

Supporting Information

**Metal Free Regio – and Stereoselective
Semireduction of CF₃-Substituted *N*-
Allenamides**

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General remarks

All reactions were carried out under an inert atmosphere of argon in dried glassware, unless otherwise noted. Conventional solvents (THF, Et₂O, CH₂Cl₂) are stored on molecular sieves and sampled under argon. Toluene, CH₃CN, acetic acid, were used as received.

NMR Spectra (¹H, ¹³C, ¹⁹F) were performed at 298 K. ¹H (500 MHz or 300 MHz) and ¹³C (126 MHz) NMR chemical shifts are reported relative to residual protiated solvent. ¹⁹F (281 MHz or 471 MHz) NMR chemical shifts are reported without any calibration. Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, hept = heptet, m = multiplet, br = broad), coupling constant *J* (Hz) and integration.

HRMS data were recorded on a microTOF spectrometer equipped with an orthogonal electrospray (ESI) interface.

Thin layer chromatography was performed using Merck TLC silica gel 60 F₂₅₄ aluminum sheets using petroleum ether/EtOAc as eluant and visualized using permanganate stain, ninhydrin stain, vanillin stain and/or UV light. Merck Geduran[®] 40-63 μm silica gel was used for column chromatography.

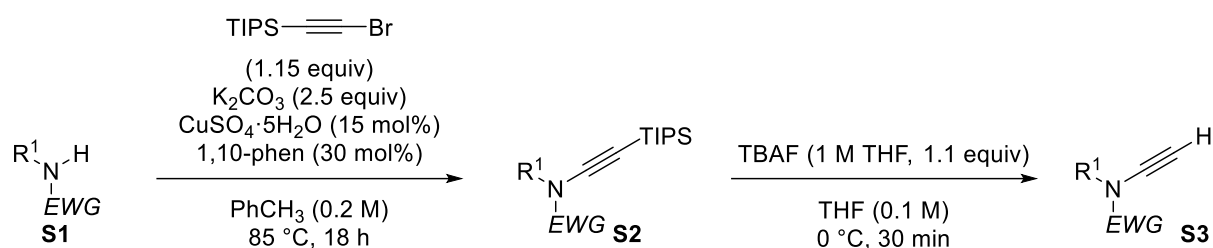
Biotage[®] Isolera[™] One system was used for *flash* chromatography. The wavelength of the UV-detector was calibrated at 254 and 365 nm.

Infrared spectra were reported in frequency of absorption using Alpha Bruker Optics spectrometer.

Melting points were recorded with a SMP3 Stuart Scientific microscope in open capillary tubes and are uncorrected

Experimental procedure

General procedure for preparation of Ynamides¹



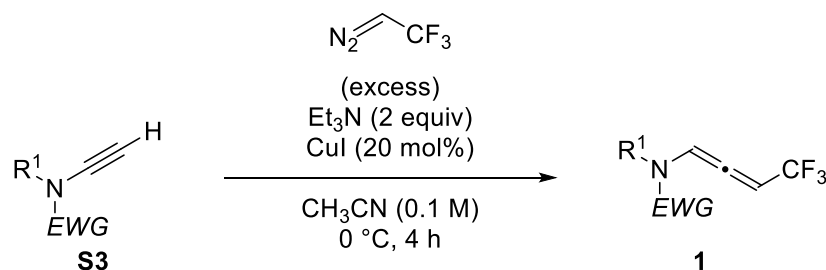
The (2-bromoethynyl)tris(propan-2-yl)silane was synthesized according to the literature.²

In a Schlenk tube was introduced CuSO₄·5H₂O (0.3 mmol, 15 mol%), 1,10-phenanthroline (0.6 mmol, 30 mol%), K₂CO₃ (5 mmol, 2.5 equiv), the sulfonamide **S1** (2 mmol, 1 equiv), anhydrous toluene (0.2 M) and the bromo-acetylenic (2.3 mmol, 1.15 equiv). The reaction mixture was heated to 85 °C with an oil bath for 18 h and then cooled down to room temperature, filtered on a pad of Celite® and washed profusely with EtOAc. The filtrate was then concentrated under vacuum. The crude material was purified by column chromatography on silica gel using a mixture petroleum ether/EtOAc as eluent to afford the desired product **S2**.

TIPS protected ynamide **S2** (2.8 mmol, 1 equiv) was dissolved in dry THF (30 mL, 0.1 M) and cooled at 0 °C. A TBAF solution (3.1 mmol, 1.1 equiv, 1 M in THF) was added dropwise and the resulting mixture was stirred at 0 °C during 30 min and then hydrolyzed with water. The aqueous layer was extracted with Et₂O (3x). The combined organic layers were washed with a saturated solution of NaCl, dried (Na₂SO₄), filtered and concentrated under vacuum. The crude material was purified by column chromatography on silica gel using a mixture petroleum ether/EtOAc, as eluent or just by washing with *n*-pentane and diethyl ether to afford the desired product **S3**.

General procedure for preparation of *N*-allenamides

Trifluorinated *N*-allenamides³ **1**



¹ (a) Y. Zhang, R. P. Hsung, M. R. Tracey, K. C. M. Kurtz and E. L. Vera, *Org. Lett.*, 2004, **6**, 1151–1154. (b) X. Zhang, R. P. Hsung, H. Li, Y. Zhang, W. L. Johnson and R. Figueroa, *Org. Lett.*, 2008, **10**, 3477–3479.

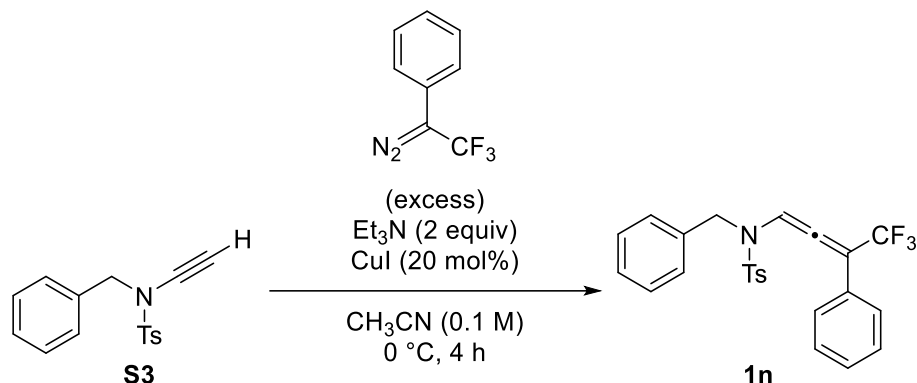
² H. Hofmeister, K. Annen, H. Laurent and R. Wiechert, *Angew. Chem. Int. Ed.* 1984, **23**, 727–729.

³ Y. Zheng, B. Moegle, S. Ghosh, A. Perfetto, D. Luise, I. Ciofini and L. Miesch, *Chem. Eur. J.* 2022, **28**, e202103598.

1,1,1-trifluoro-diazoethane was synthesized according to the previous literature and stored in diethyl ether solution in the presence of Na₂SO₄ at -18 °C for a few weeks.⁴

Ynamide **S3** (0.2 mmol, 1 equiv) was dissolved in dry CH₃CN (0.1 M) in the presence of CuI (0.04 mmol, 20 mol%), and triethylamine (0.4 mmol, 2 equiv). A diethyl ether 1,1,1-trifluoro-diazoethane solution was added dropwise (in excess) and the reaction was stirred for 4 h at 0 °C. The mixture was concentrated under vacuum and the crude material was purified by column chromatography on silica gel using a mixture petroleum ether/EtOAc, as eluent to afford the desired products **1**.

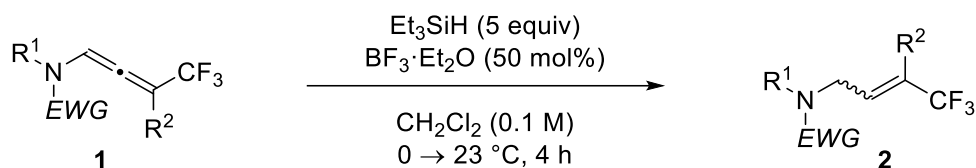
Disubstituted *N*-allenamide **1n**



(1-diazo-2,2,2-trifluoroethyl)benzene was synthesized according to the previous literature and directly used.⁵

Benzyl-ynamide **S3** (127 mg, 0.45 mmol, 1 equiv) was dissolved in dry CH₃CN (0.1 M) in the presence of CuI (0.09 mmol, 20 mol%), and triethylamine (0.9 mmol, 2 equiv). A diethyl ether (1-diazo-2,2,2-trifluoroethyl)benzene solution was added dropwise (in excess) and the reaction was stirred for 4 h at 0 °C. The mixture was concentrated under vacuum and the crude material was used without any further purification.

General procedure for the 1,2-semireduction of *N*-allenamides **1**

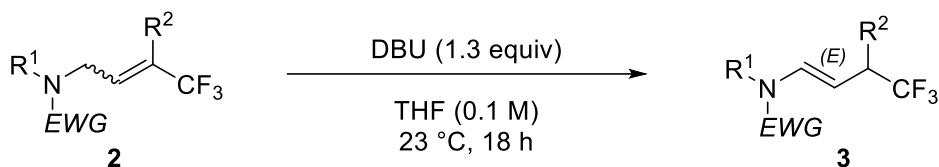


N-allenamide **1** (0.25 mmol, 1 equiv) was dissolved in dry CH₂Cl₂ (0.1 M) and cooled to 0 °C. Et₃SiH (1.25 mmol, 5 equiv) and BF₃·Et₂O (0.13 mmol, 50 mol%) were added dropwise. The reaction mixture was allowed to warm up at 23 °C and stirred for 4 h and then hydrolyzed with water. The organic layer was extracted with CH₂Cl₂ (3x) and Et₂O (1x). The organic layers were washed separately with a saturated solution of NaCl, combined, dried (Na₂SO₄), filtered and concentrated under vacuum. The crude material was purified by column chromatography on silica gel using a mixture petroleum ether/EtOAc, as eluent to afford the desired products **2**.

⁴ H. Gilman and R. G. Jones, *J. Am. Chem. Soc.*, 1943, **65**, 1458–1460.

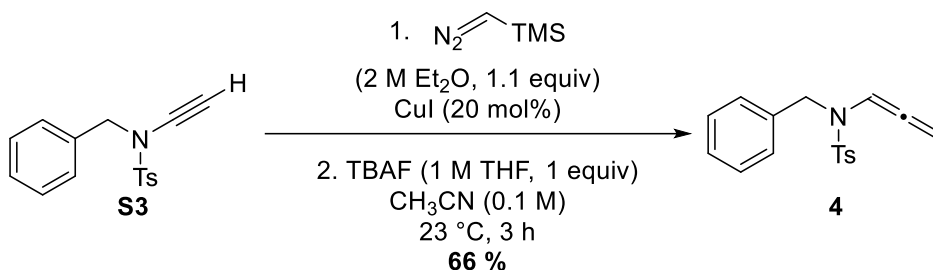
⁵ X. Huang, M. Garcia-Borràs, K. Miao, S. B. J. Kan, A. Zutshi, K. N. Houk and F. H. Arnold, *ACS Cent. Sci.*, 2019, **5**, 270–276.

General procedure for the isomerization of allylamide **2** to tertiary enamide **3**



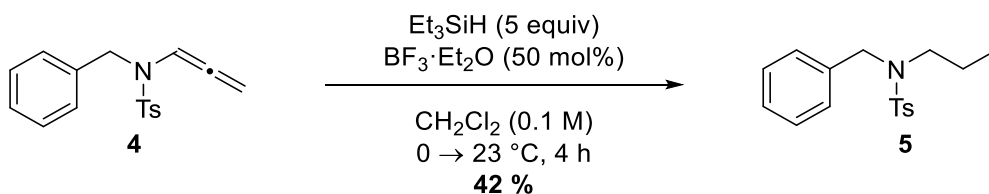
Allylamide **2** (0.1 mmol, 1 equiv) was dissolved in dry THF (0.1 M) and then DBU (0.13 mmol, 1.3 equiv) was added dropwise. The reaction mixture stirred at 23 °C for 18 h and then hydrolyzed with water. The organic layer was extracted with EtOAc (3x). The combined organic layers were washed with a saturated solution of NaCl, dried (Na₂SO₄), filtered and concentrated under vacuum. The crude material was purified by column chromatography on silica gel using a mixture petroleum ether/EtOAc, as eluent to afford the desired products **3**.

Procedure for the preparation of **4**³



Benzyl-ynamide **S3** (70 mg, 0.25 mmol, 1 equiv) was dissolved in CH₃CN (0.1 M). CuI (9 mg, 0.05 mmol, 20 mol%) and trimethylsilyldiazomethane (0.13 mL, 0.27 mmol, 1.1 equiv, 2 M Et₂O) was added dropwise and the reaction mixture was stirred at 23 °C for 3 hours. A TBAF solution (0.25 mL, 0.25 mmol, 1 equiv, 1 M in THF) was added dropwise at 0 °C and the resulting mixture was stirred during 30 min and then hydrolyzed with water. The organic layer was extracted with CH₂Cl₂ (3x) and Et₂O (1x). The organic layers were washed separately with a saturated solution of NaCl, combined, dried (Na₂SO₄), filtered and concentrated under vacuum. The crude material was purified by column chromatography on silica gel using a mixture petroleum ether/EtOAc (from 100:0 to 95:5), as eluent to afford the terminal N-allenamide **4** (49 mg, 0.17 mmol, 66 %) as a colorless oil.

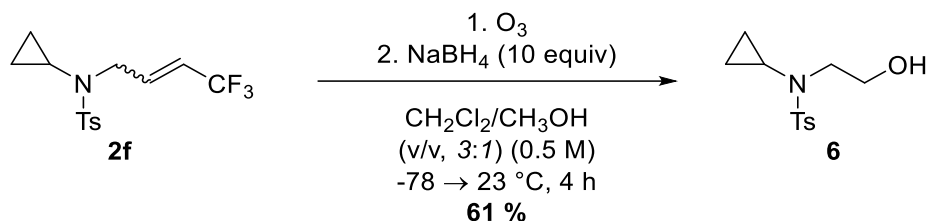
Procedure for the preparation of **5**



4 (75 mg, 0.25 mmol, 1 equiv) was dissolved in dry CH₂Cl₂ (0.1 M) and cooled to 0 °C. Et₃SiH (0.20 mL, 1.25 mmol, 5 equiv) and BF₃·Et₂O (0.02 mL, 0.13 mmol, 50 mol%) were added dropwise. The reaction mixture was allowed to warm up at 23 °C and stirred for 4 h and then hydrolyzed with water. The organic layer was extracted with CH₂Cl₂ (3x) and Et₂O (1x). The organic layers were washed separately with a saturated solution of NaCl, combined, dried

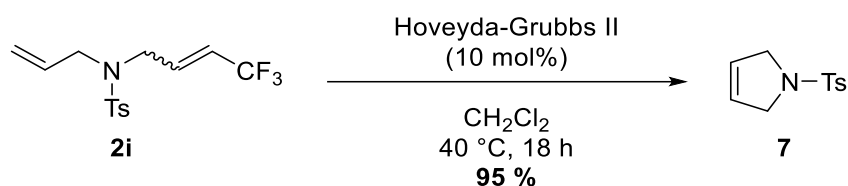
(Na₂SO₄), filtered and concentrated under vacuum. The crude material was purified by column chromatography on silica gel using a mixture petroleum ether/EtOAc (from 100:0 to 60:40), as eluent to afford the desired products **5** (31.8 mg, 0.11 mmol, 42 %) as a colorless oil.

Procedure for the preparation of **6**⁶



2f (51 mg, 0.16 mmol, 1 equiv) was dissolved in a mixture of CH₂Cl₂ (2.4 mL) and CH₃OH (0.8 mL) and the solution was cooled to -78 °C (dry-ice/acetone). To this solution was purged O₃ gas for 15 minutes followed by argon gas for additional 15 minutes. The resulting intermediate was quenched with NaBH₄ (60 mg, 1.6 mmol, 10 equiv). The reaction mixture was gently warmed to 23 °C for 3.5 hours and then cooled down to 0 °C and hydrolyzed with a saturated aqueous solution of NH₄Cl. The organic layer was extracted with CH₂Cl₂ (3x) and Et₂O (1x). The organic layers were washed separately with a saturated solution of NaCl, combined, dried (Na₂SO₄), filtered and concentrated under vacuum. The crude material was purified by *flash* chromatography on silica gel using a mixture petroleum ether/EtOAc (from 88:12 to 0:100), as eluent to afford **6** (24.9 mg, 0.01 mmol, 61 %) as a white solid .

Procedure for the preparation of **7**

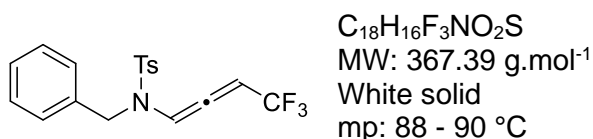


2i (83 mg, 0.26 mmol, 1 equiv) was dissolved in degassed CH₂Cl₂. Hoveyda-Grubbs II (16 mg, 0.02 mmol, 10 mol%) was then added and the reaction mixture was heated to 40 °C for 18 hours. The crude material was purified by *flash* chromatography on silica gel using a mixture petroleum ether/EtOAc (from 95:05 to 60:40), as eluent to afford **7** (55 mg, 0.25 mmol, 95 %) as a white solid .

Characterization data

N-allenamides **1a-v**

Compound 1a *N*-benzyl-4-methyl-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)benzenesulfonamide³



⁶ M. S. Manna, S. Y. Yoo, M. Sharique, H. Choi, B. Pudasaini, M. Baik and U. K. Tambar, *Angew. Chem. Int. Ed.*, 2023, **62**, e202304848.

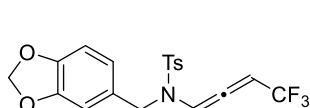
87 % (1.7 g)

The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 100:0 to 80:20) as eluent.

¹H NMR (300 MHz, CDCl₃): δ 7.79 – 7.67 (m, 2H), 7.45 – 7.38 (m, 1H), 7.38 – 7.32 (m, 2H), 7.30 – 7.18 (m, 5H), 5.68 (p, *J* = 5.6 Hz, 1H), 4.46 (d, *J* = 15.3 Hz, 1H), 4.12 (d, *J* = 15.3 Hz, 1H), 2.46 (s, 3H) ppm.

This analytical data match with those described in the literature.

Compound 1b *N*-(benzo[d][1,3]dioxol-5-ylmethyl)-4-methyl-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)benzenesulfonamide⁷



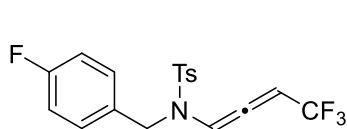
C₁₉H₁₆F₃NO₄S
MW: 411.39 g.mol⁻¹
White solid
mp: 110 - 112 °C
75 % (2.3 g)

The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 100:0 to 80:20) as eluent.

¹H NMR (400 MHz, CDCl₃): δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.41 – 7.37 (m, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 6.77 (d, *J* = 1.7 Hz, 1H), 6.73 – 6.62 (m, 2H), 5.93 (s, 2H), 5.75 (p, *J* = 5.6 Hz, 1H), 4.34 (d, *J* = 15.0 Hz, 1H), 4.06 (d, *J* = 15.0 Hz, 1H), 2.45 (s, 3H) ppm.

This analytical data match with those described in the literature.

Compound 1c *N*-(4-fluorobenzyl)-4-methyl-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)benzenesulfonamide



C₁₈H₁₅F₄NO₂S
MW: 385.38 g.mol⁻¹
White solid
mp: 99 - 101 °C

The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 100:0 to 80:20) as eluent.

¹H NMR (500 MHz, CDCl₃): δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.43 – 7.38 (m, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.22 (dd, *J* = 8.6, 5.4 Hz, 2H), 6.97 (t, *J* = 8.7 Hz, 2H), 5.71 (p, *J* = 5.6 Hz, 1H), 4.38 (d, *J* = 15.3 Hz, 1H), 4.14 (d, *J* = 15.2 Hz, 1H), 2.46 (s, 3H).

¹⁹F NMR (282 MHz, CDCl₃): δ -62.77, -114.41.

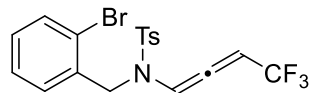
¹³C NMR (126 MHz, CDCl₃): δ 198.9 (q, *J* = 5.9 Hz), 162.5 (d, *J* = 246.8 Hz), 144.8, 135.1, 130.5 (d, *J* = 3.2 Hz), 130.2 (x2), 129.5 (d, *J* = 8.3 Hz), 127.3 (x2), 121.2 (q, *J* = 272.3 Hz), 115.6 (d, *J* = 21.7 Hz), 106.8, 96.5 (q, *J* = 39.4 Hz), 50.4, 21.8.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₈H₁₅F₄NaNO₂S 408.0652; found 408.0648.

IR (neat): ν = 3045, 1431, 1342, 1124, 944, 814, 543 cm⁻¹.

⁷ M. Hourtoule and L. Miesch, *Org. Lett.*, 2022, **24**, 3896–3900.

Compound 1d *N*-(2-bromobenzyl)-4-methyl-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)benzenesulfonamide



$C_{18}H_{15}BrF_3NO_2S$
MW: 442.28 g.mol⁻¹
White solid
mp: 94 - 96 °C

The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 100:0 to 80:20) as eluent.

¹H NMR (500 MHz, CDCl₃) δ 7.75 (dt, *J* = 8.5 Hz, 2.0 Hz, 2H), 7.49 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.46–7.44 (m, 1H), 7.42–7.41 (m, 1H), 7.39–7.36 (m, 2H), 7.30–7.27 (m, 1H), 7.14–7.10 (m, 1H), 5.69 (p, *J* = 5.5 Hz, 1H), 4.41 (s, 2H), 2.47 (s, 3H).

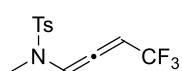
¹⁹F NMR (282 MHz, CDCl₃): δ -62.72.

¹³C NMR (126 MHz, CDCl₃): δ 198.4 (q, *J* = 5.9 Hz), 144.9, 135.0, 133.5, 132.8, 130.3 (x2), 129.2, 128.1, 127.8, 127.3 (x2), 122.4, 121.0 (q, *J* = 272.5 Hz), 106.7, 96.6 (q, *J* = 39.6 Hz), 50.8, 21.8.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₈H₁₅BrF₃NaNO₂S 467.9852; found 467.9846.

IR (neat): ν = 3016, 1447, 1352, 1110, 922, 751, 596 cm⁻¹.

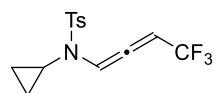
Compound 1e *N*,4-dimethyl-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)benzenesulfonamide



$C_{12}H_{12}F_3NO_2S$
MW: 291.29 g.mol⁻¹

1e was used without any further purification.

Compound 1f *N*-cyclopropyl-4-methyl-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)benzenesulfonamide⁷



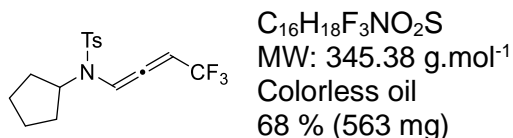
$C_{14}H_{14}F_3NO_2S$
MW: 317.33 g.mol⁻¹
White solid
mp: 53 – 56°C
74 % (760 mg)

The product was obtained by column chromatography on silica gel using Petroleum ether / EtOAc (from 95:05 to 85:15) as eluent.

¹H NMR (300 MHz, CDCl₃) δ 7.79 – 7.71 (m, 2H), 7.39 – 7.33 (m, 2H), 7.33 – 7.30 (m, 1H), 5.88 (p, *J* = 5.6 Hz, 1H), 2.45 (s, 3H), 1.73 (tt, *J* = 6.9, 3.6 Hz, 1H), 1.12 – 0.88 (m, 2H), 0.83 – 0.64 (m, 2H).

This analytical data match with those described in the literature.

Compound 1g *N*-cyclopentyl-4-methyl-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)benzenesulfonamide⁷

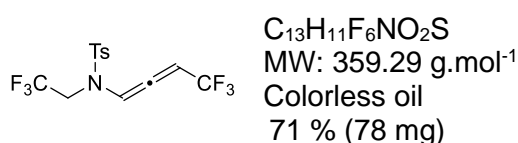


The product was obtained by column chromatography on silica gel using Petroleum ether / EtOAc (95:05 to 85:15) as eluent.

¹H NMR (500 MHz, CDCl₃) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.44 – 7.28 (m, 3H), 5.85 (p, *J* = 5.7 Hz, 1H), 4.41 (p, *J* = 8.7 Hz, 1H), 2.44 (s, 3H), 1.75 – 1.54 (m, 5H), 1.48 – 1.32 (m, 3H).

This analytical data match with those described in the literature.

Compound 1h 4-methyl-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)-*N*-(2,2,2-trifluoroethyl)benzenesulfonamide⁸

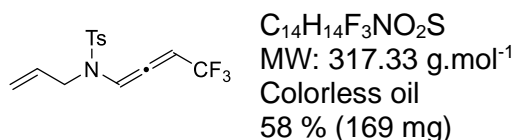


The product was obtained by column chromatography on silica gel using Petroleum ether / EtOAc (from 100:0 to 80:20) as eluent.

¹H NMR (500 MHz, CDCl₃): δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.53 – 7.33 (m, 3H), 6.07 (p, *J* = 5.5 Hz, 1H), 3.90 (dq, *J* = 15.6, 8.1, 0.8 Hz, 1H), 3.72 (dq, *J* = 16.1, 8.1 Hz, 1H), 2.49 (s, 3H).

This analytical data match with those described in the literature.

Compound 1i *N*-allyl-4-methyl-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)benzenesulfonamide⁸

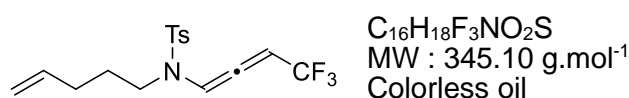


The product was obtained by column chromatography on silica gel using Petroleum ether / EtOAc (from 100:0 to 80:20) as eluent.

¹H NMR (500 MHz, CDCl₃): δ 7.73 (d, *J* = 8.6 Hz, 2H), 7.48 – 7.40 (m, 1H), 7.36 (dd, *J* = 8.6, 0.8 Hz, 2H), 5.93 (p, *J* = 5.6 Hz, 1H), 5.69 – 5.54 (m, 1H), 5.18 (dt, *J* = 1.4, 0.8 Hz, 1H), 5.16 (dq, *J* = 7.8, 1.4 Hz, 1H), 3.87 (ddtd, *J* = 16.0, 5.5, 1.6, 0.8 Hz, 1H), 3.82 – 3.73 (ddtd, *J* = 16.0, 5.5, 1.6, 0.8 Hz, 1H), 2.47 (s, 3H).

This analytical data match with those described in the literature.

Compound 1j 4-methyl-*N*-(pent-4-en-1-yl)-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)benzenesulfonamide⁷



⁸ M. Hourtoule and L. Miesch, *Org. Lett.*, 2023, **25**, 1727–1731.

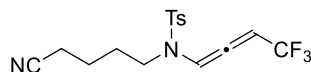
Yield: 90 % (294 mg)

The product was obtained by column chromatography on silica gel using Petroleum ether / EtOAc (from 5:1 to 4:1) as eluent.

¹H NMR (500 MHz, C₆D₆): δ = 7.55 (d, *J* = 8.3 Hz, 2H), 7.33– 7.30 (m, 1H), 6.73 (d, *J* = 8.0 Hz, 2H), 5.65– 5.57 (m, 1H), 5.36 (p, *J* = 5.6 Hz, 1H), 4.97 – 4.89 (m, 2H), 3.02 – 2.87 (m, 2H), 1.96 – 1.76 (m, 5H), 1.58 – 1.39 (m, 2H) ppm.

This analytical data match with those described in the literature.

Compound 1k *N*-(4-cyanobutyl)-4-methyl-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)benzenesulfonamide⁷



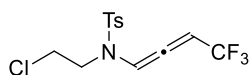
C₁₆H₁₇F₃N₂O₂S
MW: 358.38 g.mol⁻¹
Colorless oil
64 % (257 mg)

The product was obtained by column chromatography on silica gel using Petroleum ether / EtOAc (from 95:05 to 70:30) as eluent.

¹H NMR (500 MHz, CDCl₃): δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.47 – 7.38 (m, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 5.99 (p, *J* = 5.5 Hz, 1H), 3.14 (t, *J* = 6.6 Hz, 2H), 2.45 (s, 3H), 2.39 (tt, *J* = 6.6, 1.4 Hz, 2H), 1.74 – 1.65 (m, 4H) ppm.

This analytical data match with those described in the literature.

Compound 1l *N*-(2-chloroethyl)-4-methyl-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)benzenesulfonamide⁷



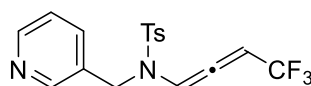
C₁₃H₁₃ClF₃NO₂S
MW: 339.76 g.mol⁻¹
White solid
mp: 56 – 57°C
74 % (281 mg)

The product was obtained by column chromatography on silica gel using Petroleum ether / EtOAc (from 95:05 to 85:15) as eluent.

¹H NMR (500 MHz, CDCl₃): δ 7.71 (d, *J* = 8.1 Hz, 1H), 7.42 (dq, *J* = 6.0, 3.0 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 6.03 (p, *J* = 5.5 Hz, 1H), 3.58 – 3.51 (m, 2H), 3.45 – 3.38 (m, 2H), 2.45 (s, 3H)

This analytical data match with those described in the literature.

Compound 1m *N,N'*-(butane-1,4-diyl)bis(4-methyl-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)benzenesulfonamide)



C₁₇H₁₅F₃N₂O₂S
MW: 368.37 g.mol⁻¹
Orange oil
52 % (244 mg) (2 steps)

The product was obtained by column chromatography on silica gel using Petroleum ether / EtOAc (from 90:10 to 0:100) as eluent.

¹H NMR (500 MHz, C₆D₆): δ 8.43 (s, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.19 – 7.17 (m, 1H), 6.72 (d, *J* = 8.1 Hz, 2H), 6.70 – 6.63 (m, 1H), 5.12 (s, 1H), 3.98 (d, *J* = 15.5 Hz, 1H), 3.74 (d, *J* = 15.4 Hz, 1H), 1.84 (s, 3H).

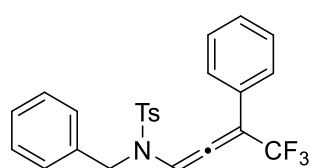
¹⁹F NMR (282 MHz, C₆D₆): δ -62.66.

¹³C NMR (126 MHz, C₆D₆): δ 199.0 (q, *J* = 6.0 Hz), 149.8, 149.8, 144.4, 135.7, 134.9, 130.1 (x2), 128.4, 128.2, 127.4 (x2), 121.7 (q, *J* = 271.7 Hz), 106.9, 96.4 (q, *J* = 41.0 Hz), 48.4, 21.1.

HRMS (ESI-TOF) *m/z*: [M+H]⁺ calcd for C₁₇H₁₆F₃N₂O₂S 369.0885; found 369.0879.

IR (neat) : ν = 3043, 2962, 1597, 1451, 1429, 1359, 1267, 1168, 1131, 930, 908, 814, 666, 600, 547 cm⁻¹.

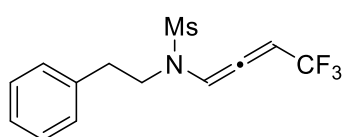
Compound 1n *N*-benzyl-4-methyl-*N*-(4,4,4-trifluoro-3-phenylbuta-1,2-dien-1-yl)benzenesulfonamide



C₂₄H₂₀F₃NO₂S
MW: 443.48 g.mol⁻¹

1n was used without any further purification.

Compound 1o *N*-phenethyl-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)methanesulfonamide⁹



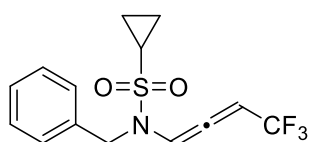
C₁₃H₁₄F₃NO₂S
MW: 305.32 g.mol⁻¹
White solid
mp: 115 – 118 °C
59 % (477 mg)

The product was obtained by column chromatography on silica gel using Petroleum ether / EtOAc (from 100:0 to 80:20) as eluent.

¹H NMR (300 MHz, C₆D₆): δ = 7.14 – 7.02 (m, 2H), 7.06 – 6.96 (m, 3H), 6.94 (dt, *J* = 6.3, 3.2 Hz, 1H), 5.46 (p, *J* = 5.6 Hz, 1H), 3.26 – 3.03 (m, 2H), 2.64 (dd, *J* = 8.6, 7.1 Hz, 2H), 1.86 (s, 3H).

This analytical data match with those described in the literature.

Compound 1p *N*-benzyl-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)cyclopropanesulfonamide



C₁₄H₁₄F₃NO₂S
MW: 317.33 g.mol⁻¹
White solid
mp: 73 – 75 °C

The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 100:0 to 80:20) as eluent.

⁹ C. Gommenginger, Y. Zheng, D. Maccarone, I. Ciofini and L. Miesch, *Org. Chem. Front.*, 2023, **10**, 4055–4060.

¹H NMR (500 MHz, CDCl₃) δ 7.30–7.25 (m, 4H), 7.24–7.20 (m, 2H), 5.73 (p, *J* = 5.5 Hz, 1H), 4.64 (d, *J* = 15.5 Hz, 1H), 4.38 (d, *J* = 15.5 Hz, 1H), 2.35–2.30 (m, 1H), 1.22–1.18 (m, 2H), 1.00–0.96 (m, 2H).

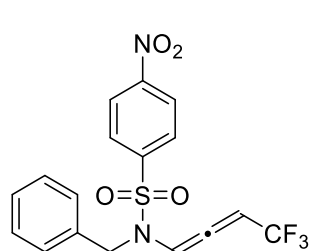
¹⁹F NMR (282 MHz, CDCl₃): δ 62.61.

¹³C NMR (126 MHz, CDCl₃): δ 198.7 (q, *J* = 5.9 Hz), 135.2, 128.7 (x2), 128.1, 127.7 (x2), 121.3 (q, *J* = 272.2 Hz), 107.2, 96.7 (q, *J* = 39.4 Hz), 51.2, 30.2, 5.7, 5.6.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₄H₁₄F₃NaNO₂S 340.0590; found 340.0574.

IR (neat) : ν = 3033, 1453, 1347, 1118, 937, 885, 607 cm⁻¹.

Compound 1q *N*-benzyl-4-nitro-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)benzenesulfonamide⁷



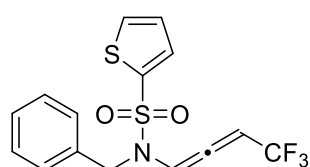
C₁₇H₁₃F₃N₂O₄S
MW: 398.36 g.mol⁻¹
White solidmp: 92 - 95°C
81 % (163 mg)

The product was obtained by column chromatography on silica gel using Petroleum ether / EtOAc (from 100:0 to 70:30) as eluent.

¹H NMR (500 MHz, CDCl₃): δ 8.37 (d, *J* = 8.9 Hz, 1H), 7.97 (d, *J* = 8.9 Hz, 1H), 7.39 (dq, *J* = 6.1, 3.1 Hz, 1H), 7.28 (dt, *J* = 4.6, 2.2 Hz, 3H), 7.24 – 7.18 (m, 2H), 5.79 (p, *J* = 5.5 Hz, 1H), 4.54 (dd, *J* = 15.3, 1.0 Hz, 1H), 4.24 (d, *J* = 15.2 Hz, 1H) ppm.

This analytical data match with those described in the literature.

Compound 1r *N*-benzyl-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)thiophene-2-sulfonamide



C₁₅H₁₂F₃NO₂S₂
MW: 359.38 g.mol⁻¹
White solid
mp: 68 – 70 °C

The product was obtained by column chromatography on silica gel using Petroleum ether / EtOAc (from 100:0 to 80:20) as eluent.

¹H NMR (500 MHz, CDCl₃): δ 7.67 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.62 (dd, *J* = 4.0, 1.5 Hz, 1H), 7.35–7.32 (m, 1H), 7.31–7.24 (m, 5H), 7.14 (dd, *J* = 5.0, 3.5 Hz, 1H), 5.72 (p, *J* = 6.0 Hz, 1H), 4.53 (d, *J* = 15.0 Hz, 1H), 4.21 (d, *J* = 15.0 Hz, 1H).

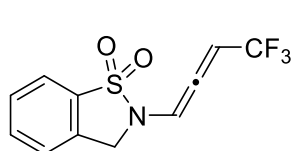
¹⁹F NMR (282 MHz, CDCl₃): δ -62.63.

¹³C NMR (126 MHz, CDCl₃): δ 199.2 (q, *J* = 6.0 Hz), 138.0, 134.6, 133.3, 133.1, 128.7 (x2), 128.1, 127.9, 127.7 (x2), 121.2 (q, *J* = 272.2 Hz), 106.4, 96.6 (q, *J* = 39.4 Hz), 51.3.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₅H₁₂F₃NaNO₂S₂ 382.0154; found 382.0150.

IR (neat) : ν = 3106, 3036, 1447, 1357, 1118, 1024, 739, 571 cm⁻¹

Compound 1s 2-(4,4,4-trifluorobuta-1,2-dien-1-yl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide⁷



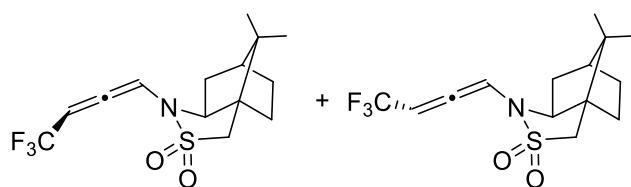
$C_{11}H_8F_3NO_2S$
 MW: 275.24 g.mol⁻¹
 White solid
 mp: 140 – 145 °C
 58 % (248 mg)

The product was obtained by column chromatography on silica gel using Petroleum ether / EtOAc (from 95:05 to 80:20) as eluent.

¹H NMR (300 MHz, CDCl₃): δ 7.85 (ddd, *J* = 7.7, 1.3, 0.6 Hz, 1H), 7.69 (td, *J* = 7.7, 1.3 Hz, 1H), 7.63 – 7.55 (m, 1H), 7.47 (dt, *J* = 7.8, 0.9 Hz, 1H), 7.32 (dq, *J* = 5.9, 2.9 Hz, 1H), 6.17 (p, *J* = 5.9 Hz, 1H), 4.46 (d, *J* = 4.8 Hz, 2H) ppm.

This analytical data match with those described in the literature.

Compound 1t 8,8-dimethyl-1-(4,4,4-trifluorobuta-1,2-dien-1-yl)hexahydro-3H-3a,6-methanobenzo[c]isothiazole 2,2-dioxide⁸



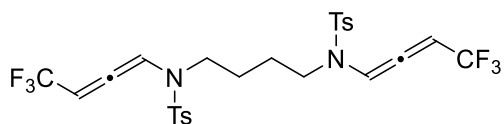
$C_{14}H_{18}F_3NO_2S$
 MW: 321.26 g.mol⁻¹
 Colorless oil
 61 % (96.3 mg)

The product was obtained by column chromatography on silica gel using Petroleum ether / EtOAc (from 95:05 to 80:20) as eluent.

¹H NMR (500 MHz, CDCl₃): δ 6.86 – 6.77 (m, 2H), 6.04 – 5.95 (m, 2H), 3.36 – 3.18 (m, 6H), 2.06 – 1.98 (m, 2H), 1.96 – 1.86 (m, 6H), 1.62 (dt, *J* = 13.0, 8.1 Hz, 2H), 1.53 – 1.42 (m, 2H), 1.38 – 1.26 (m, 2H), 1.11 (s, 6H), 0.95 (s, 6H).

This analytical data match with those described in the literature.

Compound 1u *N,N*-(butane-1,4-diyl)bis(4-methyl-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)benzenesulfonamide)



$C_{26}H_{26}F_6N_2O_4S$
 MW: 608.61 g.mol⁻¹
 White solid
 28 % (112 mg)

The product was obtained by column chromatography on silica gel using Petroleum ether / EtOAc (from 100:0 to 60:40) as eluent.

¹H NMR (300 MHz, CDCl₃): δ 7.68 (d, *J* = 8.4 Hz, 4H), 7.43 – 7.30 (m, 6H), 5.94 (p, *J* = 5.5 Hz, 2H), 3.19 – 3.01 (m, 4H), 2.45 (s, 6H), 1.53 – 1.48 (m, 4H).

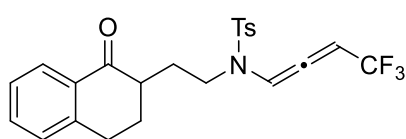
¹⁹F NMR (282 MHz, CDCl₃): δ -62.18, -62.19.

¹³C NMR (126 MHz, CDCl₃): δ 198.5 (q, *J* = 5.7 Hz) (x2), 144.7 (x2), 135.1, 135.0, 130.2 (x4), 127.3 (x4), 121.4 (q, *J* = 271.8 Hz) (x2), 107.0, 107.0, 96.4 (q, *J* = 39.2 Hz) (x2), 46.5, 46.4, 23.9, 23.8, 21.8 (x2).

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₂₆H₂₆F₆NaN₂O₄S 631.1000; found 631.1004.

IR (neat): ν = 3048, 2925, 1598, 1434, 1359, 1265, 1168, 1131, 684, 601, 547 cm⁻¹.

Compound 1v 4-methyl-*N*-(2-(1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)ethyl)-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)benzenesulfonamide

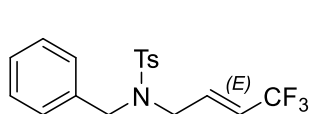


$C_{23}H_{22}F_3NO_2S$
MW: 449.49 g.mol⁻¹

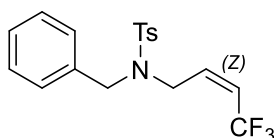
1v was used without any further purification.

Allylamides **2a-v**

Compound 2a *N*-benzyl-4-methyl-*N*-(4,4,4-trifluorobut-2-en-1-yl)benzenesulfonamide



+



$C_{18}H_{18}F_3NO_2S$
MW: 369.40 g.mol⁻¹
Colorless oil
80 % (73.6 mg)
E/Z ratio = 80:20

The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 100:0 to 60:40) as eluent.

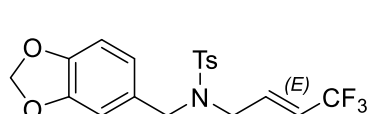
Only *E*-stereoisomer was described for ¹³C-NMR.

¹H NMR (500 MHz, CDCl₃): δ 7.73 (d, *J* = 8.3 Hz, 4H, *E* + *Z*), 7.35 (d, *J* = 8.2 Hz, 4H, *E* + *Z*), 7.33 – 7.21 (m, 10H, *E* + *Z*), 6.05 – 5.95 (m, 1H, *Z*), 5.79 (dt, *J* = 12.1, 6.2 Hz, 1H, *E*), 5.51 – 5.40 (m, 2H, *E* + *Z*), 4.38 – 4.24 (m, 4H, *E* + *Z*), 3.96 (dt, *J* = 6.3, 2.3 Hz, 2H, *E*), 3.81 (dt, *J* = 5.9, 1.9 Hz, 2H, *Z*), 2.46 (s, 6H, *E* + *Z*).

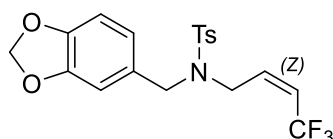
¹³C NMR (126 MHz, CDCl₃): δ 144.0, 138.8 (q, *J* = 5.0 Hz), 136.3, 135.5, 130.1 (x2), 128.8 (x2), 128.7 (x2), 128.3, 127.5 (x2), 122.8 (q, *J* = 271.9 Hz), 119.4 (q, *J* = 34.4 Hz), 52.7, 45.4 (q, *J* = 1.8 Hz), 21.7.

IR (neat): ν = 3068, 2928, 1341, 1223, 1159, 1125, 1094, 721, 656, 549 cm⁻¹.

Compound 2b *N*-(benzo[*d*][1,3]dioxol-5-ylmethyl)-4-methyl-*N*-(4,4,4-trifluorobut-2-en-1-yl)benzenesulfonamide



+



$C_{19}H_{18}F_3NO_4S$
MW: 413.41 g.mol⁻¹
White solid
mp: 65 – 68 °C
98 % (62 mg)
E/Z ratio = 80:20

The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 100:0 to 60:40) as eluent.

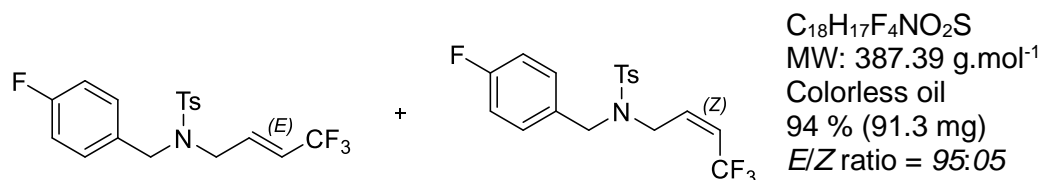
Only *E*-stereoisomer was described for ¹³C-NMR.

¹H NMR (400 MHz, CDCl₃): δ 7.72 (d, *J* = 8.3 Hz, 4H, *E* + *Z*), 7.35 (d, *J* = 7.8 Hz, 4H, *E* + *Z*), 6.87 – 6.59 (m, 6H, *E* + *Z*), 5.95 (s, 5H, *E* + *Z*), 5.81 (dt, *J* = 12.2, 6.2 Hz, 1H, *E*), 5.56 – 5.42 (m, 2H, *E* + *Z*), 4.24 – 4.15 (m, 4H, *E* + *Z*), 3.95 (dp, *J* = 6.7, 2.3 Hz, 2H, *E*), 3.80 (dt, *J* = 6.1, 2.1 Hz, 2H, *Z*), 2.46 (s, 6H, *E* + *Z*).

¹³C NMR (126 MHz, CDCl₃): δ 148.2, 147.7, 144.0, 138.9 (q, *J* = 5.0 Hz), 136.3, 130.1 (x2), 129.2, 127.4 (x2), 122.9 (q, *J* = 271.9 Hz), 122.3, 119.3 (q, *J* = 34.4 Hz), 109.1, 108.3, 101.3, 52.5, 45.2 (q, *J* = 1.7 Hz), 21.7.

IR (neat): ν = 2924, 1504, 1145, 1383, 1241, 1116, 1018, 927, 707, 697, 633, 511 cm⁻¹.

Compound 2c *N*-(4-fluorobenzyl)-4-methyl-*N*-(4,4,4-trifluorobut-2-en-1-yl)benzenesulfonamide



The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 100:0 to 60:40) as eluent.

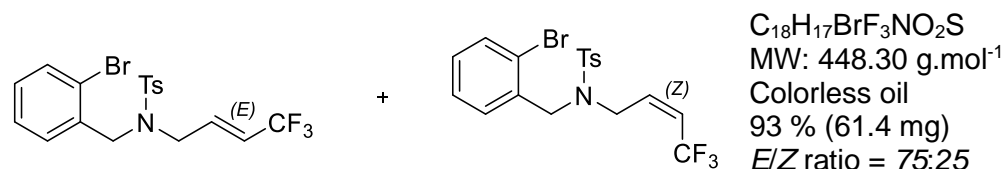
Only *E*-stereoisomer was described for ¹³C-NMR.

¹H NMR (500 MHz, CDCl₃): δ 7.65 (d, *J* = 8.4 Hz, 2H, *E*), 7.59 (d, *J* = 8.3 Hz, 2H, *Z*), 7.28 (d, *J* = 8.1 Hz, 2H, *E*), 7.25 (d, *J* = 8.1 Hz, 2H, *Z*), 7.21 – 7.12 (m, 4H, *E* + *Z*), 6.97 – 6.86 (m, 4H, *E* + *Z*), 5.97 – 5.87 (m, 1H, *Z*), 5.70 (dd, *J* = 11.9, 6.3 Hz, 1H, *E*), 5.49 – 5.31 (m, 2H, *E* + *Z*), 4.39 (s, 2H, *Z*), 4.19 (s, 2H, *E*), 3.88 (dt, *J* = 6.3, 2.2 Hz, 2H, *E*), 3.73 (dt, *J* = 3.9, 2.0 Hz, 2H, *Z*), 2.38 (s, 3H, *E*), 2.36 (s, 3H, *Z*).

¹³C NMR (126 MHz, CDCl₃): δ 162.5 (d, *J* = 246.7 Hz), 143.8, 138.4 (q, *J* = 5.0 Hz), 136.0, 131.1 (d, *J* = 3.2 Hz), 130.2 (d, *J* = 8.3 Hz), 129.9 (x2), 128.5 (d, *J* = 8.1 Hz), 127.1 (x2), 122.5 (q, *J* = 271.9 Hz), 119.4 (q, *J* = 34.4 Hz), 115.5 (d, *J* = 21.6 Hz), 99.0 (q, *J* = 3.7 Hz), 51.7, 45.2 (q, *J* = 1.6 Hz), 21.4.

IR (neat): ν = 2941, 1604, 1510, 1340, 1224, 1159, 1126, 1092, 549 cm⁻¹.

Compound 2d *N*-(2-bromobenzyl)-4-methyl-*N*-(4,4,4-trifluorobut-2-en-1-yl)benzenesulfonamide



The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 100:0 to 60:40) as eluent.

Only *E*-stereoisomer was described for ¹³C-NMR.

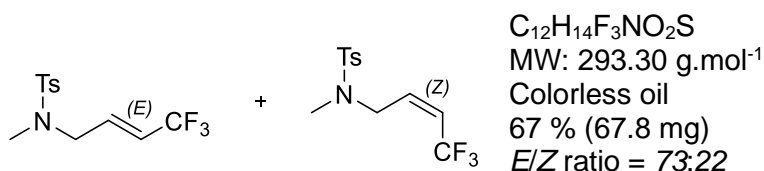
¹H NMR (500 MHz, CDCl₃): δ 7.74 (d, *J* = 8.4 Hz, 4H, *E* + *Z*), 7.56 – 7.47 (m, 4H, *E* + *Z*), 7.36 (d, *J* = 7.8 Hz, 4H, *E* + *Z*), 7.31 (td, *J* = 7.5, 1.4 Hz, 2H, *E* + *Z*), 7.19 – 7.12 (m, 2H, *E* + *Z*), 6.10

– 5.95 (m, 1H, *Z*), 5.83 (dt, *J* = 12.2, 6.2 Hz, 1H, *E*), 5.56 – 5.43 (m, 2H, *E* + *Z*), 4.45 (s, 4H, *E* + *Z*), 4.02 (dt, *J* = 6.3, 2.3 Hz, 2H, *E*), 3.86 (dd, *J* = 4.1, 2.0 Hz, 2H, *Z*), 2.46 (s, 6H, *E* + *Z*).

¹³C NMR (126 MHz, CDCl₃): δ 144.0, 138.0 (q, *J* = 5.0 Hz), 136.0, 134.7, 132.9, 130.2, 130.0 (x2), 129.5, 127.8, 127.3 (x2), 123.4, 122.6 (d, *J* = 271.9 Hz), 119.6 (q, *J* = 34.4 Hz), 52.0, 45.8 (d, *J* = 2.1 Hz), 21.6.

IR (neat): ν = 2945, 1598, 1441, 1344, 1161, 1126, 1093, 753, 633, 515 cm⁻¹.

Compound 2e *N*,4-dimethyl-*N*-(4,4,4-trifluorobut-2-en-1-yl)benzenesulfonamide



The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 100:0 to 60:40) as eluent.

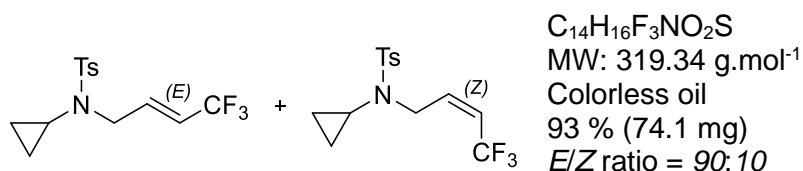
Only *E*-stereoisomer was described for ¹³C-NMR.

¹H NMR (500 MHz, CDCl₃): δ 7.70 (d, *J* = 8.3 Hz, 4H, *E* + *Z*), 7.37 (d, *J* = 8.5 Hz, 4H, *E* + *Z*), 6.36 – 6.25 (m, 1H, *Z*), 6.04 (dt, *J* = 11.8, 6.8 Hz, 1H, *E*), 5.91 – 5.73 (m, 2H, *E* + *Z*), 3.92 (dt, *J* = 6.6, 2.0 Hz, 2H, *E*), 3.79 (tt, *J* = 4.3, 2.1 Hz, 2H, *Z*), 2.73 (s, 6H, *E* + *Z*), 2.47 (s, 6H, *E* + *Z*).

¹³C NMR (126 MHz, CDCl₃): δ 144.0, 138.0 (q, *J* = 5.0 Hz), 134.3, 130.0 (x2), 127.6 (x2), 122.8 (d, *J* = 268.9 Hz), 121.4 (q, *J* = 34.4 Hz), 47.7 (q, *J* = 1.5 Hz), 35.2, 21.7.

IR (neat): ν = 2930, 1674, 1598, 1457, 1413, 1341, 1203, 1162, 1090, 694, 550 cm⁻¹.

Compound 2f *N*-cyclopropyl-4-methyl-*N*-(4,4,4-trifluorobut-2-en-1-yl)benzenesulfonamide



The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 100:0 to 60:40) as eluent.

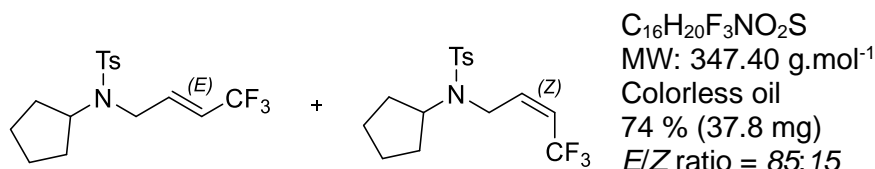
Only *E*-stereoisomer was described for ¹³C-NMR.

¹H NMR (500 MHz, CDCl₃): δ 7.74 (d, *J* = 8.3 Hz, 4H, *E* + *Z*), 7.34 (d, *J* = 8.0 Hz, 4H, *E* + *Z*), 6.36 – 6.25 (m, 1H, *Z*), 6.06 (dt, *J* = 11.8, 6.5 Hz, 1H, *E*), 5.86 – 5.73 (m, 1H, *Z*), 5.72 – 5.59 (m, 1H, *E*), 4.06 (dp, *J* = 6.5, 2.1 Hz, 2H, *E*), 3.92 (dp, *J* = 6.1, 2.1 Hz, 2H, *Z*), 2.45 (s, 6H, *E* + *Z*), 2.04 (tt, *J* = 6.9, 3.6 Hz, 2H, *E* + *Z*), 0.87 – 0.81 (m, 4H, *E* + *Z*), 0.74 – 0.67 (m, 4H, *E* + *Z*).

¹³C NMR (126 MHz, CDCl₃): δ 144.1, 139.1 (q, *J* = 5.1 Hz), 135.0, 129.9 (x2), 127.9 (x2), 123.0 (q, *J* = 271.8 Hz), 119.6 (q, *J* = 34.4 Hz), 48.6 (q, *J* = 1.5 Hz), 31.1, 21.7, 7.7 (x2).

IR (neat): ν = 2966, 2936, 1672, 1566, 1457, 1342, 1174, 1123, 817, 710, 687, 521 cm⁻¹.

Compound 2g *N*-cyclopentyl-4-methyl-*N*-(4,4,4-trifluorobut-2-en-1-yl)benzenesulfonamide



The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 100:0 to 60:40) as eluent.

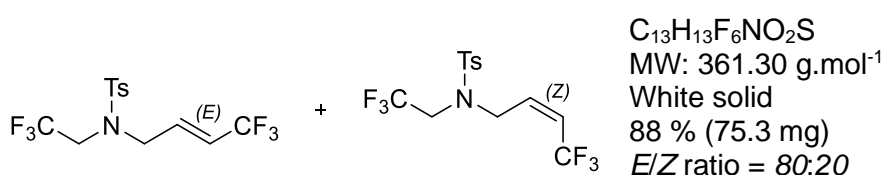
Only *E*-stereoisomer was described for ¹³C-NMR.

¹H NMR (500 MHz, CDCl₃): δ 7.69 (d, *J* = 8.3 Hz, 4H, *E* + *Z*), 7.35 – 7.28 (m, 4H; *E* + *Z*), 6.42 – 6.33 (m, 1H, *Z*), 6.19 (dt, *J* = 11.7, 5.7 Hz, 1H, *E*), 5.92 – 5.81 (m, 1H, *Z*), 5.61 (dq, *J* = 11.3, 8.9, 2.3 Hz, 1H, *E*), 4.30 (p, *J* = 8.8 Hz, 2H, *E* + *Z*), 3.95 (dt, *J* = 5.8, 2.5 Hz, 2H, *E*), 3.83 (dp, *J* = 4.8, 2.4 Hz, 2H, *Z*), 2.43 (s, 6H, *E* + *Z*), 1.78 – 1.65 (m, 4H, *E* + *Z*), 1.63 – 1.55 (m, 4H, *E* + *Z*), 1.53 – 1.42 (m, 4H, *E* + *Z*), 1.36 – 1.22 (m, 4H, *E* + *Z*).

¹³C NMR (126 MHz, CDCl₃): δ 143.6, 142.7 (q, *J* = 4.9 Hz), 137.2, 129.9 (x2), 127.3 (x2), 123.1 (q, *J* = 271.8 Hz), 117.7 (q, *J* = 34.4 Hz), 59.3, 41.2 (q, *J* = 1.6 Hz), 29.2 (x2), 23.6 (x2), 21.8.

IR (neat): ν = 2959, 2874, 1341, 1156, 1092, 659, 547 cm⁻¹.

Compound 2h 4-methyl-*N*-(4,4,4-trifluorobut-2-en-1-yl)-*N*-(2,2,2-trifluoroethyl)benzenesulfonamide



The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 100:0 to 60:40) as eluent.

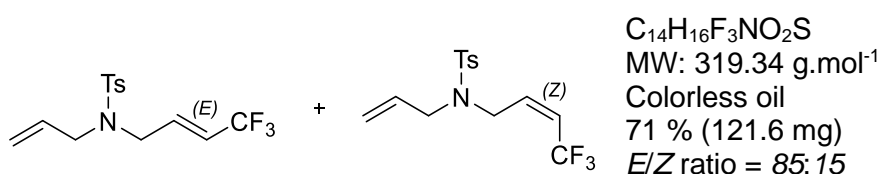
Only *E*-stereoisomer was described for ¹³C-NMR.

¹H NMR (500 MHz, CDCl₃): δ 7.72 (d, *J* = 8.4 Hz, 4H, *E* + *Z*), 7.37 – 7.31 (m, 4H, *E* + *Z*), 6.25 – 6.14 (m, 1H, *Z*), 6.02 (dt, *J* = 11.9, 6.5 Hz, 1H, *E*), 5.77 (dq, *J* = 12.6, 8.6, 2.0 Hz, 2H, *E* + *Z*), 4.10 (dt, *J* = 6.4, 2.0 Hz, 2H, *E*), 3.99 (dt, *J* = 6.3, 2.3 Hz, 2H, *Z*), 3.85 (q, *J* = 8.7 Hz, 4H, *E* + *Z*), 2.45 (s, 6H, *E* + *Z*).

¹³C NMR (126 MHz, CDCl₃): δ 144.5, 137.3 (d, *J* = 5.3 Hz), 135.6, 129.9 (x2), 127.3 (x2), 123.8 (d, *J* = 280.2 Hz), 122.4 (d, *J* = 272.1 Hz), 121.4 (q, *J* = 34.4 Hz), 48.3 (q, *J* = 35.1 Hz), 46.4, 21.5.

IR (neat): ν = 2952, 1440, 1352, 1273, 1228, 1162, 1129, 1091, 1053 cm⁻¹.

Compound 2i *N*-allyl-4-methyl-*N*-(4,4,4-trifluorobut-2-en-1-yl)benzenesulfonamide



The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 100:0 to 60:40) as eluent.

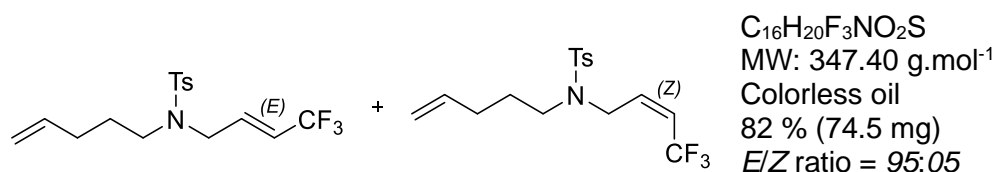
Only *E*-stereoisomer was described.

¹H NMR (500 MHz, CDCl₃): δ 7.70 (d, *J* = 8.3 Hz, 2H, *E*), 7.32 (d, *J* = 8.1 Hz, 2H, *E*), 5.99 (dt, *J* = 12.4, 6.3 Hz, 1H, *E*), 5.72 – 5.57 (m, 2H, *E*), 5.28 – 4.97 (m, 2H, *E*), 4.01 (dt, *J* = 6.4, 2.2 Hz, 2H, *E*), 3.79 (dt, *J* = 6.3, 1.4 Hz, 2H, *E*), 2.44 (s, 3H, *E*).

¹³C NMR (126 MHz, CDCl₃): δ 143.9, 139.1 (q, *J* = 5.0 Hz), 136.6, 132.2, 130.03 (x2), 127.4 (x2), 122.9 (q, *J* = 271.9 Hz), 119.9 (q, *J* = 34.5 Hz), 119.9, 51.3, 44.7 (q, *J* = 1.7 Hz), 21.7.

IR (neat): ν = 2927, 1645, 1598, 1419, 1348, 1224, 1157, 1122, 1093, 663, 548 cm⁻¹.

Compound 2j 4-methyl-*N*-(pent-4-en-1-yl)-*N*-(4,4,4-trifluorobut-2-en-1-yl)benzenesulfonamide



The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 100:0 to 60:40) as eluent.

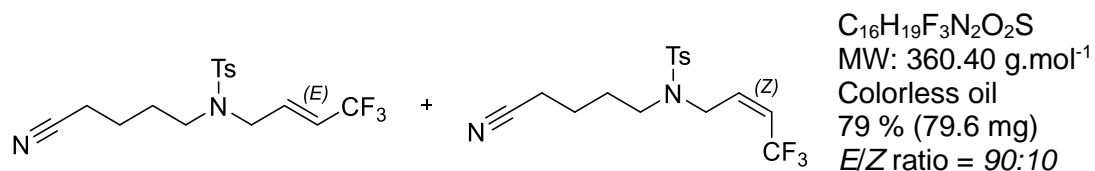
Only *E*-stereoisomer was described.

¹H NMR (500 MHz, CDCl₃): δ 7.68 (d, *J* = 8.3 Hz, 2H, *E*), 7.32 (d, *J* = 8.0 Hz, 2H, *E*), 6.00 (dt, *J* = 11.8, 6.4 Hz, 1H, *E*), 5.90 – 5.62 (m, 2H, *E*), 5.14 – 4.90 (m, 2H, *E*), 4.01 (dp, *J* = 6.5, 2.2 Hz, 2H, *E*), 3.16 – 3.09 (m, 2H, *E*), 2.44 (s, 3H, *E*), 2.04 (q, *J* = 7.1 Hz, 2H, *E*), 1.67 – 1.58 (m, 2H, *E*).

¹³C NMR (126 MHz, CDCl₃): δ 143.8, 139.5 (q, *J* = 5.0 Hz), 137.4, 136.5, 130.0 (x2), 127.3 (x2), 122.9 (d, *J* = 271.0 Hz), 120.1 (q, *J* = 34.3 Hz), 115.6, 48.5, 45.7 (q, *J* = 1.8 Hz), 30.8, 27.6, 21.7.

IR (neat): ν = 2966, 2924, 2860, 1671, 1642, 1599, 1446, 1415, 1341, 1276, 1221, 1160, 1124, 549 cm⁻¹.

Compound 2k *N*-(4-cyanobutyl)-4-methyl-*N*-(4,4,4-trifluorobut-2-en-1-yl)benzenesulfonamide



The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 100:0 to 60:40) as eluent.

Only *E*-stereoisomer was described for ¹³C-NMR.

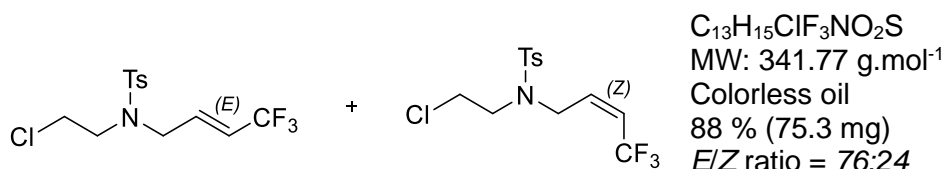
¹H NMR (500 MHz, CDCl₃): δ 7.68 (d, *J* = 8.3 Hz, 2H, *E*), 7.62 (d, *J* = 8.4 Hz, 2H, *Z*), 7.34 (d, *J* = 7.9 Hz, 4H, *E* + *Z*), 6.24 – 6.14 (m, 1H, *Z*), 5.97 (dt, *J* = 11.8, 6.6 Hz, 1H, *E*), 5.77 – 5.65

(m, 2H, *E* + *Z*), 4.00 (dp, *J* = 6.3, 2.1 Hz, 2H, *E*), 3.88 (dt, *J* = 6.0, 2.1 Hz, 2H, *Z*), 3.17 (t, *J* = 6.5 Hz, 4H, *E* + *Z*), 2.44 (s, 6H, *E* + *Z*), 2.45 – 2.37 (m, 4H, *E* + *Z*), 1.77 – 1.65 (m, 8H, *E* + *Z*).

¹³C NMR (126 MHz, CDCl₃): δ 144.1, 138.8 (d, *J* = 4.8 Hz), 136.0, 130.2 (x2), 127.3 (x2), 122.8 (d, *J* = 273.4 Hz), 120.6 (q, *J* = 34.4 Hz), 119.3, 47.8, 45.8 (q, *J* = 1.3 Hz), 27.1, 22.4, 21.7, 16.7.

IR (neat): ν = 2936, 2874, 1671, 1598, 1339, 1159, 1124, 847, 817, 549 cm⁻¹.

Compound 2l *N*-(2-chloroethyl)-4-methyl-*N*-(4,4,4-trifluorobut-2-en-1-yl)benzenesulfonamide



The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 100:0 to 60:40) as eluent.

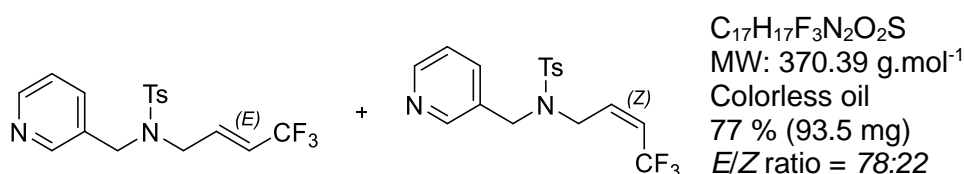
Only *E*-stereoisomer was described for ¹³C-NMR.

¹H NMR (500 MHz, CDCl₃): δ 7.71 (d, *J* = 8.3 Hz, 4H, *E* + *Z*), 7.34 (d, *J* = 7.9 Hz, 4H, *E* + *Z*), 6.32 – 6.14 (m, 1H, *Z*), 6.03 (dt, *J* = 11.8, 6.6 Hz, 1H, *E*), 5.87 – 5.61 (m, 2H, *E* + *Z*), 4.07 (dt, *J* = 6.5, 2.1 Hz, 2H, *E*), 3.99 (dt, *J* = 5.8, 2.1 Hz, 2H, *Z*), 3.76 – 3.56 (m, 4H, *E* + *Z*), 3.50 – 3.39 (m, 4H, *E* + *Z*), 2.45 (s, 6H, *E* + *Z*).

¹³C NMR (126 MHz, CDCl₃): δ 144.3, 138.6 (q, *J* = 5.2 Hz), 135.9, 130.2 (x2), 127.4 (x2), 124.3 (q, *J* = 283.9 Hz), 120.9 (q, *J* = 34.1 Hz), 50.4, 47.0 (q, *J* = 1.7 Hz), 41.9, 21.7.

IR (neat): ν = 2999, 2943, 1343, 1160, 1126, 1093, 816, 693, 550 cm⁻¹.

Compound 2m 4-methyl-*N*-(pyridin-3-ylmethyl)-*N*-(4,4,4-trifluorobut-2-en-1-yl)benzenesulfonamide



The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 100:0 to 60:40) as eluent.

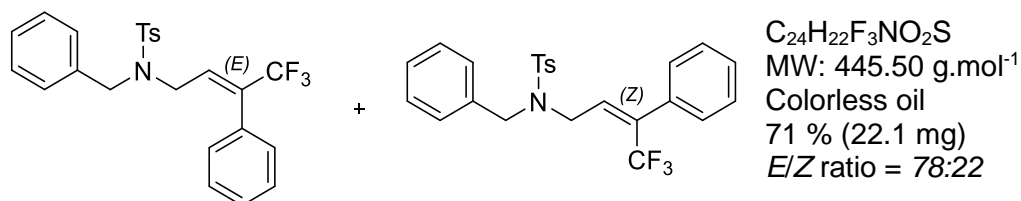
Only *E*-stereoisomer was described for ¹³C-NMR.

¹H NMR (500 MHz, CDCl₃): δ 8.53 (d, *J* = 51.4 Hz, 4H, *E* + *Z*), 7.73 (d, *J* = 8.3 Hz, 4H, *E* + *Z*), 7.73 – 7.64 (m, 2H, *E* + *Z*), 7.36 (d, *J* = 7.9 Hz, 4H, *E* + *Z*), 7.31 (dd, *J* = 20.4, 7.0 Hz, 2H, *E* + *Z*), 6.10 – 5.93 (m, 1H, *Z*), 5.79 (dt, *J* = 11.9, 6.4 Hz, 1H, *E*), 5.61 – 5.47 (m, 2H, *E* + *Z*), 4.52 (s, 2H, *Z*), 4.32 (s, 2H, *E*), 3.98 (dt, *J* = 6.5, 2.2 Hz, 2H, *E*), 3.83 (dt, *J* = 6.2, 2.0 Hz, 2H, *Z*), 2.46 (s, 6H, *E* + *Z*).

¹³C NMR (126 MHz, CDCl₃): δ 149.8, 144.7, 144.3, 138.2 (q, *J* = 5.0 Hz), 136.4, 136.0, 131.8, 130.3 (x2), 127.4 (x2), 127.1, 122.7 (d, *J* = 272.0 Hz), 120.3 (q, *J* = 34.5 Hz), 50.2, 45.7 (d, *J* = 1.8 Hz), 21.7.

IR (neat): $\nu = 3035, 2843, 1619, 1428, 1342, 1274, 1223, 1161, 1126, 1092, 815, 771, 697, 516 \text{ cm}^{-1}$.

Compound 2n *N*-benzyl-4-methyl-*N*-(4,4,4-trifluoro-3-phenylbut-2-en-1-yl)benzenesulfonamide



The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 100:0 to 60:40) as eluent.

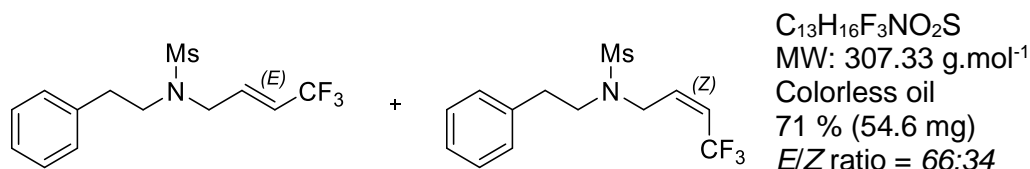
Only *E*-stereoisomer was described for ¹³C-NMR.

¹H NMR (400 MHz, CDCl₃): δ 7.76 (d, *J* = 8.3 Hz, 2H, *E*), 7.67 (d, *J* = 8.3 Hz, 2H, *Z*), 7.38 – 7.11 (m, 21H, *E* + *Z*), 6.97 (dd, *J* = 5.7, 3.5 Hz, 3H, *E* + *Z*), 6.13 (tt, *J* = 6.5, 1.7 Hz, 1H, *Z*), 5.75 (t, *J* = 6.1 Hz, 1H, *E*), 4.36 (s, 2H, *E*), 4.25 (s, 2H, *Z*), 4.11 (dd, *J* = 6.0, 2.6 Hz, 2H, *E*), 3.76 – 3.58 (m, 2H, *Z*), 2.45 (s, 3H, *E*), 2.44 (s, 3H, *Z*).

¹³C NMR (126 MHz, CDCl₃): δ 143.9, 137.5 (q, *J* = 2.8 Hz), 136.5, 135.7, 135.4, 130.1 (x2), 129.4 (x2), 128.9 (x2), 128.8 (x2), 128.6, 128.3 (x2), 128.2, 128.0, 127.4 (x2), 123.6 (q, *J* = 275.8 Hz), 52.9, 46.2 (q, *J* = 3.6 Hz), 21.7.

IR (neat): $\nu = 3064, 3033, 2923, 2863, 1598, 1495, 1455, 1446, 1344, 1289, 1202, 1161, 1099, 734, 699, 549 \text{ cm}^{-1}$.

Compound 2o *N*-phenethyl-*N*-(4,4,4-trifluorobut-2-en-1-yl)methanesulfonamide



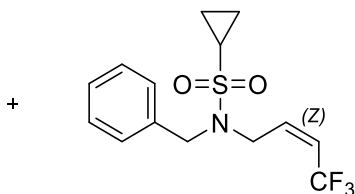
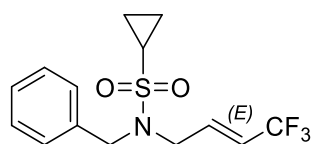
The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 100:0 to 60:40) as eluent.

Only *E*-stereoisomer was described for ¹³C-NMR.

¹H NMR (500 MHz, CDCl₃): δ 7.34 – 7.29 (m, 6H, *E* + *Z*), 7.26 – 7.18 (m, 4H, *E* + *Z*), 6.40 – 6.23 (m, 1H, *Z*), 6.03 (dt, *J* = 11.8, 6.7 Hz, 1H, *E*), 5.91 – 5.69 (m, 2H, *E* + *Z*), 4.10 (dt, *J* = 6.7, 2.0 Hz, 2H, *E*), 3.90 (dt, *J* = 6.0, 2.1 Hz, 2H, *Z*), 3.47 (dt, *J* = 7.8, 6.4 Hz, 4H, *E* + *Z*), 2.96 – 2.85 (m, 4H, *E* + *Z*), 2.69 (s, 3H, *Z*), 2.65 (s, 3H, *E*).

¹³C NMR (126 MHz, CDCl₃): δ 138.9 (q, *J* = 5.0 Hz), 138.1, 129.1 (x2), 128.9 (x2), 127.0, 122.9 (q, *J* = 270.6 Hz), 121.0 (q, *J* = 34.3 Hz), 49.8, 45.1 (q, *J* = 1.6 Hz), 39.0, 35.2.

IR (neat): $\nu = 3065, 3012, 2864, 1330, 1145, 1124, 963, 701, 519 \text{ cm}^{-1}$.

Compound 2p *N*-benzyl-*N*-(4,4,4-trifluorobut-2-en-1-yl)cyclopropanesulfonamide

$C_{14}H_{16}F_3NO_2S$
MW: 319.34 g.mol⁻¹
Colorless oil
89 % (71.4 mg)
E/Z ratio = 78:22

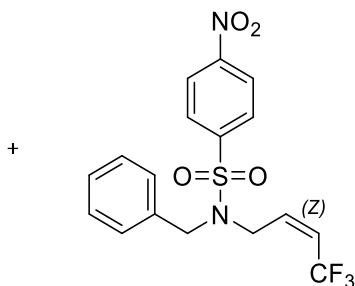
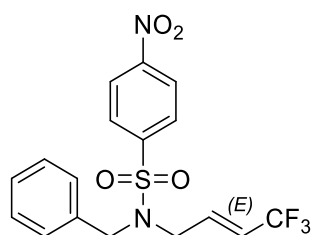
The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 100:0 to 60:40) as eluent.

Only *E*-stereoisomer was described for ¹³C-NMR.

¹H NMR (500 MHz, CDCl₃): δ 7.42 – 7.28 (m, 10H, *E* + *Z*), 6.37 – 6.21 (m, 1H, *Z*), 6.00 (dt, *J* = 11.9, 6.3 Hz, 1H, *E*), 5.72 (dddd, *J* = 15.8, 7.9, 6.2, 4.6 Hz, 1H, *Z*), 5.66 – 5.54 (m, 1H, *E*), 4.43 (s, 4H, *E* + *Z*), 4.11 (dp, *J* = 6.6, 2.2 Hz, 2H, *E*), 3.90 (dp, *J* = 6.2, 2.1 Hz, 2H, *Z*), 2.48 – 2.21 (m, 2H, *E* + *Z*), 1.35 – 1.18 (m, 4H, *E* + *Z*), 1.09 – 0.98 (m, 4H, *E* + *Z*).

¹³C NMR (126 MHz, CDCl₃): δ 139.0 (q, *J* = 5.0 Hz), 135.8, 128.9 (x2), 128.7 (x2), 128.3, 122.8 (q, *J* = 271.8 Hz), 120.0 (q, *J* = 34.5 Hz), 52.2, 45.2 (q, *J* = 1.7 Hz), 29.8, 5.5 (x2).

IR (neat): ν = 3065, 2925, 2876, 1335, 1126, 889, 703 cm⁻¹.

Compound 2q *N*-benzyl-4-nitro-*N*-(4,4,4-trifluorobut-2-en-1-yl)benzenesulfonamide

$C_{17}H_{15}F_3N_2O_4S$
MW: 400.37 g.mol⁻¹
Colorless oil
74 % (89.7 mg)
E/Z ratio = 80:20

The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 100:0 to 60:40) as eluent.

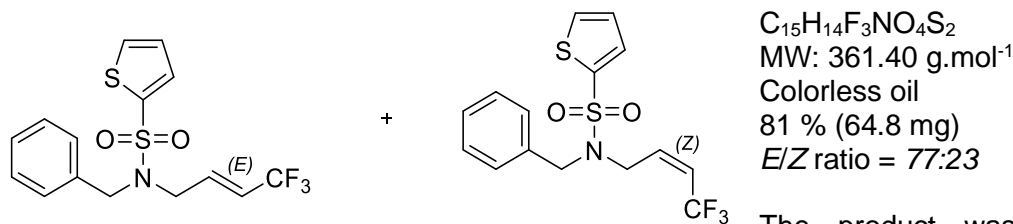
Only *E*-stereoisomer was described for ¹³C-NMR.

¹H NMR (500 MHz, CDCl₃): δ 8.38 (d, *J* = 8.8 Hz, 4H, *E* + *Z*), 7.99 (d, *J* = 8.8 Hz, 4H, *E* + *Z*), 7.37 – 7.18 (m, 10H, *E* + *Z*), 6.11 – 5.99 (m, 1H, *Z*), 5.78 (dt, *J* = 11.9, 6.3 Hz, 1H, *E*), 5.64 – 5.48 (m, 2H, *E* + *Z*), 4.39 (s, 4H, *E* + *Z*), 4.04 (dp, *J* = 6.4, 2.2 Hz, 2H, *E*), 3.89 (dp, *J* = 6.1, 2.1 Hz, 2H, *Z*).

¹³C NMR (126 MHz, CDCl₃): δ 150.3, 145.4, 137.7 (q, *J* = 5.0 Hz), 134.6, 129.0 (x2), 128.7 (x2), 128.7, 128.5 (x2), 124.7 (x2), 122.7 (q, *J* = 272.0 Hz), 120.3 (q, *J* = 34.5 Hz), 52.7, 45.5 (q, *J* = 1.7 Hz).

IR (neat): ν = 2363, 2340, 1531, 1350, 1162, 1124, 856, 738, 693, 609, 536, 463 cm⁻¹.

Compound 2r *N*-benzyl-*N*-(4,4,4-trifluorobut-2-en-1-yl)thiophene-2-sulfonamide



The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 100:0 to 60:40) as eluent.

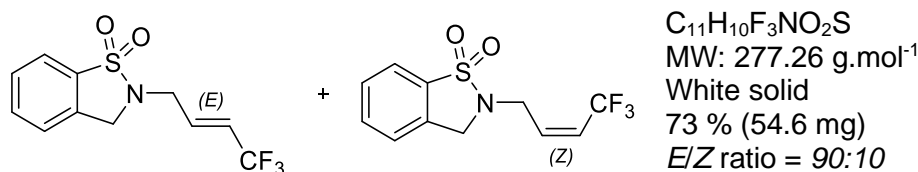
Only *E*-stereoisomer was described for ¹³C-NMR.

¹H NMR (500 MHz, CDCl₃): δ 7.75 – 7.60 (m, 4H, *E* + *Z*), 7.39 – 7.29 (m, 10H, *E* + *Z*), 7.18 (dd, *J* = 5.1, 3.7 Hz, 2H, *E* + *Z*), 6.25 – 6.00 (m, 1H, *Z*), 5.84 (dt, *J* = 12.3, 6.3 Hz, 1H, *E*), 5.64 – 5.45 (m, 2H, *E* + *Z*), 4.36 (s, 4H, *E* + *Z*), 4.04 (dq, *J* = 6.4, 2.2 Hz, 2H, *E*), 3.88 (dt, *J* = 6.1, 2.0 Hz, 2H, *Z*).

¹³C NMR (126 MHz, CDCl₃): δ 139.7, 138.4 (q, *J* = 5.1 Hz), 135.2, 132.5, 132.3, 128.9 (x2), 128.8 (x2), 128.4, 127.8, 122.8 (q, *J* = 271.8 Hz), 119.6 (q, *J* = 34.5 Hz), 53.0, 45.8 (q, *J* = 1.7 Hz).

IR (neat): ν = 3106, 2963, 2874, 1673, 1406, 1349, 1257, 1155, 722, 703, 581 cm⁻¹.

Compound 2s 2-(4,4,4-trifluorobut-2-en-1-yl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide



The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 100:0 to 60:40) as eluent.

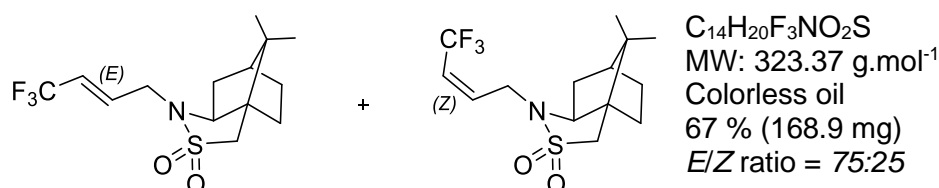
Only *E*-stereoisomer was described for ¹³C-NMR.

¹H NMR (500 MHz, CDCl₃): δ 7.80 (dd, *J* = 18.4, 8.0 Hz, 2H, *E* + *Z*), 7.63 (td, *J* = 7.6, 1.2 Hz, 2H, *E* + *Z*), 7.55 (td, *J* = 7.6, 1.0 Hz, 2H, *E* + *Z*), 7.41 (t, *J* = 0.9 Hz, 2H, *E* + *Z*), 6.56 – 6.48 (m, 1H, *Z*), 6.26 (dt, *J* = 11.8, 7.2 Hz, 1H, *E*), 5.91 (dq, *J* = 12.0, 8.5, 1.8 Hz, 2H, *E* + *Z*), 4.37 (s, 4H, *E* + *Z*), 4.21 (dp, *J* = 7.4, 2.0 Hz, 2H, *E*), 4.04 (dt, *J* = 5.9, 2.1 Hz, 2H, *Z*).

¹³C NMR (126 MHz, CDCl₃): δ 136.8 (q, *J* = 5.1 Hz), 134.8, 133.5, 133.1, 129.5, 124.7, 122.8 (d, *J* = 266.2 Hz), 122.6 (q, *J* = 34.4 Hz), 121.7, 50.3, 41.3 (q, *J* = 1.5 Hz).

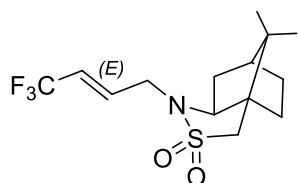
IR (neat): ν = 2943, 2865, 1675, 1299, 1225, 1175, 1127, 783, 570 cm⁻¹.

Compound 2t (6*S*,7*aS*)-8,8-dimethyl-1-(4,4,4-trifluorobut-2-en-1-yl)hexahydro-3*H*-3*a*,6-methanobenzo[*c*]isothiazole 2,2-dioxide



The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 100:0 to 60:40) as eluent. Both diastereomers are separable by column chromatography.

- **Compound 2t-E** (6S,7aS)-8,8-dimethyl-1-((E)-4,4,4-trifluorobut-2-en-1-yl)hexahydro-3H-3a,6-methanobenzo[c]isothiazole 2,2-dioxide



¹H NMR (500 MHz, CDCl₃): δ 6.47 (dddt, *J* = 15.6, 6.5, 4.3, 2.1 Hz, 1H), 6.00 – 5.79 (m, 1H), 3.83 (dtd, *J* = 15.9, 4.1, 2.0 Hz, 1H), 3.53 (dtd, *J* = 15.9, 6.4, 2.0 Hz, 1H), 3.16 (s, 2H), 3.10 (dd, *J* = 8.0, 4.4 Hz, 1H), 2.00 – 1.79 (m, 4H), 1.66 – 1.61 (m, 1H), 1.48 – 1.42 (m, 1H), 1.34 – 1.23 (m, 1H), 1.13 (s, 3H), 0.93 (s, 3H).

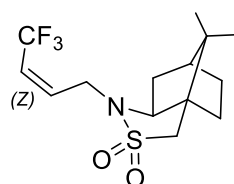
¹⁹F NMR (282 MHz, CDCl₃): δ -66.42.

¹³C NMR (126 MHz, CDCl₃): δ 135.2 (q, *J* = 6.4 Hz), 122.5 (q, *J* = 269.7 Hz), 122.3 (q, *J* = 34.2 Hz), 67.3, 50.1, 49.5, 47.8, 44.8, 43.7, 35.6, 32.4, 27.0, 20.5, 20.1.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₄H₂₀F₃NaNO₂S 346.1059; found 346.1053.

IR (neat): ν = 2958, 2883, 1673, 1456, 1308, 1222, 1117, 1063, 542 cm⁻¹.

- **Compound 2t-Z** (6S,7aS)-8,8-dimethyl-1-((Z)-4,4,4-trifluorobut-2-en-1-yl)hexahydro-3H-3a,6-methanobenzo[c]isothiazole 2,2-dioxide



¹H NMR (500 MHz, CDCl₃): δ 6.26 (dt, *J* = 11.9, 7.0 Hz, 1H), 5.88 – 5.68 (m, 1H), 3.97 (ddt, *J* = 16.6, 6.9, 2.0 Hz, 1H), 3.77 (ddt, *J* = 16.6, 6.9, 2.0 Hz, 1H), 3.15 (s, 2H), 3.15 – 3.10 (m, 1H), 1.99 – 1.93 (m, 1H), 1.93 – 1.81 (m, 3H), 1.65 (dd, *J* = 12.8, 7.9 Hz, 1H), 1.52 – 1.40 (m, 1H), 1.37 – 1.21 (m, 1H), 1.11 (s, 3H), 0.92 (s, 3H).

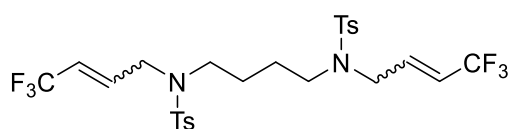
¹⁹F NMR (282 MHz, CDCl₃): δ -60.07.

¹³C NMR (126 MHz, CDCl₃): δ 137.5 (q, *J* = 5.1 Hz), 122.9 (q, *J* = 272.0 Hz), 121.1 (q, *J* = 34.3 Hz), 66.9, 50.1, 49.5, 47.8, 44.7, 40.1 (q, *J* = 1.7 Hz), 35.1, 32.3, 22.0, 20.5, 20.1.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₄H₂₀F₃NaNO₂S 346.1059; found 346.1056.

IR (neat): ν = 2958, 2883, 1719, 1306, 1226, 1130, 1062, 544 cm⁻¹.

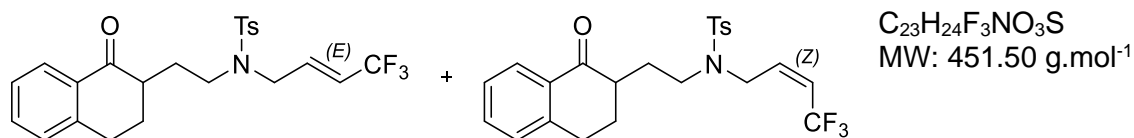
Compound 2u *N,N*-(butane-1,4-diyl)bis(4-methyl-*N*-(4,4,4-trifluorobut-2-en-1-yl)benzenesulfonamide)



C₂₆H₃₀F₆N₂O₄S₂
MW: 612.65 g.mol⁻¹

2u was obtained after short work-up and used without further purification.

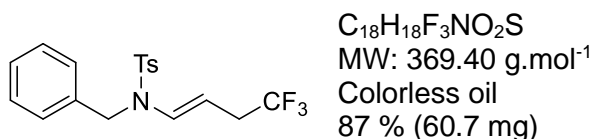
Compound 2v 4-methyl-*N*-(2-(1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)ethyl)-*N*-(4,4,4-trifluorobut-2-en-1-yl)benzenesulfonamide



2v was obtained after short work-up and used without further purification.

Enamides **3a-v**

Compound 3a (*E*)-*N*-benzyl-4-methyl-*N*-(4,4,4-trifluorobut-1-en-1-yl)benzenesulfonamide



The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 100:0 to 60:40) as eluent.

¹H NMR (500 MHz, CDCl₃): δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.38 – 7.21 (m, 7H), 6.92 (d, *J* = 14.2 Hz, 1H), 4.54 (dt, *J* = 14.2, 7.5 Hz, 1H), 4.50 (s, 2H), 2.67 (qdd, *J* = 10.4, 7.4, 1.2 Hz, 2H), 2.44 (s, 3H).

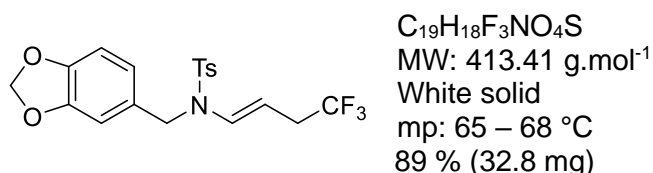
¹⁹F NMR (471 MHz, CDCl₃): δ -67.40.

¹³C NMR (126 MHz, CDCl₃): δ 144.3, 135.8, 135.0, 132.1, 130.1 (x2), 128.8 (x2), 127.7, 127.1 (2), 127.0 (x2), 126.2 (d, *J* = 276.9 Hz), 99.1 (q, *J* = 3.9 Hz), 49.5, 35.3 (q, *J* = 30.5 Hz), 21.7.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₈H₁₈F₃NNaO₂S 392.0903; found 392.0895.

IR (neat): ν = 2925, 1852, 1662, 1342, 1255, 1166, 1137, 1068, 697, 550 cm⁻¹.

Compound 3b (*E*)-*N*-(benzo[*d*][1,3]dioxol-5-ylmethyl)-4-methyl-*N*-(4,4,4-trifluorobut-1-en-1-yl)benzenesulfonamide



The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 95:05 to 60:40) as eluent.

¹H NMR (500 MHz, CDCl₃): δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 14.2 Hz, 1H), 6.81 – 6.64 (m, 3H), 5.94 (s, 2H), 4.58 (dt, *J* = 14.1, 7.5 Hz, 1H), 4.39 (s, 2H), 2.69 (qdd, *J* = 10.5, 7.5, 1.2 Hz, 2H), 2.44 (s, 3H).

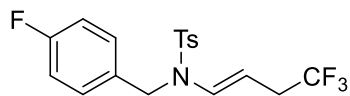
¹⁹F NMR (282 MHz, CDCl₃): δ -67.35.

¹³C NMR (126 MHz, CDCl₃): δ 148.1, 147.1, 144.2, 135.7, 132.0, 130.0 (x2), 128.7, 127.0 (x2), 125.7 (q, *J* = 275.4 Hz), 120.3, 108.2, 107.5, 101.1, 99.1 (q, *J* = 3.8 Hz), 49.2, 35.2 (q, *J* = 30.5 Hz), 21.6.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₉H₁₈F₃NNaO₄S 436.0801; found 436.0794.

IR (neat): ν = 2920, 1662, 1491, 1448, 1356, 1245, 1165, 810, 665, 549 cm⁻¹.

Compound 3c (*E*)-*N*-(4-fluorobenzyl)-4-methyl-*N*-(4,4,4-trifluorobut-1-en-1-yl)benzenesulfonamide



$C_{18}H_{17}F_4NO_2S$
MW: 387.39 g.mol⁻¹
White solid
mp: 93 – 95 °C
89 % (73 mg)

The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 100:00 to 60:40) as eluent.

¹H NMR (300 MHz, CDCl₃): δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.17 (m, 2H), 7.04 – 6.93 (m, 2H), 6.91 (d, *J* = 14.2 Hz, 1H), 4.53 (dd, *J* = 14.6, 7.1 Hz, 1H), 4.46 (s, 2H), 2.69 (qdd, *J* = 10.4, 7.5, 1.2 Hz, 2H), 2.44 (s, 3H).

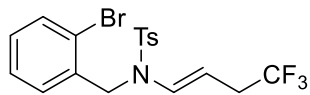
¹⁹F NMR (282 MHz, CDCl₃): δ -67.40, -114.80.

¹³C NMR (126 MHz, CDCl₃): δ 162.3 (d, *J* = 246.0 Hz), 144.5, 135.7, 132.0, 130.7 (d, *J* = 3.1 Hz), 130.1 (x2), 128.7 (d, *J* = 8.2 Hz) (x2), 127.1 (x2), 125.8 (q, *J* = 276.6 Hz), 115.7 (d, *J* = 21.7 Hz) (x2), 99.2 (q, *J* = 3.7 Hz), 48.8, 35.2 (q, *J* = 30.5 Hz), 21.7.

HRMS (ESI-TOF) m/z: [M+K]⁺ calcd for C₁₈H₁₇F₄KNO₂S 426.0548; found 426.0541.

IR (neat): ν = 3071, 2929, 1661, 1600, 1509, 1359, 1253, 1129, 1067, 811, 635, 509 cm⁻¹.

Compound 3d (*E*)-*N*-(2-bromobenzyl)-4-methyl-*N*-(4,4,4-trifluorobut-1-en-1-yl)benzenesulfonamide



$C_{18}H_{17}BrF_3NO_2S$
MW: 448.30 g.mol⁻¹
Colorless oil
80 % (44.2 mg)

The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 95:5 to 60:40) as eluent.

¹H NMR (300 MHz, CDCl₃): δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.52 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.32 – 7.22 (m, 2H), 7.18 – 7.08 (m, 1H), 6.97 (d, *J* = 14.2 Hz, 1H), 4.56 (s, 2H), 4.48 – 4.30 (m, 1H), 2.69 (qdd, *J* = 10.4, 7.5, 1.0 Hz, 2H), 2.45 (s, 3H).

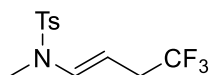
¹⁹F NMR (282 MHz, CDCl₃): δ -67.36.

¹³C NMR (126 MHz, CDCl₃): δ 144.6, 135.7, 133.6, 132.8, 131.8, 130.3 (x2), 129.2, 128.3, 127.9, 127.1 (x2), 125.8 (d, *J* = 278.6 Hz), 122.3, 98.9 (q, *J* = 3.7 Hz), 49.5, 35.2 (q, *J* = 30.5 Hz), 21.8.

HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₁₈H₁₈BrF₃NO₂S 448.0188; found 448.0187.

IR (neat): ν = 3036, 2960, 1662, 1597, 1442, 1362, 1276, 1255, 1167, 1138, 1046, 665 cm⁻¹.

Compound 3e (*E*)-*N*,4-dimethyl-*N*-(4,4,4-trifluorobut-1-en-1-yl)benzenesulfonamide



$C_{12}H_{14}F_3NO_2S$
MW: 293.30 g.mol⁻¹
Colorless oil
89 % (53.6 mg)

The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 95:05 to 60:40) as eluent.

¹H NMR (500 MHz, CDCl₃): δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 14.1 Hz, 1H), 4.58 (dt, *J* = 14.0, 7.5 Hz, 1H), 2.86 (s, 3H), 2.85 – 2.73 (m, 2H), 2.42 (s, 3H).

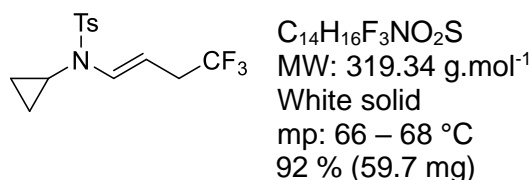
¹⁹F NMR (282 MHz, CDCl₃): δ -67.34.

¹³C NMR (126 MHz, CDCl₃): δ 144.3, 134.5, 133.8, 130.0 (x2), 127.1 (x2), 126.0 (q, *J* = 276.5 Hz), 97.6 (q, *J* = 3.8 Hz), 35.2 (q, *J* = 30.5 Hz), 32.1, 21.7.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₂H₁₄F₃NNaO₂S 316.0590; found 316.0581.

IR (neat): ν = 3064, 2931, 1662, 1598, 1356, 1335, 1276, 1248, 1162, 1137, 769, 665, 548 cm⁻¹.

Compound 3f (*E*)-*N*-cyclopropyl-4-methyl-*N*-(4,4,4-trifluorobut-1-en-1-yl)benzenesulfonamide



The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 95:05 to 60:40) as eluent.

¹H NMR (300 MHz, CDCl₃): δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 6.87 (d, *J* = 14.1 Hz, 1H), 5.00 (dt, *J* = 14.1, 7.6 Hz, 1H), 2.80 (qdd, *J* = 10.5, 7.6, 1.2 Hz, 2H), 2.43 (d, *J* = 0.8 Hz, 3H), 1.76 (tt, *J* = 6.7, 3.7 Hz, 1H), 1.01 – 0.79 (m, 4H).

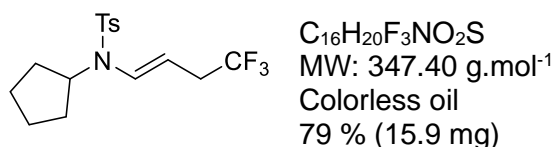
¹⁹F NMR (282 MHz, CDCl₃): δ -67.27.

¹³C NMR (126 MHz, CDCl₃): δ 144.3, 134.7, 134.2, 129.8 (x2), 127.6 (x2), 126.0 (q, *J* = 276.5 Hz), 100.8 (q, *J* = 3.7 Hz), 35.3 (q, *J* = 30.5 Hz), 27.0, 21.7, 8.2 (x2).

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₄H₁₆F₃NNaO₂S 342.0746; found 342.0746.

IR (neat): ν = 3087, 2931, 1658, 1598, 1365, 1257, 1186, 1125, 664, 601, 551 cm⁻¹.

Compound 3g (*E*)-*N*-cyclopentyl-4-methyl-*N*-(4,4,4-trifluorobut-1-en-1-yl)benzenesulfonamide



The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 95:05 to 60:40) as eluent.

¹H NMR (300 MHz, CDCl₃): δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 6.37 (d, *J* = 14.4 Hz, 1H), 5.16 (dt, *J* = 14.5, 7.5 Hz, 1H), 4.46 (p, *J* = 8.7 Hz, 1H), 2.80 (qdd, *J* = 10.5, 7.5, 1.2 Hz, 2H), 2.42 (s, 3H), 1.70 – 1.59 (m, 6H), 1.54 – 1.40 (m, 2H).

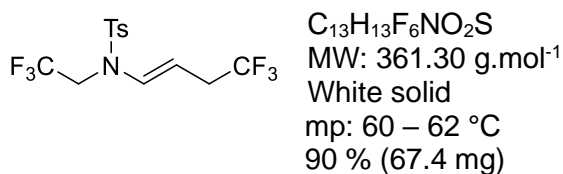
¹⁹F NMR (282 MHz, CDCl₃): δ -66.99.

¹³C NMR (126 MHz, CDCl₃): δ 143.8, 136.8, 129.7 (x2), 129.1, 127.1 (x2), 123.6 (q, *J* = 279.2 Hz), 105.4 (q, *J* = 3.5 Hz), 58.6, 35.9 (q, *J* = 30.4 Hz), 27.5 (x2), 24.4 (x2), 21.6.

HRMS (ESI-TOF) m/z: [M+K]⁺ calcd for C₁₆H₂₀F₃KNO₂S 386.0798; found 386.0801.

IR (neat): ν = 2960, 1875, 1660, 1340, 1273, 1252, 1160, 1137, 1091, 1064, 666, 548 cm⁻¹.

Compound 3h (*E*)-4-methyl-*N*-(4,4,4-trifluorobut-1-en-1-yl)-*N*-(2,2,2-trifluoroethyl)benzenesulfonamide



The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 95:05 to 60:40) as eluent.

¹H NMR (300 MHz, CDCl₃): δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.75 (d, *J* = 14.2 Hz, 1H), 4.94 (dt, *J* = 14.6, 7.4 Hz, 1H), 4.01 (q, *J* = 8.3 Hz, 2H), 2.80 (qdd, *J* = 10.3, 7.5, 1.1 Hz, 2H), 2.44 (s, 3H).

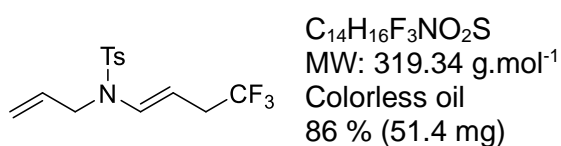
¹⁹F NMR (282 MHz, CDCl₃): δ -67.15, -68.53.

¹³C NMR (126 MHz, CDCl₃): δ 145.1, 135.2, 132.0, 130.2 (x2), 127.3 (x2), 125.7 (q, *J* = 278.1 Hz), 123.7 (q, *J* = 281.1 Hz), 101.1 (m), 47.1 (q, *J* = 36.2 Hz), 35.2 (q, *J* = 30.7 Hz), 21.7.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₃H₁₃F₆NNaO₂S 384.0463; found 384.0462.

IR (neat): ν = 2937, 1667, 1599, 1364, 1332, 1271, 1257, 1164, 1069, 1010, 666, 547 cm⁻¹.

Compound 3i (*E*)-*N*-allyl-4-methyl-*N*-(4,4,4-trifluorobut-1-en-1-yl)benzenesulfonamide



The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 95:05 to 60:40) as eluent.

¹H NMR (500 MHz, CDCl₃): δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 6.88 (d, *J* = 14.2 Hz, 1H), 5.60 (ddt, *J* = 17.2, 10.5, 5.3 Hz, 1H), 5.20 – 5.14 (m, 1H), 5.14 (t, *J* = 1.3 Hz, 1H), 4.67 (dt, *J* = 14.5, 7.4 Hz, 1H), 3.99 (dt, *J* = 5.3, 1.7 Hz, 2H), 2.77 (qdd, *J* = 10.5, 7.5, 1.2 Hz, 2H), 2.43 (s, 3H).

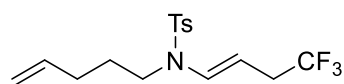
¹⁹F NMR (282 MHz, CDCl₃): δ -67.37.

¹³C NMR (126 MHz, CDCl₃): δ 144.3, 136.1, 131.9, 131.2, 130.0 (x2), 127.1 (x2), 126.0 (q, *J* = 276.5 Hz), 118.2, 98.2 (q, *J* = 3.8 Hz), 48.2, 35.3 (q, *J* = 30.5 Hz), 21.7.

HRMS (ESI-TOF) m/z: [M+K]⁺ calcd for C₁₄H₁₆F₃KNO₂S 359.0485; found 358.0476.

IR (neat): $\nu = 3070, 2929, 2874, 1662, 1598, 1357, 1274, 1254, 1164, 1133, 1089, 1067, 889, 814, 665, 593, 547 \text{ cm}^{-1}$.

Compound 3j (*E*)-4-methyl-*N*-(pent-4-en-1-yl)-*N*-(4,4,4-trifluorobut-1-en-1-yl)benzenesulfonamide



$\text{C}_{16}\text{H}_{20}\text{F}_3\text{NO}_2\text{S}$
MW: 347.40 g.mol⁻¹
Colorless oil
88 % (61.8 mg)

The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 95:05 to 60:40) as eluent.

¹H NMR (300 MHz, CDCl₃): δ 7.63 (d, $J = 8.3$ Hz, 2H), 7.30 (d, $J = 7.9$ Hz, 2H), 6.85 (d, $J = 14.3$ Hz, 1H), 5.76 (ddt, $J = 16.9, 10.2, 6.6$ Hz, 1H), 5.09 – 4.92 (m, 2H), 3.35 – 3.22 (m, 2H), 2.80 (qdd, $J = 10.4, 7.5, 1.2$ Hz, 2H), 2.42 (s, 3H), 2.15 – 1.93 (m, 2H), 1.74 – 1.58 (m, 2H), 1.29 – 1.22 (m, 1H).

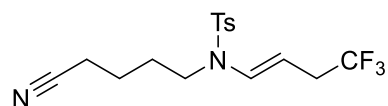
¹⁹F NMR (282 MHz, CDCl₃): δ -67.33.

¹³C NMR (126 MHz, CDCl₃): δ 144.1, 137.3, 136.0, 132.1, 130.0 (x2), 127.0 (x2), 126.0 (q, $J = 276.6$ Hz), 115.8, 97.4 (q, $J = 3.8$ Hz), 45.0, 35.4 (q, $J = 30.5$ Hz), 30.9, 25.9, 21.7.

HRMS (ESI-TOF) m/z: [M+K]⁺ calcd for C₁₆H₂₀F₃KNO₂S 386.0790; found 386.0790.

IR (neat): $\nu = 3081, 2828, 2857, 1661, 1358, 1341, 1307, 1276, 1186, 1138, 1091, 7071, 951, 911, 814, 665, 596, 560 \text{ cm}^{-1}$.

Compound 3k (*E*)-*N*-(4-cyanobutyl)-4-methyl-*N*-(4,4,4-trifluorobut-1-en-1-yl)benzenesulfonamide



$\text{C}_{16}\text{H}_{19}\text{F}_3\text{N}_2\text{O}_2\text{S}$
MW: 360.40 g.mol⁻¹
Colorless oil
82 % (57.4 mg)

The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 95:05 to 60:40) as eluent.

¹H NMR (300 MHz, CDCl₃): δ 7.62 (d, $J = 8.4$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 6.83 (d, $J = 14.3$ Hz, 1H), 4.67 (dt, $J = 14.6, 7.5$ Hz, 1H), 3.38 – 3.28 (m, 2H), 2.81 (qdd, $J = 10.4, 7.5, 1.2$ Hz, 2H), 2.43 (s, 5H), 1.77 – 1.69 (m, 4H).

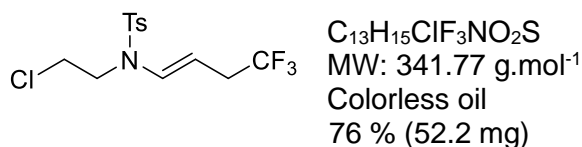
¹⁹F NMR (282 MHz, CDCl₃): δ -67.25.

¹³C NMR (126 MHz, CDCl₃): δ 144.3, 135.4, 131.8, 130.0 (x2), 126.9 (x2), 125.4 (q, $J = 274.4$ Hz), 119.2, 98.4 (q, $J = 3.7$ Hz), 44.2, 35.2 (q, $J = 30.5$ Hz), 25.3, 22.3, 21.6, 16.7.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₆H₁₉F₃N₂NaO₂S 383.1012; found 383.1008.

IR (neat): $\nu = 3060, 2944, 2876, 1661, 1598, 1340, 1255, 1162, 1099, 1063, 665, 597, 549 \text{ cm}^{-1}$.

Compound 3l (*E*)-*N*-(2-chloroethyl)-4-methyl-*N*-(4,4,4-trifluorobut-1-en-1-yl)benzenesulfonamide



The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 95:05 to 60:40) as eluent.

¹H NMR (300 MHz, CDCl₃): δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 14.3 Hz, 1H), 4.74 (dt, *J* = 14.2, 7.4 Hz, 1H), 3.59 (s, 4H), 2.81 (qdd, *J* = 10.4, 7.5, 1.2 Hz, 2H), 2.44 (s, 3H).

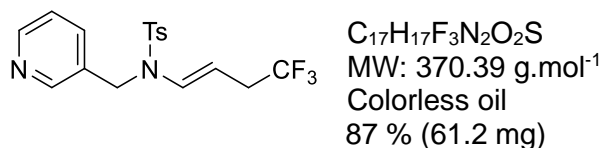
¹⁹F NMR (282 MHz, CDCl₃): δ -67.21.

¹³C NMR (126 MHz, CDCl₃): δ 144.7, 135.4, 131.9, 130.2 (x2), 127.1 (x2), 125.8 (q, *J* = 276.5 Hz), 97.7 (q, *J* = 3.8 Hz), 46.7, 39.2, 35.2 (q, *J* = 30.6 Hz), 21.7.

HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₁₃H₁₆ClF₃NO₂S 342.0537; found 342.0529.

IR (neat): ν = 3057, 2971n 1662, 1598, 1365, 1339, 1276n 1255, 1187, 1139, 1074, 905, 664, 549 cm⁻¹.

Compound 3m (*E*)-4-methyl-*N*-(pyridin-3-ylmethyl)-*N*-(4,4,4-trifluorobut-1-en-1-yl)benzenesulfonamide



The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 95:05 to 60:40) as eluent.

¹H NMR (500 MHz, CDCl₃): δ 8.50 (d, *J* = 20.9 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.22 (m, 1H), 6.92 (d, *J* = 14.3 Hz, 1H), 4.58 – 4.43 (m, 3H), 2.69 (qdd, *J* = 10.4, 7.5, 1.1 Hz, 2H), 2.44 (s, 3H).

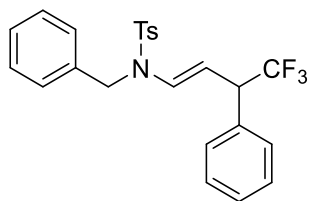
¹⁹F NMR (282 MHz, CDCl₃): δ -67.36.

¹³C NMR (126 MHz, CDCl₃): δ 149.3, 148.6, 144.7, 135.5, 135.5, 134.8, 131.8, 130.2 (x2), 123.8, 127.1 (x2), 125.7 (q, *J* = 276.6 Hz), 99.4 (q, *J* = 3.7 Hz), 47.0, 35.2 (q, *J* = 30.6 Hz), 21.7.

HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₁₇H₁₈F₃N₂O₂S 371.1036; found 371.1031.

IR (neat): ν = 3079, 2930, 1661, 1429, 1363, 1275, 1255, 1166, 1138, 1071, 666 cm⁻¹.

Compound 3n (*E*)-*N*-benzyl-4-methyl-*N*-(4,4,4-trifluoro-3-phenylbut-1-en-1-yl)benzenesulfonamide



$C_{24}H_{22}F_3NO_2S$
 MW: 445.50 g.mol⁻¹
 Colorless oil
 86 % (10.4 mg)

The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 100:00 to 60:40) as eluent.

¹H NMR (400 MHz, CDCl₃): δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.29 – 7.20 (m, 10H), 7.03 – 6.96 (m, 2H), 6.90 (d, *J* = 14.2 Hz, 1H), 4.92 (dd, *J* = 14.2, 8.8 Hz, 1H), 4.64 (d, *J* = 15.9 Hz, 1H), 4.46 (d, *J* = 15.9 Hz, 1H), 3.86 (p, *J* = 9.1 Hz, 1H), 2.44 (s, 3H).

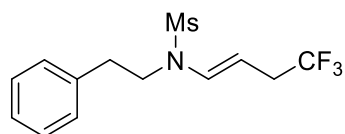
¹⁹F NMR (282 MHz, CDCl₃): δ -69.97.

¹³C NMR (126 MHz, CDCl₃): δ 144.3, 135.8, 135.0, 134.9, 131.1, 130.1 (x2), 129.4, 128.8 (x2), 128.8 (x2), 128.7 (x2), 128.2 (d, *J* = 65.5 Hz), 127.1 (x2), 127.1 (x2), 123.7 (q, *J* = 270.7 Hz), 105.4 (d, *J* = 2.9 Hz), 51.1 (q, *J* = 28.1 Hz), 49.6, 21.7.

HRMS (ESI-TOF) m/z: [M+K]⁺ calcd for C₂₄H₂₂F₃KNO₂S 484.0955; found 484.0941.

IR (neat): ν = 3090, 2957, 2872, 2357, 1659, 1520, 1455, 1363, 1250, 1165, 1107, 948, 738, 701, 666, 572 cm⁻¹.

Compound 3o (*E*)-*N*-phenethyl-*N*-(4,4,4-trifluorobut-1-en-1-yl)methanesulfonamide



$C_{13}H_{16}F_3NO_2S$
 MW: 307.33 g.mol⁻¹
 White solid
 mp: 88 – 90 °C
 69 % (32.2 mg)

The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 95:05 to 60:40) as eluent.

¹H NMR (300 MHz, CDCl₃): δ 7.37 – 7.20 (m, 5H), 6.69 (d, *J* = 14.0 Hz, 1H), 4.84 (dt, *J* = 14.3, 7.4 Hz, 1H), 3.83 – 3.67 (m, 2H), 2.99 – 2.93 (m, 2H), 2.84 (qdd, *J* = 10.4, 7.5, 1.2 Hz, 2H), 2.72 (s, 3H).

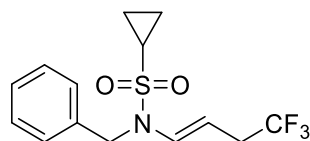
¹⁹F NMR (282 MHz, CDCl₃): δ -67.25.

¹³C NMR (126 MHz, CDCl₃): δ 138.0, 131.3, 129.0 (x2), 129.0 (x2), 127.1, 126.0 (d, *J* = 274.4 Hz), 97.3 (q, *J* = 3.8 Hz), 47.3, 39.6, 35.4 (q, *J* = 30.6 Hz), 33.6.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₃H₁₆F₃NNaO₂S 330.0746; found 330.0744.

IR (neat): ν = 3089, 3062, 3005, 2936, 1664, 1331, 1254, 1132, 1087, 967, 738, 700, 519 cm⁻¹.

Compound 3p (*E*)-*N*-benzyl-*N*-(4,4,4-trifluorobut-1-en-1-yl)cyclopropanesulfonamide



$C_{14}H_{16}F_3NO_2S$
 MW: 319.34 g.mol⁻¹
 Colorless oil
 79 % (55.5 mg)

The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 95:05 to 60:40) as eluent.

¹H NMR (300 MHz, CDCl₃): δ 7.42 – 7.19 (m, 5H), 6.80 (d, *J* = 14.2 Hz, 1H), 4.76 (s, 2H), 4.64 (dt, *J* = 14.3, 7.5 Hz, 1H), 2.70 (qdd, *J* = 10.5, 7.5, 1.1 Hz, 2H), 2.37 (tt, *J* = 8.0, 4.9 Hz, 1H), 1.31 – 1.14 (m, 2H), 1.11 – 0.91 (m, 2H).

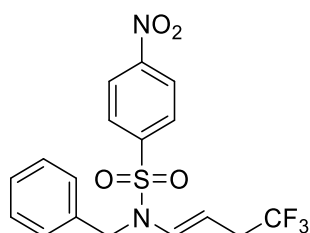
¹⁹F NMR (282 MHz, CDCl₃): δ -67.39.

¹³C NMR (126 MHz, CDCl₃): δ 135.4, 132.3, 128.8 (x2), 127.8, 126.9 (x2), 125.9 (q, *J* = 276.5 Hz), 97.8 (q, *J* = 3.8 Hz), 49.7, 35.2 (q, *J* = 30.5 Hz), 30.6, 5.7 (x2).

HRMS (ESI-TOF) *m/z*: [M+Na]⁺ calcd for C₁₄H₁₆F₃NaNO₂S 342.0746; found 342.0744.

IR (neat): ν = 3065, 2931, 1662, 1340, 1275, 1253, 1127, 1066, 946, 882, 696, 602, 541 cm⁻¹.

Compound 3q (*E*)-*N*-benzyl-4-nitro-*N*-(4,4,4-trifluorobut-1-en-1-yl)benzenesulfonamide



C₁₇H₁₅F₃N₂O₄S
MW: 400.37 g.mol⁻¹
Colorless oil
75 % (59.6 mg)

The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 95:05 to 60:40) as eluent.

¹H NMR (300 MHz, CDCl₃): δ 8.35 (d, *J* = 9.1 Hz, 2H), 7.94 (d, *J* = 9.1 Hz, 2H), 7.50 – 7.17 (m, 5H), 6.90 (d, *J* = 14.3 Hz, 1H), 4.73 (dt, *J* = 14.2, 7.5 Hz, 1H), 4.60 (s, 2H), 2.72 (qdd, *J* = 10.4, 7.5, 1.2 Hz, 2H).

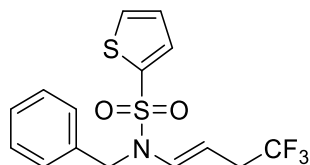
¹⁹F NMR (282 MHz, CDCl₃): δ -67.26.

¹³C NMR (126 MHz, CDCl₃): δ 150.5, 144.3, 134.1, 131.3, 128.9 (x2), 128.3 (x2), 128.1, 127.1 (x2), 125.6 (q, *J* = 280.2 Hz), 124.7 (x2), 101.4 (q, *J* = 3.8 Hz), 49.8, 35.2 (q, *J* = 30.6 Hz).

HRMS (ESI-TOF) *m/z*: [M+H]⁺ calcd for C₁₇H₁₆F₃N₂O₄S 401.0777; found 401.0777.

IR (neat): ν = 3107, 1663, 1532, 1350, 1254, 1170, 1137, 1090, 1068, 950, 855, 737, 684, 618, 545, 463 cm⁻¹.

Compound 3r (*E*)-*N*-benzyl-*N*-(4,4,4-trifluorobut-1-en-1-yl)thiophene-2-sulfonamide



C₁₅H₁₄F₃NO₂S₂
MW: 361.40 g.mol⁻¹
Colorless oil
85 % (51.2 mg)

The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 95:05 to 60:40) as eluent.

¹H NMR (500 MHz, CDCl₃): δ 7.64 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.58 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.35 – 7.23 (m, 5H), 7.11 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.88 (d, *J* = 14.2 Hz, 1H), 4.65 (dt, *J* = 14.4, 7.5 Hz, 1H), 4.58 (s, 2H), 2.70 (qdd, *J* = 10.4, 7.5, 1.0 Hz, 2H).

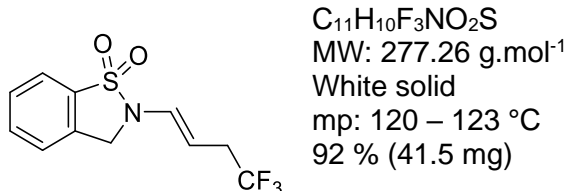
¹⁹F NMR (282 MHz, CDCl₃): δ -67.31.

¹³C NMR (126 MHz, CDCl₃): δ 139.0, 134.8, 132.8, 132.6, 131.6, 128.9 (x2), 127.9, 127.7, 127.0 (x2), 125.6 (q, *J* = 277.0 Hz), 100.6 (q, *J* = 3.8 Hz), 49.8, 35.3 (q, *J* = 30.6 Hz).

HRMS (ESI-TOF) m/z: [M+K]⁺ calcd for C₁₅H₁₄F₃KNO₂S₂ 400.0050; found 400.0039.

IR (neat): ν = 3165, 3068, 1663, 1367, 1344, 1276, 1255, 1164, 1138, 1070, 697, 607, 576 cm⁻¹.

Compound 3s (*E*)-2-(4,4,4-trifluorobut-1-en-1-yl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide



The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 95:05 to 60:40) as eluent.

¹H NMR (300 MHz, CDCl₃): δ 7.89 – 7.80 (m, 1H), 7.73 – 7.62 (m, 1H), 7.64 – 7.53 (m, 1H), 7.52 – 7.43 (m, 1H), 6.80 (d, *J* = 14.0 Hz, 1H), 4.90 (dt, *J* = 13.9, 7.4 Hz, 1H), 4.61 (s, 2H), 2.90 (qdd, *J* = 10.5, 7.4, 1.2 Hz, 2H).

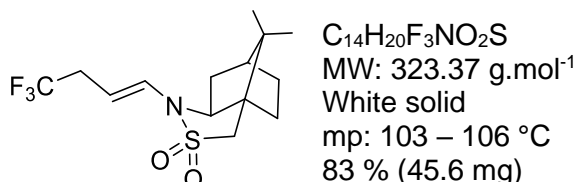
¹⁹F NMR (282 MHz, CDCl₃): δ -67.14.

¹³C NMR (126 MHz, CDCl₃): δ 134.3, 133.6, 132.0, 129.7, 127.2, 125.9 (d, *J* = 296.4 Hz), 124.8, 121.8, 98.2 (q, *J* = 3.9 Hz), 47.6, 35.4 (q, *J* = 30.7 Hz).

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₁H₁₀F₃NNaO₂S 300.0277; found 300.0275.

IR (neat): ν = 2928, 2868, 1668, 1307, 1282, 1214, 1172, 1162, 1128, 1065 cm⁻¹.

Compound 3t (6*S*,7*aS*)-8,8-dimethyl-1-((*E*)-4,4,4-trifluorobut-1-en-1-yl)hexahydro-3*H*-3*a*,6-methanobenzo[*c*]isothiazole 2,2-dioxide



The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 95:05 to 60:40) as eluent.

¹H NMR (300 MHz, CDCl₃): δ 6.32 (d, *J* = 14.1 Hz, 1H), 4.81 (ddd, *J* = 14.5, 8.0, 6.9 Hz, 1H), 3.41 (dd, *J* = 7.8, 4.8 Hz, 1H), 3.25 (d, *J* = 3.3 Hz, 2H), 2.95 – 2.69 (m, 2H), 2.15 – 2.01 (m, 1H), 1.96 – 1.89 (m, 3H), 1.87 – 1.76 (m, 1H), 1.54 – 1.44 (m, 1H), 1.39 – 1.31 (m, 1H), 1.08 (s, 3H), 0.95 (s, 3H).

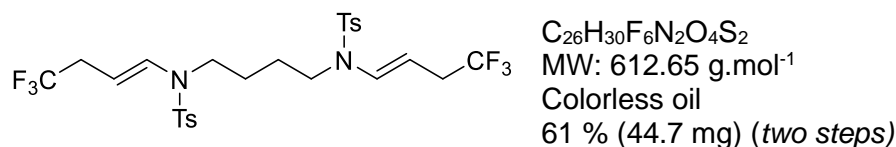
¹⁹F NMR (282 MHz, CDCl₃): δ -67.14.

¹³C NMR (126 MHz, CDCl₃): δ 126.7, 125.9 (q, *J* = 276.5 Hz), 102.2 (q, *J* = 3.7 Hz), 63.9, 50.4, 49.8, 48.1, 44.6, 36.0, 35.6 (q, *J* = 30.6 Hz), 32.2, 27.0, 20.3, 20.1.

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₄H₂₀F₃NNaO₂S 346.1059; found 346.1054.

IR (neat): ν = 2959, 2884, 1664, 1321, 1253, 1136, 1068 cm⁻¹.

Compound 3u 4-methyl-*N*-(4-((4-methyl-*N*-((*E*)-4,4,4-trifluorobut-1-en-1-yl)phenyl)sulfonamido)butyl)-*N*-((*E*)-4,4,4-trifluorobut-1-en-1-yl)benzenesulfonamide



This compound was obtained through a sequential two steps procedure from **1u**.

The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 95:05 to 60:40) as eluent.

¹H NMR (300 MHz, CDCl₃): δ 7.63 (d, *J* = 8.3 Hz, 4H), 7.31 (d, *J* = 8.5 Hz, 4H), 6.80 (d, *J* = 14.3 Hz, 2H), 4.66 (dt, *J* = 14.6, 7.5 Hz, 2H), 3.35 – 3.24 (m, 4H), 2.80 (qdd, *J* = 10.4, 7.4, 1.1 Hz, 4H), 2.43 (s, 6H), 1.66 – 1.57 (m, 4H).

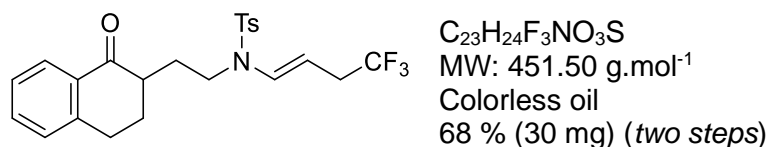
¹⁹F NMR (282 MHz, CDCl₃): δ -67.27.

¹³C NMR (126 MHz, CDCl₃): δ 144.3 (x2), 135.7 (x2), 132.0 (x2), 130.1 (x4), 127.0 (x4), 126.0 (q, *J* = 276.5 Hz) (x2), 98.4 (q, *J* = 3.7 Hz) (x2), 44.7 (x2), 35.3 (q, *J* = 30.5 Hz) (x2), 23.5 (x2), 21.7 (x2).

HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₂₆H₃₁F₆N₂O₄S₂ 613.1624; found 613.1626.

IR (neat): ν = 3089, 2931, 2882, 1661, 1339, 1253, 1163, 1063, 890, 846, 814, 664, 595, 548 cm⁻¹.

Compound 3v (*E*)-4-methyl-*N*-(2-(1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)ethyl)-*N*-(4,4,4-trifluorobut-1-en-1-yl)benzenesulfonamide



This compound was obtained through a sequential two steps procedure from **1v**.

The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 95:05 to 60:40) as eluent.

¹H NMR (500 MHz, CDCl₃): δ 7.99 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.46 (td, *J* = 7.5, 1.5 Hz, 1H), 7.36 – 7.26 (m, 3H), 7.23 (d, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 14.3 Hz, 1H), 4.96 (dt, *J* = 14.7, 7.5 Hz, 1H), 3.59 – 3.50 (m, 1H), 3.51 – 3.41 (m, 1H), 3.14 – 2.94 (m, 2H), 2.89 – 2.76 (m, 2H), 2.62 – 2.51 (m, 1H), 2.41 (s, 3H), 2.32 – 2.16 (m, 2H), 1.97 – 1.85 (m, 1H), 1.77 – 1.65 (m, 1H).

¹⁹F NMR (282 MHz, CDCl₃): δ -67.20.

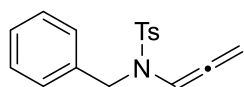
¹³C NMR (126 MHz, CDCl₃): δ 120.0, 144.2, 144.0, 135.9, 133.5, 132.6, 132.0, 130.0 (x2), 128.9, 128.9 (d, *J* = 265.6 Hz), 127.5, 127.0 (x2), 126.8, 98.2 (q, *J* = 4.0 Hz), 45.4, 43.9, 35.4 (d, *J* = 30.3 Hz), 29.7, 29.3, 27.8, 21.7.

HRMS (ESI-TOF) m/z: [M+K]⁺ calcd for C₂₃H₂₄F₃KNO₃S 490.1061; found 490.1050.

IR (neat): ν = 3072, 2930, 1681, 2661, 1600, 1342, 1276, 1255, 1186, 1136 cm⁻¹.

Terminal *N*-allenamide 4

Compound 4 *N*-benzyl-4-methyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide Erreur ! Signet non défini.



$C_{17}H_{17}NO_2S$
MW: 299.39 g.mol⁻¹
Colorless oil
66 %

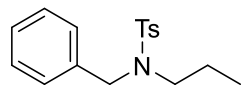
The product was obtained by column chromatography on silica gel using Petroleum ether / EtOAc (from 100:0 to 95:05) as eluent.

¹H NMR (300 MHz, CDCl₃): δ = 7.68 (d, *J* = 8.3 Hz, 2H), 7.30 – 7.20 (m, 7H), 6.79 (t, *J* = 6.2 Hz, 1H), 5.10 (d, *J* = 6.2 Hz, 2H), 4.26 (s, 2H), 2.41 (s, 3H).

This analytical data match with those described in the literature.

Various syntheses 5-7

Compound 5 *N*-benzyl-4-methyl-*N*-propylbenzenesulfonamide



$C_{17}H_{21}NO_2S$
MW: 303.42 g.mol⁻¹
Colorless oil
42 % (31.8 mg)

The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 100:0 to 80:20) as eluent.

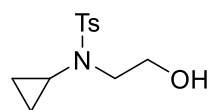
¹H NMR (500 MHz, CDCl₃): δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.25 (m, 7H), 4.32 (s, 2H), 3.08 – 3.01 (m, 2H), 2.44 (s, 3H), 1.34 (dq, *J* = 14.9, 7.4 Hz, 2H), 0.70 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃): δ 143.3, 137.3, 136.8, 129.8 (x2), 128.6 (x2), 128.4 (x2), 127.8, 127.3 (x2), 52.0, 50.0, 21.7, 21.5, 11.3.

HRMS (ESI-TOF) m/z: [M+K]⁺ calcd for C₁₇H₂₁KNO₂S 342.0925; found 342.0921.

IR (neat): ν = 3063, 3030, 2967, 2934, 2875, 1598, 1495, 1455, 1338, 1157, 1091, 1034, 940, 815, 736, 655, 549 cm⁻¹.

Compound 6 *N*-cyclopropyl-*N*-(2-hydroxyethyl)-4-methylbenzenesulfonamide



$C_{12}H_{17}NO_3S$
MW: 255.33 g.mol⁻¹
White solid
61 % (24.9 mg)

The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 88:12 to 0:100) as eluent.

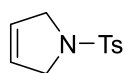
¹H NMR (400 MHz, CDCl₃): δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 3.80 (q, *J* = 5.6 Hz, 2H), 3.31 (t, *J* = 5.5 Hz, 2H), 2.44 (s, 3H), 2.18 – 2.05 (m, 2H), 0.95 – 0.85 (m, 2H), 0.76 – 0.64 (m, 2H).

¹³C NMR (126 MHz, CDCl₃): δ 143.9, 134.8, 129.8 (x2), 127.9 (x2), 61.3, 53.7, 32.0, 21.7, 7.7 (x2).

HRMS (ESI-TOF) m/z: [M+Na]⁺ calcd for C₁₂H₁₇NNaO₃S 278.0821; found 278.0814.

IR (neat): ν = 3537, 3022, 2927, 1891, 1597, 1454, 1334, 1304, 1155, 1108, 1034, 866, 816, 691, 579, 548 cm⁻¹.

Compound 7 1-tosyl-2,5-dihydro-1H-pyrrole¹⁰



C₁₁H₁₃NO₂S
MW: 223.29 g.mol⁻¹
White solid
95 % (55 mg)

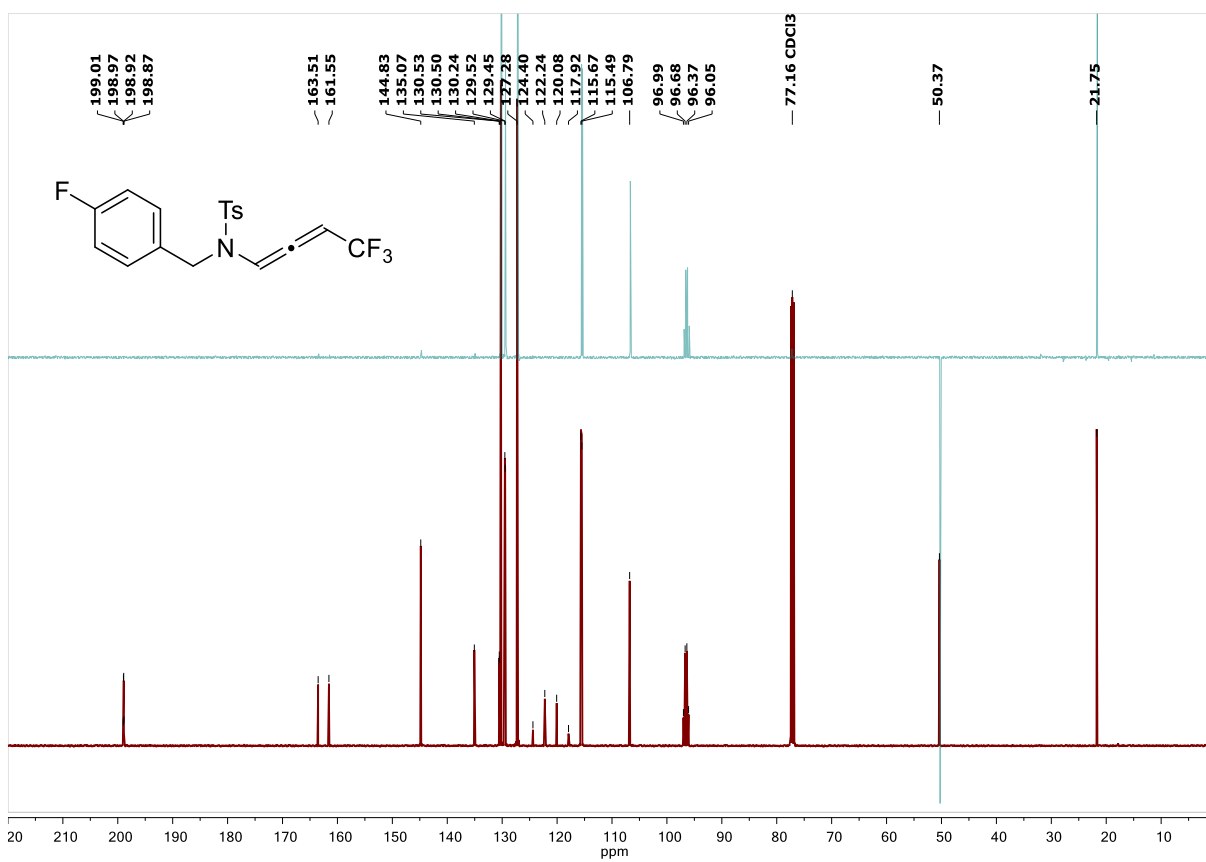
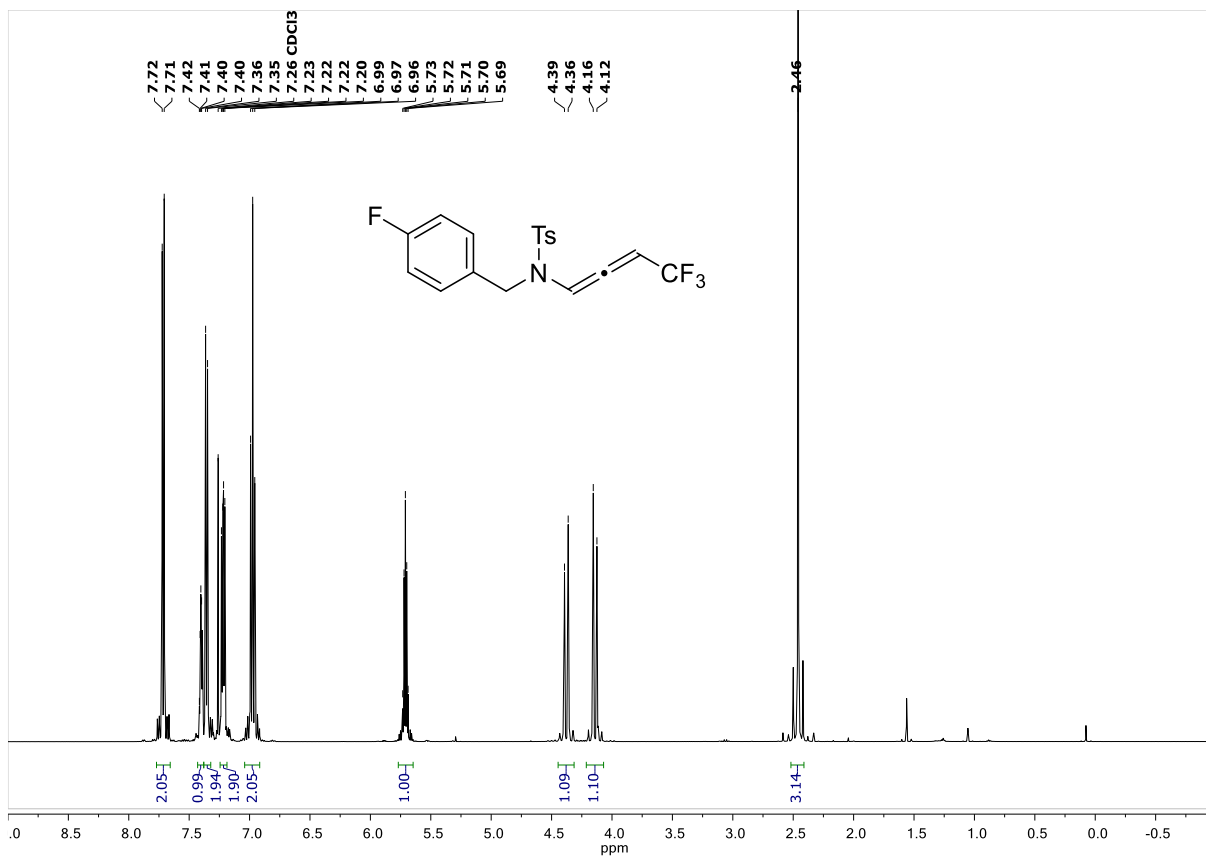
The product was obtained by column chromatography on silica gel using petroleum ether/EtOAc (from 95:05 to 60:40) as eluent.

¹H NMR (400 MHz, CDCl₃): δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.65 (s, 2H), 4.12 (s, 4H), 2.42 (s, 3H).

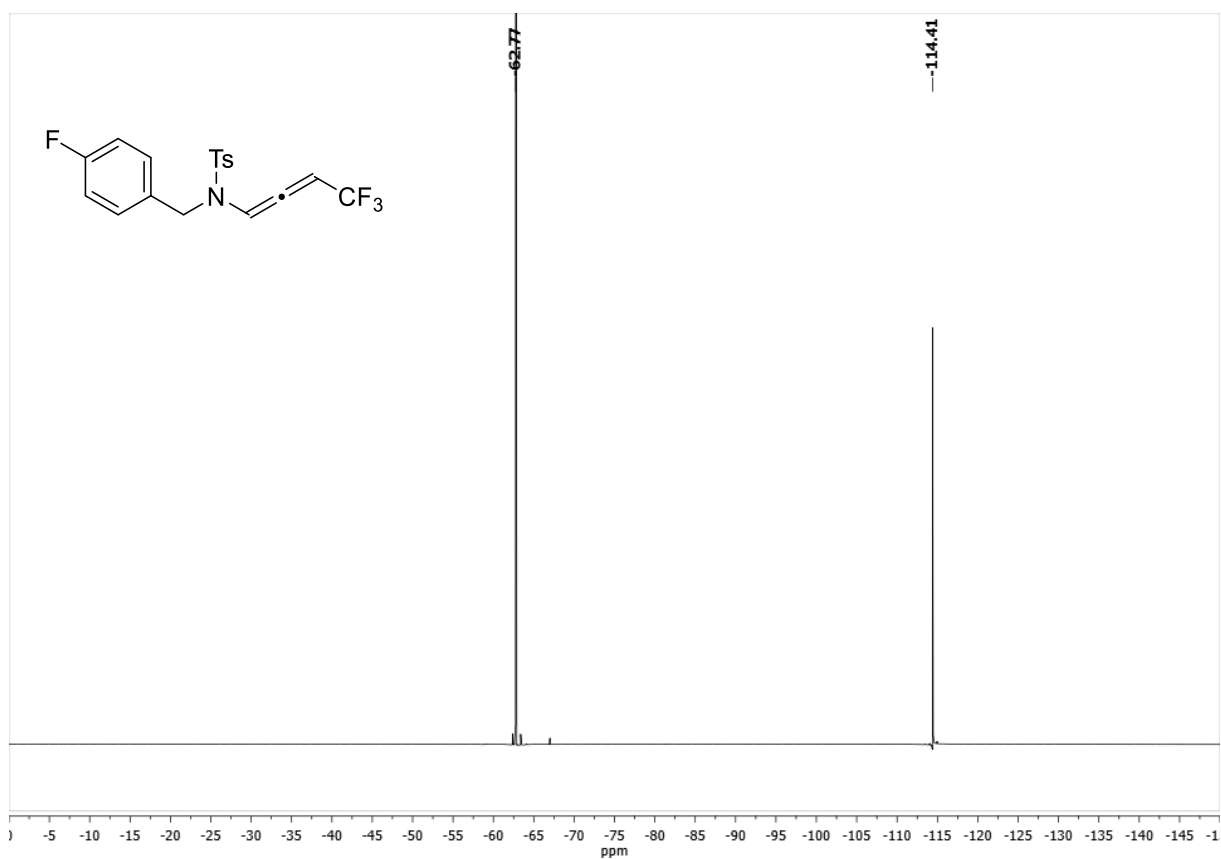
This analytical data match with those described in the literature.

NMR Spectra

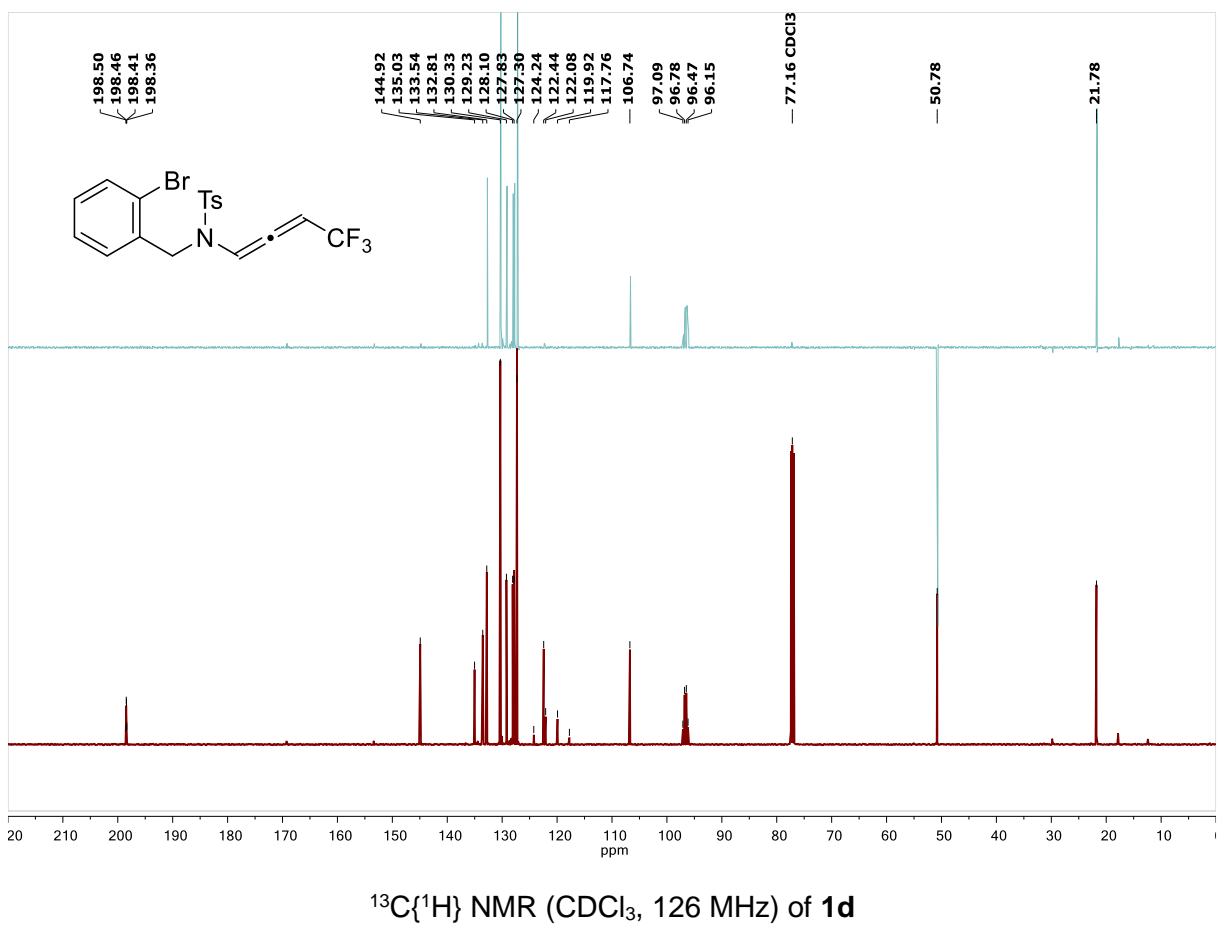
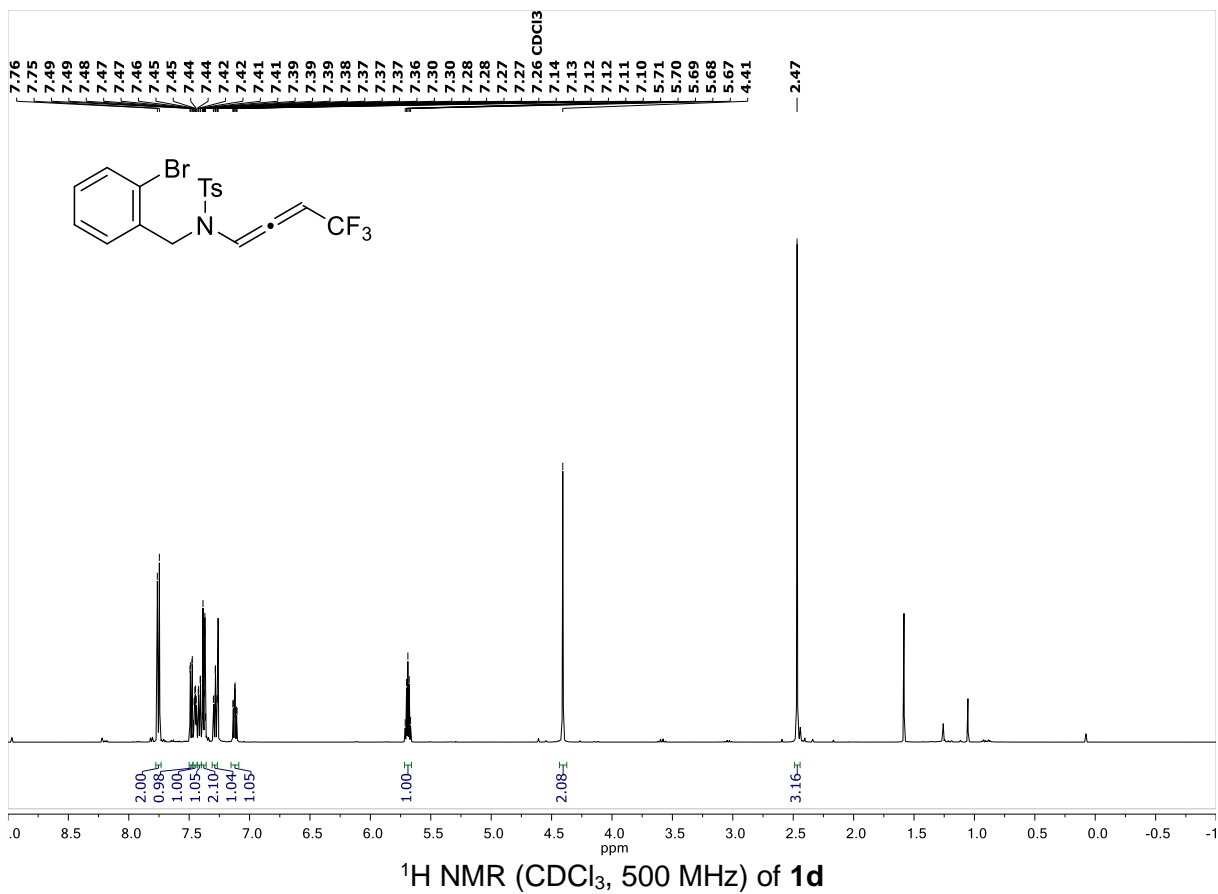
¹⁰ C. A. Urbina-Blanco, X. Bantreil, J. Wappel, T. E. Schmid, A. M. Z. Slawin, C. Slugovc and C. S. J. Cazin, *Organometallics*, 2013, **32**, 6240–6247.

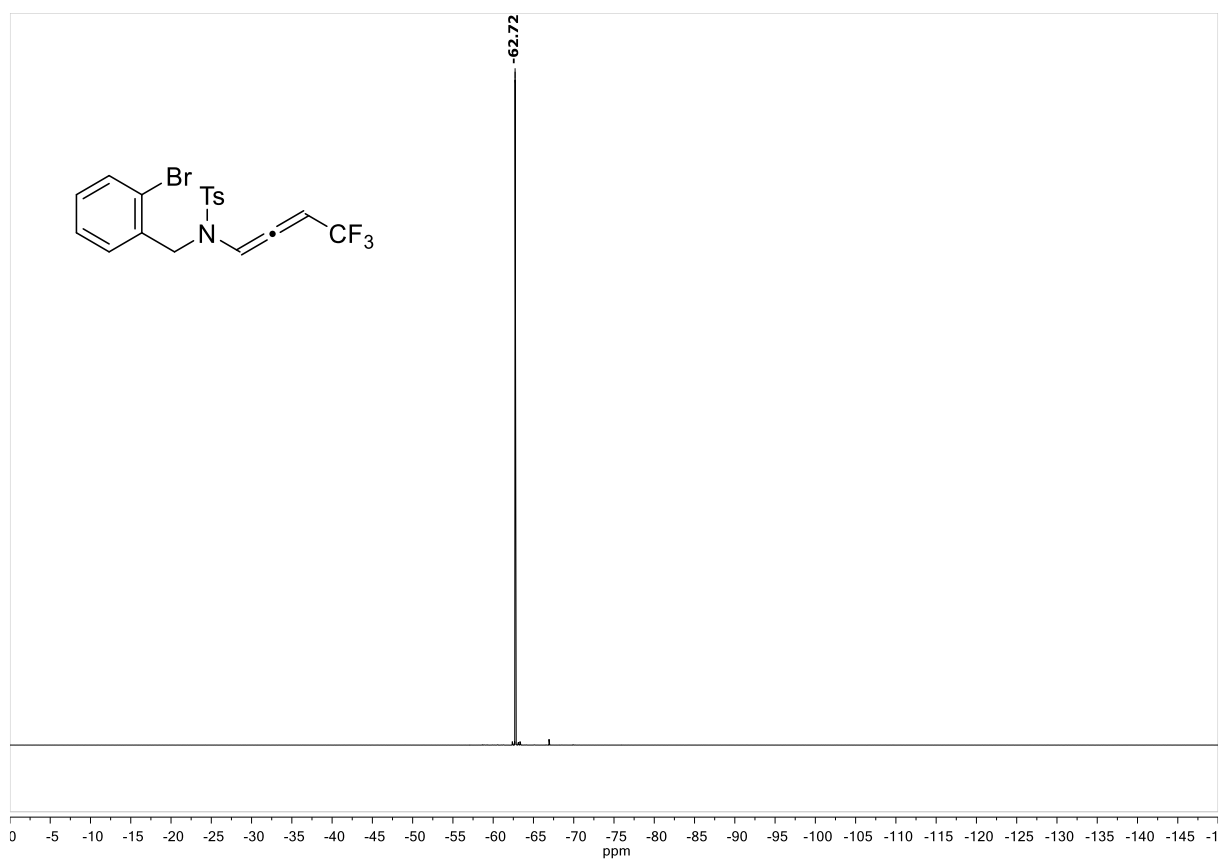


¹³C{¹H} NMR (CDCl₃, 126 MHz) of **1c**
S36

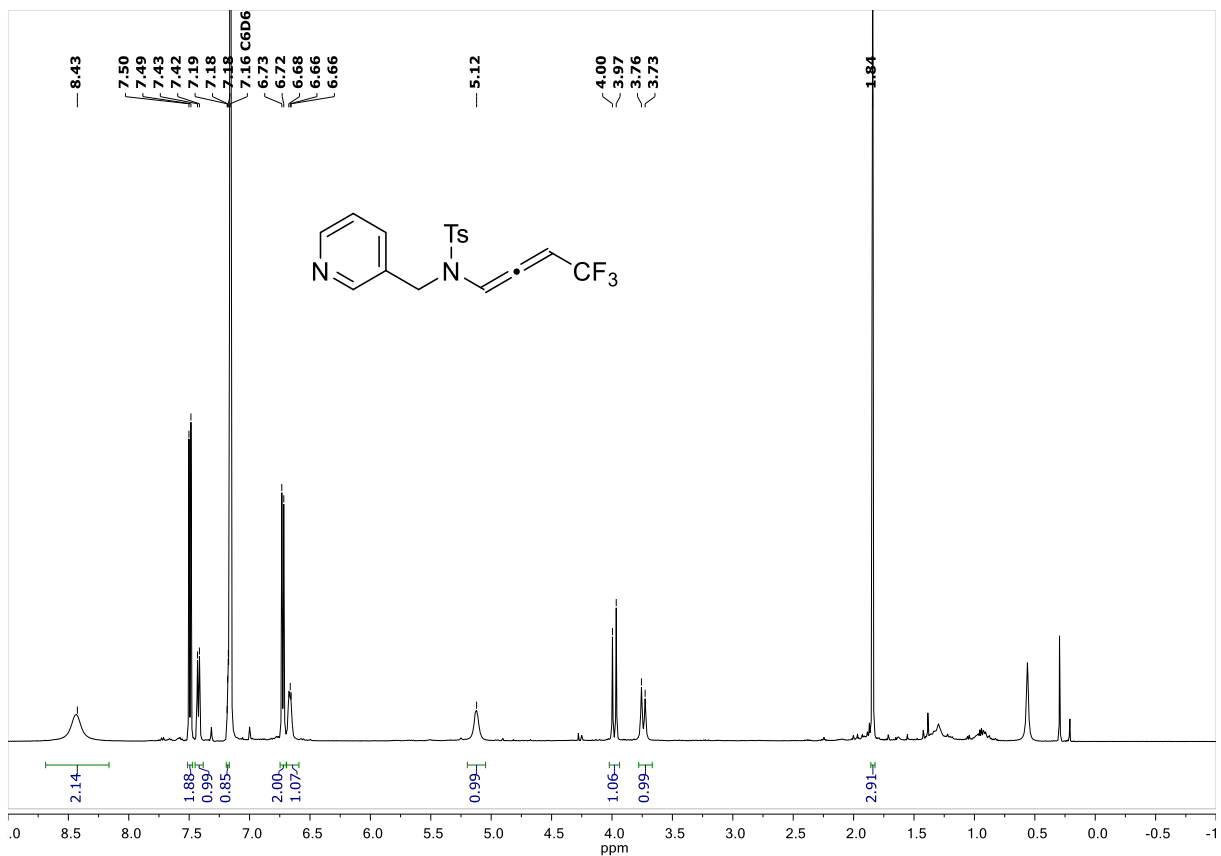


$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 282 MHz) of **1c**

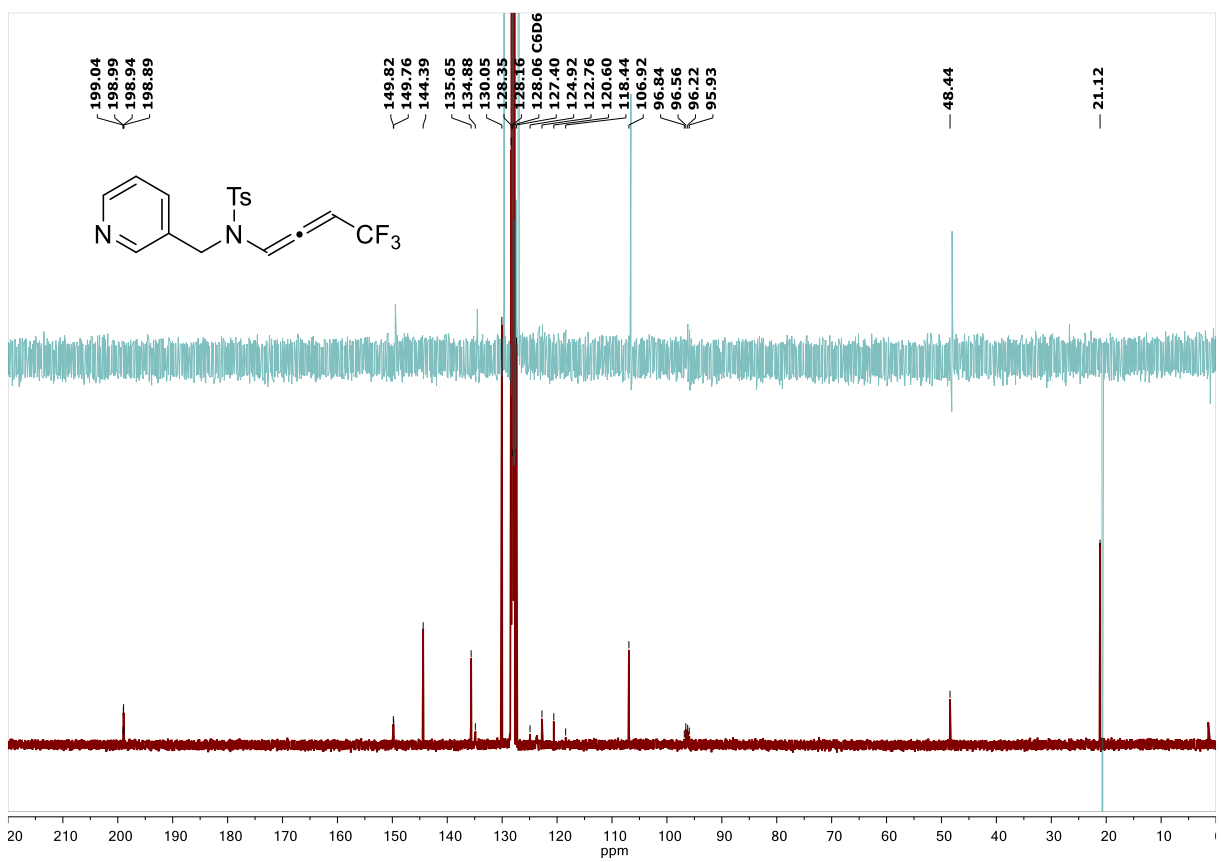




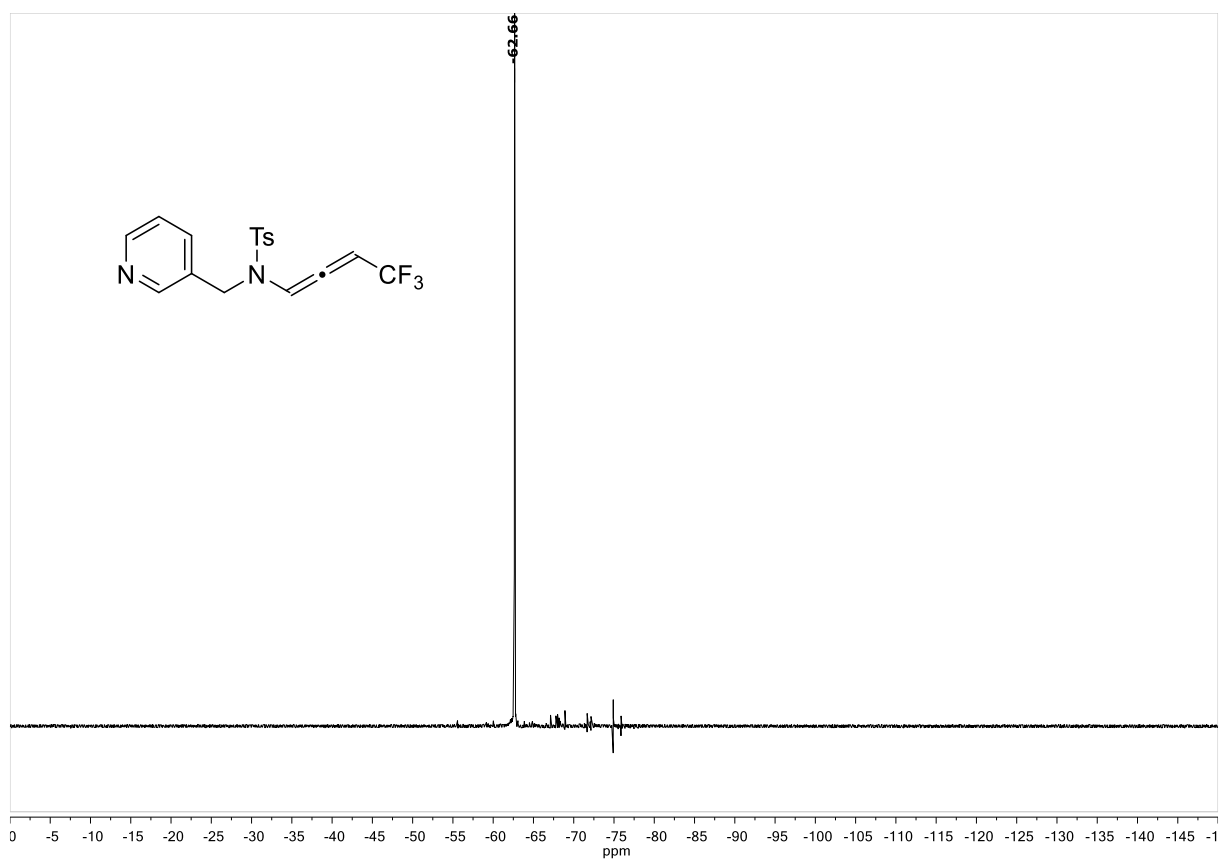
$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 282 MHz) of **1d**



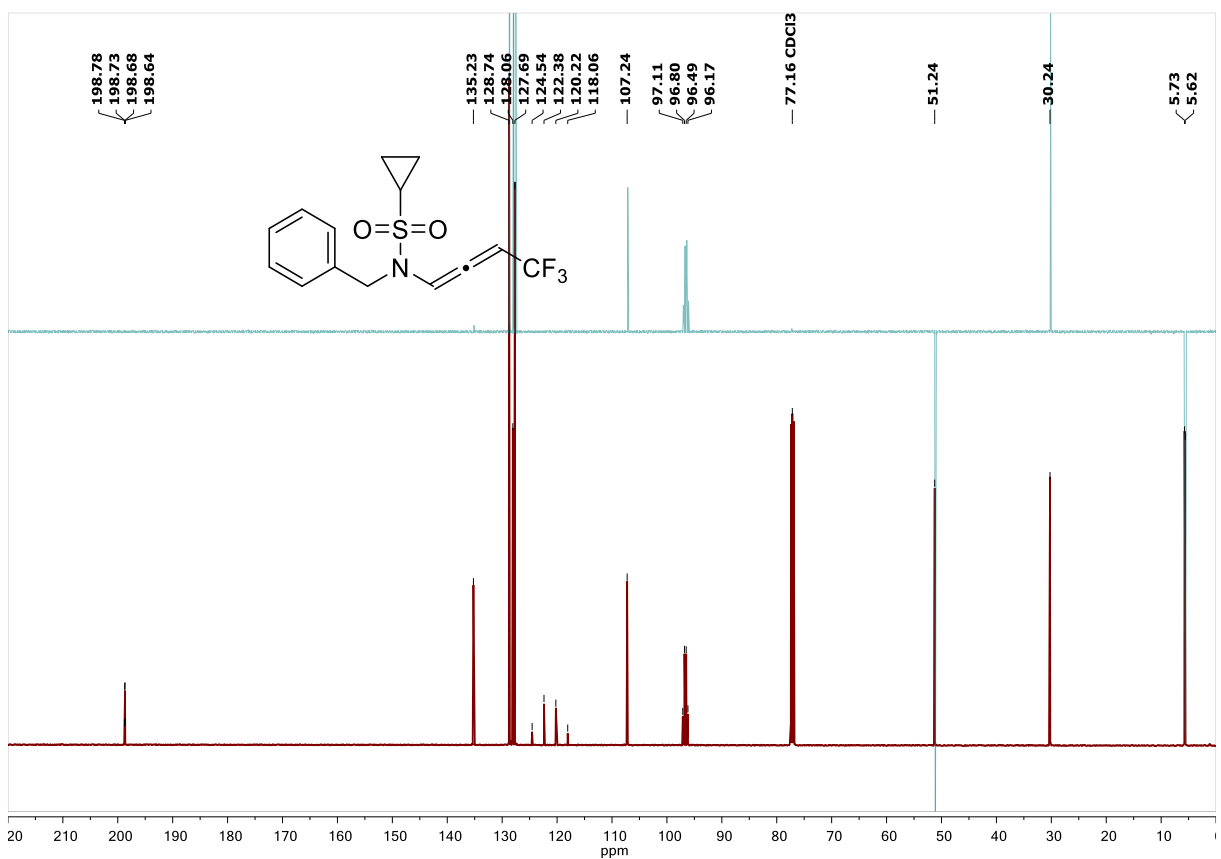
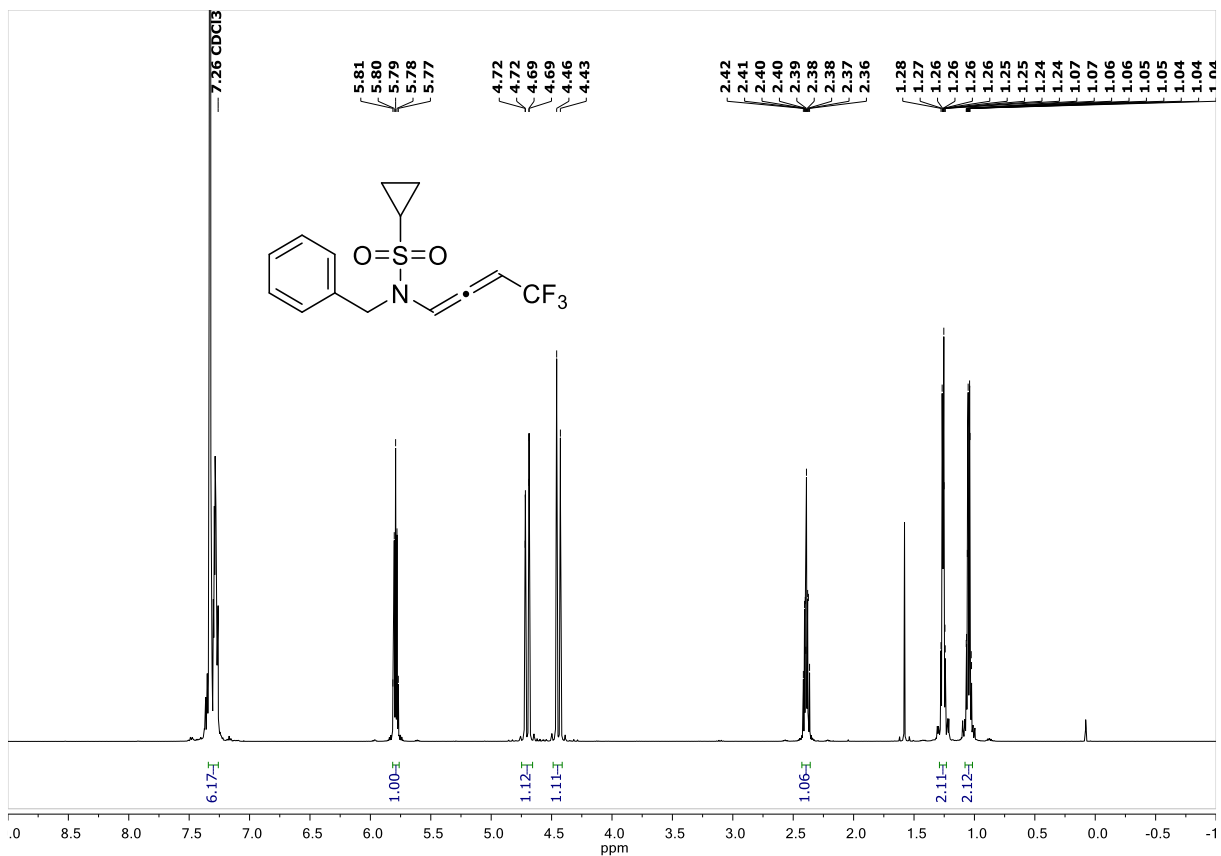
¹H NMR (C₆D₆, 500 MHz) of 1m

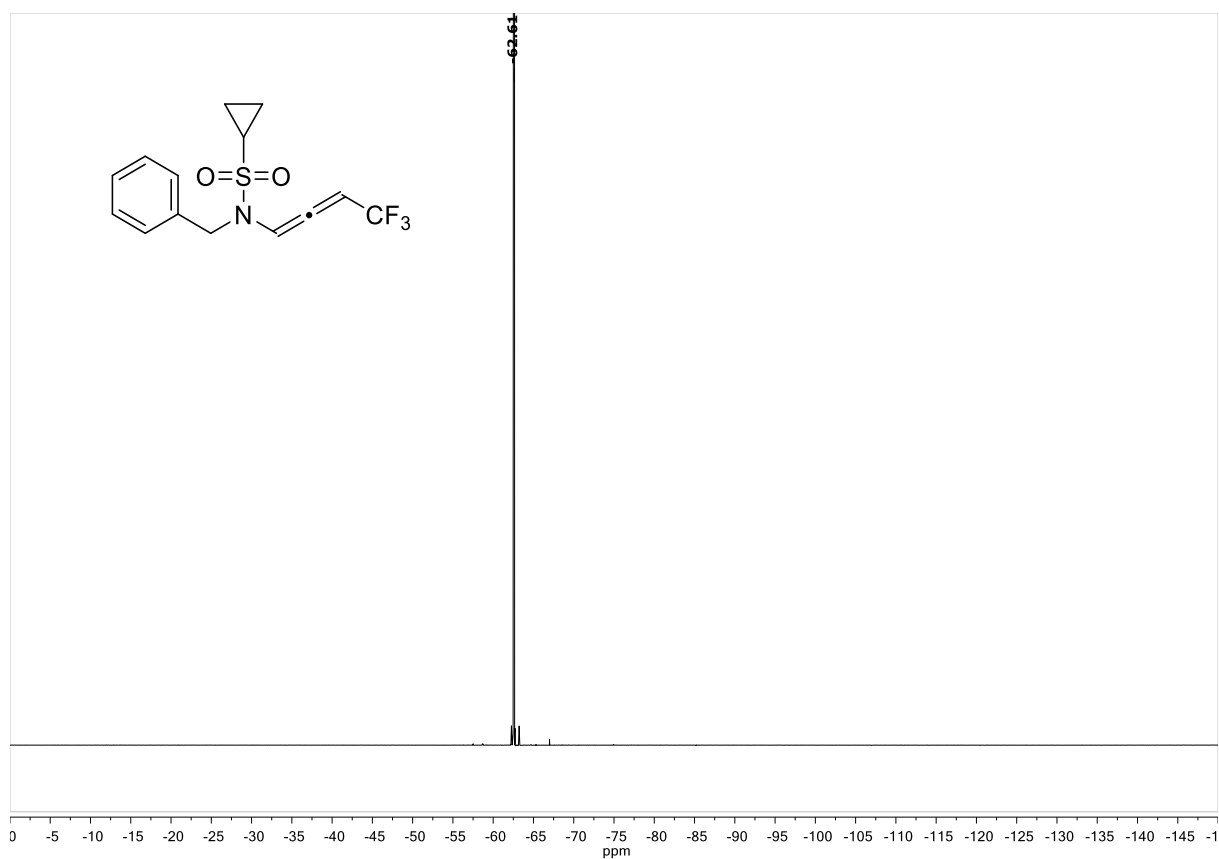


¹³C{¹H} NMR (C₆D₆, 126 MHz) of 1m
S40

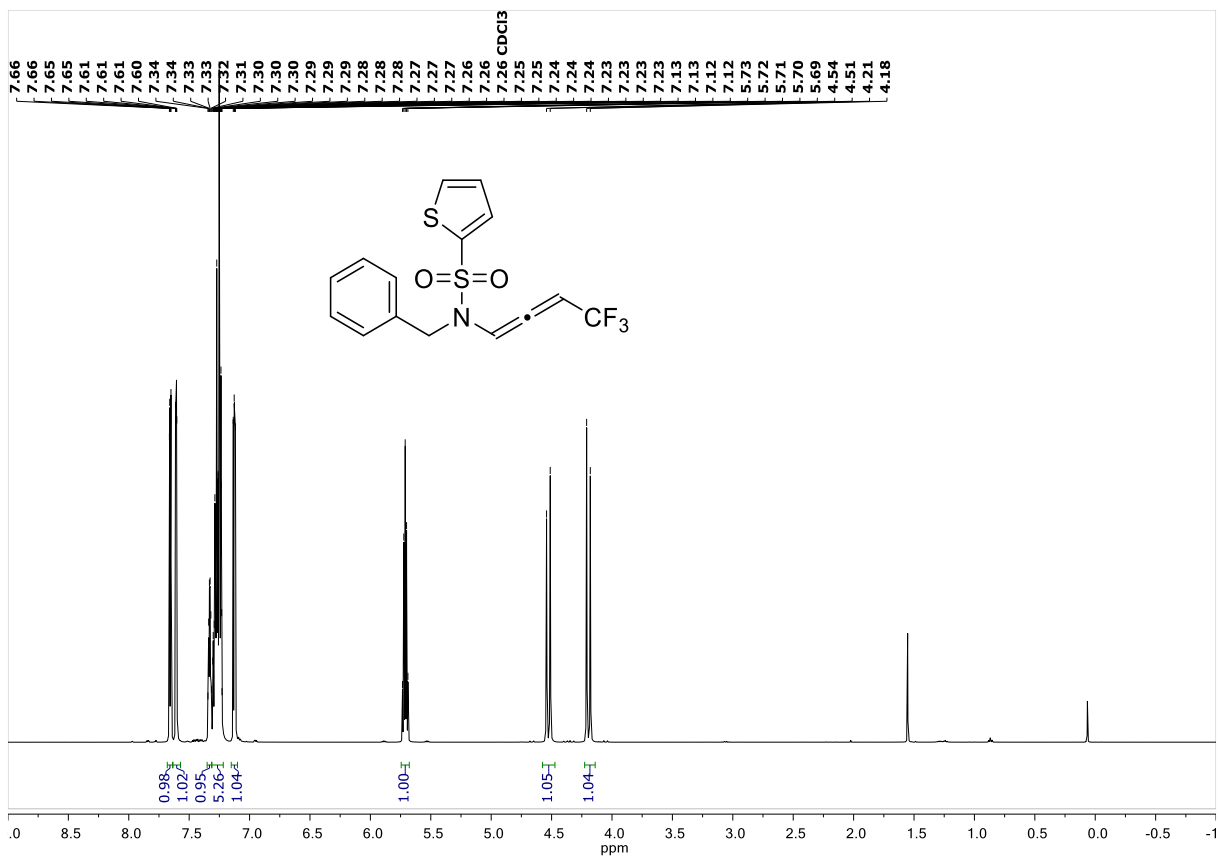


$^{19}\text{F}\{^1\text{H}\}$ NMR (C_6D_6 , 282 MHz) of **1m**

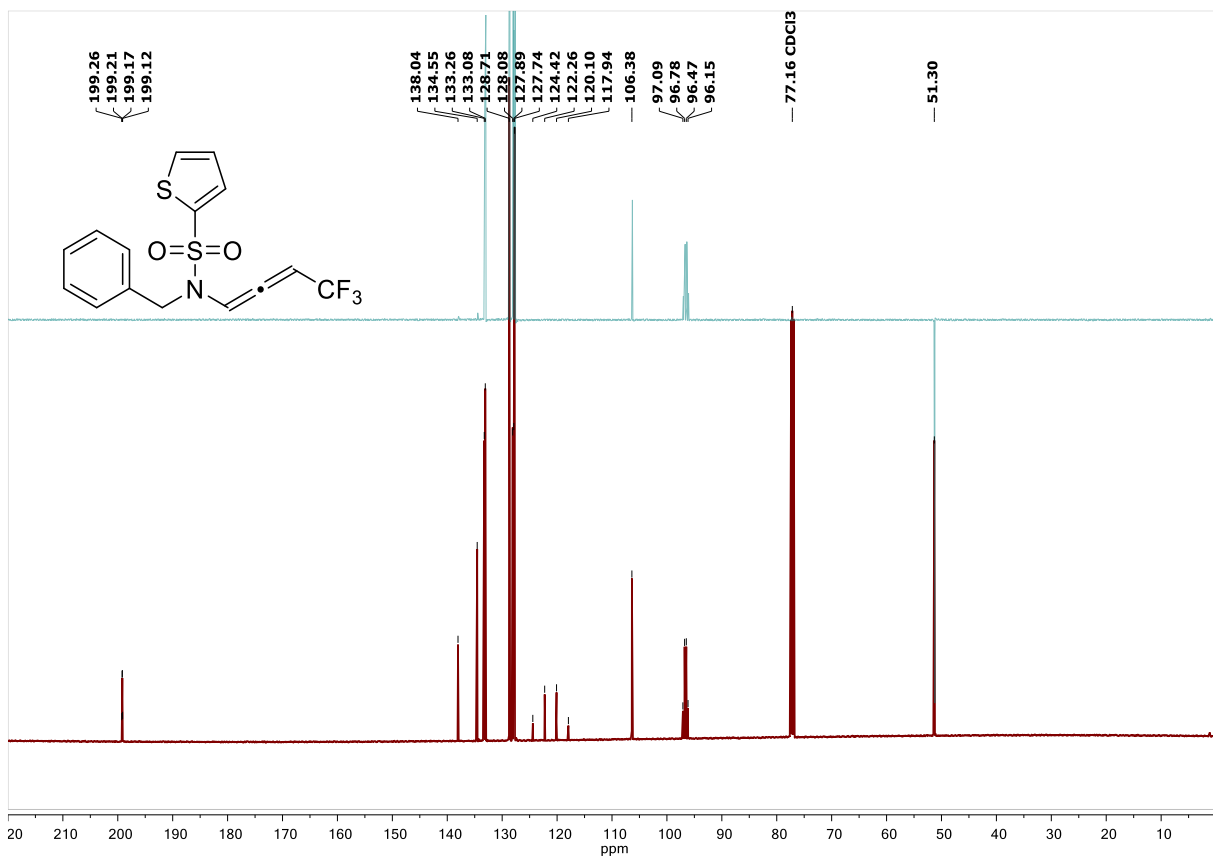




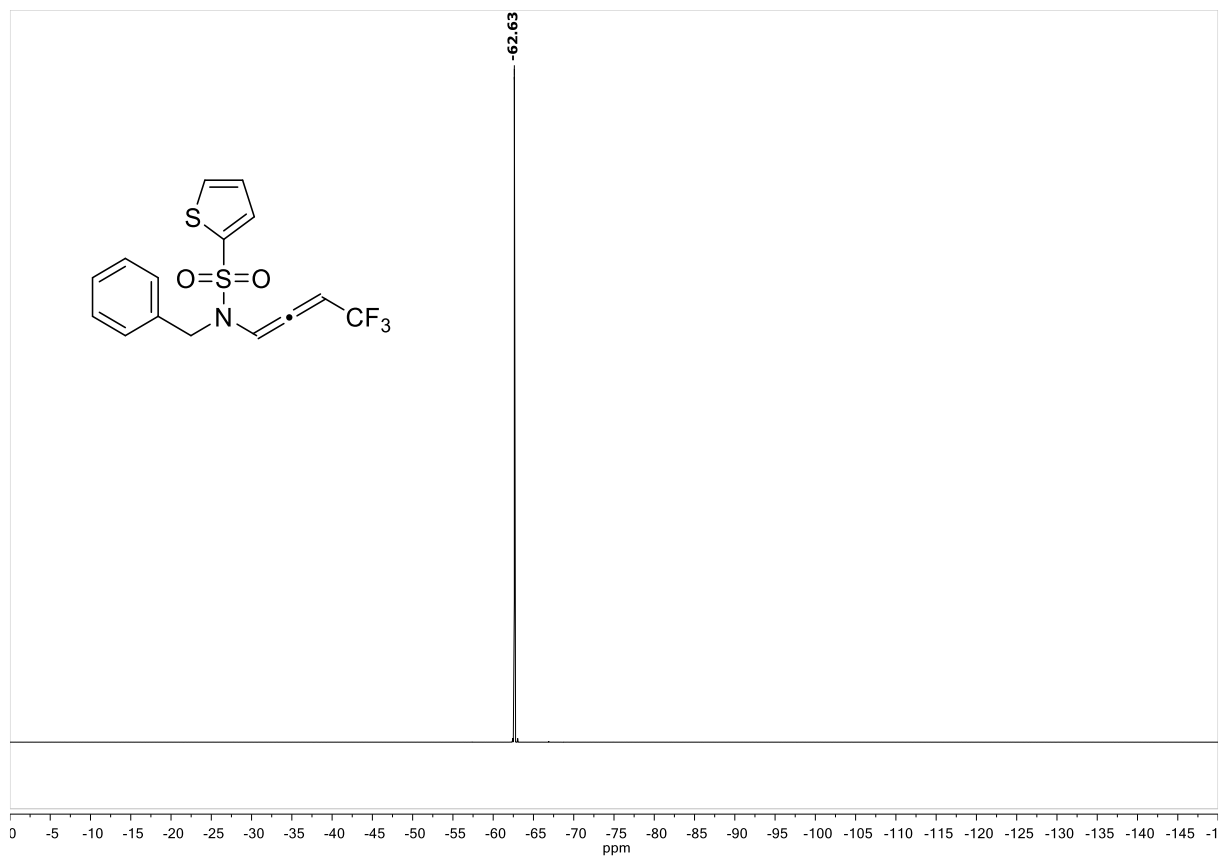
$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 282 MHz) of **1p**

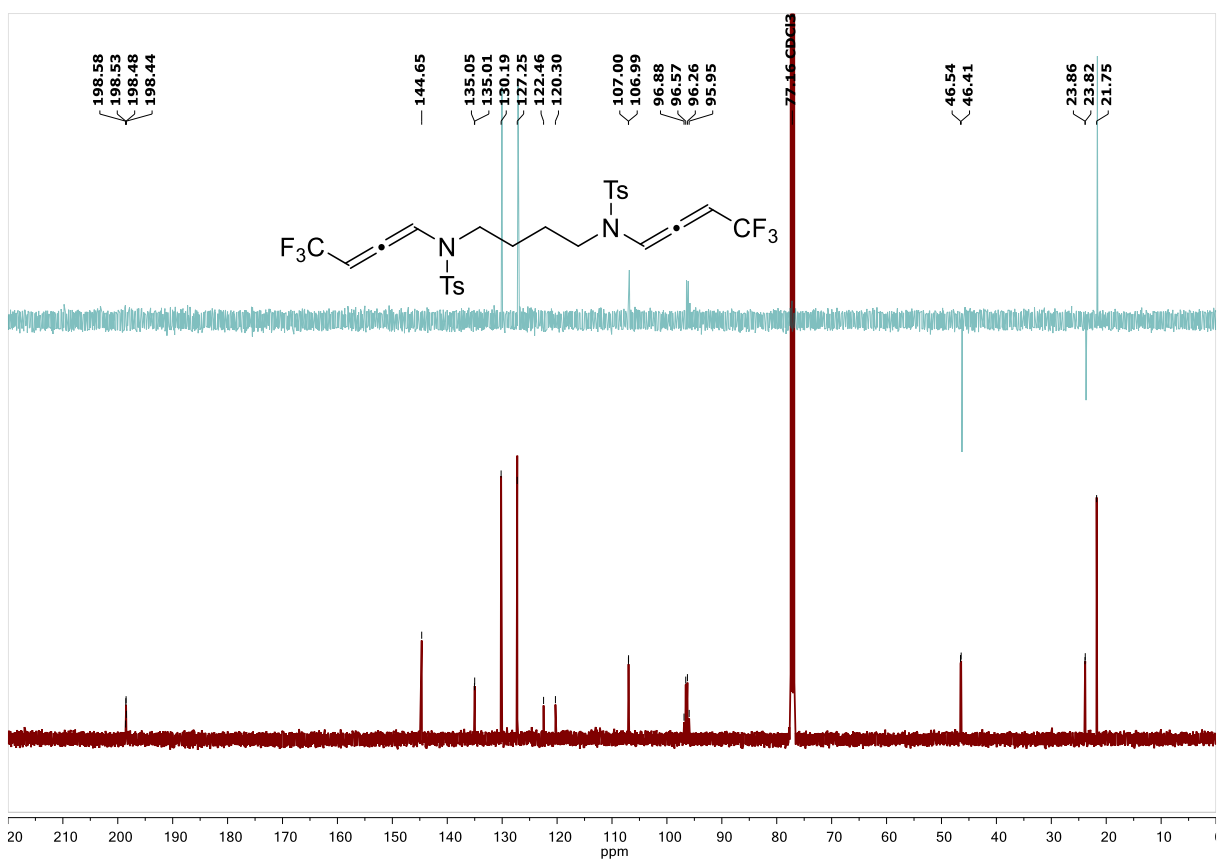
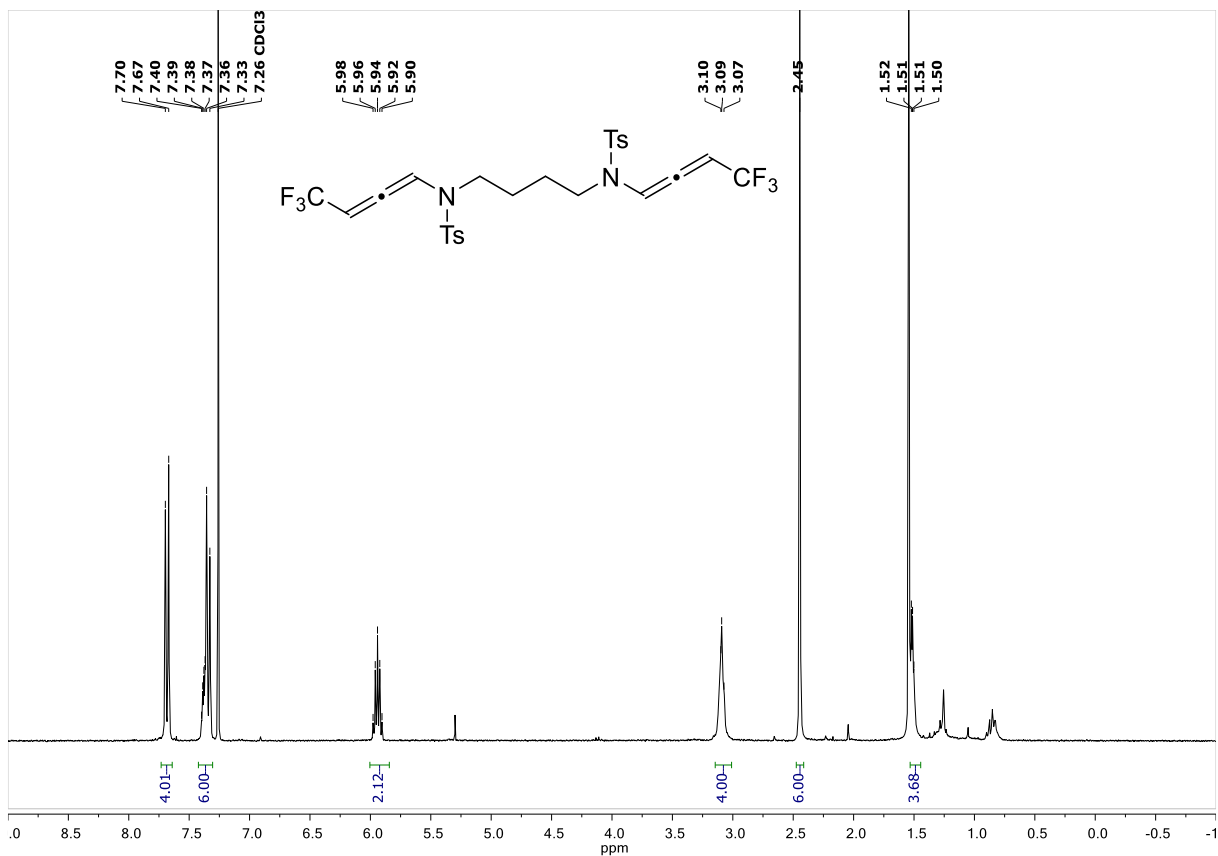


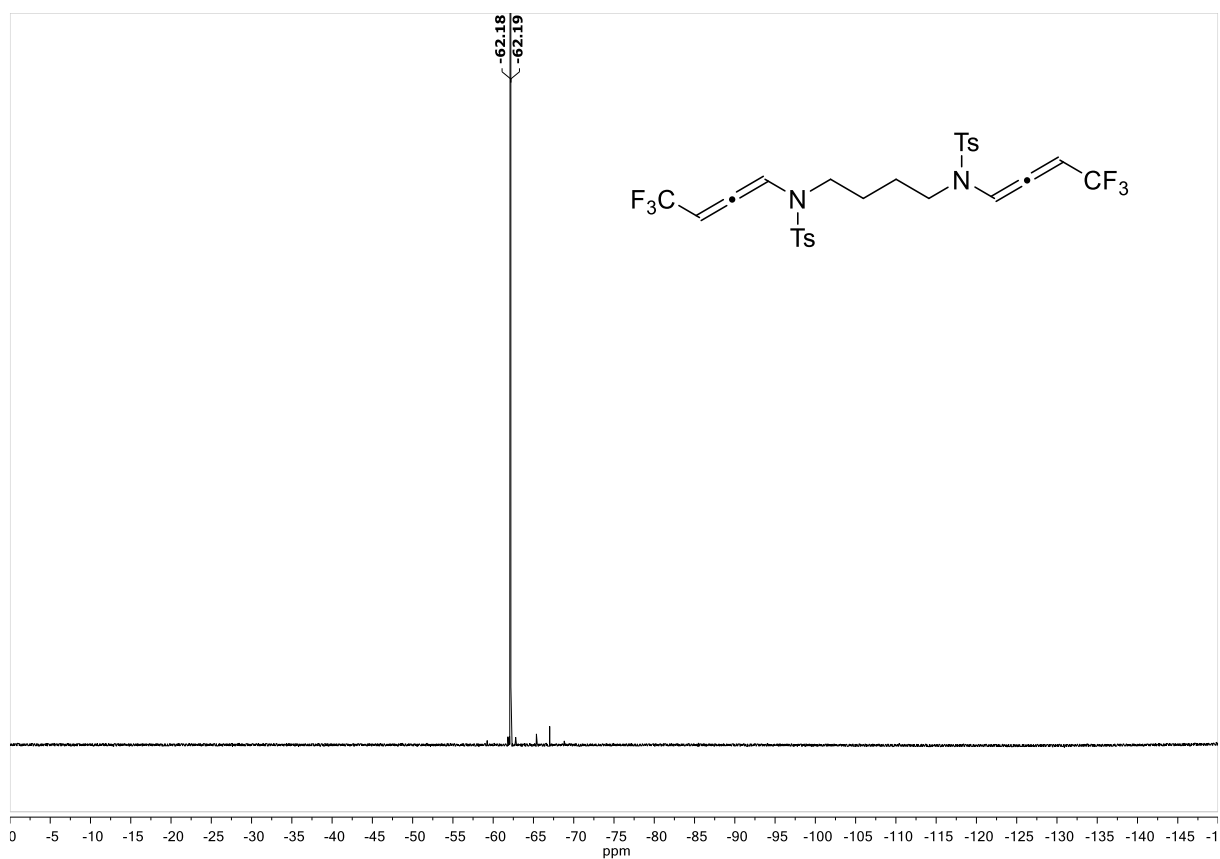
¹H NMR (CDCl₃, 500 MHz) of 1r



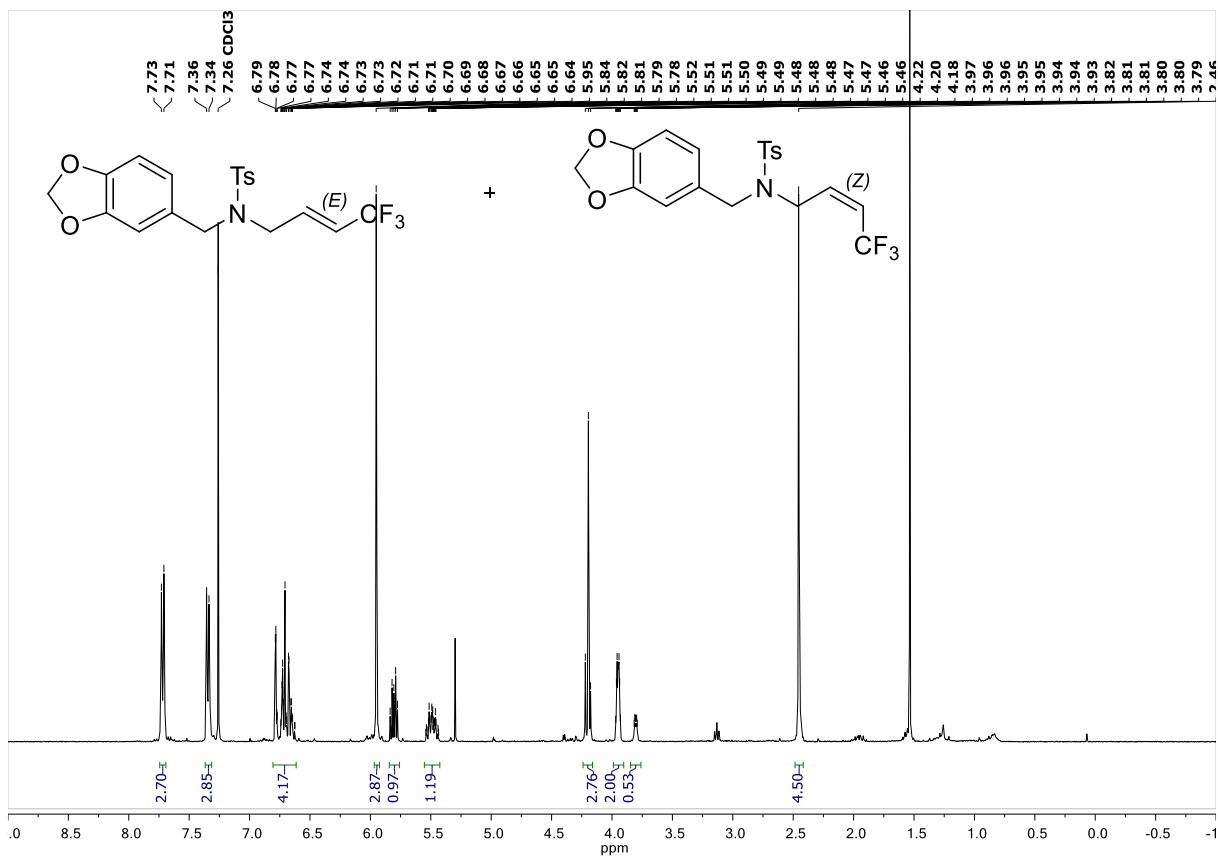
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 1r



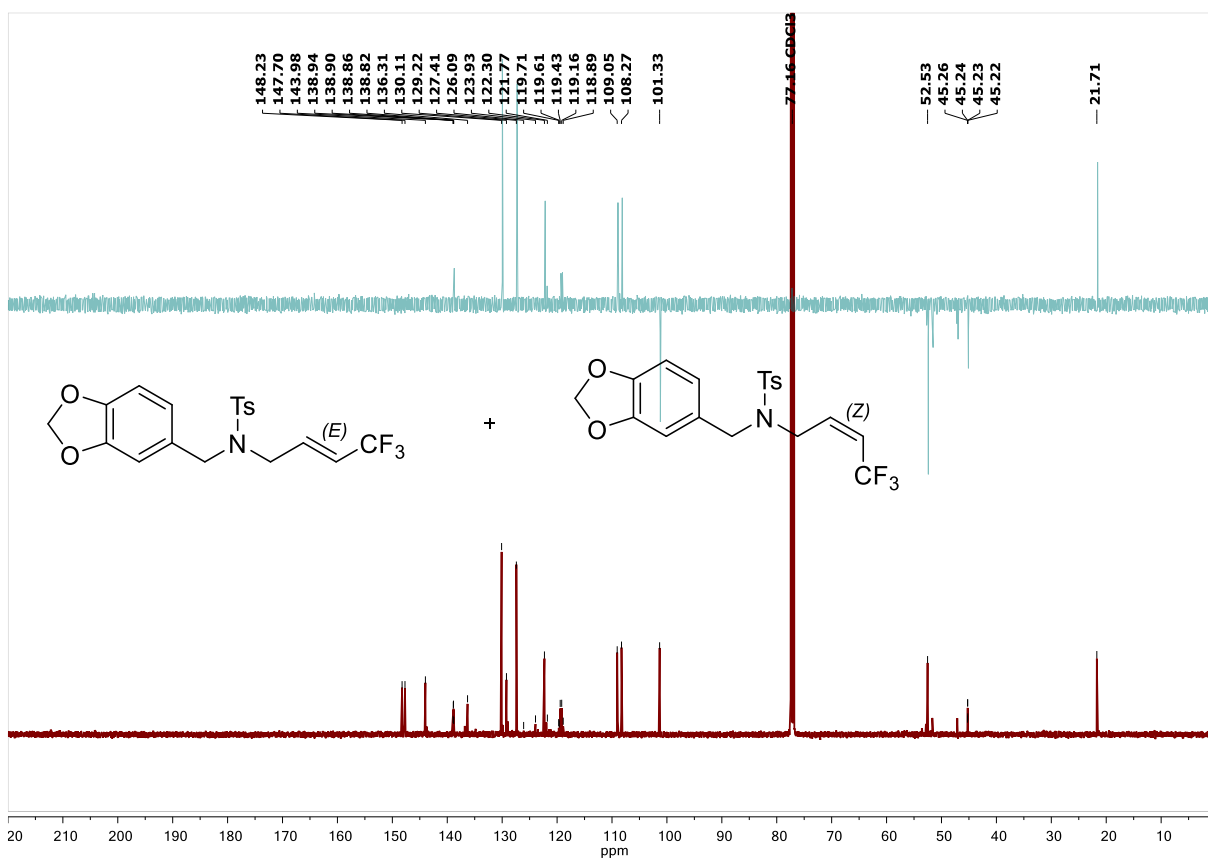




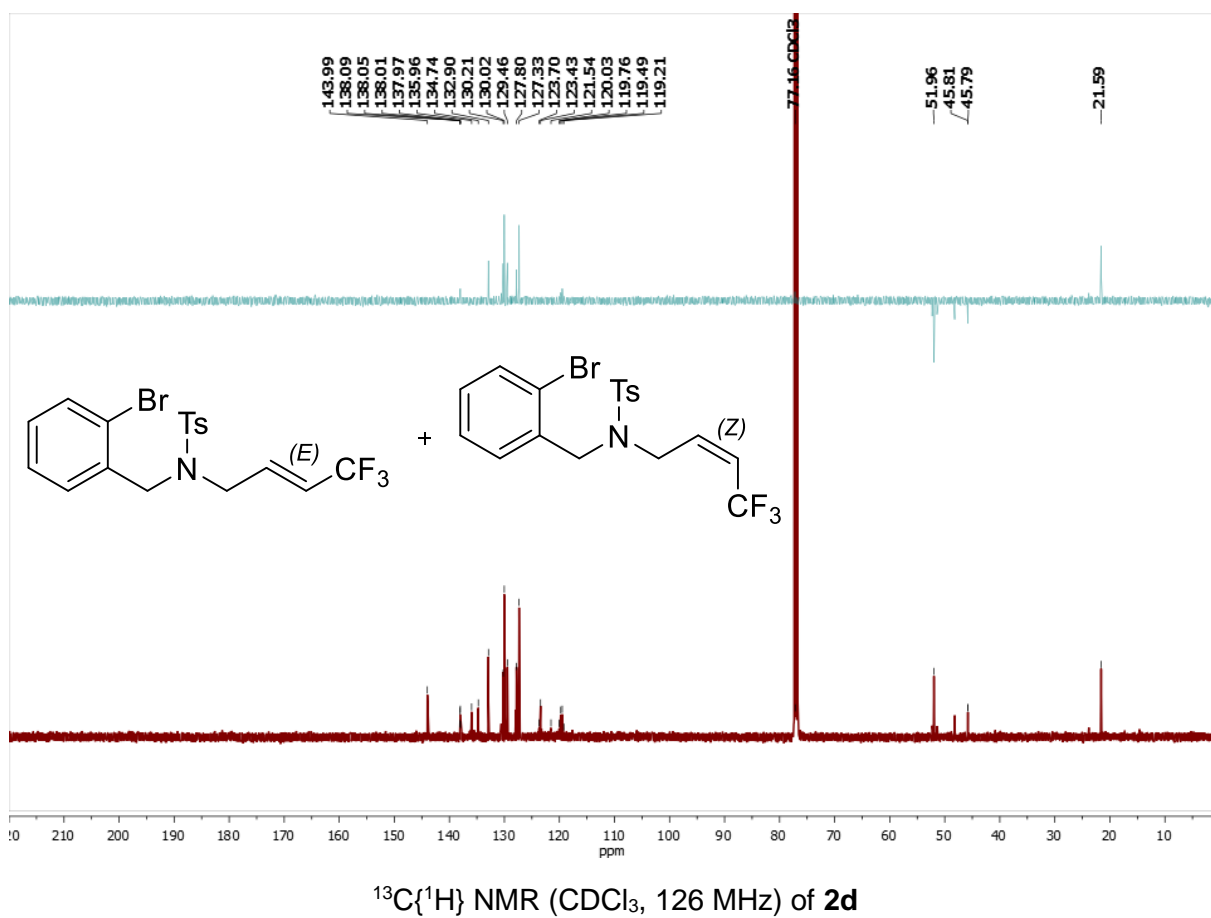
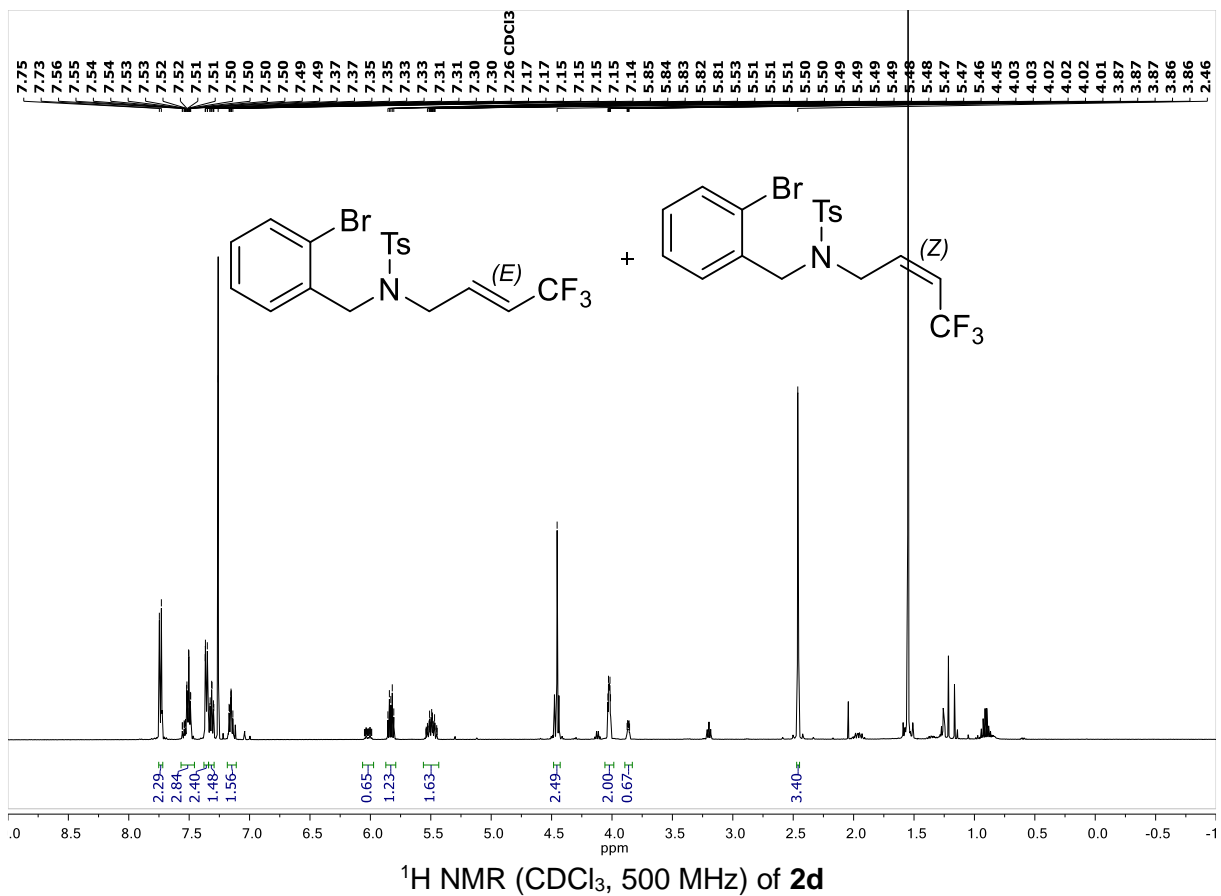
$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 282 MHz) of **1u**

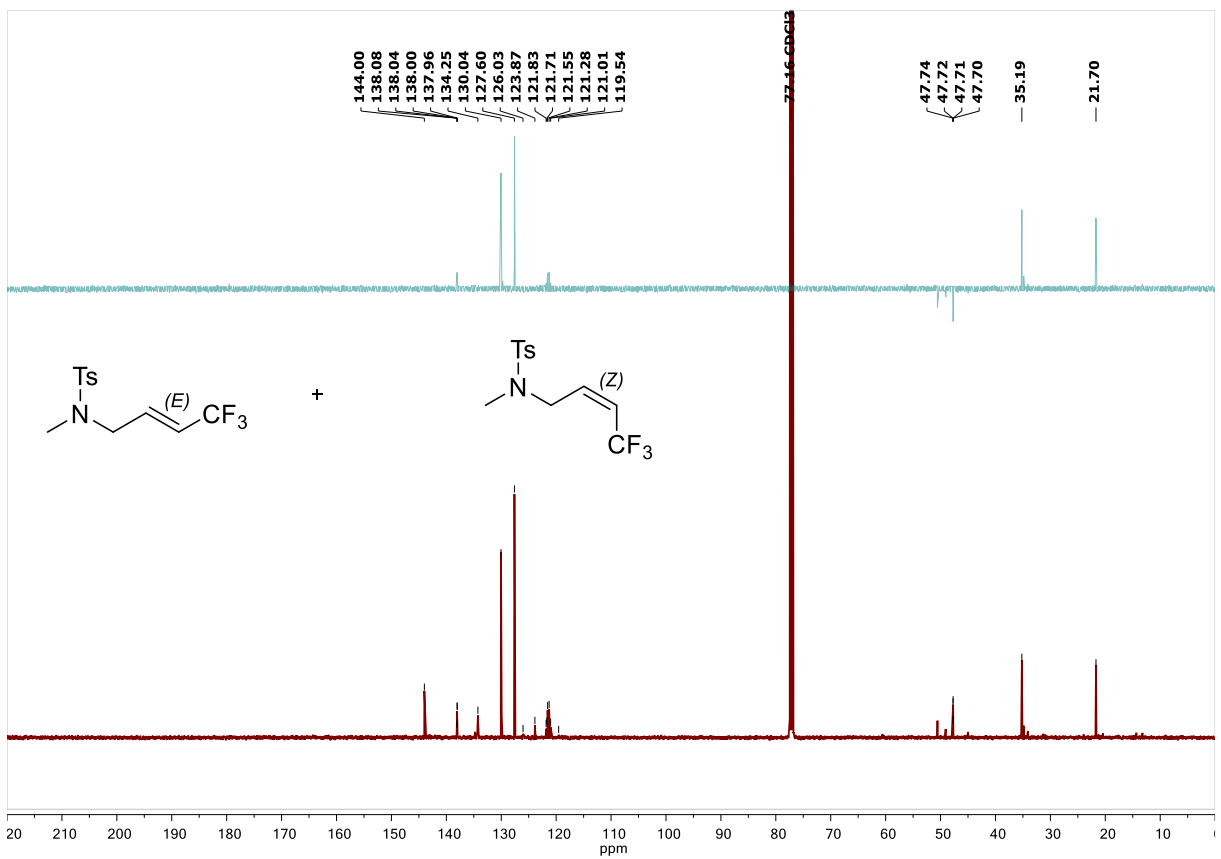
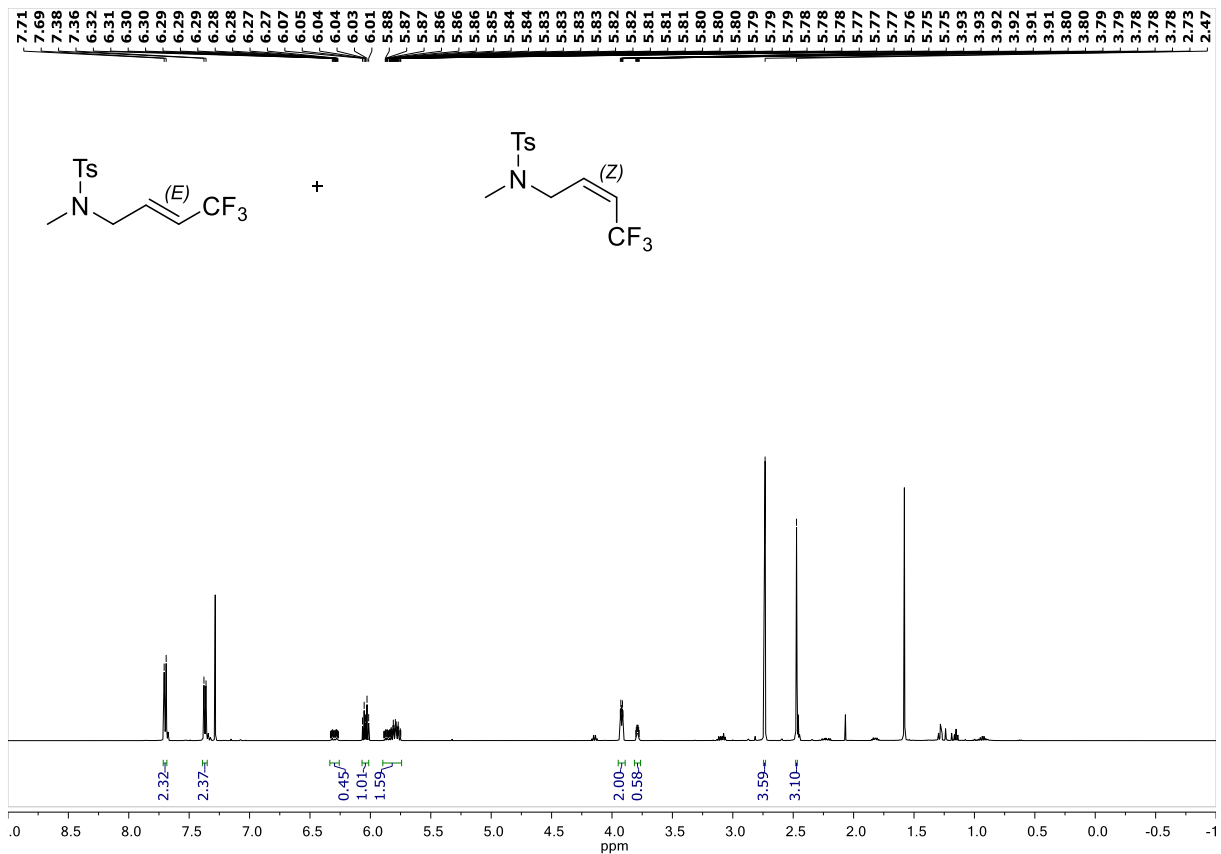


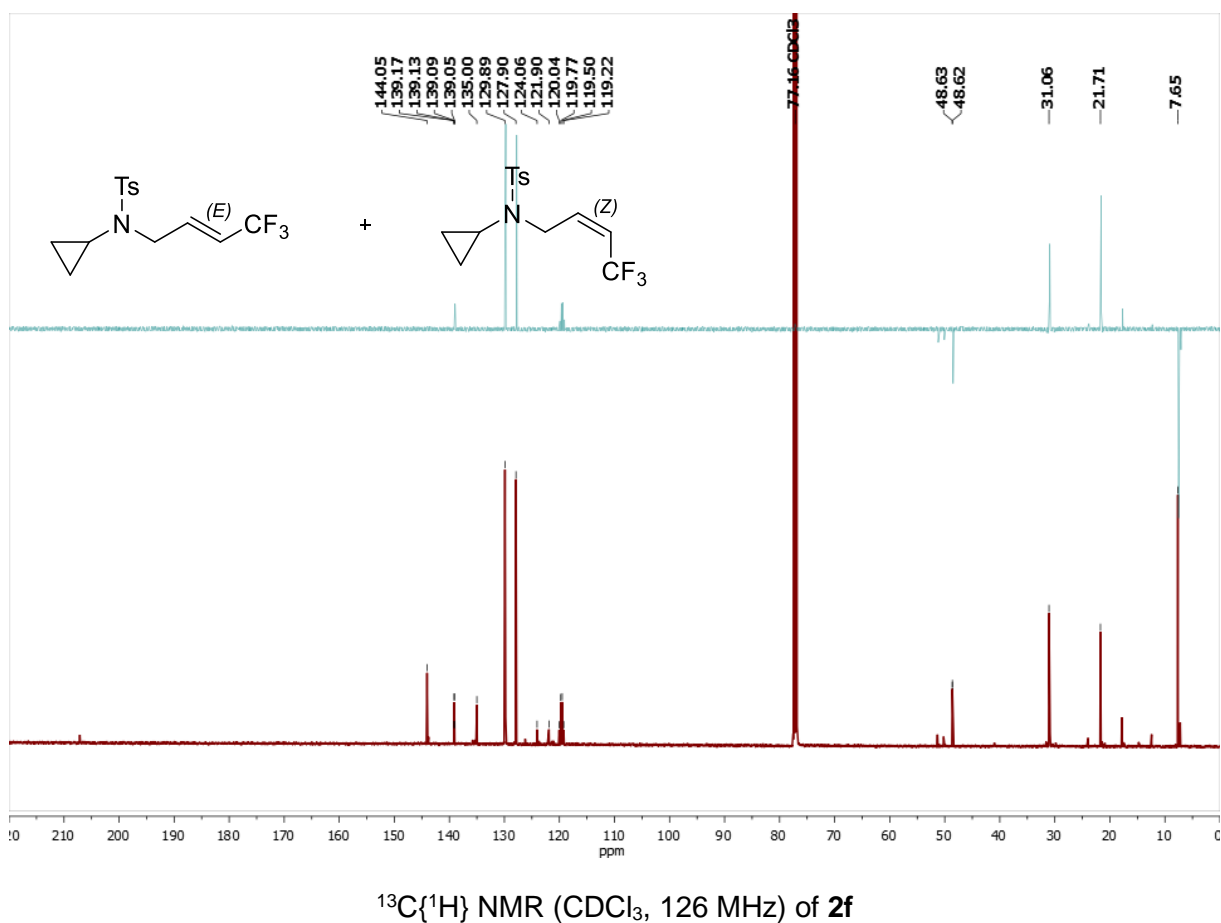
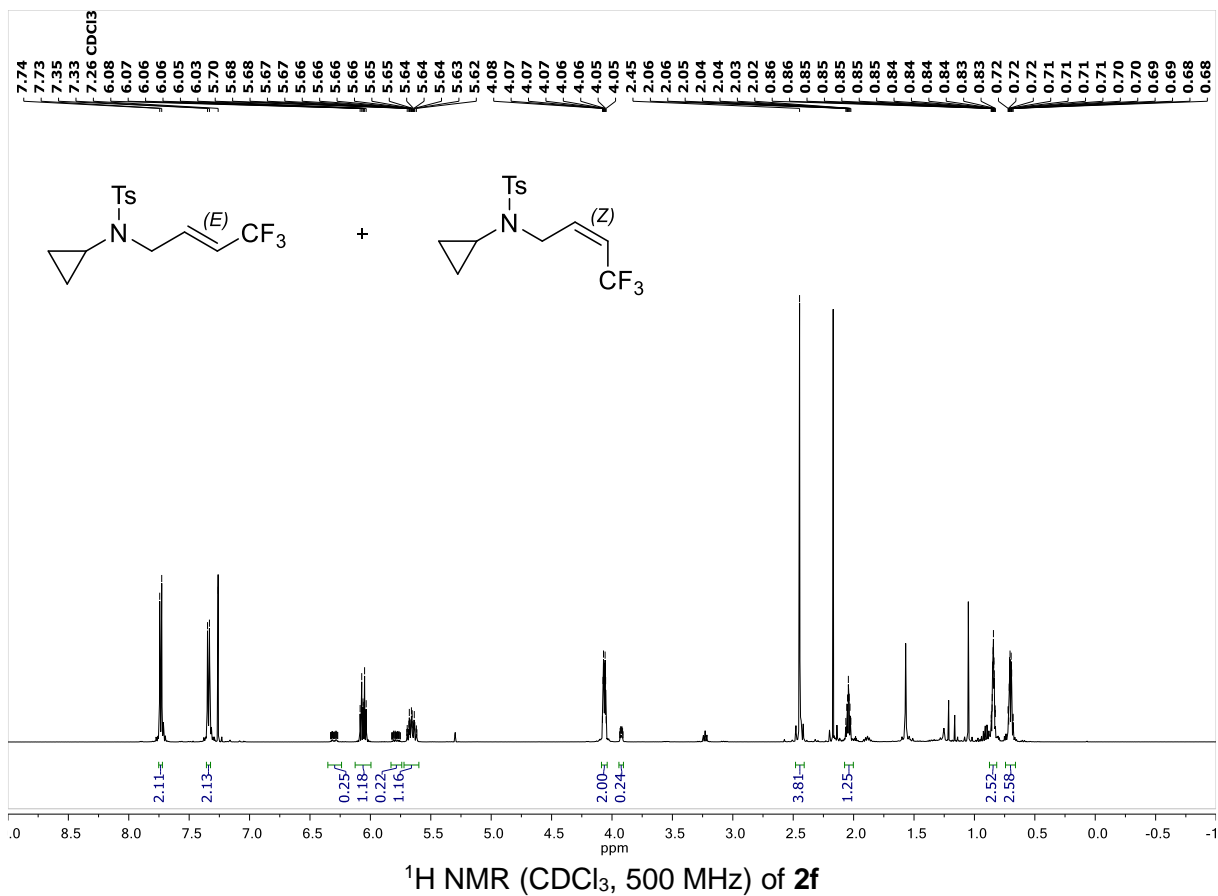
¹H NMR (CDCl₃, 300 MHz) of 2b

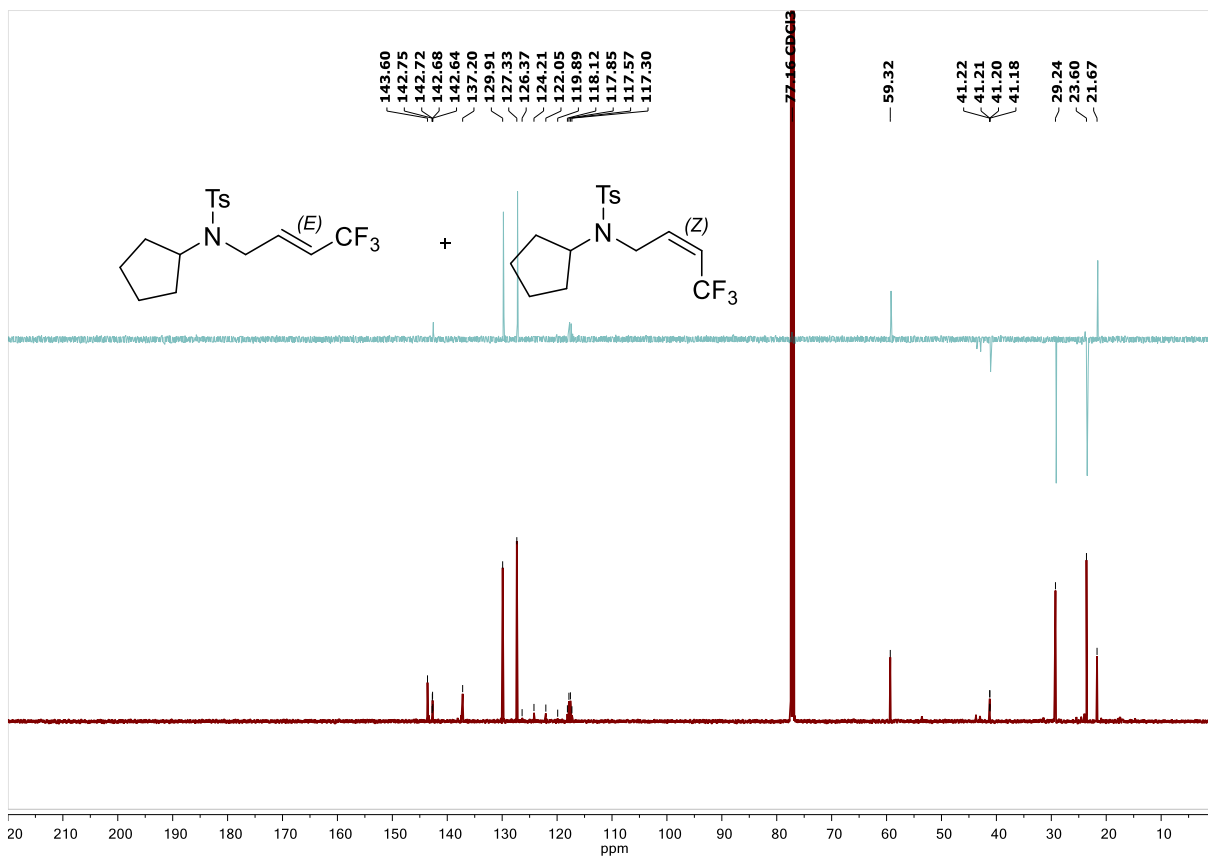
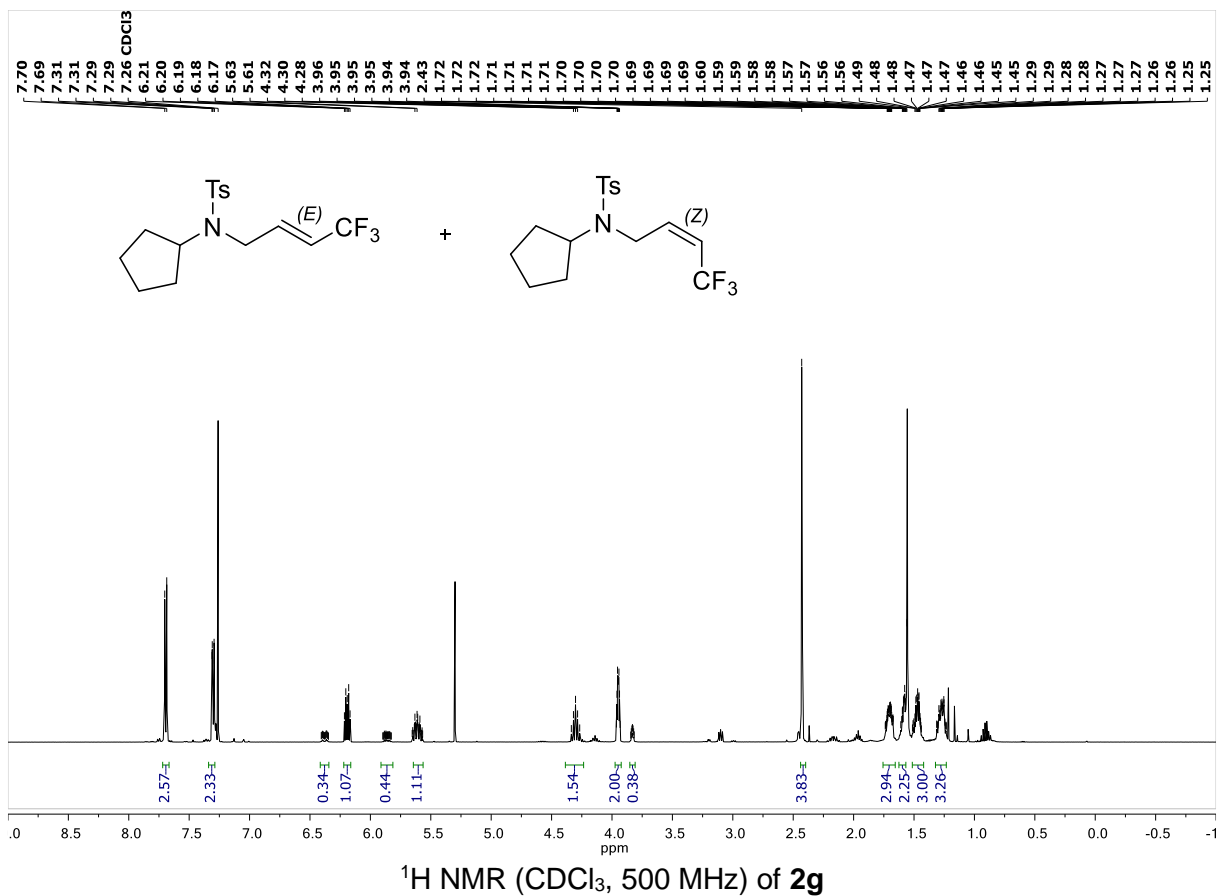


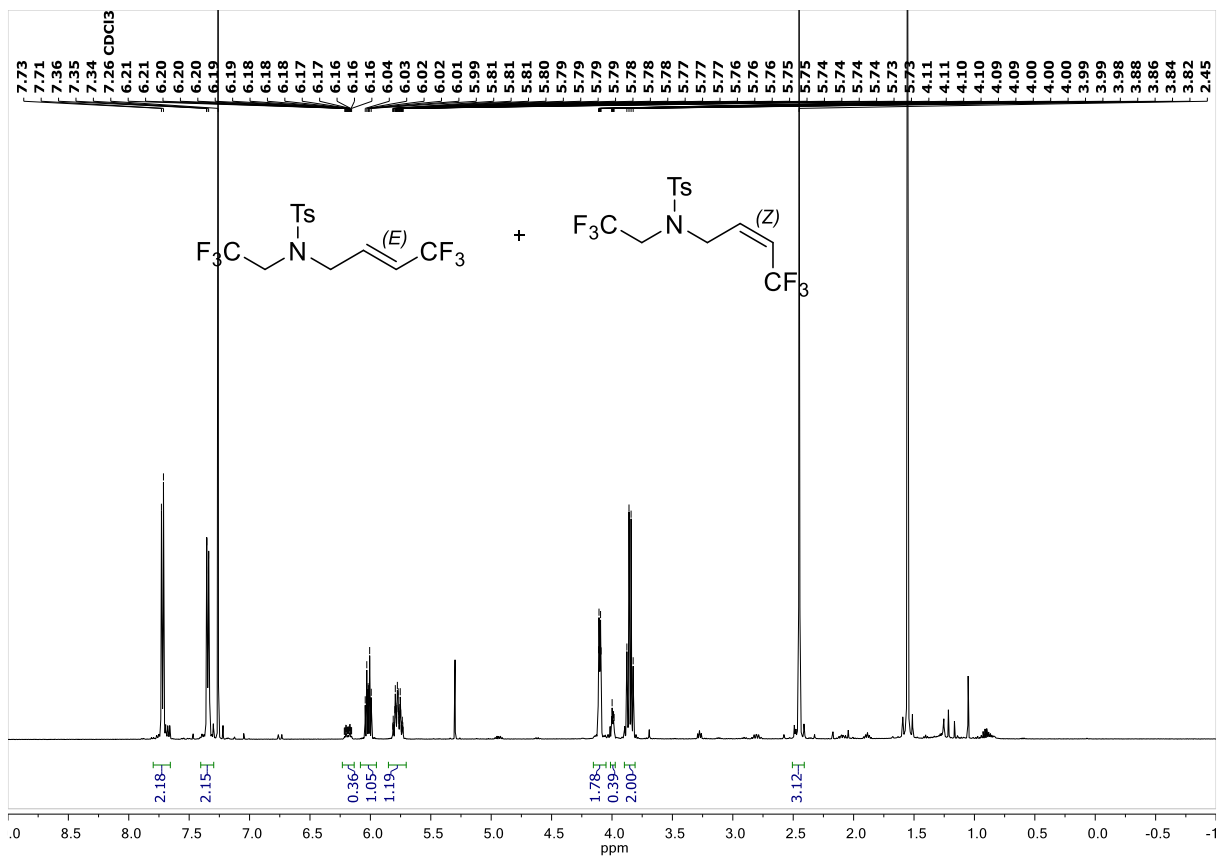
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 2b



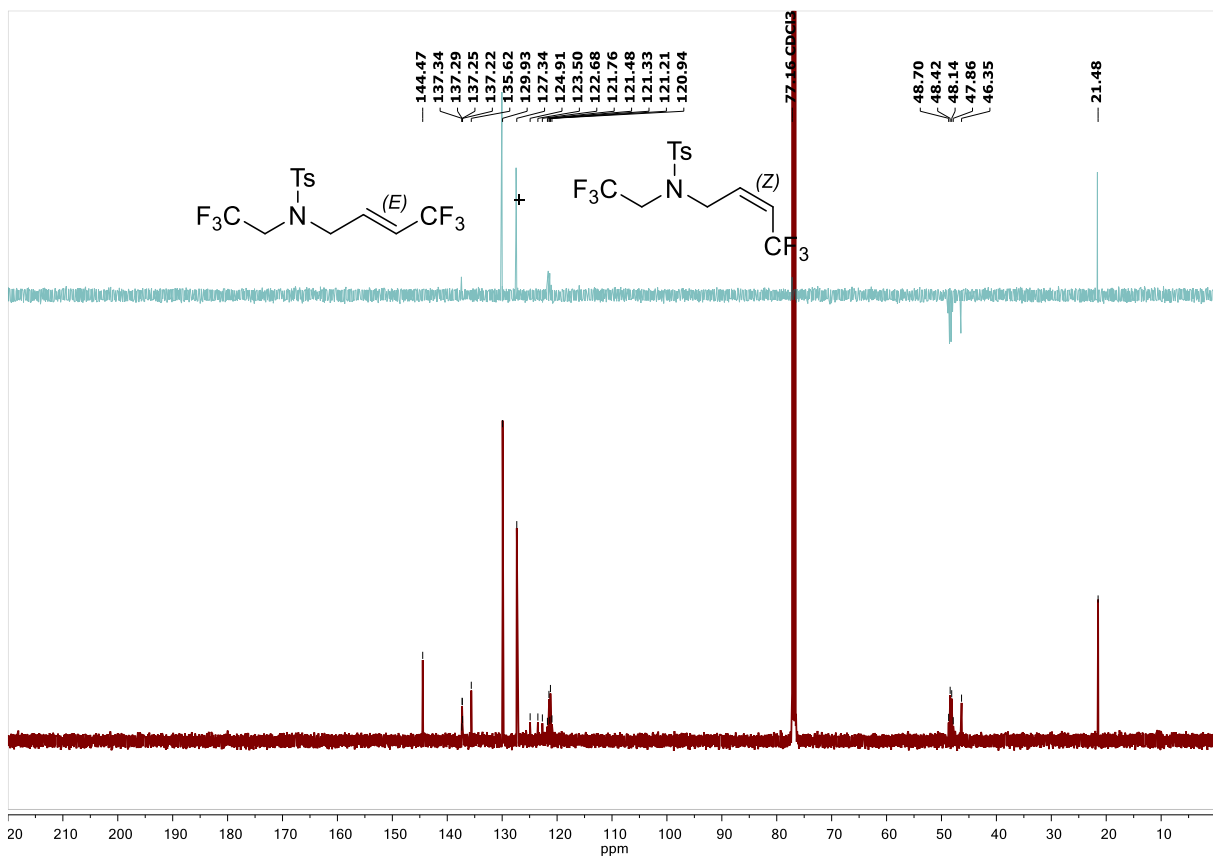






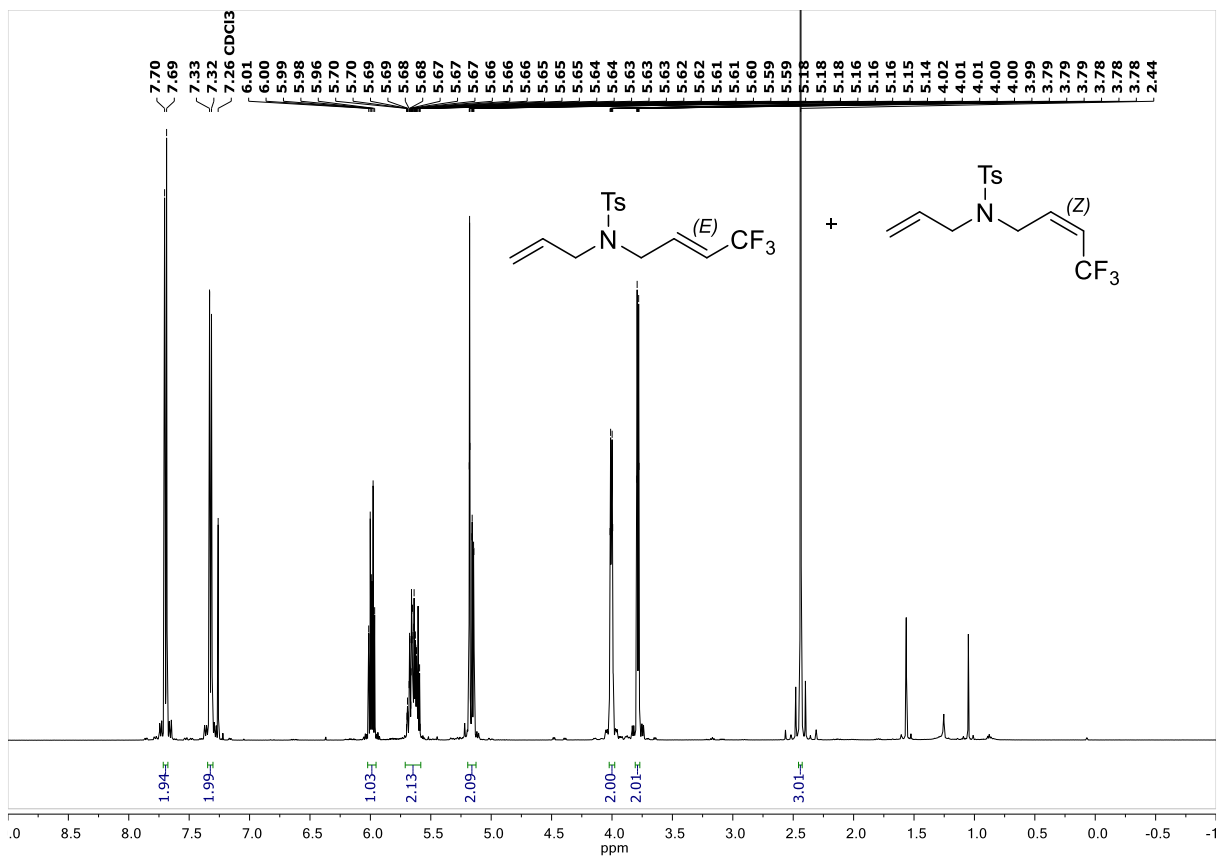


$^1\text{H NMR}$ (CDCl_3 , 500 MHz) of **2h**

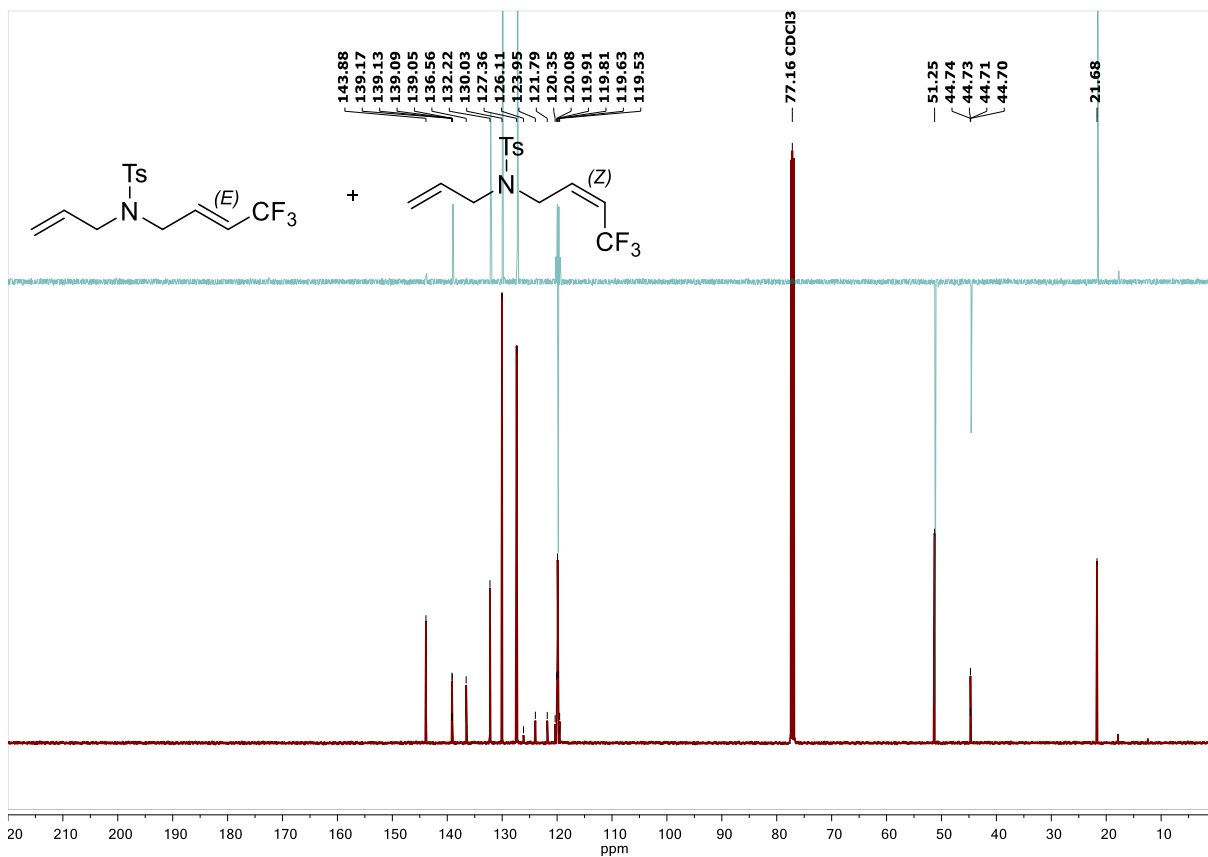


$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 126 MHz) of **2h**

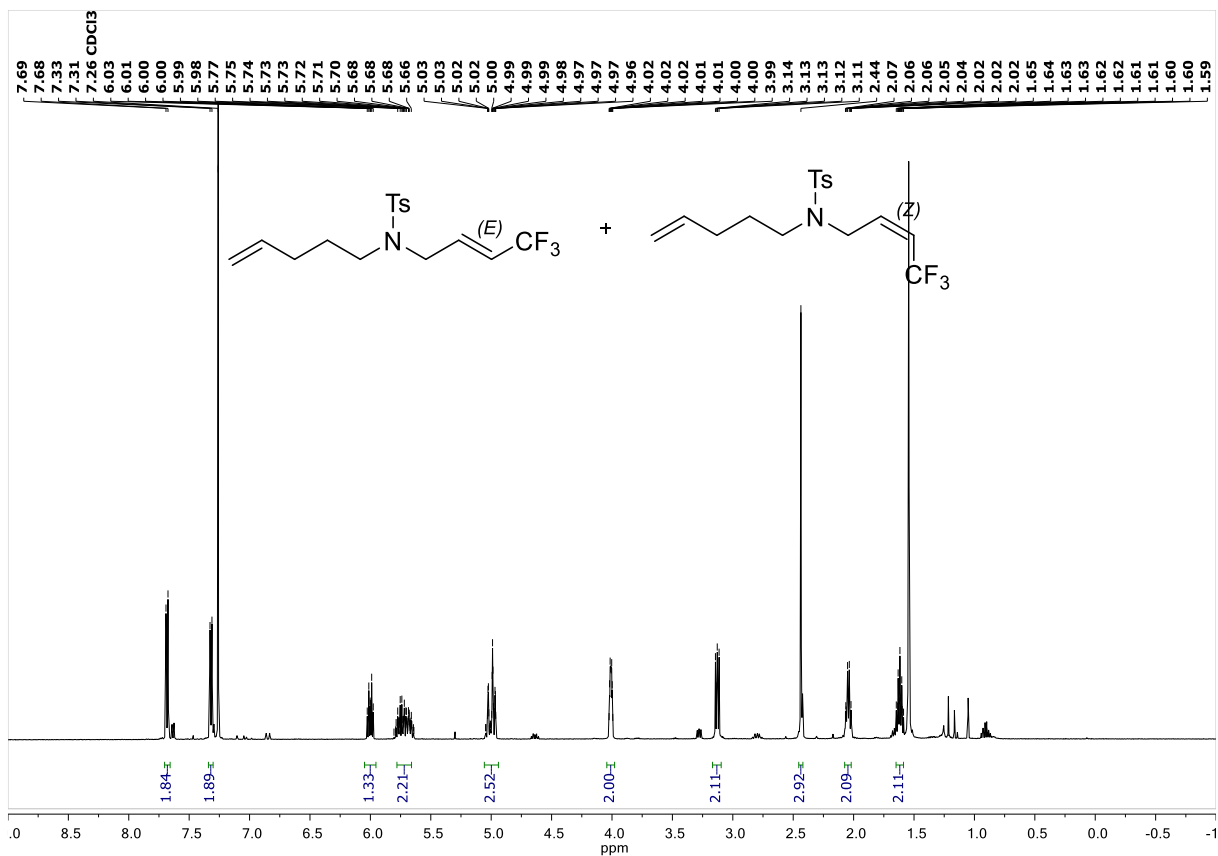
S55



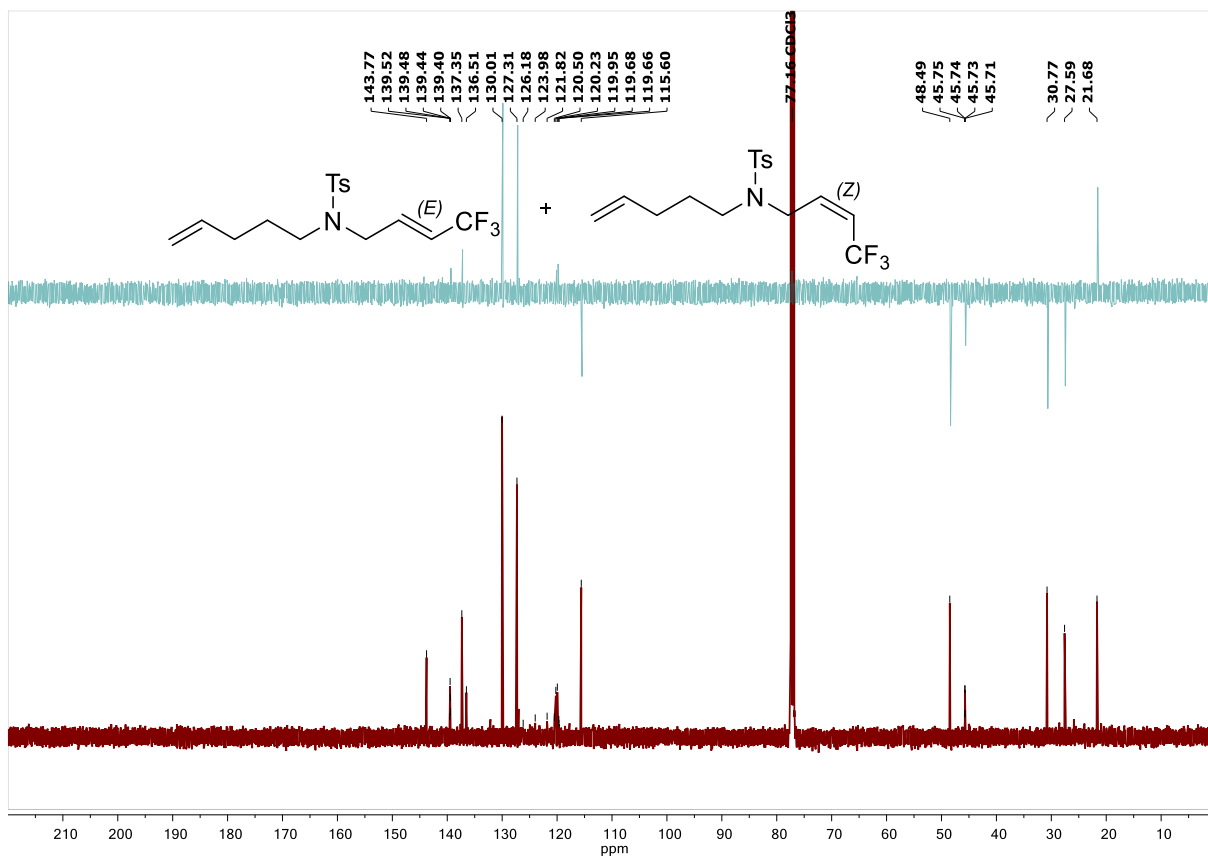
¹H NMR (CDCl₃, 500 MHz) of **2i**



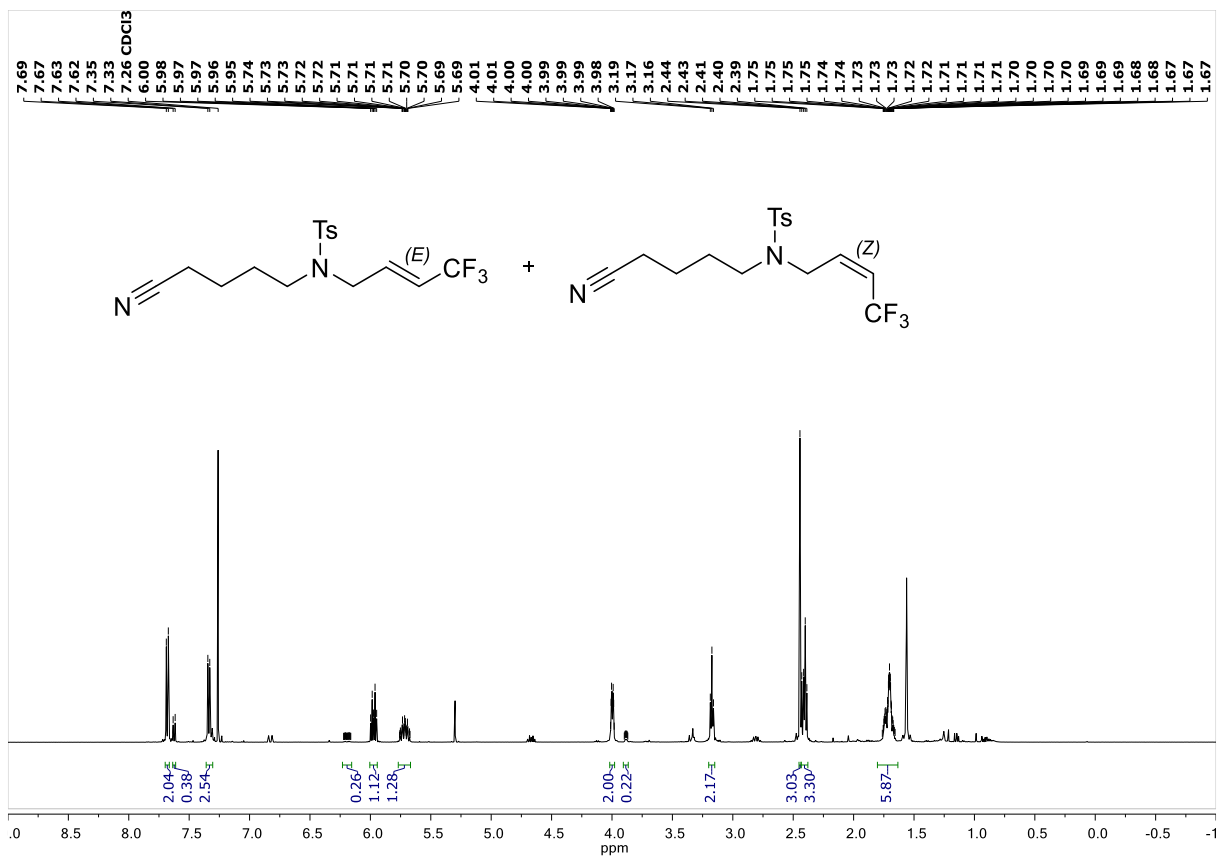
¹³C{¹H} NMR (CDCl₃, 126 MHz) of **2i**



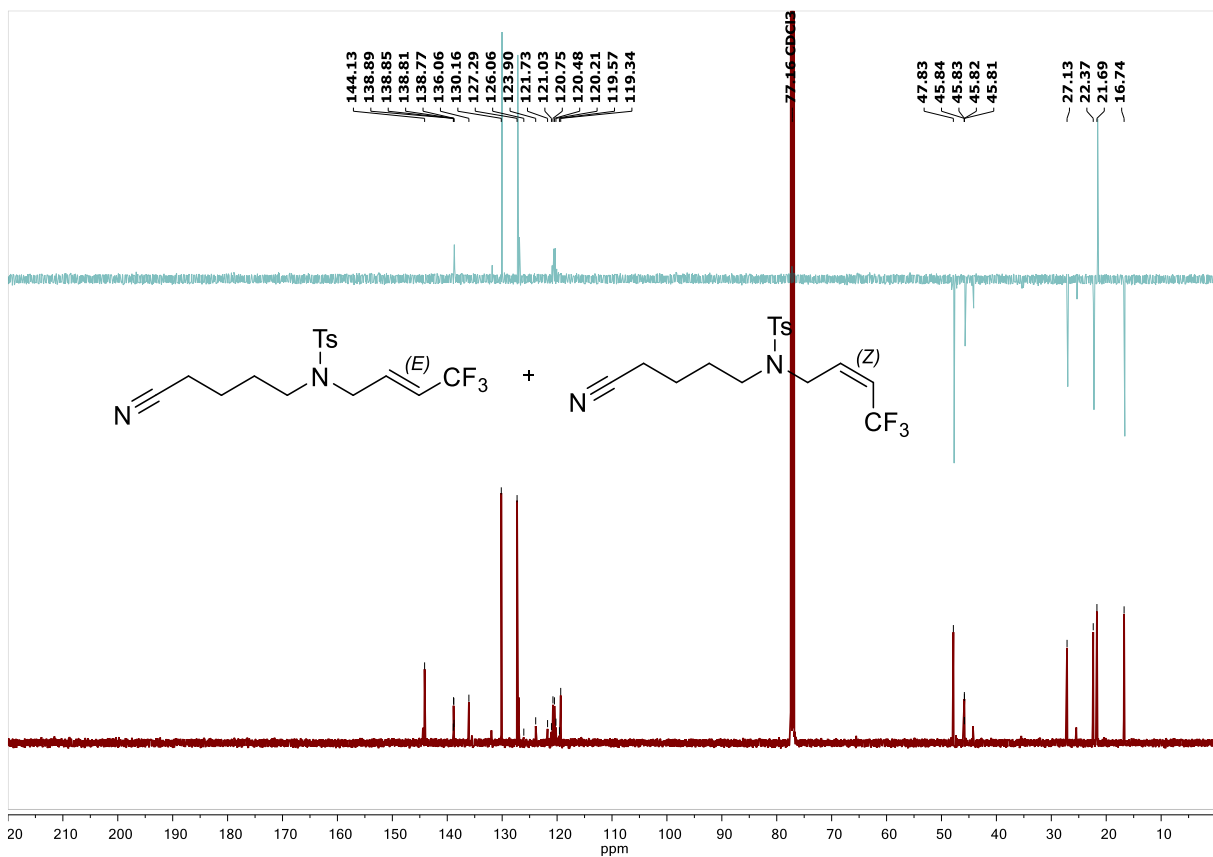
¹H NMR (CDCl₃, 500 MHz) of 2j



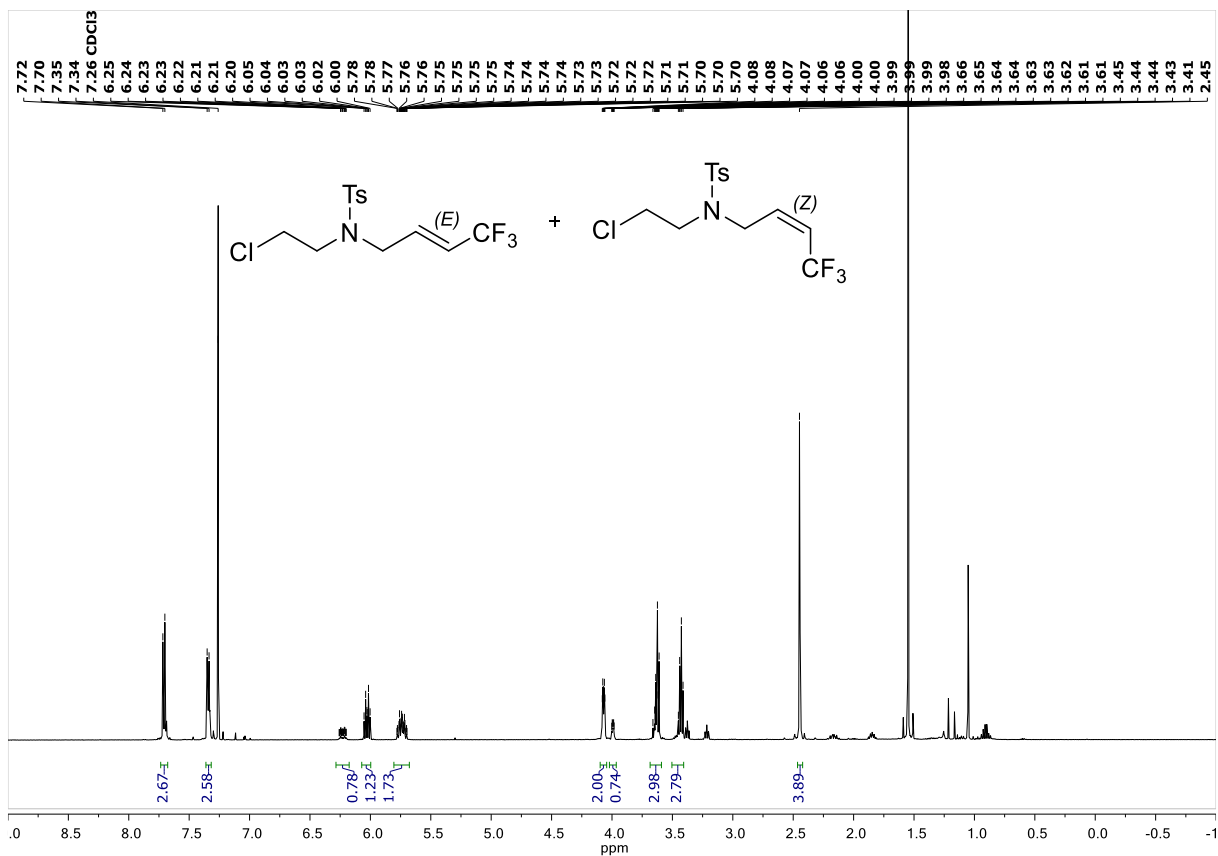
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 2j



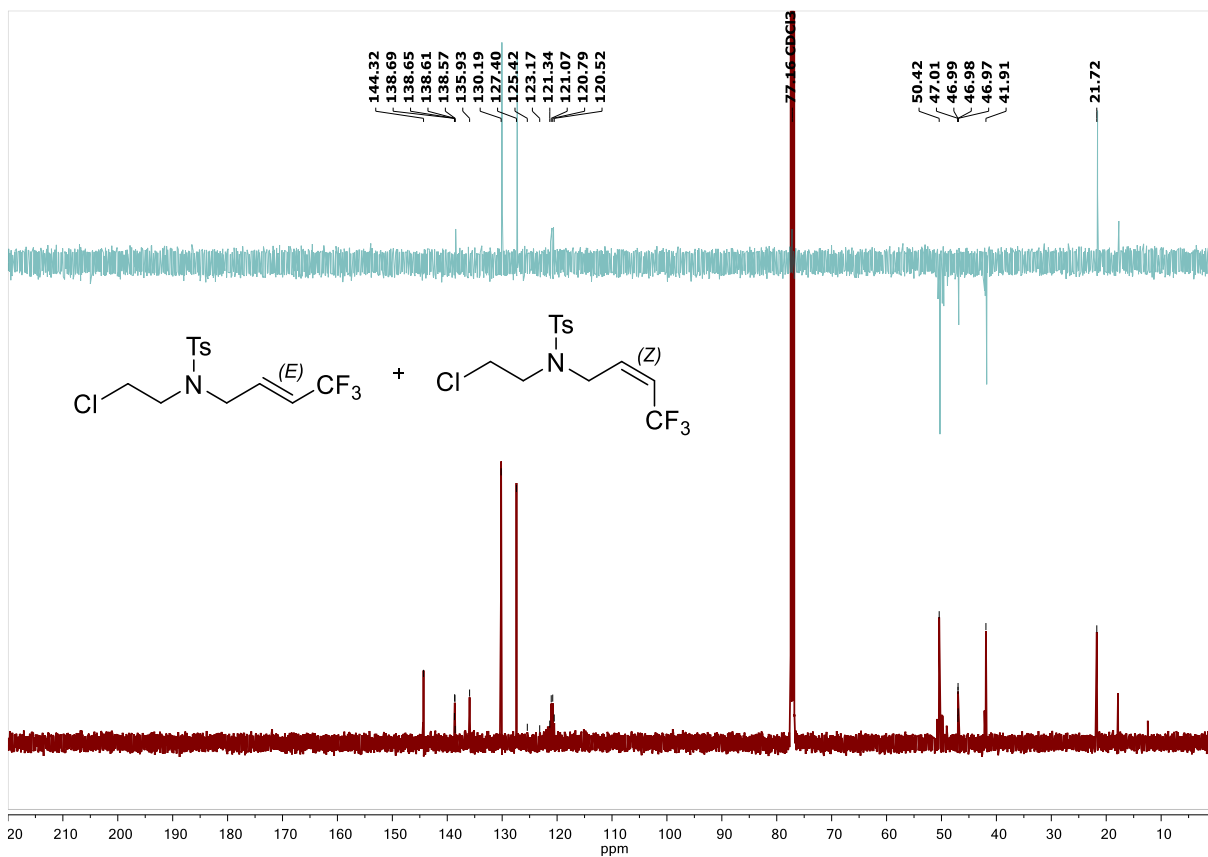
¹H NMR (CDCl₃, 500 MHz) of 2k



¹³C{¹H} NMR (CDCl₃, 126 MHz) of 2k

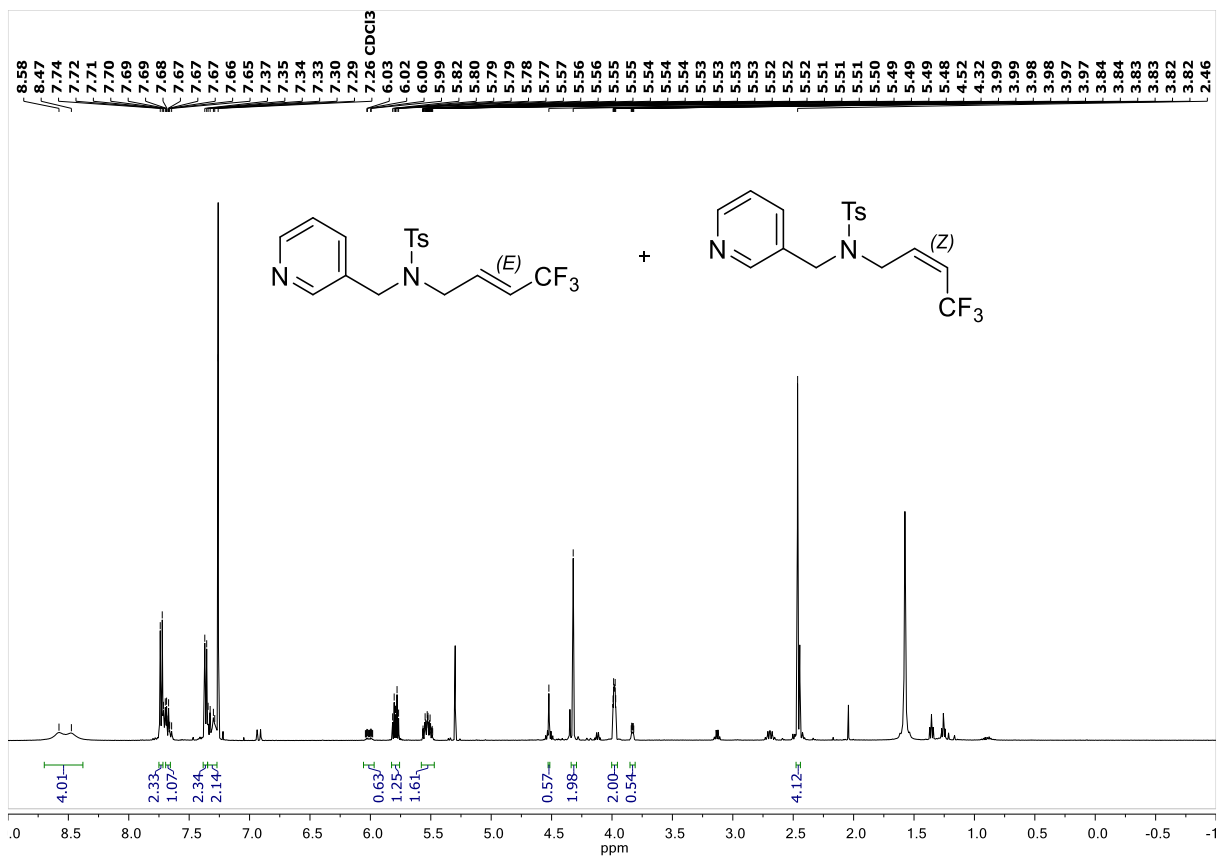


¹H NMR (CDCl₃, 500 MHz) of **2I**

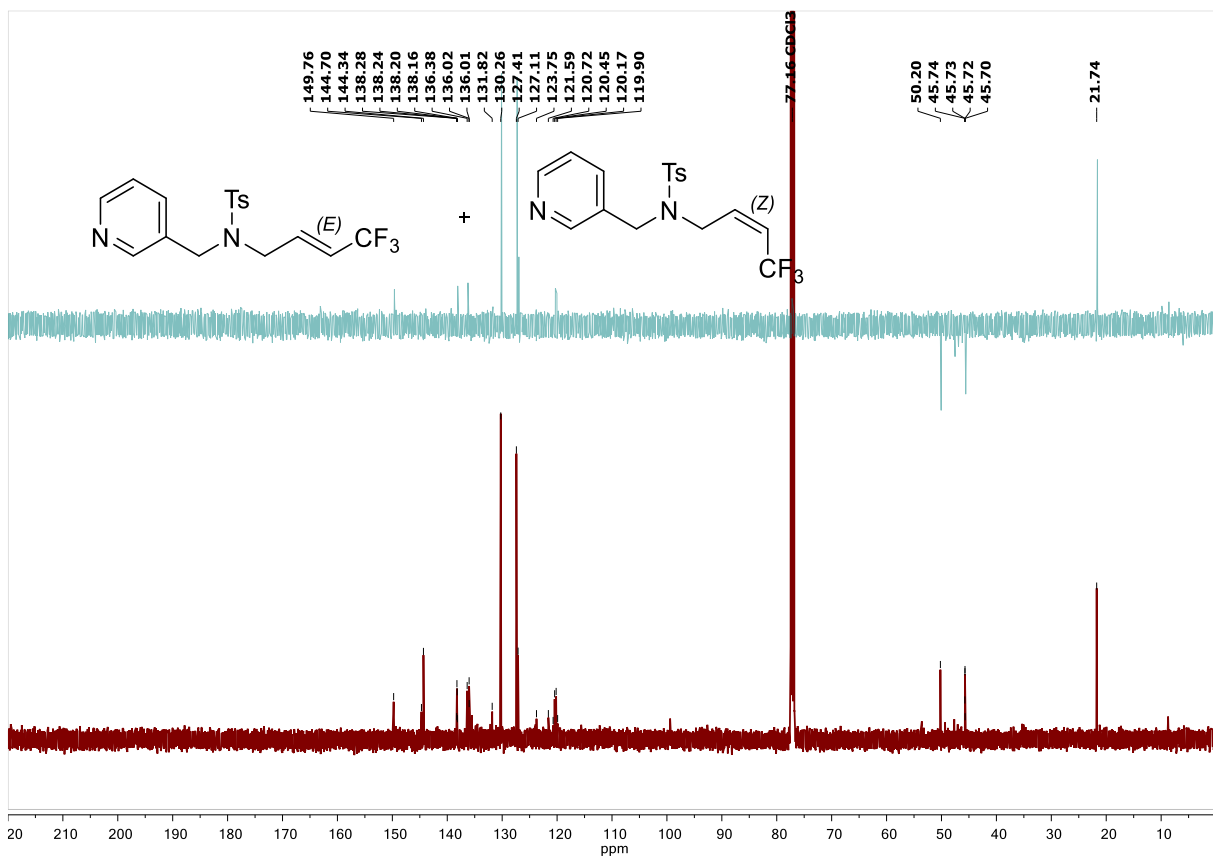


¹³C{¹H} NMR (CDCl₃, 126 MHz) of **2I**

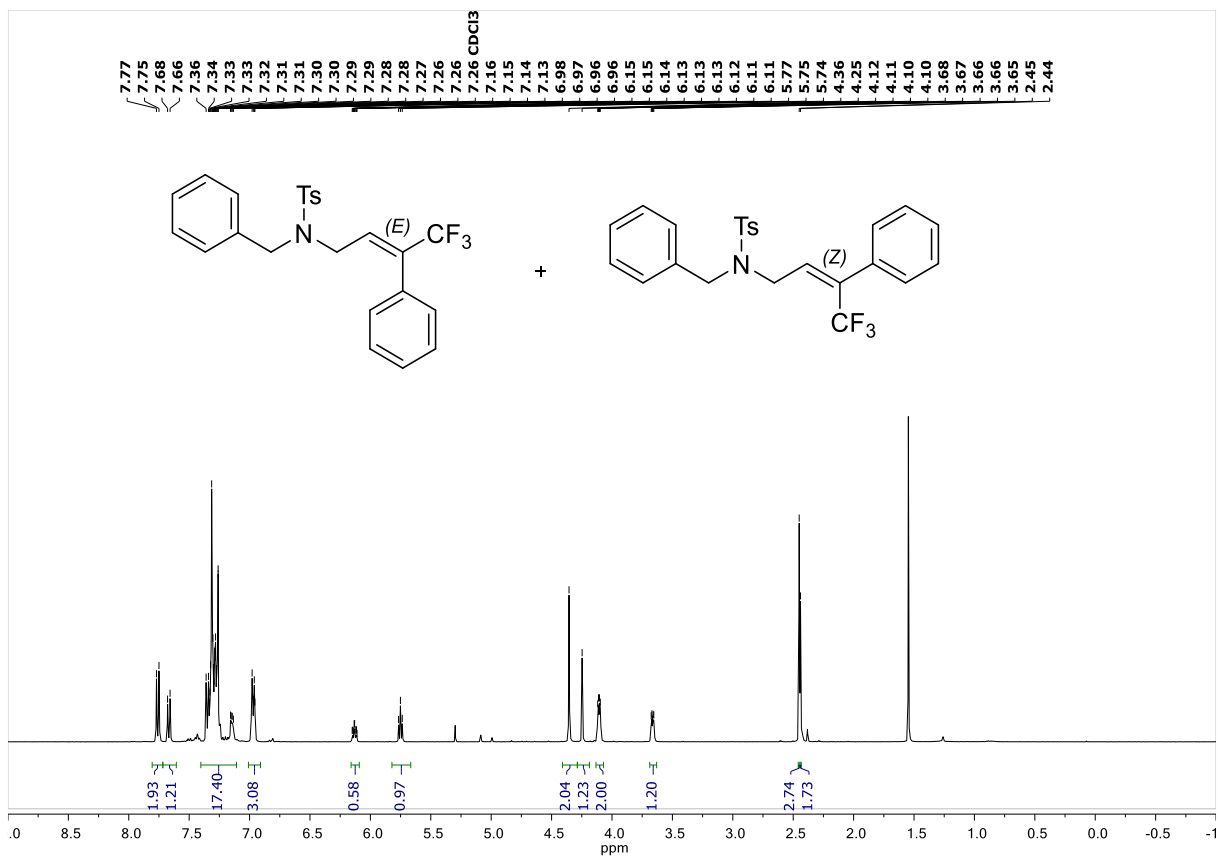
S59



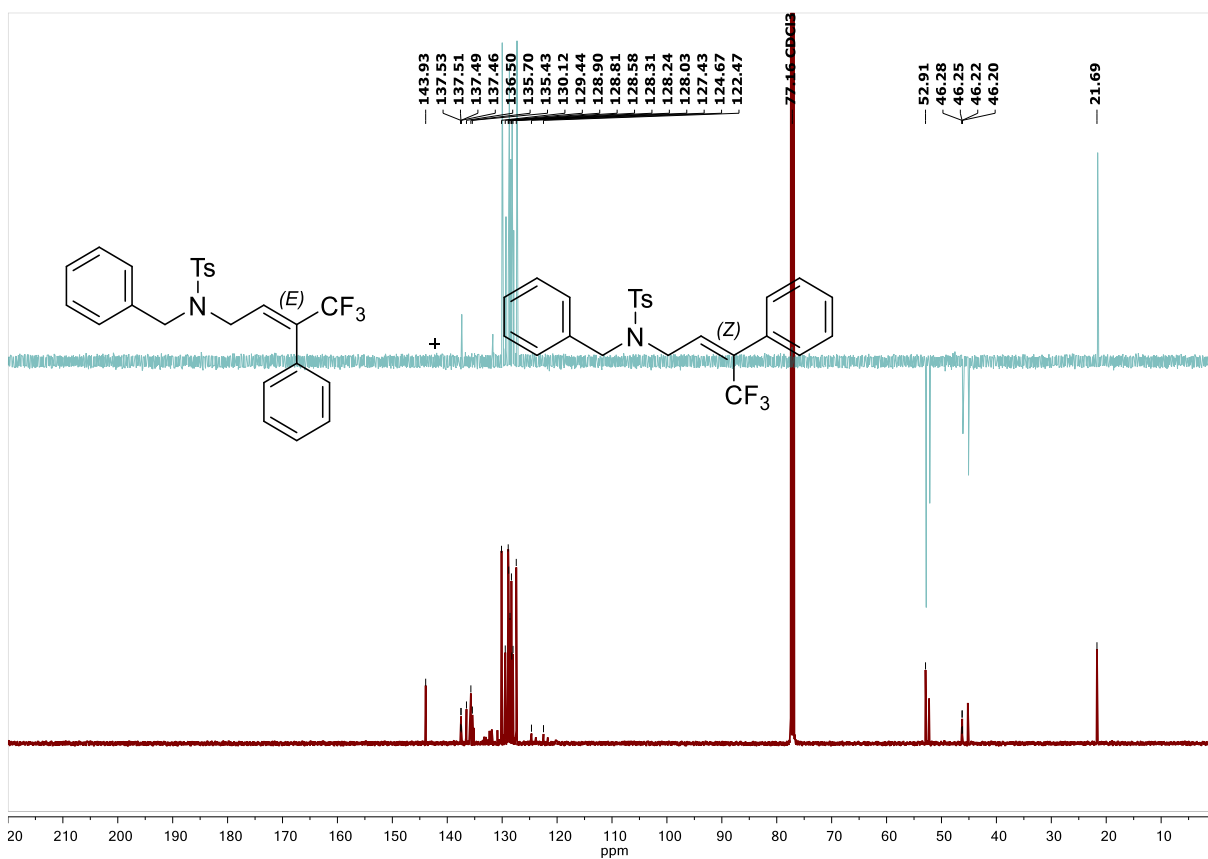
¹H NMR (CDCl₃, 500 MHz) of 2m



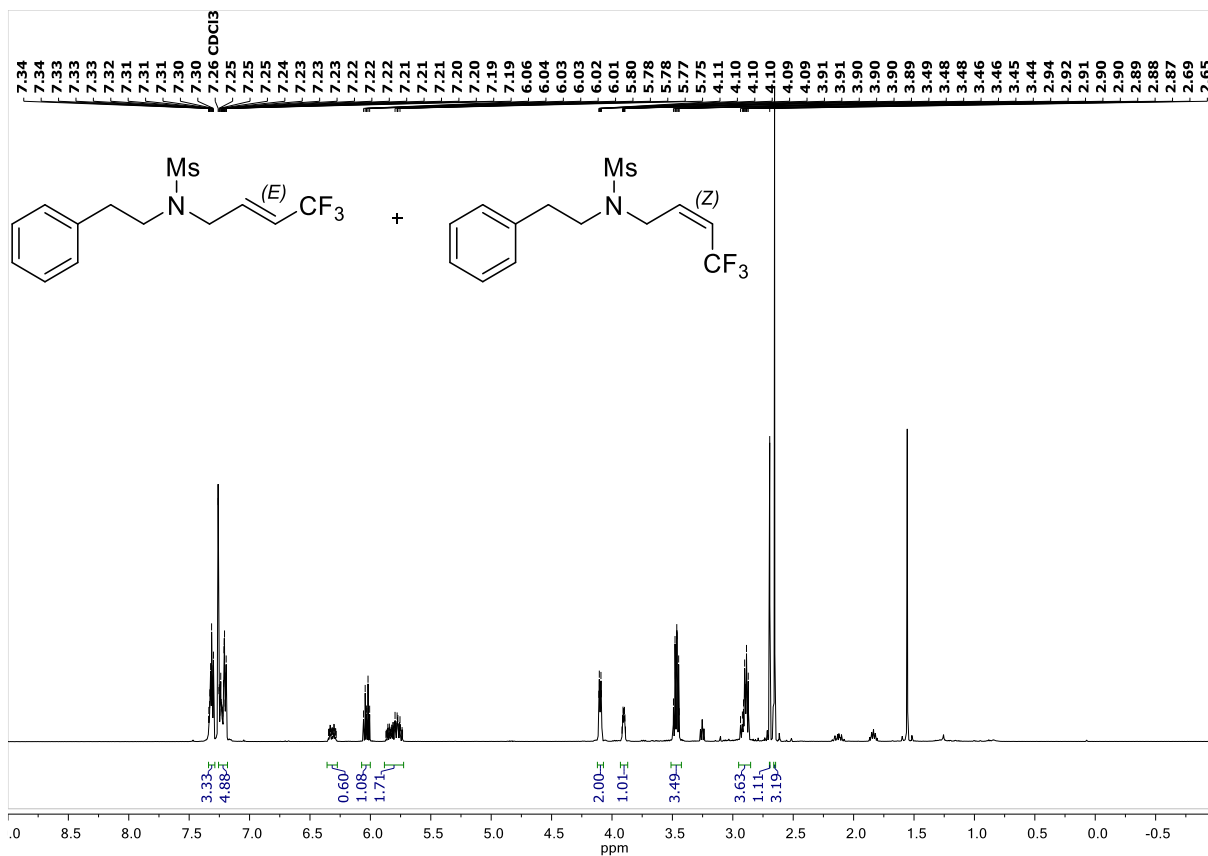
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 2m
S60



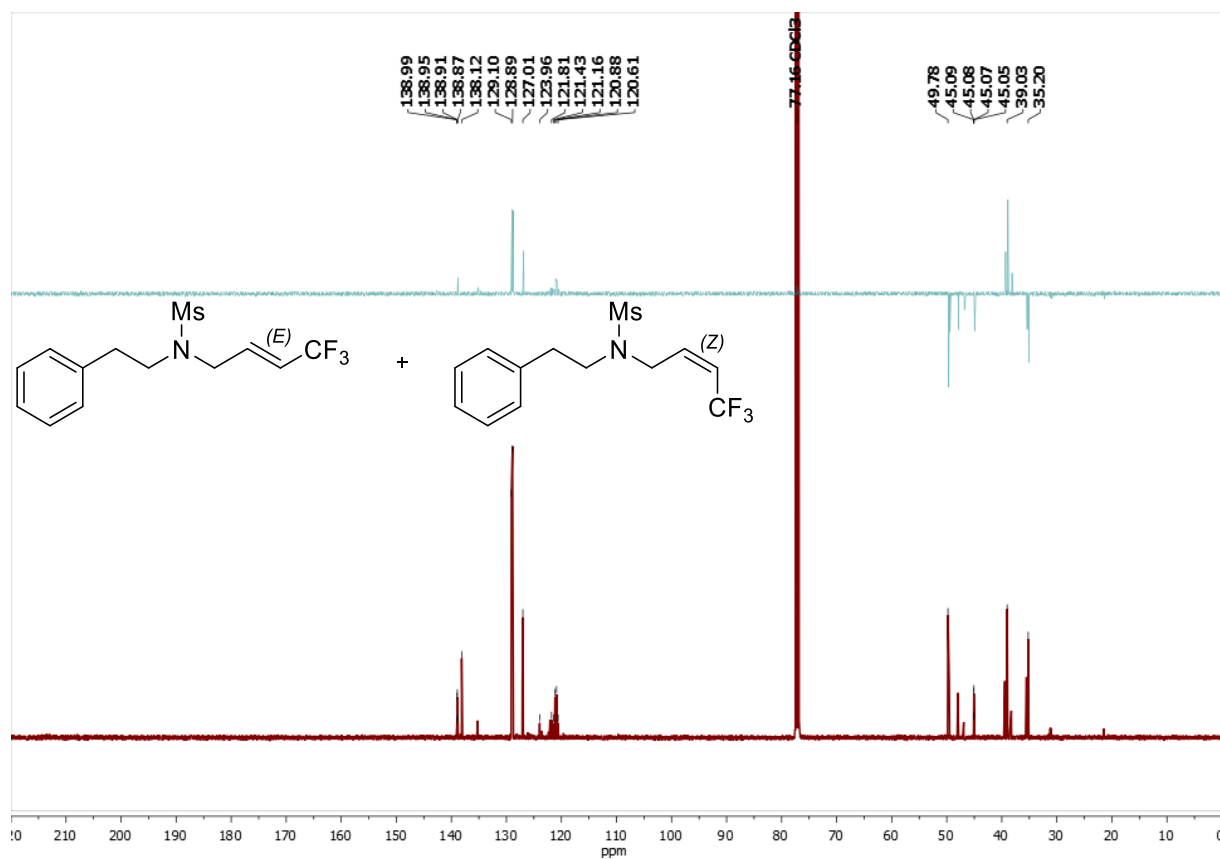
¹H NMR (CDCl₃, 400 MHz) of 2n



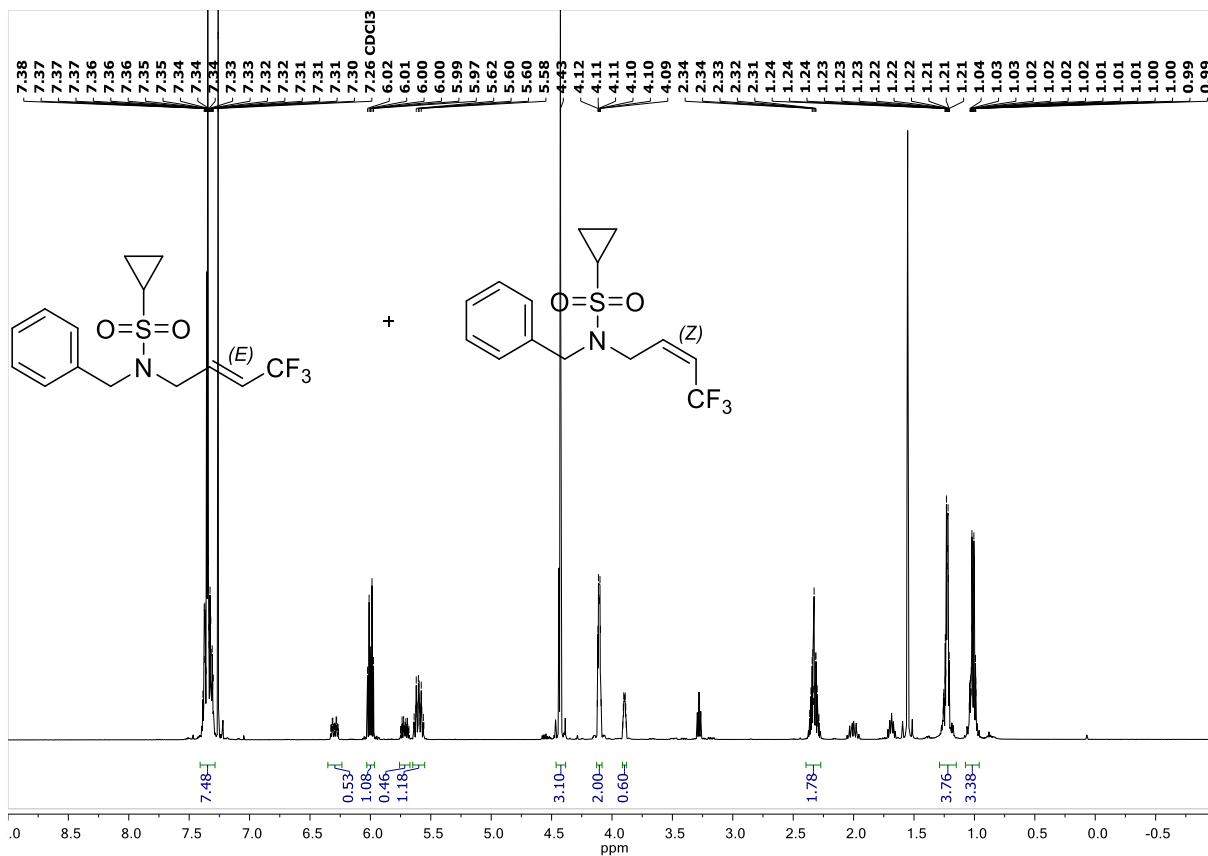
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 2n



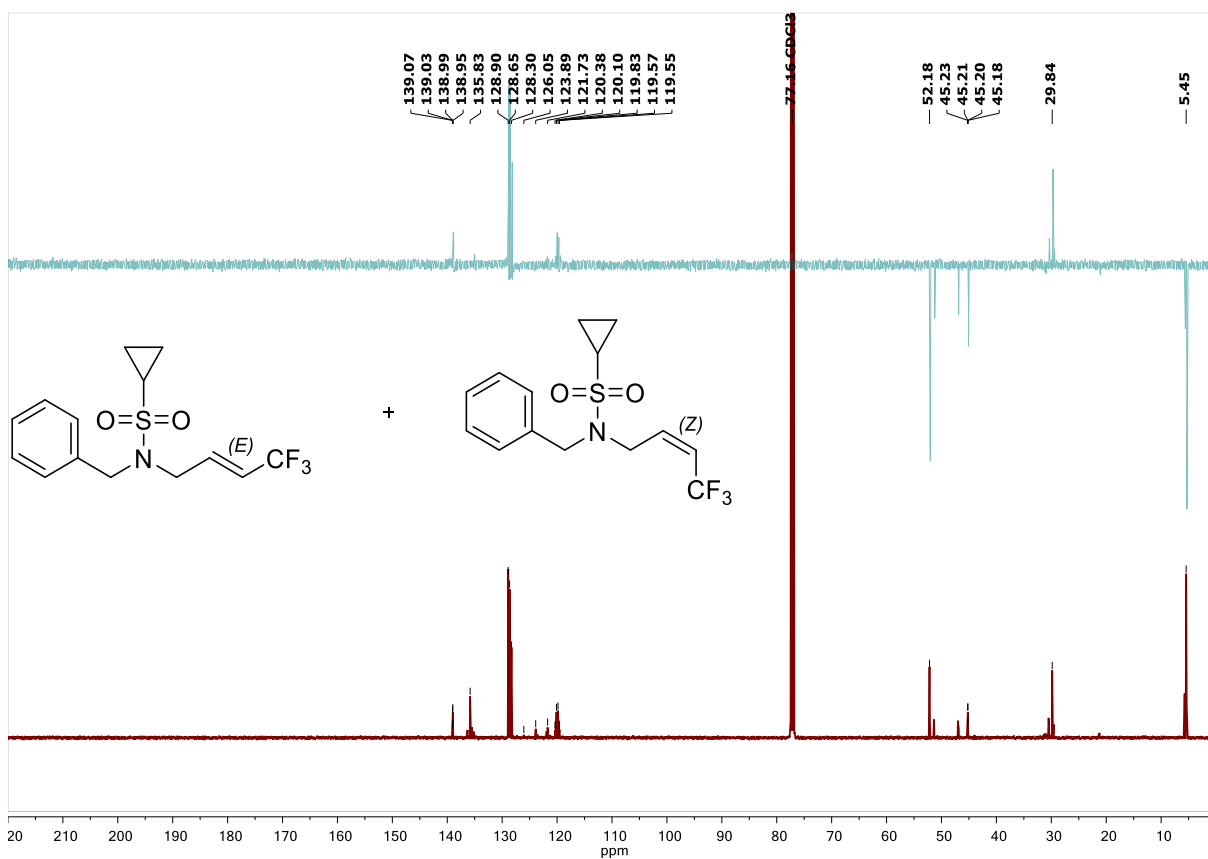
¹H NMR (CDCl₃, 500 MHz) of **2o**



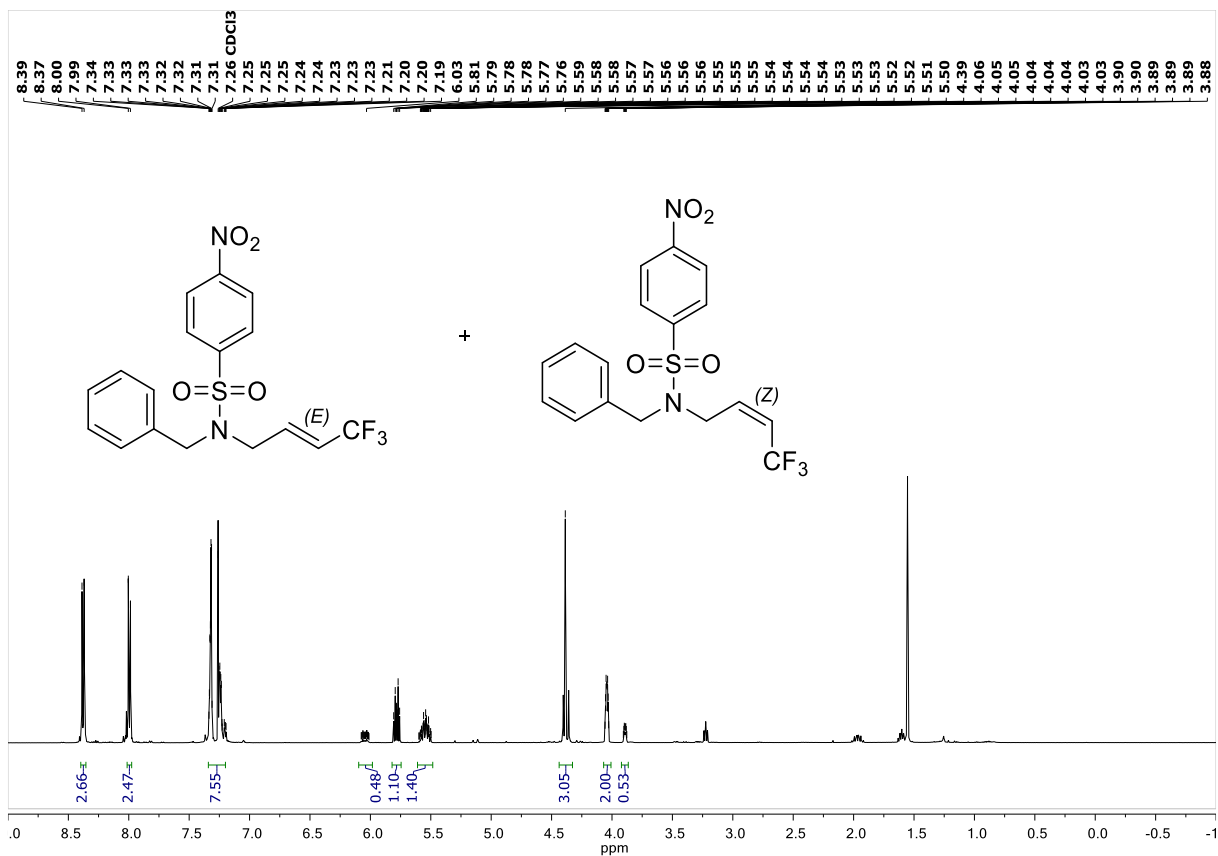
¹³C{¹H} NMR (CDCl₃, 126 MHz) of **2o**



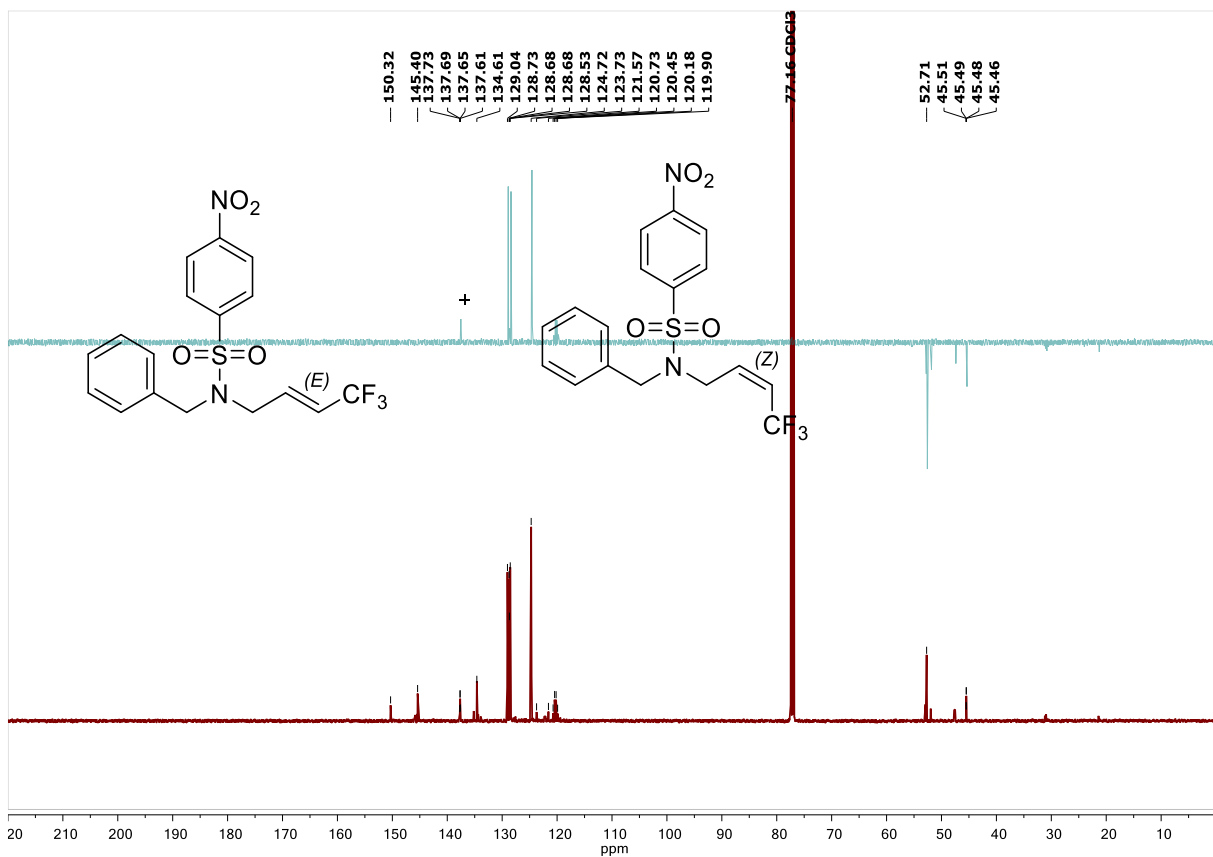
¹H NMR (CDCl₃, 500 MHz) of 2p



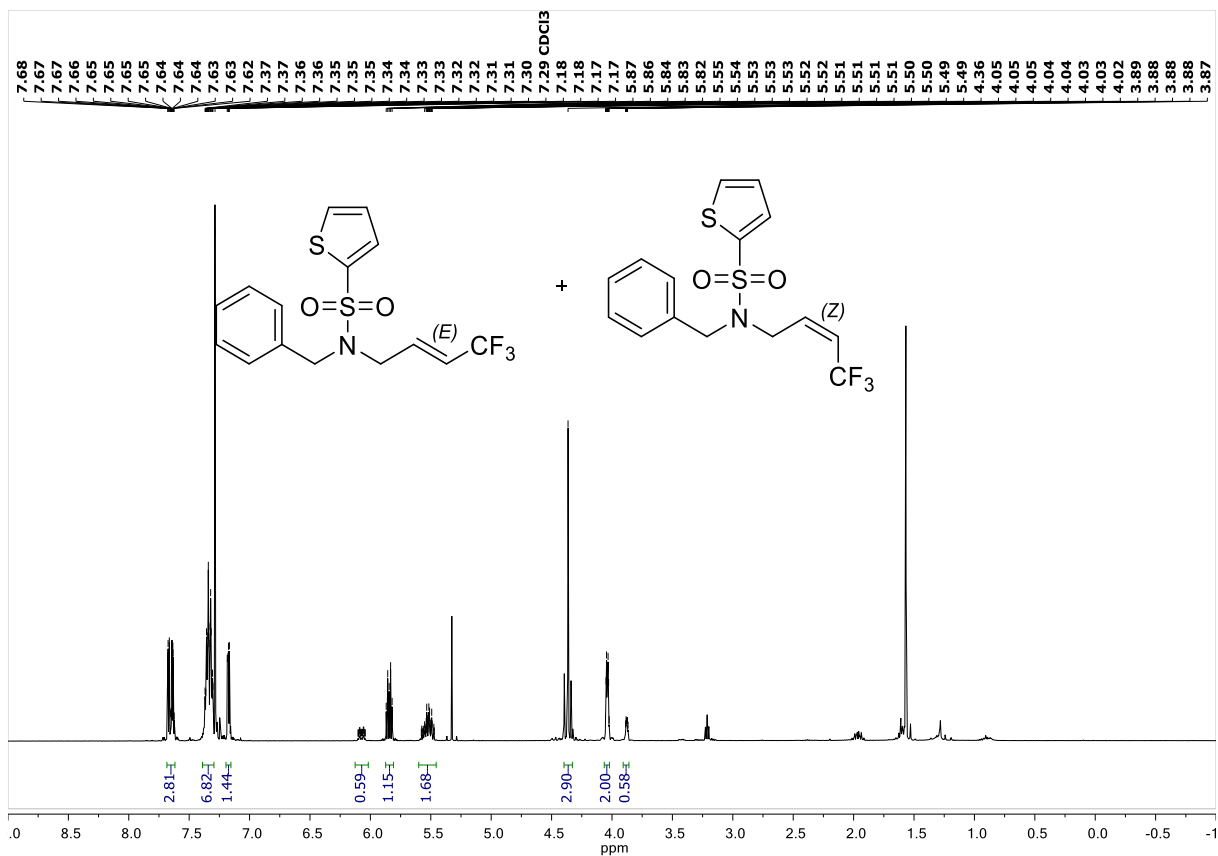
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 2p
S63



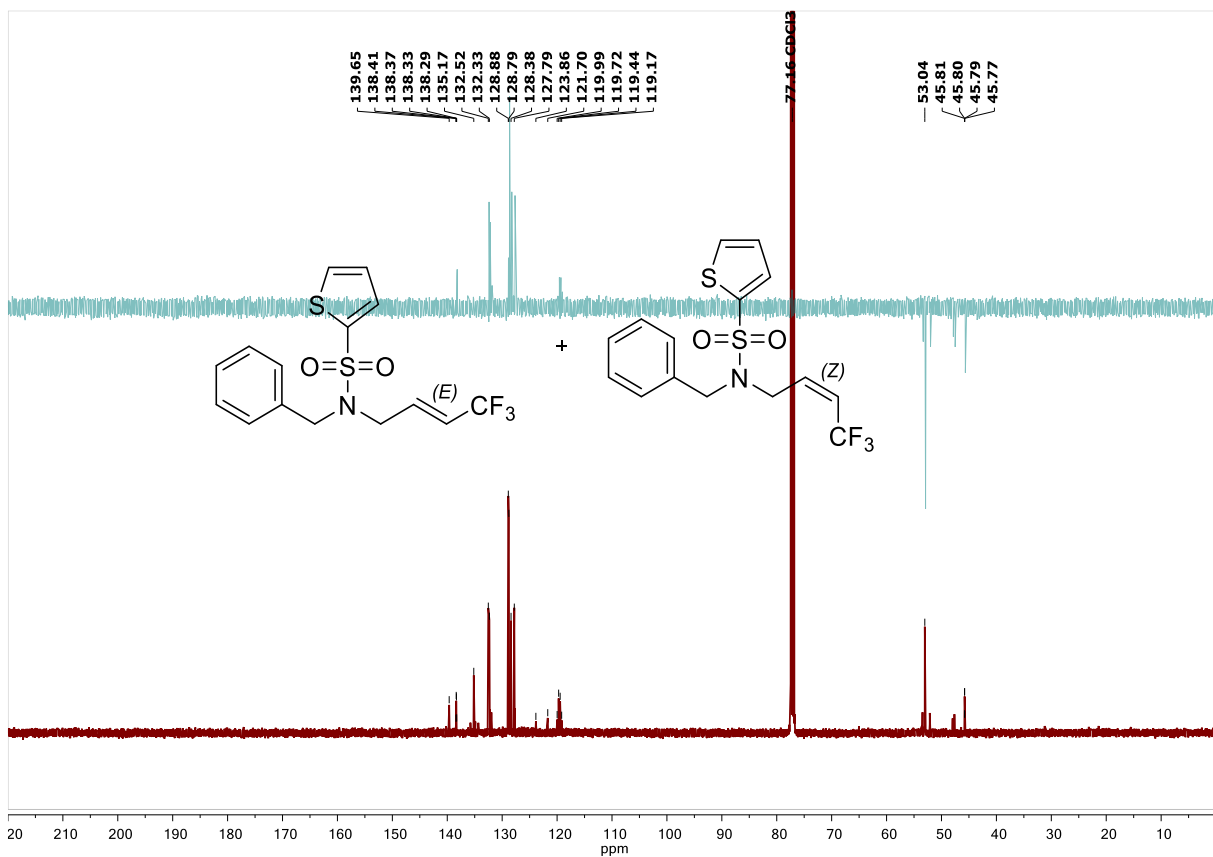
$^1\text{H NMR}$ (CDCl_3 , 500 MHz) of **2q**



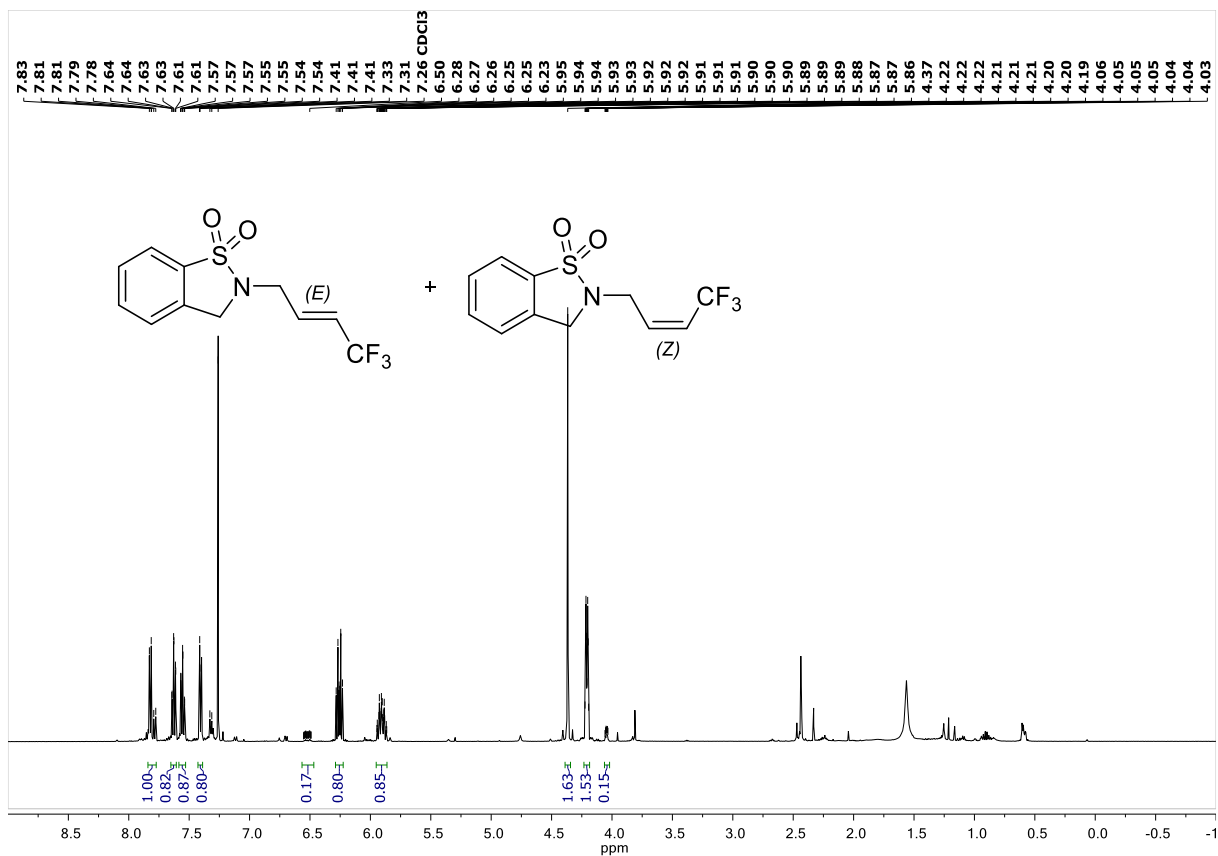
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 126 MHz) of **2q**
S64



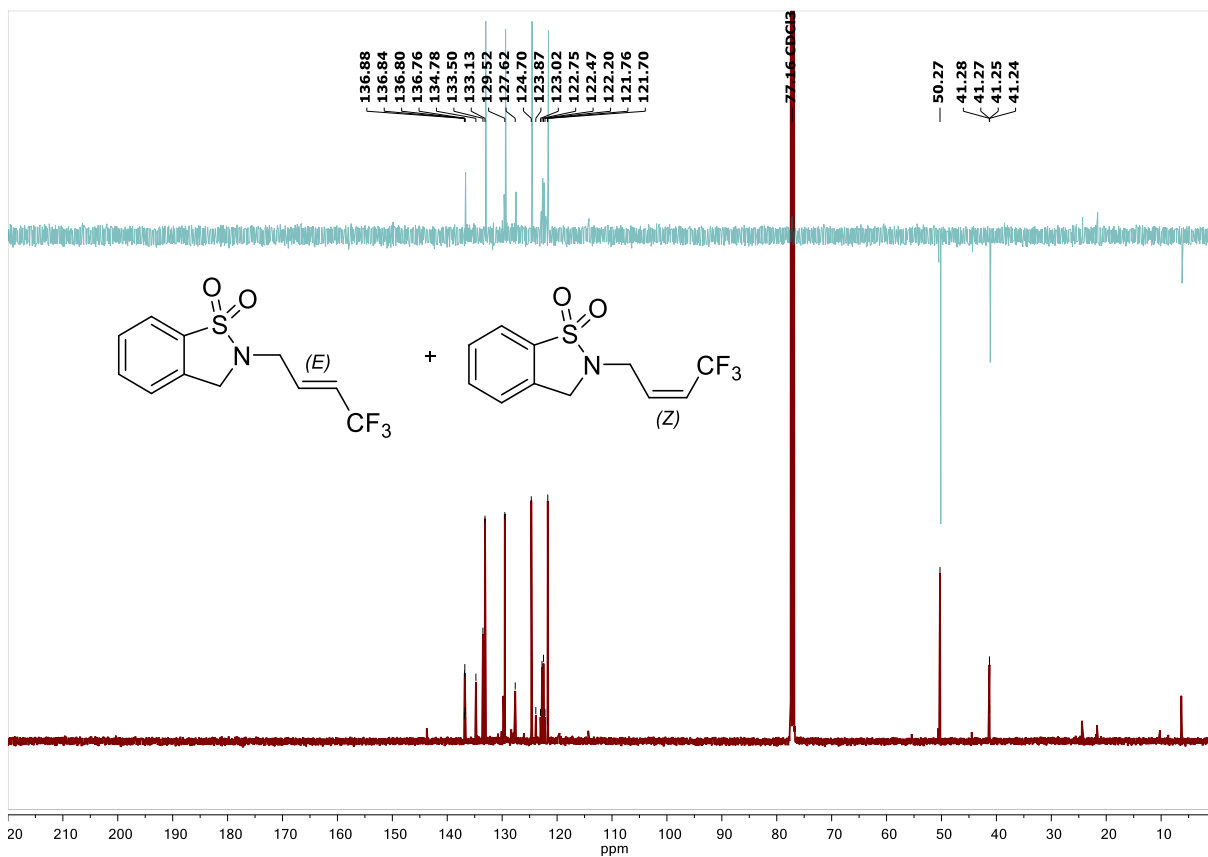
¹H NMR (CDCl₃, 500 MHz) of 2r



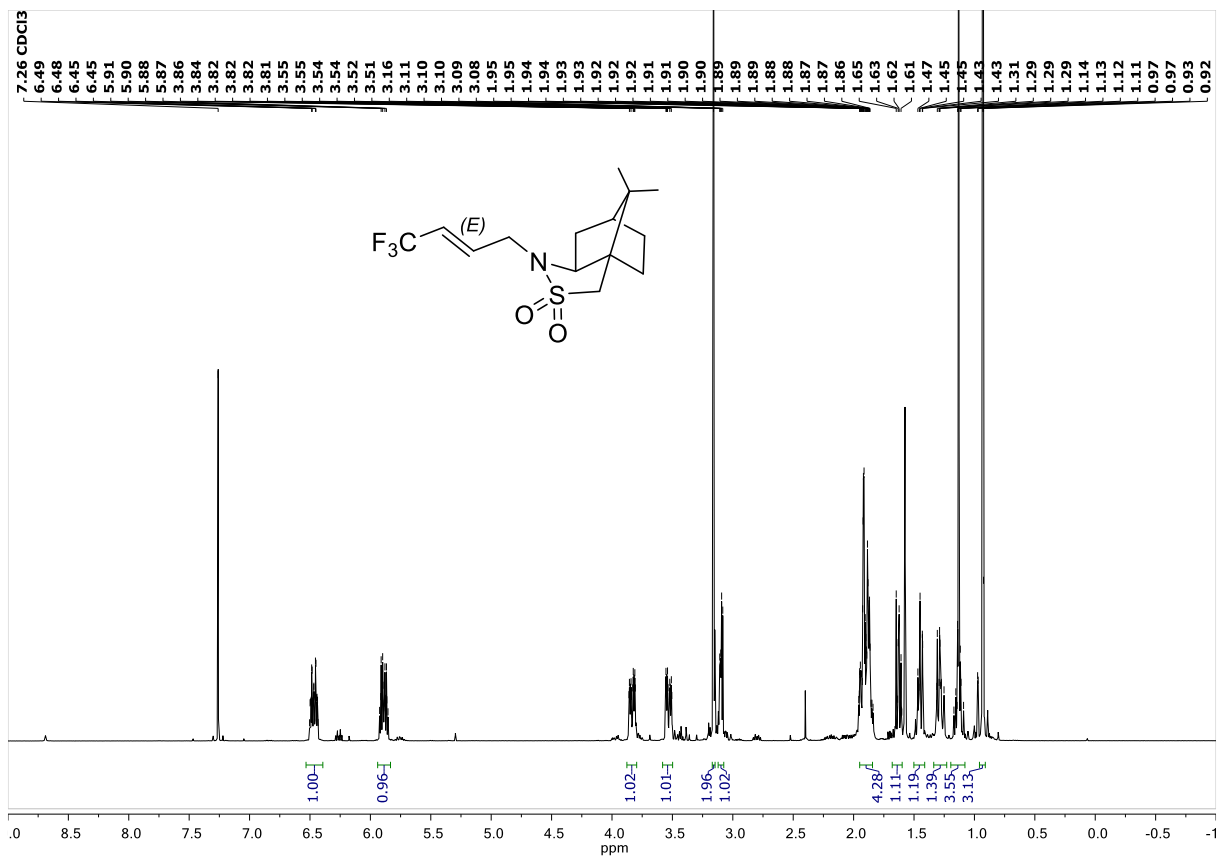
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 2r
S65



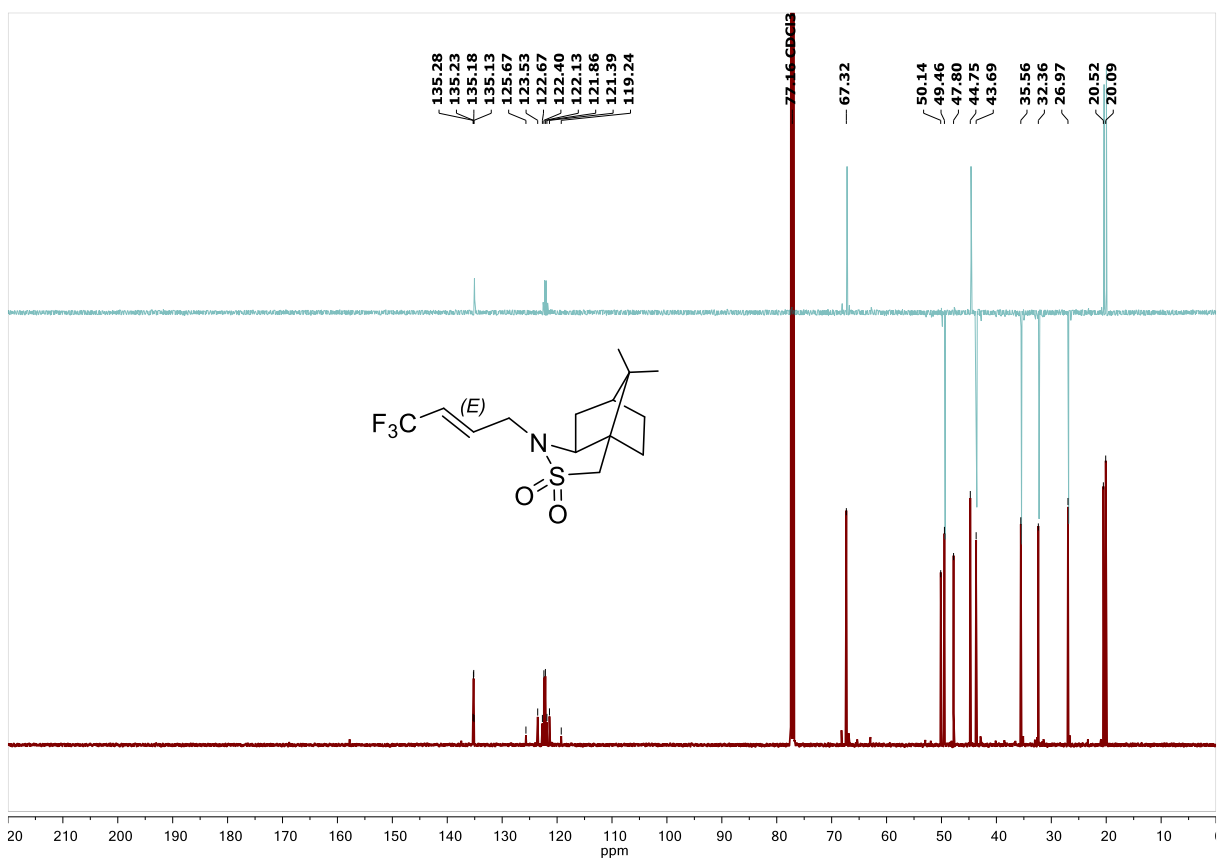
¹H NMR (CDCl₃, 500 MHz) of 2s



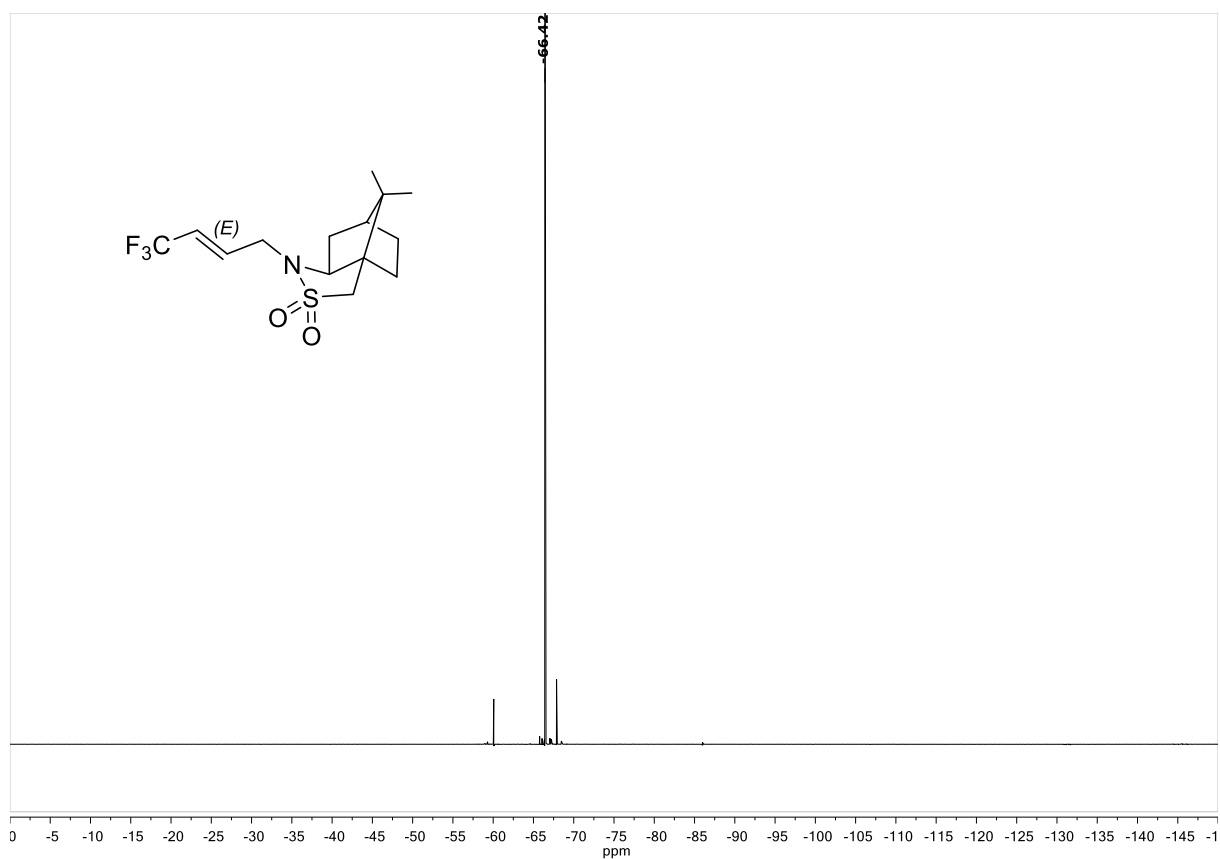
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 2s
S66



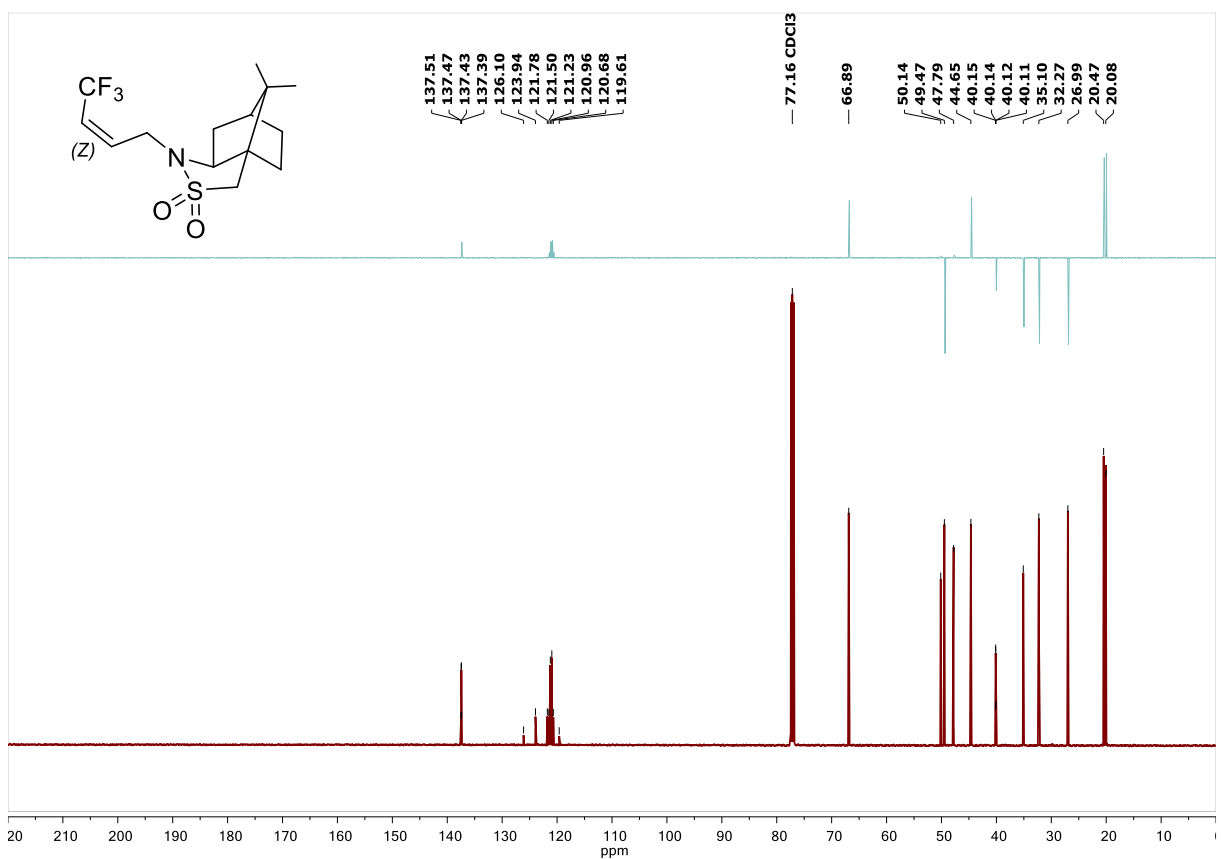
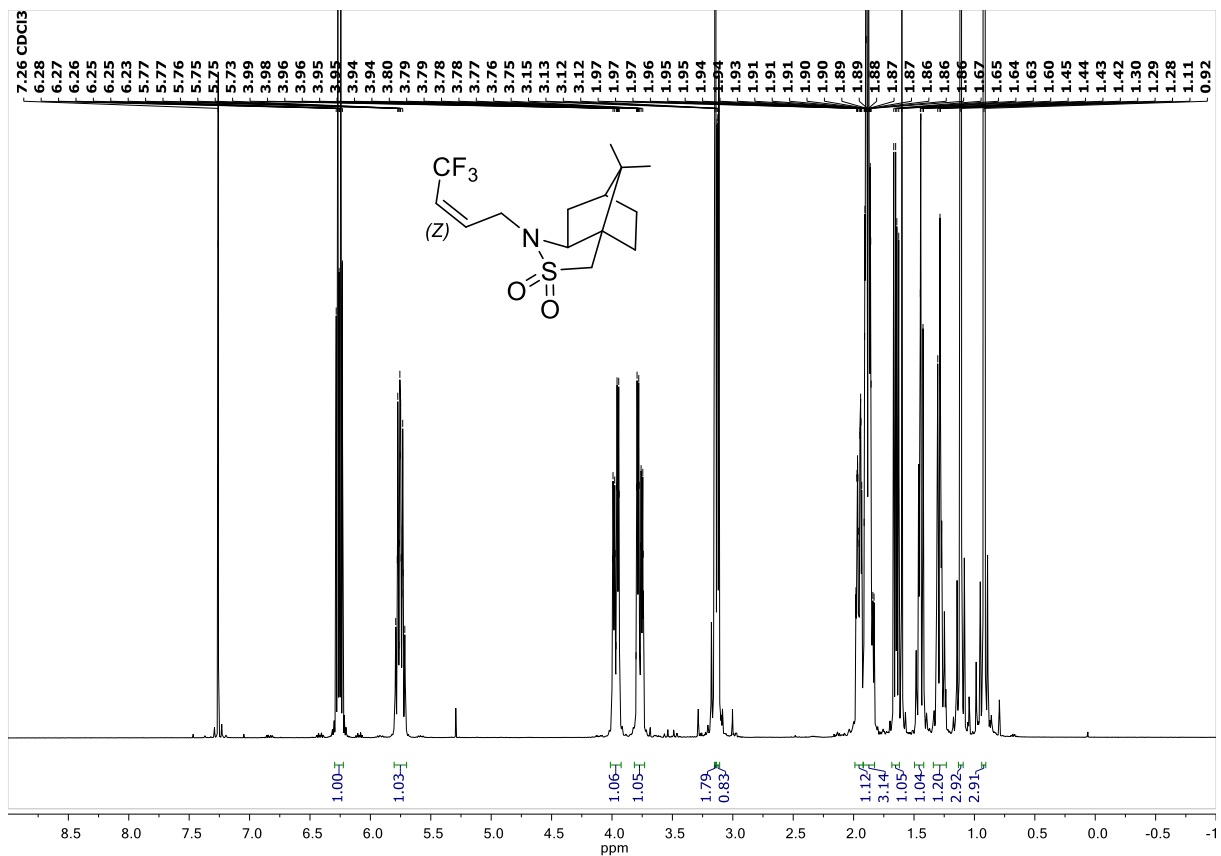
¹H NMR (CDCl₃, 500 MHz) of 2t-E



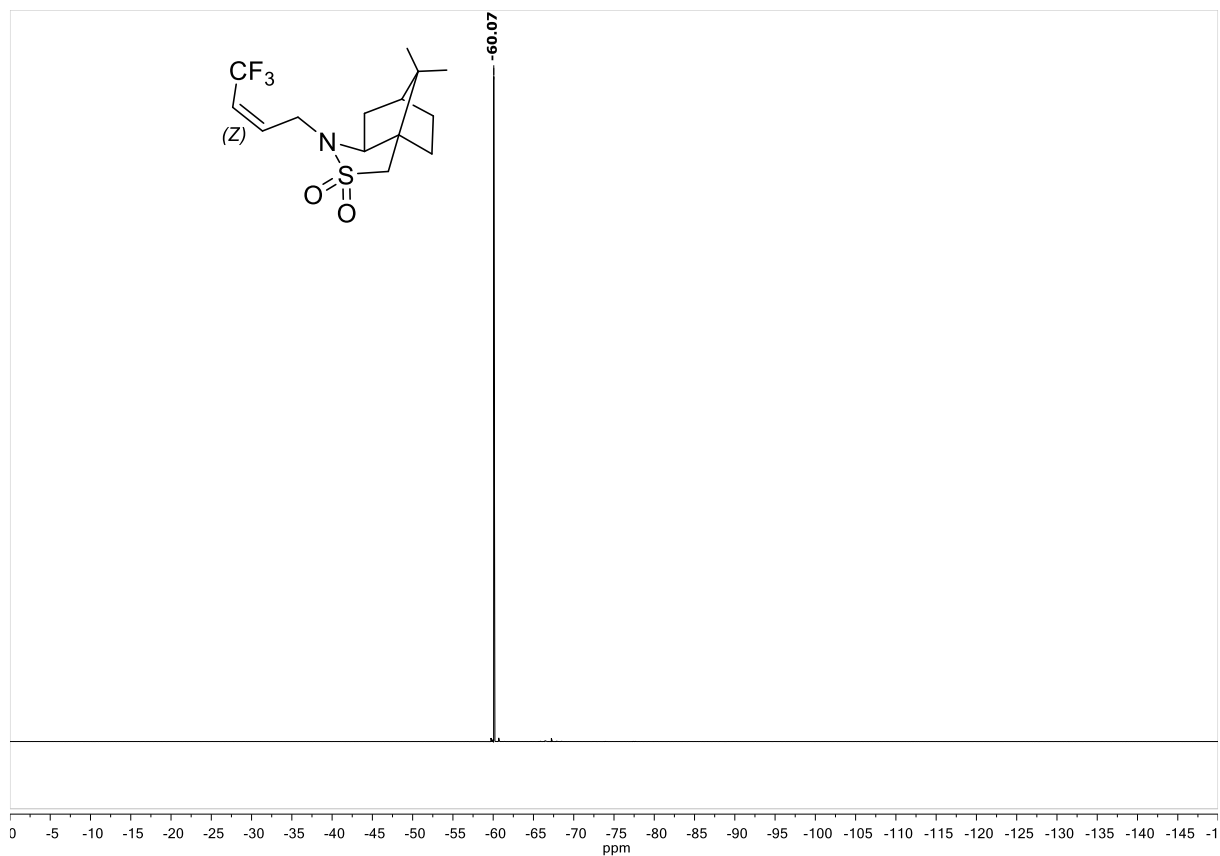
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 2t-E
S67



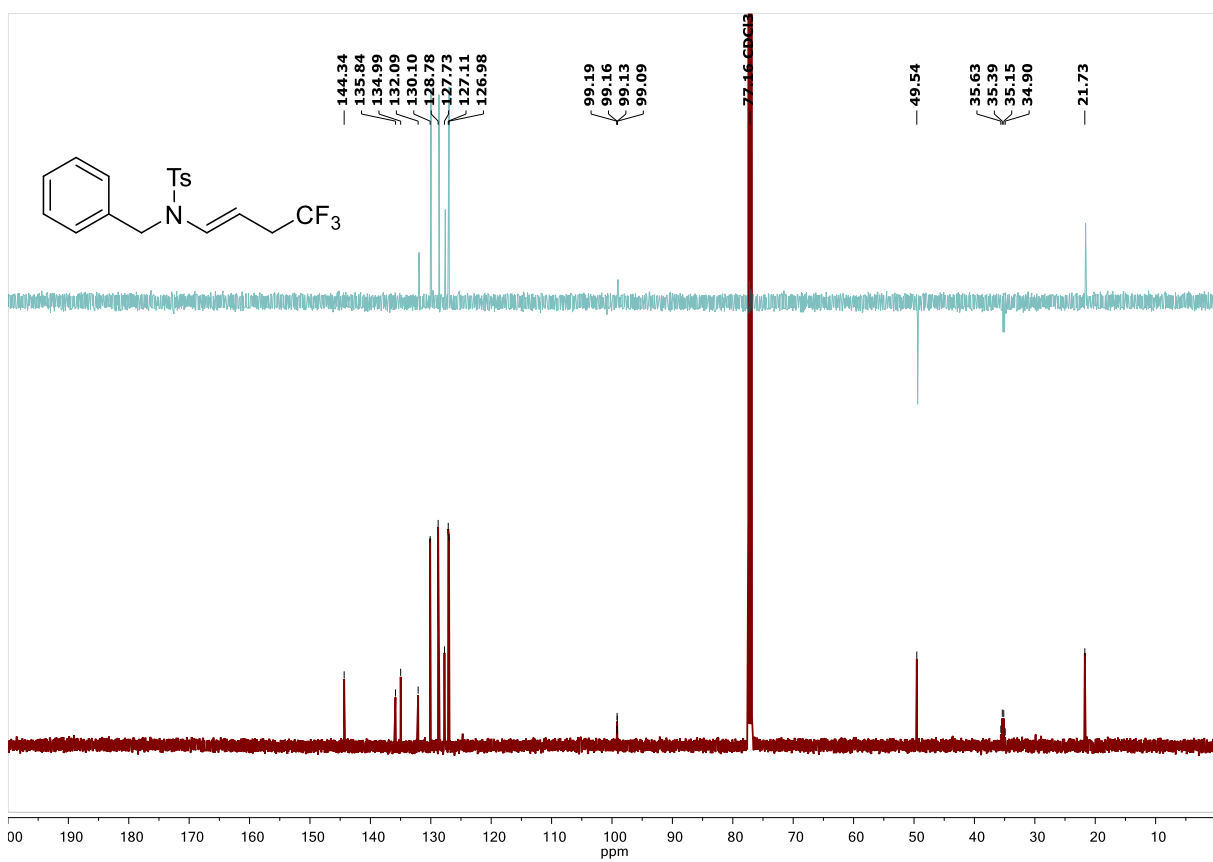
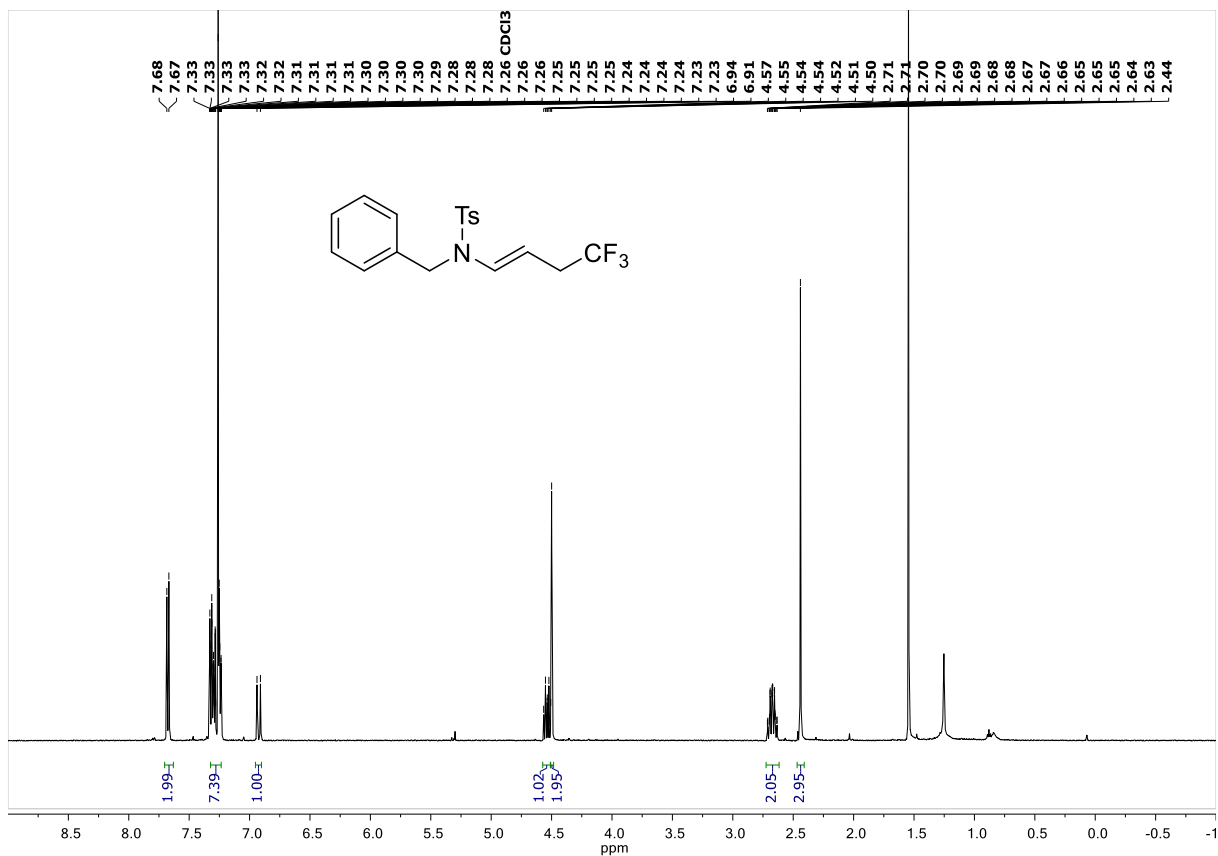
$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 282 MHz) of **2t-E**

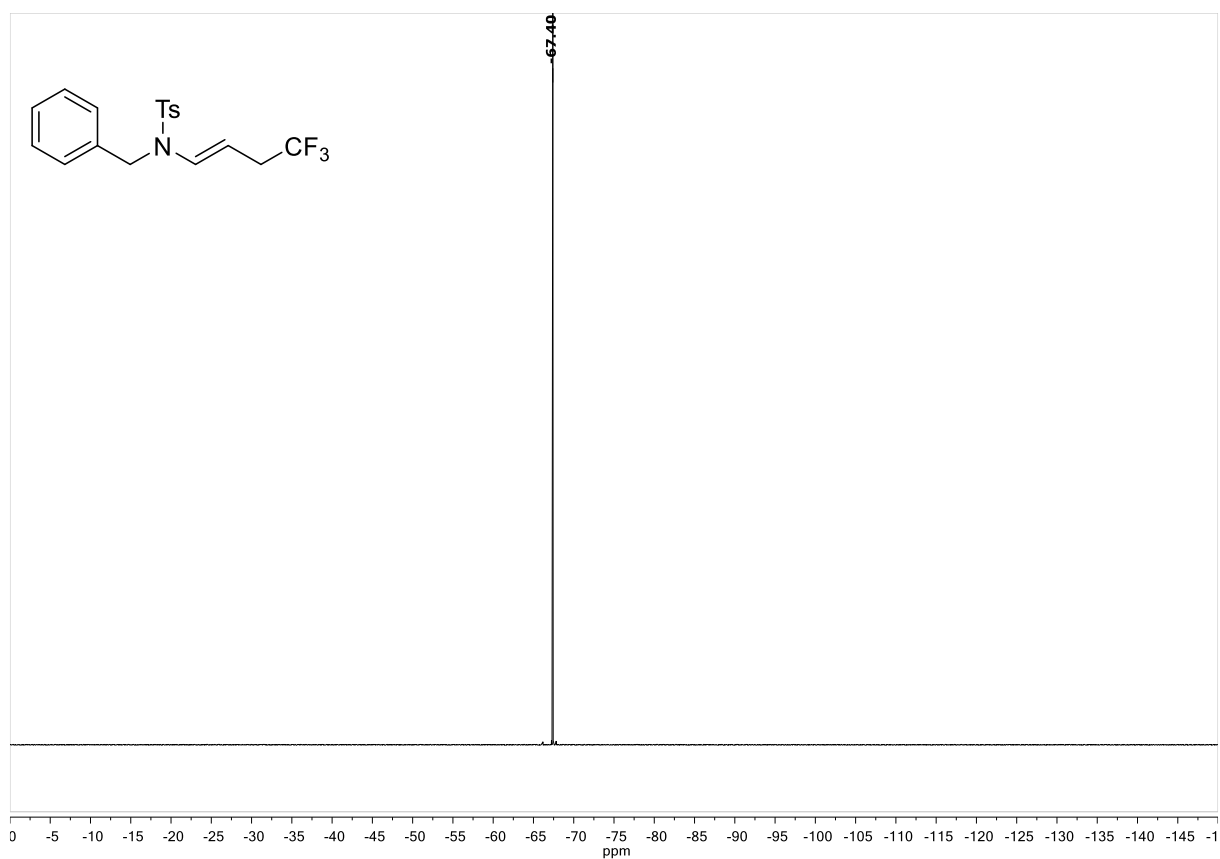


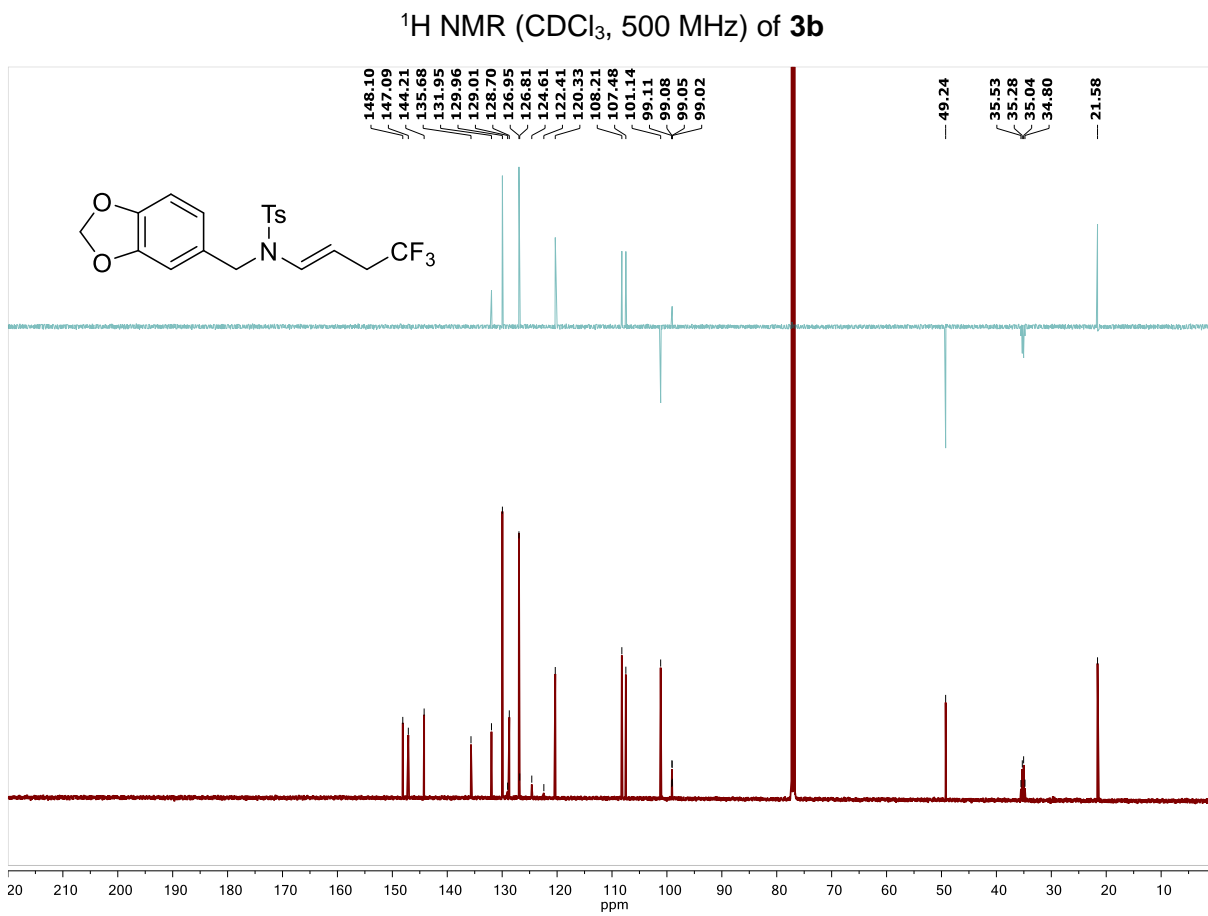
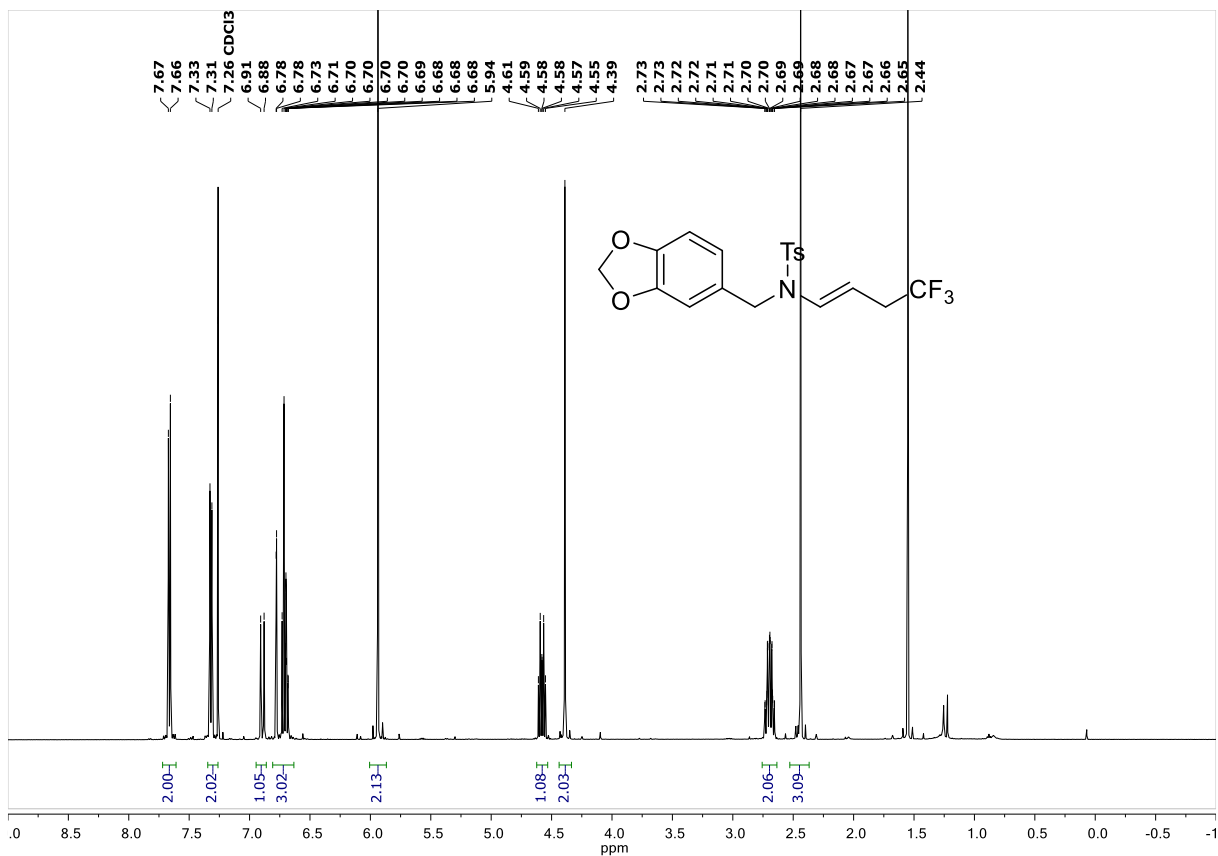
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 2t-Z
S69



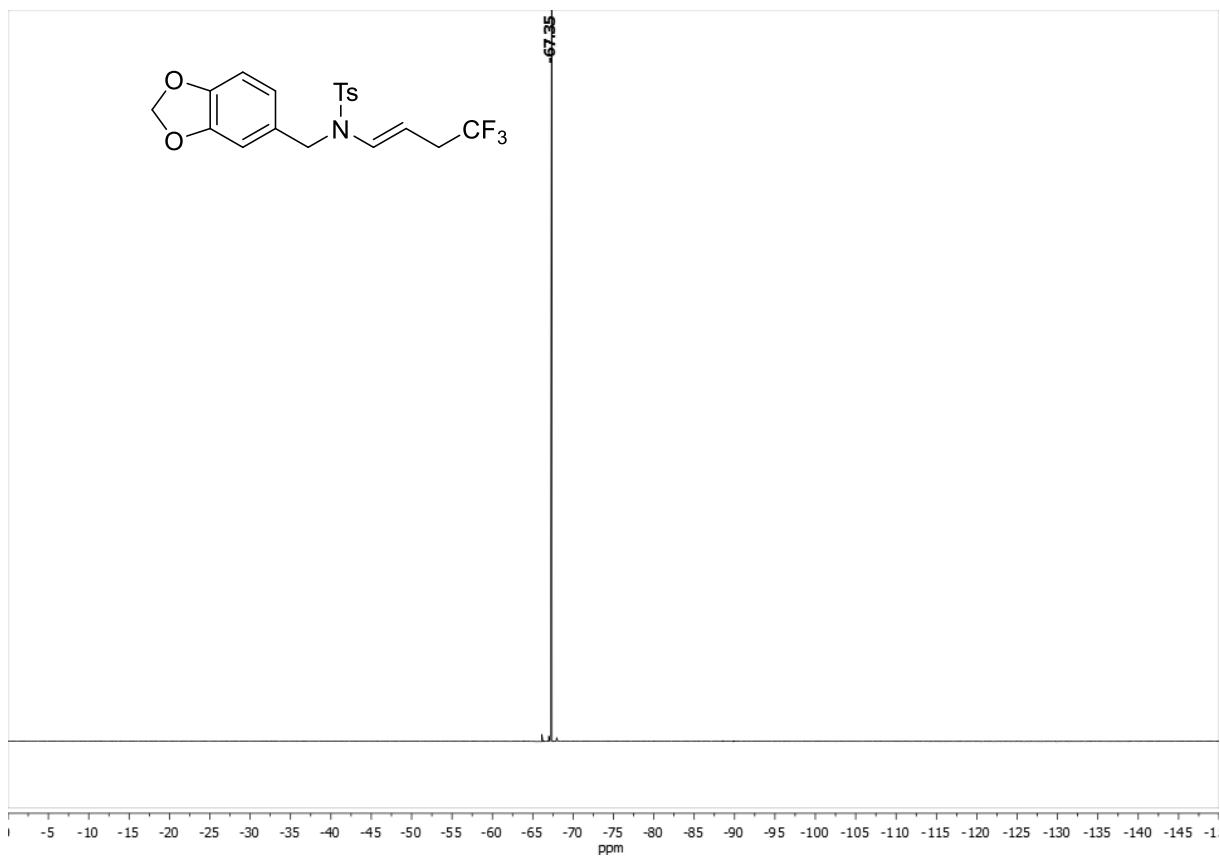
$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 282 MHz) of **2t-Z**

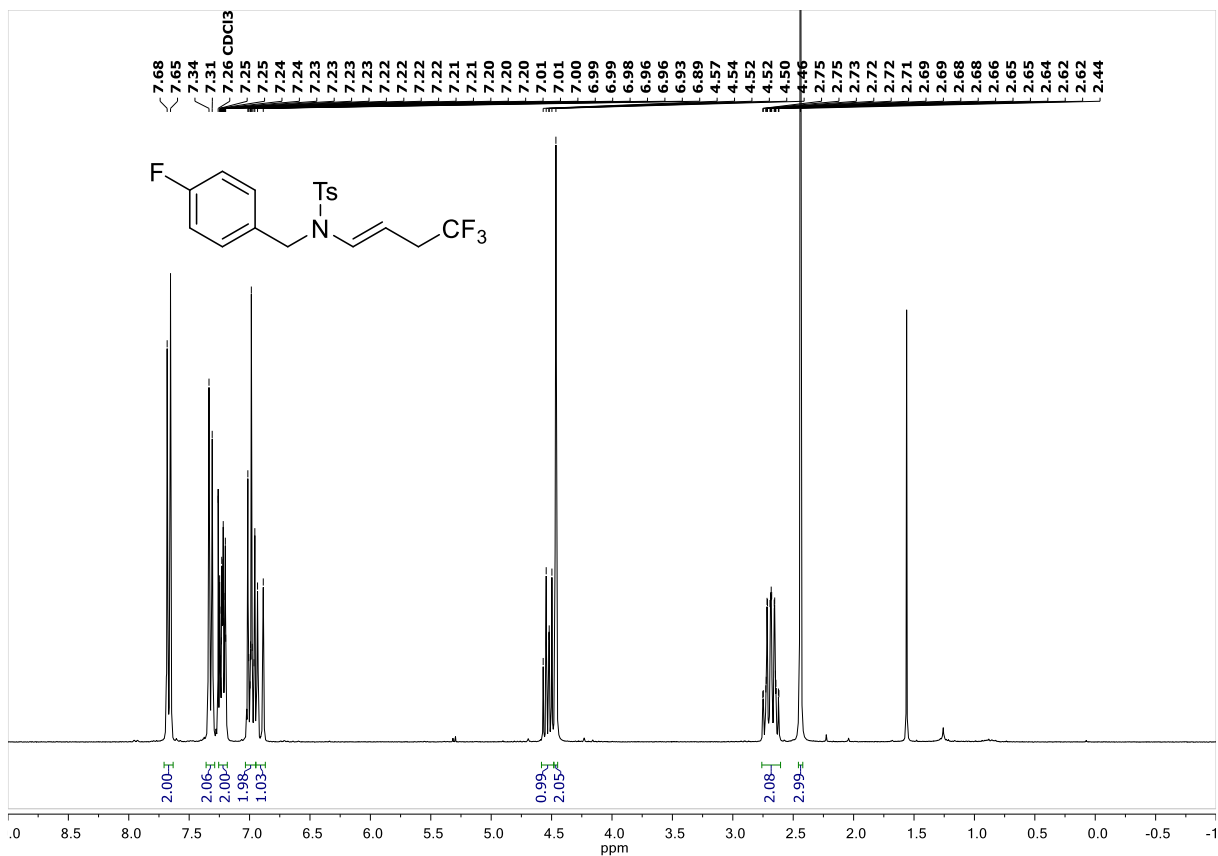




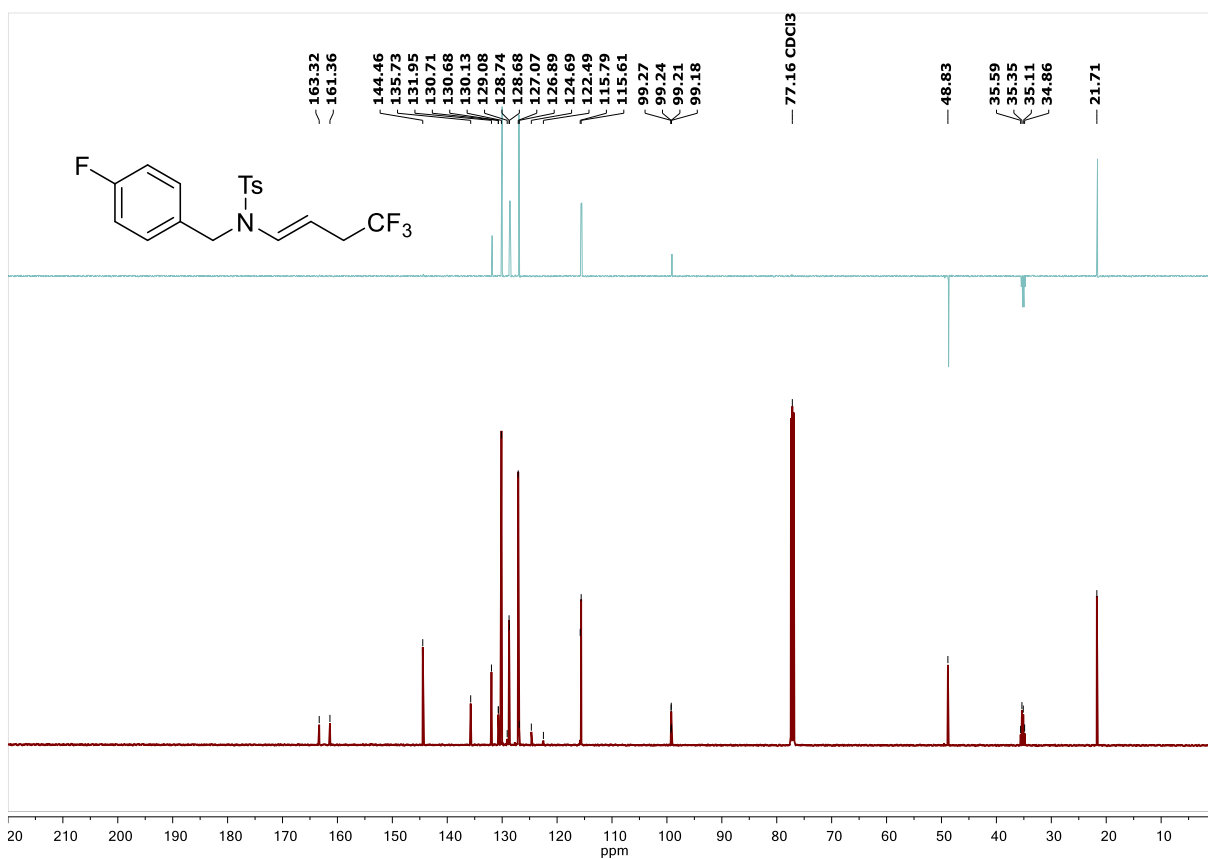


¹³C{¹H} NMR (CDCl₃, 126 MHz) of **3b**
S73



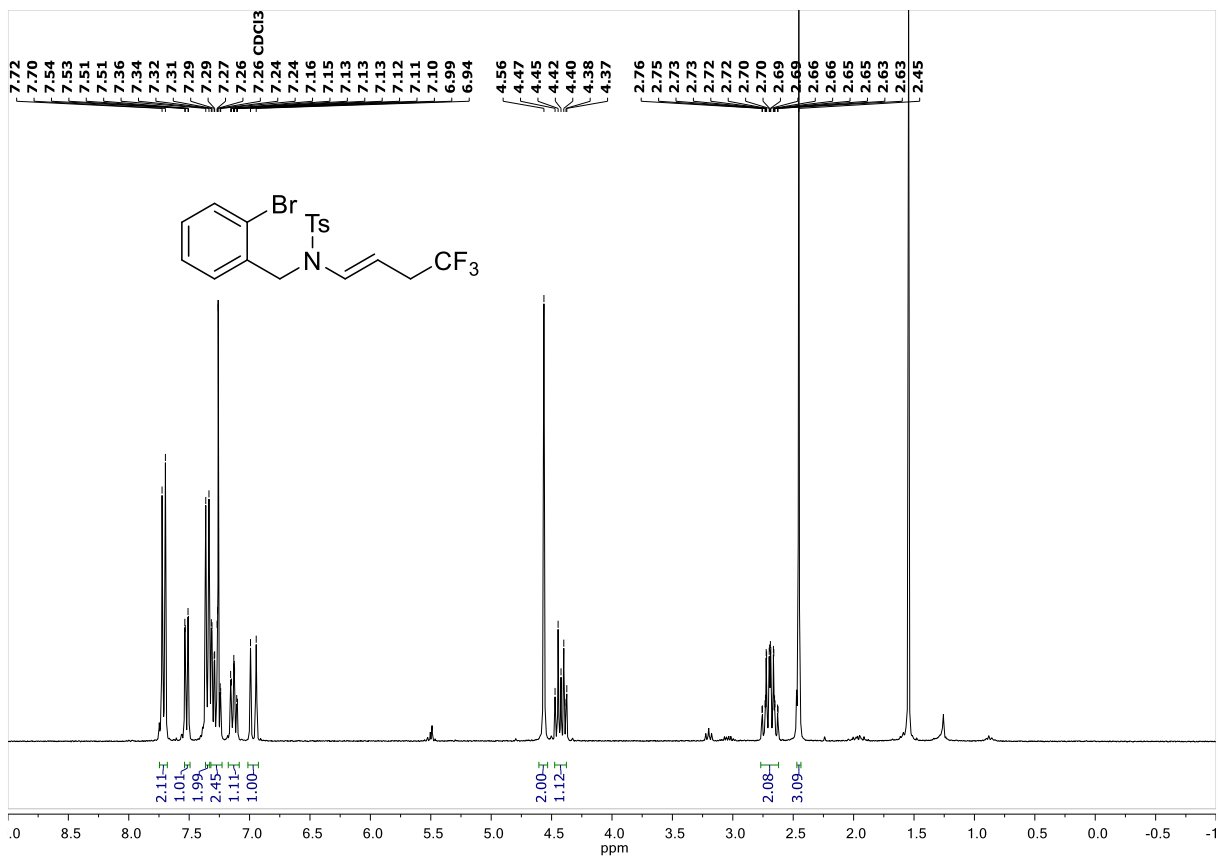


¹H NMR (CDCl₃, 300 MHz) of 3c

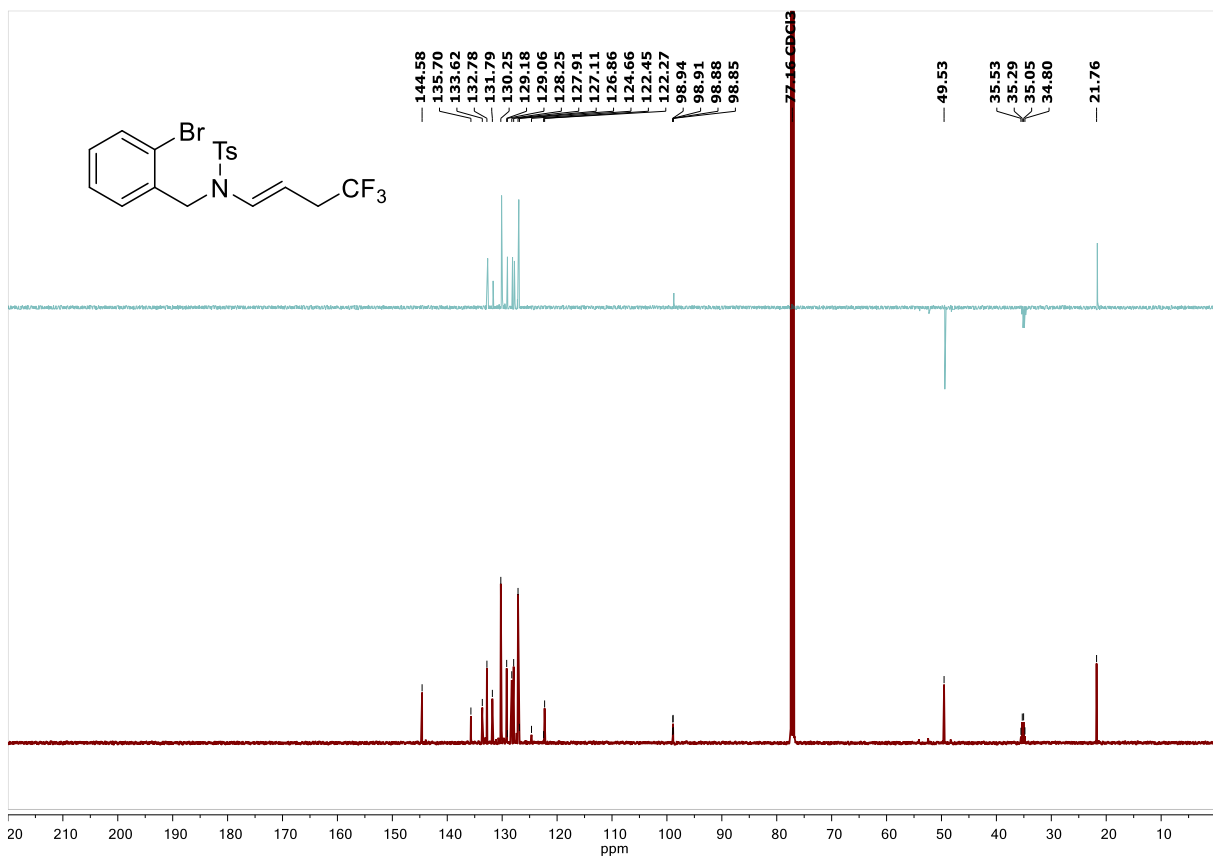


¹³C{¹H} NMR (CDCl₃, 126 MHz) of 3c

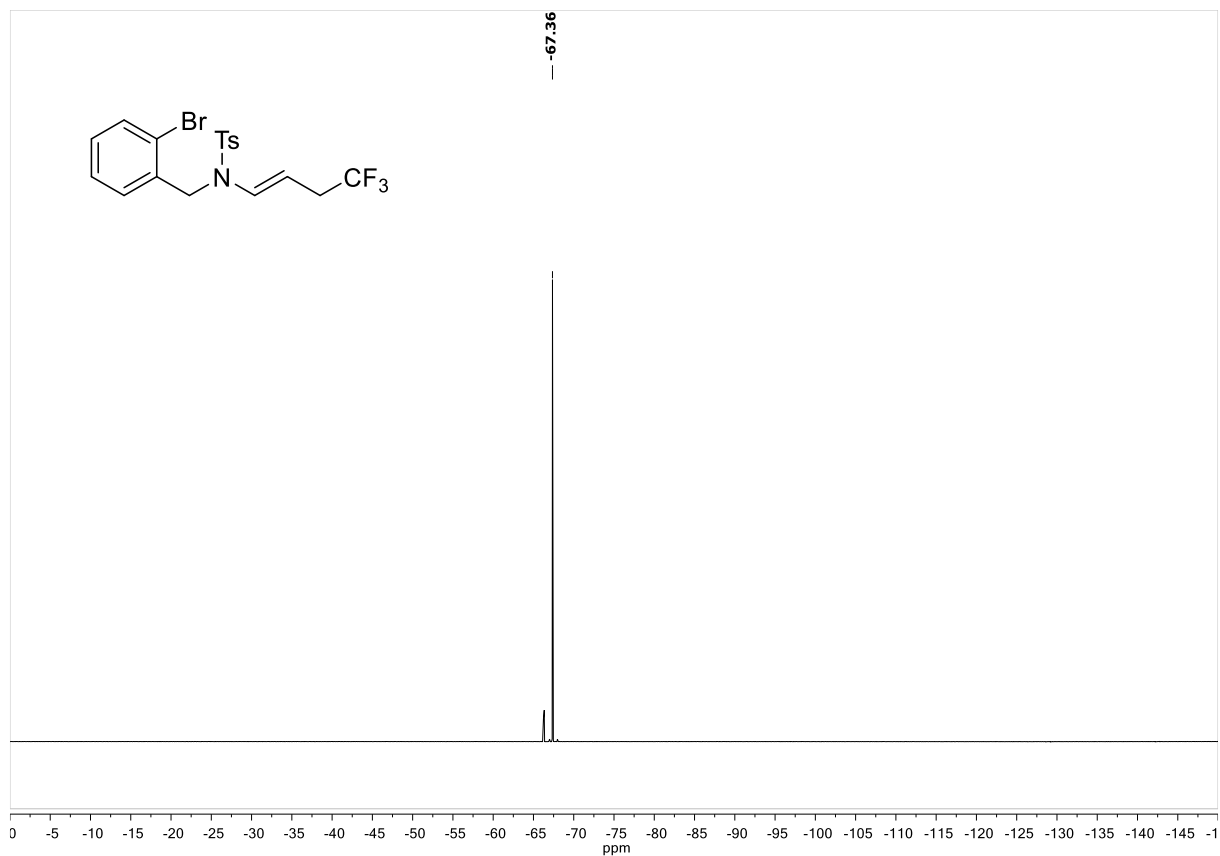


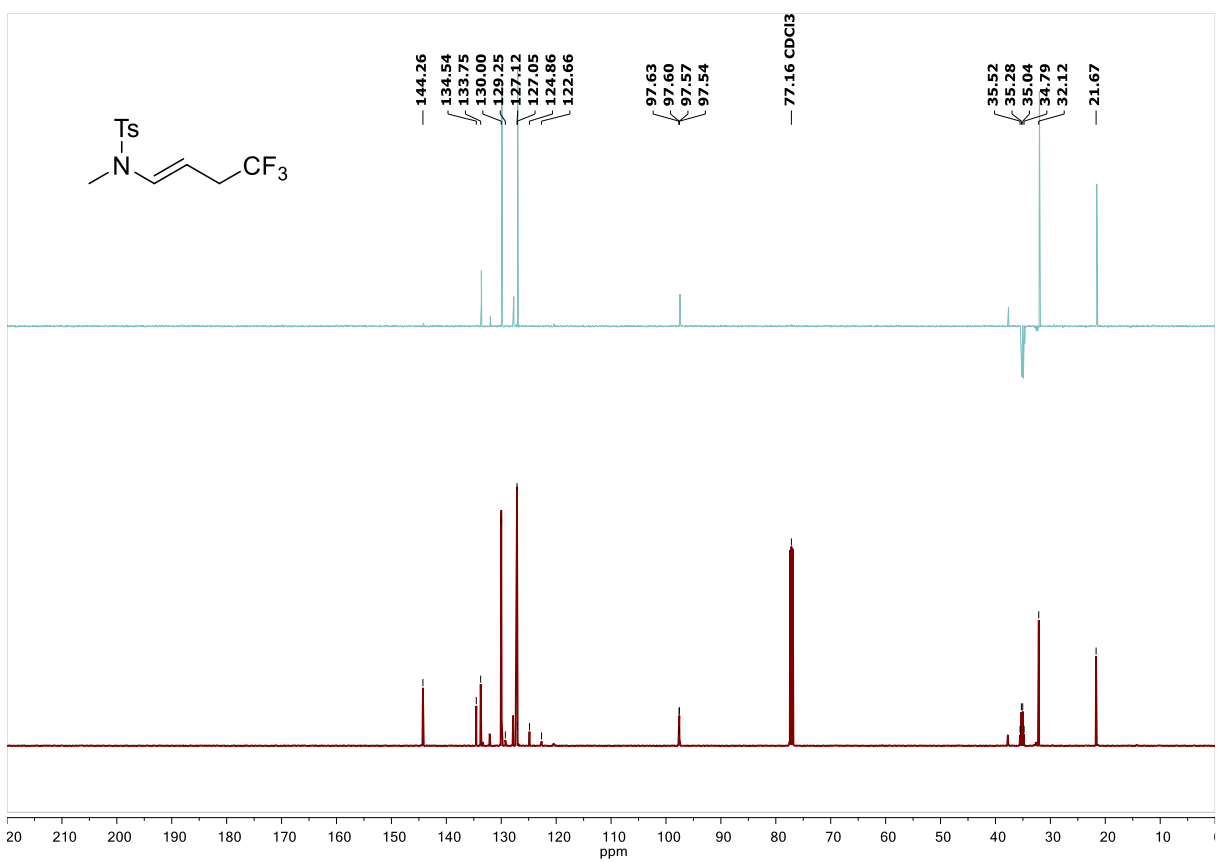
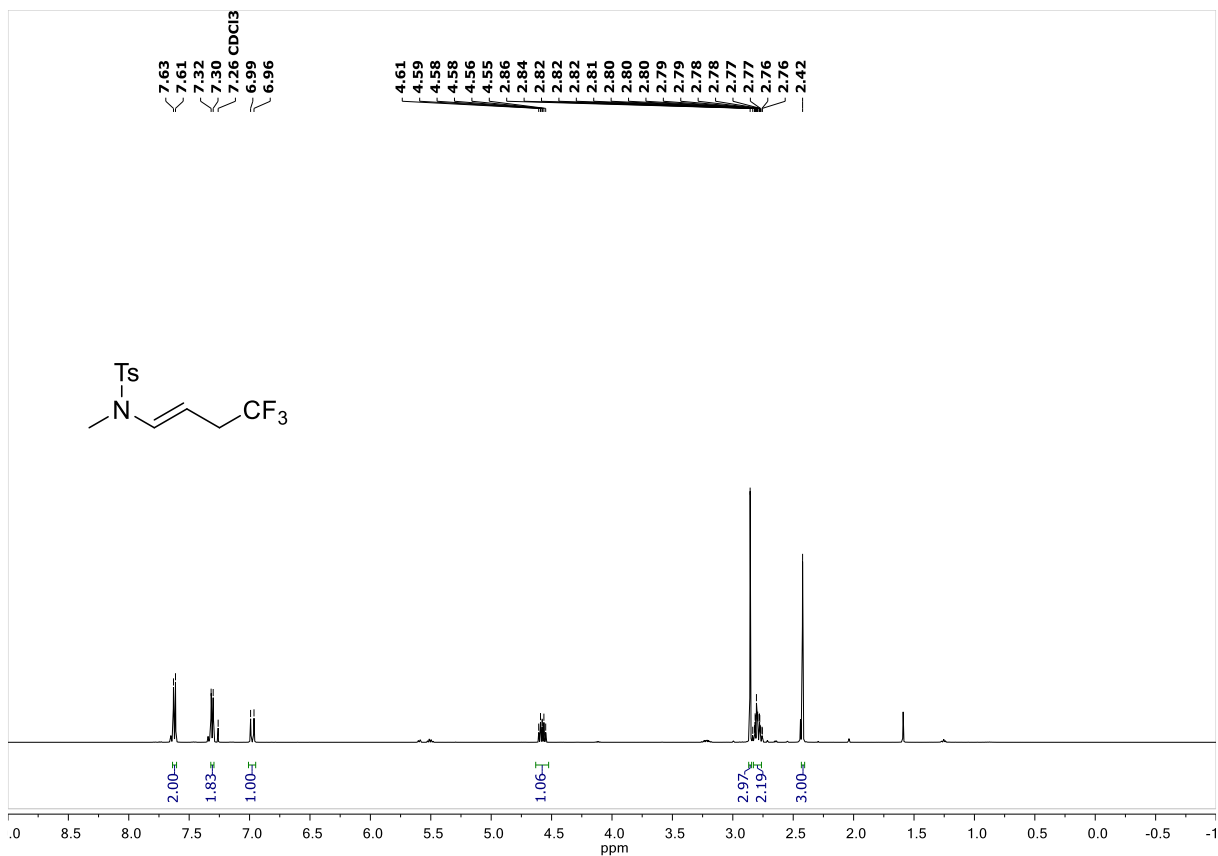


¹H NMR (CDCl₃, 300 MHz) of 3d

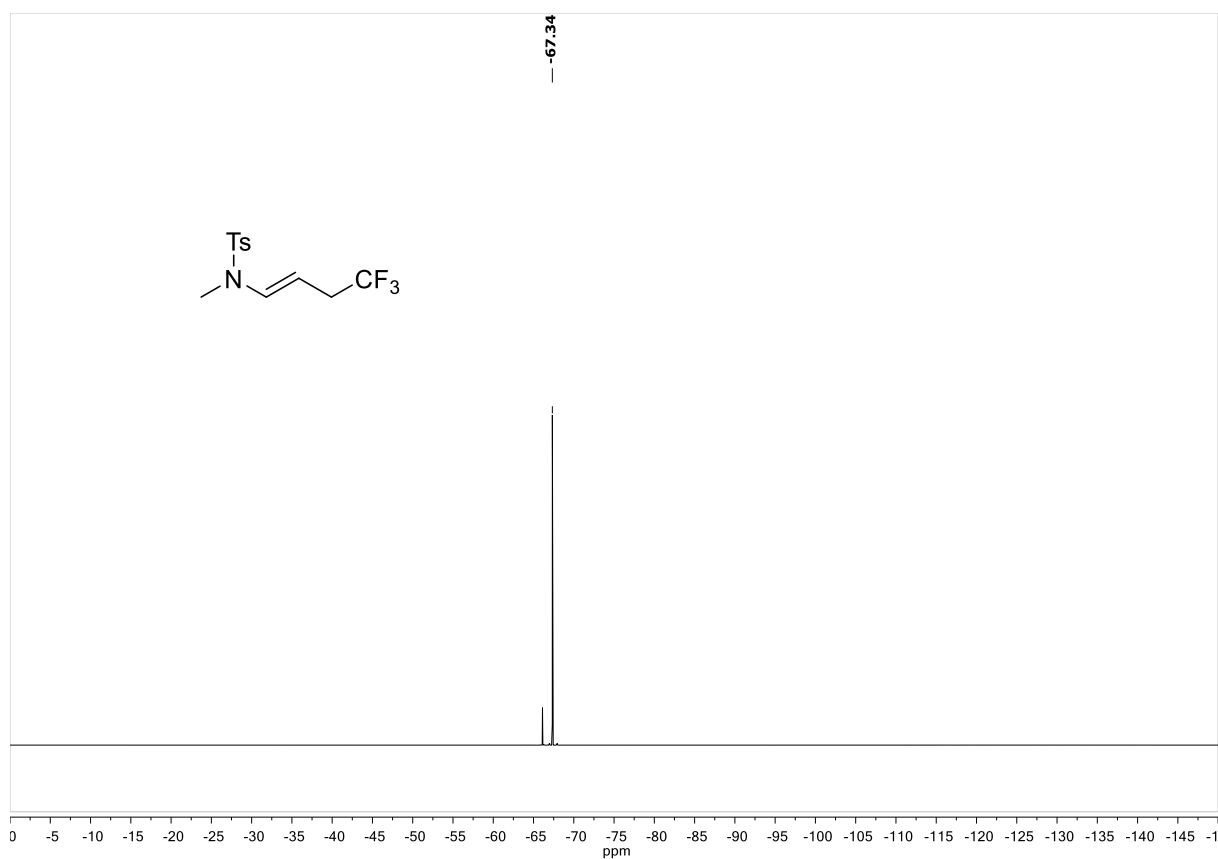


¹³C{¹H} NMR (CDCl₃, 126 MHz) of 3d

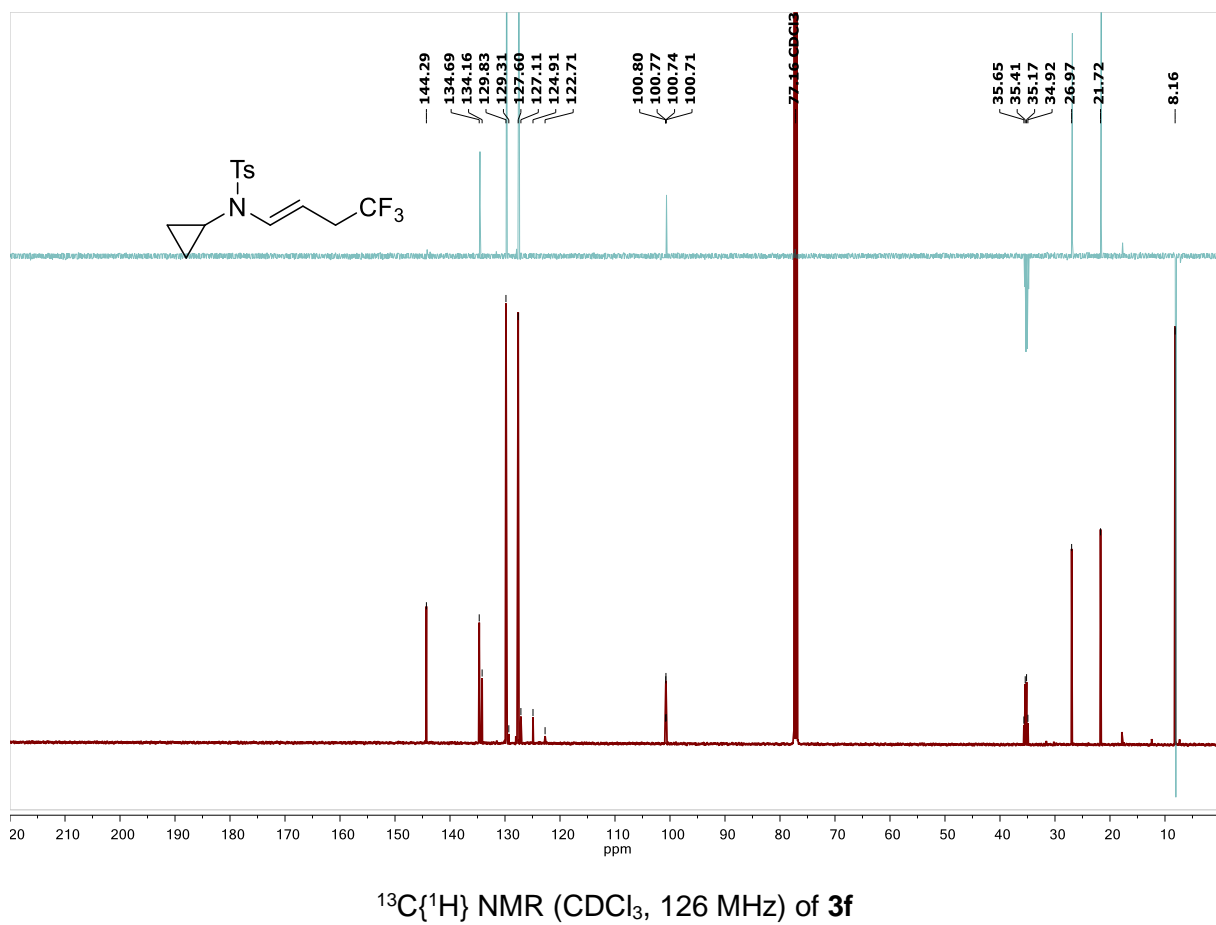
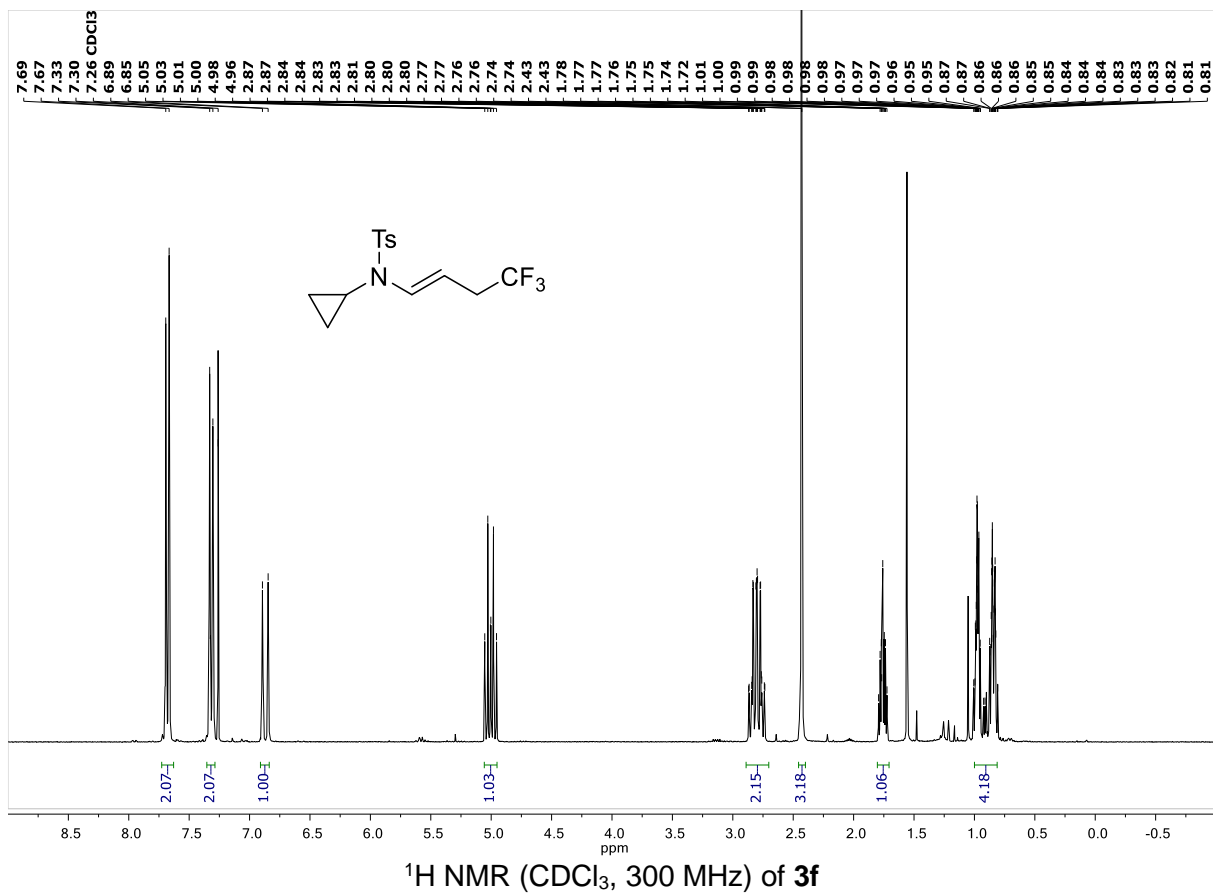


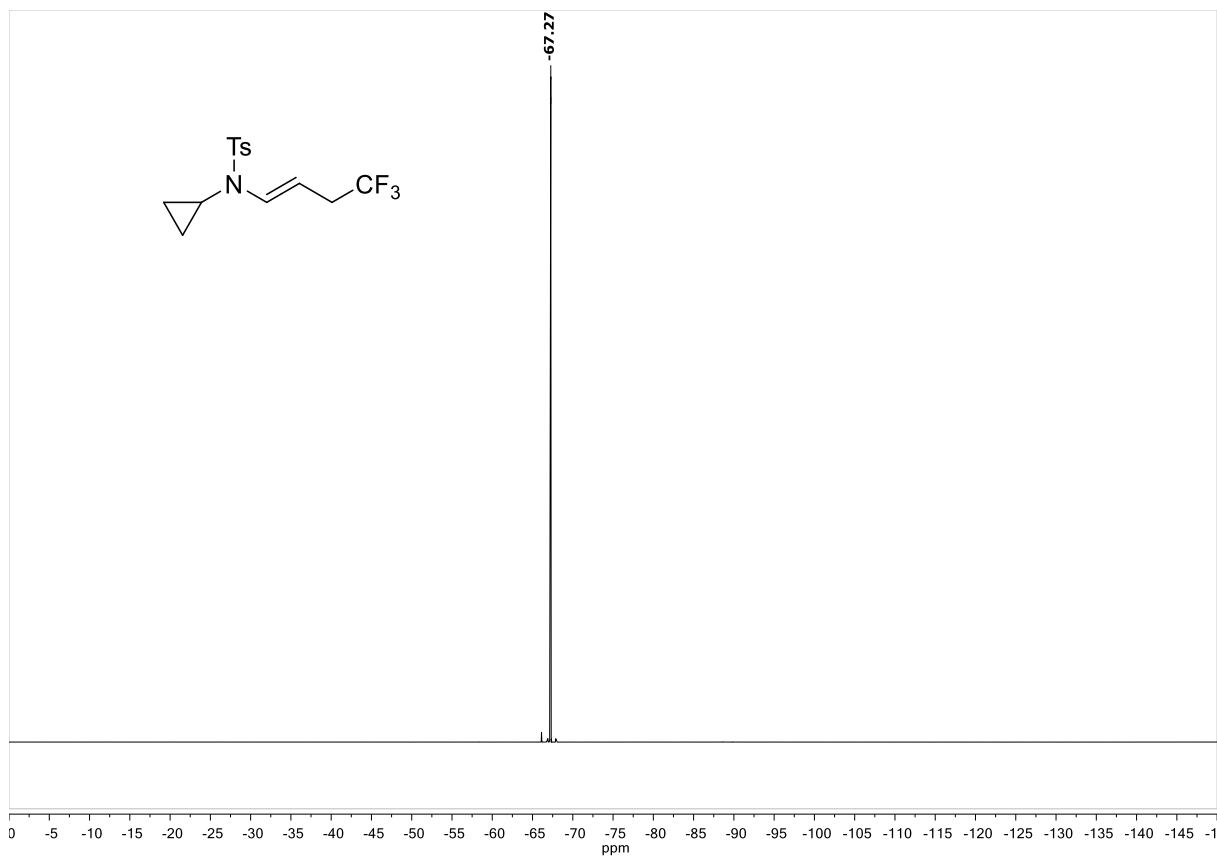


¹³C{¹H} NMR (CDCl₃, 126 MHz) of **3e**

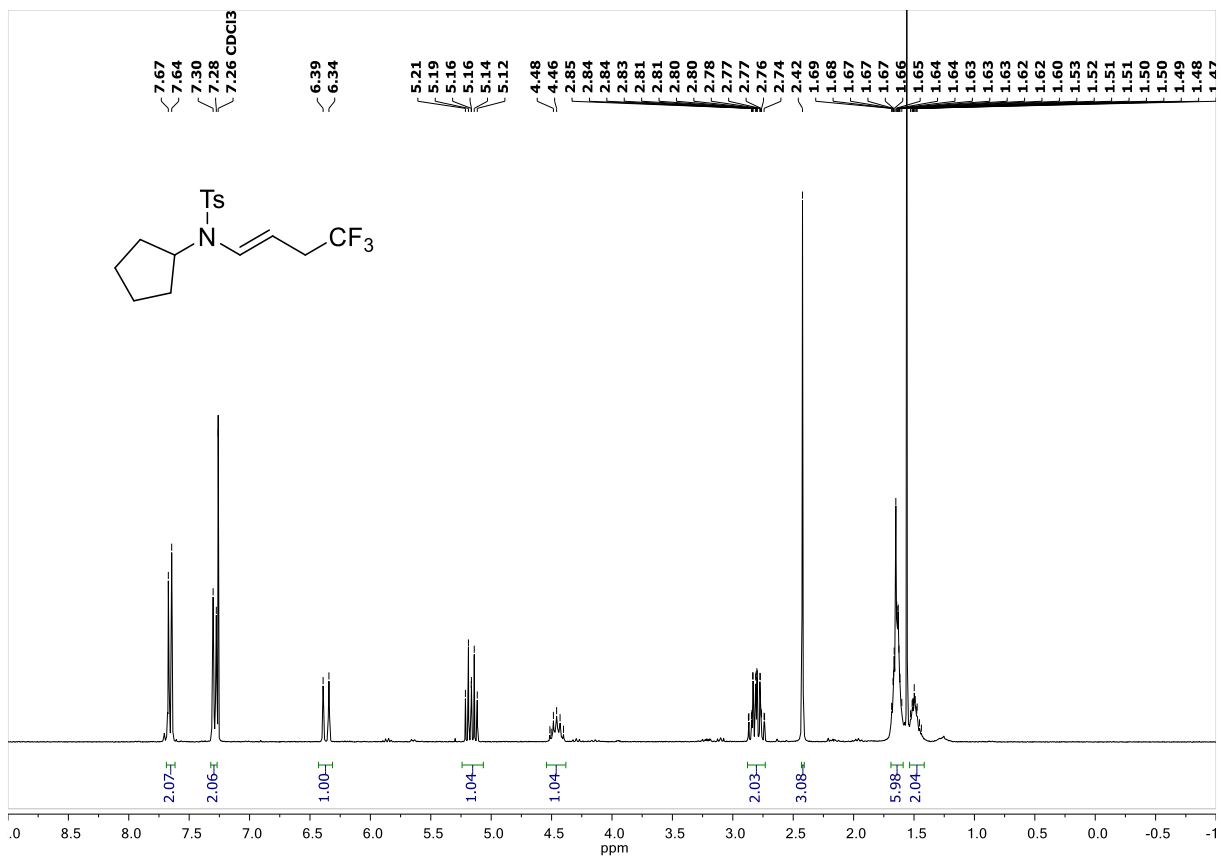


$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 282 MHz) of **3e**

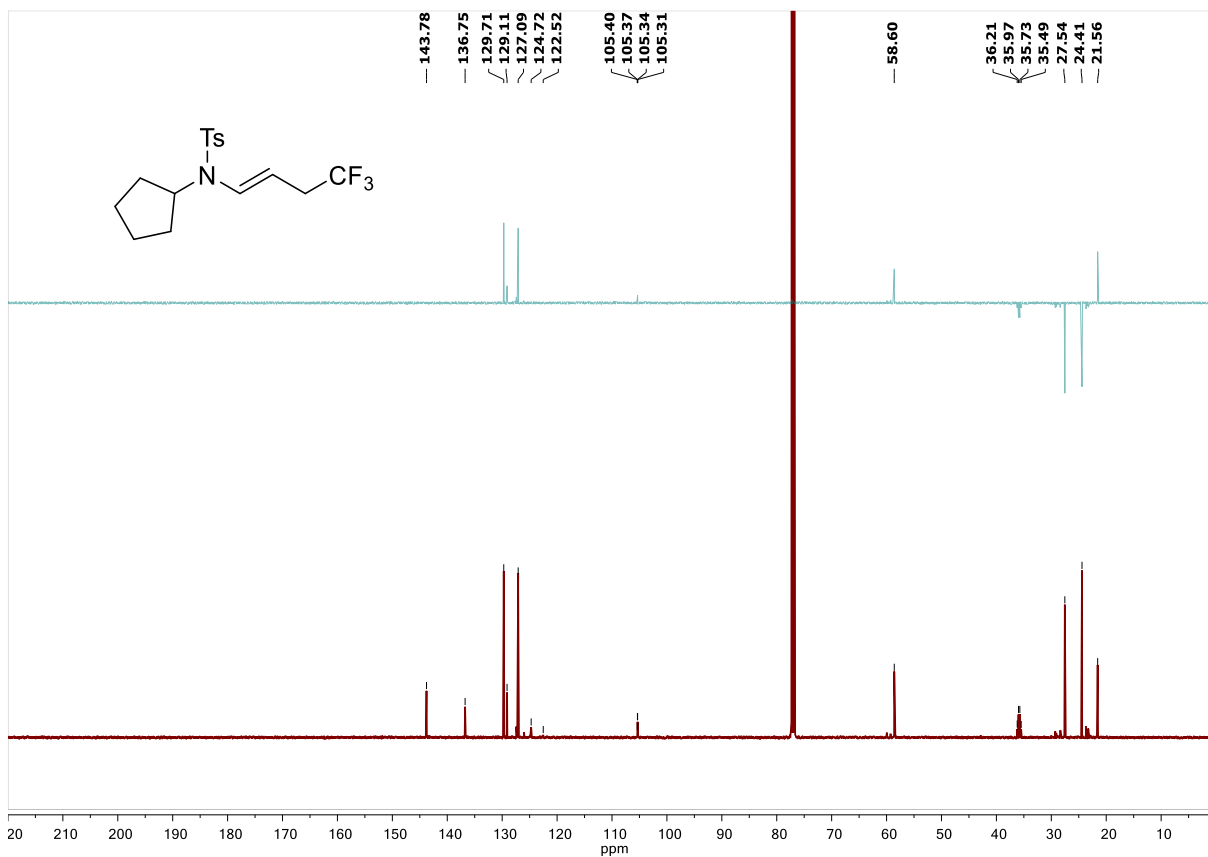




$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 282 MHz) of **3f**

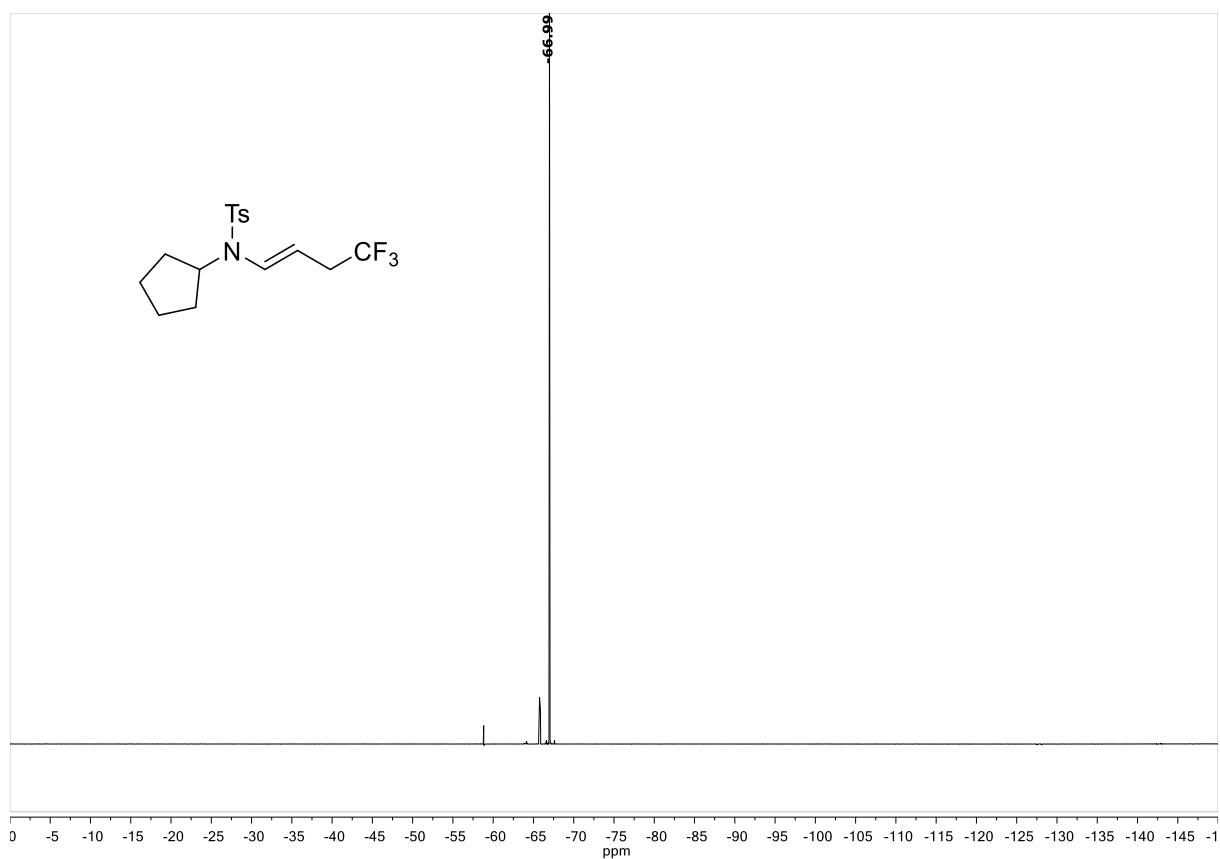


¹H NMR (CDCl₃, 300 MHz) of **3g**

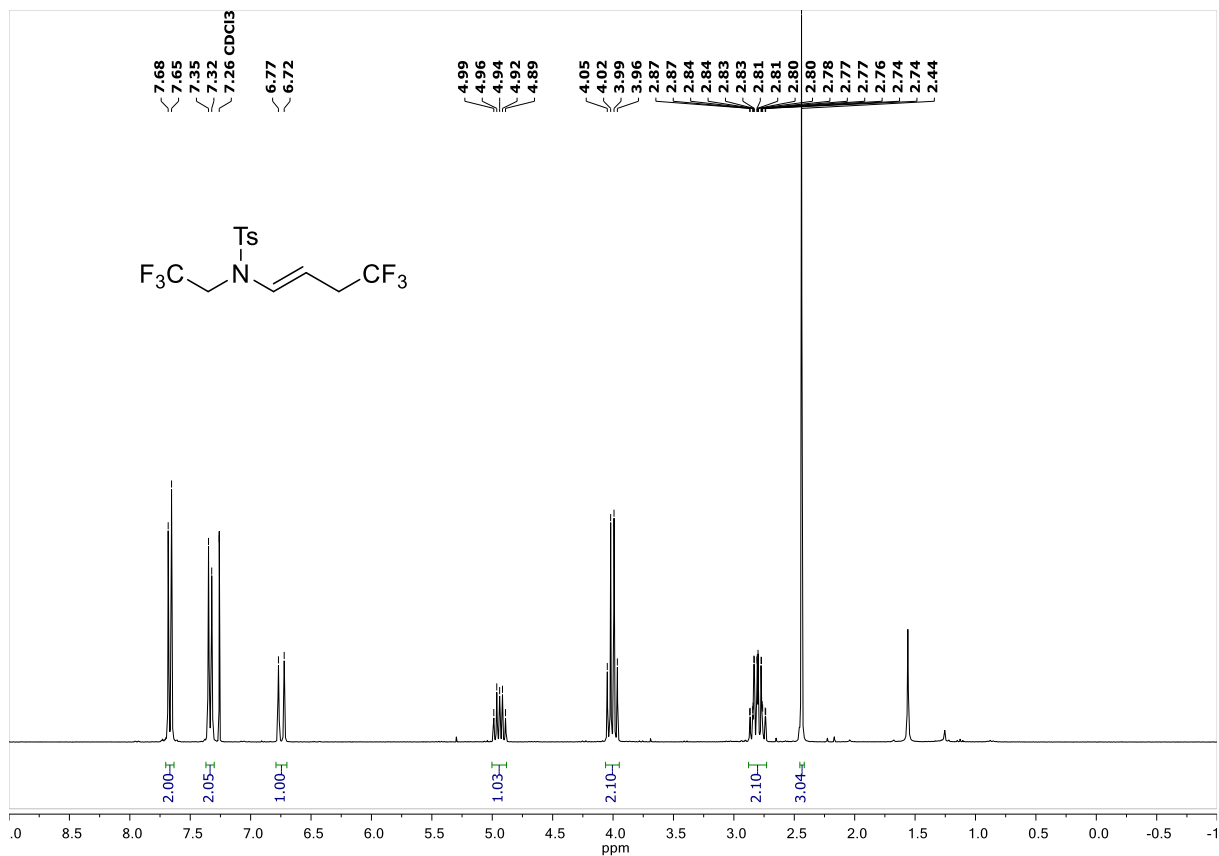


¹³C{¹H} NMR (CDCl₃, 126 MHz) of **3g**

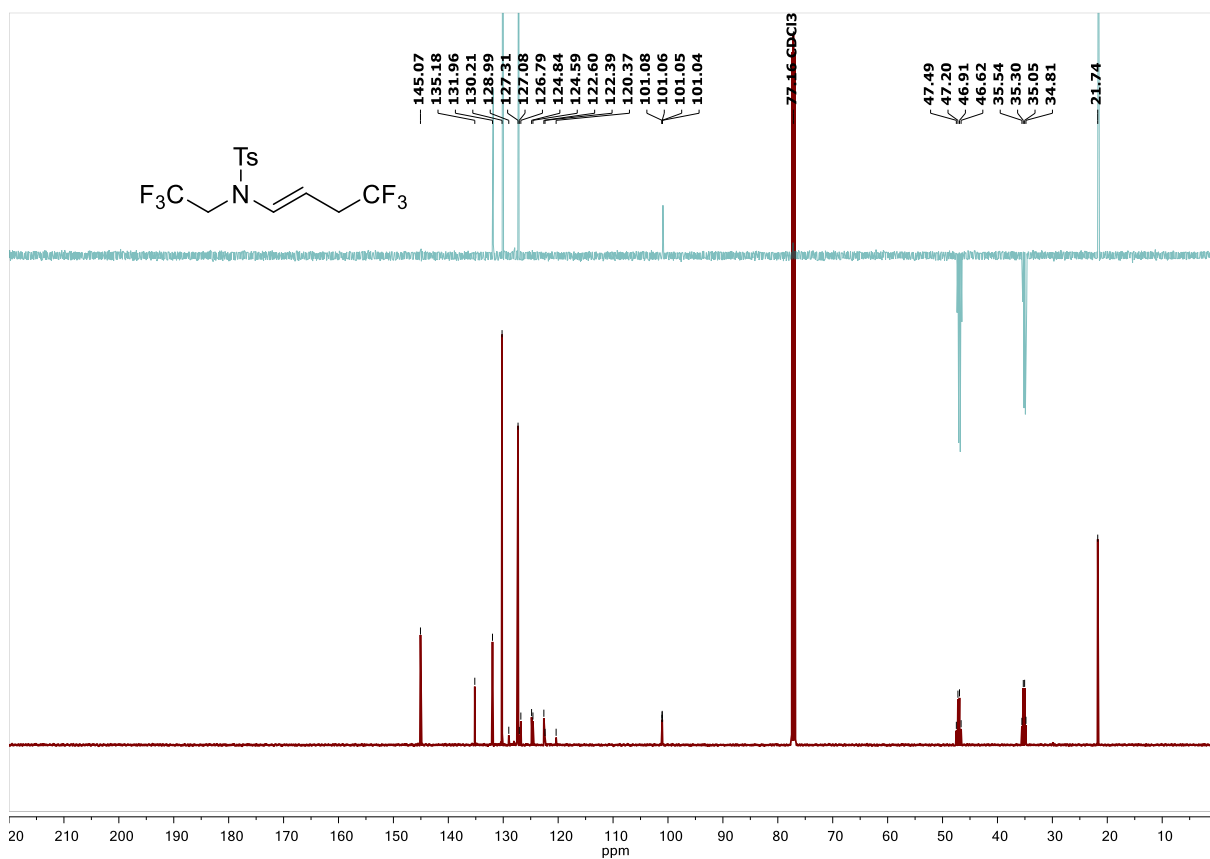
S83



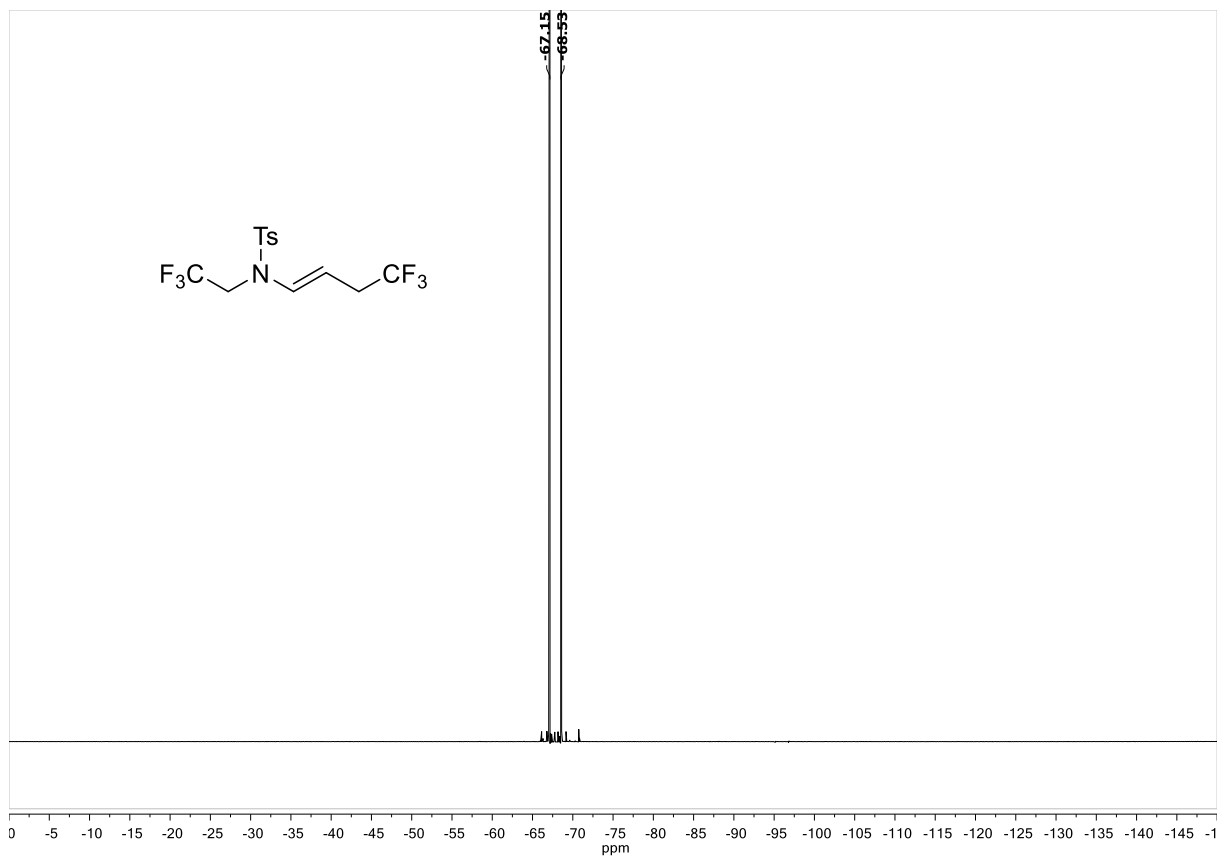
$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 282 MHz) of **3g**



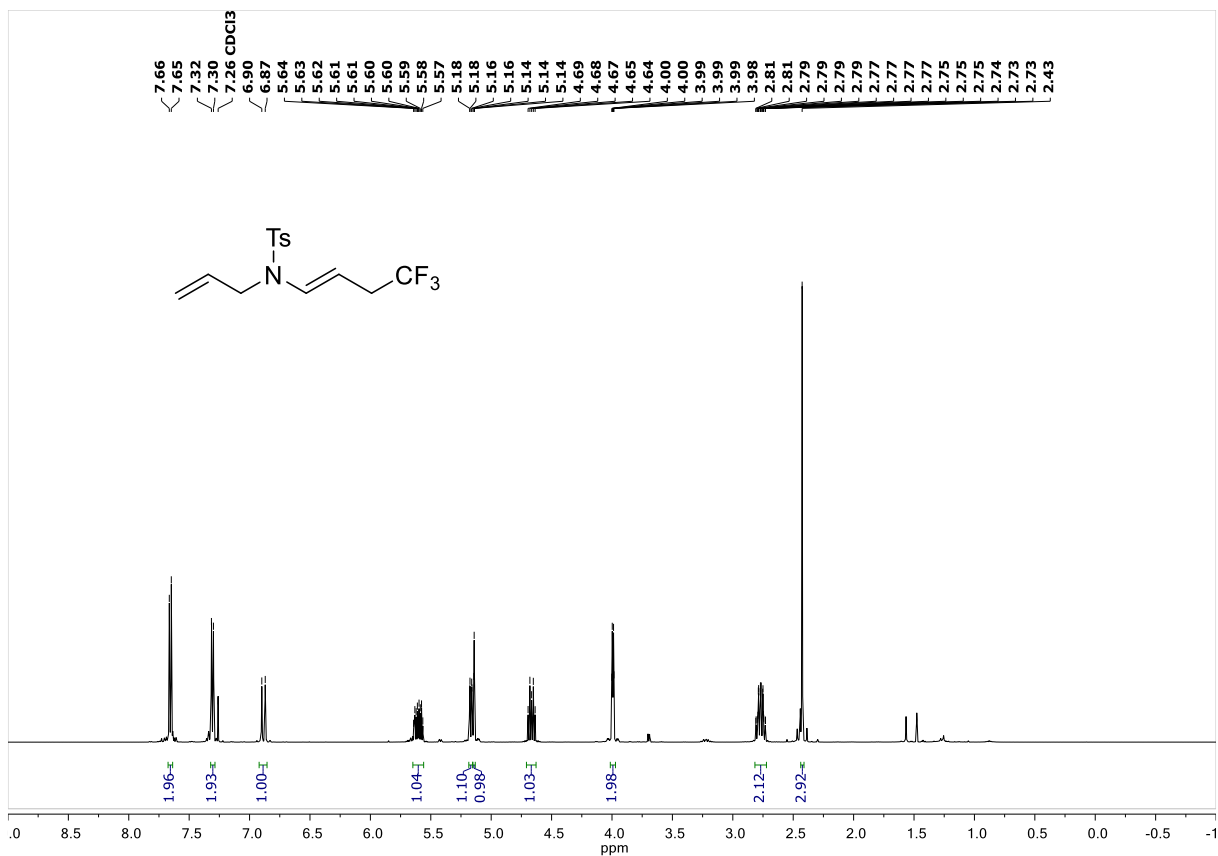
¹H NMR (CDCl₃, 300 MHz) of **3h**



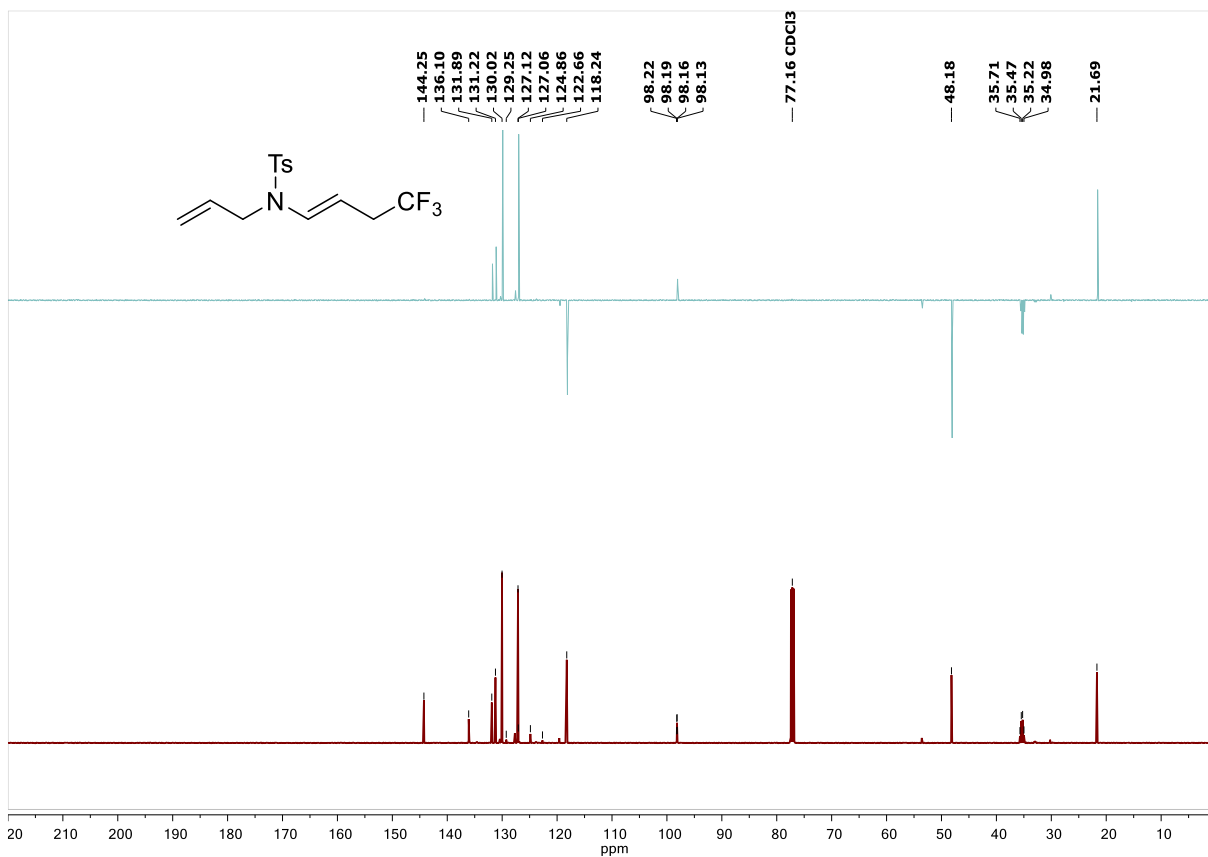
¹³C{¹H} NMR (CDCl₃, 126 MHz) of **3h**



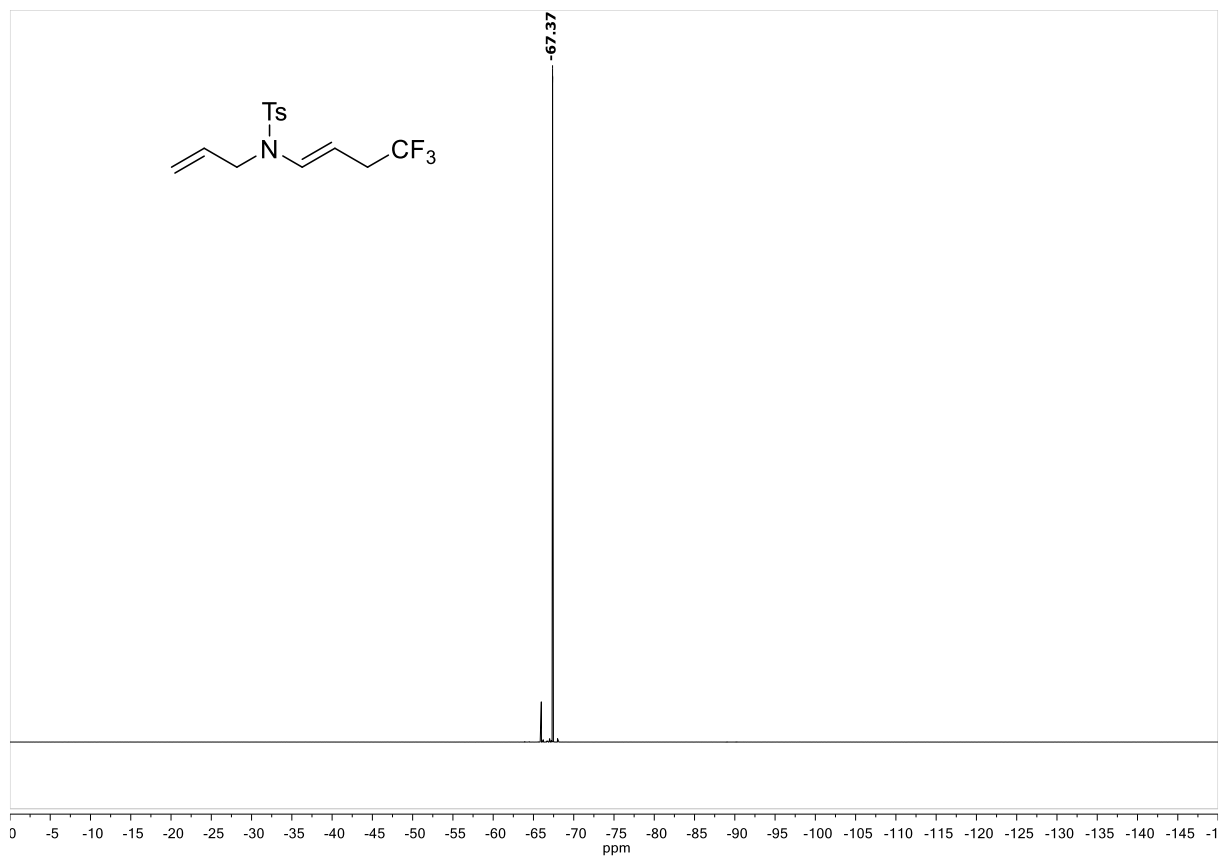
$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 282 MHz) of **3h**



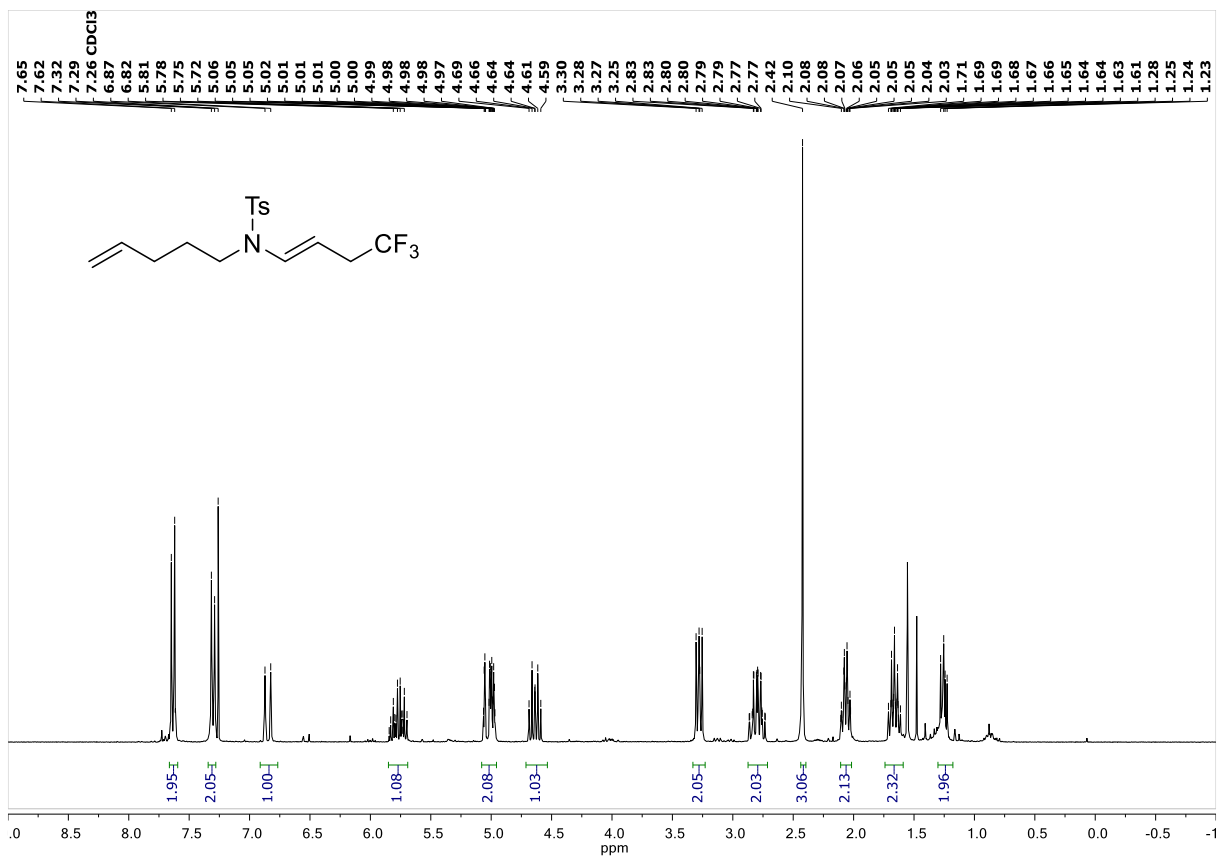
¹H NMR (CDCl₃, 500 MHz) of **3i**



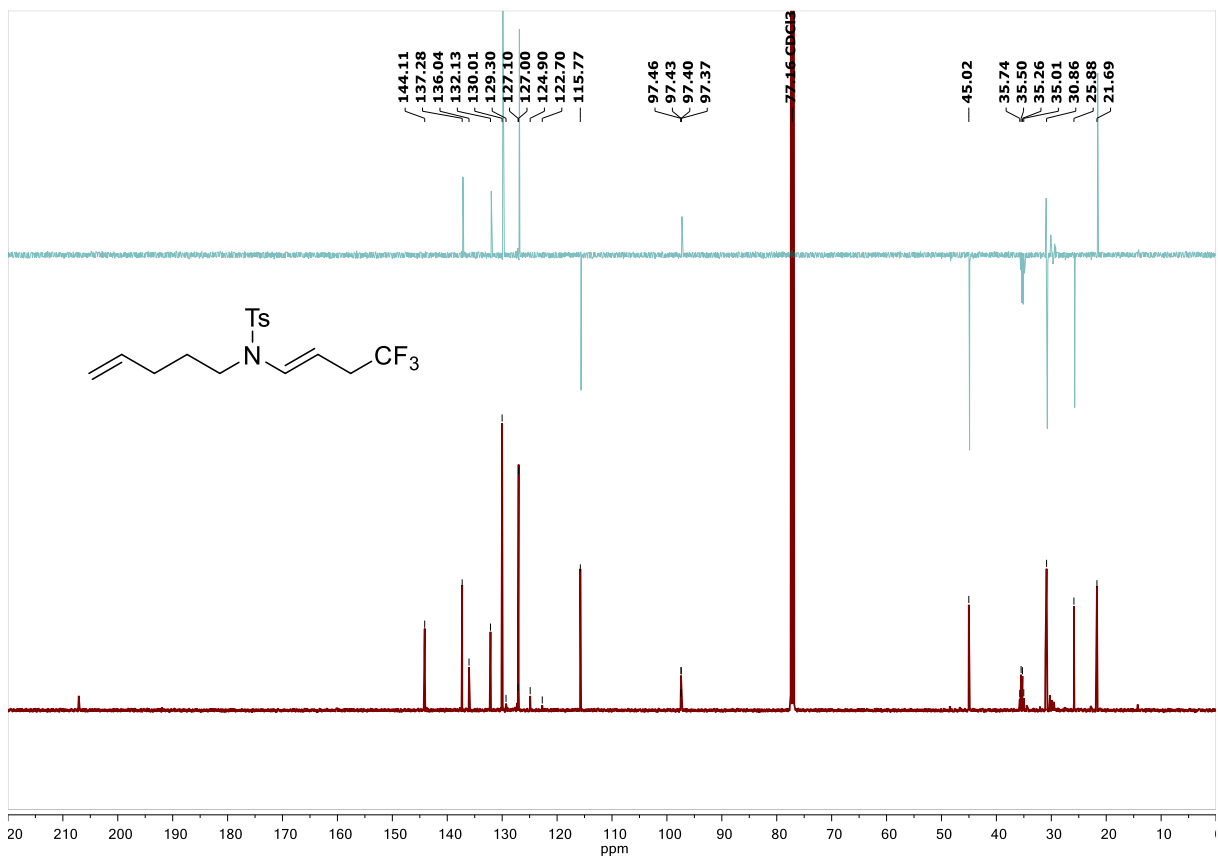
¹³C{¹H} NMR (CDCl₃, 126 MHz) of **3i**



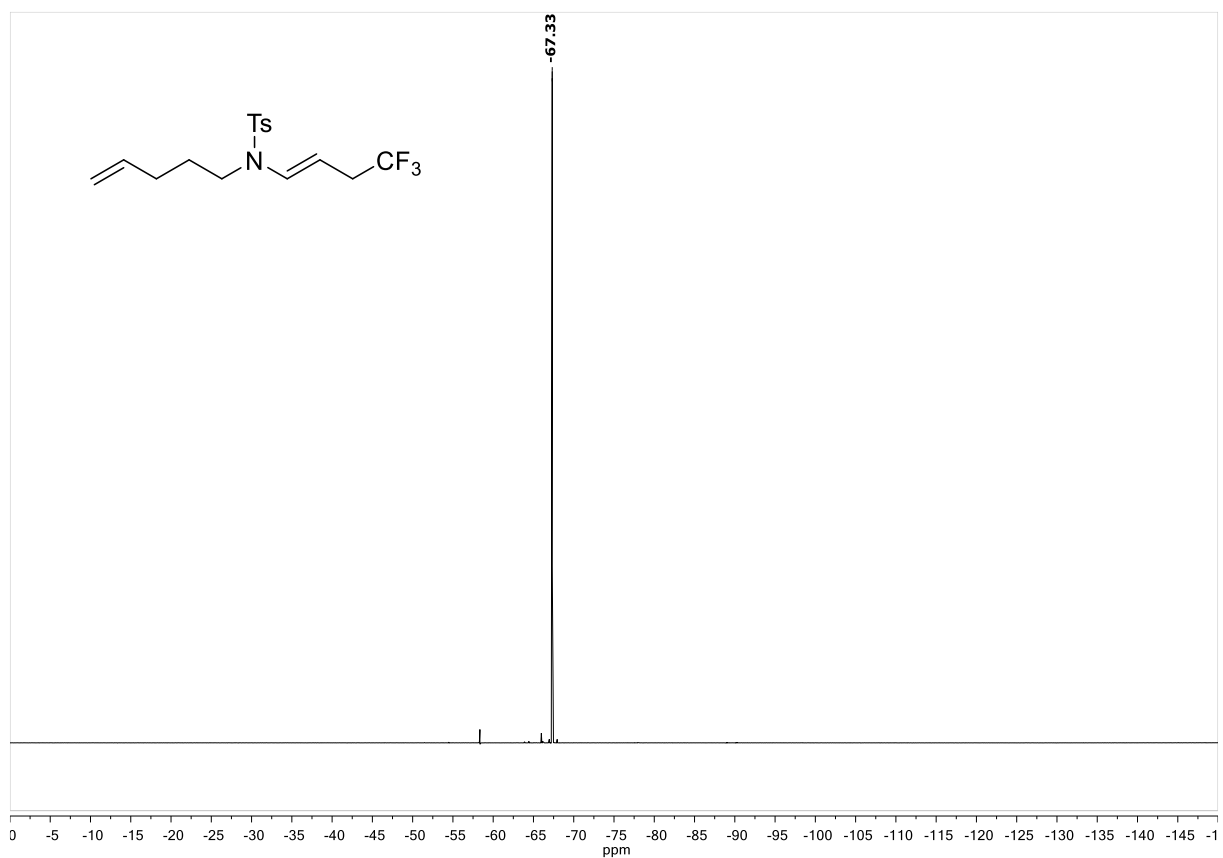
$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 282 MHz) of **3i**



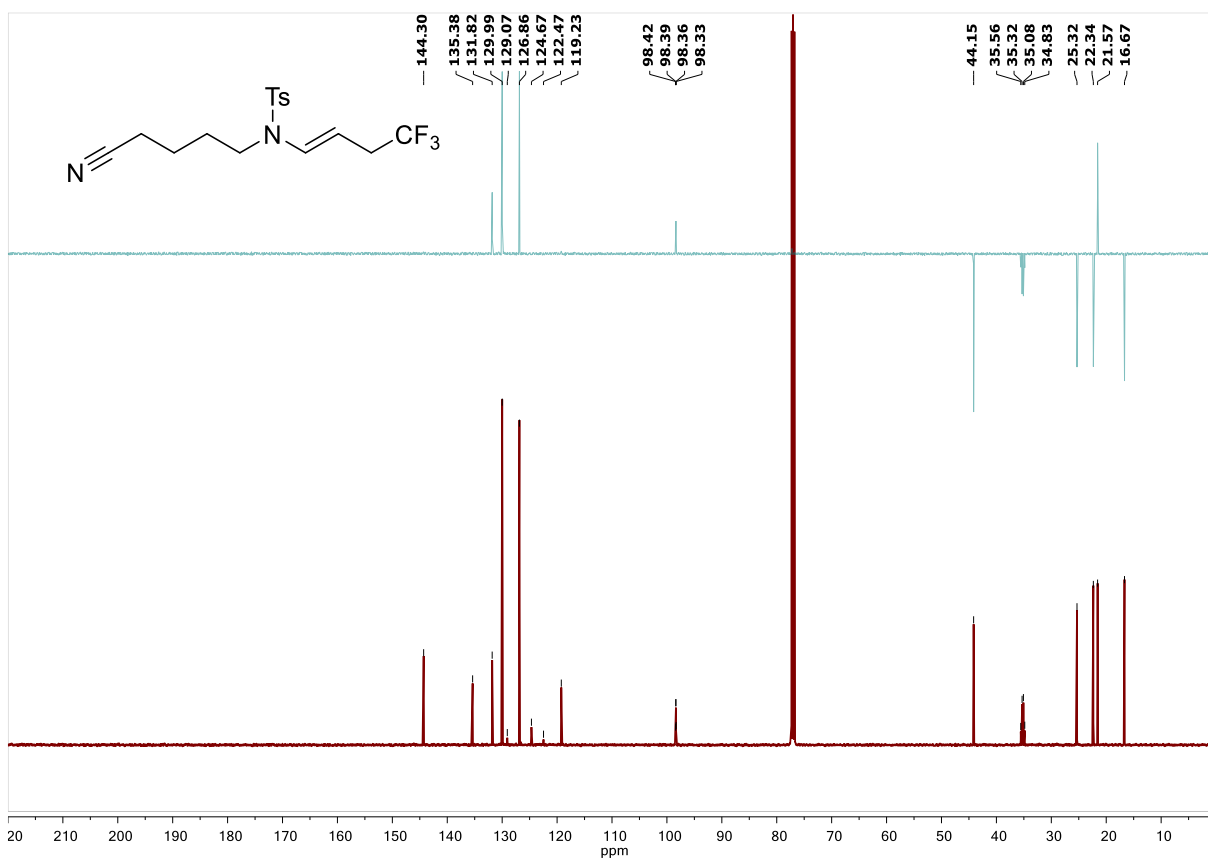
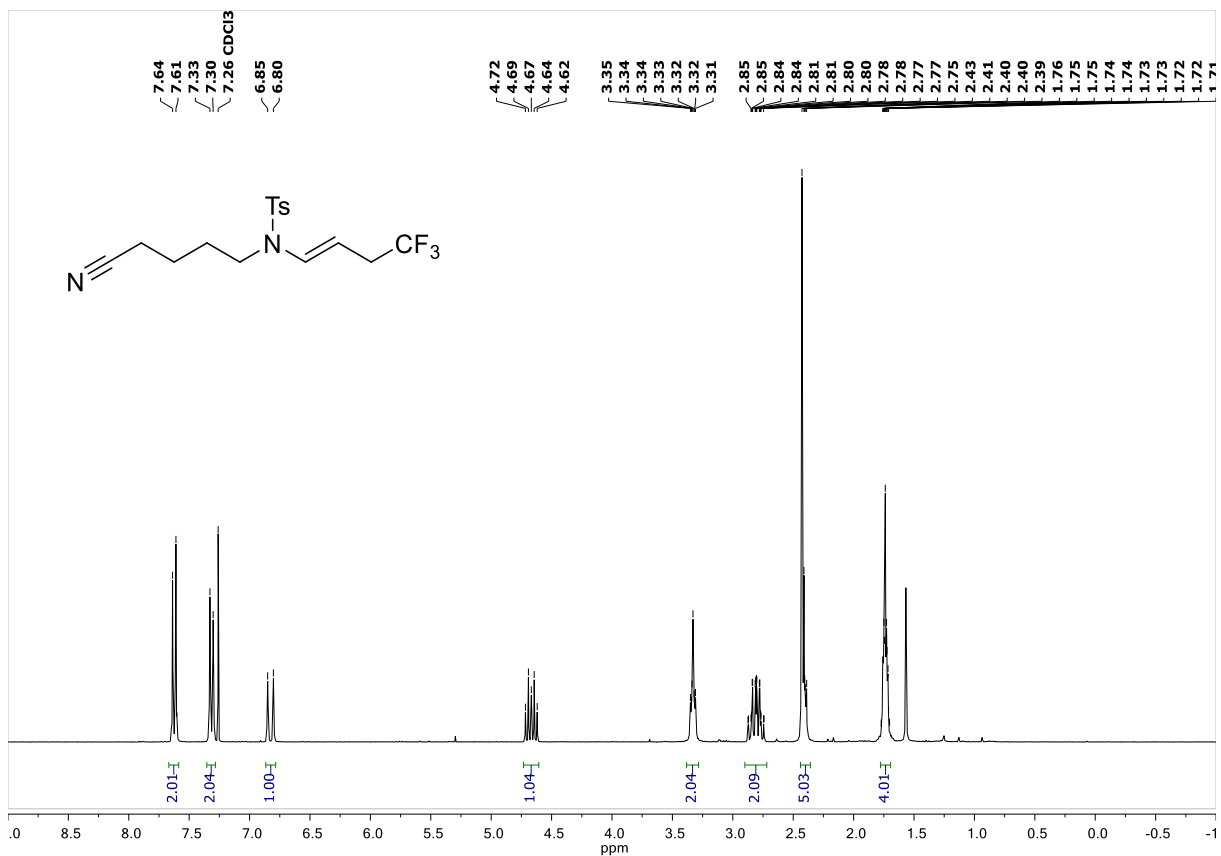
¹H NMR (CDCl₃, 300 MHz) of **3j**



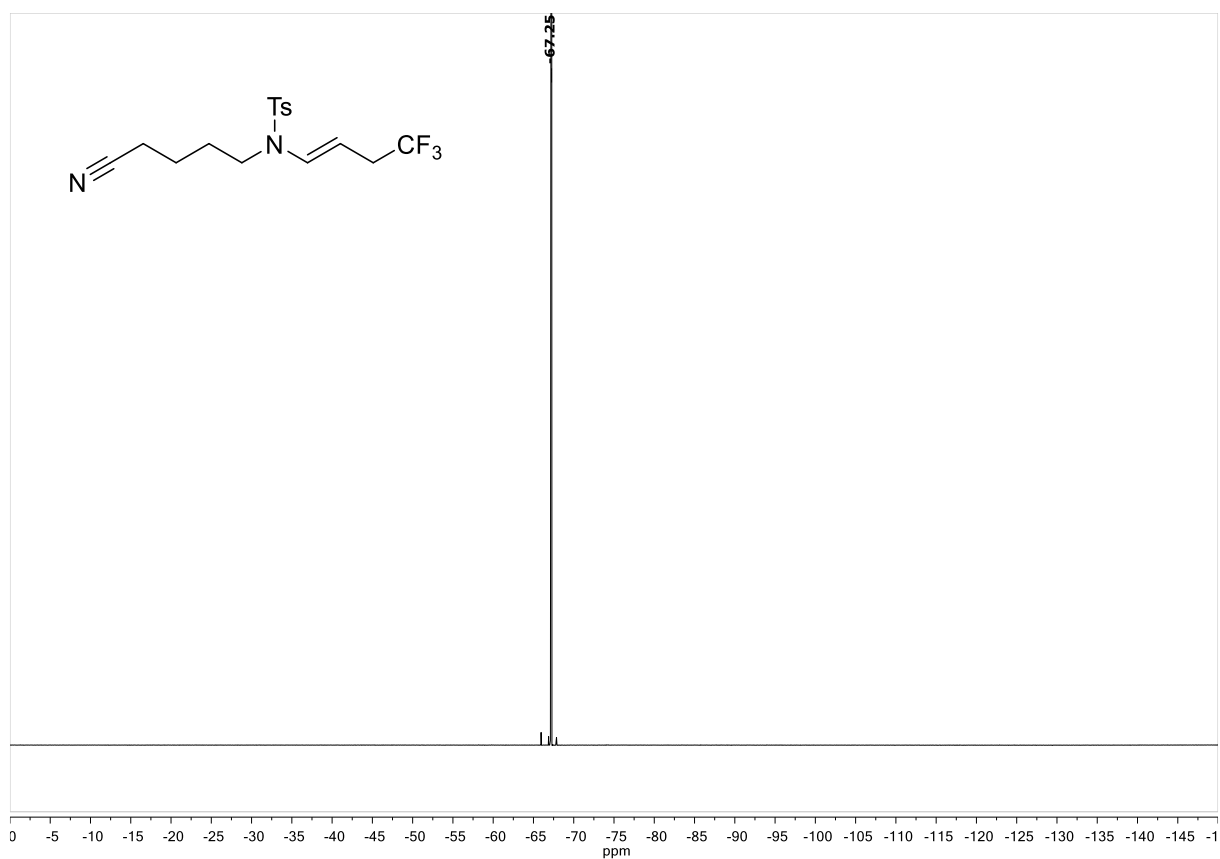
¹³C{¹H} NMR (CDCl₃, 126 MHz) of **3j**



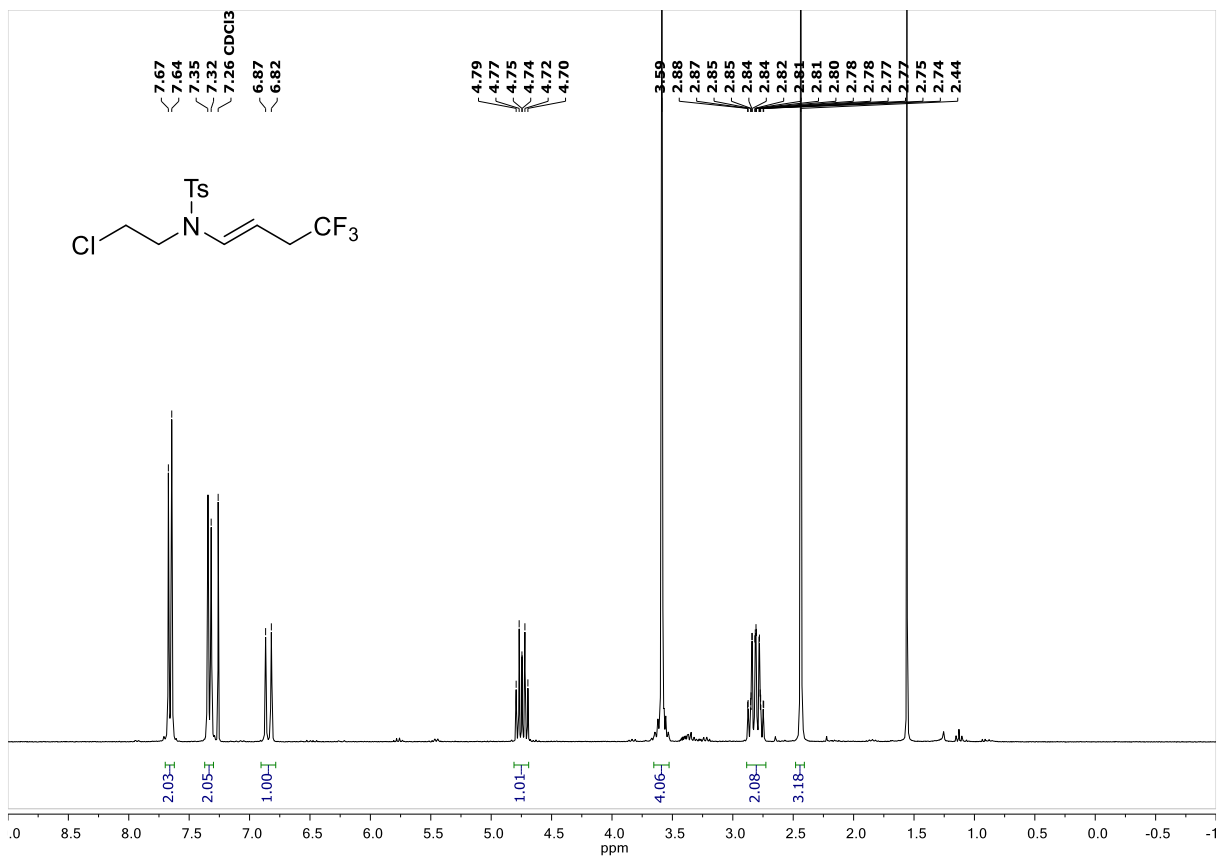
$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 282 MHz) of **3j**



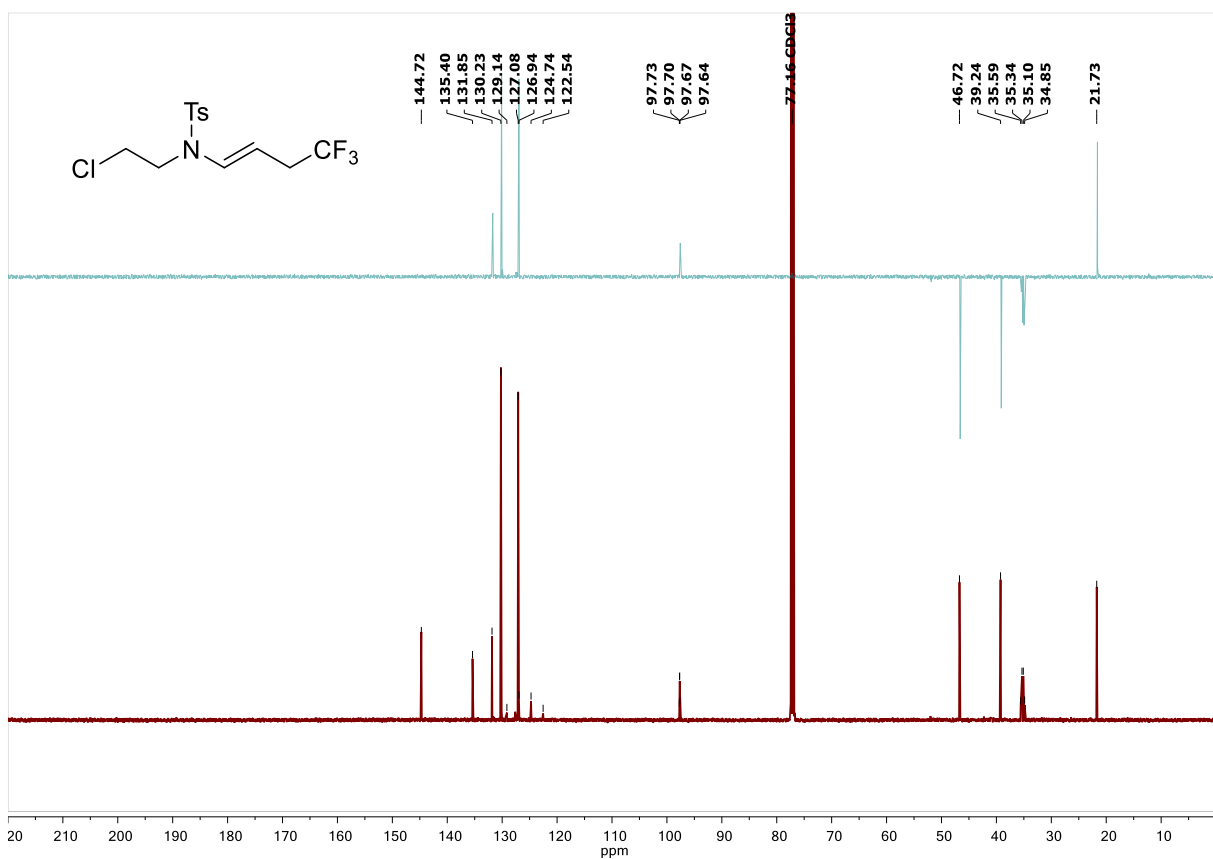
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 3k
S91



$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 282 MHz) of **3k**

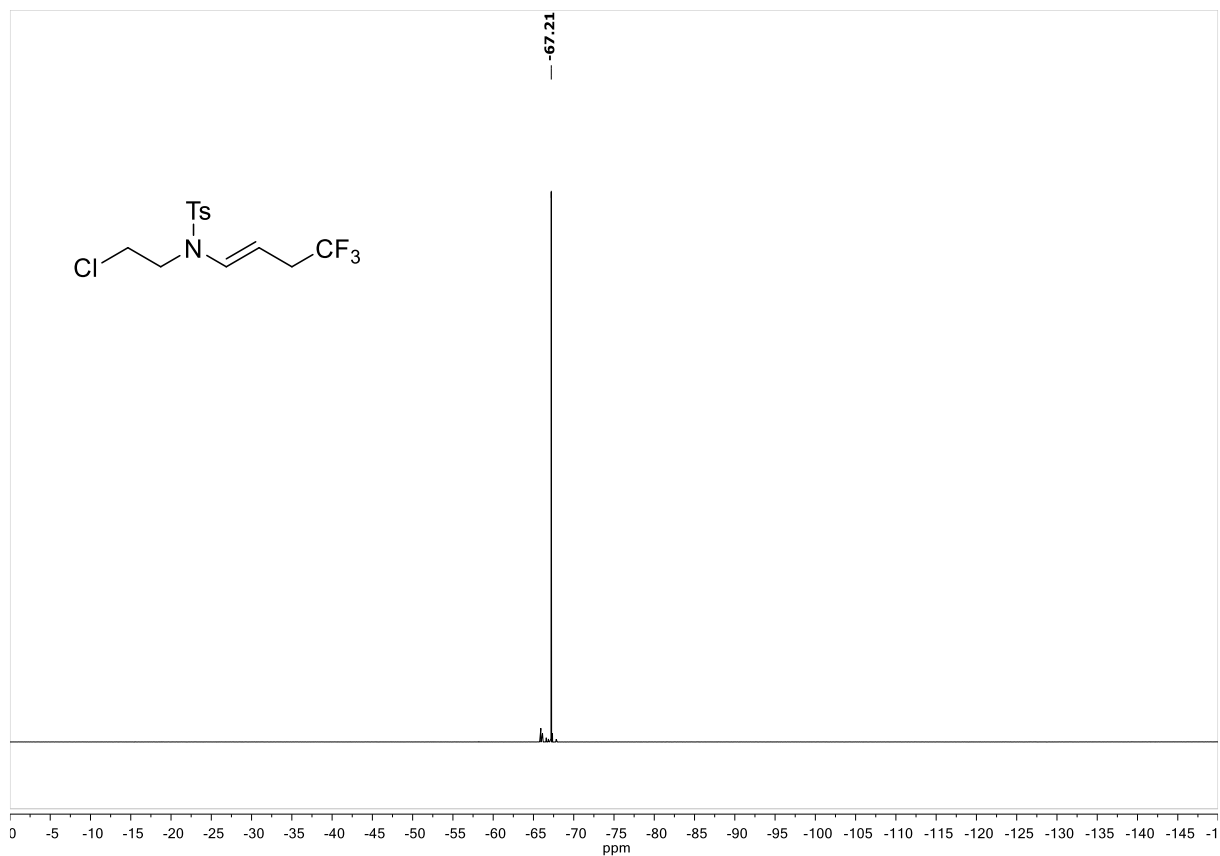


¹H NMR (CDCl₃, 300 MHz) of **31**

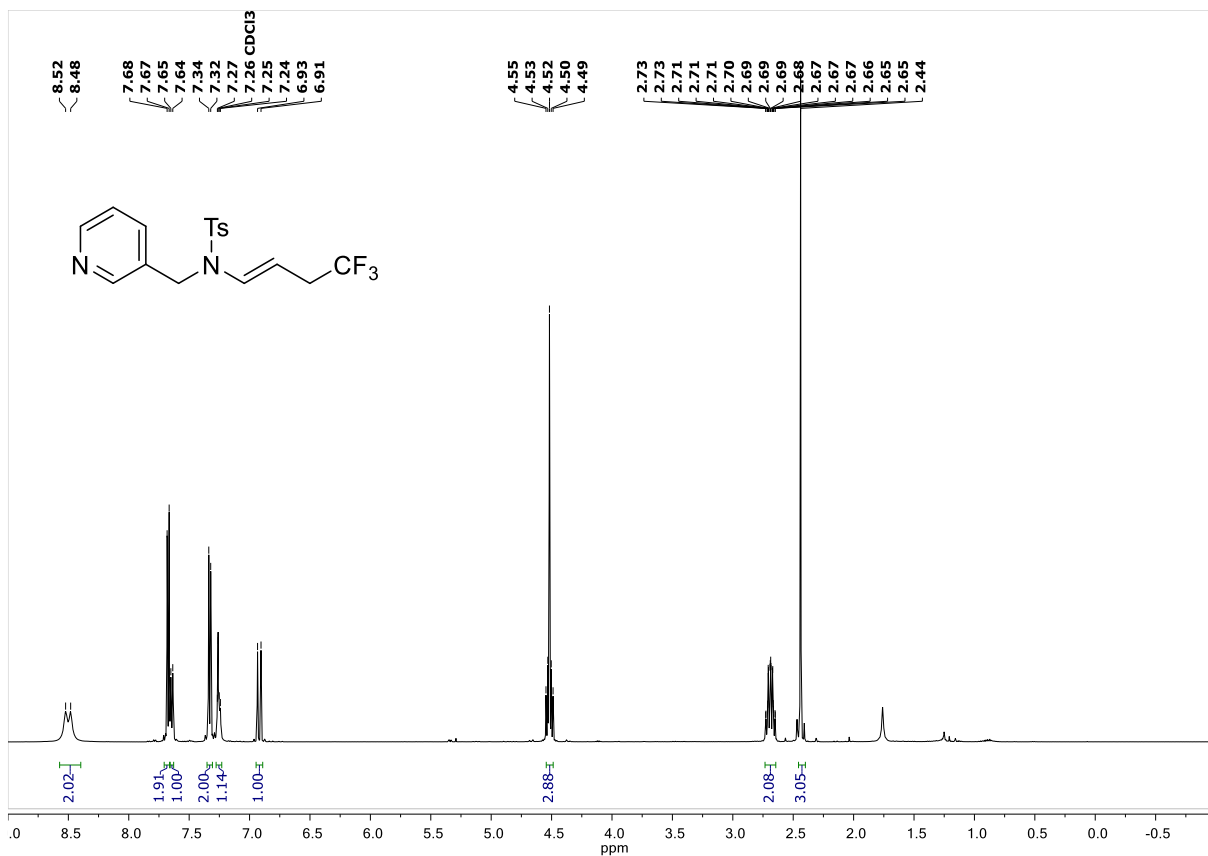


¹³C{¹H} NMR (CDCl₃, 126 MHz) of **31**

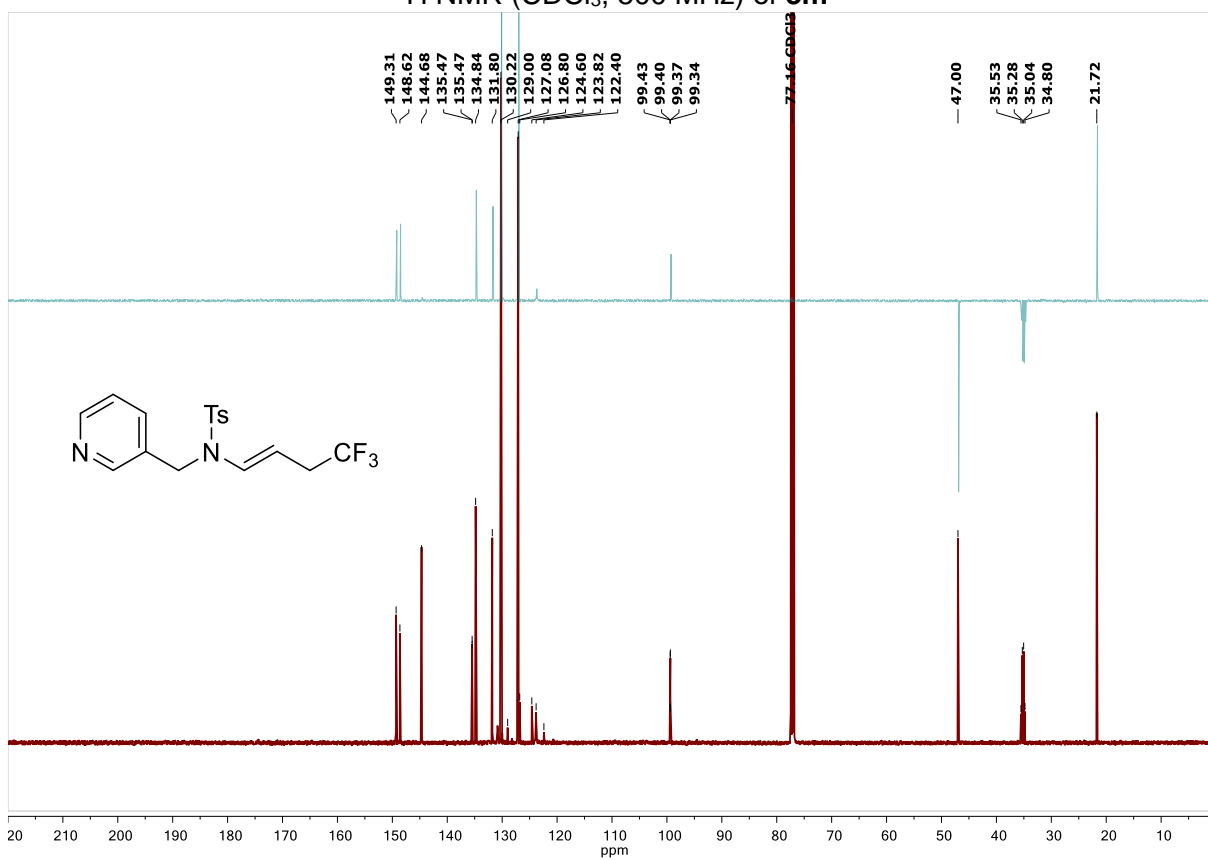
S93



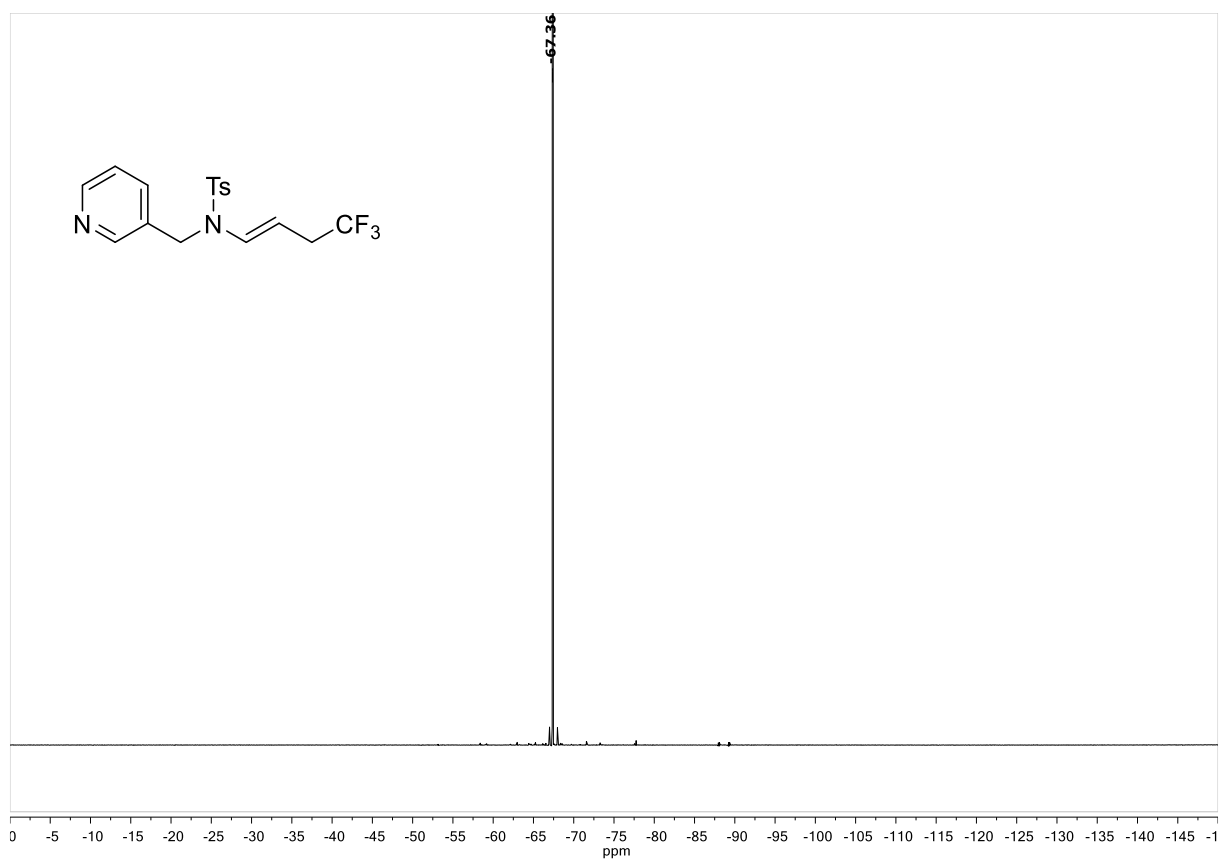
$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 282 MHz) of **3I**



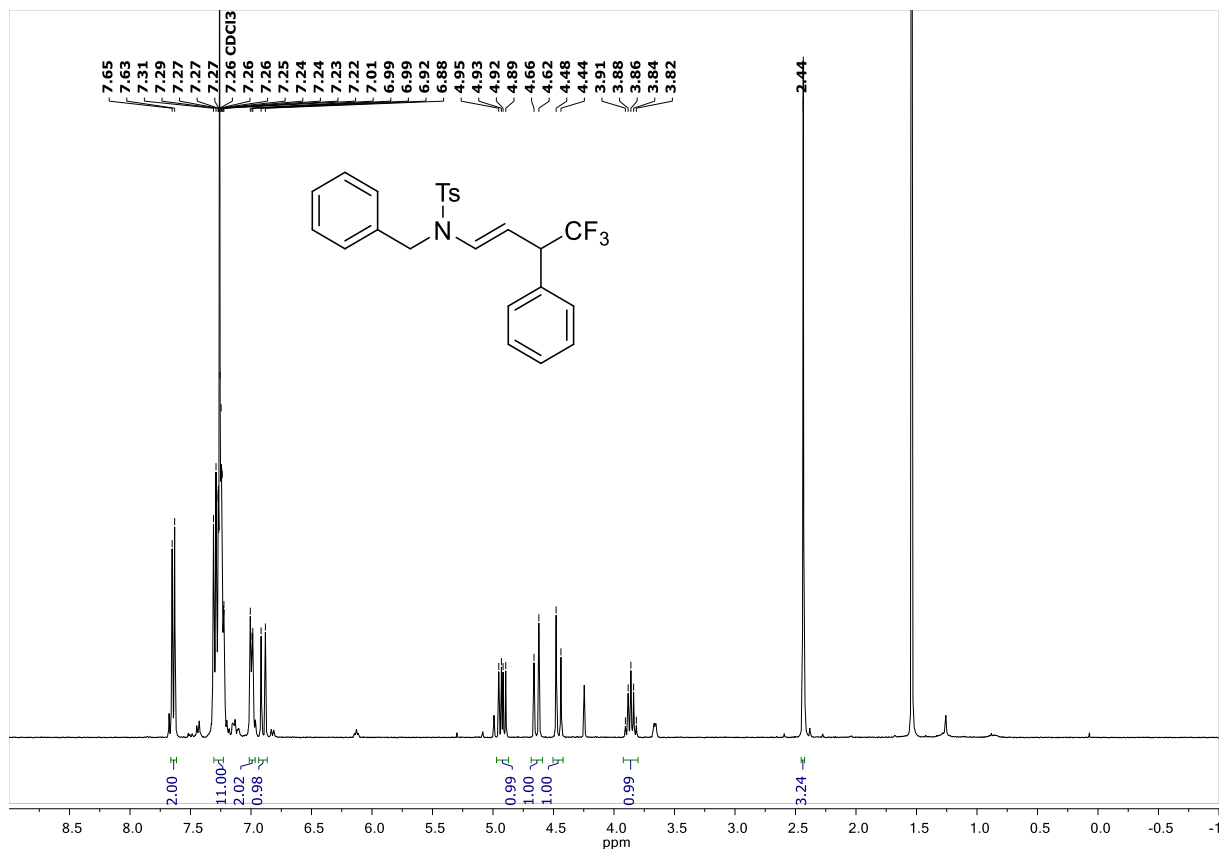
¹H NMR (CDCl₃, 500 MHz) of 3m



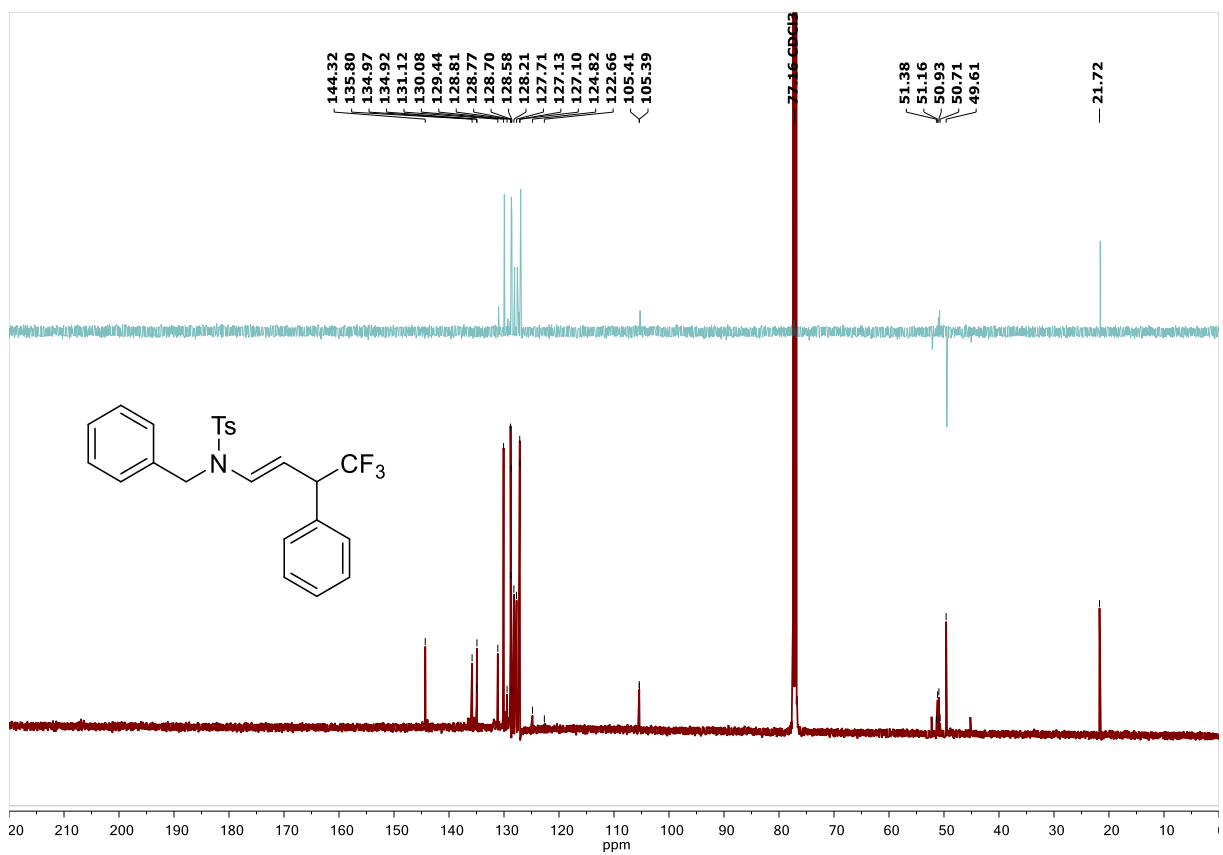
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 3m



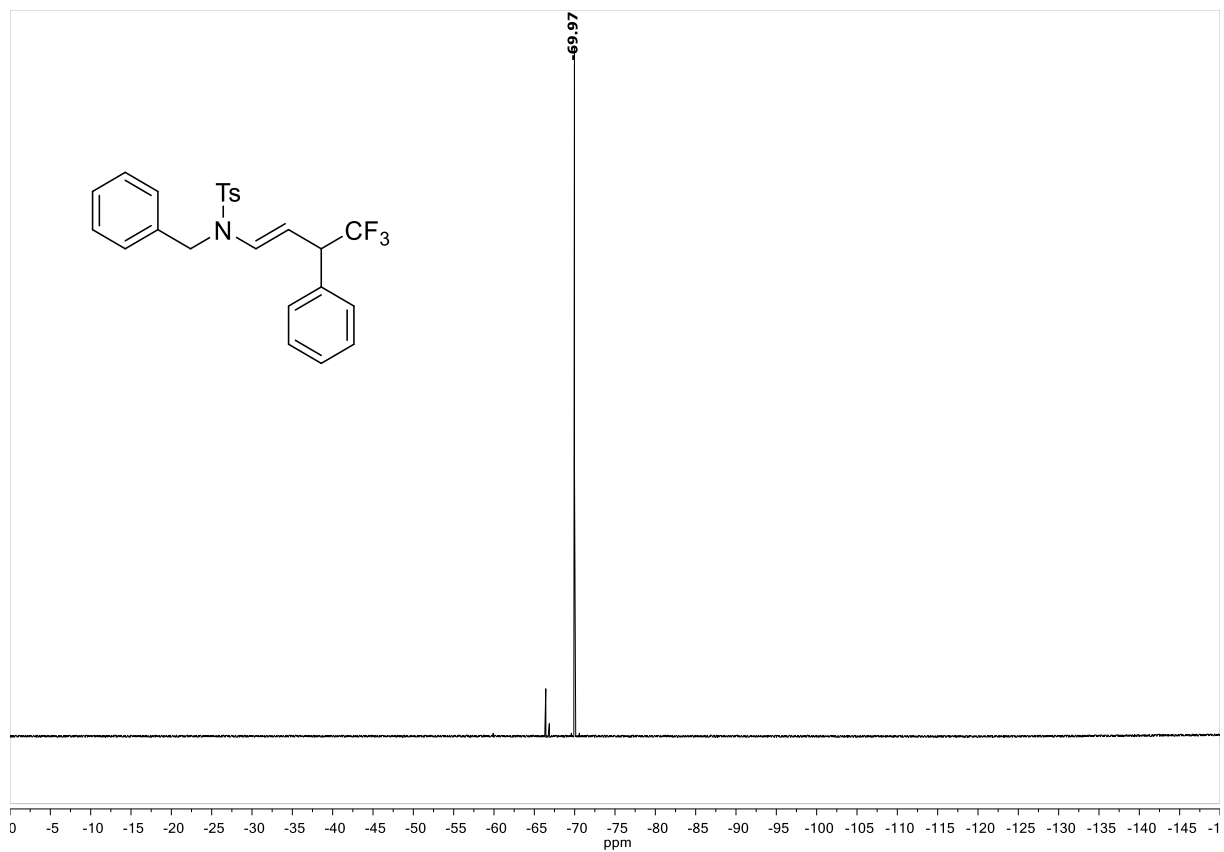
$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 282 MHz) of **3m**



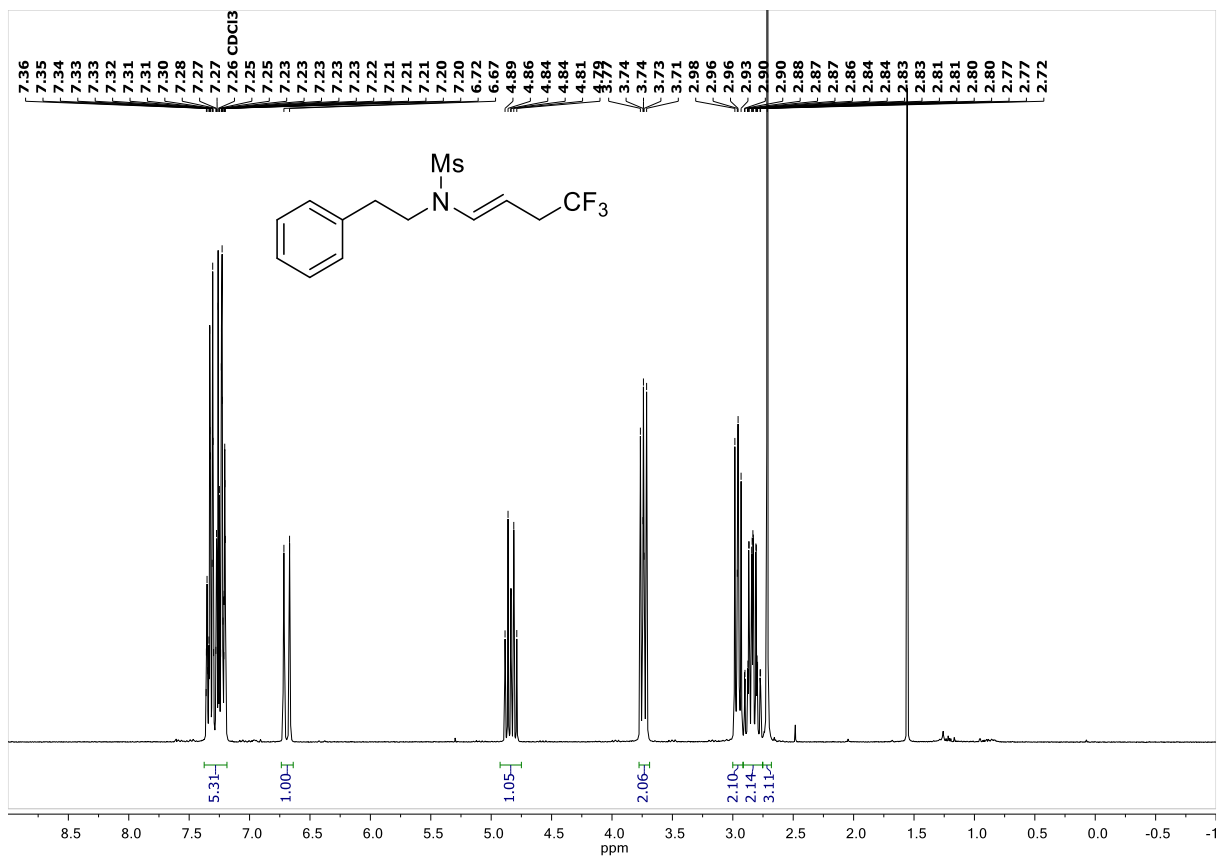
¹H NMR (CDCl₃, 400 MHz) of 3n



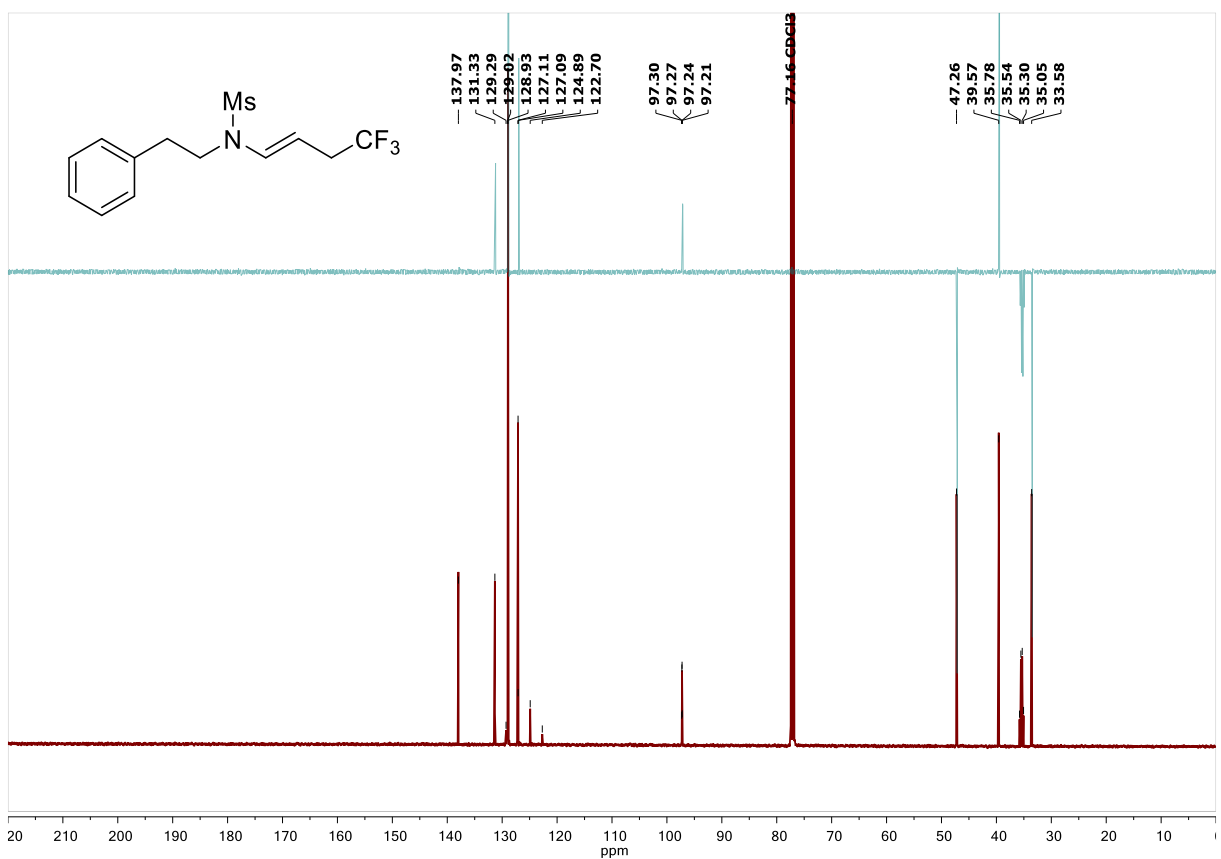
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 3n



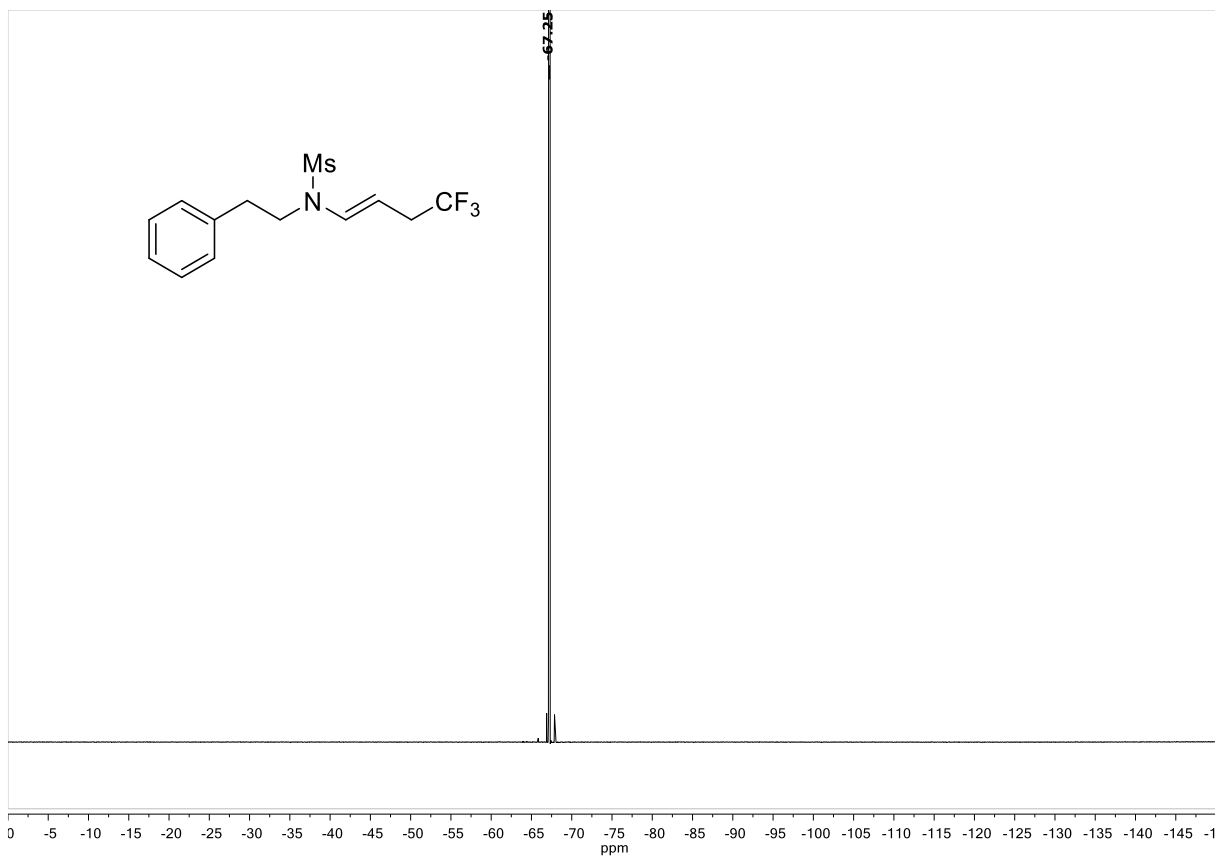
$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 282 MHz) of **3n**



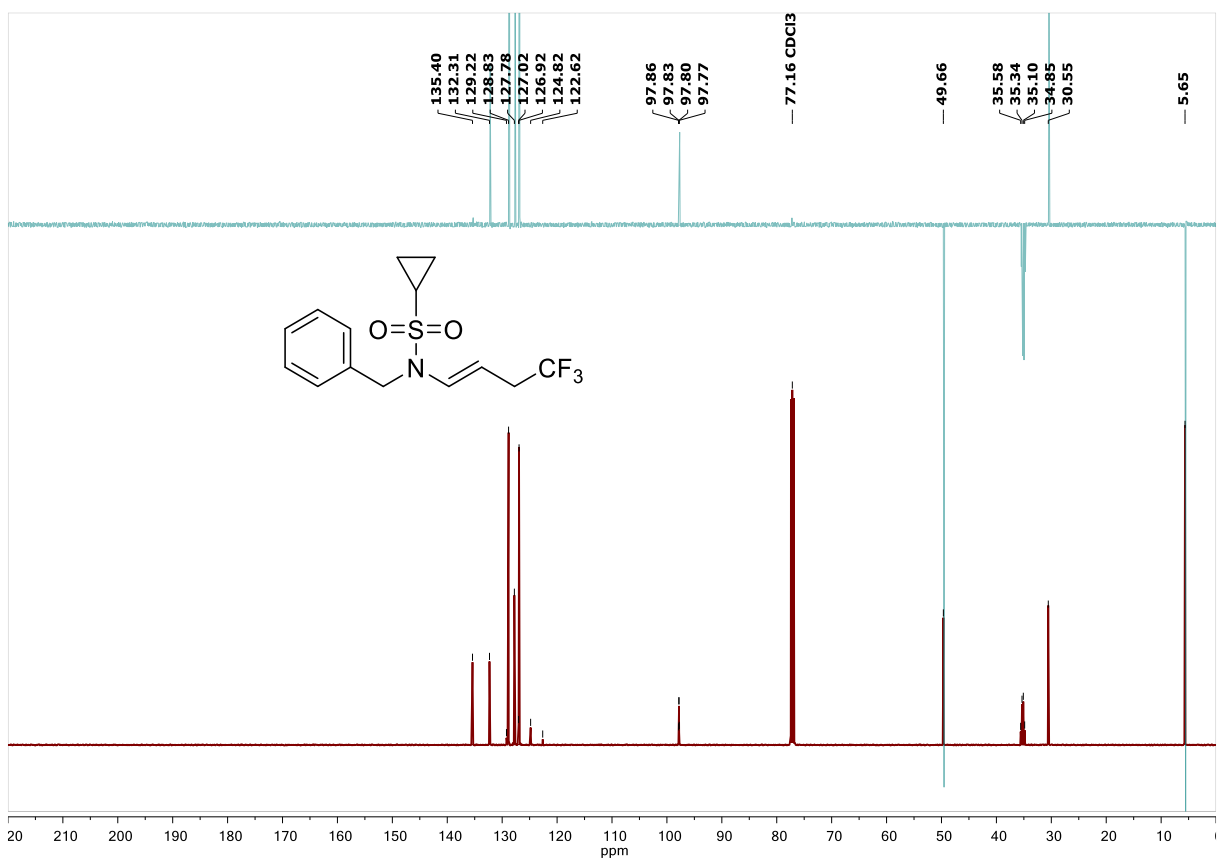
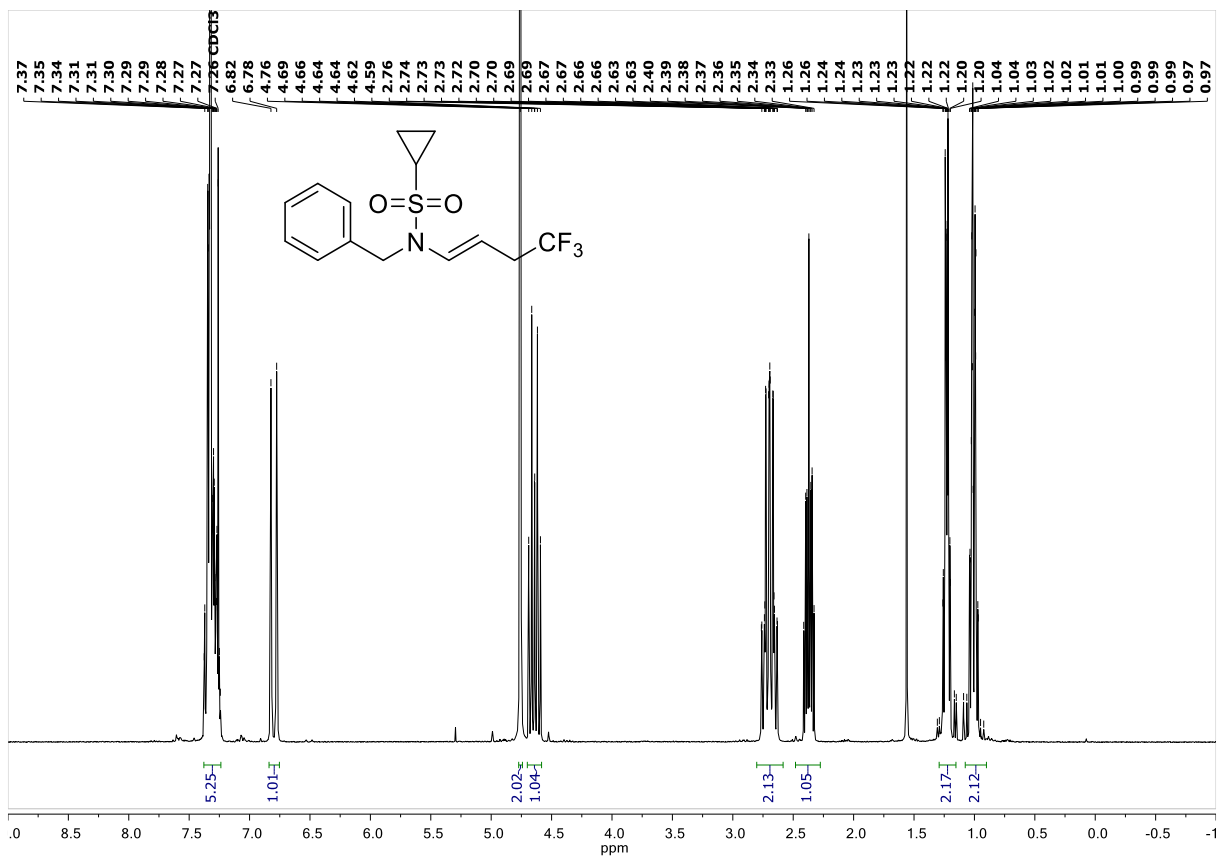
¹H NMR (CDCl₃, 300 MHz) of **3o**

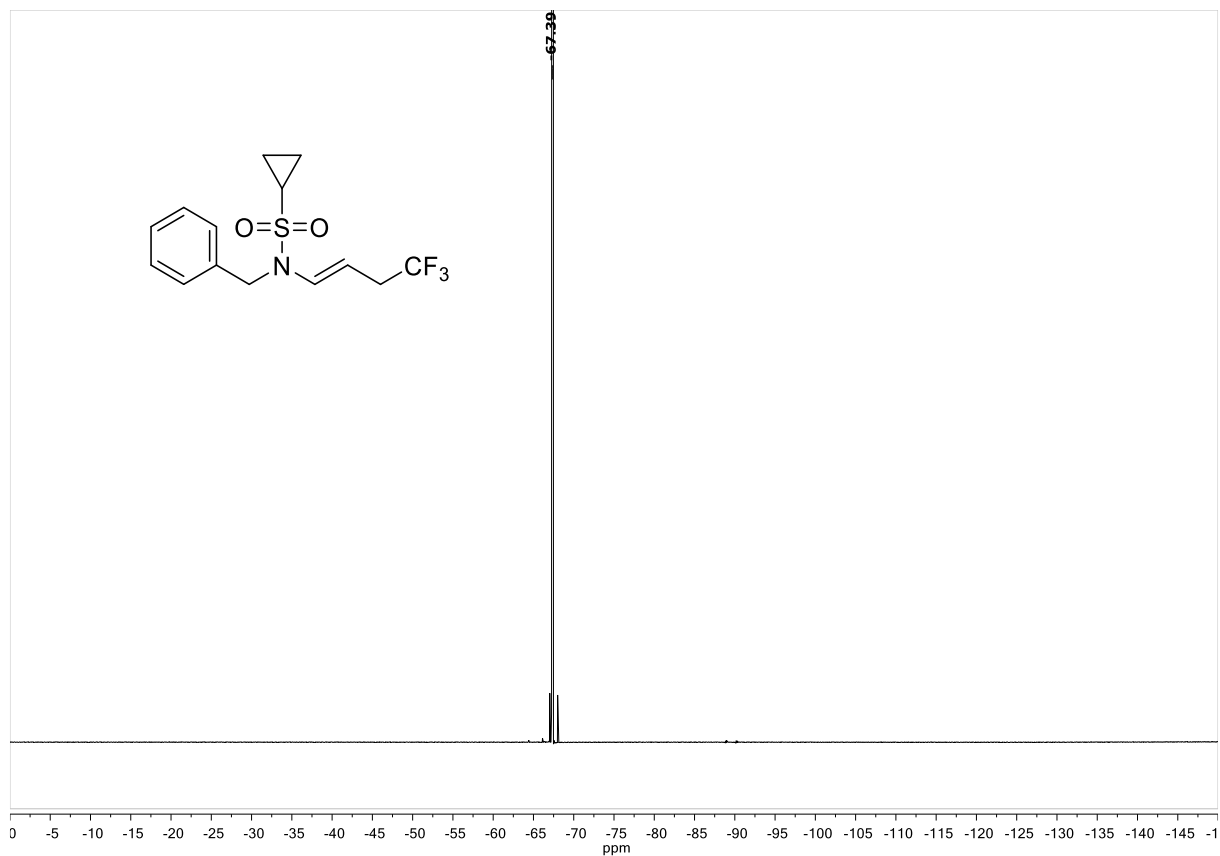


¹³C{¹H} NMR (CDCl₃, 126 MHz) of **3o**

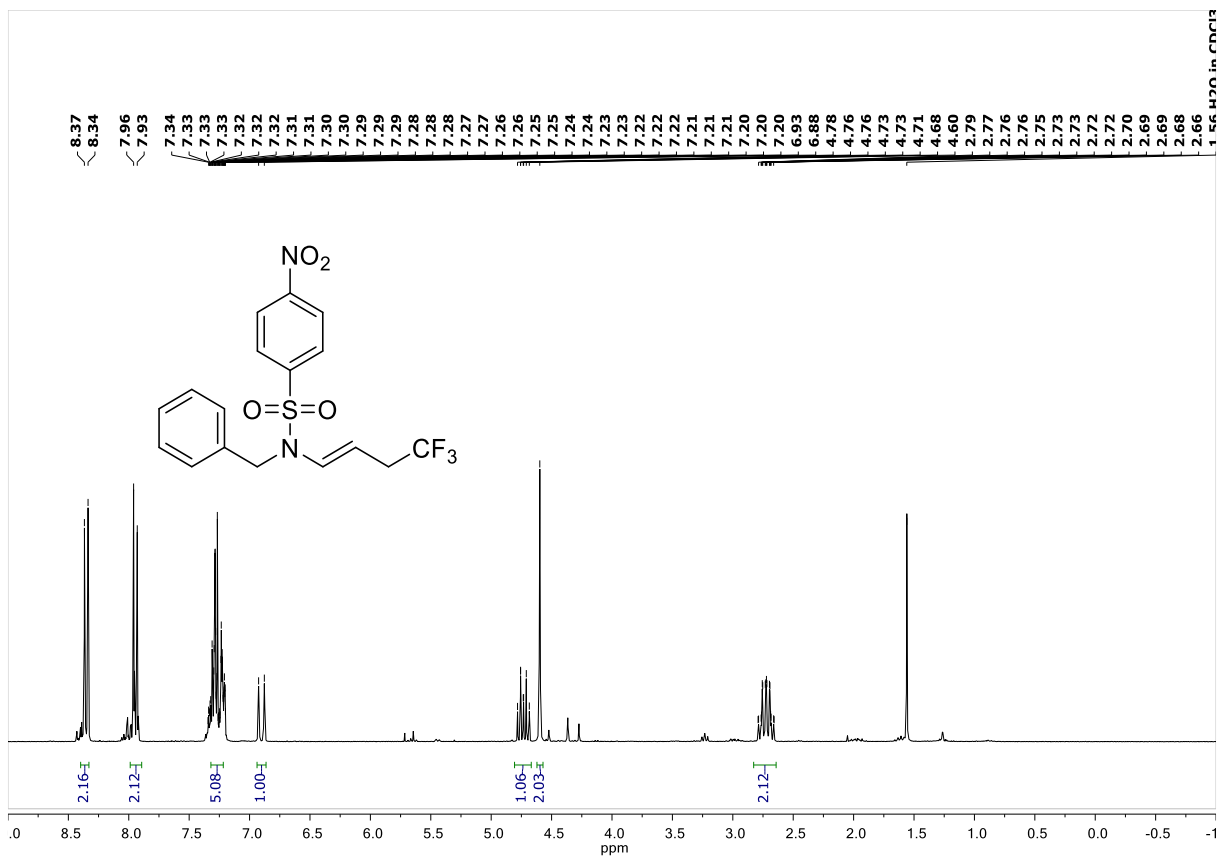


$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 282 MHz) of **3o**

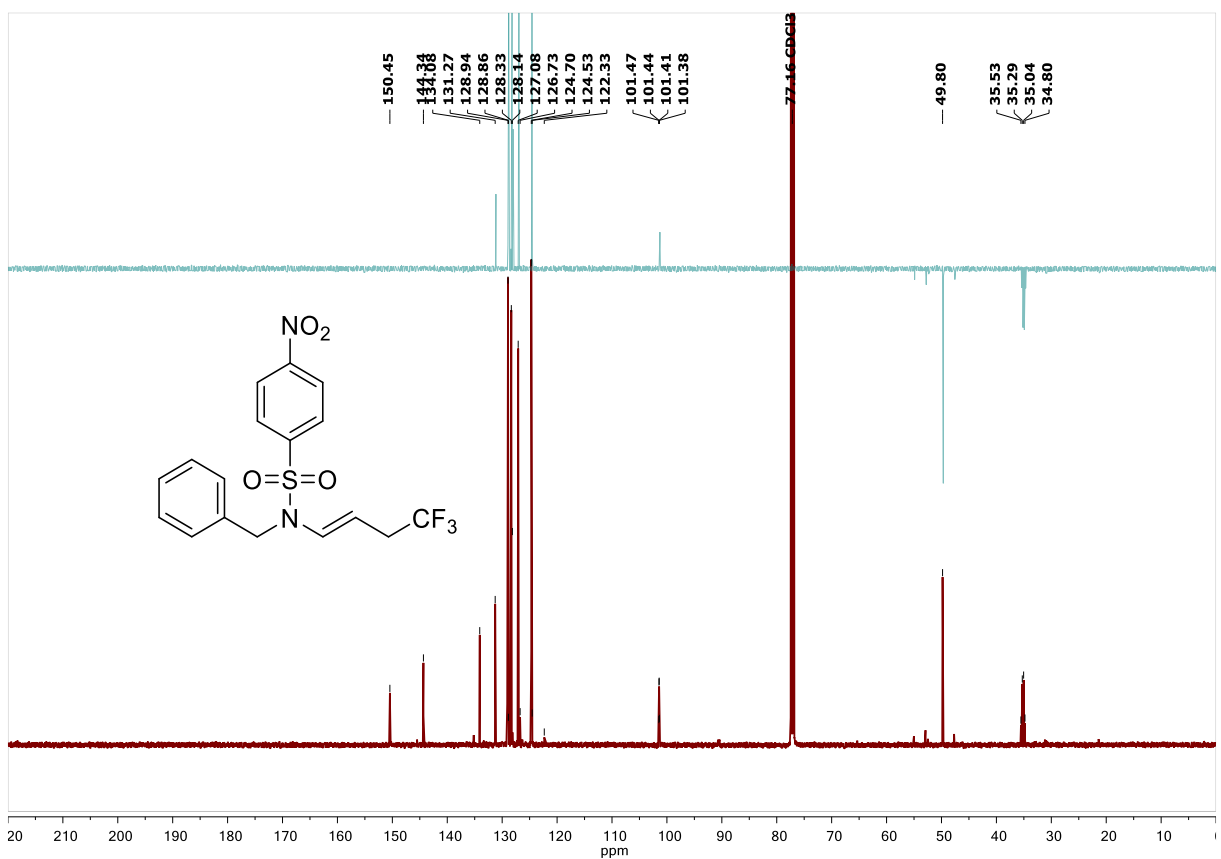




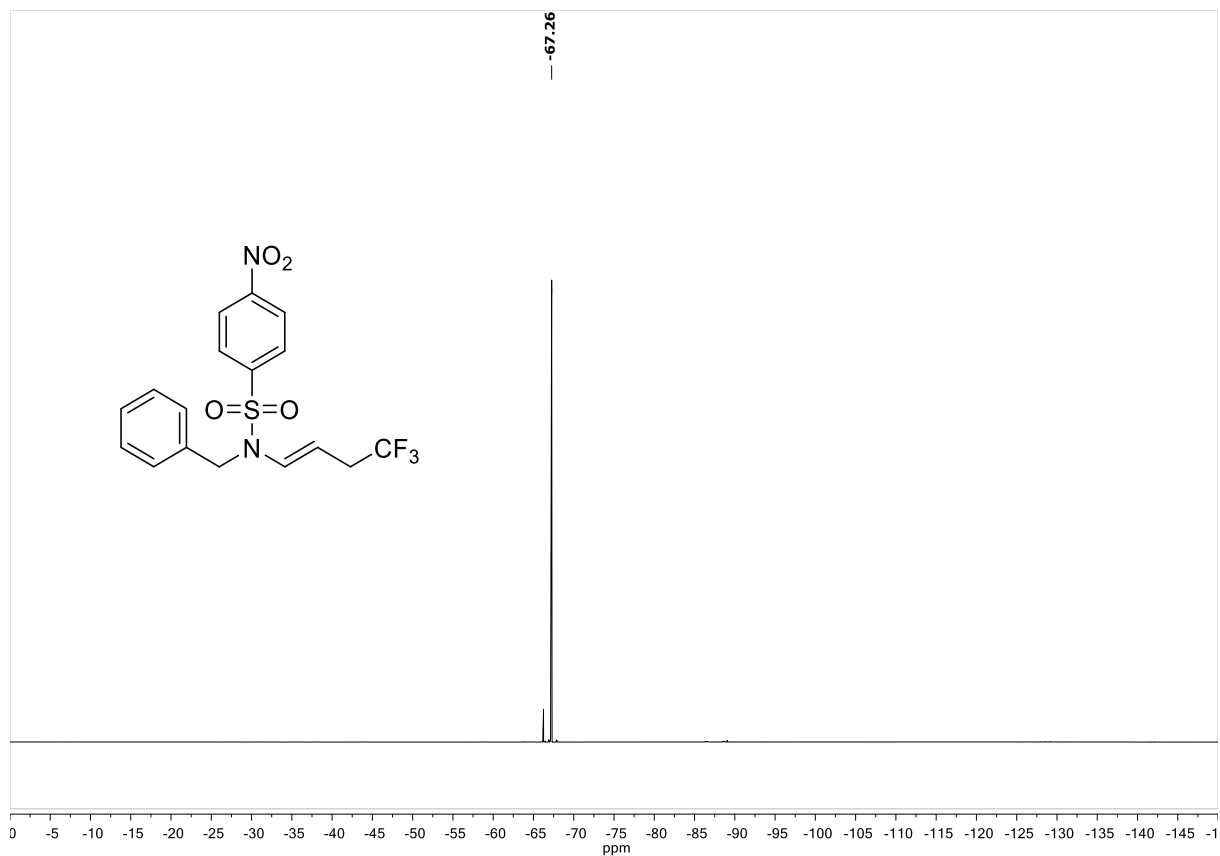
$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 282 MHz) of **3p**



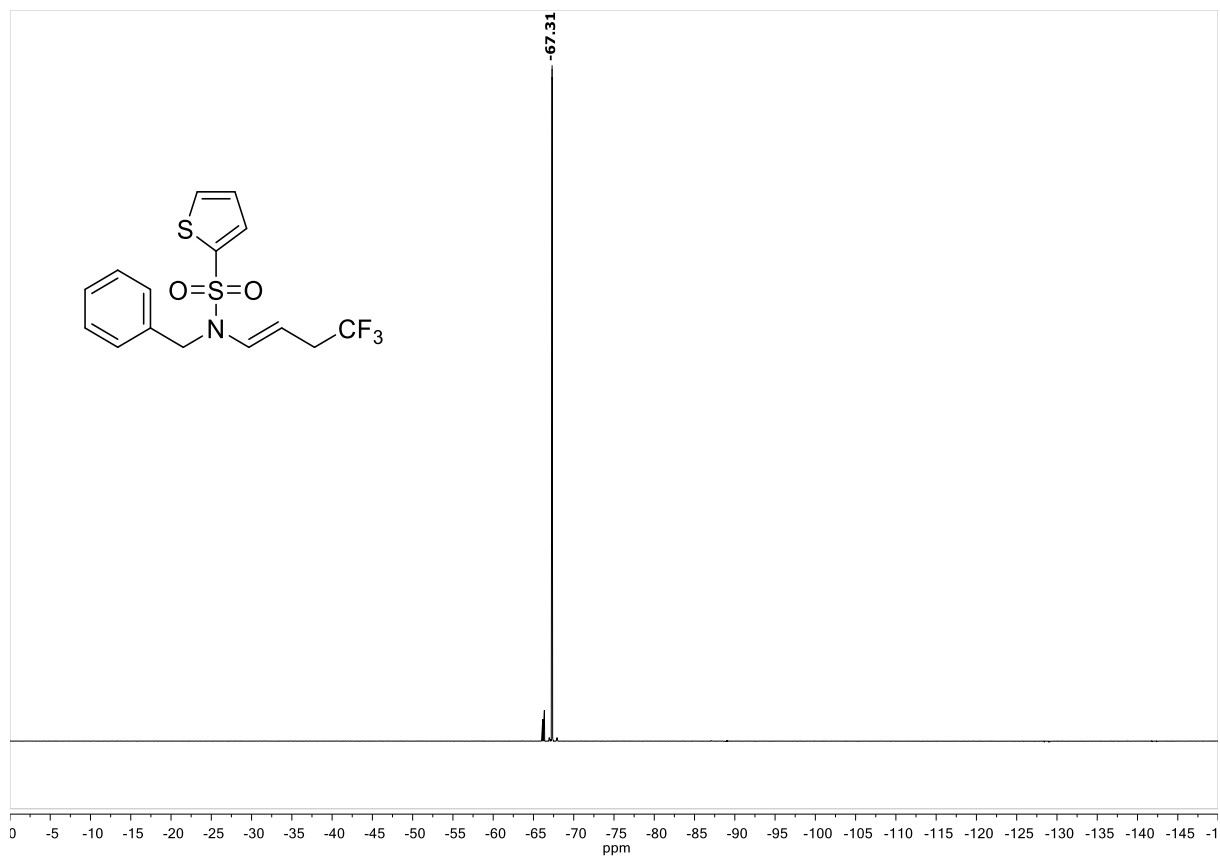
¹H NMR (CDCl₃, 300 MHz) of **3q**



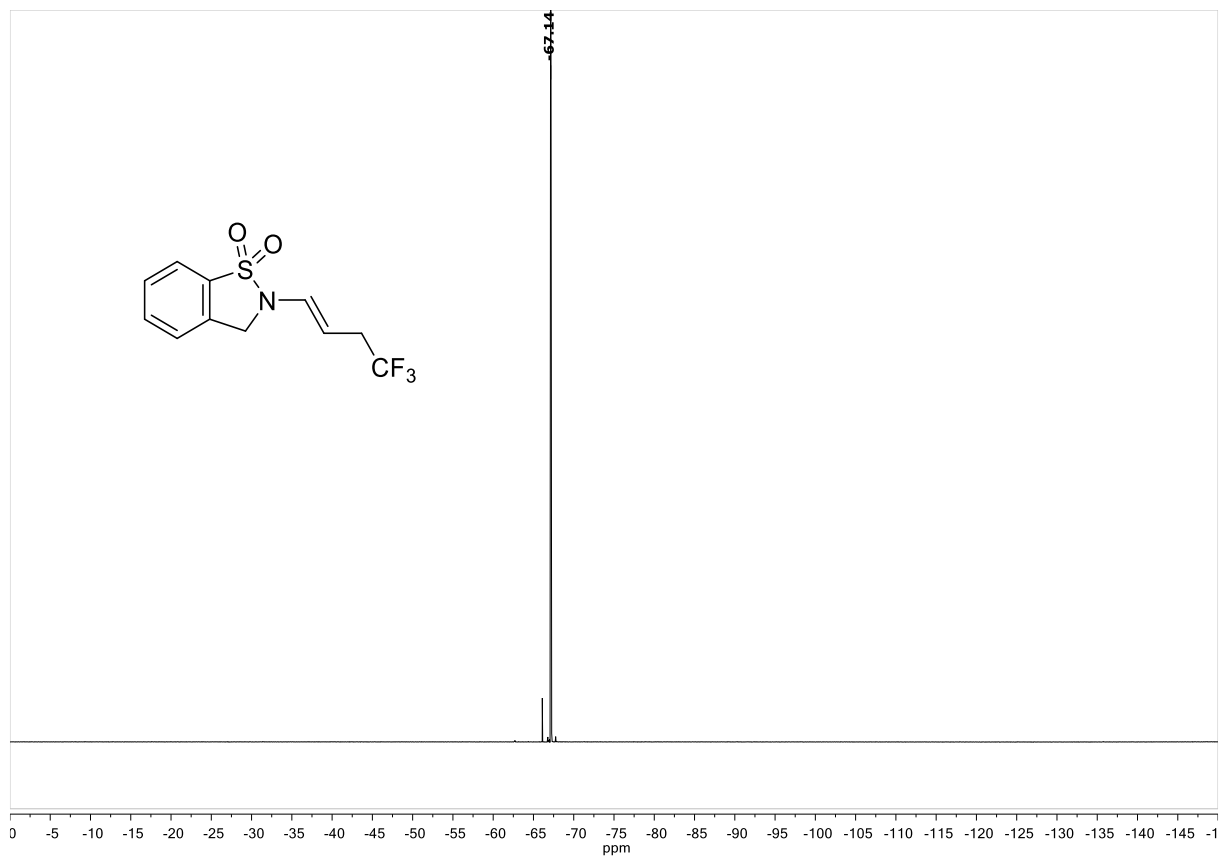
¹³C{¹H} NMR (CDCl₃, 126 MHz) of **3q**



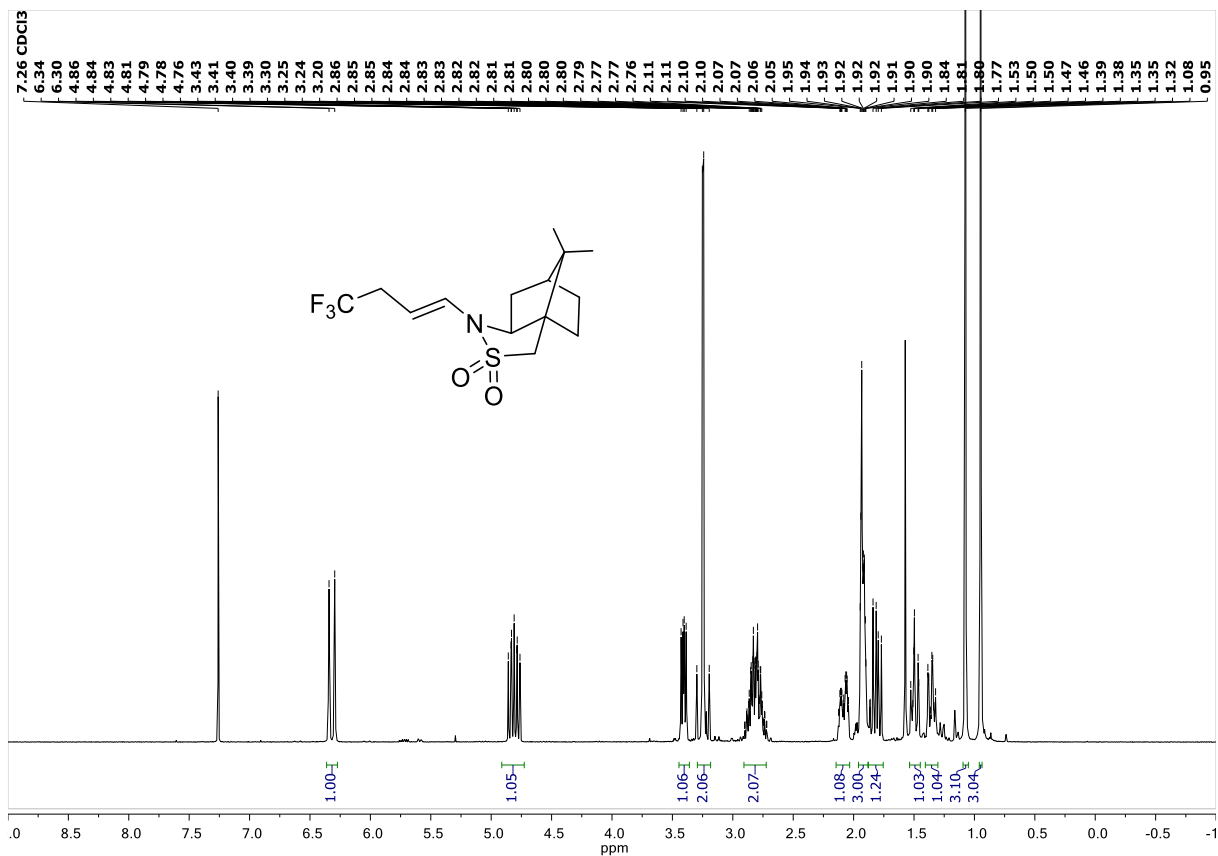
$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 282 MHz) of **3q**



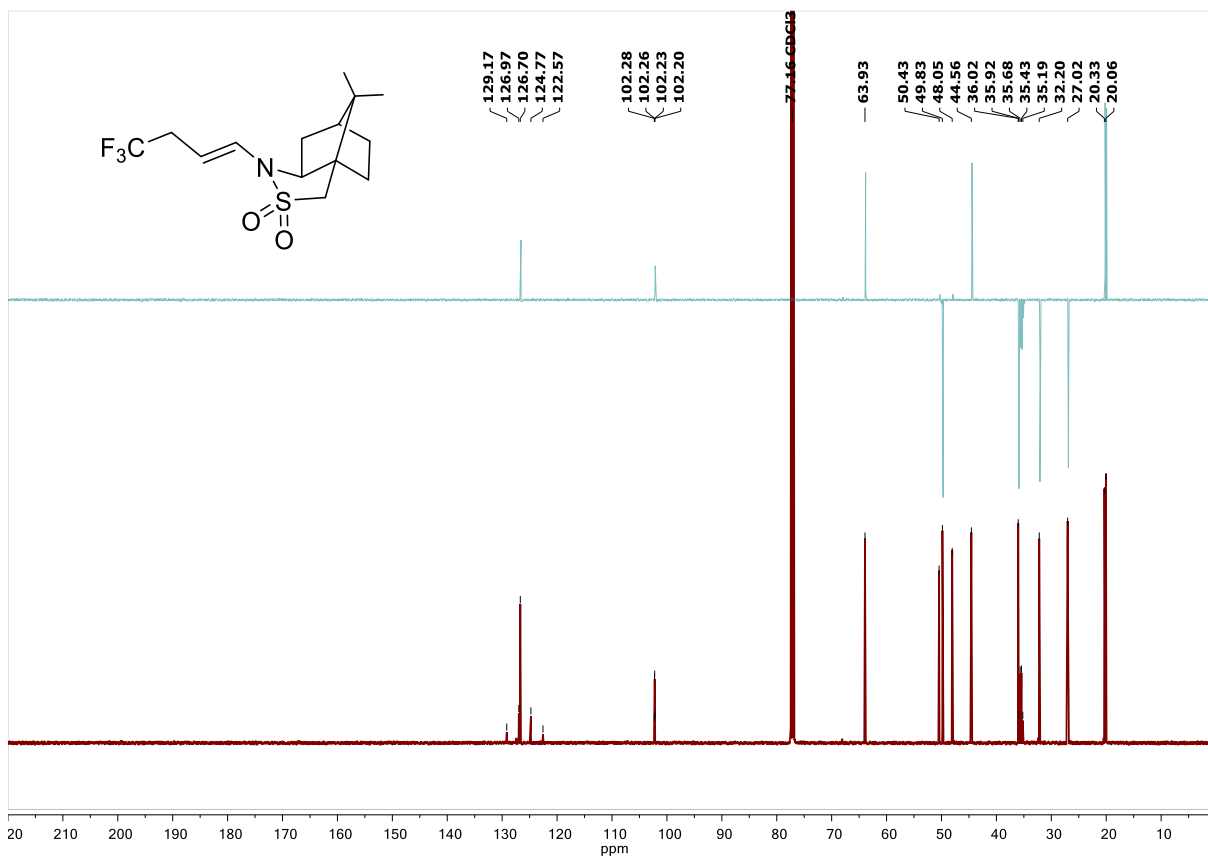
$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 282 MHz) of **3r**



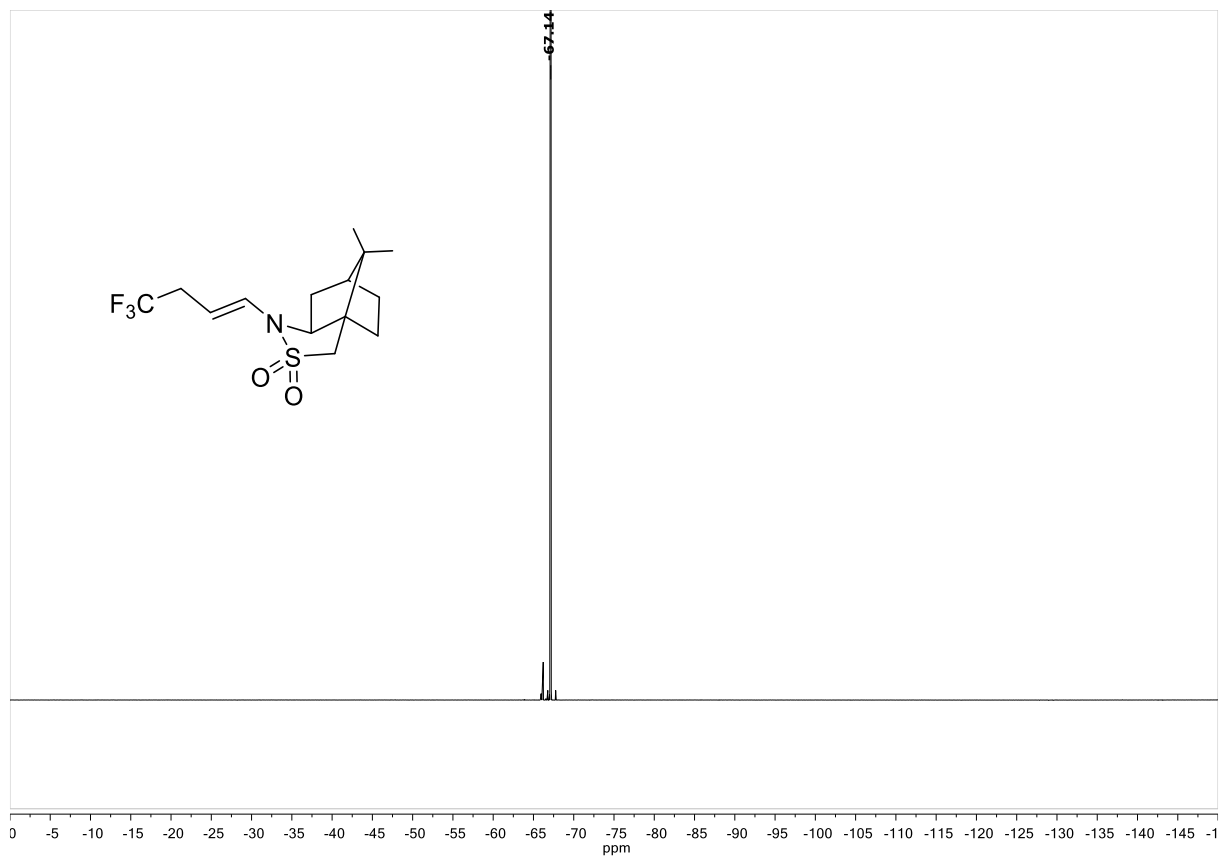
$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 282 MHz) of **3s**



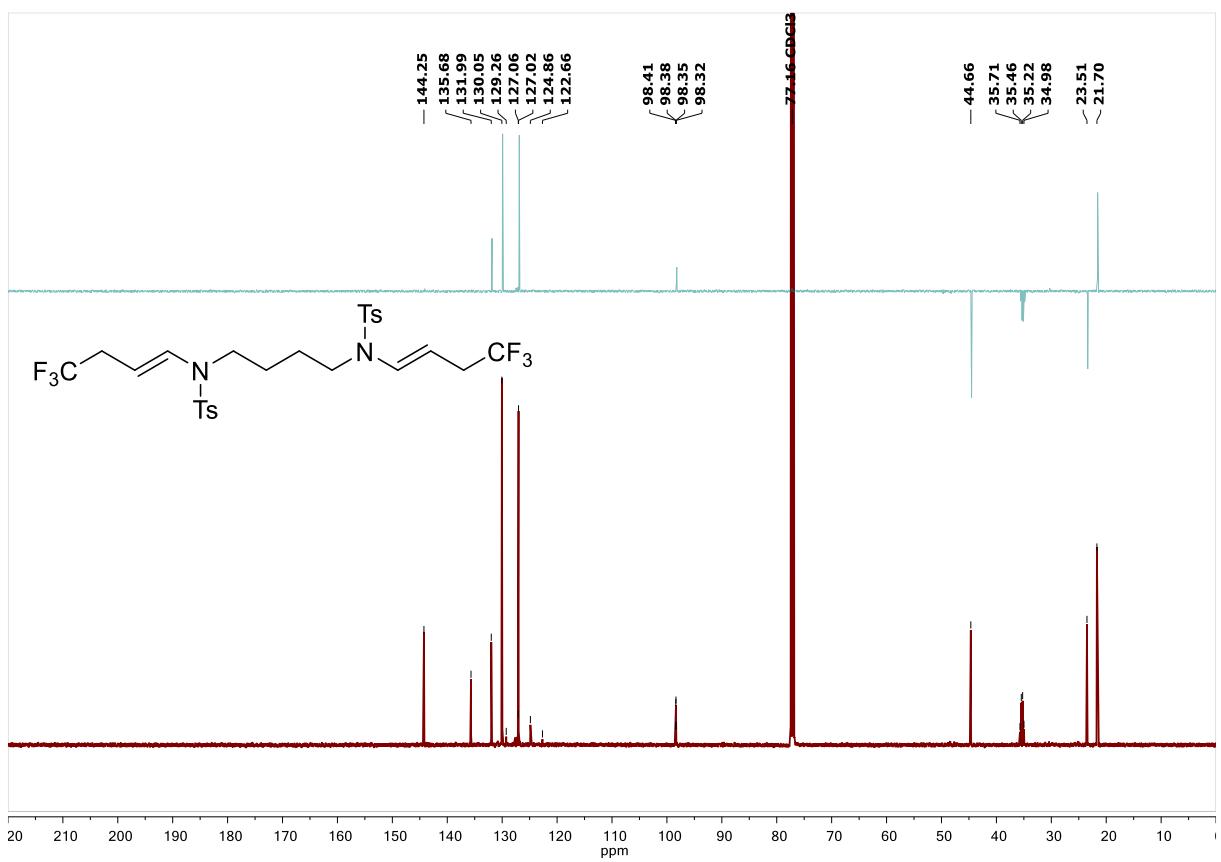
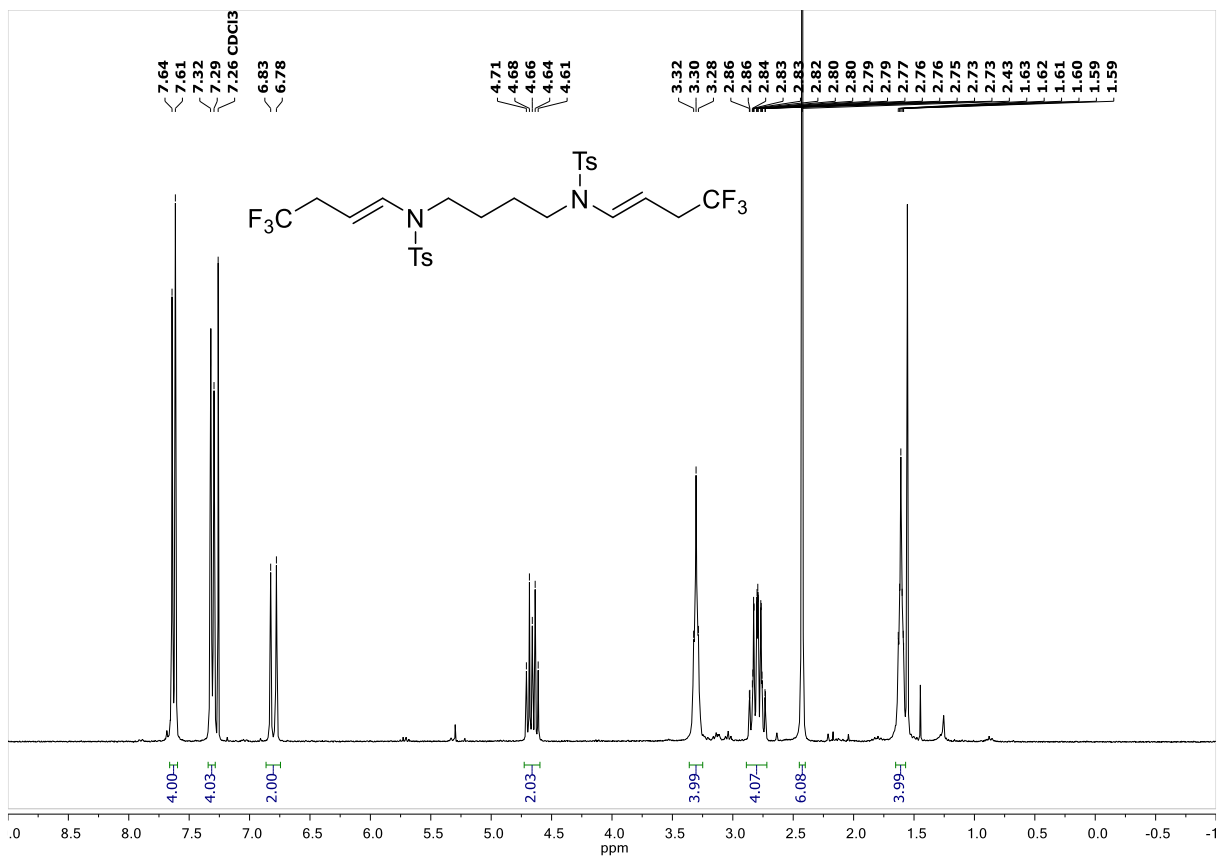
¹H NMR (CDCl₃, 300 MHz) of 3t



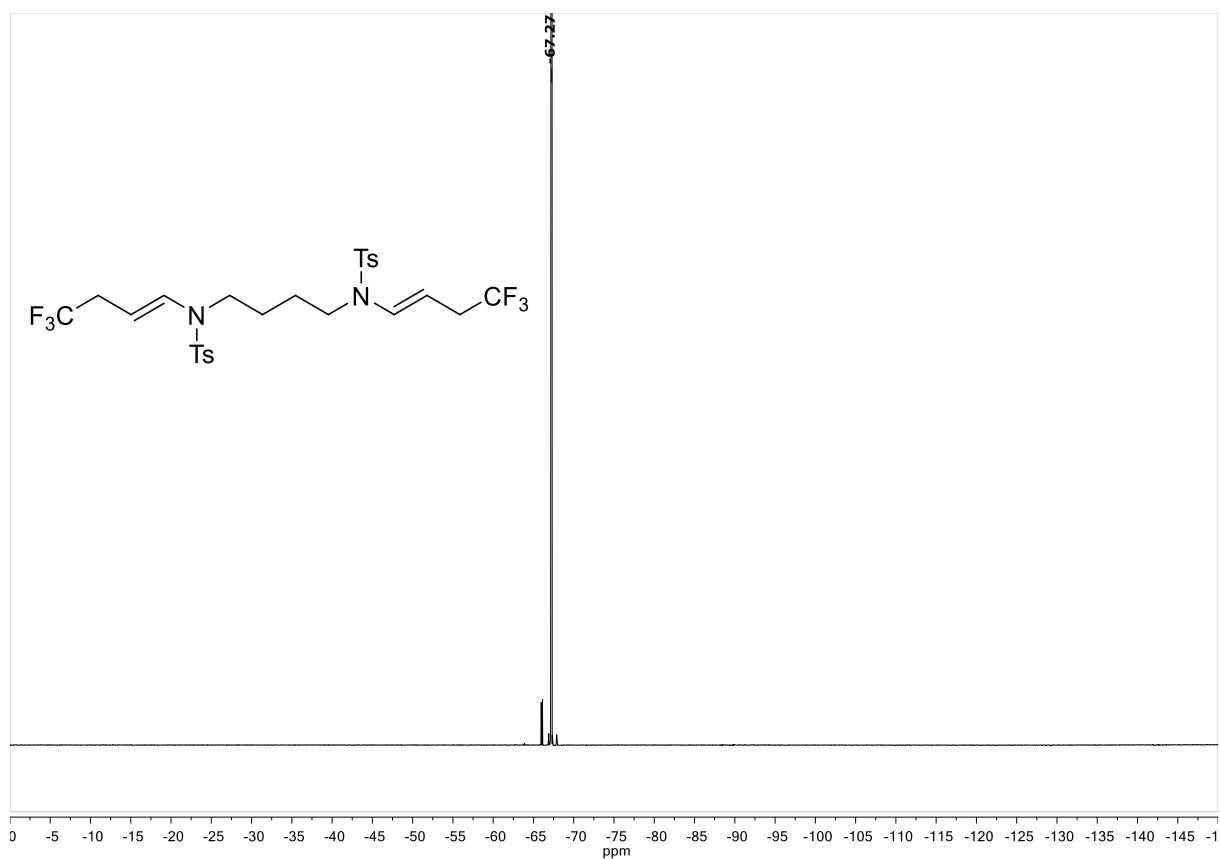
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 3t



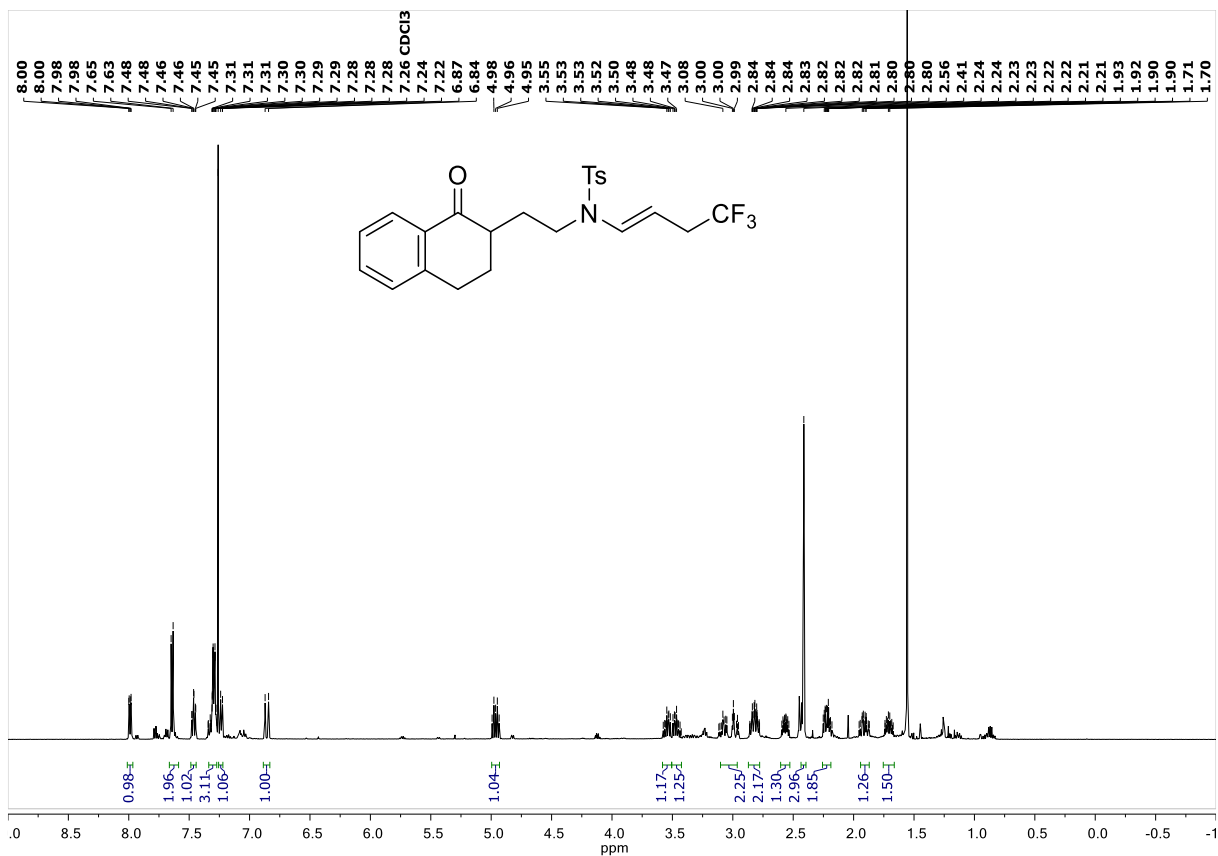
$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 282 MHz) of **3t**



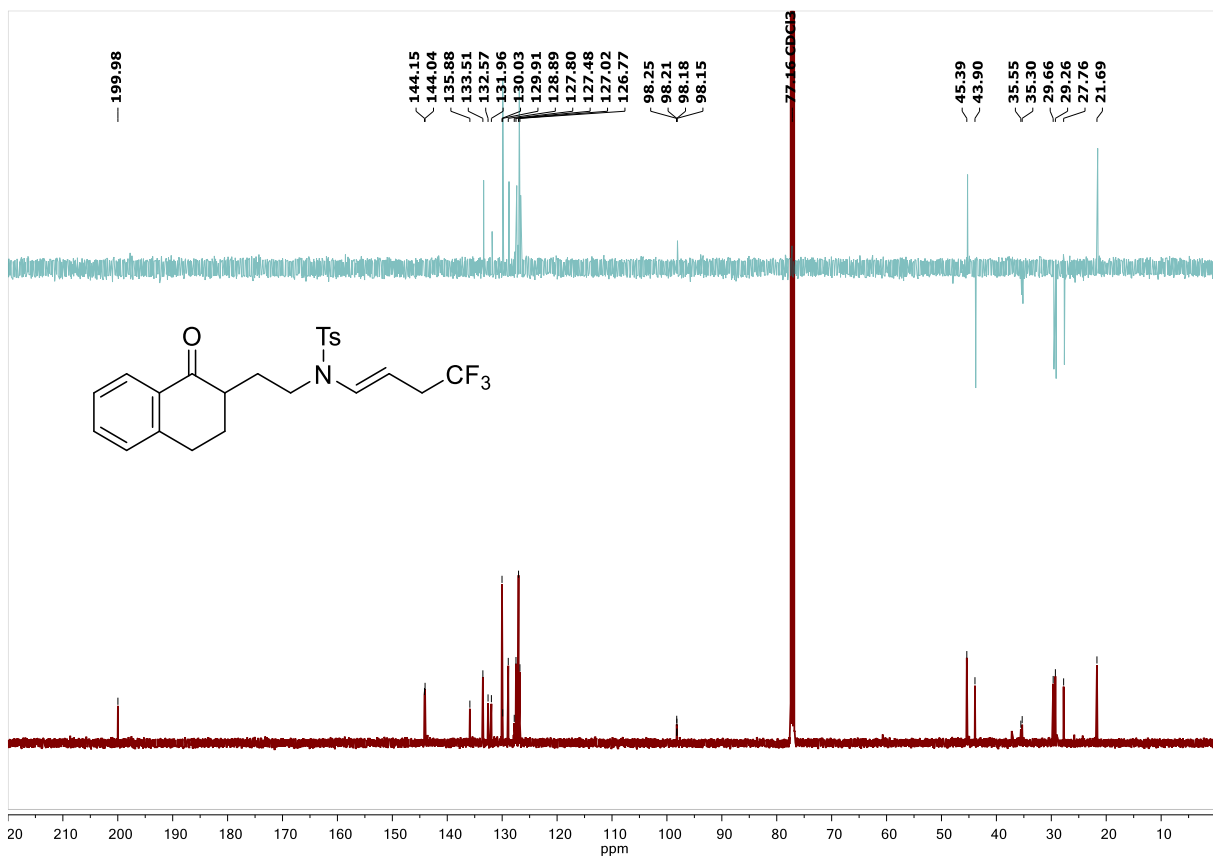
¹³C{¹H} NMR (CDCl₃, 126 MHz) of **3u**
S111



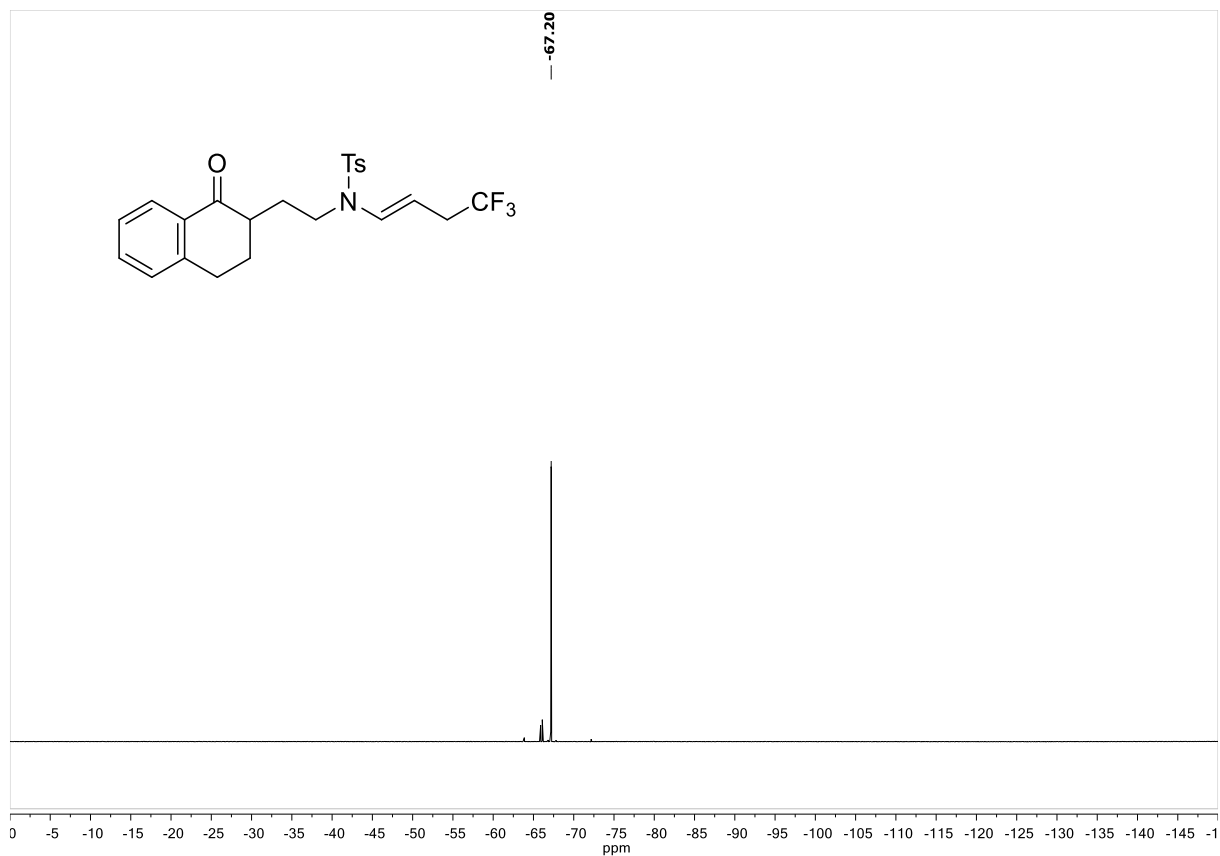
$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 282 MHz) of **3u**



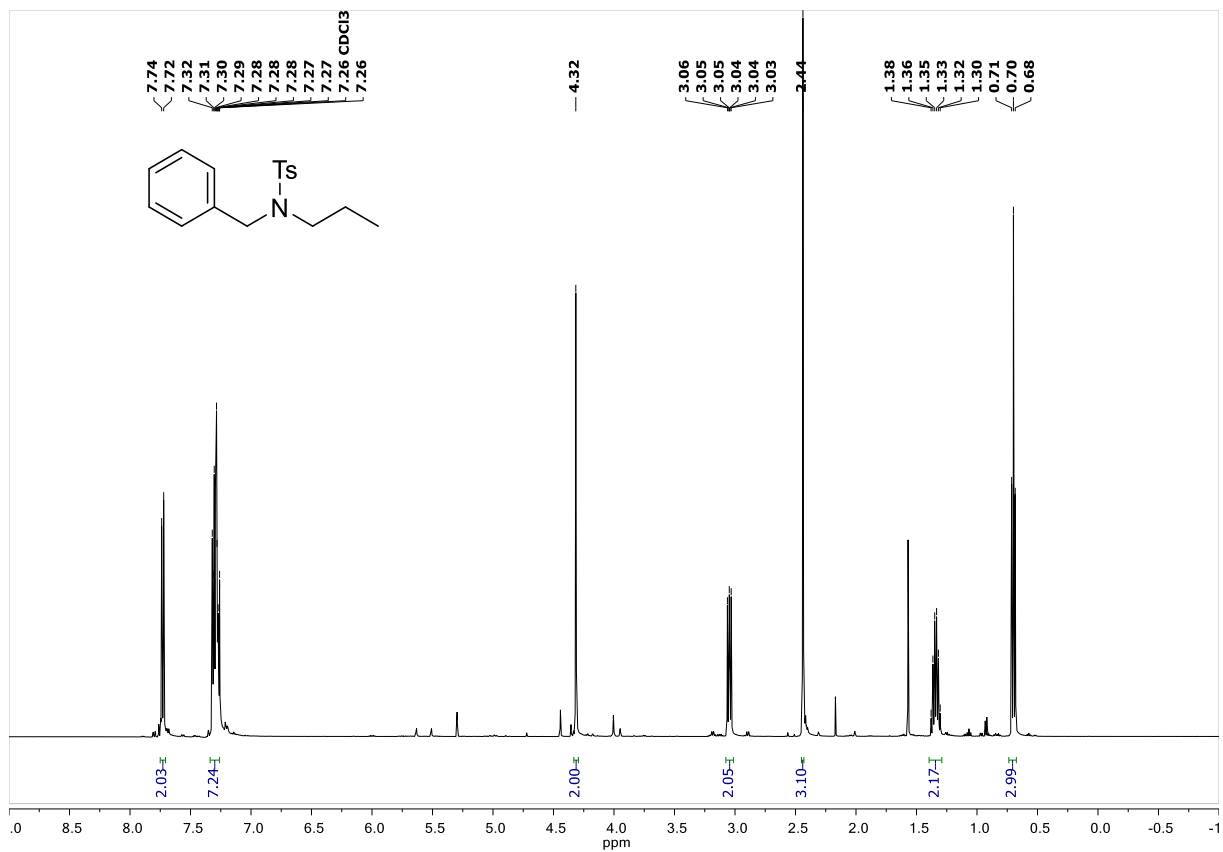
¹H NMR (CDCl₃, 500 MHz) of 3v



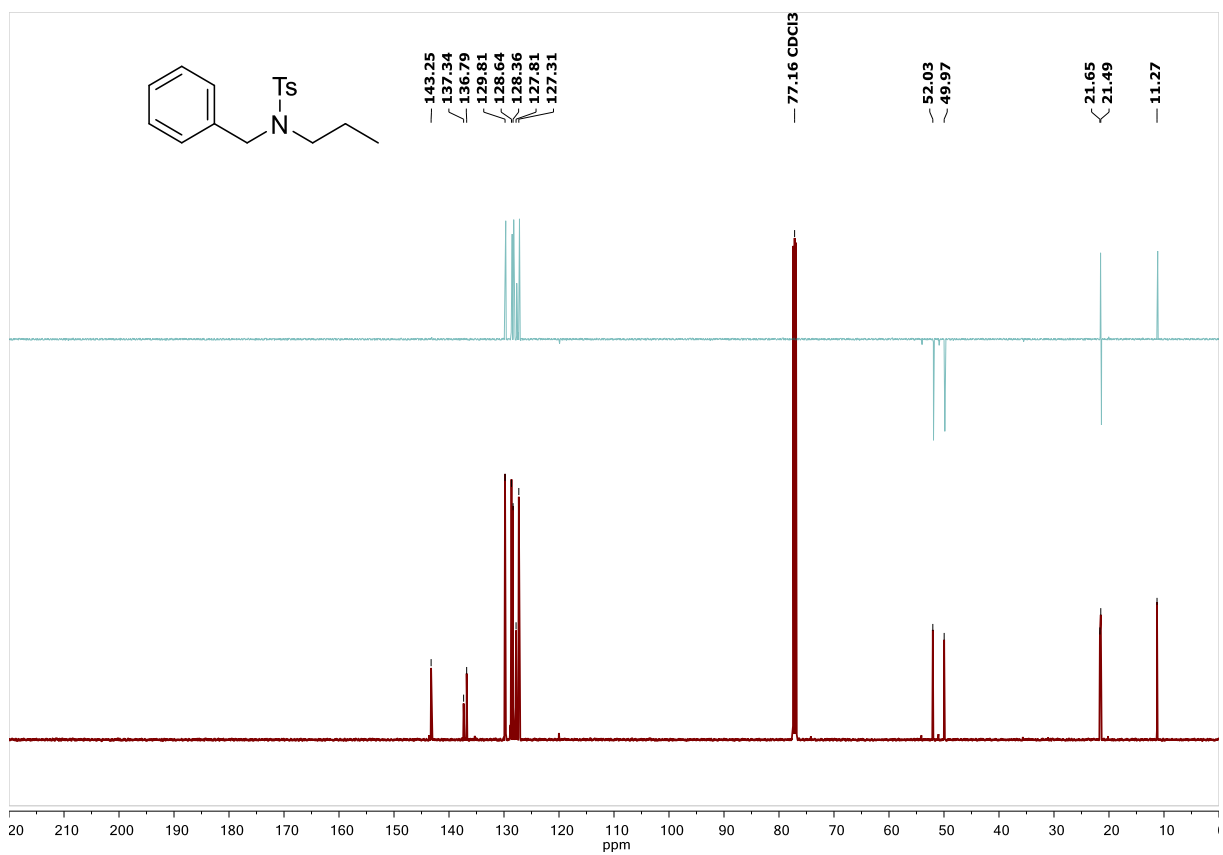
¹³C{¹H} NMR (CDCl₃, 126 MHz) of 3v
S113



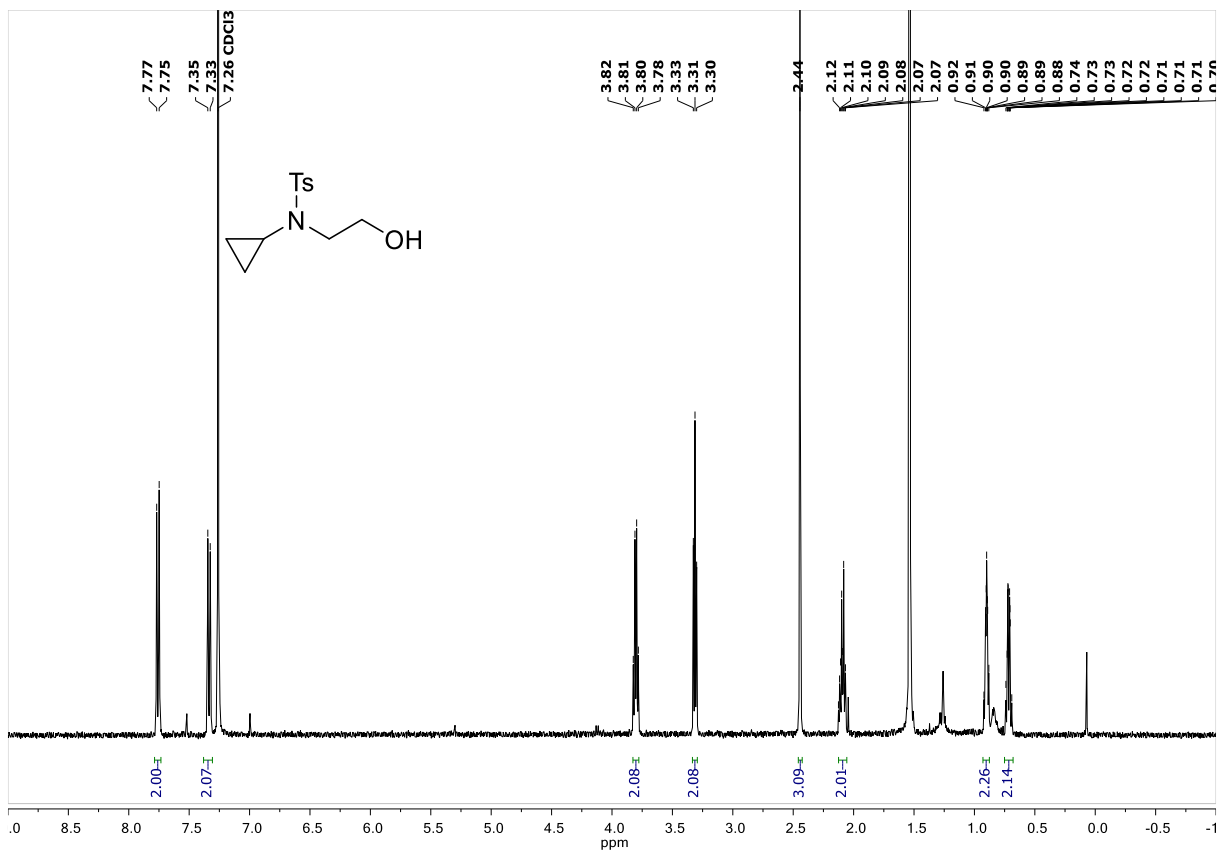
$^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 282 MHz) of **3v**



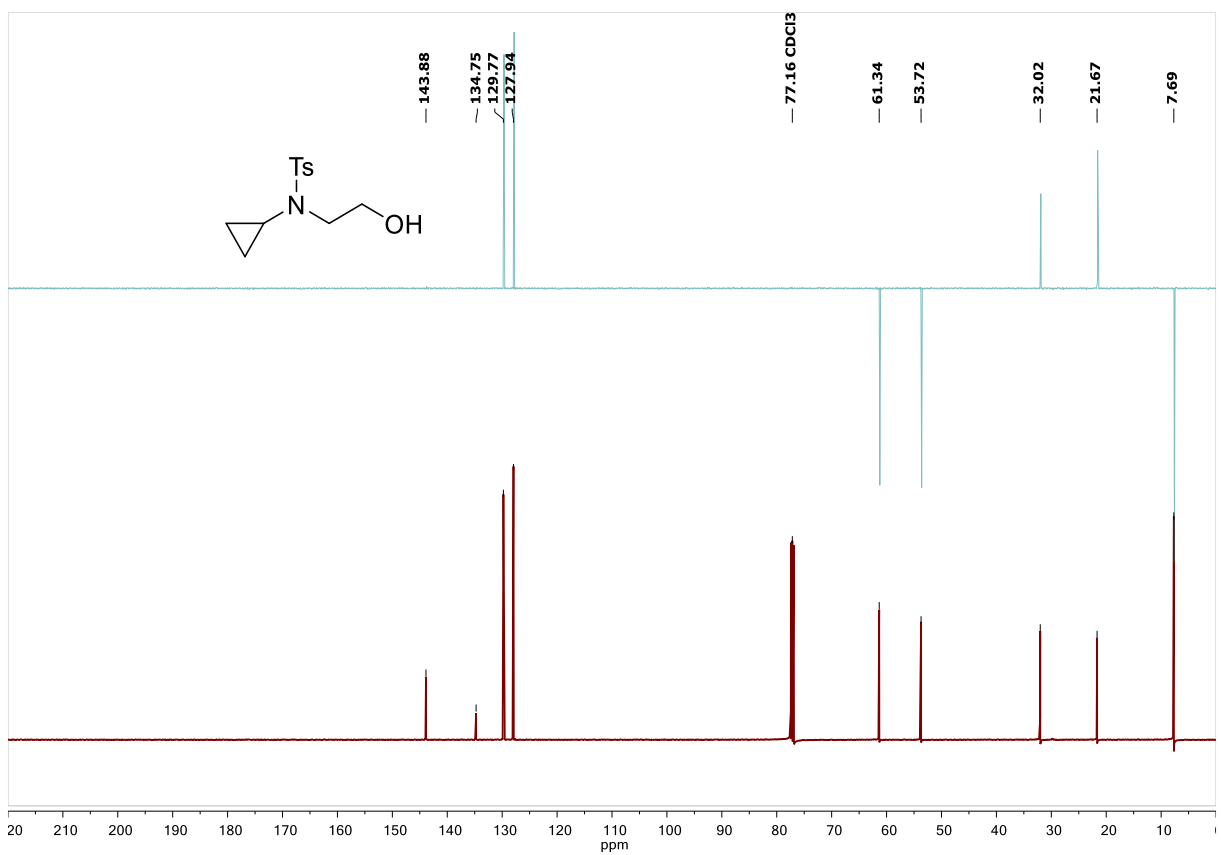
¹H NMR (CDCl₃, 500 MHz) of 5



¹³C{¹H} NMR (CDCl₃, 126 MHz) of 5



¹H NMR (CDCl₃, 400 MHz) of 6



¹³C NMR (CDCl₃, 126 MHz) of 6

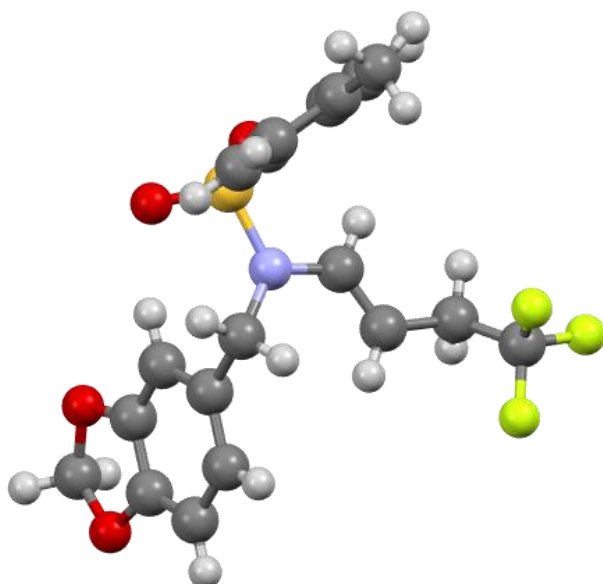
X-Ray Crystallography data

CCDC 2301994 (**3b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge crystallographic Data Centre.

Compound 4a was dissolved in a 0.5 mL dichloromethane, and *n*-hexane 2 mL were added. The sample was maintained at 4 °C for several days. Crystals were obtained through diffusion.

The X-ray diffraction data were collected at and 173 K on a Bruker SMART CCD diffractometer with MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). The diffraction data were corrected for absorption using the SADABS program. The structures were solved using SHELXS977 and refined by full matrix leastsquares on F2 using SHELXL-2014 in the anisotropic approximation for all non-hydrogen atoms. The hydrogen atoms were introduced at calculated positions and not refined (riding model).¹¹

Crystallography data of **3b**:



Structure of **3b** (CCDC 2301994): ellipsoid contour probability 50 %

¹¹ (a) Bruker. SADABS. Bruker AXS Inc.: Madison, Wisconsin, USA 2001. (b) M. Sheldrick, *Acta Crystallogr. Sect. A Found. Crystallogr.* 2008, **64**, 112–122. (c) G. M. Sheldrick, *Acta Crystallogr. Sect. C. Struct. Chem.* 2015, **71**, 3-8.

Crystal structure Report for **3b** (CCDC 2301994)

Table 1. Crystal data and structure refinement for *elmcg_b*.

Identification code	elmcg230419
Empirical formula	C ₁₉ H ₁₈ F ₃ N O ₄ S
Formula weight	413.40
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 9.9278(3) Å alpha = 90 deg. b = 16.1864(4) Å beta = 110.3770(10) deg. c = 12.2047(3) Å gamma = 90 deg.
Volume	1838.51(9) Å ³
Z, Calculated density	4, 1.494 Mg/m ³
Absorption coefficient	0.232 mm ⁻¹
F(000)	856
Crystal size	0.200 x 0.160 x 0.150 mm
Theta range for data collection	2.180 to 27.913 deg.
Limiting indices	-13 ≤ h ≤ 13, -21 ≤ k ≤ 19, -16 ≤ l ≤ 14

Reflections collected / unique 29538 / 4381 [R(int) = 0.0245]

Completeness to theta = 25.242 99.9 %

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 0.7456 and 0.6812

Refinement method Full-matrix least-squares on F²

Data / restraints / parameters 4381 / 0 / 254

Goodness-of-fit on F² 1.012

Final R indices [I > 2σ(I)] R1 = 0.0379, wR2 = 0.1034

R indices (all data) R1 = 0.0414, wR2 = 0.1070

Extinction coefficient n/a

Largest diff. peak and hole 0.728 and -0.668 e.Å⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for elmcg_b.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
N(1)	4519(1)	8077(1)	5912(1)	20(1)
S(1)	3965(1)	8971(1)	6252(1)	19(1)
O(1)	3821(1)	8855(1)	7371(1)	25(1)
O(2)	4926(1)	9586(1)	6105(1)	26(1)
C(1)	2252(1)	9145(1)	5209(1)	19(1)
C(2)	1060(2)	8865(1)	5450(1)	23(1)
C(3)	-294(2)	8938(1)	4601(1)	25(1)
C(4)	-477(2)	9291(1)	3521(1)	25(1)
C(5)	735(2)	9589(1)	3309(1)	26(1)
C(6)	2099(2)	9519(1)	4140(1)	23(1)
C(7)	-1958(2)	9357(1)	2612(2)	37(1)
C(8)	5254(1)	8039(1)	5055(1)	21(1)
C(9)	6821(1)	7789(1)	5614(1)	19(1)
C(10)	7424(2)	7214(1)	5075(1)	22(1)
C(11)	8884(2)	6992(1)	5553(1)	24(1)
C(12)	9670(1)	7362(1)	6590(1)	21(1)
O(3)	11122(1)	7280(1)	7225(1)	26(1)
C(13)	11349(2)	7740(1)	8281(1)	29(1)
O(4)	10111(1)	8247(1)	8109(1)	30(1)
C(14)	9074(2)	7935(1)	7127(1)	21(1)
C(15)	7660(2)	8168(1)	6669(1)	21(1)
C(16)	4050(2)	7350(1)	6300(1)	21(1)

C(17)	4329(2)	6580(1)	6069(1)	25(1)
C(18)	3804(2)	5871(1)	6607(2)	32(1)
C(19)	2879(2)	5282(1)	5755(2)	32(1)
F(1)	1707(1)	5636(1)	4997(1)	64(1)
F(2)	2413(1)	4661(1)	6263(1)	41(1)
F(3)	3589(2)	4913(1)	5127(1)	59(1)

Table 3. Selected bond lengths [Å] and angles [deg] for elmcg_b.

Symmetry transformations used to generate equivalent atoms:

Table 4. Bond lengths [Å] and angles [deg] for elmcg_b.

N(1)-C(16)	1.4064(18)
N(1)-C(8)	1.4701(18)
N(1)-S(1)	1.6529(12)
S(1)-O(2)	1.4323(11)
S(1)-O(1)	1.4339(11)
S(1)-C(1)	1.7559(14)
C(1)-C(2)	1.3910(19)
C(1)-C(6)	1.398(2)
C(2)-C(3)	1.387(2)
C(3)-C(4)	1.388(2)
C(4)-C(5)	1.401(2)
C(4)-C(7)	1.506(2)
C(5)-C(6)	1.386(2)
C(8)-C(9)	1.5197(18)
C(9)-C(10)	1.3888(19)
C(9)-C(15)	1.4078(19)
C(10)-C(11)	1.408(2)
C(11)-C(12)	1.372(2)
C(12)-C(14)	1.383(2)
C(12)-O(3)	1.3850(17)
O(3)-C(13)	1.436(2)
C(13)-O(4)	1.4310(19)
O(4)-C(14)	1.3752(17)
C(14)-C(15)	1.3710(19)
C(16)-C(17)	1.328(2)
C(17)-C(18)	1.503(2)
C(18)-C(19)	1.473(2)
C(19)-F(1)	1.337(2)
C(19)-F(2)	1.3445(19)

C(19)-F(3)	1.348(2)
C(16)-N(1)-C(8)	120.67(12)
C(16)-N(1)-S(1)	118.00(10)
C(8)-N(1)-S(1)	120.39(10)
O(2)-S(1)-O(1)	120.11(7)
O(2)-S(1)-N(1)	106.40(6)
O(1)-S(1)-N(1)	106.05(6)
O(2)-S(1)-C(1)	108.52(7)
O(1)-S(1)-C(1)	108.61(7)
N(1)-S(1)-C(1)	106.34(6)
C(2)-C(1)-C(6)	121.00(13)
C(2)-C(1)-S(1)	118.35(11)
C(6)-C(1)-S(1)	120.58(11)
C(3)-C(2)-C(1)	119.21(14)
C(2)-C(3)-C(4)	121.13(14)
C(3)-C(4)-C(5)	118.67(13)
C(3)-C(4)-C(7)	119.99(15)
C(5)-C(4)-C(7)	121.33(15)
C(6)-C(5)-C(4)	121.33(14)
C(5)-C(6)-C(1)	118.62(13)
N(1)-C(8)-C(9)	112.06(11)
C(10)-C(9)-C(15)	120.66(13)
C(10)-C(9)-C(8)	120.55(13)
C(15)-C(9)-C(8)	118.76(12)
C(9)-C(10)-C(11)	121.76(13)
C(12)-C(11)-C(10)	116.32(13)
C(11)-C(12)-C(14)	122.04(13)
C(11)-C(12)-O(3)	128.44(14)
C(14)-C(12)-O(3)	109.43(13)
C(12)-O(3)-C(13)	105.06(11)
O(4)-C(13)-O(3)	107.94(12)

C(14)-O(4)-C(13)	105.13(12)
C(15)-C(14)-O(4)	127.14(14)
C(15)-C(14)-C(12)	122.55(13)
O(4)-C(14)-C(12)	110.22(12)
C(14)-C(15)-C(9)	116.65(13)
C(17)-C(16)-N(1)	126.48(13)
C(16)-C(17)-C(18)	119.58(14)
C(19)-C(18)-C(17)	114.34(14)
F(1)-C(19)-F(2)	106.47(14)
F(1)-C(19)-F(3)	107.37(16)
F(2)-C(19)-F(3)	105.21(14)
F(1)-C(19)-C(18)	112.89(15)
F(2)-C(19)-C(18)	112.87(14)
F(3)-C(19)-C(18)	111.53(15)

Symmetry transformations used to generate equivalent atoms:

Table 5. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for elmcg_b.

The anisotropic displacement factor exponent takes the form:

$$-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$$

	U11	U22	U33	U23	U13	U12
N(1)	15(1)	19(1)	27(1)	1(1)	9(1)	1(1)
S(1)	14(1)	18(1)	23(1)	-2(1)	5(1)	-2(1)
O(1)	23(1)	28(1)	23(1)	-2(1)	7(1)	1(1)
O(2)	19(1)	23(1)	36(1)	-2(1)	7(1)	-7(1)
C(1)	16(1)	16(1)	23(1)	-1(1)	6(1)	-1(1)
C(2)	19(1)	21(1)	28(1)	2(1)	9(1)	0(1)
C(3)	16(1)	21(1)	36(1)	-2(1)	7(1)	-1(1)
C(4)	20(1)	22(1)	28(1)	-7(1)	2(1)	5(1)
C(5)	28(1)	28(1)	23(1)	1(1)	8(1)	6(1)
C(6)	22(1)	22(1)	25(1)	1(1)	11(1)	1(1)
C(7)	24(1)	40(1)	35(1)	-9(1)	-3(1)	9(1)
C(8)	16(1)	26(1)	21(1)	1(1)	6(1)	0(1)
C(9)	15(1)	20(1)	22(1)	1(1)	7(1)	-1(1)
C(10)	20(1)	22(1)	25(1)	-4(1)	9(1)	-3(1)
C(11)	22(1)	21(1)	34(1)	-2(1)	14(1)	1(1)
C(12)	14(1)	21(1)	30(1)	6(1)	9(1)	1(1)
O(3)	15(1)	29(1)	34(1)	6(1)	7(1)	2(1)
C(13)	18(1)	37(1)	28(1)	9(1)	4(1)	1(1)
O(4)	17(1)	40(1)	27(1)	-5(1)	0(1)	1(1)
C(14)	17(1)	25(1)	21(1)	1(1)	6(1)	-3(1)
C(15)	17(1)	24(1)	23(1)	-3(1)	8(1)	0(1)
C(16)	18(1)	22(1)	23(1)	1(1)	7(1)	-2(1)
C(17)	23(1)	23(1)	28(1)	2(1)	8(1)	0(1)

C(18)	39(1)	23(1)	33(1)	3(1)	11(1)	-4(1)
C(19)	36(1)	28(1)	32(1)	2(1)	10(1)	-6(1)
F(1)	38(1)	54(1)	73(1)	24(1)	-14(1)	-10(1)
F(2)	49(1)	29(1)	44(1)	3(1)	14(1)	-14(1)
F(3)	86(1)	44(1)	61(1)	-22(1)	44(1)	-17(1)

Table 6. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for elmcg_b.

	x	y	z	U(eq)
H(2)	1172	8627	6188	27
H(3)	-1109	8744	4760	30
H(5)	618	9845	2581	32
H(6)	2914	9721	3986	27
H(7A)	-2058	8954	1989	55
H(7B)	-2102	9915	2282	55
H(7C)	-2678	9244	2974	55
H(8A)	5200	8587	4682	25
H(8B)	4755	7636	4436	25
H(10)	6835	6965	4366	27
H(11)	9302	6607	5178	29
H(13A)	11485	7358	8944	34
H(13B)	12218	8089	8458	34
H(15)	7265	8566	7045	26
H(16)	3476	7417	6775	25
H(17)	4858	6479	5566	30
H(18A)	4646	5570	7138	39
H(18B)	3262	6096	7085	39

Table 7. Selected torsion angles [deg] for elmcg_b.

Symmetry transformations used to generate equivalent atoms:

Table 8. Torsion angles [deg] for elmcg_b.

C(16)-N(1)-S(1)-O(2)	161.56(10)
C(8)-N(1)-S(1)-O(2)	-29.42(12)
C(16)-N(1)-S(1)-O(1)	32.60(12)
C(8)-N(1)-S(1)-O(1)	-158.38(10)
C(16)-N(1)-S(1)-C(1)	-82.89(11)
C(8)-N(1)-S(1)-C(1)	86.13(11)
O(2)-S(1)-C(1)-C(2)	-154.78(11)
O(1)-S(1)-C(1)-C(2)	-22.63(13)
N(1)-S(1)-C(1)-C(2)	91.12(12)
O(2)-S(1)-C(1)-C(6)	28.30(14)
O(1)-S(1)-C(1)-C(6)	160.45(11)
N(1)-S(1)-C(1)-C(6)	-85.80(12)
C(6)-C(1)-C(2)-C(3)	1.9(2)
S(1)-C(1)-C(2)-C(3)	-175.00(11)
C(1)-C(2)-C(3)-C(4)	-0.5(2)
C(2)-C(3)-C(4)-C(5)	-1.2(2)
C(2)-C(3)-C(4)-C(7)	179.57(14)
C(3)-C(4)-C(5)-C(6)	1.6(2)
C(7)-C(4)-C(5)-C(6)	-179.18(14)
C(4)-C(5)-C(6)-C(1)	-0.3(2)
C(2)-C(1)-C(6)-C(5)	-1.5(2)
S(1)-C(1)-C(6)-C(5)	175.33(11)
C(16)-N(1)-C(8)-C(9)	-78.52(16)
S(1)-N(1)-C(8)-C(9)	112.76(12)
N(1)-C(8)-C(9)-C(10)	136.17(14)
N(1)-C(8)-C(9)-C(15)	-45.73(17)
C(15)-C(9)-C(10)-C(11)	-0.3(2)
C(8)-C(9)-C(10)-C(11)	177.79(13)
C(9)-C(10)-C(11)-C(12)	1.2(2)

C(10)-C(11)-C(12)-C(14)	-1.4(2)
C(10)-C(11)-C(12)-O(3)	-177.51(13)
C(11)-C(12)-O(3)-C(13)	-174.94(15)
C(14)-C(12)-O(3)-C(13)	8.54(15)
C(12)-O(3)-C(13)-O(4)	-14.37(15)
O(3)-C(13)-O(4)-C(14)	14.73(15)
C(13)-O(4)-C(14)-C(15)	173.86(15)
C(13)-O(4)-C(14)-C(12)	-9.54(16)
C(11)-C(12)-C(14)-C(15)	0.6(2)
O(3)-C(12)-C(14)-C(15)	177.40(13)
C(11)-C(12)-C(14)-O(4)	-176.16(13)
O(3)-C(12)-C(14)-O(4)	0.62(16)
O(4)-C(14)-C(15)-C(9)	176.59(13)
C(12)-C(14)-C(15)-C(9)	0.4(2)
C(10)-C(9)-C(15)-C(14)	-0.5(2)
C(8)-C(9)-C(15)-C(14)	-178.63(13)
C(8)-N(1)-C(16)-C(17)	7.8(2)
S(1)-N(1)-C(16)-C(17)	176.77(12)
N(1)-C(16)-C(17)-C(18)	176.88(14)
C(16)-C(17)-C(18)-C(19)	122.82(17)
C(17)-C(18)-C(19)-F(1)	-58.5(2)
C(17)-C(18)-C(19)-F(2)	-179.27(14)
C(17)-C(18)-C(19)-F(3)	62.5(2)

Symmetry transformations used to generate equivalent atoms:

Table 9. Hydrogen bonds for elmcg_b [A and deg.].

D-H...A d(D-H) d(H...A) d(D...A) <(DHA)