Supporting Information for the Paper

Unveiling the uncatalyzed reaction of alkynes with 1,2-dipoles for the room temperature synthesis of cyclobutenes

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General Methods: ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance AVIII-700 with cryoprobe, Bruker AMX-500, Bruker Avance-300, or Varian VRX-300S. NMR spectra were recorded in $CDCl_3$ solutions, except otherwise stated. Chemical shifts are given in ppm relative to TMS (^{1}H, 0.0 ppm), or $CDCl_3$ (^{13}C, 76.9 ppm). Low and high resolution mass spectra were taken on an AGILENT 6520 Accurate-Mass QTOF LC/MS spectrometer using the electronic impact (EI) or electrospray modes (ES) unless otherwise stated. IR spectra were recorded on a Bruker Tensor 27 spectrometer. X-Ray crystallographic data were collected on a Xcalibur, Atlas CCD, difractomer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) operating at 50 Kv and 40 mA with an exposure of 30.18 s in ω. All commercially available compounds were used without further purification.

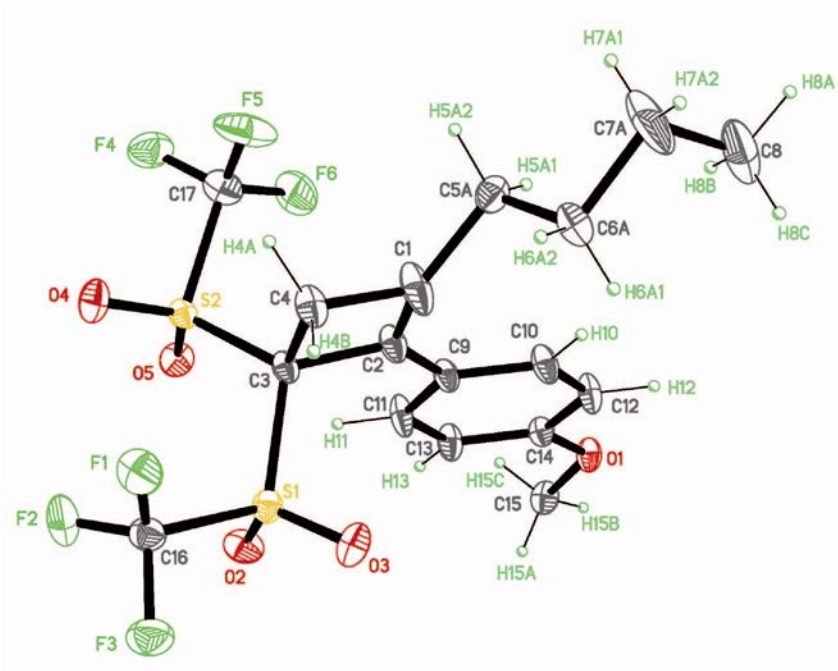


Figure S1 ORTEP drawing of cyclobutene 3c. Thermal ellipsoids shown at 50% probability.

Alkynes **2a**, **2g**, **2p**, **2s**, and **2t** were commercially available. The rest of alkynes **2** were readily obtained as described in the literature: **2b** (Byers, P. M.; Rashid, J. I.; Mohamed, R. K.; Alabugin, I. V. *Org. Lett.* **2012**, *14*, 6032); **2c** (Lu, B.; Li, C.; Zhang, L. *J. Am. Chem. Soc.* **2010**, *132*, 14070); **2d** (Zhang, X.; Larock, R. C. *Org. Lett.* **2003**, *5*, 2993); **2e** (Li, C.-W.; Pati, K.; Lin, G.-Y.; Sohel, S. Md. A.; Hung, H.-H.; Liu, R.-S. *Angew. Chem. Int. Ed.* **2010**, *49*, 9891); **2f** (Deponti, M.; Kozhushkov, S. I.; Yufit, D. S.; Ackermann, L. *Org. Biomol. Chem.* **2013**, *11*, 142); **2h** (Alcaide, B.; Almendros, P.; Quirós, M.T.; López, R.; Menéndez, M. I.; Sochacka-Ćwikła, A. *J. Am. Chem. Soc.* **2013**, *135*, 898); **2i** (Roesch, K. R.; Larock, R. C. *J. Org. Chem.* **2001**, *66*, 412); **2j** (Zhang, J.; Ugrinov, A.; Zhao, P. *Angew. Chem. Int. Ed.* **2013**, *52*, 6681); **2k** (Zhang, J.; Li, P.; Wang, L. *Org. Biomol. Chem.*, **2014**, *12*, 2969); **2l** (Caldarelli, S. A.; Fangour, S. E.; Wein, S.; Tran van Ba, C.; Périgaud, C.; Pellet, A.; Vial, H. J.; Peyrottes, S. *J. Med. Chem.* **2013**, *56*, 496); **2m** (Wang, S.; Yu, L.; Li, P.; Meng, L.; Wang, L. *Synthesis* **2011**, *10*, 1541); **2n** (Cheng, C.-C.; Chang, C.-S.; Hsu, Y.-L.; Lee, T.-Y.; Chang, L.-C.; Liu, S.-H.; Wu, Y.-T. *Eur. J. Org. Chem.* **2010**, 672); [D]-**2p** (Yabe, Y.; Sawama, Y.; Monguchi, Y.; Sajiki, H. *Chem. Eur. J.* **2013**, *19*, 484); **2q** (Ohmura, T.; Kijima, A.; Komori, Y.; Suginome, M. *Org. Lett.*, **2013**, *15*, 3510); **2r** (Seidler, A.; Svoboda , J.; Dekoj, V.; Chocholoušová, J. V.; Vacek, J.; Stará, I. G.; Stary, I. *Tetrahedron Letters* **2013**, *54*, 2795); **2u** (Machin, B. P.; Pagenkopf, B. L. *Synlett* **2011**, *19*, 2799).

Azolium salts **1a**, **1b**, **1d**, **1f**, and **1h** were synthesized according to a literature procedure: Yanai, H.; Takahashi, Y.; Fukaya, H.; Dobashi, Y.; Matsumoto, T. *Chem. Commun.* **2013**, *49*, 10091. Novel azolium salts **1c**, **1e**, and **1g** were also prepared using the above standard procedure.

General procedure for the synthesis of azolium salts 1. To a solution of bis[(trifluoromethyl)sulfonyl]methane (1.0 mmol) in 1,2-dichloroethane (6.0 mL), paraformaldehyde (90% purity, 2.0 mmol) and the appropriate azaheterocycle (2 mmol) were sequentially added at room temperature. After being stirred at 60 °C (typically 4–8 h), the reaction mixture was concentrated under reduced pressure. The resulting residue was washed with $CHCl_3$

(1.0 mL x 3) to give the corresponding azolium salt **1** as solid. Spectroscopic and analytical data for previously unreported azolium salts **1c**, **1e**, and **1g** follow.

Azolium salt 1c. From 290 mg (1.44 mmol) of 2-iodopyridine, compound **1c** (310 mg, 90%) was obtained as a colorless solid; mp 160–162 ºC; ^{1}H NMR (300 MHz, CD_3CN, 25 ^{o}C): δ = 5.67 (br s, 2H, CH_2), 8.06 (m, 2H, 2CH^{Ar}), 8.52 (m, 1H, CH^{Ar}), 9.40 (m, 1H, CH^{Ar}); ^{13}C NMR (75 MHz, CD_3CN, 25 ºC): δ = 146.4 (CH^{Ar}), 145.6 (CH^{Ar}), 142.6 (CH^{Ar}), 128.5 (CH^{Ar}), 121.6 (q, J_{CF} = 325.7 Hz, 2CF_3), 115.8 (C^{q}), 69.6 (CH_2), 68.9 (CTf_2); ^{19}F NMR (CD_3CN): δ = –80.7 (s, 6F, 2CF_3); IR (KBr): ν = 1346, 1100 (O=S=O), 1191 (C–F) cm^{-1}; HRMS (ES): calcd for C_5H_4NI [M – $C_4H_2F_6O_4S_2$]$^{+}$: 204.9388; found: 204.9390.

Azolium salt 1e. From 180 mg (1.44 mmol) of 2-methylthiopyridine, compound **1e** (350 mg, 99%) was obtained as a colorless solid; mp 190–192 ºC; ^{1}H NMR (300 MHz, CD_3CN, 25 ^{o}C): δ = 2.85 (s, 3H, SCH_3), 5.41 (br s, 2H, CH_2), 7.77 (t, 1H, J = 7.0 Hz, CH^{Ar}), 7.84 (d, 1H, J = 8.4 Hz, CH^{Ar}), 8.28 (m, 1H, CH^{Ar}), 9.14 (d, 1H, J = 6.4 Hz, CH^{Ar}); ^{13}C NMR (75 MHz, CD_3CN, 25 ^{o}C): δ = 161.5 (C^{q}), 144.2 (CH^{Ar}), 143.3 (CH^{Ar}), 125.5 (CH^{Ar}), 122.8 (CH^{Ar}), 121.6 (q, J_{CF} = 325.7 Hz, 2CF_3), 66.1 (CTf_2), 58.5 (CH_2), 16.5 (SCH_3); ^{19}F NMR (CD_3CN): δ = –80.6 (s, 6F, 2CF_3); IR (KBr): ν = 1359, 1094 (O=S=O), 1198 (C–F) cm^{-1}; HRMS (ES): calcd for C_6H_7NS [M – $C_4H_2F_6O_4S_2$]$^{+}$: 125.0299; found: 125.0304.

Azolium salt 1g. From 190 mg (1.44 mmol) of benzothiazole, compound **1g** (280 mg, 91%) was obtained as a colorless solid; mp 181–183 ºC; ^{1}H NMR (300 MHz, CD_3CN, 25 ^{o}C): δ = 5.72 (br s, 2H, CH_2), 7.90 (t, 1H, J = 7.7 Hz, CH^{Ar}), 8.00 (t, 1H, J = 7.9 Hz, CH^{Ar}), 8.37 (d, 1H, J = 8.3 Hz, CH^{Ar}), 8.52 (d, 1H, J = 8.5 Hz, CH^{Ar}), 10.27 (s, 1H, CH^{Ar}); ^{13}C NMR (75 MHz, CD_3CN, 25 ^{o}C): δ = 163.5 (CH^{Ar}), 141.2 (C^{q}), 132.5 (C^{q}), 130.9 (CH^{Ar}), 129.9 (CH^{Ar}), 125.5 (CH^{Ar}), 121.6 (q, J_{CF} = 325.6 Hz, 2CF_3), 118.3 (CH^{Ar}), 66.6 (CTf_2), 54.2 (CH_2); ^{19}F NMR (CD_3CN): δ = –81.0 (s, 6F,

$2CF_3$); IR (KBr): ν = 1350, 1103 (O=S=O), 1170 (C–F) cm^{-1}; HRMS (ES): calcd for C_7H_5NS [M – $C_4H_2F_6O_4S_2$]$^+$: 135.0143; found: 135.0141.

General procedure for the synthesis of cyclobutenes 3. 2-(2-Fluoropyridin-1-ium-1-yl)-1,1-bis[(trifluoromethyl)sulfonyl]ethan-1-ide **1d** (1.0 mmol) was added at room temperature to a solution of the appropriate alkyne **2** (1.0 mmol) in acetonitrile (8.0 mL). After disappearance of the starting material (TLC) the mixture was concentrated under reduced pressure. Chromatography of the residue gave analytically pure compounds. Spectroscopic and analytical data for cyclobutenes **3** follow.

Cyclobutene 3a. From 30 mg (0.17 mmol) of alkyne **1a**, and after flash chromatography of the residue using hexanes→hexanes/ethyl acetate (95:5) as eluent gave compound **3a** (50 mg, 64%) as a colorless oil; ^{1}H NMR (500 MHz, C_6D_6, 25 ^{o}C): δ = 3.28 (s, 2H, CH_2), 6.82 (m, 2H, $2CH^{Ar}$), 6.95 (m, 6H, $6CH^{Ar}$), 7.64 (m, 2H, $2CH^{Ar}$); ^{13}C NMR (125 MHz, C_6D_6, 25 ^{o}C): δ = 151.1 (*C*=C-CH_2), 131.2 (CH^{Ar}), 130.9 (C=*C*-CH_2), 130.8 (C^q), 130.1 (CH^{Ar}), 127.9 (C^q), 129.1 ($2CH^{Ar}$), 128.9 ($2CH^{Ar}$), 128.8 ($2CH^{Ar}$), 127.5 ($2CH^{Ar}$), 120.4 (q, J_{CF} = 331.4 Hz, $2CF_3$), 88.3 (CTf_2), 34.5 (CH_2); ^{19}F NMR (282 MHz, C_6D_6, 25 ^{o}C): δ = –70.40 (s, 6F, $2CF_3$); IR ($CHCl_3$): ν = 1380, 1104 (O=S=O), 1203 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{18}H_{12}O_4S_2F_6$ [M]$^+$: 470.0081; found: 470.0077.

Cyclobutene 3b. From 40 mg (0.17 mmol) of alkyne **1b**, and after chromatography of the residue using hexanes/ethyl acetate (97:3) as eluent gave compound **3b** (53 mg, 59%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 0.87 (t, 3H, J = 7.2 Hz, CH_3), 1.34 (m, 2H, CH_2), 1.50 (m, 2H, CH_2), 2.40 (t, 2H, J = 7.6 Hz, CH_2), 3.35 (s, 2H, CH_2-*allylic*), 7.26 (td, 1H, J = 7.7, 1.7 Hz, CH^{Ar}), 7.36 (td, 1H, J = 7.6, 1.3 Hz, CH^{Ar}), 7.58 (dd, 1H, J = 7.8, 1.7 Hz, CH^{Ar}), 7.65 (dd, 1H, J = 8.0, 1.2 Hz, CH^{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 162.6 [*C*=C-$(CH_2)_3CH_3$], 133.3 (CH^{Ar}), 131.0 (CH^{Ar}), 130.8 (C^q), 130.6 (CH^{Ar}), 130.3 (C^q), 125.2 (CH^{Ar}), 123.8 [C=*C*-

(CH_2)$_3$$CH_3$], 119.7 (q, J_{CF} = 331.3 Hz, 2CF_3), 88.1 (CTf_2), 35.0 (CH_2-*allylic*), 30.8 (CH_2), 27.4 (CH_2), 22.4 (CH_2), 13.6 (CH_3); ^{19}F NMR (282 MHz, $CDCl_3$, 25 ^{o}C): δ = –69.6 (s, 6F, 2CF_3); IR ($CHCl_3$): ν = 1381, 1106 (O=S=O), 1199 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{16}H_{15}O_4S_2F_6Br$ [*M*]$^+$: 527.9499; found: 527.9473.

Cyclobutene 3c. From 40 mg (0.21 mmol) of alkyne **1c**, and after chromatography of the residue using hexanes/diethyl ether (9:1) as eluent gave compound **3c** (97 mg, 96%) as a colorless solid; mp 59–61 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 0.95 (t, 3H, *J* = 7.2 Hz, CH_3), 1.42 (m, 2H, CH_2), 1.55 (m, 2H, CH_2), 2.55 (t, 2H, *J* = 7.6 Hz, CH_2), 3.34 (s, 2H, CH_2-*allylic*), 3.84 (s, 3H, OCH_3), 6.93 (m, 2H, 2CH^{Ar}), 7.50 (m, 2H, 2CH^{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 160.2 (C^q-OCH_3), 154.9 [*C*=C-(CH_2)$_3$$CH_3$], 131.7 [C=*C*-($CH_2$)$_3$$CH_3$], 129.4 (2$CH^{Ar}$), 122.3 ($C^q$), 119.8 (q, J_{CF} = 331.4 Hz, 2CF_3), 114.0 (2CH^{Ar}), 86.6 (CTf_2), 55.2 (OCH_3), 36.1 (CH_2-*allylic*), 29.3 (CH_2), 28.1 (CH_2), 22.5 (CH_2), 13.7 (CH_3); ^{19}F NMR (282 MHz, $CDCl_3$, 25 ^{o}C): δ = –70.68 (s, 6F, 2CF_3); IR ($CHCl_3$): ν = 1607 (C=C), 1375, 1102 (O=S=O), 1193 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{17}H_{18}O_5S_2F_6$ [*M*]$^+$: 480.0500; found: 480.0504. X-ray data of **3c**: crystallized from ethyl acetate/*n*-hexane at 20 ^{o}C; $C_{17}H_{18}F_6O_5S_2$ (M_r = 480.43); monoclinic; space group = P2(1)/c; a = 9.8939(5) Å, b = 13.2500(6) Å; c = 15.9721(8) Å; α = 90°; β = 102.881(5)°; γ = 90°; V = 2041.2(2) Å^3; Z = 4; cd = 1.563 mg m^{-3}; μ = 0.341 mm^{-1}; F(000) = 984. 3596 (R_{int} = 0.0332) independent reflections were collected on a Xcalibur, Atlas CCD difractomer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) operating at 50 Kv and 40 mA. The structure was solved by direct methods and was refined by full-matrix least-squares procedures on F^2 (SHELXL-97). All non-hydrogen atoms were refined anisotropically. Two C-atoms of the butyl chain (C5A-C5B and C6A-C6B) are disordered over two sites with 50% occupancies and were refined using geometrical restrained and variable common C–C distances. All hydrogen atoms were included in calculated positions and refined riding on the respective carbon atoms. Final R indices [I>2σ(I)] values were

R1 (reflns obsd) = 0.0581 (2382), *w*R2 (all data) = 0.1711. CCDC 1007421 contains 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.

Cyclobutene 3d. From 60 mg (0.28 mmol) of alkyne **1d**, and after chromatography of the residue using hexanes/ethyl acetate (97:3) as eluent gave compound **3d** (36 mg, 25%) as a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C): δ = 0.96 (t, 3H, *J* = 7.3 Hz, CH_3), 1.46 (m, 2H, CH_2), 1.60 (m, 2H, CH_2), 2.62 (t, 2H, *J* = 7.7 Hz, CH_2), 3.43 (s, 2H, CH_2-*allylic*), 7.75 (m, 2H, $2CH^{Ar}$), 8.29 (m, 2H, $2CH^{Ar}$); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ^{o}C): δ = 161.5 [*C*=C-$(CH_2)_3CH_3$], 147.9 (C^{q}-NO_2), 135.5 (C^{q}), 130.1 [C=*C*-$(CH_2)_3CH_3$], 128.8 ($2CH^{Ar}$), 124.0 ($2CH^{Ar}$), 119.7 (q, J_{CF} = 331.1 Hz, $2CF_3$), 86.2 (CTf_2), 36.8 (CH_2-*allylic*), 29.8 (CH_2), 28.0 (CH_2), 22.5 (CH_2), 13.7 (CH_3); ^{19}F NMR (282 MHz, $CDCl_3$, 25 ^{o}C): δ = –70.44 (s, 6F, $2CF_3$); IR ($CHCl_3$): ν = 1641 (C=C), 1381, 1107 (O=S=O), 1208 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{16}H_{15}O_6NS_2F_6$ $[M]^+$: 495.0245; found: 495.0224.

Cyclobutene 3e. From 30 mg (0.21 mmol) of alkyne **1e**, and after chromatography of the residue using hexanes/diethyl ether (95:5) as eluent gave compound **3e** (39 mg, 41%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 0.52 (m, 1H,C*H*H), 0.77 (m, 1H,CH*H*), 0.91 (m, 1H,C*H*H), 1.07 (m, 1H,CH*H*), 1.99 (m, 1H, CH), 2.54 (d, 1H, *J* = 14.6 Hz, C*H*H-*allylic*), 3.26 (d, 1H, *J* = 14.6 Hz CH*H*-*allylic*), 7.50 (m, 3H, $3CH^{Ar}$), 8.00 (m, 2H, $2CH^{Ar}$); ^{13}C NMR (175 MHz, $CDCl_3$, 25 ^{o}C): δ = 161.7 (*C*=C-*cyclopropane*), 133.2 (CH^{Ar}), 130.3 ($2CH^{Ar}$), 129.0 ($2CH^{Ar}$), 127.7 (C^{q}), 127.4 (C=*C*-*cyclopropane*), 120.1 (q, J_{CF} = 330.6 Hz, CF_3), 119.8 (q, J_{CF} = 336.6 Hz, CF_3), 72.8 (CTf_2), 31.9 (CH_2-*allylic*), 9.8 (CH), 5.8 (CH_2), 1.5 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$, 25 ^{o}C): δ = –71.80 and –77.79 (s, each 3F, CF_3); IR ($CHCl_3$): ν = 1598 (C=C), 1366, 1103 (O=S=O), 1206 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{15}H_{12}O_4S_2F_6$ $[M]^+$: 434.0081; found: 434.0078.

Cyclobutene 3f. From 30 mg (0.21 mmol) of alkyne **1f**, and after chromatography of the residue using hexanes/ethyl acetate (95:5) as eluent gave compound **3f** (40 mg, 51%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 0.50 (m, 1H,C*H*H), 0.76 (m, 1H,C*H*H), 0.87 (m, 1H,CH*H*), 1.03 (m, 1H,CH*H*), 1.98 (m, 1H,CH), 2.49 (d, 1H, *J* = 14.3 Hz, C*H*H-*allylic*), 3.21 (d, 1H, *J* = 14.3 Hz CH*H*-*allylic*), 3.89 (s, 3H, CH_3O), 6.98 (m, 2H, $2CH^{Ar}$), 8.09 (m, 2H, $2CH^{Ar}$); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 163.7 (C^{q}-OCH_3), 160.8 (*C*=C-*cyclopropane*), 133.2 ($2CH^{Ar}$), 122.1 (C=*C*-*cyclopropane*), 120.6 (C^{q}), 120.2 (q, J_{CF} = 330.8 Hz, CF_3), 120.0 (q, J_{CF} = 326.7 Hz, CF_3), 114.6 ($2CH^{Ar}$), 72.4 (CTf_2), 55.6 (CH_3O), 31.5 (CH_2-*allylic*), 10.0 (CH), 5.7 (CH_2), 1.4 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$, 25 ^{o}C): δ = –71.82 and –78.09 (s, each 3F, CF_3); IR ($CHCl_3$): ν = 1603 (C=C), 1367, 1107 (O=S=O), 1208 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{16}H_{14}O_5S_2F_6$ $[M]^+$: 464.0187; found: 464.0183.

Cyclobutene 3g. From 50 mg (0.38 mmol) of alkyne **1g**, and after chromatography of the residue using hexanes/diethyl ether (9:1) as eluent gave compound **3g** (116 mg, 72%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 1.86 (s, 1H, OH), 3.52 (s, 2H, CH_2-*cyclobutene*), 4.66 (s, 2H, CH_2), 7.46 (m, 5H, $5CH^{Ar}$); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 153.6 (*C*=C-CH_2), 132.5 (C=*C*-CH_2), 129.9 (CH^{Ar}), 129.1 (C^{q}), 128.8 ($2CH^{Ar}$), 127.9 ($2CH^{Ar}$), 119.8 (q, J_{CF} = 331.3 Hz, $2CF_3$), 85.9 (CTf_2), 58.5 (CH_2OH), 35.2 (CH_2-*cyclobutene*); ^{19}F NMR (282 MHz, $CDCl_3$, 25 ^{o}C): δ = –70.46 (s, 6F, $2CF_3$); IR ($CHCl_3$): ν = 3412 (OH), 1381, 1103 (O=S=O), 1204 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{13}H_{10}O_5S_2F_6$ $[M]^+$: 423.9874; found: 423.9872.

Cyclobutene 3h. From 40 mg (0.22 mmol) of alkyne **1h**, and after chromatography of the residue using hexanes/diethyl ether (9:1) as eluent gave compound **3h** (72 mg, 68%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 1.86 (s, 1H, OOH), 3.48 (s, 2H, CH_2-*cyclobutene*), 3.86 (s, 3H, OCH_3), 5.31 (s, 2H, CH_2), 6.98 (m, 2H, $2CH^{Ar}$), 7.53 (m, 2H, $2CH^{Ar}$); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 161.4 (C^{q}-OCH_3), 141.3 (*C*=C-CH_2), 137.8 (C=*C*-CH_2), 129.9 ($2CH^{Ar}$), 120.8

(C^q), 119.7 (q, J_{CF} = 331.2 Hz, $2CF_3$) 114.5 ($2CH^{Ar}$), 86.1 (CTf_2), 66.5 (CH_2OOH), 55.4 (OCH_3), 35.7 (CH_2-*cyclobutene*); ^{19}F NMR (282 MHz, $CDCl_3$, 25 ^oC): δ = –70.40 (s, 6F, $2CF_3$); IR ($CHCl_3$): ν = 1651 (C=C), 1383, 1104 (O=S=O), 1277 (C–O), 1209 (C–F), 840 (O–OH) cm^{-1}; HRMS (ES): calcd for $C_{14}H_{12}O_7S_2F_6$ $[M]^+$: 469.9929; found: 469.9917.

Cyclobutene 3i. From 50 mg (0.30 mmol) of alkyne **1i**, and after chromatography of the residue using hexanes/ethyl acetate (97:3) as eluent gave compound **3i** (102 mg, 74%) as a colorless solid; mp 52–54 ºC; ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC): δ = 0.97 (t, 3H, *J* = 7.2 Hz, CH_3), 1.42 (m, 2H, CH_2), 1.56 (m, 2H, CH_2), 2.60 (t, 2H, *J* = 7.5 Hz, CH_2), 3.39 (s, 2H, CH_2-*allylic*), 7.07 (dd, 1H, *J* = 5.0, 3.8 Hz, CH^{Ar}), 7.41 (d, 1H, *J* = 4.6 Hz, CH^{Ar}), 7.52 (d, 1H, *J* = 3.7 Hz, CH^{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^oC): δ = 153.5 [*C*=C-$(CH_2)_3CH_3$], 130.9 [C=*C*-$(CH_2)_3CH_3$], 129.1 (CH^{Ar}), 127.7 (CH^{Ar}), 127.6 (CH^{Ar}), 125.1 (C^q), 119.8 (q, J_{CF} = 331.4 Hz, $2CF_3$), 85.5 (CTf_2), 37.1 (CH_2-*allylic*), 29.6 (CH_2), 28.0 (CH_2), 22.5 (CH_2), 13.7 (CH_3); ^{19}F NMR (282 MHz, $CDCl_3$, 25 ^oC): δ = –71.08 (s, 6F, $2CF_3$); IR ($CHCl_3$): ν = 1383, 1107 (O=S=O), 1202 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{14}H_{14}O_4S_3F_6$ $[M]^+$: 455.9958; found: 455.9939.

Cyclobutene 3j. From 40 mg (0.22 mmol) of alkyne **1j**, and after flash chromatography of the residue using hexanes/ethyl acetate (95:5) as eluent gave compound **3j** (59 mg, 56%) as a colorless solid; mp 100–102 ºC; ^1H NMR (300 MHz, C_6D_6, 25 ^oC): δ = 3.24 (s, 2H, CH_2), 6.51 (dd, 1H, *J* = 5.1, 3.7 Hz, CH^{Ar}), 6.67 (dd, 1H, *J* = 5.1, 1.1 Hz, CH^{Ar}), 6.96 (m, 3H, $3CH^{Ar}$), 7.16 (m, 2H, $2CH^{Ar}$), 7.63 (d, 1H, *J* = 2.9 Hz, CH^{Ar}); ^{13}C NMR (75 MHz, C_6D_6, 25 ^oC): δ = 149.8 (*C*=C-Thf), 131.4 (CH^{Ar}), 131.3 (CH^{Ar}), 130.9 (C=*C*-Ph), 130.8 (C^q), 128.9 ($2CH^{Ar}$), 128.4 (CH^{Ar}), 127.9 (CH^{Ar}), 127.6 ($2CH^{Ar}$), 123.0 (C^q), 120.4 (q, J_{CF} = 331.6 Hz, $2CF_3$), 87.3 (CTf_2), 35.3 (CH_2); ^{19}F NMR (282 MHz, C_6D_6, 25 ^oC): δ = –70.89 (s, 6F, $2CF_3$); IR ($CHCl_3$): ν = 1381, 1105 (O=S=O), 1202 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{16}H_{10}O_4S_3F_6$ $[M]^+$: 475.96454; found: 475.96517.

Cyclobutene 3k. From 20 mg (0.21 mmol) of alkyne **1k**, and after chromatography of the residue using hexanes/ethyl acetate (97:3) as eluent gave compound **3k** (36 mg, 75%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 1.88 (m, 1H, C*H*H), 2.02 (m, 2H, CH_2), 2.31 (m, 1H, CH*H*), 3.34 (d, 1H, *J* = 15.7 Hz, C*H*H-*allylic*), 3.48 (d, 1H, *J* = 15.7 Hz, CH*H*-*allylic*), 3.84 (s, 3H, OCH_3), 3.91 (m, 2H, CH_2), 4.90 (t, 2H, *J* = 7.2 Hz, CH), 6.93 (m, 2H, $2CH^{Ar}$), 7.50 (m, 2H, $2CH^{Ar}$); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 160.5 (C^{q}-OCH_3), 153.4 (*C*=C-THF), 131.3 (C=*C*-THF), 129.7 ($2CH^{Ar}$), 121.8 (C^{q}), 119.8 (q, J_{CF} = 331.4 Hz, $2CF_3$), 114.1 ($2CH^{Ar}$), 85.8 (CTf_2), 74.1 (CH), 69.1 (CH_2), 55.3 (OCH_3), 34.4 (CH_2-*allylic*), 30.6 (CH_2), 26.2 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$, 25 ^{o}C): δ = –70.59 and –70.75 (s, each 3F, CF_3); IR ($CHCl_3$): ν = 1608 (C=C), 1381, 1105 (O=S=O), 1024 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{17}H_{16}O_6S_2F_6$ $[M]^{+}$: 494.0292; found: 494.0297.

Cyclobutene 3l. From 30 mg (0.1 mmol) of alkyne **1l**, and after chromatography of the residue using hexanes/ethyl acetate (95:5) as eluent gave compound **3l** (32 mg, 55%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 3.55 (s, 2H, CH_2-*cyclobutene*), 4.17 (s, 2H, C≡C-*C*H_2), 4.22 (s, 2H, CH_2Br), 7.54 (m, 4H, $4CH^{Ar}$); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 148.9 (*C*=C-CH_2), 134.5 (*C*=C-CH_2), 132.4 ($2CH^{Ar}$), 128.7 (C^{q}), 128.0 ($2CH^{Ar}$), 124.5 (C^{q}), 119.7 (q, J_{CF} = 331.2 Hz, $2CF_3$), 87.0 (C≡*C*-CH_2), 85.8 (CTf_2), 85.5 (*C*≡C-CH_2), 36.3 (CH_2-*cyclobutene*), 23.0 (CH_2Br), 14.6 (C≡C-*C*H_2); ^{19}F NMR (282 MHz, $CDCl_3$, 25 ^{o}C): δ = –70.34 (s, 6F, $2CF_3$); IR ($CHCl_3$): ν = 1603 (C=C), 1366, 1108 (O=S=O), 1207 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{16}H_{10}O_4S_2F_6Br_2$ $[M]^{+}$: 601.8291; found: 601.8307.

Cyclobutene 3m. From 40 mg (0.19 mmol) of alkyne **1m**, and after chromatography of the residue using hexanes/ethyl acetate (95:5) as eluent gave compound **3m** (50 mg, 53%) as a colorless oil; ^{1}H NMR (300 MHz, C_6D_6, 25 ^{o}C): δ = 1.39 (m, 2H, CH_2), 1.88 (t, 3H, *J* = 7.4 Hz, CH_3), 2.68 (s, 2H, CH_2-*allylic*), 2.98 (t, 2H, *J* = 6.4 Hz, CH_2), 6.89 (m, 3H, $3CH^{Ar}$), 7.31 (m, 2H, $2CH^{Ar}$); ^{13}C NMR (75 MHz, C_6D_6, 25 ^{o}C): δ = 165.3 (*C*=C-C≡C), 132.0 ($2CH^{Ar}$), 129.9 (CH^{Ar}), 128.7 ($2CH^{Ar}$), 121.1

(C^q), 120.3 (q, J_{CF} = 330.8 Hz, $2CF_3$), 115.2 (C=*C*-C≡C), 98.3 [C≡*C*-$(CH_2)_2CH_2Cl$], 86.4 (CTf_2), 77.9 [*C*≡C-$(CH_2)_2CH_2Cl$], 43.4 (CH_2), 36.3 (CH_2-*allylic*), 28.3 (CH_2), 28.0 (CH_2); ^{19}F NMR (282 MHz, C_6D_6, 25 ^oC): δ = –70.39 (s, 6F, $2CF_3$); IR ($CHCl_3$): ν = 2213 (C≡C), 1384, 1104 (O=S=O), 1201 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{17}H_{13}O_4S_2F_6Cl$ $[M]^+$: 493.9848; found: 493.98697.

Cyclobutene 3n. From 50 mg (0.16 mmol) of alkyne **1n**, and after chromatography of the residue using hexanes/ethyl acetate (9:1) as eluent gave compound **3n** (44 mg, 47%) as a colorless oil; ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC): δ = 1.86 (m, 2H, CH_2), 2.53 (t, 2H, *J* = 6.8 Hz, CH_2), 2.75 (t, 2H, *J* = 7.7 Hz, CH_2), 3.37 (s, 2H, CH_2-*allylic*), 3.80 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 6.83 (m, 2H, $2CH^{Ar}$), 6.88 (m, 2H, $2CH^{Ar}$), 7.31 (m, 2H, $2CH^{Ar}$), 7.55 (m, 2H, $2CH^{Ar}$); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ^oC): δ = 160.3 (C^q-OCH_3), 159.3 (C^q-OCH_3), 153.7 [*C*=C-$(CH_2)_3$-], 132.9 ($2C^{Ar}H$), 132.7 [C=*C*-$(CH_2)_3$-], 129.5 ($2C^{Ar}H$), 122.2 (C^q), 119.8 (q, J_{CF} = 331.3 Hz, $2CF_3$), 115.5 (C^q), 114.1 ($2C^{Ar}H$), 113.9 ($2C^{Ar}H$), 86.7 (CTf_2), 86.6 (*C*≡C-PMP), 81.9 (C≡*C*-PMP), 55.3 (OCH_3), 55.2 (OCH_3), 36.1 (CH_2-a*llylic*), 28.5 (CH_2), 25.2 (CH_2), 19.0 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$, 25 ^oC): δ = –70.63 (s, 6F, $2CF_3$); IR ($CHCl_3$): ν = 1605 (C=C), 1379, 1104 (O=S=O), 1203 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{25}H_{22}O_6S_2F_6$ $[M]^+$: 596.0762; found: 596.0767.

Cyclobutene 3o. From 50 mg (0.16 mmol) of alkyne **1n**, and after chromatography of the residue using hexanes/ethyl acetate (9:1 → 8:2) as eluent gave compound **3o** (122 mg, 86%) as a colorless oil; ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC): δ = 1.81 (q, 2H, *J* = 7.3 Hz, CH_2), 2.62 (t, 4H, *J* = 7.3 Hz, $2CH_2$), 3.27 (s, 4H, $2CH_2$-*allylic*), 3.82 (s, 6H, $2OCH_3$), 6.88 (m, 4H, $4CH^{Ar}$), 7.44 (m, 4H, $4CH^{Ar}$); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^oC): δ = 160.5 ($2C^q$-OCH_3), 152.5 [2*C*=C-$(CH_2)_3$-], 133.5 [2C=*C*-$(CH_2)_3$-], 129.4 ($4C^{Ar}H$), 121.8 ($2C^q$), 119.8 (q, J_{CF} = 331.1 Hz, $4CF_3$), 114.1 ($4C^{Ar}H$), 86.5 ($2CTf_2$), 55.2 ($2OCH_3$), 35.8 ($2CH_2$-*allylic*), 28.6 ($2CH_2$), 22.4 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$, 25 ^oC): δ = –70.55 (s, 12F, $4F_3$); IR ($CHCl_3$): ν = 1607 (C=C), 1378, 1103 (O=S=O), 1200 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{29}H_{24}O_{10}S_4F_{12}$ $[M]^+$: 888.0061; found: 888.0047.

Cyclobutene 3p. From 30 mg (0.22 mmol) of alkyne **2p**, and after chromatography of the residue using hexanes/diethyl ether (95:5) as eluent gave compound **3p** (53 mg, 57%) as a yellow solid; mp 58–60 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 3.46 (s, 2H, CH_2), 3.84 (s, 3H, CH_3O), 6.83 (s, 1H, CH), 6.93 (m, 2H, $2CH^{Ar}$), 7.63 (m, 2H, $2CH^{Ar}$); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 161.1 (C^{q}-OCH_3), 139.3 (*C*=CH), 134.6 (C=*C*H), 128.0 ($2C^{Ar}H$), 121.6 (C^{q}), 119.8 (q, J_{CF} = 331.3 Hz, $2CF_3$), 114.2 ($2C^{Ar}H$), 87.3 (CTf_2), 55.3 (CH_3O), 35.6 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$, 25 ^{o}C): δ = –70.85 (s, 6F, $2CF_3$); IR ($CHCl_3$): ν = 1607 (C=C), 1383, 1105 (O=S=O), 1205 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{13}H_{10}O_5S_2F_6$ $[M]^{+}$: 423.9874; found: 423.9875.

Cyclobutene [D]-**3p.** From 40 mg (0.30 mmol) of alkyne [D]-**2p**, and after chromatography of the residue using hexanes/ethyl acetate (97:3) as eluent gave compound [D]-**3p** (82 mg, 65%) as a yellow solid; mp 50–52 ºC; ^{1}H NMR (300 MHz, C_6D_6, 25 ^{o}C): δ = 2.87 (s, 2H, CH_2), 3.15 (s, 3H, CH_3O), 5.70 [s, 1H, CH (92% D)], 6.54 (m, 2H, $2CH^{Ar}$), 7.51 (m, 2H, $2CH^{Ar}$); ^{13}C NMR (75 MHz, C_6D_6, 25 ^{o}C): δ = 161.5 (C^{q}-OCH_3), 139.1 (*C*=CD), 134.9 (t, J_{CD} = 27.2 Hz, C=*C*D), 128.3 ($2CH^{Ar}$ – *overlapped with the solvent signal*), 122.6 (C^{q}), 120.4 (q, J_{CF} = 331.4 Hz, $2CF_3$), 114.4 ($2CH^{Ar}$), 87.8 (CTf_2), 54.8 (CH_3O), 35.4 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$, 25 ^{o}C): δ = –71.21 (s, 6F, $2CF_3$); IR ($CHCl_3$): ν = 1606 (C=C), 1385, 1104 (O=S=O), 1210 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{13}H_9DO_5S_2F_6$ $[M]^{+}$: 424.9937; found: 424.9955.

Cyclobutene 3q. From 50 mg (0.46 mmol) of alkyne **2q**, and after chromatography of the residue using hexanes/ethyl acetate (97:3) as eluent gave compound **3q** (125 mg, 68%) as a colorless solid; mp 52–54 ºC; ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C): δ = 3.50 (s, 2H, CH_2), 6.72 (s, 1H, CH), 7.07 (dd, 1H, *J* = 5.0, 3.8 Hz, CH^{Ar}), 7.42 (d, 1H, *J* = 4.9 Hz, CH^{Ar}), 7.55 (d, 1H, *J* = 3.6 Hz, CH^{Ar}); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ^{o}C): δ = 135.2 (C=*C*H), 133.3 (*C*=CH), 131.4 (C^{q}), 129.8 (CH^{Ar}), 128.4 (CH^{Ar}), 128.2 (CH^{Ar}), 119.8 (q, J_{CF} = 331.2 Hz, $2CF_3$), 87.0 (CTf_2), 36.3 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$, 25 ^{o}C): δ = –70.77 (s, 6F, $2CF_3$); IR ($CHCl_3$): ν = 1621 (C=C), 1384, 1105

(O=S=O), 1203 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{10}H_6O_4S_3F_6$ $[M]^+$: 399.9332; found: 399.9344.

Cyclobutene 3r. From 50 mg (0.38 mmol) of alkyne **2r**, and after chromatography of the residue using hexanes/ethyl acetate (9:1 → 8:2) as eluent gave compound **3r** (158 mg, 58%) as a colorless oil; ^{1}H NMR (300 MHz, C_6D_6, 25 ^{o}C): δ = 2.69 (s, 4H, $2CH_2$), 5.44 (t, 2H, *J* = 1.3 Hz, 2CH), 7.25 (s, 2H, $2CH^{Ar}$); ^{13}C NMR (75 MHz, C_6D_6, 25 ^{o}C): δ = 139.3 (2C=*C*H), 133.7 (2*C*=CH), 131.9 ($2C^q$), 130.4 ($2CH^{Ar}$), 120.2 (q, J_{CF} = 331.2 Hz, $4CF_3$), 87.3 ($2CTf_2$), 36.2 ($2CH_2$); ^{19}F NMR (282 MHz, $CDCl_3$, 25 ^{o}C): δ = –70.99 (s, 12F, $4CF_3$); IR ($CHCl_3$): ν = 1384, 1103 (O=S=O), 1203 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{16}H_8O_8S_5F_{12}$ $[M]^+$: 715.86311; found: 715.86223.

Preparation of cyclobutene 3s and pyridine 4s. From 40 mg (0.39 mmol) of alkyne **2s**, and after chromatography of the residue using hexanes/diethyl ether (9:1) as eluent, 15 mg (32%) of the more polar compound **3s** and 35 mg (30%) of the less polar compound **4s** were obtained.

Cyclobutene 3s. Colorless solid; mp 39–40 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 3.50 (s, 2H, CH_2), 7.01 (s, 1H, CH), 7.43 (m, 3H, $3CH^{Ar}$), 7.68 (m, 3H, $3CH^{Ar}$); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 140.0 (*C*=CH), 137.7 (C=*C*H), 130.4 (CH^{Ar}), 128.9 (C^q), 128.8 ($2CH^{Ar}$), 126.3 ($2CH^{Ar}$), 119.8 (q, J_{CF} = 331.3 Hz, $2CF_3$), 87.4 (CTf_2), 35.7 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$, 25 ^{o}C): δ = –70.72 (s, 6F, $2CF_3$); IR ($CHCl_3$): ν = 1379, 1100 (O=S=O), 1194 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{12}H_8O_4S_2F_6$ $[M]^+$: 393.9768; found: 393.9778.

Pyridine 4s. Colorless solid; mp 68–70 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 3.02 (s, 3H, CH_3), 7.55 (m, 3H, $3CH^{Ar}$), 7.85 (d, 1H, *J* = 8.5 Hz, CH^{Ar}), 8.14 (m, 2H, $2CH^{Ar}$), 8.38 (d, 1H, *J* = 8.5 Hz, CH^{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 162.9 (C^q-CH_3), 161.2 (C^q-N), 142.0 (CH^{Ar}-*Piridina*), 136.7 (C^q-*Ph*), 131.2 (CH^{Ar}-*Ph*), 129.1 ($2CH^{Ar}$), 127.8 ($2CH^{Ar}$), 124.6 (C^q-Tf), 120.1 (q, J_{CF} = 326.3 Hz, CF_3), 118.1 (CH^{Ar}-*pyridine*), 24.3 (CH_3); ^{19}F NMR (282 MHz, $CDCl_3$,

25 ^{o}C): δ = –78.26 (s, 3F, CF_3); IR ($CHCl_3$): ν = 1377, 1126 (O=S=O), 1215 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{13}H_{10}O_2NSF_3$ $[M]^+$: 301.0384; found: 301.0394.

Preparation of cyclobutene 3t and pyridine 4t. From 40 mg (0.31 mmol) of alkyne **2t**, and after chromatography of the residue using hexanes/diethyl ether (99:1) as eluent, 45 mg (35%) of the more polar compound **3t** and 31 mg (31%) of the less polar compound **4t** were obtained.

Cyclobutene 3t. Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C): δ = 3.14 (s, 1H, C≡CH), 3.50 (s, 2H, CH_2), 7.05 (s, 1H, CH), 7.40 (t, 1H, *J* = 7.8 Hz, CH^{Ar}), 7.54 (d, 1H, *J* = 7.7 Hz, CH^{Ar}), 7.69 (t, 1H, *J* = 7.9 Hz, CH^{Ar}), 7.76 (s, 1H, CH^{Ar}); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ^{o}C): δ = 139.5 (*C*=CH), 139.4 (C=*C*H), 134.3 (CH^{Ar}), 130.1 (CH^{Ar}), 129.5 (C^{q}), 129.4 (CH^{Ar}), 127.2 (CH^{Ar}), 123.4 (C^{q}), 120.2 (q, J_{CF} = 331.1 Hz, $2CF_3$), 87.7 (CTf_2), 82.8 (*C*≡CH), 78.9 (C≡*C*H), 36.2 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$, 25 ^{o}C): δ = –70.65 (s, 6F, $2CF_3$); IR ($CHCl_3$): ν = 3301 (≡CH), 1382, 1101 (O=S=O), 1210 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{14}H_8O_4S_2F_6$ $[M]^+$: 417.9768; found: 417.9773.

Pyridine 4t. Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C): δ = 3.02 (s, 3H, CH_3), 3.17 (s, 1H, C≡CH), 7.51 (t, 1H, *J* = 7.8 Hz, CH^{Ar}), 7.66 (d, 1H, *J* = 7.7 Hz, CH^{Ar}), 7.84 (d, 1H, *J* = 8.4 Hz, CH^{Ar}), 8.12 (d, 1H, *J* = 7.9 Hz, CH^{Ar}), 8.26 (s, H, CH^{Ar}), 8.39 (d, 1H, *J* = 8.4 Hz, CH^{Ar}); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ^{o}C): δ = 161.8 (C^{q}-CH_3), 161.3 (C^{q}-N), 142.2 (CH^{Ar}-*pyridine*), 137.0 (C^{q}), 134.5 (CH^{Ar}), 131.5 (CH^{Ar}), 129.2 (CH^{Ar}), 128.1 (CH^{Ar}), 125.1 (C^{q}-Tf), 123.2 (C^{q}-C≡CH), 120.0 (q, J_{CF} = 326.3 Hz, CF_3), 118.2 (CH^{Ar}-*pyridine*), 82.9 (*C*≡CH), 78.2 (C≡*C*H), 24.3 (CH_3); ^{19}F NMR (282 MHz, $CDCl_3$, 25 ^{o}C): δ = –78.18 (s, 3F, CF_3); IR ($CHCl_3$): ν = 1370, 1124 (O=S=O), 1208 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{15}H_{10}O_2NSF_3$ $[M]^+$: 325.0384; found: 325.0382.

Pyridine 4u. From 30 mg (0.20 mmol) of alkyne **2u**, and after chromatography of the residue using hexanes/ethyl acetate (9:1) as eluent gave compound **3u** (20 mg, 28%) as a colorless oil; ^{1}H NMR

(500 MHz, $CDCl_3$, 25 ^oC): δ = 3.05 (s, 3H, CH_3), 7.94 (d, 1H, *J* = 8.4 Hz, CH^{Ar}), 8.31 (m, 2H, $2CH^{Ar}$), 8.40 (m, 2H, $2CH^{Ar}$), 8.47 (d, 1H, *J* = 8.4 Hz, CH^{Ar}); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ^oC): δ = 161.6 (C^q-CH_3), 160.2 (C^q-N), 149.4 (C^q-NO_2), 142.6 (CH^{Ar}-*pyridine*), 142.3(C^q-*Ph*), 128.8 ($2CH^{Ar}$), 126.3 (C^q-Tf), 124.2 ($2CH^{Ar}$), 119.9 (q, J_{CF} = 326.4 Hz, CF_3), 118.9 (CH^{Ar}-*pyridine*), 24.3 (CH_3); ^{19}F NMR (282 MHz, $CDCl_3$, 25 ^oC): δ = –79.99 (s, 3F, CF_3); IR ($CHCl_3$): ν = 1562, 1369 (NO_2), 1347, 1120 (O=S=O), 1197 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{13}H_9O_4N_2SF_3$ $[M]^+$: 346.0235; found: 346.0251.

Computational Details

All the calculations reported in this paper were obtained with the GAUSSIAN 09 suite of programs[1] at the dispersion corrected M06-2X[2]/6-31+(d) level. Reactants and products were characterized by frequency calculations,[3] and have positive definite Hessian matrices. Transition structures (TS's) show only one negative eigenvalue in their diagonalized force constant matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration using the Intrinsic Reaction Coordinate (IRC) method.[4] Solvents effects were taken into account using the Polarizable Continuum Model (PCM)[5] in the geometry

[1] Gaussian 09, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

[2] Y. Zhao, D. G. Truhlar, *Acc. Chem. Res*. **2008**, *41*, 157.

[3] McIver, J. W.; Komornicki, A. K. *J. Am. Chem. Soc*. **1972**, *94*, 2625.

[4] González, C.; Schlegel, H. B. *J. Phys. Chem*. **1990**, *94*, 5523.

[5] (a) Miertuš, S.; Scrocco, E.; Tomasi, J. *Chem. Phys*. **1981**, *55*, 117. (b) Pascual-Ahuir, J. L.; Silla, E.; Tuñón, I. *J. Comp. Chem*. **1994**, *15*, 1127. (c) Barone, V.; Cossi, M. *J. Phys. Chem. A*, 1998, *102*, 1995.

optimizations and frequency calculations (solvent = acetonitrile). This level is denoted PCM(acetonitrile)-M06-2X/6-31+G(d).

Cartesian coordinates (in Å) and free energies (in a. u.) of all the stationary points discussed in the text. All calculations have been performed at the PCM-M06-2X/6-31+G(d) level.

1d: E= -2196.692112

C	0.315494000	-1.244033000	0.934852000
H	0.484990000	-1.065367000	1.993493000
H	-0.169299000	-2.213414000	0.809875000
N	1.682762000	-1.383164000	0.299607000
C	1.759087000	-1.700153000	-1.017200000
C	2.803321000	-1.141587000	0.991533000
C	2.974669000	-1.775227000	-1.655334000
C	4.059664000	-1.183965000	0.415648000
C	4.141245000	-1.504832000	-0.930676000
H	0.804838000	-1.875895000	-1.504624000
H	3.007263000	-2.034955000	-2.705947000
H	4.925349000	-0.967282000	1.029355000
H	5.110544000	-1.547625000	-1.415695000
C	-0.486680000	-0.161970000	0.300179000
S	-0.149858000	1.448028000	0.725452000
O	-1.310129000	2.330291000	0.715152000
O	0.768284000	1.421800000	1.867046000
S	-1.756931000	-0.554070000	-0.748360000
O	-2.146222000	0.553573000	-1.612710000
O	-1.514467000	-1.889885000	-1.303098000
C	-3.255745000	-0.829762000	0.314662000
F	-4.272633000	-1.241704000	-0.439155000
F	-2.989762000	-1.764137000	1.228489000
F	-3.602819000	0.291829000	0.935690000
C	0.929978000	2.139132000	-0.624330000
F	2.011890000	1.367289000	-0.772372000
F	0.286147000	2.194267000	-1.783135000
F	1.325058000	3.364566000	-0.286897000
F	2.657637000	-0.859722000	2.268013000

TS1: E= -2196.673104

C	0.121384000	-0.889699000	1.284274000
H	0.661028000	-0.451467000	2.116773000
H	0.001132000	-1.967171000	1.264186000
N	2.126653000	-1.223041000	0.295963000
C	2.166949000	-1.259777000	-1.042303000
C	3.264256000	-1.167233000	0.948320000
C	3.361480000	-1.243626000	-1.746585000
C	4.522579000	-1.141179000	0.362997000
C	4.557329000	-1.181102000	-1.025434000
H	1.204525000	-1.305448000	-1.548361000
H	3.356264000	-1.277518000	-2.829640000
H	5.414209000	-1.091074000	0.976453000
H	5.511370000	-1.162527000	-1.542374000
C	-0.640446000	-0.098007000	0.482655000
S	-0.580637000	1.648459000	0.693673000
O	-1.825433000	2.264851000	0.270100000
O	0.014469000	1.929649000	1.991179000
S	-1.695998000	-0.837658000	-0.715035000
O	-2.010196000	0.081702000	-1.793869000
O	-1.202360000	-2.183597000	-0.972987000
C	-3.283703000	-1.096356000	0.224465000
F	-4.143008000	-1.710505000	-0.576739000
F	-3.047719000	-1.853547000	1.288419000
F	-3.784402000	0.066553000	0.609347000
C	0.705936000	2.196953000	-0.538666000
F	1.899136000	1.752514000	-0.164481000

F	0.418058000	1.726042000	-1.743629000
F	0.713497000	3.522123000	-0.566281000
F	3.158286000	-1.127294000	2.284396000

2-Fluoropyridine: E= -347.354529

N	-0.312562000	-1.196483000	0.000046000
C	1.030541000	-1.206698000	0.000026000
C	-0.886799000	-0.019840000	-0.000002000
C	1.798943000	-0.049155000	-0.000052000
C	-0.245924000	1.213913000	0.000037000
C	1.142843000	1.184101000	0.000010000
H	1.497860000	-2.187396000	0.000130000
H	2.881184000	-0.112092000	-0.000257000
H	-0.817936000	2.134220000	0.000208000
H	1.706703000	2.111570000	0.000010000
F	-2.235278000	-0.033872000	-0.000059000

INT1: E= -1849.329923

C	0.217172000	-1.676935000	1.663220000
H	-0.621527000	-1.915362000	2.311974000
H	1.219561000	-1.945928000	1.987461000
C	0.013154000	-1.079513000	0.488553000
S	-1.676200000	-0.818530000	-0.058056000
O	-1.824815000	-1.227148000	-1.440353000
O	-2.537801000	-1.323728000	0.996675000
S	1.410701000	-0.710365000	-0.567412000
O	0.947971000	-0.263668000	-1.866139000
O	2.406934000	-1.750650000	-0.397514000
C	2.116839000	0.796399000	0.280358000
F	2.560851000	0.465012000	1.483457000
F	3.112015000	1.252864000	-0.460123000
F	1.175219000	1.723011000	0.393593000
C	-1.889959000	1.034476000	-0.011091000
F	-1.508005000	1.488013000	1.173627000
F	-1.170048000	1.600954000	-0.964614000
F	-3.173543000	1.292213000	-0.199221000

Phenylacetylene: E= -308.190279

C	0.000000000	0.000000000	0.586411000
C	0.000000000	1.212477000	-0.119332000
C	0.000000000	-1.212477000	-0.119332000
C	0.000000000	1.208299000	-1.511412000
C	0.000000000	-1.208299000	-1.511412000
C	0.000000000	0.000000000	-2.209630000
H	0.000000000	2.149538000	0.429299000
H	0.000000000	-2.149538000	0.429299000
H	0.000000000	2.150009000	-2.052014000
H	0.000000000	-2.150009000	-2.052014000
H	0.000000000	0.000000000	-3.295540000
C	0.000000000	0.000000000	2.024216000
C	0.000000000	0.000000000	3.233453000
H	0.000000000	0.000000000	4.303194000

TS2: E= -2157.492232

C	0.302224000	-0.541105000	2.001249000
H	0.174858000	0.261754000	2.721451000
H	0.953695000	-1.354675000	2.310332000
C	0.350601000	-0.178111000	0.643784000
S	-0.333917000	1.345953000	0.162633000
O	-0.971561000	1.322022000	-1.143188000

O	-1.024262000	1.883807000	1.332007000
S	1.002251000	-1.303433000	-0.497507000
O	0.821989000	-0.857106000	-1.870647000
O	0.669372000	-2.662830000	-0.084686000
C	-1.268452000	-1.549128000	2.690187000
H	-0.957317000	-1.995331000	3.617475000
C	-2.124569000	-1.349958000	1.822583000
C	-2.819633000	-0.979271000	0.661729000
C	-3.692289000	0.131329000	0.673921000
C	-2.581541000	-1.692639000	-0.533481000
C	-4.321167000	0.511780000	-0.499120000
C	-3.209607000	-1.288453000	-1.703956000
C	-4.077045000	-0.194957000	-1.683045000
H	-3.852554000	0.672673000	1.600708000
H	-1.912655000	-2.547969000	-0.518709000
H	-4.994457000	1.362496000	-0.502863000
H	-3.027052000	-1.823577000	-2.629989000
C	2.842395000	-1.209871000	-0.216293000
F	3.447973000	-2.017633000	-1.078194000
F	3.275083000	0.032021000	-0.398844000
F	3.135775000	-1.593030000	1.023972000
C	1.123821000	2.480306000	-0.063557000
F	1.920441000	2.420751000	0.998446000
F	1.808076000	2.134800000	-1.147630000
F	0.676994000	3.723441000	-0.205774000
H	-4.569678000	0.114476000	-2.600097000

TS2-B: E= -2157.462544

C	-0.664697000	-0.554496000	-0.687676000
H	-0.412375000	-1.189725000	-1.532557000
H	-1.238052000	0.314245000	-1.016228000
C	0.442532000	-0.214822000	0.181317000
S	1.579710000	-1.449153000	0.524482000
O	2.133220000	-1.427873000	1.869076000
O	0.966874000	-2.675272000	-0.009374000
S	0.566050000	1.344308000	0.873988000
O	1.654496000	1.426111000	1.837461000
O	-0.759358000	1.877524000	1.178678000
C	-2.029937000	-1.430787000	0.013377000
C	-1.578218000	-2.548580000	0.347168000
C	1.124964000	2.425219000	-0.534741000
F	1.225940000	3.680362000	-0.112299000
F	2.306136000	2.019899000	-0.988433000
F	0.238466000	2.368402000	-1.528333000
C	3.065866000	-1.194977000	-0.566679000
F	2.674590000	-1.013464000	-1.824398000
F	3.750507000	-0.132221000	-0.161953000
F	3.841837000	-2.270939000	-0.499834000
C	-3.358264000	-0.789973000	-0.070380000
C	-4.464092000	-1.598291000	-0.369121000
C	-3.521899000	0.578410000	0.156501000
C	-5.730648000	-1.028827000	-0.443627000
H	-4.325136000	-2.658902000	-0.554209000
C	-4.797556000	1.135248000	0.088367000
H	-2.671543000	1.201070000	0.413586000
C	-5.899760000	0.337451000	-0.213853000
H	-6.585066000	-1.653680000	-0.683832000
H	-4.925973000	2.197026000	0.273532000
H	-6.890059000	0.778526000	-0.272916000
H	-1.112838000	-3.476749000	0.623726000

INT2: E= -2157.507311

C	-0.236362000	0.001826000	2.066052000

H	-0.789707000	-0.801195000	2.560607000
H	-0.616683000	0.943019000	2.475950000
C	-0.433756000	-0.067061000	0.570034000
S	-0.725556000	-1.579811000	-0.129497000
O	-0.284430000	-1.711885000	-1.514203000
O	-0.369222000	-2.603966000	0.857004000
S	-0.280548000	1.358511000	-0.321446000
O	-0.204042000	1.155713000	-1.764772000
O	0.674375000	2.243659000	0.354148000
C	1.219060000	-0.113635000	2.513527000
H	1.450215000	-0.136019000	3.580075000
C	2.182049000	-0.161983000	1.663050000
C	3.154082000	-0.191916000	0.708981000
C	3.596220000	-1.444805000	0.182839000
C	3.691104000	1.038595000	0.219231000
C	4.555609000	-1.453957000	-0.806032000
C	4.649670000	1.003110000	-0.770576000
C	5.074674000	-0.236020000	-1.274557000
H	3.165987000	-2.362430000	0.571281000
H	3.316998000	1.971644000	0.626949000
H	4.908509000	-2.390131000	-1.223336000
H	5.070392000	1.921827000	-1.163102000
C	-1.872933000	2.301540000	-0.117150000
F	-2.134260000	2.493773000	1.178375000
F	-1.773407000	3.488661000	-0.713178000
F	-2.889052000	1.634436000	-0.658135000
C	-2.568432000	-1.791690000	-0.266270000
F	-3.151094000	-1.479485000	0.892795000
F	-3.062088000	-1.004867000	-1.219498000
F	-2.860810000	-3.057394000	-0.563613000
H	5.829011000	-0.254224000	-2.056228000

TS3: E= -2157.502508

C	-1.892427000	-0.301855000	1.565813000
C	-1.092780000	-0.382555000	2.589059000
C	0.349498000	-0.244955000	2.200481000
C	0.307998000	-0.058105000	0.681492000
H	-1.475909000	-0.540007000	3.597434000
H	0.813276000	0.610523000	2.699869000
H	0.912795000	-1.137475000	2.487275000
C	-2.902714000	-0.228014000	0.629377000
C	-3.498003000	1.030522000	0.343293000
C	-3.321972000	-1.404155000	-0.050151000
C	-4.511231000	1.097770000	-0.593534000
C	-4.334525000	-1.313763000	-0.985507000
C	-4.922396000	-0.069000000	-1.251856000
H	-3.146813000	1.914170000	0.867651000
H	-2.832766000	-2.346839000	0.175437000
H	-4.983894000	2.046549000	-0.822115000
H	-4.671844000	-2.198186000	-1.514586000
S	0.239630000	1.528479000	0.049339000
O	-0.147035000	2.413411000	1.149776000
O	-0.451339000	1.606328000	-1.231509000
S	0.546975000	-1.428453000	-0.302972000
O	0.323365000	-1.153478000	-1.717216000
O	-0.070861000	-2.588761000	0.340069000
C	1.970191000	2.099341000	-0.349128000
F	2.381654000	1.571823000	-1.496614000
F	1.986647000	3.425018000	-0.452712000
F	2.803159000	1.730929000	0.624069000
C	2.359916000	-1.853146000	-0.215398000
F	2.584842000	-2.968957000	-0.902474000
F	3.093712000	-0.871198000	-0.730157000
F	2.729241000	-2.042677000	1.051765000

H	-5.716186000	-0.006092000	-1.990335000

3s: E= -2157.552022

C	-1.491580000	0.001365000	1.112299000
C	-1.154468000	0.006676000	2.413302000
C	0.332276000	-0.013095000	2.196179000
C	-0.024272000	0.047551000	0.671255000
H	-1.736149000	0.003310000	3.328587000
H	0.902260000	0.845531000	2.559289000
H	0.827419000	-0.938727000	2.496686000
C	-2.745329000	-0.035082000	0.358057000
C	-3.953420000	0.007958000	1.071532000
C	-2.775411000	-0.138374000	-1.037694000
C	-5.167750000	-0.053745000	0.399454000
C	-3.996853000	-0.202420000	-1.707017000
C	-5.192835000	-0.160955000	-0.993706000
H	-3.939357000	0.090091000	2.155011000
H	-1.852668000	-0.160177000	-1.609883000
H	-6.096113000	-0.019125000	0.961337000
H	-4.009582000	-0.284168000	-2.789556000
S	0.317448000	1.686055000	-0.097587000
O	0.001608000	2.671091000	0.923125000
O	-0.256707000	1.759254000	-1.427900000
S	0.432664000	-1.431790000	-0.328316000
O	0.376056000	-1.118656000	-1.747116000
O	-0.314653000	-2.532108000	0.256406000
C	2.181641000	1.778407000	-0.294729000
F	2.532107000	1.333550000	-1.486811000
F	2.553171000	3.035425000	-0.151203000
F	2.748669000	1.030444000	0.651720000
C	2.239124000	-1.884217000	-0.017314000
F	2.342730000	-3.169240000	-0.312343000
F	3.020992000	-1.181168000	-0.816365000
F	2.589828000	-1.688430000	1.244497000
H	-6.142245000	-0.211272000	-1.518318000

TS4: E= -2290.171677

C	0.006947000	-0.662661000	-0.956526000
H	0.270511000	0.271593000	-1.450782000
H	-0.406416000	-1.330058000	-1.717848000
C	-1.016236000	-0.441857000	0.133535000
S	-1.001064000	1.020388000	0.975037000
O	-1.954257000	1.070118000	2.079962000
O	0.376264000	1.484983000	1.166362000
S	-2.084549000	-1.702111000	0.488145000
O	-2.605480000	-1.711344000	1.850781000
O	-1.522842000	-2.926719000	-0.093075000
C	1.264670000	-1.312736000	-0.423790000
H	1.139059000	-2.303687000	0.030996000
C	2.497102000	-0.933300000	-0.370396000
C	3.868793000	-0.968584000	-0.099509000
C	4.751065000	-1.542447000	-1.042358000
C	4.350521000	-0.449976000	1.123816000
C	6.102493000	-1.611330000	-0.747673000
C	5.704521000	-0.527213000	1.403442000
C	6.572727000	-1.104813000	0.469402000
H	4.356972000	-1.924345000	-1.978679000
H	3.651548000	-0.003756000	1.824582000
H	6.793848000	-2.053925000	-1.456410000
H	6.091294000	-0.141166000	2.340206000
C	-3.615398000	-1.443775000	-0.533425000
F	-3.284495000	-1.268282000	-1.814196000
F	-4.413149000	-2.506904000	-0.440248000

F	-4.281250000	-0.370351000	-0.112821000
C	-1.656640000	2.309794000	-0.199769000
F	-0.860826000	2.408958000	-1.270744000
F	-2.883428000	2.002008000	-0.610315000
F	-1.690303000	3.494260000	0.409379000
H	7.633874000	-1.160290000	0.693530000
N	2.403445000	1.106828000	-1.280240000
C	2.276962000	2.213444000	-0.969404000
C	2.098605000	3.606827000	-0.581864000
H	1.589034000	4.146272000	-1.382866000
H	1.489709000	3.632449000	0.325068000
H	3.071046000	4.064918000	-0.391654000

INT3: E= -2290.222144

C	0.054892000	0.090901000	-1.426161000
H	0.005508000	1.135403000	-1.758102000
H	-0.403225000	-0.511120000	-2.216371000
C	-0.724800000	-0.015543000	-0.123023000
S	-1.627109000	1.299665000	0.414158000
O	-2.257305000	1.072633000	1.711643000
O	-0.907318000	2.554575000	0.155152000
S	-0.831780000	-1.537257000	0.617826000
O	-0.928127000	-1.510885000	2.073917000
O	0.163670000	-2.395075000	-0.035042000
C	1.501785000	-0.312109000	-1.289664000
H	1.831019000	-1.200351000	-1.819469000
C	2.427217000	0.326314000	-0.559159000
C	3.835740000	-0.082906000	-0.351628000
C	4.845247000	0.871401000	-0.184141000
C	4.159784000	-1.444751000	-0.333124000
C	6.167567000	0.467280000	-0.018512000
C	5.484327000	-1.842983000	-0.174411000
C	6.491004000	-0.889465000	-0.017669000
H	4.605932000	1.931483000	-0.196815000
H	3.374059000	-2.190146000	-0.420563000
H	6.944837000	1.214714000	0.106502000
H	5.727242000	-2.901036000	-0.157463000
C	-2.433673000	-2.349043000	0.119448000
F	-2.617678000	-2.226287000	-1.196268000
F	-2.388824000	-3.645469000	0.424758000
F	-3.465656000	-1.797672000	0.752044000
C	-3.076469000	1.487852000	-0.740813000
F	-2.643317000	1.618575000	-1.997492000
F	-3.870377000	0.421617000	-0.676880000
F	-3.782696000	2.569320000	-0.416114000
H	7.522094000	-1.203422000	0.113597000
N	2.043624000	1.500235000	0.097512000
C	1.756155000	2.466753000	0.645380000
C	1.452603000	3.696159000	1.346406000
H	2.381773000	4.095182000	1.760526000
H	1.011778000	4.400938000	0.638449000
H	0.737119000	3.478281000	2.142014000

TS5: E= -2290.209725

C	-0.110803000	-0.383315000	-1.295464000
H	0.074890000	-1.392748000	-1.688340000
H	0.317639000	0.301231000	-2.036606000
C	0.615025000	-0.256659000	0.041704000
S	1.891117000	-1.385352000	0.305864000
O	2.705814000	-1.011145000	1.455672000
O	1.353102000	-2.740016000	0.183304000
S	0.705619000	1.325457000	0.746158000
O	0.988529000	1.271099000	2.176638000

O	-0.458715000	2.059807000	0.253106000
C	-1.606134000	-0.180977000	-1.314389000
H	-2.001679000	0.178720000	-2.259799000
C	-2.488947000	-0.418963000	-0.337360000
C	-3.948867000	-0.193270000	-0.365437000
C	-4.789662000	-0.924754000	0.481400000
C	-4.505051000	0.752552000	-1.236020000
C	-6.168309000	-0.727749000	0.443461000
C	-5.883142000	0.942638000	-1.274375000
C	-6.719357000	0.203056000	-0.436332000
H	-4.366753000	-1.655754000	1.164959000
H	-3.862294000	1.358547000	-1.867841000
H	-6.810636000	-1.305442000	1.101217000
H	-6.303068000	1.681143000	-1.950435000
C	2.133617000	2.310439000	0.057341000
F	2.110044000	2.272688000	-1.273505000
F	1.999758000	3.571363000	0.456307000
F	3.293796000	1.838336000	0.494067000
C	3.069326000	-1.297887000	-1.144819000
F	3.448050000	-0.042718000	-1.360973000
F	4.137425000	-2.037077000	-0.871611000
F	2.484987000	-1.765730000	-2.244708000
H	-7.793643000	0.358204000	-0.463849000
N	-1.981561000	-0.946185000	0.862903000
C	-1.023182000	-1.146275000	1.509500000
C	-0.314730000	-1.646481000	2.683736000
H	0.371591000	-0.879452000	3.049519000
H	-1.073276000	-1.875296000	3.438309000
H	0.235304000	-2.551399000	2.416579000

INT4: E= -2290.241653

C	-0.099978000	-0.430663000	-1.252904000
H	0.177392000	-1.405548000	-1.683895000
H	0.397102000	0.329185000	-1.860174000
C	0.403501000	-0.383953000	0.200050000
S	1.932095000	-1.425896000	0.370979000
O	2.725567000	-0.977599000	1.498950000
O	1.476490000	-2.799558000	0.235266000
S	0.590257000	1.364040000	0.832023000
O	0.940348000	1.332110000	2.240002000
O	-0.573161000	2.089117000	0.350693000
C	-1.583566000	-0.256855000	-1.360754000
H	-1.972656000	0.022451000	-2.334325000
C	-2.391476000	-0.458082000	-0.314323000
C	-3.855384000	-0.232881000	-0.338994000
C	-4.706529000	-0.988926000	0.476915000
C	-4.408719000	0.739705000	-1.182535000
C	-6.085422000	-0.793079000	0.429082000
C	-5.786711000	0.933896000	-1.228836000
C	-6.630426000	0.166277000	-0.424498000
H	-4.283075000	-1.734469000	1.142218000
H	-3.757157000	1.363336000	-1.788579000
H	-6.734883000	-1.392177000	1.060722000
H	-6.200659000	1.694632000	-1.884146000
C	2.045018000	2.205027000	-0.006931000
F	1.808593000	2.356282000	-1.299882000
F	2.152187000	3.389400000	0.569268000
F	3.161027000	1.515399000	0.178929000
C	3.011465000	-1.149286000	-1.178737000
F	2.665475000	-0.053616000	-1.842833000
F	4.257014000	-1.037689000	-0.761765000
F	2.881614000	-2.198747000	-1.964618000
H	-7.704830000	0.321408000	-0.457059000
N	-1.885047000	-0.968797000	0.903845000

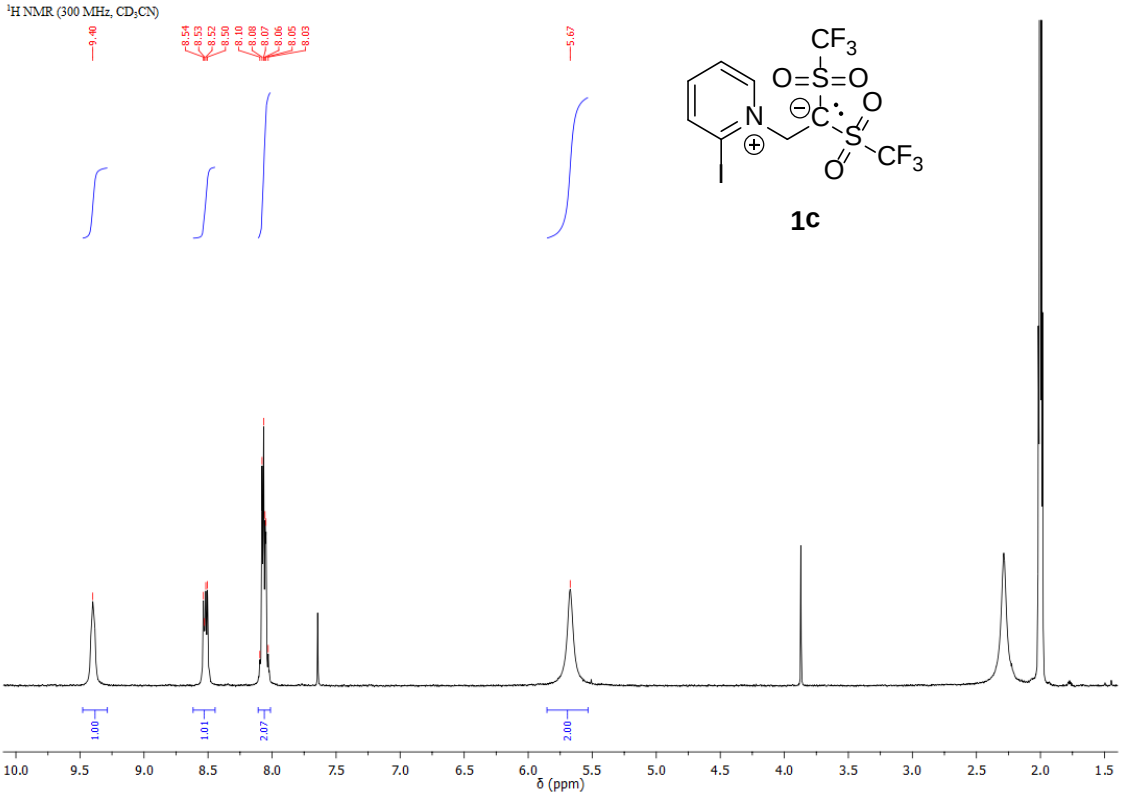
C	-0.650505000	-0.989844000	1.197663000
C	-0.204495000	-1.560331000	2.515796000
H	-1.090148000	-1.692566000	3.137804000
H	0.274724000	-2.534032000	2.375759000
H	0.504130000	-0.898804000	3.019575000

TfH: E= -886.590323

H	-1.013319000	0.000019000	1.629489000
S	-0.975880000	0.000003000	0.274611000
O	-1.463621000	-1.272555000	-0.226997000
O	-1.463162000	1.272787000	-0.226883000
C	0.861998000	-0.000086000	-0.010167000
F	1.402388000	-1.083244000	0.530322000
F	1.069753000	-0.000571000	-1.318691000
F	1.402268000	1.083658000	0.529344000

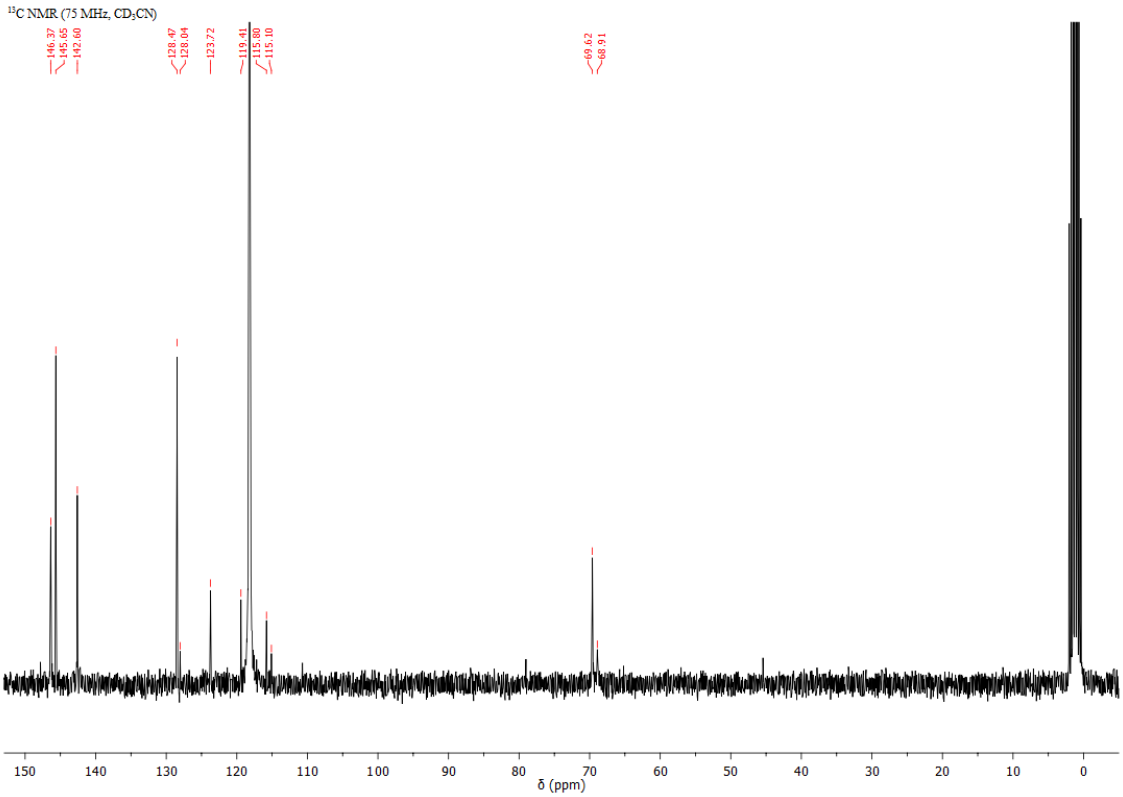
4s: E= -1403.709931

C	-0.253314000	-1.165989000	-0.868803000
H	-0.823264000	-2.007930000	-1.249676000
C	-0.896451000	0.031137000	-0.551112000
S	-2.648080000	0.058471000	-0.776354000
O	-3.142208000	1.407070000	-1.013284000
O	-3.039256000	-1.047926000	-1.641192000
C	1.117910000	-1.243867000	-0.707864000
H	1.649101000	-2.148949000	-0.976965000
C	1.797128000	-0.118356000	-0.222400000
C	3.268006000	-0.128890000	-0.021350000
C	3.986420000	1.072697000	-0.078516000
C	3.955572000	-1.324210000	0.226098000
C	5.367651000	1.075760000	0.093950000
C	5.336593000	-1.317635000	0.408478000
C	6.046528000	-0.119006000	0.338396000
H	3.453546000	1.998910000	-0.267986000
H	3.414947000	-2.263012000	0.304698000
H	5.915373000	2.011742000	0.036685000
H	5.856186000	-2.249350000	0.610557000
C	-3.297576000	-0.420080000	0.902762000
F	-2.892563000	0.451636000	1.819874000
F	-4.622789000	-0.428036000	0.855655000
F	-2.856452000	-1.630113000	1.224568000
H	7.123588000	-0.115443000	0.476866000
N	1.161464000	1.028032000	0.068050000
C	-0.159419000	1.137509000	-0.082188000
C	-0.749056000	2.480811000	0.253427000
H	0.033811000	3.090579000	0.705074000
H	-1.115992000	2.975068000	-0.650256000
H	-1.590278000	2.402814000	0.945989000

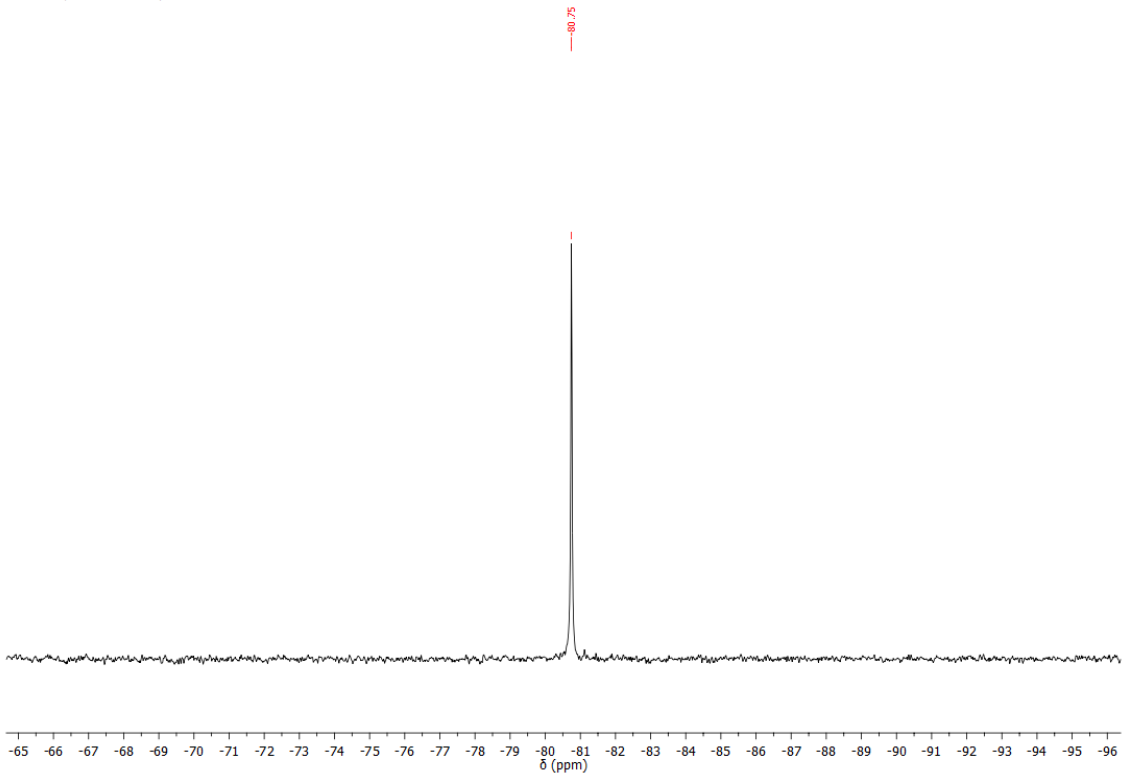

^{1}H NMR (300 MHz, CD_3CN)
9.40
8.54
8.53
8.52
8.50
8.10
8.08
8.07
8.06
8.05
8.03
5.67
1.00
1.01
2.07
2.00
δ (ppm)

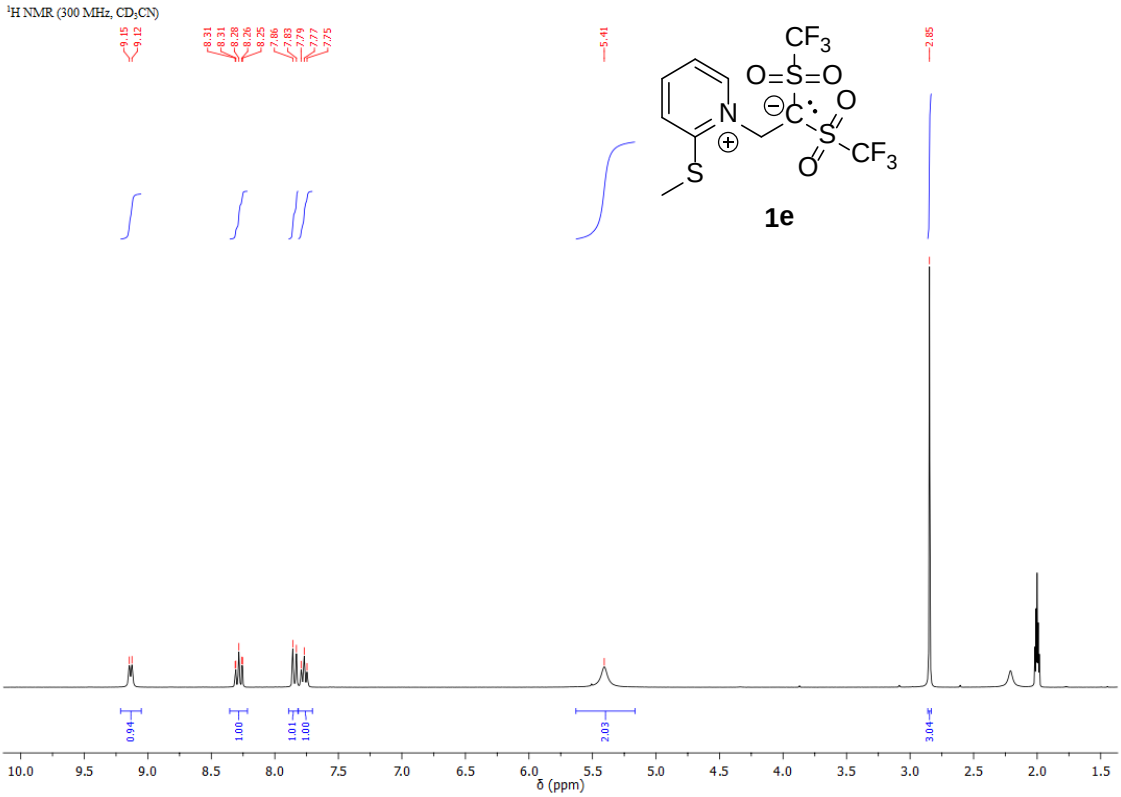
CF3
O=S=O
N
C
O
S
O
CF3

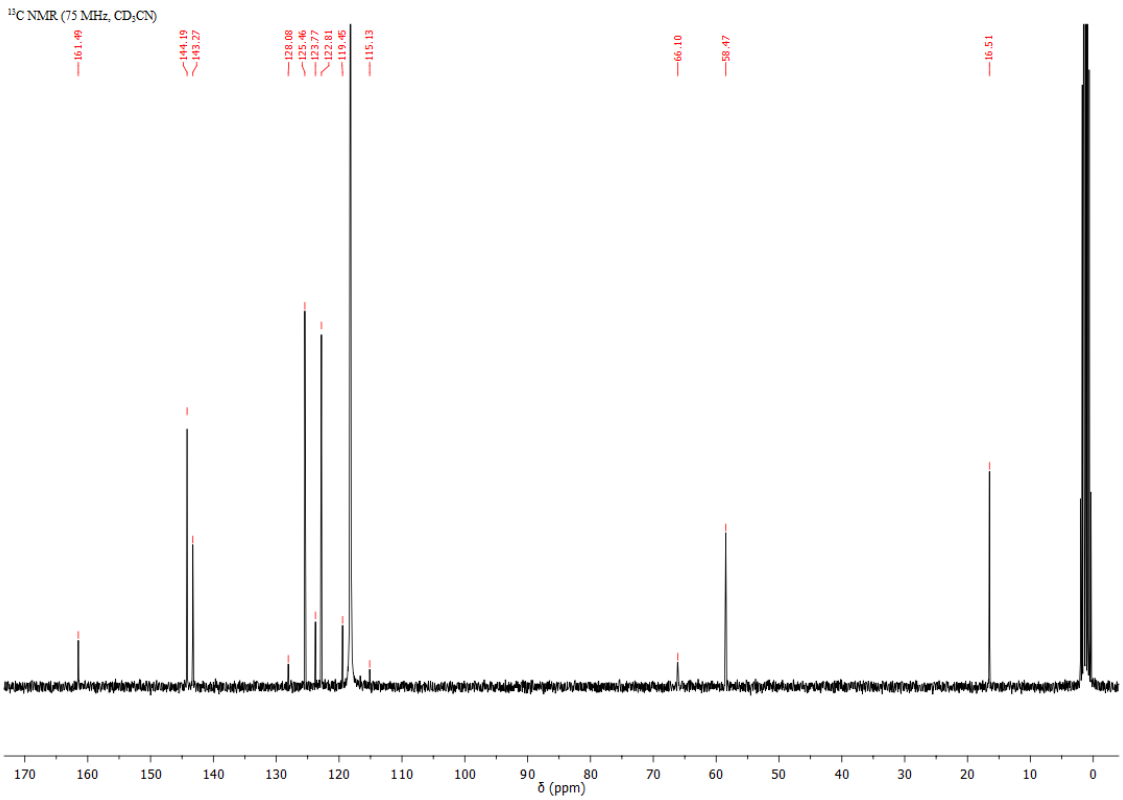
1c


^{13}C NMR (75 MHz, CD_3CN)
146.37
145.65
142.60
128.47
128.04
123.72
119.41
115.80
115.10
69.62
68.91
δ (ppm)

^{19}F NMR (282 MHz, CD_3CN)



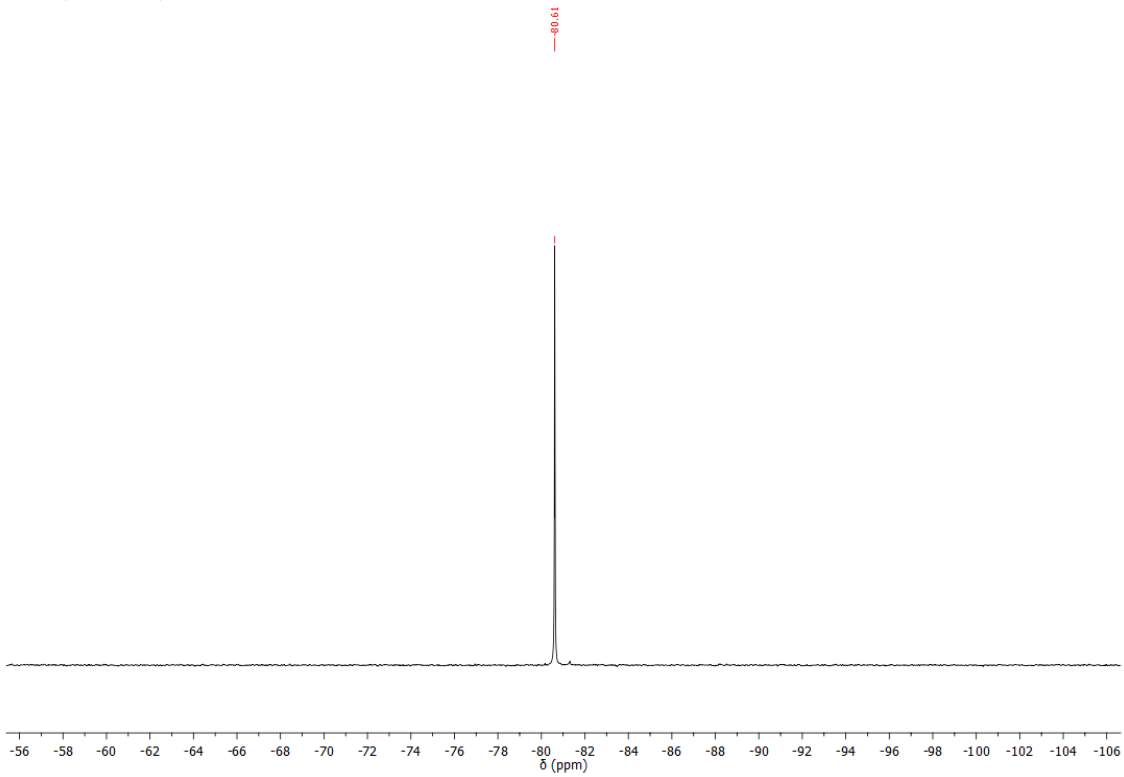

^{1}H NMR (300 MHz, CD_3CN)
9.15
9.12
8.31
8.31
8.28
8.26
8.25
7.86
7.83
7.79
7.77
7.75
5.41
2.85
0.94
1.00
1.01
1.00
2.03
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
δ (ppm)

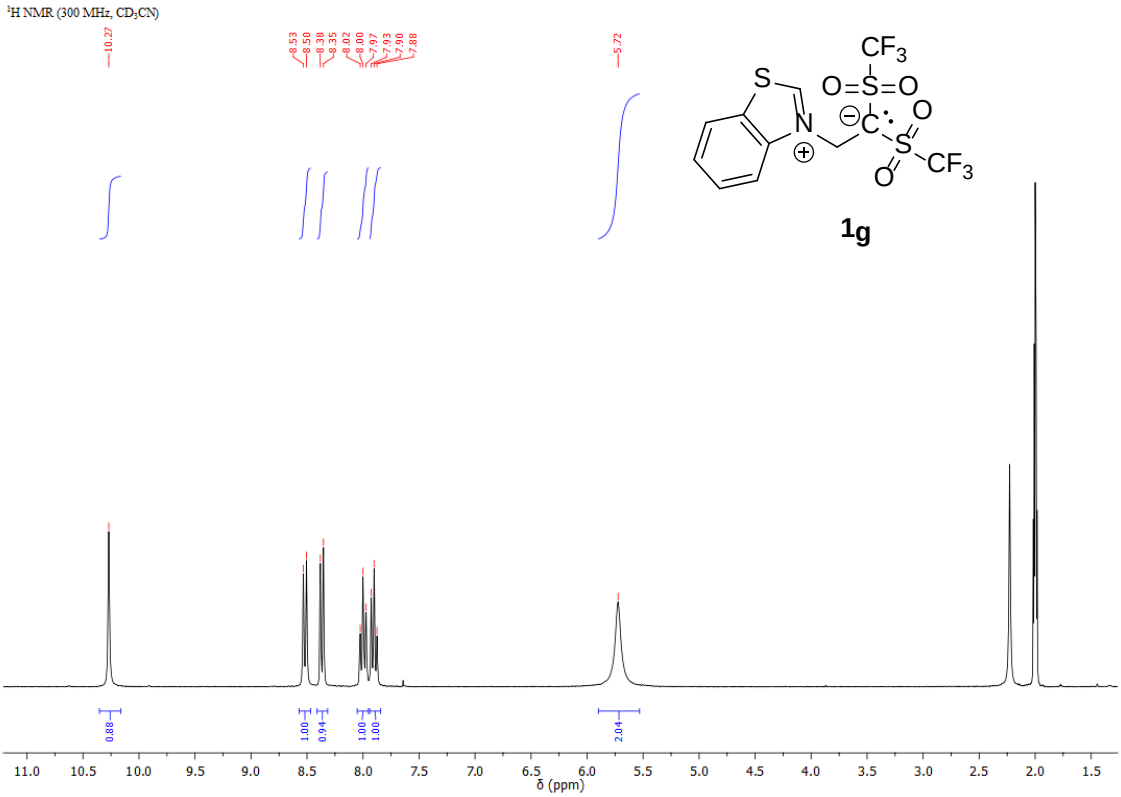

^{13}C NMR (75 MHz, CD_3CN)
161.49
144.19
143.27
128.08
125.46
123.77
122.81
119.45
115.13
66.10
58.47
16.51
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

CF_3
O=S=O
N
C
O
S
CF_3
O
S

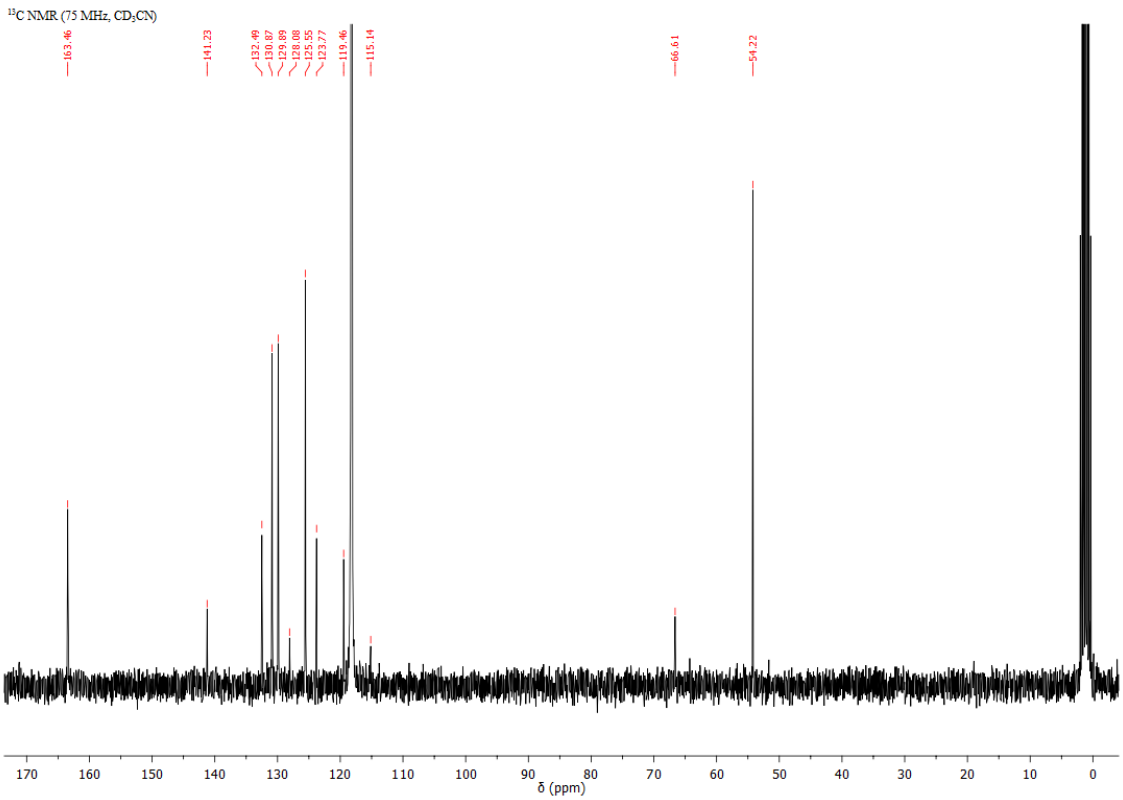
1e

^{19}F NMR (282 MHz, CD_3CN)

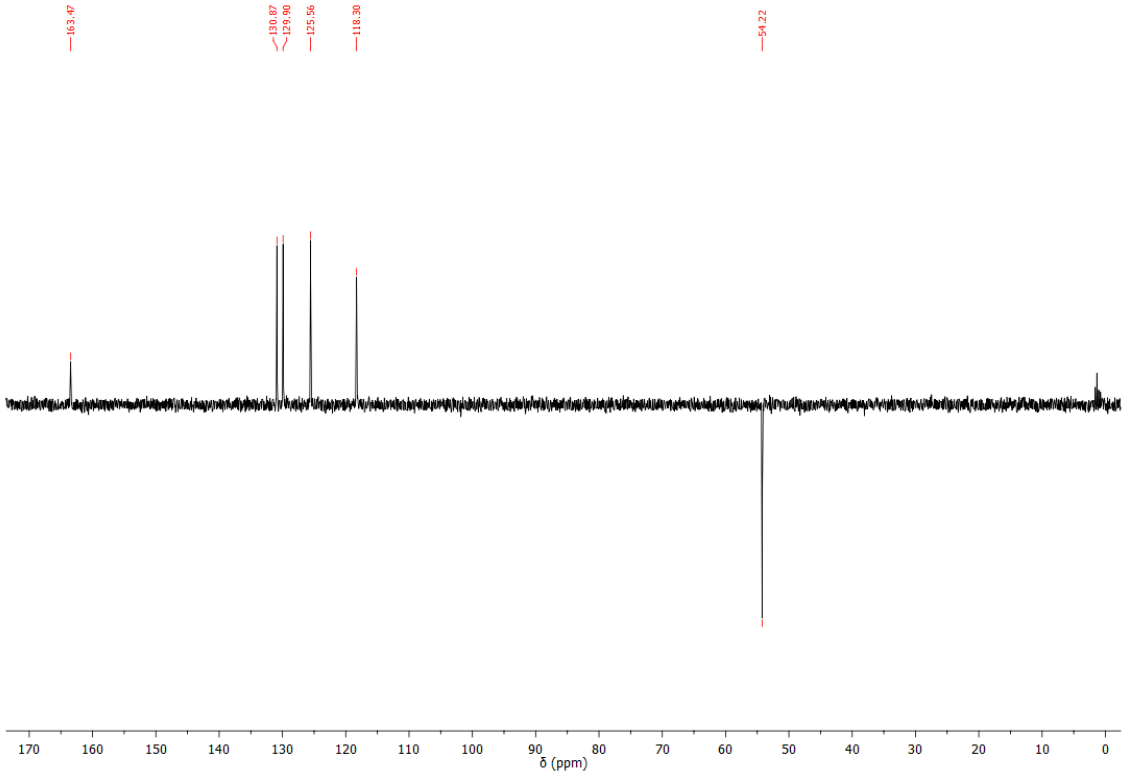



^{1}H NMR (300 MHz, CD_3CN)
10.27
8.53
8.50
8.38
8.35
8.02
8.00
7.97
7.93
7.90
7.88
5.72
0.88
1.00
0.94
1.00
1.00
2.04
δ (ppm)

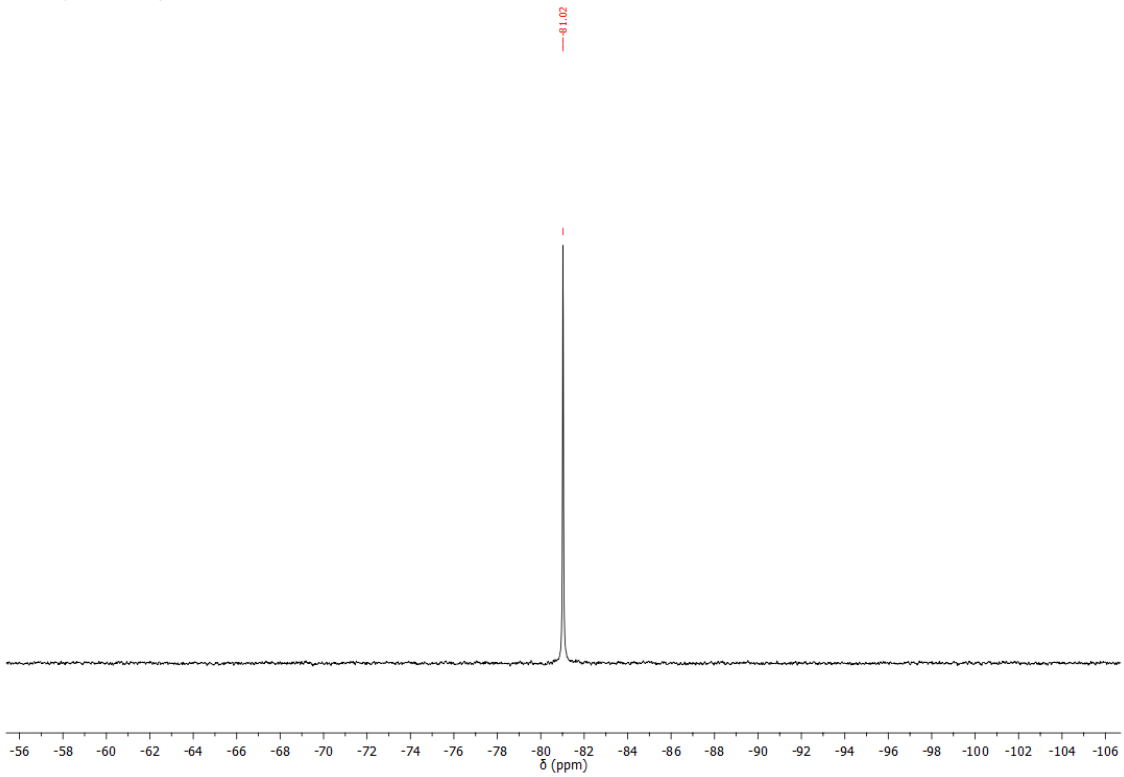
1g


^{13}C NMR (75 MHz, CD_3CN)
163.46
141.23
132.49
130.87
129.89
128.08
125.55
123.77
119.46
115.14
66.61
54.22
δ (ppm)

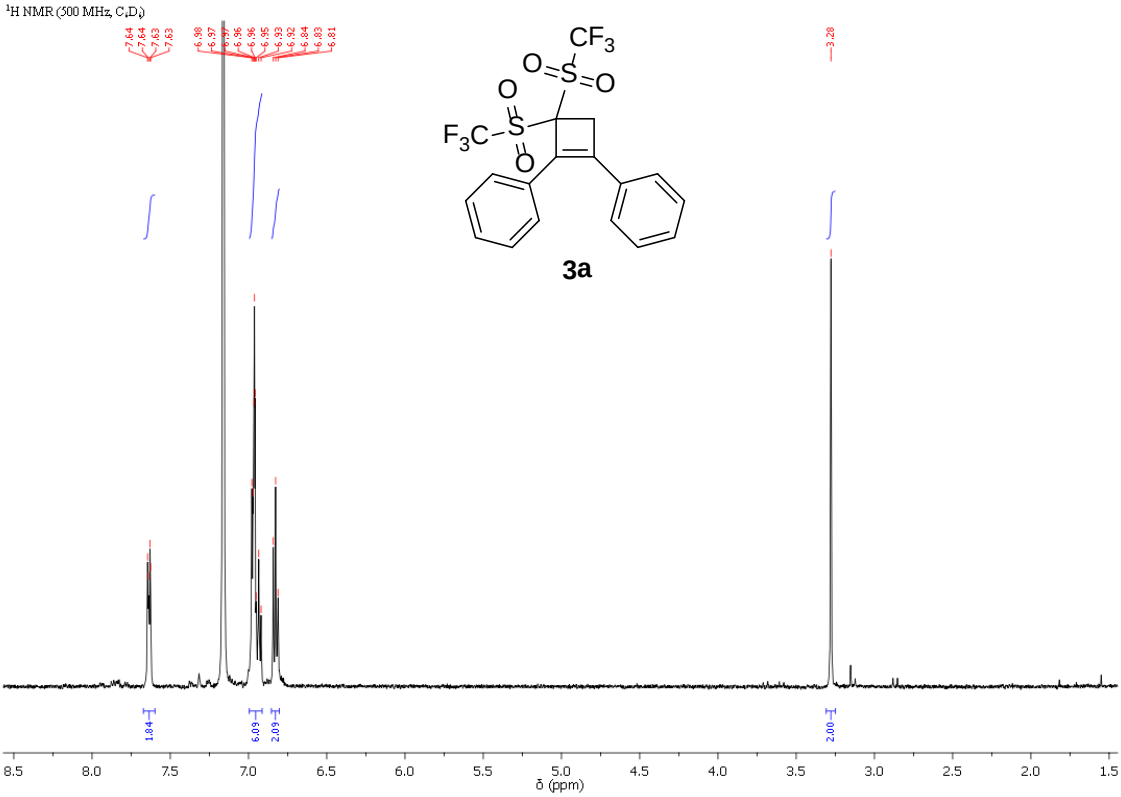
^{13}C-DEPT-135 NMR (75 MHz, CD_3CN)



^{19}F NMR (282 MHz, CD_3CN)

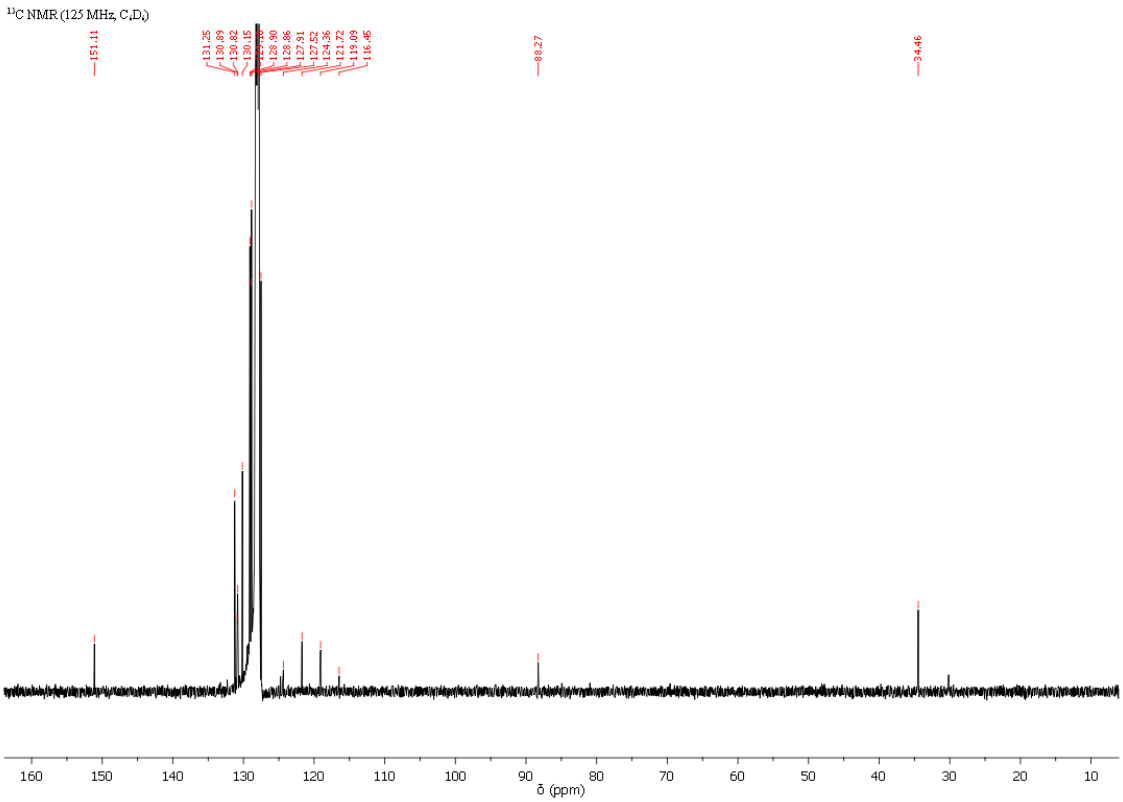


^{1}H NMR (500 MHz, C_4D_8)

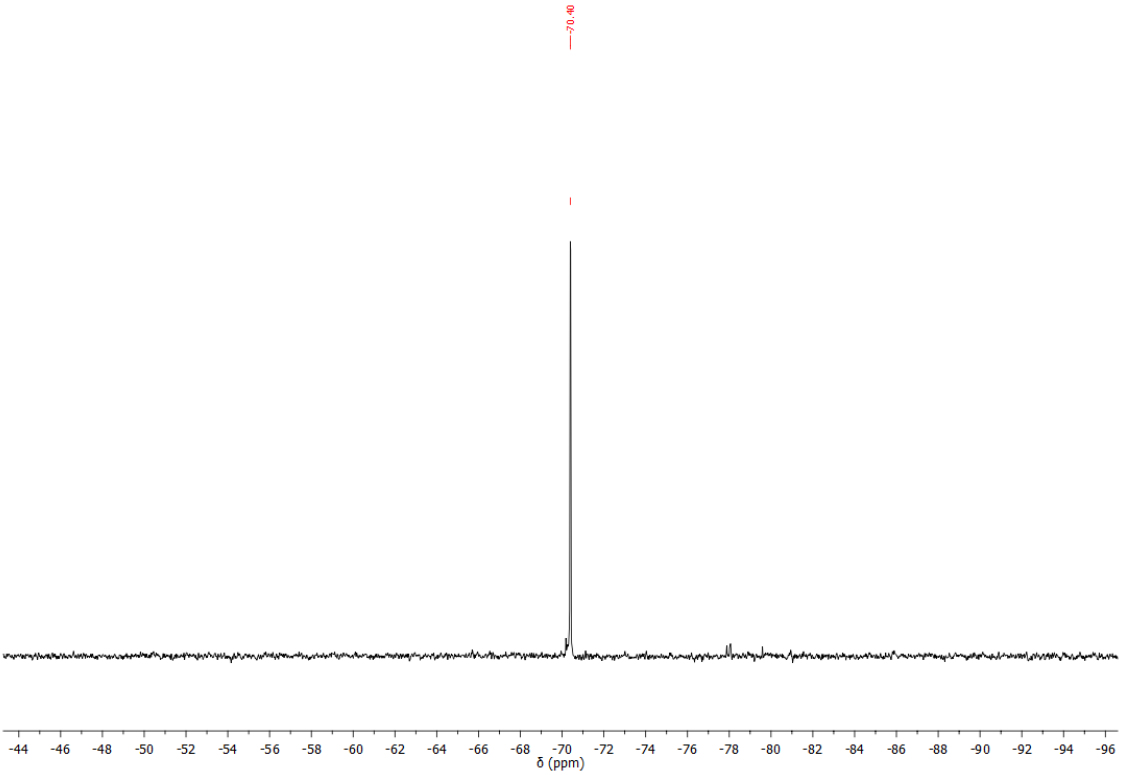


3a

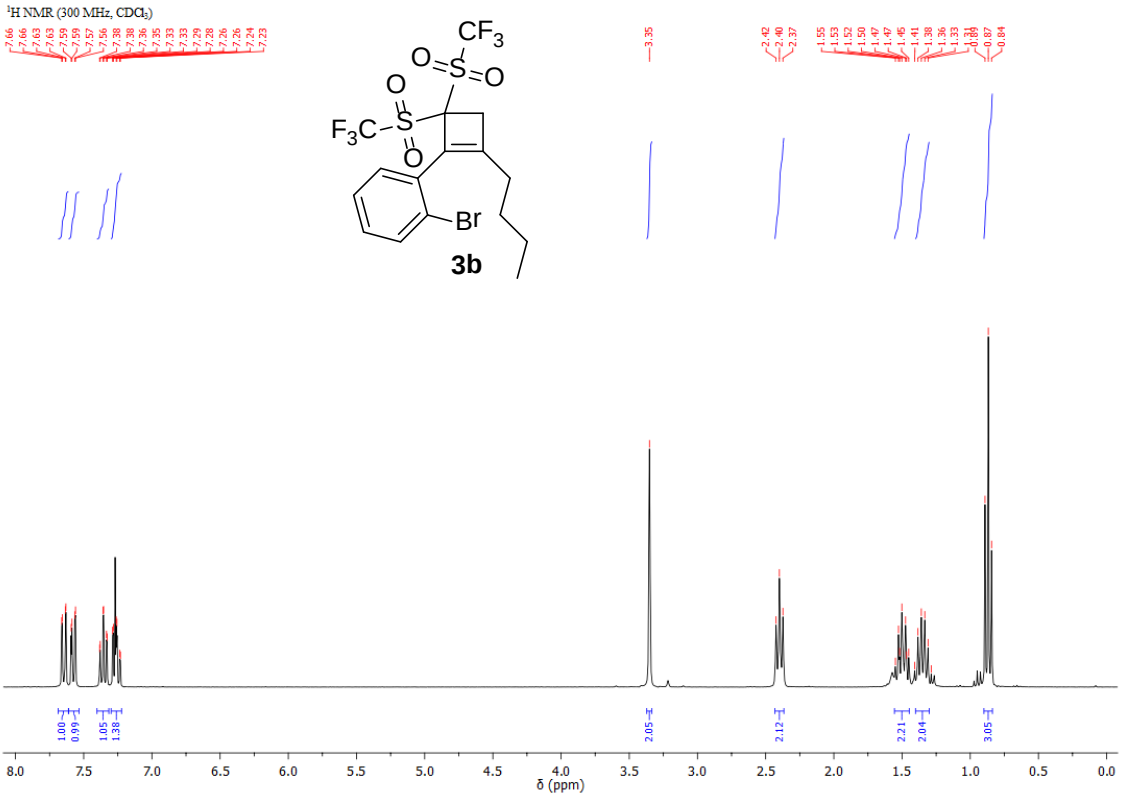
^{13}C NMR (125 MHz, C_4D_8)



^{19}F NMR (282 MHz, C_6D_6)

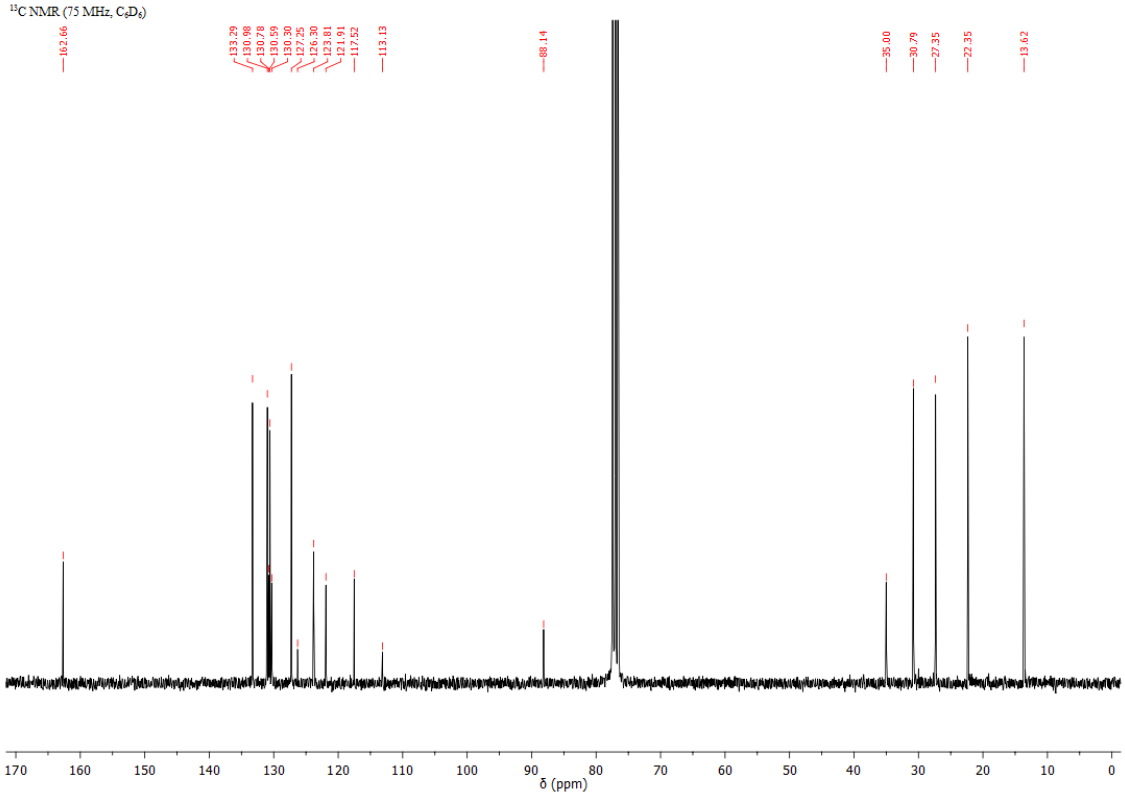


^{1}H NMR (300 MHz, $CDCl_3$)

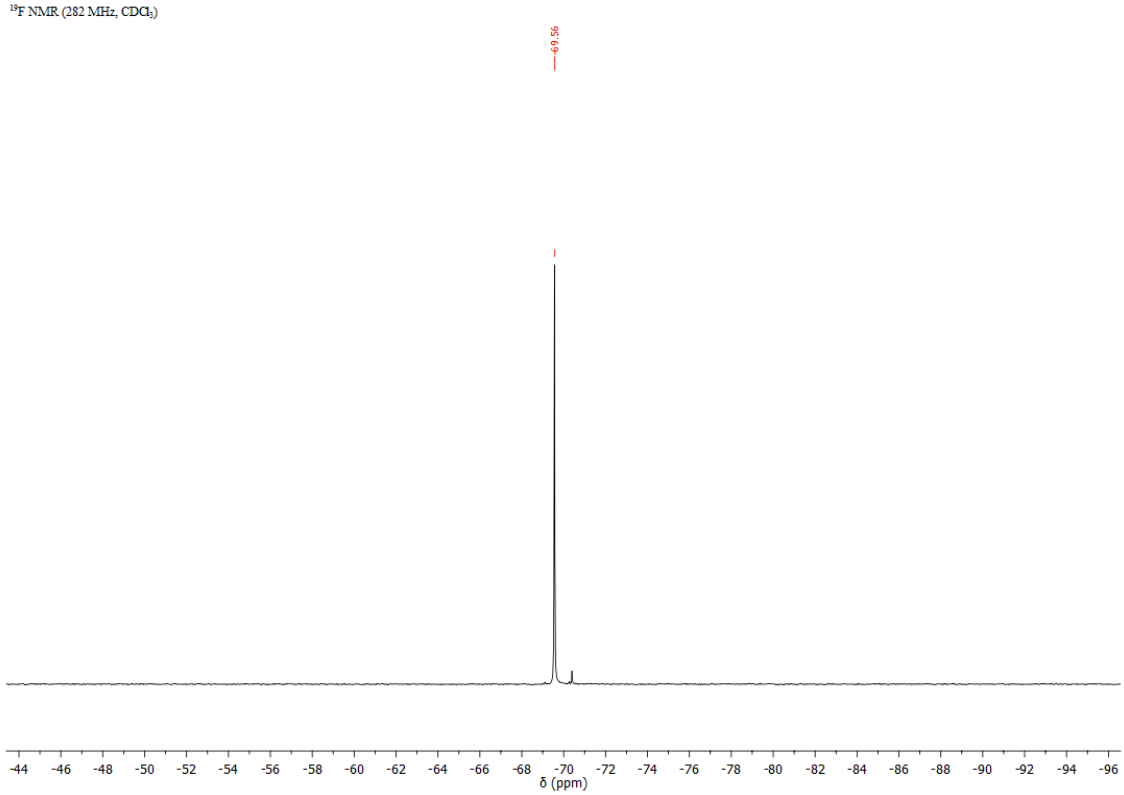


3b

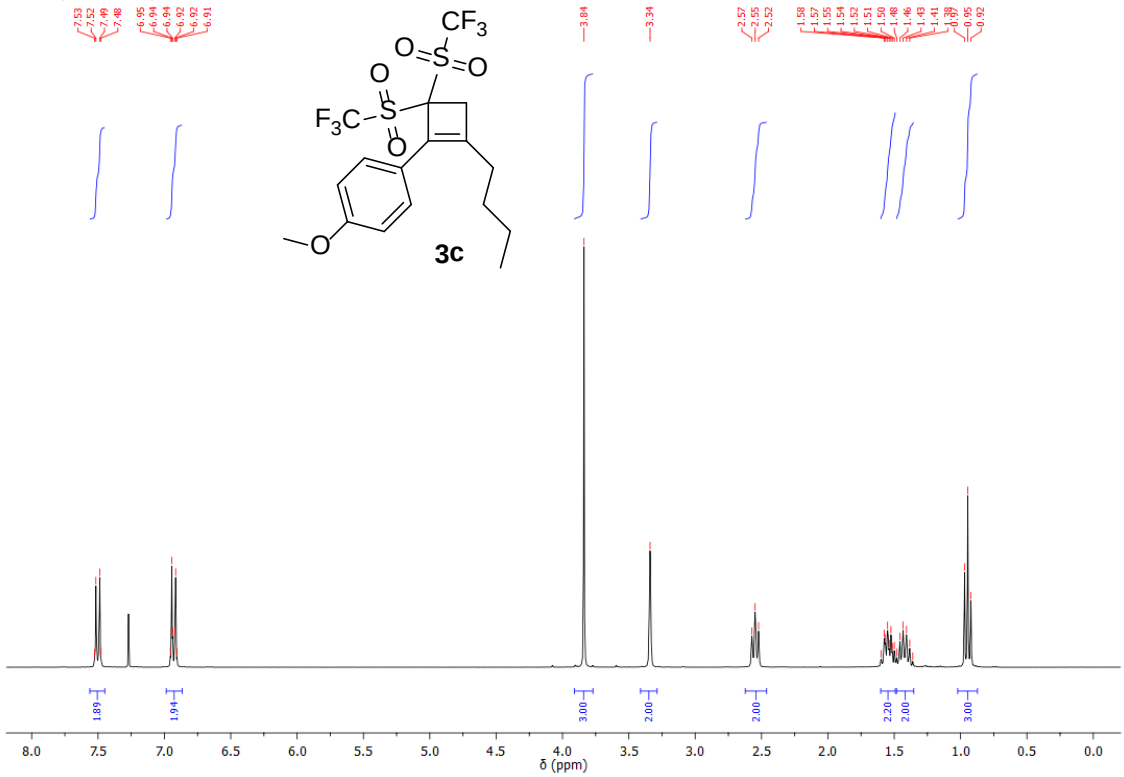
^{13}C NMR (75 MHz, C_6D_6)



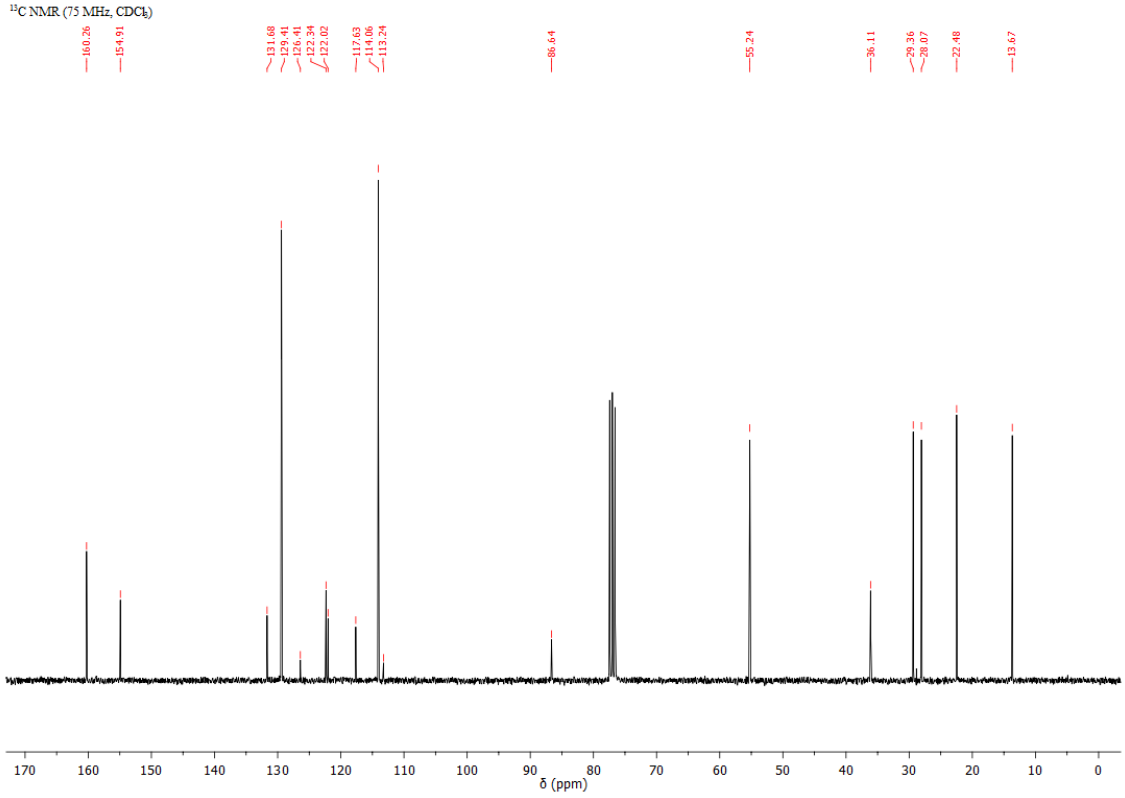
^{19}F NMR (282 MHz, $CDCl_3$)



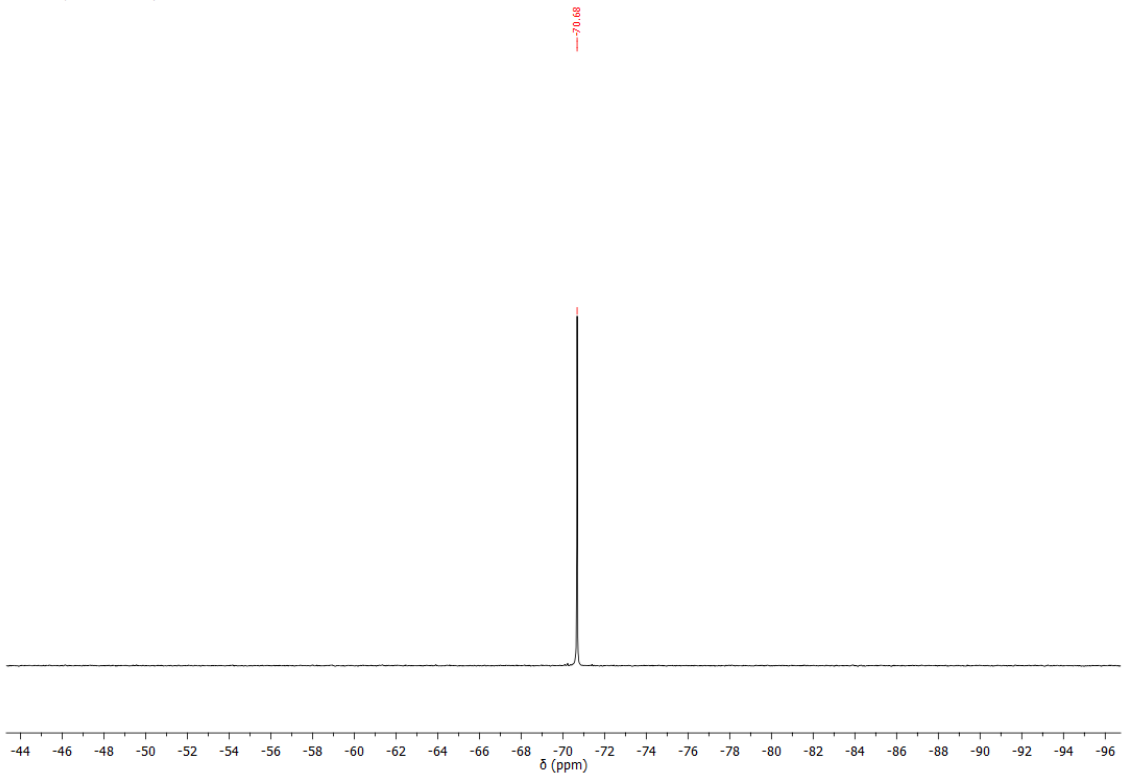
^{1}H NMR (300 MHz, $CDCl_3$)

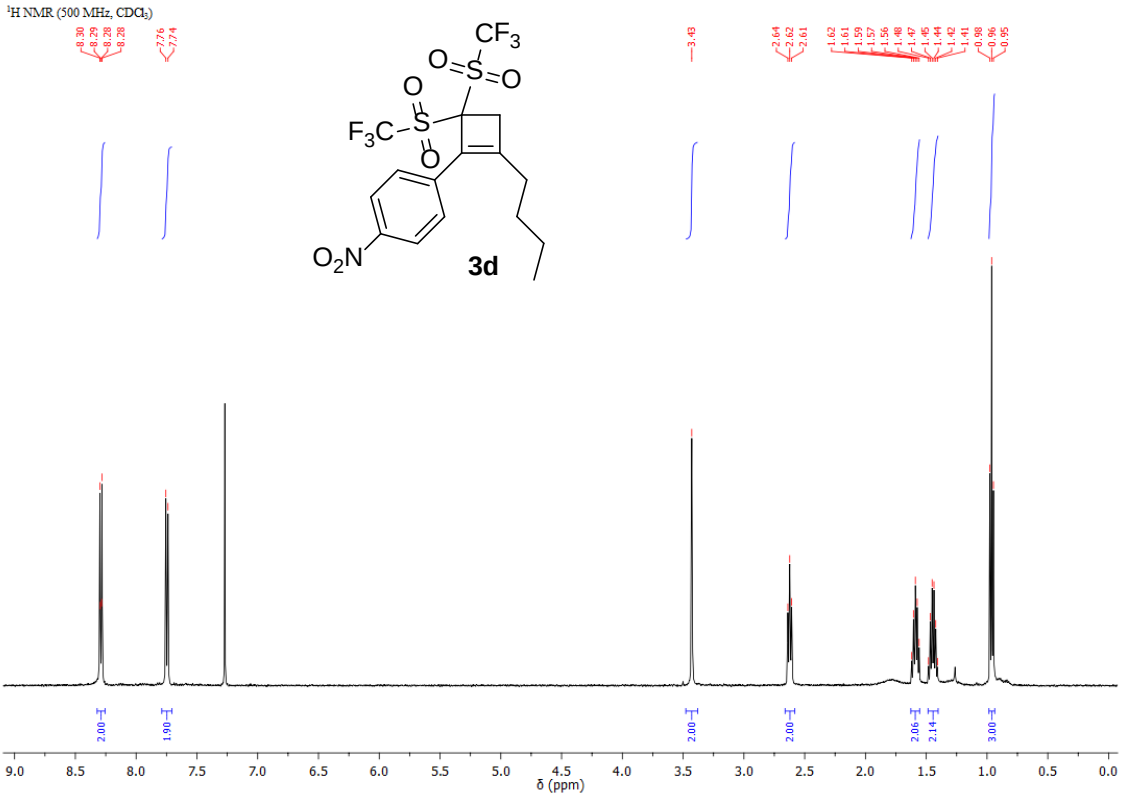


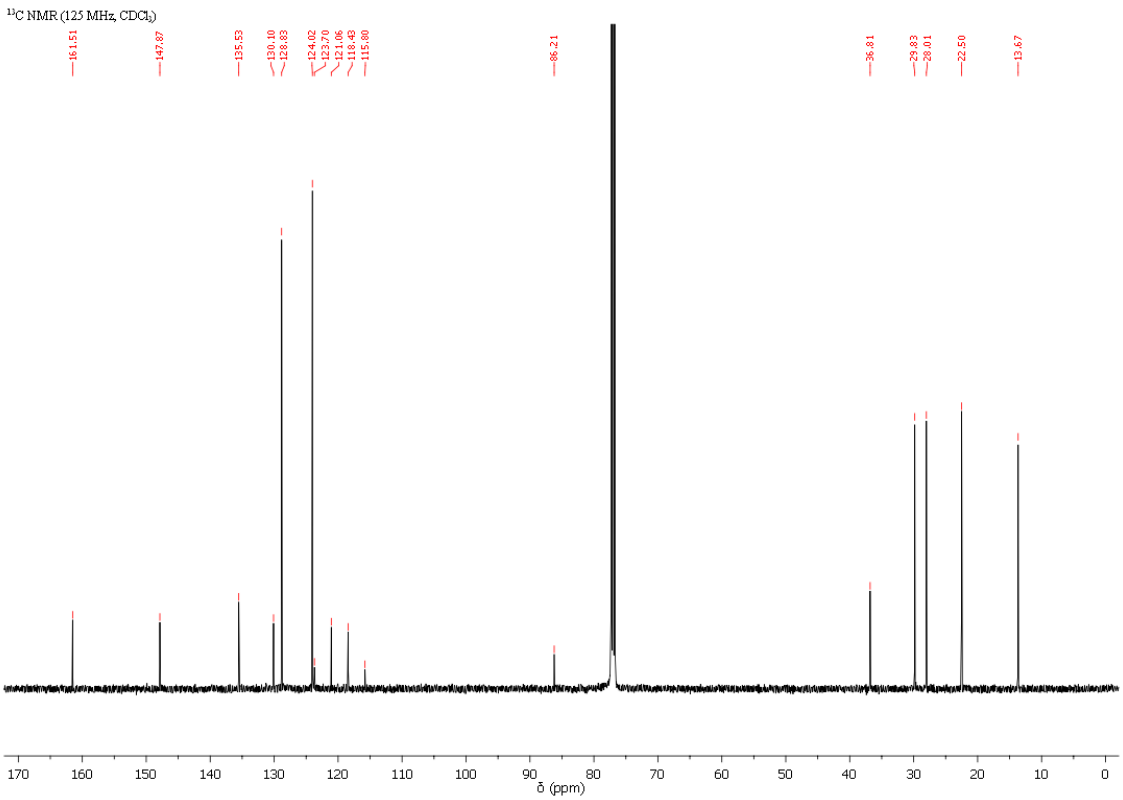
^{13}C NMR (75 MHz, $CDCl_3$)



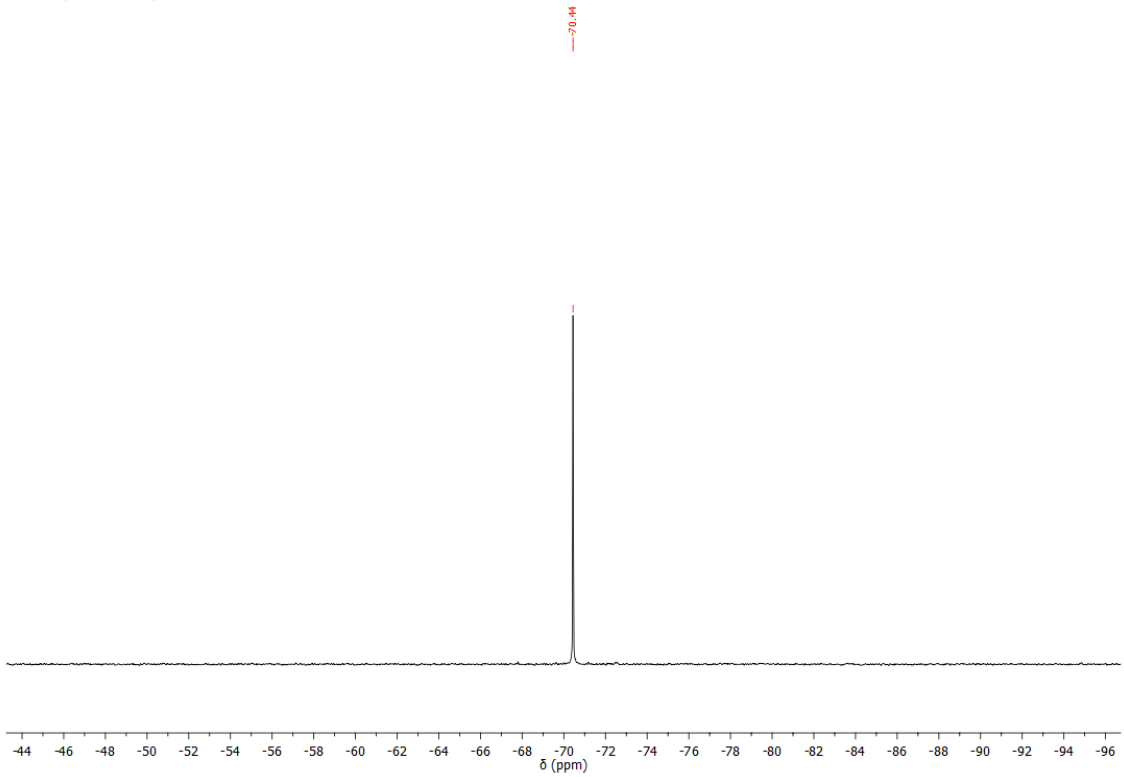
^{19}F NMR (282 MHz, $CDCl_3$)



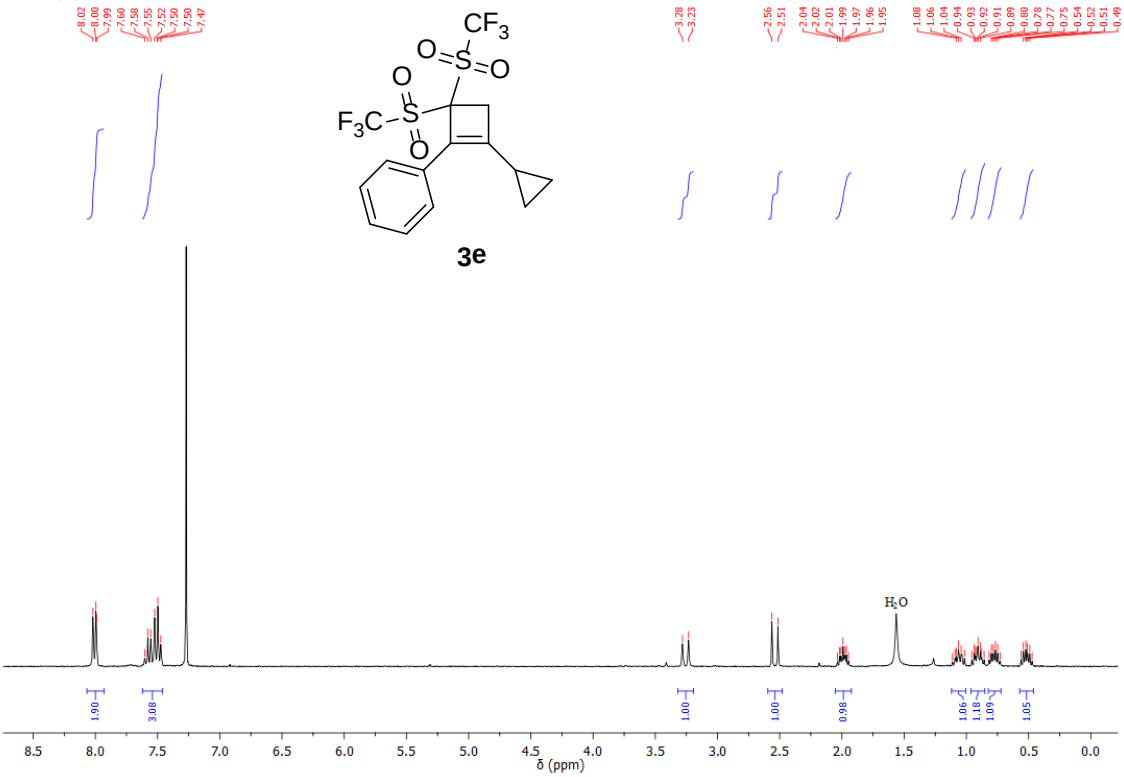

^{1}H NMR (500 MHz, CDCl$_3$)
8.30
8.29
8.28
8.28
7.76
7.74
3.43
2.64
2.62
2.61
1.62
1.61
1.59
1.57
1.56
1.48
1.47
1.45
1.44
1.42
1.41
0.98
0.96
0.95
CF$_3$
O
S
O
O
F$_3$C
S
O
O$_2$N
3d
2.00
1.90
2.00
2.00
2.06
2.14
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)


^{13}C NMR (125 MHz, CDCl$_3$)
161.51
147.87
135.53
130.10
128.83
124.02
123.70
121.06
118.43
115.80
86.21
36.81
29.83
28.01
22.50
13.67
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

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

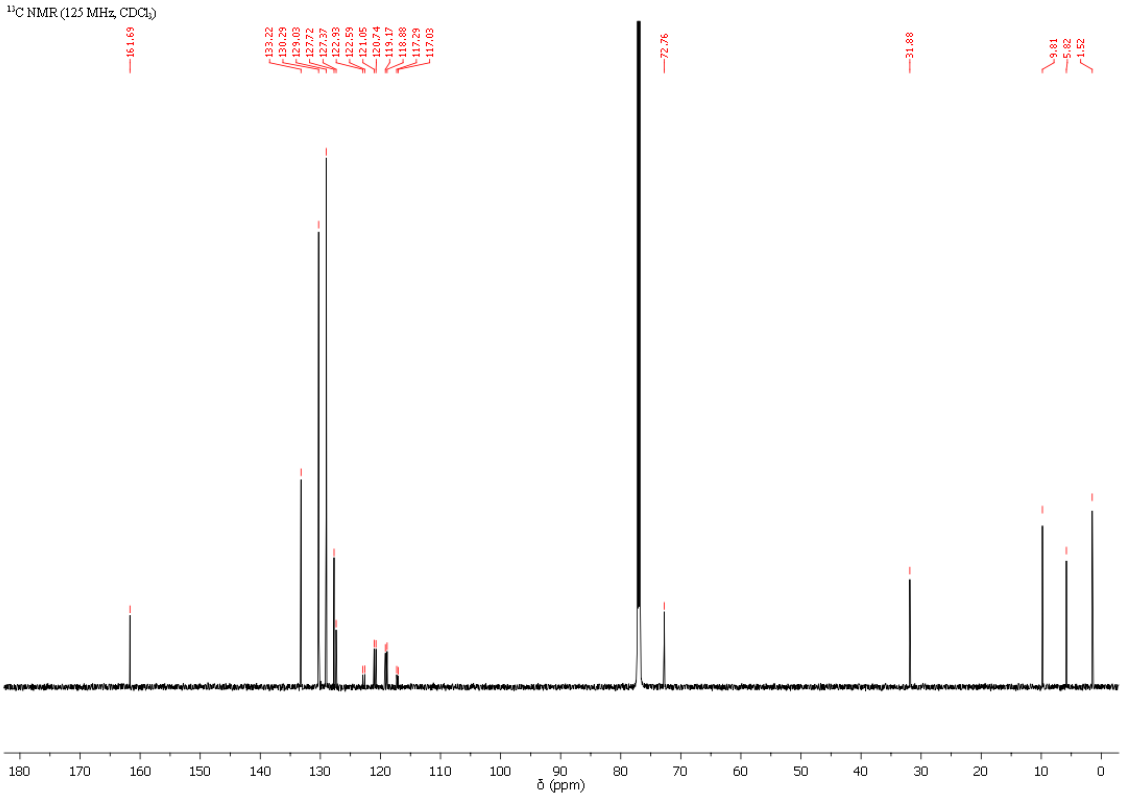


^{1}H NMR (300 MHz, $CDCl_3$)

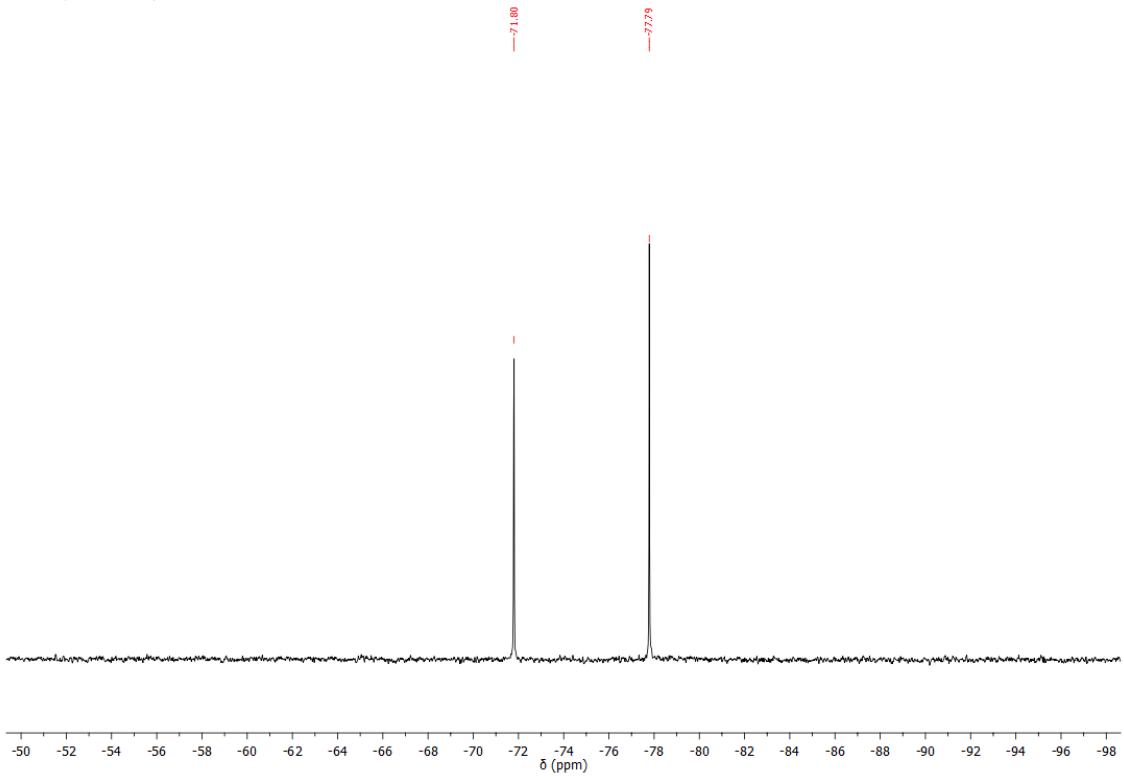


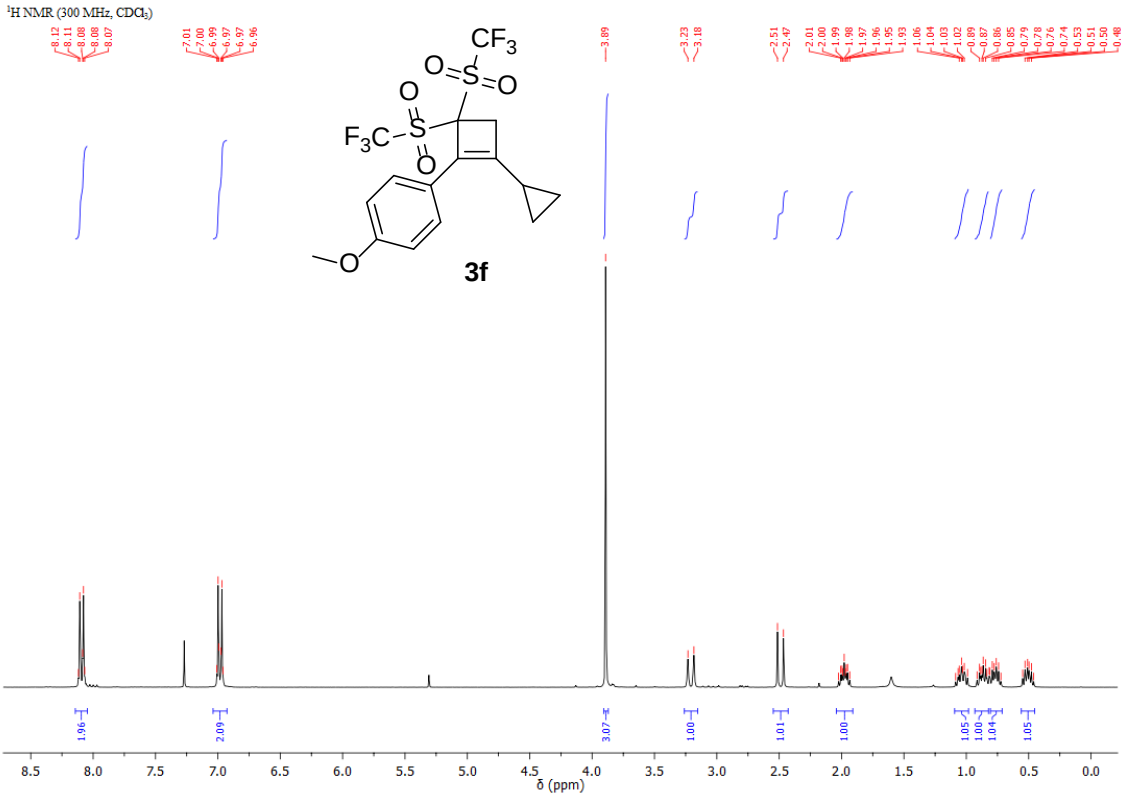
3e

^{13}C NMR (125 MHz, $CDCl_3$)

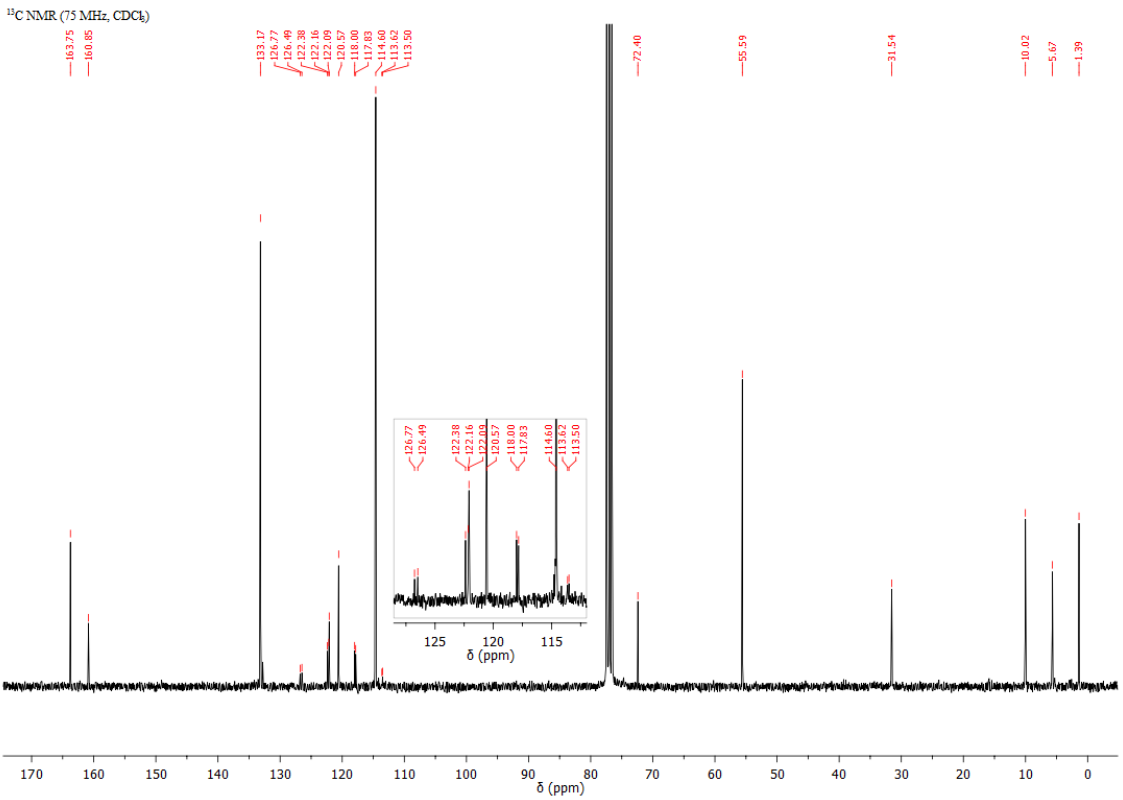


^{19}F NMR (282 MHz, $CDCl_3$)

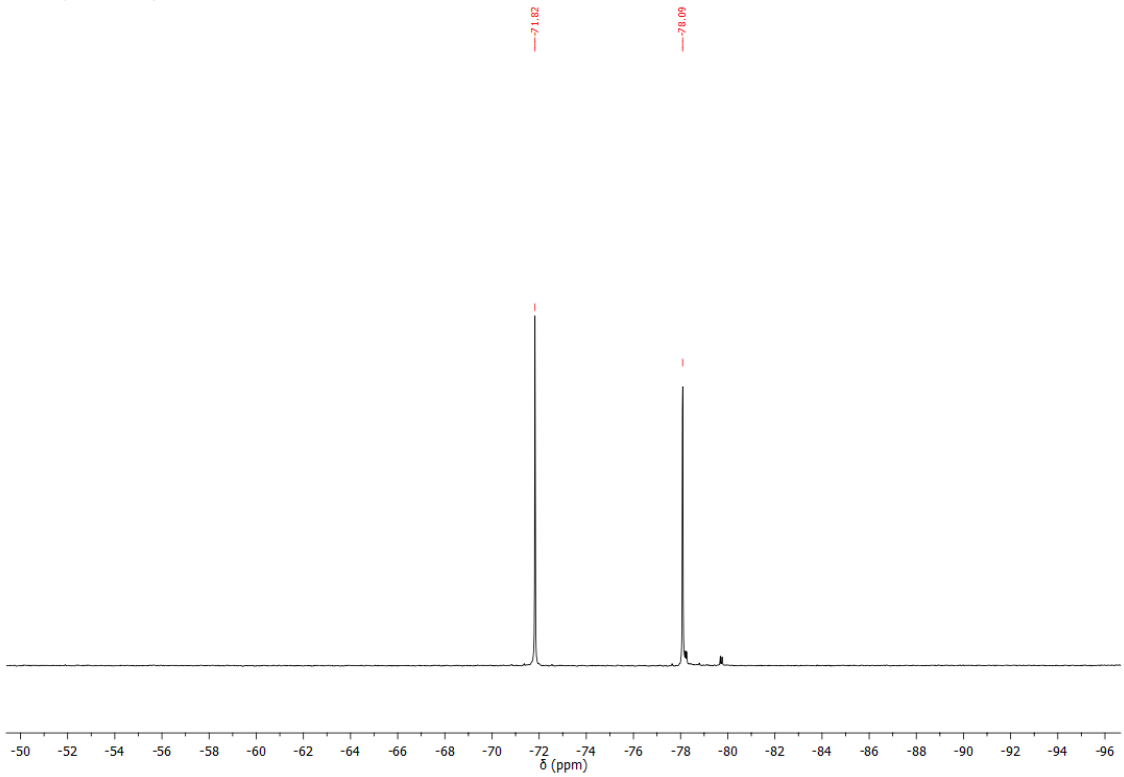




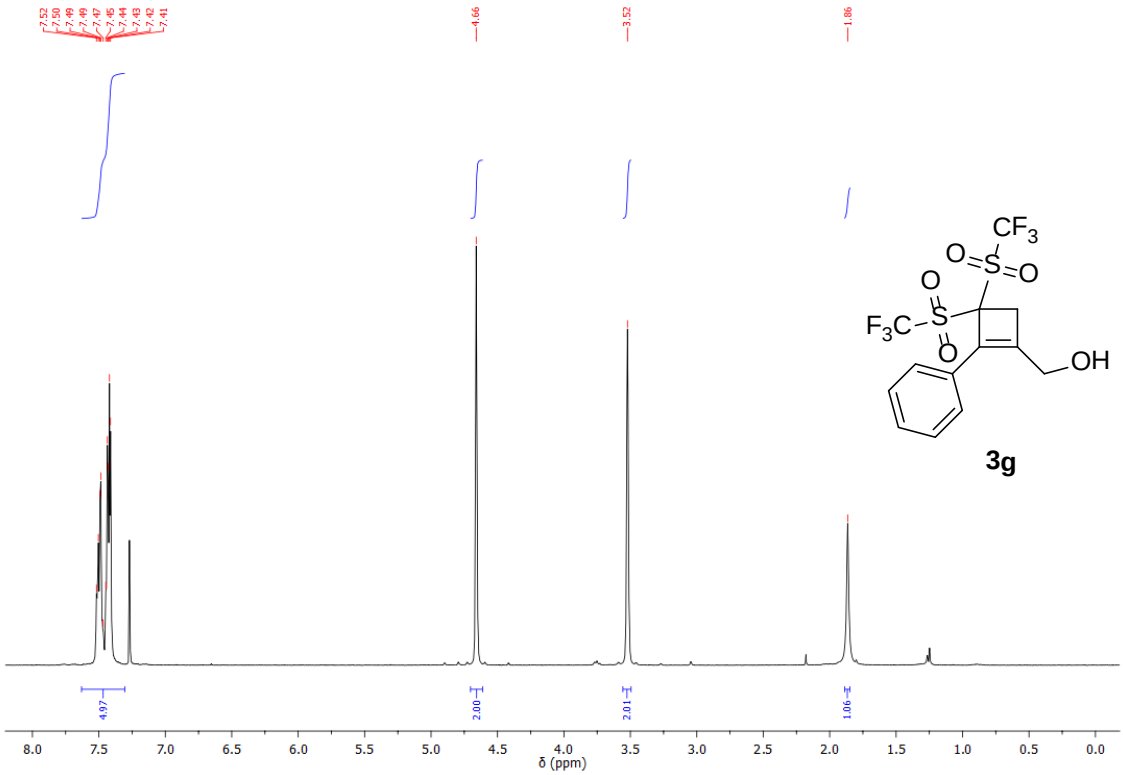
3f



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

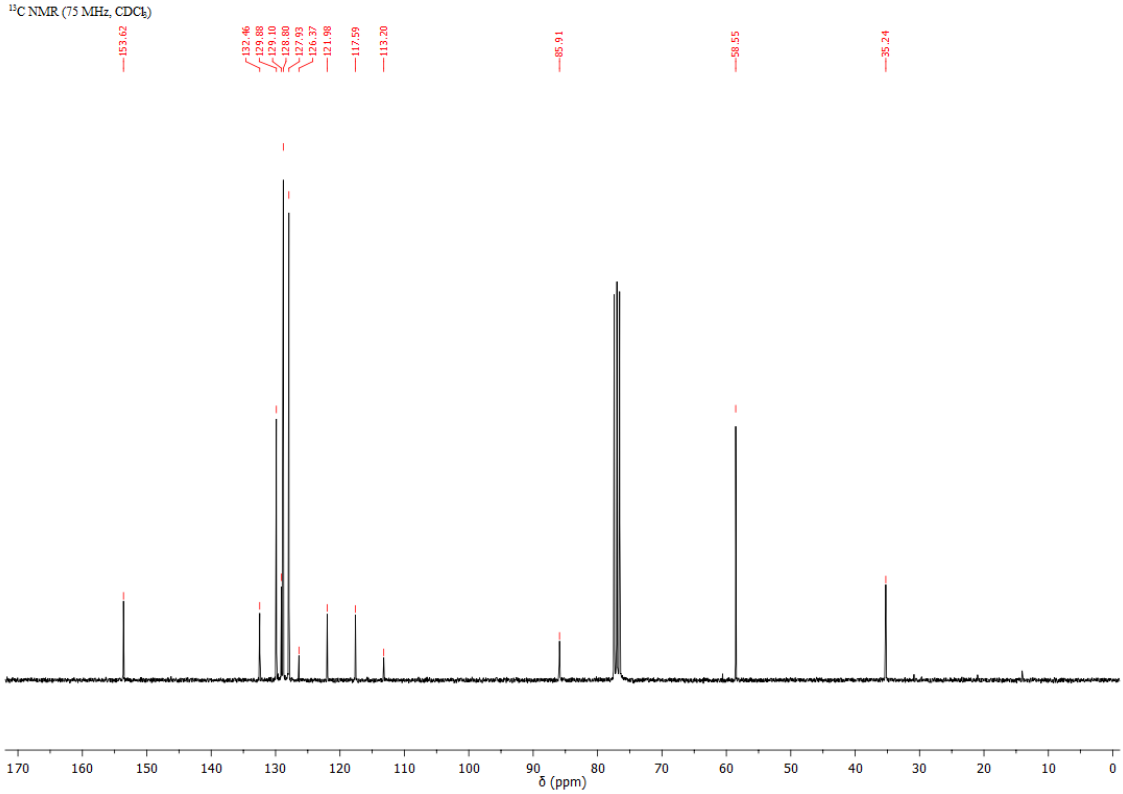


^{1}H NMR (300 MHz, $CDCl_3$)

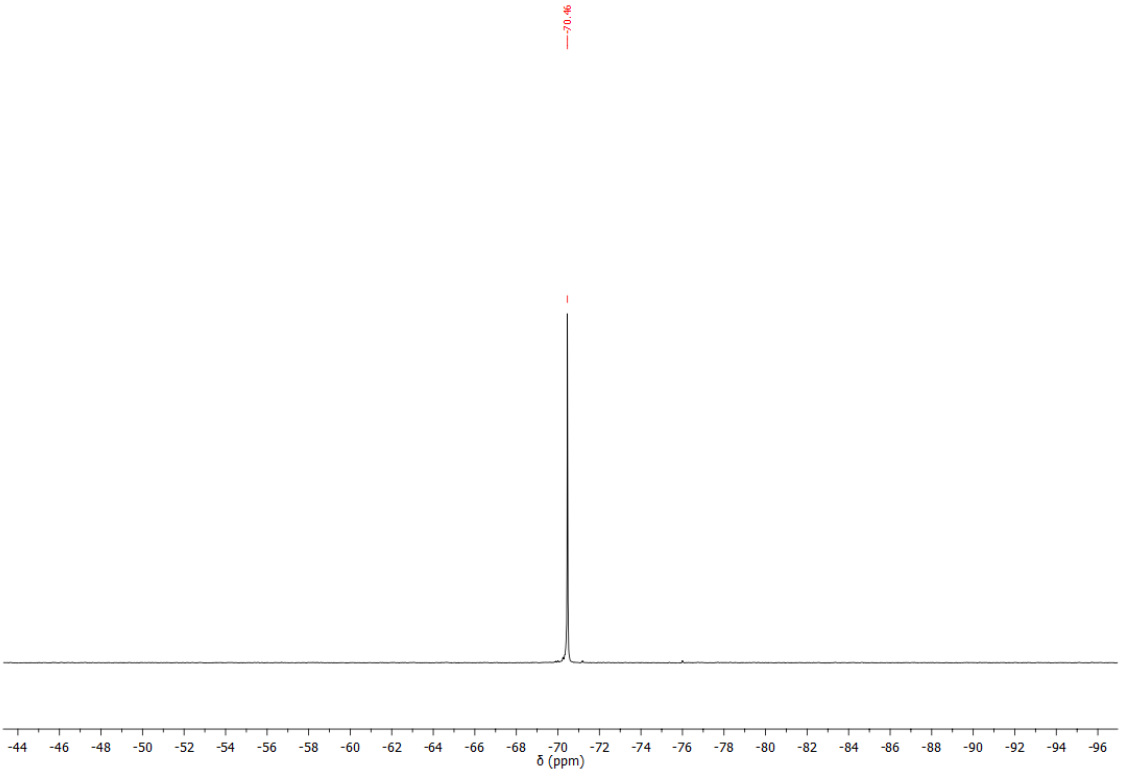


3g

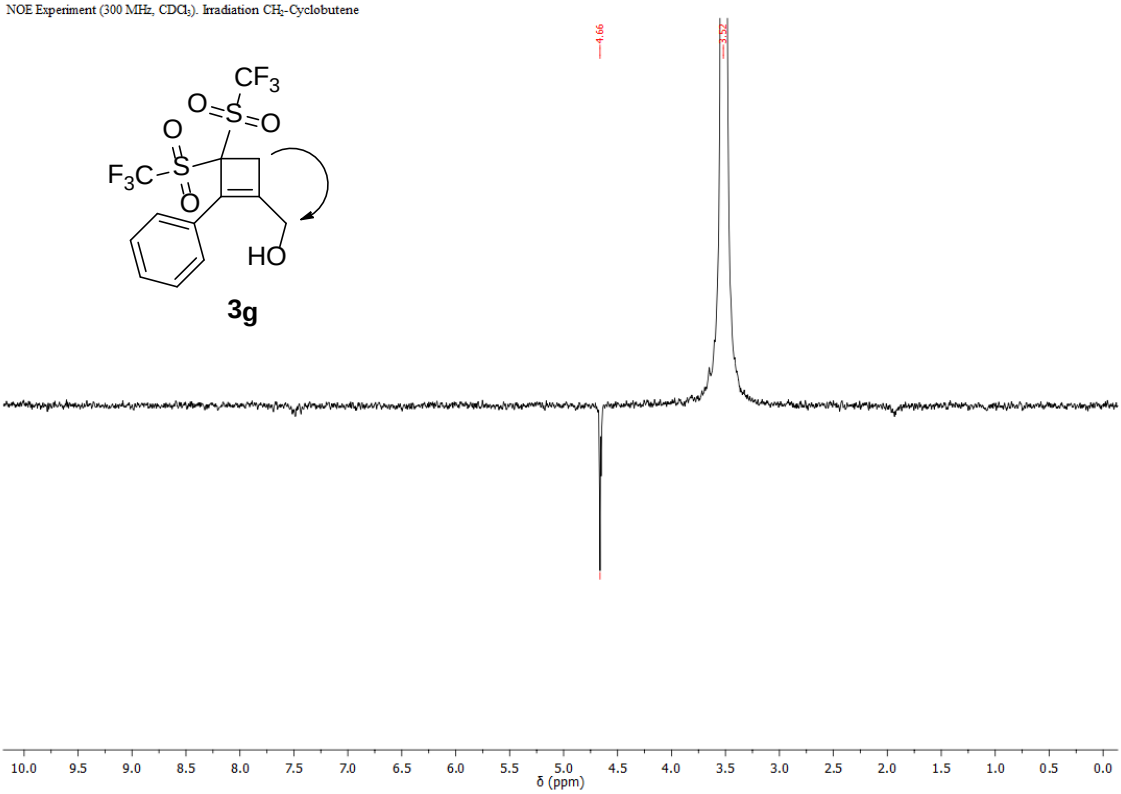
^{13}C NMR (75 MHz, $CDCl_3$)



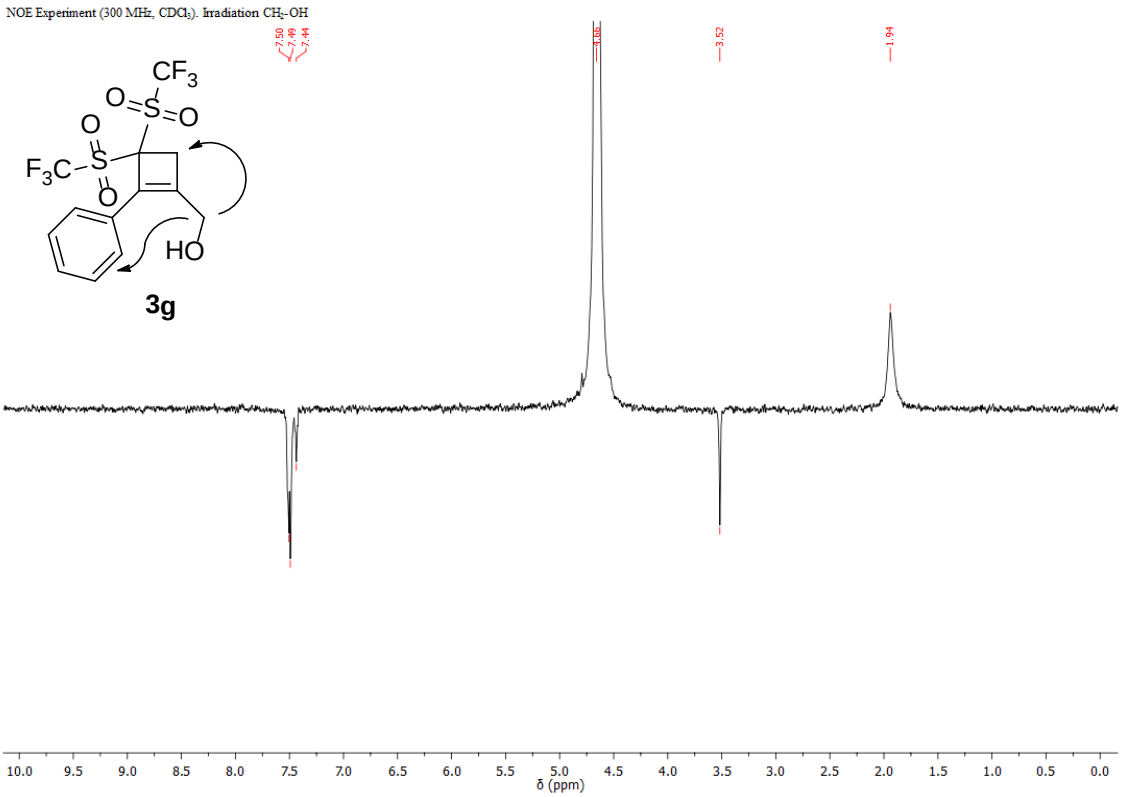
^{19}F NMR (282 MHz, $CDCl_3$)



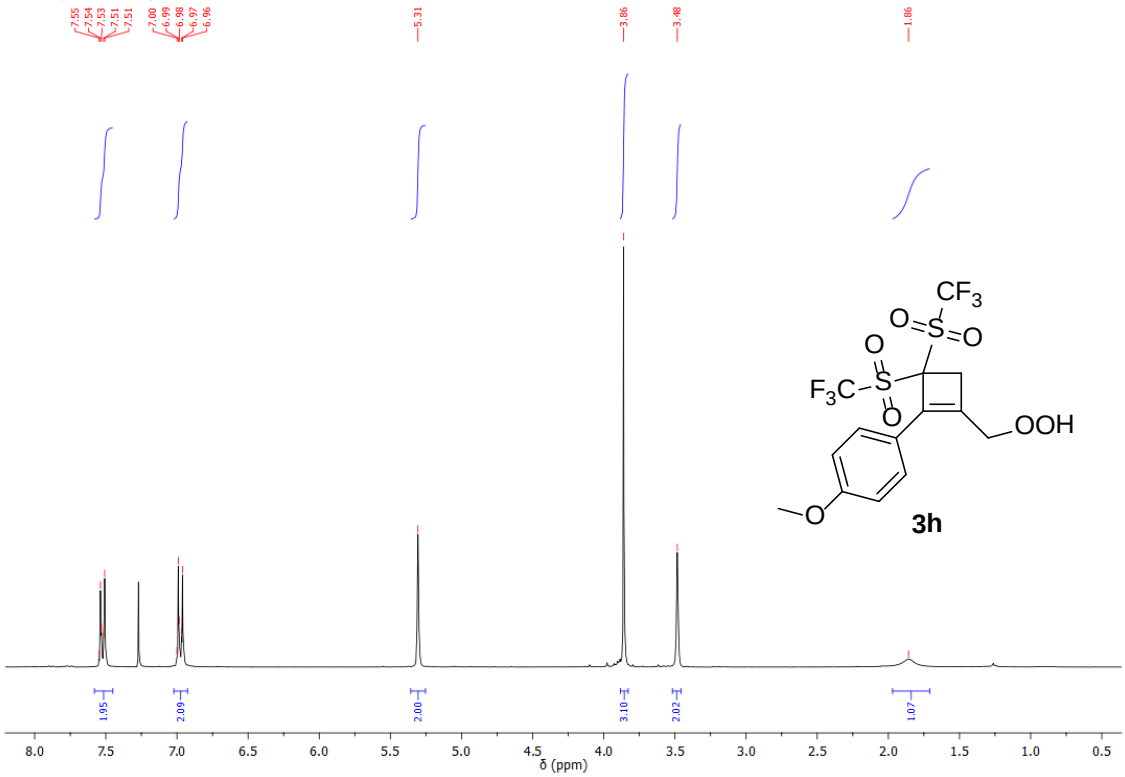
NOE Experiment (300 MHz, $CDCl_3$). Irradiation CH_2-Cyclobutene



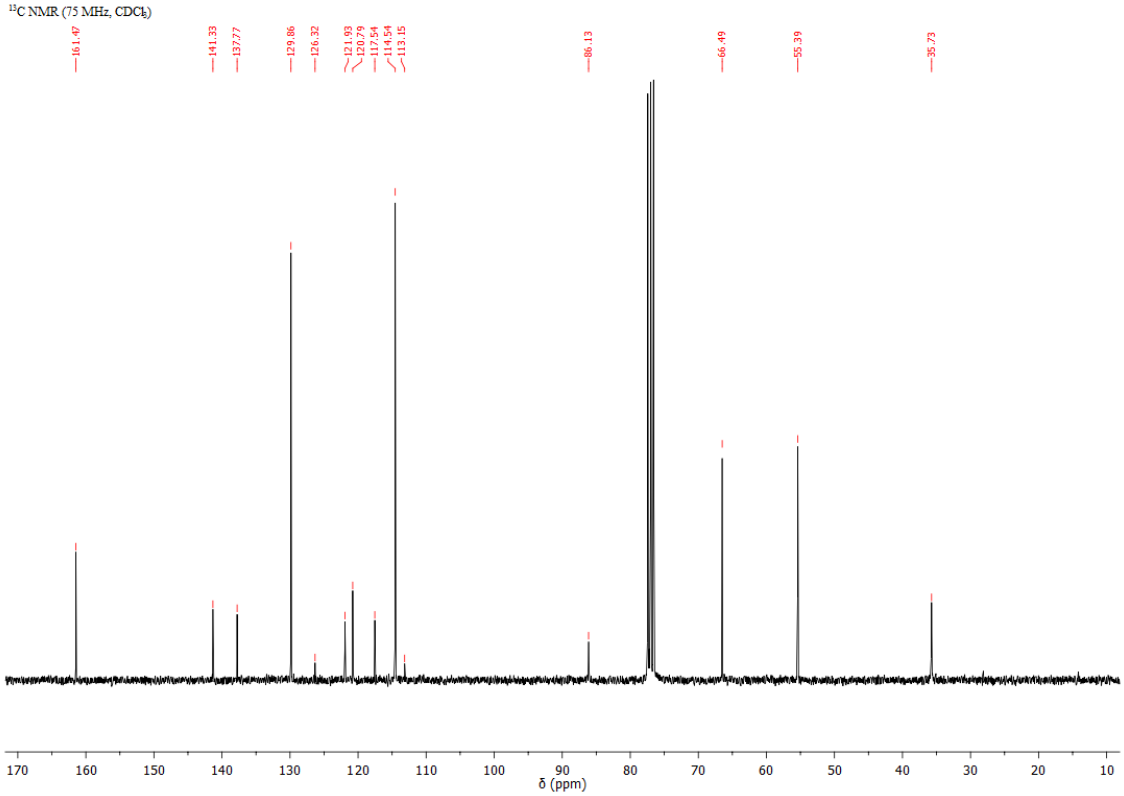
3g


NOE Experiment (300 MHz, CDCl3). Irradiation CH2-OH
7.50
7.49
7.44
5.06
3.52
1.94
CF3
O
S
O
O
F3C
S
O
HO
3g
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
δ (ppm)

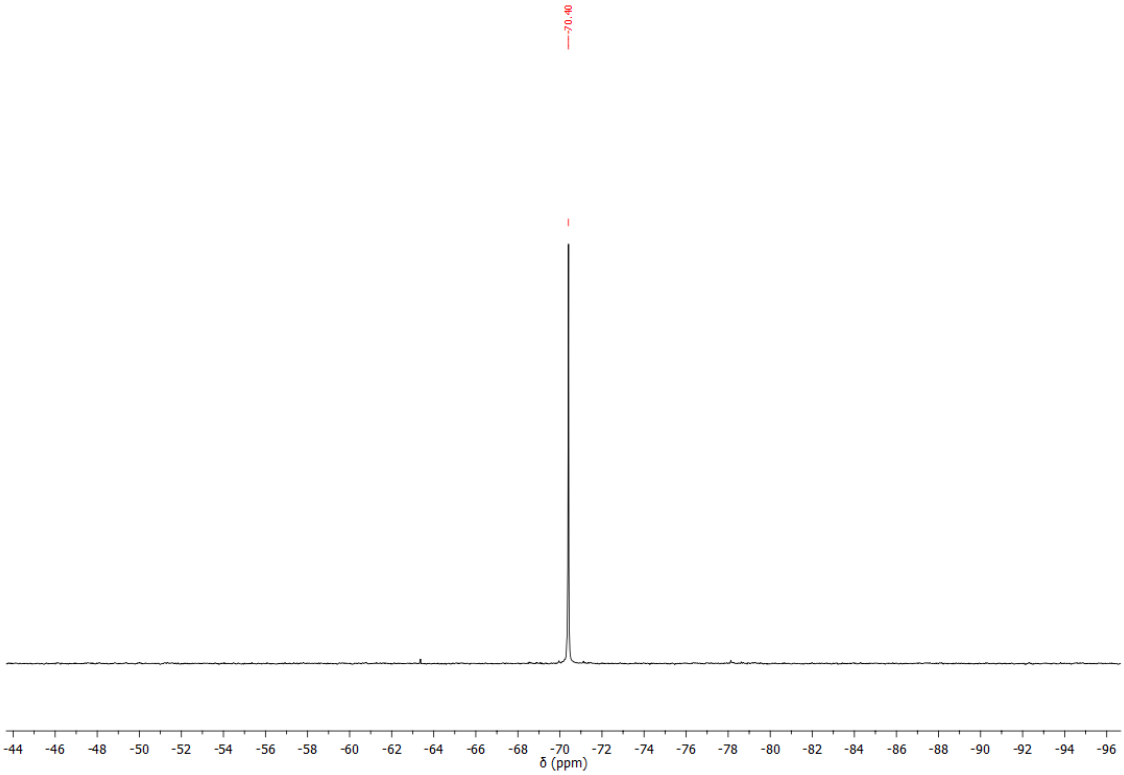
^{1}H NMR (300 MHz, $CDCl_3$)



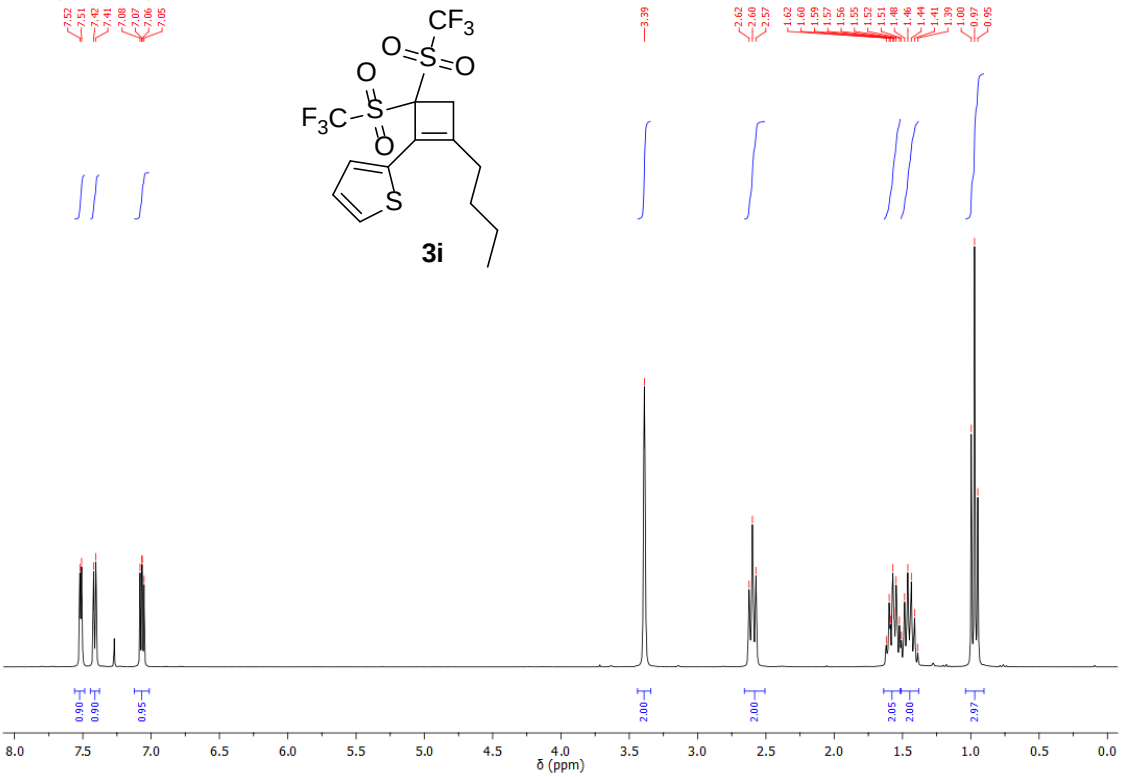
^{13}C NMR (75 MHz, $CDCl_3$)



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

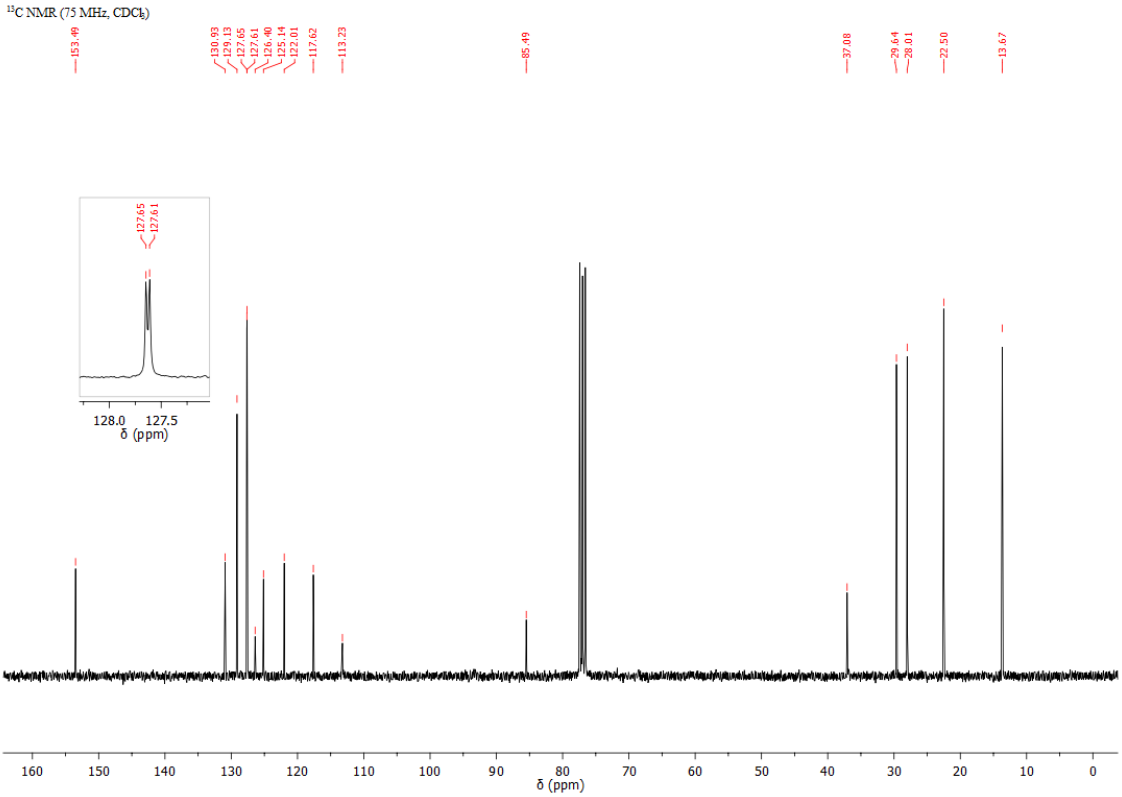


^{1}H NMR (300 MHz, $CDCl_3$)

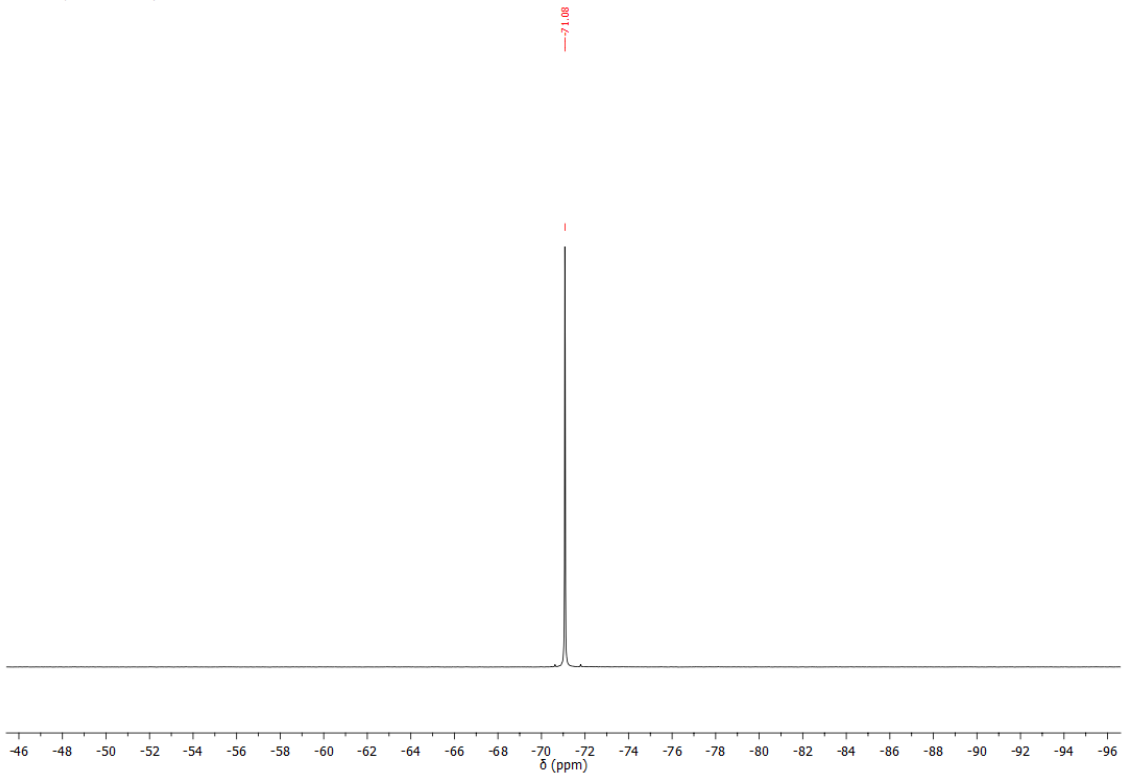


3i

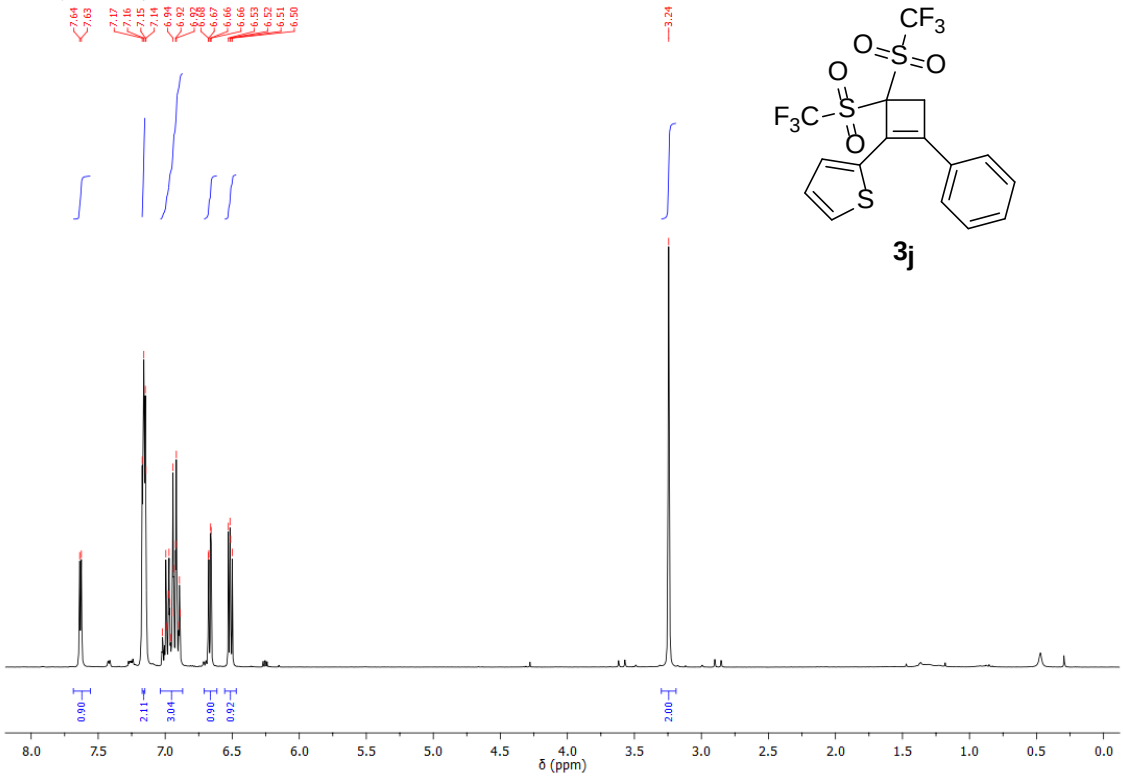
^{13}C NMR (75 MHz, $CDCl_3$)



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

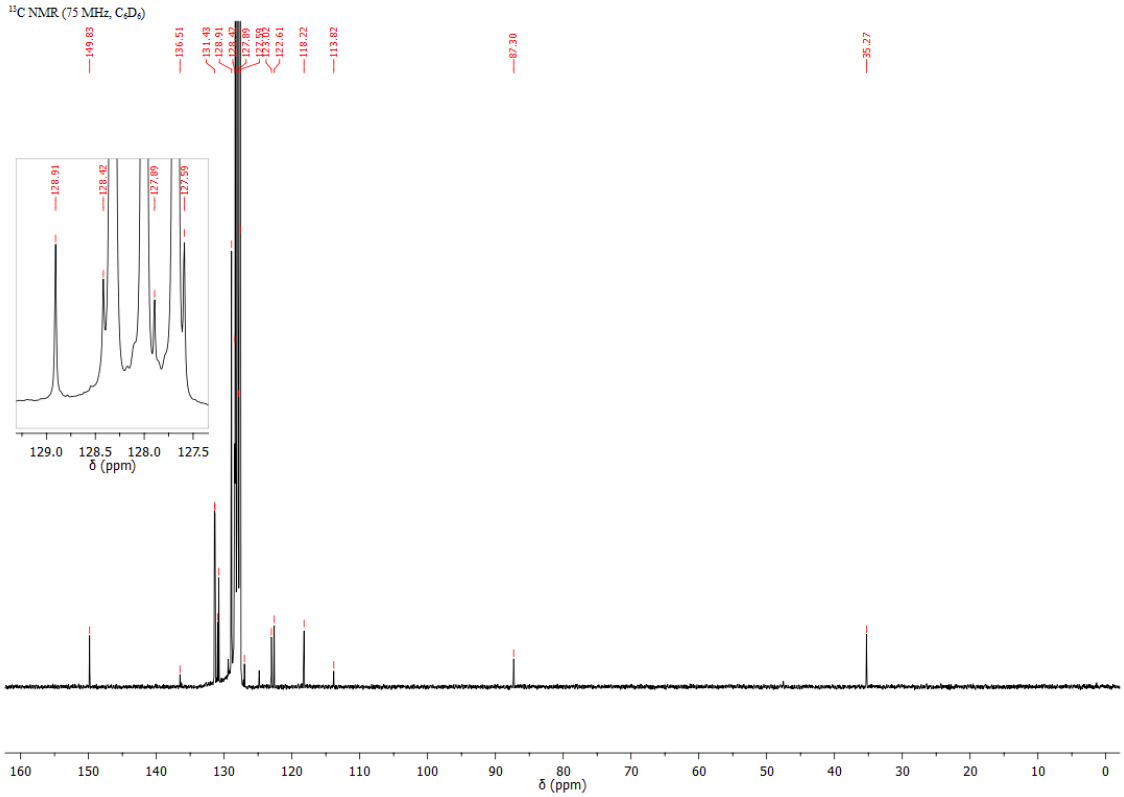


^{1}H NMR (300 MHz, C_6D_6)

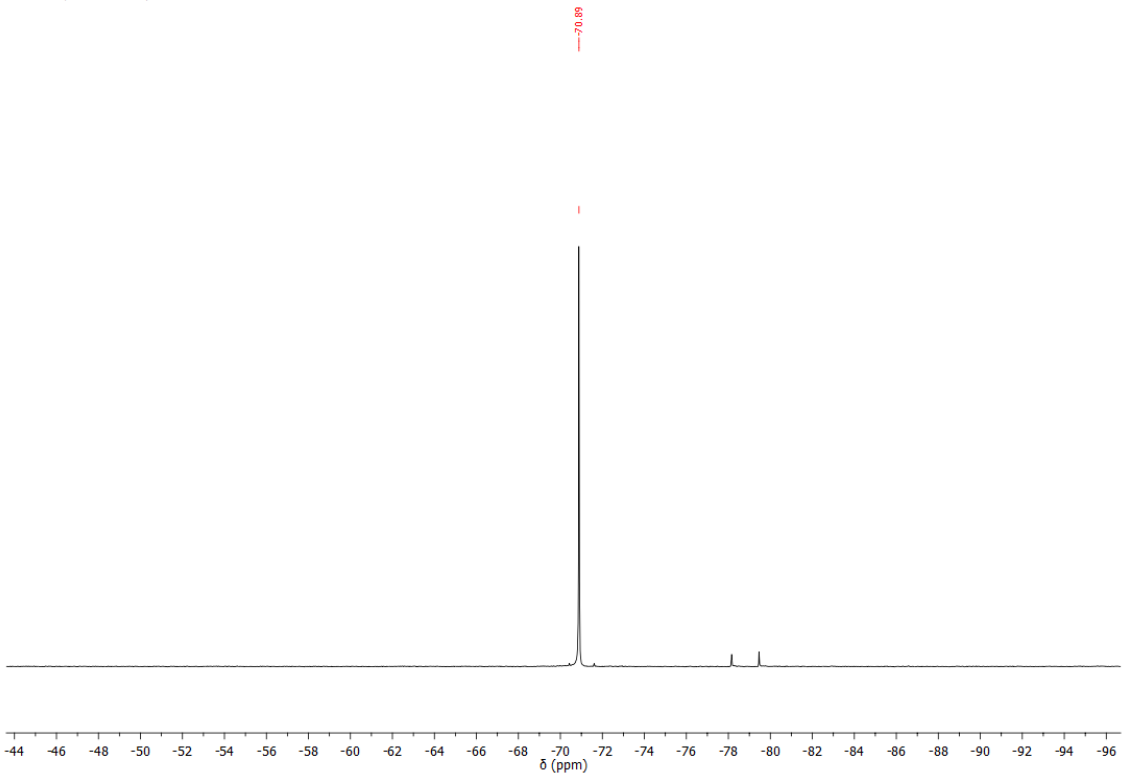


3j

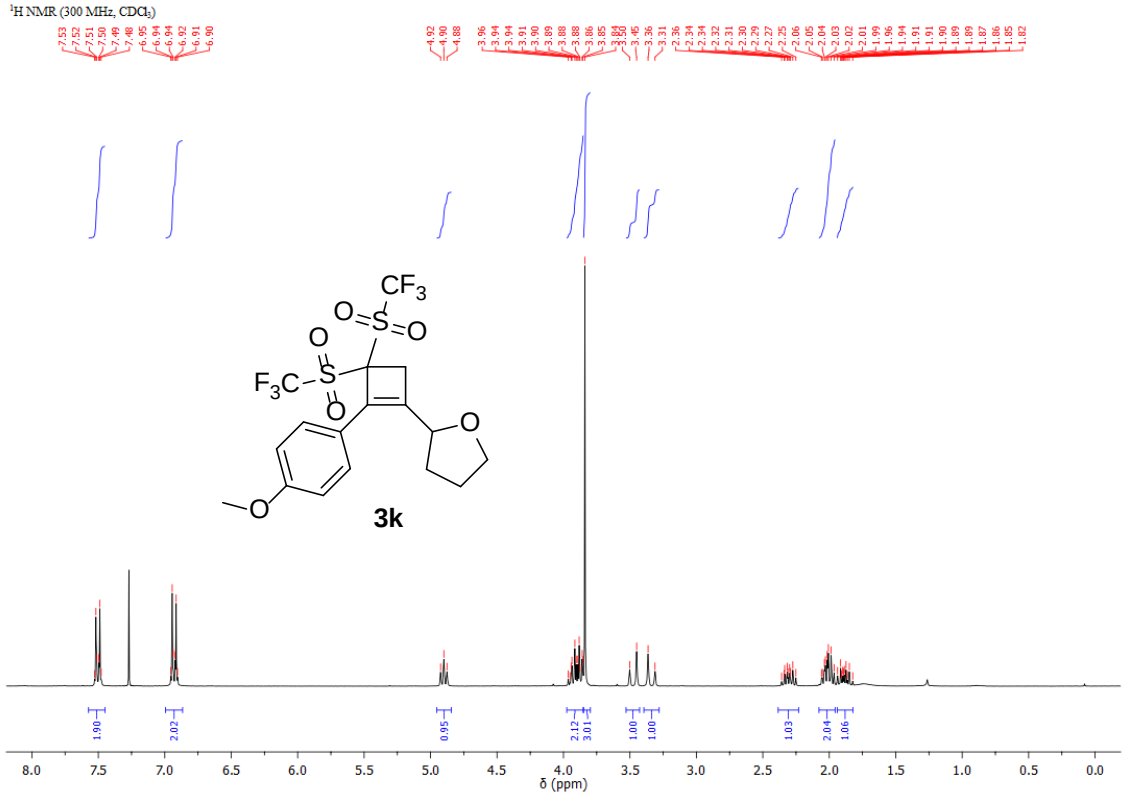
^{13}C NMR (75 MHz, C_6D_6)



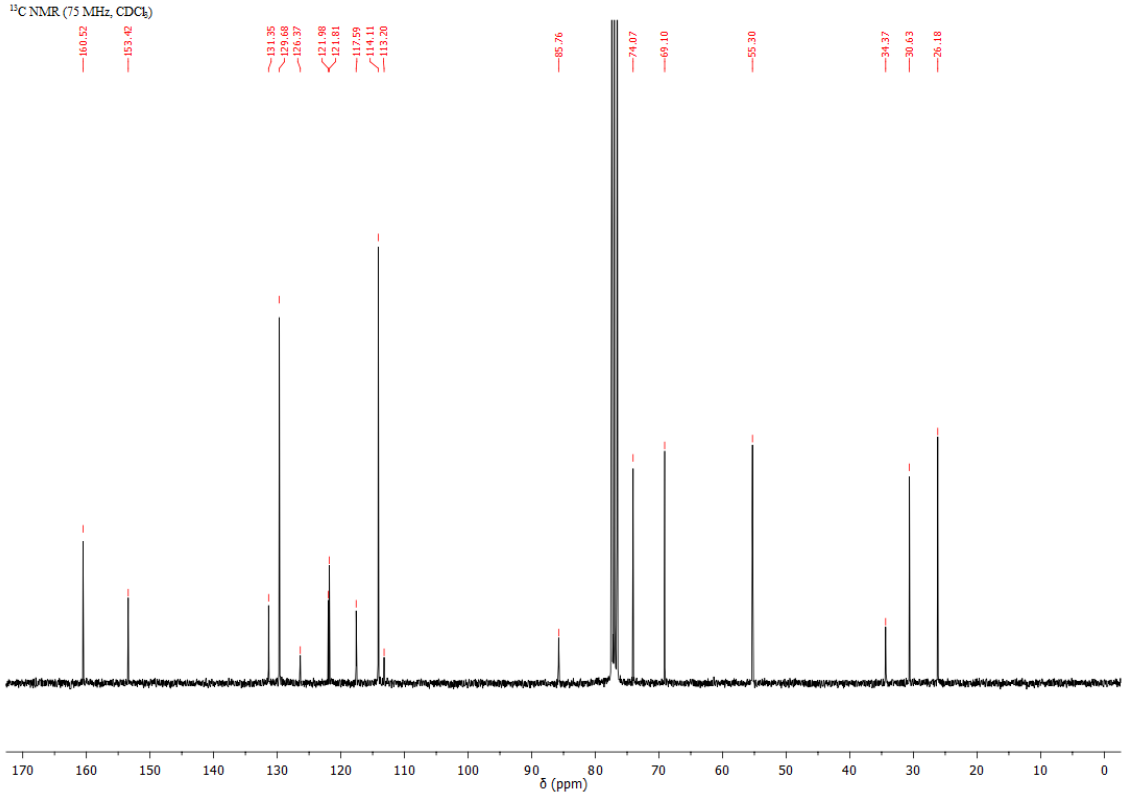
^{19}F NMR (282 MHz, C_6D_6)



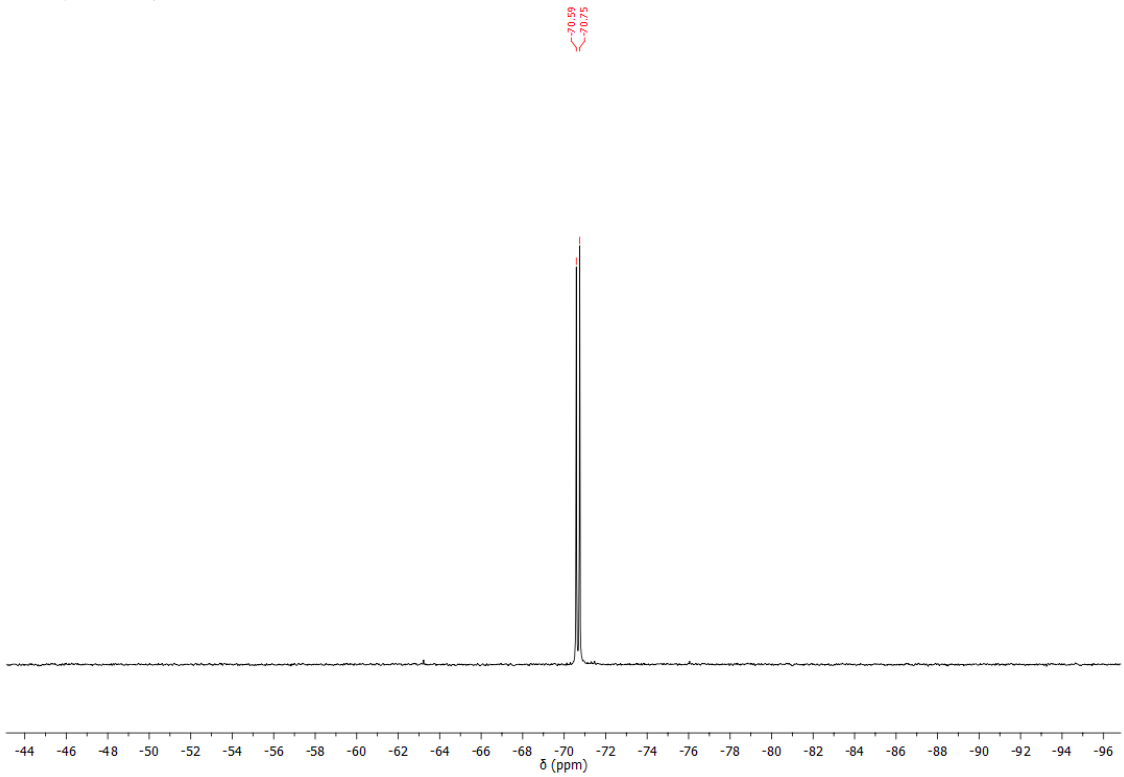
^{1}H NMR (300 MHz, $CDCl_3$)



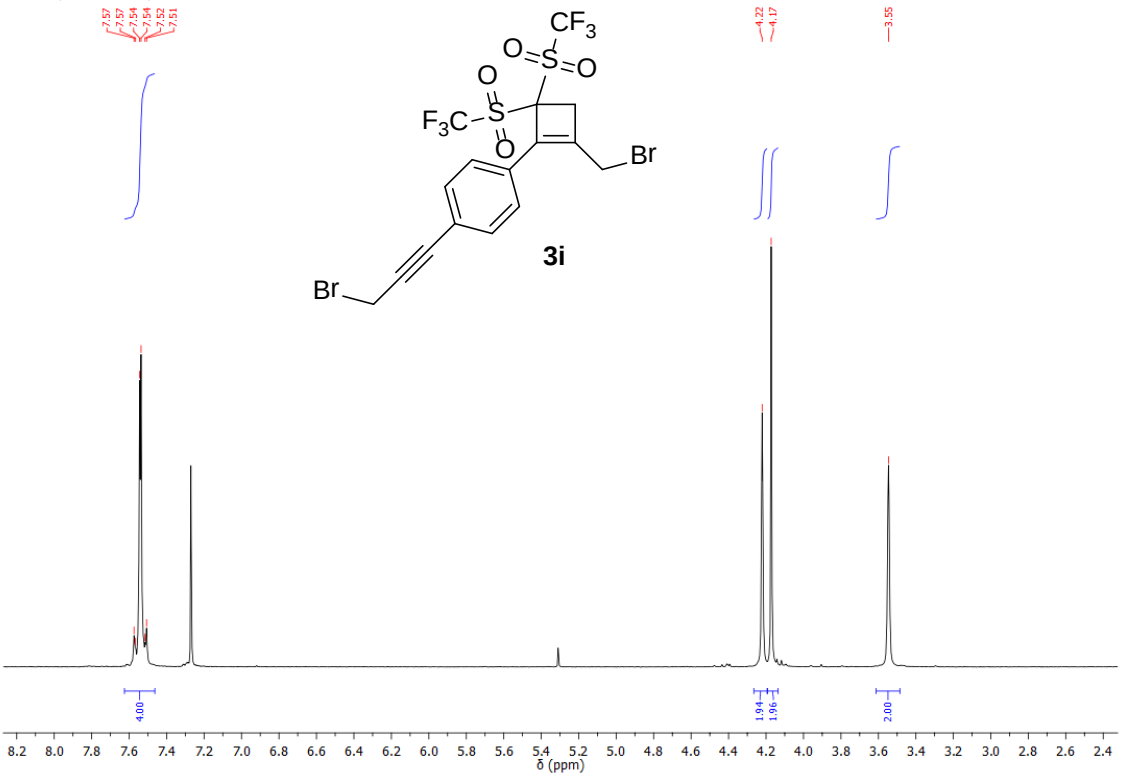
^{13}C NMR (75 MHz, $CDCl_3$)



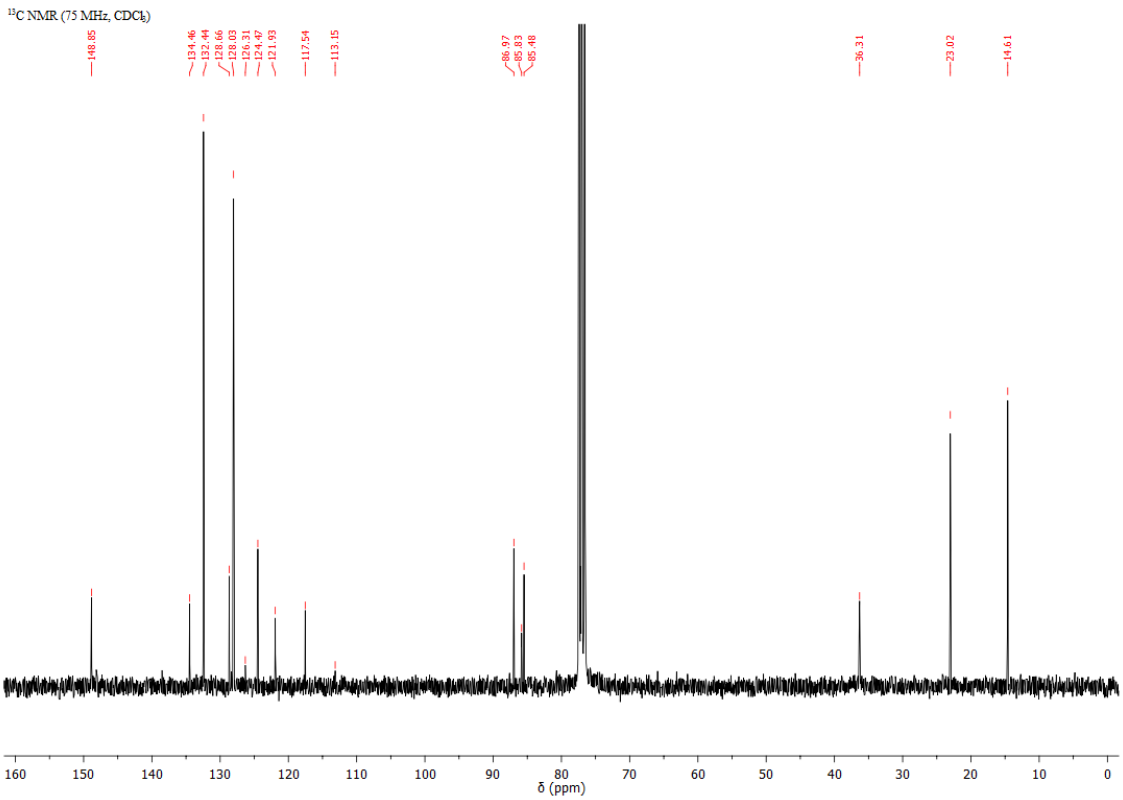
^{19}F NMR (282 MHz, $CDCl_3$)

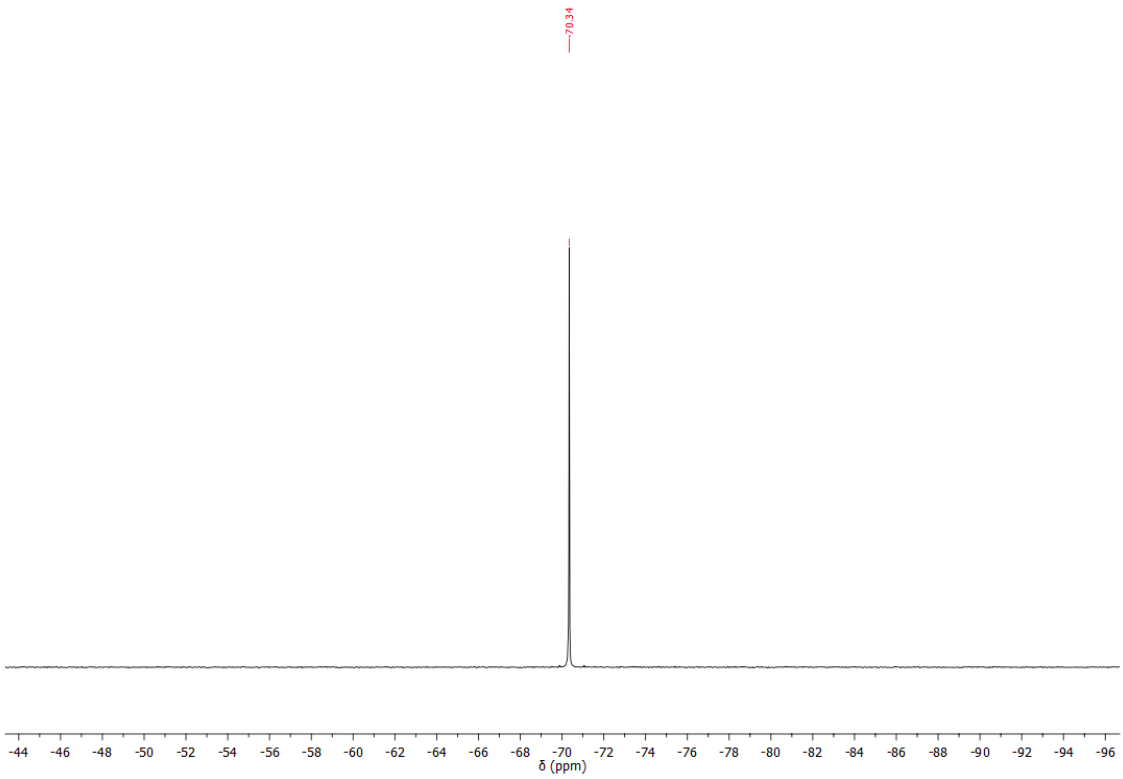


^{1}H NMR (300 MHz, $CDCl_3$)

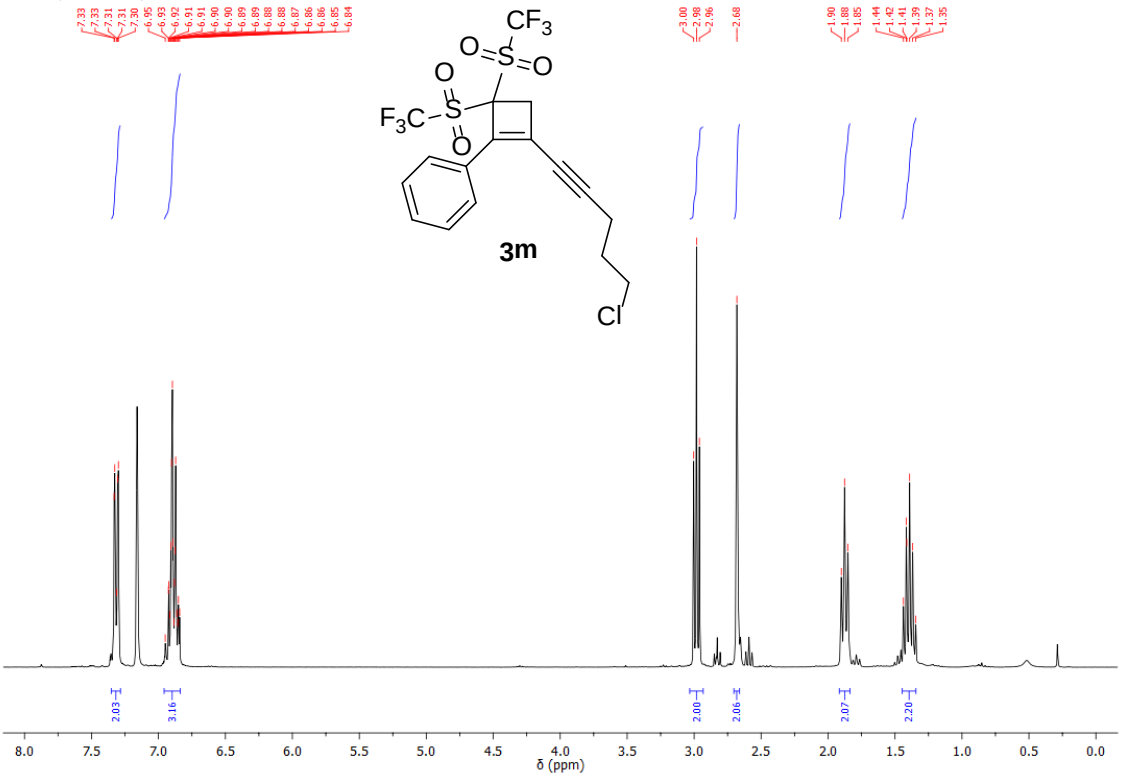


^{13}C NMR (75 MHz, $CDCl_3$)

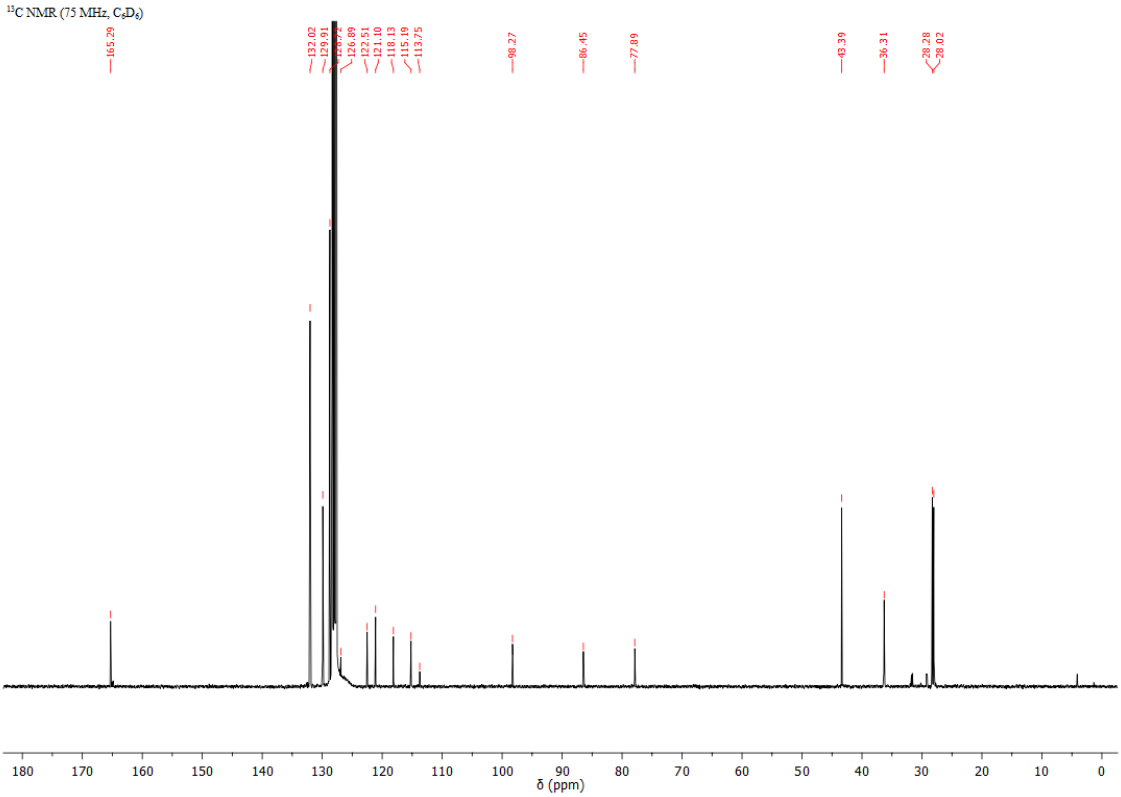



-70.34
-44 -46 -48 -50 -52 -54 -56 -58 -60 -62 -64 -66 -68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88 -90 -92 -94 -96
δ (ppm)

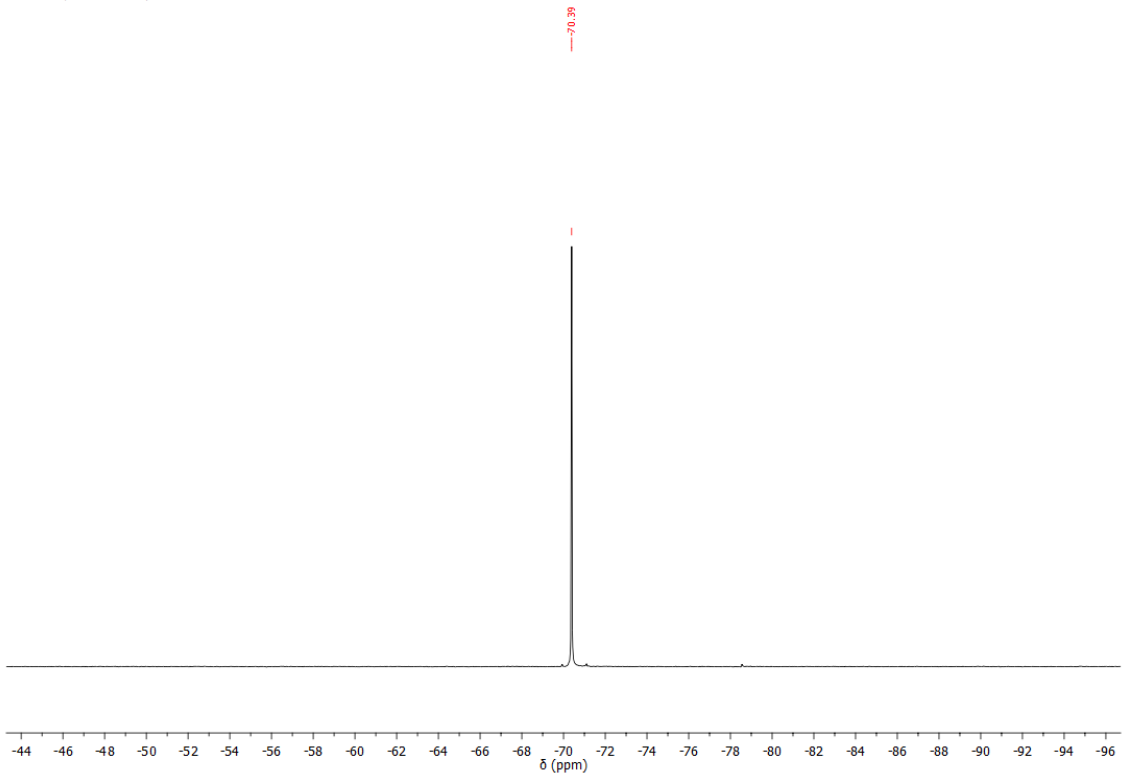
^{1}H NMR (300 MHz, C_6D_6)

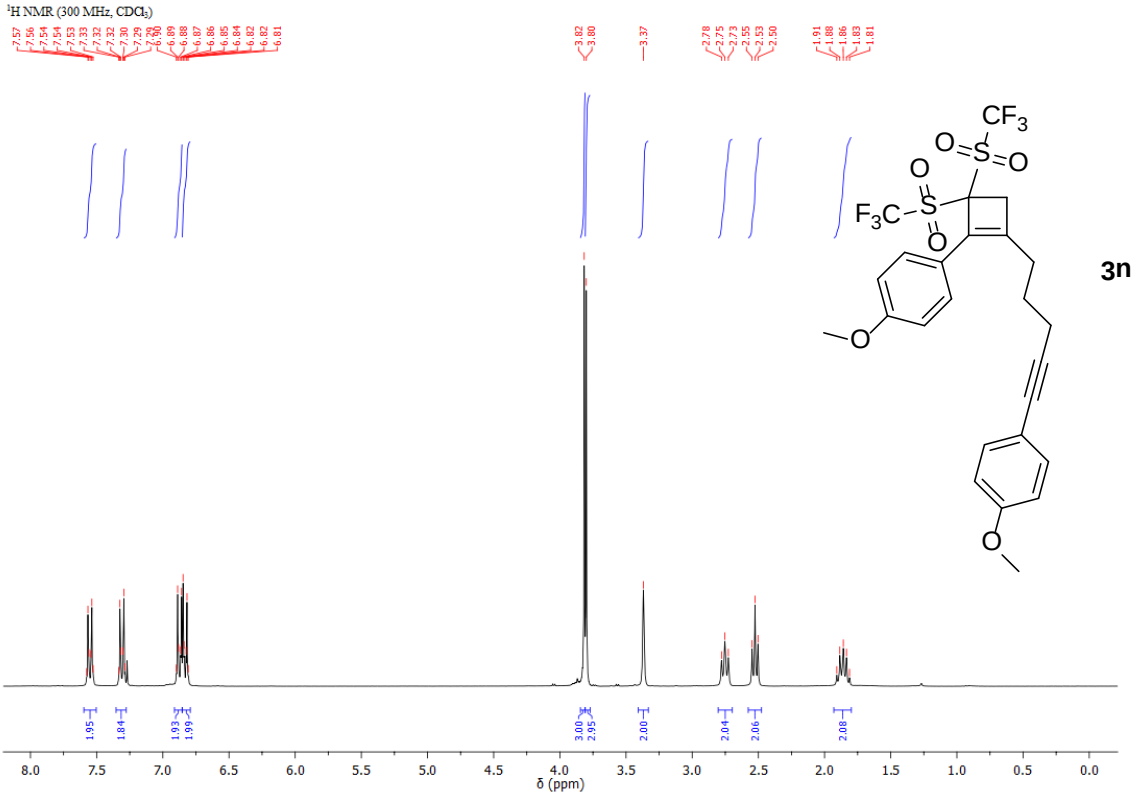


^{13}C NMR (75 MHz, C_6D_6)

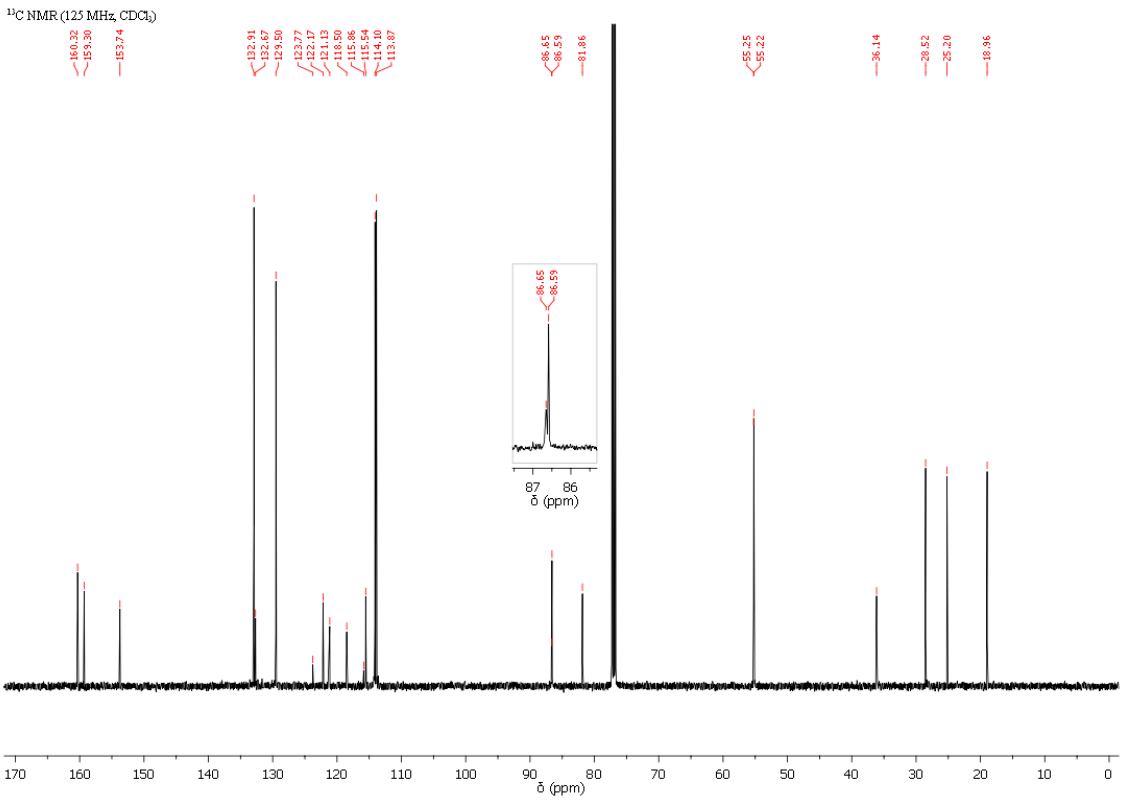


^{19}F NMR (282 MHz, C_6D_6)

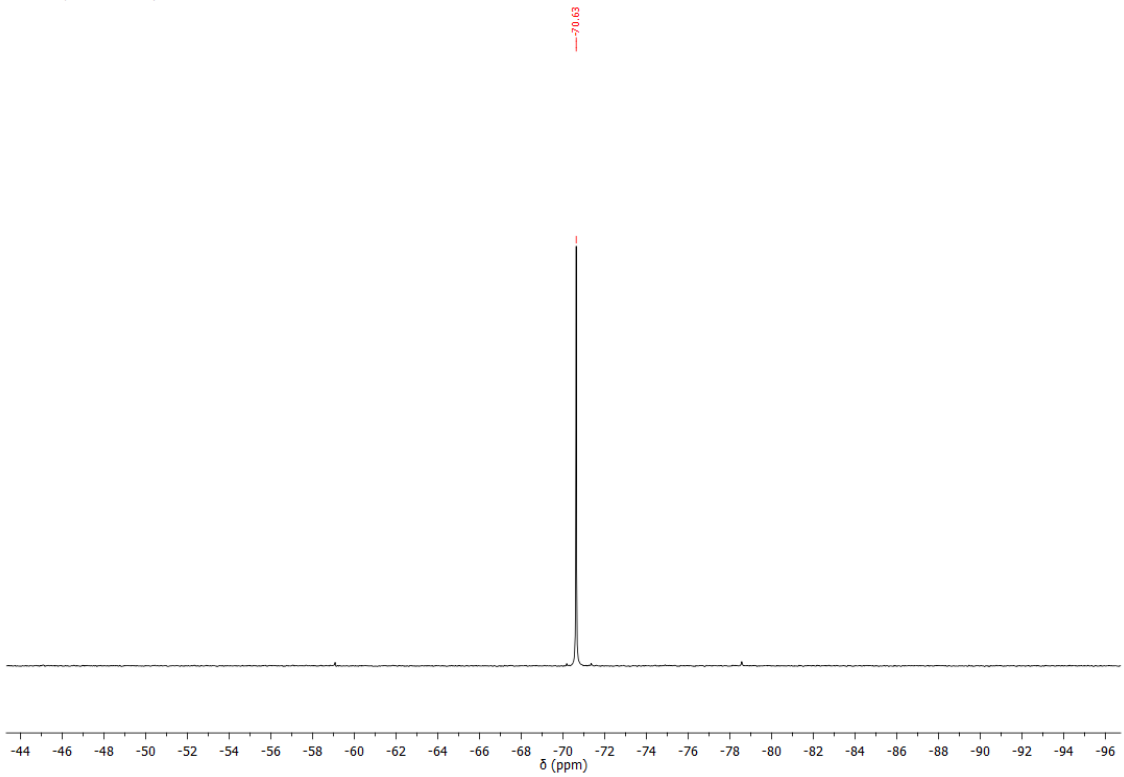




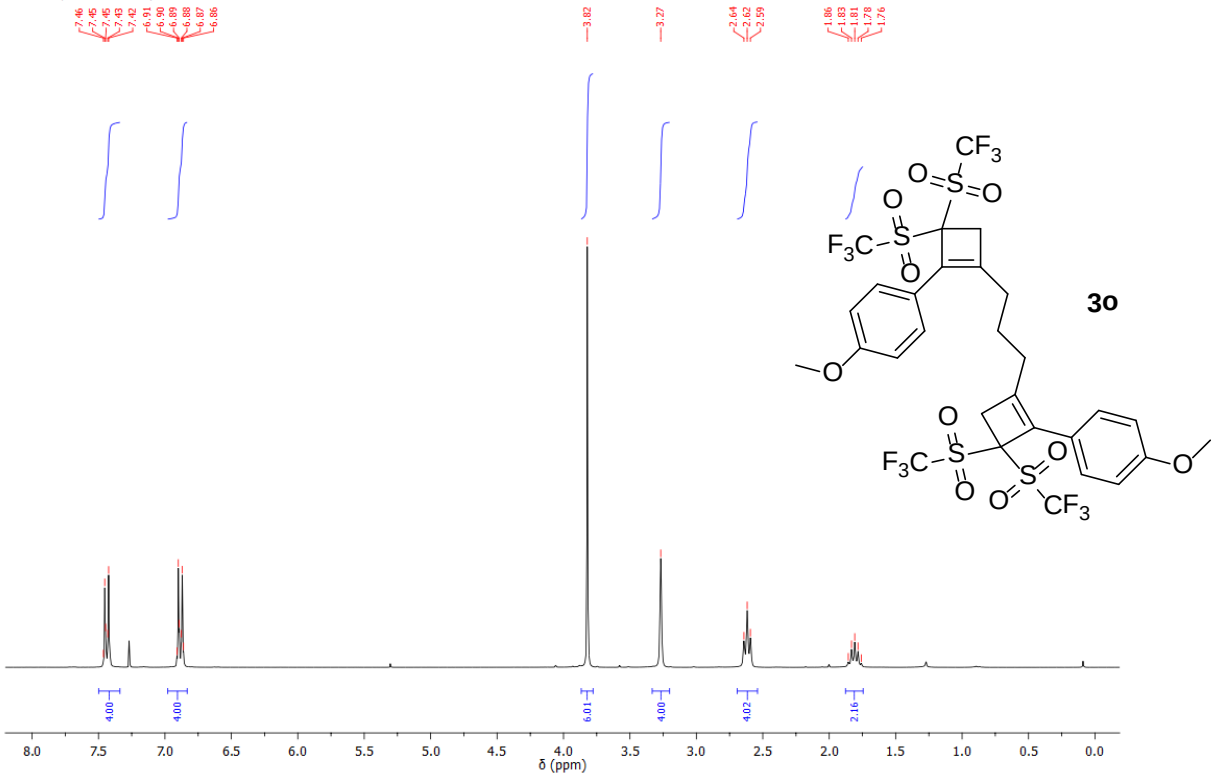
3n



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

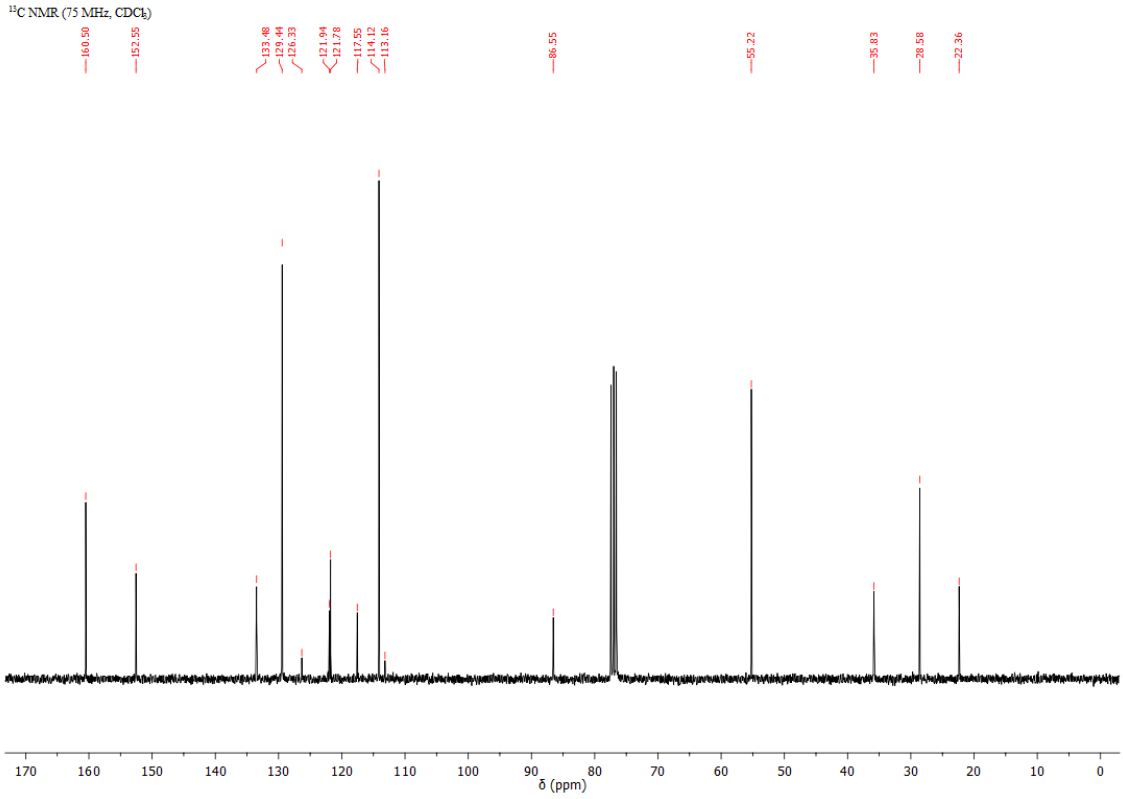


^{1}H NMR (300 MHz, $CDCl_3$)

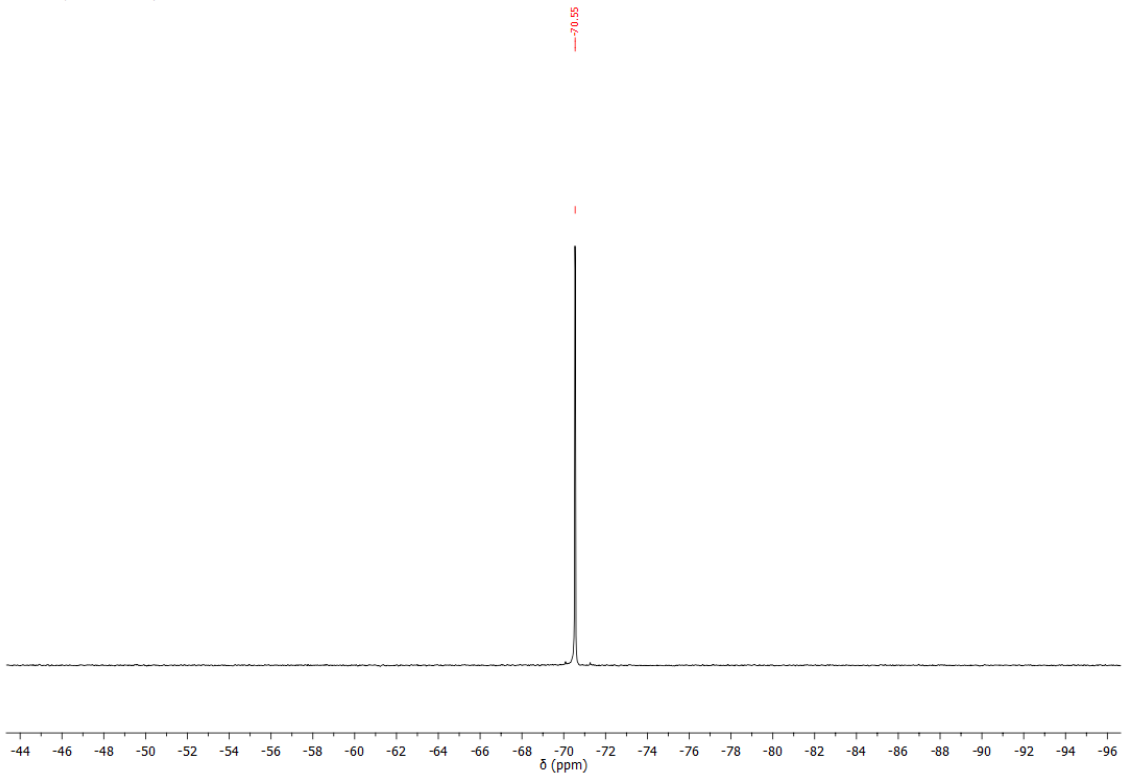


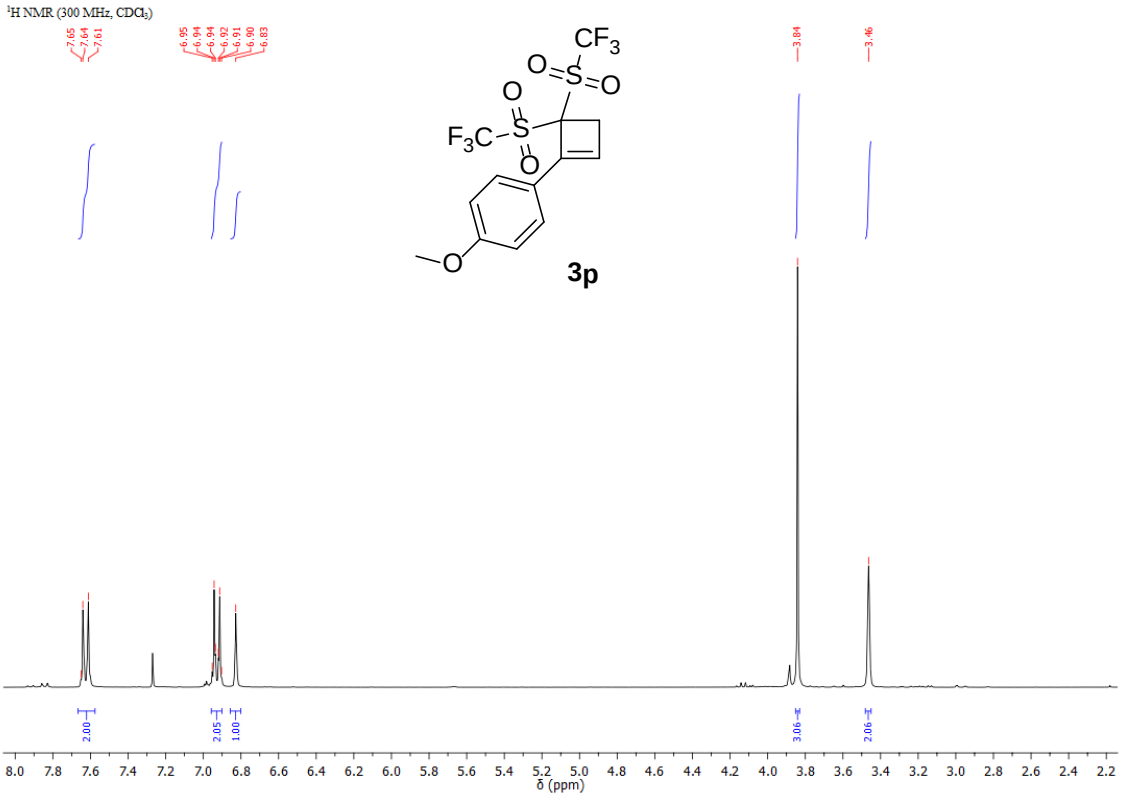
3o

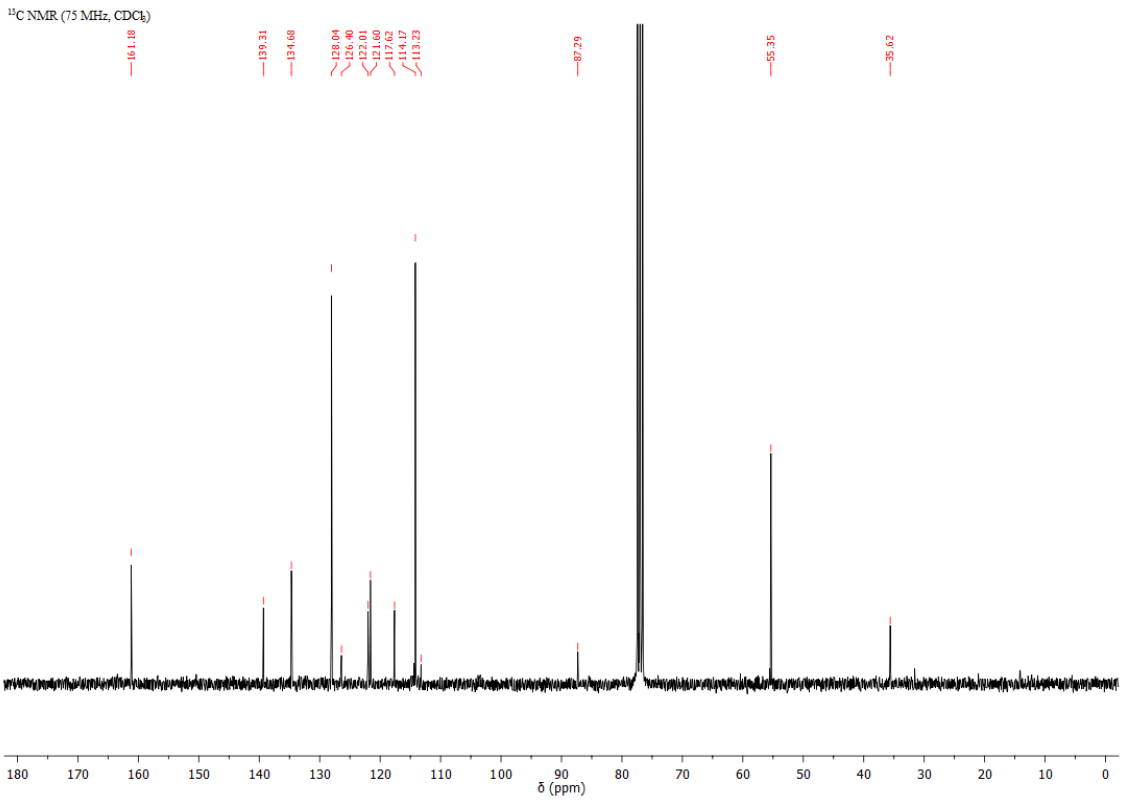
^{13}C NMR (75 MHz, $CDCl_3$)



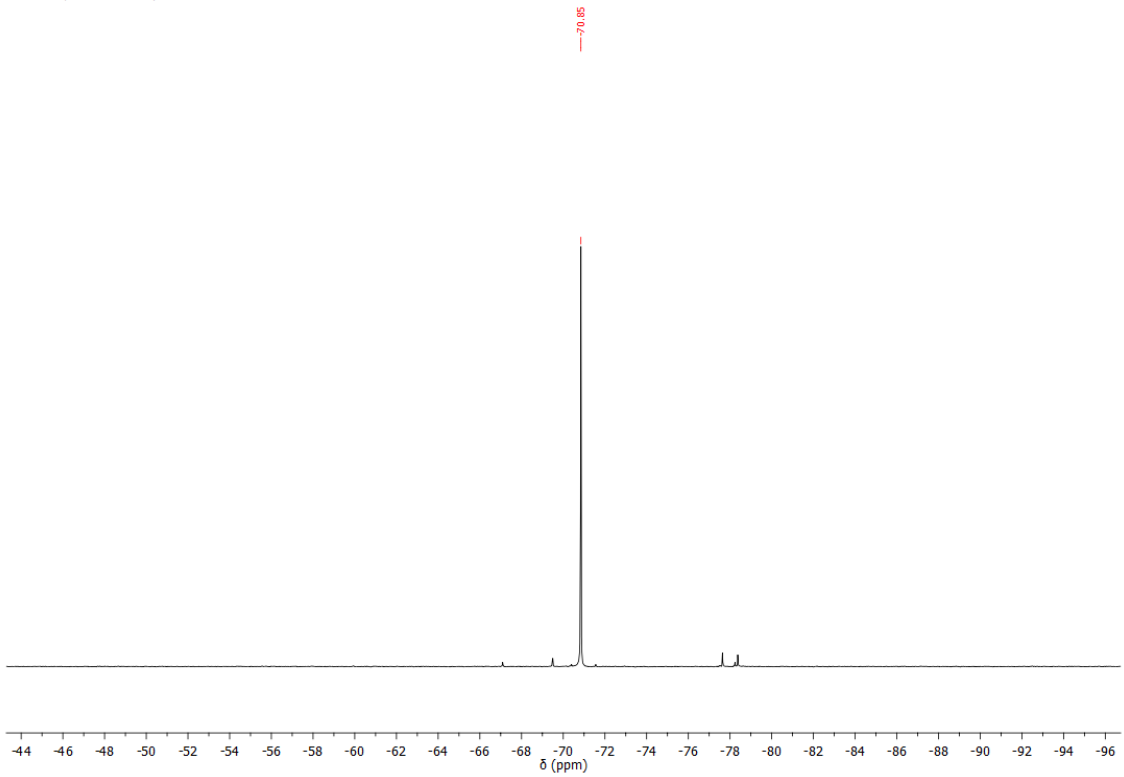
^{19}F NMR (282 MHz, $CDCl_3$)

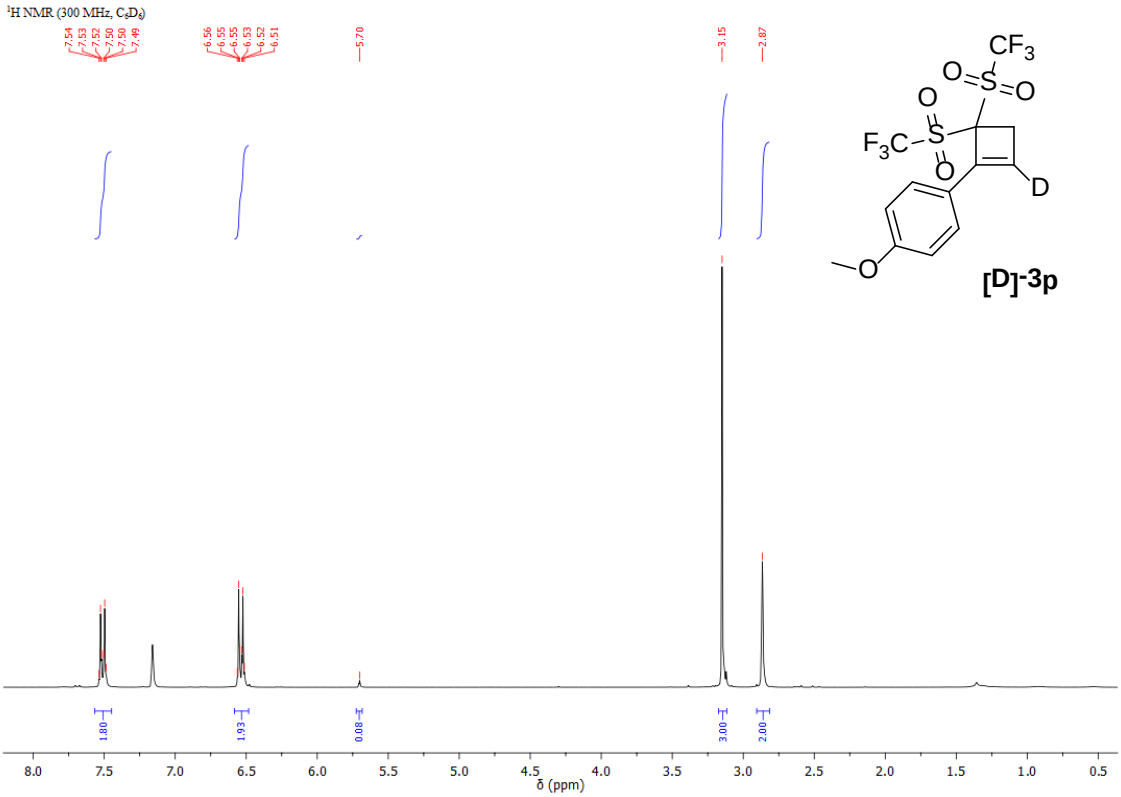


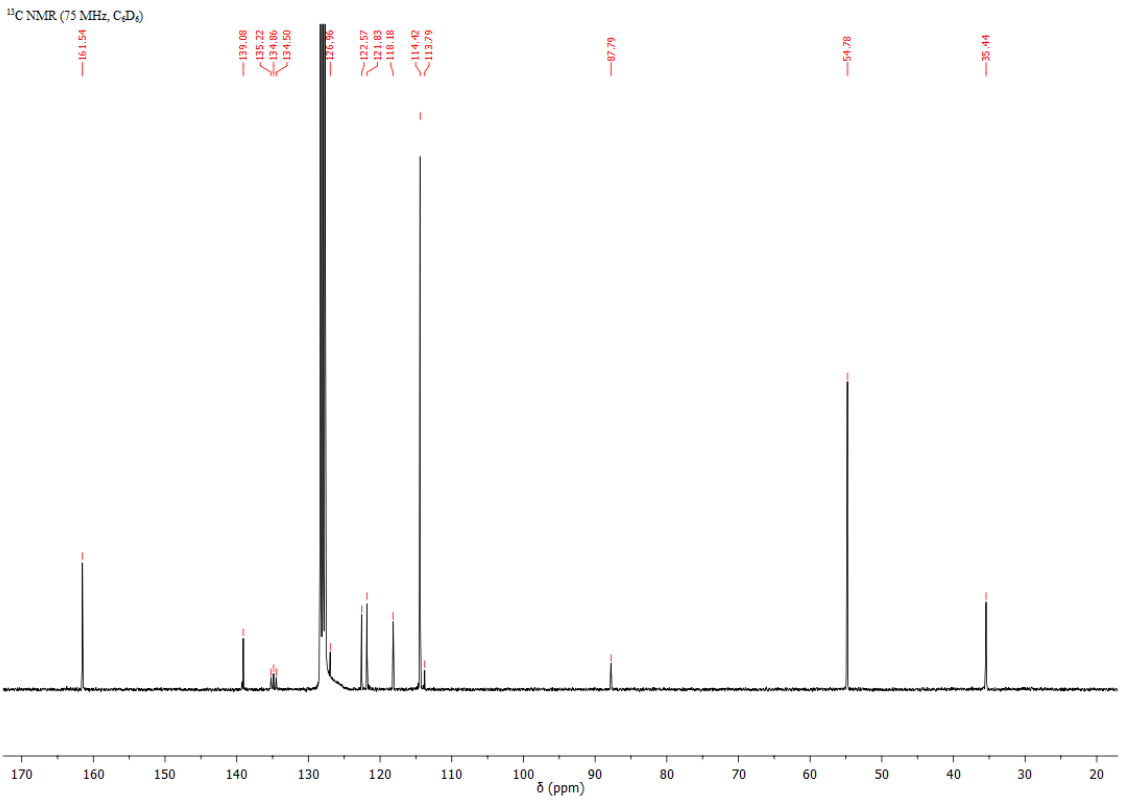

^{1}H NMR (300 MHz, $CDCl_3$)
7.65
7.64
7.61
6.95
6.94
6.94
6.92
6.91
6.90
6.83
3.84
3.46
CF_3
F_3C
O
S
3p
2.00
2.05
1.00
3.06
2.06
δ (ppm)


^{13}C NMR (75 MHz, $CDCl_3$)
161.18
139.31
134.68
128.04
126.40
122.01
121.60
117.62
114.17
113.23
87.29
55.35
35.62
δ (ppm)

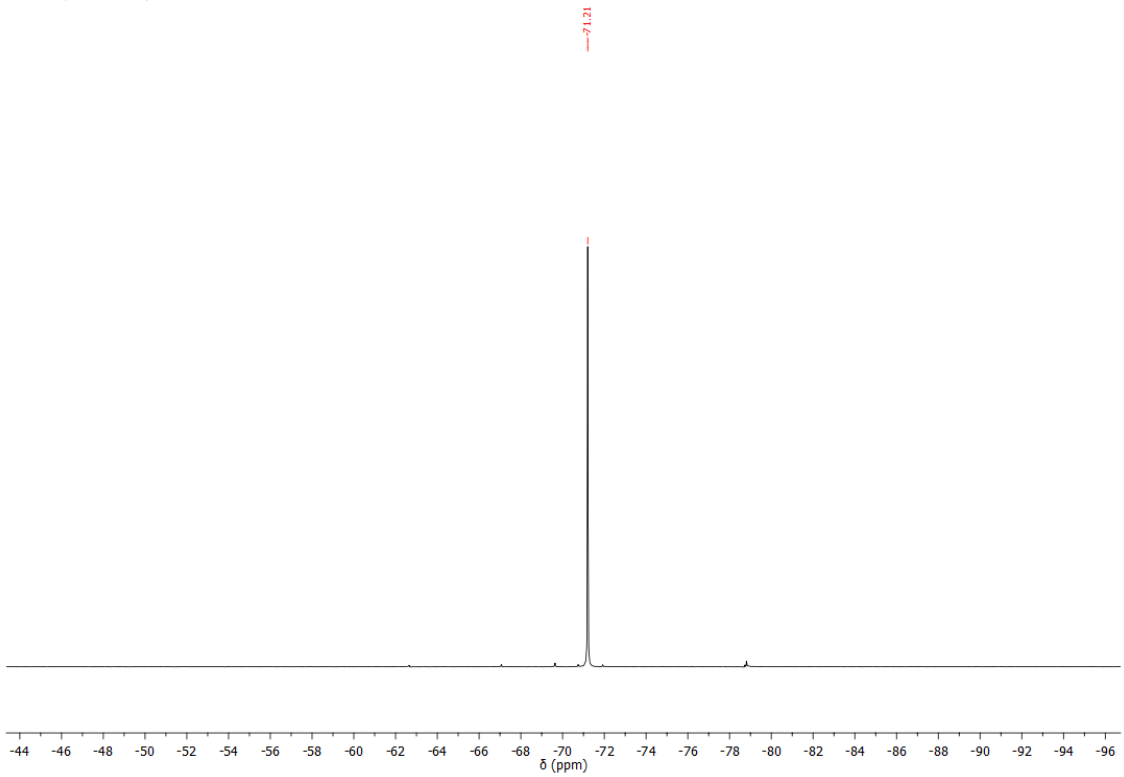
^{19}F NMR (282 MHz, $CDCl_3$)



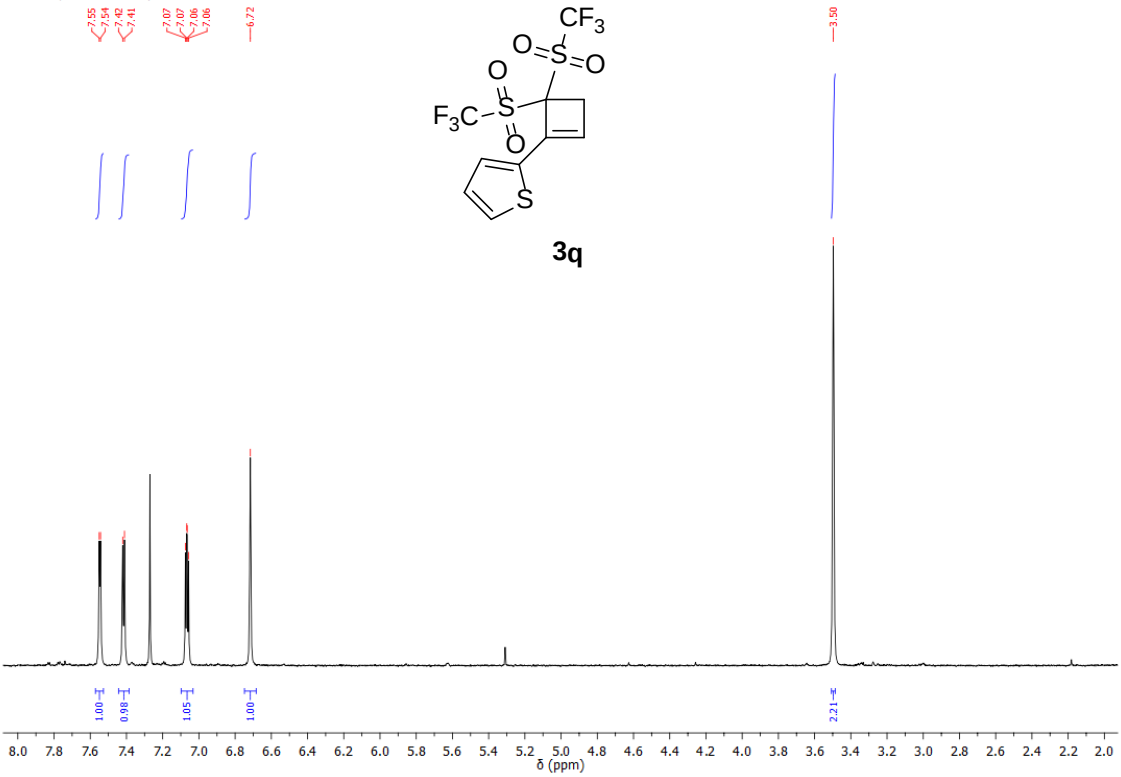

^{1}H NMR (300 MHz, C_6D_6)
7.54
7.53
7.52
7.50
7.50
7.49
6.56
6.55
6.55
6.53
6.52
6.51
5.70
3.15
2.87
1.80
1.93
0.08
3.00
2.00
δ (ppm)
[D]-3p


^{13}C NMR (75 MHz, C_6D_6)
161.54
139.08
135.22
134.86
134.50
126.98
122.57
121.83
118.18
114.42
113.79
87.79
54.78
35.44
δ (ppm)

^{19}F NMR (282 MHz, C_6D_6)

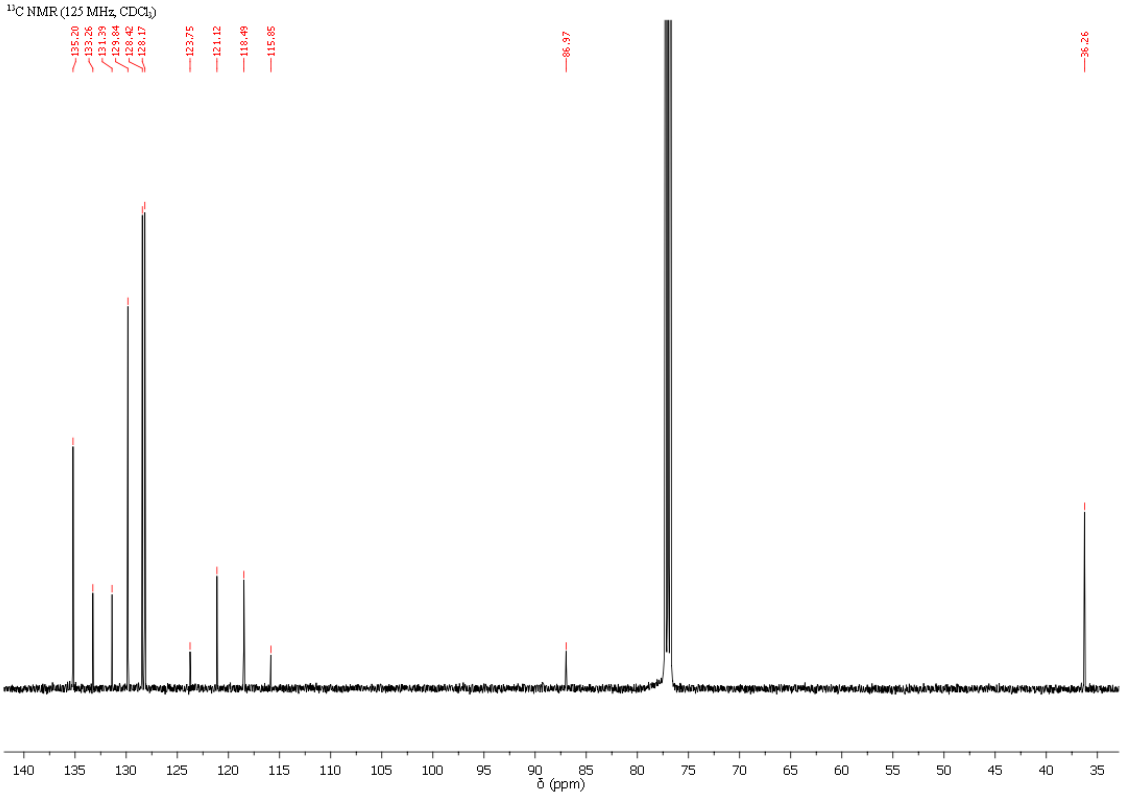


^{1}H NMR (500 MHz, $CDCl_3$)

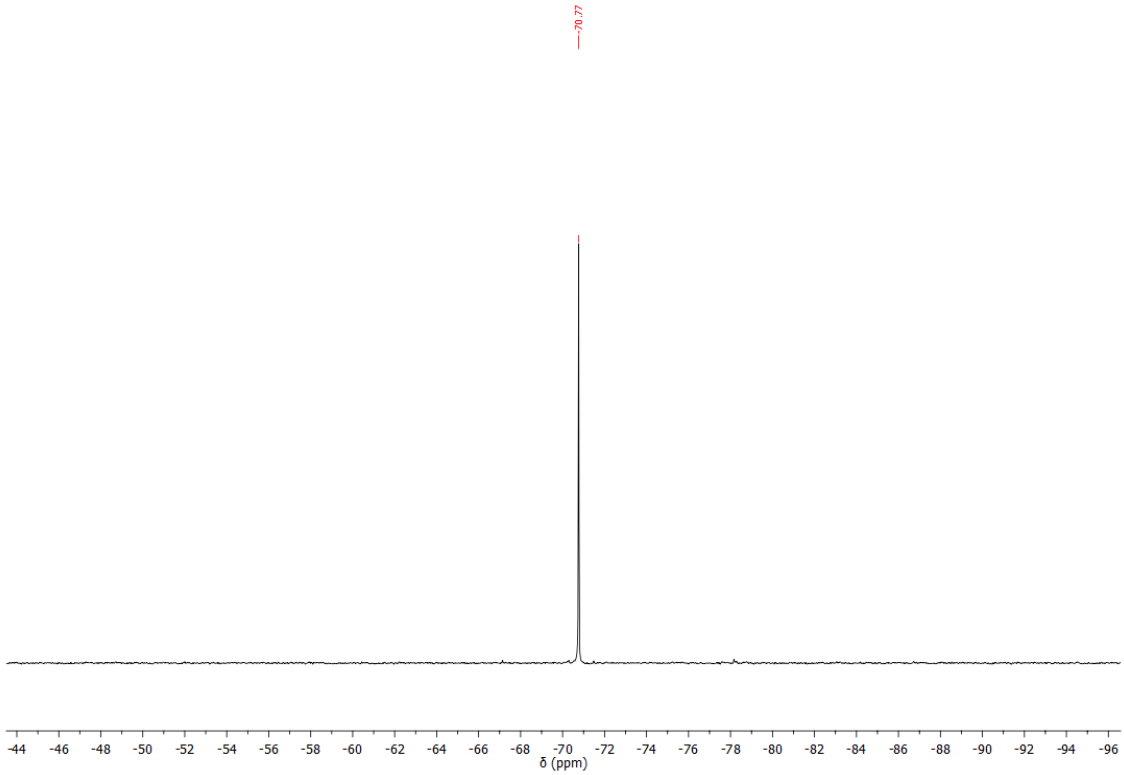


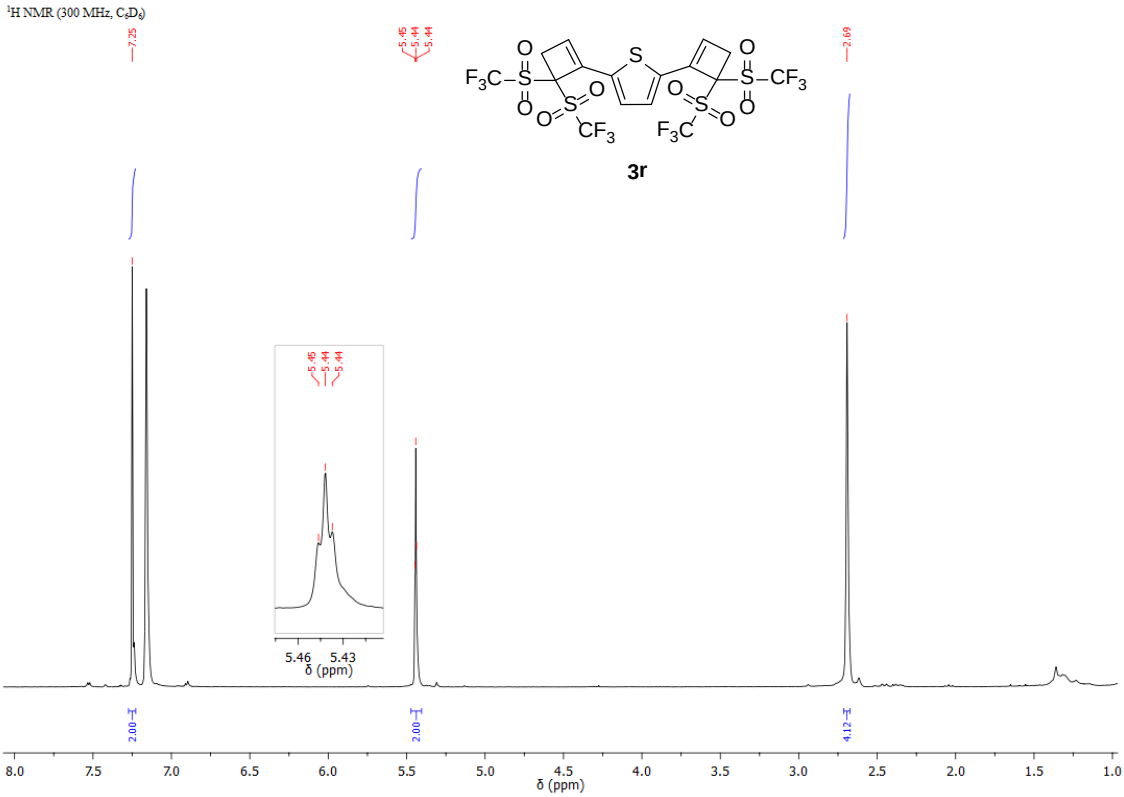
3q

^{13}C NMR (125 MHz, $CDCl_3$)

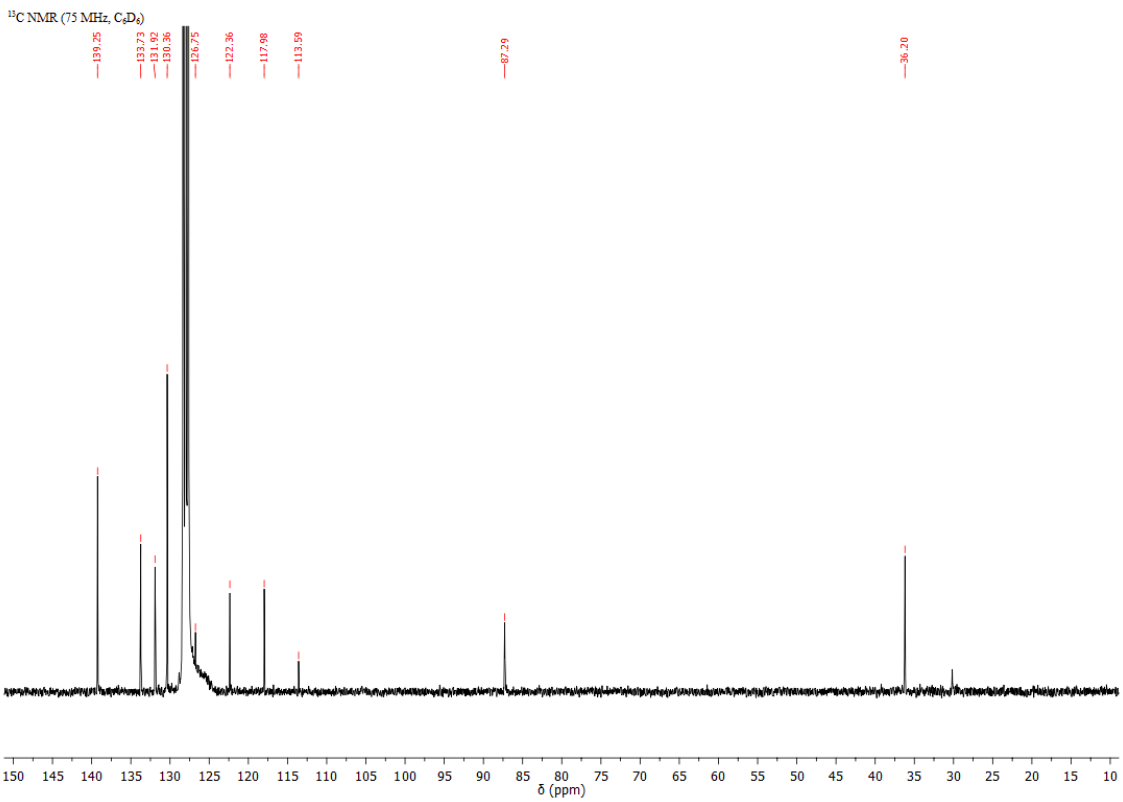


^{19}F NMR (282 MHz, $CDCl_3$)

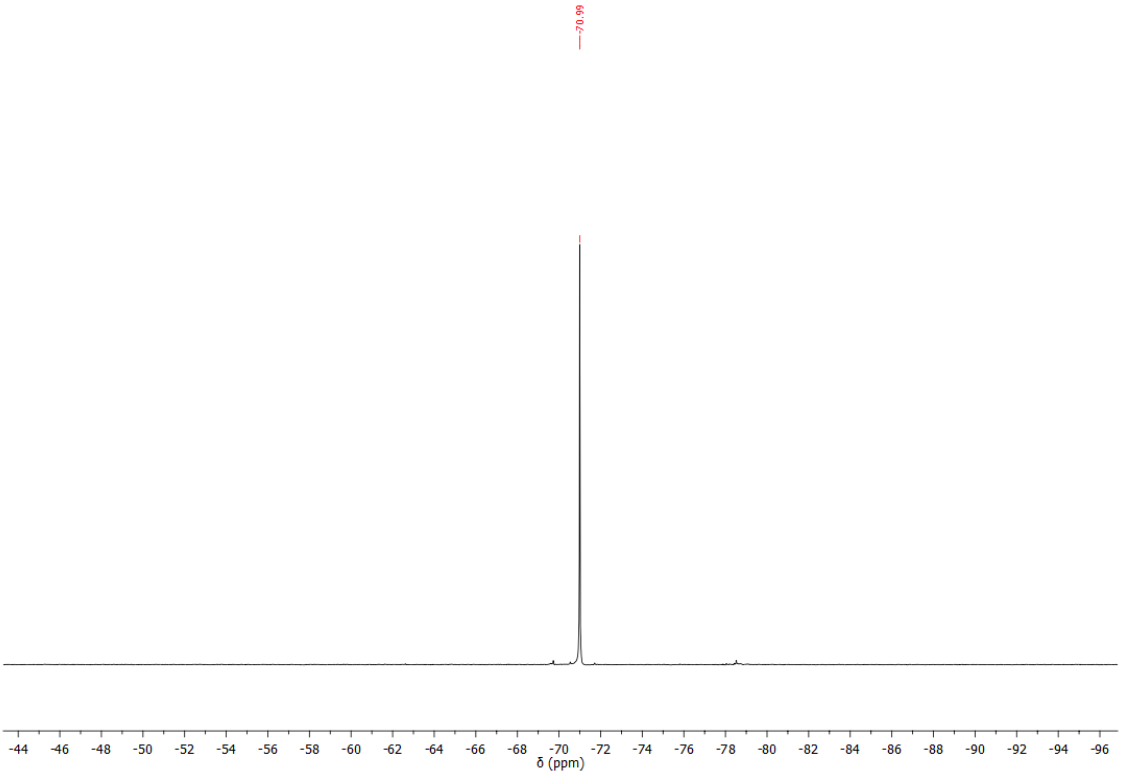


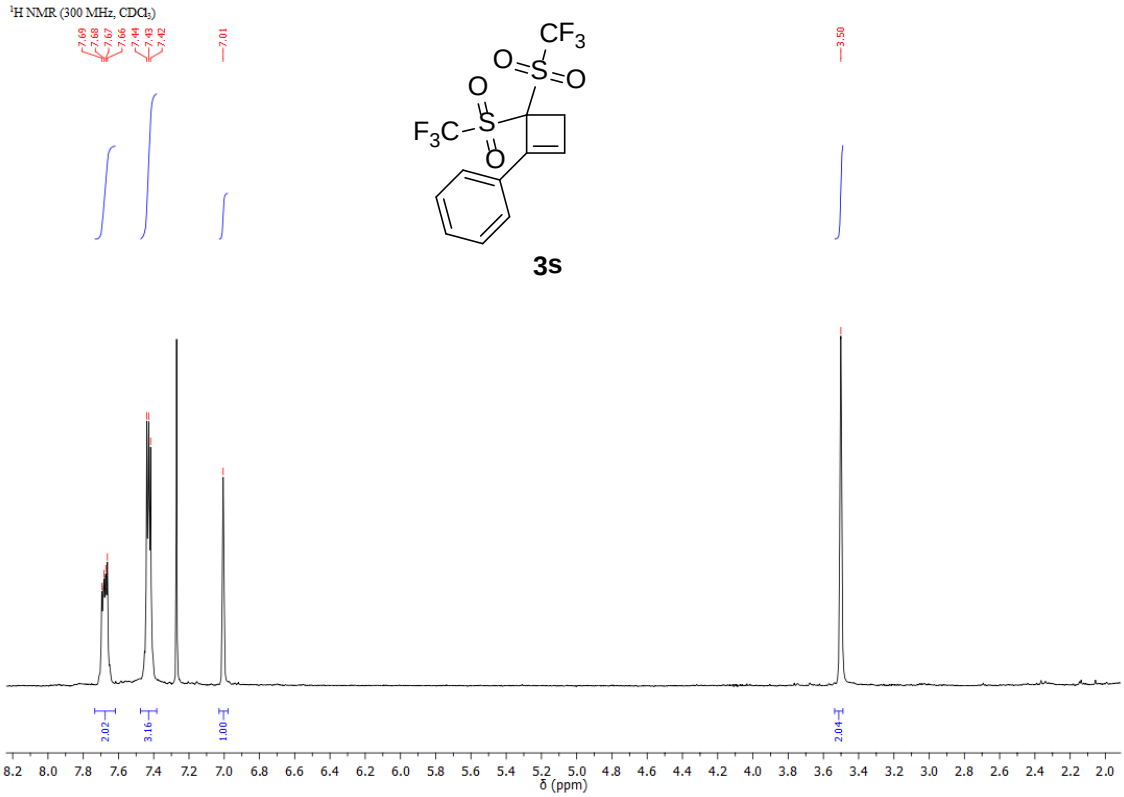

^{1}H NMR (300 MHz, C_6D_6)
7.25
5.45
5.44
5.44
2.69
5.46
5.43
δ (ppm)
2.00
2.00
4.12
δ (ppm)

3r

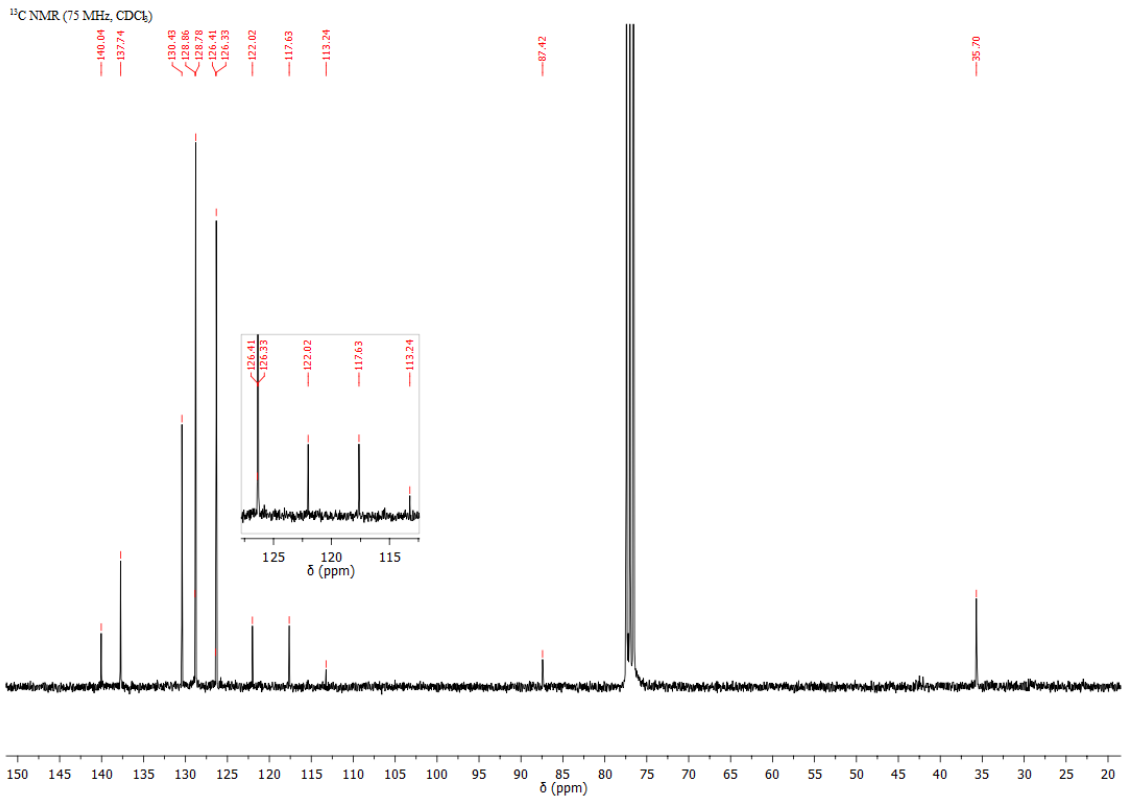

^{13}C NMR (75 MHz, C_6D_6)
139.25
133.73
131.92
130.36
126.75
122.36
117.98
113.59
87.29
36.20
δ (ppm)

^{19}F NMR (282 MHz, C_6D_6)

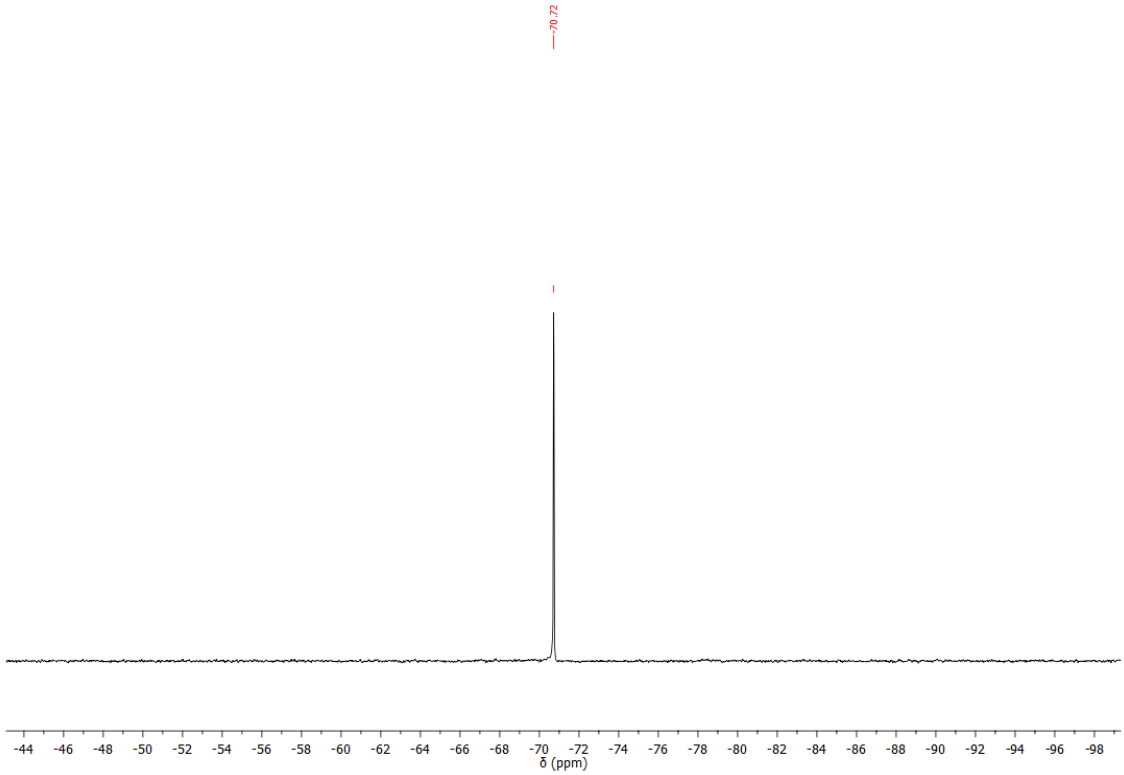


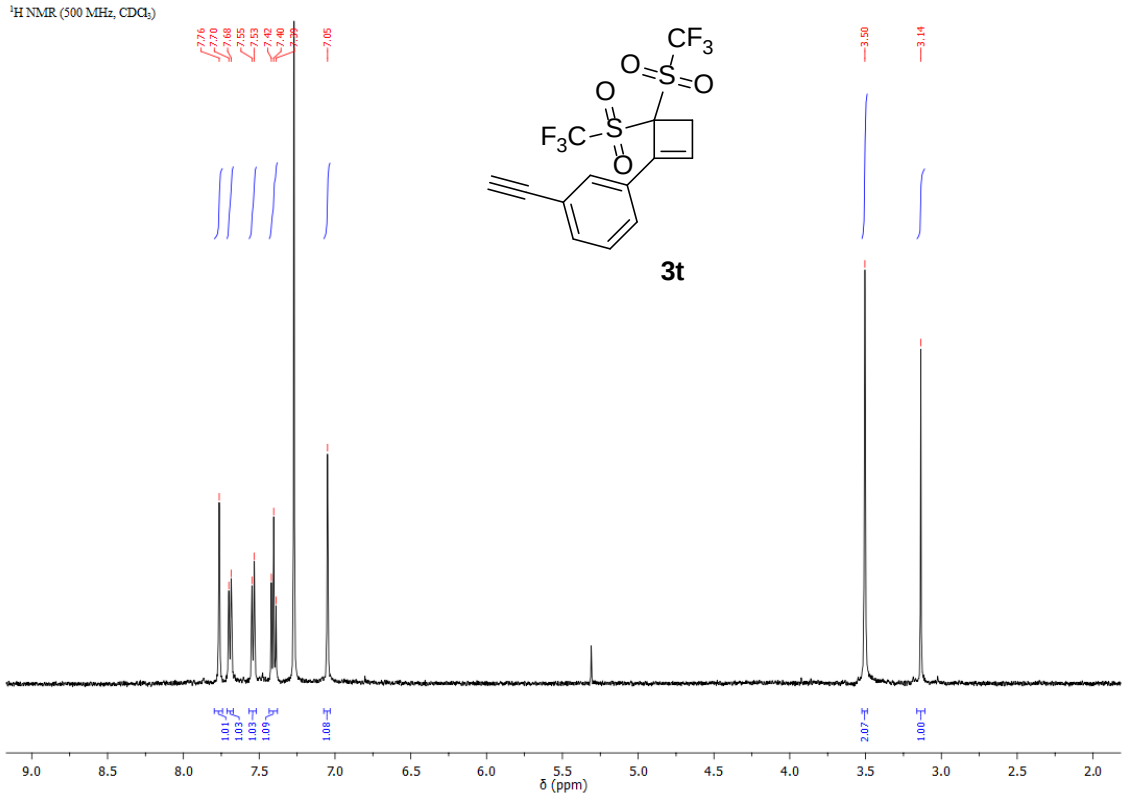

^{1}H NMR (300 MHz, $CDCl_3$)
7.69
7.68
7.67
7.66
7.44
7.43
7.42
7.01
3.50
2.02
3.16
1.00
2.04
δ (ppm)

3s


^{13}C NMR (75 MHz, $CDCl_3$)
140.04
137.74
130.43
128.86
128.78
126.41
126.33
122.02
117.63
113.24
87.42
35.70
δ (ppm)

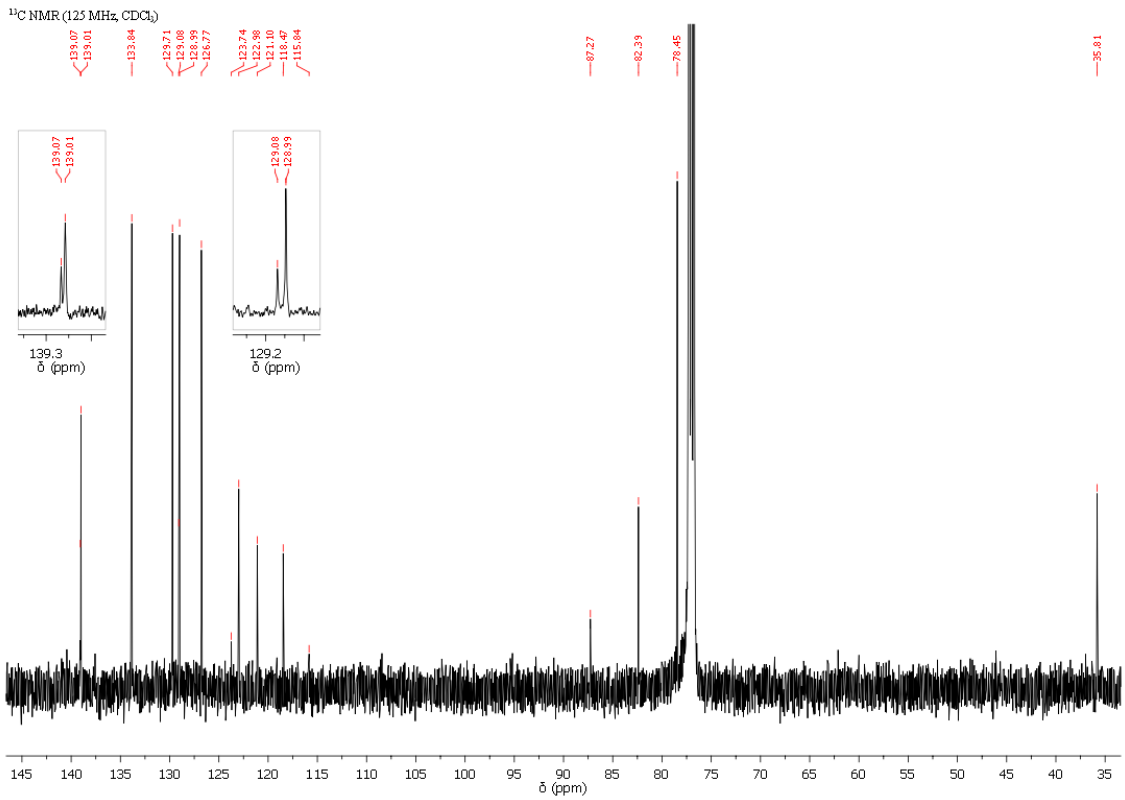
^{19}F NMR (282 MHz, $CDCl_3$)



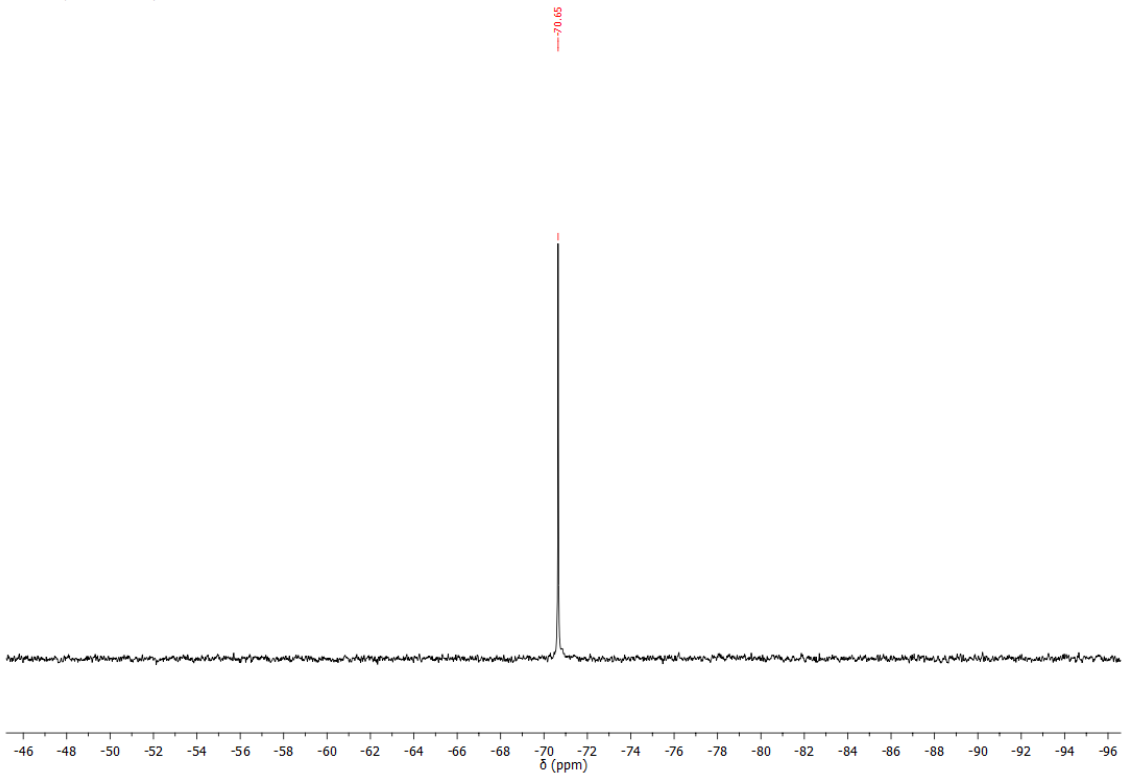

^{1}H NMR (500 MHz, CDCl$_3$)
7.76
7.70
7.68
7.55
7.53
7.42
7.40
7.39
7.05
3.50
3.14
1.01
1.03
1.03
1.09
1.08
2.07
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
δ (ppm)

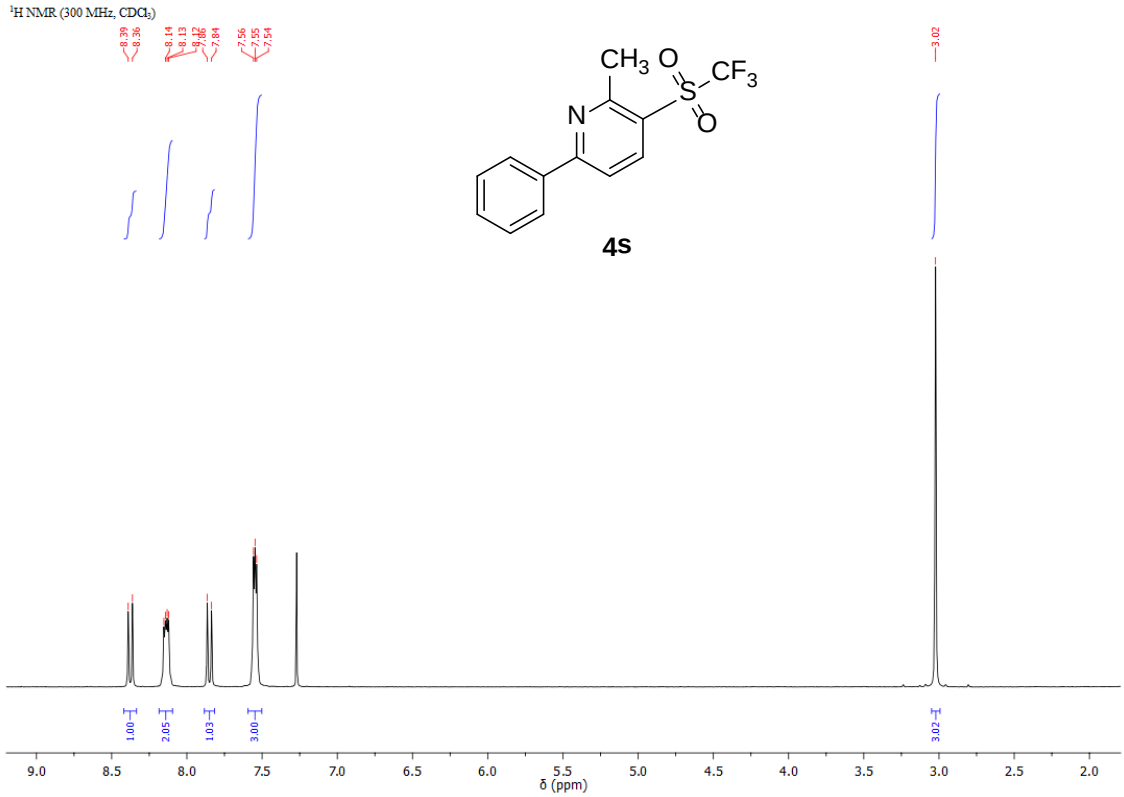
CF3
O
S
O
O
F3C
S
O
O

3t


^{13}C NMR (125 MHz, CDCl$_3$)
139.07
139.01
133.84
129.71
129.08
128.99
126.77
123.74
122.98
121.10
118.47
115.84
87.27
82.39
78.45
35.81
139.07
139.01
139.3
δ (ppm)
129.08
128.99
129.2
δ (ppm)
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
δ (ppm)

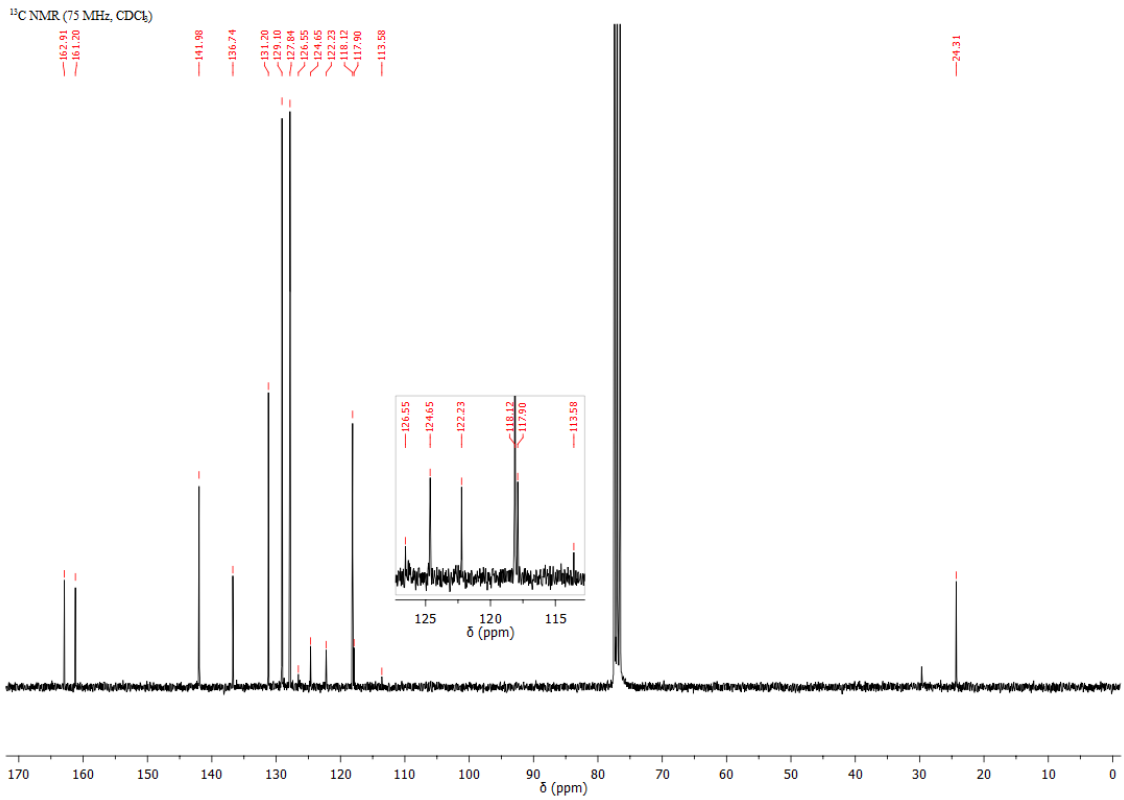
^{19}F NMR (282 MHz, $CDCl_3$)



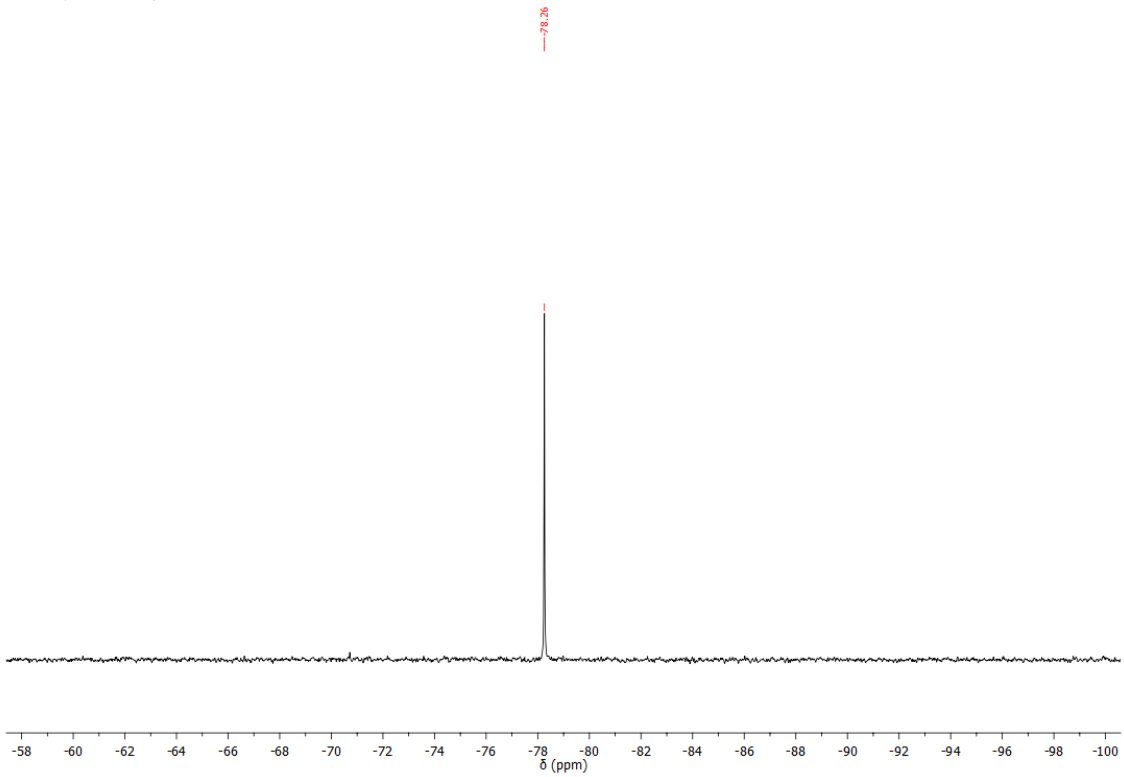

^{1}H NMR (300 MHz, CDCl$_3$)
8.39
8.36
8.14
8.13
7.86
7.84
7.56
7.55
7.54
3.02
1.00
2.05
1.03
3.00
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
δ (ppm)

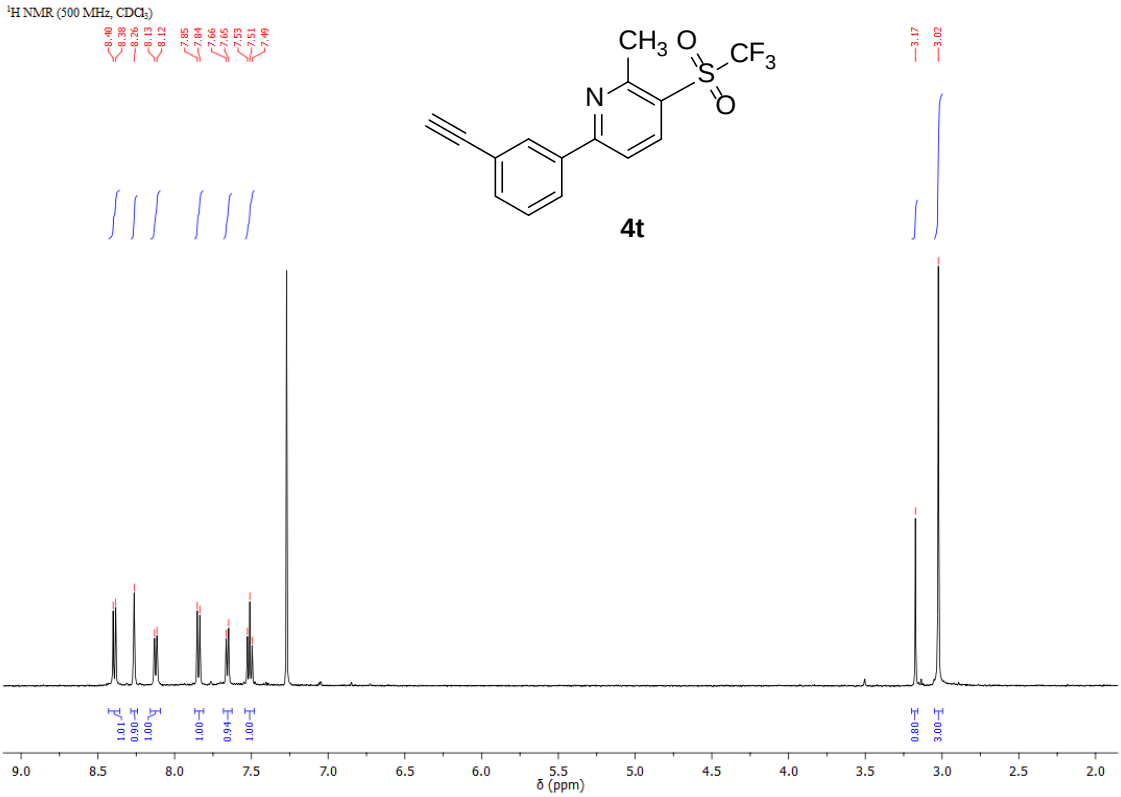
CH3
O
S
CF3
N
O

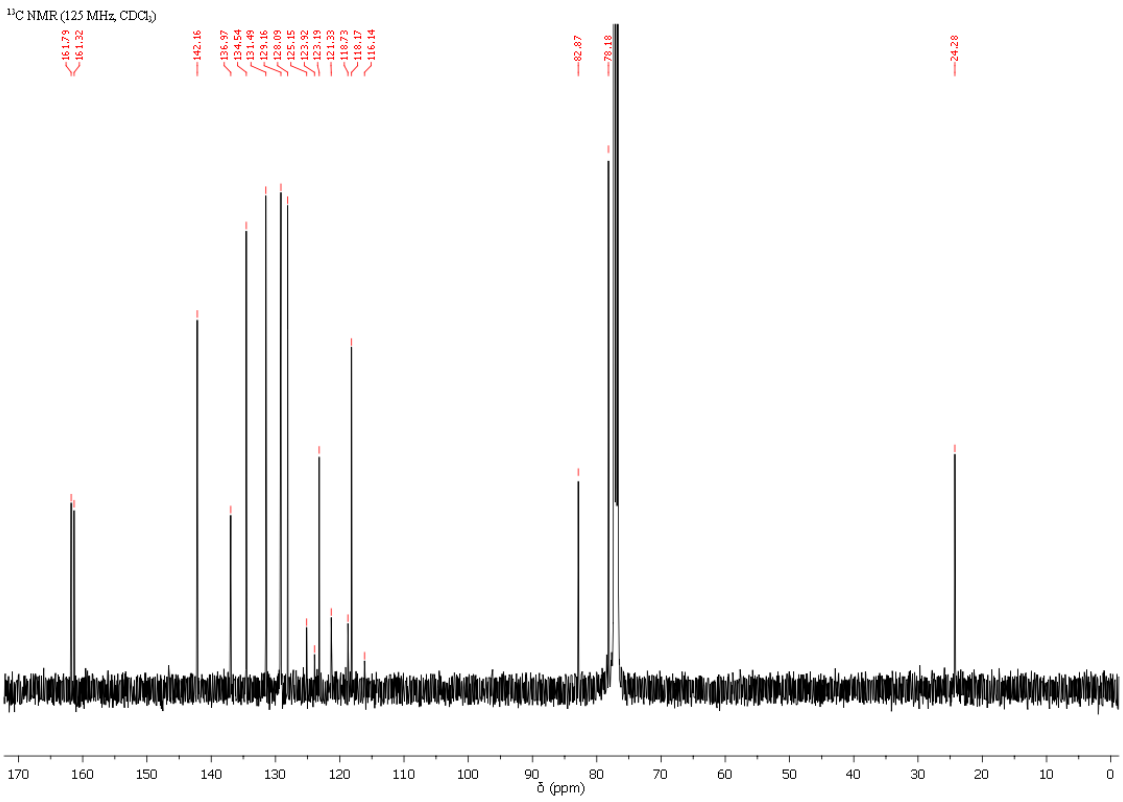
4s


^{13}C NMR (75 MHz, CDCl$_3$)
162.91
161.20
141.98
136.74
131.20
129.10
127.84
126.55
124.65
122.23
118.12
117.90
113.58
24.31
126.55
124.65
122.23
118.12
117.90
113.58
125
120
115
δ (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

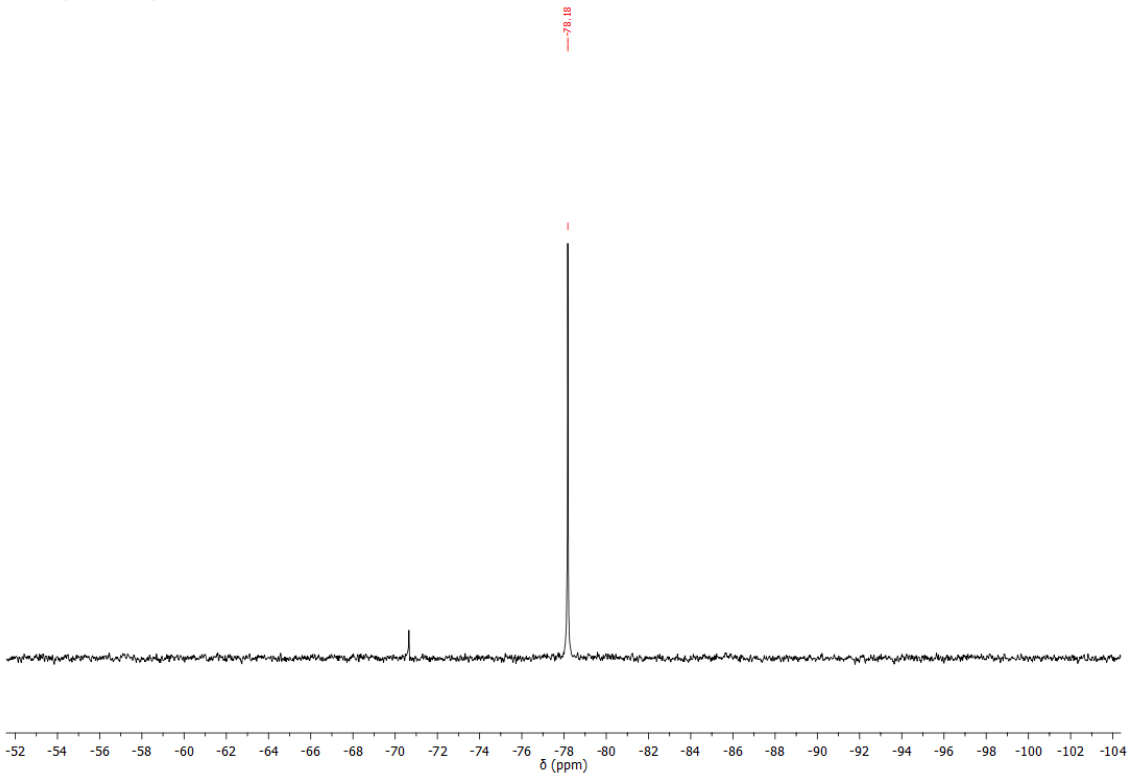
^{19}F NMR (282 MHz, $CDCl_3$)

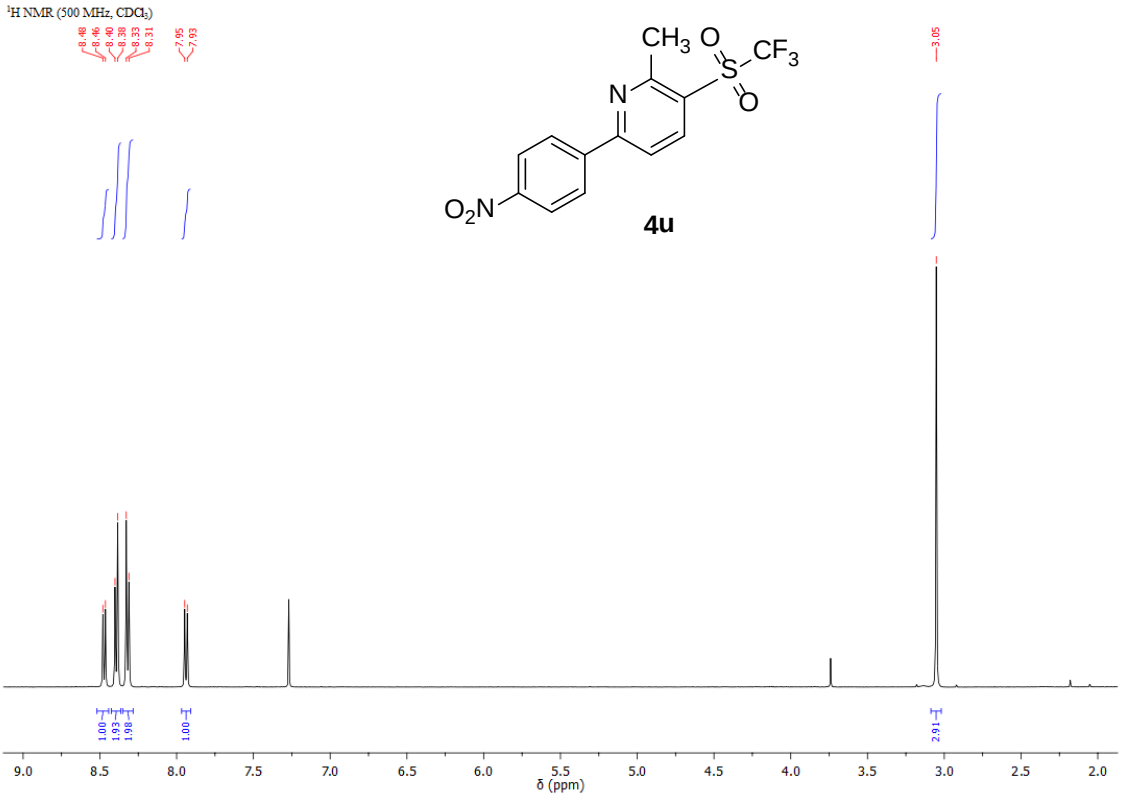



^{1}H NMR (500 MHz, CDCl$_3$)
8.40
8.38
8.26
8.13
8.12
7.85
7.84
7.66
7.65
7.53
7.51
7.49
3.17
3.02
CH$_3$
O
S
CF$_3$
N
O
4t
1.01
0.90
1.00
1.00
0.94
1.00
0.80
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
δ (ppm)


^{13}C NMR (125 MHz, CDCl$_3$)
161.79
161.32
142.16
136.97
134.54
131.49
129.16
126.09
125.15
123.92
123.18
121.33
118.73
118.17
116.14
82.87
78.18
24.28
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

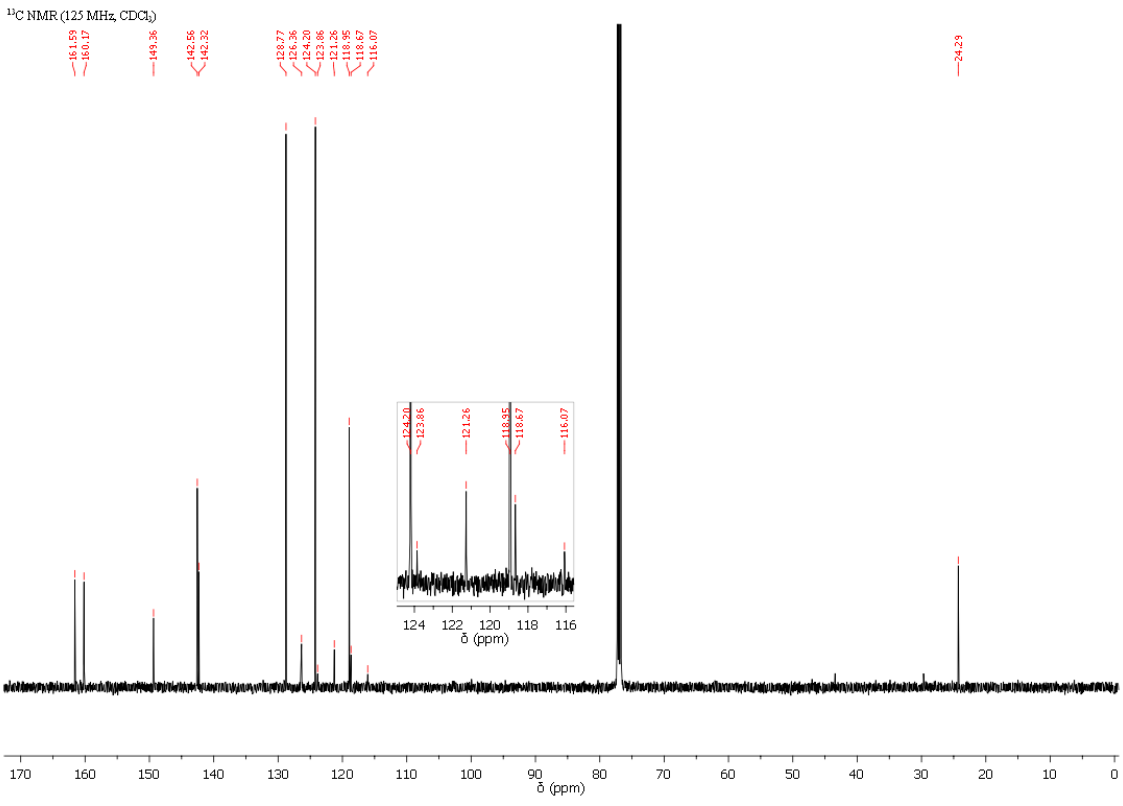
^{19}F NMR (282 MHz, $CDCl_3$)




^{1}H NMR (500 MHz, CDCl$_3$)
8.48
8.46
8.40
8.38
8.33
8.31
7.95
7.93
3.05
1.00
1.93
1.98
1.00
2.91
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
δ (ppm)

CH3
O
S
CF3
N
O
O2N

4u


^{13}C NMR (125 MHz, CDCl$_3$)
161.59
160.17
149.36
142.56
142.32
128.77
126.36
124.20
123.86
121.26
118.45
118.67
116.07
24.23
124.20
123.86
121.26
118.45
118.67
116.07
124
122
120
118
116
δ (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

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