Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2015

Supporting Information for the Paper

Metal-Free [3+2] Cycloaddition of Azides with $Tf_2C=CH_2$ for the Regioselective Preparation of Elusive 4-(Trifluoromethylsulfonyl)- 1,2,3-triazoles

Benito Alcaide,*[1] Pedro Almendros,*[2] and Carlos Lázaro-Milla[1]

[1]*Grupo de Lactamas y Heterociclos Bioactivos, Departamento de Química Orgánica I, Unidad Asociada al CSIC, Facultad de Química, Universidad Complutense de Madrid, 28040-Madrid, Spain*

[2]*Instituto de Química Orgánica General, IQOG-CSIC, Consejo Superior de Investigaciones Científicas, Juan de la Cierva 3, 28006-Madrid, Spain*

E-mail: alcaideb@quim.ucm.es; Palmendros@iqog.csic.es

Table of Contents

General Methods: ^1H NMR and ^{13}C NMR spectra were recorded on a 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 (^1H, 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. All commercially available compounds were used without further purification.

Azolium salt **2** was easily synthesized according to a convenient literature procedure: Yanai, H.; Takahashi, Y.; Fukaya, H.; Dobashi, Y.; Matsumoto, T. *Chem. Commun.* **2013**, *49*, 10091.

Procedure for the synthesis of azolium salt 2. 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 2-fluoropyridine (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 **2** as solid.

Azides **3m** and **3t** were commercially available. Azides **3a–i**, **3k**, **3l**, **3o–s**, and **3v** were readily obtained as described in the literature: **3a** and **3v** (L. Hong, W. Lin, F. Zhang, R. Liu, X. Zhou, *Chem. Commun.* **2013**, *49*, 5589); **3b** and **3c** (P. Ramírez-López, M. C. de la Torre, H. E. Montenegro, M. Asenjo, M. A. Sierra, *Org. Lett.* **2008**, *10*, 3555); **3d** (W. Wu, G. Xu, C. Li, G. Yu, Y. Liu, C. Ye, J. Qin, Z. Li, *Chem. Eur. J.* **2013**, *19*, 6874); **3e** (A. Cuetos, F. R. Bisogno, I.

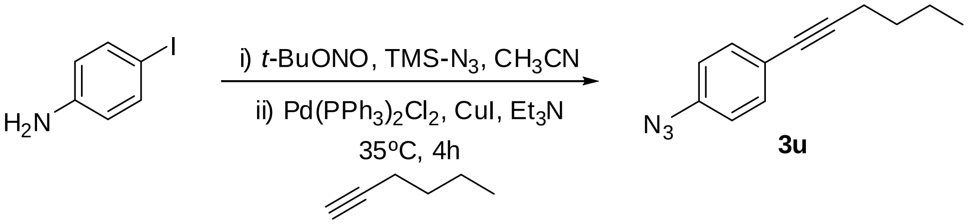
Lavandera, V. Gotor, *Chem. Commun.* **2013**, *49*, 2625); **3f** (Z. Wang, Y.-T. Cui, Z.-B. Xu, J. Qu, *J. Org. Chem.* **2008**, *73*, 2270); **3g** (K. Shin, Y. Baek, S. Chang, *Angew. Chem. Int. Ed.* **2013**, *52*, 8031); **3h** (M. Rueping, C. Vila, U. Uria, *Org. Lett.* **2012**, *14*, 768); **3i** (J.-C. Lee, S.-W. Chang, C.-C. Liao, F.-C. Chi, C.-S. Chen, Y.-S. Wen, C.-C. Wang, S. S. Kulkarni, R. Puranik, Y.-H. Liu, S.-C. Hung, *Chem. Eur. J.* **2004**, *10*, 399); **3j** (D. R. Wagle, C. Garai, J. Chiang, M. G. Monteleone, B. E. Kurys, T. W. Strohmeyer, V. R. Hegde, M. S. Manhas, A. K. Bose, *J. Org. Chem.* **1988**, *53*, 4229); **3k** (D. Fischer, H. Tomeba, N. K. Pahadi, N. T. Patil, Y. Yamamoto, *Angew. Chem. Int. Ed.* **2007**, *46*, 4764); **3l** (H.-Y. Hsieh, W.-C. Lee, G. C. Senadi, W.-P. Hu, J.-J. Liang, T.-R. Tsai, Y.-W. Chou, K.-K. Kuo, C.-Y. Chen, J.-J. Wang, *J. Med. Chem.* **2013**, *56*, 5422); **3o** (K. Barral, A. D. Moorhouse, J. E. Moses, *Org. Lett.* **2007**, *9*, 1809); **3p** (Q. Zhang, J. P. Shrestha, C.-W. T. Chang, *Tetrahedron Lett.* **2014**, *55*, 1839); **3q** and **3r** (S. Pagoti, S. Surana, A. Chauhan, B. Parasar, J. Dash, *Catal. Sci. Technol.* **2013**, *3*, 584); **3s** (S. W. Kwok, J. R. Fotsing, R. J. Fraser, V. O. Rodionov, V. V. Fokin, *Org. Lett.* **2010**, *12*, 4217).

Azide **3n** has been previously described in the literature through a multistep procedure. We have prepared compound **3n** using a more direct protocol:

i) Anthranilic acid (200 mg, 1.46 mmol) was solved in CH_3CN (4 mL) and cooled to 0°C in an ice bath. *t*-BuONO (226 mg, 260 μL, 2.18 mmol) was added to this stirred mixture, followed by the dropwise addition of TMS-N_3 (200 mg, 230 μL, 1.75 mmol). The resulting solution was stirred at room temperature for 2 h. The reaction mixture was concentrated under vacuum. The resulting precipitate was filtered off, and washed with water and hexane to give 2-azidobenzoic acid as a beige solid (192 mg, 81%).

ii) A solution of 2-azidobenzoic acid (163 mg, 1.0 mmol) and concentrated H_2SO_4 (three drops) in metanol (10 mL) was heated at 80ºC for 12h in a sealed tube. The mixture was allowed to cool at RT and was concentrated under reduced pressure. Chromatography of the residue on silica gel using hexanes/ethyl acetate (95:5) as eluent gave analytically pure methyl 2-azidobenzoate (159 mg, 90%) **3n** as a yellow oil.

Azide **3u** was synthesized using the following procedure:



i) To a stirred and cooled solution of 4-iodoaniline (200 mg, 0.91 mmol) in CH_3CN (2 mL) at 0°C, was added *t*-BuONO (141 mg, 162 µL, 1.36 mmol). Next, it was followed by the dropwise addition of TMS-N_3 (125 mg, 145 µL, 1.09 mmol). The resulting solution was stirred at room temperature for 2 h. The reaction mixture was concentrated under vacuum and the crude product was purified by chromatography on silica gel using hexanes as eluent to give 1-azido-4-iodobenzene (200 mg, 90%) as a brown solid.

ii) A solution of 1-azido-4-iodobenzene (200 mg, 0.81 mmol) and 1-hexyne (0.11 ml, 0.97 mmol) in anhydrous Et_3N (1 ml) was stirred under argon. $Pd(PPh_3)_2Cl_2$ (5 mg) and CuI (2 mg) were sequentially added and the resulting mixture was stirred for 4 h at 35ºC. The reaction mixture was concentrated under vacuum and the crude product was purified by chromatography on silica gel using hexanes as eluent to give 1-azido-4-(hex-1-yn-1-yl)benzene (81 mg, 50%) **3u** as a dark orange oil.

Azide 3u. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.96 (t, 3H, *J* = 7.2 Hz, CH_3), 1.48 (m, 2H, CH_2), 1.59 (m, 2H, CH_2), 2.41 (t, 2H, *J* = 7.0 Hz, CH_2), 6.94 (m, 2H, $2CH^{Ar}$), 7.38 (m, 2H, $2CH^{Ar}$); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 139.1 ($C^{Ar\text{-}q}$-N_3), 132.9 ($2CH^{Ar}$), 120.7 ($C^{Ar\text{-}q}$), 118.8 ($2CH^{Ar}$), 90.7 ($\mathit{C}{\equiv}C$), 79.8 ($C{\equiv}\mathit{C}$), 30.8 (CH_2), 22.0 (CH_2), 19.1 (CH_2), 13.6 (CH_3); IR

($CHCl_3$): ν = 2125, 2092 (N_3-*asymmetric stretching*), 1294 (N_3-*symmetric stretching*) cm^{-1}; HRMS (ES): calcd for $C_{12}H_{13}N_3$ $[M]^+$: 199.1109; found: 199.1122.

General experimental procedure for the 4-triflyl triazole formation. 2-(2-Fluoropyridin-1-ium-1-yl)-1,1-bis[(trifluoromethyl)sulfonyl]ethan-1-ide **2** (1.0 mmol) was added at room temperature to a solution of the appropriate organic azide **3** (1.0 mmol) in acetonitrile (8.0 mL). After disappearance of the starting material (TLC) the mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired heterocycle **4**. Spectroscopic and analytical data for 4-triflyl triazoles **4** follow.

4-Triflyl triazole 4a. From 40 mg (0.30 mmol) of azide **3a**, and after flash chromatography of the residue using hexanes/ethyl acetate (9:1) as eluent gave compound **4a** (79 mg, 91%) as a colorless solid; mp 81–83 ºC; ^1H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 5.67 (s, 2H, CH_2), 7.36 (m, 2H, $2CH^{Ar}$), 7.45 (m, 3H, $3CH^{Ar}$), 8.24 (s, 1H, CH-*Triazole*); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 139.4 (C-Tf), 132.2 ($C^{Ar\text{-}q}$), 130.7 (CH-*Triazole*), 129.7 (CH^{Ar}), 129.6 ($2CH^{Ar}$), 128.6 ($2CH^{Ar}$), 119.3 (q, J_{CF} = 324.7 Hz, CF_3), 55.3 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$, 25 ºC): δ = –78.62 (s, 3F, CF_3); IR ($CHCl_3$): ν = 1375, 1118 (O=S=O), 1222 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{10}H_8N_3O_2SF_3$ $[M]^+$: 291.0289; found: 291.0286.

Bis(4-triflyl triazole) 4b. From 20 mg (0.10 mmol) of azide **3b**, and after recrystallization (acetonitrile) gave compound **4b** (41 mg, 80%) as a colorless solid; mp 206–208 ºC; ^1H NMR (300 MHz, DMSO-d_6, 25 ºC): δ = 5.80 (s, 4H, $2CH_2$), 7.45 (s, 4H, $4CH^{Ar}$), 9.71 (s, 2H, 2CH-*Triazole*); ^{13}C NMR (75 MHz, DMSO-d_6, 25 ºC): δ = 136.9 (2C-Tf), 134.9 ($2C^{Ar\text{-}q}$), 134.2 (2CH-*Triazole*), 129.0 ($4CH^{Ar}$), 119.0 (q, J_{CF} = 324.8 Hz, $2CF_3$), 53.8 ($2CH_2$); ^{19}F NMR (282 MHz, $CDCl_3$, 25 ºC): δ = –79.14 (s, 6F, $2CF_3$); IR ($CHCl_3$): ν = 1376 (O=S=O), 1221 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{14}H_{10}N_6O_4S_2F_6$ $[M]^+$: 504.0109; found: 504.0123.

Bis(4-triflyl triazole) 4c. From 20 mg (0.10 mmol) of azide **3c**, and after recrystallization (acetonitrile) gave compound **4c** (46 mg, 91%) as a colorless solid; mp 202–204 ºC; ^{1}H NMR (300 MHz, $(CD_3)_2CO$, 25 ºC): δ = 6.16 (s, 4H, $2CH_2$), 7.46 (m, 4H, $4CH^{Ar}$), 9.26 (s, 2H, 2CH-*Triazole*); ^{13}C NMR (75 MHz, $(CD_3)_2CO$, 25 ºC): δ = 139.3 (2C-Tf), 134.4 (2CH-*Triazole*), 134.0 ($2C^{Ar-q}$), 131.7 ($2CH^{Ar}$), 131.0 ($2CH^{Ar}$), 120.5 (q, J_{CF} = 323.8 Hz, $2CF_3$), 52.7 ($2CH_2$); ^{19}F NMR (282 MHz, $(CD_3)_2CO$, 25 ºC): δ = –80.34 (s, 6F, $2CF_3$); IR (acetone): ν = 1374, 1120 (O=S=O), 1215 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{14}H_{10}N_6O_4S_2F_6$ $[M]^+$: 504.0109; found: 504.0086.

Tris(4-triflyl triazole) 4d. From 20 mg (0.08 mmol) of azide **3d**, and after recrystallization (acetonitrile) gave compound **4d** (59 mg, quantitative yield) as a colorless solid; mp 228–230 ºC; ^{1}H NMR (300 MHz, $(CD_3)_2CO$, 25 ºC): δ = 5.90 (s, 6H, $3CH_2$), 7.67 (s, 3H, $3CH^{Ar}$), 9.19 (s, 3H, 3CH-*Triazole*); ^{13}C NMR (75 MHz, $(CD_3)_2CO$, 25 ºC): δ = 139.1 (3C-Tf), 137.1 ($3C^{Ar-q}$), 134.1 (3CH-*Triazole*), 130.4 ($3CH^{Ar}$), 120.3 (q, J_{CF} = 323.7 Hz, $3CF_3$), 54.9 ($3CH_2$); ^{19}F NMR (282 MHz, $(CD_3)_2CO$, 25 ºC): δ = –80.37 (s, 9F, $3CF_3$); IR (acetone): ν = 1378, 1112 (O=S=O), 1194 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{18}H_{12}N_9O_6S_3F_9$ $[M]^+$: 716.9929; found: 716.9913.

4-Triflyl triazole 4e. From 22 mg (0.13 mmol) of azide **3e**, and after flash chromatography of the residue using hexanes/dichloromethane (8:2→1:1) as eluent gave compound **4e** (42 mg, 96%) as a colorless solid; mp 144–146 ºC; ^{1}H NMR (300 MHz, $(CD_3)_2CO$, 25 ºC): δ = 6.44 (s, 2H, CH_2), 7.59 (t, 2H, J = 7.6 Hz, $2CH^{Ar}$), 7.72 (t, 1H, J = 7.4 Hz, CH^{Ar}), 8.11 (d, 2H, J = 7.6 Hz, $2CH^{Ar}$), 9.18 (s, 1H, CH-*Triazole*); ^{13}C NMR (75 MHz, $(CD_3)_2CO$, 25 ºC): δ = 191.0 (C=O), 139.0 (C-Tf), 135.9 (CH-*Triazole*), 135.4 (CH^{Ar}), 134.9 (C^{Ar-q}), 130.0 ($2CH^{Ar}$), 129.2 ($2CH^{Ar}$), 120.5 (q, J_{CF} = 323.8 Hz, CF_3), 57.9 (CH_2); ^{19}F NMR (282 MHz, $(CD_3)_2CO$, 25 ºC): δ = –80.37 (s, 3F, CF_3); IR (acetone): ν = 1693 (C=O), 1380, 1122 (O=S=O), 1222 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{11}H_8N_3O_3SF_3$ $[M]^+$: 319.0238; found: 319.0239.

4-Triflyl triazole (±)-4f. From 20 mg (0.12 mmol) of azide (±)-**3f**, and after flash chromatography of the residue using hexanes/ethyl acetate (9:1→8:2) as eluent gave compound (±)-**4f** (36 mg, 94%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 2.64 (s, 1H, OH), 4.29 (dd, 1H, *J* = 12.3, 4.0 Hz, C*H*H), 4.59 (dd, 1H, *J* = 12.3, 7.7 Hz, CH*H*), 5.85 (dd, 1H, *J* = 7.7, 3.9 Hz, CH), 7.33 (m, 2H, 2CH^{Ar}), 7.43 (m, 3H, 3CH^{Ar}), 8.45 (s, 1H, CH-*Triazole*); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 139.0 (C-Tf), 134.0 (C^{Ar-q}), 131.7 (CH-*Triazole*), 129.8 (CH^{Ar}), 129.6 (2CH^{Ar}), 127.3 (2CH^{Ar}), 119.3 (q, J_{CF} = 324.7 Hz, CF_3), 68.3 (CH), 64.2 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$, 25 ^{o}C): δ = –78.52 (s, 3F, CF_3); IR ($CHCl_3$): ν = 3426 (OH), 1381, 1119 (O=S=O), 1217 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{11}H_{10}N_3O_3SF_3$ [*M*]$^+$: 321.0395; found: 321.0397.

4-Triflyl triazole 4g. From 20 mg (0.09 mmol) of azide **3g**, and after recrystallization (acetonitrile) gave compound **4g** (30 mg, 86%) as a colorless solid; mp 227–229 ºC; ^{1}H NMR (300 MHz, $(CD_3)_2CO$, 25 ^{o}C): δ = 4.22 (m, 2H, CH_2), 4.95 (m, 2H, CH_2), 7.80 (m, 4H, 4CH^{Ar}), 9.26 (s, 1H, CH-*Triazole*); ^{13}C NMR (75 MHz, $(CD_3)_2CO$, 25 ^{o}C): δ = 168.4 (2C=O), 139.2 (C-Tf), 135.4 (2CH^{Ar}), 134.8 (CH-*Triazole*), 132.9 (2C^{Ar-q}), 124.1 (2CH^{Ar}), 120.5 (q, J_{CF} = 323.8 Hz, CF_3), 50.9 (CH_2), 38.7 (CH_2); ^{19}F NMR (282 MHz, $(CD_3)_2CO$, 25 ^{o}C): δ = –80.45 (s, 3F, CF_3); IR ($CHCl_3$): ν = 1717 (C=O), 1373, 1134 (O=S=O), 1201 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{13}H_9N_4O_4SF_3$ [*M*]$^+$: 374.02966; found: 374.03092.

4-Triflyl triazole 4h. From 20 mg (0.16 mmol) of azide **3h**, and after flash chromatography of the residue using hexanes/ethyl acetate (9:1) as eluent gave compound **4h** (45 mg, 90%) as a colorless solid; mp 113–115 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 5.30 (dd, 2H, *J* = 7.0, 0.9 Hz, CH_2), 6.37 (dt, 1H, *J* = 15.7, 7.0 Hz, CH=C*H*-CH_2), 6.83 (d, 1H, *J* = 15.8 Hz, C*H*=CH-CH_2), 7.40 (m, 5H, 5CH^{Ar}), 8.39 (s, 1H, CH-*Triazole*); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 139.4 (C-Tf), 138.1 (CH=*C*H-CH_2), 134.6 (C^{Ar-q}), 130.5 (CH-*Triazole*), 129.2 (CH^{Ar}), 128.8 (2CH^{Ar}), 126.9 (2CH^{Ar}), 119.3 (q, J_{CF} = 324.7 Hz, CF_3), 119.0 (*C*H=CH-CH_2), 53.6 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$, 25

^{o}C): δ = –78.56 (s, 3F, CF_3); IR ($CHCl_3$): ν = 1379, 1118 (O=S=O), 1215 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{12}H_{10}N_3O_2SF_3$ $[M]^+$: 317.0446; found: 317.0450.

4-Triflyl triazole (+)-4i. From 34 mg (0.12 mmol) of azide (+)-**3i**, and after recrystallization (acetonitrile) gave compound (+)-**4i** (40 mg, 82%) as a colorless solid; mp 151–153 ºC; $[\alpha]_D$ = +5.1 (*c* 9.7, acetone); ^{1}H NMR (300 MHz, $(CD_3)_2CO$, 25 ^{o}C): δ = 1.33 (s, 3H, CH_3), 1.50 (s, 3H, CH_3), 3.08 (ddd, 1H, *J* = 9.0, 6.0, 5.0 Hz, CHOH), 3.80 (dd, 1H, *J* = 8.6, 4.9 Hz, C*H*H-OH), 3.94 (dd, 1H, *J* = 8.6, 6.1 Hz, CH*H*-OH), 4.42 (dd, 1H, *J* = 9.0, 4.0 Hz, CH), 5.24 (d, 1H, *J* = 3.6 Hz, CH), 5.47 (d, 1H, *J* = 4.0 Hz, CH), 6.22 (d, 1H, *J* = 3.6 Hz, CH), 9.14 (s, 1H, CH-*Triazole*); ^{13}C NMR (75 MHz, $(CD_3)_2CO$, 25 ^{o}C): δ = 138.7 (C-Tf), 135.9 (CH-*Triazole*), 120.5 (q, J_{CF} = 323.9 Hz, CF_3), 113.3 (C^q-*Acetonide*), 107.3 (CH), 84.4 (CH), 81.3 (CH), 73.4 (CHOH), 68.2 (CH), 68.1 (CH_2OH), 27.0 (CH_3), 26.4 (CH_3); ^{19}F NMR (282 MHz, $(CD_3)_2CO$, 25 ^{o}C): δ = –80.37 (s, 3F, CF_3); IR (acetone): ν = 1383, 1028 (O=S=O), 1216 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{12}H_{16}N_3O_7SF_3$ $[M]^+$: 403.0661; found: 403.0681.

4-Triflyl triazole (–)-4j. From 30 mg (0.09 mmol) of azide (–)-**3j**, and after flash chromatography of the residue using hexanes/ethyl acetate (8:2→1:1) as eluent gave compound (–)-**4j** (25 mg, 63%) as a colorless solid; mp 115–117 ºC; $[\alpha]_D$ = –27.8 (*c* 3.5, acetone); ^{1}H NMR (500 MHz, $(CD_3)_2CO$, 25 ^{o}C): δ = 3.16 (s, 2H, 2OH), 3.77 (s, 3H, OCH_3), 4.00 (dd, 1H, *J* = 9.0, 5.9 Hz, C*H*H-OH), 4.24 (dd, 1H, *J* = 9.0, 6.8 Hz, CH*H*-OH), 4.73 (m, 1H, CH-OH), 4.93 (dd, 1H, *J* = 6.1, 2.4 Hz, CH-N), 6.15 (d, 1H, *J* = 2.4 Hz, CH-C=O), 6.94 (m, 2H, $2CH^{Ar}$), 7.56 (m, 2H, $2CH^{Ar}$), 9.44 (s, 1H, CH-*Triazole*); ^{13}C NMR (125 MHz, $(CD_3)_2CO$, 25 ^{o}C): δ = 158.7 (C=O), 158.4 ($C^{Ar\text{-}q}$-OCH_3), 139.6 (C-Tf), 134.5 (CH-*Triazole*), 131.1 ($C^{Ar\text{-}q}$), 121.7 ($2CH^{Ar}$), 120.5 (q, J_{CF} = 323.8 Hz, CF_3), 115.1 ($2CH^{Ar}$), 76.5 (CHOH), 67.1 (CH-C=O), 66.4 (CH_2OH), 63.4 (CH-N), 55.9 (OCH_3); ^{19}F NMR (282 MHz, $(CD_3)_2CO$, 25 ^{o}C): δ = –80.26 (s, 3F, CF_3); IR (acetone): ν = 3450 (OH), 1757 (C=O),

1381, 1102 (O=S=O), 1207 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{15}H_{15}N_4O_6SF_3$ $[M]^+$: 436.0664; found: 436.0664.

4-Triflyl triazole 4k. From 20 mg (0.12 mmol) of azide **3k**, and after flash chromatography of the residue using hexanes/ethyl acetate (95:5→9:1) as eluent gave compound **4k** (33 mg, 87%) as a colorless solid; mp 85–87 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 3.42 (s, 1H, C≡CH), 5.84 (s, 2H, CH_2), 7.44 (m, 3H, $3CH^{Ar}$), 7.63 (m, 1H, CH^{Ar}), 8.30 (s, 1H, CH-*Triazole*); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 139.3 (C-Tf), 134.2 (C^{Ar-q}), 133.8 (CH^{Ar}), 130.8 (CH-*Triazole*), 130.1 (CH^{Ar}), 129.9 (CH^{Ar}), 129.8 (CH^{Ar}), 122.2 (C^{Ar-q}), 119.3 (q, J_{CF} = 324.7 Hz, CF_3), 83.7 (C≡*C*H), 80.2 (*C*≡CH), 53.6 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$, 25 ºC): δ = –78.56 (s, 3F, CF_3); IR ($CHCl_3$): ν = 3288 (≡C-H), 1381, 1119 (O=S=O), 1217 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{12}H_8N_3O_2SF_3$ $[M]^+$: 315.0289; found: 315.0285.

4-Triflyl triazole 4l. From 20 mg (0.10 mmol) of azide **3l**, and after flash chromatography of the residue using hexanes/ethyl acetate (95:5→85:15) as eluent gave compound **4l** (30 mg, 87%) as a colorless solid; mp 99–101 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 2.31 (m, 2H, J = 6.8 Hz, CH_2), 2.53 (t, 2H, J = 6.6 Hz, CH_2), 4.74 (t, 2H, J = 6.9 Hz, CH_2), 7.33 (m, 3H, $3CH^{Ar}$), 7.41 (m, 2H, $2CH^{Ar}$), 8.40 (s, 1H, CH-*Triazole*); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 139.2 (C-Tf), 131.6 ($2CH^{Ar}$), 131.1 (CH-*Triazole*), 128.4 ($2CH^{Ar}$), 128.3 (CH^{Ar}), 122.8 (C^{Ar-q}), 119.4 (q, J_{CF} = 324.8 Hz, CF_3), 86.2 (*C*≡C), 83.0 (C≡*C*), 50.3 (CH_2), 28.4 (CH_2), 16.4 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$, 25 ºC): δ = –78.58 (s, 3F, CF_3); IR ($CHCl_3$): ν = 1381, 1120 (O=S=O), 1217 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{14}H_{12}N_3O_2SF_3$ $[M]^+$: 343.0602; found: 343.0604.

4-Triflyl triazole 4m. From 50 mg (0.42 mmol) of azide **3m**, and after flash chromatography of the residue using hexanes/ethyl acetate (90:10) as eluent gave compound **4m** (83 mg, 72%) as a colorless solid; mp 135–137 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 7.62 (m, 3H, $3CH^{Ar}$), 7.79 (m, 2H, $2CH^{Ar}$), 8.76 (s, 1H, CH-*Triazole*); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 140.0 (C-Tf), 135.4 (C^{Ar-q}), 130.7 (CH^{Ar}), 130.3 ($2CH^{Ar}$), 128.8 (CH-*Triazole*), 121.1 ($2CH^{Ar}$), 119.4 (q, J_{CF} = 324.8 Hz, CF_3); ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –78.38 (s, 3F, CF_3); IR ($CHCl_3$): ν = 1382, 1111 (O=S=O), 1213 (C–F) cm^{-1}; HRMS (ES): calcd for $C_9H_6N_3O_2SF_3$ $[M]^+$: 277.0133; found: 277.0136.

4-Triflyl triazole 4n. From 26 mg (0.14 mmol) of azide **3n**, and after flash chromatography of the residue using hexanes/dichloromethane (1:1) as eluent gave compound **4n** (46 mg, 94%) as a colorless solid; mp 119–121 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.73 (s, 3H, CH_3), 7.57 (dd, 1H, J = 7.5, 1.5 Hz, CH^{Ar}), 7.77 (m, 2H, $2CH^{Ar}$), 8.19 (dd, 3H, J = 7.2, 2.1 Hz, CH^{Ar}), 8.64 (s, 1H, CH-*Triazole*); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 164.2 (C=O), 138.9 (C-Tf), 134.6 (C^{Ar-q}), 133.5 (CH^{Ar}), 133.4 (CH-*Triazole*), 132.1 (CH^{Ar}), 131.6 (CH^{Ar}), 127.5 (CH^{Ar}), 126.8 (C^{Ar-q}), 119.4 (q, J_{CF} = 324.8 Hz, CF_3), 52.8 (CH_3); ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –78.59 (s, 3F, CF_3); IR ($CHCl_3$): ν = 1725 (C=O), 1381, 1108 (O=S=O), 1216 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{11}H_8N_3O_4SF_3$ $[M]^+$: 335.0188; found: 335.0176.

4-Triflyl triazole 4o. From 23 mg (0.09 mmol) of azide **3o**, and after flash chromatography of the residue using hexanes/dichloromethane (8:2→1:1) as eluent gave compound **4o** (37 mg, 99%) as a colorless solid; mp 158–160 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.56 (m, 2H, $2CH^{Ar}$), 7.97 (m, 2H, $2CH^{Ar}$), 8.76 (s, 1H, CH-*Triazole*); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 140.3 (C-Tf), 139.4 ($2CH^{Ar}$), 135.0 (C^{Ar-q}), 128.6 (CH-*Triazole*), 122.5 ($2CH^{Ar}$), 119.3 (q, J_{CF} = 324.8 Hz, CF_3), 96.2 (C^{Ar-q}-I); ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –78.27 (s, 3F, CF_3); IR ($CHCl_3$): ν = 1382, 1110 (O=S=O), 1217 (C–F) cm^{-1}; HRMS (ES): calcd for $C_9H_5N_3O_2SIF_3$ $[M]^+$: 402.9099; found: 402.9115.

4-Triflyl triazole 4p. From 25 mg (0.14 mmol) of azide **3p**, and after flash chromatography of the residue using hexanes/ethyl acetate (9:1) as eluent gave compound **4p** (42 mg, 89%) as a colorless solid; mp 103–105 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.90 (s, 3H, OCH_3), 3.92 (s, 3H,

OCH_3), 6.65 (m, 2H, 2CH^{Ar}), 7.77 (m, 1H, CH^{Ar}), 8.83 (s, 1H, CH-*Triazole*); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 162.3 (C$^{Ar\text{-}q}$-OCH_3), 152.0 (C$^{Ar\text{-}q}$-OCH_3), 138.5 (C-Tf), 132.3 (CH-*Triazole*), 126.0 (CH^{Ar}), 119.5 (q, J_{CF} = 324.7 Hz, CF_3), 118.0 (C$^{Ar\text{-}q}$), 105.3 (CH^{Ar}), 99.5 (CH^{Ar}), 56.2 (OCH_3), 55.8 (OCH_3); ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –78.62 (s, 3F, CF_3); IR ($CHCl_3$): ν = 1380, 1106 (O=S=O), 1213 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{11}H_{10}N_3O_4SF_3$ [*M*]$^+$: 337.0344; found: 337.0341.

4-Triflyl triazole 4q. From 20 mg (0.16 mmol) of azide **3q**, and after flash chromatography of the residue using hexanes/ethyl acetate (9:1→8:2) as eluent gave compound **4q** (23 mg, 50%) as a colorless solid; mp 132–133 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.23 (d, 1H, *J* = 4.6 Hz, CH^{Ar}), 7.64 (d, 1H, *J* = 4.6 Hz, CH^{Ar}), 8.36 (s, 1H, CH-*Triazole*); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 152.8 (C$^{Ar\text{-}q}$), 136.7 (C-Tf), 121.3 (CH-*Triazole*), 119.6 (q, J_{CF} = 325.2 Hz, CF_3), 118.4 (CH^{Ar}), 118.2 (CH^{Ar}); ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –78.32 (s, 3F, CF_3); IR ($CHCl_3$): ν = 1364, 1101 (O=S=O), 1206 (C–F) cm^{-1}; HRMS (ES): calcd for $C_6H_3N_4O_2S_2F_3$ [*M*]$^+$: 283.9649; found: 283.9637.

4-Triflyl triazole 4r. From 27 mg (0.22 mmol) of azide **3r**, and after flash chromatography of the residue using hexanes/ethyl acetate (95:5) as eluent gave compound **4r** (35 mg, 57%) as a colorless solid; mp 102–104 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.53 (ddd, 1H, *J* = 7.5, 4.9, 0.9 Hz, CH^{Ar}), 8.06 (td, 1H, *J* = 7.9, 1.8 Hz, CH^{Ar}), 8.28 (d, 1H, *J* = 8.2 Hz, CH^{Ar}), 8.59 (m, 1H, CH^{Ar}), 9.35 (s, 1H, CH-*Triazole*); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 149.2 (CH^{Ar}), 147.6 (C-Tf), 139.9 (CH^{Ar}), 128.2 (CH-*Triazole*), 125.5 (CH^{Ar}), 119.4 (q, J_{CF} = 324.7 Hz, CF_3), 114.3 (CH^{Ar}), (*the signal for a C$^{Ar\text{-}q}$ was not detected because of the quadropole effect of the two nitrogen atoms bonded to it*); ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –78.43 (s, 3F, CF_3); IR ($CHCl_3$): ν = 1381, 1111 (O=S=O), 1213 (C–F) cm^{-1}; HRMS (ES): calcd for $C_8H_5N_4O_2SF_3$ [*M*]$^+$: 278.0085; found: 278.0086.

4-Triflyl triazole 4t. From 20 mg (0.17 mmol) of azide **3t**, and after flash chromatography of the residue using hexanes/ethyl acetate (9:1) as eluent gave compound **4t** (25 mg, 73%) as a colorless solid; mp 107–109 ºC; ^{1}H NMR (300 MHz, CD_3CN, 25 ºC): δ = 8.79 (s, 1H, CH-*Triazole*); ^{13}C NMR (75 MHz, CD_3CN, 25 ºC): δ = 138.8 (C-Tf), 134.1 (CH-*Triazole*), 120.2 (q, J_{CF} = 323.6 Hz, CF_3); ^{19}F NMR (282 MHz, CD_3CN, 25 ºC): δ = –80.39 (s, 3F, CF_3); IR (acetone): ν = 1379, 1105 (O=S=O), 1214 (C–F) cm^{-1}; HRMS (ES): calcd for $C_3H_2N_3O_2SF_3$ $[M]^+$: 200.9820; found: 200.9827.

4-Triflyl triazole 4u. From 20 mg (0.10 mmol) of azide **3u**, and after flash chromatography of the residue using hexanes/ethyl acetate (97:3→9:1) as eluent gave compound **4u** (21 mg, 55%) as a colorless solid; mp 144–146 ºC; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 0.98 (t, 3H, *J* = 7.2 Hz, CH_3), 1.47 (m, 2H, CH_2), 1.63 (m, 2H, CH_2), 2.46 (t, 2H, *J* = 7.0 Hz, CH_2), 7.61 (d, 2H, *J* = 8.7 Hz, 2CH^{Ar}), 7.72 (d, 2H, *J* = 8.7 Hz, 2CH^{Ar}), 8.71 (s, 1H, CH-*Triazole*); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 140.2 (C-Tf), 134.0 (C$^{Ar\text{-}q}$), 133.3 (2CH^{Ar}), 128.5 (CH-*Triazole*), 127.1 (C$^{Ar\text{-}q}$), 120.7 (2CH^{Ar}), 119.4 (q, J_{CF} = 324.8 Hz, CF_3), 94.3 (C≡*C*), 78.9 (*C*≡C), 30.5 (CH_2), 22.0 (CH_2), 19.1 (CH_2), 13.6 (CH_3); ^{19}F NMR (282 MHz, $CDCl_3$, 25 ºC): δ = –78.31 (s, 3F, CF_3); IR ($CHCl_3$): ν = 1362, 1111 (O=S=O), 1204 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{15}H_{14}N_3O_2SF_3$ $[M]^+$: 357.0759; found: 357.0748.

4-Triflyl triazole 4v. From 20 mg (0.10 mmol) of azide **3u**, and after flash chromatography of the residue using hexanes/ethyl acetate (97:3→9:1) as eluent gave compound **4v** (45 mg, 70%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 0.97 (t, 3H, *J* = 7.2 Hz, CH_3), 1.46 (m, 2H, CH_2), 1.61 (m, 2H, CH_2), 2.63 (t, 2H, *J* = 7.6 Hz, CH_2), 3.43 (s, 2H, CH_2-*Cyclobutene*), 7.82 (d, 2H, *J* = 8.9 Hz, 2CH^{Ar}), 7.88 (d, 2H, *J* = 8.9 Hz, 2CH^{Ar}), 8.78 (s, 1H, CH-*Triazole*); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 160.3 (*C*=C-*n*Bu), 140.4 (C-Tf), 135.5 (C$^{Ar\text{-}q}$), 132.0 (C$^{Ar\text{-}q}$), 130.0 (C=*C*-*n*Bu), 129.9 (2CH^{Ar}), 128.6 (CH-*Triazole*), 121.2 (2CH^{Ar}), 119.7 (q, J_{CF} = 331.2 Hz, 2CF_3), 119.4

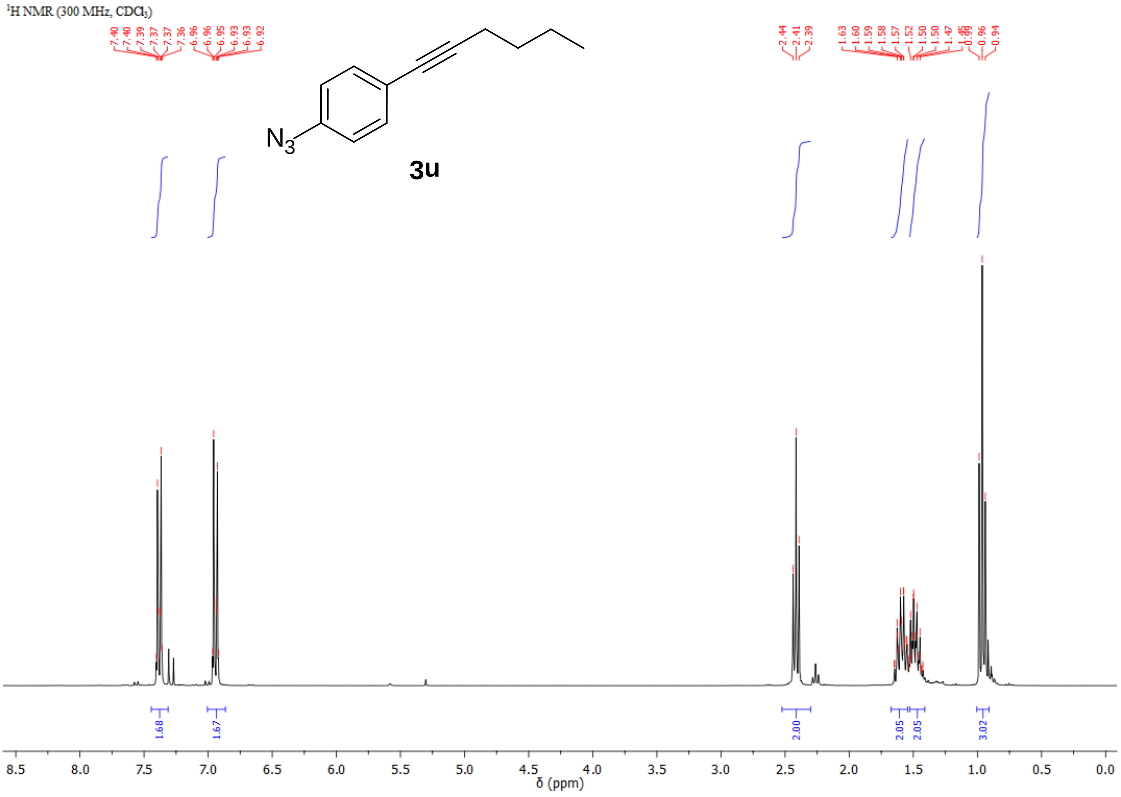
(q, J_{CF} = 324.8 Hz, CF_3), 86.3 (CTf_2), 36.7 (CH_2-*Cyclobutene*), 29.7 (CH_2), 28.0 (CH_2), 22.5 (CH_2), 13.7 (CH_3); ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –70.48 (s, 6F, $2CF_3$), –70.28 (s, 3F, CF_3); IR ($CHCl_3$): ν = 1382, 1107 (O=S=O), 1216 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{19}H_{16}N_3O_6S_3F_9$ $[M]^+$: 649.0058; found: 649.0066.

4-Triflyl triazole 4w. From 20 mg (0.11 mmol) of azide **3v**, and after flash chromatography of the residue using hexanes/ethyl acetate (95:5→9:1) as eluent gave compound **4w** (37 mg, 98%) as a colorless solid; mp 102–104 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 5.65 (s, 2H, CH_2), 7.10 (d, 2H, J = 8.0 Hz, $2CH^{Ar}$), 7.36 (d, 2H, J = 8.5 Hz, $2CH^{Ar}$), 8.22 (s, 1H, CH-*Triazole*); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 141.9 ($C^{Ar\text{-}q}$), 139.6 (C-Tf), 130.5 (CH-*Triazole*), 130.3 ($2CH^{Ar}$), 128.6 ($C^{Ar\text{-}q}$), 120.1 ($2CH^{Ar}$), 119.3 (q, J_{CF} = 324.6 Hz, CF_3), 54.7 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$, 25 °C): δ = –78.55 (s, 3F, CF_3); IR ($CHCl_3$): ν = 2114 (N_3), 1379, 1114 (O=S=O), 1216 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{10}H_7N_6O_2SF_3$ $[M]^+$: 332.0303; found: 332.0310.

Bis(4-triflyl triazole) 4x. From 20 mg (0.11 mmol) of azide **3v**, and after recrystallization (acetonitrile) gave compound **4x** (42 mg, 78%) as a colorless solid; mp 181–183 °C; ^{1}H NMR (300 MHz, $(CD_3)_2CO$, 25 °C): δ = 6.02 (s, 2H, CH_2), 7.79 (d, 2H, J = 8.6 Hz, $2CH^{Ar}$), 8.09 (d, 2H, J = 8.6 Hz, $2CH^{Ar}$), 9.33 (s, 1H, CH-*Triazole*), 9.74 (s, 1H, CH-*Triazole*); ^{13}C NMR (75 MHz, $(CD_3)_2CO$, 25 °C): δ = 140.0 (C-Tf), 139.3 (C-Tf), 137.6 ($C^{Ar\text{-}q}$), 137.3 ($C^{Ar\text{-}q}$), 134.4 (CH-*Triazole*), 132.6 (CH-*Triazole*), 131.4 ($2CH^{Ar}$), 123.0 ($2CH^{Ar}$), 120.52 (q, J_{CF} = 323.9 Hz, CF_3), 120.49 (q, J_{CF} = 323.9 Hz, CF_3), 54.9 (CH_2); ^{19}F NMR (282 MHz, $(CD_3)_2CO$, 25 °C): δ = –80.18 (s, 3F, CF_3), –80.38 (s, 3F, CF_3); IR ($CHCl_3$): ν = 1379, 1108 (O=S=O), 1216 (C–F) cm^{-1}; HRMS (ES): calcd for $C_{13}H_8N_6O_4S_2F_6$ $[M]^+$: 489.9953; found: 489.9955.

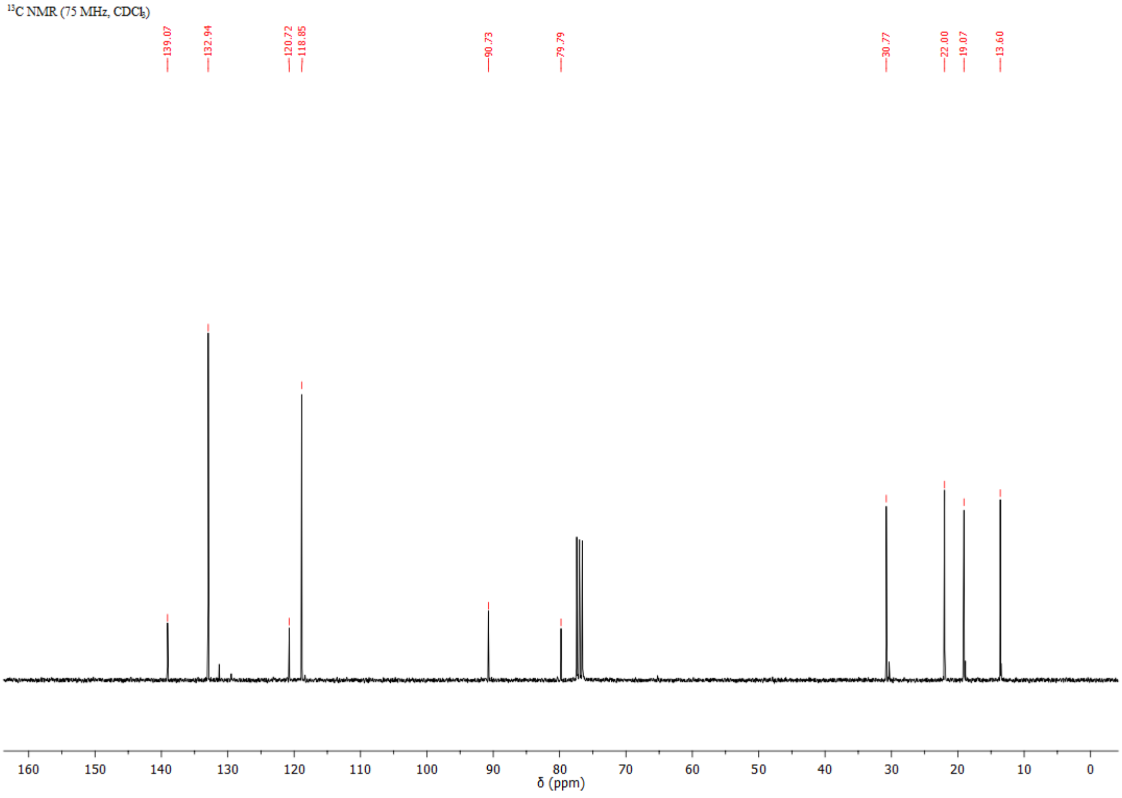
Bis(4,5-dihydro-1*H*-1,2,3-triazole) 5s. From 21 mg (0.17 mmol) of azide **3s**, and after recrystallization (acetonitrile) gave compound **5s** (72 mg, quantitative yield) as a colorless solid; mp

147–149 ºC; ^{1}H NMR (300 MHz, $(CD_3)_2CO$, 25 ºC): δ = 5.44 (s, 2H, CH_2), 7.79 (d, 2H, *J* = 7.3 Hz, $2CH^{Ar}$), 8.88 (d, 2H, *J* = 7.3 Hz, $2CH^{Ar}$); ^{13}C NMR (75 MHz, $(CD_3)_2CO$, 25 ºC): δ = 159.3 ($C^{Ar\text{-}q}$), 145.6 ($2CH^{Ar}$), 121.7 (q, J_{CF} = 326.0 Hz, $2CF_3$), 118.4 ($2CH^{Ar}$), 69.1 (CTf_2), 61.3 (CH_2); ^{19}F NMR (282 MHz, $(CD_3)_2CO$, 25 ºC): δ = –81.03 (s, 6F, $2CF_3$); IR ($CHCl_3$): ν = 2124 (N–N=N), 1339, 1116 (O=S=O), 1167 (C–F) cm^{-1}; HRMS (ES): calcd for $C_9H_6N_4O_4S_2F_6$ $[M]^+$: 411.9735; found: 411.9742.



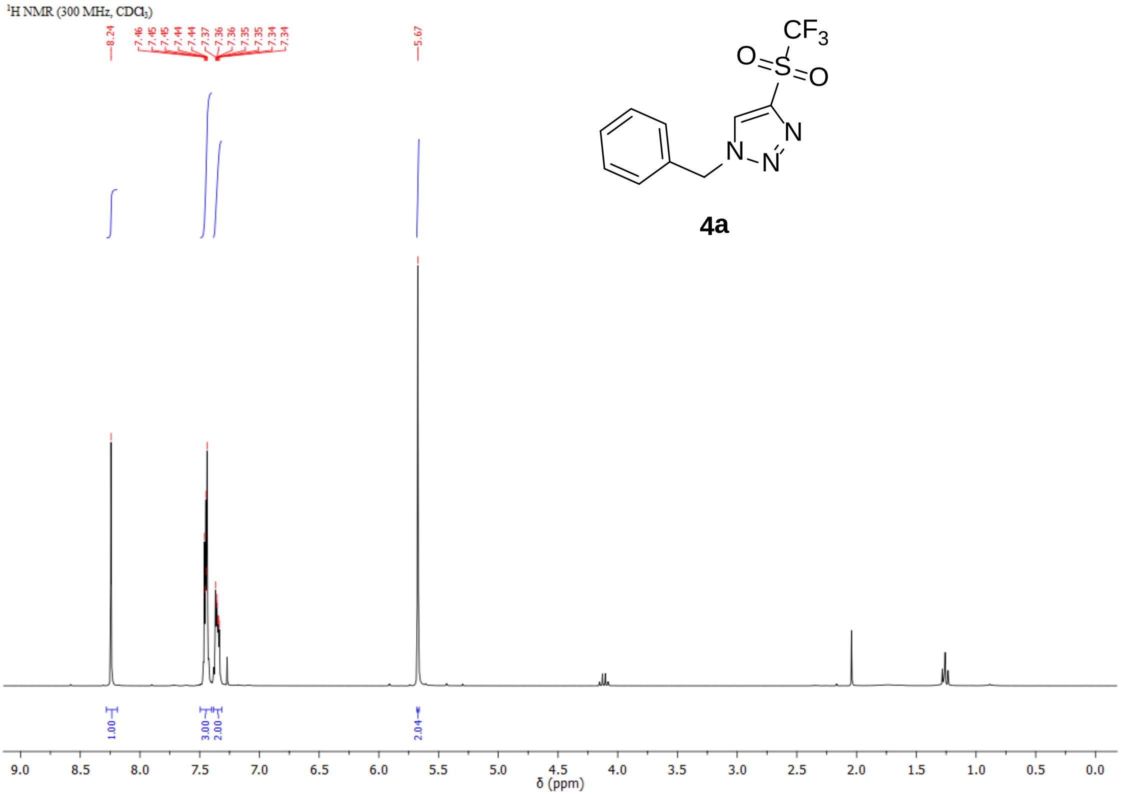
^{1}H NMR (300 MHz, CDCl$_3$)

3u



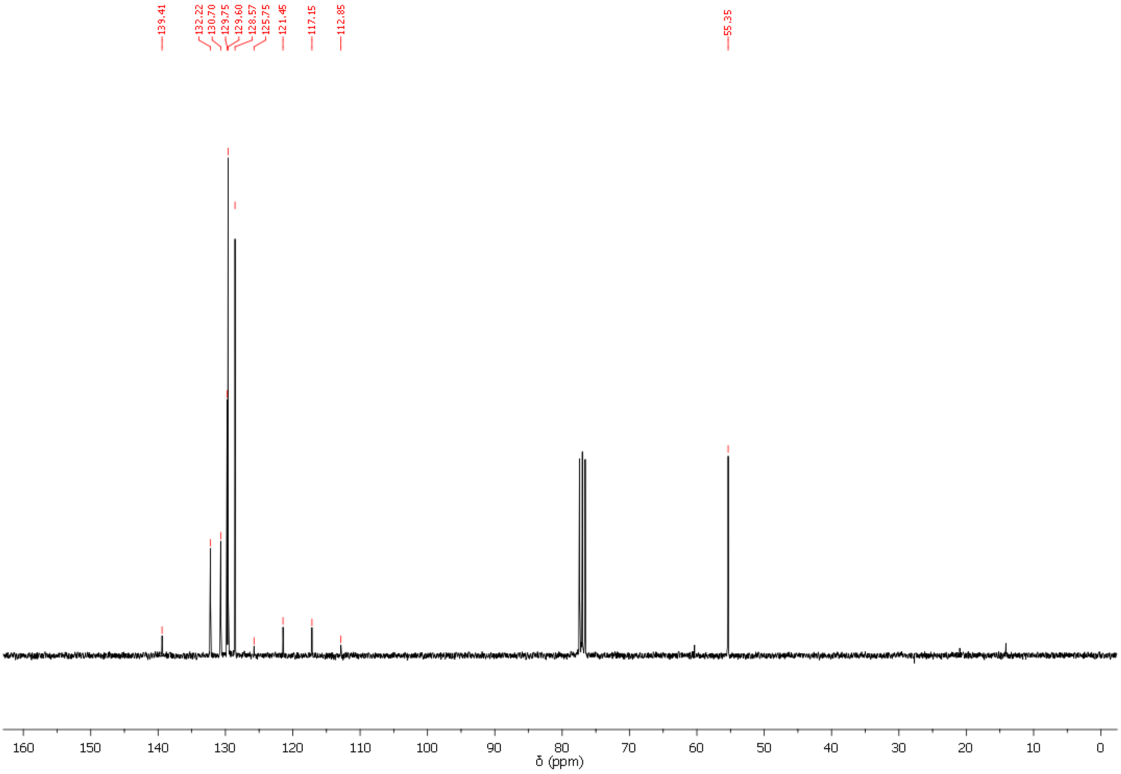
^{13}C NMR (75 MHz, CDCl$_3$)

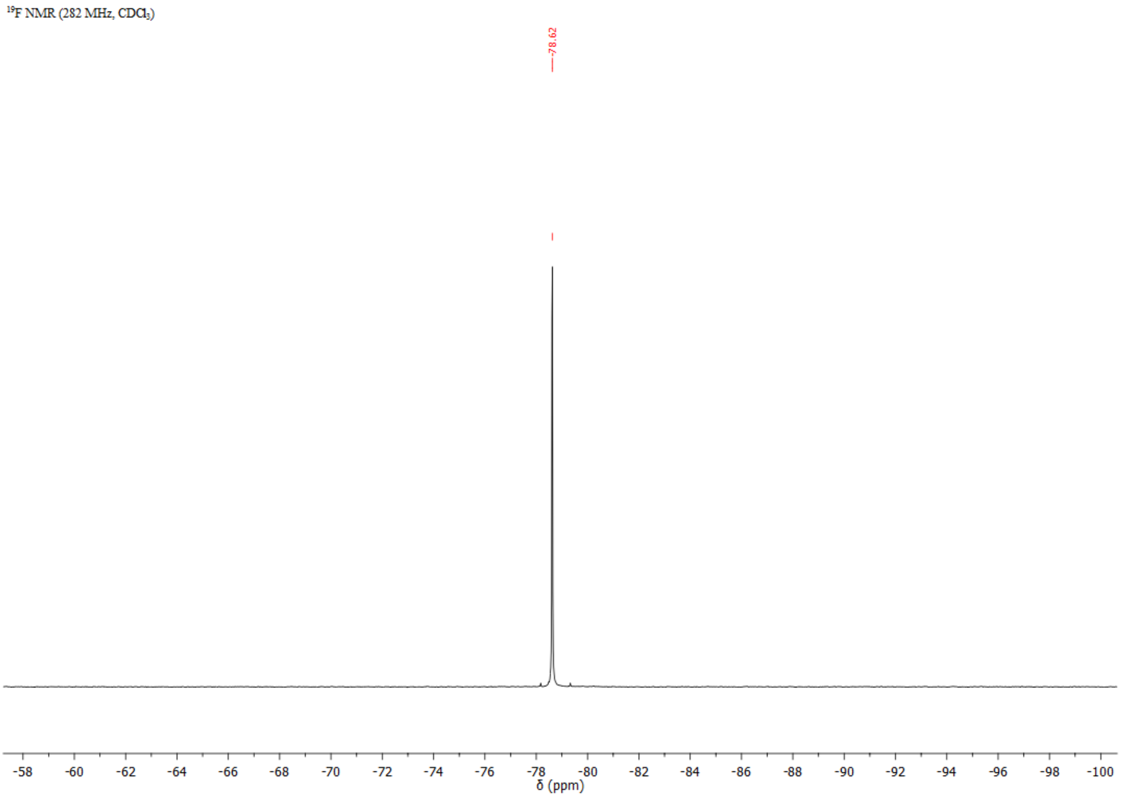
^{1}H NMR (300 MHz, CDCl$_3$)

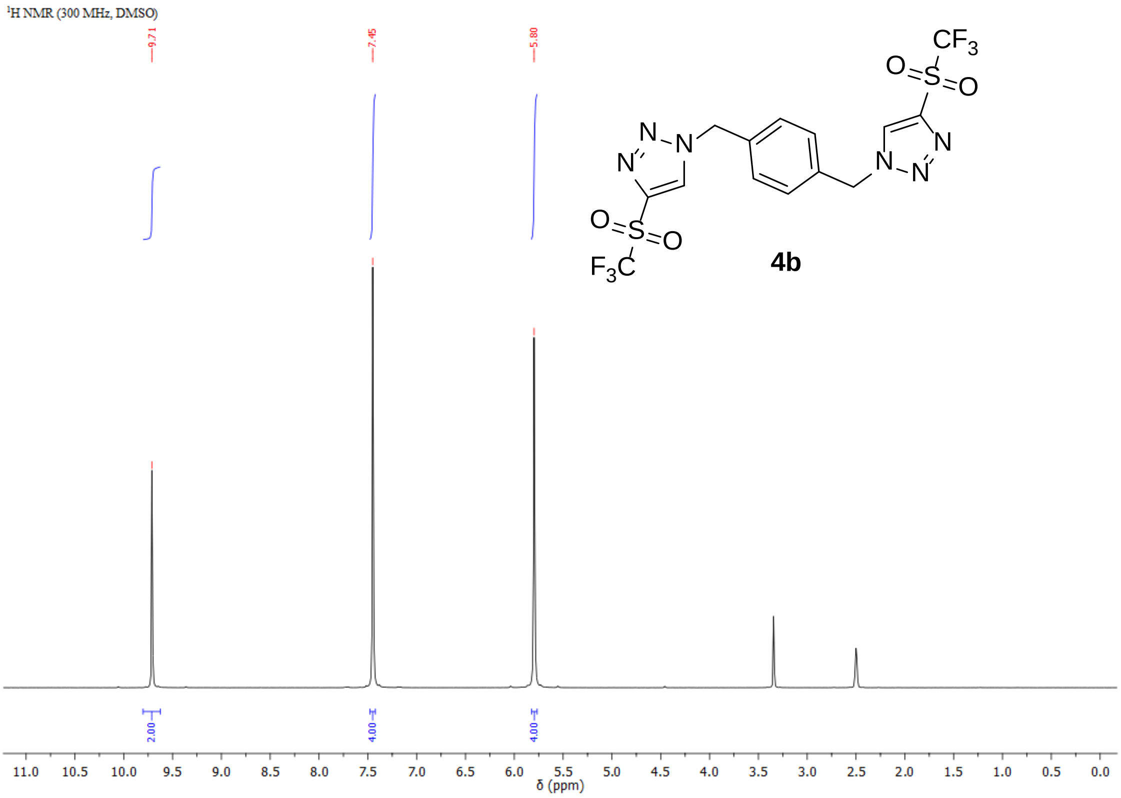


4a

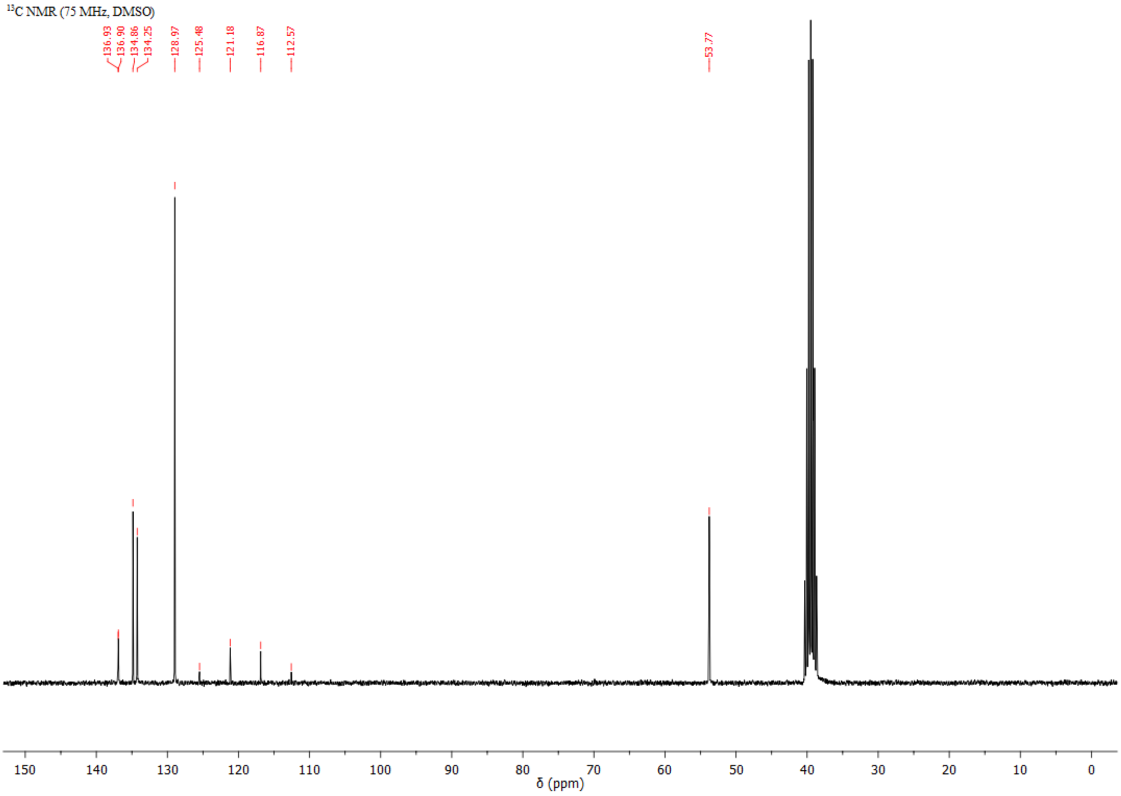
^{13}C NMR (75 MHz, CDCl$_3$)

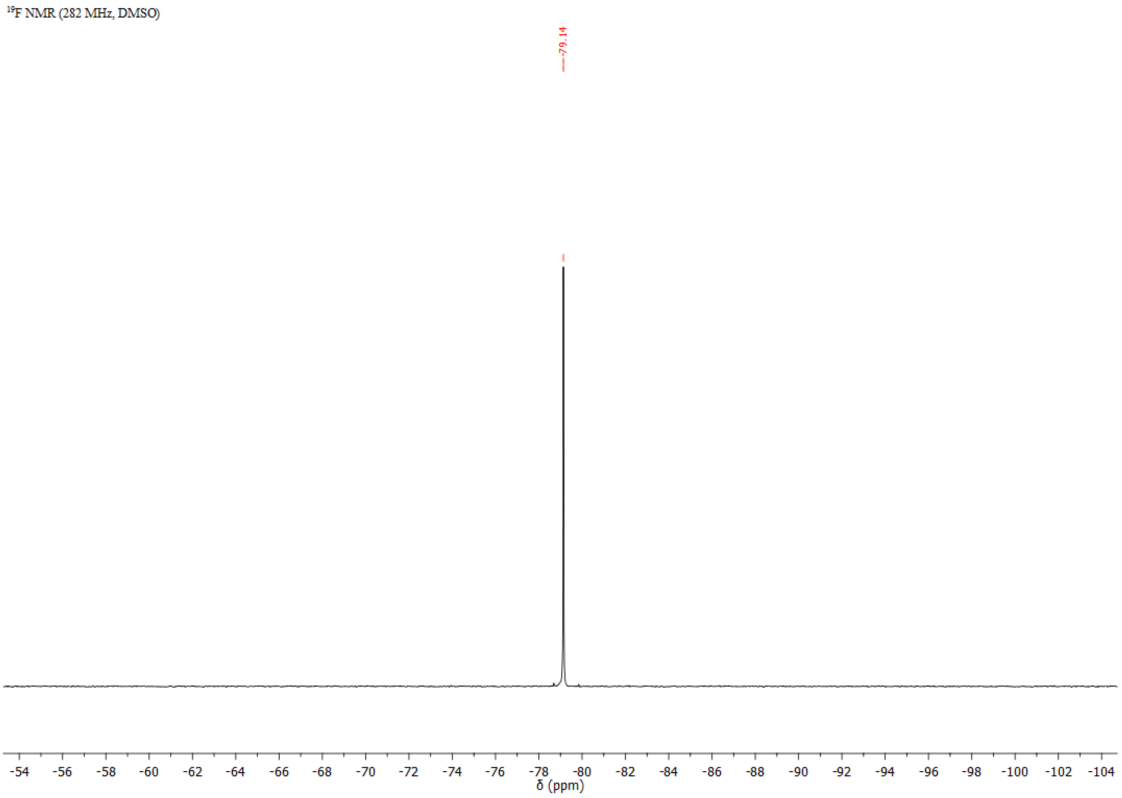



^{19}F NMR (282 MHz, $CDCl_3$)
-78.62
-58
-60
-62
-64
-66
-68
-70
-72
-74
-76
-78
-80
-82
-84
-86
-88
-90
-92
-94
-96
-98
-100
δ (ppm)

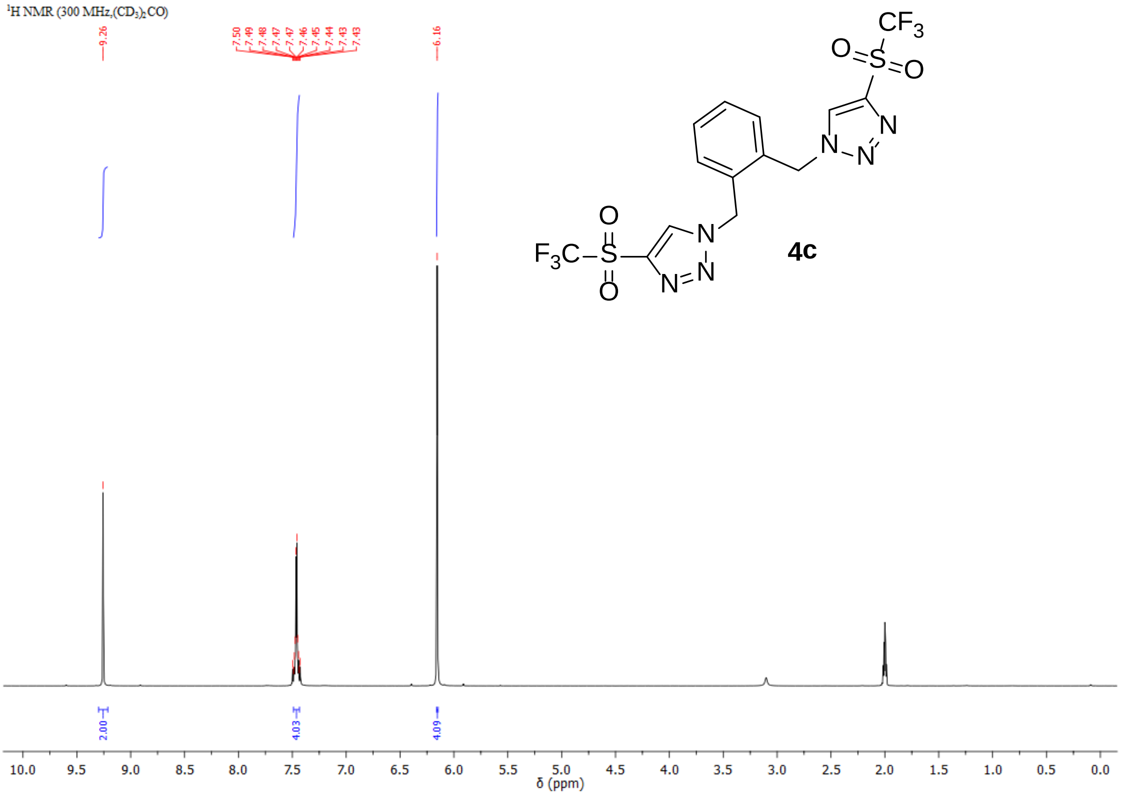

^{1}H NMR (300 MHz, DMSO)
9.71
7.45
5.80
2.00
4.00
4.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)
N
N
N
O
S
O
F3C
CF3
O
S
O
N
N
N

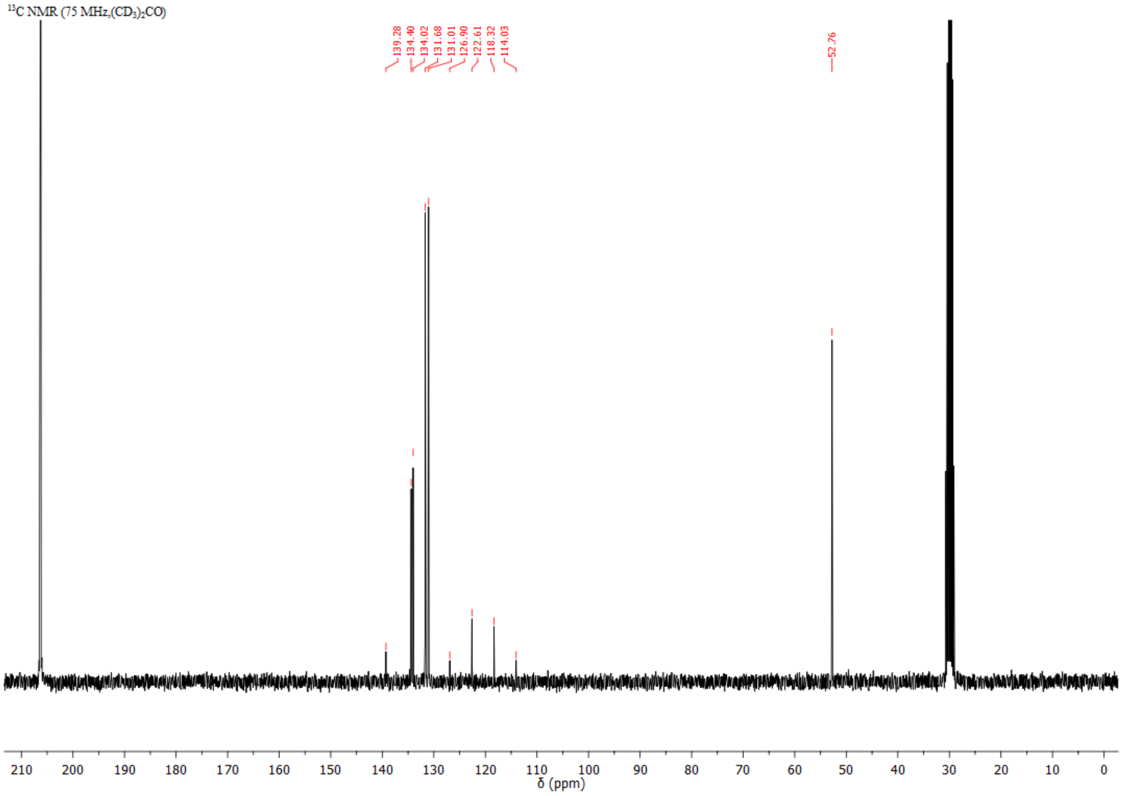
4b


^{13}C NMR (75 MHz, DMSO)
136.93
136.90
134.86
134.25
128.97
125.48
121.18
116.87
112.57
53.77
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

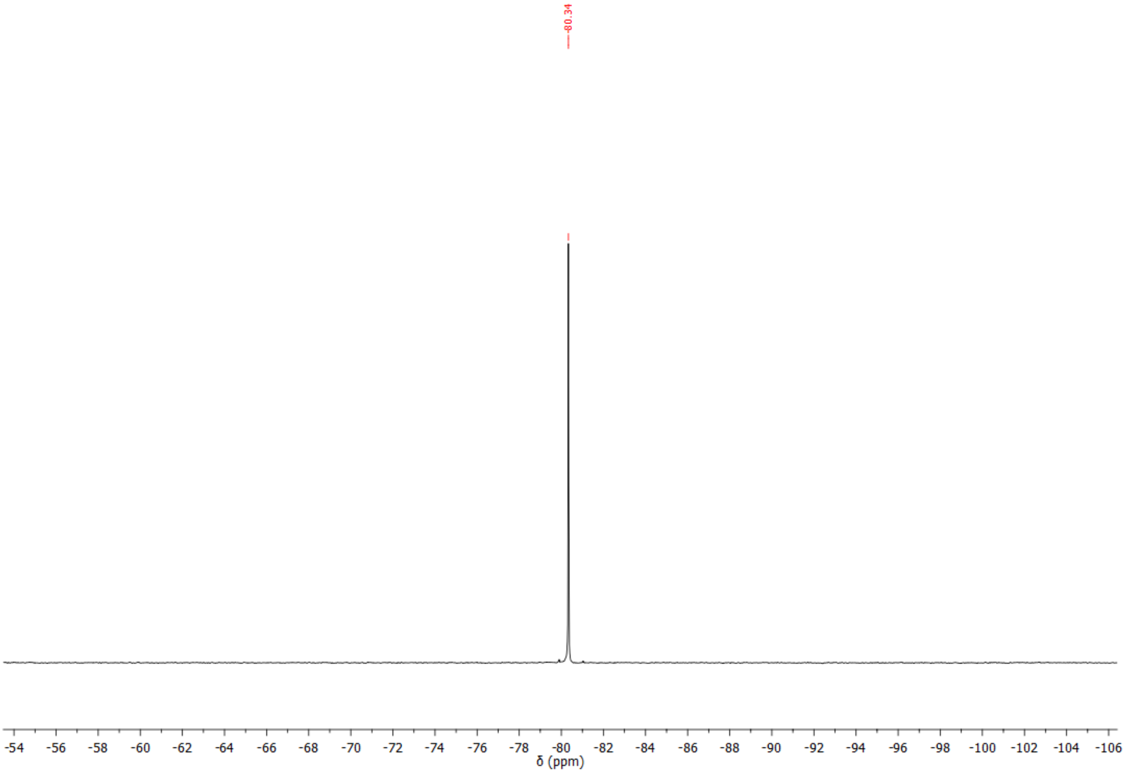


^{19}F NMR (282 MHz, DMSO)
-79.14
-54
-56
-58
-60
-62
-64
-66
-68
-70
-72
-74
-76
-78
-80
-82
-84
-86
-88
-90
-92
-94
-96
-98
-100
-102
-104
δ (ppm)

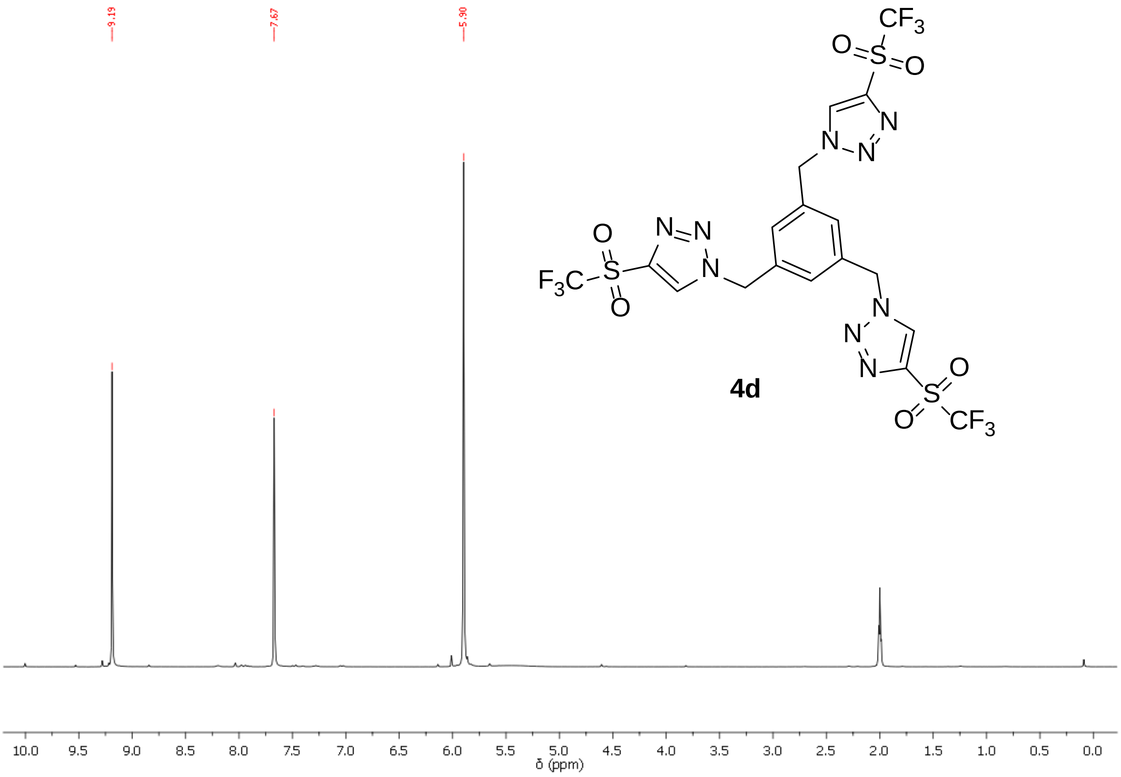

^{1}H NMR (300 MHz,(CD$_3$)$_2$CO)
9.26
7.50
7.49
7.48
7.47
7.47
7.46
7.45
7.44
7.43
7.43
6.16
CF$_3$
O
S
O
N
N
N
O
F$_3$C
S
O
N
N
N
4c
2.00
4.03
4.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)


^{13}C NMR (75 MHz,(CD$_3$)$_2$CO)
139.28
134.40
134.02
131.68
131.01
126.90
122.61
118.32
114.03
52.76
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

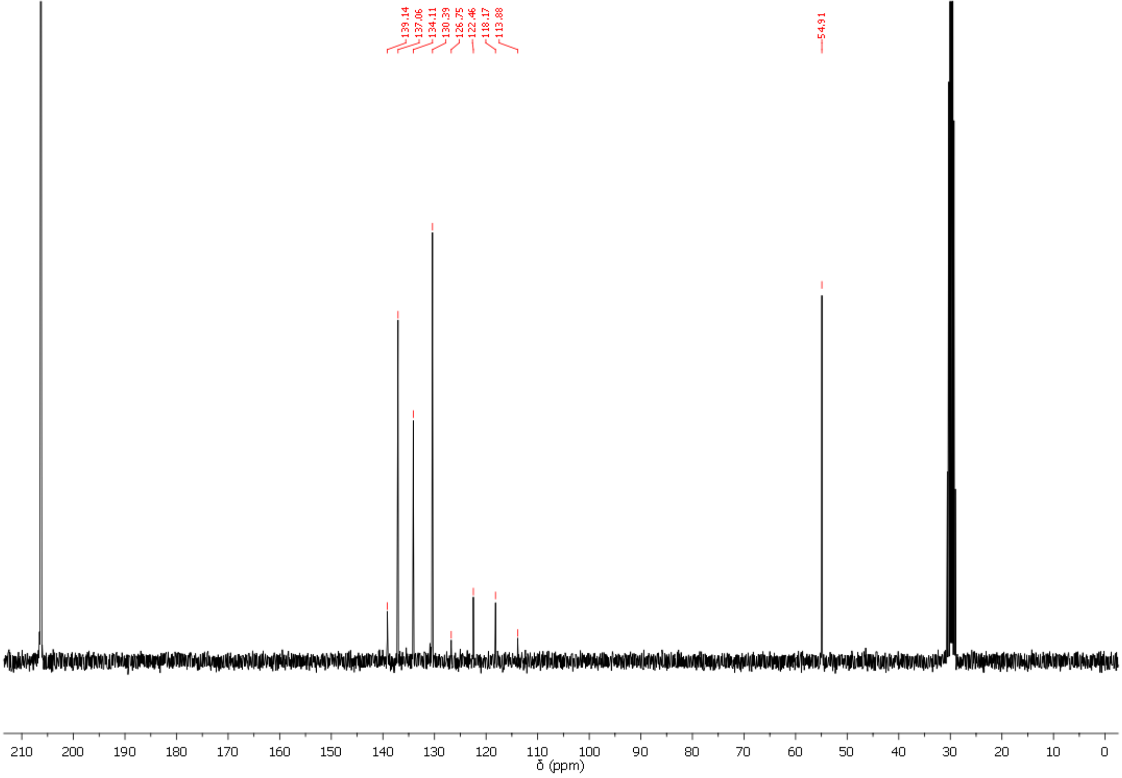
^{19}F NMR (282 MHz,$(CD_3)_2CO$)

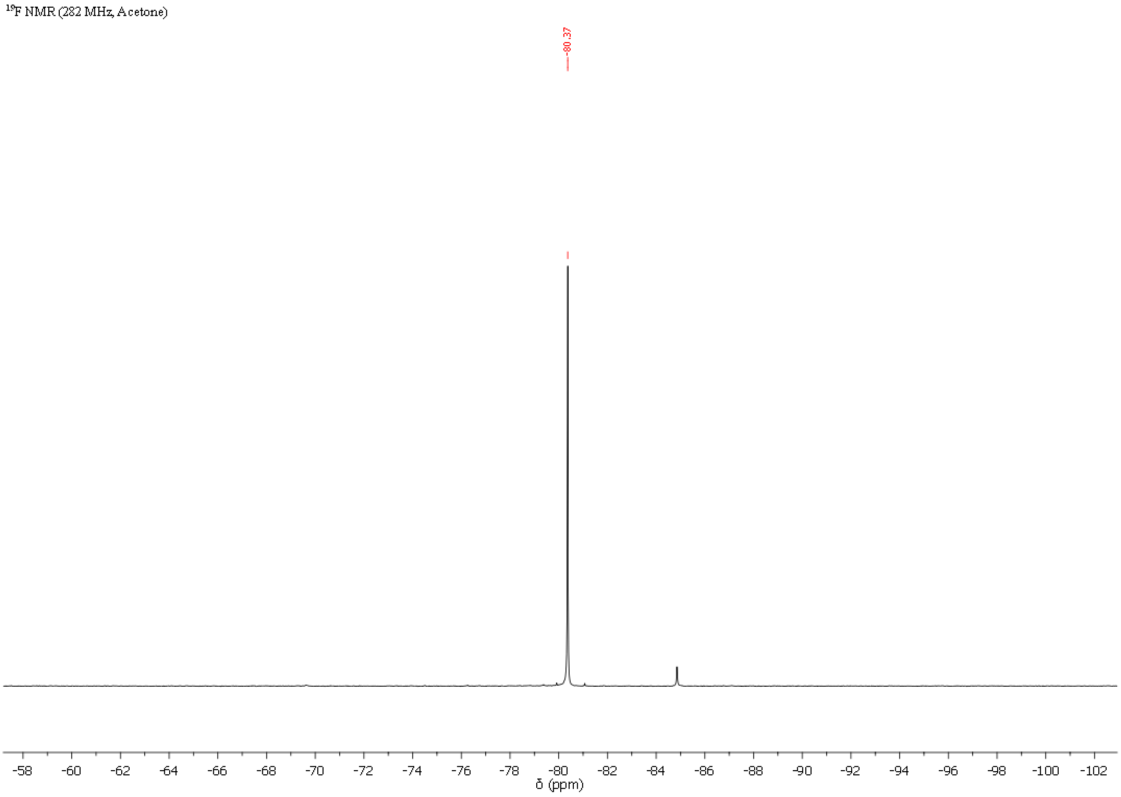


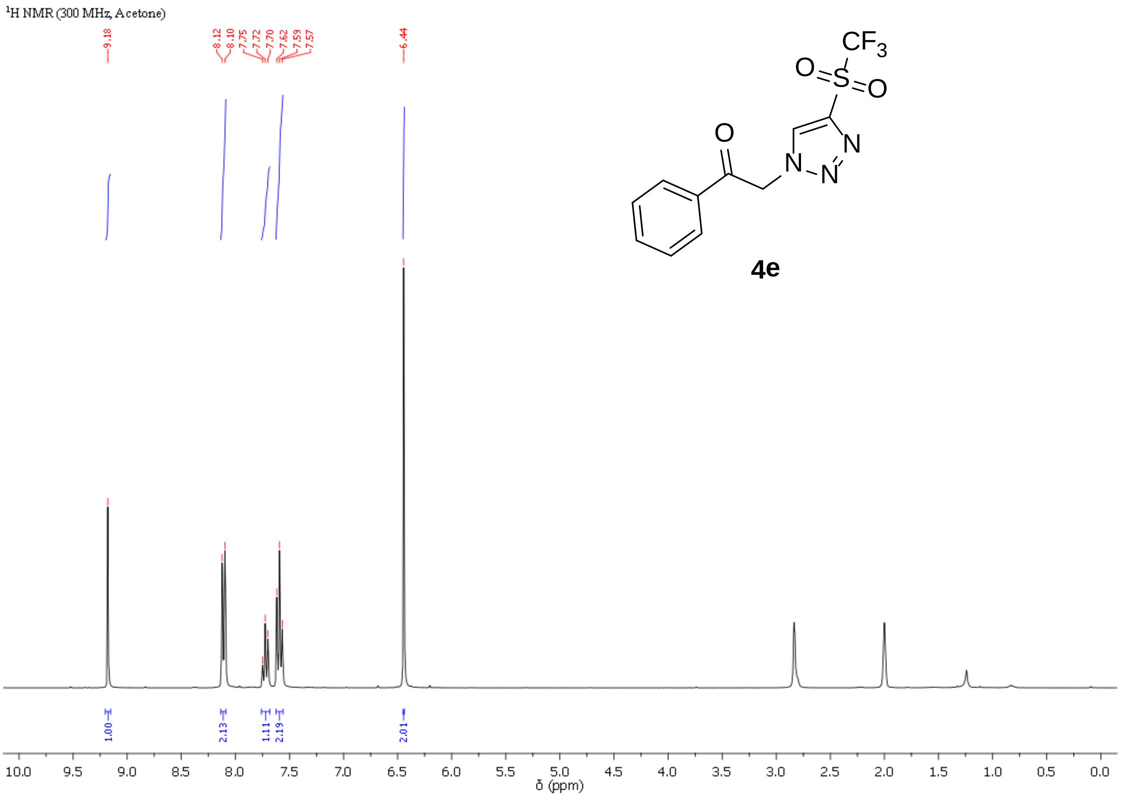
^{1}H NMR (300 MHz, Acetone)



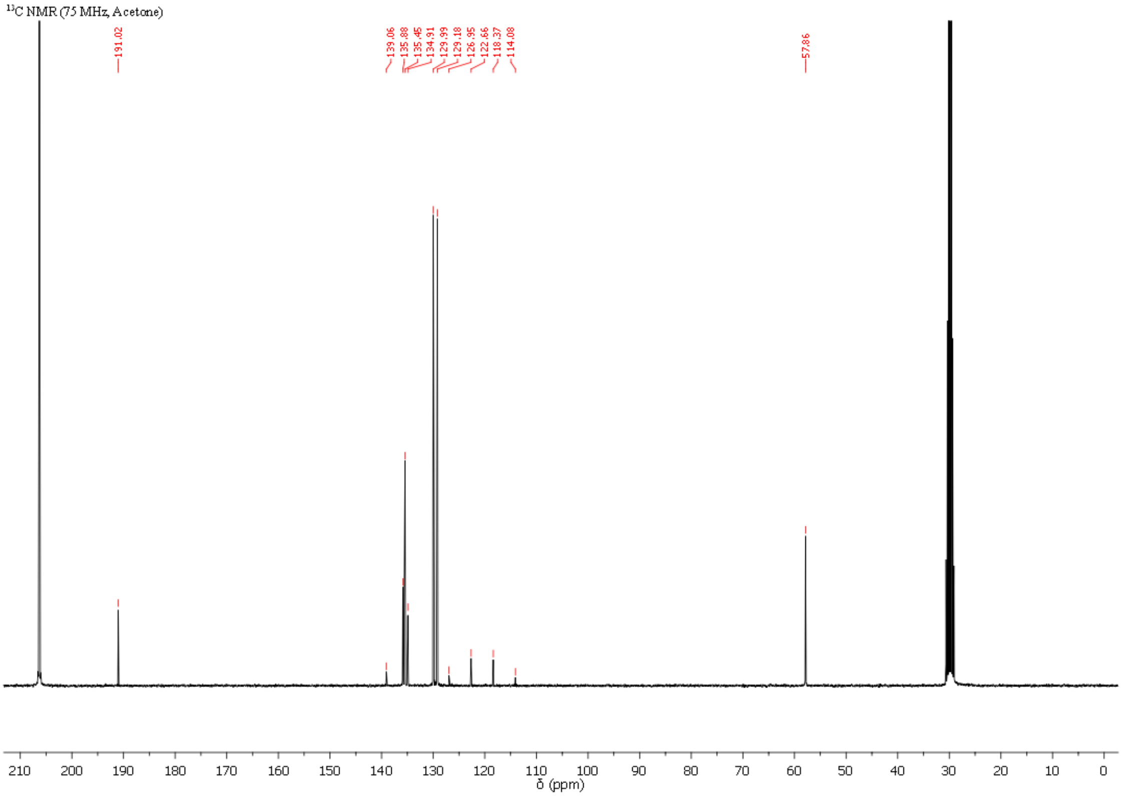
^{13}C NMR (75 MHz, Acetone)




^{19}F NMR (282 MHz, Acetone)
-80.37
-58
-60
-62
-64
-66
-68
-70
-72
-74
-76
-78
-80
-82
-84
-86
-88
-90
-92
-94
-96
-98
-100
-102
δ (ppm)

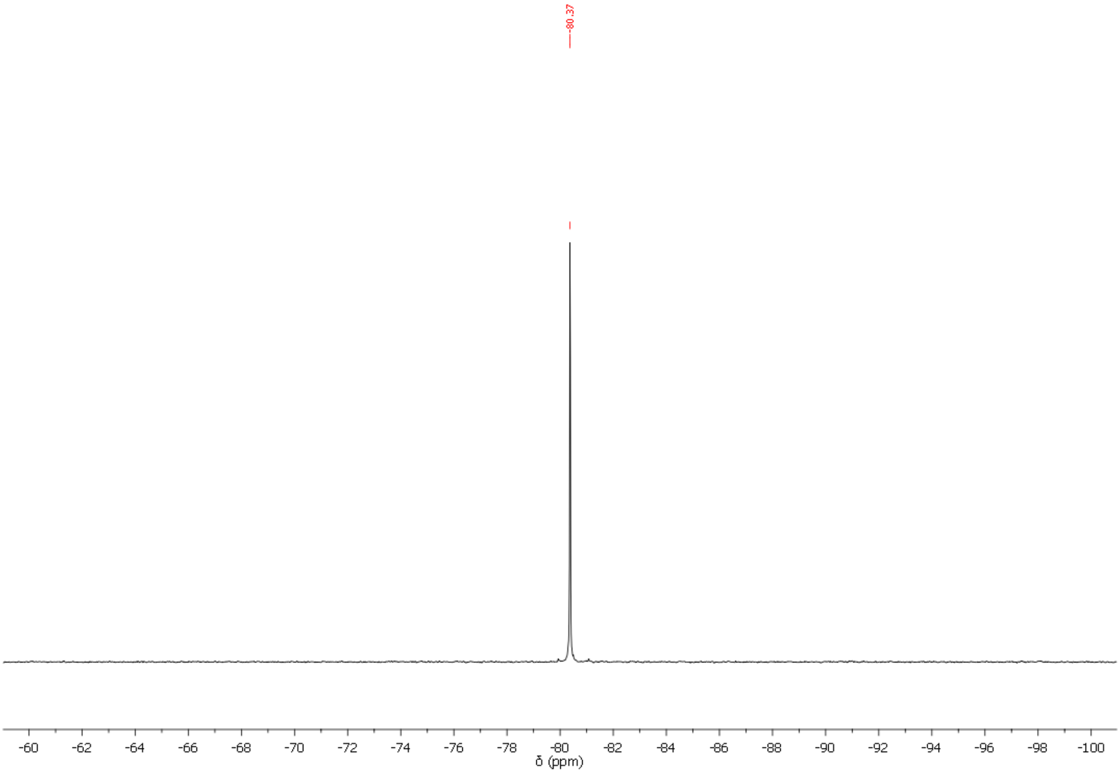


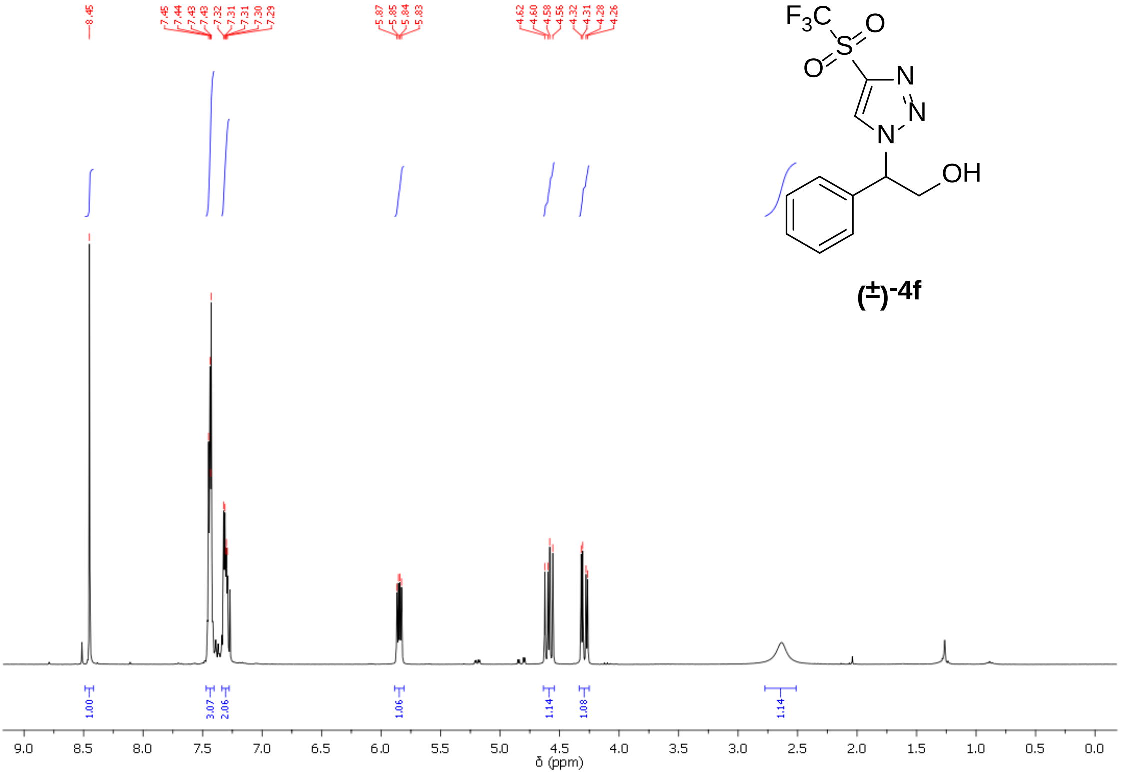
^{1}H NMR (300 MHz, Acetone)



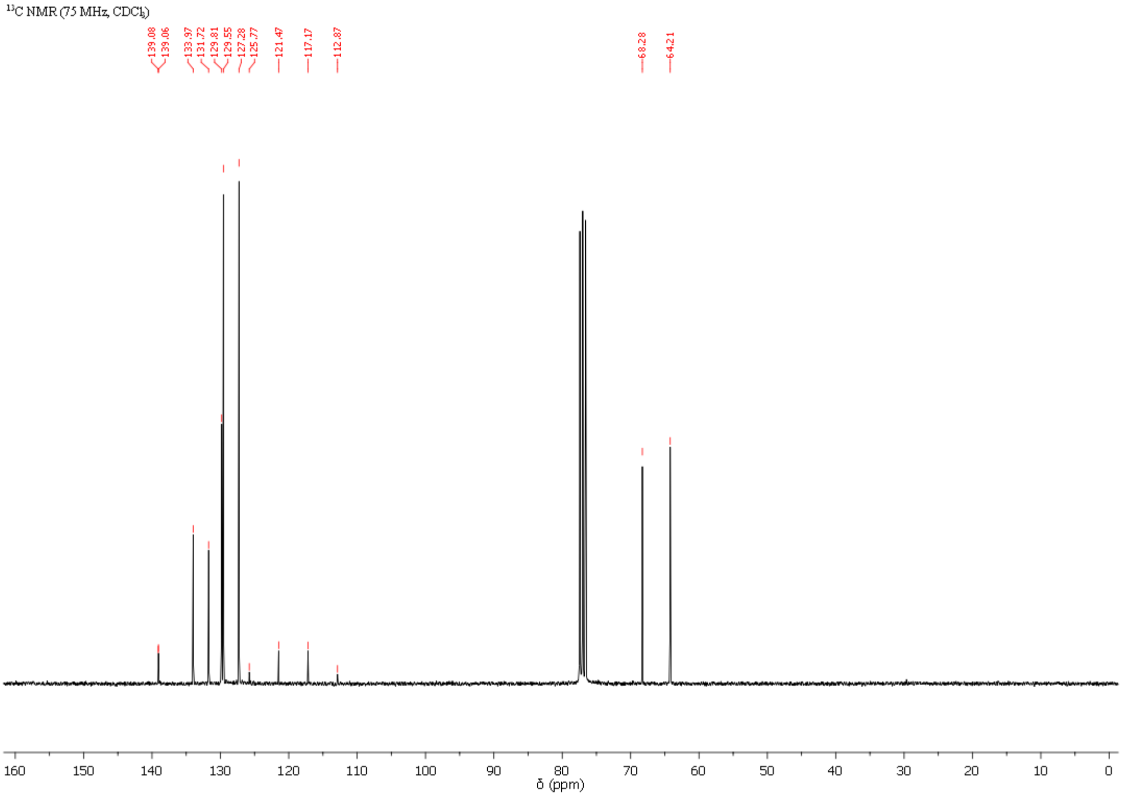
^{13}C NMR (75 MHz, Acetone)

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



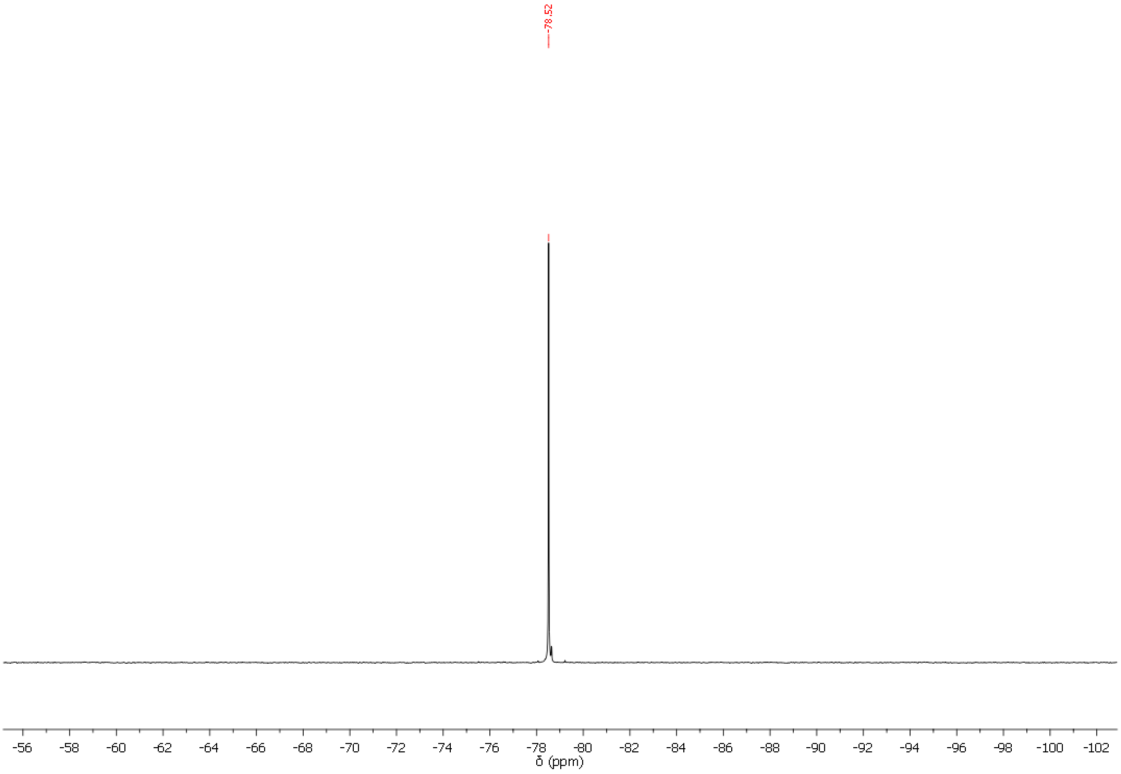


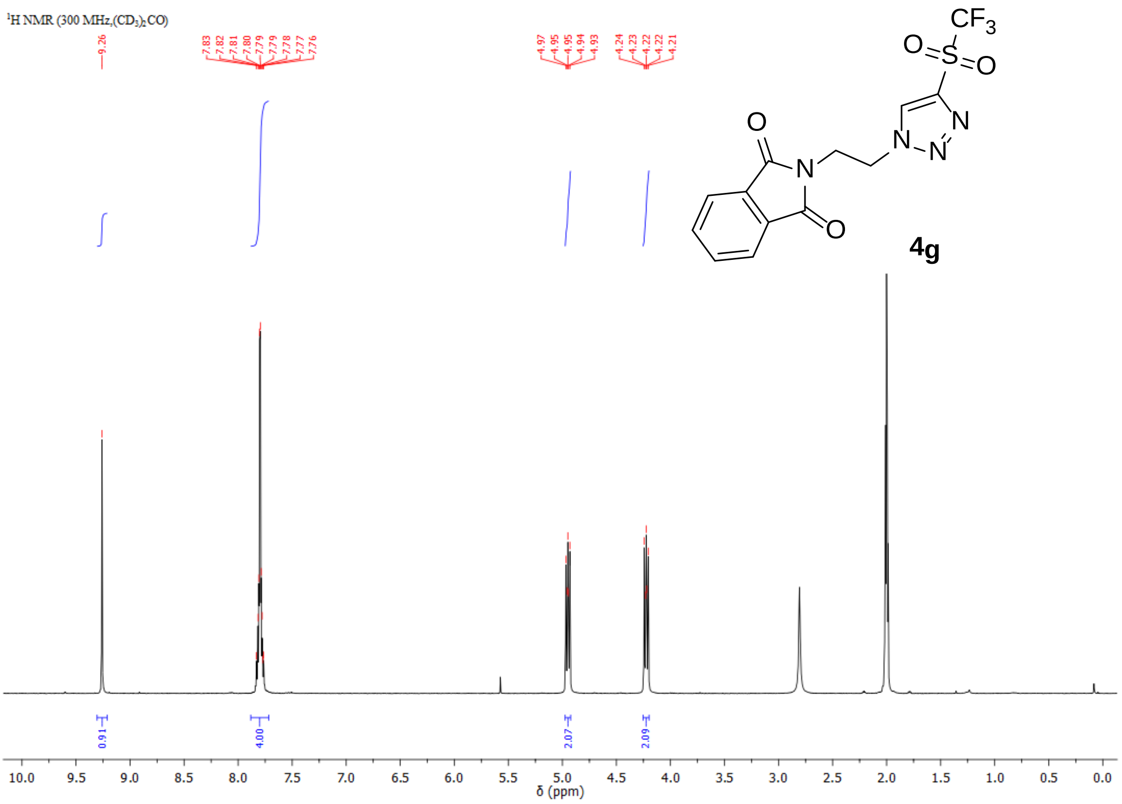
^{1}H NMR (300 MHz, $CDCl_3$)

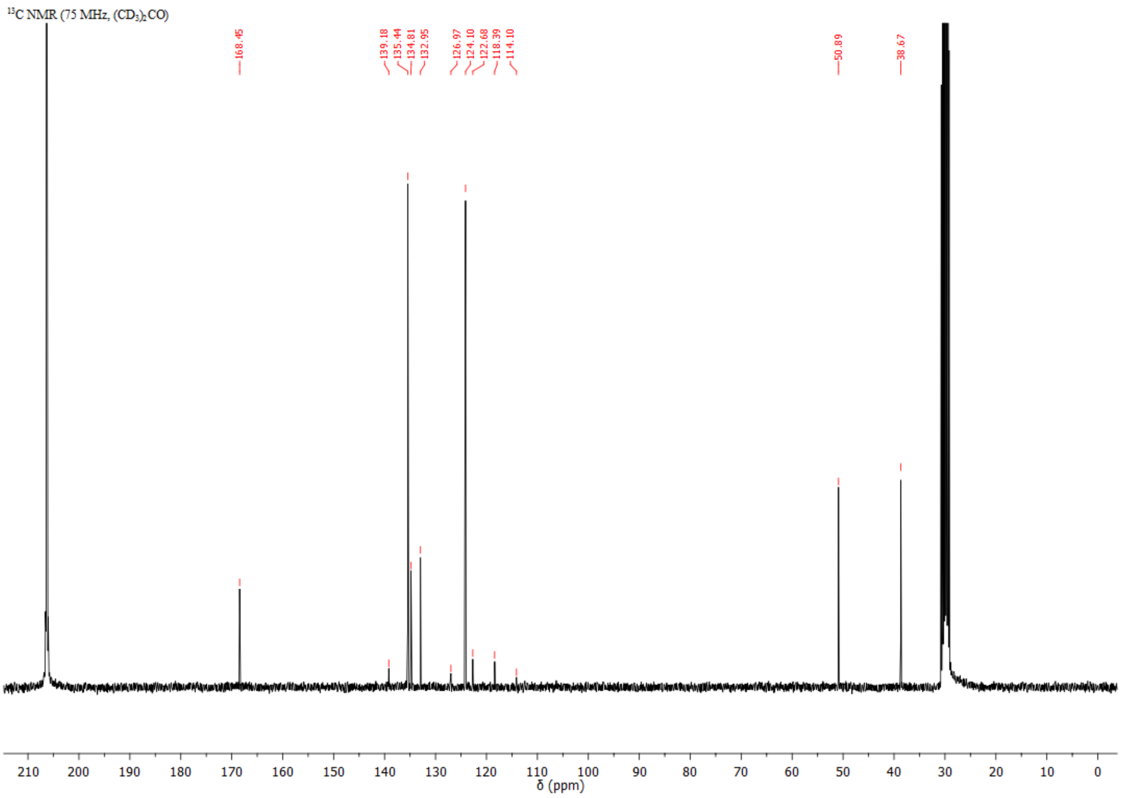


^{13}C NMR (75 MHz, $CDCl_3$)

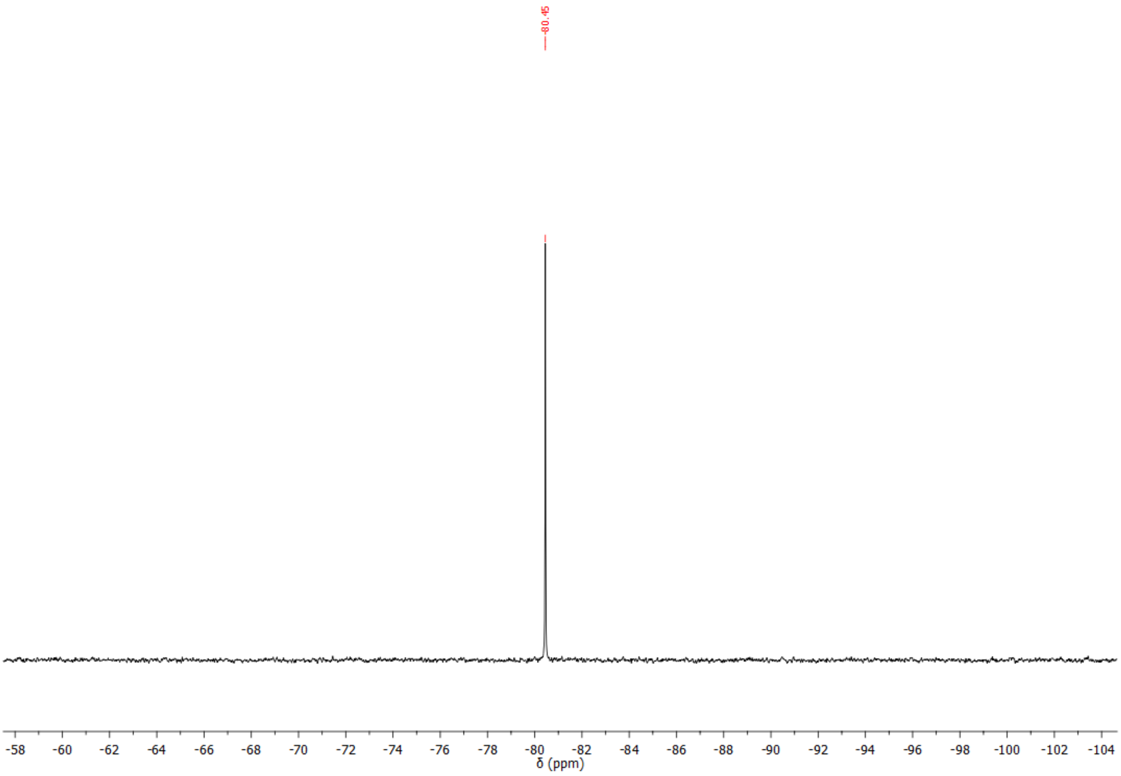
^{19}F NMR (282 MHz, CDCl$_3$)

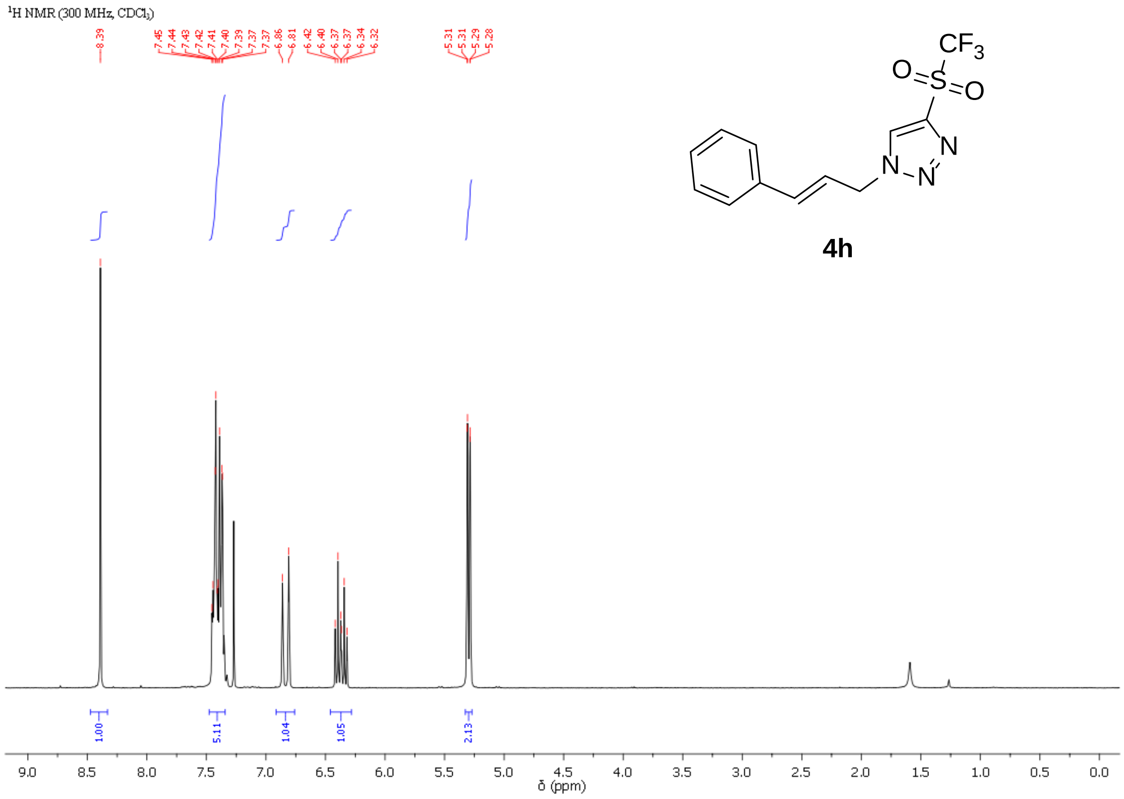



^{1}H NMR (300 MHz,(CD$_3$)$_2$CO)
9.26
7.83
7.82
7.81
7.80
7.79
7.79
7.78
7.77
7.76
4.97
4.95
4.95
4.94
4.93
4.24
4.23
4.22
4.22
4.21
CF$_3$
O
S
O
N
N
N
O
N
O
4g
0.91
4.00
2.07
2.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

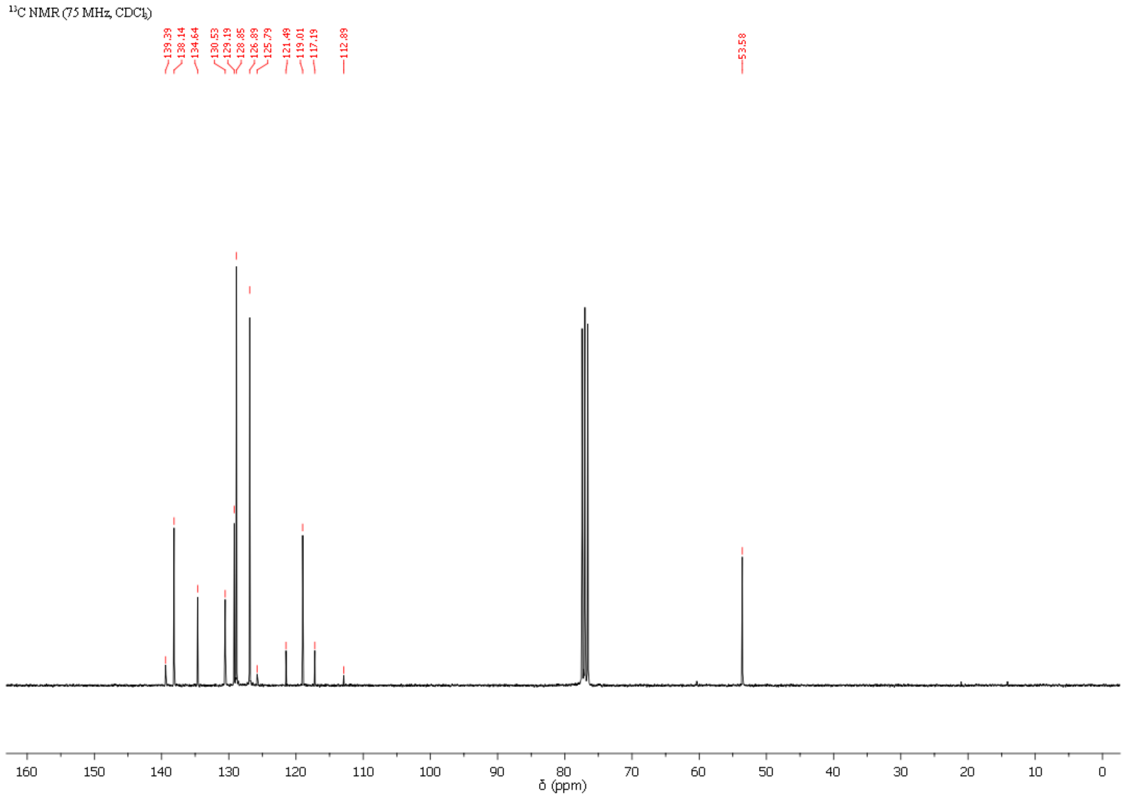

^{13}C NMR (75 MHz, (CD$_3$)$_2$CO)
168.45
139.18
135.44
134.81
132.95
126.97
124.10
122.68
118.39
114.10
50.89
38.67
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

^{19}F NMR (282 MHz, $(CD_3)_2CO$)

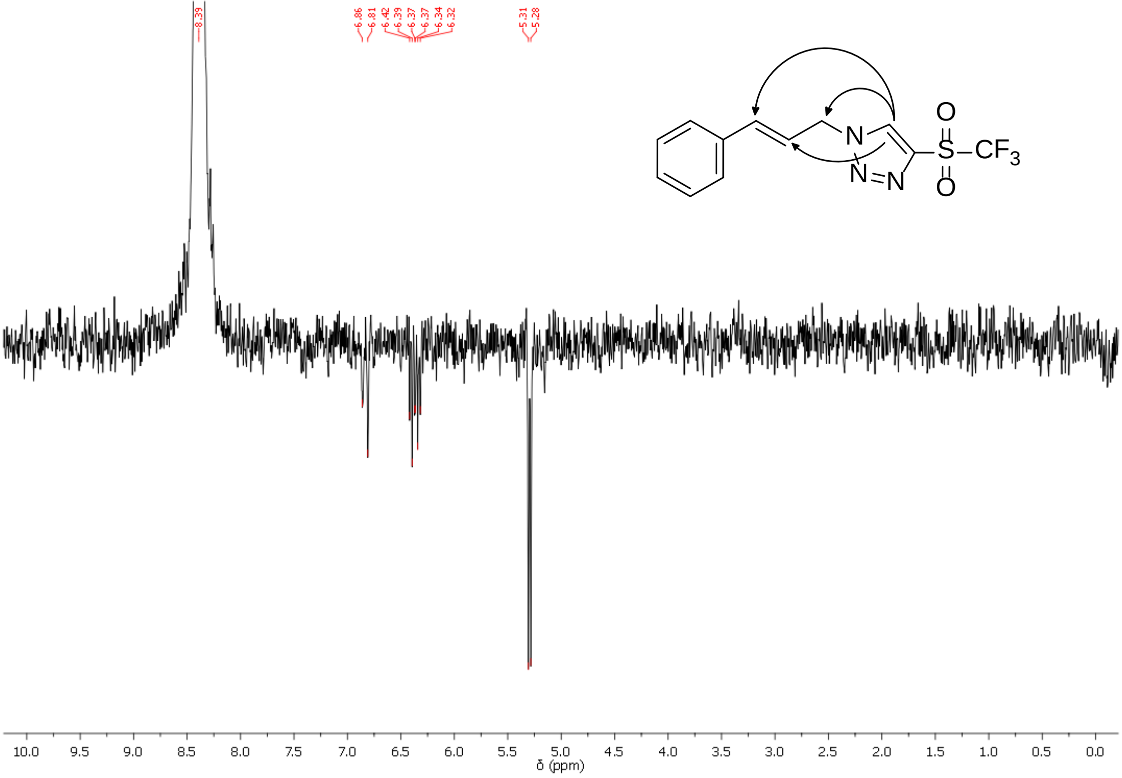



^{1}H NMR (300 MHz, CDCl$_3$)
8.39
7.45
7.44
7.43
7.42
7.41
7.40
7.39
7.37
7.37
6.86
6.81
6.42
6.40
6.37
6.37
6.34
6.32
5.31
5.31
5.29
5.28
1.00
5.11
1.04
1.05
2.13
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)
CF3
O
S
O
N
N
N

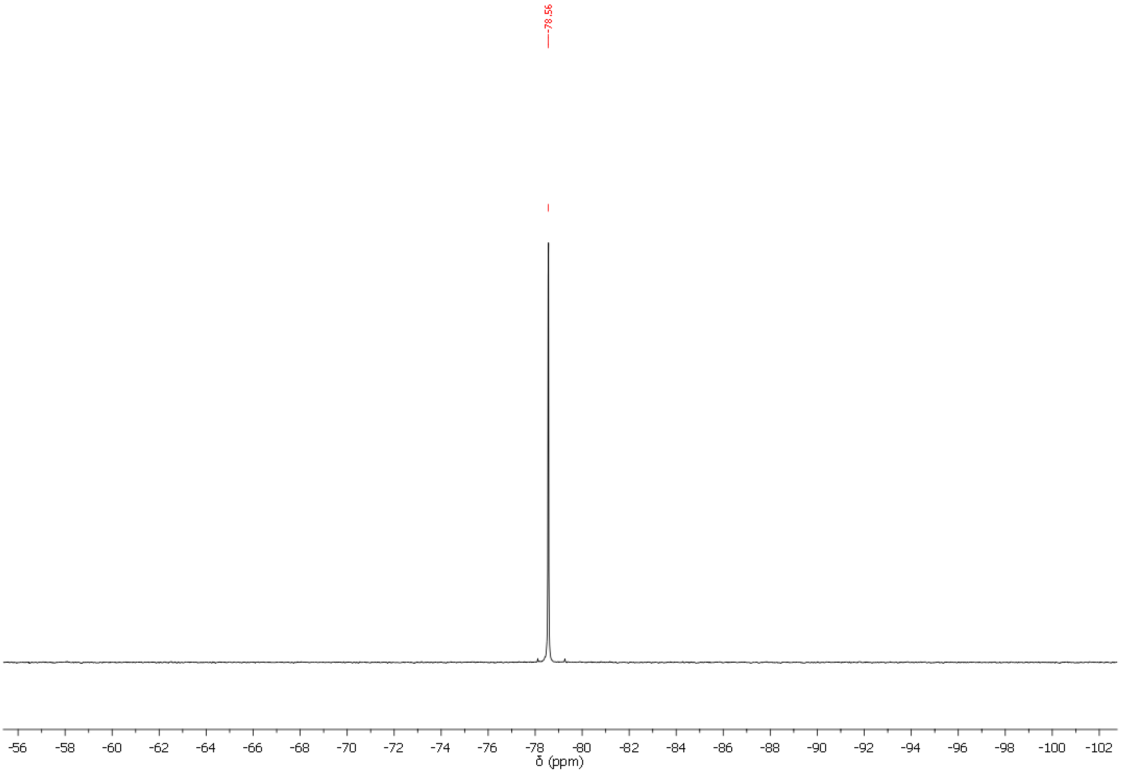
4h

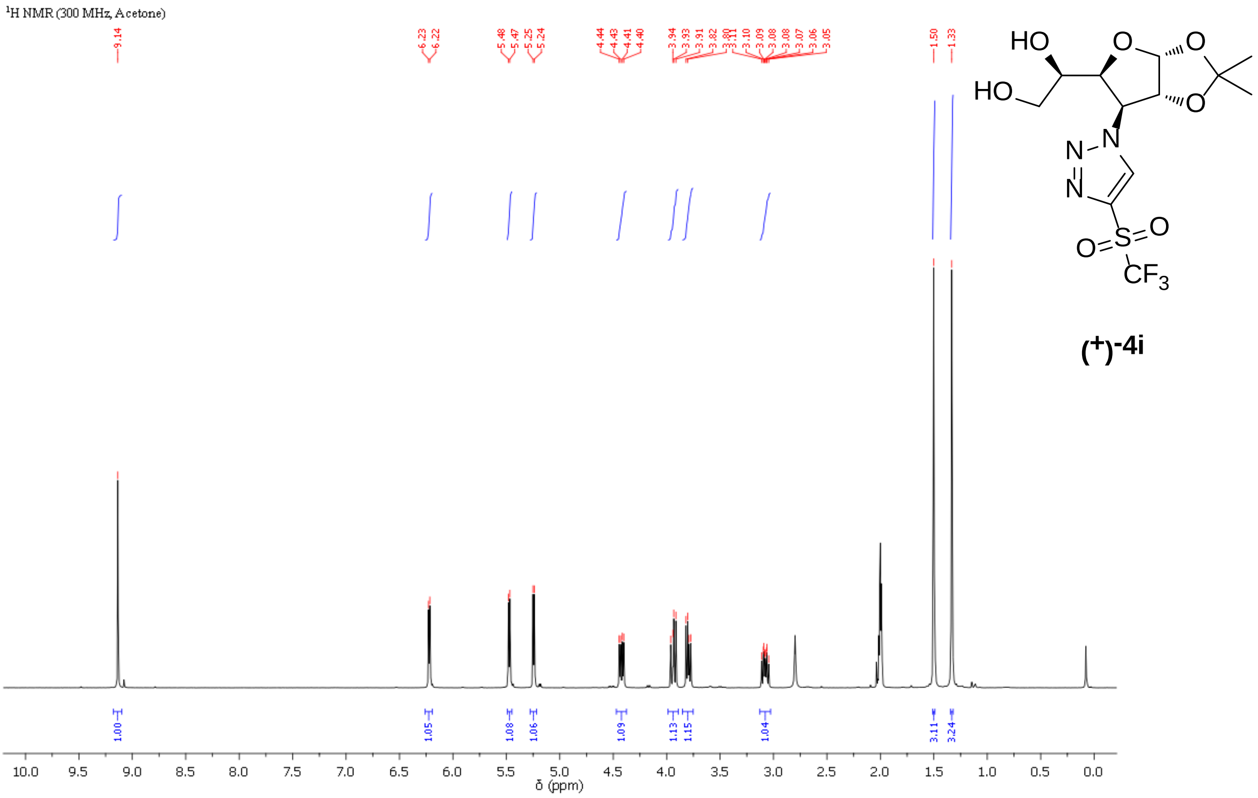

^{13}C NMR (75 MHz, CDCl$_3$)
139.39
138.14
134.64
130.53
129.19
128.85
126.89
125.79
121.49
119.01
117.19
112.89
53.58
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

NOE Experiment (300 MHz, $CDCl_3$). Irradiation CH-Triazole



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

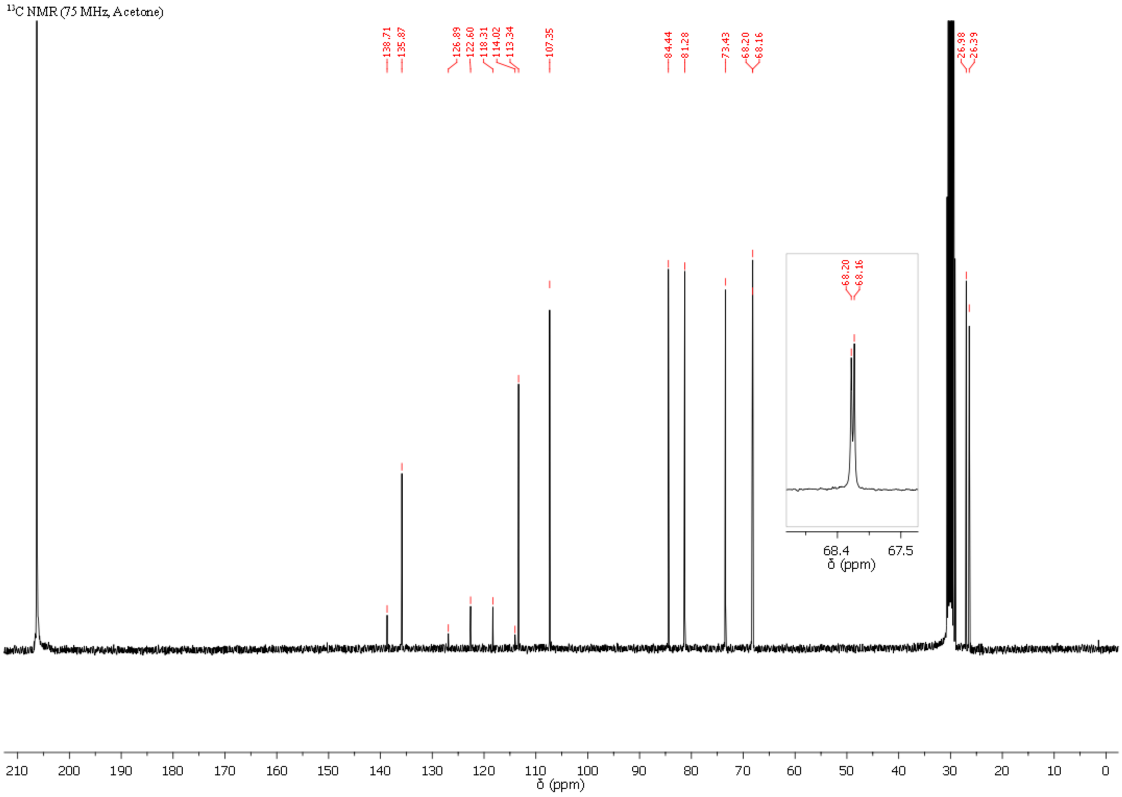




^{1}H NMR (300 MHz, Acetone)
9.14
6.23
6.22
5.48
5.47
5.25
5.24
4.44
4.43
4.41
4.40
3.94
3.93
3.91
3.82
3.80
3.11
3.10
3.09
3.08
3.08
3.07
3.06
3.05
1.50
1.33
1.00
1.05
1.08
1.06
1.09
1.13
1.15
1.04
3.11
3.24
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

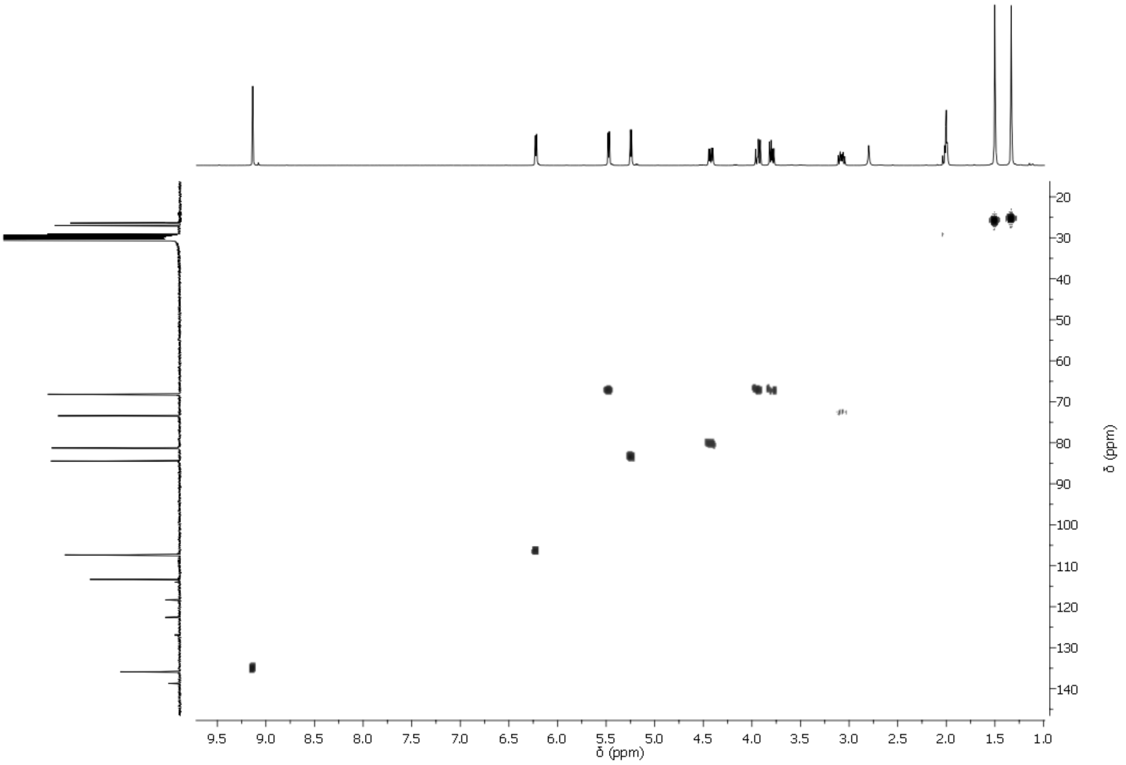
HO
HO
O
O
O
N
N
N
S
O
O
CF3

(+)-4i

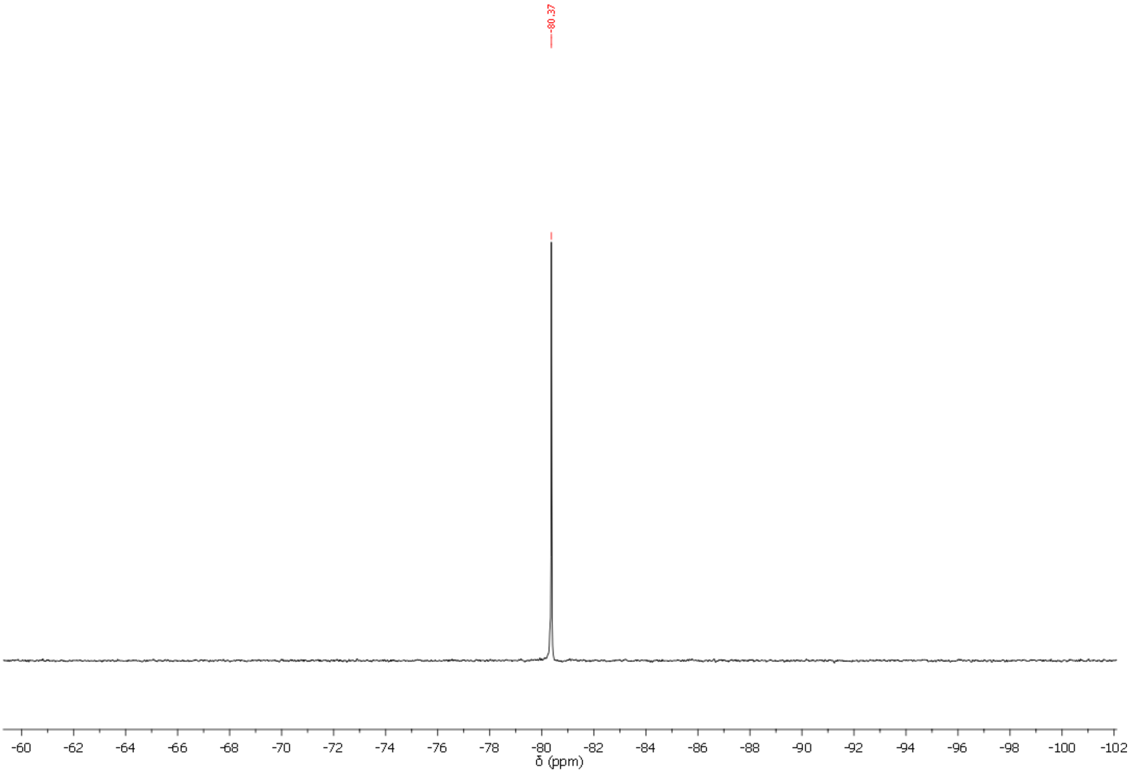


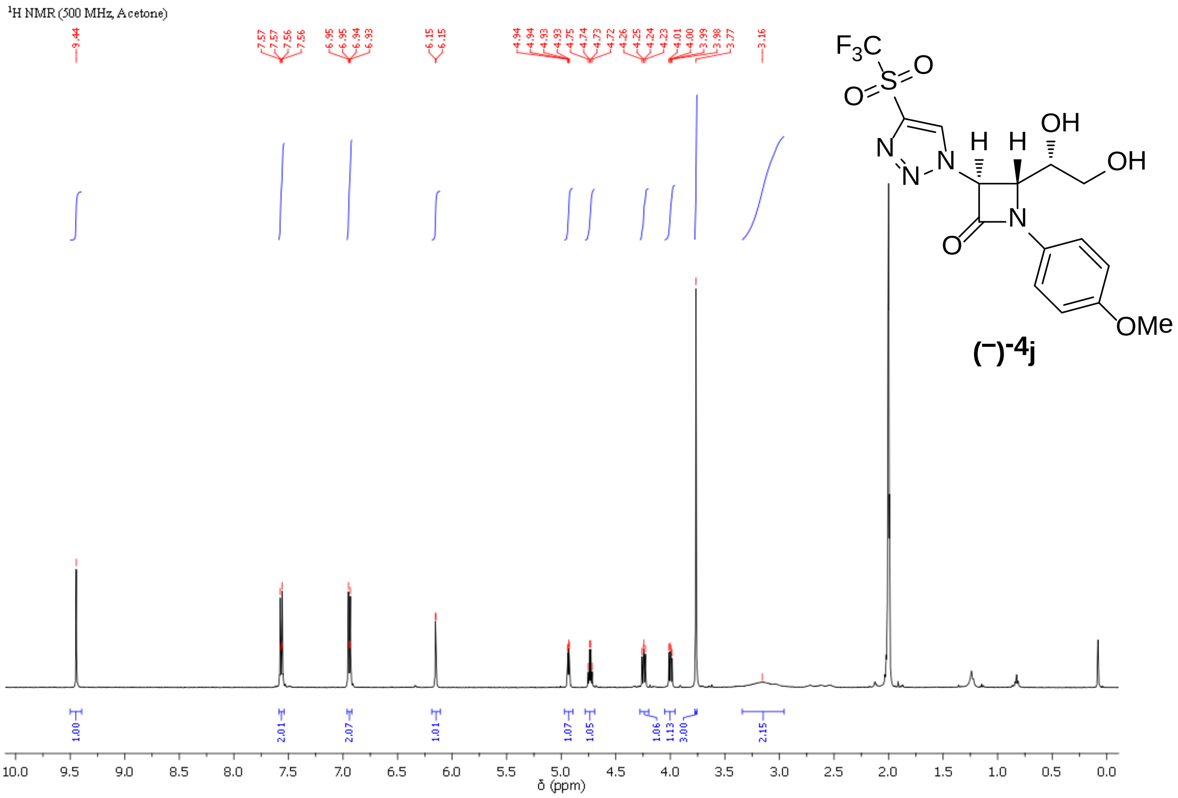
^{13}C NMR (75 MHz, Acetone)
138.71
135.87
126.89
122.60
118.31
114.02
113.34
107.35
84.44
81.28
73.43
68.20
68.16
26.98
26.39
68.20
68.16
68.4
67.5
δ (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

2D-HMQC NMR (Acetone)



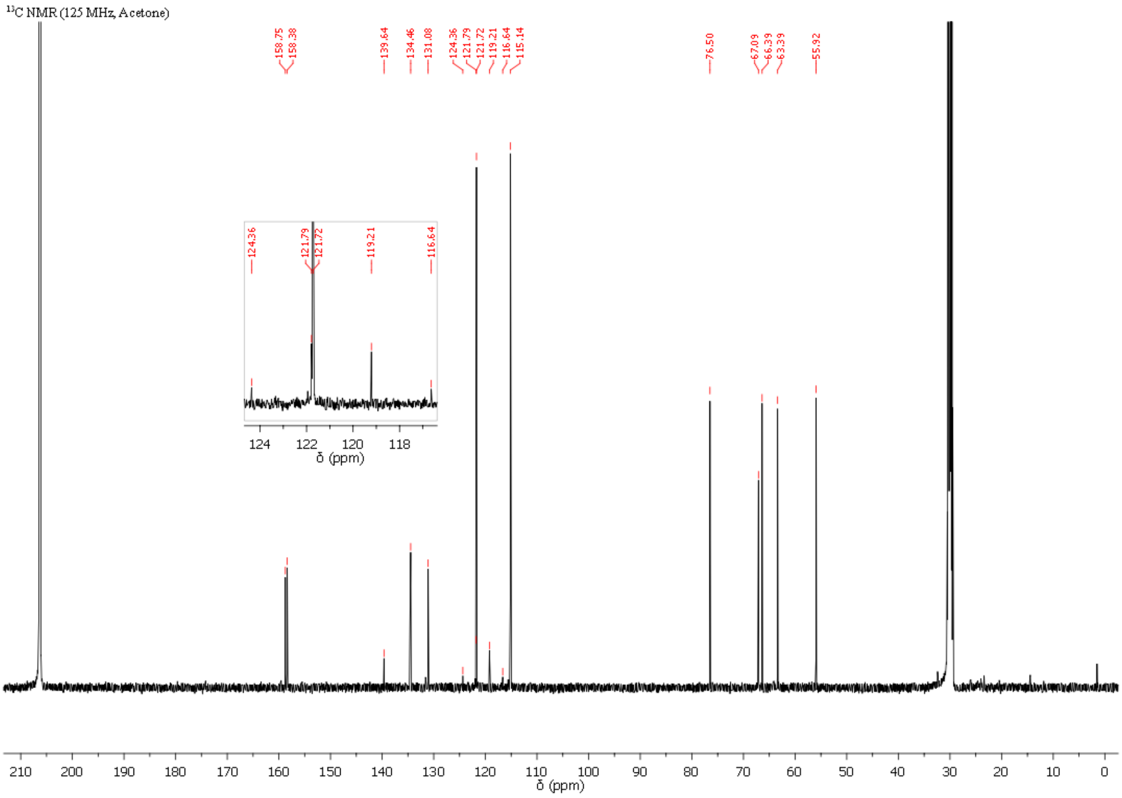
^{19}F NMR (282 MHz, Acetone)





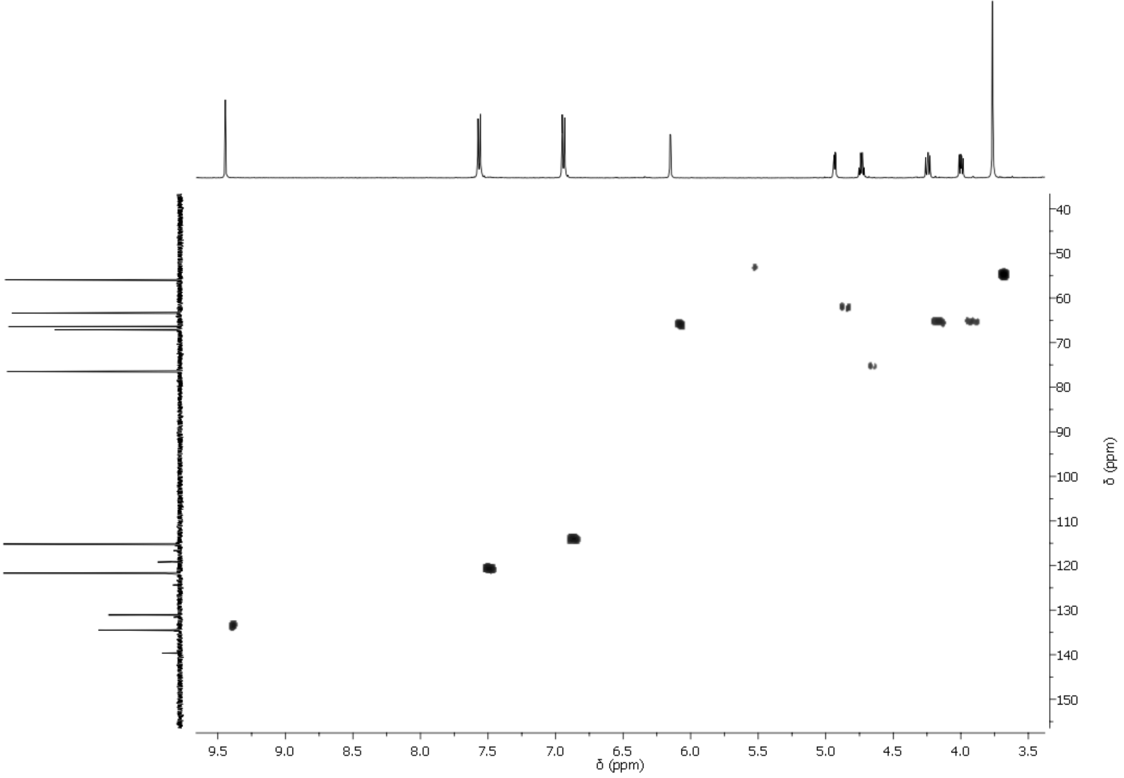
^{1}H NMR (500 MHz, Acetone)

(−)-4j

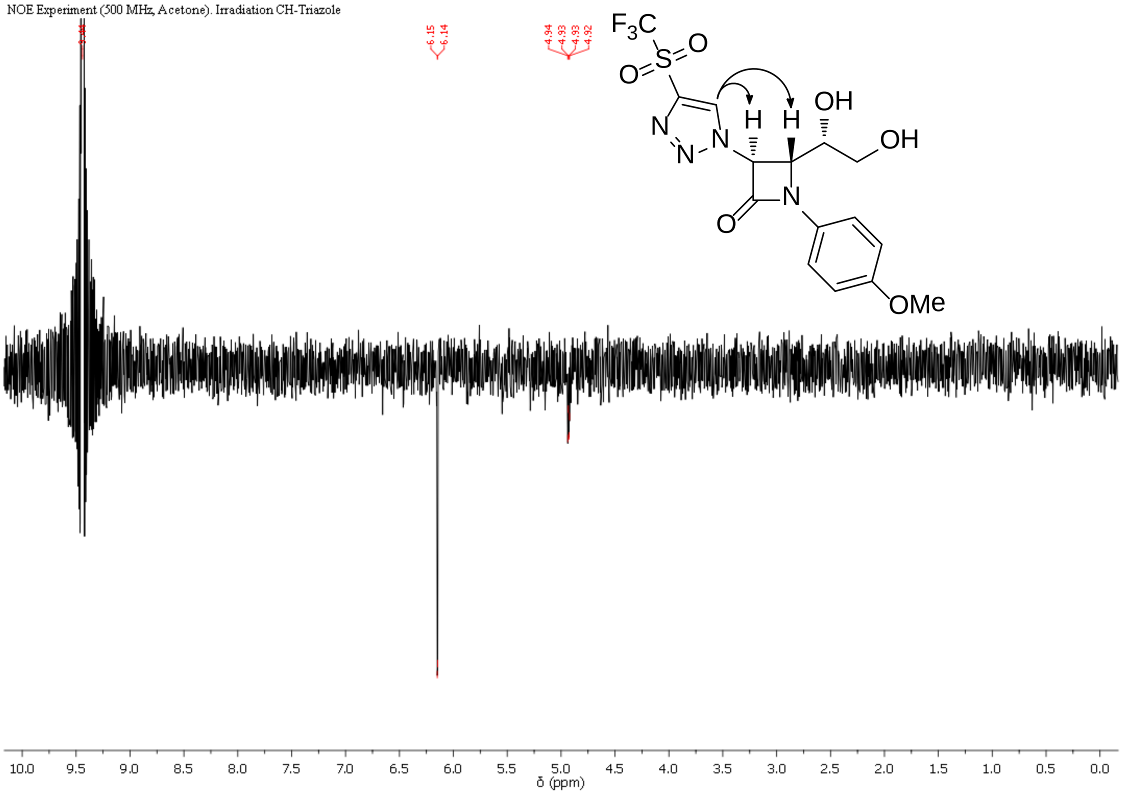


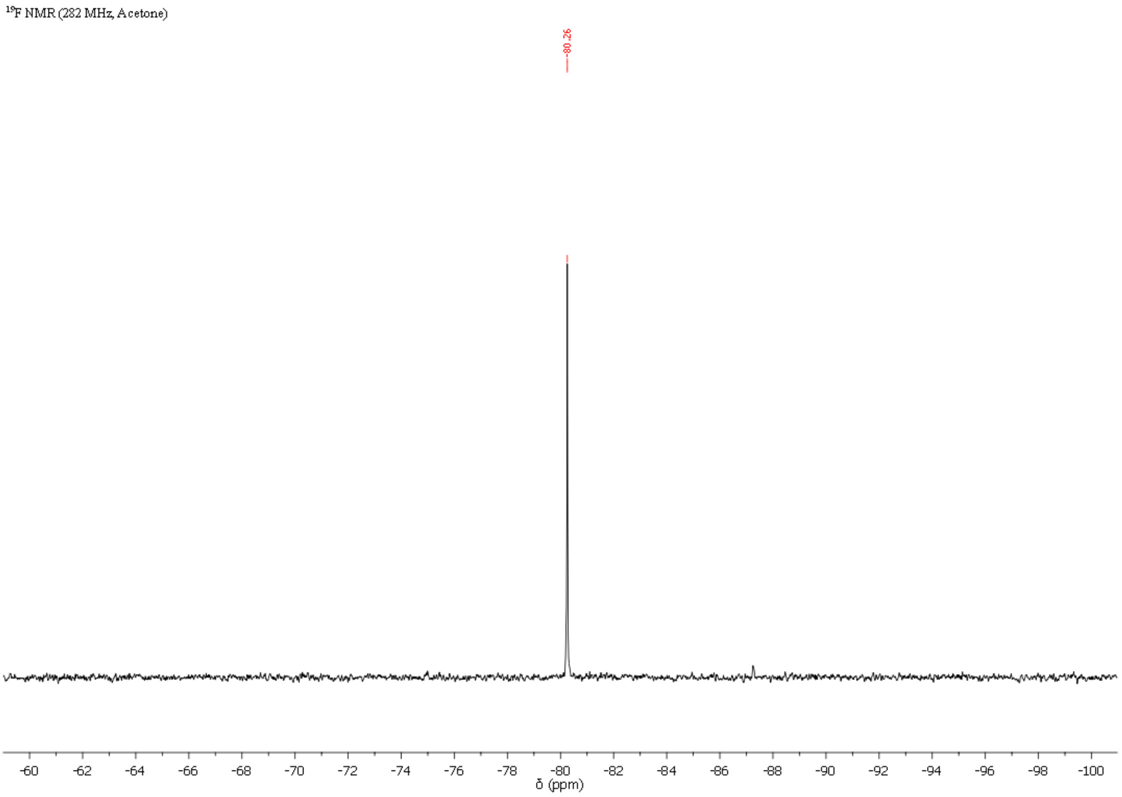
^{13}C NMR (125 MHz, Acetone)

2D-HMQC NMR (Acetone)

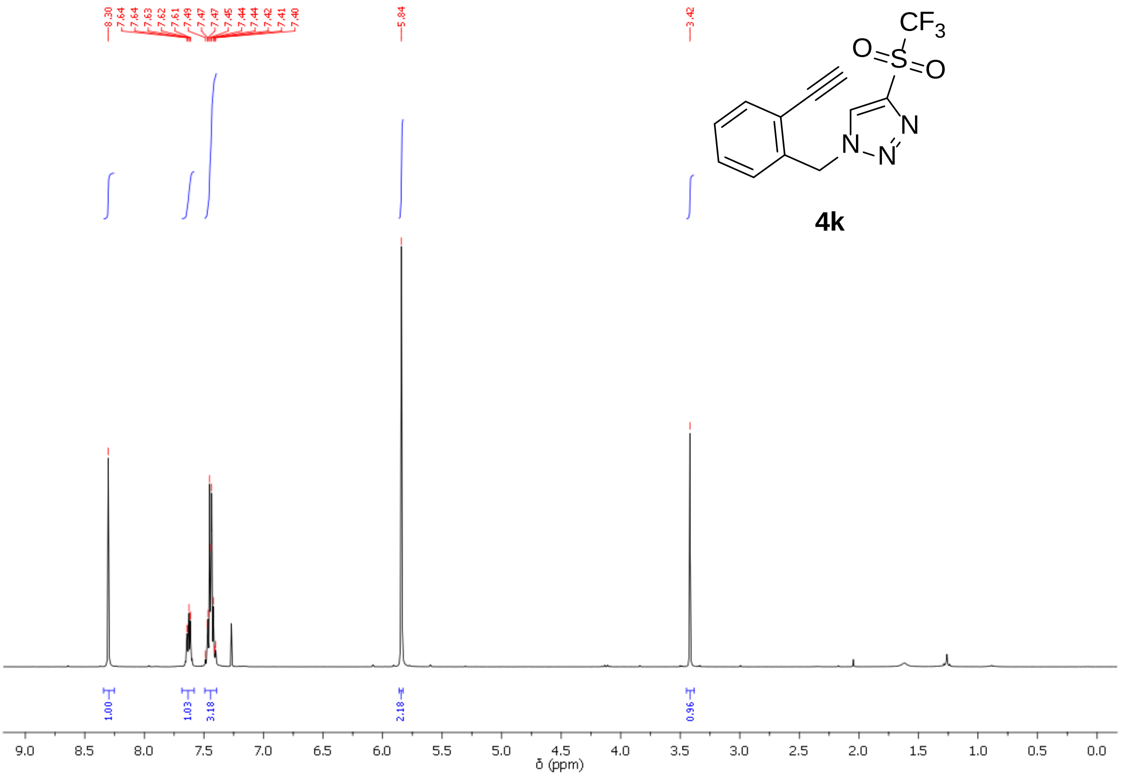


NOE Experiment (500 MHz, Acetone). Irradiation CH-Triazole



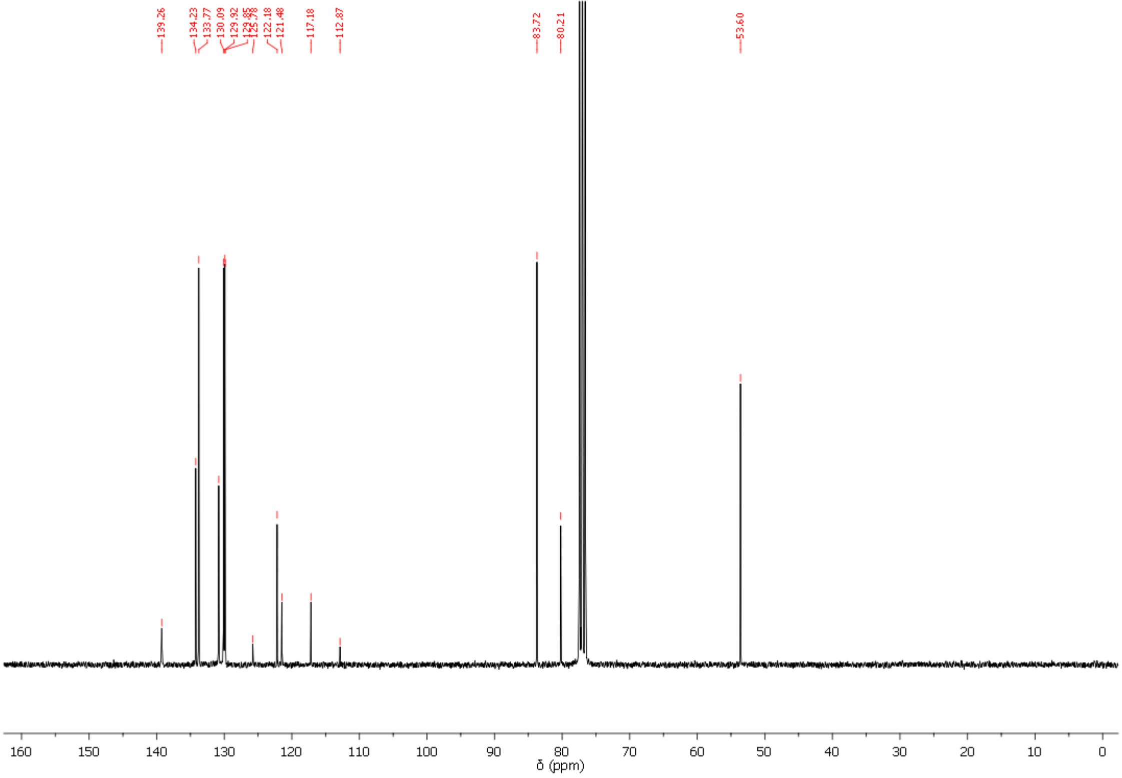

^{19}F NMR (282 MHz, Acetone)
-80.26
-60
-62
-64
-66
-68
-70
-72
-74
-76
-78
-80
-82
-84
-86
-88
-90
-92
-94
-96
-98
-100
δ (ppm)

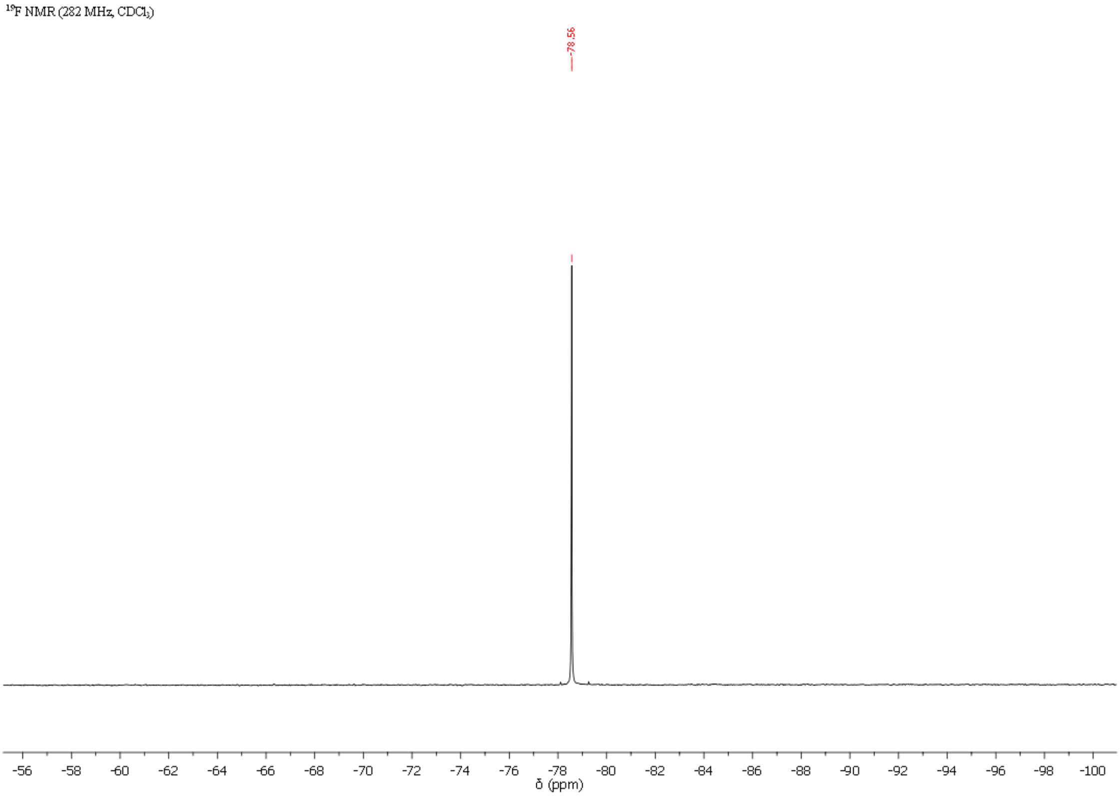
^{1}H NMR (300 MHz, $CDCl_3$)



4k

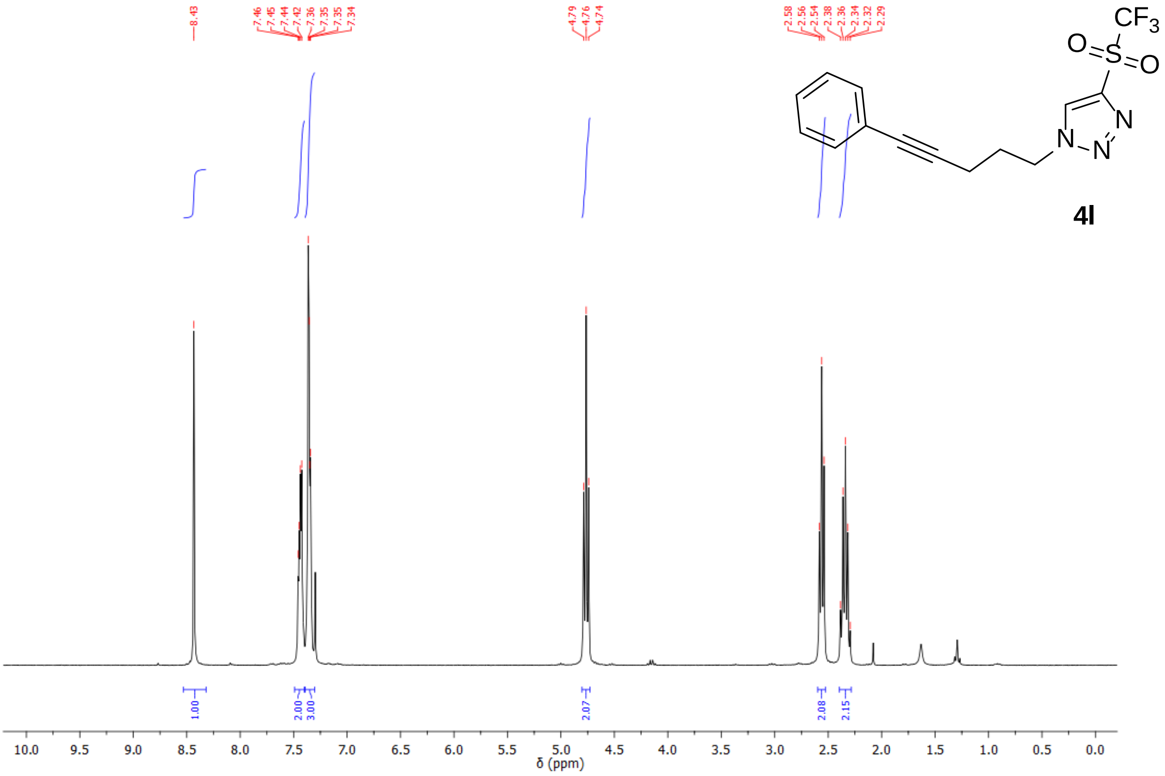
^{13}C NMR (75 MHz, $CDCl_3$)





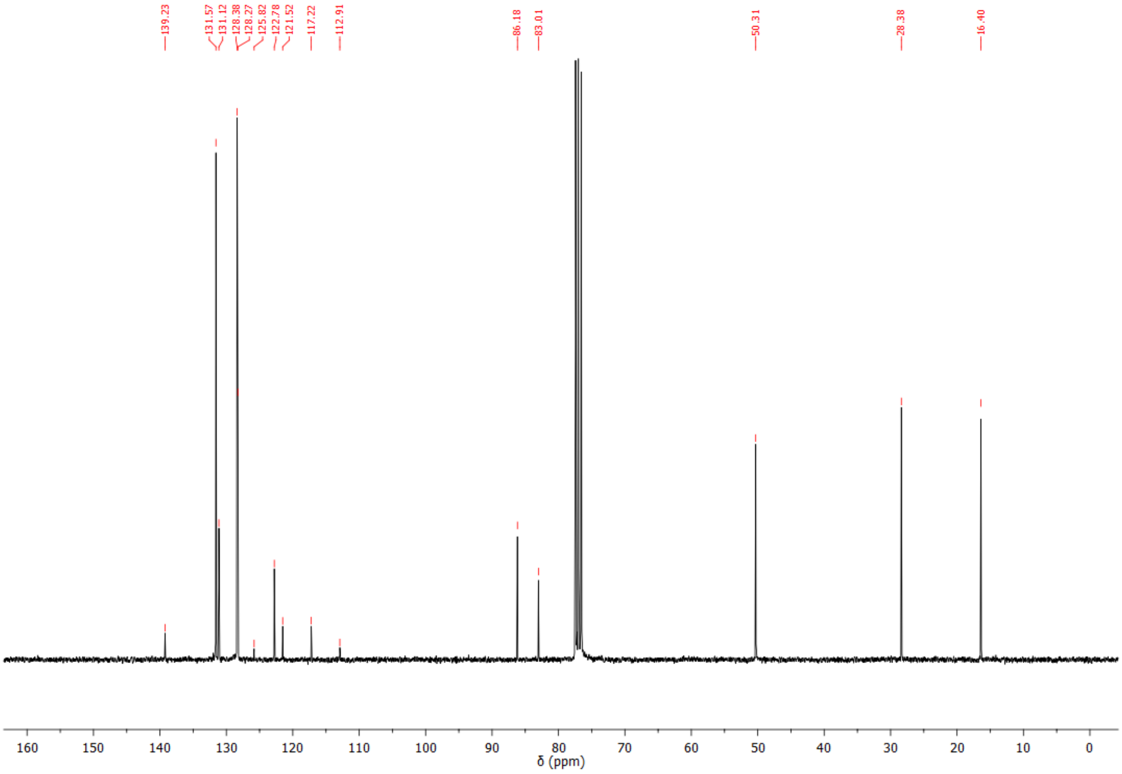
^{19}F NMR (282 MHz, CDCl$_3$)
-78.56
-56
-58
-60
-62
-64
-66
-68
-70
-72
-74
-76
-78
-80
-82
-84
-86
-88
-90
-92
-94
-96
-98
-100
δ (ppm)

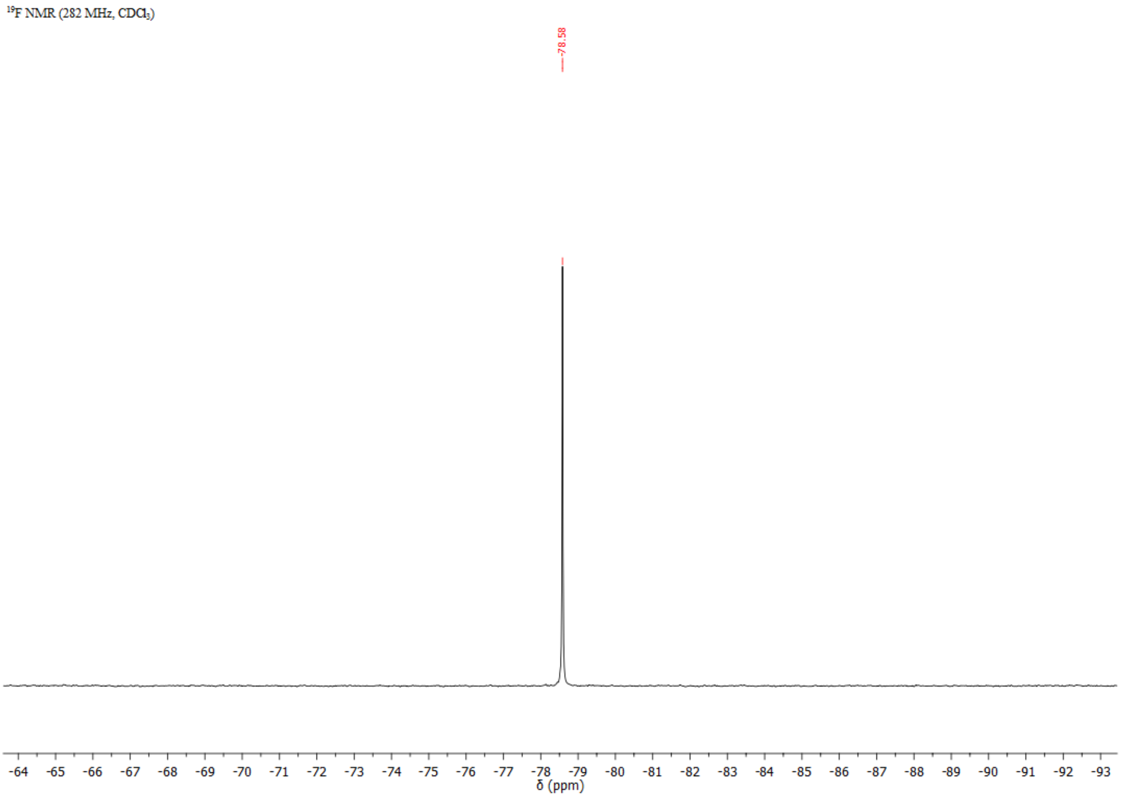
^{1}H NMR (300 MHz, CDCl$_3$)



4l

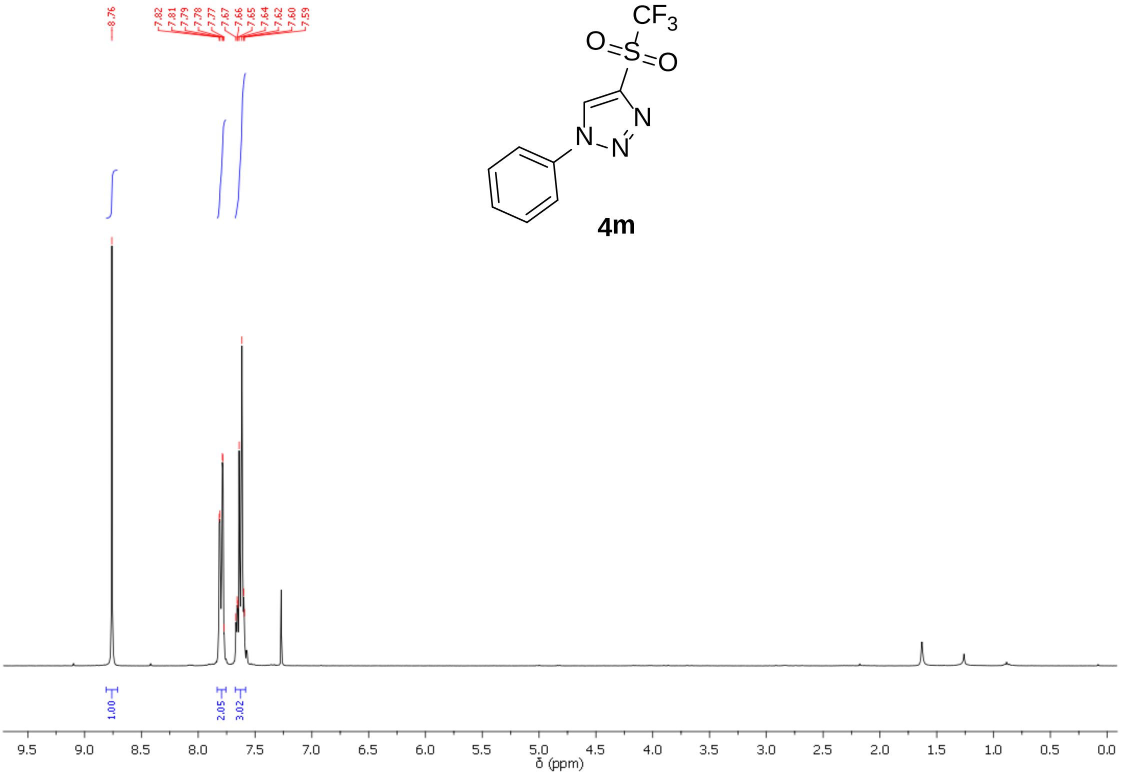
^{13}C NMR (75 MHz, CDCl$_3$)



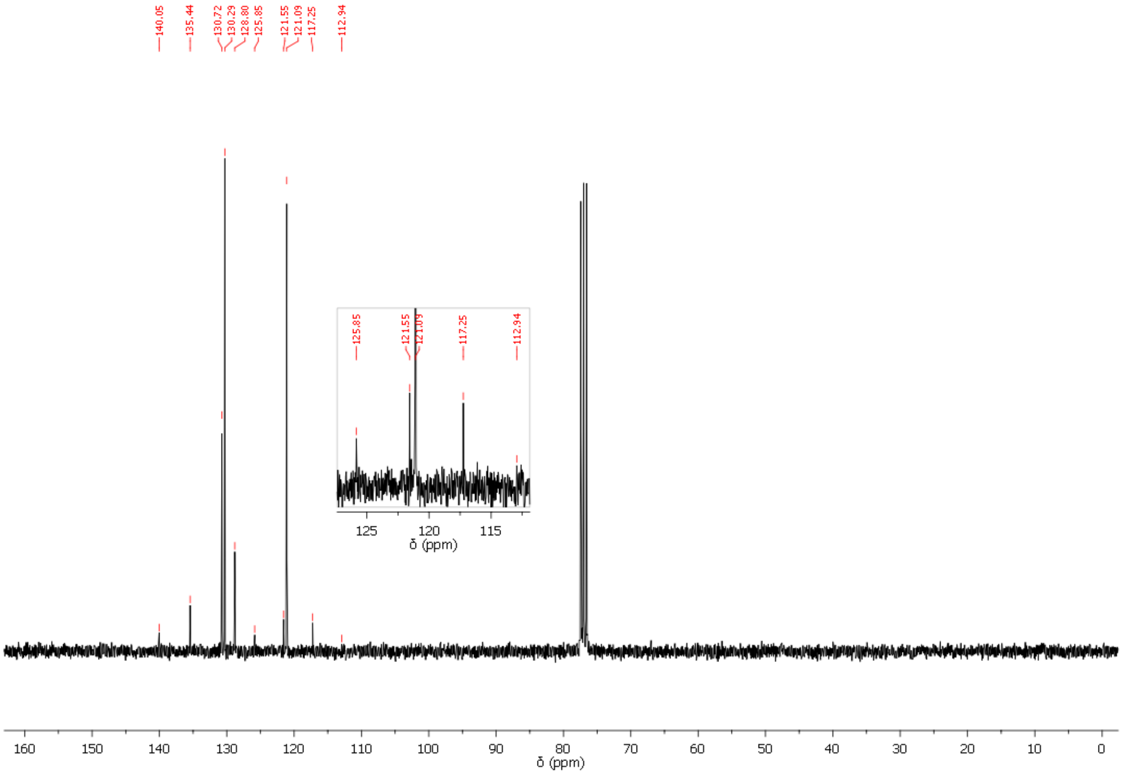


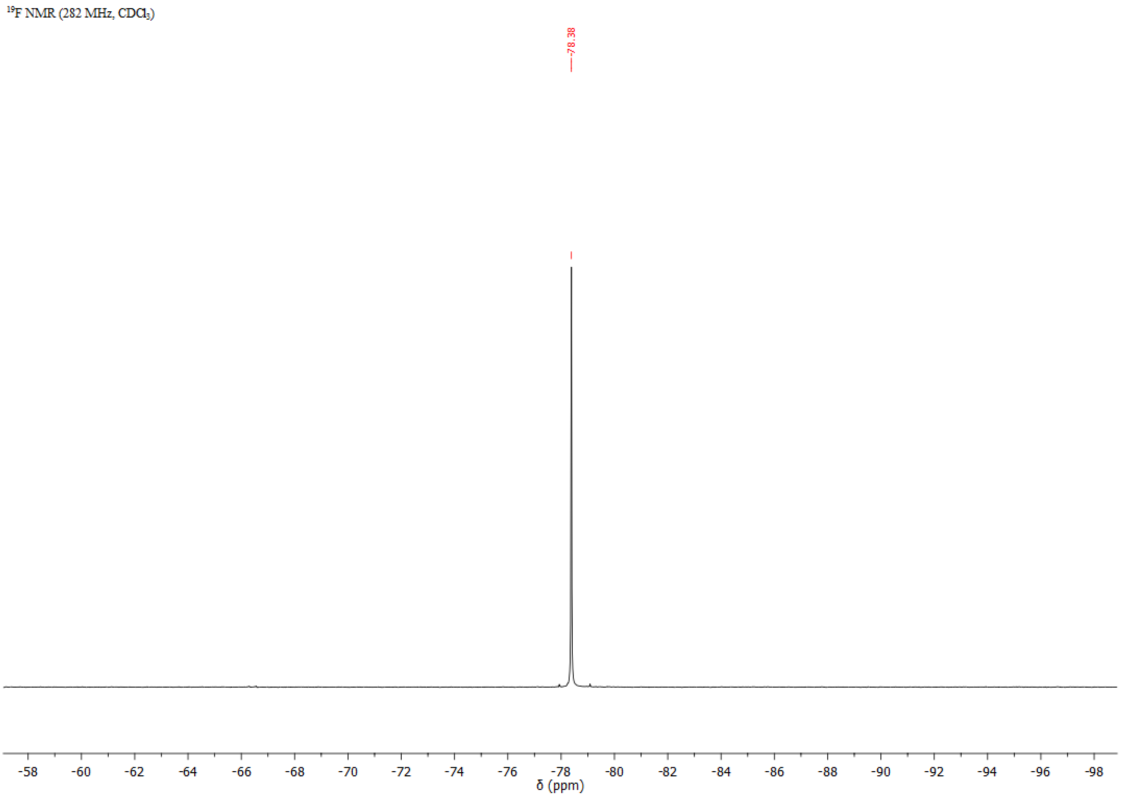
^{19}F NMR (282 MHz, CDCl$_3$)
-78.58
-64
-65
-66
-67
-68
-69
-70
-71
-72
-73
-74
-75
-76
-77
-78
-79
-80
-81
-82
-83
-84
-85
-86
-87
-88
-89
-90
-91
-92
-93
δ (ppm)

^{1}H NMR (300 MHz, CDCl$_3$)

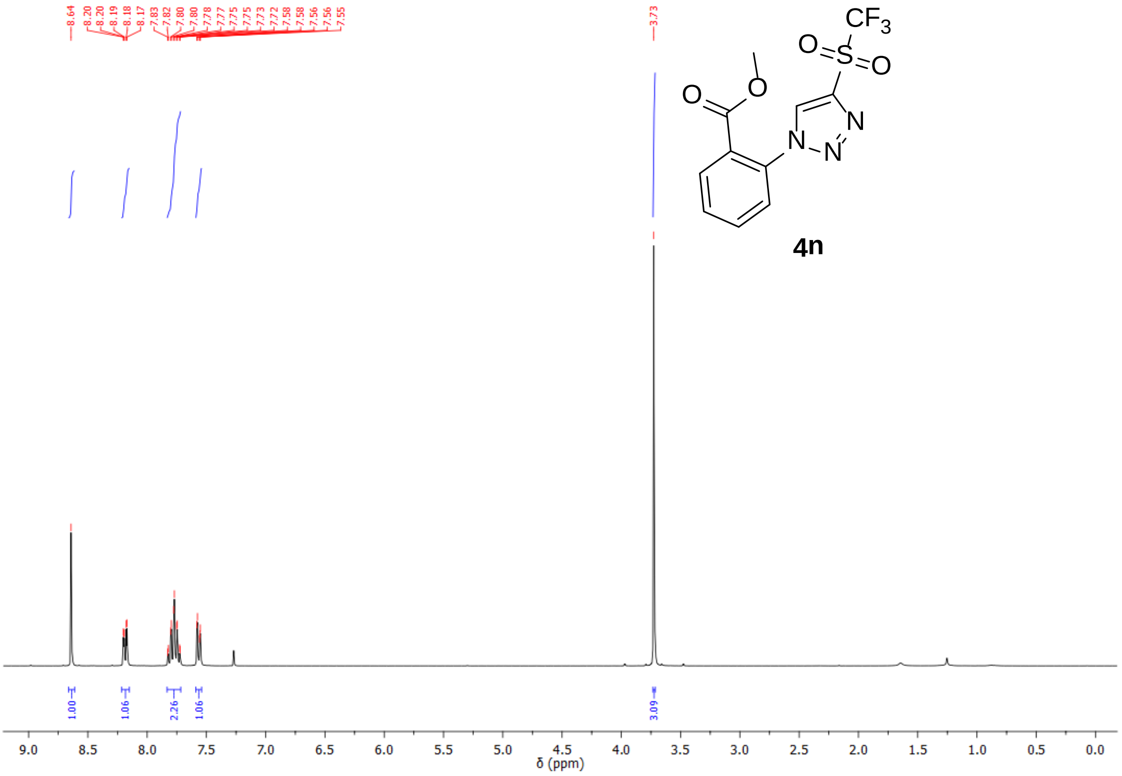


^{13}C NMR (75 MHz, CDCl$_3$)



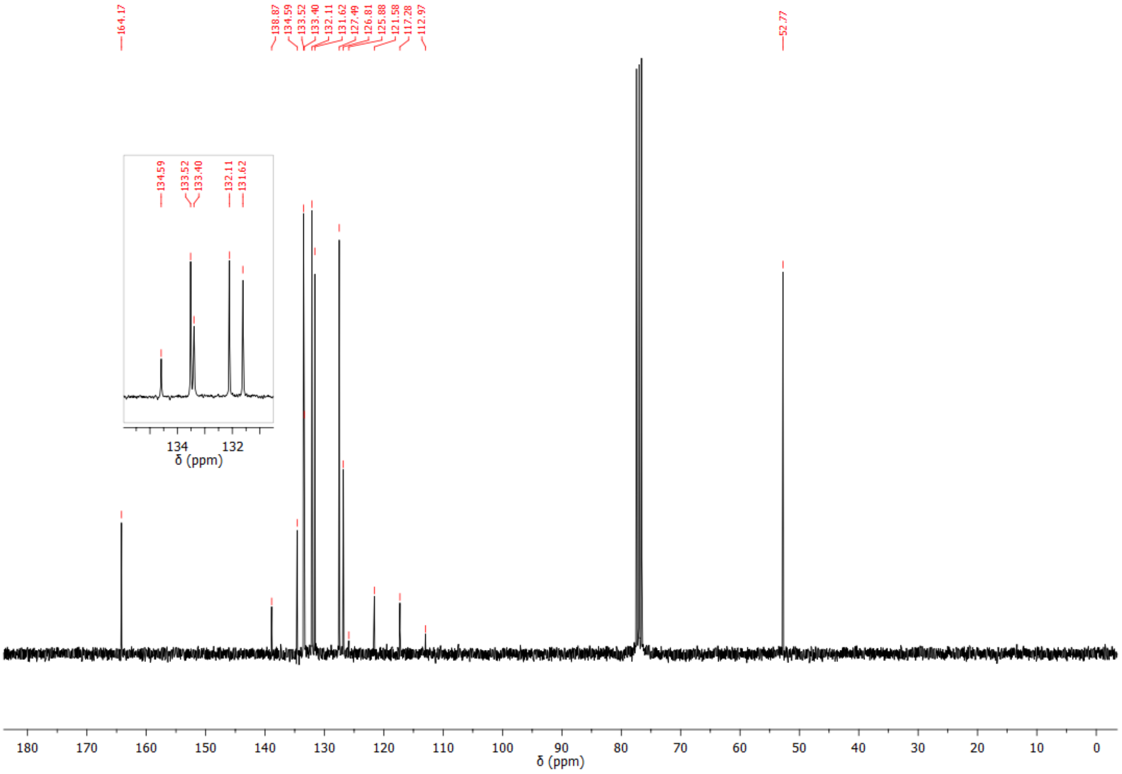

^{19}F NMR (282 MHz, CDCl$_3$)
—78.38
-58
-60
-62
-64
-66
-68
-70
-72
-74
-76
-78
-80
-82
-84
-86
-88
-90
-92
-94
-96
-98
δ (ppm)

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

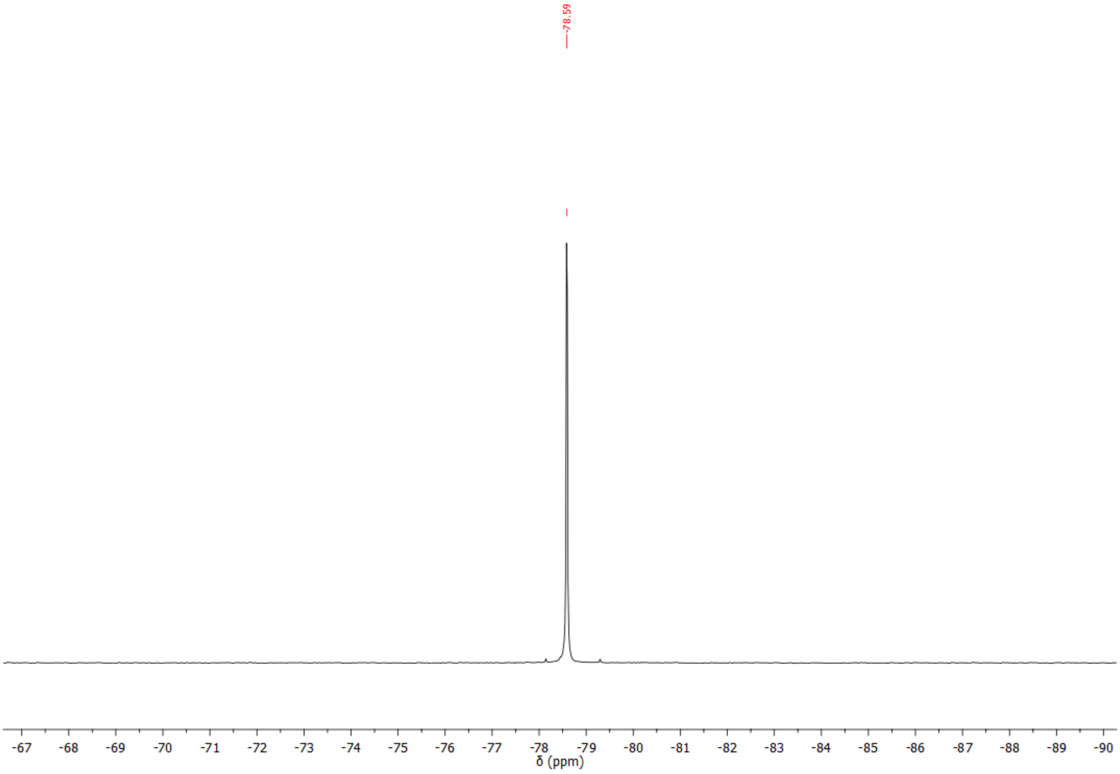


4n

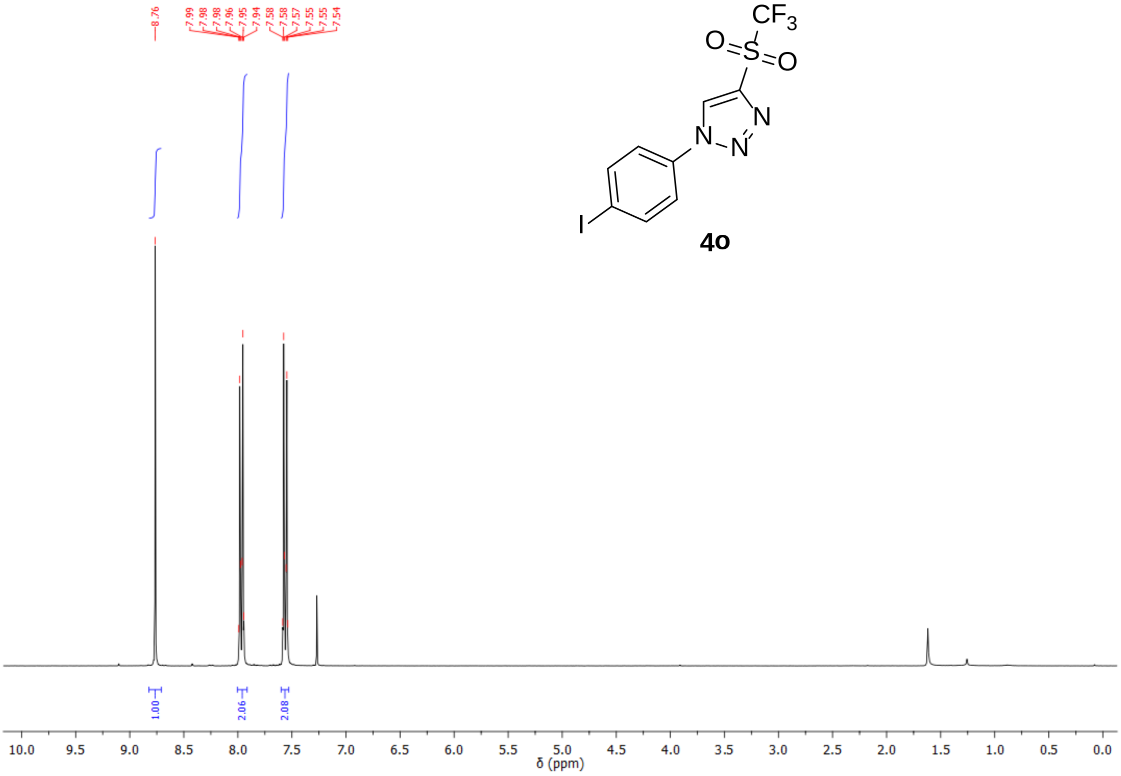
^{13}C NMR (75 MHz, $CDCl_3$)



^{19}F NMR (282 MHz, CDCl$_3$)

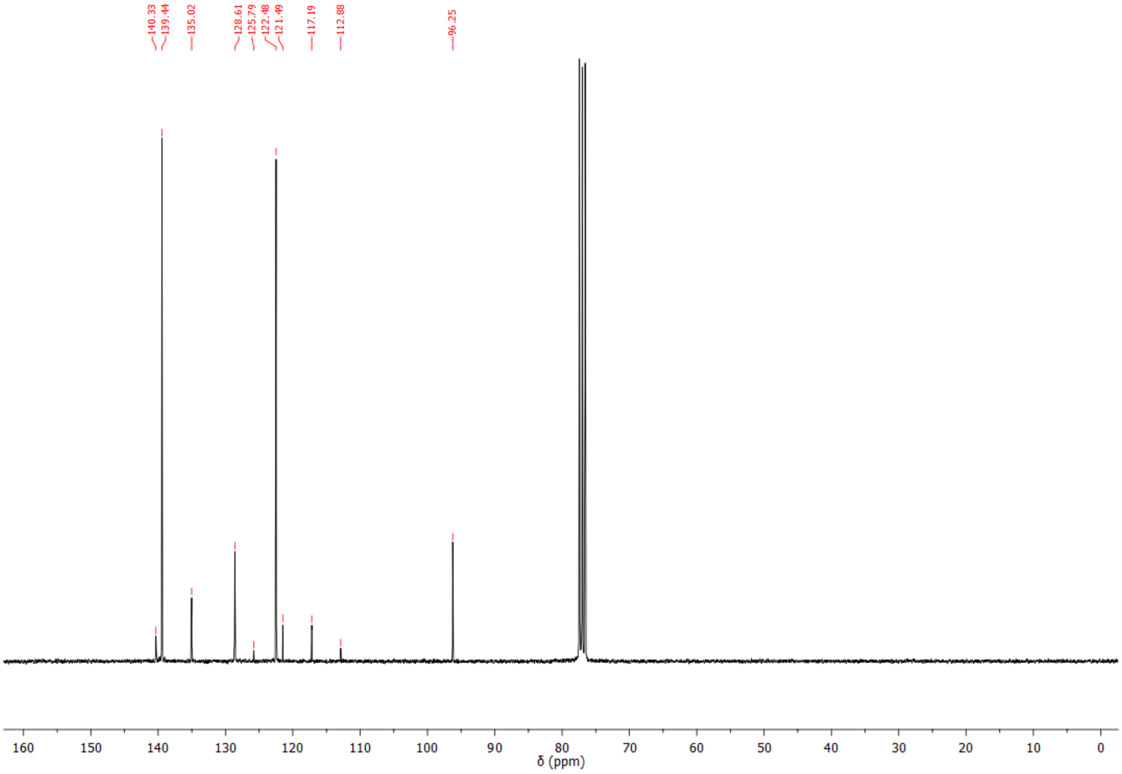


^{1}H NMR (300 MHz, CDCl$_3$)

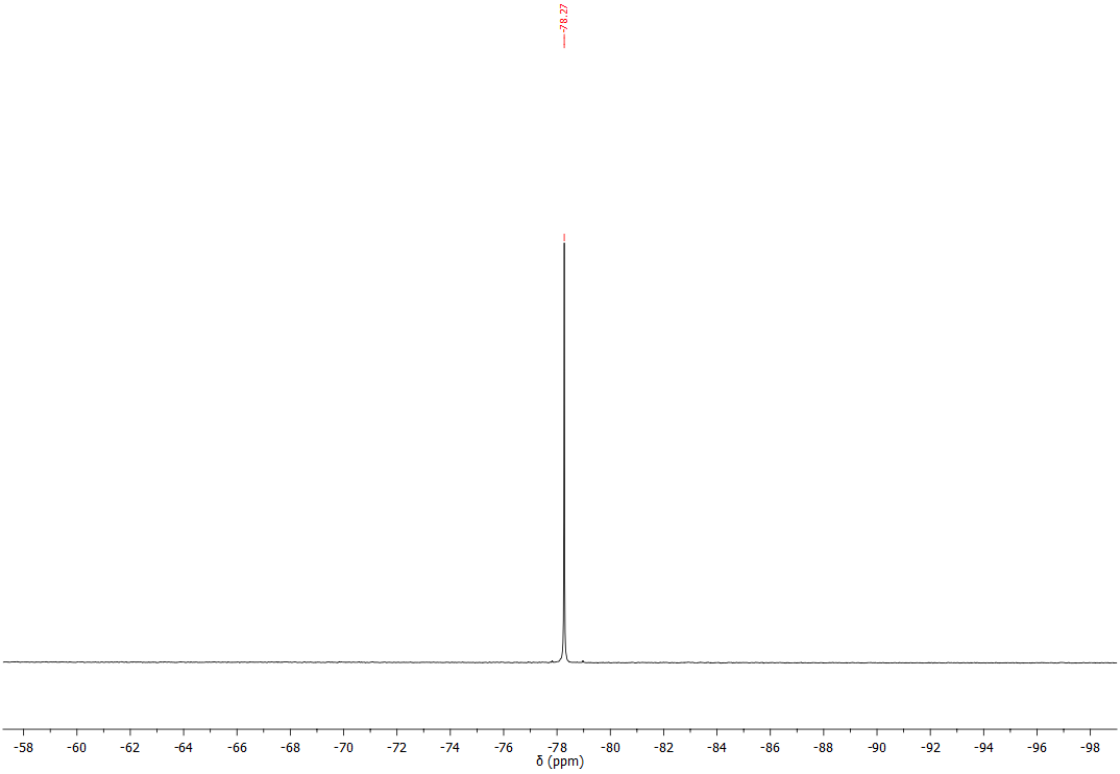


4o

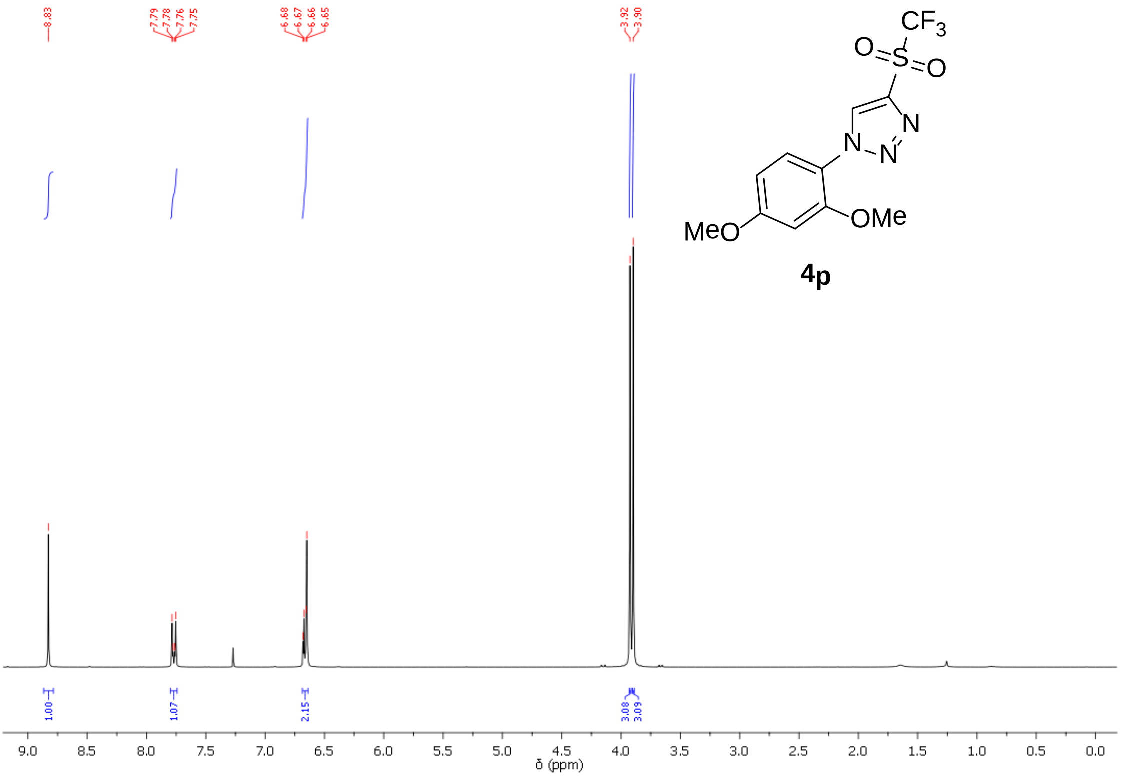
^{13}C NMR (75 MHz, CDCl$_3$)



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

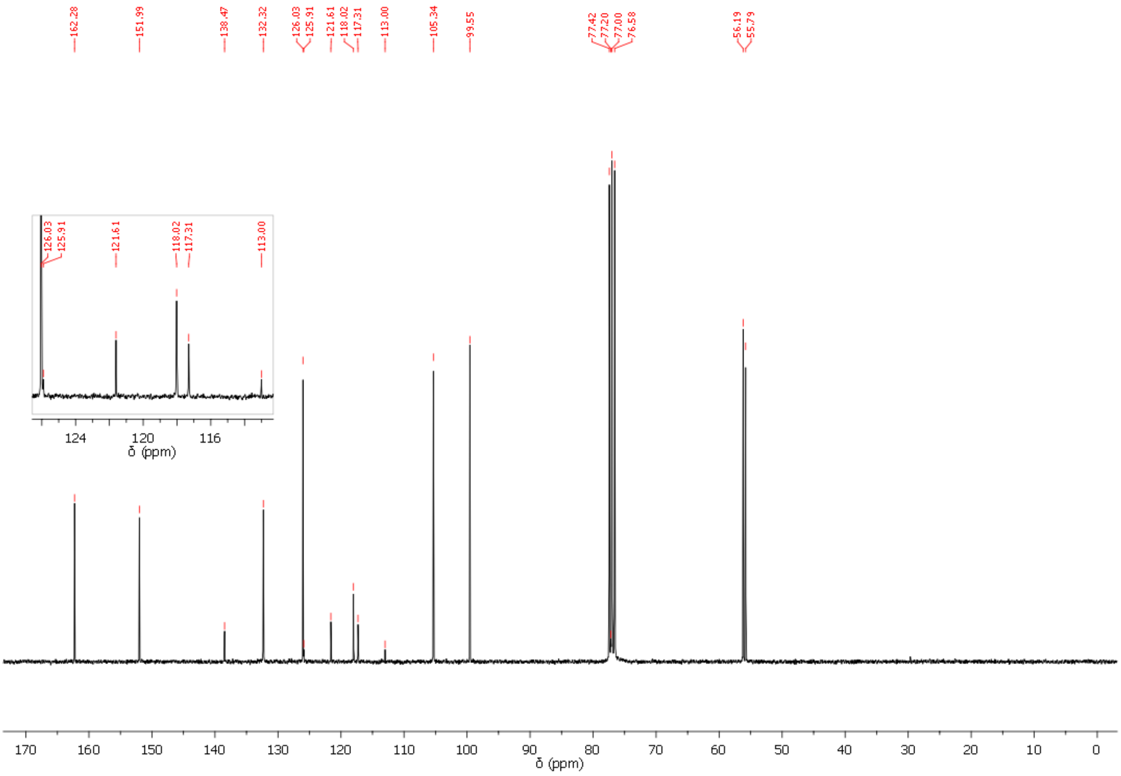


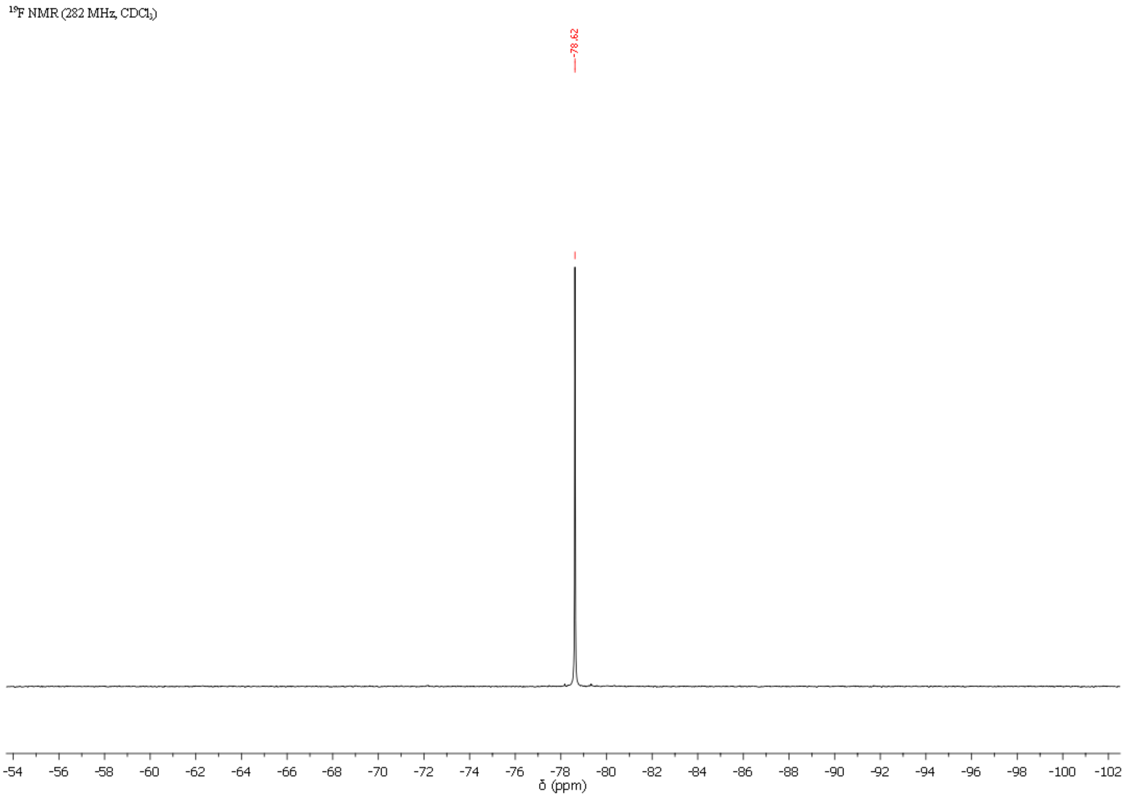
^{1}H NMR (300 MHz, CDCl$_3$)



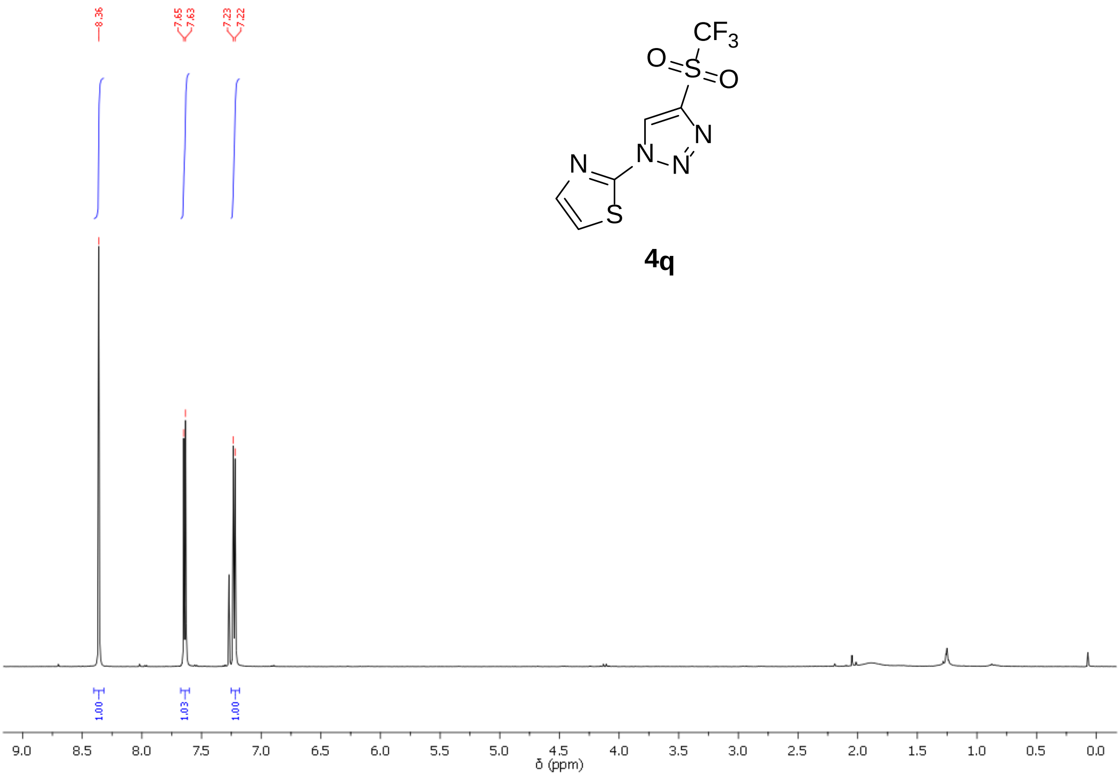
4p

^{13}C NMR (75 MHz, CDCl$_3$)



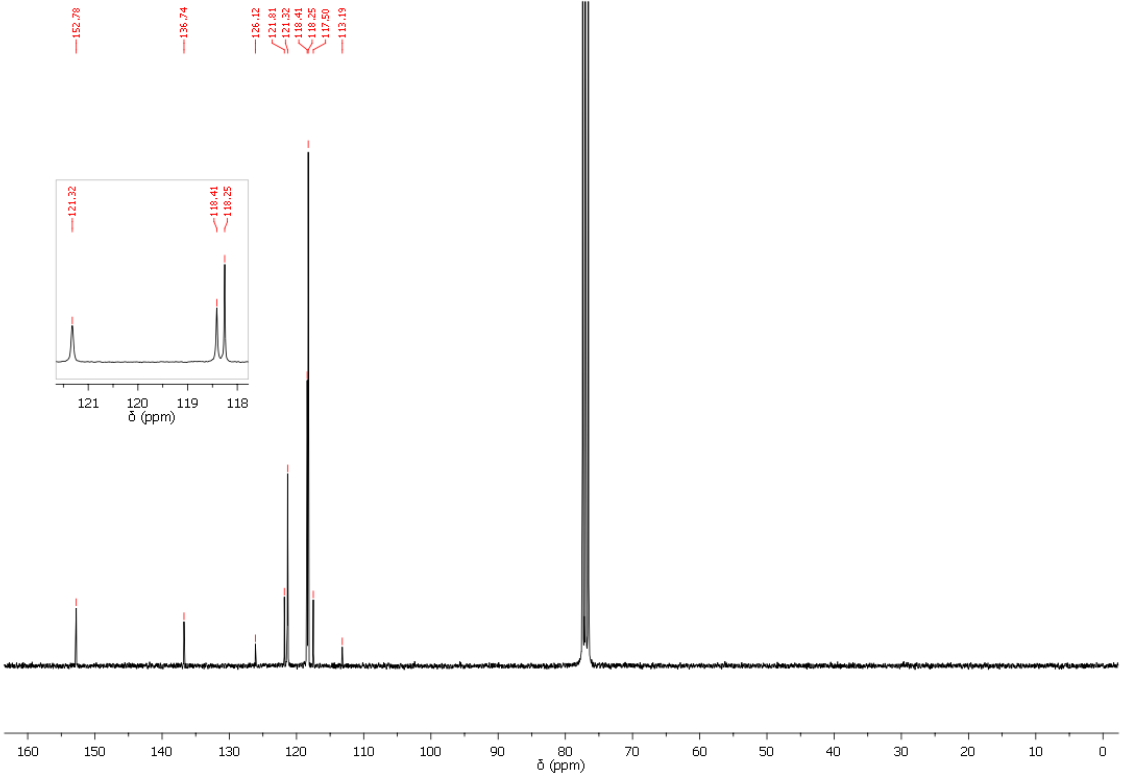

^{19}F NMR (282 MHz, $CDCl_3$)
-78.62
-54
-56
-58
-60
-62
-64
-66
-68
-70
-72
-74
-76
-78
-80
-82
-84
-86
-88
-90
-92
-94
-96
-98
-100
-102
δ (ppm)

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

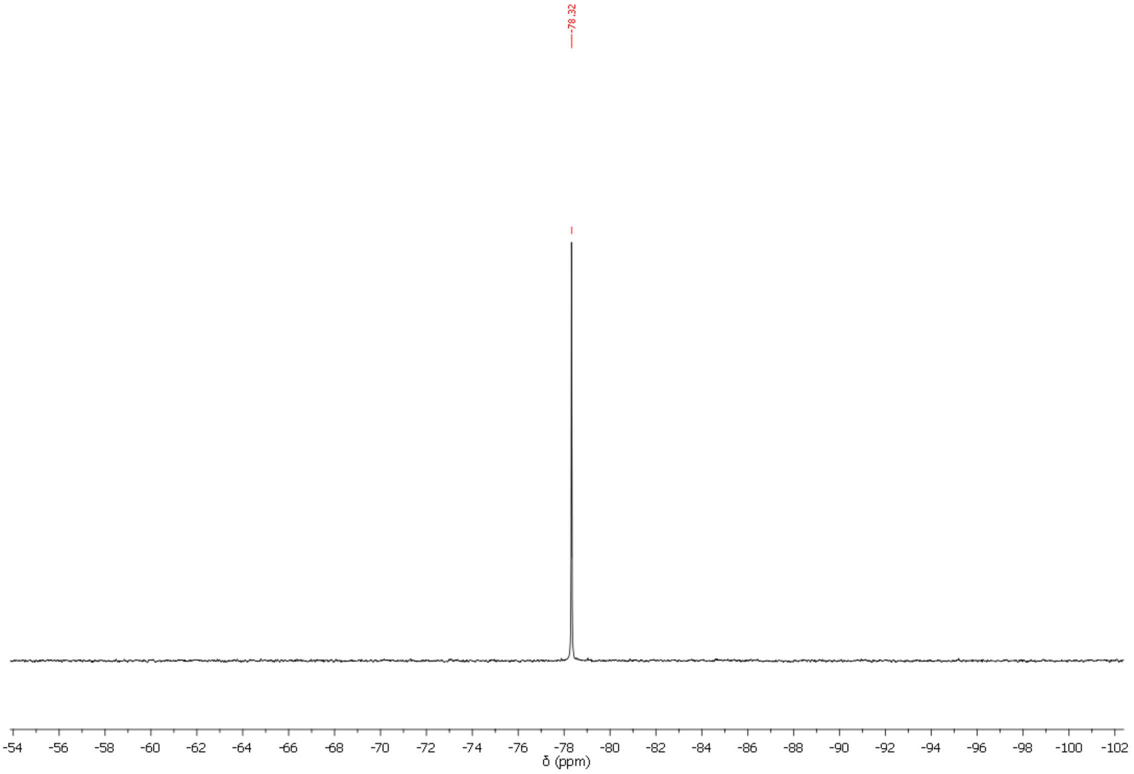


4q

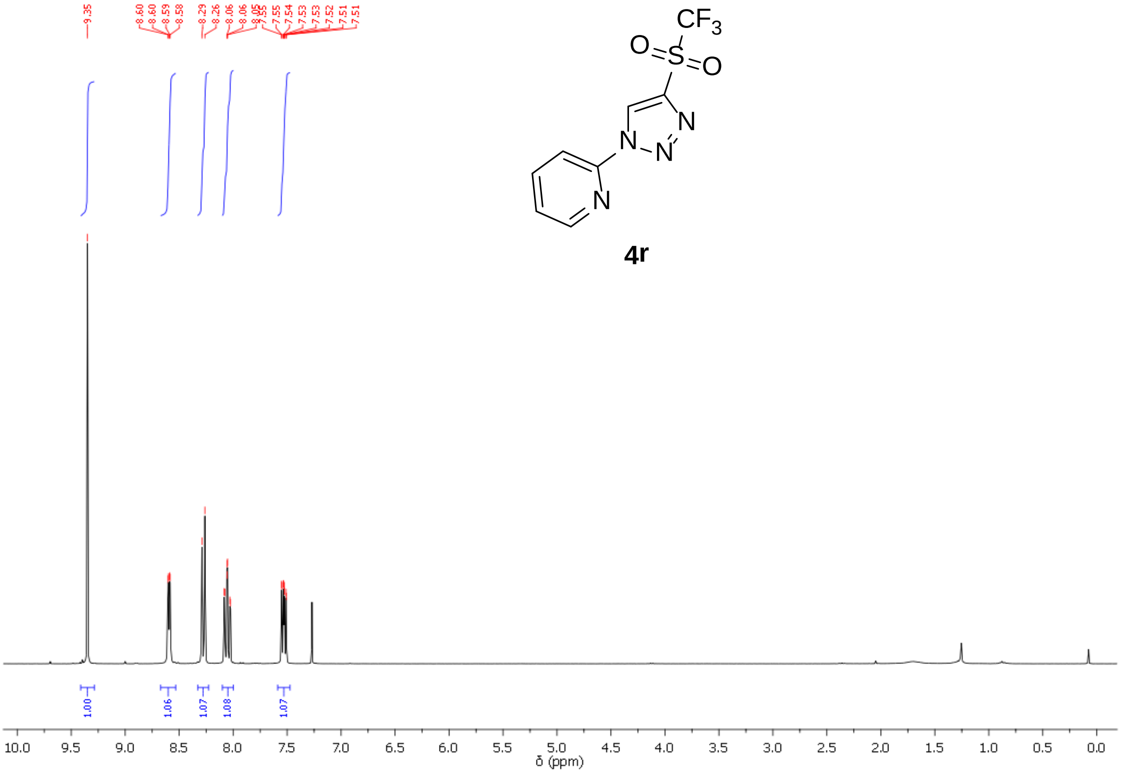
^{13}C NMR (75 MHz, $CDCl_3$)



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

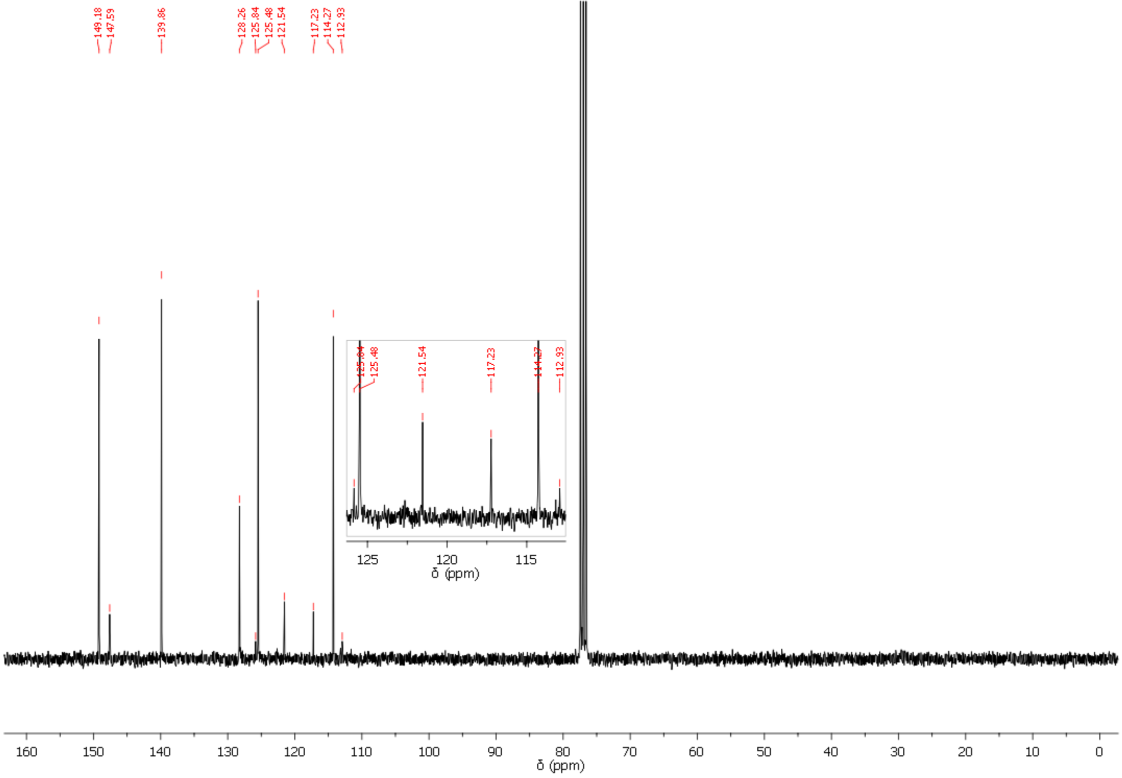


^{1}H NMR (300 MHz, CDCl$_3$)

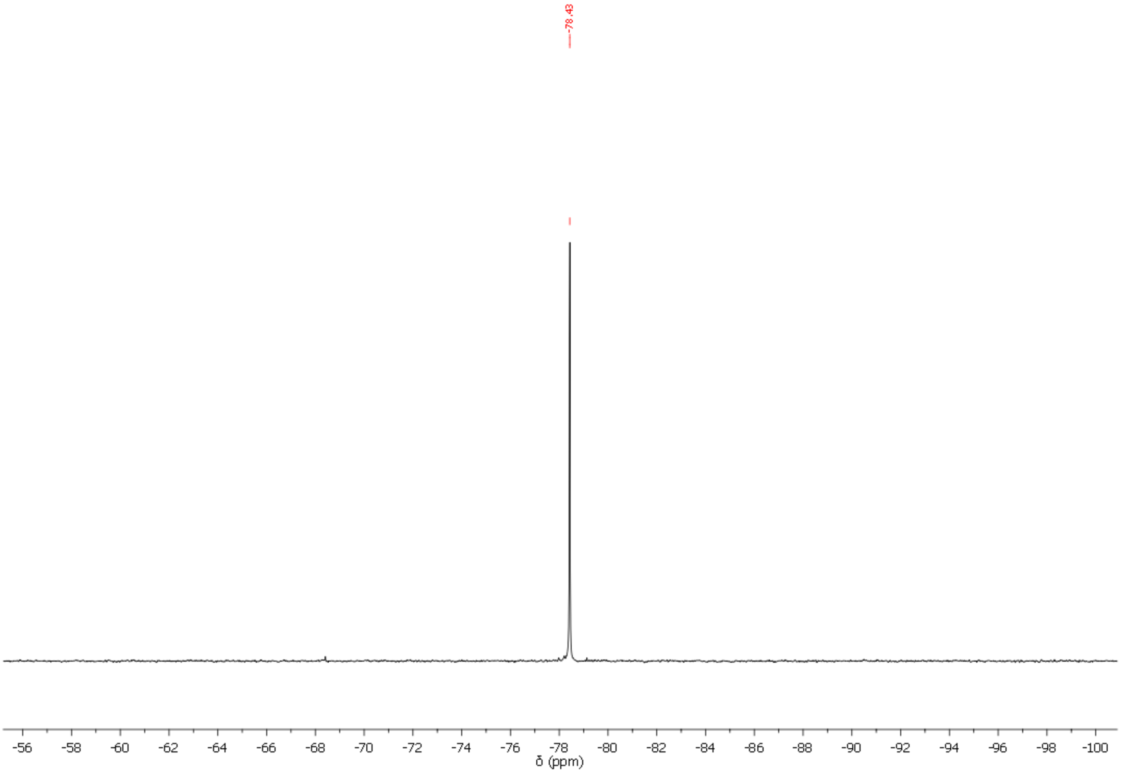


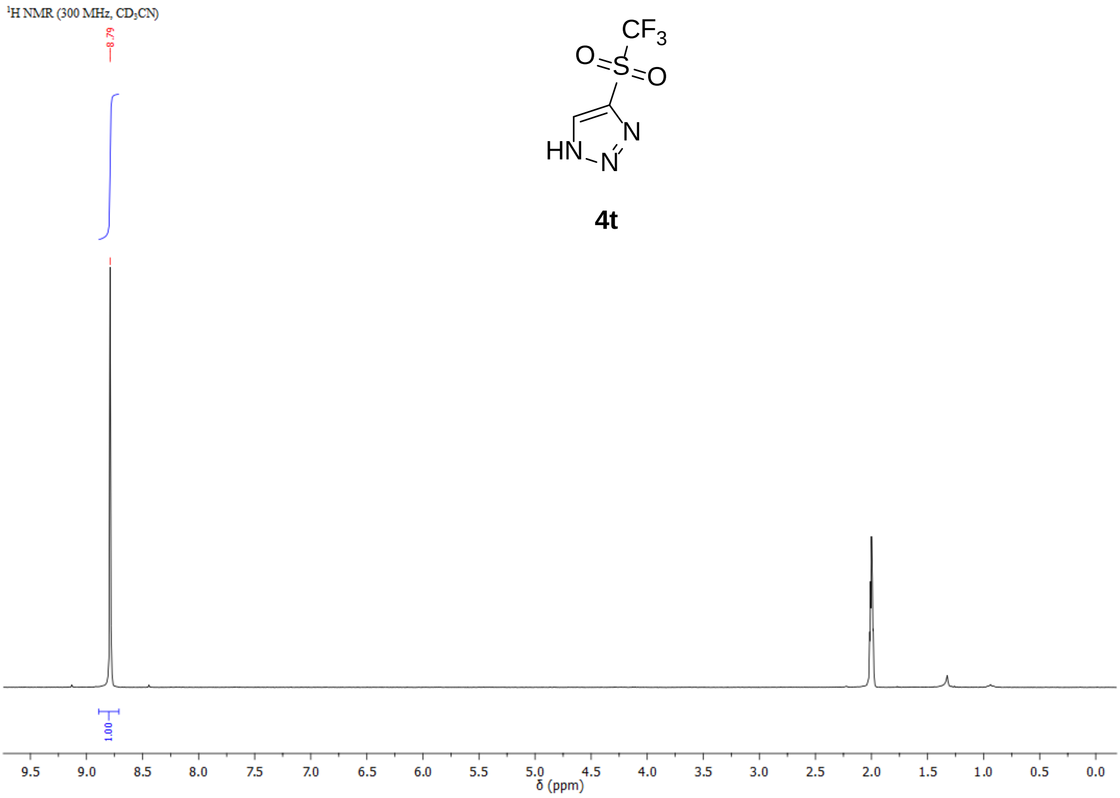
4r

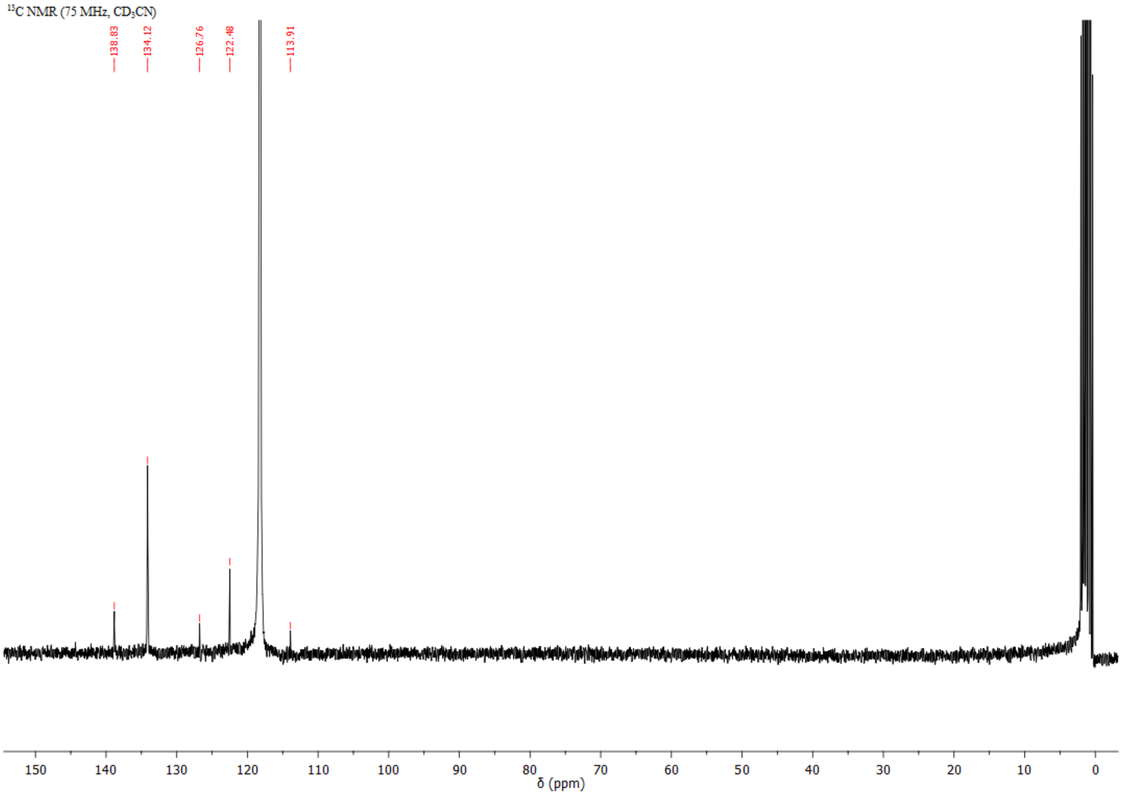
^{13}C NMR (75 MHz, CDCl$_3$)



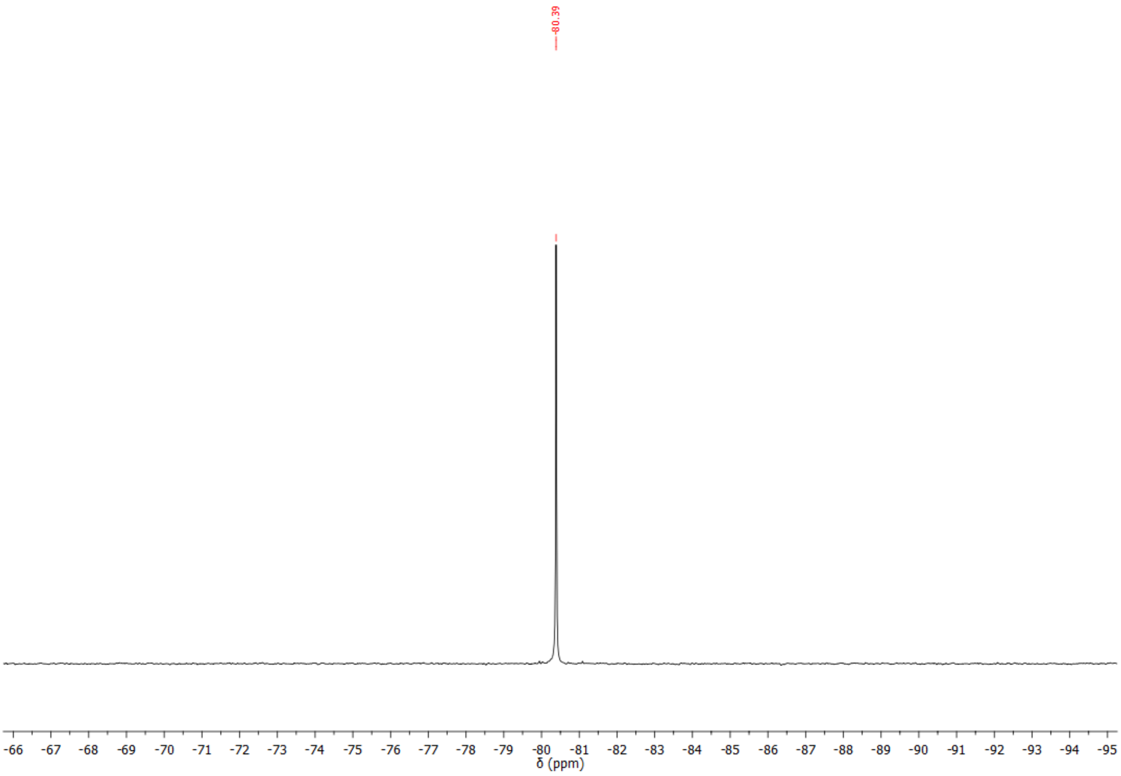
^{19}F NMR (282 MHz, $CDCl_3$)

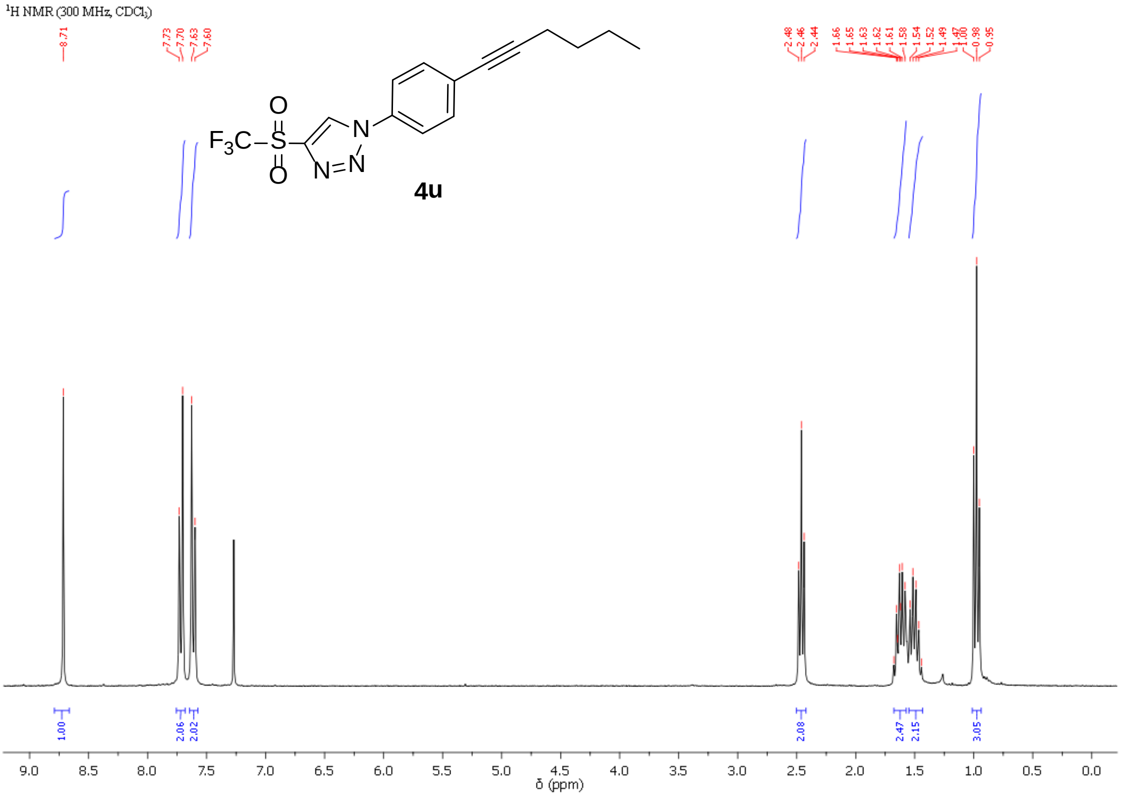


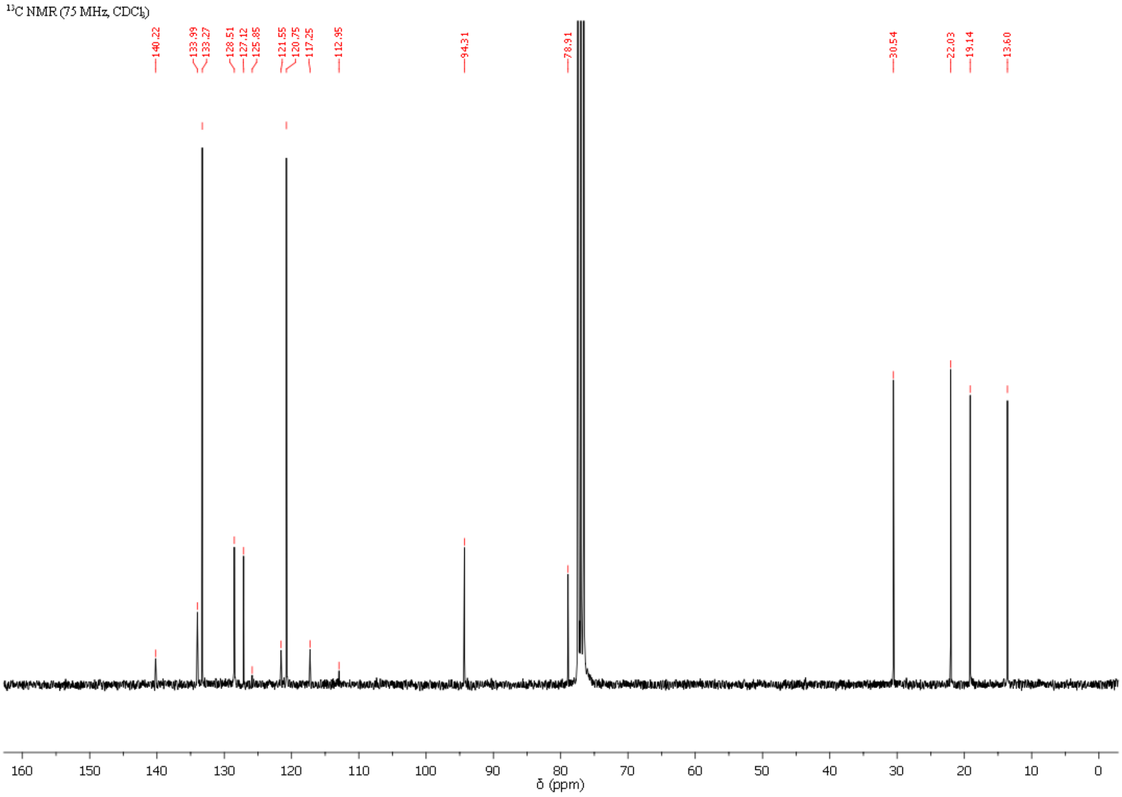

4t
^{1}H NMR (300 MHz, CD$_3$CN)
8.79
1.00
CF_3
O
S
O
N
HN
N
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)


^{13}C NMR (75 MHz, CD$_3$CN)
138.83
134.12
126.76
122.48
113.91
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

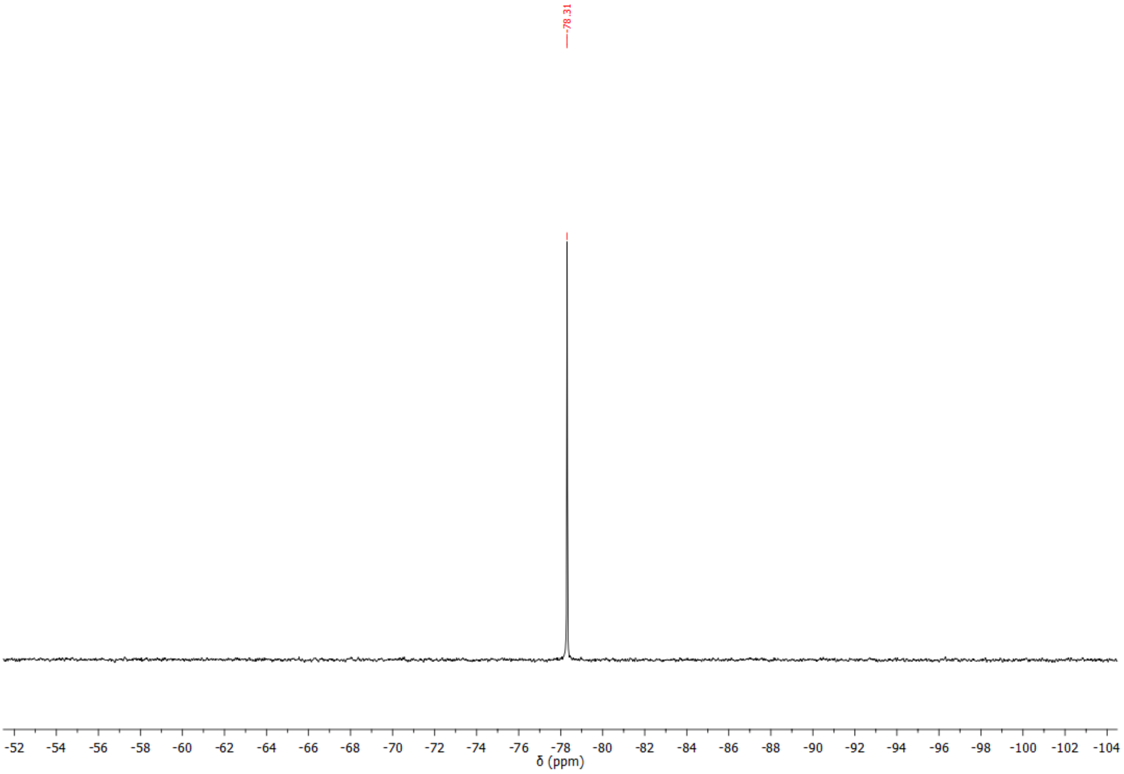
^{19}F NMR (282 MHz, CD_3CN)

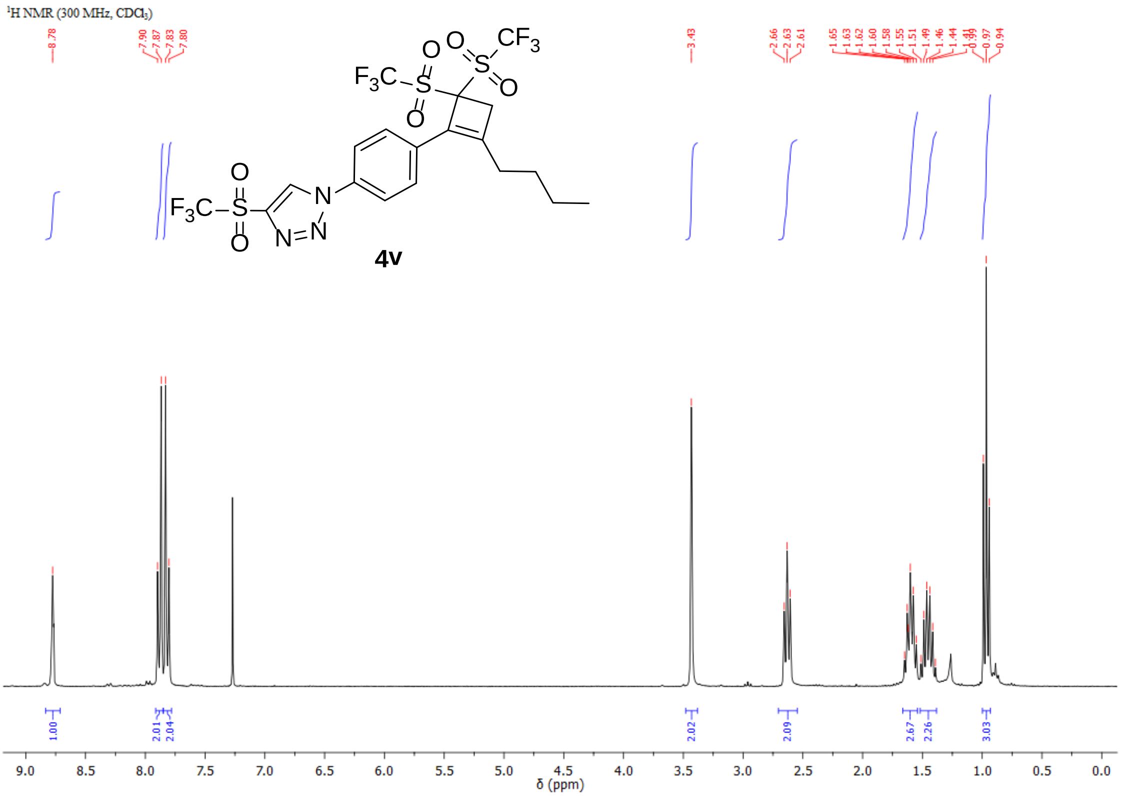


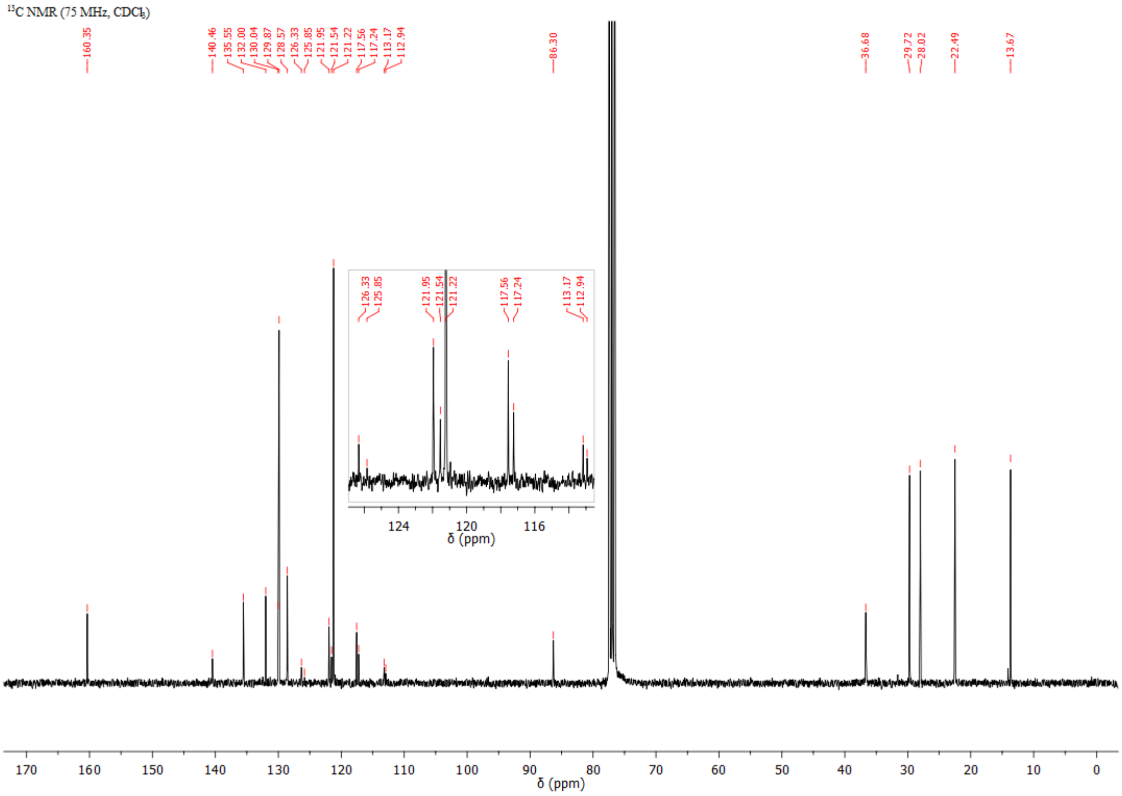

^{1}H NMR (300 MHz, CDCl$_3$)
8.71
7.73
7.70
7.63
7.60
2.48
2.46
2.44
1.66
1.65
1.63
1.62
1.61
1.58
1.54
1.52
1.49
1.47
1.00
0.98
0.95
F_3C
S
O
N
N=N
4u
1.00
2.06
2.02
2.08
2.47
2.15
3.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

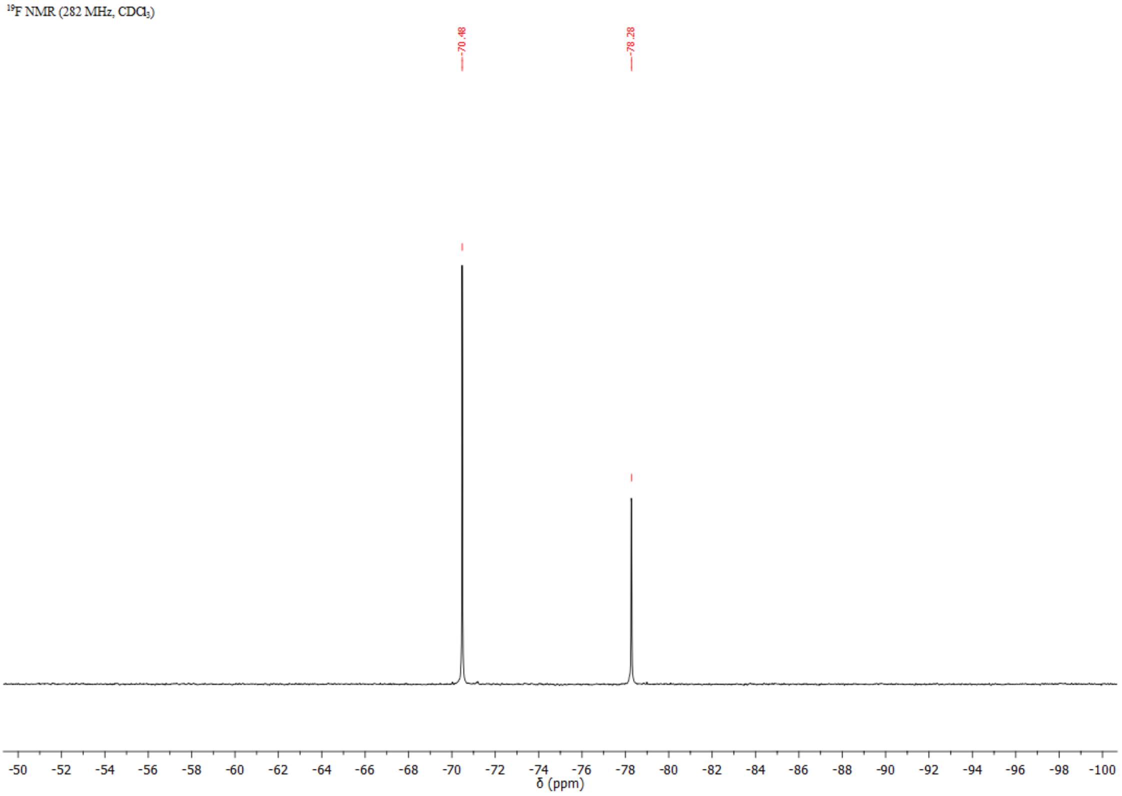

^{13}C NMR (75 MHz, CDCl$_3$)
140.22
133.99
133.27
128.51
127.12
125.85
121.55
120.75
117.25
112.95
94.31
78.91
30.54
22.03
19.14
13.60
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

^{19}F NMR (282 MHz, CDCl$_3$)



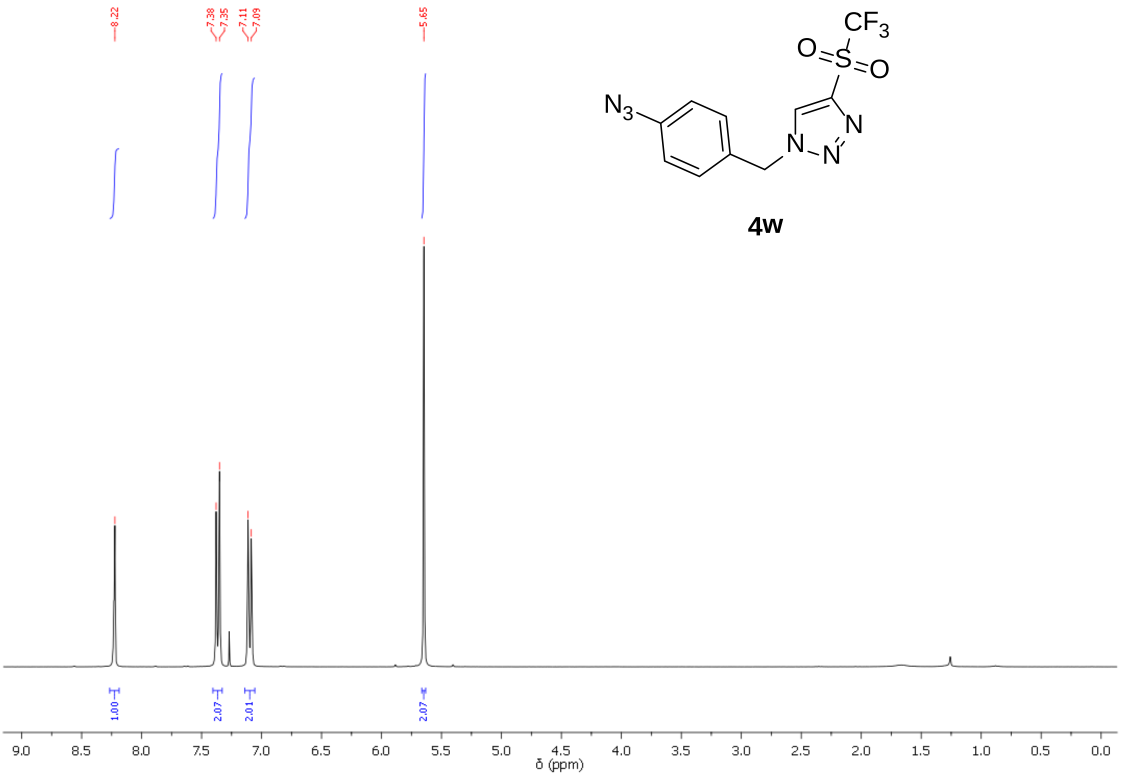

1H NMR (300 MHz, CDCl3)
8.78
7.90
7.87
7.83
7.80
3.43
2.66
2.63
2.61
1.65
1.63
1.62
1.60
1.58
1.55
1.51
1.49
1.46
1.44
1.41
0.99
0.97
0.94
F3C
O
S
N
N=N
O
F3C
S
O
O
O
S
CF3
O
4v
1.00
2.01
2.04
2.02
2.09
2.67
2.26
3.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)


13C NMR (75 MHz, CDCl3)
160.35
140.46
135.55
132.00
130.04
129.87
128.57
126.33
125.85
121.95
121.54
121.22
117.56
117.24
113.17
112.94
86.30
36.68
29.72
28.02
22.49
13.67
126.33
125.85
121.95
121.54
121.22
117.56
117.24
113.17
112.94
124
120
116
δ (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

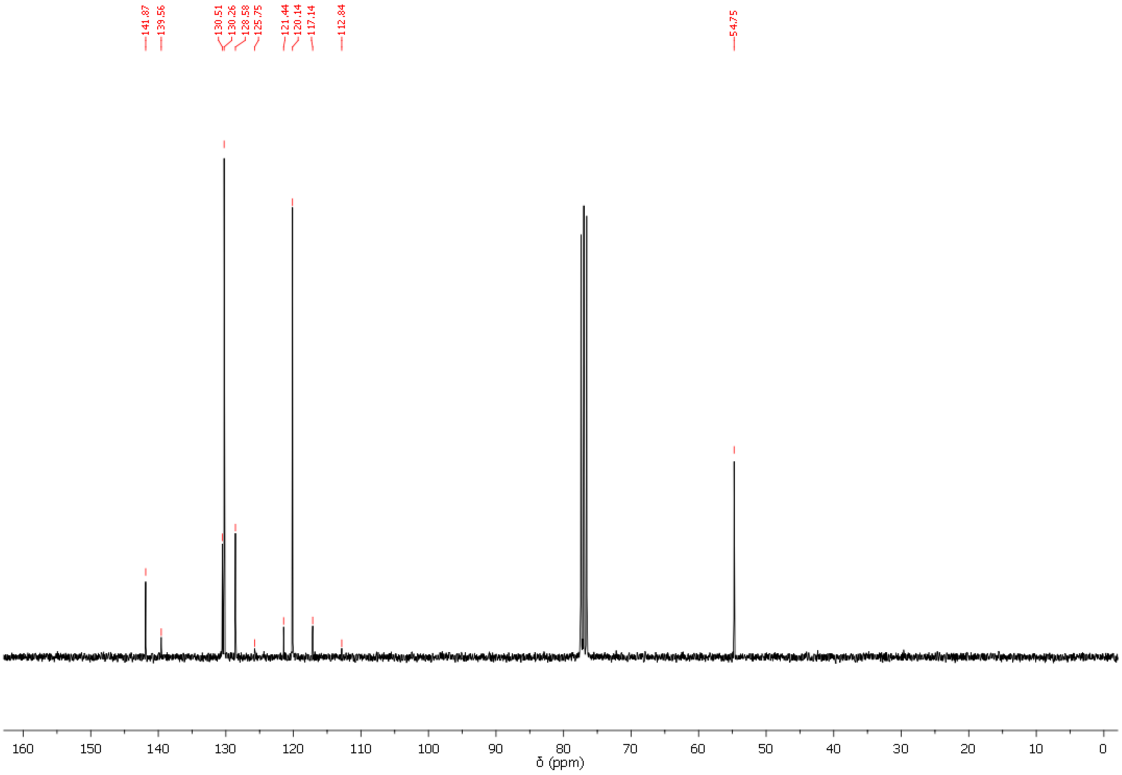


^{19}F NMR (282 MHz, CDCl$_3$)
-70.48
-78.28
-50
-52
-54
-56
-58
-60
-62
-64
-66
-68
-70
-72
-74
-76
-78
-80
-82
-84
-86
-88
-90
-92
-94
-96
-98
-100
δ (ppm)

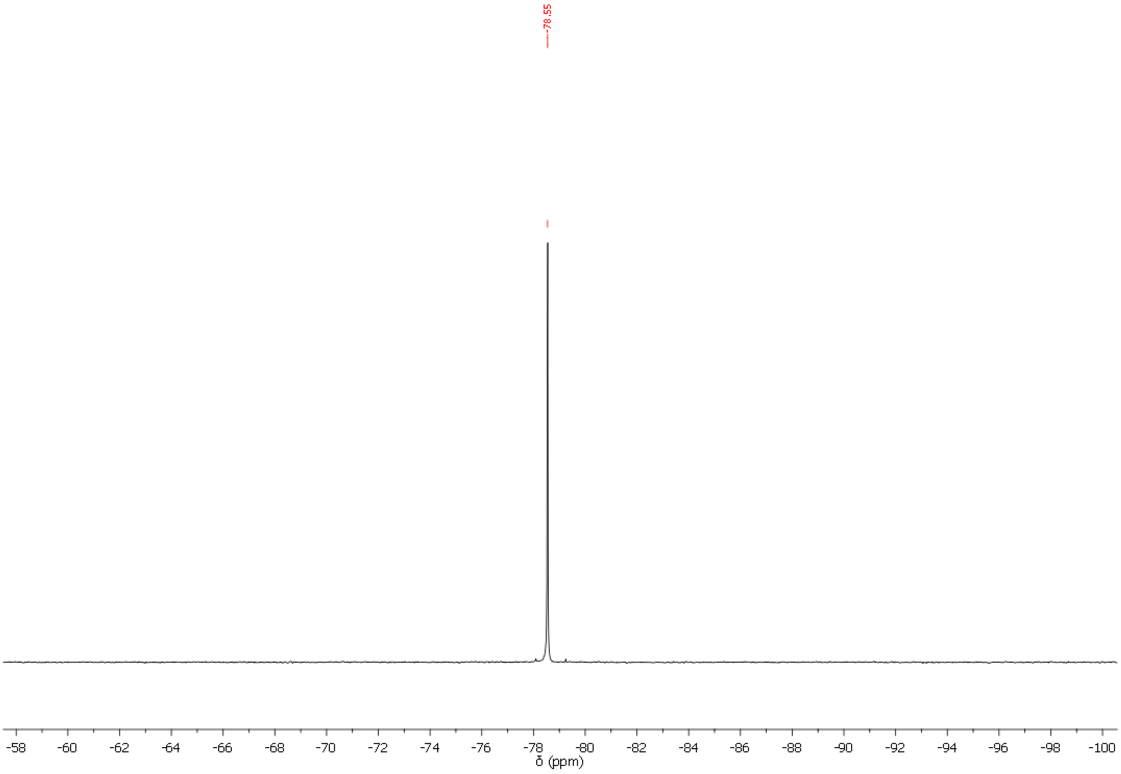
^{1}H NMR (300 MHz, CDCl$_3$)

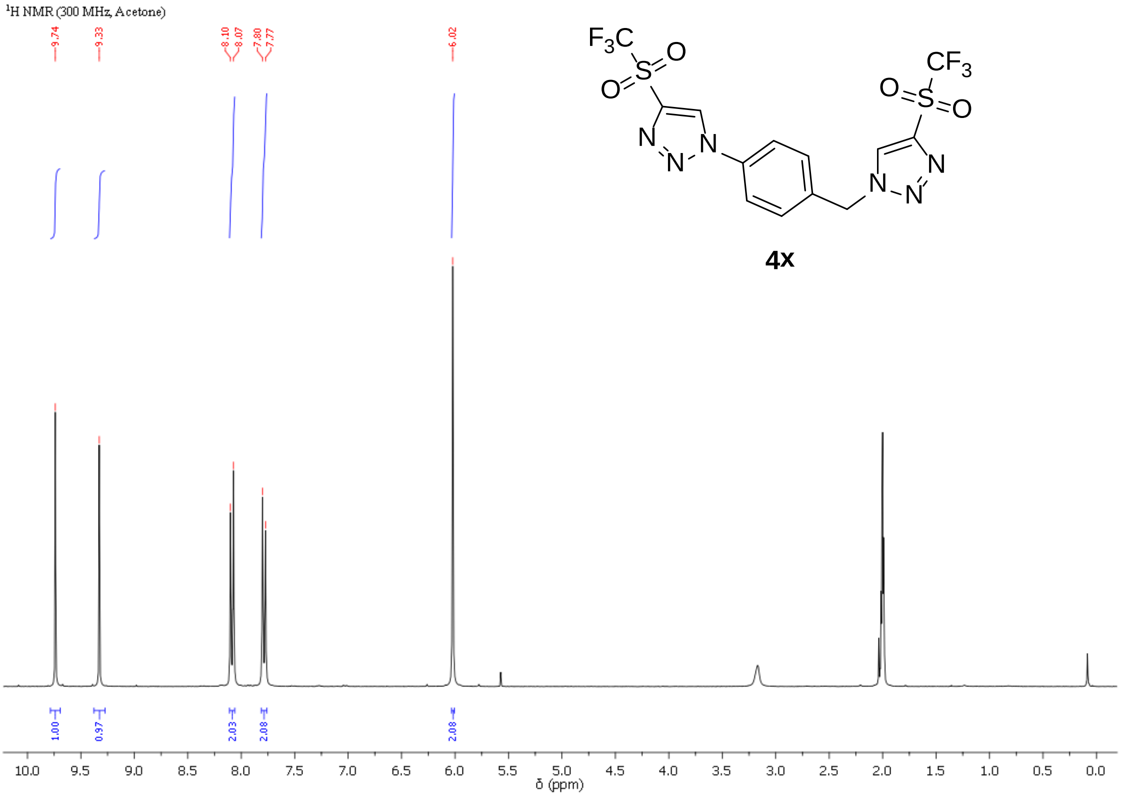


^{13}C NMR (75 MHz, CDCl$_3$)

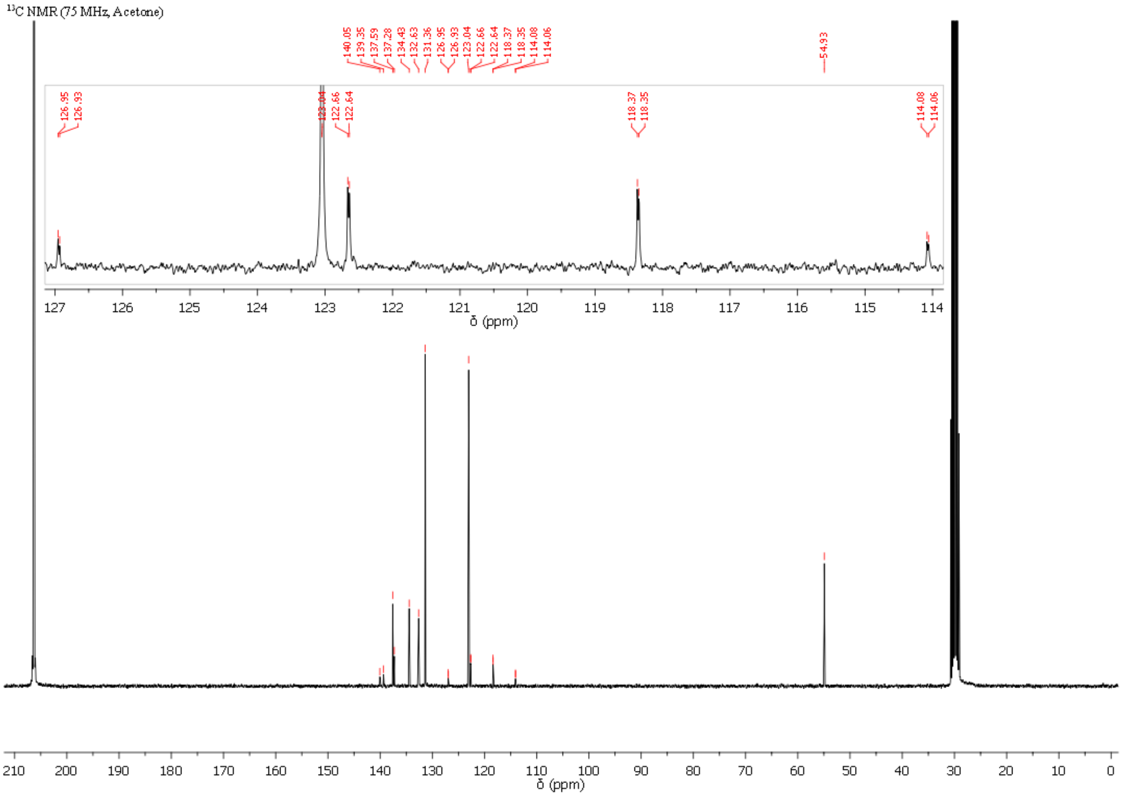


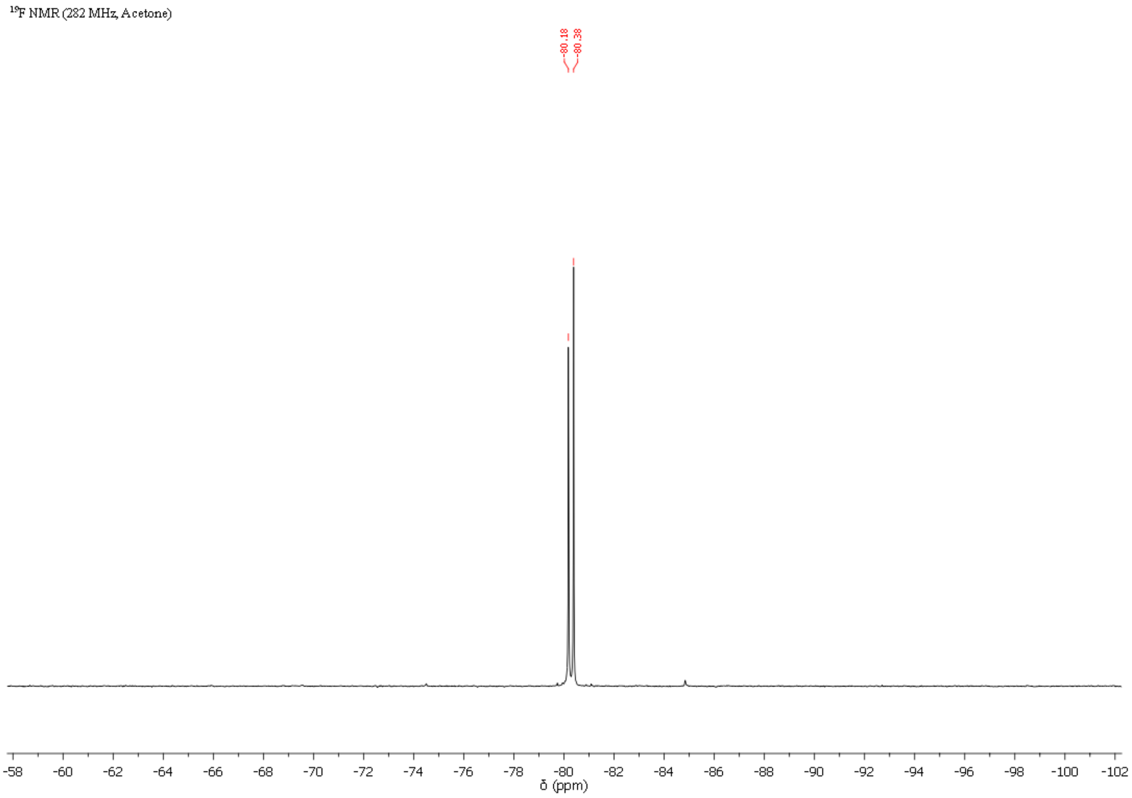
^{19}F NMR (282 MHz, $CDCl_3$)



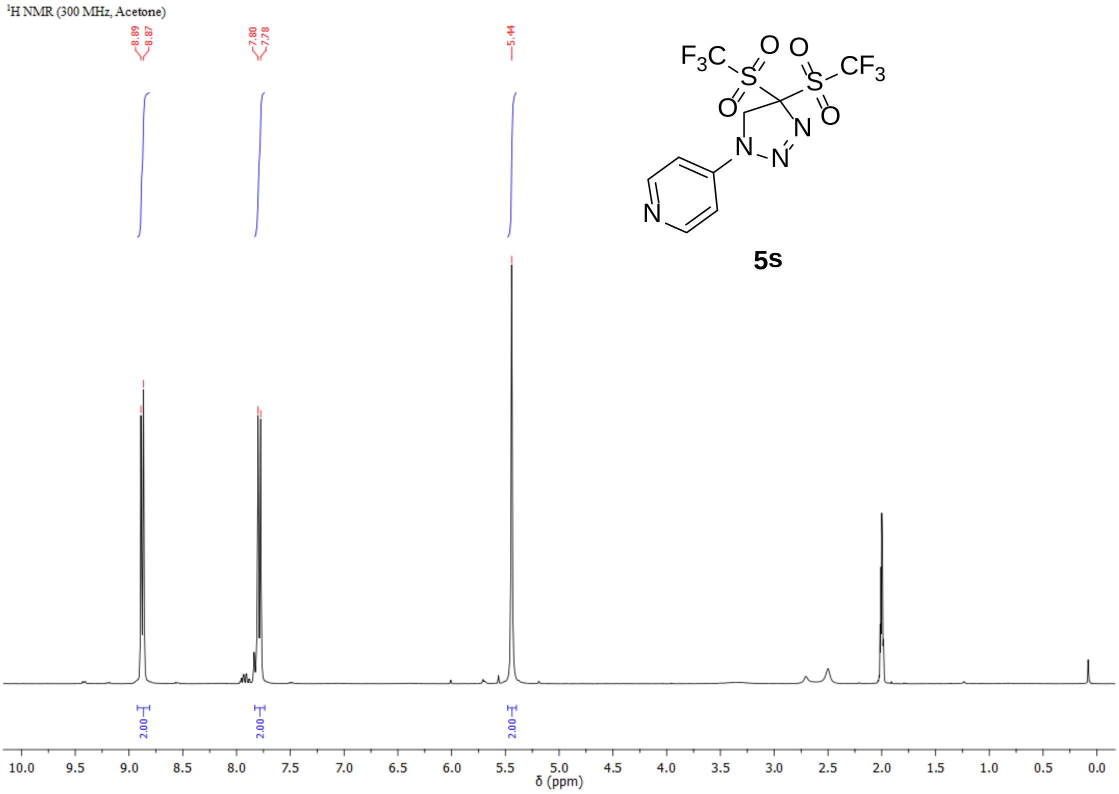

¹H NMR (300 MHz, Acetone)
9.74
9.33
8.10
8.07
7.80
7.77
6.02
1.00
0.97
2.03
2.08
2.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)
F3C
O
S
O
N
N
N
CF3
O
S
O
N
N
N

4x


¹³C NMR (75 MHz, Acetone)
140.05
139.35
137.59
137.28
134.43
132.63
131.36
126.95
126.93
123.04
122.66
122.64
118.37
118.35
114.08
114.06
54.93
126.95
126.93
123.04
122.66
122.64
118.37
118.35
114.08
114.06
127
126
125
124
123
122
121
120
119
118
117
116
115
114
δ (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
δ (ppm)

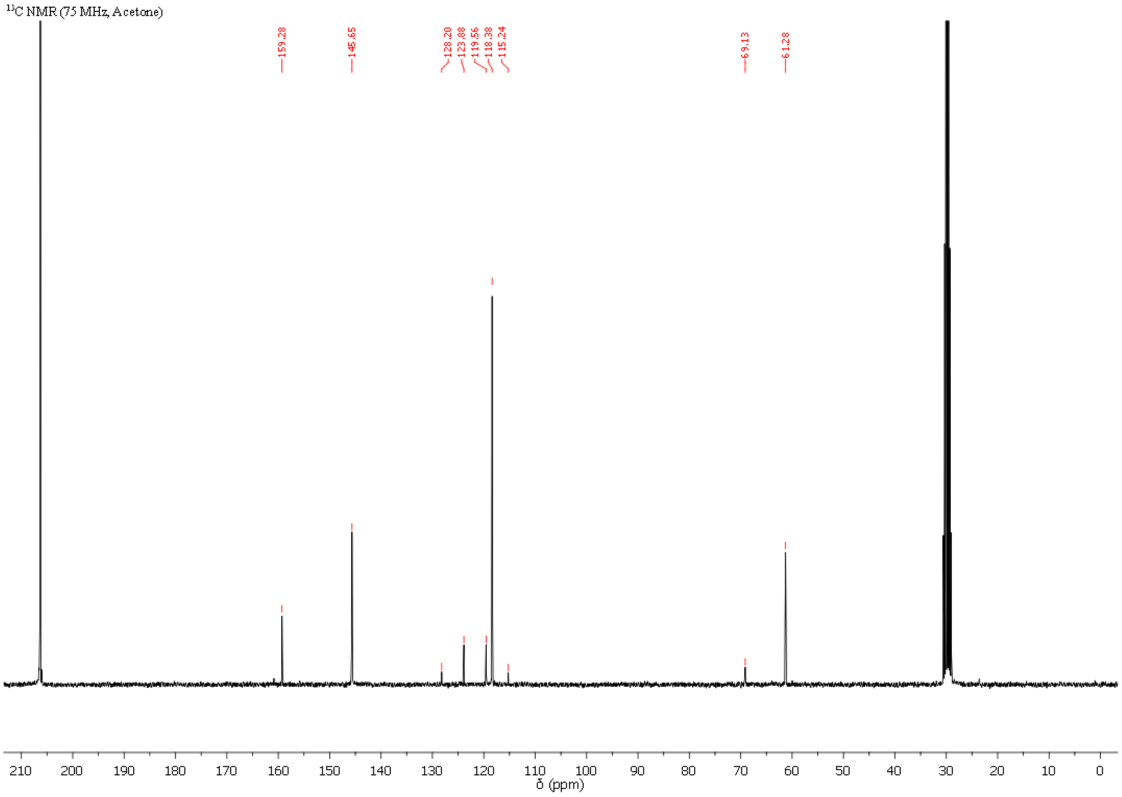


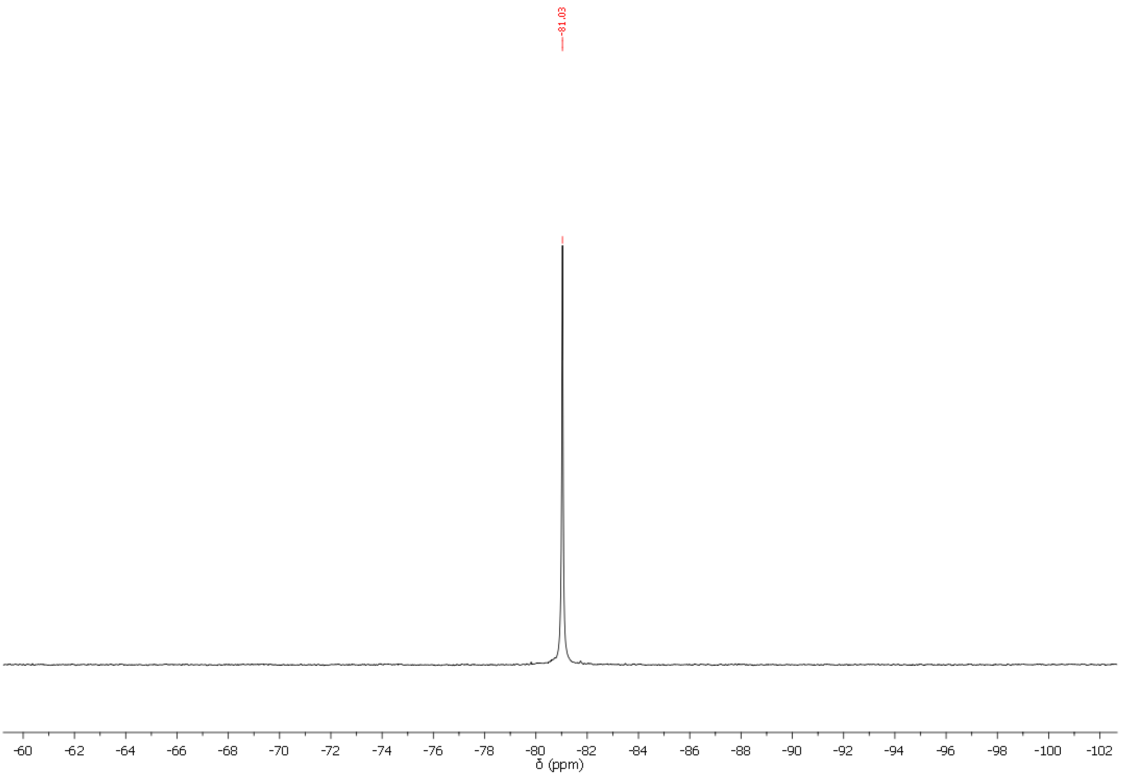
^{19}F NMR (282 MHz, Acetone)
-80.18
-80.38
-58
-60
-62
-64
-66
-68
-70
-72
-74
-76
-78
-80
-82
-84
-86
-88
-90
-92
-94
-96
-98
-100
-102
δ (ppm)


^{1}H NMR (300 MHz, Acetone)
8.89
8.87
7.80
7.78
5.44
2.00
2.00
2.00
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)

F_3C
S
O
O
O
S
CF_3
O
N
N
N
N

5s


^{13}C NMR (75 MHz, Acetone)
159.28
145.65
128.20
123.88
119.56
118.38
115.24
69.13
61.28
210
200
190
180
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, Acetone)