanobenzoate



$C_9H_7NO_2$, 161.16 g/mol

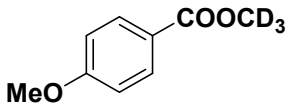
Yield 45.1 mg, 0.28 mmol, 31% (isolated)

^{1}H-NMR (300 MHz, $CDCl_3$): δ_H [ppm] = 8.17 – 8.11 (m, 1H), 7.84 – 7.78 (m, 1H), 7.73 – 7.68 (m, 2H), 4.00 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ_C [ppm] = 164.5, 134.8, 132.7, 132.4, 132.3, 131.1, 117.5, 112.9, 52.8.

LR MS (EI, 70 eV, m/z): 161.0 [M^+]

Methyl-d_3 4-methoxybenzoate



$C_9H_7D_3O_3$, 169.19 g/mol

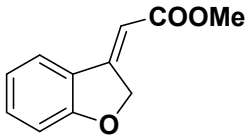
Yield 84.6 mg, 0.50 mmol, 56% (isolated)

^{1}H-NMR (400 MHz, $CDCl_3$): δ_H [ppm] = 7.99 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 3.85 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ_C [ppm] = 166.8, 163.3, 131.5, 122.6, 113.6, 55.4, 51.0 (q, *J* = 22.3 Hz).

LR MS (EI, 70 eV, m/z): 169.1 [M^+]

Methyl 2-(benzofuran-3(2*H*)-ylidene)acetate



$C_{11}H_{10}O_3$, 190.20 g/mol

Yield 89.4 mg, 0.47 mmol, 52% (isolated)

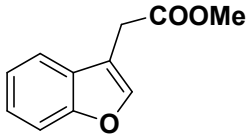
^{1}H-NMR (300 MHz, $CDCl_3$): δ_H [ppm] = 7.52 (dd, *J* = 7.9 Hz, *J* = 1.2 Hz, 1H), 7.37 (td, *J* = 7.8 Hz, *J* = 1.3 Hz, 1H), 7.01 – 6.94 (m, 2H), 6.18 (t, *J* = 3.1 Hz, 1H), 5.52 (d, *J* = 3.1 Hz, 2H), 3.77 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ_C [ppm] = 167.5, 165.4, 156.2, 133.6, 124.0, 122.2, 121.1, 111.4, 103.9, 76.6, 51.4.

LR MS (EI, 70 eV, m/z): 190.0 [M^+]

HR MS (EI, m/z): found: 190.06253 [M^+] (calculated: 190.06245)

Methyl 2-(benzofuran-3-yl)acetate



$C_{11}H_{10}O_3$, 190.20 g/mol

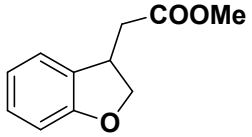
^{1}H-NMR (400 MHz, $CDCl_3$): δ_H [ppm] = 7.63 (s, 1H), 7.59 – 7.55 (m, 1H), 7.50 – 7.46 (m, 1H), 7.24 – 7.23 (m, 2H), 3.74 (s, 1H), 3.72 (d, *J* = 0.6 Hz, 2H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ_C [ppm] = 171.1, 155.1, 142.8, 127.5, 124.5, 122.6, 119.6, 113.0, 111.5, 52.2, 29.5.

LR MS (EI, 70 eV, m/z): 190.0 [M^+]

HR MS (EI, m/z): found: 190.06293 [M^+] (calculated: 190.06245)

Methyl 2-(2,3-dihydrobenzofuran-3-yl)acetate



$C_{11}H_{12}O_3$, 192.21 g/mol

Yield 69.2 mg, 0.36 mmol, 40% (isolated)

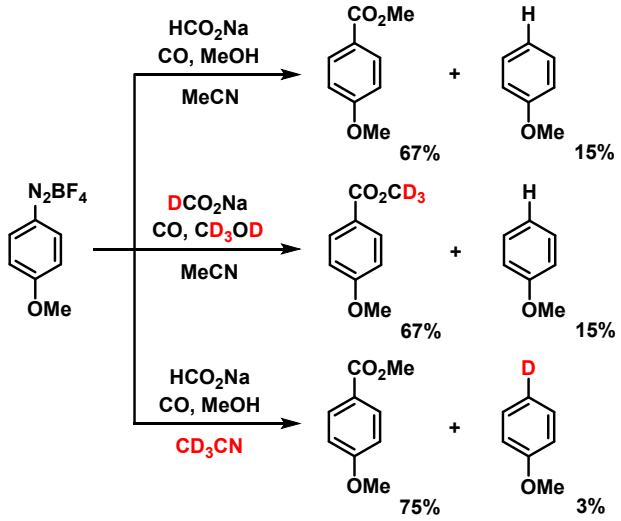
^{1}H-NMR (400 MHz, $CDCl_3$): δ_H [ppm] = 7.15 (t, *J* = 7.6 Hz, 2H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 4.75 (t, *J* = 9.1 Hz, 1H), 4.25 (dd, *J* = 9.2 Hz, *J* = 6.9 Hz, 1H), 3.93 – 3.87 (m, 1H), 3.73 (s, 3H), 2.84 – 1.76 (m, 1H), 2.65 – 2.55 (m, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ_C [ppm] = 172.2, 159.8, 129.0, 128.7, 124.2, 120.6, 109.7, 76.7, 51.8, 39.2, 38.3.

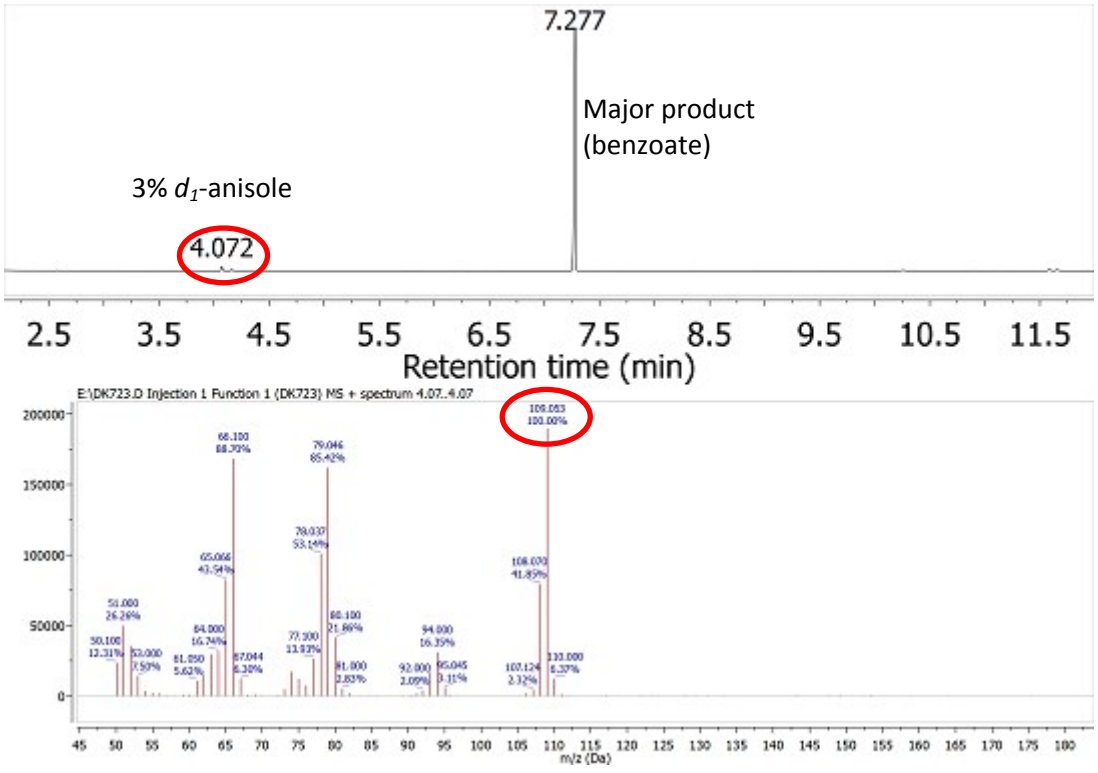
LR MS (EI, 70 eV, m/z): 192.0 [M^+]

HR MS (EI, m/z): found: 192.07782 [M^+] (calculated: 192.07810)

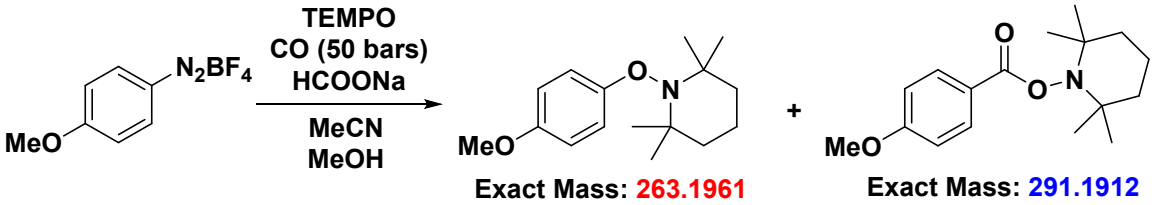
Deuteration experiment in CD_3CN



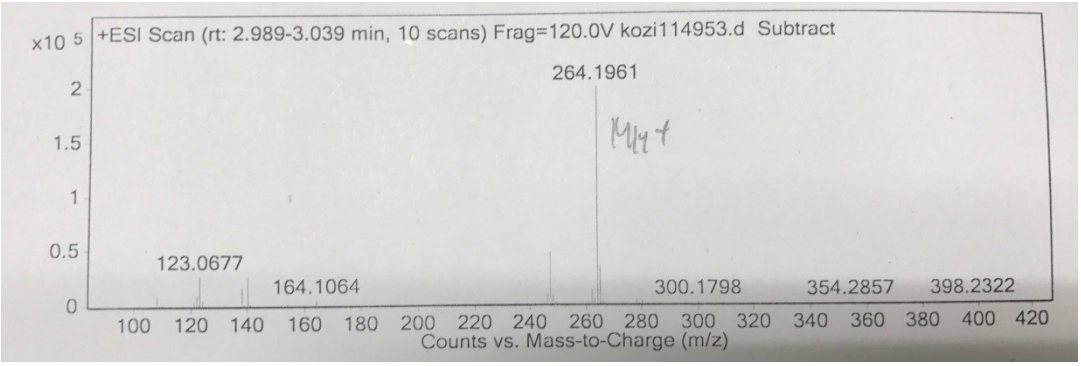
GC-MS spectrum of deutero anisole (4.072 min) in crude reaction mixture:

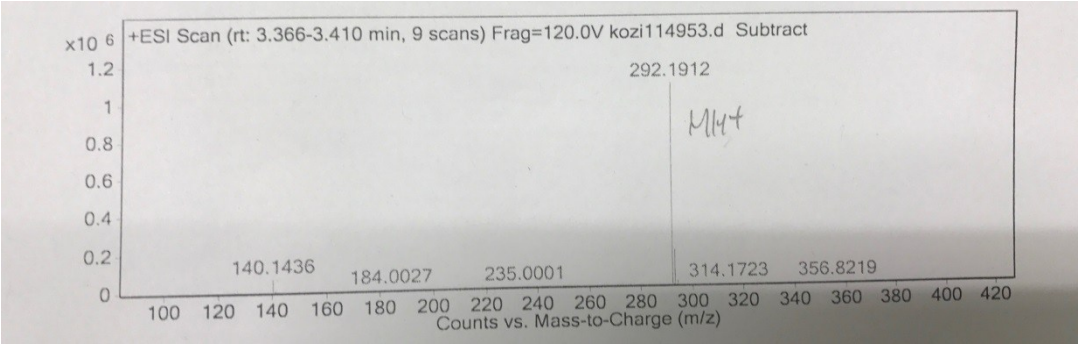


Mass spectra of radical trapping experiments with TEMPO



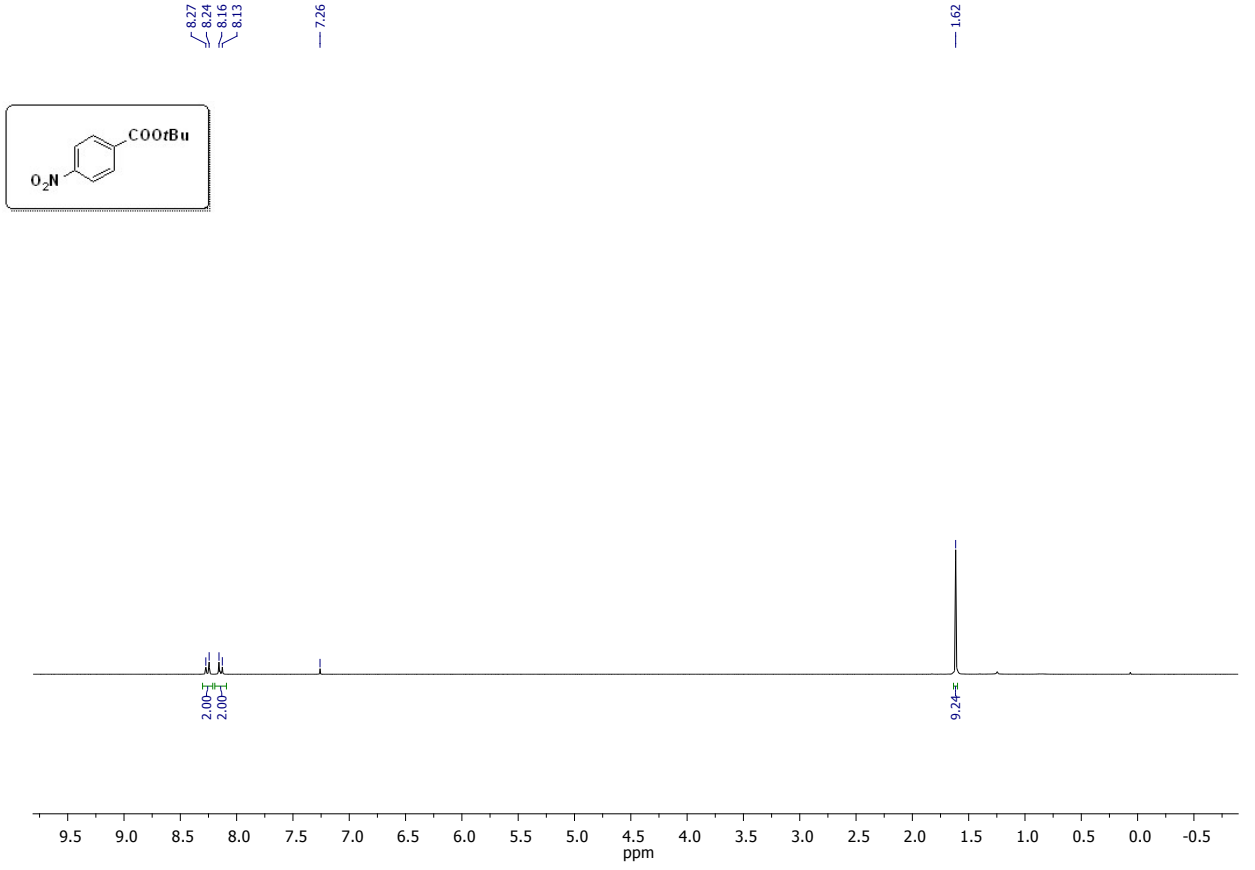
Exact Mass: 263.1961 Exact Mass: 291.1912



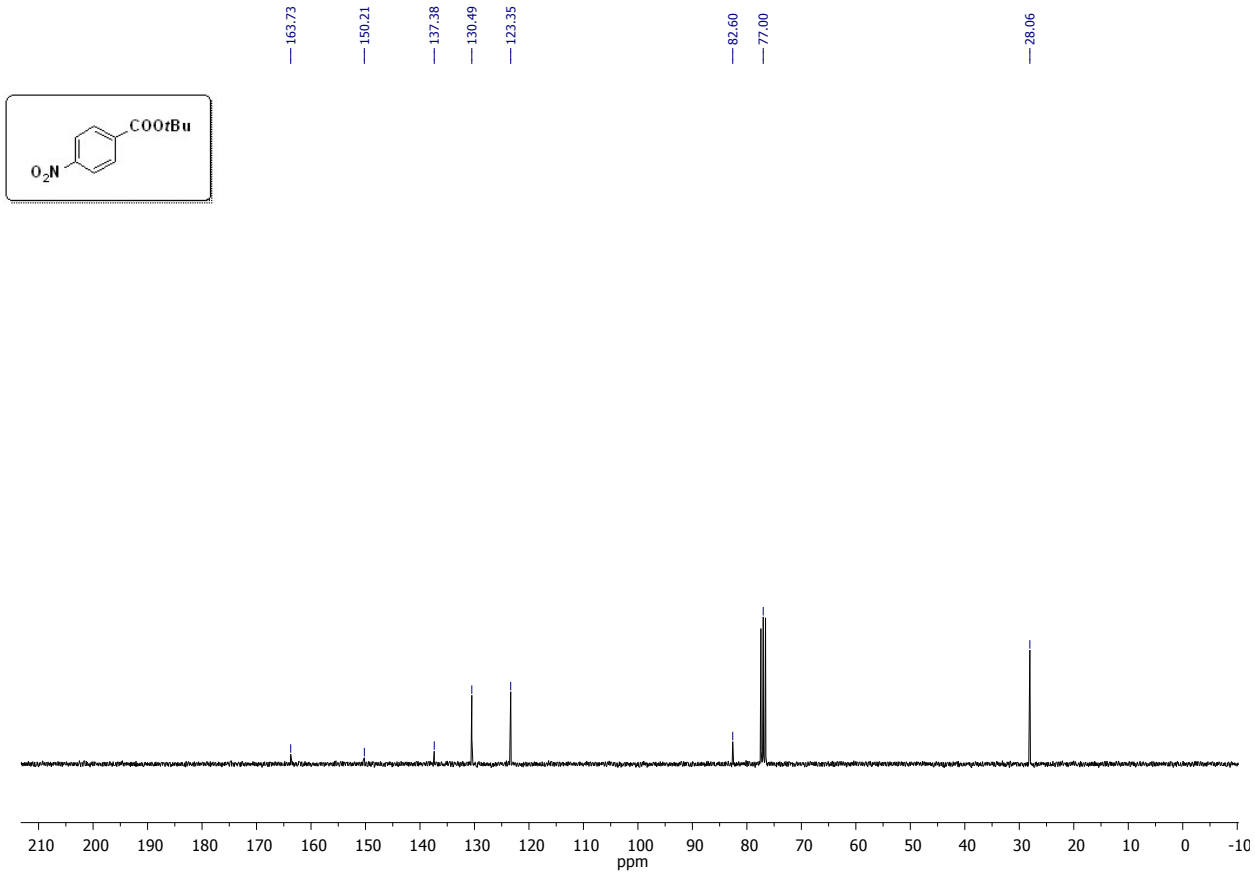


^{1}H and ^{13}C NMR Spectra of all compounds

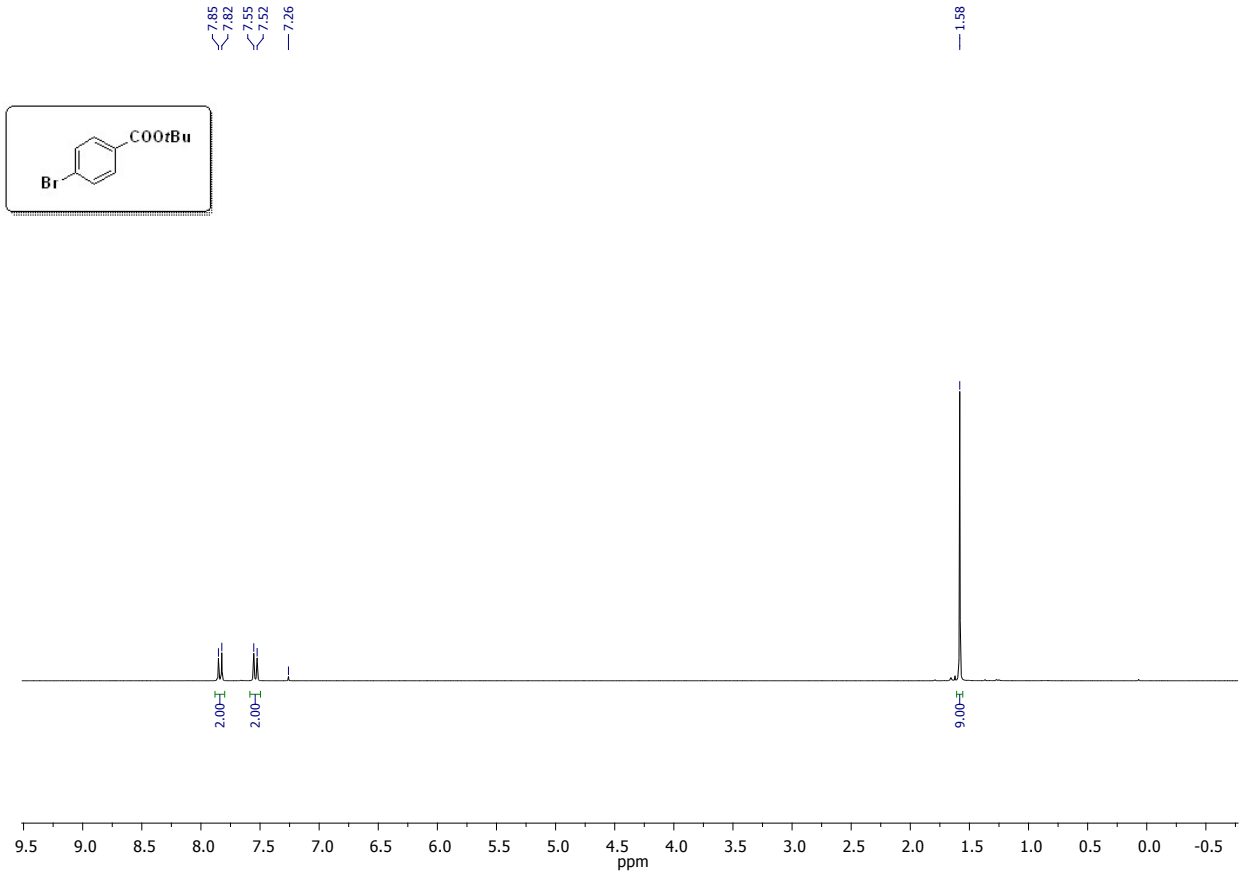
^{1}H-NMR (300 MHz, $CDCl_3$)



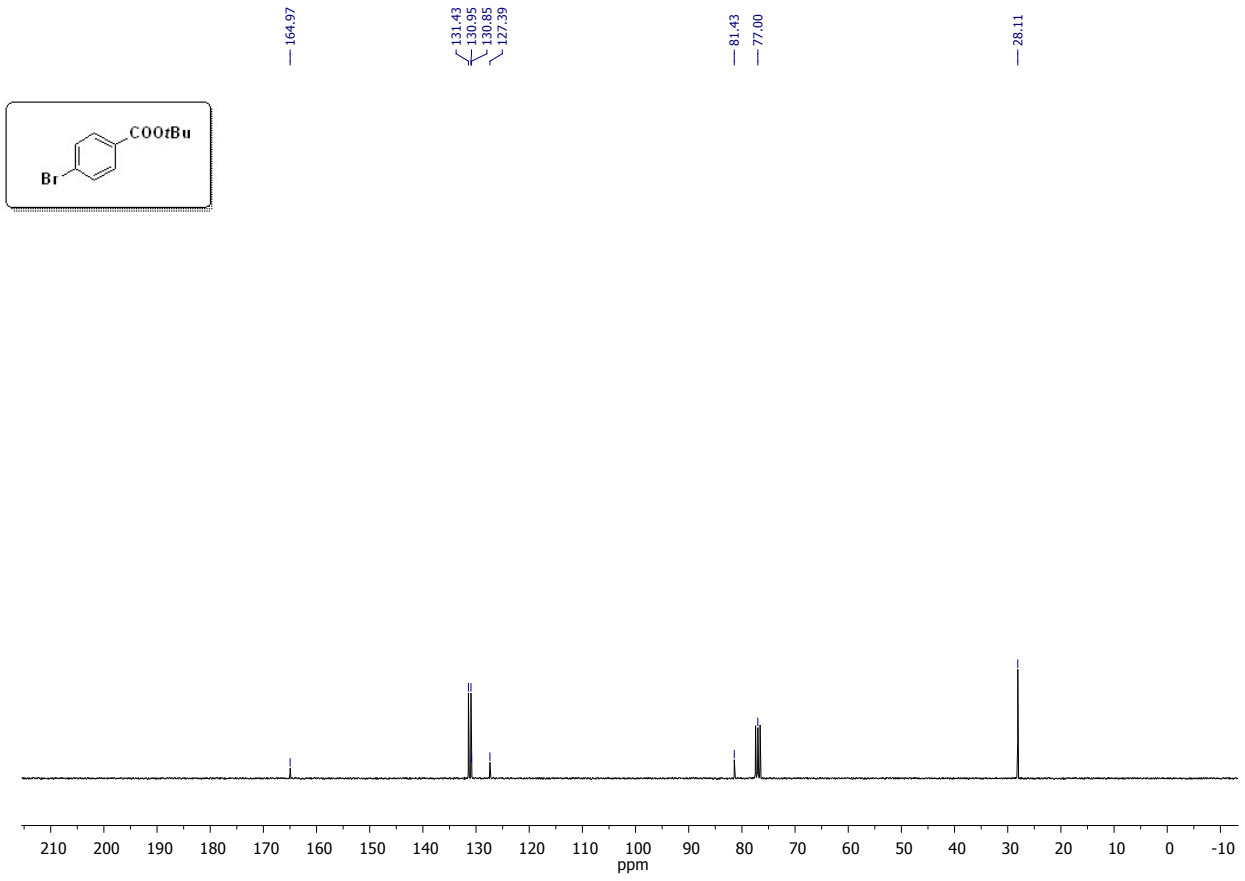
^{13}C-NMR (75 MHz, $CDCl_3$)



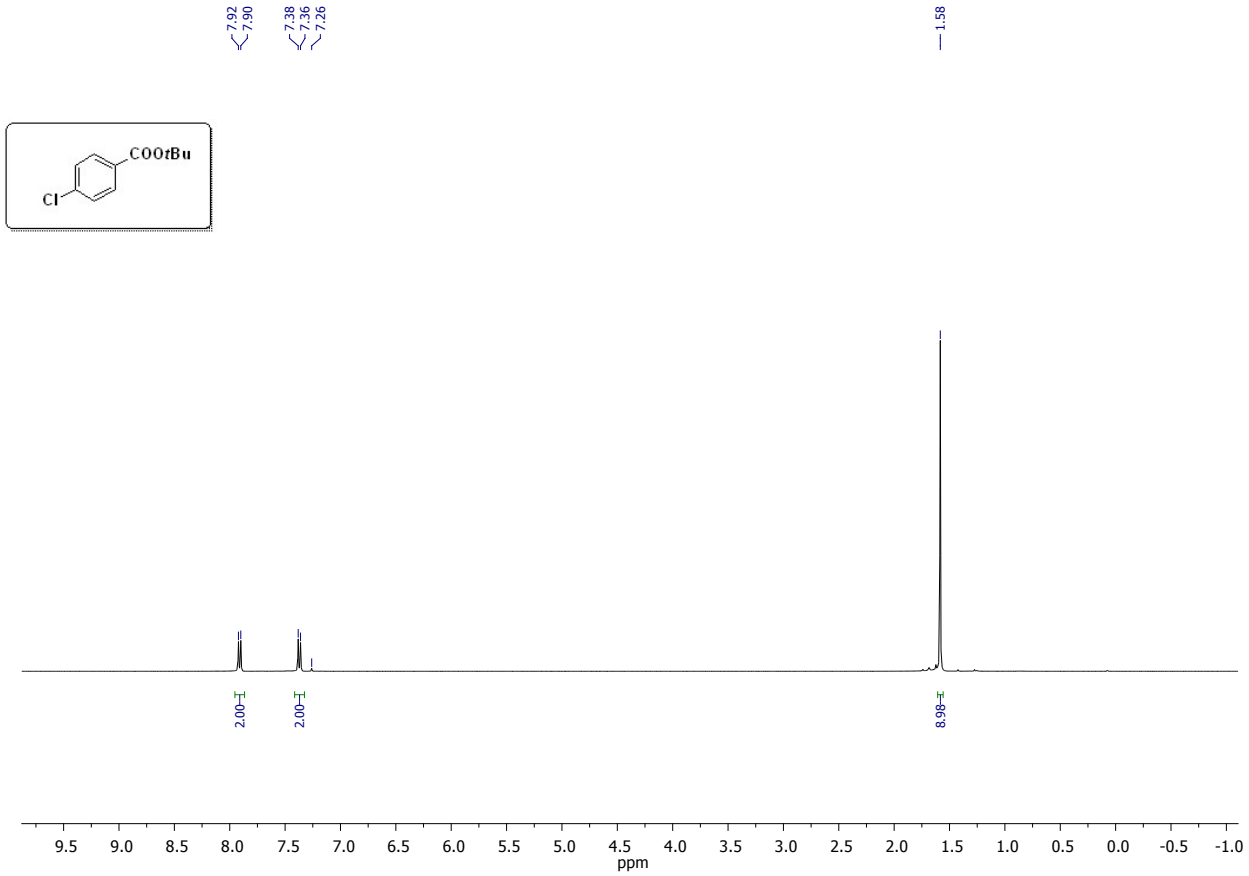
^{1}H-NMR (300 MHz, $CDCl_3$)



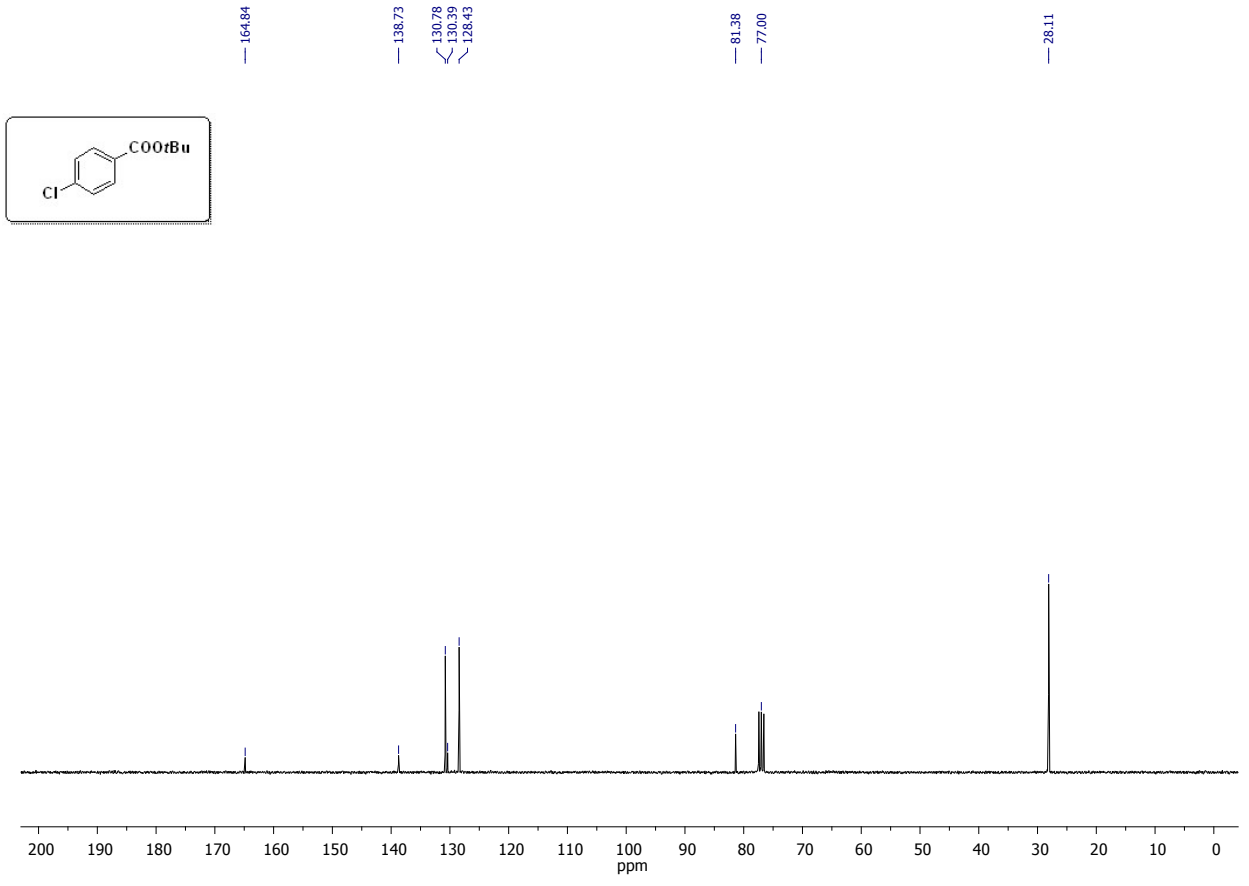
^{13}C-NMR (75 MHz, $CDCl_3$)



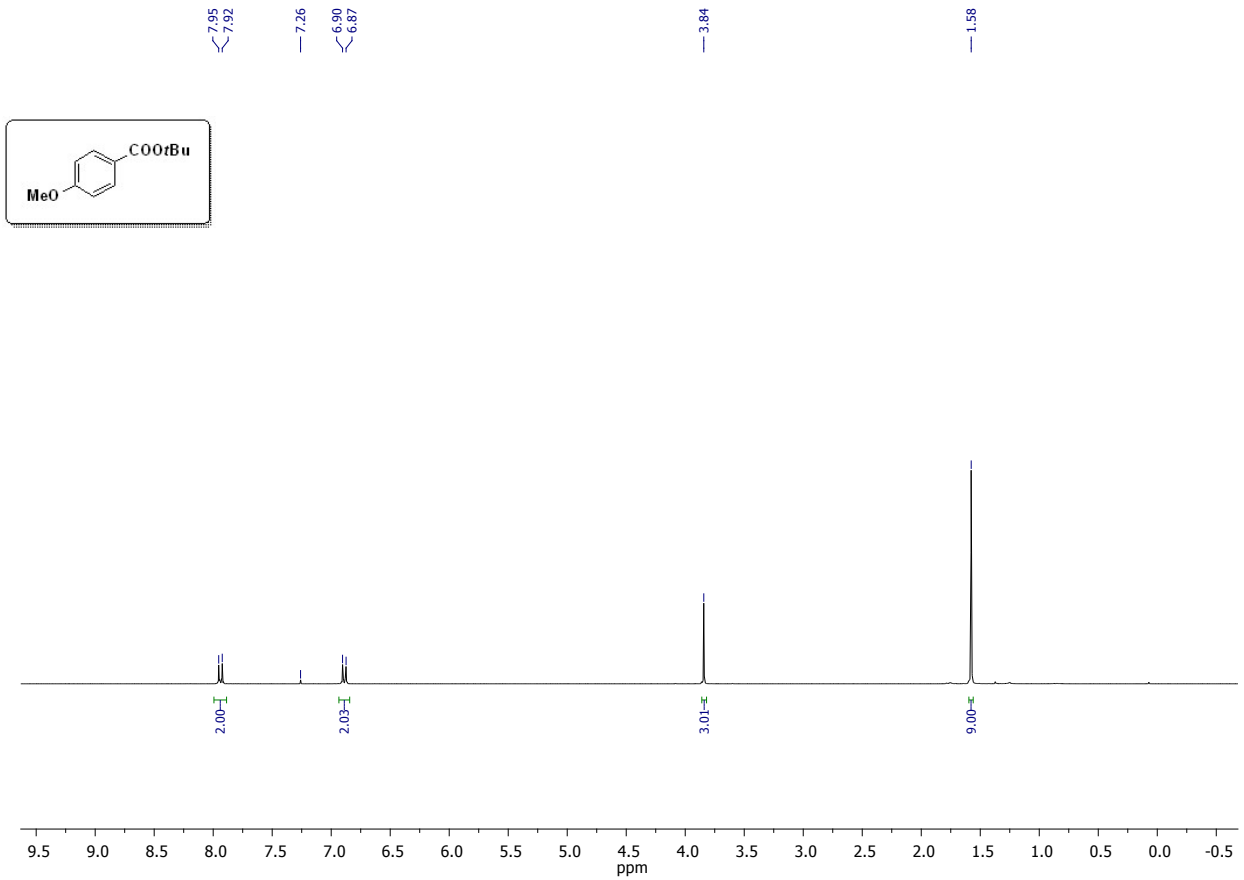
^{1}H-NMR (400 MHz, $CDCl_3$)



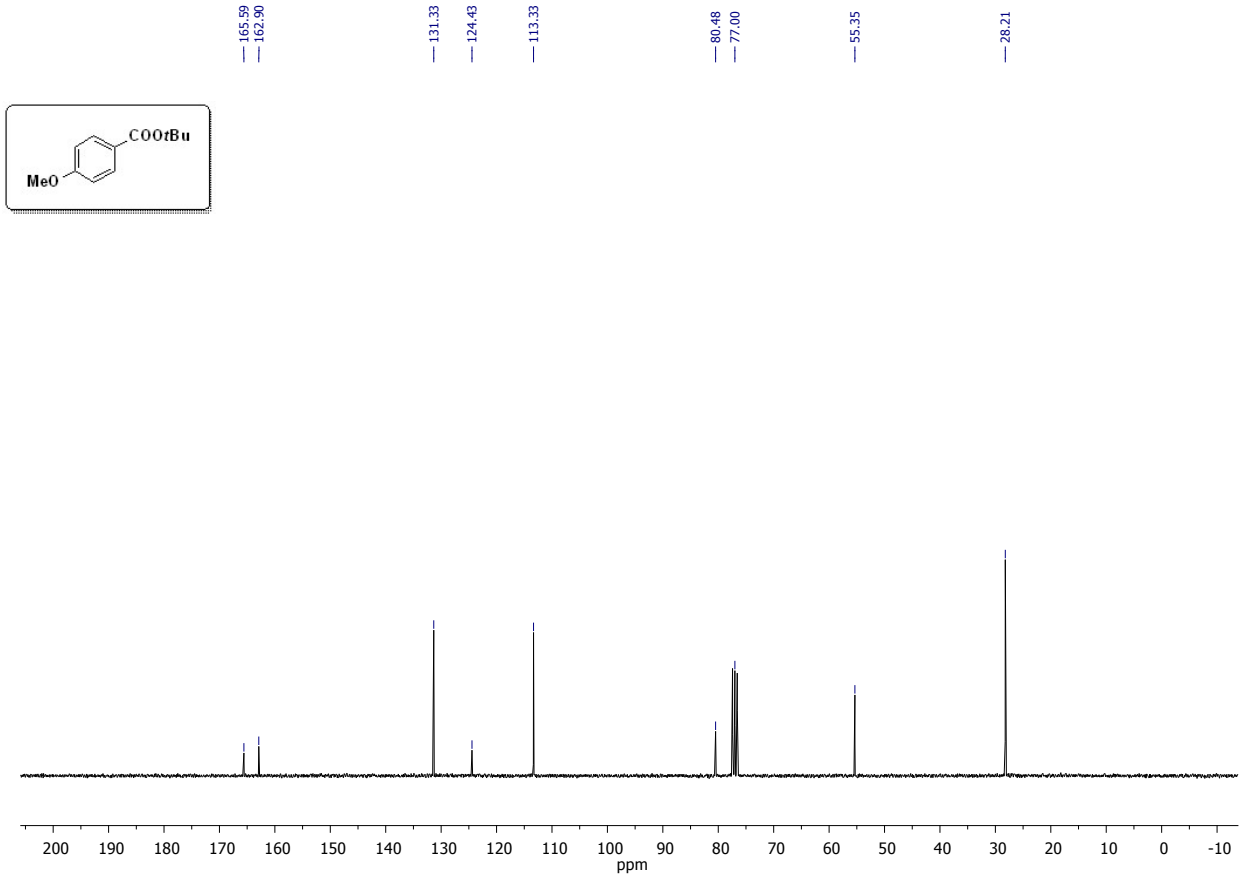
^{13}C-NMR (75 MHz, $CDCl_3$)



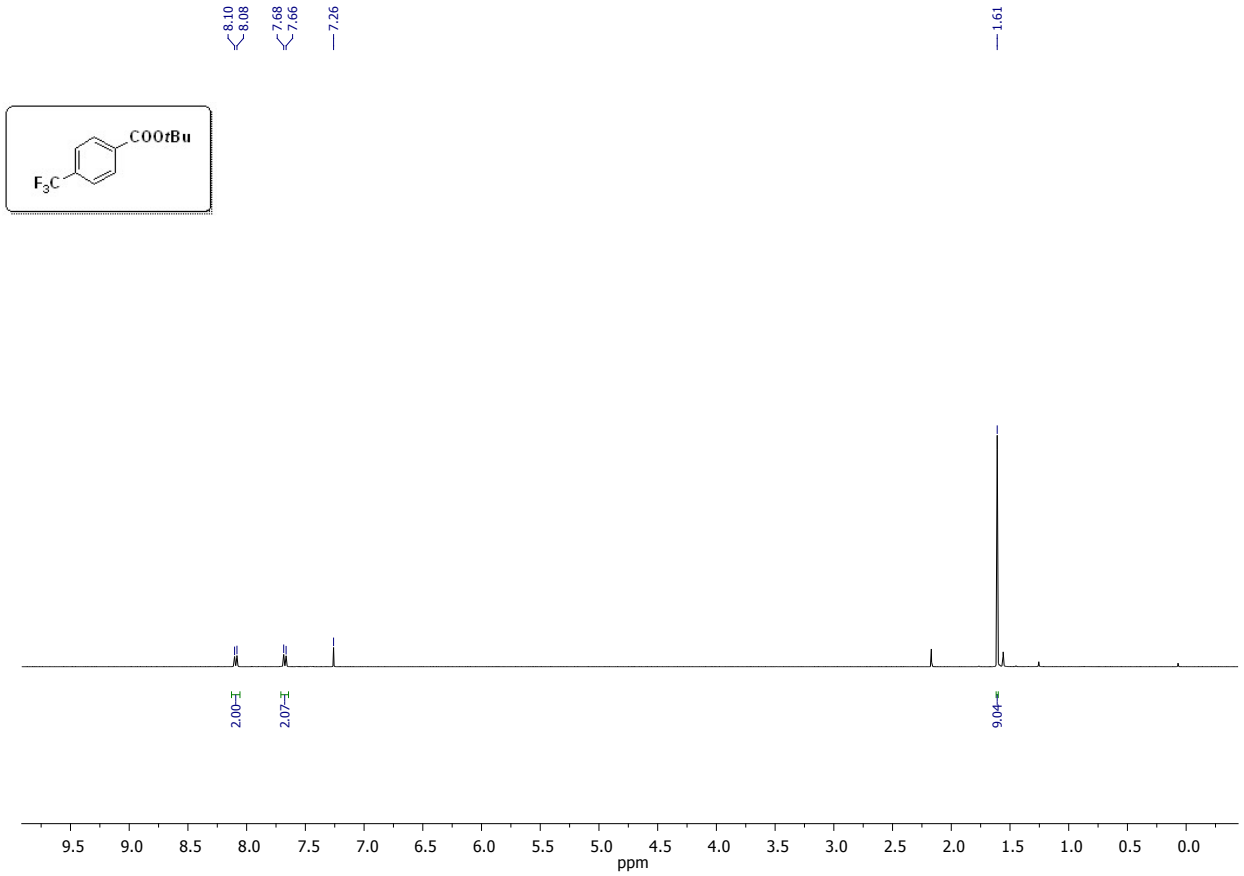
^{1}H-NMR (300 MHz, $CDCl_3$)



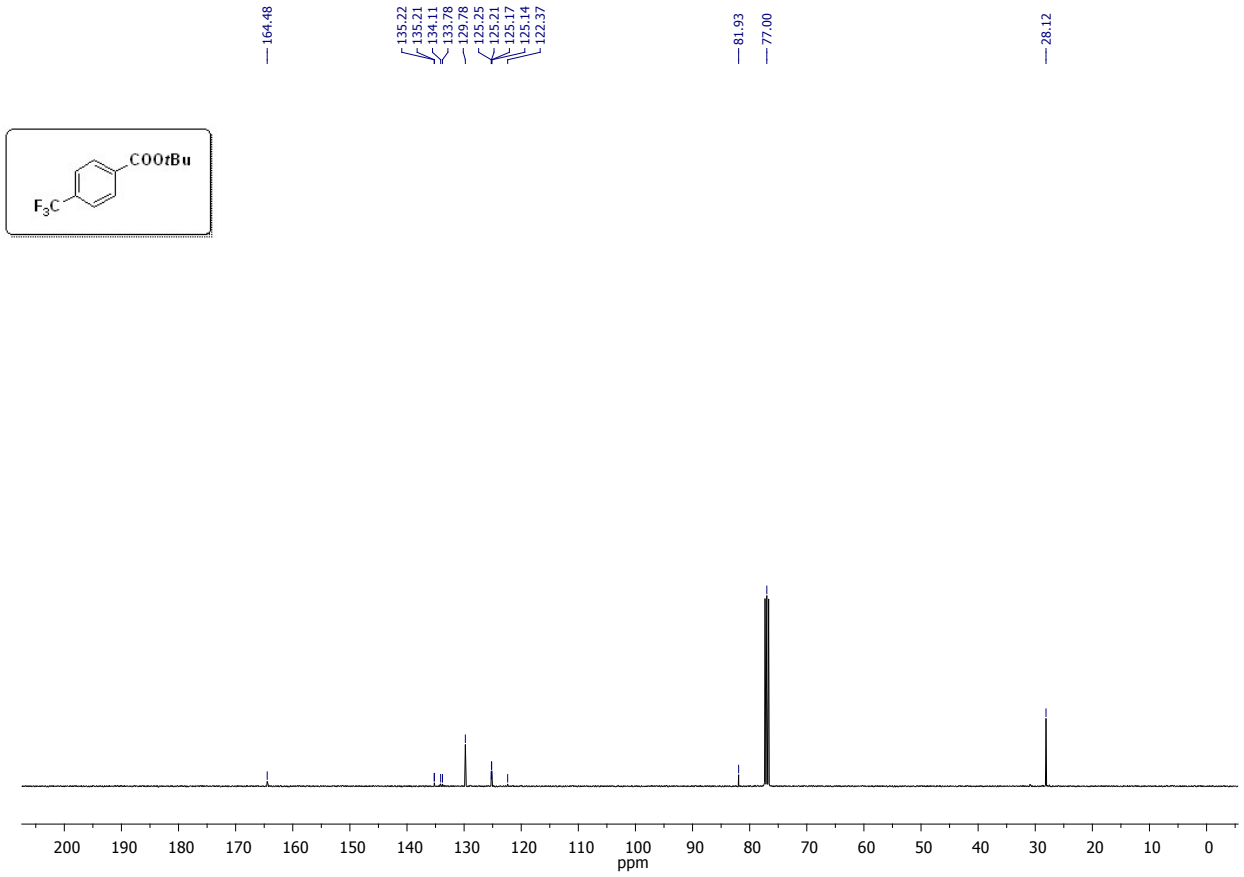
^{13}C-NMR (75 MHz, $CDCl_3$)



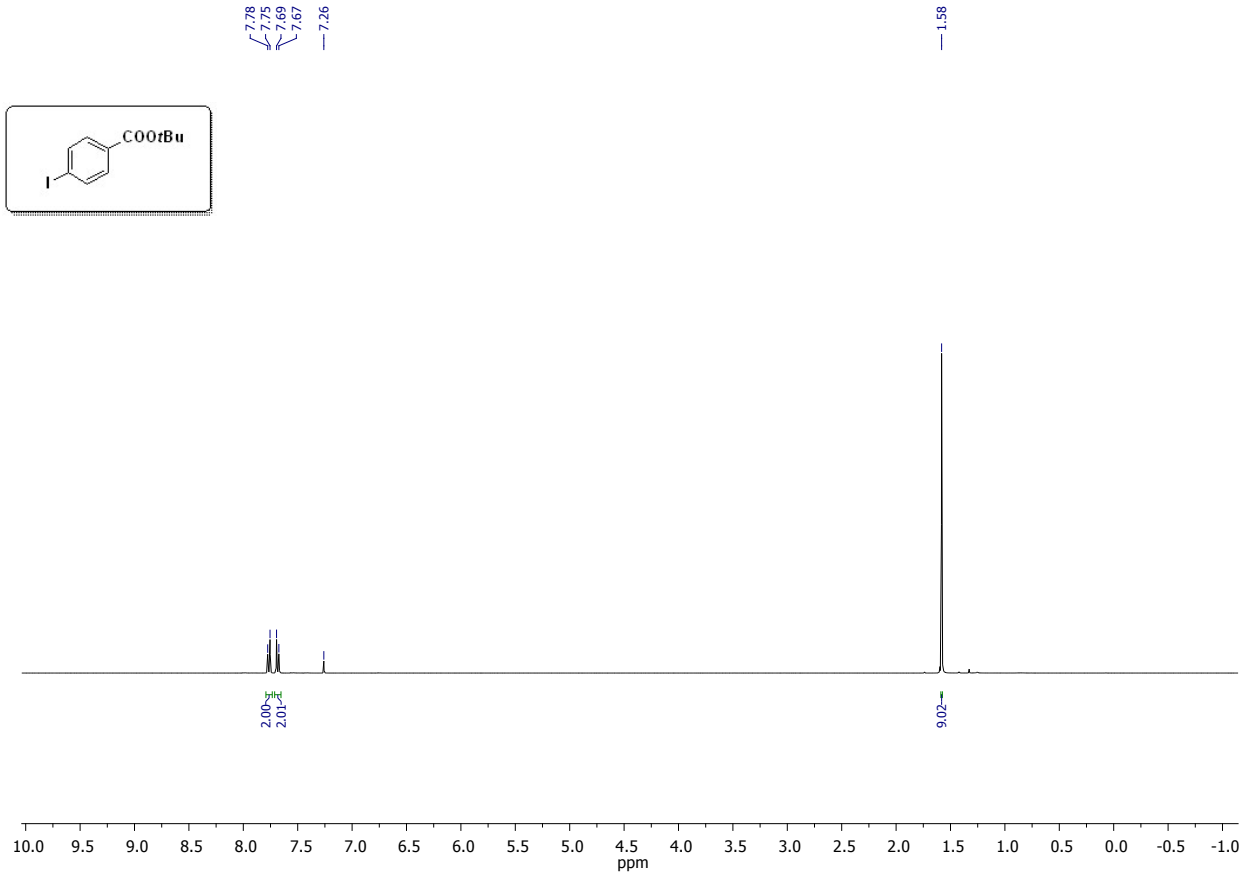
^{1}H-NMR (400 MHz, $CDCl_3$)



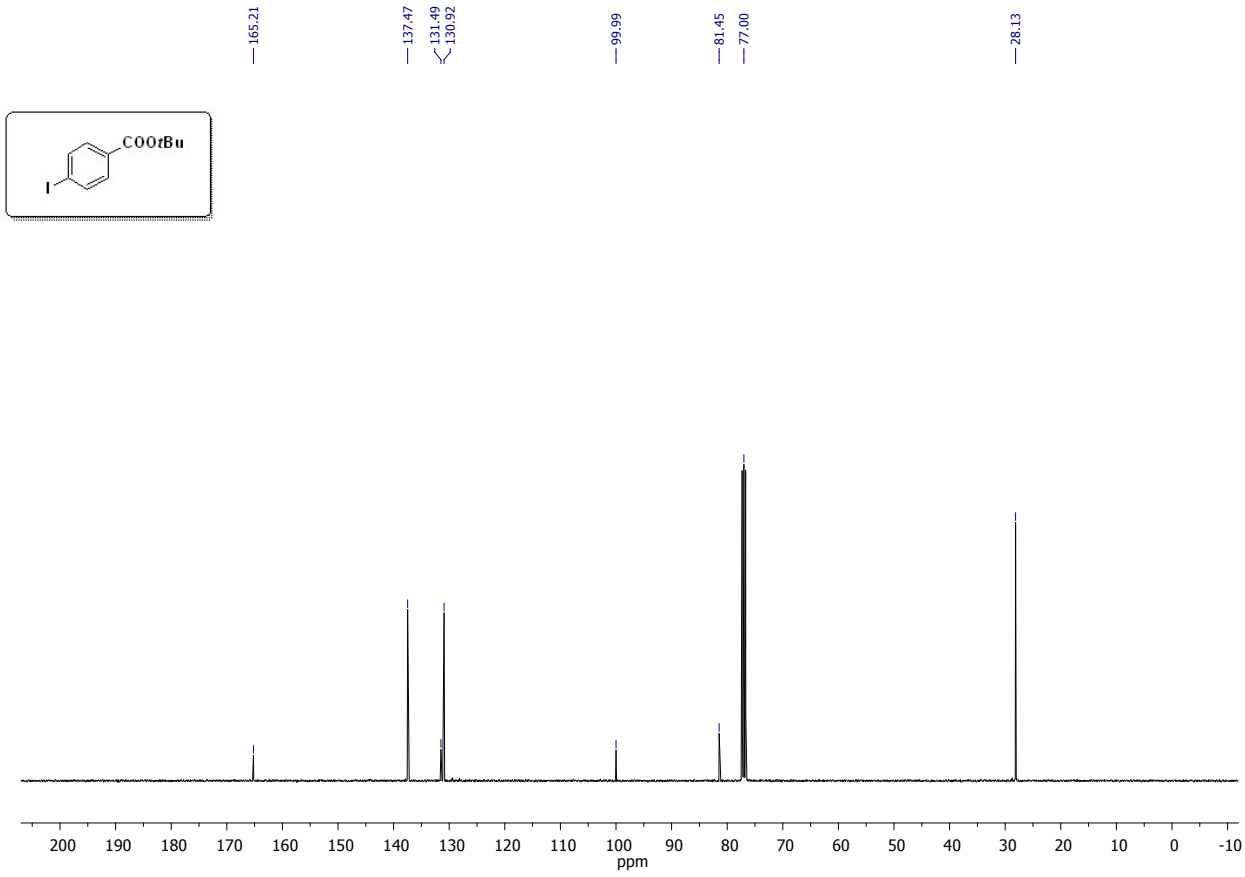
^{13}C-NMR (101 MHz, $CDCl_3$)



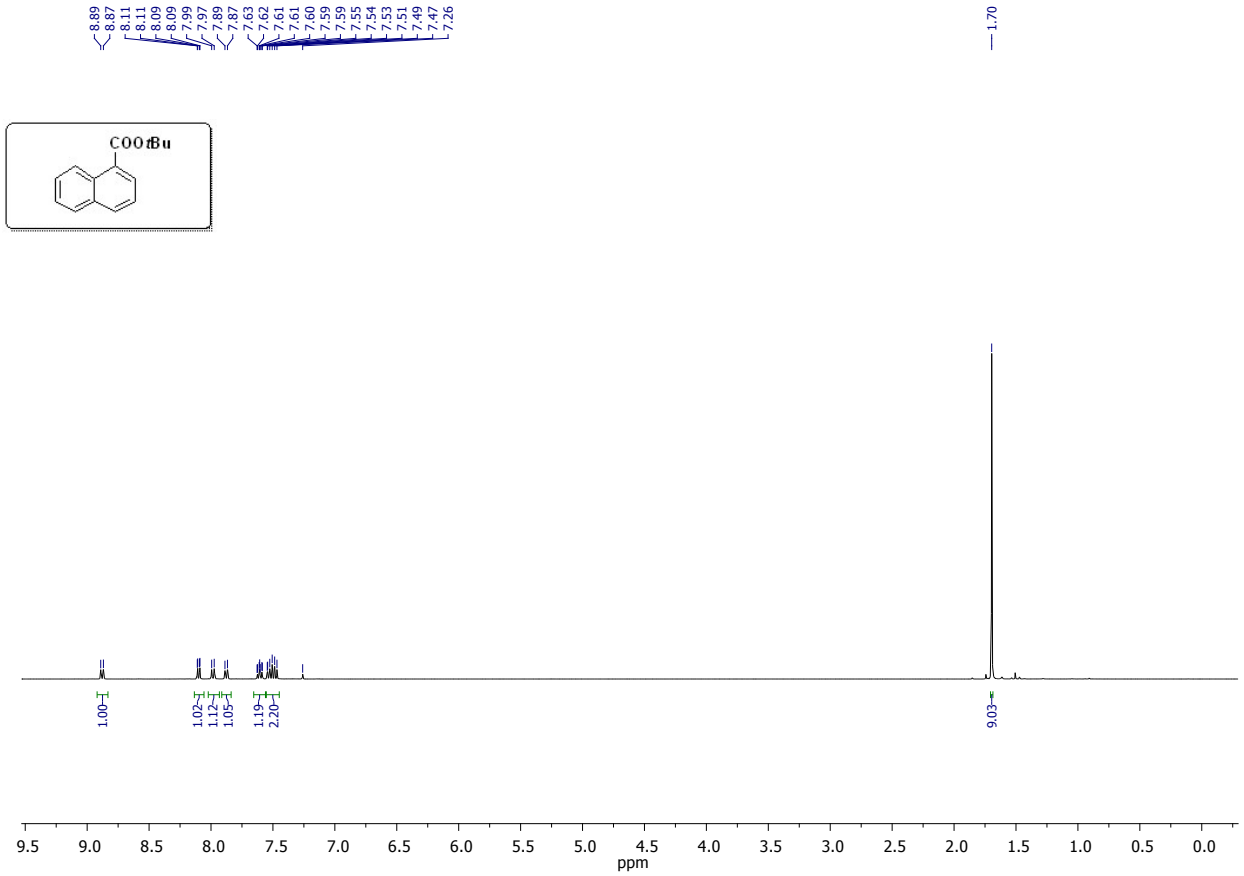
^{1}H-NMR (400 MHz, $CDCl_3$)



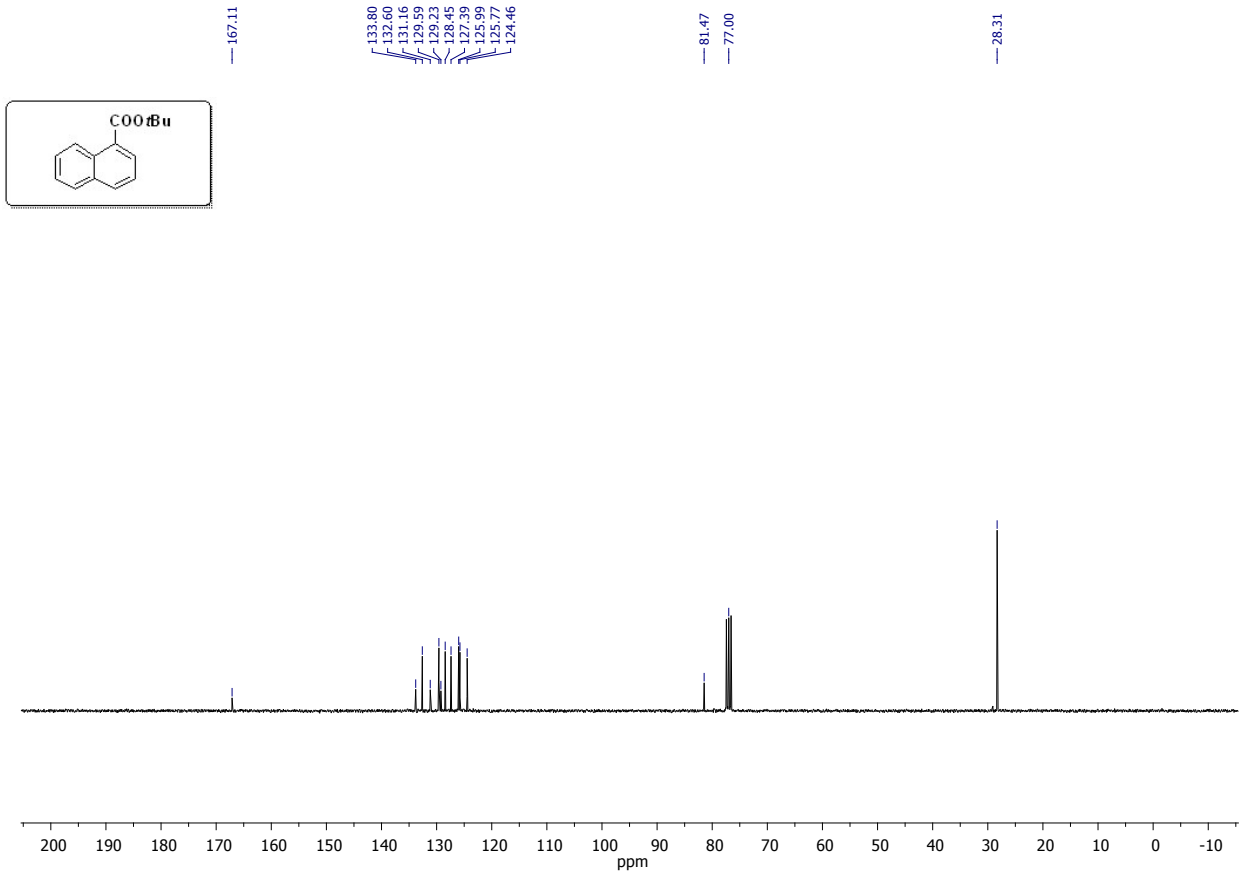
^{13}C-NMR (101 MHz, $CDCl_3$)



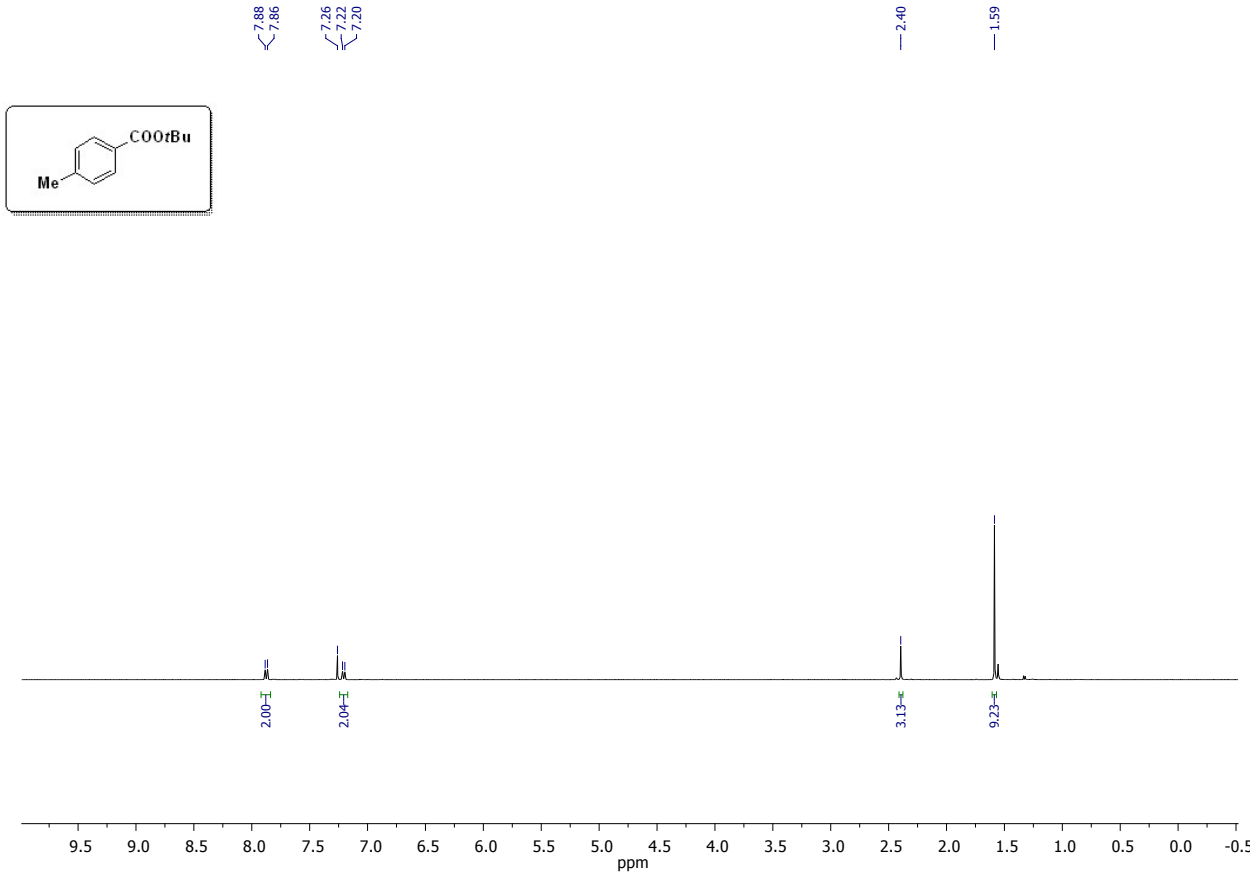
^{1}H-NMR (400 MHz, $CDCl_3$)



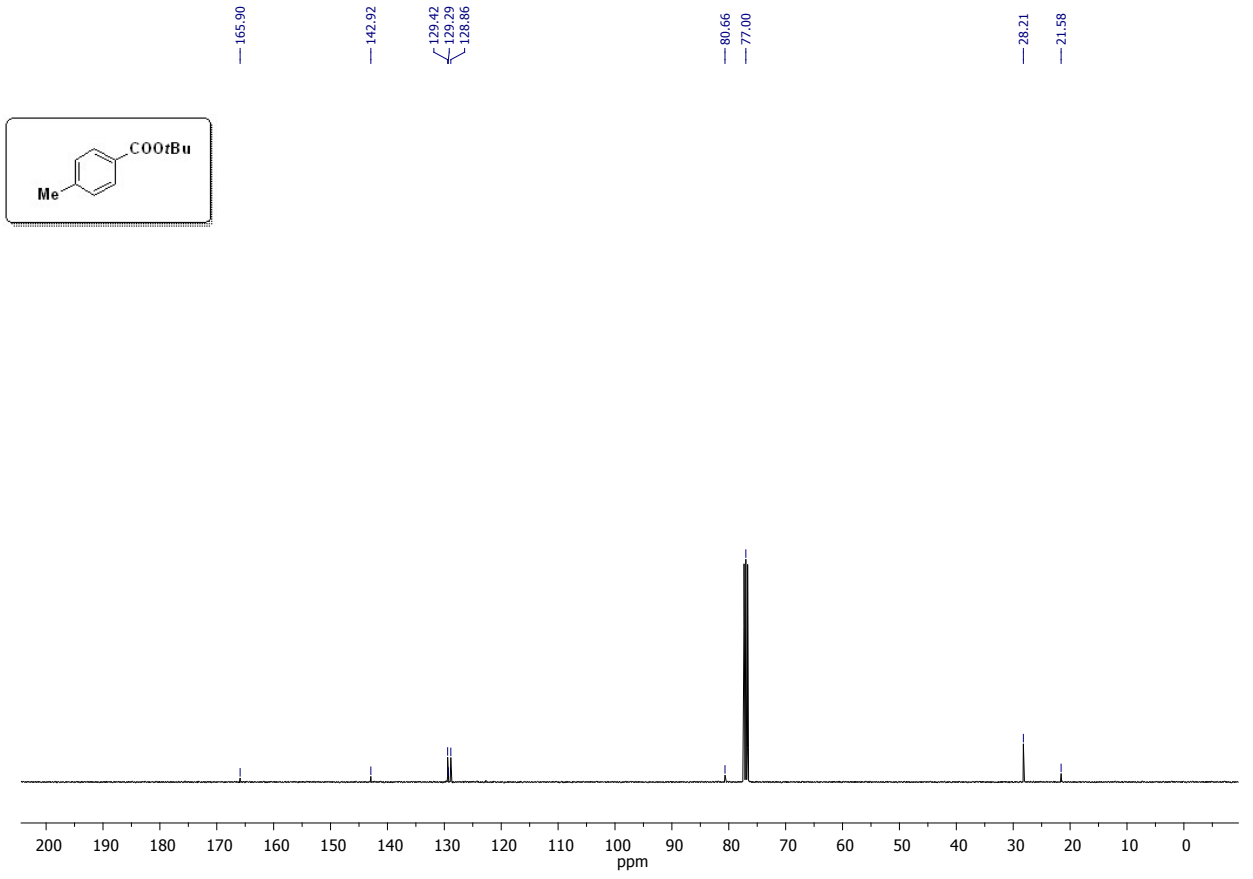
^{13}C-NMR (75 MHz, $CDCl_3$)



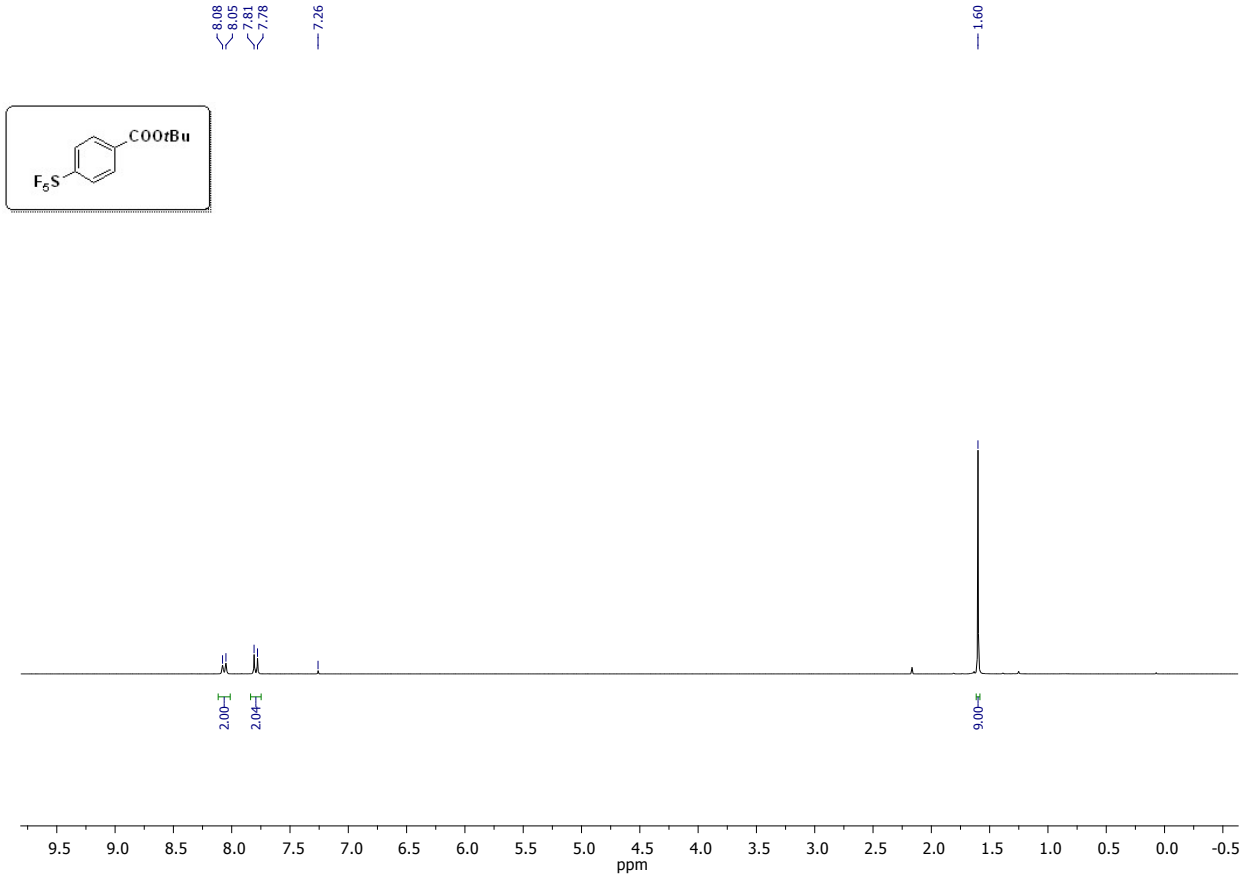
^{1}H-NMR (400 MHz, $CDCl_3$)



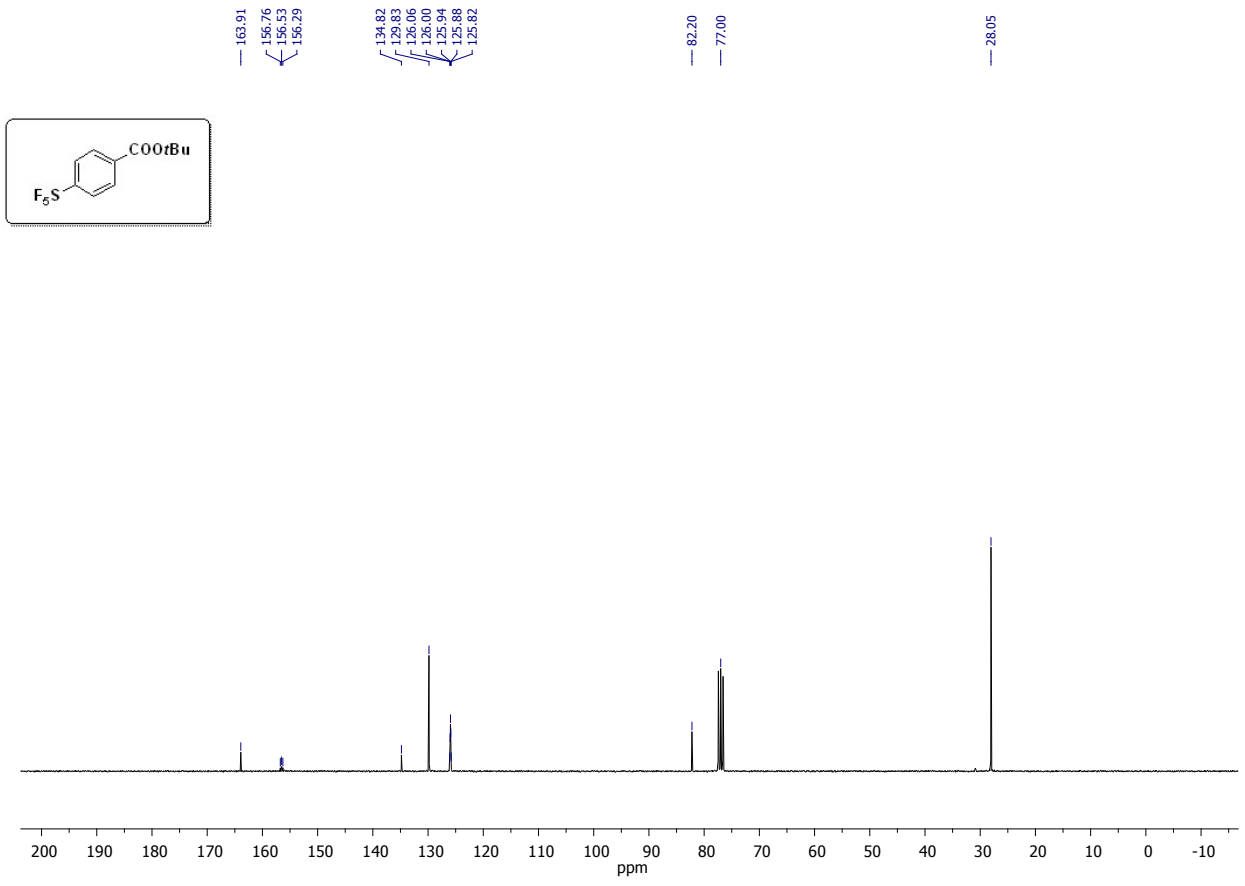
^{13}C-NMR (101 MHz, $CDCl_3$)



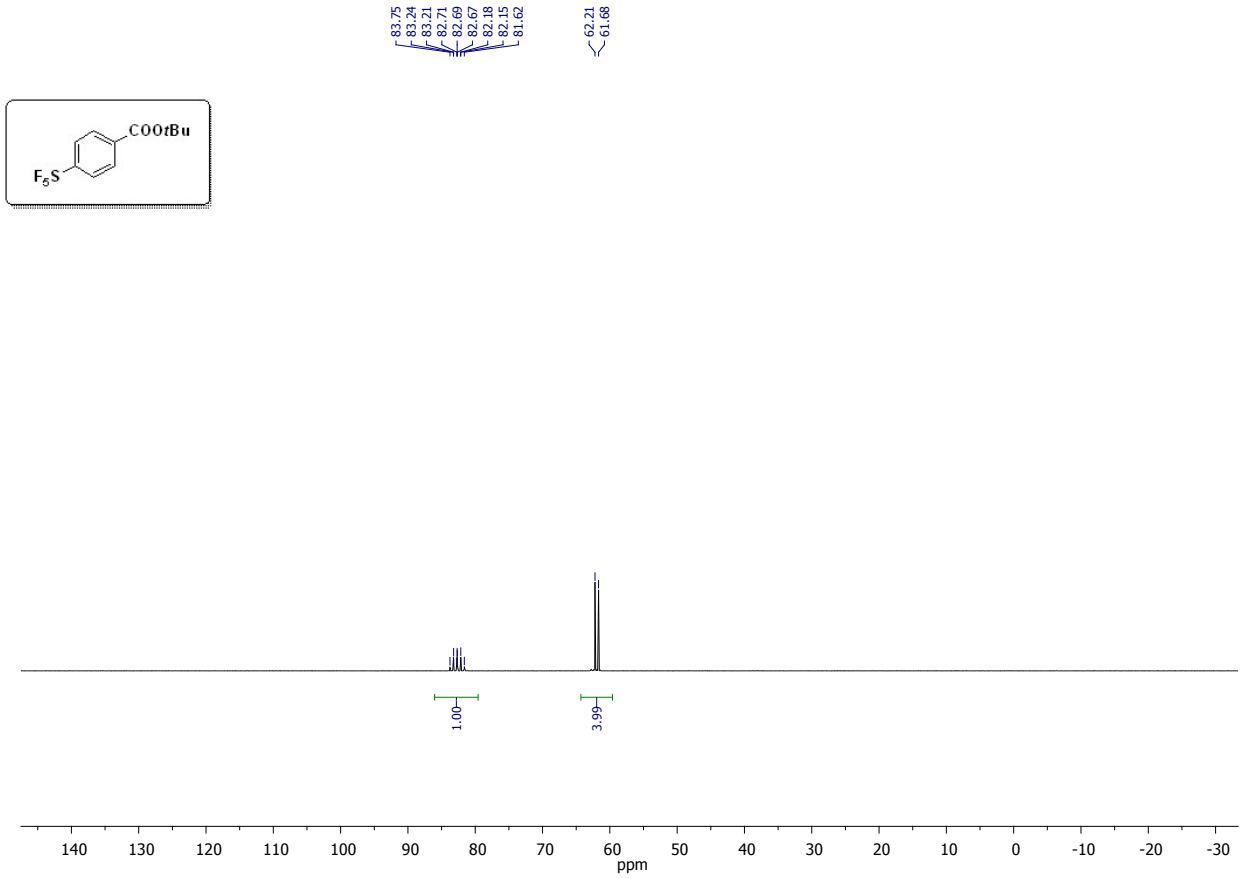
^{1}H-NMR (300 MHz, $CDCl_3$)



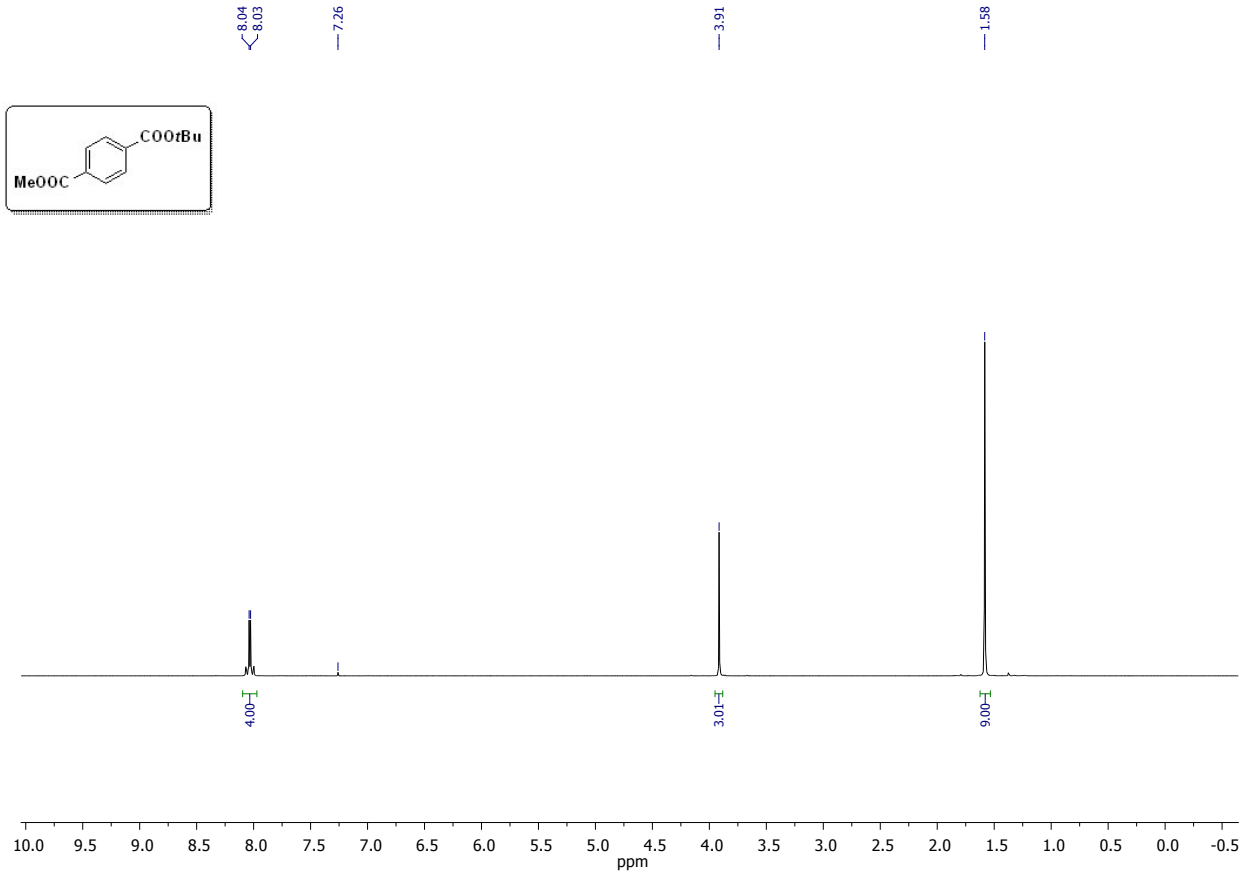
^{13}C-NMR (75 MHz, $CDCl_3$)



^{19}F-NMR (282 MHz, $CDCl_3$)



^{1}H-NMR (300 MHz, $CDCl_3$)



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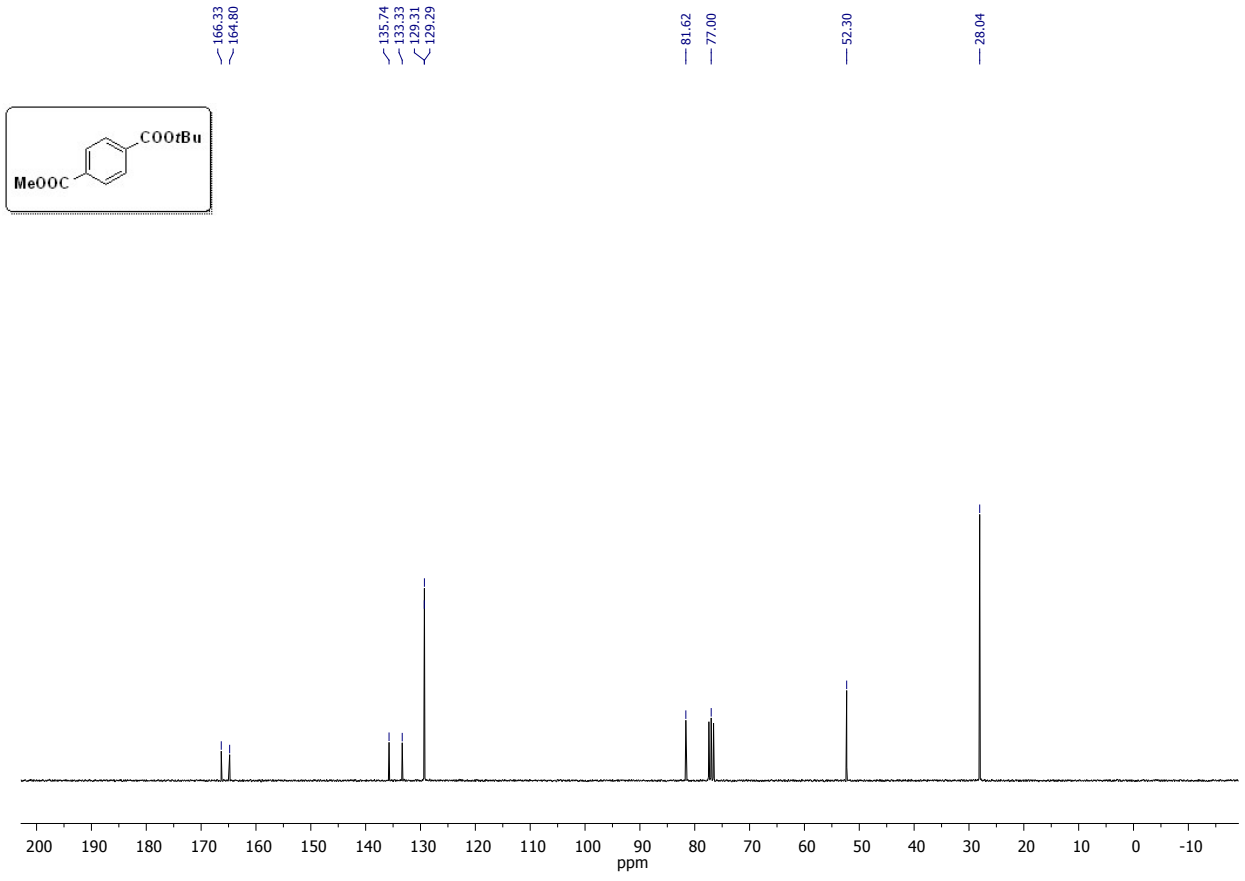

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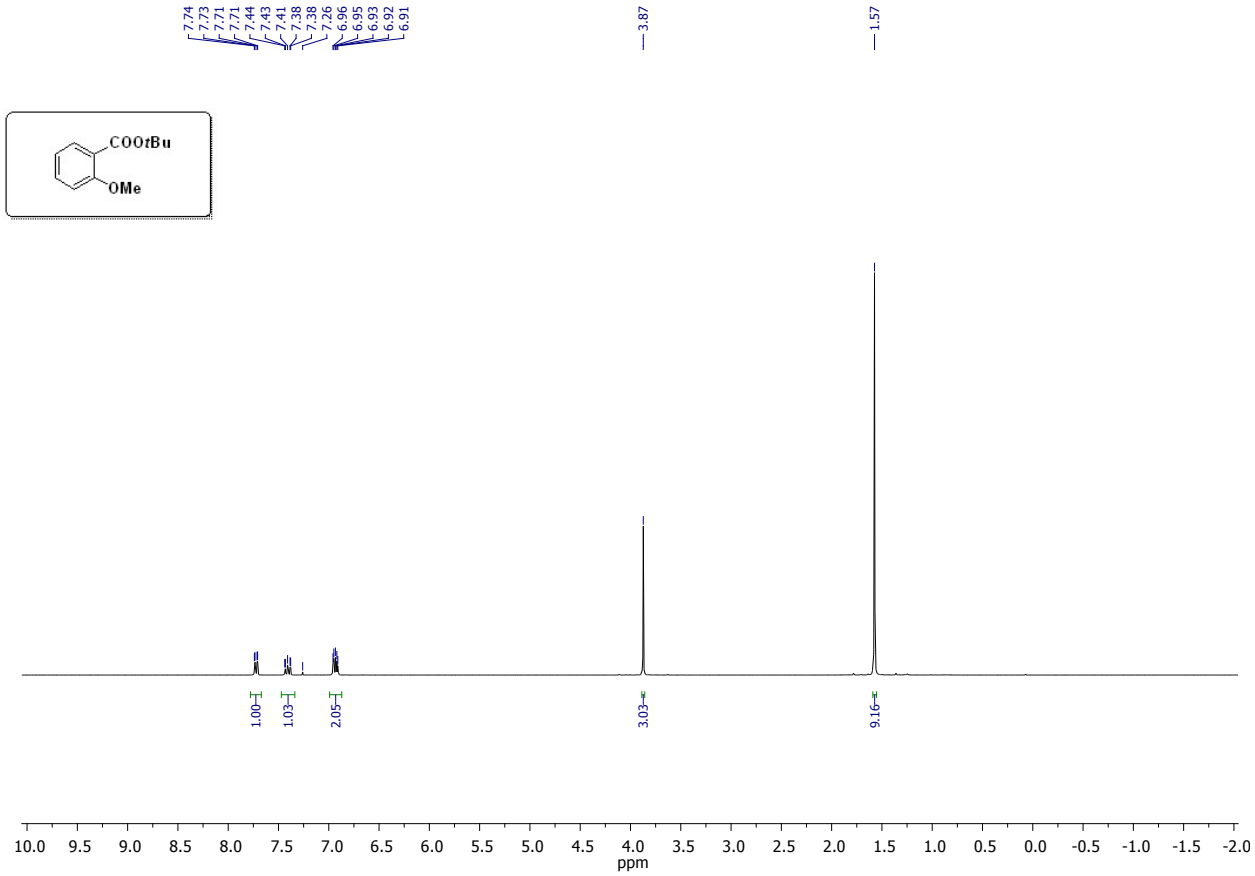
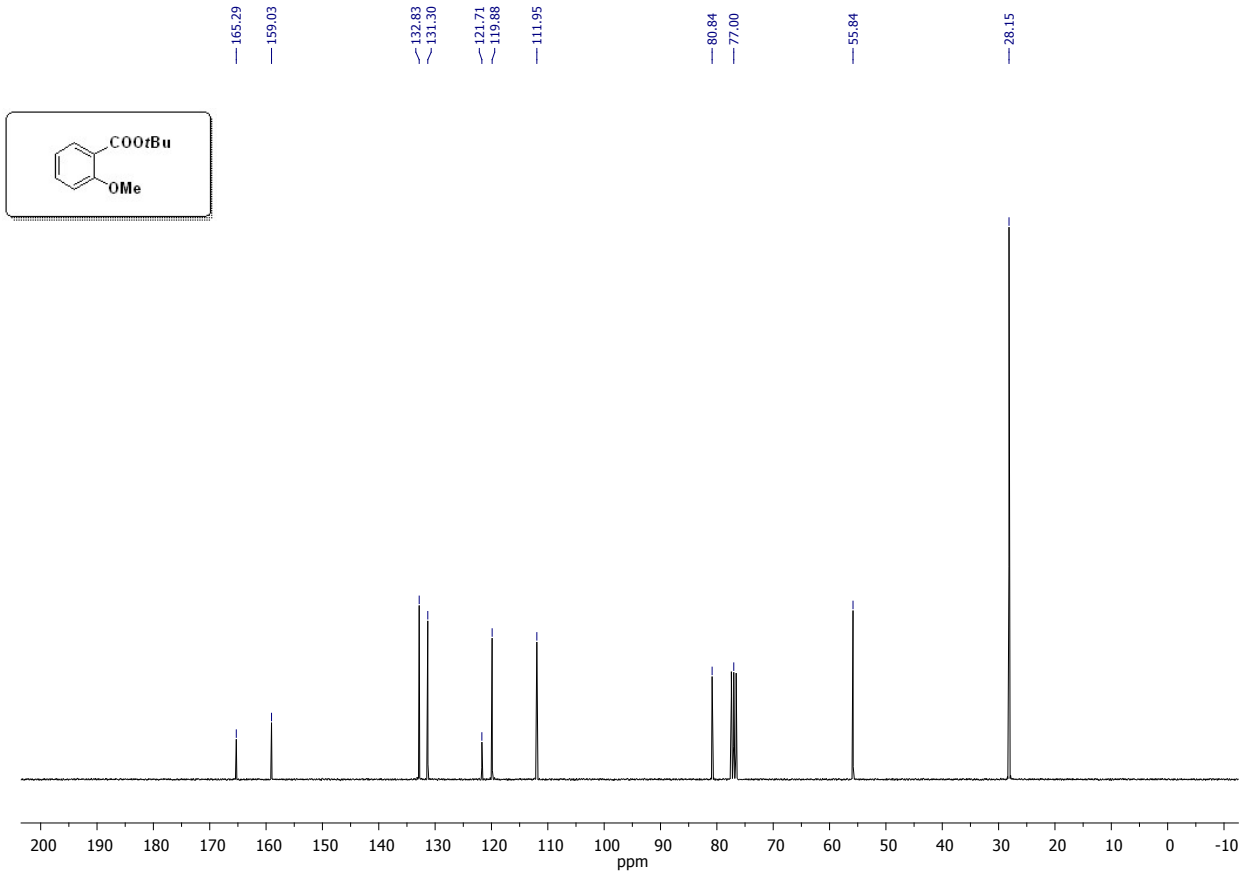
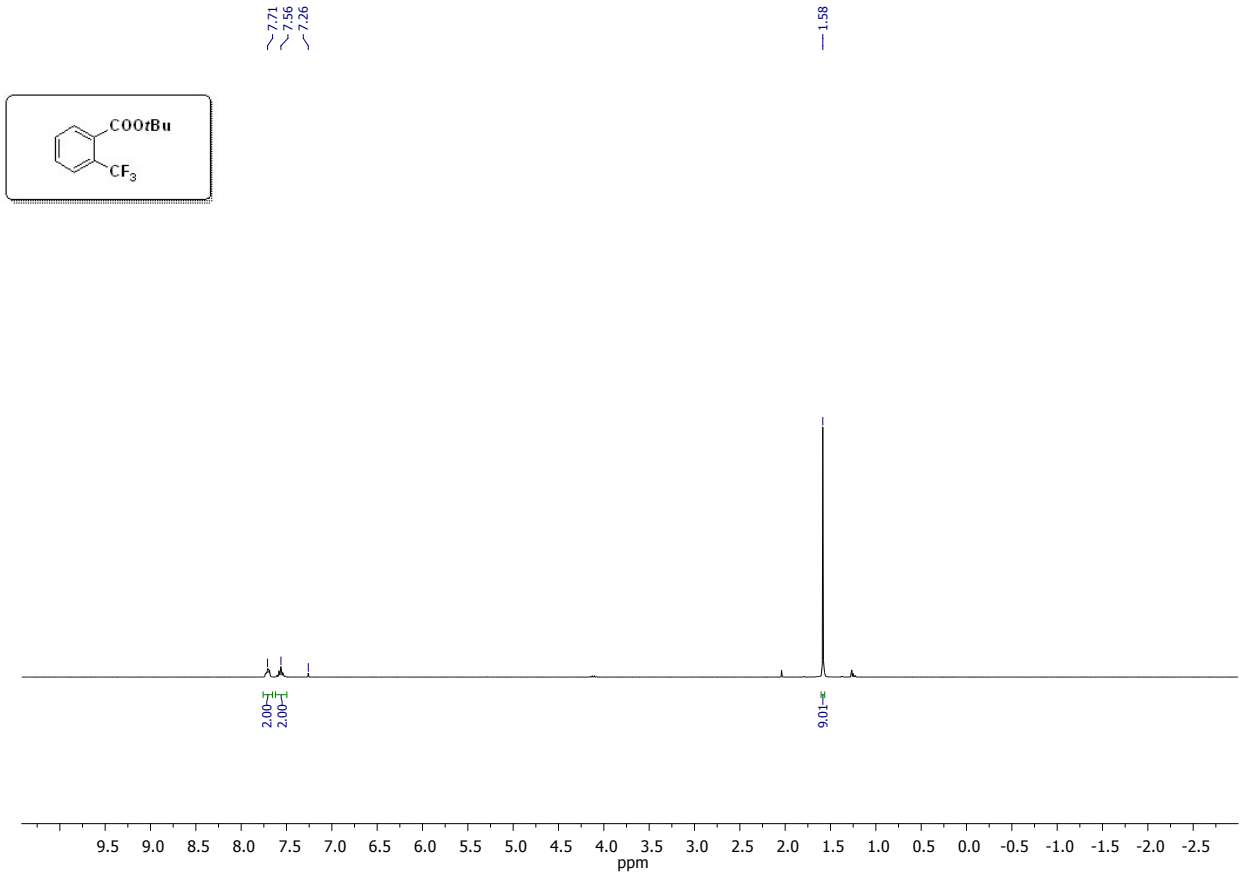


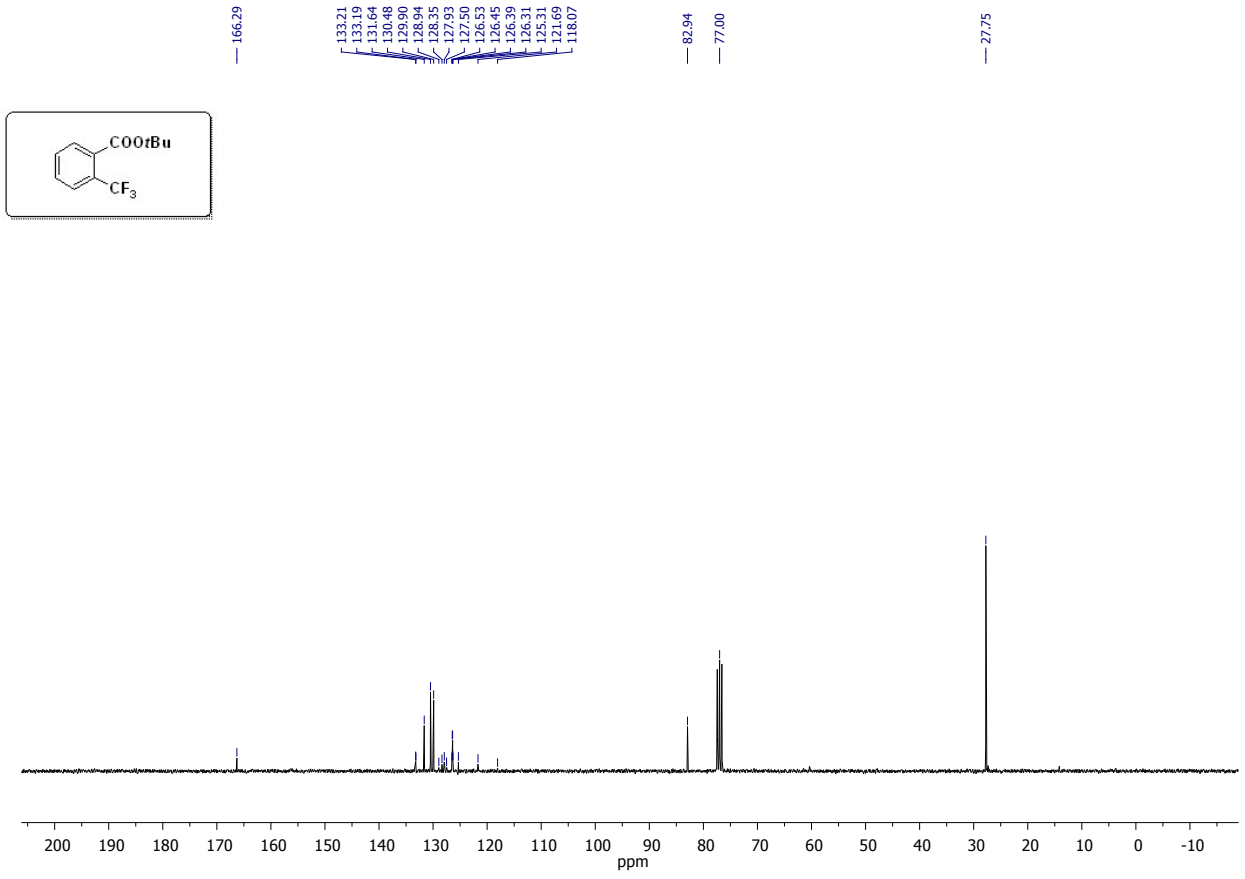
^{13}C-NMR (75 MHz, $CDCl_3$)



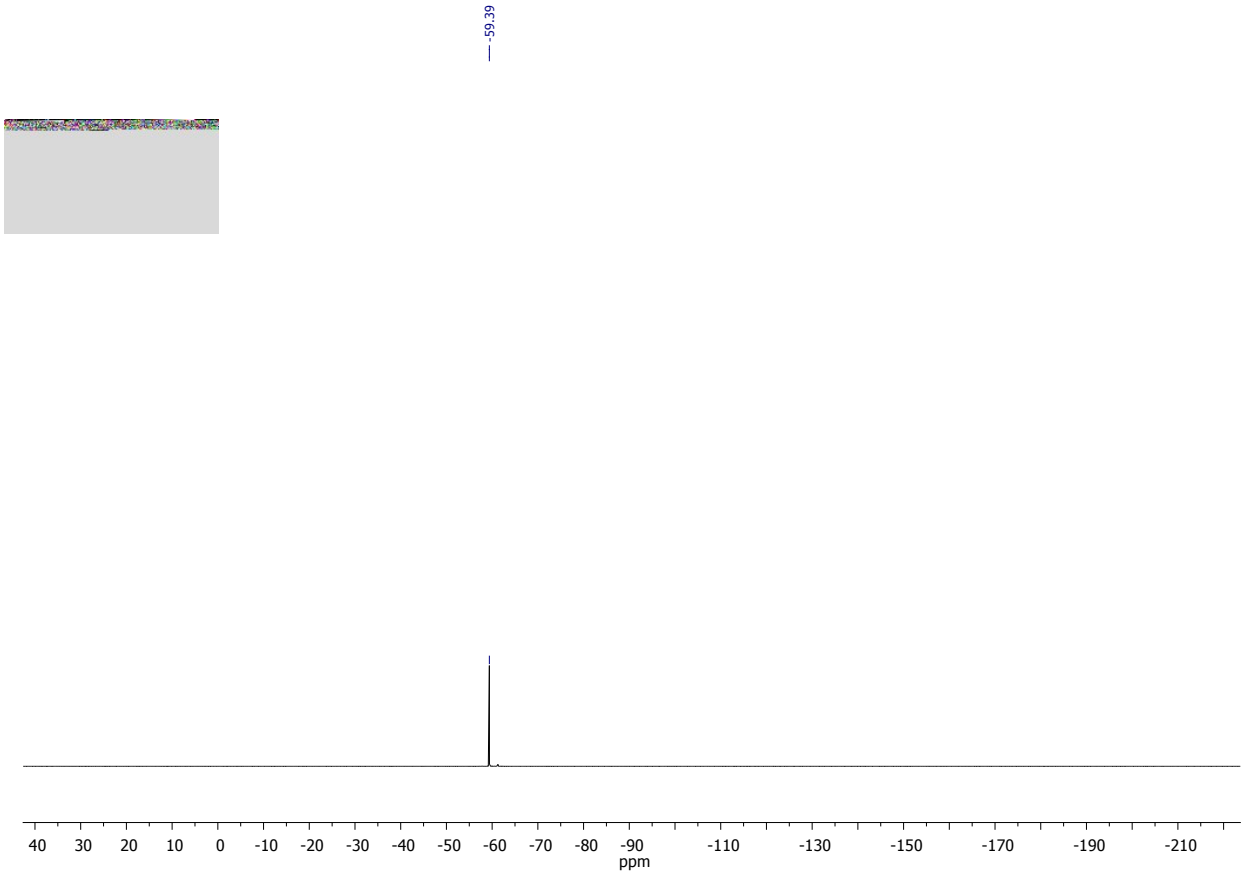
^{1}H-NMR (300 MHz, $CDCl_3$)



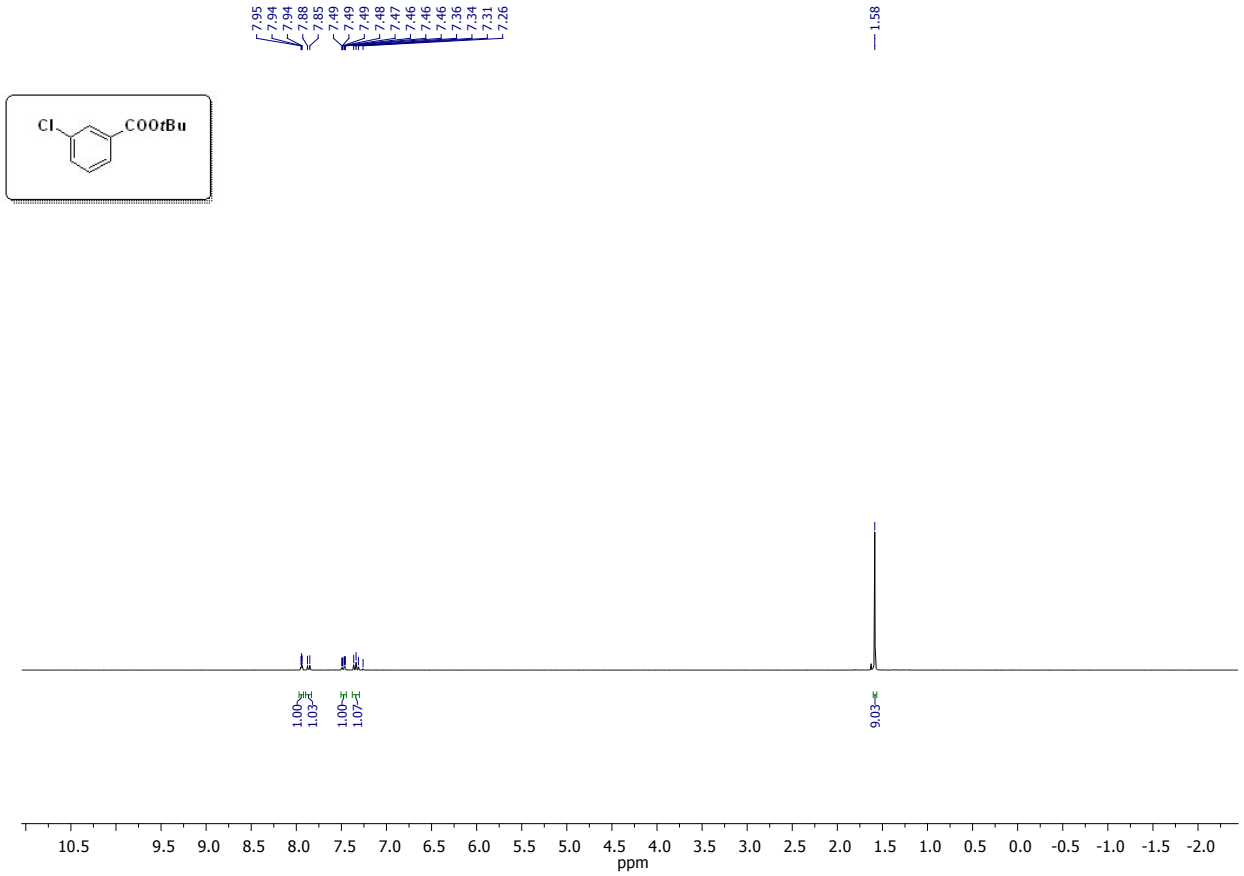
^{13}C-NMR (75 MHz, $CDCl_3$)



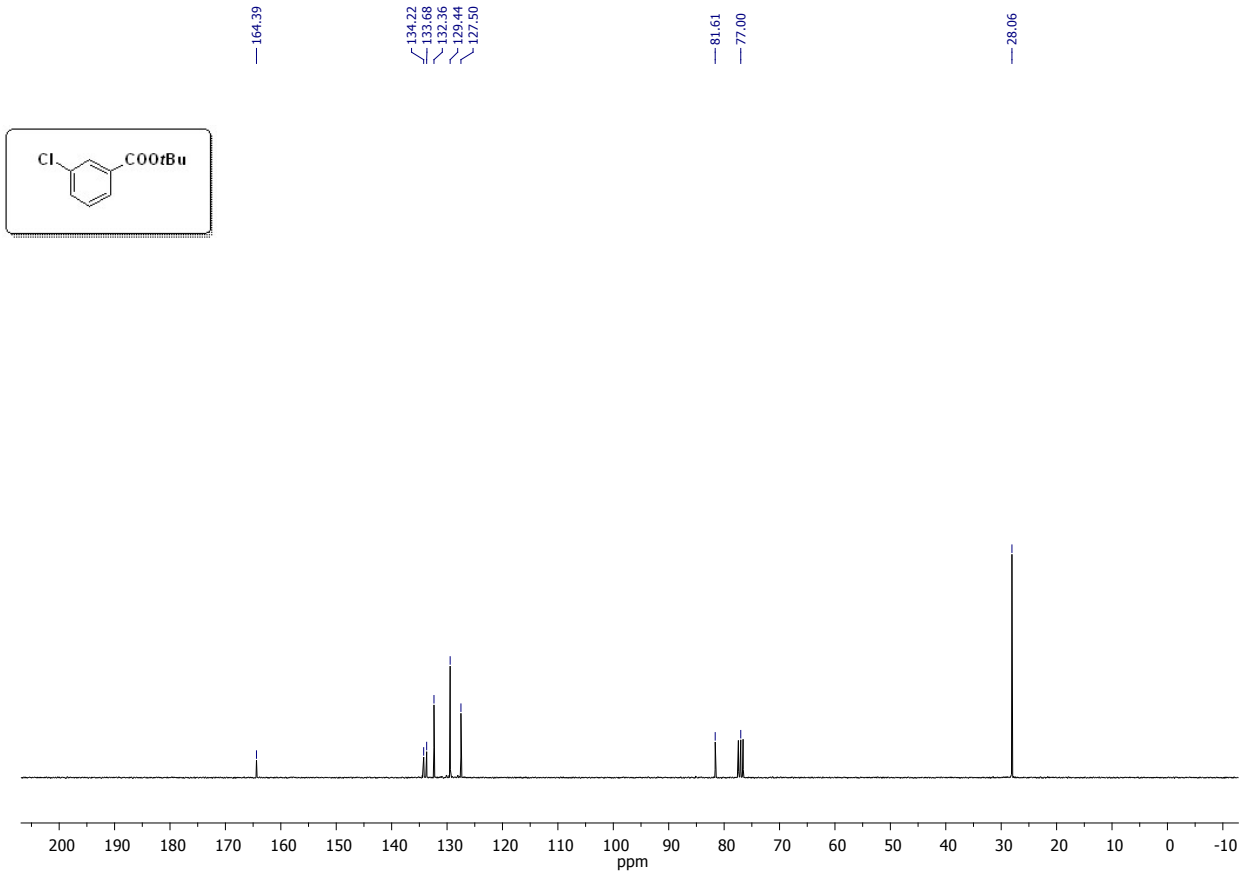
^{19}F-NMR (282 MHz, $CDCl_3$)



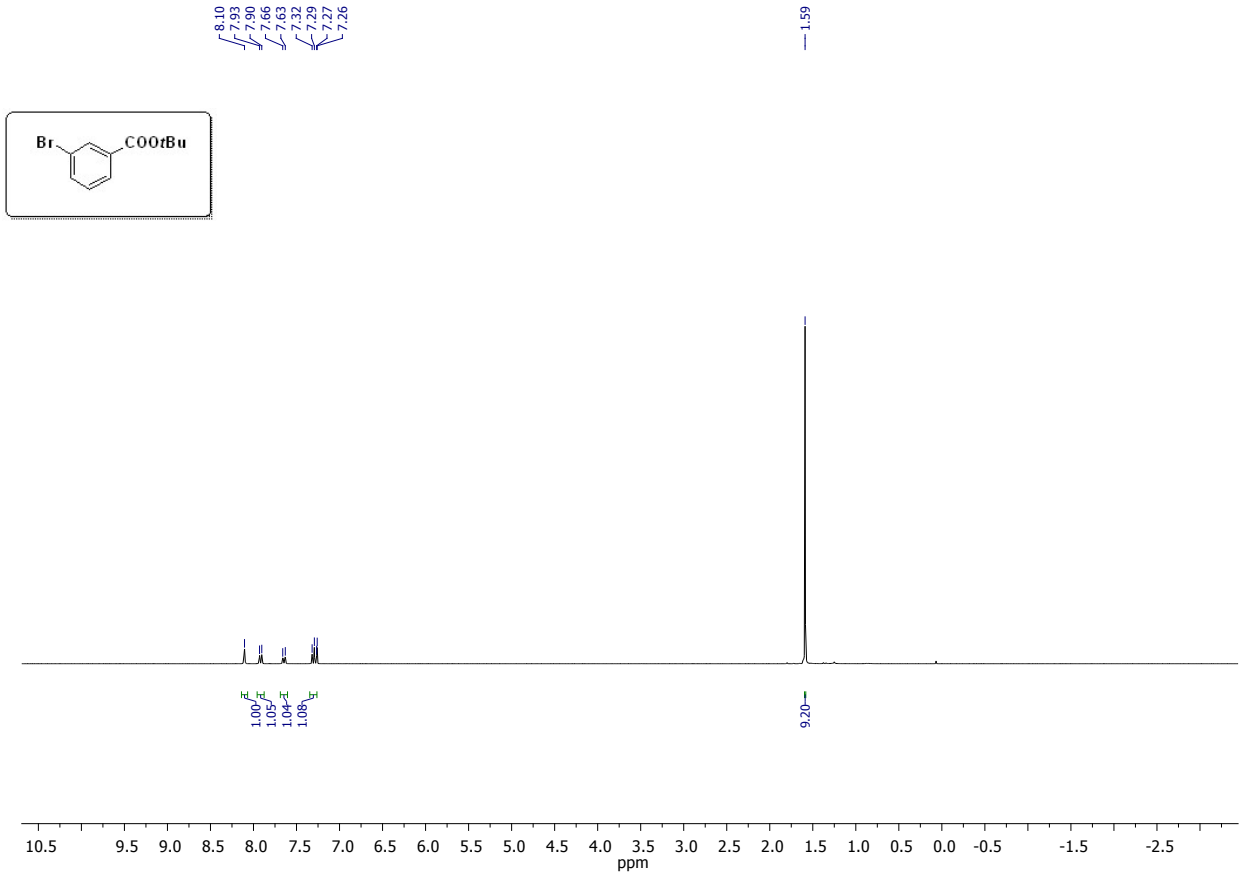
^{1}H-NMR (300 MHz, $CDCl_3$)



^{13}C-NMR (75 MHz, $CDCl_3$)



^{1}H-NMR (300 MHz, $CDCl_3$)



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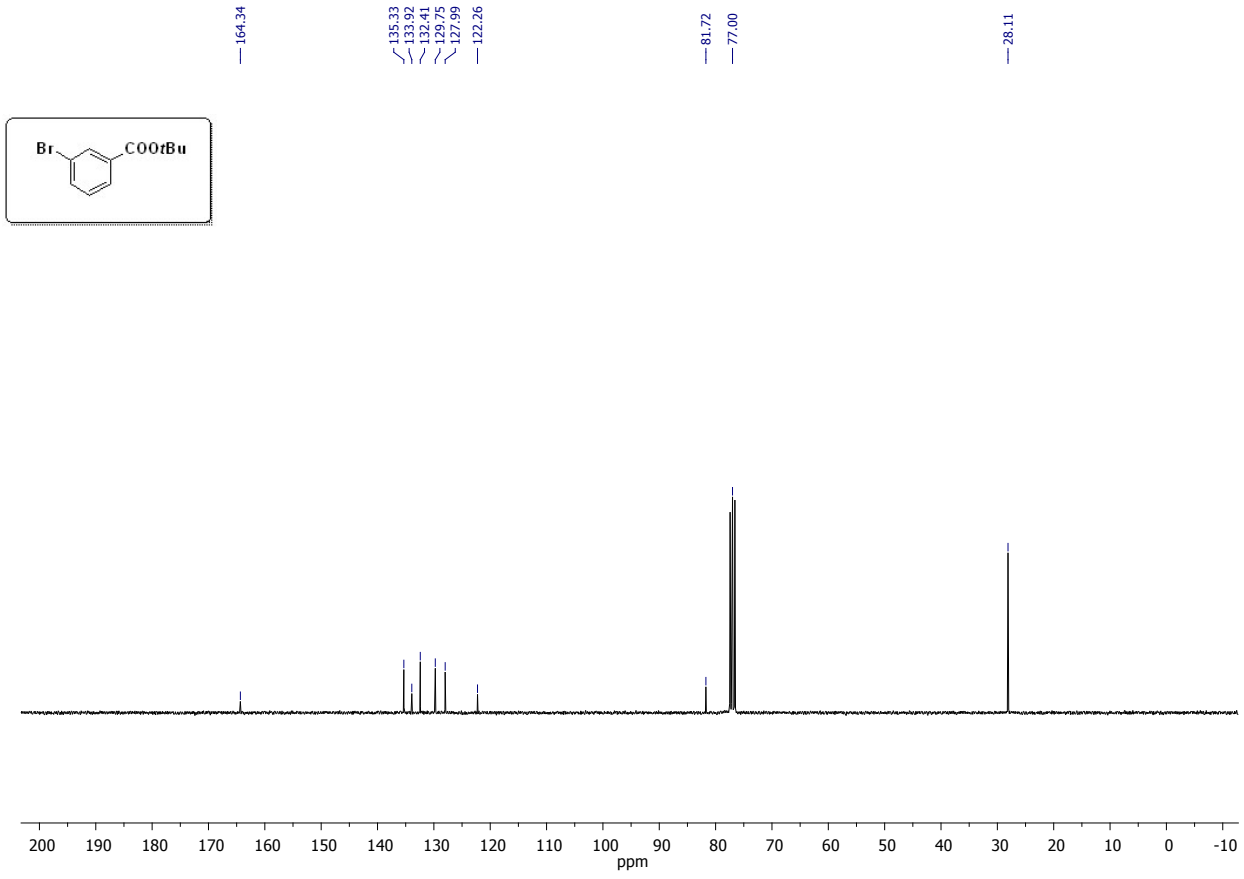
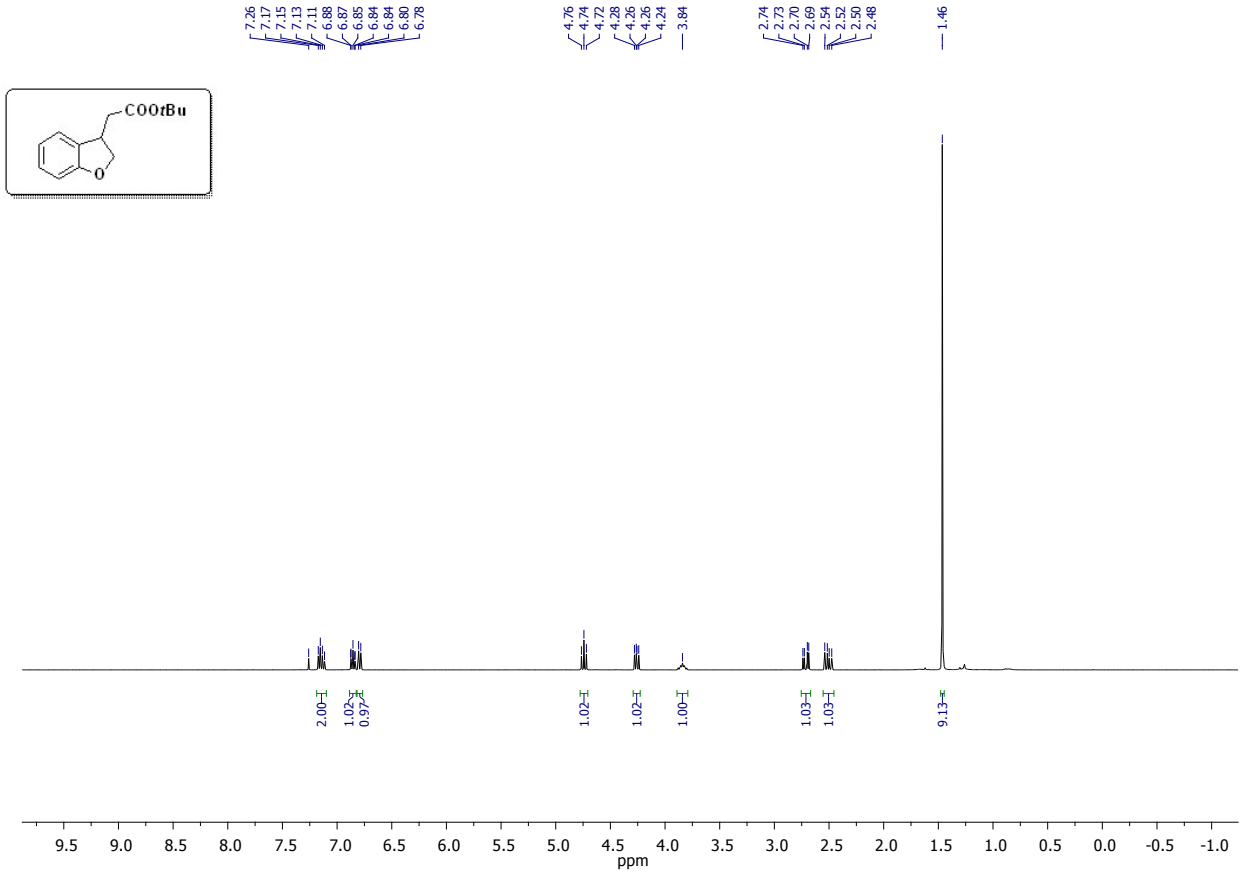
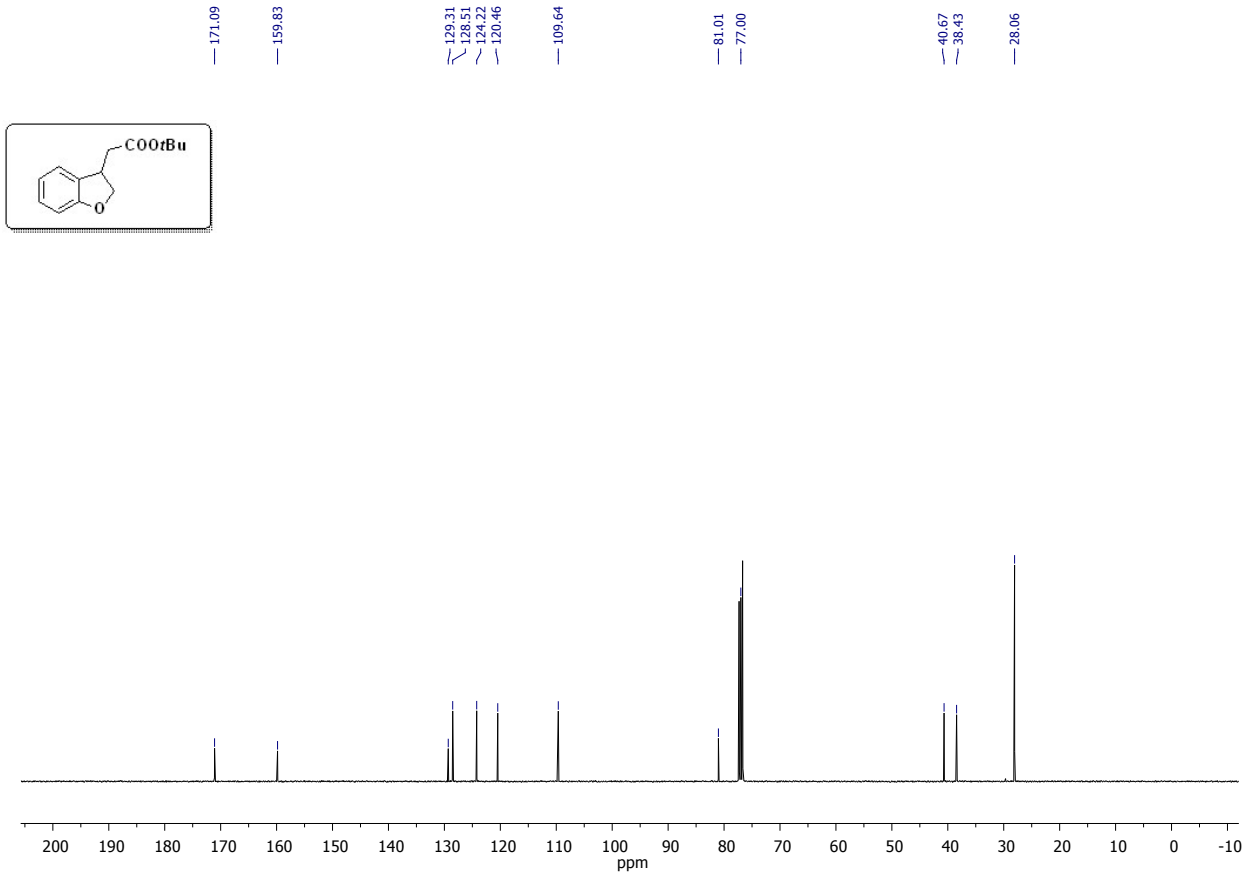


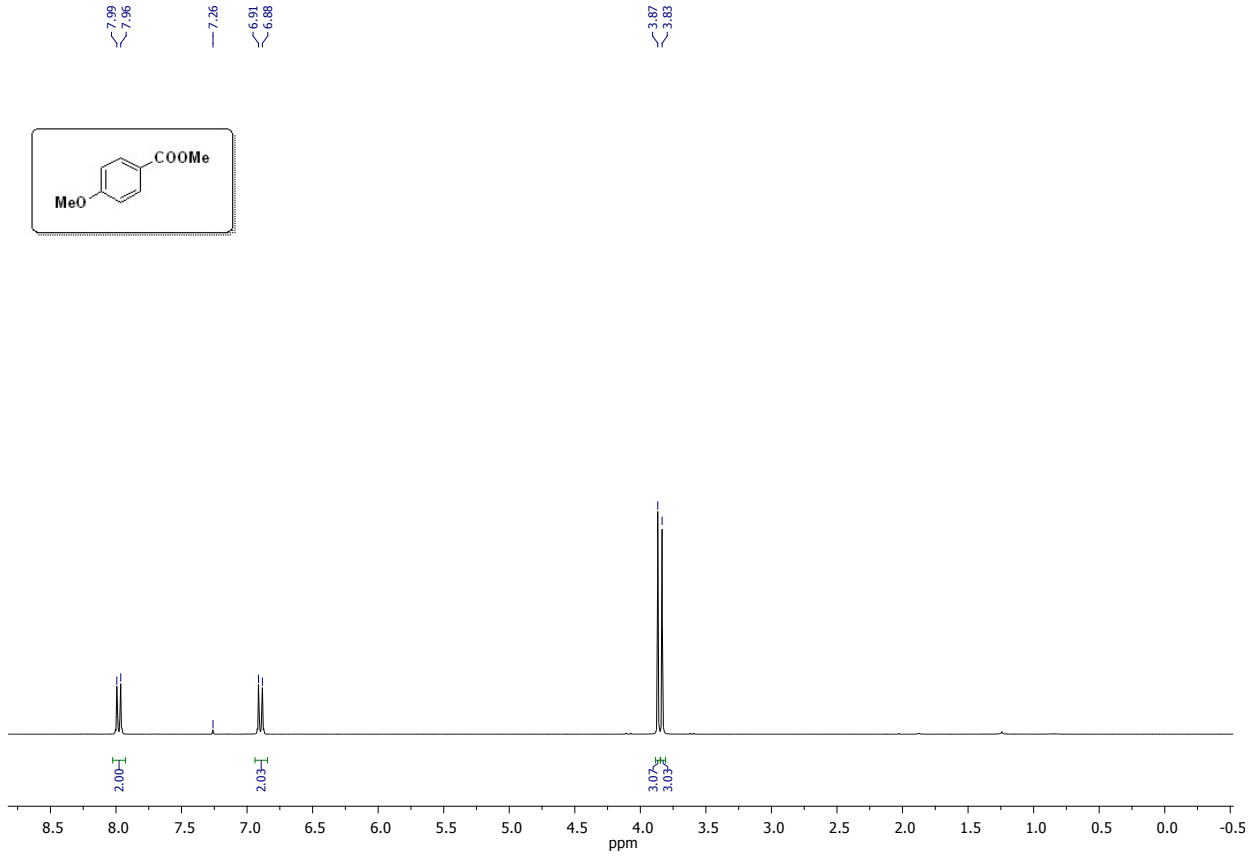
^{1}H-NMR (400 MHz, $CDCl_3$)



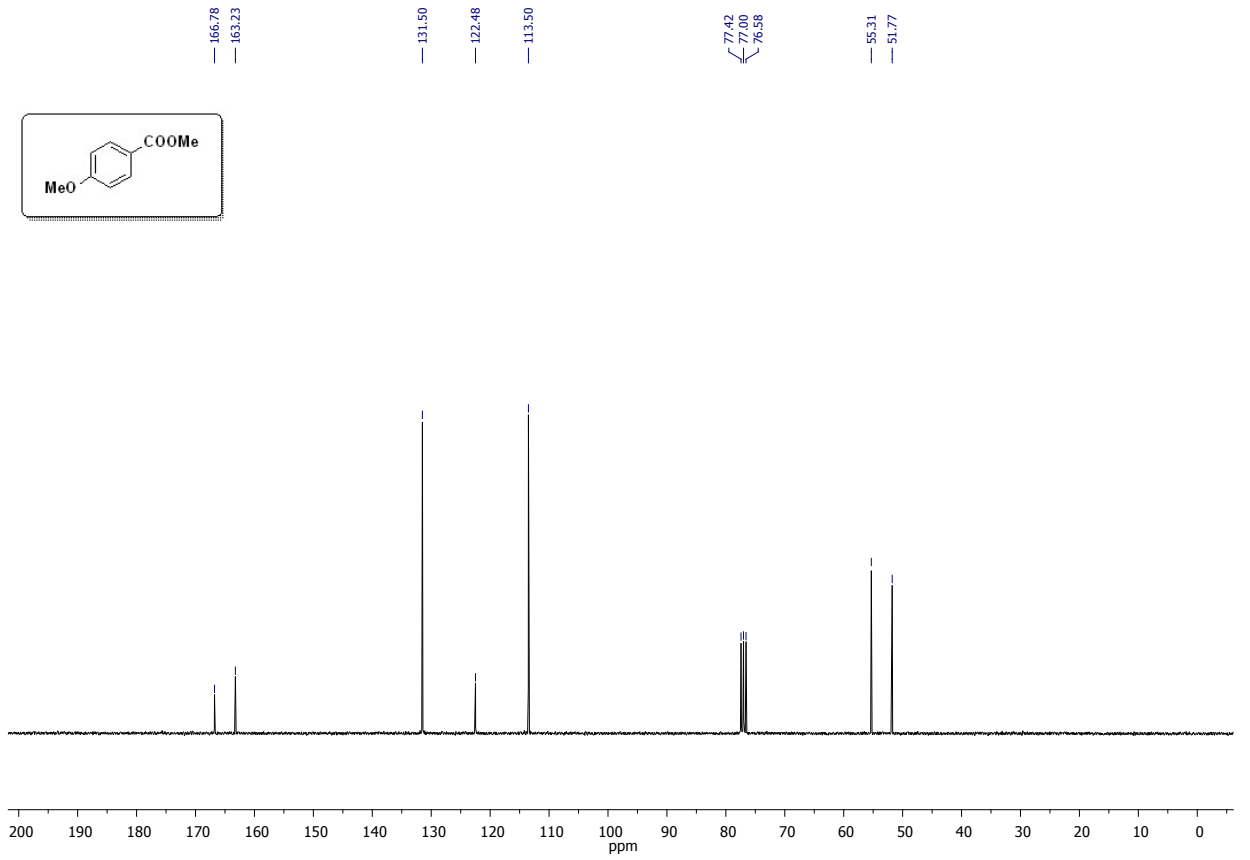
^{13}C-NMR (101 MHz, $CDCl_3$)



^{1}H-NMR (300 MHz, $CDCl_3$)



^{13}C-NMR (75 MHz, $CDCl_3$)



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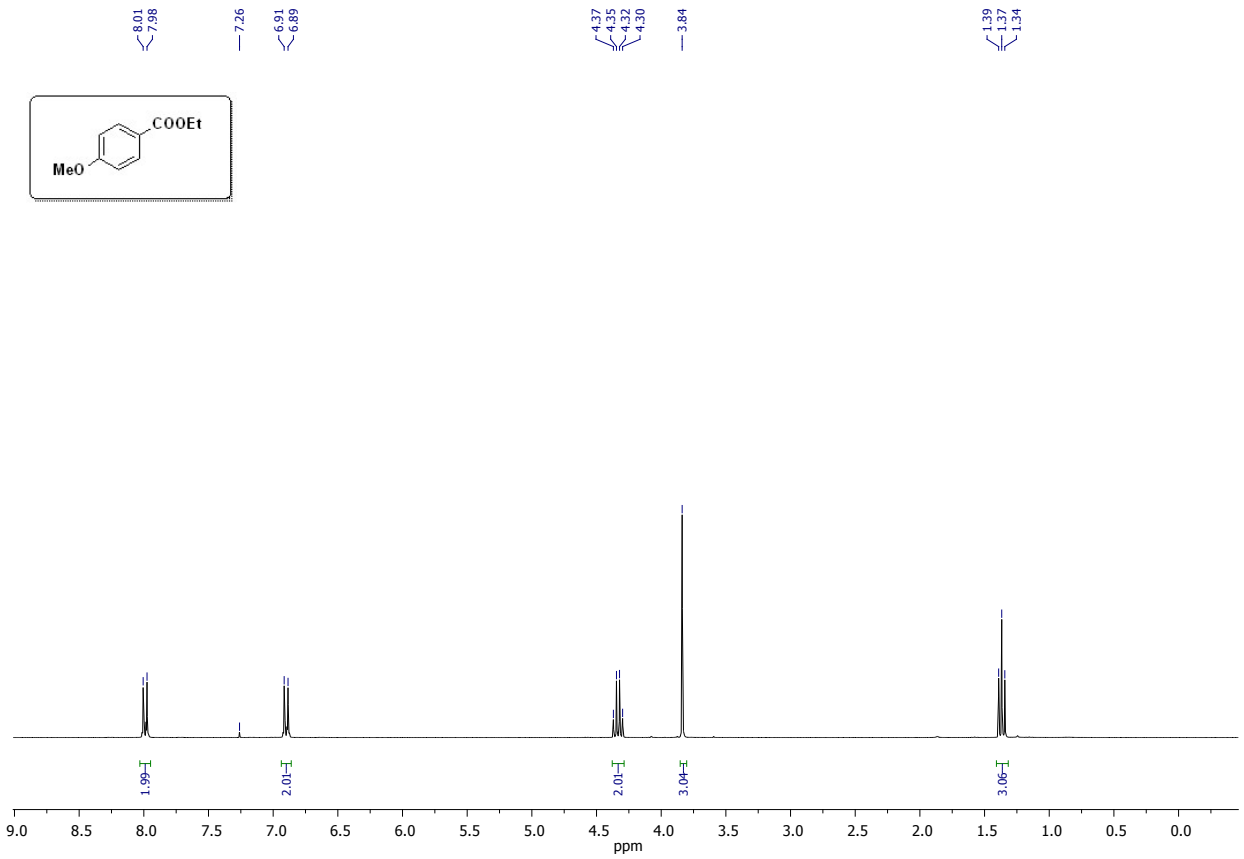

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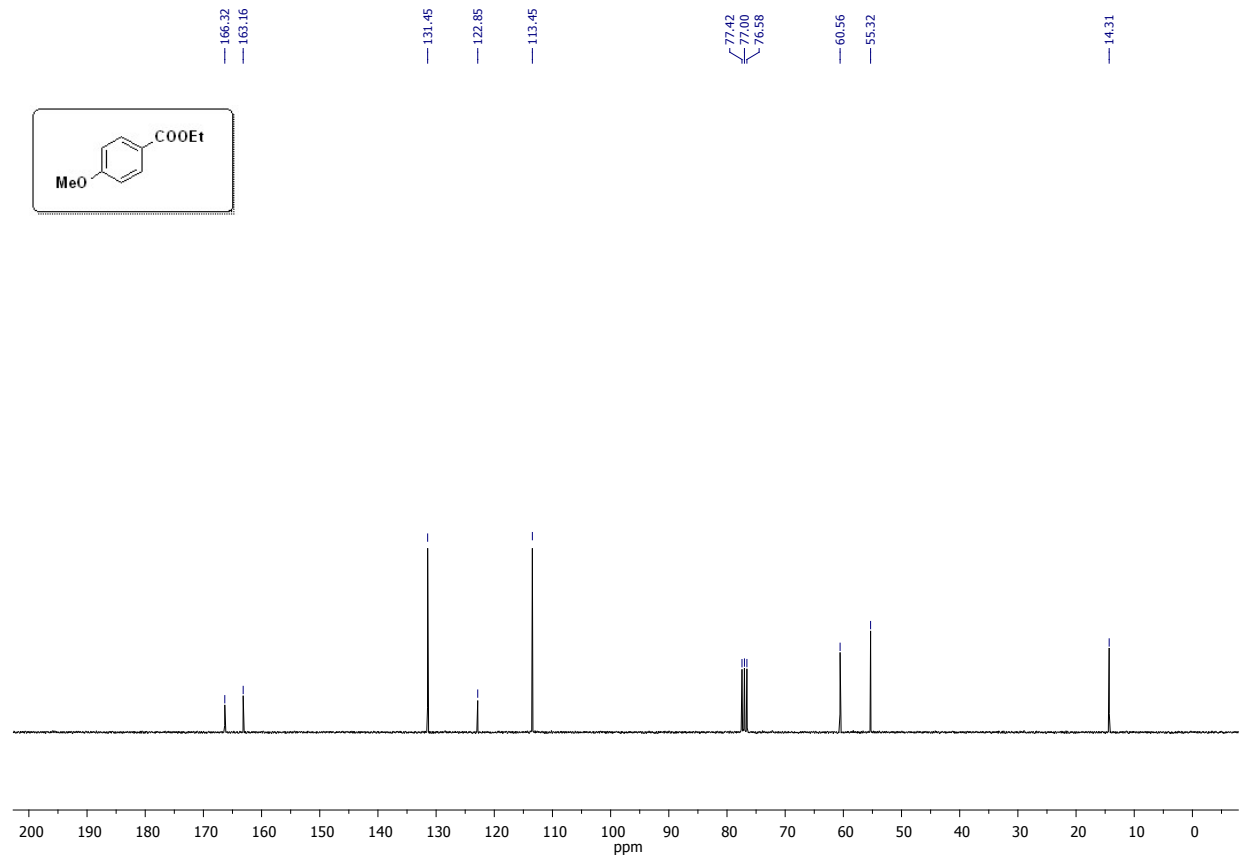

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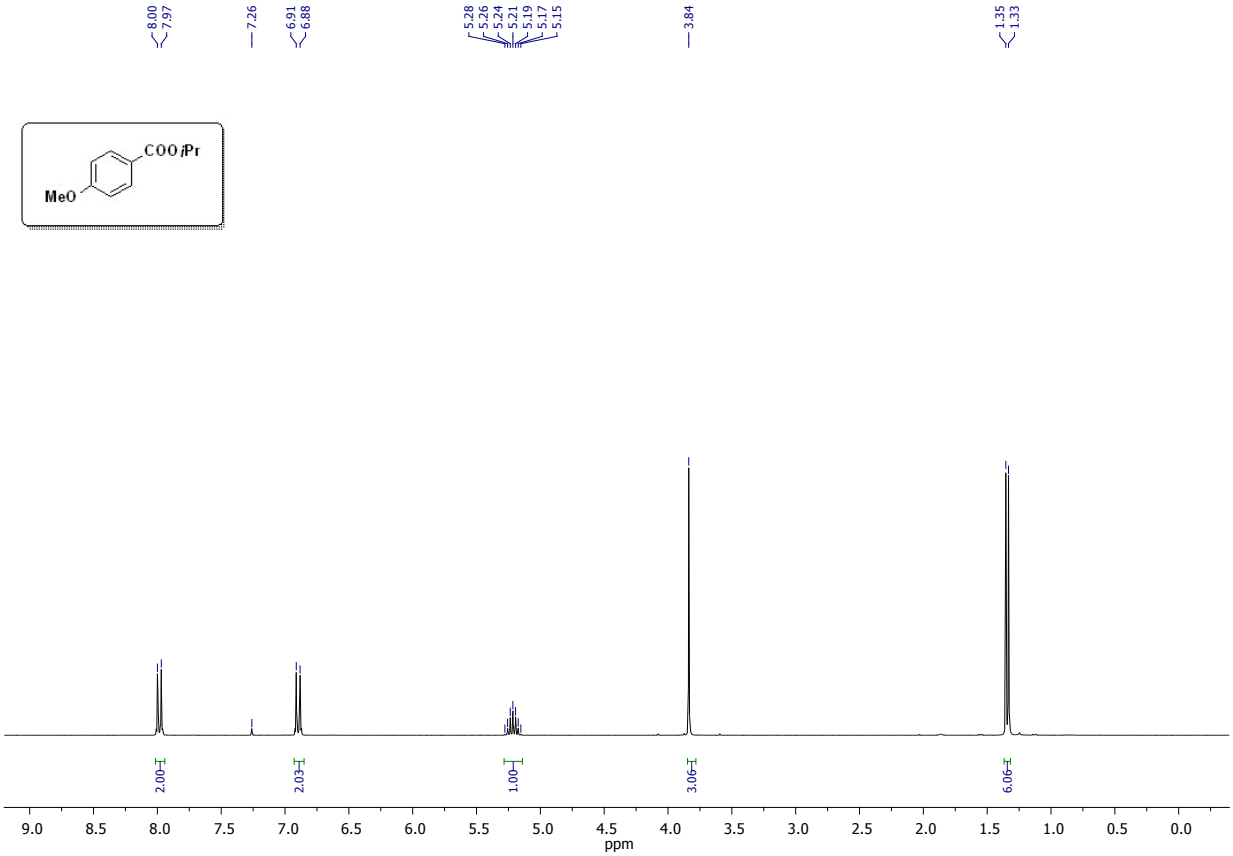

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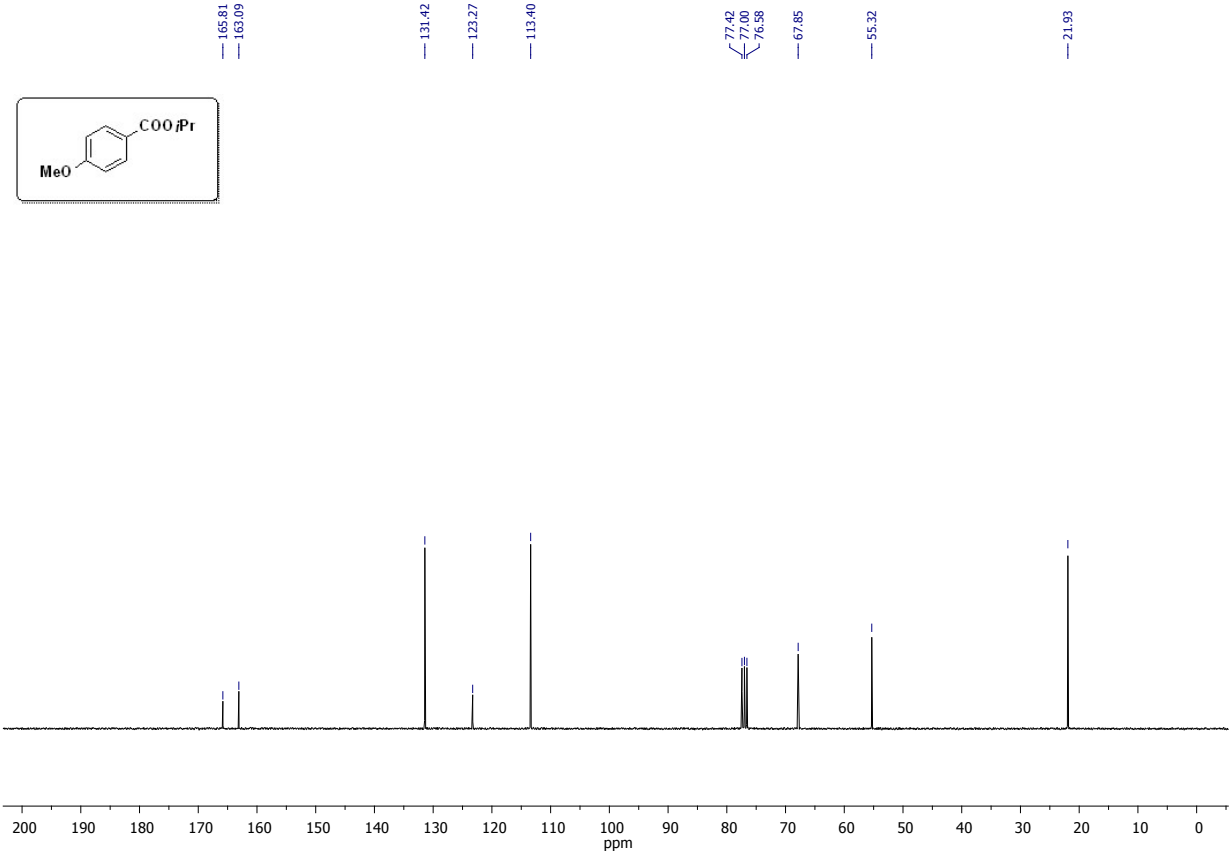

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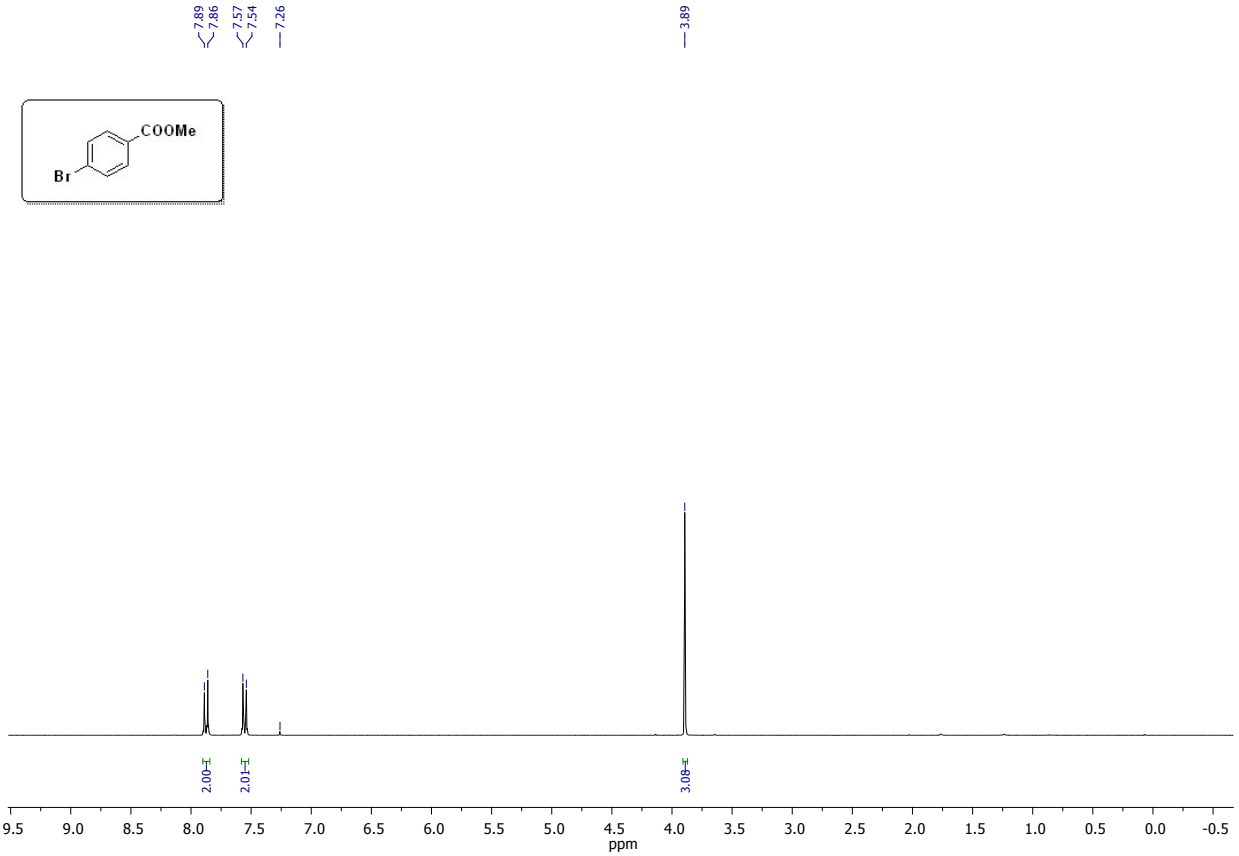

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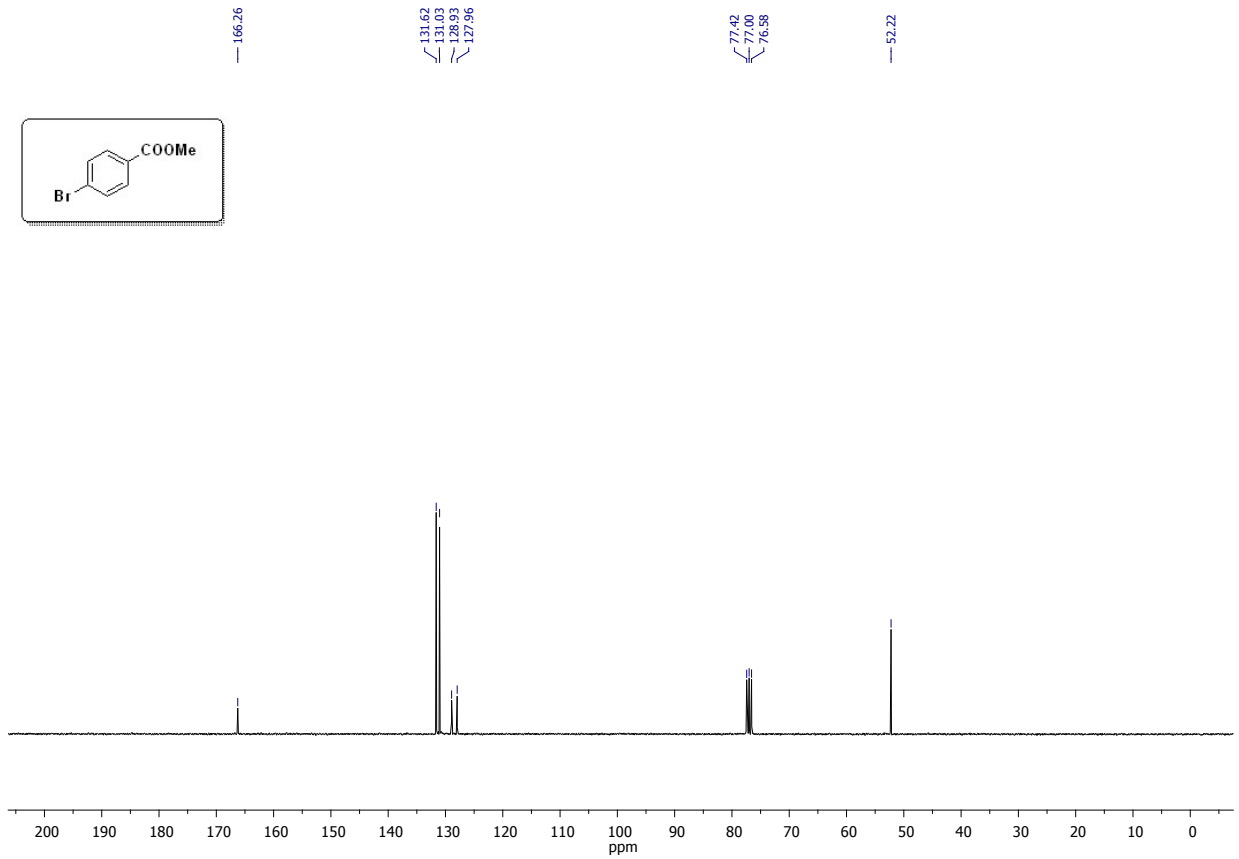

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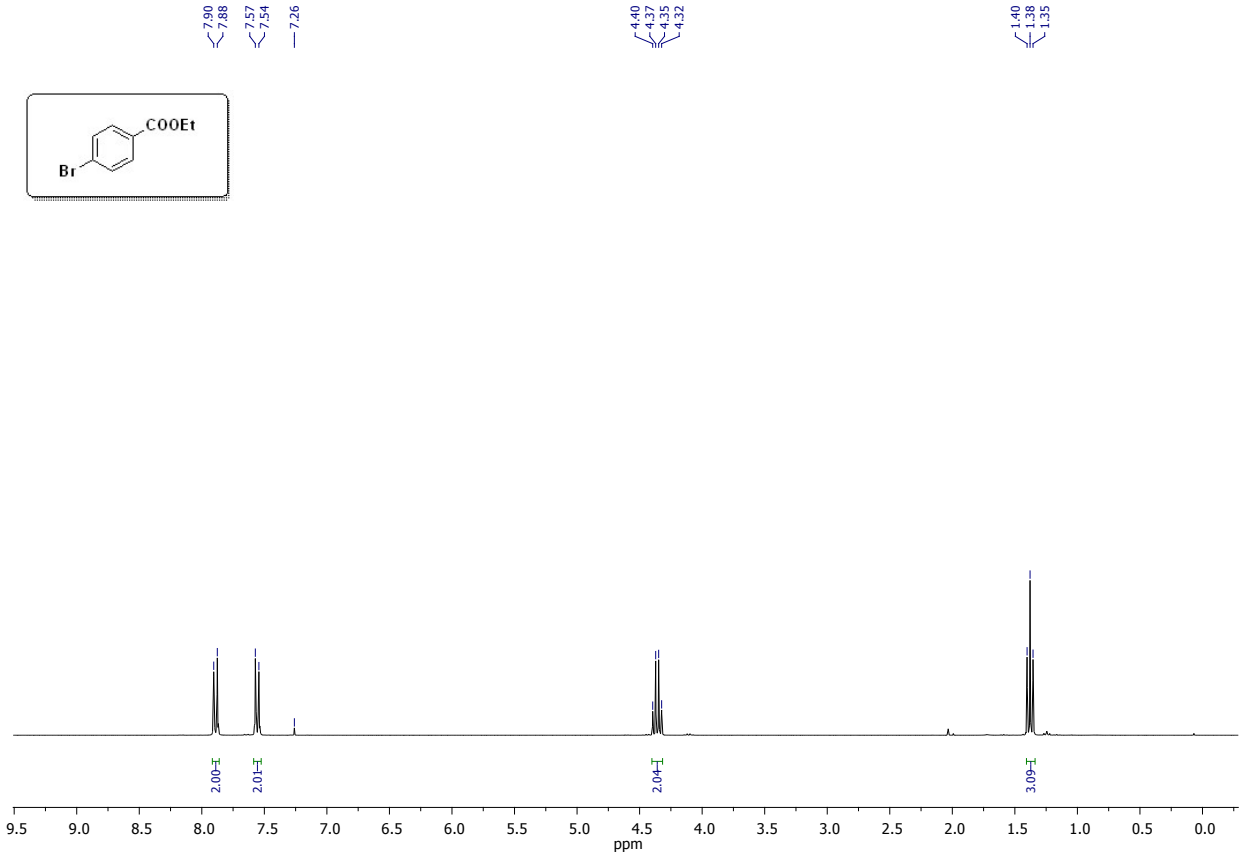

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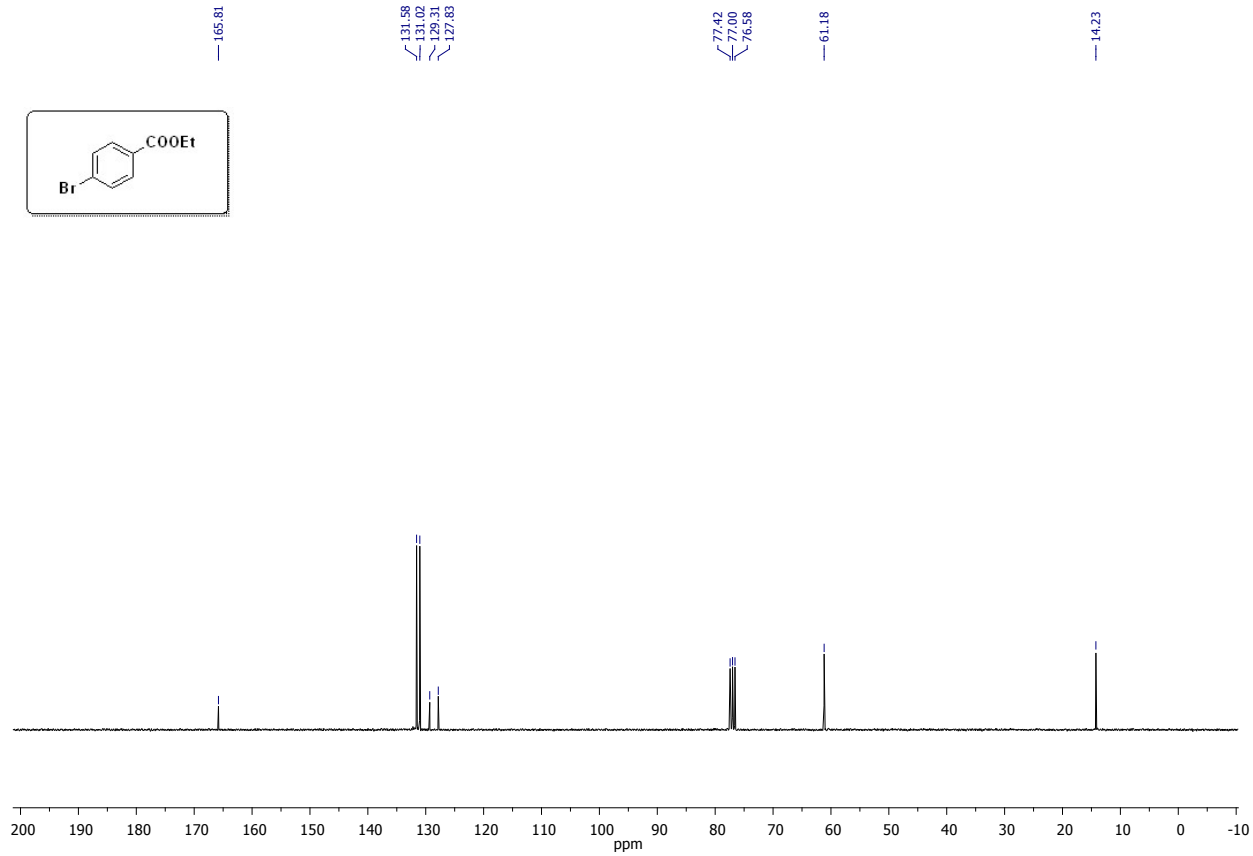
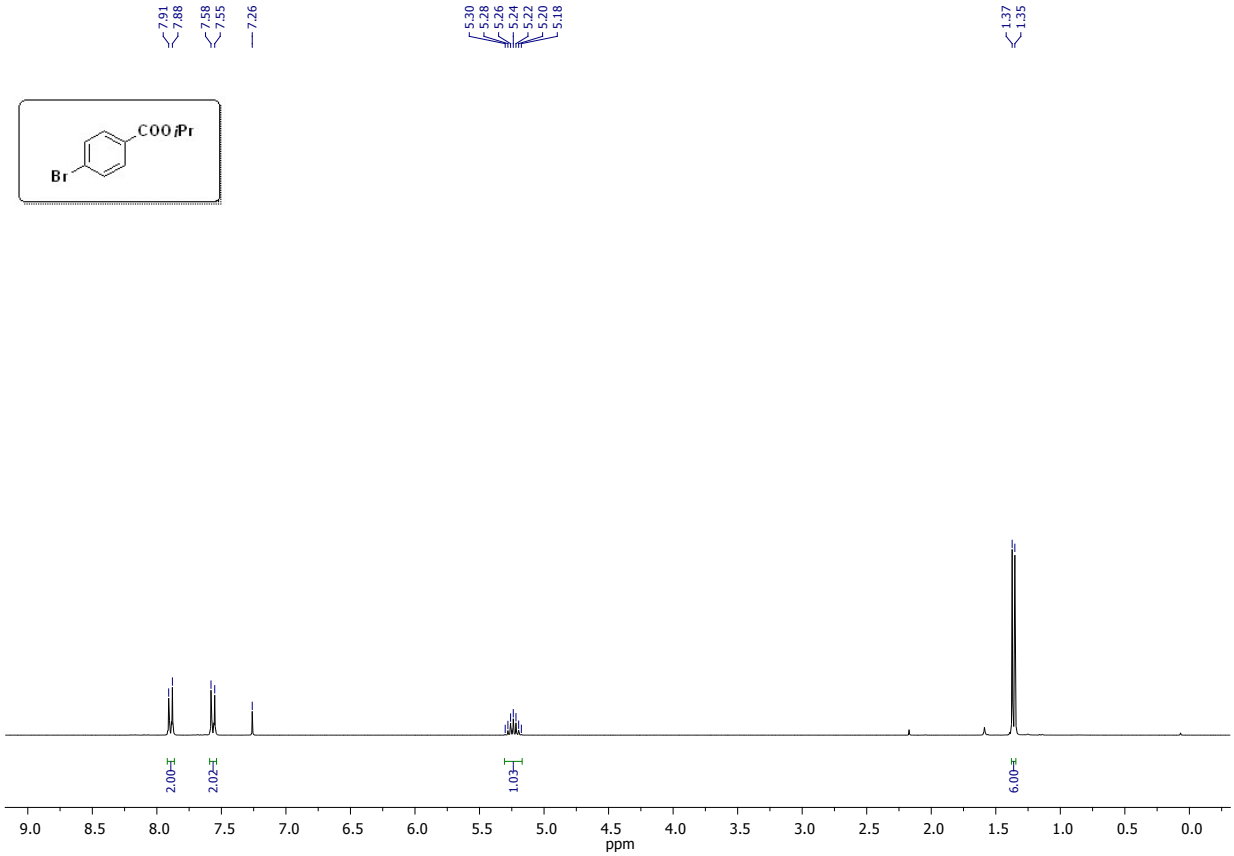


^{1}H-NMR (300 MHz, $CDCl_3$)



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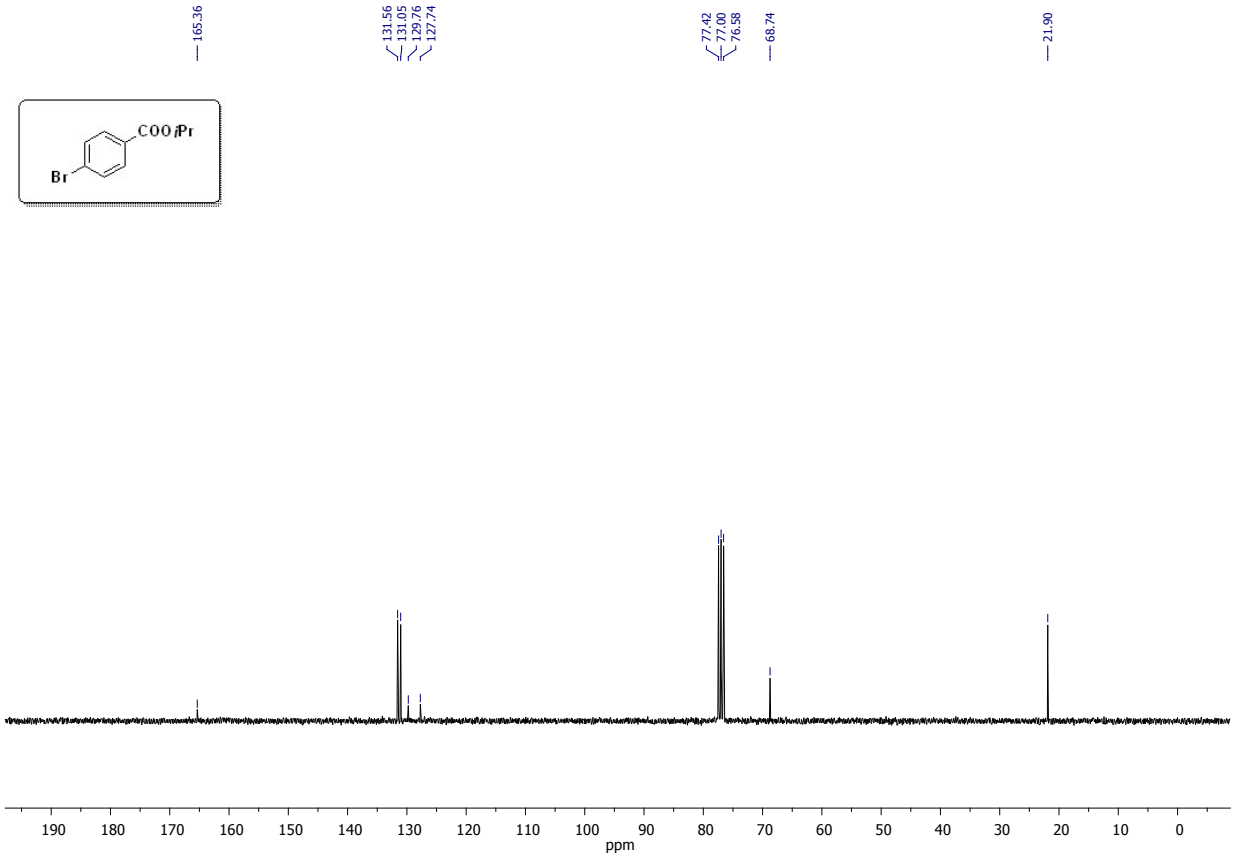

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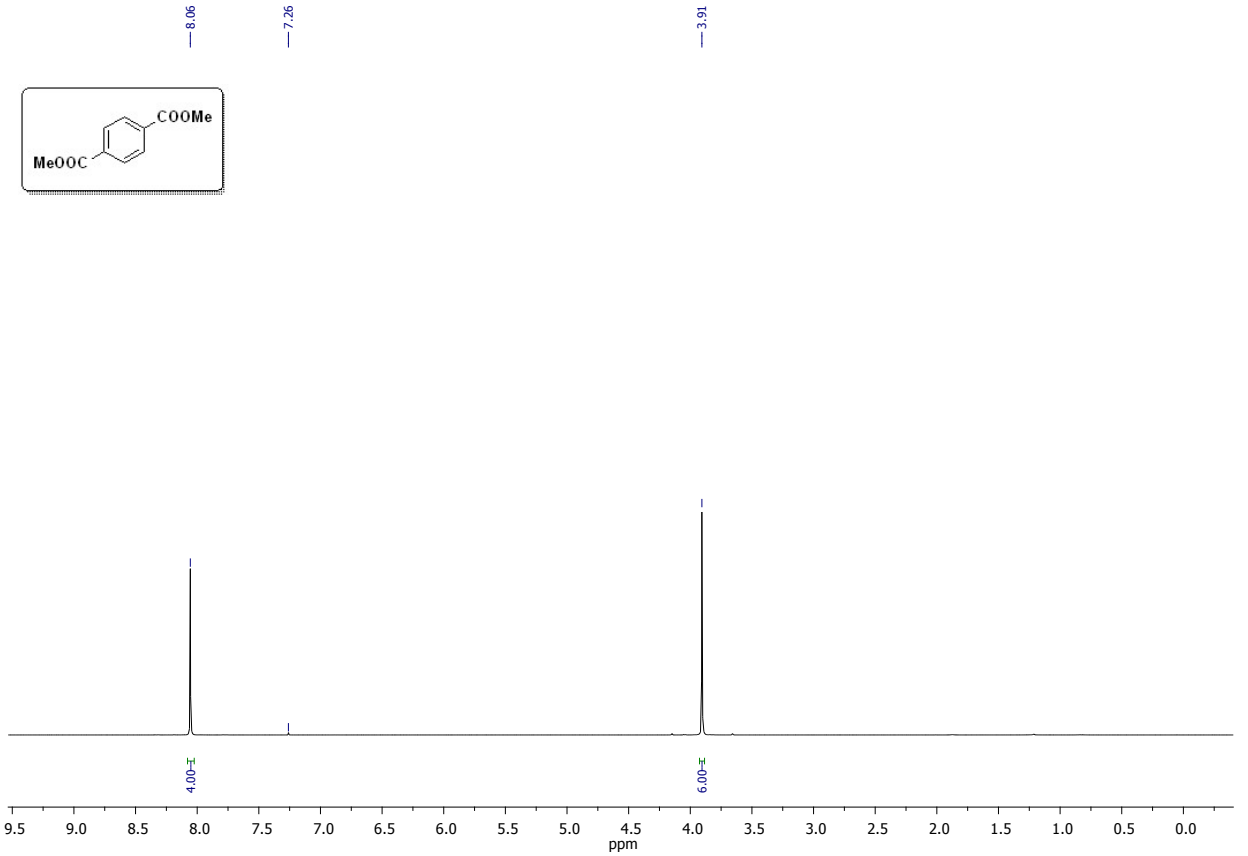
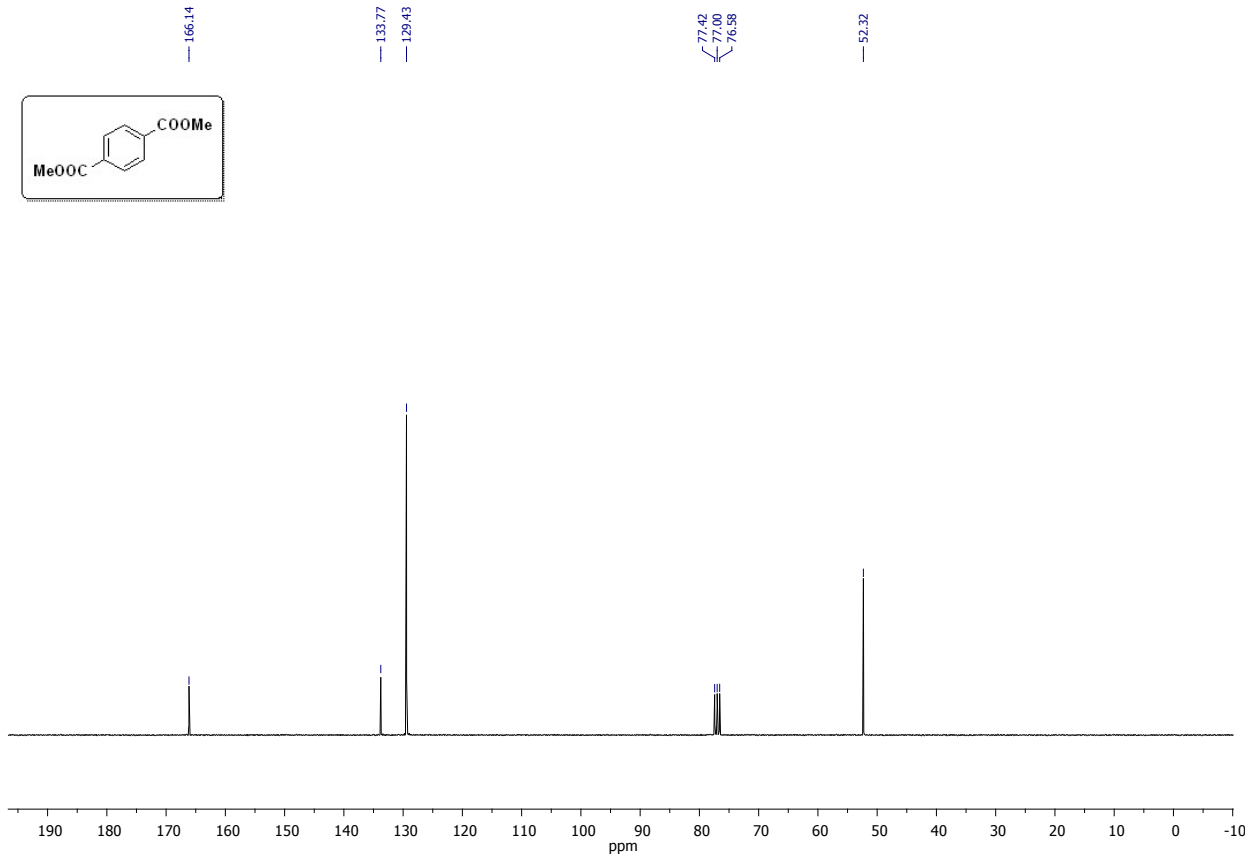


^{13}C-NMR (75 MHz, $CDCl_3$)



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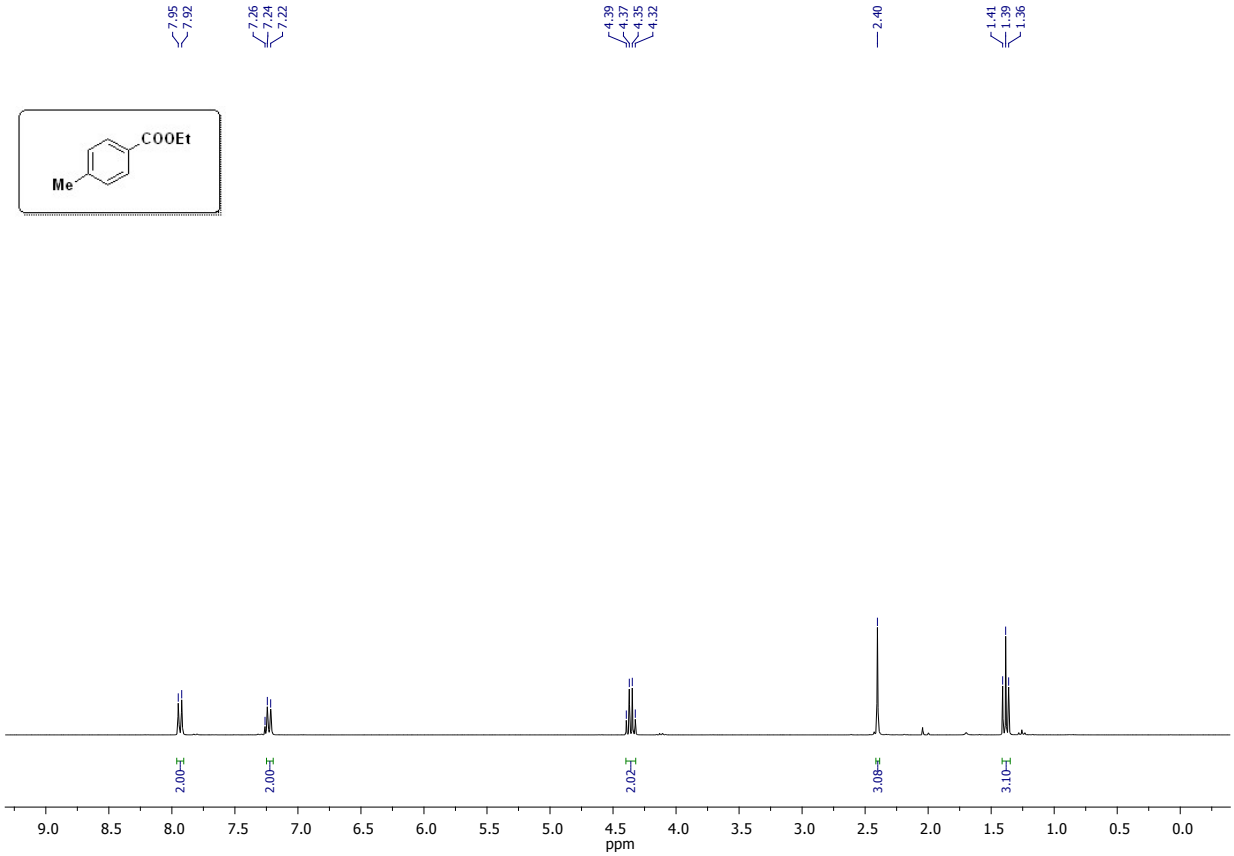

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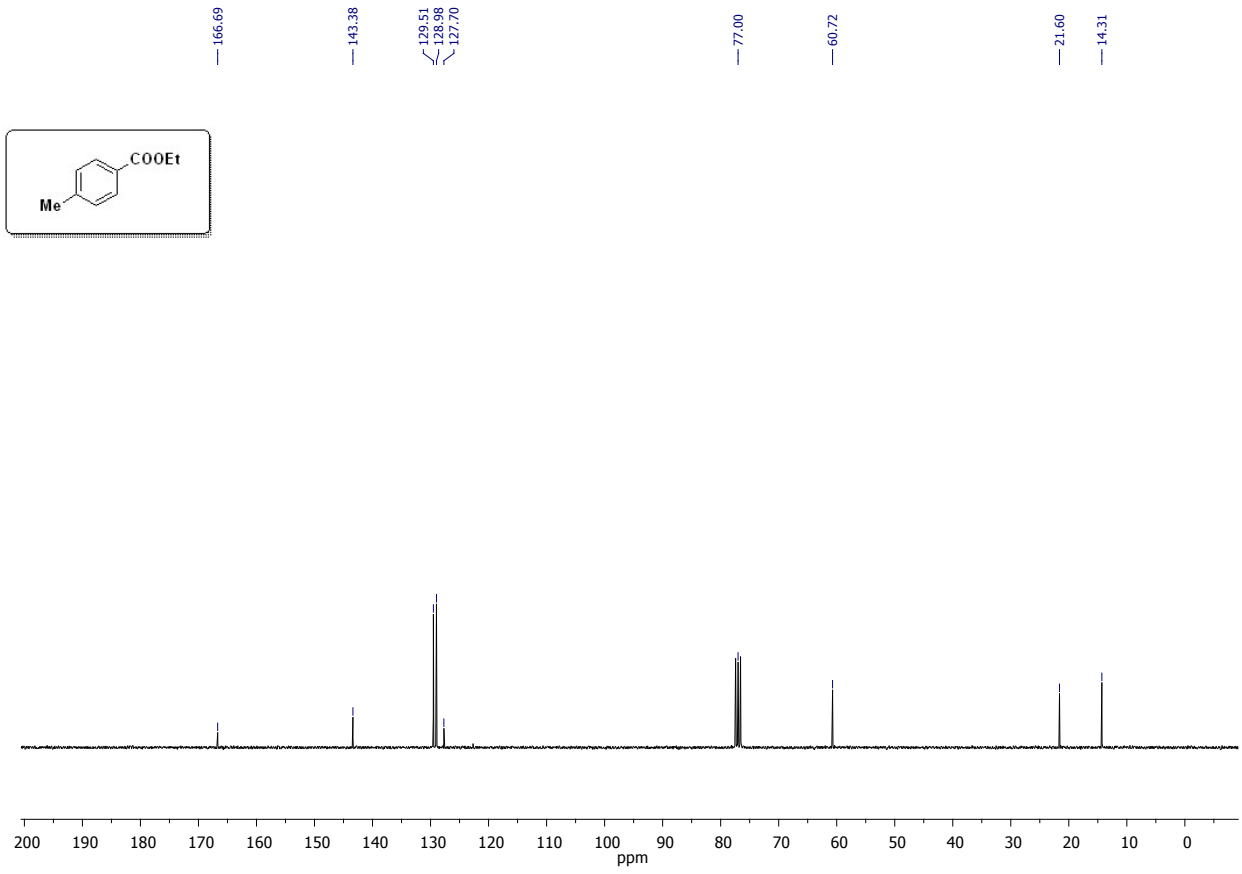
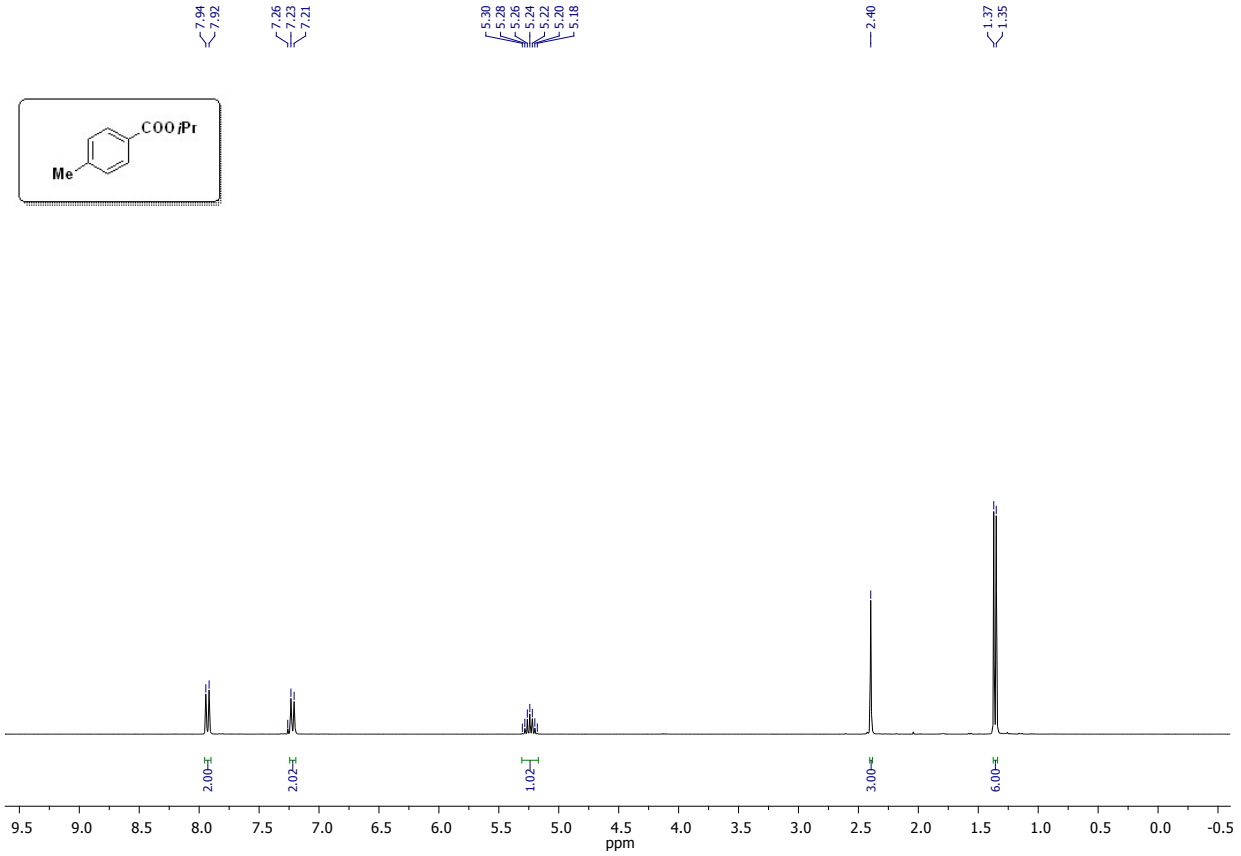


^{1}H-NMR (300 MHz, $CDCl_3$)



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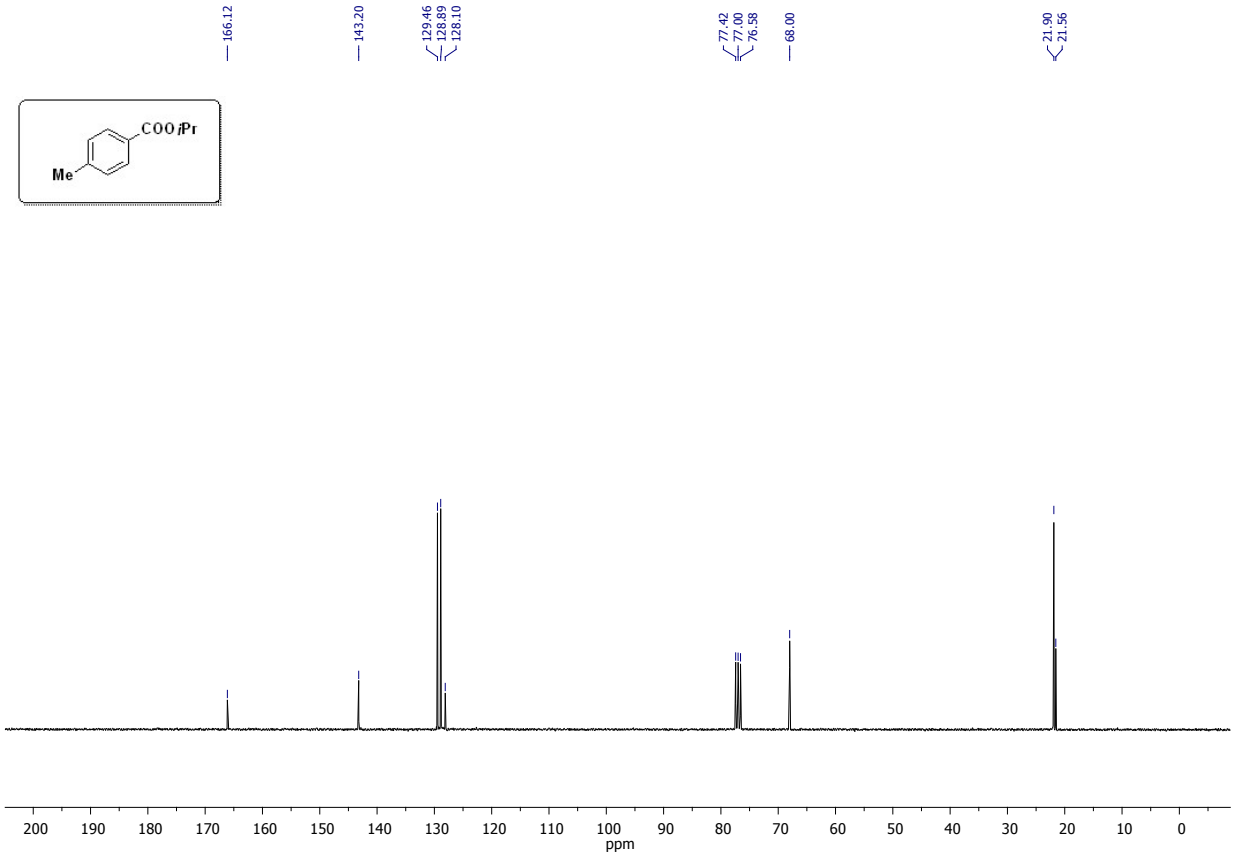

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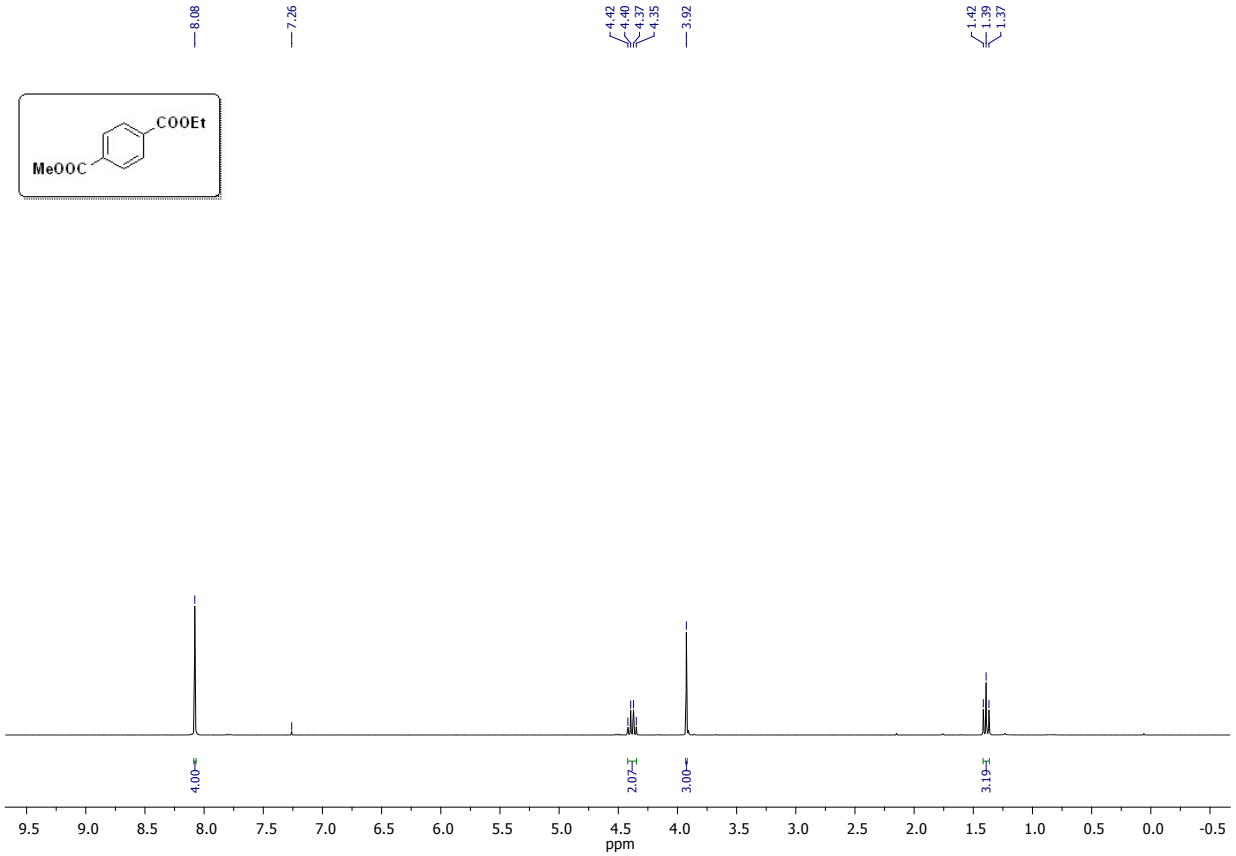
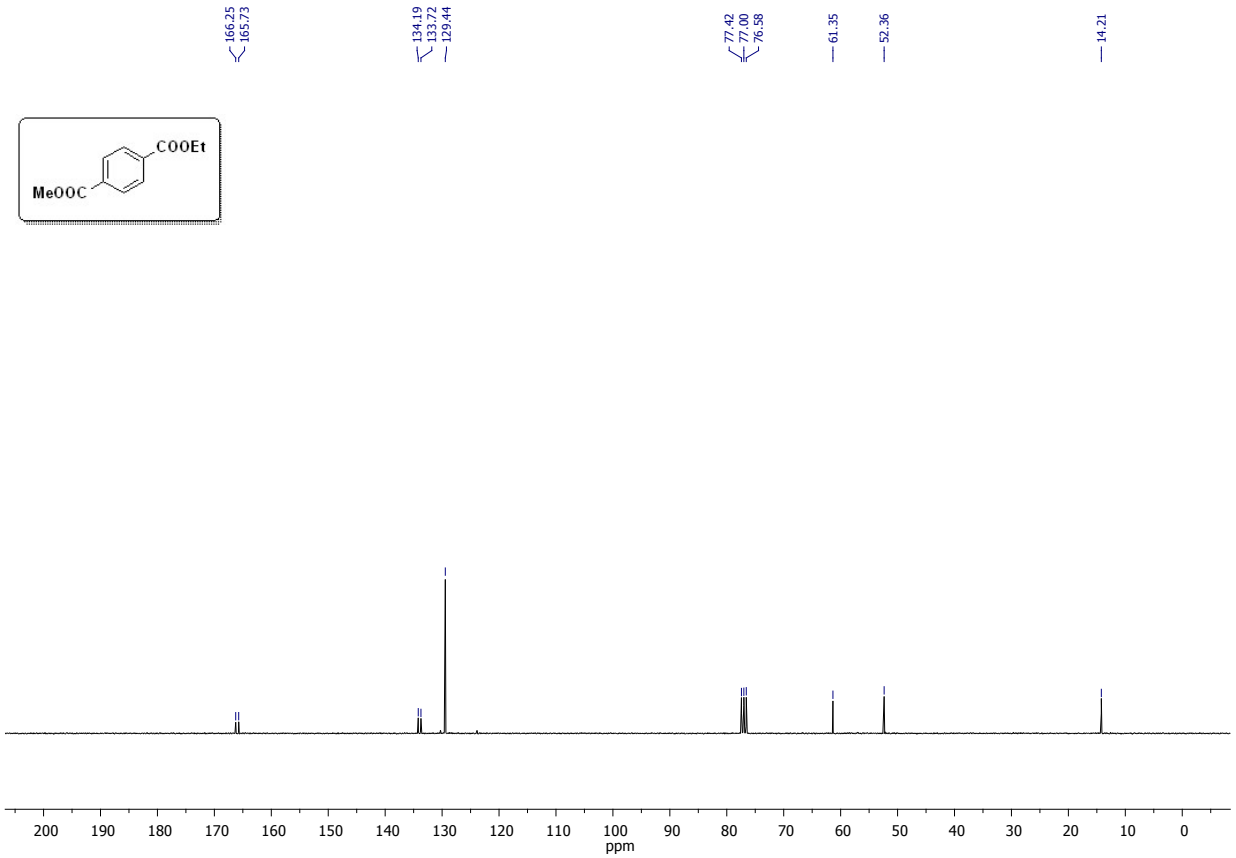


^{13}C-NMR (75 MHz, $CDCl_3$)



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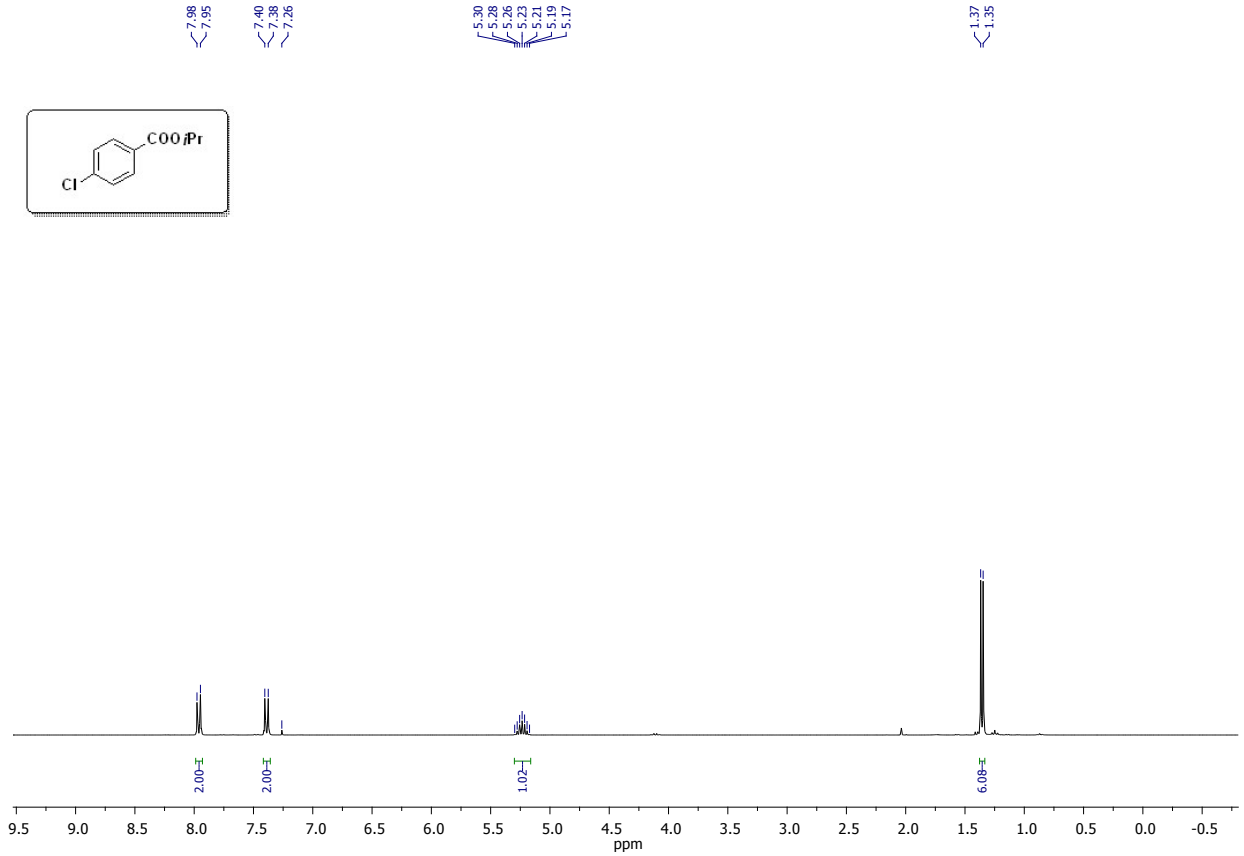
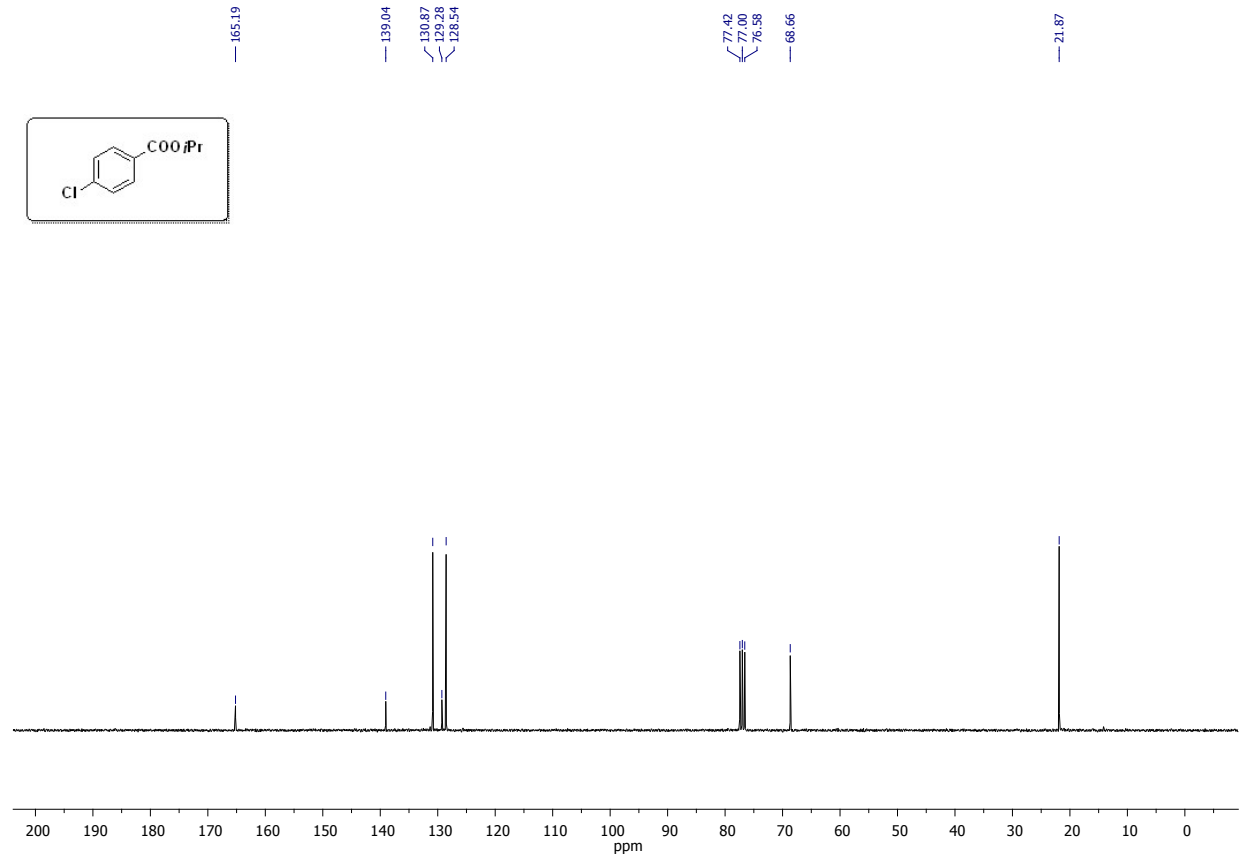
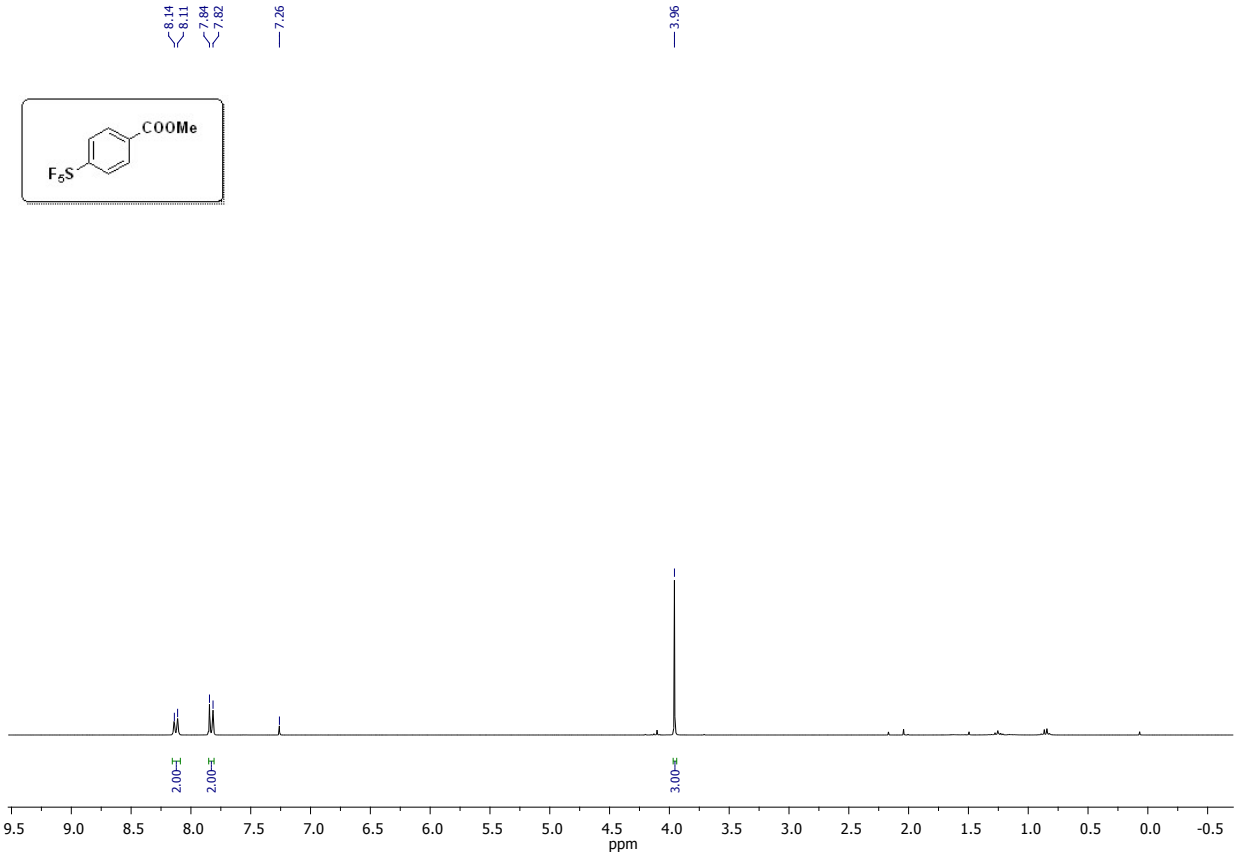


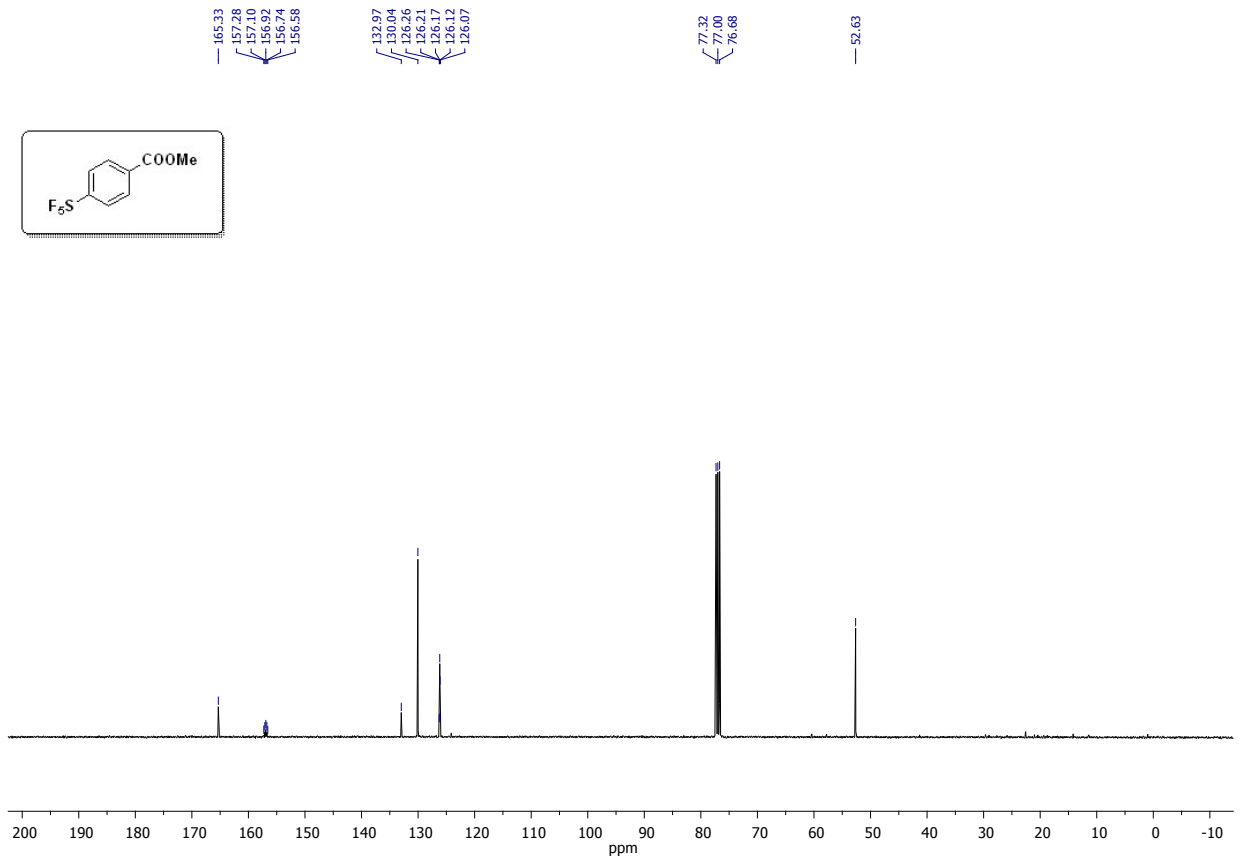
^{13}C-NMR (75 MHz, $CDCl_3$)



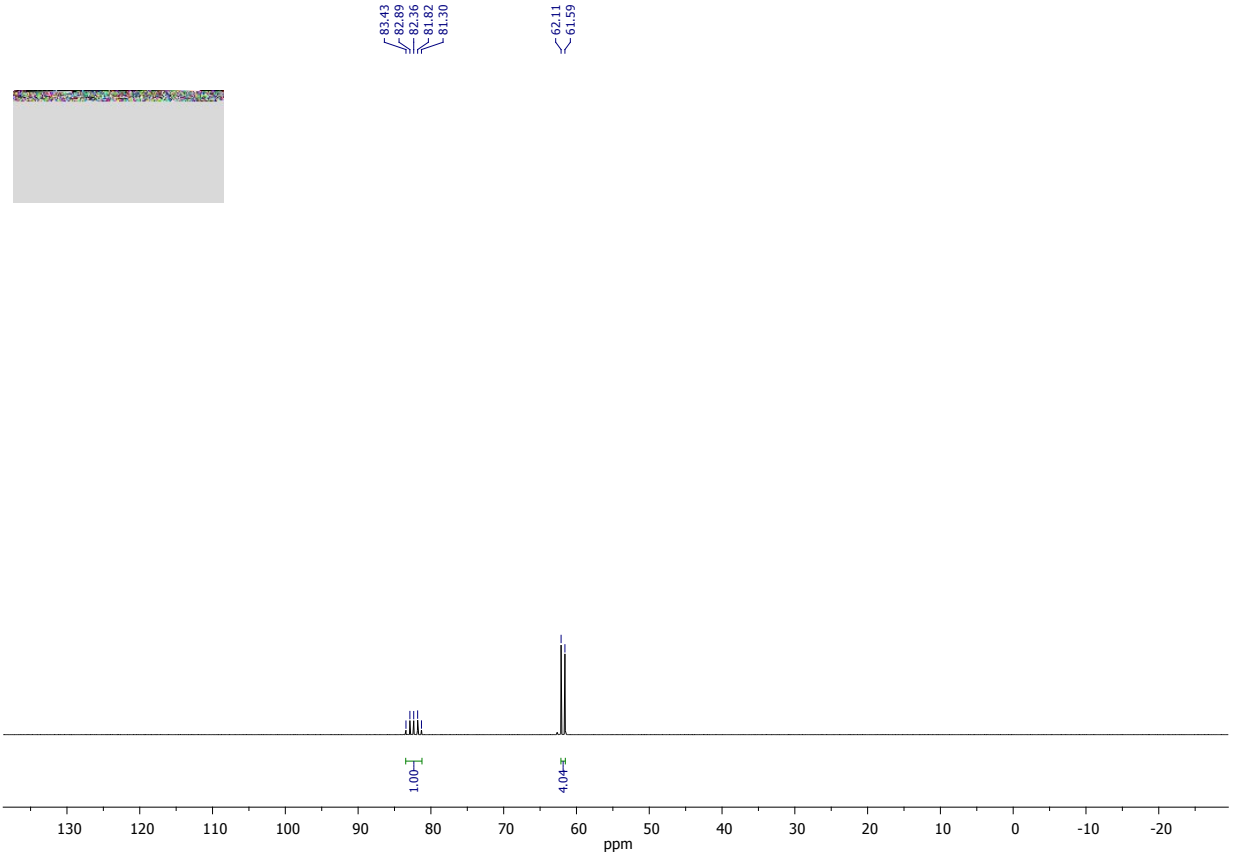
^{1}H-NMR (300 MHz, $CDCl_3$)



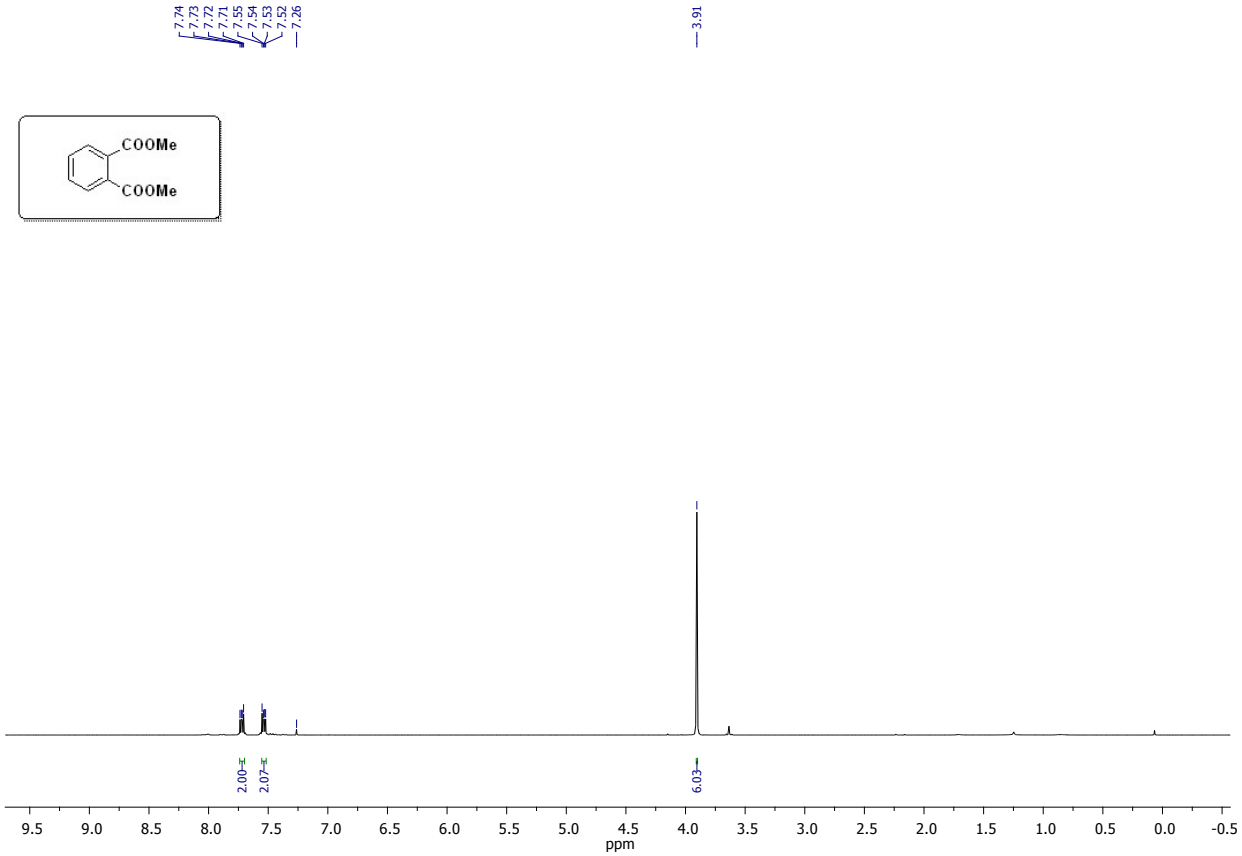
^{13}C-NMR (101 MHz, $CDCl_3$)



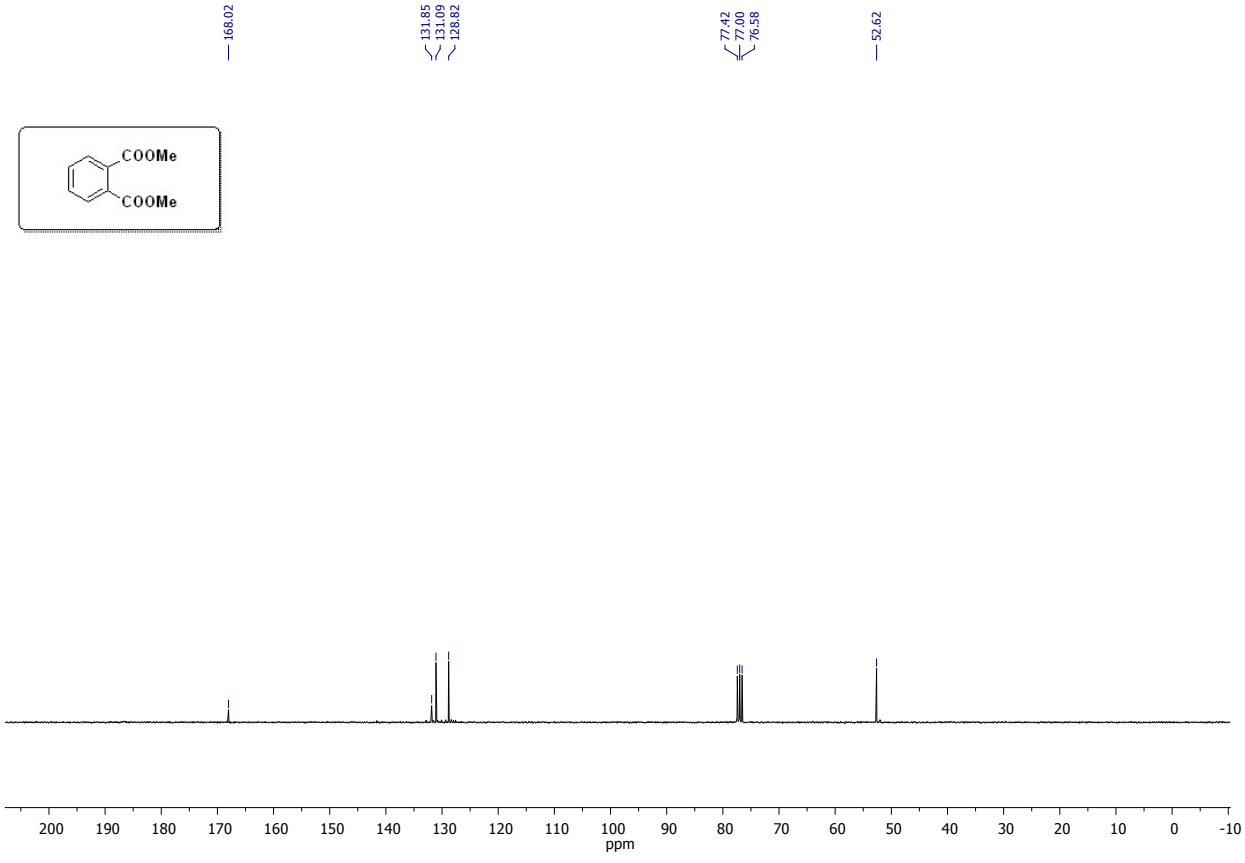
^{19}F-NMR (282 MHz, $CDCl_3$)



^{1}H-NMR (300 MHz, $CDCl_3$)



^{13}C-NMR (75 MHz, $CDCl_3$)



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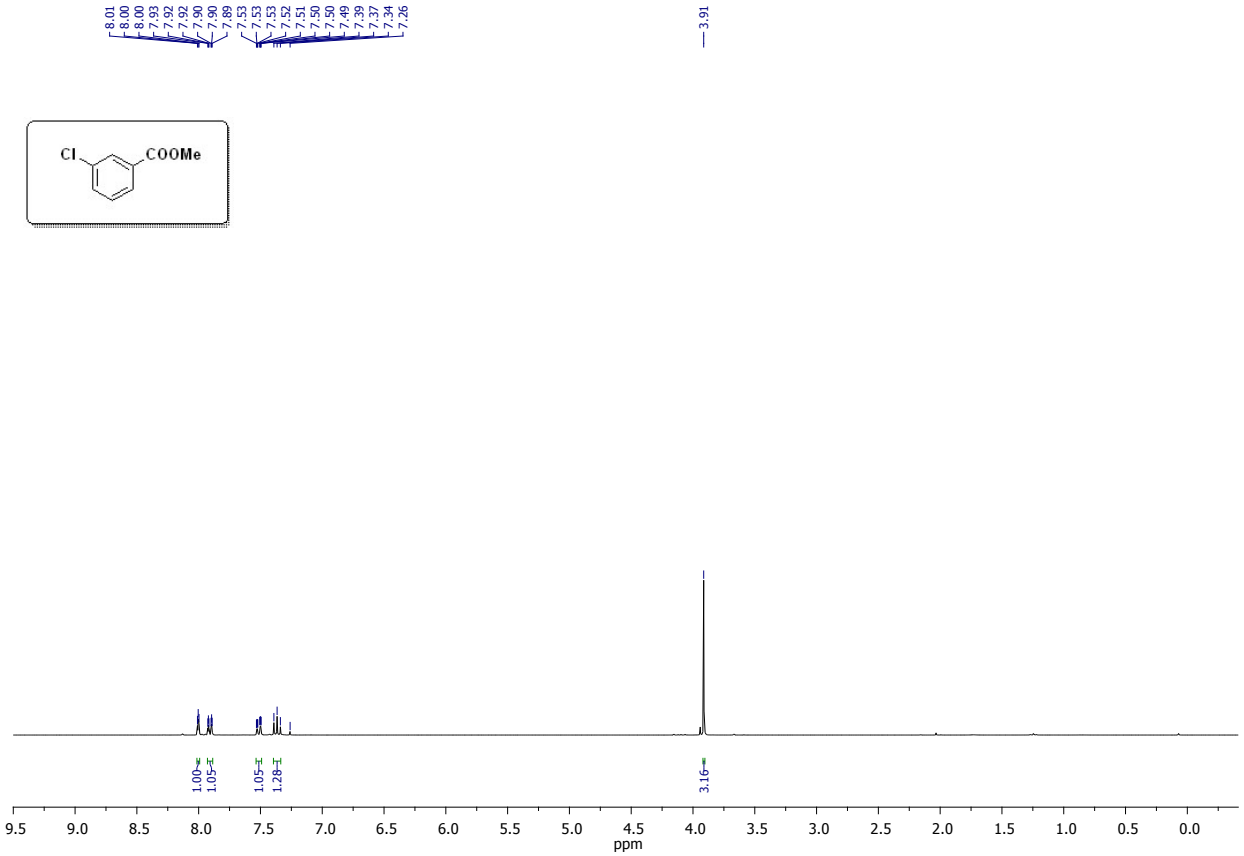
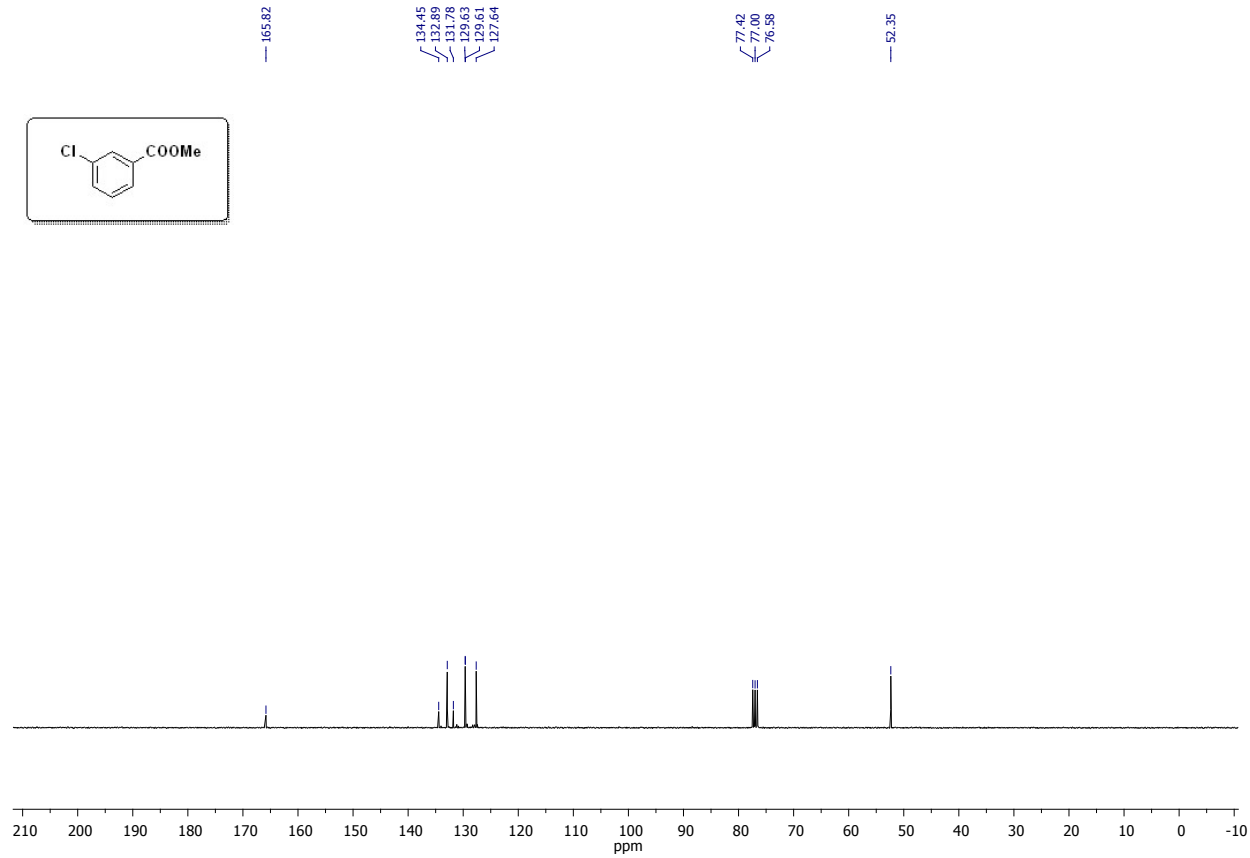


^{13}C-NMR (75 MHz, $CDCl_3$)



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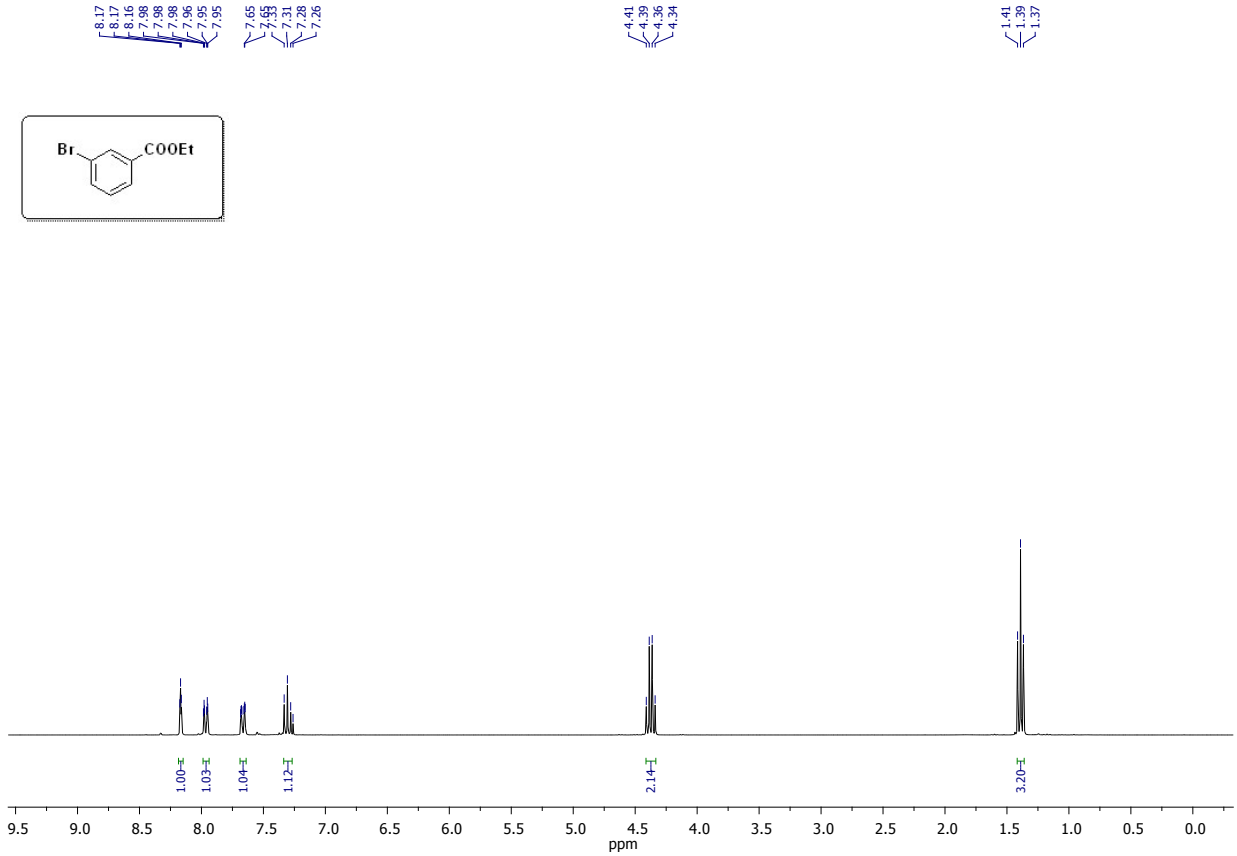
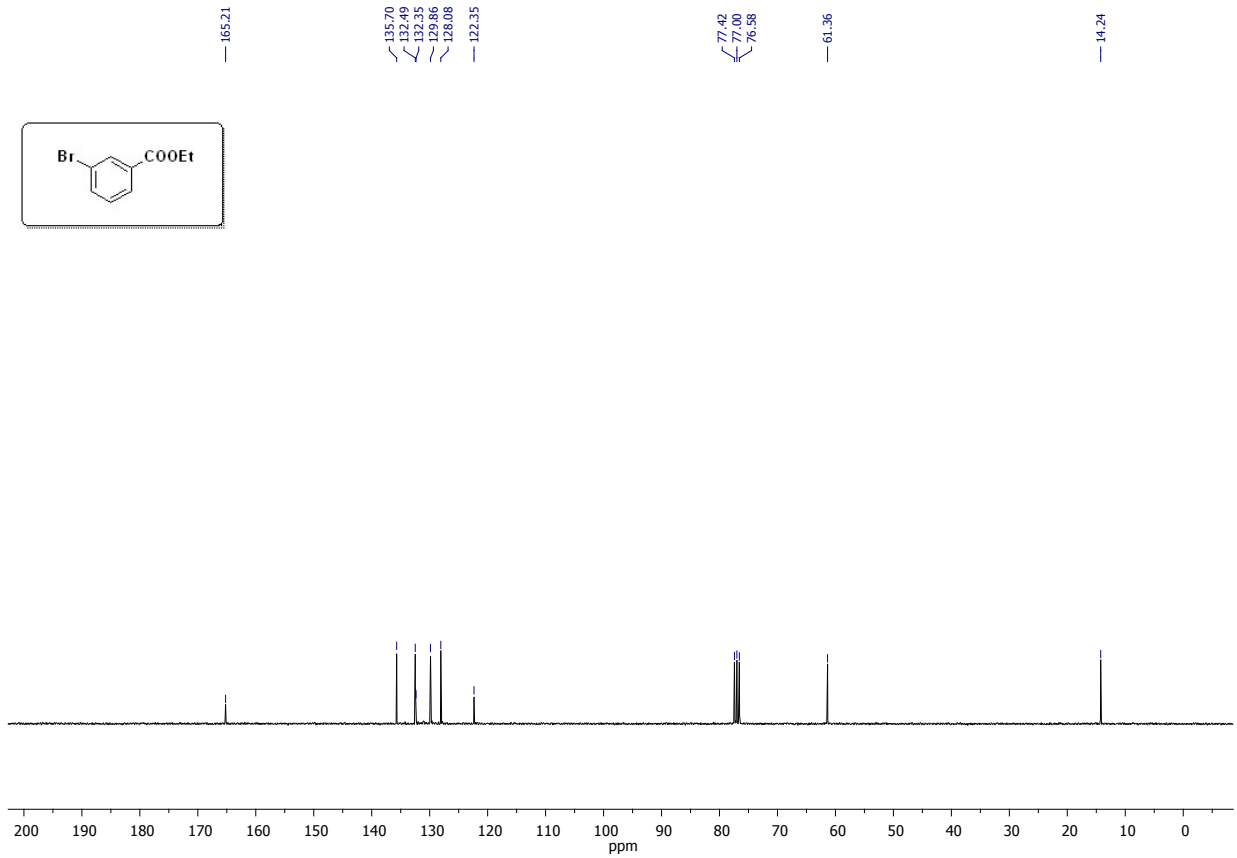
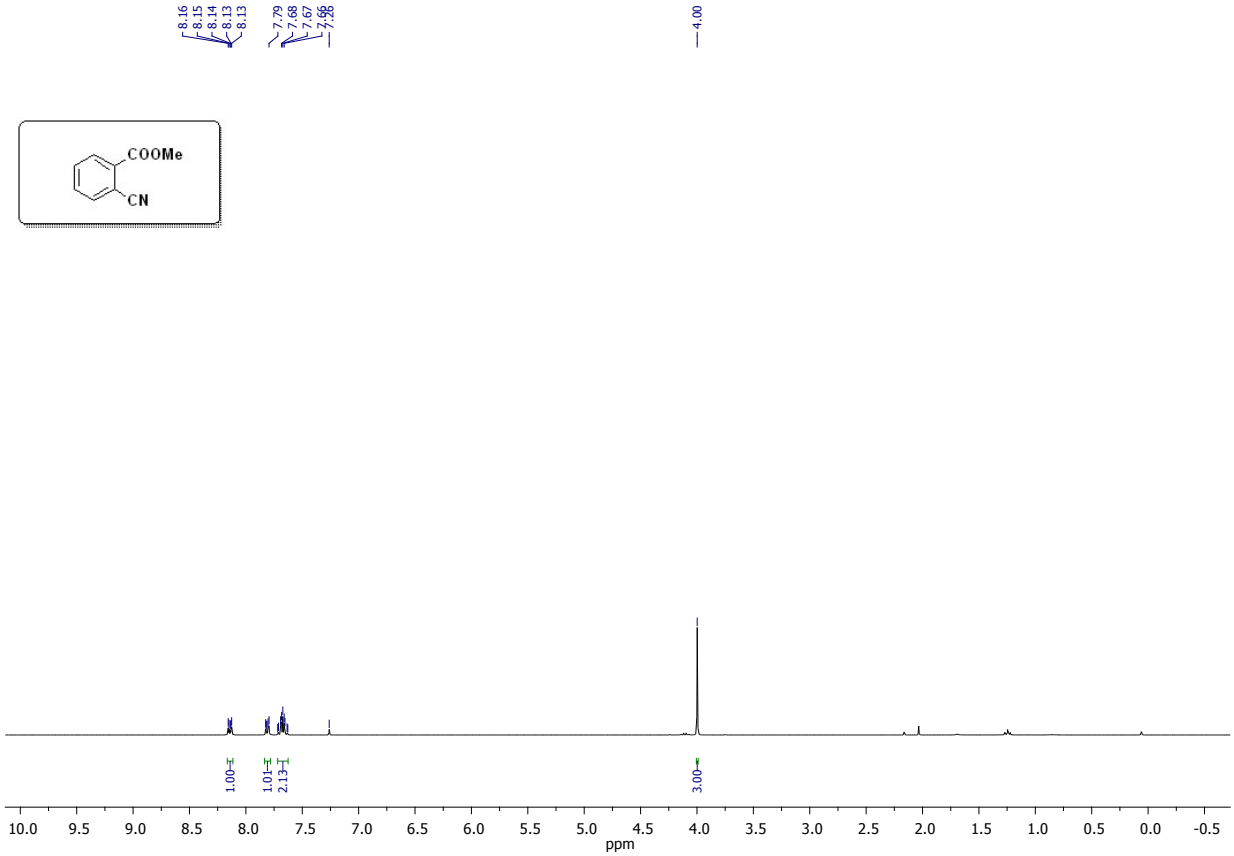


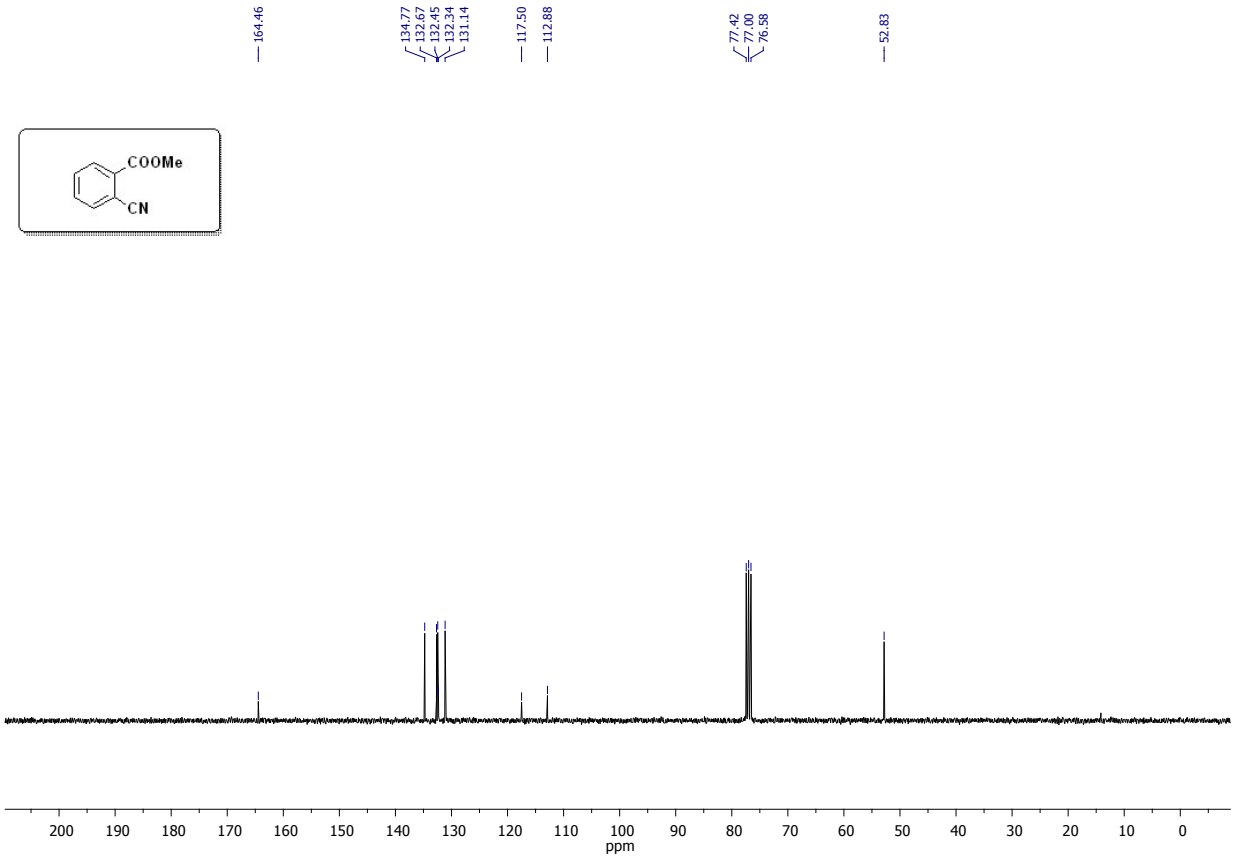
^{13}C-NMR (75 MHz, $CDCl_3$)



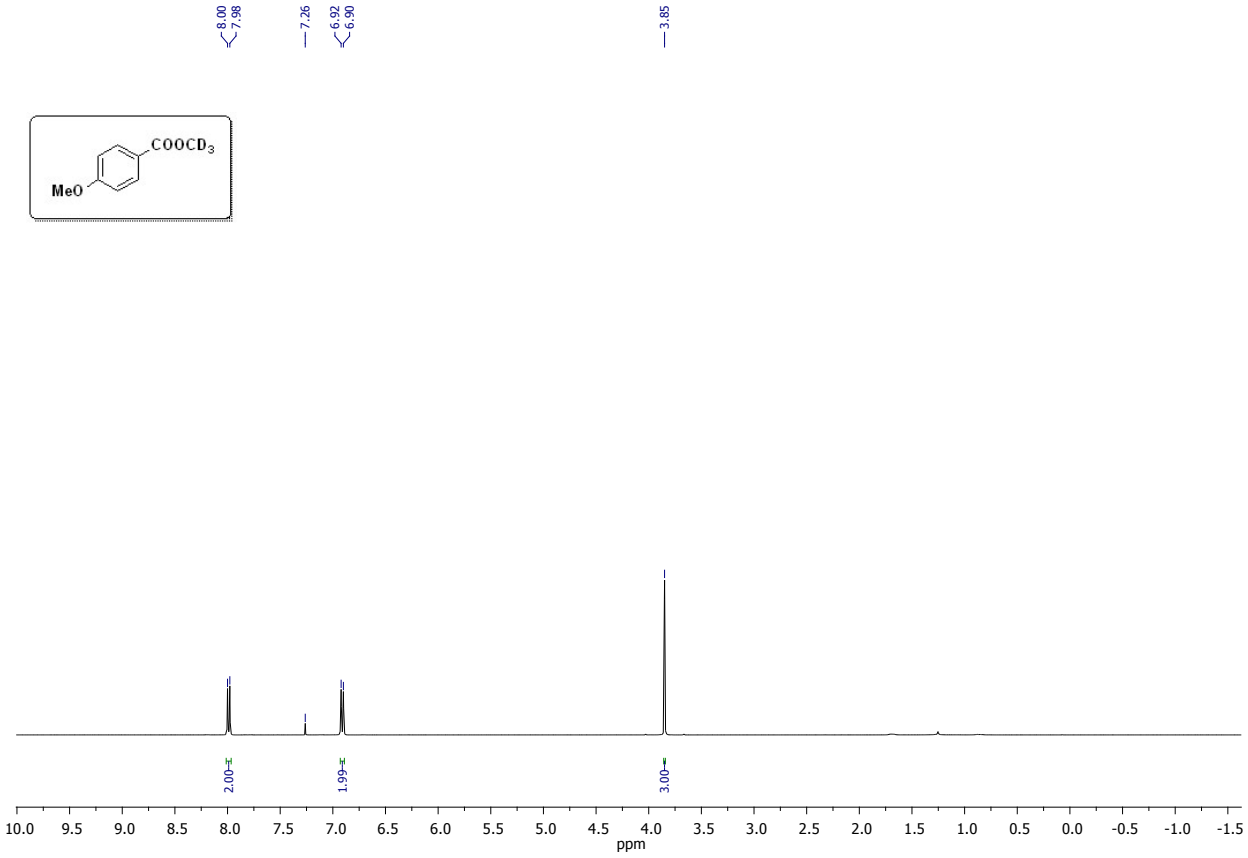
^{1}H-NMR (300 MHz, $CDCl_3$)



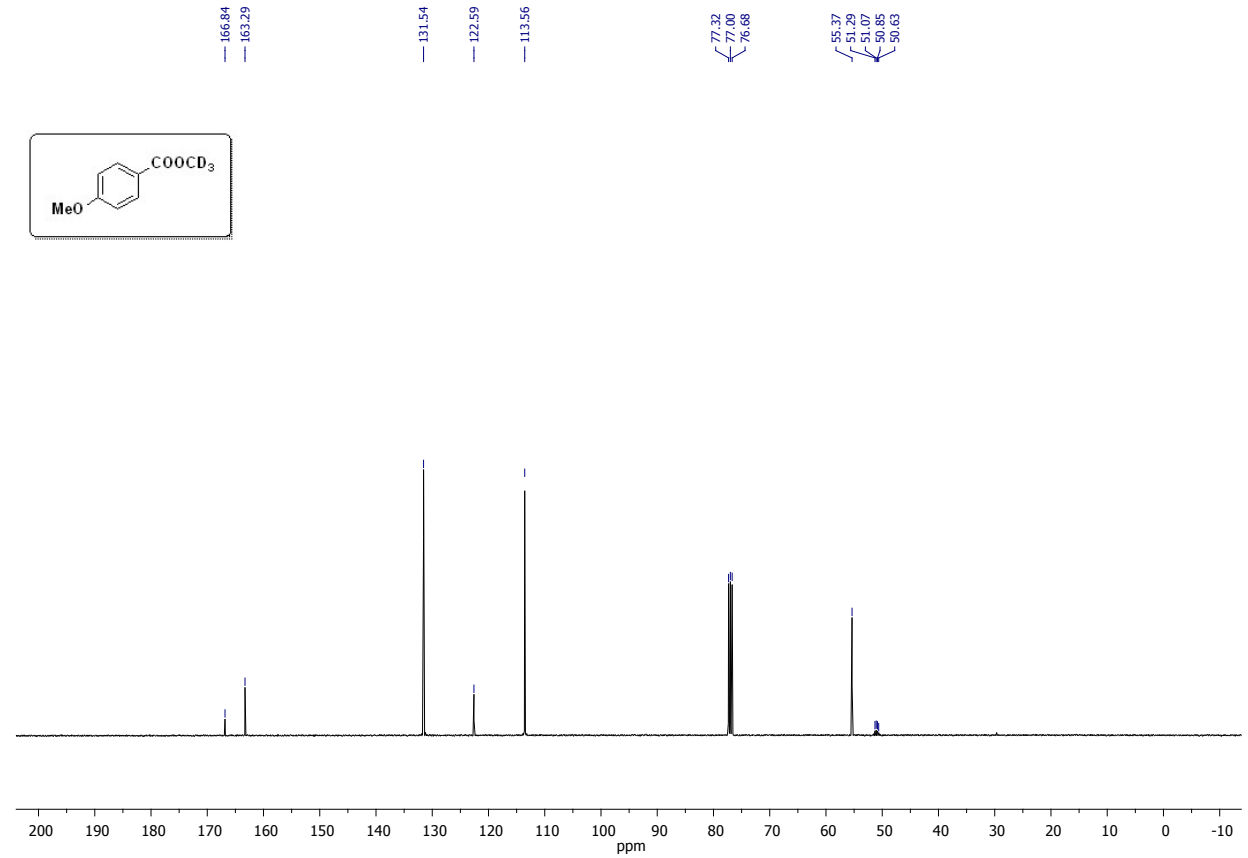
^{13}C-NMR (75 MHz, $CDCl_3$)



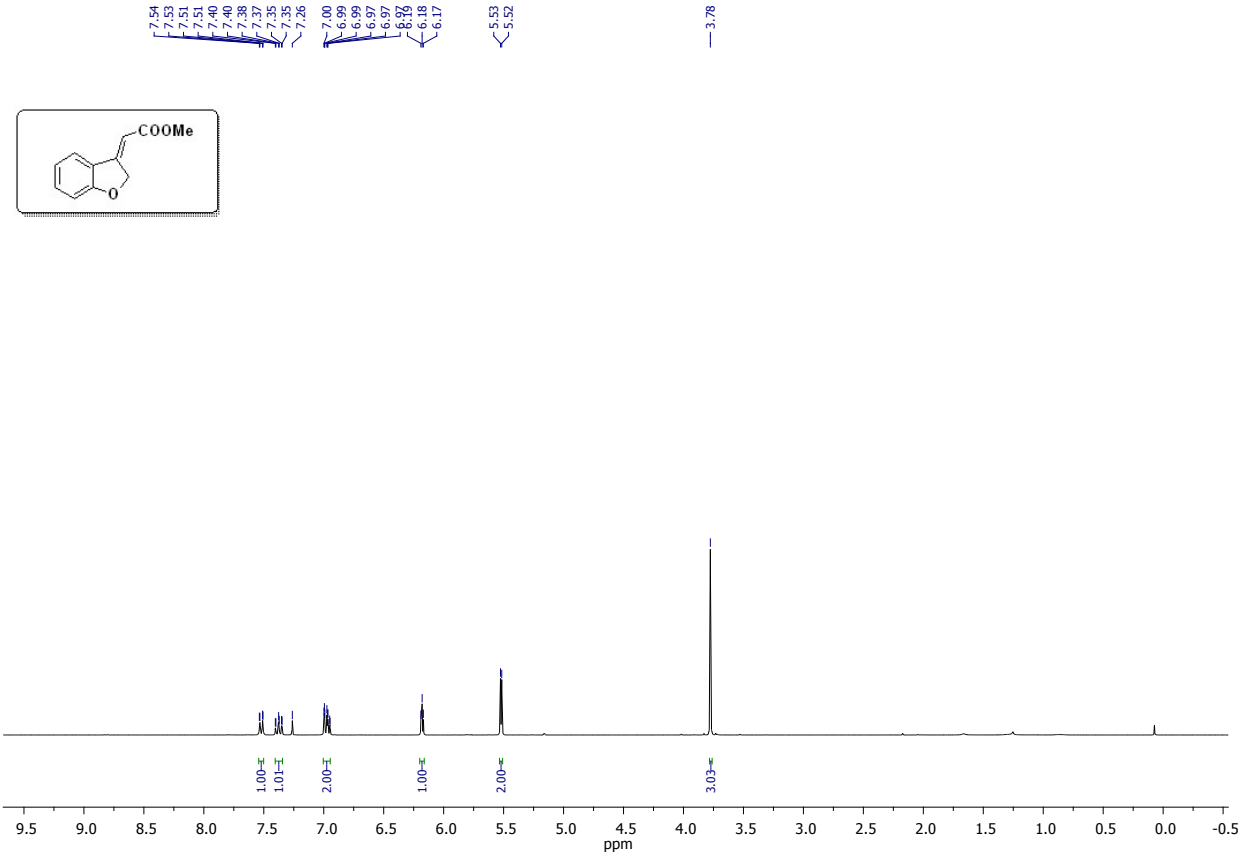
^{1}H-NMR (400 MHz, $CDCl_3$)



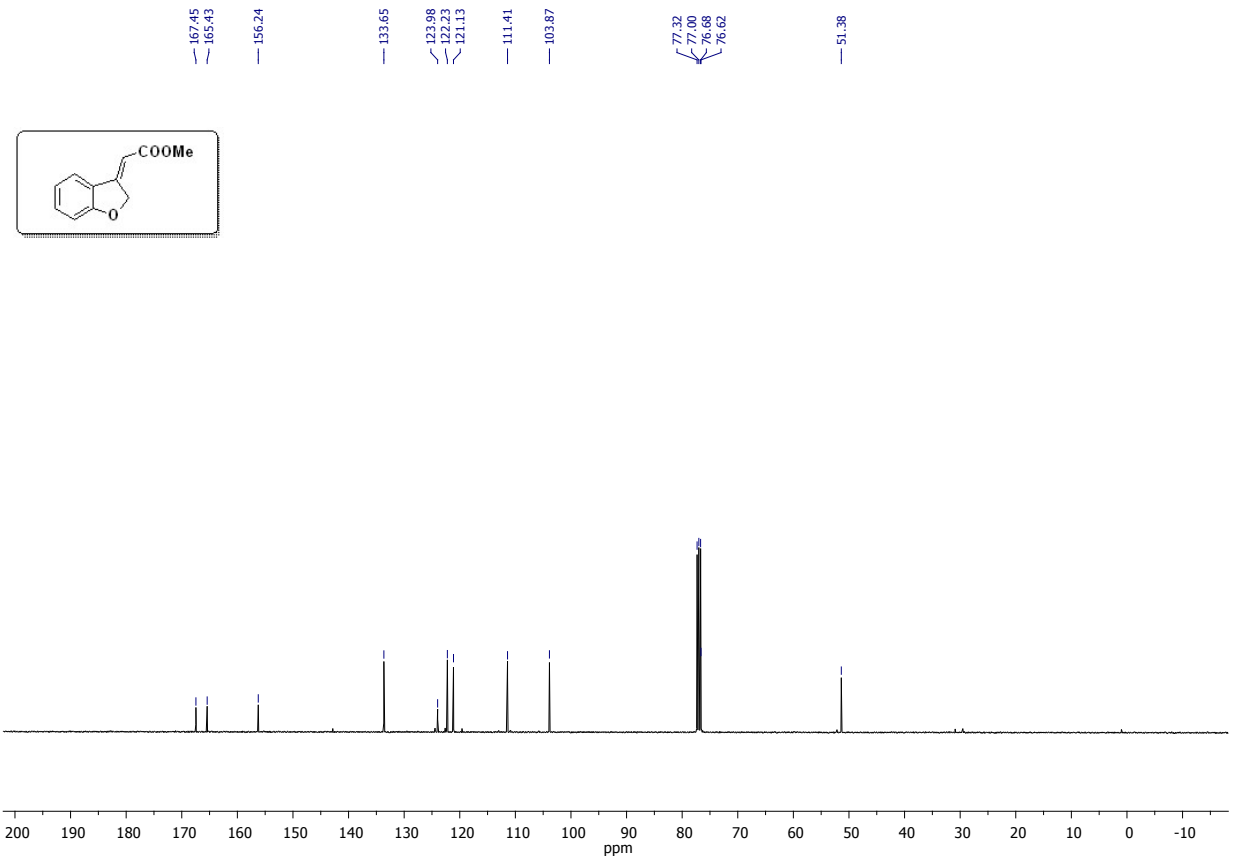
^{13}C-NMR (101 MHz, $CDCl_3$)



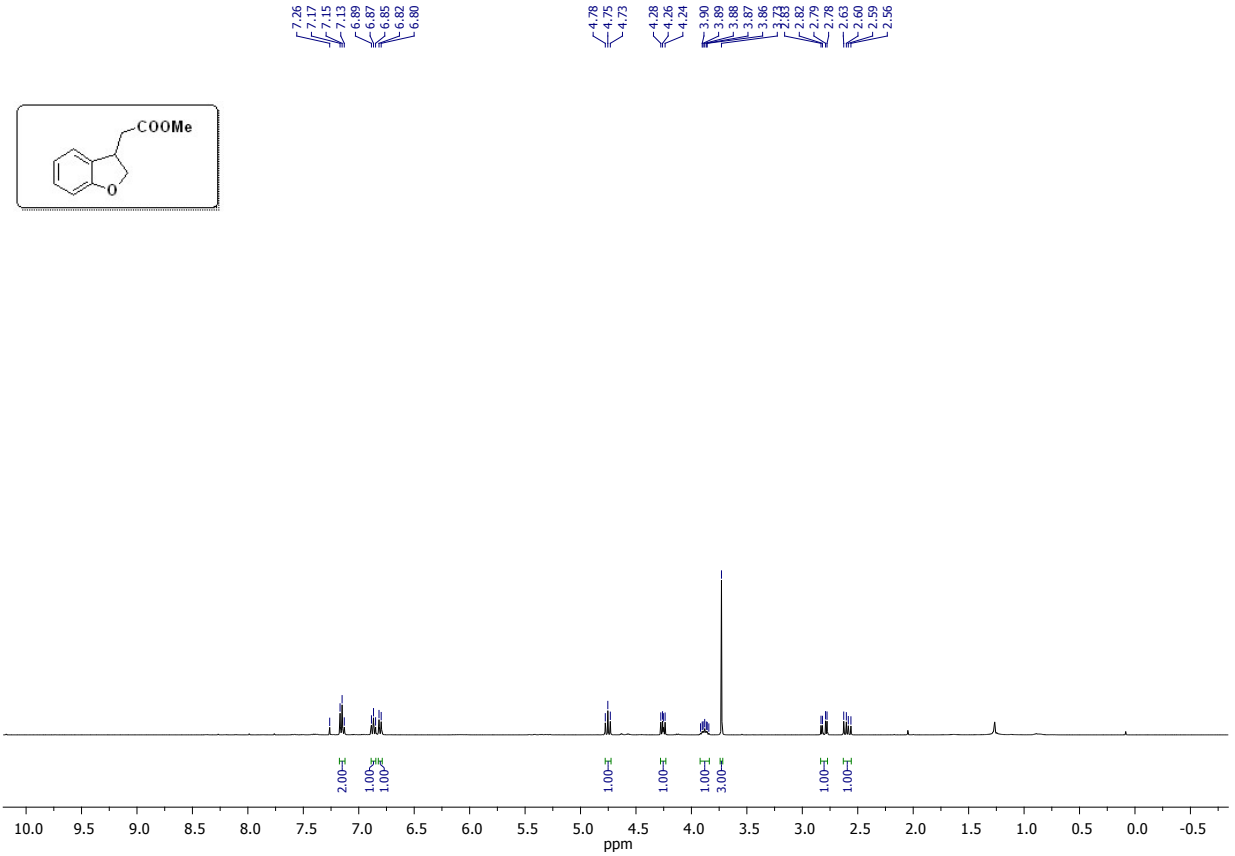
^{1}H-NMR (300 MHz, $CDCl_3$)



^{13}C-NMR (101 MHz, $CDCl_3$)



^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C-NMR (101 MHz, $CDCl_3$)