Supporting Information

Installation of Trifluoromethylated Quaternary Carbon Stereocenters via Asymmetric Epoxidation of Tetrasubstituted Alkenes

Vincenzo Battaglia,[a] Isaac G. Sonsona,[a] Andrea Pellegrini,[b] Andrea Mazzanti,[b] and Alessandra Lattanzi[a,*]

[a] *Dipartimento di Chimica e Biologia "A. Zambelli", University of Salerno, Via Giovanni Paolo II 132, 84084, Fisciano, Italy, e-mail: lattanzi@unisa.it*

[b] *Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna, Via P. Gobetti 85, 40129, Bologna, Italy*

CONTENT

General Methods

All reactions requiring anhydrous and inert conditions were conducted in flame-dried glassware under a positive pressure of nitrogen. Anhydrous dimethyl carbonate, anhydrous *tert*-butyl methyl ether (both from Aldrich), anhydrous hexafluorobenzene and anhydrous tetrahydrofuran (both from TCI- Europe) were used as received; all other solvents were dried over molecular sieves. Molecular sieves (Aldrich Molecular Sieves, 3 Å, 1.6 mm pellets) were activated under vacuum at 200 °C overnight. Reactions were monitored by thin layer chromatography (TLC) on Merck pre-coated silica gel plates (0.25 mm) and visualized by UV light, and if necessary, by phosphomolybdic acid, potassium permanganate or ninhydrin solutions. Flash chromatography was performed on Merck silica gel (60, particle size: 0.040–0.063 mm. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on Bruker Avance III HD 600, Bruker Avance-400, Bruker Avance-300 or Bruker Avance-250 spectrometer in $CDCl_3$ and acetone-d_6. Chemical shifts for protons are reported using residual solvent protons (δ = 7.26 ppm for $CDCl_3$, δ = 2.05 ppm for acetone-d_6) as internal standard. Carbon spectra were referenced to the shift of the ^{13}C signal of $CDCl_3$ (δ = 77.0 ppm) or acetone d_6 (δ = 29.8 ppm).

The following abbreviations are used to indicate the multiplicity in NMR spectra: s - singlet; d - doublet; t - triplet; q – quadruplet; dd – double doublet; m - multiplet; bs - broad signal.

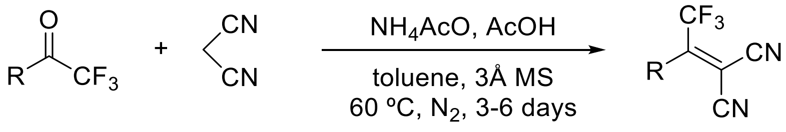
Optical rotation of compounds was performed on a Jasco P-2000 digital polarimeter using WI (Tungsten-Halogen) lamp (λ = 589 nm). Elemental analyses were carried out by using Flash EA 1112 (Thermo Electron Corporation) analyzer. High resolution mass spectra (HRMS) were acquired using a Bruker solariX XR Fourier transform ion cyclotron resonance mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 7 T refrigerated actively-shielded superconducting magnet. The samples were ionized in positive ion mode using a MALDI ionization source. Melting points were measured with a Stuart Model SMP 30 melting point apparatus and are uncorrected. All starting materials (unless otherwise noted) were purchased from Merck-Sigma Aldrich or TCI-Europe and used as received. Organocatalyst **I** was purchased from Aldrich and organocatalyst **II** was purchased from Strem Chemicals and used as received. Catalysts **eQNU**,[1] **eQNT**,[2] **III**,[3] **IV**,[4] **V**[5] and **VI**[6] were prepared according to the literature. Enantiomeric excess of products **2**, **3**, **4**, **5**, **6**, **7** and **9** were determined by HPLC (Waters-Breeze 2487, UV dual λ

[1] a) Miyaji, R.; Asano, K.; Matsubara, S. *Org. Lett.*, **2013**, *15*, 3658–3661; b) Amere, M.; Lasne, M.-C.; Rouden, J. *Org. Lett.*, **2007**, *9*, 2621–2624; c) Wu, W.; Min, L.; Zhu, L.; Lee, C.-S. *Adv. Synth. Catal.*, **2011**, *353*, 1135–1145.
[2] Vakulya, B.; Varga, S.; Csámpai, A.; Soós, T. *Org. Lett.*, **2005**, *7*, 1967–1969.
[3] Meninno, S.; Zullo, L.; Overgaard, J.; Lattanzi, A. *Adv. Synth. Catal.*, **2017**, *359*, 913–918.
[4] Meninno, S.; Vidal-Albalat, A.; Lattanzi, A. *Org. Lett.*, **2015**, *17*, 4348–4351.
[5] Meninno, S.; Croce, G.; Lattanzi, A. *Org. Lett.*, **2013**, *15*, 3436–3439.
[6] Meninno, S.; Overgaard, J.; Lattanzi, A. *Synthesis*, **2017**, *49*, 1509–1518.

absorbance detector or Waters-Breeze 2998 photodiode array detector and 1525 Binary HPLC Pump) using Daicel chiral columns.

Experimental Procedures and Compounds Characterization

General procedure for the synthesis of alkenes 1



1a-n

Alkenes **1** were prepared under a slightly modified procedure from the literature.[7]

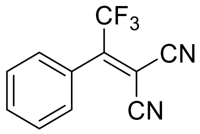
To a solution of malononitrile (132 mg, 2.0 mmol) in an ace tube, anhydrous toluene (1.3 mL) ketone (2.0 mmol), ammonium acetate (31.8 mg, 0.40 mmol), glacial acetic acid (126 µL, 2.2 mmol) and molecular sieves (~100 mg) are added. The tube is sealed under N_2 and the reaction mixture warmed at 60 °C without stirring for 3-6 days, monitored by TLC (eluent PE/ethyl acetate 90/10). Additional aliquots of molecular sieves (~100 mg) are added after 24 h and 48 h from the start. Upon completion, the crude reaction mixture is diluted with $CHCl_3$ (50 mL) and washed with a saturated solution of $NaHCO_3$ (1x40 mL) and brine (2x40mL). The organic layer is dried over Na_2SO_4, filtered and the solvent removed under reduced pressure to give a mixture of alkylidene **1** and starting ketone. ATTENTION! Purification of the crude by flash chromatography leads to a significant decomposition of the alkyne in most of the cases and should be avoided. The different crudes were further purified as follows and the purity of the compound **1** analyzed by ^{1}H-NMR and ^{19}F-NMR:

- For compounds **1a** and **1h**, starting ketone is removed by evaporation at 40 °C and 4 mbar, giving the product as an oil, pure from NMR.
- Compounds **1b**, **1d**, **1i** and are purified by a quick filtration through a silica plug with pentane to remove the ketone and a mixture of pentane/diethyl ether 90/10 to recover the product as an oil (**1b** pure, **1d** 90% pure, **1i** 95% pure from NMR).
- For compounds **1j** and **1k**, the crude is washed with pentane (3x3mL) to afford the product as a solid (**1j** 94% pure, **1k** pure from NMR).
- For compounds **1c**, **1m** and **1l**, the crude is suspended in pentane (3 mL) and the top layer is carefully removed using a Pasteur pipette. The process is repeated two times more, affording the products as oils (**1c** 95% pure, **1m** 95% pure, **1l** 97% pure from NMR).

[7] a) Mowry, D. T. *J. Am. Chem. Soc.*, **1945**, *67*, 1050–1051; b) Xue, D.; Chen, Y.-C.; Cui, X.; Wang, Q.-W.; Zhu, J.; Deng, J.-G. *J. Org. Chem.*, **2005**, *70*, 3584–3591.

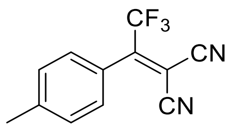
- For compounds **1e**, **1f** and **1g**, the crude is quickly filtered through a silica plug with diethyl ether, evaporated and the residue washed with pentane (3x3mL). The product is recovered as a solid, pure from NMR.
- For the compound **1n**, the crude is suspended in Et_2O (3 mL), and the top layer is removed carefully using a Pasteur pipette. The process is repeated two times more, affording the product as a solid (90% pure from NMR).

2-(2,2,2-trifluoro-1-phenylethylidene)malononitrile 1a



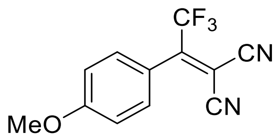
Colourless liquid, 262.0 mg, 59% yield. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.66 (t, 1H, J = 7.4 Hz), 7.60-7.56 (m, 2H), 7.50 (d, 2H, J = 7.8 Hz).**^{13}C NMR:** ($CDCl_3$, 100 MHz): δ 160.0 (q, $^2J_{CF}$ = 33.3 Hz), 135.5, 133.2, 129.5, 128.5, 120.3 (q, $^1J_{CF}$ = 278 Hz), 110.7, 109.2, 92.3. **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -61.5. **HRMS (MALDI-FT ICR)** m/z: $[M+H]^+$ calculated for $C_{11}H_6F_3N_2$: 223.0478, found: 223.0501.

2-(2,2,2-trifluoro-1-(*p*-tolyl)ethylidene)malononitrile 1b



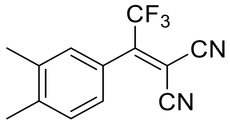
Pale yellow oil, 99.2 mg, 21% yield. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.42 (d, 2H, J = 8.2 Hz), 7.37 (d, 2H, J = 8.2 Hz), 2.46 (s, 3H).**^{13}C NMR:** ($CDCl_3$, 150 MHz): δ 159.9 (q, $^2J_{CF}$ = 32.8 Hz), 144.5, 133.1, 128.6, 125.2, 120.4 (q, $^1J_{CF}$ = 281 Hz), 111.1, 109.4, 91.0, 21.7. **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -61.2. **HRMS (MALDI-FT ICR)** m/z: $[M]^+$ calculated for $C_{12}H_7F_3N_2$: 236.0556, found: 236.0558.

2-(2,2,2-trifluoro-1-(4-methoxyphenyl)ethylidene)malononitrile 1c



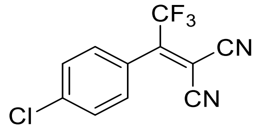
Yellow oil, 70.6 mg, 14% yield. **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 7.53 (d, 2H, J = 9.0 Hz), 7.04 (d, 2H, J = 9.0 Hz), 3.90 (s, 3H). **^{13}C NMR:** ($CDCl_3$, 150 MHz): δ 163.9, 159.2 (q, $^2J_{CF}$ = 32.7 Hz), 131.1, 120.5 (q, $^1J_{CF}$ = 279 Hz), 120.1, 114.9, 111.6, 109.7, 89.0, 55.6. **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -60.7. **HRMS (MALDI-FT ICR)** m/z: $[M+H]^+$ calculated for $C_{12}H_8F_3N_2O$: 253.0583, found: 253.0597.

2-(1-(3,4-dimethylphenyl)-2,2,2-trifluoroethylidene)malononitrile 1d



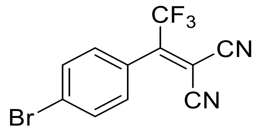
Yellow solid, 190.2 mg, 38% yield. **m.p**. = 56.2-58.1 °C. **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 7.28 (d, 1H, J = 7.8 Hz), 7.24 (s, 1H), 7.23 (d, 1H, J = 7.8 Hz), 2.32 (s, 3H), 2.31 (s, 3H).**^{13}C NMR:** ($CDCl_3$, 150 MHz): δ 160.1 (q, $^2J_{CF}$ = 32.8 Hz), 143.3, 138.2, 130.6, 129.4, 126.3, 125.7, 120.4 (q, $^1J_{CF}$ = 278 Hz), 111.2, 109.5, 90.8 (q, $^3J_{CF}$ = 3.6 Hz), 20.0, 19.8. **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -61.2. **HRMS (MALDI-FT ICR)** m/z: $[M+Na]^+$ calculated for $C_{13}H_9F_3N_2Na$: 273.0610, found: 273.0600.

2-(1-(4-chlorophenyl)-2,2,2-trifluoroethylidene)malononitrile 1e



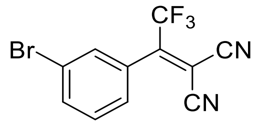
Pale yellow wax, 261.7 mg, 51% yield. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.56 (d, 2H, J = 8.4 Hz), 7.45 (d, 2H, J = 8.4 Hz). **^{13}C NMR:** ($CDCl_3$, 150 MHz): δ 158.6 (q, $^2J_{CF}$ = 33.5 Hz), 140.0, 129.9, 126.3, 120.0 (q, $^1J_{CF}$ = 278 Hz), 110.5, 108.9, 92.5 (q, $^3J_{CF}$ = 3.3 Hz). **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -61.5. **HRMS (MALDI-FT ICR)** m/z: $[M+H]^+$ calculated for $C_{11}H_5ClF_3N_2$: 257.0088, found: 257.0090.

2-(1-(4-bromophenyl)-2,2,2-trifluoroethylidene)malononitrile 1f



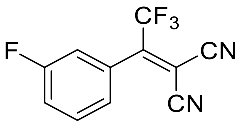
White solid, 102.4 mg, 17% yield. **m.p**. = 53.1-55.2 °C. **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 7.72 (d, 2H, J = 8.5 Hz), 7.37 (d, 2H, J = 8.5 Hz).**^{13}C NMR:** ($CDCl_3$, 150 MHz): δ 158.6 (q, $^2J_{CF}$ = 33.4 Hz), 132.8, 129.9, 128.4, 126.7, 119.9 (q, $^1J_{CF}$ = 278 Hz), 110.5, 108.9, 92.5 (q, $^3J_{CF}$ = 3.2 Hz). **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -61.5. **HRMS (MALDI-FT ICR)** m/z: $[M+H]^+$ calculated for $C_{11}H_5BrF_3N_2$: 300.9583, found: 300.9583.

2-(1-(3-bromophenyl)-2,2,2-trifluoroethylidene)malononitrile 1g



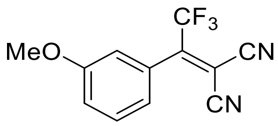
White solid, 72.3 mg, 12% yield. **m.p**. = 48.8-49.8 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.78 (d, 1H, J = 7.5 Hz), 7.62 (s, 1H), 7.48-7.44 (m, 1H), 7.43 (d, 1H, J = 7.9 Hz). **^{13}C NMR:** ($CDCl_3$, 100 MHz): δ 158.1 (q, $^2J_{CF}$ = 33.3 Hz), 136.1, 131.0, 129.7, 127.1, 123.5, 119.9 (q, $^1J_{CF}$ = 278 Hz), 110.2, 108.7, 93.4 (q, $^3J_{CF}$ = 3.3 Hz). **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -61.7. **HRMS (MALDI-FT ICR)** m/z: $[M+H]^+$ calculated for $C_{11}H_5BrF_3N_2$: 300.9583, found: 300.9583.

2-(2,2,2-trifluoro-1-(3-fluorophenyl)ethylidene)malononitrile 1h



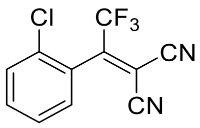
Yellow liquid, 297.8 mg, 62% yield. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.60-7.55 (m, 1H), 7.38-7.34 (m, 1H), 7.30 (d, 1H, J = 8.0 Hz), 7.21 (d, 1H, J = 8.4 Hz). **^{13}C NMR:** ($CDCl_3$, 100 MHz): δ 162.6 (d, ^1J_F = 251 Hz), 158.2 (q, $^2J_{CF}$ = 33.6 Hz), 131.5 (d, ^3J_F = 8.3 Hz), 129.7-129.6 (m), 124.5 (d, ^4J_F = 3.1 Hz), 120.3 (d, ^2J_F = 21.0 Hz), 120.0 (q, $^1J_{CF}$ = 279 Hz), 115.7 (d, ^2J_F = 24.2 Hz), 110.2, 108.7, 93.4. **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -61.7, -108.9. **HRMS (MALDI-FT ICR)** m/z: $[M+H]^+$ calculated for $C_{11}H_5F_4N_2$: 241.0383, found: 241.0408.

2-(2,2,2-trifluoro-1-(3-methoxyphenyl)ethylidene)malononitrile 1i



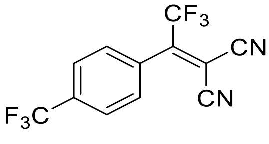
Pale yellow oil, 131.2 mg, 26% yield. **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 7.47 (t, 1H, J = 8.1 Hz), 7.16 (dd, 1H, J = 8.4 Hz, J = 2.4 Hz), 7.06 (d, 1H, J = 7.7 Hz), 6.97 (s, 1H), 3.86 (s, 3H). **^{13}C NMR:** ($CDCl_3$, 150 MHz): δ 159.9, 159.7 (q, $^2J_{CF}$ = 32.9 Hz), 130.7, 129.1, 120.6, 120.2 (q, $^1J_{CF}$ = 278 Hz), 118.9, 113.8, 110.7, 109.1, 92.3 (q, $^3J_{CF}$ = J = 3.4 Hz), 55.6. **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -61.5. **HRMS (MALDI-FT ICR)** m/z: $[M+H]^+$ calculated for $C_{12}H_8F_3N_2O$: 253.0583, found: 253.0605.

2-(1-(2-chlorophenyl)-2,2,2-trifluoroethylidene)malononitrile 1j



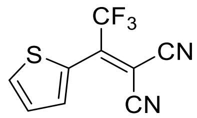
Pale yellow oil, 333.6 mg, 65% yield. **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 7.60 (d, 1H, J = 7.6 Hz), 7.58-7.55 (m, 1H), 7.49-7.46 (m, 1H), 7.31 (d, 1H, *J* = 7.7 Hz). **^{13}C NMR:** ($CDCl_3$, 150 MHz): δ 158.5 (q, $^2J_{CF}$ = 35.3 Hz), 133.5, 132.9, 130.8, 129.4, 127.7, 127.5, 119.6 (q, $^1J_{CF}$ = 277 Hz), 109.5, 108.3, 96.5 (q, $^3J_{CF}$ = 3.1 Hz). **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -62.9. **HRMS (MALDI-FT ICR)** m/z: $[M+H]^+$ calculated for $C_{11}H_5ClF_3N_2$: 257.0088, found: 257.0089.

2-(2,2,2-trifluoro-1-(4-(trifluoromethyl)phenyl)ethylidene)malononitrile 1k



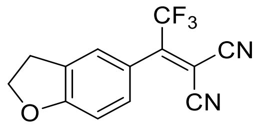
Light orange solid, 307.6 mg, 53% yield. **m.p**. = 51.0-52.1 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.85 (d, 2H, J = 8.1 Hz), 7.63 (d, 2H, J = 8.1 Hz).**^{13}C NMR:** ($CDCl_3$, 100 MHz): δ 158.3 (q, $^2J_{CF}$ = 33.9 Hz), 134.8 (q, $^2J_{CF}$ = 33.6 Hz), 131.4, 129.1, 126.6 (q, $^3J_{CF}$ = 3.6 Hz), 123.0 (q, $^1J_{CF}$ = 273 Hz), 119.9 (q, $^1J_{CF}$ = 278 Hz), 110.1, 108.6, 94.0 (q, $^3J_{CF}$ = 2.9 Hz). **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -61.7, -63.4. **HRMS (MALDI-FT ICR)** m/z: $[M]^+$ calculated for $C_{12}H_4F_6N_2$: 290.0273, found: 290.0256.

2-(2,2,2-trifluoro-1-(thiophen-3-yl)ethylidene)malononitrile 1l



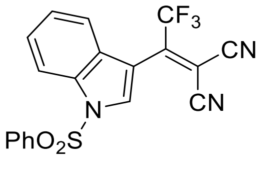
Brown oil, 105.0 mg, 23% yield. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.95-7.92 (m, 2H), 7.31 (dd, 1H, J = 5.0 Hz, 4.1 Hz).**^{13}C NMR:** ($CDCl_3$, 75 MHz): δ 158.1 (q, $^2J_{CF}$ = 32.6 Hz), 136.8, 136.7, 129.3, 129.2, 120.4 (q, $^1J_{CF}$ = 280 Hz), 112.5, 110.1, 84.4. **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -59.7. **HRMS (MALDI-FT ICR)** m/z: $[M+Na]^+$ calculated for $C_9H_3F_3N_2NaS$: 250.9861, found: 250.9873.

2-(1-(2,3-dihydrobenzofuran-5-yl)-2,2,2-trifluoroethylidene)malononitrile 1m



Yellow oil, 121.5 mg, 23% yield. **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 7.41 (s, 1H), 7.38 (d, 1H, J = 8.5 Hz), 6.92 (d, 1H, J = 8.5 Hz), 4.72 (t, 2H, J = 8.8 Hz), 3.31 (t, 2H, J = 8.8 Hz).**^{13}C NMR:** ($CDCl_3$, 150 MHz): δ 165.1, 159.5 (q, $^2J_{CF}$ = 32.6 Hz), 130.9, 129.2, 126.1, 120.6 (q, $^1J_{CF}$ = 279 Hz), 120.1, 111.9, 110.5, 109.9, 88.4 (q, $^3J_{CF}$ = 3.1 Hz), 72.6, 29.0. **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -60.5. **HRMS (MALDI-FT ICR)** m/z: $[M+Na]^+$ calculated for $C_{13}H_7F_3N_2NaO$: 287.0403, found: 287.0428.

2-(2,2,2-trifluoro-1-(1-(phenylsulfonyl)-1H-indol-3-yl)ethylidene)malononitrile 1n



Dark violet wax, 160.5 mg, 20% yield. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.18 (s, 1H), 8.03 (d, 1H, J = 8.4 Hz), 7.98 (d, 2H, J = 7.6 Hz), 7.64 (t, 1H, J = 7.3 Hz), 7.56-7.51 (m, 3H), 7.47 (t, 1H, J = 7.3 Hz), 7.40 (t, 1H, J = 7.3 Hz).**^{13}C NMR:** ($CDCl_3$, 100 MHz): δ 152.7 (q, $^2J_{CF}$ = 34.7 Hz), 136.8, 135.0, 134.7, 130.7, 129.9, 127.3, 126.7, 126.3, 124.9, 121.0, 120.3 (q, $^1J_{CF}$ = 279 Hz), 114.0, 111.4, 110.7, 109.4, 90.1.**^{19}F NMR** ($CDCl_3$, 376 MHz): δ -61.2. **HRMS (MALDI-FT ICR)** m/z: $[M+Na]^+$ calculated for $C_{19}H_{10}F_3KN_3O_2S$: 440.0077, found: 440.0079.

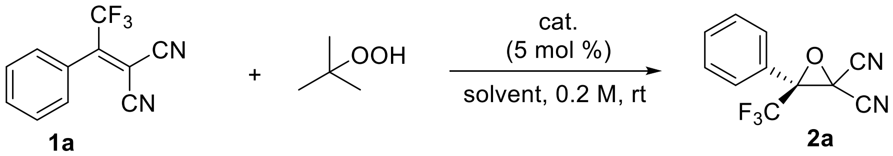
General procedure for the synthesis of racemic epoxides 2 from alkenes 1

In a sample vial containing a solution of alkene **1** (0.1 mmol), quinine (3.6 mg, 0.01 mmol, 90%) and quinidine (3.2 mg, 0.01 mmol) in anhydrous toluene (5 mL), *tert*-butyl hydroperoxide (~5.5 M in decane, 23 µL, 0.12 mmol) is added. The reaction is stirred at room temperature, monitored by TLC (eluent PE/ethyl acetate 90/10). The products **2** are isolated by flash chromatography (eluting from PE/ethyl acetate 100/0 to 95/5).

General procedure for the asymmetric synthesis of epoxides 2 from alkenes 1

In a sample vial containing a solution of alkene **1** (0.1 mmol) and (*R*,*R*)-**V** catalyst or (*S*,*S*)-**V** catalyst (2.1 mg, 0.005 mmol) in anhydrous toluene (5 mL) at -20°C, *tert*-butyl hydroperoxide (~5.5 M in decane, 23 µL, 0.12 mmol) is added. The reaction is stirred at -20°C for 13-23 hours, monitored by TLC (eluent PE/ethyl acetate 90/10). Purification of the crude reaction mixture by flash chromatography (eluting with PE/ethyl acetate 100/0 to 95/5) gives enantioenriched epoxides **2**. ATTENTION to the volatility of these compounds: carefully evaporate the solvent (40 mbar, 40°C) to concentrate the product after purification, particularly for compounds **2a, 2k, 2h** and **2l**. Compound **2j** was isolated by preparative TLC (eluent PE/ethyl acetate 80/20), separating it from the unreacted alkene.

Table S1. Solvent screening for the asymmetric epoxidation of alkenes **1a**[a]

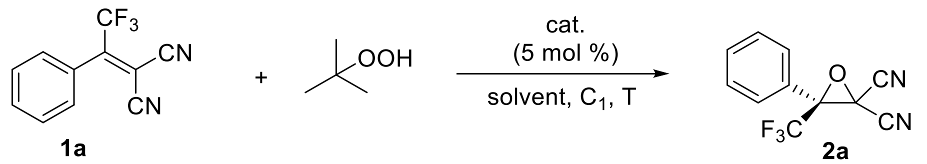


entry	solvent	t(h)	yield **2a** [%][b]	unreacted **1a** [%][b]	ee **2a** [%]
1	toluene	2	85	-	74
2[c]	toluene	16	74	-	60
3	pentane	3	91	-	58
4	hexane	3.5	95	-	60
5	methyl-*t*-butyl ether	1.5	91	-	50
6	hexafluorobenzene	2	83	-	74
7	THF	3	72	-	26
8	CH_2Cl_2	2	75	-	51
9	chlorobenzene	2	47	-	65
10	hexane/toluene 1/1	5	71	-	74

11	$CHCl_3$	6	82	-	48
12	hexane/toluene 2/1	5	89	11	71
13	dimethyl carbonate	2.5	72	-	40

[a]*Reaction conditions*: **1** (0.1 mmol), TBHP (0.12 mmol, 1.2 eq.) and (*R*,*R*)-**V** (2.1 mg, 5 mol%, 0.005 mmol) in anhydrous solvent (0.5 mL, C = 0.2 M). [b]Yield determined by ^{19}F NMR analysis on the crude mixture. [c]Cumene hydroperoxide (CHP) used as oxidant.

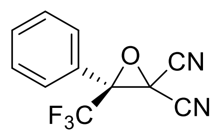
Table S2. Concentration and temperature screening for the asymmetric epoxidation of alkene **1a**[a]



entry	solvent	C_1	t(h)	T	yield **2a** [%][b]	unreacted **1a** [%][b]	ee **2a** [%]
1	hexane/toluene 2/1	0.05	5	rt	82	2	73
2[c]	toluene	0.02	16	rt	63	13	63
3	hexane/toluene 2/1	0.02	16	-25	94	3	86
4	hexane	0.02	24	-25	76	11	64
5	hexane/toluene 2/1	0.02	30	-40	61	23	81
6	toluene	0.2	3	-20	86	2	80
7	toluene	0.02	20	-20	93	-	86
8	toluene	0.02	30	-40	71	18	84
9	toluene	0.01	64	-20	87	12	84
10[d]	toluene	0.02	65	-20	83	14	81

[a]*Reaction conditions*: **1a** (0.1 mmol), TBHP (0.12 mmol, 1.2 eq.) and (*R*,*R*)-**V** (2.1 mg, 5 mol%, 0.005 mmol) in anhydrous solvent. [b]Yield determined by ^{19}F NMR analysis on the crude mixture. [c]Molecular sieves ~4 Å (100 mg) added to the reaction. [d]Reaction conducted with 3% mol of the catalyst (*R*,*R*)-**V.**

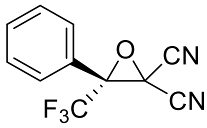
(*S*)-3-phenyl-3-(trifluoromethyl)oxirane-2,2-dicarbonitrile 2a



Colourless liquid, 22.1 mg, 93% yield. $[\alpha]_D^{23}$ = -1.7 (*c* = 0.51, $CHCl_3$), 86% ee. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.61-7.59 (m, 1H), 7.56 (s, 4H). **^{13}C NMR:** ($CDCl_3$, 100 MHz): δ 132.3, 129.5, 127.3, 124.1, 120.3 (q, $^1J_{CF}$ = 281 Hz), 108.7, 108.3, 69.4 (q, $^2J_{CF}$ = 38.9 Hz), 42.7. **^{19}F NMR** ($CDCl_3$, 376

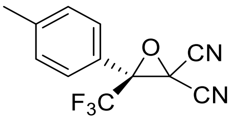
MHz): δ -69.1. Elemental analysis calcd (%) for $C_{11}H_5F_3N_2O$: C, 55.47; H, 2.12; N, 11.76; found C, 55.73; H, 2.19; N, 11.66. HPLC (OD-H, 2-propanol/n-hexane = 2/98, flow rate = 1 mL/min, λ = 220 nm) major enantiomer t_R = 5.6 min, minor enantiomer t_R = 10.2 min.

(*R*)-3-phenyl-3-(trifluoromethyl)oxirane-2,2-dicarbonitrile 2a



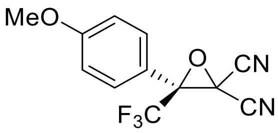
Colourless liquid, 23.1 mg, 97% yield. $[\alpha]_D^{23}$ = +1.7 (*c* = 0.15, $CHCl_3$), 86% ee. HPLC (OD-H, 2-propanol/n-hexane = 2/98, flow rate = 1 mL/min, λ = 220 nm) major enantiomer t_R = 11.2 min, minor enantiomer t_R = 5.9 min.

(*S*)-3-(*p*-tolyl)-3-(trifluoromethyl)oxirane-2,2-dicarbonitrile 2b



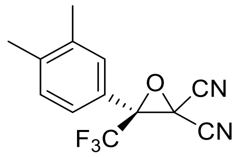
Yellow oil, 23.4 mg, 93% yield. $[\alpha]_D^{23}$ = -7.3 (*c* = 0.70, $CHCl_3$), 82% ee. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.44 (d, 2H, J = 8.7 Hz), 7.34 (d, 2H, J = 8.7 Hz), 2.43 (s, 3H).**^{13}C NMR:** ($CDCl_3$, 100 MHz): δ 142.9, 130.2, 127.1, 124.6, 121.1, 120.4 (q, $^1J_{CF}$ = 282 Hz), 108.8, 108.3, 69.5 (q, $^2J_{CF}$ = 38.9 Hz), 42.8, 21.5. **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -69.2. Elemental analysis calcd (%) for $C_{12}H_7F_3N_2O$: C, 57.15; H, 2.80; N, 11.11; found C, 57.43; H, 2.74; N, 11.01. HPLC (AD-H, 2-propanol/n-hexane = 2/98, flow rate = 1 mL/min, λ = 230 nm) major enantiomer t_R = 4.5 min, minor enantiomer t_R = 4.1 min.

(*S*)-3-(4-methoxyphenyl)-3-(trifluoromethyl)oxirane-2,2-dicarbonitrile 2c



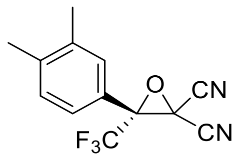
Yellow oil, 24.4 mg, 91% yield. $[\alpha]_D^{23}$ = -5.7 (*c* = 0.50, $CHCl_3$), 89% ee. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.48 (d, 2H, J = 8.8 Hz), 7.02 (d, 2H, J = 8.8 Hz), 3.86 (s, 3H).**^{13}C NMR:** ($CDCl_3$, 75 MHz): δ 162.4, 128.9, 120.4 (q, $^1J_{CF}$ = 281 Hz), 115.6, 115.0, 108.9, 108.4, 69.6 (q, $^2J_{CF}$ = 41.9 Hz), 55.5, 42.9. **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -69.3. Elemental analysis calcd (%) for $C_{12}H_7F_3N_2O_2$: C, 53.74; H, 2.63; N, 10.45; found C, 53.93; H, 2.58; N, 10.37. HPLC (OD-H, 2-propanol/n-hexane = 2/98, flow rate = 1 mL/min, λ = 255 nm) major enantiomer t_R = 6.2 min, minor enantiomer t_R = 7.3 min.

(*S*)-3-(3,4-dimethylphenyl)-3-(trifluoromethyl)oxirane-2,2-dicarbonitrile 2d



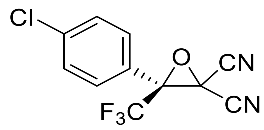
Light brown oil, 24.8 mg, 94% yield. $[\alpha]_D^{23}$ = -11.6 (*c* = 0.14, $CHCl_3$), 87% ee. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 7.28 (m, 3H), 2.33 (m, 6H). **^{13}C NMR:** ($CDCl_3$, 75 MHz): δ 141.6, 138.3, 130.6, 128.0, 124.6, 121.3, 120.4 (q, $^1J_{CF}$ = 282 Hz), 108.9, 108.4, 69.5 (q, $^2J_{CF}$ = 39.1 Hz), 42.7, 19.85 (2C). **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -69.2. Elemental analysis calcd (%) for $C_{13}H_9F_3N_2O$: C, 58.65; H, 3.41; N, 10.52; found C, 58.96; H, 3.49; N, 10.33. HPLC (AD-H, 2-propanol/n-hexane = 2/98, flow rate = 1 mL/min, λ = 220 nm) major enantiomer t_R = 4.1 min, minor enantiomer t_R = 3.7 min.

(*R*)-3-(3,4-dimethylphenyl)-3-(trifluoromethyl)oxirane-2,2-dicarbonitrile 2d



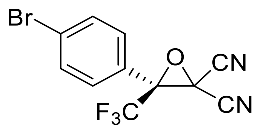
Light brown oil, 26.1 mg, 98% yield. $[\alpha]_D^{21}$ = +2.8 (*c* = 0.75, $CHCl_3$), 85% ee. HPLC (AD-H, 2-propanol/n-hexane = 2/98, flow rate = 1 mL/min, λ = 220 nm) major enantiomer t_R = 3.6 min, minor enantiomer t_R = 4.1 min.

(*S*)-3-(4-chlorophenyl)-3-(trifluoromethyl)oxirane-2,2-dicarbonitrile 2e



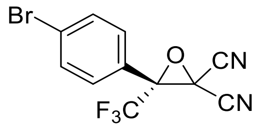
White wax, 24.0 mg, 88% yield. $[\alpha]_D^{24}$ = -9.3 (*c* = 0.74, $CHCl_3$), 83% ee. **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 7.54 (d, 2H, J = 8.8 Hz), 7.51 (d, 2H, J = 8.8 Hz). **^{13}C NMR:** ($CDCl_3$, 150 MHz): δ 139.0, 130.0, 128.7, 122.5, 120.2 (q, $^1J_{CF}$ = 282 Hz), 108.5, 108.0, 69.0 (q, $^2J_{CF}$ = 39.0 Hz), 42.7.**^{19}F NMR** ($CDCl_3$, 564 MHz): δ -69.1. Elemental analysis calcd (%) for $C_{11}H_5F_3ClN_2O$: C, 48.46; H, 1.48; N, 10.28; found C, 48.75; H, 1.55; N, 10.17. HPLC (OD-H, 2-propanol/n-hexane = 2/98, flow rate = 1 mL/min, λ = 220 nm) major enantiomer t_R = 6.6 min, minor enantiomer t_R = 10.4 min.

(*S*)-3-(4-bromophenyl)-3-(trifluoromethyl)oxirane-2,2-dicarbonitrile 2f



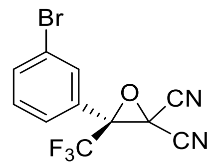
White wax, 27.3 mg, 86% yield. $[\alpha]_D^{23}$ = -14.7 (*c* = 0.96, $CHCl_3$), 89% ee. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.71 (d, 2H, J = 8.1 Hz), 7.44 (d, 2H, J = 8.1 Hz). **^{13}C NMR:** ($CDCl_3$, 100 MHz): δ 133.0, 128.8, 127.4, 123.1, 120.1 (q, $^1J_{CF}$ = 282 Hz), 108.6, 108.0, 69.1 (q, $^2J_{CF}$ = 39.3 Hz), 42.8. **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -69.0. Elemental analysis calcd (%) for $C_{11}H_5F_3BrN_2O$: C, 41.67; H, 1.27; N, 8.84; found C, 41.44; H, 1.18; N, 8.91. HPLC (OD-H, 2-propanol/n-hexane = 2/98, flow rate = 1 mL/min, λ = 230 nm) major enantiomer t_R = 6.8 min, minor enantiomer t_R = 9.8 min.

(*R*)-3-(4-bromophenyl)-3-(trifluoromethyl)oxirane-2,2-dicarbonitrile 2f



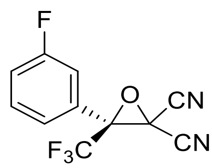
White wax, 27.2 mg, 86% yield. $[\alpha]_D^{20}$ = +14.2 (*c* = 0.72, $CHCl_3$), 87% ee. HPLC (OD-H, 2-propanol/n-hexane = 2/98, flow rate = 1 mL/min, λ = 230 nm) major enantiomer t_R = 9.3 min, minor enantiomer t_R = 6.8 min.

(*S*)-3-(3-bromophenyl)-3-(trifluoromethyl)oxirane-2,2-dicarbonitrile 2g



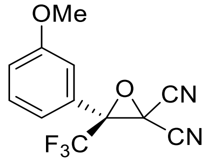
Yellow oil, 25,4 mg, 80% yield. $[\alpha]_D^{24}$ = -12.0 (*c* = 0.49, $CHCl_3$), 78% ee. **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 7.76 (dd, 1H, J = 7.8, 0.6 Hz), 7.71 (s, 1H), 7.52 (d, 1H, J = 7.9 Hz), 7.45-7.42 (m, 1H). **^{13}C NMR:** ($CDCl_3$, 150 MHz): δ 135.7, 131.1, 130.3, 126.1, 125.9, 123.6, 120.1 (q, $^1J_{CF}$ = 282 Hz), 108.4, 107.9, 68.6 (q, $^2J_{CF}$ 39.4 Hz), 42.6. **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -69.0. Elemental analysis calcd (%) for $C_{11}H_5F_3BrN_2O$: C, 41.67; H, 1.27; N, 8.84; found C, 41.43; H, 1.15; N, 8.93. HPLC (AD-H, 2-propanol/n-hexane = 2/98, flow rate = 1 mL/min, λ = 210 nm) major enantiomer t_R = 5.6 min, minor enantiomer t_R = 4.7 min.

(*S*)-3-(3-fluorophenyl)-3-(trifluoromethyl)oxirane-2,2-dicarbonitrile 2h



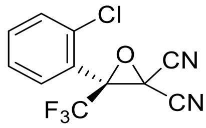
Colourless liquid, 15.1 mg, 59% yield. $[\alpha]_D^{24}$ = -2.4 (*c* = 0.63, $CHCl_3$), 78% ee. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.59-7.53 (m, 1H), 7.38-7.28 (m, 3H). **^{13}C NMR:** ($CDCl_3$, 100 MHz): δ 162.8 (d, ^1J_F = 251 Hz), 131.7 (d, ^3J_F = 8.2 Hz), 126.2 (d, ^3J_F = 7.6 Hz), 123.1, 120.1 (q, $^1J_{CF}$ = 282 Hz), 119.8 (d, ^2J_F = 30.0 Hz), 114.8 (d, ^2J_F = 24.6 Hz), 108.4, 107.9, 68.8 (q, $^2J_{CF}$ = 41.4 Hz), 42.7. **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -69.0, -108.7 Elemental analysis calcd (%) for $C_{11}H_5F_4N_2O$: C, 51.58; H, 1.57; N, 10.94; found C, 51.87; H, 1.45; N, 10.81. HPLC (OD-H, 2-propanol/n-hexane = 2/98, flow rate = 1 mL/min, λ = 228 nm) major enantiomer t_R = 6.2 min, minor enantiomer t_R = 10.7 min.

(*S*)-3-(3-methoxyphenyl)-3-(trifluoromethyl)oxirane-2,2-dicarbonitrile 2i



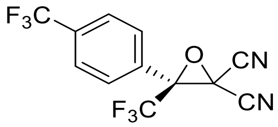
Light brown oil, 24.9 mg, 93% yield. $[\alpha]_D^{23}$ = -12.7 (c = 0.70, $CHCl_3$), 76% ee. **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 7.47-7.44 (m, 1H), 7.14 (d, 1H, J = 7.7 Hz), 7.12(dd, 1H, J = 8.4 Hz, 2.2 Hz), 7.04 (s, 1H), 3.86 (s, 3H).**^{13}C NMR:** ($CDCl_3$, 150 MHz): δ 160.1, 130.8, 125.3, 120.3 (q, $^1J_{CF}$ = 282 Hz), 119.4, 117.8, 112.8, 108.7, 108.2, 69.3 (q, $^2J_{CF}$ = 39.0 Hz), 55.5, 42.6.**^{19}F NMR** ($CDCl_3$, 376 MHz): δ -69.1. Elemental analysis calcd (%) for $C_{12}H_7F_3N_2O_2$: C, 53.74; H, 2.63; N, 10.45; found C, 53.99; H, 2.54; N, 10.59. HPLC (OD-H, 2-propanol/n-hexane = 2/98, flow rate = 1 mL/min, λ = 210 nm) major enantiomer t_R = 6.4 min, minor enantiomer t_R = 8.5 min.

(*S*)-3-(2-chlorophenyl)-3-(trifluoromethyl)oxirane-2,2-dicarbonitrile 2j



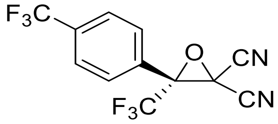
Colourless oil, 13.1 mg, 48% yield. $[\alpha]_D^{26}$ = +4.4 (c = 1.29, $CHCl_3$), 77% ee. **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 7.58-7.56 (m, 2H), 7.52 (d, 1H, J = 7.6 Hz), 7.48-7.45 (m, 1H). **^{13}C NMR:** ($CDCl_3$, 150 MHz): δ 133.9, 133.6, 130.9, 130.6, 127.9, 124.1, 120.0 (q, $^1J_{CF}$ = 282 Hz), 108.9, 108.1, 68.1 (q, $^2J_{CF}$ 39.2 Hz), 43.8. **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -69.8. Elemental analysis calcd (%) for $C_{11}H_5F_3ClN_2O$: C, 48.46; H, 1.48; N, 10.28; found C, 48.75; H, 1.41; N, 10.17. HPLC (AD-H, 2-propanol/n-hexane = 2/98, flow rate = 1 mL/min, λ = 220 nm) major enantiomer t_R = 4.6 min, minor enantiomer t_R = 4.3 min.

(*S*)-3-(trifluoromethyl)-3-(4-(trifluoromethyl)phenyl)oxirane-2,2-dicarbonitrile 2k



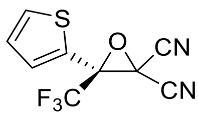
Light brown wax, 26.3 mg, 86% yield. $[\alpha]_D^{25}$ = -4.0 (c = 0.90, $CHCl_3$), 84% ee. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.84 (d, 2H, J = 8.1 Hz), 7.73 (d, 2H, J = 8.1 Hz).**^{13}C NMR:** ($CDCl_3$, 75 MHz): δ 134.5 (q, $^2J_{CF}$ = 33.2 Hz), 128.0, 127.9, 126.7 (q, $^3J_{CF}$ = 3.7 Hz), 123.1 (q, $^1J_{CF}$ = 273 Hz), 120.1 (q, $^1J_{CF}$ = 282 Hz), 108.3, 107.7, 68.8 (q, $^2J_{CF}$ = 39.5 Hz), 42.6.**^{19}F NMR** ($CDCl_3$, 376 MHz): δ -63.3, -68.9. Elemental analysis calcd (%) for $C_{12}H_4F_6N_2O$: C, 47.08; H, 1.32; N, 9.15; found C, 46.87; H, 1.24; N, 9.30. HPLC (OD-H, 2-propanol/n-hexane = 2/98, flow rate = 1 mL/min, λ = 220 nm) major enantiomer t_R = 6.7 min, minor enantiomer t_R = 7.3 min.

(*R*)-3-(trifluoromethyl)-3-(4-(trifluoromethyl)phenyl)oxirane-2,2-dicarbonitrile 2k



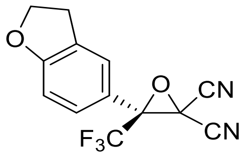
Light brown wax, 23.9 mg, 78% yield. $[\alpha]_D^{21}$ = +5.0 (*c* = 0.76, $CHCl_3$), 86% ee. HPLC (OD-H, 2-propanol/n-hexane = 2/98, flow rate = 1 mL/min, λ = 220 nm) major enantiomer t_R = 7.6 min, minor enantiomer t_R = 6.9 min.

(*S*)-3-(thiophen-3-yl)-3-(trifluoromethyl)oxirane-2,2-dicarbonitrile 2l



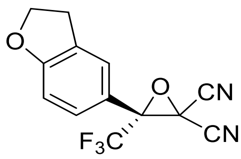
Yellow oil, 15.1 mg, 62% yield. $[\alpha]_D^{24}$ = -10.2 (*c* = 0.53, $CHCl_3$), 84% ee. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.62 (d, 1H, J = 4.8 Hz), 7.48 (d, 1H, J = 3.2 Hz), 7.19 (t, 1H, J = 4.4 Hz).**^{13}C NMR:** ($CDCl_3$, 100 MHz): δ 131.5, 130.8, 128.1, 124.7, 119.9 (q, $^1J_{CF}$ = 282 Hz), 108.6, 107.9, 67.7 (q, $^2J_{CF}$ = 40.8 Hz), 44.3. **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -69.9. Elemental analysis calcd (%) for $C_9H_3F_3N_2OS$: C, 44.27; H, 1.24; N, 11.47; S, 13.13; found C, 44.01; H, 1.13; N, 11.59, S, 12.99. HPLC (OD-H, 2-propanol/n-hexane = 2/98, flow rate = 1 mL/min, λ = 240 nm) major enantiomer t_R = 6.5 min, minor enantiomer t_R = 11.5 min.

(*S*)-3-(2,3-dihydrobenzofuran-5-yl)-3-(trifluoromethyl)oxirane-2,2-dicarbonitrile 2m



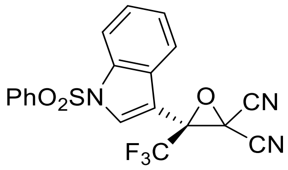
Yellow oil, 24.9 mg, 89% yield. $[\alpha]_D^{24}$ = -0.65 (*c* = 0.81, $CHCl_3$), 86% ee. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.35 (s, 1H), 7.30 (d, 1H, J = 8.3 Hz), 6.88 (d, 1H, J = 8.3 Hz), 4.67 (t, 2H, J = 8.8 Hz), 3.28 (t, 2H, J = 8.8 Hz).**^{13}C NMR:** ($CDCl_3$, 62.5 MHz): δ 163.3, 128.9, 128.1, 124.0, 120.4 (q, $^1J_{CF}$ = 281 Hz), 115.4, 110.3, 109.0, 108.4, 72.0, 69.7 (q, $^2J_{CF}$ = 37.8 Hz), 42.9, 29.2. **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -69.4. Elemental analysis calcd (%) for $C_{13}H_7F_3N_2O_2$: C, 55.72; H, 2.52; N, 10.00; found C, 55.52; H, 2.66; N, 10.21. HPLC (OD-H, 2-propanol/n-hexane = 2/98, flow rate = 1 mL/min, λ = 255 nm) major enantiomer t_R = 7.0 min, minor enantiomer t_R = 7.7 min.

(*R*)-3-(2,3-dihydrobenzofuran-5-yl)-3-(trifluoromethyl)oxirane-2,2-dicarbonitrile 2m



Yellow oil, 25.8 mg, 92% yield. $[\alpha]_D^{26}$ = +0.62 (*c* = 0.83, $CHCl_3$), 89% ee. HPLC (OD-H, 2-propanol/n-hexane = 2/98, flow rate = 1 mL/min, λ = 255 nm) major enantiomer t_R = 8.2 min, minor enantiomer t_R = 7.4 min.

(*S*)-3-(1-(phenylsulfonyl)-1H-indol-3-yl)-3-(trifluoromethyl)oxirane-2,2-dicarbonitrile 2n

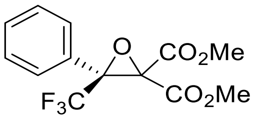


White solid, 17.5 mg, 47% yield. $[\alpha]_D^{24}$ = -1.5 (*c* = 0.74, $CHCl_3$), 49% ee. **m.p**. = 62.1-63.3 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz): *δ* 8.01 (m, 2H), 7.88 (d, 2H, J = 8.1 Hz), 7.64 (d, 1H, J = 8.0 Hz), 7.60-7.57 (m, 1H), 7.49-7.42 (m, 3H), 7.36 (t, 1H, J = 7.6 Hz). **^{13}C NMR:** ($CDCl_3$, 150 MHz): *δ* 137.1, 134.7, 129.9, 129.7, 128.8, 127.3, 127.0, 126.5, 124.8, 120.1 (q, $^1J_{CF}$ = 282 Hz), 119.9, 114.0, 108.8, 108.0, 66.5 (q, $^2J_{CF}$ = 41.4 Hz), 42.6. **^{19}F NMR** ($CDCl_3$, 376 MHz): *δ* -69.9. Elemental analysis calcd (%) for $C_{19}H_{10}F_3N_3O_3S$: C, 54.68; H, 2.42; N, 10.07; S, 7.68. found C, 54.49; H, 2.55; N, 10.29, S, 7.53. HPLC (OD-H, 2-propanol/n-hexane = 2/98, flow rate = 1 mL/min, λ = 260 nm) major enantiomer t_R = 15.9 min, minor enantiomer t_R = 14.6 min.

One-pot synthesis of compounds 3 from 2

The synthesis of compounds **3** was performed under a slightly modified procedure from the literature.[8] In a sample vial, a solution of enantiomerically enriched epoxide **2** (238 mg, 1 mmol, 85% ee for diester **3a**; 158 mg, 0.5 mmol, 84% ee for diester **3b**) in MeOH (1.8 mL; 0.9 mL for diester **3b**) is prepared. Then MeONa (46 μL, 0.2 mmol, 25% wt in MeOH for diester **3a**; 23 μL, 0.1 mmol, 25% wt in MeOH for diester **3b**) is added at room temperature and stirred until the disappearance of **2** (2 h), monitored by TLC (eluent PE/ ethyl acetate 8/2). Then, aqueous HCl (5 mL, 1M for diester **3a**; 2.5 mL, 2M for diester **3b**) is added to the reaction solution at 0 °C and stirred for 3-4h. After completion, the mixture is diluted with ethyl acetate (50 mL) and washed with water (2x30 mL), dried over anhydrous Na_2SO_4 and concentrated under vacuum. The reaction mixture is purified by flash chromatography (eluent: n-hexane/ethyl acetate 100/0 to 80/20) to give the final products **3** in 72-84% yield and 78-82% ee. A final enantioenrichment of compound **3a** up to 98% ee was obtained after crystallization in a mixture of n-hexane/ethyl acetate 8/2.

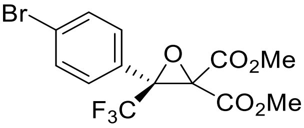
Dimethyl (*S*)-3-phenyl-3-(trifluoromethyl)oxirane-2,2-dicarboxylate 3a



[8] a) Hurtaud, D.; Baudy-Floc'h, M.; Le Grel, P. *Tetrahedron Lett.*, **1999**, *40*, 5001-5004; b) Nanjo, K.; Suzuki, K.; Sekiya, M. *Chem. Pharm. Bull.,* **1981**, *29*, 336-343.

White solid, 219.0 mg, 72% yield. $[\alpha]_D^{26}$ = -46.8 (c = 0.69, $CHCl_3$), 82% ee. **m.p**. = 78.2-79.8 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.53-7.51 (m, 2H), 7.44 -7.39 (m, 3H), 3.93 (s, 3H), 3.48 (s, 3H). **^{13}C NMR:** ($CDCl_3$, 150 MHz): δ 162.4, 162.2, 130.3, 128.4, 127.9, 127.1, 121.7 (q, $^1J_{CF}$ = 280 Hz), 65.9 (q, $^2J_{CF}$ = 37.6 Hz), 64.4, 53.6, 53.4. **^{19}F NMR** ($CDCl_3$, 564 MHz): δ -71.7. **HRMS (MALDI-FT ICR)** m/z: $[M+Na]^+$ calculated for $C_{13}H_{11}F_3NaO_5$: 327.0451, found: 327.0499. HPLC (IE-3, 2-propanol/n-hexane = 10/90, flow rate = 0.6 mL/min, λ = 210 nm) major enantiomer t_R = 10.7 min, minor enantiomer t_R = 11.4 min.

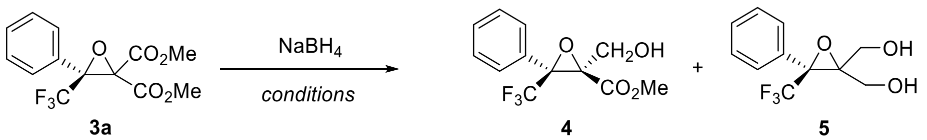
Dimethyl (*S*)-3-(4-bromophenyl)-3-(trifluoromethyl)oxirane-2,2-dicarboxylate 3b



Yellow wax, 173.8 mg, 84% yield. $[\alpha]_D^{25}$ = -48.1 (c = 0.86, $CHCl_3$), 78% ee. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.55 (d, 2H, J = 7.8 Hz), 7.36 (d, 2H, J = 7.8 Hz), 3.92 (s, 3H), 3.54 (s, 3H). **^{13}C NMR:** ($CDCl_3$, 100 MHz): δ 162.1, 160.9, 131.8, 129.5, 126.1, 125.0, 121.5 (q, $^1J_{CF}$ = 280 Hz), 108.9, 108.4, 65.6 (q, $^2J_{CF}$ = 37.8 Hz), 64.3, 53.7, 53.6. **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -71.6. **HRMS (MALDI-FT ICR)** m/z: $[M+K]^+$ calculated for $C_{13}H_{10}BrF_3O_5$: 420.9295, found: 420.9338. HPLC (IE-3, 2-propanol/n-hexane = 10/90, flow rate = 0.6 mL/min, λ = 235 nm) major enantiomer t_R = 10.0 min, minor enantiomer t_R = 9.4 min.

Reduction of the diester 3a into the alcohol 4 and the diol 5

Table S3. Reaction conditions for the reduction of the diester **3a** into the products **4** and **5**[a]



entry	$NaBH_4$ (eq.)	solvent	C_0 [M]	t (h)	T (ºC)	yield **4**[b] [%]	yield **5**[b] [%]
1	1.20[c]	MeOH	0.1	4.5	0	46 (48)	(20)
2	2.25[c]	MeOH	0.1	5.5	0	59	n.d.[d]
3[e]	3.70[c]	MeOH	0.2	4.5	rt	(14)	74 (78)
4	2.00[c]	THF/MeOH 4:1	0.1	4.5	0	(14)	83 (78)

[a] *Conditions*: To a solution of **3a** (0.15 mmol) in the indicated solvent or solvent mixture, at the corresponding temperature, sodium borohydride (1.2–3.7 equiv) is added. [b]Yields provided after isolation by column chromatography. Between brackets, yields determined by ^{1}H-NMR from the crude using tetrachloroethane as internal standard. [c]The total amount of reducing agent is sequentially added in three portions during the reaction time. [d]Not determined. [e]Sodium methoxide (10 mol%) was added.

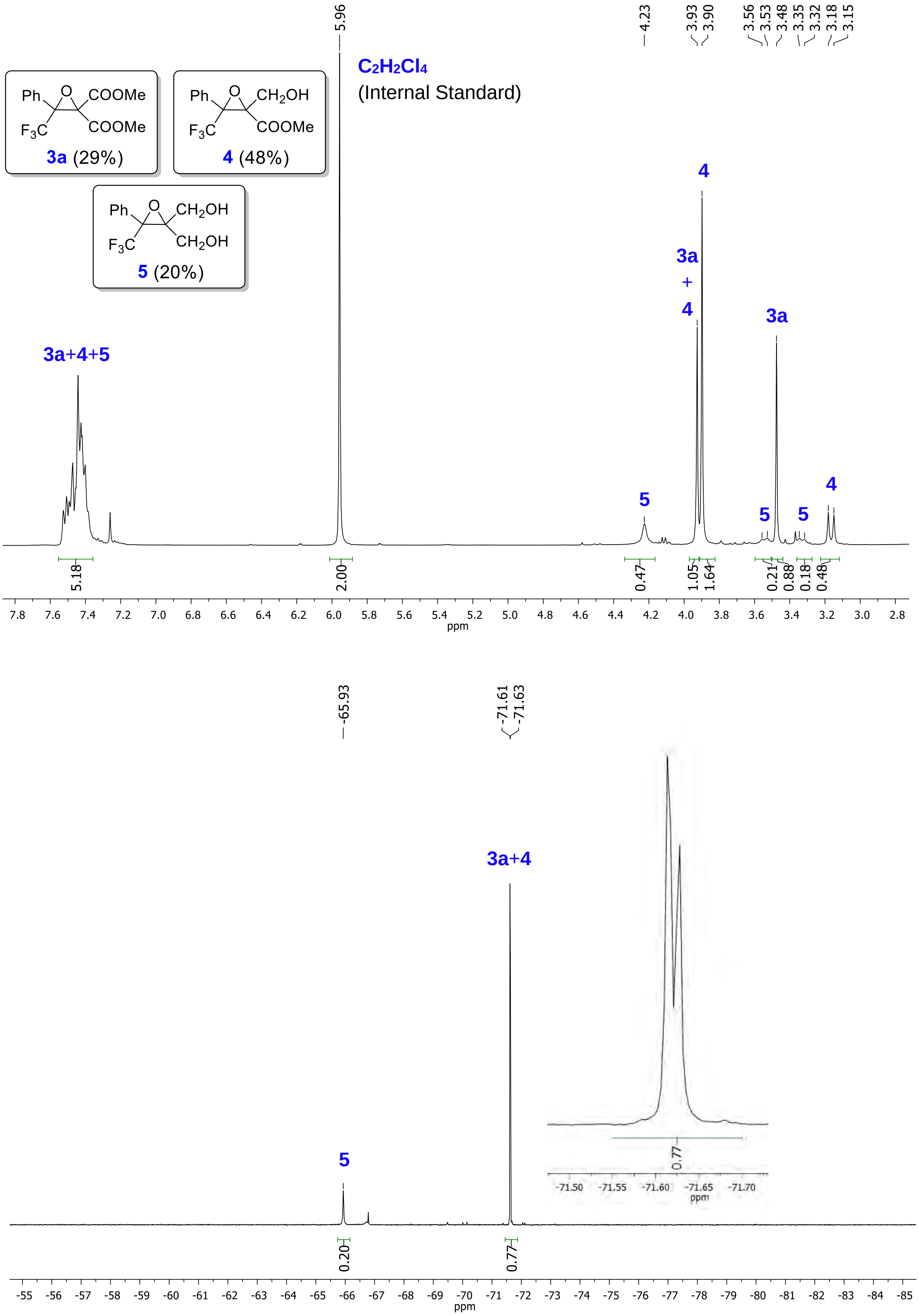
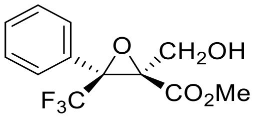


Figure S1. ^{1}H-NMR and ^{19}F-NMR spectra ($CDCl_3$, 400 MHz) of the crude in the reduction of the diester **3a** in presence of 1.2 eq. of sodium borohydride, in methanol as solvent and at 0ºC. 1,1,2,2-Tetrachloroethane is used as internal standard (0.15 mmol, 1.0 equiv). Under these conditions, only one diastereoisomer of the alcohol **4** is observed. Partial overreduction of the alcohol **4** to give the diol **5** is observed.

The synthesis of compound **4** was performed under a slightly modified procedure from the literature.[9] Enantiomerically enriched diester **3a** (45.6 mg, 0.15 mmol, 82% ee) is dissolved in anhydrous MeOH (1.5 mL) in a dried round-bottom flask and the solution cooled at 0°C. After 10 min, $NaBH_4$ is added in three portions (13.0 mg, 0.34 mmol) waiting 2 hours between two subsequent additions. The reaction mixture is left under stirring for overall 5.5 hours (TLC eluent, PE/ ethyl acetate 6:4). After completion the reaction is quenched with brine (10 mL) and extracted with ethyl acetate (3 x 10 mL). The combined organic layer is washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The reaction mixture is purified by flash chromatography (eluent: n-hexane/ethyl acetate 100/0 to 80/20) to give the final product **4** in 59% yield and 83% ee.

The synthesis of compound **5** was performed under a slightly modified procedure from the literature.[2] Enantiomerically enriched diester **3a** (30.4 mg, 0.1 mmol, 82% ee) is dissolved in a mixture of THF/MeOH 4/1 (1.0 mL) in a dried round-bottomed flask and the solution is cooled at 0°C. After 10 min, $NaBH_4$ is added in three portions (8.0 mg, 0.2 mmol) waiting 1.5 hours between two subsequent additions and the reaction mixture is left under stirring for overall 4.5 hours at 0 °C (TLC eluent, PE/ ethyl acetate 6:4). After completion the reaction is quenched with saturated aqueous disodium tartrate solution (20 mL) and extracted with chloroform (3 x 20 mL) and ethyl acetate (3 x 20 mL). The combined organic layer is dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The reaction mixture is purified by flash chromatography (eluent: PE/ethyl acetate 4/1 to 3/2) to give the final product **5** in 83% yield and 82% ee.

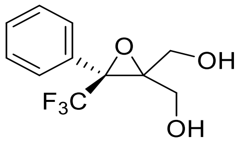
Methyl (*2R,3S*)-2-(hydroxymethyl)-3-phenyl-3-(trifluoromethyl)oxirane-2-carboxylate 4



White solid, 24.4 mg, 59% yield. $[\alpha]_D^{26}$ = -0.62 (*c* = 0.83, $CHCl_3$), 83% ee. **m.p.** = 54.2-56.0 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.49-7.42 (m, 5H), 3.92 (d, 1H, J = 12.3 Hz), 3.90 (s, 3H), 3.17 (d, 1H, J = 12.3 Hz), 2.08 (bs, 1H).**^{13}C NMR:** ($CDCl_3$, 150 MHz): δ 166.1, 130.1, 128.8, 128.4, 127.7, 122.4 (q, $^1J_{CF}$ = 280 Hz), 66.9, 65.6 (q, $^2J_{CF}$ = 36.9 Hz), 63.5, 53.1. **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -71.6. **HRMS (MALDI-FT ICR)** m/z: $[M+Na]^+$ calculated for $C_{12}H_{11}F_3NaO_4$: 299.0502, found: 299.0523. HPLC (AD-H, 2-propanol/n-hexane = 2/98, flow rate = 1 mL/min, λ = 210 nm) major enantiomer t_R =22.7 min, minor enantiomer t_R = 24.4 min.

[9] Meninno, S.; Zullo, L.; Overgaard, J.; Lattanzi, A. *Adv. Synth. Catal.*, **2017**, *359*, 913-918.

(*S*)-(3-phenyl-3-(trifluoromethyl)oxirane-2,2-diyl)dimethanol 5

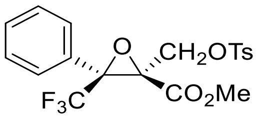


White solid, 20.6 mg, 83% yield. $[\alpha]_D^{25}$ = +12.6 (*c* = 0.76, $CHCl_3$), 82% ee. **m.p.** = 80.5-81.9 °C. **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 7.46-7.40 (m, 5H), 4.24 (d, 2H, J = 5.0 Hz), 3.57 (dd, 1H, J = 12.0 Hz, J = 4.5 Hz), 3.34 (dd, 1H, J = 12.0 Hz, J = 4.5 Hz), 2.37 (t, 1H, J = 5.7 Hz), 2.06 (t, 1H, J = 5.7 Hz).**^{13}C NMR:** ($CDCl_3$, 150 MHz): δ 130.6, 129.5, 128.9, 128.4, 127.7, 126.9, 123.5 (q, $^1J_{CF}$ = 280 Hz), 67.3, 66.9 (q, $^2J_{CF}$ = 36.1 Hz), 62.4, 60.7 (q, $^3J_{CF}$ = 3.7 Hz). **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -65.9. **HRMS (MALDI-FT ICR)** m/z: $[M+H]^+$ calculated for $C_{11}H_{12}F_3O_3$: 249.0733, found: 249.0755. HPLC (AD-H, 2-propanol/n-hexane = 5/95, flow rate = 1 mL/min, λ = 210 nm) major enantiomer t_R = 13.5 min, minor enantiomer t_R = 14.3 min.

Tosylation of product 4 into product 6

The synthesis of compound **6** was performed according to the literature.[10] To a solution of enantioenriched **4** (27.6 mg, 0.1 mmol, 83% ee) in anhydrous Et_2O (0.5 mL) at 0 ºC, *p*-toluensulfonic chloride (0.15 mmol, 28.6 mg) is added. Then, sodium hydroxide (40.0 mg, 1.0 mmol) is added in three portions in a period of 30 min. After this time, the reaction is stirred at 0 ºC for 1 hour. Then, the cooling bath is removed and the reaction is stirred at room temperature for 2 h. (TLC eluent, PE/ethyl acetate 9/1). After completion, the reaction is quenched with distilled water (20 mL) and extracted with dichloromethane (3 x 20 mL). The combined organic layer is washed with brine (2 x 30 mL), dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure to give the final product **6** in 96% yield and 84% ee.

Methyl (2*R*,3*S*)-3-phenyl-2-((tosyloxy)methyl)-3-(trifluoromethyl)oxirane-2-carboxylate 6



White solid, 41.3 mg, 96% yield. $[\alpha]_D^{24}$ = +8.0 (*c* = 0.73, $CHCl_3$), 84% ee. **m.p.** = 94.3-95.7 °C. **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 7.66 (d, 2H, J = 8.2 Hz), 7.46 (t, 1H, J = 7.5 Hz), 7.42-7.38 (m, 4H), 7.32 (d, 2H, J = 8.1 Hz), 4.38 (d, 1H, J = 11.7 Hz), 3.81 (s, 3H), 3.46 (d, 1H, J = 11.7 Hz), 2.45 (s, 3H).**^{13}C NMR:** ($CDCl_3$, 150 MHz): δ 164.1, 145.4, 132.0, 130.5, 130.0, 129.9, 129.0, 128.0, 127.4, 121.9 (q, $^1J_{CF}$ = 280 Hz), 68.6, 65.4 (q, $^2J_{CF}$ = 37.5 Hz), 53.3, 21.7. **^{19}F NMR** ($CDCl_3$, 564 MHz): δ -71.3. **HRMS (MALDI-FT ICR)** m/z: $[M+Na]^+$ calculated for $C_{19}H_{17}F_3NaO_6S$: 453.0590, found:

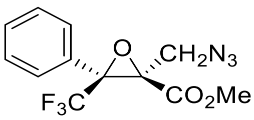
[10] Padín, D.; Cambeiro, F.; Fañanás-Mastral, M.; Varela, J. A.; Saá, C. *ACS Catal.,* **2017**, *7*, 992-996.

453.0610. HPLC (AD-H, 2-propanol/n-hexane = 2/98, flow rate = 1 mL/min, λ = 230 nm) major enantiomer t_R =30.0 min, minor enantiomer t_R = 40.4 min.

Synthesis of azide 7 from compound 6

To a solution of **6** (21.5 mg, 0.05 mmol, 84% ee) in anhydrous dimethylformamide (0.5 mL) in a reaction tube, sodium azide is added (4.2 mg, 0.065 mmol). After the addition, the reaction tube is filled with nitrogen and sealed. The tube is placed in a heating bath at 50 ºC, and the reaction is stirred for 19 hours. After completion (TLC eluent, PE/ethyl acetate 9/1), the reaction was dissolved in $CHCl_3$ (30 mL) and washed with brine (3 x 30 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The reaction mixture was purified by flash chromatography (eluent: PE/ethyl acetate 95/5) to give the final product **7** in 57% yield and 82% ee.

Methyl (*2R,3S*)-2-(azidomethyl)-3-phenyl-3-(trifluoromethyl)oxirane-2-carboxylate 7



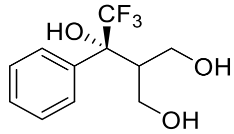
Colorless oil, 8.6 mg, 57% yield. $[\alpha]_D^{26}$ = +20.9 (*c* = 0.39, $CHCl_3$), 82% ee. **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 7.50-7.46 (m, 5H), 3.93 (s, 3H), 3.58 (d, 1H, J = 13.7 Hz), 2.88 (d, 1H, J = 13.7 Hz).**^{13}C NMR:** ($CDCl_3$, 150 MHz): δ 165.4, 130.4, 129.0, 128.0, 127.7, 122.2 (q, $^1J_{CF}$ = 280 Hz), 65.5 (q, $^2J_{CF}$ = 37.2 Hz), 65.4, 53.4, 52.4. **^{19}F NMR** ($CDCl_3$, 564 MHz): δ -71.4. **HRMS (MALDI-FT ICR)** m/z: $[M+K]^+$ calculated for $C_{12}H_{10}F_3KN_3O_3$: 340.0306, found: 340.0313. HPLC (AD-H, 2-propanol/n-hexane = 2/98, flow rate = 1 mL/min, λ = 210 nm) major enantiomer t_R =5.3 min, minor enantiomer t_R = 5.8 min.

Synthesis of triol 8 from diester 3a

The synthesis of compound **8** was performed under a slightly modified procedure from the literature.[11] To a solution of compound **3a** (60.8 mg, 0.2 mmol, 82% ee) in THF (2.8 mL) in a round-bottom flask, sodium bis(2-methoxyethoxy)aluminum hydride (RedAl) (65% wt in toluene, 0.31 mL, 1.0 mmol) is added at 0 °C. After the addition, the reaction mixture is warmed to room temperature and stirred for 3 hours. Upon completion, the flask is placed in an ice-water cooling bath and the reaction is quenched with methanol (2 mL). The resulting solution is poured over a saturated aqueous disodium tartrate solution (20 mL) and the mixture is vigorously stirred for 3 hours. The product is extracted with ethyl acetate (4 x 20 mL). The combined organic layer is dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure to give the final product **8** in 98% yield.

[11] Kano, T.; Yamamoto, A.; Song, S.; Maruoka, K. *Chem. Commun.,* **2011**, *47*, 4358-4360.

(*R*)-4,4,4-trifluoro-2-(hydroxymethyl)-3-phenylbutane-1,3-diol 8

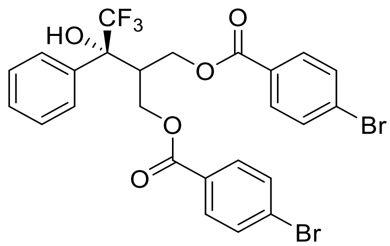


Pale yellow wax, 48.9 mg, 98% yield. $[\alpha]_D^{26}$ = +17.6 (*c* = 0.72, acetone). **^{1}H NMR** (Acetone d$_6$, 600 MHz): δ 7.61 (d, 2H, J = 7.8 Hz), 7.44 (t, 2H, J = 7.6 Hz), 7.38 (t, 1H, J = 7.3 Hz), 6.17 (s, 1H), 4.89 (t, 1H, J = 3.9 Hz), 4.34-4.33 (m, 1H), 4.24-4.22 (m, 1H), 3.86-3.84 (m, 1H), 3.70-3.65 (m, 1H), 3.35-3.33 (m, 1H), 2.42-2.40 (m, 1H).**^{13}C NMR:** (Acetone d$_6$, 150 MHz): δ 139.6, 129.0, 128.9, 127.0 (q, $^1J_{CF}$ = 287 Hz), 126.6, 80.6 (q, $^2J_{CF}$ = 27.5 Hz), 59.5, 58.5, 46.3 (q, $^3J_{CF}$ = 3.0 Hz). **^{19}F NMR** (Acetone d$_6$, 564 MHz): δ -75.2. **HRMS (MALDI-FT ICR)** m/z: $[M+Na]^+$ calculated for $C_{11}H_{13}F_3NaO_3$: 273.0709, found: 273.0731.

Synthesis of compound 9 from 8

The synthesis of compound **9** was performed under a slightly modified procedure from the literature.[12] In a sample vial, a solution of compound **8** (37.5 mg, 0.15 mmol) in CH_2Cl_2 (1.5 mL) is prepared. Then Et_3N (78.4 uL,0.68 mmol) and *p*-bromobenzoyl chloride (115 mg, 0.53 mmol) are added at 0 °C. After the addition, the cooling bath is removed and the reaction is stirred at room temperature for 92 hours, monitored by TLC (eluent PE/ethyl acetate 8/2). After completion, the solvent is removed under reduced pressure and the residue purified by flash chromatography (eluent: PE/ethyl acetate 95/5 to 9/1) to give the final product **9** in 80% yield and 82% ee. Enantiopure crystals were grown by crystallization of the enantioenriched compound **9** (83% ee) in a mixture of heptane/acetonitrile 3/1.

(*R*)-2-(2,2,2-trifluoro-1-hydroxy-1-phenylethyl)propane-1,3-diyl bis(4-bromobenzoate) 9



White solid, 67.0 mg, 80% yield. $[\alpha]_D^{25}$ = +31.9 (*c* = 0.76, $CHCl_3$), 83% ee. **m.p.** = 119.4-121.0 °C. (Acetone d$_6$, 600 MHz): δ 7.88 (d, 2H, J = 8.6 Hz), 7.76 (d, 2H, J = 7.2 Hz), 7.75 (d, 2H, J = 8.6 Hz), 7.65 (d, 2H, J = 8.6 Hz), 7.60 (d, 2H, J = 8.6 Hz), 7.48-7.45 (m, 2H), 7.40 (t, 1H, J = 7.4 Hz), 6.09 (s, 1H), 4.97 (dd, 1H, J = 11.7 Hz, 5.1 Hz), 4.76 (dd, 1H, J = 11.7 Hz, 6.3 Hz), 4.41 (dd, 1H, J = 11.6 Hz, 6.3 Hz), 4.37 (dd, 1H, J = 11.6 Hz, 4.4 Hz), 3.39 (quint, 1H, J = 5.7 Hz).**^{13}C NMR:** (Acetone d$_6$, 150 MHz): δ 166.1, 165.8, 138.6, 132.8, 132.6, 132.3, 132.2, 130.2, 130.0, 129.7,

[12] Yoon, W. S.; Han, J. T.; Yun, J. *Adv. Synth. Catal.,* **2021**, *363*, 4953-4959.

129.6, 128.6, 128.5, 127.1, 127.0 (q, $^{1}J_{CF}$ = 287 Hz), 79.2 (q, $^{2}J_{CF}$ = 27.9 Hz), 63.4, 62.9, 44.6. **^{19}F NMR** (Acetone d_6, 564 MHz): δ -74.4. **HRMS (MALDI-FT ICR)** m/z: $[M+Na]^+$ calculated for $C_{25}H_{19}Br_2F_3NaO_5$: 638.9425, found: 638.9455. HPLC (AD-H, 2-propanol/n-hexane = 10/90, flow rate = 1 mL/min, λ = 240 nm) major enantiomer t_R = 13.6 min, minor enantiomer t_R = 20.4 min.

Scale-up for the asymmetric synthesis of epoxides 2a and 2f from alkenes 1a and 1f

In a round-bottom flask containing a solution of alkenes **1** (1.0 mmol) and (*R*,*R*)-**V** catalyst (21.0 mg, 0.05 mmol) in anhydrous toluene (50 mL) at -20°C, *tert*-butyl hydroperoxide (~5.5 M in decane, 230 µL, 1.2 mmol) is added. The reaction is stirred at -20°C for 19-20 h, monitored by TLC (eluent PE/ethyl acetate 90/10). Direct purification of the reaction mixture by flash chromatography (eluting with PE/ethyl acetate 100/0 to 98/2) gives enantioenriched epoxide **2a** and **2f** in 87-89% yield and 84-85% ee. ATTENTION to the volatility of compound **2a**: carefully evaporate the solvent (40 mbar, 40°C) to concentrate the product after purification.

Linear effect study in the asymmetric epoxidation of alkene 1a

In a sample vial containing alkene **1a** (11.1 mg, 0.05 mmol), different volumes of stock solutions (1.25 mM) in anhydrous toluene of catalyst (*R*,*R*)-**V** and catalyst (*S*,*S*)-**V** are added (in total, 5 mol% catalyst **V**). Pure anhydrous toluene is added to obtain a final volume of 2.5 mL. To the prepared solution, *tert*-butyl hydroperoxide (~5.5 M in decane, 11 µL, 0.06 mmol) is added at -20°C. The reaction is stirred at -20°C for 20 hours. After this time, product **2a** is purified by preparative thin layer chromatography (PE/ethyl acetate 95/05) and the ee determined by chiral HPLC (OD-H, 2-propanol/n-hexane = 2/98, flow rate = 1 mL/min, λ = 220 nm) major enantiomer t_R = 5.6 min, minor enantiomer t_R = 10.2 min.

Table S4. Data of the linear effect study on the epoxidation of **1a**

entry	(*R*,*R*)-**V** (µmol)	(*S*,*S*)-**V** (µmol)	(*R*,*R*)-**V** [ee%]	**2a** [ee%]
1	1.50	1.00	20	10
2	1.75	0.75	40	25
3	2.00	0.50	60	41
4	2.25	0.25	80	59
5	2.50	0.00	100	83

ECD Spectra of 3b

The enantioenriched mixture of diester **3b** was further purified using CSP-preparative HPLC with Chiralpak AD-H column (250x21.2 mm) using n-hexane:iPrOH 98:2 v/v. The ECD spectra of the enantiopure compound was recorded using a JASCO J-810 spectropolarimeter. The acquisition was carried out in the 190-400 nm range, using hypergrade LC-MS acetonitrile (Merck), at a concentration of about $1\cdot10^{-4}$ M. The concentration was optimized to obtain a maximum absorbance between 0.8 and 1 of the UV/vis spectra, with a cell path of 0.2 cm. The acquisition is an average of 8 scans at a scan rate of 50 $nm\cdot min^{-1}$.

The ECD calculations[13] have been performed on the *S* enantiomer of **3b** using acetonitrile as implicit solvent and Solvation Model Based (SMD), after a conformational search and the following refinement, considering only the three conformation populated above the 5%.[14] The actual electronic transitions have been calculated using ωB97X-D4[15,16], CAM-B3LYP-D4[17,16], and M06-2x[18] functionals within the time-dependent density functional theory (TD-DFT). The def2-TZVPP basis set has been used in all calculations, and 40 states were calculated to cover the complete UV range. Each transition was then shifted and convoluted with a gaussian function, optimized to overlap with the experimental. For both the UV and ECD spectra the shift is always toward the blue (0.2 ÷ 0.5 eV, and 0.4 ÷0.5 eV, respectively).

Figure S2 shows the UV and the ECD spectra, calculated compared with the experimental ones normalized which are in very good agreement, in particular when using ωB97X-D4/def2-TZVPP.

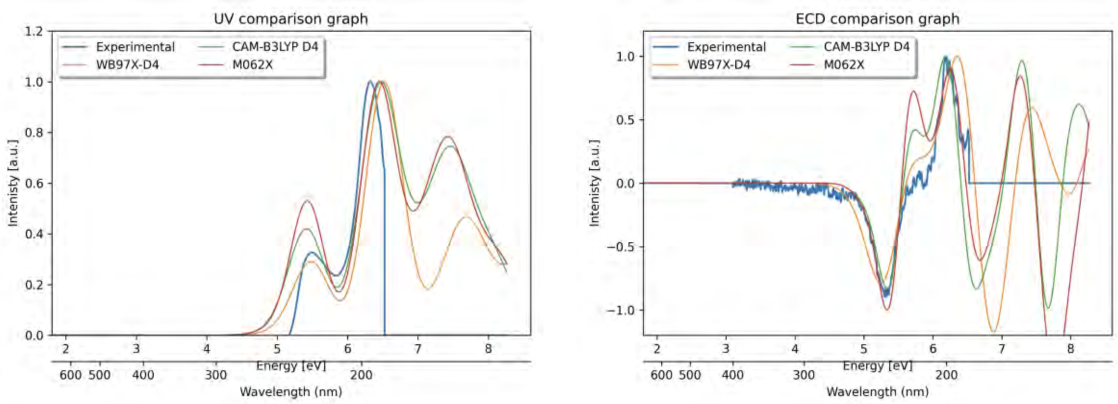
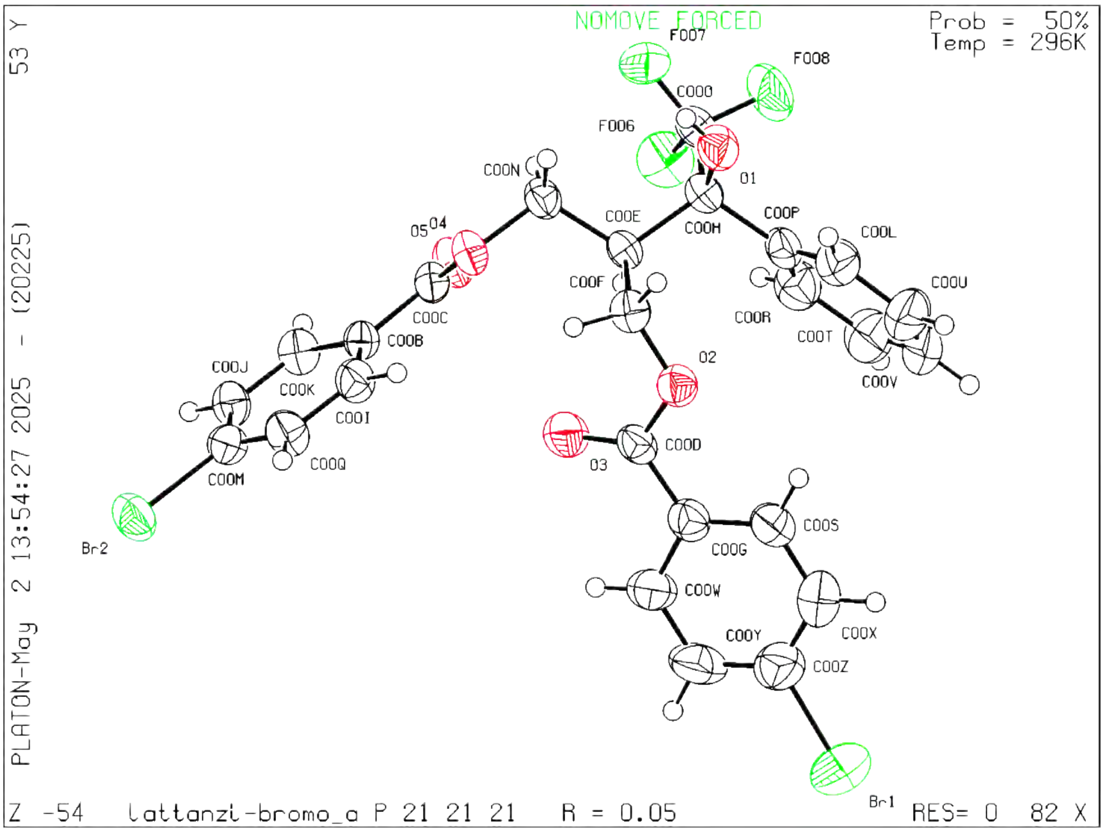


Figure S2. Comparison between the experimental and the computed electronic graphs.

[13] Pescitelli, G.; Bruhn, T. *Chirality* **2016**, *28*, 466–474.
[14] Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, *113*, 6378–6396.
[15] Chai, J.-D.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615–6620.
[16] Caldeweyher, E.; Ehlert, S.; Hansen, A.; Neugebauer, H.; Spicher, S.; Bannwarth, C.; Grimme, S. *J. Chem. Phys.* **2019**, *150*, 154122.
[17] Yanai, T.; Tew, D. P.; Handy, N. C. *Chem. Phys. Lett.* **2004**, *393*, 51–57.
[18] Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215–241.

X-Ray Diffraction data



A specimen of $C_{23}H_{15}Br_2F_3O_5$, approximate dimensions 0.080 mm x 0.100 mm x 0.400 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 0.71073 Å). The total exposure time was 20.33 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 31534 reflections to a maximum θ angle of 26.00° (0.81 Å resolution), of which 4693 were independent (average redundancy 6.719, completeness = 99.9%, R_{int} = 6.83%, R_{sig} = 4.84%) and 3977 (84.74%) were greater than $2\sigma(F^2)$. The final cell constants of a = 5.8988(12) Å, b = 8.0273(16) Å, c = 50.508(10) Å, volume = 2391.6(8) Å^3, are based upon the refinement of the XYZ-centroids of 8484 reflections above 20 σ(I) with 5.138° < 2θ < 47.73°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.679. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.3400 and 0.7700.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 21 21 21, with Z = 4 for the formula unit, $C_{23}H_{15}Br_2F_3O_5$. The final anisotropic full-matrix least-squares refinement on F^2 with 321 variables converged at R1 = 4.75%, for the observed data and wR2 = 10.64% for all data. The goodness-of-fit was 1.065. The largest peak in the final difference electron density synthesis was 0.425 e-/Å^3 and the largest hole was -0.458 e-/Å3 with an RMS deviation of 0.062 e-/Å3. On the basis of the final model, the calculated density was 1.633 g/cm^3 and F(000), 1160 e-. Flack parameter using 1338 quotients and *R* configuration at C00H was 0.051(6). CCDC deposition number 2448374.

Table 1. Sample and crystal data

Identification code	mazza2408AL	
Chemical formula	$C_{23}H_{15}Br_2F_3O_5$	
Formula weight	588.17 g/mol	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.080 x 0.100 x 0.400 mm	
Crystal system	orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 5.8988(12) Å	α = 90°
	b = 8.0273(16) Å	β = 90°
	c = 50.508(10) Å	γ = 90°
Volume	2391.6(8) $Å^3$	
Z	4	
Density (calculated)	1.633 g/cm^3	
Absorption coefficient	3.444 mm^{-1}	
F(000)	1160	

Table 2. Data collection and structure refinement.

Theta range for data collection	1.61 to 26.00°	
Index ranges	-7<=h<=7, -9<=k<=9, -62<=l<=61	
Reflections collected	31534	
Independent reflections	4693 [R(int) = 0.0683]	
Coverage of independent reflections	99.9%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.7700 and 0.3400	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2017/1 (Sheldrick, 2017)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	4693 / 0 / 321	
Goodness-of-fit on F^2	1.065	
Final R indices	3977 data; $I>2\sigma(I)$	R1 = 0.0475, wR2 = 0.1027
	all data	R1 = 0.0577, wR2 = 0.1064
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0282P)^2+2.4766P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.051(6)	
Extinction coefficient	0.0025(5)	
Largest diff. peak and hole	0.425 and -0.458 $eÅ^{-3}$	
R.M.S. deviation from mean	0.062 $eÅ^{-3}$	

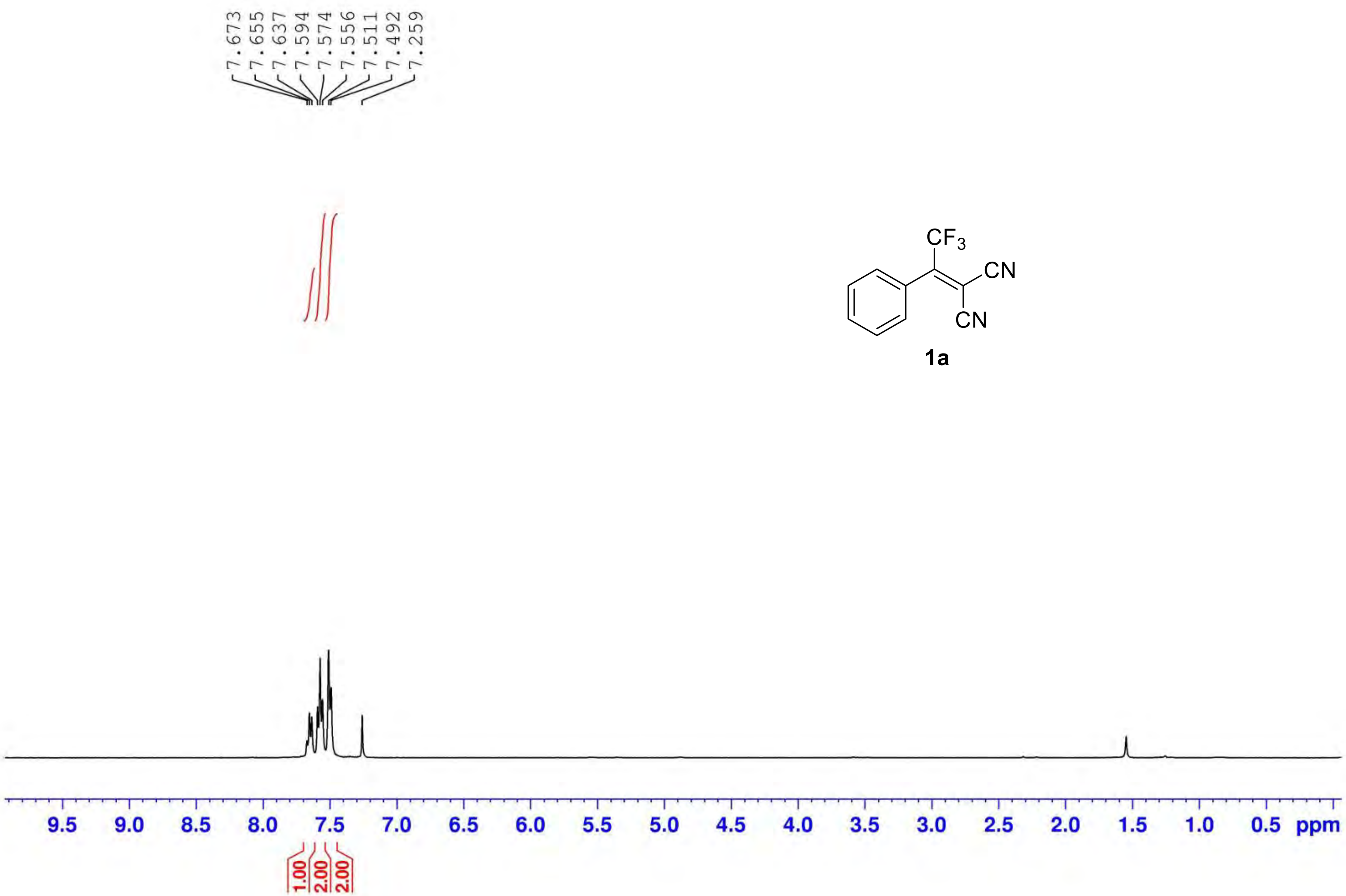
Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

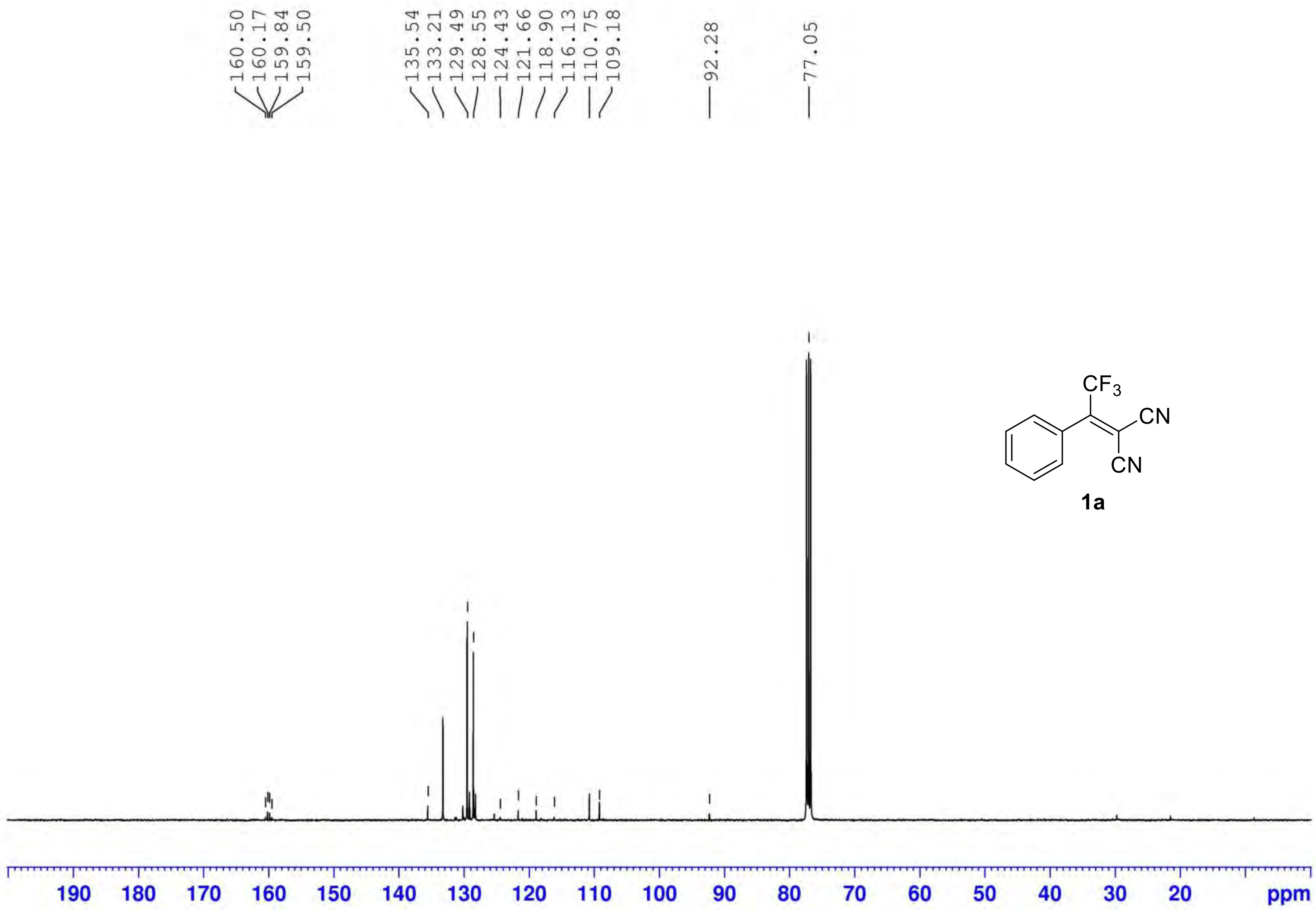
	x/a	y/b	z/c	U(eq)
Br2	0.71002(14)	0.87566(8)	0.48809(2)	0.0633(3)
Br1	0.9134(2)	0.08678(18)	0.25608(2)	0.1210(5)
O4	0.3676(7)	0.4884(5)	0.43784(8)	0.0420(10)
O2	0.4691(7)	0.4006(5)	0.36208(8)	0.0459(10)
O5	0.0407(7)	0.6284(6)	0.43733(8)	0.0493(10)
F006	0.3239(8)	0.9521(5)	0.39507(9)	0.0721(12)
F007	0.6304(9)	0.9626(5)	0.41793(8)	0.0738(14)
F008	0.6246(9)	0.0571(5)	0.37842(9)	0.0859(16)
O1	0.8536(8)	0.7477(7)	0.38819(11)	0.0521(12)
O3	0.1454(8)	0.3391(6)	0.38276(9)	0.0612(13)
C00B	0.0458(10)	0.3467(7)	0.45245(11)	0.0368(13)
C00C	0.1444(10)	0.5022(8)	0.44175(12)	0.0381(13)
C00D	0.2565(11)	0.3433(6)	0.36273(12)	0.0432(14)
C00E	0.4804(9)	0.6215(7)	0.39593(10)	0.0350(12)
C00F	0.5636(11)	0.4505(7)	0.38686(12)	0.0425(14)
C00G	0.1776(12)	0.2883(7)	0.33654(13)	0.0482(15)
C00H	0.6213(10)	0.7621(7)	0.38303(13)	0.0382(14)
C00I	0.1499(11)	0.1941(8)	0.44986(12)	0.0477(16)
C00J	0.7431(11)	0.2190(7)	0.47666(12)	0.0439(14)
C00K	0.8423(10)	0.3584(8)	0.46606(12)	0.0433(14)
C00L	0.7669(13)	0.6965(9)	0.33741(14)	0.0592(18)
C00M	0.8483(10)	0.0685(8)	0.47344(12)	0.0436(15)
C00N	0.4825(10)	0.6307(9)	0.42618(11)	0.0427(13)
C00O	0.5470(14)	0.9348(8)	0.39349(14)	0.0543(18)
C00P	0.5932(11)	0.7570(8)	0.35265(12)	0.0440(15)
C00Q	0.0516(12)	0.0531(8)	0.46058(13)	0.0510(16)
C00R	0.3943(13)	0.8045(9)	0.34110(15)	0.0601(19)
C00S	0.3028(14)	0.3110(9)	0.31379(14)	0.0635(19)
C00T	0.3720(16)	0.7953(11)	0.31366(17)	0.076(2)
C00U	0.7408(17)	0.6842(12)	0.31019(16)	0.083(3)
C00V	0.5427(18)	0.7353(12)	0.29866(15)	0.085(3)
C00W	0.9709(13)	0.2081(9)	0.33493(16)	0.063(2)
C00X	0.2238(16)	0.2526(11)	0.28951(16)	0.077(2)
C00Y	0.8926(14)	0.1497(10)	0.31068(17)	0.074(2)
C00Z	0.0203(16)	0.1728(10)	0.28887(16)	0.070(2)

NMR Spectra

^{1}H NMR in $CDCl_3$ (400 MHz)

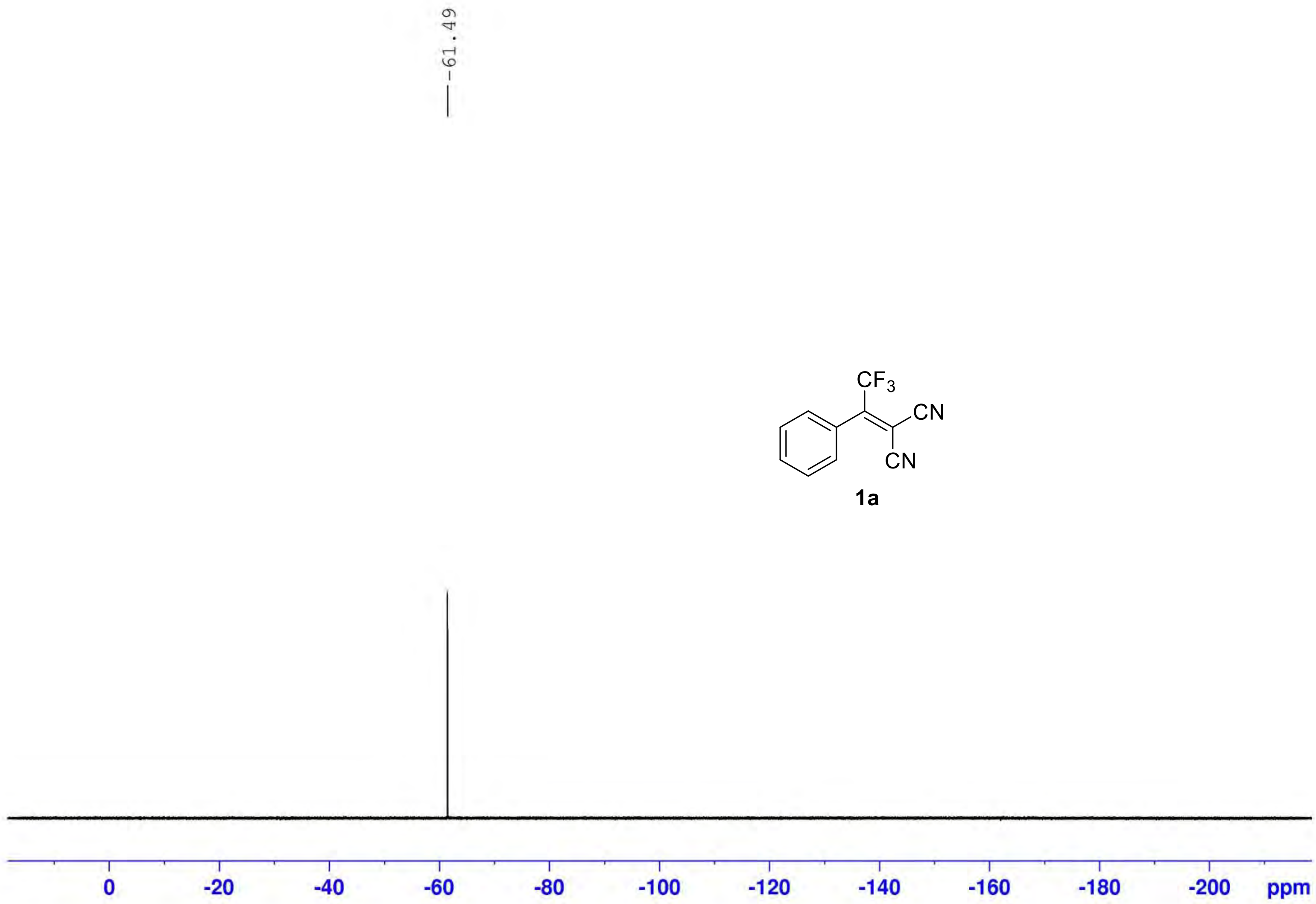


^{13}C NMR in $CDCl_3$ (100 MHz)

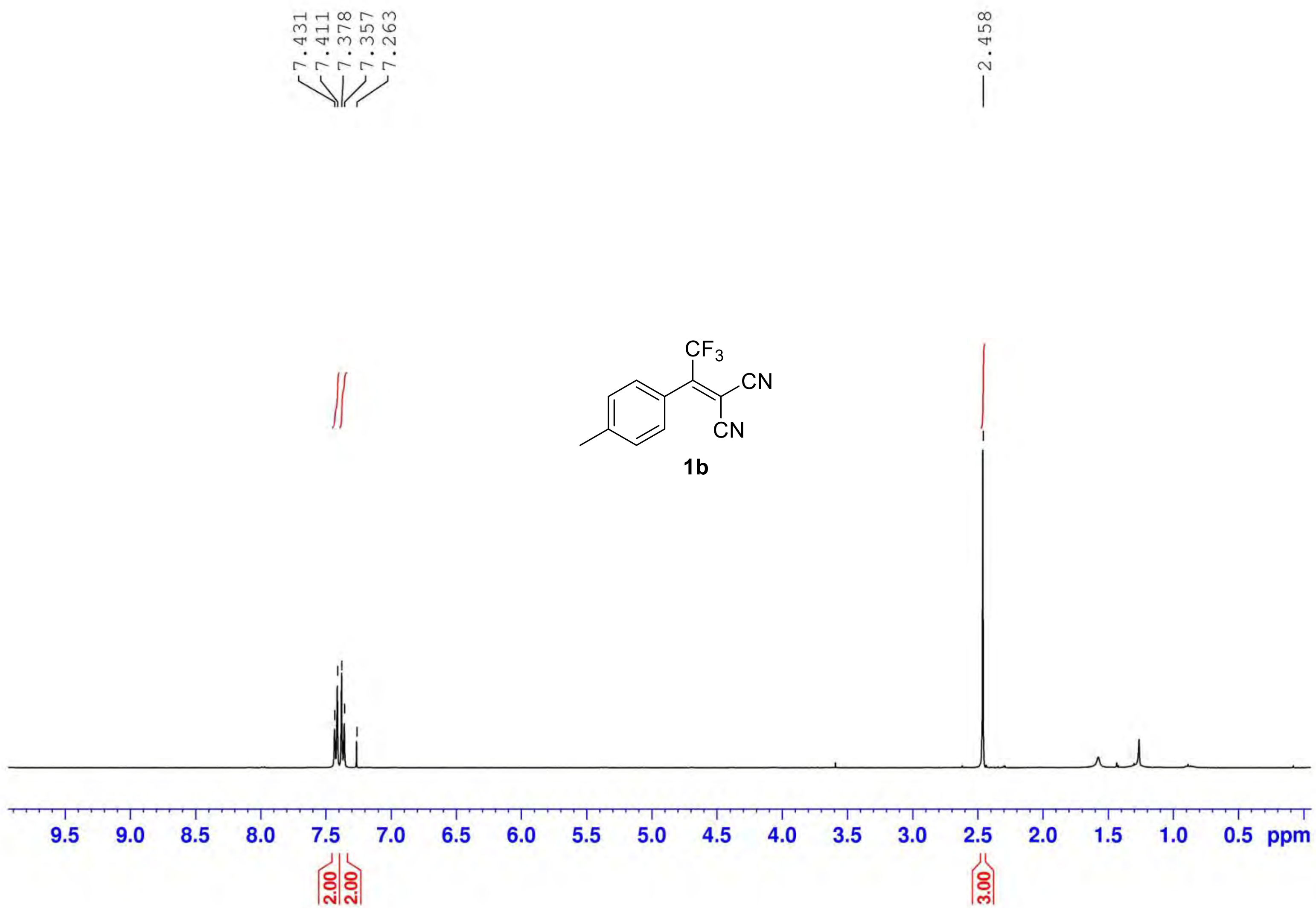


1a

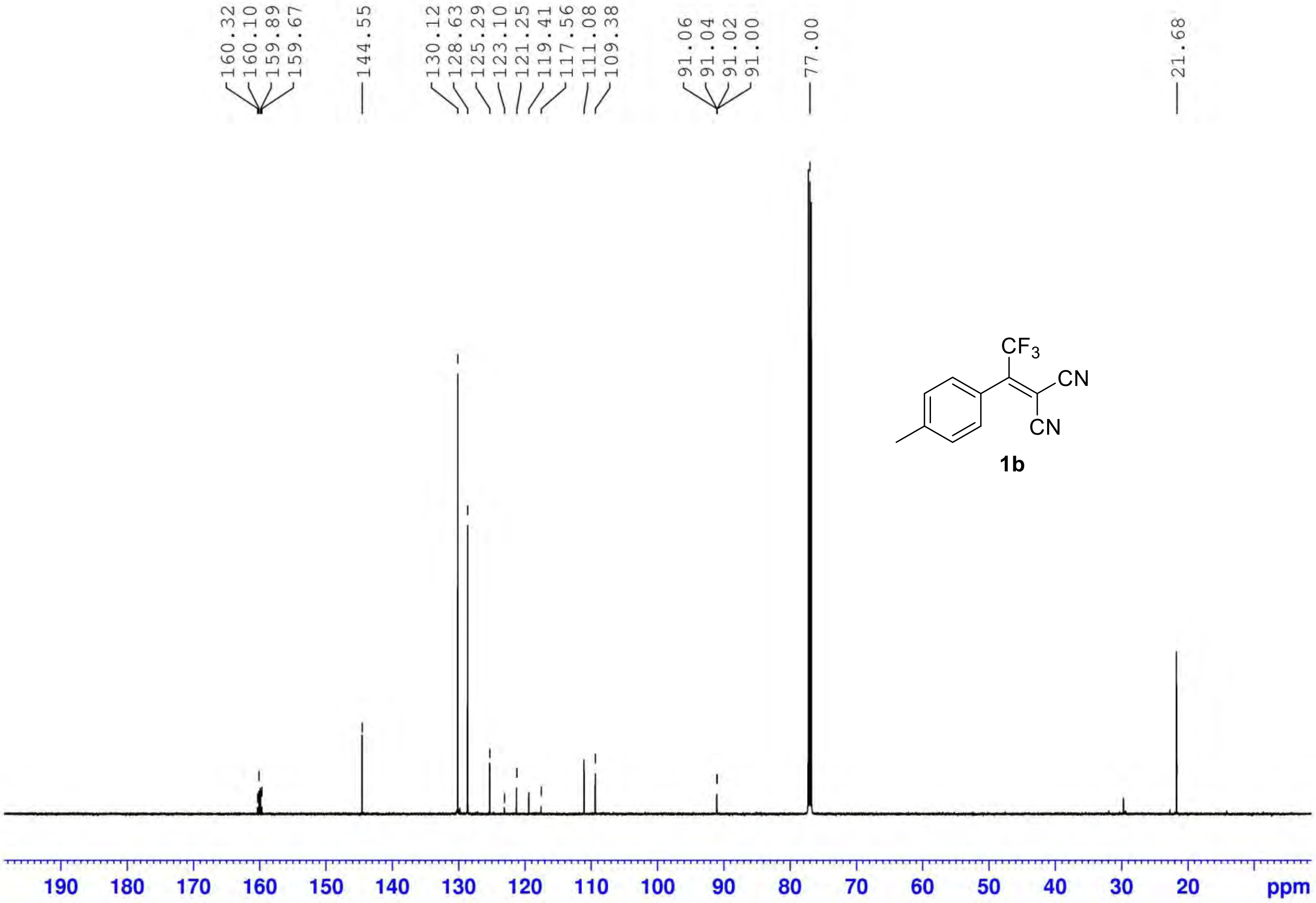
^{19}F NMR in $CDCl_3$ (376 MHz)



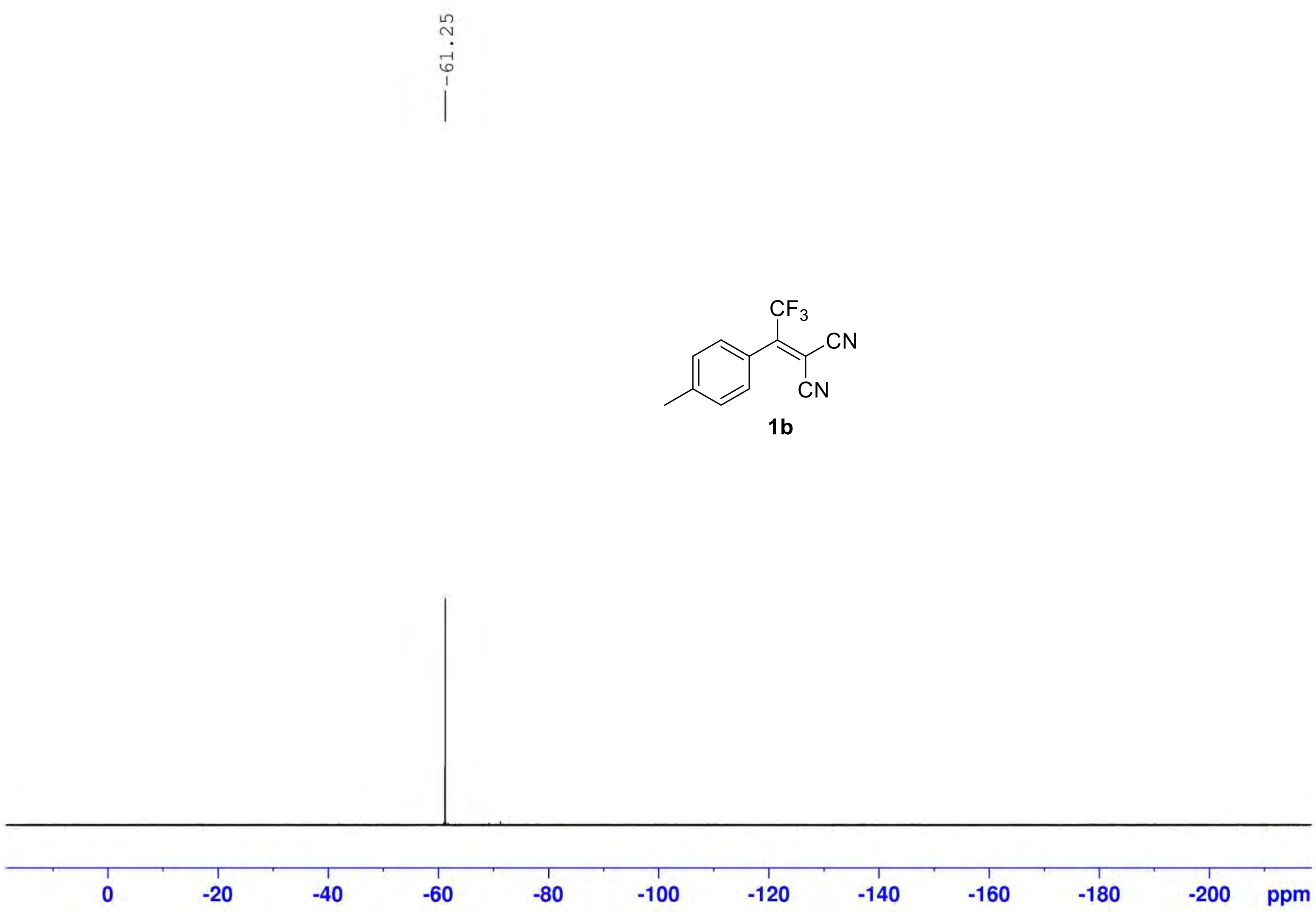
[1]H NMR in $CDCl_3$ (400 MHz)



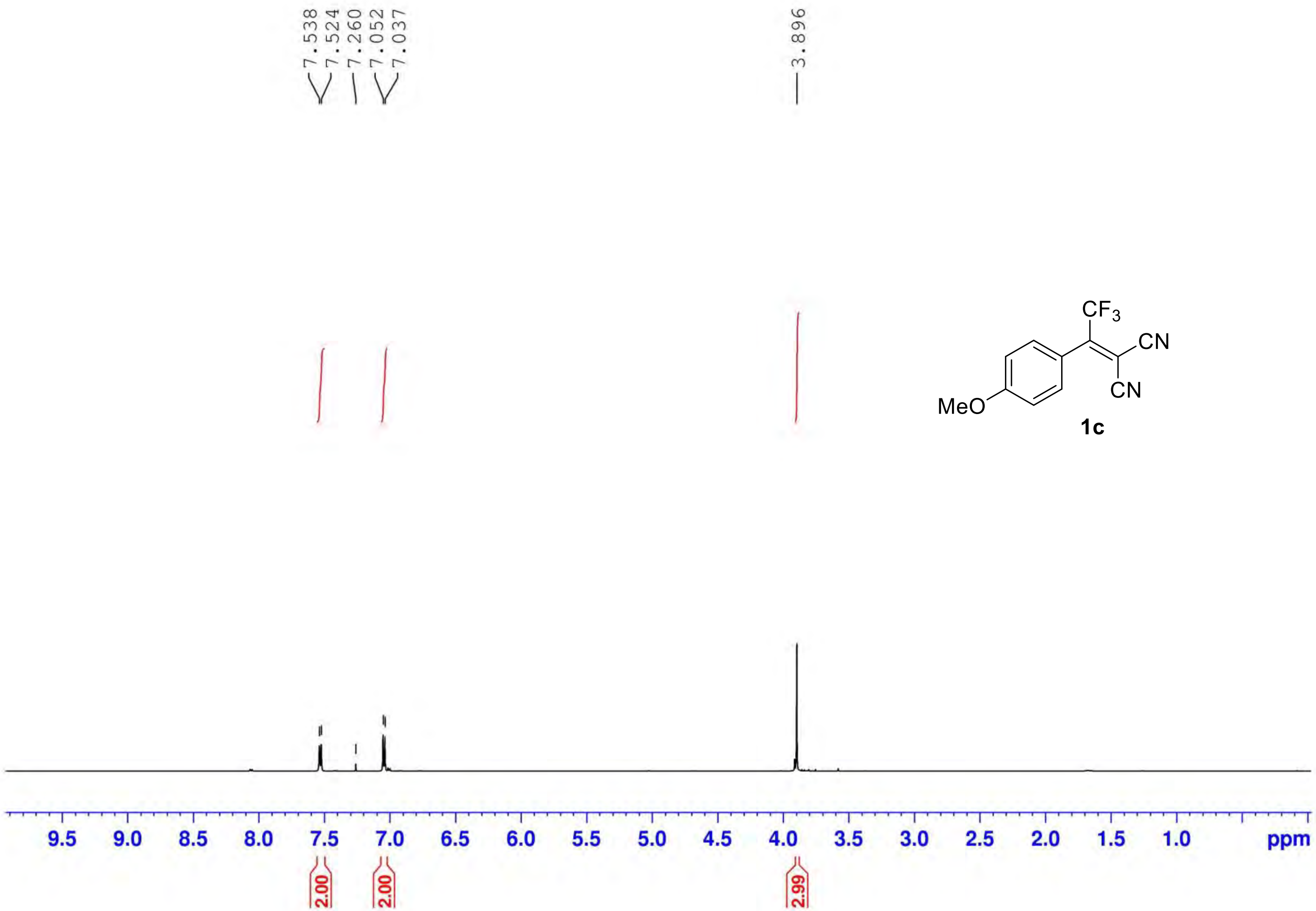
^{13}C NMR in $CDCl_3$ (150 MHz)



^{19}F NMR in $CDCl_3$ (376 MHz)

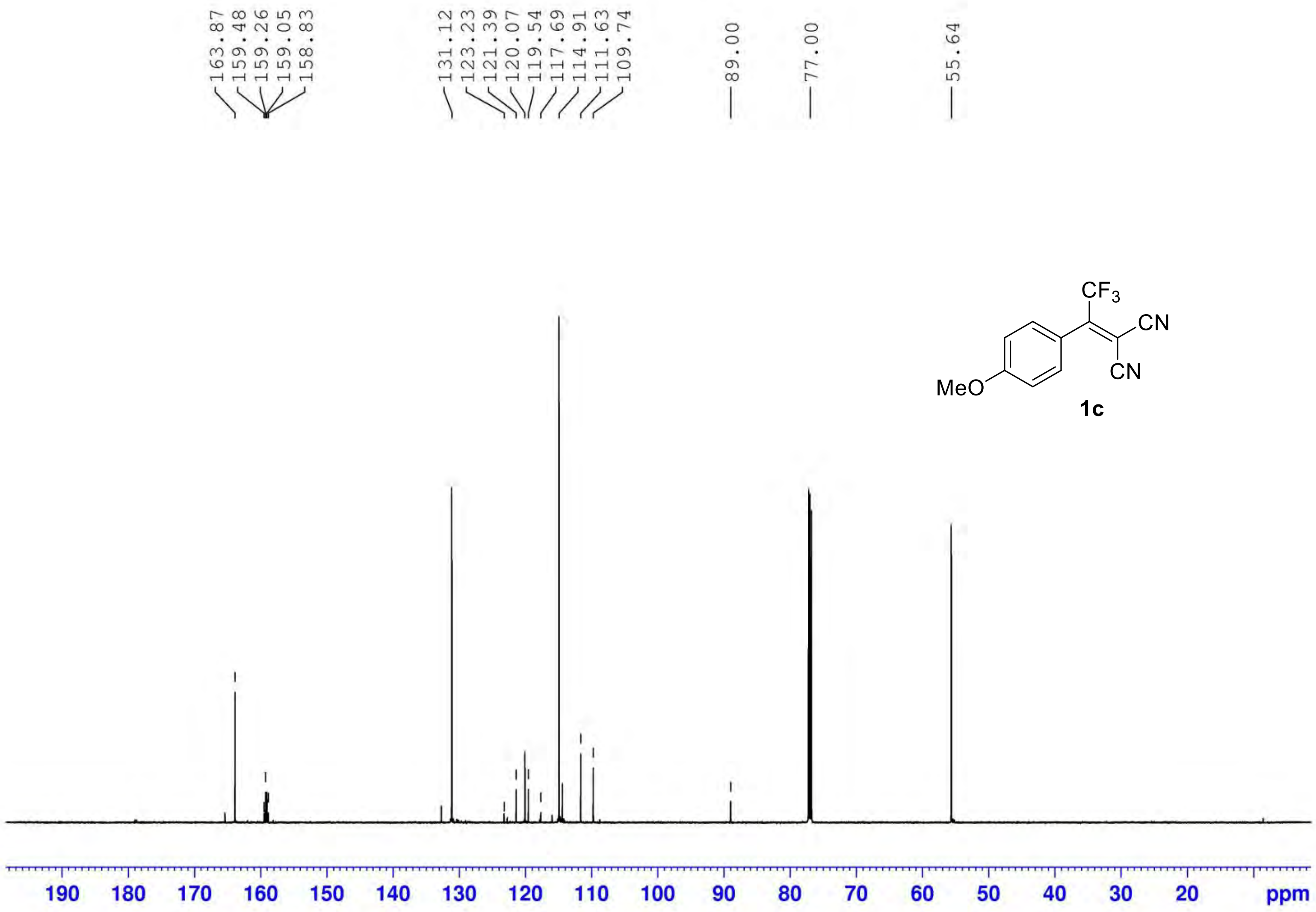


[1]H NMR in $CDCl_3$ (600 MHz)



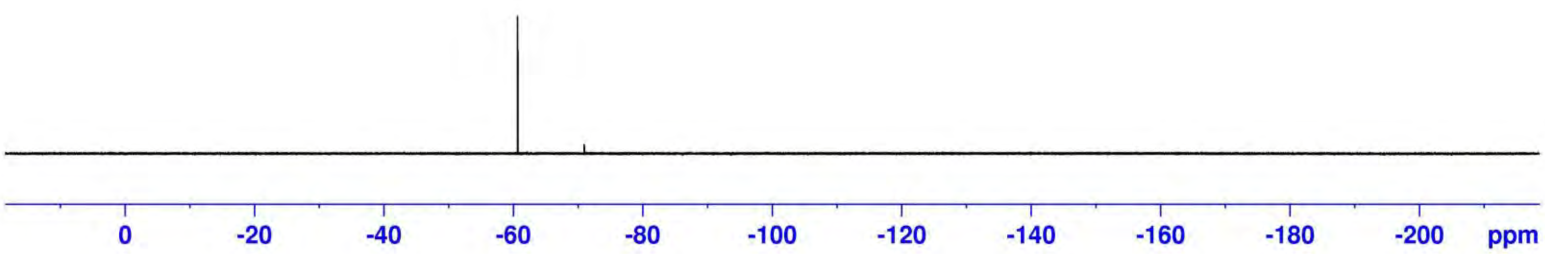
1c

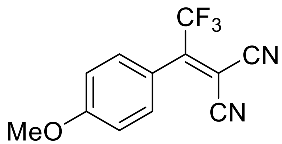
^{13}C NMR in $CDCl_3$ (150 MHz)



1c

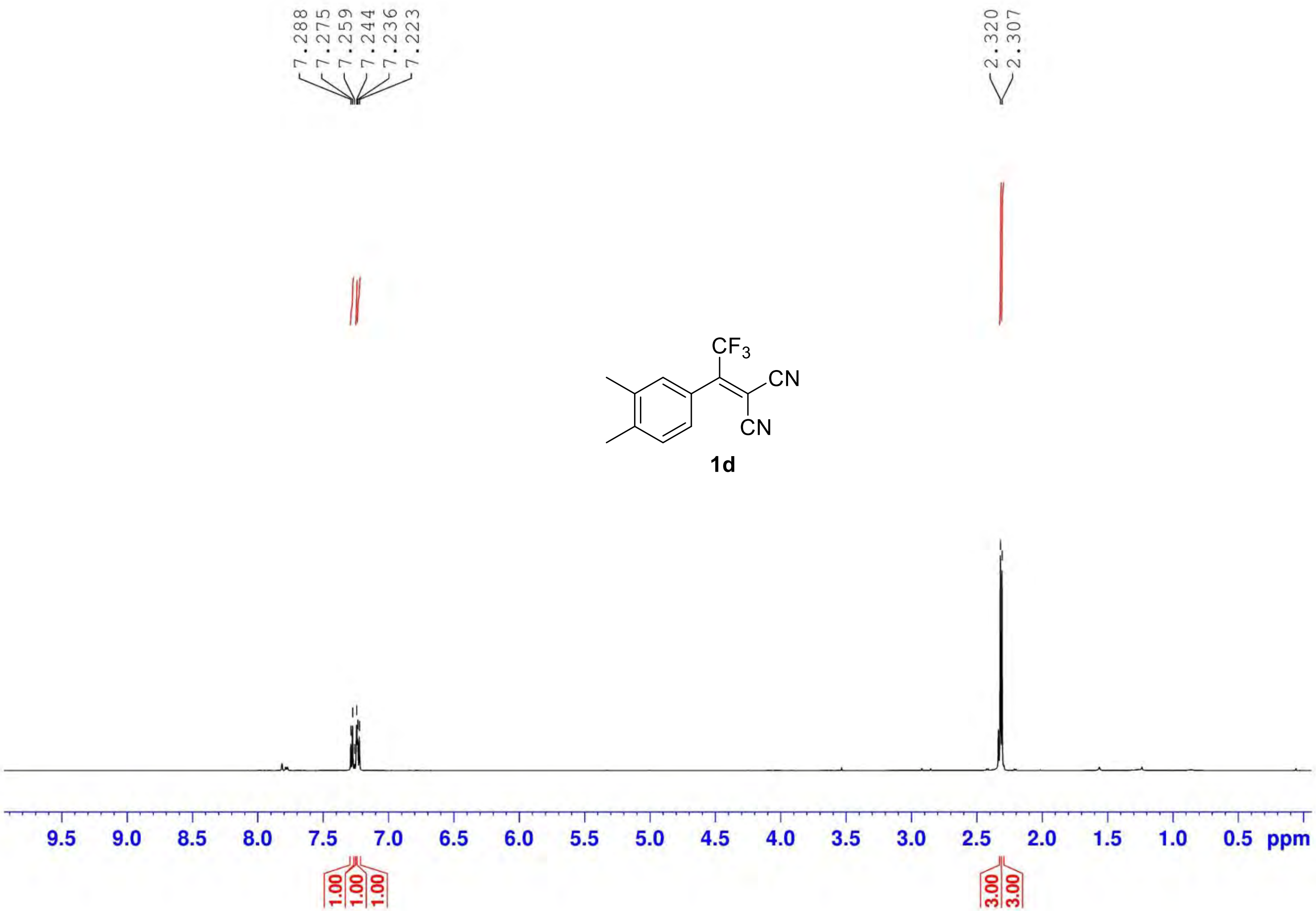
^{19}F NMR in $CDCl_3$ (376 MHz)



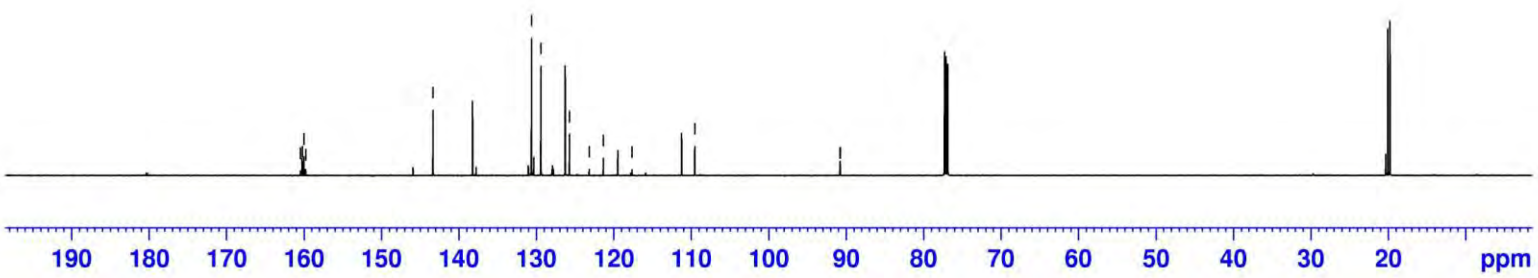


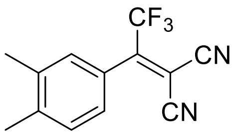
1c

^{1}H NMR in $CDCl_3$ (600 MHz)



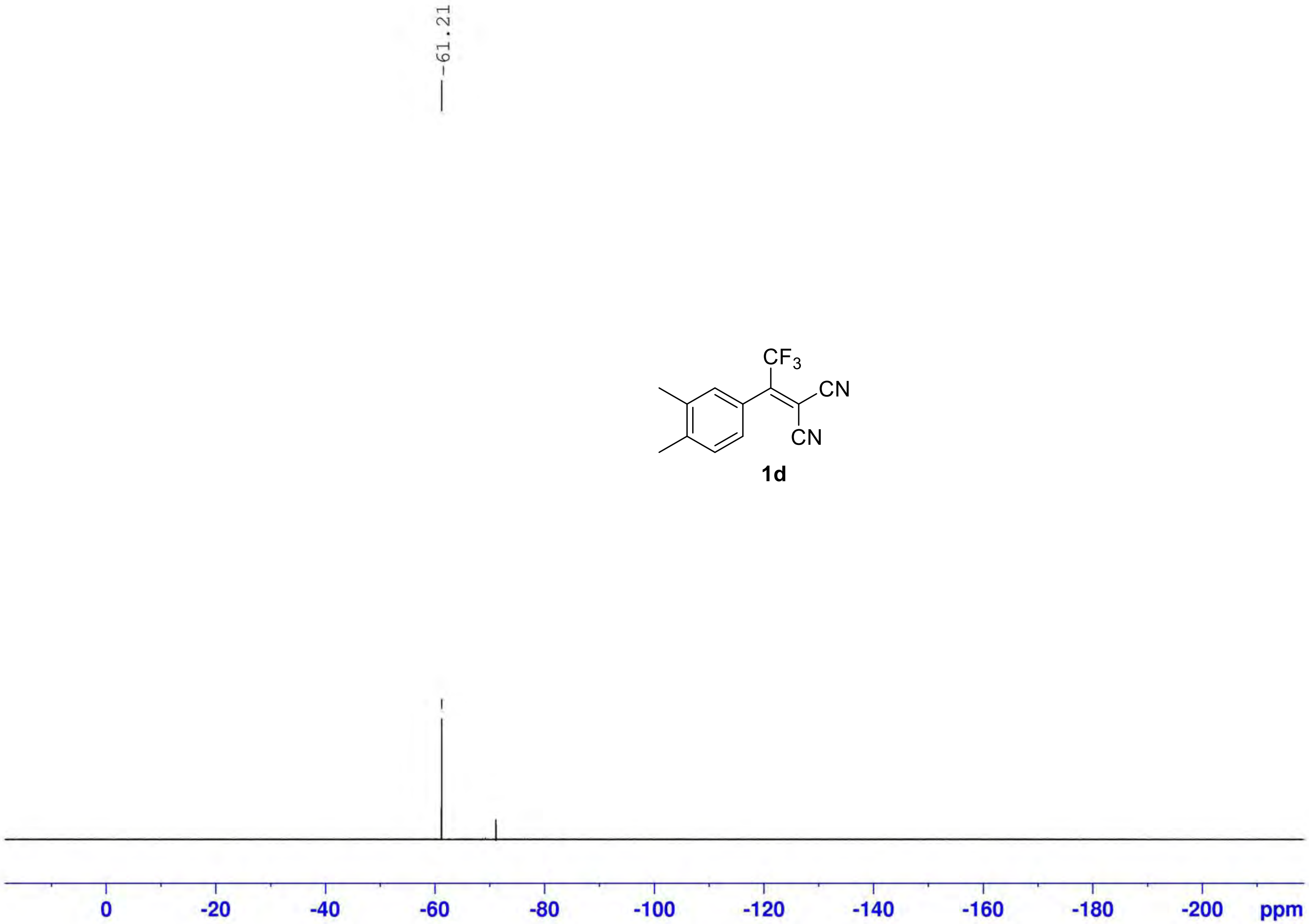
^{13}C NMR in $CDCl_3$ (150 MHz)





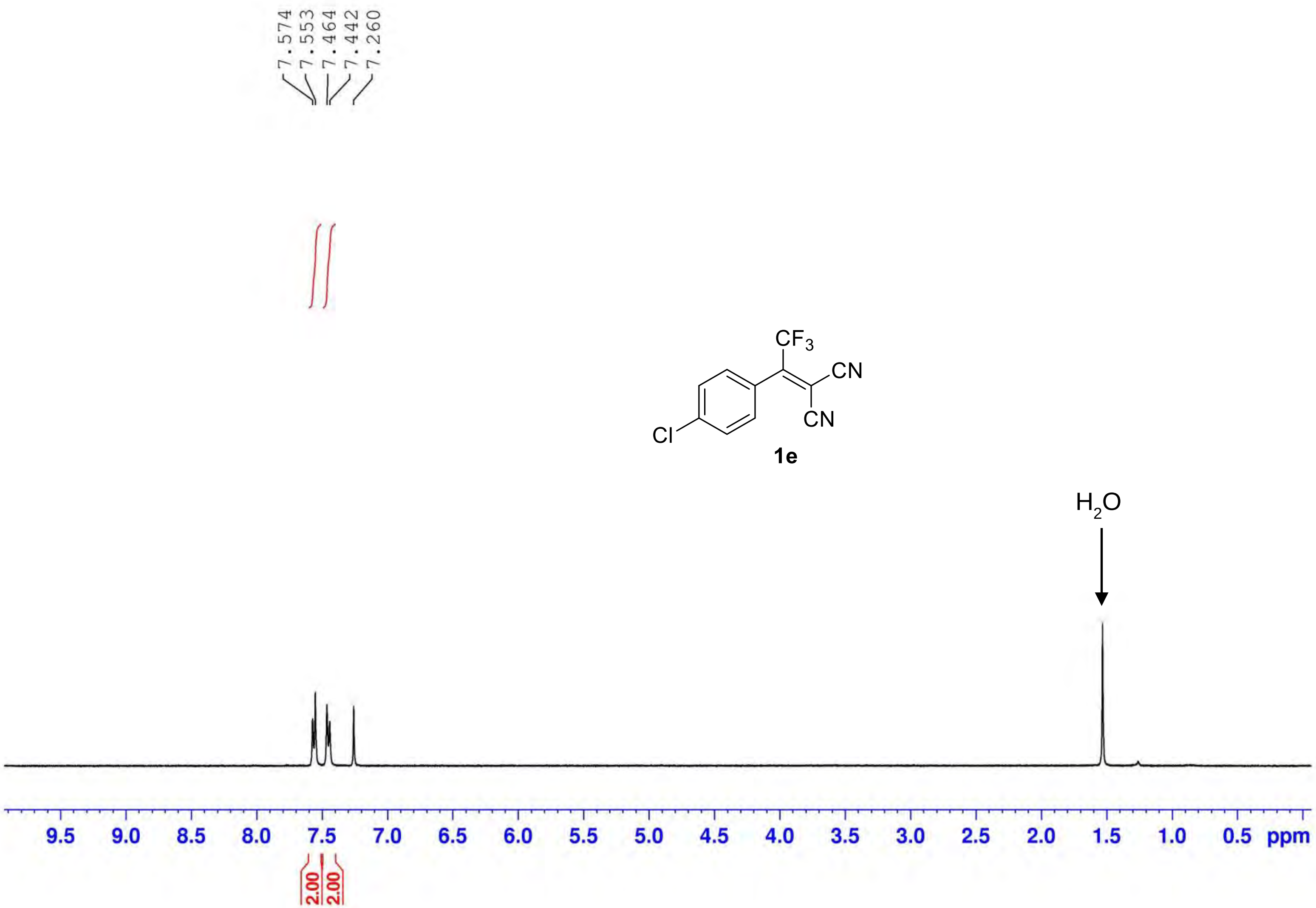
1d

^{19}F NMR in $CDCl_3$ (376 MHz)

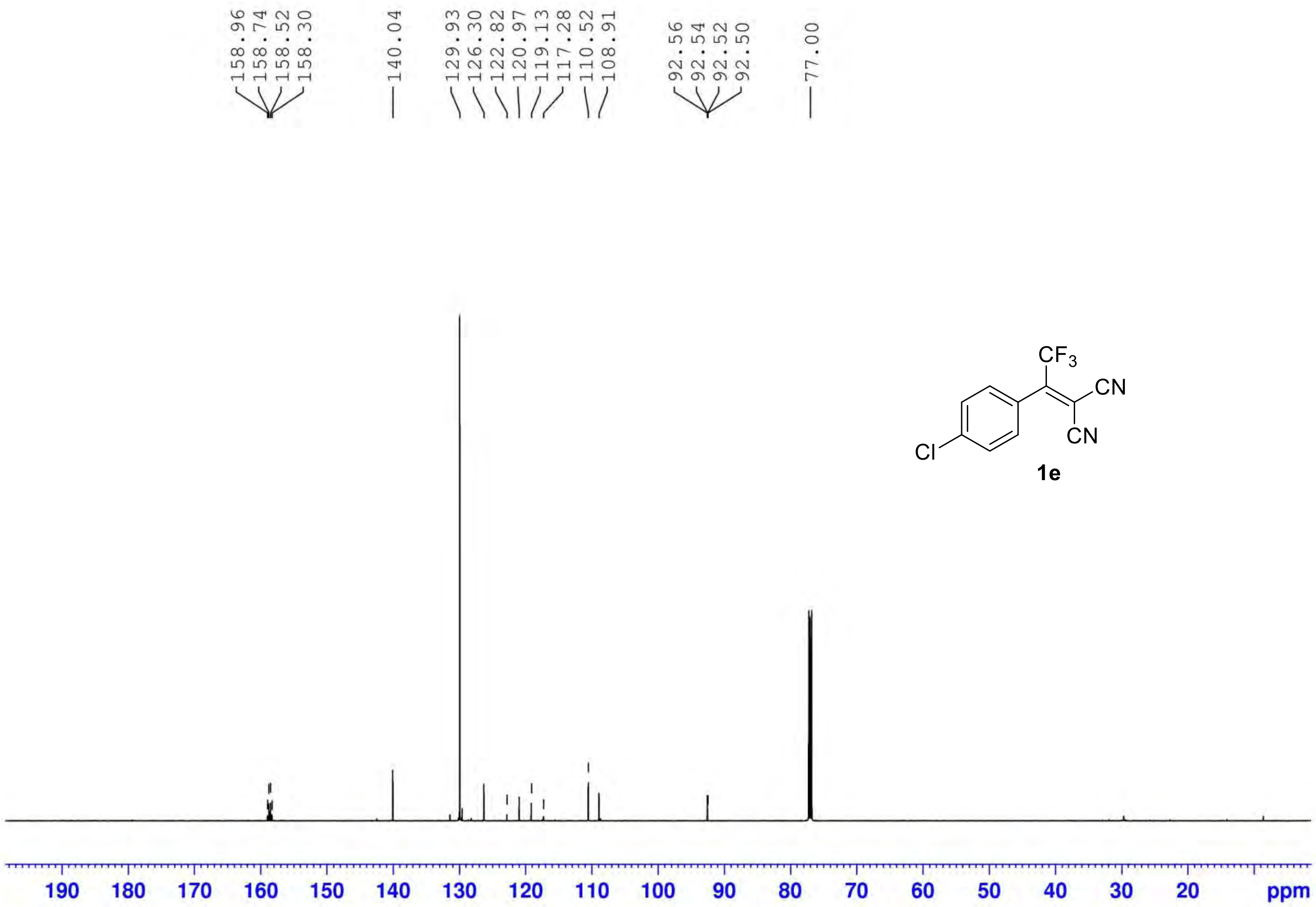


1d

^1H NMR in $CDCl_3$ (400 MHz)

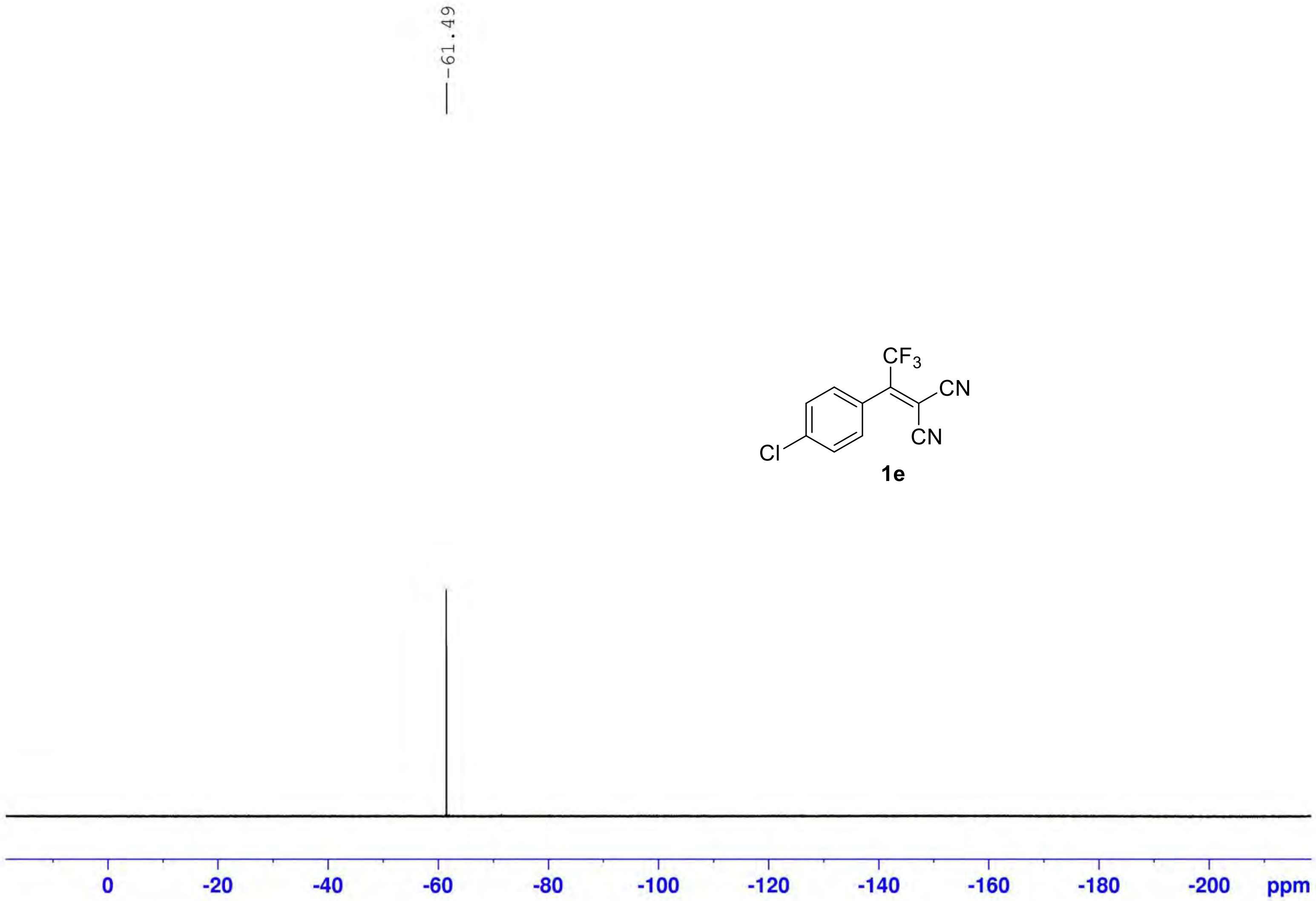


^{13}C NMR in $CDCl_3$ (150 MHz)

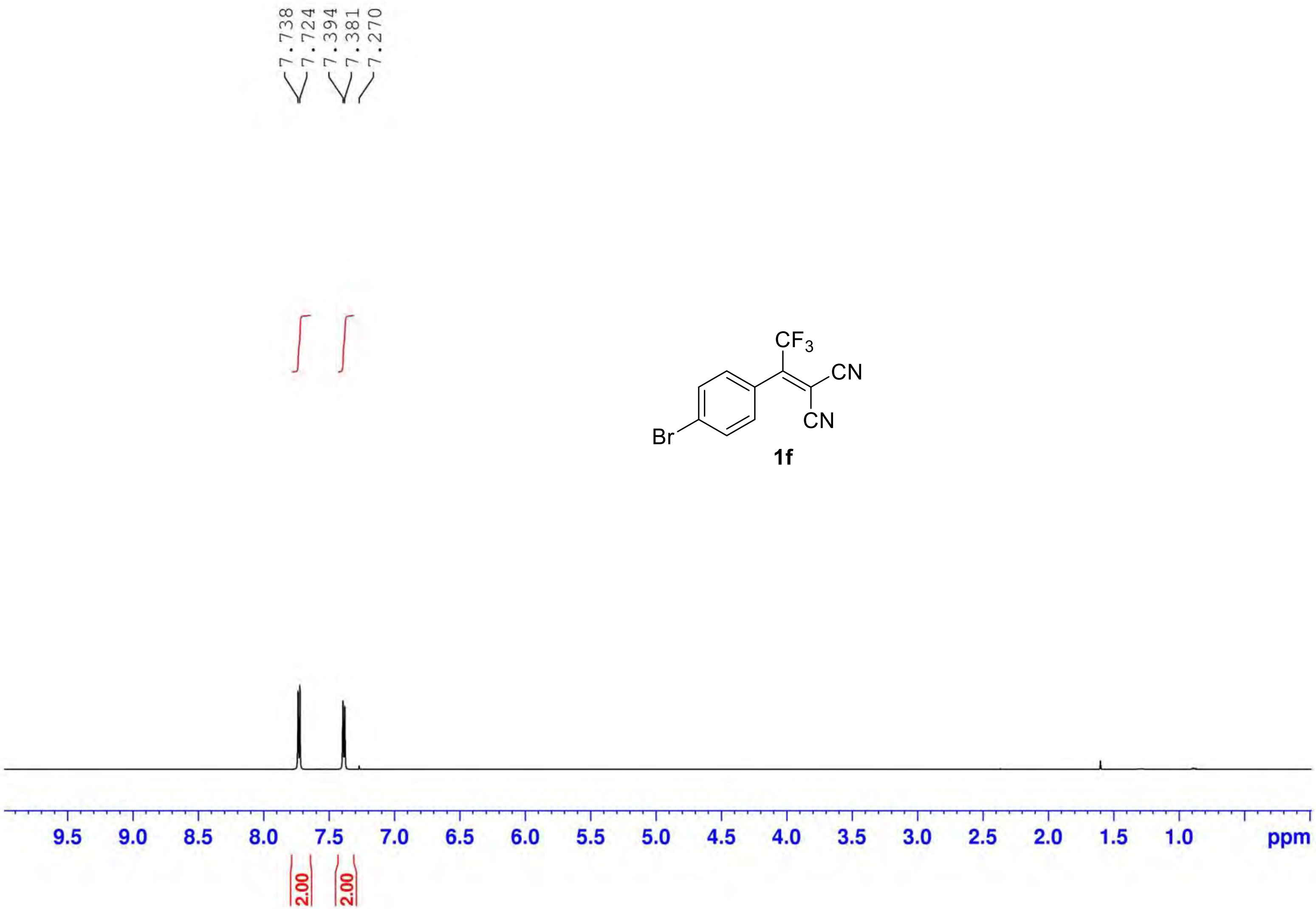


1e

^{19}F NMR in $CDCl_3$ (376 MHz)

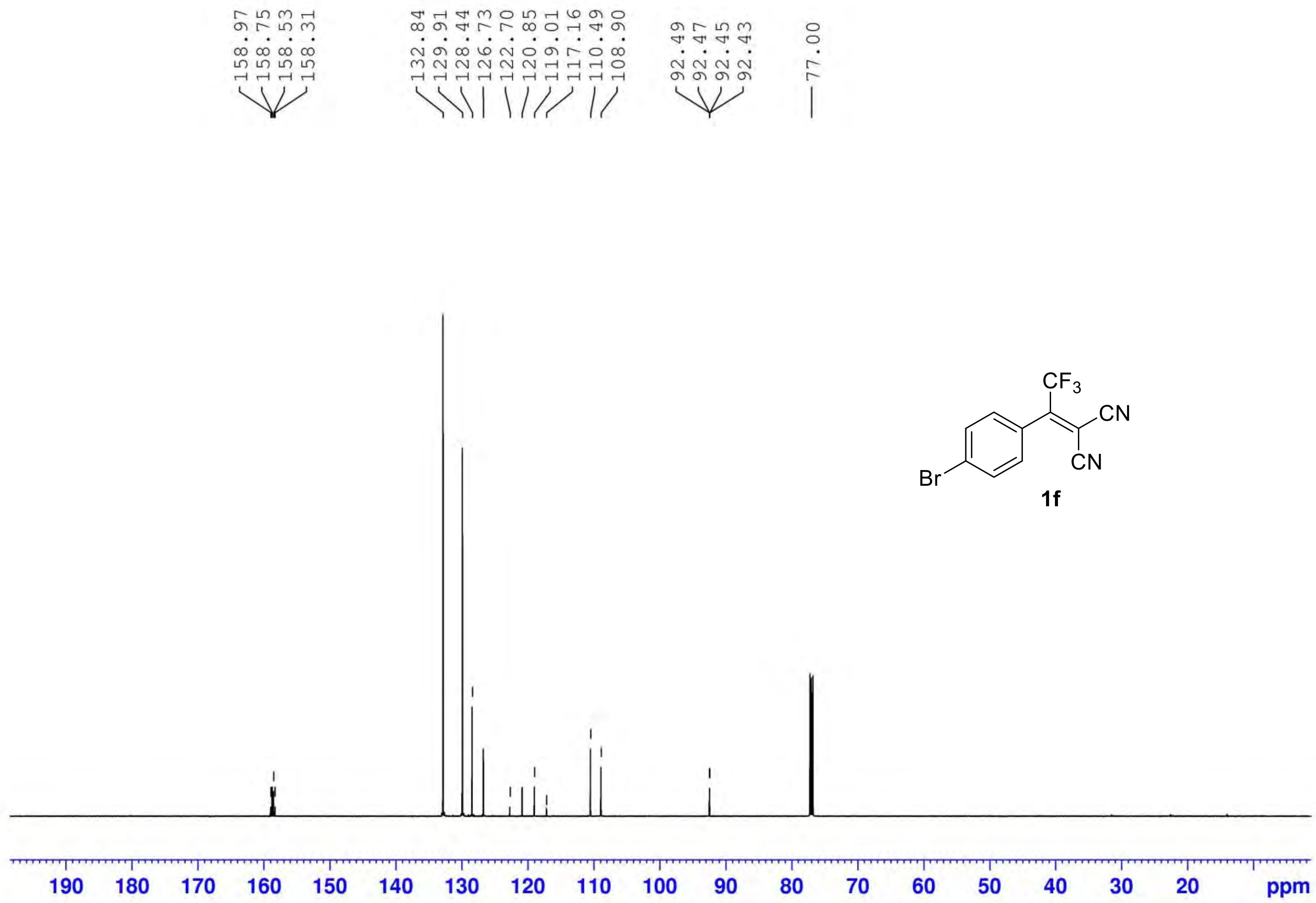


^{1}H NMR in $CDCl_3$ (600 MHz)

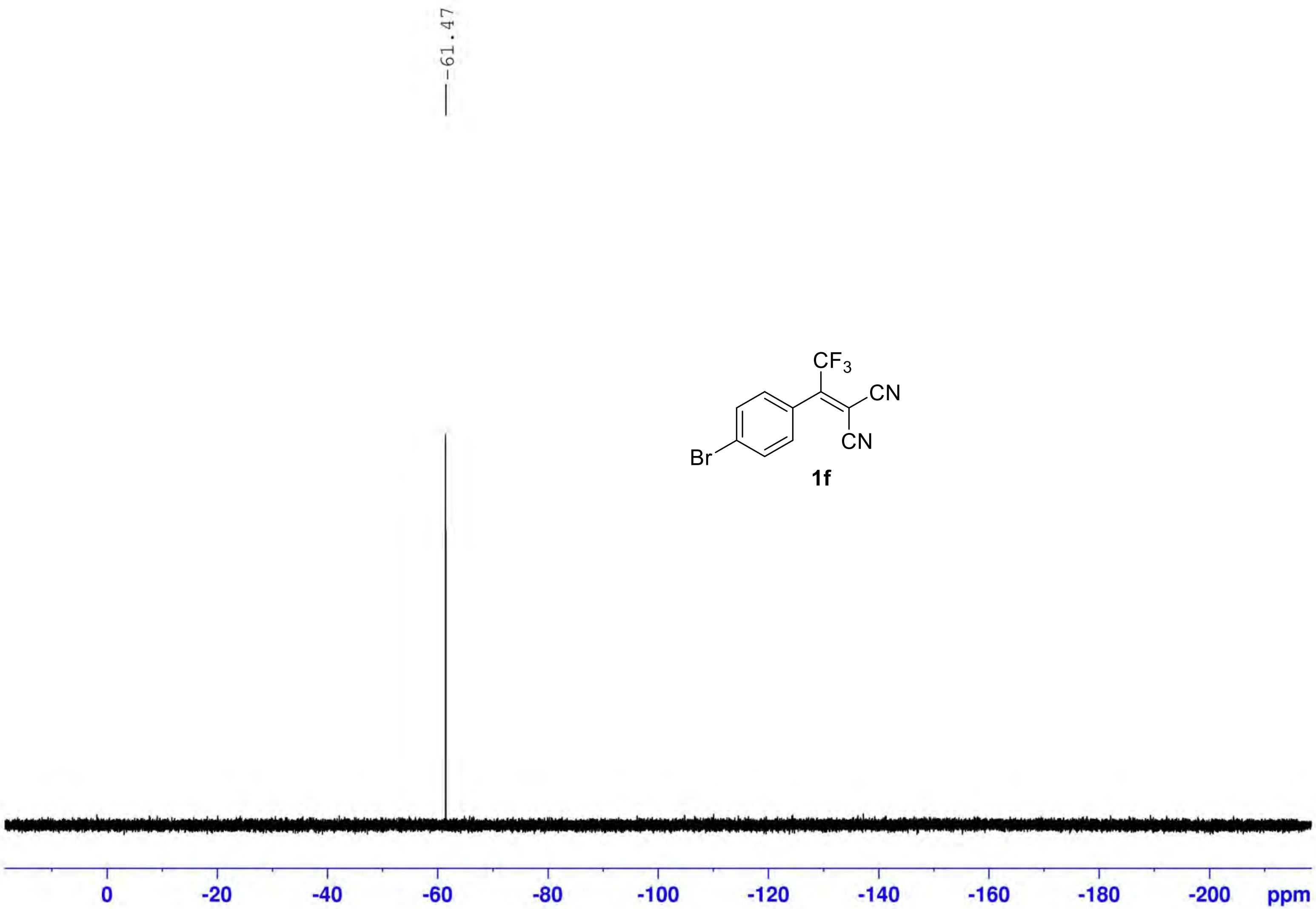


1f

^{13}C NMR in $CDCl_3$ (150 MHz)

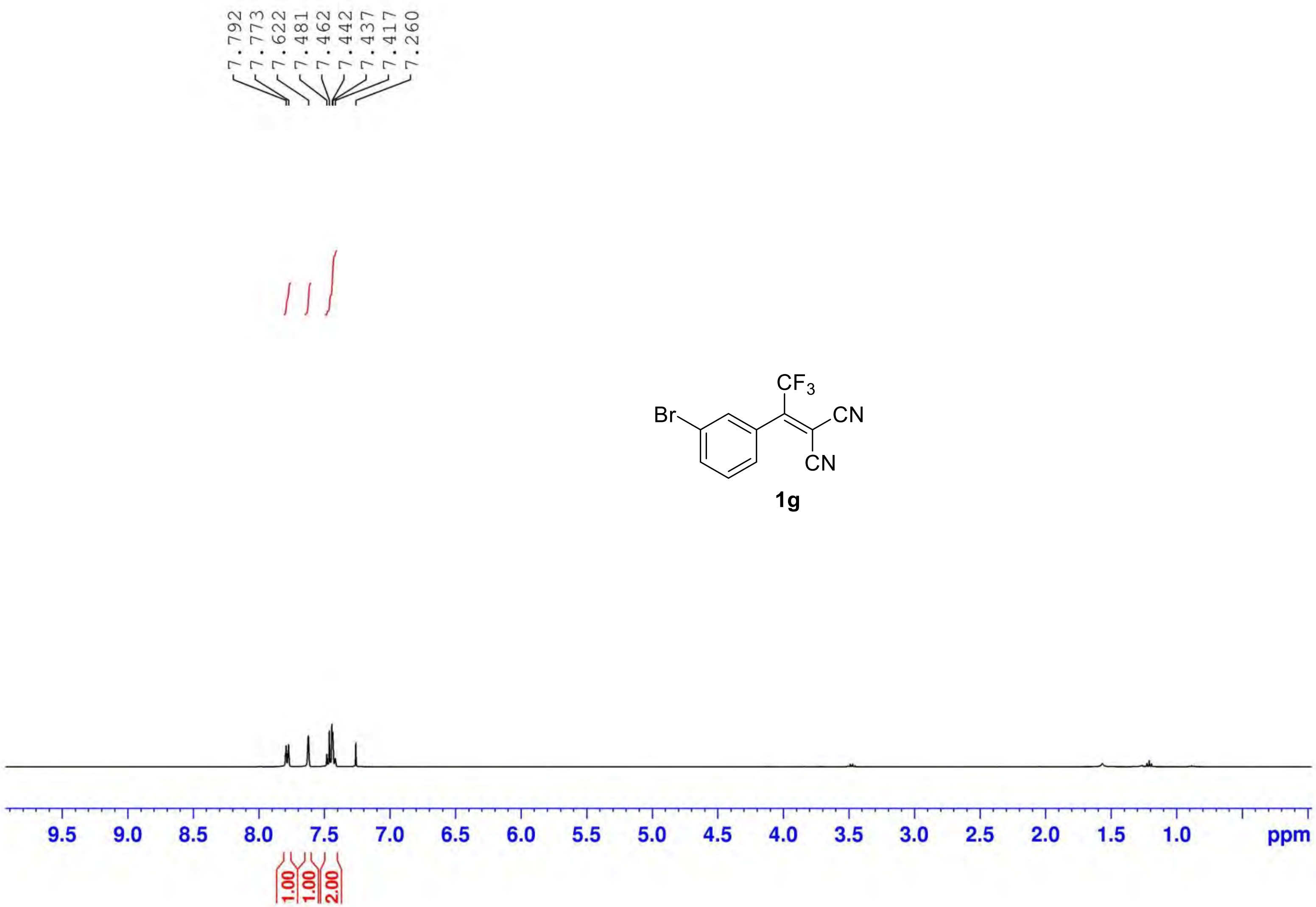


^{19}F NMR in $CDCl_3$ (376 MHz)

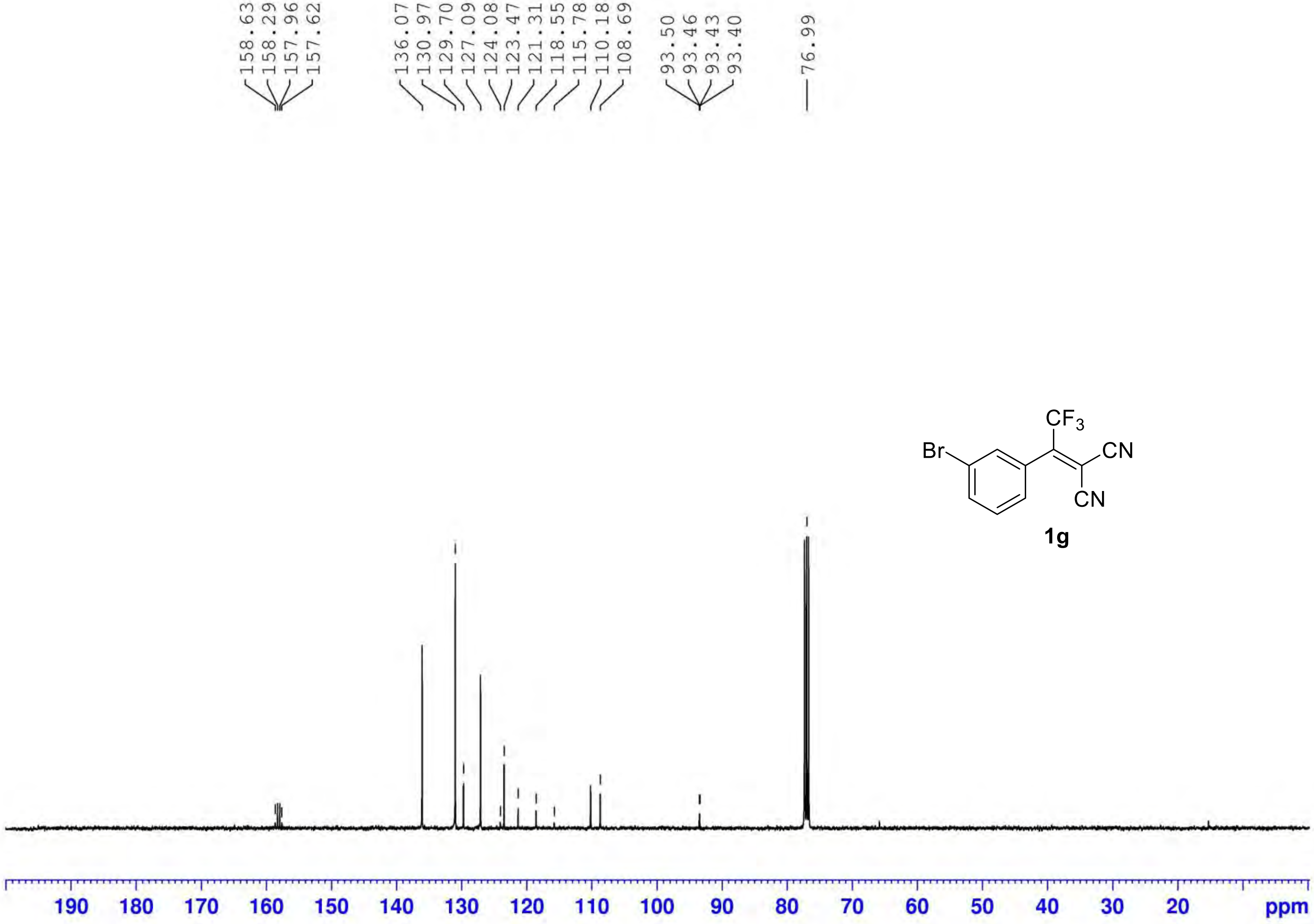


1f

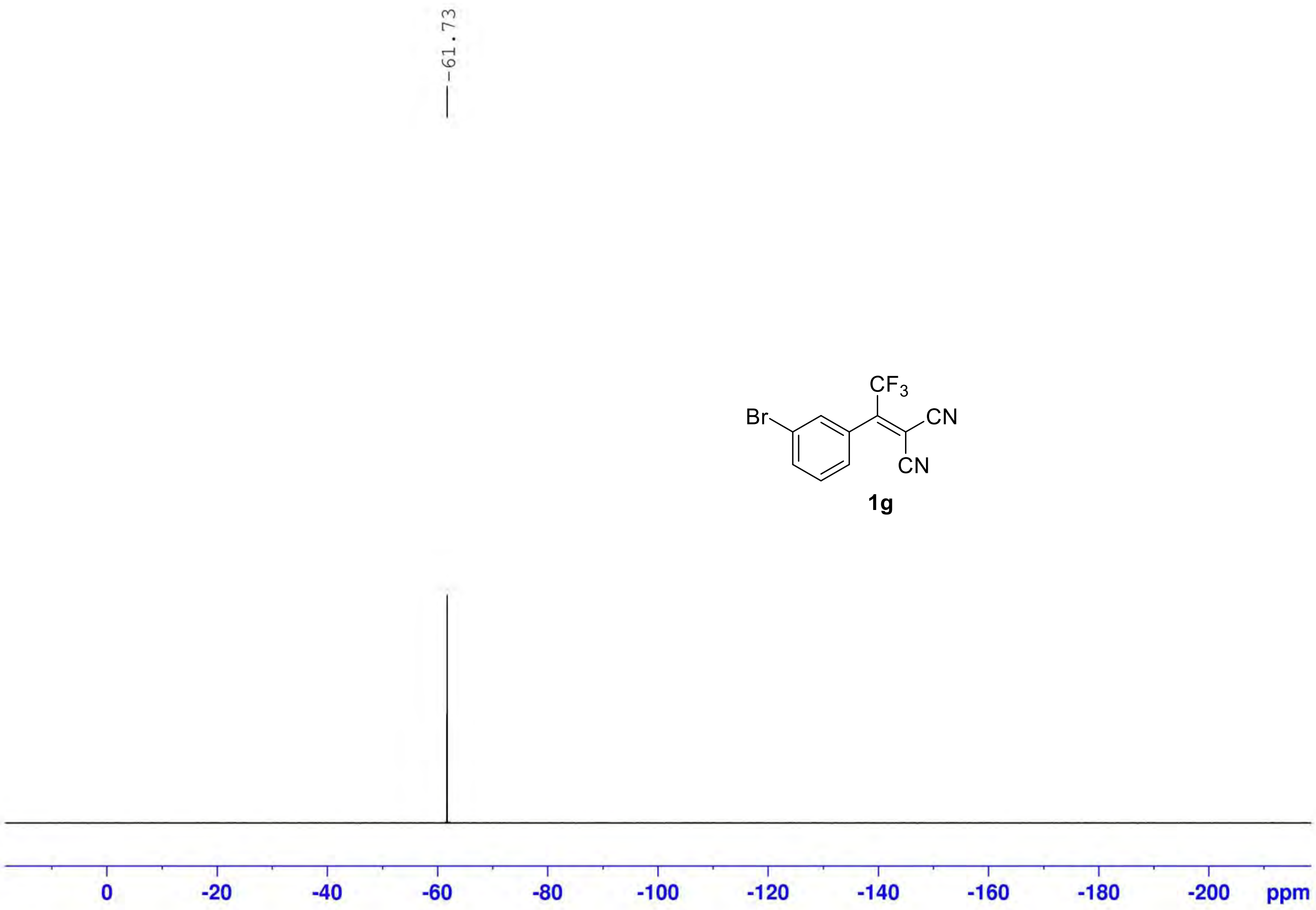
[1]H NMR in $CDCl_3$ (400 MHz)



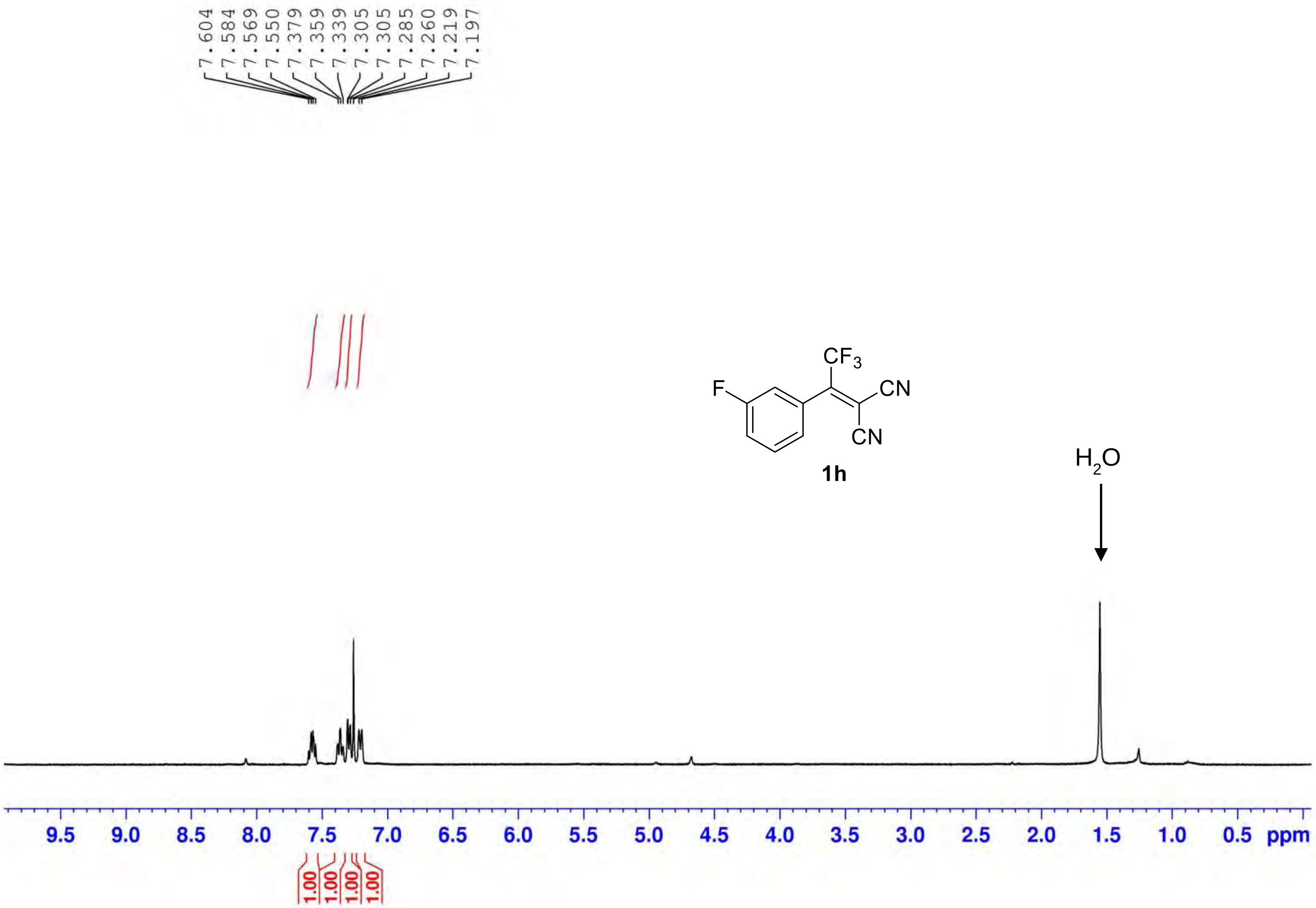
^{13}C NMR in $CDCl_3$ (100 MHz)



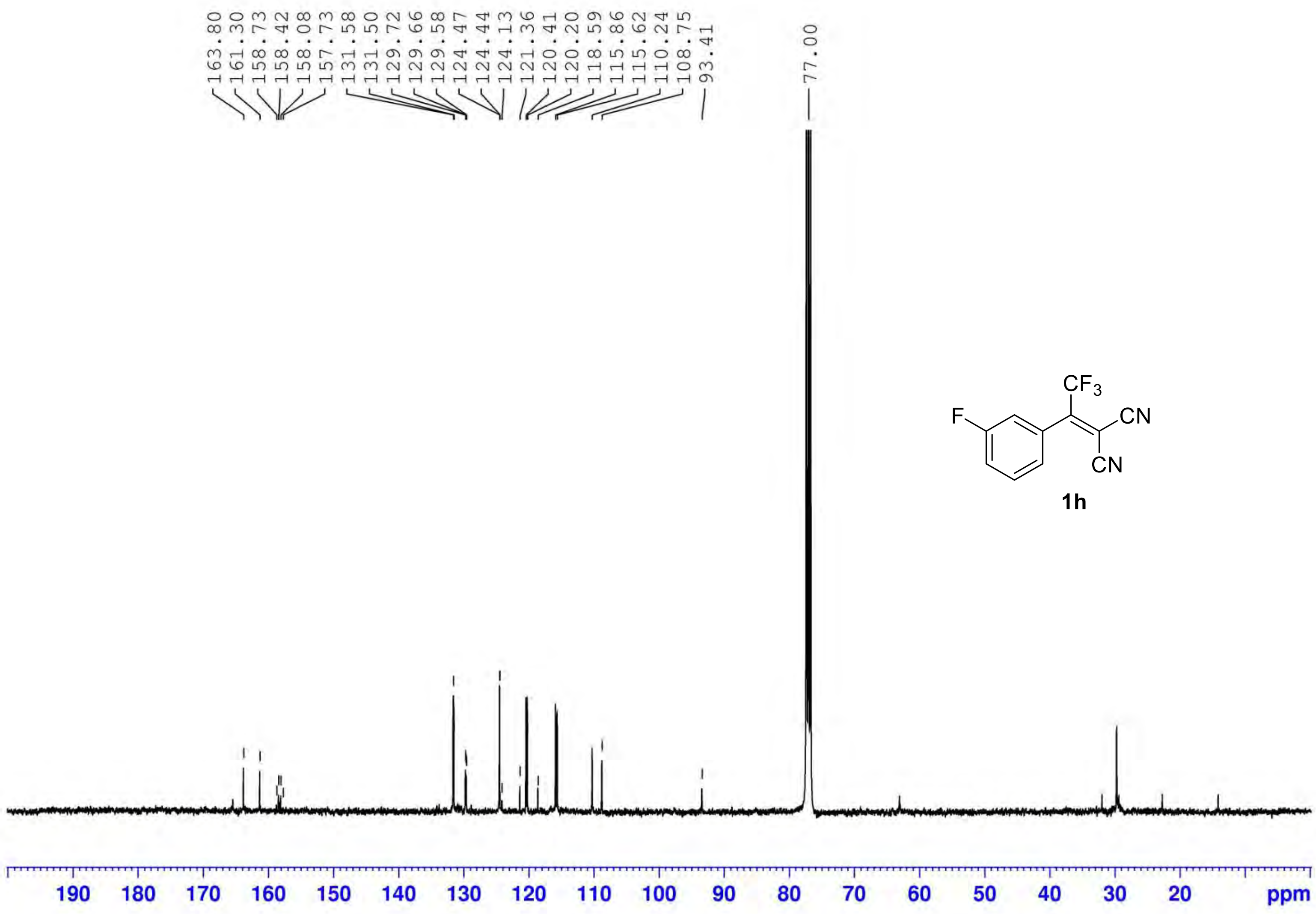
^{19}F NMR in $CDCl_3$ (376 MHz)



[1]H NMR in $CDCl_3$ (400 MHz)

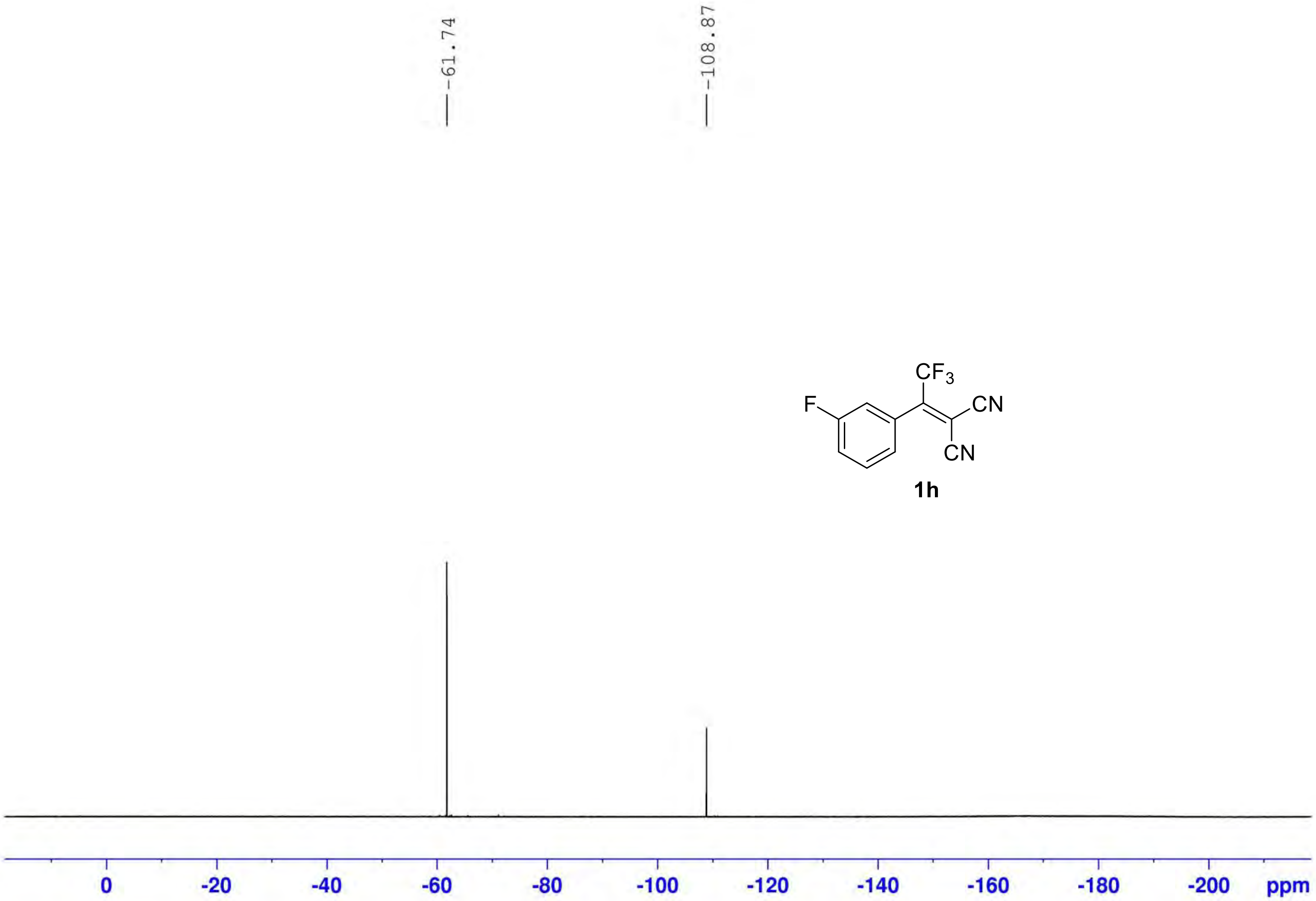


^{13}C NMR in $CDCl_3$ (100 MHz)

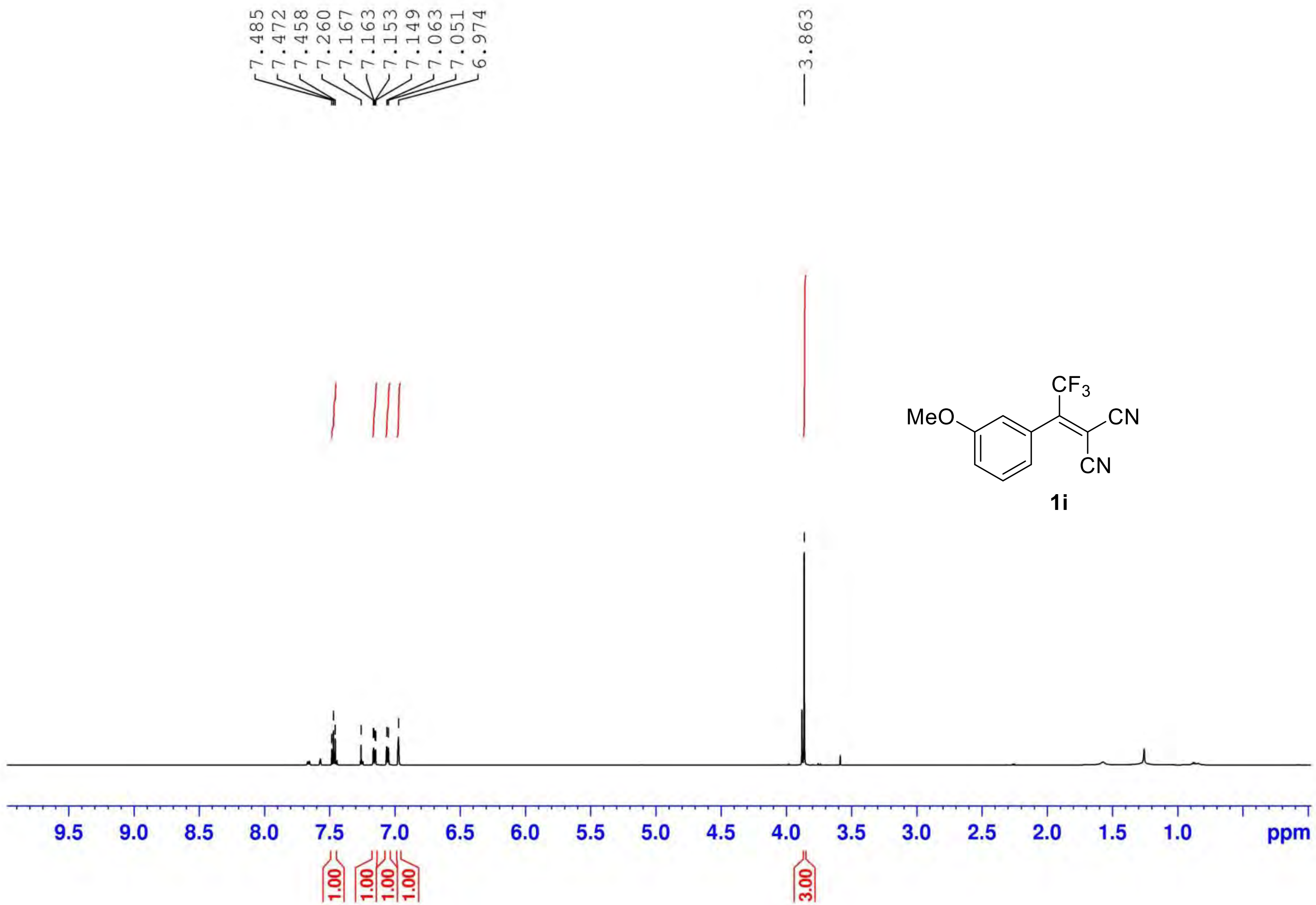


1h

^{19}F NMR in $CDCl_3$ (376 MHz)

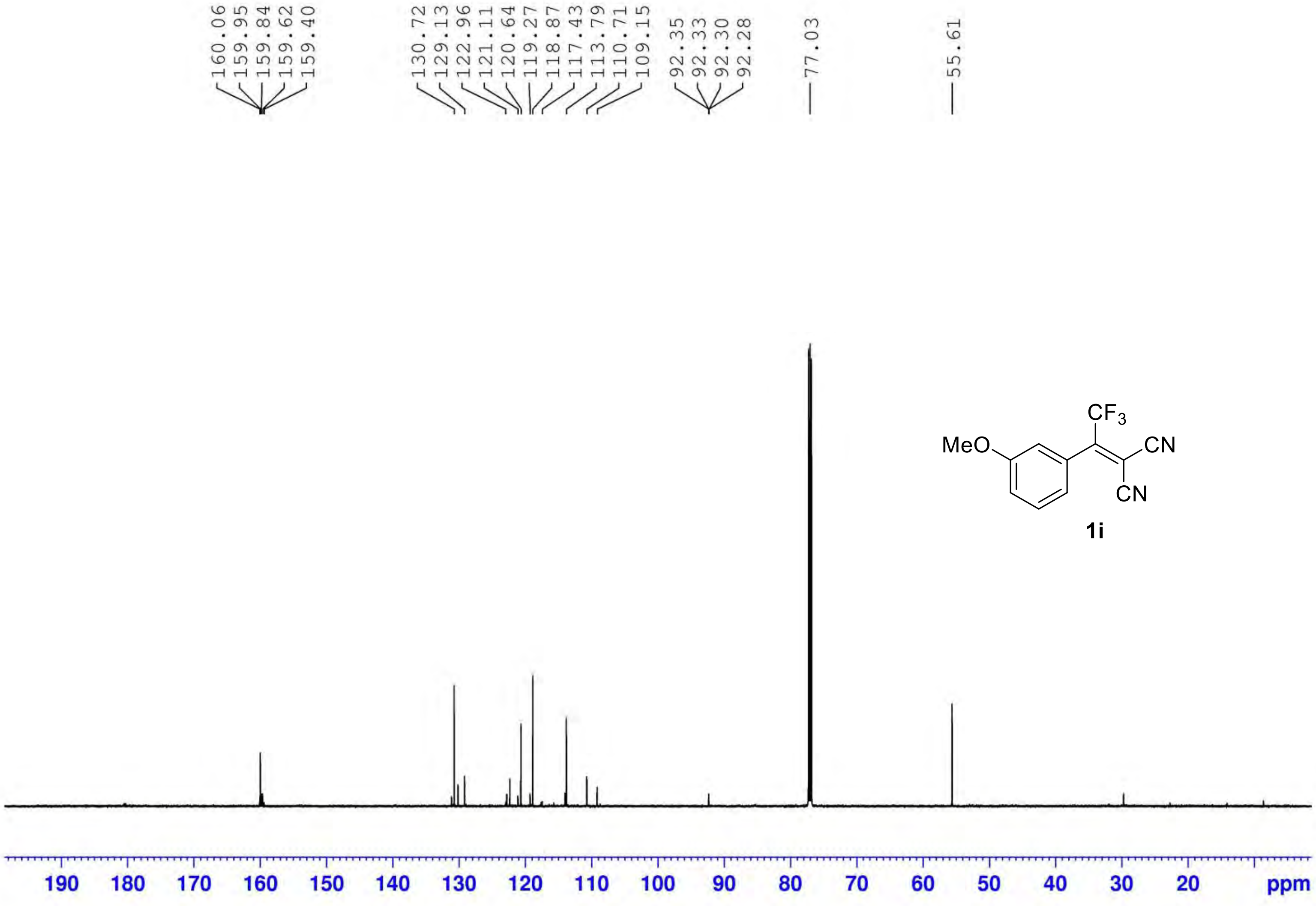


[1]H NMR in $CDCl_3$ (600 MHz)



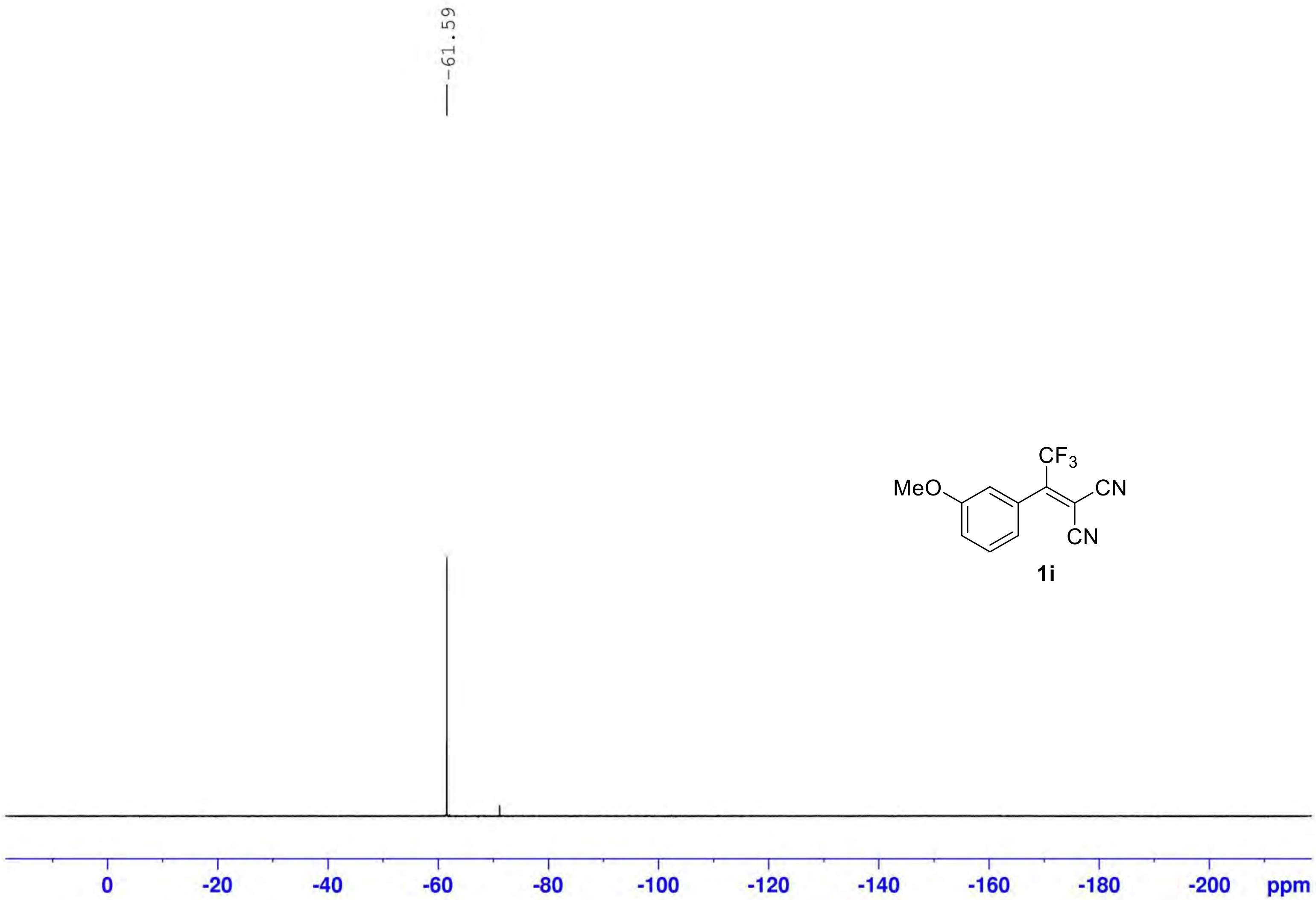
1i

^{13}C NMR in $CDCl_3$ (150 MHz)

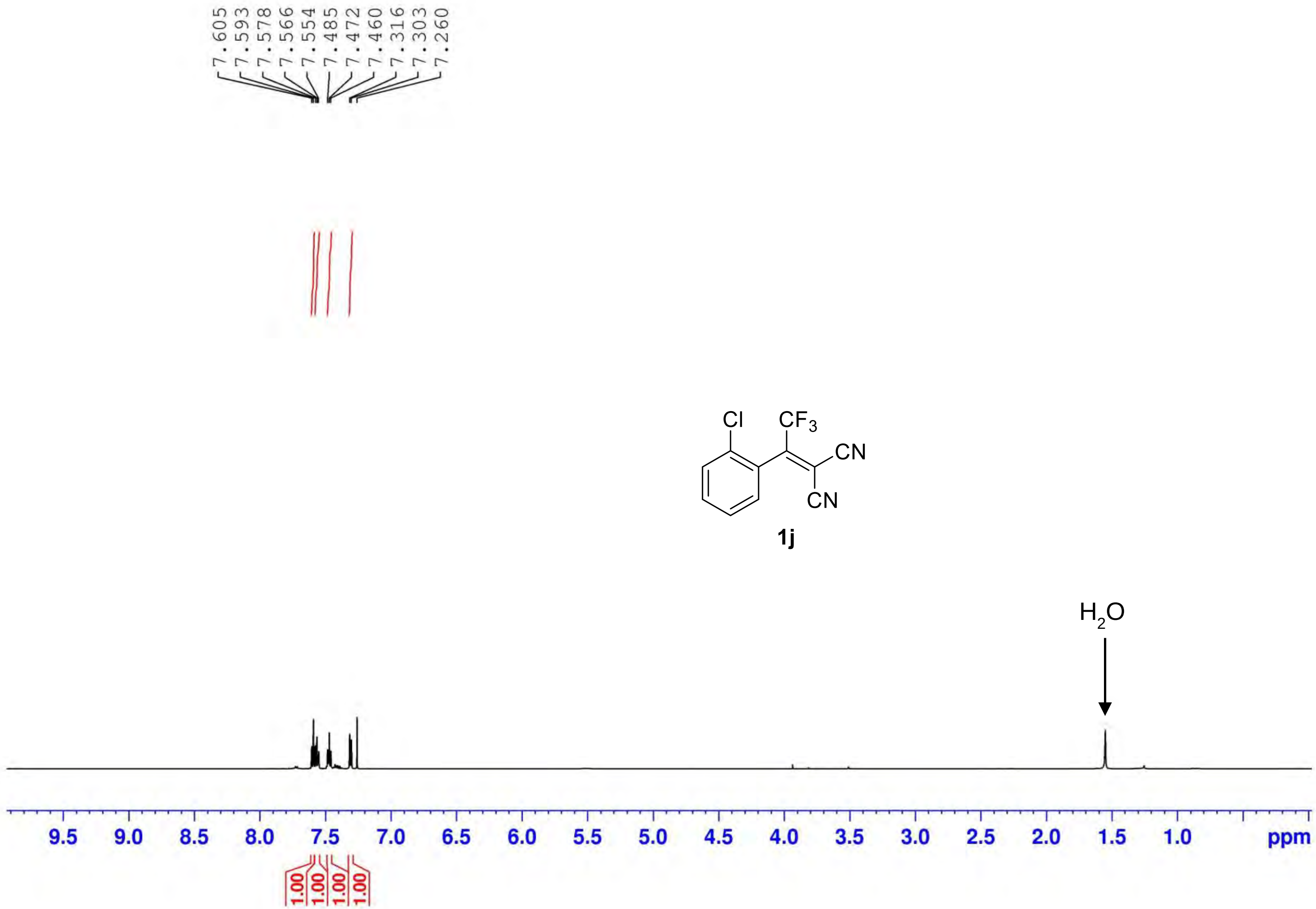


1i

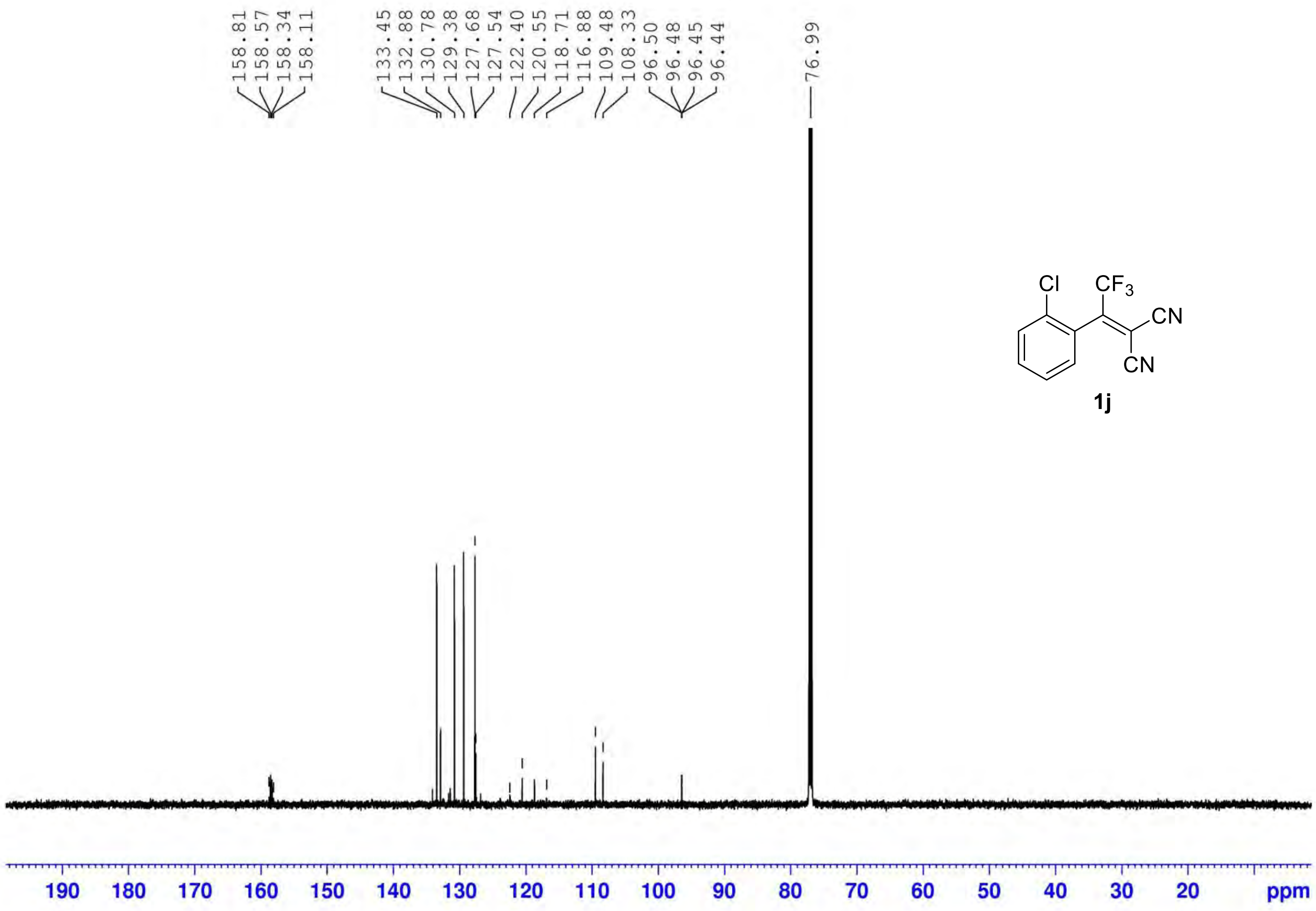
^{19}F NMR in $CDCl_3$ (376 MHz)



[1]H NMR in $CDCl_3$ (600 MHz)

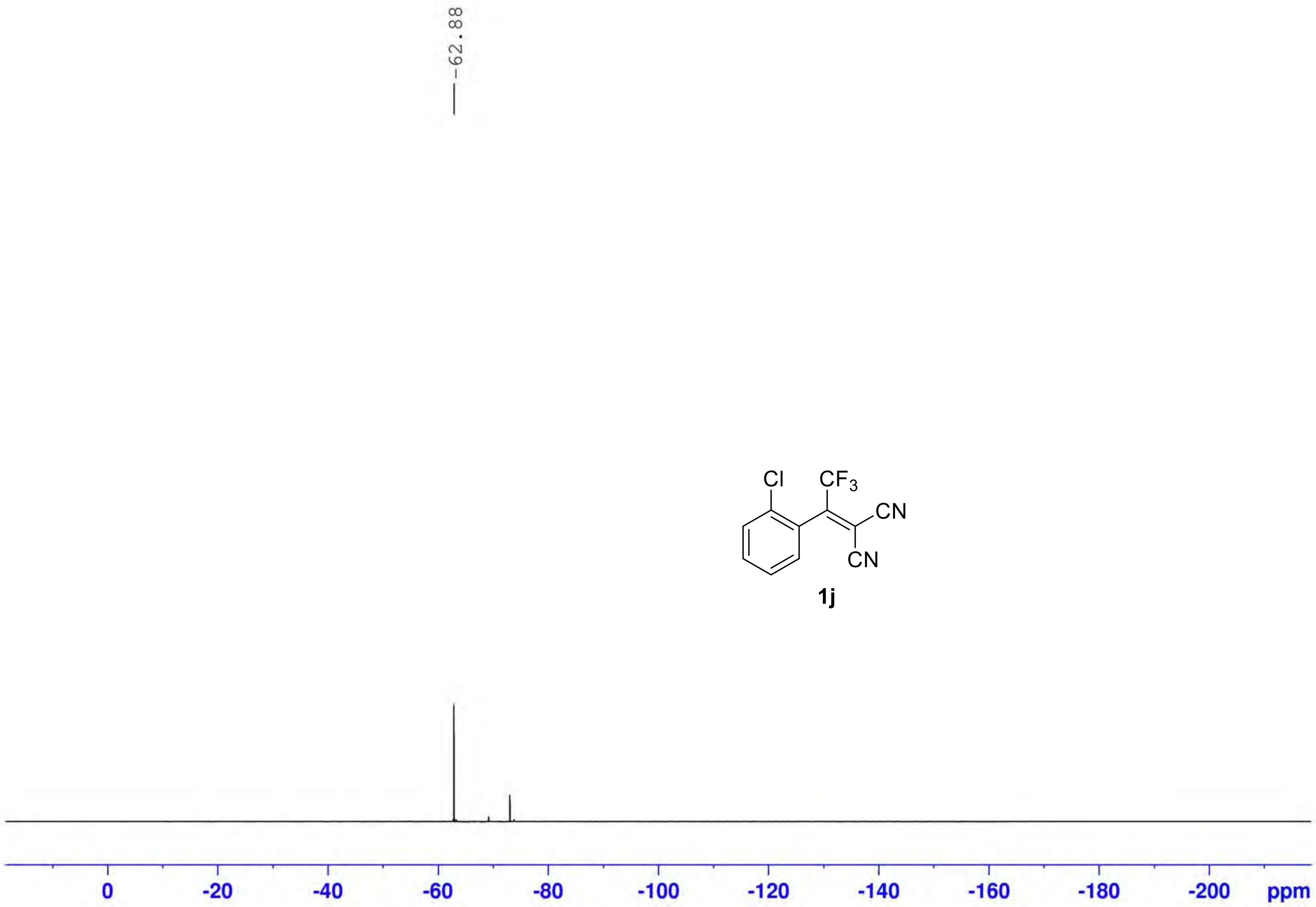


^{13}C NMR in $CDCl_3$ (150 MHz)



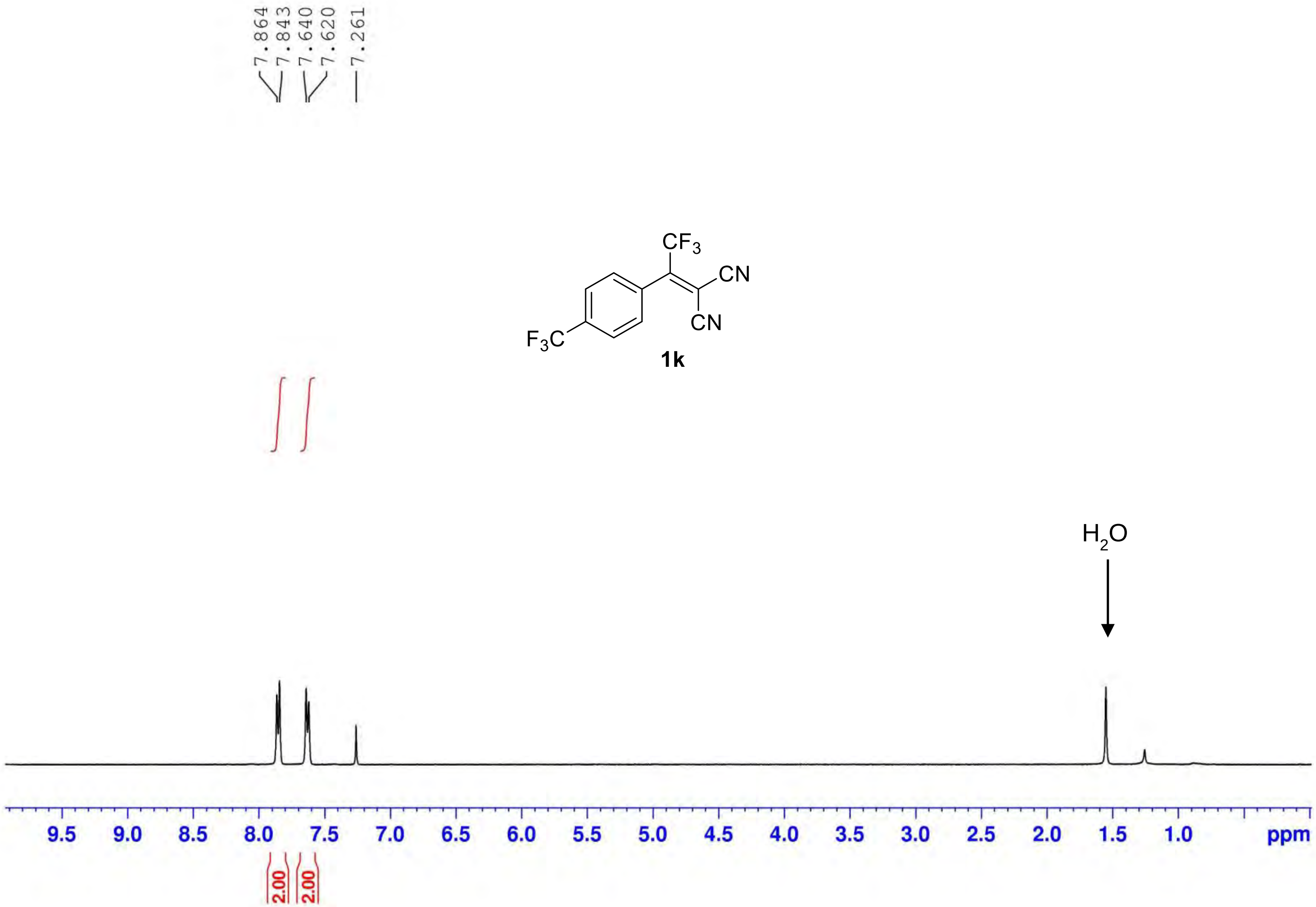
1j

^{19}F NMR in $CDCl_3$ (376 MHz)

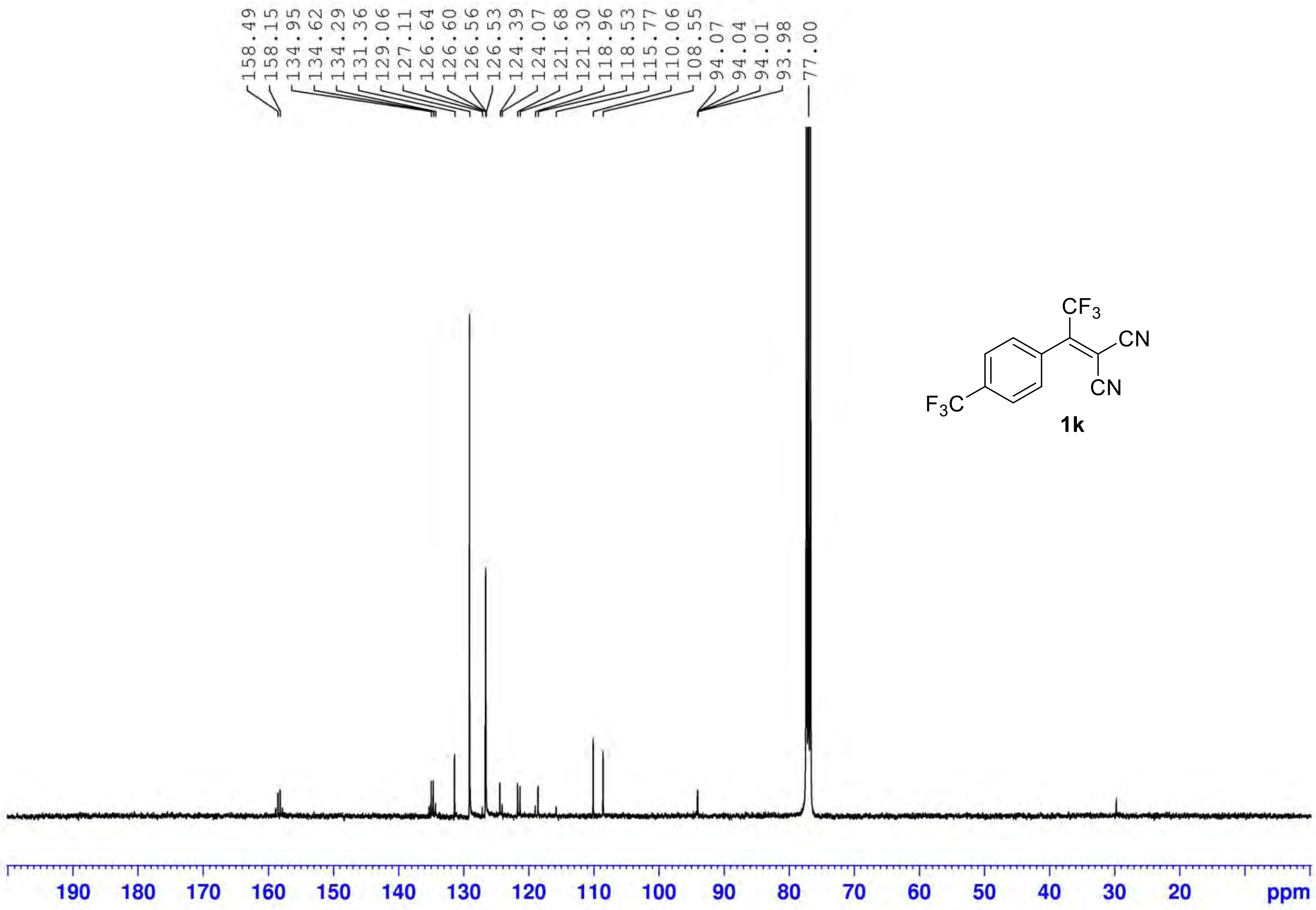


1j

^1H NMR in $CDCl_3$ (400 MHz)

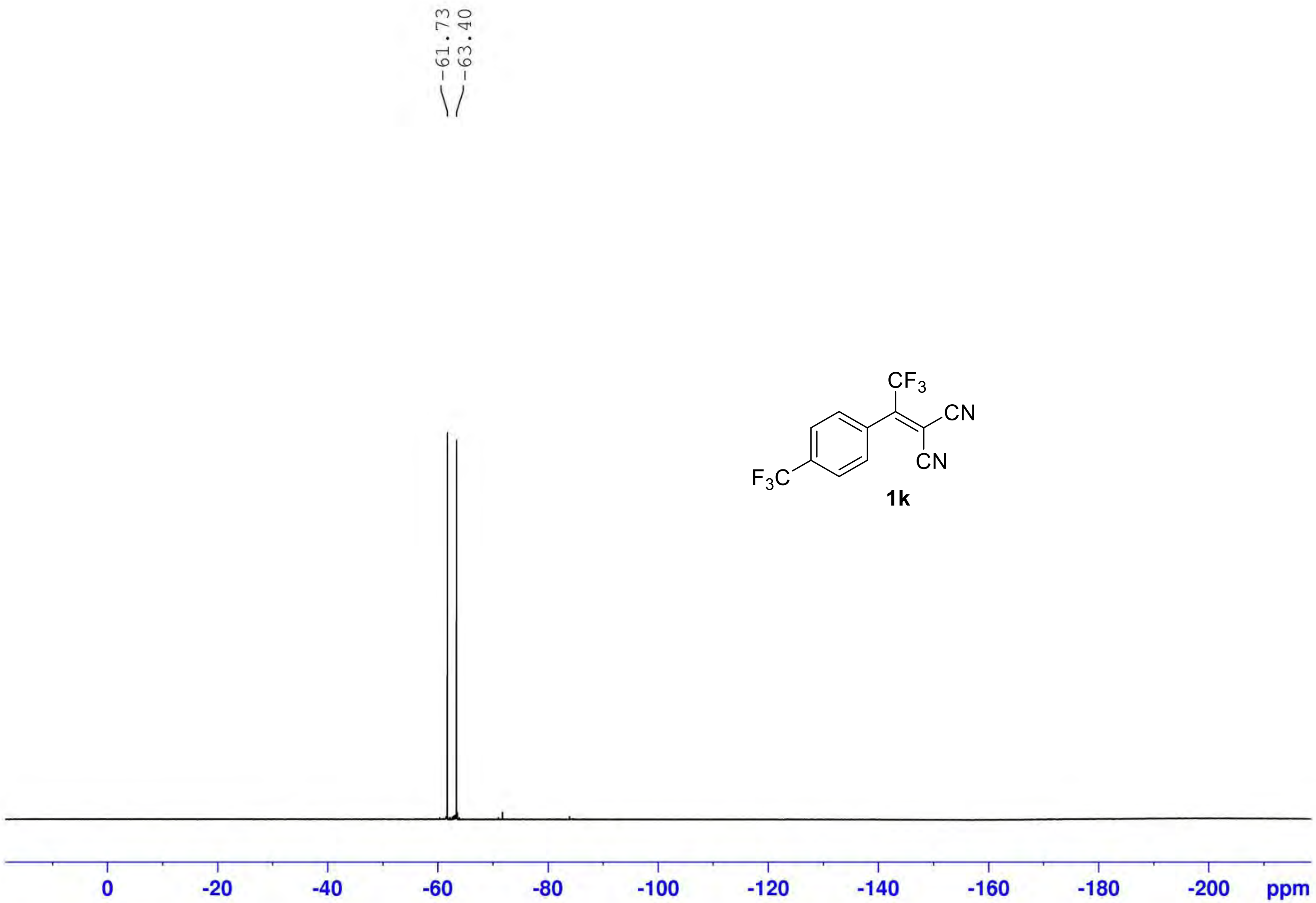


^{13}C NMR in $CDCl_3$ (100 MHz)



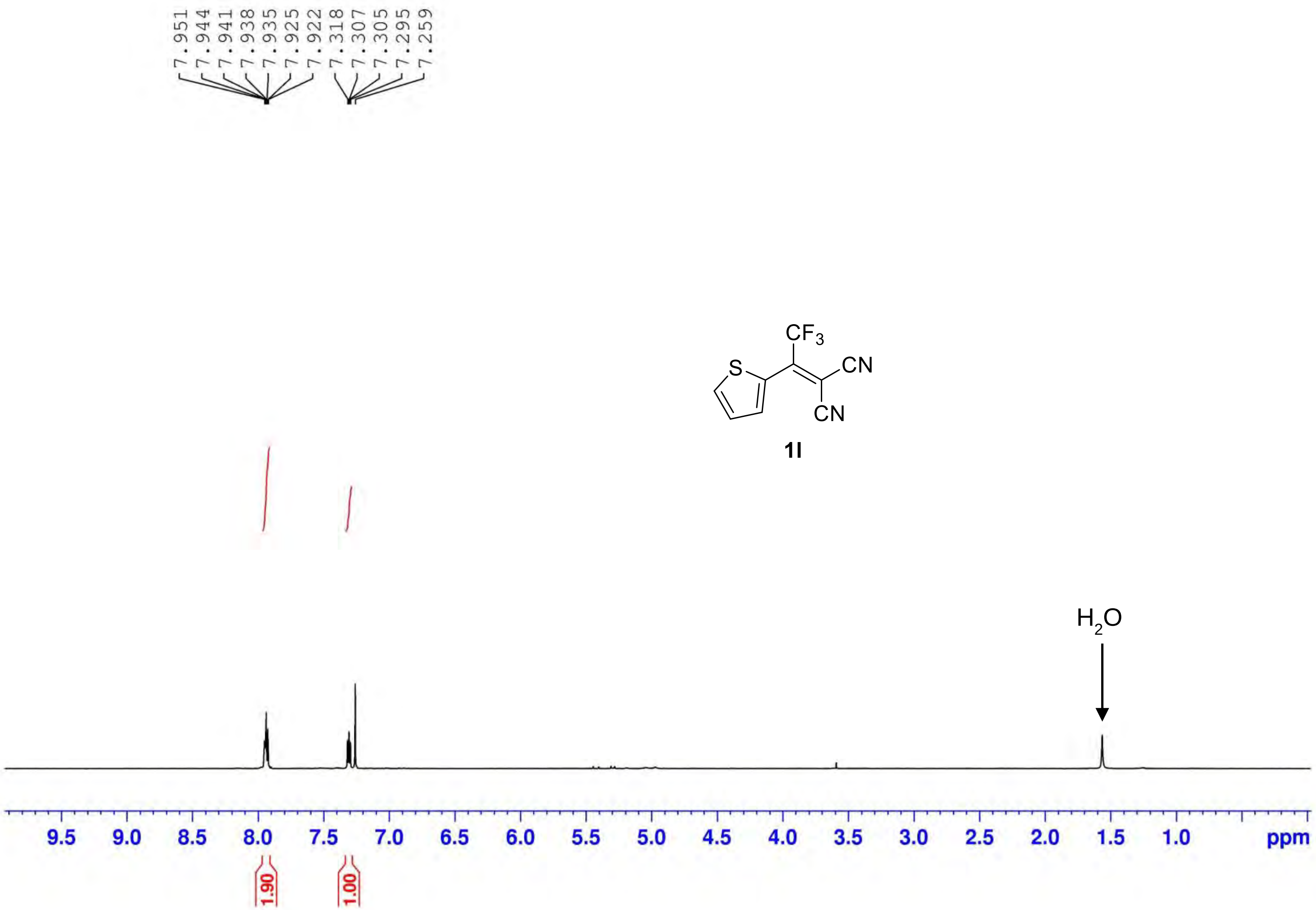
1k

^{19}F NMR in $CDCl_3$ (376 MHz)



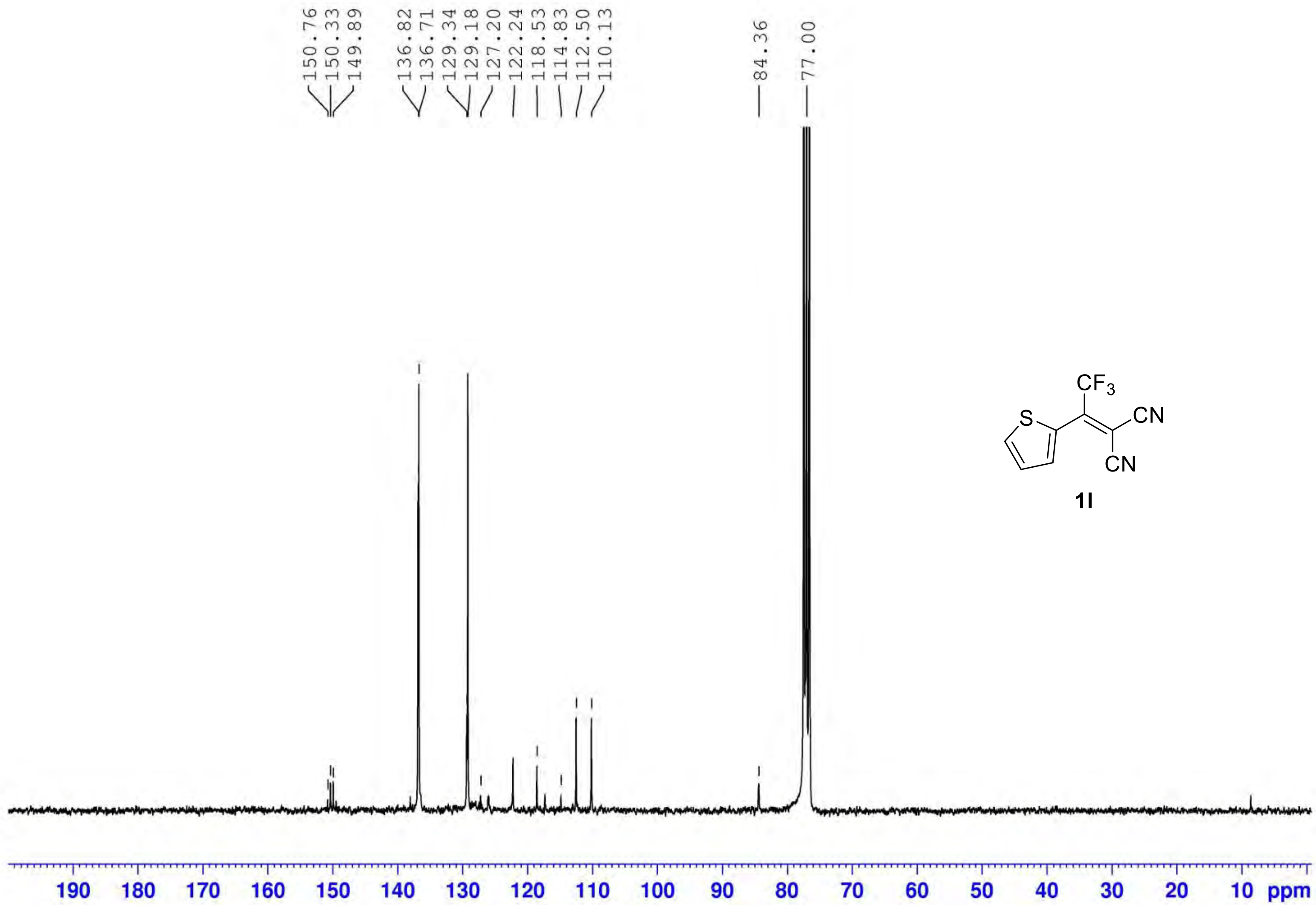
1k

[1]H NMR in $CDCl_3$ (400 MHz)



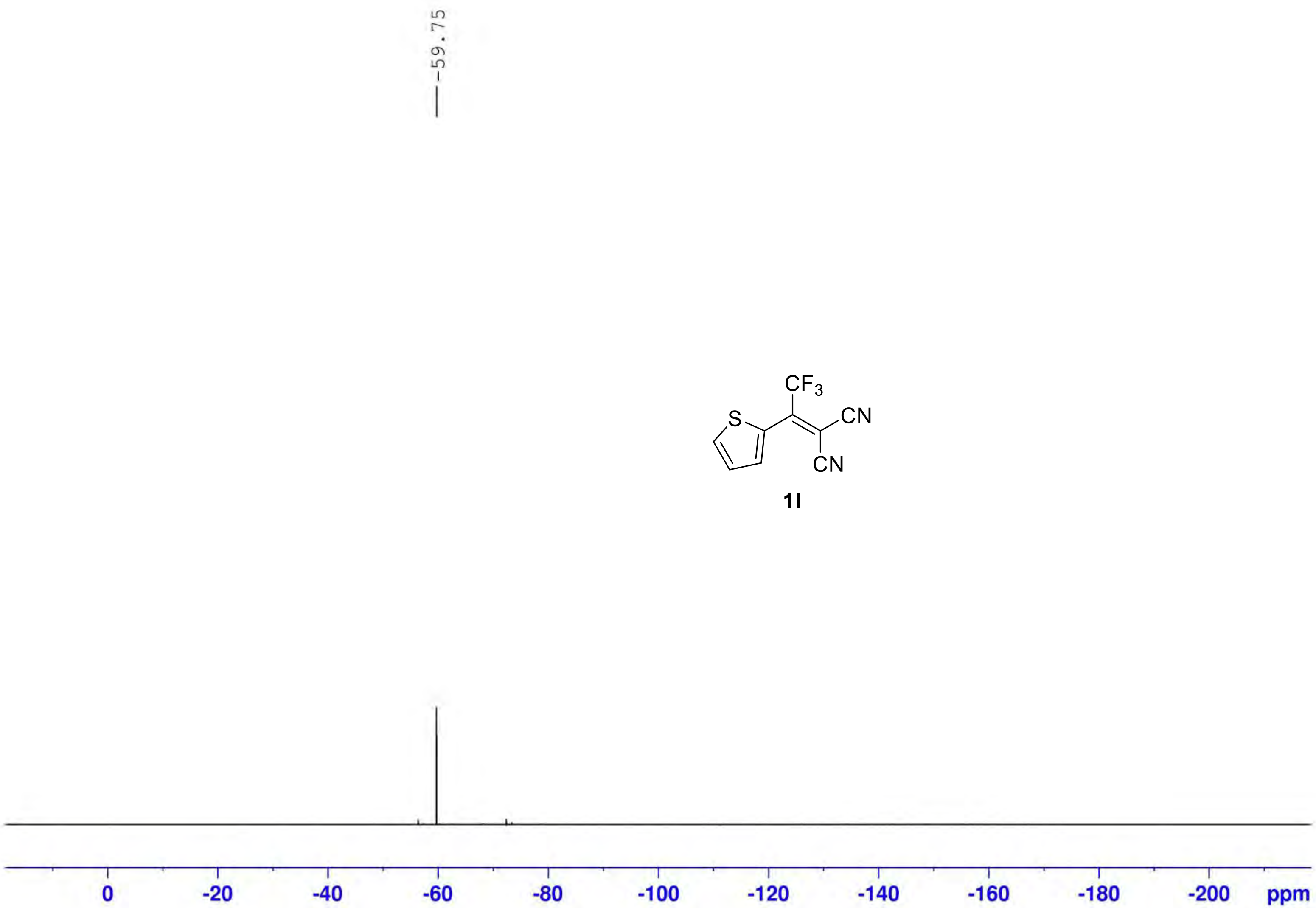
1l

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



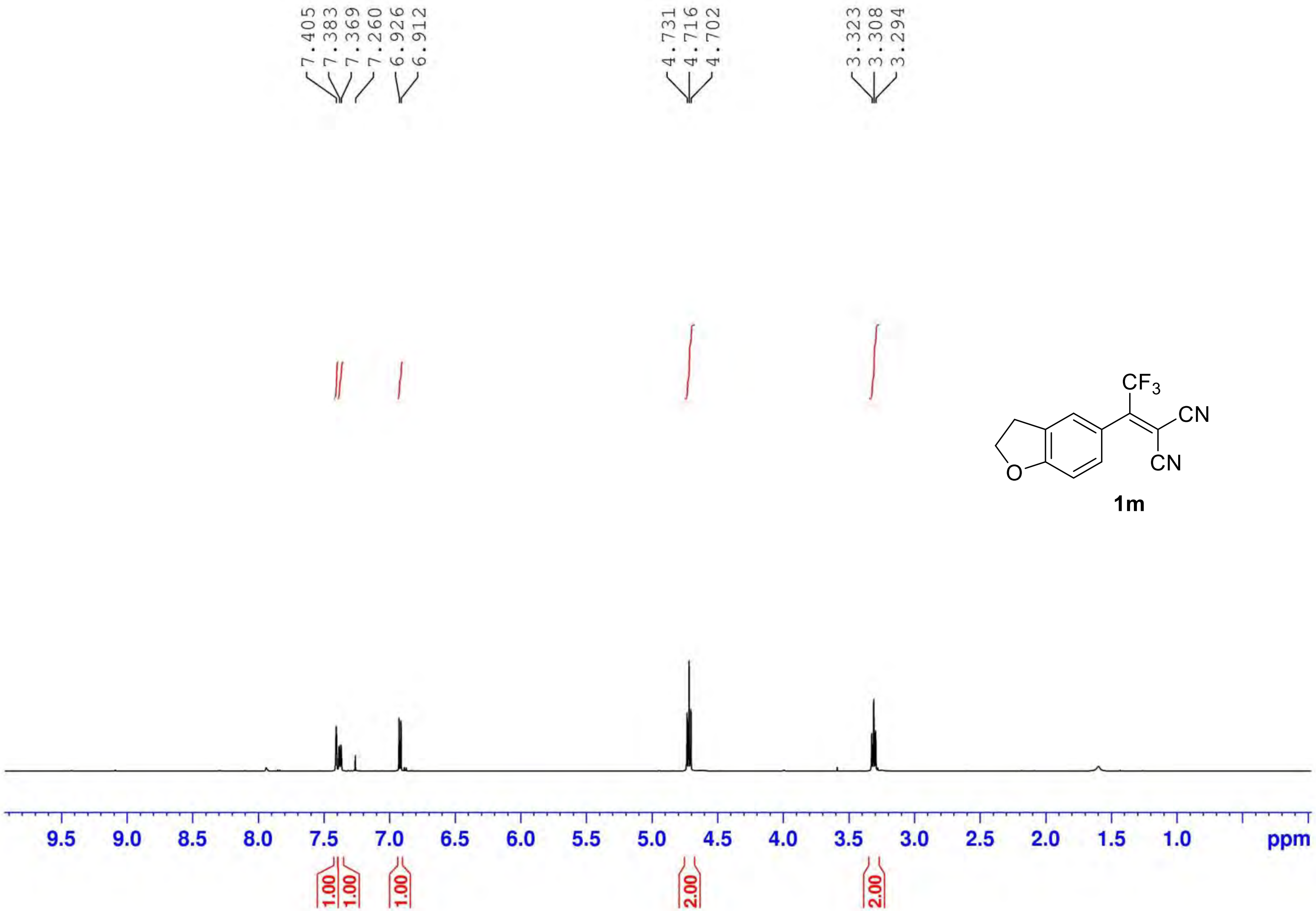
1l

^{19}F NMR in $CDCl_3$ (376 MHz)

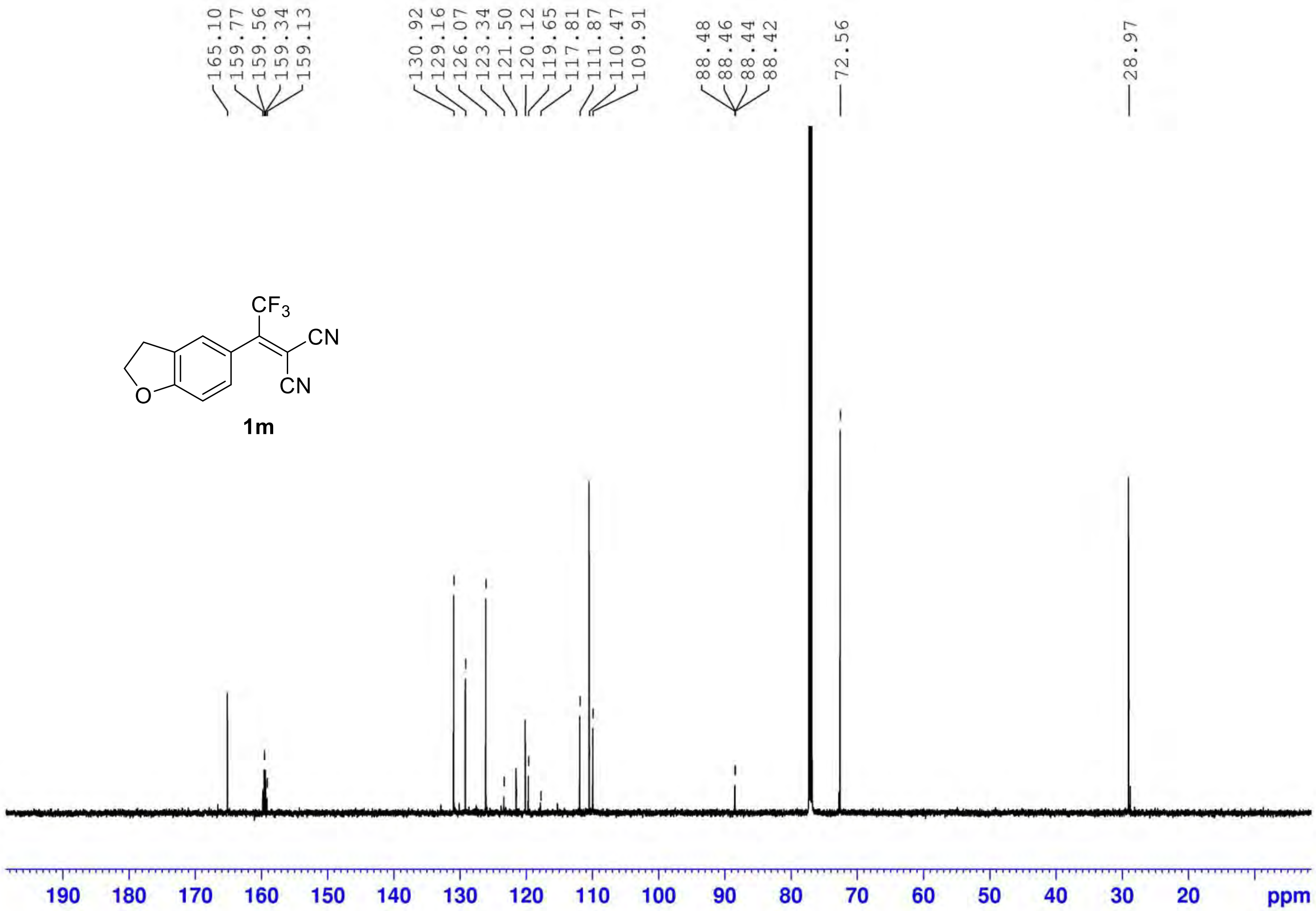


1l

^{1}H NMR in $CDCl_3$ (600 MHz)

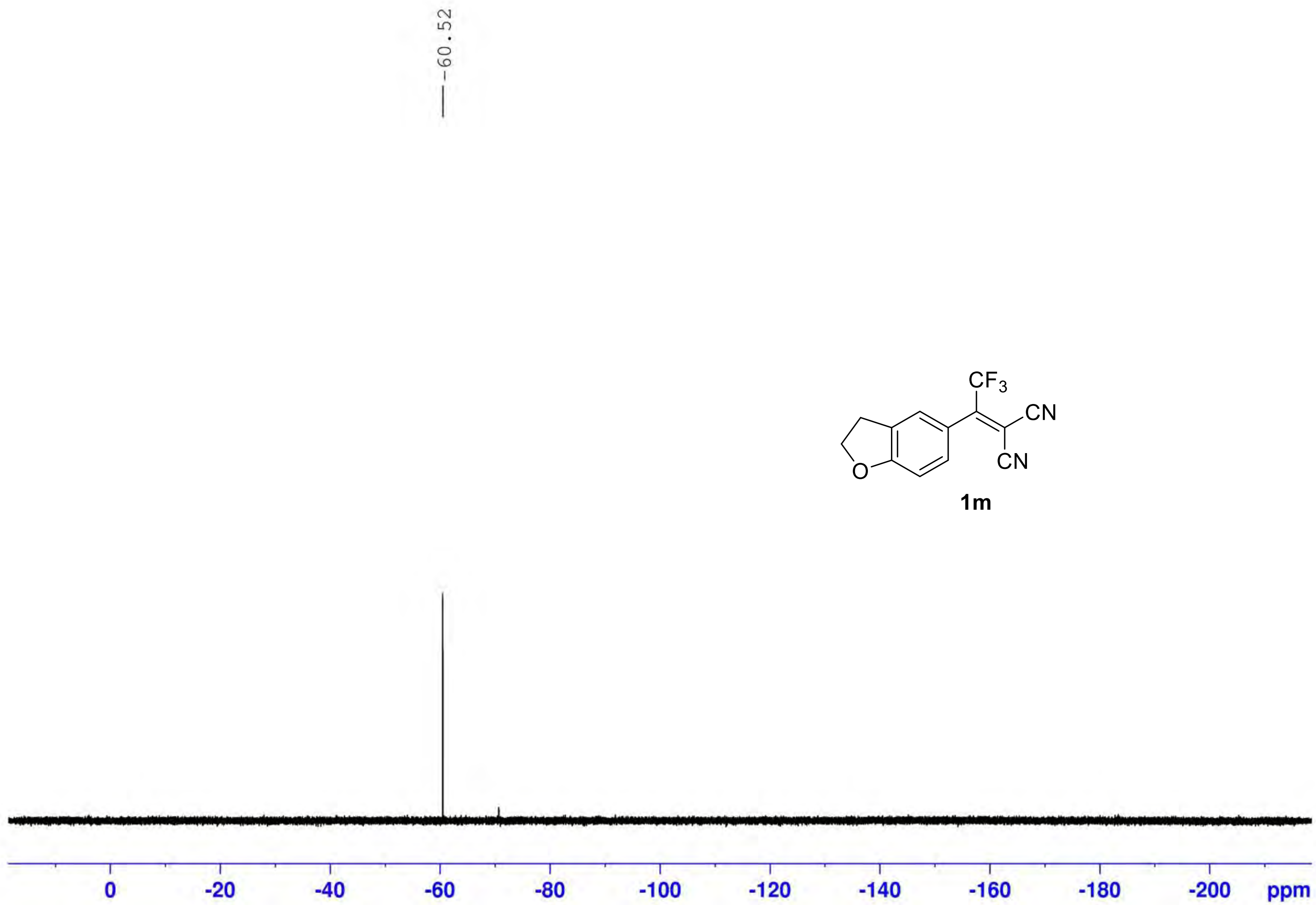


^{13}C NMR in $CDCl_3$ (150 MHz)



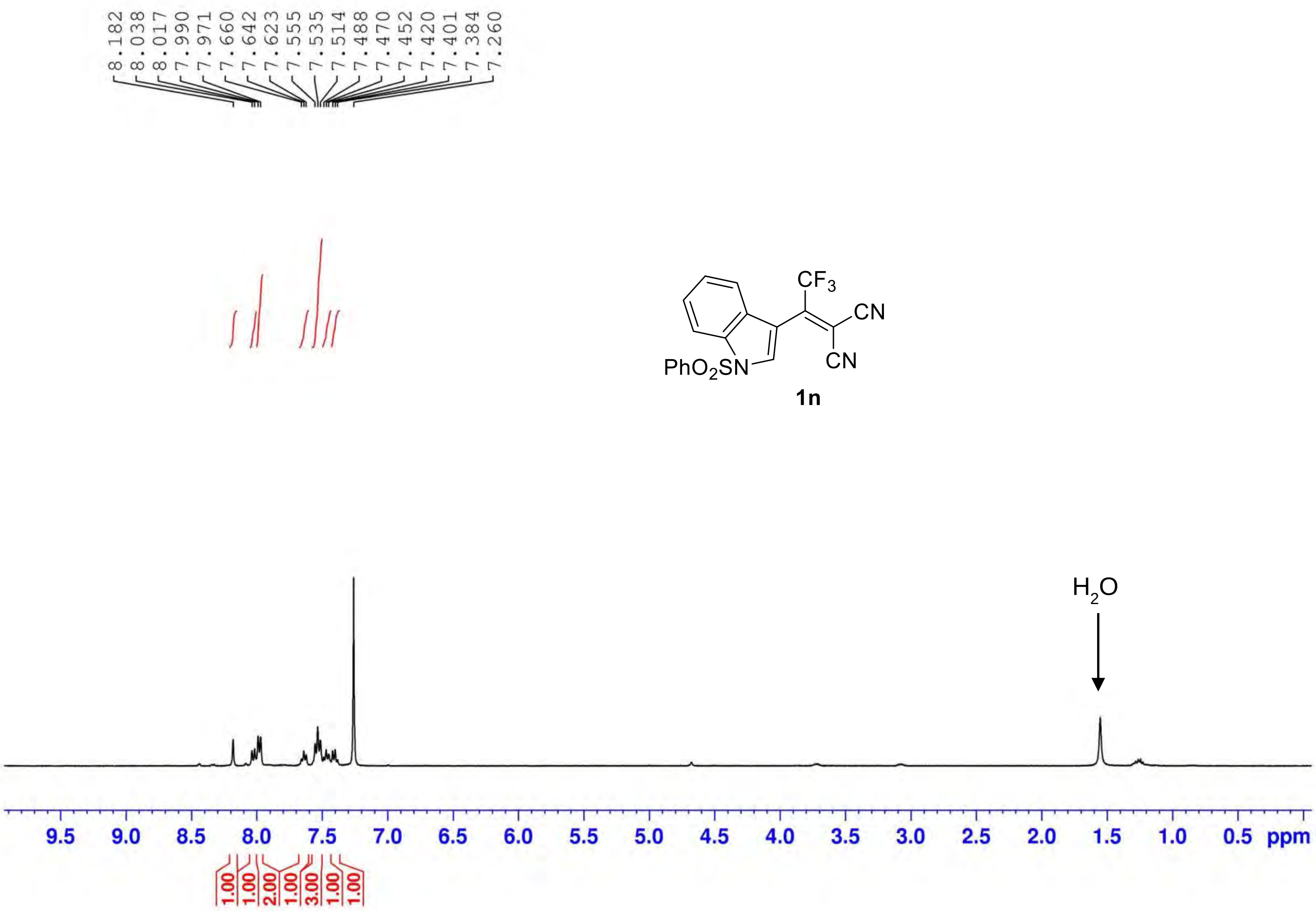
1m

^{19}F NMR in $CDCl_3$ (376 MHz)

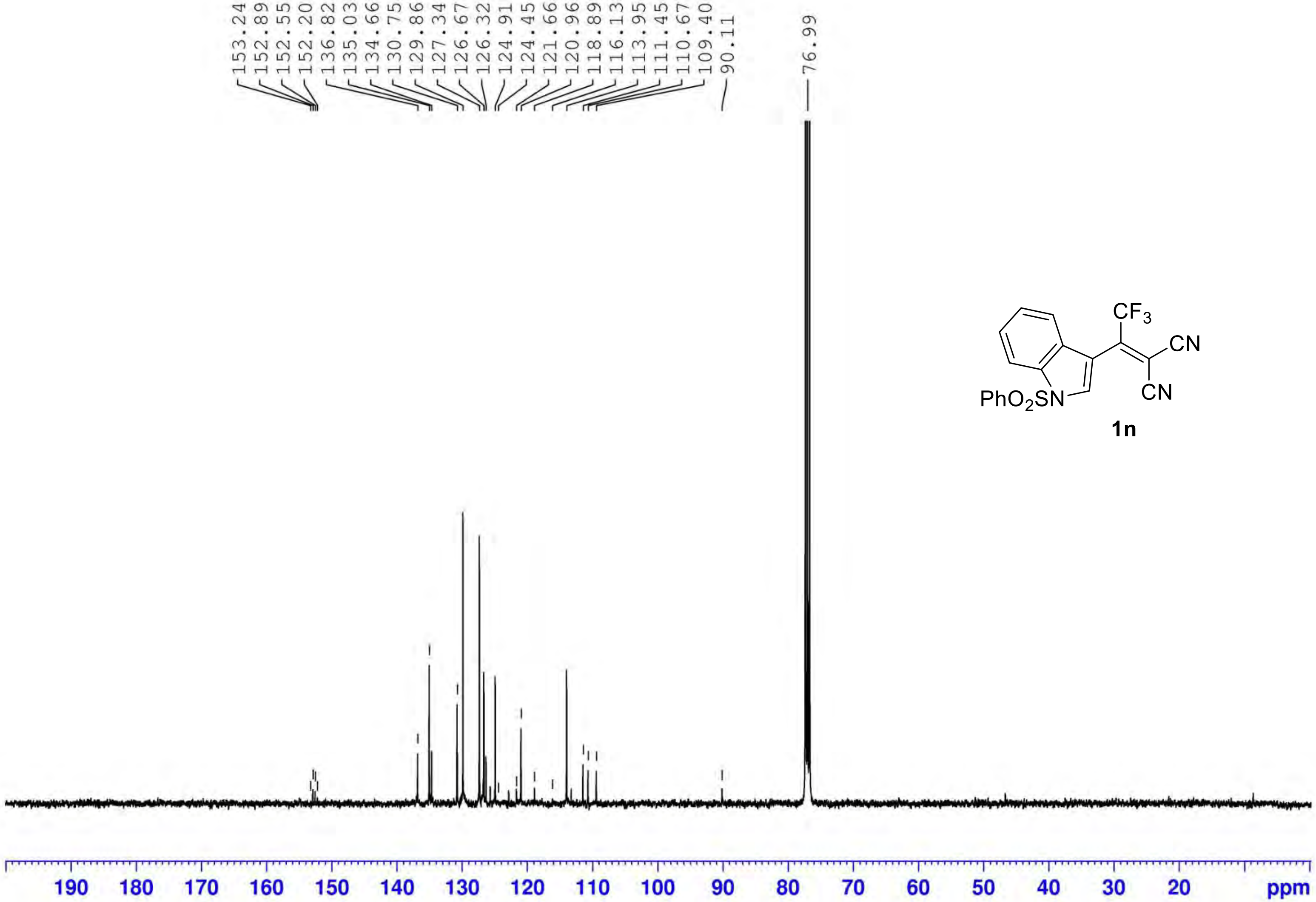


1m

^{1}H NMR in $CDCl_3$ (400 MHz)

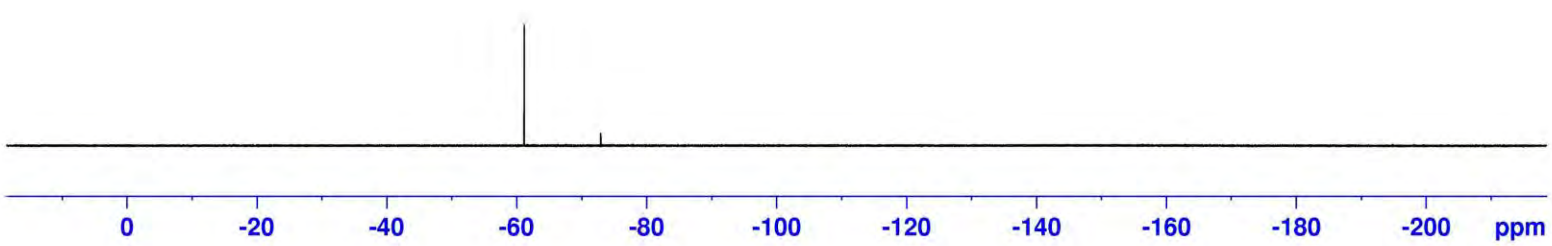


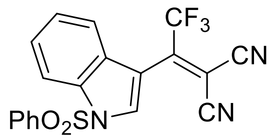
^{13}C NMR in $CDCl_3$ (100 MHz)



1n

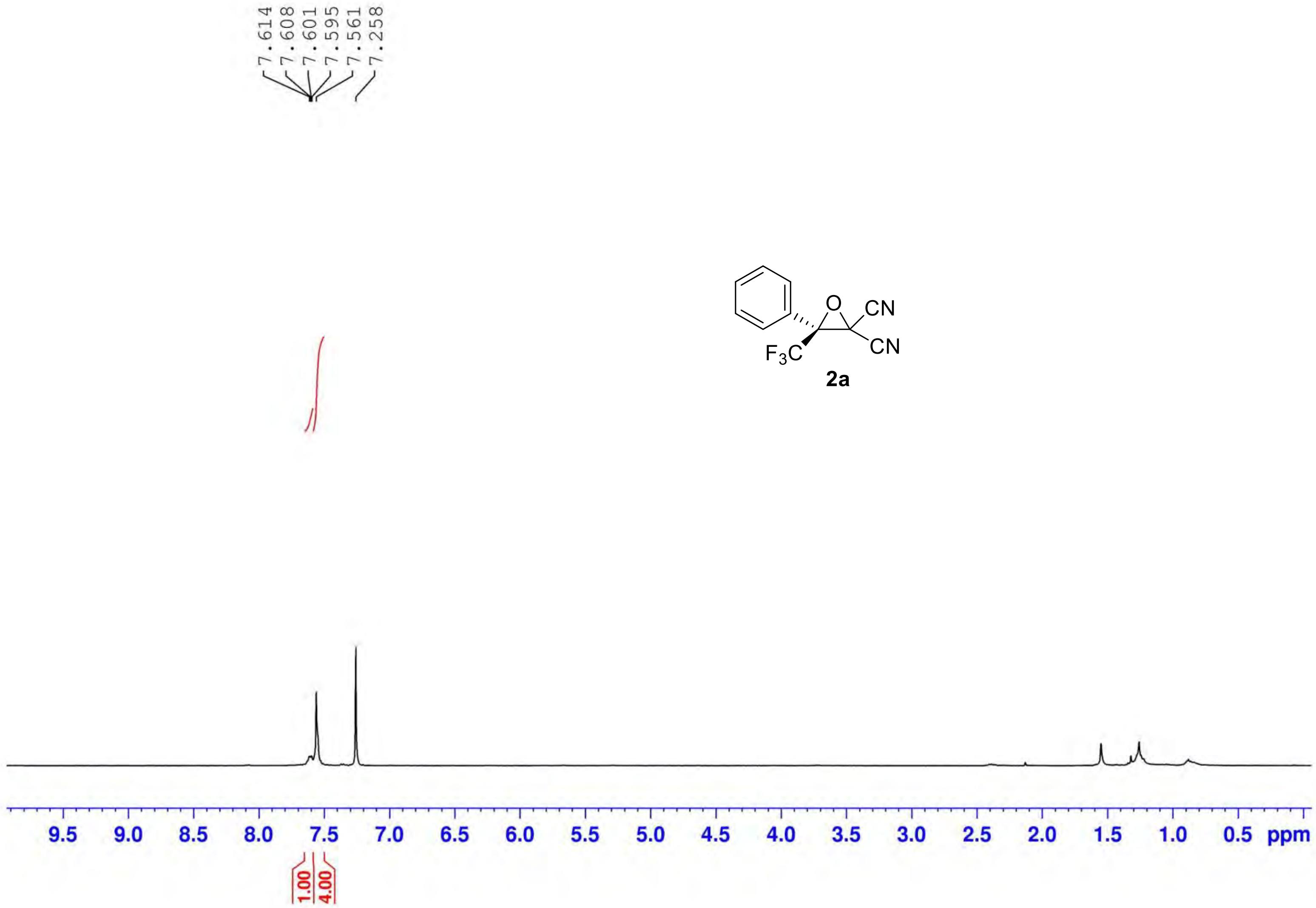
^{19}F NMR in $CDCl_3$ (376 MHz)





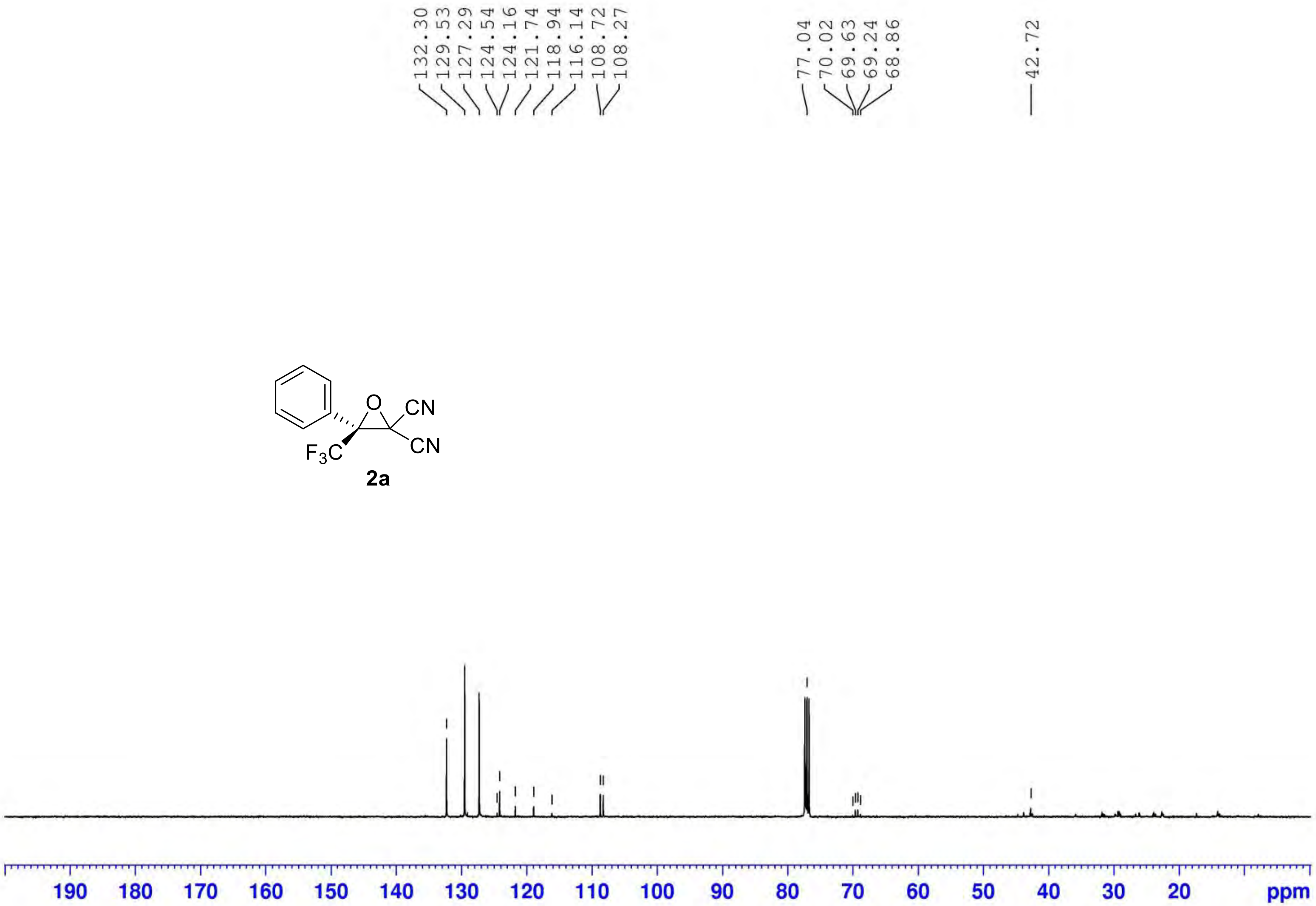
1n

^{1}H NMR in $CDCl_3$ (400 MHz)

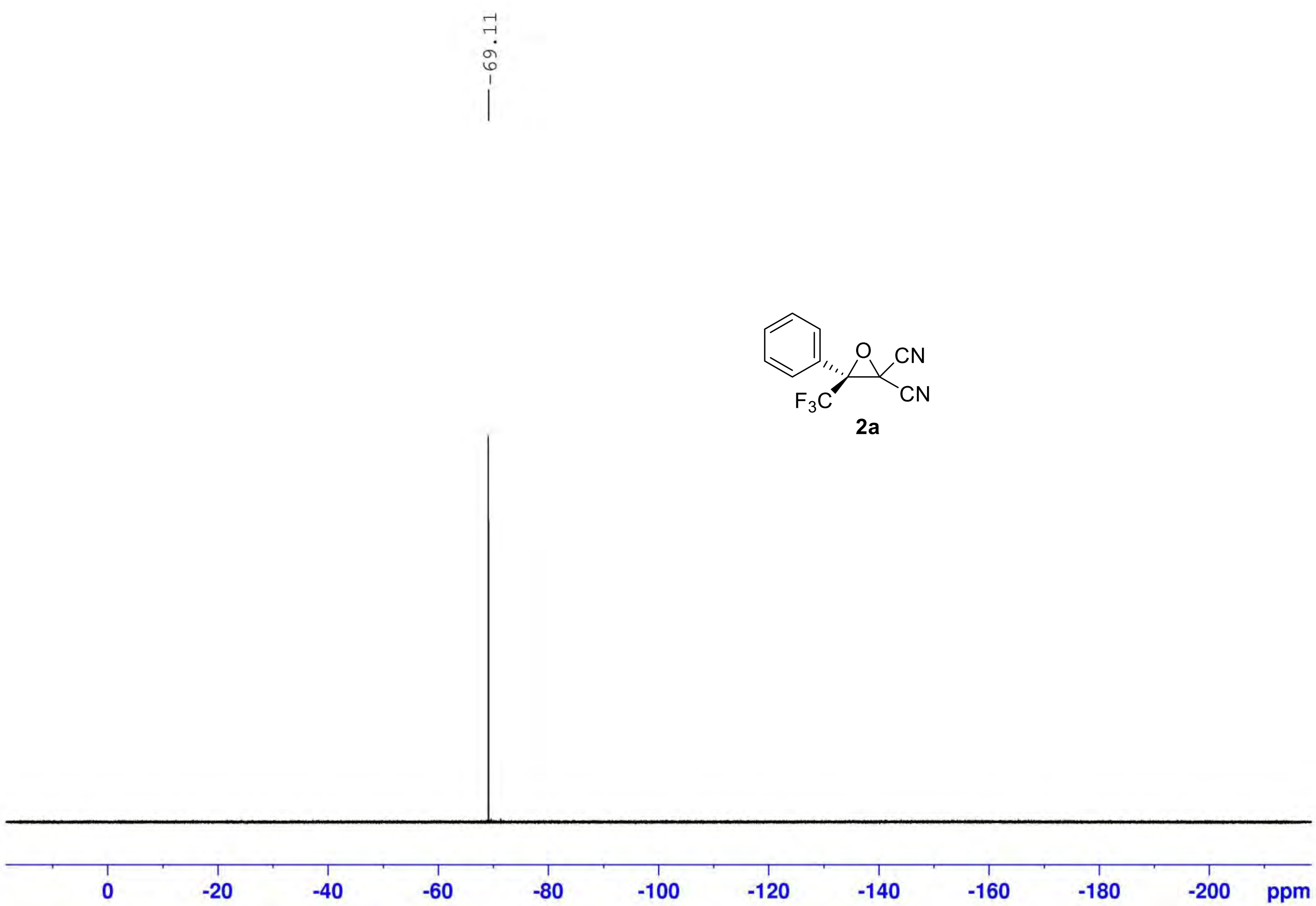


2a

^{13}C NMR in $CDCl_3$ (100 MHz)

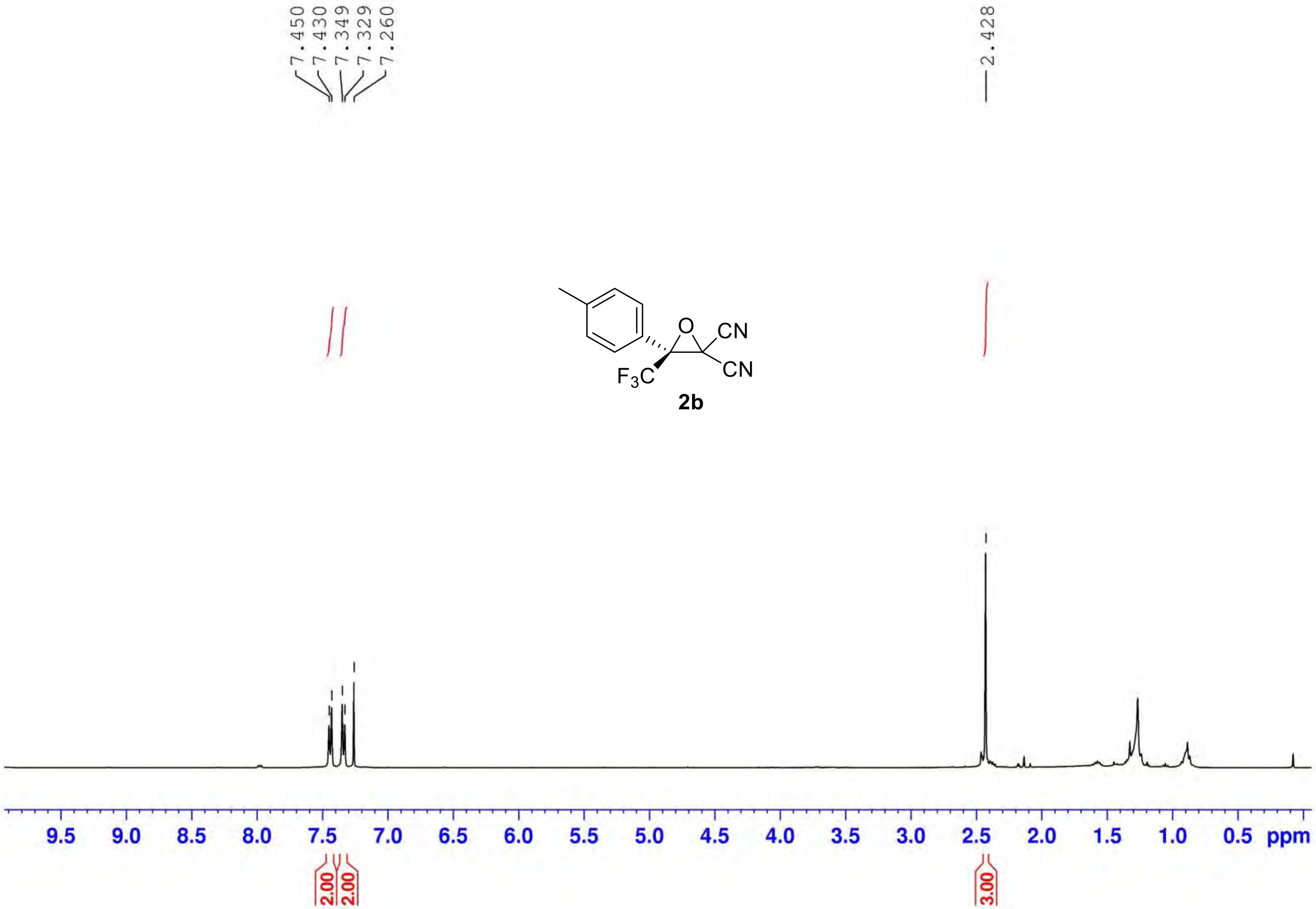


^{19}F NMR in $CDCl_3$ (376 MHz)

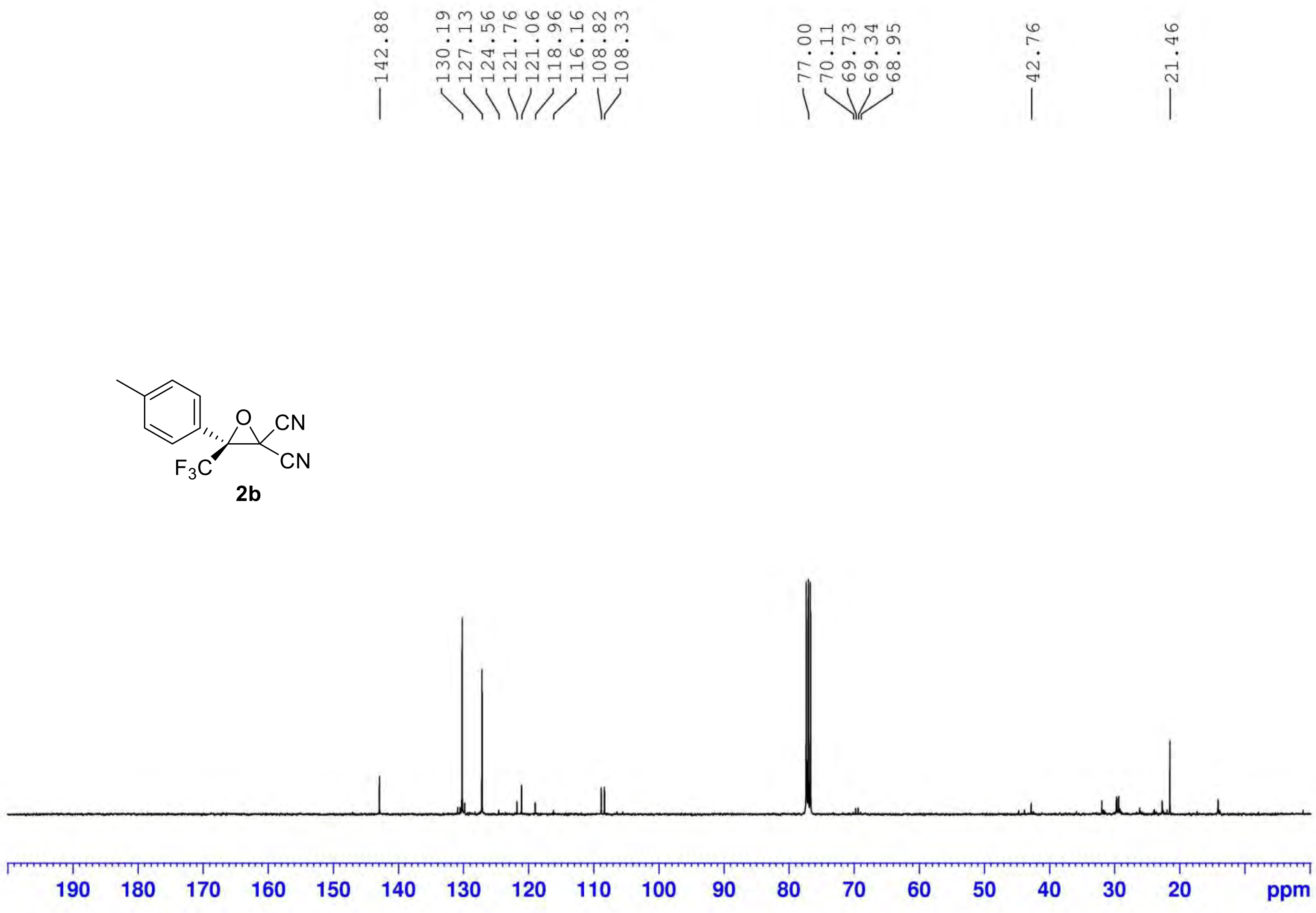


2a

^1H NMR in $CDCl_3$ (400 MHz)

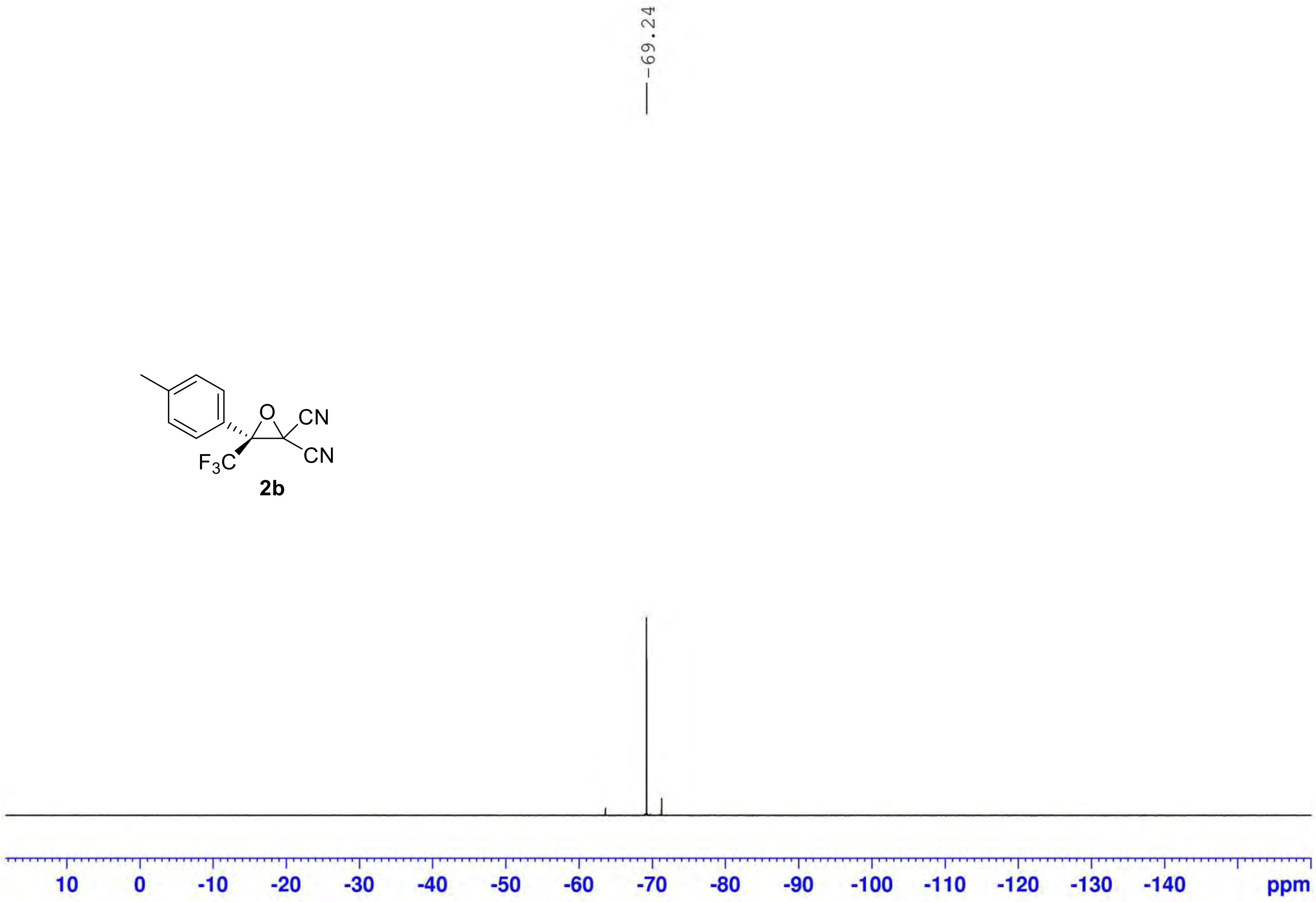


^{13}C NMR in $CDCl_3$ (100 MHz)

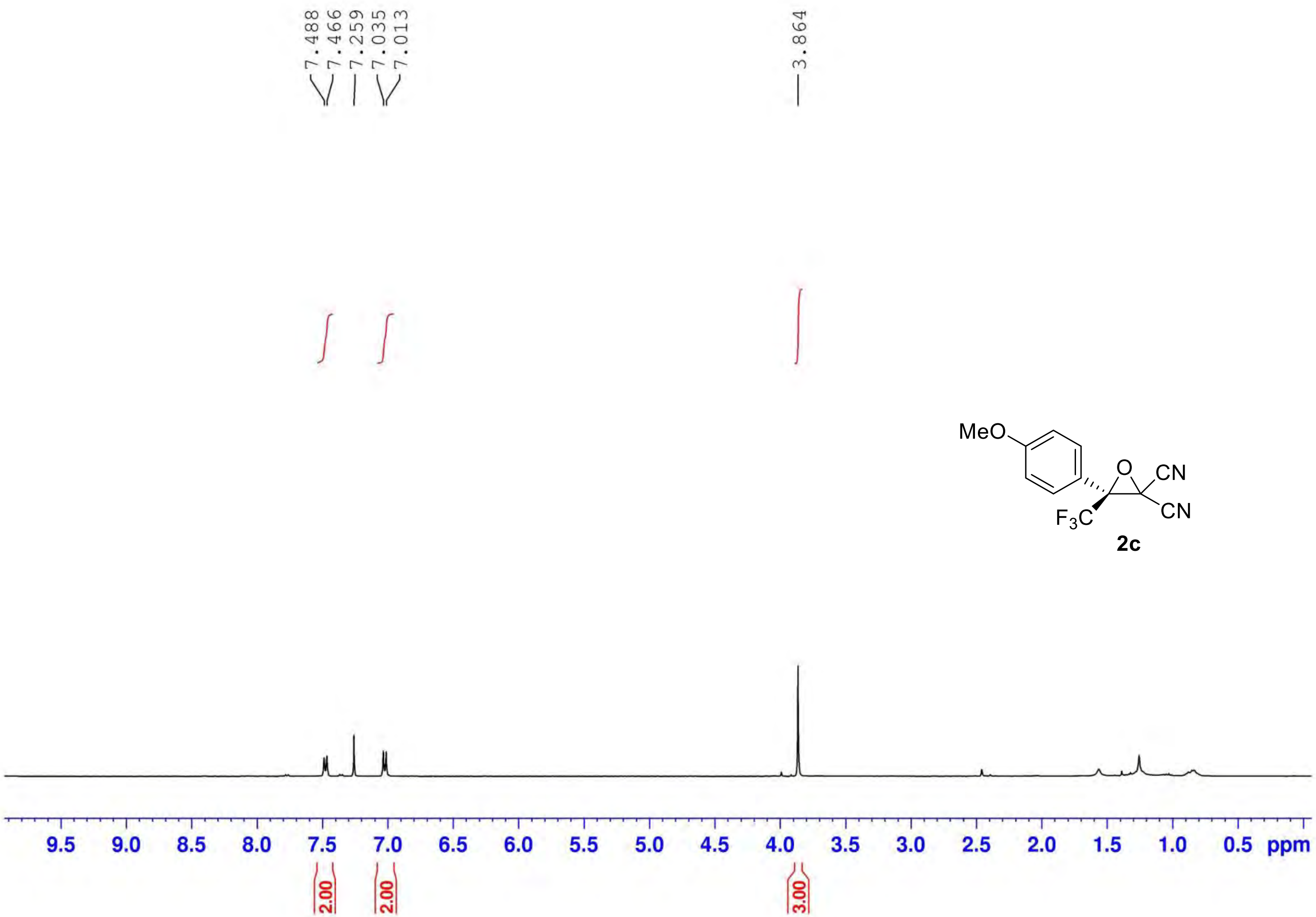


2b

^{19}F NMR in $CDCl_3$ (376 MHz)

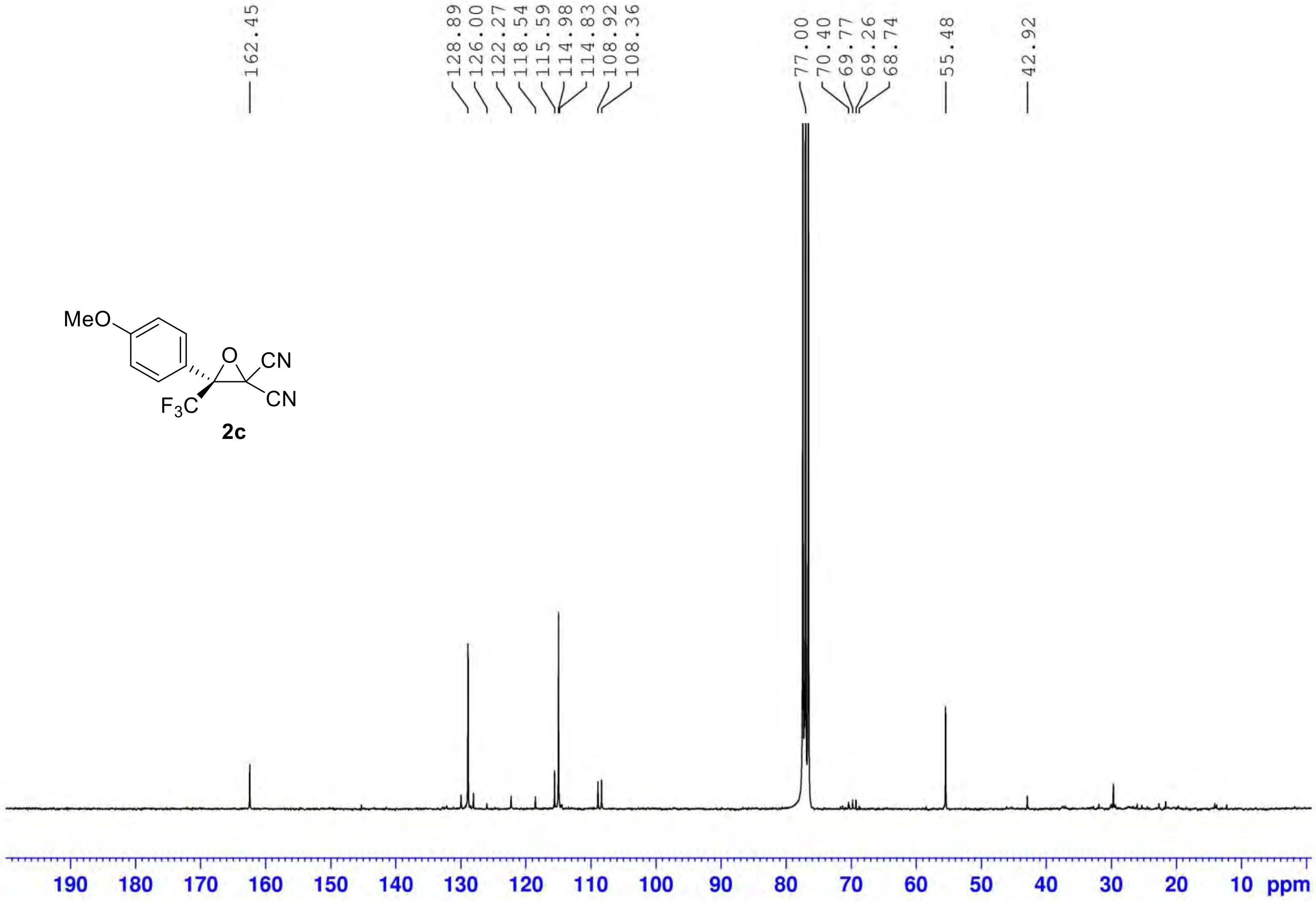


^{1}H NMR in $CDCl_3$ (400 MHz)



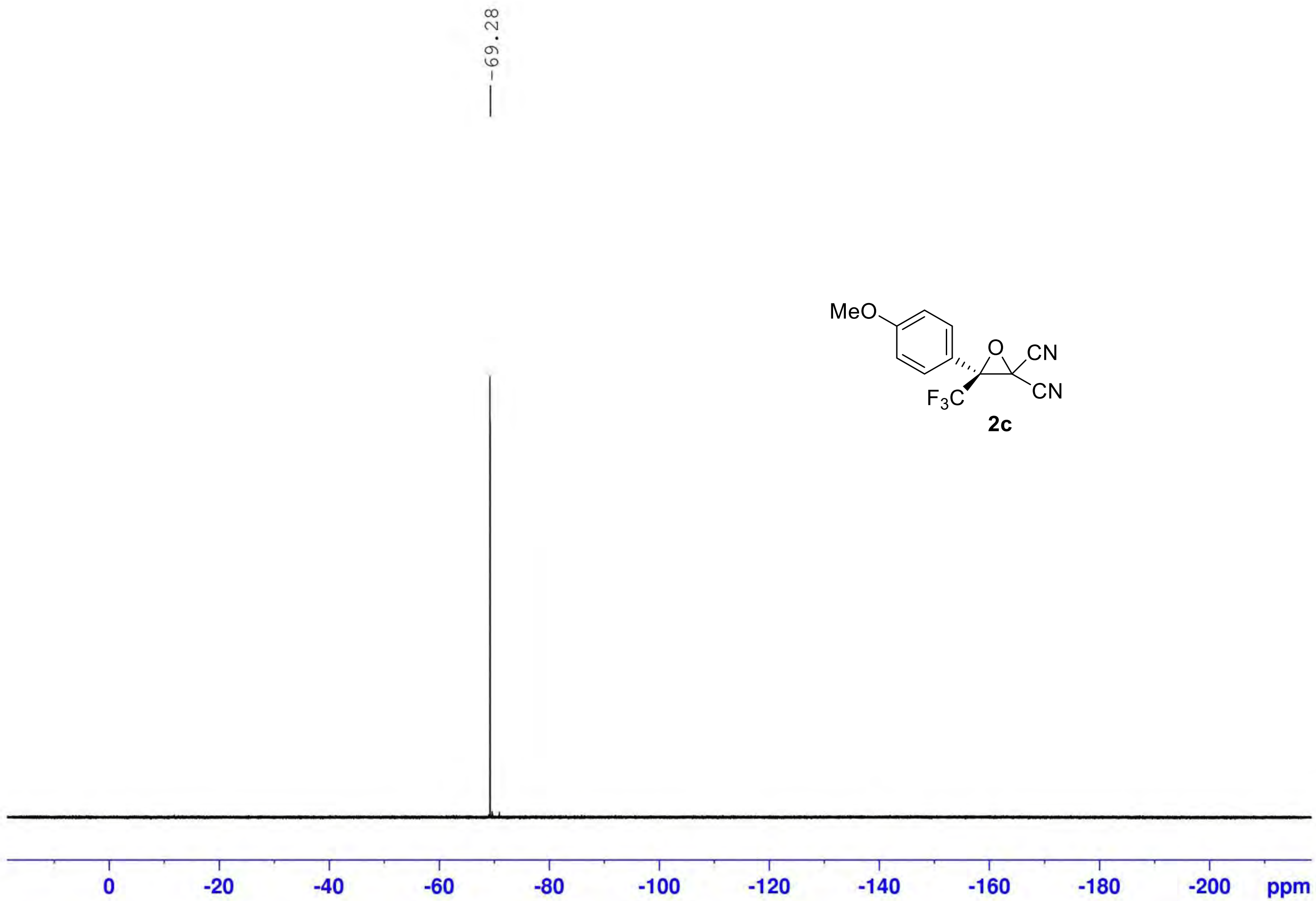
2c

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

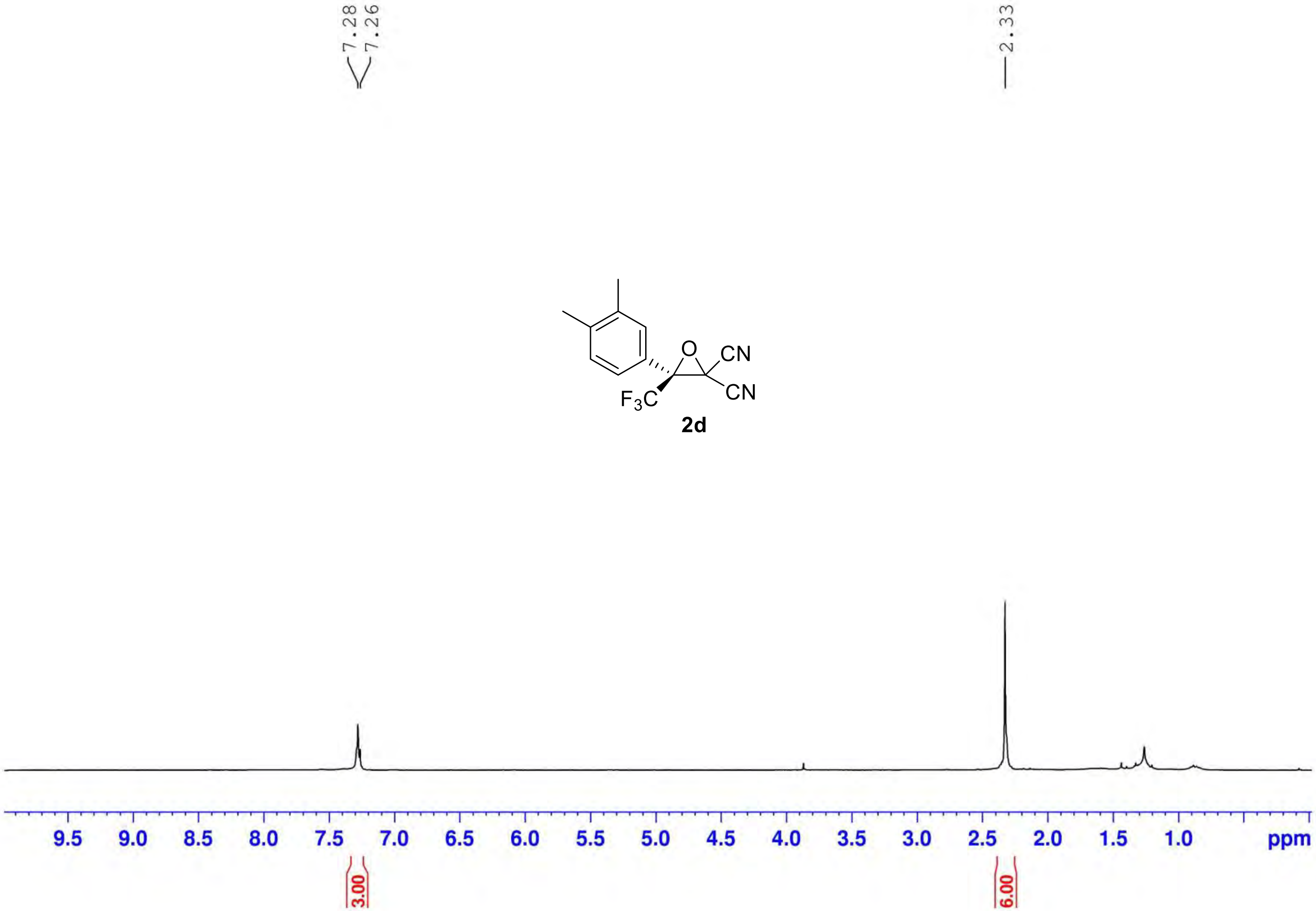


2c

^{19}F NMR in $CDCl_3$ (376 MHz)

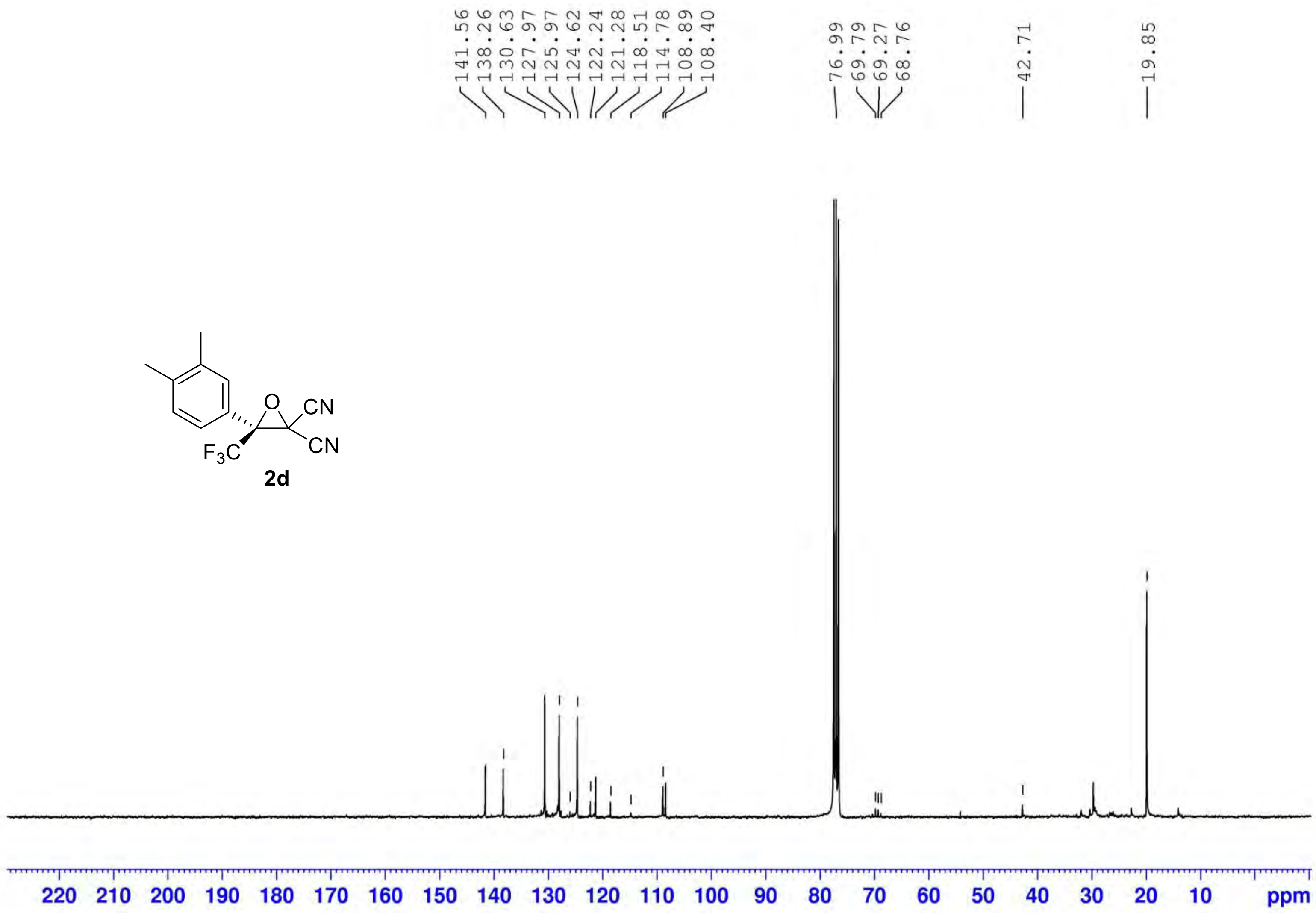


[1]H NMR in $CDCl_3$ (300 MHz)

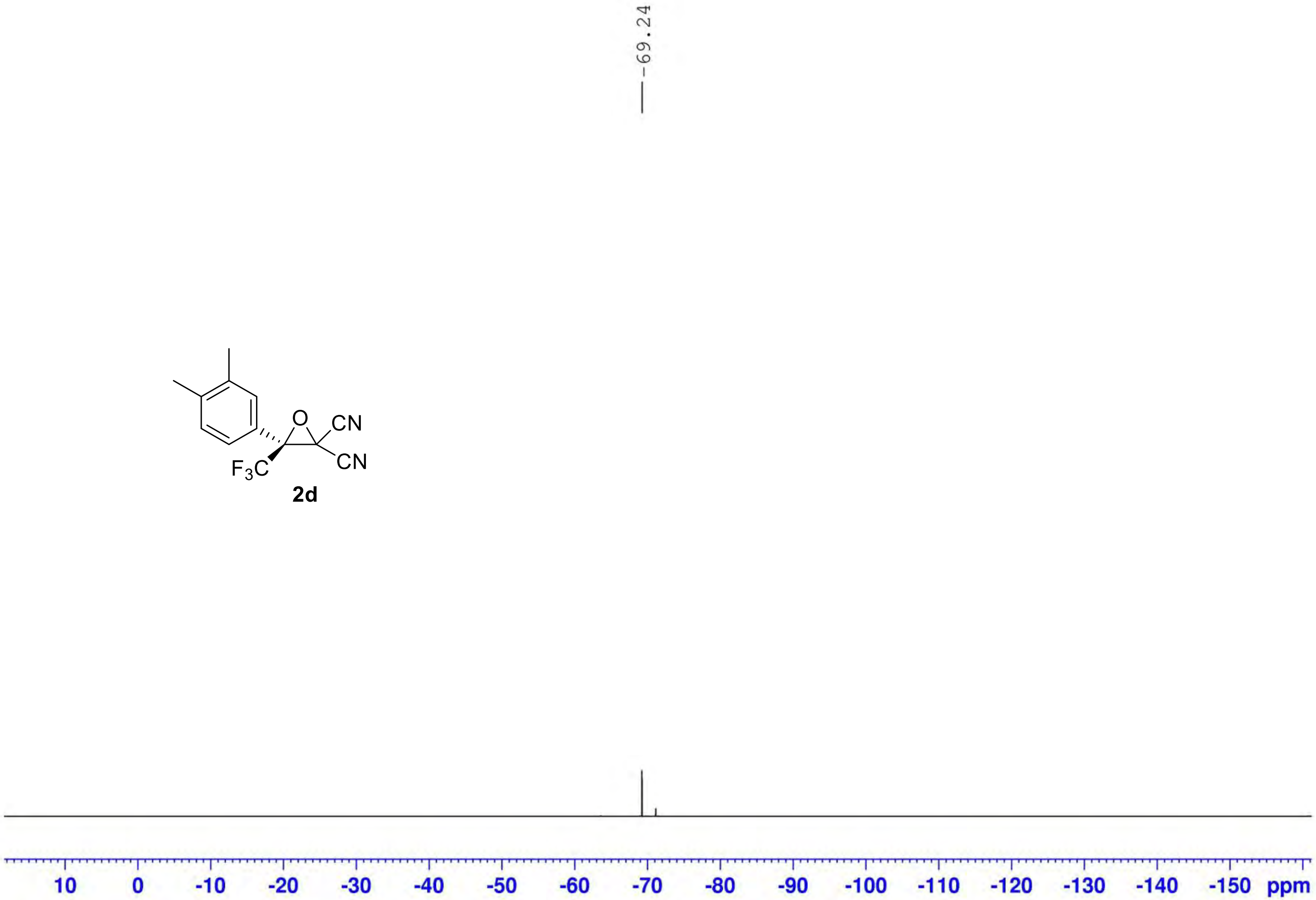


2d

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

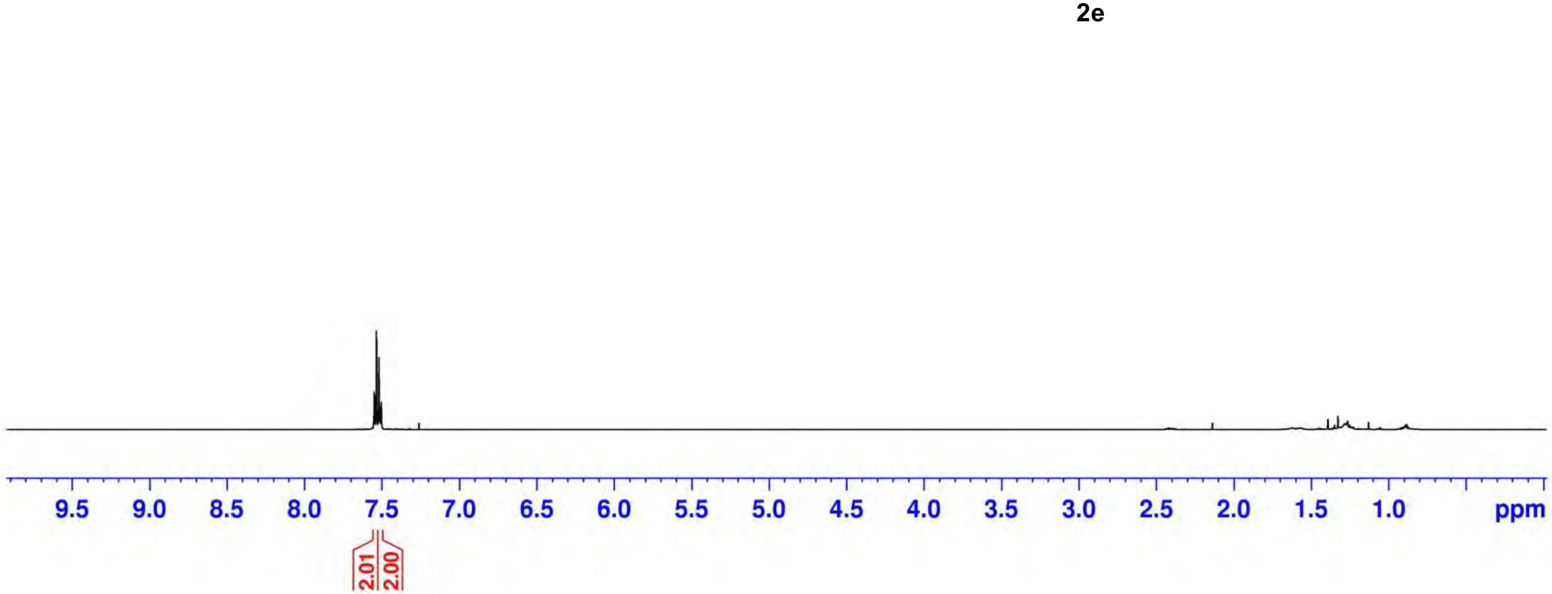


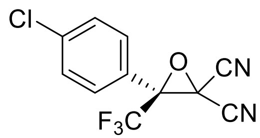
^{19}F NMR in $CDCl_3$ (376 MHz)



2d

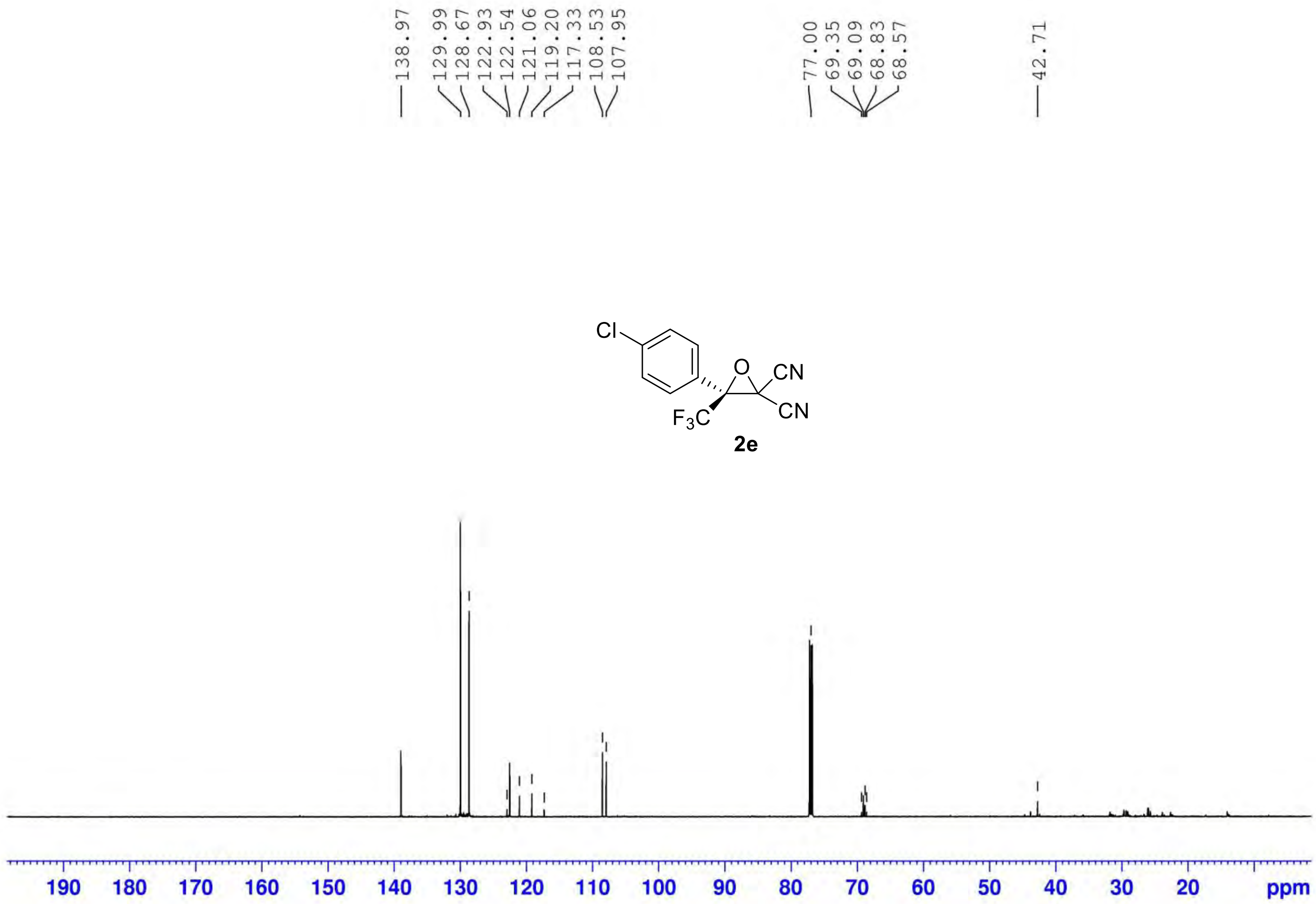
[1]H NMR in $CDCl_3$ (600 MHz)





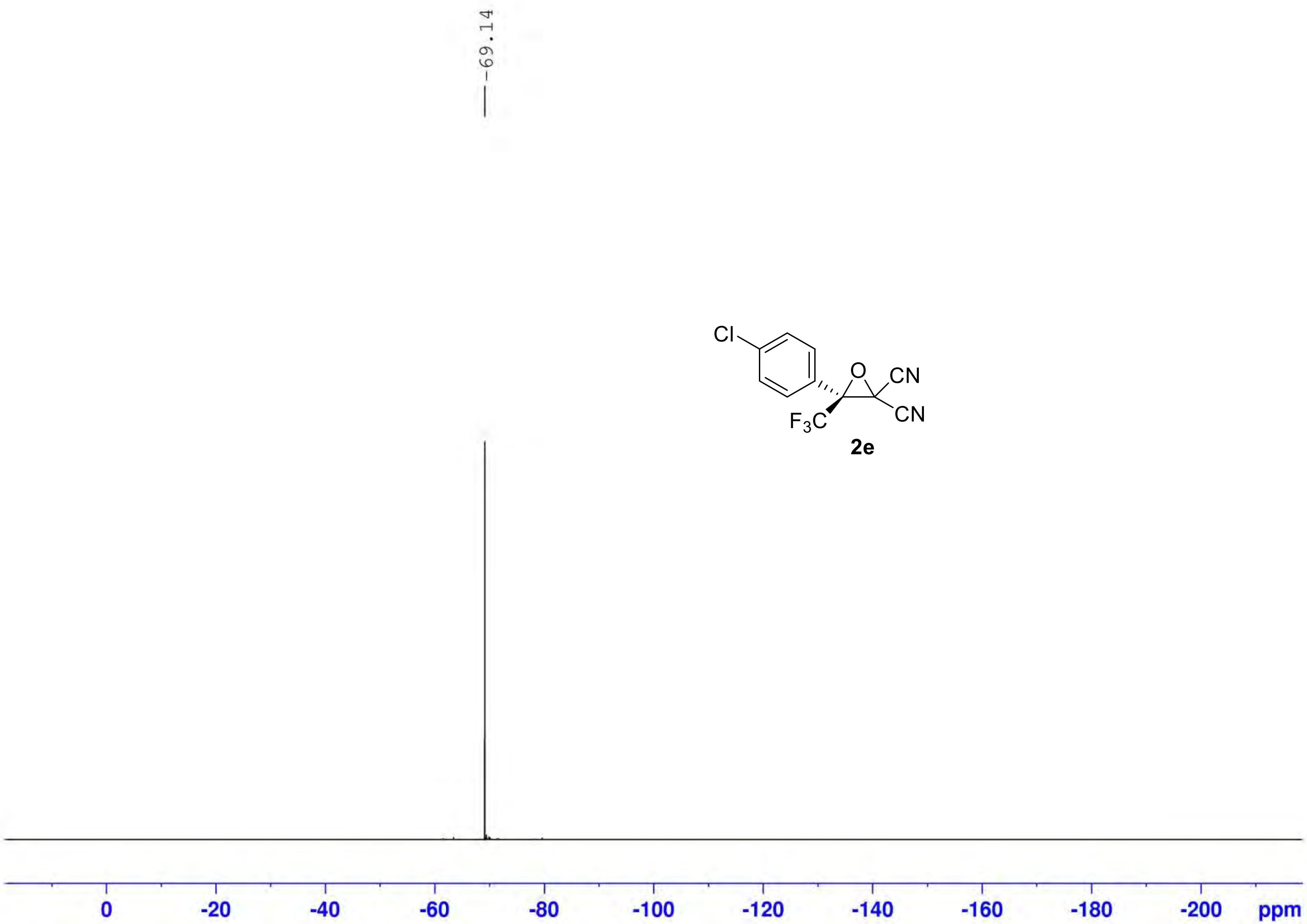
2e

[13]C NMR in $CDCl_3$ (150 MHz)

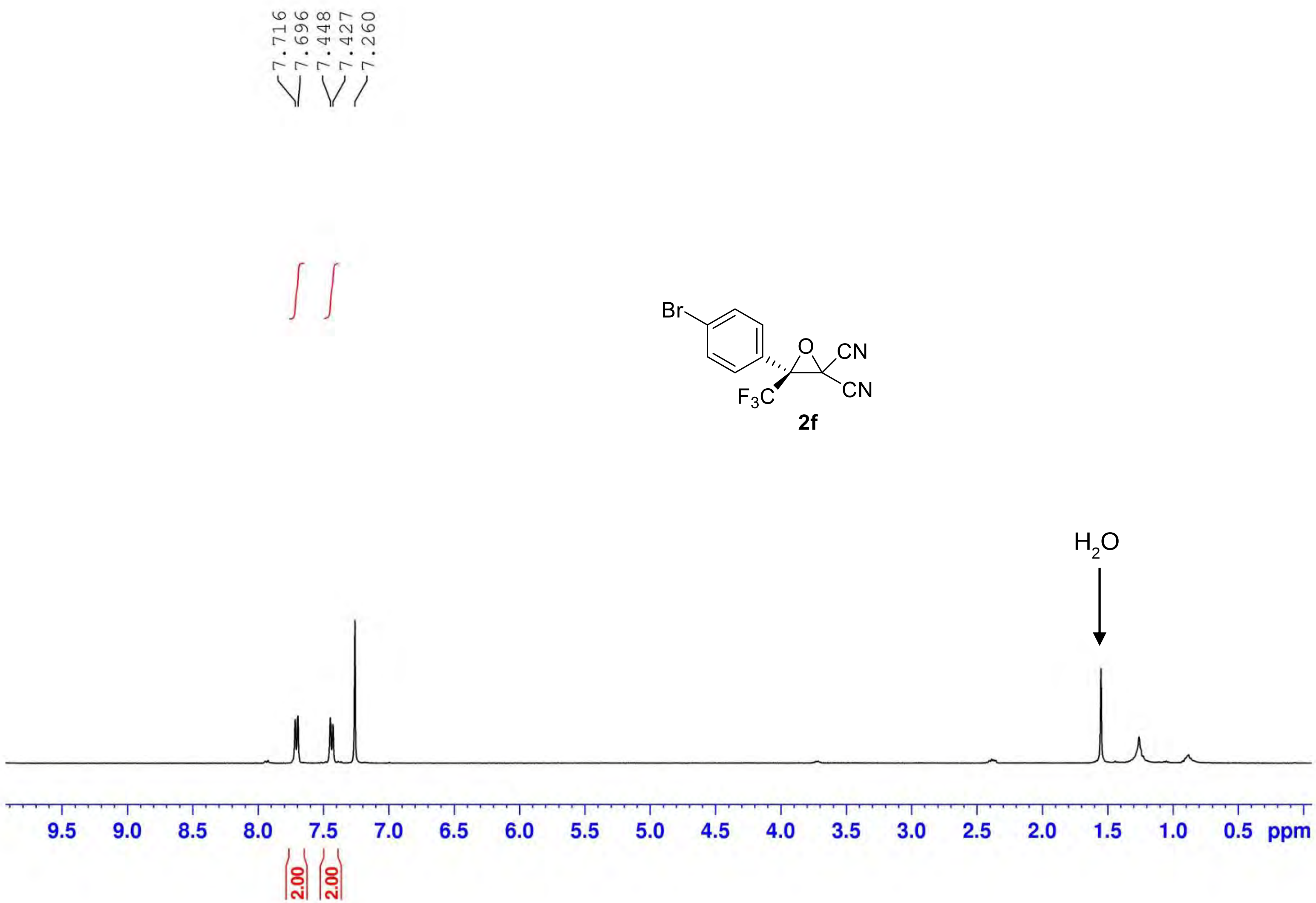


2e

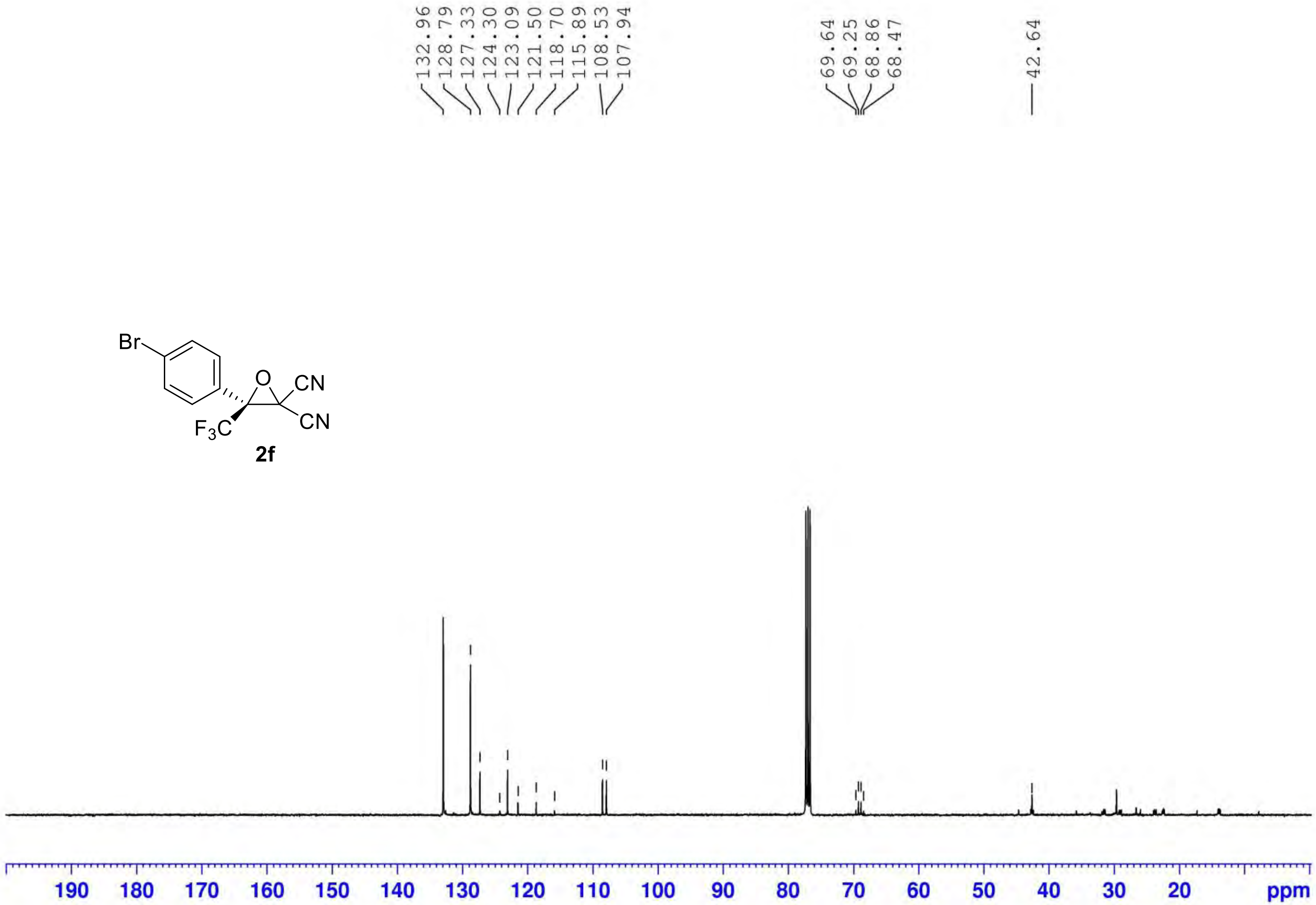
^{19}F NMR in $CDCl_3$ (564 MHz)



[1]H NMR in $CDCl_3$ (400 MHz)

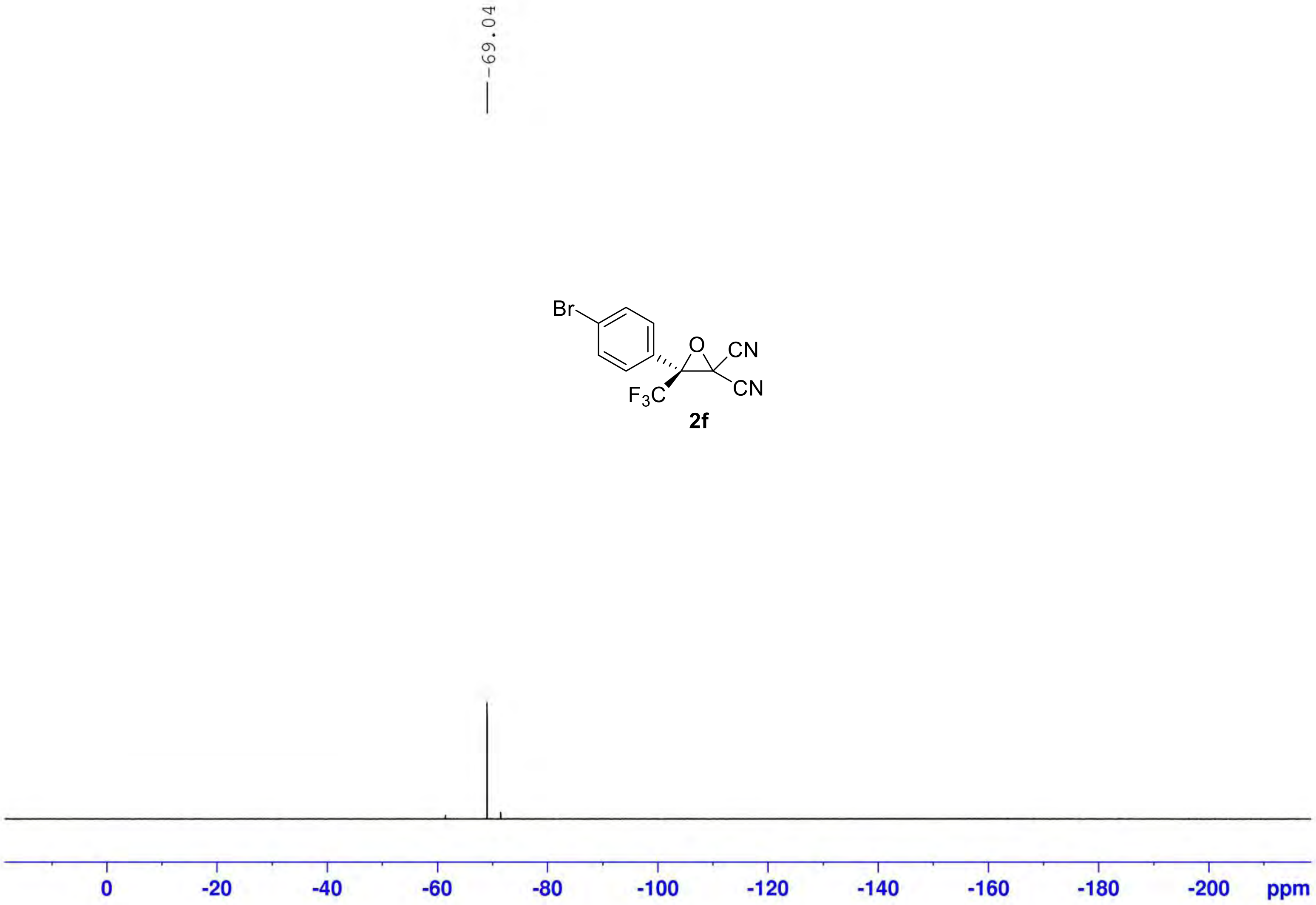


[13]C NMR in CDCl$_3$ (100 MHz)



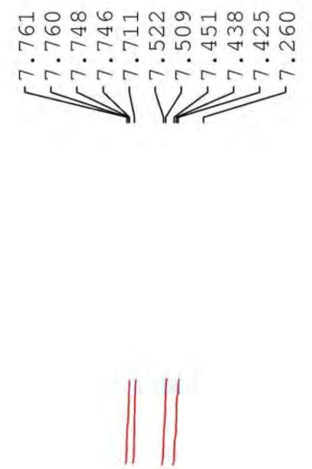
2f

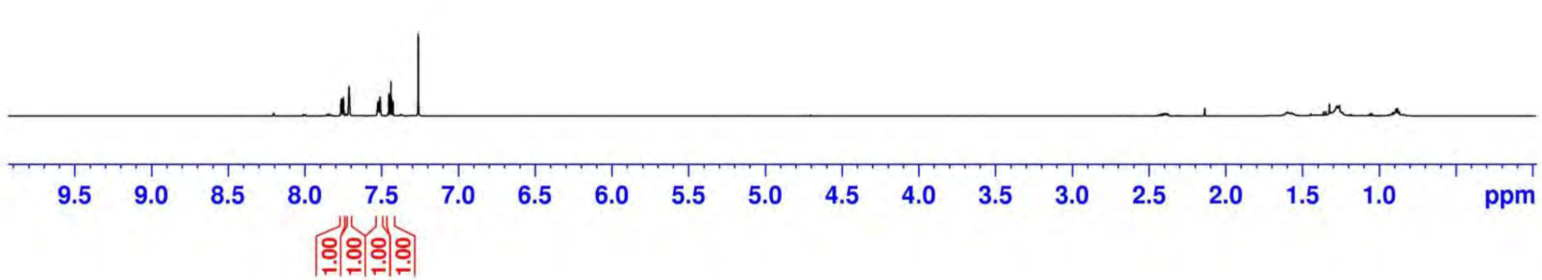
^{19}F NMR in $CDCl_3$ (376 MHz)

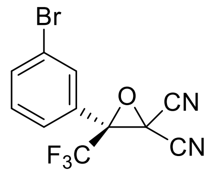


2f

^{1}H NMR in $CDCl_3$ (600 MHz)

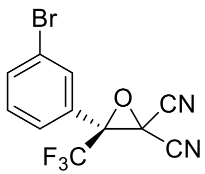




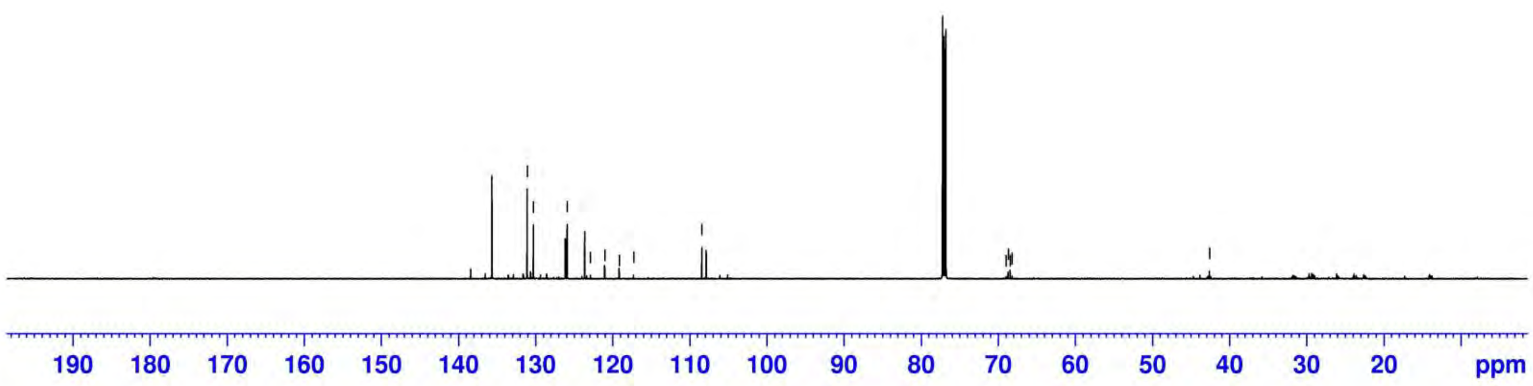


2g

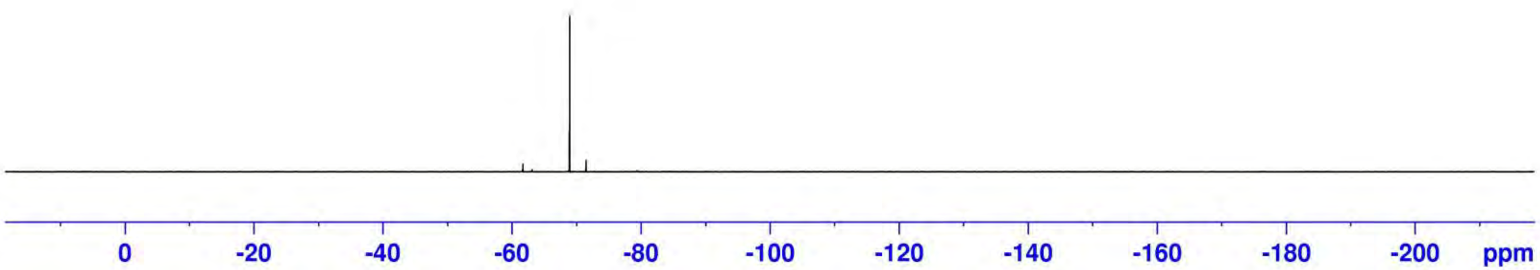
^{13}C NMR in $CDCl_3$ (150 MHz)

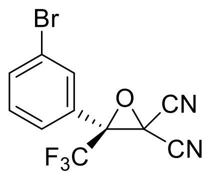


2g



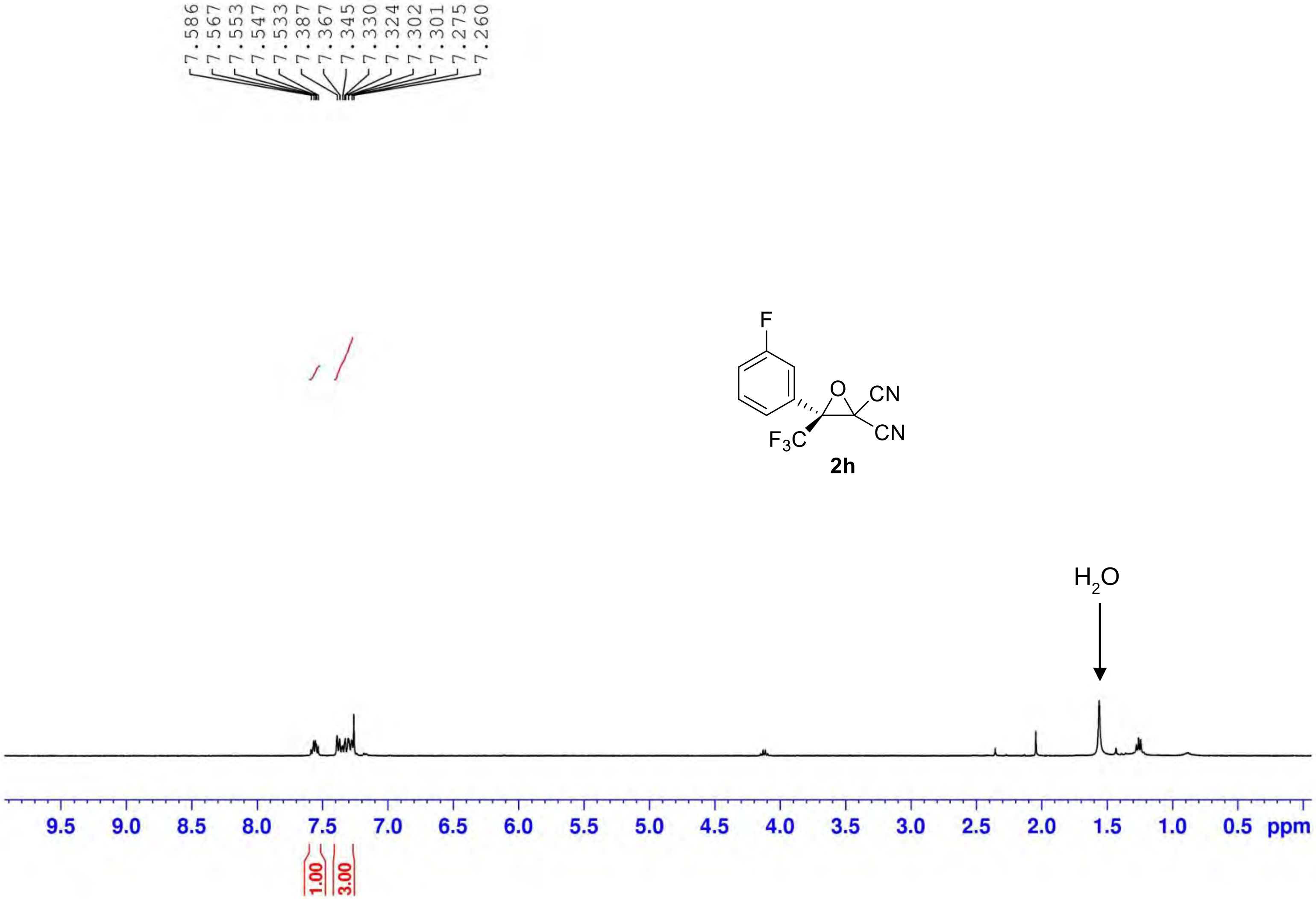
^{19}F NMR in $CDCl_3$ (376 MHz)



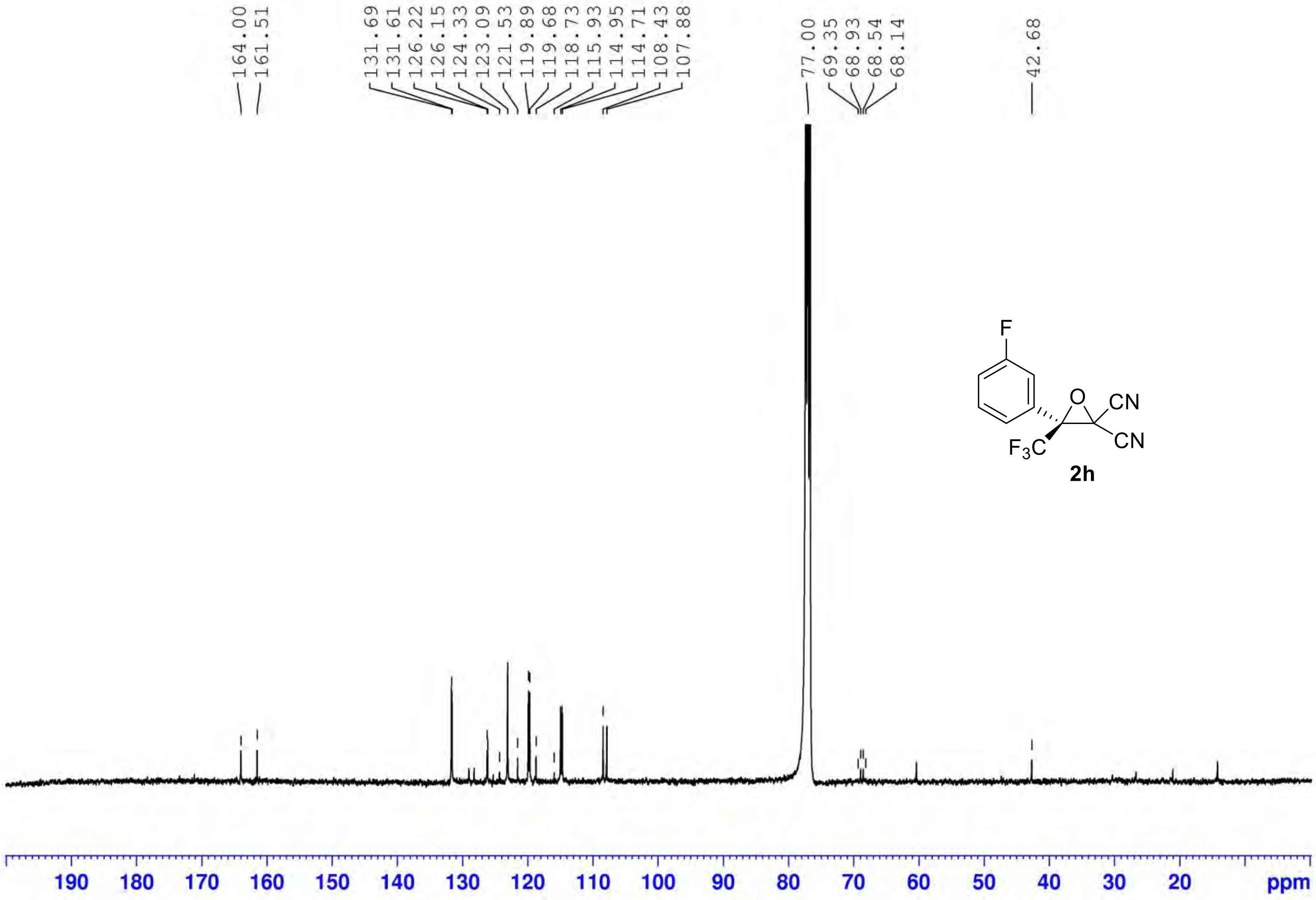


2g

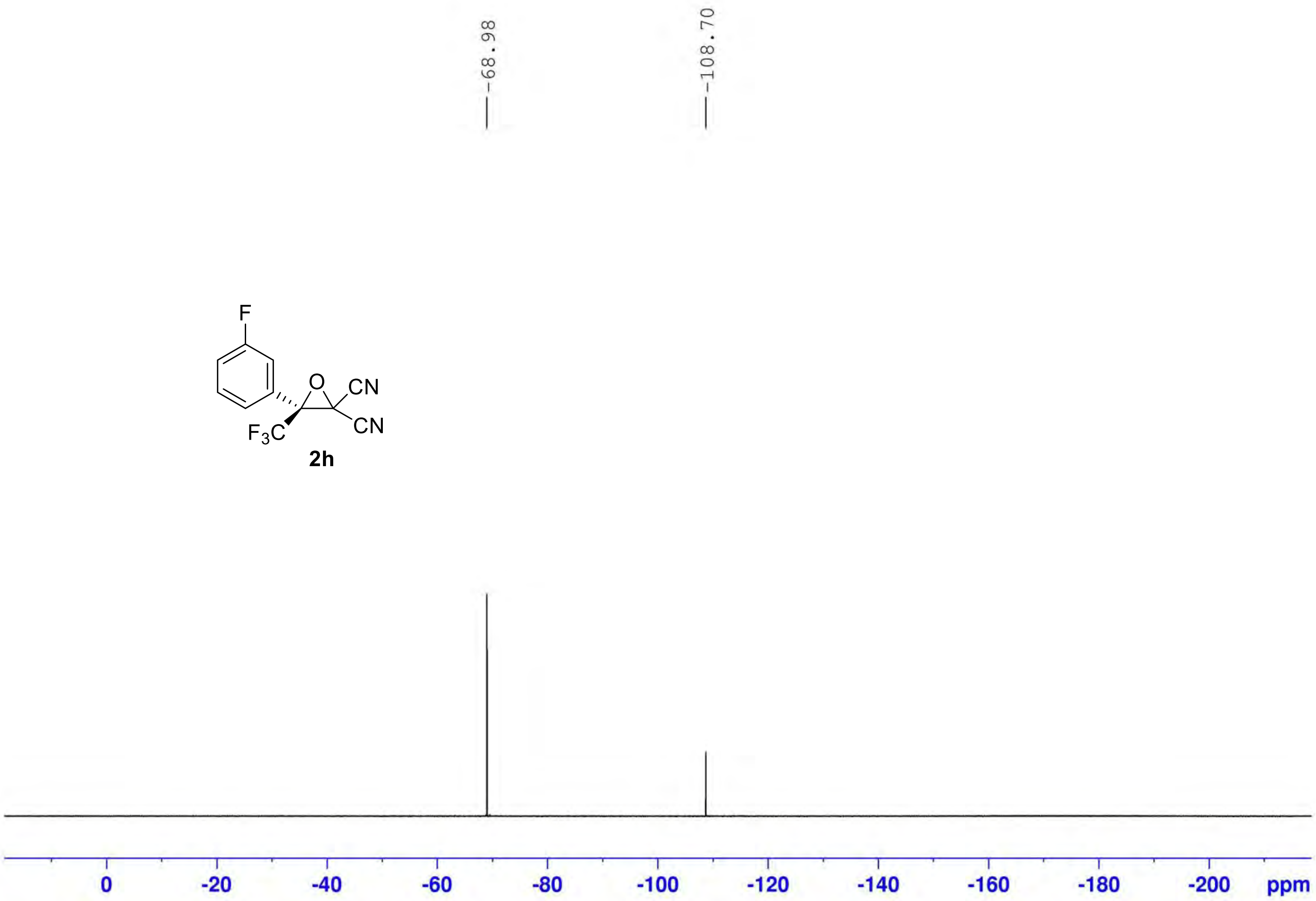
^{1}H NMR in $CDCl_3$ (400 MHz)



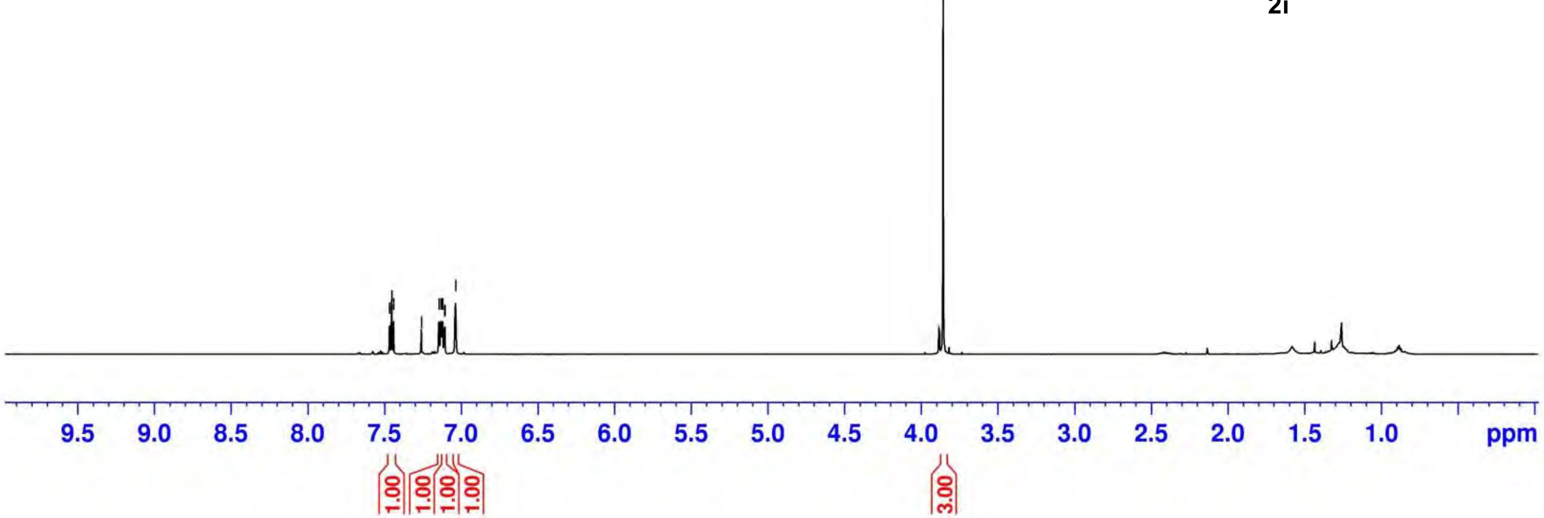
^{13}C NMR in $CDCl_3$ (100 MHz)

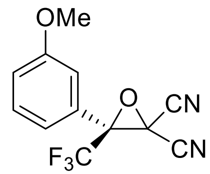


^{19}F NMR in $CDCl_3$ (376 MHz)



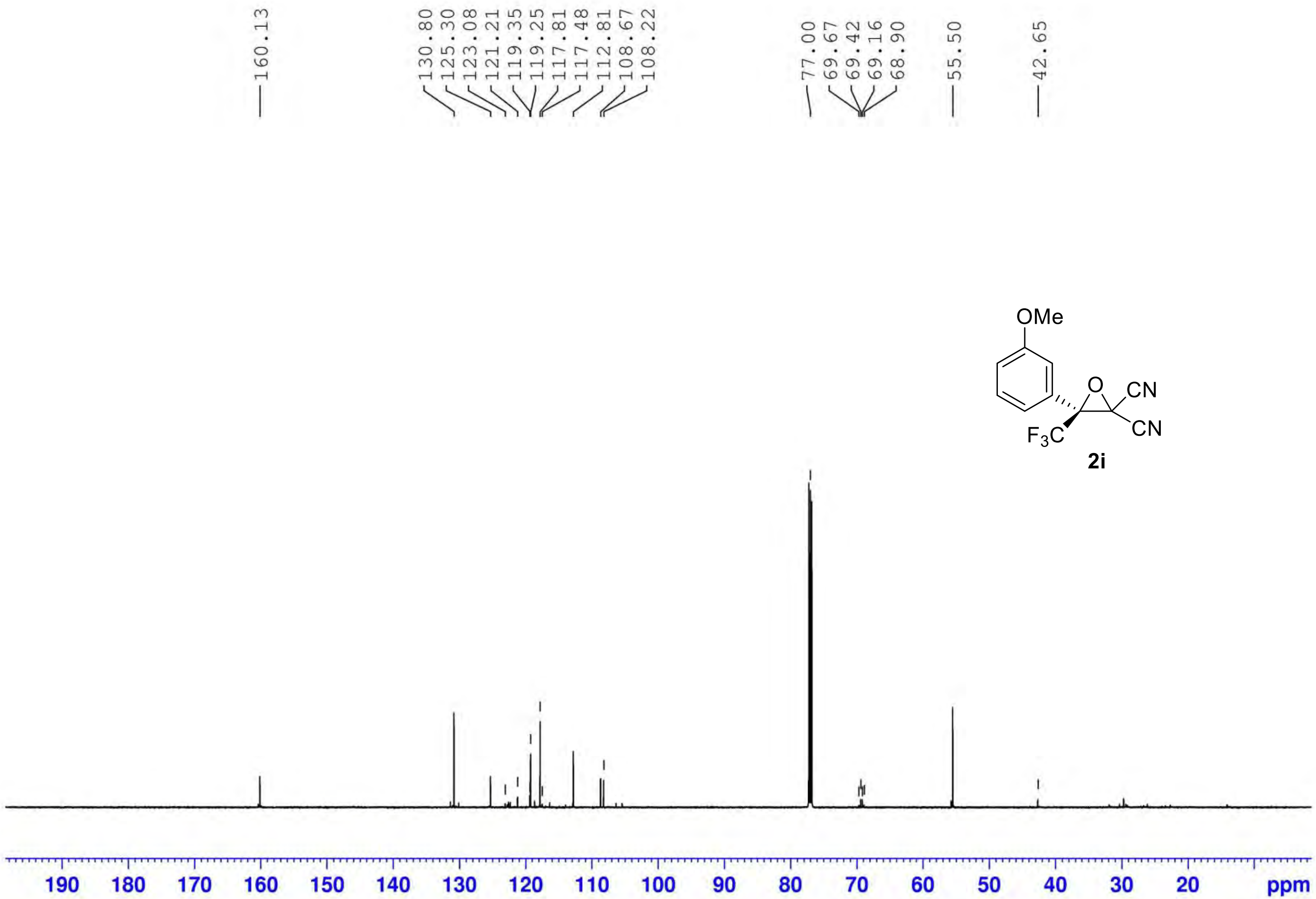
^1H NMR in $CDCl_3$ (600 MHz)





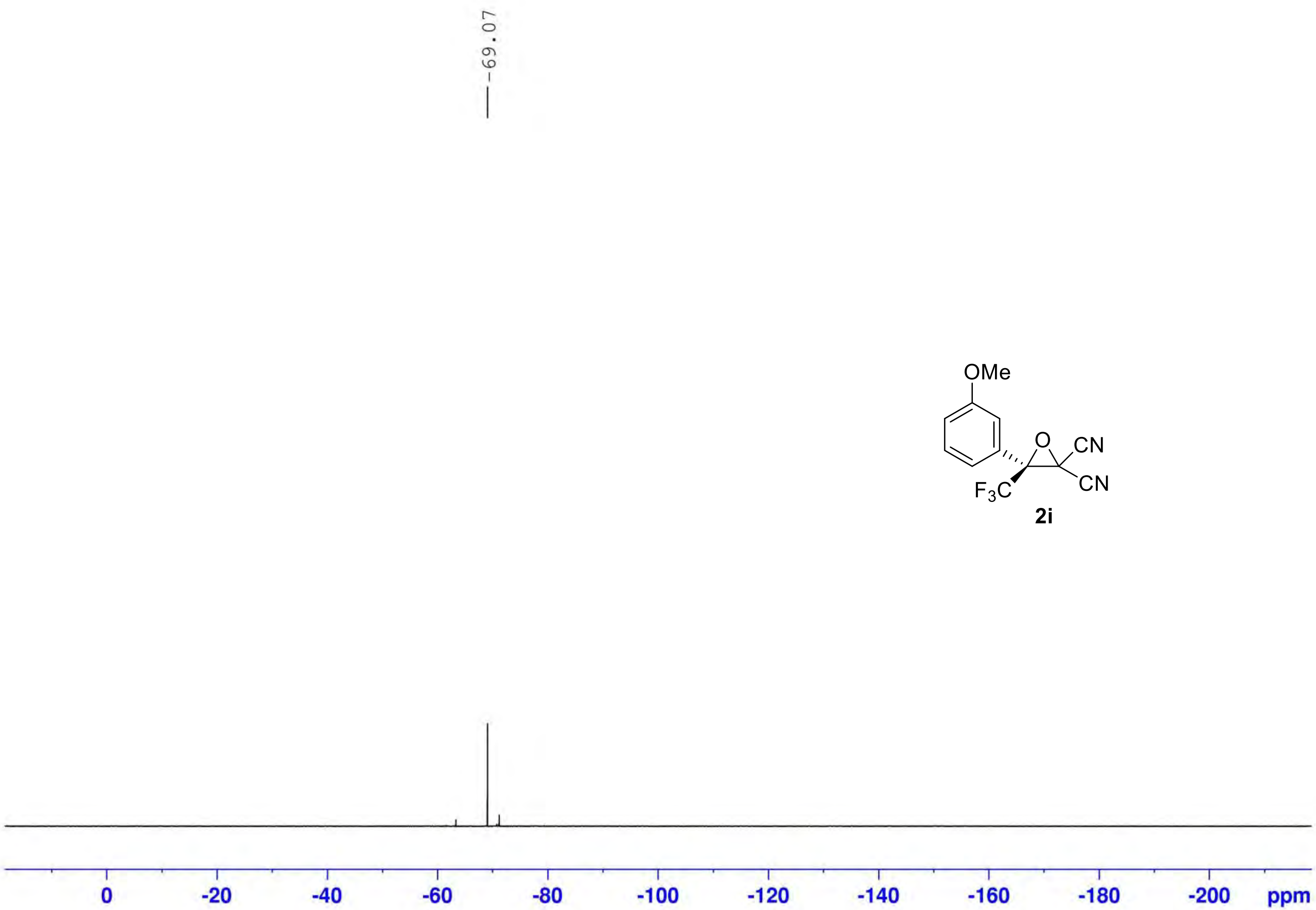
2i

^{13}C NMR in $CDCl_3$ (150 MHz)



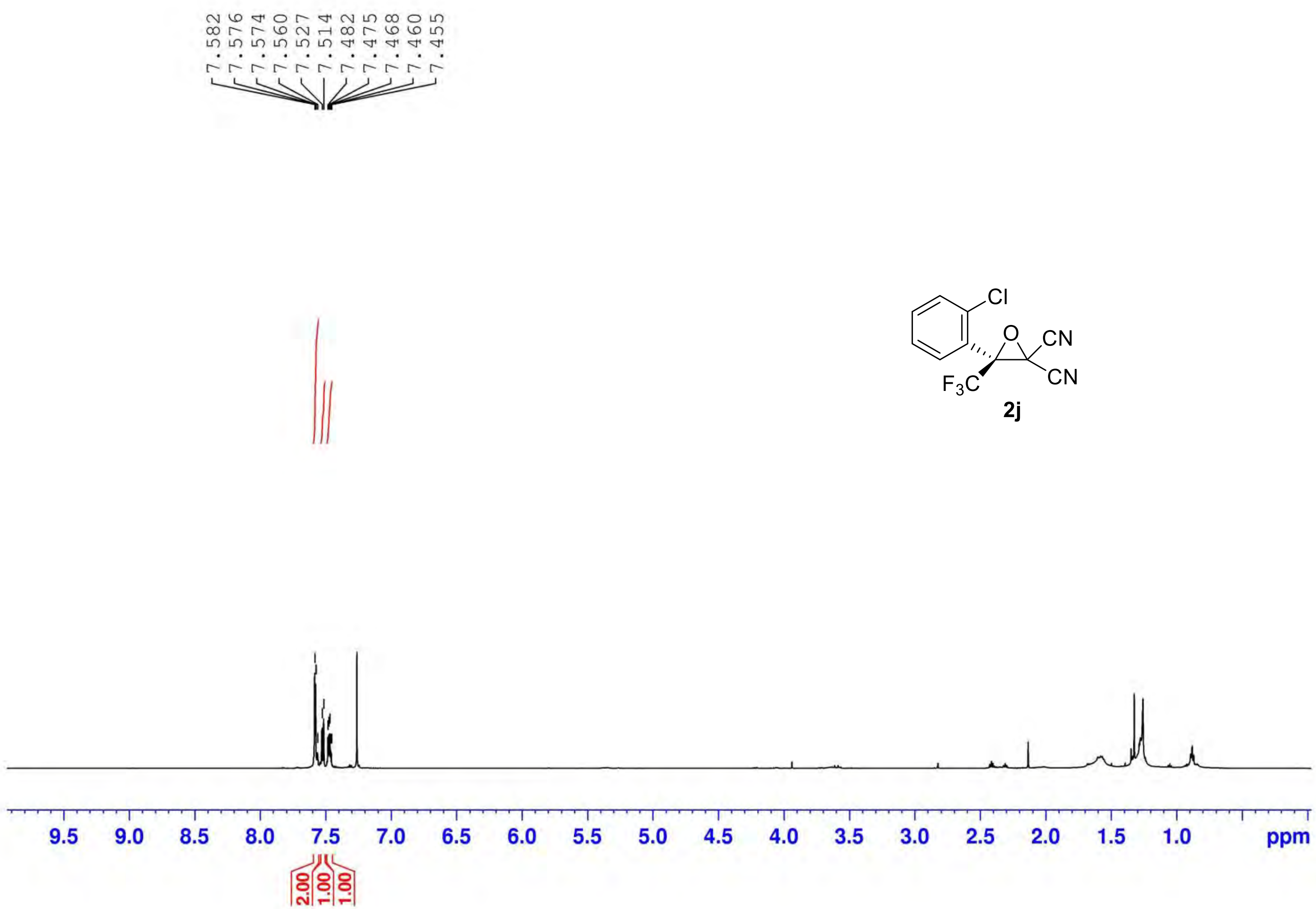
2i

^{19}F NMR in $CDCl_3$ (376 MHz)

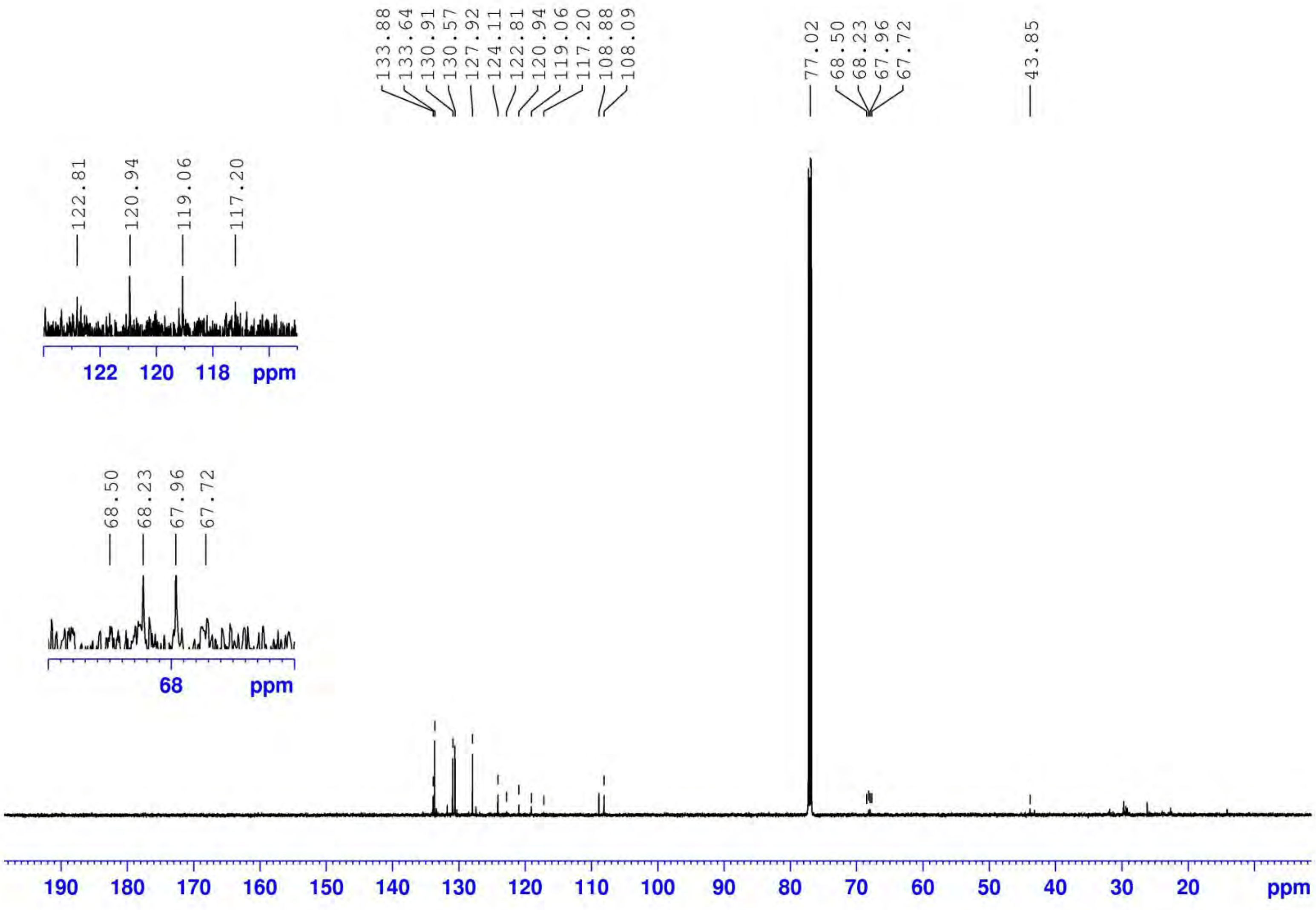


2i

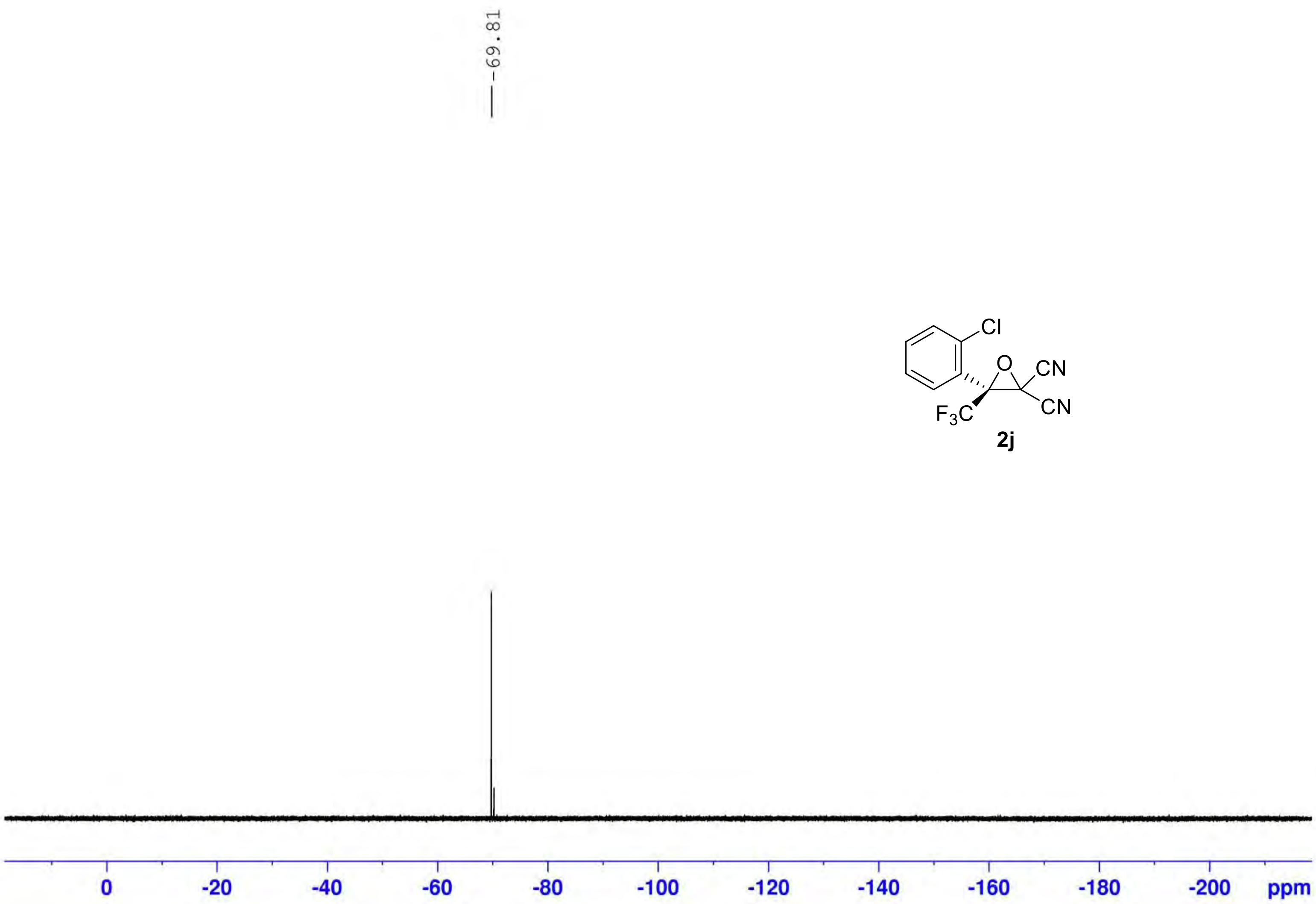
^{1}H NMR in $CDCl_3$ (600 MHz)



^{13}C NMR in $CDCl_3$ (150 MHz)

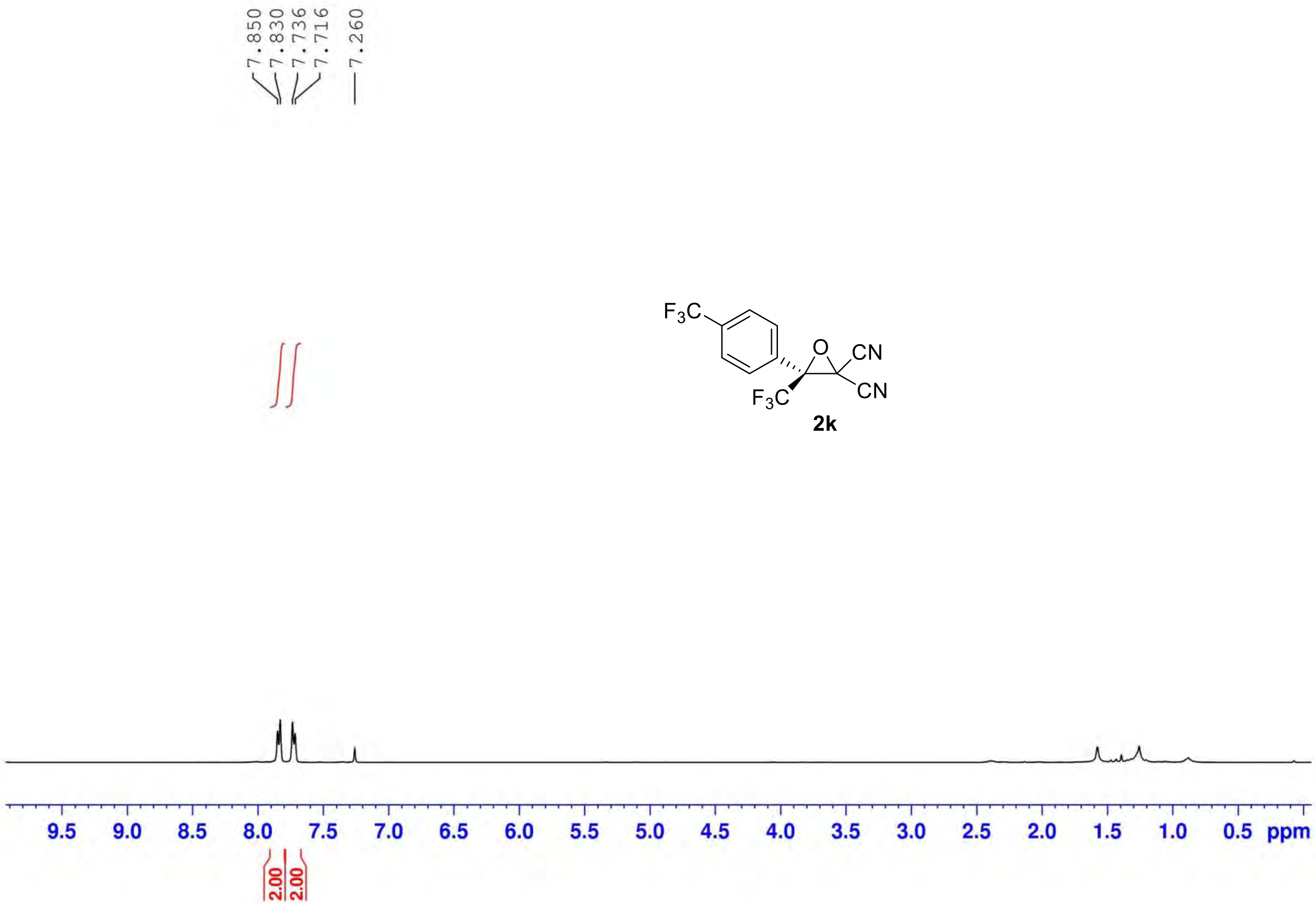


^{19}F NMR in $CDCl_3$ (376 MHz)

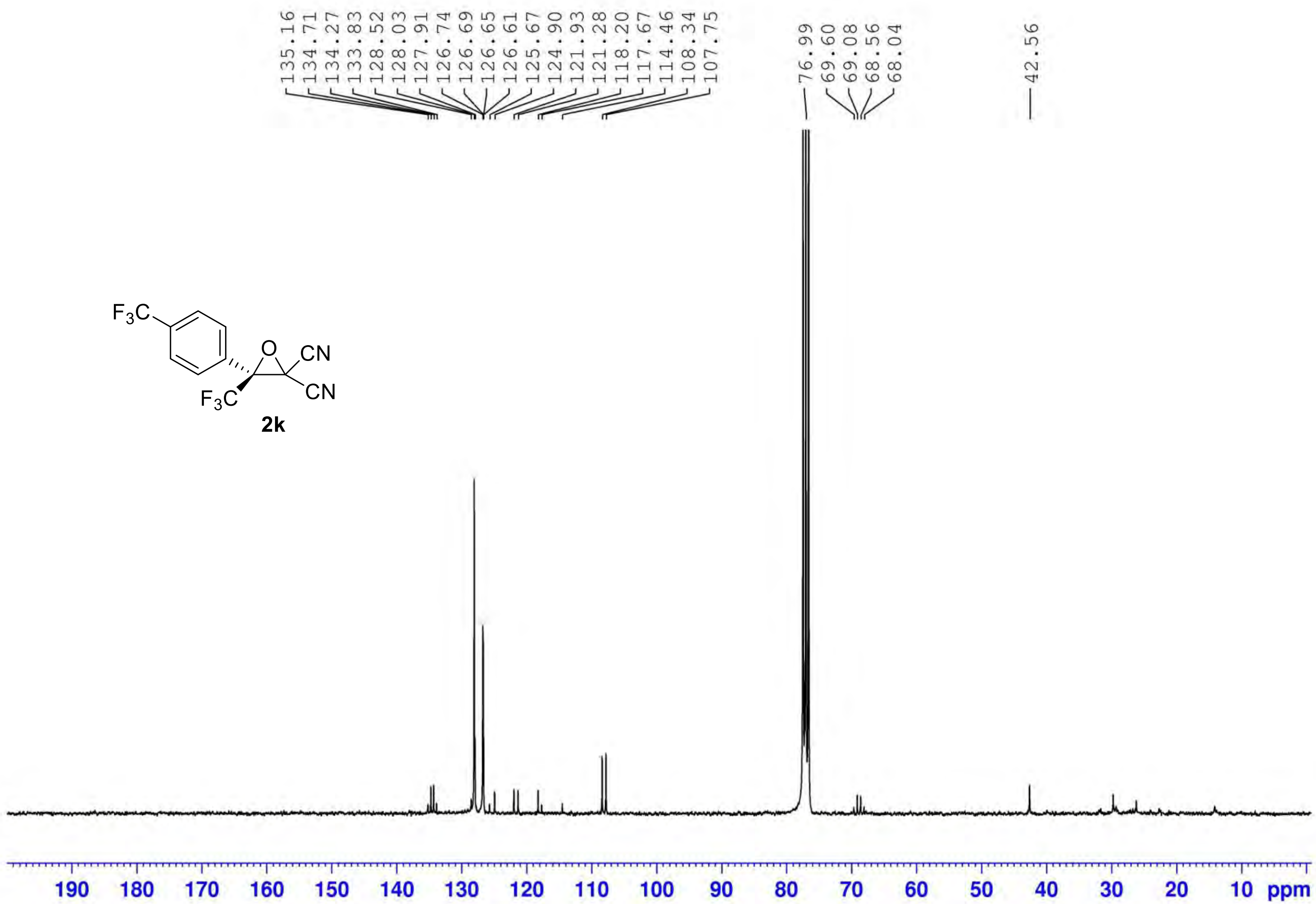


2j

^{1}H NMR in $CDCl_3$ (400 MHz)

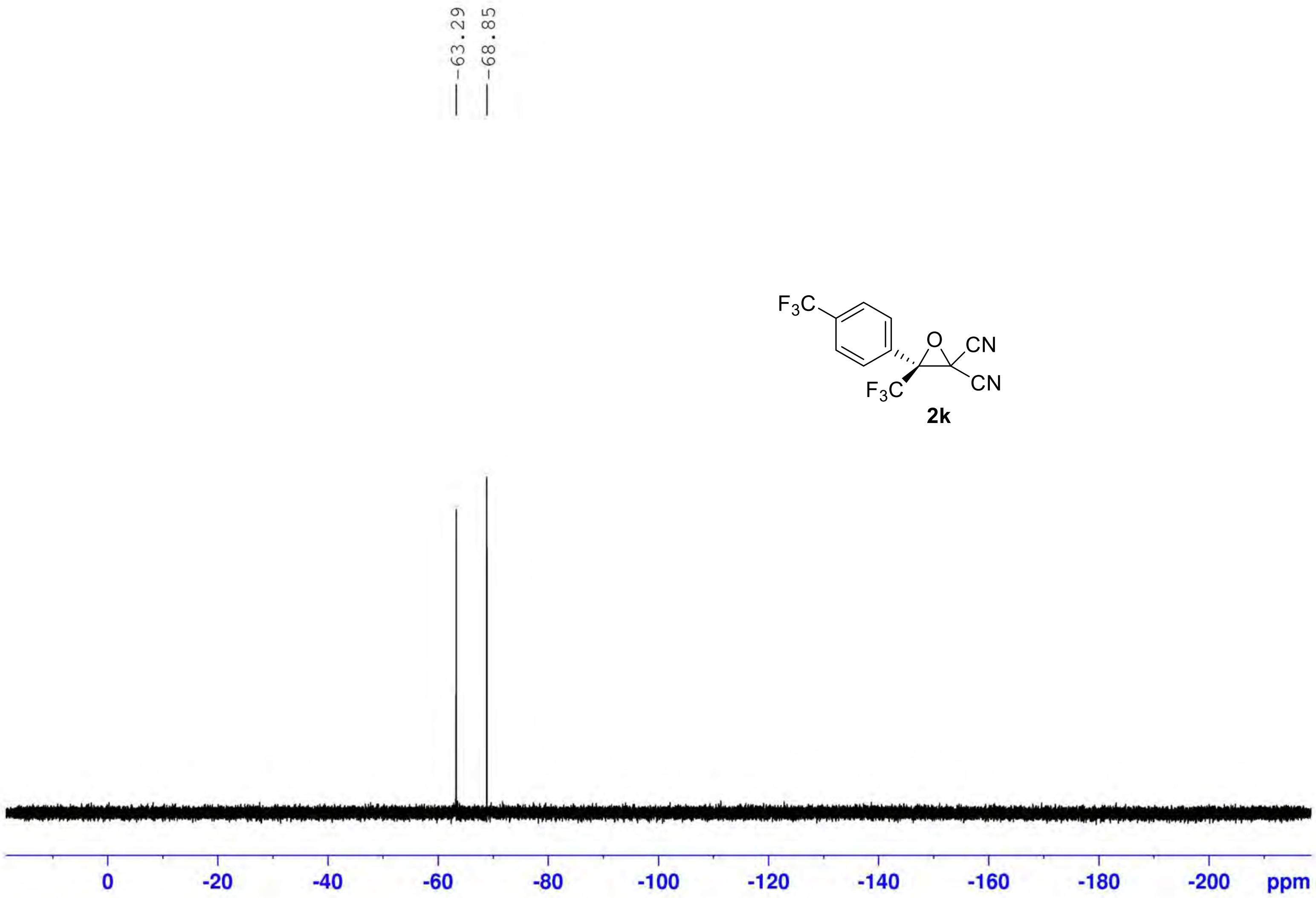


^{13}C NMR in $CDCl_3$ (75 MHz)



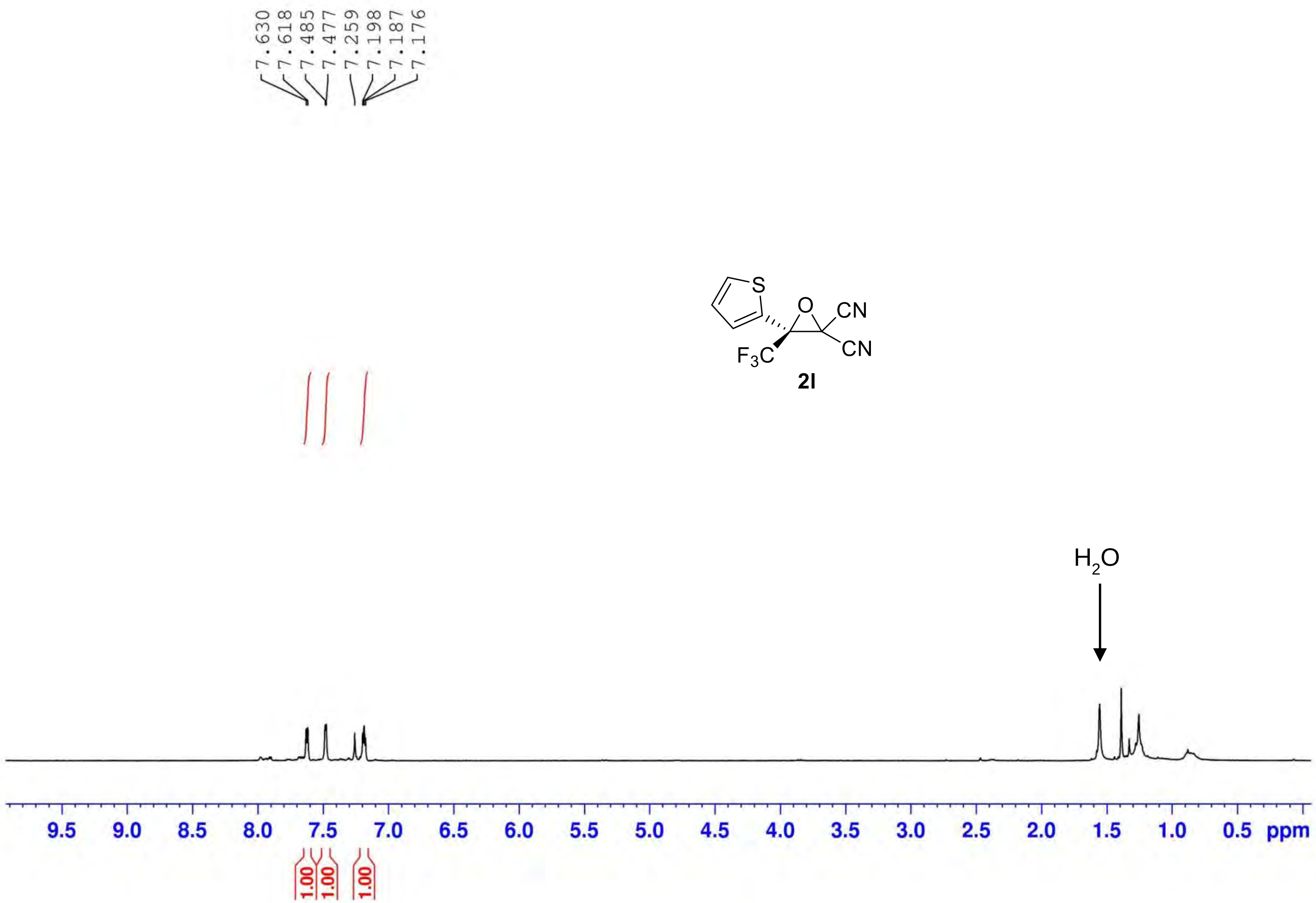
2k

^{19}F NMR in $CDCl_3$ (376 MHz)

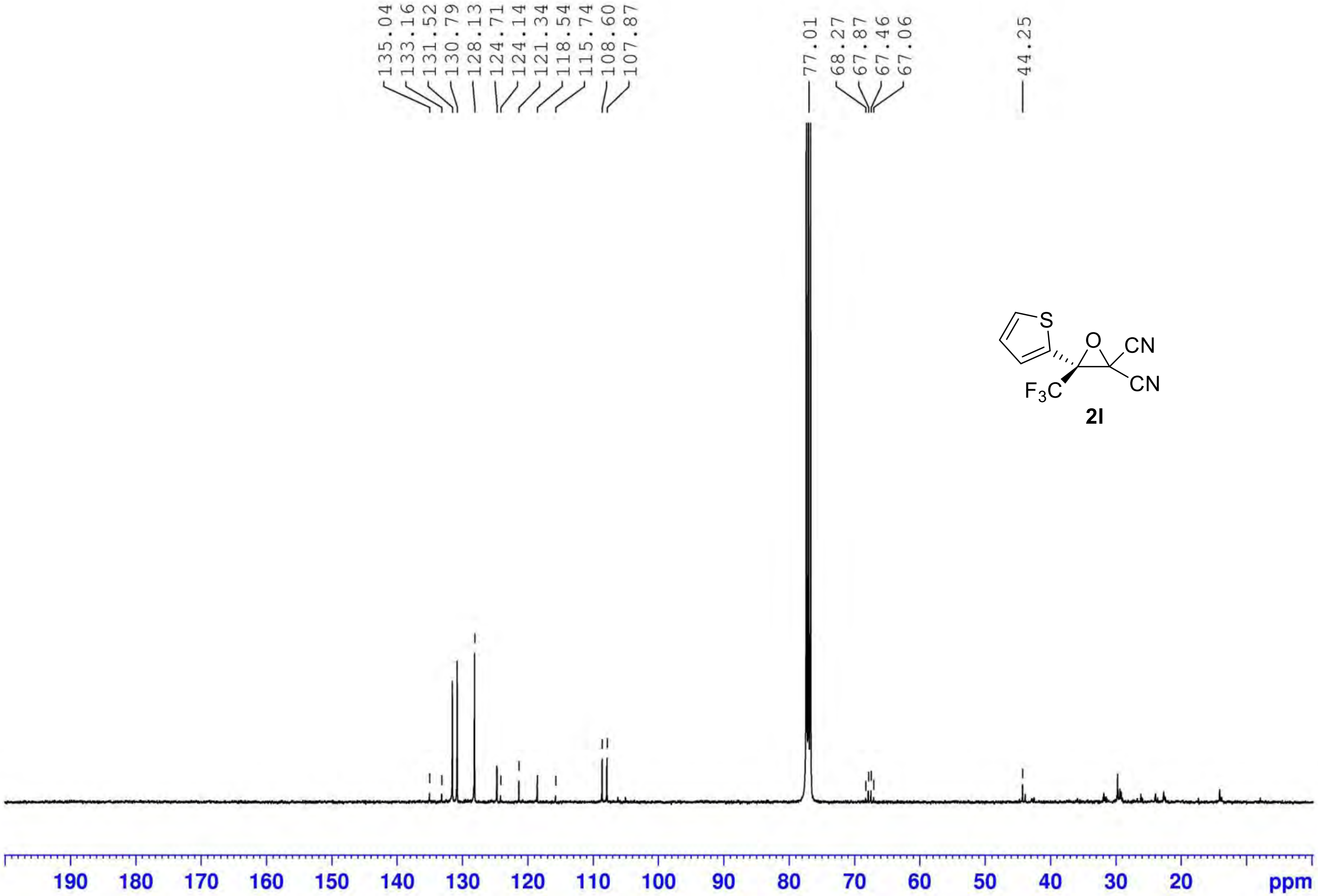


2k

^1H NMR in $CDCl_3$ (400 MHz)

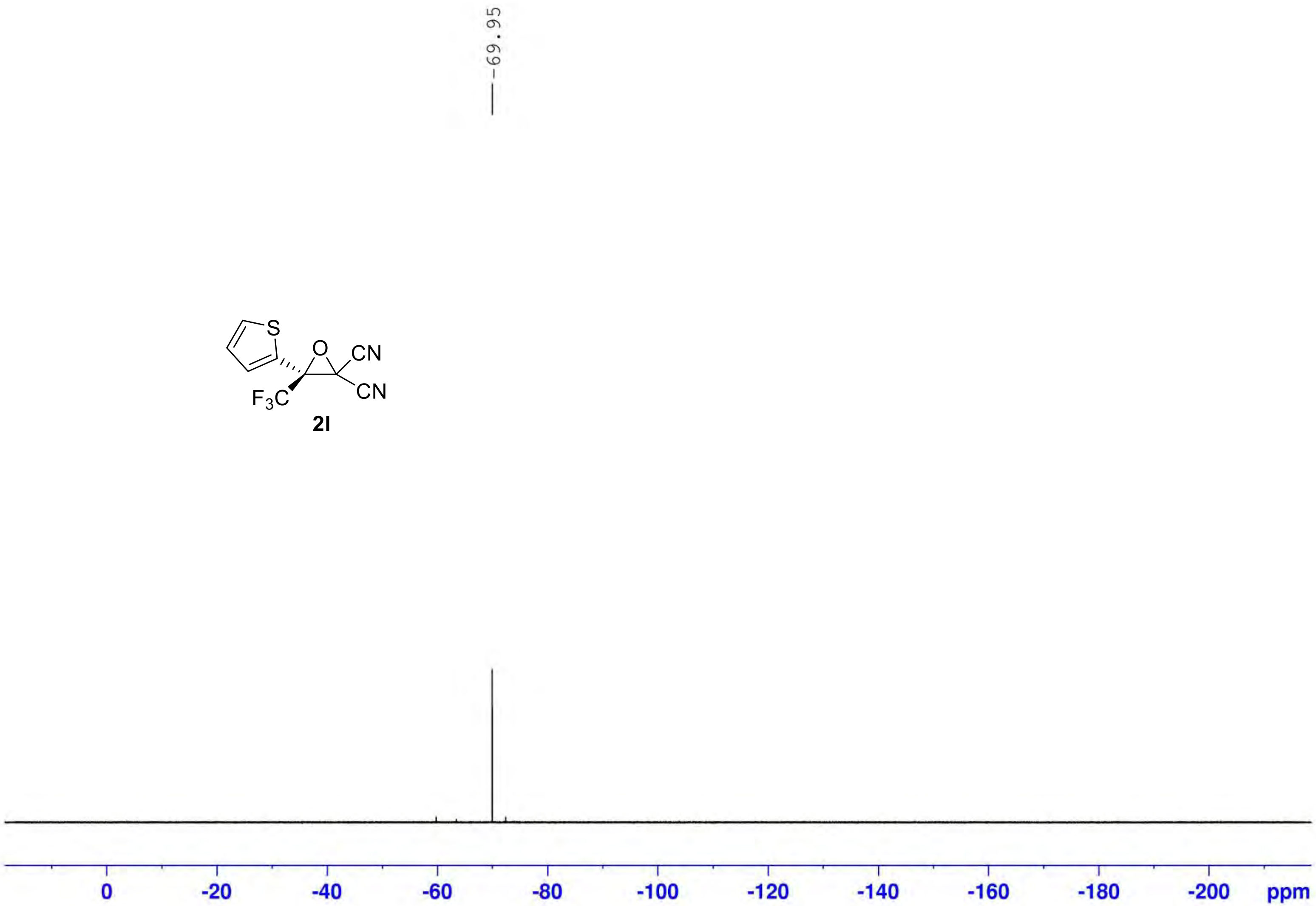


^{13}C NMR in $CDCl_3$ (100 MHz)

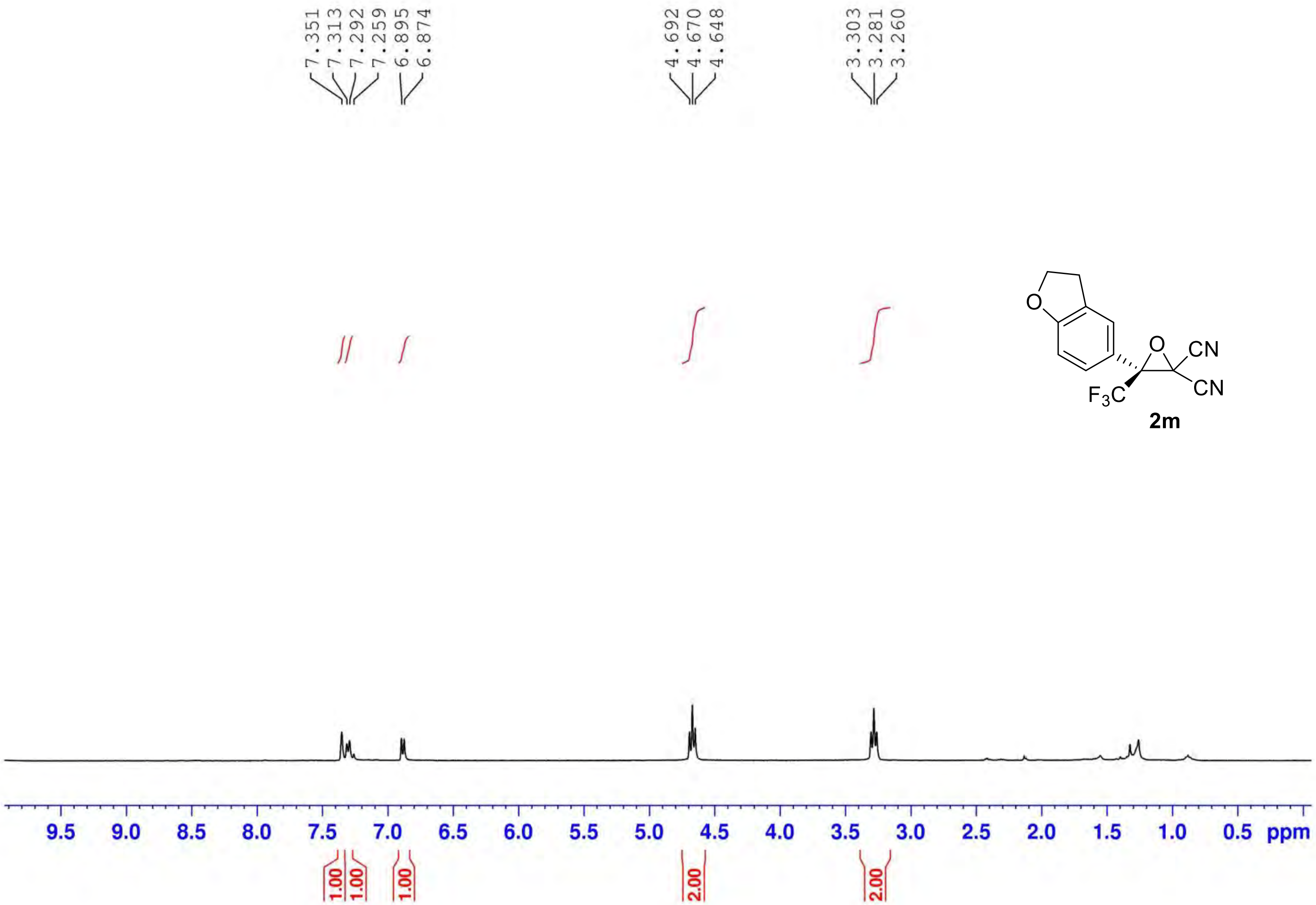


2l

^{19}F NMR in $CDCl_3$ (376 MHz)

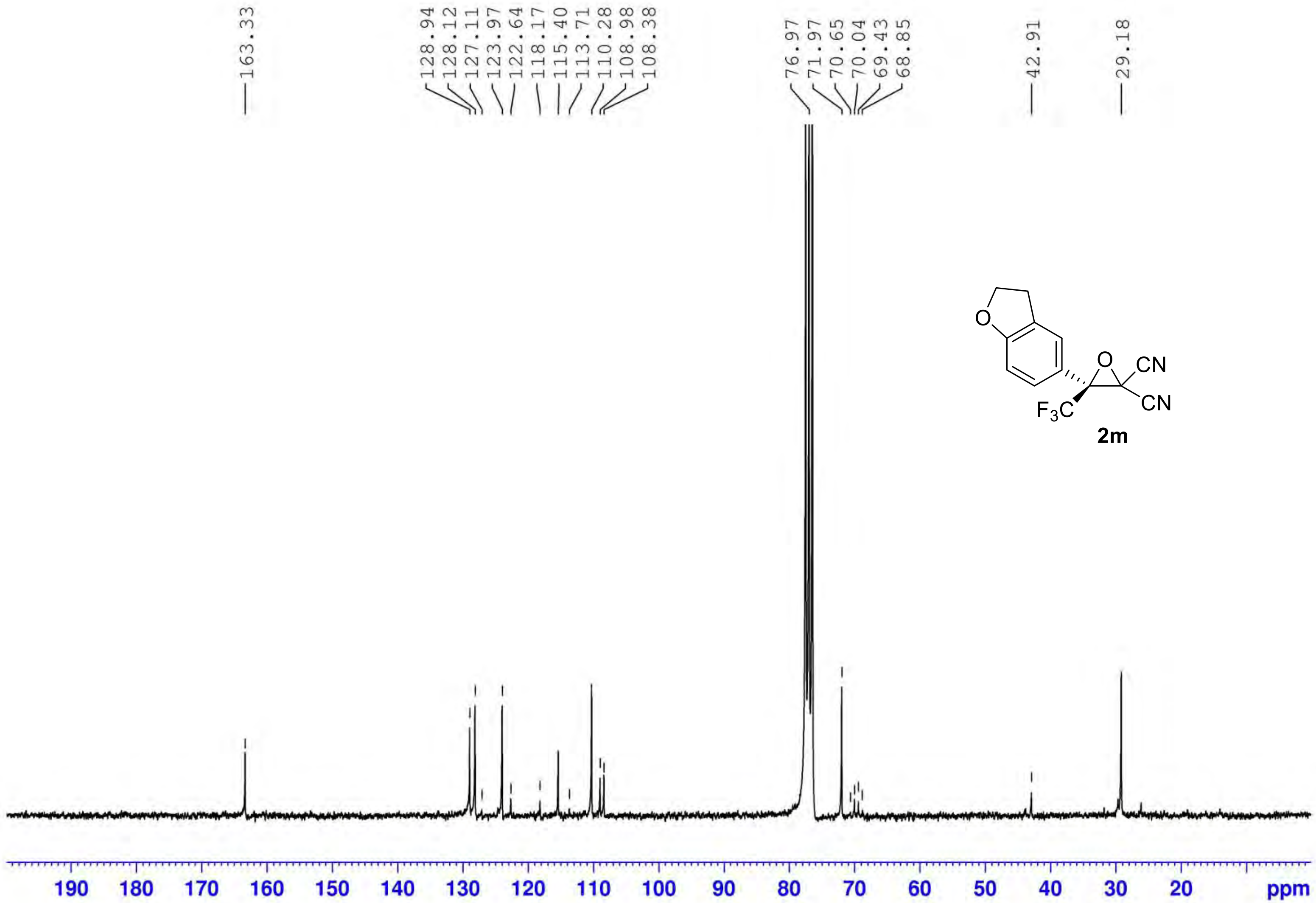


^{1}H NMR in $CDCl_3$ (400 MHz)



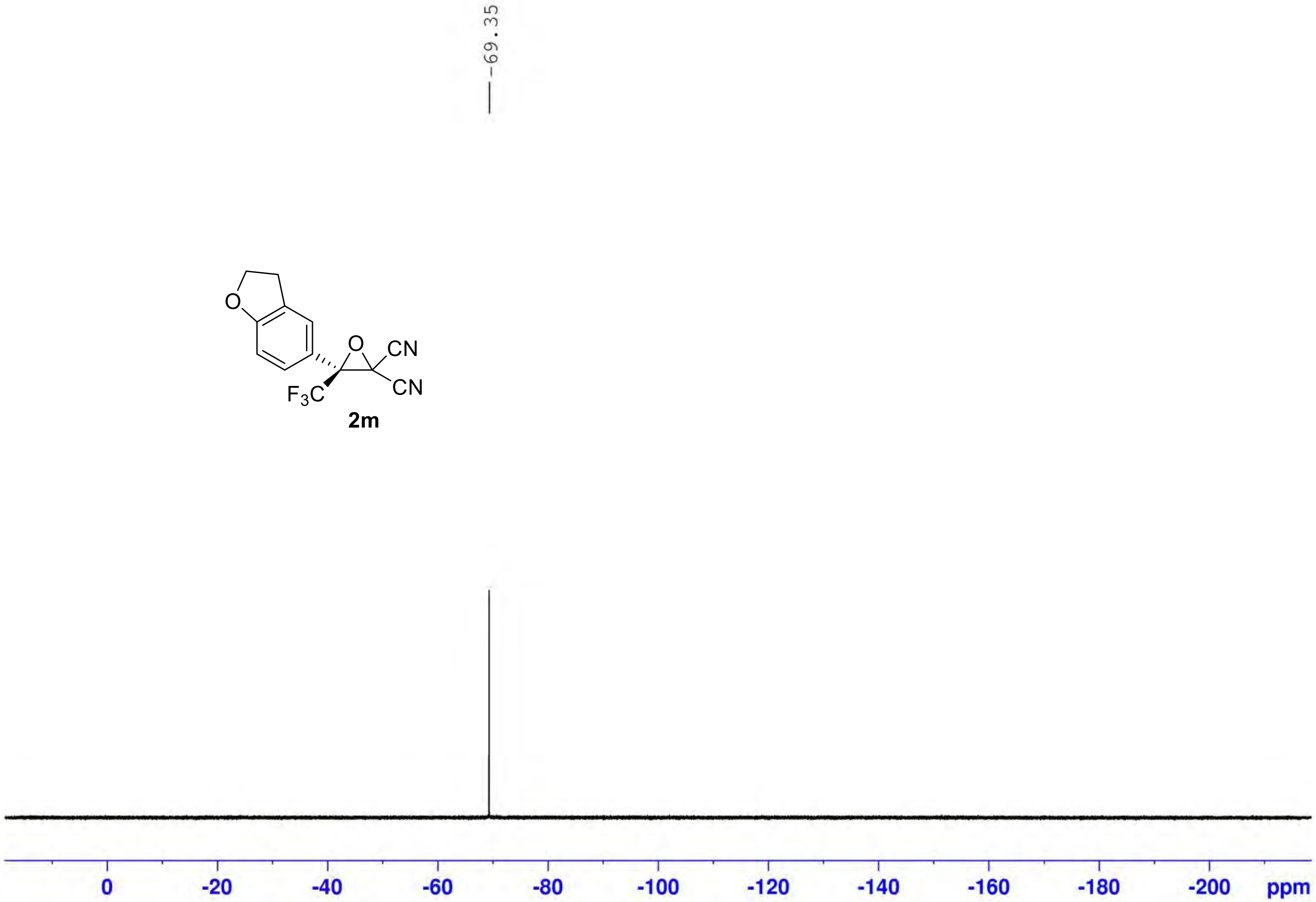
2m

^{13}C NMR in $CDCl_3$ (62.5 MHz)

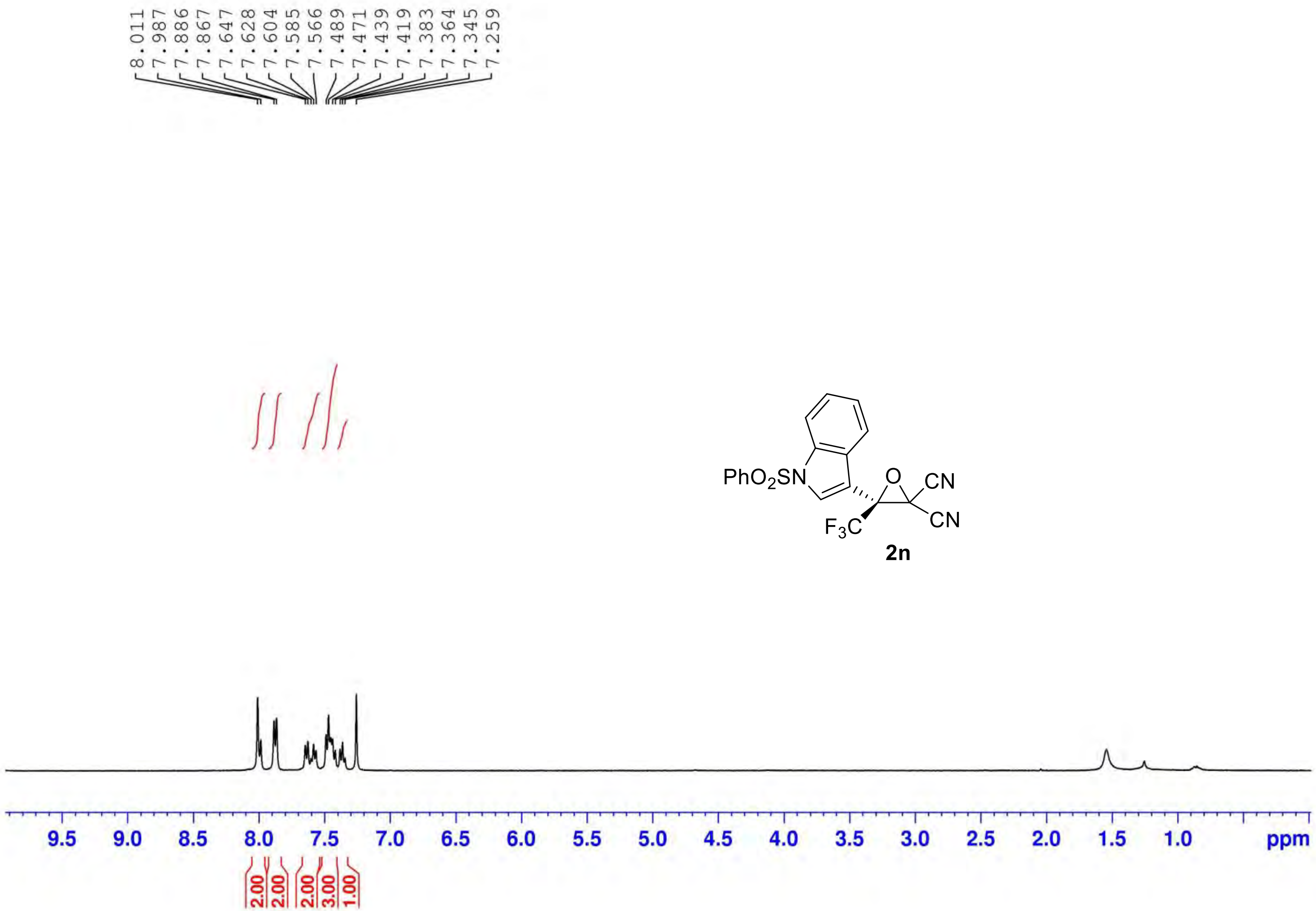


2m

^{19}F NMR in $CDCl_3$ (376 MHz)

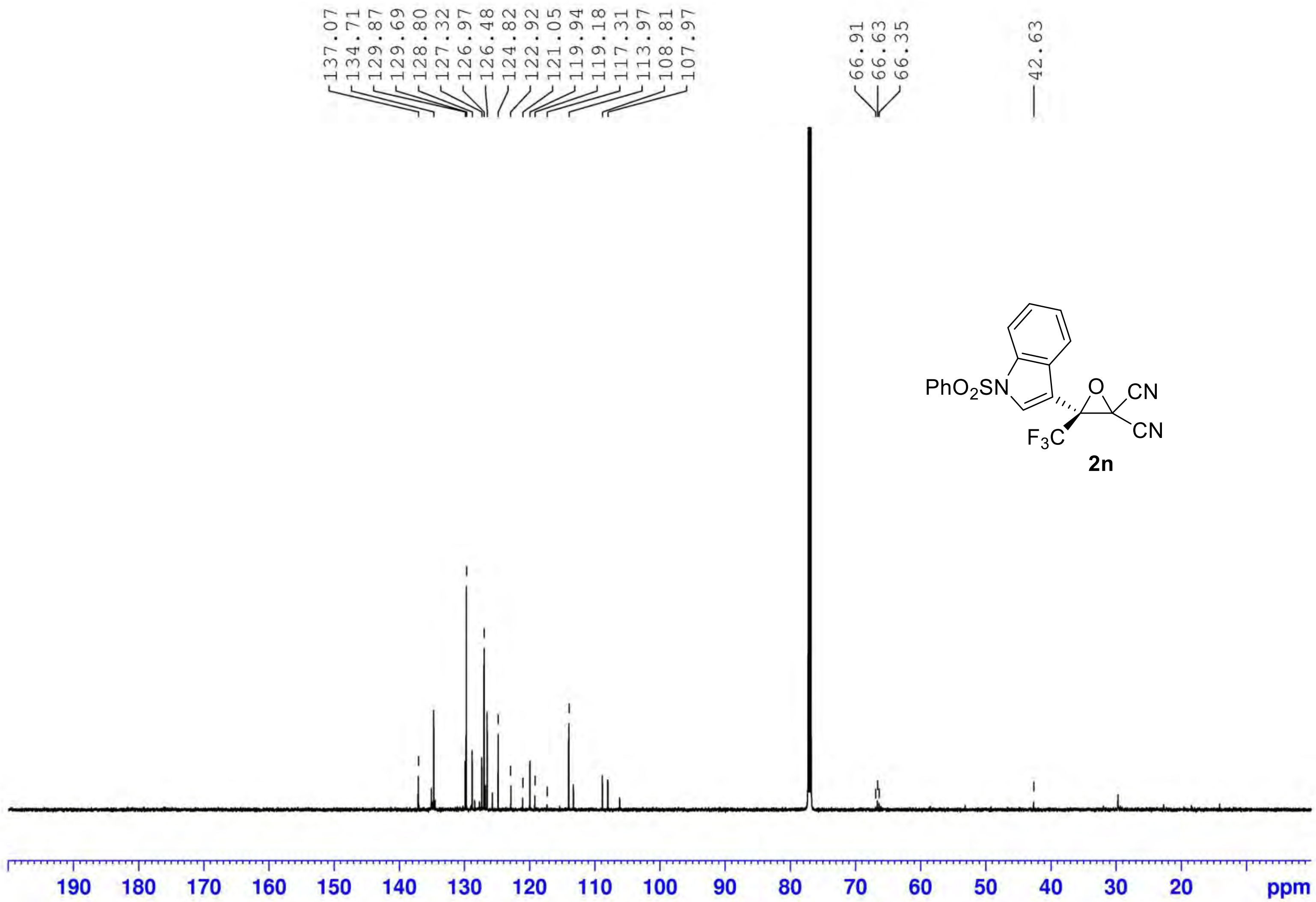


[1]H NMR in $CDCl_3$ (400 MHz)



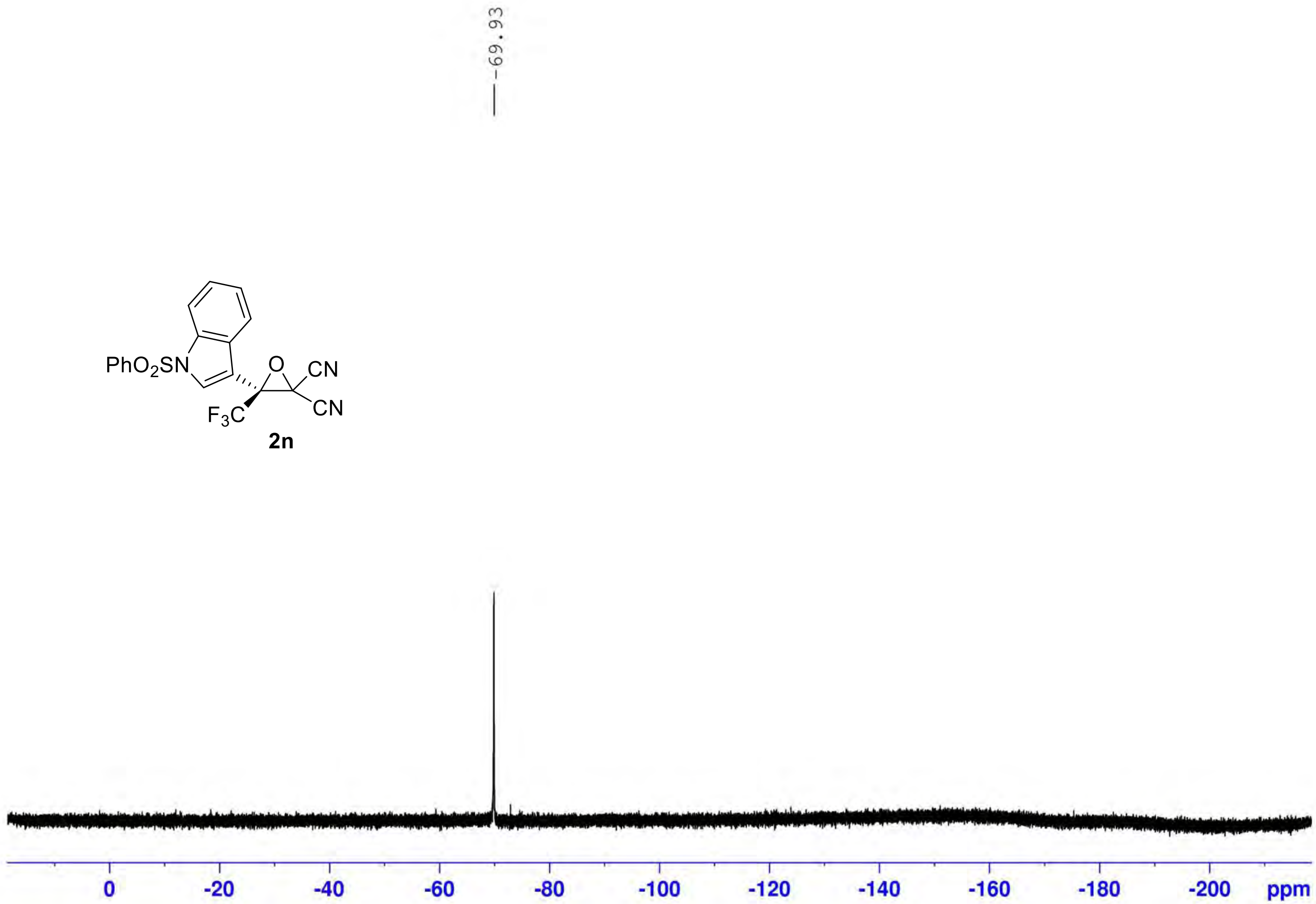
2n

^{13}C NMR in $CDCl_3$ (150 MHz)

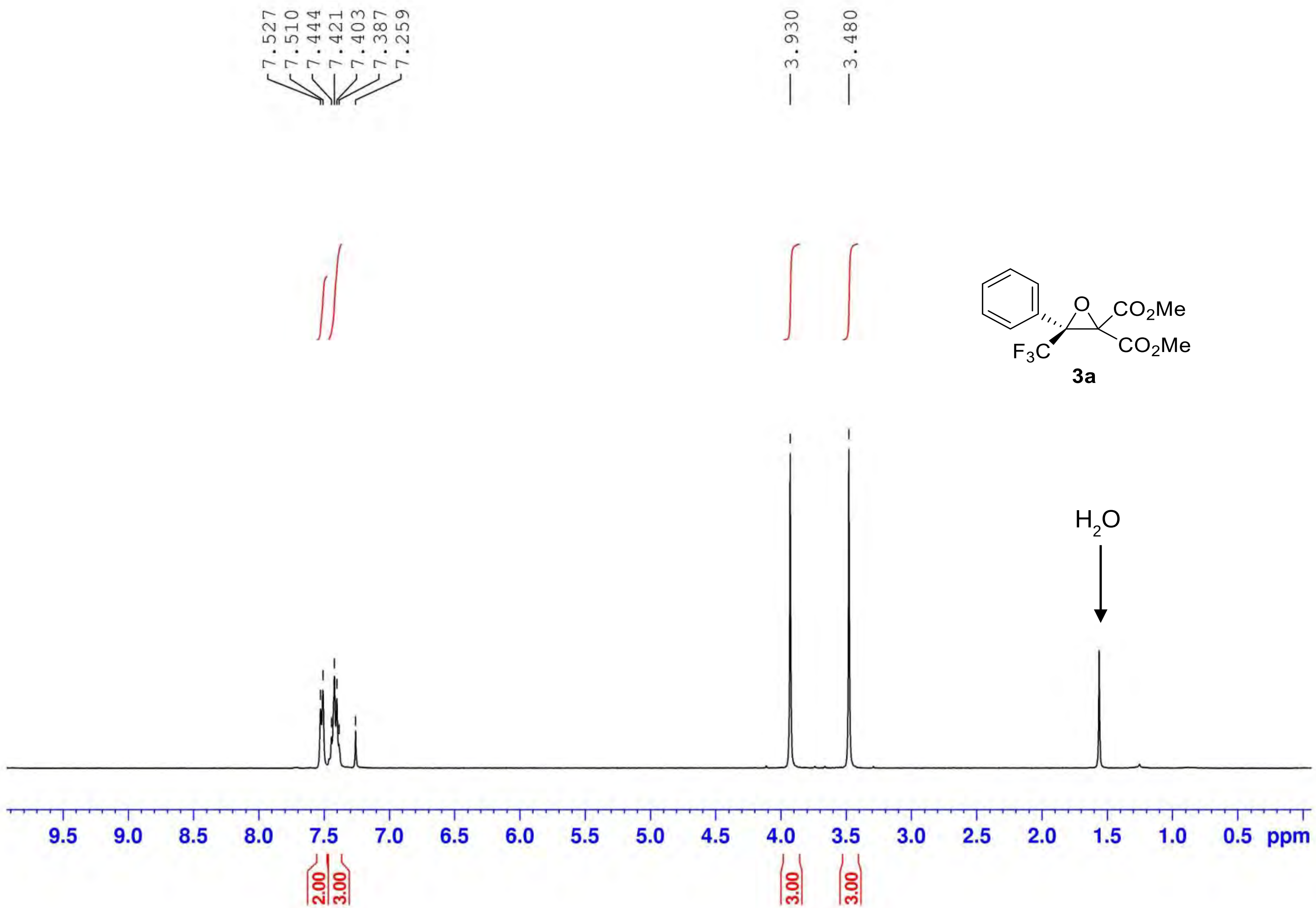


2n

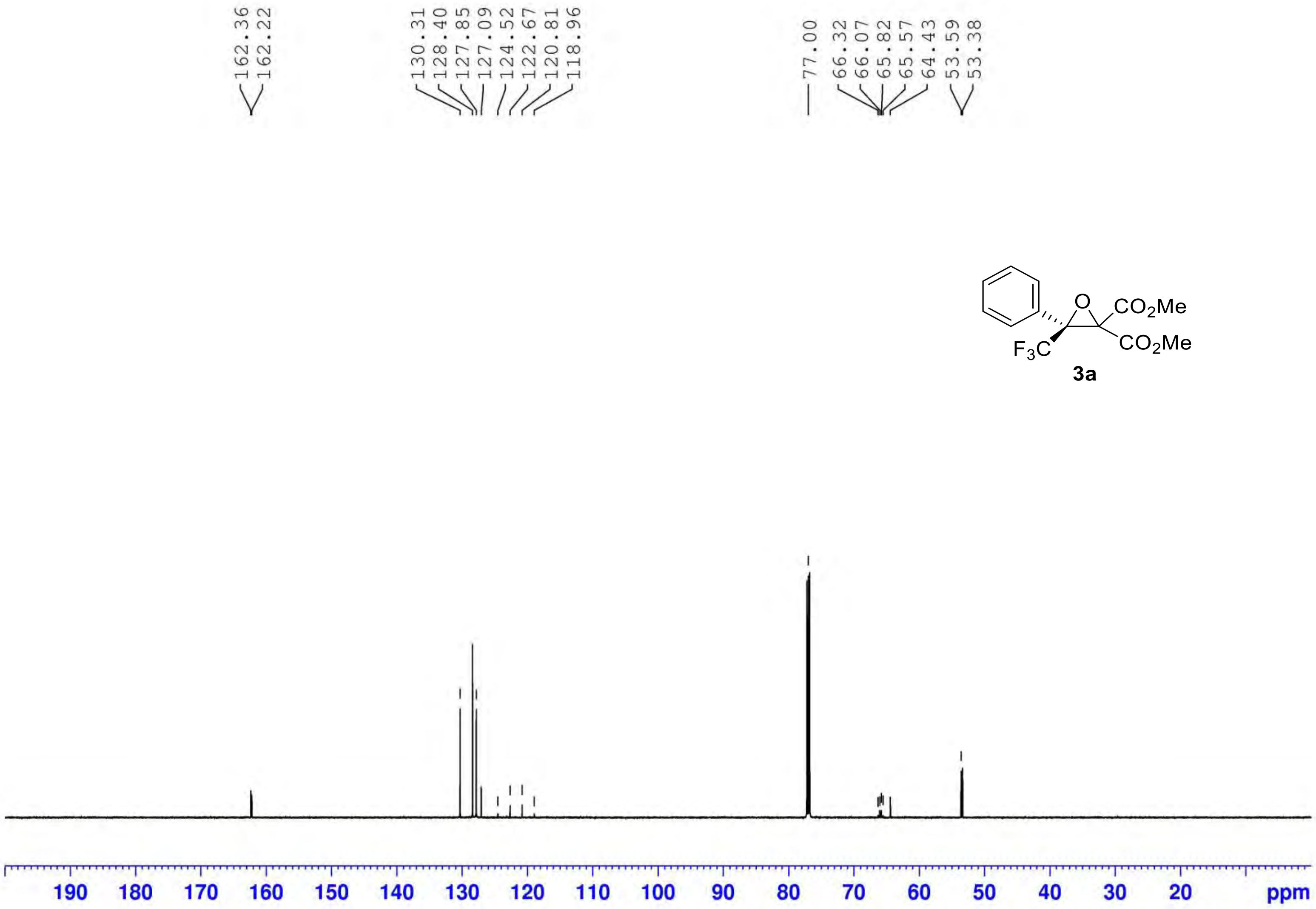
^{19}F NMR in $CDCl_3$ (376 MHz)



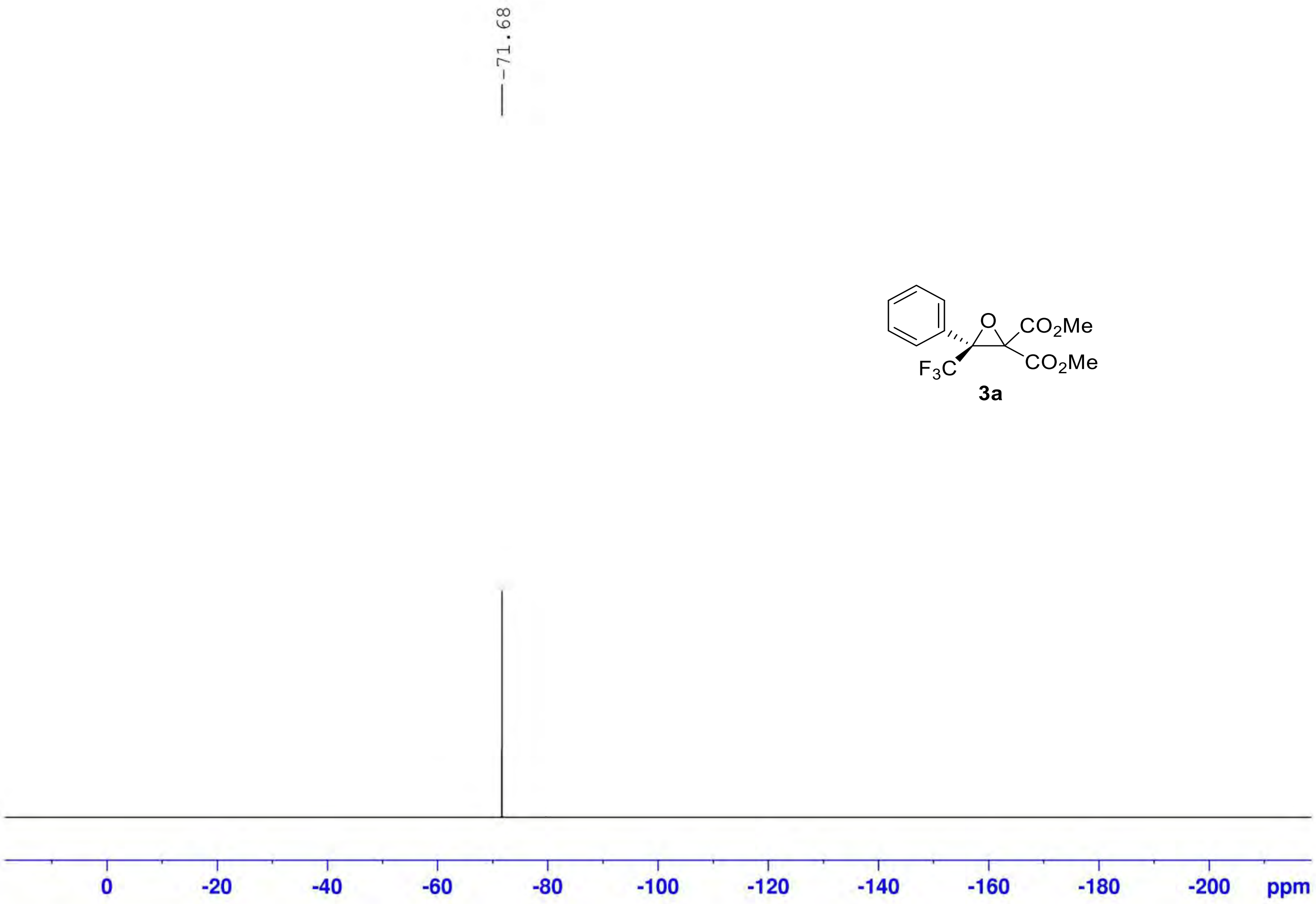
[1]H NMR in $CDCl_3$ (400 MHz)



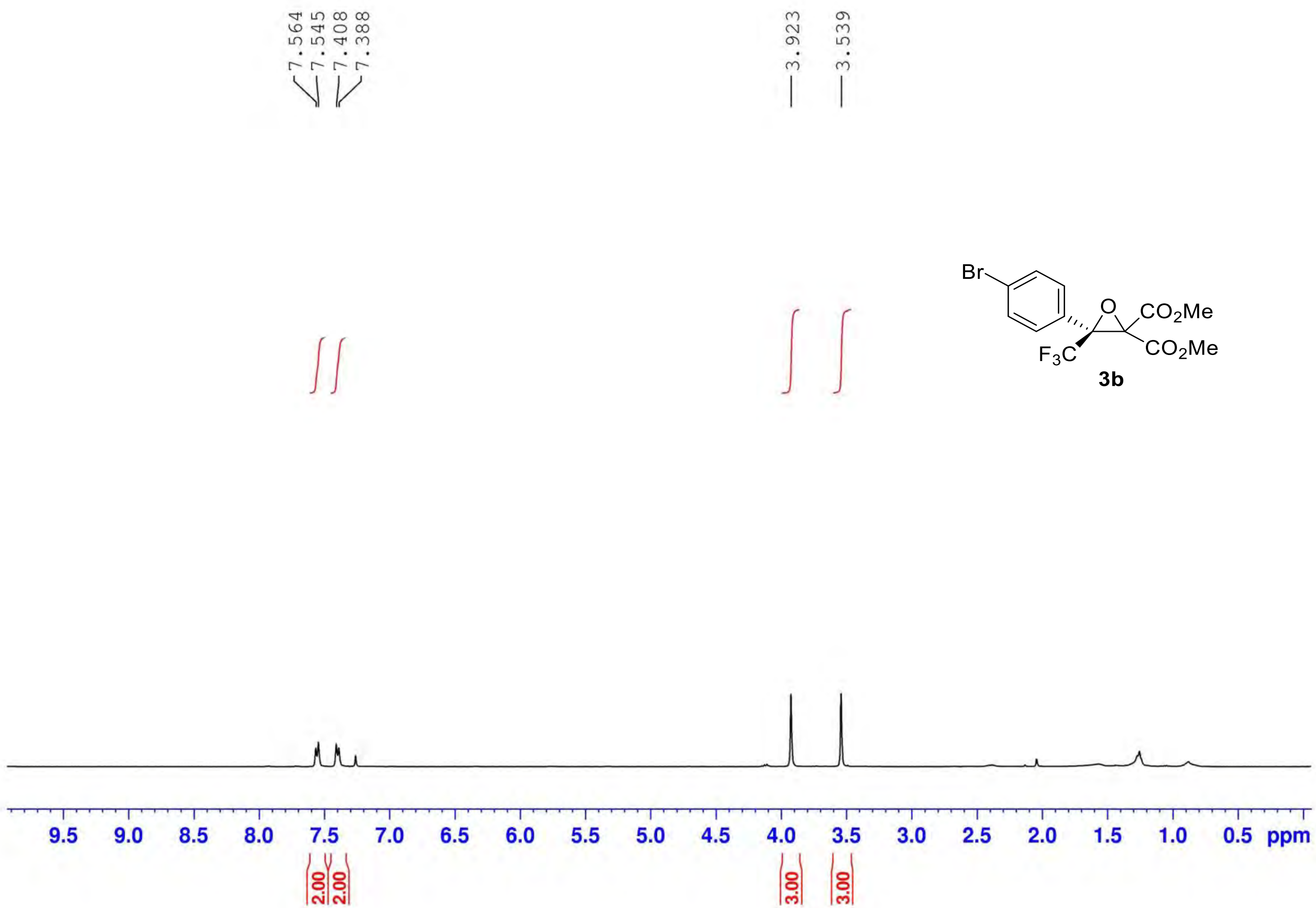
^{13}C NMR in $CDCl_3$ (150 MHz)



^{19}F NMR in $CDCl_3$ (564 MHz)

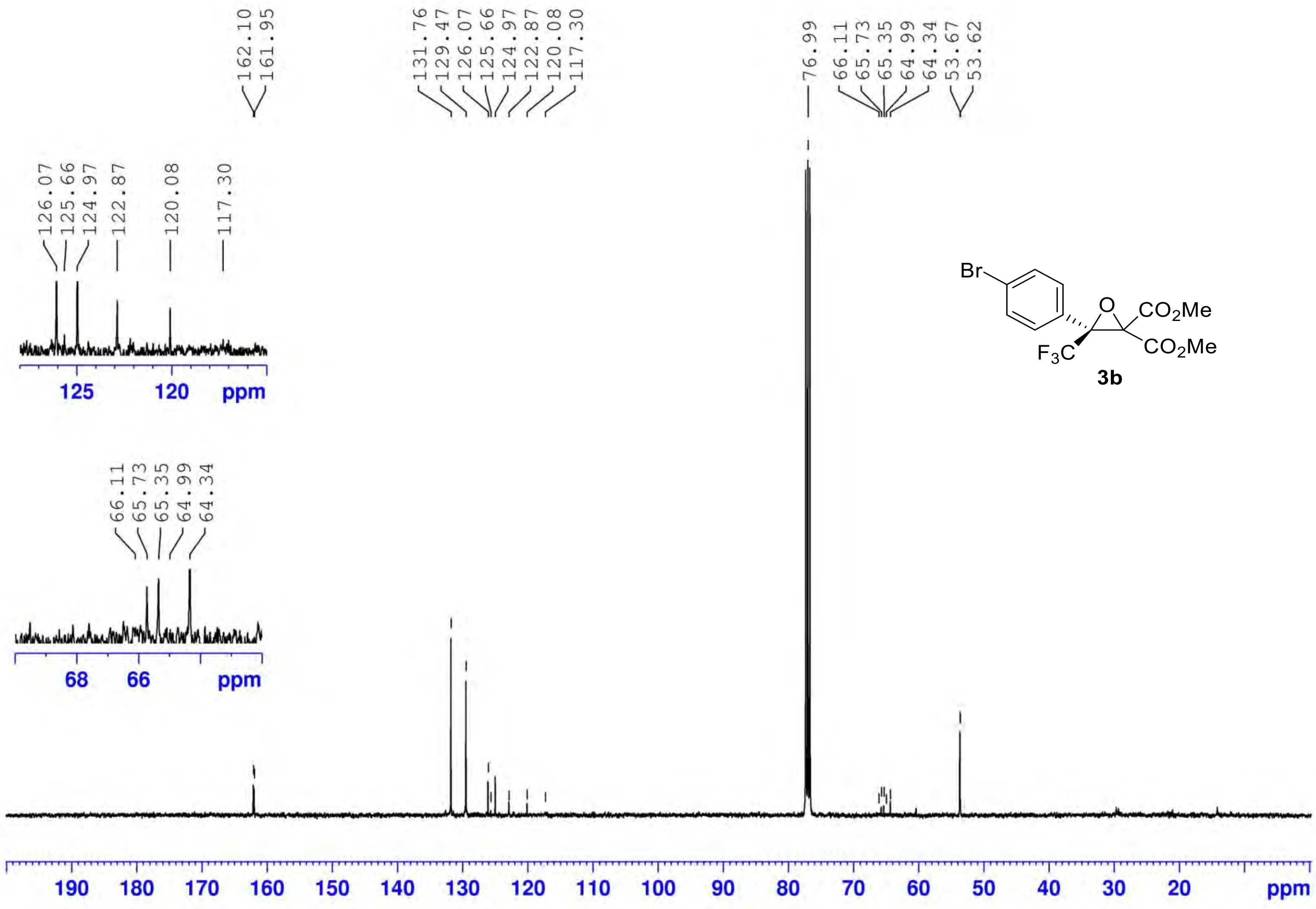


^1H NMR in $CDCl_3$ (400 MHz)

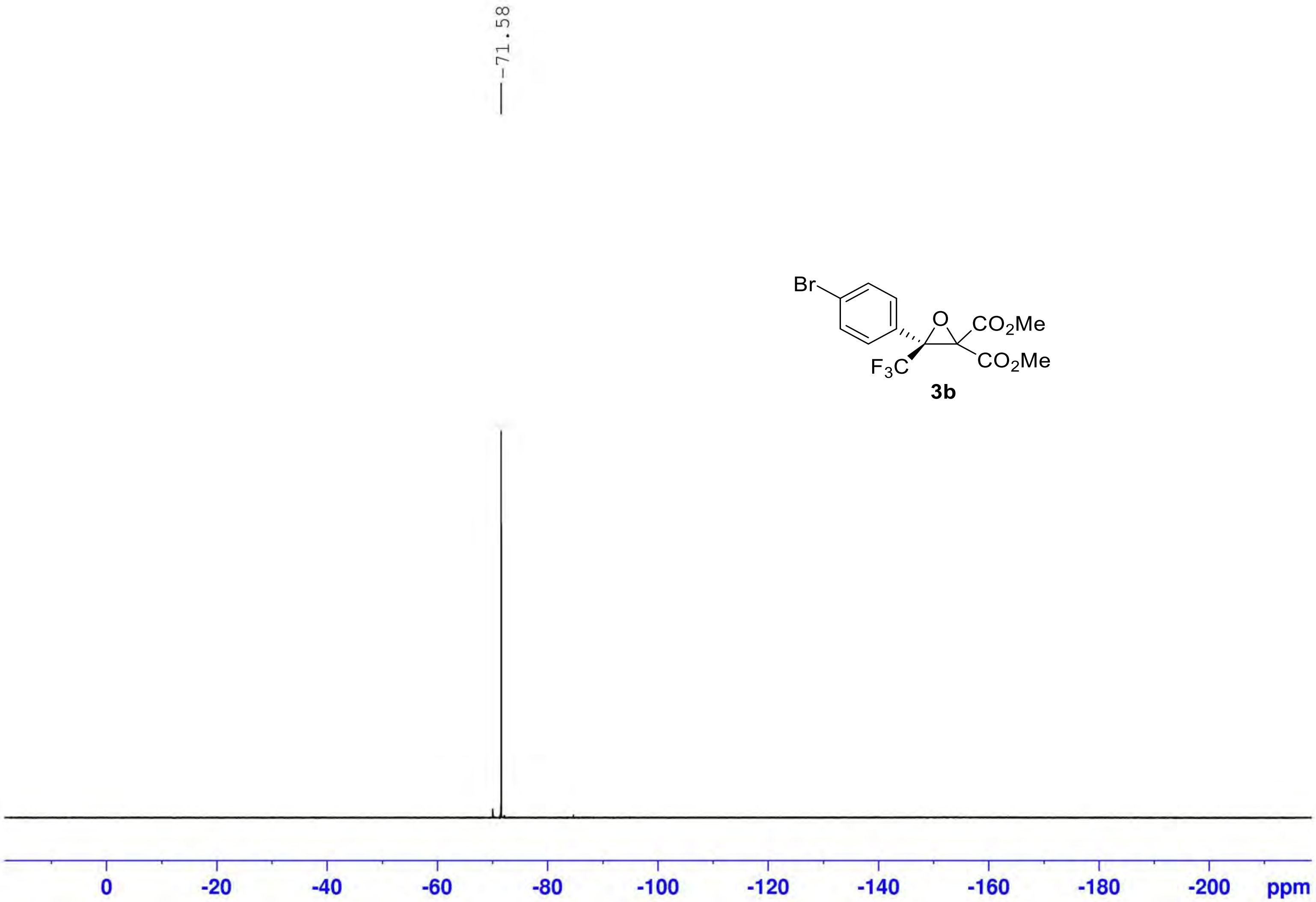


3b

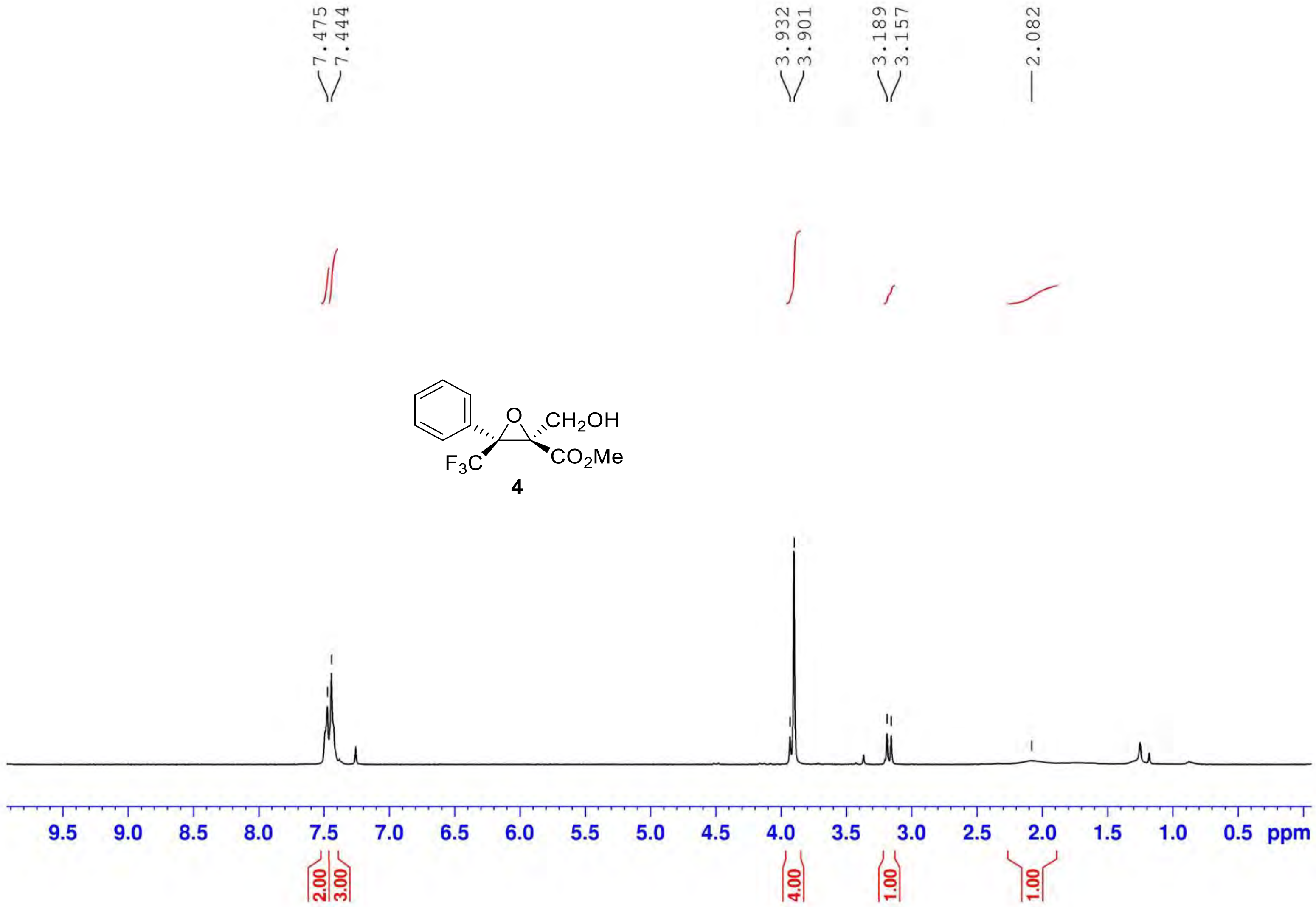
[13]C NMR in $CDCl_3$ (100 MHz)



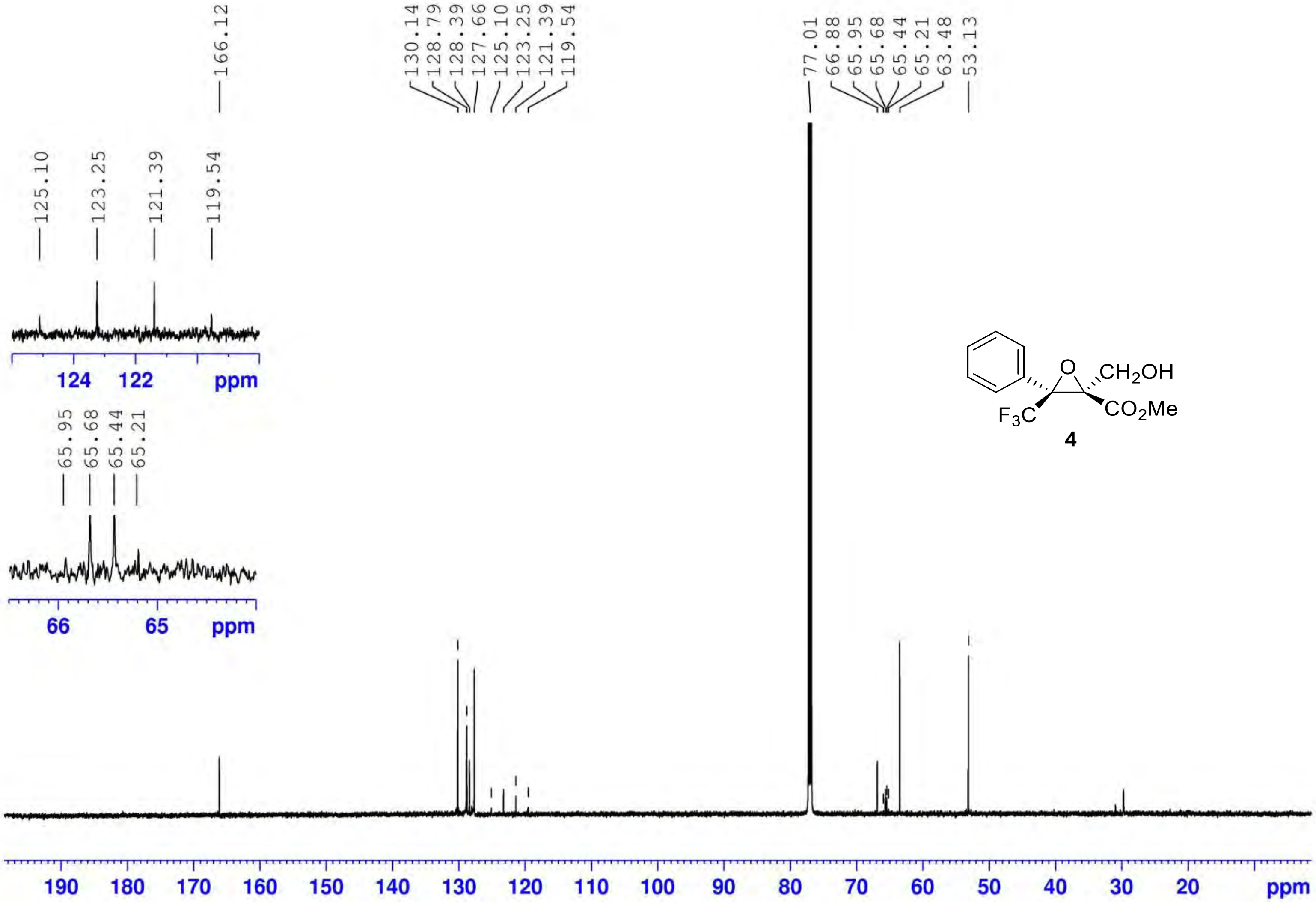
^{19}F NMR in $CDCl_3$ (376 MHz)



[1]H NMR in $CDCl_3$ (400 MHz)

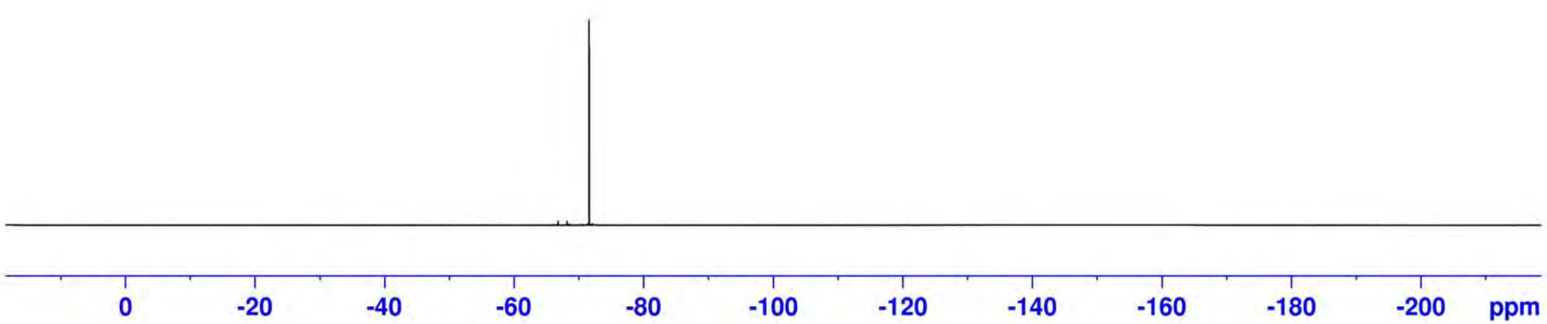


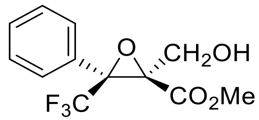
^{13}C NMR in $CDCl_3$ (150 MHz)



4

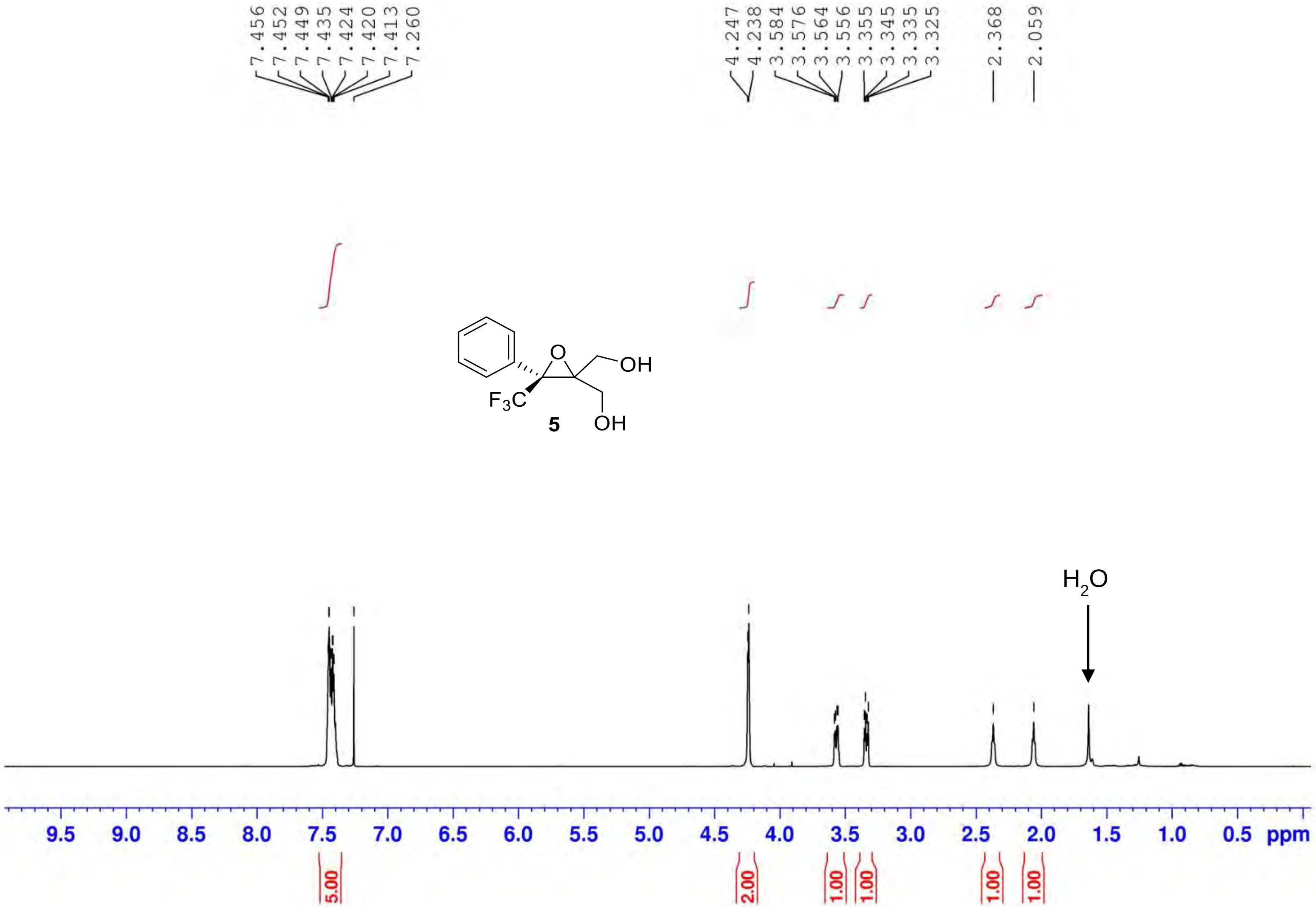
[19]F NMR in $CDCl_3$ (376 MHz)



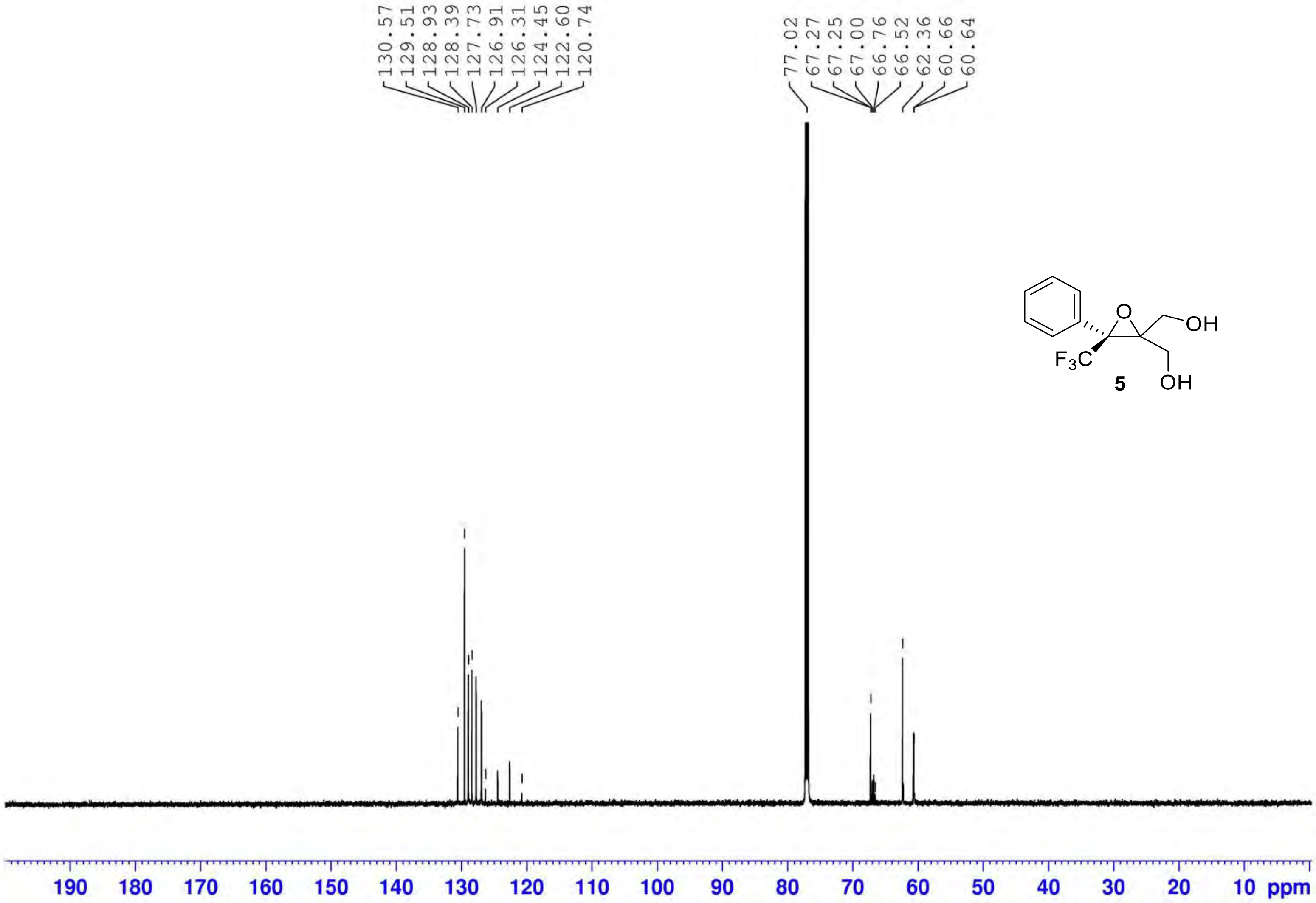


4

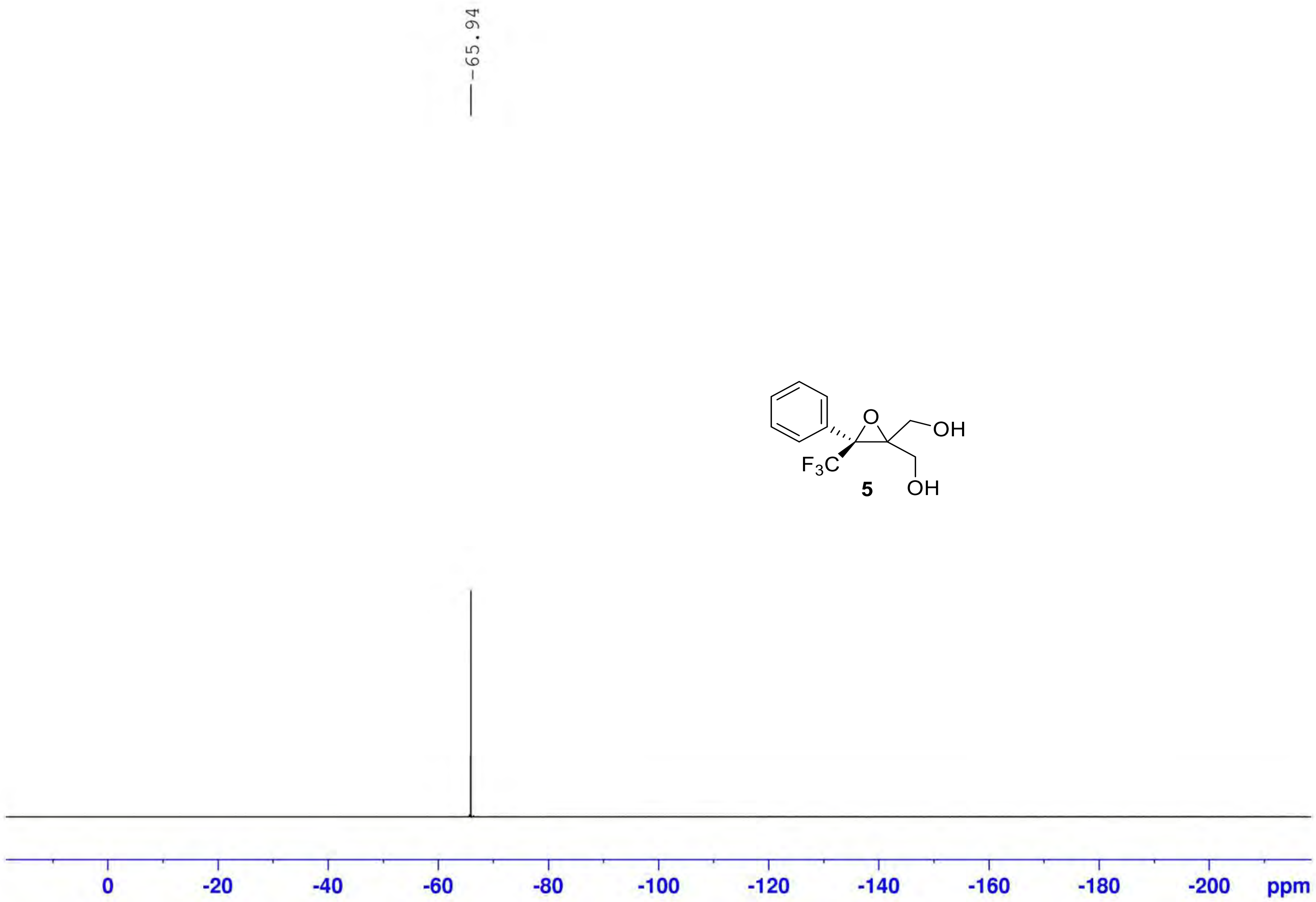
^1H NMR in $CDCl_3$ (600 MHz)



^{13}C NMR in $CDCl_3$ (150 MHz)

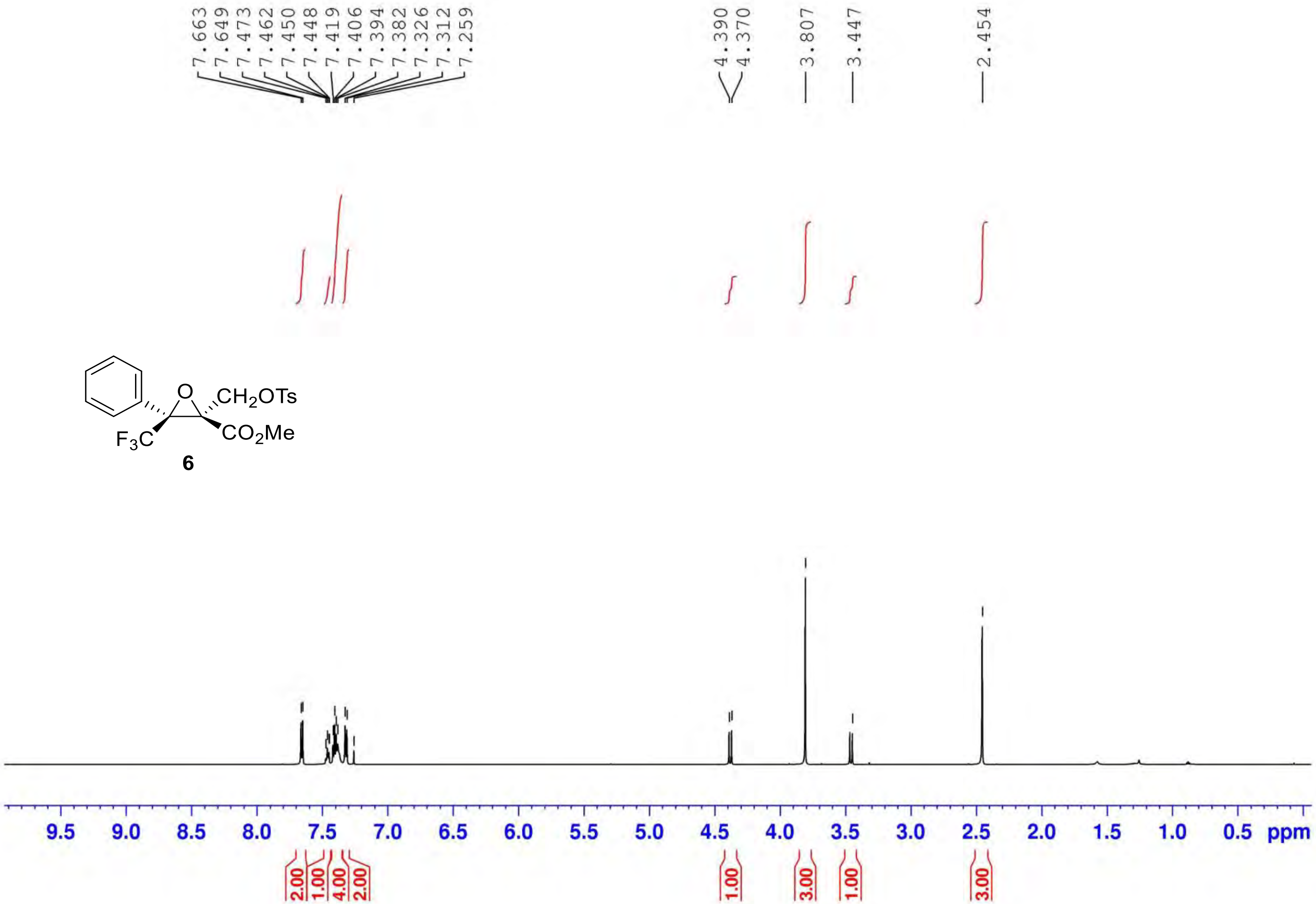


^{19}F NMR in $CDCl_3$ (376 MHz)

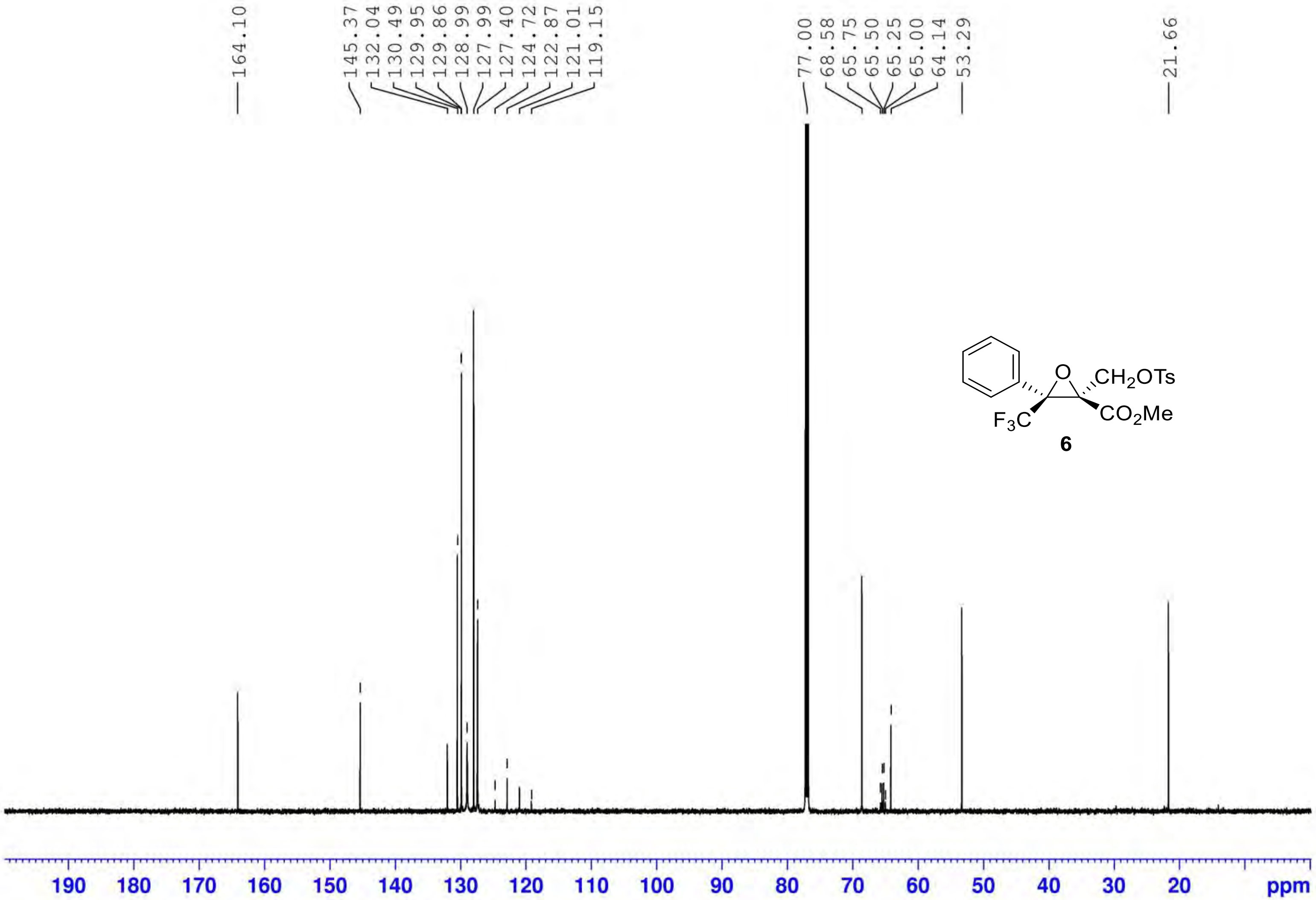


5

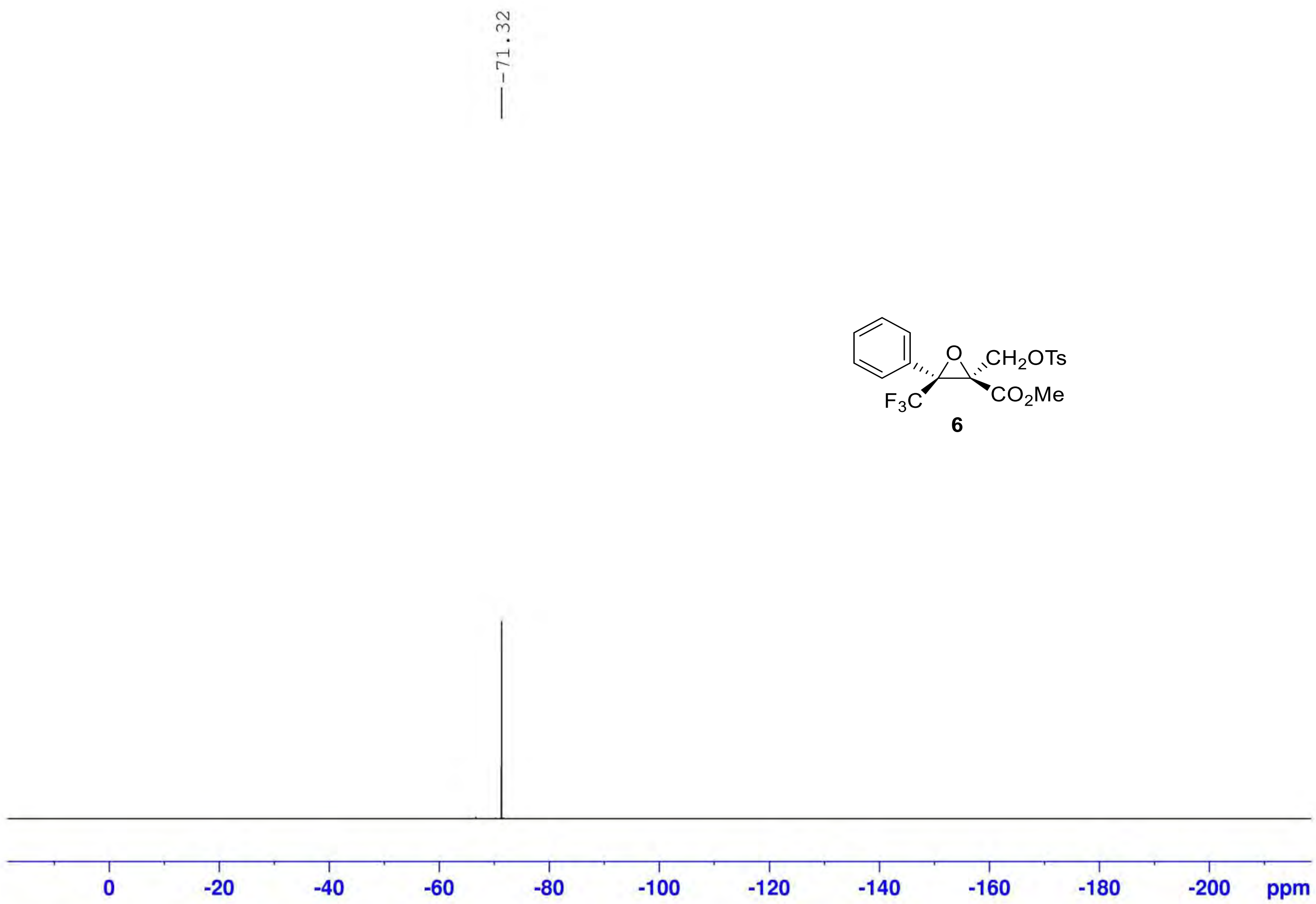
[1]H NMR in $CDCl_3$ (600 MHz)



^{13}C NMR in $CDCl_3$ (150 MHz)

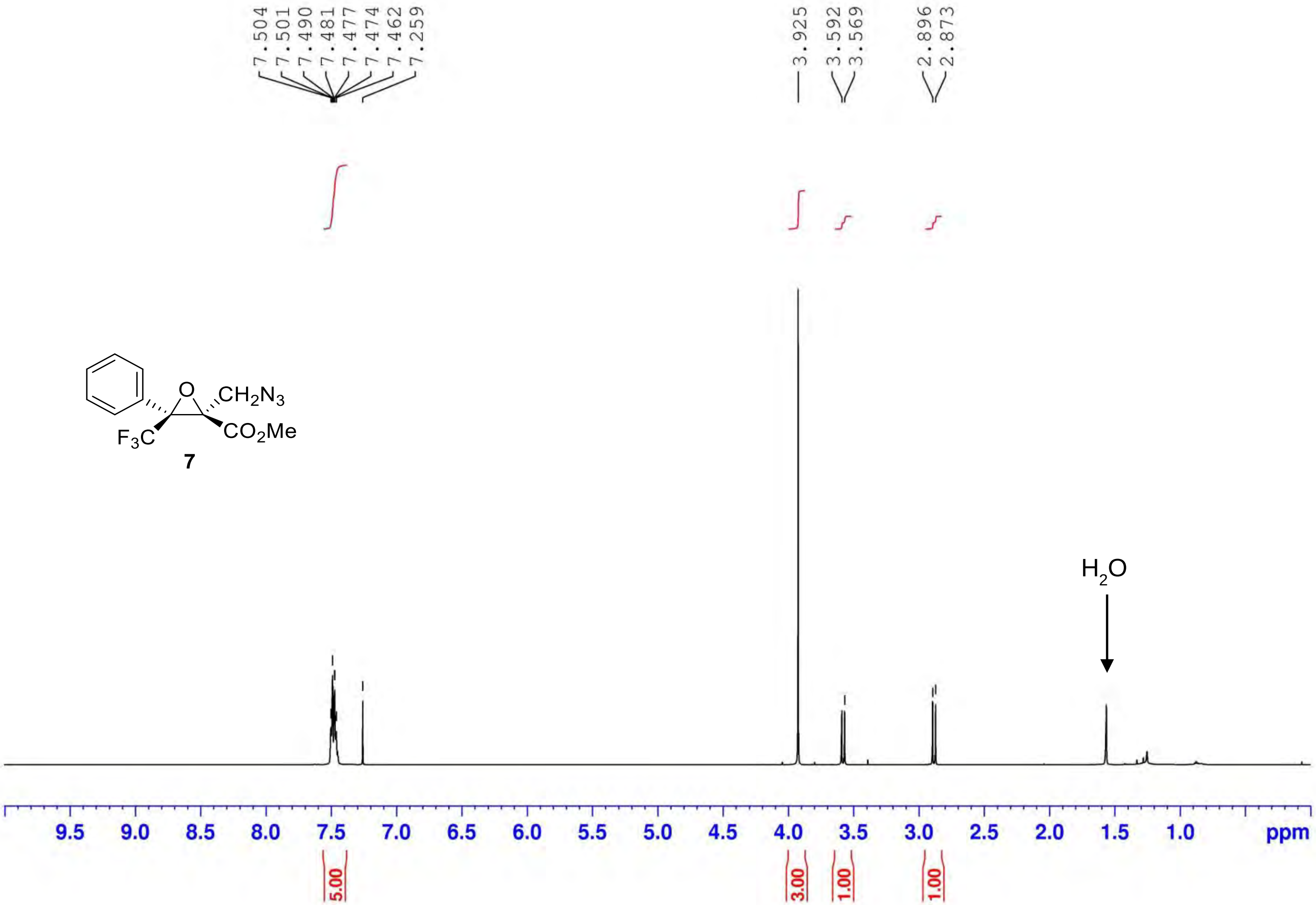


^{19}F NMR in $CDCl_3$ (564 MHz)

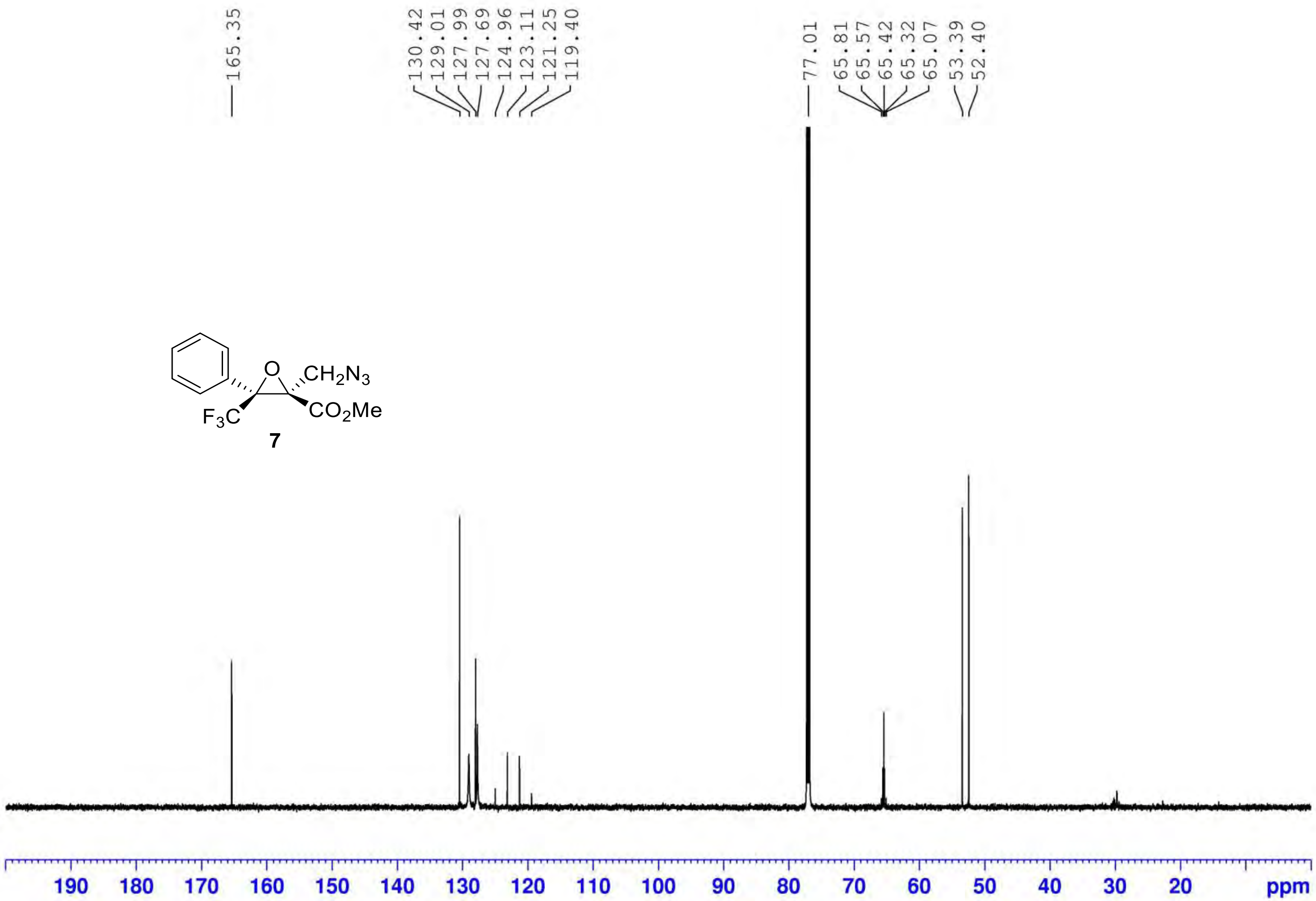


6

[1]H NMR in $CDCl_3$ (600 MHz)

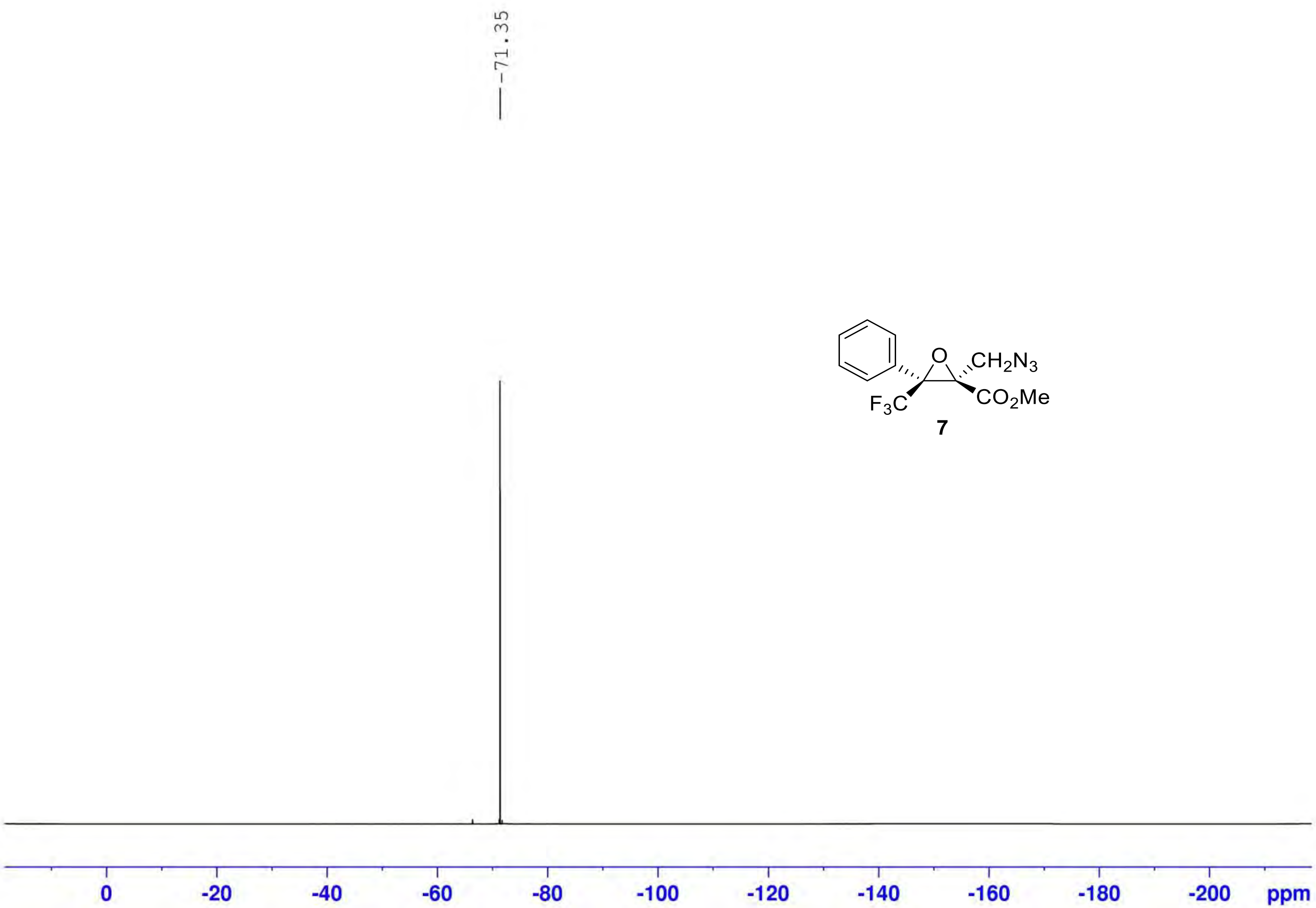


^{13}C NMR in $CDCl_3$ (150 MHz)

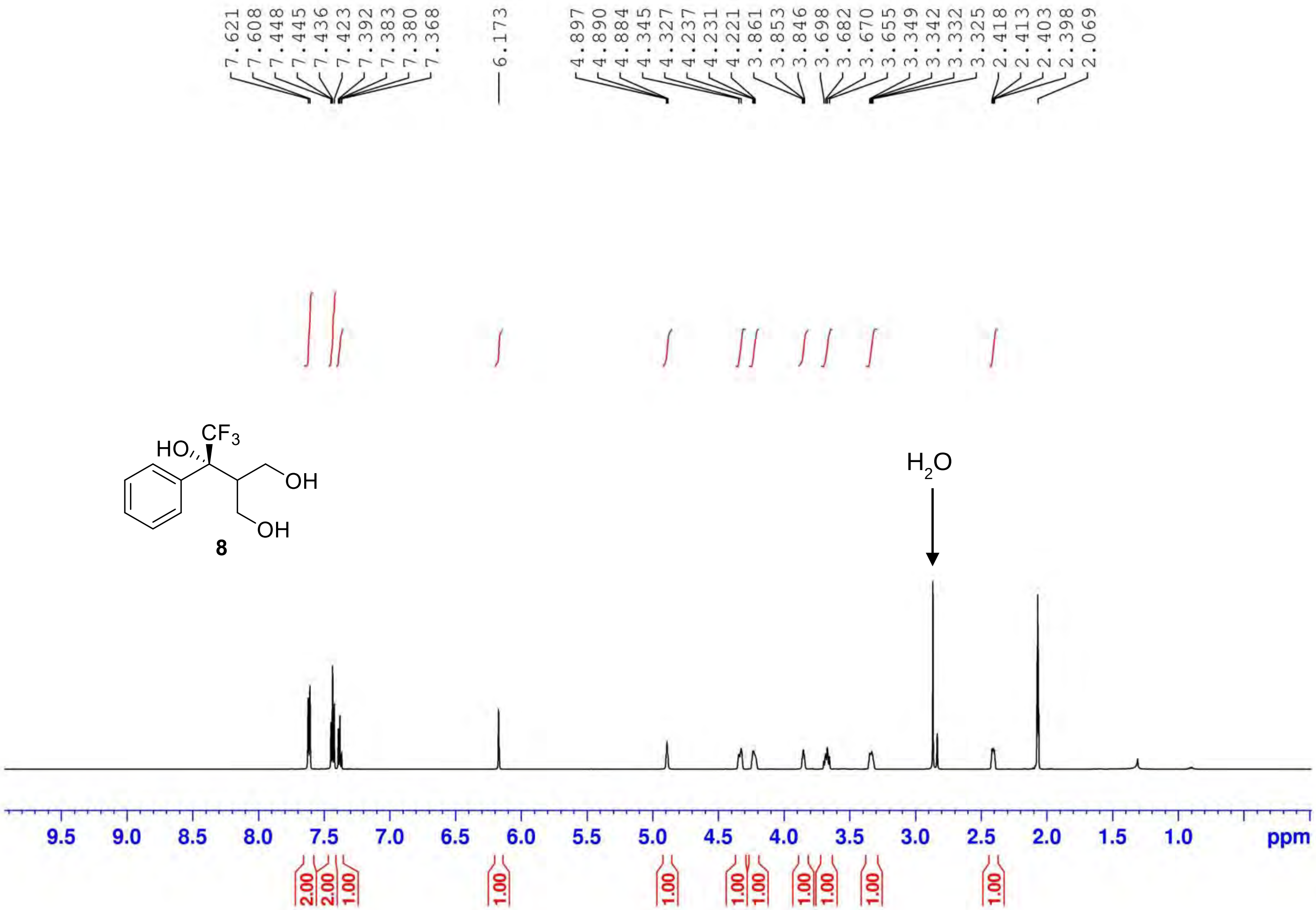


7

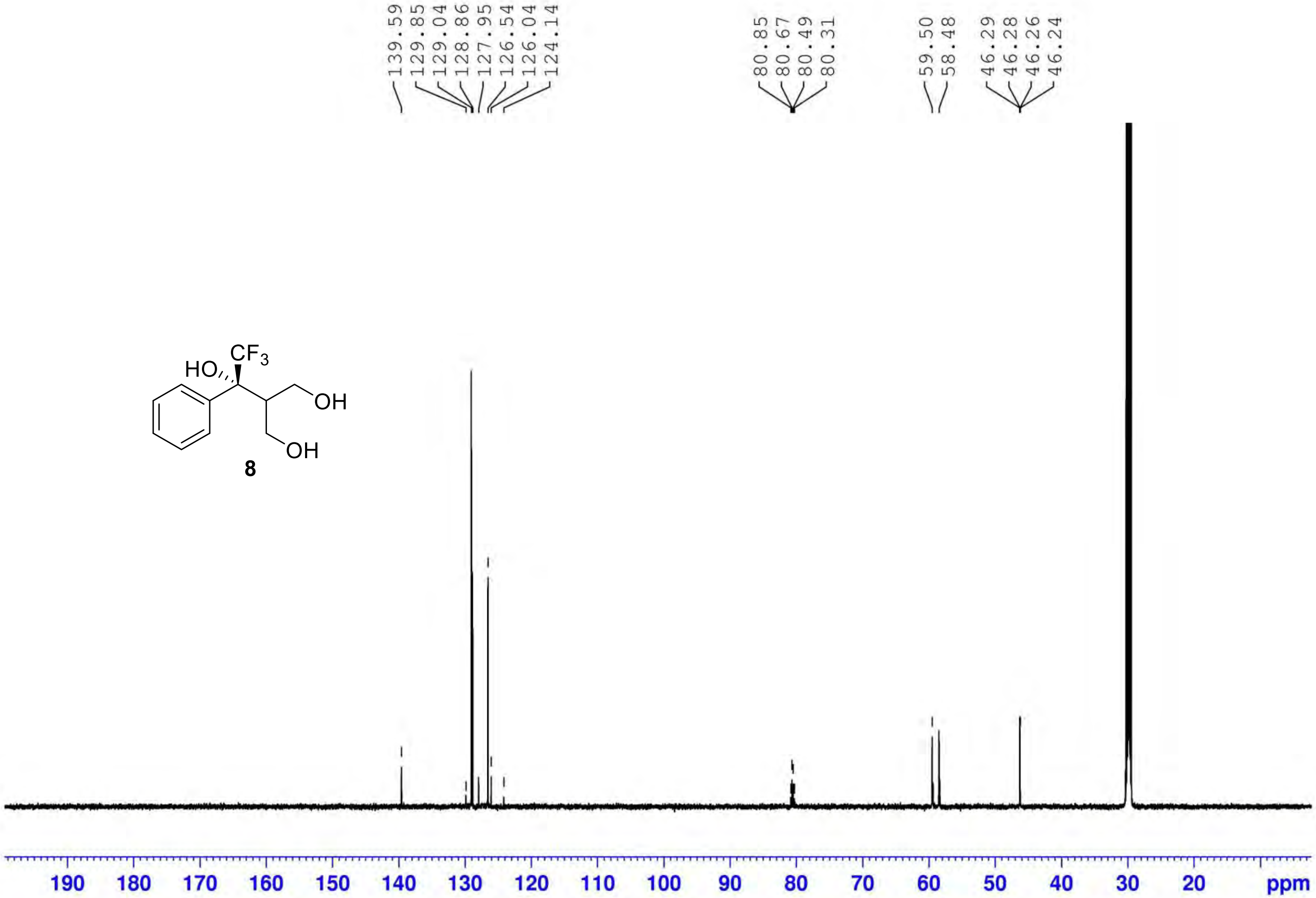
^{19}F NMR in $CDCl_3$ (564 MHz)



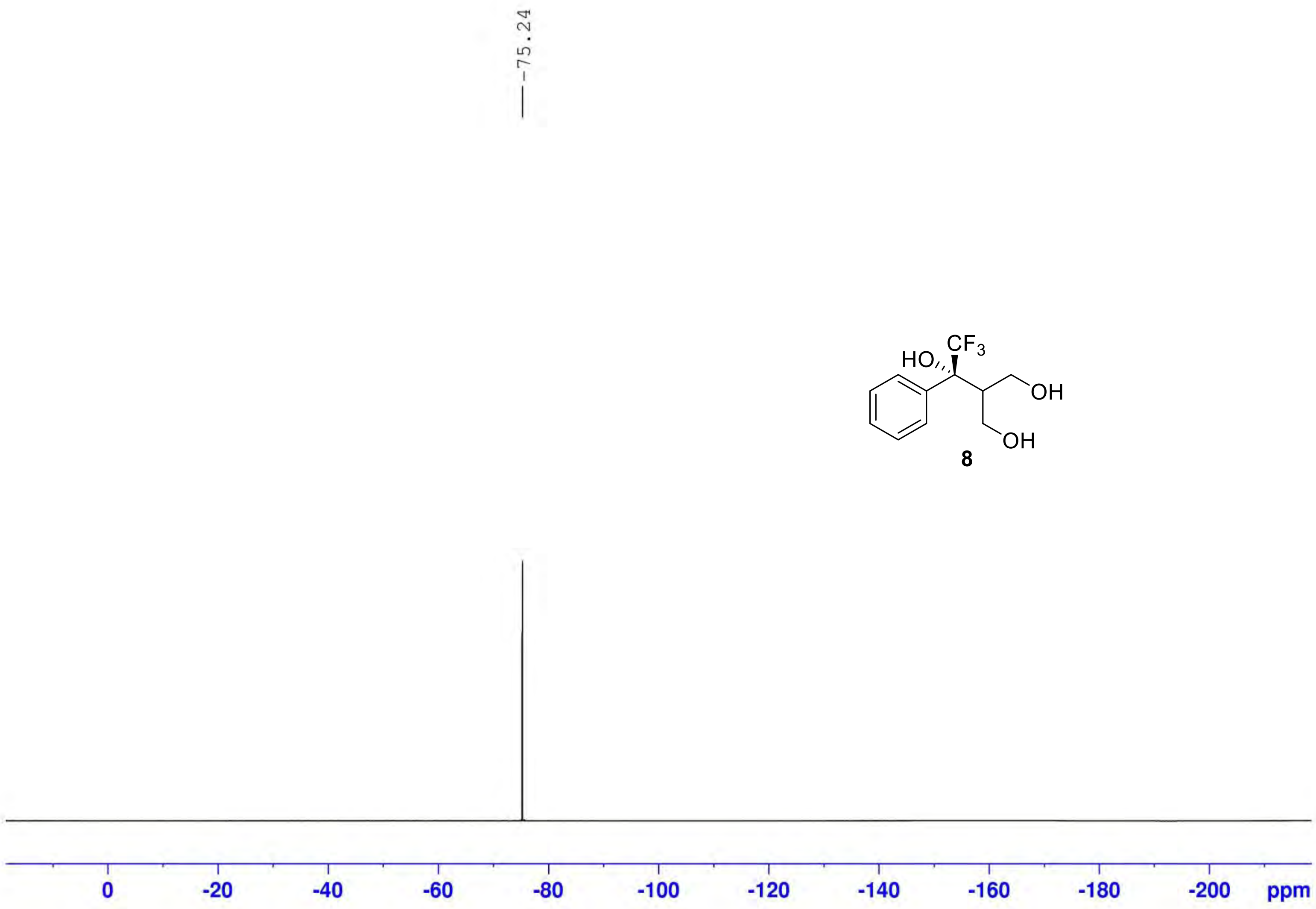
^1H NMR in acetone-d_6 (600 MHz)



^{13}C NMR in acetone-d_6 (150 MHz)

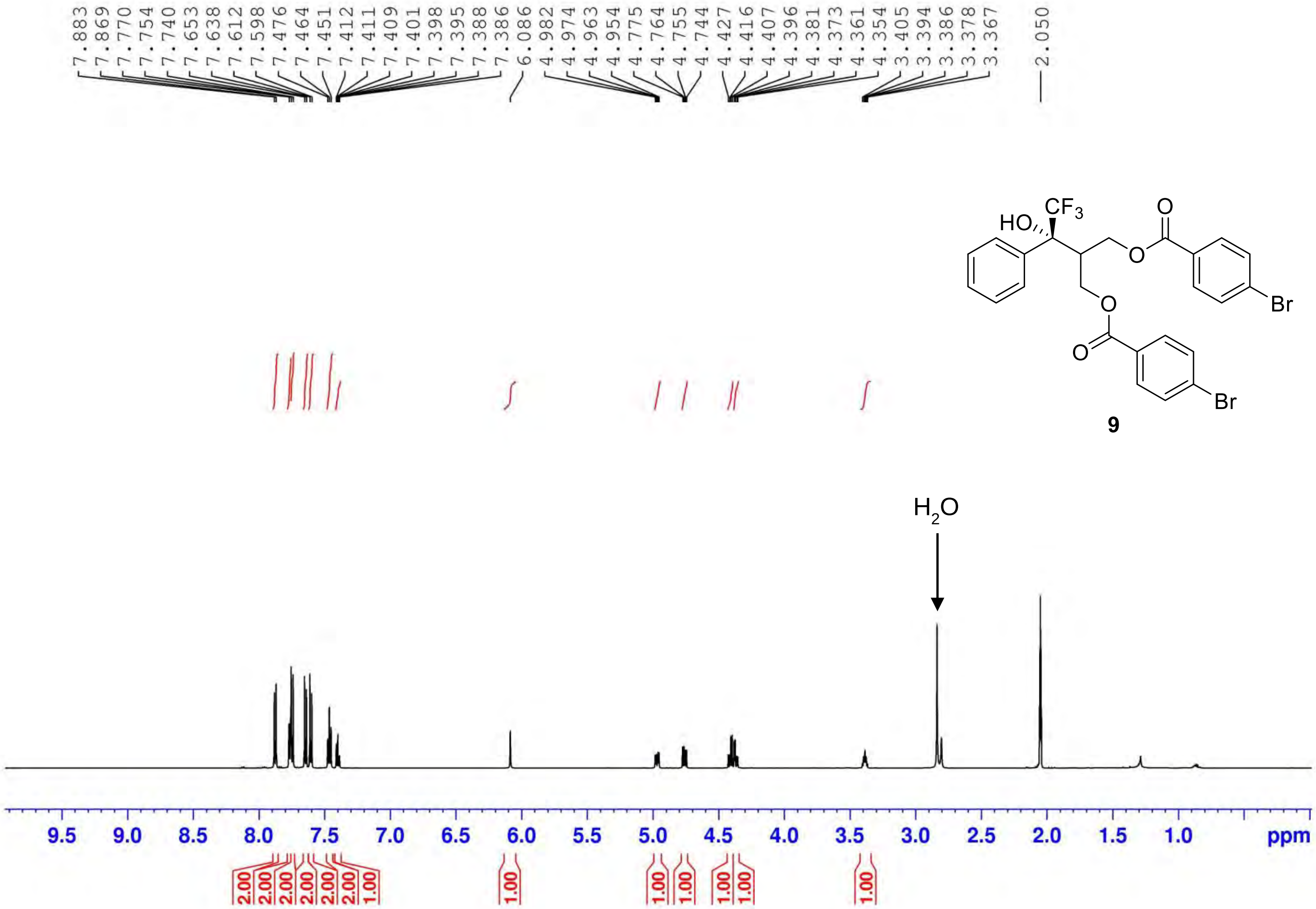


^{19}F NMR in acetone-d_6 (564 MHz)

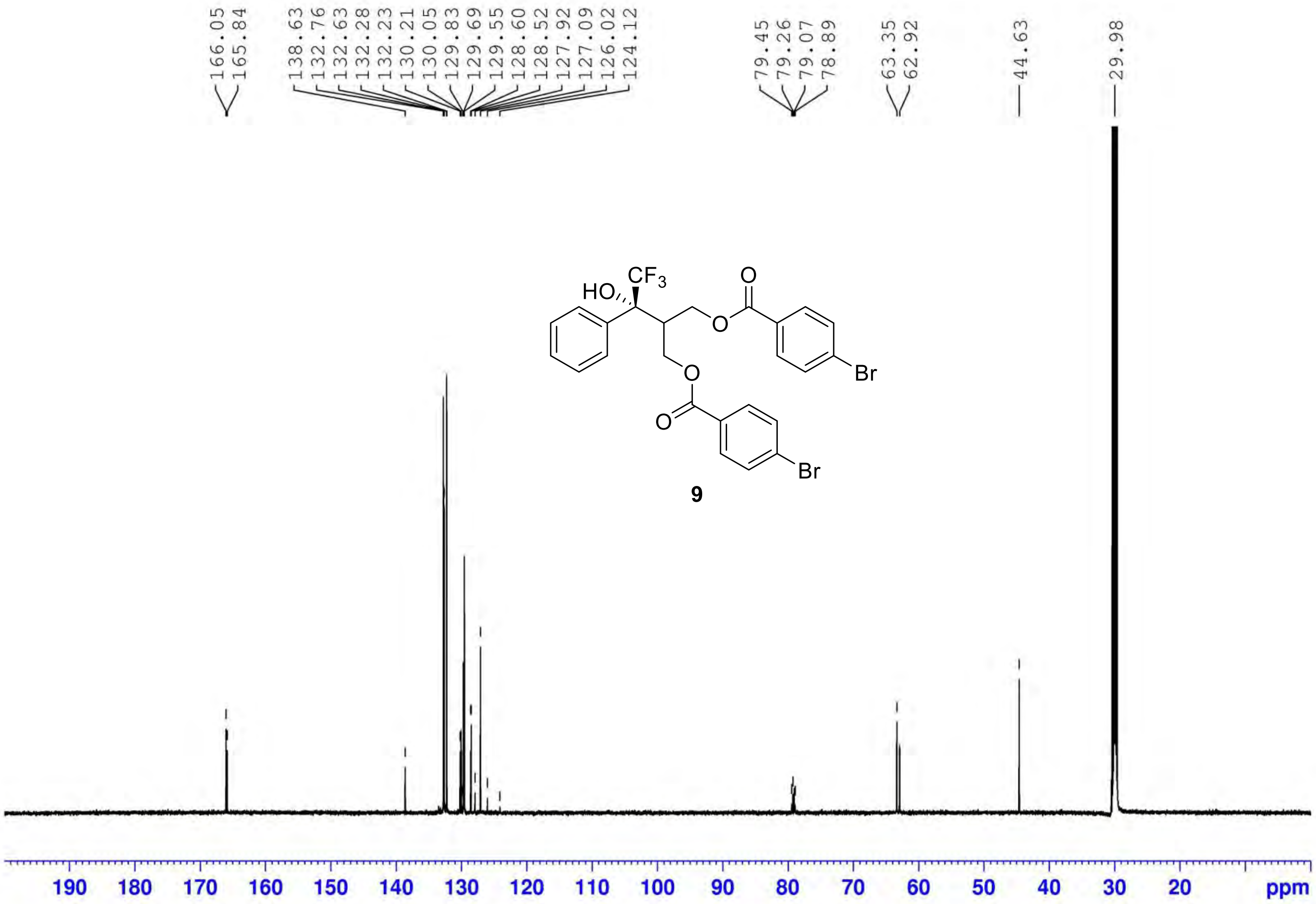


8

^{1}H NMR in acetone-d_6 (600 MHz)

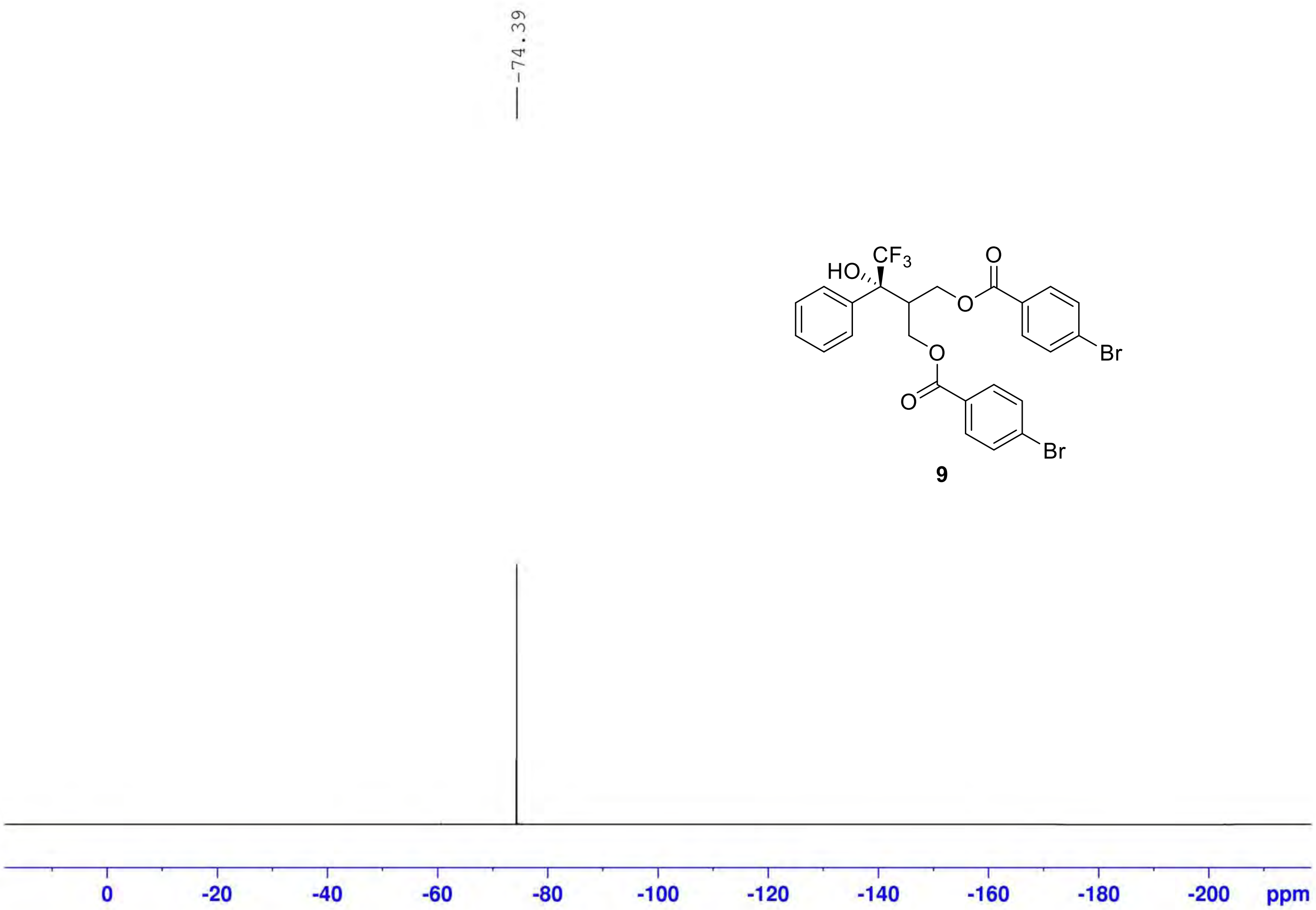


^{13}C NMR in acetone-d$_6$ (150 MHz)



9

^{19}F NMR in acetone-d_6 (564 MHz)



Configuration assignment of methyl (*2R, 3S*)-2-(hydroxymethyl)-3-phenyl-3-(trifluoromethyl)oxirane-2-carboxylate 4 by NOESY

Figure S3. NOESY spectrum of compound **4** (600 MHz, $CDCl_3$)

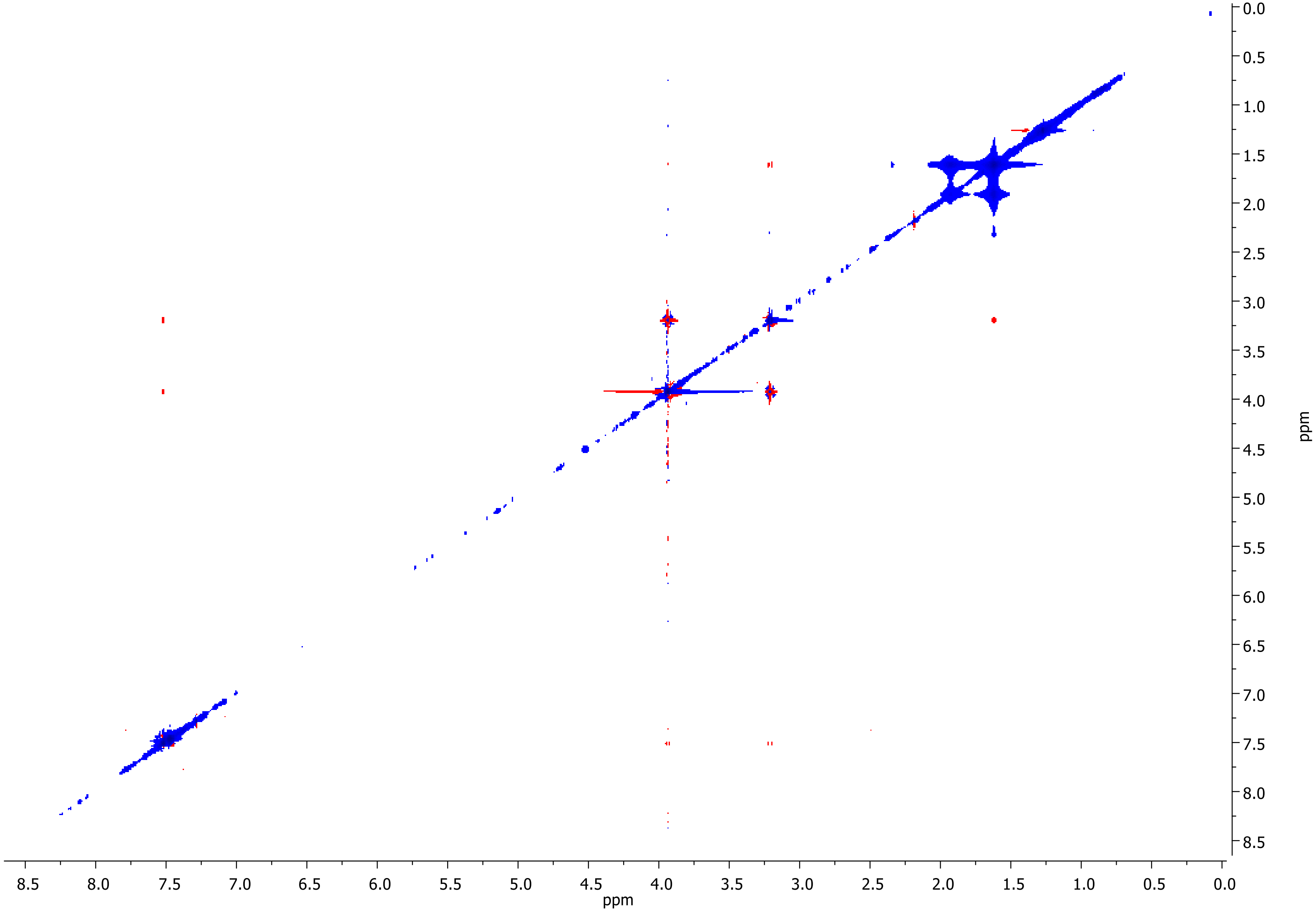
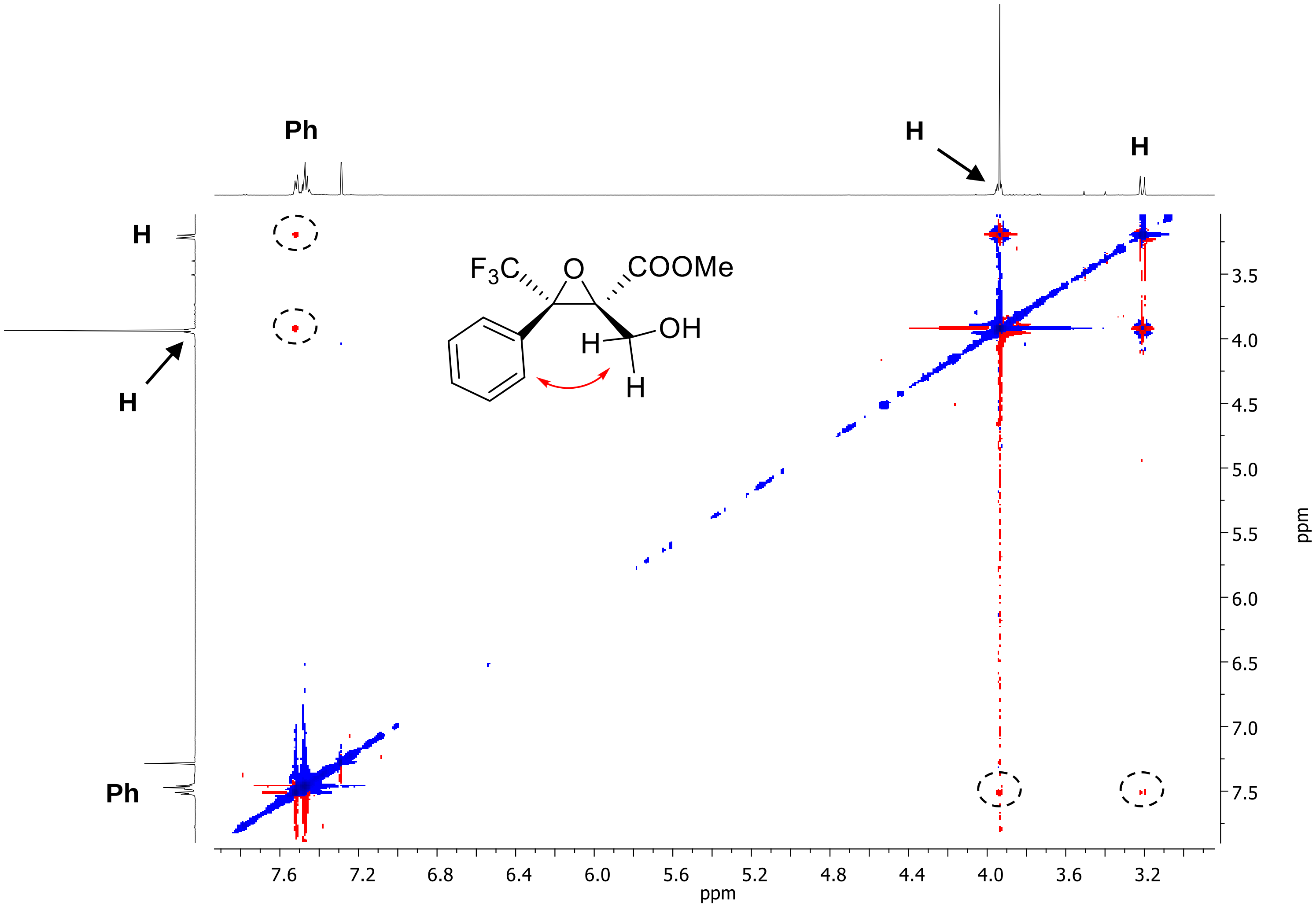
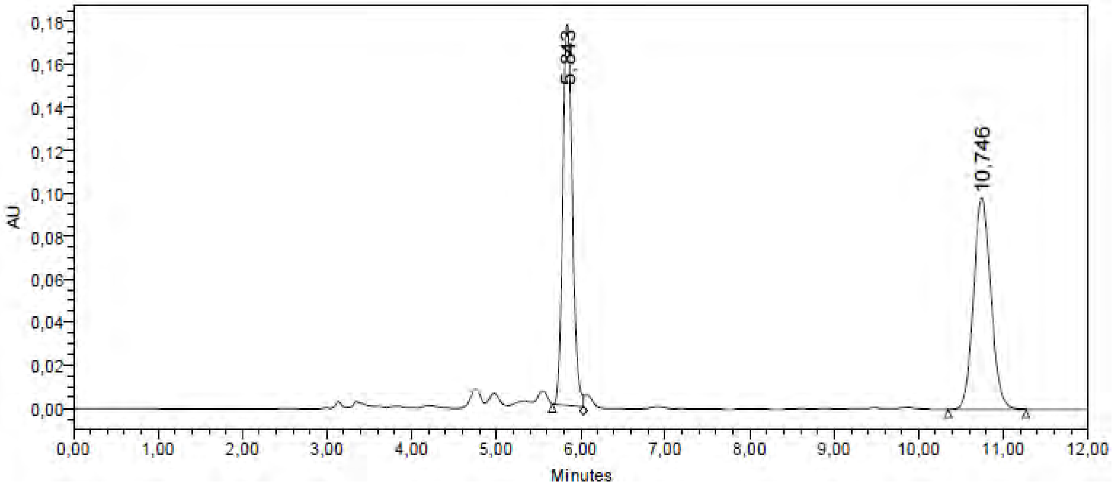


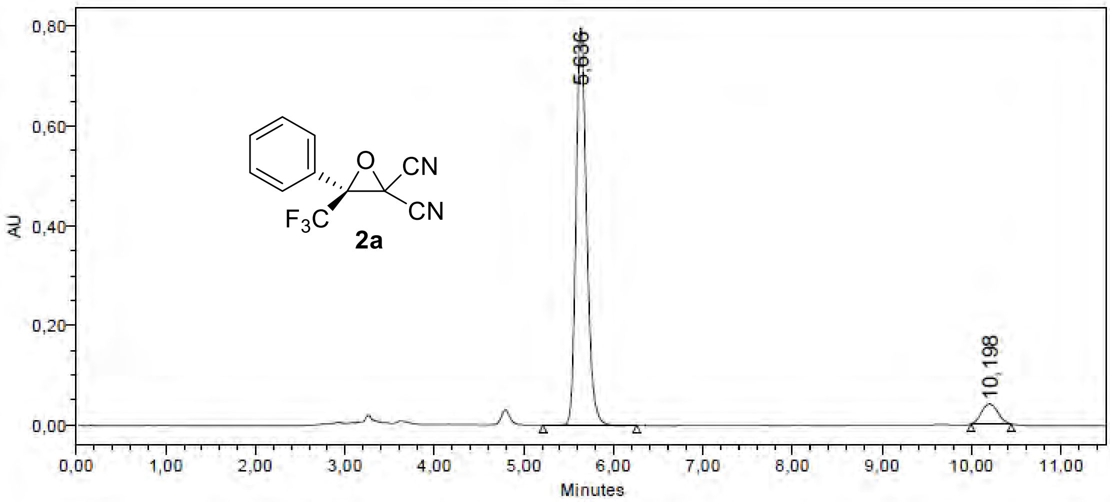
Figure S4. Expansion of the NOESY spectrum of compound **4** (600 MHz, $CDCl_3$). The cross peaks corresponding to the dipolar coupling between protons of the hydroxymethyl group and aromatic protons are observed, thus indicating that the *anti* carbomethoxy group to the CF_3 moiety has been reduced.



HPLC Chromatograms

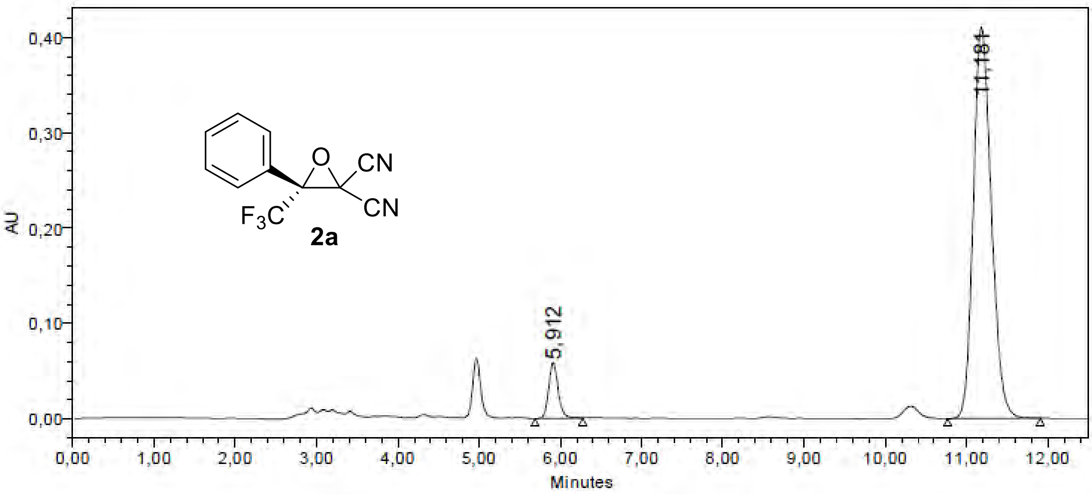


	RT (min)	Area (µV*sec)	% Area	Height (µV)
1	5,843	1376306	49,51	177959
2	10,746	1403390	50,49	98639



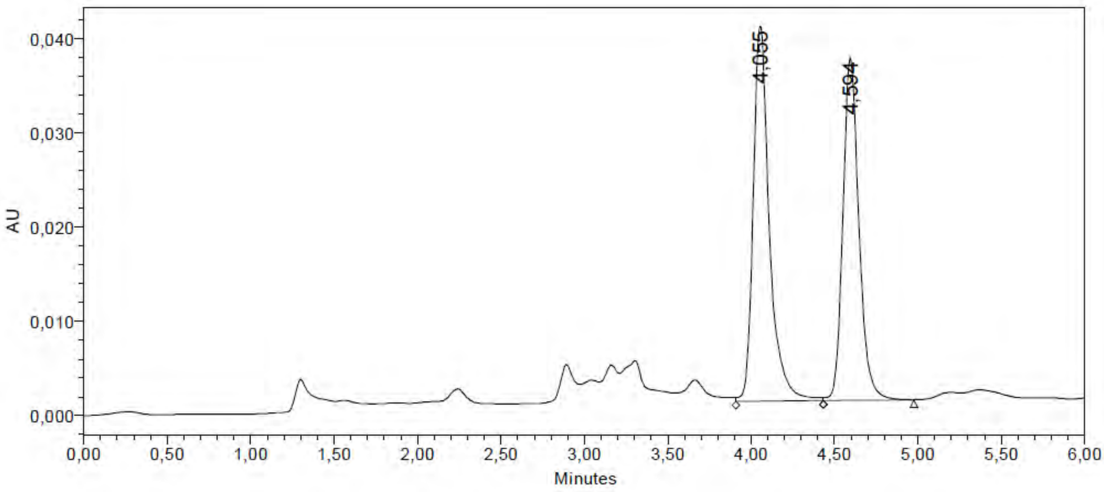
Processed Channel Descr.: 2998 PDA 220,0 nm (2998 (210-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220,0 nm (2998 (210-300)nm)	5,636	6544955	92,78	797388
2	2998 PDA 220,0 nm (2998 (210-300)nm)	10,198	509250	7,22	39776



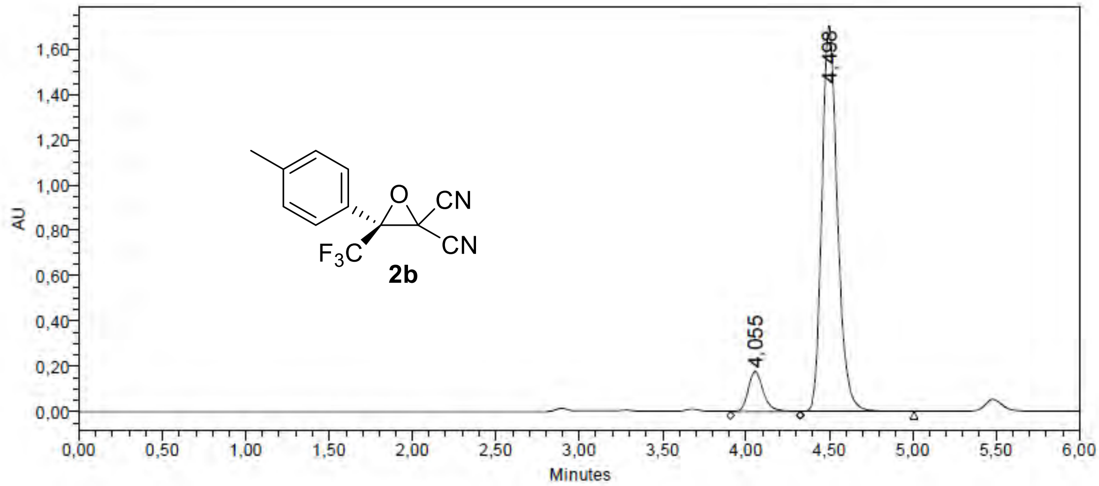
Processed Channel Descr.: 2998 PDA 220,0 nm (2998 (210-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220,0 nm (2998 (210-300)nm)	5,912	465413	6,87	58340
2	2998 PDA 220,0 nm (2998 (210-300)nm)	11,181	6307653	93,13	410674



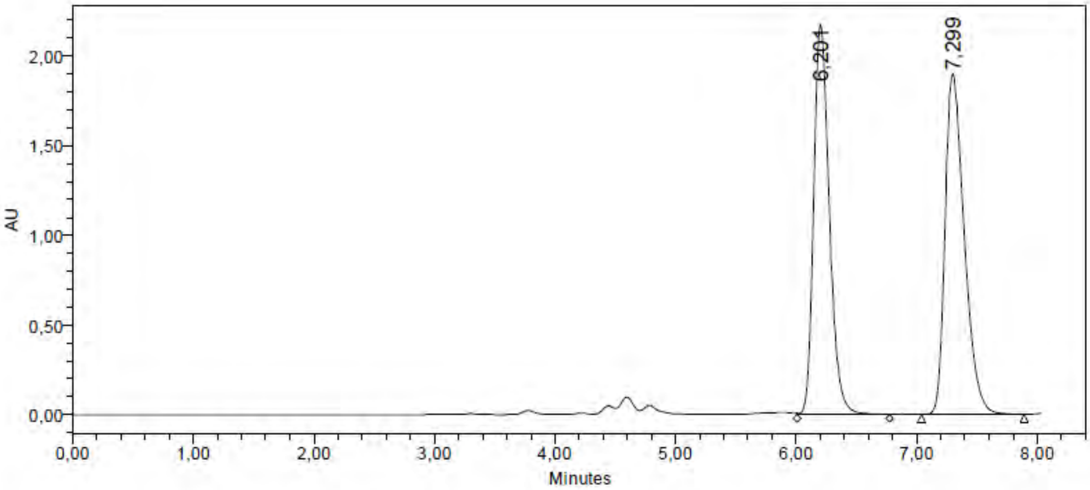
Processed Channel Descr.: 2998 PDA 230,0 nm (2998 (210-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 230,0 nm (2998 (210-300)nm)	4,055	269887	52,63	39885
2	2998 PDA 230,0 nm (2998 (210-300)nm)	4,594	242881	47,37	36447



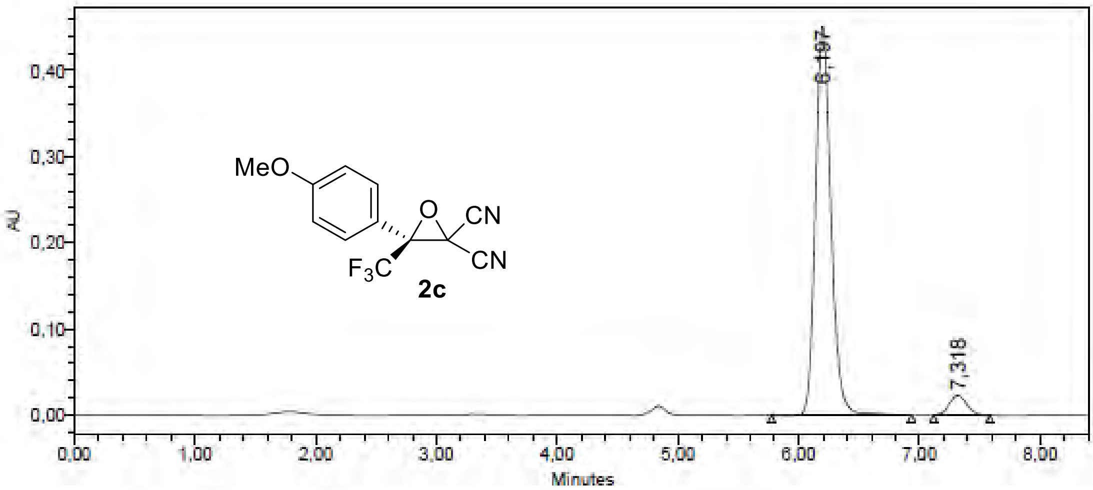
Processed Channel Descr.: 2998 PDA 230,0 nm (2998 (210-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 230,0 nm (2998 (210-300)nm)	4,055	1096052	9,00	176407
2	2998 PDA 230,0 nm (2998 (210-300)nm)	4,498	11075886	91,00	1705033



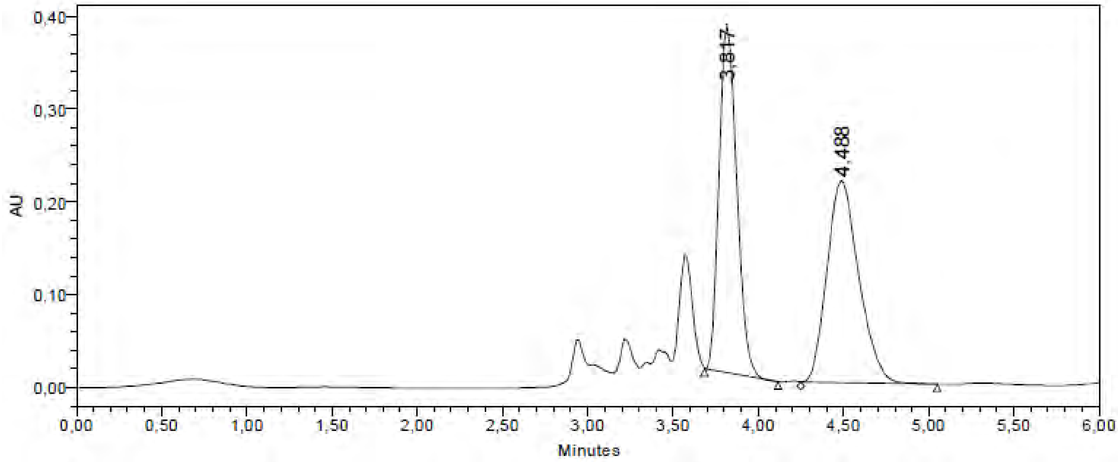
Processed Channel Descr.: 2998 PDA 255,0 nm (2998 (210-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 255,0 nm (2998 (210-300)nm)	6,201	19589504	48,03	2174057
2	2998 PDA 255,0 nm (2998 (210-300)nm)	7,299	21195407	51,97	1896908

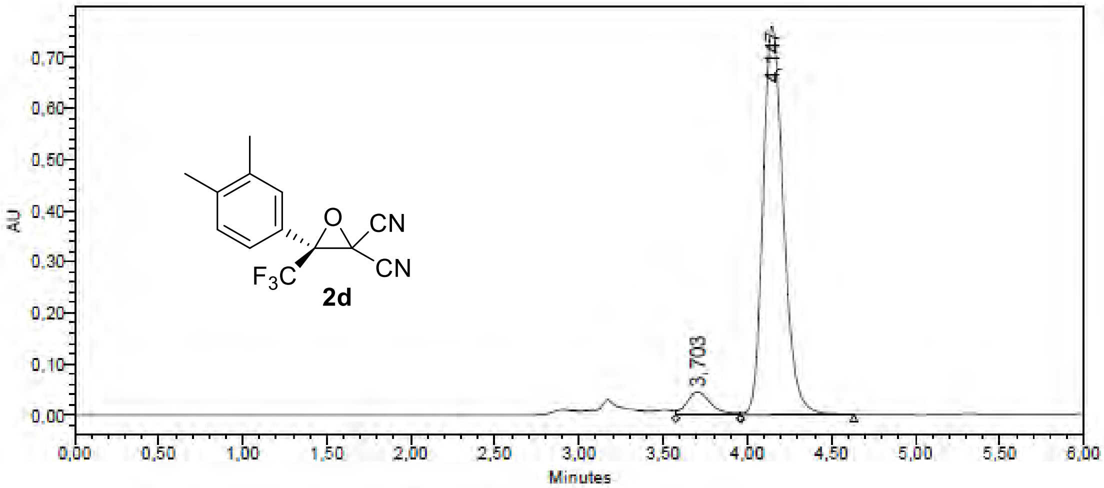


Processed Channel Descr.: 2998 PDA 255,0 nm (2998 (210-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 255,0 nm (2998 (210-300)nm)	6,197	4011727	94,56	452231
2	2998 PDA 255,0 nm (2998 (210-300)nm)	7,318	230832	5,44	22988

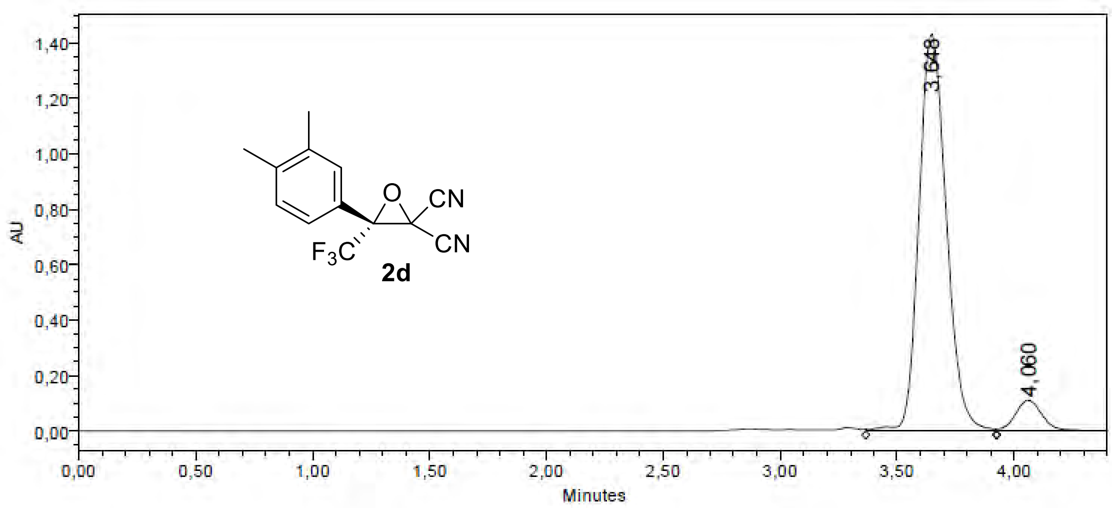


	RT (min)	Area (µV*sec)	% Area	Height (µV)
1	3,817	2710975	49,03	374386
2	4,488	2818657	50,97	217830



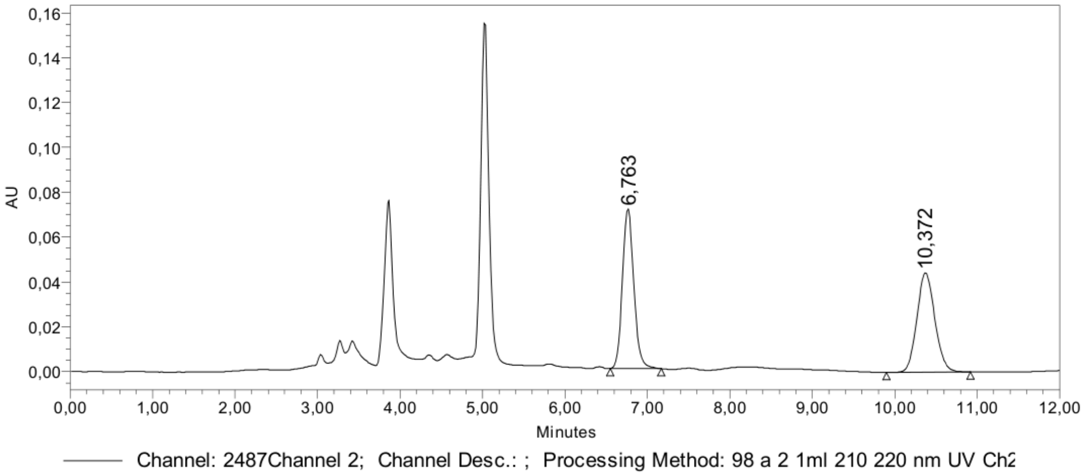
Processed Channel Descr.: 2998 PDA 220,0 nm (2998 (210-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220,0 nm (2998 (210-300)nm)	3,703	440728	6,40	44933
2	2998 PDA 220,0 nm (2998 (210-300)nm)	4,147	6450183	93,60	759629

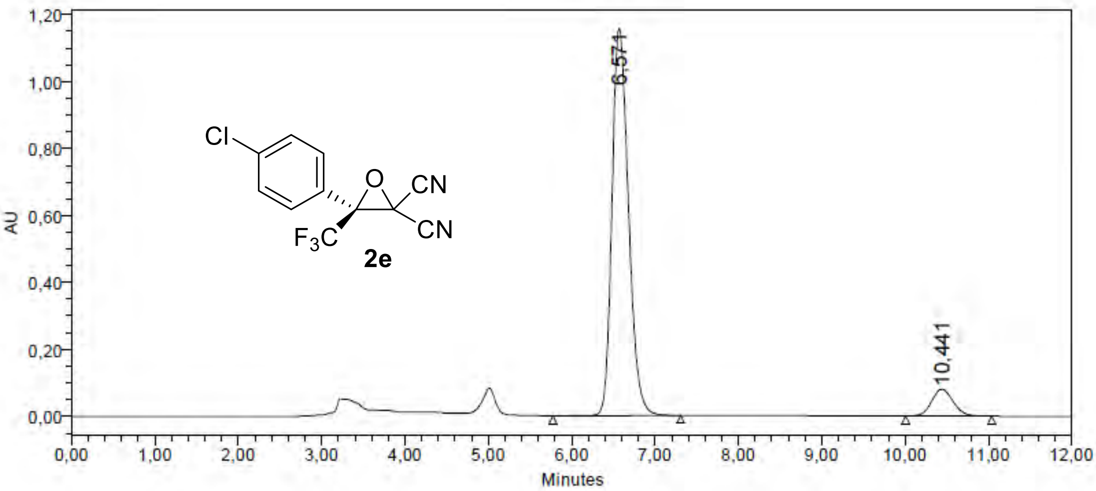


Processed Channel Descr.: 2998 PDA 220,0 nm (2998 (210-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220,0 nm (2998 (210-300)nm)	3,648	11645637	92,92	1432515
2	2998 PDA 220,0 nm (2998 (210-300)nm)	4,060	887070	7,08	111246

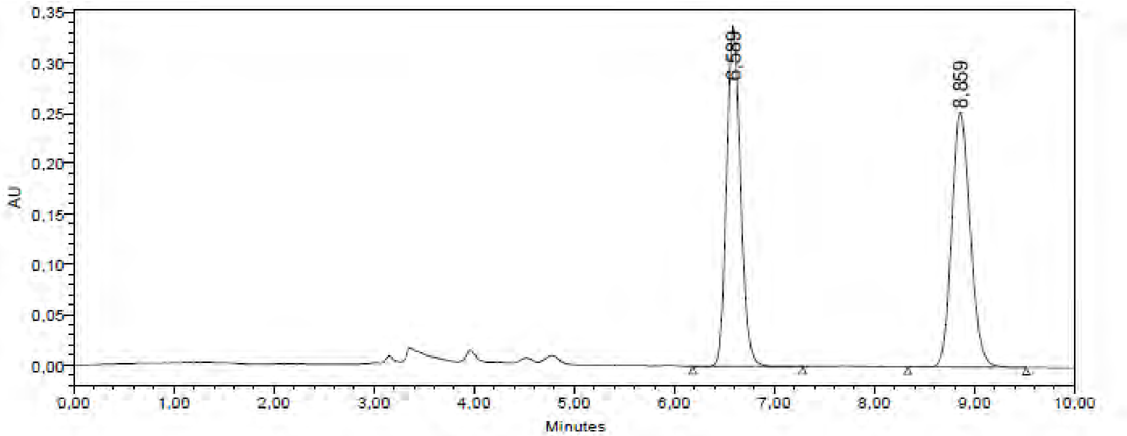


	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	6,763	685536	50,51	71396
2	10,372	671628	49,49	44322

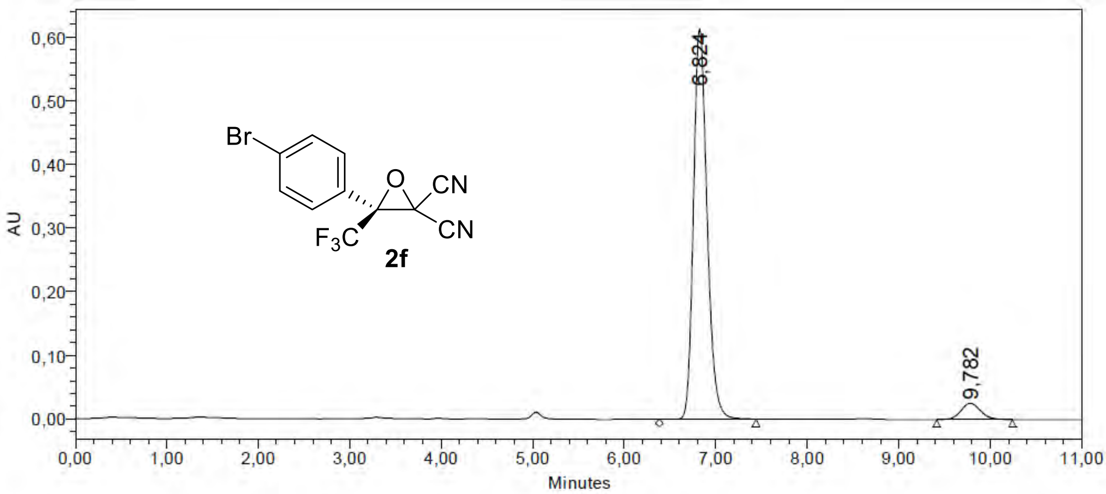


Processed Channel Descr.: 2998 PDA 220,0 nm (2998 (210-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220,0 nm (2998 (210-300)nm)	6,571	15938550	91,70	1157164
2	2998 PDA 220,0 nm (2998 (210-300)nm)	10,441	1442367	8,30	80355

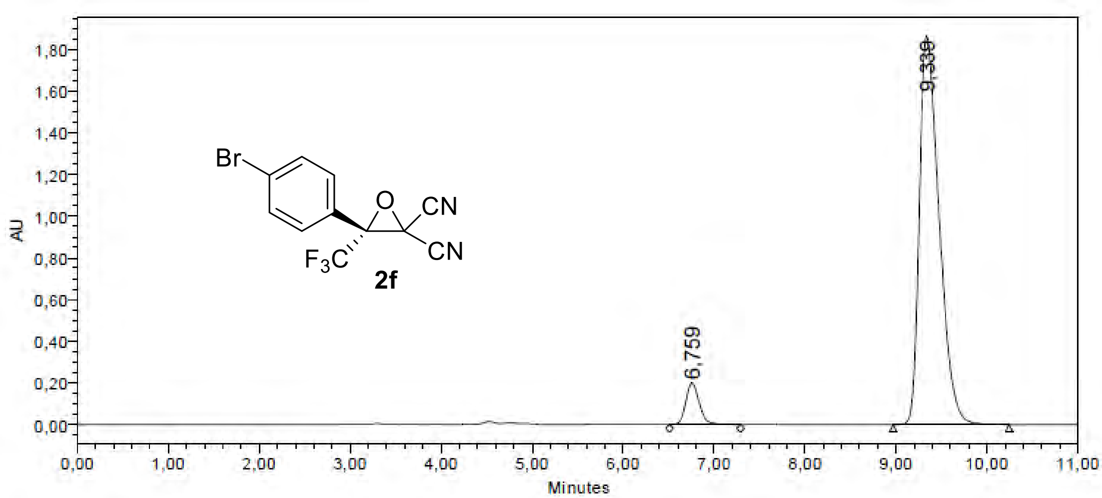


	RT (min)	Area (µV*sec)	% Area	Height (µV)
1	6,589	3258215	49,88	338330
2	8,859	3273848	50,12	253879



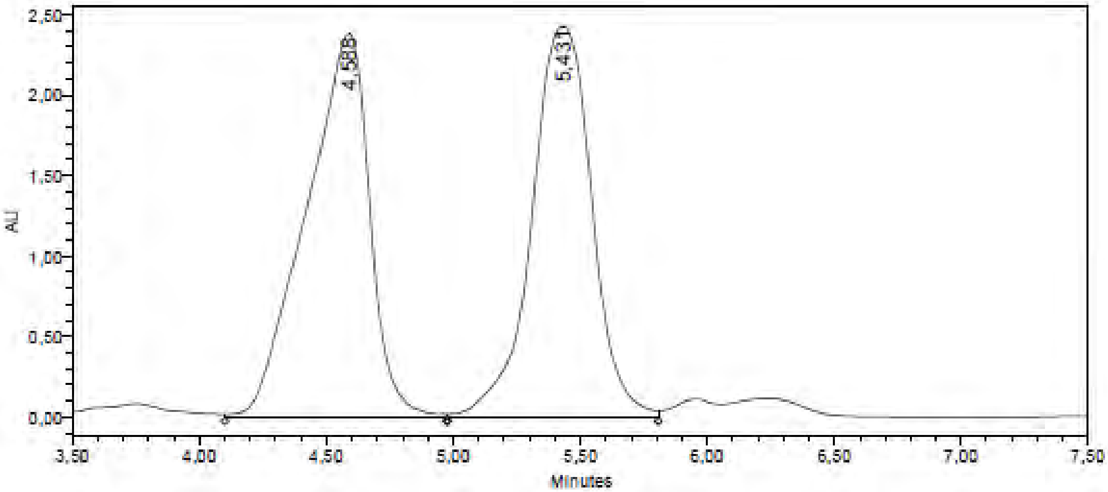
Processed Channel Descr.: 2998 PDA 230,0 nm (2998 (210-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 230,0 nm (2998 (210-300)nm)	6,824	6261907	94,39	613320
2	2998 PDA 230,0 nm (2998 (210-300)nm)	9,782	372426	5,61	25574



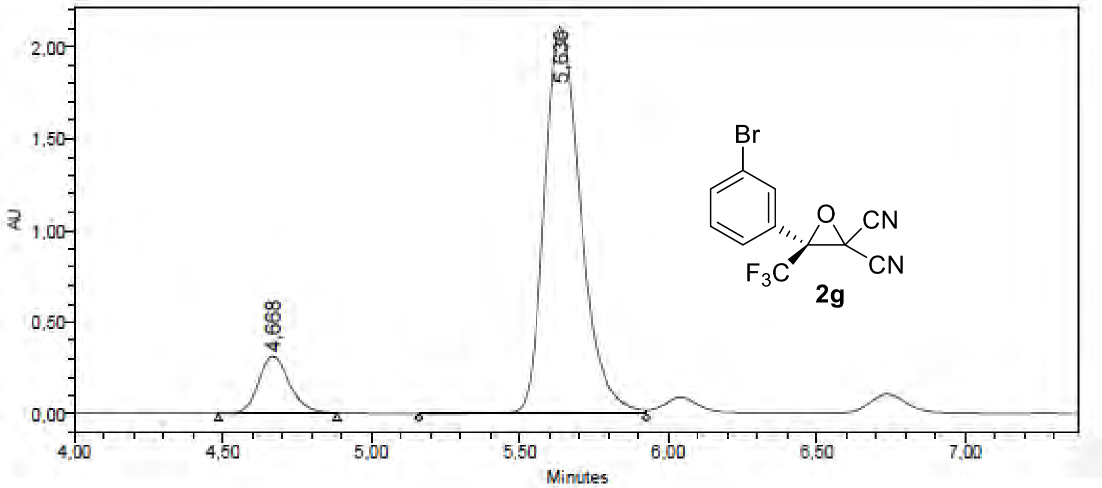
Processed Channel Descr.: 2998 PDA 230,0 nm (2998 (210-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 230,0 nm (2998 (210-300)nm)	6,759	1998964	6,62	198811
2	2998 PDA 230,0 nm (2998 (210-300)nm)	9,339	28197621	93,38	1863768



Processed Channel Descr.: 2998 PDA 210,0 nm (2998 (210-300)nm)

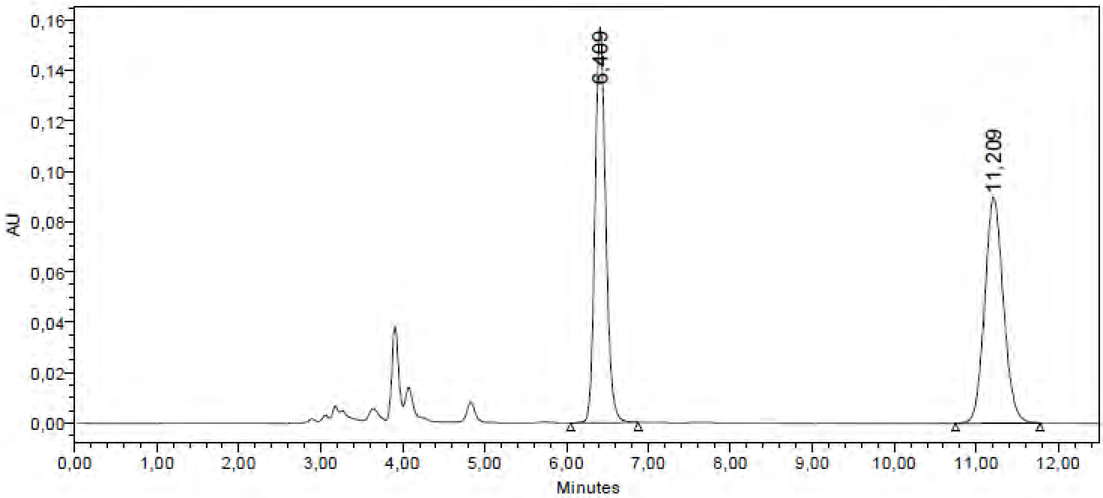
	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 210,0 nm (2998 (210-300)nm)	4,588	41325843	50,84	2380636
2	2998 PDA 210,0 nm (2998 (210-300)nm)	5,431	39954553	49,16	2427212



2g

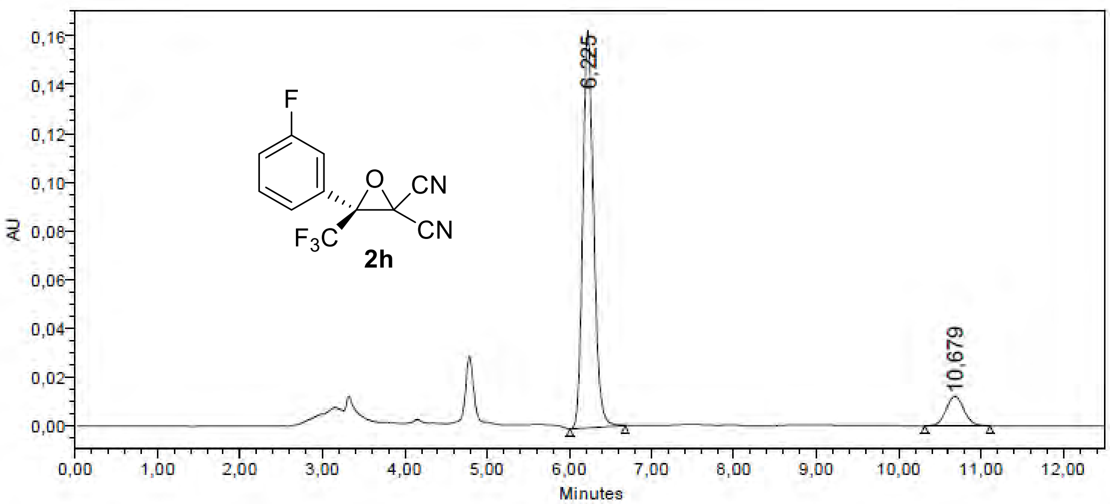
Processed Channel Descr.: 2998 PDA 210,0 nm (2998 (210-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 210,0 nm (2998 (210-300)nm)	4,668	2237169	11,04	312300
2	2998 PDA 210,0 nm (2998 (210-300)nm)	5,636	18028407	88,96	2114355



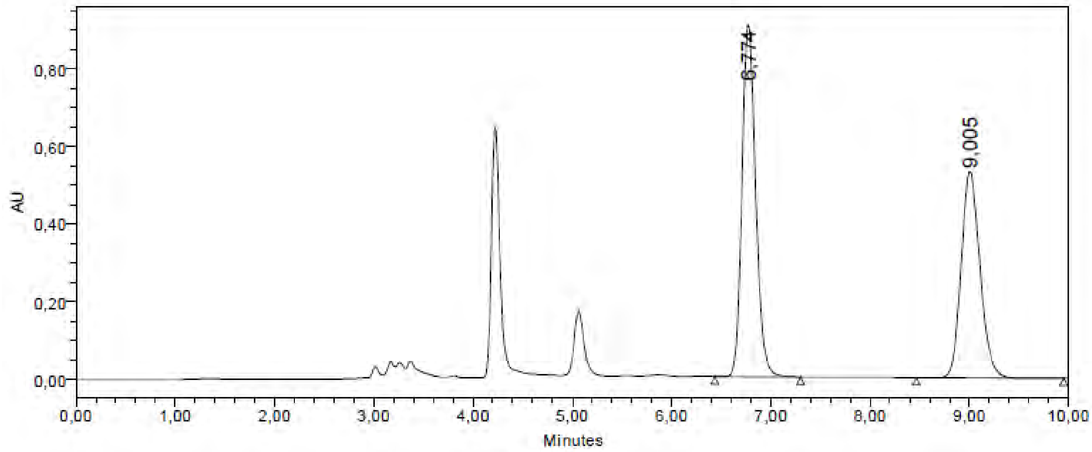
Processed Channel Descr.: 2998 PDA 228,0 nm (2998 (210-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 228,0 nm (2998 (210-300)nm)	6,409	1432399	50,41	157193
2	2998 PDA 228,0 nm (2998 (210-300)nm)	11,209	1408958	49,59	89392

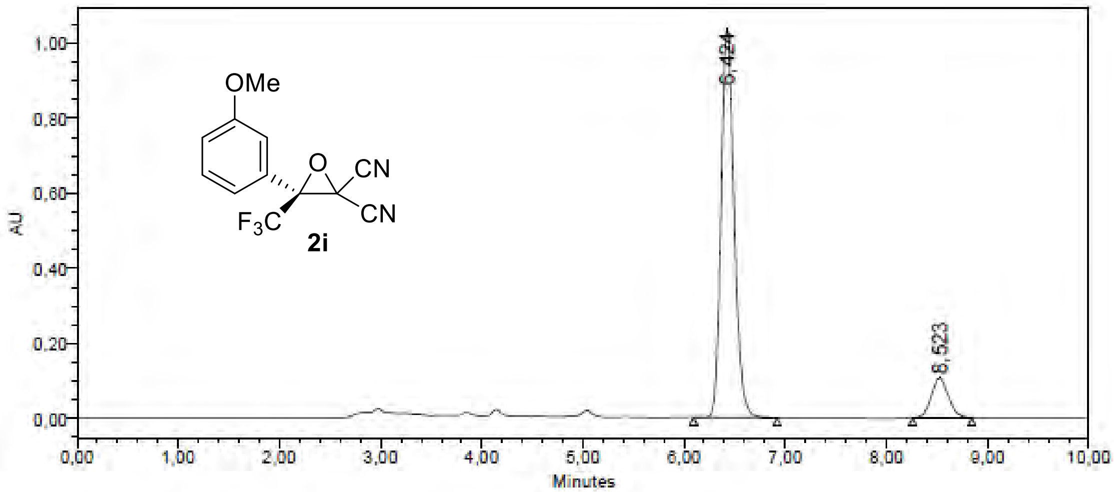


Processed Channel Descr.: 2998 PDA 228,0 nm (2998 (210-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 228,0 nm (2998 (210-300)nm)	6,225	1457802	88,96	162766
2	2998 PDA 228,0 nm (2998 (210-300)nm)	10,679	180999	11,04	12109

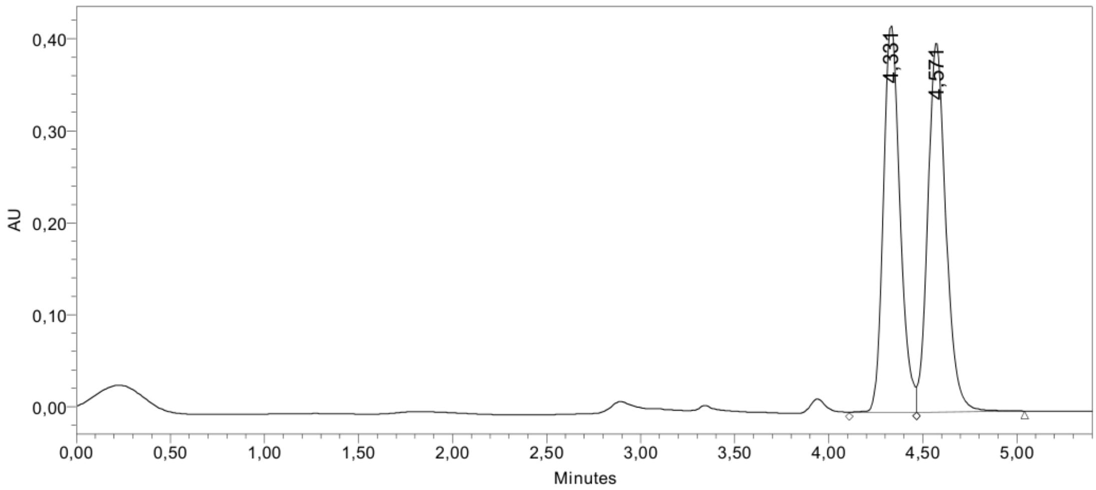


	RT (min)	Area (µV*sec)	% Area	Height (µV)
1	6,774	8610850	55,21	909247
2	9,005	6986953	44,79	531635



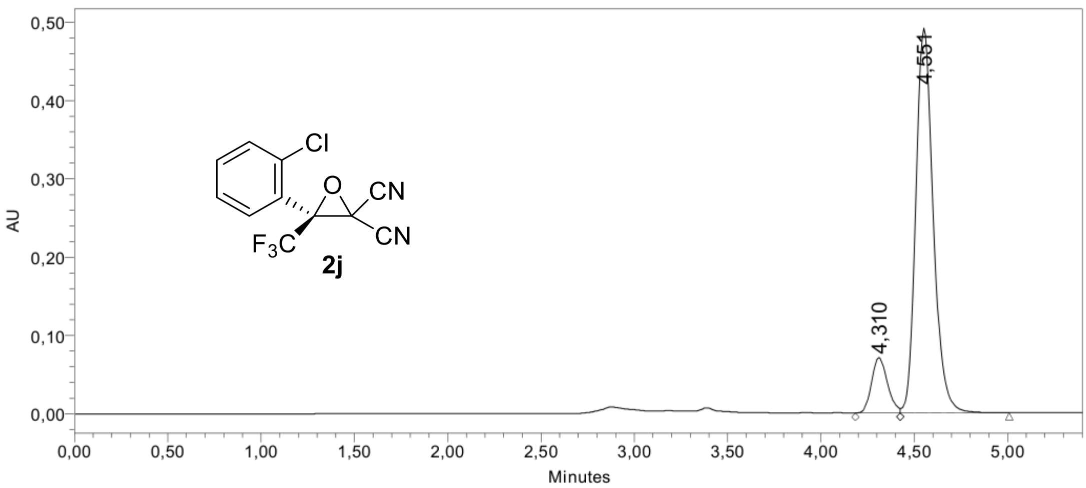
Processed Channel Descr.: 2998 PDA 210,0 nm (2998 (210-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 210,0 nm (2998 (210-300)nm)	6,424	9280529	88,10	1038747
2	2998 PDA 210,0 nm (2998 (210-300)nm)	8,523	1253505	11,90	105724



Processed Channel Descr.: 2998 PDA 220,0 nm (2998 (210-300)nm)

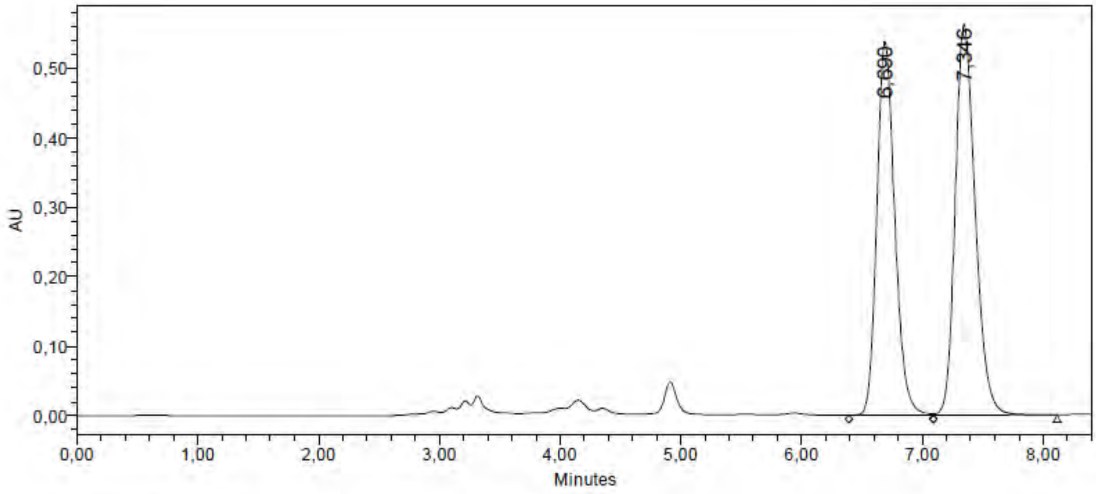
	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220,0 nm (2998 (210-300)nm)	4,331	2598356	49,14	420852
2	2998 PDA 220,0 nm (2998 (210-300)nm)	4,571	2689604	50,86	402135



2j

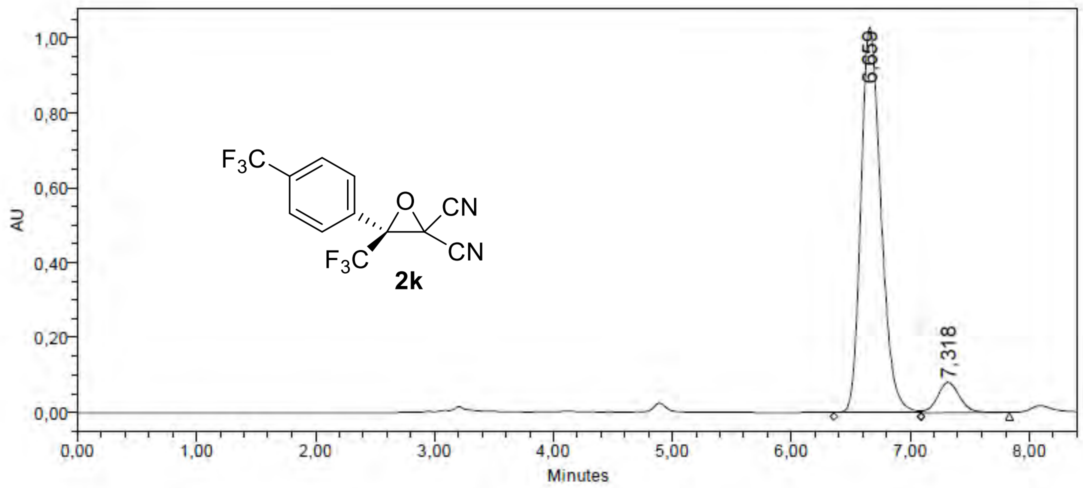
Processed Channel Descr.: 2998 PDA 220,0 nm (2998 (210-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220,0 nm (2998 (210-300)nm)	4,310	418451	11,65	70810
2	2998 PDA 220,0 nm (2998 (210-300)nm)	4,551	3172861	88,35	491254



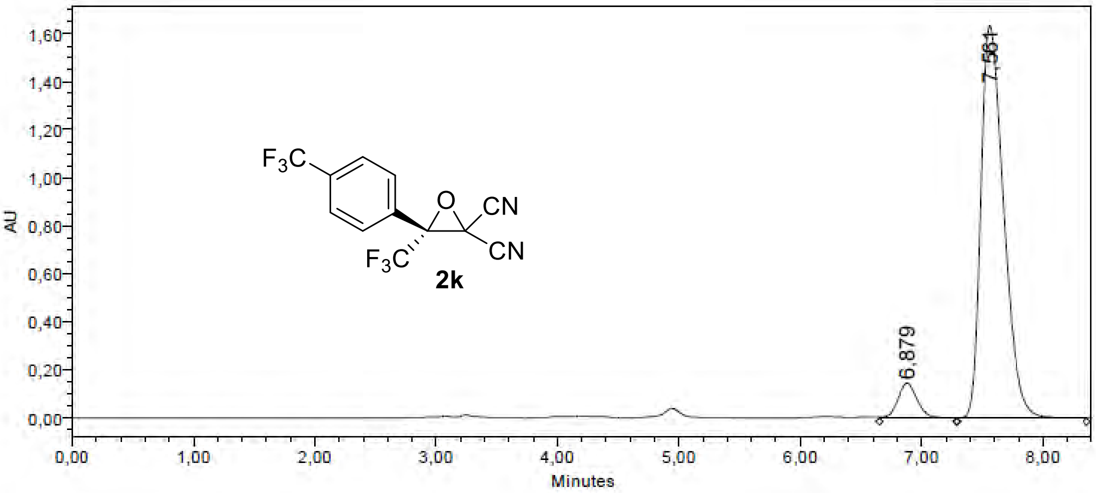
Processed Channel Descr.: 2998 PDA 220,0 nm (2998 (210-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220,0 nm (2998 (210-300)nm)	6,690	5558653	46,14	537419
2	2998 PDA 220,0 nm (2998 (210-300)nm)	7,346	6488426	53,86	562757



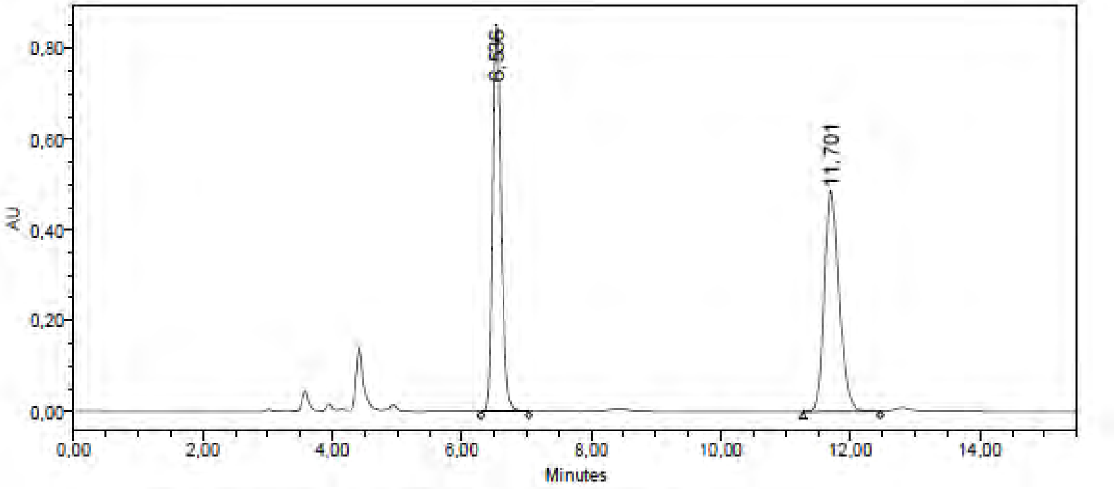
Processed Channel Descr.: 2998 PDA 220,0 nm (2998 (210-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220,0 nm (2998 (210-300)nm)	6,659	12022941	92,17	1028285
2	2998 PDA 220,0 nm (2998 (210-300)nm)	7,318	1021371	7,83	80308



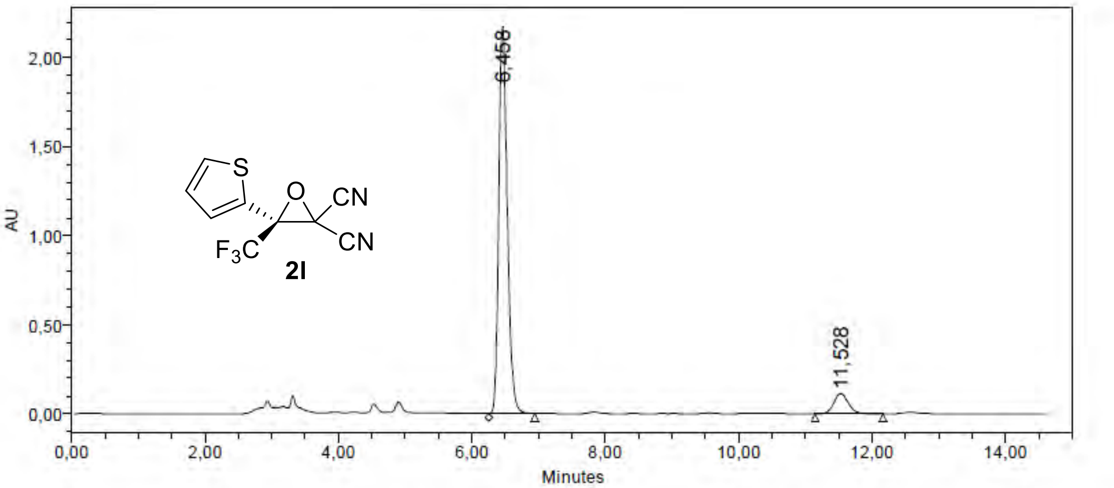
Processed Channel Descr.: 2998 PDA 220,0 nm (2998 (210-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 220,0 nm (2998 (210-300)nm)	6,879	1547351	6,86	143931
2	2998 PDA 220,0 nm (2998 (210-300)nm)	7,561	21019854	93,14	1634482



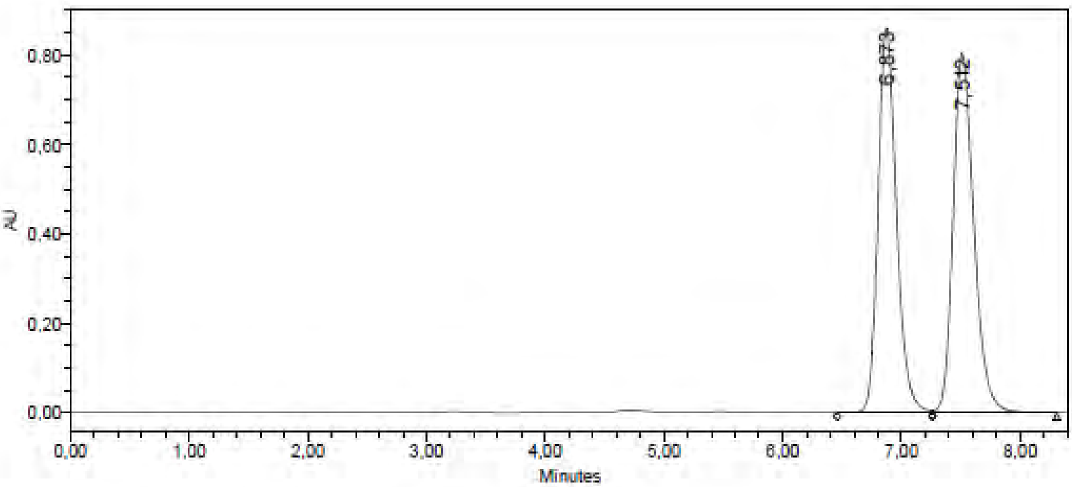
Processed Channel Descr.: 2998 PDA 240,0 nm (2998 (210-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 240,0 nm (2998 (210-300)nm)	6,536	7698831	49,71	853524
2	2998 PDA 240,0 nm (2998 (210-300)nm)	11,701	7789506	50,29	486414



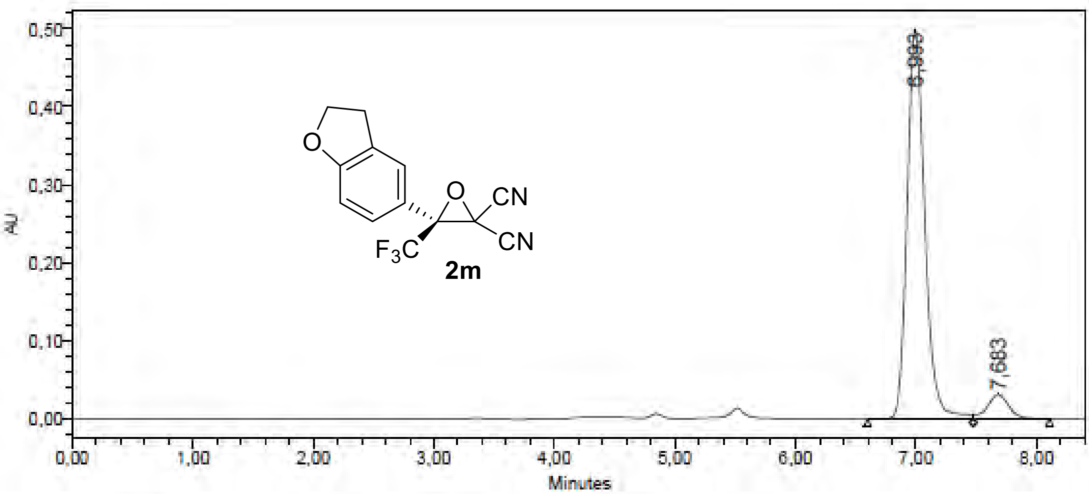
Processed Channel Descr.: 2998 PDA MaxPlot (190,0 nm to 800,0 nm) (2998 (210-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA MaxPlot (190,0 nm to 800,0 nm) (2998 (210-300)nm)	6,458	19292968	91,85	2171552
2	2998 PDA MaxPlot (190,0 nm to 800,0 nm) (2998 (210-300)nm)	11,528	1712542	8,15	113755



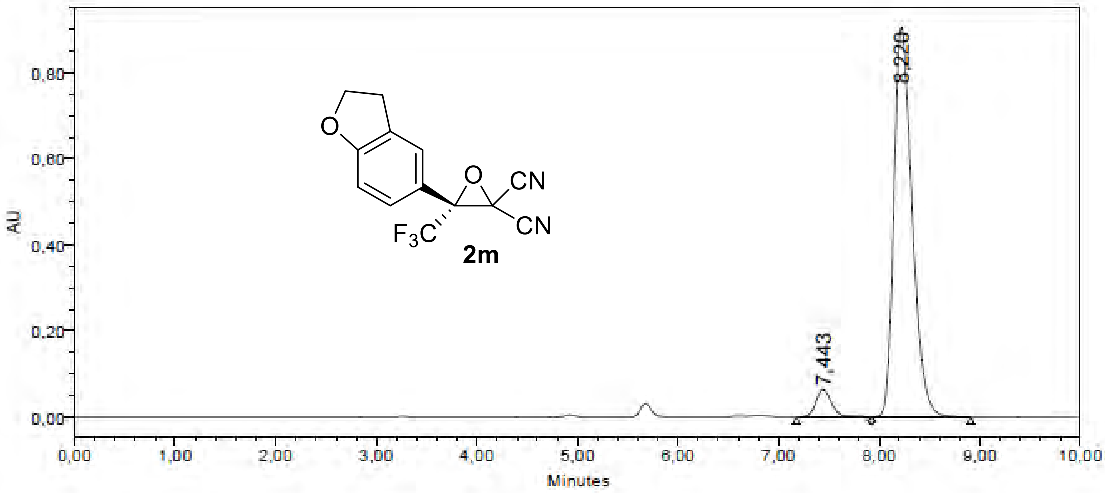
Processed Channel Descr.: 2998 PDA 255,0 nm (2998 (210-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 255,0 nm (2998 (210-300)nm)	6,873	9311975	49,04	860036
2	2998 PDA 255,0 nm (2998 (210-300)nm)	7,512	9676980	50,96	802927



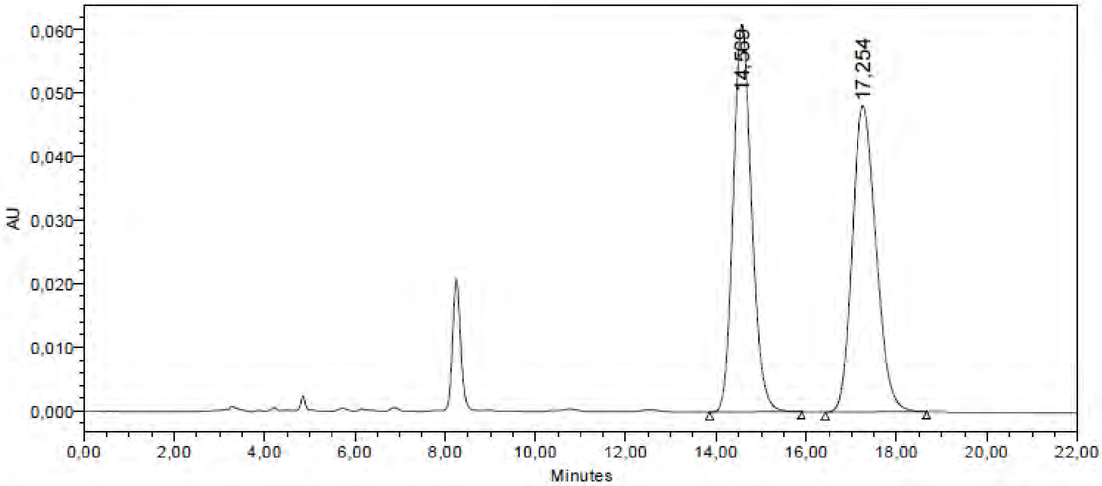
Processed Channel Descr.: 2998 PDA 255,0 nm (2998 (210-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 255,0 nm (2998 (210-300)nm)	6,993	5034945	92,87	499185
2	2998 PDA 255,0 nm (2998 (210-300)nm)	7,683	386587	7,13	31636



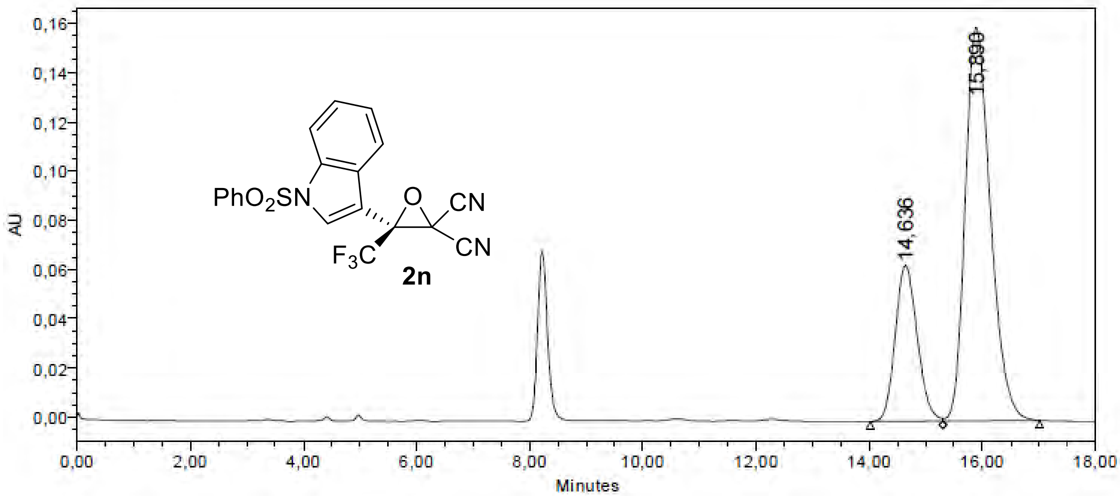
Processed Channel Descr.: 2998 PDA 255,0 nm (2998 (210-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 255,0 nm (2998 (210-300)nm)	7,443	690889	5,74	63482
2	2998 PDA 255,0 nm (2998 (210-300)nm)	8,220	11340401	94,26	906077



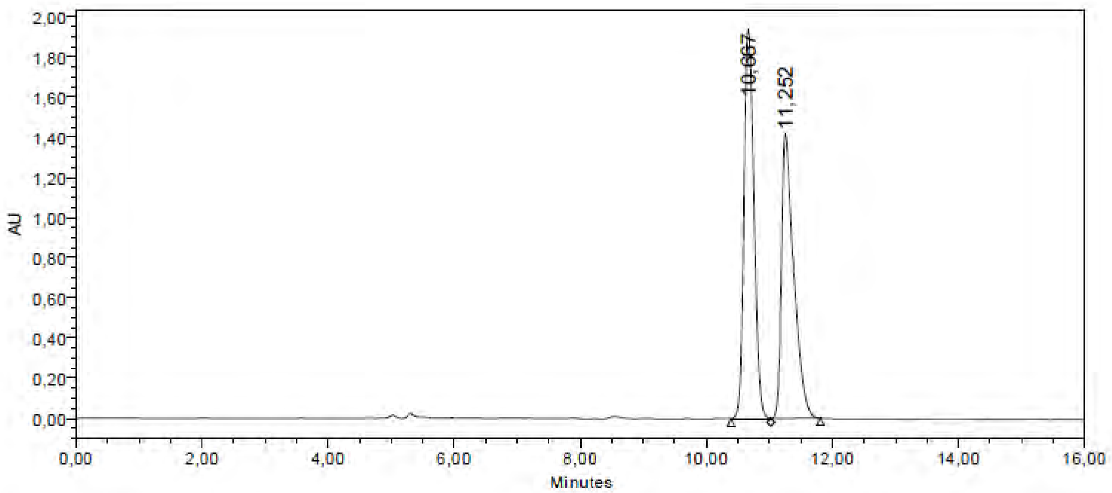
Processed Channel Descr.: 2998 PDA 260,0 nm (2998 (210-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 260,0 nm (2998 (210-300)nm)	14,569	1734209	49,74	60902
2	2998 PDA 260,0 nm (2998 (210-300)nm)	17,254	1752198	50,26	48159



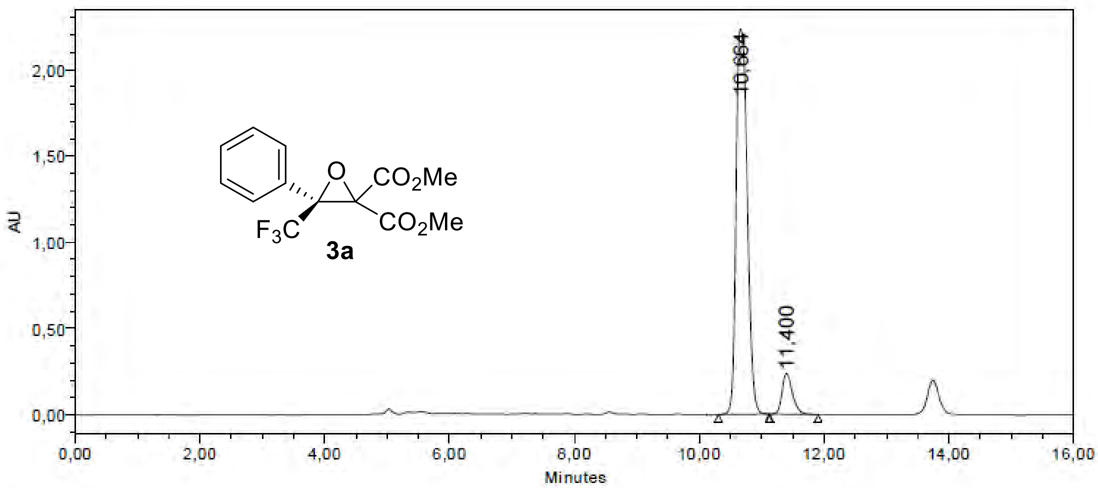
Processed Channel Descr.: 2998 PDA 260,0 nm (2998 (210-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 260,0 nm (2998 (210-300)nm)	14,636	1708142	25,70	63122
2	2998 PDA 260,0 nm (2998 (210-300)nm)	15,890	4938958	74,30	159606



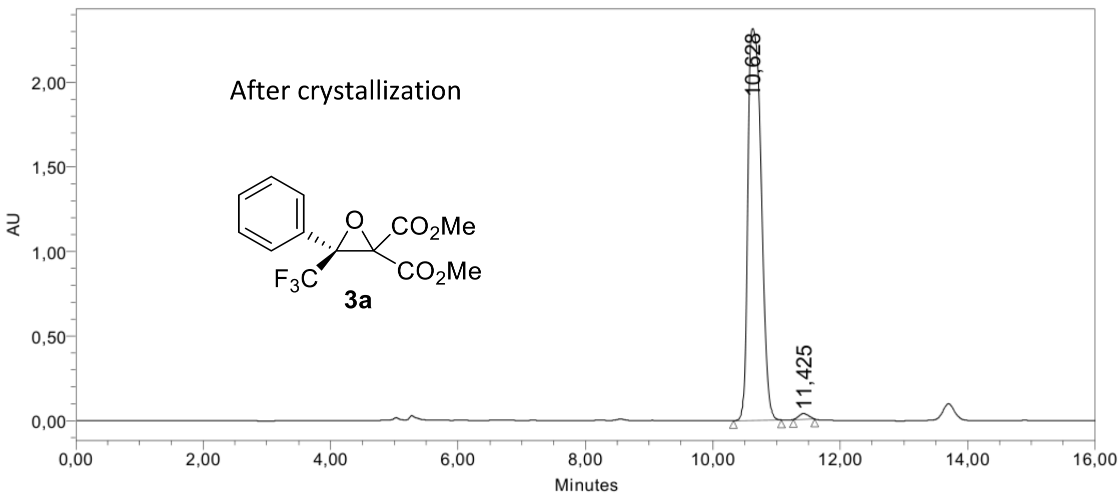
Processed Channel Descr.: 2998 PDA 210,0 nm (2998 (200-400)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 210,0 nm (2998 (200-400)nm)	10,667	21789501	52,65	1937494
2	2998 PDA 210,0 nm (2998 (200-400)nm)	11,252	19594514	47,35	1417546



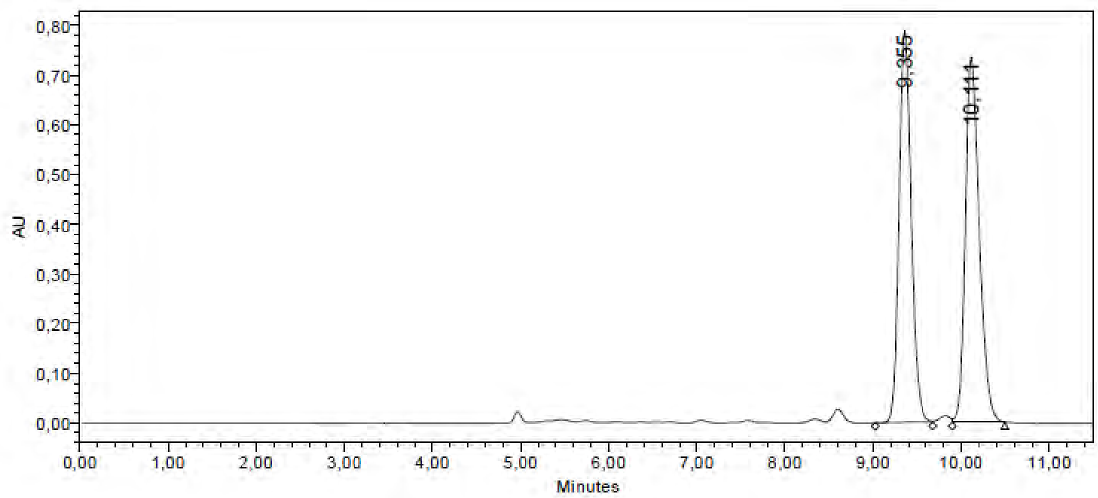
Processed Channel Descr.: 2998 PDA 210,0 nm (2998 (200-400)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 210,0 nm (2998 (200-400)nm)	10,664	27712106	90,92	2235007
2	2998 PDA 210,0 nm (2998 (200-400)nm)	11,400	2767620	9,08	237330



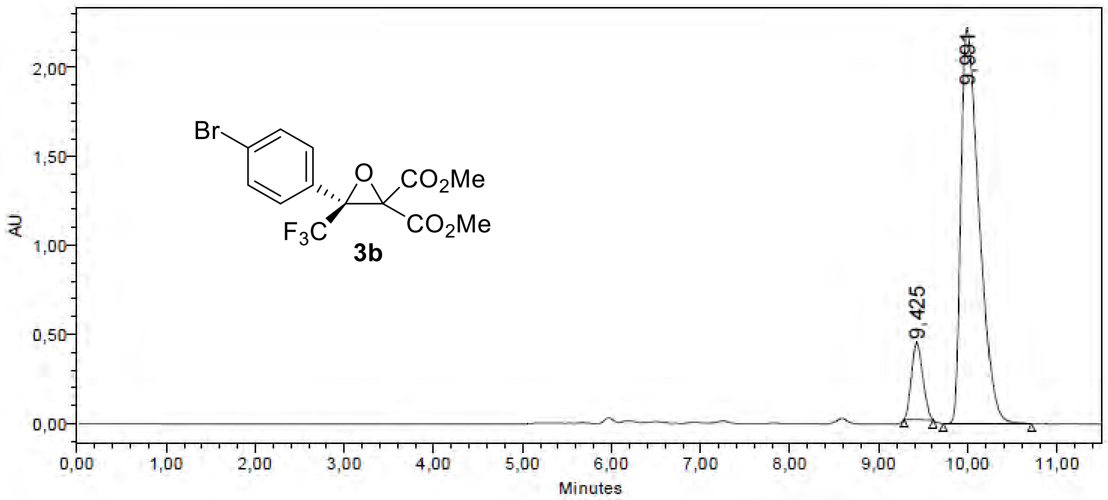
Processed Channel Descr.: 2998 PDA 210,0 nm (2998 (200-400)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 210,0 nm (2998 (200-400)nm)	10,628	33697761	98,93	2316545
2	2998 PDA 210,0 nm (2998 (200-400)nm)	11,425	363359	1,07	33902



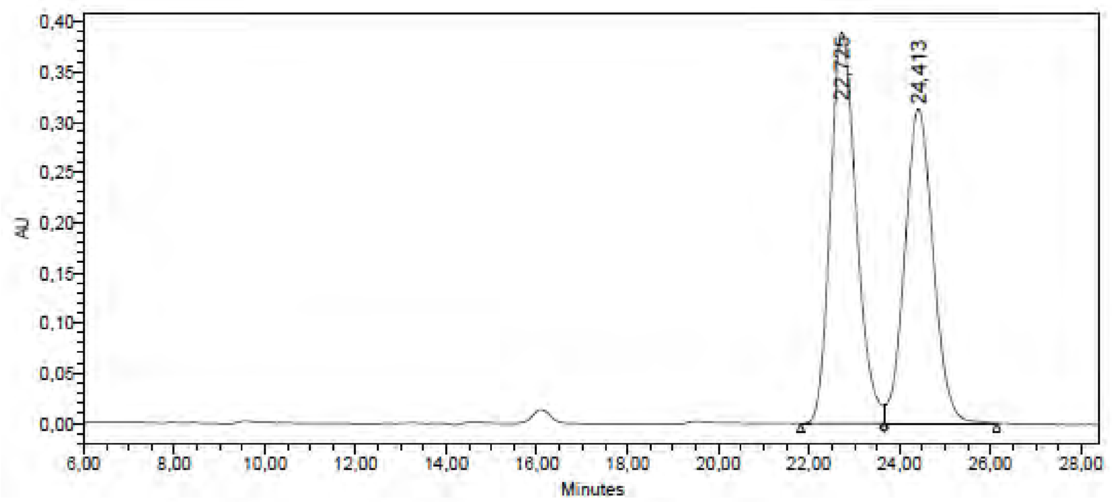
Processed Channel Descr.: 2998 PDA 235,0 nm (2998 (200-400)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 235,0 nm (2998 (200-400)nm)	9,355	7502686	48,02	788632
2	2998 PDA 235,0 nm (2998 (200-400)nm)	10,111	8121303	51,98	735097



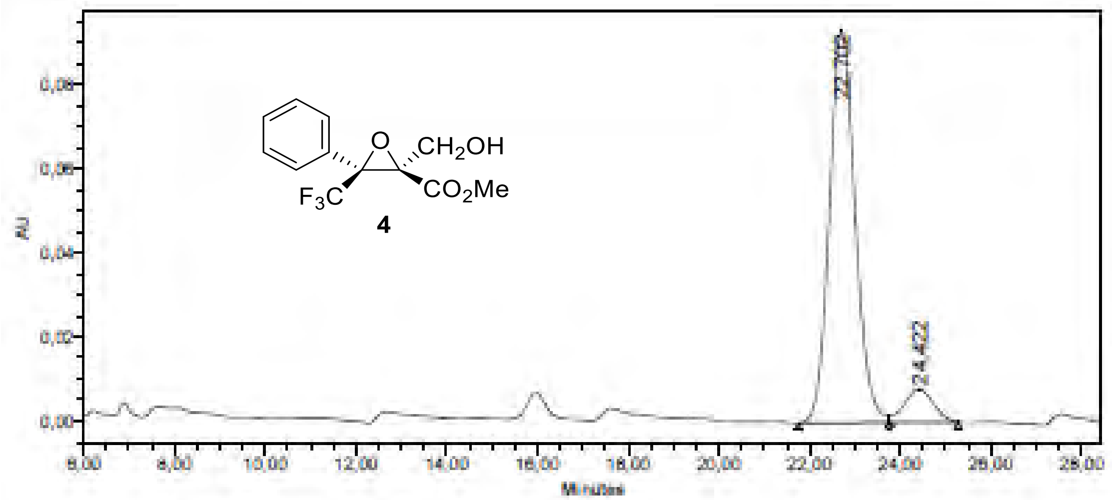
Processed Channel Descr.: 2998 PDA 236,2 nm (2998 (200-400)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 236,2 nm (2998 (200-400)nm)	9,425	3836149	10,88	431963
2	2998 PDA 236,2 nm (2998 (200-400)nm)	9,991	31415832	89,12	2220476



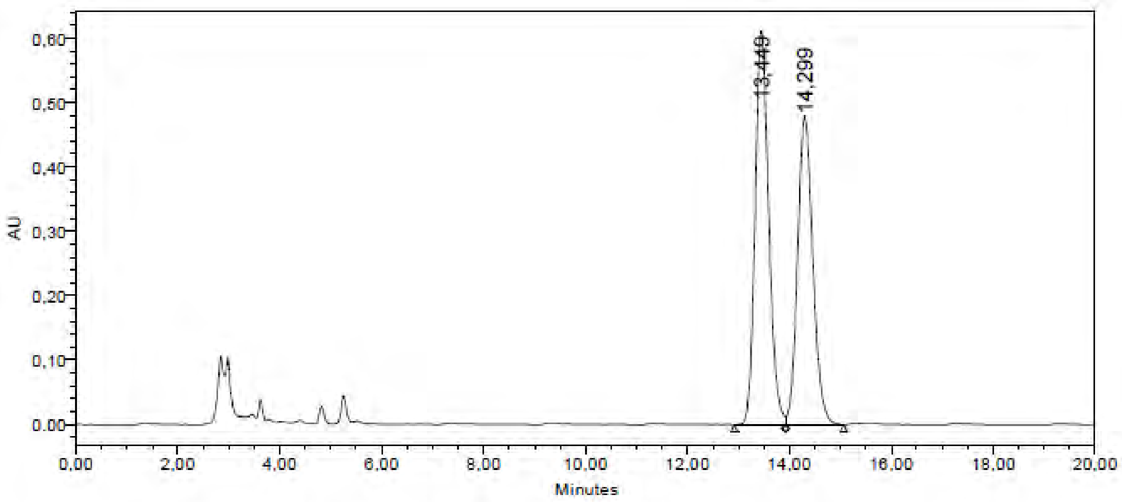
Processed Channel Descr.: 2998 PDA 210,0 nm (2998 (210-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 210,0 nm (2998 (210-300)nm)	22,725	15566427	53,29	389537
2	2998 PDA 210,0 nm (2998 (210-300)nm)	24,413	13642297	46,71	313092



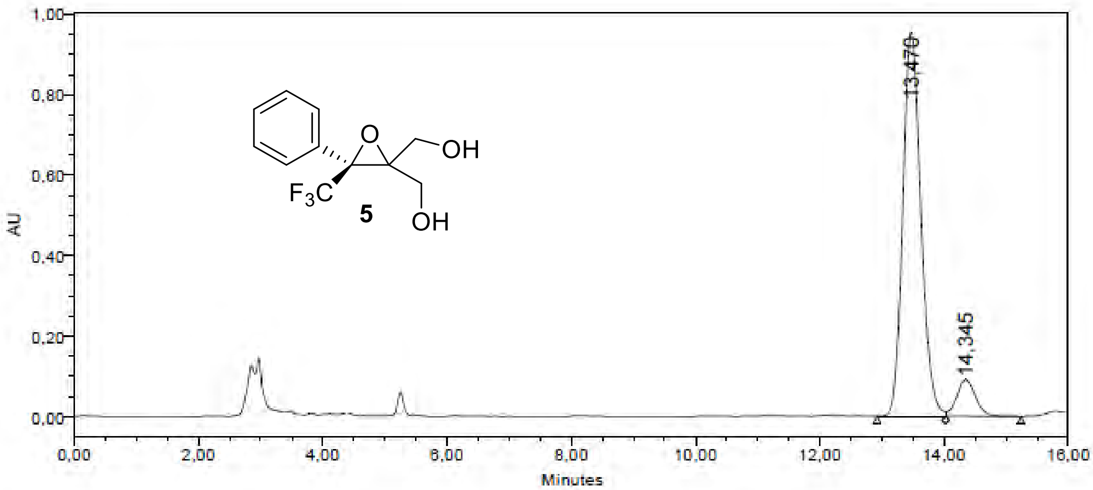
Processed Channel Descr.: 2998 PDA 210,0 nm (2998 (210-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 210,0 nm (2998 (210-300)nm)	22,702	3668810	91,34	93336
2	2998 PDA 210,0 nm (2998 (210-300)nm)	24,422	347913	8,66	7897



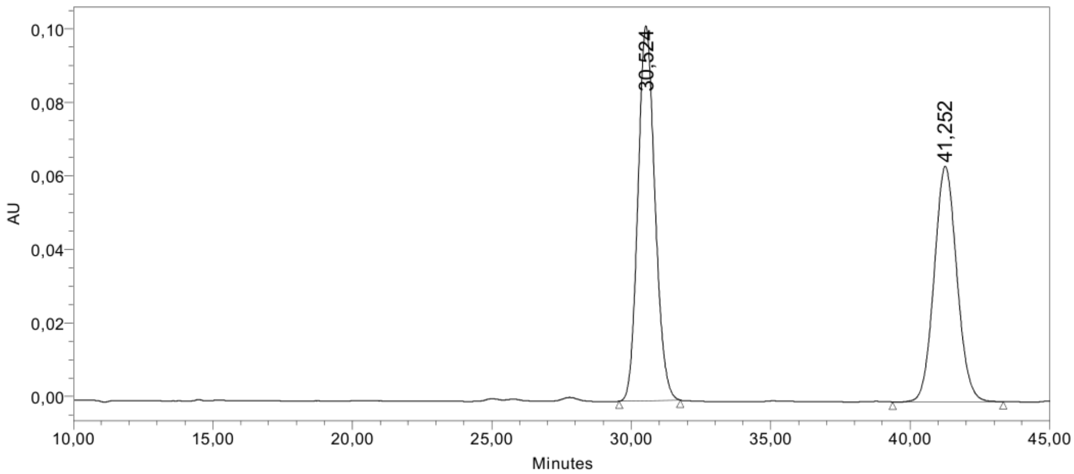
Processed Channel Descr.: 2998 PDA 210,0 nm (2998 (195-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 210,0 nm (2998 (195-300)nm)	13,449	11368072	53,25	610473
2	2998 PDA 210,0 nm (2998 (195-300)nm)	14,299	9979456	46,75	478231



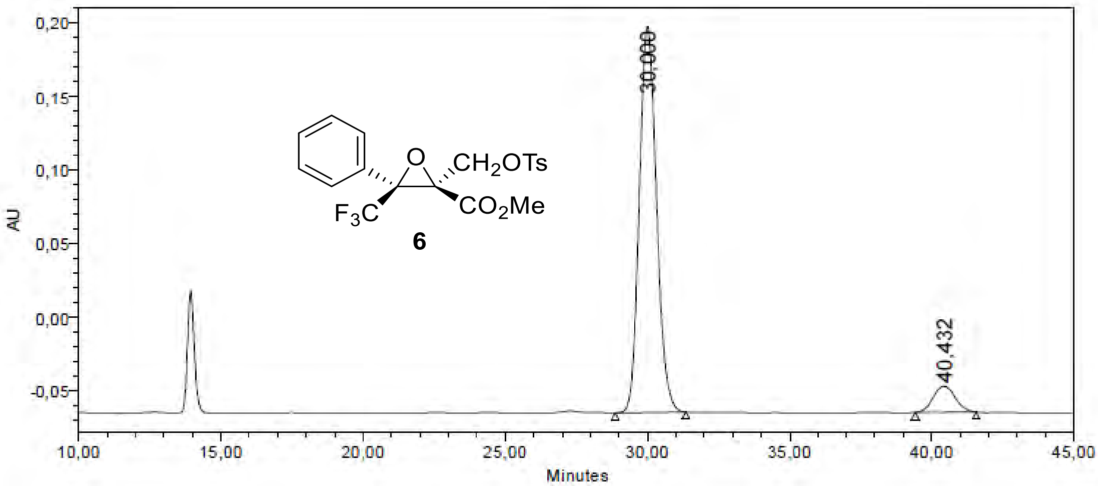
Processed Channel Descr.: 2998 PDA 210,0 nm (2998 (195-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 210,0 nm (2998 (195-300)nm)	13,470	19244210	90,90	954017
2	2998 PDA 210,0 nm (2998 (195-300)nm)	14,345	1927354	9,10	91694



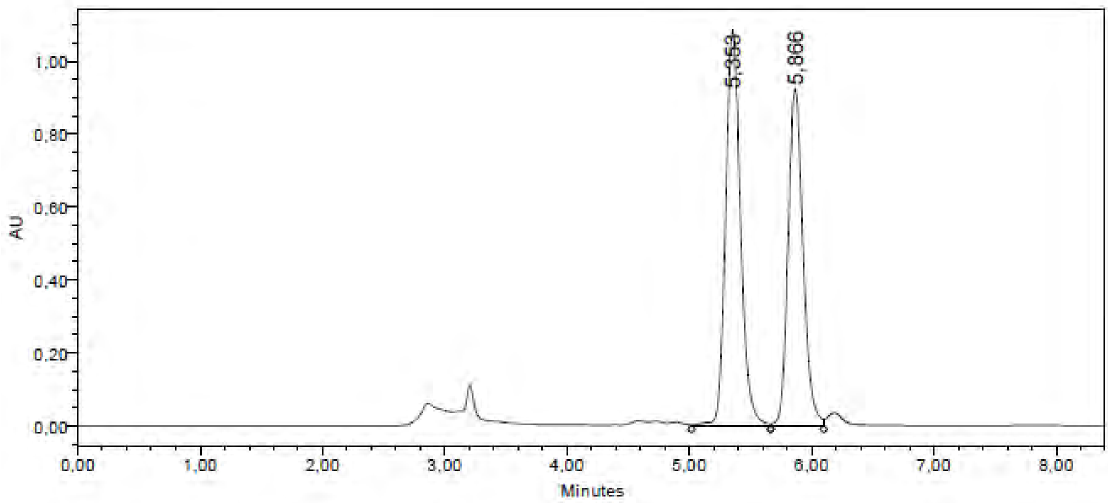
Processed Channel Descr.: 2998 PDA 230,0 nm (2998 (210-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 230,0 nm (2998 (210-300)nm)	30,524	4320586	54,42	101960
2	2998 PDA 230,0 nm (2998 (210-300)nm)	41,252	3618175	45,58	64068



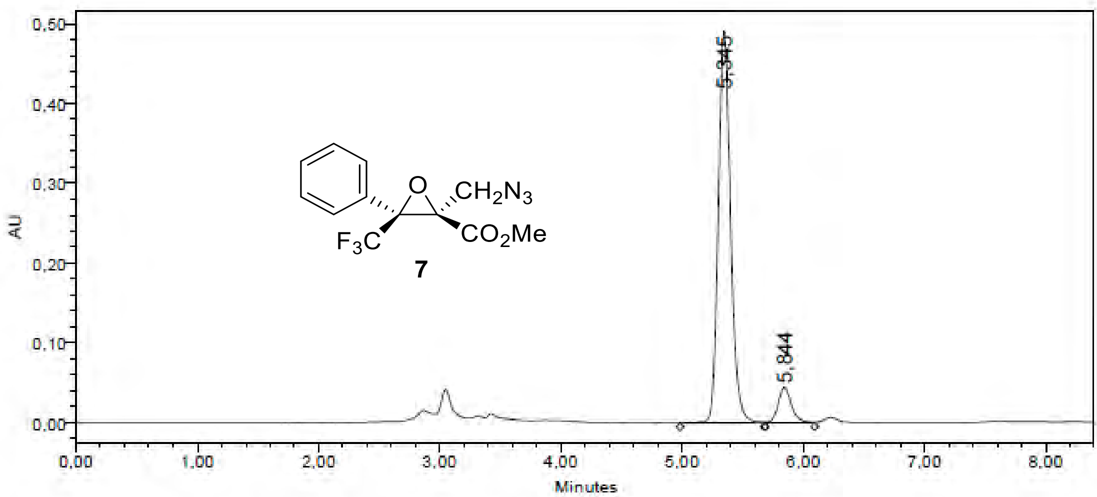
Processed Channel Descr.: 2998 PDA 230,0 nm (2998 (210-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 230,0 nm (2998 (210-300)nm)	30,000	10930888	92,02	261728
2	2998 PDA 230,0 nm (2998 (210-300)nm)	40,432	947393	7,98	17688



Processed Channel Descr.: 2998 PDA 210,0 nm (2998 (210-300)nm)

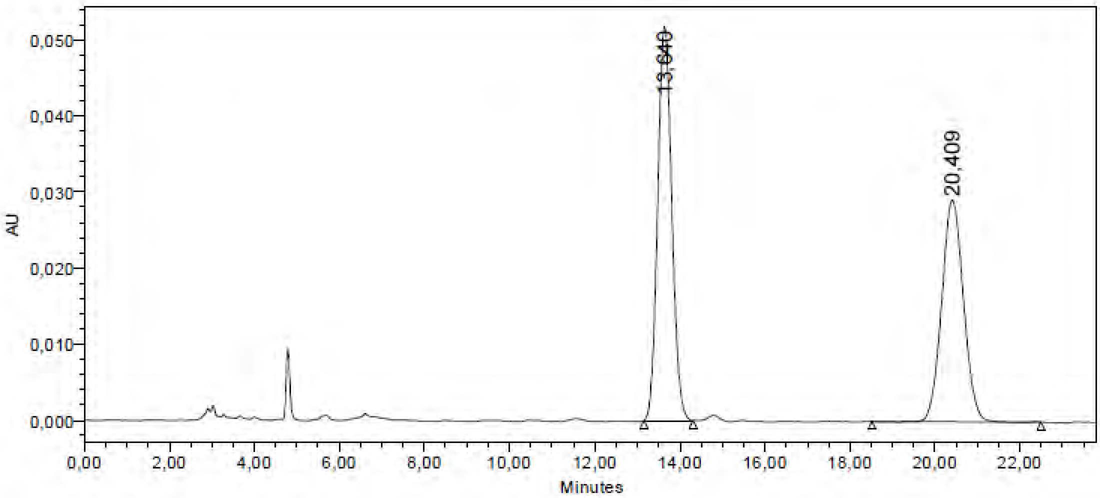
	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 210,0 nm (2998 (210-300)nm)	5,353	9287647	54,06	1086035
2	2998 PDA 210,0 nm (2998 (210-300)nm)	5,866	7892237	45,94	924064



7

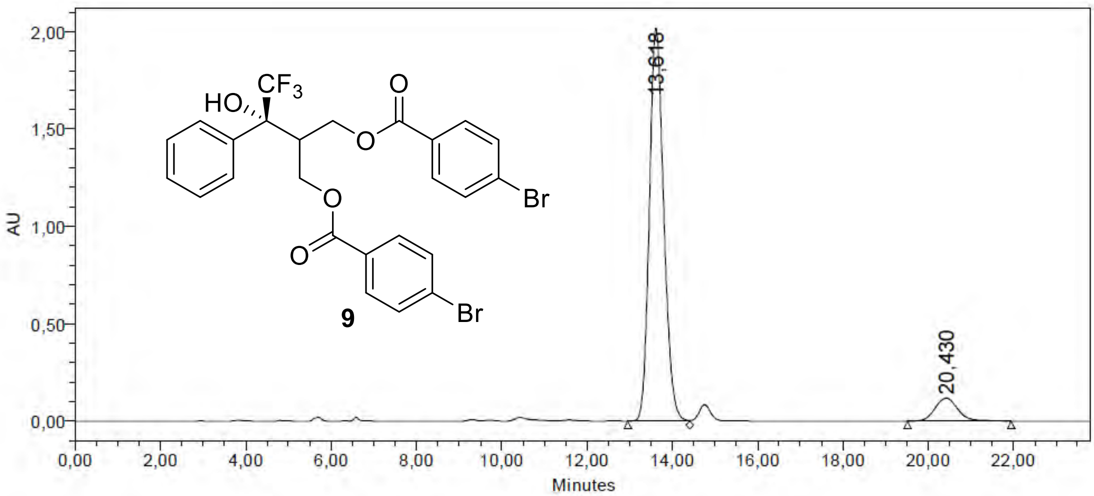
Processed Channel Descr.: 2998 PDA 210,0 nm (2998 (210-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 210,0 nm (2998 (210-300)nm)	5,345	3505198	91,14	492719
2	2998 PDA 210,0 nm (2998 (210-300)nm)	5,844	340890	8,86	44177



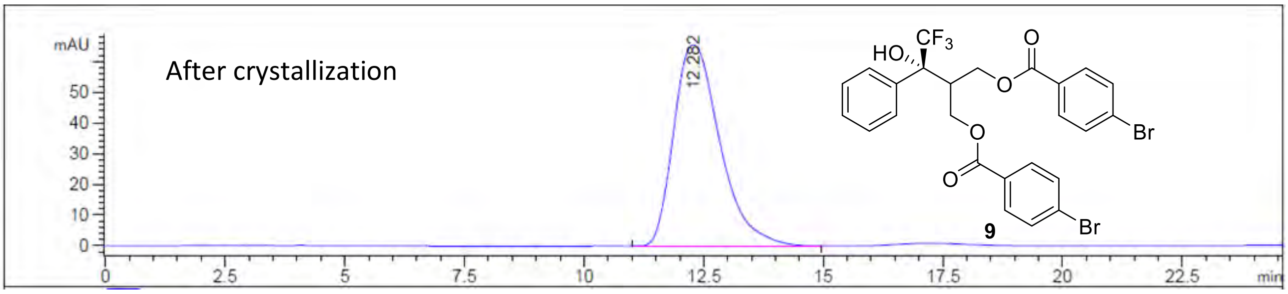
Processed Channel Descr.: 2998 PDA 240,0 nm (2998 (195-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 240,0 nm (2998 (195-300)nm)	13,640	1189232	53,32	51780
2	2998 PDA 240,0 nm (2998 (195-300)nm)	20,409	1041006	46,68	29093



Processed Channel Descr.: 2998 PDA 240,0 nm (2998 (195-300)nm)

	Processed Channel Descr.	RT	Area	% Area	Height
1	2998 PDA 240,0 nm (2998 (195-300)nm)	13,618	47286638	91,47	2017872
2	2998 PDA 240,0 nm (2998 (195-300)nm)	20,430	4407214	8,53	117332



mAU
After crystallization
12.282
HO
CF3
O
O
Br
O
O
9
Br
min

DFT Calculations

Computational method

The conformational space of the initial system has been analyzed using CREST (version 2.12)[19], so using a meta-dynamic calculation at the tight-binding GFN2-xTB[20] level considering toluene as an implicit solvation thanks to the ALPB[21] theory. The conformers have been clustered using PCA analysis on the dihedral angles and the so formed families have been further optimized, sorted and pruned using ORCA[22] (version 6.0.0) following the workflow: i) single point energy calculation at B3LYP[23]/def2-SVP[24] – CPCM(toluene); ii) optimization and thermochemistry value calculation at r^2SCAN-3c[25] d4[26]/def2-mTZVPP – CPCM(toluene). Starting from the best conformer found by this sorting, the reagents have been approached with a scan at GFN2-xTB level, the maximum has been then optimized first with constrained atoms and then freely towards the saddle point. All the points have been characterized as a minimum if all the frequencies calculated from the diagonalization of the hessian matrix are positive or a transition state if only one frequency is negative and stronger then 10*i* cm^{-1}; frequencies below this arbitrarily chosen value have been ignored because it is associate to a conformational vibration (such as a vibration of a CF_3 group) and wasn't canceled by more tight optimization's thresholds.

For thermochemistry values, frequencies were then dumped using mRRHO[27] theory (with cut-off at 100 cm^{-1}, ignoring imaginary frequencies greater than 10*i* cm^{-1}) using 253.15K as temperature, 1M as concentration and 1 bar as pressure.

Later, for the two enantio-determining transition states the Non-Covalent Interaction (NCI) surface have been computed and analyzed with NCIPLOT[28] software (version 4.2) to better understand the enantioselective key interactions.

Geometries, vibrational analysis and surface visualization were visualized using ChimeraX.[29]

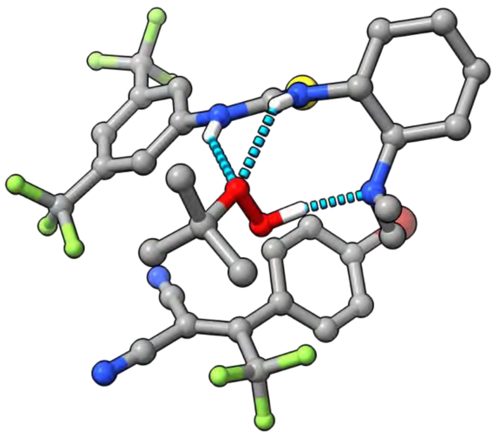
[19] Pracht, P.; Grimme, S; Bannwarth, C; Bohle, F.; Ehlert, S; Feldmann, G.; Gorges, J.; Müller, M.; Neudecker, T.; Plett, C.; Spicher, S.; Steinbach, P.; Wesołowski, P. A.; Zeller, F. *J. Chem. Phys.* **2024**, *160*, 114110.
[20] Bannwarth, C.; Ehlert, S.; Grimme, S. *J. Chem. Theory Comput.* **2019**, *15*, 1652–1671.
[21] Ehlert, S.; Stahn, M.; Spicher, S.; Grimme, S. *J. Chem. Theory Comput.* **2021**, *17*, 4250–4261.
[22] Neese, F. *WIREs Comput. Mol. Sci.* **2022**, *12*, e1606.
[23] Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623–11627
[24] Weigend, F.; Ahlrichs R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.
[25] Grimme, S.; Hansen, A.; Ehlert, S.; Mewes, J.-M. *J. Chem. Phys.* **2021**, *154*, 064103.
[26] Caldeweyher, E.; Mewes, J.-M.; Ehlert, S.; Grimme, S. *Phys. Chem. Chem. Phys.* **2020**, *22*, 8499–8512.
[27] Pracht, P.; Grimme, S. *Chem. Sci.* **2021**, *12*, 6551–6568.
[28] Contreras-García, J.; Johnson, E. R.; Keinan, S.; Chaudret, R.; Piquemal, J.-P.; Beratan, D. N.; Yang, W. *J. Chem. Theory Comput.* **2011**, *7*, 625–632.
[29] a) Pettersen, E. F.; Goddard, T. D.; Huang, C. C.; Couch, G. S.; Greenblatt, D. M.; Meng, E. C.; Ferrin, T. E. *J. Comput. Chem.* **2004**, *25*, 1605–1612; b) Schaefer, A. J.; Ingman, V. M.; Wheeler, S. E. *J. Comput. Chem.* **2021**, *42*, 1750–1754.

Mechanism Study

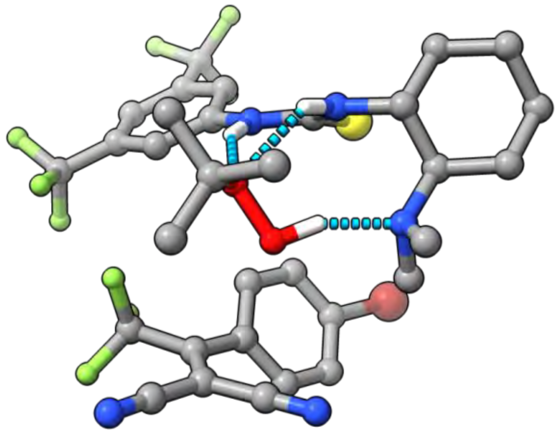
The reaction has been divided into two elementary steps: i) the attack of the TBHP to the C=C bond; and ii) the S_N2 reaction that drives the epoxide formation and the cleavage of *t*-BuOH.

For both the approaches, the initial conformation (**Pre-I**) involves the first coordination of TBHP to the Takemoto catalyst *via* a network of H-bonds.

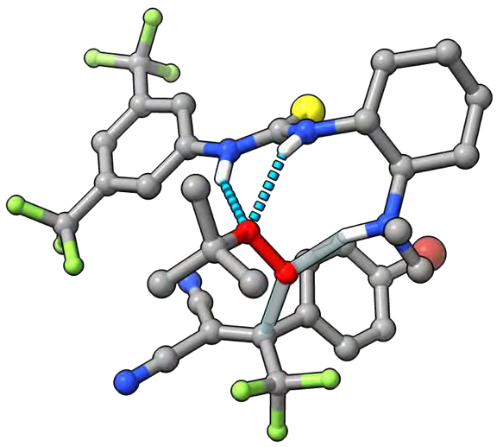
During the approach (**TS-I**) is possible to observe two concerted movements: i) approach of the peroxide oxygen atom to the Michael acceptor carbon, and ii) the deprotonation of the peroxide by the tertiary amine. Following the atom displacement corresponding to the single imaginary frequency found for **TS-I** geometry, the intermediate geometry **Post-I** has been found.



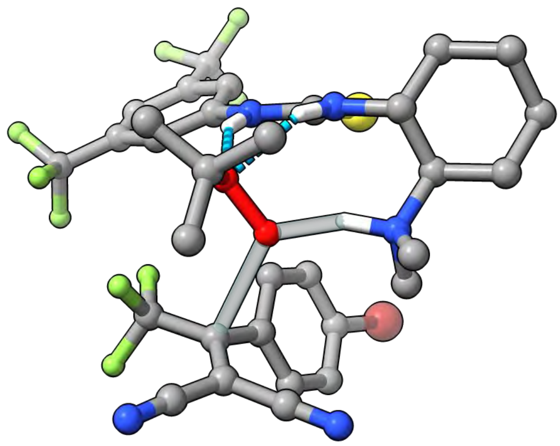
Pre-I Re face



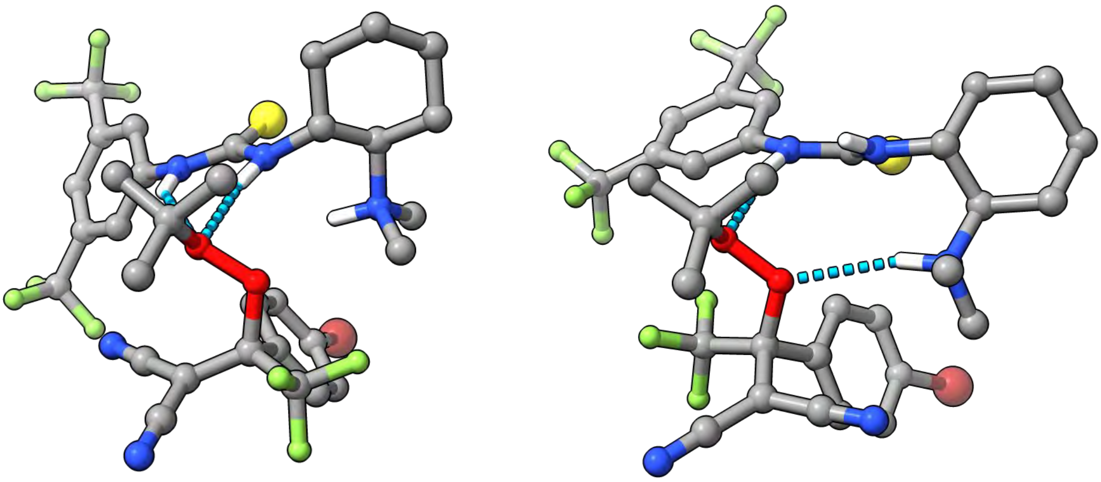
Pre-I Si Face



TS-I Re face



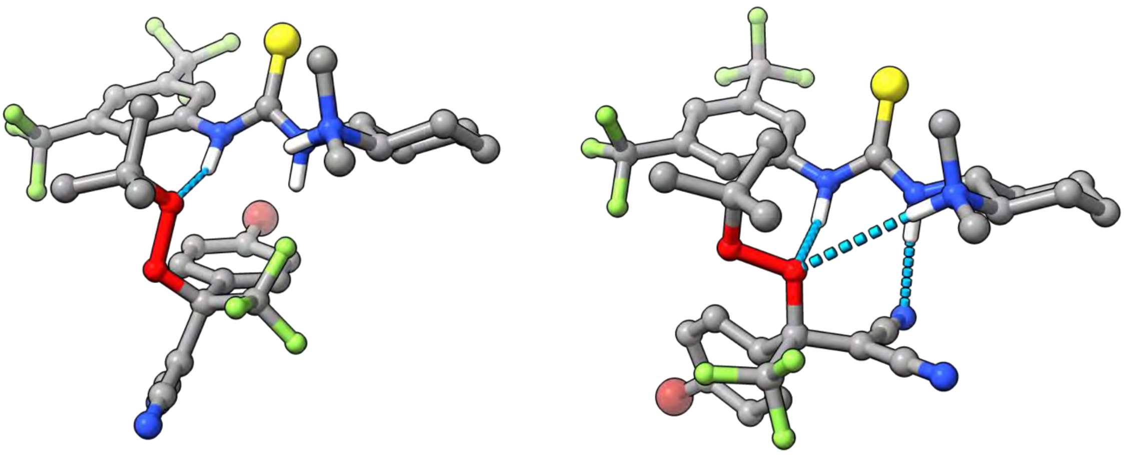
TS-I Si Face



Post-I Re Face **Post-I Si Face**

Figure S5. 3D representation of the critical point geometries obtained at r2scan-3c d4/def2-mTZVPP – CPCM(toluene) level. *Non-relevant* hydrogen atoms have been omitted for clarity

From **Post-I** geometries, possible TS structure for the closure step to epoxide have been detected by a scan approaching the two reactive atoms by bending the key O-C-C angle. From these guess geometries, the **TS-II** structures were found using the same methodology as previously described. The two **Pre-II** and **Post-II** have been located following the projection of the imaginary frequency and then optimizing towards the minimum the so formed geometries. For this reason, it is worth tom mention that **Pre-II** and **Post-I** are two different conformers, linked by a conformational rearrangement that was not modelled.



Pre-II Re Face **Pre-II Si Face**

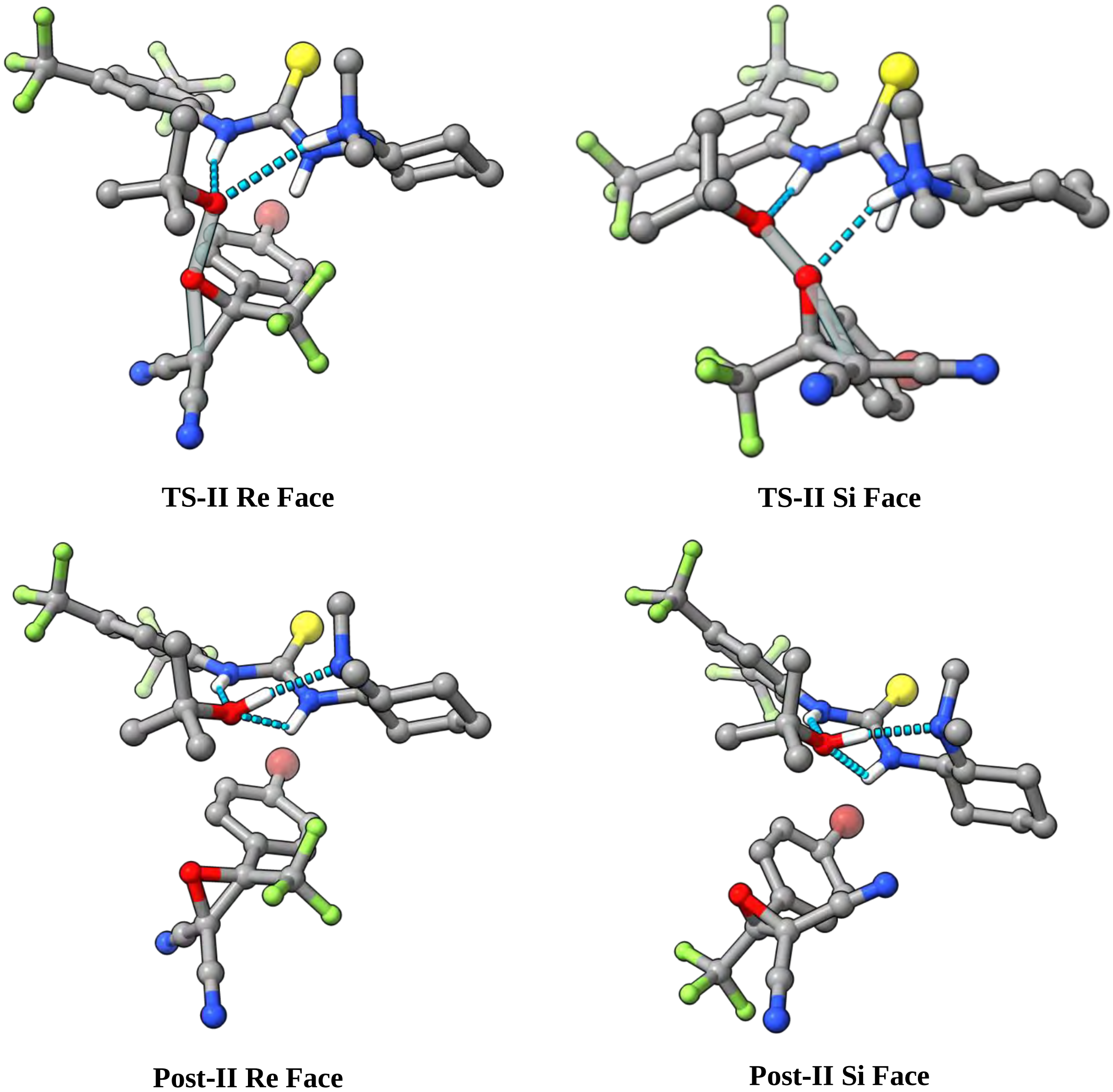
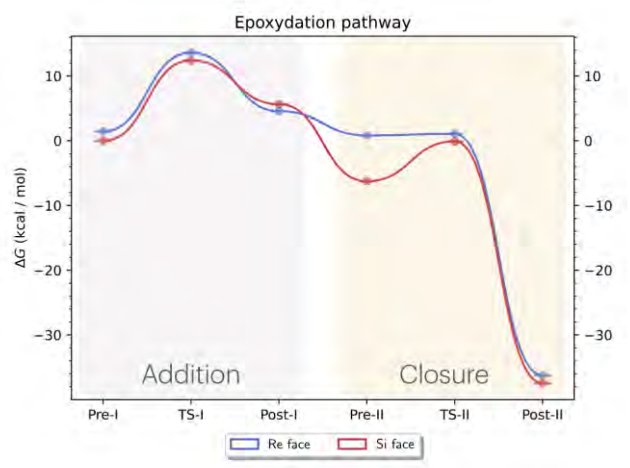


Figure S6. 3D representation of the critical point geometries obtained at r^{2}scan-3c d4/def2-mTZVPP – CPCM(toluene) level. Non relevant hydrogen atoms have been omitted for clarity

The energy pathway as the relative energy is shown in Table S5.

Table S5. Relative energy values of the critical points obtained at r2scan-3c d4/def2-mTZVPP – CPCM(Toluene) at 253.15K. Conformational reorganizational imaginary frequency: a: 7.98i cm^{-1}; b: 2.14i cm^{-1}; c: 2.98i cm^{-1}.

ΔG [kcal/mol]	Re face	Si face
Pre-I	1.4[a]	0.0
TS-I	13.6	12.4
Post-I	4.6	5.7
Pre-II	-0.5	-6.2[b]
TS-II	1.1	-0.1
Post-II	-36.2[c]	-37.4



From the energy point of view, calculations suggest that the first addition step is the rate determining step for the whole reaction, while the ring-closure has lower activation energy.

Based on the energy values reported in Table S5, the enantioselectivity and enantiomeric excess can be estimated. The $\Delta\Delta G^{\neq}$ between the two diastereomeric transition states (**TS-I**) is 1.2 kcal/mol at 253 °K, favoring the **S** pathway. This corresponds to a predicted enantiomeric excess of 83.2%, which is in good agreement with the experimental value of 89%.

To further investigate the key factors influencing the enantioselectivity of the catalyst, non-covalent interaction (NCI) surfaces were computed (Figure S3). The highlighted interactions are those deemed relevant and occur within the catalytic complex formed between the catalyst and TBHP. These interactions suggest that addition to the **Si** face of the alkene is favored due to two halogen bonds involving the CF_3 group: one with an aromatic hydrogen and the other with a methyl group of TBHP. In contrast, addition to the **Re** face benefits from only one such interaction with TBHP, being the CF_3 on the opposite side with respect the aromatic branch of the catalyst.

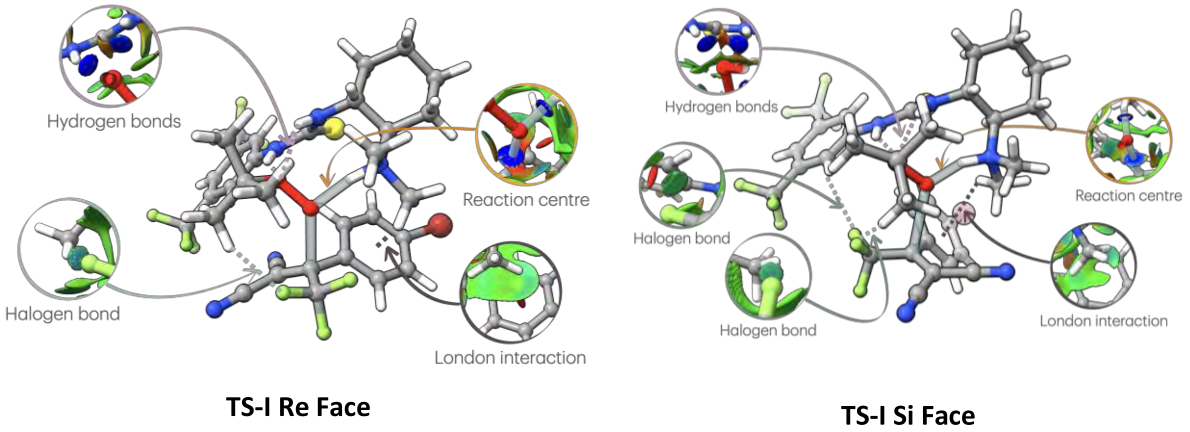
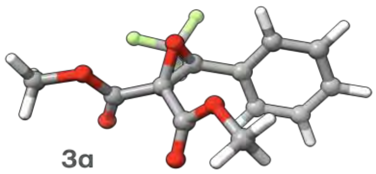


Figure S7. NCI surfaces. Color scheme for the surfaces: red repulsive, green mild interaction (e.g. Van Der Waals), blue strong interaction (e.g. H-bonds)

To study the electronic structure, instead, two qualitative analyses have been performed: the study of the Mulliken charges and the condensed Fukui positive function (related so to the electrophilicity of the atom). Both results are shown in Table S6.

Table S6. Mulliken charge and Fukui condensed positive function calculated for **3a**.

 3a	q Mulliken	Fukui positive function f^+
C *anti*	0.40	0.103
C *syn*	0.38	0.098

Geometries

Pre-I-Re

```
Inner Energy (Hartree)     :  -5535.2084230830
Zero Point Energy (Hartree):  0.6380214200
Enthalpy (Hartree)         :  -5534.5005461300
Entropy (Hartree)          :  -0.1282910900
Gibbs Energy (Hartree)     :  -5534.6288372300
Imaginary Frequency (cm-1) :  -7.96

N       0.39964  -0.98323  -1.27340
C       1.32223  -1.75465  -2.11636
C       2.30493  -0.85539  -2.88215
C       3.32242  -1.67947  -3.66868
C       2.60758  -2.63853  -4.61850
C       1.67460  -3.55655  -3.82917
C       0.61697  -2.75870  -3.04936
N      -0.36371  -3.61080  -2.31960
C      -1.34973  -4.18209  -3.25095
C       0.24834  -4.68994  -1.52749
C      -0.59094  -0.14030  -1.64324
N      -1.38915   0.20820  -0.57006
S      -0.85244   0.41736  -3.21582
C      -2.44135   1.12426  -0.51552
C      -2.43958   2.34260  -1.20082
C      -3.50708   3.21816  -1.03259
C      -4.56541   2.93297  -0.17601
C      -4.53611   1.73178   0.52438
C      -3.50010   0.82491   0.34981
C      -5.60709   1.45043   1.53965
C      -3.51829   4.49684  -1.82406
F      -4.25405   5.46121  -1.22713
F      -2.27346   4.99600  -2.00236
F      -6.81711   1.89870   1.14853
F      -5.72818   0.12804   1.80845
F      -4.04519   4.31062  -3.06176
F      -5.32922   2.05986   2.72406
H       0.38133  -1.28150  -0.30628
H       1.91661  -2.33309  -1.39357
H       1.74250  -0.21655  -3.56984
H       2.80516  -0.19775  -2.16099
H       3.98715  -1.00647  -4.22293
H       3.95587  -2.25666  -2.97868
H       2.02758  -2.06255  -5.35335
H       3.33294  -3.23923  -5.18032
H       1.17662  -4.26653  -4.49995
H       2.28165  -4.14598  -3.12808
H       0.02668  -2.17170  -3.76470
H      -1.82598  -3.37524  -3.81494
H      -0.90592  -4.89803  -3.96203
H      -2.12170  -4.70840  -2.68080
H       1.00239  -4.28644  -0.84419
H      -0.53273  -5.16359  -0.92369
H       0.71516  -5.46814  -2.15135
H      -1.39005  -0.46937   0.19120
H      -1.61021   2.60540  -1.84319
H      -5.38450   3.63114  -0.04727
H      -3.50313  -0.12006   0.88449
C      -1.59660  -3.08004   1.98918
C      -2.97157  -2.58042   2.41675
C      -0.51322  -2.59989   2.95131
C      -1.56290  -4.59454   1.83177
O      -1.19442  -2.43124   0.74858
O      -2.11883  -2.78480  -0.33569
H      -3.29650  -3.09964   3.32354
H      -3.70963  -2.77120   1.63488
H      -2.94435  -1.50698   2.63020
H      -0.50351  -1.50682   3.01325
H       0.47430  -2.95082   2.63545
H      -0.72042  -2.99780   3.94919
H      -2.27404  -4.92004   1.06889
H      -1.83452  -5.06774   2.78045
H      -0.55937  -4.92968   1.55161
H      -1.45185  -2.97985  -1.07550
C      -5.35067  -3.37963  -1.16055
C      -6.04679  -2.48692  -0.39607
C      -4.87819  -3.06779  -2.50539
C      -4.28035  -1.82777  -2.77711
C      -5.04715  -3.98989  -3.55326
C      -3.89049  -1.49783  -4.06522
C      -4.67068  -3.66284  -4.84540
C      -4.09865  -2.41687  -5.08667
C      -6.45376  -1.22258  -0.91730
C      -6.53555  -2.73684   0.91919
N      -6.84132  -0.20619  -1.31292
N      -6.97703  -2.87806   1.97957
C      -5.14637  -4.80111  -0.65334
F      -6.20264  -5.57306  -1.00578
F      -4.04317  -5.35988  -1.18394
H      -4.07594  -1.12718  -1.97352
H      -5.50875  -4.95490  -3.37174
H      -3.40244  -0.54837  -4.25393
H      -4.82082  -4.36901  -5.65454
Br     -3.54114  -1.97838  -6.85409
F      -5.02357  -4.86770   0.68209
```

TS-I-Re

```
Inner Energy (Hartree)     :  -5535.1898585395
Zero Point Energy (Hartree):  0.6390692300
Enthalpy (Hartree)         :  -5534.4819815700
Entropy (Hartree)          :  -0.1278950600
```

Gibbs Energy (Hartree) : -5534.6098766300

Imaginary Frequency (cm-1) : -43.38

N	-0.00044	-1.11698	-1.24509
C	0.97710	-1.83056	-2.06937
C	2.02133	-0.89678	-2.70225
C	3.00998	-1.66690	-3.56946
C	2.25031	-2.41813	-4.65795
C	1.30059	-3.43911	-4.02989
C	0.29949	-2.77540	-3.07979
N	-0.54365	-3.82818	-2.35340
C	-1.29584	-4.67685	-3.32885
C	0.20803	-4.71658	-1.41411
C	-0.88780	-0.15470	-1.61565
N	-1.78183	0.11539	-0.60338
S	-0.94004	0.59357	-3.12763
C	-2.65101	1.19692	-0.44508
C	-2.40762	2.47267	-0.95589
C	-3.31485	3.49523	-0.69165
C	-4.45213	3.28706	0.07777
C	-4.66306	2.01568	0.60616
C	-3.78056	0.97947	0.35308
C	-5.88008	1.78727	1.45776
C	-3.05149	4.84755	-1.29327
F	-3.72846	5.83229	-0.66338
F	-1.73681	5.17324	-1.24778
F	-7.01634	2.12525	0.80577
F	-6.00559	0.50209	1.85009
F	-3.41550	4.89133	-2.60046
F	-5.84304	2.54569	2.58570
H	-0.18023	-1.54041	-0.33955
H	1.53511	-2.45162	-1.35614
H	1.51917	-0.14394	-3.31297
H	2.52742	-0.37067	-1.88448
H	3.72873	-0.96761	-4.01078
H	3.58677	-2.38190	-2.96381
H	1.68225	-1.70395	-5.26973
H	2.93852	-2.94256	-5.33030
H	0.76169	-3.97640	-4.81654
H	1.90892	-4.17438	-3.48694
H	-0.42760	-2.19161	-3.65973
H	-1.75172	-4.03521	-4.08504
H	-0.61845	-5.39234	-3.79842
H	-2.07323	-5.21087	-2.78240
H	0.64029	-4.12442	-0.60758
H	-0.51311	-5.41127	-0.98005
H	0.98441	-5.26688	-1.94720
H	-1.94606	-0.66740	0.03553
H	-1.51972	2.66840	-1.54209
H	-5.15309	4.09152	0.27096
H	-3.96405	-0.00857	0.76345
C	-1.81507	-3.00477	1.85986
C	-3.15065	-2.76485	2.54913
C	-0.73219	-2.11468	2.46910
C	-1.41265	-4.46995	1.91114
O	-1.87147	-2.51068	0.47986
O	-2.43711	-3.41447	-0.49153
H	-3.08189	-3.03006	3.60947
H	-3.93592	-3.37093	2.10164
H	-3.43755	-1.71020	2.47928
H	-0.99135	-1.05484	2.36258
H	0.23853	-2.29499	1.99308
H	-0.63613	-2.33045	3.53763
H	-2.13649	-5.08871	1.37732
H	-1.37761	-4.79299	2.95644
H	-0.42138	-4.62259	1.47367
H	-1.30399	-3.39201	-1.71585
C	-4.74646	-3.42990	-1.16578
C	-5.51638	-2.48729	-0.50599
C	-4.38067	-3.22226	-2.57942
C	-3.71460	-2.05585	-2.97323
C	-4.76601	-4.14331	-3.56408
C	-3.44535	-1.80347	-4.31106
C	-4.49897	-3.90370	-4.90654
C	-3.83971	-2.73501	-5.26398
C	-5.86526	-1.25563	-1.12002
C	-6.13318	-2.68591	0.75658
N	-6.19759	-0.25040	-1.59400
N	-6.68665	-2.80406	1.76883
C	-4.79021	-4.86272	-0.66792
F	-5.99089	-5.41968	-1.00890
F	-3.84085	-5.63941	-1.22917
H	-3.38620	-1.34206	-2.22569
H	-5.30194	-5.04843	-3.30074
H	-2.92257	-0.89609	-4.59268
H	-4.80933	-4.61928	-5.66018
Br	-3.44064	-2.41201	-7.10535
F	-4.68151	-4.98668	0.66190

Post-I-Re

Inner Energy (Hartree) : -5535.2056173526

Zero Point Energy (Hartree): 0.6424664300

Enthalpy (Hartree) : -5534.4953172800

Entropy (Hartree) : -0.1287813100

Gibbs Energy (Hartree) : -5534.6240985900

Imaginary Frequency (cm-1) : None

N	-0.70720	-1.48811	-1.36506
C	0.44217	-2.22719	-1.89230
C	1.79668	-1.58189	-1.56474
C	2.94319	-2.50461	-1.98415
C	2.84364	-2.88195	-3.46288

C	1.48020	-3.51186	-3.77802
C	0.38773	-2.52007	-3.40012
N	-1.00963	-2.96556	-3.80501
C	-1.27358	-2.72055	-5.25915
C	-1.35036	-4.37221	-3.41905
C	-1.09952	-0.22010	-1.66369
N	-1.96426	0.30443	-0.73914
S	-0.64545	0.60327	-3.06903
C	-2.71115	1.50077	-0.86694
C	-2.08240	2.71559	-1.14226
C	-2.85246	3.86727	-1.23298
C	-4.23247	3.83539	-1.03896
C	-4.83195	2.62191	-0.73327
C	-4.08352	1.44958	-0.64507
C	-6.31186	2.54013	-0.47250
C	-2.19226	5.17196	-1.58129
F	-2.79648	6.22116	-0.97913
F	-0.88901	5.19760	-1.22307
F	-6.88765	1.54246	-1.18071
F	-6.57069	2.29675	0.83443
F	-2.23630	5.41037	-2.91801
F	-6.95241	3.68530	-0.79807
H	-1.14101	-1.92193	-0.54691
H	0.40064	-3.19100	-1.36486
H	1.86826	-0.61887	-2.08390
H	1.83352	-1.38088	-0.48802
H	3.90263	-2.01636	-1.78111
H	2.91567	-3.41969	-1.37513
H	2.98134	-1.98658	-4.08409
H	3.63863	-3.58545	-3.73261
H	1.42078	-3.76837	-4.84197
H	1.37246	-4.44034	-3.20215
H	0.53814	-1.57876	-3.93709
H	-1.13221	-1.65658	-5.45977
H	-0.58411	-3.32283	-5.85290
H	-2.30402	-3.00893	-5.47552
H	-1.18907	-4.50353	-2.34780
H	-2.40615	-4.53388	-3.64325
H	-0.73167	-5.05929	-3.99750
H	-2.28066	-0.31450	0.00103
H	-1.00849	2.75637	-1.26852
H	-4.82192	4.74195	-1.11264
H	-4.56929	0.50602	-0.39980
C	-1.67715	-2.99603	2.00380
C	-2.56687	-3.76657	2.96232
C	-1.44917	-1.56753	2.49396
C	-0.36031	-3.71973	1.75413
O	-2.36185	-2.73937	0.72328
O	-2.51618	-3.95960	-0.05003
H	-2.04073	-3.88716	3.91499
H	-2.79942	-4.75993	2.57526
H	-3.50290	-3.23371	3.14517
H	-2.39974	-1.02776	2.56635
H	-0.76564	-1.01973	1.83528
H	-1.00197	-1.60337	3.49156
H	-0.53748	-4.71151	1.32990
H	0.17045	-3.84264	2.70331
H	0.28488	-3.14599	1.07901
H	-1.65221	-2.35428	-3.27990
C	-3.99410	-4.26748	-0.33239
C	-4.96008	-3.80680	0.68838
C	-4.30425	-3.67356	-1.70349
C	-3.93343	-2.34830	-1.94383
C	-4.98366	-4.35785	-2.71538
C	-4.20128	-1.71609	-3.15358
C	-5.24859	-3.74813	-3.93976
C	-4.84823	-2.43596	-4.15035
C	-5.34953	-2.46724	0.69621
C	-5.43423	-4.62104	1.72016
N	-5.64643	-1.33660	0.69962
N	-5.84464	-5.29629	2.57921
C	-3.89131	-5.81242	-0.37545
F	-5.08656	-6.39784	-0.58367
F	-3.06833	-6.20994	-1.38427
H	-3.45135	-1.78386	-1.15969
H	-5.32154	-5.37773	-2.57895
H	-3.91833	-0.67841	-3.30540
H	-5.76910	-4.29837	-4.71635
Br	-5.19984	-1.59923	-5.83580
F	-3.38700	-6.32541	0.75736

Pre-I-Si

Inner Energy (Hartree) : -5535.2079819411
Zero Point Energy (Hartree): 0.6377509500
Enthalpy (Hartree) : -5534.4994608600
Entropy (Hartree) : -0.1314141000
Gibbs Energy (Hartree) : -5534.6308749600
Imaginary Frequency (cm-1) : None

N	-1.19115	-0.57925	-1.94562
C	0.22176	-0.79422	-2.29924
C	0.79192	0.40356	-3.07514
C	2.25339	0.19032	-3.46123
C	2.40543	-1.10403	-4.25762
C	1.93323	-2.28706	-3.41290
C	0.45989	-2.14200	-3.00604
N	-0.06096	-3.27083	-2.18387
C	-0.55335	-4.35848	-3.04378
C	0.90553	-3.80807	-1.21211
C	-2.27240	-0.51504	-2.75382
N	-3.45150	-0.47625	-2.02670
S	-2.22908	-0.52239	-4.44294

C	-4.74499	-0.14455	-2.42839
C	-5.03717	0.69080	-3.51121
C	-6.36330	0.99288	-3.80218
C	-7.41566	0.50514	-3.03733
C	-7.10905	-0.29180	-1.93770
C	-5.79712	-0.62296	-1.63250
C	-8.23760	-0.82783	-1.10183
C	-6.65237	1.84971	-5.00425
F	-7.85311	2.46361	-4.91770
F	-5.71953	2.81359	-5.17824
F	-8.86121	-1.86661	-1.71542
F	-7.82256	-1.27353	0.10389
F	-6.66852	1.11179	-6.14450
F	-9.18524	0.11309	-0.87893
H	-1.39150	-0.62666	-0.95367
H	0.73704	-0.83670	-1.32738
H	0.19615	0.54988	-3.98156
H	0.67349	1.30264	-2.45808
H	2.60636	1.05055	-4.04202
H	2.87999	0.13451	-2.55853
H	1.81176	-1.04068	-5.18047
H	3.44996	-1.25482	-4.55560
H	2.06573	-3.23051	-3.95699
H	2.56824	-2.34025	-2.51833
H	-0.14055	-2.12830	-3.92287
H	-1.32758	-3.97214	-3.71291
H	0.24660	-4.81368	-3.65275
H	-0.99111	-5.14535	-2.42027
H	1.31616	-3.00228	-0.59545
H	0.38421	-4.51098	-0.55295
H	1.73978	-4.34710	-1.68846
H	-3.38698	-0.85252	-1.08262
H	-4.23862	1.10780	-4.10908
H	-8.44373	0.75367	-3.27482
H	-5.58002	-1.24368	-0.76756
C	-2.15083	-2.09489	1.63810
C	-2.79207	-3.25635	2.38328
C	-2.70202	-0.75207	2.11045
C	-0.63163	-2.14002	1.73208
O	-2.57050	-2.10053	0.24051
O	-2.20732	-3.34930	-0.41503
H	-2.54770	-3.19344	3.44836
H	-2.41558	-4.20975	2.00425
H	-3.88037	-3.23414	2.27469
H	-3.79005	-0.71670	1.99463
H	-2.25586	0.07562	1.54806
H	-2.46257	-0.61600	3.16894
H	-0.25151	-3.09737	1.36749
H	-0.32113	-2.02489	2.77531
H	-0.18012	-1.32993	1.14762
H	-1.45888	-3.08583	-1.04123
C	-4.81221	-5.36249	-0.85648
C	-4.05211	-6.05318	0.04106
C	-4.43646	-5.18100	-2.25219
C	-3.95876	-6.26715	-3.00092
C	-4.53928	-3.92115	-2.86350
C	-3.58738	-6.10140	-4.32646
C	-4.15101	-3.74071	-4.17945
C	-3.67949	-4.83621	-4.89677
C	-4.41832	-6.28254	1.39884
C	-2.75220	-6.53780	-0.28466
N	-4.65248	-6.48658	2.51377
N	-1.68232	-6.93407	-0.48021
C	-6.10120	-4.71885	-0.35271
F	-6.82048	-5.57916	0.39230
F	-5.82043	-3.64165	0.41805
H	-3.91463	-7.25762	-2.55932
H	-4.88166	-3.06173	-2.29849
H	-3.23605	-6.94732	-4.90689
H	-4.18980	-2.75369	-4.62844
Br	-3.12858	-4.58792	-6.70233
F	-6.88628	-4.30914	-1.35927

TS-I-Si

Inner Energy (Hartree) : -5535.1915054425
Zero Point Energy (Hartree): 0.6384971900
Enthalpy (Hartree) : -5534.4829394600
Entropy (Hartree) : -0.1286649600
Gibbs Energy (Hartree) : -5534.6116044200
Imaginary Frequency (cm-1) : -62.18

N	-1.27632	-0.62116	-1.82644
C	0.12731	-0.90811	-2.12938
C	0.82134	0.27186	-2.82905
C	2.28042	-0.03431	-3.15426
C	2.37700	-1.30225	-3.99976
C	1.78080	-2.48413	-3.23258
C	0.31268	-2.22320	-2.90118
N	-0.32295	-3.38846	-2.15042
C	-0.79026	-4.42262	-3.12121
C	0.56328	-4.03220	-1.13262
C	-2.31392	-0.43191	-2.68163
N	-3.50425	-0.33481	-1.99573
S	-2.18069	-0.36179	-4.36529
C	-4.79407	-0.03541	-2.43645
C	-5.09423	0.72023	-3.57265
C	-6.42665	0.97608	-3.88653
C	-7.47243	0.51433	-3.09849
C	-7.15519	-0.20378	-1.94728
C	-5.83985	-0.47825	-1.61295
C	-8.27433	-0.72133	-1.08764
C	-6.72468	1.75173	-5.14019

F	-7.94384	2.33327	-5.10478
F	-5.81777	2.73213	-5.35736
F	-8.88859	-1.78672	-1.66356
F	-7.85074	-1.12053	0.13058
F	-6.70263	0.95098	-6.23742
F	-9.23156	0.21731	-0.89384
H	-1.55088	-0.80722	-0.86443
H	0.60088	-1.02474	-1.14264
H	0.28242	0.50028	-3.75347
H	0.73458	1.14668	-2.17451
H	2.72187	0.81805	-3.68276
H	2.85789	-0.17117	-2.22816
H	1.83847	-1.15861	-4.94647
H	3.42003	-1.52486	-4.25091
H	1.87545	-3.40713	-3.81659
H	2.36252	-2.61848	-2.31173
H	-0.25788	-2.14038	-3.83280
H	-1.53126	-3.97370	-3.78311
H	0.06066	-4.79051	-3.69997
H	-1.23673	-5.24867	-2.56741
H	1.05106	-3.26913	-0.52454
H	-0.06538	-4.65901	-0.49696
H	1.31759	-4.64562	-1.62991
H	-3.46928	-0.71595	-1.04727
H	-4.30136	1.11030	-4.19531
H	-8.50439	0.72173	-3.35809
H	-5.61115	-1.03377	-0.70886
C	-2.25057	-2.00953	1.58441
C	-2.40926	-3.36334	2.25898
C	-3.07253	-0.93406	2.28836
C	-0.77730	-1.61175	1.52063
O	-2.81925	-2.00614	0.23841
O	-2.46585	-3.16244	-0.56295
H	-1.98049	-3.31858	3.26527
H	-1.88841	-4.13738	1.68946
H	-3.46034	-3.64030	2.34559
H	-4.12303	-1.23370	2.35243
H	-3.00794	0.01783	1.74873
H	-2.68974	-0.77793	3.30185
H	-0.23014	-2.31634	0.88977
H	-0.32810	-1.63625	2.51875
H	-0.65479	-0.59543	1.12633
H	-1.20763	-3.07045	-1.57843
C	-4.29093	-5.12146	-0.89028
C	-3.63038	-6.03252	-0.09978
C	-4.11954	-5.04202	-2.34407
C	-3.97928	-6.22830	-3.08124
C	-4.16341	-3.82091	-3.03609
C	-3.86854	-6.20056	-4.46502
C	-4.06893	-3.78192	-4.41767
C	-3.91619	-4.97490	-5.11787
C	-3.99174	-6.33280	1.24004
C	-2.44913	-6.68495	-0.53889
N	-4.26226	-6.62484	2.32859
N	-1.46291	-7.21209	-0.84784
C	-5.53014	-4.46330	-0.29034
F	-6.47644	-5.41851	-0.09399
F	-5.30412	-3.87521	0.89443
H	-3.99403	-7.18913	-2.57673
H	-4.21849	-2.89252	-2.48414
H	-3.76814	-7.12435	-5.02411
H	-4.08249	-2.82733	-4.93354
Br	-3.75956	-4.92398	-7.01857
F	-6.07419	-3.54157	-1.10140

Post-I-Si

Inner Energy (Hartree) : -5535.2048722892
Zero Point Energy (Hartree): 0.6422718600
Enthalpy (Hartree) : -5534.4946721800
Entropy (Hartree) : -0.1277014300
Gibbs Energy (Hartree) : -5534.6223736100
Imaginary Frequency (cm-1) : None

N	-1.24494	-0.92219	-2.03585
C	0.13208	-1.06281	-2.52778
C	0.63620	0.14372	-3.33605
C	2.10354	-0.03400	-3.72105
C	2.29190	-1.32913	-4.50748
C	1.83196	-2.53236	-3.67867
C	0.36500	-2.37656	-3.29103
N	-0.13939	-3.56335	-2.46968
C	-0.22566	-4.82121	-3.28521
C	0.62637	-3.83274	-1.20675
C	-2.37896	-0.65415	-2.74656
N	-3.46277	-0.46766	-1.91813
S	-2.46363	-0.64386	-4.42727
C	-4.72796	0.04804	-2.23398
C	-4.93528	1.02365	-3.21095
C	-6.21815	1.52284	-3.41008
C	-7.30101	1.08789	-2.65375
C	-7.06766	0.14381	-1.65881
C	-5.80043	-0.37842	-1.44548
C	-8.21649	-0.36582	-0.83315
C	-6.42855	2.54404	-4.49397
F	-7.53301	3.29223	-4.28263
F	-5.38056	3.39498	-4.59818
F	-8.83445	-1.41270	-1.43562
F	-7.81611	-0.79418	0.38514
F	-6.57560	1.95738	-5.70943
F	-9.15865	0.58437	-0.63766
H	-1.31138	-0.77953	-1.03719
H	0.73942	-1.09532	-1.61267

H	0.02797	0.25696	-4.23711
H	0.49230	1.04257	-2.72537
H	2.43061	0.82657	-4.31483
H	2.73264	-0.05898	-2.81926
H	1.71493	-1.28254	-5.44107
H	3.34254	-1.46731	-4.78442
H	1.97877	-3.45560	-4.24855
H	2.45653	-2.59423	-2.77799
H	-0.26655	-2.37322	-4.18805
H	-0.78505	-4.61186	-4.19803
H	0.78367	-5.16157	-3.51756
H	-0.74015	-5.57590	-2.68669
H	0.71686	-2.91746	-0.62225
H	0.08180	-4.59348	-0.64162
H	1.61411	-4.21302	-1.46867
H	-3.43162	-0.94836	-1.01643
H	-4.10682	1.40114	-3.79527
H	-8.29426	1.48875	-2.81925
H	-5.63584	-1.11370	-0.66552
C	-3.10930	-2.25172	1.62742
C	-3.03276	-3.51903	2.45838
C	-4.07849	-1.24006	2.23963
C	-1.72556	-1.64229	1.43152
O	-3.75463	-2.46763	0.32862
O	-3.07326	-3.46758	-0.51282
H	-2.64842	-3.26702	3.45198
H	-2.35919	-4.24728	1.99997
H	-4.01574	-3.97979	2.57417
H	-5.06607	-1.68862	2.37957
H	-4.17521	-0.35215	1.60530
H	-3.69356	-0.92645	3.21471
H	-1.10400	-2.30343	0.81991
H	-1.23179	-1.51901	2.40020
H	-1.79519	-0.64860	0.97095
H	-1.10225	-3.32520	-2.18973
C	-3.85092	-4.73889	-0.71068
C	-3.36833	-5.84207	0.16766
C	-3.62456	-5.02271	-2.20493
C	-3.53846	-6.33971	-2.66251
C	-3.61274	-3.98543	-3.14199
C	-3.40774	-6.61932	-4.01844
C	-3.48939	-4.24772	-4.50248
C	-3.37863	-5.56600	-4.92279
C	-4.08038	-6.39785	1.23018
C	-2.06152	-6.27337	-0.03527
N	-4.66118	-6.88389	2.11910
N	-0.95883	-6.60949	-0.24532
C	-5.37526	-4.49599	-0.53365
F	-6.04647	-5.59699	-0.93415
F	-5.75273	-4.24000	0.72890
H	-3.58270	-7.15849	-1.95250
H	-3.72070	-2.95645	-2.82119
H	-3.33698	-7.64637	-4.35987
H	-3.48215	-3.42804	-5.21295
Br	-3.17276	-5.93672	-6.78942
F	-5.80562	-3.46835	-1.29929

Pre-II-Re

Inner Energy (Hartree) : -5535.2098744862
Zero Point Energy (Hartree): 0.6407725300
Enthalpy (Hartree) : -5534.5012180100
Entropy (Hartree) : -0.1305770800
Gibbs Energy (Hartree) : -5534.6317951000
Imaginary Frequency (cm-1) : None

N	-0.40491	-5.30516	-3.07610
C	-0.47402	-6.57984	-3.77836
C	-1.24010	-6.46501	-5.10243
C	-1.27115	-7.81091	-5.82771
C	-1.85480	-8.90621	-4.93516
C	-1.09249	-9.00781	-3.60643
C	-1.13893	-7.65358	-2.90924
N	-0.52413	-7.65877	-1.51101
C	-1.31092	-8.49293	-0.54522
C	0.93090	-8.02268	-1.47253
C	0.67791	-4.46710	-3.15306
N	0.43996	-3.26508	-2.54974
S	2.14968	-4.91074	-3.84109
C	1.17406	-2.07745	-2.66718
C	1.76869	-1.68207	-3.86969
C	2.40485	-0.45269	-3.93684
C	2.45061	0.41232	-2.84237
C	1.83198	0.01463	-1.66720
C	1.19854	-1.22098	-1.57034
C	1.82068	0.90014	-0.45361
C	3.00606	0.00917	-5.23538
F	2.23545	0.95885	-5.82596
F	4.22810	0.56380	-5.05024
F	2.44171	2.07687	-0.66242
F	0.55250	1.17551	-0.05723
F	3.15009	-0.99303	-6.12644
F	2.43186	0.30289	0.60190
H	-1.29889	-4.84637	-2.91681
H	0.55851	-6.87138	-4.00481
H	-2.26363	-6.11866	-4.89566
H	-0.75064	-5.69925	-5.71463
H	-1.85516	-7.72265	-6.75015
H	-0.24829	-8.08406	-6.12162
H	-2.91213	-8.69077	-4.72813
H	-1.81987	-9.87575	-5.44304
H	-1.54298	-9.78622	-2.98144
H	-0.05271	-9.29483	-3.80898

H	-2.18755	-7.37770	-2.73532
H	-2.36447	-8.21616	-0.60973
H	-1.17406	-9.54626	-0.79185
H	-0.93572	-8.29826	0.46102
H	1.49555	-7.34638	-2.11850
H	1.27451	-7.91858	-0.44138
H	1.04573	-9.05672	-1.79952
H	-0.28884	-3.24739	-1.83542
H	1.71365	-2.32129	-4.74071
H	2.94747	1.37311	-2.91475
H	0.70454	-1.51311	-0.64819
C	-0.13957	-4.05466	1.31002
C	0.01287	-2.78724	2.14864
C	1.20067	-4.45358	0.68741
C	-0.71452	-5.19715	2.14267
O	-0.96615	-3.81604	0.14762
O	-2.30658	-3.22443	0.66705
H	0.74197	-2.96168	2.94636
H	-0.93740	-2.50425	2.60712
H	0.36887	-1.95233	1.53692
H	1.65060	-3.62366	0.13517
H	1.08106	-5.30007	0.00183
H	1.89062	-4.75289	1.48247
H	-1.70541	-4.93808	2.52265
H	-0.05805	-5.40898	2.99280
H	-0.79974	-6.10463	1.53431
H	-0.59374	-6.68015	-1.20101
C	-3.35723	-3.44370	-0.27835
C	-4.51219	-2.76229	0.38858
C	-3.00415	-2.80712	-1.61895
C	-3.34132	-3.34585	-2.86262
C	-2.32284	-1.58730	-1.57764
C	-2.95215	-2.71170	-4.04155
C	-1.95057	-0.93192	-2.74373
C	-2.24785	-1.51810	-3.96662
C	-4.98466	-1.53838	-0.08998
C	-5.06095	-3.27370	1.56954
N	-5.39436	-0.52368	-0.49694
N	-5.52701	-3.70634	2.54818
C	-3.63593	-4.96857	-0.39527
F	-4.81876	-5.21989	-0.99042
F	-2.69279	-5.62747	-1.15370
H	-3.91695	-4.26154	-2.94453
H	-2.07812	-1.14650	-0.61642
H	-3.20378	-3.14577	-5.00343
H	-1.42011	0.01302	-2.69509
Br	-1.65584	-0.67319	-5.57626
F	-3.63870	-5.58051	0.79525

TS-II-Re

Inner Energy (Hartree) : -5535.2082071026
Zero Point Energy (Hartree): 0.6395488600
Enthalpy (Hartree) : -5534.5007869400
Entropy (Hartree) : -0.1286478100
Gibbs Energy (Hartree) : -5534.6294347400
Imaginary Frequency (cm-1) : -17.60

N	-0.36944	-5.15942	-2.91996
C	-0.49043	-6.43135	-3.60888
C	-1.49829	-6.40182	-4.76327
C	-1.51353	-7.75155	-5.48386
C	-1.79126	-8.90099	-4.51319
C	-0.79817	-8.90291	-3.34076
C	-0.88372	-7.55371	-2.63871
N	-0.06180	-7.45554	-1.35660
C	-0.61254	-8.32144	-0.26586
C	1.40609	-7.68701	-1.55382
C	0.68196	-4.30478	-3.08351
N	0.62635	-3.22826	-2.24905
S	1.95634	-4.59675	-4.15519
C	1.35832	-2.04027	-2.41018
C	1.45819	-1.42489	-3.66243
C	2.14459	-0.22706	-3.78085
C	2.71888	0.39615	-2.67192
C	2.59369	-0.21672	-1.43454
C	1.92847	-1.43410	-1.29639
C	3.22831	0.38572	-0.21311
C	2.21675	0.45677	-5.11846
F	1.25474	1.40754	-5.24422
F	3.40442	1.08045	-5.29930
F	3.59717	1.66869	-0.40097
F	2.39134	0.35572	0.85226
F	2.05406	-0.40596	-6.14324
F	4.34315	-0.29980	0.15439
H	-1.18963	-4.80027	-2.44000
H	0.49876	-6.64469	-4.03300
H	-2.49653	-6.16407	-4.36903
H	-1.21277	-5.59369	-5.44588
H	-2.26707	-7.74070	-6.27883
H	-0.54023	-7.90951	-5.96889
H	-2.81223	-8.81097	-4.11694
H	-1.73417	-9.86345	-5.03267
H	-1.03983	-9.72232	-2.65525
H	0.21640	-9.06894	-3.72467
H	-1.91352	-7.39957	-2.29952
H	-1.67253	-8.09211	-0.13760
H	-0.47469	-9.36934	-0.53437
H	-0.07115	-8.10225	0.65651
H	1.78759	-6.98787	-2.30175
H	1.91118	-7.51787	-0.60102
H	1.56019	-8.71802	-1.87463
H	0.01938	-3.31760	-1.41881

H	0.99031	-1.87979	-4.52733
H	3.24758	1.33651	-2.77715
H	1.86802	-1.91427	-0.32541
C	-0.42852	-4.17524	1.24647
C	-0.29077	-2.74173	1.77564
C	0.97272	-4.77903	1.03520
C	-1.20297	-5.03889	2.24739
O	-1.04645	-4.19997	-0.03113
O	-2.66715	-3.29894	0.30415
H	0.31827	-2.72383	2.68565
H	-1.27172	-2.32188	2.00770
H	0.18377	-2.09872	1.02762
H	1.51954	-4.26749	0.23678
H	0.90040	-5.84358	0.78643
H	1.55333	-4.69998	1.96055
H	-2.20094	-4.62698	2.41383
H	-0.67647	-5.08464	3.20730
H	-1.31243	-6.05872	1.86071
H	-0.17705	-6.47561	-1.05028
C	-3.59560	-3.52647	-0.69062
C	-4.61643	-2.69934	0.04633
C	-3.20291	-2.95393	-2.04810
C	-3.73007	-3.40399	-3.26143
C	-2.31131	-1.88058	-2.05462
C	-3.33751	-2.82329	-4.46318
C	-1.93178	-1.27240	-3.24481
C	-2.43449	-1.76808	-4.43896
C	-4.73940	-1.33339	-0.23851
C	-5.36085	-3.22073	1.11381
N	-4.86384	-0.20268	-0.48448
N	-6.00718	-3.65290	1.97959
C	-4.01692	-5.01751	-0.76476
F	-5.25809	-5.16557	-1.27612
F	-3.17886	-5.73517	-1.56981
H	-4.45277	-4.21196	-3.29555
H	-1.91031	-1.51713	-1.11380
H	-3.73739	-3.18751	-5.40336
H	-1.24530	-0.43276	-3.23733
Br	-1.86796	-0.97933	-6.08728
F	-3.99420	-5.61317	0.43345

Post-II-Re

Inner Energy (Hartree) : -5535.2654973240
Zero Point Energy (Hartree): 0.6379918300
Enthalpy (Hartree) : -5534.5596568900
Entropy (Hartree) : -0.1288905100
Gibbs Energy (Hartree) : -5534.6885474000
Imaginary Frequency (cm-1) : -2.81

N	-0.30276	-4.98948	-3.07906
C	-0.45473	-6.32563	-3.63486
C	-1.53519	-6.36510	-4.72186
C	-1.62841	-7.75755	-5.34206
C	-1.88881	-8.80804	-4.26401
C	-0.82965	-8.74578	-3.15894
C	-0.77217	-7.34389	-2.52504
N	0.13414	-7.20359	-1.35567
C	-0.22319	-8.13910	-0.28224
C	1.56164	-7.32984	-1.68168
C	0.71558	-4.14935	-3.36279
N	0.86422	-3.16237	-2.41306
S	1.73070	-4.33243	-4.70058
C	1.62387	-1.99729	-2.52222
C	1.65653	-1.24515	-3.70369
C	2.37523	-0.06104	-3.73822
C	3.05657	0.41803	-2.61805
C	3.00247	-0.32993	-1.45138
C	2.30422	-1.53428	-1.39739
C	3.72935	0.11676	-0.21551
C	2.36140	0.77689	-4.98627
F	1.45728	1.78906	-4.89069
F	3.56323	1.35477	-5.21855
F	4.22664	1.36481	-0.32728
F	2.91684	0.10276	0.87270
F	2.03633	0.06391	-6.08430
F	4.77173	-0.70357	0.07690
H	-0.90644	-4.74714	-2.30085
H	0.50286	-6.58107	-4.10605
H	-2.50047	-6.08703	-4.27449
H	-1.29317	-5.60826	-5.47750
H	-2.41969	-7.77969	-6.10063
H	-0.68523	-7.98663	-5.85826
H	-2.88031	-8.63417	-3.82047
H	-1.90947	-9.81316	-4.70181
H	-1.05835	-9.49478	-2.39323
H	0.15262	-8.99979	-3.58031
H	-1.77955	-7.11467	-2.14040
H	-1.29400	-8.05867	-0.06164
H	0.00678	-9.19006	-0.52259
H	0.33732	-7.87924	0.62288
H	1.86247	-6.57068	-2.40955
H	2.14408	-7.16669	-0.76836
H	1.82807	-8.32371	-2.07866
H	0.52545	-3.41316	-1.47858
H	1.11446	-1.58794	-4.57576
H	3.60844	1.34980	-2.66076
H	2.30066	-2.12142	-0.48361
C	-0.08160	-4.38881	1.25126
C	-0.29502	-2.90009	1.49863
C	1.35685	-4.79476	1.56872
C	-1.07611	-5.20878	2.07246
O	-0.33324	-4.59205	-0.15964

O	-3.87209	-2.83358	0.47244
H	-0.11797	-2.65866	2.55107
H	-1.32197	-2.61587	1.24826
H	0.39023	-2.29983	0.89077
H	2.06011	-4.22793	0.94881
H	1.50785	-5.86273	1.37337
H	1.59129	-4.60675	2.62170
H	-2.10257	-4.92109	1.82284
H	-0.92097	-5.04096	3.14360
H	-0.95623	-6.27920	1.87563
H	-0.11851	-5.52339	-0.43140
C	-4.25159	-3.52644	-0.70383
C	-5.19521	-2.57300	-0.00720
C	-3.59537	-3.12066	-1.97954
C	-4.00584	-3.66521	-3.19998
C	-2.59449	-2.14843	-1.95355
C	-3.41489	-3.24618	-4.38374
C	-2.00468	-1.71864	-3.13565
C	-2.41941	-2.27688	-4.33779
C	-5.40811	-1.27529	-0.61158
C	-6.29519	-3.02215	0.81588
N	-5.59198	-0.24412	-1.09609
N	-7.20009	-3.35329	1.45147
C	-4.51480	-5.02718	-0.49414
F	-5.59192	-5.41766	-1.20583
F	-3.45803	-5.74943	-0.90716
H	-4.79208	-4.41145	-3.24376
H	-2.27421	-1.71844	-1.01034
H	-3.72948	-3.66962	-5.33112
H	-1.23001	-0.95976	-3.11494
Br	-1.60905	-1.70207	-5.96471
F	-4.73681	-5.31814	0.79346

Pre-II-Si

Inner Energy (Hartree)   : -5535.2098744862
Zero Point Energy (Hartree): 0.6407725300
Enthalpy (Hartree)   : -5534.5012180100
Entropy (Hartree)   : -0.1305770800
Gibbs Energy (Hartree)   : -5534.6317951000
Imaginary Frequency (cm-1) : None

N	-0.40491	-5.30516	-3.07610
C	-0.47402	-6.57984	-3.77836
C	-1.24010	-6.46501	-5.10243
C	-1.27115	-7.81091	-5.82771
C	-1.85480	-8.90621	-4.93516
C	-1.09249	-9.00781	-3.60643
C	-1.13893	-7.65358	-2.90924
N	-0.52413	-7.65877	-1.51101
C	-1.31092	-8.49293	-0.54522
C	0.93090	-8.02268	-1.47253
C	0.67791	-4.46710	-3.15306
N	0.43996	-3.26508	-2.54974
S	2.14968	-4.91074	-3.84109
C	1.17406	-2.07745	-2.66718
C	1.76869	-1.68207	-3.86969
C	2.40485	-0.45269	-3.93684
C	2.45061	0.41232	-2.84237
C	1.83198	0.01463	-1.66720
C	1.19854	-1.22098	-1.57034
C	1.82068	0.90014	-0.45361
C	3.00606	0.00917	-5.23538
F	2.23545	0.95885	-5.82596
F	4.22810	0.56380	-5.05024
F	2.44171	2.07687	-0.66242
F	0.55250	1.17551	-0.05723
F	3.15009	-0.99303	-6.12644
F	2.43186	0.30289	0.60190
H	-1.29889	-4.84637	-2.91681
H	0.55851	-6.87138	-4.00481
H	-2.26363	-6.11866	-4.89566
H	-0.75064	-5.69925	-5.71463
H	-1.85516	-7.72265	-6.75015
H	-0.24829	-8.08406	-6.12162
H	-2.91213	-8.69077	-4.72813
H	-1.81987	-9.87575	-5.44304
H	-1.54298	-9.78622	-2.98144
H	-0.05271	-9.29483	-3.80898
H	-2.18755	-7.37770	-2.73532
H	-2.36447	-8.21616	-0.60973
H	-1.17406	-9.54626	-0.79185
H	-0.93572	-8.29826	0.46102
H	1.49555	-7.34638	-2.11850
H	1.27451	-7.91858	-0.44138
H	1.04573	-9.05672	-1.79952
H	-0.28884	-3.24739	-1.83542
H	1.71365	-2.32129	-4.74071
H	2.94747	1.37311	-2.91475
H	0.70454	-1.51311	-0.64819
C	-0.13957	-4.05466	1.31002
C	0.01287	-2.78724	2.14864
C	1.20067	-4.45358	0.68741
C	-0.71452	-5.19715	2.14267
O	-0.96615	-3.81604	0.14762
O	-2.30658	-3.22443	0.66705
H	0.74197	-2.96168	2.94636
H	-0.93740	-2.50425	2.60712
H	0.36887	-1.95233	1.53692
H	1.65060	-3.62366	0.13517
H	1.08106	-5.30007	0.00183
H	1.89062	-4.75289	1.48247
H	-1.70541	-4.93808	2.52265

H	-0.05805	-5.40898	2.99280
H	-0.79974	-6.10463	1.53431
H	-0.59374	-6.68015	-1.20101
C	-3.35723	-3.44370	-0.27835
C	-4.51219	-2.76229	0.38858
C	-3.00415	-2.80712	-1.61895
C	-3.34132	-3.34585	-2.86262
C	-2.32284	-1.58730	-1.57764
C	-2.95215	-2.71170	-4.04155
C	-1.95057	-0.93192	-2.74373
C	-2.24785	-1.51810	-3.96662
C	-4.98466	-1.53838	-0.08998
C	-5.06095	-3.27370	1.56954
N	-5.39436	-0.52368	-0.49694
N	-5.52701	-3.70634	2.54818
C	-3.63593	-4.96857	-0.39527
F	-4.81876	-5.21989	-0.99042
F	-2.69279	-5.62747	-1.15370
H	-3.91695	-4.26154	-2.94453
H	-2.07812	-1.14650	-0.61642
H	-3.20378	-3.14577	-5.00343
H	-1.42011	0.01302	-2.69509
Br	-1.65584	-0.67319	-5.57626
F	-3.63870	-5.58051	0.79525

TS-II-Si

Inner Energy (Hartree) : -5535.2082071026
Zero Point Energy (Hartree): 0.6395488600
Enthalpy (Hartree) : -5534.5007869400
Entropy (Hartree) : -0.1286478100
Gibbs Energy (Hartree) : -5534.6294347400
Imaginary Frequency (cm-1) : -17.60

N	-0.36944	-5.15942	-2.91996
C	-0.49043	-6.43135	-3.60888
C	-1.49829	-6.40182	-4.76327
C	-1.51353	-7.75155	-5.48386
C	-1.79126	-8.90099	-4.51319
C	-0.79817	-8.90291	-3.34076
C	-0.88372	-7.55371	-2.63871
N	-0.06180	-7.45554	-1.35660
C	-0.61254	-8.32144	-0.26586
C	1.40609	-7.68701	-1.55382
C	0.68196	-4.30478	-3.08351
N	0.62635	-3.22826	-2.24905
S	1.95634	-4.59675	-4.15519
C	1.35832	-2.04027	-2.41018
C	1.45819	-1.42489	-3.66243
C	2.14459	-0.22706	-3.78085
C	2.71888	0.39615	-2.67192
C	2.59369	-0.21672	-1.43454
C	1.92847	-1.43410	-1.29639
C	3.22831	0.38572	-0.21311
C	2.21675	0.45677	-5.11846
F	1.25474	1.40754	-5.24422
F	3.40442	1.08045	-5.29930
F	3.59717	1.66869	-0.40097
F	2.39134	0.35572	0.85226
F	2.05406	-0.40596	-6.14324
F	4.34315	-0.29980	0.15439
H	-1.18963	-4.80027	-2.44000
H	0.49876	-6.64469	-4.03300
H	-2.49653	-6.16407	-4.36903
H	-1.21277	-5.59369	-5.44588
H	-2.26707	-7.74070	-6.27883
H	-0.54023	-7.90951	-5.96889
H	-2.81223	-8.81097	-4.11694
H	-1.73417	-9.86345	-5.03267
H	-1.03983	-9.72232	-2.65525
H	0.21640	-9.06894	-3.72467
H	-1.91352	-7.39957	-2.29952
H	-1.67253	-8.09211	-0.13760
H	-0.47469	-9.36934	-0.53437
H	-0.07115	-8.10225	0.65651
H	1.78759	-6.98787	-2.30175
H	1.91118	-7.51787	-0.60102
H	1.56019	-8.71802	-1.87463
H	0.01938	-3.31760	-1.41881
H	0.99031	-1.87979	-4.52733
H	3.24758	1.33651	-2.77715
H	1.86802	-1.91427	-0.32541
C	-0.42852	-4.17524	1.24647
C	-0.29077	-2.74173	1.77564
C	0.97272	-4.77903	1.03520
C	-1.20297	-5.03889	2.24739
O	-1.04645	-4.19997	-0.03113
O	-2.66715	-3.29894	0.30415
H	0.31827	-2.72383	2.68565
H	-1.27172	-2.32188	2.00770
H	0.18377	-2.09872	1.02762
H	1.51954	-4.26749	0.23678
H	0.90040	-5.84358	0.78643
H	1.55333	-4.69998	1.96055
H	-2.20094	-4.62698	2.41383
H	-0.67647	-5.08464	3.20730
H	-1.31243	-6.05872	1.86071
H	-0.17705	-6.47561	-1.05028
C	-3.59560	-3.52647	-0.69062
C	-4.61643	-2.69934	0.04633
C	-3.20291	-2.95393	-2.04810
C	-3.73007	-3.40399	-3.26143
C	-2.31131	-1.88058	-2.05462

C	-3.33751	-2.82329	-4.46318
C	-1.93178	-1.27240	-3.24481
C	-2.43449	-1.76808	-4.43896
C	-4.73940	-1.33339	-0.23851
C	-5.36085	-3.22073	1.11381
N	-4.86384	-0.20268	-0.48448
N	-6.00718	-3.65290	1.97959
C	-4.01692	-5.01751	-0.76476
F	-5.25809	-5.16557	-1.27612
F	-3.17886	-5.73517	-1.56981
H	-4.45277	-4.21196	-3.29555
H	-1.91031	-1.51713	-1.11380
H	-3.73739	-3.18751	-5.40336
H	-1.24530	-0.43276	-3.23733
Br	-1.86796	-0.97933	-6.08728
F	-3.99420	-5.61317	0.43345

Post-II-Si

Inner Energy (Hartree) : -5535.2654973240
Zero Point Energy (Hartree): 0.6379918300
Enthalpy (Hartree) : -5534.5596568900
Entropy (Hartree) : -0.1288905100
Gibbs Energy (Hartree) : -5534.6885474000
Imaginary Frequency (cm-1) : -2.81

N	-0.30276	-4.98948	-3.07906
C	-0.45473	-6.32563	-3.63486
C	-1.53519	-6.36510	-4.72186
C	-1.62841	-7.75755	-5.34206
C	-1.88881	-8.80804	-4.26401
C	-0.82965	-8.74578	-3.15894
C	-0.77217	-7.34389	-2.52504
N	0.13414	-7.20359	-1.35567
C	-0.22319	-8.13910	-0.28224
C	1.56164	-7.32984	-1.68168
C	0.71558	-4.14935	-3.36279
N	0.86422	-3.16237	-2.41306
S	1.73070	-4.33243	-4.70058
C	1.62387	-1.99729	-2.52222
C	1.65653	-1.24515	-3.70369
C	2.37523	-0.06104	-3.73822
C	3.05657	0.41803	-2.61805
C	3.00247	-0.32993	-1.45138
C	2.30422	-1.53428	-1.39739
C	3.72935	0.11676	-0.21551
C	2.36140	0.77689	-4.98627
F	1.45728	1.78906	-4.89069
F	3.56323	1.35477	-5.21855
F	4.22664	1.36481	-0.32728
F	2.91684	0.10276	0.87270
F	2.03633	0.06391	-6.08430
F	4.77173	-0.70357	0.07690
H	-0.90644	-4.74714	-2.30085
H	0.50286	-6.58107	-4.10605
H	-2.50047	-6.08703	-4.27449
H	-1.29317	-5.60826	-5.47750
H	-2.41969	-7.77969	-6.10063
H	-0.68523	-7.98663	-5.85826
H	-2.88031	-8.63417	-3.82047
H	-1.90947	-9.81316	-4.70181
H	-1.05835	-9.49478	-2.39323
H	0.15262	-8.99979	-3.58031
H	-1.77955	-7.11467	-2.14040
H	-1.29400	-8.05867	-0.06164
H	0.00678	-9.19006	-0.52259
H	0.33732	-7.87924	0.62288
H	1.86247	-6.57068	-2.40955
H	2.14408	-7.16669	-0.76836
H	1.82807	-8.32371	-2.07866
H	0.52545	-3.41316	-1.47858
H	1.11446	-1.58794	-4.57576
H	3.60844	1.34980	-2.66076
H	2.30066	-2.12142	-0.48361
C	-0.08160	-4.38881	1.25126
C	-0.29502	-2.90009	1.49863
C	1.35685	-4.79476	1.56872
C	-1.07611	-5.20878	2.07246
O	-0.33324	-4.59205	-0.15964
O	-3.87209	-2.83358	0.47244
H	-0.11797	-2.65866	2.55107
H	-1.32197	-2.61587	1.24826
H	0.39023	-2.29983	0.89077
H	2.06011	-4.22793	0.94881
H	1.50785	-5.86273	1.37337
H	1.59129	-4.60675	2.62170
H	-2.10257	-4.92109	1.82284
H	-0.92097	-5.04096	3.14360
H	-0.95623	-6.27920	1.87563
H	-0.11851	-5.52339	-0.43140
C	-4.25159	-3.52644	-0.70383
C	-5.19521	-2.57300	-0.00720
C	-3.59537	-3.12066	-1.97954
C	-4.00584	-3.66521	-3.19998
C	-2.59449	-2.14843	-1.95355
C	-3.41489	-3.24618	-4.38374
C	-2.00468	-1.71864	-3.13565
C	-2.41941	-2.27688	-4.33779
C	-5.40811	-1.27529	-0.61158
C	-6.29519	-3.02215	0.81588
N	-5.59198	-0.24412	-1.09609
N	-7.20009	-3.35329	1.45147
C	-4.51480	-5.02718	-0.49414

F	-5.59192	-5.41766	-1.20583
F	-3.45803	-5.74943	-0.90716
H	-4.79208	-4.41145	-3.24376
H	-2.27421	-1.71844	-1.01034
H	-3.72948	-3.66962	-5.33112
H	-1.23001	-0.95976	-3.11494
Br	-1.60905	-1.70207	-5.96471
F	-4.73681	-5.31814	0.79346