Redox-ligand sustains controlled generation of CF_3 radicals by well-defined copper complex

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SUPPORTING INFORMATION

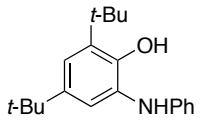
General Information

All reactions were performed under argon atmosphere, in flame dried glassware with magnetic stirring using standard Schlenk techniques, unless mentionned otherwise. NMP and CH_2Cl_2 were distilled over calcium hydride and were sparged with argon prior to use. All other commercially available reagents were used without purification, unless otherwise noted. 5-(Trifluoromethyl)dibenzothiophenium triflate was purchased from Sigma Aldrich and Togni II reagent was prepared following the procedure developed by A. Togni.[1] Thin layer chromatography (TLC) was performed on Merck 60 F254 silica gel and visualized with a UV lamp (254 nm) or with a potassium permanganate solution. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded at room temperature unless otherwise required on Bruker Avance 300 MHz, Bruker Avance 400 MHz. Fluorobenzene was used as an internal standard to determine ^{19}F NMR yields, with 12 seconds relaxation delays. Shifts (δ) are given in parts per million (ppm) and coupling constants (J) are given in Hertz (Hz). IR spectra were measured using Tensor 27 (ATR Diamond) Bruker spectrometer, and JASCO FT/IR-4100 for KBr pellets. IR data are reported as characteristic bands (cm^{-1}). UV spectra were recorded using Agilent 8453 UV-visible Spectrophotometer. Wavelengths (λ) are given in nanometer (nm) and molar extinction coefficients (ε) are given in $M^{-1}.cm^{-1}$.

[1] K. Stanek, R. Koller and A. Togni, *J. Org. Chem.* 2008, **73**, 7678–7685.

Preparation of ligands and complexes

2-anilino-4,6-di-*tert*-butylphenol

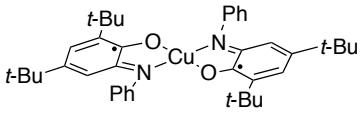


To a pale brown solution of 3,5-di-*tert*-butylcatechol (5.72 g, 25.7 mmol, 1 equiv.) in heptane (30 mL), were added dropwise the corresponding aniline (25.7 mmol, 1 equiv.) and triethylamine (358 µL, 2.57 mmol, 0.1 equiv.). The resulting dark brown mixture was refluxed for 5 h under air. After cooling down to room temperature, a white solid precipitated, which was filtered and washed with cold heptane, to afford the desired product (5.2 g, 68 %).

The characterization data were identical to those previously reported.[2]

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.29 (s, 9H), 1.47 (s, 9H), 5.00 (bs, 1H), 6.45 (bs, 1H), 6.69 (d, *J* = 7.7 Hz, 2H), 6.87 (t, *J* = 7.3 Hz, 1H), 7.06 (d, *J* = 2.2 Hz, 1H), 7.20-7.26 (m, 3H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 29.7, 31.7, 34.5, 35.2, 115.3, 119.9, 121.6, 122.1, 127.9, 129.5, 135.5, 142.3, 146.9, 149.5. **IR** (neat, cm^{-1}): 3350, 2958m, 2868w, 1598m, 1495m, 1487m, 1417m, 1363m, 1311m, 1229m, 1077w, 1026w, 971w, 882w, 825w, 808w, 748m, 691m.

$Cu^{II}(L^{SQ})_2$ complex (1)



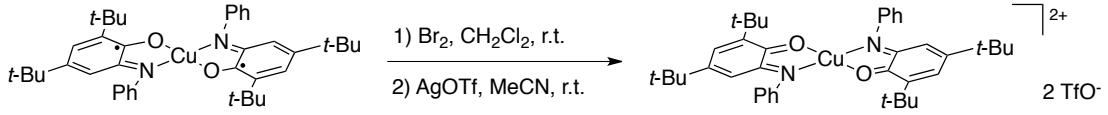
To a colorless solution of 2-anilino-4,6-di-*tert*-butylphenol (1.06 g, 3.56 mmol, 2 equiv.) in acetonitrile (40 mL), were added at 40 °C, CuCl (176 mg, 1.78 mmol, 1 equiv.) and triethylamine (992 µL, 7.12 mmol, 4 equiv.). The resulting dark green mixture was refluxed for 2 h under air. After cooling down to room temperature, a dark green solid precipitated, which was filtered and washed with cold acetonitrile, to afford complex **1** (789 mg, 68 %).

The characterization data were identical to those previously reported.[2]

ESI-MS: *m/z* 653 $[C_{40}H_{50}CuN_2O_2]^+$. **IR** (KBr, cm^{-1}): 2961-2866s, 1582m, 1485s, 1464s, 1442m, 1386m, 1356m, 1334m, 1256s, 1203m, 1179m, 1105m, 1026m, 994m, 860m, 764m, 701m, 692m. **UV-vis** [CH_2Cl_2; λ, nm (ε, $M^{-1}.cm^{-1}$)]: 307 (21000), 460 (4610), 795 (7470).

[2] P. Chaudhuri, C. N. Verani, E. Bill, E. Bothe, T. Weyhermüller and K. Wieghardt, *J. Am. Chem. Soc.* 2001, **123**, 2213–2223.

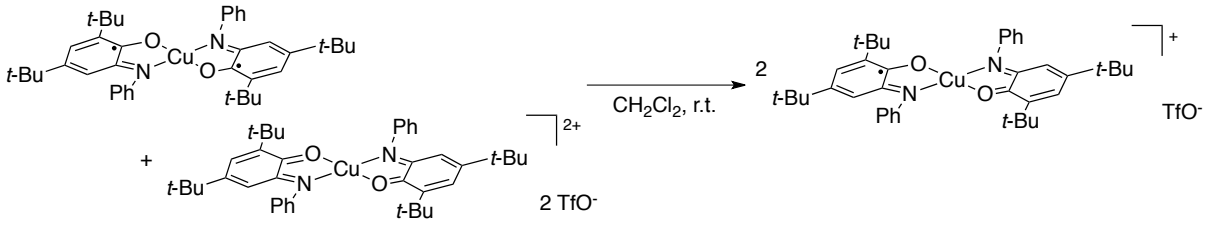
$[Cu^{II}(L^{BQ})_2](OTf)_2$ complex (6)



Into a Schlenk flask under an argon atmosphere, were introduced complex **1** (200 mg, 0.31 mmol, 1 equiv.) and degassed CH_2Cl_2 (9 mL). A 2.8 M solution of bromine in CH_2Cl_2 (111 µL, 0.31 mmol, 1 equiv.) was added and the resulting dark-red solution was stirred for 1 h at room temperature. After evaporation of the solvent, the residue was triturated in hexane and filtered to afford a red-brown solid[3] (249 mg, quantitative). This $Cu(L_{BQ})_2Br_2$ complex (249 mg, 0.31 mmol, 1 equiv.) and silver triflate (157 mg, 0.62 mmol, 2 equiv.) were introduced into a Schlenk flask under an argon atmosphere. Degassed acetonitrile (5 mL) was added and the resulting mixture was stirred for 2 h at room temperature. The suspension was filtered, and the filtrate was evaporated. The residue was dissolved in CH_2Cl_2 and filtered. The filtrate was evaporated to give complex **6** (245 mg, 83 %).

HRMS (ESI) calculated for $[C_{41}H_{50}CuF_3N_2O_5S]^+$ 802.2683, found 802.2679. **IR** (neat, cm^{-1}): 2961w, 2872w, 1606m, 1537m, 1484m, 1389m, 1367m, 1285s, 1237s, 1221s, 1166s, 1152s, 1025s, 902m, 867m, 800m, 763m, 704m, 637s. **UV-vis** [CH_2Cl_2; λ, nm (ε, $M^{-1}.cm^{-1}$)]: 290 (14100), 434 (6870), 504 (7370).

$[Cu^{II}(L^{SQ})(L^{BQ})]OTf$ complex (3)



Into a Schlenk flask under an argon atmosphere, were introduced complex **1** (42 mg, 64 µmol, 1 equiv.) and complex **6** (61 mg, 64 µmol, 1 equiv.). Degassed CH_2Cl_2 was added and the resulting mixture was stirred for 2 h at room temperature. The solvent was evaporated to give complex **3** (103 mg, quantitative).

HRMS (ESI) calculated for $[C_{40}H_{50}CuN_2O_2]^+$ 654.3163, found 654.3152. **IR** (neat, cm^{-1}): 2961m, 2905w, 2870w, 1606m, 1581w, 1536m, 1484m, 1463m, 1388m, 1365m, 1333w, 1286s, 1237s, 1222s, 1166s, 1152s, 1026s, 901m, 861m, 800m, 762m, 740m, 702m, 637s. **UV-vis** [CH_2Cl_2; λ, nm (ε, $M^{-1}.cm^{-1}$)]: 429 (8510), 525 (8650), 692 (6150).

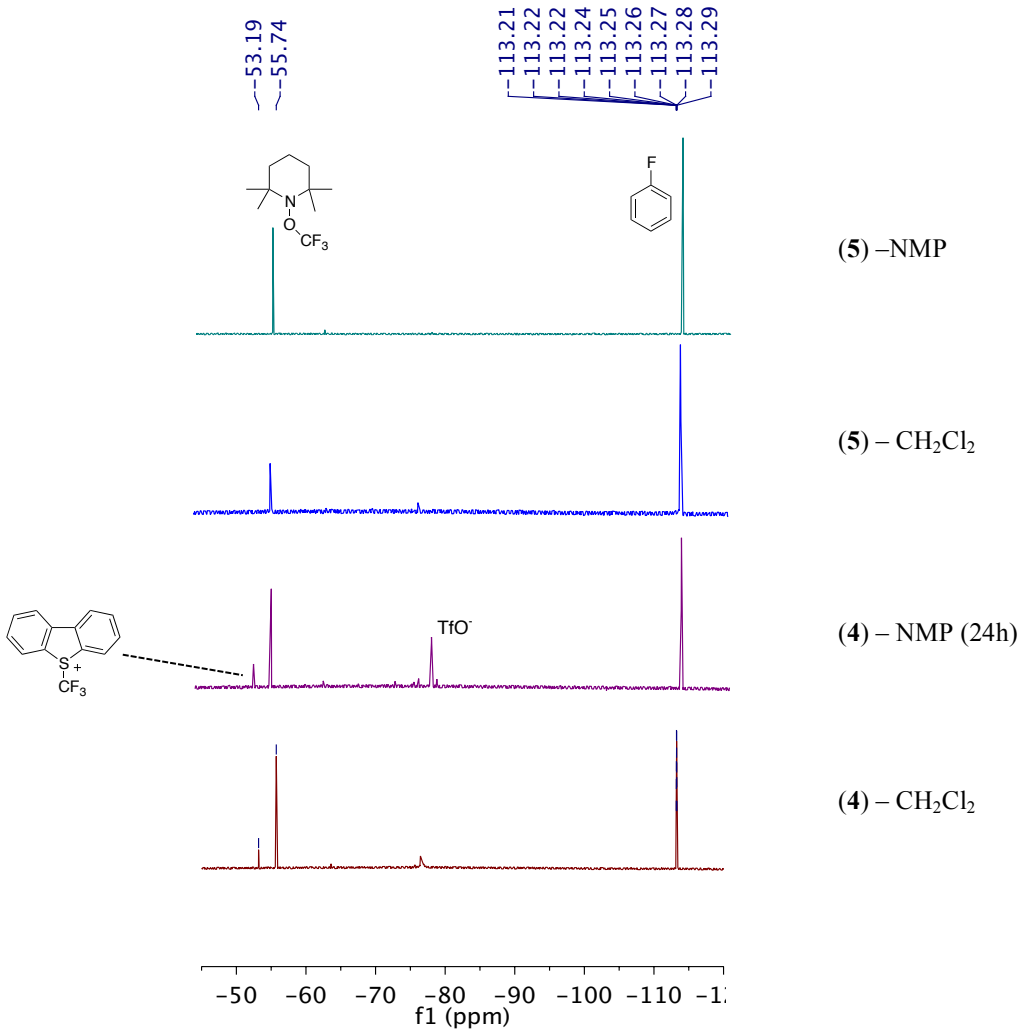
[3] C. Mukherjee, T. Weyhermüller, E. Bothe and P. Chaudhuri, *Inorg. Chem.* 2008, **47**, 2740–2746.

General Procedure for experiments with TEMPO

Into a Schlenk flask under an argon atmosphere, were introduced complex **1** (48 mg, 0.073 mmol, 1 equiv.) and the solvent (CH_2Cl_2 or NMP, 4 mL). TEMPO (13 mg, 0.081 mmol, 1.1 equiv.) and the electrophilic trifluoromethylating agent **4** or **5** (0.073 mmol, 1 equiv.) were added at the same time, and the resulting mixture was stirred for 3-24 h at room temperature.

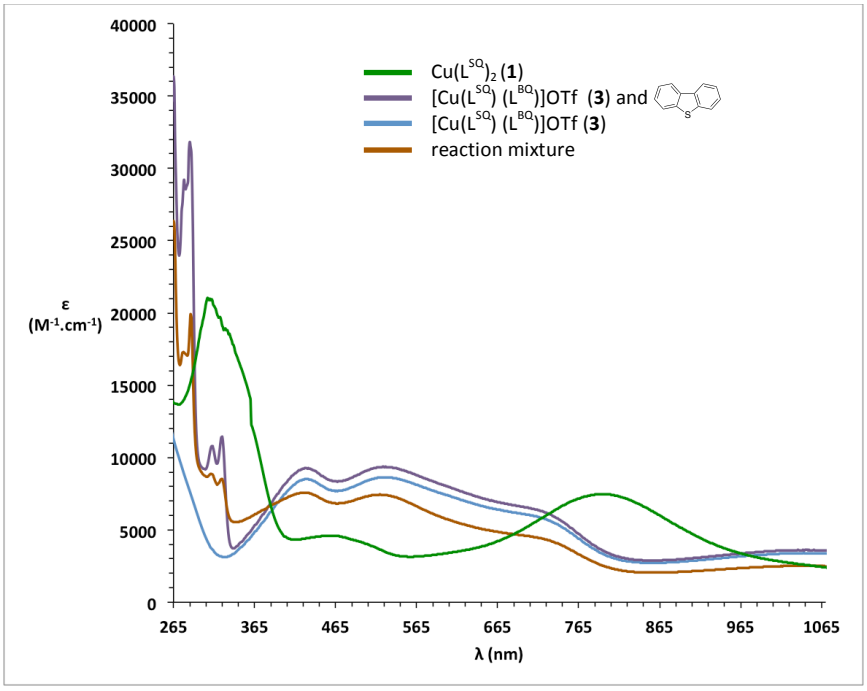
NMR yields of TEMPO-CF_3 (^{19}F NMR ($CDCl_3$, 376 MHz) δ -55.7 ppm), were determined with fluorobenzene as internal standard.

	NMR Yield (conversion)	
	Umemoto reagent (4)	**Togni II reagent (5)**
CH_2Cl_2	3 h: 67 % (95 %)	3 h: 47 % (100 %)
NMP	6 h: 36 % (64 %) 24 h: 62 % (92 %)	3 h: 69 % (100 %)



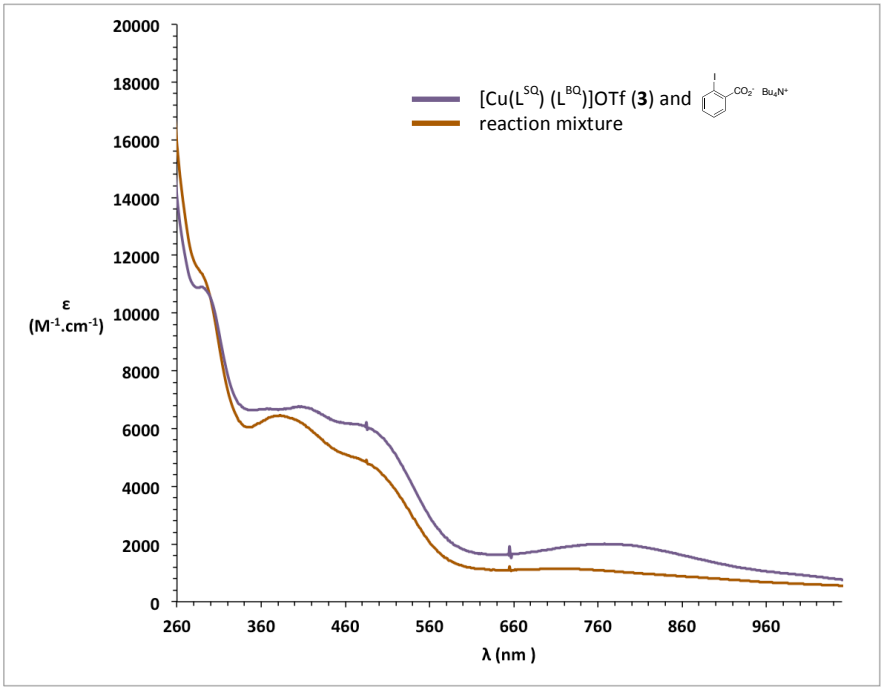
UV-vis studies

1) with Umemoto reagent (4) in CH_2Cl_2:



An aliquot of the reaction mixture, diluted in CH_2Cl_2 (C = $1.19.10^{-4}$ M), compared to complex **3** (C = $1.07.10^{-4}$ M).

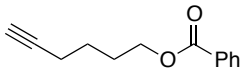
2) with Togni II reagent (5) in CH_2Cl_2:



An aliquot of the reaction mixture, diluted in CH_2Cl_2 (C = $1.19.10^{-4}$ M), compared to a mixture of complex **3** (C = $7.09.10^{-5}$ M) with 1 equiv. of tetrabutylammonium 2-iodobenzoate.

Preparation of alkynes

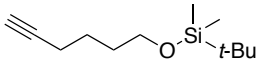
Hex-5-yn-1-yl benzoate (11a)



To a solution of hex-5-yn-1-ol (1.58 mL, 14.3 mmol, 1 equiv.) in CH_2Cl_2 (24 mL), were added successively at 0 °C, DMAP (175 mg, 1.43 mmol, 0.1 equiv.) and pyridine (3.5 mL, 43.0 mmol, 3 equiv.), followed by a dropwise addition of benzoyl chloride (5 mL, 43.0 mmol, 3 equiv.). The resulting mixture was allowed to warm to room temperature and stirred for 2 h. The reaction was quenched with water, and the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude mixture was purified by silica gel column chromatography (pentane/ethyl acetate 99:1 to 97:3) to afford **11a** (2.23 g, 78 %). The characterization data were identical to those previously reported.[4]

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.65-1.76 (m, 2H), 1.86-1.96 (m, 2H), 1.97 (t, *J* = 2.7 Hz, 1H), 2.29 (td, *J* = 7.0, 2.6 Hz, 2H), 4.35 (t, *J* = 6.4 Hz, 2H), 7.41-7.46 (m, 2H), 7.53-7.59 (m, 1H), 8.03-8.06 (m, 2H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 18.28, 25.22, 27.94, 64.58, 68.92, 84.01, 128.48, 129.69, 130.51, 133.02, 166.74. **IR** (neat, cm^{-1}): 3306m, 2117w, 1714s, 1271s, 1115s, 710s.

4-*Tert*-butyldimethylsiloxyhex-5-yne (11c)

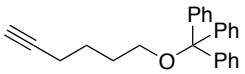


To a solution of hex-5-yn-1-ol (2.2 mL, 20.0 mmol, 1 equiv.) in CH_2Cl_2 (15 mL), was added imidazole (2.04 g, 30.0 mmol, 1.5 equiv.), followed by the addition of *tert*-butyldimethylsilyl chloride (3.62 g, 24.0 mmol, 1.2 equiv.) at 0 °C. The resulting mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched with a saturated aqueous NH_4Cl solution, and the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude mixture was purified by silica gel column chromatography (pentane/CH_2Cl_2 9:1) to afford **11c** (4.43 g, quantitative). The characterization data were identical to those previously reported.[5]

[4] S. Atobe, H. Masuno, M. Sonoda, Y. Suzuki, H. Shinohara, S. Shibata and A. Ogawa, *Tetrahedron Lett.* 2012, **53**, 1764–1767.
[5] B. Guay and P. Deslongchamps, *J. Org. Chem.* 2003, **68**, 6140–6148.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.04 (s, 6H), 0.89 (s, 9H), 1,58-1,62 (m, 4H), 1.93 (t, *J* = 2.6 Hz, 1H), 2.21 (td, *J* = 6.9, 2.7 Hz, 2H), 3.63 (t, *J* = 6.0 Hz, 2H). **^{13}C NMR** ($CDCl_3$, 101 MHz) δ -5.16, 18.37, 18.48, 25.13, 26.10, 31.97, 62.72, 68.39, 84.64. **IR** (neat, cm^{-1}): 3316m, 2100w, 1256m, 1106s, 835s, 775s, 628s.

1-Trityloxyhex-5-yne (11d)



To a solution of hex-5-yn-1-ol (1.5 mL, 13.6 mmol, 1 equiv.) in CH_2Cl_2 (35 mL) were added successively at 0 °C, DMAP (166 mg, 1.36 mmol, 0.1 equiv.), pyridine (1.65 mL, 20.4 mmol, 1.5 equiv.), and trityl chloride (3.98 g, 14.3 mmol, 1.05 equiv.). The resulting mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched with water, and the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude mixture was purified by silica gel column chromatography (pentane/CH_2Cl_2 85:15) to afford **11d** (3.7 g, 80 %). The characterization data were identical to those previously reported.[6]

^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.61-1.69 (m, 2H), 1.71-1.78 (m, 2H), 1.94 (t, *J* = 2.6 Hz, 1H), 2.18 (td, *J* = 7.0, 2.6 Hz, 2H), 3.10 (t, *J* = 6.2 Hz, 2H), 7.21-7.32 (m, 9H), 7.44-7.47 (m, 6H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 18.44, 25.58, 29.28, 63.09, 68.45, 84.62, 86.51, 126.99, 127.86, 128.83, 144.55. **IR** (neat, cm^{-1}): 3293m, 2117w, 1490m, 1448m, 1070s, 630s.

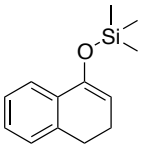
Preparation of silyl enol ethers[7]

General Procedure (A): To a solution of the ketone (30 mmol), triethylamine (5.02 mL, 36 mmol, 1.2 equiv.) and trimethylchlorosilane (4.57 mL, 36 mmol, 1.2 equiv.), was added dropwise a solution of sodium iodide (5.40 g, 36 mmol, 1.2 equiv.) in acetonitrile (30 mL), at room temperature, and the resulting mixture was stirred for 1 h - 24 h. The reaction was quenched with ice water and the aqueous phase was extracted with pentane. The combined organic layers were washed with ice water, dried over Na_2SO_4, filtered and concentrated *in vacuo*.

The crude mixture was purified by Kugelrohr distillation, under argon or under reduced pressure.

[6] A. Lumbroso, P. Koschker, N. R. Vautravers and B. Breit, *J. Am. Chem. Soc.* 2011, **133**, 2386–2389.
[7] P. Cazeau, F. Duboudin, F. Moulines, O. Babot and J. Dunogues, *Tetrahedron Lett.* 1987, **43**, 2075–2088.

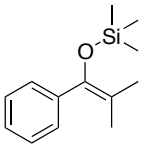
Trimethyl((2-methyl-3,4-dihydronaphthalen-1-yl)oxy)silane (7c)



This compound was prepared according to the general procedure (**A**) in 69 % yield. The characterization data were identical to those previously reported.[8]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.27 (s, 9H), 2.33 (ddd, *J* = 9.3, 7.2, 4.7 Hz, 2H), 2.77 (t, *J* = 8.0 Hz, 2H), 5.20 (t, *J* = 4.6 Hz, 1H), 7.10-7.12 (m, 1H), 7.16 (td, *J* = 7.3, 1.7 Hz, 1H), 7.16-7.22 (m, 1H), 7.42 (dd, *J* = 7.5, 1.6 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 0.36, 22.32, 28.32, 105.44, 121.96, 126.30, 127.07, 127.40, 133.67, 137.20, 148.21. **IR** (neat, cm^{-1}): 1638m, 1247s, 839s, 770s.

Trimethyl((2-methyl-1-phenylprop-1-en-1-yl)oxy)silane (7d)



This compound was prepared according to the general procedure (**A**) in 51 % yield. The characterization data were identical to those previously reported.[9]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.07 (s, 9H), 1.63 (s, 3H), 1.74 (s, 3H), 7.16-7.20 (m, 1H), 7.22-7.26 (m, 2H). **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 0.54, 18.38, 19.87, 112.99, 127.20, 127.78, 129.29, 139.18, 143.67. **IR** (neat, cm^{-1}): 1688m, 1250m, 838s, 766m.

General Procedures for Radical Trifluoromethylation

NMR yields were determined with fluorobenzene as internal standard and calculated considering the trifluoromethylating agent as limiting reactant.
Isolated yields: purification by silica gel column chromatography.

General procedure for the trifluoromethylation of silyl enol ethers and heteroaromatics (B)

(B1): Into a Schlenk flask under an argon atmosphere, were introduced complex **1** (10 mg, 0.015 mmol, 5 mol%), the substrate (0.308 mmol, 1 equiv.) and CH_2Cl_2 (1.5 mL), under an argon stream. To this solution, was added the trifluoromethylating agent **5** (146 mg, 0.462 mmol, 1.5 equiv.). The resulting mixture was stirred at room temperature for 18 h. The reaction was quenched with water and

[8] M. Pouliot, P. Renaud, K. Schenk, A. Studer and T. Vogler, *Angew. Chem. Int Ed.* 2009, **48**, 6037–6040.
[9] J. Eames, G. S. Coumbarides, M. J. Suggate and N. Weerasooriya, *Eur. J. Org. Chem.* 2003, 634–641.

the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*.

(B2): Into a Schlenk flask under an argon atmosphere, were introduced complex **1** (10 mg, 0.015 mmol, 5 mol%), the substrate (1.228 mmol, 4 equiv.) and CH_2Cl_2 (6 mL), under an argon stream. To this solution, was added the trifluoromethylating agent **5** (97 mg, 0.307 mmol, 1 equiv.). The resulting mixture was stirred at room temperature for 18 h. The reaction was quenched with water and the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*.

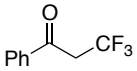
General procedure for the trifluoromethylation of alkynes in NMP (C)

Into a Schlenk flask under an argon atmosphere, were introduced complex **1** (40 mg, 0.061 mmol, 20 mol%), the substrate (1.22 mmol, 4 equiv.) and NMP (6 mL), under an argon stream. To this solution, was added the trifluoromethylating agent **5** (97mg, 0.307 mmol, 1 equiv.). The resulting mixture was stirred at room temperature for 18 h. The reaction was quenched with water and the aqueous phase was extracted with diethyl ether. The combined organic layers were washed with water, dried over Na_2SO_4, filtered and concentrated *in vacuo*.

Procedure for the trifluoromethylation of alkene 13 in NMP (D)

Into a Schlenk flask under an argon atmosphere, were introduced complex **1** (21 mg, 0.032 mmol, 20 mol%), alkene **13** (130 mg, 0.644 mmol, 4 equiv.), 1,4-CHD (15 µL, 0.161 mmol, 1 equiv.) and NMP (3 mL), under an argon stream. To this solution, was added the trifluoromethylating agent **4** or **5** (0.161 mmol, 1 equiv.). The resulting mixture was stirred at room temperature for 18 h. The reaction was quenched with water and the aqueous phase was extracted with diethyl ether. The combined organic layers were washed with water, dried over Na_2SO_4, filtered and concentrated *in vacuo*.

3,3,3-Trifluoro-1-phenylpropan-1-one (8a)[10]

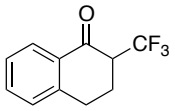


(**B1**): 79 %. Purification by silica gel column chromatography (pentane/CH_2Cl_2 90:10 to 75:25) afforded **8a** (41 mg, 71 %).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.80 (q, *J* = 10.0 Hz, 2H), 7.49-7.52 (m, 2H), 7.61-7.65 (m, 1H), 7.92-7.94 (m, 2H). **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 42.21 (q, *J* = 28.3 Hz), 124.17 (q, *J* = 277.0 Hz), 128.46, 129.06, 134.31, 135.96 (q, *J* = 1.9 Hz), 189.84 (q, *J* = 2.7 Hz). **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -62.06 (t, *J* = 10.0 Hz, 3F). **IR** (neat, cm^{-1}): 1699s, 1228s, 1129s, 1102s.

[10] P.V. Pham, D. A. Nagib and D. W. C. MacMillan, *Angew. Chem. Int. Ed.* 2011, **50**, 6119–6122.

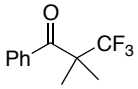
2-(Trifluoromethyl)-3,4-dihydronaphthalen-1(2*H*)-one (8c)[11]



(**B1**): 94 %. Purification by silica gel column chromatography (pentane/CH_2Cl_2 90:10 to 80:20) afforded **8c** (58 mg, 88 %).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.28 (dddd, *J* = 13.5, 11.8, 10.1, 5.6 Hz, 1H), 2.50 (dq, *J* = 13.8, 4.7 Hz, 2H), 3.09 (dt, *J* = 9.7, 4.9 Hz, 1H), 3.27 (dqd, *J* = 11.8, 8.8, 4.5 Hz, 1H), 7.26-7.30 (m, 1H), 7.32-7.38 (m, 1H), 7.52 (td, *J* = 7.5, 1.5 Hz, 1H), 8.06 (dd, *J* = 7.9, 0.8 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 23.60 (q, *J* = 2.7 Hz), 27.68, 51.04 (q, *J* = 25.6 Hz), 125.21 (q, *J* = 280.0 Hz), 127.25, 128.02, 128.91, 132.09 (q, *J* = 1.8 Hz), 134.32, 143.20, 190.33 (q, *J* = 1.4 Hz). **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -67.53 (s, 3F). **IR** (neat, cm^{-1}): 1692s, 1123s, 1097s.

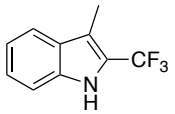
3,3,3-Trifluoro-2,2-dimethyl-1-phenylpropan-1-one (8d)[12]



(**B1**): 56 %. Purification by silica gel column chromatography (pentane/CH_2Cl_2 90:10 to 80:20) afforded **8d** (36 mg, 53 %).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.57 (s, 6H), 7.42 (ddt, *J* = 8.3, 6.6, 1.2 Hz, 2H), 7.51 (ddt, *J* = 8.4, 6.6, 1.3 Hz, 1H), 7.63 – 7.66 (m, 2H). **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 20.88 (q, *J* = 2.5 Hz), 53.44 (q, *J* = 24.5 Hz), 126.92 (q, *J* = 283.8 Hz), 127.83, 128.37, 131.64, 138.22, 200.88. **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -72.66 (s, 3F). **IR** (neat, cm^{-1}): 1686s, 1122s.

3-Methyl-2-(trifluoromethyl)-1*H*-indole (10a)[13]

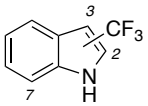


(**B1**): 72 % (57 % with 2 mol% of complex **1**). Purification by silica gel column chromatography (pentane/CH_2Cl_2 85:15) afforded **10a** (41 mg, 67 %).
(**B2**): 83 % (48 % with 2 mol% of complex **1**).

[11] J. Ma and D. Cahard, *J. Org. Chem.* 2003, **68**, 8726–8729.
[12] K. Sato, T. Yuki, R. Yamaguchi, T. Hamano, A. Tarui, M. Omote, I. Kumadaki and A. Ando, *J. Org. Chem.* 2009, **74**, 3815–3819.
[13] E. Mejía and A. Togni, *ACS Catal.* 2012, **2**, 521–527.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.46 (q, *J* = 1.9 Hz, 3H), 7.21 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.32-7.40 (m, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 8.14 (bs, 1H). **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 8.45, 111.69, 114.24 (q, *J* = 3.0 Hz), 120.24, 120.54, 121.70 (q, *J* = 36.7 Hz), 122.28 (q, *J* = 268.4 Hz), 124.92, 128.23, 135.35. **^{19}F NMR** ($CDCl_3$, 282 MHz) δ -58.61 (q, *J* = 2.0 Hz, 3F). **IR** (neat, cm^{-1}): 3388m, 1592m, 1316m, 1257m, 1109s.

Trifluoromethyl-1*H*-indole (10b)[14]



(**B1**): 59 % (*2*:*3*:*7* = 2.8:1.1:1).

(**B2**): 75 % (*2*:*3*:*7* = 2.9:1.1:1). Purification by silica gel column chromatography (pentane/CH_2Cl_2 90:10) afforded ***2*-10b** (23 mg, 42 %).

*2-(Trifluoromethyl)-1H-indole (**2-10b**)*

^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.95 (dt, *J* = 2.2, 1.1 Hz, 1H), 7.21 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 7.32– 7.37 (m, 1H),7.42-7.45 (m, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 8.36 (bs, 1H). **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 104.45 (q, *J*= 3.3 Hz), 111.84, 121.31, 121.40 (q, *J* = 267.6 Hz), 122.25, 124.95, 125.88 (q, *J* = 39.1 Hz), 126.76, 136.28. **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -60.56 (d, *J* = 1.7 Hz, 3F). **IR** (neat, cm^{-1}): 3388m, 1558w, 1167s, 1149m, 1101s, 1085m.

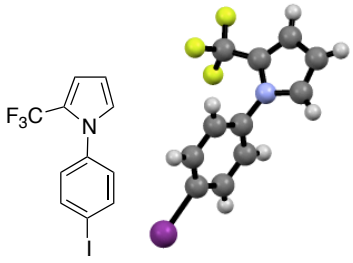
*3-(Trifluoromethyl)-1H-indole (**3-10b**)*

^{19}F NMR ($CDCl_3$, 376 MHz) δ -57.34 (s, 3F).

*7-(Trifluoromethyl)-1H-indole (**7-10b**)*

^{19}F NMR ($CDCl_3$, 376 MHz) δ -61.52 (s, 3F).

1-(4-Iodophenyl)-2-(trifluoromethyl)-1*H*-pyrrole (10c)



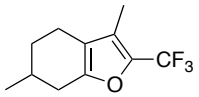
(**B1**): 57 %.

[14] (a) M. S. Wiehn, E. V. Vinogradova and A. Togni, *J. Fluorine Chem.* 2010, **131**, 951–957; (b) Q.-Y. Chen, Z.-T. Li, *J. Chem. Soc. Perkin Trans. 1* 1993, 645–648.

(**B2**): Reaction performed with 4 equiv. of **9c** (253 mg, 0.94 mmol), 1 equiv. of **5** (74 mg, 0.235 mmol), 5 mol% of **1** (7 mg, 0.012 mmol) in CH_2Cl_2 (4.5 mL): 87 %. Purification by silica gel column chromatography (pentane 100 %) afforded **10c** (63 mg, 80 %).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.28 (t, *J* = 3.3 Hz, 1H), 6.73-6.74 (m, 1H), 6.84-6.85 (m, 1H), 7.12-7.14 (m, 2H), 7.77-7.79 (m, 2H). **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 94.00, 108.84, 113.32 (q, *J* = 3.5 Hz), 121.20 (q, *J* = 266.9 Hz), 122.36 (q, *J* = 38.4 Hz), 127.20 (q, *J* = 2.1 Hz), 128.41, 138.40, 138.97. **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -55.86 (s, 3F). **IR** (neat, cm^{-1}): 1552m, 1493s, 1283m, 1098s.

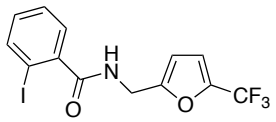
3,6-Dimethyl-2-(trifluoromethyl)-4,5,6,7-tetrahydrobenzofuran (10d)[15]



(**B1**): 74 %.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.08 (d, *J* = 6.7 Hz, 3H), 1.36 (dddd, *J* = 13.2, 10.7, 9.8, 5.9 Hz, 1H), 1.82-1.86 (m, 1H), 1.90-1.98 (m, 1H), 2.04 (q, *J* = 2.0 Hz, 3H), 2.14-2.22 (m, 1H), 2.28-2.40 (m, 2H), 2.67 (dd, *J* = 16.5, 5.3 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 8.01, 19.70, 21.41, 29.53, 30.98, 31.23, 119.14, 120.87 (q, *J* = 266.8 Hz), 122.62 (q, *J* = 2.4 Hz), 135.09 (q, *J* = 39.9 Hz), 152.56 (q, *J* = 2.0 Hz). **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -61.21 (q, *J* = 1.8 Hz, 3F). **IR** (neat, cm^{-1}) : 1590w, 1460w, 1445w, 1369m, 1183m, 1152m, 1114m.

2-iodo-*N*-((5-(trifluoromethyl)furan-2-yl)methyl)benzamide (10e)



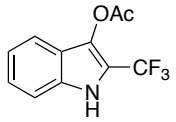
(**B1**): Reaction performed with 1 equiv. of **9e** (89 mg, 0.268 mmol), 1.5 equiv. of **5** (127 mg, 0.402 mmol), 10 mol% of **1** (18 mg, 0.027 mmol) in CH_2Cl_2 (1.3 mL) for 48 h: 51 % (conversion: 60 %). Purification by silica gel column chromatography (pentane/ethyl acetate 80:20 to 70:30) afforded a mixture of **10e** with unreacted starting material **9e** (87 mg, **9e**/**10e** = 0.7/1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.59 (d, *J* = 5.9 Hz, 2H), 6.40-6.41 (m, 1H), 6.59 (bs, 1H), 6.71-6.72 (m, 1H), 7.05-7.09 (m, 1H), 7.31-7.35 (m, 2H), 7.81 (d, *J* = 7.9 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 36.75, 92.33, 108.80, 112.65 (q, *J* = 3.0 Hz), 119.06 (q, *J* = 267.6 Hz), 128.22, 128.39, 131.39,

[15] M. Baar and S. Blechert, *Chem. Eur. J.* 2015, **21**, 526–530.

139.99, 141.30 (q, J = 43.4 Hz), 141.45, 154.00, 169.34. **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -63.90 (s, 3F). **HRMS** (ESI) calculated for $[C_{13}H_9F_3INO_2Na]^+$ 417.9522, found 417.9535.

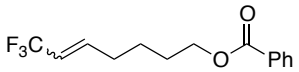
2-(trifluoromethyl)-1*H*-indol-3-yl acetate (10f)



(**B1**): 63 %. Purification by silica gel column chromatography (pentane/ethyl acetate 95:5) afforded **10f** (45 mg, 60 %).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.42 (s, 3H), 7.19 (ddd, *J* = 8.0, 6.7, 1.2 Hz, 1H), 7.24-7.32 (m, 2H), 7.49 (d, *J* = 8.1 Hz, 1H), 8.32 (s, 1H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 20.47, 112.33, 114.61 (q, *J* = 38.4 Hz), 119.05, 120.49, 120.82 (q, J = 268.0 Hz), 121.45, 125.64, 129.75 (q, *J* = 2.9 Hz), 169.09. **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -59.90 (s, 3F). **IR** (neat, cm^{-1}): 3340b, 1750s, 1607m, 1325s, 1116s, 1078s. **HRMS** (ESI) calculated for $[C_{11}H_8F_3NO_2Na]^+$ 266.0399, found 266.0408.

7,7,7-Trifluorohept-5-en-1-yl benzoate (12a)[16]

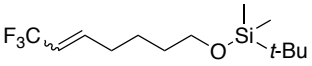


(**C**): 61 % (E/Z = 4.0:1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.57-1.68 (m, 2H, *E*+*Z*), 1.77-1.84 (m, 2H, *E*+*Z*), 2.19-2.28 (m, 2H, *E*), 2.35-2.42 (m, 2H, *Z*), 4.32-4.36 (m, 2H, *E*+*Z*), 5.60-5.69 (m, 1H, *E*+*Z*), 6.00 (dt, *J* = 11.6, 7.9 Hz, 1H, *Z*), 6.39 (dtq, *J* = 15.8, 6.7, 2.2 Hz, 1H, *E*), 7.42-7.46 (m, 2H, *E*+*Z*), 7.53-7.58 (m, 1H, *E*+*Z*), 8.03-8.06 (m, 2H, *E*+*Z*). **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 24.60 (*E*), 25.54 (*Z*), 28.06 (*Z*), 28.28 (*E*), 28.34 (*Z*), 31.13 (*E*), 64.58 (*E*), 64.64 (*Z*), 119.03 (q, *J* = 33.2 Hz, *E*), 119.05 (q, *J* = 33.2 Hz, *Z*), 123.13 (q, *J* = 269.2 Hz, *E*), 123.41 (q, *J* = 272.2 Hz, *Z*), 128.47 (*Z*), 128.49 (*E*), 129.65 (*E*+*Z*), 130.43 (*E*), 130.47 (*Z*), 133.01 (*Z*), 133.05 (*E*), 140.12 (q, *J* = 6.5 Hz, *E*), 142.41 (q, *J* = 5.4 Hz, *Z*), 166.69 (*E*+*Z*). **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -63.99 (dq, *J* = 6.5, 2.3 Hz, *E*), -58.12 (dt, *J* = 8.5, 2.2 Hz, *Z*). **IR** (neat, cm^{-1}): 1717s, 1680m, 1270s, 1113s.

[16] S. Mizuta, S. Verhoog, K. M. Engle, T. Khotavivattana, M. O'Duill, K. Wheelhouse, G. Rassias, M. Médebielle and V. Gouverneur, *J. Am. Chem. Soc.* 2013, **135**, 2505–2508.

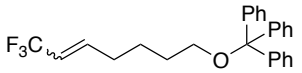
(*E*)-*tert*-butyldimethyl((7,7,7-trifluorohept-5-en-1-yl)oxy)silane (12c)[17]



(**C**): 52 % (E/Z = 3.6:1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.05 (s, 6H, *E*+*Z*), 0.89 (s, 9H, *E*+*Z*), 1.47-1.57 (m, 4H, *E*+*Z*), 2.14-2.22 (m, 2H, *E*), 2.27-2.37 (m, 2H, *Z*), 3.60-3.64 (m, 2H, *E*+*Z*), 5.53-5.66 (m, 1H, *E*+*Z*), 5.98 (dt, *J* = 11.6, 7.9 Hz, 1H, *Z*), 6.38 (dtq, *J* = 15.8, 6.7, 2.2 Hz, 1H, *E*). **^{13}C NMR** ($CDCl_3$, 101 MHz) δ -5.17 (*E*+*Z*), 18.50 (*E*+*Z*), 24.51 (*E*), 25.38 (*Z*), 26.10 (*E*+*Z*), 28.23 (*Z*), 31.35 (*E*), 32.24 (*E*), 32.32 (*Z*), 62.82 (*Z*), 62.86 (*E*), 118.60 (q, *J* = 33.2 Hz, *Z*), 118,64 (q, *J* = 33.2 Hz, *E*), 123.25 (q, *J* = 269.1 Hz, *E*), 123.51 (q, *J* = 271.1 Hz, *Z*), 140.75 (q, *J* = 6.5 Hz, *E*), 143.11 (q, *J* = 5.4 Hz, *Z*). **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -63.95 (dq, *J* = 6.8, 2.4 Hz, *E*), -58.13 (dt, *J* = 8.5, 2.4 Hz, *Z*). **IR** (neat, cm^{-1}): 1255m, 1124s, 1103s, 835m, 776m.

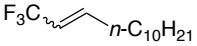
(((7,7,7-Trifluorohept-5-en-1-yl)oxy)methanetriyl)tribenzene (12d)



(**C**): 57 % (E/Z = 3.8:1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.45-1.54 (m, 2H, *E*+*Z*), 1.56-1.63 (m, 2H, *E*+*Z*), 2.06-2.08 (m, 2H, *E*), 2.23-2.27 (m, 2H, *Z*), 3.03-3.07 (m, 2H, *E*+*Z*), 5.49-5.58 (m, 1H, *E*+*Z*), 5.92 (dt, *J* = 11.7, 7.8 Hz, 1H, *Z*), 6.31 (dtq, *J* = 15.7, 6.6, 2.1 Hz, 1H, *E*), 7.17-7.28 (m, 9H, *E*+*Z*), 7.39-7.42 (m, 6H, *E*+*Z*). **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 24.88 *(E)*, 25.84 (*Z*), 28.32 (*Z*), 29.48 (*E*), 29.65 (*Z*), 31.32 (*E*), 63.16 (*E*), 63.22 (*Z*), 86.52 (*Z*), 86.58 (*E*), 118.62 (q, *J* = 33.2 Hz, *Z*), 118.68 (q, *J* = 33.2 Hz, *E*), 123.23 (q, *J* = 269.1 Hz, *E*), 123.48 (q, *J* = 270.0 Hz, *Z*), 127.00 (*Z*), 127.04 (*E*), 127.88 (*E*+*Z*), 128.81 (*E*+*Z*), 140.64 (q, *J* = 6.5 Hz, *E*), 143.02 (q, *J* = 5.4 Hz, *Z*), 144.50 (*E*), 144.54 (*Z*). **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -63.86 (dq, *J* = 6.3, 2.2 Hz, 3F, *E*), -58.06 (dt, *J* = 8.5, 2.3 Hz, 3F, *Z*). **HRMS** (ESI) calculated for $[C_{26}H_{25}F_3ONa]^+$ 433.1750, found 433.1751. **IR** (neat, cm^{-1}): 1680m, 1448m, 1272m, 1115s, 1089s, 1073s.

1,1,1-trifluorotridec-2-ene (12e)



(**C**): 53 % (E/Z = 3.6:1). Purification by silica gel column chromatography (hexane 100 %) afforded **12e** (38 mg, 52 %).

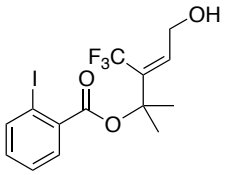
[17] N. Iqbal, S. Choi, E. Kim and E. J. Cho, *J. Org. Chem.* 2012, **77**, 11383–11387.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.87-0.90 (m, 3H, *E*+*Z*), 1.23-1.32 (m, 14H, *E*+*Z*), 1.40-1.45 (m, 2H, *E*+*Z*), 2.14-2.16 (m, 2H, *E*), 2.27-2.32 (m, 2H, *Z*), 5.54-5.64 (m, 1H, *E*+*Z*), 5.98 (dt, *J* = 11.6, 7.9 Hz, 1H, *Z*), 6.38 (dtq, *J* = 15.8, 6.7, 2.2 Hz, 1H, *E*). **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 14.25 (*E*+*Z*), 22.85 (*E*+*Z*), 28.14 (*E*), 28.51 (*Z*), 29.04 (*Z*), 29.20 (*E*+*Z*), 29.27 (*Z*), 29.48 (*E*+*Z*), 29.51 (*Z*), 29.53 (*E*), 29.68 (*E*+*Z*), 29.74 (*E*+*Z*), 31.62 (*E*), 32.07 (*E*), 118.38 (q, *J* = 33.1 Hz, *Z*), 118.45 (q, *J* = 33.1 Hz, *E*), 123.30 (q, *J* = 269.1 Hz, *E*), 123.56 (q, J = 272.1 Hz, *Z*), 140.99 (q, *J* = 6.5 Hz, *E*), 143.36 (q, *J* = 5.3 Hz, *Z*). **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -63.93 (dq, *J* = 6.9, 2.4 Hz, *E*), -58.10 (dt, *J* = 8.6, 2.3 Hz, *Z*). **IR** (neat, cm^{-1}): 2925w, 2913w, 2847w, 1250w, 1114m.

7,7,7-trifluoroheptyl benzoate (14a),[16] (*E*)-7,7,7-trifluorohept-5-en-1-yl benzoate (14b)[16] and (*E*)-7,7,7-trifluorohept-4-en-1-yl benzoate (14c)[18]

^{19}F NMR ($CDCl_3$, 376 MHz) δ -66.69 (t, *J* = 10.7 Hz, 3F, **14c**), -66.41 (t, *J* = 11.0 Hz, 3F, **14a**), -63.99 (dq, *J* = 6.4, 2.0 Hz, 3F, **14b**).

5-hydroxy-2-methyl-3-(trifluoromethyl)pent-3-en-2-yl 2-iodobenzoate (16)



(**B1**): 43 %. Purification by silica gel column chromatography (pentane/ethyl acetate 80:20) afforded **16** (52 mg, 41 %).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.80 (s, 6H), 2.59 (s, 1H), 4.48 (dq, *J* = 5.3, 2.6 Hz, 2H), 6.32 (t, *J* = 5.5 Hz, 1H), 7.09 – 7.15 (m, 1H), 7.38 (td, *J* = 7.6, 1.2 Hz, 1H), 7.69 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.94 (dd, *J* = 8.0, 1.0 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 27.33, 59.46 (q, *J* = 3.8 Hz), 81.42, 93.73, 123.77 (q, *J* = 277.8 Hz), 128.07, 130.71, 132.00 (q, *J* = 28.1 Hz), 132.56, 135.95, 138.98 (q, *J* = 3.1 Hz), 141.21, 165.62. **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -56, 15 (s, 3F). **IR** (neat, cm^{-1}): 3420b, 1717s, 1294s, 1042s. **HRMS** (ESI) calculated for $[C_{14}H_{14}F_3IO_3Na]^+$ 436.9832, found 436.9847.

[18] L. Chu and F.-L. Qing, *Org. Lett.* 2012, **14**, 2106–2109.

Crystal structure determination of compound 10c

A single crystal of the compound was selected, mounted onto a cryoloop, and transferred in a cold nitrogen gas stream. Intensity data were collected with a BRUKER Kappa-APEXII diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Data collection were performed with APEX2 suite (BRUKER). Unit-cell parameters refinement, integration and data reduction were carried out with SAINT program (BRUKER). SADABS (BRUKER) was used for scaling and multi-scan absorption corrections.

In the WinGX suite of programs[19], the structure were solved with Sir2014[20] program and refined by full-matrix least-squares methods using SHELXL-14[]21.

CCDC 1413274 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystal data and structure refinement for compound 10c.

Empirical formula	C11 H7 F3 I N	
Formula weight	337.08	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 7.7762(3) Å	α= 90°.
	b = 19.2554(8) Å	β= 98.728(2)°.
	c = 7.6287(3) Å	γ = 90°.
Volume	1129.05(8) $Å^3$	
Z	4	
Density (calculated)	1.983 Mg/m^3	
Theta range for data collection	2.115 to 30.174°.	
Reflections collected	11530	
Independent reflections	3323 [R(int) = 0.0174]	
Completeness to theta = 25.242°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3323 / 0 / 145	
Goodness-of-fit on F^2	1.046	
Final R indices [I>2sigma(I)]	R1 = 0.0250, wR2 = 0.0516	
R indices (all data)	R1 = 0.0323, wR2 = 0.0545	

[19] L. J. Farrugia, *Journal of Applied Crystallography* 1999, **32**, 837–838.
[20] M. C. Burla, R. Caliandro, B. Carrozzini, G. L. Cascarano, C. Cuocci, C. Giacovazzo, M. Mallamo, A. Mazzone and G. Polidori, *Journal of Applied Crystallography* 2015, **48**, 306–309.
[21] G. M. Sheldrick, *Acta Crystallographica Section C* 2015, **71**, 3–8.

Extinction coefficient n/a

XYZ data for calculated complex 3

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N	7.0	-1.85011733	-0.30709809	-0.01608500
O	8.0	0.33621761	0.88533360	1.61407244
O	8.0	-0.07294050	-1.13690805	-1.71164858
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C	6.0	2.58972931	0.76664972	0.94705898
C	6.0	-2.32762098	-0.97665107	-1.05576837
C	6.0	-1.26850450	-1.46489811	-1.98147225
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C	6.0	3.24816680	2.30240512	3.17337418
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C	6.0	3.95242238	1.11418426	1.17886925
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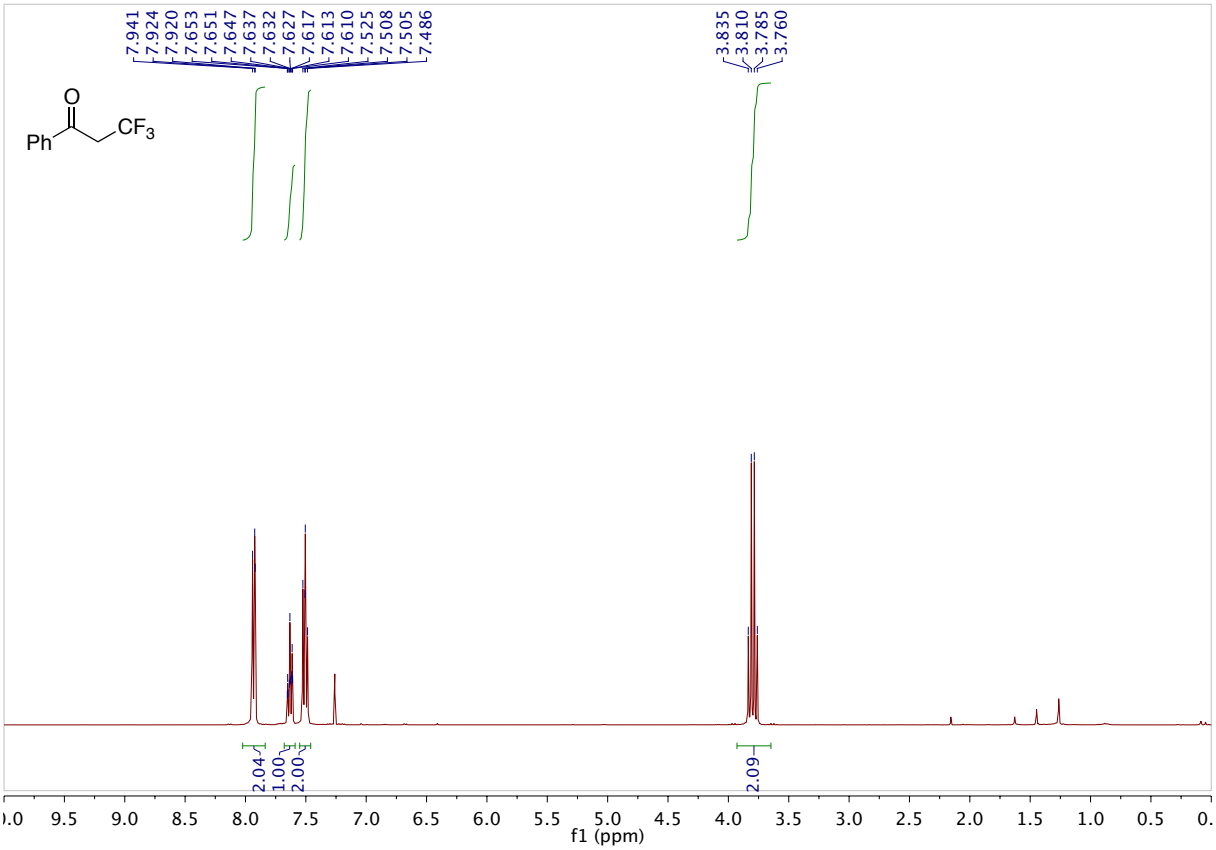
NMR Spectra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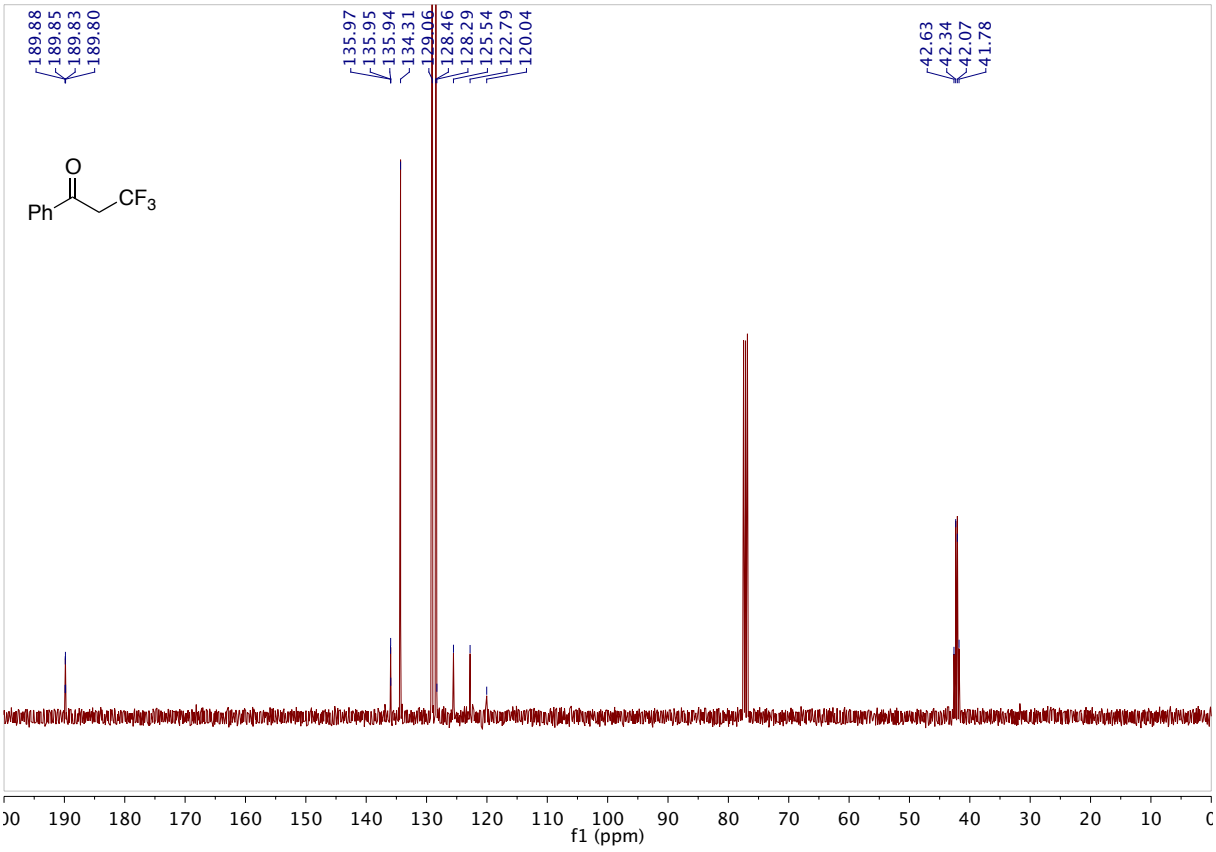
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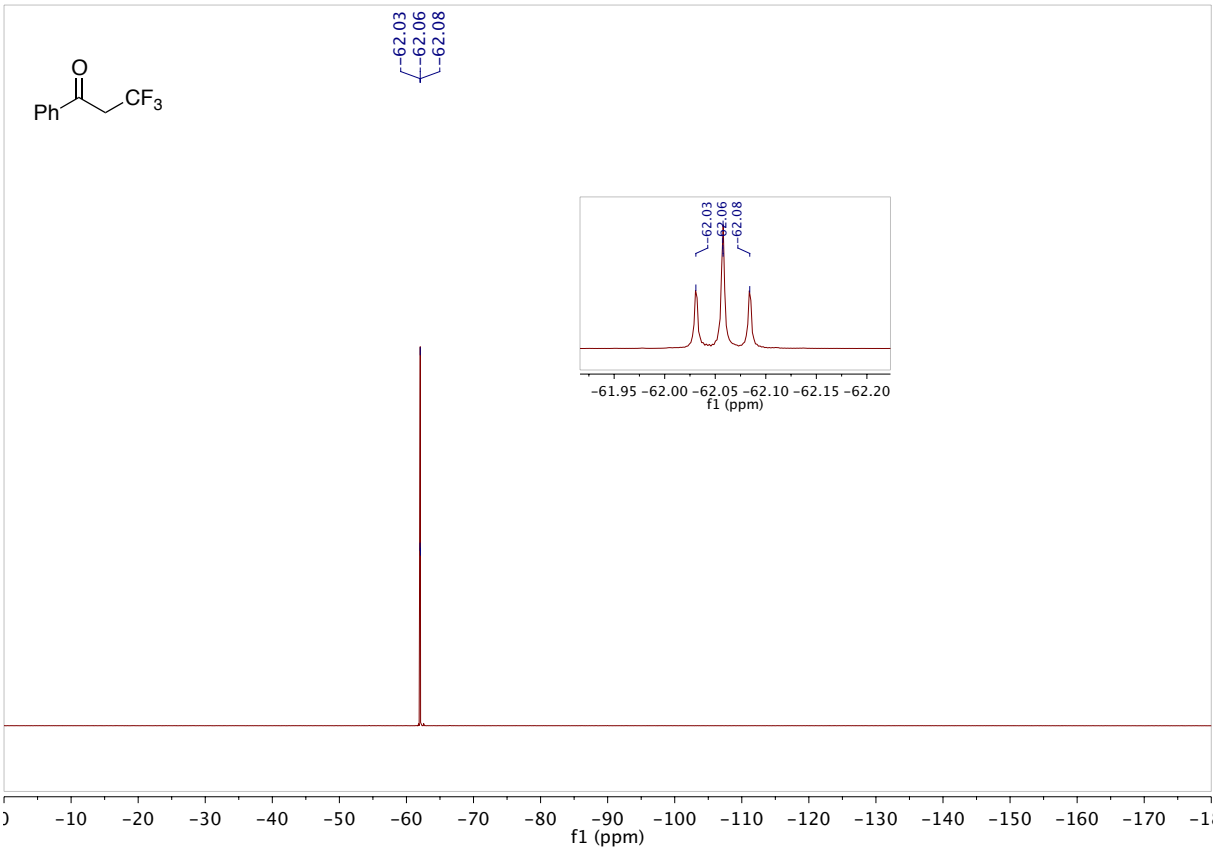
Ph
CF3
f1 (ppm)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-62.06
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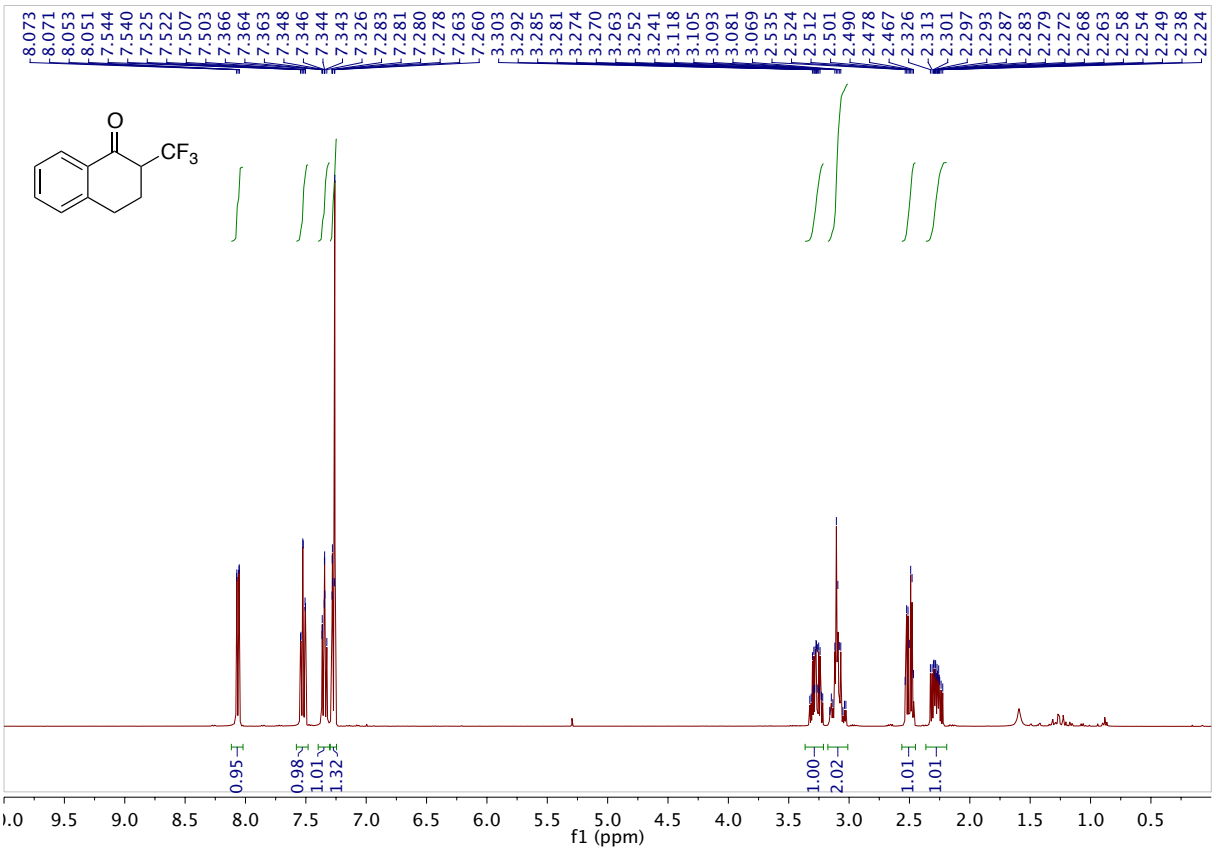
f1 (ppm)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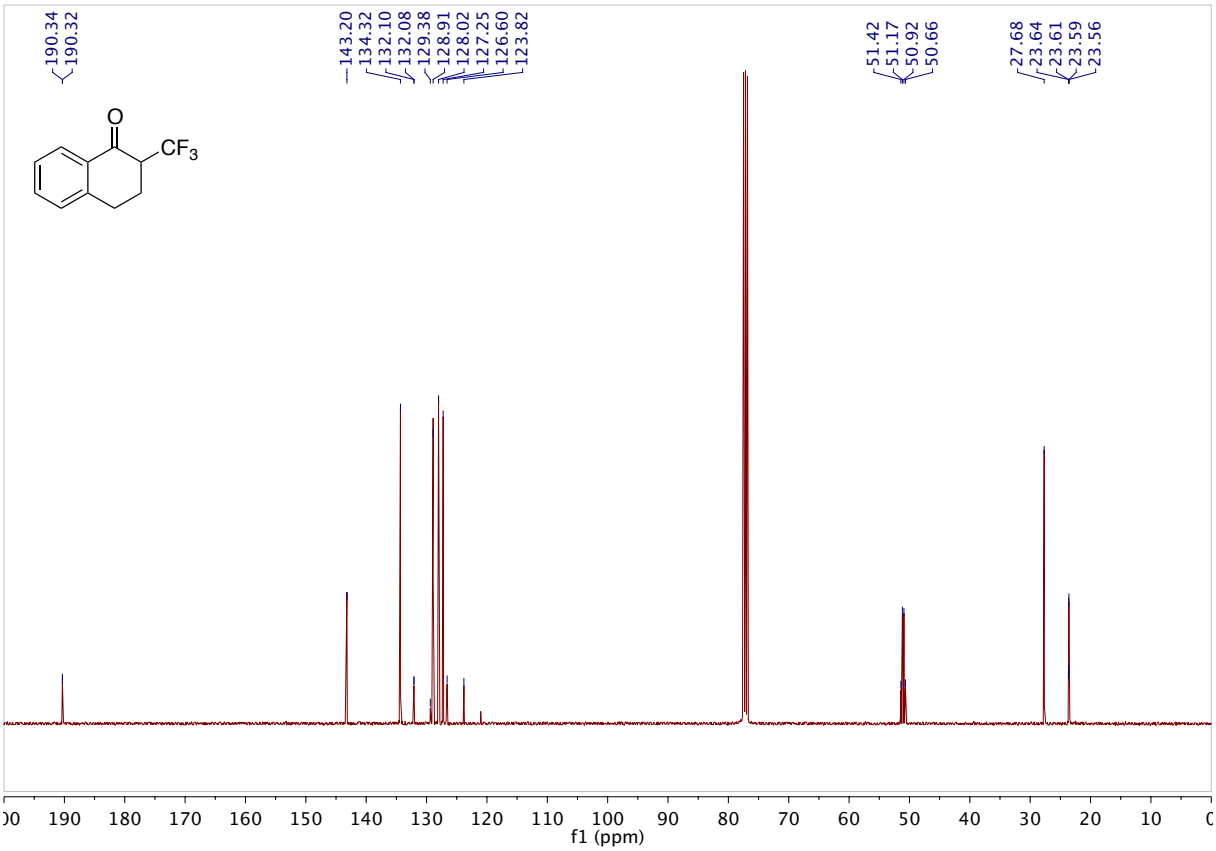
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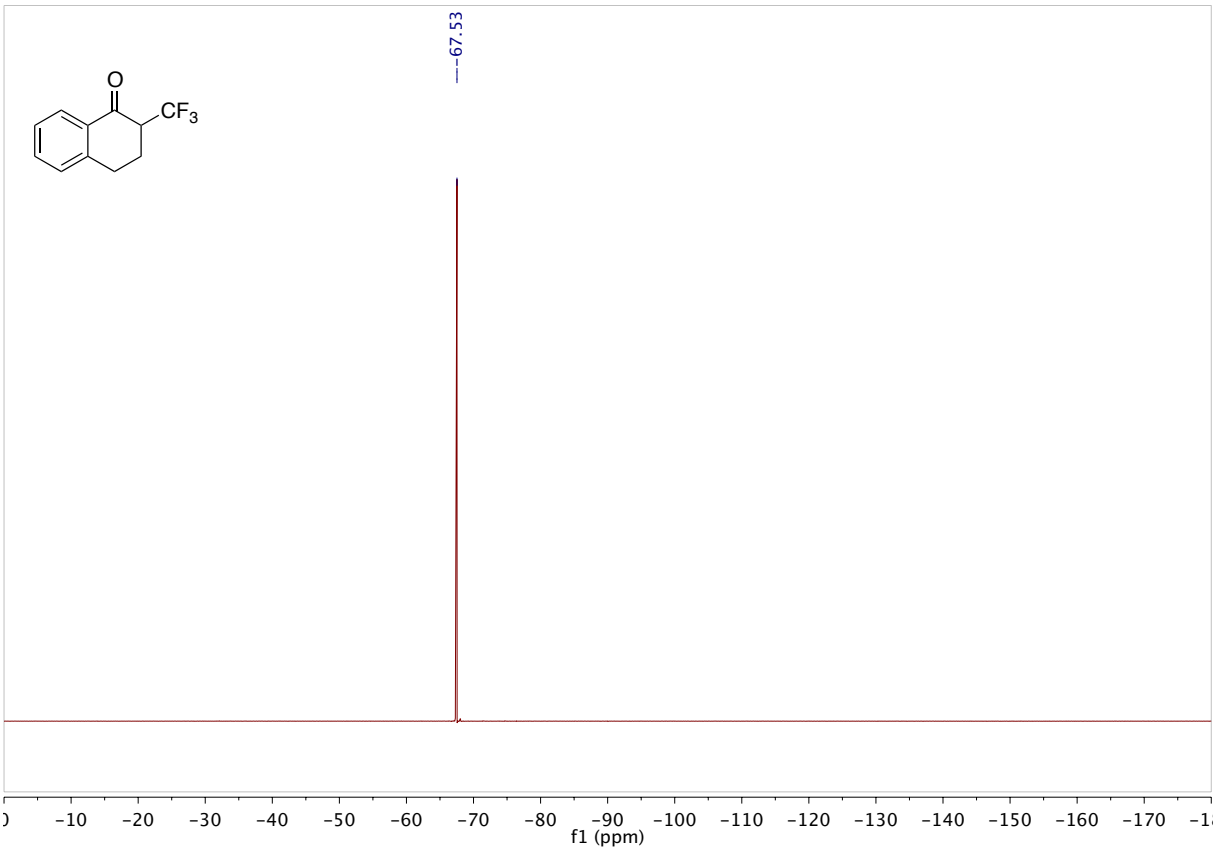
CF3
f1 (ppm)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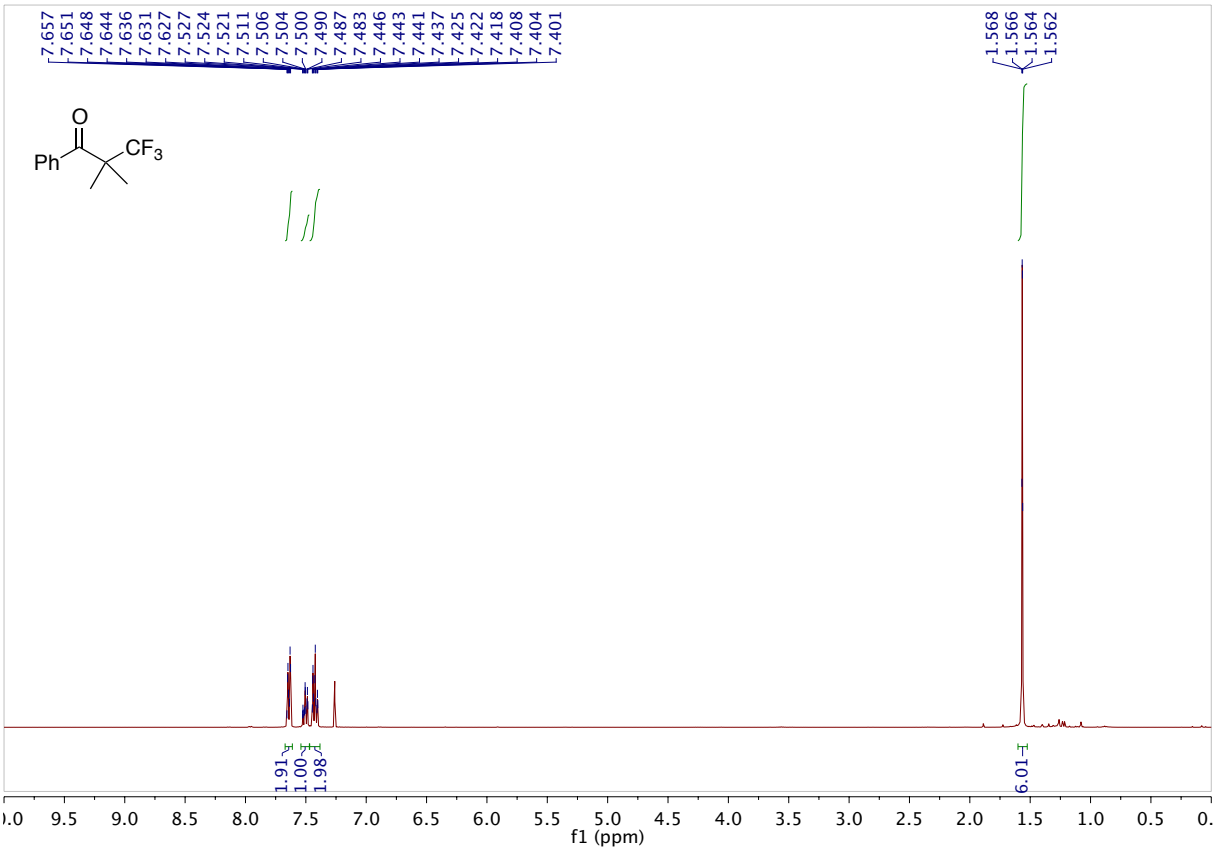
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7.422
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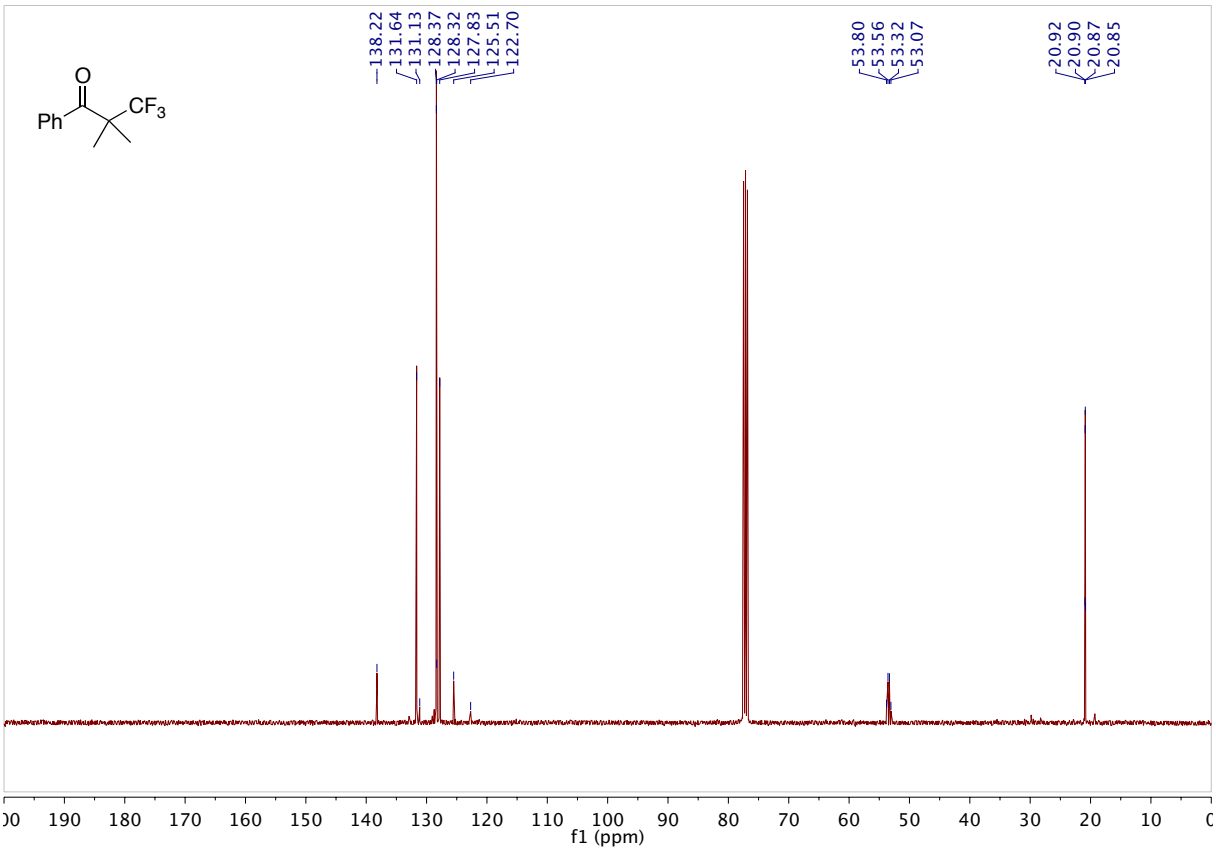
f1 (ppm)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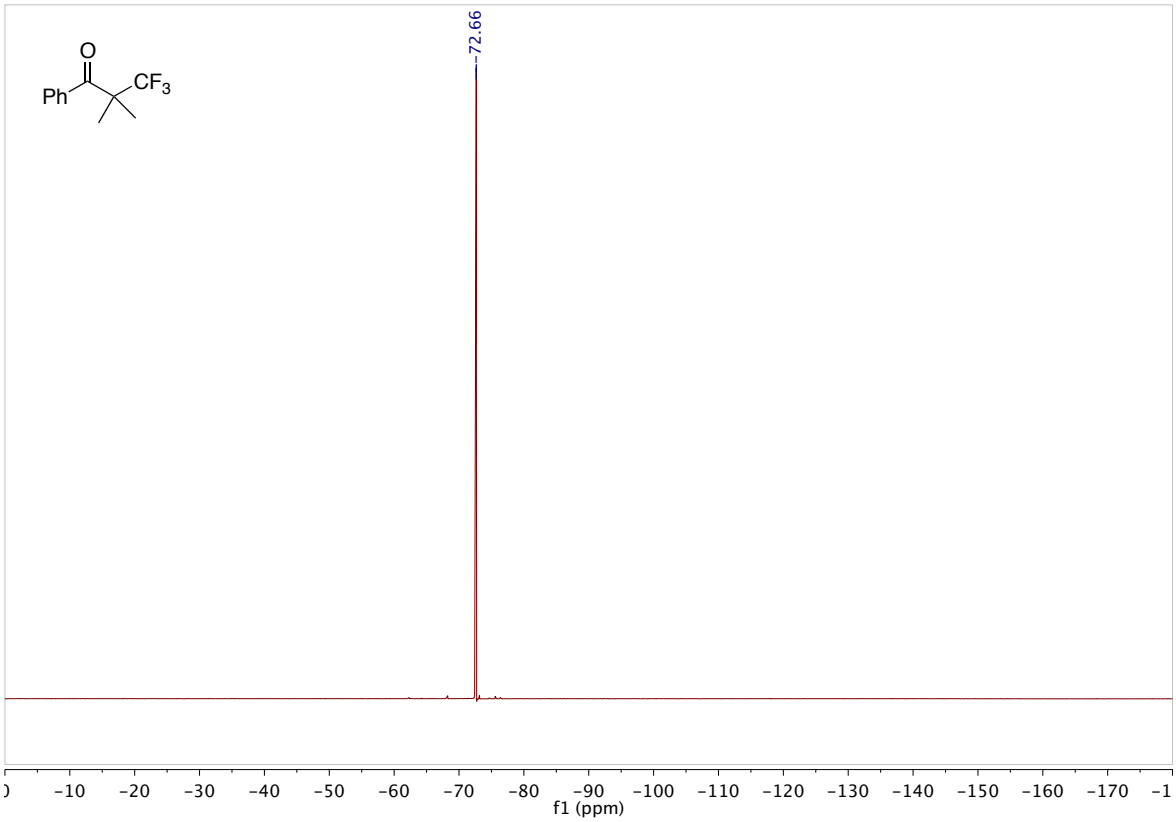
f1 (ppm)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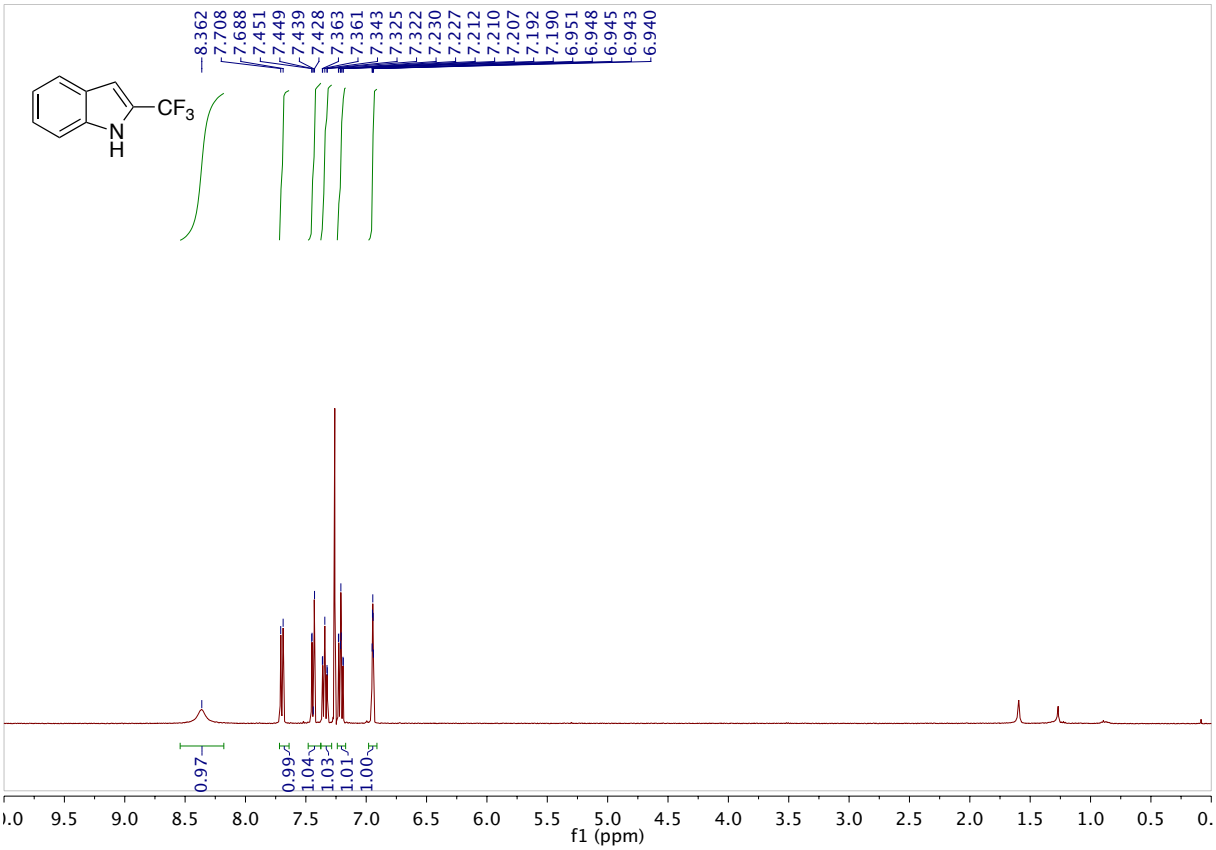
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7.190
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6.948
6.945
6.943
6.940
CF3
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0.99
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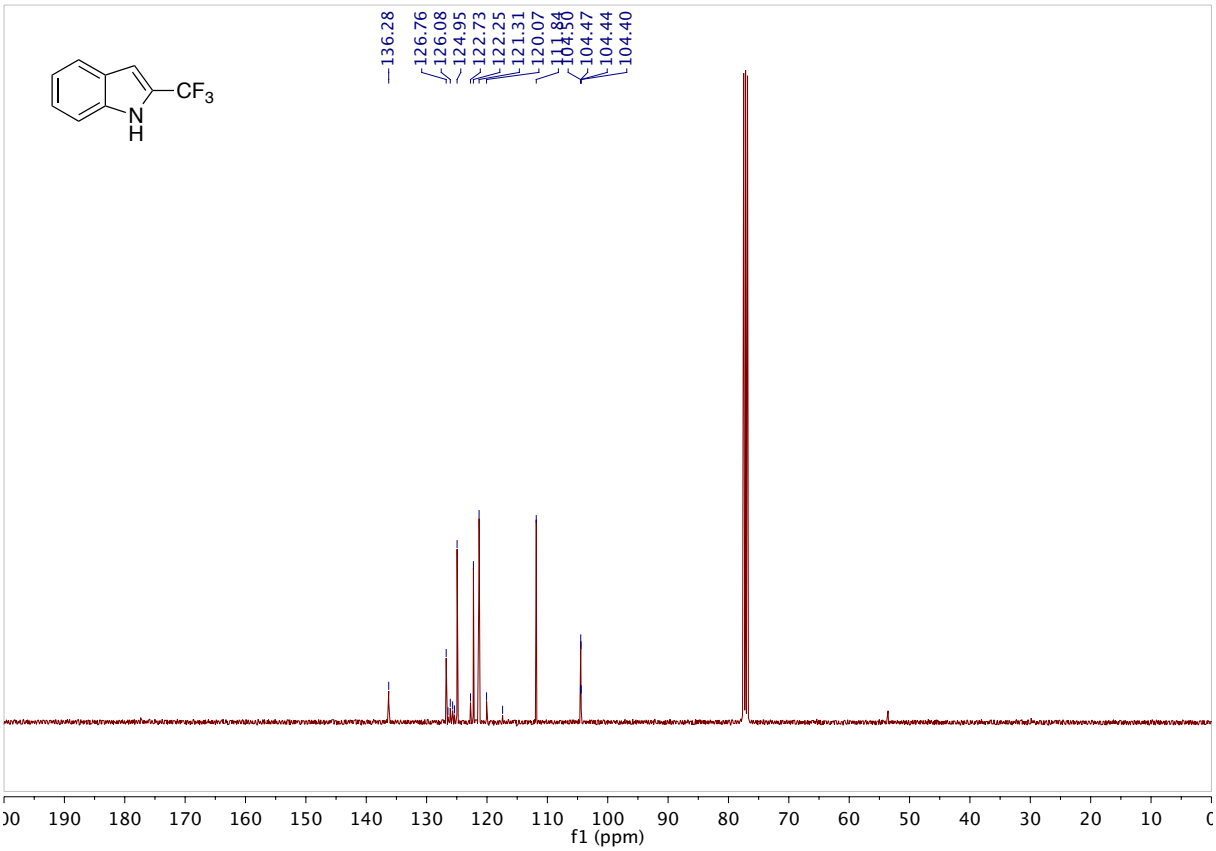
1.03
1.01
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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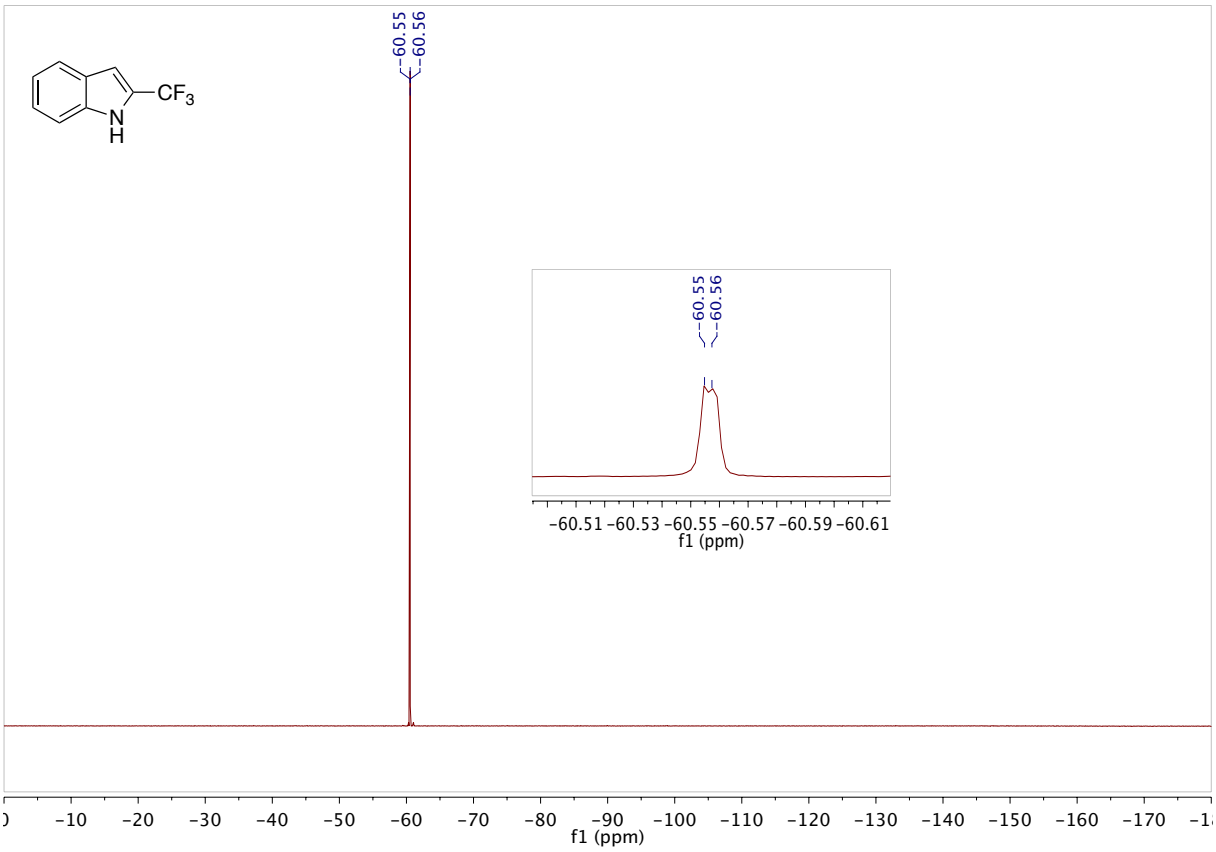
CF3
N
H
f1 (ppm)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60.56
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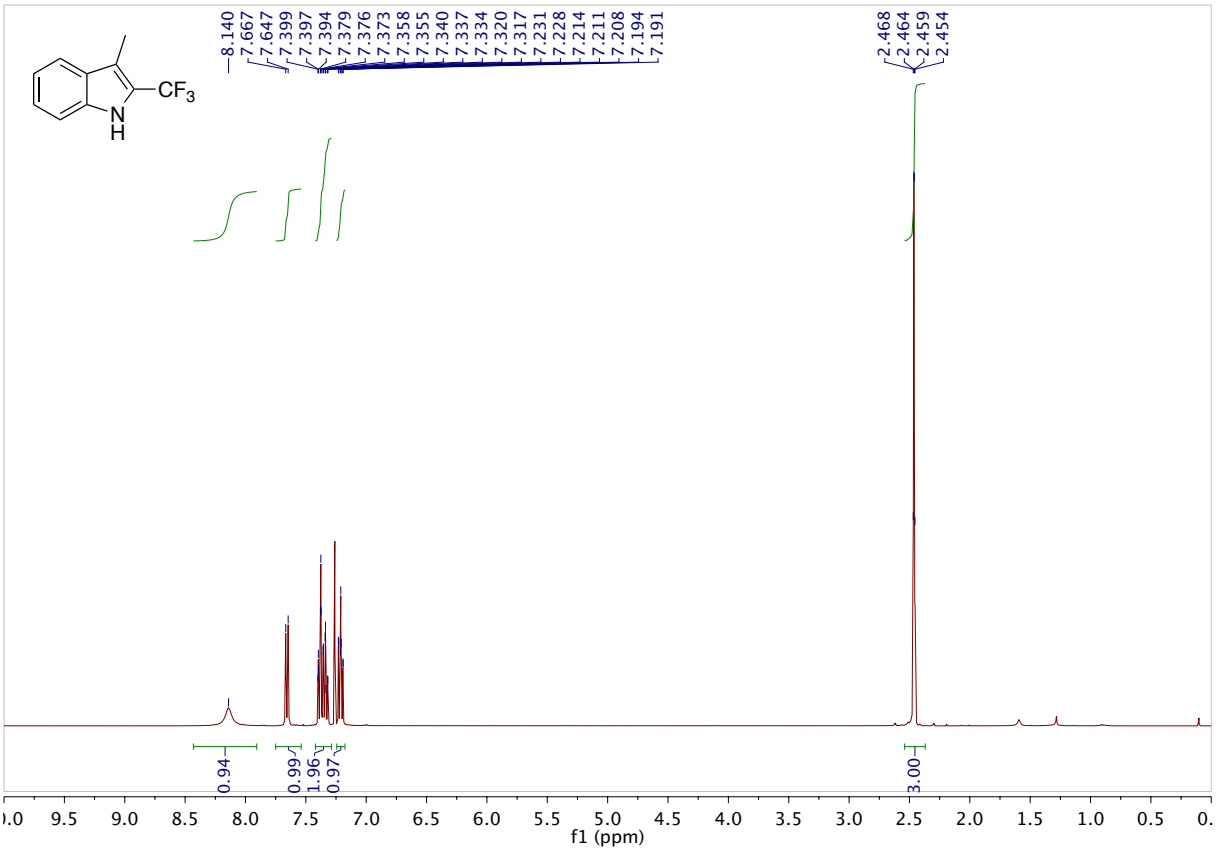
f1 (ppm)
f1 (ppm)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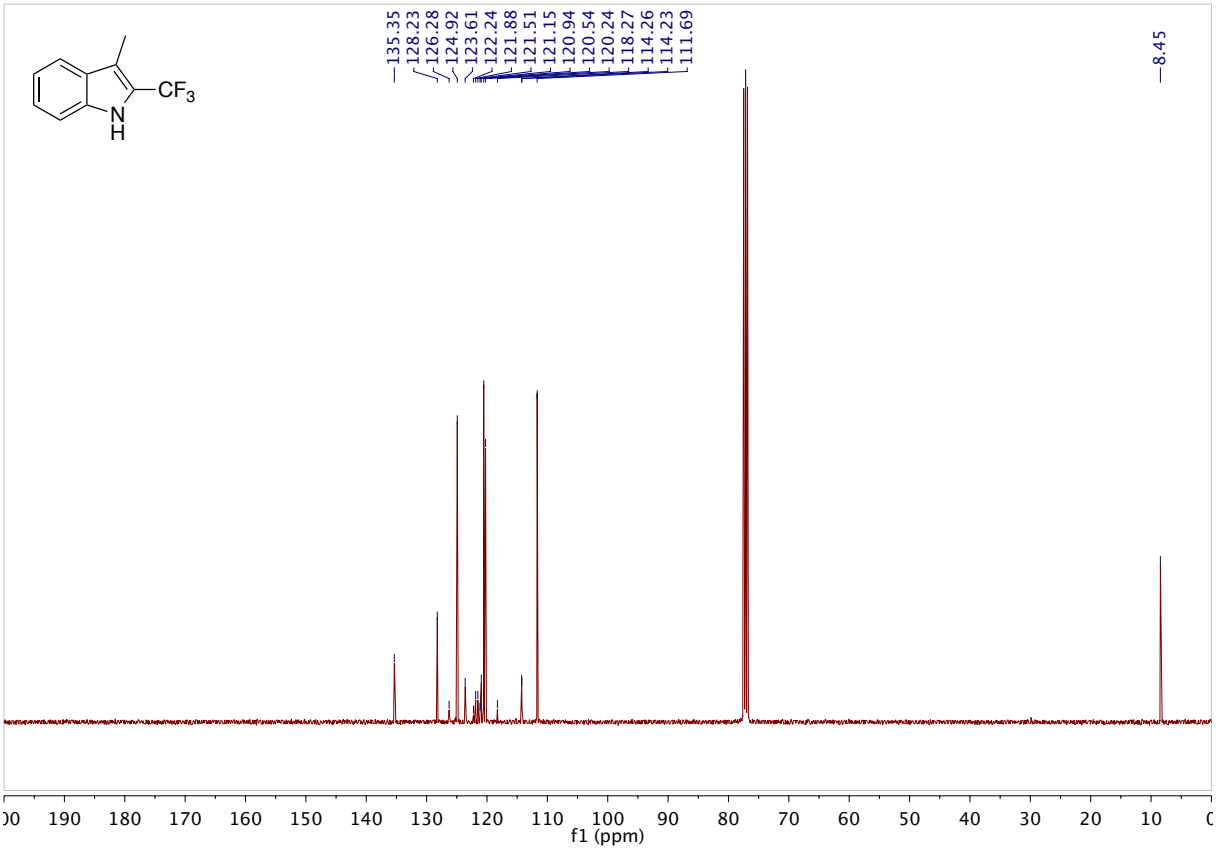
f1 (ppm)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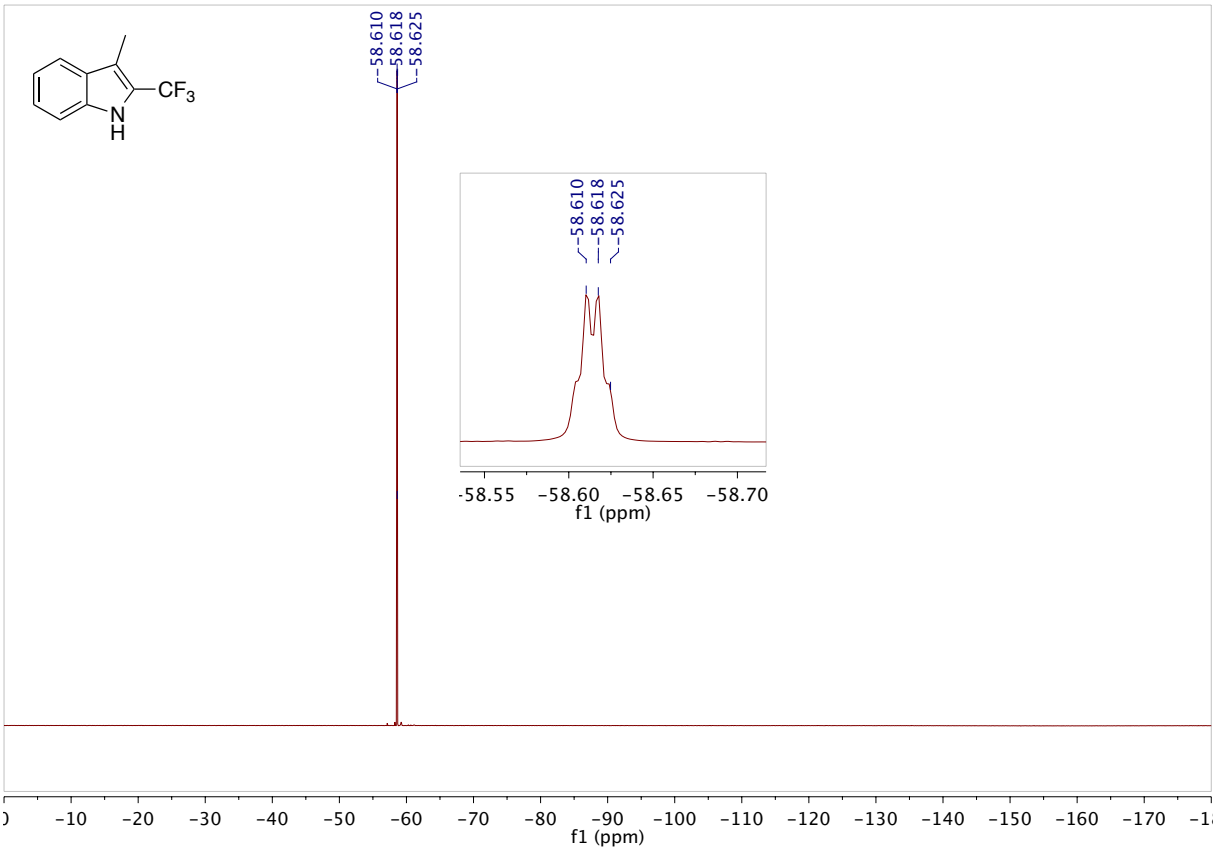
N
H
f1 (ppm)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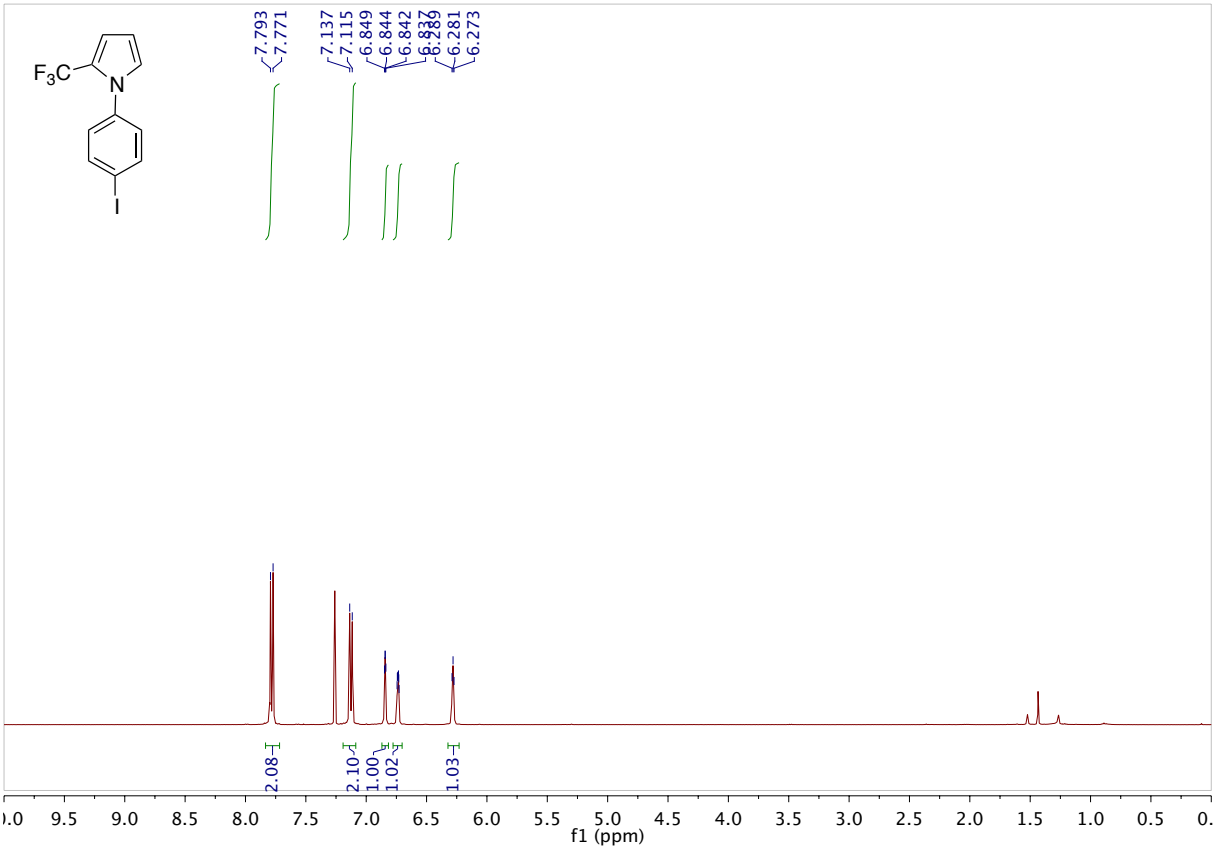
f1 (ppm)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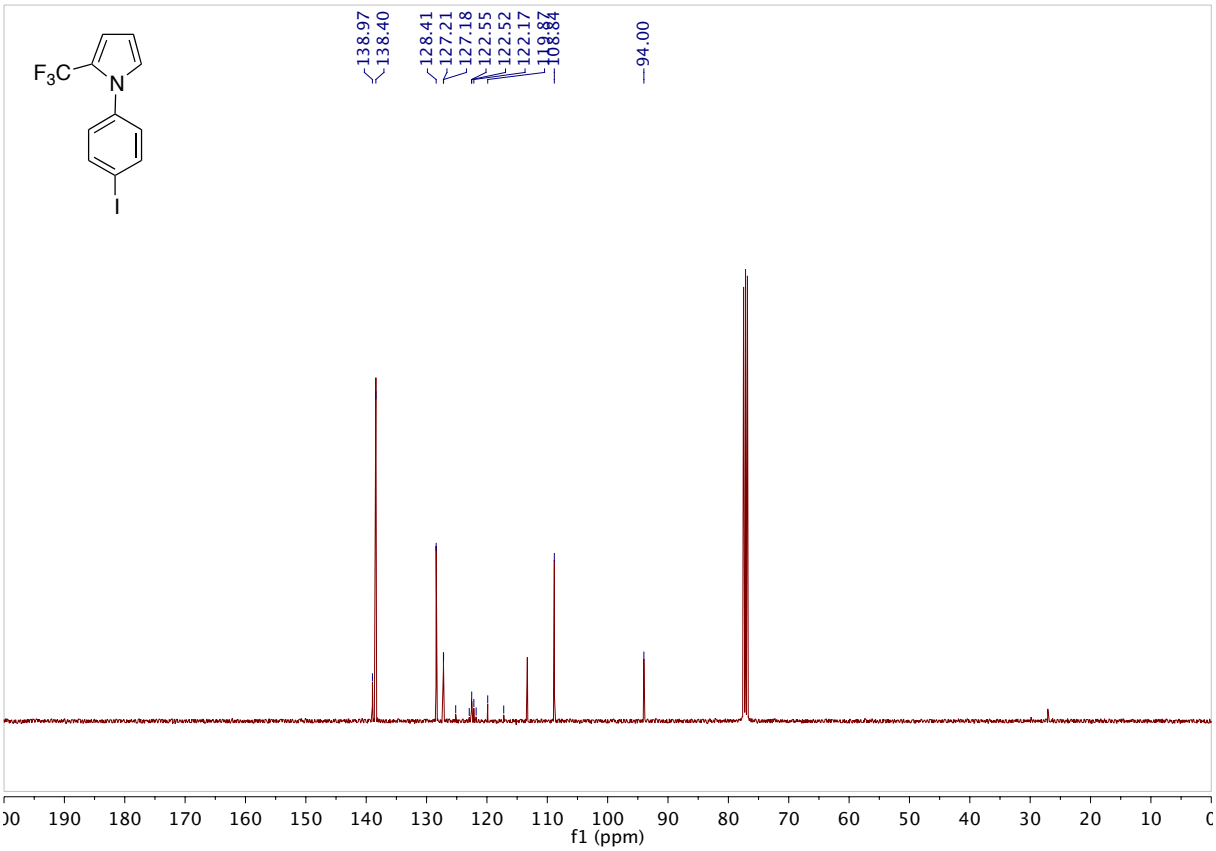
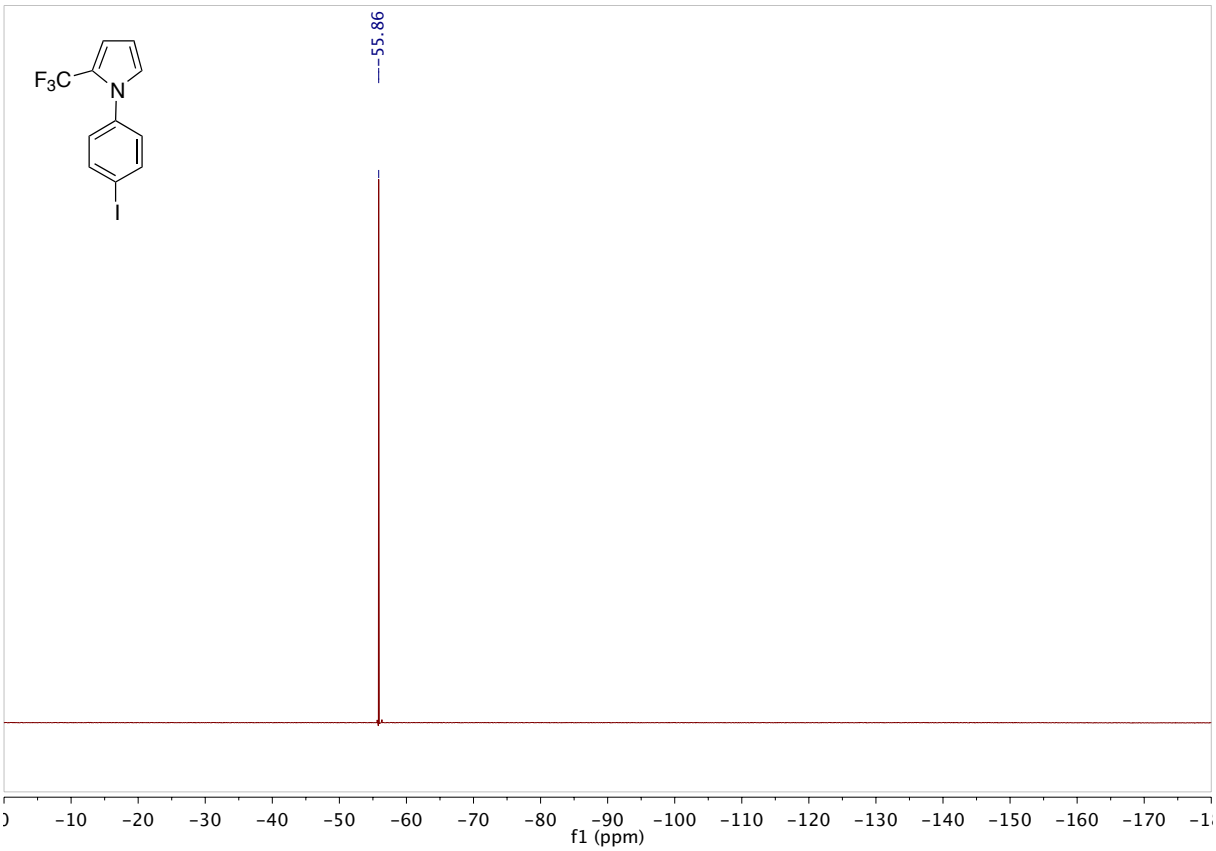
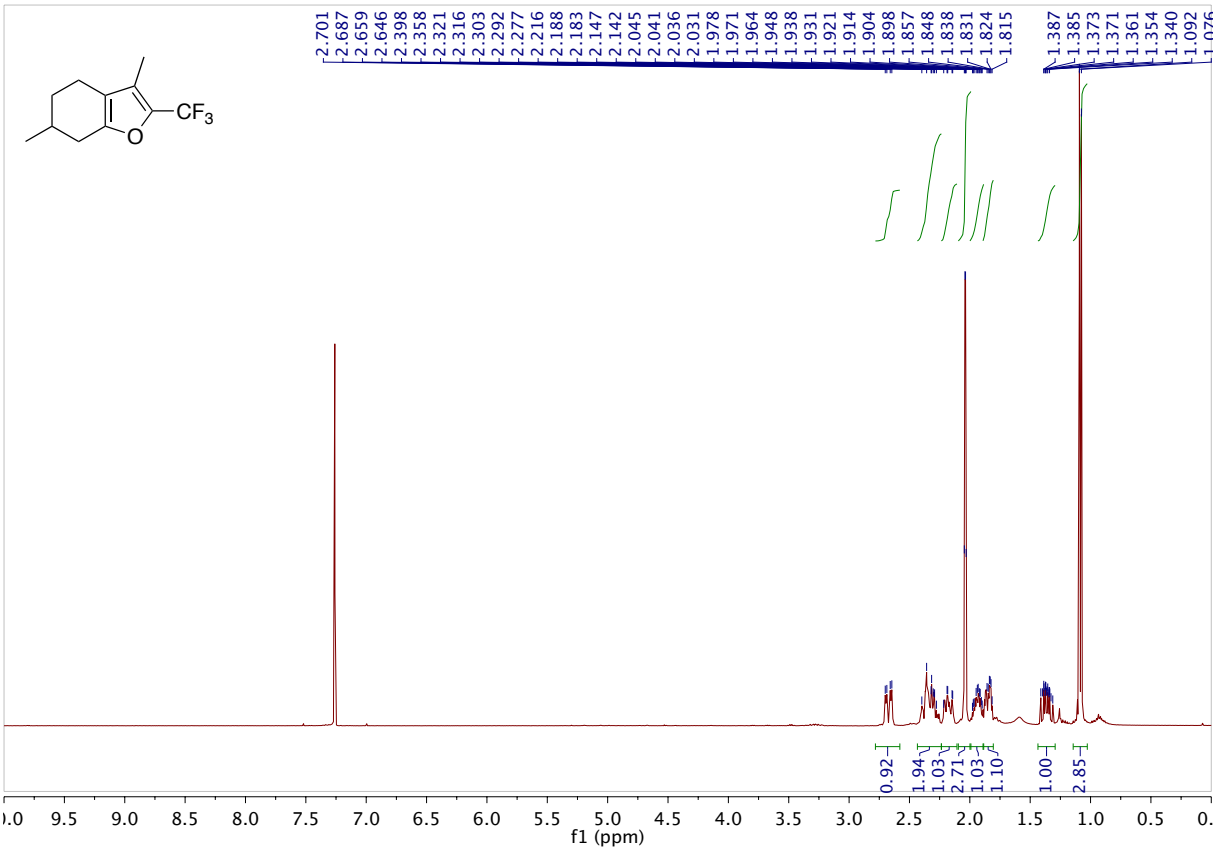
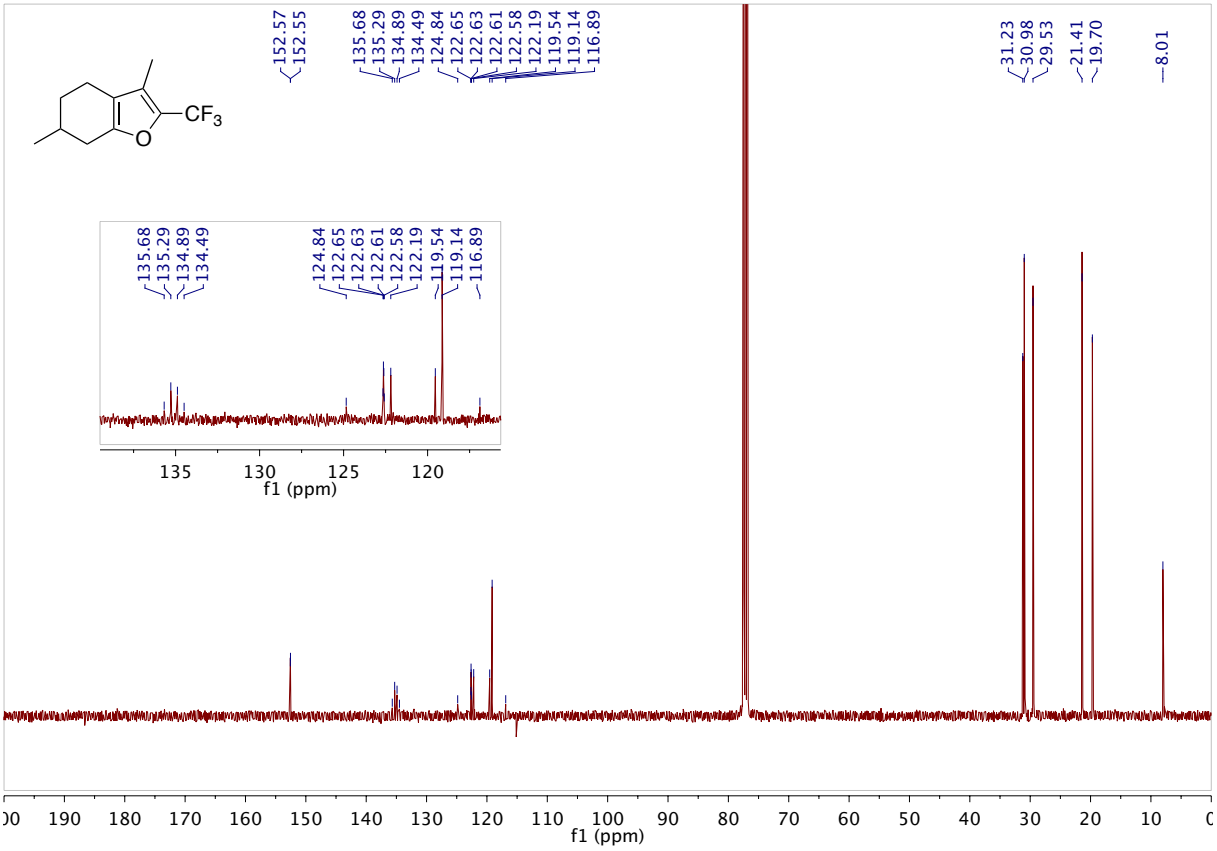
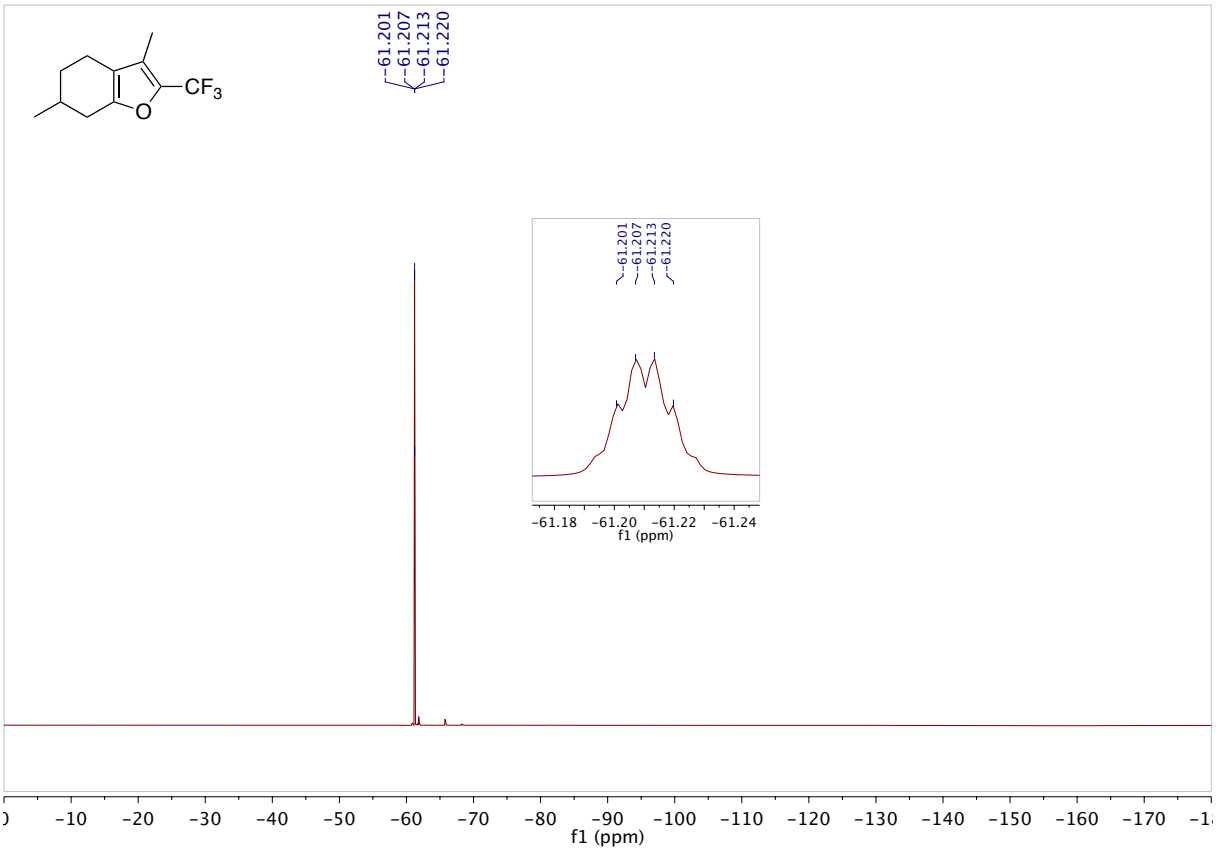
1.03
f1 (ppm)

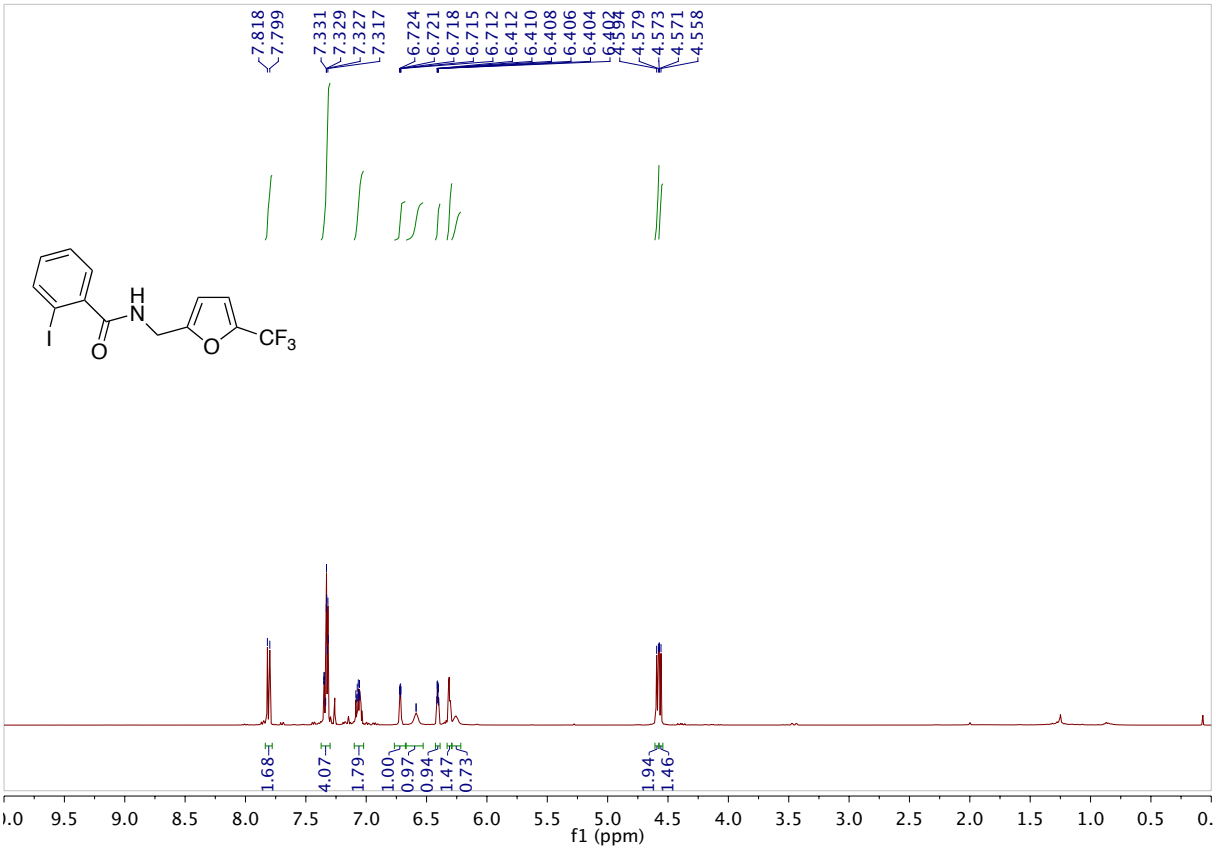

F3C
N
I
138.97
138.40
128.41
127.21
127.18
122.55
122.52
122.17
119.87
108.84
94.00
f1 (ppm)

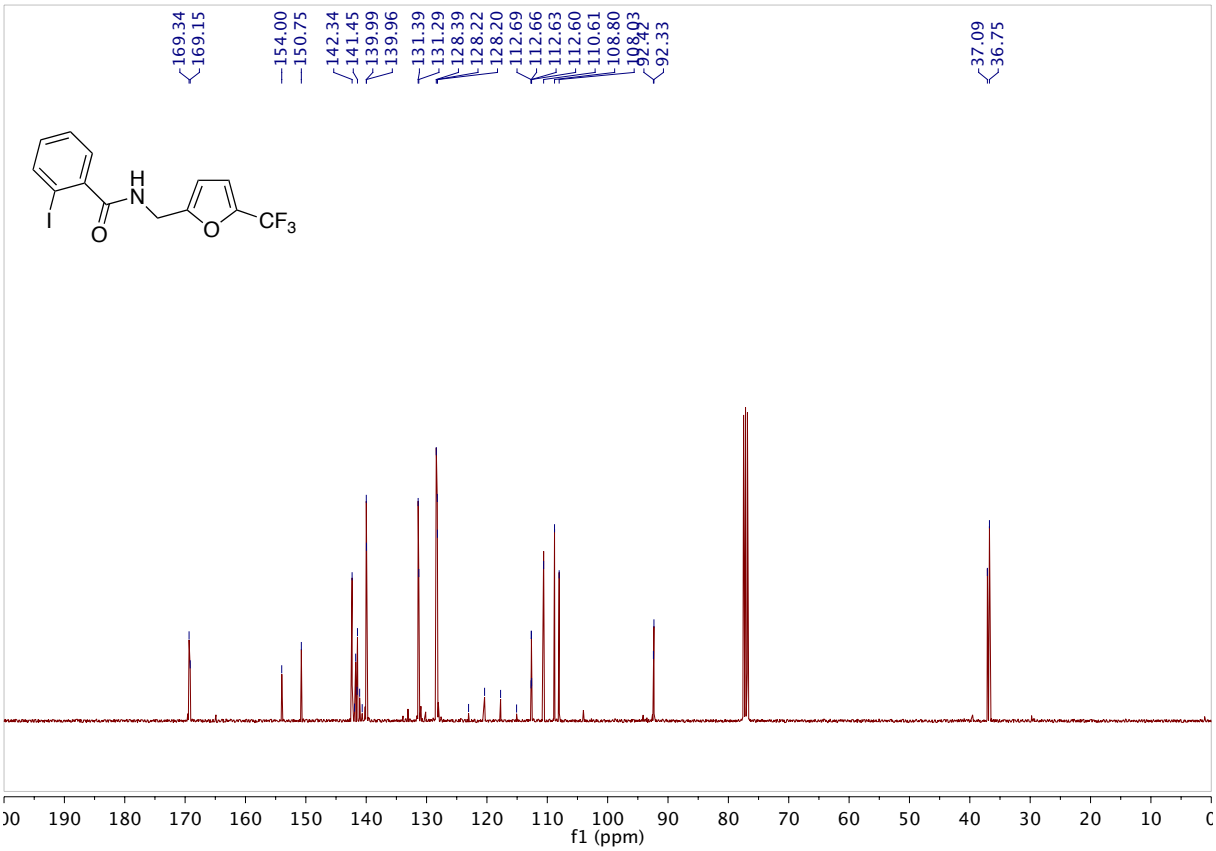

F3C
N
I
-55.86
f1 (ppm)

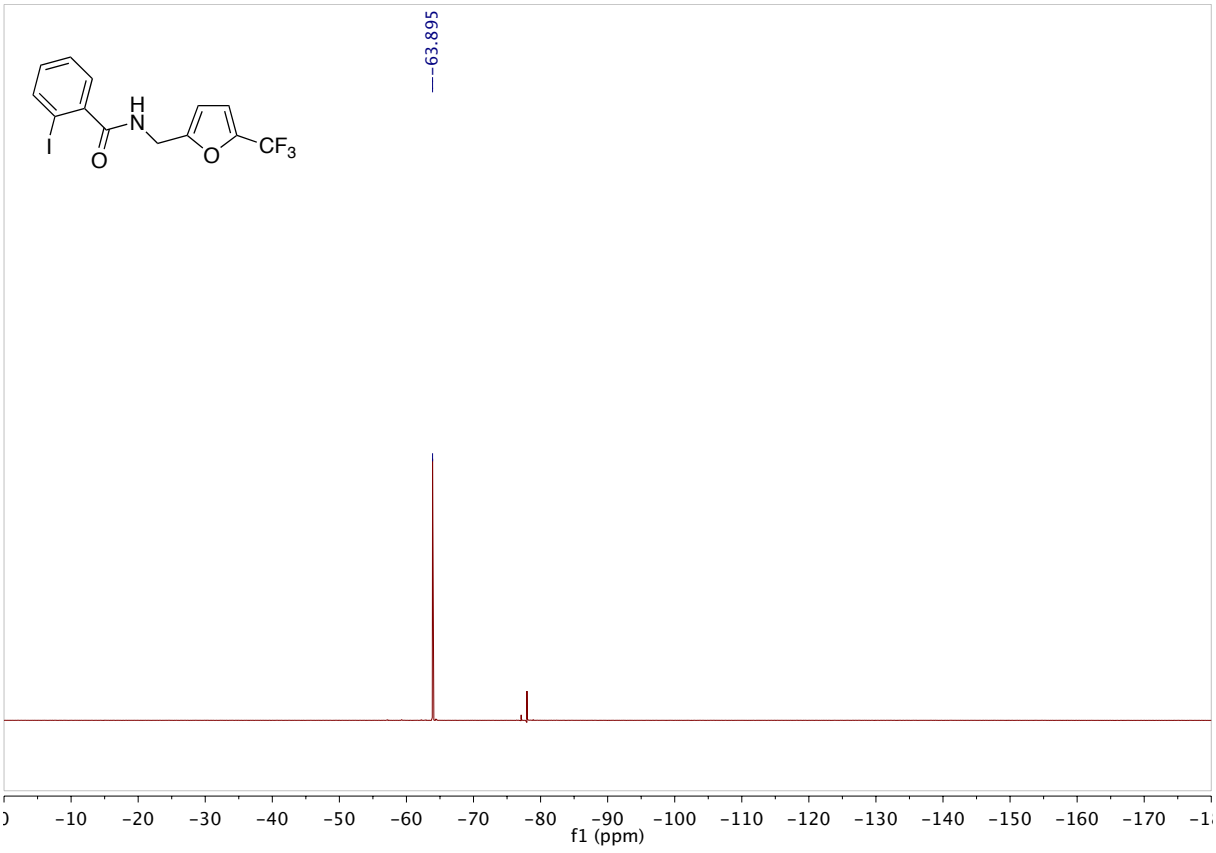

CF3
O
f1 (ppm)

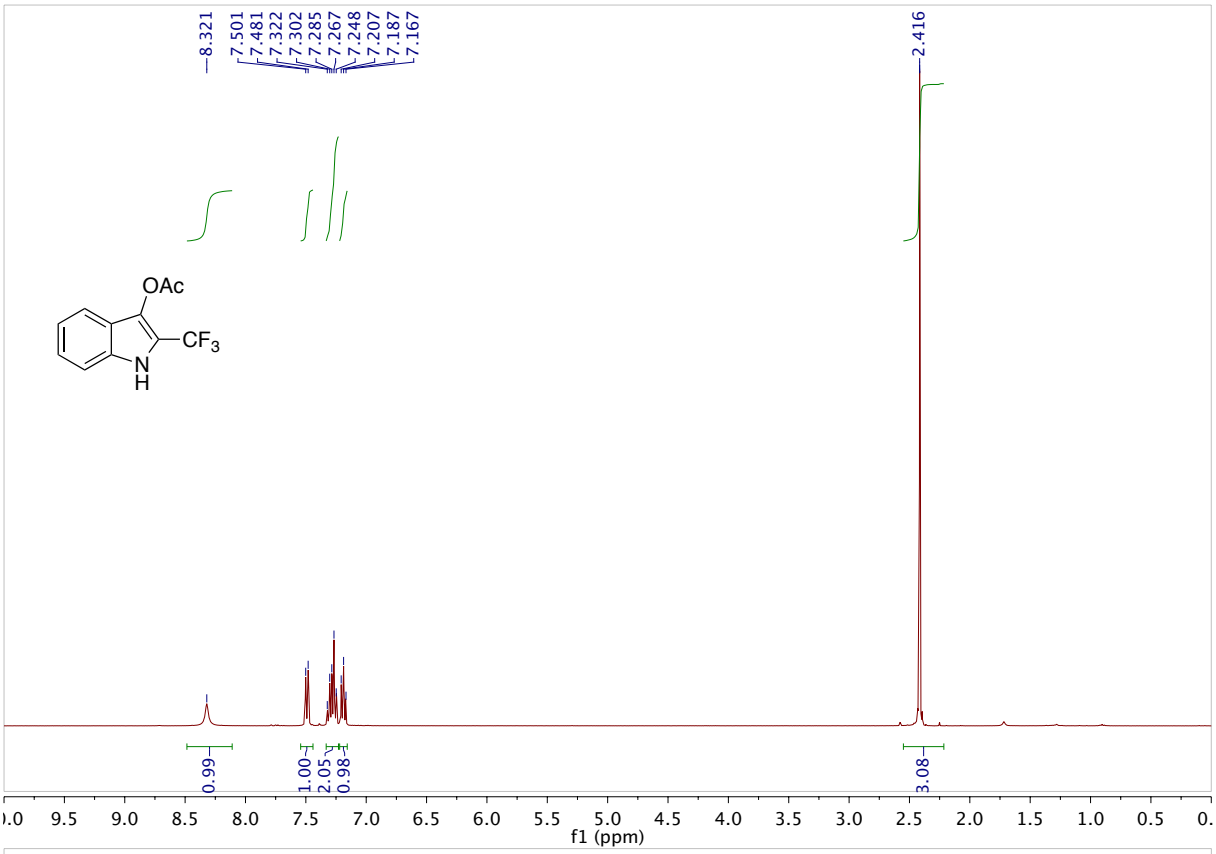

CF3
O
f1 (ppm)

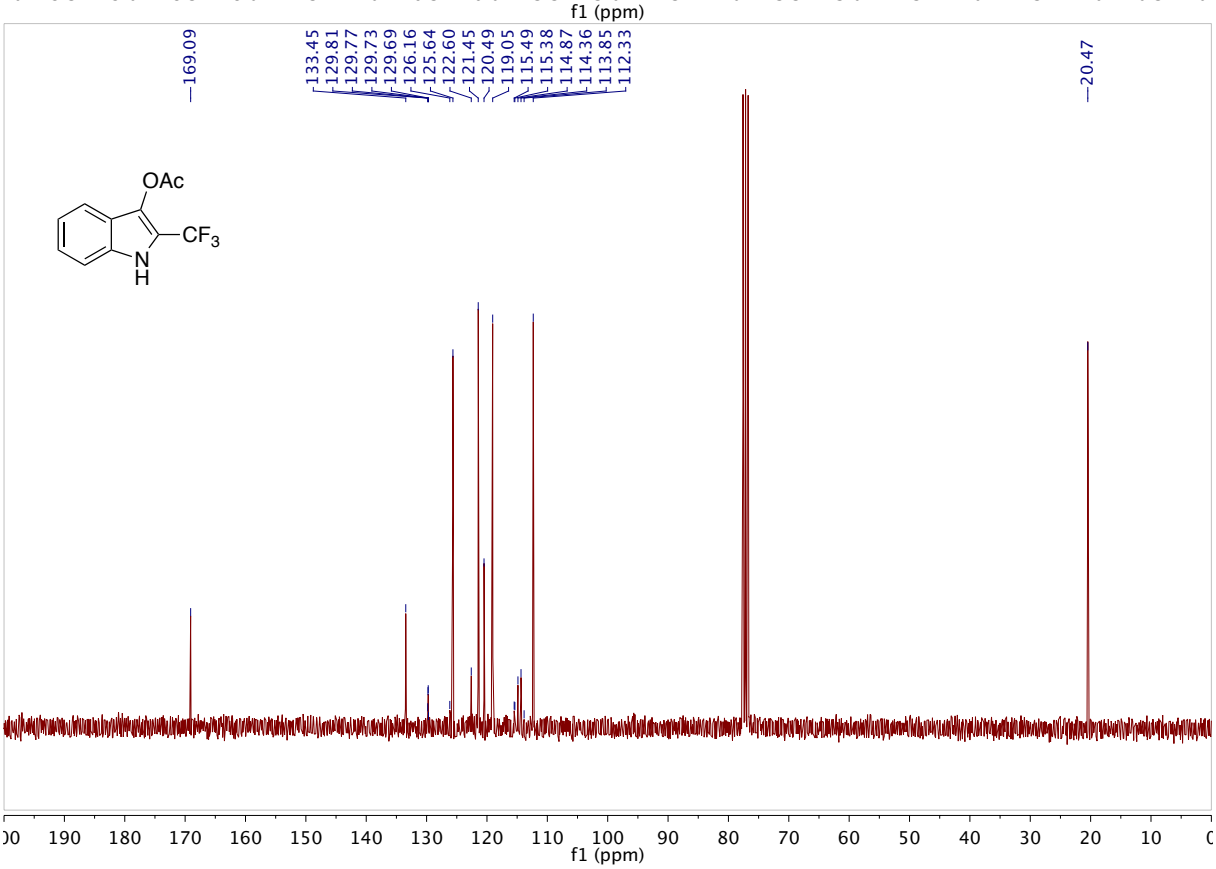

61.201
61.207
61.213
61.220
CF3
O
-61.18 -61.20 -61.22 -61.24
f1 (ppm)
f1 (ppm)

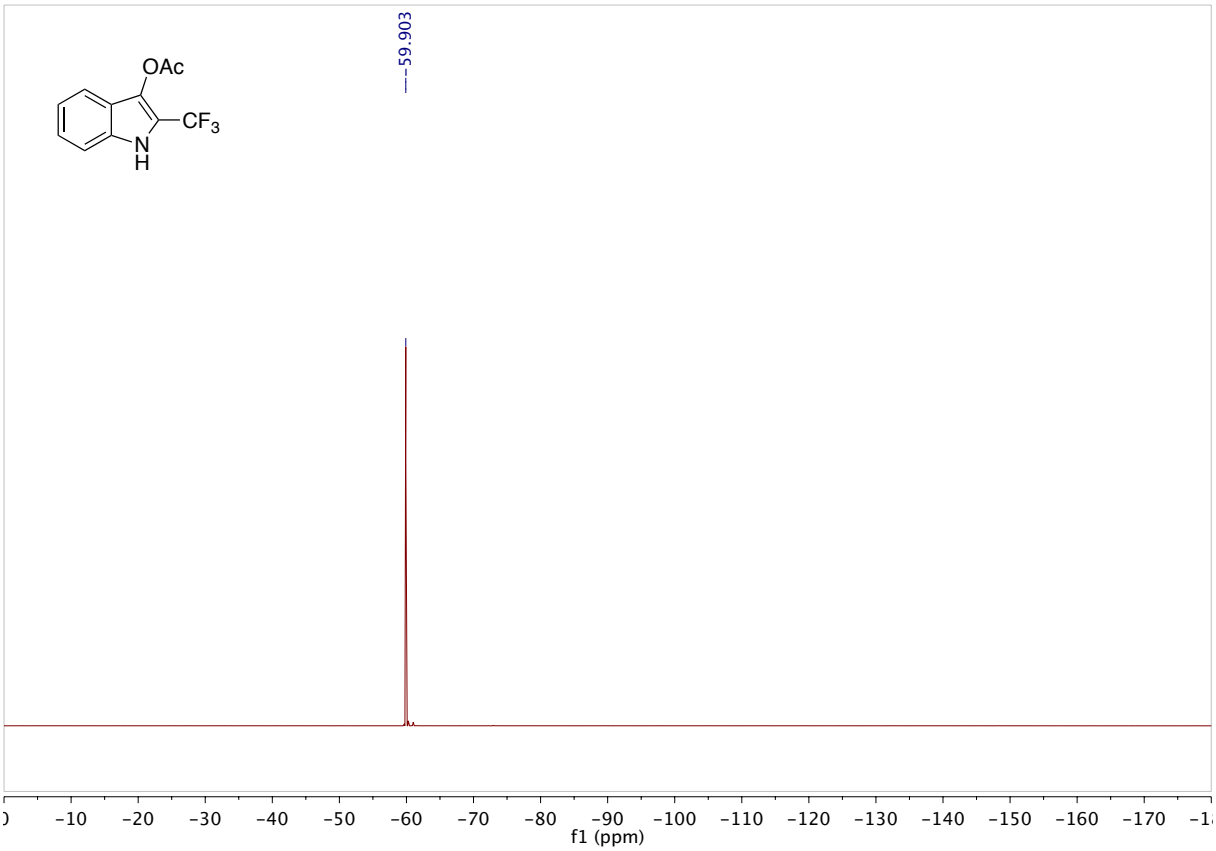

7.818
7.799
7.331
7.329
7.327
7.317
6.724
6.721
6.718
6.715
6.712
6.412
6.410
6.408
6.406
6.404
4.579
4.573
4.571
4.558
H
N
O
I
O
CF3
1.68
4.07
1.79
1.00
0.97
0.94
1.47
0.73
1.94
1.46
f1 (ppm)

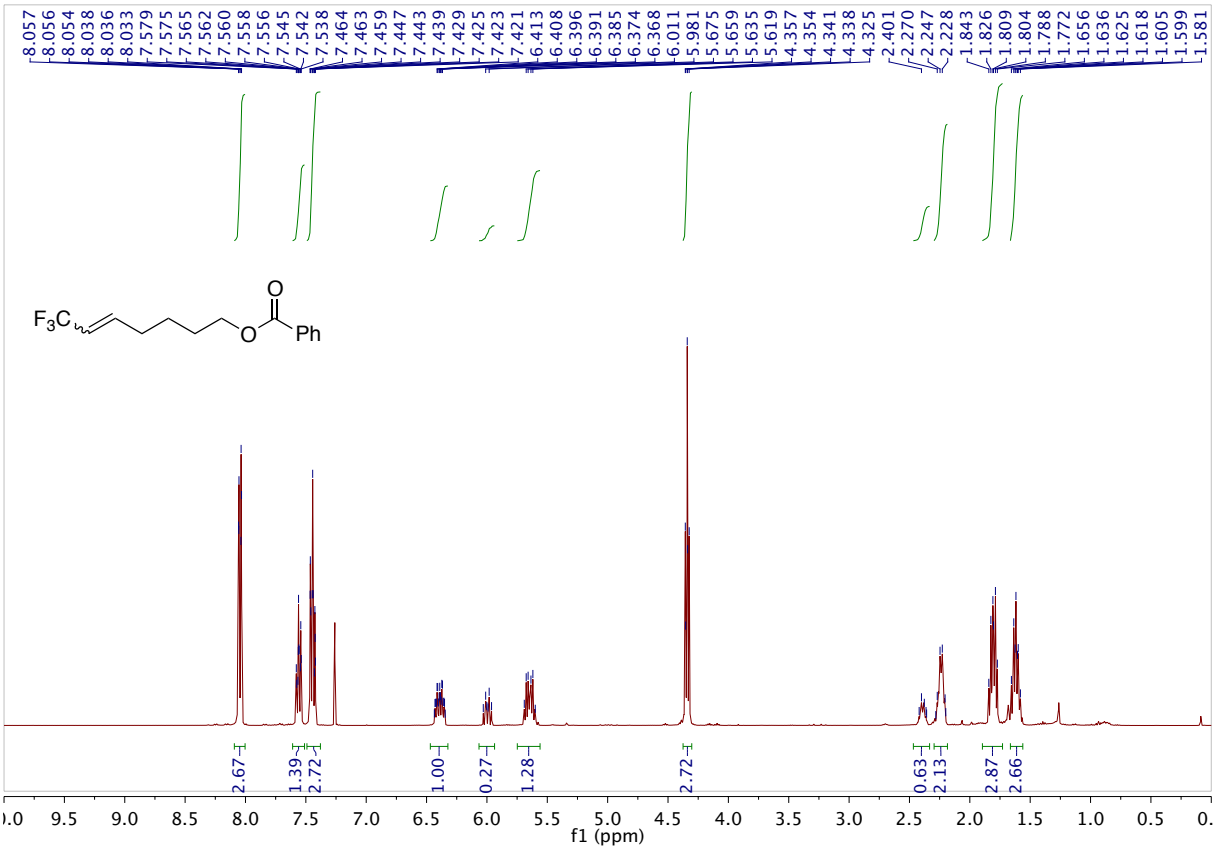

169.34
169.15
154.00
150.75
142.34
141.45
139.99
139.96
131.39
131.29
128.39
128.22
128.20
112.69
112.66
112.63
112.60
110.61
108.80
92.42
92.33
37.09
36.75
H
N
O
I
O
CF3
f1 (ppm)

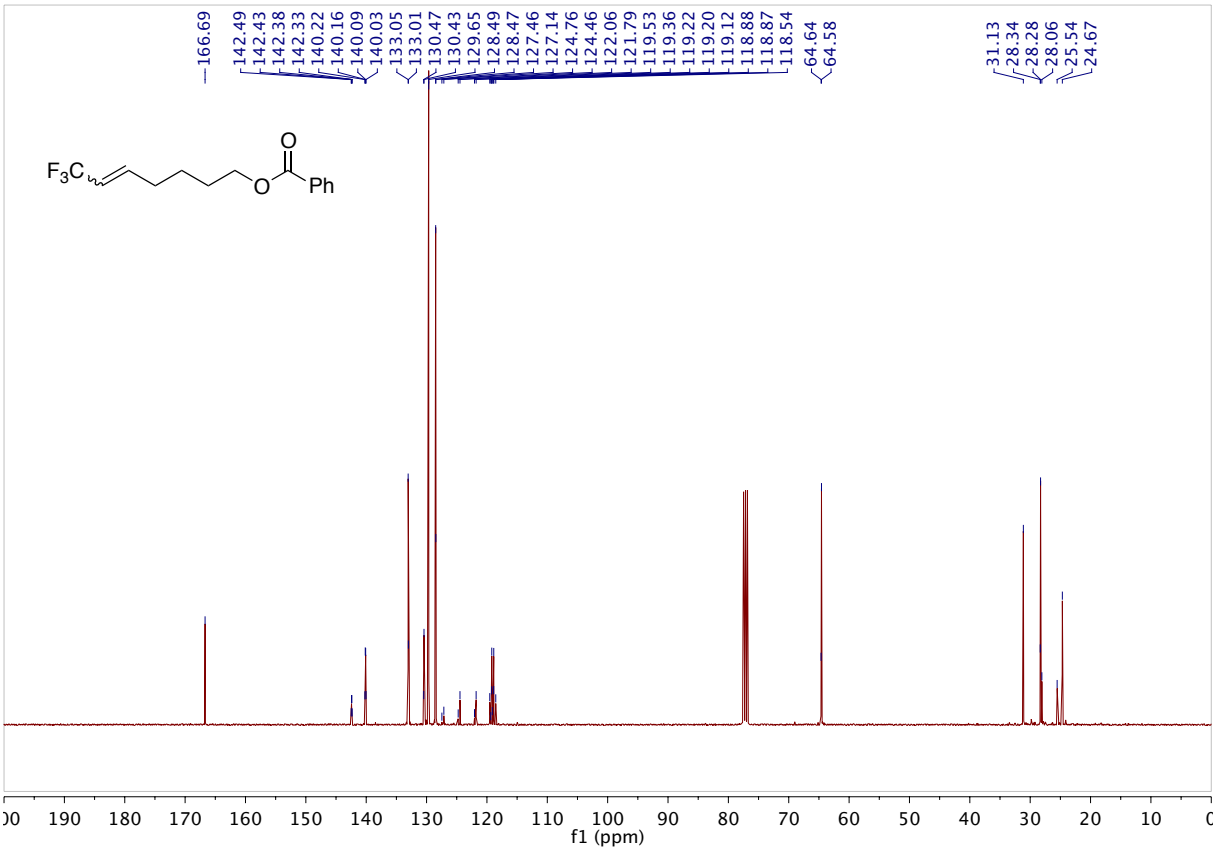

-63.895
H
N
O
I
O
CF3
f1 (ppm)

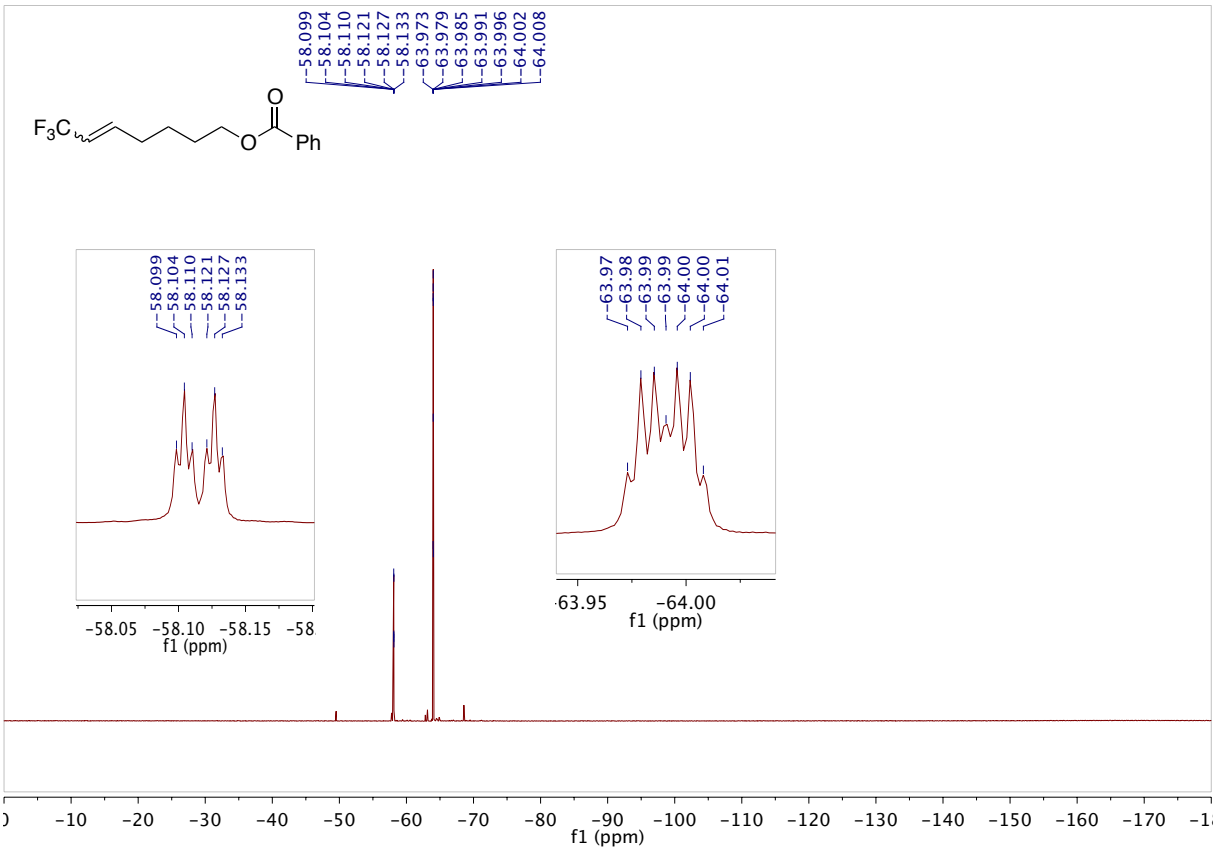

8.321
7.501
7.481
7.322
7.302
7.285
7.267
7.248
7.207
7.187
7.167
2.416
OAc
CF3
N
H
0.99
1.00
2.05
0.98
3.08
f1 (ppm)

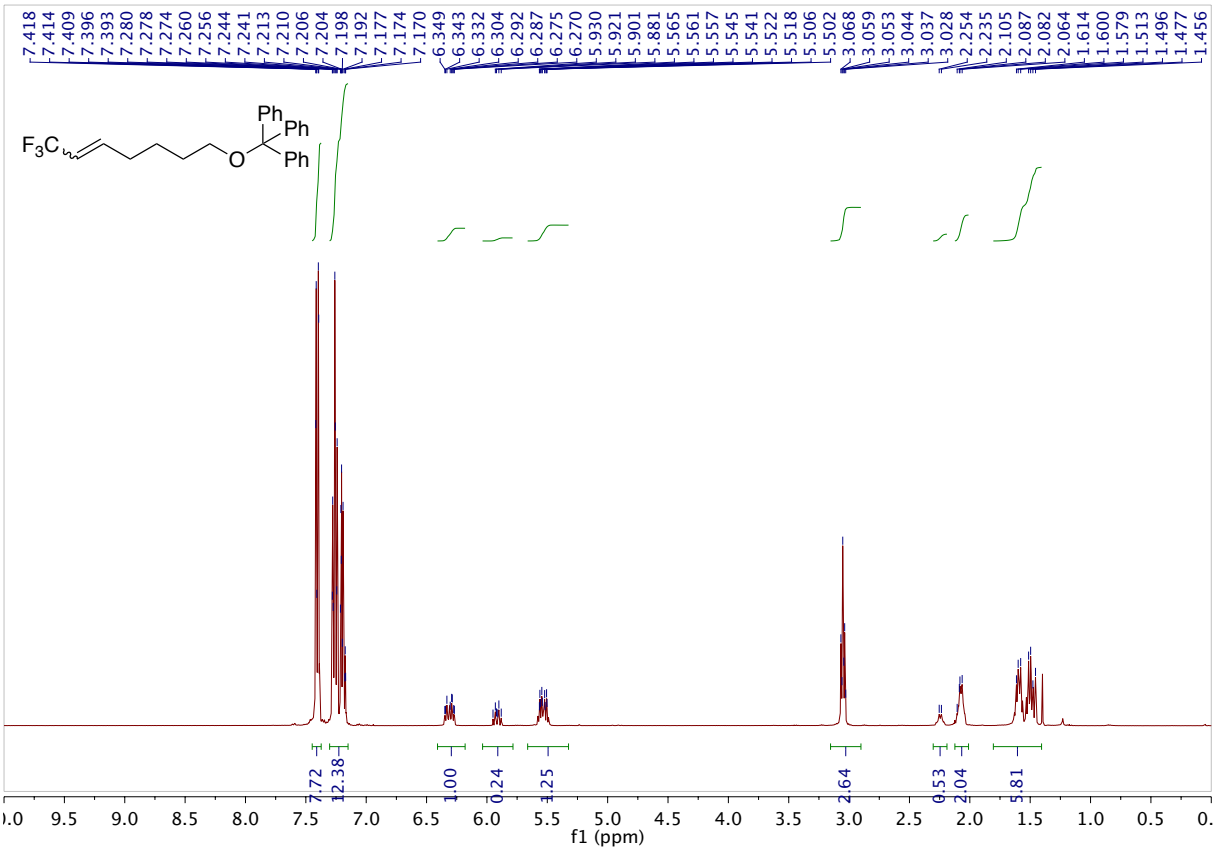

169.09
133.45
129.81
129.77
129.73
129.69
126.16
125.64
122.60
121.45
120.49
119.05
115.49
115.38
114.87
114.36
113.85
112.33
20.47
OAc
CF3
N
H
f1 (ppm)

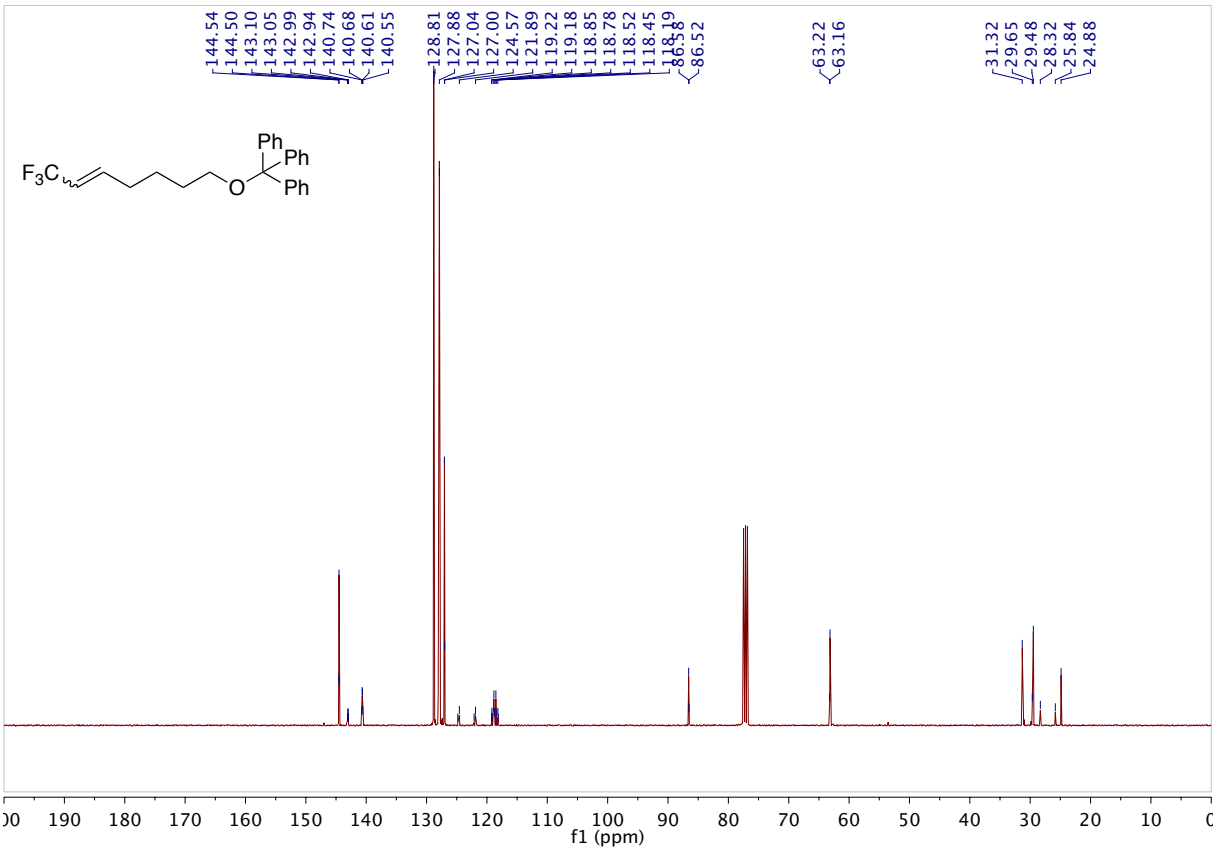

OAc
CF3
N
H
-59.903
f1 (ppm)

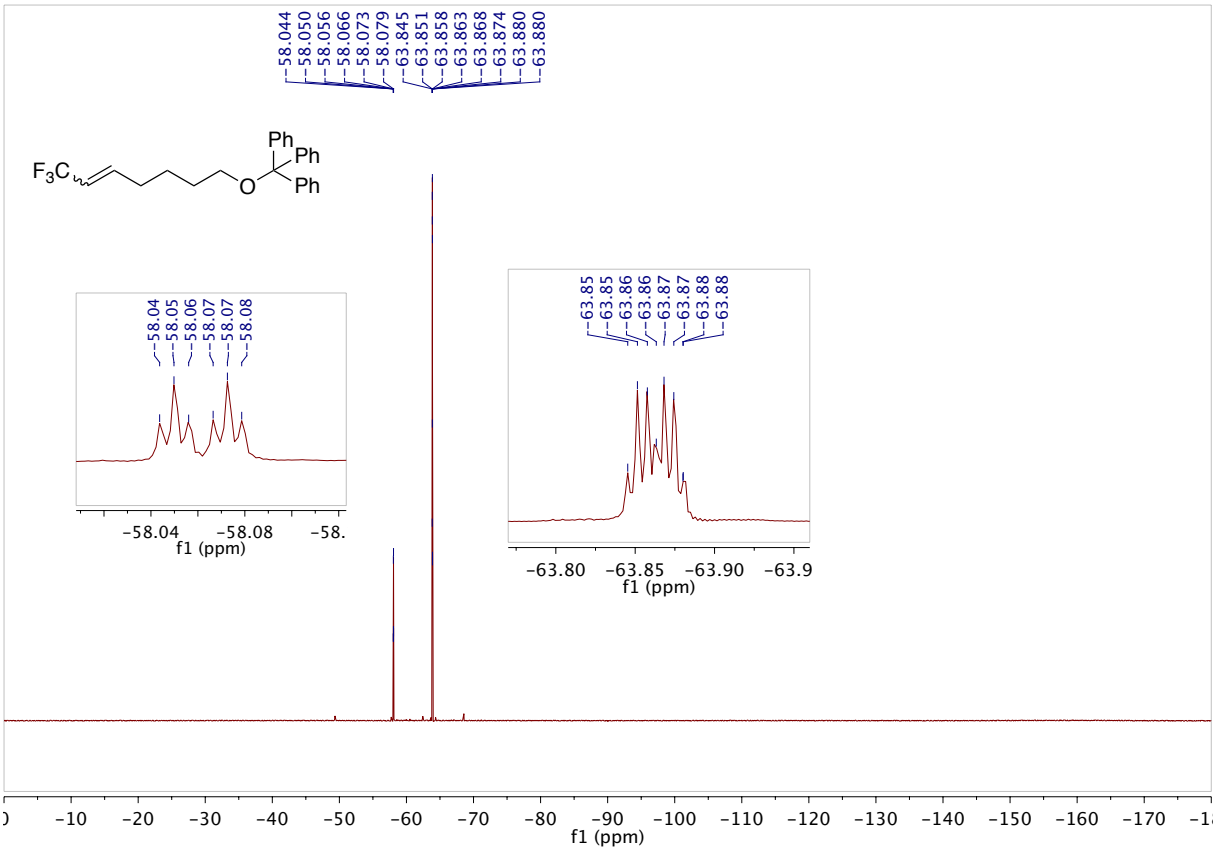

F3C
O
O
Ph
2.67
1.39
2.72
1.00
0.27
1.28
2.72
0.63
2.13
2.87
2.66
f1 (ppm)

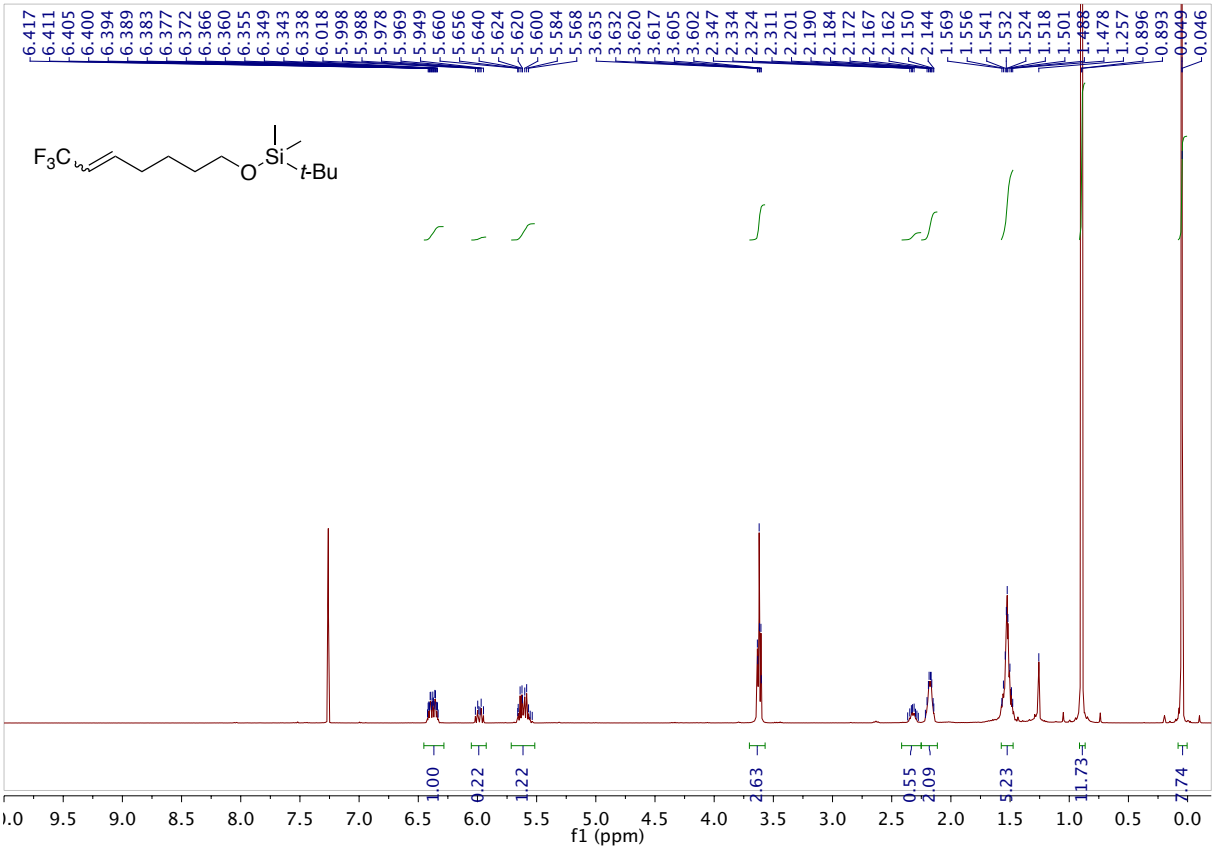

166.69
142.49
142.43
142.38
142.33
140.22
140.16
140.09
140.03
133.05
133.01
130.47
130.43
129.65
128.49
128.47
127.46
127.14
124.76
124.46
122.06
121.79
119.53
119.36
119.22
119.20
119.12
118.88
118.87
118.54
64.64
64.58
31.13
28.34
28.28
28.06
25.54
24.67
F3C
O
O
Ph
f1 (ppm)

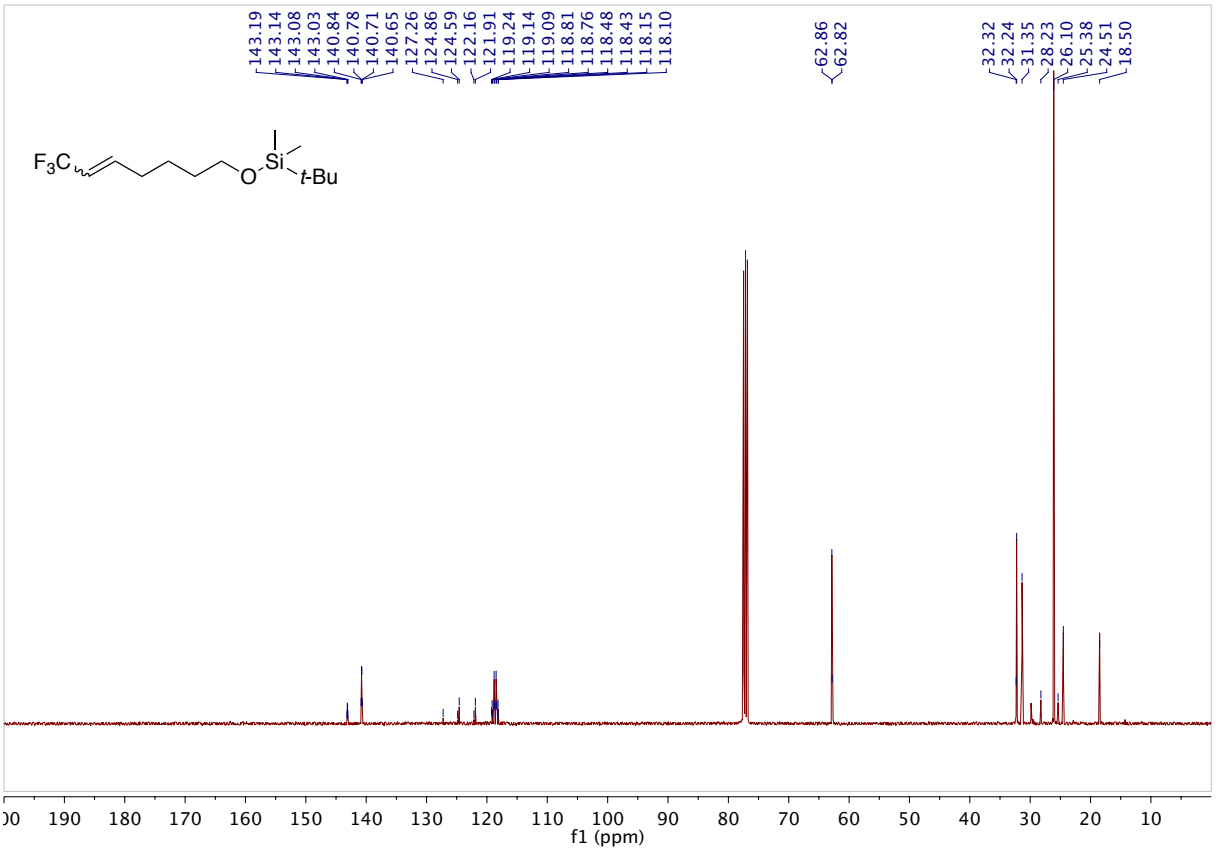

58.099
58.104
58.110
58.121
58.127
58.133
63.973
63.979
63.985
63.991
63.996
64.002
64.008
F3C
O
O
Ph
58.099
58.104
58.110
58.121
58.127
58.133
-58.05
-58.10
-58.15
-58
f1 (ppm)
63.97
63.98
63.99
63.99
64.00
64.00
64.01
63.95
-64.00
f1 (ppm)
f1 (ppm)


7.418
7.414
7.409
7.396
7.393
7.280
7.278
7.274
7.260
7.256
7.244
7.241
7.213
7.210
7.206
7.204
7.198
7.192
7.177
7.174
7.170
6.349
6.343
6.332
6.304
6.292
6.287
6.275
6.270
5.930
5.921
5.901
5.881
5.565
5.561
5.557
5.545
5.541
5.522
5.518
5.506
5.502
3.068
3.059
3.053
3.044
3.037
3.028
2.254
2.235
2.105
2.087
2.082
2.064
1.614
1.600
1.579
1.513
1.496
1.477
1.456
Ph
Ph
Ph
F3C
O
7.72
12.38
1.00
0.24
1.25
2.64
0.53
2.04
5.81
f1 (ppm)


144.54
144.50
143.10
143.05
142.99
142.94
140.74
140.68
140.61
140.55
128.81
127.88
127.04
127.00
124.57
121.89
119.22
119.18
118.85
118.78
118.52
118.45
118.19
86.52
63.22
63.16
31.32
29.65
29.48
28.32
25.84
24.88
Ph
Ph
Ph
F3C
O
f1 (ppm)


58.044
58.050
58.056
58.066
58.073
58.079
63.845
63.851
63.858
63.863
63.868
63.874
63.880
63.880
Ph
Ph
Ph
F3C
O
58.04
58.05
58.06
58.07
58.07
58.08
-58.04
-58.08
f1 (ppm)
63.85
63.85
63.86
63.86
63.87
63.87
63.88
63.88
-63.80
-63.85
-63.90
-63.9
f1 (ppm)
f1 (ppm)


6.417
6.411
6.405
6.400
6.394
6.389
6.383
6.377
6.372
6.366
6.360
6.355
6.349
6.343
6.338
6.018
5.998
5.988
5.978
5.969
5.949
5.660
5.656
5.640
5.624
5.620
5.600
5.584
5.568
3.635
3.632
3.620
3.617
3.605
3.602
2.347
2.334
2.324
2.311
2.201
2.190
2.184
2.172
2.167
2.162
2.150
2.144
1.569
1.556
1.541
1.532
1.524
1.518
1.501
1.488
1.478
1.257
0.896
0.893
0.049
0.046
F3C
O
Si
t-Bu
1.00
0.22
1.22
2.63
0.55
2.09
5.23
11.73
2.74
f1 (ppm)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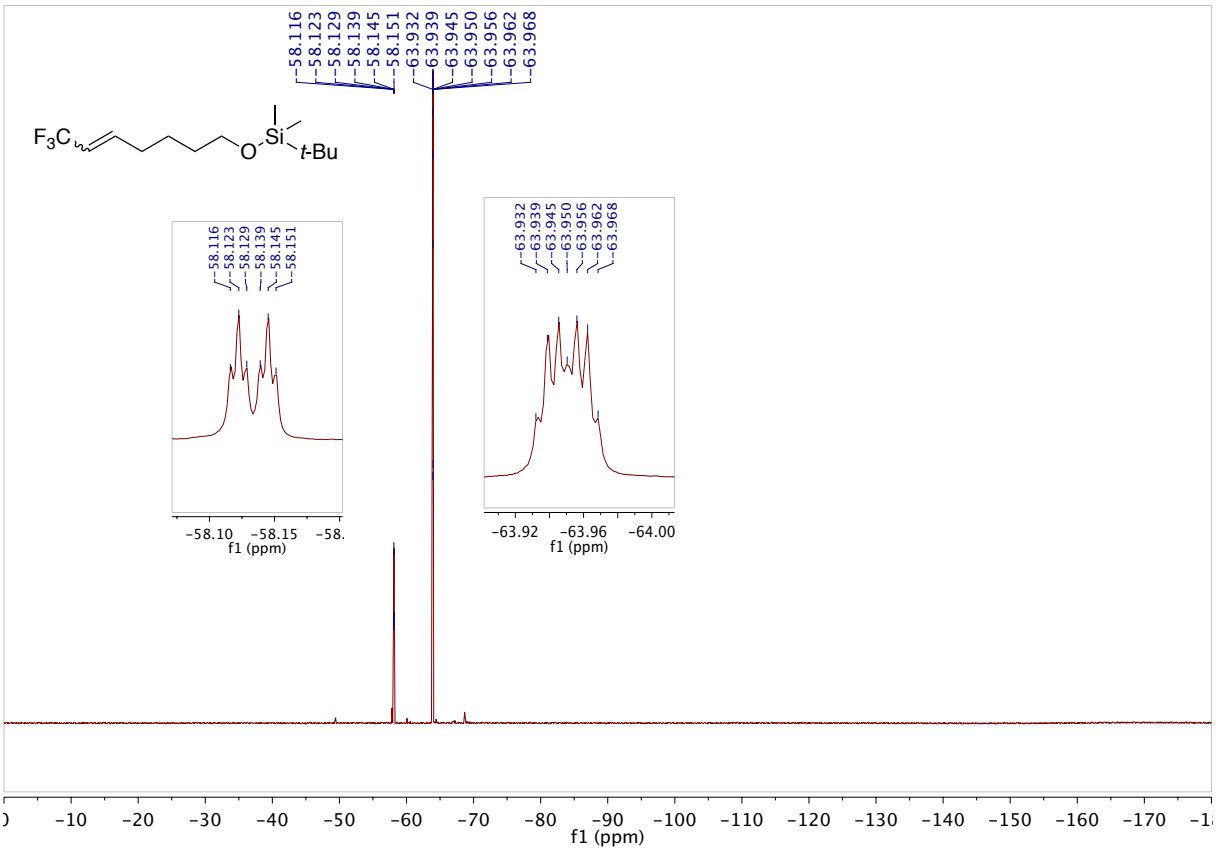
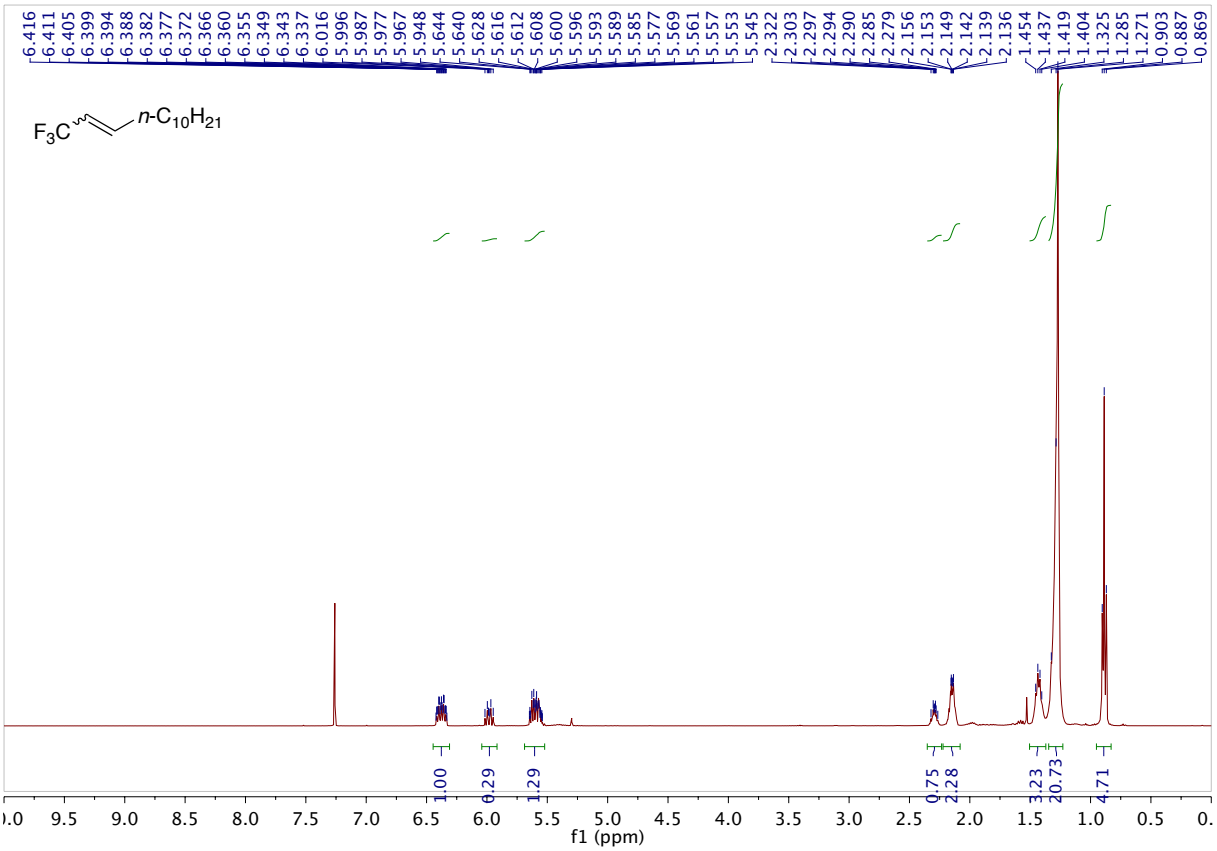
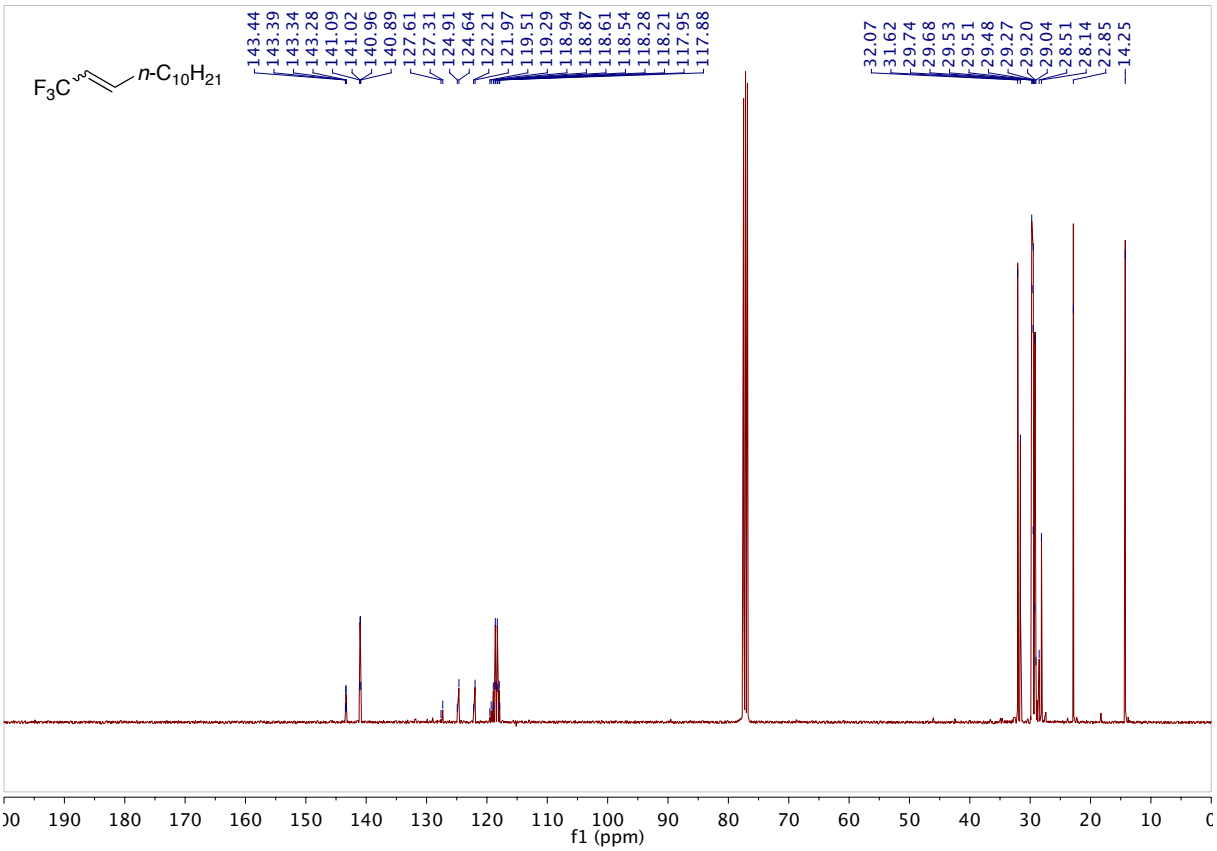
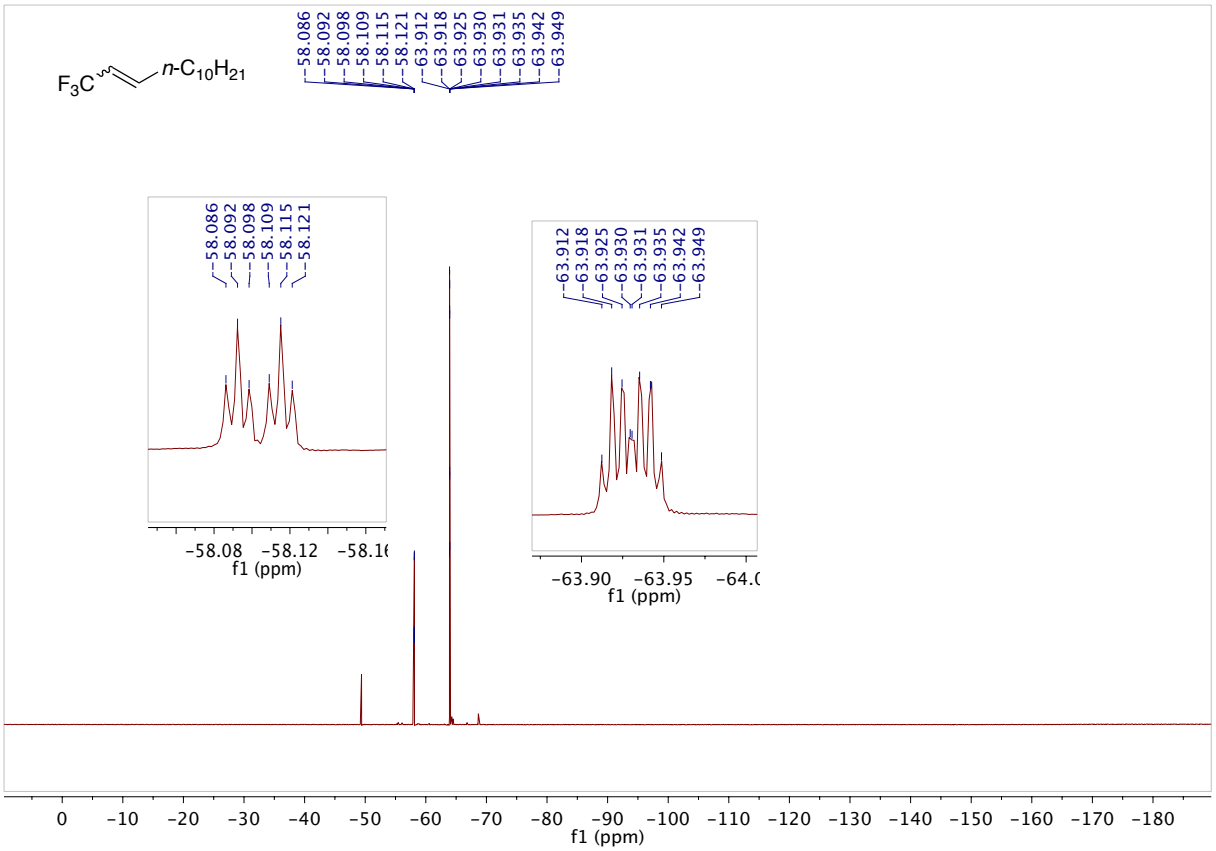
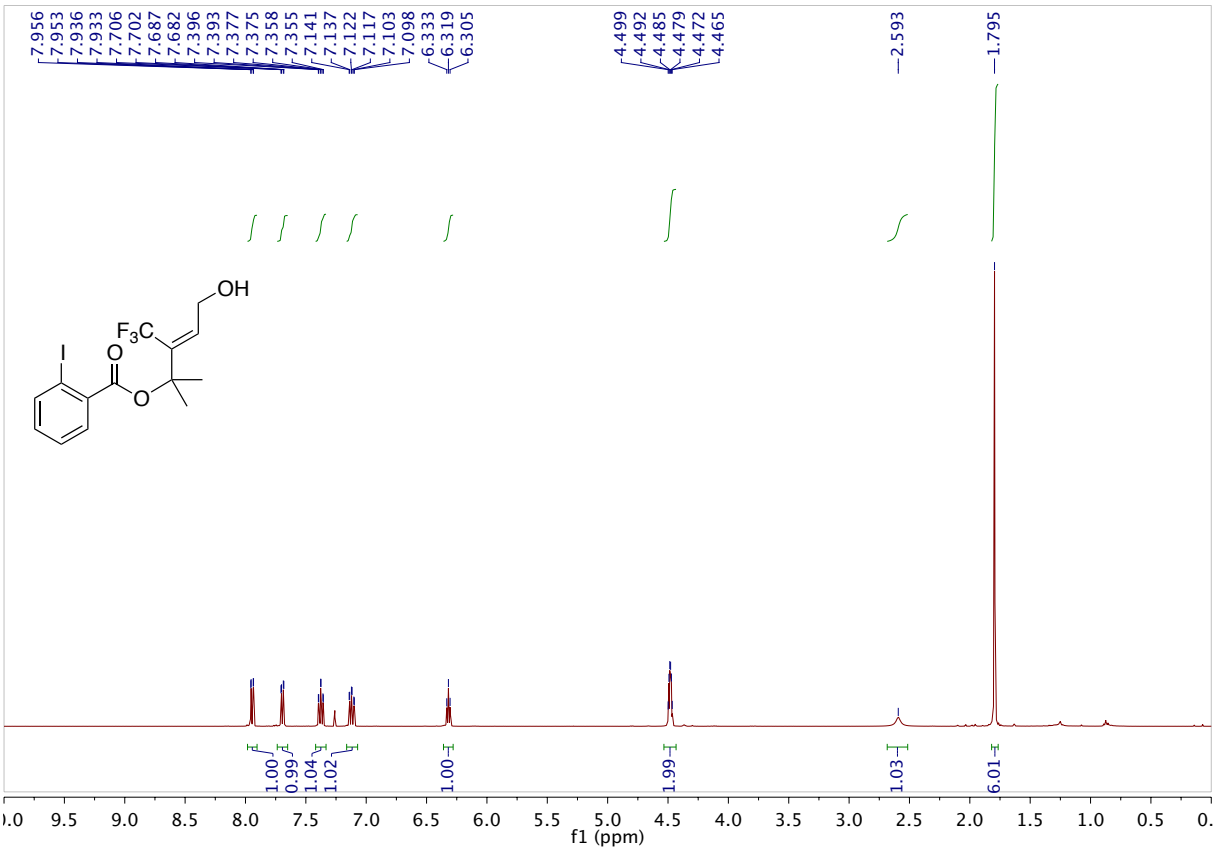
143.14
143.08
143.03
140.84
140.78
140.71
140.65
127.26
124.86
124.59
122.16
121.91
119.24
119.14
119.09
118.81
118.76
118.48
118.43
118.15
118.10
62.86
62.82
32.32
32.24
31.35
28.23
26.10
25.38
24.51
18.50
F3C
O
Si
t-Bu
f1 (ppm)

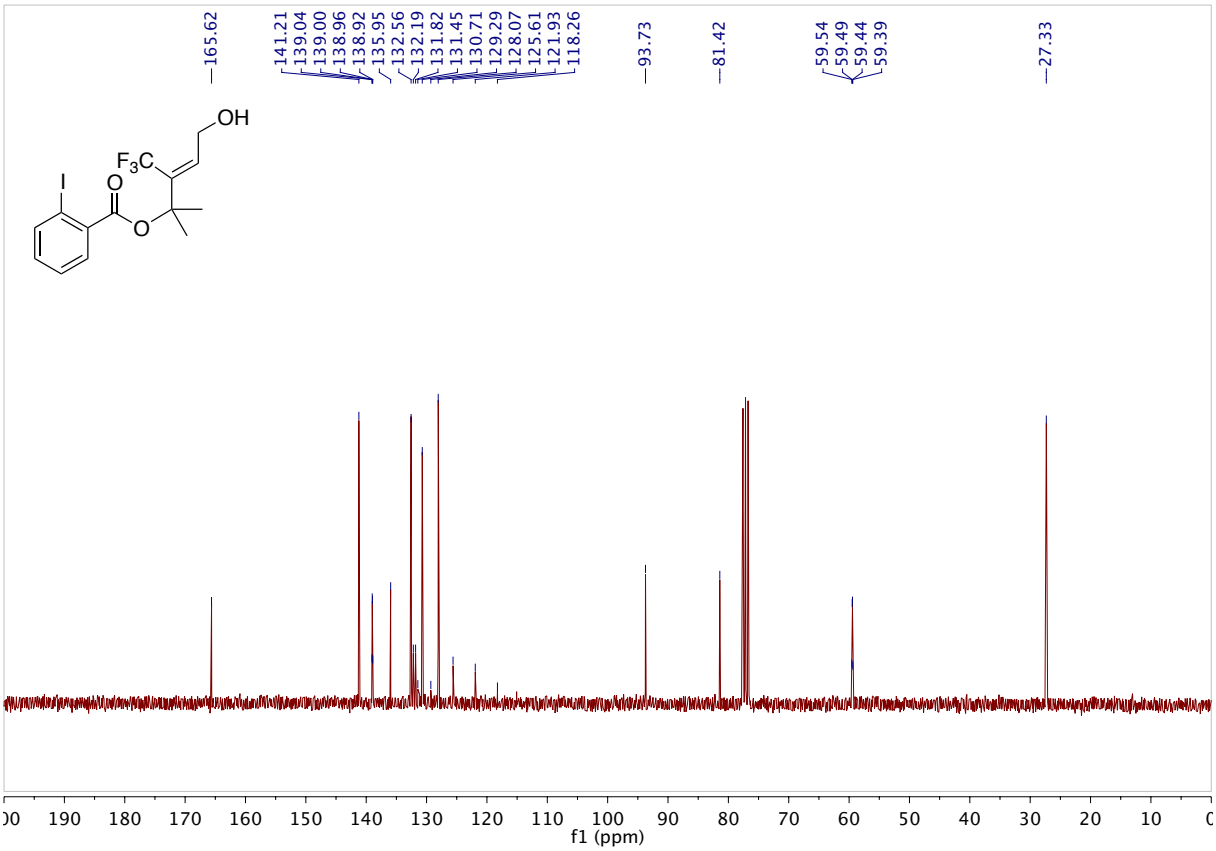

58.116
58.123
58.129
58.139
58.145
58.151
63.932
63.939
63.945
63.950
63.956
63.962
63.968
F3C
O
Si
t-Bu
f1 (ppm)

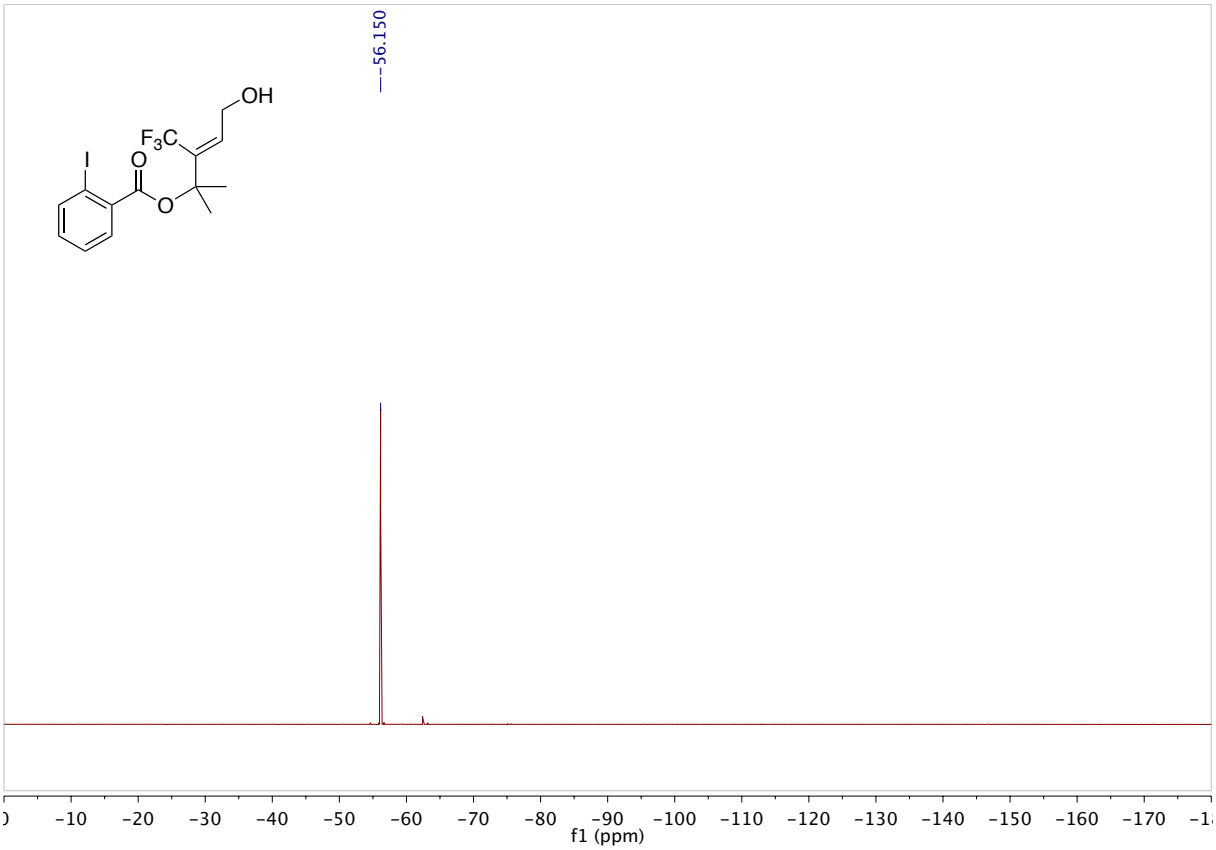

F3C
n-C10H21
6.416
6.411
6.405
6.399
6.394
6.388
6.382
6.377
6.372
6.366
6.360
6.355
6.349
6.343
6.337
6.016
5.996
5.987
5.977
5.967
5.948
5.644
5.640
5.628
5.616
5.612
5.608
5.600
5.596
5.593
5.589
5.585
5.577
5.569
5.561
5.557
5.553
5.545
2.322
2.303
2.297
2.294
2.290
2.285
2.279
2.156
2.153
2.149
2.142
2.139
2.136
1.454
1.437
1.419
1.404
1.325
1.285
1.271
0.903
0.887
0.869
1.00
0.29
1.29
0.75
2.28
3.23
20.73
4.71
f1 (ppm)


F3C
n-C10H21
143.44
143.39
143.34
143.28
141.09
141.02
140.96
140.89
127.61
127.31
124.91
124.64
122.21
121.97
119.51
119.29
118.94
118.87
118.61
118.54
118.28
118.21
117.95
117.88
32.07
31.62
29.74
29.68
29.53
29.51
29.48
29.27
29.20
29.04
28.51
28.14
22.85
14.25
f1 (ppm)


58.086
58.092
58.098
58.109
58.115
58.121
63.912
63.918
63.925
63.930
63.931
63.935
63.942
63.949
F3C
n-C10H21
-58.08 -58.12 -58.16
f1 (ppm)
-63.90 -63.95 -64.0
f1 (ppm)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)


7.956
7.953
7.936
7.933
7.706
7.702
7.687
7.682
7.396
7.393
7.377
7.375
7.358
7.355
7.141
7.137
7.122
7.117
7.103
7.098
6.333
6.319
6.305
4.499
4.492
4.485
4.479
4.472
4.465
2.593
1.795
OH
F3C
I
O
O
1.00
0.99
1.04
1.02
1.00
1.99
1.03
6.01
f1 (ppm)


165.62
141.21
139.04
139.00
138.96
138.92
135.95
132.56
132.19
131.82
131.45
130.71
129.29
128.07
125.61
121.93
118.26
93.73
81.42
59.54
59.49
59.44
59.39
27.33
OH
F3C
I
O
O
f1 (ppm)


56.150
OH
F3C
I
O
O
f1 (ppm)