Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Material

Copper(I)-Photocatalyzed Trifluoromethylation of Alkenes

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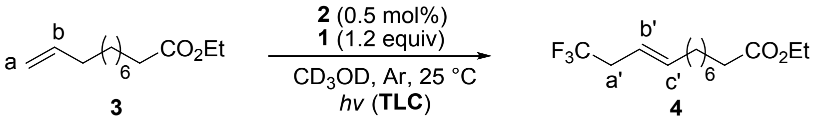
General information

All reagents were obtained from commercial sources and used as received. Togni's reagent **1** was prepared according to published procedures.[1-3] NMR analyses were carried out on a Bruker avanceII-400 (400 MHz for proton, 101 MHz for ^{13}C, 376.5 MHz for ^{19}F) in deuterated chloroform or methanol as solvent. The chemical shifts (δ) for carbon and proton resonances are given compared to the residual solvent peak and are expressed in ppm. The ESI-TOF mass spectra (figure 2 in the article and figure S10) were recorded at the CESAMO analytical center (Institut des Sciences Moléculaires, Université Bordeaux) on a QSTAR Elite spectrometer from Applied Biosystem. The ESI-MS experiment of figure S11, was performed on a Bruker Esquire 3000 Plus ion trap spectrometer equipped with an electrospray ion source (ESI). The sample was analyzed in positive ionization mode by direct perfusion in the ESI-MS interface. X-band ESR spectra were recording at 100 K on a Bruker EMX apparatus, equipped with an ER-4192 ST Bruker cavity and an ER-4131 VT. Photoirradiation at 365 nm was performed with a portable Fisher Bioblock mercury lamp (type "TLC") with a power of 6 watts. Absorption spectra were recorded on a Varian Cary 5000 spectrophotometer in 1 cm pathlength quartz cells. Cyclic voltammetry (CV) experiments were recorded with an Autolab PGSTAT302N potentiostat interfaced to a PC, using a three electrode: glassy carbon working electrode, silver wire pseudo-reference electrode and platinum foil counter electrode. The electrode surface was polished routinely with 0.05 µm alumina-water slurry on a felt surface immediately before use. CV measurements were carried out under an atmosphere of argon in the dark at room temperature, solutions were degassed by argon bubbling before use. Experiments were performed in methanol (HPLC grade dried over alumina) with tetrabutylammonium hexafluorophosphate (0.1 M; Sigma-Aldrich electrochemical grade) as supporting electrolyte. Redox potentials were referenced internally against ferrocenium/ferrocene (Fc^+/Fc).

General procedure for the trifluoromethylation of terminal alkenes conducted in NMR tubes:

In a vial, the complex **2** (0.5 mol%) and the Togni's reagent **1** (1.2 equiv) were dissolved in CD_3OD (0.5 or 1 mL). The resulting solution was then transferred to the NMR tube, the alkene (1 equiv) was added and the tube capped with a rubber septum. The reaction mixture, protected from light by aluminium foil, was then degassed by gentle argon bubbling for 20 minutes. At that stage, a ^1H NMR spectrum is recorded to allow further determination of the conversion and NMR yield using the resonance of CHD_2OD as internal reference (see figures S1-S4). The reaction is initiated by irradiating the tube at 365 nm using a TLC lamp placed at ~ 1 cm from the tube or, by placing the tube behind a window under direct sun light illumination (sunny day). In the latter conditions, the temperature of the reaction mixture was 27 °C. Once the reaction was completed, the CD_3OD solvent was evaporated and the residue was purified by flash chromatography over silica gel to afford the trifluoromethylated product.

Procedures for the trifluoromethylation of terminal alkenes conducted in round-bottom flaks on 2 mmole scale: See S19



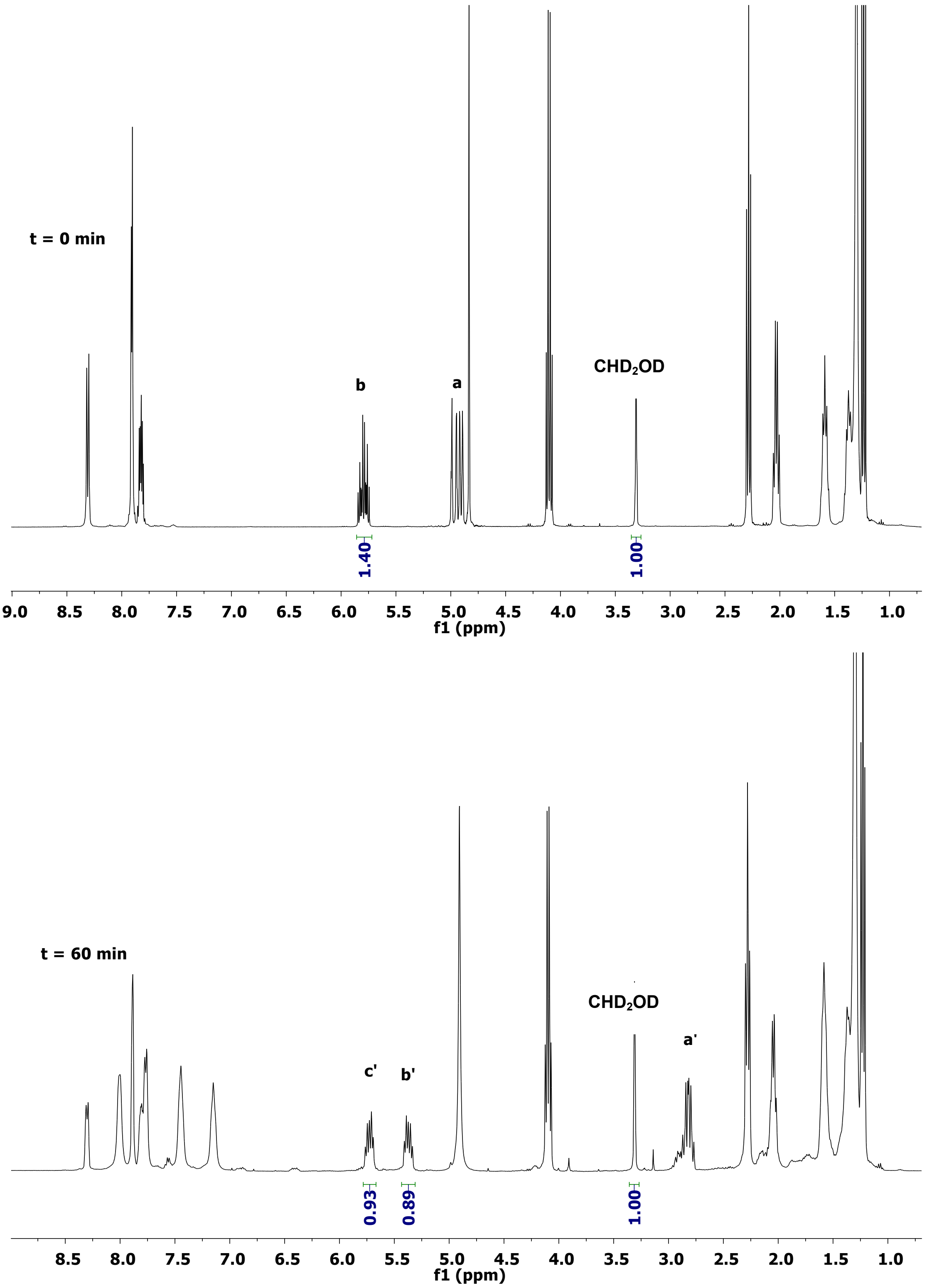


Figure S1. ^{1}H NMR spectra of reaction of entry 4 in table 1 at the start of the reaction (top) and after 60 min (bottom).

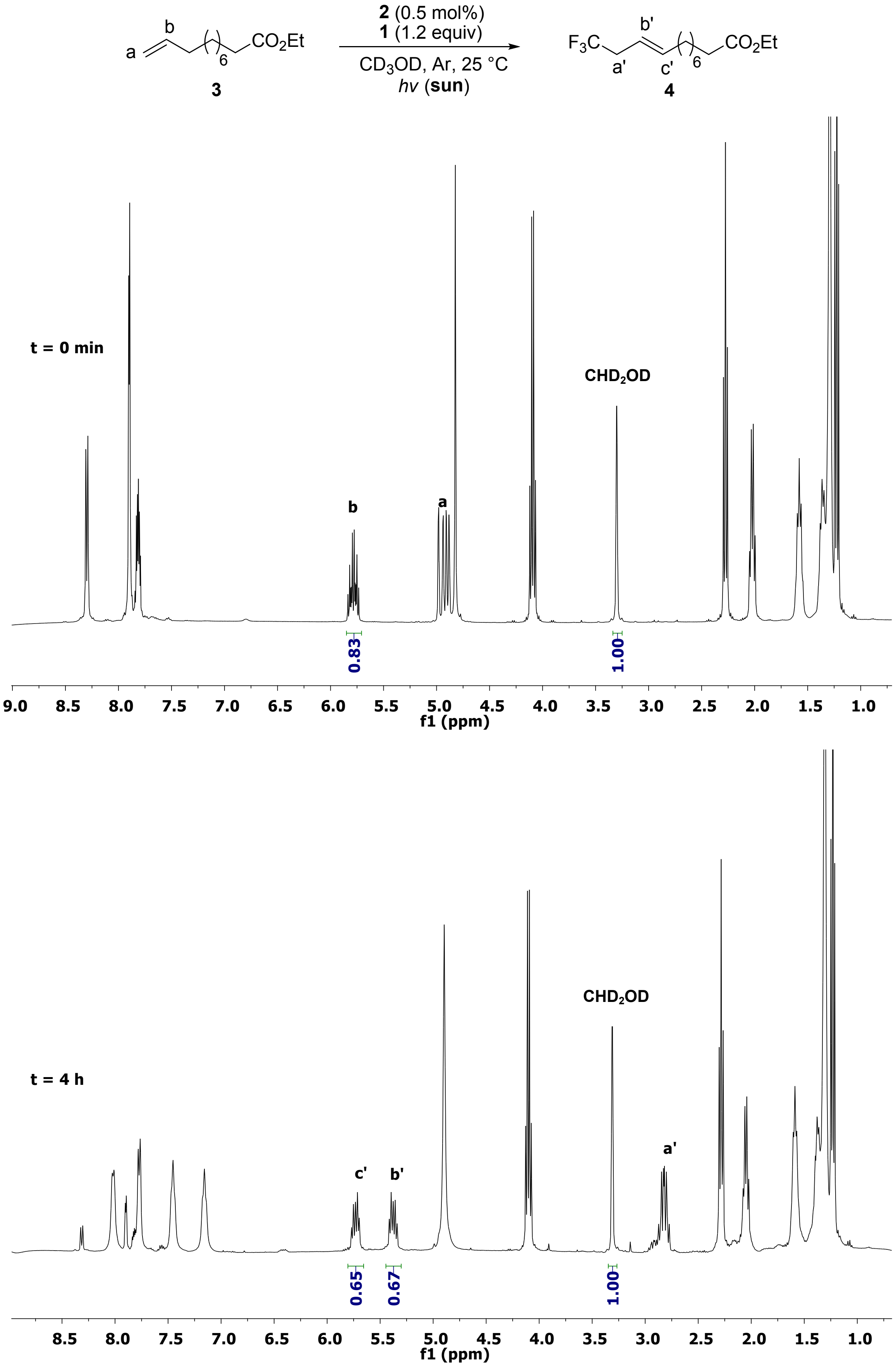
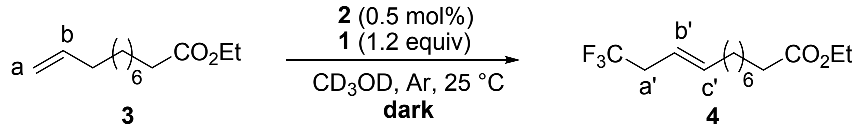


Figure S2. ^{1}H NMR spectra of reaction of entry 1 in table 1 at the start of the reaction (top) and after 4 h (bottom).



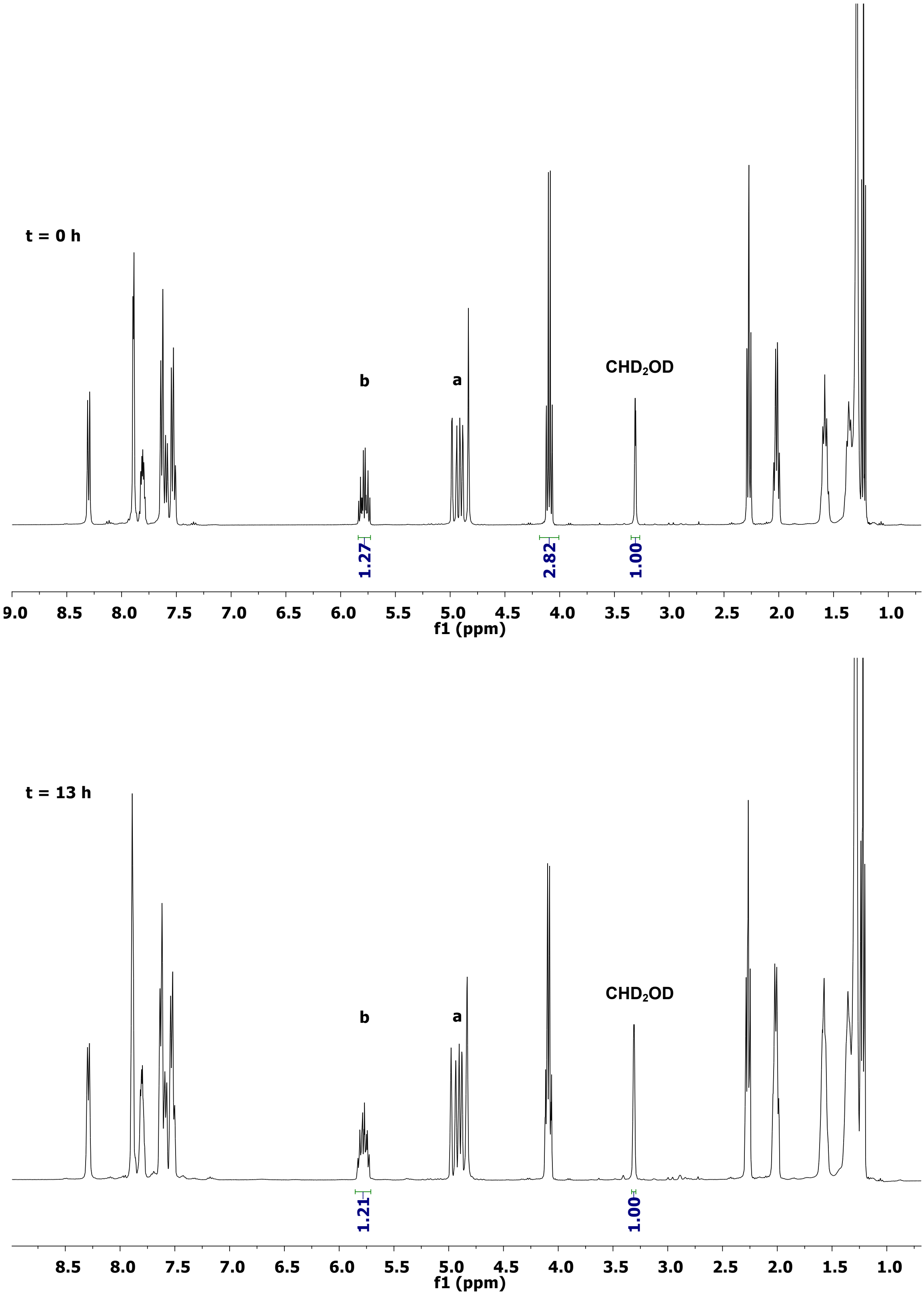
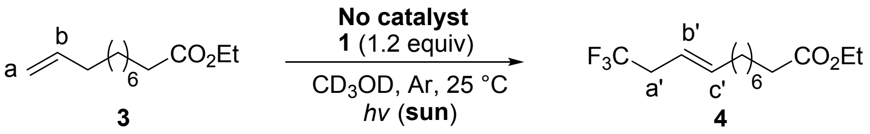


Figure S3. ^{1}H NMR spectra of reaction of entry 2 in table 1 at the start of the reaction (top) and after 13 h (bottom)



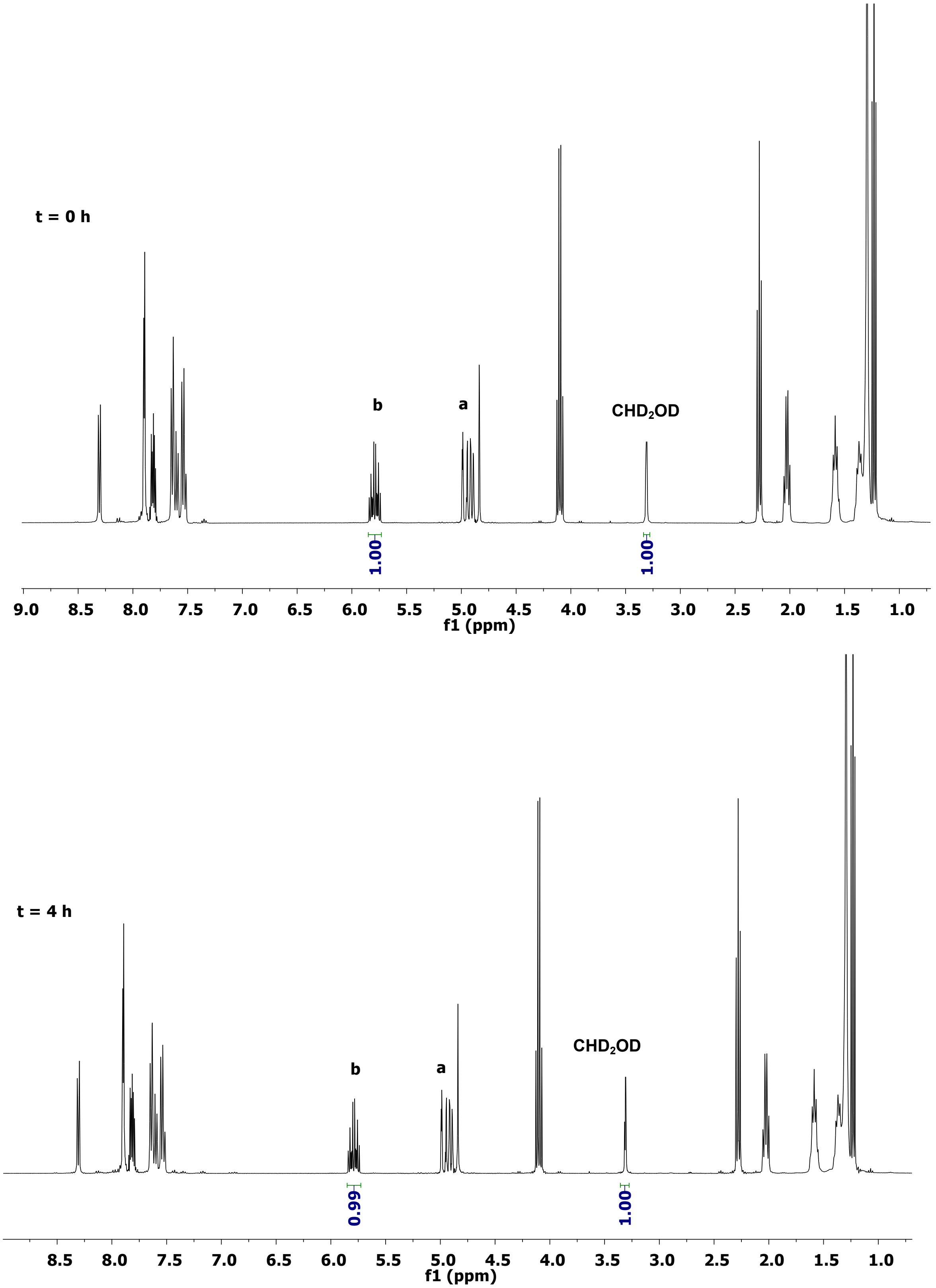


Figure S4. Evolution of the ^{1}H NMR spectra of the reaction entry 5 in table 1 at the start of the reaction (top) and after 4 h (bottom)

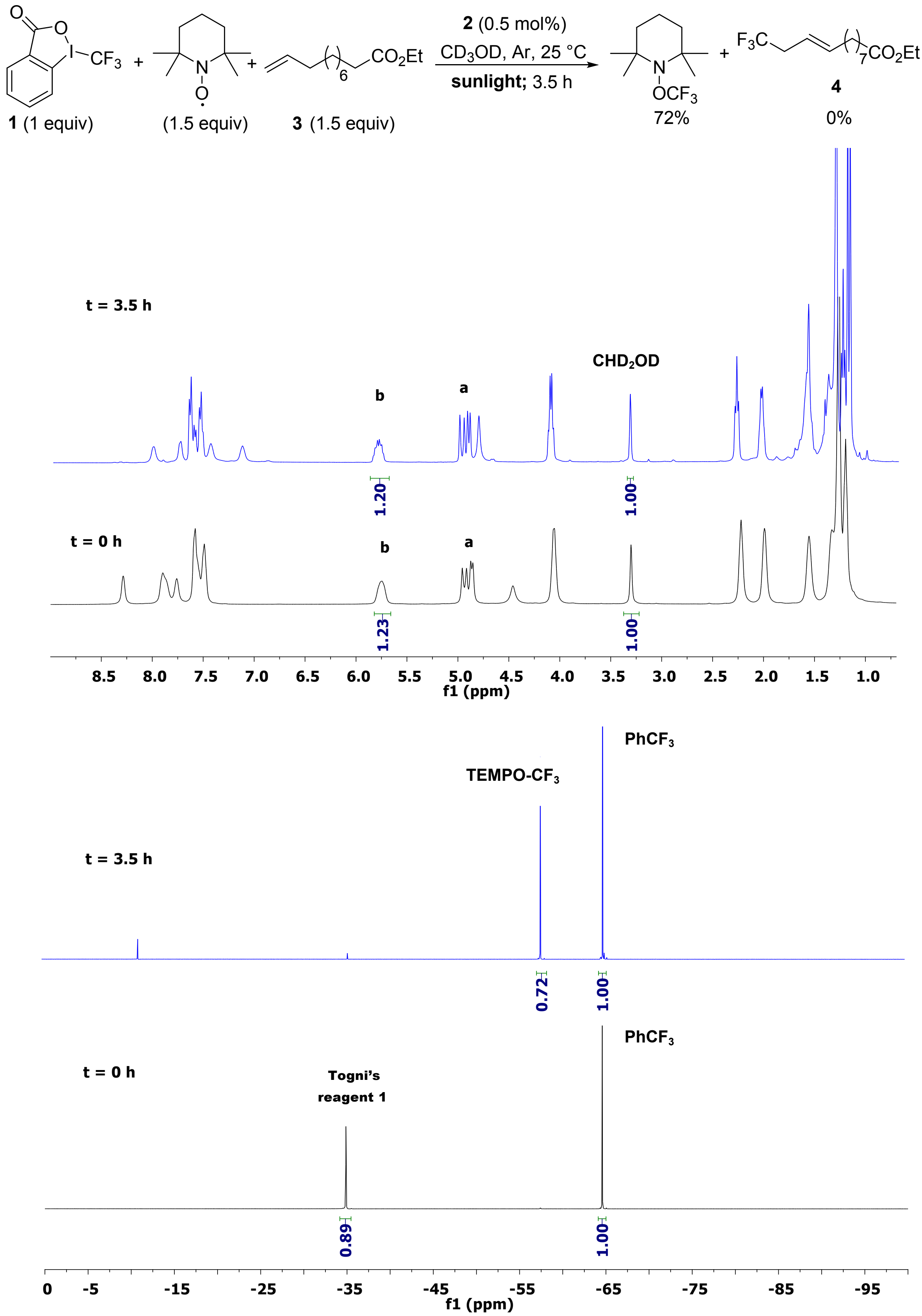
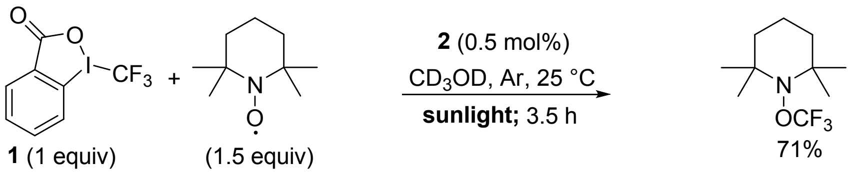


Figure S5. ^{1}H NMR (top) and ^{19}F NMR spectra (bottom) of a reaction of **1** (0.1 mmol), **3** (0.15 mmol), TEMPO radical (0.15 mmol) in CD_3OD solution (0.5 mL) with **2** (0.5 mol%) under sunlight illumination at time = 0 (black) and after 3.5 h (blue). $PhCF_3$ (0.1 mmol) was added as an internal standard.



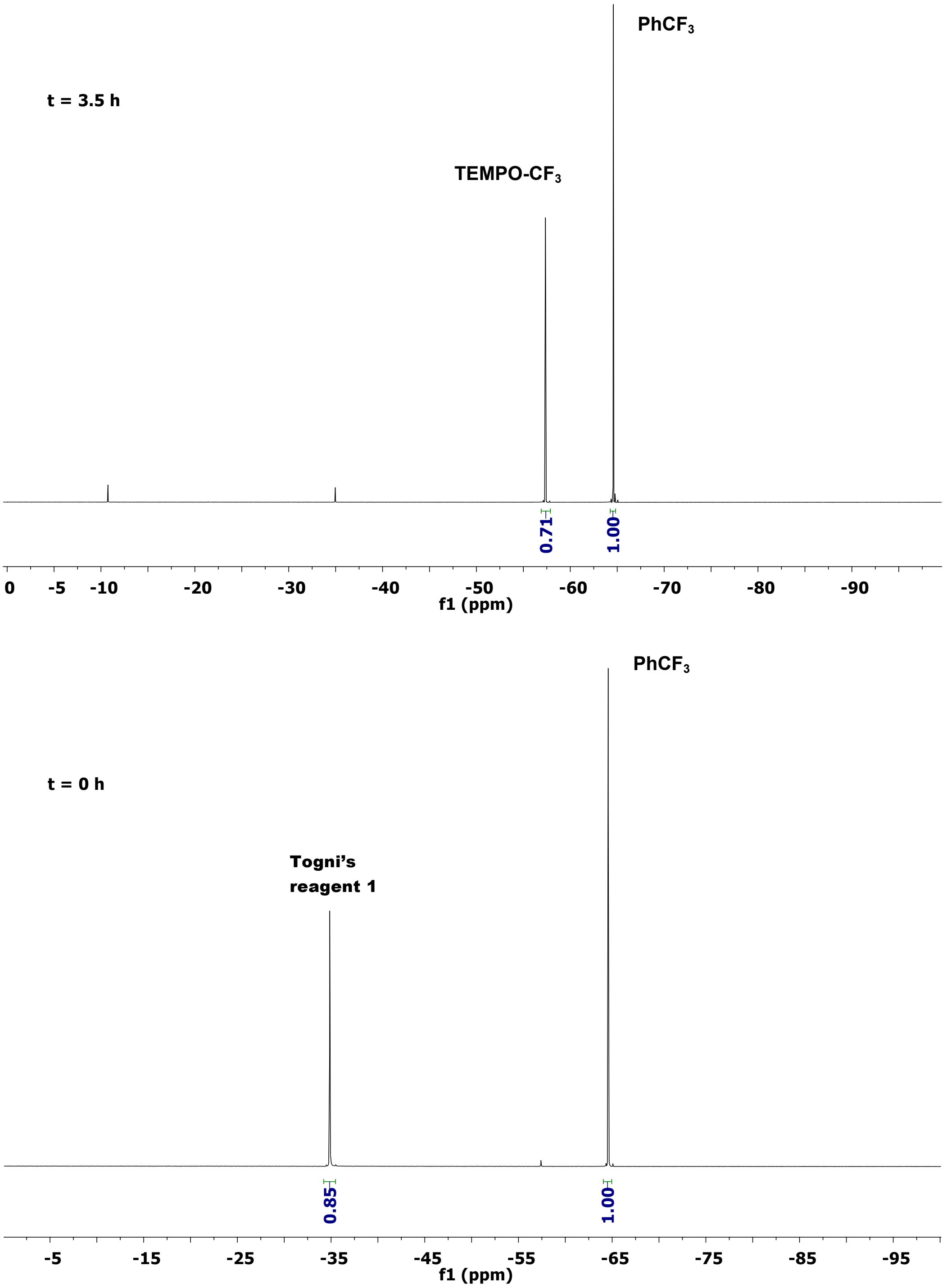
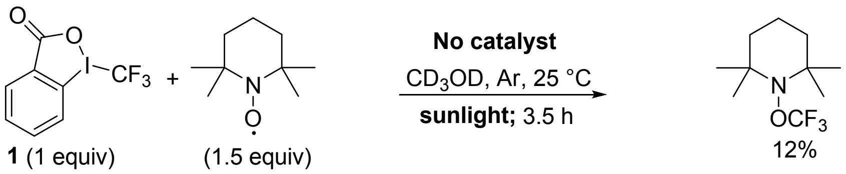


Figure S6. ^{19}F NMR spectra of a reaction of **1** (0.1 mmol) and TEMPO radical (0.15 mmol) in CD_3OD solution (0.5 mL) with **2** (0.5 mol%) under sunlight at time = 0 (bottom) and after 3.5 h (top). $PhCF_3$ (0.1 mmol) was added as an internal standard.



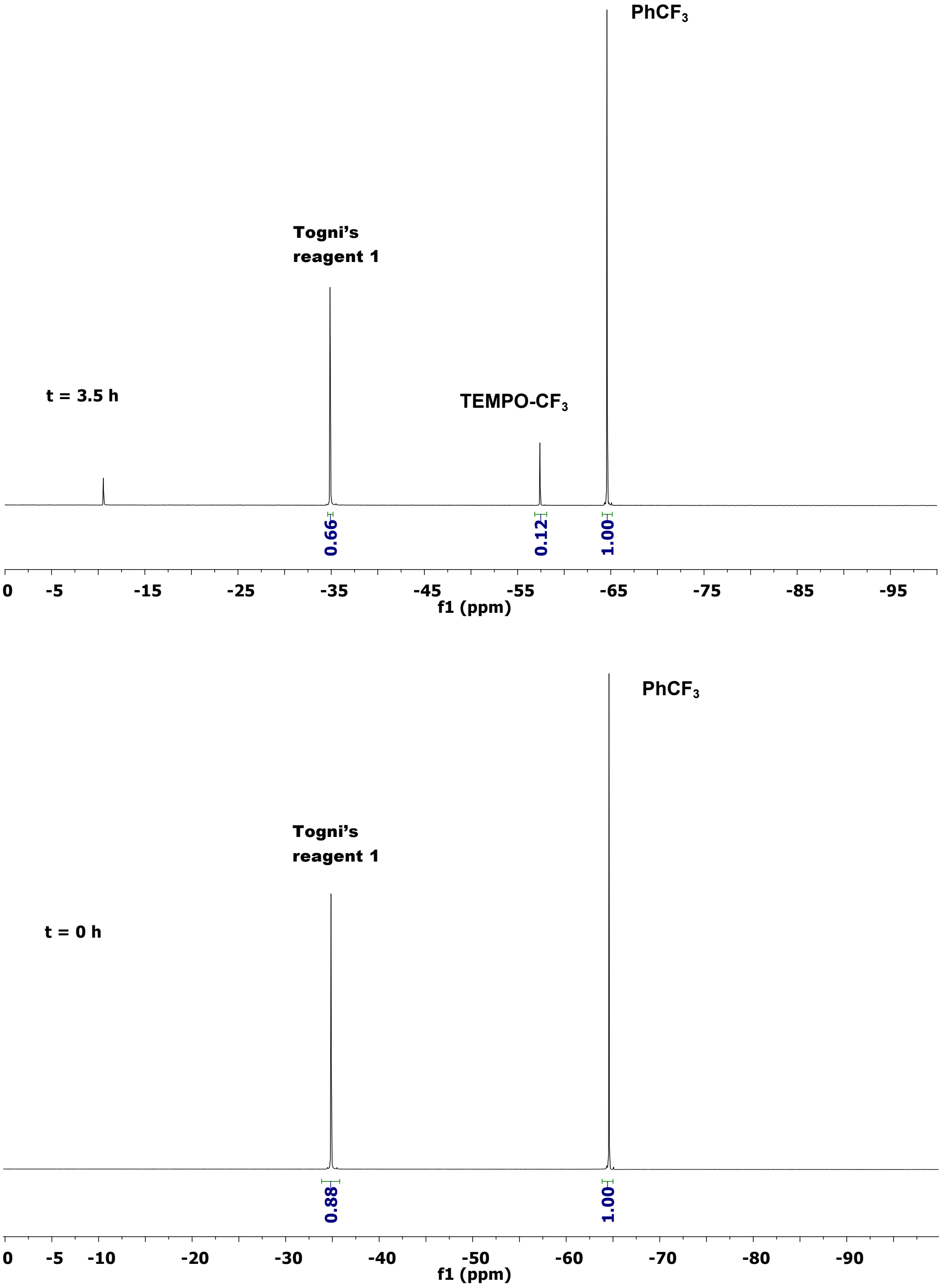


Figure S7. ^{19}F NMR spectra of a reaction of **1** (0.1 mmol) and TEMPO radical (0.15 mmol) in CD_3OD solution (0.5 mL) under sunlight at time = 0 (bottom) and after 3.5 h (top). $PhCF_3$ (0.1 mmol) was added as an internal standard.

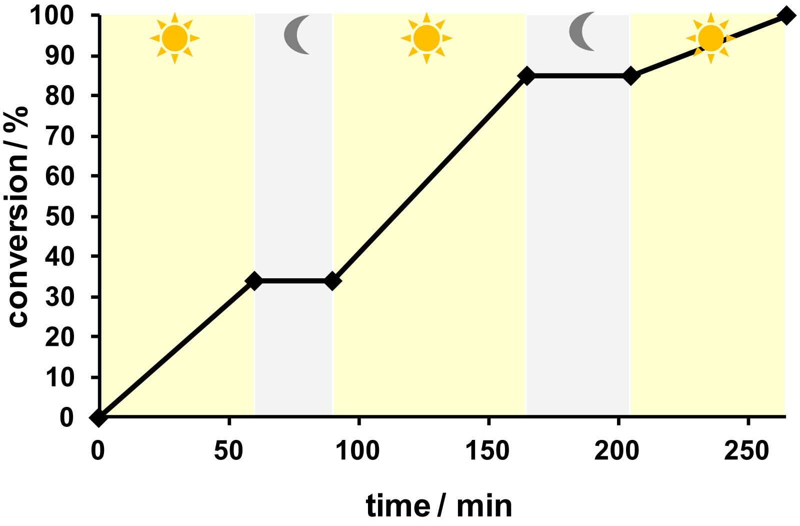


Figure S8. Reaction profile for the photocatalytic reduction of Togni's reagent **1** by **2** alternating the illumination conditions, e.g. direct sunlight or absence of light (Tube kept in the NMR probe). The reaction was conducted in CD_3OD (0.5 mL) in a NMR tube containing **1** (0.1 mmol) and **2** (0.5 mol%). The solution was deaerated by gentle Ar bubbling for 20 min keeping the tube in the dark (aluminium foil). The conversion was determined by ^1H NMR spectroscopy using the peak of CHD_2OD as an internal standard.

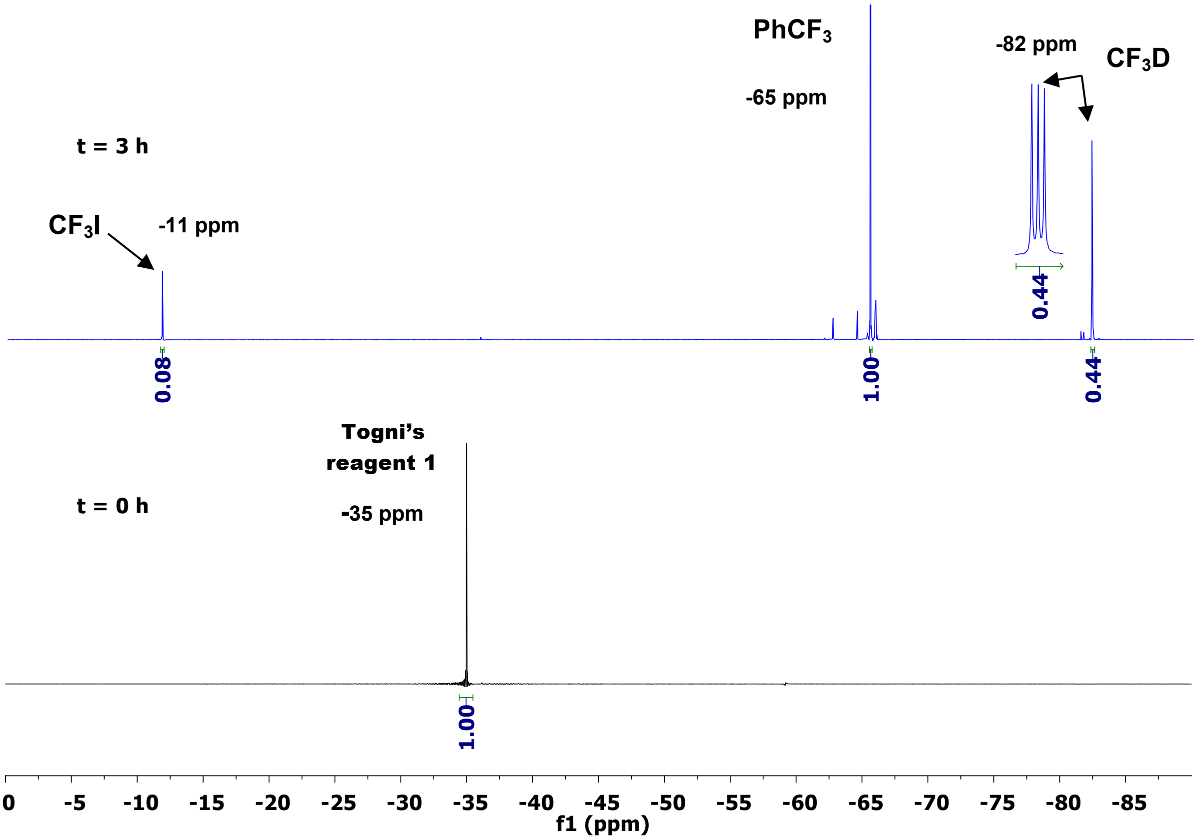


Figure S9. ^{19}F NMR spectra of a reaction of **1** (0.1 mmol) with **2** (0.5 mol%) in CD_3OD solution (0.5 mL) before irradiation (black) and after 3 h sunlight irradiation (blue). $PhCF_3$ (0.1 mmol) was added as an internal standard at the end of the reaction.

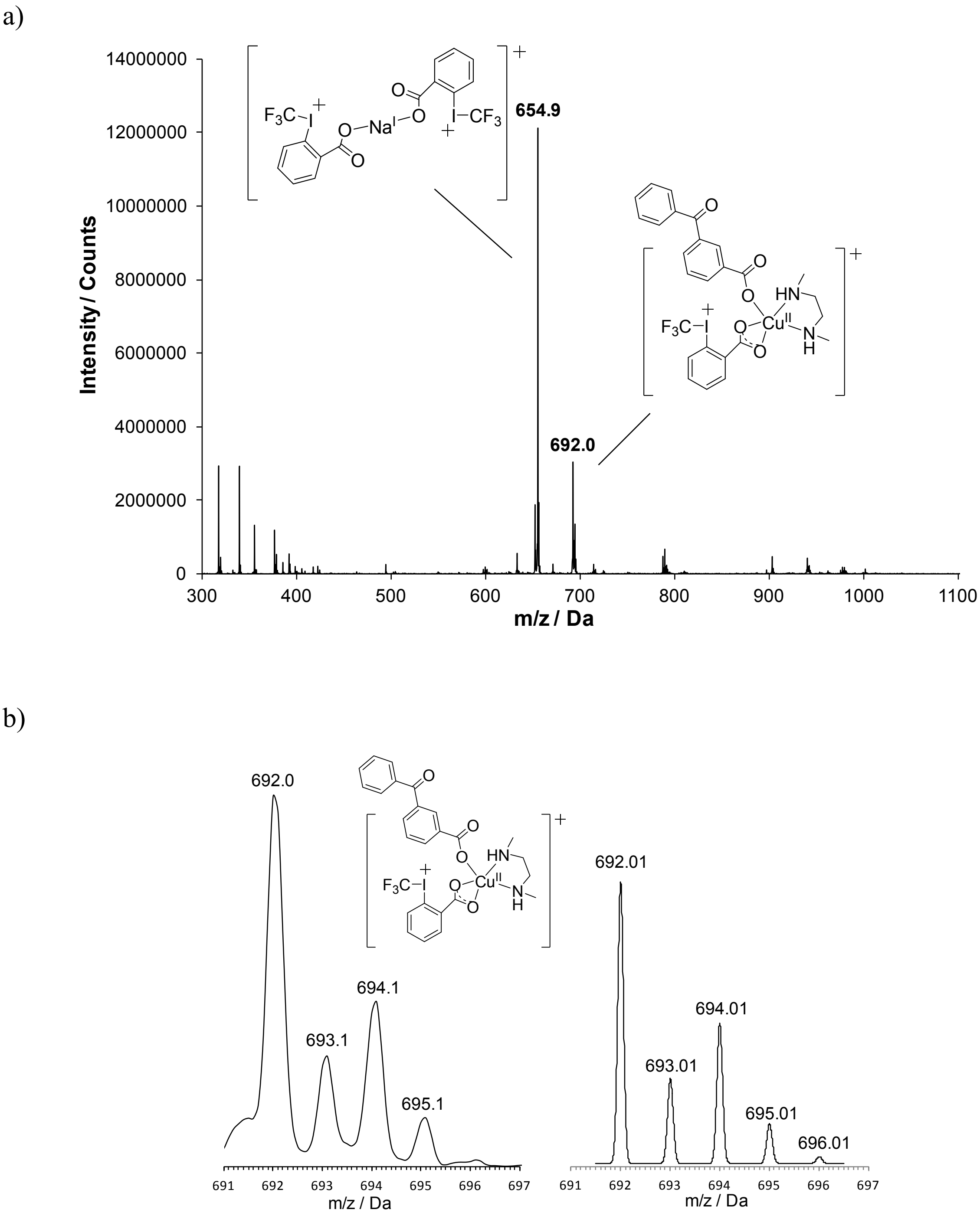


Figure S10. a) ESI-MS spectrum of a freshly prepared air-equilibrated CH_3OH solution (0.3 mL) of **1** (20 mmol) and **2** (1 mmol). The solution was prepared and kept in the dark for 2 min until injection (diluted 100-fold in CH_3OH) in the spectrometer. b) Experimental (left) and calculated (right) isotopic patterns. The spectrometer was not calibrated for high resolution molecular weight determination.

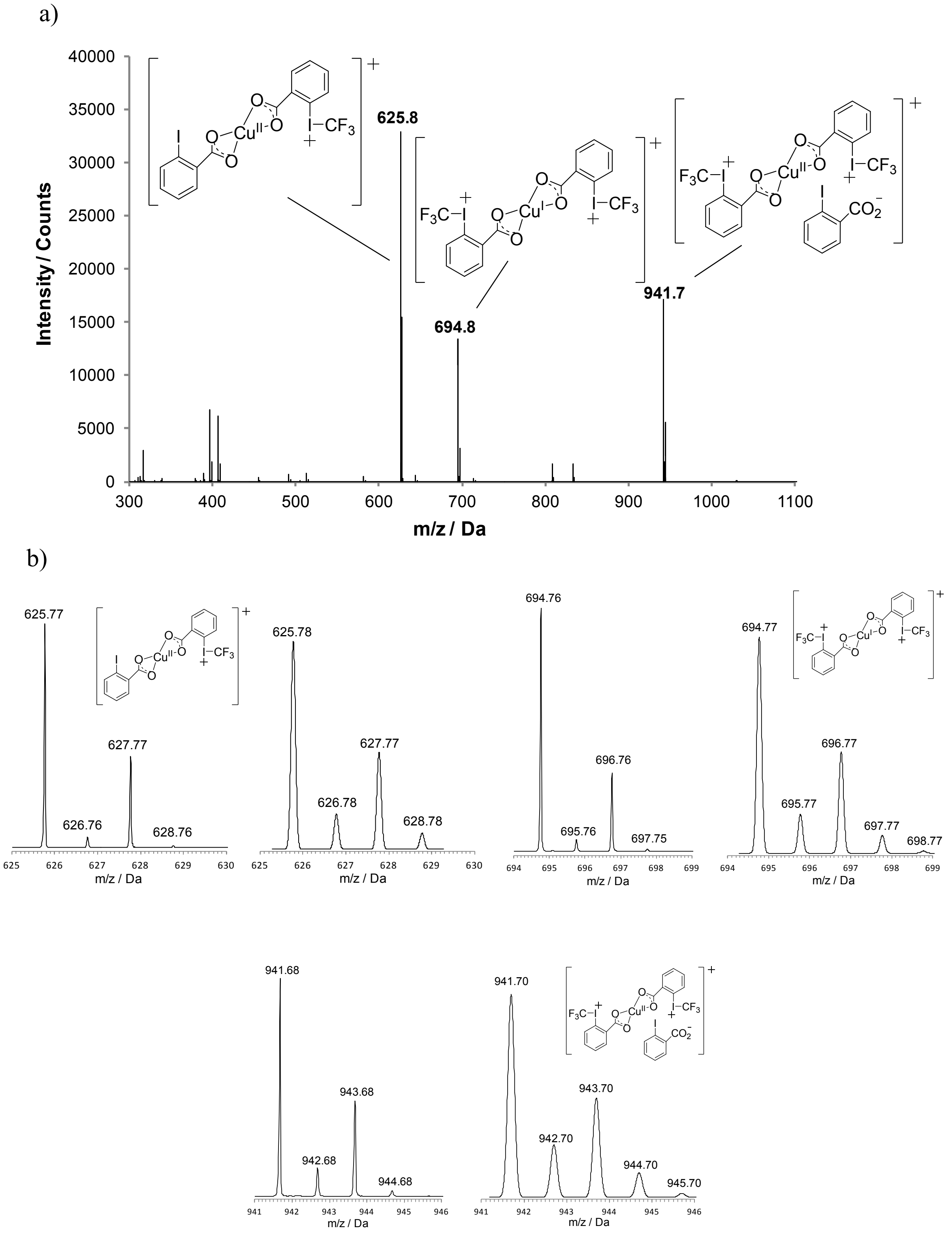


Figure S11. a) ESI-MS spectrum of a freshly prepared CD_3OD solution (0.5 mL) of **2** (0.1 mmol) and $[Cu(MeCN)_4]PF_6$ (0.05 mmol). The solution was prepared and kept in the dark until injection (diluted 100-fold in CH_3OH) in the spectrometer. b) Experimental (left) and calculated (right) isotopic patterns.

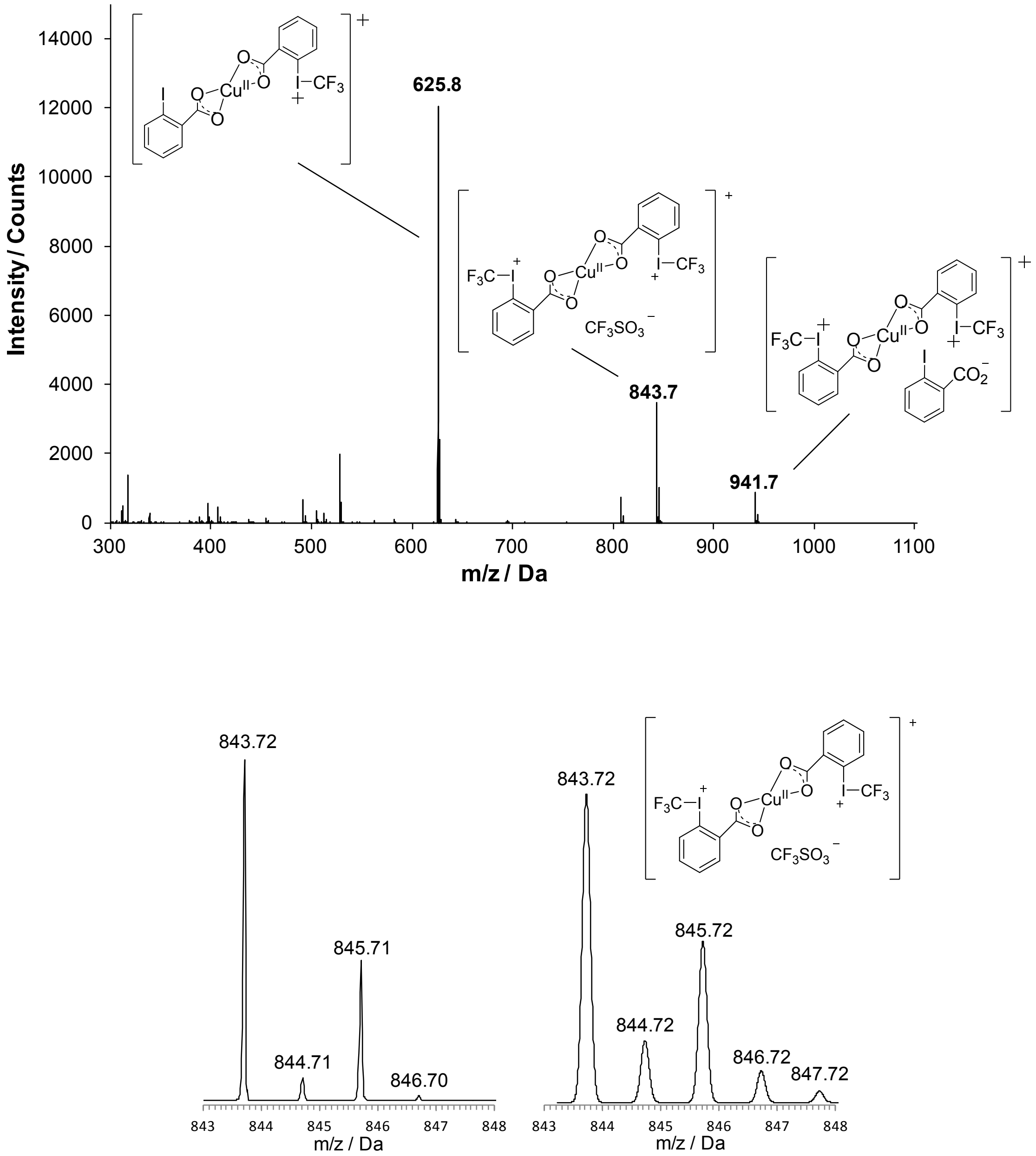


Figure S12. a) ESI-MS spectrum of a freshly prepared CD_3OD solution (0.5 mL) of **2** (0.1 mmol) and $CuOTf_2$ (0.05 mmol). The solution was prepared and kept in the dark until injection (diluted 100-fold in CH_3OH) in the spectrometer. b) Experimental (left) and calculated (right) isotopic patterns.

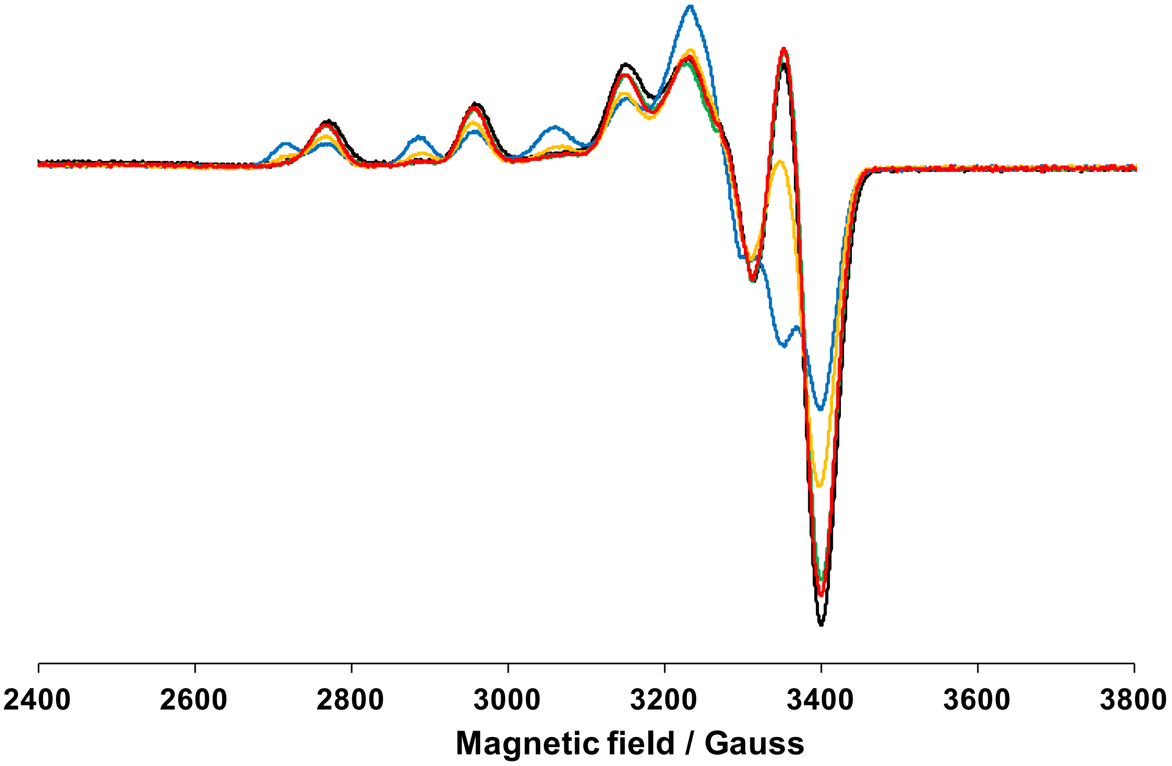


Figure S13. EPR (X-band) spectroscopic monitoring of the reaction of **2** with ethyl benzoate, or the benzoate and 2-iodobenzoate sodium salts in the dark. The spectra were recorded at 100 K. Black spectrum: Air-equilibrated MeOH solution (0.3 mL) of **2** (1 mM); Green spectrum: Air-equilibrated MeOH solution (0.3 mL) of **2** (1 mM) and ethyl benzoate (20 mM) left for 240 min in the dark; Red spectrum: Air-equilibrated MeOH solution (0.3 mL) of **2** (1 mM) and sodium benzoate (20 mM) left for 240 min in the dark; Orange spectrum: Air-equilibrated MeOH solution (0.3 mL) of **2** (1 mM) and sodium benzoate + 15-crown-5 ether (20 mM) left for 240 min in the dark; Blue spectrum: Air-equilibrated MeOH solution (0.3 mL) of **2** (1 mM) and 2-iodobenzoate + 15-crown-5 ether (20 mM) left for 240 min in the dark.

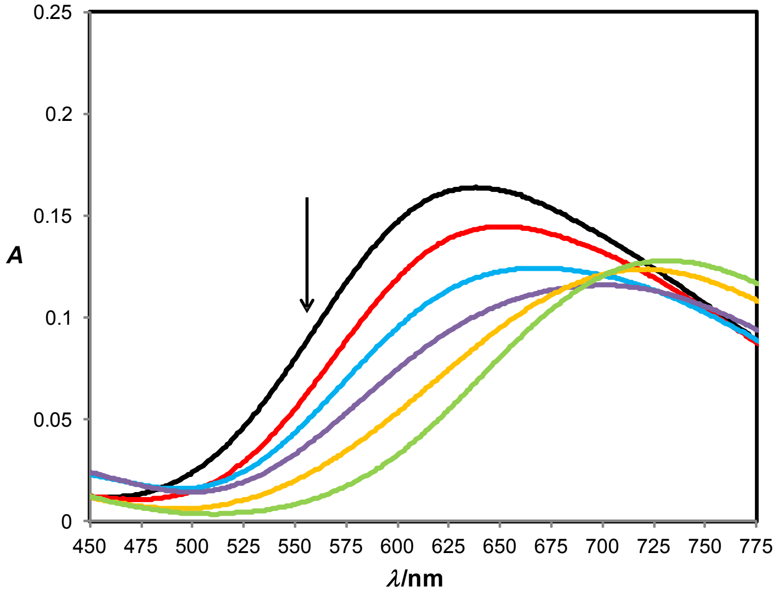


Figure S14. UV-vis spectroscopic monitoring of the reaction of **2** with **1** in the dark. Black spectrum: Air equilibrated MeOH solution (3 mL) of **2** (5×10^{-3} mmol, 5 mol%); Keeping the sample in the dark, **1** is added (0.1 mmol) and the spectra are recorded after 10 min (red), 30 min (blue), 60 min (purple), 80 min (orange) and 160 min (green).

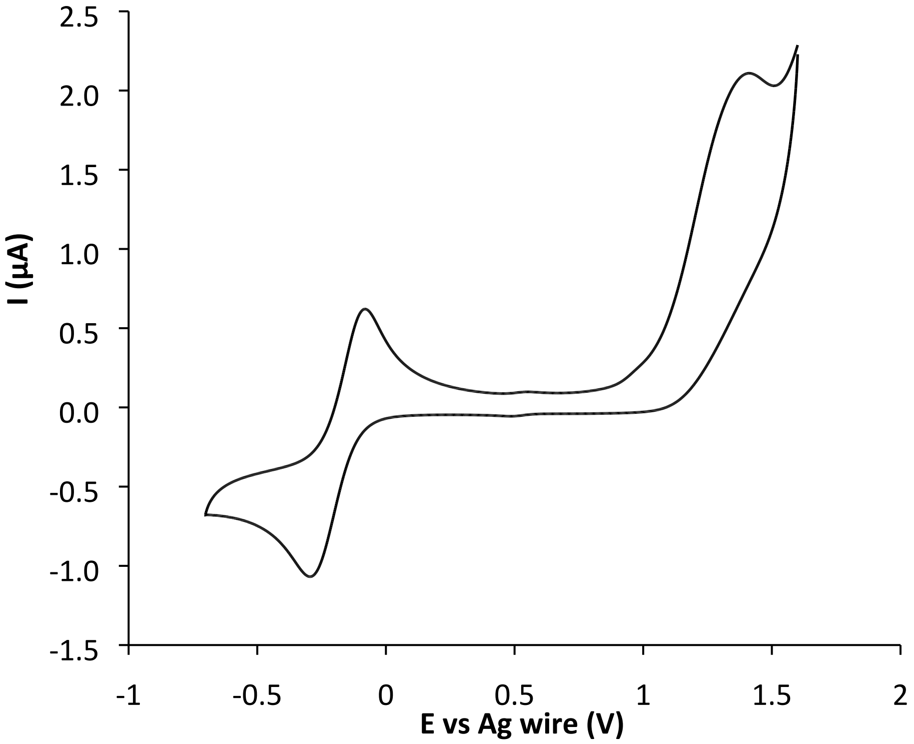
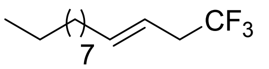


Figure S15. Cyclic voltammogram of complex **2** in the dark at room temperature at a concentration of 1 mM in methanol with 0.1 mM of $TBAPF_6$ supporting electrolyte and ferrocene internal reference, at a scan rate of 50 mV/s.

Syntheses and Characterization of Compounds 4, 5a-e, 6a-b.

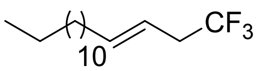
(*E*)-1,1,1-Trifluorotetradec-3-ene (5a): Synthesized according to a general procedure from a mixture of complex **2** (0.73 mg, 0.001 mmol), dodec-1-ene (46 µL, 0.2 mmol) and Togni's reagent **1** (78 mg, 0.24 mmol) in CD_3OD (1 mL) under sunlight illumination for 6 h. The residue was purified by flash chromatography over silica gel (100% pentane) to afford the trifluoromethylated product **5a** (36 mg, 74%) as a clear, and colorless oil (*E*/*Z*/other isomer = 86:8:6).



5a

^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 5.75-5.61 (m, 1 H), 5.45-5.32 (m, 1H), 2.90-2.66 (m, 2H), 2.05 (q, J = 6.4 Hz, 2H), 1.36-1.14 (m, 16H), 0.88 (t, J = 6.4 Hz, 3H); **^{13}C-NMR** ($CDCl_3$, 101 MHz) δ (ppm) = 138.5, 126.2 (q, J = 274.7 Hz), 117.4, 37.4 (q, J = 29.2 Hz), 32.5, 31.9, 29.6, 29.4, 29.3, 29.0, 28.9, 22.7, 14.1; **^{19}F-NMR** ($CDCl_3$, 376.5 MHz,) δ (ppm) = -68.0 (t, J = 10.9 Hz);. **EI-MS** (*m/z*, relative intensity): 236 (M, 8), 97 ($C_3H_4F_3^+$, 53), 83 ($C_2H_2F_3^+$, 82), 70 (CF_3H or C_5H_{10}, 100), 56 (C_4H_8, 94), 43 ($C_4H_9^+$, 87); **HRMS** (EI): Calcd. for $C_{16}H_{29}F_3$: 236.1751; Found: 236.1741.

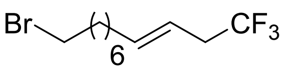
(*E*)-1,1,1-Trifluorohexadec-3-ene (5b): Synthesized according to a general procedure from a mixture of complex **2** (0.73 mg, 0.001 mmol), pentadec-1-ene (55.5 µL, 0.2 mmol) and Togni's reagent **1** (78 mg, 0.24 mmol) in CD_3OD (1 mL) under sunlight illumination for 6 h. The residue was purified by flash chromatography over silica gel (100% pentane) to afford the trifluoromethylated product **5b** (46 mg, 83%) as a clear, and colorless oil (*E*/*Z*/other isomer = 88:8:4).



5b

^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 5.76-5.61 (m, 1 H), 5.43-5.29 (m, 1H), 2.86-2.68 (m, 2H), 2.04 (q, J = 6.8 Hz, 2H), 1.43-1.12 (m, 20H), 0.88 (t, J = 6.4 Hz, 3H); **^{13}C-NMR** ($CDCl_3$, 101 MHz) δ (ppm) = 138.7, 126.3 (q, J = 274.8 Hz), 117.6, 37.5 (q, J = 29.2 Hz), 32.7, 32.1, 29.8, 29.6, 29.5, 29.3, 29.2, 29.1, 22.9, 14.2; **^{19}F-NMR** ($CDCl_3$, 376.5 MHz,) δ (ppm) = -67.8 (t, J = 10.9 Hz);. **EI-MS** (*m/z*, relative intensity): 278 (M, 5), 125 ($C_9H_{17}^+$, 24), 111 ($C_8H_{15}^+$, 48), 97 ($C_3H_4F_3^+$, 83), 83 ($C_2H_2F_3^+$, 96), 69 (CF_3^+, 84), 57 ($C_4H_9^+$, 100), 43 ($C_3H_7^+$, 80); **HRMS** (EI): Calcd. for $C_{16}H_{29}F_3$: 278.2221; Found: 278.2231.

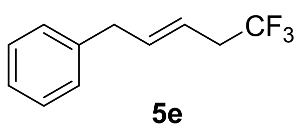
(*E*)-11-Bromo-1,1,1-trifluoroundec-3-ene (5c): Synthesized according to the general procedure from a mixture of complex **2** (0.73 mg, 0.001 mmol), 10-bromodec-1-ene (40 µL, 0.2 mmol) and Togni's reagent **1** (78 mg, 0.24 mmol) in CD_3OD (1 mL) under sunlight illumination for 6 h. The residue was purified by flash chromatography over silica gel (100% pentane) to afford the trifluoromethylated product **5c** (43 mg, 75%) as a colorless oil (*E*/*Z* = 91:9).



5c

^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 5.74-5.63 (m, 1 H), 5.41-5.29 (m, 1H), 3.40 (t, J = 6.8 Hz, 2H), 2.86-2.67 (m, 2H), 2.02 (q, J = 6.4 Hz, 2H), 1.90-1.78 (m, 2H), 1.46-1.24 (m, 8H); **^{13}C-NMR** ($CDCl_3$, 101 MHz) δ (ppm) = 138.1, 125.9 (q, J = 274.8 Hz), 117.4, 37.2 (q, J = 29.3 Hz), 33.8, 32.6, 32.2, 28.6, 28.5, 28.4, 27.9; **^{19}F-NMR** ($CDCl_3$, 376.5 MHz,) δ (ppm) = -67.7 (t, J = 10.5 Hz);. **EI-MS** (*m/z*, relative intensity): 286 (M, 20), 137 ($C_{11}H_{17}^+$, 18), 97 ($C_3H_4F_3^+$, 47), 83 ($C_2H_2F_3^+$, 42), 69 (CF_3^+, 32), 55 ($C_4H_7^+$, 100); **HRMS** (EI): Calcd. for $C_{11}H_{18}BrF_3$: 286.0544; Found: 286.0550.

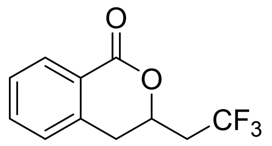
(*E*)-(5,5,5-Trifluoropent-2-enyl)benzene (5e): Synthesized according to the general procedure from a mixture of complex **2** (0.73 mg, 0.001 mmol), but-3-enylbenzene (30 µL, 0.2 mmol) and Togni's reagent **1** (78 mg, 0.24 mmol) in CD_3OD (1 mL) under sunlight illumination for 8 h. The residue was purified by flash chromatography over silica gel (100% pentane) to afford the trifluoromethylated product **5e** (19 mg, 47%) as a clear and colorless oil (*E*/*Z* = 97:3).



5e

^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.40-7.31 (m, 2H), 7.30-7.18 (m, 3H), 5.96-5.83 (m, 1H), 5.57-5.45 (m, 1H), 3.44 (d, J = 10.8 Hz, 2H), 2.92-2.78 (m, 2H); **^{13}C-NMR** ($CDCl_3$, 101 MHz) δ (ppm) = 139.7, 136.9, 128.7, 128.5, 126.4, 126.2 (q, J = 275.0 Hz), 119.3, 39.0, 37.3 (q, J = 29.5 Hz); **^{19}F-NMR** ($CDCl_3$, 376.5 MHz,) δ (ppm) = -67.5(t, J = 10.5 Hz);. **EI-MS** (*m/z*, relative intensity): 200 (M, 50), 117 ($C_9H_9^+$, 100), 91 ($C_7H_7^+$, 26); **HRMS** (EI): Calcd. for $C_{11}H_{11}F_3$: 200.0812; Found: 200.0818.

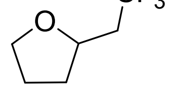
3-(2,2,2-Trifluoroethyl)isochroman-1-one (6a): Synthesized in a test tube (5 mL) from a mixture of complex **2** (1.56 mg, 0.0021 mmol), 2-allylbenzoic acid (70 mg, 0.43 mmol) and Togni's reagent **1** (163 mg, 0.515 mmol) in CD_3OD (2.5 mL) under irradiation at 365 nm (TLC lamp) for 2 h at 70 °C (water bath). The mixture was allowed to cool to room temperature, then diluted with diethyl ether (10 mL) and washed with saturated $NaHCO_3$ solution (5 mL). The aqueous layer was separated and extracted with Et_2O (5 mL × 2). The combined organic layers were dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash chromatography over silica gel (Pentane /EtOAc, 95/5, v/v to 90/10, v/v) to afford the trifluoromethylated product **6a** (71 mg, 71%) as a white solid.



6a

^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 8.09 (d, J = 7.6 Hz, 1H), 7.57 (td, J = 7.3 Hz and 1.2 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.27 (d, J = 7.6 Hz, 1H), 4.90-4.81 (m, 1H), 3.11-3.06 (m, 2H), 2.87-2.72 (m, 1H), 2.64-2.48 (m, 1H); **^{13}C-NMR** ($CDCl_3$, 101 MHz) δ (ppm) = 164.3, 137.9, 134.3, 130.6, 128.3, 127.6, 125.2 (q, J = 275.1 Hz), 124.8, 72.4, 39.3 (q, J = 28.5 Hz), 33.1; **^{19}F-NMR** ($CDCl_3$, 376.5 MHz,) δ (ppm) = -64.3(t, J = 10.9 Hz);. **EI-MS** (*m/z*, relative intensity): 230 (M^+, 32), 118 (C_9H_{10}, 100), 91 (44); **HRMS** (EI): Calcd. for $C_{11}H_9F_3O_2$: 230.0554; Found: 230.0549.

2-(2,2,2-Trifluoroethyl)tetrahydrofuran (6b): Synthesized according to the general procedure from a mixture of complex **2** (0.73 mg, 0.001 mmol), hex-5-en-1-ol (20.5 µL, 0.2 mmol) and Togni's reagent **1** (78 mg, 0.24 mmol) in CD_3OD (1 mL) under irradiation at 365 nm using a TLC lamp for 2 h at 70 °C (water bath). Due to its high volatility, isolation of this compound was not possible. The yield of **6b** was 80 % as determined by ^{1}H NMR spectroscopy using the peak of CHD_2OD as an internal standard.



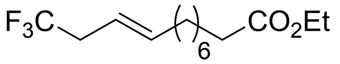
6b

^{1}H-NMR (CD_3OD, 400 MHz) δ (ppm) = 4.12-4.02 (m, 1H), 3.84 (dd, J = 15.2 Hz and 7.6 Hz, 1H), 3.73 (td, J = 8.0 Hz and 6.1 Hz, 1H), 2.47-2.31 (m, 2H), 2.16-2.04 (m, 1H), 1.97-1.85 (m, 1H), 1.64-1.50 (m, 1 H); **^{19}F-NMR** (CD_3OD, 376.5 MHz,) δ (ppm) = -68.1 (t, J = 10.9 Hz);. **CI-**

MS (*m/z*, relative intensity): 195 (M+$C_3H_5^+$, 5), 183 (M+$C_2H_5^+$, 8), 155 (M+H^+, 100), 137 ($C_9H_9F_3$, 58).

Procedure for the Trifluoromethylation of Ethyl undec-10-enoate (2 mmol scale):

(*E*)-Ethyl 12,12,12-trifluorododec-9-enoate (4): In a round-bottom flask (25 mL), a MeOH solution (12 mL) containing the complex **2** (1.45 mg, 0.002 mmol, 0.1 mol%), the Togni's reagent **1** (758 mg, 2.4 mmol) and the ethyl undec-10-enoate **3** (0.48 mL, 2 mmol) was degassed by gentle argon bubbling for 30 minutes. Then the flask was placed behind a window under sunlight illumination. The solution was stirred for a total of 14 h of sunlight illumination. The solvent was evaporated and the residue was purified by flash chromatography over silica gel (100% pentane to pentane/EtOAc, 98/2, v/v) to afford the trifluoromethylated product **4** (458 mg, 81%) as a clear oil (*E*/*Z* = 91:9).

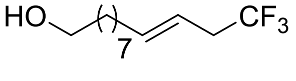


4

^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 5.72-5.61 (m, 1 H), 5.41-5.29 (m, 1H), 4.11 (q, J = 7.2 Hz, 2H), 2.83-2.67 (m, 2H), 2.27 (t, J = 7.2 Hz, 2H), 2.03 (q, J = 6.8 Hz, 2H), 1.66-1.53 (m, 2H), 1.41-1.28 (m, 8H), 1.24 (t, J = 7.2 Hz, 3H); **^{13}C-NMR** ($CDCl_3$, 101 MHz) δ (ppm) = 174.0, 138.5, 126.2 (q, J = 274.8 Hz), 117.7, 60.2, 37.5 (q, J = 29.3 Hz), 34.5, 32.5, 29.2, 28.9, 25.1, 14.4; **^{19}F-NMR** ($CDCl_3$, 376.5 MHz,) δ (ppm) = -67.7 (t, J = 10.9 Hz);. **EI-MS** (*m/z*, relative intensity): 281 (M+H^+, 58), 235 (C_9H_{10}, 82), 217 (54), 151 (56), 97 ($C_3H_4F_3^+$, 56), 88 (83), 69 (CF_3^+, 100).

Procedure for the Trifluoromethylation of Undec-10-en-1-ol (2 mmol scale):

(*E*)-12,12,12-Trifluorododec-9-en-1-ol (5d): In a round-bottom flask, a MeOH solution (12 mL) containing the complex **2** (1.45 mg, 0.002 mmol, 0.1 mol%), Togni's reagent **1** (758 mg, 2.4 mmol) and the undec-10-en-1-ol (0.4 mL, 2 mmol) was degassed by gentle argon bubbling for 30 minutes. Then the flask was placed behind a window under sunlight illumination. The solution was stirred for a total of 16 h of sunlight illumination. The solvent was evaporated and the residue was diluted with diethyl ether (20 mL), and washed with saturated $NaHCO_3$ solution (15 mL). The aqueous layer was separated and extracted with Et_2O (10 mL x 2). The combined organic layers were dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash chromatography over silica gel (pentane /EtOAc, 92/8, v/v to 90/10, v/v) to afford the trifluoromethylated product **5d** (363 mg, 76%) as a clear and colorless oil (*E*/*Z* = 90:10).



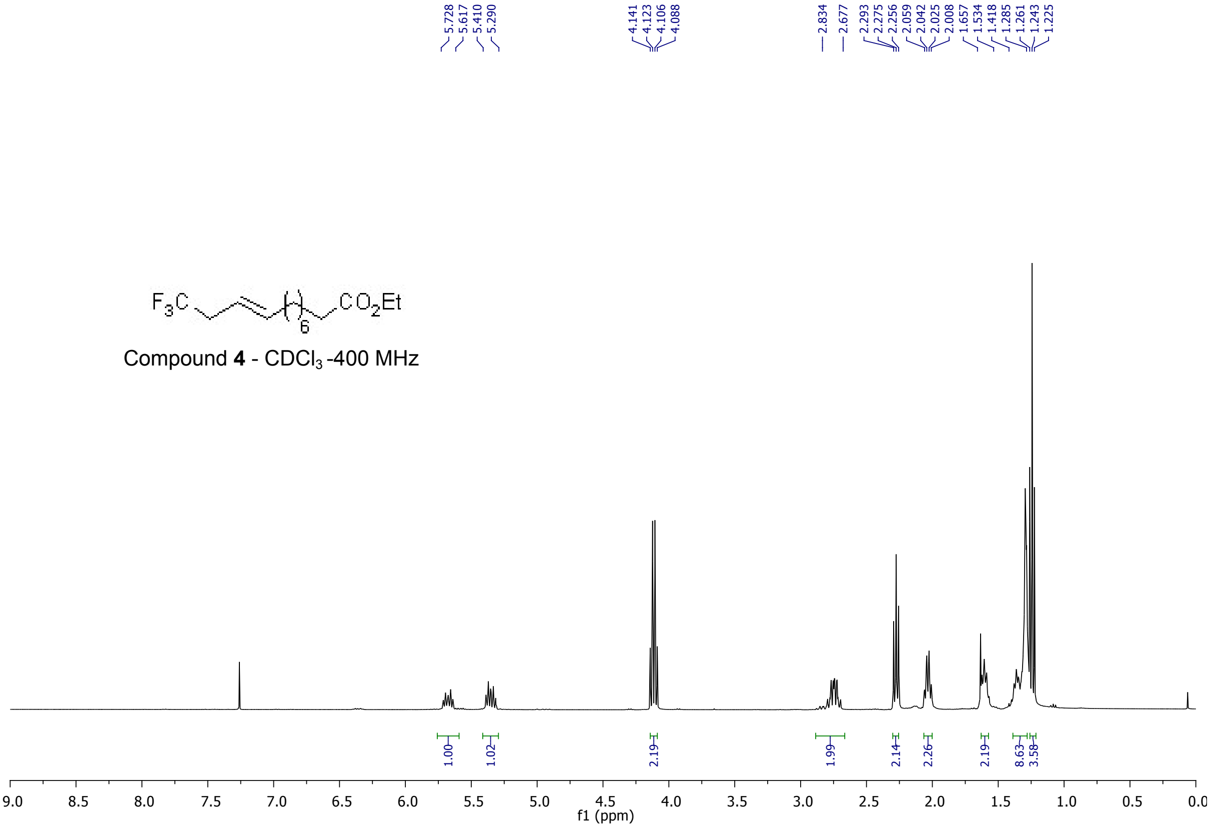
5d

^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) = 5.76-5.60 (m, 1 H), 5.41-5.26 (m, 1H), 3.59 (t, J = 6.8 Hz, 2H), 2.86-2.64 (m, 2H), 2.02 (q, J = 6.8 Hz, 2H), 1.61-1.50 (m, 2H), 1.38-1.15 (m, 10H); **^{13}C-NMR** ($CDCl_3$, 101 MHz) δ (ppm) = 138.5, 126.2 (q, J = 274.6 Hz), 117.6, 63.0, 37.4 (q, J = 29.3 Hz), 32.8, 32.5, 29.4, 29.2, 29.1, 29.0, 25.8; **^{19}F-NMR** ($CDCl_3$, 376.5 MHz,) δ (ppm) = -67.8 (t, J = 10.9 Hz); **CI-MS** (*m/z*, relative intensity): 279 (M+$C_3H_5^+$, 2), 239 (M+H, 5), 219 ($C_{12}H_{18}F_3^+$, 18), 179 ($C_{13}H_{24}^+$, 57), 165 ($C_{12}H_{21}^+$, 100), 151 ($C_{11}H_{20}^+$,27), 151 ($C_{10}H_{17}^+$, 16), 97 ($C_3H_4F_3^+$, 27), 83 ($C_2H_2F_3^+$, 56), 69 (CF^+, 32).

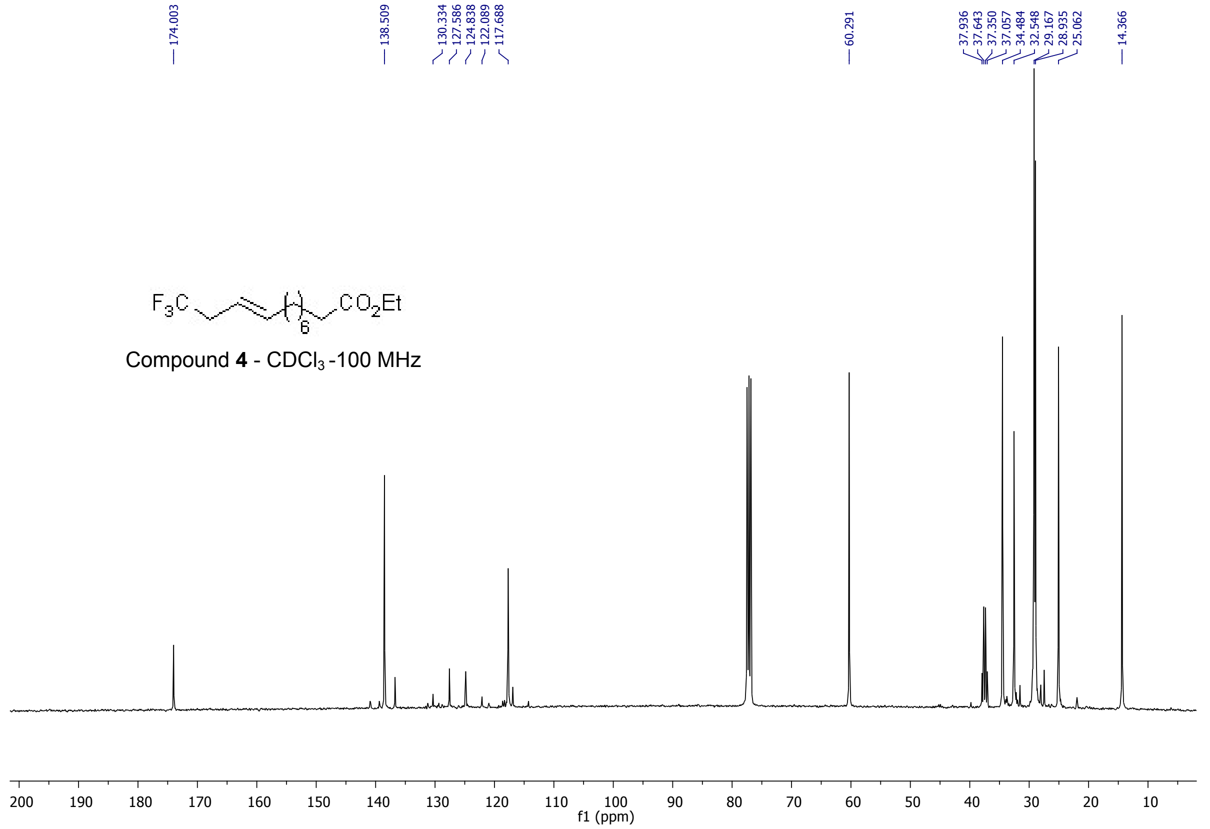
References

[1] K. Stanek, R. Koller, A. Togni, *J. Org. Chem.* **2008**, *73*, 7678.
[2] P. Eisenberger, S. Gischig, A. Togni, *Chem. – Eur. J.* **2006**, *12*, 2579.
[3] J. P. Brand, J. Charpentier, J. Waser, *Angew. Chem., Int. Ed.* **2009**, *48*, 9346.

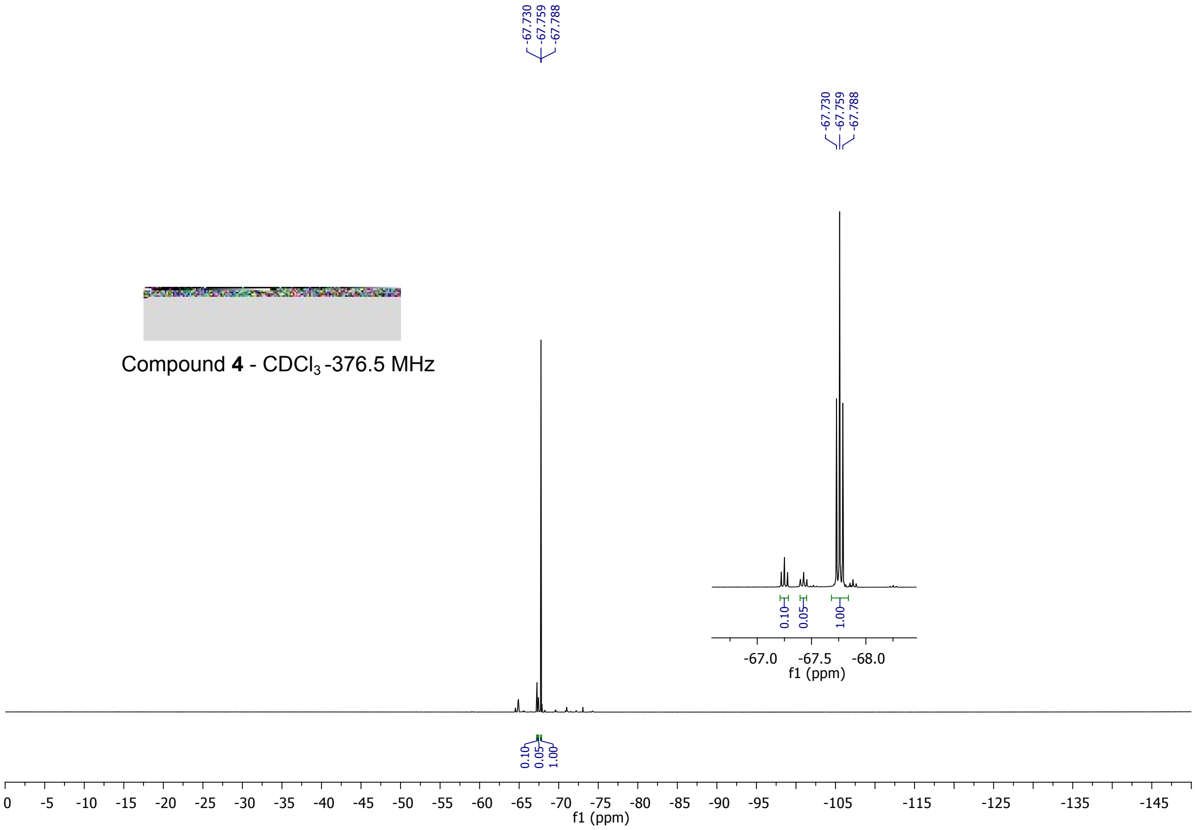
^{1}H-, ^{13}C and ^{19}F-NMR Spectra

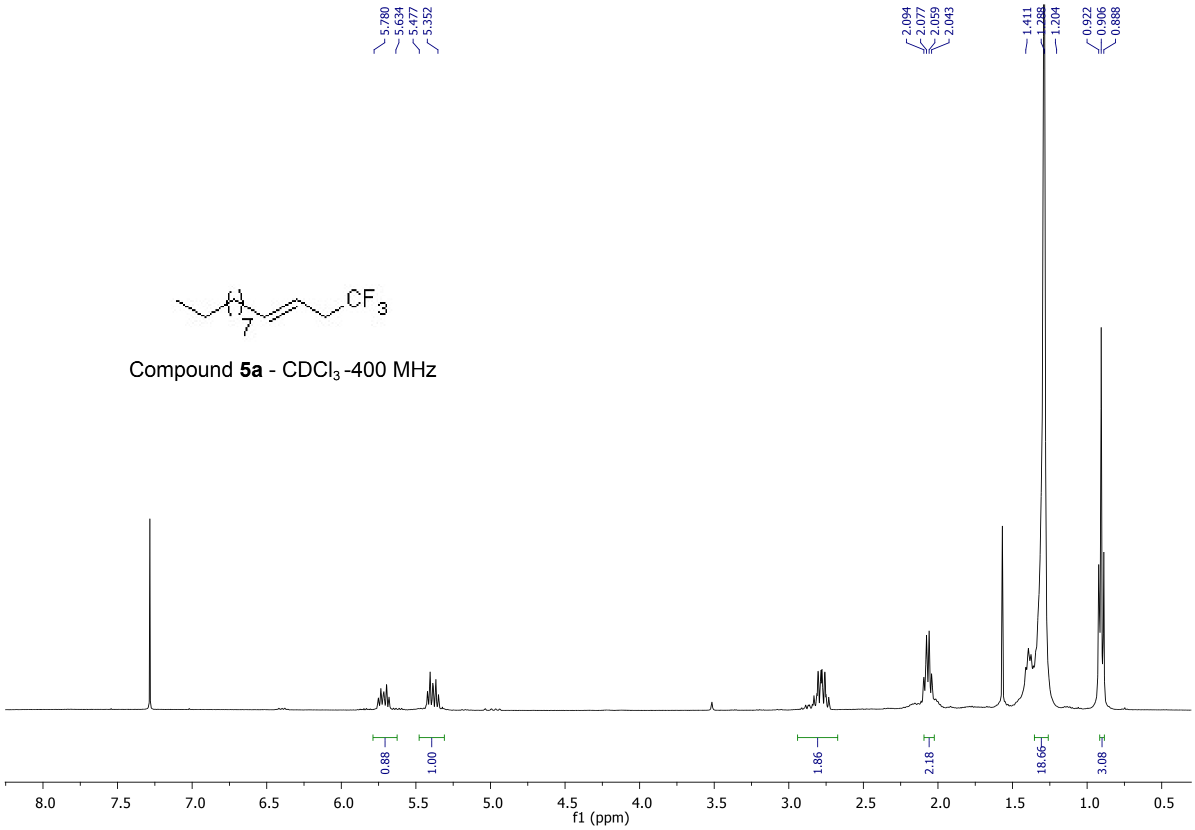


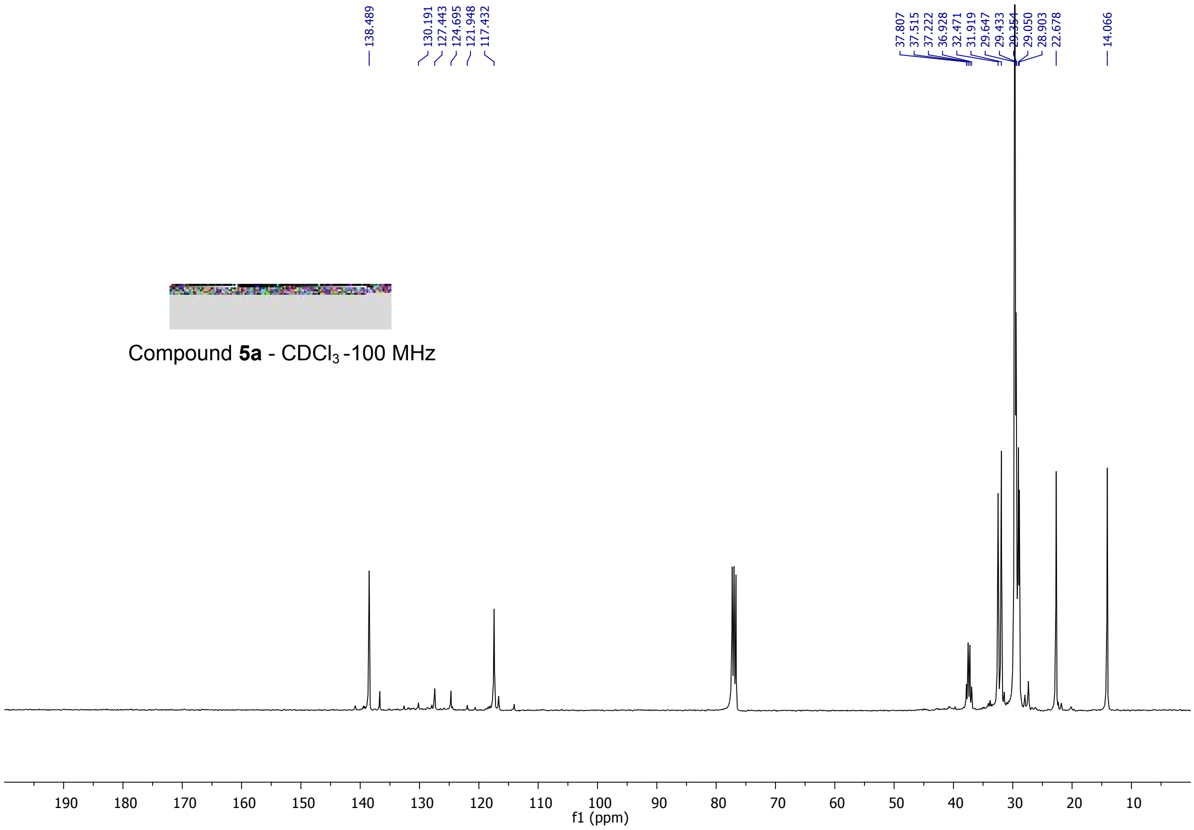
Compound **4** - $CDCl_3$ -400 MHz

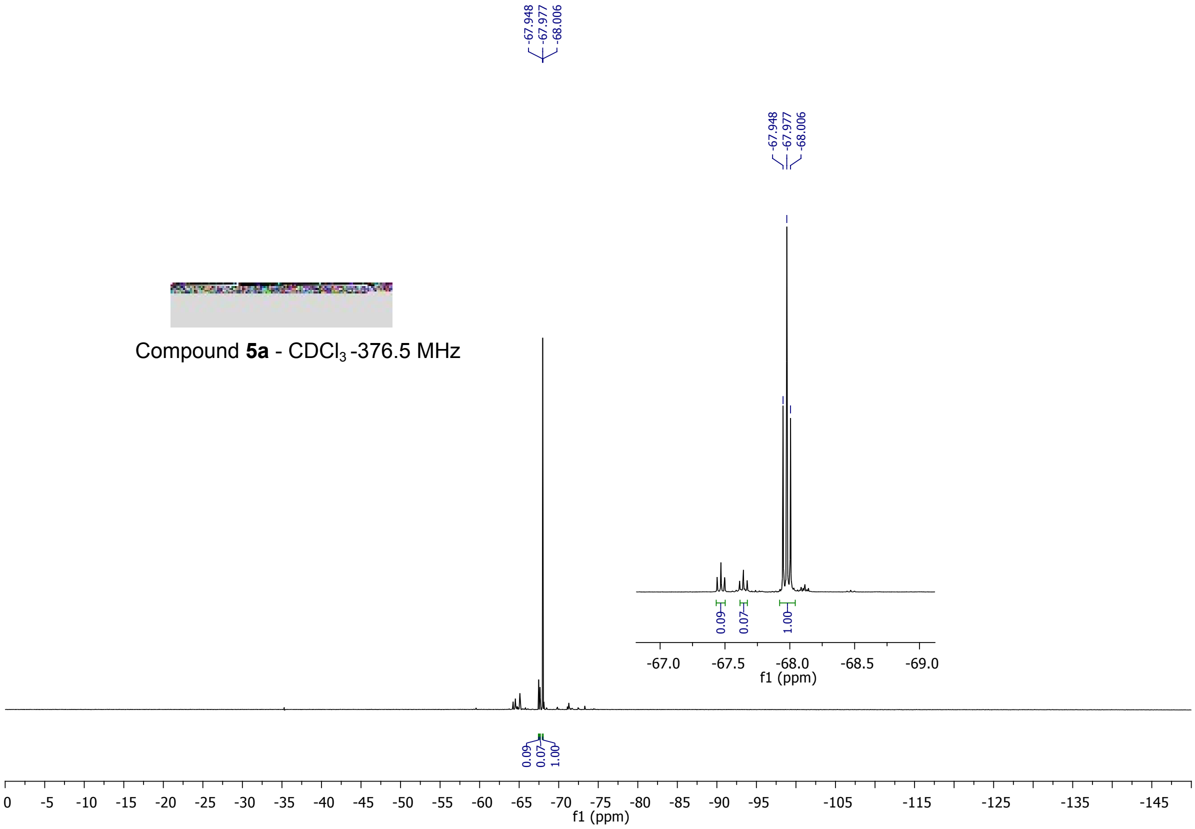


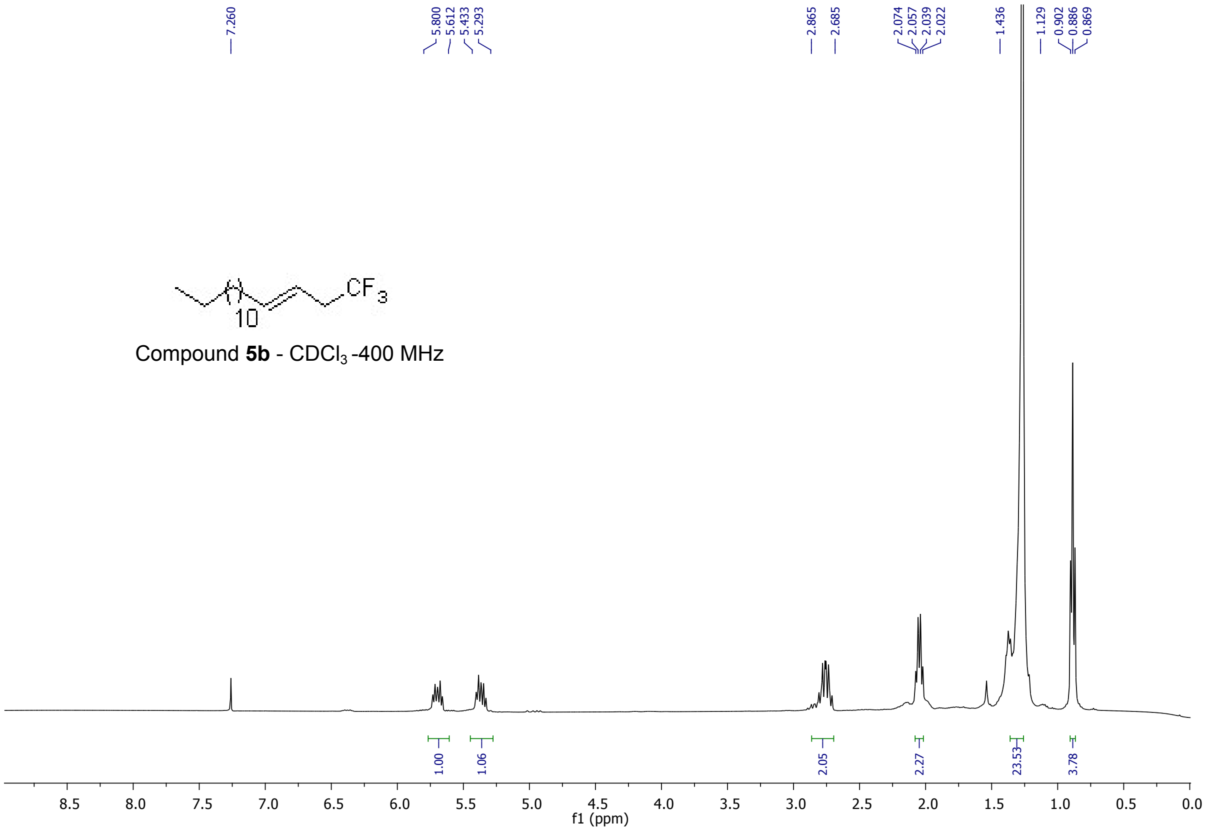
Compound **4** - $CDCl_3$ -100 MHz

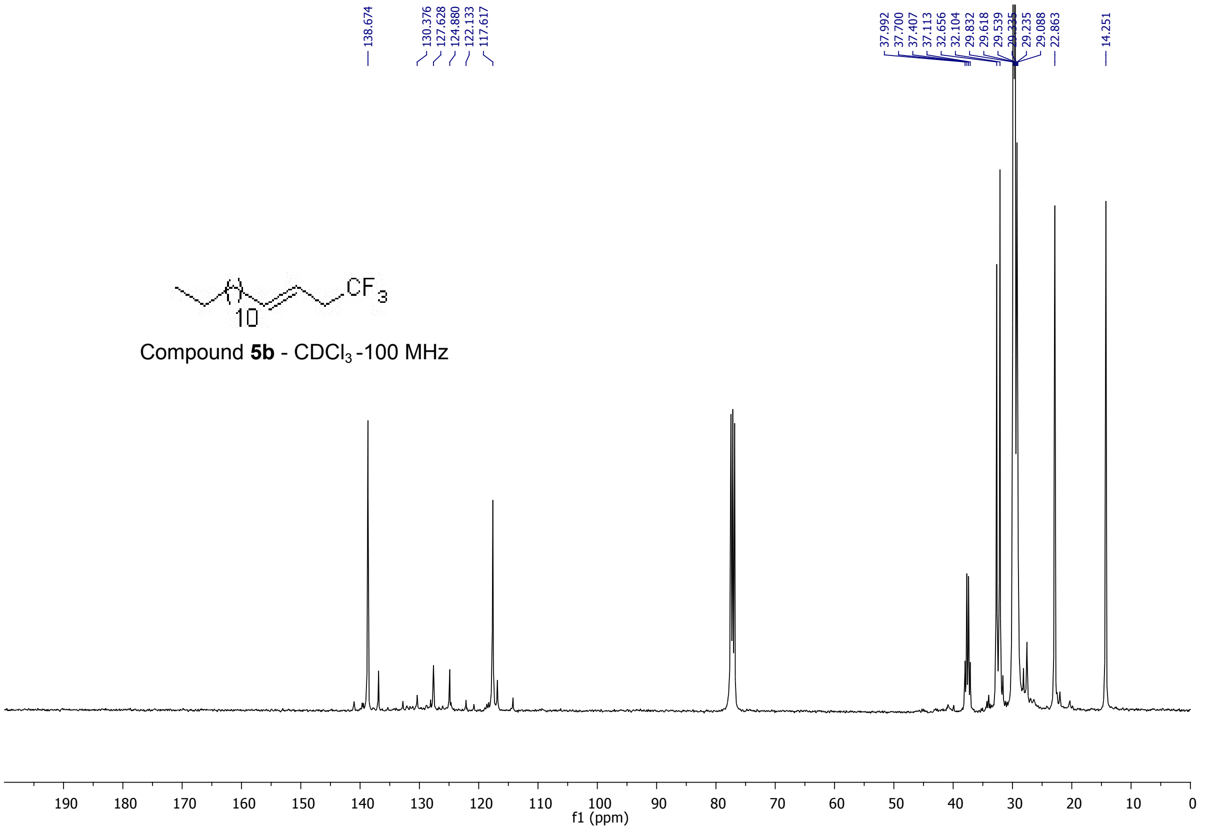

Compound **4** - $CDCl_3$ -376.5 MHz

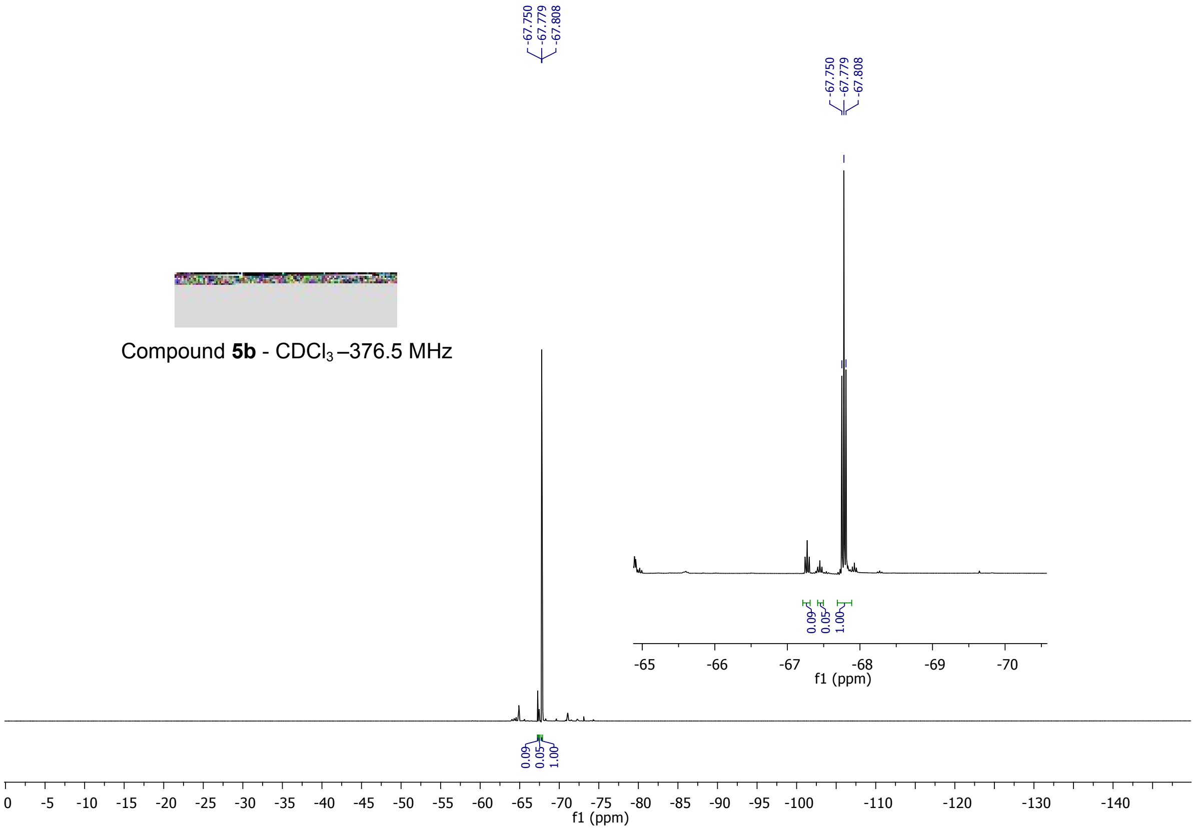

Compound **5a** - $CDCl_3$ -400 MHz

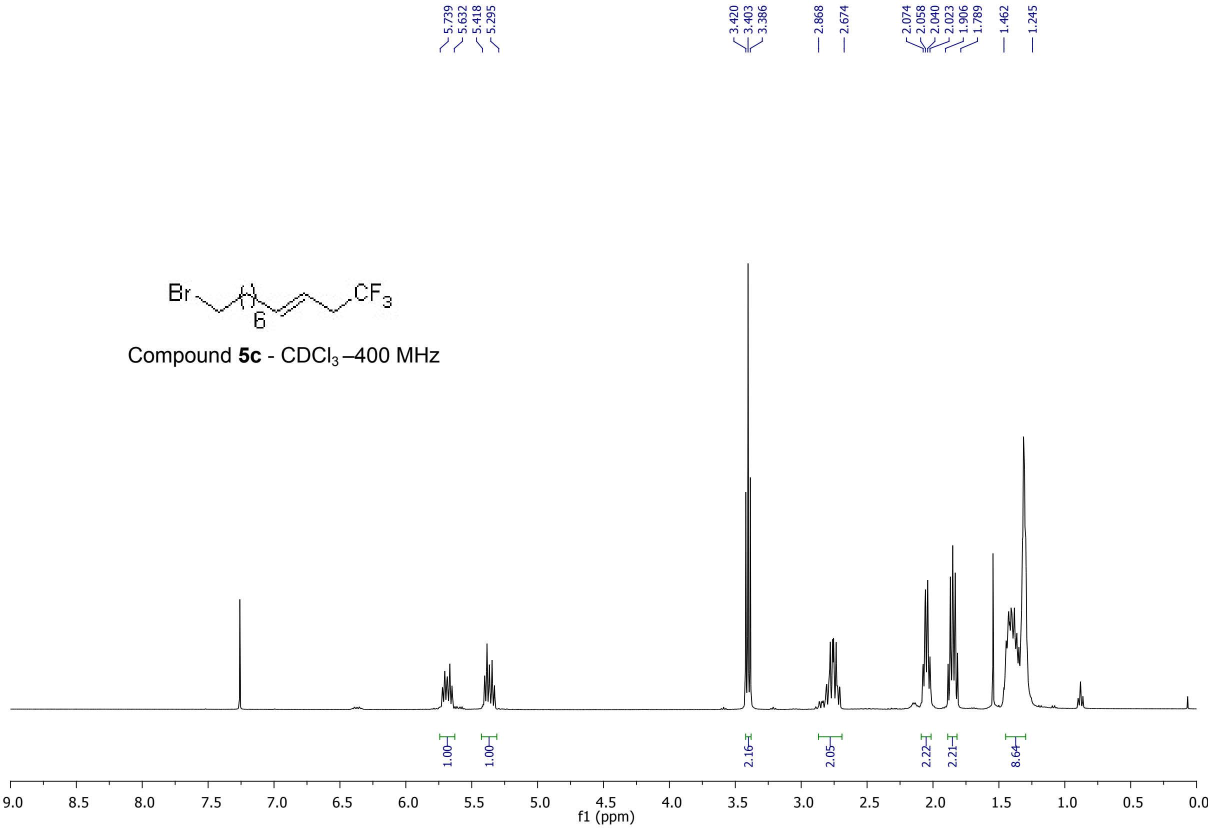

Compound **5a** - $CDCl_3$ -100 MHz

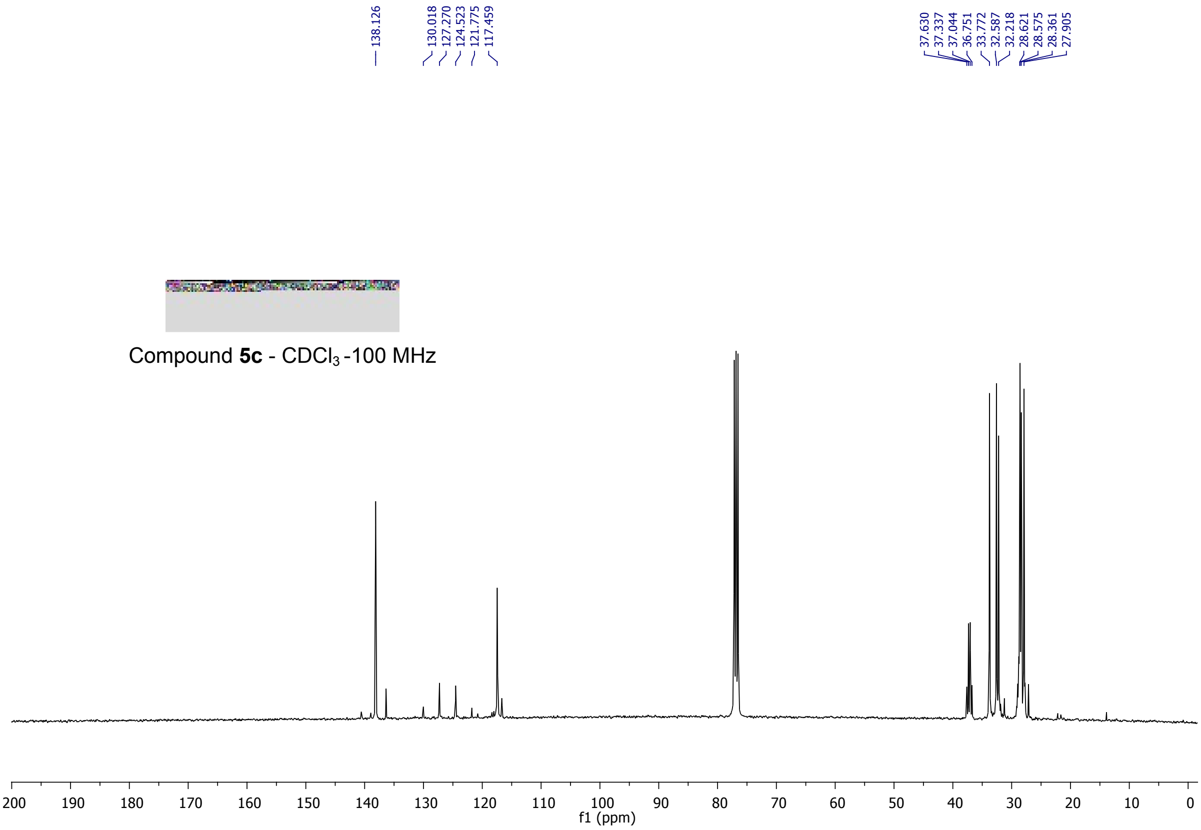

Compound **5a** - $CDCl_3$ -376.5 MHz

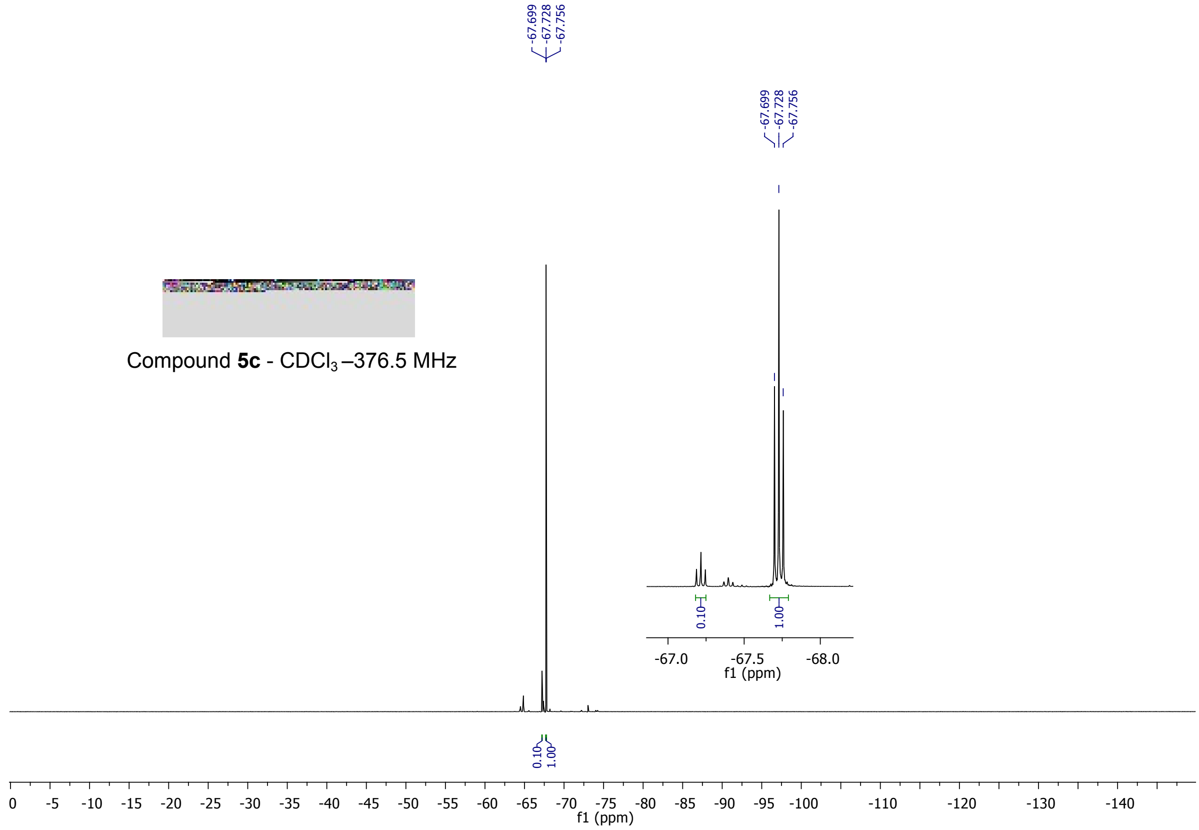

7.260
5.800
5.612
5.433
5.293
2.865
2.685
2.074
2.057
2.039
2.022
1.436
1.129
0.902
0.886
0.869
CF3
10
Compound 5b - CDCl3-400 MHz
1.00
1.06
2.05
2.27
23.53
3.78
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

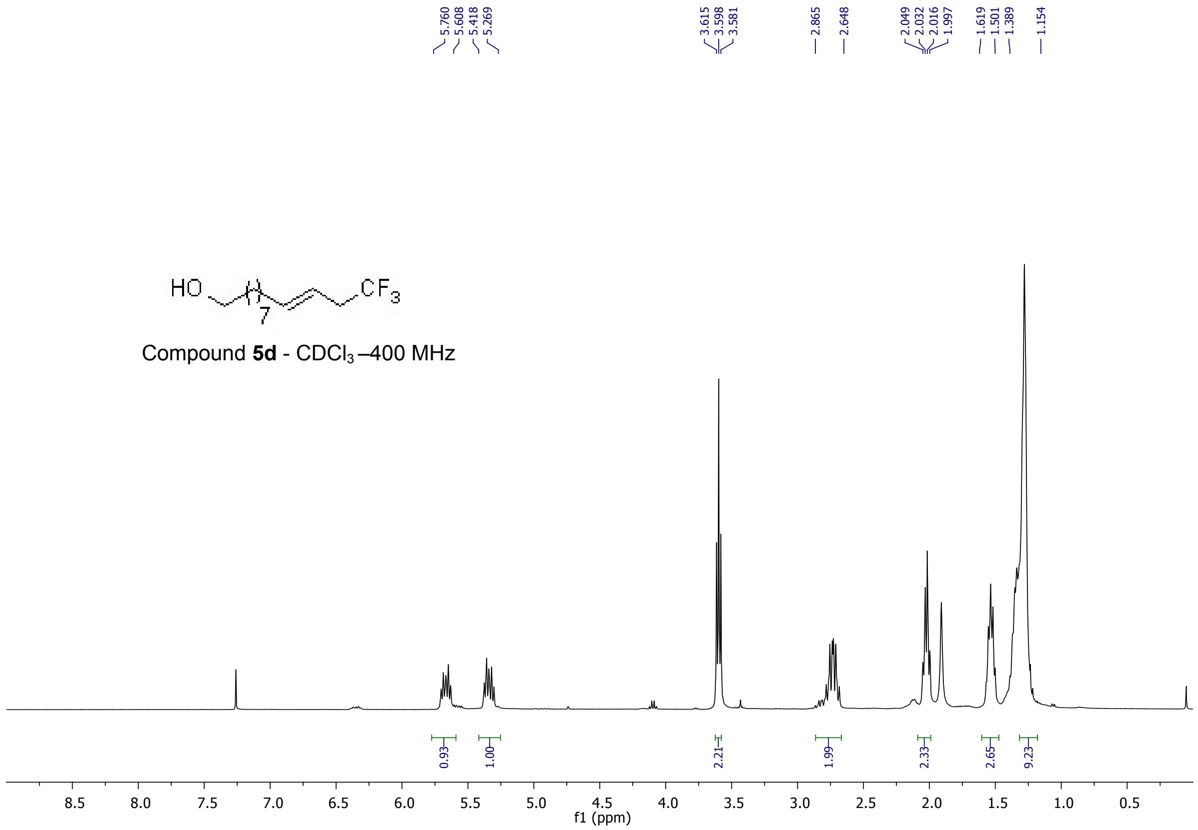

138.674
130.376
127.628
124.880
122.133
117.617
37.992
37.700
37.407
37.113
32.656
32.104
29.832
29.618
29.539
29.335
29.235
29.088
22.863
14.251
CF3
10
Compound 5b - CDCl3-100 MHz
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Compound **5b** - $CDCl_3$ –376.5 MHz

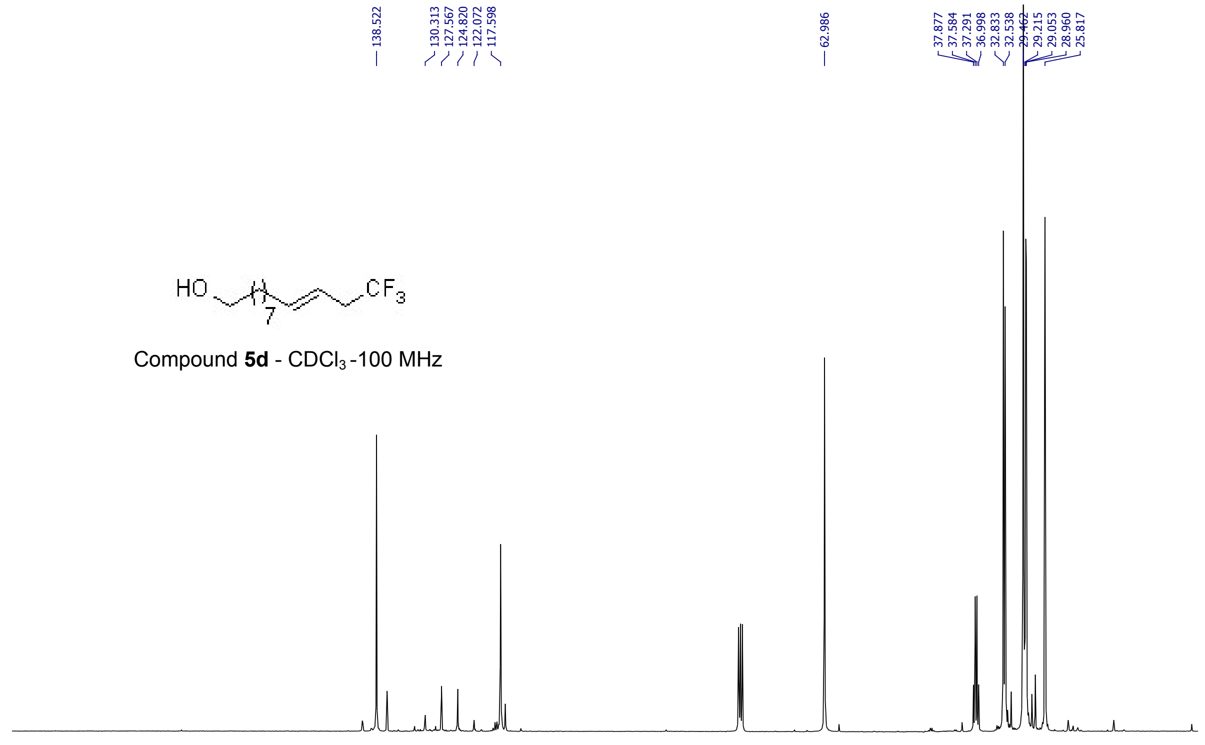

Compound **5c** - $CDCl_3$ –400 MHz


Compound **5c** - $CDCl_3$ -100 MHz

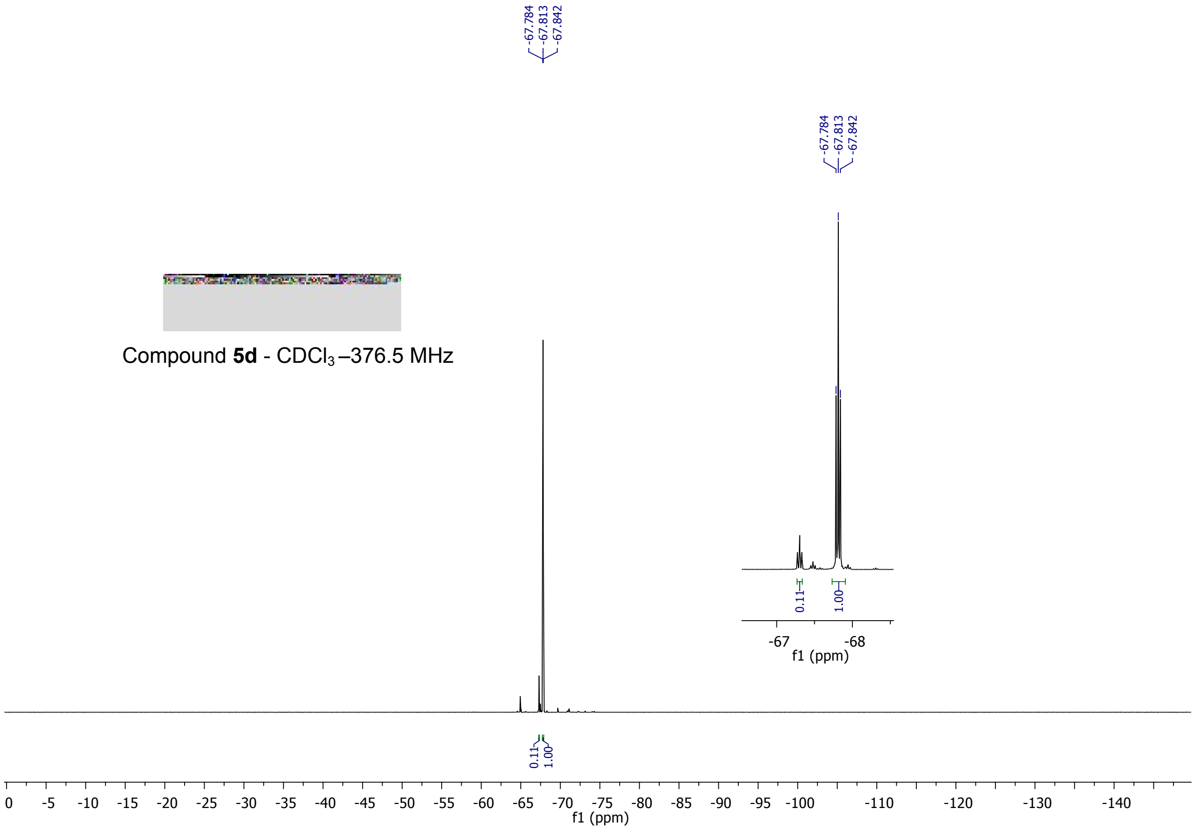

Compound **5c** - $CDCl_3$ –376.5 MHz



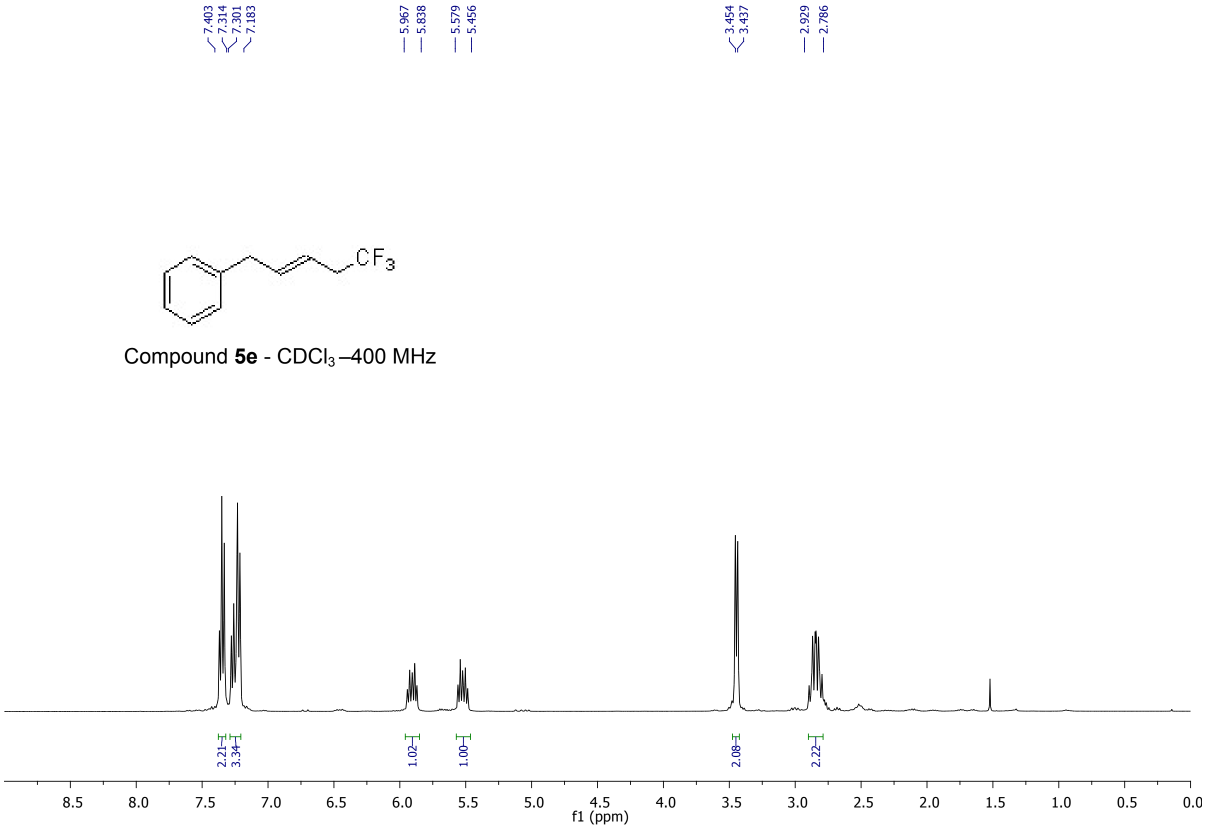
Compound **5d** - $CDCl_3$ –400 MHz



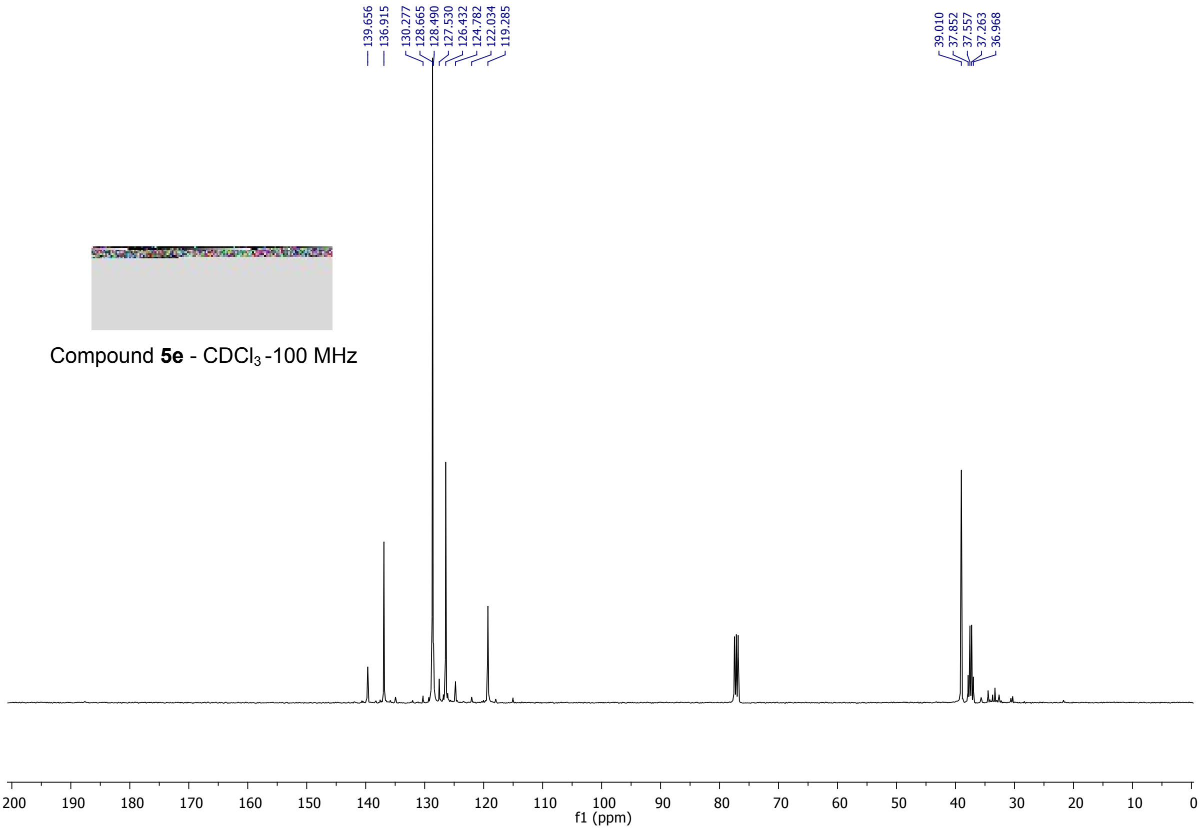
Compound **5d** - $CDCl_3$ -100 MHz



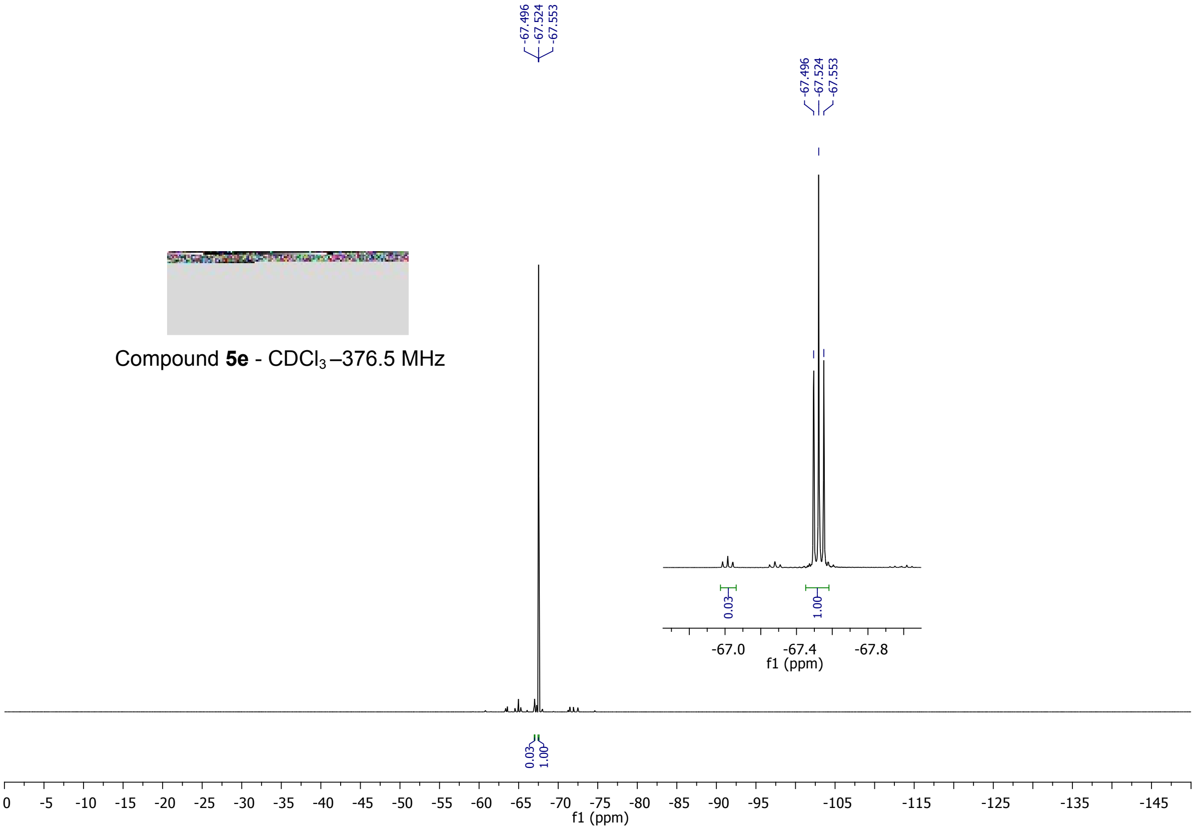
Compound **5d** - $CDCl_3$–376.5 MHz



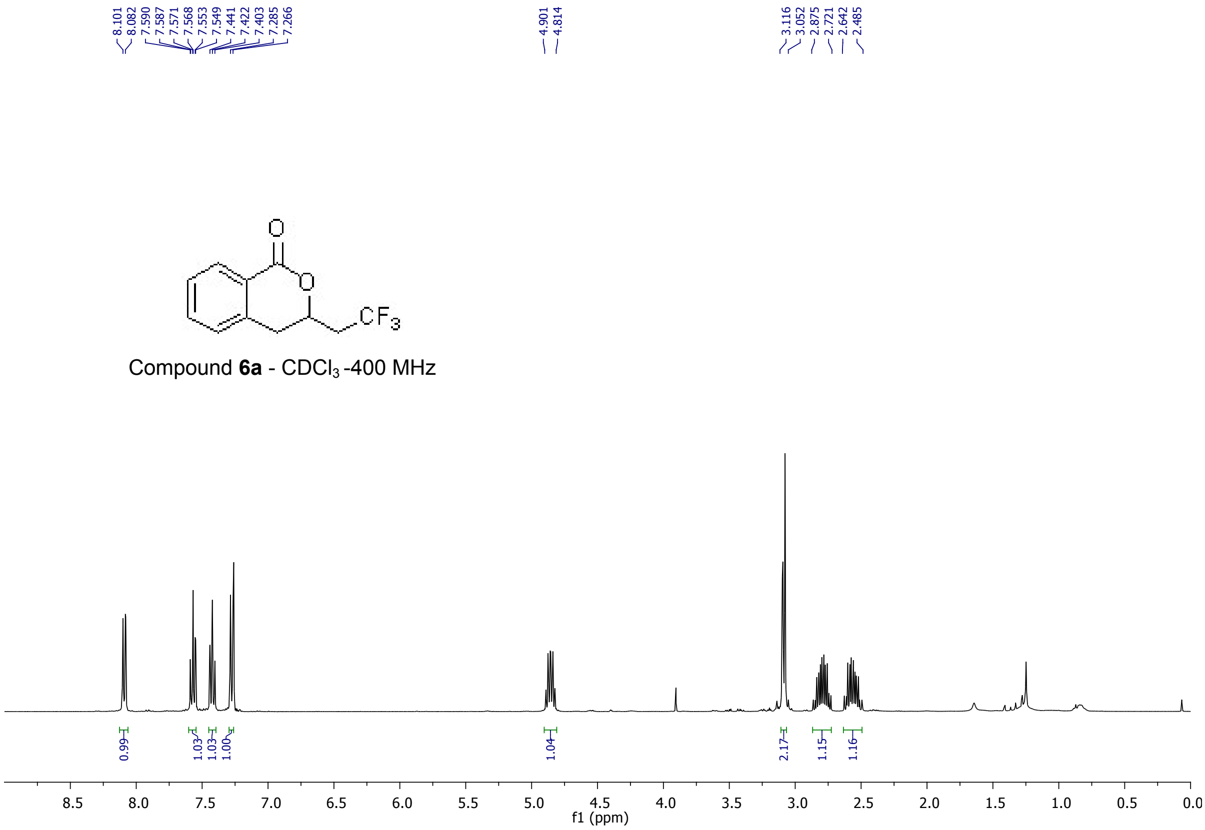
Compound **5e** - $CDCl_3$–400 MHz



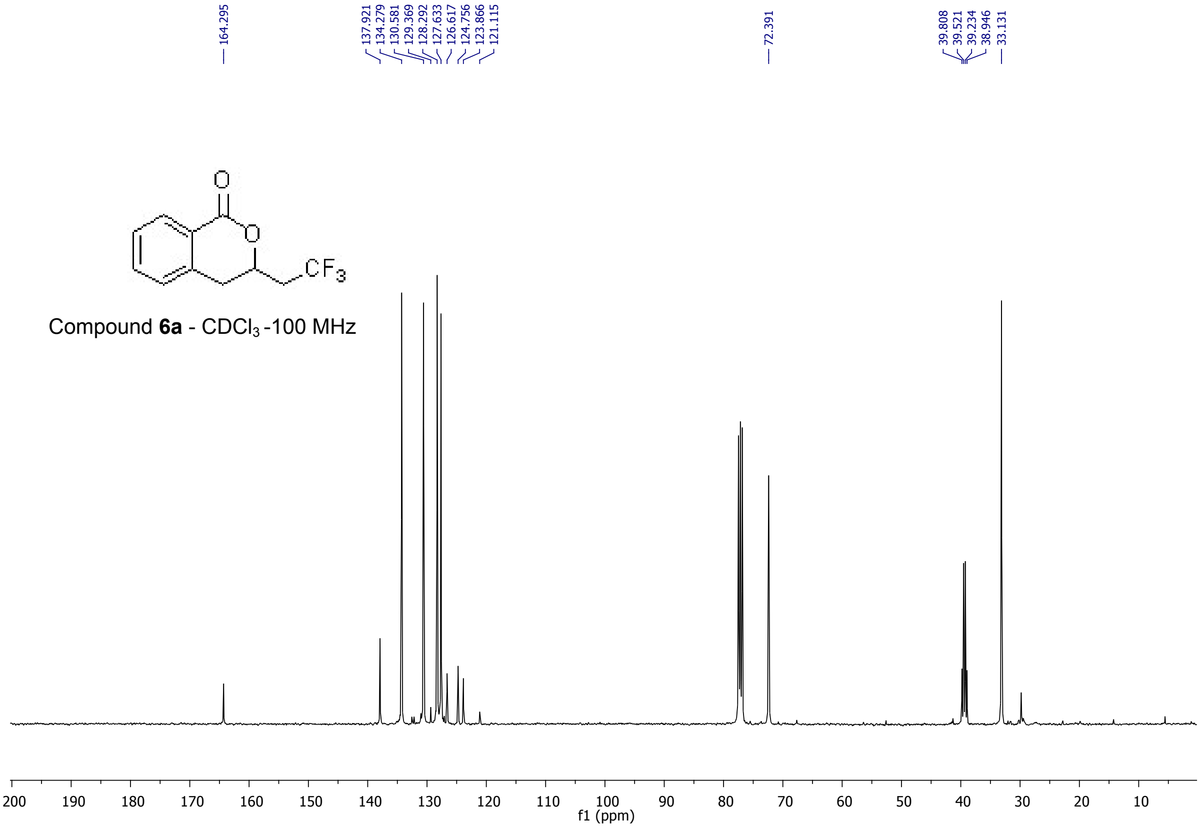
Compound **5e** - $CDCl_3$ -100 MHz



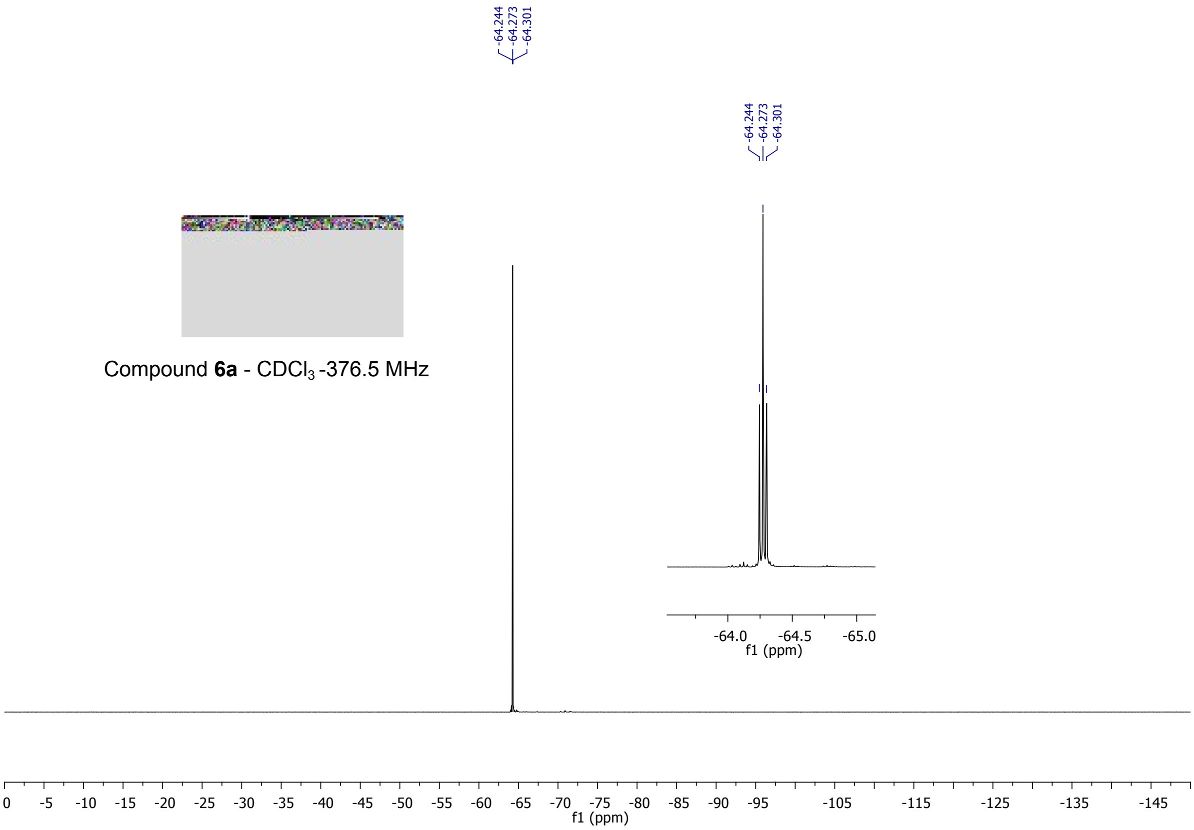
Compound **5e** - $CDCl_3$ –376.5 MHz



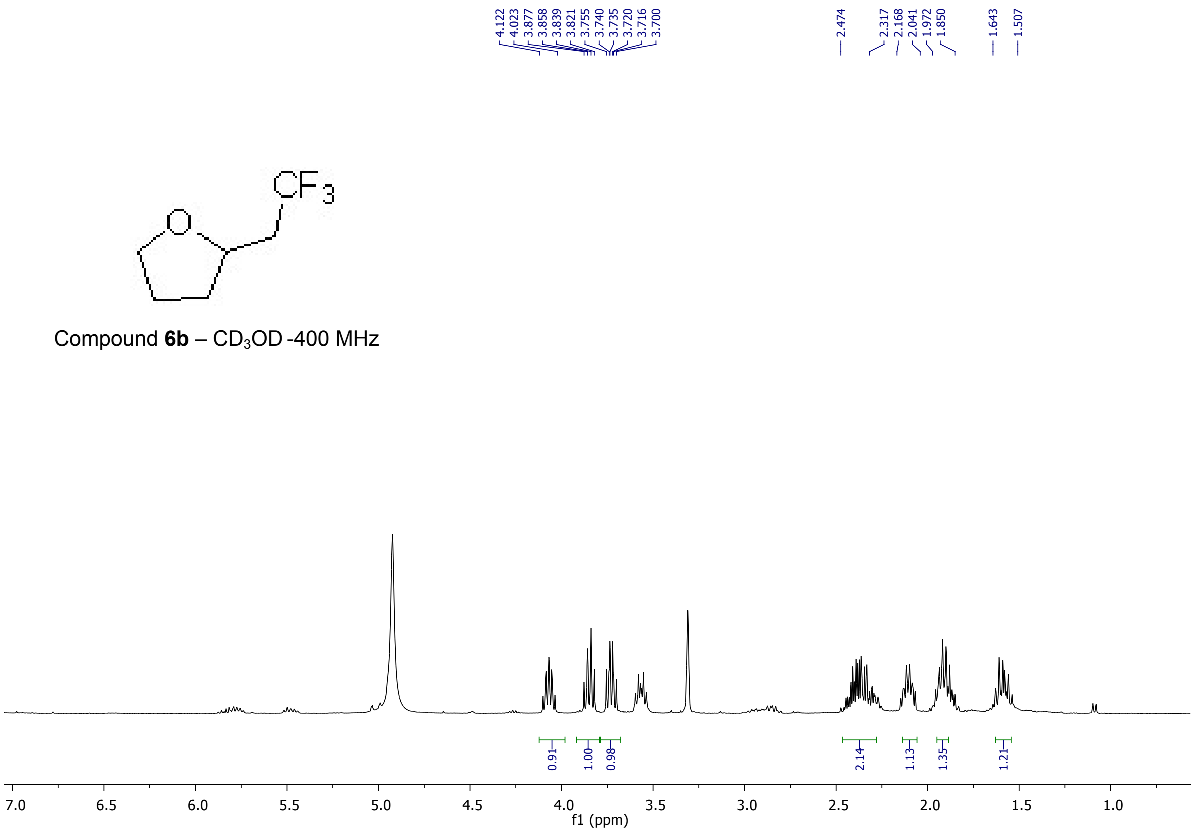
Compound **6a** - $CDCl_3$ -400 MHz



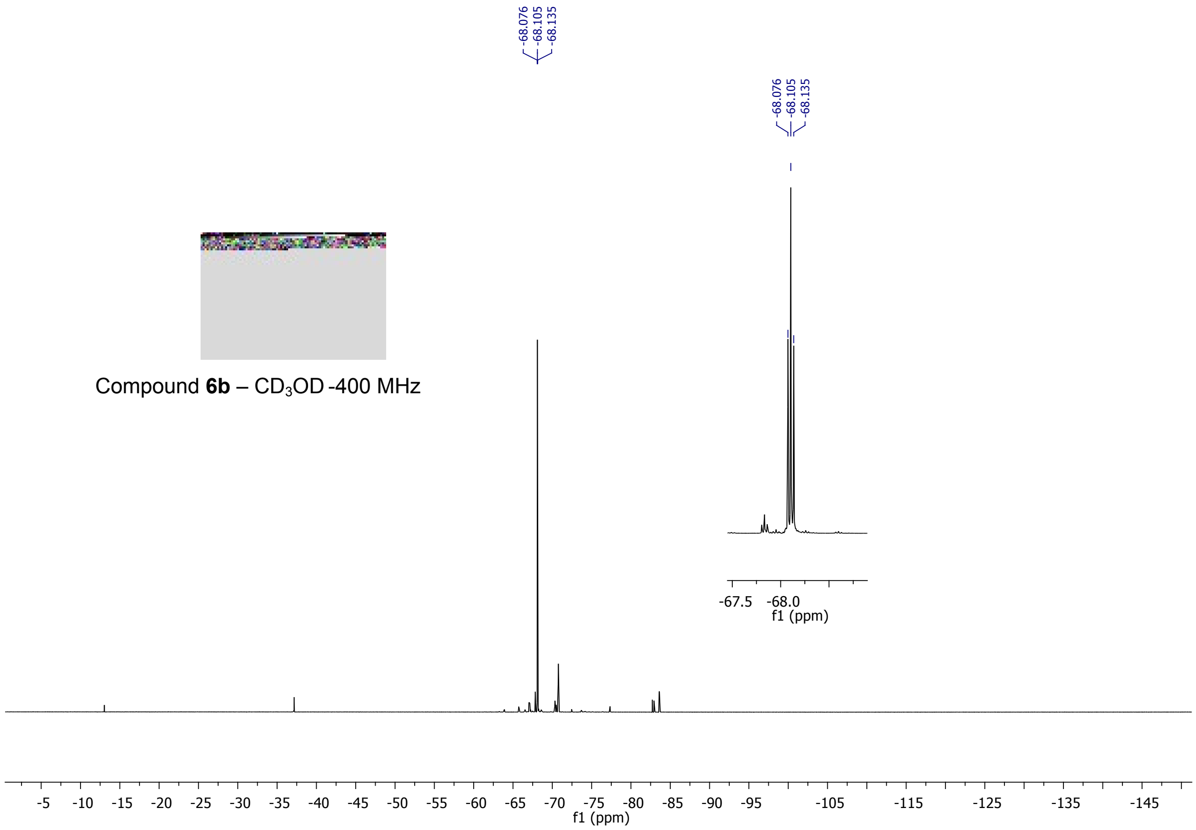
Compound **6a** - $CDCl_3$ -100 MHz



Compound **6a** - $CDCl_3$ -376.5 MHz



Compound **6b** – CD_3OD -400 MHz



Compound **6b** – CD_3OD -400 MHz