Rhodium-Catalyzed Arylative Cyclization of Alkynyl Malonates by 1,4-Rhodium(I) Migration

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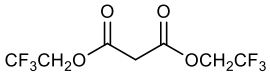
Supplementary Information

1. General Information

All air-sensitive reactions were carried out under an inert atmosphere using oven-dried apparatus. 1,4-Dioxane was purchased from Acros Organics and degassed before use using a stream of argon (30 min). All commercially available reagents were used as received unless otherwise stated. Petroleum ether refers to Sigma-Aldrich product 24587 (petroleum ether boiling point 40-60 °C). Thin layer chromatography (TLC) was performed on Merck DF-Alufoilien 60F254 0.2 mm precoated plates. Compounds were visualized by exposure to UV light or by dipping the plates into solutions of potassium permanganate or vanillin followed by gentle heating. Flash column chromatography was carried out using silica gel (Fisher Scientific 60 Å particle size 35-70 micron or Fluorochem 60 Å particle size 40-63 micron). Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. The solvent of recrystallization is reported in parentheses. Infrared (IR) spectra were recorded on Bruker platinum ALPHA FTIR spectrometer on the neat compound using the attenuated total refraction technique. NMR spectra were acquired on Bruker Ascend 400 or Ascend 500 spectrometers. ^{1}H and ^{13}C NMR spectra were referenced to external tetramethylsilane via the residual protonated solvent (^{1}H) or the solvent itself (^{13}C). ^{19}F NMR spectra were referenced through the solvent lock (^{2}H) signal according to the IUPAC-recommended secondary referencing method following Bruker protocols. All chemical shifts are reported in parts per million (ppm). For $CDCl_3$, the shifts are referenced to 7.26 ppm for ^{1}H NMR spectroscopy and 77.16 ppm for ^{13}C NMR spectroscopy. ^{13}C NMR assignments were made using the DEPT sequence with secondary pulses at 90° and 135°. Coupling constants (*J*) are quoted to the nearest 0.1 Hz. High-resolution mass spectra were recorded using electrospray ionization (ESI) techniques. X-ray diffraction data were collected at 120 K on an Agilent SuperNova diffractometer using CuKα radiation.

2. Preparation of Substrates



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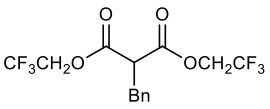

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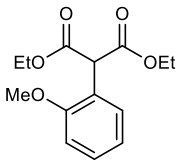

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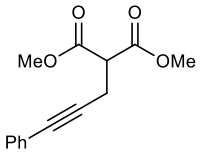

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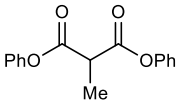

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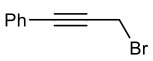

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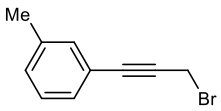
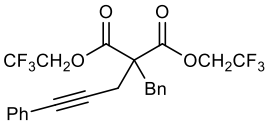
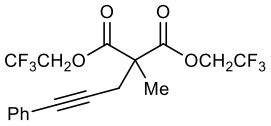


S7



1a



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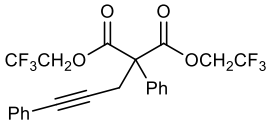

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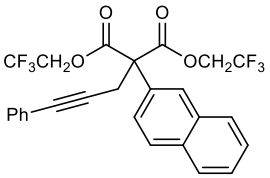
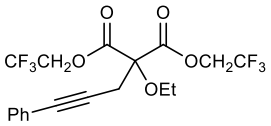
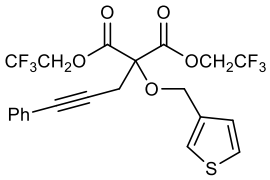


1h



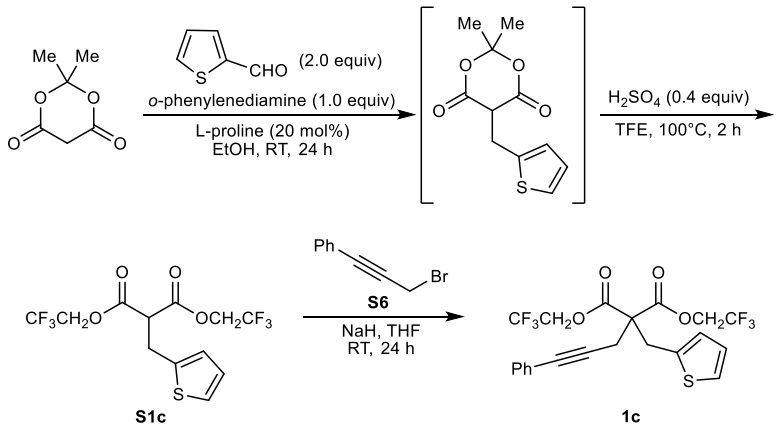
1p

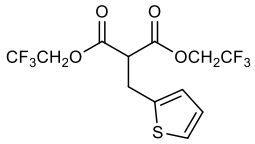


1q

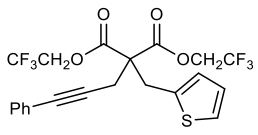
Known procedures were used for the preparation of **S1**,[1] **S2**,[2] **S3**,[3] **S4**,[4] **S5**,[5] **S6**,[6] and **S7**.[7] Substrates **1a**,[2] **1b**,[2] **1f**,[2] **1h**,[2] **1p**,[2] **1q**,[2] were prepared by known methods.

Preparation of Substrate 1c





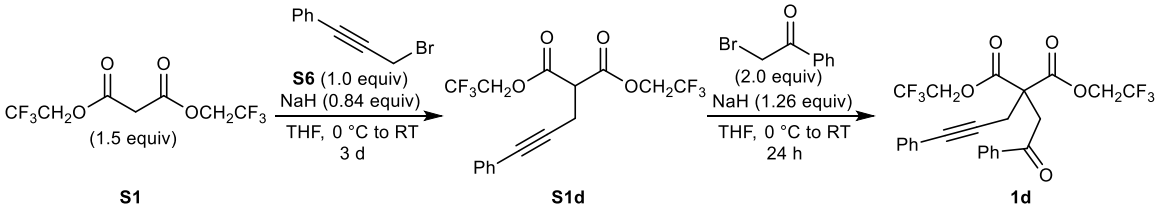
Bis(2,2,2-trifluoroethyl) 2-(2-thienylmethyl)malonate (S1c). To a solution of *ortho*-phenylenediamine (1.88 g, 17.4 mmol) in EtOH (300 mL) at 25 °C were added 2-thienylcarboxaldehyde (3.24 mL, 34.7 mmol), Meldrum's acid (2.51 g, 17.4 mmol), and L-proline (399 mg, 3.47 mmol). The resulting mixture was vigorously stirred for 24 h and concentrated *in vacuo* to leave a residue, which was dissolved in CH_2Cl_2 (200 mL) and washed with 1 M aqueous HCl solution (150 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 100 mL). The combined organic layers were washed with H_2O, dried ($MgSO_4$), filtered, and concentrated in *vacuo* to leave a residue (4.80 g), which was used directly in the next step without further purification. In a sealed vessel containing a stirrer bar, a solution of this crude compound (4.80 g) and concentrated H_2SO_4 (433 µL, 8.1 mmol) in TFE (45 mL) were stirred at 100 °C for 2 h. The reaction was cooled to room temperature, diluted with Et_2O (200 mL), and washed with saturated aqueous $NaHCO_3$ solution (3 × 100 mL), H_2O (100 mL), and brine (100 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated in *vacuo*. The residue was passed through a plug of silica gel using 2% EtOAc/petroleum ether as the eluent to give **S1c** (674 mg) as a yellow oil which was not pure, but which was used directly in the next step. R_f = 0.30 (10% EtOAc/petroleum ether).

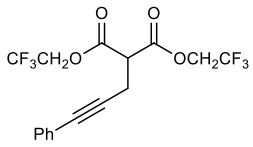


Bis(2,2,2-trifluoroethyl) 2-(3-phenylprop-2-yn-1-yl)-2-(2-thienylmethyl)malonate (1c). A flask was charged with NaH (60% dispersion in mineral oil, 85.6 mg, 2.14 mmol), purged with argon for 30 min, and then suspended in THF (5 mL) at 0 °C. A proportion of impure malonate **S1c** (650 mg out of the 674 mg prepared as above) in THF (2 mL) was added to the ice-cooled suspension. The resulting solution was warmed to room temperature and stirred for 45 min. Alkynyl bromide **S6**[6] (80 wt. % in toluene, 868 µL, 3.56 mmol) was added dropwise and the resulting solution was stirred at room temperature for 3 h. The reaction was quenched with H_2O (25 mL), extracted with Et_2O (3 × 25 mL), and the combined organic layers were washed with brine (25 mL), dried ($MgSO_4$), filtered, and concentrated

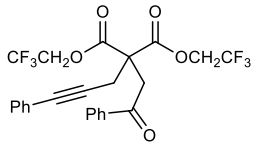
in *vacuo*. The residue was purified by column chromatography (0% to 2% EtOAc/petroleum ether) to give the title compound **1c** (950 mg, 12% over two steps) as an orange oil. R_f = 0.30 (10% EtOAc/petroleum ether); IR 1758 (C=O), 1411, 1279, 1157, 1067, 972, 906, 756, 690, 531 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (2H, dd, *J* = 6.7, 3.0 Hz, Ar**H**), 7.34-7.30 (3H, m, Ar**H**), 7.21 (1H, dd, *J* = 5.0, 1.2 Hz, Ar**H**), 7.00-6.92 (2H, m, Ar**H**), 4.63-4.46 (4H, m, 2 × C**H**$_2$CF$_3$), 3.76 (2H, s, C**H**$_2$CS), 3.08 (2H, s, C**H**$_2$C≡C); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4 (2 × C), 135.5 (C), 131.9 (2 × CH), 128.5 (CH), 128.5 (2 × CH), 128.3 (CH), 127.4 (CH), 125.6 (CH), 122.8 (C), 122.6 (q, J_{C-F} = 277.4 Hz, 2 × C), 85.3 (C), 82.7 (C), 61.6 (q, J_{C-F} = 37.4 Hz, 2 × CH_2), 58.6 (C), 32.1 (CH_2), 23.6 (CH_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ –73.8 (t, *J* = 8.2 Hz, 6 × F); HRMS (ESI) Exact mass calculated for $[C_{21}H_{16}F_6NaO_4S]^+$ $[M+Na]^+$: 501.0568, found 501.0566.

Preparation of Substrate 1d



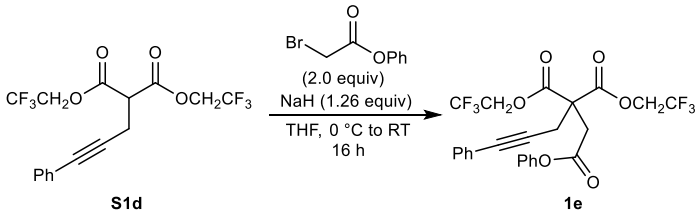


Bis(2,2,2-trifluoroethyl) 2-(3-phenylprop-2-yn-1-yl)malonate (S1d). A flask was charged with NaH (60% dispersion in mineral oil, 251 mg, 6.28 mmol), purged with argon for 30 min, and then suspended in THF (25 mL) at 0 °C. A solution of bis(2,2,2-trifluoroethyl) malonate (3.00 g, 11.2 mmol) in THF (5 mL) was added to the ice-cooled suspension. The resulting solution was stirred at 0 °C for 45 min. Alkynyl bromide **S6**[6] (80 wt. % solution in toluene, 1.82 mL, 7.47 mmol) was added dropwise and the resulting solution was stirred at room temperature for 3 d. The reaction was quenched with H_2O (30 mL), extracted with Et_2O (3 × 30 mL), and the combined organic layers were washed with brine (50 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (0% to 1% EtOAc/petroleum ether) to give the title compound **S1d** (978 mg, 41%) as a yellow oil. R_f = 0.26 (10% EtOAc/petroleum ether); IR 1756 (C=O), 1492, 1280, 1158, 1067, 965, 757, 691, 659, 535 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.34 (2H, m, Ar**H**), 7.32-7.27 (3H, m, Ar**H**), 4.58 (4H, q, *J* = 8.2 Hz, 2 × C**H**$_2$CF$_3$), 3.91 (1H, t, *J* = 7.6 Hz, CH$_2$C**H**), 3.09 (2H, d, *J* = 7.6 Hz, C**H**$_2$C≡C); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9 (2 × C), 131.8 (2 × CH), 128.4 (CH), 128.4 (2 × CH), 122.8 (C), 122.6 (q, J_{C-F} = 277.4 Hz, 2 × C), 83.7 (C), 83.5 (C), 61.5 (q, J_{C-F} = 37.4 Hz, 2 × CH_2), 50.7 (CH), 19.5 (CH_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ –73.5 (t, *J* = 8.3 Hz, 6 × F); HRMS (ESI) Exact mass calculated for $[C_{16}H_{12}F_6NaO_4]^+$ $[M+Na]^+$: 405.0537, found 405.0535.



Bis(2,2,2-trifluoroethyl) 2-(2-oxo-2-phenylethyl)-2-(3-phenylprop-2-yn-1-yl)malonate (1d). A flask was charged with NaH (60% dispersion in mineral oil, 66 mg, 1.65 mmol), purged with argon for 30 min, and then suspended in THF (15 mL) at 0 °C. A solution of malonate **S1d** (500 mg, 1.31 mmol) in THF (3 mL) was added to the ice-cooled suspension. The resulting solution was stirred at 0 °C for 45 min. A solution of 2-bromoacetophenone (521 mg, 2.62 mmol) in THF (3 mL) was added dropwise and the resulting solution was stirred at room temperature for 24 h. The reaction was quenched with H_2O (20 mL), extracted with Et_2O (3 × 20 mL), and the combined organic layers were washed with brine (25 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (0% to 5% EtOAc/petroleum ether) to give the title compound **1d** (385 mg, 59%) as a white solid. R_f = 0.31 (20% EtOAc/petroleum ether); m.p. 91-92 °C (Et_2O); IR 2921, 1754 (C=O), 1681 (C=O), 1434, 1283, 1165, 1065, 973, 751, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.05-7.97 (2H, m, Ar**H**), 7.65-7.57 (1H, m, Ar**H**), 7.53-7.46 (2H, m, Ar**H**), 7.33-7.26 (5H, m, Ar**H**), 4.68-4.49 (4H, m, 2 × C**H**$_2$CF$_3$), 4.02 (2H, s, C**H**$_2$C=O), 3.38 (2H, s, C**H**$_2$C≡C); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4 (C), 167.5 (2 × C), 136.3 (C), 134.0 (CH), 131.8 (2 × CH), 129.0 (2 × CH), 128.5 (CH), 128.4 (2 × CH), 128.3 (2 × CH), 122.7 (C), 122.7 (q, $J_{C\text{-}F}$ = 277.4 Hz, 2 × C), 84.9 (C), 83.0 (C), 61.7 (q, $J_{C\text{-}F}$ = 37.4 Hz, 2 × CH_2), 55.2 (C), 41.4 (CH_2), 24.6 (CH_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ –73.8 (t, J = 8.2 Hz, 6 × F); HRMS (ESI) Exact mass calculated for $[C_{24}H_{18}F_6NaO_5]^+$ $[M+Na]^+$: 523.0951, found 523.0951.

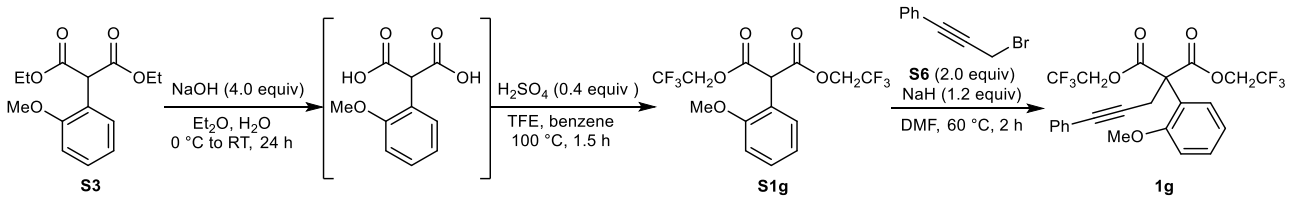
1-Phenyl 2,2-bis(2,2,2-trifluoroethyl) 5-phenylpent-4-yne-1,2,2-tricarboxylate (1e)

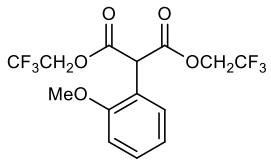


A flask was charged with NaH (60% dispersion in mineral oil, 53 mg, 1.26 mmol), purged with argon for 30 min, and then suspended in THF (15 mL) at 0 °C. A solution of malonate **S1d** (400 mg, 1.05 mmol) in THF (3 mL) was added to the ice-cooled suspension. The resulting solution was stirred at 0 °C for 45 min. A solution of phenyl bromoacetate (452 mg, 2.10 mmol) in THF (3 mL) was added dropwise and the resulting solution was stirred at room temperature for 16 h. The reaction was quenched with H_2O (30 mL), extracted with Et_2O (3 × 20 mL), and the combined organic layers were washed with brine (25 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (0% to 4% EtOAc/petroleum ether) to give the title compound **1e** (481 mg, 89%) as a pale yellow oil. R_f = 0.28 (20% EtOAc/petroleum ether); IR 1755 (C=O), 1593

(C=O), 1411, 1281, 1160, 1065, 973, 756, 689, 496 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.35 (4H, m, Ar**H**), 7.34-7.28 (3H, m, Ar**H**), 7.25-7.21 (1H, m, Ar**H**), 7.11-7.05 (2H, m, Ar**H**), 4.65-4.51 (4H, m, 2 × C**H**$_2$CF$_3$), 3.56 (2H, s, C**H**$_2$C=O), 3.35 (2H, s, C**H**$_2$C≡C); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8 (C), 167.0 (2 × C), 150.3 (C), 131.9 (2 × CH), 129.7 (2 × CH), 128.7 (CH), 128.5 (2 × CH), 126.4 (CH), 122.6 (q, J_{C-F} = 277.4 Hz, 2 × C), 122.6 (C), 121.5 (2 × CH), 85.2 (C), 82.2 (C), 61.9 (q, J_{C-F} = 37.2 Hz, 2 × CH_2), 55.5 (C), 37.4 (CH_2), 25.0 (CH_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ –73.8 (t, J = 8.2 Hz, 6 × F); HRMS (ESI) Exact mass calculated for $[C_{24}H_{18}F_6NaO_6]^+$ $[M+Na]^+$: 539.0905, found 539.0906.

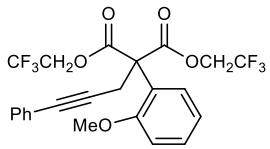
Preparation of Substrate 1g





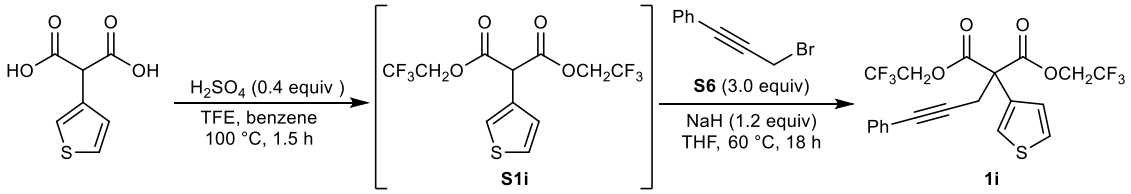
Bis(2,2,2-trifluoroethyl) 2-(2-methoxyphenyl)malonate (S1g). To a stirred solution of diethyl 2-(2-methoxyphenyl)malonate (**S3**,[3] 4.65 g, 17.5 mmol) in Et_2O (32 mL) at 0 °C was added a solution of NaOH (2.79 g, 69.9 mmol) in H_2O (60 mL) and the resulting mixture was stirred vigorously at room temperature for 24 h. The aqueous layer was separated and washed with Et_2O (2 × 50 mL), acidified to pH 2 with 6 M aqueous HCl solution, and extracted with EtOAc (5 × 50 mL). The combined organic extracts were washed with brine (50 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo* to leave the malonic acid as an off-white solid (3.31 g) that was used in the next step without further purification. A microwave vial fitted with a stirrer bar was charged with this malonic acid (3.31 g, 15.8 mmol), TFE (20 mL), benzene (20 mL) and concentrated H_2SO_4 (335 µL, 6.30 mmol). The vial was then capped with a crimp capped PTFE seal and stirred at 100 °C for 7 h. The reaction was cooled to room temperature and diluted with Et_2O (250 mL). The solution was then washed with saturated aqueous $NaHCO_3$ solution (3 × 100 mL) and brine (50 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (0% to 3% EtOAc/petroleum ether) to give the title compound **S1g** (2.20 g, 34% over two steps) as a brown oil. R_f = 0.33 (10% EtOAc/petroleum ether); IR 1771 (C=O), 1747, 1416, 1254, 1135, 955, 865, 749, 654, 543 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.34 (1H, m, Ar**H**), 7.28 (1H, dd, J = 7.7, 1.7 Hz, Ar**H**), 6.99 (1H, td, J = 7.6, 1.1 Hz, Ar**H**), 6.93 (1H, dd, J = 8.3, 1.1 Hz, Ar**H**), 5.28 (1H, s, ArC**H**), 4.59-4.52 (4H, m, 2 × C**H**$_2$CF$_3$), 3.83 (3H, s, OC**H**$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5 (2 × C), 157.0 (C), 130.4 (CH), 129.5 (CH), 122.7 (q, J_{C-F} = 277.3 Hz, 2 × C), 121.0 (CH), 120.0 (C), 111.0

(CH), 61.3 (q, $J_{C\text{-}F}$ = 37.3 Hz, 2 × CH_2), 55.7 (CH), 50.8 (CH_3); ^{19}F NMR (376 MHz, $CDCl_3$) δ –73.9 (t, *J* = 8.3 Hz, 6 × F); HRMS (ESI) Exact mass calculated for $[C_{14}H_{12}F_6O_5Na]^+$ $[M+Na]^+$: 397.0481, found 397.0483.



Bis(2,2,2-trifluoroethyl) 2-(2-methoxyphenyl)-2-(3-phenylprop-2-yn-1-yl)malonate (1g). A solution of malonate **S1g** (1.00 g, 2.67 mmol) in DMF (3 mL) was added to an ice-cooled suspension of NaH (60% dispersion in mineral oil, 128.2 mg, 3.21 mmol) in DMF (7 mL). The resulting solution was warmed to room temperature and stirred for 30 min. Alkynyl bromide **S6**[6] (80 wt. % in toluene, 1.30 mL, 5.34 mmol) was added dropwise and the resulting solution was warmed to 60 °C and stirred for 2 h. The reaction was cooled to room temperature and quenched with saturated aqueous NH_4Cl solution (50 mL). This solution was extracted with EtOAc (3 × 50 mL), and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated in *vacuo*. The residue was purified by column chromatography (0% to 2% EtOAc/petroleum ether) to give title compound **1g** (951 mg, 73%) as a yellow oil. R_f = 0.27 (10% EtOAc/petroleum ether); IR 2973, 1756 (C=O), 1493, 1282, 1155, 972, 753, 692, 651, 556 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.31 (2H, m, Ar**H**), 7.25-7.23 (5H, m, Ar**H**), 7.01 (1H, td, *J* = 8.3, 1.2 Hz, Ar**H**), 6.92 (1H, dd, *J* = 8.2, 1.2 Hz, Ar**H**), 4.63-4.50 (4H, m, 2 × C**H**$_2$CF$_3$), 3.78 (3H, s, OC**H**$_3$), 3.47 (2H, s, C**H**$_2$C≡C); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8 (2 × C), 156.6 (C), 131.7 (2 × CH), 130.1 (CH), 128.6 (CH), 128.3 (2 × CH), 128.1 (CH), 124.7 (C), 123.3 (C), 122.8 (q, $J_{C\text{-}F}$ = 277.5 Hz, 2 × C), 120.8 (CH), 111.3 (CH), 84.9 (C), 83.7 (C), 61.5 (q, $J_{C\text{-}F}$ = 37.1 Hz, 2 × CH_2), 60.8 (C), 55.6 (CH_3), 26.5 (CH_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ –73.6 (t, *J* = 8.3 Hz, 6 × F); HRMS (ESI) Exact mass calculated for $[C_{23}H_{22}F_6NO_5]^+$ $[M+NH_4]^+$: 506.1398, found 506.1397.

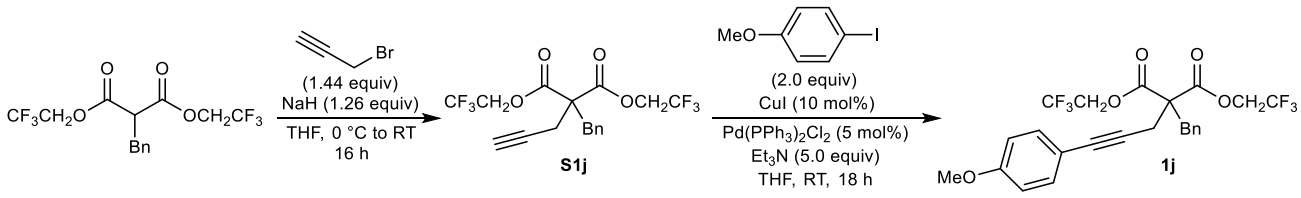
Bis(2,2,2-trifluoroethyl) 2-(3-phenylprop-2-yn-1-yl)-2-(3-thienyl)malonate (1i)

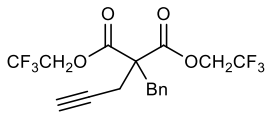


A sealed tube was charged with the 3-thienylmalonic acid (2.50 g, 13.4 mmol), concentrated H_2SO_4 (163 µL, 2.69 mmol), TFE (30 mL), and a stirrer bar. The mixture was then stirred at 100 °C for 1.5 h. The reaction was cooled to room temperature and diluted with Et_2O (200 mL). The solution was then washed with saturated aqueous $NaHCO_3$ solution (3 × 100 mL), H_2O (100 mL), and brine (100 mL). The organic layer was dried ($MgSO_4$) and concentrated in *vacuo*. The residual solvent was removed under high vacuum to leave the crude malonate ester **S1i** (2.52 g), which was used in the next step without further purification. A solution of this malonate ester in THF (5 mL) was added to

an ice-cooled suspension of NaH (60% dispersion in mineral oil, 864 mg, 21.6 mmol) in THF (20 mL). The resulting solution was warmed to room temperature and stirred for 30 min. Alkynyl bromide **S6**[6] (80 wt. % in toluene, 5.27 mL, 21.6 mmol) was added dropwise and the resulting solution was warmed to 60 °C and stirred for 18 h. The reaction was cooled to room temperature and quenched with saturated aqueous NH_4Cl solution (50 mL). This solution was extracted with EtOAc (3 × 50 mL), and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated in *vacuo*. The residue was purified by column chromatography (0% to 2% EtOAc/petroleum ether) to give title compound **1i** (908 mg, 14% over two steps) as a pale brown solid. R_f = 0.25 (7% EtOAc/petroleum ether); IR 1757 (C=O), 1415, 1241, 1157, 1085, 1009, 974, 762, 696, 625 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (1H, dd, *J* = 3.0, 1.4 Hz, Ar**H**), 7.37-7.23 (7H, m, Ar**H**), 4.66-4.55 (4H, m, 2 × C**H**$_2$CF$_3$), 3.49 (2H, s, C**H**$_2$C≡C); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1 (2 × C), 133.8 (C), 131.8 (2 × CH), 128.43 (CH), 128.36 (2 × CH), 127.4 (CH), 126.8 (CH), 124.7 (CH), 122.8 (C), 122.6 (q, J_{C-F} = 277.3 Hz, 2 × C), 84.8 (C), 83.2 (C), 61.6 (q, J_{C-F} = 37.4 Hz, 2 × CH_2), 59.7 (C), 27.5 (CH_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ –73.7 (t, *J* = 8.1 Hz, 6 × F); HRMS (ESI) Exact mass calculated for $[C_{20}H_{14}F_6O_4SNa]^+$ [M+Na]$^+$: 487.0409, found 487.0414.

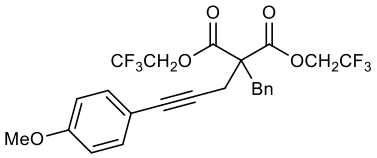
Preparation of Substrate 1j





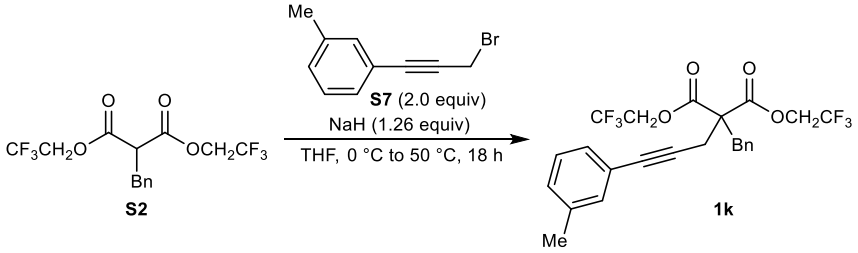
Bis(2,2,2-trifluoroethyl) 2-benzyl-2-(prop-2-yn-1-yl)malonate (S1j). A flask was charged with NaH (60% dispersion in mineral oil, 844 mg, 21.1 mmol), purged with argon for 30 min, and then suspended in THF (200 mL) at 0 °C. A solution malonate **S2**[2] (6.00 g, 16.7 mmol) in THF (20 mL) was added to the ice-cooled suspension. The resulting solution was stirred at 0 °C for 45 min. Propargyl bromide (80 wt. % in toluene, 3.58 mL, 24.1 mmol) was added dropwise and the resulting solution was stirred at room temperature for 16 h. The reaction was quenched with H_2O (150 mL), extracted with Et_2O (3 × 120 mL), and the combined organic layers were washed with brine (150 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (0% to 1% EtOAc/petroleum ether) to give the title compound **S1j** (2.01 g, 30%) as a pale yellow oil. R_f = 0.33 (10% EtOAc/petroleum ether); IR 1756 (C=O), 1412, 1281, 1155, 1086, 994, 908, 742, 702, 648 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.27 (3H, m, Ar**H**), 7.20-7.10 (2H, m, Ar**H**), 4.61-4.43 (4H, m, 2 × C**H**$_2$CF$_3$), 3.47 (2H, s, C**H**$_2$Ph), 2.76 (2H, d, *J* = 2.7 Hz, C**H**$_2$C≡C), 2.21 (1H, t, *J* = 2.6 Hz,

C≡C**H**); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5 (2 × C), 134.3 (C), 129.9 (2 × CH), 128.9 (2 × CH), 127.9 (CH), 122.6 (q, $J_{C\text{-}F}$ = 277.3 Hz, 2 × C), 77.9 (C), 73.3 (CH), 61.5 (q, $J_{C\text{-}F}$ = 37.4 Hz, 2 × CH_2), 58.4 (C), 37.4 (CH_2), 22.4 (CH_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ –73.6 (t, *J* = 8.2 Hz, 6 × F); HRMS (ESI) Exact mass calculated for $[C_{17}H_{14}F_6NaO_4]^+$ $[M+Na]^+$: 419.0678, found 419.0688.



Bis(2,2,2-trifluoroethyl) 2-benzyl-2-[3-(4-methoxyphenyl)prop-2-yn-1-yl]malonate (1j). A flask was charged with CuI (24.0 mg, 0.13 mmol), $Pd(PPh_3)_2Cl_2$ (44.2 mg, 0.06 mmol), 4-iodoanisole (591 mg, 2.52 mmol) and purged with argon for 20 min. Freshly degassed (purging with argon for 30 min) THF (25 mL), and Et_3N (1.05 mL, 6.30 mmol) were added and the mixture was degassed with a stream of argon for 15 min. Malonate **S1j** (500 mg, 1.26 mmol) was added and the mixture was stirred at room temperature for 18 h. The reaction was quenched with saturated aqueous NH_4Cl solution (10 mL), extracted with EtOAc (3 × 20 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (0% to 3% EtOAc/petroleum ether) to give the title compound **1j** (345 mg, 54%) as a yellow oil. R_f = 0.29 (10% EtOAc/petroleum ether); IR 2969, 1757 (C=O), 1510, 1443, 1284, 1157, 973, 907, 742, 535 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.35 (2H, m, Ar**H**), 7.33-7.27 (3H, m, Ar**H**), 7.20 (2H, dd, *J* = 7.5, 1.9 Hz, Ar**H**), 6.98 (1H, dd, *J* = 5.2, 3.6 Hz, Ar**H**), 6.88-6.83 (2H, m, Ar**H**), 4.60-4.51 (4H, m, 2 × C**H**$_2$CF$_3$), 3.82 (3H, s, OC**H**$_3$), 3.51 (2H, s, C**H**$_2$Ph), 2.96 (2H, s, C**H**$_2$C≡C); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8 (2 × C), 159.8 (C), 134.5 (C), 133.3 (2 × CH), 130.0 (2 × CH), 128.9 (2 × CH), 127.8 (CH), 122.6 (q, $J_{C\text{-}F}$ = 277.4 Hz, 2 × C), 115.0 (C), 114.1 (2 × CH), 85.2 (C), 81.5 (C), 61.4 (q, $J_{C\text{-}F}$ = 37.3 Hz, 2 × CH_2), 58.8 (C), 55.5 (CH_3), 37.6 (CH_2), 23.4 (CH_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ –73.7 (t, *J* = 8.2 Hz, 6 × F); HRMS (ESI) Exact mass calculated for $[C_{24}H_{20}F_6NaO_5]^+$ $[M+Na]^+$: 525.1108, found 525.1107.

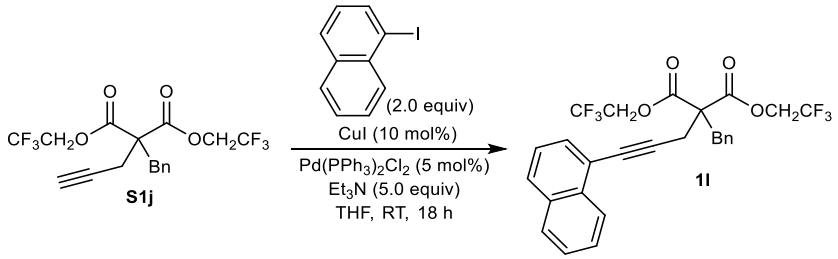
Bis(2,2,2-trifluoroethyl) 2-benzyl-2-(3-(3-methylphenyl)prop-2-yn-1-yl)malonate (1k)



A flask was charged with NaH (60% dispersion in mineral oil, 141 mg, 3.53 mmol), purged with argon for 30 min, and then suspended in THF (15 mL) at 0 °C. A solution of malonate **S2**[2] (1.00 g, 2.79 mmol) in THF (3 mL) was added to the ice-cooled suspension. The resulting solution was stirred at 0 °C for 45 min. Alkynyl bromide **S7**[7] (72 wt. % in toluene, 1.48 mL, 5.58 mmol) was added dropwise and the resulting solution was stirred at 50 °C for 18 h. The reaction was quenched with

H_2O (20 mL), extracted with Et_2O (3 × 20 mL), and the combined organic layers were washed with brine (25 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (0% to 1% EtOAc/petroleum ether) to give the title compound **1k** (870 mg, 64%) as a pale yellow oil. R_f = 0.36 (10% EtOAc/petroleum ether); IR 1757 (C=O), 1486, 1282, 1155, 1085, 974, 784, 742, 702, 651 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34-7.27 (3H, m, Ar**H**), 7.25-7.18 (5H, m, Ar**H**), 7.15 (1H, d, *J* = 7.4 Hz, Ar**H**), 4.58-4.50 (4H, m, 2 × C**H**$_2$CF$_3$), 3.53 (2H, s, C**H**$_2$Ph), 2.98 (2H, s, C**H**$_2$C≡C), (3H, s, C**H**$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7 (2 × C), 138.2 (C), 134.4 (C), 132.4 (CH), 130.0 (2 × CH), 129.4 (CH), 129.0 (CH), 128.9 (2 × CH), 128.4 (CH), 127.8 (CH), 122.7 (C), 122.7 (q, $J_{C\text{-}F}$ = 277.2 Hz, 2 × C), 85.5 (C), 82.56 (C), 61.4 (q, $J_{C\text{-}F}$ = 37.4 Hz, 2 × CH_2), 58.8 (C), 37.6 (CH_2), 23.4 (CH_2), 21.4 (CH_3); ^{19}F NMR (376 MHz, $CDCl_3$) δ –73.7 (t, *J* = 8.2 Hz, 6 × F); HRMS (ESI) Exact mass calculated for $[C_{24}H_{20}F_6NaO_4]^+$ $[M+Na]^+$: 509.1158, found 509.1158.

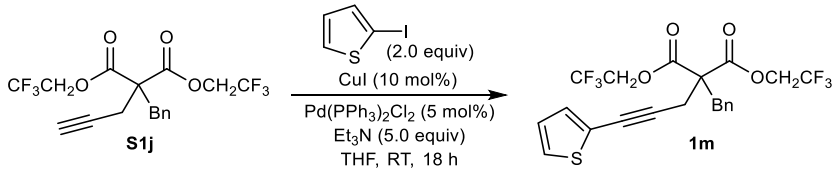
Bis(2,2,2-trifluoroethyl) 2-benzyl-2-(3-(naphthalen-1-yl)prop-2-yn-1-yl)malonate (1l)



A flask was charged with CuI (24.0 mg, 0.13 mmol) and $Pd(PPh_3)_2Cl_2$ (44.2 mg, 0.06 mmol), and was then purged with argon for 20 min. Freshly degassed (purging with argon for 30 min) THF (25 mL), and Et_3N (1.05 mL, 6.30 mmol) were added and the mixture was degassed with a stream of argon for 15 min. Malonate **S1j** (500 mg, 1.26 mmol) and 1-iodonaphthalene (0.37 mL, 2.52 mmol) were added and the mixture was stirred at room temperature for 40 h. The reaction was quenched with saturated aqueous NH_4Cl solution (10 mL), extracted with EtOAc (3 × 20 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (0% to 5% EtOAc/petroleum ether) to give the title compound **1l** (426 mg, 65%) as a yellow oil. R_f = 0.39 (10% EtOAc/petroleum ether); IR 1755 (C=O), 1281, 1148, 1085, 968, 841, 800, 701, 652, 523 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.32-8.29 (1H, m, Ar**H**), 7.88-7.83 (2H, m, Ar**H**), 7.69 (1H, dd, *J* = 7.2, 1.2 Hz, Ar**H**), 7.60 (1H, ddd, *J* = 8.3, 6.9, 1.4 Hz, Ar**H**), 7.53 (1H, ddd, J = 8.2, 6.8, 1.4 Hz, Ar**H**), 7.44 (1H, dd, J = 8.3, 7.1 Hz, Ar**H**), 7.35-7.29 (3H, m, Ar**H**), 7.26-7.23 (2H, m, Ar**H**), 4.63-4.50 (4H, m, 2 × C**H**$_2$CF$_3$), 3.62 (2H, s, C**H**$_2$Ph), 3.16 (2H, s, C**H**$_2$C≡C); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8 (2 × C), 134.4 (C), 133.5 (C), 133.3 (C), 130.9 (CH), 130.0 (2 × CH), 129.0 (CH), 128.9 (2 × CH), 128.5 (CH), 127.9 (CH), 127.0 (CH), 126.6 (CH), 126.1 (CH), 125.3 (CH), 122.7 (q, $J_{C\text{-}F}$ = 277.3 Hz, 2 × C), 120.5 (C), 87.9 (C), 83.4 (C), 61.5 (q, $J_{C\text{-}F}$ = 37.4 Hz, 2 × CH_2), 58.8 (C), 37.8 (CH_2), 23.8

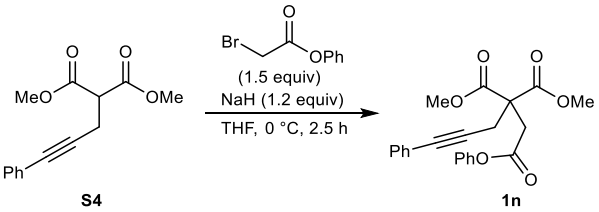
(CH_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ –73.6 (t, J = 8.1 Hz, 6 × F); HRMS (ESI) Exact mass calculated for $[C_{27}H_{20}F_6NO_4]^+$ $[M+NH_4]^+$: 540.1604, found 540.1606.

Bis(2,2,2-trifluoroethyl) 2-benzyl-2-(3-(2-thienyl)prop-2-yn-1-yl)malonate (1m)



A flask was charged with CuI (24.0 mg, 0.13 mmol) and $Pd(PPh_3)_2Cl_2$ (44.2 mg, 0.06 mmol), and was then purged with argon for 20 min. Freshly degassed (purging with argon for 30 min) THF (25 mL), and Et_3N (1.05 mL, 6.30 mmol) were added and the mixture was degassed with a stream of argon for 15 min. Malonate **S1j** (500 mg, 1.26 mmol) and 2-iodothiophene (0.28 mL, 2.52 mmol) were added and the mixture was stirred at room temperature for 18 h. The reaction was quenched with saturated aqueous NH_4Cl solution (10 mL), extracted with EtOAc (3 × 20 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (0% to 1% EtOAc/petroleum ether) to give the title compound **1m** (591 mg, 98%) as an orange oil. R_f = 0.35 (10% EtOAc/petroleum ether); IR 1754 (C=O), 1443, 1279, 1159, 1073, 972, 958, 838, 700, 528 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.28 (3H, m, Ar**H**), 7.26-7.24 (1H, m, Ar**H**), 7.22-7.17 (3H, m, Ar**H**), 6.98 (1H, dd, J = 5.2, 3.6 Hz, Ar**H**), 4.59-4.50 (4H, m, 2 × C**H**$_2$CF$_3$), 3.50 (2H, s, C**H**$_2$Ph), 3.00 (2H, s, C**H**$_2$C≡C); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6 (2 × C), 134.3 (C), 132.3 (CH), 130.0 (2 × CH), 128.9 (2 × CH), 127.9 (CH), 127.2 (CH), 127.1 (CH), 122.7 (C), 122.6 (q, $J_{C\text{-}F}$ = 277.4 Hz, 2 × C), 87.1 (C), 78.4 (C), 61.5 (q, $J_{C\text{-}F}$ = 37.4 Hz, 2 × CH_2), 58.7 (C), 37.7 (CH_2), 23.7 (CH_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ –73.6 (t, J = 8.3 Hz, 6 × F); HRMS (ESI) Exact mass calculated for $[C_{21}H_{16}F_6NaO_4S]^+$ $[M+Na]^+$: 501.0565, found 501.0566.

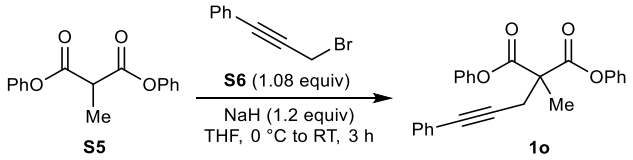
2,2-Dimethyl 1-phenyl 5-phenylpent-4-yne-1,2,2-tricarboxylate (1n)



A solution of malonate **S4**[4] (2.00 g, 8.12 mmol) in THF (10 mL) was added over 10 min to an ice-cooled suspension of NaH (60% dispersion in mineral oil, 389.7 mg, 9.75 mmol) in THF (40 mL). The resulting solution was warmed to room temperature, stirred for 45 min and recooled to 0 °C. A solution of phenyl 2-bromoacetate (2.62 g, 12.2 mmol) in THF (10 mL) was added dropwise and the resulting solution was stirred at 0 °C for 2.5 h. The reaction was quenched with saturated aqueous

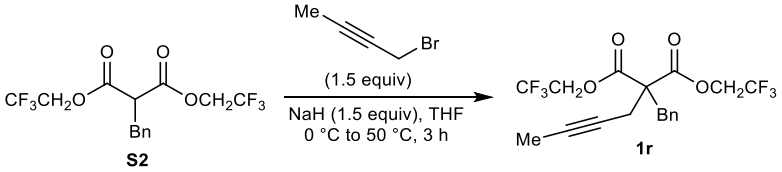
NH_4Cl solution (50 mL). This mixture was extracted with EtOAc (3 × 50 mL), and the combined organic layers were washed with H_2O (50 mL), brine (50 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (0% to 5% EtOAc/petroleum ether) to give the title compound **1n** (2.34 g, 76%) as a colorless oil. R_f = 0.26 (10% EtOAc/petroleum ether); IR 2953, 1750 (C=O), 1727 (C=O), 1491, 1431, 1275, 1192, 1080, 756, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42-7.35 (4H, m, Ar**H**), 7.32-7.21 (4H, m, Ar**H**), 7.12-7.08 (2H, m, Ar**H**), 3.81 (6H, s, 2 × OC**H**$_3$), 3.51 (2H, s, C**H**$_2$C=O), 3.31 (2H, s, C**H**$_2$C≡C); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5 (2 × C), 169.2 (C), 150.5 (C), 138.8 (2 × CH), 129.6 (2 × CH), 128.4 (2 × CH), 128.3 (CH), 126.1 (CH), 123.0 (C), 121.6 (2 × CH), 84.4 (C), 83.9 (C), 55.5 (C), 53.4 (2 × CH_3), 37.5 (CH_2), 24.9 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{22}H_{20}NaO_6]^+$ $[M+Na]^+$: 403.1152, found 403.1155.

Diphenyl 2-methyl-2-(3-phenylprop-2-yn-1-yl)malonate (1o)



A flask was charged with NaH (60% dispersion in mineral oil, 177 mg, 4.43 mmol), purged with argon for 30 min, and then suspended in THF (14 mL) at 0 °C. A solution of diphenyl 2-methylmalonate **S5**[5] (1.00 g, 3.70 mmol) in THF (4 mL) was added to the ice-cooled suspension. The resulting solution was stirred at 0 °C for 45 min. Alkynyl bromide **S6**[6] (80 wt. % in toluene, 978 µL, 4.01 mmol) was added dropwise and the resulting solution was stirred at room temperature for 3 h. The reaction was quenched with H_2O (25 mL), extracted with Et_2O (3 × 25 mL), and the combined organic layers were washed with brine (25 mL), dried ($MgSO_4$), filtered, and concentrated in *vacuo*. The residue was purified by column chromatography (0% to 2% EtOAc/petroleum ether) to give the title compound **1o** (950 mg, 67%) as a white solid. R_f = 0.27 (10% EtOAc/petroleum ether); m.p. 81-82 °C (Et_2O); IR 3060, 1749 (C=O), 1590, 1488, 1193, 1158, 1085, 915, 743, 687 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44-7.38 (6H, m, Ar**H**), 7.33-7.25 (5H, m, Ar**H**), 7.18-7.14 (4H, m, Ar**H**), 3.30 (2H, s, C**H**$_2$C≡C), 1.91 (3H, s, C**H**$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5 (2 × C), 150.7 (2 × C), 131.9 (2 × CH), 129.8 (4 × CH), 128.4 (2 × CH), 128.3 (CH), 126.4 (2 × CH), 123.1 (C), 121.4 (4 × CH), 84.2 (C), 84.1 (C), 54.2 (C), 27.2 (CH_2), 20.3 (CH_3); HRMS (ESI) Exact mass calculated for $[C_{25}H_{20}NaO_4]^+$ $[M+Na]^+$: 407.1254, found 407.1263.

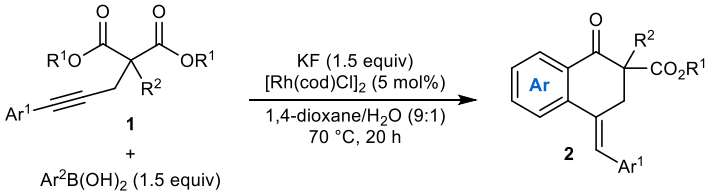
Bis(2,2,2-trifluoroethyl) 2-benzyl-2-(but-2-yn-1-yl)malonate (1r)



A flask was charged with NaH (60% dispersion in mineral oil, 83.6 mg, 2.09 mmol), purged with argon for 30 min, and then suspended in THF (12 mL) at 0 °C. A solution of malonate **S2**[2] (500 mg, 1.40 mmol) in THF (3 mL) was added to the ice-cooled suspension. The resulting solution was stirred at 0 °C for 45 min. 1-Bromo-2-butyne (183 μL, 2.09 mmol) was added dropwise and the resulting solution was stirred at 50 °C for 16 h. The reaction was quenched with H_2O (25 mL), extracted with Et_2O (3 × 25 mL), and the combined organic layers were washed with brine (25 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (0% to 1% EtOAc/petroleum ether) to give the title compound **1r** (444 mg, 77%) as a pale yellow oil. R_f = 0.49 (10% EtOAc/petroleum ether); IR 1756 (C=O), 1497, 1412, 1282, 1158, 1085, 965, 743, 702, 651 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31-7.25 (3H, m, Ar**H**), 7.16-7.14 (2H, m, Ar**H**), 4.58-4.43 (4H, m, 2 × C**H**$_2$CF$_3$), 3.43 (2H, s, C**H**$_2$Ph), 2.70 (2H, q, *J* = 2.4 Hz, C**H**$_2$C≡C), 1.84 (3H, t, *J* = 2.5 Hz, C**H**$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9 (2 × C), 134.6 (C), 129.9 (2 × CH), 128.8 (2 × CH), 127.7 (CH), 122.7 (q, $J_{C\text{-}F}$ = 277.3 Hz, 2 × C), 80.8 (C), 72.5 (C), 61.4 (q, $J_{C\text{-}F}$ = 37.3 Hz, 2 × CH_2), 58.8 (C), 37.4 (CH_2), 22.8 (CH_2), 3.6 (CH_3); ^{19}F NMR (376 MHz, $CDCl_3$) δ –73.7 (t, *J* = 8.1 Hz, 6 × F); HRMS (ESI) Exact mass calculated for $[C_{18}H_{20}F_6NO_4]^+$ $[M+NH_4]^+$: 428.1291, found 428.1289.

3. Rhodium-Catalyzed Arylative Cyclization of Alkynyl Malonates

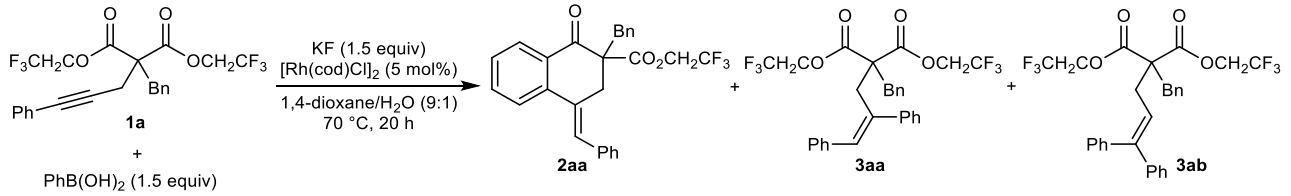
General Procedure A



An oven-dried microwave vial fitted with a stirrer bar was charged with the appropriate substrate **1** (0.30 mmol), the appropriate arylboronic acid (0.45 mmol), KF (26.1 mg, 0.45 mmol) and $[Rh(cod)Cl]_2$ (7.4 mg, 0.015 mmol). The vial was sealed with a septum-lined cap and purged with argon for 30 min. 1,4-Dioxane (2.7 mL) and H_2O (0.3 mL), both of which were freshly degassed separately (purging with argon for 30 min) were added. The mixture was stirred at 70 °C for 20 h. The reaction was cooled to room temperature, H_2O (15 mL) was added, and the mixture was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (20 mL), dried

($MgSO_4$), filtered, and concentrated in *vacuo*. The residue was purified by column chromatography using EtOAc/*n*-pentane to give the arylative cyclization product **2**.

2,2,2-Trifluoroethyl (*E*)-2-benzyl-4-benzylidene-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2aa), bis(2,2,2-trifluoroethyl) (*E*)-2-benzyl-2-(2,3-diphenylallyl)malonate (3aa), and bis(2,2,2-trifluoroethyl) 2-benzyl-2-(3,3-diphenylallyl)malonate (3ab)



General Procedure A was followed using malonate ester **1a** (236 mg, 0.50 mmol) and phenylboronic acid (91.4 mg, 0.75 mmol). Purification by column chromatography (0% to 1% EtOAc/*n*-pentane) gave a 1:1.25 mixture of inseparable *alkyne hydroarylation products* **3aa** and **3ab**, respectively (53.4 mg, 19%) as a yellow oil followed by *arylative cyclization product* **2aa** (152 mg, 67%) as a yellow oil.

Data for **2aa**: R_f = 0.32 (10% EtOAc/petroleum ether); IR 2922, 1742 (C=O), 1685 (C=O), 1454, 1273, 1156, 925, 848, 760, 656 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (1H, dd, *J* = 7.9, 1.4 Hz, Ar**H**), 7.77 (1H, dd, *J* = 8.1, 1.1 Hz, Ar**H**), 7.60 (1H, ddd, *J* = 8.3, 7.2, 1.5 Hz, Ar**H**), 7.45-7.40 (4H, m, Ar**H**), 7.36-7.33 (3H, m, Ar**H** and =C**H**Ph), 7.17-7.09 (5H, m, Ar**H**), 4.48 (1H, dq, *J* = 12.7, 8.4 Hz, C$\mathbf{H}_a$$H_b$$CF_3$), 4.26 (1H, dq, *J* = 12.7, 8.4 Hz, $CH_a$$\mathbf{H}_b$$CF_3$), 3.66 (1H, dd, *J* = 14.6, 1.4 Hz, =CC$\mathbf{H}_a$$H_b$), 3.40 (1H, d, *J* = 13.7 Hz, C$\mathbf{H}_a$$H_b$Ph), 3.25 (1H, d, *J* = 13.7 Hz, $CH_a$$\mathbf{H}_b$Ph), 3.04 (1H, dd, *J* = 14.6, 1.6 Hz, =$CCH_a$$\mathbf{H}_b$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.6 (C), 169.9 (C), 141.1 (C), 136.7 (C), 135.4 (C), 134.3 (CH), 131.0 (C), 130.8 (2 × CH), 130.3 (C), 129.8 (CH), 129.2 (2 × CH), 128.6 (2 × CH), 128.6 (CH), 128.4 (CH), 128.2 (2 × CH), 127.8 (CH), 127.0 (CH), 124.5 (CH), 122.7 (q, J_{C-F} = 277.6 Hz, C), 61.0 (q, J_{C-F} = 36.9 Hz, CH_2), 60.3 (C), 38.8 (CH_2), 34.1 (CH_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ –73.5 (t, *J* = 8.3 Hz, 3 × F); HRMS (ESI) Exact mass calculated for $[C_{27}H_{21}F_3NaO_3]^+$ $[M+Na]^+$: 473.1332, found 473.1335.

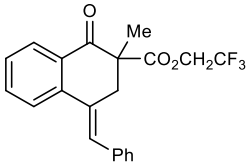
Data for 1:1.25 mixture of **3aa** and **3ab**, respectively: R_f = 0.38 (10% EtOAc/petroleum ether); IR 3029, 1751 (C=O), 1413, 1280, 1155, 1086, 961, 767, 699, 649 cm^{-1}; ^{19}F NMR (376 MHz, $CDCl_3$) δ –73.5-(–73.6) (m, 6 × F for each of **3aa** and **3ab**); HRMS (ESI) Exact mass calculated for $[C_{29}H_{28}F_6NO_4]^+$ $[M+NH_4]^+$: 568.1917, found 568.1921.

Characteristic signals for minor regioisomer **3aa**: ^1H NMR (400 MHz, $CDCl_3$) δ 6.82 (1H, s, =C**H**), 6.76-6.73 (2H, m, Ar**H**), 3.94-3.85 (2H, m, C$\mathbf{H}_2$$CF_3$), 3.80-3.72 (2H, m, C$\mathbf{H}_2$$CF_3$), 3.68 (2H, s, C$\mathbf{H}_2$Ph), 3.05 (2H, s, C$\mathbf{H}_2$C=CH), [9 × Ar**H** concealed within the multiplet 7.43-7.28 and 4 × Ar**H**

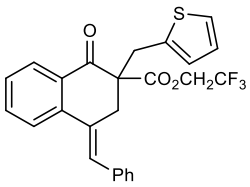
concealed within the multiplet at 7.23-7.01 ppm]; ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5 (2 × C), 142.7 (C), 137.5 (C), 137.2 (C), 135.4 (CH), 135.3 (C), 130.0 (2 × CH), 129.2 (2 × CH), 128.9 (2 × CH), 128.3 (2 × CH), 128.2 (2 × CH), 128.0 (2 × CH), 127.8 (2 × CH), 127.4 (CH), 127.2 (CH), 122.6 (q, $J_{C\text{-}F}$ = 276.3 Hz, 2 × C), 61.1 (q, $J_{C\text{-}F}$ = 37.1 Hz, 2 × CH_2), 59.1 (C), 38.7 (CH_2), 34.0 (CH_2).

Data for major regioisomer **3ab**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93-6.91 (2H, m, Ar**H**), 5.95 (1H, t, *J* = 7.2 Hz, **H**C=C), 4.52-4.34 (4H, m, 2 × C**H**$_2$CF$_3$), 3.33 (2H, s, CC**H**$_2$CCH), 2.84 (2H, d, *J* = 7.2 Hz, CC**H**$_2$CH), [6 × Ar**H** concealed within the multiplet 7.43-7.28 and 7 × Ar**H** concealed within the multiplet at 7.23-7.01 ppm]; ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6 (2 × C), 146.5 (C), 142.6 (C), 139.2 (C), 134.5 (C), 130.0 (2 × CH), 129.9 (2 × CH), 128.6 (2 × CH), 128.5 (2 × CH), 128.4 (2 × CH), 127.8 (4 × CH), 127.5 (CH), 122.7 (q, $J_{C\text{-}F}$ = 276.3 Hz, 2 × C), 121.3 (CH), 61.3 (q, $J_{C\text{-}F}$ = 37.3 Hz, 2 × CH_2), 59.3 (C), 38.2 (CH_2), 32.0 (CH_2).

Note: Assignment of the NMR data for **3aa** and **3ab** was made simpler by the isolation of **3ab** in a purer form from the enantioselective reaction described on page 28.

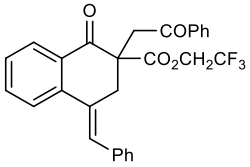


2,2,2-Trifluoroethyl (*E*)-4-benzylidene-2-methyl-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2ba). The title compound was prepared according to General Procedure A, using malonate ester **1b** (119 mg, 0.30 mmol) and phenylboronic acid (54.9 mg, 0.45 mmol), and purified by column chromatography (0% to 1.5% EtOAc/*n*-pentane) to give a pale yellow oil (65.5 mg, 58%). R_f = 0.30 (10% EtOAc/petroleum ether); IR 2956, 1744 (C=O), 1684 (C=O), 1452, 1270, 1156, 920, 850, 758, 659 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (1H, dd, *J* = 7.9, 1.5 Hz, Ar**H**), 7.74 (1H, dd, *J* = 8.1, 1.1 Hz, Ar**H**), 7.62 (1H, ddd, *J* = 8.0, 7.3, 1.5 Hz, Ar**H**), 7.46-7.31 (7H, m, Ar**H** and =C**H**Ph), 4.55 (1H, dq, *J* = 12.6, 8.4 Hz, C**H**$_a$H$_b$CF$_3$), 4.30 (1H, dq, *J* = 12.6, 8.4 Hz, CH$_a$**H**$_b$CF$_3$), 3.59 (1H, dd, *J* = 14.1, 1.5 Hz, =CC**H**$_a$H$_b$), 3.07 (1H, dd, *J* = 14.1, 1.2 Hz, =CCH$_a$**H**$_b$) 1.46 (3H, s, C**H**$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.1 (C), 171.0 (C), 141.5 (C), 136.7 (C), 134.4 (CH), 131.3 (C), 130.2 (CH), 129.6 (C), 129.1 (2 × CH), 128.7 (2 × CH), 128.7 (CH), 128.3 (CH), 127.8 (CH), 124.7 (CH), 122.7 (q, $J_{C\text{-}F}$ = 277.5 Hz, C), 60.9 (q, $J_{C\text{-}F}$ = 36.9 Hz, CH_2), 55.4 (C), 37.4 (CH_2), 19.8 (CH_3); ^{19}F NMR (376 MHz, $CDCl_3$) δ –73.8 (t, *J* = 8.3 Hz, 3 × F); HRMS (ESI) Exact mass calculated for $[C_{21}H_{18}F_3O_3]^+$ $[M+H]^+$: 375.1203, found 375.1202.

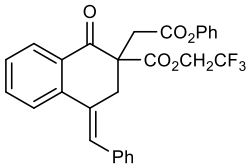


2,2,2-Trifluoroethyl (*E*)-4-benzylidene-1-oxo-2-(2-thienylmethyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2ca). The title compound was prepared according to General Procedure A, using malonate ester **1c** (144 mg, 0.30 mmol) and phenylboronic acid (54.9 mg, 0.45 mmol), and purified by column chromatography (0% to 1.5% EtOAc/*n*-pentane) to give a yellow oil (68.8 mg, 50%). R_f =

0.46 (10% EtOAc/petroleum ether); IR 2925, 1751 (C=O), 1684 (C=O), 1595, 1278, 1155, 1070, 972, 758, 697, 510 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (1H, dd, *J* = 7.9, 1.4 Hz, Ar**H**), 7.75 (1H, dd, *J* = 8.1, 1.1 Hz, Ar**H**), 7.60 (1H, ddd, *J* = 8.2, 7.3, 1.5 Hz, Ar**H**), 7.45-7.29 (7H, m, Ar**H** and =C**H**Ph), 7.05 (1H, dd, *J* = 5.1, 1.3 Hz, Ar**H**), 6.73-6.69 (2H, m, Ar**H**), 4.53 (1H, dq, *J* = 12.7, 8.4 Hz, C**H**$_a$H$_b$CF$_3$), 4.25 (1H, dq, *J* = 12.7, 8.4 Hz, CH$_a$**H**$_b$CF$_3$), 3.65-3.59 (2H, m, =CC**H**$_a$H$_b$ and C**H**$_a$H$_b$CS), 3.43 (1H, d, *J* = 14.7 Hz, CH$_a$**H**$_b$CS), 3.06 (1H, dd, *J* = 14.5, 1.6 Hz, =CCH$_a$**H**$_b$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.4 (C), 169.8 (C), 141.4 (C), 136.9 (C), 136.6 (C), 134.4 (CH), 130.8 (C), 130.2 (CH), 130.1 (C), 129.2 (2 × CH), 128.8 (CH), 128.6 (3 × CH), 128.4 (CH), 127.8 (CH), 126.6 (CH), 125.3 (CH), 124.6 (CH), 122.6 (q, $J_{C\text{-}F}$ = 277.6 Hz, C), 61.1 (q, $J_{C\text{-}F}$ = 37.0 Hz, CH_2), 60.3 (C), 34.1 (CH_2), 33.5 (CH_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ –73.5 (t, *J* = 8.3 Hz, 3 × F); HRMS (ESI) Exact mass calculated for $[C_{25}H_{19}F_3NaO_3S]^+$ $[M+Na]^+$: 479.0899, found 479.0900.



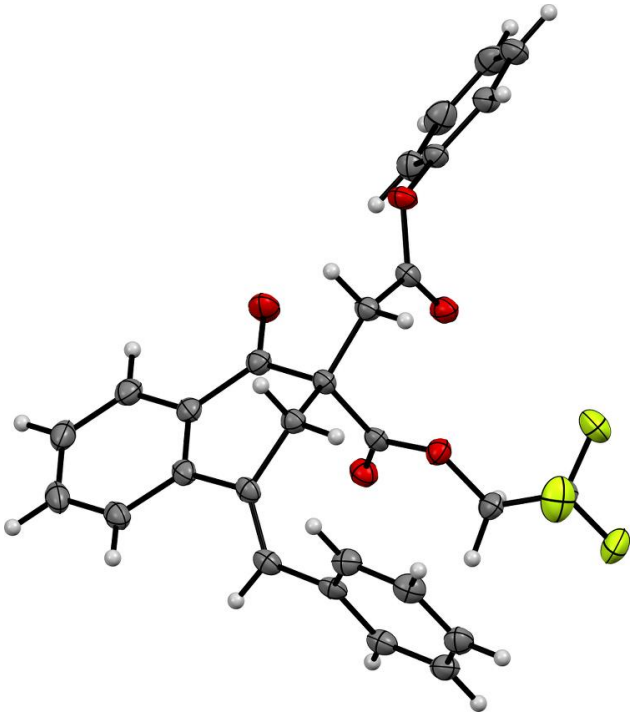
2,2,2-Trifluoroethyl (*E*)-4-benzylidene-1-oxo-2-(2-oxo-2-phenylethyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2da). The title compound was prepared according to a slight modification of General Procedure A (in that the reaction was left for 24 h), using malonate ester **1d** (150 mg, 0.30 mmol) and phenylboronic acid (54.9 mg, 0.45 mmol), and purified by column chromatography (0% to 4% EtOAc/*n*-pentane) to give a pale yellow oil (52.3 mg, 36%). R_f = 0.26 (10% EtOAc/petroleum ether); IR 1751 (C=O), 1682 (C=O), 1598, 1452, 1156, 1079, 909, 727, 694, 657 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (1H, dd, *J* = 7.9, 1.5 Hz, Ar**H**), 7.81-7.79 (2H, m, Ar**H**), 7.73 (1H, dd, *J* = 8.0, 1.1 Hz, Ar**H**), 7.64-7.60 (1H, m, Ar**H**), 7.58-7.54 (1H, m, Ar**H**), 7.47-7.40 (3H, m, Ar**H**), 7.34-7.27 (4H, m, Ar**H** and =C**H**), 7.20-7.17 (2H, m, Ar**H**), 4.55 (1H, dq, *J* = 12.6, 8.4 Hz, C**H**$_a$H$_b$CF$_3$), 4.29 (1H, dq, *J* = 12.6, 8.4 Hz, CH$_a$**H**$_b$CF$_3$), 3.66-3.54 (4H, m, =CC**H**$_2$ and C**H**$_2$C=O); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.8 (C), 193.8 (C), 169.9 (C), 141.8 (C), 136.4 (2 × C), 134.4 (CH), 133.5 (CH), 131.6 (C), 130.4 (CH), 130.3 (C), 129.0 (2 × CH), 128.7 (3 × CH), 128.6 (2 × CH), 128.3 (CH), 128.1 (2 × CH), 127.7 (CH), 124.7 (CH), 122.7 (q, $J_{C\text{-}F}$ = 277.4 Hz, C), 61.1 (q, $J_{C\text{-}F}$ = 36.9 Hz, CH_2), 57.0 (C), 41.8 (CH_2), 35.0 (CH_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ –73.7 (t, *J* = 8.4 Hz, 3 × F); HRMS (ESI) Exact mass calculated for $[C_{28}H_{25}NF_3O_4]^+$ $[M+NH_4]^+$: 496.1730, found 496.1738.

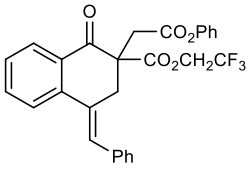


2,2,2-Trifluoroethyl (*E*)-4-benzylidene-1-oxo-2-(2-oxo-2-phenoxyethyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2ea). The title compound was prepared according to General Procedure A, using malonate ester **1e** (155 mg, 0.30 mmol) and phenylboronic acid (54.9 mg, 0.45 mmol), and purified by column chromatography (0% to 3% EtOAc/*n*-pentane) to give a white solid (81.6 mg, 55%). R_f = 0.31 (20% EtOAc/petroleum ether); m.p. 138-140 °C (Et_2O); IR 3062, 1754 (C=O), 1687 (C=O),

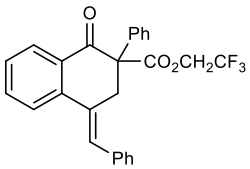
1594, 1278, 1145, 958, 758, 698, 496 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (1H, dd, *J* = 7.9, 1.5 Hz, Ar**H**), 7.75 (1H, dd, *J* = 8.0, 1.1 Hz, Ar**H**), 7.65-7.61 (1H, m, Ar**H**), 7.47-7.40 (9H, m, Ar**H** and =C**H**Ph), 7.22-7.17 (1H, m, Ar**H**), 6.94-6.90 (2H, m, Ar**H**), 4.53 (1H, dq, *J* = 12.6, 8.3 Hz, C**H**$_a$H$_b$CF$_3$), 4.22 (1H, dq, *J* = 12.6, 8.3 Hz, CH$_a$**H**$_b$CF$_3$), 3.71 (1H, dd, *J* = 14.2, 1.0 Hz, =CC**H**$_a$H$_b$), 3.46 (1H, dd, *J* = 14.2, 1.6 Hz, =CCH$_a$**H**$_b$), 3.18-3.09 (2H, m, C**H**$_2$C=O); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.2 (C), 169.3 (C), 168.8 (C), 150.4 (C), 141.6 (C), 136.4 (C), 134.6 (CH), 130.7 (C and CH), 130.0 (C), 129.4 (2 × CH), 129.1 (2 × CH), 128.8 (2 × CH), 128.8 (CH), 128.3 (CH), 127.9 (CH), 126.0 (CH), 124.7 (CH), 122.6 (q, $J_{C\text{-}F}$ = 277.4 Hz, C), 121.5 (2 × CH), 61.2 (q, $J_{C\text{-}F}$ = 36.9 Hz, CH_2), 57.1 (C), 38.1 (CH_2), 35.7 (CH_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ –73.7 (t, *J* = 8.4 Hz, 3 × F); HRMS (ESI) Exact mass calculated for $[C_{28}H_{21}F_3NaO_5]^+$ $[M+Na]^+$: 517.1233, found 517.1233.

Slow evaporation of a solution of **2ea** in CH_2Cl_2/petroleum ether gave crystals that were suitable for X-ray crystallography.



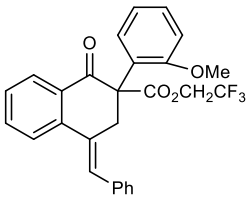


2ea
CCDC 1938497

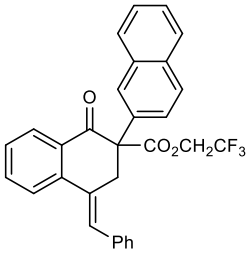


2,2,2-Trifluoroethyl (*E*)-4-benzylidene-1-oxo-2-phenyl-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2fa). The title compound was prepared according to General Procedure A, using malonate ester **1f** (137 mg, 0.30 mmol) and phenylboronic acid (54.9 mg, 0.45 mmol), and purified by column chromatography (0% to 1.5% EtOAc/*n*-pentane) to give a yellow oil (81.0 mg, 62%). R_f = 0.42 (10% EtOAc/petroleum ether); IR 2919, 1749 (C=O), 1682 (C=O), 1596, 1447, 1280, 1158, 972, 732, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (1H, dd, *J* = 7.9, 1.4 Hz, Ar**H**), 7.65 (1H, dd, *J* = 8.0, 1.1 Hz, Ar**H**), 7.58-7.53 (1H, m, Ar**H**), 7.48-7.29 (6H, m, Ar**H** and =C**H**Ph), 7.24-7.15 (4H,

m, Ar**H**), 6.96-6.93 (2H, m, Ar**H**), 4.54 (1H, dq, *J* = 12.7, 8.4 Hz, C**H**$_a$H$_b$CF$_3$), 4.39 (1H, dq, *J* = 12.7, 8.4 Hz, CH$_a$**H**$_b$CF$_3$), 3.92 (1H, dd, *J* = 14.5, 0.8 Hz, =CC**H**$_a$H$_b$), 3.82 (1H, dd, *J* = 14.5, 1.9 Hz, =CCH$_a$**H**$_b$); ^{13}C NMR (101 MHz, CDCl$_3$) δ 193.5 (C), 169.9 (C), 141.1 (C), 136.9 (C), 134.4 (CH), 134.0 (C), 131.1 (C), 130.3 (CH), 130.2 (C), 129.1 (2 × CH), 128.8 (2 × CH), 128.7 (CH), 128.5 (CH), 128.3 (2 × CH), 128.2 (CH), 128.0 (CH), 127.9 (2 × CH), 124.6 (CH), 122.7 (q, J_{C-F} = 277.5 Hz, C), 64.3 (C), 61.2 (q, J_{C-F} = 36.9 Hz, CH$_2$), 35.2 (CH$_2$); ^{19}F NMR (376 MHz, CDCl$_3$) δ –73.7 (t, *J* = 8.3 Hz, 3 × F); HRMS (ESI) Exact mass calculated for [C$_{26}$H$_{20}$F$_3$O$_3$]$^+$ [M+H]$^+$: 437.1359, found 437.1343.

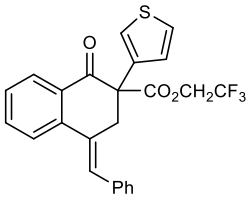


2,2,2-Trifluoroethyl (*E*)-4-benzylidene-2-(2-methoxyphenyl)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2ga). The title compound was prepared according to General Procedure A, using malonate ester **1g** (147 mg, 0.30 mmol) and phenylboronic acid (54.9 mg, 0.45 mmol), and purified by column chromatography (0% to 1.5% EtOAc/*n*-pentane) to give a pale yellow oil (75.1 mg, 54%). R$_f$ = 0.29 (10% EtOAc/petroleum ether); IR 2923, 1751 (C=O), 1682 (C=O), 1596, 1494, 1157, 1029, 973, 774, 698 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.19 (1H, dt, *J* = 7.8, 1.1 Hz, Ar**H**), 7.61-7.57 (2H, m, Ar**H**), 7.49-7.43 (1H, m, Ar**H**), 7.34-7.29 (2H, m, Ar**H**), 7.26-7.22 (1H, m, Ar**H**), 7.17 (1H, ddd, *J* = 8.2, 6.9, 2.2 Hz, Ar**H**), 7.04-6.99 (3H, m, Ar**H** and =C**H**Ph), 6.70-6.63 (2H, m, Ar**H**), 6.58-6.56 (1H, m, Ar**H**), 4.66 (1H, dq, *J* = 12.7, 8.4 Hz, C**H**$_a$H$_b$CF$_3$), 4.36 (1H, dq, *J* = 12.7 8.4 Hz, CH$_a$**H**$_b$CF$_3$), 4.27 (1H, d, *J* = 13.8 Hz, =CC**H**$_a$H$_b$), 3.52 (1H, dd, *J* = 13.8, 1.8 Hz, =CCH$_a$**H**$_b$), 3.15 (3H, s, OC**H**$_3$); ^{13}C NMR (101 MHz, CDCl$_3$) δ 194.9 (C), 170.2 (C), 156.9 (C), 142.5 (C), 137.0 (C), 134.4 (CH), 132.9 (C), 131.0 (C), 130.1 (CH), 129.1 (CH), 129.0 (2 × CH), 128.6 (CH), 128.3 (2 × CH), 128.1 (CH), 128.0 (CH), 127.3 (CH), 124.9 (C), 124.8 (CH), 122.9 (q, J_{C-F} = 277.7 Hz, C), 120.0 (CH), 110.4 (CH), 63.2 (C), 60.8 (q, J_{C-F} = 36.7 Hz, CH$_2$), 54.3 (CH$_3$), 34.8 (CH$_2$); ^{19}F NMR (376 MHz, CDCl$_3$) δ –73.7 (t, *J* = 8.5 Hz, 3 × F); HRMS (ESI) Exact mass calculated for [C$_{27}$H$_{22}$F$_3$O$_4$]$^+$ [M+H]$^+$: 467.1465, found 467.1464.

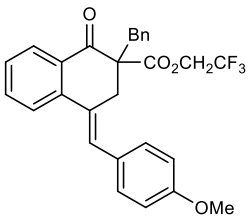


2,2,2-Trifluoroethyl (*E*)-4-benzylidene-1-oxo-3,4-dihydro-[2,2'-binaphthalene]-2(1*H*)-carboxylate (2ha). The title compound was prepared according to a slight modification of General Procedure A (in that 2.0 equivalents of the boronic acid and 10 mol% catalyst loading was used), using malonate ester **1h** (153 mg, 0.30 mmol) and phenylboronic acid (73.2 mg, 0.60 mmol), and purified by column chromatography (0% to 1% EtOAc/*n*-pentane) to give a yellow oil (82.3 mg, 56%). R$_f$ = 0.41 (10% EtOAc/petroleum ether); IR 2924, 1745 (C=O), 1682 (C=O), 1596, 1278, 1157, 1081, 967, 777, 699 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.25 (1H, dt, *J* = 7.8, 1.2 Hz,

Ar**H**), 7.77-7.70 (2H, m, Ar**H**), 7.64-7.59 (2H, m, Ar**H**), 7.50 (1H, ddd, *J* = 8.3, 5.9, 2.6 Hz, Ar**H**), 7.31-7.27 (2H, m, Ar**H**), 7.17 (1H, dd, *J* = 8.2, 7.3 Hz, Ar**H**), 7.09-6.93 (6H, m, Ar**H** and =C**H**Ph), 6.57-6.54 (2H, m, Ar**H**), 4.60-4.43 (2H, m, C$\mathbf{H}_2$CF$_3$), 4.27 (1H, d, *J* = 14.0 Hz, =CC$\mathbf{H}_a$H$_b$), 3.74 (1H, dd, *J* = 14.0, 1.7 Hz, =CCH$_a$$\mathbf{H}_b$); ^{13}C NMR (101 MHz, CDCl$_3$) δ 194.8 (C), 170.9 (C), 141.7 (C), 136.3 (C), 134.6 (CH), 134.2 (C), 132.4 (C), 131.6 (C), 131.0 (C), 130.9 (C), 130.5 (CH), 129.2 (CH), 129.2 (CH), 128.8 (CH), 128.3 (CH), 128.2 (2 × CH), 128.1 (2 × CH), 127.0 (CH), 126.2 (CH), 125.9 (CH), 125.5 (CH), 124.8 (CH), 124.5 (CH), 123.7 (CH), 122.6 (q, $J_{C\text{-}F}$ = 277.8 Hz, C), 65.2 (C), 61.2 (q, $J_{C\text{-}F}$ = 36.9 Hz, CH$_2$), 36.6 (CH$_2$); ^{19}F NMR (376 MHz, CDCl$_3$) δ –73.3 (t, *J* = 8.4 Hz, 3 × F); HRMS (ESI) Exact mass calculated for [C$_{30}$H$_{25}$F$_3$NO$_3$]$^+$ [M+NH$_4$]$^+$: 504.1781, found 504.1783.

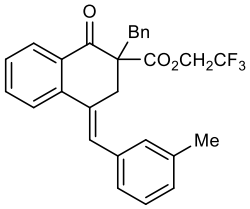


2,2,2-Trifluoroethyl (*E*)-4-benzylidene-1-oxo-2-(3-thienyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2ia). The title compound was prepared according to General Procedure A, using malonate ester **1i** (139 mg, 0.30 mmol) and phenylboronic acid (54.9 mg, 0.45 mmol), and purified by column chromatography (0% to 2% EtOAc/*n*-pentane) to give a yellow oil (75.7 mg, 57%). R$_f$ = 0.25 (10% EtOAc/petroleum ether); IR 2924, 1749 (C=O), 1682 (C=O), 1596, 1445, 1280, 1156, 908, 731, 698 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.15 (1H, ddd, *J* = 7.9, 1.5, 0.5 Hz, Ar**H**), 7.69 (1H, dd, *J* = 8.1, 1.2 Hz, Ar**H**), 7.58 (1H, ddd, *J* = 8.0, 7.2, 1.5 Hz, Ar**H**), 7.48-7.33 (6H, m, Ar**H**), 7.30 (1H, s, =C**H**Ph), 7.16 (1H, dd, *J* = 5.1, 3.0 Hz, Ar**H**), 6.89 (1H, dd, *J* = 3.0, 1.4 Hz, Ar**H**), 6.76 (1H, dd, *J* = 5.1, 1.4 Hz, Ar**H**), 4.57 (1H, dq, *J* = 12.6, 8.3 Hz, C$\mathbf{H}_a$H$_b$CF$_3$), 4.40 (1H, dq, *J* = 12.6, 8.3 Hz, CH$_a$$\mathbf{H}_bCF_3$), 3.89-3.80 (2H, m, =CC$\mathbf{H}_2$); ^{13}C NMR (101 MHz, CDCl$_3$) δ 192.4 (C), 169.5 (C), 141.1 (C), 136.7 (C), 134.5 (CH), 134.4 (C), 131.0 (C), 130.4 (CH), 129.7 (C), 129.2 (2 × CH), 128.9 (2 × CH), 128.7 (CH), 128.6 (CH), 128.0 (CH), 127.6 (CH), 125.4 (CH), 124.7 (CH), 123.9 (CH), 122.7 (q, $J_{C\text{-}F}$ = 277.5 Hz, C), 61.5 (C), 61.3 (q, $J_{C\text{-}F}$ = 36.8 Hz, CH$_2$), 35.6 (CH$_2$); ^{19}F NMR (376 MHz, CDCl$_3$) δ –73.7 (t, *J* = 8.3 Hz, 3 × F); HRMS (ESI) Exact mass calculated for [C$_{24}$H$_{18}$F$_3$O$_3$S]$^+$ [M+H]$^+$: 443.0923, found 443.0923.

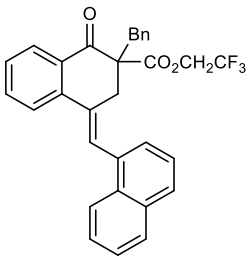


2,2,2-Trifluoroethyl (*E*)-2-benzyl-4-(4-methoxybenzylidene)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2ja). The title compound was prepared according to General Procedure A, using malonate ester **1j** (151 mg, 0.30 mmol) and phenylboronic acid (54.9 mg, 0.45 mmol), and purified by column chromatography (0% to 2% EtOAc/*n*-pentane) to give a yellow oil (91.8 mg, 64%). R$_f$ = 0.31 (10% EtOAc/petroleum ether); IR 2964, 1750 (C=O), 1686 (C=O), 1605, 1510, 1279, 1249, 1157, 1031, 701 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.10 (1H, dd, *J* = 7.9, 1.5 Hz, Ar**H**), 7.73 (1H, dd, *J* = 8.1, 1.1 Hz, Ar**H**), 7.60-7.55 (1H, m, Ar**H**), 7.39 (1H, ddd, *J* = 8.1, 7.2, 1.1

Hz, Ar**H**), 7.34 (1H, s, =C**H**Ar), 7.29-7.26 (3H, m, Ar**H**), 7.14-7.10 (4H, m, Ar**H**), 6.96-6.92 (2H, m, Ar**H**), 4.47 (1H, dq, *J* = 12.6, 8.4 Hz, C**H**$_a$H$_b$CF$_3$), 4.27 (1H, dq, *J* = 12.6, 8.4 Hz, CH$_a$**H**$_b$CF$_3$), 3.86 (3H, s, OC**H**$_3$), 3.63 (1H, dd, *J* = 14.6, 1.4 Hz, =CC**H**$_a$H$_b$), 3.37 (1H, d, *J* = 13.7 Hz, C**H**$_a$H$_b$Ph), 3.24 (1H, d, *J* = 13.7 Hz, CH$_a$**H**$_b$Ph), 3.02 (1H, dd, *J* = 14.7, 1.5 Hz, =CCH$_a$**H**$_b$); ^{13}C NMR (101 MHz, CDCl$_3$) δ 193.8 (C), 170.0 (C), 159.2 (C), 141.4 (C), 135.4 (C), 134.3 (CH), 130.9 (2 × CH), 130.7 (2 × CH), 130.0 (C), 129.6 (CH), 129.4 (C), 129.3 (C), 128.4 (CH), 128.3 (CH), 128.2 (2 × CH), 127.0 (CH), 124.4 (CH), 122.7 (q, $J_{C\text{-}F}$ = 277.5 Hz, C), 114.1 (2 × CH), 61.0 (q, $J_{C\text{-}F}$ = 36.9 Hz, CH$_2$), 60.3 (C), 55.5 (CH$_3$), 38.8 (CH$_2$), 34.1 (CH$_2$); ^{19}F NMR (376 MHz, CDCl$_3$) δ –73.5 (t, *J* = 8.4 Hz, 3 × F); HRMS (ESI) Exact mass calculated for [C$_{28}$H$_{24}$F$_3$O$_4$]$^+$ [M+H]$^+$: 481.1621, found 481.1616.

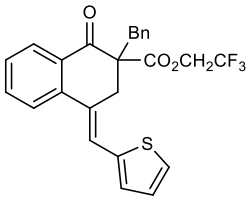


2,2,2-Trifluoroethyl (*E*)-2-benzyl-4-(3-methylbenzylidene)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2ka). The title compound was prepared according to General Procedure A, using malonate ester **1k** (146 mg, 0.30 mmol) and phenylboronic acid (54.9 mg, 0.45 mmol), and purified by column chromatography (0% to 1.5% EtOAc/*n*-pentane) to give a yellow oil (103 mg, 74%). R$_f$ = 0.31 (10% EtOAc/petroleum ether); IR 1752 (C=O), 1695 (C=O), 1602, 1455, 1281, 1153, 1060, 913, 729, 698 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.11 (1H, dd, *J* = 7.9, 1.4 Hz, Ar**H**), 7.76 (1H, dd, *J* = 8.1, 1.1 Hz, Ar**H**), 7.59 (1H, ddd, *J* = 8.3, 7.2, 1.5 Hz, Ar**H**), 7.42 (1H, ddd, *J* = 8.2, 7.3, 1.1 Hz, Ar**H**), 7.37 (1H, s, =C**H**Ar), 7.31-7.27 (1H, m, Ar**H**), 7.13-7.10 (8H, m, Ar**H**), 4.47 (1H, dq, *J* = 12.6, 8.4 Hz, C**H**$_a$H$_b$CF$_3$), 4.31-4.20 (1H, m, CH$_a$**H**$_b$CF$_3$), 3.65 (1H, dd, *J* = 14.7, 1.4 Hz, =CC**H**$_a$H$_b$), 3.38 (1H, d, *J* = 13.8 Hz, C**H**$_a$H$_b$Ph), 3.26 (1H, d, *J* = 13.8 Hz, CH$_a$**H**$_b$Ph), 3.01 (1H, dd, *J* = 14.7, 1.7 Hz, =CCH$_a$**H**$_b$), 2.39 (3H, s, C**H**$_3$); ^{13}C NMR (101 MHz, CDCl$_3$) δ 193.7 (C), 169.9 (C), 141.1 (C), 138.2 (C), 136.6 (C), 135.4 (C), 134.3 (CH), 130.8 (2 × CH), 130.7 (C), 130.3 (C), 130.0 (CH), 129.9 (CH), 128.6 (CH), 128.5 (CH), 128.5 (CH), 128.4 (CH), 128.2 (2 × CH), 127.0 (CH), 126.3 (CH), 124.4 (CH), 122.7 (q, $J_{C\text{-}F}$ = 277.6 Hz, C), 61.0 (q, $J_{C\text{-}F}$ = 36.9 Hz, CH$_2$), 60.2 (C), 38.9 (CH$_2$), 34.2 (CH$_2$), 21.6 (CH$_3$); ^{19}F NMR (376 MHz, CDCl$_3$) δ –73.5 (t, *J* = 8.4 Hz, 3 × F); HRMS (ESI) Exact mass calculated for [C$_{28}$H$_{24}$F$_3$O$_3$]$^+$ [M+H]$^+$: 465.1672, found 465.1669.

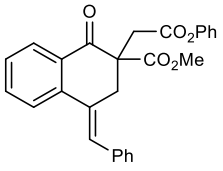


2,2,2-Trifluoroethyl (*E*)-2-benzyl-4-(naphthalen-1-ylmethylene)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2la). The title compound was prepared according to General Procedure A, using malonate ester **1l** (157 mg, 0.30 mmol) and phenylboronic acid (54.9 mg, 0.45 mmol), and purified by column chromatography (0% to 1.5% EtOAc/*n*-pentane) to give a yellow oil (102 mg, 68%). R$_f$ = 0.38 (10% EtOAc/petroleum ether); IR 3061, 1757 (C=O), 1683 (C=O), 1282, 1152, 974, 908, 778, 752, 663 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.14 (1H, dd, *J* = 7.9, 1.4 Hz,

Ar**H**), 7.98 (1H, dd, *J* = 7.8, 1.7 Hz, Ar**H**), 7.94 (1H, dd, *J* = 7.6, 1.8 Hz, Ar**H**), 7.89-7.86 (3H, m, Ar**H**), 7.65 (1H, td, *J* = 7.7, 1.5 Hz, Ar**H**), 7.58-7.45 (4H, m, Ar**H**), 7.38 (1H, d, *J* = 7.0 Hz, Ar**H**), 7.04-7.00 (3H, m, Ar**H** and =C**H**Ph), 6.90-6.86 (2H, m, Ar**H**), 4.45 (1H, dq, *J* = 12.7, 8.4 Hz, C**H**$_a$H$_b$CF$_3$), 4.00 (1H, dq, *J* = 12.7, 8.4 Hz, CH$_a$**H**$_b$CF$_3$), 3.50 (1H, dd, *J* = 14.6, 1.3 Hz, =CC**H**$_a$H$_b$), 3.37 (1H, d, *J* = 13.7 Hz, C**H**$_a$H$_b$Ph), 3.12 (1H, d, *J* = 13.7 Hz, CH$_a$**H**$_b$Ph), 2.96 (1H, dd, *J* = 14.6, 1.5 Hz, =CCH$_a$**H**$_b$); ^{13}C NMR (101 MHz, CDCl$_3$) δ 193.7 (C), 170.0 (C), 140.9 (C), 135.3 (C), 134.4 (CH), 133.8 (C), 133.6 (C), 132.6 (C), 132.2 (C), 130.9 (2 × CH), 130.4 (C), 128.9 (CH), 128.8 (CH), 128.6 (CH), 128.5 (CH), 128.0 (2 × CH), 127.8 (CH), 126.9 (2 × CH), 126.5 (CH), 126.2 (CH), 125.5 (CH), 124.6 (2 × CH), 122.6 (q, $J_{C\text{-}F}$ = 277.5 Hz, C), 60.9 (q, $J_{C\text{-}F}$ = 36.9 Hz, CH$_2$), 60.5 (C), 38.6 (CH$_2$), 34.7 (CH$_2$); ^{19}F NMR (376 MHz, CDCl$_3$) δ –73.7 (t, *J* = 8.3 Hz, 3 × F); HRMS (ESI) Exact mass calculated for [C$_{31}$H$_{24}$F$_3$O$_3$]$^+$ [M+H]$^+$: 501.1672, found 501.1667.

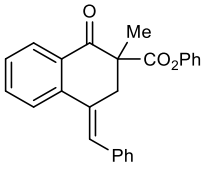


2,2,2-Trifluoroethyl (*E*)-2-benzyl-1-oxo-4-(2-thienylmethylene)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2ma). The title compound was prepared according to General Procedure A, using malonate ester **1m** (144 mg, 0.30 mmol) and phenylboronic acid (54.9 mg, 0.45 mmol), and purified by column chromatography (0% to 1.5% EtOAc/*n*-pentane) to give a yellow oil (91.7 mg, 66%). R$_f$ = 0.29 (10% EtOAc/petroleum ether); IR 2930, 1759 (C=O), 1681 (C=O), 1283, 1148, 974, 923, 857, 750, 690 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.08 (1H, dd, *J* = 7.9, 1.5 Hz, Ar**H**), 7.73 (1H, dd, *J* = 8.1, 1.0 Hz, Ar**H**), 7.57 (1H, ddd, *J* = 8.3, 7.2, 1.5 Hz, Ar**H**), 7.45 (1H, s, =C**H**Ar), 7.41-7.35 (2H, m, Ar**H**), 7.22-7.14 (6H, m, Ar**H**), 7.06 (1H, dd, *J* = 5.1, 3.6 Hz, Ar**H**), 4.45 (1H, dq, *J* = 12.6, 8.3 Hz, C**H**$_a$H$_b$CF$_3$), 4.29 (1H, dq, *J* = 12.6, 8.3 Hz, CH$_a$**H**$_b$CF$_3$), 3.80 (1H, dd, *J* = 14.8, 1.3 Hz, =CC**H**$_a$H$_b$), 3.43-3.36 (2H, m, C**H**$_2$Ph), 3.02 (1H, dd, *J* = 14.8, 1.7 Hz, =CCH$_a$**H**$_b$); ^{13}C NMR (101 MHz, CDCl$_3$) δ 193.5 (C), 169.7 (C), 140.9 (C), 139.8 (C), 135.4 (C), 134.3 (CH), 130.8 (2 × CH), 130.2 (C), 130.0 (CH), 128.7 (C), 128.6 (CH), 128.4 (3 × CH), 127.3 (CH), 127.2 (CH), 126.9 (CH), 123.9 (CH), 122.7 (q, $J_{C\text{-}F}$ = 277.5 Hz, C), 122.1 (CH), 61.0 (q, $J_{C\text{-}F}$ = 36.9 Hz, CH$_2$), 60.0 (C), 39.2 (CH$_2$), 34.3 (CH$_2$); ^{19}F NMR (376 MHz, CDCl$_3$) δ –73.6 (t, *J* = 8.3 Hz, 3 × F); HRMS (ESI) Exact mass calculated for [C$_{25}$H$_{19}$F$_3$NaO$_3$S]$^+$ [M+Na]$^+$: 479.0899, found 479.0903.

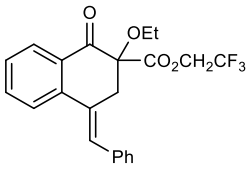


Methyl (*E*)-4-benzylidene-1-oxo-2-(2-oxo-2-phenoxyethyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2na). The title compound was prepared according to General Procedure A, using malonate ester **1n** (114 mg, 0.30 mmol) and phenylboronic acid (54.9 mg, 0.45 mmol), and purified by column chromatography (0% to 7.5% EtOAc/*n*-pentane) to give a white solid (91.2 mg, 71%). R$_f$ = 0.38 (20% EtOAc/petroleum ether); m.p. 136-137 °C (Et$_2$O); IR 2938, 1756 (C=O), 1685 (C=O), 1593, 1280,

1224, 1156, 1064, 973, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (1H, dd, *J* = 8.0, 1.3 Hz, Ar**H**), 7.73 (1H, dd, *J* = 8.0, 1.1 Hz, Ar**H**), 7.60 (1H, ddd, *J* = 8.0, 7.3, 1.5 Hz, Ar**H**), 7.45-7.29 (9H, m, Ar**H** and =C**H**Ph), 7.20-7.16 (1H, m, Ar**H**), 6.97-6.93 (2H, m, Ar**H**), 3.69 (1H, dd, *J* = 14.0, 0.9 Hz, =CC**H**$_a$H$_b$), 3.59 (3H, s, OC**H**$_3$), 3.38 (1H, dd, *J* = 14.0, 1.6 Hz, =CCH$_a$**H**$_b$), 3.18 (1H, d, *J* = 16.6 Hz, C**H**$_a$H$_b$C=O), 3.06 (1H, d, *J* = 16.6 Hz, CH$_a$**H**$_b$C=O); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.1 (C), 171.1 (C), 169.1 (C), 150.6 (C), 141.8 (C), 136.7 (C), 134.3 (CH), 131.7 (C), 130.4 (C), 130.1 (C), 129.4 (2 × CH), 129.1 (2 × CH), 128.7 (2 × CH), 128.6 (CH), 128.3 (CH), 127.8 (CH), 125.9 (CH), 124.7 (CH), 121.6 (2 × CH), 57.2 (C), 52.9 (CH_3), 38.5 (CH_2), 35.9 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{27}H_{23}O_5]^+$ $[M+H]^+$: 427.1540, found 427.1541.

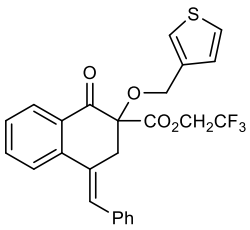


Phenyl (*E*)-4-benzylidene-2-methyl-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2oa). The title compound was prepared according to General Procedure A, using malonate ester **1o** (115 mg, 0.30 mmol) and phenylboronic acid (54.9 mg, 0.45 mmol), and purified by column chromatography (0% to 1.5% EtOAc/*n*-pentane) to give a white solid (60.5 mg, 55%). R_f = 0.32 (10% EtOAc/petroleum ether); m.p. 95-96 °C (Et_2O); IR 2968, 1758 (C=O), 1682 (C=O), 1514, 1412, 1282, 1156, 974, 808, 758 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (1H, dd, *J* = 7.9, 1.4 Hz, Ar**H**), 7.78 (1H, dd, *J* = 8.0, 1.3 Hz, Ar**H**), 7.62 (1H, ddd, *J* = 8.0, 7.2, 1.5 Hz, Ar**H**), 7.47-7.28 (9H, m, Ar**H** and =C**H**Ph), 7.20-7.16 (1H, m, Ar**H**), 6.97-6.94 (2H, m, Ar**H**), 3.77 (1H, dd, *J* = 14.0, 1.5 Hz, =CC**H**$_a$H$_b$), 3.15 (1H, dd, *J* = 14.0, 1.3 Hz, =CCH$_a$**H**$_b$), 1.57 (3H, s, C**H**$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.7 (C), 171.2 (C), 150.7 (C), 141.6 (C), 136.8 (C), 134.3 (CH), 131.8 (C), 130.0 (C), 129.9 (CH), 129.4 (2 × CH), 129.3 (2 × CH), 128.7 (2 × CH), 128.6 (CH), 128.3 (CH), 127.8 (CH), 126.0 (CH), 124.7 (CH), 121.5 (2 × CH), 55.4 (C), 37.7 (CH_2), 20.1 (CH_3); HRMS (ESI) Exact mass calculated for $[C_{25}H_{21}O_3]^+$ $[M+H]^+$: 369.1485, found 369.1484.

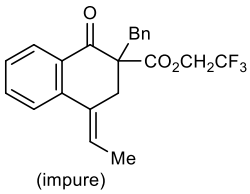


2,2,2-Trifluoroethyl (*E*)-4-benzylidene-2-ethoxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2pa). The title compound was prepared according to a slight modification of General Procedure A (in that 2.0 equivalents of the boronic acid and 10 mol% catalyst loading was used), using malonate ester **1p** (128 mg, 0.30 mmol) and phenylboronic acid (73.2 mg, 0.60 mmol), and purified by column chromatography (0% to 1.5% EtOAc/*n*-pentane) to give a yellow oil (43.5 mg, 36%). R_f = 0.27 (10% EtOAc/petroleum ether); IR 2979, 1768 (C=O), 1688 (C=O), 1596, 1282, 1226, 1162, 1041, 755, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (1H, dd, *J* = 7.8, 1.5 Hz, Ar**H**), 7.79 (1H, d, *J* = 8.0 Hz, Ar**H**), 7.63 (1H, ddd, *J* = 8.1, 7.2, 1.5 Hz, Ar**H**), 7.46-7.30 (7H, m, Ar**H** and =C**H**Ph), 4.62 (1H, dq, *J* = 12.6, 8.3 Hz, C**H**$_a$H$_b$CF$_3$), 4.43 (1H, dq, *J* = 12.6, 8.3 Hz, CH$_a$**H**$_b$CF$_3$), 3.65-3.56

(2H, m, OC**H**$_a$H$_b$ and =CC**H**$_a$H$_b$), 3.50-3.41 (2H, m, OCH$_a$**H**$_b$ and =CCH$_a$**H**$_b$), 1.10 (3H, t, J = 7.0 Hz, CH$_2$C**H**$_3$); ^{13}C NMR (101 MHz, CDCl$_3$) δ 191.5 (C), 169.0 (C), 141.5 (C), 136.6 (C), 134.6 (CH), 130.5 (CH), 130.0 (C), 129.3 (C), 129.2 (2 × CH), 128.7 (2 × CH), 128.6 (CH), 128.4 (CH), 127.9 (CH), 124.5 (CH), 122.7 (q, $J_{C\text{-}F}$ = 277.3 Hz, C), 84.0 (CH$_2$), 63.2 (C), 61.0 (q, $J_{C\text{-}F}$ = 37.0 Hz, CH$_2$), 36.3 (CH$_2$), 15.5 (CH$_3$); ^{19}F NMR (376 MHz, CDCl$_3$) δ –73.7 (t, J = 8.3 Hz, 3 × F); HRMS (ESI) Exact mass calculated for [C$_{22}$H$_{20}$F$_3$O$_4$]$^+$ [M+H]$^+$: 405.1308, found 405.1311.



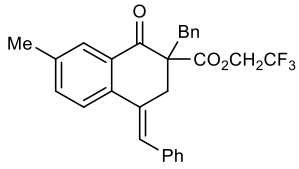
2,2,2-Trifluoroethyl (*E*)-4-benzylidene-1-oxo-2-(3-thienylmethoxy)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2qa). The title compound was prepared according to a slight modification of General Procedure A (in that 2.0 equivalents of the boronic acid and 10 mol% catalyst loading was used), using malonate ester **1q** (148 mg, 0.30 mmol) and phenylboronic acid (73.2 mg, 0.60 mmol), and purified by column chromatography (0% to 2% EtOAc/*n*-pentane) to give a pale yellow oil (47.4 mg, 33%). R$_f$ = 0.28 (10% EtOAc/petroleum ether); IR 2924, 1766 (C=O), 1684 (C=O), 1596, 1282, 1162, 1070, 908, 731, 698 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.04 (1H, dd, J = 7.9, 1.5 Hz, Ar**H**), 7.78 (1H, d, J = 8.1 Hz, Ar**H**), 7.65-7.61 (1H, m, Ar**H**), 7.44-7.30 (7H, m, Ar**H** and =C**H**Ph), 7.15 (1H, dd, J = 5.0, 3.0 Hz, Ar**H**), 7.06 (1H, m, Ar**H**), 6.93 (1H, dd, J = 4.9, 1.2 Hz, Ar**H**), 4.71 (1H, d, J = 11.2 Hz, C**H**$_a$H$_b$Ar), 4.64 (1H, dq, J = 12.5, 8.3 Hz, C**H**$_a$H$_b$CF$_3$), 4.55 (1H, d, J = 11.2 Hz, CH$_a$**H**$_b$Ar), 4.46 (1H, dq, J = 12.5, 8.3 Hz, CH$_a$**H**$_b$CF$_3$) 3.67 (1H, dd, J = 14.7, 0.8 Hz, =CC**H**$_a$H$_b$), 3.51 (1H, dd, J = 14.7, 1.9 Hz, =CCH$_a$**H**$_b$); ^{13}C NMR (101 MHz, CDCl$_3$) δ 191.3 (C), 168.8 (C), 141.5 (C), 138.5 (C), 136.5 (C), 134.7 (CH), 130.7 (CH), 129.9 (C), 129.3 (C), 129.2 (2 × CH), 128.8 (2 × CH), 128.7 (CH), 128.4 (CH), 127.9 (CH), 127.3 (CH), 125.6 (CH), 124.5 (CH), 122.9 (CH), 122.7 (q, $J_{C\text{-}F}$ = 277.3 Hz, C), 83.8 (CH$_2$), 65.0 (C), 61.1 (q, $J_{C\text{-}F}$ = 37.0 Hz, CH$_2$), 36.6 (CH$_2$); ^{19}F NMR (376 MHz, CDCl$_3$) δ –73.5 (t, J = 8.3 Hz, 3 × F); HRMS (ESI) Exact mass calculated for [C$_{25}$H$_{23}$F$_3$NSO$_4$]$^+$ [M+NH$_4$]$^+$: 490.1294, found 490.1295.



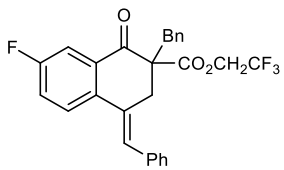
(impure)

2,2,2-Trifluoroethyl (*E*)-2-benzyl-4-ethylidene-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**2ra**). The title compound was prepared according to General Procedure A, using malonate ester **1r** (123 mg, 0.30 mmol) and phenylboronic acid (54.9 mg, 0.45 mmol), and purified by column chromatography (0% to 1.5% EtOAc/n-pentane) to give a brown oil that contained unidentified, inseparable impurities (30.0 mg, <26%). The exact yield was not determined. R$_f$ = 0.39 (10% EtOAc/petroleum ether); IR 2926, 1750 (C=O), 1686 (C=O), 1597, 1410, 1282, 1158, 1084, 914, 700 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.05 (1H, dd, J = 7.9, 1.4 Hz, Ar**H**), 7.57 (1H, d, J = 7.8 Hz, Ar**H**), 7.50 (1H, ddd, J = 8.1, 7.6, 1.4 Hz, Ar**H**), 7.35-7.31 (1H, m, Ar**H**), 7.25-7.19 (5H, m,

Ar**H**), 6.40 (1H, q, *J* = 7.0 Hz, =C**H**CH_3), 4.53-4.43 (1H, m, C**H**$_a$H$_b$$CF_3$), 4.34 (1H, dq, *J* = 12.7, 8.4 Hz, CH_a**H**$_b$$CF_3$), 3.42 (1H, d, *J* = 13.8, C**H**$_a$H$_b$Ph), 3.36-3.28 (2H, m, =CC**H**$_a$H$_b$ and CH_a**H**$_b$Ph), 2.61 (1H, d, *J* = 14.5 Hz, =CCH_a**H**$_b$), 1.77 (3H, d, *J* = 7.0 Hz, =CHC**H**$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.9 (C), 170.3 (C), 141.4 (C), 135.9 (C), 134.1 (CH), 130.8 (2 x CH), 129.8 (C), 129.6 (C), 128.4 (2 × CH), 128.3 (CH), 127.7 (CH), 127.1 (CH), 125.4 (CH), 123.7 (CH), 122.7 (q, J_{C-F} = 277.6 Hz, C), 61.0 (q, J_{C-F} = 36.9 Hz, CH_2), 59.9 (C), 39.2 (CH_2), 32.7 (CH_2), 14.3 (CH_3); ^{19}F NMR (376 MHz, $CDCl_3$) δ –73.5 (t, *J* = 8.4 Hz, 3 × F); HRMS (ESI) Exact mass calculated for $[C_{22}H_{19}F_3NaO_3]^+$ $[M+Na]^+$: 411.1178, found 411.1181.

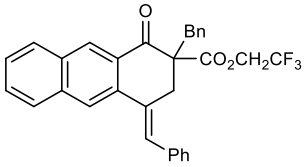


2,2,2-Trifluoroethyl (*E*)-2-benzyl-4-benzylidene-7-methyl-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2ab). The title compound was prepared according to General Procedure A, using malonate ester **1a** (142 mg, 0.30 mmol) and 4-methylphenylboronic acid (61.2 mg, 0.45 mmol), and purified by column chromatography (0% to 1% EtOAc/*n*-pentane) to give a yellow oil (110 mg, 79%). R_f = 0.32 (10% EtOAc/petroleum ether); IR 2924, 1751 (C=O), 1686 (C=O), 1495, 1280, 1158, 963, 732, 698, 513 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (1H, dd, *J* = 2.0, 0.9 Hz, Ar**H**), 7.66 (1H, d, *J* = 8.1 Hz, Ar**H**), 7.42-7.38 (3H, m, Ar**H**), 7.35-7.28 (4H, m, Ar**H** and =C**H**Ph), 7.14-7.07 (5H, m, Ar**H**), 4.46 (1H, dq, *J* = 12.6, 8.4 Hz, C**H**$_a$H$_b$$CF_3$), 4.27 (1H, dq, *J* = 12.6, 8.4 Hz, CH_a**H**$_b$$CF_3$), 3.62 (1H, dd, *J* = 14.6, 1.4 Hz, =CC**H**$_a$H$_b$), 3.37 (1H, d, *J* = 13.7 Hz, C**H**$_a$H$_b$Ph), 3.23 (1H, d, *J* = 13.7 Hz, CH_a**H**$_b$Ph), 3.01 (1H, dd, *J* = 14.6, 1.6 Hz, =CCH_a**H**$_b$), 2.42 (3H, s, C**H**$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.9 (C), 170.0 (C), 138.7 (C), 138.5 (C), 136.8 (C), 135.4 (C), 135.4 (CH), 131.0 (C), 130.8 (2 × CH), 130.0 (C), 129.2 (2 × CH), 128.9 (CH), 128.6 (2 × CH), 128.4 (CH), 128.2 (2 × CH), 127.6 (CH), 127.0 (CH), 124.4 (CH), 122.7 (q, J_{C-F} = 277.5 Hz, C), 61.0 (q, J_{C-F} = 37.0 Hz, CH_2), 60.3 (C), 38.8 (CH_2), 34.1 (CH_2), 21.2 (CH_3); ^{19}F NMR (376 MHz, $CDCl_3$) δ –73.5 (t, *J* = 8.3 Hz, 3 × F); HRMS (ESI) Exact mass calculated for $[C_{28}H_{24}F_3O_3]^+$ $[M+H]^+$: 465.1675, found 465.1672.

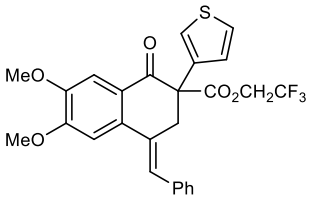


2,2,2-Trifluoroethyl (*E*)-2-benzyl-4-benzylidene-7-fluoro-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2ac). The title compound was prepared according to General Procedure A, using malonate ester **1a** (142 mg, 0.30 mmol) and 4-fluorophenylboronic acid (63.0 mg, 0.45 mmol), and purified by column chromatography (0% to 1% EtOAc/*n*-pentane) to give a yellow solid (95.1 mg, 68%). R_f = 0.31 (10% EtOAc/petroleum ether); m.p. 135-136 °C (Et_2O); IR 3022, 1743 (C=O), 1686 (C=O), 1493, 1270, 1156, 971, 824, 767, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.72 (2H, m, Ar**H**), 7.43-7.39 (2H, m, Ar**H**), 7.35-7.29 (5H, m, Ar**H** and =C**H**Ph), 7.15-7.10 (5H, m, Ar**H**), 4.48

(1H, dq, *J* = 12.6, 8.4 Hz, C**H**$_a$H$_b$CF$_3$), 4.23 (1H, dq, *J* = 12.6, 8.4 Hz, CH$_a$**H**$_b$CF$_3$), 3.63 (1H, dd, *J* = 14.6, 1.2 Hz, =CC**H**$_a$H$_b$), 3.42 (1H, d, *J* = 13.7 Hz, C**H**$_a$H$_b$Ph), 3.20 (1H, d, *J* = 13.7 Hz, CH$_a$**H**$_b$Ph), 2.98 (1H, dd, *J* = 14.6, 1.5 Hz, =CCH$_a$**H**$_b$); ^{13}C NMR (101 MHz, CDCl$_3$) δ 192.6 (C), 169.7 (C), 162.8 (d, $J_{C\text{-}F}$ = 250.2 Hz, C), 137.5 (d, $J_{C\text{-}F}$ = 3.3 Hz, C), 136.5 (C), 135.2 (CH), 132.0 (d, $J_{C\text{-}F}$ = 6.4 Hz, C), 130.8 (2 × CH), 130.1 (C), 129.8 (d, $J_{C\text{-}F}$ = 1.5 Hz, C), 129.2 (2 × CH), 128.7 (2 × CH), 128.3 (2 × CH), 127.9 (CH), 127.1 (CH), 126.9 (d, $J_{C\text{-}F}$ = 7.3 Hz, CH), 122.6 (q, $J_{C\text{-}F}$ = 277.4 Hz, C), 121.9 (d, $J_{C\text{-}F}$ = 22.6 Hz, CH), 114.1 (d, $J_{C\text{-}F}$ = 22.5 Hz, CH), 61.0 (q, $J_{C\text{-}F}$ = 37.1 Hz, CH$_2$), 60.0 (C), 38.8 (CH$_2$), 34.2 (CH$_2$); ^{19}F NMR (376 MHz, CDCl$_3$) δ –73.6 (t, *J* = 8.3 Hz, 3 × F), –112.1 (td, *J* = 8.3, 5.0 Hz, 1 × F); HRMS (ESI) Exact mass calculated for [C$_{27}$H$_{24}$F$_4$NO$_3$]$^+$ [M+NH$_4$]$^+$: 486.1687, found 486.1684.

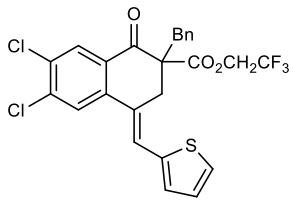


2,2,2-Trifluoroethyl (*E*)-2-benzyl-4-benzylidene-1-oxo-1,2,3,4-tetrahydroanthracene-2-carboxylate (2ad). The title compound was prepared according to General Procedure A, using malonate ester **1a** (142 mg, 0.30 mmol) and 2-naphthylboronic acid (77.4 mg, 0.45 mmol), and purified by column chromatography (0% to 1% EtOAc/*n*-pentane) to give a yellow oil (84.5 mg, 56%). R$_f$ = 0.33 (10% EtOAc/petroleum ether); IR 2924, 1749 (C=O), 1687 (C=O), 1586, 1443, 1281, 1156, 972, 734, 698 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.70 (1H, s, Ar**H**), 8.16 (1H, s, Ar**H**), 7.98 (1H, dd, *J* = 8.3, 1.2 Hz, Ar**H**), 7.89 (1H, dd, *J* = 8.3, 1.1 Hz, Ar**H**), 7.60 (1H, ddd, *J* = 8.2, 6.8, 1.3 Hz, Ar**H**), 7.54-7.50 (2H, m, Ar**H** and =C**H**Ph), 7.45-7.41 (2H, m, Ar**H**), 7.39-7.33 (3H, m, Ar**H**), 7.17-7.11 (5H, m, Ar**H**), 4.49 (1H, dq, *J* = 12.6, 8.4 Hz, C**H**$_a$H$_b$CF$_3$), 4.23 (1H, dq, *J* = 12.6, 8.4 Hz, CH$_a$**H**$_b$CF$_3$), 3.70 (1H, dd, *J* = 14.4, 1.3 Hz, =CC**H**$_a$H$_b$), 3.49 (1H, d, *J* = 13.8 Hz, C**H**$_a$H$_b$Ph), 3.26 (1H, d, *J* = 13.8 Hz, CH$_a$**H**$_b$Ph), 3.09 (1H, dd, *J* = 14.4, 1.6 Hz, =CCH$_a$**H**$_b$); ^{13}C NMR (101 MHz, CDCl$_3$) δ 194.0 (C), 170.1 (C), 136.9 (2 × C), 136.3 (C), 135.5 (C), 132.6 (C), 131.4 (C), 130.9 (2 × CH), 130.3 (CH), 130.0 (CH), 129.3 (2 × CH), 129.3 (CH), 129.2 (CH), 128.7 (2 × CH), 128.5 (C), 128.2 (2 × CH), 128.1 (CH), 127.7 (CH), 127.0 (2 × CH), 123.6 (CH), 122.7 (q, $J_{C\text{-}F}$ = 277.4 Hz, C), 61.0 (q, $J_{C\text{-}F}$ = 37.1 Hz, CH$_2$), 60.7 (C), 38.9 (CH$_2$), 34.2 (CH$_2$); ^{19}F NMR (376 MHz, CDCl$_3$) δ –73.5 (t, *J* = 8.3 Hz, 3 × F); HRMS (ESI) Exact mass calculated for [C$_{31}$H$_{24}$F$_3$O$_3$]$^+$ [M+H]$^+$: 501.1672, found 501.1670.

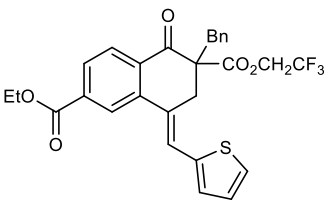


2,2,2-Trifluoroethyl (*E*)-4-benzylidene-6,7-dimethoxy-1-oxo-2-(3-thienyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2ie). The title compound was prepared according to General Procedure A, using malonate ester **1i** (139 mg, 0.30 mmol) and 3,4-dimethoxyphenylboronic acid (81.9 mg, 0.45 mmol), and purified by column chromatography (0% to 10% EtOAc/*n*-pentane) to give a yellow oil (74.6 mg, 50%). R$_f$ = 0.29 (10% EtOAc/petroleum ether); IR 2941, 1737 (C=O),

1668 (C=O), 1594, 1509, 1241, 1209, 1154, 763, 729 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (1H, s, Ar**H**), 7.48-7.43 (2H, m, Ar**H**), 7.38-7.32 (3H, m, Ar**H** and =C**H**Ph), 7.17-7.14 (2H, m, Ar**H**), 7.06 (1H, s, Ar**H**), 6.87 (1H, dd, *J* = 2.9, 1.4 Hz, Ar**H**), 6.77 (1H, dd, *J* = 5.1, 1.4 Hz, Ar**H**), 4.58 (1H, dq, *J* = 12.7, 8.4 Hz, C**H**$_a$H$_b$CF$_3$), 4.39 (1H, dq, *J* = 12.7, 8.4 Hz, CH$_a$**H**$_b$CF$_3$), 3.98 (3H, s, OC**H**$_3$), 3.96 (3H, s, OC**H**$_3$), 3.82-3.81 (2H, m, =CC**H**$_2$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.3 (C), 169.8 (C), 154.5 (C), 150.0 (C), 136.8 (C), 136.2 (C), 134.8 (C), 131.3 (C), 129.1 (2 × CH), 129.0 (CH), 128.9 (2 × CH), 127.9 (CH), 127.6 (CH), 125.2 (CH), 123.7 (CH), 123.2 (C), 122.8 (q, $J_{C\text{-}F}$ = 277.4 Hz, C), 109.2 (CH), 106.1 (CH), 61.3 (q, $J_{C\text{-}F}$ = 36.8 Hz, CH_2), 61.2 (C), 56.3 (2 × CH_3), 36.1 (CH_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ –73.6 (t, *J* = 8.3 Hz, 3 × F); HRMS (ESI) Exact mass calculated for $[C_{26}H_{22}F_3O_5S]^+$ $[M+H]^+$: 503.1135, found 503.1135.

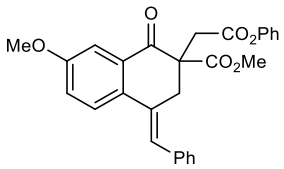


2,2,2-Trifluoroethyl (*E*)-2-benzyl-6,7-dichloro-1-oxo-4-(2-thienylmethylene)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2mf). The title compound was prepared according to General Procedure A, using malonate ester **1m** (144 mg, 0.30 mmol) and 3,4-dichlorophenylboronic acid (96.5 mg, 0.45 mmol), and purified by column chromatography (0% to 1% EtOAc/*n*-pentane) followed by a preparative TLC (8% EtOAc/*n*-pentane) to give a yellow oil (80.4 mg, 51%). R_f = 0.32 (10% EtOAc/petroleum ether); IR 2927, 1749 (C=O), 1691 (C=O), 1579, 1455, 1282, 1160, 907, 732, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (1H, s, Ar**H**), 7.79 (1H, s, Ar**H**), 7.40 (1H, dd, *J* = 5.1, 1.2 Hz, Ar**H**), 7.37 (1H, s, =C**H**Ar), 7.21-7.17 (6H, m, Ar**H**), 7.08 (1H, dd, *J* = 5.1, 3.6 Hz, Ar**H**), 4.43 (1H, dq, *J* = 12.6, 8.4 Hz, C**H**$_a$H$_b$CF$_3$), 4.28 (1H, dq, *J* = 12.6, 8.4 Hz, CH$_a$**H**$_b$CF$_3$), 3.81 (1H, dd, *J* = 15.0, 1.2 Hz, =CC**H**$_a$H$_b$), 3.43 (1H, d, *J* = 13.8 Hz, C**H**$_a$H$_b$Ph), 3.35 (1H, d, *J* = 13.8 Hz, CH$_a$**H**$_b$Ph), 2.94 (1H, dd, *J* = 15.0, 1.7 Hz, =CCH$_a$**H**$_b$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.6 (C), 169.3 (C), 140.4 (C), 139.0 (C), 139.0 (C), 135.0 (C), 132.9 (C), 130.9 (CH), 130.8 (2 × CH), 130.2 (CH), 129.5 (C), 128.5 (2 × CH), 127.7 (CH), 127.5 (CH), 127.4 (CH), 126.4 (C), 125.9 (CH), 123.6 (CH), 122.5 (q, $J_{C\text{-}F}$ = 277.4 Hz, C), 61.1 (q, $J_{C\text{-}F}$ = 37.1 Hz, CH_2), 59.7 (C), 39.2 (CH_2), 34.2 (CH_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ –73.6 (t, *J* = 8.3 Hz, 3 × F); HRMS (ESI) Exact mass calculated for $[C_{25}H_{21}Cl_2F_3NO_3S]^+$ $[M+NH_4]^+$: 542.0566, found 542.0557.

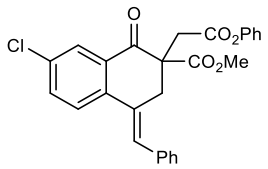


6-Ethyl 2-(2,2,2-trifluoroethyl) (*E*)-2-benzyl-1-oxo-4-(2-thienylmethylene)-1,2,3,4-tetrahydronaphthalene-2,7-dicarboxylate (2mg). The title compound was prepared according to General Procedure A, using malonate ester **1m** (144 mg, 0.30 mmol) and 3-ethoxycarbonylphenylboronic acid (87.3 mg, 0.45 mmol), and purified by column chromatography (0% to 2.5% EtOAc/*n*-pentane) to give a yellow solid (88.9 mg, 56%). R_f = 0.24 (10%

EtOAc/petroleum ether); m.p. 117-118 °C (Et_2O); IR 2938, 1754 (C=O), 1724 (C=O), 1695 (C=O), 1433, 1272, 1253, 1052, 771, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.41 (1H, d, *J* = 1.5 Hz, Ar**H**), 8.11 (1H, dd, *J* = 8.2, 0.5 Hz, Ar**H**), 7.98 (1H, dd, *J* = 8.2, 1.5 Hz, Ar**H**), 7.55 (1H, s, =C**H**Ar), 7.39 (1H, dd, *J* = 5.1, 1.1 Hz, Ar**H**), 7.22-7.17 (6H, m, Ar**H**), 7.08 (1H, dd, *J* = 5.1, 3.6 Hz, Ar**H**), 4.48-4.38 (3H, m, C**H**$_a$H$_b$CF$_3$ and OC**H**$_2$), 4.32-4.22 (1H, m, CH$_a$**H**$_b$CF$_3$), 3.83 (1H, dd, *J* = 15.1, 1.2 Hz, =CC**H**$_a$H$_b$), 3.43-3.36 (2H, m, C**H**$_2$Ph), 3.00 (1H, dd, *J* = 15.1, 1.7 Hz, =CCH$_a$**H**$_b$), 1.43 (3H, t, *J* = 7.1 Hz, CH$_2$C**H**$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.2 (C), 169.5 (C), 165.8 (C), 140.9 (C), 139.4 (C), 135.3 (C), 135.2 (C), 132.8 (C), 130.8 (2 × CH), 130.6 (CH), 128.7 (CH), 128.5 (CH), 128.4 (2 × CH), 127.5 (C), 127.4 (CH), 127.3 (2 × CH), 125.5 (CH), 123.2 (CH), 122.6 (q, J_{C-F} = 277.4 Hz, C), 61.9 (CH_2), 61.1 (q, J_{C-F} = 37.0 Hz, CH_2), 60.0 (C), 39.2 (CH_2), 34.3 (CH_2), 14.4 (CH_3); ^{19}F NMR (376 MHz, $CDCl_3$) δ –73.6 (t, *J* = 8.3 Hz, 3 × F); HRMS (ESI) Exact mass calculated for $[C_{28}H_{27}F_3NO_5S]^+$ $[M+NH_4]^+$: 546.1557, found 546.1546.



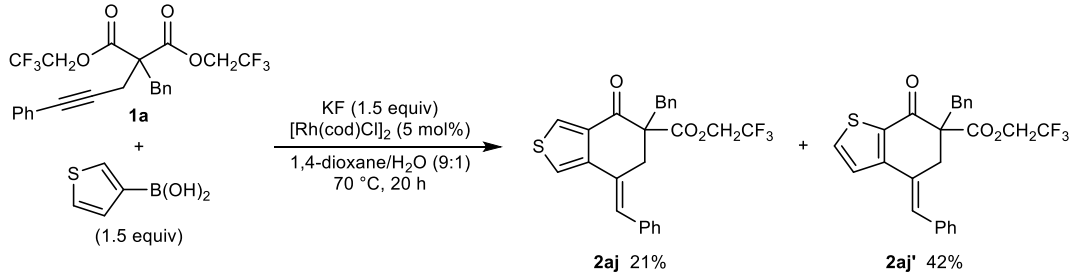
Methyl (*E*)-4-benzylidene-7-methoxy-1-oxo-2-(2-oxo-2-phenoxyethyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2nh). The title compound was prepared according to General Procedure A, using malonate ester **1n** (114 mg, 0.30 mmol) and 4-methoxyphenylboronic acid (68.4 mg, 0.45 mmol), and purified by column chromatography (0% to 5% EtOAc/*n*-pentane) to give a pale yellow oil (69.8 mg, 51%). R_f = 0.28 (15% EtOAc/petroleum ether); IR 2952, 1736 (C=O), 1684 (C=O), 1603, 1492, 1282, 1142, 909, 727, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (1H, d, *J* = 8.7 Hz, Ar**H**), 7.57 (1H, d, *J* = 2.8 Hz, Ar**H**), 7.42-7.28 (7H, m, Ar**H**), 7.24 (1H, s, =C**H**Ph), 7.21-7.16 (2H, m, Ar**H**), 6.99-6.96 (2H, m, Ar**H**), 3.89 (3H, s, OC**H**$_3$) 3.66 (1H, dd, *J* = 13.9, 0.9 Hz, =CC**H**$_a$H$_b$), 3.60 (3H, s, OC**H**$_3$), 3.33 (1H, dd, *J* = 13.9, 1.7 Hz, =CCH$_a$**H**$_b$), 3.18 (1H, d, *J* = 16.6 Hz, C**H**$_a$H$_b$C=O), 3.04 (1H, d, *J* = 16.6 Hz, CH$_a$**H**$_b$C=O); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.1 (C), 171.1 (C), 169.1 (C), 160.0 (C), 150.6 (C), 136.9 (C), 134.9 (C), 131.4 (C), 131.2 (2 × C), 129.4 (2 × CH), 129.1 (2 × CH), 128.7 (2 × CH), 128.4 (CH), 127.5 (CH), 126.3 (CH), 125.9 (CH), 122.9 (CH), 109.7 (2 × CH), 57.1 (C), 55.8 (CH_3), 52.9 (CH_3), 38.7 (CH_2), 36.1 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{28}H_{28}NO_6]^+$ $[M+NH_4]^+$: 474.1911, found 474.1913.



Methyl (*E*)-4-benzylidene-7-chloro-1-oxo-2-(2-oxo-2-phenoxyethyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2ni). The title compound was prepared according to General Procedure A, using malonate ester **1n** (114 mg, 0.30 mmol) and 4-chlorophenylboronic acid (70.4 mg, 0.45 mmol), and purified by column chromatography (0% to 5% EtOAc/*n*-pentane) to give a pale yellow oil (62.4 mg, 45%). R_f = 0.21 (10% EtOAc/petroleum ether); IR 2927, 1737 (C=O), 1692 (C=O), 1591, 1492,

1192, 1144, 907, 730, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (1H, d, *J* = 2.3 Hz, Ar**H**), 7.67 (1H, d, *J* = 8.5 Hz, Ar**H**), 7.54 (1H, dd, *J* = 8.5, 2.4 Hz, Ar**H**), 7.44-7.39 (2H, m, Ar**H**), 7.35-7.29 (6H, m, Ar**H** and =C**H**Ph), 7.21-7.17 (1H, m, Ar**H**), 7.00-6.96 (2H, m, Ar**H**), 3.67 (1H, dd, *J* = 14.0, 0.8 Hz, =CC**H**$_a$H$_b$), 3.58 (3H, s, OC**H**$_3$), 3.33 (1H, dd, *J* = 14.0, 1.8 Hz, =CCH$_a$**H**$_b$), 3.22 (1H, d, *J* = 16.7 Hz, C**H**$_a$H$_b$C=O), 3.03 (1H, d, *J* = 16.7 Hz, CH$_a$**H**$_b$C=O); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.0 (C), 170.8 (C), 169.1 (C), 150.5 (C), 140.1 (C), 136.4 (C), 134.9 (C), 134.2 (C), 131.6 (C), 130.7 (C), 130.6 (CH), 129.5 (2 × CH), 129.1 (2 × CH), 128.8 (2 × CH), 128.0 (CH), 127.9 (CH), 126.4 (CH), 126.0 (CH), 121.6 (2 × CH), 57.0 (C), 53.0 (CH_3), 38.6 (CH_2), 35.9 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{27}H_{25}ClNO_5]^+$ $[M+NH_4]^+$: 478.1416, found 478.1418.

2,2,2-Trifluoroethyl (*E*)-5-benzyl-7-benzylidene-4-oxo-4,5,6,7-tetrahydrobenzo[*c*]thiophene-5-carboxylate (2aj) and 2,2,2-trifluoroethyl (*E*)-6-benzyl-4-benzylidene-7-oxo-4,5,6,7-tetrahydrobenzo[*b*]thiophene-6-carboxylate (2aj')



General Procedure A was followed using malonate ester **1a** (142 mg, 0.30 mmol) and 3-thienylboronic acid (57.6 mg, 0.45 mmol). Purification by column chromatography (0% to 2% EtOAc/*n*-pentane) gave *arylative cyclization product* **2aj** (29.0 mg, 21%) as a brown oil followed by *arylative cyclization product* **2aj'** (57.5 mg, 42%) as a brown oil.

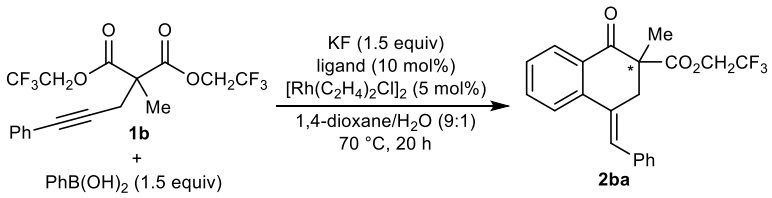
Data for **2aj**: R_f = 0.26 (10% EtOAc/petroleum ether); IR 2927, 1730 (C=O), 1686 (C=O), 1518, 1433, 1283, 1163, 1083, 972, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 (1H, d, *J* = 3.1 Hz, Ar**H**), 7.47 (1H, d, *J* = 3.1 Hz, Ar**H**), 7.40-7.30 (5H, m, Ar**H**), 7.23 (1H, s, =C**H**Ph), 7.12-7.08 (5H, m, Ar**H**), 4.48 (1H, dq, *J* = 12.6, 8.4 Hz, C**H**$_a$H$_b$CF$_3$), 4.32 (1H, dq, *J* = 12.6, 8.4 Hz, CH$_a$**H**$_b$CF$_3$), 3.56 (1H, dd, *J* = 15.0, 1.4 Hz, =CC**H**$_a$H$_b$), 3.33 (1H, d, *J* = 13.7 Hz, C**H**$_a$H$_b$Ph), 3.24 (1H, d, *J* = 13.7 Hz, CH$_a$**H**$_b$Ph), 2.98 (1H, dd, *J* = 15.0, 1.4 Hz, =CCH$_a$**H**$_b$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.0 (C), 169.8 (C), 141.8 (C), 136.4 (C), 135.3 (C), 135.3 (C), 132.9 (CH), 130.9 (2 × CH), 129.2 (2 x CH), 128.6 (2 x CH), 128.2 (2 x CH), 127.9 (CH), 127.7 (C), 127.6 (CH), 127.0 (CH), 122.7 (q, J_{C-F} = 277.6 Hz, C), 119.1 (CH), 61.3 (C), 61.1 (q, J_{C-F} = 37.0 Hz, CH_2), 38.7 (CH_2), 34.3 (CH_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ –73.5 (t, *J* = 8.3 Hz, 3 × F); HRMS (ESI) Exact mass calculated for $[C_{25}H_{20}F_3O_3S]^+$ $[M+H]^+$: 457.1080, found 457.1087.

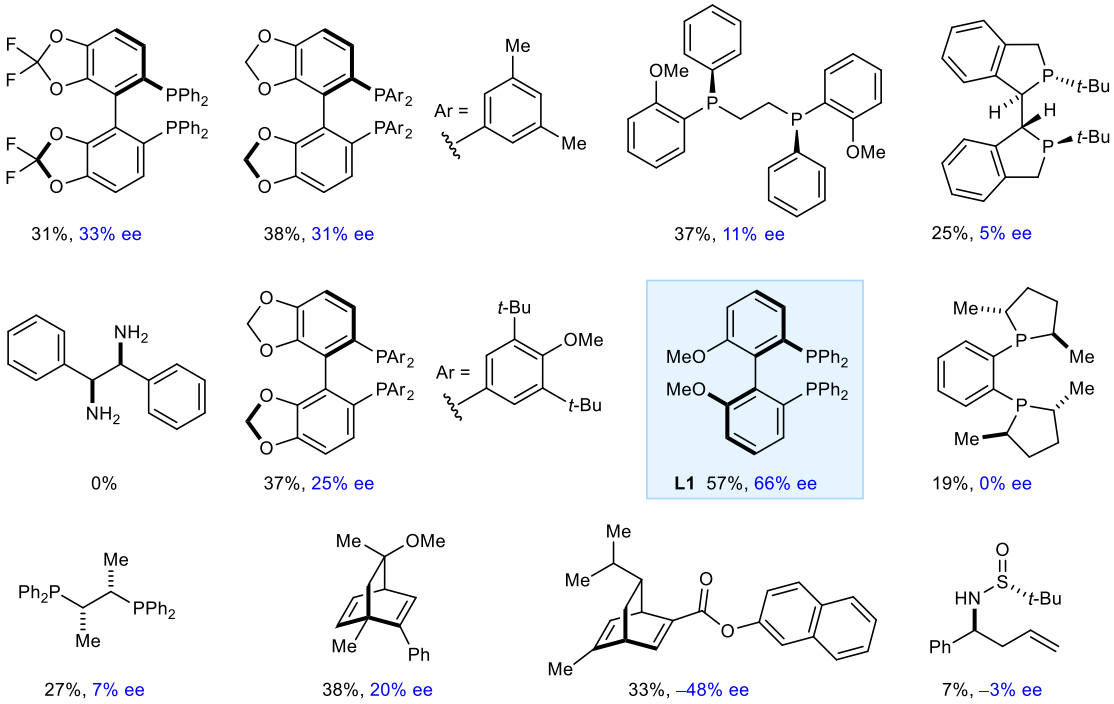
Data for **2aj'**: R_f = 0.24 (10% EtOAc/petroleum ether); IR 2927, 1749 (C=O), 1664 (C=O), 1494, 1430, 1283, 1162, 972, 757, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (1H, d, *J* = 5.2 Hz, Ar**H**), 7.41-7.30 (6H, m, Ar**H**), 7.24 (1H, s, =C**H**Ph), 7.15-7.06 (5H, m, Ar**H**), 4.49 (1H, dq, *J* = 12.7, 8.4 Hz, C**H**$_a$H$_b$CF$_3$), 4.37 (1H, dq, *J* = 12.7, 8.4 Hz, CH$_a$**H**$_b$CF$_3$), 3.63 (1H, dd, *J* = 15.2, 1.4 Hz, =CC**H**$_a$H$_b$), 3.35 (1H, d, *J* = 13.7 Hz, C**H**$_a$H$_b$Ph), 3.28 (1H, d, *J* = 13.7 Hz, CH$_a$**H**$_b$Ph), 3.04 (1H, dd, *J* = 15.2, 1.4 Hz, =CCH$_a$**H**$_b$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.1 (C), 169.7 (C), 150.1 (C), 136.1 (C), 135.5 (CH), 135.3 (C), 134.6 (C), 130.8 (2 × CH), 130.7 (CH), 129.2 (2 x CH), 128.7 (2 x CH), 128.6 (C), 128.2 (2 x CH), 128.0 (CH), 127.1 (CH), 124.4 (CH), 122.7 (q, J_{C-F} = 277.5 Hz, C), 61.1 (q, J_{C-F} = 36.9 Hz, CH_2), 60.7 (C), 39.4 (CH_2), 34.7 (CH_2); ^{19}F NMR (376 MHz, $CDCl_3$) δ –73.5 (t, *J* = 8.4 Hz, 3 × F); HRMS (ESI) Exact mass calculated for $[C_{25}H_{20}F_3O_3S]^+$ $[M+H]^+$: 457.1080, found 457.1085.

4. Enantioselective Cyclizations

Evaluation of Chiral Ligands

The reaction of substrate **1b** with $PhB(OH)_2$ to give **2ba** was conducted in the presence of $[Rh(C_2H_4)_2Cl]_2$ (5 mol%, 10 mol% Rh) and various chiral ligands (10 mol%) as shown in the Table below:

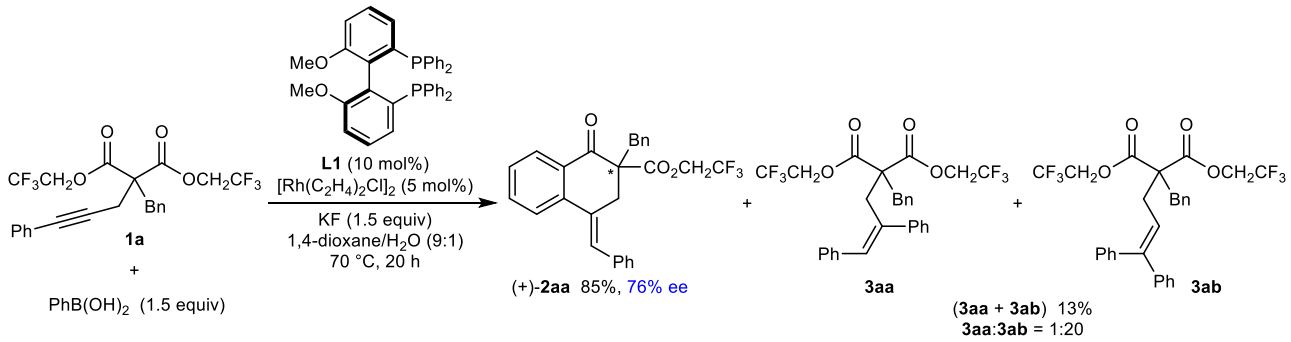




Reactions were conducted using 0.05 mmol of **1b**. Yields determined by ^{1}H NMR spectroscopy using 1,4-dimethoxybenzene as an internal standard.

From these studies, (*R*)-MeO-BIPHEP (**L1**) emerged as a promising ligand, which was then employed in the reaction of substrate **1a** with $PhB(OH)_2$ as described below:

2,2,2-Trifluoroethyl (*E*)-2-benzyl-4-benzylidene-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate [(+)-2aa]



An oven-dried microwave vial was fitted with a stirrer bar and charged with $[Rh(C_2H_4)_2Cl]_2$ (5.8 mg, 0.015 mmol) and (*R*)-MeO-BIPHEP (**L1**, 17.5 mg, 0.03 mmol). The vial was sealed with a septum-lined cap and purged with argon for 30 min. 1,4-Dioxane (1.8 mL) and H_2O (0.2 mL), both of which were freshly degassed separately (purging with argon for 30 min) were added. The mixture was stirred at room temperature for 30 min. Meanwhile, a separate oven-dried microwave vial was fitted with a stirrer bar and charged with malonic ester **1a** (142 mg, 0.30 mmol), phenylboronic acid (54.9 mg, 0.45 mmol), and KF (26.1 mg, 0.45 mmol). The vial was sealed with a septum-lined cap and purged with argon for 30 min. Degassed 1,4-dioxane (0.9 mL), degassed H_2O (0.1 mL) and the solution of catalyst (see above) were added. The mixture was stirred at 70 °C for 20 h. The reaction was cooled to room temperature, H_2O (15 mL) was added, and the mixture was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine (20 mL), dried ($MgSO_4$), filtered, and concentrated in *vacuo*. The residue was purified by column chromatography (0% to 1% EtOAc/*n*-pentane) to give a 1:20 inseparable mixture of alkyne hydroarylation products **3aa** and **3ab**, respectively (20.9 mg, 13%) as a yellow oil followed by arylative cyclization product **2aa** (115 mg, 85%) as a yellow oil and.

Data for (+)-**2aa**: See above (page 15) and $[\alpha]_D^{25}$ +36.0 (*c* 1.00, $CHCl_3$); Enantiomeric excess was determined by HPLC using a Chiralpak AD-H column (95:5 *iso*-hexane:*i*-PrOH, 1.0 mL/min, 254 nm, 25 °C) t_r (major) = 8.9 min, t_r (minor) = 16.3 min, 76% ee.

Data for 1:20 mixture of **3aa** and **3ab**, respectively. R_f = 0.38 (10% EtOAc/petroleum ether); IR 3030, 1752 (C=O), 1411, 1281, 1159, 1084, 975, 759, 699, 650 cm^{-1}; ^{19}F NMR (376 MHz, $CDCl_3$) δ –73.6 (t, *J* = 8.2 Hz, 6 × F); HRMS (ESI) Exact mass calculated for $[C_{29}H_{28}F_6NO_4]^+$ $[M+NH_4]^+$: 568.1917, found 568.1919.

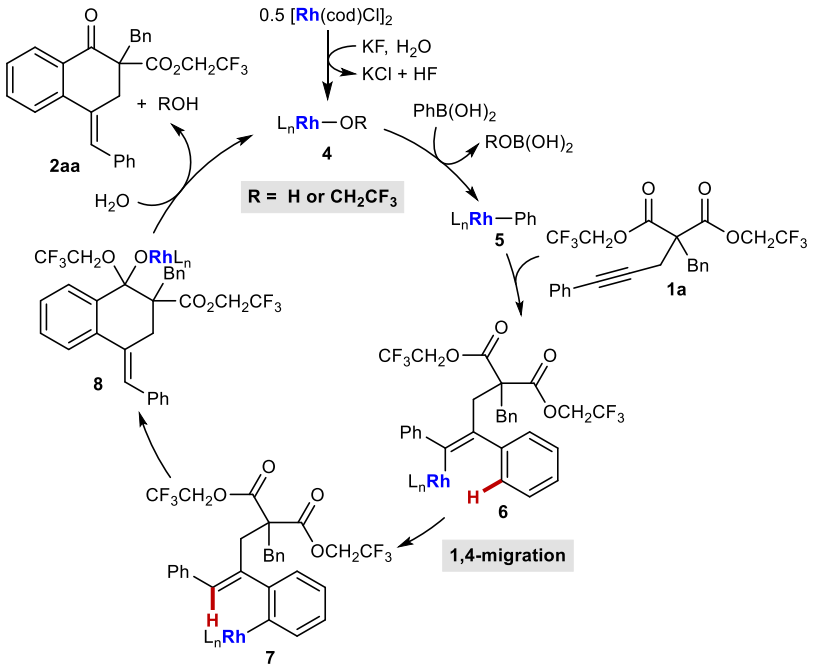
Data for major regioisomer: ^1H NMR (400 MHz, $CDCl_3$) 7.41-7.28 (6H, m, Ar**H**), 7.24-7.13 (7H, m, Ar**H**), 6.94-6.91 (2H, m, Ar**H**), 5.95 (1H, t, *J* = 7.2 Hz, =C**H**CH_2), 4.56-4.34 (4H, m, 2 × C**H**$_2CF_3$), 3.33 (2H, s, C**H**$_2$Ph), 2.84 (2H, d, *J* = 7.2 Hz, =CHC**H**$_2$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6 (2 ×

C), 146.5 (C), 142.6 (C), 139.2 (C), 134.5 (C), 130.0 (2 × CH), 129.9 (2 × CH), 128.6 (2 × CH), 128.5 (2 × CH), 128.4 (2 × CH), 127.8 (4 × CH), 127.5 (CH), 122.7 (q, $J_{C\text{-}F}$ = 277.4 Hz, 2 × C), 121.3 (CH), 61.2 (q, $J_{C\text{-}F}$ = 37.3 Hz, 2 × CH_2), 59.3 (C), 38.2 (CH_2), 32.0 (CH_2).

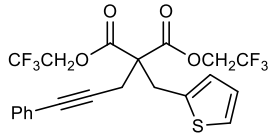
Characteristic signals for minor regioisomer: ^{1}H NMR (400 MHz, $CDCl_3$) 6.82 (1H, s, =C**H**Ph), 6.76-6.73 (2H, m, Ar**H**), 3.93-3.84 (2H, m, C**H**$_2$$CF_3$), 3.80-3.73 (2H, m, C**H**$_2$$CF_3$), 3.69 (2H, s, C**H**$_2$Ph), 3.05 (2H, s, C**H**$_2$C=CH).

5. Possible Catalytic Cycle

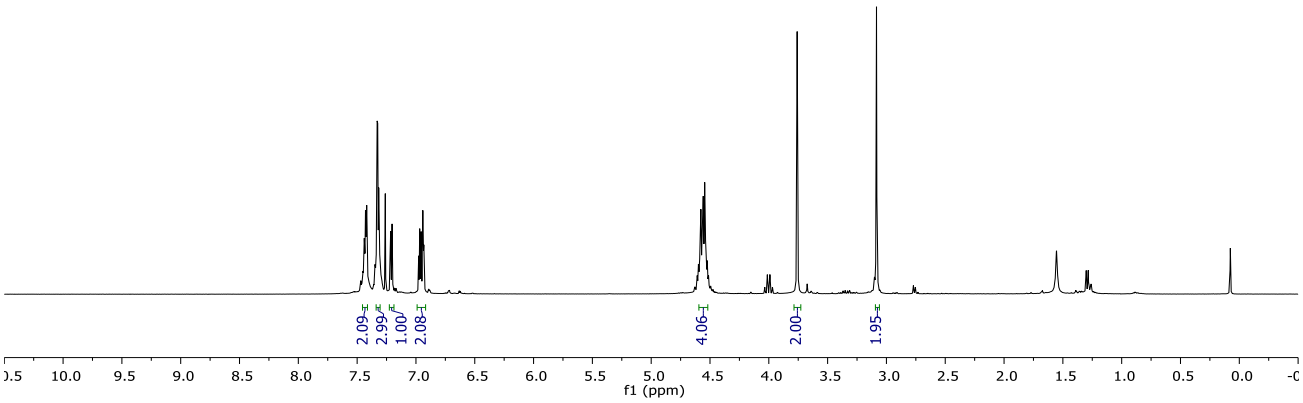
A possible catalytic cycle for these reactions is depicted below, using substrate **1a** and $PhB(OH)_2$ as example reaction partners. Heating a mixture of $[Rh(cod)Cl]_2$, KF, and H_2O may generate rhodium hydroxide **4** (R = H), which can undergo transmetalation with $PhB(OH)_2$ to give arylrhodium species **5**. Phenylrhodation of the alkyne of **1a** gives alkenylrhodium species **6**, which then undergoes alkenyl-to-aryl 1,4-Rh(I) migration to give arylrhodium species **7**. Cyclization of **7** by 1,2-addition onto one of the esters produces rhodium alkoxide **8**, which collapses to release the product **2aa** and regenerate the active rhodium complex **4** (which could have a either a trifluoroethoxide or hydroxide counterion).

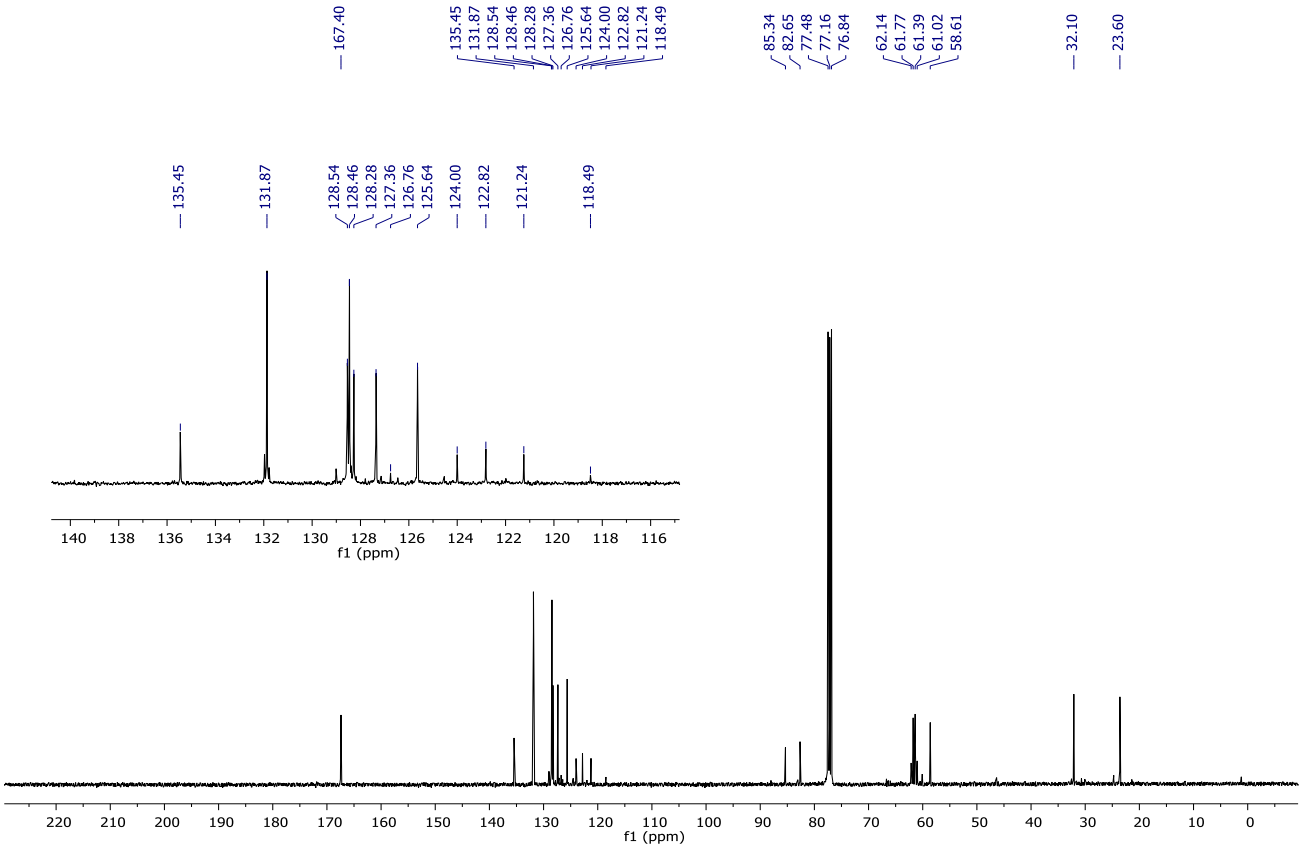


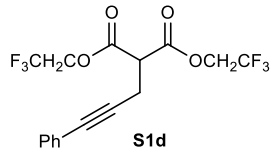
6. NMR Spectra



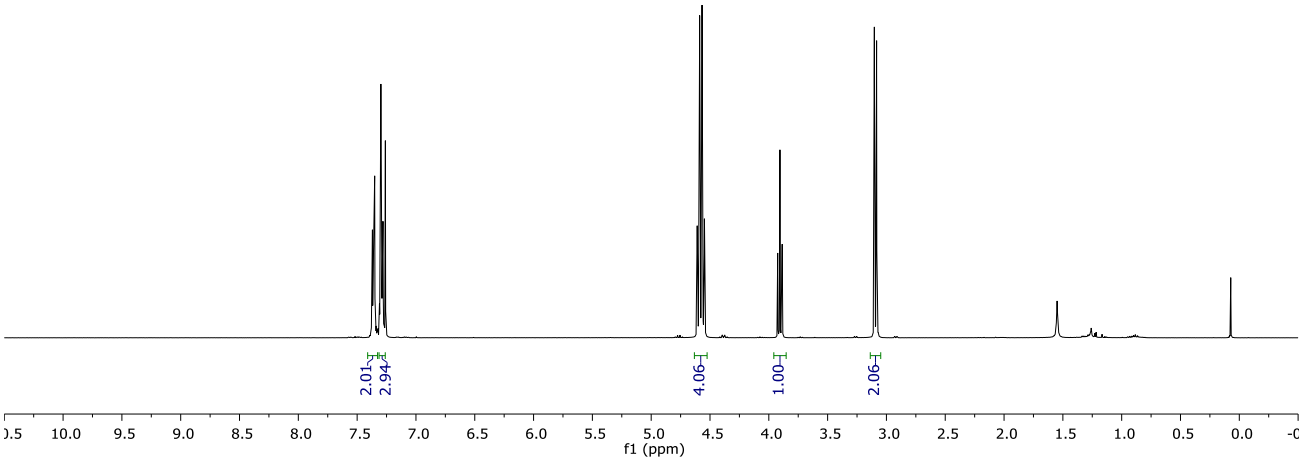
1c

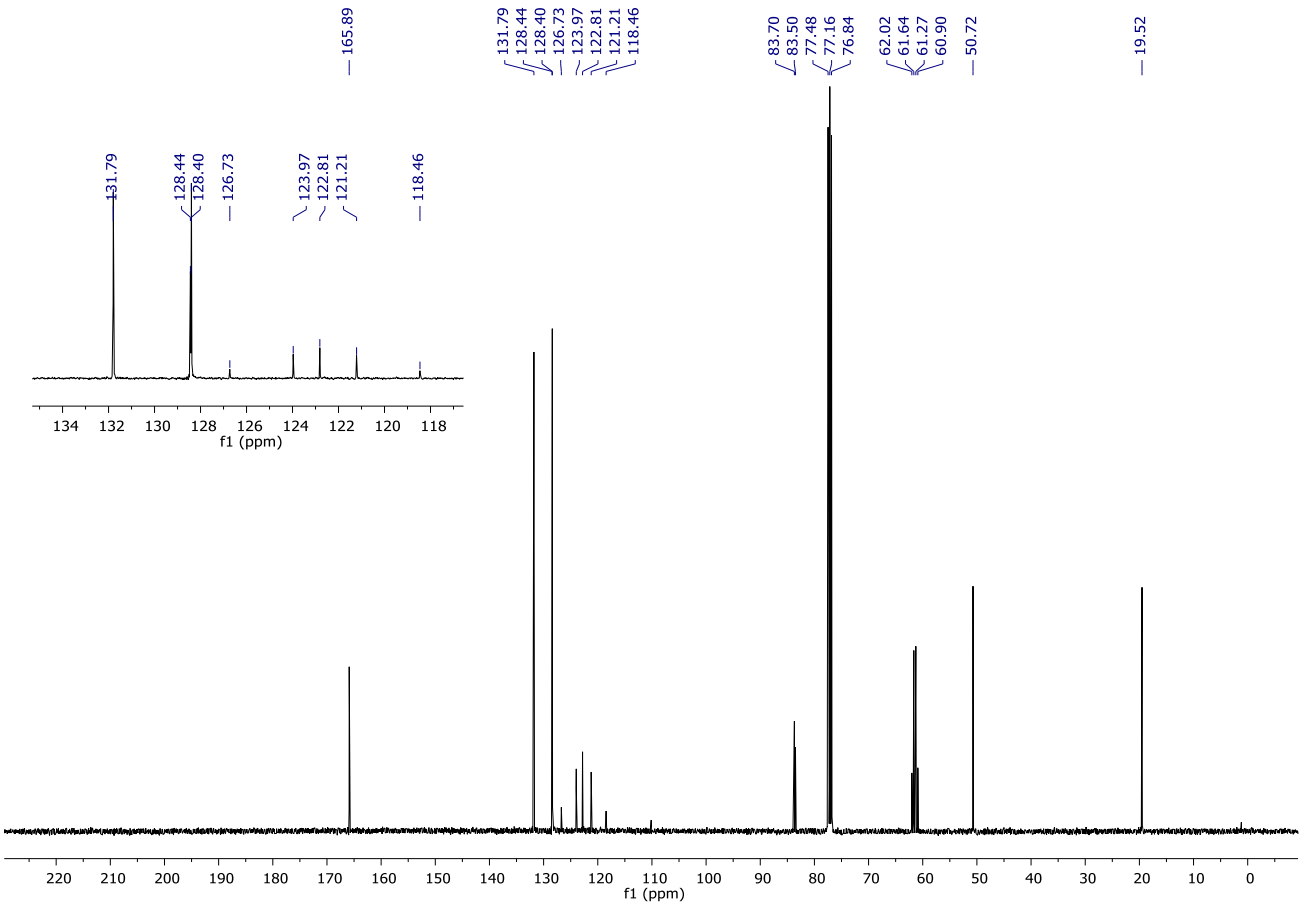


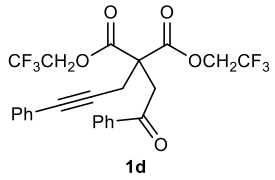



O
O
F3CH2CO
OCH2CF3
Ph

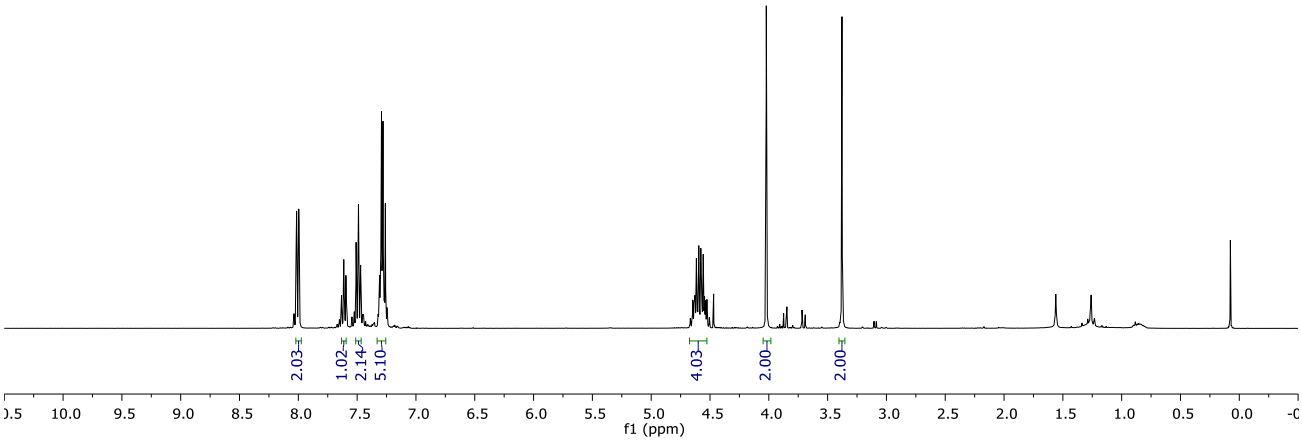
S1d


2.01
2.94
4.06
1.00
2.06
f1 (ppm)


165.89
131.79
128.44
128.40
126.73
123.97
122.81
121.21
118.46
83.70
83.50
77.48
77.16
76.84
62.02
61.64
61.27
60.90
50.72
19.52
f1 (ppm)


O
O
CF3CH2O
OCH2CF3
Ph
Ph
O

1d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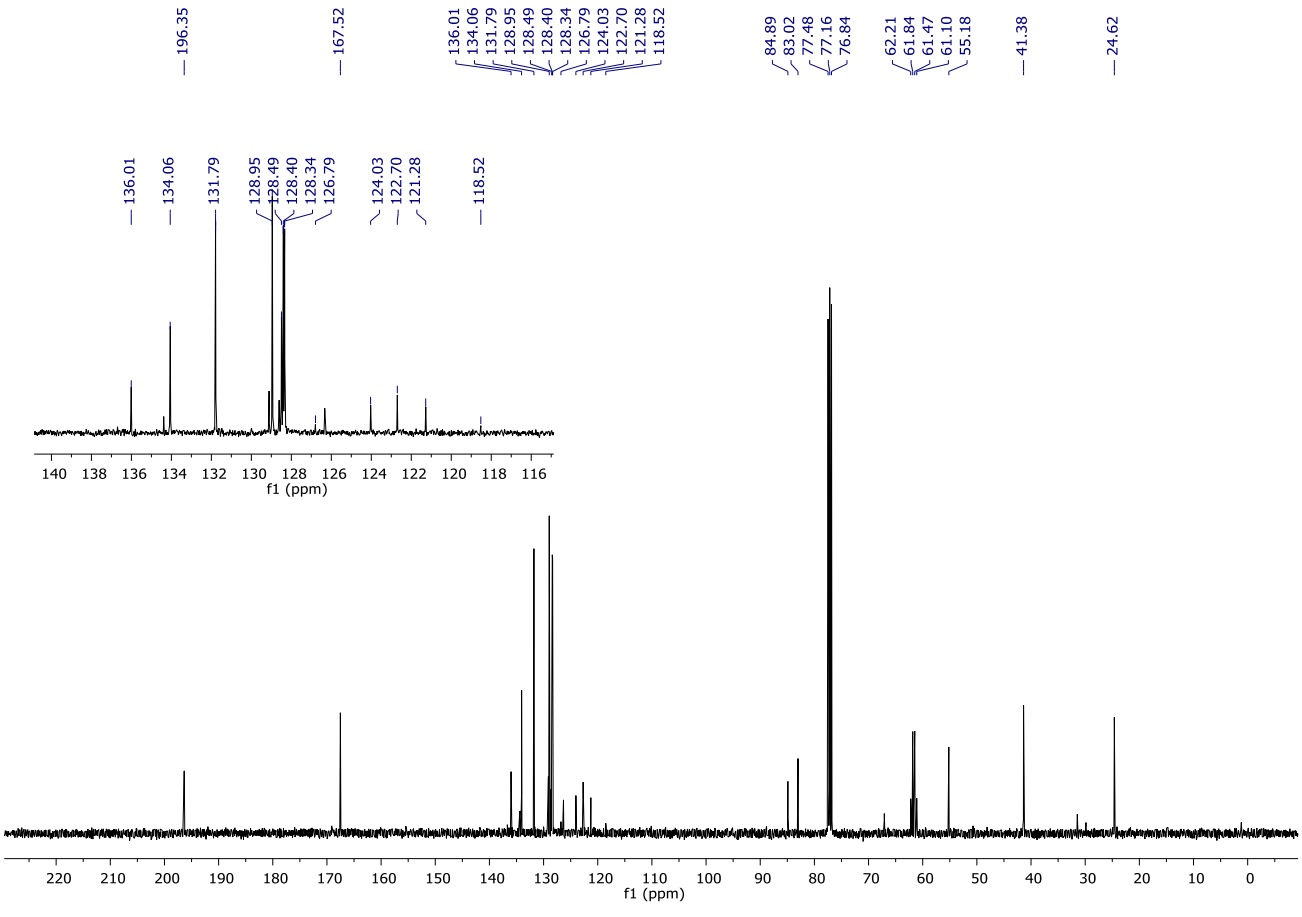
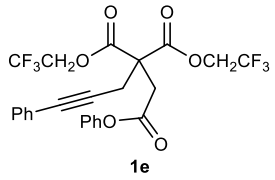
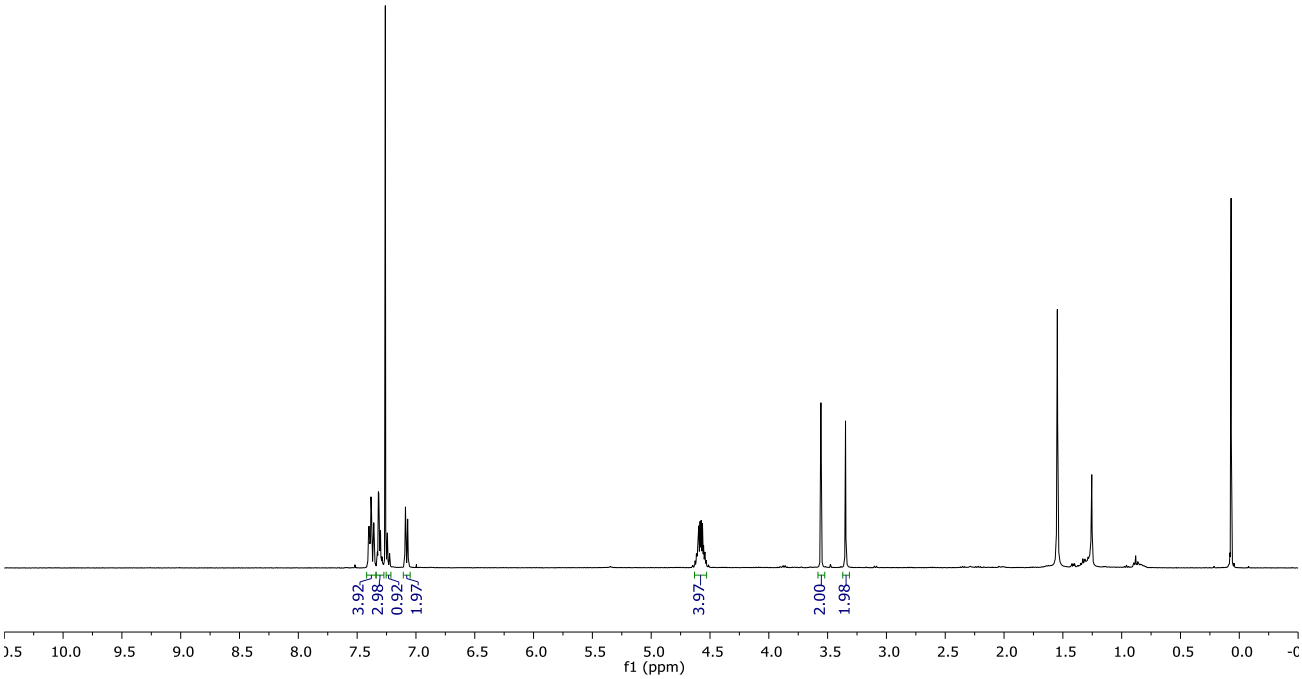
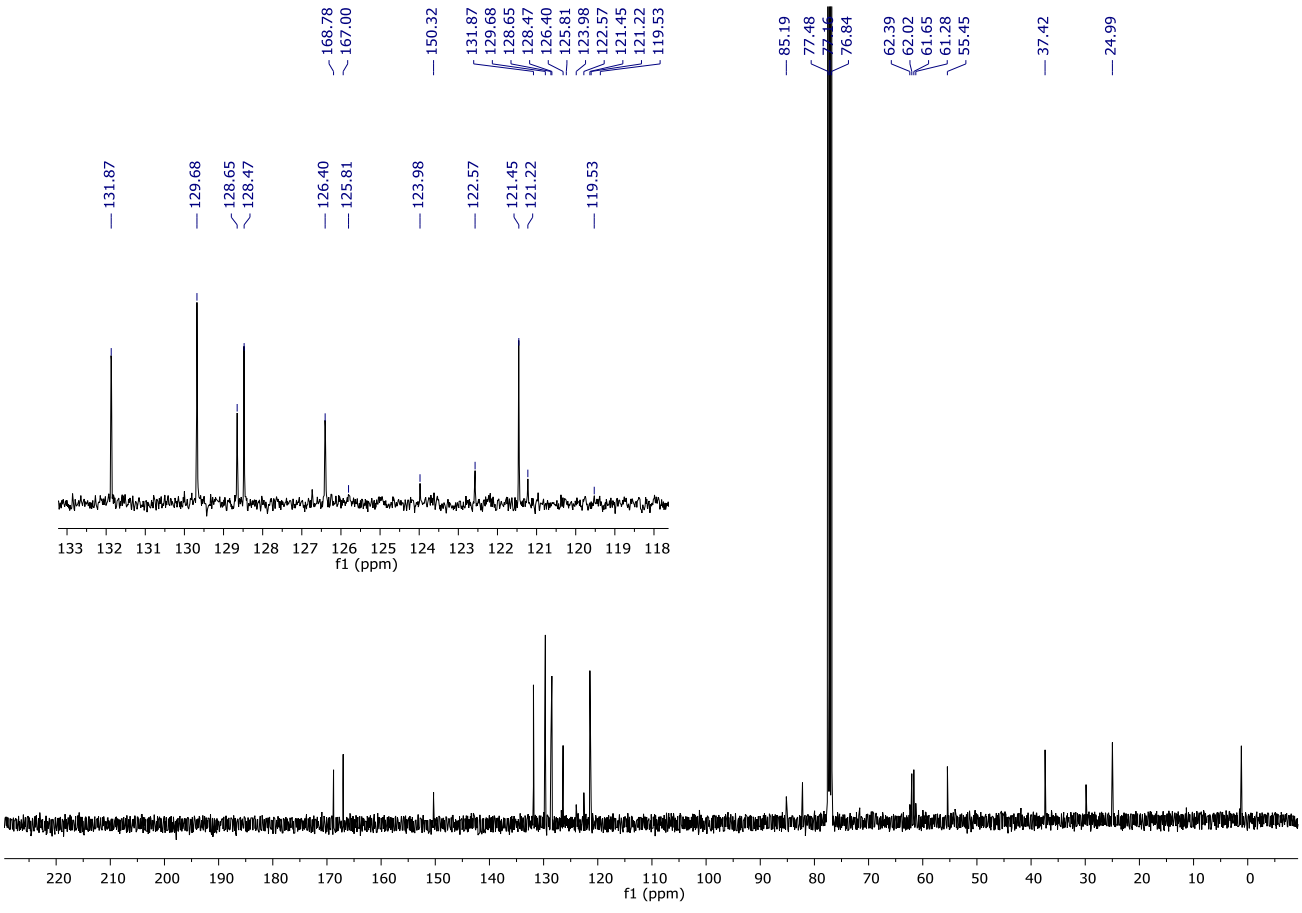
1.02
2.14
5.10
4.03
2.00
2.00
f1 (ppm)

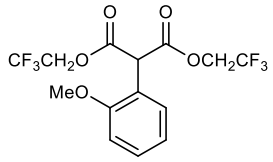

196.35
167.52
136.01
134.06
131.79
128.95
128.49
128.40
128.34
126.79
124.03
122.70
121.28
118.52
84.89
83.02
77.48
77.16
76.84
62.21
61.84
61.47
61.10
55.18
41.38
24.62
f1 (ppm)


O
O
CF3CH2O
OCH2CF3
Ph
PhO
O

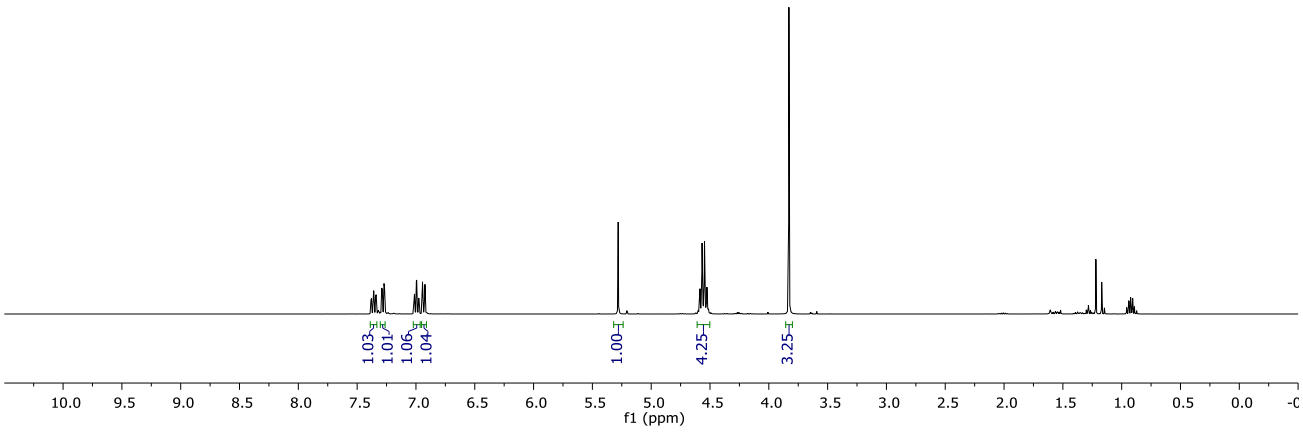
1e

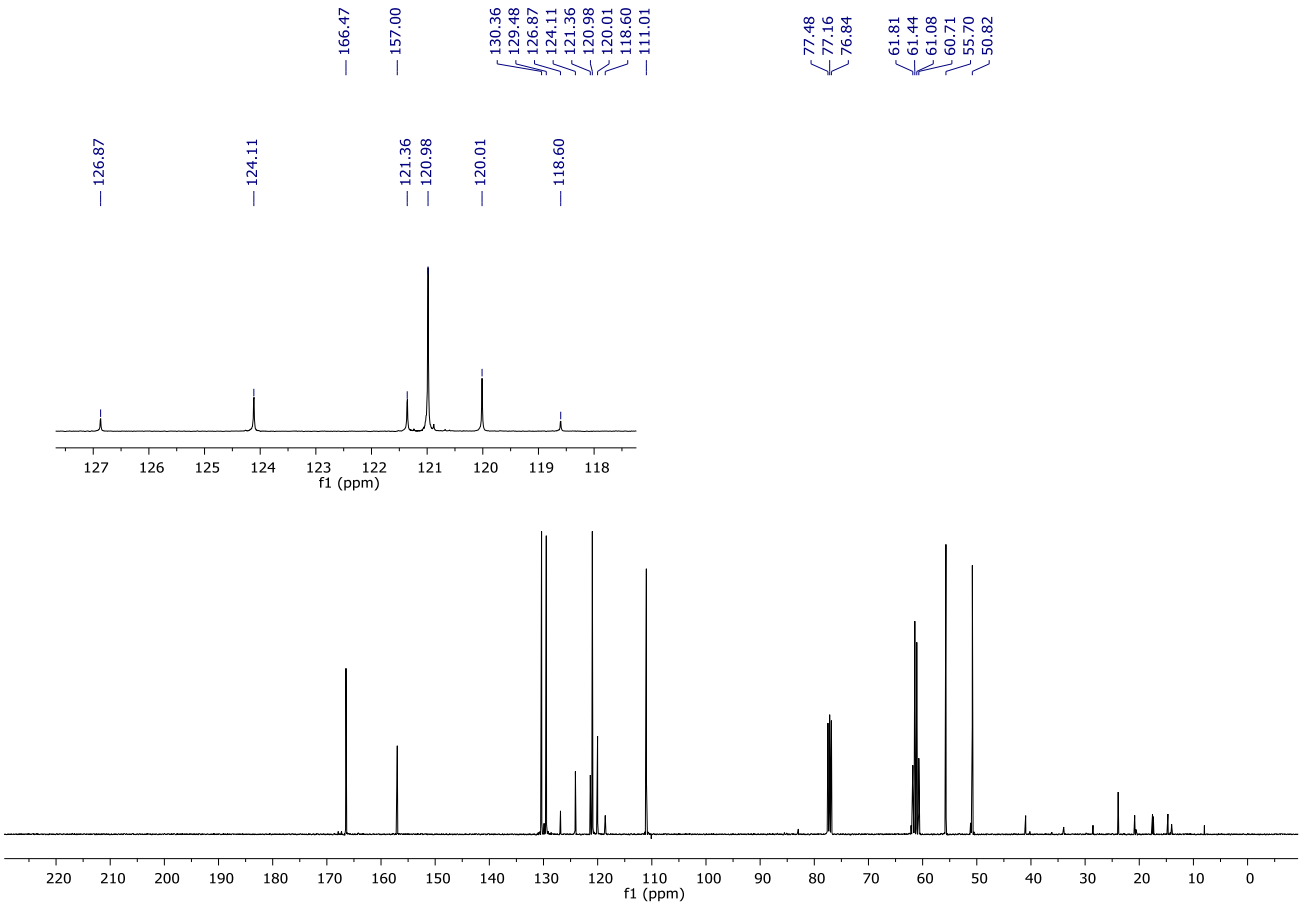

3.92
2.98
0.92
1.97
3.97
2.00
1.98
f1 (ppm)

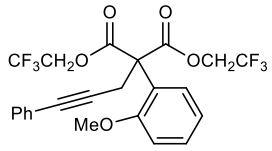

168.78
167.00
150.32
131.87
129.68
128.65
128.47
126.40
125.81
123.98
122.57
121.45
121.22
119.53
85.19
77.48
77.16
76.84
62.39
62.02
61.65
61.28
55.45
37.42
24.99
f1 (ppm)


O
O
CF3CH2O
OCH2CF3
MeO

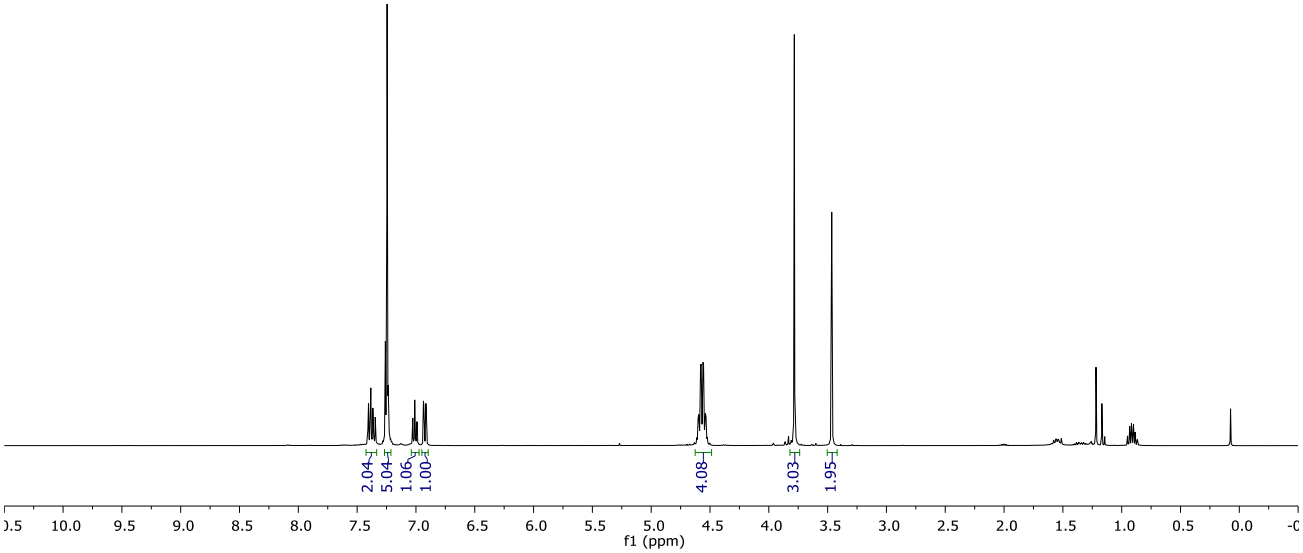
S1g


1.03
1.01
1.06
1.04
1.00
4.25
3.25
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
f1 (ppm)


166.47
157.00
130.36
129.48
126.87
124.11
121.36
120.98
120.01
118.60
111.01
77.48
77.16
76.84
61.81
61.44
61.08
60.71
55.70
50.82
126.87
124.11
121.36
120.98
120.01
118.60
127 126 125 124 123 122 121 120 119 118
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
O
CF3CH2O
OCH2CF3
Ph
MeO

1g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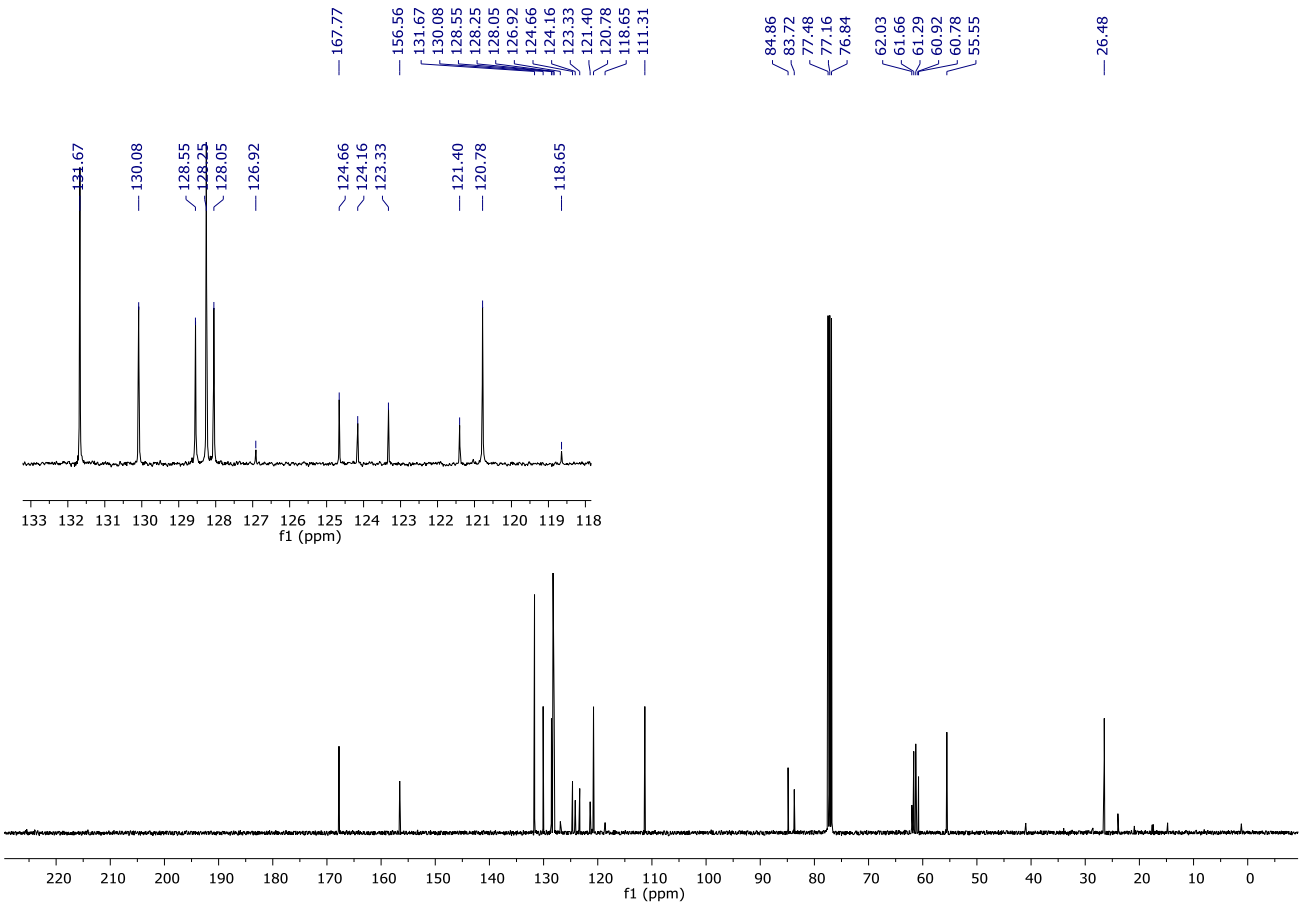
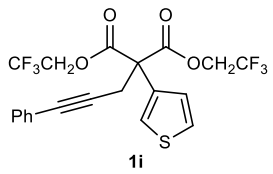
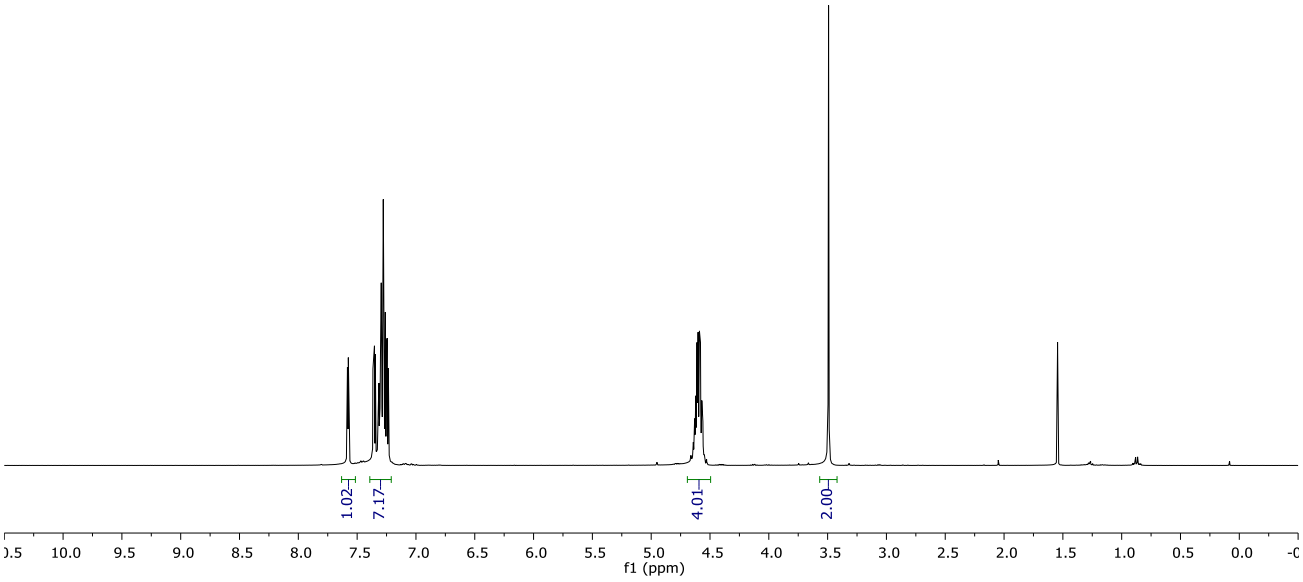
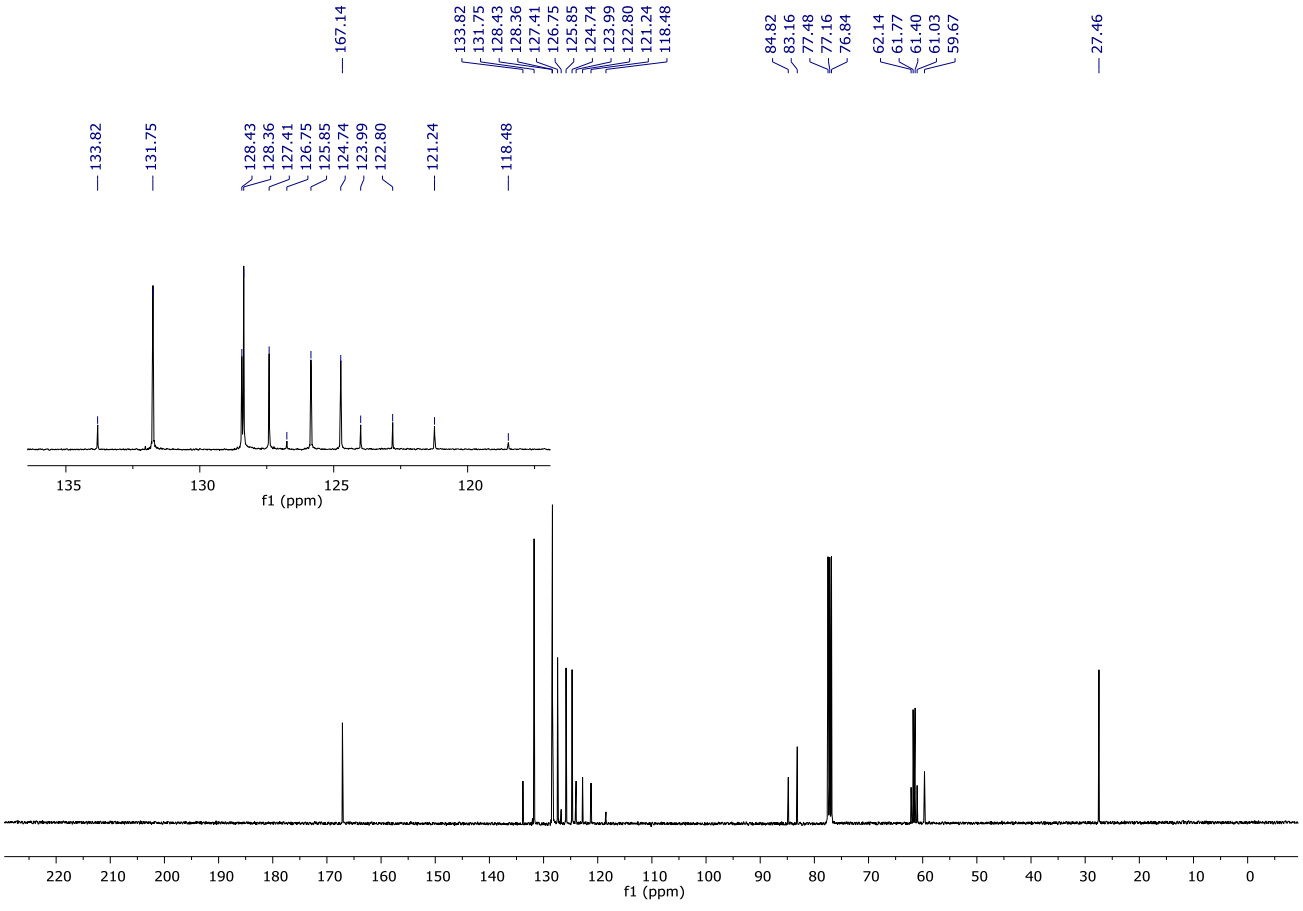
5.04
1.06
1.00
4.08
3.03
1.95
f1 (ppm)


167.77
156.56
131.67
130.08
128.55
128.25
128.05
126.92
124.66
124.16
123.33
121.40
120.78
118.65
111.31
84.86
83.72
77.48
77.16
76.84
62.03
61.66
61.29
60.92
60.78
55.55
26.48
f1 (ppm)


O
O
CF3CH2O
OCH2CF3
Ph
S

1i


1.02
7.17
4.01
2.00
f1 (ppm)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133.82
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128.36
127.41
126.75
125.85
124.74
123.99
122.80
121.24
118.48
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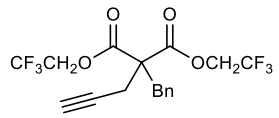
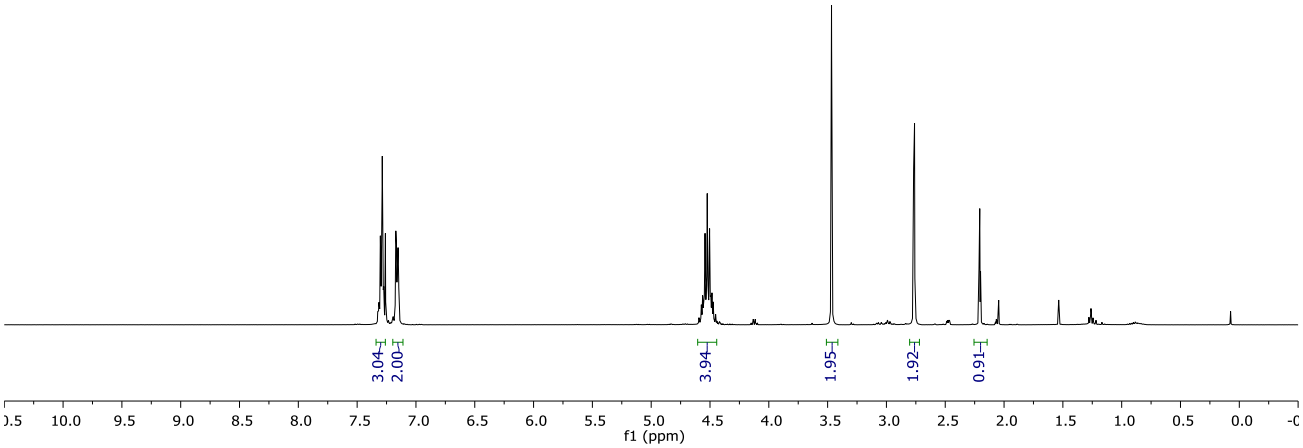
61.40
61.03
59.67
27.46
f1 (ppm)


O
O
CF3CH2O
OCH2CF3
Bn

S1j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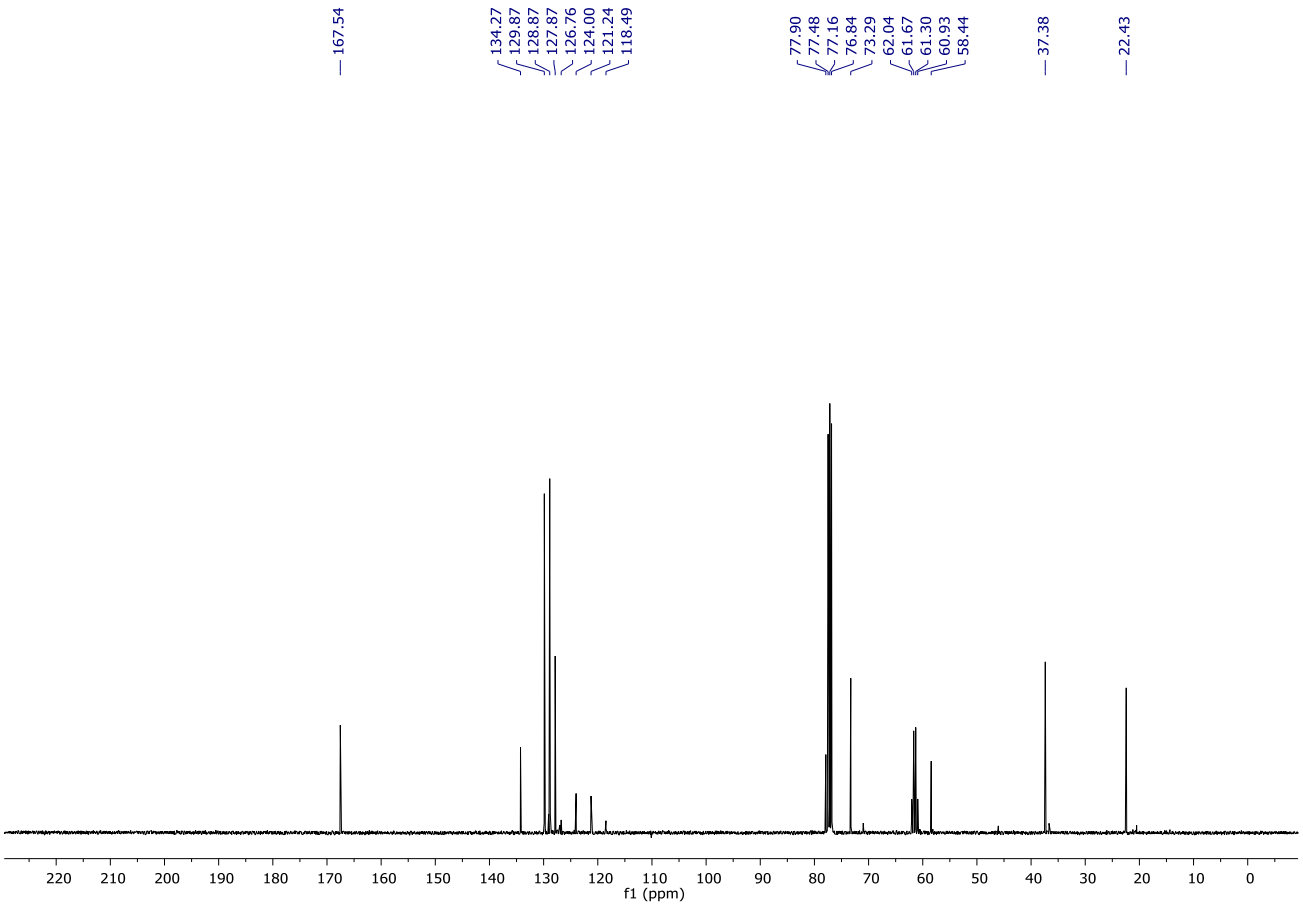
1.95
1.92
0.91
f1 (ppm)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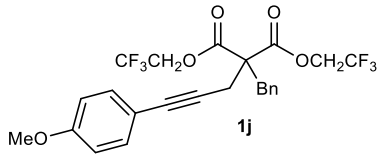
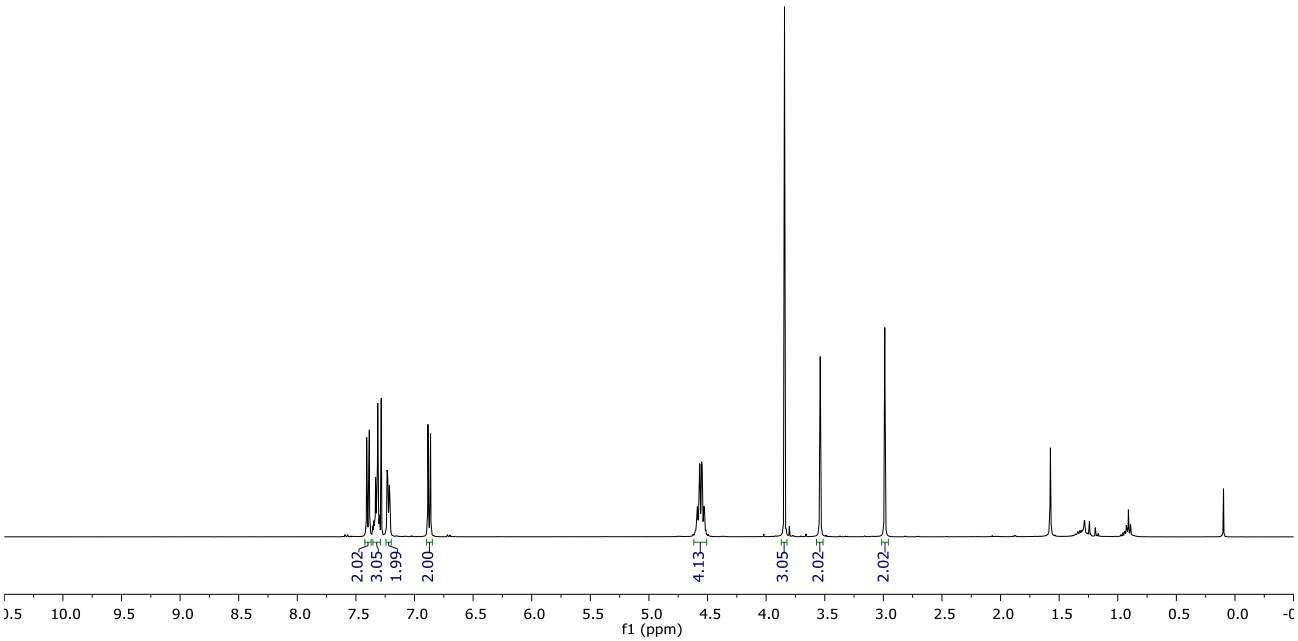
128.87
127.87
126.76
124.00
121.24
118.49
77.90
77.48
77.16
76.84
73.29
62.04
61.67
61.30
60.93
58.44
37.38
22.43
f1 (ppm)


O
O
CF3CH2O
OCH2CF3
Bn
MeO

1j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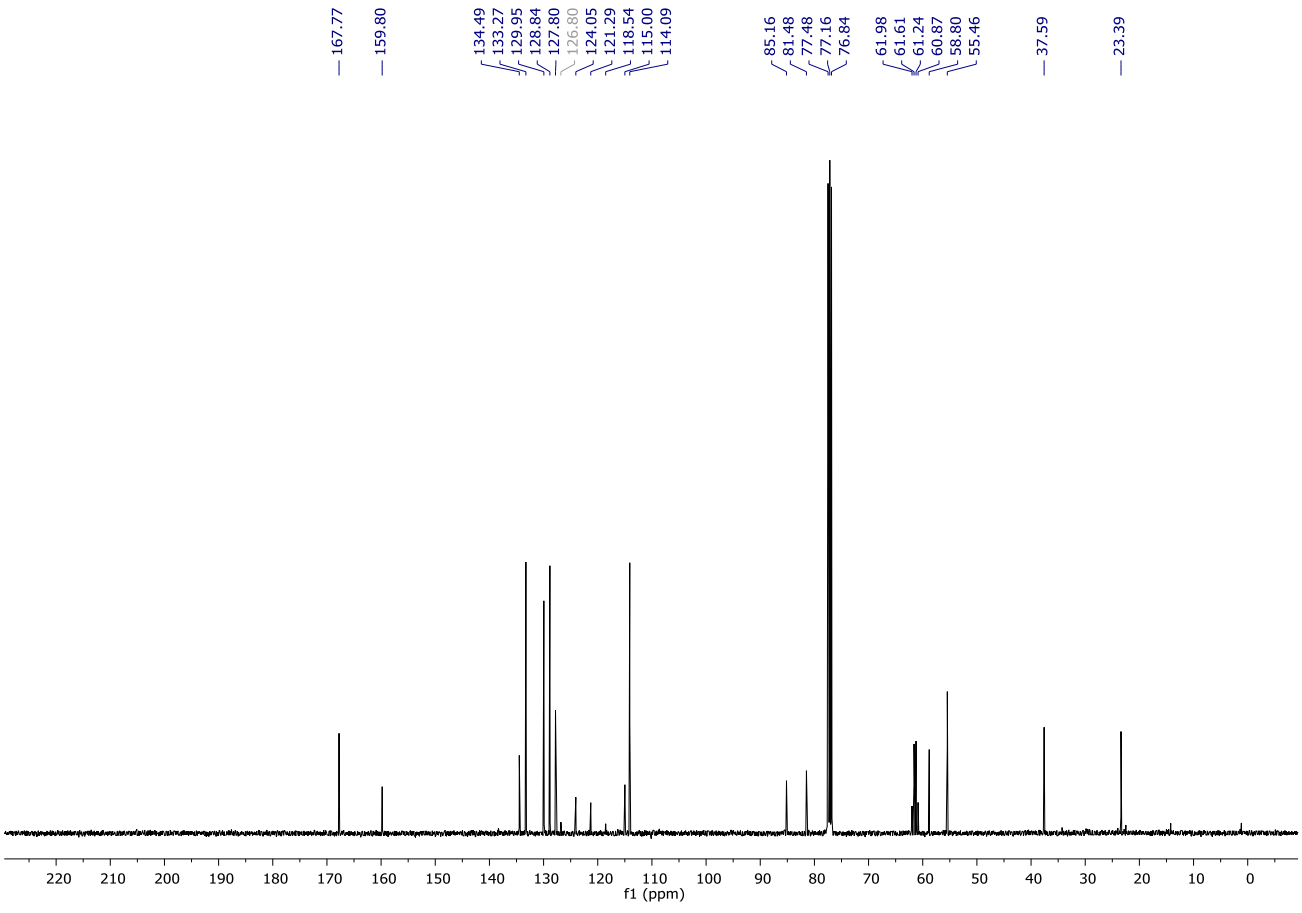
1.99
2.00
4.13
3.05
2.02
2.02
f1 (ppm)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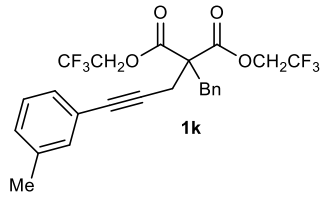
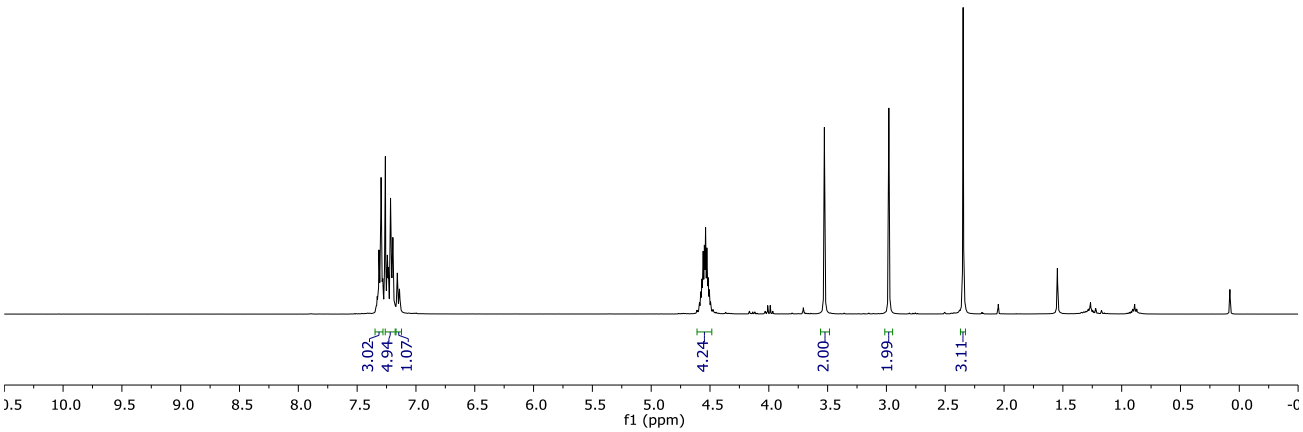
128.84
127.80
126.80
124.05
121.29
118.54
115.00
114.09
85.16
81.48
77.48
77.16
76.84
61.98
61.61
61.24
60.87
58.80
55.46
37.59
23.39
f1 (ppm)


O
O
CF3CH2O
OCH2CF3
Bn
Me

1k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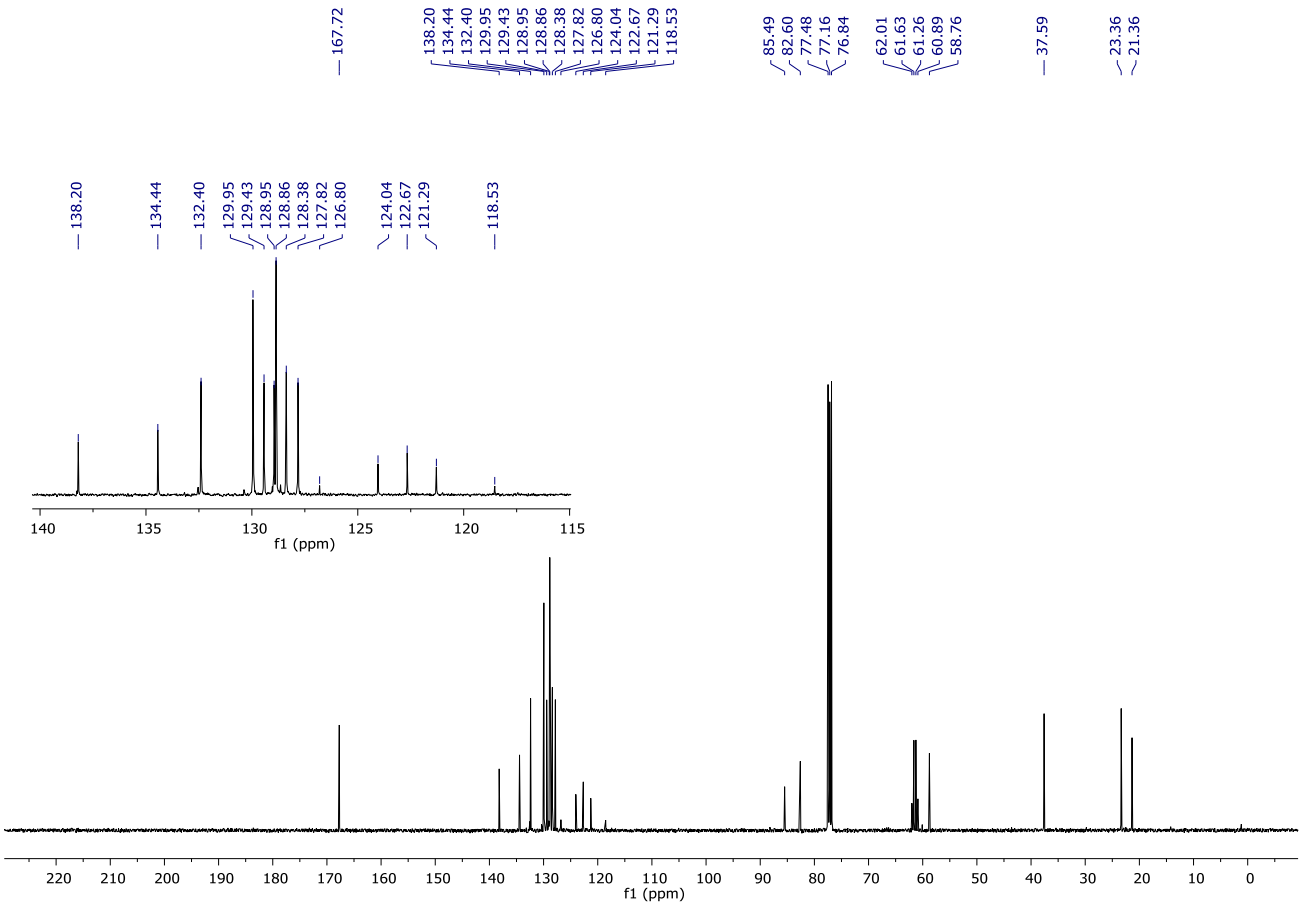
1.07
4.24
2.00
1.99
3.11
f1 (ppm)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127.82
126.80
124.04
122.67
121.29
118.53
85.49
82.60
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77.16
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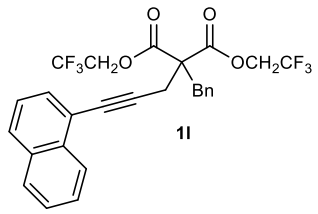
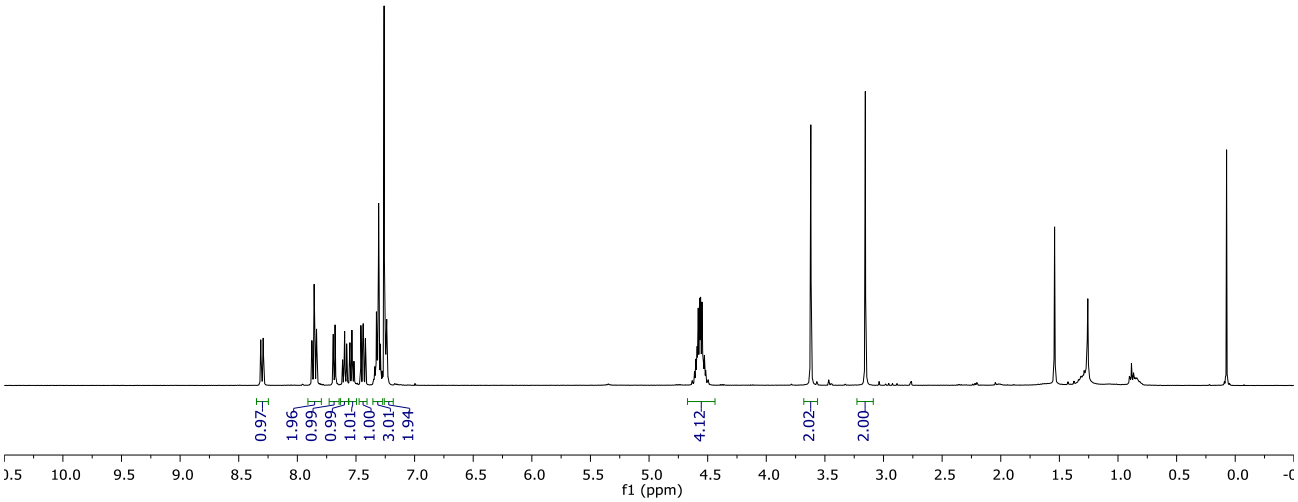
62.01
61.63
61.26
60.89
58.76
37.59
23.36
21.36
f1 (ppm)


O
O
CF3CH2O
OCH2CF3
Bn

1l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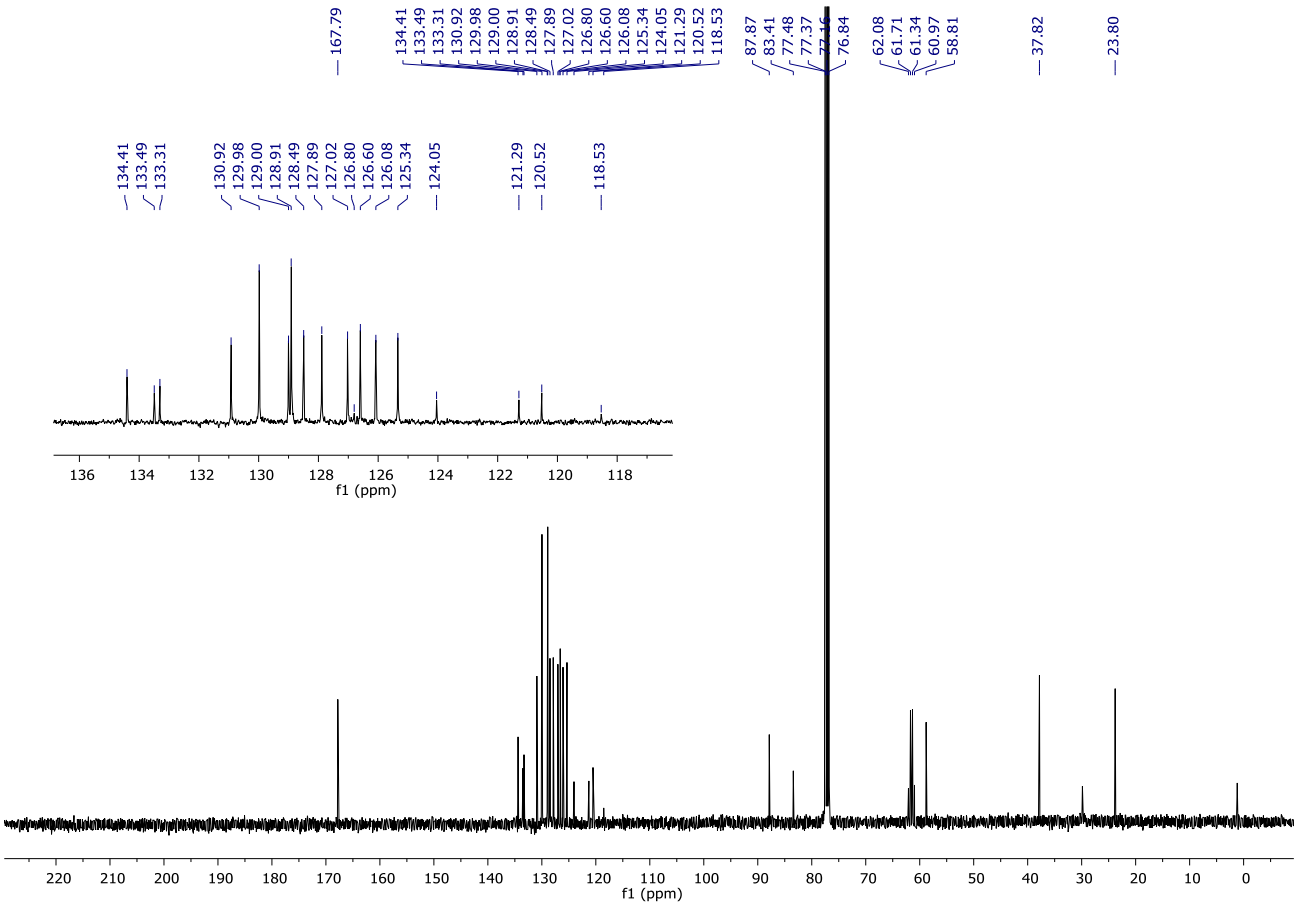
0.99
1.01
1.00
3.01
1.94
4.12
2.02
2.00
f1 (ppm)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129.98
129.00
128.91
128.49
127.89
127.02
126.80
126.60
126.08
125.34
124.05
121.29
120.52
118.53
87.87
83.41
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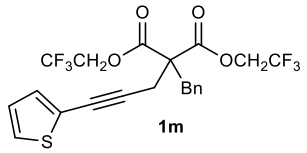
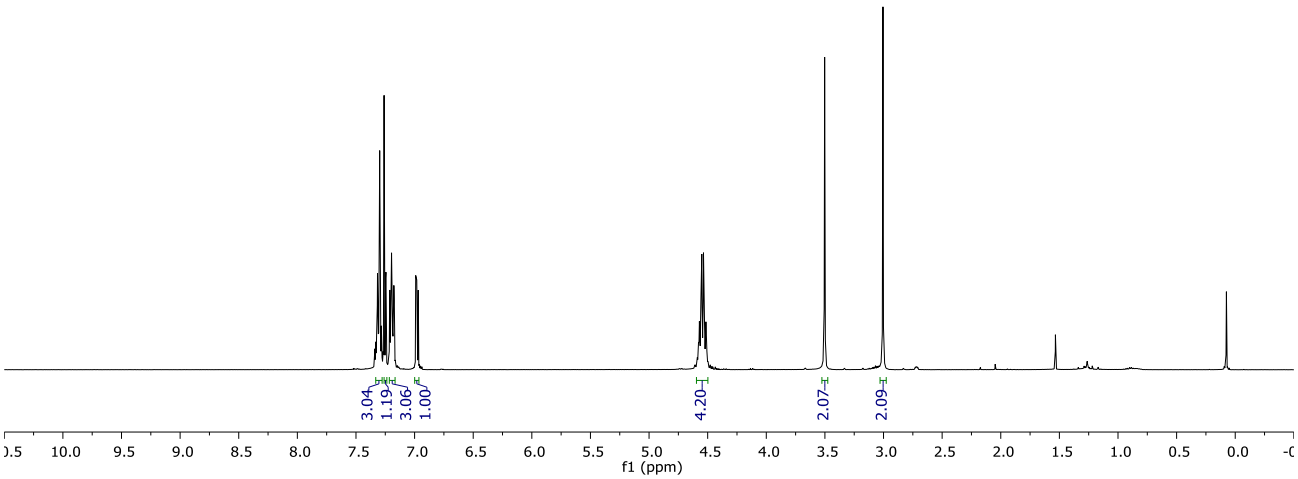
60.97
58.81
37.82
23.80
f1 (ppm)


O
O
CF3CH2O
OCH2CF3
Bn
S

1m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1.19
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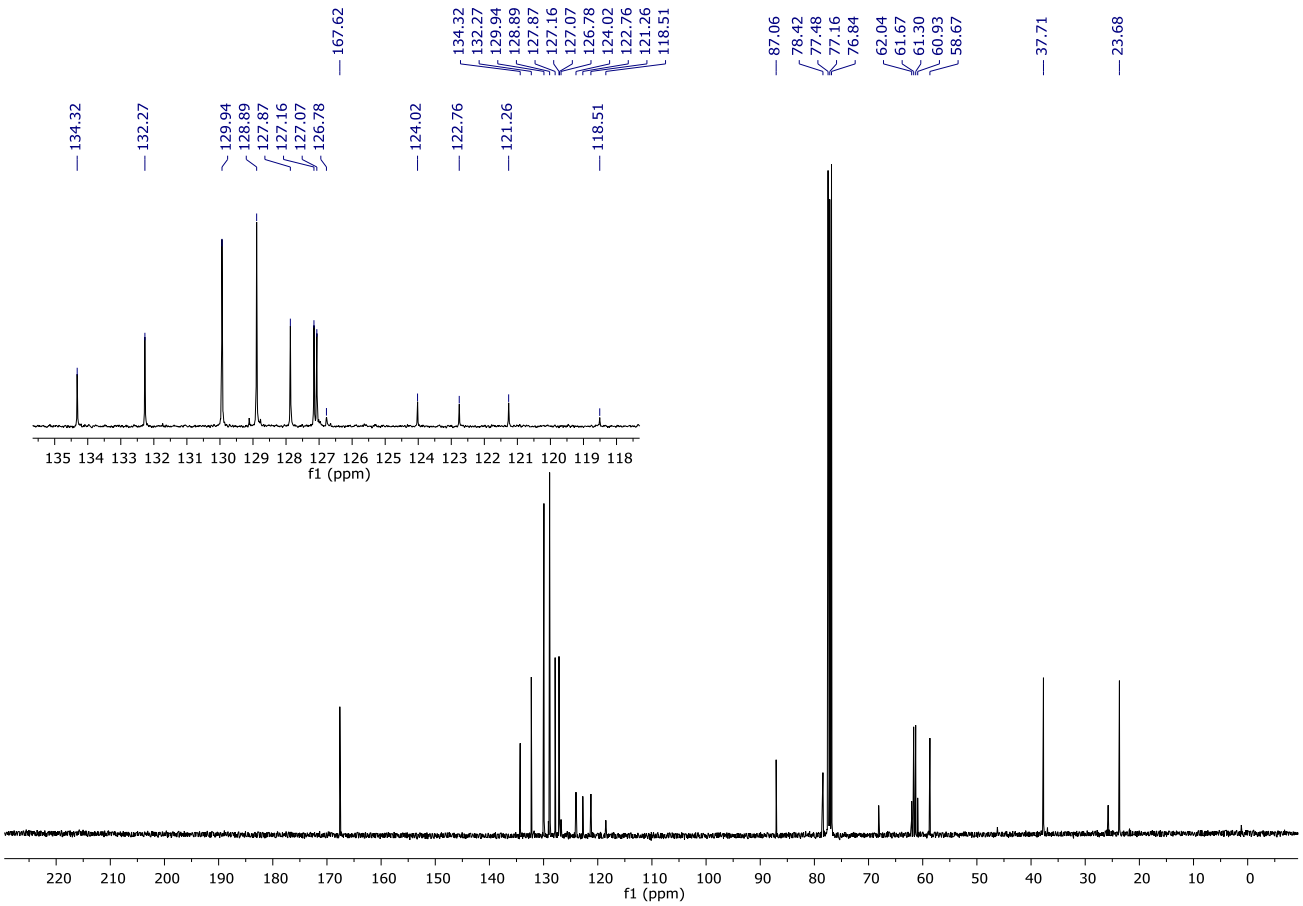
1.00
4.20
2.07
2.09
f1 (ppm)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128.89
127.87
127.16
127.07
126.78
124.02
122.76
121.26
118.51
87.06
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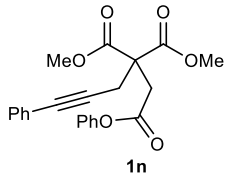
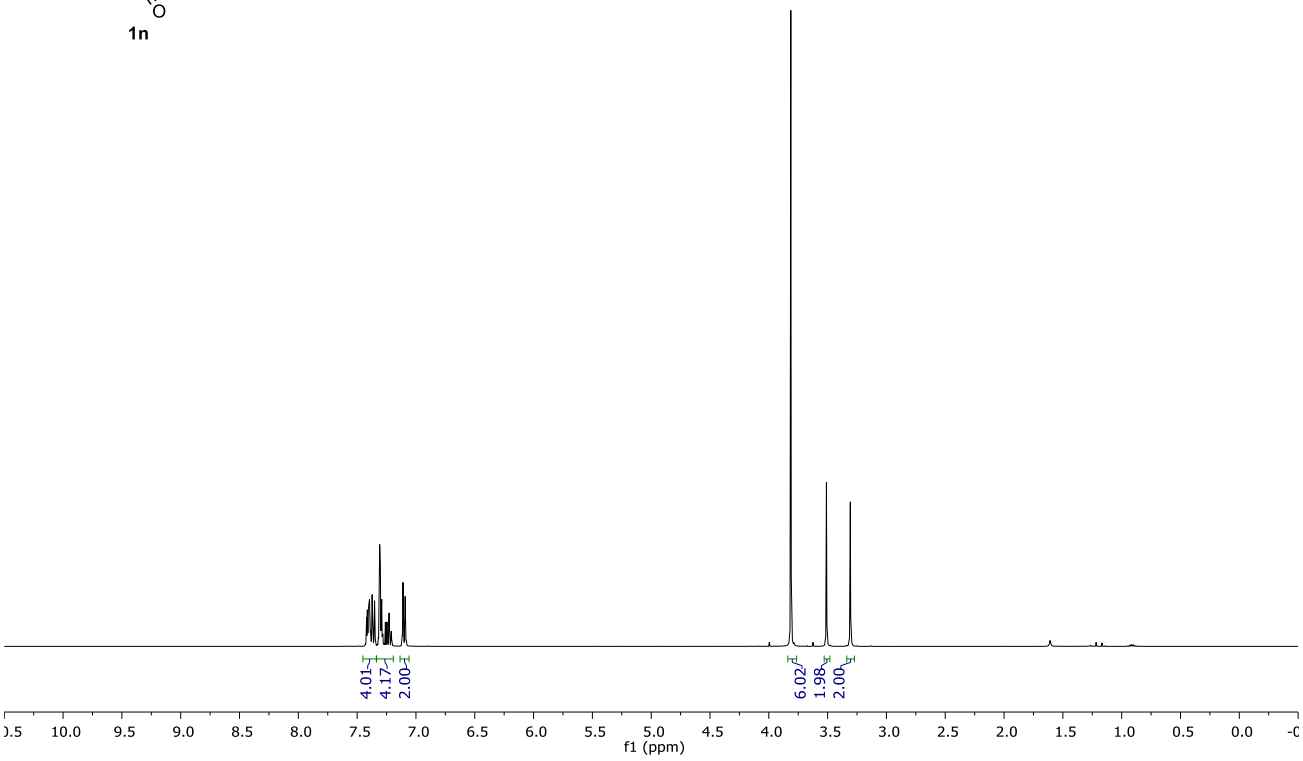
60.93
58.67
37.71
23.68
f1 (ppm)


MeO
OMe
Ph
PhO
O
O
O
O

1n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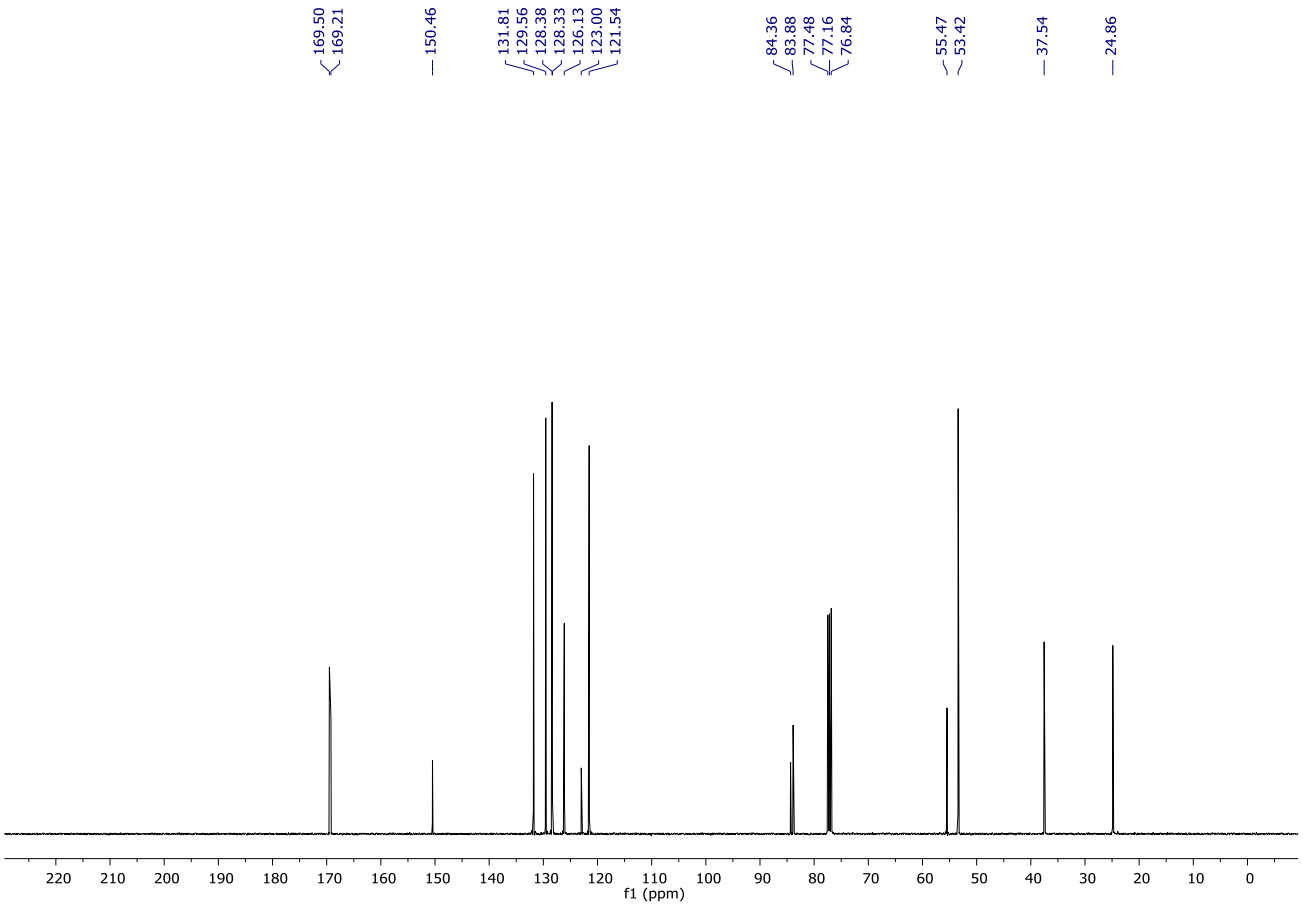
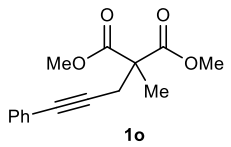
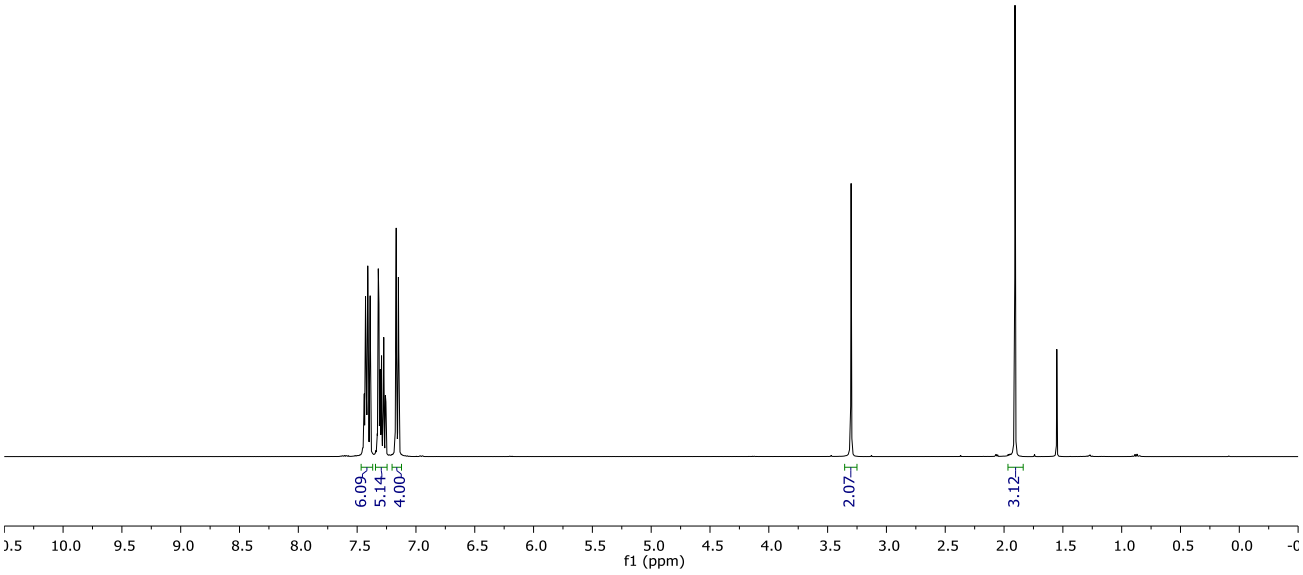
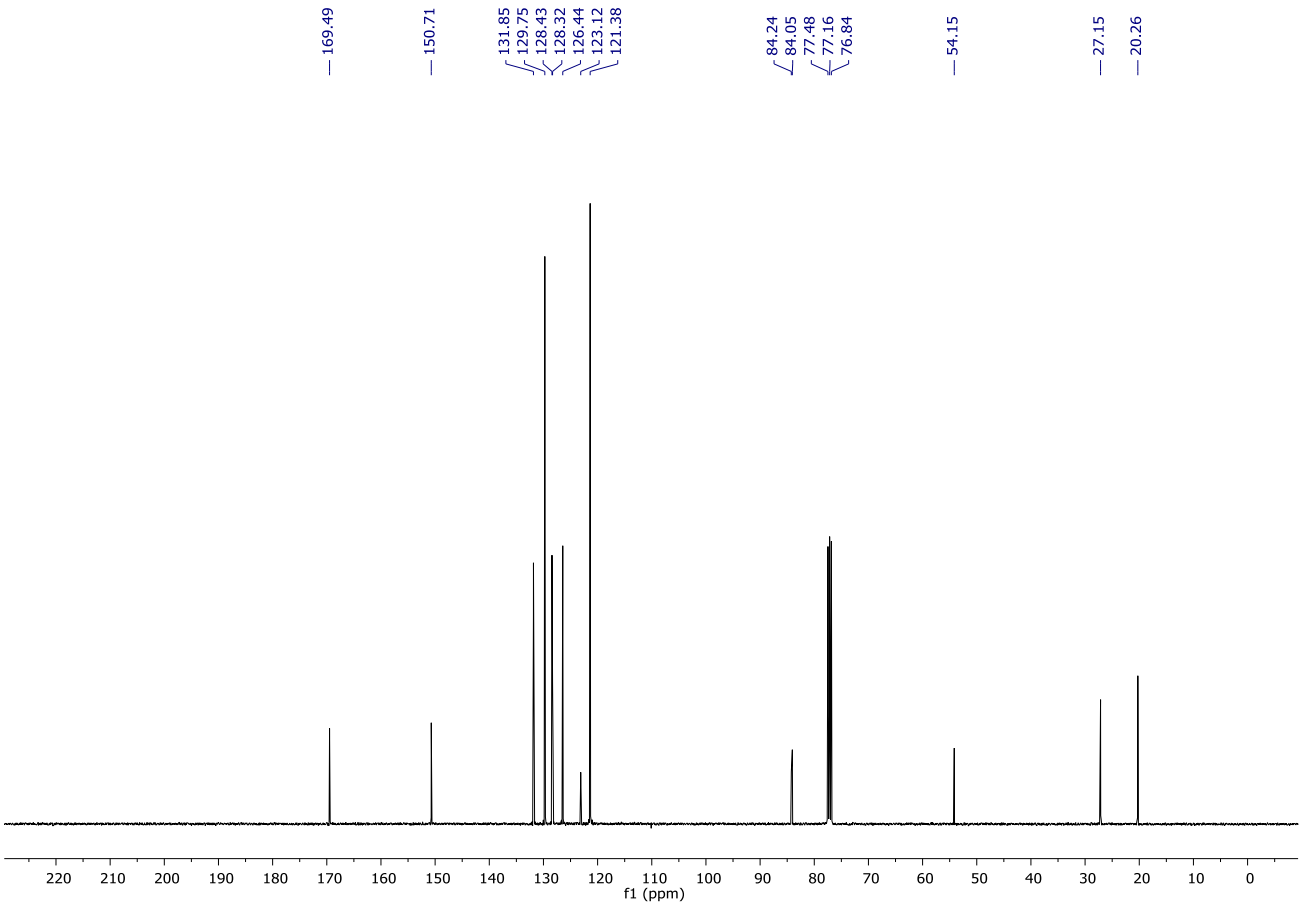
4.17
2.00
6.02
1.98
2.00
f1 (ppm)

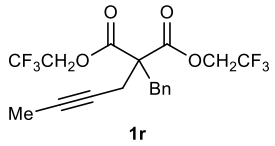

169.50
169.21
150.46
131.81
129.56
128.38
128.33
126.13
123.00
121.54
84.36
83.88
77.48
77.16
76.84
55.47
53.42
37.54
24.86
f1 (ppm)


O
O
MeO
OMe
Me
Ph

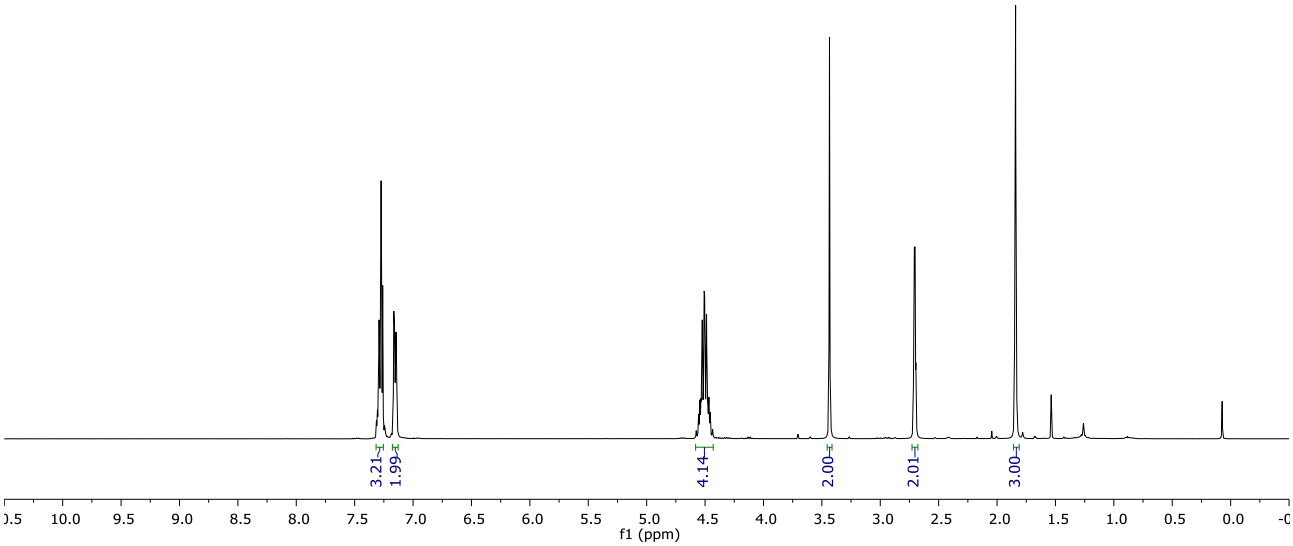
1o

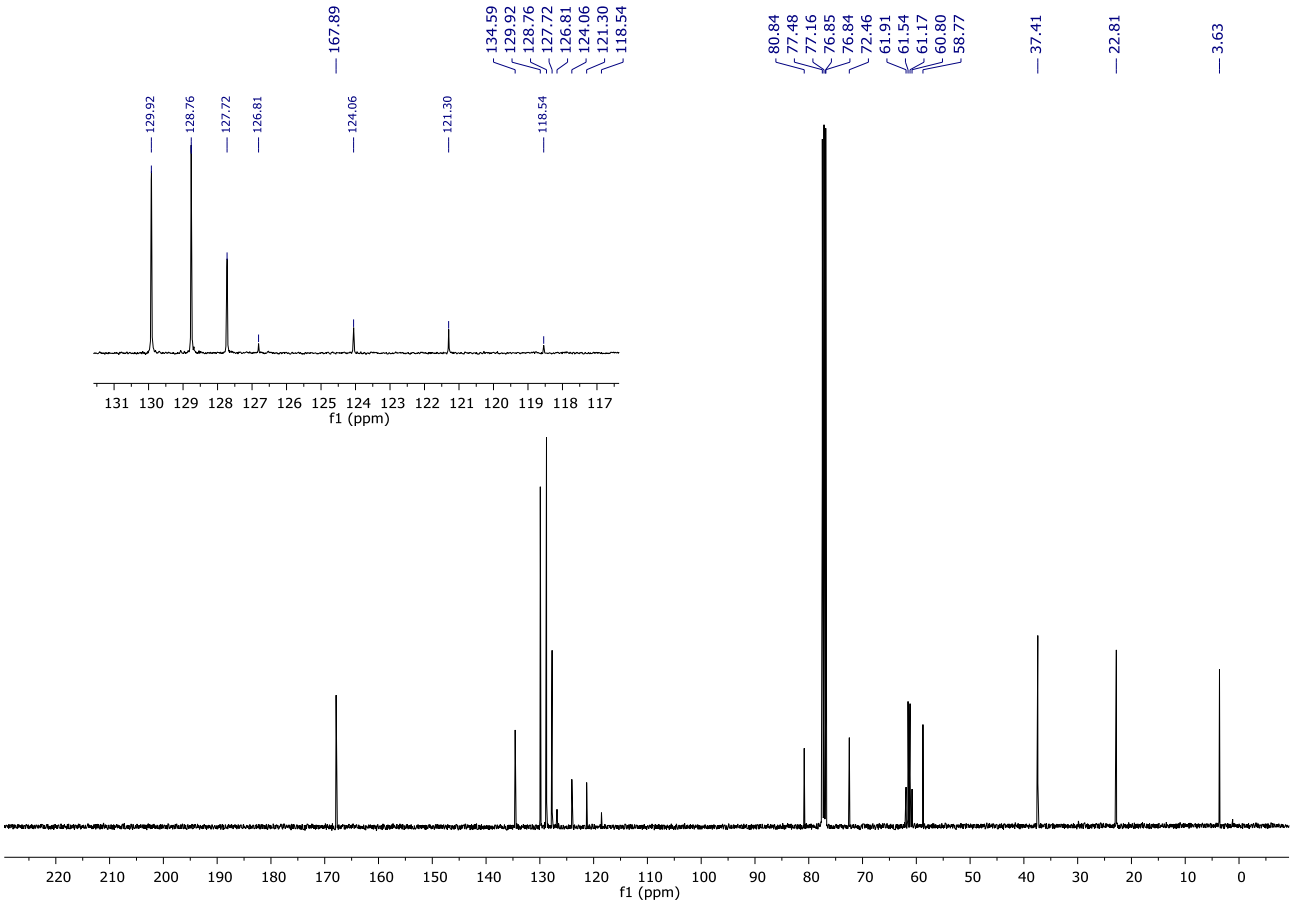

6.09
5.14
4.00
2.07
3.12
f1 (ppm)

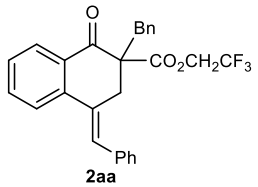

169.49
150.71
131.85
129.75
128.43
128.32
126.44
123.12
121.38
84.24
84.05
77.48
77.16
76.84
54.15
27.15
20.26
f1 (ppm)


O
O
CF3CH2O
OCH2CF3
Bn
Me

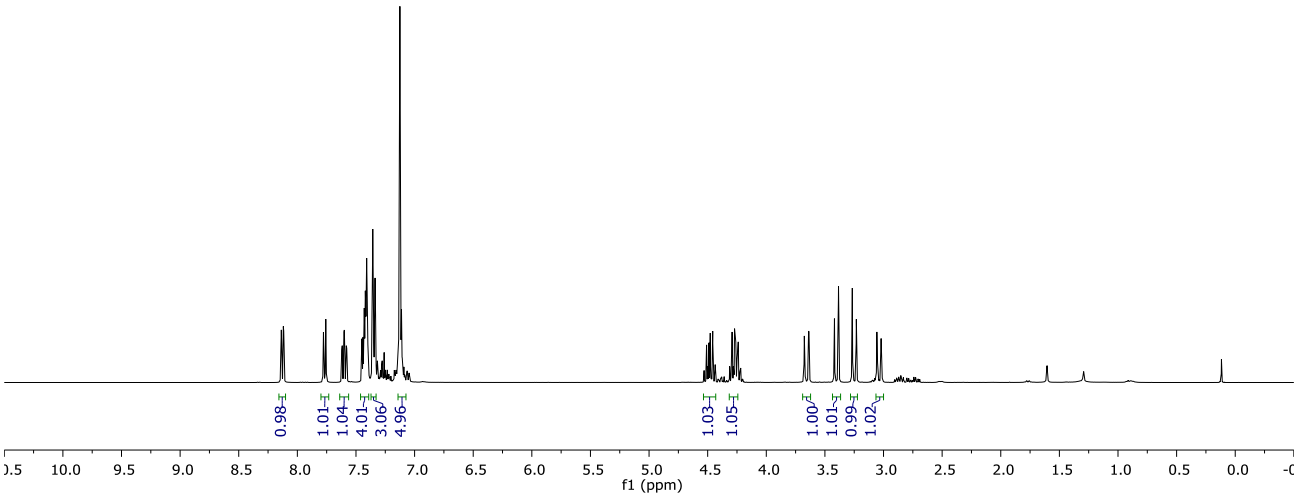
1r

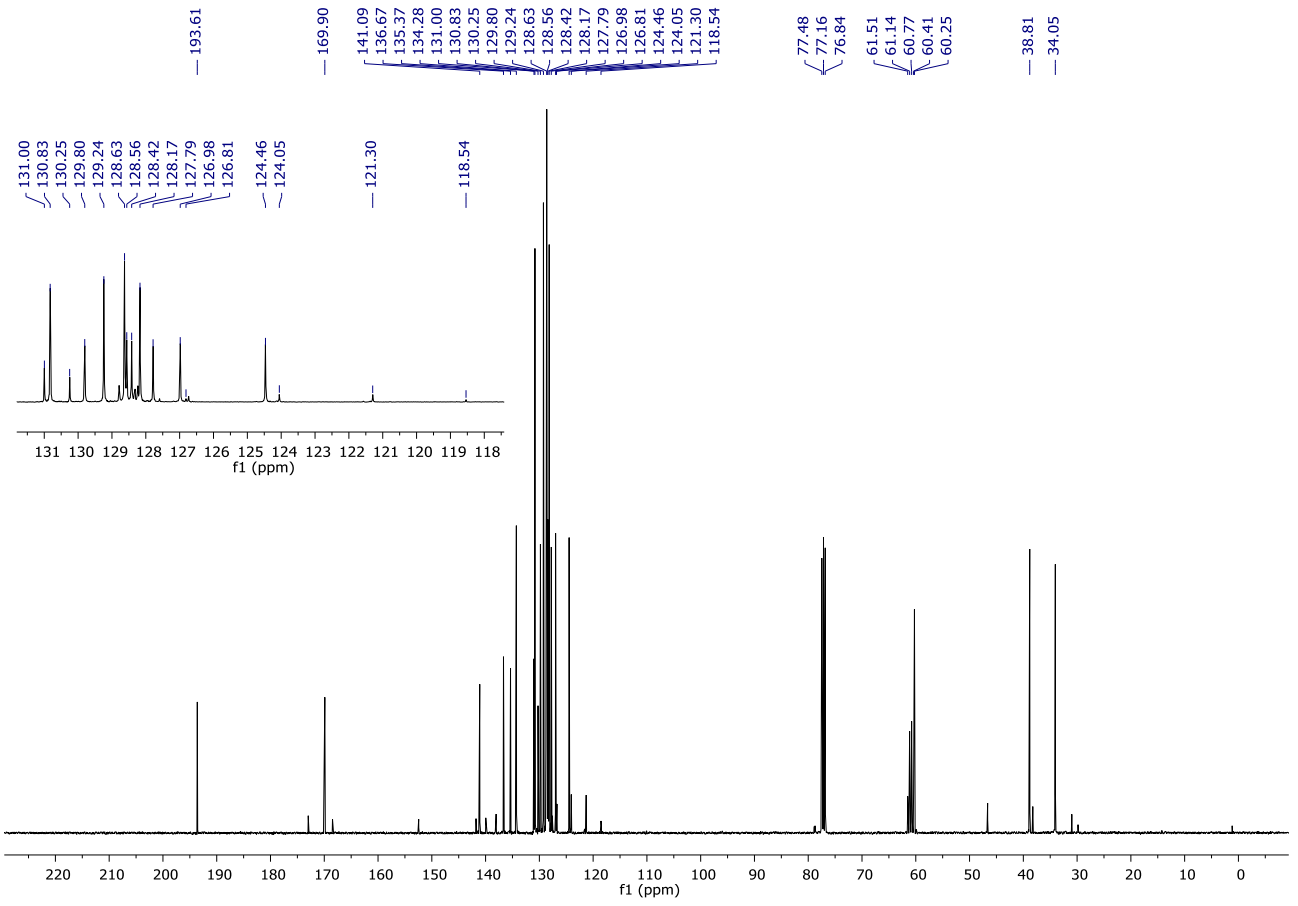

3.21
1.99
4.14
2.00
2.01
3.00
f1 (ppm)

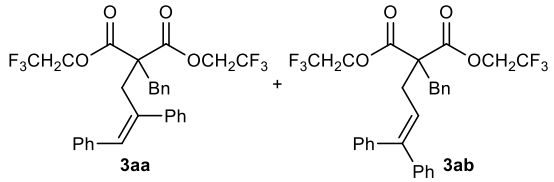

167.89
134.59
129.92
128.76
127.72
126.81
124.06
121.30
118.54
80.84
77.48
77.16
76.85
76.84
72.46
61.91
61.54
61.17
60.80
58.77
37.41
22.81
3.63
f1 (ppm)


O
Bn
CO2CH2CF3
Ph

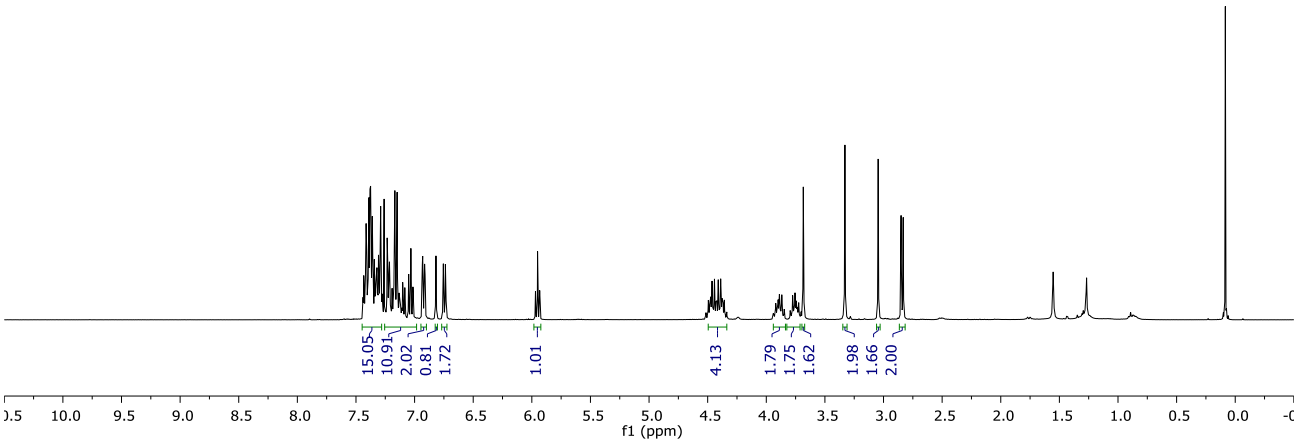
2aa

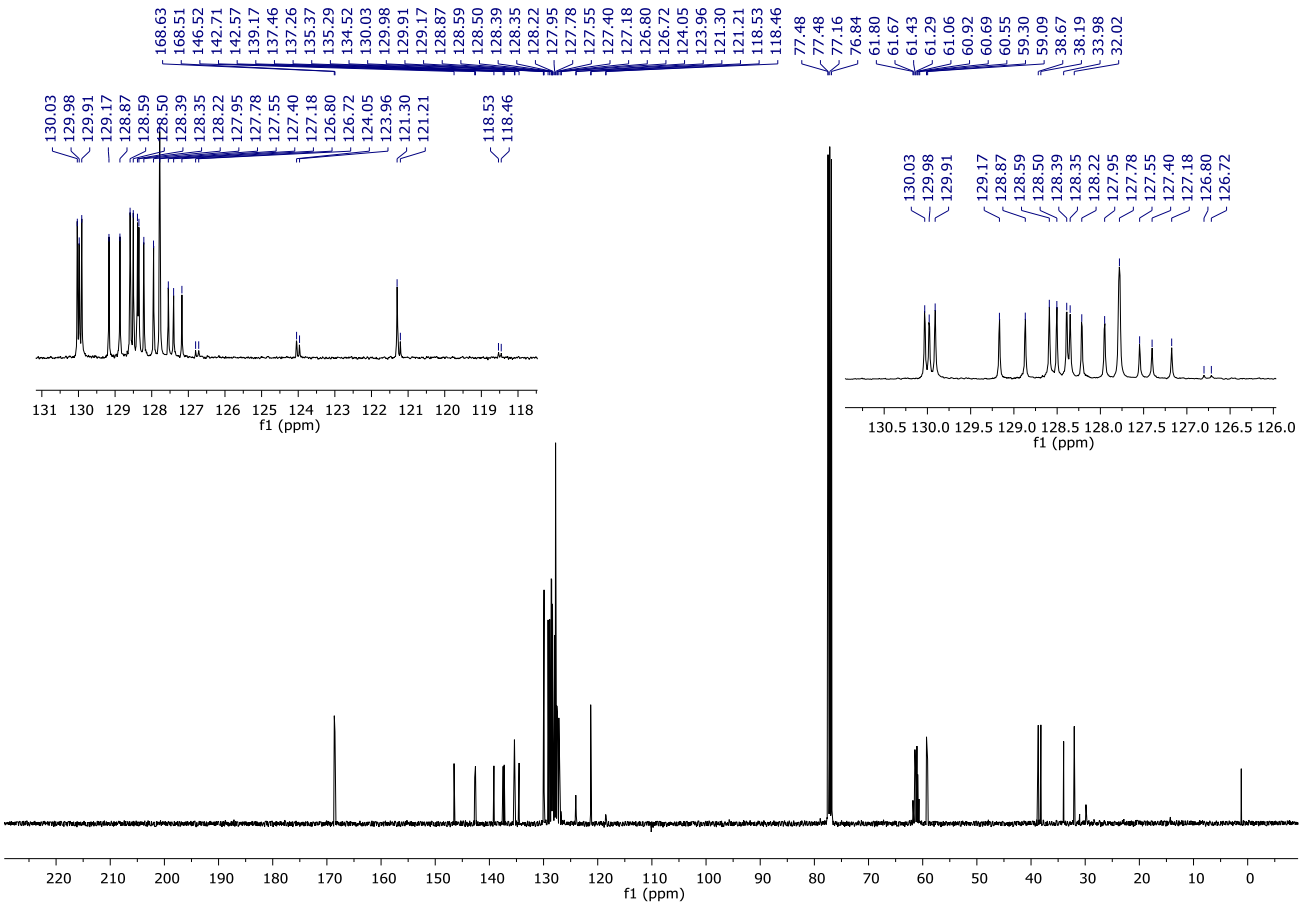

0.98
1.01
1.04
4.01
3.06
4.96
1.03
1.05
1.00
1.01
0.99
1.02
f1 (ppm)

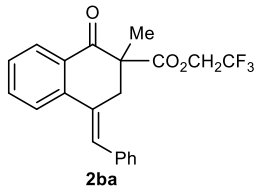

193.61
169.90
141.09
136.67
135.37
134.28
131.00
130.83
130.25
129.80
129.24
128.63
128.56
128.42
128.17
127.79
126.98
126.81
124.46
124.05
121.30
118.54
77.48
77.16
76.84
61.51
61.14
60.77
60.41
60.25
38.81
34.05
f1 (ppm)


F3CH2CO
OCH2CF3
Bn
Ph
Ph
3aa
+
F3CH2CO
OCH2CF3
Bn
Ph
Ph
Ph
3ab

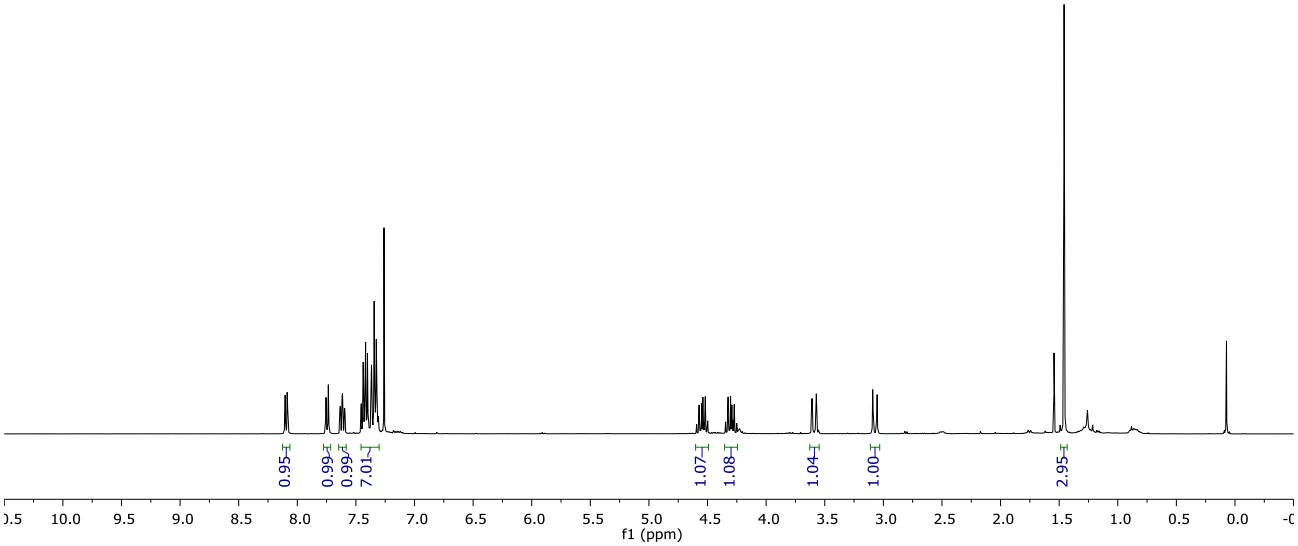
3aa:**3ab** = 1:1.25

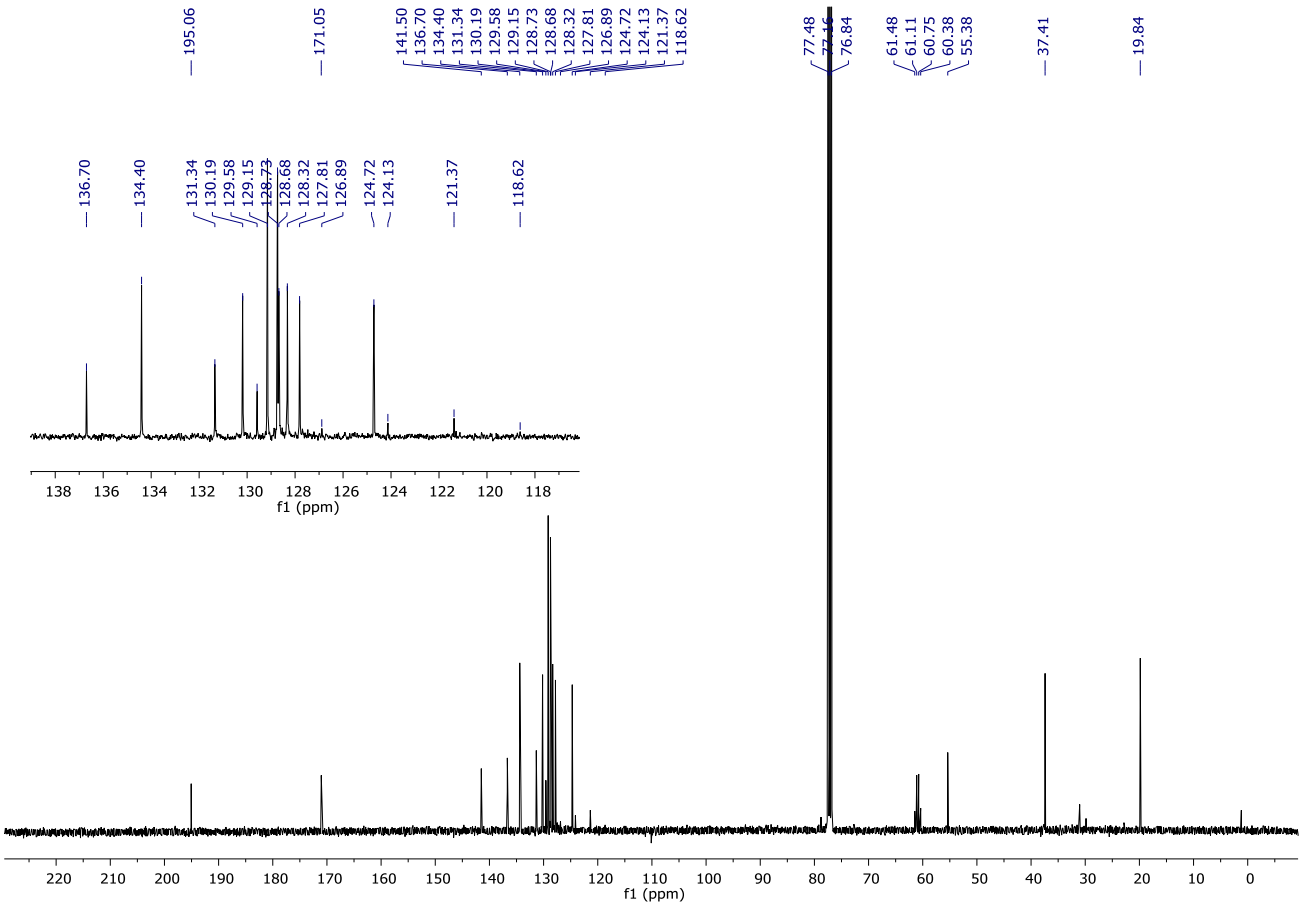

15.05
10.91
2.02
0.81
1.72
1.01
4.13
1.79
1.75
1.62
1.98
1.66
2.00
f1 (ppm)

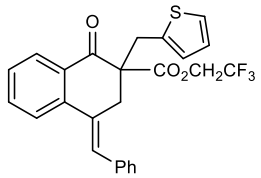

168.63
168.51
146.52
142.71
142.57
139.17
137.46
137.26
135.37
135.29
134.52
130.03
129.98
129.91
129.17
128.87
128.59
128.50
128.39
128.35
128.22
127.95
127.78
127.55
127.40
127.18
126.80
126.72
124.05
123.96
121.30
121.21
118.53
118.46
77.48
77.16
76.84
61.80
61.67
61.43
61.29
61.06
60.92
60.69
60.55
59.30
59.09
38.67
38.19
33.98
32.02
f1 (ppm)


O
Me
$CO_2CH_2CF_3$
Ph

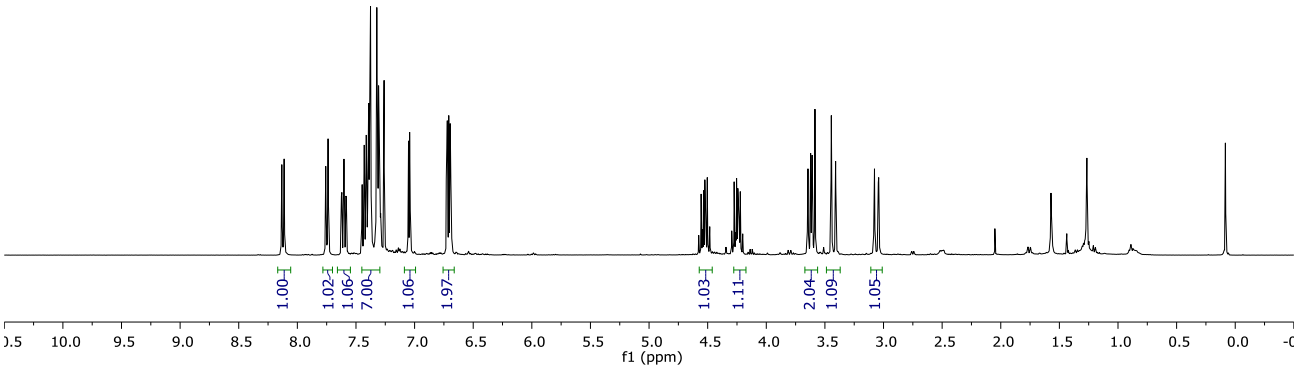
2ba

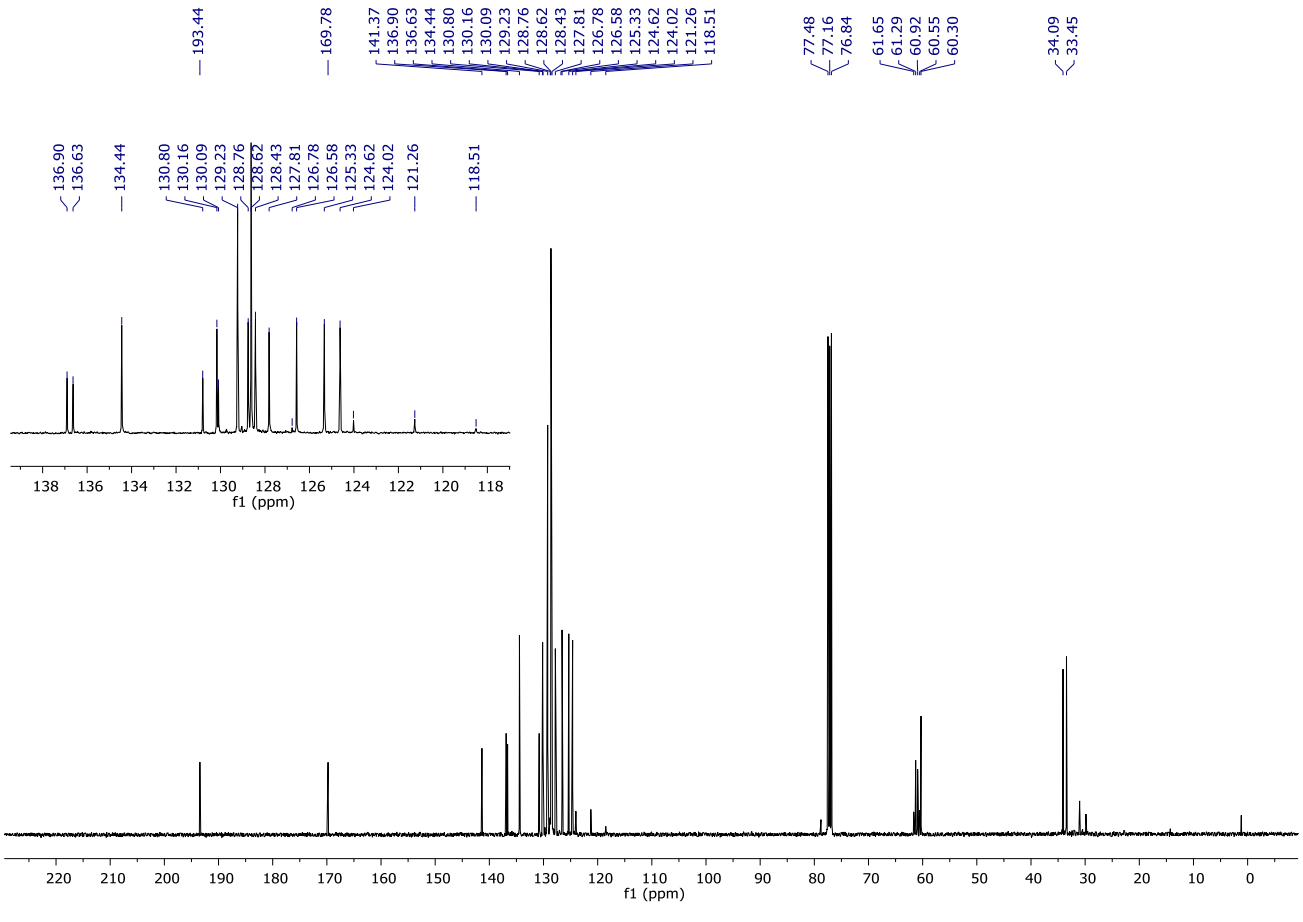

0.95
0.99
0.99
7.01
1.07
1.08
1.04
1.00
2.95
f1 (ppm)

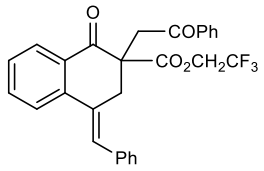

195.06
171.05
141.50
136.70
134.40
131.34
130.19
129.58
129.15
128.73
128.68
128.32
127.81
126.89
124.72
124.13
121.37
118.62
77.48
77.16
76.84
61.48
61.11
60.75
60.38
55.38
37.41
19.84
f1 (ppm)


O
S
$CO_2CH_2CF_3$
Ph

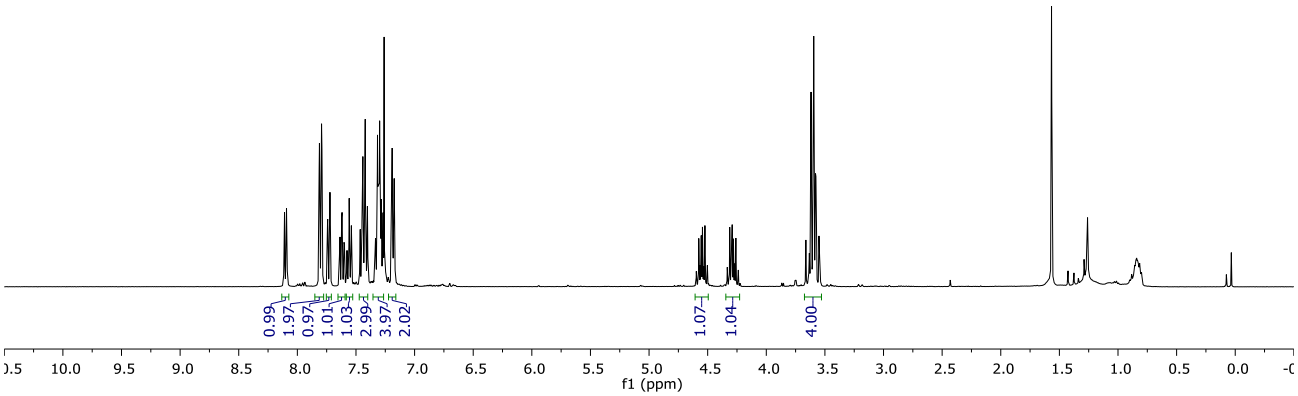
2ca

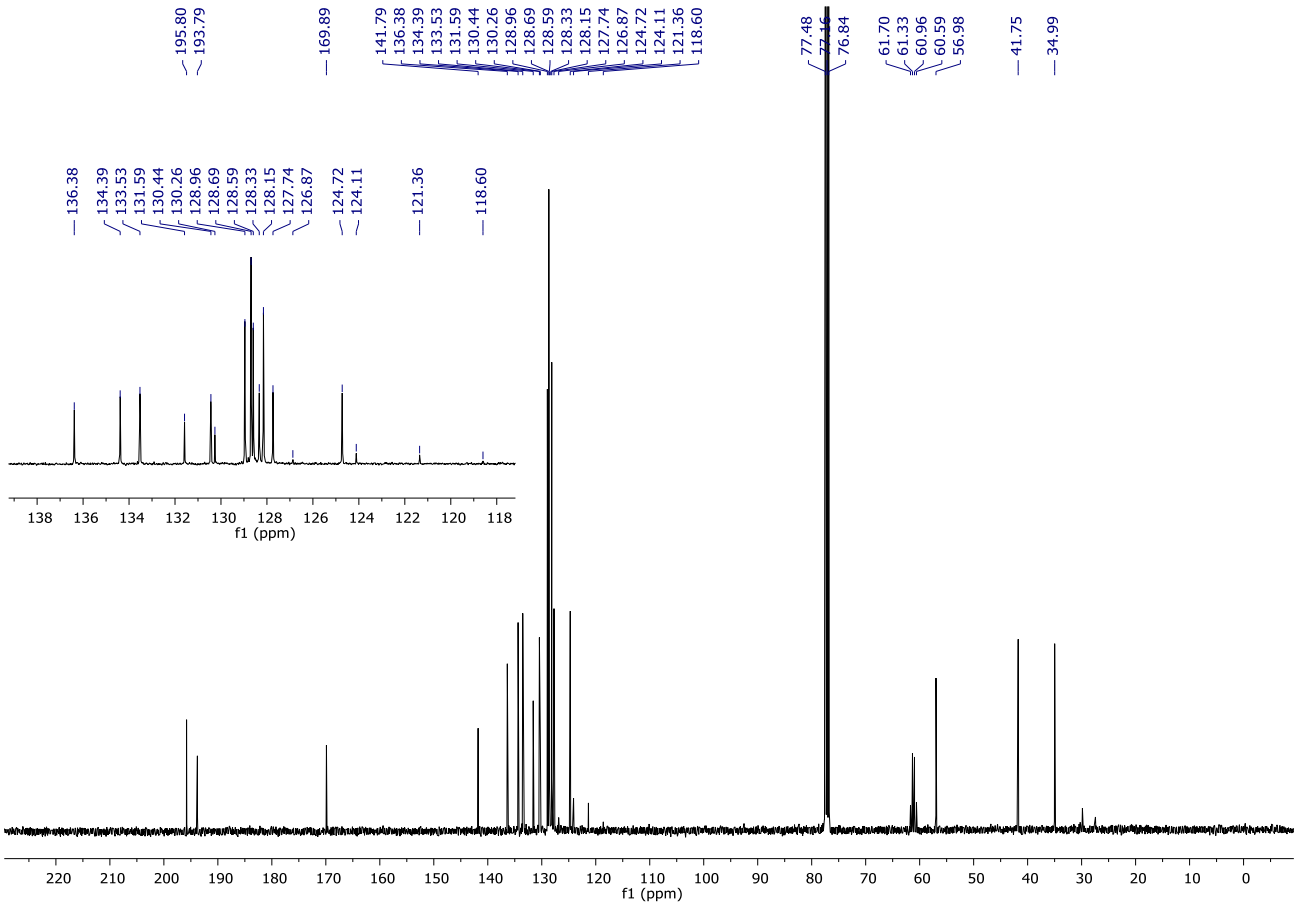

1.00
1.02
1.06
7.00
1.06
1.97
1.03
1.11
2.04
1.09
1.05
f1 (ppm)

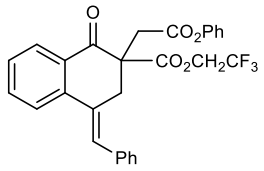

193.44
169.78
141.37
136.90
136.63
134.44
130.80
130.16
130.09
129.23
128.76
128.62
128.43
127.81
126.78
126.58
125.33
124.62
124.02
121.26
118.51
77.48
77.16
76.84
61.65
61.29
60.92
60.55
60.30
34.09
33.45
f1 (ppm)


O
COPh
$CO_2CH_2CF_3$
Ph

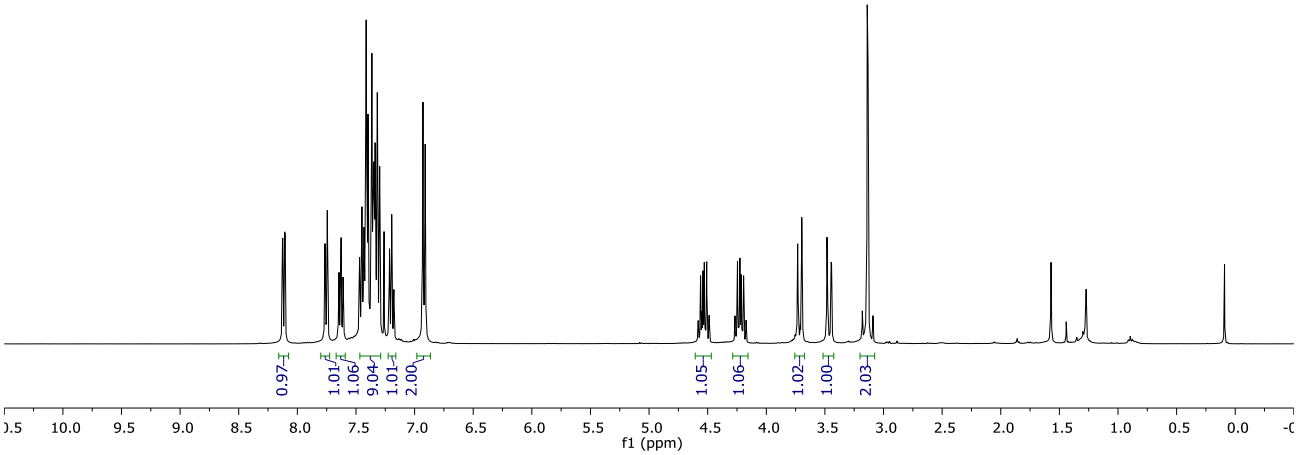
2da

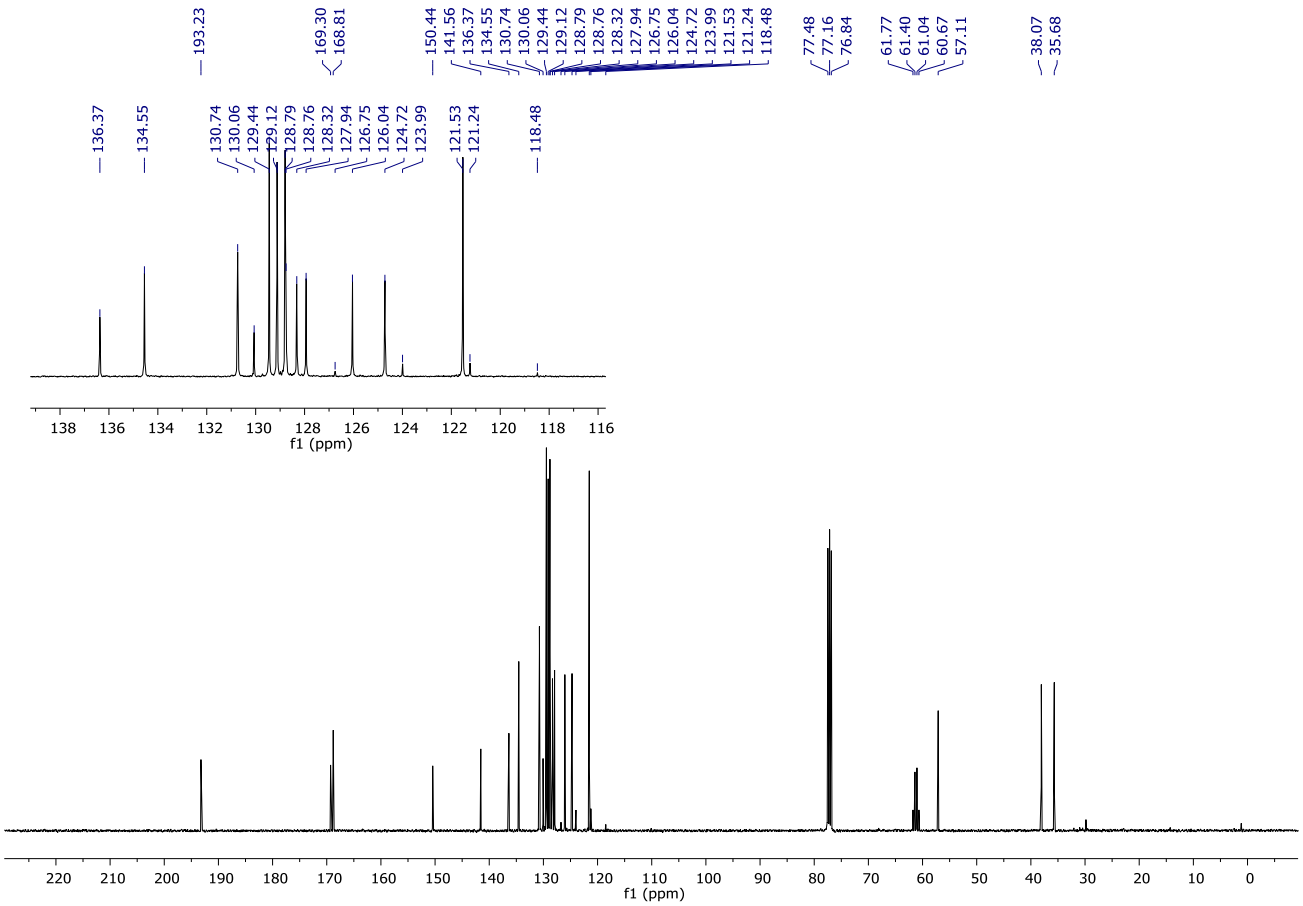

0.99
1.97
0.97
1.01
1.03
2.99
3.97
2.02
1.07
1.04
4.00
f1 (ppm)

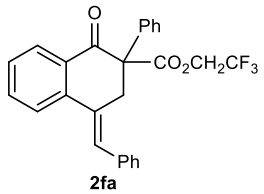

195.80
193.79
169.89
141.79
136.38
134.39
133.53
131.59
130.44
130.26
128.96
128.69
128.59
128.33
128.15
127.74
126.87
124.72
124.11
121.36
118.60
77.48
77.16
76.84
61.70
61.33
60.96
60.59
56.98
41.75
34.99
f1 (ppm)


O
CO2Ph
CO2CH2CF3
Ph

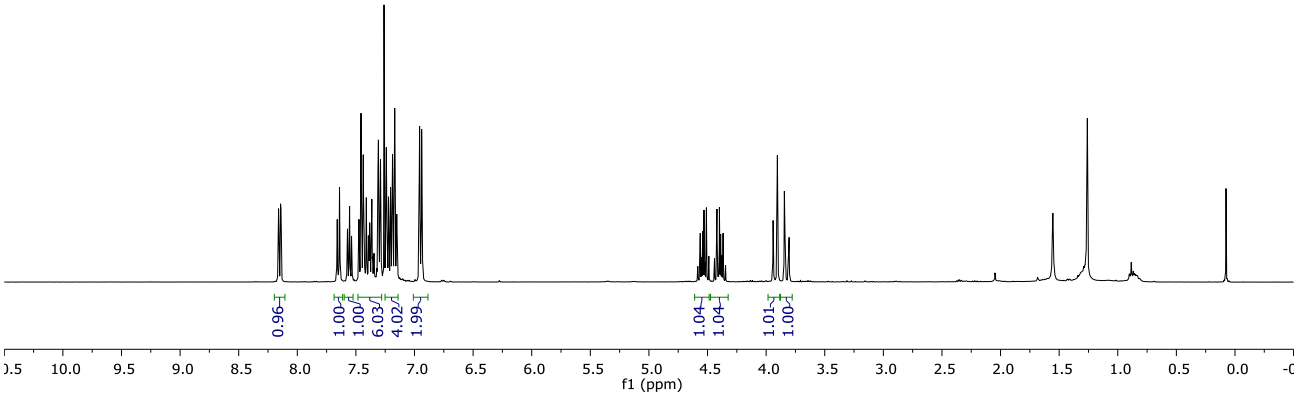
2ea

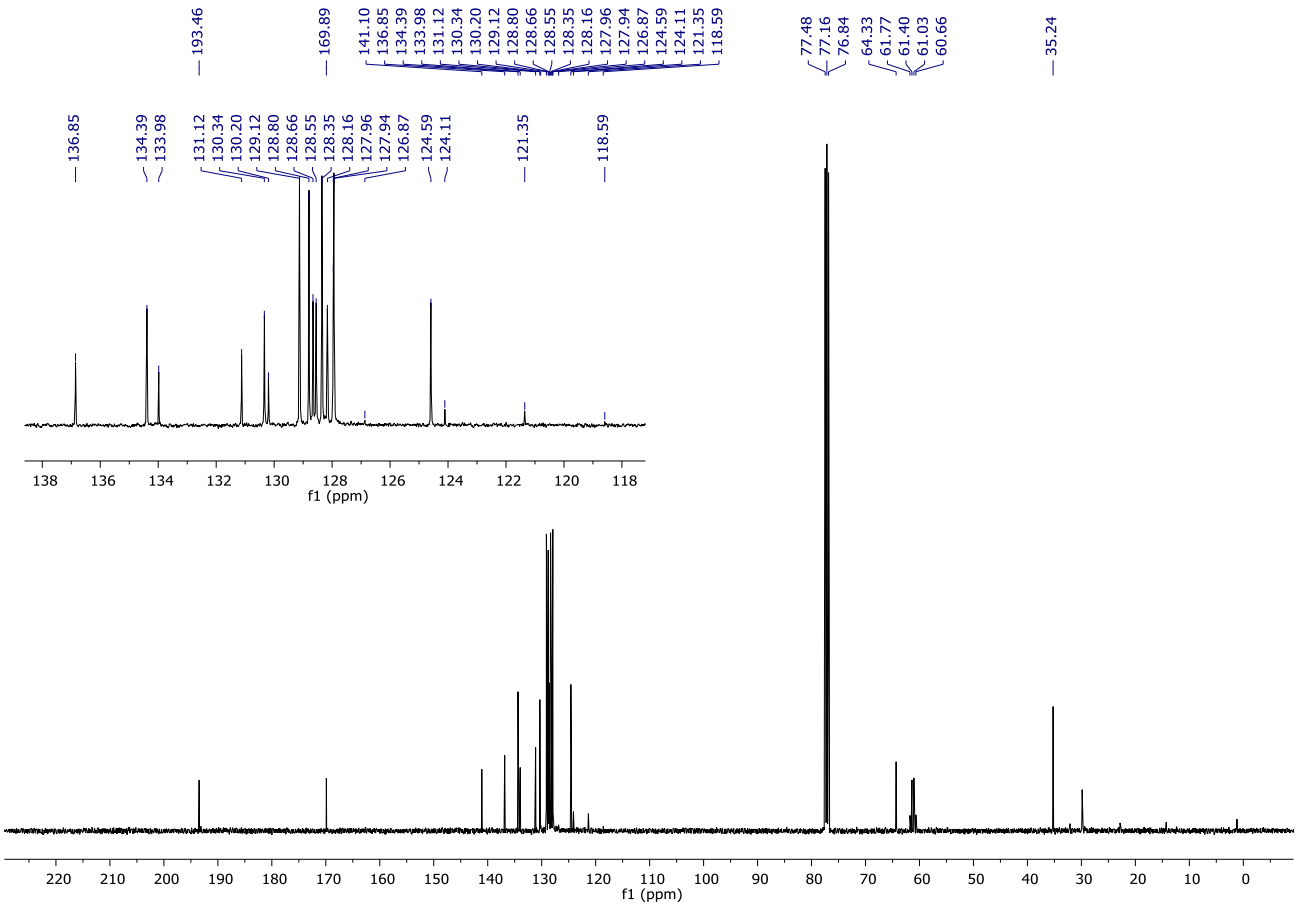

0.97
1.01
1.06
9.04
1.01
2.00
1.05
1.06
1.02
1.00
2.03
f1 (ppm)

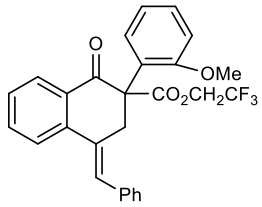

193.23
169.30
168.81
150.44
141.56
136.37
134.55
130.74
130.06
129.44
129.12
128.79
128.76
128.32
127.94
126.75
126.04
124.72
123.99
121.53
121.24
118.48
77.48
77.16
76.84
61.77
61.40
61.04
60.67
57.11
38.07
35.68
f1 (ppm)


O
Ph
$CO_2CH_2CF_3$
Ph

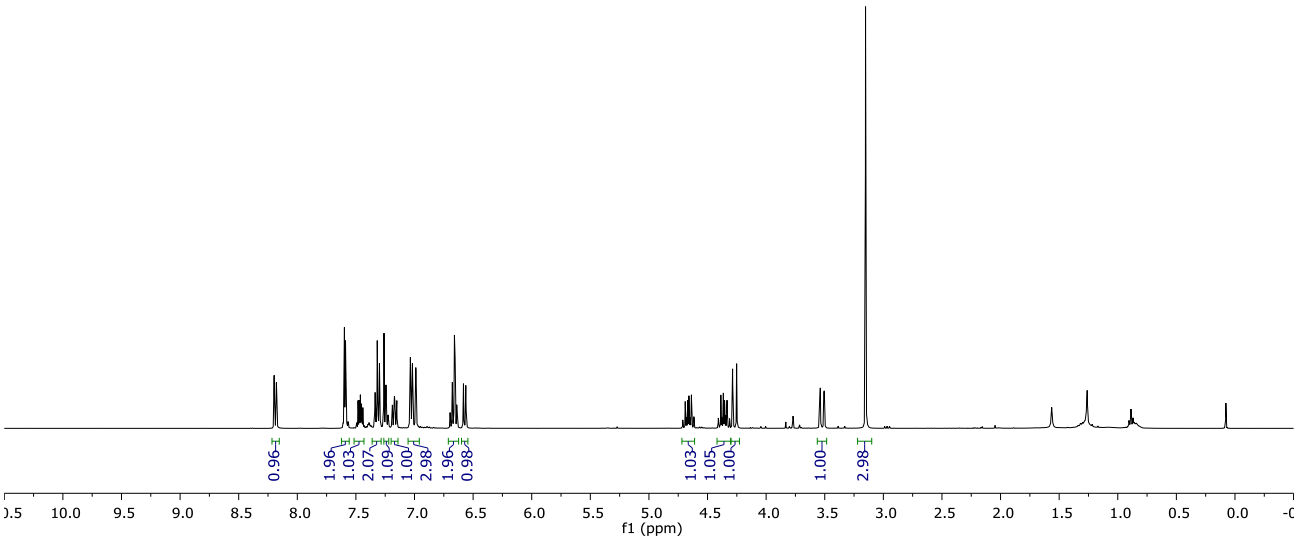
2fa

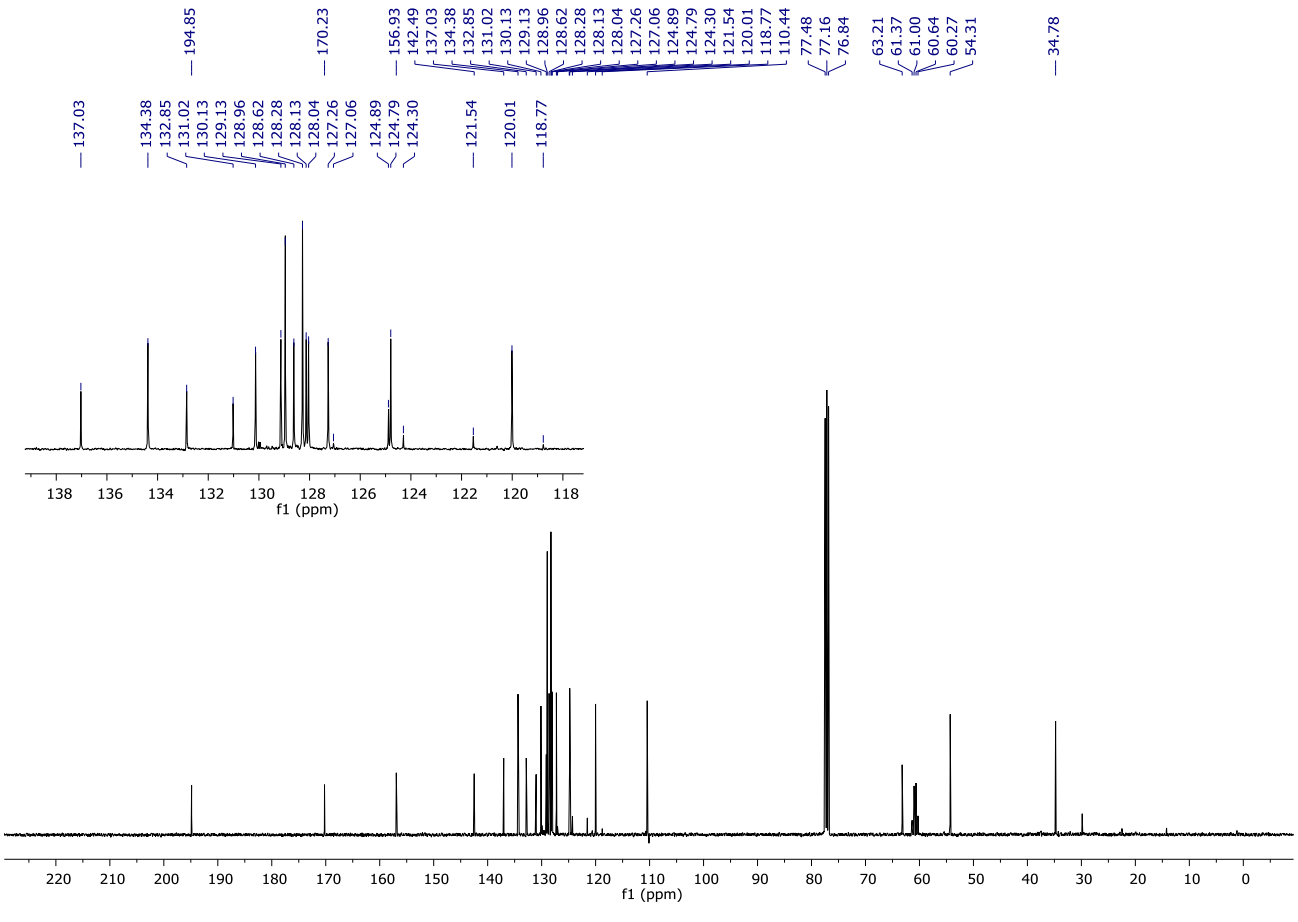

0.96
1.00
1.00
6.03
4.02
1.99
1.04
1.04
1.01
1.00
f1 (ppm)

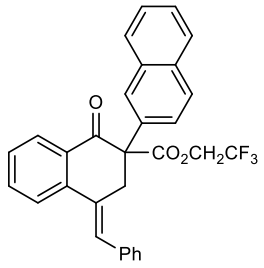

193.46
169.89
141.10
136.85
134.39
133.98
131.12
130.34
130.20
129.12
128.80
128.66
128.55
128.35
128.16
127.96
127.94
126.87
124.59
124.11
121.35
118.59
77.48
77.16
76.84
64.33
61.77
61.40
61.03
60.66
35.24
f1 (ppm)


O
OMe
$CO_2CH_2CF_3$
Ph

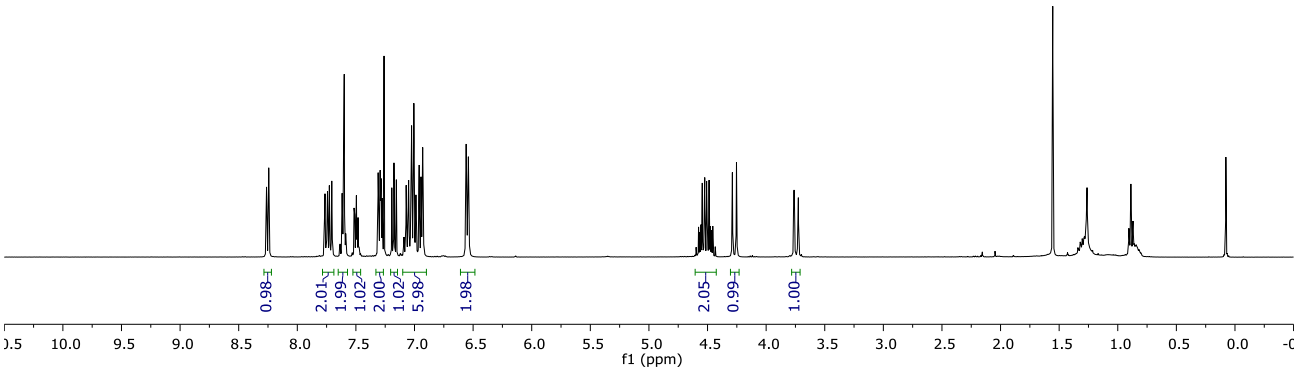
2ga

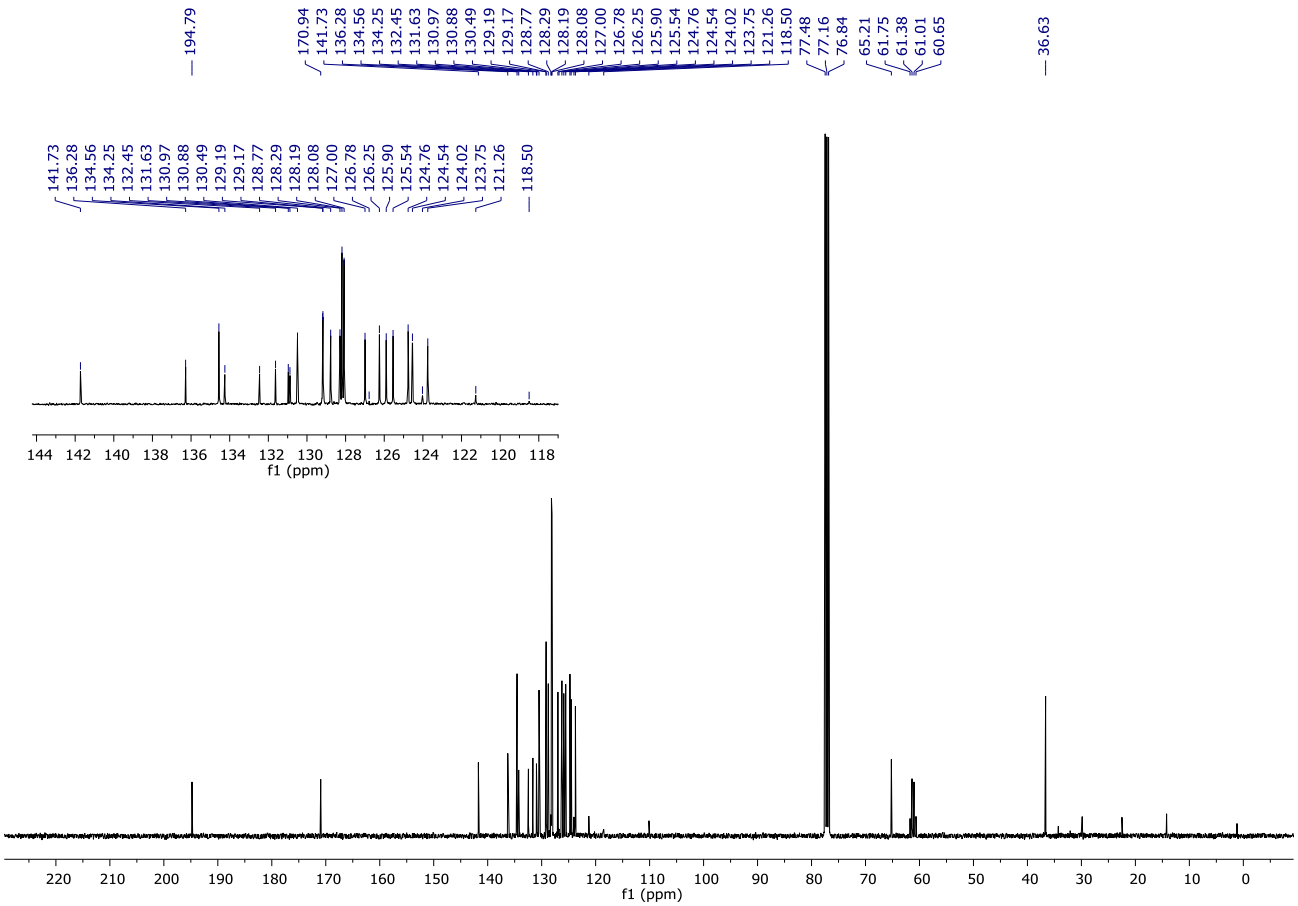

0.96
1.96
1.03
2.07
1.09
1.00
2.98
1.96
0.98
1.03
1.05
1.00
1.00
2.98
f1 (ppm)


194.85
170.23
156.93
142.49
137.03
134.38
132.85
131.02
130.13
129.13
128.96
128.62
128.28
128.13
128.04
127.26
127.06
124.89
124.79
124.30
121.54
120.01
118.77
110.44
77.48
77.16
76.84
63.21
61.37
61.00
60.64
60.27
54.31
34.78
f1 (ppm)


O
CO2CH2CF3
Ph

2ha


0.98
2.01
1.99
1.02
2.00
1.02
5.98
1.98
2.05
0.99
1.00
f1 (ppm)


194.79
170.94
141.73
136.28
134.56
134.25
132.45
131.63
130.97
130.88
130.49
129.19
129.17
128.77
128.29
128.19
128.08
127.00
126.78
126.25
125.90
125.54
124.76
124.54
124.02
123.75
121.26
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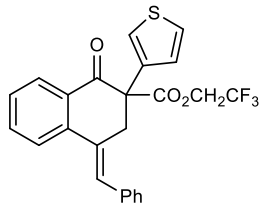
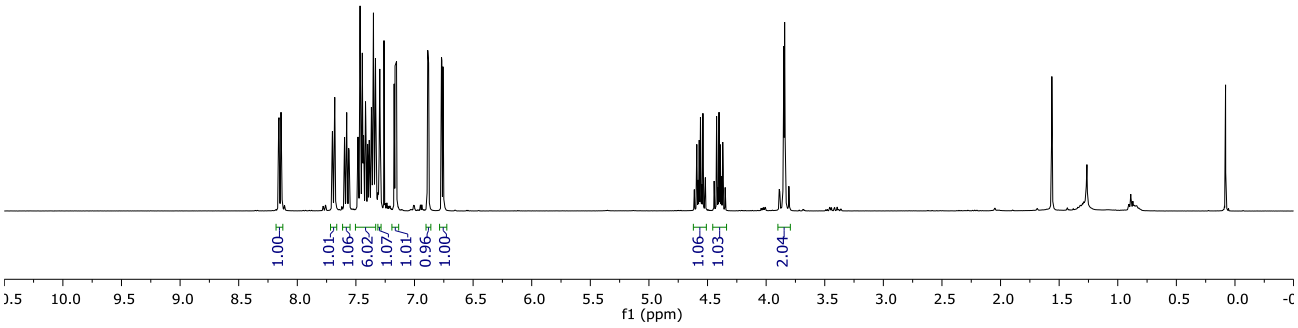
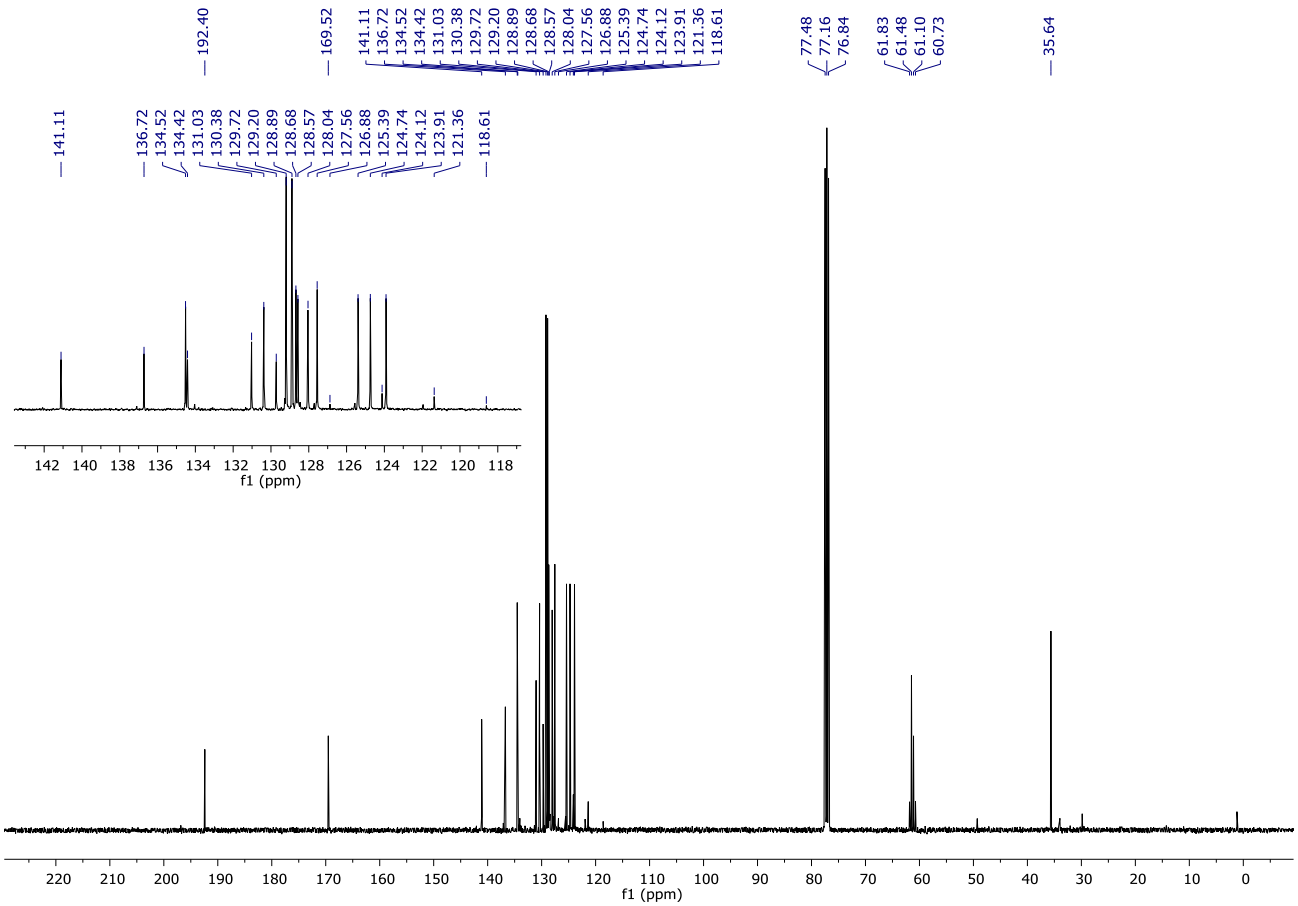
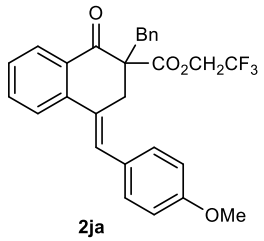
77.16
76.84
65.21
61.75
61.38
61.01
60.65
36.63
f1 (ppm)


S
O
$CO_2CH_2CF_3$
Ph

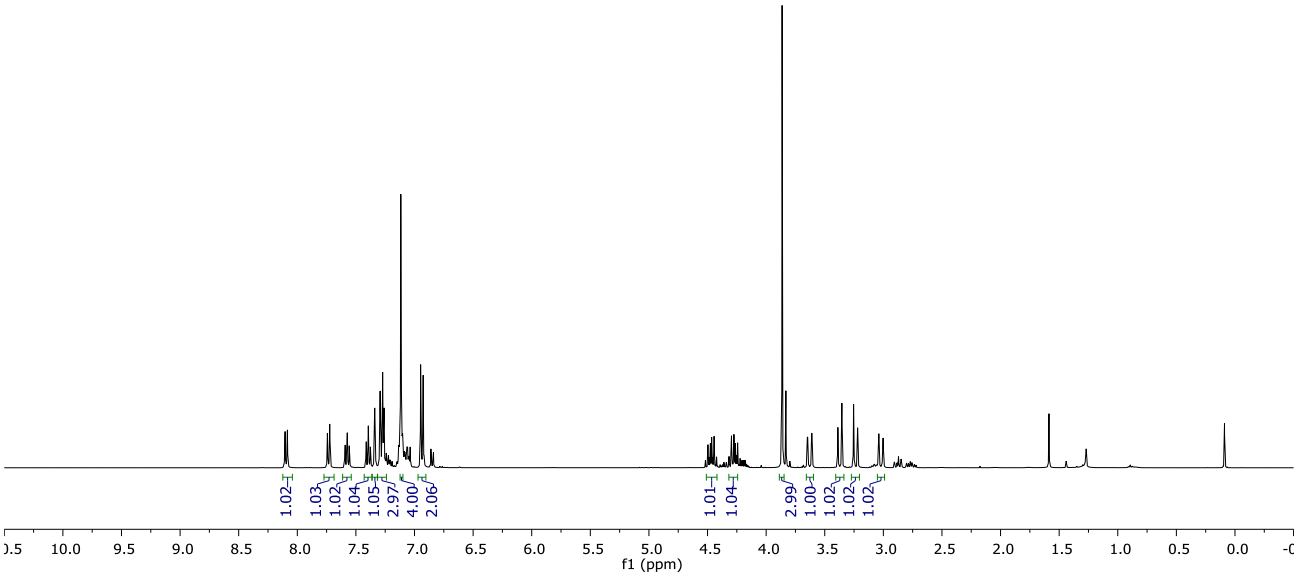
2ia

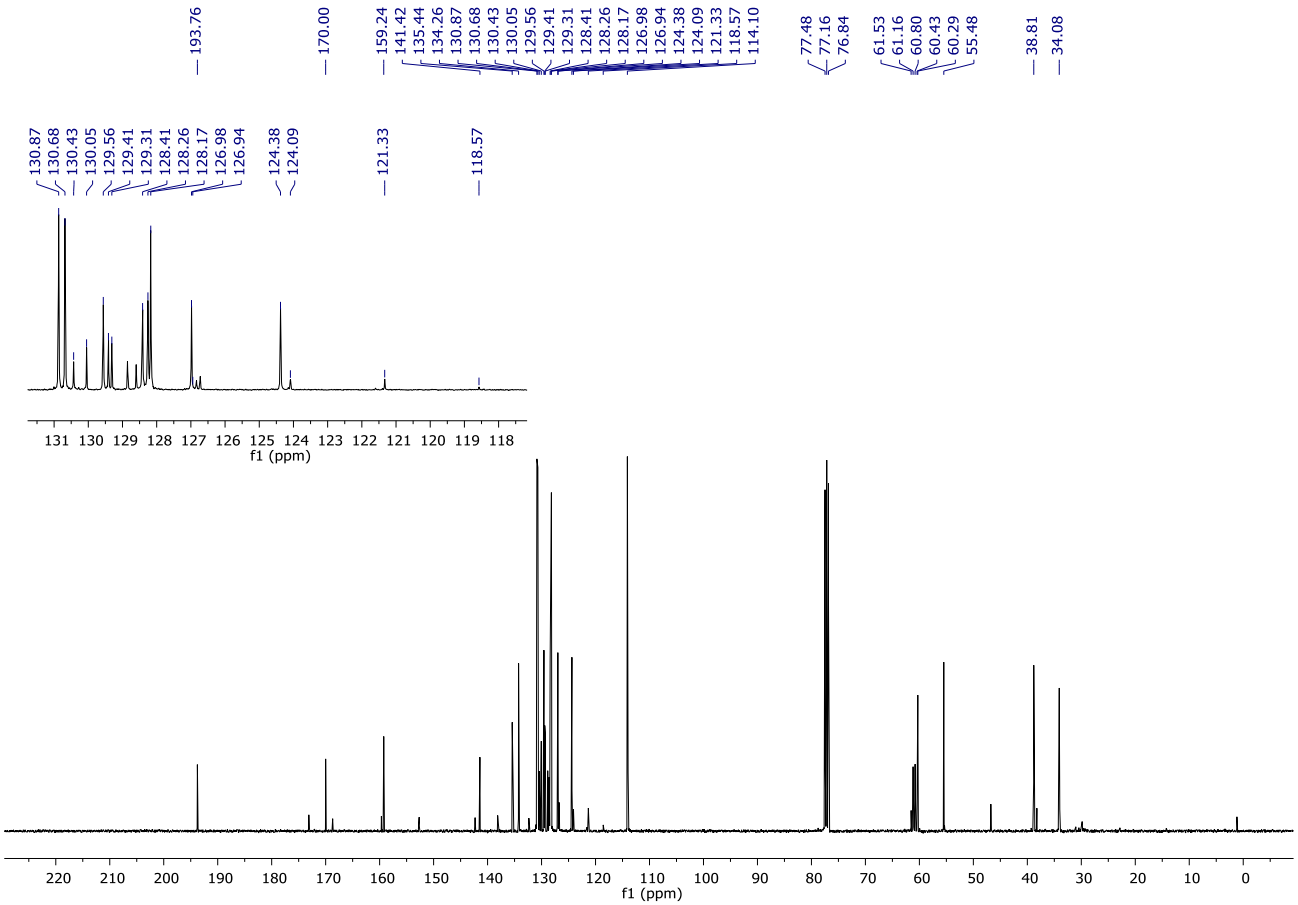

1.00
1.01
1.06
6.02
1.07
1.01
0.96
1.00
1.06
1.03
2.04
f1 (ppm)


192.40
169.52
141.11
136.72
134.52
134.42
131.03
130.38
129.72
129.20
128.89
128.68
128.57
128.04
127.56
126.88
125.39
124.74
124.12
123.91
121.36
118.61
77.48
77.16
76.84
61.83
61.48
61.10
60.73
35.64
f1 (ppm)


O
Bn
$CO_2CH_2CF_3$
OMe

2ja


1.02
1.03
1.02
1.04
1.05
2.97
4.00
2.06
1.01
1.04
2.99
1.00
1.02
1.02
1.02
f1 (ppm)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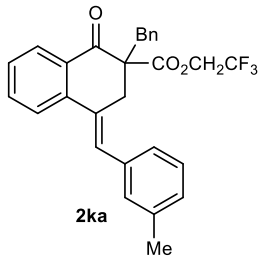
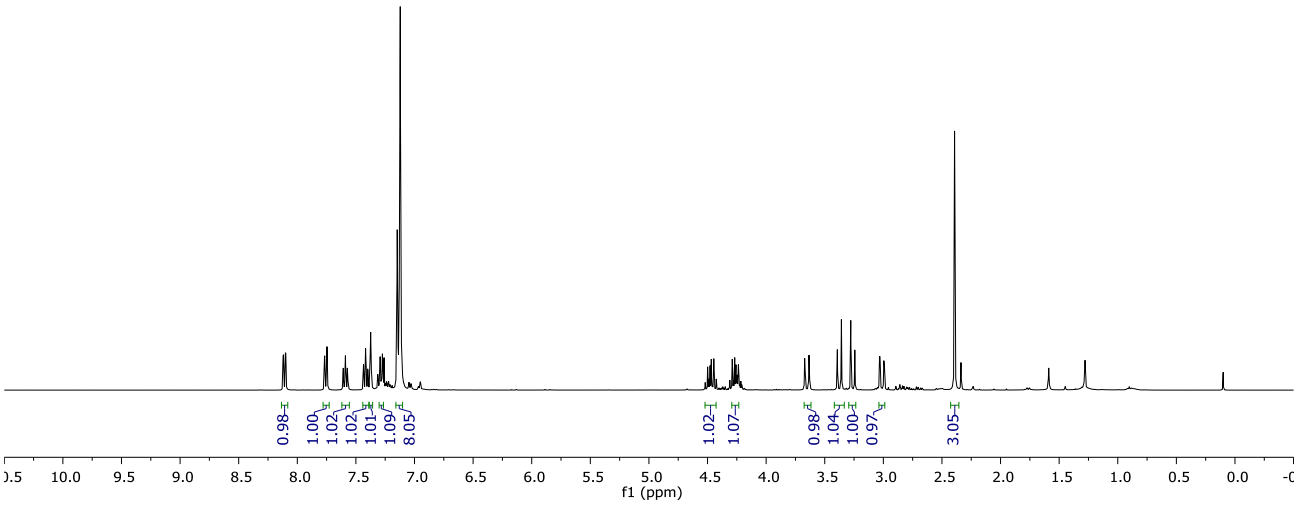
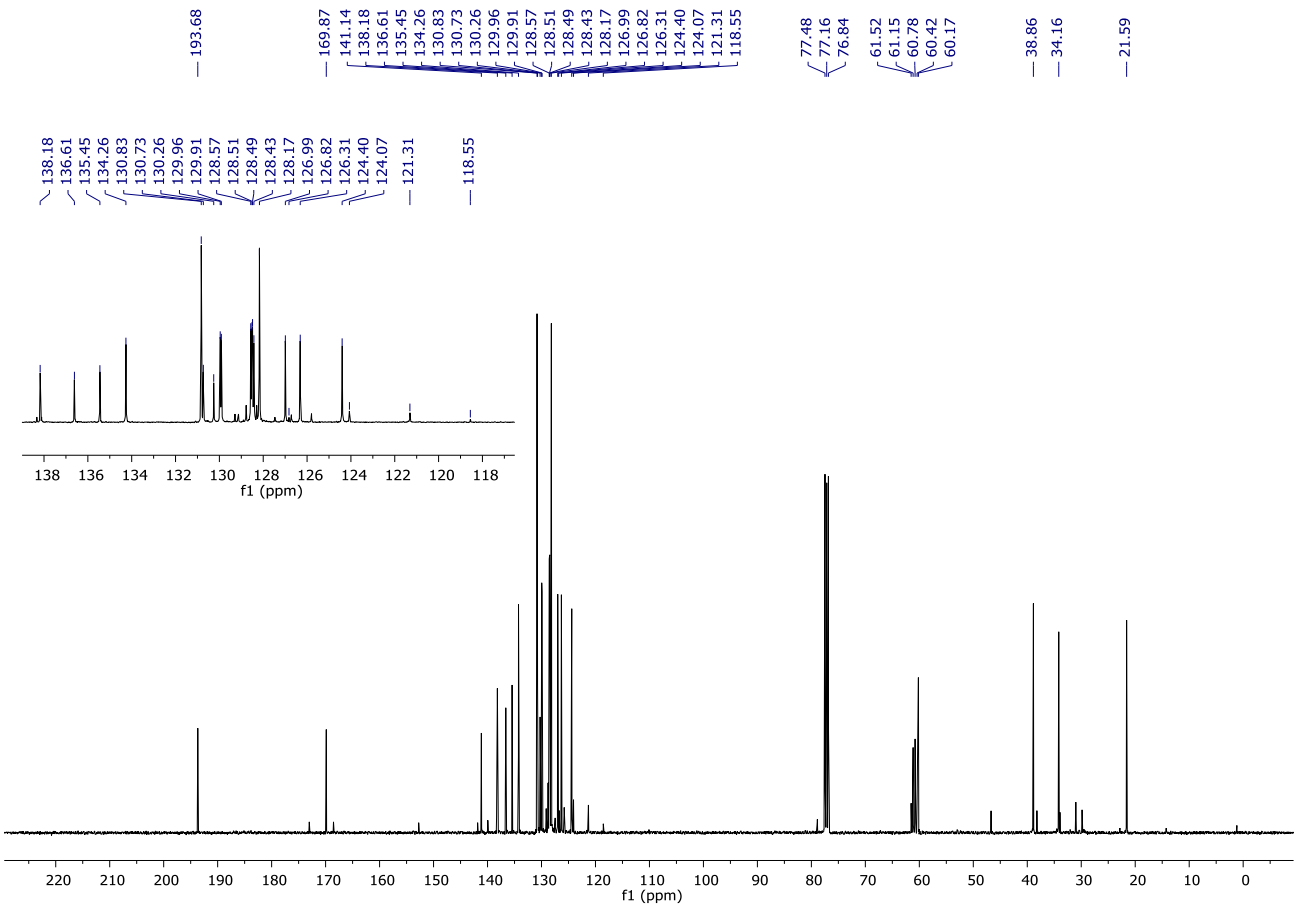
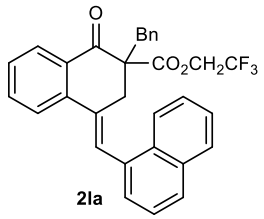
170.00
159.24
141.42
135.44
134.26
130.87
130.68
130.43
130.05
129.56
129.41
129.31
128.41
128.26
128.17
126.98
126.94
124.38
124.09
121.33
118.57
114.10
77.48
77.16
76.84
61.53
61.16
60.80
60.43
60.29
55.48
38.81
34.08
f1 (ppm)

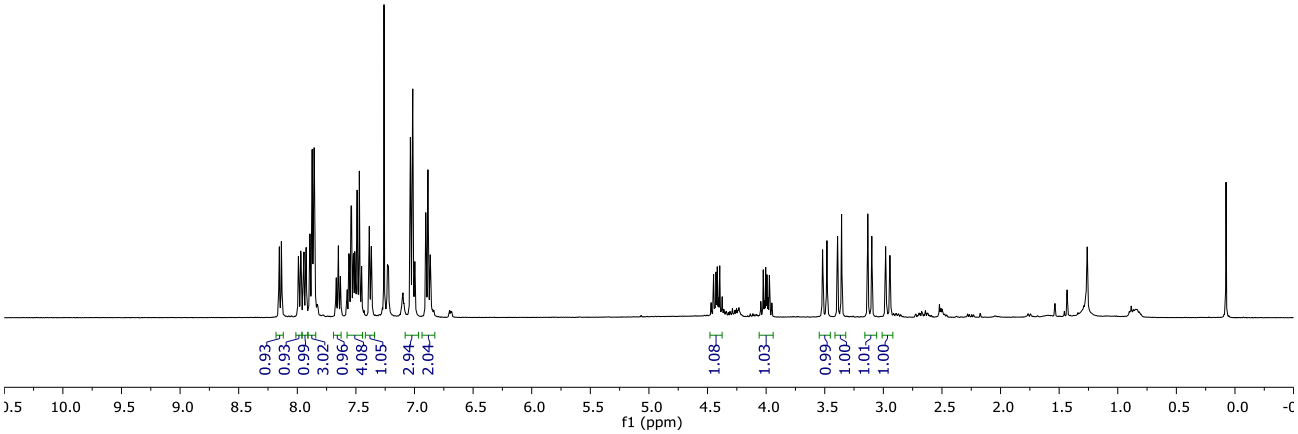

O
Bn
$CO_2CH_2CF_3$
2ka
Me

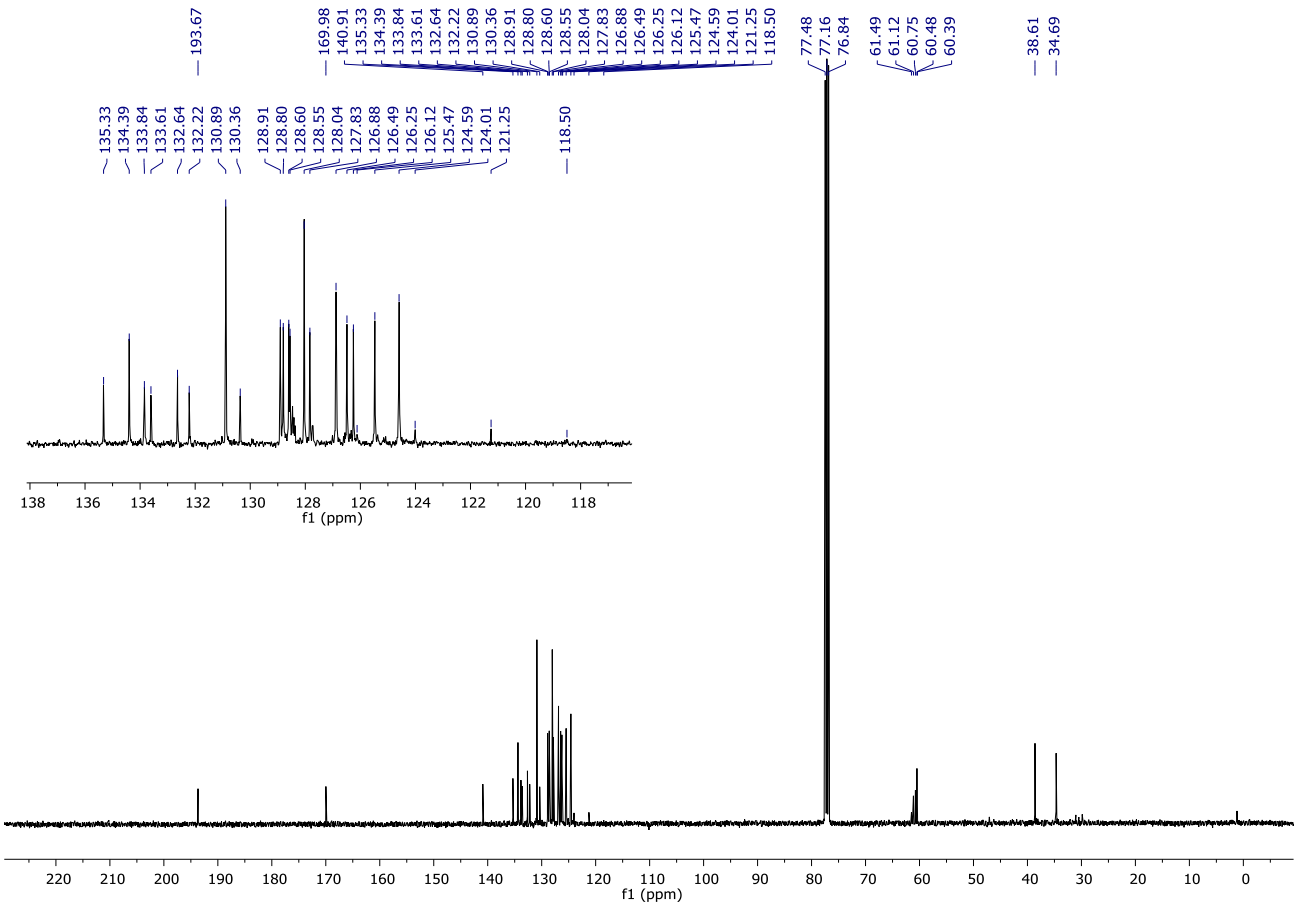

0.98
1.00
1.02
1.01
1.09
8.05
1.02
1.07
0.98
1.04
1.00
0.97
3.05
f1 (ppm)

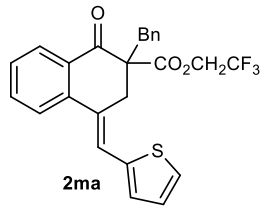

193.68
169.87
141.14
138.18
136.61
135.45
134.26
130.83
130.73
130.26
129.96
129.91
128.57
128.51
128.49
128.43
128.17
126.99
126.82
126.31
124.40
124.07
121.31
118.55
77.48
77.16
76.84
61.52
61.15
60.78
60.42
60.17
38.86
34.16
21.59
f1 (ppm)


O
Bn
$CO_2CH_2CF_3$

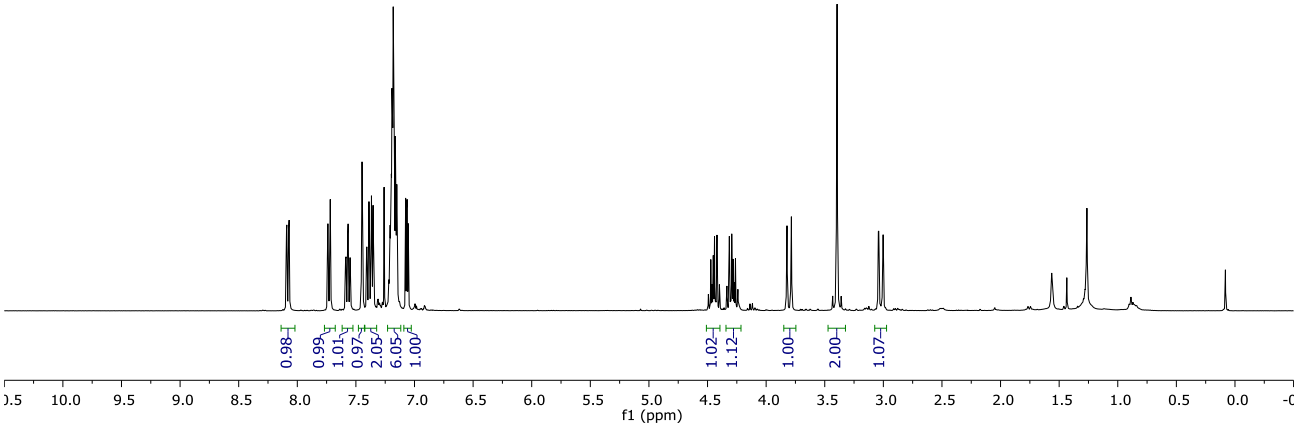
2la

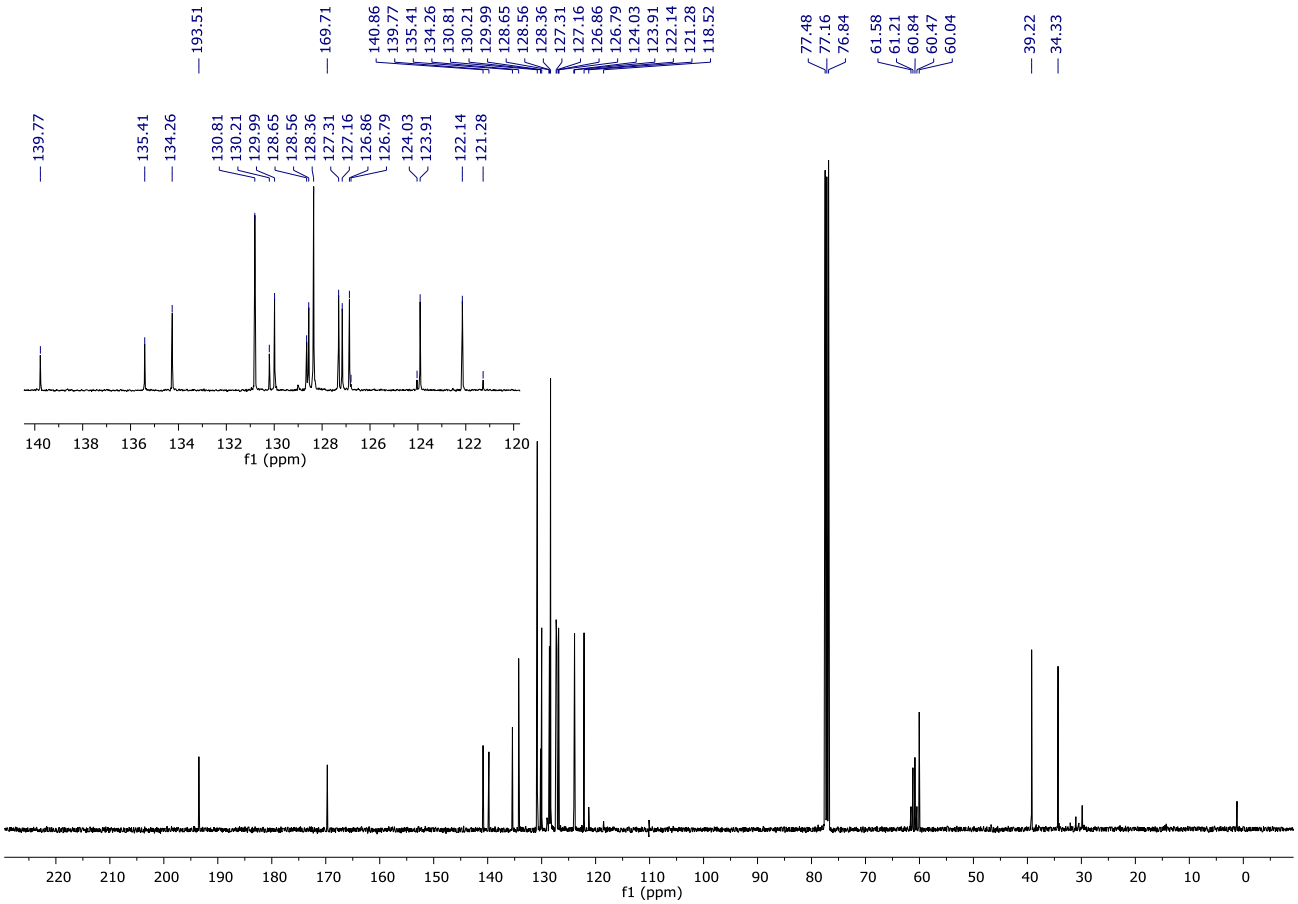

0.93
0.93
0.99
3.02
0.96
4.08
1.05
2.94
2.04
1.08
1.03
0.99
1.00
1.01
1.00
f1 (ppm)

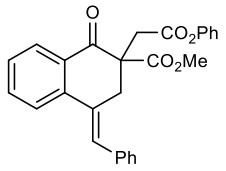

193.67
169.98
140.91
135.33
134.39
133.84
133.61
132.64
132.22
130.89
130.36
128.91
128.80
128.60
128.55
128.04
127.83
126.88
126.49
126.25
126.12
125.47
124.59
124.01
121.25
118.50
77.48
77.16
76.84
61.49
61.12
60.75
60.48
60.39
38.61
34.69
f1 (ppm)


O
Bn
$CO_2CH_2CF_3$
S

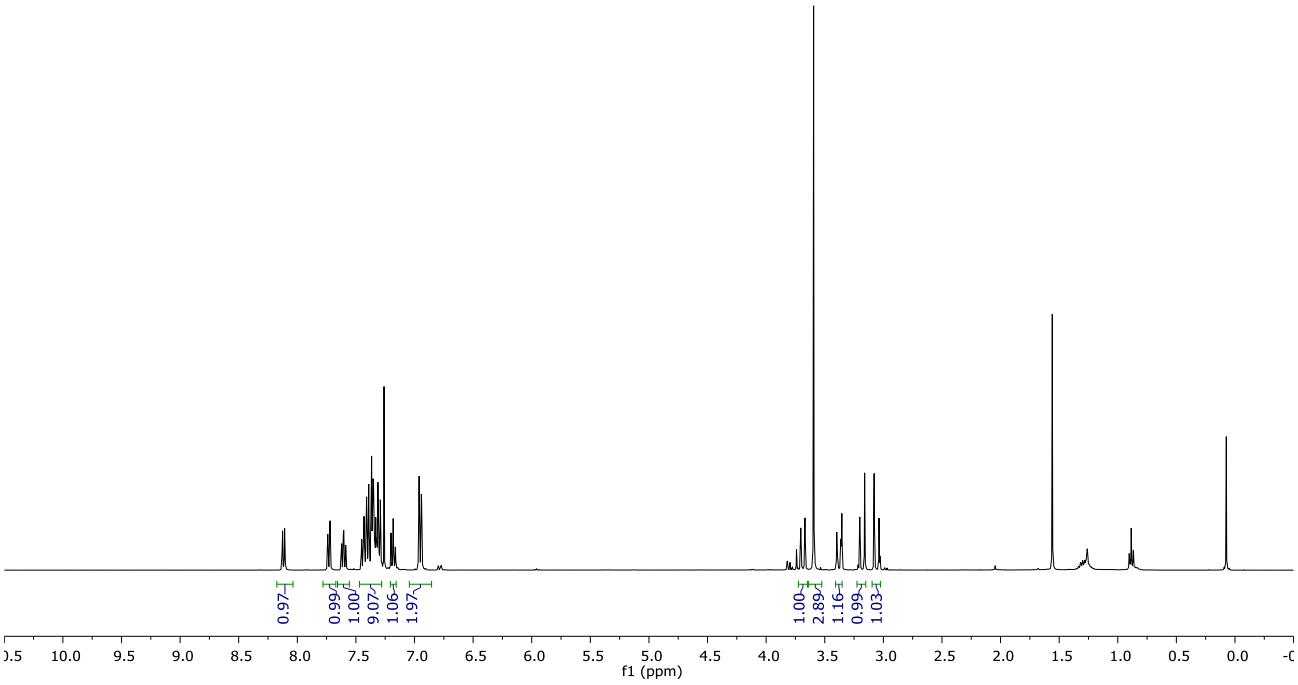
2ma

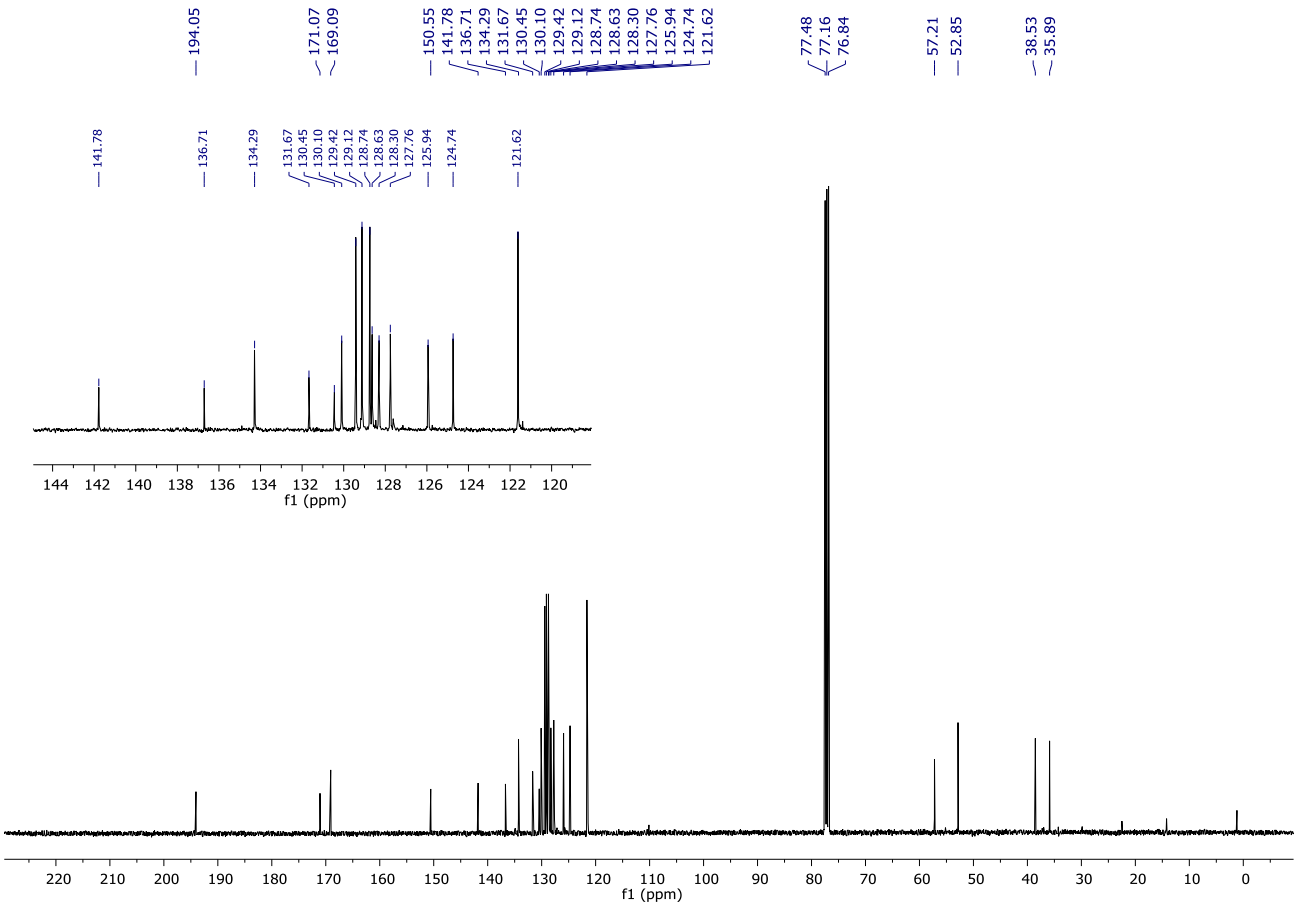

0.98
0.99
1.01
0.97
2.05
6.05
1.00
1.02
1.12
1.00
2.00
1.07
f1 (ppm)

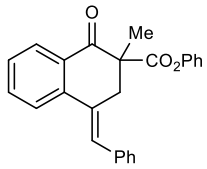

193.51
169.71
140.86
139.77
135.41
134.26
130.81
130.21
129.99
128.65
128.56
128.36
127.31
127.16
126.86
126.79
124.03
123.91
122.14
121.28
118.52
77.48
77.16
76.84
61.58
61.21
60.84
60.47
60.04
39.22
34.33
f1 (ppm)


O
CO2Ph
CO2Me
Ph

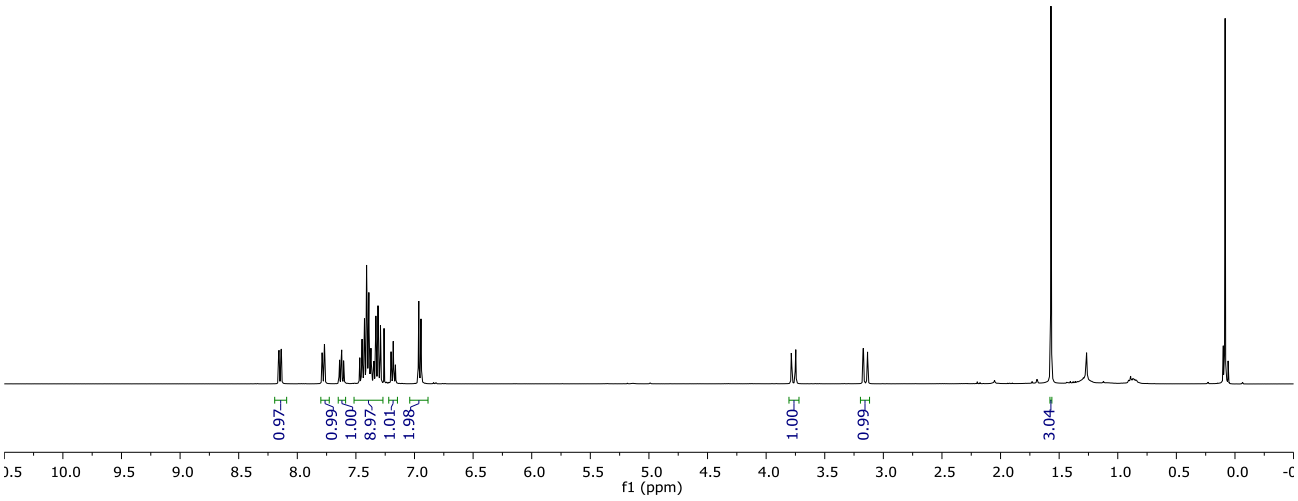
2na

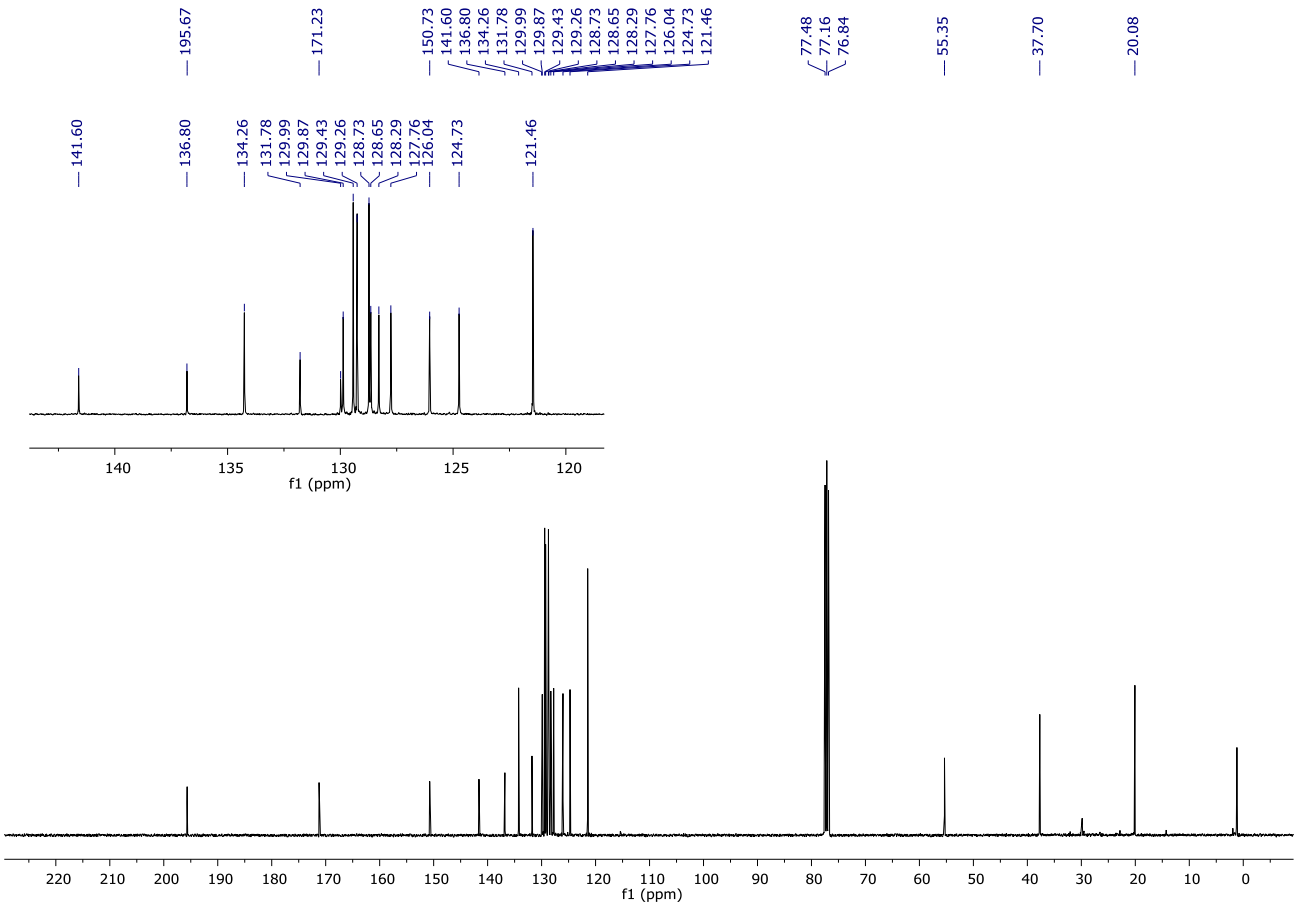

0.97
0.99
1.00
9.07
1.06
1.97
1.00
2.89
1.16
0.99
1.03
f1 (ppm)

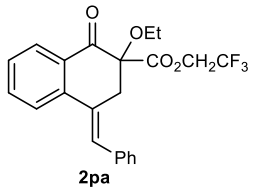

194.05
171.07
169.09
150.55
141.78
136.71
134.29
131.67
130.45
130.10
129.42
129.12
128.74
128.63
128.30
127.76
125.94
124.74
121.62
77.48
77.16
76.84
57.21
52.85
38.53
35.89
f1 (ppm)


O
Me
CO2Ph
Ph

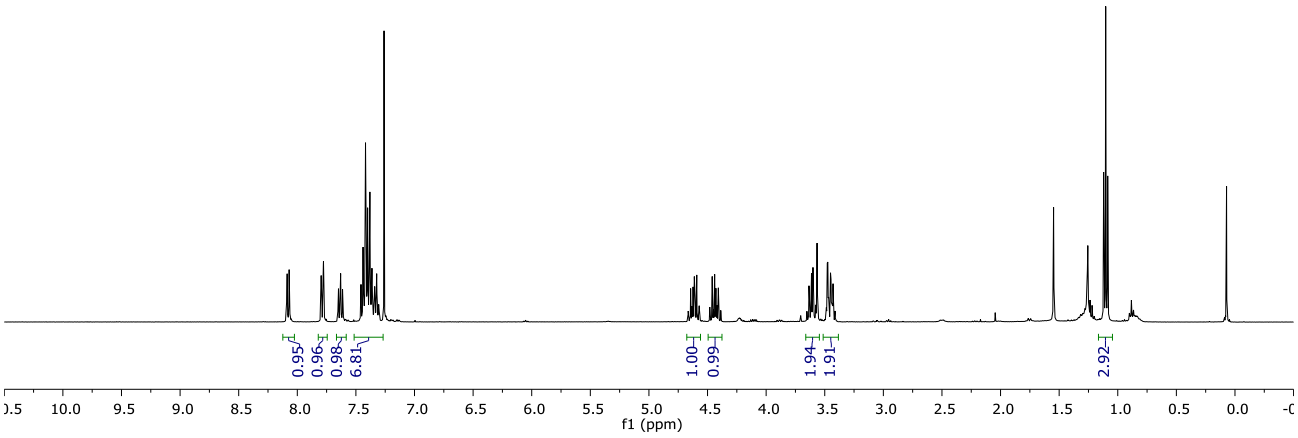
2oa

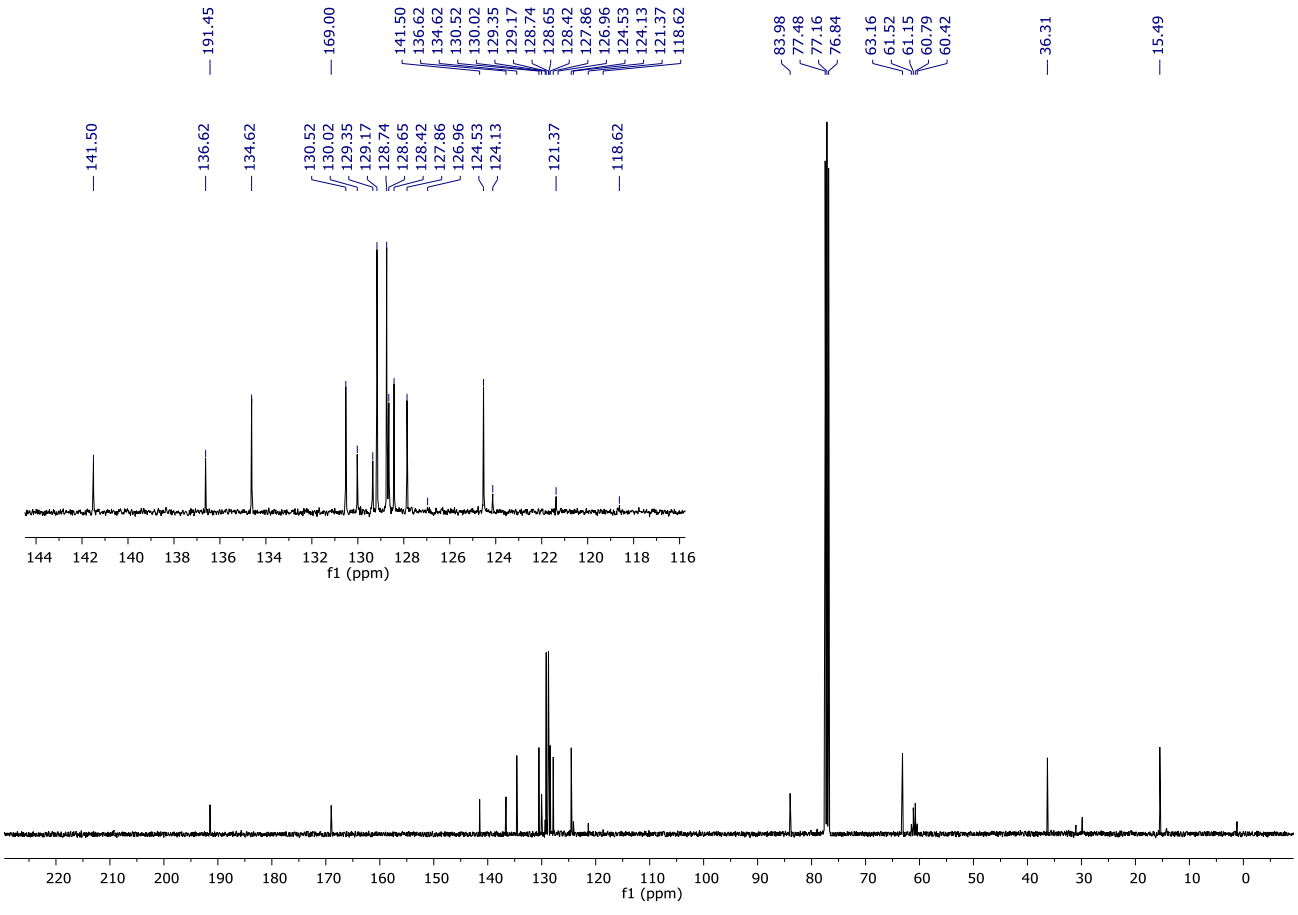

0.97
0.99
1.00
8.97
1.01
1.98
1.00
0.99
3.04
f1 (ppm)

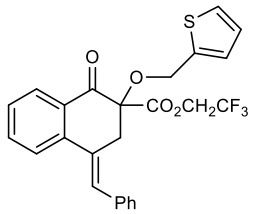

195.67
171.23
150.73
141.60
136.80
134.26
131.78
129.99
129.87
129.43
129.26
128.73
128.65
128.29
127.76
126.04
124.73
121.46
77.48
77.16
76.84
55.35
37.70
20.08
f1 (ppm)


O
OEt
$CO_2CH_2CF_3$
Ph

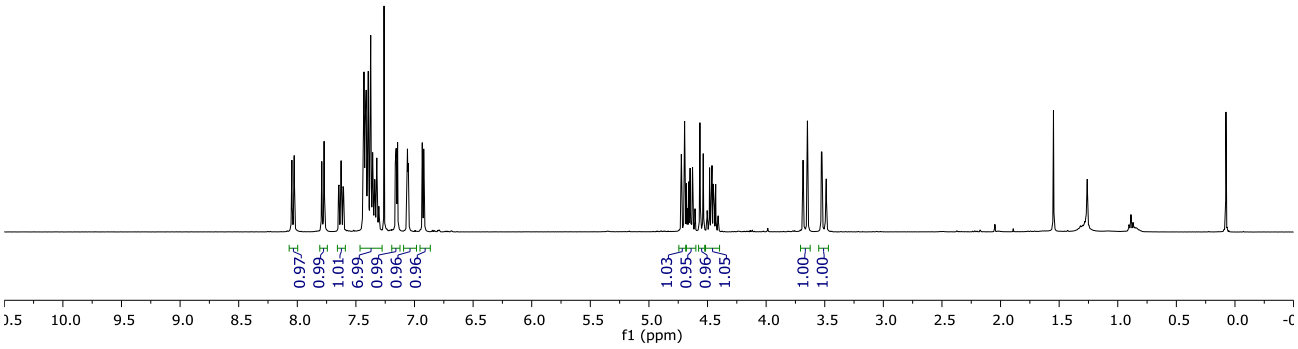
2pa

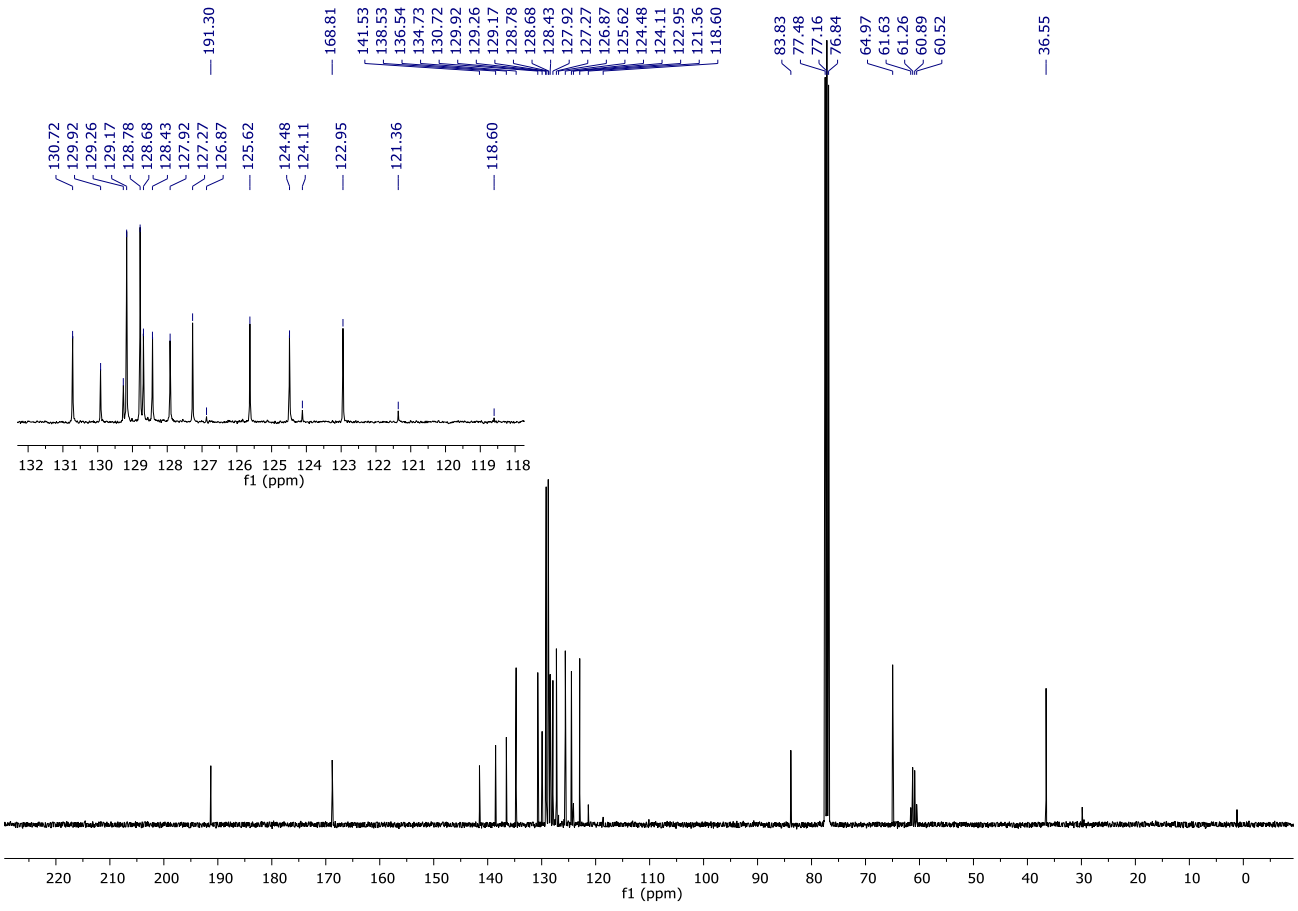

0.95
0.96
0.98
6.81
1.00
0.99
1.94
1.91
2.92
f1 (ppm)

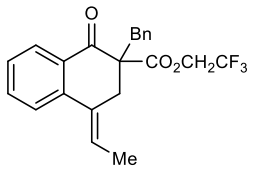

191.45
169.00
141.50
136.62
134.62
130.52
130.02
129.35
129.17
128.74
128.65
128.42
127.86
126.96
124.53
124.13
121.37
118.62
83.98
77.48
77.16
76.84
63.16
61.52
61.15
60.79
60.42
36.31
15.49
f1 (ppm)


S
O
O
CO2CH2CF3
Ph

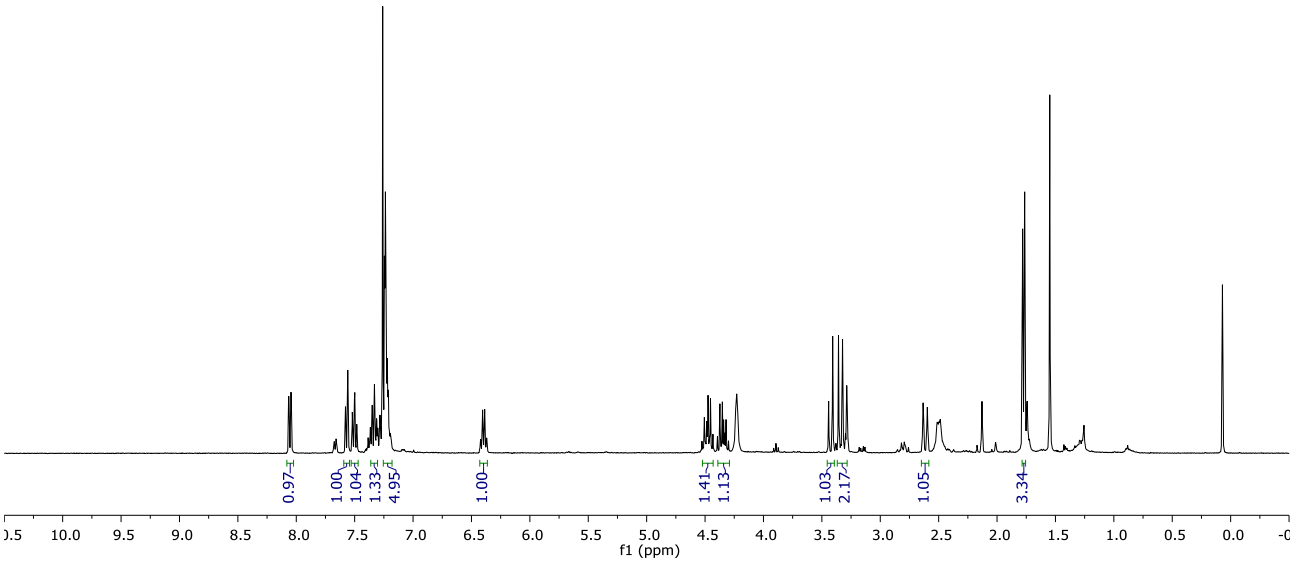
2qa

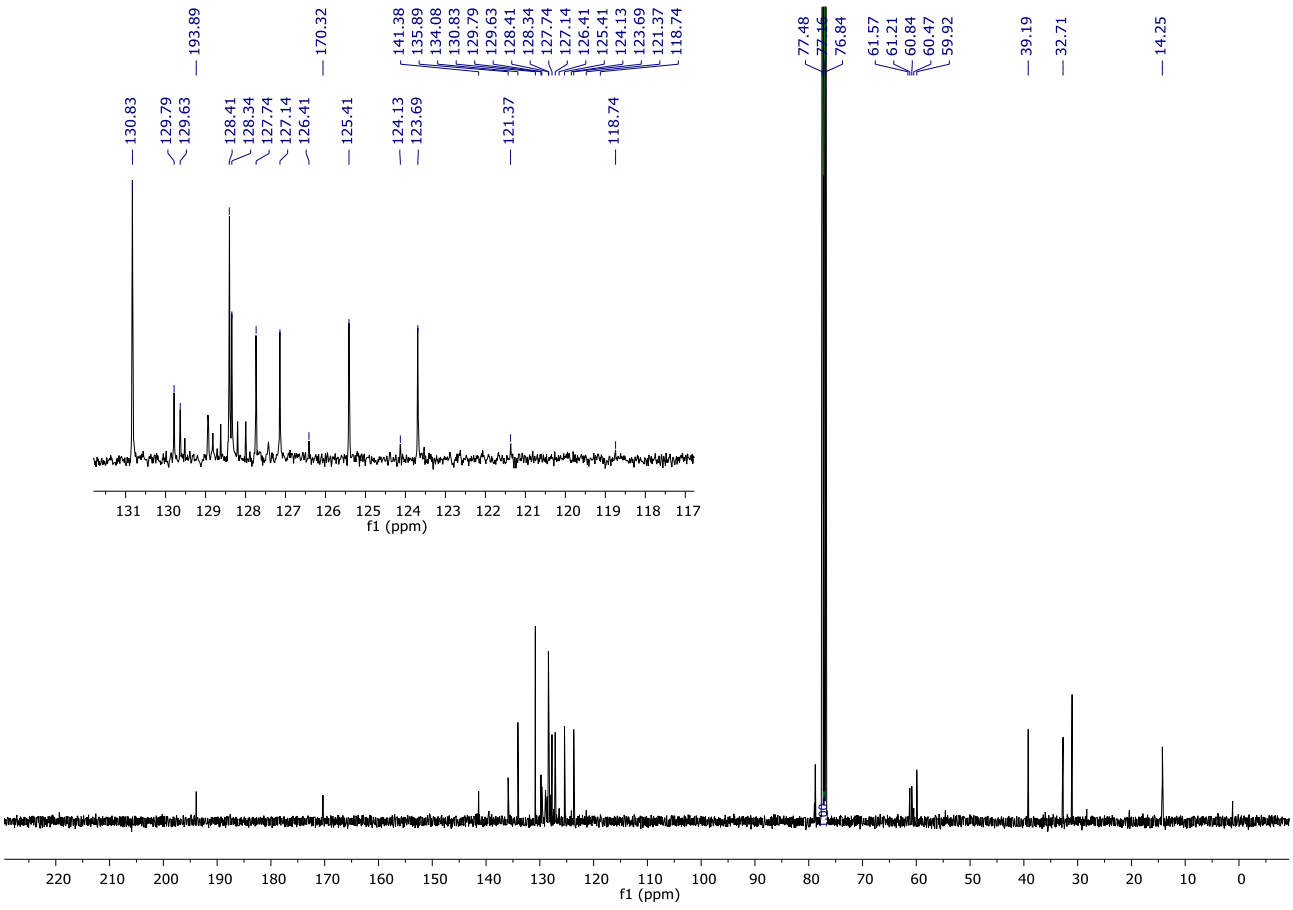

0.97
0.99
1.01
6.99
0.99
0.96
0.96
1.03
0.95
0.96
1.05
1.00
1.00
f1 (ppm)

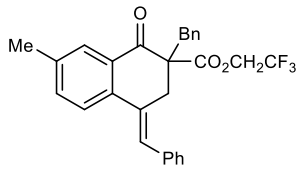

191.30
168.81
141.53
138.53
136.54
134.73
130.72
129.92
129.26
129.17
128.78
128.68
128.43
127.92
127.27
126.87
125.62
124.48
124.11
122.95
121.36
118.60
83.83
77.48
77.16
76.84
64.97
61.63
61.26
60.89
60.52
36.55
f1 (ppm)


O
Bn
$CO_2CH_2CF_3$
Me

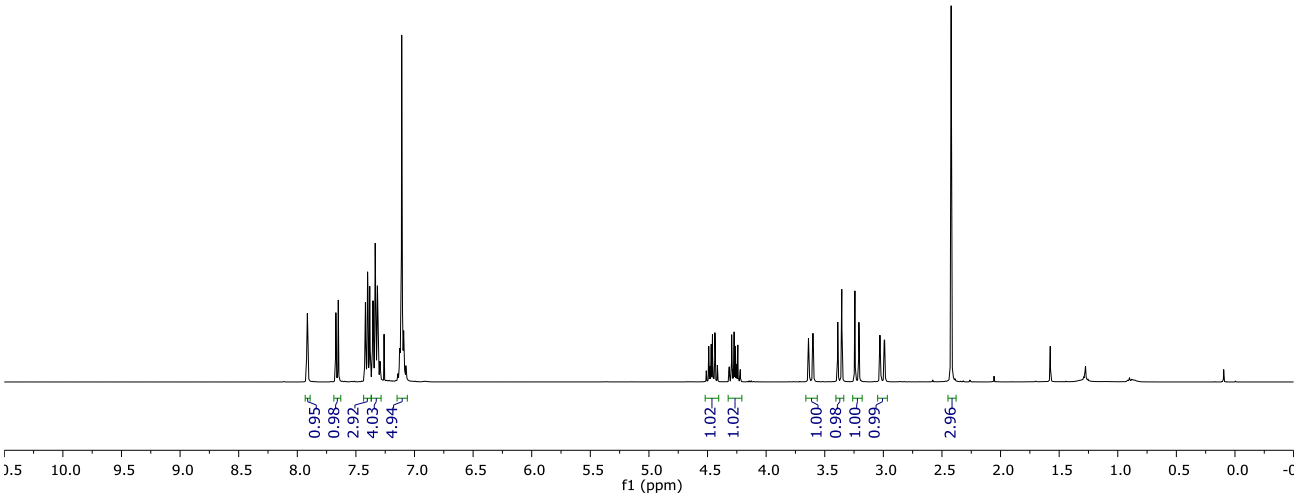
2ra
(impure)

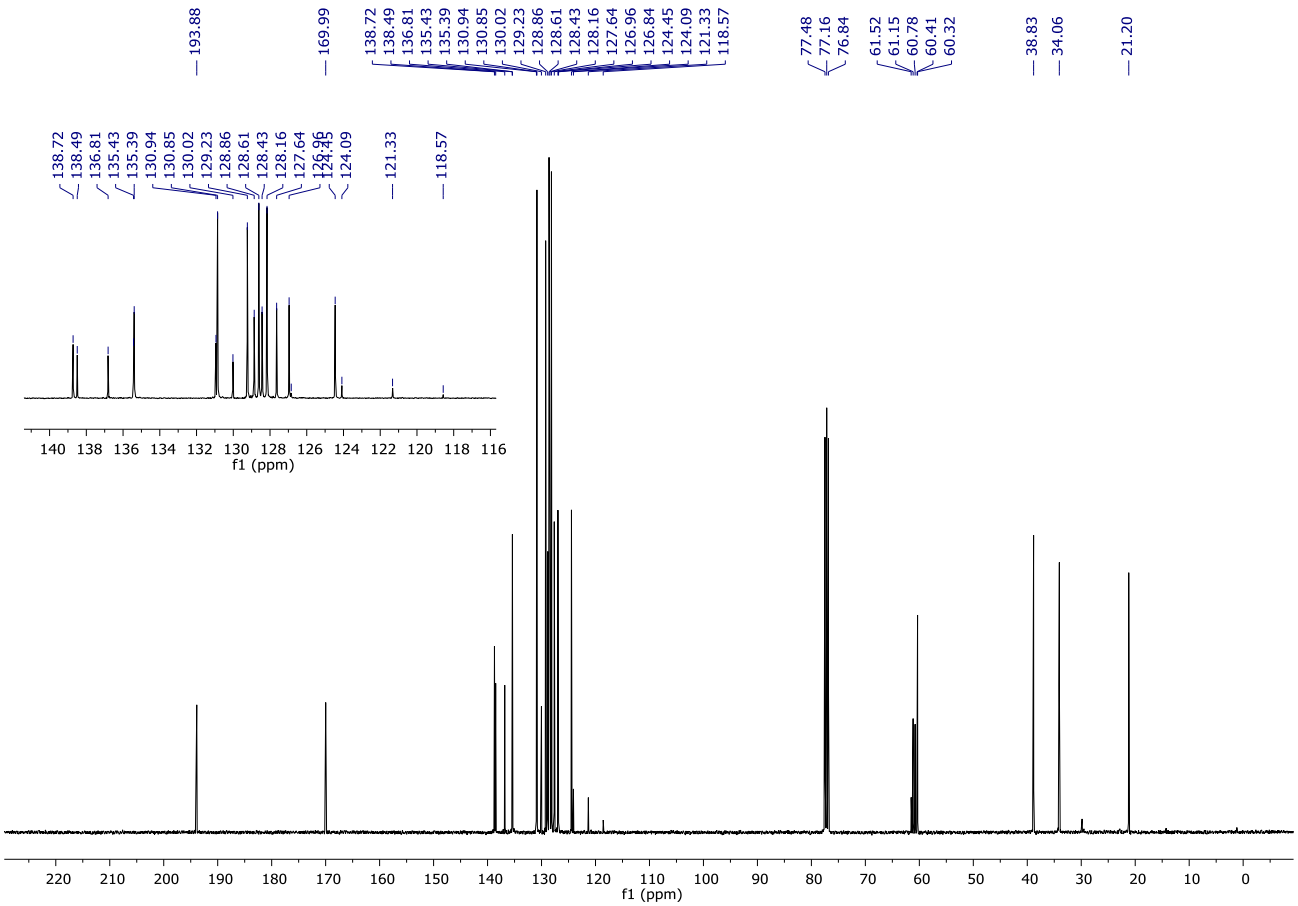

0.97
1.00
1.04
1.33
4.95
1.00
1.41
1.13
1.03
2.17
1.05
3.34
f1 (ppm)

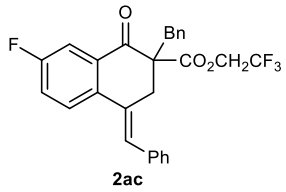

193.89
170.32
141.38
135.89
134.08
130.83
129.79
129.63
128.41
128.34
127.74
127.14
126.41
125.41
124.13
123.69
121.37
118.74
77.48
77.16
76.84
61.57
61.21
60.84
60.47
59.92
39.19
32.71
14.25
f1 (ppm)


O
Bn
Me
$CO_2CH_2CF_3$
Ph

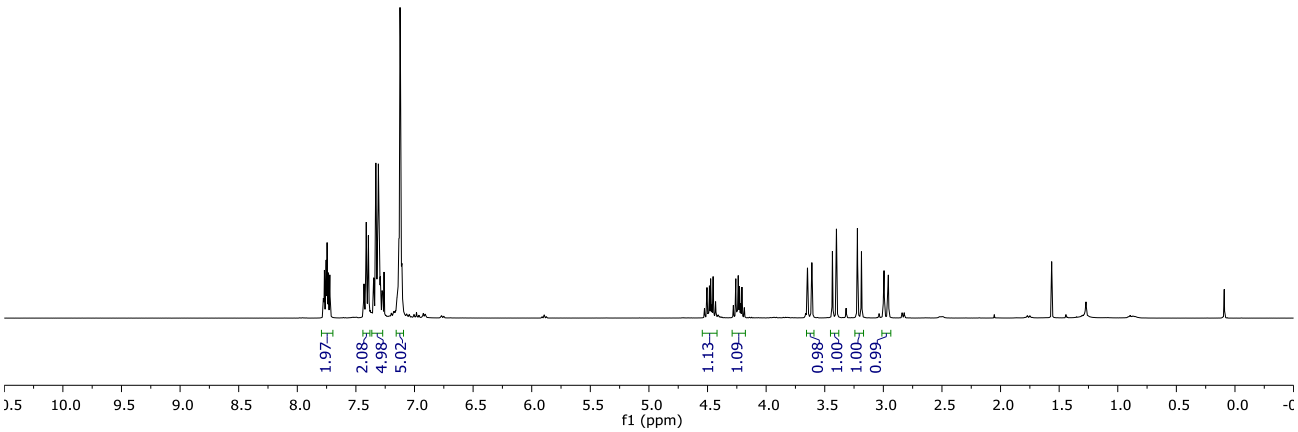
2ab

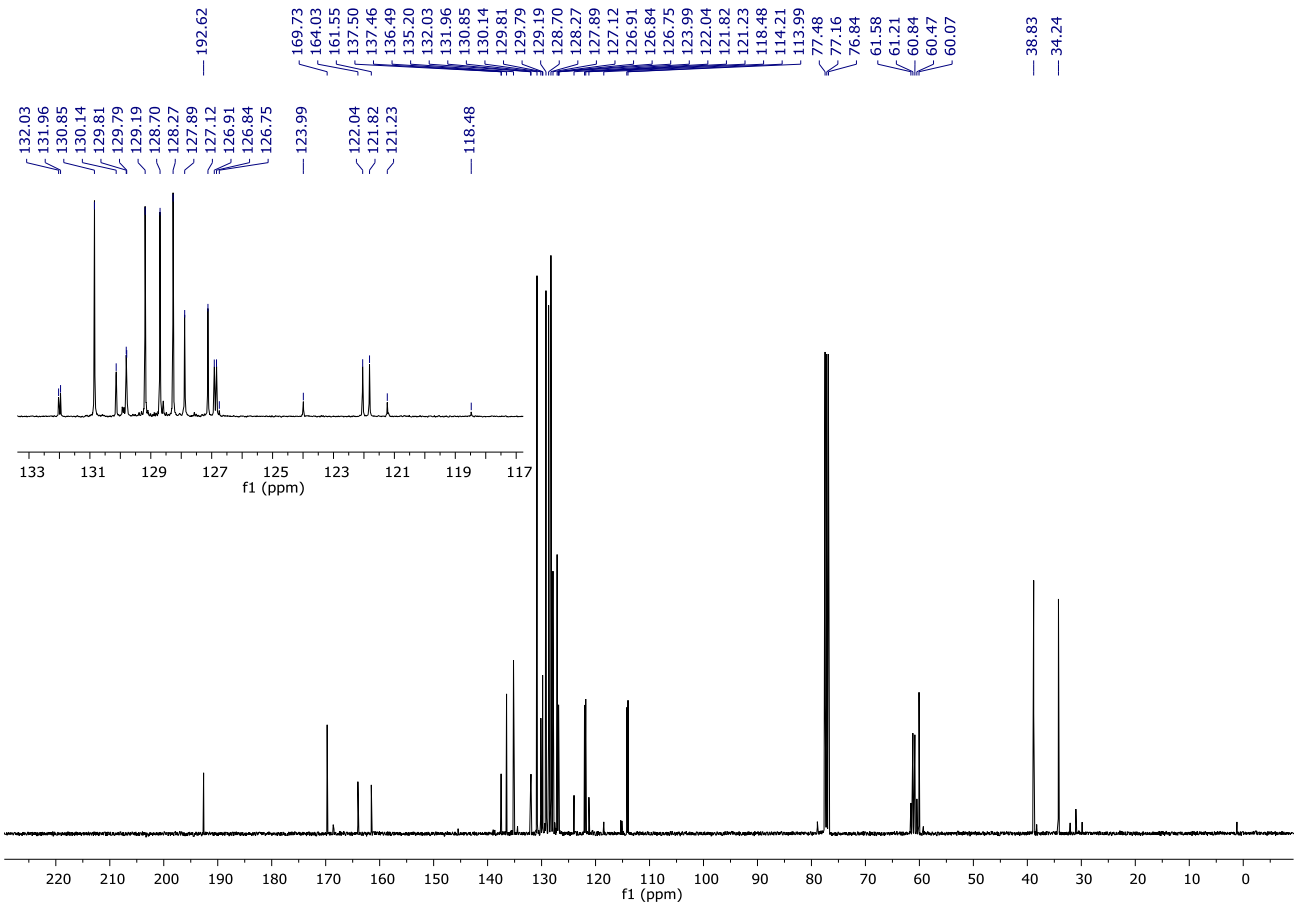

0.95
0.98
2.92
4.03
4.94
1.02
1.02
1.00
0.98
1.00
0.99
2.96
f1 (ppm)

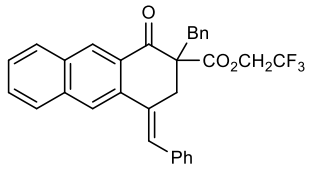

193.88
169.99
138.72
138.49
136.81
135.43
135.39
130.94
130.85
130.02
129.23
128.86
128.61
128.43
128.16
127.64
126.96
126.84
124.45
124.09
121.33
118.57
77.48
77.16
76.84
61.52
61.15
60.78
60.41
60.32
38.83
34.06
21.20
f1 (ppm)


O
Bn
F
$CO_2CH_2CF_3$
Ph

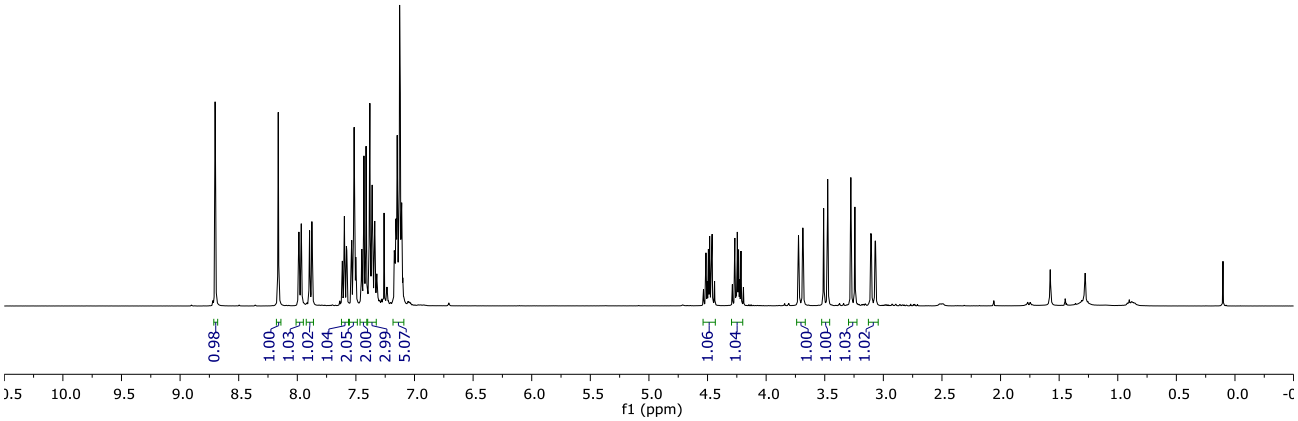
2ac

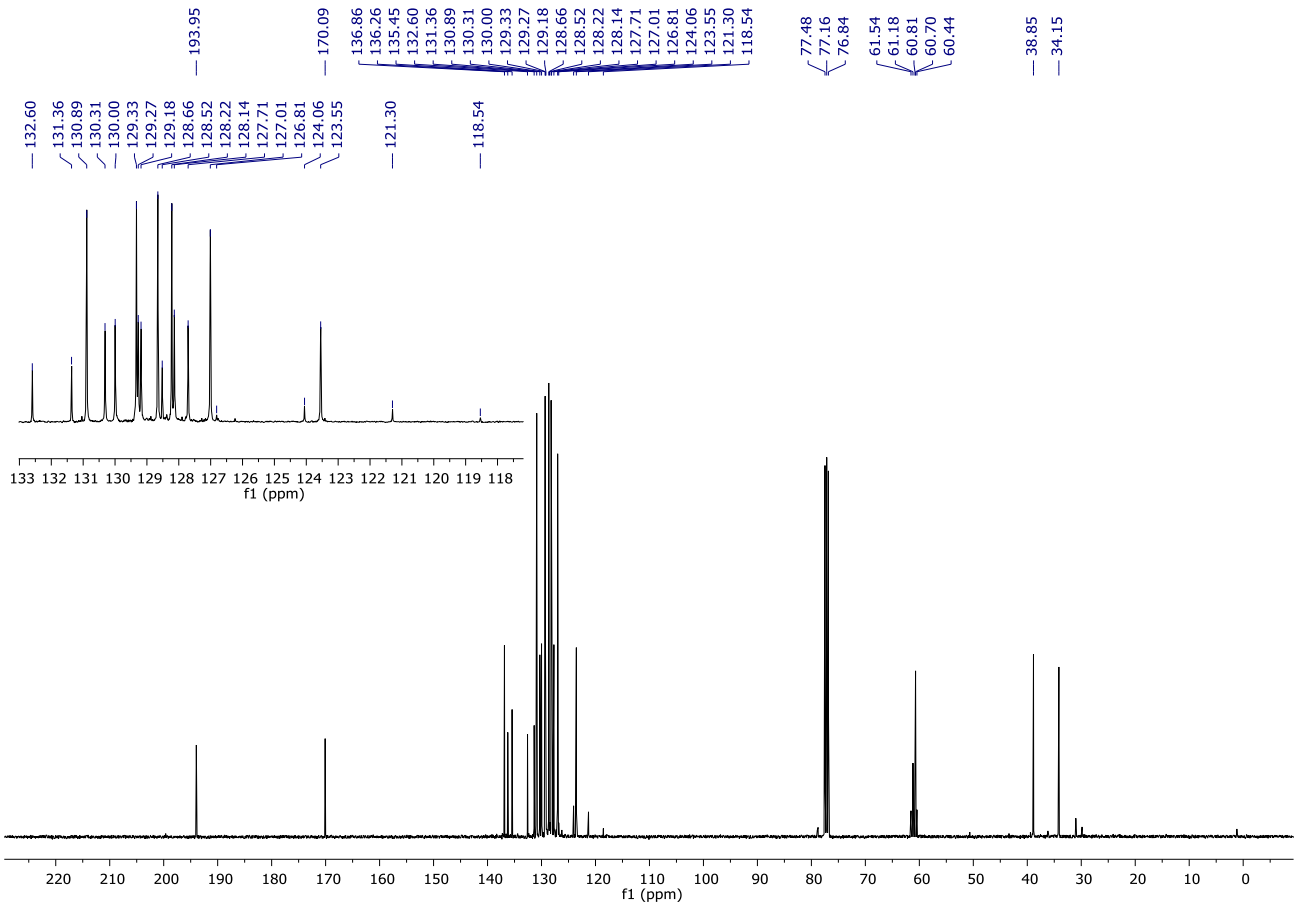

1.97
2.08
4.98
5.02
1.13
1.09
0.98
1.00
1.00
0.99
f1 (ppm)

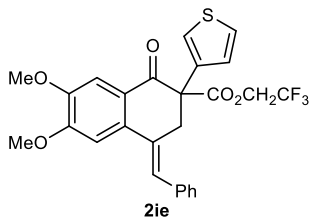

192.62
169.73
164.03
161.55
137.50
137.46
136.49
135.20
132.03
131.96
130.85
130.14
129.81
129.79
129.19
128.70
128.27
127.89
127.12
126.91
126.84
126.75
123.99
122.04
121.82
121.23
118.48
114.21
113.99
77.48
77.16
76.84
61.58
61.21
60.84
60.47
60.07
38.83
34.24
f1 (ppm)


O
Bn
CO2CH2CF3
Ph

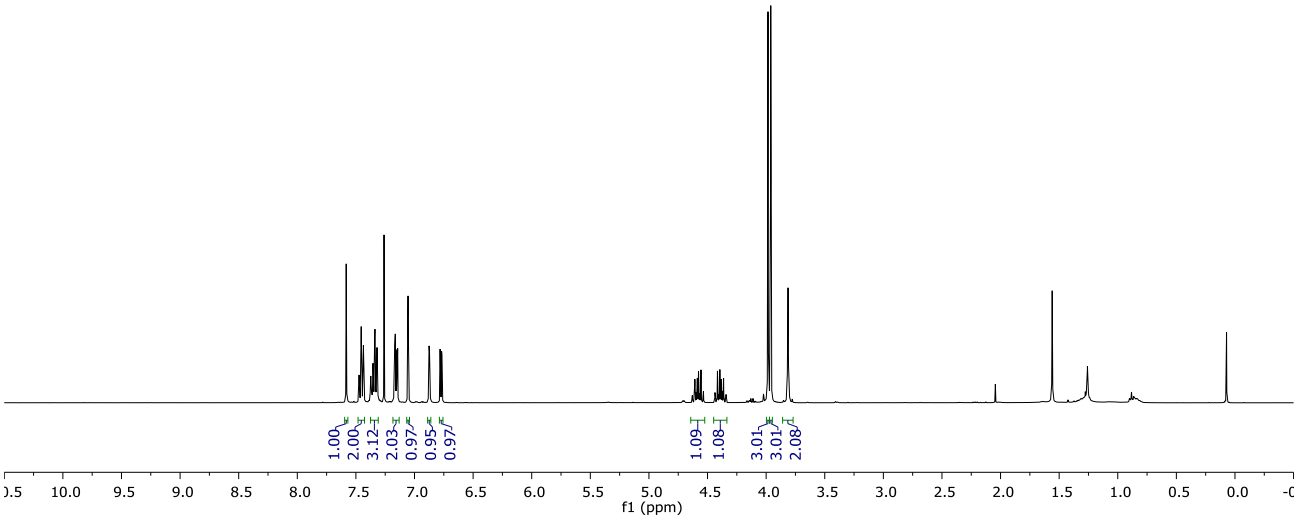
2ad

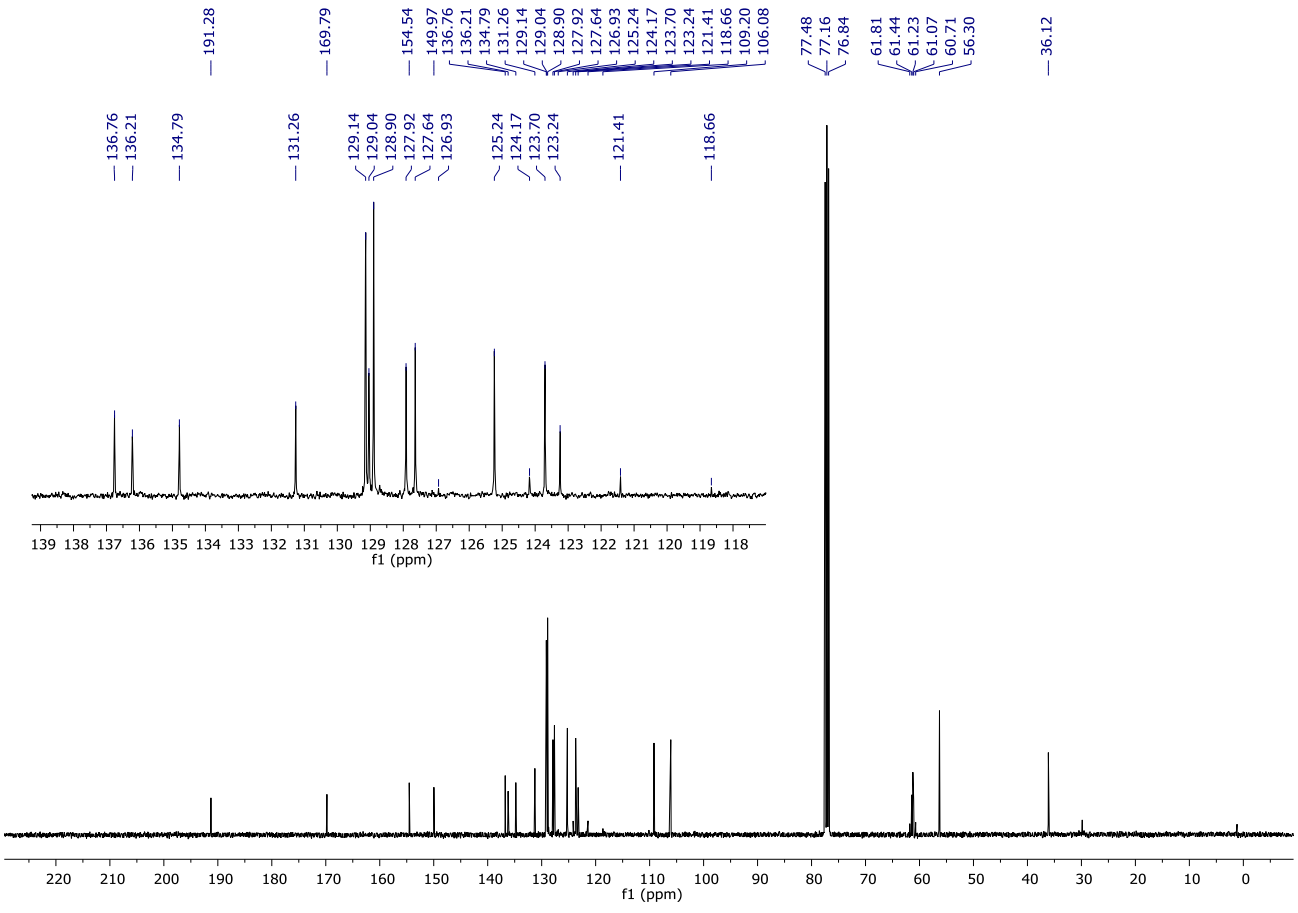

0.98
1.00
1.03
1.02
1.04
2.05
2.00
2.99
5.07
1.06
1.04
1.00
1.00
1.03
1.02
f1 (ppm)

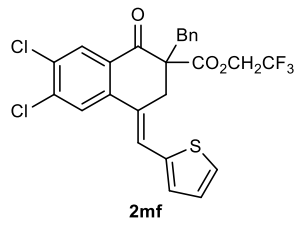

193.95
170.09
136.86
136.26
135.45
132.60
131.36
130.89
130.31
130.00
129.33
129.27
129.18
128.66
128.52
128.22
128.14
127.71
127.01
126.81
124.06
123.55
121.30
118.54
77.48
77.16
76.84
61.54
61.18
60.81
60.70
60.44
38.85
34.15
f1 (ppm)


S
O
MeO
MeO
$CO_2CH_2CF_3$
Ph

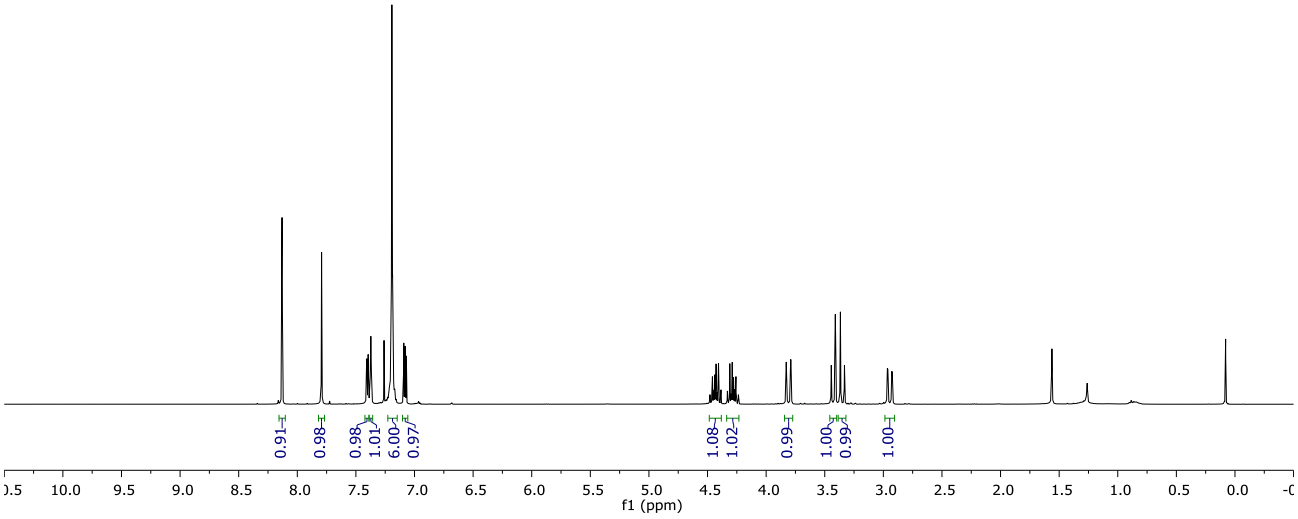
2ie

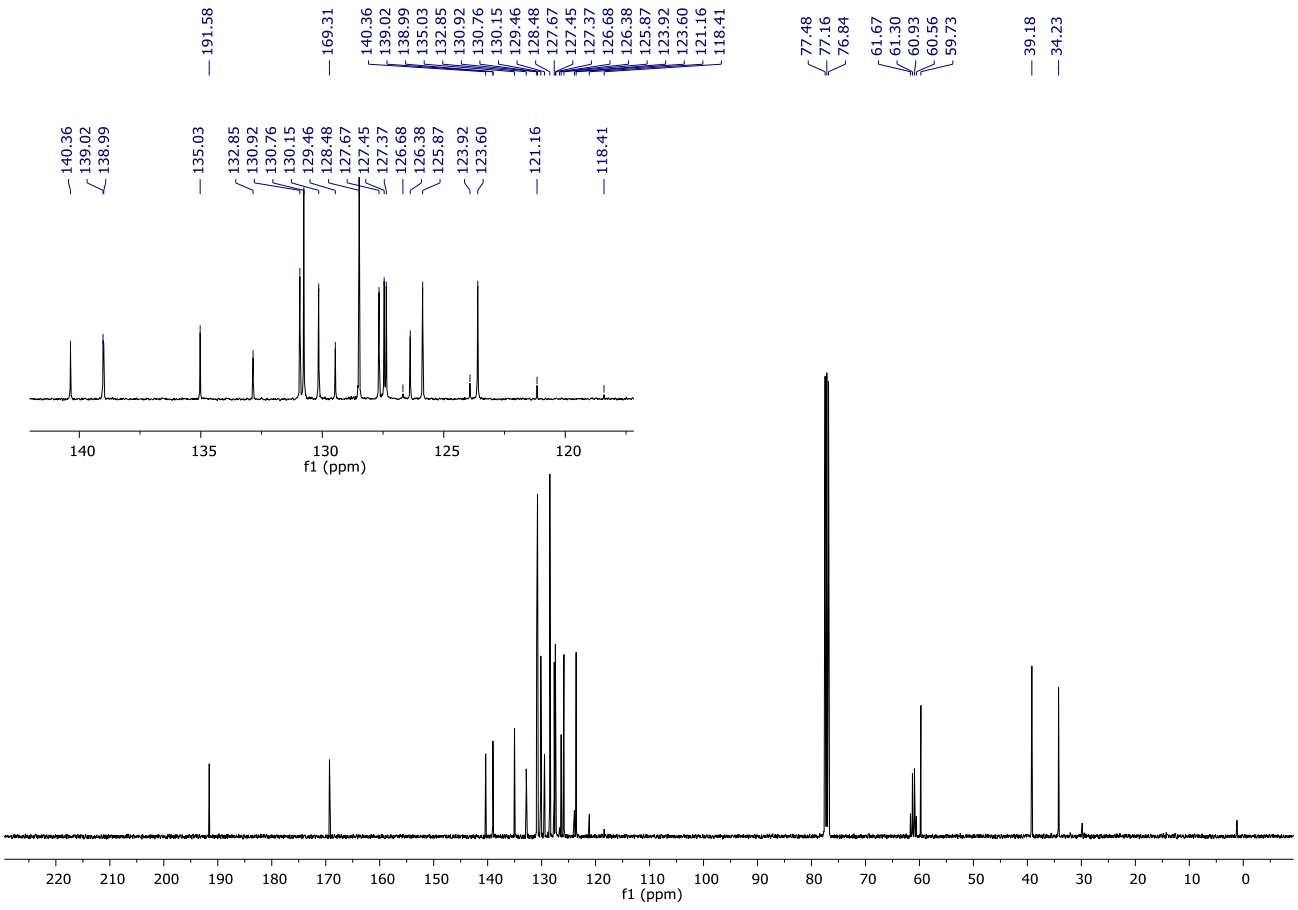

1.00
2.00
3.12
2.03
0.97
0.95
0.97
1.09
1.08
3.01
3.01
2.08
f1 (ppm)

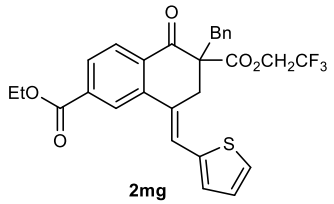

191.28
169.79
154.54
149.97
136.76
136.21
134.79
131.26
129.14
129.04
128.90
127.92
127.64
126.93
125.24
124.17
123.70
123.24
121.41
118.66
109.20
106.08
77.48
77.16
76.84
61.81
61.44
61.23
61.07
60.71
56.30
36.12
f1 (ppm)


O
Bn
Cl
$CO_2CH_2CF_3$
Cl
S

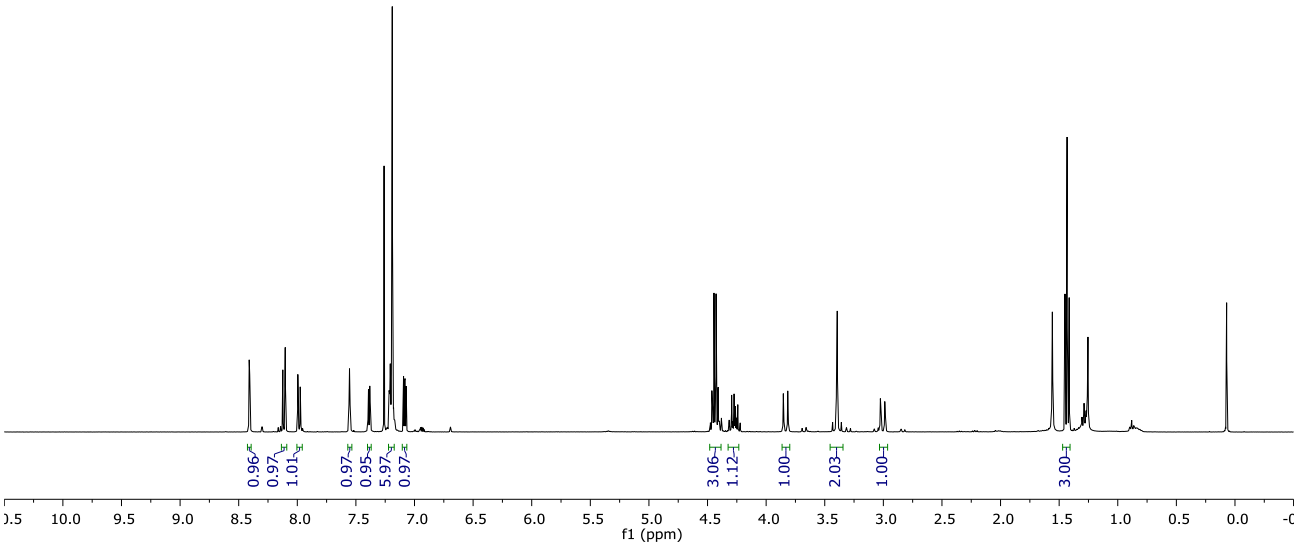
2mf

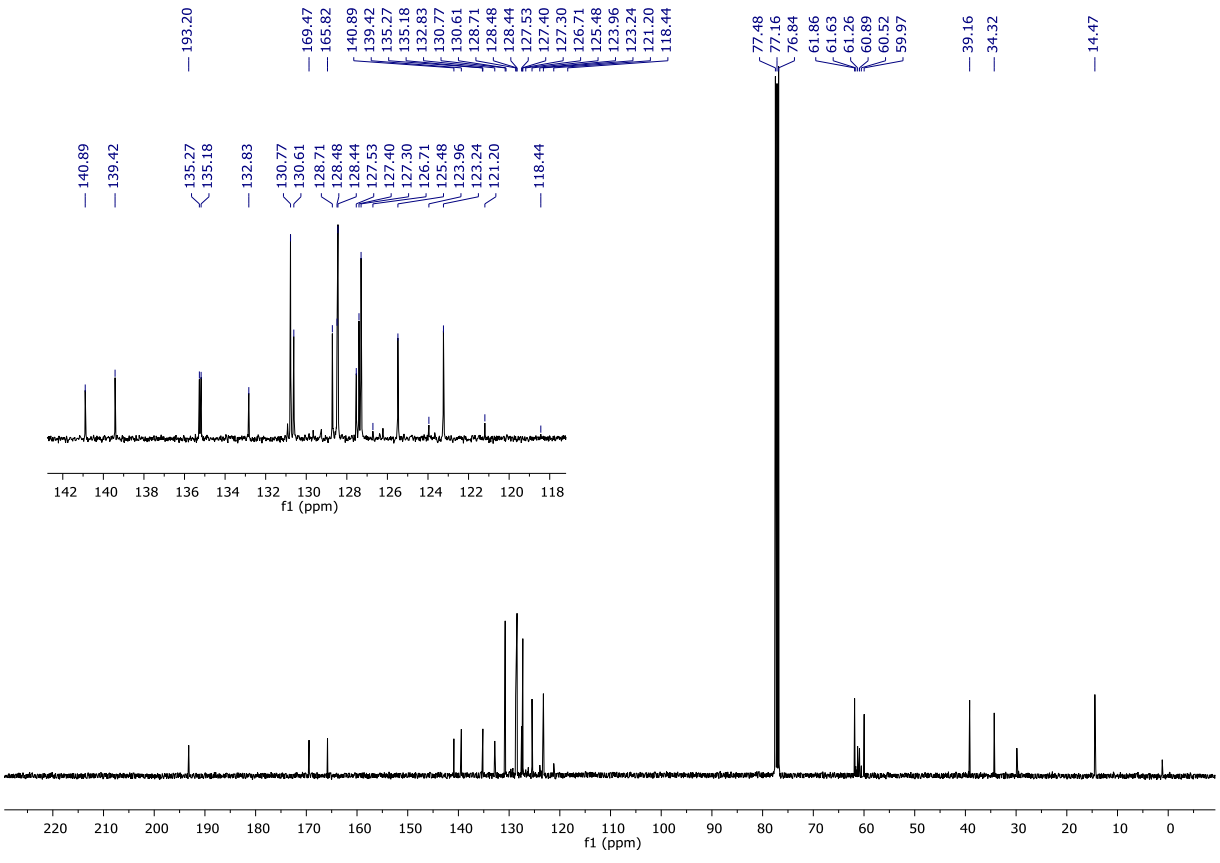

0.91
0.98
0.98
1.01
6.00
0.97
1.08
1.02
0.99
1.00
0.99
1.00
f1 (ppm)

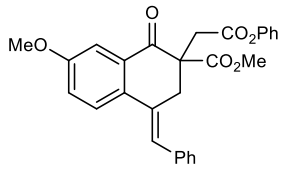

191.58
169.31
140.36
139.02
138.99
135.03
132.85
130.92
130.76
130.15
129.46
128.48
127.67
127.45
127.37
126.68
126.38
125.87
123.92
123.60
121.16
118.41
77.48
77.16
76.84
61.67
61.30
60.93
60.56
59.73
39.18
34.23
f1 (ppm)


O
Bn
CO2CH2CF3
EtO
O
S

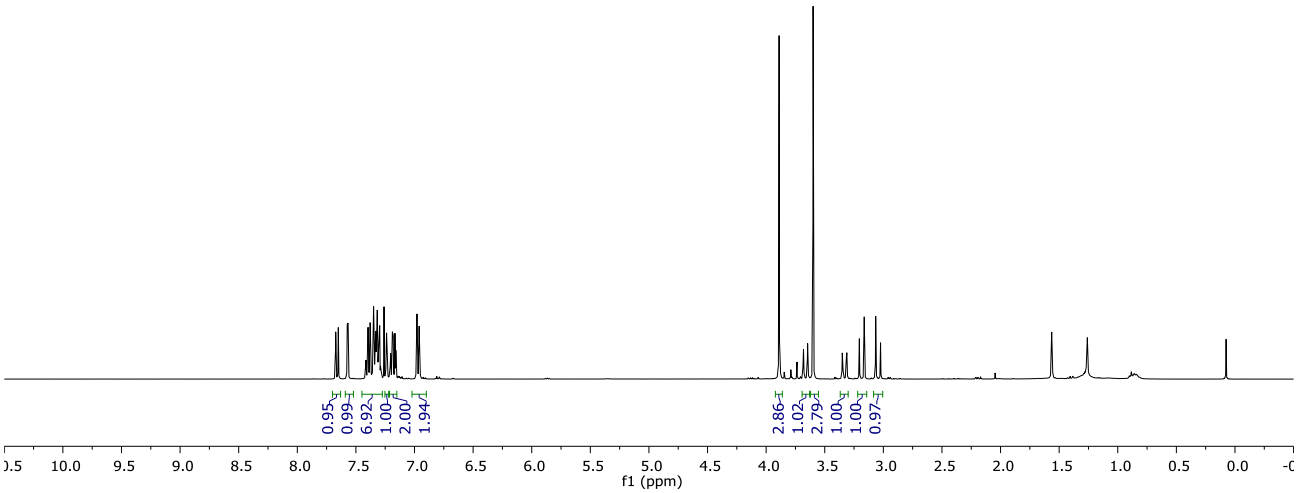
2mg

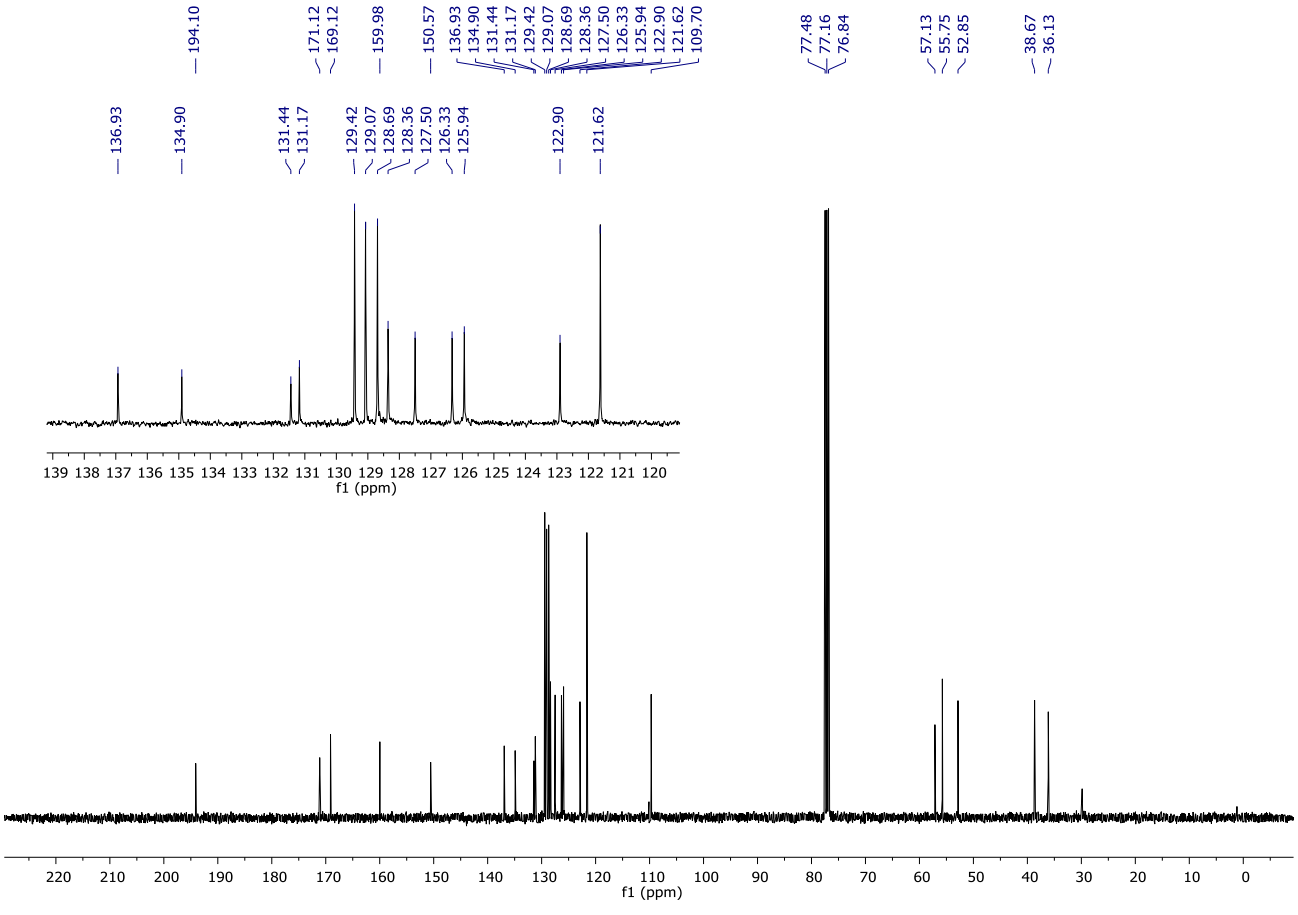

0.96
0.97
1.01
0.97
0.95
5.97
0.97
3.06
1.12
1.00
2.03
1.00
3.00
f1 (ppm)

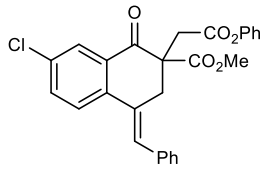

193.20
169.47
165.82
140.89
139.42
135.27
135.18
132.83
130.77
130.61
128.71
128.48
128.44
127.53
127.40
127.30
126.71
125.48
123.96
123.24
121.20
118.44
77.48
77.16
76.84
61.86
61.63
61.26
60.89
60.52
59.97
39.16
34.32
14.47
f1 (ppm)


O
MeO
CO2Ph
CO2Me
Ph

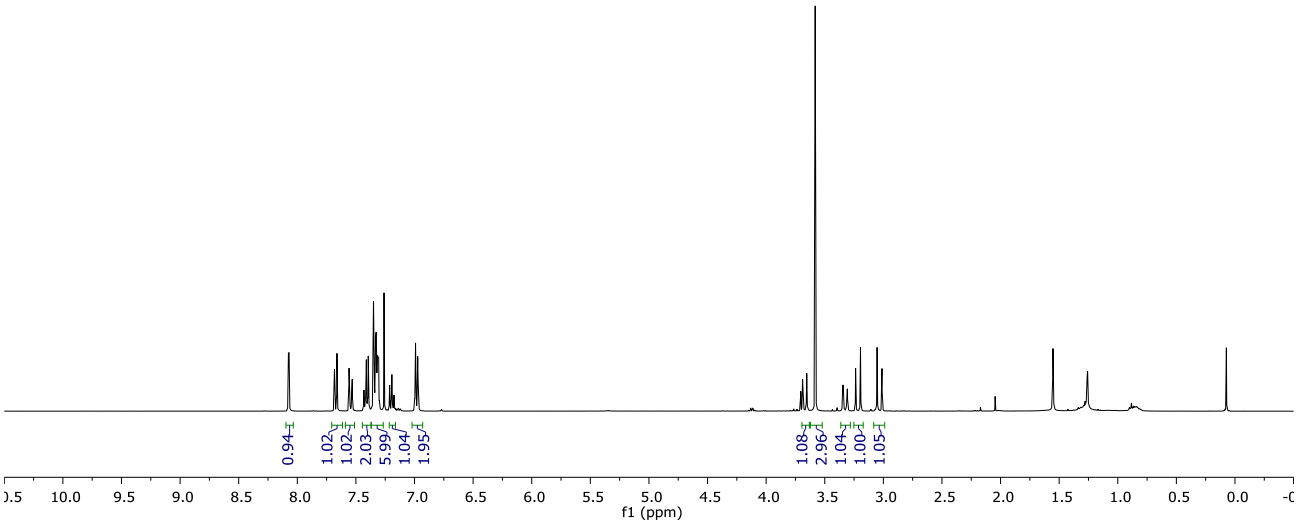
2nh

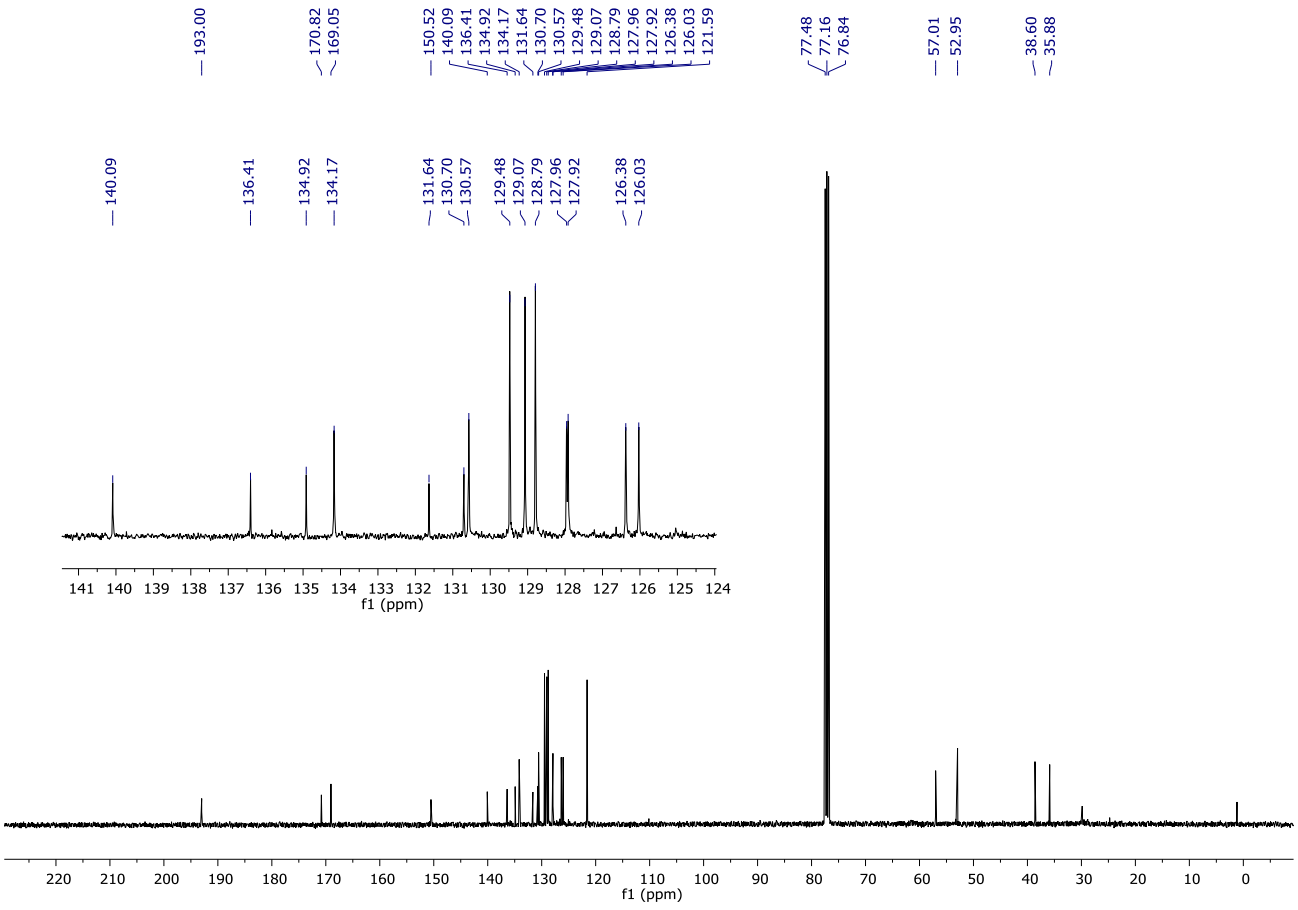

0.95
0.99
6.92
1.00
2.00
1.94
2.86
1.02
2.79
1.00
1.00
0.97
f1 (ppm)


194.10
171.12
169.12
159.98
150.57
136.93
134.90
131.44
131.17
129.42
129.07
128.69
128.36
127.50
126.33
125.94
122.90
121.62
109.70
77.48
77.16
76.84
57.13
55.75
52.85
38.67
36.13
f1 (ppm)


O
Cl
CO2Ph
CO2Me
Ph

2ni


0.94
1.02
1.02
2.03
5.99
1.04
1.95
1.08
2.96
1.04
1.00
1.05
f1 (ppm)


193.00
170.82
169.05
150.52
140.09
136.41
134.92
134.17
131.64
130.70
130.57
129.48
129.07
128.79
127.96
127.92
126.38
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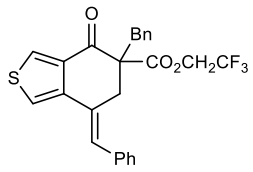
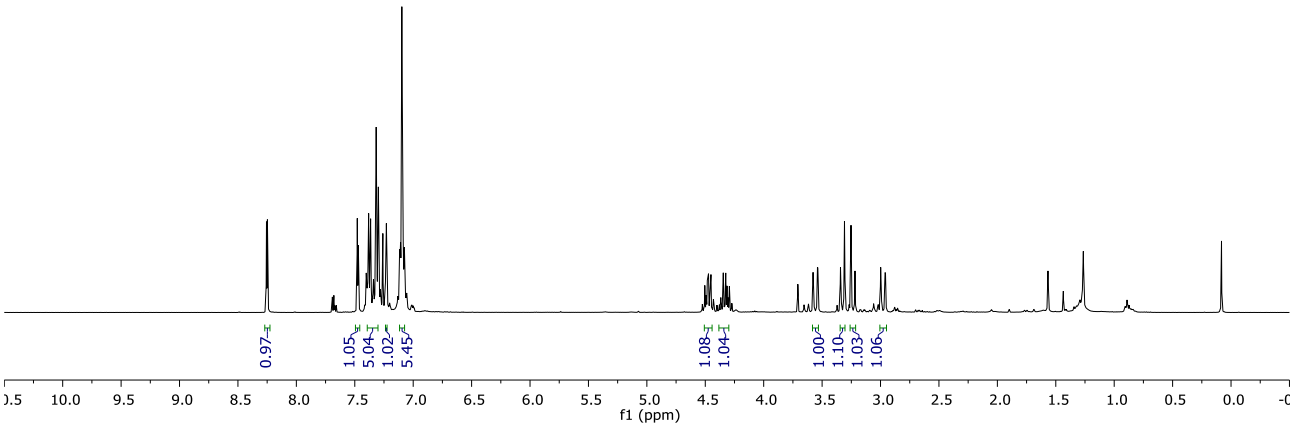
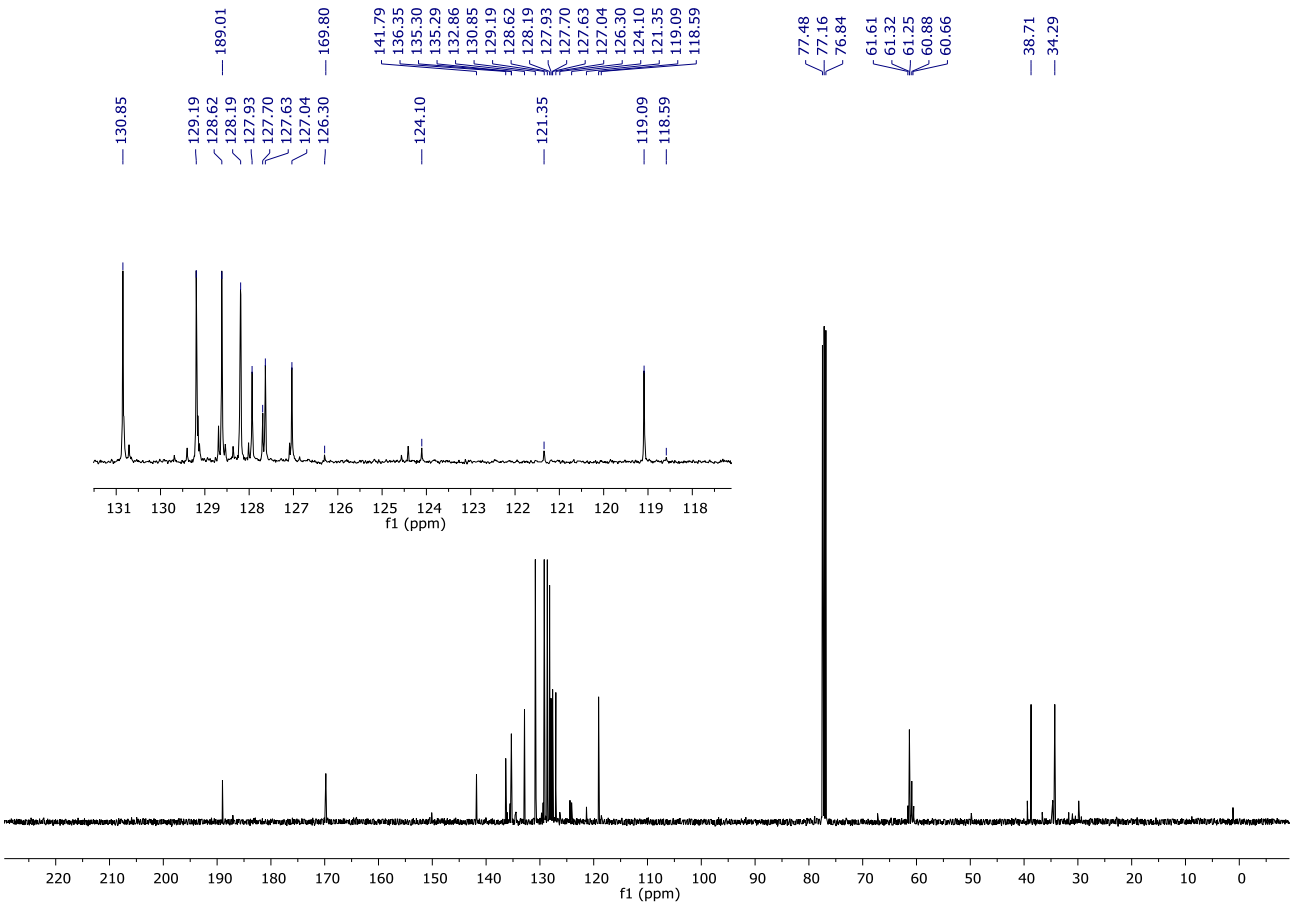
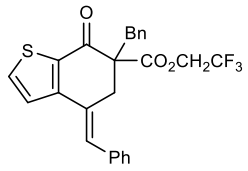
121.59
77.48
77.16
76.84
57.01
52.95
38.60
35.88
f1 (ppm)


O
Bn
CO2CH2CF3
S
Ph

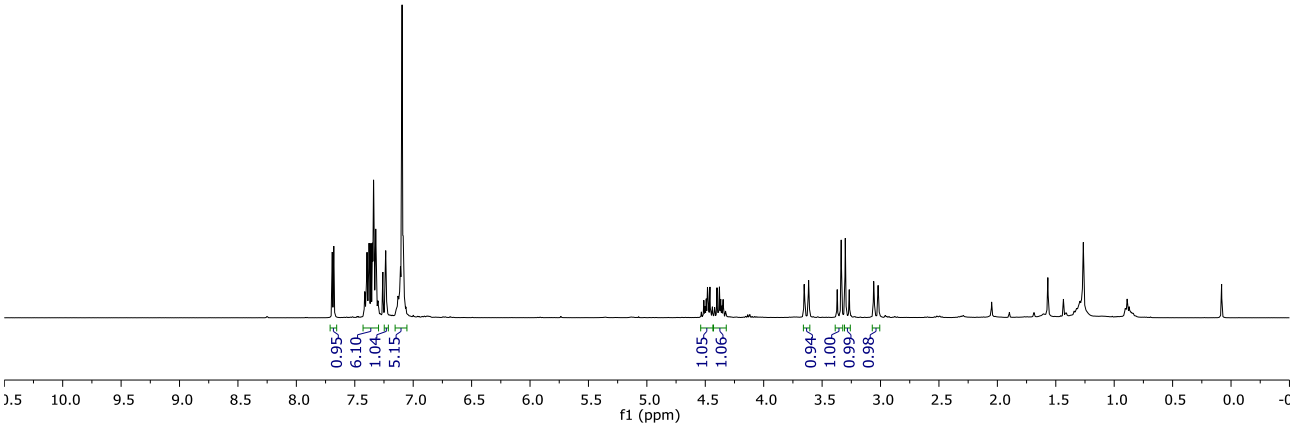
2aj

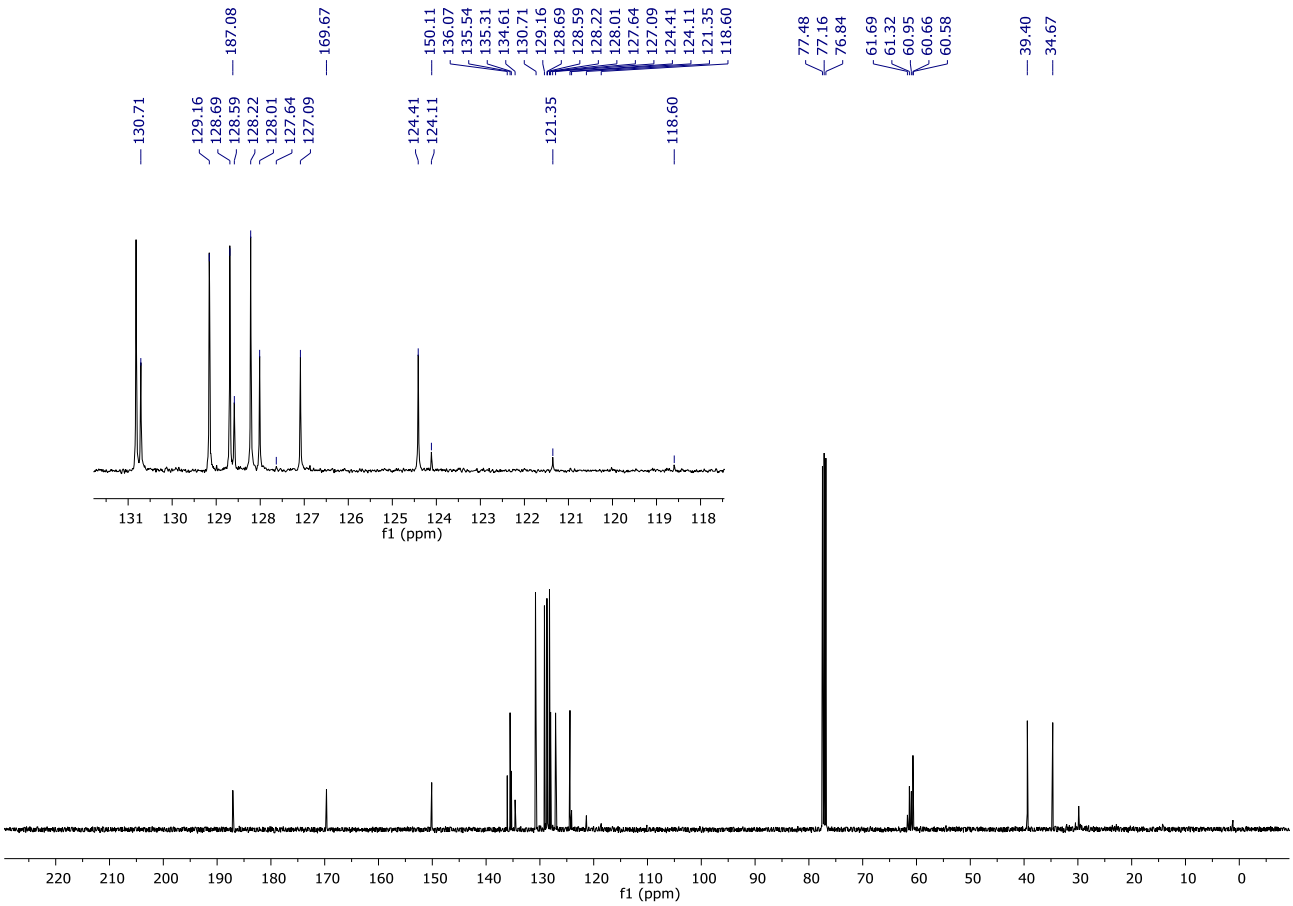

0.97
1.05
5.04
1.02
5.45
1.08
1.04
1.00
1.10
1.03
1.06
f1 (ppm)

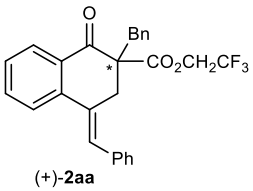

189.01
169.80
141.79
136.35
135.30
135.29
132.86
130.85
129.19
128.62
128.19
127.93
127.70
127.63
127.04
126.30
124.10
121.35
119.09
118.59
77.48
77.16
76.84
61.61
61.32
61.25
60.88
60.66
38.71
34.29
f1 (ppm)


O
Bn
S
$CO_2CH_2CF_3$
Ph

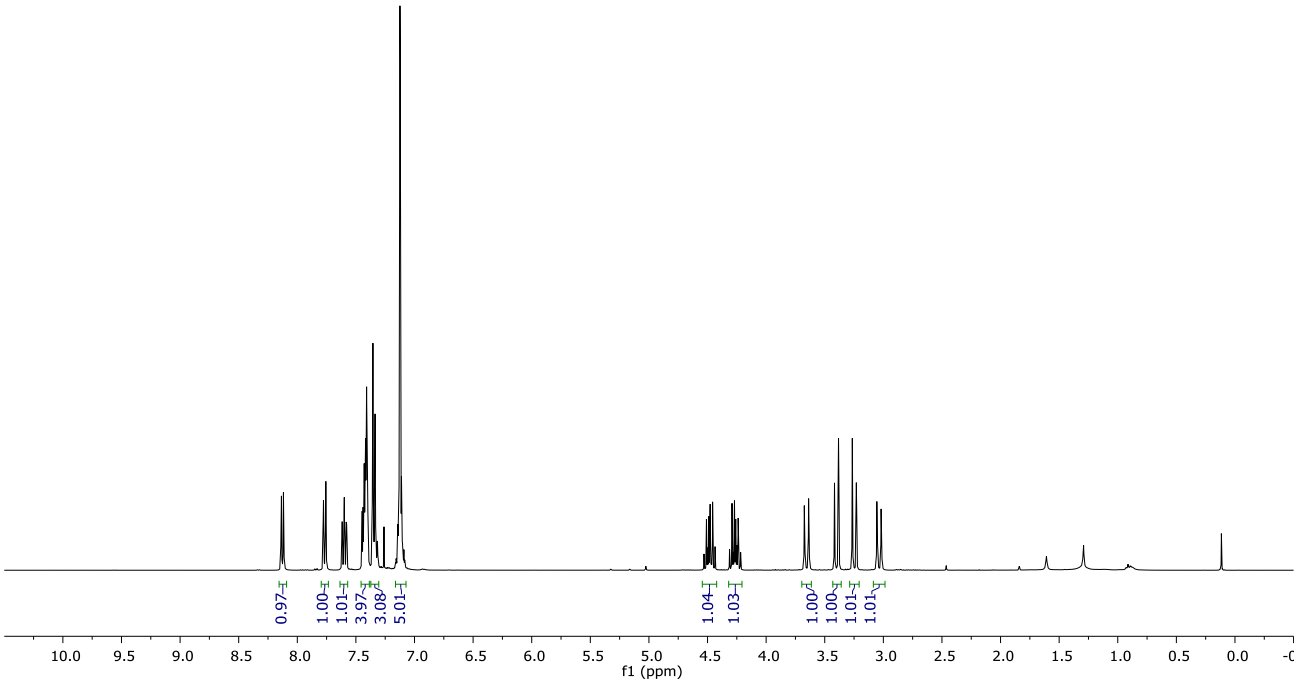
2aj'

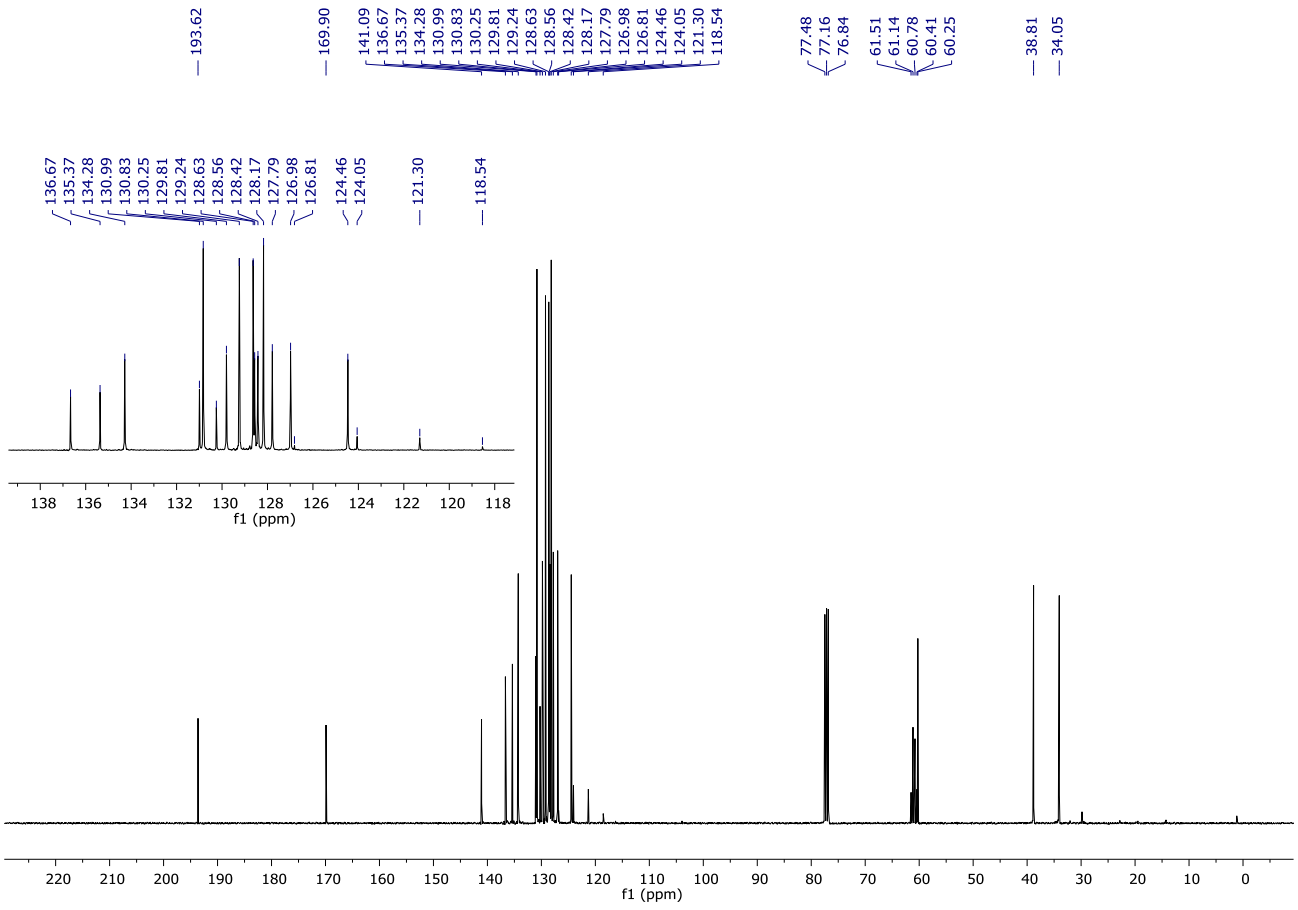

0.95
6.10
1.04
5.15
1.05
1.06
0.94
1.00
0.99
0.98
f1 (ppm)

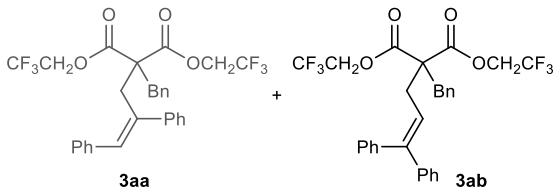

187.08
169.67
150.11
136.07
135.54
135.31
134.61
130.71
129.16
128.69
128.59
128.22
128.01
127.64
127.09
124.41
124.11
121.35
118.60
77.48
77.16
76.84
61.69
61.32
60.95
60.66
60.58
39.40
34.67
f1 (ppm)



(+)-**2aa**
(from enantioselective reaction)

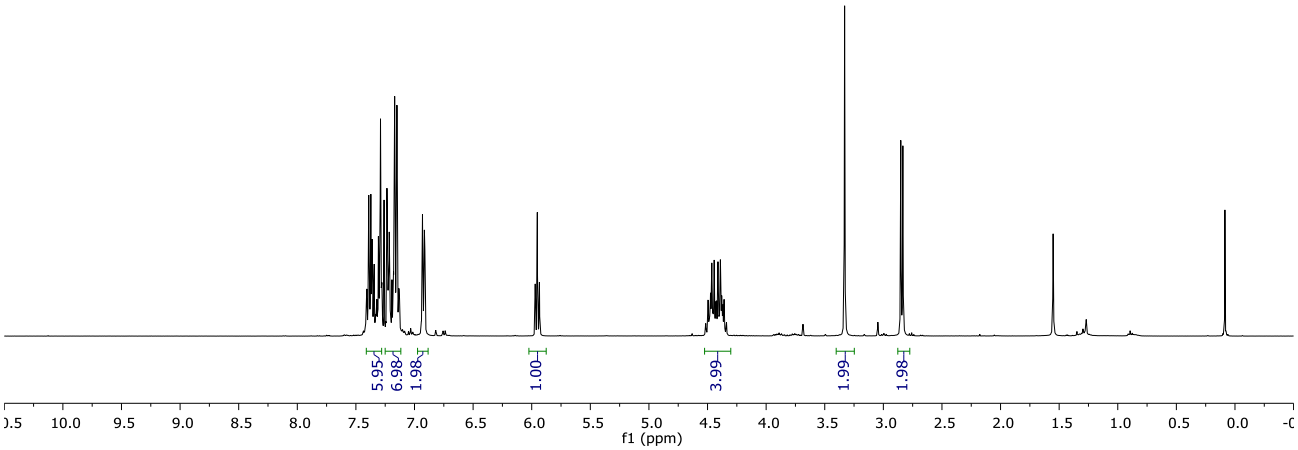


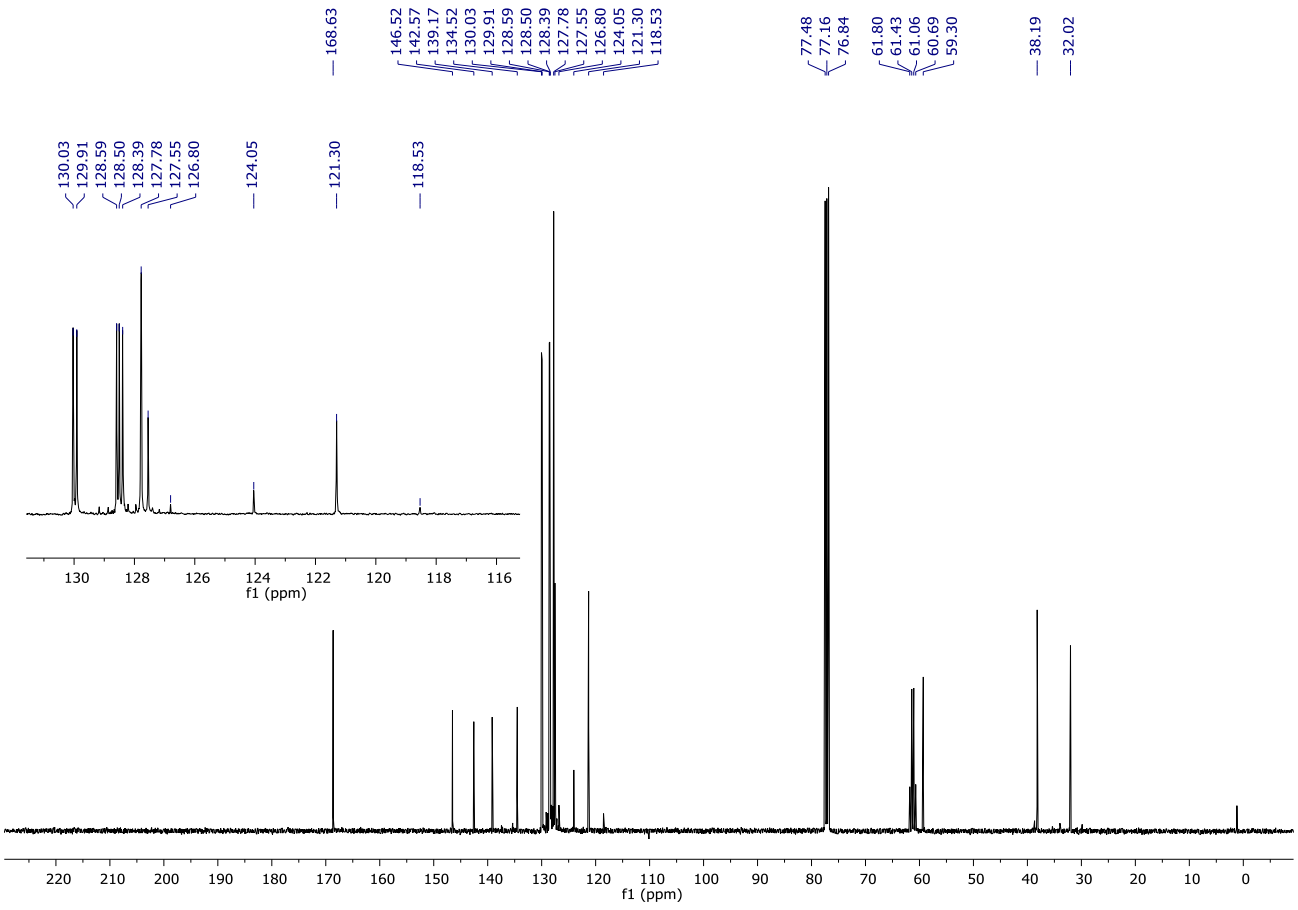




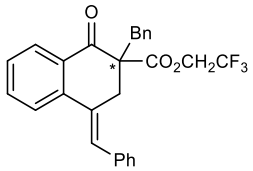
3aa **3ab**

3aa:**3ab** = 1:20

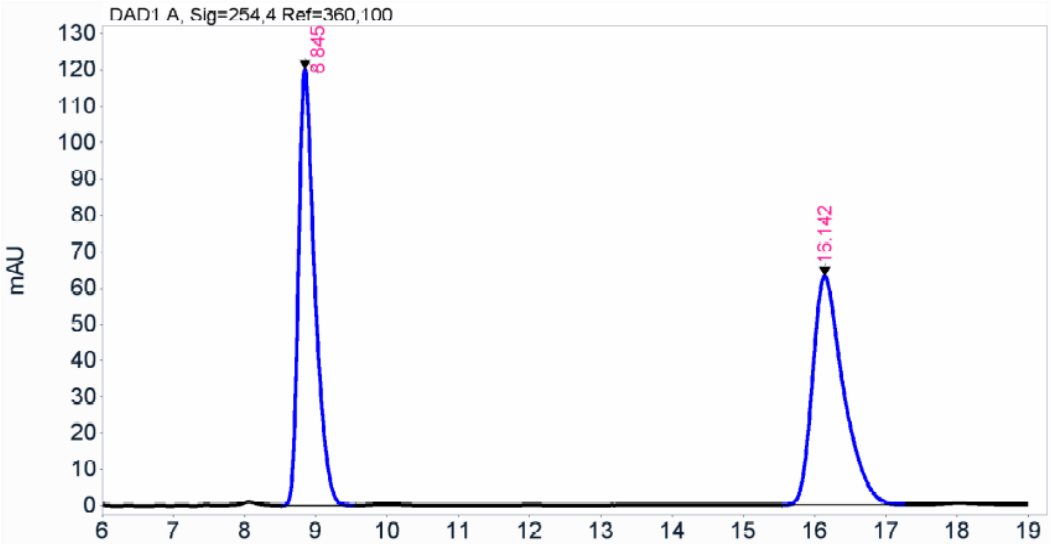




7. HPLC Traces

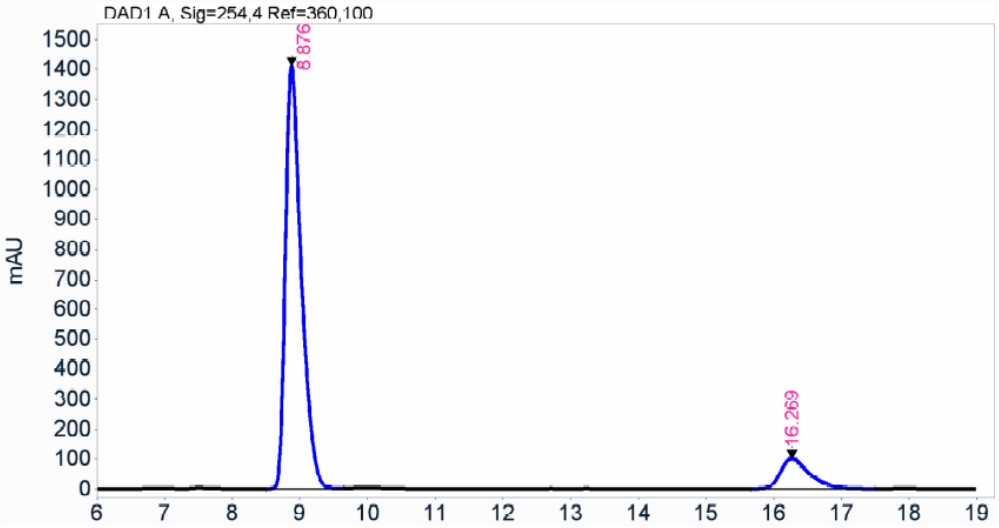


(+)-**2aa**



Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
8.845	BB	0.2352	1907.724	120.1835	50.13
16.142	BB	0.4457	1898.094	62.9687	49.87



Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
8.876	BV	0.2419	22966.697	1411.1356	88.24
16.269	BB	0.4523	3060.150	100.7775	11.76

8. References

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