Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Visible light enabled γ-trifluoromethylation of Baylis-Hillman acetates: stereoselective synthesis of trisubstituted alkenes

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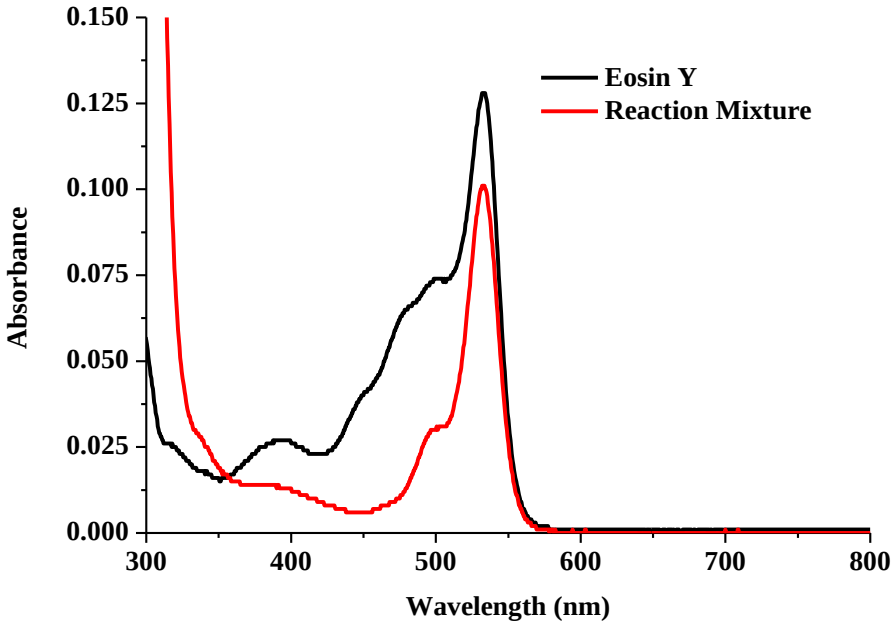
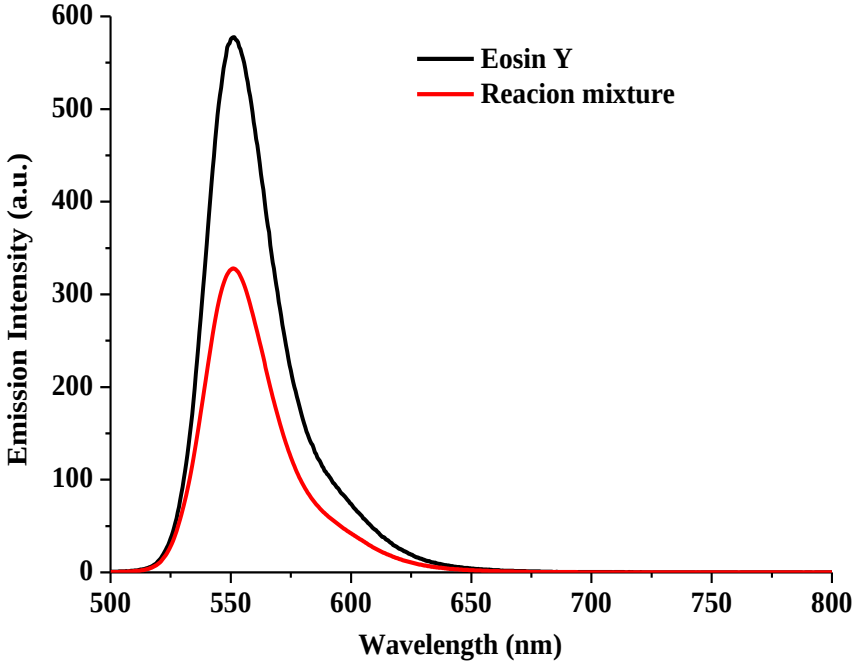


(UV-Visible Spectrum)



(Fluorescence spectrum)

General information: All the reagents used were procured from Aldrich/Merck and were used without further purification unless otherwise specified. The solvents were purified by distillation methods and were stored over 4 A° molecular sieves prior to its use. All the reactions were performed using oven-dried glassware. Organic solutions were concentrated using a Buchi rotary evaporator. Column chromatography was carried out over silica gel (Merck 100–200 mesh), whereas thin layer chromatography (TLC) was performed using silica gel GF254 (Merck) plates. ^{1}H (500 MHz), ^{13}C (125.7 MHz) and ^{19}F (470 MHz) NMR spectra were recorded on a JEOL spectrometer JNM-ECZ500R/S1 in $CDCl_3$ using TMS as internal reference. All the chemical shifts are reported in δ/ppm, and coupling constants (*J*) in Hertz (Hz). High-resolution mass spectra (HRMS) were obtained at the Centre of Biomedical Research Mass Spectrometry Service Centre using a Waters GCT Premier instrument run on electron ionization (EI) direct probe or a Waters QTOF Ultima instrument run on electro-spray ionization (ESI+). Green LED (2.50 W, λ = 535 nm) Rebel LED mounted on a 25 mm cool base was purchased from commercial supplier Luxeon Star LEDs Quadica Developments Inc Canada. The quantum yield of the reaction was determined using Shimadzu UV-1601 and Perkin Elmer LS 55 fluorescence spectrophotometer in EtOH.

General procedure for the Synthesis of Baylis-Hillman acetates 1.[1]

Step I: Preparation of Baylis-Hillman alcohols. A mixture of the aldehyde (10.0 mmol), acrylate/acrylonitrile (10.5 mmol) and DABCO (10.0 mmol), contained in a glass vessel, was stirred at 0°C to RT for 12 h. After completion of reaction (TLC), the mixture was diluted with diethyl ether (25 mL) and then washed with 0.5 M HCl solution (3 × 30 mL). The organic phase was dried over anhydrous sodium sulphate, filtered and concentrated under reduced pressure to yield the crude product, which was purified by silica gel column chromatography using a mixture of ethyl acetate-hexane (1:9) to give the pure Baylis-Hillman alcohol.

Step II: Preparation of Baylis-Hillman acetates 1. To a solution of Et_3N (5.0 mmol), Ac_2O (5.0 mmol), and 4-dimethylaminopyridine (DMAP) (10 mol%) in dichloromethane (25 mL) was added the Baylis-Hillman alcohol (5.0 mmol) prepared by Step I at 0°C to RT, and the resulting mixture was stirred for 30 min. Upon

completion of the reaction (TLC), the mixture was shaken with aqueous saturated solution of $NaHCO_3$. The organic phase was taken out, dried using anhydrous sodium sulfate, filtered and concentrated to yield the crude product, which was purified by column chromatography using a mixture of ethyl acetate/hexane (0.5:9.5) to furnish the pure product **1**. All the synthesized products **1** were characterized by the comparison of their NMR data with literature values.[2] The NMR data and spectra of **1** are given are given below.

II. Physical and spectra data of the Baylis-Hillman acetates 1:

2-(Acetoxy-p-tolyl-methyl)-acrylic acid ethyl ester (1a):[2a] Colourless Oily Liquid; Yield: 89%, 1.16 g; **^{1}H NMR** (500 MHz, $CDCl_3$): 1.13 (t, *J* = 7.0 Hz, 3H), 2.02 (s, 3H), 4.05 (q, *J* = 6.5 Hz, 2H), 5.75 (s, 1H), 6.31 (s, 1H), 6.58 (s, 1H), 7.106 (d, *J* = 7.5 Hz, 2H), 7.18 (d, *J* = 7.5 Hz, 2H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): 14.0, 21.2, 61.0, 73.1, 125.3, 127.8, 129.2, 134.9, 138.3, 140.0, 165.1, 169.5.

2-(Acetoxy-p-tolyl-methyl)-acrylic acid butyl ester (1b): Colourless Oily Liquid; Yield: 92%, 1.33 g; **^{1}H NMR** (500 MHz, $CDCl_3$): 0.86 (t, *J* = 7.5 Hz, 3H), 1.24 (sextet, *J* = 7.0 Hz, 2H), 1.53 (quintet, *J* = 6.5 Hz, 2H), 2.08 (s, 3H), 2.32 (s, 3H), 4.04 (m, 2H), 5.83 (s, 1H), 6.38 (s, 1H), 6.64 (s, 1H), 7.13 (d, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): 13.7, 19.1, 21.2, 30.6, 64.9, 73.2, 125.4, 127.8, 129.2, 135.0, 138.3, 140.0, 165.2, 169.6.

2-(Acetoxy-phenyl-methyl)-acrylic acid butyl ester (1c): Colourless Oily Liquid; Yield: 90%, 1.24 g; **^{1}H NMR** (500 MHz, $CDCl_3$): 0.84 (t, *J* = 7.0 Hz, 3H), 1.22 (sextet, *J* = 7.5 Hz, 2H), 1.50 (quintet, *J* = 6.5 Hz, 2H), 2.07 (s, 3H), 4.03 (m, 2H), 5.81 (s, 1H), 6.38 (s, 1H), 6.66 (s, 1H), 7.25-7.35 (m, 5H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): 13.6, 19.0, 20.8, 30.5, 64.9, 73.2, 125.7, 127.7, 128.4, 128.5, 137.8, 139.8, 165.1, 169.6.

2-(Acetoxy-phenyl-methyl)-acrylic acid isobutyl ester (1d): Colourless Oily Liquid; Yield: 85%, 1.17 g; **^{1}H NMR** (500 MHz, $CDCl_3$): 0.83 (m, 3H), 0.96 (d, *J* = 6.5 Hz, 3H), 1.84-2.04 (m, 1H), 2.08 (s, 3H), 4.01 (d, *J* = 6.5 Hz, 2H), 4.94 (s, 1H), 5.82 (s, 1H), 6.31 (s, 1H), 7.33-7.39 (m, 5H).

2-(Acetoxy-phenyl-methyl)-acrylic acid methyl ester (1e):[2b] Colourless Oily Liquid; Yield: 87%, 1.02 g; **^{1}H NMR** (500 MHz, $CDCl_3$): 2.02 (s, 3H), 3.62 (s, 3H), 5.78 (s, 1H), 6.31 (s, 1H), 6.60 (s, 1H), 7.23-7.31 (m, 5H).

2-(Acetoxy-phenyl-methyl)-acrylic acid ethyl ester (1f):[2a] Colourless Oily Liquid; Yield: 85%, 1.05 g; **^{1}H NMR** (500 MHz, $CDCl_3$): 1.19 (t, *J* = 5.0 Hz, 3H), 2.10 (s, 3H), 4.14 (q, *J* = 3.5 Hz, 2H), 5.83 (s, 1H), 6.39 (s, 1H), 6.68 (s, 1H), 7.29-7.38 (m, 5H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): 14.0, 21.1, 60.9, 73.1, 125.5, 127.7, 128.3, 128.4, 137.8, 139.9, 164.9, 169.4.

2-(Acetoxy-phenyl-methyl)-acrylic acid tert-butyl ester (1g):[2c] Colourless Oily Liquid; Yield: 82%, 1.13 g; **^{1}H NMR** (500 MHz, $CDCl_3$): 0.80 (t, *J* = 7.5, 3H), 1.18 (sextet, *J* = 7.5 Hz, 2H), 1.47 (q, *J* = 6.5 Hz, 2H), 2.03 (s, 3H), 4.00 (q, *J* = 9.5 Hz, 2H), 5.79 (s, 1H), 6.35 (s, 1H), 6.55 (s, 1H), 7.19-7.28 (m, 5H).

Acetic acid 2-cyano-1-(4-methoxy-phenyl)-allyl ester (1h):[2d] Colourless Oily Liquid; Yield: 80%, 0.92 g; **^{1}H NMR** (500 MHz, $CDCl_3$): 2.15 (s, 3H), 3.80 (s, 3H), 5.98 (s, 1H), 6.05 (s, 1H), 6.28 (s, 1H), 6.91 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): 21.0, 55.4, 74.1, 114.4, 116.4, 123.5, 127.7, 128.6, 131.5, 160.3, 169.4.

2-[Acetoxy-(4-fluoro-phenyl)-methyl]-acrylic acid methyl ester (1i):[2e] Colourless Oily Liquid; Yield: 86%, 1.08 g; **^{1}H NMR** (500 MHz, $CDCl_3$): 2.09 (s, 3H), 3.70 (s, 3H), 5.88 (s, 1H), 6.39 (s, 1H), 6.65 (s, 1H), 7.01 (s, 2H), 7.36 (s, 2H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): 21.0, 52.0, 72.5, 115.3 (d, *J* = 21.0 Hz), 125.6, 129.6 (d, *J* = 7.8 Hz), 128.5, 133.7, 139.5, 161.7, 163.6, 165.3, 166.4, 169.4.

2-[Acetoxy-(4-chloro-phenyl)-methyl]-acrylic acid methyl ester (1j): Colourless Oil; Yield: 92%, 1.23 g; **^{1}H NMR** (500 MHz, $CDCl_3$): 2.10 (s, 3H), 3.70 (s, 3H), 5.89 (s, 1H), 6.40 (s, 1H), 6.63 (s, 1H), 7.31 (s, 4H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): 21.1, 52.1, 72.5, 125.9, 128.7, 129.2, 134.3, 136.5, 139.3, 165.3, 169.4.

2-[Acetoxy-(4-chloro-phenyl)-methyl]-acrylic acid ethyl ester (1k):[2f] Colourless Oily Liquid; Yield: 90%, 1.26 g; **^{1}H NMR** (500 MHz, $CDCl_3$): 1.20 (t, *J* = 5.0 Hz, 3H), 2.10 (s, 3H), 4.13 (q, *J* = 4.5 Hz, 2H), 5.86 (s, 1H), 6.40 (s, 1H), 6.63 (s, 1H), 7.29-7.33 (m, 4H);

^{13}C NMR (125.7 MHz, $CDCl_3$): 14.0, 21.1, 61.1, 72.5, 125.7, 128.7, 129.2, 134.2, 136.5, 139.5, 164.8, 169.3.

2-[Acetoxy-(4-chloro-phenyl)-methyl]-acrylic acid butyl ester (1l): Colourless Oily Liquid; Yield: 94%, 1.45 g; **^{1}H NMR** (500 MHz, $CDCl_3$): 0.92 (t, *J* = 7.5 Hz, 3H), 1.40-1.41 (m, 2H), 1.65-1.68 (m, 2H), 2.07 (s, 3H), 4.21 (t, *J* = 6.5 Hz, 2H), 5.83 (s, 1H), 6.38 (s, 1H), 6.60 (s, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H).

Acetic acid 1-(3-chloro-phenyl)-2-cyano-allyl ester (1m): Colourless Oily Liquid; Yield: 86%, 1.01 g; **^{1}H NMR** (500 MHz, $CDCl_3$): 2.10 (s, 3H), 6.02 (s, 1H), 6.09 (s, 1H), 6.27 (s, 1H), 7.26 (d, *J* = 5.0 Hz, 1H), 7.30-7.36 (m, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): 20.9, 73.6.1, 115.9, 127.7, 125.2, 127.0, 129.5, 130.3, 132.5, 135.0, 137.6, 169.2.

2-[Acetoxy-(3-chloro-phenyl)-methyl]-acrylic acid ethyl ester (1n): Colourless Oily Liquid; Yield: 84%, 1.18 g; **^{1}H NMR** (500 MHz, $CDCl_3$): 1.21 (t, *J* = 7.5 Hz, 3H), 2.11 (s, 3H), 4.14 (q, *J* = 5.5 Hz, 2H), 5.86 (s, 1H), 6.41 (s, 1H), 6.62 (s, 1H), 7.26 (s, 3H), 7.35 (s, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): 14.0, 21.1, 61.2, 72.5, 126.1, 127.8, 128.6, 129.8, 134.4, 139.4, 140.0, 164.8, 169.4.

2-[Acetoxy-(3-chloro-phenyl)-methyl]-acrylic acid butyl ester (1o): Colourless Oily Liquid; Yield: 89%, 1.37 g; **^{1}H NMR** (500 MHz, $CDCl_3$): 0.81 (t, *J* = 7.5 Hz, 3H), 1.20 (quintet, *J* = 7.5 Hz, 2H), 1.49 (q, *J* = 10.5 Hz, 2H), 2.04 (s, 3H), 4.02 (q, *J* = 7.0 Hz, 2H), 5.80 (s, 1H), 6.35 (s, 1H), 6.56 (s, 1H), 7.20 (s, 3H), 7.29 (s, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): 13.7, 19.1, 21.1, 30.6, 65.0, 72.5, 126.1, 127.8, 128.6, 129.8, 134.4, 139.4, 140.1, 164.9, 169.4.

2-[Acetoxy-(3-chloro-phenyl)-methyl]-acrylic acid tert-butyl ester (1p): Colourless Oily Liquid; 83%, 1.28 g; **^{1}H NMR** (500 MHz, $CDCl_3$): 1.35 (s, 9H), 2.07 (s, 3H), 5.73 (s, 2H), 6.30 (s, 1H), 6.51 (s, 1H), 7.21-7.24 (m, 3H), 7.32 (s, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): 22.2, 27.9, 72.7, 81.8, 125.2, 126.1, 127.9, 128.5, 129.7, 134.3, 140.6, 164.0, 166.4, 169.4.

2-[Acetoxy-(2-bromo-phenyl)-methyl]-acrylic acid methyl ester (1q):[2g] Yellowish Oily Liquid; Yield: 82%, 1.27 g; **^{1}H NMR** (500 MHz, $CDCl_3$): 2.06 (s, 3H), 3.69 (s, 3H), 5.56 (s, 1H), 6.42 (s, 1H), 6.93 (s, 1H), 7.11 (t, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 5.5 Hz, 2H),

7.51 (t, *J* = 8.0 Hz, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): 21.2, 52.2, 72.3, 123.7, 127.6, 128.1, 128.6, 129.9, 133.2, 136.9, 138.2, 165.4, 169.3.

2-[Acetoxy-(2-bromo-phenyl)-methyl]-acrylic acid ethyl ester (1r): Yellowish Oily Liquid; Yield: 82%, 1.33 g; **^{1}H NMR** (500 MHz, $CDCl_3$): 1.22 (t, *J* = 7.0 Hz, 3H), 2.12 (s, 3H), 4.17 (q, *J* = 8.5 Hz, 2H), 5.59 (s, 1H), 6.47 (s, 1H), 7.00 (s, 1H), 7.16-7.20 (m, 1H), 7.29-7.35 (m, 2H), 7.57 (t, *J* = 7.5 Hz, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): 14.1, 20.9, 61.1, 72.4, 123.9, 127.6, 127.7, 128.7, 129.9, 133.2, 137.2, 138.6, 165.9, 169.2.

2-[Acetoxy-(2-bromo-phenyl)-methyl]-acrylic acid butyl ester (1s): Yellowish Oily Liquid; Yield: 86%, 1.52 g; **^{1}H NMR** (500 MHz, $CDCl_3$): 0.86 (t, *J* = 7.0 Hz, 3H), 1.24-1.31 (sextet, 2H), 1.55 (quintet, *J* = 7.5 Hz, 2H), 2.12 (s, 3H), 4.11 (q, *J* = 4.5 Hz, 2H), 5.60 (s, 1H), 6.48 (s, 1H), 7.00 (t, *J* = 4.5 Hz, 1H), 7.19-7.57 (m, 2H), 7.58 (s, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): 13.5, 19.08, 20.8, 22.2, 30.5, 65.0, 72.4, 124.0, 127.5, 127.7, 128.7, 129.9, 133.2, 137.1, 138.5, 165.0, 166.5, 169.2.

2-[Acetoxy-(3-bromo-phenyl)-methyl]-acrylic acid butyl ester (1t): Yellowish Oily Liquid; Yield: 88%, 1.55 g; **^{1}H NMR** (500 MHz, $CDCl_3$): 0.88 (t, *J* = 7.5 Hz, 3H), 1.25 (sextet, *J* = 7.5 Hz, 2H), 1.54 (quintet, *J* = 7.0 Hz, 2H), 2.11 (s, 3H), 4.06-4.16 (m, 2H), 5.87 (s, 1H), 6.42 (s, 1H), 6.63 (s, 1H), 7.26-7.27 (m, 3H), 7.35 (s, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): 13.7, 19.1, 21.1, 30.6, 65.0, 72.5, 126.1, 126.2, 127.8, 128.6, 129.8, 134.4, 139.4, 140.1, 164.9, 169.4.

2-(Acetoxy-m-tolyl-methyl)-acrylic acid butyl ester (1u): Colourless Oily Liquid; Yield: 83%, 1.20 g; **^{1}H NMR** (500 MHz, $CDCl_3$): 0.79 (t, *J* = 7.5 Hz, 3H), 1.18-1.22 (m, 2H), 1.49-1.52 (m, 2H), 2.03 (s, 3H), 2.26 (s, 3H), 4.01 (q, *J* = 7.0 Hz, 2H), 5.75 (s, 1H), 6.32 (s, 1H), 6.57 (s, 1H), 7.08-7.19 (m, 4H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): 13.7, 19.1, 21.2, 21.4, 30.5, 64.8, 73.3, 124.8, 125.5, 128.3, 128.5, 129.2, 137.7, 138.1, 139.9, 165.1, 169.5.

2-(Acetoxy-thiophen-2-yl-methyl)-acrylic acid methyl ester (1v):[2b] Yellow Oily Liquid; Yield: 85%, 1.02 g; **^{1}H NMR** (500 MHz, $CDCl_3$): 2.10 (s, 3H), 3.70 (s, 3H), 5.87 (s, 1H), 6.40 (s, 1H), 6.60 (s, 1H), 7.17 (t, *J* = 8.0, 1H), 7.29 (d, *J* = 8.0, 1H), 7.40 (d, *J* = 8.0,

1H), 7.49 (s, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): 21.1, 52.1, 72.4, 122.5, 126.3, 126.5, 130.1, 130.6, 131.5, 139.1, 140.2, 165.2, 169.3.

2-[Acetoxy-(3-methoxy-phenyl)-methyl]-acrylic acid butyl ester (1w): Colourless Oily Liquid; Yield: 83%, 1.20 g; **^{1}H NMR** (500 MHz, $CDCl_3$): 0.88 (t, *J* = 7.5 Hz, 3H), 1.27 (sextet, *J* = 7.0 Hz, 2H), 1.55(quintet, *J* = 6.5 Hz, 2H), 2.1 (s, 3H), 3.8 (s, 3H), 4.07-4.16 (m, 2H), 5.83 (s, 1H), 6.41 (s, 1H), 6.67 (s, 1H), 6.84-6.86 (m, 1H), 6.92-6.98 (m, 2H), 7.25 (t, *J* = 7.5 Hz, 1H). **^{13}C NMR** (125.7 MHz, $CDCl_3$): 13.7, 19.1, 21.1, 30.6, 55.3, 64.9, 73.1, 113.4, 113.8, 120.1, 125.9, 129.5, 139.4, 139.8, 159.7, 165.1, 169.5.

2-[Acetoxy-(4-cyano-phenyl)-methyl]-acrylic acid methyl ester (1x): Colourless solid; Yield: 94%, 2.40 g; **^{1}H NMR** (500 MHz, $CDCl_3$): 2.12 (s, 3H), 3.71 (s, 3H), 5.93 (s, 1H), 6.43 (s, 1H), 6.66 (s, 1H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): 21.0, 52.3, 72.5, 112.3, 126.8, 128.4, 129.9, 132.4, 142.8, 143.3, 165.1, 169.3

2-[Acetoxy-(2,4-dichloro-phenyl)-methyl]-acrylic acid methyl ester (1y): Colourless solid; Yield: 97%, 2.92 g; **^{1}H NMR** (500 MHz, $CDCl_3$): 2.12 (s, 3H), 3.74 (s, 3H), 5.69 (s, 1H), 6.47 (s, 1H), 6.96 (s, 1H), 7.24-7.26 (m, 1H), 7.28 (d, *J* = 8.5 Hz, 1H), 7.41 (d, *J* = 2.0 Hz, 2H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): 20.9, 52.3, 69.8, 127.4, 128.0, 129.5, 129.8, 134.2, 134.6, 135.0, 137.9, 165.2, 169.2

General Procedure for the synthesis of products 2: A mixture of Baylis-Hillman acetate **1** (1.0 mmol), CF_3SO_2Na (3.0 equiv.), eosin Y (2.0 mol %) and DMSO (3mL), placed in a closed vessel, was irradiated with Luxeon Rebel high power green LED [2.50 W, λ = 535 nm] from the bottom side at room temperature for 12-15 h. After completion of the reaction (as indicated by TLC), the mixture was quenched with water (5 mL), and then extracted with diethyl ether (3 × 5 mL). The combined organic phase was dried over anhydrous sodium sulfate and concentrated under reduced pressure to yield the crude product, which was purified by silica gel column chromatography using a mixture of ethyl acetate-hexane (0.5:9.5) to give the pure product **2**. All the products were characterized by ^{1}H, ^{13}C, ^{19}F and HRMS data as given below.

Physical and spectra data of the products 2:

4,4,4-Trifluoro-2-(4-methyl-benzylidene)-butyric acid ethyl ester (2a): Rf (5%, EA/PE) = 0.65; Colourless oily liquid (73%, 198.63 mg); (*E*/*Z* = 95/5); **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.26 (t, *J* = 7.0 Hz, 3H), 2.3 (s, 3H), 3.34 (q, $^{3}J_{H\text{-}F}$ = 10.0 Hz, 2H), 4.22 (q, *J* = 7.5 Hz, 2H), 7.15 (d, *J* = 7.5 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.87 (s, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ = 14.2, 21.3, 31.8 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz), 61.4, 121.8, 122.5 (q, $^{1}J_{C\text{-}F}$ = 276.4 Hz), 129.2, 129.5, 131.4, 139.6, 144.9, 167.2; **^{19}F NMR** (470 MHz, $CDCl_3$): δ = -63.09 (s, 3F). **HRMS** (ESI+): $(M+H)^+$ calcd for $C_{14}H_{16}F_3O_2$ 273.1097, found 273.1108.

4,4,4-Trifluoro-2-(4-methyl-benzylidene)-butyric acid butyl ester (2b): Rf (5%, EA/PE) = 0.62; Colourless oily liquid (76%, 228.09 mg); (*E*/*Z* = 94/6); **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7.5 Hz, 3H), 1.34 (sextet, *J* = 8.5 Hz, 2H), 1.60 (quintet, *J* = 6.5 Hz, 2H), 3.33 (q, $^{3}J_{H\text{-}F}$ = 10.0 Hz, 2H), 4.16 (t, *J* = 7.0 Hz, 2H), 7.14 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.86 (s, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ = 13.7, 19.2, 21.3, 30.6, 31.8 (q, $^{2}J_{C\text{-}F}$ = 30.0 Hz), 65.3, 121.8, 122.5 (q, $^{1}J_{C\text{-}F}$ = 276.1 Hz), 129.2, 129.5, 131.4, 139.6, 144.9, 167.3; **^{19}F NMR** (470 MHz, $CDCl_3$): δ = -63.4 (s, 3F). **HRMS** (ESI+): $(M+H)^+$ calcd for $C_{16}H_{20}F_3O_2$ 301.1410, found 301.1409.

2-Benzylidene-4,4,4-trifluoro-butyric acid butyl ester (2c): Rf (5%, EA/PE) = 0.65; Colourless oily liquid (69%, 197.41 mg); (*E*/*Z* = 93/7); **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.5 Hz, 3H), 1.34 (sextet, *J* = 5.5 Hz, 2H), 1.61 (quintet, *J* = 6.5 Hz, 2H), 3.33 (q, $^{3}J_{H\text{-}F}$ = 10.0 Hz, 2H), 4.17 (t, *J* = 7.0 Hz, 2H), 7.30-7.35 (m, 5H), 7.90 (s, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ = 13.6, 19.1, 30.6, 31.7 (q, $^{2}J_{C\text{-}F}$ = 30.5 Hz), 65.3, 122.3 (q, $^{1}J_{C\text{-}F}$ = 276.5 Hz), 128.7, 128.8, 129.2, 134.3, 144.9, 167.0; **^{19}F NMR** (470 MHz, $CDCl_3$): δ = -62.9 (s, 3F). **HRMS** (ESI+): $(M+H)^+$ calcd for $C_{15}H_{18}F_3O_2$ 287.1253, found 287.1246.

2-Benzylidene-4,4,4-trifluoro-butyric acid isobutyl ester (2d): Rf (5%, EA/PE) = 0.66; Colourless oily liquid (63%, 180.24 mg); (*E*/*Z* = 81/19); **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.92 (d, *J* = 6.5 Hz, 6H), 1.92-2.10 (m, 1H), 3.33 (q, $^{3}J_{H\text{-}F}$ = 10.0 Hz, 2H), 3.96 (d, *J* = 6.5 Hz, 2H), 7.18-7.20 (m, 1H), 7.26-7.27 (m, 1H), 7.30-7.38 (m, 2H), 7.91 (s, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ = 19.2, 27.9, 31.8 (q, $^{2}J_{C\text{-}F}$ = 30.1 Hz), 71.7, 122.4 (q, $^{1}J_{C\text{-}F}$ =

275.0 Hz), 122.9, 128.8, 128.9, 129.3, 134.4, 145.1, 167.1; **^{19}F NMR** (470 MHz, $CDCl_3$): δ = -63.0 (s, 3F). **HRMS** (ESI+): $(M+H)^+$ calcd for $C_{15}H_{18}F_3O_2$ 287.1253, found 287.1251.

2-Benzylidene-4,4,4-trifluoro-butyric acid methyl ester (2e):[2d] Rf (5%, EA/PE) = 0.70; Colourless oily liquid (67%, 163.52 mg); (*E*/*Z* = 96/4); **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 3.40 (q, $^3J_{H-F}$ = 10.5 Hz, 2H), 3.86 (s, 3H), 7.38-7.40 (m, 5H), 7.90 (s, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ = 31.8 (q, $^2J_{C-F}$ = 28.8 Hz), 52.5, 119.2 (q, $^1J_{C-F}$ = 279.2 Hz), 122.5, 126.3, 128.9, 129.4, 145.3, 175.5; **^{19}F NMR** (470 MHz, $CDCl_3$): δ = -63.0 (s, 3F). **HRMS** (ESI+): $(M+H)^+$ calcd for $C_{12}H_{12}F_3O_2$ 245.0784, found 245.0781.

2-Benzylidene-4,4,4-trifluoro-butyric acid ethyl ester (2f): Rf (5%, EA/PE) = 0.70; Colourless oily liquid (67%, 167.75 mg); (*E*/*Z* = 95/5); **^{1}H NMR (500 MHz, $CDCl_3$)**: δ = 1.27 (t, *J* = 7.0 Hz, 3H), 3.30 (q, $^3J_{H-F}$ = 10.0 Hz, 2H), 4.2 (q, *J* = 7.0 Hz, 2H), 7.31-7.37 (m, 5H, 7.91 (s, 1H); **^{13}C NMR (126 MHz, $CDCl_3$)**: δ = 14.2, 31.7 (q, $^2J_{C-F}$ = 30.1 Hz), 61.5, 120.8 (q, $^1J_{C-F}$ = 256.5 Hz), 122.0, 128.9, 129.3, 134.4, 145.0, 167.1; **^{19}F NMR (470 MHz, $CDCl_3$)**: δ = -63.0 (s, 3F). **HRMS** (ESI+): $(M+H)^+$ calcd for $C_{13}H_{14}F_3O_2$ 259.0940, found 259.0938.

2-Benzylidene-4,4,4-trifluoro-butyric acid tert-butyl ester (2g): Rf (5%, EA/PE) = 0.72; Colourless oily liquid (67%, 205.99 mg); (*E*/*Z* = 95/5); **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.47 (s, 9H), 3.26 (q, $^3J_{H-F}$ = 10.5 Hz, 2H), 7.28-7.35 (m, 5H), 7.81 (s, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ = 27.9, 31.8 (q, $^2J_{C-F}$ = 30.2 Hz), 81.65, 122.4 (q, $^1J_{C-F}$ = 276.5 Hz), 124.4, 128.7, 128.9, 129.0, 134.6, 143.9, 166.1; **^{19}F NMR** (470 MHz, $CDCl_3$): δ = -63.0 (s, 3F). **HRMS** (ESI+): $(M+H)^+$ calcd for $C_{15}H_{18}F_3O_2$ 287.1257, found 287.1251.

4,4,4-Trifluoro-2-(4-methoxy-benzylidene)-butyronitrile (2h): Rf (5%, EA/PE) = 0.55; Colourless oily liquid (78%, 188.03 mg); (*E*/*Z* = 99/1); **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 3.03 (q, $^3J_{H-F}$ = 10.0 Hz, 2H), 3.8 (s, 3H), 6.88-6.91 (m, 2H), 7.0 (s, 1H), 7.70-7.73 (m, 2H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ = 39.7 (q, $^2J_{C-F}$ = 31.2 Hz), 55.4, 95.8, 114.4, 118.1, 121.6 (q, $^1J_{C-F}$ = 256.4 Hz), 125.3, 131.2, 149.7, 161.9; **^{19}F NMR** (470 MHz, $CDCl_3$): δ = -66.0 (s, 3F). **HRMS** (ESI+): $(M+H)^+$ calcd for $C_{12}H_{11}F_3NO$ 242.0787, found 242.0790.

4,4,4-Trifluoro-2-(4-fluoro-benzylidene)-butyric acid methyl ester (2i): Rf (5%, EA/PE) = 0.62; Colourless oily liquid (63%, 165.09 mg); (*E*/*Z* = 95/5); **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 3.3 (q, $^{3}J_{H-F}$ = 10.5 Hz, 2H), 3.79 (s, 3H), 7.03-7.07 (m, 2H), 7.30-7.34 (m, 2H), 7.87 (s, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ = 32.5 (q, $^{2}J_{C-F}$ = 30.1 Hz), 52.5, 115.9, 116.0, 120.2 (q, $^{1}J_{C-F}$ = 219.5 Hz), 130.3, 131.0 (d, $^{1}J_{C-F}$ = 8.5 Hz), 144.1, 164.2, 167.4; **^{19}F NMR** (470 MHz, $CDCl_3$): δ = -110.6 (s, 1F), -63.0 (s, 3F). **HRMS** (ESI+): $(M+H)^+$ calcd for $C_{12}H_{11}F_4O_2$ 263.0690, found 263.0687.

2-(4-Chloro-benzylidene)-4,4,4-trifluoro-butyric acid methyl ester (2j): Rf (5%, EA/PE) = 0.57; Colourless oily liquid (60%, 166.80 mg); (*E*/*Z* = 89/11); **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 3.30 (q, $^{3}J_{H-F}$ = 10.0 Hz, 2H), 3.38 (s, 3H), 7.26 (d, *J* = 8.5 Hz, 2H), 7.33 (d , J = 8.5 Hz, 2H), 7.86 (s, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ = 31.7 (q, $^{2}J_{C-F}$ = 30.7 Hz), 52.5, 122.1 (q, $^{1}J_{C-F}$ = 276.7 Hz), 123.0, 129.0, 130.2, 132.6, 135.4, 143.8, 167.1; **^{19}F NMR** (470 MHz, $CDCl_3$): δ = -63.3 (s, 3F). **HRMS** (ESI+): $(M+H)^+$ calcd for $C_{12}H_{11}ClF_3O_2$ 279.0394, found 279.0401.

2-(4-Chloro-benzylidene)-4,4,4-trifluoro-butyric acid ethyl ester (2k): Rf (5%, EA/PE) = 0.57; Colourless oily liquid (67%, 196.09 mg); (*E*/*Z* = 89/11); **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.27 (t, *J* = 7.0 Hz, 3H), 3.29 (q, $^{3}J_{H-F}$ = 10.5 Hz, 2H), 4.22 (q, *J* = 7.0 Hz, 2H), 7.24-7.26 (m, 2H), 7.32-7.34 (m, 2H), 7.84 (s, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ = 14.1, 31.7(q, $^{2}J_{C-F}$ = 30.3 Hz), 61.6, 122.2 (q, $^{1}J_{C-F}$ = 276.7 Hz), 123.4, 129.0, 130.1, 132.7, 135.4, 143.6, 166.7; **^{19}F NMR** (470 MHz, $CDCl_3$): δ = -63.1 (s, 3F). **HRMS** (ESI+): $(M+H)^+$ calcd for $C_{13}H_{13}ClF_3O_2$ 293.0551, found 293.0563.

2-(4-Chloro-benzylidene)-4,4,4-trifluoro-butyric acid butyl ester (2l): Rf (5%, EA/PE) = 0.55; Colourless oily liquid (62%, 198.44 mg); (*E*/*Z* = 91/9); **^{1}H NMR (500 MHz, $CDCl_3$)**: δ = 0.88 (t, *J* = 7.5 Hz, 3H), 1.35 (sextet, *J* = 3.5 Hz, 2H), 1.61 (quintet, *J* = 7.0 Hz, 2H), 3.29 (q, $^{3}J_{H-F}$ = 10.5 Hz, 2H), 4.18 (t, *J* = 6.5 Hz, 2H), 7.24-7.26 (m, 2H), 7.32-7.34 (m, 2H), 7.84 (s, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ = 13.7, 19.2, 30.7, 31.8 (q, $^{2}J_{C-F}$ = 30.2 Hz), 65.5, 123.5, 126.0 (q, $^{1}J_{C-F}$ = 302.8 Hz), 129.2, 130.9, 133.1, 135.5,

143.6, 166.8; **^{19}F NMR** (470 MHz, $CDCl_3$): δ = -63.4 (s, 3F). **HRMS** (ESI+): $(M+H)^+$ calcd for $C_{15}H_{17}ClF_3O_2$ 321.0864, found 321.0859.

2-(3-Chloro-benzylidene)-4,4,4-trifluoro-butyronitrile (2m): Rf (5%, EA/PE) = 0.55; Colourless oily liquid (67%, 164.16 mg); (*E*/*Z* = 79/21); **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 3.09 (q, $^3J_{H-F}$ = 10.0 Hz, 2H), 7.0 (s, 1H), 7.33-7.39 (m, 2H), 7.64 (s, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ = 39.7 (q, $^2J_{C-F}$ = 31.1 Hz), 101.2, 116.9, 124.5 (q, $^1J_{C-F}$ = 248.0 Hz), 126.9, 129.2, 130.3, 131.2, 134.1, 135.1, 148.6, 149.3; **^{19}F NMR** (470 MHz, $CDCl_3$): δ = -65.7 (s, 3F). **HRMS** (ESI+): $(M+H)^+$ calcd for $C_{11}H_8ClF_3N$ 246.0292, found 246.0291.

2-(3-Chloro-benzylidene)-4,4,4-trifluoro-butyric acid ethyl ester (2n): Rf (5%, EA/PE) = 0.57; Colourless oily liquid (65%, 189.82 mg; (*E*/*Z* = 93/7); **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.26 (t, *J* = 7.5 Hz, 3H), 3.28 (q, $^3J_{H-F}$ = 10.0 Hz, 2H), 4.20 (q, *J* = 6.5 Hz, 2H), 7.18-7.20 (m, 2H), 7.28 (d, *J* = 5.0 Hz, 2H), 7.80 (s, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ = 14.1, 31.7(q, $^2J_{C-F}$ = 30.8 Hz), 61.6, 124.3, 124.6 (q, $^1J_{C-F}$ = 251.8 Hz), 126.7, 128.8, 129.2, 130.1, 134.8, 136.1, 143.4, 166.6; **^{19}F NMR** (470 MHz, $CDCl_3$): δ = -63.3 (s, 3F). **HRMS** (ESI+): $(M+H)^+$ calcd for $C_{13}H_{13}ClF_3O_2$ 293.0551, found 293.0547.

2-(3-Chloro-benzylidene)-4,4,4-trifluoro-butyric acid butyl ester (2o): Rf (5%, EA/PE) = 0.57; Colourless oily liquid (63%, 201.66 mg; (*E*/*Z* = 90/10); **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.95 (t, *J* = 7.5 Hz, 3H), 1.40 (sextet, *J* = 7.5 Hz, 2H), 1.68 (quintet, *J* = 7.0 Hz, 2H), 3.35 (q, $^3J_{H-F}$ = 10.5 Hz, 2H), 4.20 (t, *J* = 6.5 Hz, 2H), 7.25-7.28 (m, 1H), 7.35 (d, *J* = 4.5 Hz, 3H), 7.89 (s, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ = 13.7, 19.2, 30.7, 31.7 (q, $^2J_{C-F}$ = 30.6 Hz), 65.6, 124.3, 124.4 (q, $^1J_{C-F}$ = 263.2 Hz), 126.8, 128.8, 129.2, 130.1, 134.8, 136.2, 143.4, 166.7; **^{19}F NMR** (470 MHz, $CDCl_3$): δ = -63.3 (s, 3F). **HRMS** (ESI+): $(M+H)^+$ calcd for $C_{15}H_{17}ClF_3O_2$ 321.0864, found 321.0874.

2-(3-Chloro-benzylidene)-4,4,4-trifluoro-butyric acid tert-butyl ester (2p): Rf (5%, EA/PE) = 0.60; Colourless oily liquid (60%, 192.04 mg; (*E*/*Z* = 89/11); **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.46(s, 9H), 3.21 (q, $^3J_{H-F}$ = 10.0 Hz, 2H), 7.14-7.19 (m, 2H), 7.25-7.28 (m, 2H), 7.7 (s, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ = 27.9, 31.8 (q, $^2J_{C-F}$ = 30.1 Hz),

81.9, 122.2 (q, $^{1}J_{C\text{-}F}$ = 263.2 Hz), 125.7, 128.7, 128.9, 129.9, 134.7, 136.4, 144.2, 165.6; **^{19}F NMR** (470 MHz, $CDCl_3$): δ = -63.1 (s, 3F). **HRMS** (ESI+): $(M+H)^+$ calcd for $C_{15}H_{17}ClF_3O_2$ 321.0864, found 321.0874.

2-(2-Bromo-benzylidene)-4,4,4-trifluoro-butyric acid methyl ester (2q): Rf (5%, EA/PE) = 0.65; Colourless oily liquid (68%, 225.14 mg; (*E*/*Z* = 92/8); **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 3.17 (q, $^{3}J_{H\text{-}F}$ = 10.5 Hz, 2H), 3.81 (s, 3H), 7.13-7.19 (m, 1H), 7.22 (d, *J* = 7.0 Hz, 1H), 7.28-7.31 (m, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.86 (s, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ = 31.7 (q, $^{2}J_{C\text{-}F}$ = 30.7 Hz), 52.6, 121.9, 123.5, 124.2 (q, $^{1}J_{C\text{-}F}$ = 276.6 Hz), 124.5, 127.5, 129.4, 132.9, 134.95, 144.5, 166.8; **^{19}F NMR** (470 MHz, $CDCl_3$): δ = -63.7 (s, 3F). **HRMS** (ESI+): $(M+H)^+$ calcd for $C_{12}H_{11}BrF_3O_2$ 322.9889, found 322.9907.

2-(2-Bromo-benzylidene)-4,4,4-trifluoro-butyric acid ethyl ester (2r): Rf (5%, EA/PE) = 0.65; Colourless oily liquid (65%, 218.39 mg; (*E*/*Z* = 89/11); **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.28 (t, *J* = 7.5 Hz, 3H), 3.16 (q, $^{3}J_{H\text{-}F}$ = 10.0 Hz, 2H), 4.25(q, *J* = 7.0 Hz, 2H), 7.15-7.22 (m, 1H), 7.23 (d, *J* = 6.0 Hz, 1H), 7.28-7.31 (m, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.86 (s, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ = 14.12, 31.7 (q, $^{2}J_{C\text{-}F}$ = 30.3 Hz), 61.6, 122.0 (q, $^{1}J_{C\text{-}F}$ = 276.0 Hz), 123.5, 124.8, 127.5, 129.5, 130.3, 132.9, 135.0, 144.3, 166.4; **^{19}F NMR** (470 MHz, $CDCl_3$): δ = -63.1 (s, 3F). **HRMS** (ESI+): $(M+H)^+$ calcd for $C_{13}H_{13}BrF_3O_2$ 337.0046, found 337.0054.

2-(2-Bromo-benzylidene)-4,4,4-trifluoro-butyric acid butyl ester (2s): Rf (5%, EA/PE) = 0.62; Colourless oily liquid (63%, 229.33 mg; (*E*/*Z* = 91/9); **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.5 Hz, 3H), 1.36 (sextet, *J* = 7.5 Hz, 2H), 1.62 (quintet, *J* = 7.0 Hz, 2H), 3.16 (q, $^{3}J_{H\text{-}F}$ = 10.0 Hz, 2H), 4.19 (t, *J* = 7.0 Hz, 2H), 7.04-7.17 (m, 1H), 7.23 (d, *J* = 7.0 Hz, 1H), 7.28-7.31 (m, 1H), 7.56 (s, 1H), 7.86 (s, 1H); **^{13}C** NMR (125.7 MHz, $CDCl_3$): δ = 13.6, 19.1, 30.5, 31.6 (q, $^{2}J_{C\text{-}F}$ = 30.5 Hz), 65.5, 122.0 (q, $^{1}J_{C\text{-}F}$ = 276.7 Hz), 123.5, 124.7, 127.5, 129.5, 130.3, 132.9, 135.0, 144.2, 166.4; **^{19}F NMR** (470 MHz, $CDCl_3$): δ = -63.3 (s, 3F). **HRMS** (ESI+): $(M+H)^+$ calcd for $C_{15}H_{17}BrF_3O_2$ 365.0359, found 365.0355.

2-(3-Bromo-benzylidene)-4,4,4-trifluoro-butyric acid butyl ester (2t): Rf (5%, EA/PE) = 0.65; Colourless oily liquid (67%, 243.89 mg; (E/Z = 90/10); **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.5 Hz, 3H), 1.34 (sextet, *J* = 9.0 Hz, 2H), 1.61 (quintet, *J* = 7.0 Hz, 2H), 3.28 (q, $^{3}J_{H\text{-}F}$ = 10.0 Hz, 2H), 4.18 (t, *J* = 7.0 Hz, 2H), 7.18-7.20 (m, 1H), 7.28 (d, *J* = 5.0 Hz, 3H), 7.80 (s, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ = 13.7, 19.2, 30.6, 31.7 (q, $^{2}J_{C\text{-}F}$ = 30.5 Hz), 65.6, 124.3, 124.5 (q, $^{1}J_{C\text{-}F}$ = 246.4 Hz), 126.7, 128.8, 130.0, 130.4, 134.8, 136.1, 143.3, 166.7; **^{19}F NMR** (470 MHz, $CDCl_3$): δ = -62.9 (s, 3F). **HRMS** (ESI+): $(M+H)^+$ calcd for $C_{15}H_{17}BrF_3O_2$ 365.0359, found 365.0357.

4,4,4-Trifluoro-2-(3-methyl-benzylidene)-butyric acid butyl ester (2u): Rf (5%, EA/PE) = 0.65; Colourless oily liquid (73%, 219.09 mg; (*E*/*Z* = 92/8); **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.5 Hz, 3H), 1.36 (sextet, *J* = 4.5 Hz, 2H), 1.60 (quintet, *J* = 6.5 Hz, 2H), 2.33 (s, 3H), 3.34 (q, $^{3}J_{H\text{-}F}$ = 10.0 Hz, 2H), 4.19 (t, *J* = 7.0 Hz, 2H), 7.14 (d, *J* = 7.5 Hz, 3H), 7.24-7.27 (m, 1H), 7.89 (s, 1H); **^{13}C NMR (**125.7 MHz, $CDCl_3$): δ = 13.8, 19.2, 21.5. 30.7, 31.8 (q, $^{2}J_{C\text{-}F}$ = 30.0Hz), 65.4, 112.5, 122.6 (q, $^{1}J_{C\text{-}F}$ = 251.0 Hz), 125.9, 129.1, 129.7, 130.1, 134.4, 138.5, 145.2, 167.2; **^{19}F** NMR (470 MHz, $CDCl_3$): δ = -63.0 (s, 3F). **HRMS** (ESI+): $(M+H)^+$ calcd for $C_{16}H_{20}F_3O_2$ 301.1410, found 301.1409.

4,4,4-Trifluoro-2-thiophen-2-ylmethylene-butyric acid methyl ester (2v): Rf (5%, EA/PE) = 0.70; Colourless oily liquid (65%, 162.51 mg; (*E*/*Z* = 91/9); **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 3.28 (q, $^{3}J_{H\text{-}F}$ = 10.0 Hz, 2H), 3.79 (s, 3H), 7.22 (s, 1H), 7.44 (d, *J* = 7.5 Hz, 2H), 7.83 (s, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ = 31.78 (q, $^{2}J_{C\text{-}F}$ = 30.6Hz), 52.7, 122.2 (q, $^{1}J_{C\text{-}F}$ = 270.4 Hz), 122.9, 127.2, 130.4, 131.7, 132.3, 136.4, 143.6, 167.1; **^{19}F NMR** (470 MHz, $CDCl_3$): δ = -63.7 (s, 3F). **HRMS** (ESI+): $(M+H)^+$ calcd for $C_{10}H_{10}F_3O_2S$ 251.0348, found 251.0346.

4,4,4-Trifluoro-2-(3-methoxy-benzylidene)-butyric acid butyl ester (2w): Rf (5%, EA/PE) = 0.55; Colourless oily liquid (76%, 240.25 mg; (*E*/*Z* = 98/2); **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.5 Hz, 3H), 1.36 (sextet, *J* = 4.5 Hz, 2H), 1.60 (quintet, *J* = 6.5 Hz, 2H), 2.33 (s, 3H), 3.34 (q, $^{3}J_{H\text{-}F}$ = 10.0 Hz, 2H), 4.19 (t, *J* = 7.0 Hz, 2H), 7.14 (d, *J* = 7.5 Hz, 3H), 7.24-7.27 (m, 1H), 7.89 (s, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ = 13.7, 19.2, 30.7, 31.9 (q, $^{2}J_{C\text{-}F}$ = 30.6 Hz), 55.3, 65.4, 114.1, 115.1, 121.2, 122.4 (q, $^{1}J_{C\text{-}F}$ =

278.7 Hz), 123.1, 129.9, 135.7, 144.9, 159.8, 167.1; **^{19}F NMR** (470 MHz, $CDCl_3$): δ = -62.9 (s, 3F). **HRMS** (ESI+): $(M)^+$ calcd for $C_{16}H_{19}F_3O_3$ 316.1286, found 316.1289.

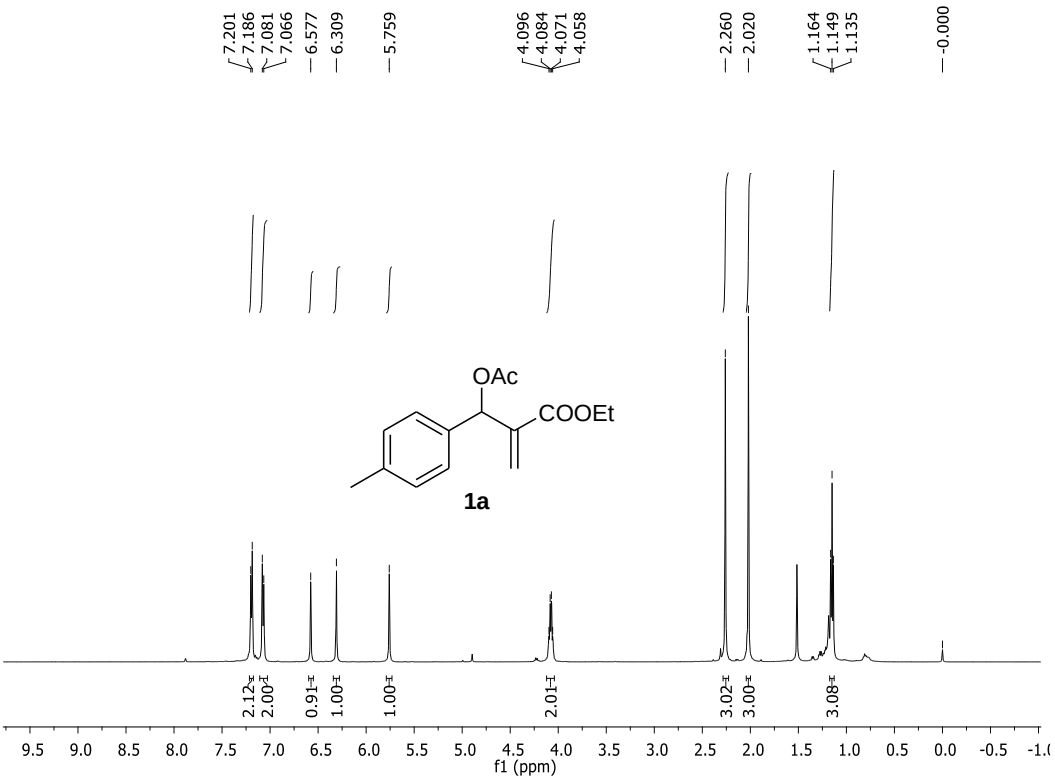
2-(4-Cyano-benzylidene)-4,4,4-trifluoro-butyric acid methyl ester (2x): Rf (5%, EA/PE) = 0.20; Colourless oily liquid (52%, 139.90 mg; (*E*/*Z* = 89/11); **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 3.33 (q, $^3J_{H\text{-}F}$ = 10.0 Hz, 2H), 3.88 (s, 3H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.96 (s, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ = 31.9 (q, $^2J_{C\text{-}F}$ = 17.8 Hz), 52.9, 113.0, 118.3, 125.4 (q, $^1J_{C\text{-}F}$ = 278.0 Hz), 129.3, 132.7, 133.0, 138.9, 143.1, 166.8; **^{19}F NMR** (470 MHz, $CDCl_3$): δ = -63.2 (s, 3F). **HRMS** (ESI+): $(M+H)^+$ calcd for $C_{13}H_{11}F_3NO_2$ 270.0736, found 2700749.

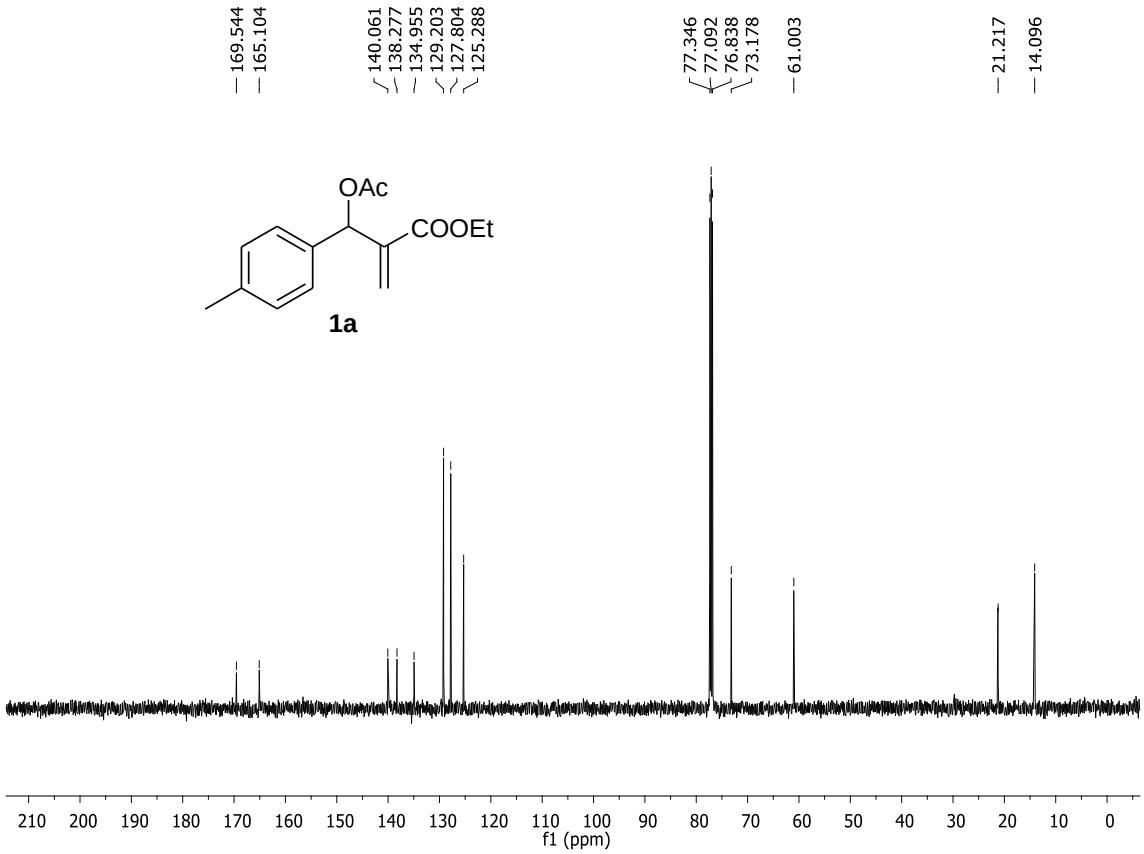
2-(2,4-Dichloro-benzylidene)-4,4,4-trifluoro-butyric acid methyl ester (2y): Rf (5%, EA/PE) = 0.40; Colourless oily liquid (57%, 177.80 mg; (*E*/*Z* = 90/10); **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 3.23 (q, $^3J_{H\text{-}F}$ = 10.5 Hz, 2H), 3.88 (s, 3H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.31-7.33 (m, 1H), 7.47 (d, *J* = 1.5, 1H), 7.92 (s, 1H); **^{13}C NMR** (125.7 MHz, $CDCl_3$): δ = 31.9 (q, $^2J_{C\text{-}F}$ = 30.8 Hz), 52.8, 122.0 (q, $^1J_{C\text{-}F}$ = 275.2 Hz), 127.5, 129.2, 129.9, 130.3, 131.7, 134.7, 135.8, 141.5, 166.7; **^{19}F NMR** (470 MHz, $CDCl_3$): δ = -63.4 (s, 3F). **HRMS** (ESI+): $(M+H)^+$ calcd for $C_{12}H_{10}Cl_2F_3O_2$ 313.0004, found 313.0019.

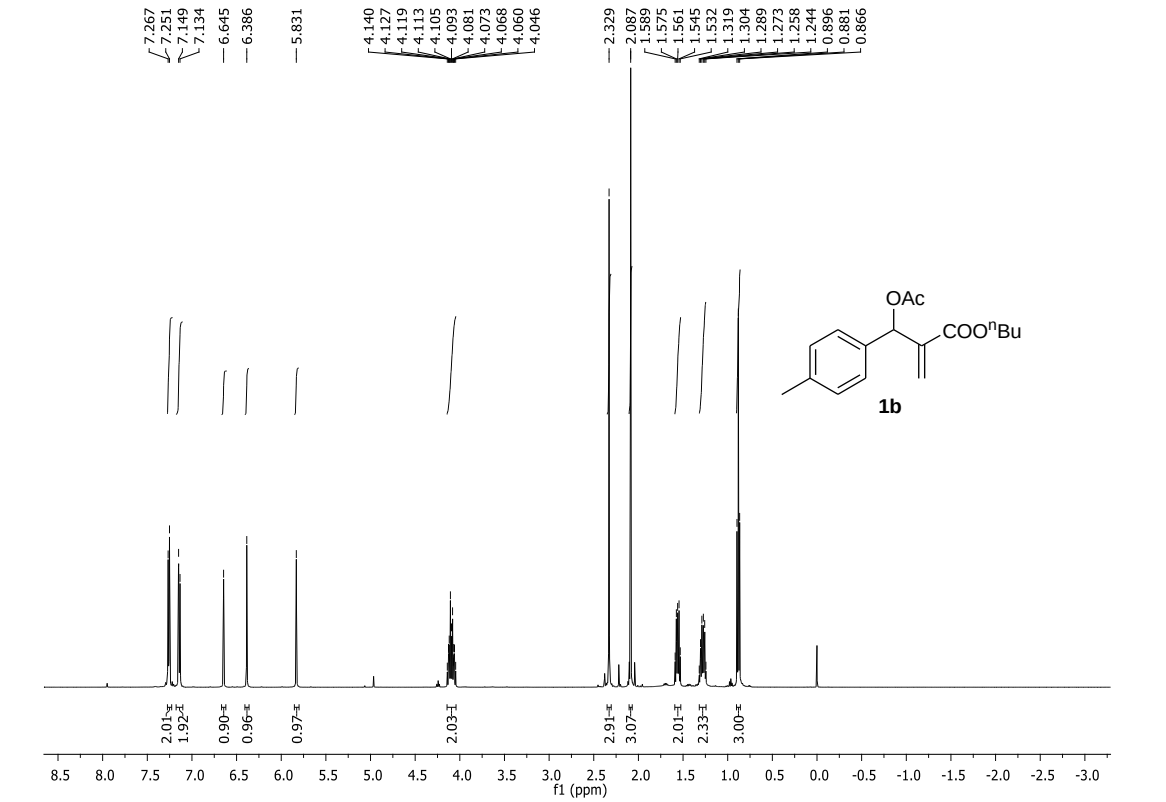
References

1. W. P. Juma, V. Chhiba, D. Brady and M. L. Bode*, Tetrahedron Asymmetry,* 2017, **28**, 1169.
2. (*a*) P. Zhou, Y. Liang, H. Zhang, H. Jiang, K. Feng, P. Xu, J. Wang, X. Wang, K. Ding, C. Luo, M. Liu and Y. Wang, *Eur. J. Med. Chem.*, 2018, **144**, 817; (*b*) S. Nag, S. Bhowmik, H. M. Gauniyal and S. Batra, *Eur. J. Org. Chem*., 2010, 4705; (*c*) M. Nayak and S. Batra, *Eur. J. Org. Chem*., 2009, 3505; (*d*) A. A. Zemtsov, V. V. Levin, A. D. Dilman, M. I. Sttruchkova, A. B. Pavel and V. A. Tartakovsky, *Eur. J. Org. Chem*., 2010, 6779; (*e*) M. Nayak G. Pandey and S. Batra, *Tetrahedron,* 2011, **67**, 7563; (*f*) B. Das, P. R. Thirupathi, A. Kumar and K. Laxminarayana, *D. Cluster*, 2007, **349**, 2677; (*g*) T. Ollevier, T. M. Mwene-Mbeja, *Tetrahedron,* 2008, **64**, 5150.

IX. Copies of ^{1}H & ^{13}C NMR Spectra of the Baylis-Hillman Acetate (1)



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1.575
1.561
1.545
1.532
1.319
1.304
1.289
1.273
1.258
1.244
0.896
0.881
0.866
OAc
COO^{n}Bu
1b
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0.96
0.97
2.03
2.91
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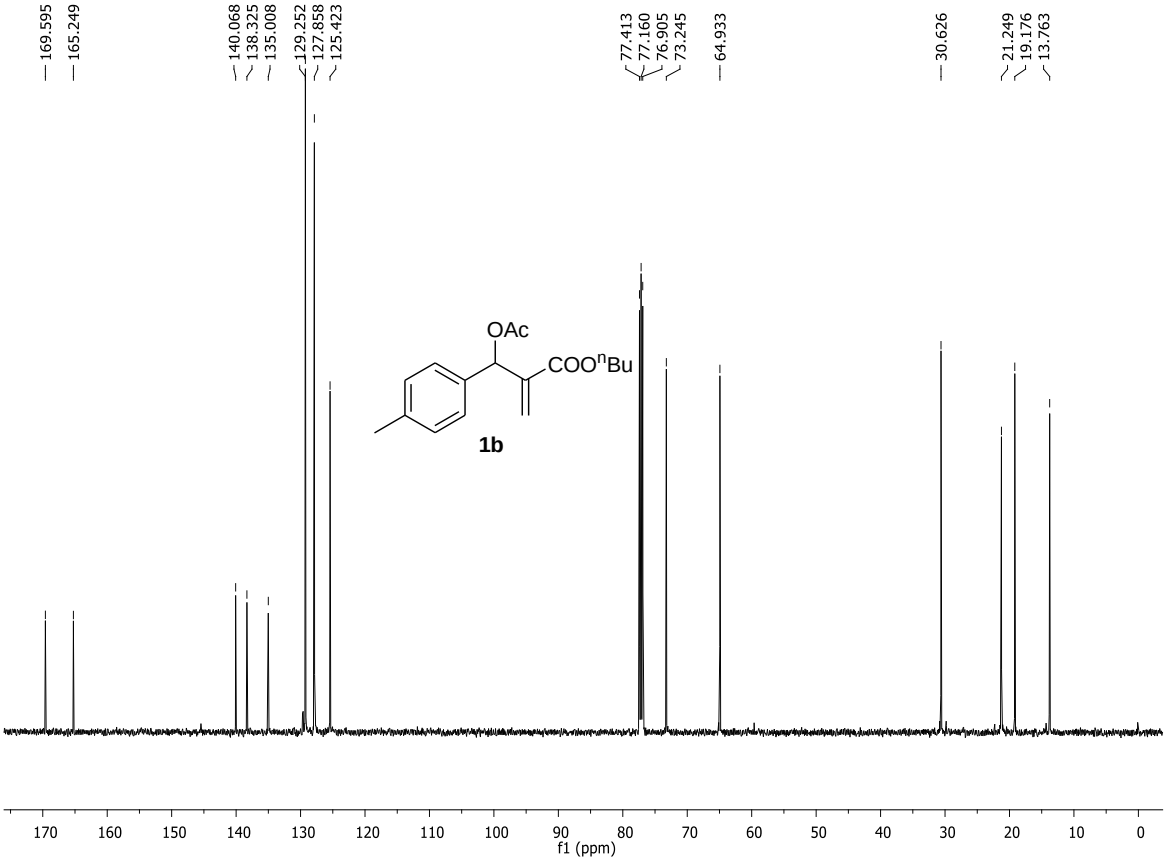
2.01
2.33
3.00
f1 (ppm)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21.249
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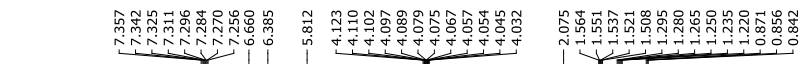
OAc
COO^{n}Bu
1b
f1 (ppm)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4.110
4.102
4.097
4.089
4.079
4.075
4.067
4.057
4.054
4.045
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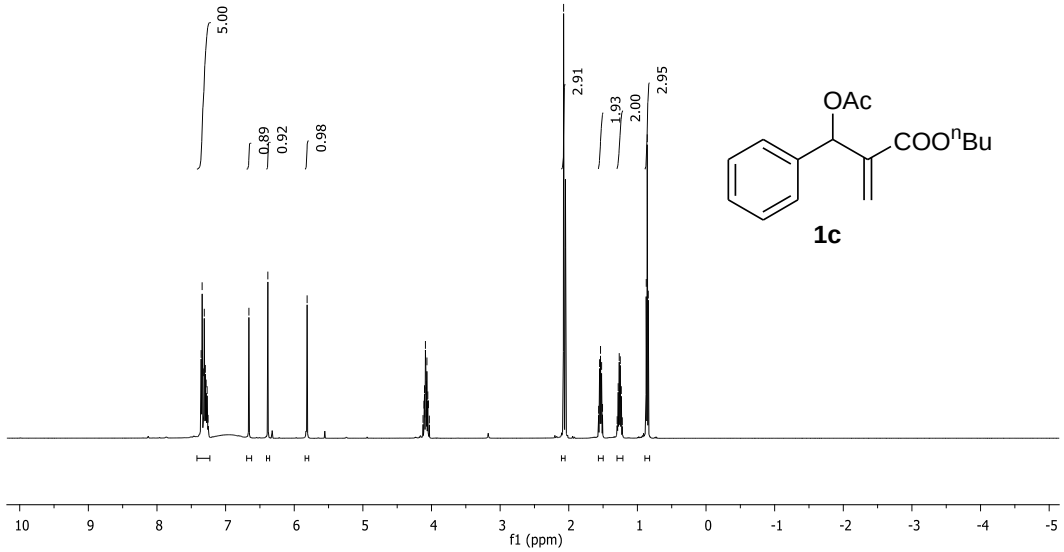
0.842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2.00
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COO^{n}Bu
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1c


169.629
165.182
139.891
137.873
128.482
128.420
127.775
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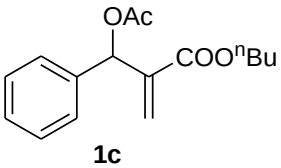
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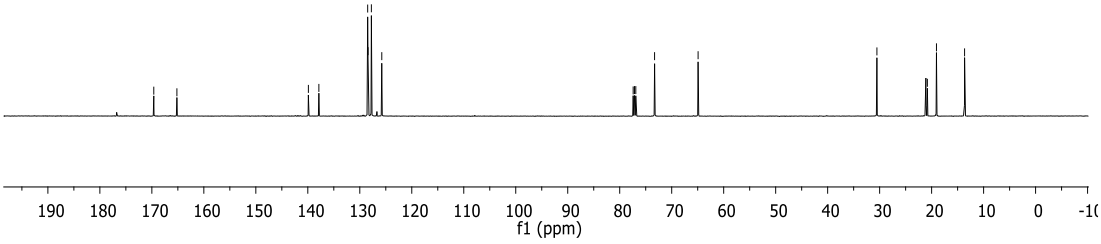
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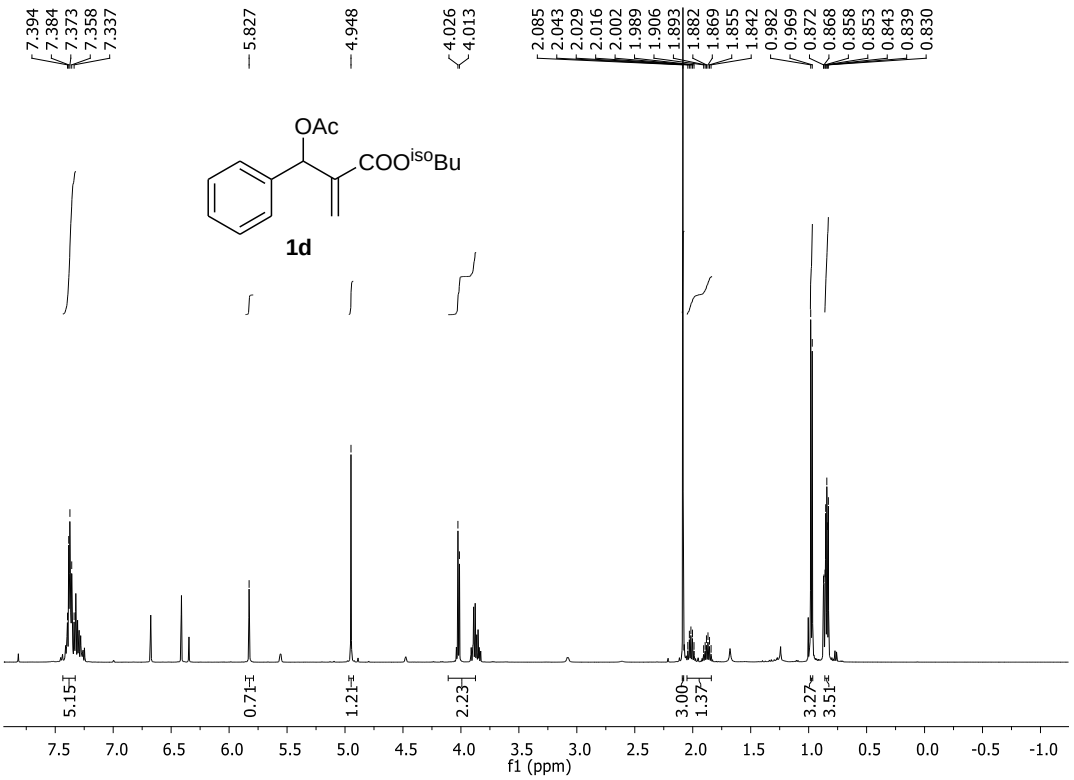
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2.016
2.002
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1.906
1.893
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0.969
0.872
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0.858
0.853
0.843
0.839
0.830
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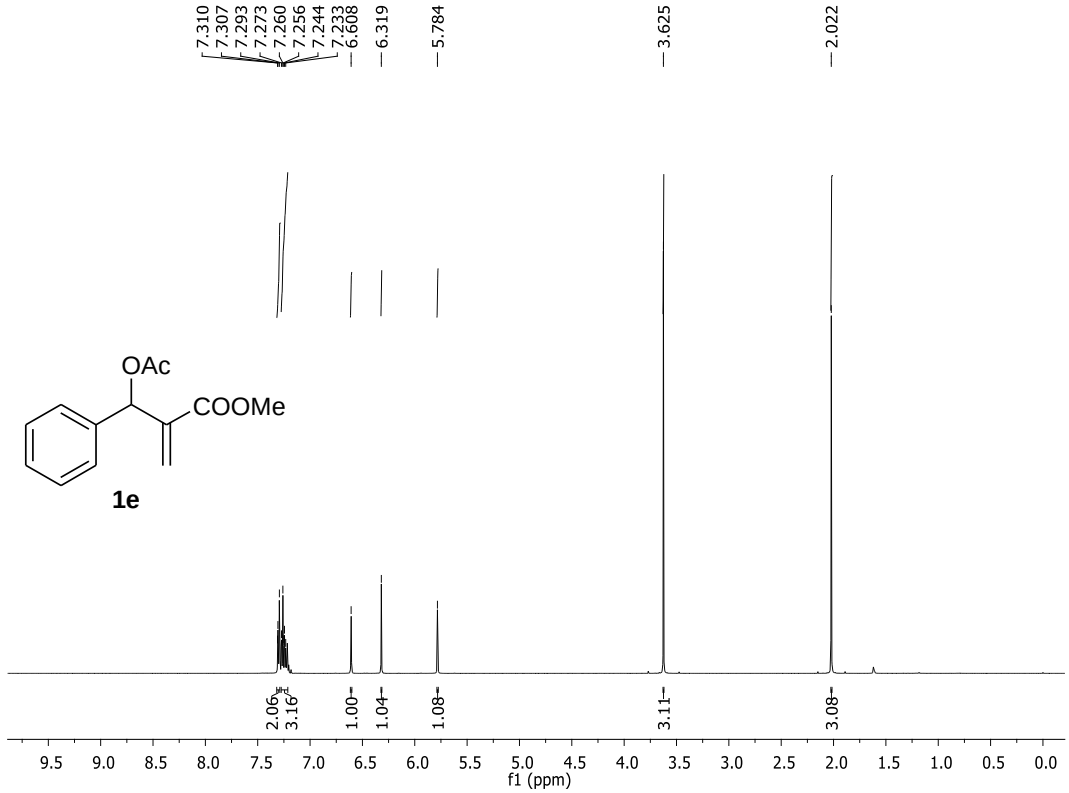
3.51
f1 (ppm)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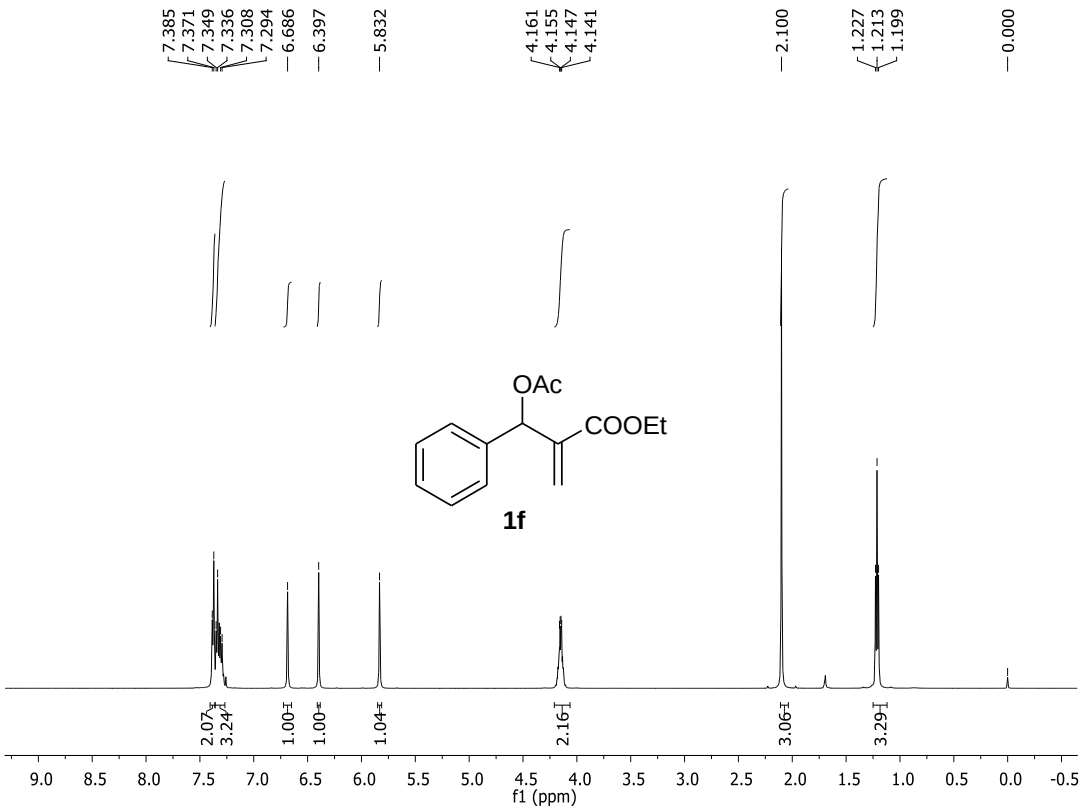
3.08
f1 (ppm)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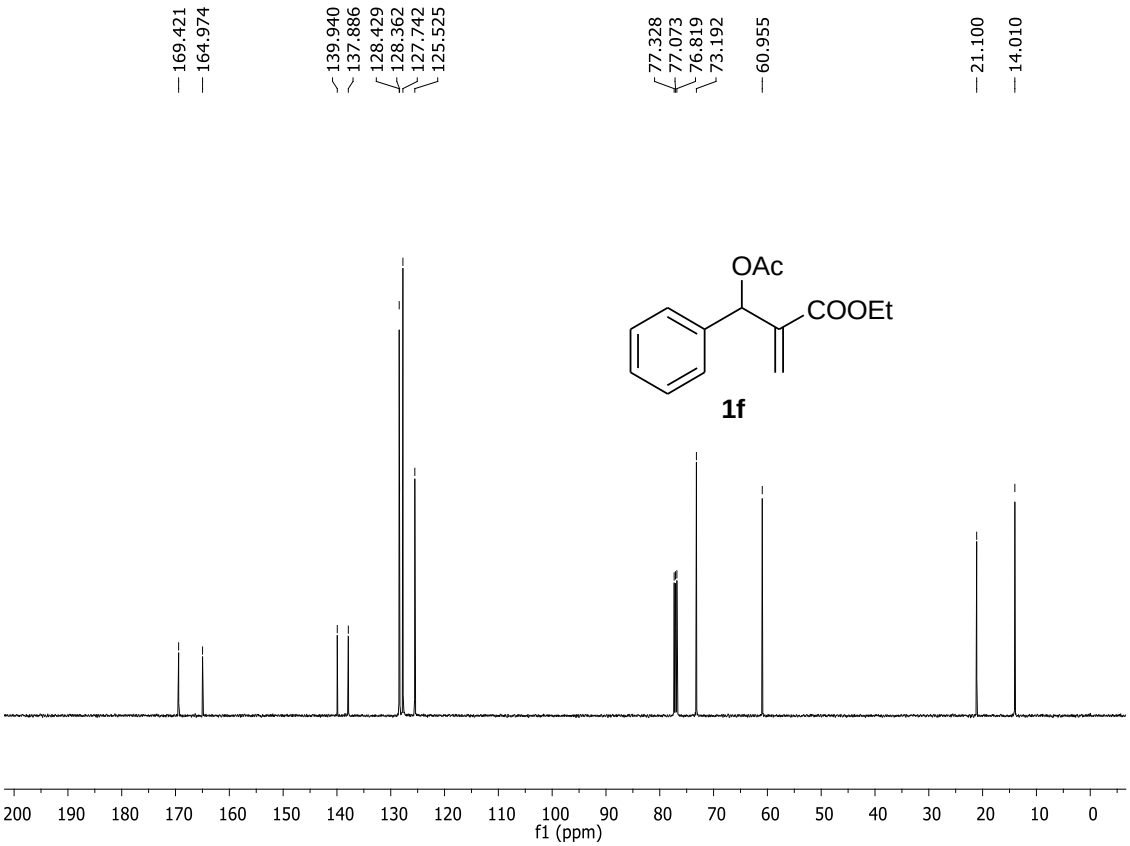
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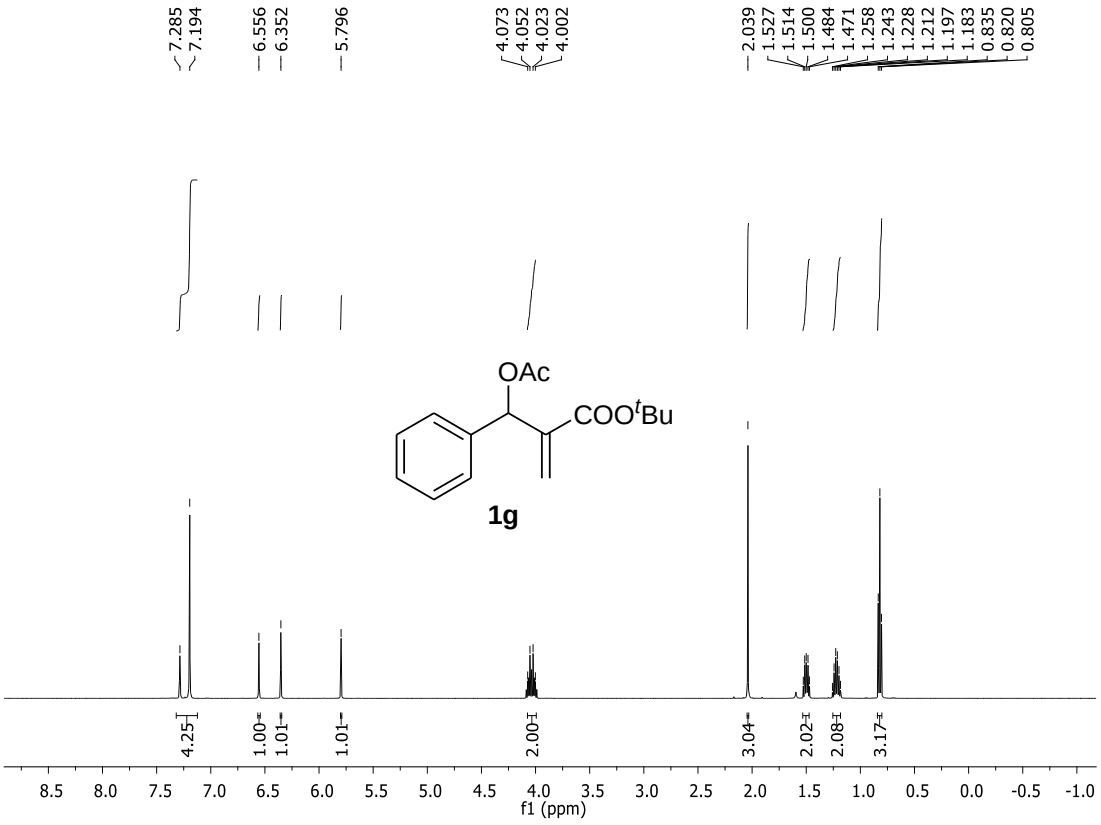
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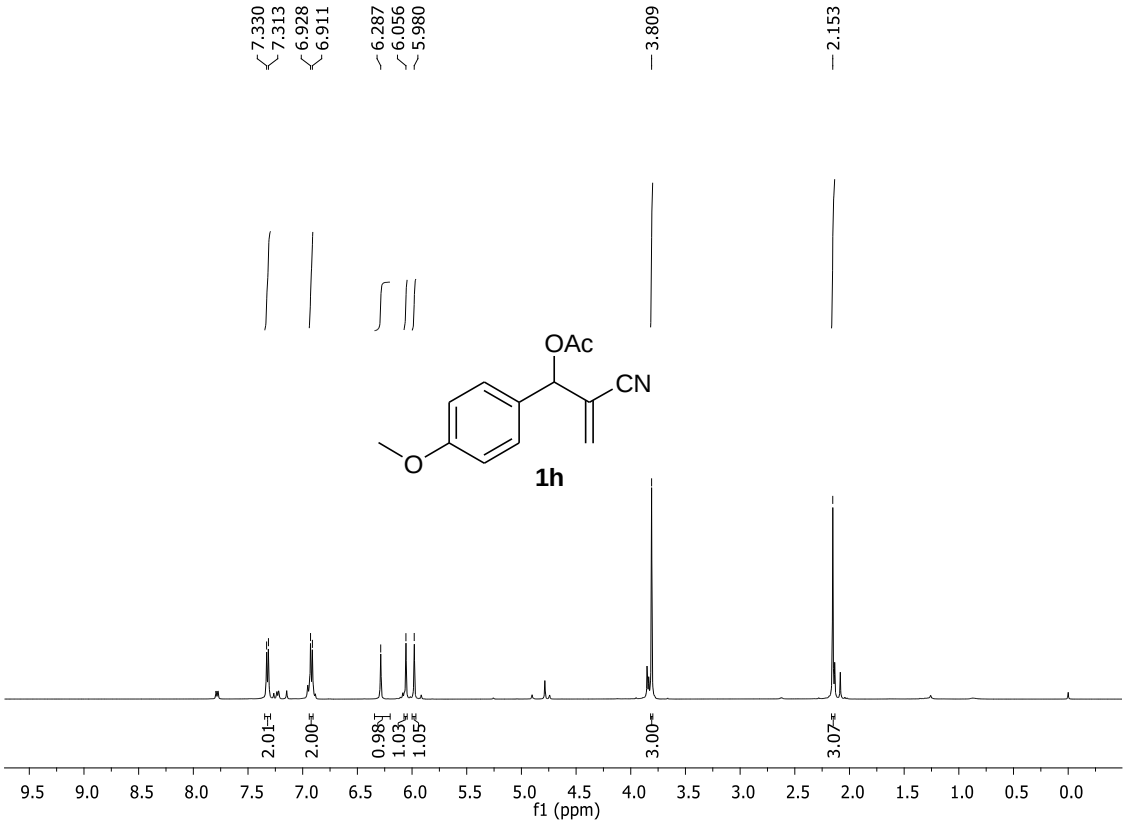
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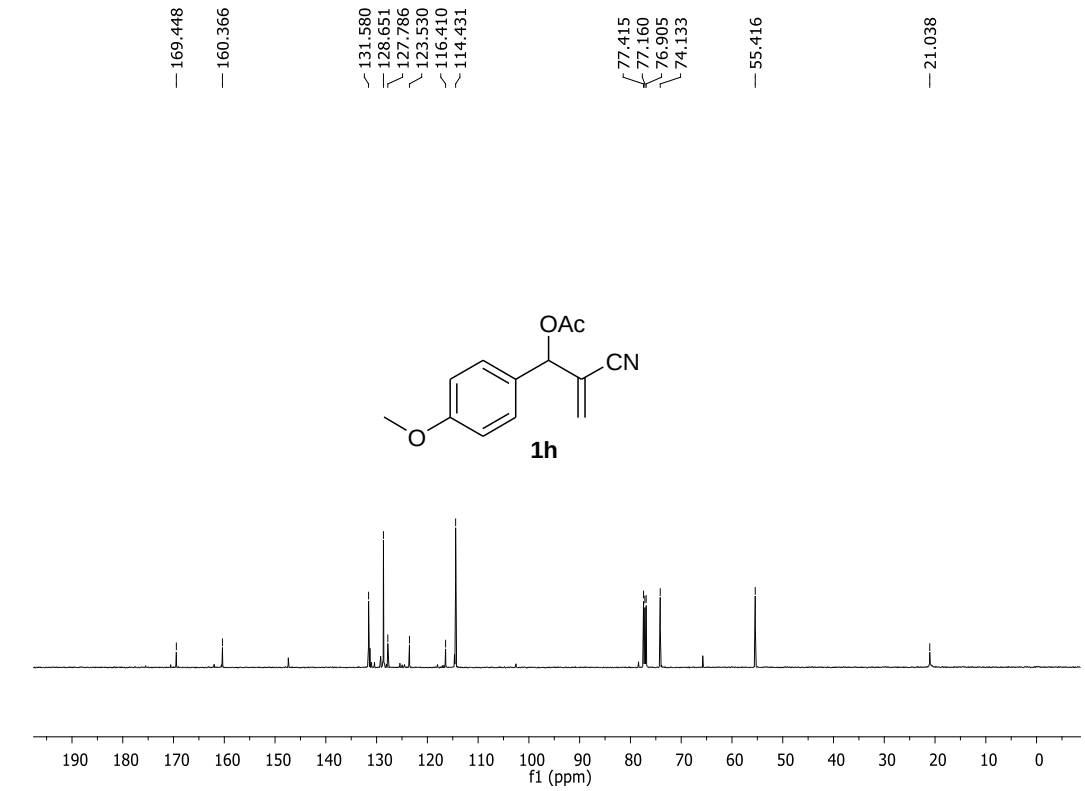
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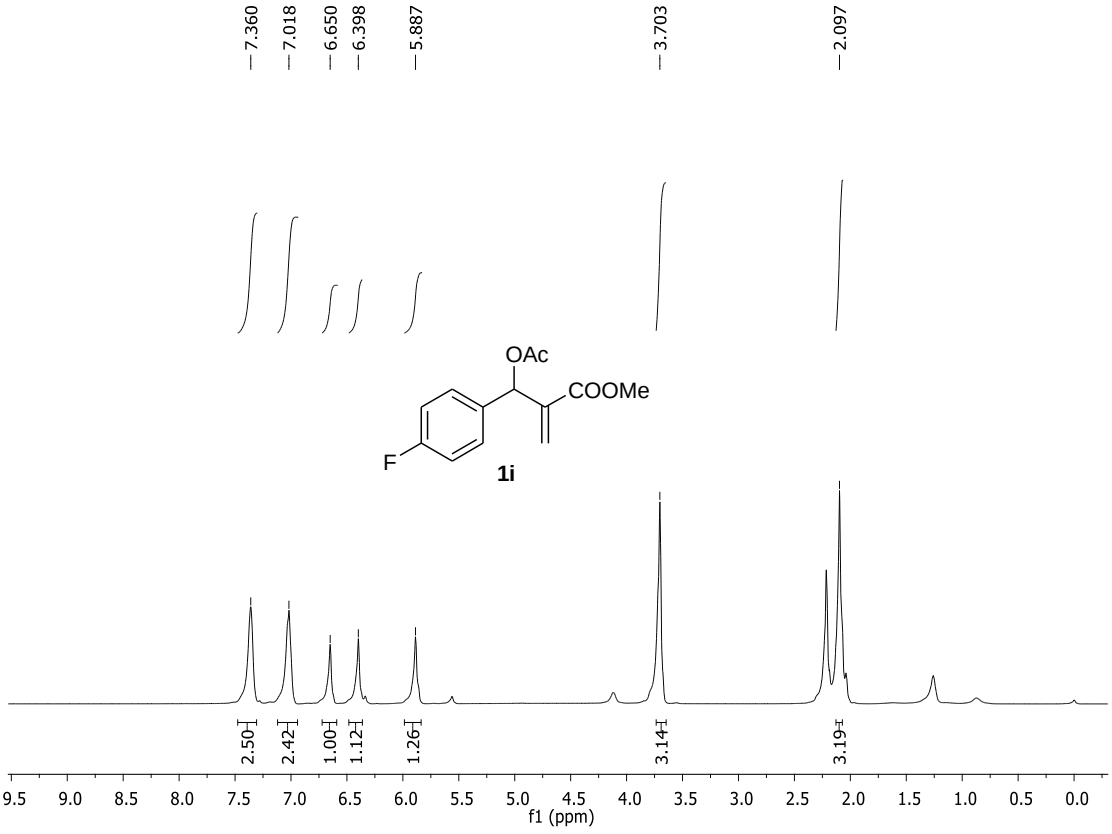
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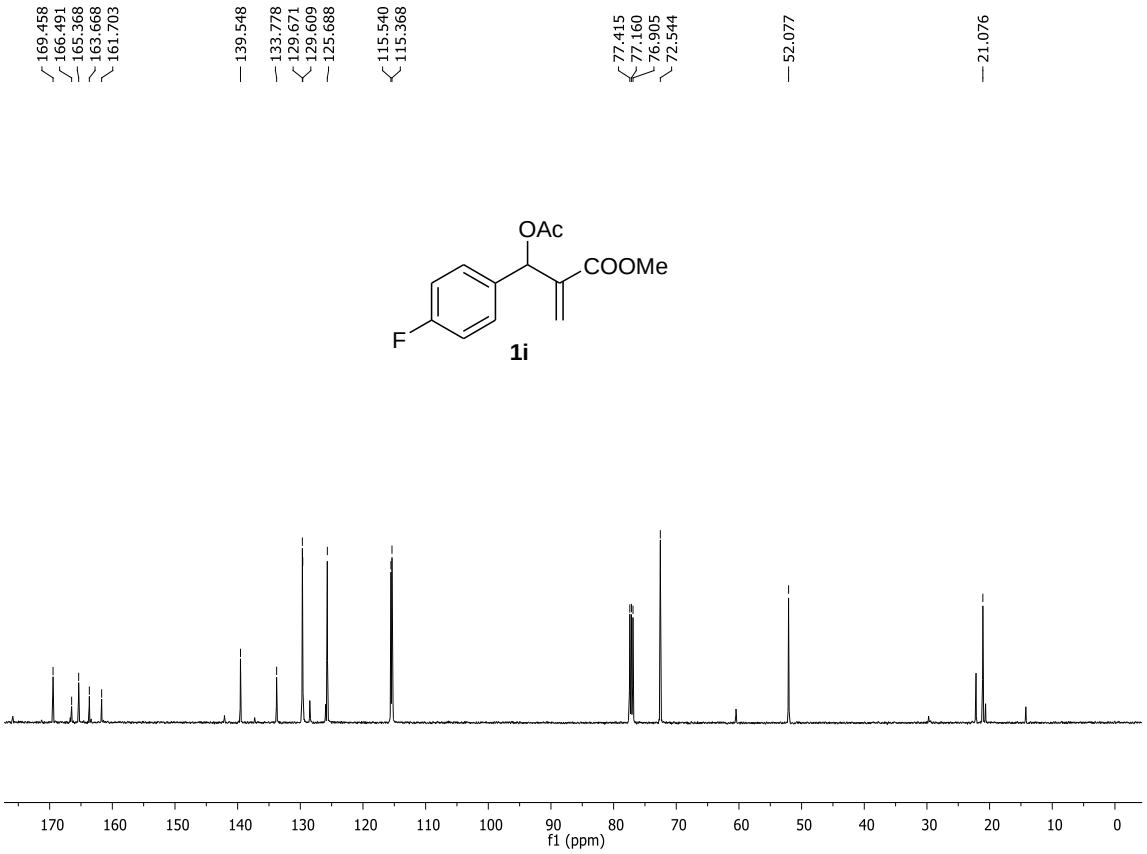
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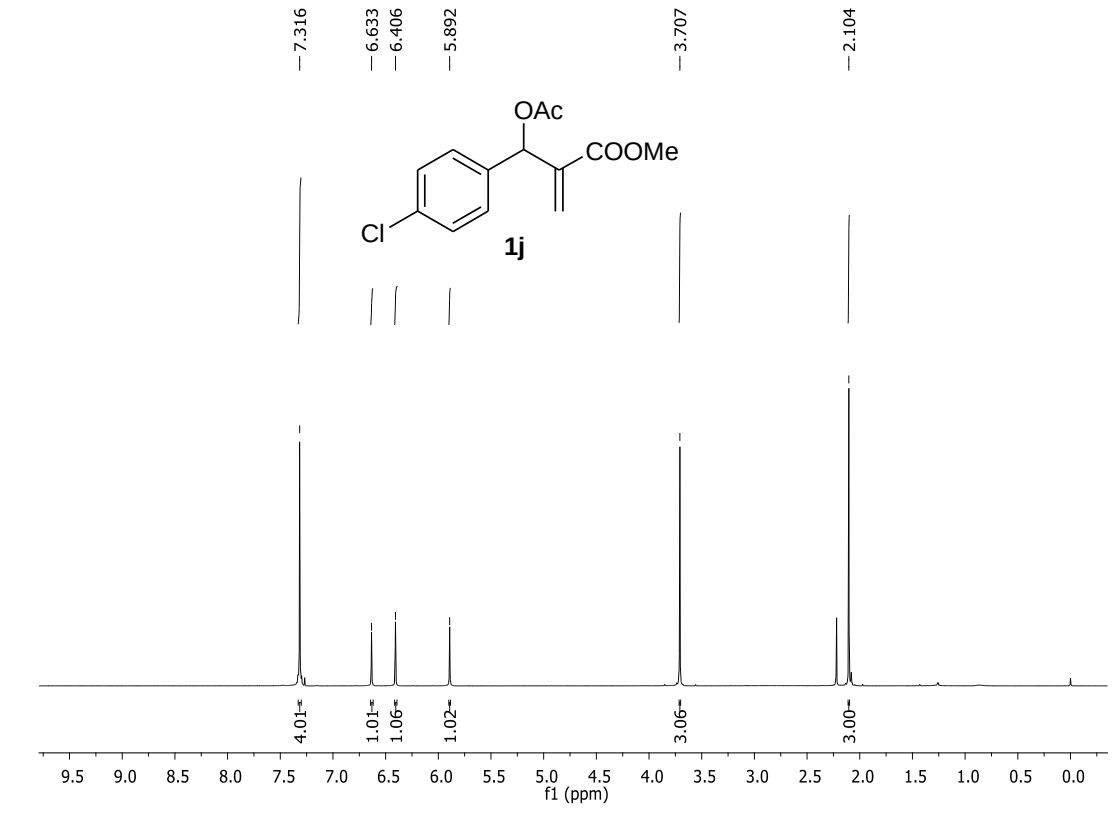
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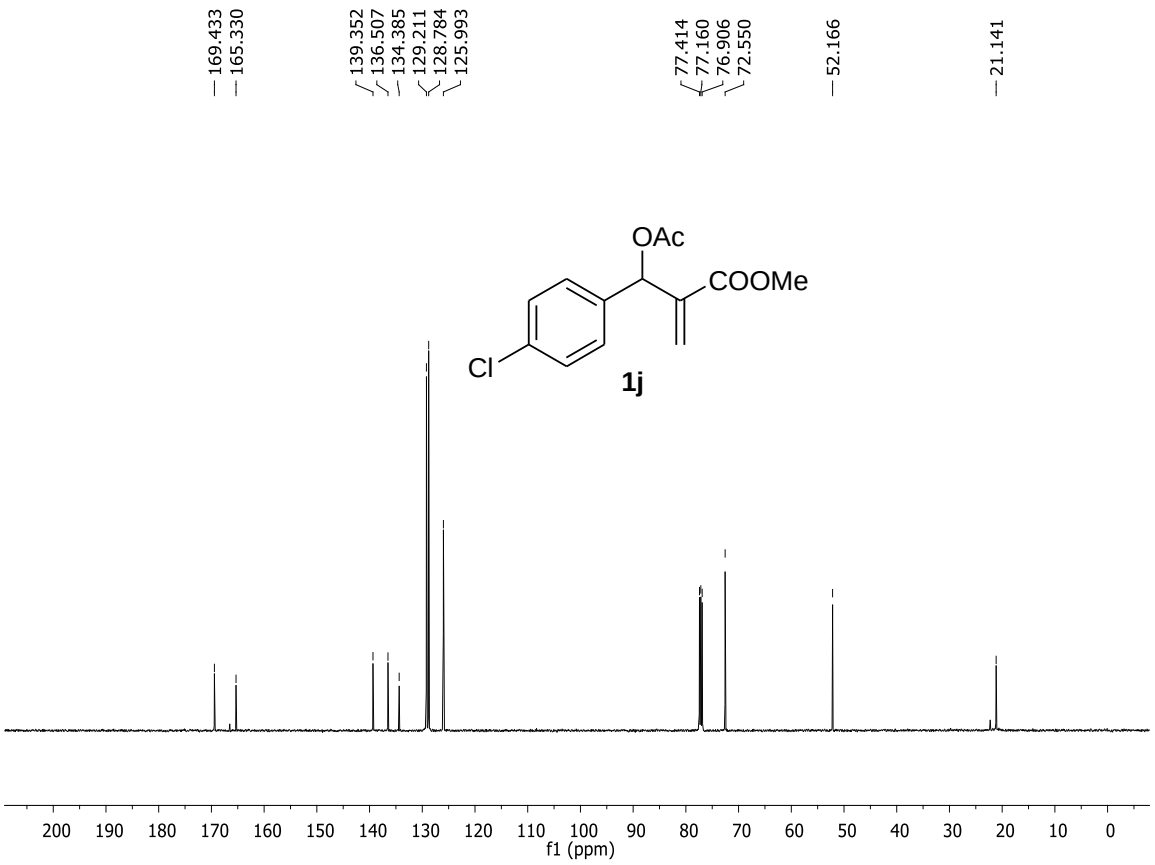
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1j
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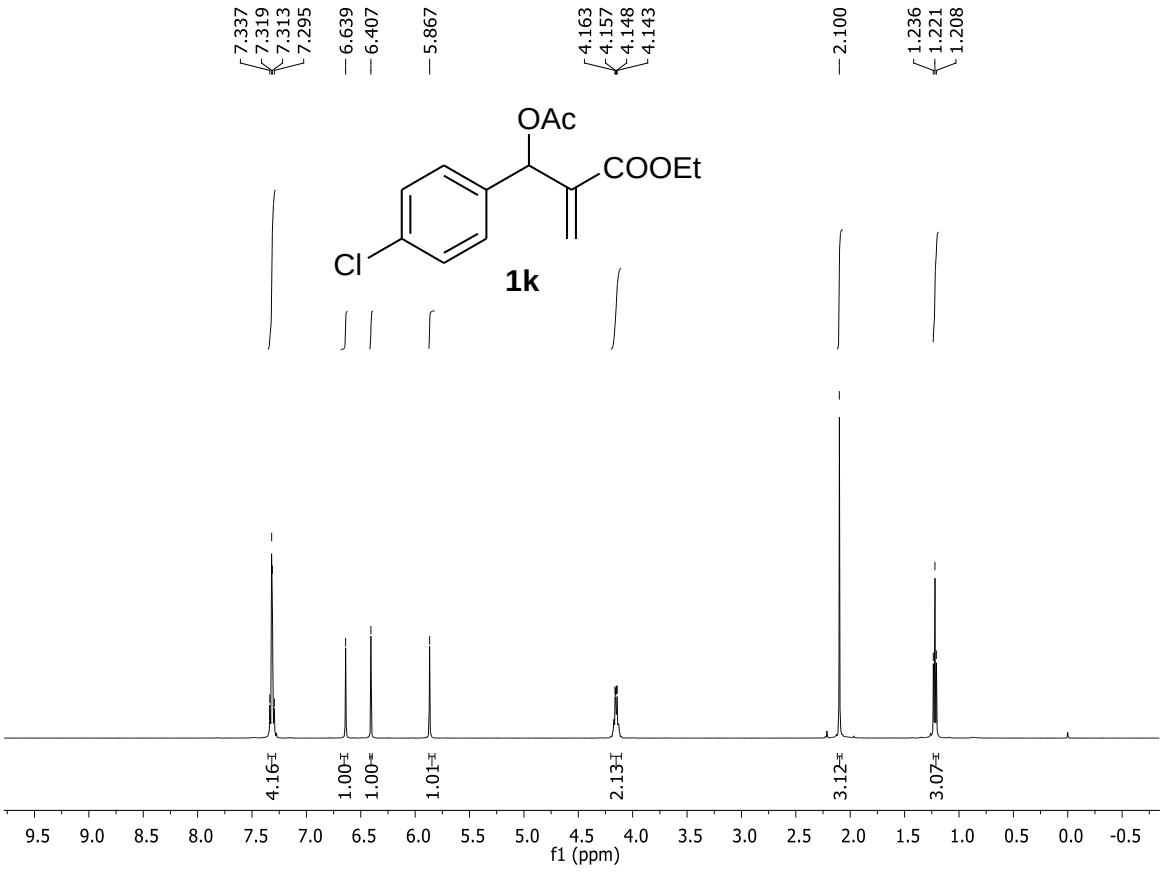
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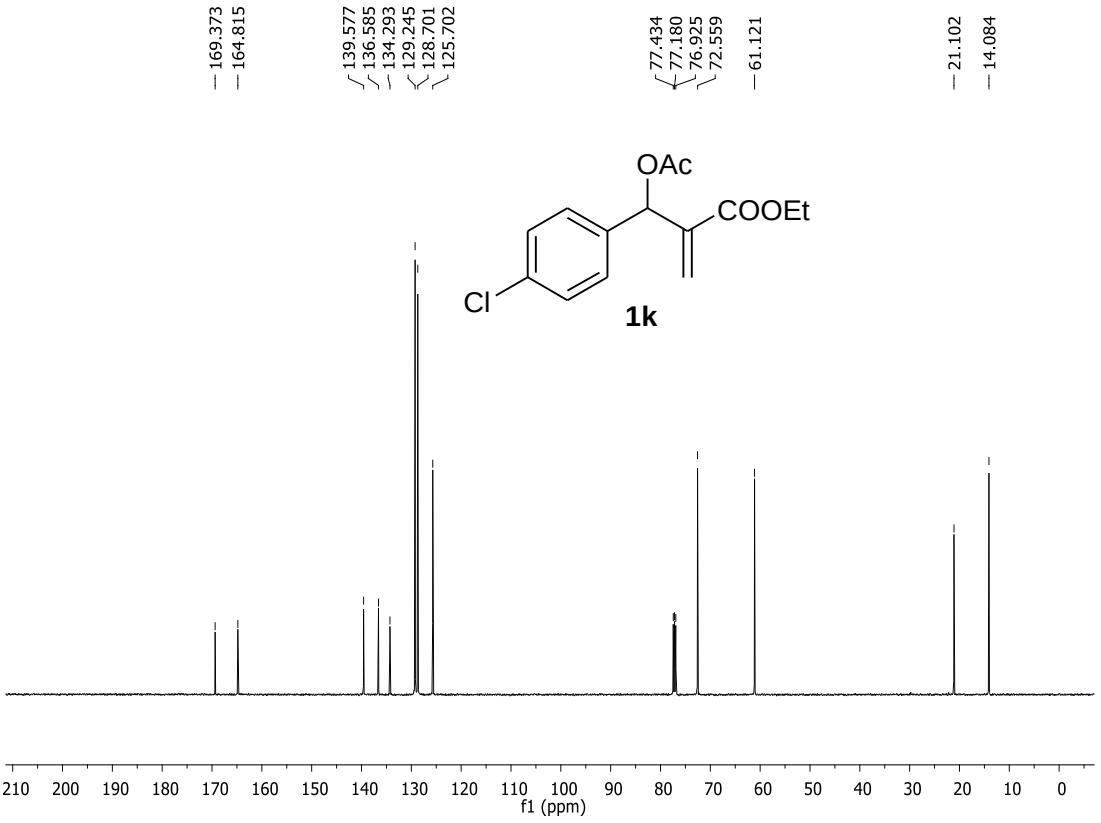
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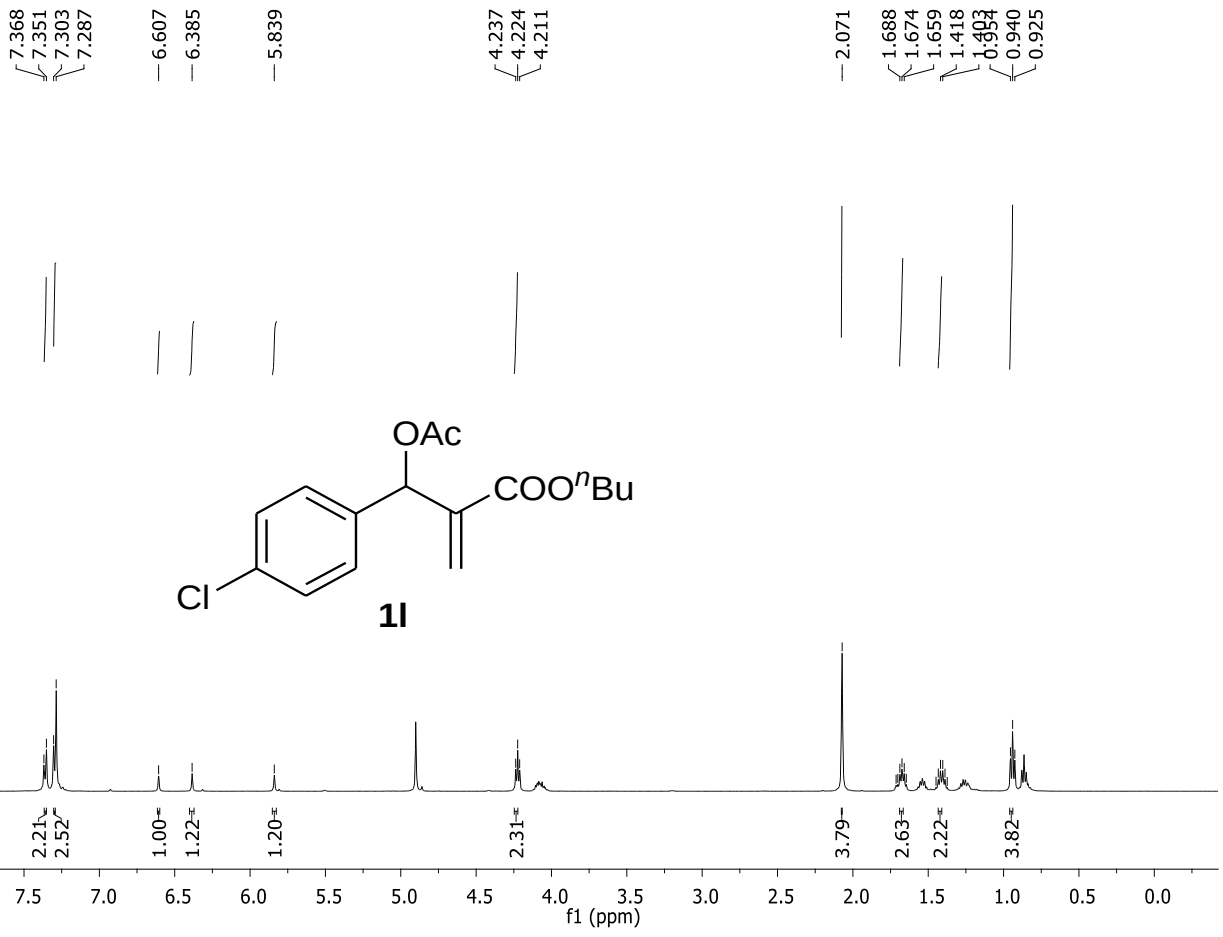
f1 (ppm)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7.303
7.287
6.607
6.385
5.839
4.237
4.224
4.211
2.071
1.688
1.674
1.659
1.418
1.403
0.954
0.940
0.925
OAc
COO^{n}Bu
Cl
1l
2.21
2.52
1.00
1.22
1.20
2.31
3.79
2.63
2.22
3.82
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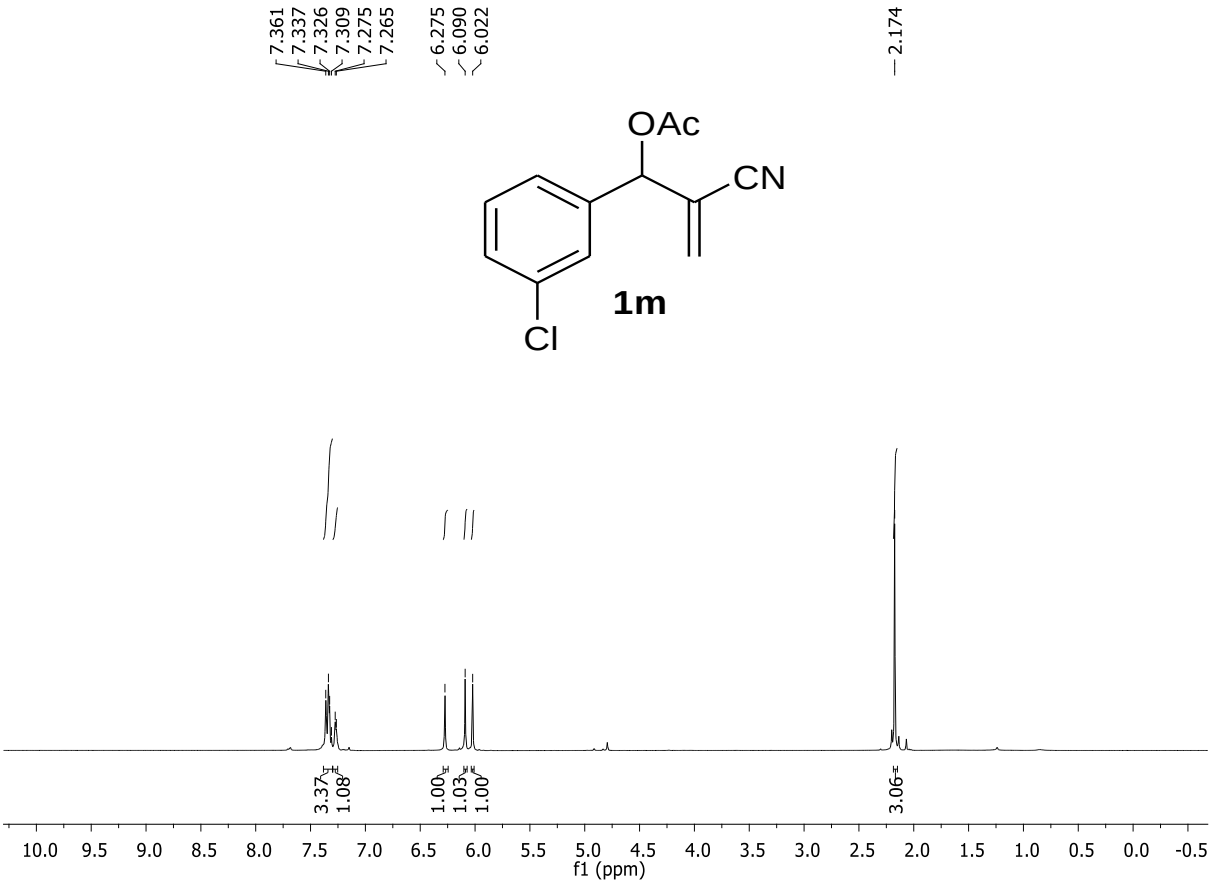
f1 (ppm)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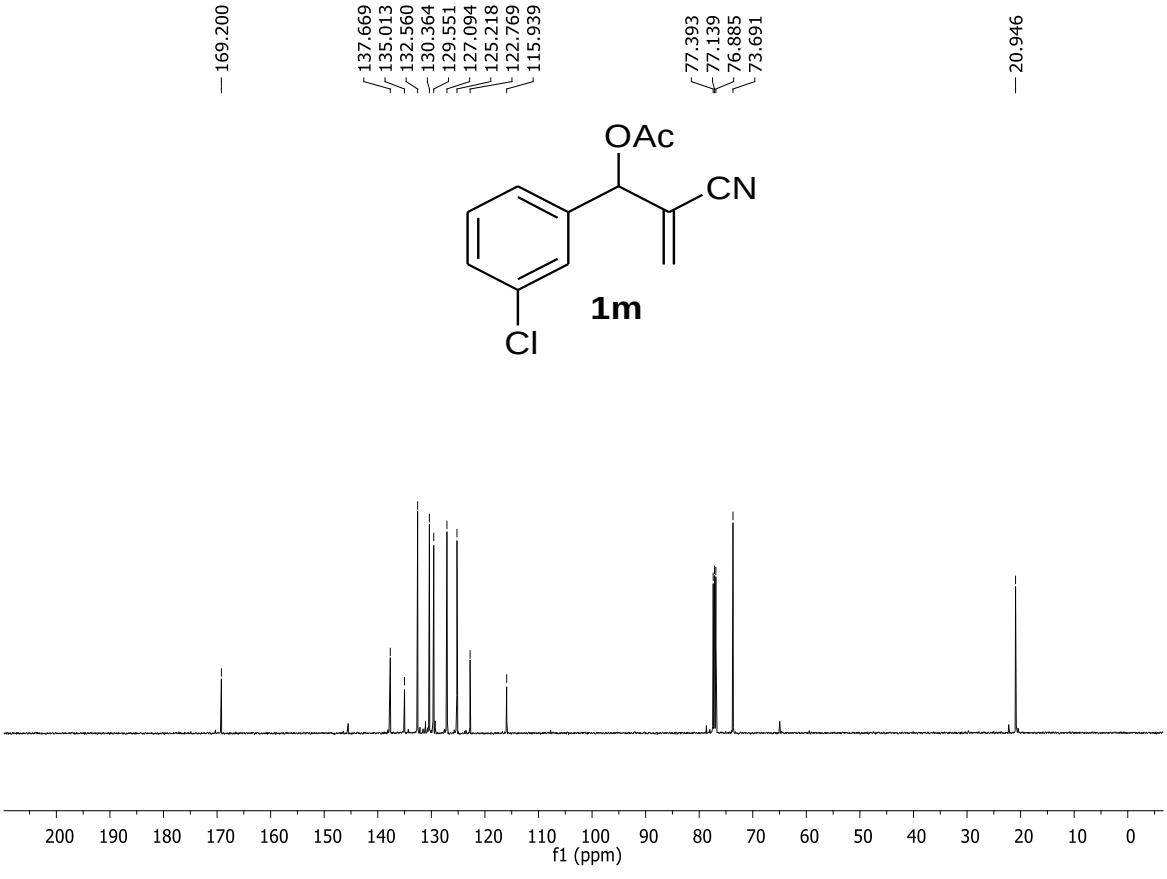
7.337
7.326
7.309
7.275
7.265
6.275
6.090
6.022
2.174
OAc
CN
Cl
1m
3.37
1.08
1.00
1.03
1.00
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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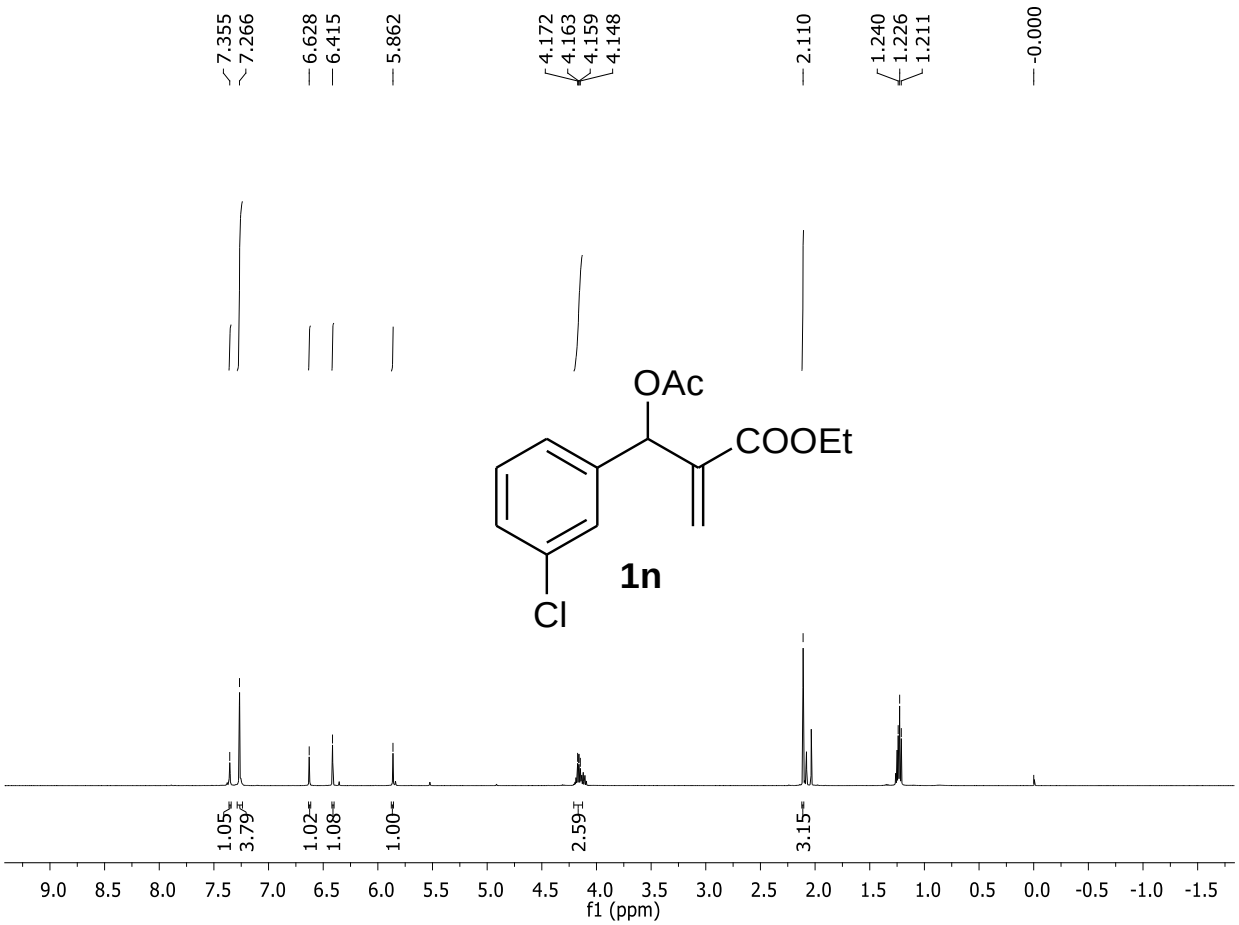
135.013
132.560
130.364
129.551
127.094
125.218
122.769
115.939
77.393
77.139
76.885
73.691
20.946
OAc
CN
Cl
1m
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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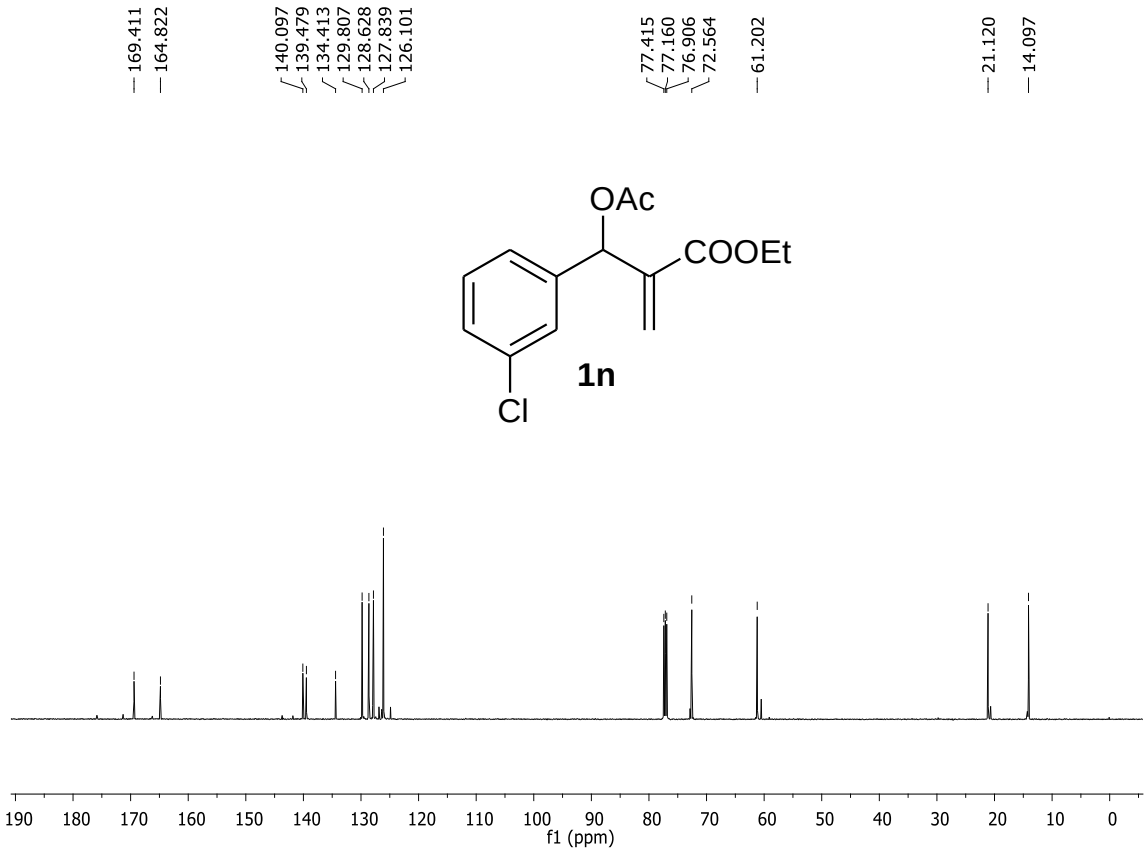
7.266
6.628
6.415
5.862
4.172
4.163
4.159
4.148
2.110
1.240
1.226
1.211
-0.000
OAc
COOEt
Cl
1n
1.05
3.79
1.02
1.08
1.00
2.59
3.15
f1 (ppm)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164.822
140.097
139.479
134.413
129.807
128.628
127.839
126.101
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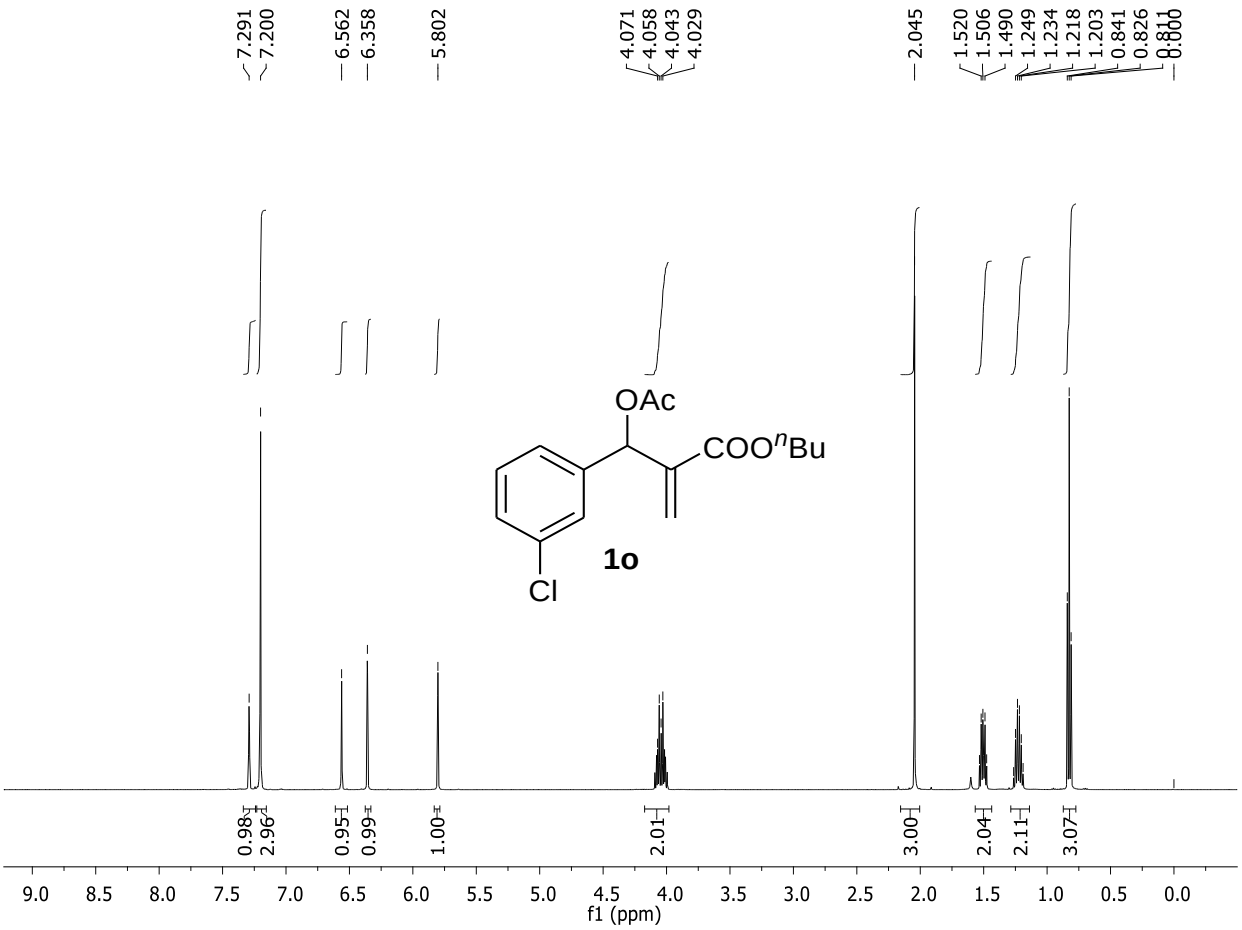
76.906
72.564
61.202
21.120
14.097
OAc
COOEt
Cl
1n
f1 (ppm)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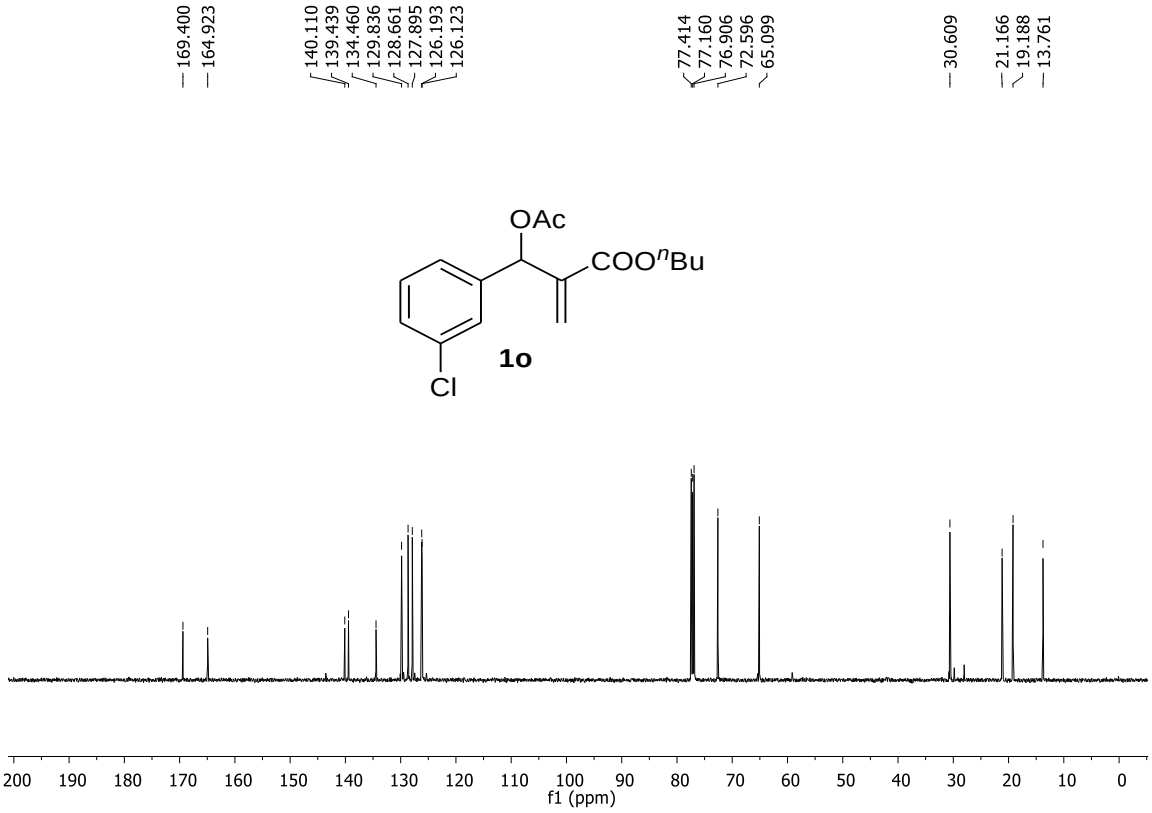
7.200
6.562
6.358
5.802
4.071
4.058
4.043
4.029
2.045
1.520
1.506
1.490
1.249
1.234
1.218
1.203
0.841
0.826
0.811
0.800
OAc
COO^{n}Bu
Cl
1o
0.98
2.96
0.95
0.99
1.00
2.01
3.00
2.04
2.11
3.07
f1 (ppm)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164.923
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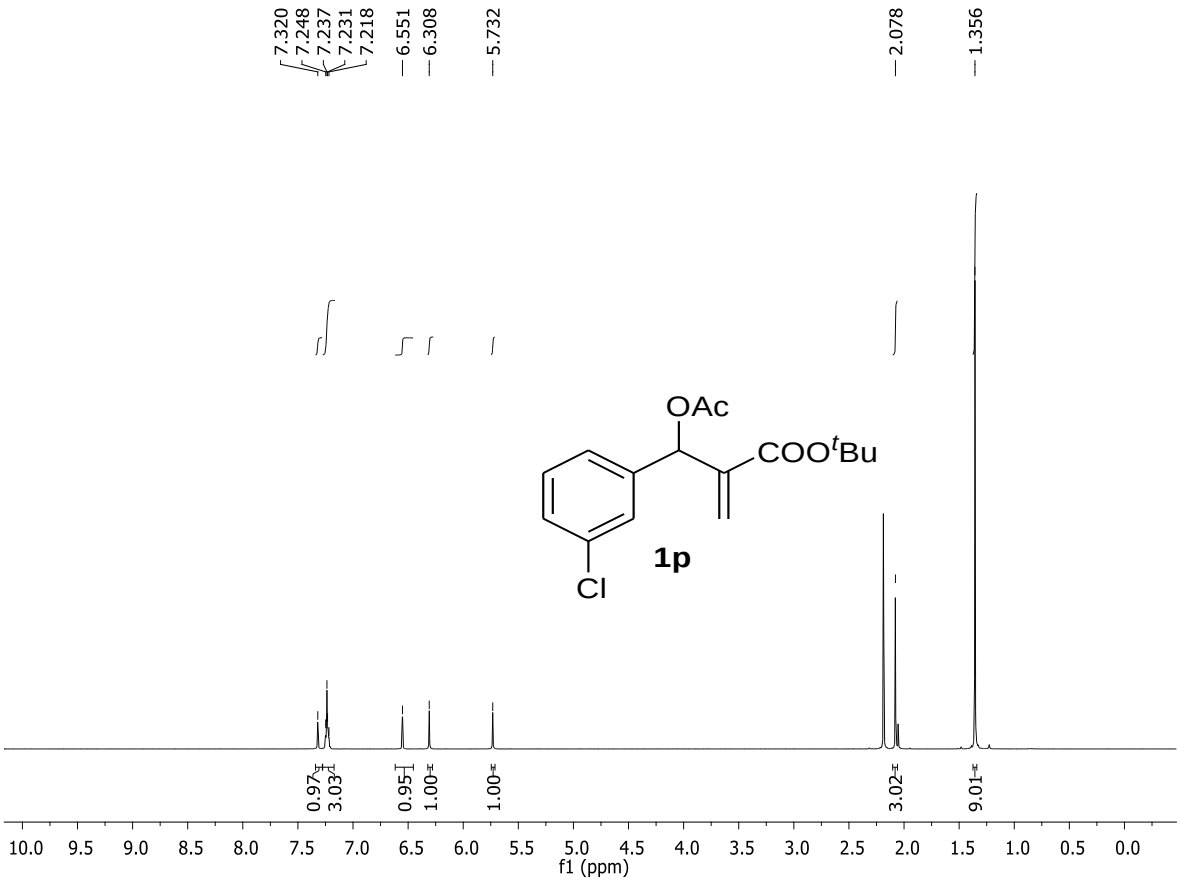
139.439
134.460
129.836
128.661
127.895
126.193
126.123
77.414
77.160
76.906
72.596
65.099
30.609
21.166
19.188
13.761
OAc
COO^{n}Bu
Cl
1o
f1 (ppm)


7.320
7.248
7.237
7.231
7.218
6.551
6.308
5.732
2.078
1.356
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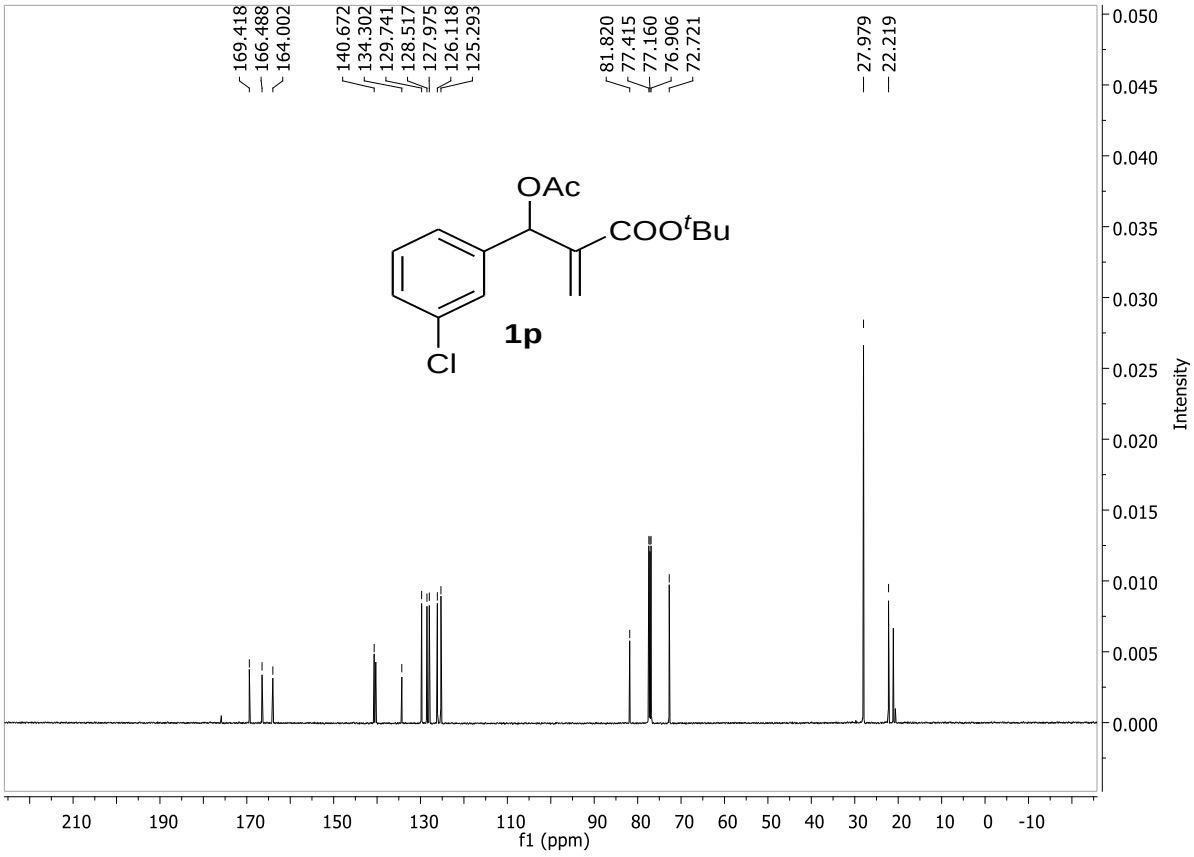
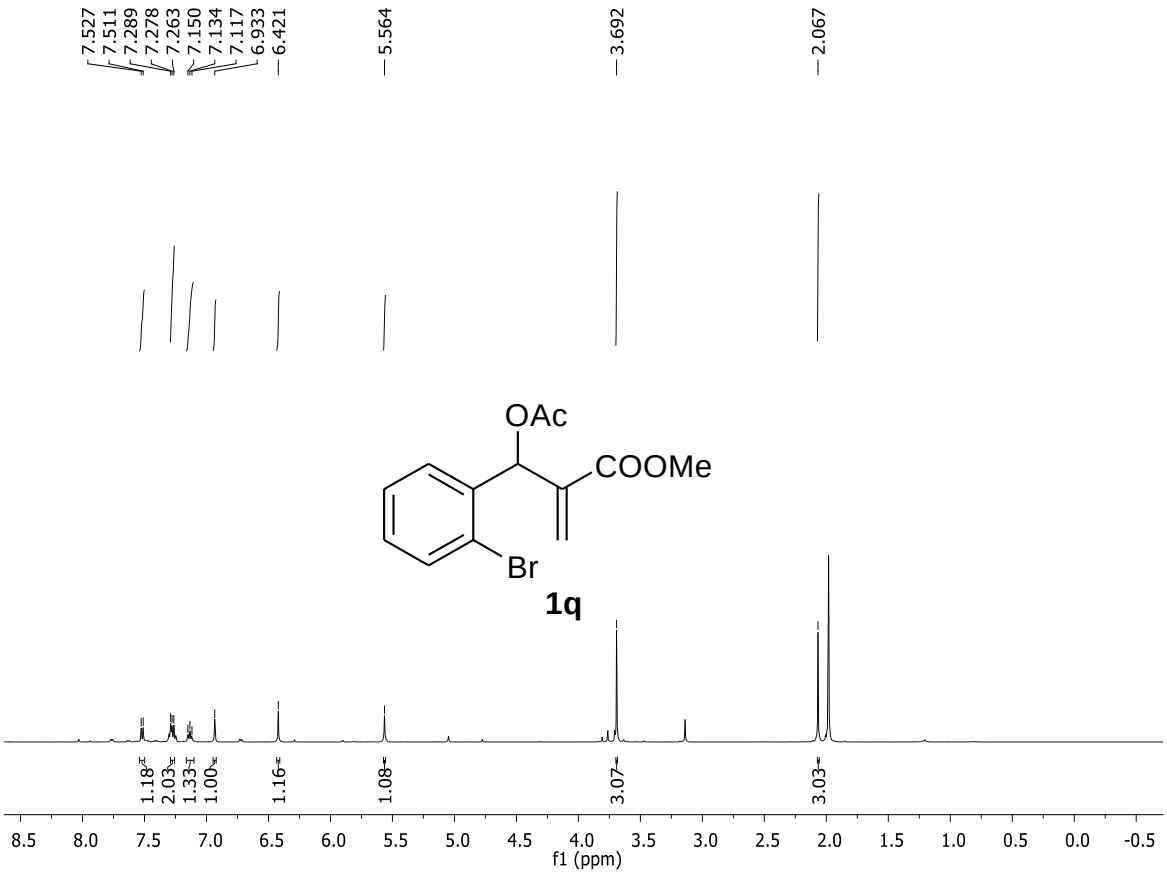
COO^{t}Bu
Cl
1p
0.97
3.03
0.95
1.00
1.00
3.02
9.01
f1 (ppm)


169.418
166.488
164.002
140.672
134.302
129.741
128.517
127.975
126.118
125.293
81.820
77.415
77.160
76.906
72.721
27.979
22.219
OAc
COO^{t}Bu
Cl
1p
Intensity
f1 (ppm)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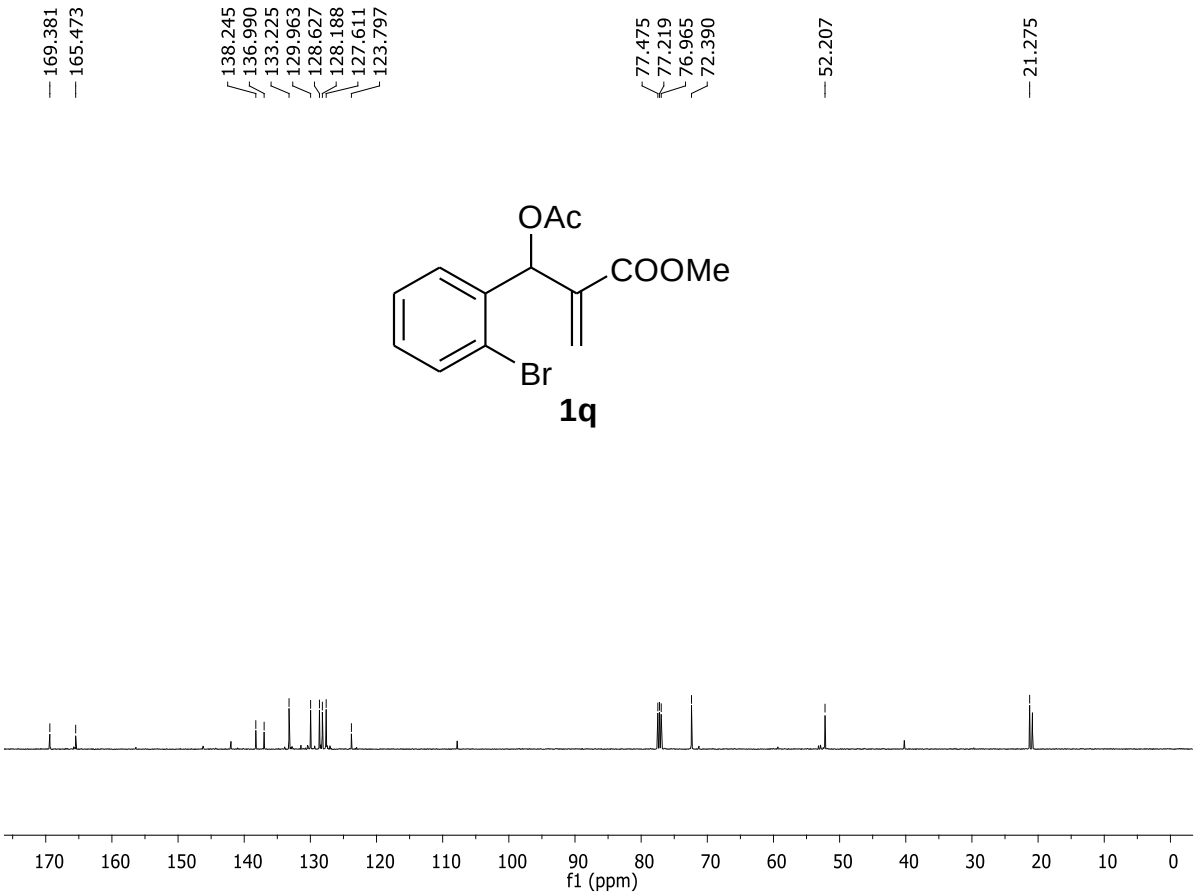
7.511
7.289
7.278
7.263
7.150
7.134
7.117
6.933
6.421
5.564
3.692
2.067
OAc
COOMe
Br
1q
1.18
2.03
1.33
1.00
1.16
1.08
3.07
3.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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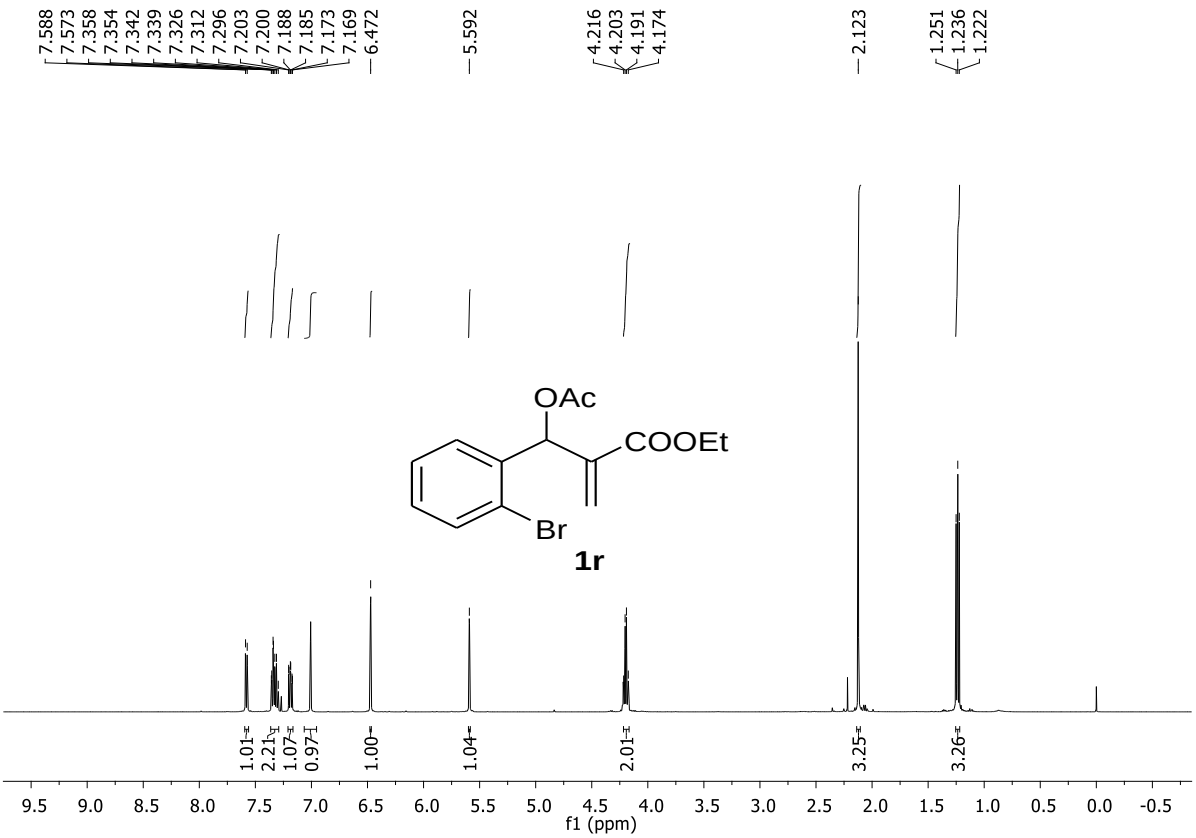
138.245
136.990
133.225
129.963
128.627
128.188
127.611
123.797
77.475
77.219
76.965
72.390
52.207
21.275
OAc
COOMe
Br
1q
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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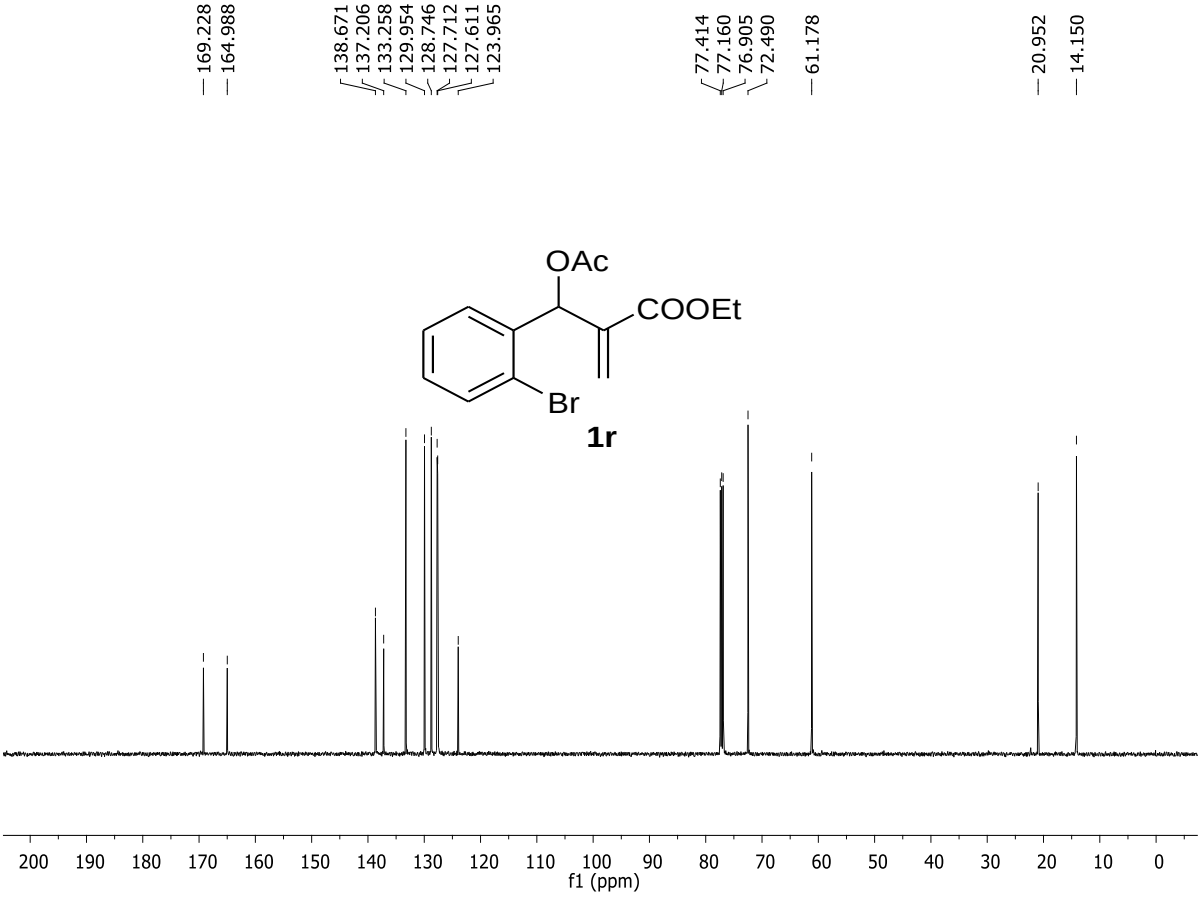
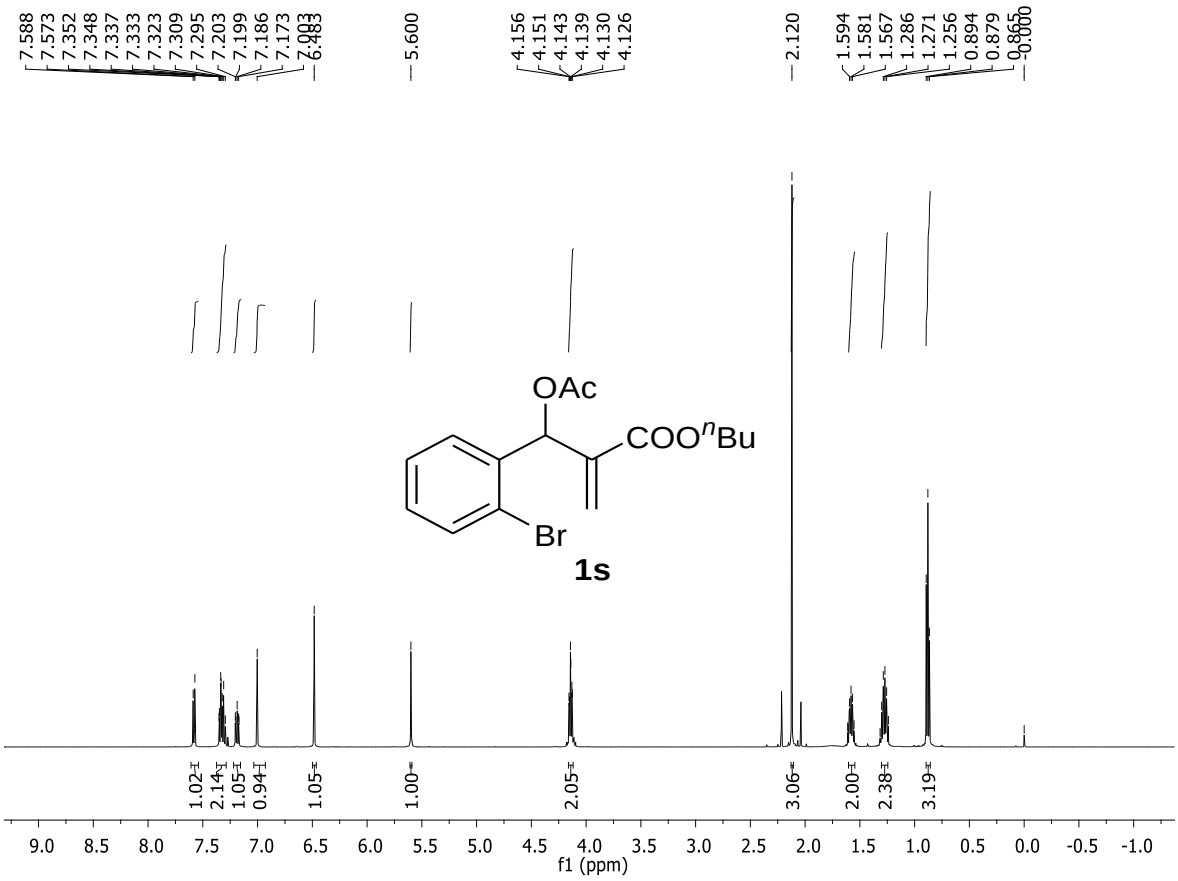
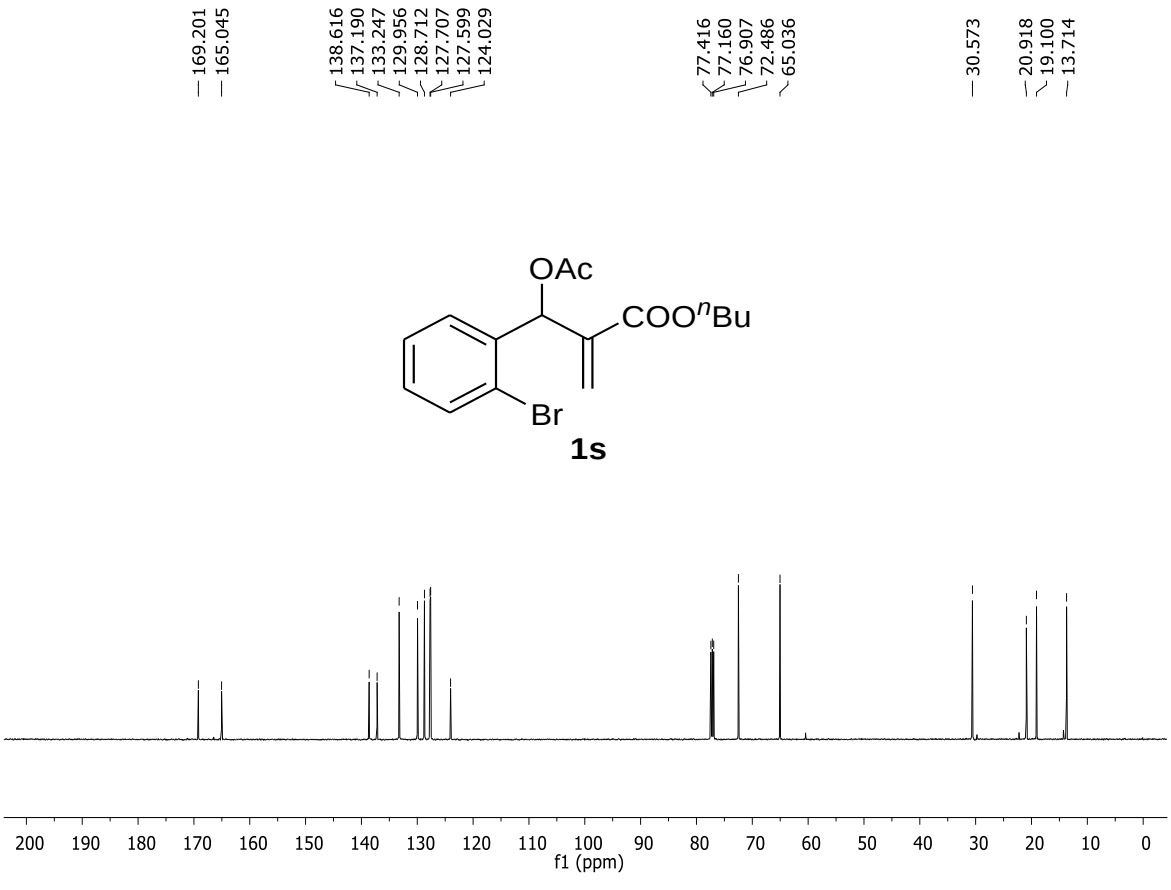
7.573
7.358
7.354
7.342
7.339
7.326
7.312
7.296
7.203
7.200
7.188
7.185
7.173
7.169
6.472
5.592
4.216
4.203
4.191
4.174
2.123
1.251
1.236
1.222
OAc
COOEt
Br
1r
1.01
2.21
1.07
0.97
1.00
1.04
2.01
3.25
3.26
f1 (ppm)


169.228
164.988
138.671
137.206
133.258
129.954
128.746
127.712
127.611
123.965
77.414
77.160
76.905
72.490
61.178
20.952
14.150
OAc
COOEt
Br
1r
f1 (ppm)


7.588
7.573
7.352
7.348
7.337
7.333
7.323
7.309
7.295
7.203
7.199
7.186
7.173
7.003
6.483
5.600
4.156
4.151
4.143
4.139
4.130
4.126
2.120
1.594
1.581
1.567
1.286
1.271
1.256
0.894
0.879
0.865
0.000
OAc
COO^{n}Bu
Br
1s
1.02
2.14
1.05
0.94
1.05
1.00
2.05
3.06
2.00
2.38
3.19
f1 (ppm)


169.201
165.045
138.616
137.190
133.247
129.956
128.712
127.707
127.599
124.029
77.416
77.160
76.907
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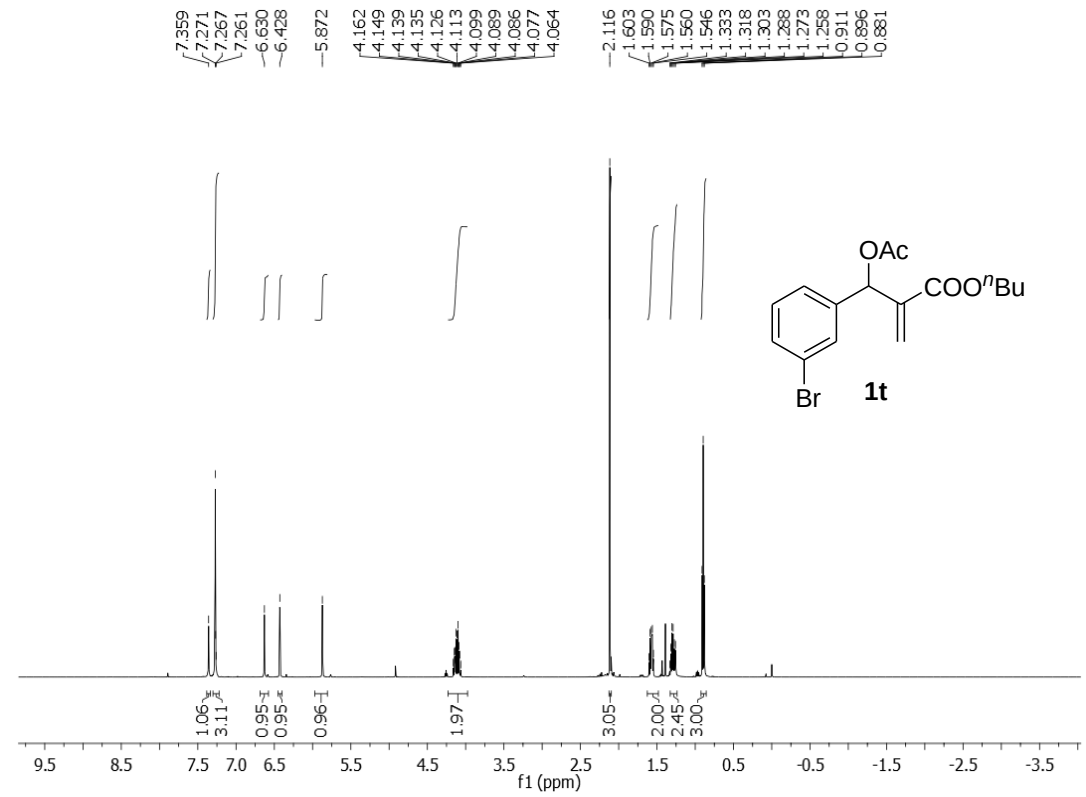
30.573
20.918
19.100
13.714
OAc
COO^{n}Bu
Br
1s
f1 (ppm)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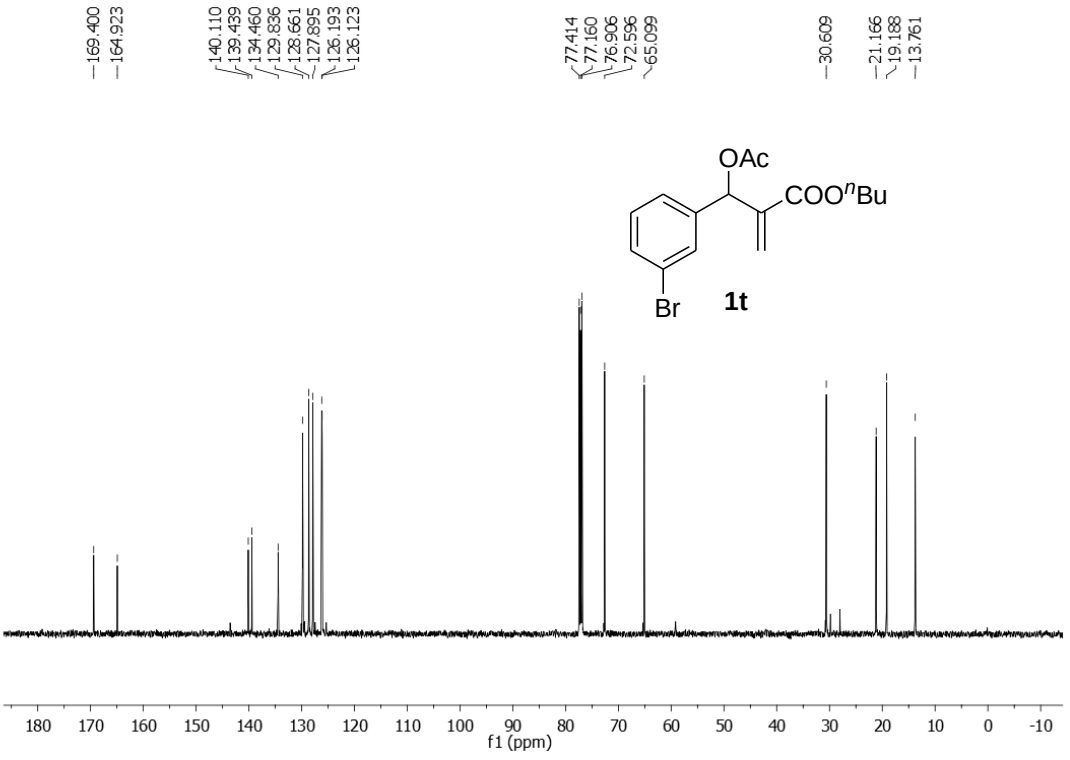
7.267
7.261
6.630
6.428
5.872
4.162
4.149
4.139
4.135
4.126
4.113
4.099
4.089
4.086
4.077
4.064
2.116
1.603
1.590
1.575
1.560
1.546
1.333
1.318
1.303
1.288
1.273
1.258
0.911
0.896
0.881
OAc
COO^{n}Bu
Br
1t
1.06
3.11
0.95
0.95
0.96
1.97
3.05
2.00
2.45
3.00
f1 (ppm)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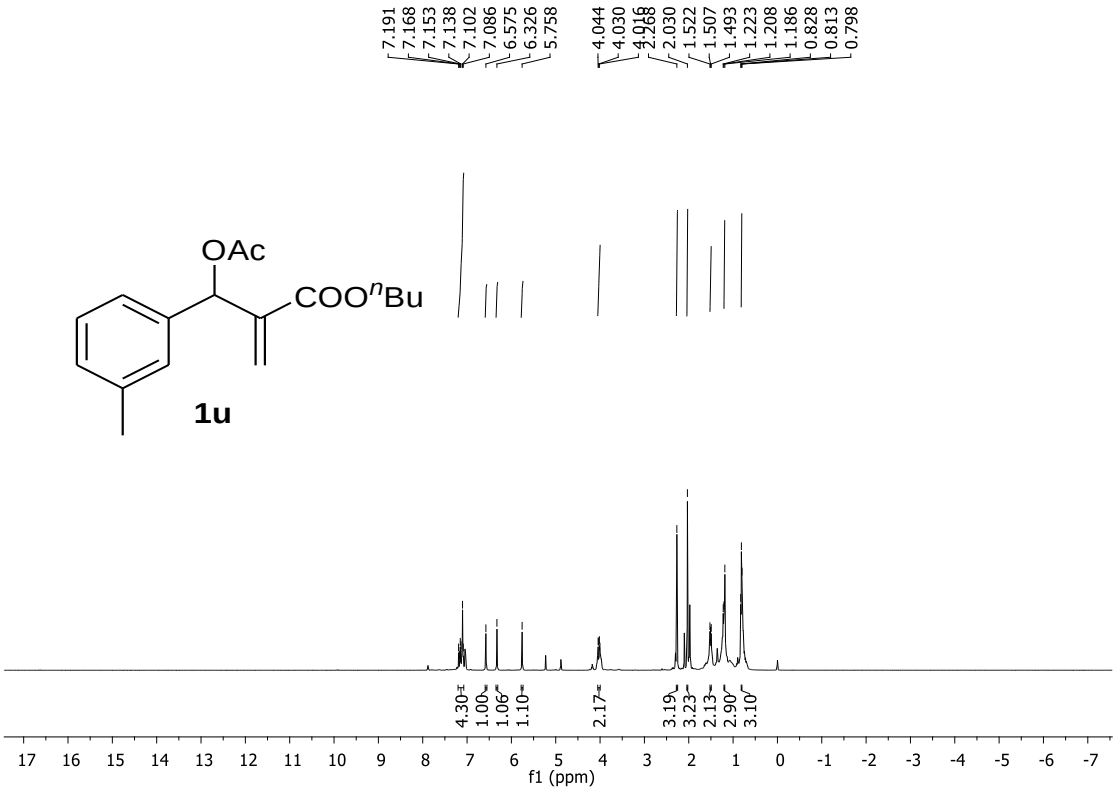
164.923
140.110
139.439
134.460
129.836
128.661
127.895
126.193
126.123
77.414
77.160
76.906
72.596
65.099
30.609
21.166
19.188
13.761
OAc
COO^{n}Bu
Br
1t
f1 (ppm)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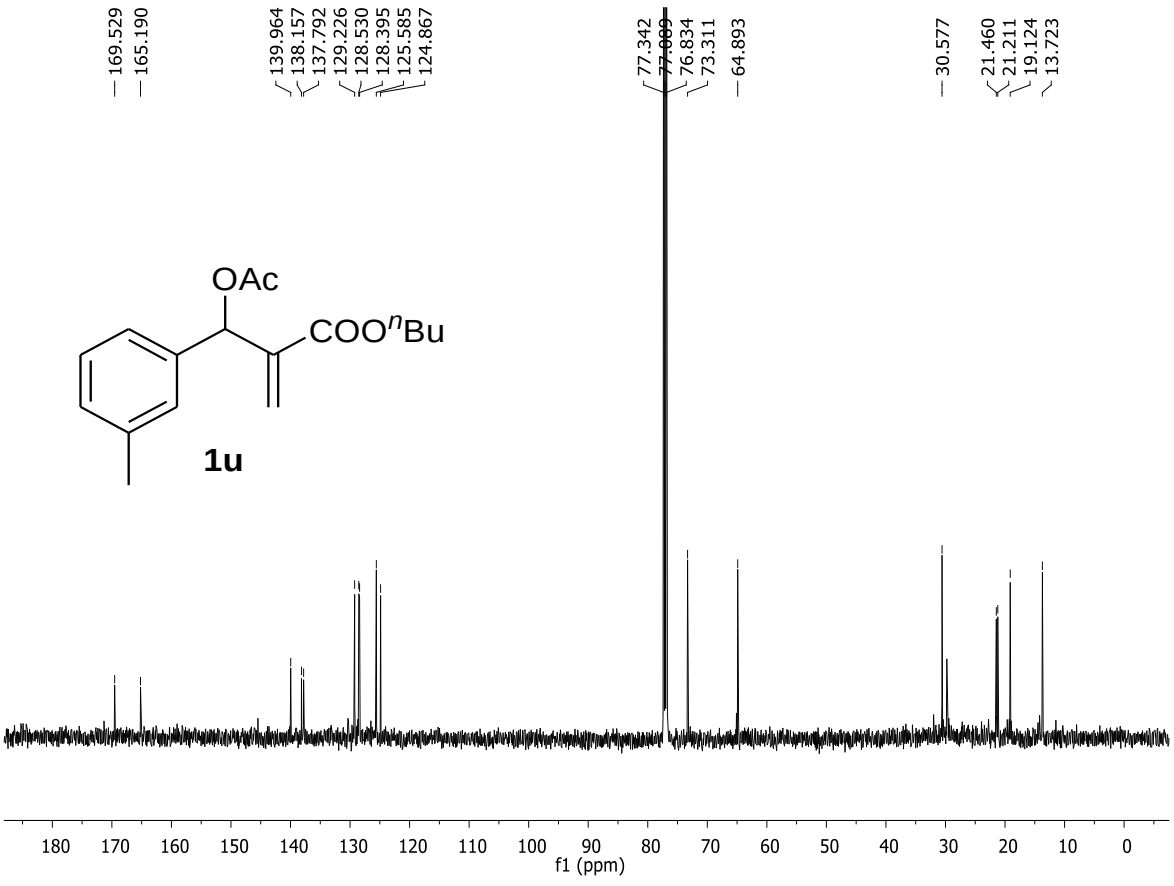
7.153
7.138
7.102
7.086
6.575
6.326
5.758
4.044
4.030
4.016
2.268
2.030
1.522
1.507
1.493
1.223
1.208
1.186
0.828
0.813
0.798
OAc
COO^{n}Bu
1u
4.30
1.00
1.06
1.10
2.17
3.19
3.23
2.13
2.90
3.10
f1 (ppm)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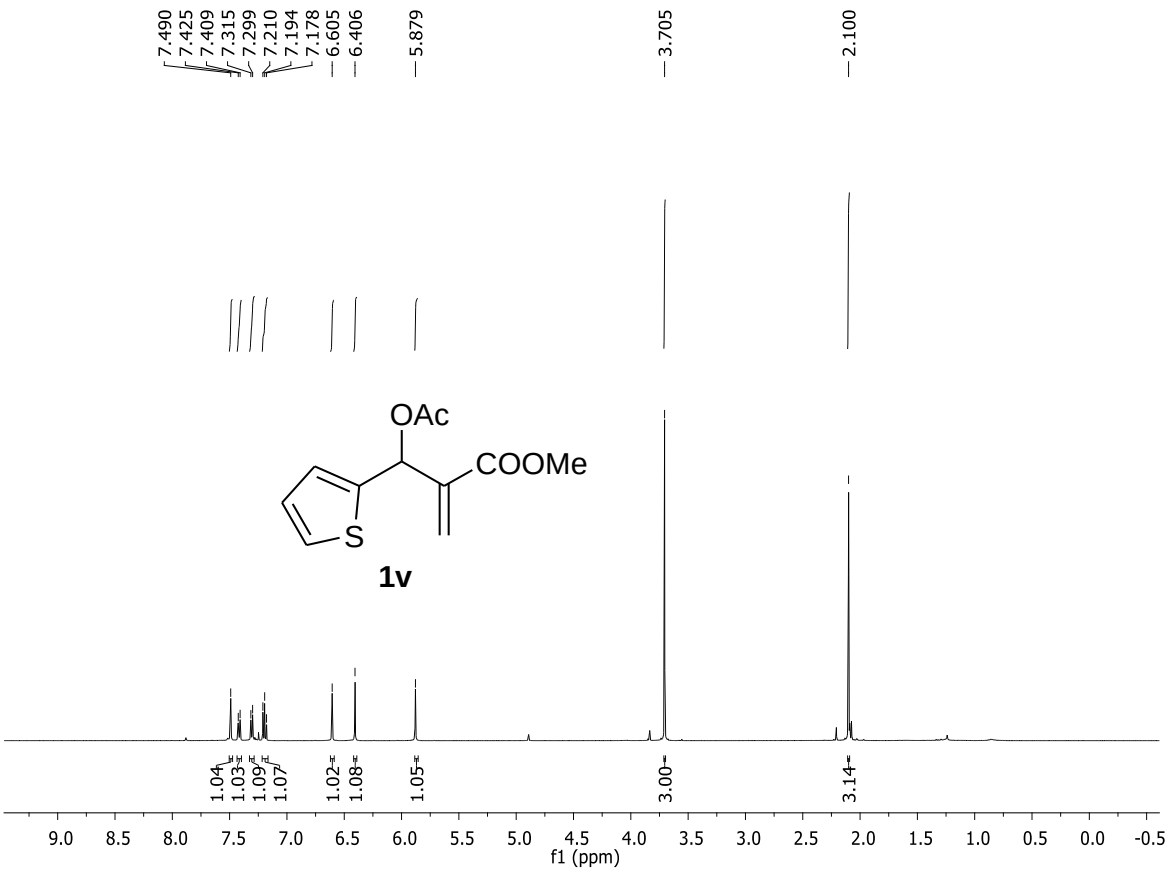
137.792
129.226
128.530
128.395
125.585
124.867
77.342
77.089
76.834
73.311
64.893
30.577
21.460
21.211
19.124
13.723
OAc
COO^{n}Bu
1u
f1 (ppm)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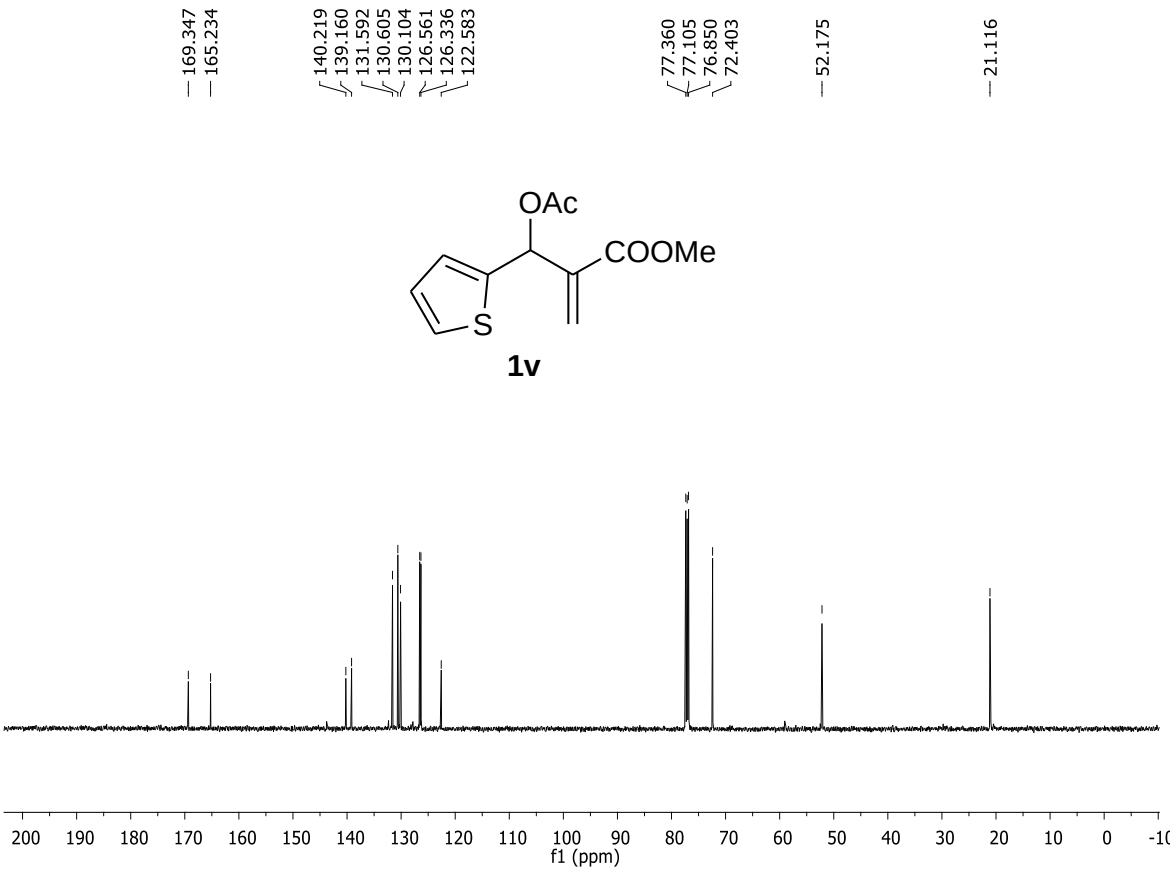
7.425
7.409
7.315
7.299
7.210
7.194
7.178
6.605
6.406
5.879
3.705
2.100
OAc
COOMe
S
1v
1.04
1.03
1.09
1.07
1.02
1.08
1.05
3.00
3.14
f1 (ppm)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130.605
130.104
126.561
126.336
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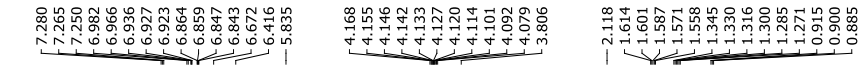
21.116
OAc
COOMe
S
1v
f1 (ppm)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6.966
6.936
6.927
6.923
6.864
6.859
6.847
6.843
6.672
6.416
5.835
4.168
4.155
4.146
4.142
4.133
4.127
4.120
4.114
4.101
4.092
4.079
3.806
2.118
1.614
1.601
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1.285
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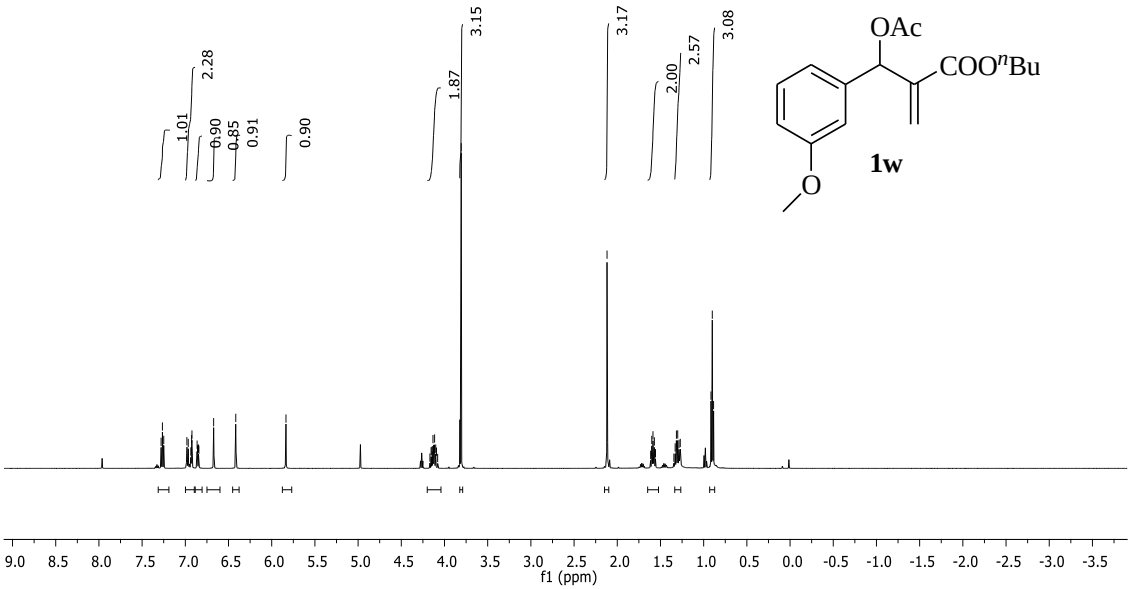
0.900
0.885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0.85
0.91
0.90
1.87
3.15
3.17
2.00
2.57
3.08
OAc
COO^{n}Bu
1w
O
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2.5 -3.0 -3.5
f1 (ppm)


169.504
165.143
159.680
139.834
139.449
129.548
125.917
120.085
113.815
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77.140
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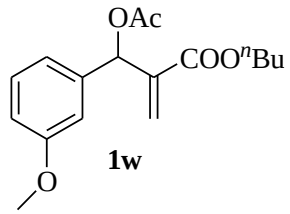
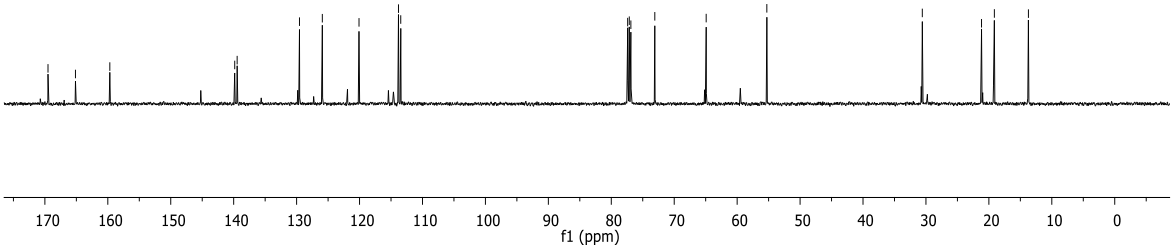
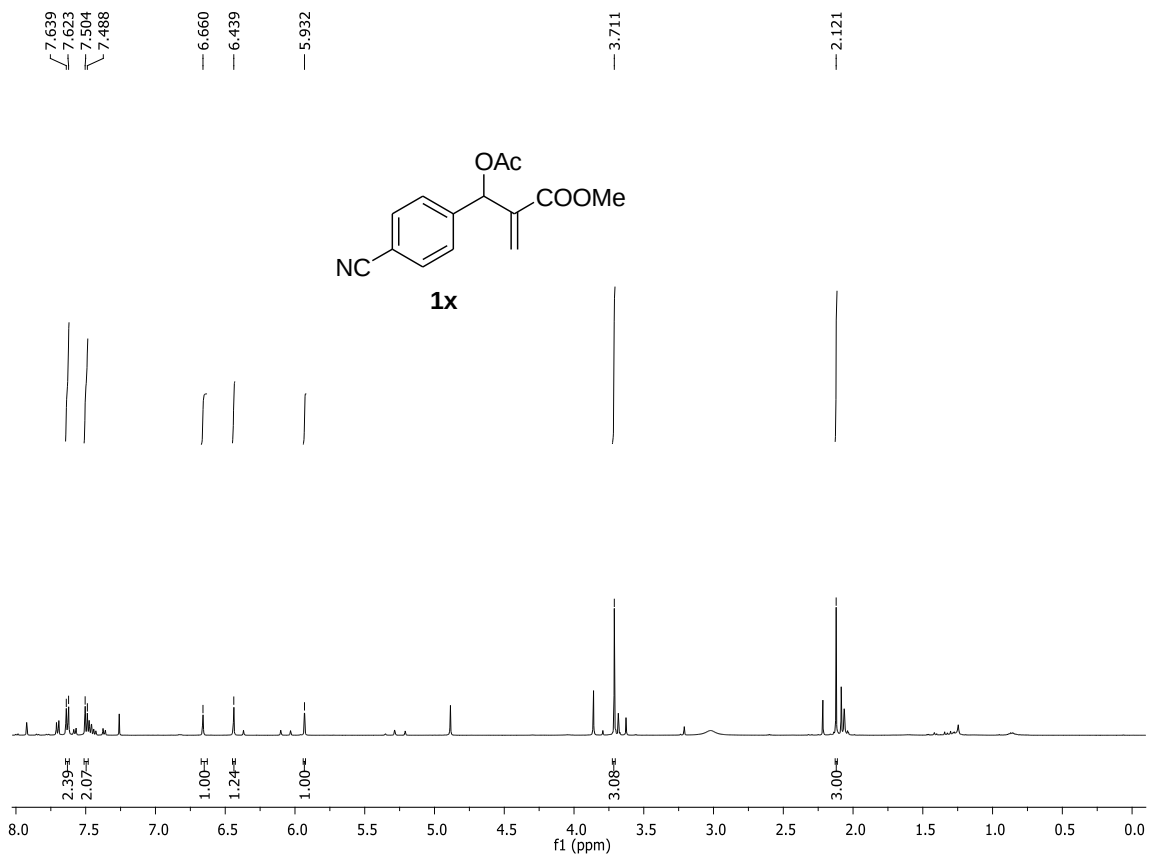
19.130
13.719


OAc
COO^{n}Bu
1w
O


170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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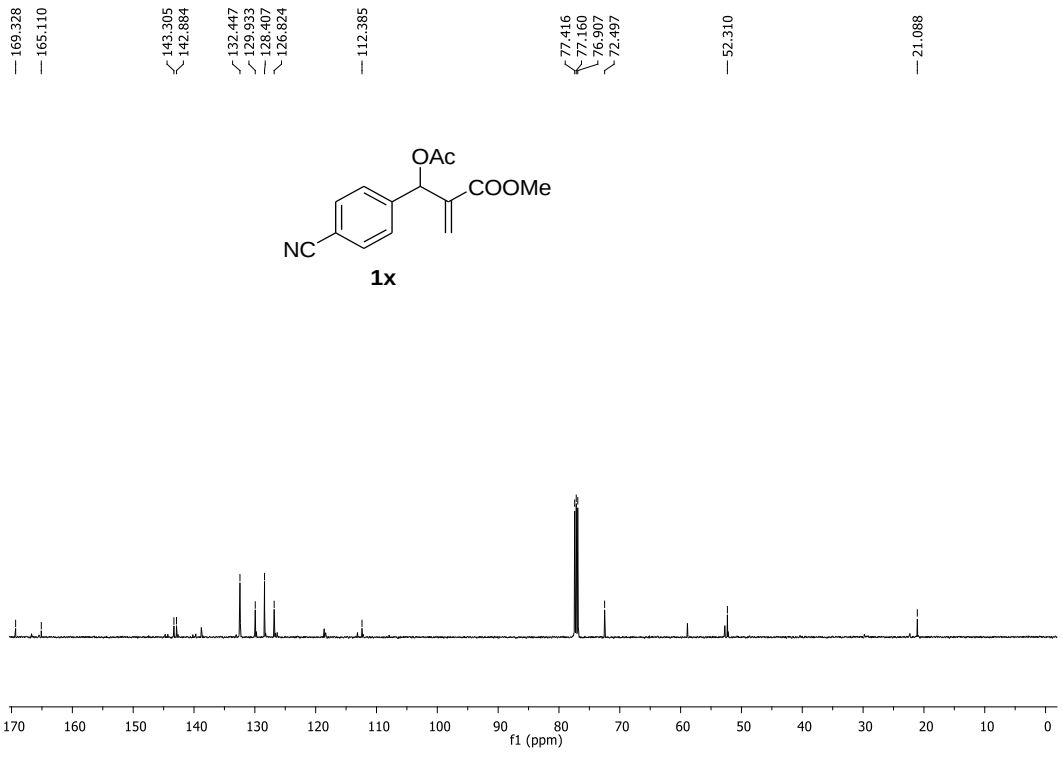
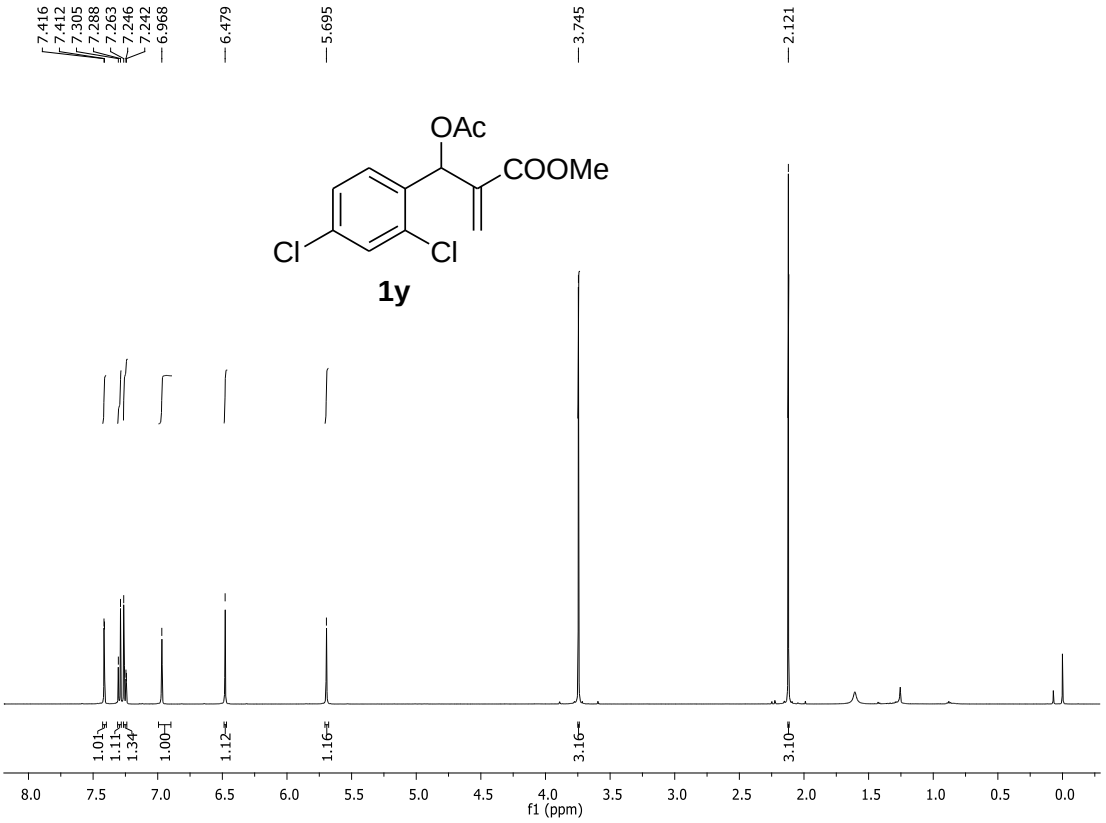
7.504
7.488
6.660
6.439
5.932
3.711
2.121
OAc
COOMe
NC
1x
2.39
2.07
1.00
1.24
1.00
3.08
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


169.328
165.110
143.305
142.884
132.447
129.933
128.407
126.824
112.385
77.416
77.160
76.907
72.497
52.310
21.088
OAc
COOMe
NC
1x
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.412
7.305
7.288
7.263
7.246
7.242
6.968
6.479
5.695
3.745
2.121
OAc
COOMe
Cl
Cl
1y
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1.11
1.34
1.00
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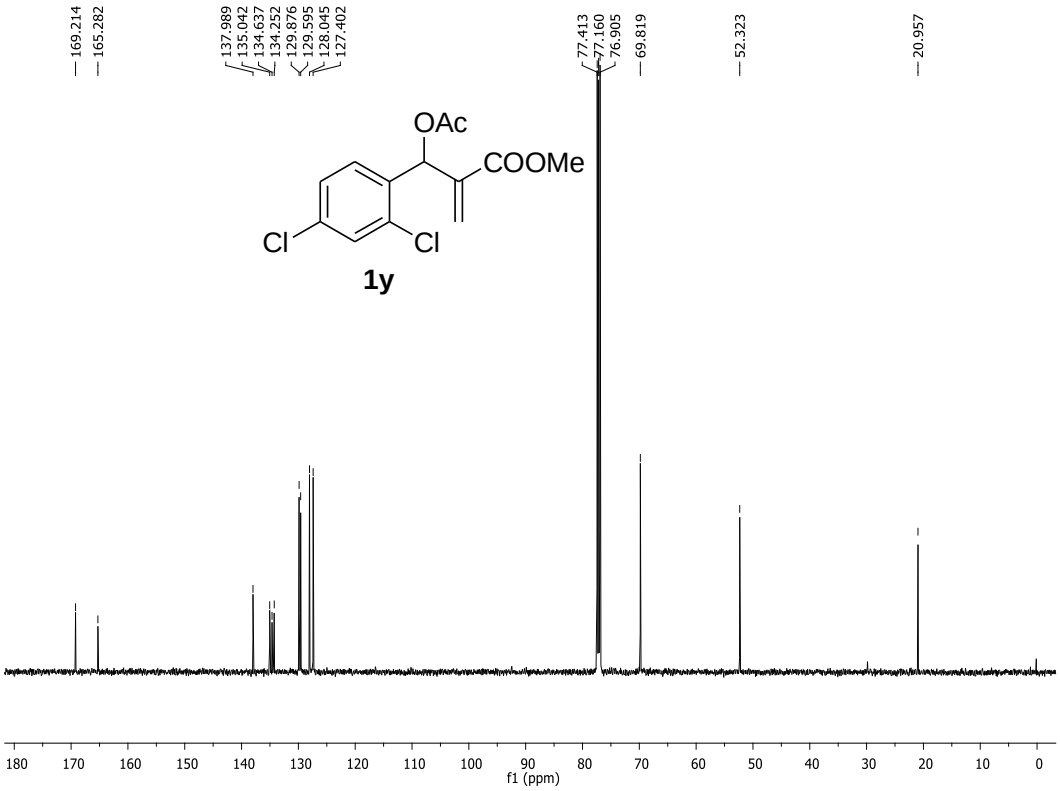
1.16
3.16
3.10
f1 (ppm)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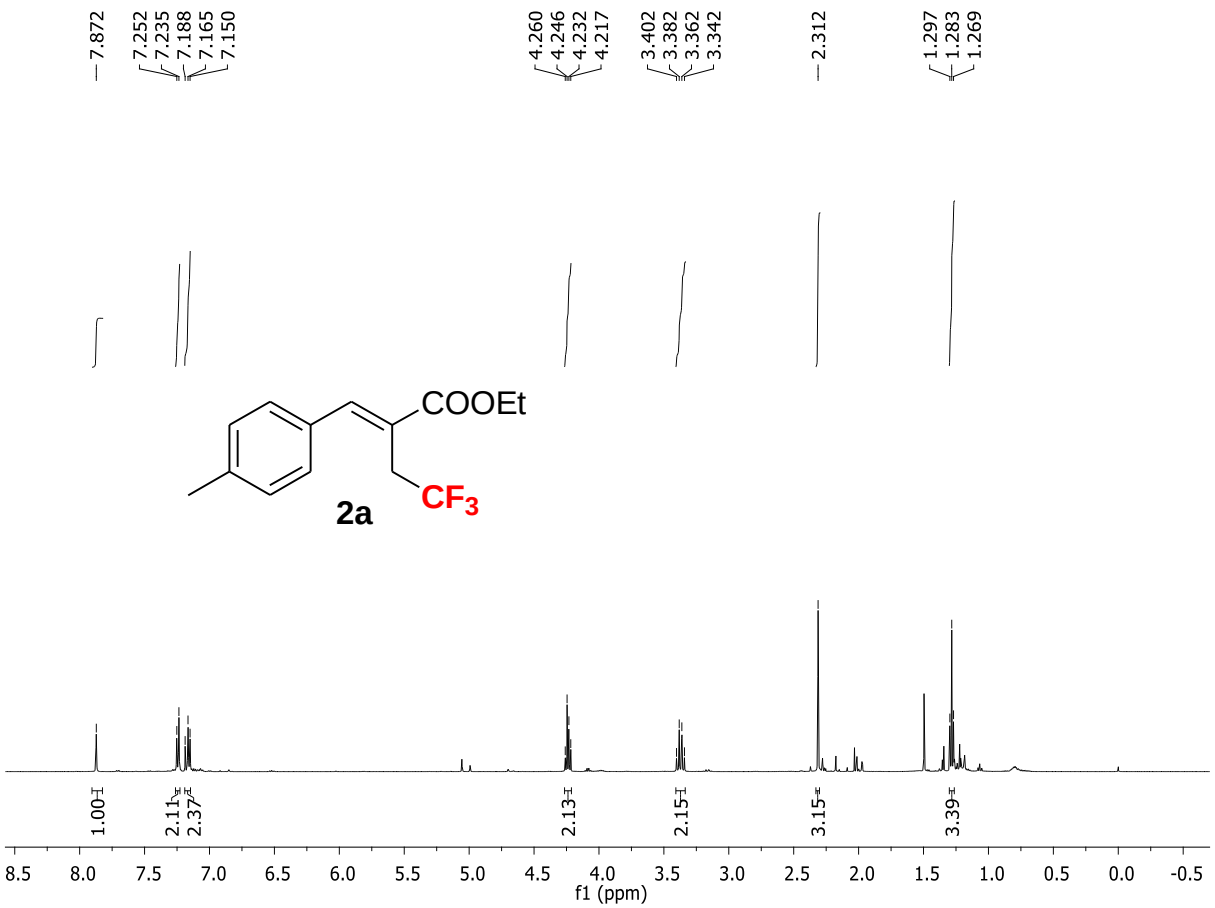
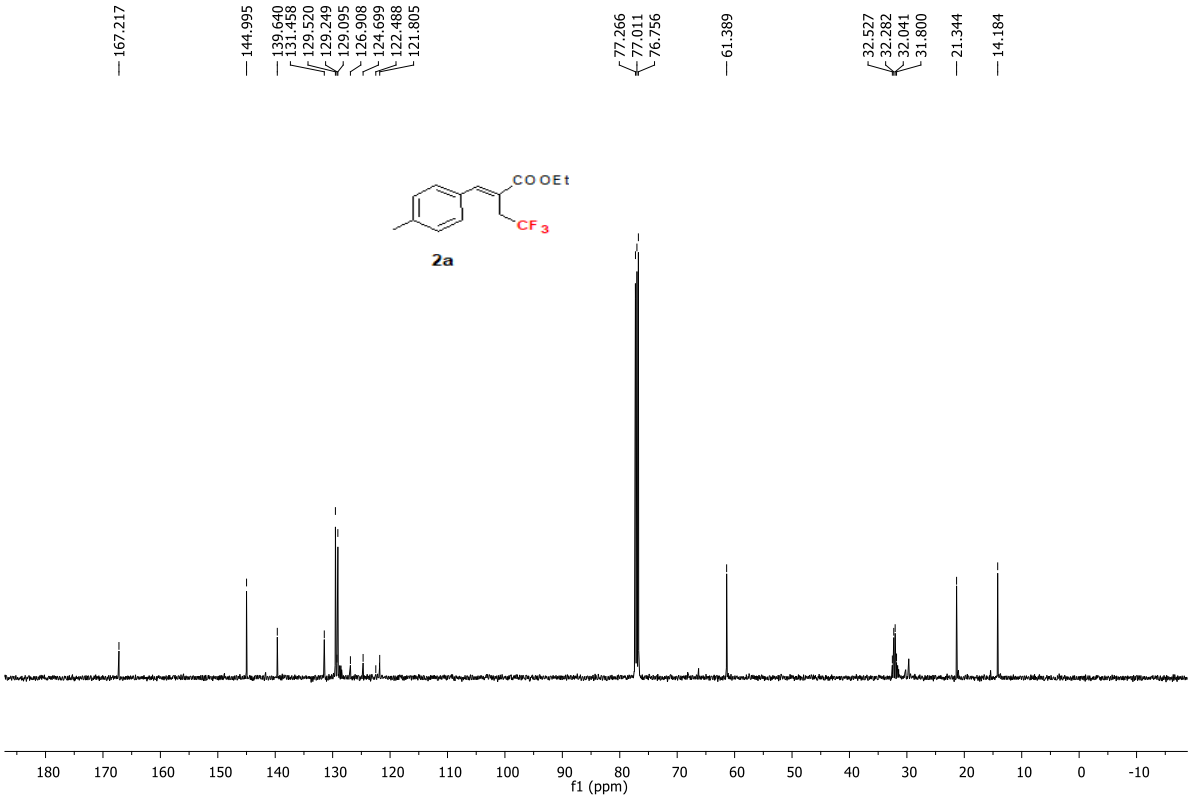
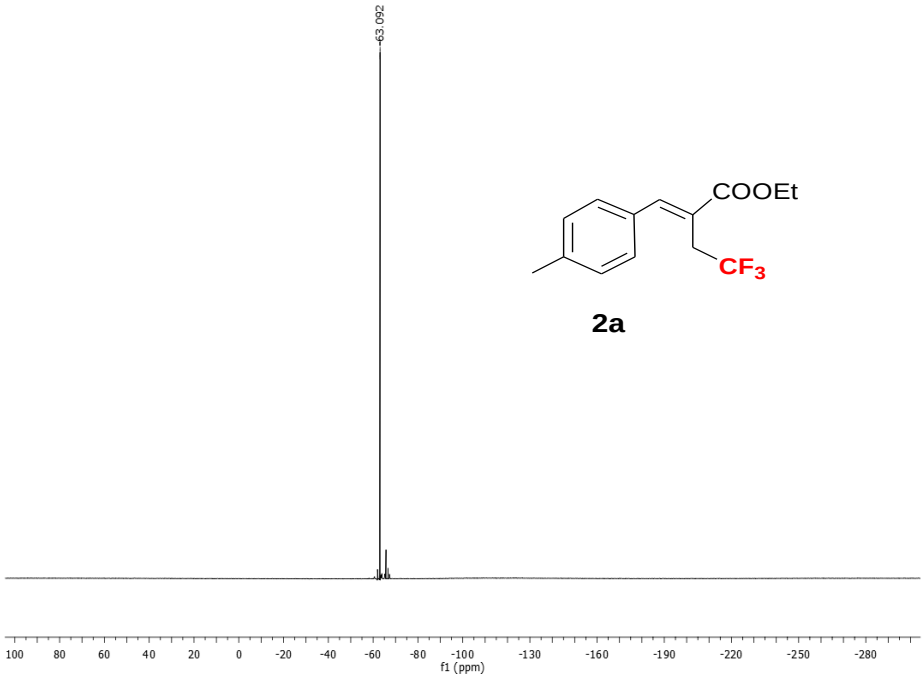
135.042
134.637
134.252
129.876
129.595
128.045
127.402
77.413
77.160
76.905
69.819
52.323
20.957
OAc
COOMe
Cl
Cl
1y
f1 (ppm)

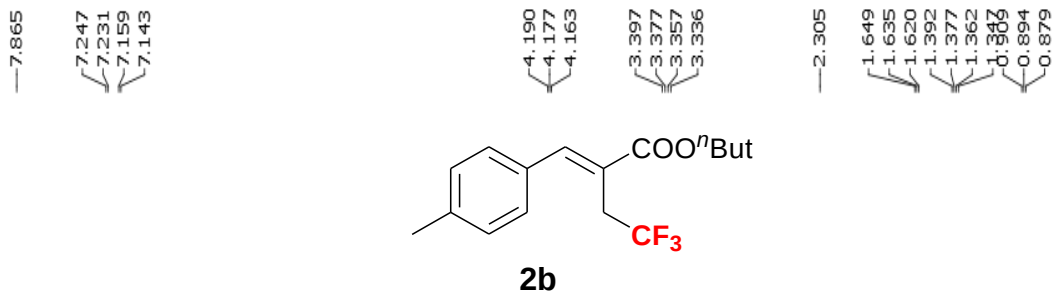
X. Copies of ^{1}H, ^{13}C NMR & ^{19}F Spectra of the Products 2



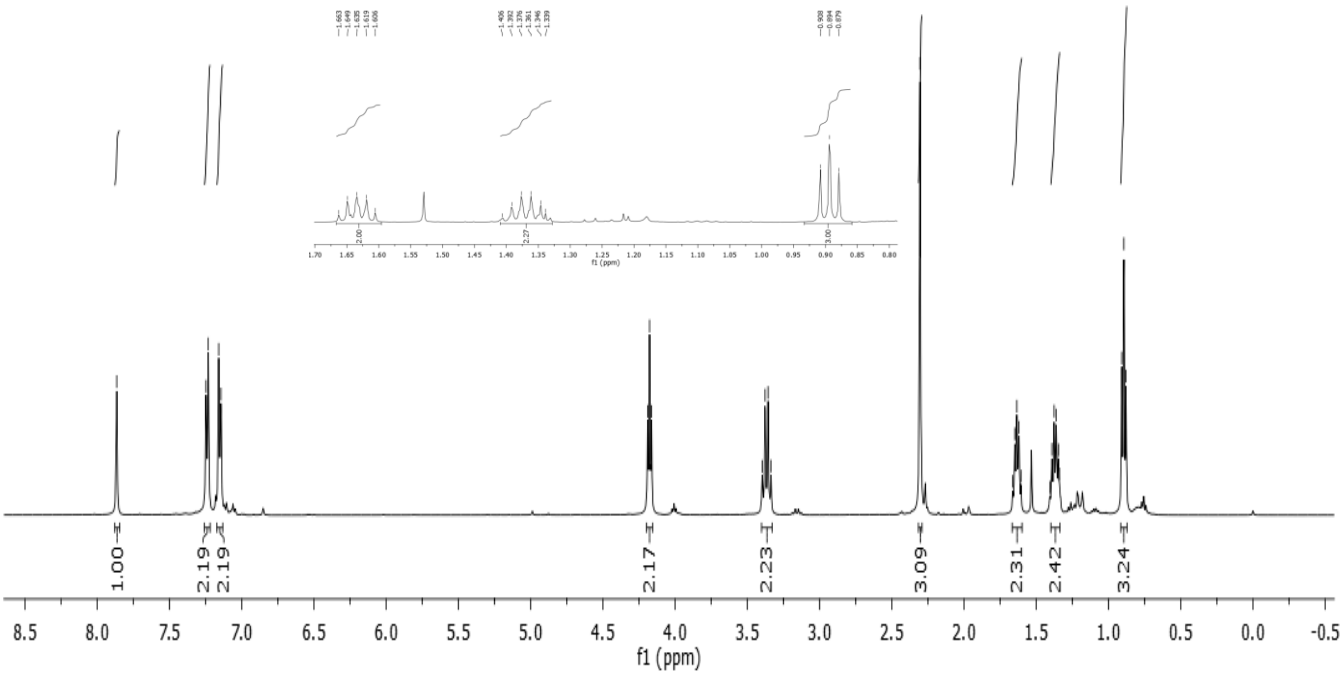


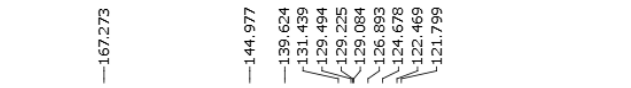

63.092
COOEt
CF3
100 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220 -250 -280
f1 (ppm)

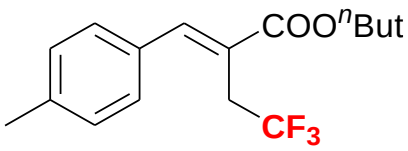
2a


7.865
7.247
7.231
7.159
7.143
4.190
4.177
4.163
3.397
3.377
3.357
3.336
2.305
1.649
1.635
1.620
1.392
1.377
1.362
0.909
0.894
0.879
COO^nBut
CF3

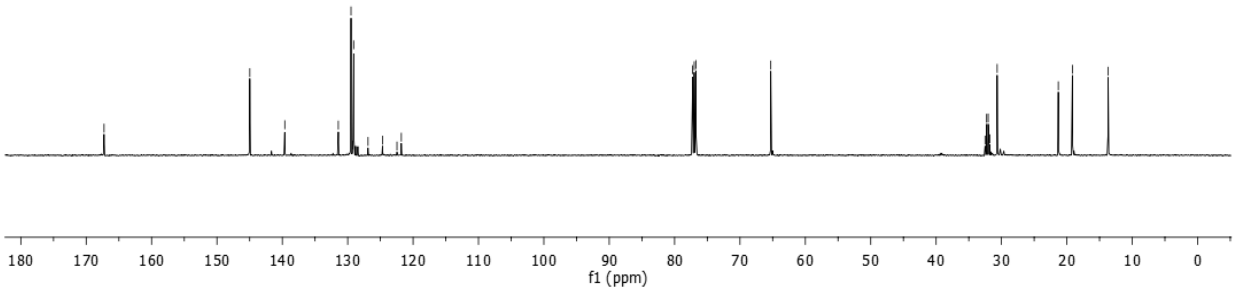
2b

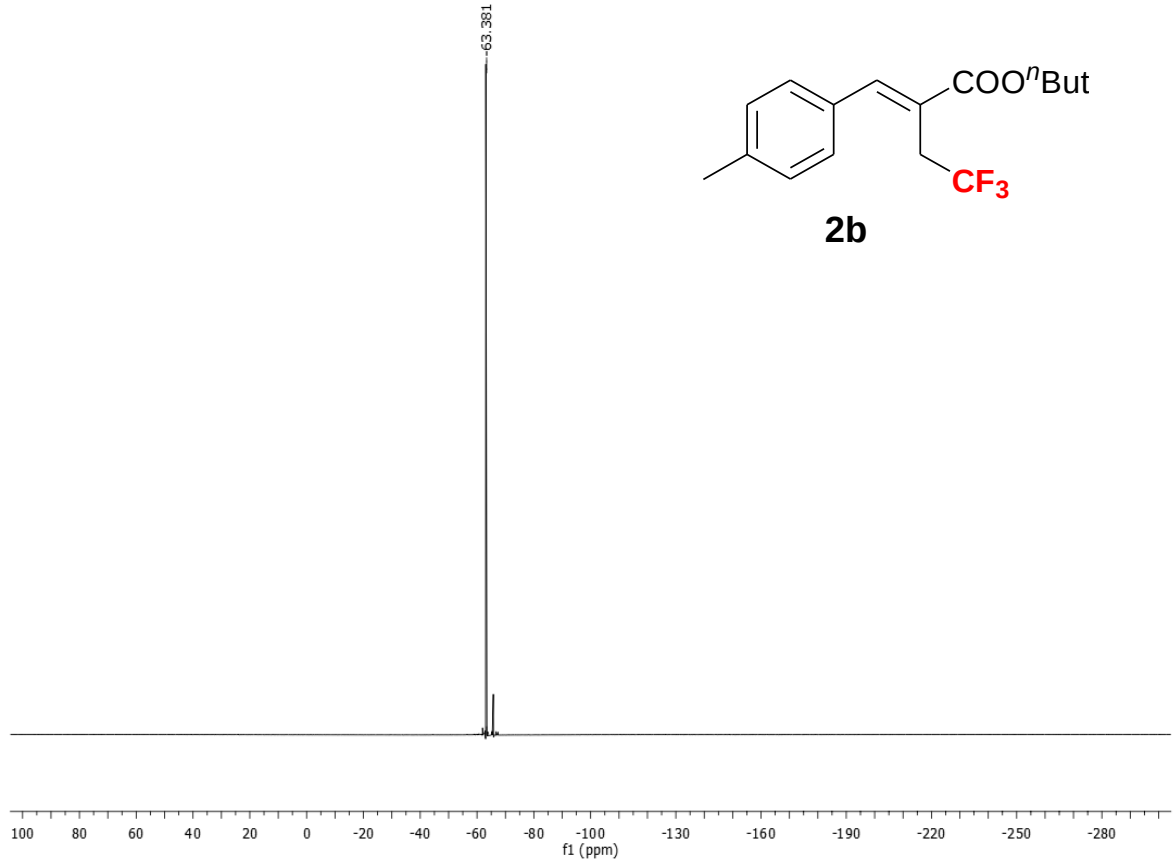

1.00
2.19
2.19
2.17
2.23
3.09
2.31
2.42
3.24
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


167.273
144.977
139.624
131.439
129.494
129.225
129.084
126.893
124.678
122.469
121.799
77.253
76.999
76.745
65.289
32.512
32.271
32.031
31.790
30.660
21.308
19.154
13.685


COO^{n}But
CF$_3$

2b

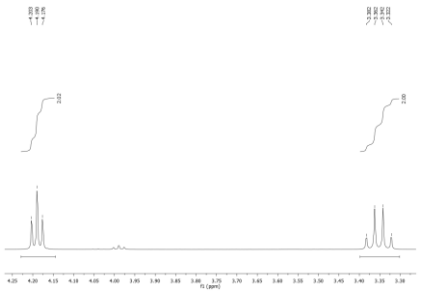

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

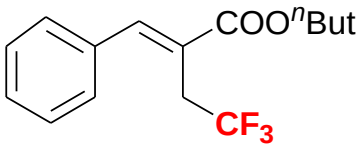

-63.381
100
80
60
40
20
0
-20
-40
-60
-80
-100
-130
-160
-190
-220
-250
-280
f1 (ppm)

COO^{n}But
CF$_3$

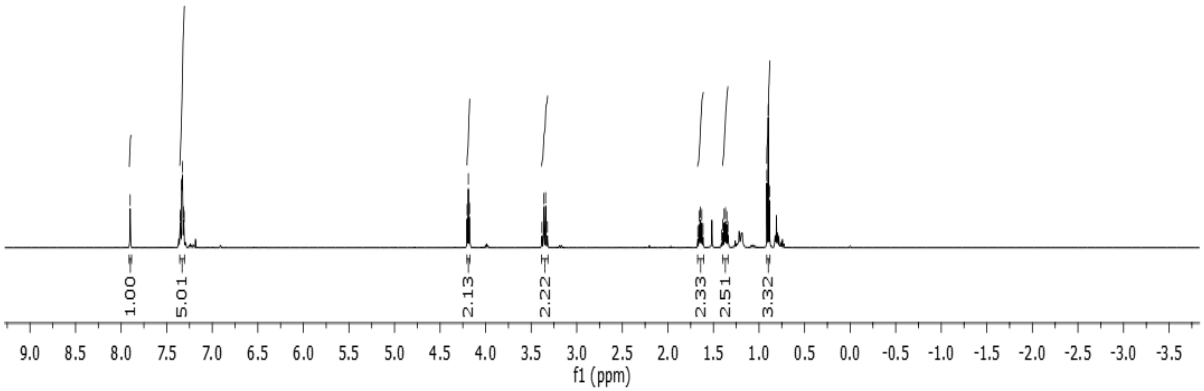
2b


7.901
7.351
7.348
7.338
7.327
7.313
7.308
4.203
4.190
4.176
3.382
3.362
3.342
3.322
1.658
1.643
1.628
1.397
1.383
1.368
1.353
1.342
0.914
0.899
0.884

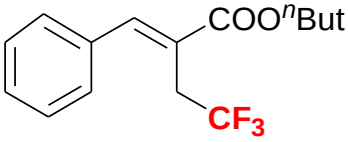



COO^{n}But
CF$_3$

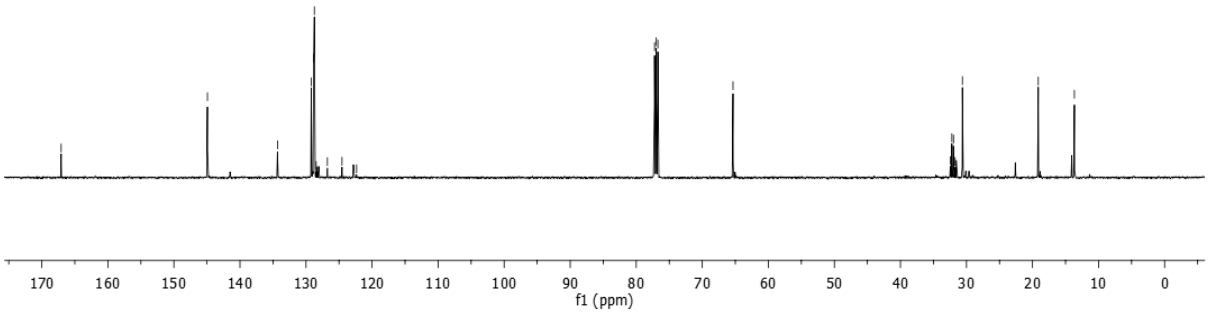
2c

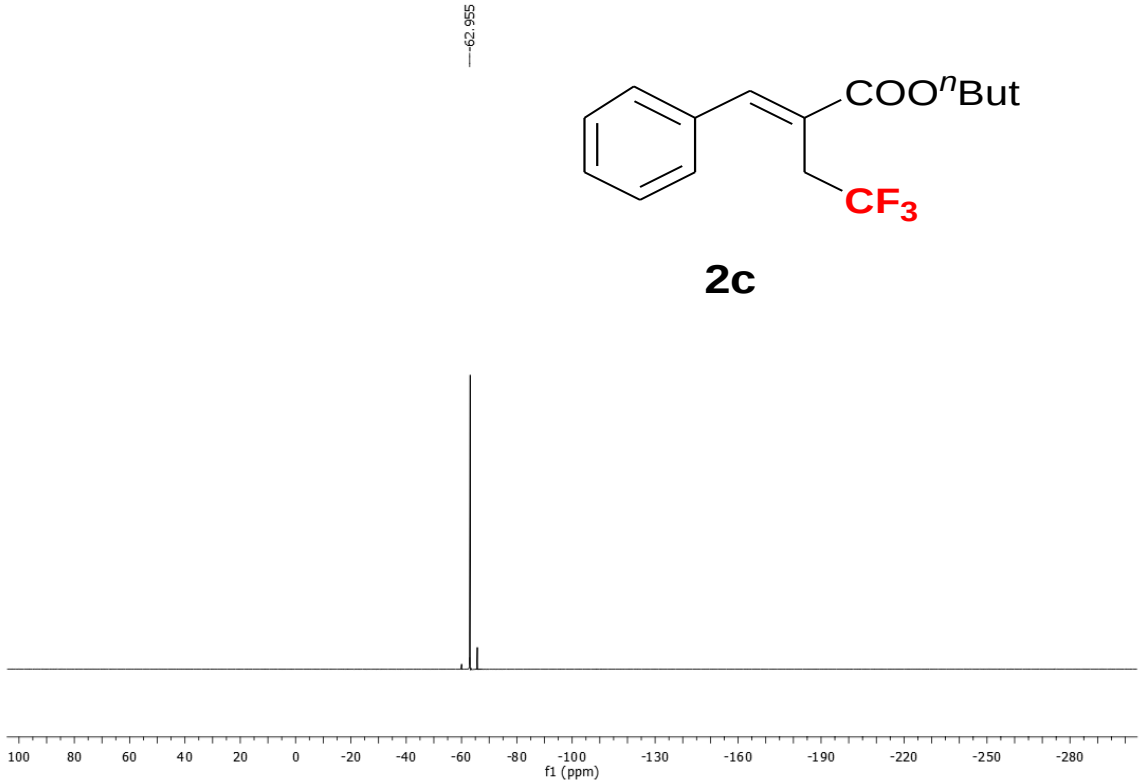

1.00
5.01
2.13
2.22
2.33
2.51
3.32
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2.5 -3.0 -3.5
f1 (ppm)


167.072
144.924
134.318
129.206
128.850
128.736
128.464
126.762
124.550
122.338
77.225
76.971
76.717
65.348
32.452
32.210
31.968
31.724
30.616
19.128
13.661

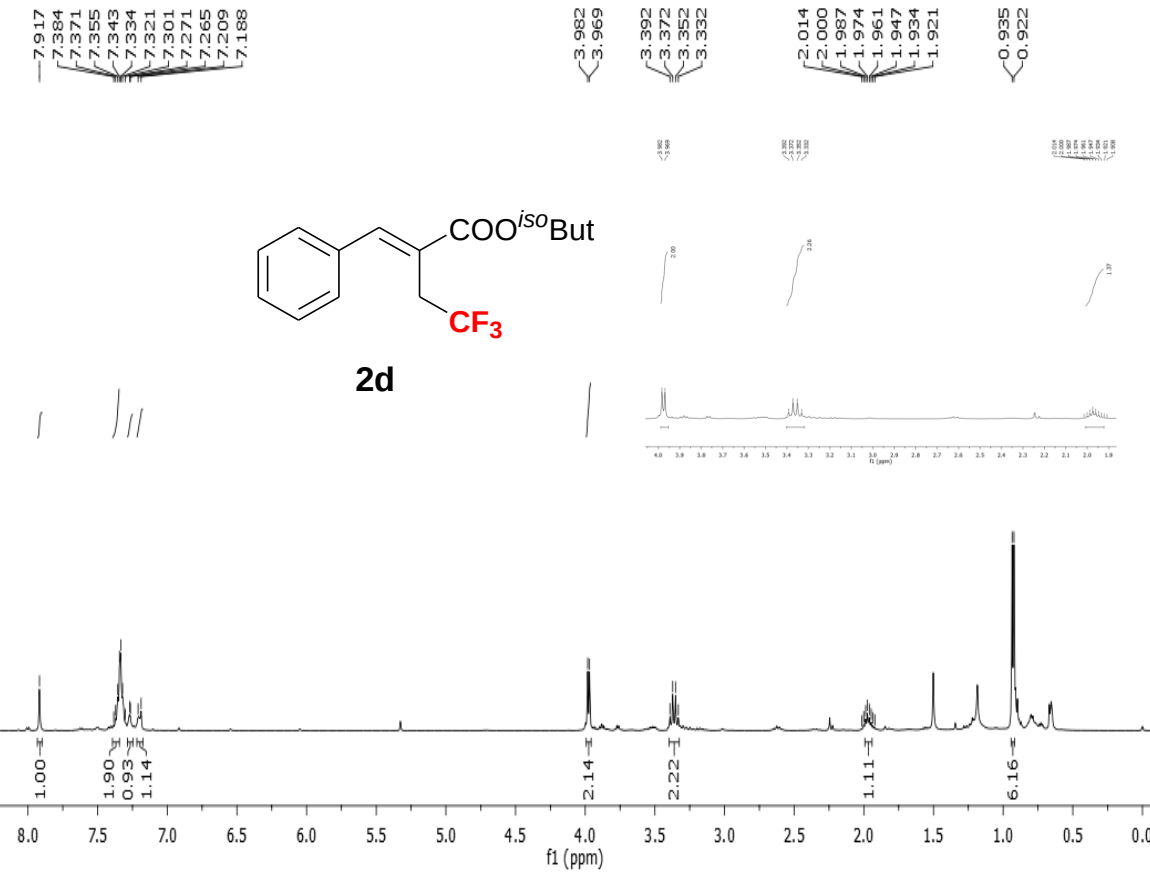

COO^{n}But
CF$_3$

2c

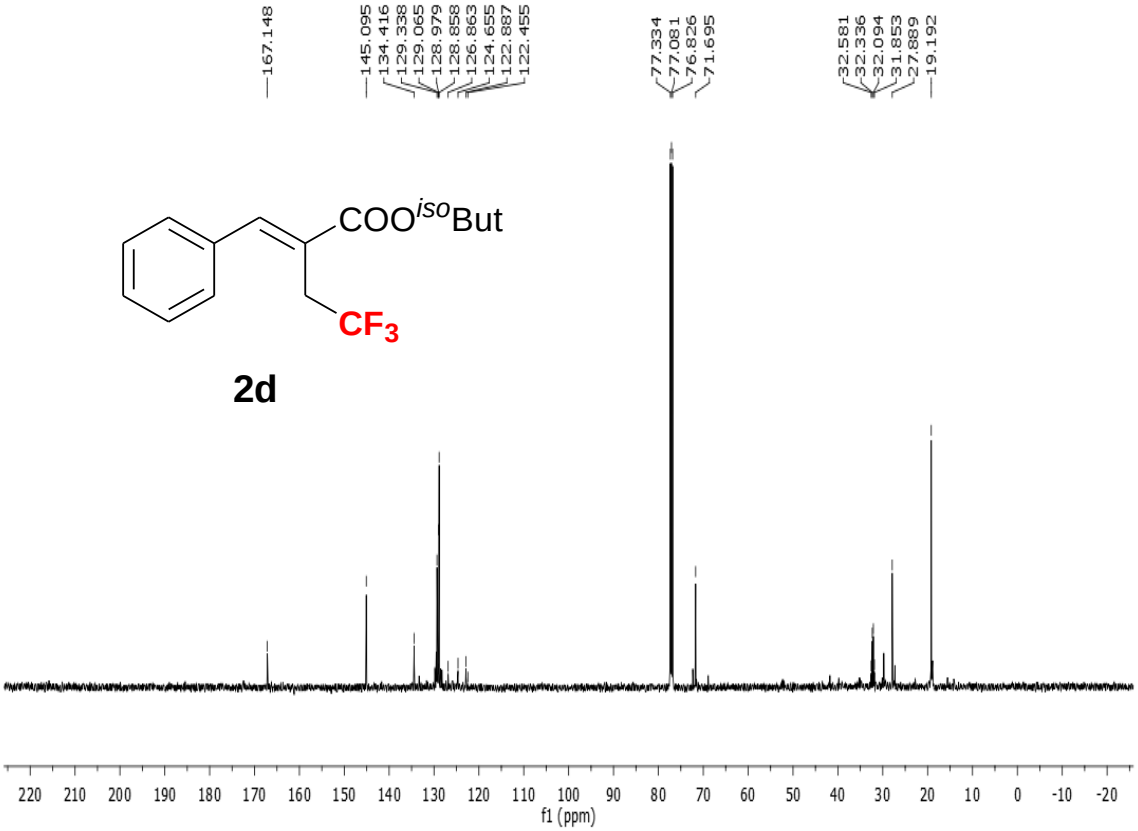

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

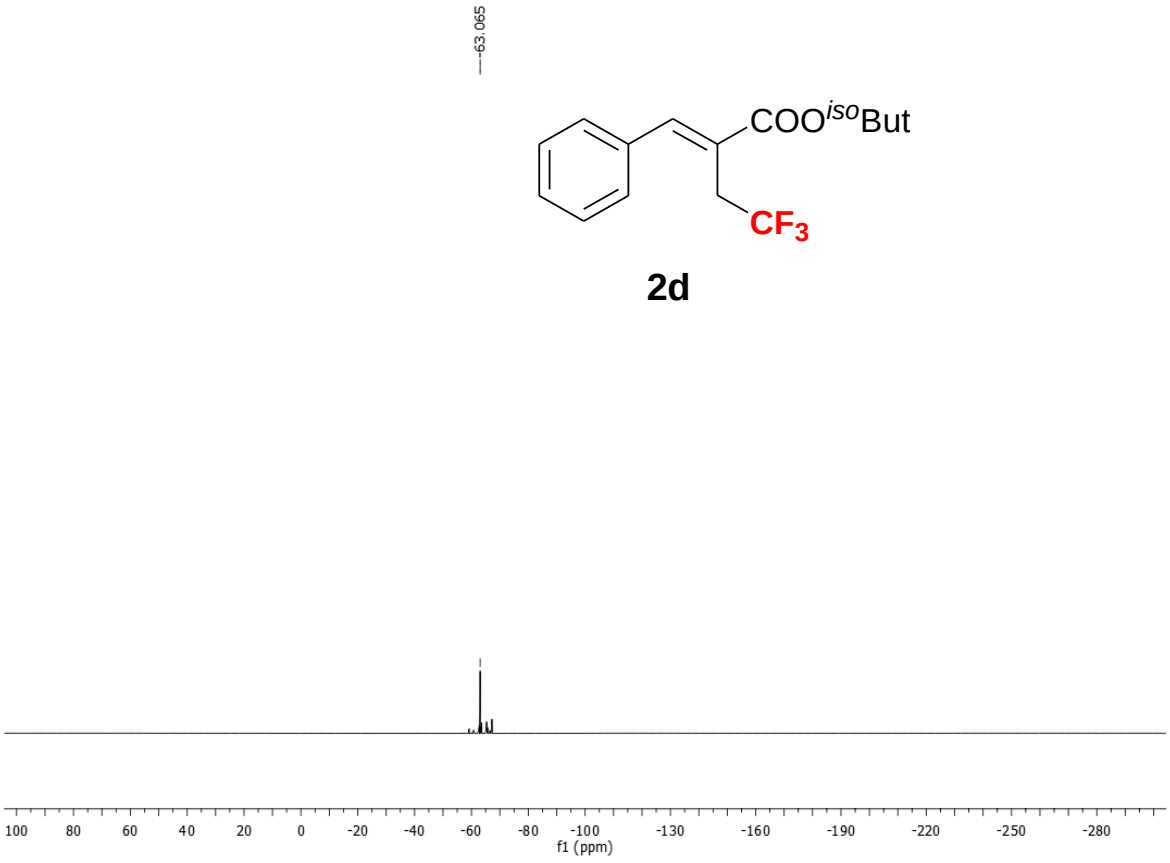

-62.955
COO^{n}But
CF$_3$
100 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220 -250 -280
f1 (ppm)

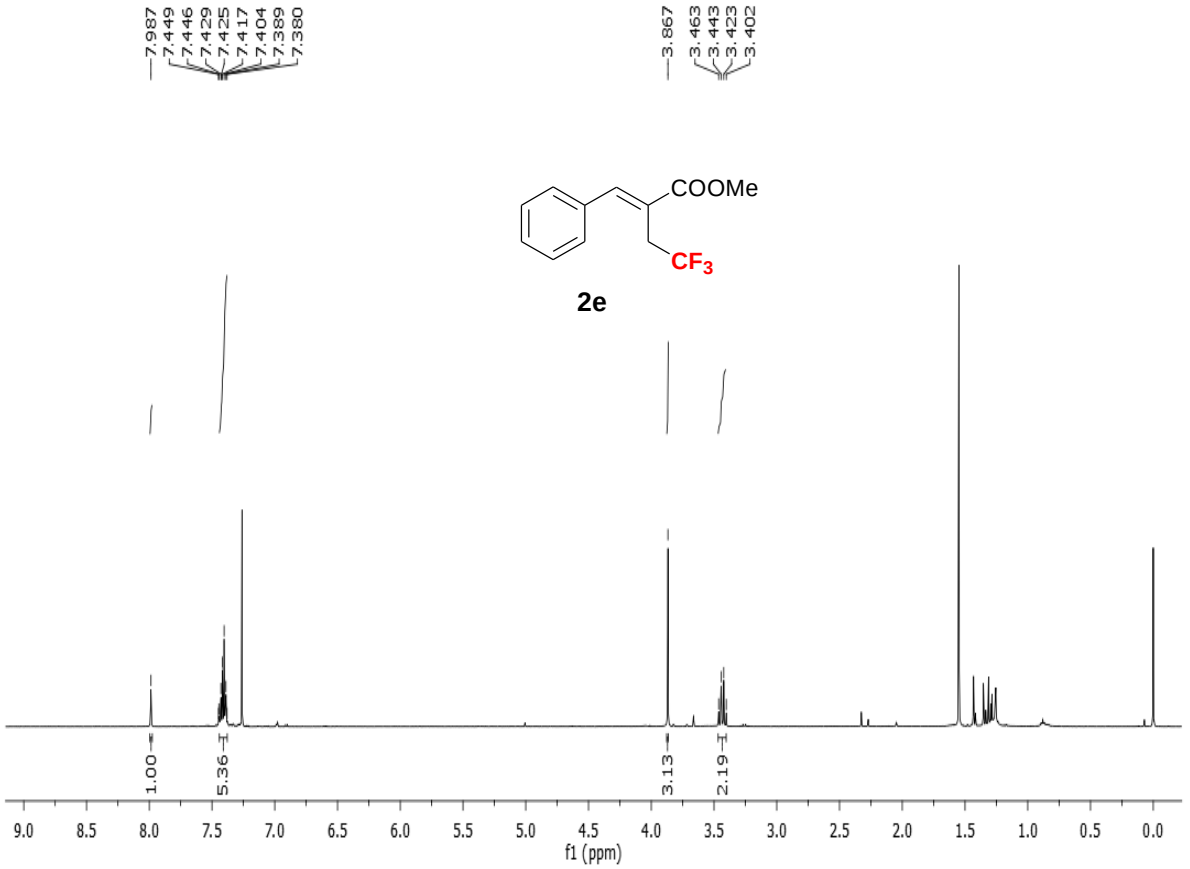
2c

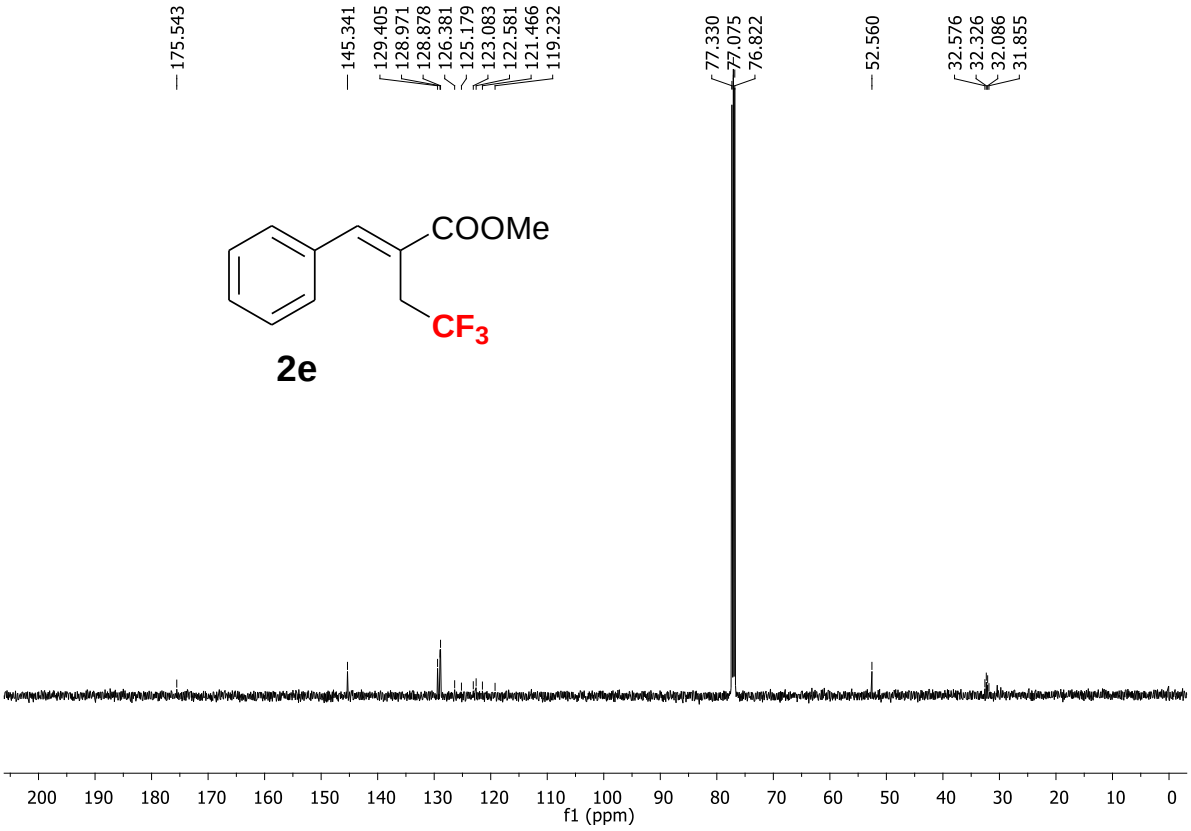

7.917
7.384
7.371
7.355
7.343
7.334
7.321
7.301
7.271
7.265
7.209
7.188
3.982
3.969
3.392
3.372
3.352
3.332
2.014
2.000
1.987
1.974
1.961
1.947
1.934
1.921
0.935
0.922
COO^{iso}But
CF$_3$
1.00
1.90
0.93
1.14
2.14
2.22
1.11
6.16
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

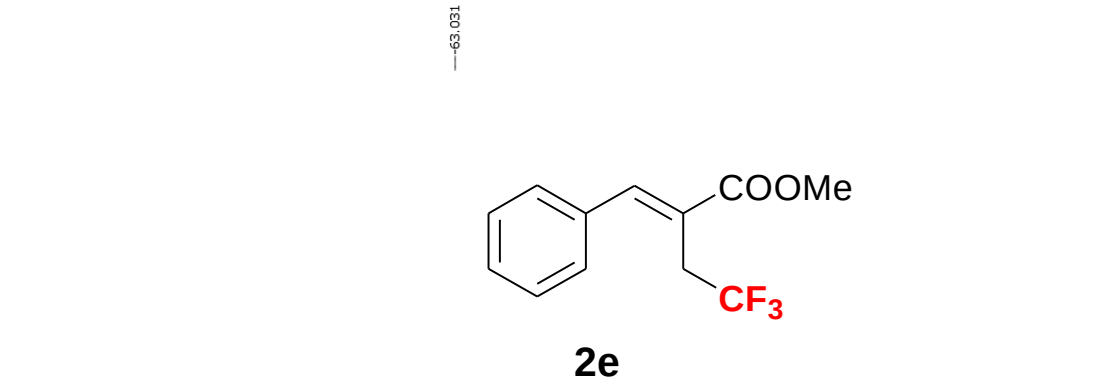
2d


167.148
145.095
134.416
129.338
129.065
128.979
128.858
126.863
124.655
122.887
122.455
77.334
77.081
76.826
71.695
32.581
32.336
32.094
31.853
27.889
19.192
COO^isoBut
CF3
2d
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

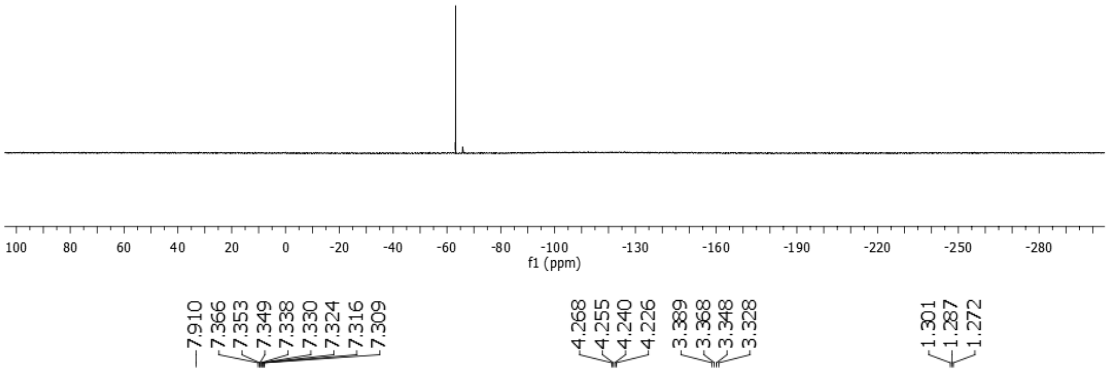

-63.065
COO^isoBut
CF3
2d
100 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220 -250 -280
f1 (ppm)


7.987
7.449
7.446
7.429
7.425
7.417
7.404
7.389
7.380
3.867
3.463
3.443
3.423
3.402
COOMe
CF3
2e
1.00
5.36
3.13
2.19
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

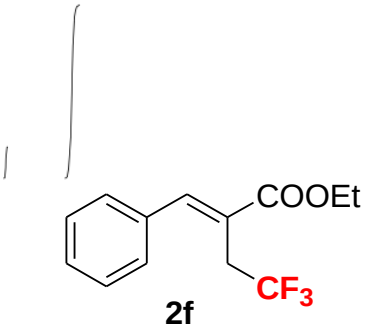

175.543
145.341
129.405
128.971
128.878
126.381
125.179
123.083
122.581
121.466
119.232
77.330
77.075
76.822
52.560
32.576
32.326
32.086
31.855
COOMe
CF3
2e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-63.031
COOMe
CF3

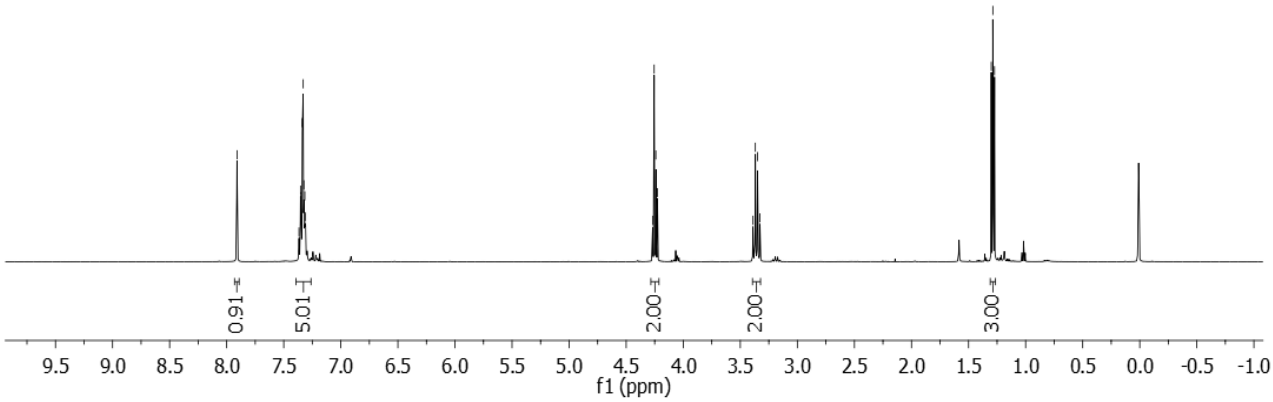
2e

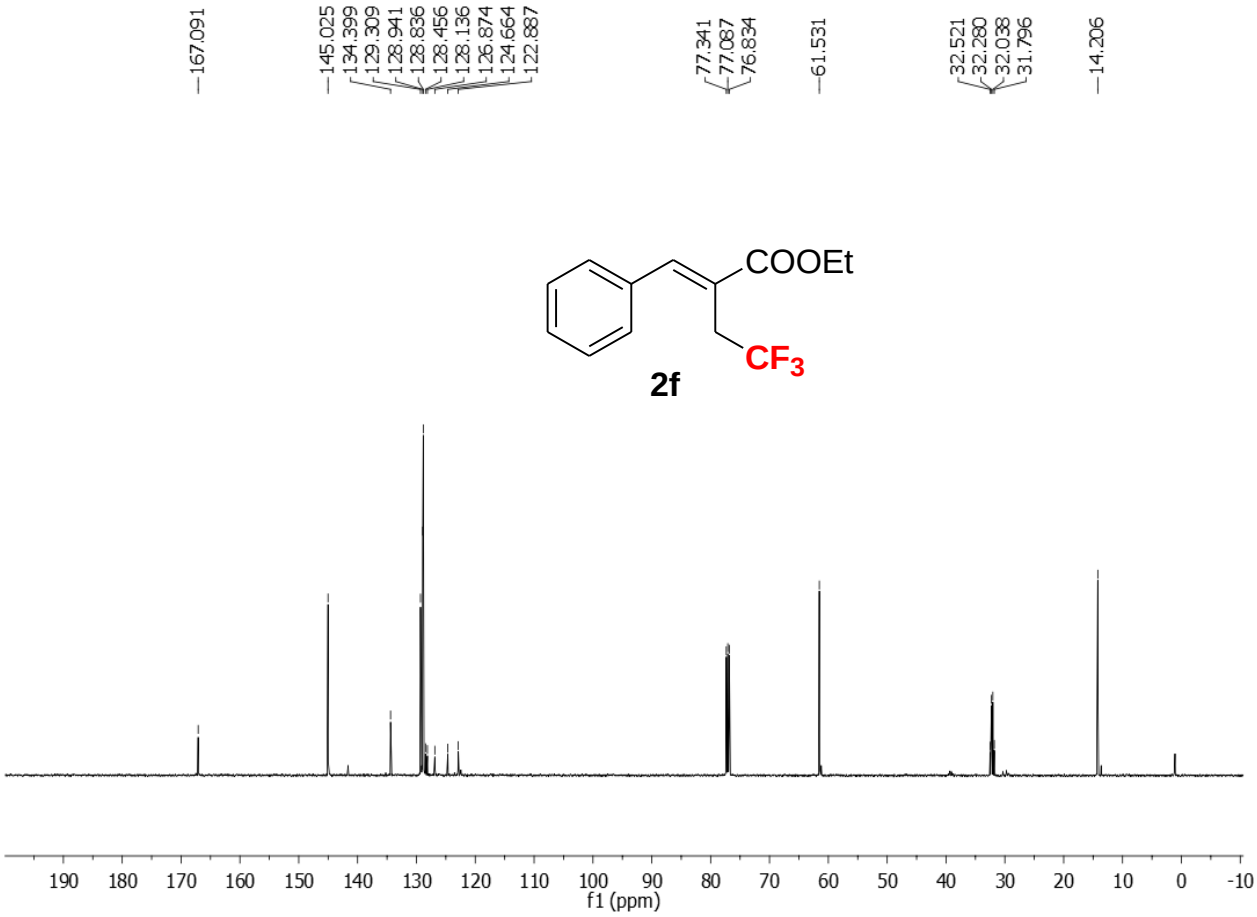

100 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220 -250 -280
f1 (ppm)

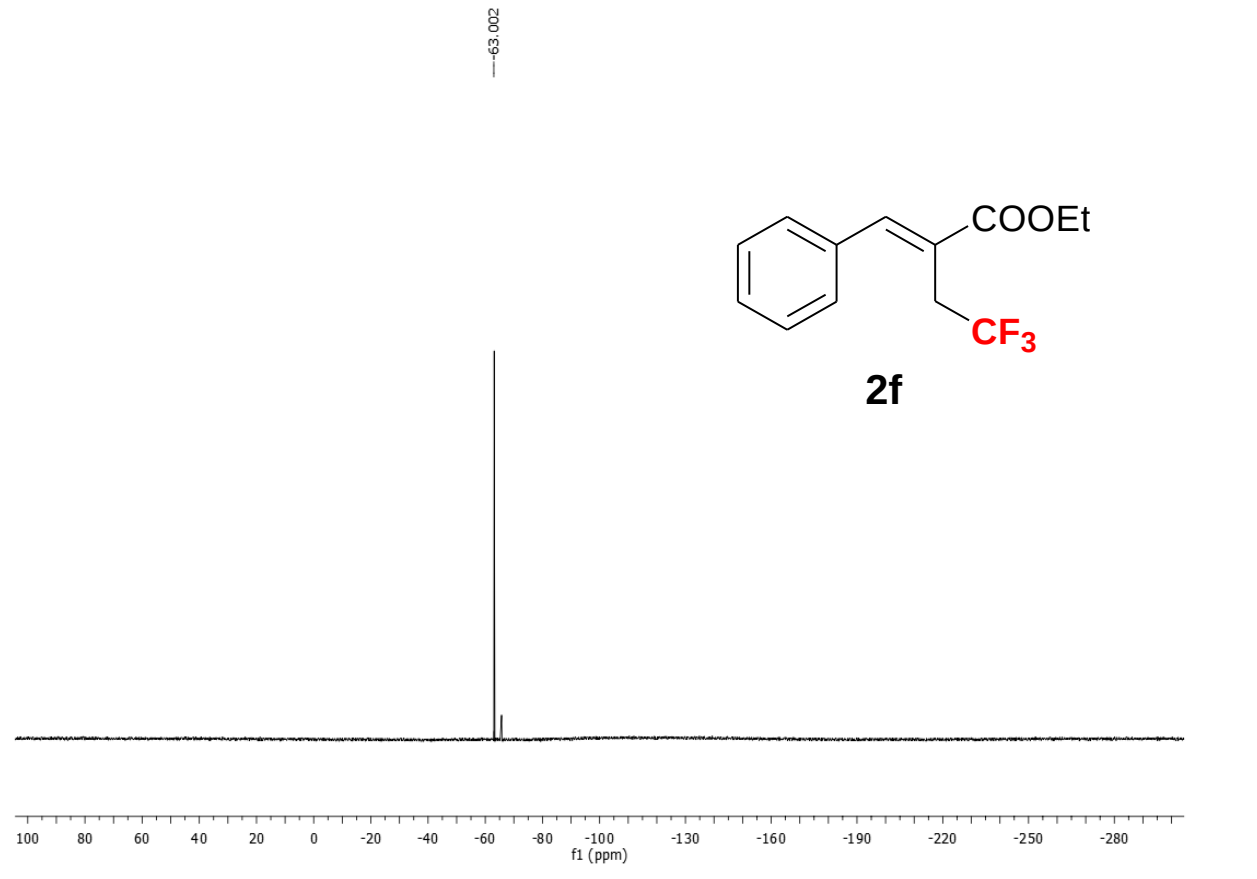
7.910
7.366
7.353
7.349
7.338
7.330
7.324
7.316
7.309
4.268
4.255
4.240
4.226
3.389
3.368
3.348
3.328
1.301
1.287
1.272

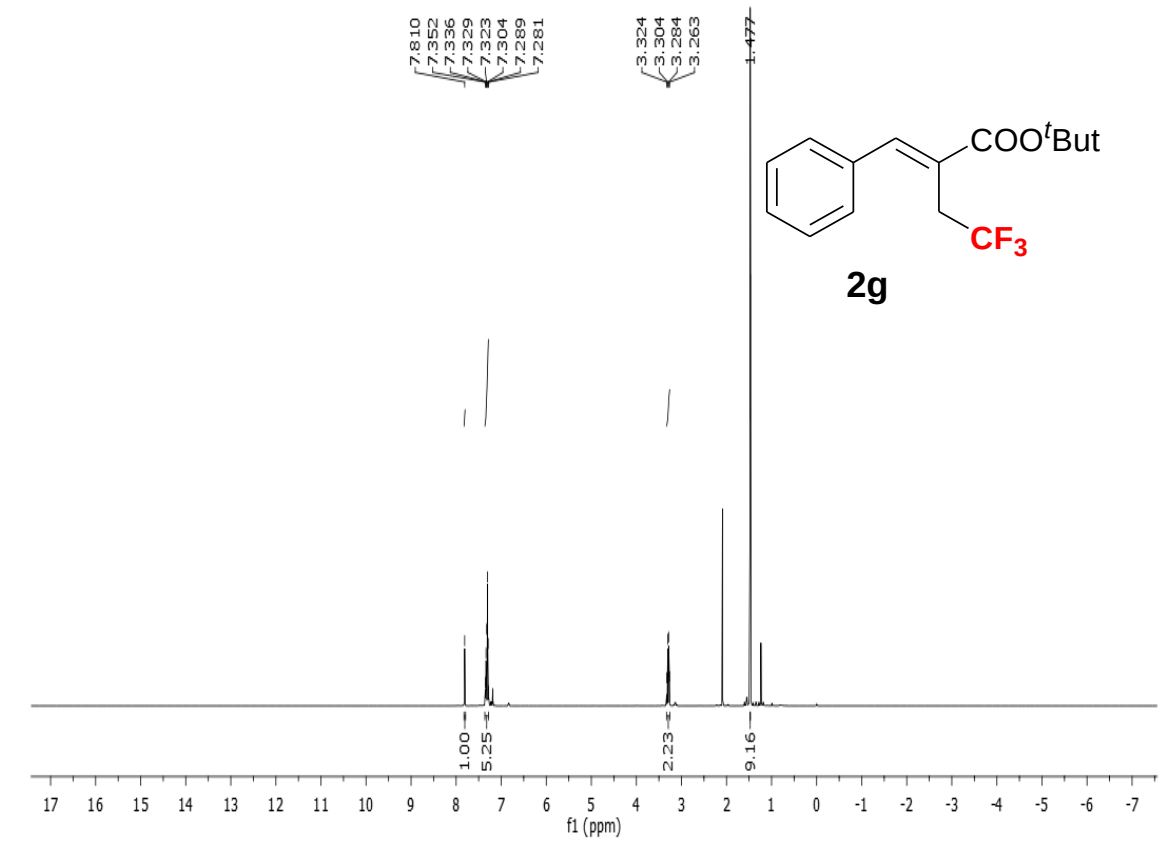

COOEt
CF3

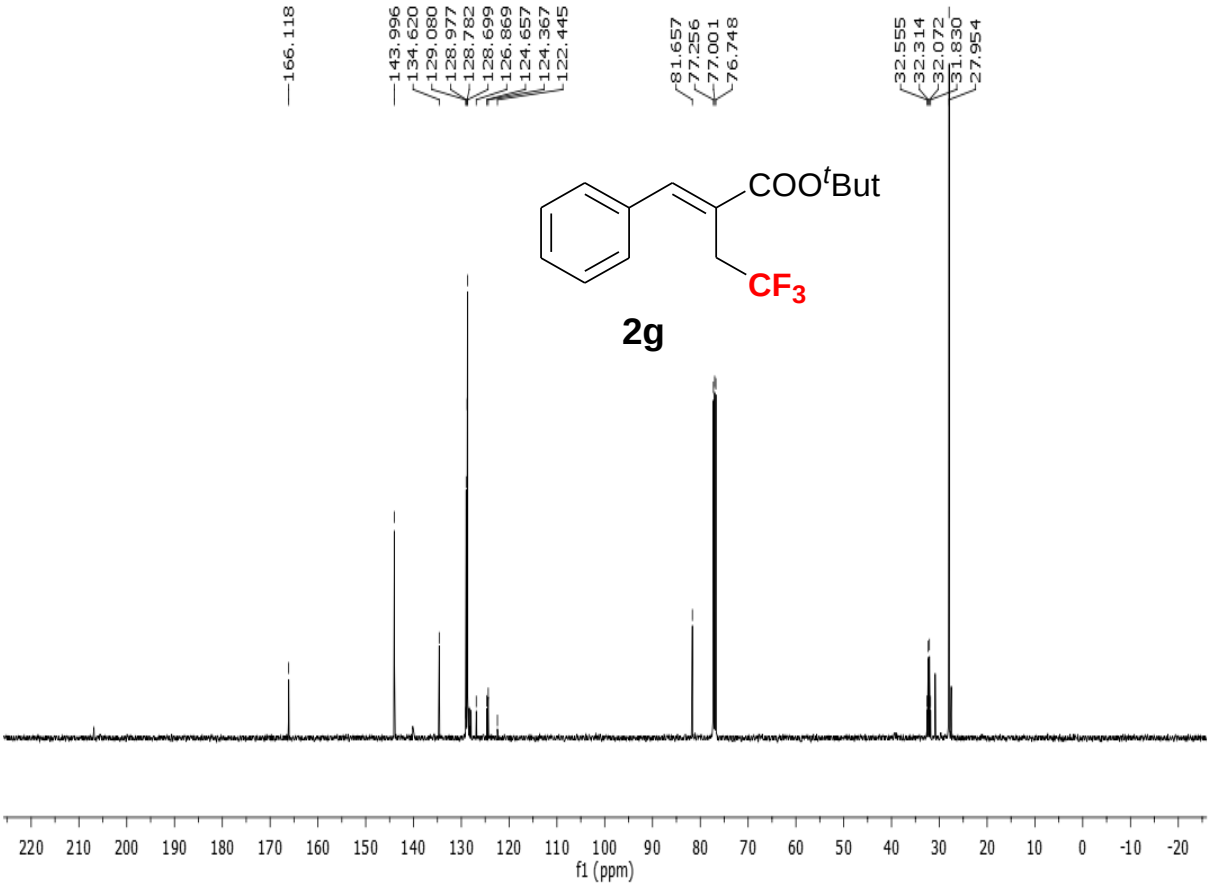
2f

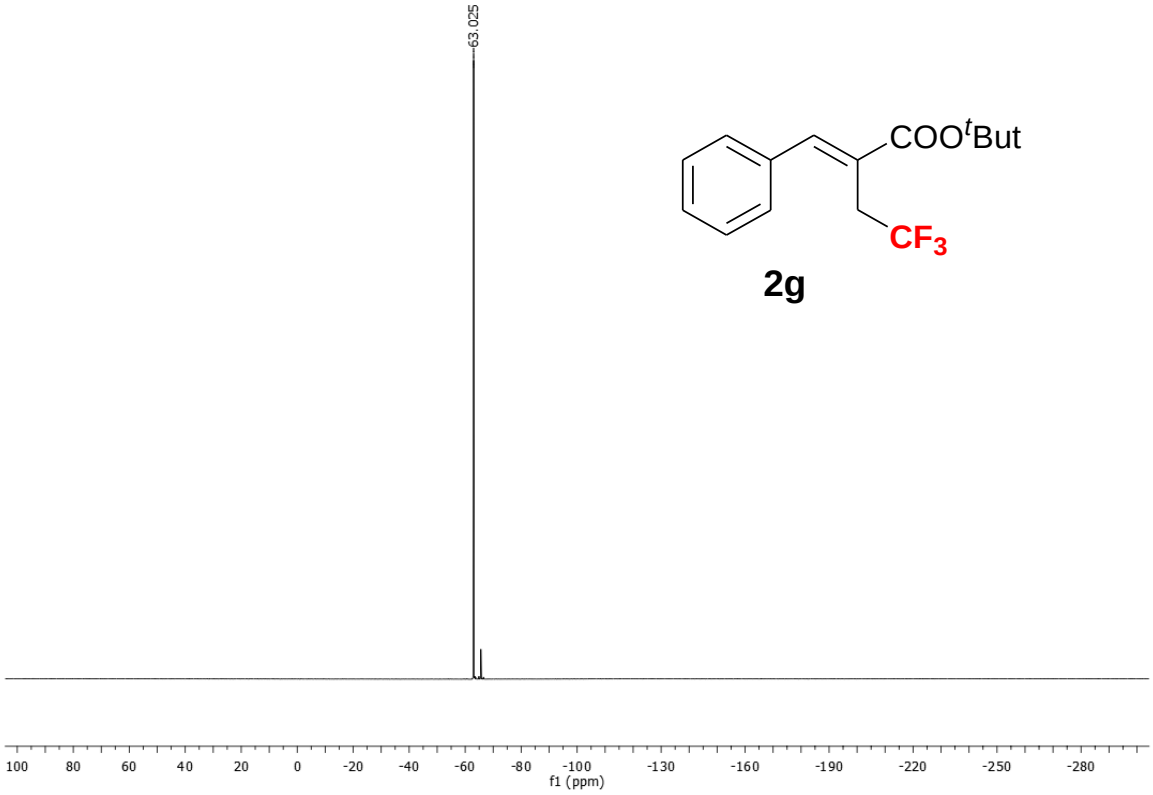

0.91
5.01
2.00
2.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


167.091
145.025
134.399
129.309
128.941
128.836
128.456
128.136
126.874
124.664
122.887
77.341
77.087
76.834
61.531
32.521
32.280
32.038
31.796
14.206
COOEt
CF3
2f
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

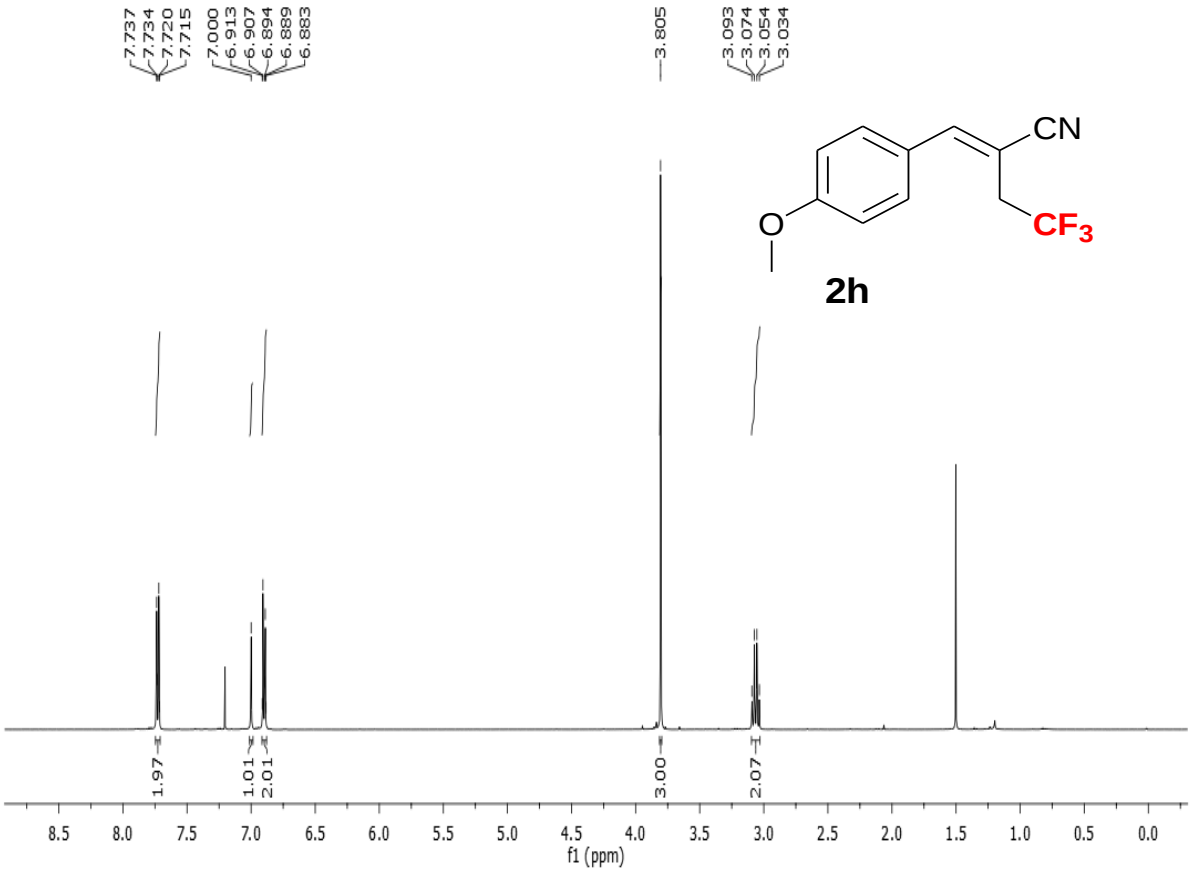

-63.002
COOEt
CF3
2f
100 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220 -250 -280
f1 (ppm)


7.810
7.352
7.336
7.329
7.323
7.304
7.289
7.281
3.324
3.304
3.284
3.263
1.477
COO^{t}But
CF$_3$
2g
1.00
5.25
2.23
9.16
f1 (ppm)

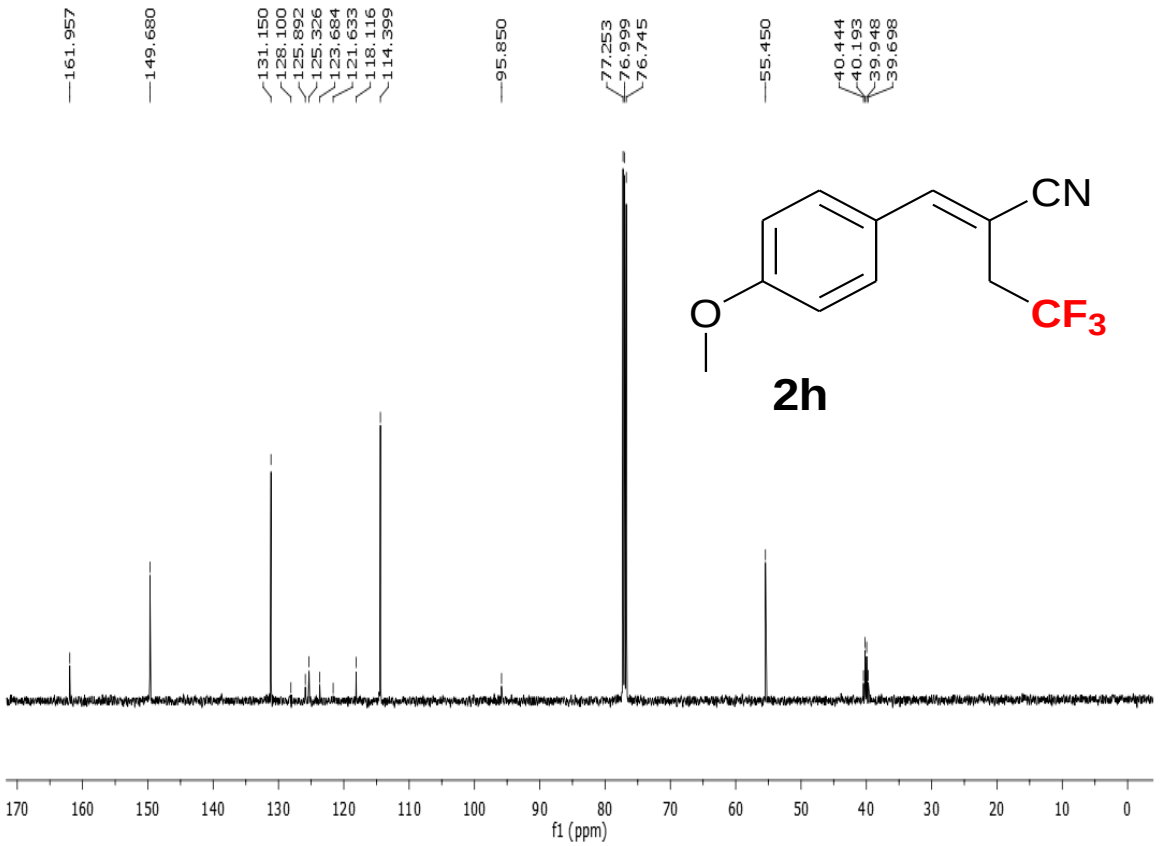

166.118
143.996
134.620
129.080
128.977
128.782
128.699
126.869
124.657
124.367
122.445
81.657
77.256
77.001
76.748
32.555
32.314
32.072
31.830
27.954
COO^{t}But
CF$_3$
2g
f1 (ppm)

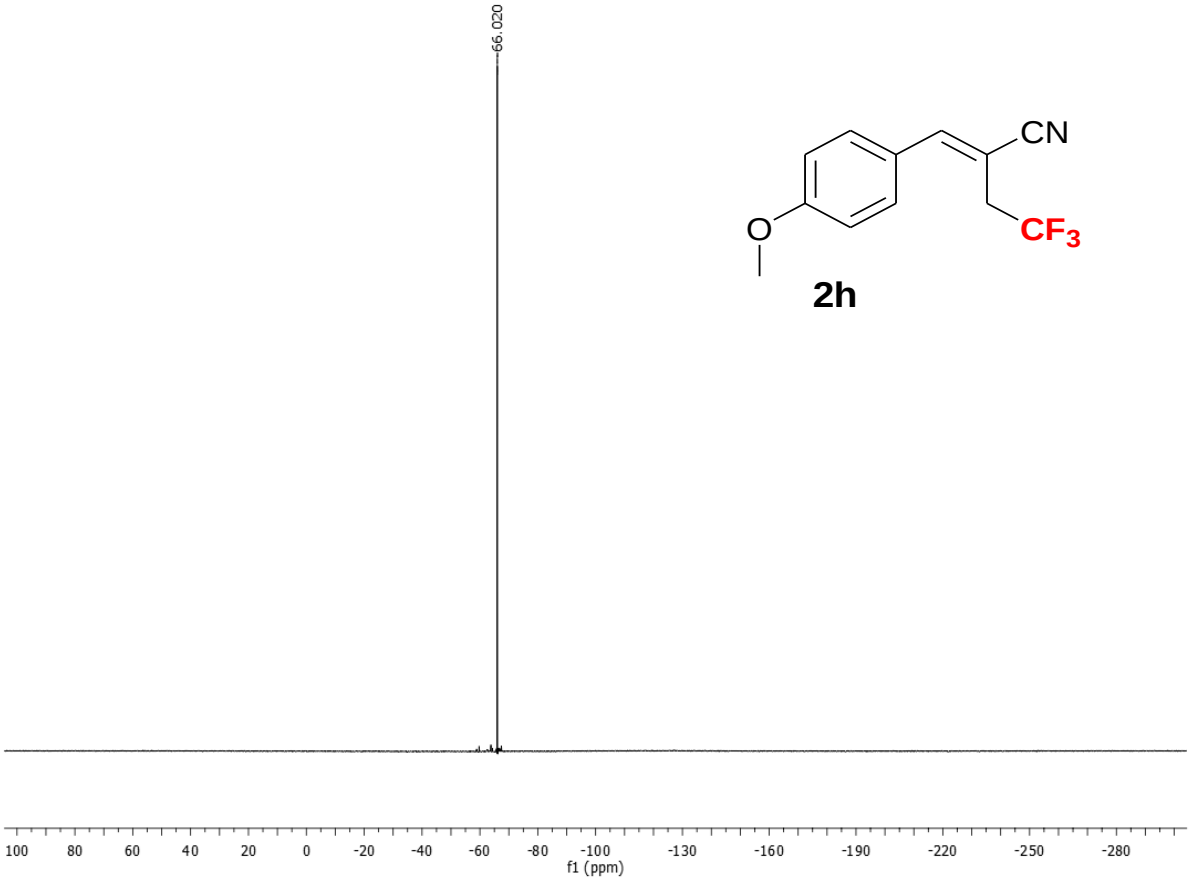

63.025
COO^{t}But
CF$_3$
100 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220 -250 -280
f1 (ppm)

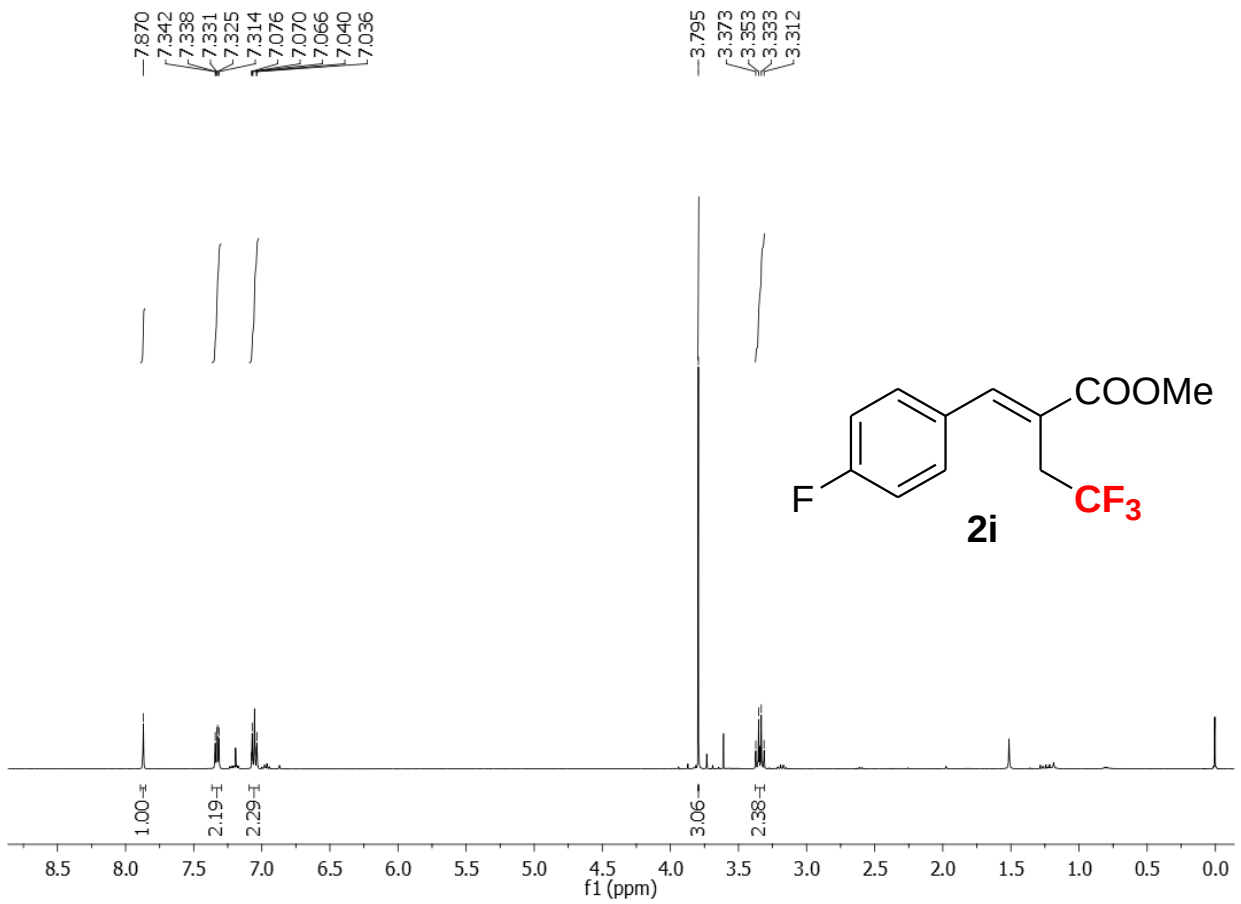
2g

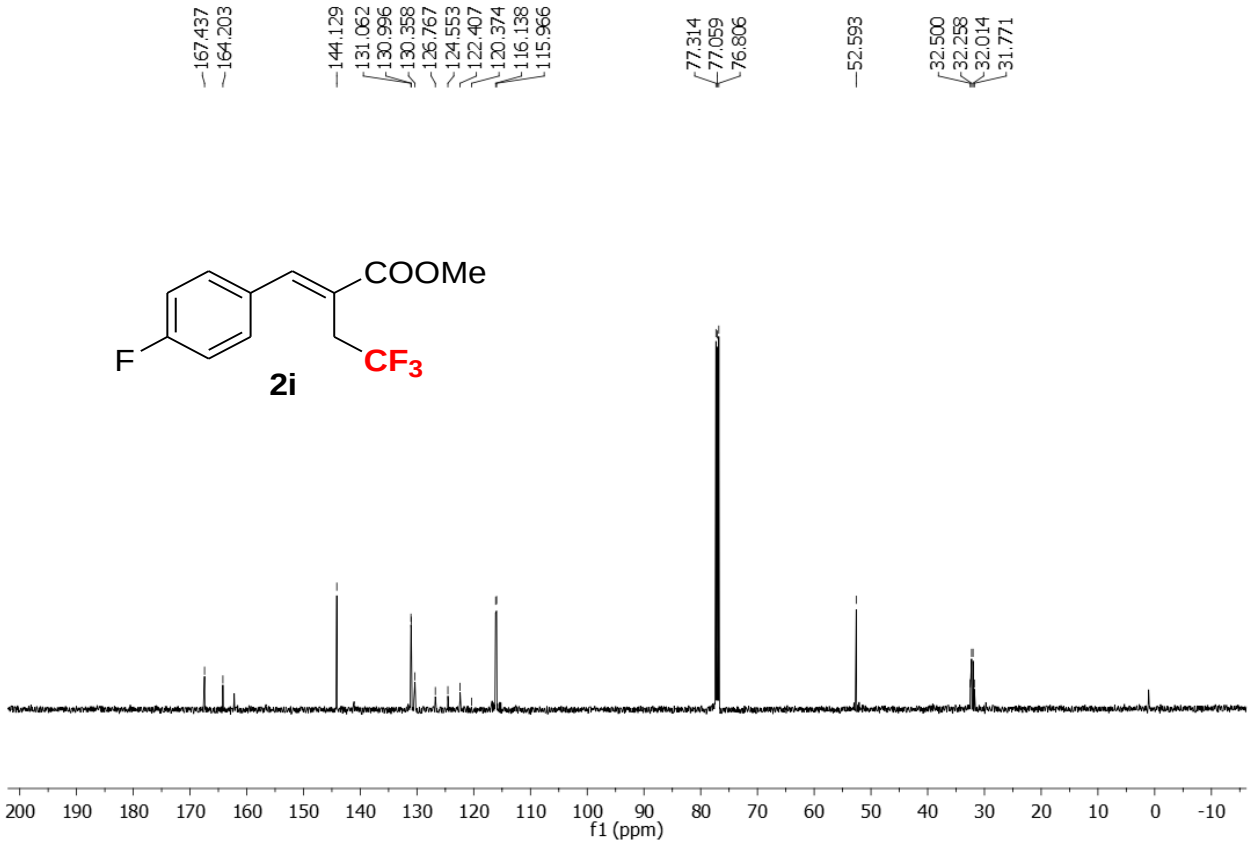

7.737
7.734
7.720
7.715
7.000
6.913
6.907
6.894
6.889
6.883
3.805
3.093
3.074
3.054
3.034
CN
O
CF$_3$
1.97
1.01
2.01
3.00
2.07
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

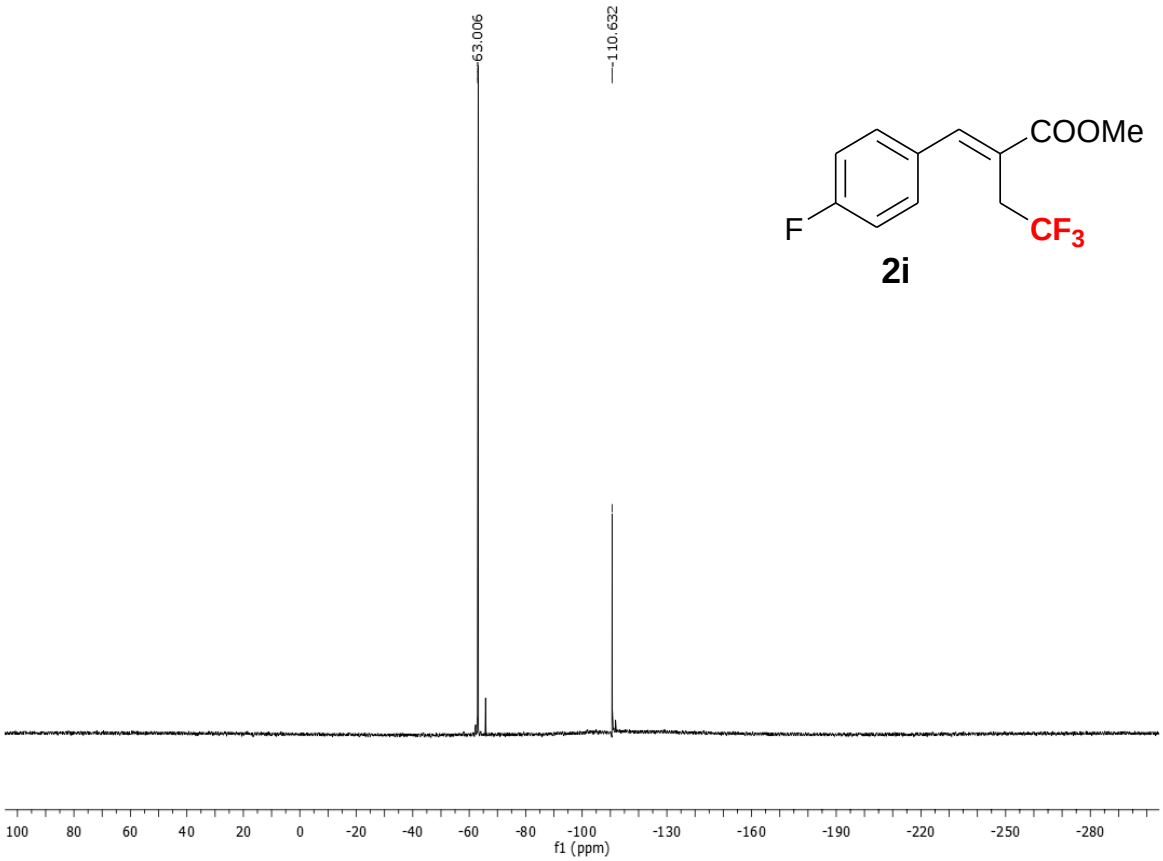
2h


161.957
149.680
131.150
128.100
125.892
125.326
123.684
121.633
118.116
114.399
95.850
77.253
76.999
76.745
55.450
40.444
40.193
39.948
39.698
CN
O
CF3
2h
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

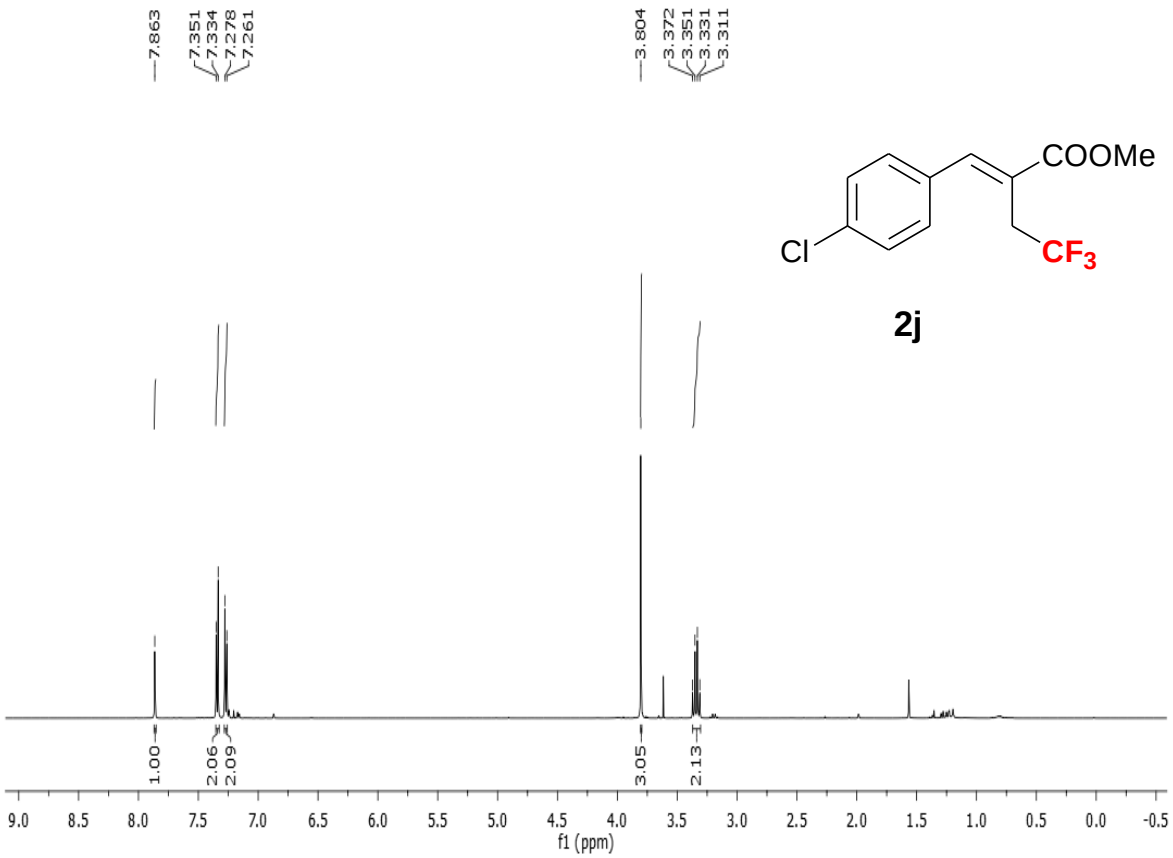

-66.020
CN
O
CF3
2h
100 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220 -250 -280
f1 (ppm)


7.870
7.342
7.338
7.331
7.325
7.314
7.076
7.070
7.066
7.040
7.036
3.795
3.373
3.353
3.333
3.312
COOMe
F
CF3
2i
1.00
2.19
2.29
3.06
2.38
f1 (ppm)

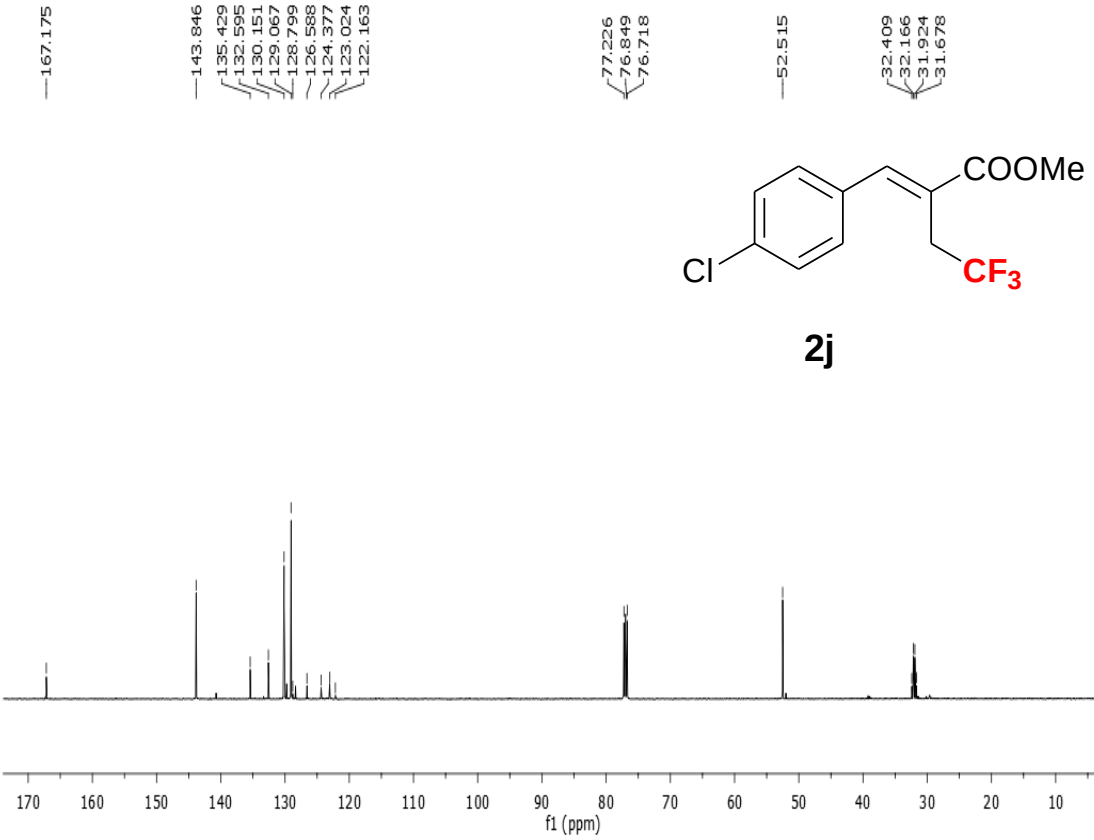

167.437
164.203
144.129
131.062
130.996
130.358
126.767
124.553
122.407
120.374
116.138
115.966
77.314
77.059
76.806
52.593
32.500
32.258
32.014
31.771
COOMe
F
CF3
2i
f1 (ppm)

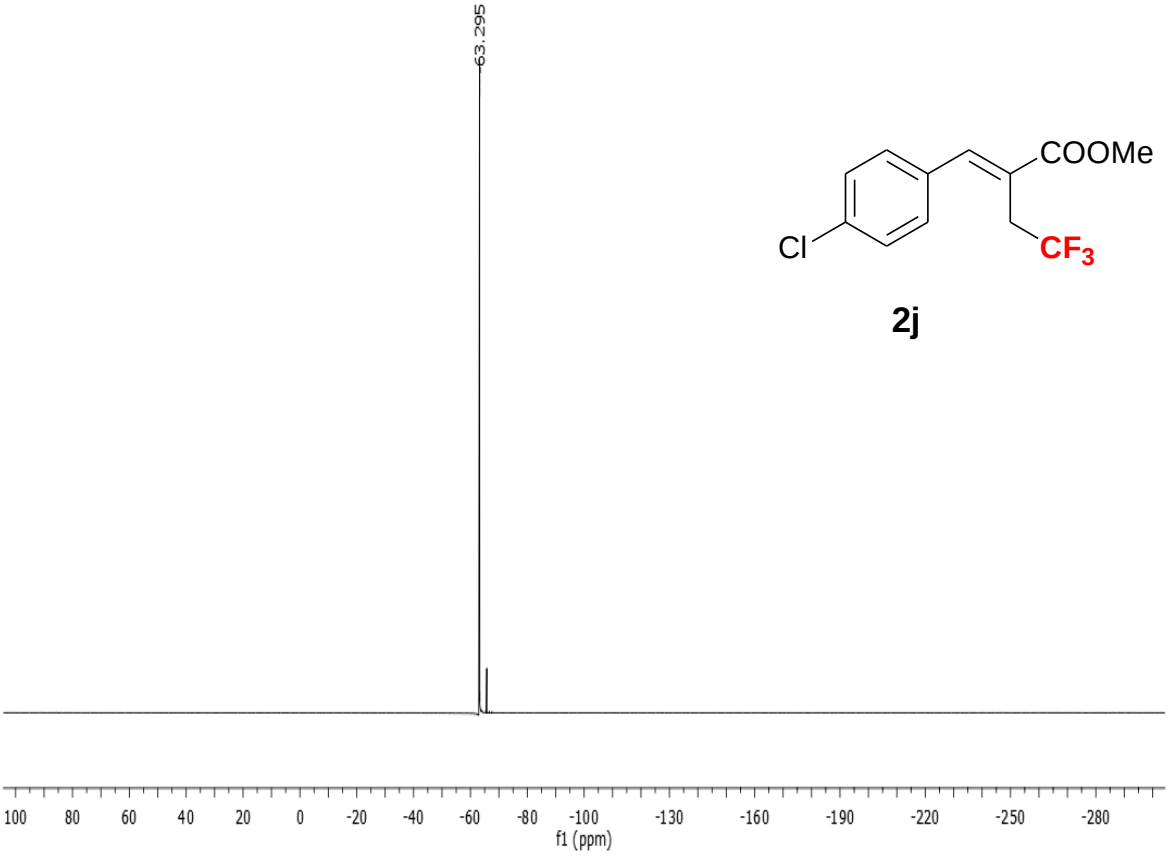

63.006
110.632
COOMe
F
CF3
100 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220 -250 -280
f1 (ppm)

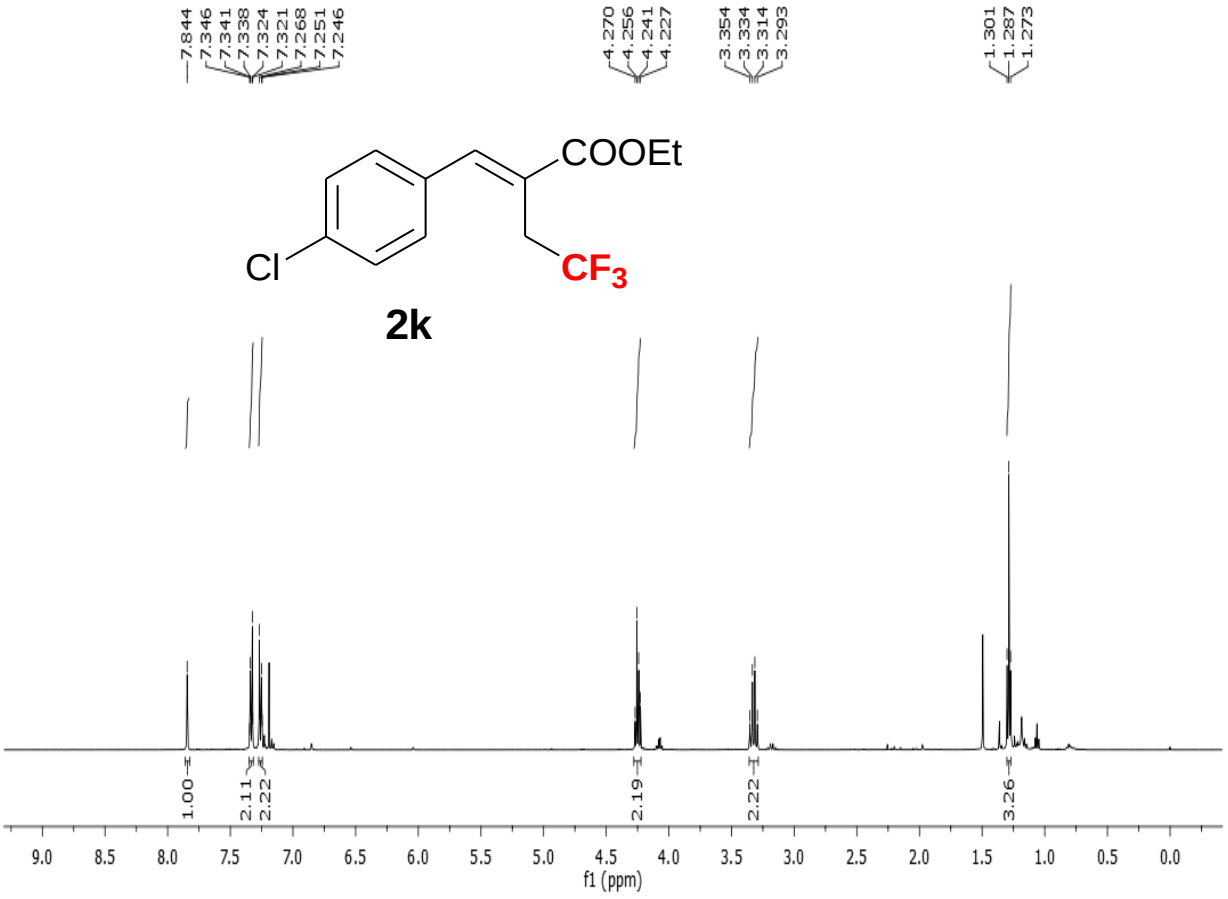
2i

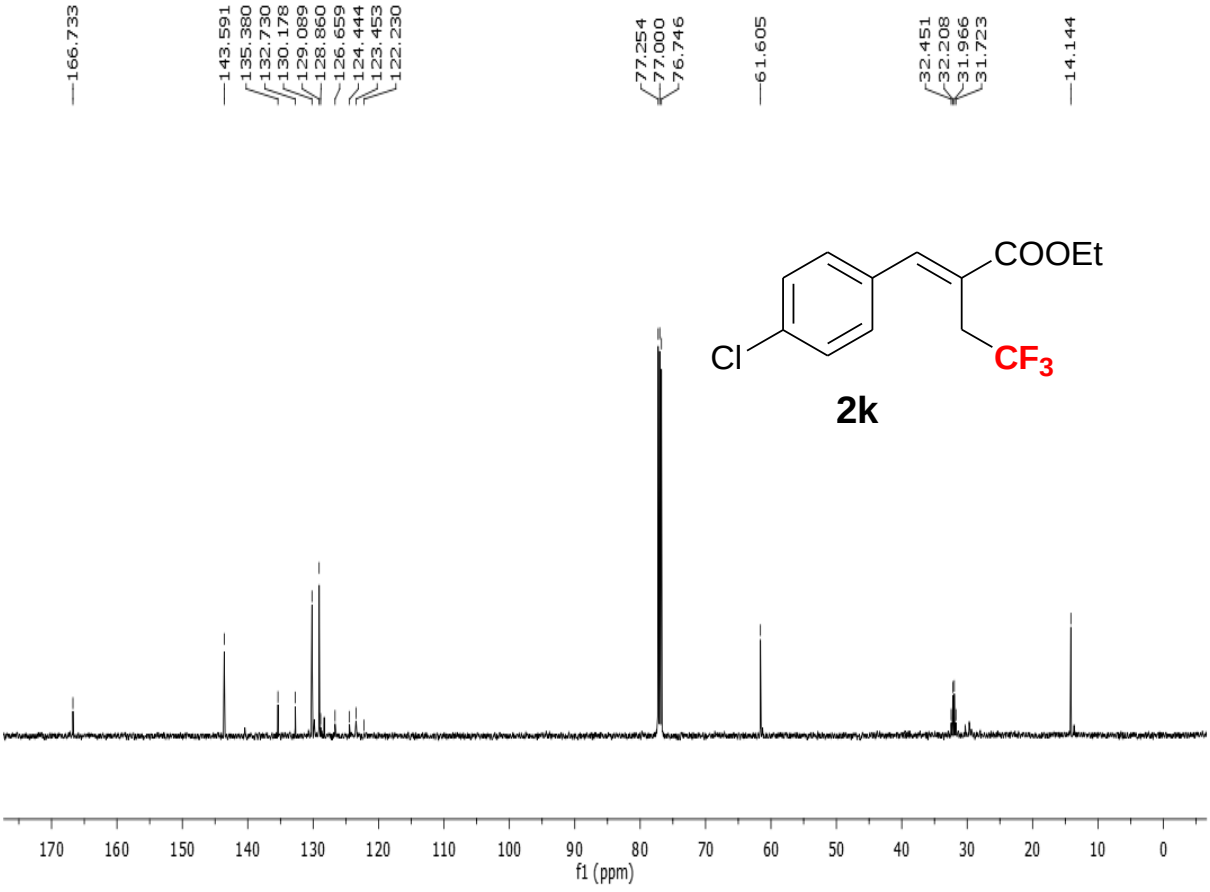

7.863
7.351
7.334
7.278
7.261
3.804
3.372
3.351
3.331
3.311
COOMe
Cl
CF3
1.00
2.06
2.09
3.05
2.13
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

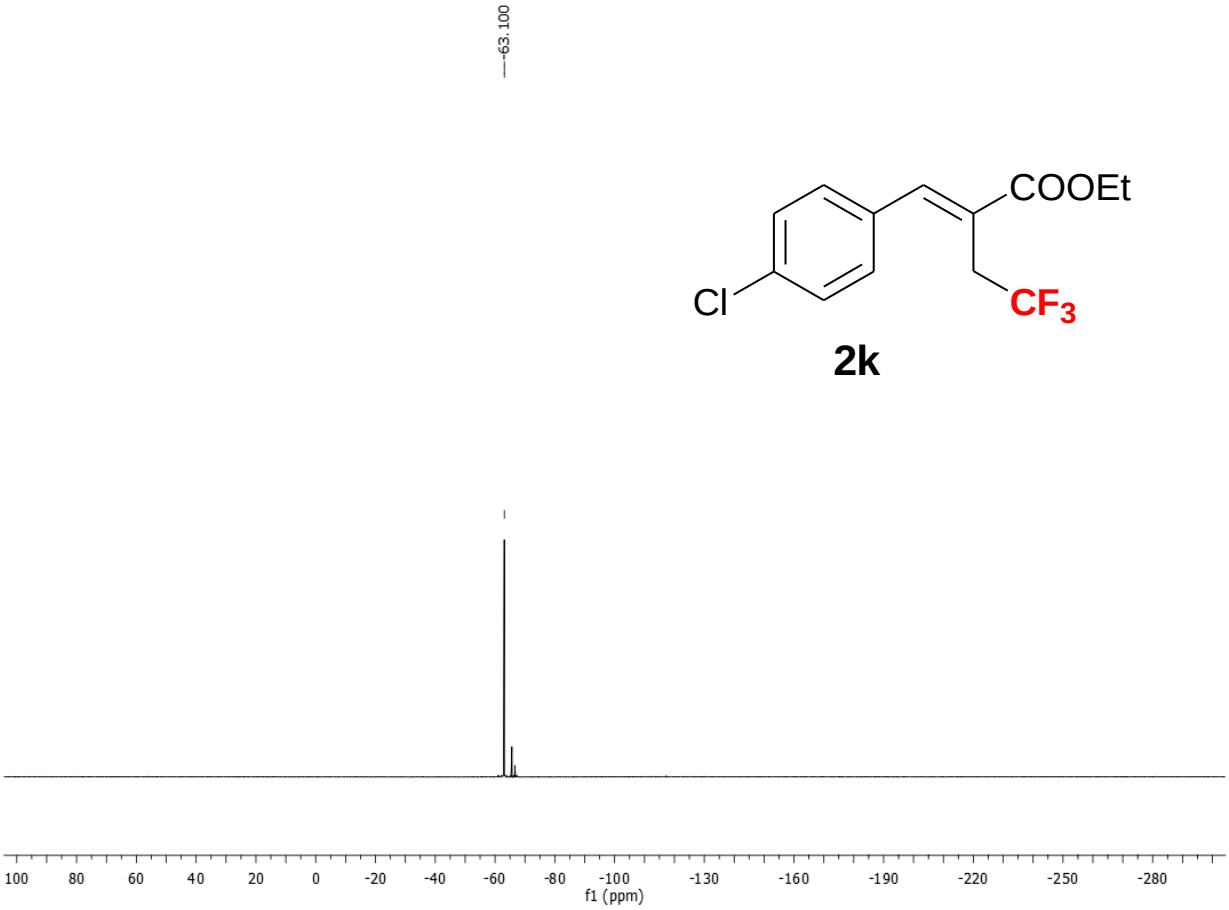
2j

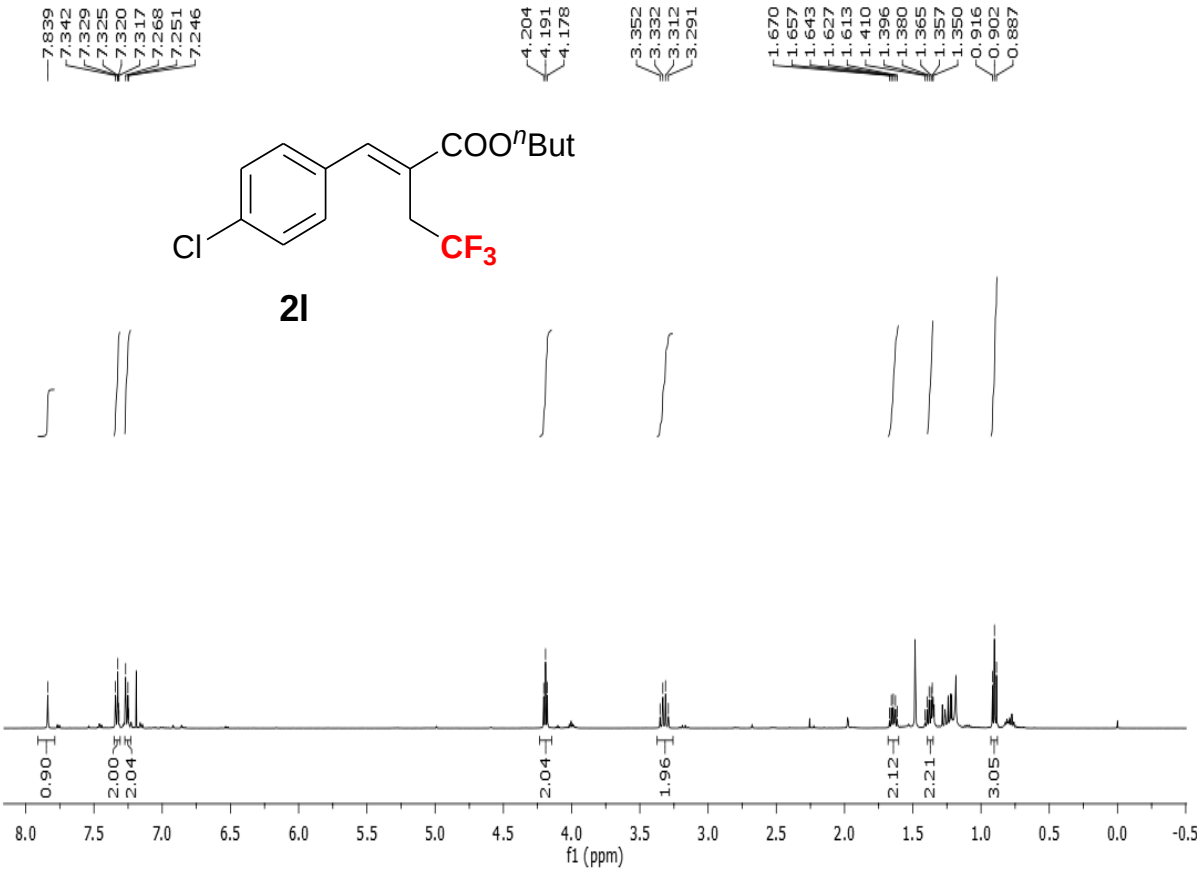

167.175
143.846
135.429
132.595
130.151
129.067
128.799
126.588
124.377
123.024
122.163
77.226
76.849
76.718
52.515
32.409
32.166
31.924
31.678
COOMe
Cl
CF3
2j
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

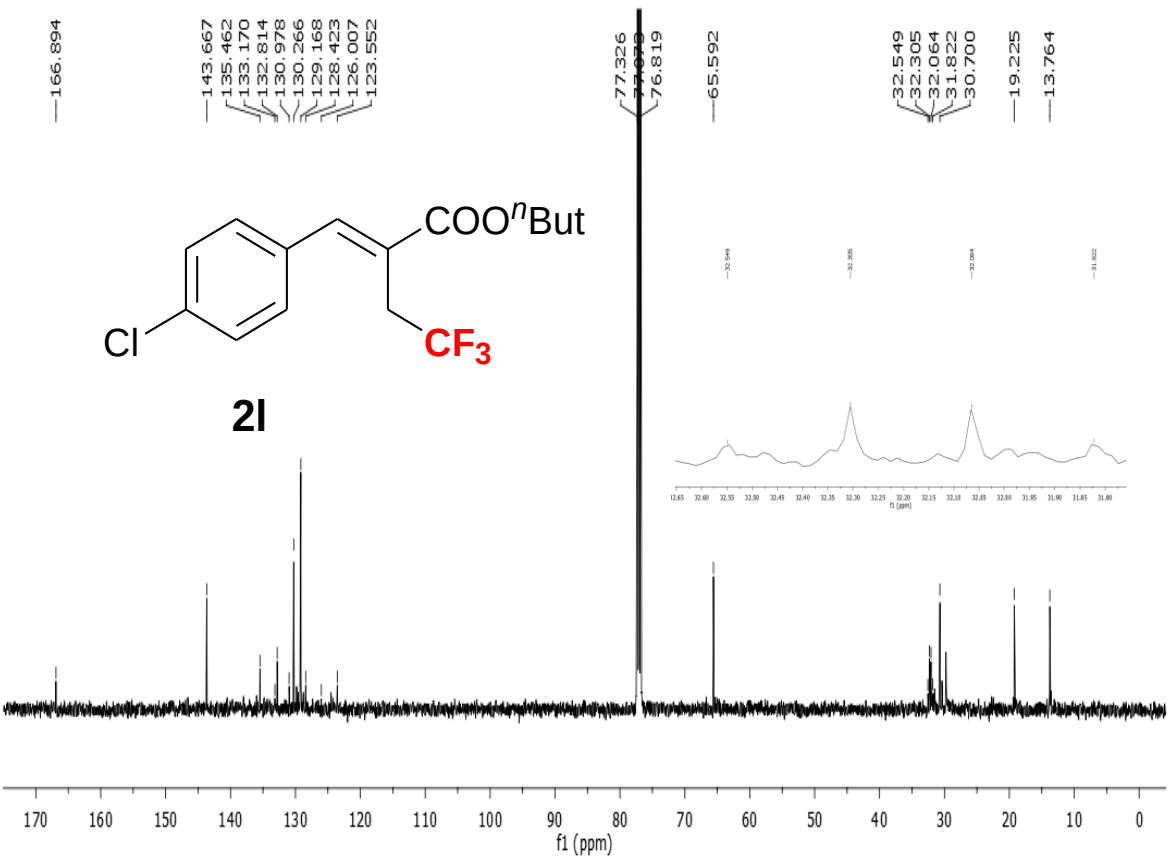

63.295
COOMe
Cl
CF3
2j
100 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220 -250 -280
f1 (ppm)

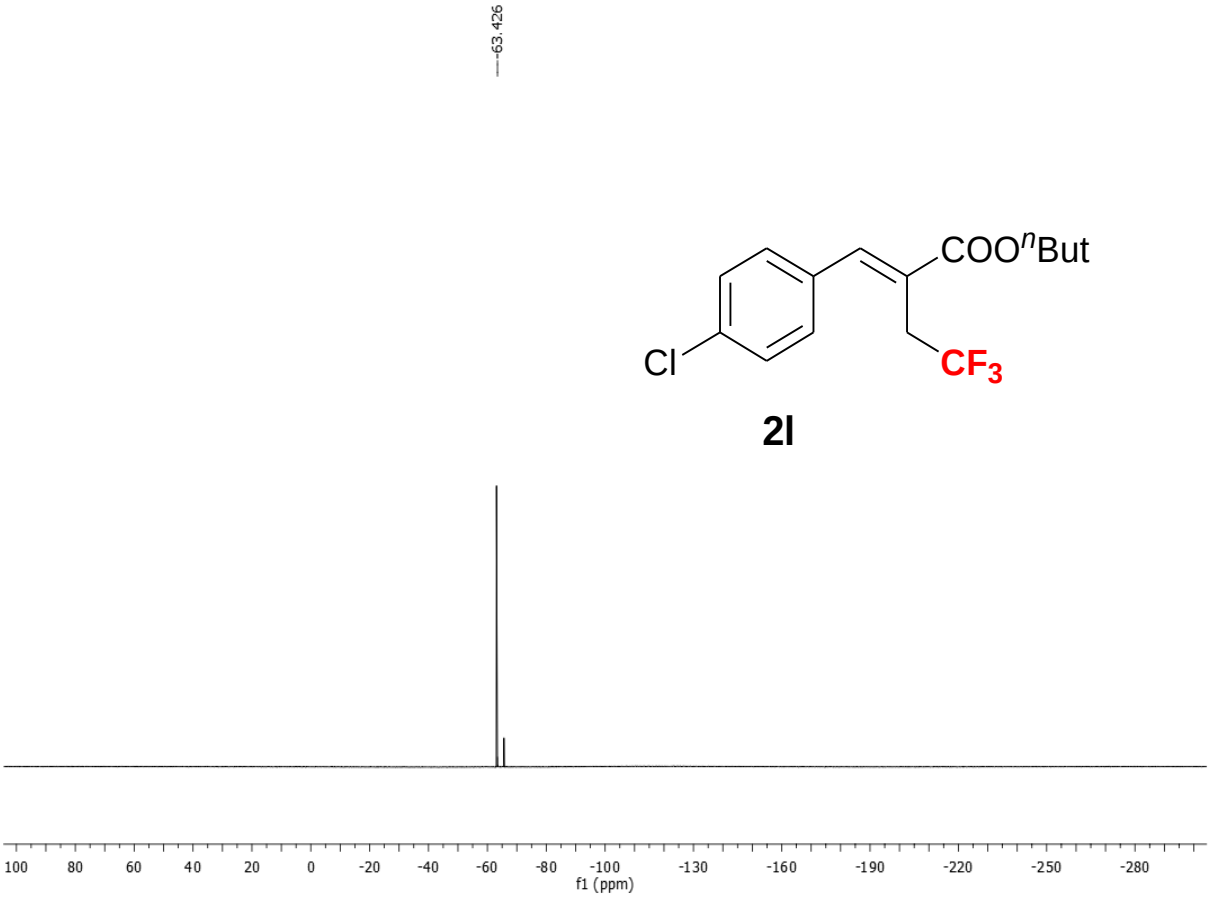

7.844
7.346
7.341
7.338
7.324
7.321
7.268
7.251
7.246
4.270
4.256
4.241
4.227
3.354
3.334
3.314
3.293
1.301
1.287
1.273
COOEt
Cl
CF3
2k
1.00
2.11
2.22
2.19
2.22
3.26
f1 (ppm)

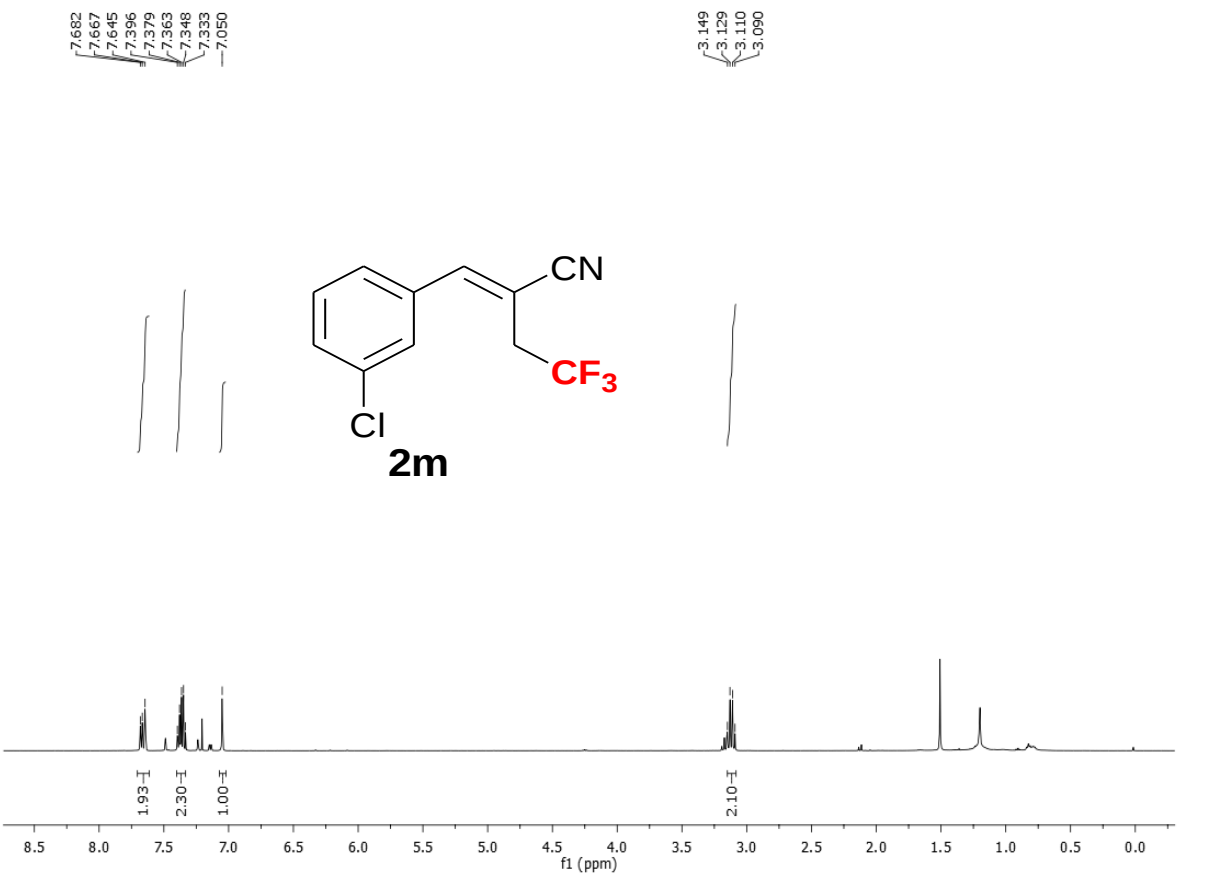

166.733
143.591
135.380
132.730
130.178
129.089
128.860
126.659
124.444
123.453
122.230
77.254
77.000
76.746
61.605
32.451
32.208
31.966
31.723
14.144
COOEt
Cl
CF3
2k
f1 (ppm)

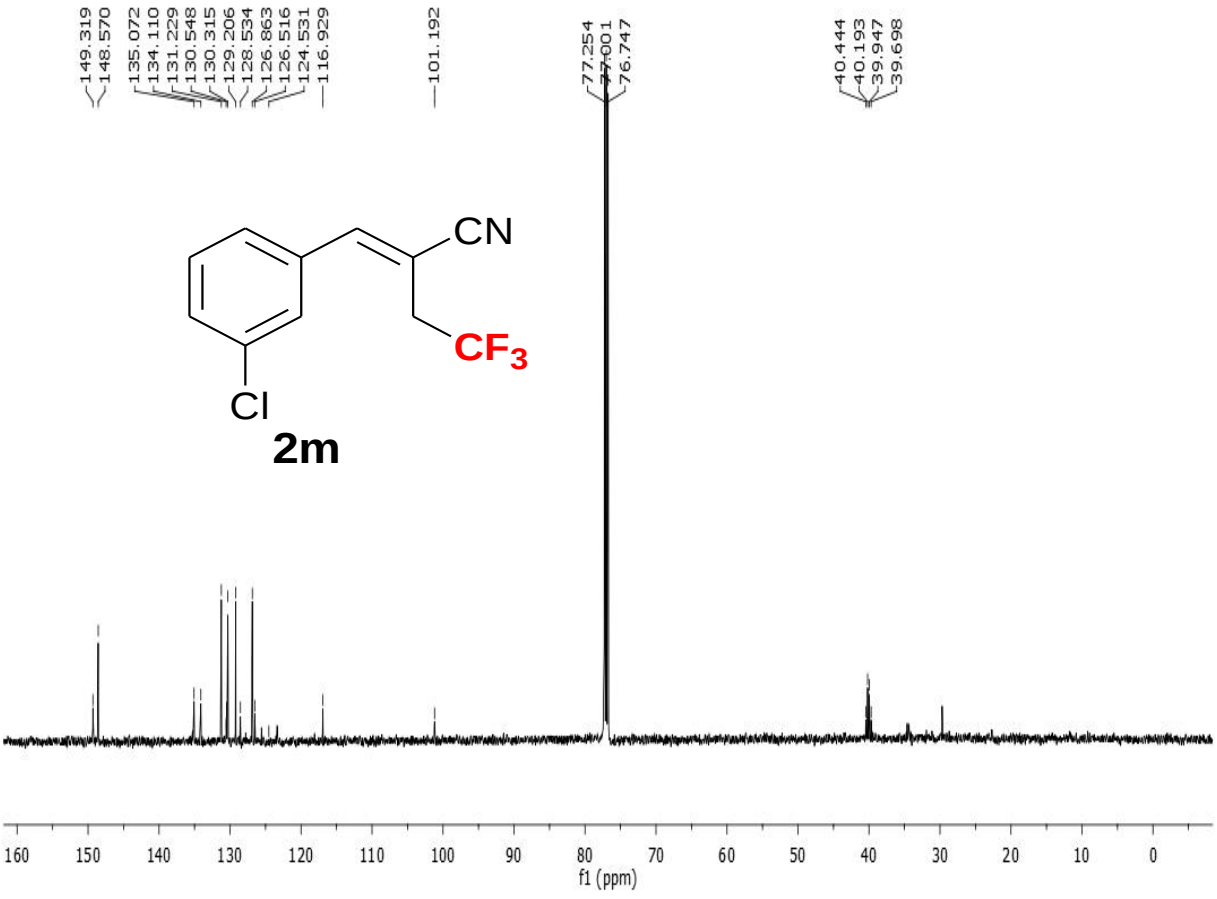

-63.100
COOEt
Cl
CF3
2k
100 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220 -250 -280
f1 (ppm)

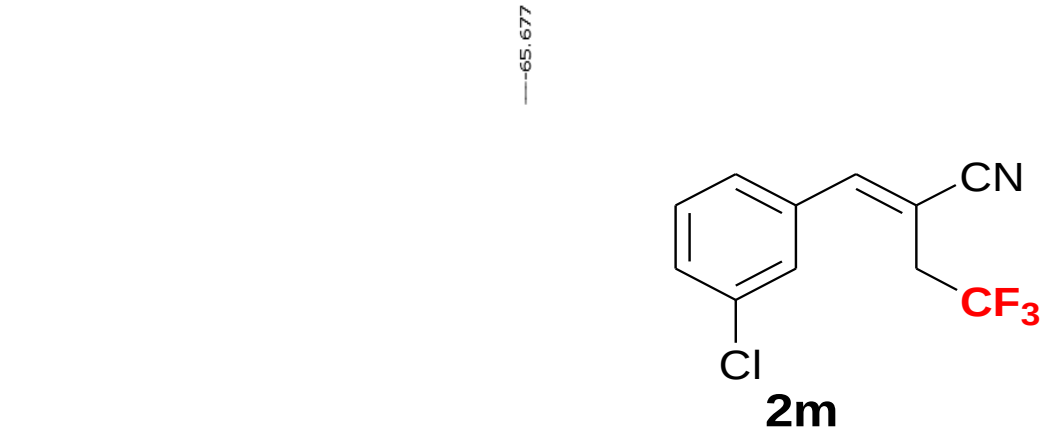

7.839
7.342
7.329
7.325
7.320
7.317
7.268
7.251
7.246
4.204
4.191
4.178
3.352
3.332
3.312
3.291
1.670
1.657
1.643
1.627
1.613
1.410
1.396
1.380
1.365
1.357
1.350
0.916
0.902
0.887
COO^nBut
Cl
CF3
2l
0.90
2.00
2.04
2.04
1.96
2.12
2.21
3.05
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

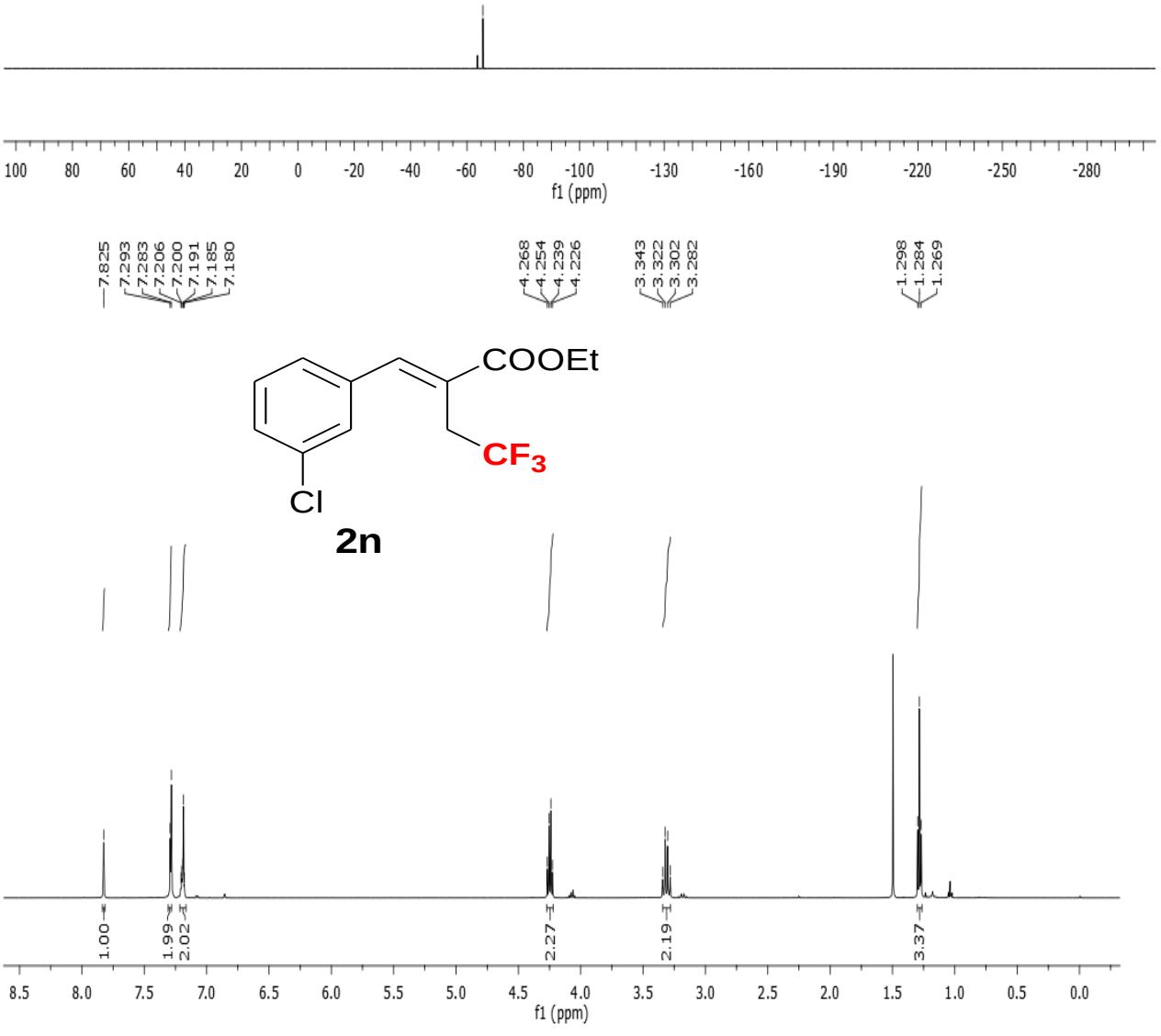

166.894
143.667
135.462
133.170
132.814
130.978
130.266
129.168
128.423
126.007
123.552
77.326
77.070
76.819
65.592
32.549
32.305
32.064
31.822
30.700
19.225
13.764
COO^{n}But
Cl
CF$_3$
2l
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

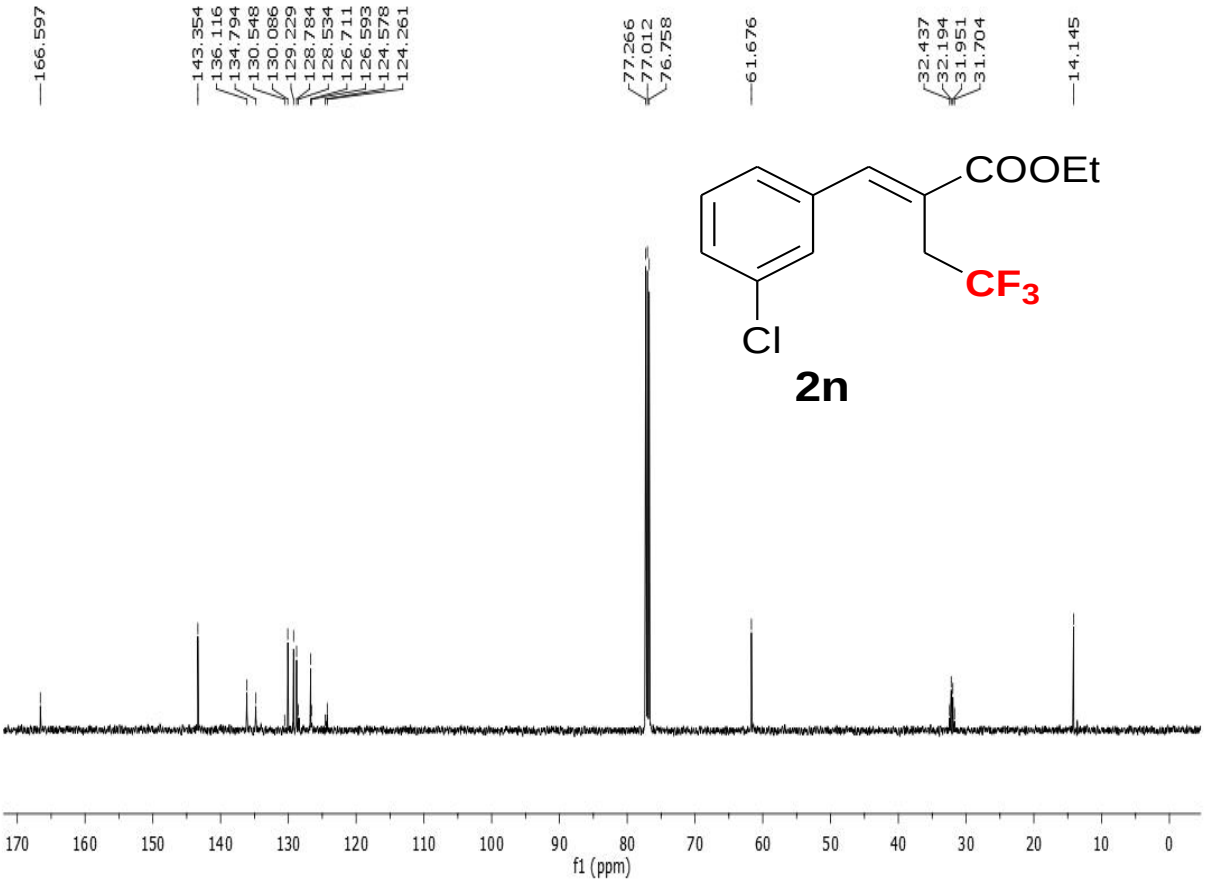

63.426
COO^{n}But
Cl
CF$_3$
2l
100 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220 -250 -280
f1 (ppm)

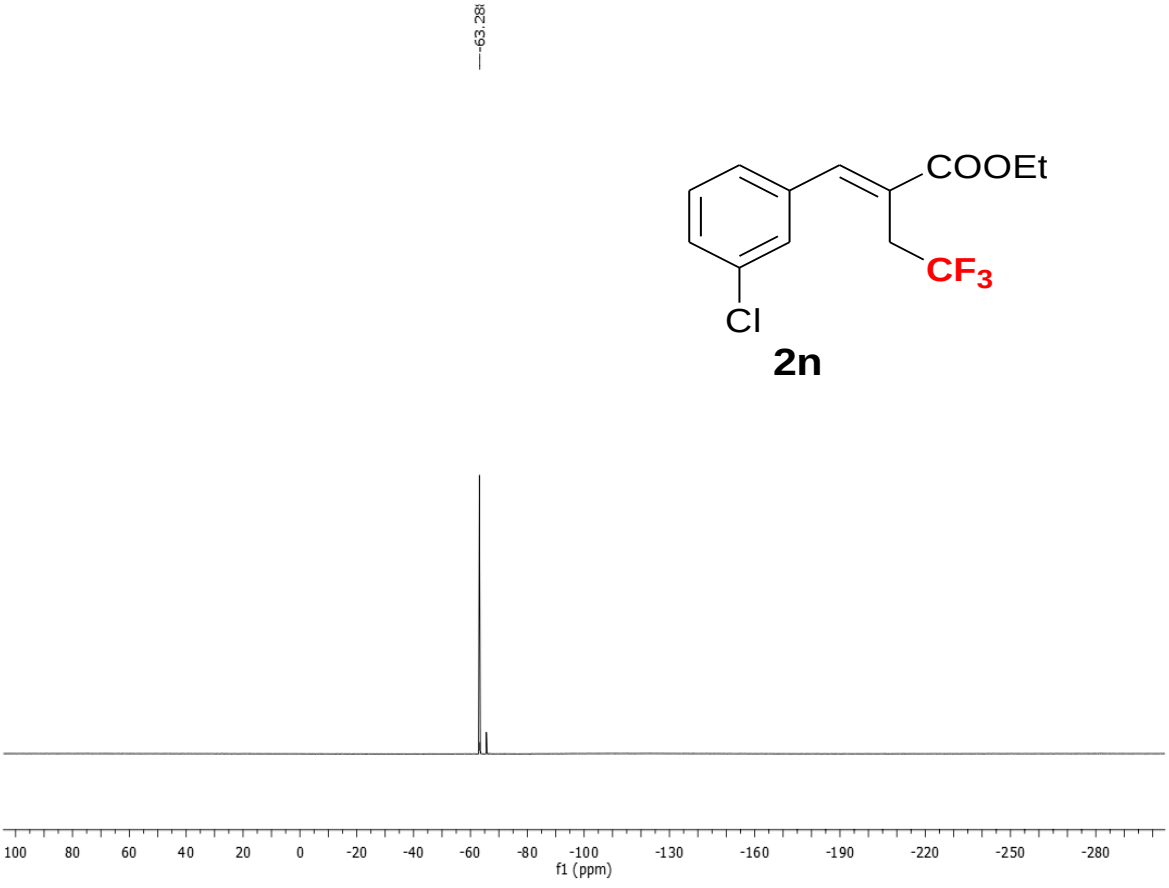

7.682
7.667
7.645
7.396
7.379
7.363
7.348
7.333
7.050
3.149
3.129
3.110
3.090
CN
CF3
Cl
2m
1.93
2.30
1.00
2.10
f1 (ppm)

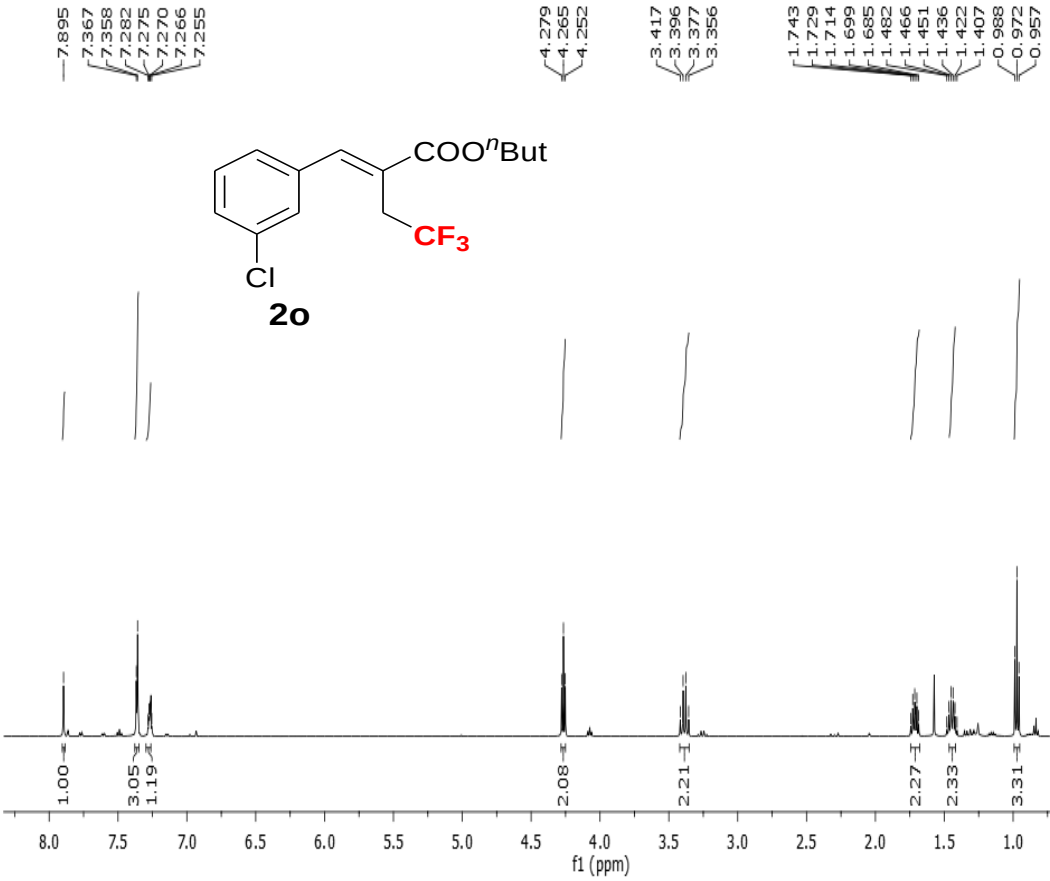

149.319
148.570
135.072
134.110
131.229
130.548
130.315
129.206
128.534
126.863
126.516
124.531
116.929
101.192
77.254
77.001
76.747
40.444
40.193
39.947
39.698
CN
CF3
Cl
2m
f1 (ppm)

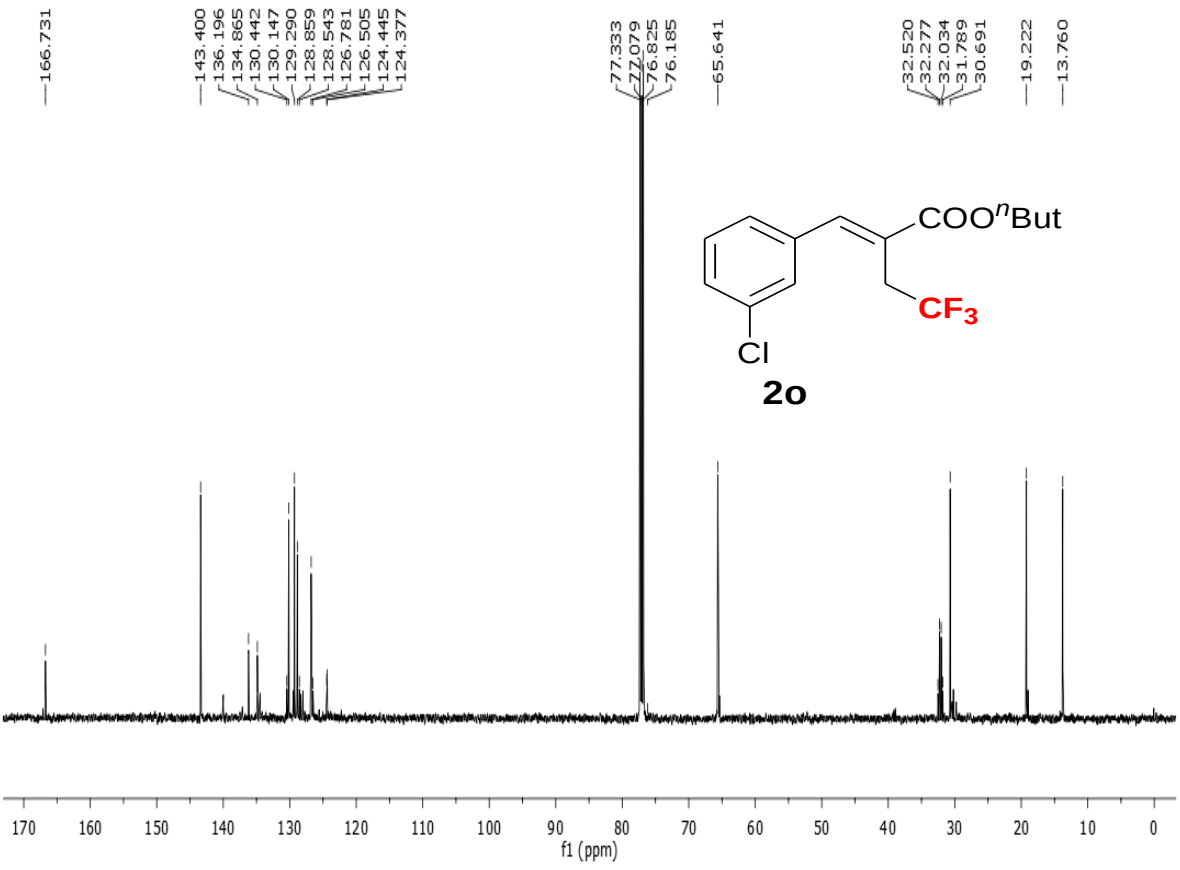

-65.677
CN
CF3
Cl
2m

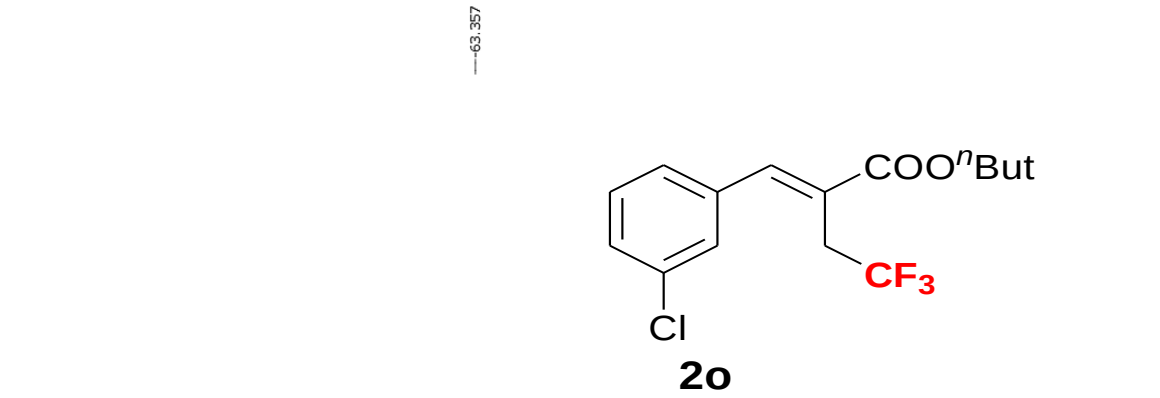

7.825
7.293
7.283
7.206
7.200
7.191
7.185
7.180
4.268
4.254
4.239
4.226
3.343
3.322
3.302
3.282
1.298
1.284
1.269
COOEt
CF3
Cl
2n
1.00
1.99
2.02
2.27
2.19
3.37
f1 (ppm)


166.597
143.354
136.116
134.794
130.548
130.086
129.229
128.784
128.534
126.711
126.593
124.578
124.261
77.266
77.012
76.758
61.676
32.437
32.194
31.951
31.704
14.145
COOEt
CF3
Cl
2n
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

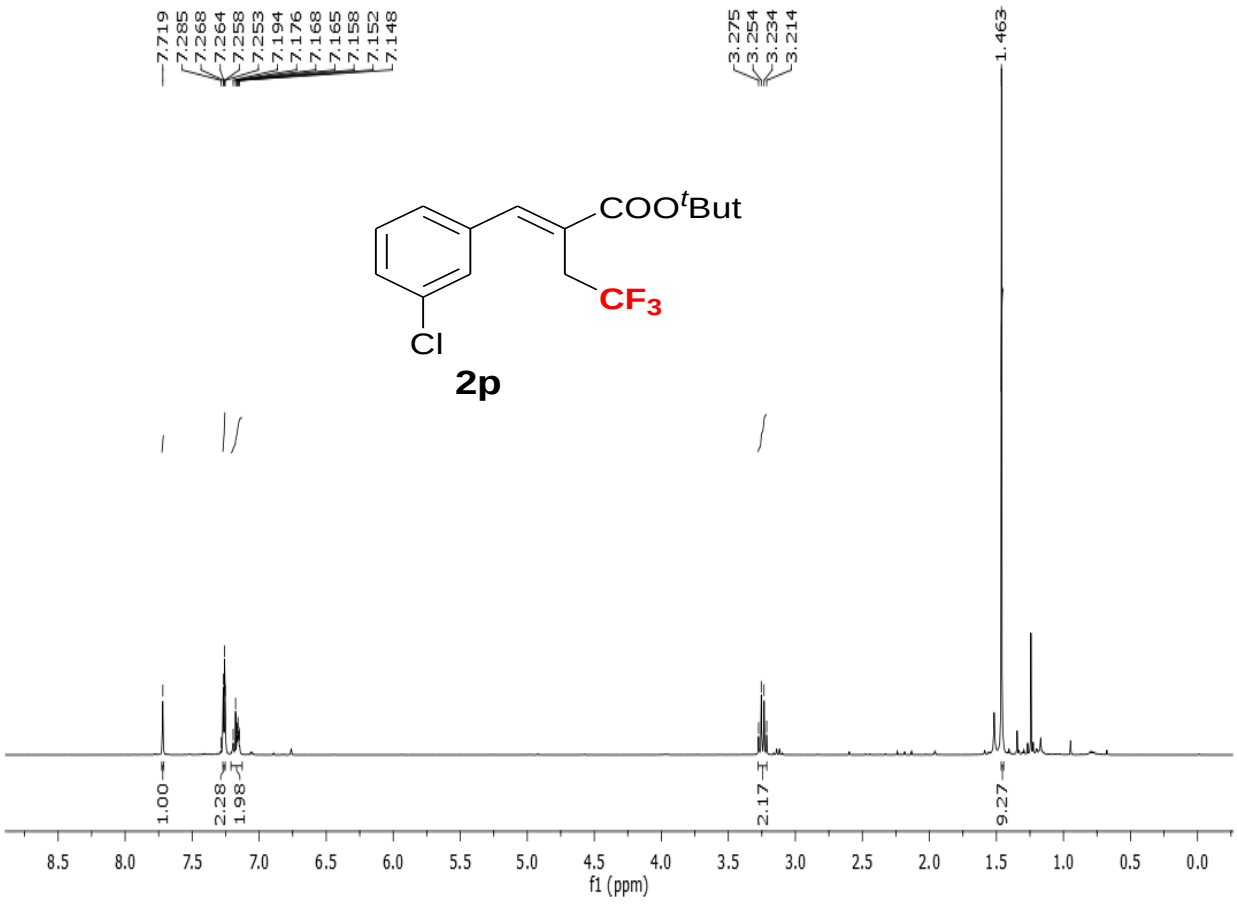

63.28
COOEt
CF3
Cl
2n
100
80
60
40
20
0
-20
-40
-60
-80
-100
-130
-160
-190
-220
-250
-280
f1 (ppm)


7.895
7.367
7.358
7.282
7.275
7.270
7.266
7.255
4.279
4.265
4.252
3.417
3.396
3.377
3.356
1.743
1.729
1.714
1.699
1.685
1.482
1.466
1.451
1.436
1.422
1.407
0.988
0.972
0.957
COO^{n}But
CF$_3$
Cl
2o
1.00
3.05
1.19
2.08
2.21
2.27
2.33
3.31
f1 (ppm)

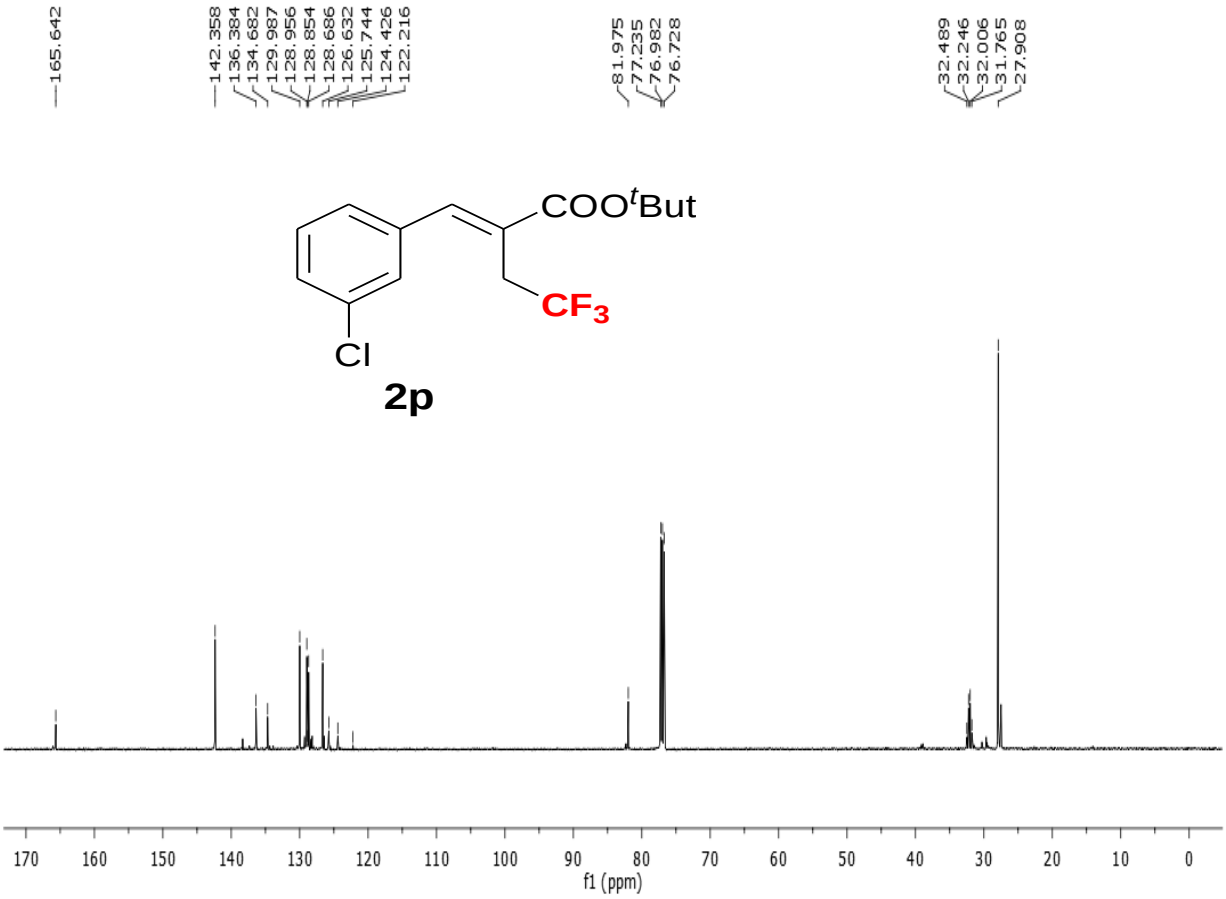

166.731
143.400
136.196
134.865
130.442
130.147
129.290
128.859
128.543
126.781
126.505
124.445
124.377
77.333
77.079
76.825
76.185
65.641
32.520
32.277
32.034
31.789
30.691
19.222
13.760
COO^{n}But
CF$_3$
Cl
2o
f1 (ppm)

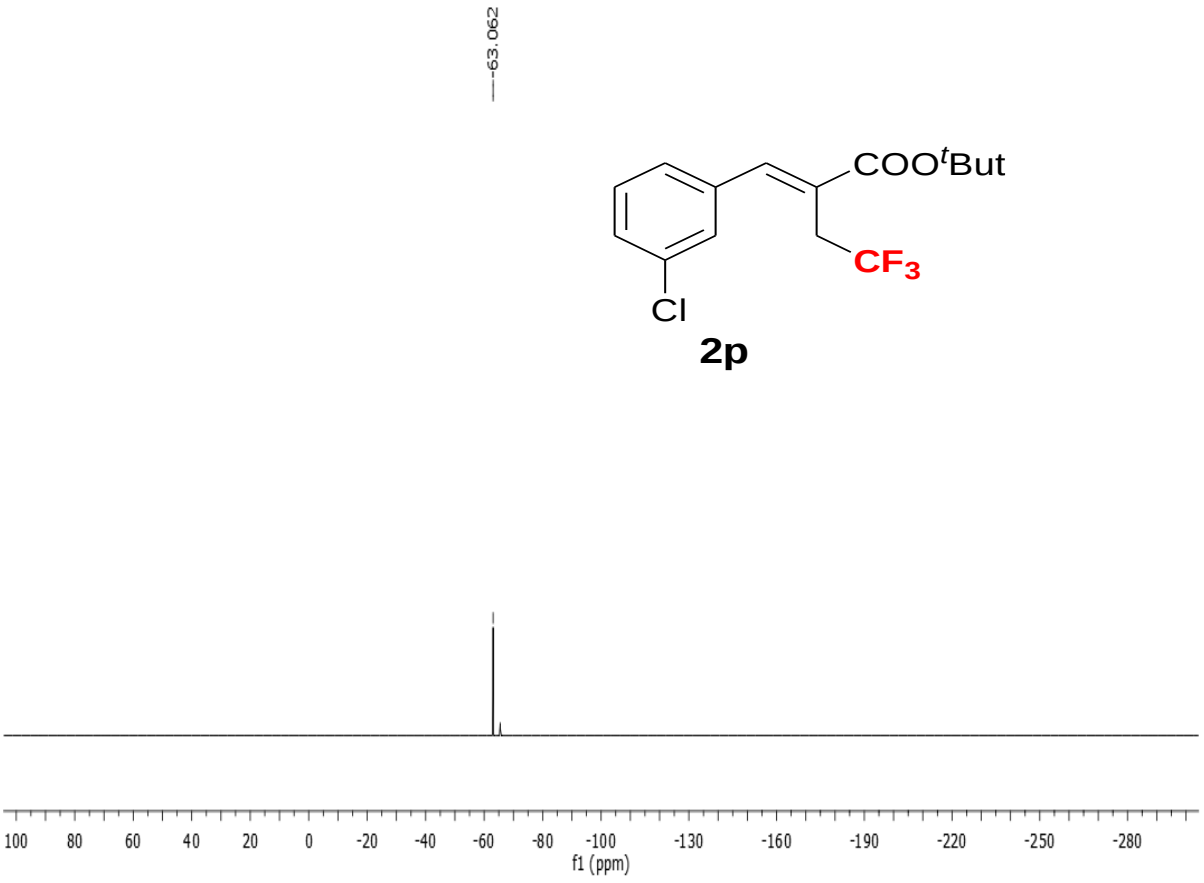

-63.357
COO^{n}But
CF$_3$
Cl
100 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220 -250 -280
f1 (ppm)

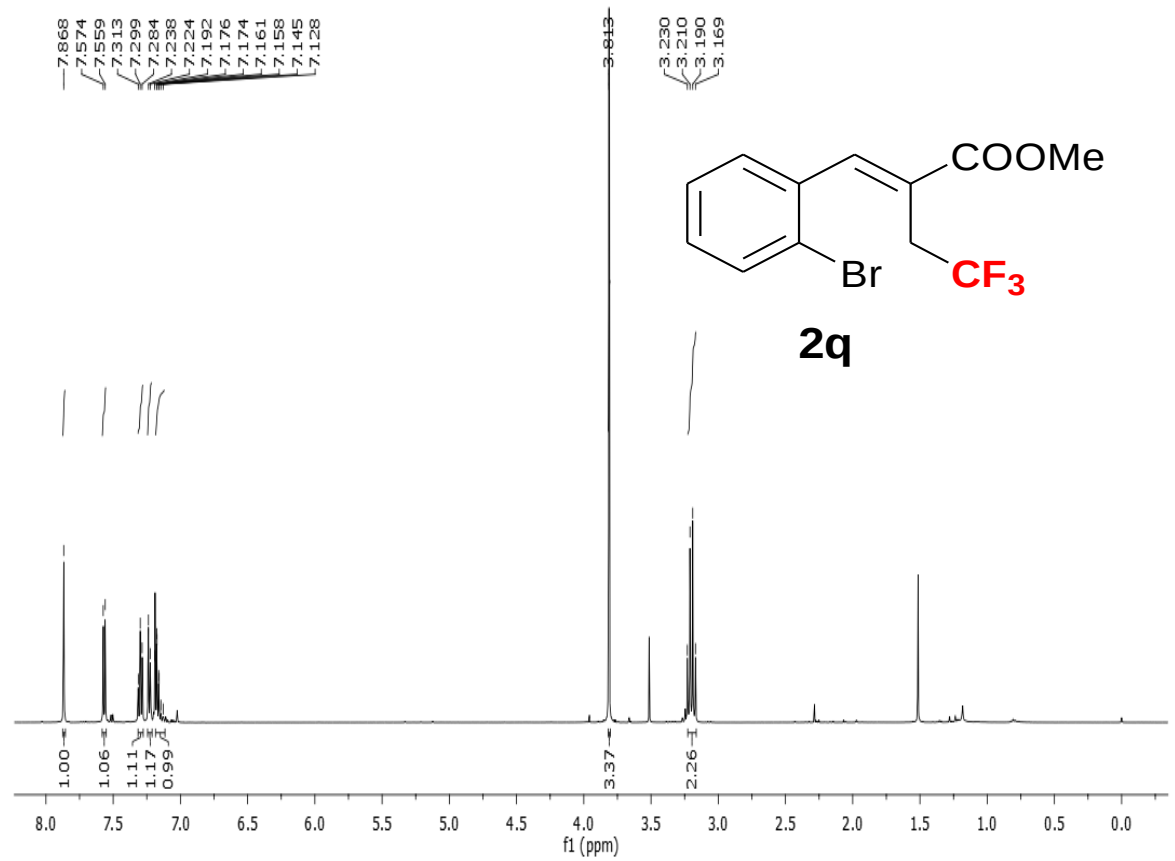
2o


7.719
7.285
7.268
7.264
7.258
7.253
7.194
7.176
7.168
7.165
7.158
7.152
7.148
3.275
3.254
3.234
3.214
1.463
COO^{t}But
CF$_3$
Cl
1.00
2.28
1.98
2.17
9.27
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

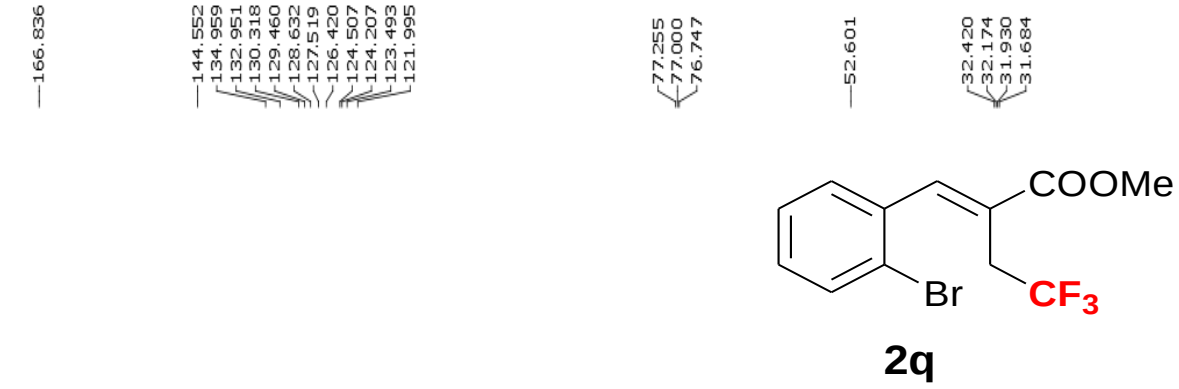
2p


165.642
142.358
136.384
134.682
129.987
128.956
128.854
128.686
126.632
125.744
124.426
122.216
81.975
77.235
76.982
76.728
32.489
32.246
32.006
31.765
27.908
COO^{t}But
CF$_3$
Cl
2p
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

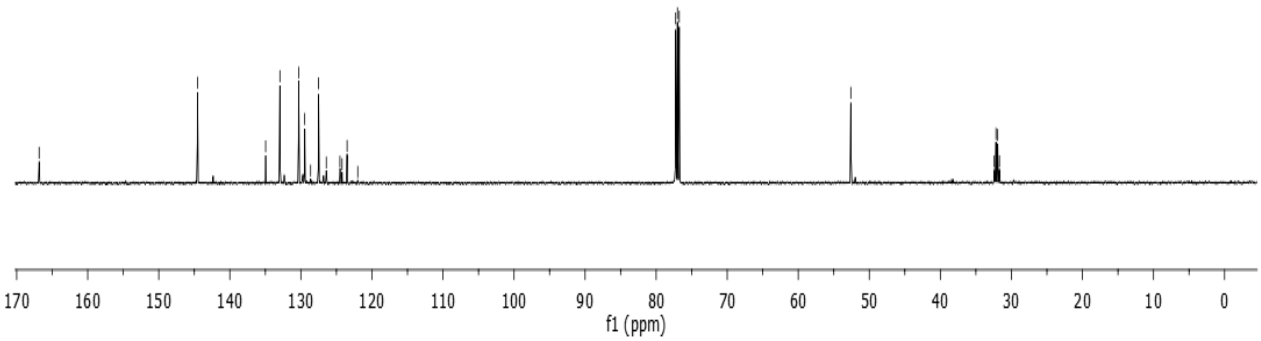

-63.062
COO^{t}But
CF$_3$
Cl
2p
100 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220 -250 -280
f1 (ppm)

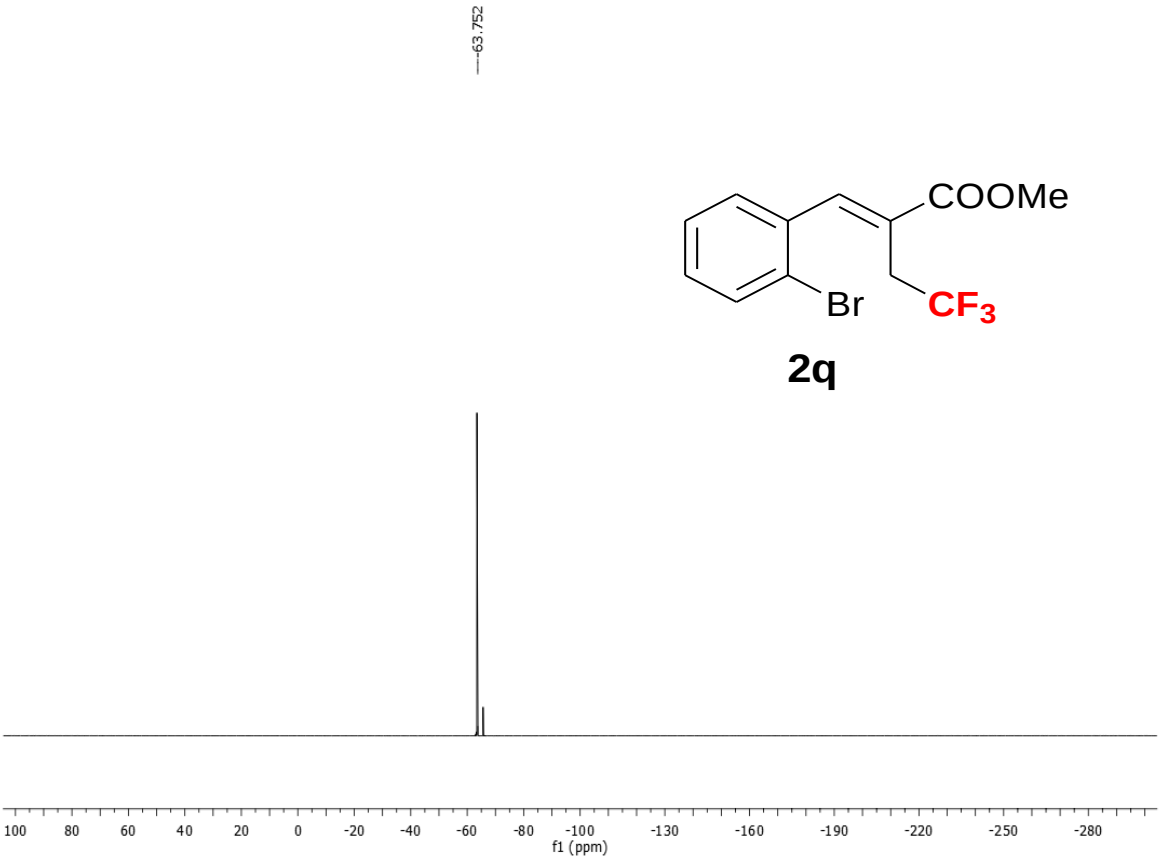

7.868
7.574
7.559
7.313
7.299
7.284
7.238
7.224
7.192
7.176
7.174
7.161
7.158
7.145
7.128
3.813
3.230
3.210
3.190
3.169
COOMe
Br
CF3
1.00
1.06
1.11
1.17
0.99
3.37
2.26
f1 (ppm)

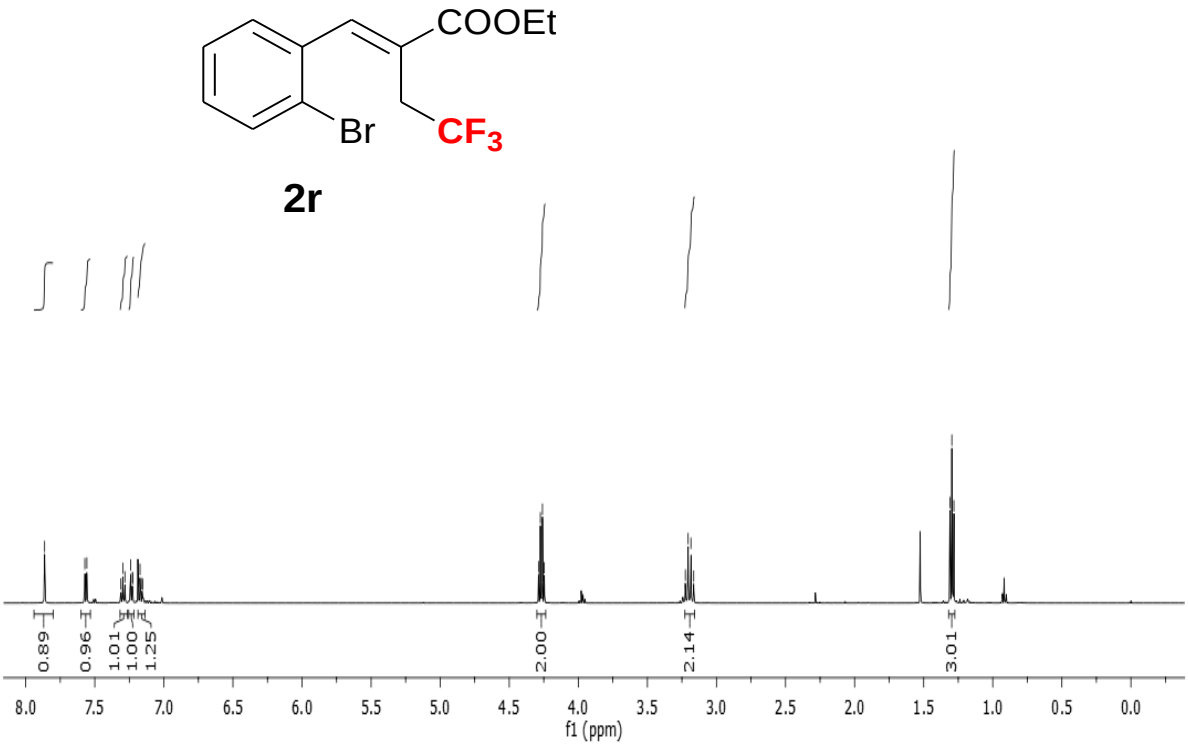
2q


166.836
144.552
134.959
132.951
130.318
129.460
128.632
127.519
126.420
124.507
124.207
123.493
121.995
77.255
77.000
76.747
52.601
32.420
32.174
31.930
31.684
COOMe
Br
CF3

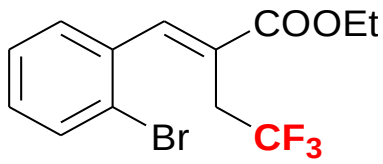
2q


f1 (ppm)

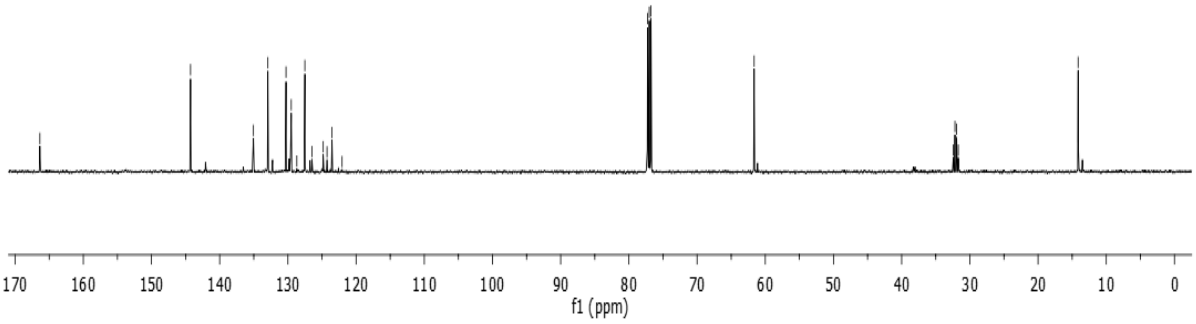

-63.752
COOMe
Br
CF3
2q
100 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220 -250 -280
f1 (ppm)
7.863 7.572 7.557 7.311 7.296 7.282 7.240 7.228 7.225 7.185 7.172 7.157 7.154
4.288 4.275 4.260 4.246
3.225 3.205 3.185 3.165
1.310 1.296 1.281


COOEt
Br
CF3
2r
0.89 0.96 1.01 1.00 1.25 2.00 2.14 3.01
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

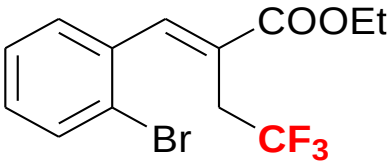

166.369
144.275
135.053
132.940
130.275
129.509
128.691
127.512
126.475
124.820
124.264
123.532
122.055
77.265
77.012
76.758
61.632
32.430
32.189
31.941
31.698
14.126


COOEt
Br
CF3

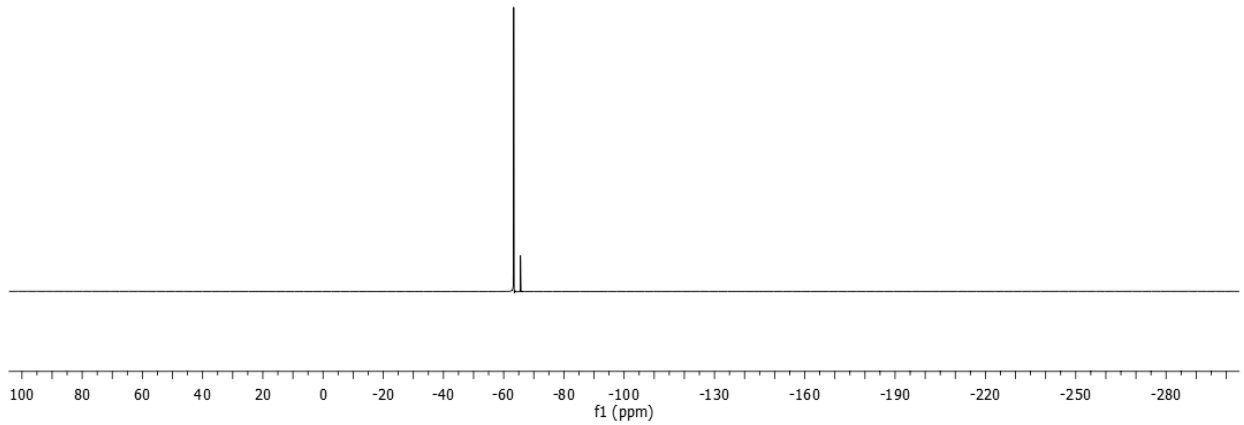
2r

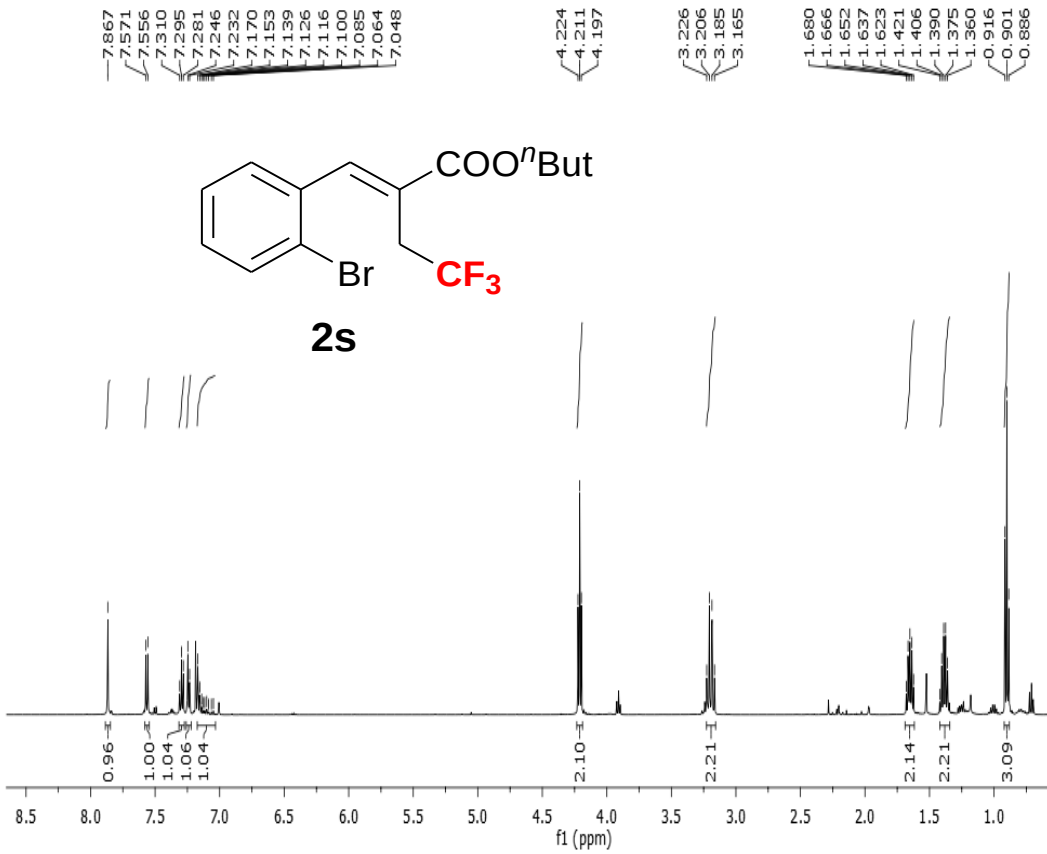

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-63.165

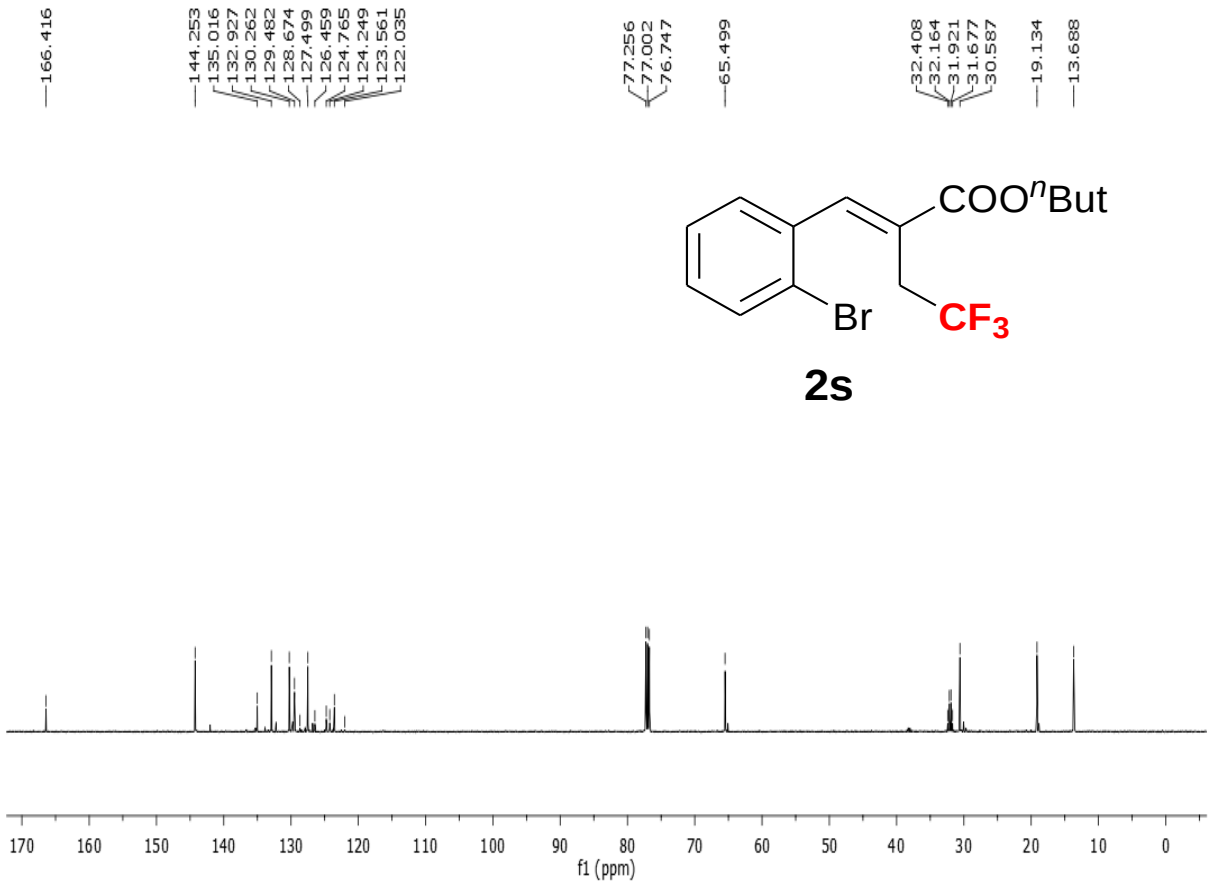

COOEt
Br
CF3

2r

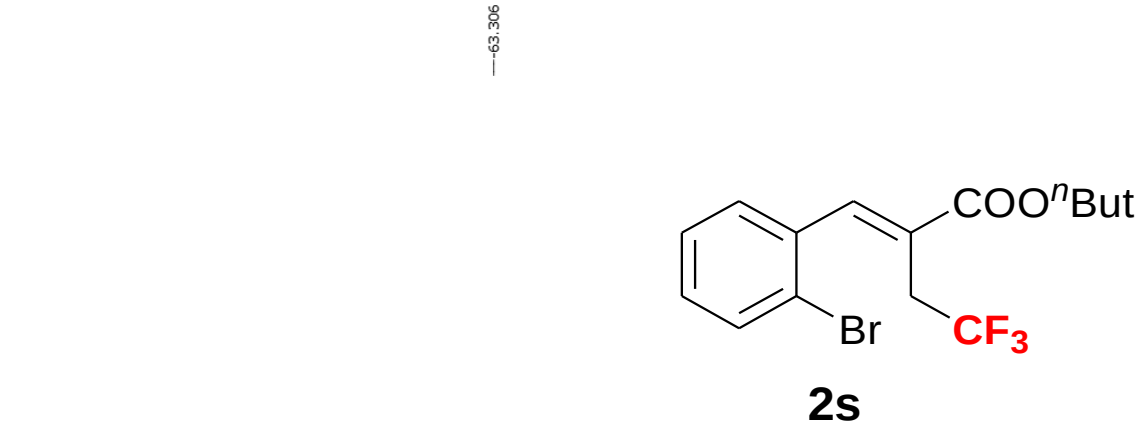

100
80
60
40
20
0
-20
-40
-60
-80
-100
-130
-160
-190
-220
-250
-280
f1 (ppm)


7.867
7.571
7.556
7.310
7.295
7.281
7.246
7.232
7.170
7.153
7.139
7.126
7.116
7.100
7.085
7.064
7.048
4.224
4.211
4.197
3.226
3.206
3.185
3.165
1.680
1.666
1.652
1.637
1.623
1.421
1.406
1.390
1.375
1.360
0.916
0.901
0.886
COO^{n}But
Br
CF$_3$
0.96
1.00
1.04
1.06
1.04
2.10
2.21
2.14
2.21
3.09
f1 (ppm)

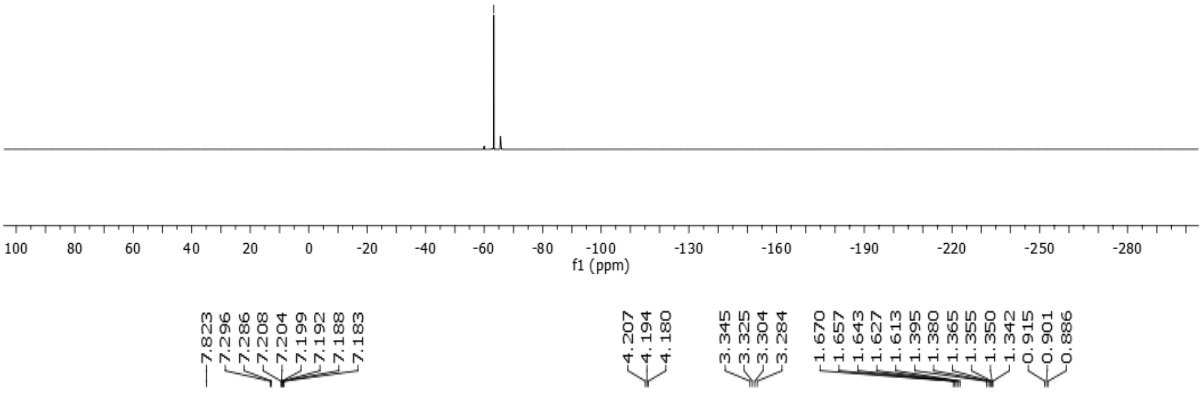
2s


166.416
144.253
135.016
132.927
130.262
129.482
128.674
127.499
126.459
124.765
124.249
123.561
122.035
77.256
77.002
76.747
65.499
32.408
32.164
31.921
31.677
30.587
19.134
13.688
COO^{n}But
Br
CF$_3$
f1 (ppm)

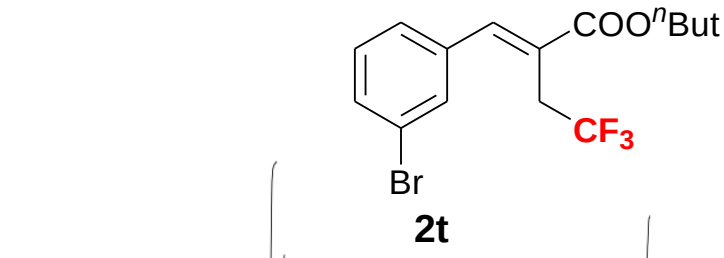
2s


-63.306
COO^{n}But
Br
CF_3

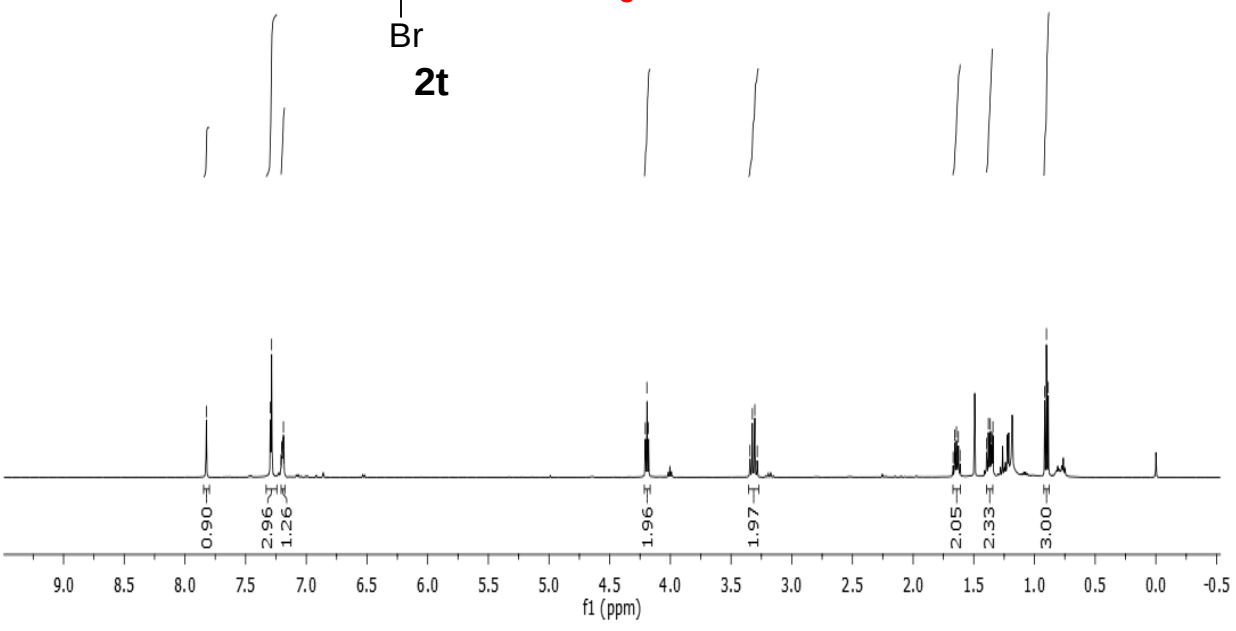
2s

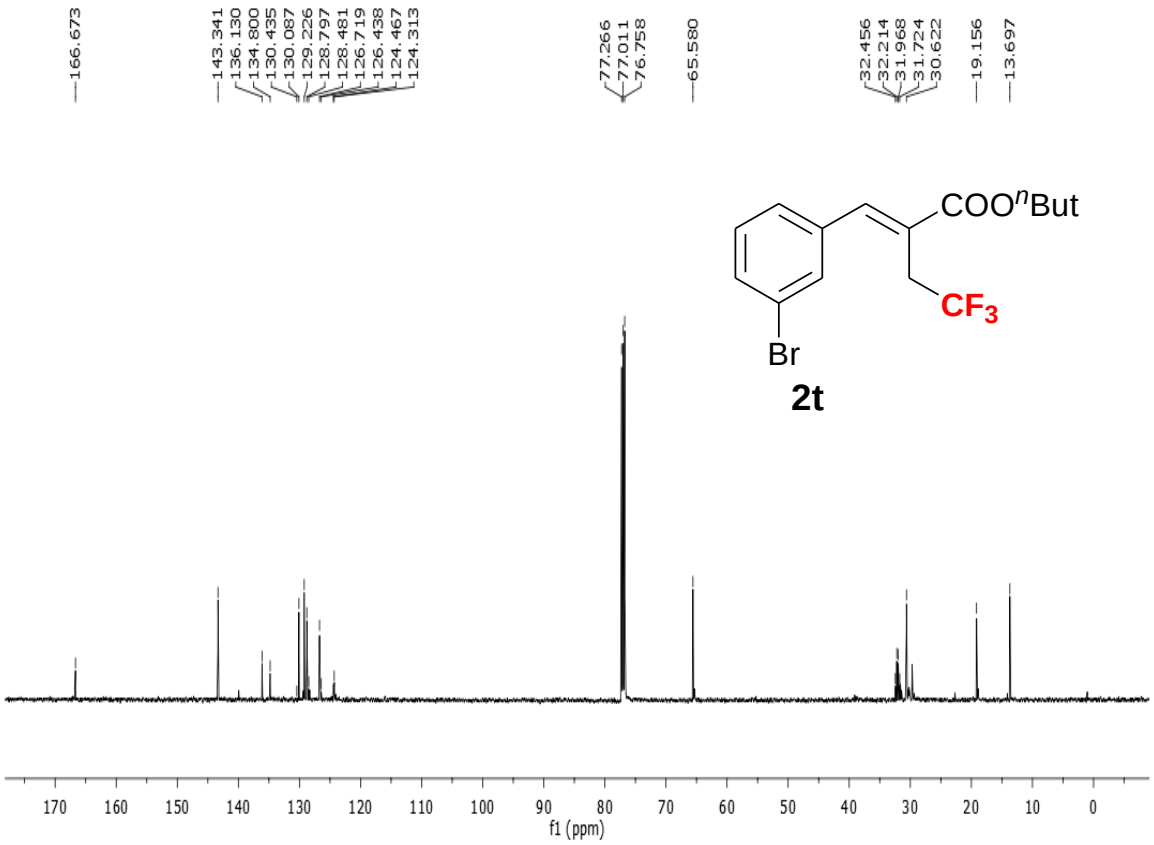

100 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220 -250 -280
f1 (ppm)

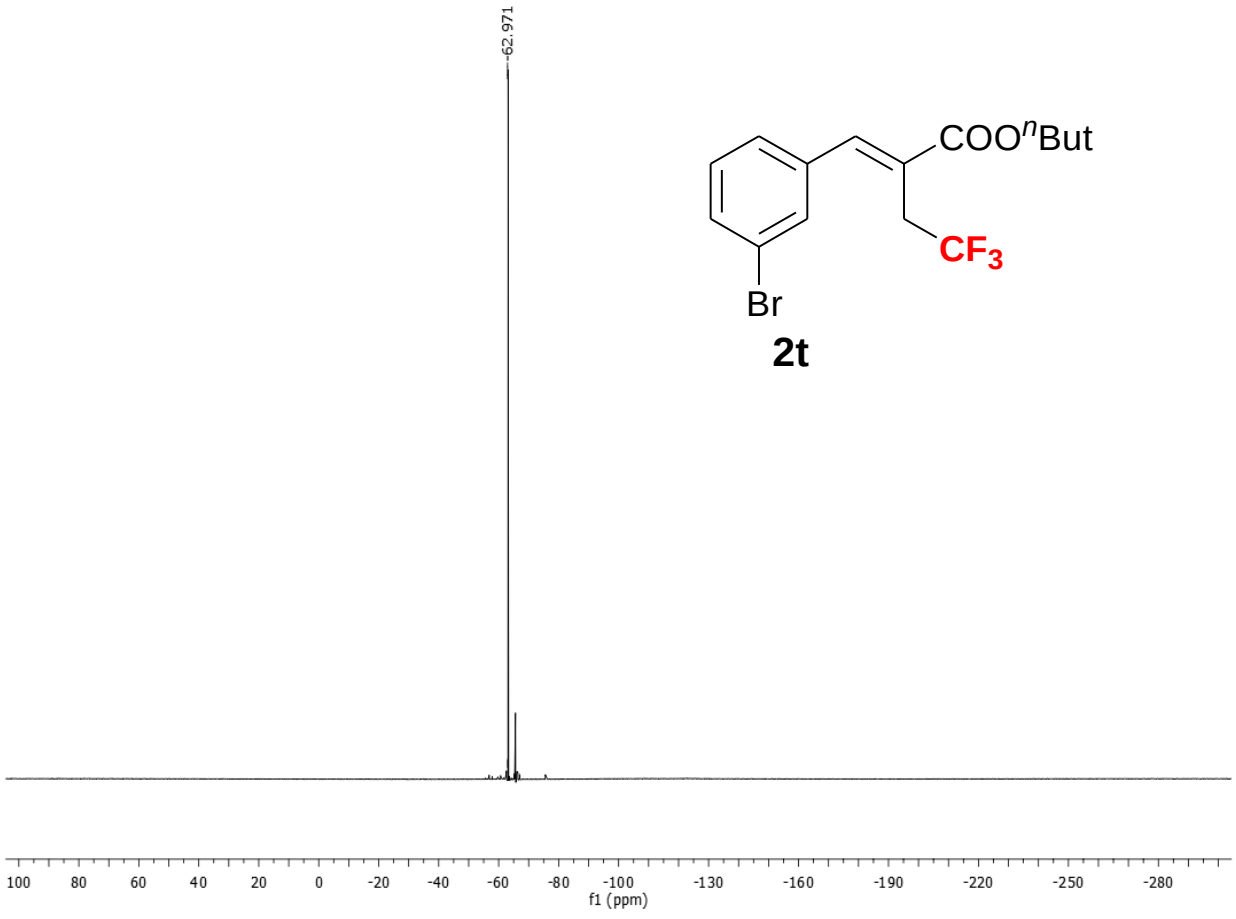
7.823
7.296
7.286
7.208
7.204
7.199
7.192
7.188
7.183
4.207
4.194
4.180
3.345
3.325
3.304
3.284
1.670
1.657
1.643
1.627
1.613
1.395
1.380
1.365
1.355
1.350
1.342
0.915
0.901
0.886

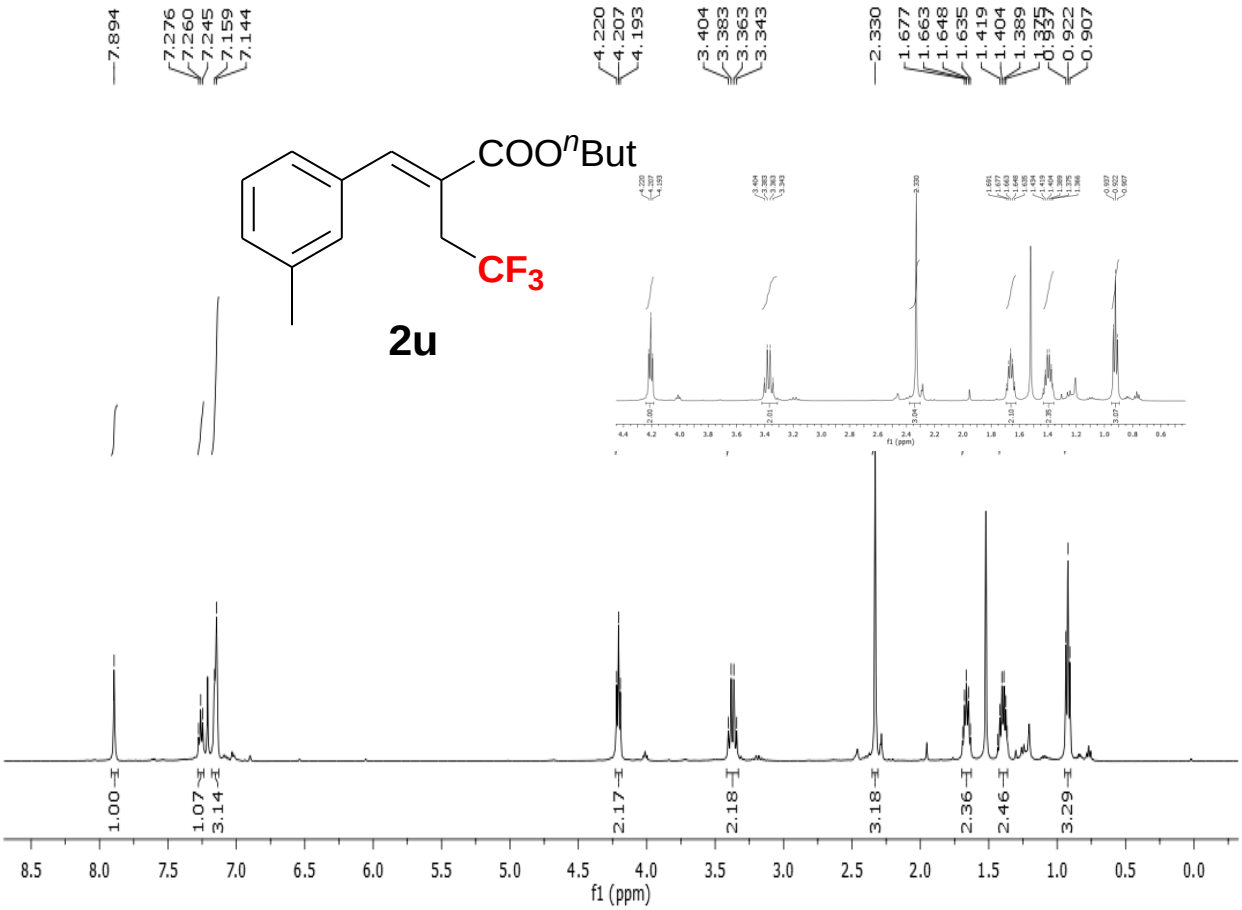

COO^{n}But
CF_3
Br

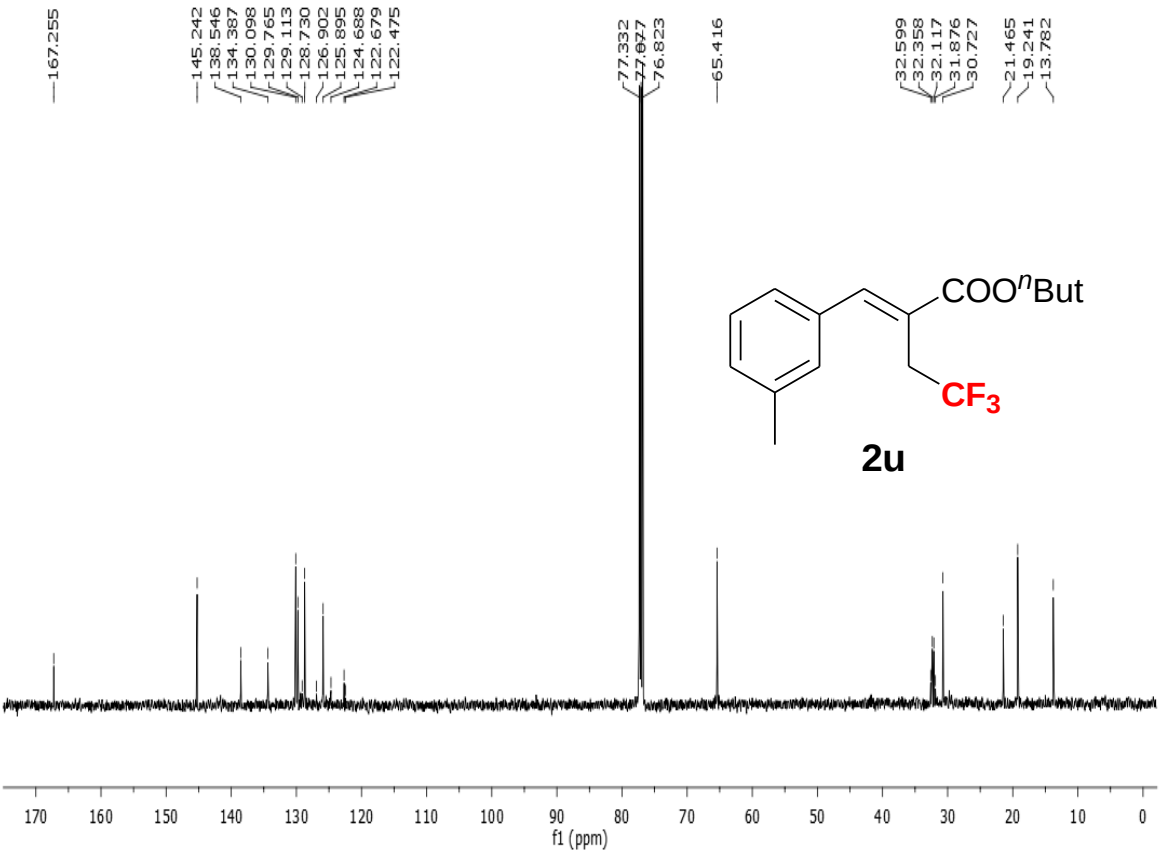
2t

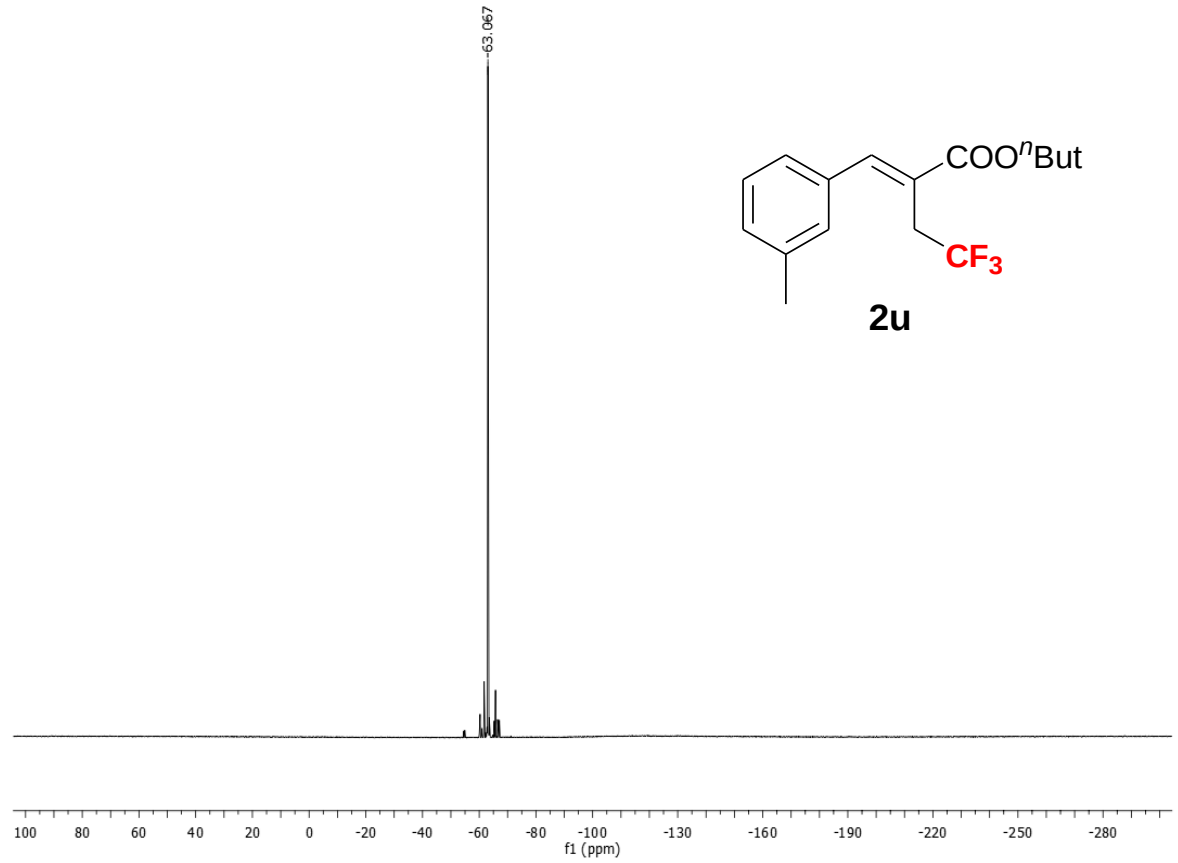

0.90
2.96
1.26
1.96
1.97
2.05
2.33
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

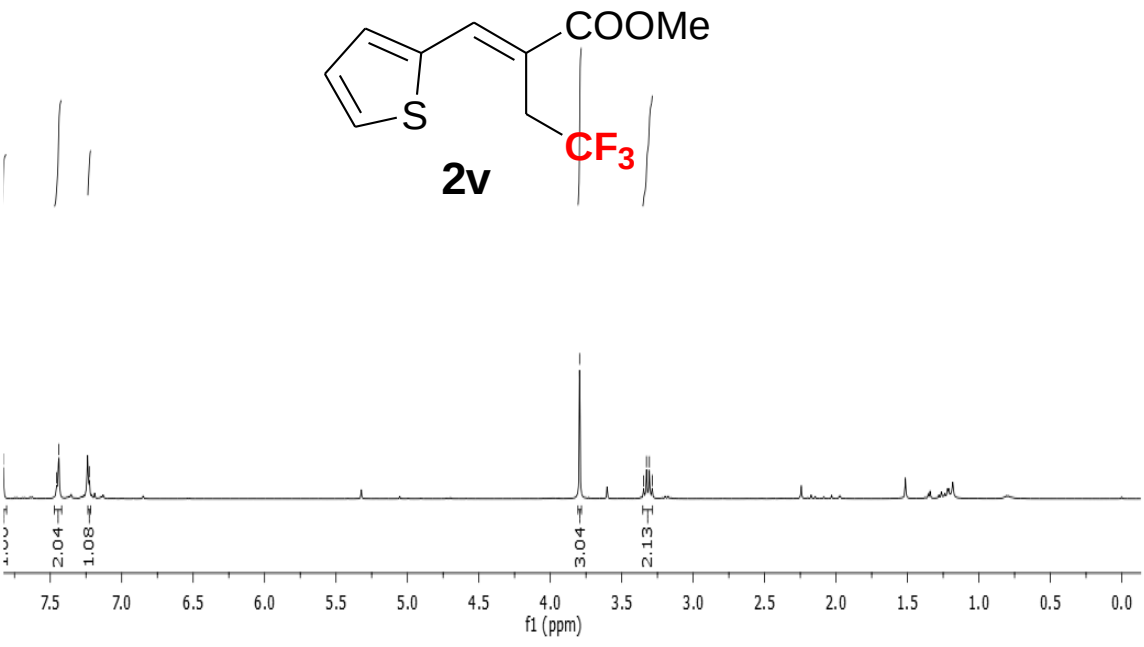

166.673
143.341
136.130
134.800
130.435
130.087
129.226
128.797
128.481
126.719
126.438
124.467
124.313
77.266
77.011
76.758
65.580
32.456
32.214
31.968
31.724
30.622
19.156
13.697
COO^{n}But
CF$_3$
Br
2t
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

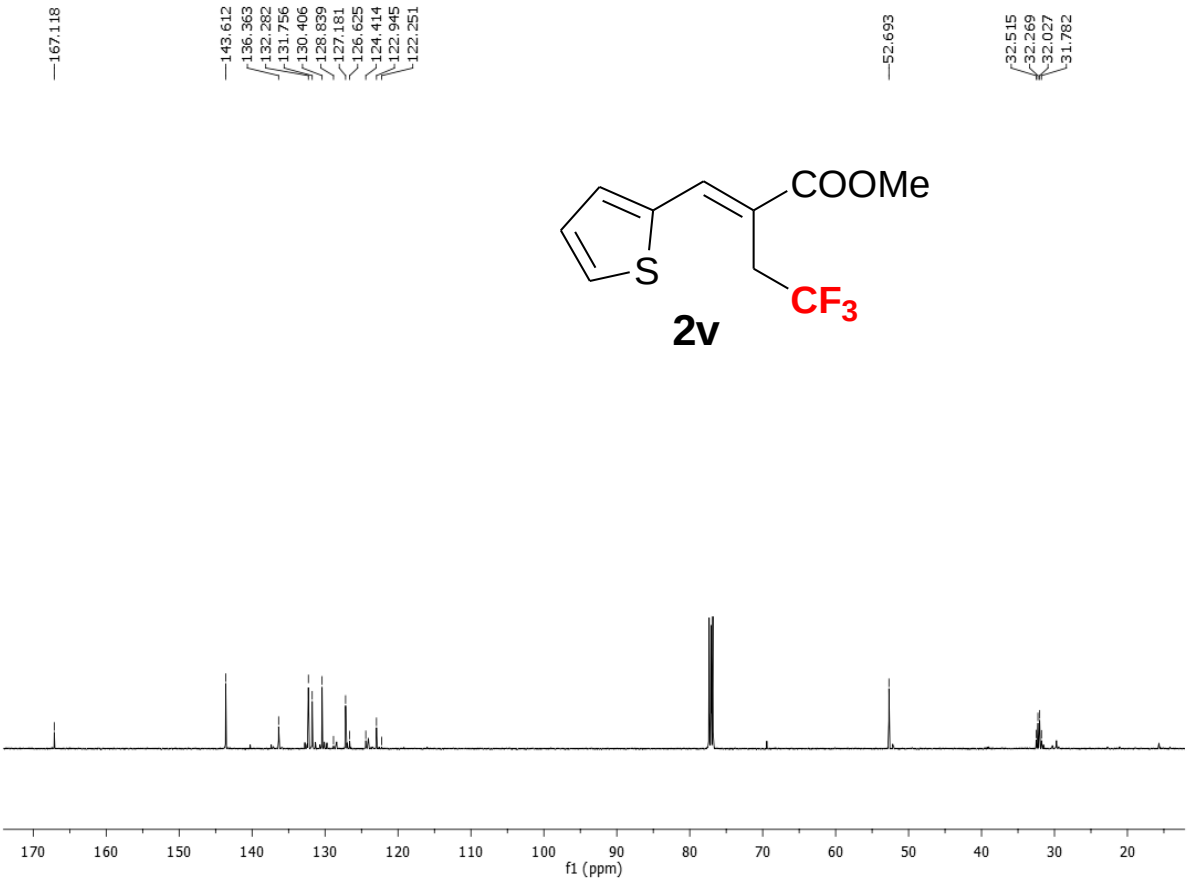

-62.971
COO^{n}But
CF$_3$
Br
2t
100 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220 -250 -280
f1 (ppm)

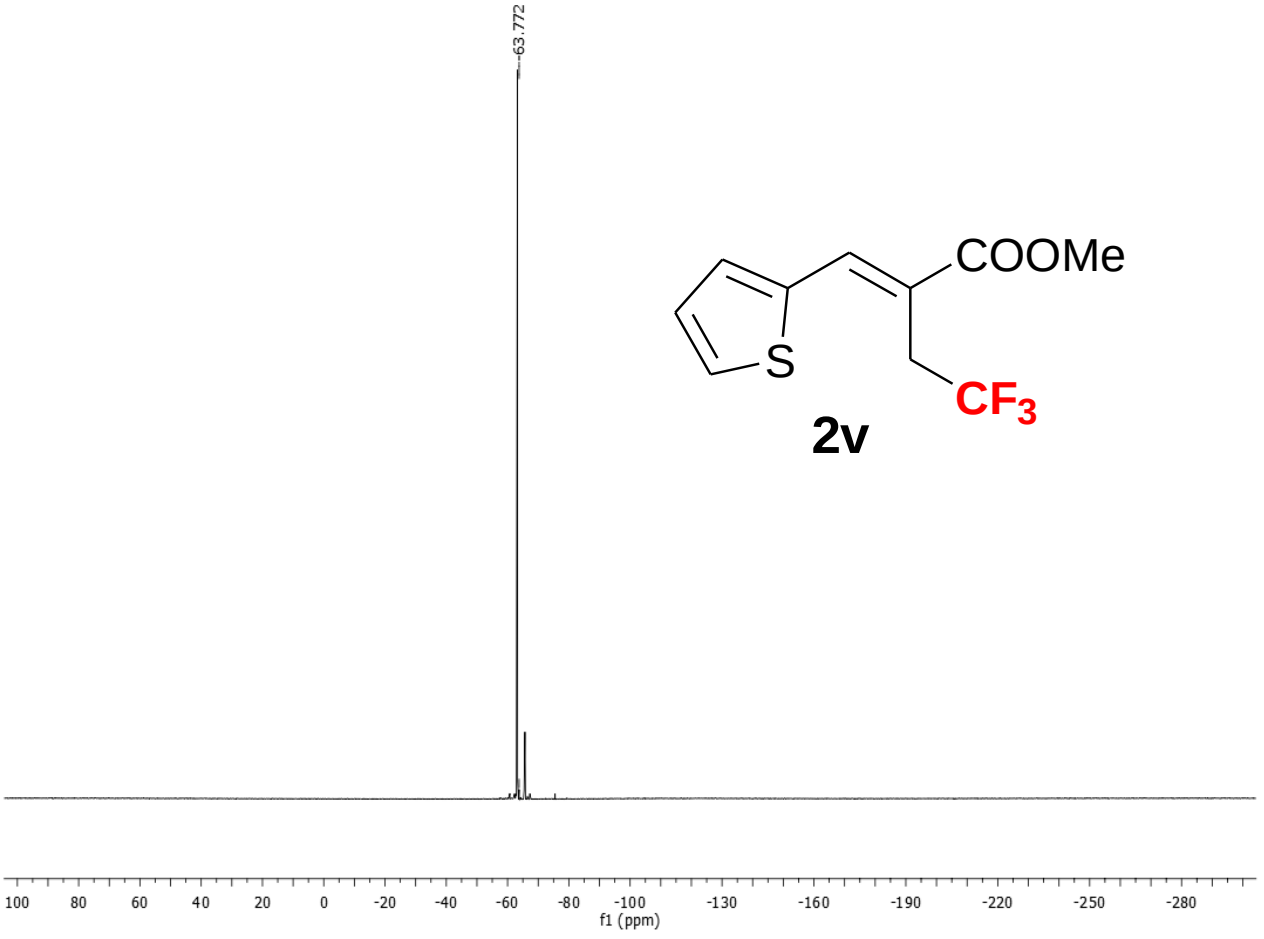

7.894
7.276
7.260
7.245
7.159
7.144
4.220
4.207
4.193
3.404
3.383
3.363
3.343
2.330
1.677
1.663
1.648
1.635
1.419
1.404
1.389
0.922
0.907
COO^{n}But
CF$_3$
2u
1.00
1.07
3.14
2.17
2.18
3.18
2.36
2.46
3.29
f1 (ppm)

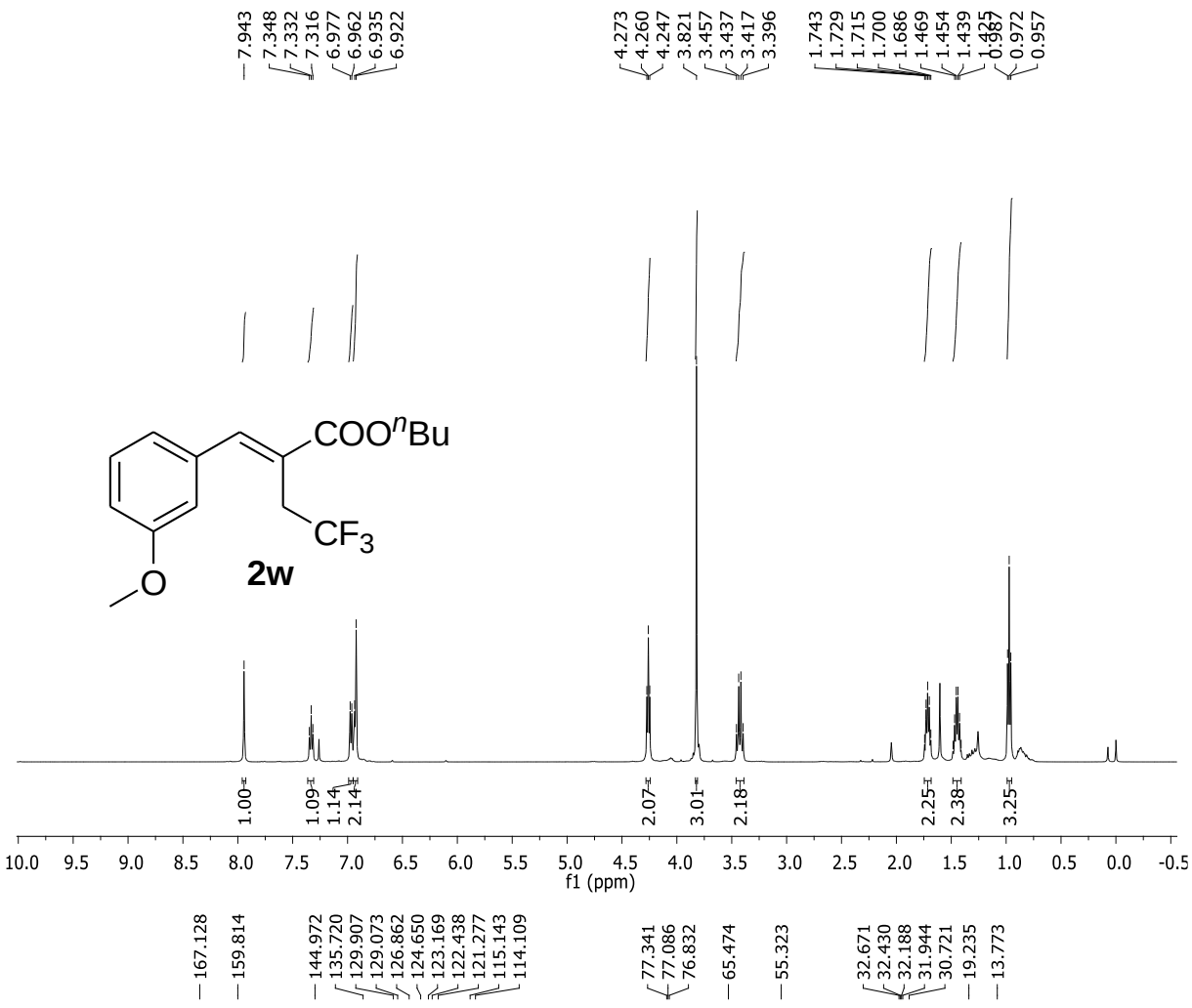

167.255
145.242
138.546
134.387
130.098
129.765
129.113
128.730
126.902
125.895
124.688
122.679
122.475
77.332
77.077
76.823
65.416
32.599
32.358
32.117
31.876
30.727
21.465
19.241
13.782
COO^{n}But
CF$_3$
2u
f1 (ppm)

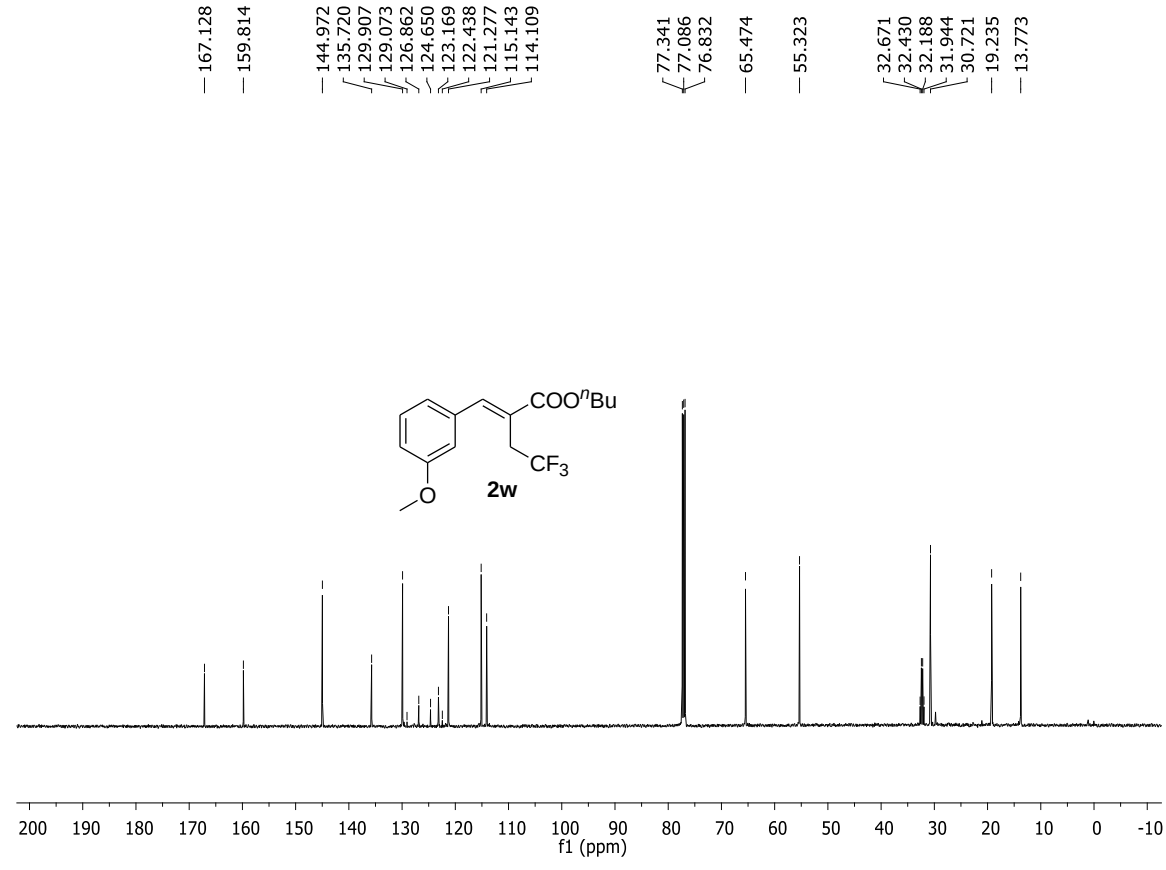

-63.067
COO^{n}But
CF_3
2u
100 80 60 40 20 0 -20 -40 -60 -80 -100 -130 -160 -190 -220 -250 -280
f1 (ppm)
7.455
7.440
7.226
3.795
3.347
3.326
3.306
3.286

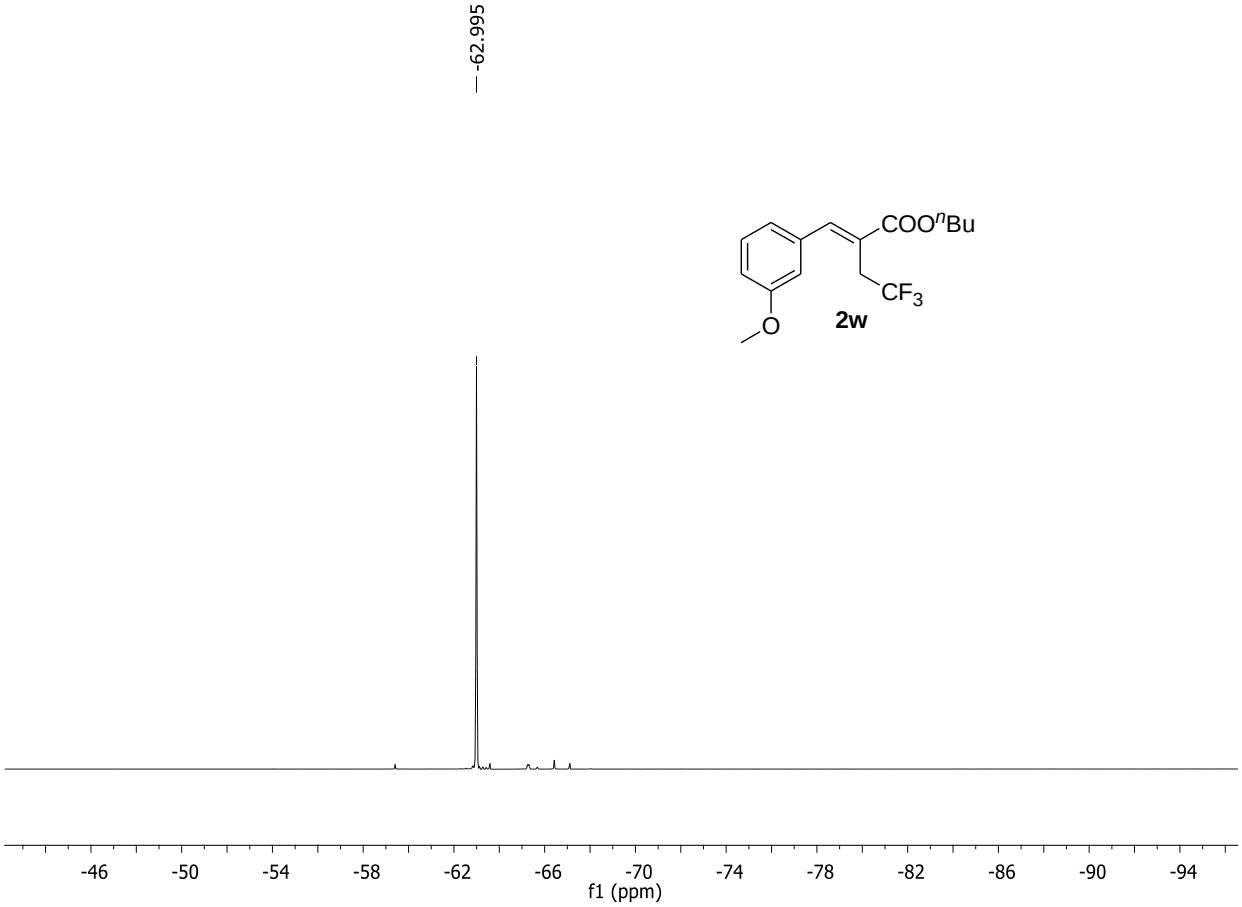

COOMe
S
CF_3
2v
2.04
1.08
3.04
2.13
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

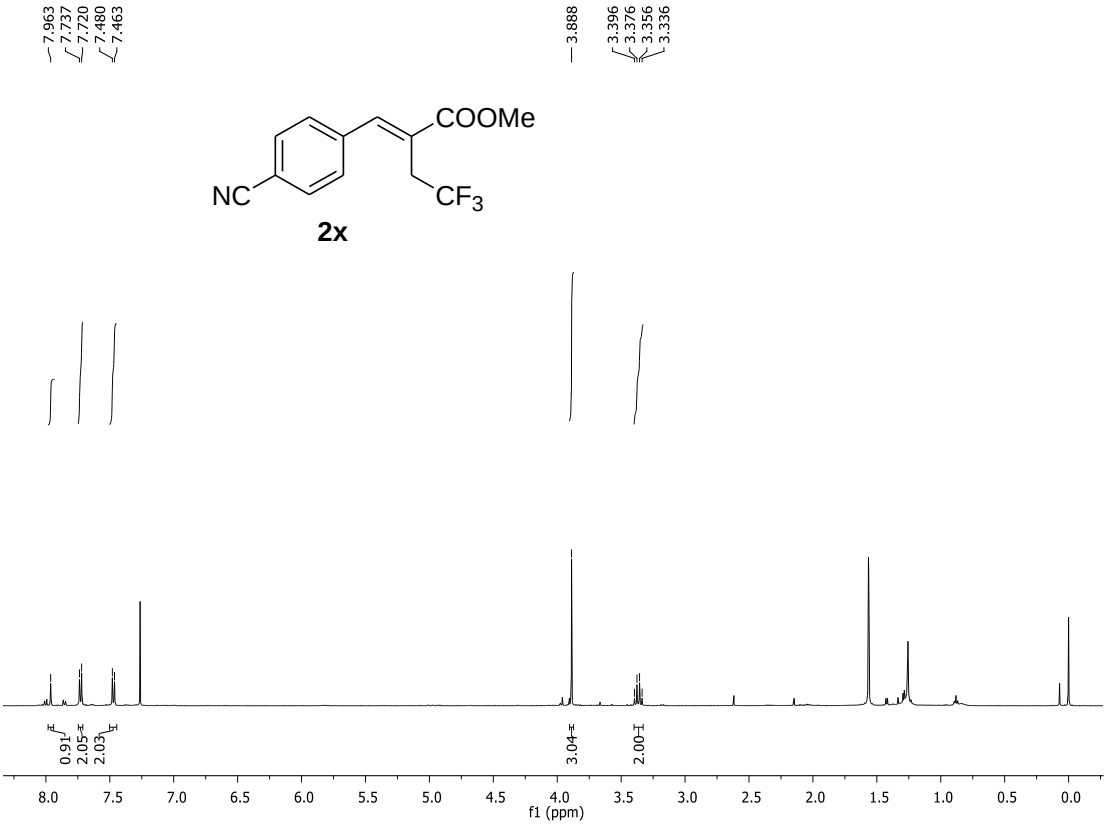

167.118
143.612
136.363
132.282
131.756
130.406
128.839
127.181
126.625
124.414
122.945
122.251
52.693
32.515
32.269
32.027
31.782
COOMe
S
CF3
2v
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

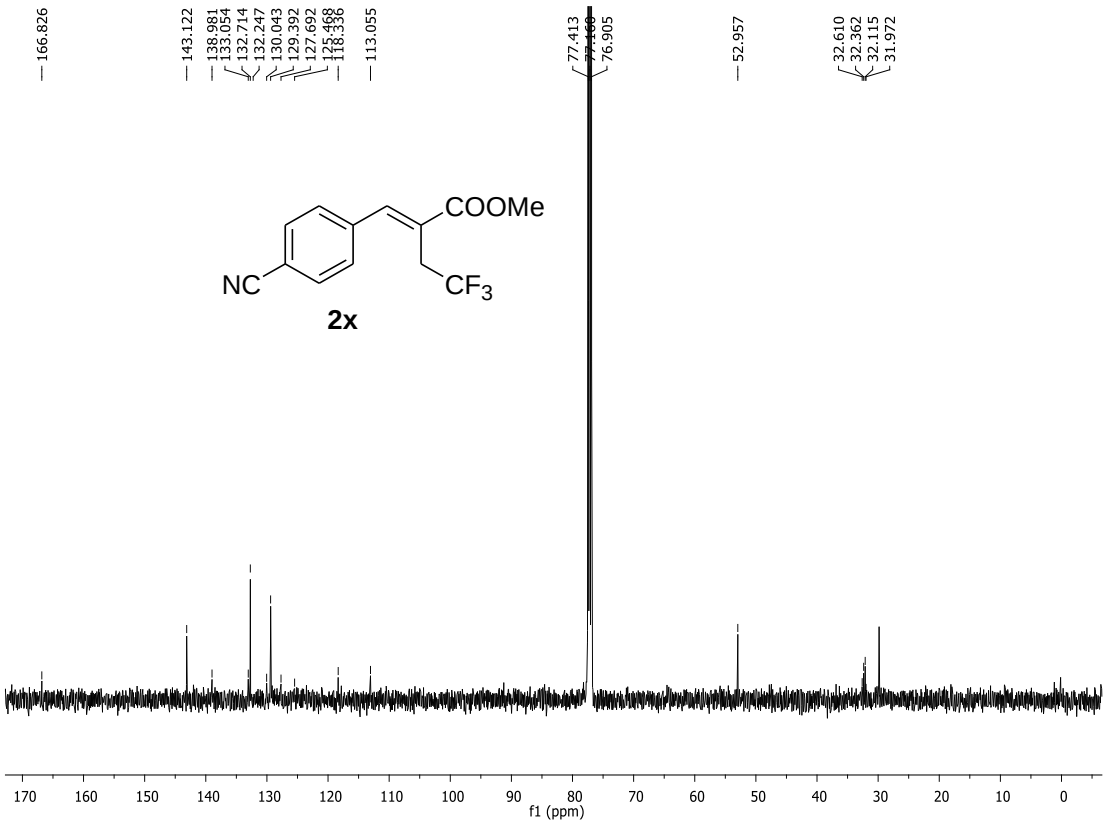

-63.772
COOMe
S
CF3
2v
100
80
60
40
20
0
-20
-40
-60
-80
-100
-130
-160
-190
-220
-250
-280
f1 (ppm)

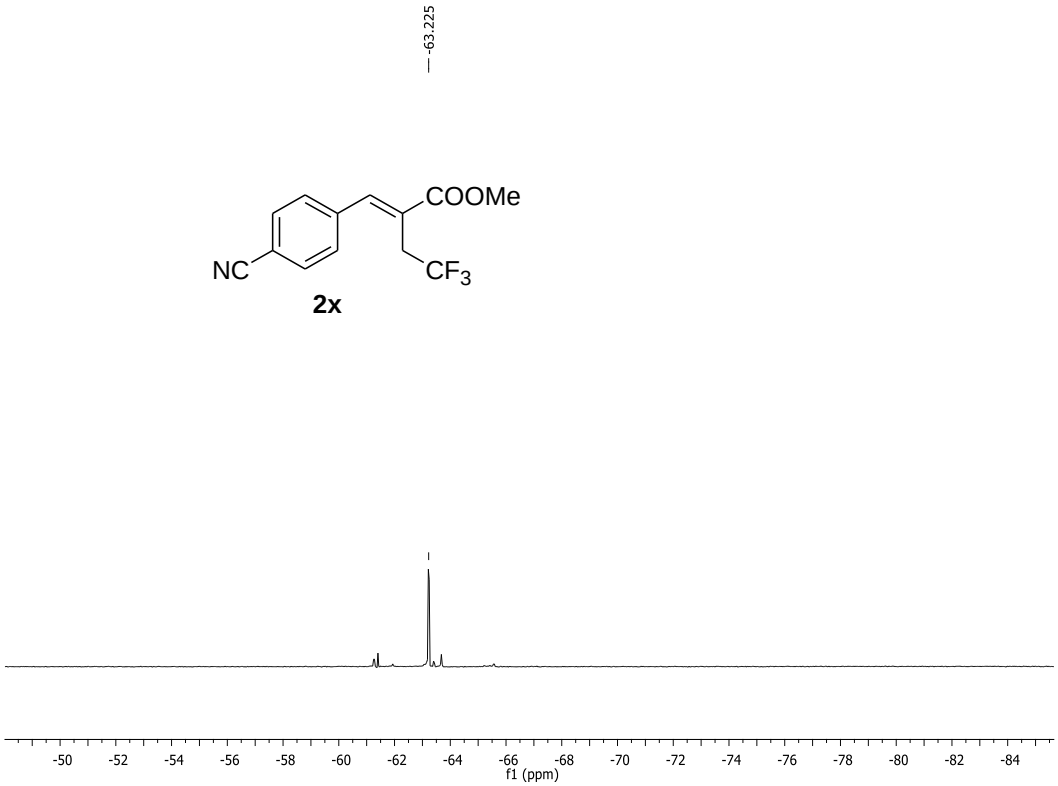

7.943
7.348
7.332
7.316
6.977
6.962
6.935
6.922
4.273
4.260
4.247
3.821
3.457
3.437
3.417
3.396
1.743
1.729
1.715
1.700
1.686
1.469
1.454
1.439
0.987
0.972
0.957
COO^{n}Bu
CF$_3$
O
2w
1.00
1.09
1.14
2.14
2.07
3.01
2.18
2.25
2.38
3.25
f1 (ppm)

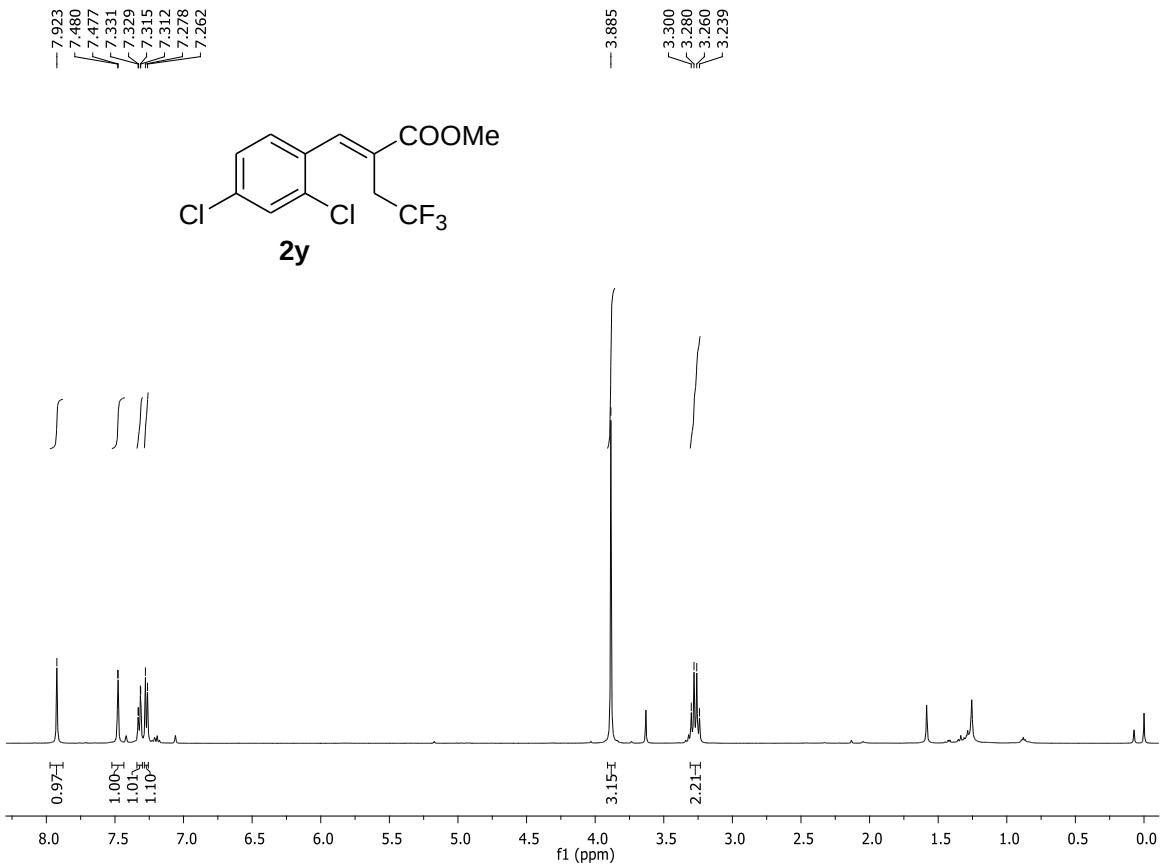

167.128
159.814
144.972
135.720
129.907
129.073
126.862
124.650
123.169
122.438
121.277
115.143
114.109
77.341
77.086
76.832
65.474
55.323
32.671
32.430
32.188
31.944
30.721
19.235
13.773
COO^{n}Bu
CF$_3$
O
2w
f1 (ppm)

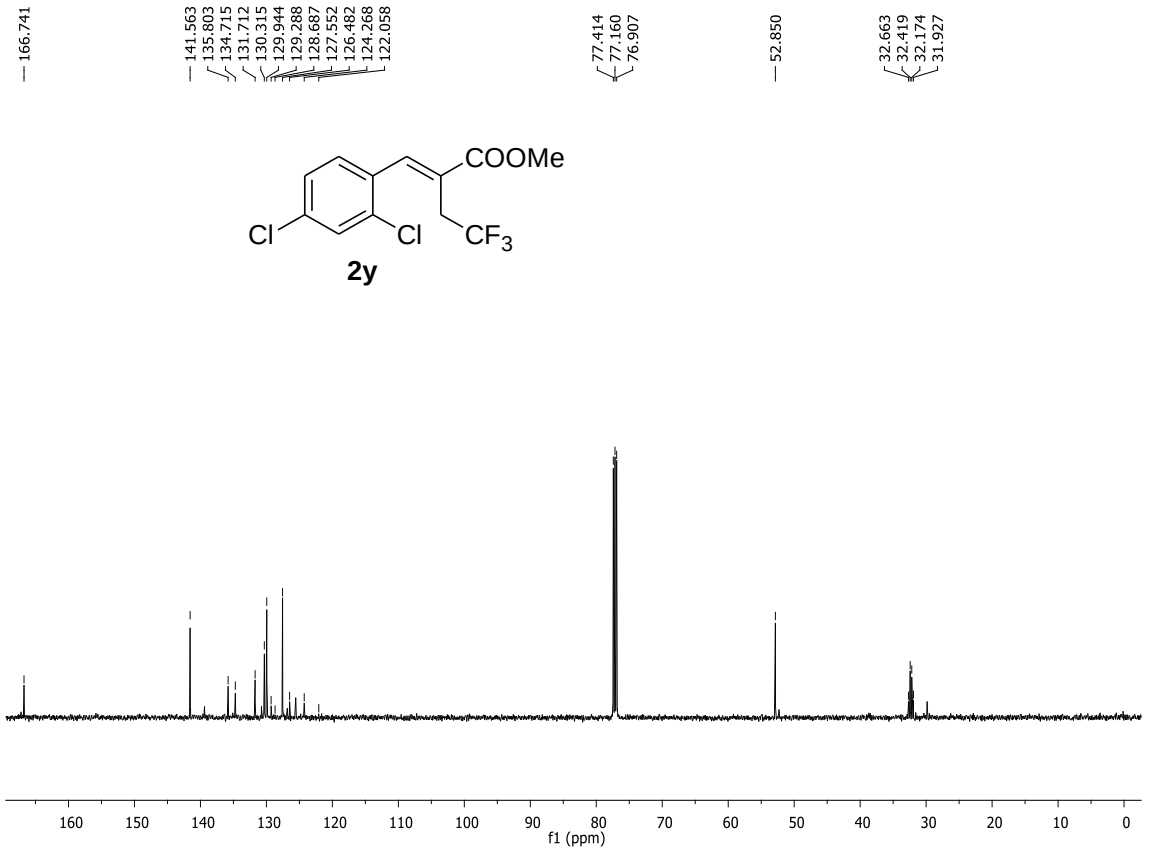

-62.995
COO^{n}Bu
CF$_3$
O
2w
-46
-50
-54
-58
-62
-66
-70
-74
-78
-82
-86
-90
-94
f1 (ppm)

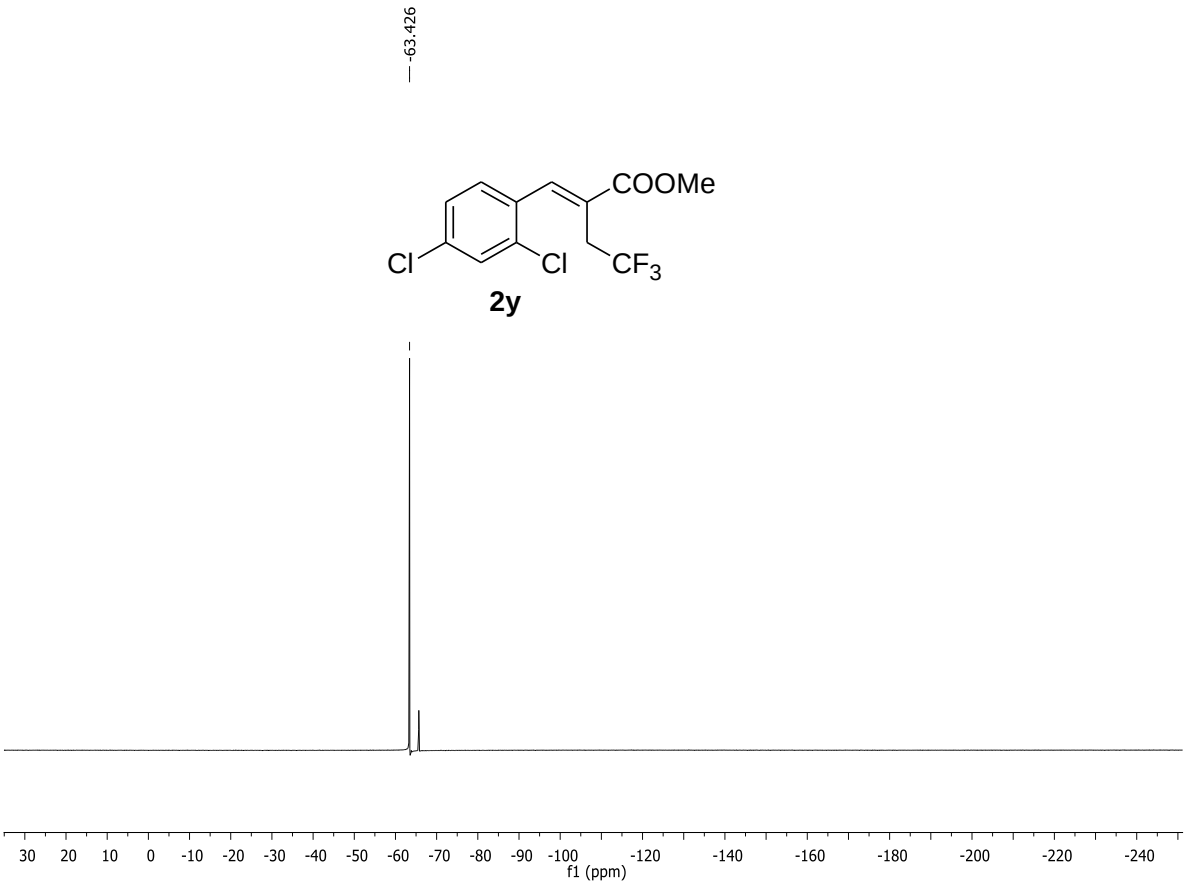

7.963
7.737
7.720
7.480
7.463
3.888
3.396
3.376
3.356
3.336
COOMe
NC
CF$_3$
2x
0.91
2.05
2.03
3.04
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


166.826
143.122
138.981
133.054
132.714
132.247
130.043
129.392
127.692
125.468
118.336
113.055
77.413
77.160
76.905
52.957
32.610
32.362
32.115
31.972
COOMe
NC
CF3
2x
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-63.225
COOMe
NC
CF3
2x
-50
-52
-54
-56
-58
-60
-62
-64
-66
-68
-70
-72
-74
-76
-78
-80
-82
-84
f1 (ppm)


7.923
7.480
7.477
7.331
7.329
7.315
7.312
7.278
7.262
3.885
3.300
3.280
3.260
3.239
COOMe
Cl
Cl
CF3
2y
0.97
1.00
1.01
1.10
3.15
2.21
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


166.741
141.563
135.803
134.715
131.712
130.315
129.944
129.288
128.687
127.552
126.482
124.268
122.058
77.414
77.160
76.907
52.850
32.663
32.419
32.174
31.927
COOMe
Cl
Cl
CF3
2y
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-63.426
COOMe
Cl
Cl
CF3
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

2y