Supporting Information

Regio-and Stereoselective Azidation of Activated *N*-allenamides: an entry to α, β, γ and δ-amido-azides

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Contents

General remarks

All reactions were carried out under an inert atmosphere of argon in dried glassware, unless otherwise noted. Conventional solvents (THF, CH_2Cl_2) are stored on molecular sieves and sampled under argon. Toluene, CH_3CN, $CHCl_3$ were used as received.

NMR Spectra (^1H, ^{13}C, ^{19}F) were performed at 298 K. ^1H (500 MHz or 300 MHz) and ^{13}C (126 MHz) NMR chemical shifts are reported relative to residual protiated solvent. ^{19}F (282 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, p = quintet, m = multiplet), coupling constant J (Hz) and integration.

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

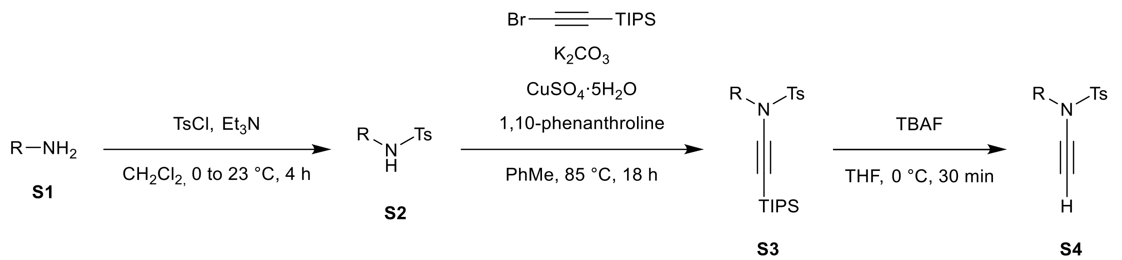
Thin layer chromatography was performed using Merck TLC silica gel 60 F254 aluminum sheets using petroleum ether/EtOAc as eluant and visualized using permanganate stain, ninhydrin stain, vanillin stain and/or UV light. Merck Geduran® 40-63 µm silica gel was used for column chromatography.

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 & characterization data

General procedure for the preparation of ynamides **S4**[1]



Primary amine **S1** (4.5 mmol, 1 equiv) was dissolved in CH_2Cl_2 (0.3 M), TsCl (4.95 mmol, 1.1 equiv) and Et_3N (11.25 mmol, 2.5 equiv) were added successively at 0 °C. After stirring at room temperature for 4 hours, the mixture was diluted with aqueous solution of HCl (1 N). The aqueous layer was extracted with CH_2Cl_2 (3x) and Et_2O (1x). The combined organic layers were washed with a saturated aqueous solution of NaCl, dried over $MgSO_4$, concentrated under reduce pressure and purified by column chromatography on silica gel using a mixture of petroleum ether/EtOAc as eluent to afford the desired sulfonamide **S2**.

[1] Y. Zhang, R. P. Hsung, M. R. Tracey, K. C. M. Kurtz, E. L. Vera, *Org. Lett.* 2004, **6**, 1151–1154.

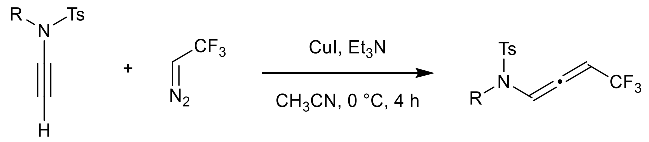
Sulfonamide **S2** (2 mmol, 1 equiv), $CuSO_4{\cdot}5H_2O$ (0.3 mmol, 15 mol%), 1,10-phenanthroline (0.6 mmol, 30 mol%), K_2CO_3 (5 mmol, 2.5 equiv), the bromoacetylenic derivative (2.3 mmol, 1.15 equiv) were dissolved in PhMe (0.08 M) and the reaction mixture was heated to 85 °C with a heating block for 18 h. After cooling down to room temperature, the mixture was filtered on a pad of silica gel and washed with EtOAc. The filtrate was then concentrated under reduced pressure and the crude material was purified by column chromatography on silica gel using a mixture petroleum ether/EtOAc as eluent to afford the desired TIPS protected ynamide **S3**.

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

TIPS protected ynamide **S3** (2.8 mmol, 1 equiv) was dissolved in THF (0.1 M) and cooled at 0 °C. A TBAF solution (3.1 mmol, 1.1 equiv, 1 M) was added dropwise and the resulting mixture was stirred at 0 °C for 30 min. The mixture was allowed to warm up to room temperature and was hydrolyzed with H_2O. The aqueous layer was extracted three times with EtOAc, washed with a saturated aqueous solution of NaCl, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel using a mixture petroleum ether/EtOAc as eluent or just by washing with cold *n*-pentane to afford the desired ynamide **S4**.

General procedure for the preparation of *N*-allenamides **1**

Trifluoromethylated *N*-allenamides **1a-q**[3]



S4 **1a-q**

The corresponding ynamide **S4** (0.2 mmol, 1 equiv) was solubilized in CH_3CN (0.1 M) in the presence of CuI (0.2 mmol, 20 mol%), and Et_3N (0.4 mmol, 2 equiv). 1,1,1-trifluoro-diazoethane was added dropwise (in excess) at 0 °C and the reaction was stirred for 4 h. 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 trifluoromethylated *N*-allenamides **1a-q**.

1,1,1-trifluoro-diazoethane was synthesized according to the previous literature and stored in diethyl ether solution in the presence of $MgSO_4$ at -18 °C for a few weeks.[4]

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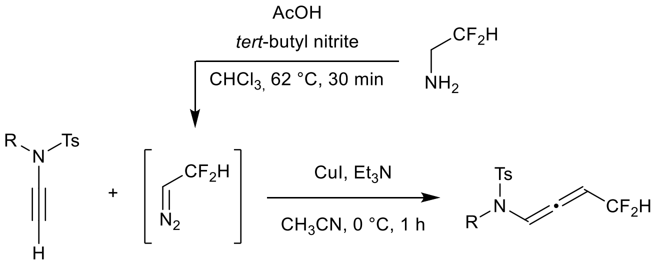
[2] H. Hofmeister, K. Annen, H. Laurent, R. Wiechert, *Angew. Chem. Int. Ed. Engl.* 1984, **23**, 727–729.
[3] Y. Zheng, B. Moegle, S. Ghosh, A. Perfetto, D. Luise, I. Ciofini, L. Miesch, *Chem. – Eur. J.* 2022, **28**, e202103598.
[4] H. Gilman, R. G. Jones, *J. Am. Chem. Soc.* 1943, **65**, 1458–1460.

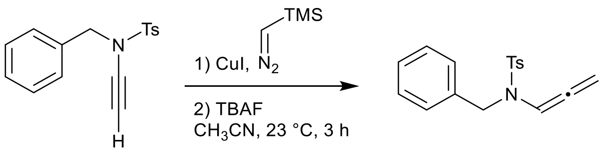
Difluoromethylated *N*-allenamides **1r-t**



S4 **1r-t**

2,2-difluoroethan-1-amine (3.0 mmol, 6 equiv), *tert*-butyl nitrite (4.5 mmol, 9 equiv) and AcOH (0.25 mmol, 50 mol%) were dissolved in $CHCl_3$ and heated to 62 °C with a heating block for 30 min. The reaction mixture was subsequently cooled down at room temperature with a water bath for 10 min. The reaction mixture was then slowly added at 0 °C to another round-bottom flask previously charged with ynamide **S4** (0.5 mmol, 1 equiv), CuI (0.15 mmol, 0.3 equiv) and Et_3N (1.25 mmol, 2.5 equiv) dissolved in CH_3CN (0.05 M). The resulting mixture was stirred for 1 h. The solvent was removed 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 difluoromethylated *N*-allenamides **1r-t**.

Terminal *N*-allenamides **1u**[3]

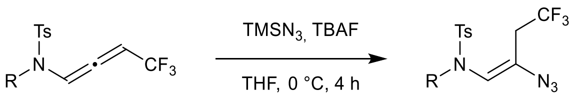


S4 **1u**

Benzyl-ynamide **S3** (0.5 mmol, 1 equiv) was dissolved in CH_3CN (0.1 M). CuI (0.1 mmol, 20 mol%) and trimethylsilyldiazomethane (0.54 mmol, 1.1 equiv, 2 M Et_2O) was added dropwise and the reaction mixture was stirred at 23 °C for 3 hours. A TBAF solution (0.50 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 H_2O. The aqueous layer was extracted with CH_2Cl_2 (x3) and with Et_2O (1x). The combined organic layers were washed with a saturated aqueous solution of NaCl, dried over $MgSO_4$, concentrated under reduced pressure and purified by column chromatography on silica gel using a mixture of petroleum ether/EtOAc as eluent to afford the desired terminal *N*-allenamide **1u** (0.34 mmol, 66 %) as a colorless oil.

General procedure for the preparation of β–amido azides **2**

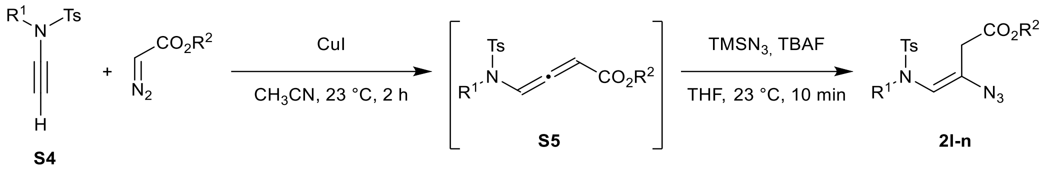
Synthesis of trifluoromethylated β–amido azides **2a-k**



1 **2a-k**

Trifluoromethylated *N*-allenamide **1** (0.1 mmol, 1 equiv) was dissolved in THF (0.1 M) and cooled to 0 °C. $TMSN_3$ (2.0 mmol, 2 equiv) and a TBAF solution (0.2 mmol, 2 equiv, 1 M in THF) were subsequently added and the solution was stirred at 0 °C for 4 h. The solvent was removed 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 fluorinated β–amido azides **2a-k**.

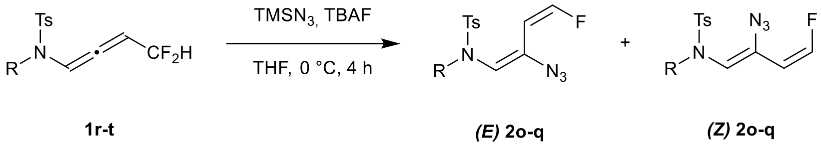
Sequential one-pot synthesis of ester β–amido azides **2l-n**



The corresponding ynamide **S4** (0.2 mmol, 1 equiv) was solubilized in CH_3CN (0.1 M) in the presence of CuI (0.2 mmol, 1 equiv) and the diazo ester derivative (0.3 mmol, 1.5 equiv) was added dropwise at room temperature and the reaction was stirred for 2 h. $TMSN_3$ (0.22 mmol, 1.1 equiv) and a TBAF solution (0.22 mmol, 1.1 equiv, 1 M in THF) were then subsequently added to the reaction mixture at room temperature and stirred for 10 min. The solvent was removed 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 ester β–amido azides **2l-n**.

The corresponding diazo ester derivatives were synthesized according to the literature.[5]

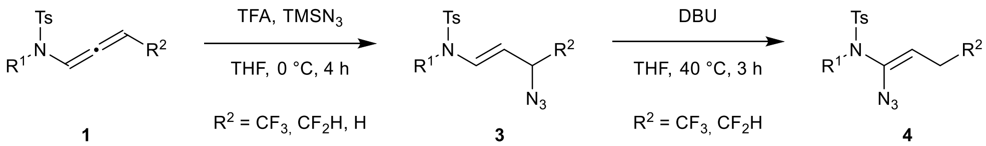
Synthesis of difluoromethylated β–amido azides **2o-q**



Difluoromethylated *N*-allenamide **1r-t** (0.1 mmol, 1 equiv) was dissolved in THF (0.1 M) and cooled to 0 °C. $TMSN_3$ (2.0 mmol, 2 equiv) and a TBAF solution (0.2 mmol, 2 equiv, 1 M in THF) were subsequently added and the solution was stirred at 0 °C for 4 h. The solvent was removed 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 mono-fluorinated β–amido azides **2o-q** as a diastereoisomeric mixture.

General procedure for the preparation of α–amido azides **4**

Caution! Handle with care. This protocol generates hydrazoic acid (HN3), which is acutely toxic and extremely shock sensitive.



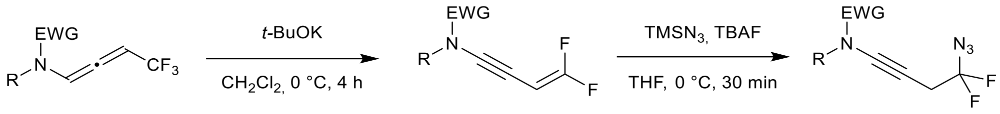
N-allenamide **1** (0.1 mmol, 1 equiv) was dissolved in THF (0.1 M) and cooled to 0 °C. TFA (0.02 mmol, 0.2 equiv) and $TMSN_3$ (0.2 mmol, 2 equiv) were subsequently added and the solution was stirred at 0 °C for 4 h. The reaction mixture was hydrolyzed with a saturated aqueous solution of

[5] T. Toma, J. Shimokawa, T. Fukuyama, *Org. Lett.* 2007, **9**, 3195–3197.

$NaHCO_3$. The aqueous layer was extracted with EtOAc (3x). The combined organic layers were washed with a saturated aqueous solution of NaCl, dried over $MgSO_4$, concentrated under reduced pressure and purified by column chromatography on silica gel using a mixture of petroleum ether/EtOAc as eluent to afford the desired γ–amido azides **3a-j**.

Allyl azide **3a-j** (0.1 mmol, 1 equiv) was dissolved in THF (0.05 M) in the presence of DBU (0.15 mmol, 1.2 equiv). The reaction mixture was stirred at 40 °C for 3 h. The reaction was cooled down to room temperature and hydrolyzed with H_2O. The aqueous layer was extracted with EtOAc (3x). The combined organic layers were washed with a saturated aqueous solution of NaCl, dried over $MgSO_4$, concentrated under reduced pressure and purified by column chromatography on silica gel using a mixture of petroleum ether/EtOAc as eluent to afford the desired α–amido azides **4a-i**.

General procedure for the preparation of difluoromethylated δ–amido azides **6**



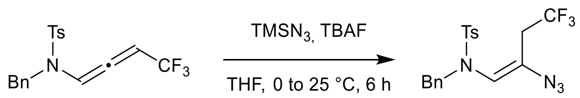
1a-q **5** **6**

Trifluoromethylated *N*-allenamide **1a-q** (0.2 mmol, 1 equiv) was dissolved in CH_2Cl_2 (0.05 M) and cooled to 0 °C. *t*-BuOK (0.4 mmol, 2 equiv) was then added portion by portion and the resulting reaction mixture was stirred for 4 h at 0 °C before being hydrolyzed with H_2O. The aqueous layer was extracted three times with CH_2Cl_2. The combined organic layers were washed with a saturated aqueous solution of NaCl, dried over $MgSO_4$, concentrated under reduced pressure and purified by column chromatography on silica gel using a mixture of petroleum ether/EtOAc as eluent to afford the desired ene-ynamide **5a-c**.[6]

To a stirring solution of $TMSN_3$ (0.4 mmol, 2 equiv) and TBAF (0.22 mmol, 1.1 equiv, 1 M in THF) in THF (2 mL) at 0 °C was added dropwise a solution of ene-ynamide **5a-c** (0.2 mmol, 1 equiv) in THF (2 mL). After stirring for 30 min, the solvent was removed 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 difluoromethylated δ–amido azides **6a-c**.

Extension and post-functionalization procedures

Large scale synthesis of trifluoromethylated amido azide **2a**, **3a** & **4a**

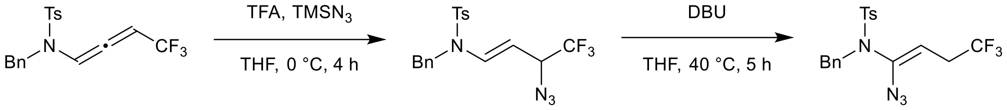


1a (1.0 mmol) **2a** (0.75 mmol)

Trifluoromethylated *N*-allenamide **1a** (1 mmol, 1 equiv) was dissolved in THF (0.1 M) and cooled to 0 °C. $TMSN_3$ (2.0 mmol, 2 equiv) and a TBAF solution (2.0 mmol, 2 equiv, 1 M in THF) were subsequently added and the solution was stirred at 0 °C for 6 h. The solvent was removed under vacuum and the crude material was purified by column chromatography on silica gel using a

[6] M. Hourtoule, L. Miesch, *Org. Lett.* 2022, **24**, 3896–3900.

mixture petroleum ether/EtOAc, as eluent to afford the desired fluorinated β–amido azides **2a** (0.75 mmol, 75 %) as a white solid.

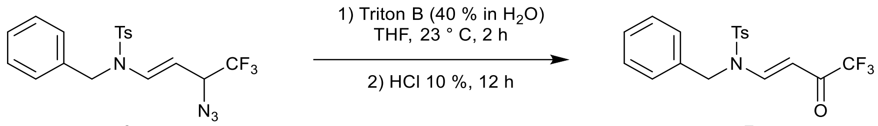


1a (1.5 mmol) **3a** (1.3 mmol) **4a** (0.9 mmol)

N-allenamide **1a** (1.5 mmol, 1 equiv) was dissolved in THF (0.1 M) and cooled to 0 °C. TFA (0.3 mmol, 0.3 equiv) and $TMSN_3$ (3.0 mmol, 3 equiv) were subsequently added and the solution was stirred at 0 °C for 4 h. The reaction mixture was hydrolyzed with a saturated aqueous solution of $NaHCO_3$. The aqueous layer was extracted with EtOAc (3x). The combined organic layers were washed with a saturated aqueous solution of NaCl, dried over $MgSO_4$, concentrated under reduced pressure and purified by column chromatography on silica gel using a mixture of petroleum ether/EtOAc as eluent to afford the desired γ–amido azides **3a** (1.3 mmol, 88 %) as a white solid.

Allyl azide **3a** (1.3 mmol, 1 equiv) was dissolved in THF (0.05 M) in the presence of DBU (1.9 mmol, 1.5 equiv). The reaction mixture was stirred at 40 °C for 5 h. The reaction was cooled down to room temperature and hydrolyzed with H_2O. The aqueous layer was extracted with EtOAc (3x). The combined organic layers were washed with a saturated aqueous solution of NaCl, dried over $MgSO_4$, concentrated under reduced pressure and purified by column chromatography on silica gel using a mixture of petroleum ether/EtOAc as eluent to afford the desired α–amido azides **4a** (0.9 mmol, 67 %) as a white solid.

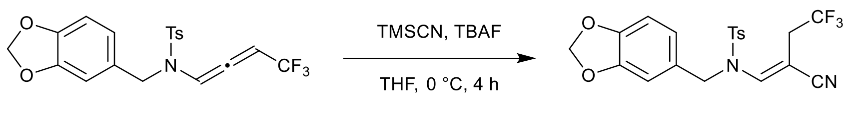
Hydration of trifluoromethylated γ–amido azide **3a**



3a **7**

Allyl azide **3a** (0.1 mmol, 1 equiv) was dissolved in THF (0.1 M) and Triton B (0.15 mmol, 1.5 equiv) was added dropwise at 0 °C and the resulting mixture was stirred for 2 h at room temperature. The reaction was then hydrolyzed with an aqueous solution of HCl (10 %) and stirred for another 12 h. The aqueous layer was then extracted with EtOAc (3x), the combined organic layers were washed with a saturated aqueous solution of NaCl, dried over $MgSO_4$, concentrated under reduced pressure and purified by column chromatography on silica gel using a mixture of petroleum ether/EtOAc as eluent to afford the trifluoromethyl ketone **7** (0.09 mmol, 35 mg, 91 %) as a colorless oil.

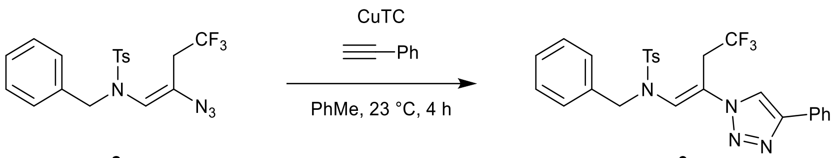
Hydrocyanation of trifluoromethylated *N*-allenamide **1c**



1c **8**

Trifluoromethylated *N*-allenamide **1c** (0.1 mmol, 1 equiv) was dissolved in THF (0.1 M) and cooled to 0 °C. TMSCN (2.0 mmol, 2 equiv) and a TBAF solution (0.2 mmol, 2 equiv, 1 M in THF) were subsequently added and the solution was stirred at 0 °C for 4 h. The solvent was removed 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 fluorinated vinyl nitrile **8** (0.07 mmol, 29.5 mg, 69 %) as a colorless oil.

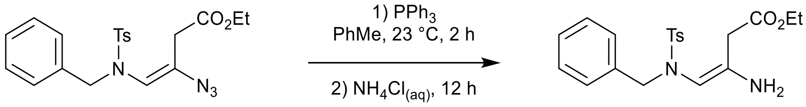
Cu(I)-catalyzed Alkyne Azide Cyclisation of trifluoromethylated β–amido azide **2a**[7]



2a **9**

To a solution of phenyl acetylene (0.22 mmol, 1.1 equiv) and CuTC (0.06 mmol, 30 mol%) in PhMe (0.1 M) was added vinyl azide **2a** (0.2 mmol, 1 equiv) and the resulting mixture was stirred at room temperature for 4 h. The aqueous layer was then extracted with EtOAc (3x), the combined organic layers were washed with a saturated aqueous solution of NaCl, dried over $MgSO_4$, concentrated under reduced pressure and purified by column chromatography on silica gel using a mixture of petroleum ether/EtOAc as eluent to afford the triazole **9** (0.2 mmol, 98 %) as a white solid.

Azide reduction of ester vinyl azide **2l**



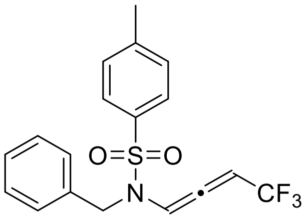
2l **10**

Ester vinyl azide **2l** (0.1 mmol, 1 equiv) and PPh_3 (0.2 mmol, 2 equiv) were dissolved in PhMe (0.05 M) and stirred at room temperature for 2 h. The reaction was hydrolyzed with a saturated solution of NH_4Cl and stirred for an additional 12 h. The aqueous layer was then extracted with EtOAc (3x), the combined organic layers were washed with a saturated aqueous solution of NaCl, dried over $MgSO_4$, concentrated under reduced pressure and purified by column chromatography on silica gel using a mixture of petroleum ether/EtOAc as eluent to afford the desired primary enamine **10** (0.09 mmol, 87 %) as a colorless oil.

[7] Z. Liu, P. Liao, X. Bi, *Org. Lett.* 2014, **16**, 3668–3671.

Characterization data

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

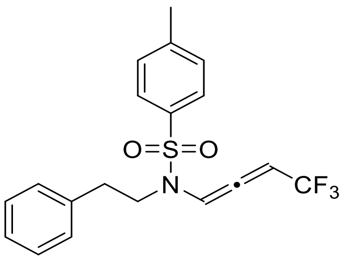


$C_{18}H_{16}F_3NO_2S$
MW: 367.39 g.mol^{-1}
White solid
87%

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

Data match with those described in the literature[6]

Compound **1b** 4-methyl-*N*-phenethyl-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)benzenesulfonamide



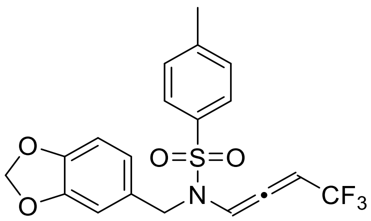
$C_{19}H_{18}F_3NO_2S$
MW: 381.41 g.mol^{-1}
White solid
65%

^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.74 – 7.63 (m, 2H), 7.46 (dq, J = 6.2, 3.1 Hz, 1H), 7.32 (d, J = 8.1 Hz, 2H), 7.31 – 7.27 (m, 2H), 7.24 – 7.18 (m, 1H), 7.17 – 7.09 (m, 2H), 5.99 (p, J = 5.6 Hz, 1H), 3.37 – 3.23 (m, 2H), 2.90 – 2.77 (m, 2H), 2.43 (s, 3H) ppm.

Data match with those described in the literature[6]

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

yl)benzenesulfonamide

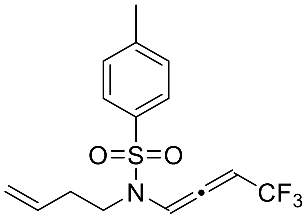


$C_{19}H_{16}F_3NO_4S$
MW: 411.40 g.mol^{-1}
White solid
75%

^{1}H NMR (400 MHz, CDCl$_3$): 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.

Data match with those described in the literature[6]

Compound **1d** *N*-(but-3-en-1-yl)-4-methyl-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)benzenesulfonamide

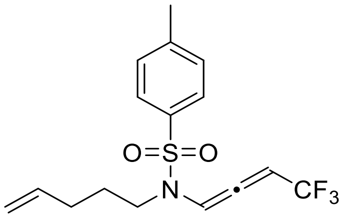


$C_{15}H_{16}F_3NO_2S$
MW: 331.35 g.mol^{-1}
Colorless oil
95%

^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.52 (d, J = 8.1 Hz, 2H), 7.31 – 7.29 (m, 1H), 6.70 (d, J = 8.0 Hz, 2H), 5.57 – 5.48 (m, 1H), 5.35 (p, J = 5.6 Hz, 1H), 5.00 – 4.85 (m, 2H), 3.07 – 2.95 (m, 2H), 2.24 – 2.07 (m, 2H), 1.82 (s, 3H) ppm.

Data match with those described in the literature[6]

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



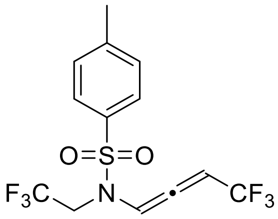
$C_{16}H_{18}F_3NO_2S$
MW: 345.38 g.mol^{-1}
Colorless oil
90%

^{1}H NMR (500 MHz, CDCl$_3$): 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.

Data match with those described in the literature[6]

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

trifluoroethyl)benzenesulfonamide



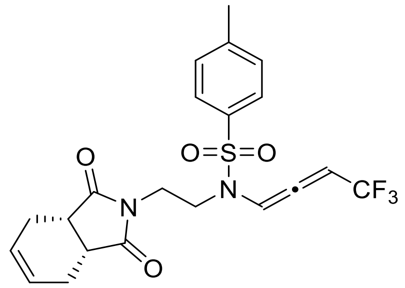
$C_{13}H_{11}F_6NO_2S$
MW: 359.29 g.mol^{-1}
Colorless oil
71%

^{1}H NMR (500 MHz, CDCl$_3$): 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 (dqd, J = 15.6, 8.1, 0.8 Hz, 1H), 3.72 (dq, J = 16.1, 8.1 Hz, 1H), 2.49 (s, 3H) ppm.

Data match with those described in the literature[8]

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

Compound **1g** *N*-(2-((3aR,7aS)-1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2H-isoindol-2-yl)ethyl)-4-methyl-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)benzenesulfonamide



$C_{21}H_{21}F_3N_2O_4S$
MW: 454.46 g.mol^{-1}
White solid
91%

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 8.1 Hz, 2H), 7.41 – 7.34 (m, 1H), 7.32 (d, *J* = 7.9 Hz, 2H), 6.08 (p, *J* = 5.5 Hz, 1H), 5.90 (m, 2H), 3.65 – 3.54 (m, 2H), 3.42 – 3.33 (m, 1H), 3.21 – 3.14 (m, 2H), 3.10 (dt, *J* = 14.8, 5.1 Hz, 1H), 2.62 – 2.54 (m, 2H), 2.43 (s, 3H), 2.26 – 2.25 (m, 2H) ppm.

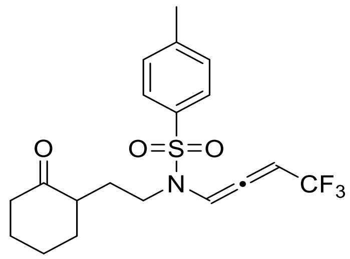
^{13}C NMR (126 MHz, $CDCl_3$): δ = 198.1 (q, *J* = 5.8 Hz), 180.3, 180.3, 144.8, 134.7, 130.2, 128.0, 128.0, 127.2, 121.3 (q, *J* = 271.9 Hz,), 106.9, 97.3 (q, *J* = 39.2 Hz), 44.0, 39.3, 39.3, 35.3, 23.4, 23.4, 21.7 ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = -62.08 ppm.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{21}H_{21}F_3N_2NaO_4S$ 477.1066; Found 477.1056.

IR (neat): ν = 3046, 1703, 1402, 1360, 1166, 1127 cm^{-1}

Compound **1h** 4-methyl-*N*-(2-(2-oxocyclohexyl)ethyl)-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)benzenesulfonamide



$C_{19}H_{22}F_3NO_3S$
MW: 401.44 g.mol^{-1}
White solid
62%

Only one diastereoisomer was described for ^{13}C-NMR.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.68 – 7.62 (m, 2H), 7.42 – 7.34 (m, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 6.02 – 5.90 (m, 1H), 3.30 – 3.01 (m, 2H), 2.42 (s, 4H), 2.40 – 2.29 (m, 2H), 2.13 – 1.98 (m, 2H), 1.98 – 1.81 (m, 2H), 1.78 – 1.56 (m, 2H), 1.41 – 1.27 (m, 2H) ppm.

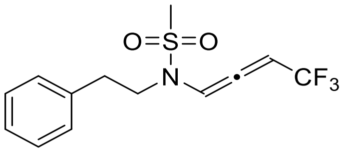
^{13}C NMR (126 MHz, $CDCl_3$): δ = 212.8, 198.4 (q, *J* = 5.8 Hz), 144.5, 134.9, 130.1, 127.2, 121.4 (q, *J* = 272.0 Hz), 107.0, 96.3 (q, *J* = 39.2 Hz), 47.4, 45.5, 42.3, 34.8, 28.3, 27.0, 25.4, 21.7 ppm.

^{19}F NMR (471 MHz, $CDCl_3$): δ = -62.10, -62.31 ppm.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{19}H_{22}F_3NNaO_3S$ 424.1165; Found 424.1159.

IR (neat): ν = 3046, 2934, 1708, 1356, 1265, 1121 cm^{-1}

Compound **1i** *N*-phenethyl-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)methanesulfonamide

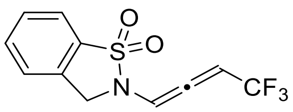


$C_{13}H_{14}F_3NO_2S$
MW: 305.32 g.mol^{-1}
White solid
59%

^{1}H NMR (500 MHz, CDCl$_3$): 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) ppm.

Data match with those described in the literature[9]

Compound **1j** 2-(4,4,4-trifluorobuta-1,2-dien-1-yl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide

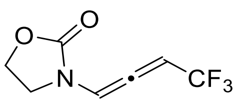


$C_{11}H_8F_3NO_2S$
MW: 275.24 g.mol^{-1}
White solid
58%

^{1}H NMR (500 MHz, CDCl$_3$): 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.

Data match with those described in the literature[6]

Compound **1k** 3-(4,4,4-trifluorobuta-1,2-dien-1-yl)oxazolidin-2-one

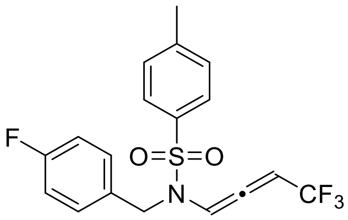


$C_7H_6F_3NO_2$
MW: 193.13 g.mol^{-1}
Colorless oil
73%

^{1}H NMR (500 MHz, CDCl$_3$): δ = 6.85 (dq, *J* = 6.2, 3.1 Hz, 1H), 5.36 (p, *J* = 5.6 Hz, 1H), 3.05 (pd, *J* = 8.9, 6.5 Hz, 2H), 2.07 (dtd, *J* = 22.0, 8.9, 6.5 Hz, 2H) ppm.

Data match with those described in the literature[3]

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



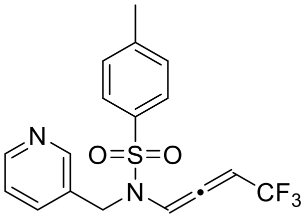
$C_{18}H_{15}F_4NO_2S$
MW: 385.38 g.mol^{-1}
White solid
78%

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

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

Data match with those described in the literature[10]

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

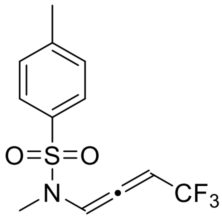


$C_{17}H_{15}F_3N_2O_2S$
MW: 368.37 g.mol^{-1}
Orange oil
52%

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

Data match with those described in the literature[10]

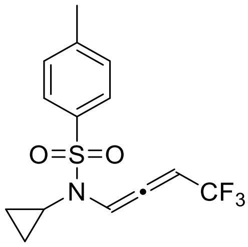
Compound **1n** *N*,4-dimethyl-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)benzenesulfonamide



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

1n was used without any further purification.

Compound **1o** *N*-cyclopropyl-4-methyl-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)benzenesulfonamide



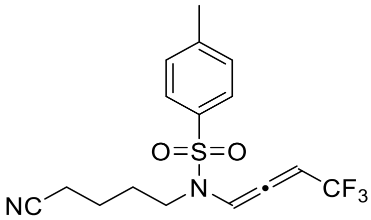
$C_{14}H_{14}F_3NO_2S$
MW: 317.33 g.mol^{-1}
White solid
74%

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

Data match with those described in the literature[6]

[10] C. Gommenginger, M. Hourtoule, M. Menghini, L. Miesch, *Org. Biomol. Chem.* 2024, **22**, 940–944.

Compound **1p** *N*-(4-cyanobutyl)-4-methyl-*N*-(4,4,4-trifluorobuta-1,2-dien-1-yl)benzenesulfonamide

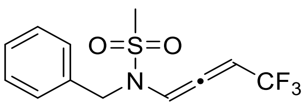


$C_{16}H_{17}F_3N_2O_2S$
MW: 358.38 g.mol^{-1}
Colorless oil
64%

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

Data match with those described in the literature[6]

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

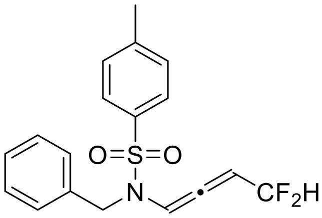


$C_{12}H_{12}F_3NO_2S$
MW: 291.29 g.mol^{-1}
White solid
81%

^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.56 – 7.13 (m, 6H), 5.85 (p, *J* = 5.6 Hz, 1H), 4.66 (d, *J* = 15.3 Hz, 1H), 4.41 (d, *J* = 15.3 Hz, 1H), 2.93 (s, 3H) ppm.

Data match with those described in the literature[6]

Compound **1r** *N*-benzyl-*N*-(4,4-difluorobuta-1,2-dien-1-yl)-4-methylbenzenesulfonamide

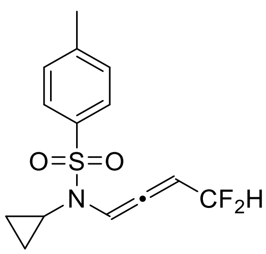


$C_{18}H_{17}F_2NO_2S$
MW: 349.40 g.mol^{-1}
Colorless oil
82%

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.76 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.35 – 7.26 (m, 5H), 7.23 (dd, *J* = 11.0, 5.7 Hz, 1H), 5.68 (p, *J* = 6.0 Hz, 1H), 5.39 (td, *J* = 56.0, 6.0 Hz, 1H), 4.48 (d, *J* = 15.1 Hz, 1H), 4.18 (d, *J* = 15.1 Hz, 1H), 2.49 (s, 3H) ppm.

Data match with those described in the literature[3]

Compound **1s** *N*-cyclopropyl-*N*-(4,4-difluorobuta-1,2-dien-1-yl)-4-methylbenzenesulfonamide



$C_{14}H_{15}F_2NO_2S$
MW: 299.34 g.mol^{-1}
White solid
89%

^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.74 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 7.17 (td, *J* = 5.8, 4.9 Hz, 1H), 6.10 – 5.80 (m, 2H), 2.45 (s, 3H), 1.72 (tt, *J* = 6.9, 3.6 Hz, 1H), 1.08 – 0.98 (m, 1H), 0.96 – 0.84 (m, 1H), 0.80 – 0.68 (m, 2H) ppm.

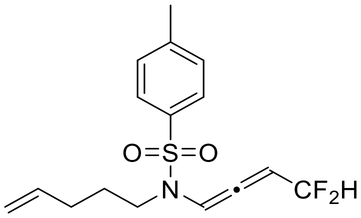
^{13}C NMR (126 MHz, CDCl$_3$): δ = 200.3 (t, *J* = 12.1 Hz), 144.6, 133.6, 129.9, 127.9, 113.5 (t, *J* = 239.4 Hz), 107.1 (t, *J* = 1.3 Hz), 98.2 (t, *J* = 28.7 Hz), 29.0, 21.8, 8.2, 7.7 ppm.

^{19}F NMR (471 MHz, CDCl$_3$): δ = -109.84 ppm.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for $C_{14}H_{15}F_2NNaO_2S$ 322.0689; Found 322.0694.

IR (neat): ν = 1350, 1171, 901, 814 cm^{-1}

Compound **1t** *N*-(4,4-difluorobuta-1,2-dien-1-yl)-4-methyl-*N*-(pent-4-en-1-yl)benzenesulfonamide



$C_{16}H_{19}F_2NO_2S$
MW: 327.40 g.mol^{-1}
Colorless oil
62%

Only one isomer was described for ^{13}C-NMR.

^{1}H NMR (500 MHz, CDCl$_3$) δ = 7.68 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.26 – 7.22 (m, 1H), 6.12 – 5.86 (m, 2H), 5.81 – 5.69 (m, 1H), 5.06 – 4.93 (m, 2H), 3.13 – 3.04 (m, 2H), 2.44 (s, 3H), 2.08 – 1.98 (m, 2H), 1.67 – 1.58 (m, 2H) ppm.

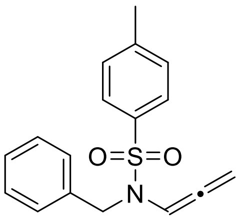
^{13}C NMR (126 MHz, CDCl$_3$): δ = 198.6, 144.2, 137.2, 135.3, 129.9, 127.1, 115.5, 113.0 (t, *J* = 239.8 Hz), 105.1, 99.3 (t, *J* = 28.2 Hz), 46.6, 30.6, 26.5, 21.6 ppm.

^{19}F NMR (471 MHz, CDCl$_3$): δ = -109.52 (d, *J* = 298.5 Hz), -110.30 (d, *J* = 299.5 Hz) ppm.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for $C_{16}H_{19}F_2NNaO_2S$ 350.0997; Found 350.0994.

IR (neat): ν = 1354, 1166, 904, 725 cm^{-1}

Compound **1u** *N*-benzyl-4-methyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide

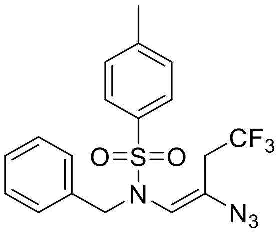


$C_{17}H_{17}NO_2S$
MW: 299.39 g.mol^{-1}
Colorless oil
66%

^{1}H NMR (500 MHz, CDCl$_3$): 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) ppm.

Data match with those described in the literature[3]

Compound **2a** (*E*)-*N*-(2-azido-4,4,4-trifluorobut-1-en-1-yl)-*N*-benzyl-4-methylbenzenesulfonamide



$C_{18}H_{17}F_3N_4O_2S$
MW: 410.42 g.mol^{-1}
Colorless oil
84%

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.7 – 7.67 (m, 2H), 7.41 – 7.35 (m, 2H), 7.31 – 7.28 (m, 3H), 7.22 – 7.18 (m, 2H), 5.20 (s, 1H), 4.21 (s, 2H), 3.08 (qd, *J* = 10.2, 0.8 Hz, 2H), 2.48 (s, 3H) ppm.

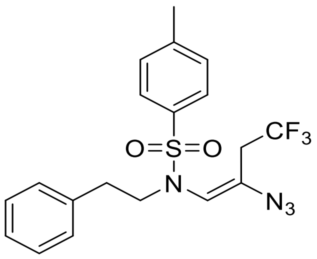
^{13}C NMR (126 MHz, $CDCl_3$): δ = 144.5, 138.3 (q, *J* = 3.0 Hz), 134.2, 133.9, 130.0, 129.2, 128.7, 128.3, 127.7, 123.9 (q, *J* = 278,3 Hz), 117.8, 55.6, 33.4 (q, *J* = 31.5 Hz), 21.6 ppm.

^{19}F NMR (282 MHz, $CDCl_3$): δ = -62.88 ppm.

HRMS (ESI-TOF) m/z: $[M+K]^+$ calcd for $C_{18}H_{17}F_3KN_4O_2S$ 449.0656; Found 449.0668.

IR (neat): ν = 2960, 2112, 1271, 1164 cm^{-1}

Compound **2b** (*E*)-*N*-(2-azido-4,4,4-trifluorobut-1-en-1-yl)-4-methyl-*N*-phenethylbenzenesulfonamide



$C_{19}H_{19}F_3N_4O_2S$
MW: 424.44 g.mol^{-1}
Colorless oil
91%

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66 – 7.59 (m, 2H), 7.35 – 7.22 (m, 5H), 7.16 – 7.11 (m, 2H), 5.22 (s, 1H), 3.32 (m, 4H), 2.79 (m, 2H), 2.44 (s, 3H) ppm.

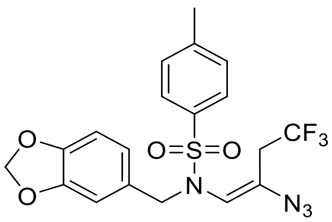
^{13}C NMR (126 MHz, $CDCl_3$): δ = 144.5, 138.0 (q, *J* = 3.1 Hz), 137.7, 133.5, 129.0, 128.7, 128.7, 127.6, 126.8, 124.4 (q, *J* = 275.7 Hz), 118.3, 52.8, 34.6, 33.5 (q, *J* = 30.7 Hz), 21.6 ppm.

^{19}F NMR (282 MHz, $CDCl_3$): δ = -62.75 ppm.

HRMS (ESI-TOF) m/z: $[M+K]^+$ calcd for $C_{19}H_{19}F_3KN_4O_2S$ 463.0812; Found 463.0815.

IR (neat): ν = 2928, 2109, 1341, 1270, 1162, 1091 cm^{-1}

Compound **2c** (*E*)-*N*-(2-azido-4,4,4-trifluorobut-1-en-1-yl)-*N*-(benzo[d][1,3]dioxol-5-ylmethyl)-4-methylbenzenesulfonamide



$C_{19}H_{17}F_3N_4O_4S$
MW: 454.42 g.mol-1
White solid
mp = 105 - 107 °C
85%

^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.67 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 6.74 – 6.60 (m, 3H), 5.94 (s, 2H), 5.18 (s, 1H), 4.11 (s, 2H), 3.12 (q, *J* = 10.2 Hz, 2H), 2.47 (s, 3H) ppm.

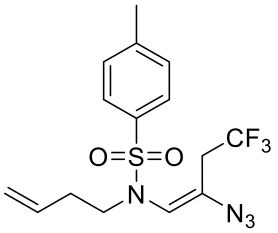
^{13}C NMR (126 MHz, CDCl$_3$): δ = 148.1, 147.8, 144.6, 138.5 (q, *J* = 3.0 Hz), 134.1, 130.1, 128.1, 127.8, 124.2 (q, *J* = 278.4 Hz), 122.9, 117.8, 109.5, 108.3, 101.3, 55.6, 33.5 (q, *J* = 31.5 Hz), 21.7 ppm.

^{19}F NMR (282 MHz, CDCl$_3$): δ = -62.86 ppm.

HRMS (ESI-TOF) m/z: [M+K]$^+$ calcd for $C_{19}H_{17}F_3KN_4O_4S$ 493.0554; Found 493.0565.

IR (neat): ν = 2920, 2115, 1655, 1246, 1167, 1127 cm^{-1}

Compound **2d** (*E*)-*N*-(2-azido-4,4,4-trifluorobut-1-en-1-yl)-*N*-(but-3-en-1-yl)-4-methylbenzenesulfonamide



$C_{15}H_{17}F_3N_4O_2S$
MW : 374.38 g.mol^{-1}
colorless oil
81%

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.62 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 5.70 (ddt, *J* = 17.0, 10.3, 6.6 Hz, 1H), 5.16 (s, 1H), 5.12 – 5.03 (m, 2H), 3.37 (qd, *J* = 10.3, 0.7 Hz, 2H), 3.01 (m, 2H), 2.45 (s, 3H), 2.22 (m, 2H) ppm.

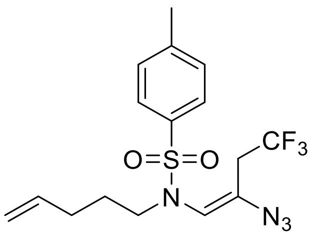
^{13}C NMR (126 MHz, CDCl$_3$): δ = 144.6, 138.1 (q, *J* = 3.1 Hz), 134.3, 133.7, 130.1, 127.8, 121.2 (q, *J* = 270.0 Hz), 118.4, 117.5, 50.9, 33.8 (q, *J* = 30.7 Hz), 32.2, 21.7 ppm.

^{19}F NMR (282 MHz, CDCl$_3$): δ = -62.74 ppm.

HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for $C_{15}H_{18}F_3N_4O_2S$ 375.1097; Found 375.1105.

IR (neat): ν = 2111, 1343, 1271, 1164 cm^{-1}

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



$C_{16}H_{19}F_3N_4O_2S$
MW : 388.41 g.mol^{-1}
colorless oil
81%

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.61 – 7.65 (m, 2H), 7.38– 7.32 (m, 2H), 5.74 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.14 (s, 1H), 5.05 – 4.96 (m, 2H), 3.39 (q, *J* = 10.2 Hz, 2H) 3.02 – 2.99 (m, 2H), 2.45 (s, 3H), 2.08 – 2.02 (m, 2H), 1.59 – 1.52 (m, 2H) ppm.

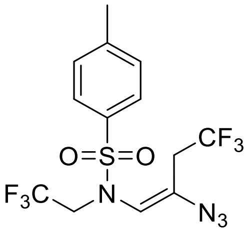
^{13}C NMR (126 MHz, CDCl$_3$): δ = 144.5, 137.8 (q, *J* = 3.08 Hz), 137.2, 133.7, 130.0, 127.7, 124.5 (q, *J* = 279.0 Hz), 118.7, 115.7, 51.1, 33.7 (q, *J* = 31.2 Hz), 30.9, 27.1, 21.7 ppm.

^{19}F NMR (282 MHz, CDCl$_3$): δ = -62.91 ppm.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for $C_{16}H_{19}F_3NaN_4O_2S$ 411.1073; Found 411.1078.

IR (neat): ν = 2928, 2861, 2110, 1271, 1163 cm^{-1}

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



$C_{13}H_{12}F_6N_4O_2S$
MW: 402.32 g.mol^{-1}
white solid
88%

^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.67 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 5.35 (s, 1H), 3.75 (q, *J* = 8.3 Hz, 2H), 3.32 (q, *J* = 10.2 Hz, 2H), 2.49 (s, 3H) ppm.

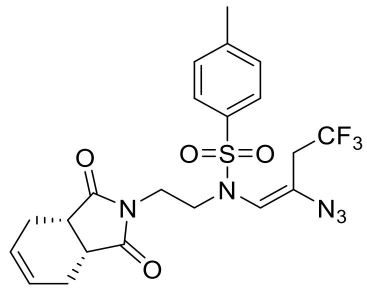
^{13}C NMR (125 MHz, CDCl$_3$): δ = 145.5 , 140.1 (q, *J* = 3.0 Hz), 133.7, 130.4, 127.8, 124.2 (q, *J* = 277.9 Hz) 123.6 (q, *J* = 280.4 Hz), 117.1, 51.9 (q, *J* = 34.1 Hz), 33.3 (q, *J* = 31.9 Hz), 21.8 ppm.

^{19}F NMR (282 MHz, CDCl$_3$): δ = -62.55 (q, *J* = 3.0 Hz), -69.39 (q, *J* = 3.0 Hz) ppm.

HRMS (ESI-TOF) m/z: [M+K]$^+$ calcd for $C_{13}H_{12}F_6KN_4O_2S$ 441.0217; Found 441.0226.

IR (neat): ν = 2933, 2117, 1270, 1166, 1089 cm^{-1}

Compound **2g** *N*-((*E*)-2-azido-4,4,4-trifluorobut-1-en-1-yl)-*N*-(2-((3a*R*,7a*S*)-1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2H-isoindol-2-yl)ethyl)-4-methylbenzenesulfonamide



$C_{21}H_{22}F_3N_5O_4S$
MW: 497.49 g.mol^{-1}
Colorless oil
63%

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.58 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 5.94 – 5.83 (m, 2H), 5.29 (s, 1H), 3.70 – 3.54 (m, 2H), 3.32 (q, *J* = 10.1 Hz, 2H), 3.23 – 3.13 (m, 4H), 2.60 (m, 2H), 2.44 (s, 3H), 2.31 – 2.21 (m, 2H) ppm.

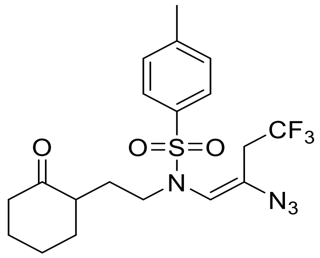
^{13}C NMR (126 MHz, CDCl$_3$): δ = 180.4, 144.8, 138.9 (q, *J* = 3.1 Hz), 133.8, 130.2, 127.9, 127.7, 124.6 (q, *J* = 278.3 Hz), 118.4, 49.1, 39.3, 37.2, 33.4 (q, *J* = 31.4 Hz), 23.5, 21.7 ppm.

^{19}F NMR (282 MHz, CDCl$_3$): δ = -62.56 ppm.

HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for $C_{21}H_{23}F_3N_5O_4S$ 498.1417; Found 498.1429.

IR (neat): ν = 2927, 2361, 2113, 1699, 1162, 906, 727 cm^{-1}

Compound **2h** (*E*)-*N*-(2-azido-4,4,4-trifluorobut-1-en-1-yl)-4-methyl-*N*-(2-(2-oxocyclohexyl)ethyl)benzenesulfonamide



$C_{19}H_{23}F_3N_4O_3S$
MW: 444.47 g.mol^{-1}
Colorless oil
74%

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.61 – 7.56 (m, 2H), 7.36 – 7.31 (m, 2H), 5.17 (s, 1H), 3.59 – 3.44 (m, 1H), 3.31 – 3.14 (m, 2H), 2.97 – 2.89 (m, 1H), 2.44 (s, 3H), 2.43 – 2.31 (m, 3H), 2.12 – 1.25 (m, 8H) ppm.

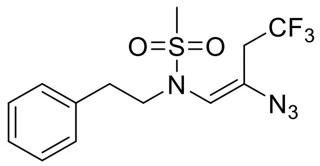
^{13}C NMR (126 MHz, CDCl$_3$): δ = 212.6, 144.6, 137.6 (q, *J* = 2.8 Hz), 133.6, 130.1, 127.7, 124.5 (q, *J* = 278.2 Hz), 118.9, 49.7, 47.7, 42.4, 34.6, 33.8 (q, *J* = 32.1 Hz), 28.3, 28.1, 25.4, 21.7 ppm.

^{19}F NMR (282 MHz, CDCl$_3$): δ = -62.88 ppm.

HRMS (ESI-TOF) m/z: [M+K]$^+$ calcd for $C_{19}H_{23}F_3KN_4O_3S$ 483.1075; Found 483.1092.

IR (neat): ν = 2935, 2864, 2112, 1710, 1342, 1272, 1164 cm^{-1}

Compound **2i** (*E*)-*N*-(2-azido-4,4,4-trifluorobut-1-en-1-yl)-*N*-phenethylmethanesulfonamide



$C_{13}H_{15}F_3N_4O_2S$
MW: 348.34 g.mol^{-1}
Colorless oil
73%

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.26 – 7.12 (m, 5H), 5.57 (s, 1H), 3.45 (m, 2H), 3.19 (q, *J* = 10.2, 2H), 2.82 (m, 2H), 2.70 (s, 3H) ppm.

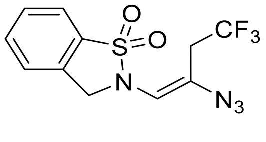
^{13}C NMR (126 MHz, CDCl$_3$): δ = 138.6 (q, *J* = 3.0 Hz), 137.7, 128.9, 128.9, 127.1, 124.4 (q, *J* = 277.6 Hz), 117.5, 53.2, 36.3, 34.9, 33.6 (q, *J* = 31.4 Hz) ppm.

^{19}F NMR (282 MHz, CDCl$_3$): δ = -62.76 ppm.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for $C_{13}H_{15}F_3N_4NaO_2S$ 371.0760; Found 371.0750.

IR (neat): ν = 3028, 2112, 1336, 1270, 1150 cm^{-1}

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



$C_{11}H_9F_3N_4O_2S$
MW: 318.27 g.mol^{-1}
White solid
81%

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.83 (ddd, *J* = 7.7, 1.2, 0.6 Hz, 1H), 7.67 (td, *J* = 7.5, 1.2 Hz, 1H), 7.62 – 7.54 (m, 1H), 7.43 (dt, *J* = 7.7, 1.0 Hz, 1H), 5.93 (s, 1H), 4.46 (s, 2H), 3.34 (q, *J* = 10.2 Hz, 2H) ppm.

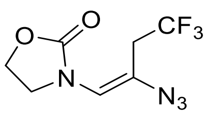
^{13}C NMR (126 MHz, CDCl$_3$): δ = 139.3 (q, *J* = 2.9 Hz), 134.2, 133.5, 133.3, 129.7, 124.8, 124.5 (q, *J* = 277.9 Hz), 122.0, 114.4, 53.1, 33.4 (q, *J* = 31.4 Hz) ppm.

^{19}F NMR (282 MHz, CDCl$_3$): δ = -64.15 ppm.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for $C_{11}H_9F_3N_4NaO_2S$ 341.0291; Found 341.0290.

IR (neat): ν = 3267, 2114, 2114, 1654, 1251, 1156, 756 cm^{-1}

Compound **2k** (*E*)-3-(2-azido-4,4,4-trifluorobut-1-en-1-yl)oxazolidin-2-one



$C_7H_7F_3N_4O_2$
MW: 236.15 g.mol^{-1}
Colorless oil
45%

^{1}H NMR (500 MHz, C$_6$D$_6$): δ = 4.86 (qt, *J* = 8.0, 0.7 Hz, 1H), 3.61 (dt, *J* = 1.9, 0.9 Hz, 2H), 3.31 – 3.23 (m, 2H), 2.30 – 2.23 (m, 2H) ppm.

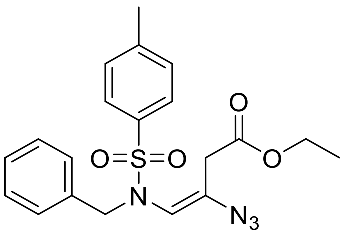
^{13}C NMR (126 MHz, C$_6$D$_6$): δ = 157.5, 147.9 (q, *J* = 5.3 Hz), 123.7 (q, *J* = 269.3 Hz), 105.7 (q, *J* = 36.4 Hz), 61.2, 43.4, 42.4 (q, *J* = 2.1 Hz) ppm.

^{19}F NMR (471 MHz, C$_6$D$_6$): δ = -53.94 ppm.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for $C_7H_7F_3N_4NaO_2$ 259.0413; Found 259.0410.

IR (neat): ν = 2992, 2110, 1712 cm^{-1}

Compound **2l** ethyl (*E*)-3-azido-4-((*N*-benzyl-4-methylphenyl)sulfonamido)but-3-enoate



$C_{20}H_{22}N_4O_4S$
MW: 414.48 g.mol-1
White solid
mp = 76 - 78 °C
65% over 2 steps

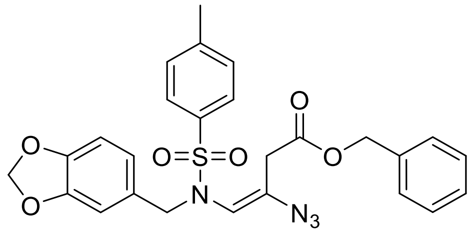
^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.69 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 7.32 – 7.27 (m, 3H), 7.25 – 7.22 (m, 2H), 5.05 (s, 1H), 4.06 (q, *J* = 7.2 Hz, 2H), 3.31 (s, 2H), 2.46 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ = 168.2, 144.3, 140.8, 135.2, 134.3, 130.0, 129.1, 128.7, 128.1, 127.8, 115.6, 61.3, 55.6, 34.0, 21.7, 14.2 ppm.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for $C_{20}H_{22}N_4NaO_4S$ 437.1254; Found 437.1283.

IR (neat): ν = 2982, 2360, 2109, 1737, 1348, 1164, 740 cm^{-1}

Compound **2m** benzyl (*E*)-3-azido-4-((*N*-(benzo[d][1,3]dioxol-5-ylmethyl)-4-methylphenyl)sulfonamido)but-3-enoate



$C_{26}H_{24}N_4O_6S$
MW: 520.56 g.mol^{-1}
White solid
61% over 2 steps

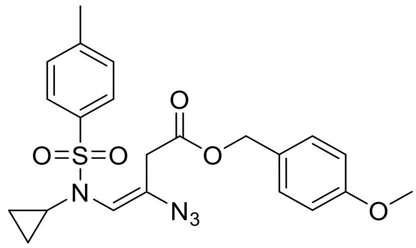
^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.66 (d, *J* = 8.4 Hz, 2H), 7.41 – 7.29 (m, 7H), 6.77 – 6.71 (m, 1H), 6.69 – 6.59 (m, 2H), 5.90 (s, 2H), 5.09 (s, 2H), 5.04 (s, 1H), 4.09 (s, 2H), 3.40 (s, 2H), 2.45 (s, 3H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ = 168.1, 147.9, 147.4, 144.2, 140.5, 135.4, 134.1, 129.9, 128.8, 128.6, 128.4, 128.3, 127.7, 122.5, 115.5, 109.2, 108.2, 101.2, 67.0, 55.3, 33.9, 21.7 ppm.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for $C_{26}H_{24}N_4NaS$ 543.1308; Found 543.1315.

IR (neat): ν = 3033, 2897, 2108, 1737, 1489, 1445, 1243, 1160, 1036, 730 cm^{-1}

Compound **2n** 4-methoxybenzyl (*E*)-3-azido-4-((*N*-cyclopropyl-4-methylphenyl)sulfonamido)but-3-enoate



$C_{22}H_{24}N_4O_5S$
MW: 456.52 g.mol^{-1}
Colorless oil
36% over 2 steps

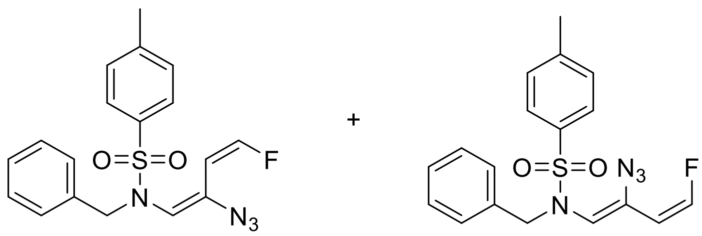
^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.68 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.29 (m, 6H), 6.89 (d, *J* = 8.7 Hz, 2H), 5.20 (s, 1H), 5.11 (s, 2H), 3.81 (s, 3H), 3.47 (s, 2H), 2.44 (s, 3H), 2.02 (tt, *J* = 6.8, 3.5 Hz, 1H), 0.82 – 0.74 (m, 2H), 0.74 – 0.53 (m, 2H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ = 168.8, 159.9, 144.4, 138.7, 133.3, 130.4, 129.9, 128.2, 127.6, 117.2, 114.1, 67.2, 55.5, 34.4, 32.5, 21.7, 7.2, 6.3 ppm.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for $C_{22}H_{24}N_4NaO_5S$ 479.1360; Found 479.1354.

IR (neat): ν = 3275, 2925, 2110, 1737, 1516, 1164, 816 cm^{-1}

Compound **2o** *N*-((1E)-2-azido-4-fluorobuta-1,3-dien-1-yl)-*N*-benzyl-4-methylbenzenesulfonamide



$C_{18}H_{17}FN_4O_2S$
MW: 374.42 g.mol^{-1}
White solid
80%, **6:4 *dr***

Only one diastereoisomer was described for ^{13}C-NMR.

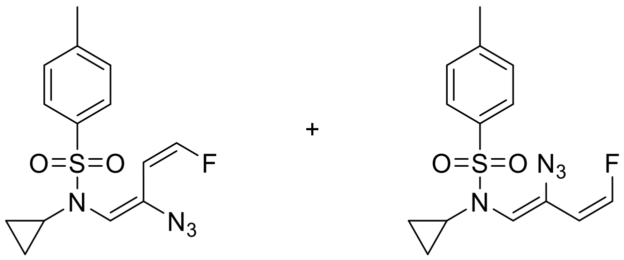
^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.77 – 7.67 (m, 4H), 7.39 – 7.27 (m, 11H), 7.25 – 7.22 (m, 3H), 6.88 (ddd, *J* = 58.8, 11.0, 0.5 Hz, 1H), 6.87 (ddd, *J* = 82.0, 10.9, 0.5 Hz, 1H), 6.07 (ddd, *J* = 17.6, 11.0, 0.7 Hz, 1H), 5.62 (ddd, *J* = 16.6, 10.8, 0.6 Hz, 1H), 5.12 – 5.10 (m, 2H), 5.06 – 5.06 (m, 2H), 4.30 (s, 2H), 4.25 (s, 2H), 2.47 (s, 6H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ = 154.2 (d, *J* = 268.0 Hz), 144.4, 140.6, 135.0, 134.4, 130.1, 129.1, 128.8, 128.3, 127.8, 113.6 (d, *J* = 10.8 Hz), 106.2 (d, *J* = 21.9 Hz), 55.7, 21.7 ppm.

^{19}F NMR (471 MHz, CDCl$_3$): δ = -122.76, -124.58 ppm.

IR (neat): ν = 3032, 2926, 1018, 1663, 1349, 1164, 1092 cm^{-1}

Compound **2p** *N*-((3*Z*)-2-azido-4-fluorobuta-1,3-dien-1-yl)-*N*-cyclopropyl-4-methylbenzenesulfonamide



$C_{14}H_{15}FN_4O_2S$
MW: 322.36 g.mol^{-1}
Colorless oil
82%, **8:2 *dr***

Only one diastereoisomer was described for ^{13}C-NMR.

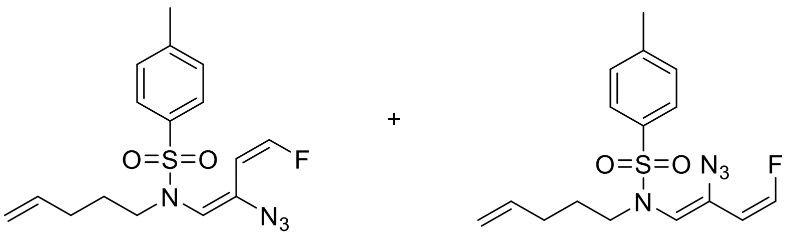
^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.77 – 7.66 (m, 4H), 7.39 – 7.30 (m, 4H), 7.05 (ddd, *J* = 82.0, 11.1, 0.3 Hz, 1H), 7.04 (ddd, *J* = 81.8, 10.6, 0.7 Hz, 1H), 6.22 (ddd, *J* = 17.6, 11.0, 0.7 Hz, 1H), 5.72 (ddd, *J* = 17.3, 10.8, 0.4 Hz, 1H), 5.25 (dt, *J* = 1.5, 0.7 Hz, 2H), 5.21 – 5.20 (m, 2H), 2.45 (s, 6H), 2.16 (tt, *J* = 6.8, 3.4 Hz, 1H), 2.10 (tt, *J* = 6.8, 3.5 Hz, 1H), 0.89 (m, 8H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ = 154.2 (d, *J* = 267.7 Hz), 144.4, 138.6, 133.5, 129.9, 128.1, 115.1 (d, *J* = 11.1 Hz), 106.2 (d, *J* = 21.6 Hz), 32.7, 21.7, 7.4 ppm.

^{19}F NMR (471 MHz, CDCl$_3$): δ = -122.91, -125.12 ppm.

IR (neat): ν = 2934, 2117, 1648, 1358, 1170, 1132 cm^{-1}

Compound **2q** *N*-((3*Z*)-2-azido-4-fluorobuta-1,3-dien-1-yl)-4-methyl-*N*-(pent-4-en-1-yl)benzenesulfonamide



$C_{16}H_{19}FN_4O_2S$
MW: 350.41 g.mol^{-1}
Colorless oil
75%, **8:2 *dr***

Only one diastereoisomer was described for ^{13}C-NMR.

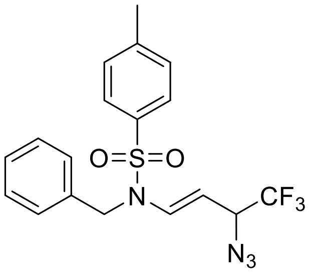
^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.72 – 7.59 (m, 4H), 7.38 – 7.31 (m, 4H), 7.08 (ddd, *J* = 81.8, 10.9, 0.5 Hz, 1H), 7.06 (ddd, *J* = 82.0, 10.8, 0.5 Hz, 1H), 6.37 (ddd, *J* = 17.5, 11.0, 0.6 Hz, 1H), 5.82 – 5.68 (m, 3H), 5.10 – 4.97 (m, 6H), 3.14 – 3.03 (m, 4H), 2.44 (s, 6H), 2.08 (m, 4H), 1.69 – 1.52 (m, 4H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ = 154.5 (d, *J* = 268.1 Hz), 144.2, 140.3 (d, *J* = 11.9 Hz), 137.3, 134.2, 130.0, 127.7, 115.8, 114.0 (d, *J* = 11.1 Hz), 106.5 (d, *J* = 21.8 Hz), 51.0, 30.9, 27.6, 21.7 ppm.

^{19}F NMR (471 MHz, CDCl$_3$): δ = -122.37, -124.94 ppm.

IR (neat): ν = 3099, 2926, 2110, 1349, 1164, 1109 cm^{-1}

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



$C_{18}H_{17}F_3N_4O_2S$
MW: 410.42 g.mol^{-1}
Colorless oil
91%

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.69 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.31 – 7.19 (m, 6H), 4.63 – 4.49 (m, 3H), 4.28 – 4.13 (m, 1H), 2.45 (s, 3H) ppm.

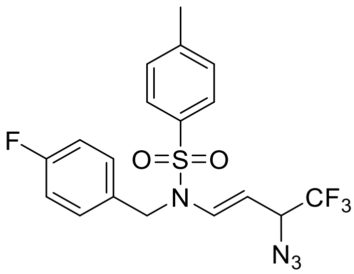
^{13}C NMR (126 MHz, CDCl$_3$): δ = 144.8, 135.5, 134.9, 133.9, 130.3, 128.9, 128.0, 127.2, 126.9, 123.5 (q, *J* = 280.9 Hz), 98.0 (q, *J* = 1.9 Hz), 62.7 (q, *J* = 32.0 Hz), 49.6, 21.8 ppm.

^{19}F NMR (282 MHz, CDCl$_3$): δ = -75.85 ppm.

HRMS (ESI-TOF) m/z: $[M+K]^+$ calcd for $C_{18}H_{17}F_3KN_4O_2S$ 449.0656; Found 449.0649.

IR (neat): ν = 2113, 1655, 1262, 1167, 1126 cm^{-1}

Compound **3b** (*E*)-*N*-(3-azido-4,4,4-trifluorobut-1-en-1-yl)-*N*-(4-fluorobenzyl)-4-methylbenzenesulfonamide



$C_{18}H_{16}F_4N_4O_2S$
MW: 428.41 g.mol^{-1}
Colorless oil
94%

^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.68 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.24 (d, *J* = 14.5 Hz, 1H), 7.22 – 7.18 (m, 2H), 7.03 – 6.95 (m, 2H), 4.58 – 4.45 (m, 3H), 4.25 – 4.15 (m, 1H), 2.45 (s, 3H) ppm.

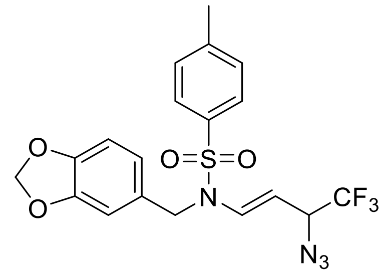
^{13}C NMR (126 MHz, CDCl$_3$): δ = 162.5 (d, *J* = 246.6 Hz), 145.0, 135.4, 134.8, 130.3, 129.7 (d, *J* = 3.1 Hz), 128.7 (d, *J* = 8.2 Hz), 127.1, 123.5 (q, *J* = 280.8 Hz), 115.9 (d, *J* = 21.8 Hz), 98.1 (q, *J* = 2.2 Hz), 62.7 (q, *J* = 32.0 Hz), 48.9, 21.7 ppm.

^{19}F NMR (282 MHz, CDCl$_3$): δ = -75.84, -114.31 ppm.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{16}F_4N_4NaO_2S$ 451.0828; Found 451.0831.

IR (neat): ν = 2112, 1654, 1510, 1165, 1123, 1035, 812 cm^{-1}

Compound **3c** (*E*)-*N*-(3-azido-4,4,4-trifluorobut-1-en-1-yl)-*N*-(benzo[d][1,3]dioxol-5-ylmethyl)-4-methylbenzenesulfonamide



$C_{19}H_{17}F_3N_4O_4S$
MW: 454.42 g.mol^{-1}
Colorless oil
95%

^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.61 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 14.1 Hz, 1H), 6.72 – 6.54 (m, 3H), 5.86 (q, *J* = 1.4 Hz, 2H), 4.52 (dd, *J* = 14.1, 8.9 Hz, 1H), 4.43 (d, *J* = 15.9 Hz, 1H), 4.28 (d, *J* = 15.9 H, 1H), 4.13 (dq, *J* = 8.4, 6.5 Hz, 1H), 2.38 (s, 2H) ppm.

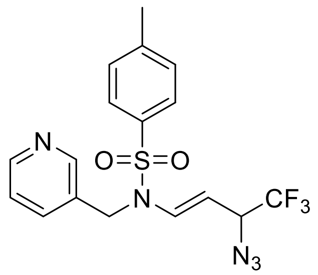
^{13}C NMR (126 MHz, CDCl$_3$): δ = 148.3, 147.3, 144.7, 135.3, 134.7, 130.1, 127.6, 127.0, 123.4 (q, *J* = 280.9 Hz), 120.4, 108.3, 107.3, 101.2, 97.9 (q, *J* = 1.8 Hz), 62.6 (q, *J* = 32.0 Hz), 49.3, 21.6 ppm.

^{19}F NMR (282 MHz, CDCl$_3$): δ = -75.79 ppm.

HRMS (ESI-TOF) m/z: [M+K]$^+$ calcd for $C_{19}H_{17}F_3KN_4O_4S$ 493.0554; Found 493.0565.

IR (neat): ν = 2361, 2114, 1655, 1491, 1245, 1167, 1126, 1038 cm^{-1}

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



$C_{17}H_{16}F_3N_5O_2S$
MW: 411.40 g.mol^{-1}
Colorless oil
83%

^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.52 (d, *J* = 21.8 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.64 (dt, *J* = 8.1, 1.9 Hz, 1H), 7.35 (dt, *J* = 8.0, 0.7 Hz, 2H), 7.31 – 7.24 (m, 3H), 4.63 – 4.53 (m, 2H), 4.52 (dd, *J* = 14.1, 8.7 Hz, 1H), 4.29 – 4.17 (m, 1H), 2.45 (s, 3H) ppm.

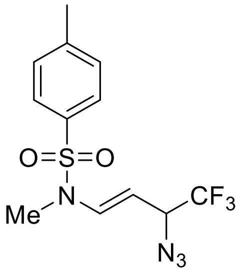
^{13}C NMR (126 MHz, CDCl$_3$): δ = 149.2, 148.2, 145.2, 135.1, 135.0, 134.5, 130.4, 130.1, 127.2, 124.0, 123.5 (d, *J* = 281.0 Hz), 98.2 (q, *J* = 1.8 Hz), 62.5 (q, *J* = 32.1 Hz), 47.0, 21.8 ppm.

^{19}F NMR (471 MHz, CDCl$_3$): δ = -75.78 ppm.

HRMS (ESI-TOF) m/z: [M+K]$^+$ calcd for $C_{19}H_{17}F_3KN_4O_4S$ 412.1055; Found 412.1060.

IR (neat): ν = 2958, 2112, 1658, 1129 cm^{-1}

Compound **3e** (*E*)-*N*-(3-azido-4,4,4-trifluorobut-1-en-1-yl)-*N*,4-dimethylbenzenesulfonamide



$C_{12}H_{13}F_3N_4O_2S$
MW: 334.32 g.mol^{-1}
Colorless oil
89%

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.64 (d, *J* = 8.4 Hz, 2H), 7.36 – 7.26 (m, 3H), 4.61 (dd, *J* = 13.9, 8.9 Hz, 1H), 4.40 – 4.24 (m, 1H), 2.91 (s, 3H), 2.44 (s, 3H) ppm.

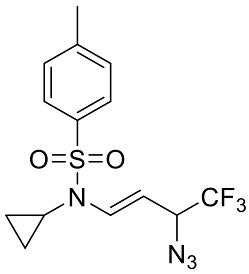
^{13}C NMR (126 MHz, CDCl$_3$): δ = 144.8, 136.8, 134.3, 130.2, 127.1, 123.7 (q, *J* = 280.4 Hz), 96.4 (q, *J* = 1.9 Hz), 62.8 (q, *J* = 32.1 Hz), 32.1, 21.7 ppm.

^{19}F NMR (282 MHz, CDCl$_3$): δ = -75.65 ppm.

HRMS (ESI-TOF) m/z: [M+K]$^+$ calcd for $C_{12}H_{13}F_3KN_4O_2S$ 373.0348; Found 373.0341.

IR (neat): ν = 2113, 1652, 1161, 1126 cm^{-1}

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



$C_{14}H_{15}F_3N_4O_2S$
MW: 360.36 g.mol^{-1}
Colorless oil
86%

^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.69 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 14.0 Hz, 1H), 5.06 (dd, *J* = 14.0, 9.1 Hz, 1H), 4.37 – 4.26 (m, 1H), 2.44 (s, 3H), 1.81 (tt, *J* = 6.9, 3.7 Hz, 1H), 1.10 – 0.95 (m, 2H), 0.95 – 0.82 (m, 2H) ppm.

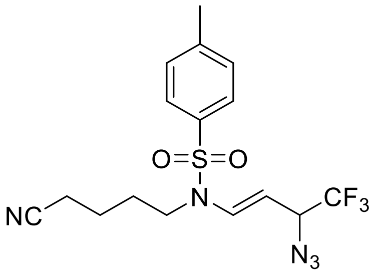
^{13}C NMR (126 MHz, CDCl$_3$): δ = 144.8, 137.9, 134.0, 130.0, 127.6, 123.7 (q, *J* = 280.6 Hz), 99.4 (d, *J* = 2.2 Hz), 62.8 (q, *J* = 32.0 Hz), 27.0, 21.7, 8.1, 8.1 ppm.

^{19}F NMR (282 MHz, CDCl$_3$): δ = -75.70 ppm.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for $C_{14}H_{15}F_3N_4NaO_2S$ 383.0766; Found 383.0772.

IR (neat): ν = 2114, 1651, 1366, 1171, 1131 cm^{-1}

Compound **3g** (*E*)-*N*-(3-azido-4,4,4-trifluorobut-1-en-1-yl)-*N*-(4-cyanobutyl)-4-methylbenzenesulfonamide



$C_{16}H_{18}F_3N_5O_2S$
MW: 401.41 g.mol^{-1}
Colorless oil
65%

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.64 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.6, Hz, 2H), 7.18 (d, *J* = 14.2, 1H), 4.67 (dd, *J* = 14.2, 8.8 Hz, 1H), 4.39 – 4.27 (m, 1H), 3.43 – 3.34 (m, 2H), 2.44 (s, 3H), 2.42 – 2.38 (m, 2H), 1.82 – 1.65 (m, 4H) ppm.

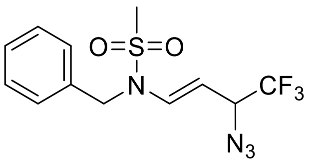
^{13}C NMR (126 MHz, CDCl$_3$): δ = 145.0, 135.1, 135.0, 130.3, 127.0, 123.6 (q, *J* = 280.8 Hz), 119.2, 96.9 (q, *J* = 1.9 Hz), 62.9 (q, *J* = 32.0 Hz), 44.4, 25.3, 22.5, 21.7, 16.8 ppm.

HRMS (ESI-TOF) m/z: [M+K]$^+$ calcd for $C_{16}H_{18}F_3KN_5O_2S$ 440.0770; Found 440.0779.

^{19}F NMR (471 MHz, CDCl$_3$): δ = -75.61 ppm.

IR (neat): ν = 2935, 2115, 1652, 1164, 1126 cm^{-1}

Compound **3h** (*E*)-*N*-(3-azido-4,4,4-trifluorobut-1-en-1-yl)-*N*-benzylmethanesulfonamide



$C_{12}H_{13}F_3N_4O_2S$
MW: 334.07 g.mol^{-1}
Colorless oil
89%

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.43 – 7.23 (m, 5H), 7.11 (dd, *J* = 14.1, 0.7 Hz, 1H), 4.88 – 4.65 (m, 3H), 4.22 (dqd, *J* = 8.8, 6.5, 0.7 Hz, 1H), 2.96 (s, 3H) ppm.

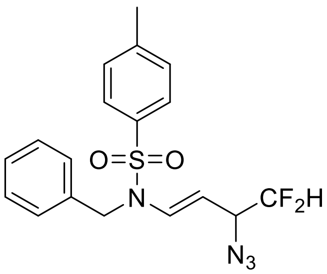
^{13}C NMR (126 MHz, CDCl$_3$): δ = 134.6, 134.0, 129.1, 128.2, 127.0, 123.6 (q, *J* = 280.9 Hz), 97.7 (q, *J* = 1.9 Hz), 62.7 (q, *J* = 32.1 Hz), 49.5, 40.5 ppm.

^{19}F NMR (282 MHz, CDCl$_3$): δ = -75.76 ppm.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for $C_{12}H_{13}F_3N_4NaO_2S$ 357.0609; Found 357.0615.

IR (neat): ν = 2114, 1657, 1342, 1262, 1159, 1124 cm^{-1}

Compound **3i** (*E*)-*N*-(3-azido-4,4-difluorobut-1-en-1-yl)-*N*-benzyl-4-methylbenzenesulfonamide



$C_{18}H_{18}F_2N_4O_2S$
MW: 392.42 g.mol^{-1}
Colorless oil
92%

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.69 (d, *J* = 8.4 Hz, 2H), 7.38 – 7.17 (m, 8H), 5.72 – 5.23 (m, 1H), 4.65 – 4.47 (m, 3H), 4.11 – 3.93 (m, 1H), 2.44 (s, 3H) ppm.

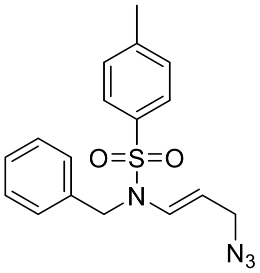
^{13}C NMR (126 MHz, CDCl$_3$): δ = 144.7, 135.6, 134.2, 133.9, 130.2, 127.9, 127.2, 126.9, 114.2 (t, *J* = 246.4 Hz), 99.3 (t, *J* = 4.3 Hz), 63.3 (t, *J* = 24.4 Hz), 49.6, 21.7 ppm.

^{19}F NMR (282 MHz, CDCl$_3$): δ = -124.53 (d, *J* = 282.8 Hz), -126.69 (d, *J* = 282.8 Hz) ppm.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for $C_{18}H_{18}F_2N_4NaO_2S$ 415.1011; Found 415.1008.

IR (neat): ν = 2110, 1654, 1363, 1166, 1069 cm^{-1}

Compound **3j** (*E*)-*N*-(3-azidoprop-1-en-1-yl)-*N*-benzyl-4-methylbenzenesulfonamide



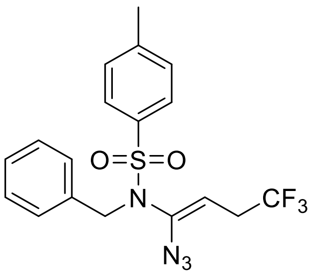
$C_{17}H_{18}N_4O_2S$
MW: 342.42 g.mol^{-1}
Colorless oil
90%

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.70 (d, *J* = 8.4 Hz, 2H), 7.35 – 7.20 (m, 7H), 7.03 (d, *J* = 14.1 Hz, 1H), 4.70 (dt, *J* = 14.3, 7.3 Hz, 1H), 4.52 (s, 2H), 3.66 – 3.60 (m, 2H), 2.43 (s, 3H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ = 144.4, 135.8, 134.8, 131.7, 130.1, 128.8, 127.8, 126.9, 103.7, 51.4, 49.6, 21.7 ppm.

Data match with those described in the literature[11]

Compound **4a** (*E*)-*N*-(1-azido-4,4,4-trifluorobut-1-en-1-yl)-*N*-benzyl-4-methylbenzenesulfonamide



$C_{18}H_{17}F_3N_4O_2S$
MW: 410.42 g.mol-1
White solid
mp = 49 - 51 °C
78%

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.76 (d, *J* = 8.3 Hz, 2H), 7.42 – 7.25 (m, 7H), 4.40 (s, 2H), 4.19 (t, *J* = 7.4 Hz, 1H), 2.75 (qd, *J* = 10.6, 7.4 Hz, 2H), 2.48 (s, 3H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ = 145.0, 137.7, 134.2, 133.6, 129.9, 129.4, 128.9, 128.9, 128.4, 125.5 (q, *J* = 277.0 Hz), 105.4 (q, *J* = 3.7 Hz), 55.9, 31.7 (q, *J* = 30.9 Hz), 21.8 ppm.

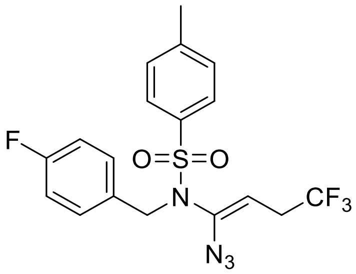
^{19}F NMR (282 MHz, CDCl$_3$): δ = -65.78 ppm.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for $C_{18}H_{17}F_3N_4NaO_2S$ 433.0917; Found 433.0935.

IR (neat): ν = 2130, 1660, 1370, 1170, 1082 cm^{-1}

[11] Y. Liu, N. Ding, X. Tan, X. Li, Z. Zhao, *Chem. Commun.* 2020, **56**, 7507–7510.

Compound **4b** (*E*)-*N*-(1-azido-4,4,4-trifluorobut-1-en-1-yl)-*N*-(4-fluorobenzyl)-4-methylbenzenesulfonamide



$C_{18}H_{16}F_4N_4O_2S$
MW: 428.41 g.mol^{-1}
White solid
68%

^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.75 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.29 – 7.21 (m, 2H), 7.08 – 6.99 (m, 2H), 4.38 (s, 2H), 4.19 (t, *J* = 7.4 Hz, 1H), 2.77 (qd, *J* = 10.6, 7.4 Hz, 2H), 2.48 (s, 3H) ppm.

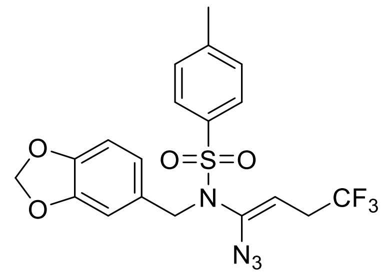
^{13}C NMR (126 MHz, CDCl$_3$) δ = 163.1 (d, *J* = 248.0 Hz), 145.1, 137.7, 133.6, 131.2 (d, *J* = 8.4 Hz), 130.1 (d, *J* = 3.3 Hz), 130.0, 128.4, 125.4 (q, *J* = 277.1 Hz), 116.0 (d, *J* = 21.7 Hz), 105.6 (q, *J* = 3.4 Hz), 55.2, 31.7 (q, *J* = 30.7 Hz), 21.8 ppm.

^{19}F NMR (282 MHz, CDCl$_3$): δ = -65.78, -112.83 ppm.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for $C_{18}H_{16}F_4N_4NaO_2S$ 451.0828; Found 451.0841.

IR (neat): ν = 2360, 2131, 1510, 1358, 1251, 1065 cm^{-1}

Compound **4c** (*E*)-*N*-(1-azido-4,4,4-trifluorobut-1-en-1-yl)-*N*-(benzo[d][1,3]dioxol-5-ylmethyl)-4-methylbenzenesulfonamide



$C_{19}H_{17}F_3N_4O_4S$
MW: 454.42 g.mol^{-1}
White solid
81%

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.74 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 6.83 – 6.62 (m, 3H), 5.97 (s, 2H), 4.31 (s, 2H), 4.18 (t, *J* = 7.4 Hz, 1H), 2.78 (qd, *J* = 10.6, 7.4 Hz, 2H), 2.47 (s, 3H) ppm.

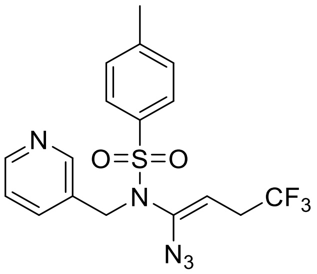
^{13}C NMR (126 MHz, CDCl$_3$): δ = 148.2, 148.1, 144.9, 137.7, 133.7, 129.9, 128.4, 127.8, 125.5 (q, *J* = 277.0 Hz), 123.2, 109.6, 108.5, 105.5 (q, *J* = 3.6 Hz), 101.4, 55.8, 31.7 (q, *J* = 30.9 Hz), 21.8 ppm.

^{19}F NMR (282 MHz, CDCl$_3$): δ = -65.76 ppm.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for $C_{19}H_{17}F_3N_4NaO_4S$ 477.0815; Found 477.0801.

IR (neat): ν = 2907, 2132, 1661, 1348, 1244, 1036 cm^{-1}

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



$C_{17}H_{16}F_3N_5O_2S$
MW: 411.40 g.mol^{-1}
Colorless oil
62%

^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.61 (d, *J* = 3.9 Hz, 1H), 8.42 (s, 1H), 7.80 – 7.70 (m, 3H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.36 – 7.32 (m, 1H), 4.43 (s, 2H), 4.23 (t, *J* = 7.4 Hz, 1H), 2.77 (qd, *J* = 10.6, 7.4 Hz, 2H), 2.48 (s, 3H) ppm.

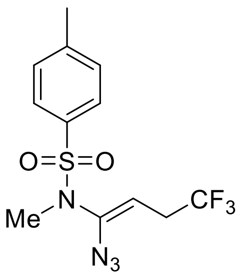
^{13}C NMR (126 MHz, CDCl$_3$): δ = 150.2, 150.0, 145.2, 137.4, 137.0, 133.1, 130.1, 129.9, 128.3, 125.2 (q, *J* = 277.1 Hz), 123.9, 105.9 (q, *J* = 3.7 Hz), 53.1, 31.6 (q, *J* = 31.0 Hz), 21.7 ppm.

^{19}F NMR (471 MHz, CDCl$_3$): δ = -65.76 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{17}F_3N_5O_2S$ 412.1050; Found 412.1043.

IR (neat): ν = 2127, 1660, 1595, 1428, 1249, 1163, 1055 cm^{-1}

Compound **4e** (*E*)-*N*-(1-azido-4,4,4-trifluorobut-1-en-1-yl)-*N*,4-dimethylbenzenesulfonamide



$C_{12}H_{13}F_3N_4O_2S$
MW: 334.32 g.mol^{-1}
Colorless oil
61%

^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.70 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 4.10 (t, *J* = 7.4 Hz, 1H), 3.02 (s, 3H), 2.84 (qd, *J* = 10.6, 7.4 Hz, 2H), 2.46 (s, 3H) ppm.

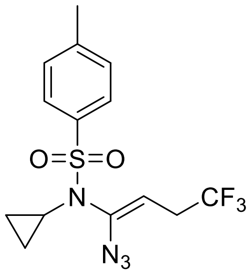
^{13}C NMR (126 MHz, CDCl$_3$): δ = 145.0, 140.0, 131.9, 129.8, 128.7, 125.5 (q, *J* = 276.8 Hz), 103.3 (q, *J* = 3.8 Hz), 39.4, 31.7 (q, *J* = 31.0 Hz), 21.8 ppm.

^{19}F NMR (471 MHz, CDCl$_3$): δ = -65.87 ppm.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd $C_{12}H_{13}F_3N_4NaO_2S$ 357.0603; Found 357.0602.

IR (neat): ν = 2981, 2122, 1660, 1356, 1250, 1138, 1062 cm^{-1}

Compound **4f** (*E*)-*N*-(1-azido-4,4,4-trifluorobut-1-en-1-yl)-*N*-cyclopropyl-4-methylbenzenesulfonamide



$C_{14}H_{15}F_3N_4O_2S$
MW: 360.36 g.mol^{-1}
Colorless oil
67%

^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.77 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.24 (t, *J* = 7.4 Hz, 1H), 2.87 (qd, *J* = 10.6, 7.4 Hz, 2H), 2.46 (s, 3H), 2.46 – 2.39 (m, 1H), 0.90 – 0.77 (m, 4H) ppm.

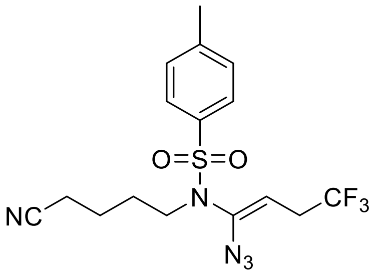
^{13}C NMR (126 MHz, CDCl$_3$): δ = 145.0, 139.5, 133.0, 129.8, 128.8, 125.6 (d, *J* = 276.9 Hz), 104.2 (q, *J* = 3.7 Hz), 32.6, 31.8 (q, *J* = 30.9 Hz), 21.8, 8.1 ppm.

^{19}F NMR (471 MHz, CDCl$_3$): δ = -65.95 ppm.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd $C_{14}H_{15}F_3N_4NaO_2S$ 383.0760; Found 383.0765.

IR (neat): ν = 2123, 1662, 1363, 1250, 1139, 1064 cm^{-1}

Compound **4g** (*E*)-*N*-(1-azido-4,4,4-trifluorobut-1-en-1-yl)-*N*-(4-cyanobutyl)-4-methylbenzenesulfonamide



$C_{16}H_{18}F_3N_5O_2S$
MW: 401.41 g.mol^{-1}
Colorless oil
59%

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.69 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.19 (t, *J* = 7.4 Hz, 1H), 3.35 (td, *J* = 5.8, 1.1 Hz, 2H), 2.88 (qd, *J* = 10.6, 7.4 Hz, 2H), 2.46 (s, 3H), 2.45 – 2.41 (m, 2H), 1.76 (dq, *J* = 4.1, 2.8 Hz, 4H) ppm.

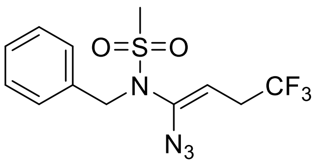
^{13}C NMR (126 MHz, CDCl$_3$): δ = 145.1, 138.0, 133.1, 129.9, 128.4, 125.4 (q, *J* = 277.0 Hz), 119.1, 105.5 (q, *J* = 3.4 Hz), 50.9, 31.9 (q, *J* = 31.0 Hz), 27.2, 22.3, 21.8, 16.8 ppm.

^{19}F NMR (471 MHz, CDCl$_3$): δ = -65.74 ppm.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd $C_{16}H_{18}F_3N_5NaO_2S$ 424.1025; Found 424.1018.

IR (neat): ν = 2941, 2126, 1660, 1353, 1249, 1135, 1060 cm^{-1}

Compound **4h** (*E*)-*N*-(1-azido-4,4,4-trifluorobut-1-en-1-yl)-*N*-benzylmethanesulfonamide



$C_{12}H_{13}F_3N_4O_2S$
MW: 334.07 g.mol^{-1}
Colorless oil
80%

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.47 – 7.28 (m, 5H), 4.82 (t, *J* = 7.3 Hz, 1H), 4.59 (s, 2H), 3.01 (s, 3H), 2.89 (qd, *J* = 10.6, 7.3 Hz, 2H) ppm.

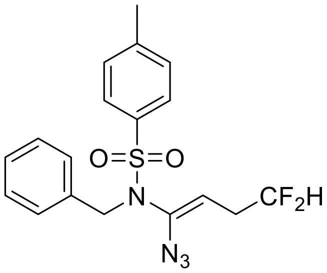
^{13}C NMR (126 MHz, CDCl$_3$): δ = 137.7, 134.2, 129.5, 129.1, 129.1, 125.5 (q, *J* = 276.9 Hz), 106.1 (q, *J* = 3.7 Hz), 55.5, 38.2, 32.0 (q, *J* = 31.0 Hz) ppm.

^{19}F NMR (282 MHz, CDCl$_3$): δ = -65.87 ppm.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd $C_{12}H_{13}F_3N_4NaO_2S$ 357.0604; Found 357.0610.

IR (neat): ν = 2133, 1662, 1349, 1251, 1143, 1065 cm^{-1}

Compound **4i** (*E*)-*N*-(1-azido-4,4-difluorobut-1-en-1-yl)-*N*-benzyl-4-methylbenzenesulfonamide



$C_{18}H_{18}F_2N_4O_2S$
MW: 392.42 g.mol^{-1}
White solid
32%

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.76 (d, *J* = 8.0 Hz, 2H), 7.40 – 7.27 (m, 7H), 5.79 – 5.40 (m, 1H), 4.40 (s, 2H), 4.25 (t, *J* = 7.5 Hz, 1H), 2.58 – 2.36 (m, 5H) ppm.

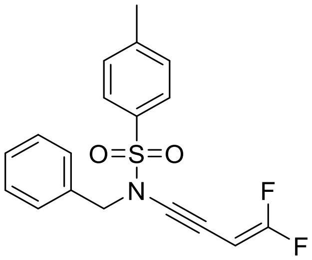
^{13}C NMR (126 MHz, CDCl$_3$): δ = 144.9, 136.4, 134.3, 133.7, 129.9, 129.5, 128.9, 128.8, 128.4, 115.1 (t, *J* = 241.1 Hz), 107.7 (t, *J* = 6.5 Hz), 55.9, 31.8 (t, *J* = 22.5 Hz), 21.8 ppm.

^{19}F NMR (282 MHz, CDCl$_3$): δ = -115.54 ppm.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for $C_{18}H_{18}F_2N_4NaO_2S$ 415.1011; Found 415.1008.

IR (neat): ν = 2126, 168, 1353, 1165, 1049 cm^{-1}

Compound **5a** *N*-benzyl-*N*-(4,4-difluorobut-3-en-1-yn-1-yl)-4-methylbenzenesulfonamide

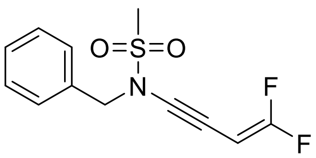


$C_{18}H_{15}F_2NO_2S$
MW: 347.38 g.mol^{-1}
Colorless oil
79%

^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.92 – 7.65 (d, 2H, *J* = 8.3 Hz, 2H), 7.45 – 7.10 (m, 7H), 4.57 (dd, *J* = 22.8, 1.1 Hz, 1H), 4.50 (s, 2H), 2.44 (s, 3H).

Data match with those described in the literature[6]

Compound **5b** *N*-benzyl-*N*-(4,4-difluorobut-3-en-1-yn-1-yl)-4-methanesulfonamide

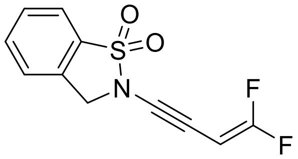


$C_{12}H_{11}F_2NO_2S$
MW: 271.28 g.mol^{-1}
Colorless oil
75%

^{1}H NMR (500 MHz, CDCl$_3$): 7.60 – 7.32 (m, 5H), 4.72 – 4.63 (m, 1H), 4.64 (s, 2H), 2.87 (s, 3H) ppm.

Data match with those described in the literature[6]

Compound **5c** 2-(4,4-difluorobut-3-en-1-yn-1-yl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide

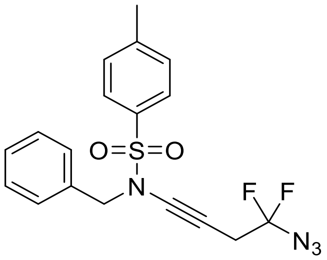


$C_{11}H_7F_2NO_2S$
MW: 255.24 g.mol^{-1}
Colorless oil
52%

^{1}H NMR (500 MHz, CDCl$_3$): 7.88 – 7.79 (m, 1H), 7.69 (td, *J* = 7.6, 1.2 Hz, 1H), 7.64 – 7.56 (m, 1H), 7.42 (dp, *J* = 7.9, 0.9 Hz, 1H), 4.81 (s, 2H), 4.77 (dd, *J* = 22.6, 1.2 Hz, 1H).

Data match with those described in the literature[6]

Compound **6a** *N*-(4-azido-4,4-difluorobut-1-yn-1-yl)-*N*-benzyl-4-methylbenzenesulfonamide



$C_{18}H_{16}F_2N_4O_2S$
MW: 390.40 g.mol^{-1}
Colorless oil
52%

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.75 (d, *J* = 8.4 Hz, 2H), 7.33 – 7.27 (m, 7H), 4.47 (s, 2H), 2.92 (t, *J* = 10.9 Hz, 2H), 2.45 (s, 3H) ppm.

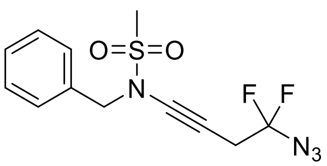
^{13}C NMR (126 MHz, CDCl$_3$): δ = 144.9, 134.7, 134.4, 129.8, 128.9, 128.6, 128.5, 127.9, 121.4 (d, *J* = 267.0 Hz), 76.9, 61.2 (t, *J* = 6.3 Hz), 55.5, 28.2 (d, *J* = 33.2 Hz), 21.8 ppm.

^{19}F NMR (471 MHz, CDCl$_3$): δ = -74.00 ppm.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for $C_{18}H_{16}F_2N_4NaO_2S$ 413.0854; Found 413.0856.

IR (neat): ν = 2930, 2361, 2148, 1366, 1168, 1060 cm^{-1}

Compound **6b** *N*-(4-azido-4,4-difluorobut-1-yn-1-yl)-*N*-benzylmethanesulfonamide



$C_{12}H_{12}F_2N_4O_2S$
MW: 314.31 g.mol^{-1}
Colorless oil
44%

^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.47 – 7.32 (m, 5H), 4.61 (s, 2H), 3.01 (t, *J* = 10.9 Hz, 2H), 2.86 (s, 3H) ppm.

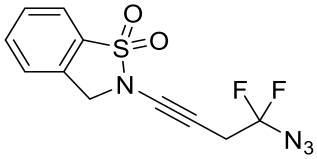
^{13}C NMR (126 MHz, CDCl$_3$): δ = 134.4, 129.1, 129.0, 129.0, 121.4 (t, *J* = 266.8 Hz), 77.0, 61.8 (t, *J* = 6.0 Hz), 55.7, 39.0, 28.2 (t, *J* = 32.7 Hz) ppm.

^{19}F NMR (471 MHz, CDCl$_3$): δ = -73.96 ppm.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for $C_{12}H_{12}F_2N_4NaO_2S$ 337.0541; Found 337.0522.

IR (neat): ν = 2932, 2264, 2149, 1361, 1164, 1059 cm^{-1}

Compound **6c** 2-(4-azido-4,4-difluorobut-1-yn-1-yl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide



$C_{11}H_8F_2N_4O_2S$
MW: 298.27 g.mol^{-1}
Colorless oil
47%

^{1}H NMR (500 MHz, C_6D_6): δ = 7.22 (dq, *J* = 7.8, 0.6 Hz, 1H), 6.73 (td, *J* = 7.6, 1.2 Hz, 1H), 6.64 (td, *J* = 7.6, 0.9 Hz, 1H), 6.15 (dt, *J* = 7.7, 0.9 Hz, 1H), 3.65 (s, 2H), 2.54 (t, *J* = 11.2 Hz, 2H) ppm.

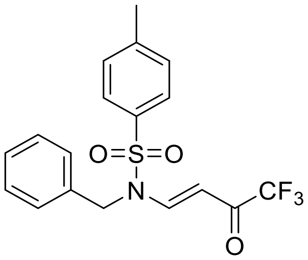
^{13}C NMR (126 MHz, C_6D_6): δ = 133.7, 132.6, 131.6, 129.3, 124.3, 121.8 (t, *J* = 265.8 Hz), 121.6, 73.9, 63.1 (t, *J* = 6.0 Hz), 51.7, 28.0 (t, *J* = 32.8 Hz) ppm.

^{19}F NMR (471 MHz, C_6D_6): δ = -74.11 ppm.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for $C_{11}H_8F_2N_4NaO_2S$ 321.0228; Found 321.0213.

IR (neat): ν = 2951, 2261, 2151, 1327, 1179, 1059 cm^{-1}

Compound **7** (*E*)-*N*-benzyl-4-methyl-*N*-(4,4,4-trifluoro-3-oxobut-1-en-1-yl)benzenesulfonamide



$C_{18}H_{16}F_3NO_3S$
MW: 383.38 g.mol^{-1}
Colorless oil
91%

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.5 (d, *J* = 13.7 Hz, 1H), 7.7 (d, *J* = 8.4 Hz, 2H), 7.4 – 7.3 (m, 2H), 7.2 – 7.1 (m, 5H), 5.57 (dq, J = 13.7, 0.8 Hz, 1H), 4.7 (s, 2H), 2.5 (s, 3H) ppm.

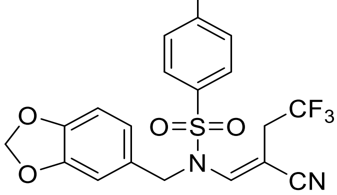
^{13}C NMR (126 MHz, $CDCl_3$): δ = 179.1 (q, *J* = 35.1 Hz), 147.1 (d, *J* = 1.4 Hz), 146.0, 134.6, 133.0, 130.6, 129.1, 128.4, 127.7, 126.9, 116.5 (q, *J* = 290.9 Hz), 98.5, 50.4, 21.8 ppm.

^{19}F NMR (282 MHz, $CDCl_3$): δ = -77.81 ppm.

HRMS (ESI-TOF) m/z: [M+Na]$^+$ calcd for $C_{18}H_{16}F_3NNaO_3S$ 406.0695; Found 406.0686.

IR (neat): ν = 2939, 1579, 1170, 1022 cm^{-1}

Compound **8** (*E*)-*N*-(benzo[d][1,3]dioxol-5-ylmethyl)-*N*-(2-cyano-4,4,4-trifluorobut-1-en-1-yl)-4-methylbenzenesulfonamide



$C_{20}H_{17}F_3N_2O_4S$
MW: 438.42 g.mol^{-1}
Colorless oil
69%

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.03 (s, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.74 – 6.61 (m, 1H), 6.61 – 6.51 (m, 1H), 5.97 (s, 2H), 4.42 (s, 2H), 3.02 (qd, *J* = 9.8, 0.9 Hz, 2H), 2.48 (s, 3H) ppm.

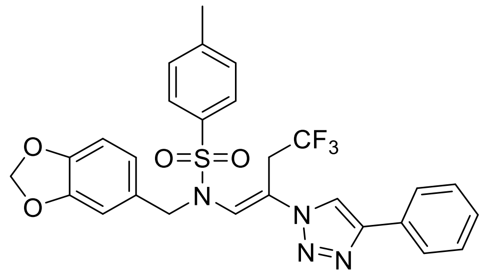
^{13}C NMR (126 MHz, CDCl$_3$): δ = 148.7, 148.0, 145.8, 144.0, 134.2, 130.6, 127.7, 127.6, 124.3 (q, *J* = 278.0 Hz), 120.6, 118.4, 108.9, 107.4, 101.6, 94.6 (q, *J* = 3.6 Hz), 52.3, 33.6 (q, *J* = 31.5 Hz), 21.8 ppm.

^{19}F NMR (282 MHz, CDCl$_3$): δ = -64.71 ppm.

HRMS (ESI-TOF) m/z: $[M+K]^+$ calcd for $C_{20}H_{17}F_3KN_2O_4S$ 477.0493; Found 477.0504.

IR (neat): ν = 2905, 1626, 1361, 1247, 1168, 1039 cm^{-1}

Compound **9** (*E*)-*N*-benzyl-4-methyl-*N*-(4,4,4-trifluoro-3-oxobut-1-en-1-yl)benzenesulfonamide



$C_{27}H_{23}F_3N_4O_4S$
MW: 556.56 g.mol^{-1}
White solid
98%

^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.86 – 7.79 (m, 2H), 7.73 (s, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.49 – 7.40 (m, 2H), 7.40 – 7.33 (m, 3H), 6.78 – 6.63 (m, 3H), 6.16 (s, 1H), 5.95 (s, 2H), 4.27 (s, 2H), 3.80 (q, *J* = 9.8 Hz, 2H), 2.46 (s, 3H) ppm.

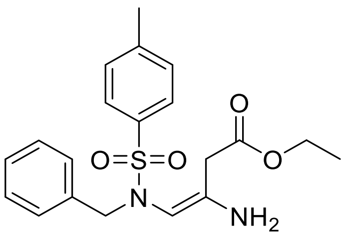
^{13}C NMR (126 MHz, CDCl$_3$): δ = 148.3, 148.2, 148.0, 145.1, 134.0, 133.3 (q, *J* = 3.1 Hz), 130.4, 129.8, 129.1, 128.8, 127.8, 127.7, 127.0, 126.0, 124.1 (q, *J* = 279.0 Hz), 122.9, 118.8 (q, *J* = 1.4 Hz), 109.5, 108.5, 101.4, 55.5, 34.1 (q, *J* = 31.7 Hz), 21.8 ppm.

^{19}F NMR (282 MHz, CDCl$_3$): δ = -62.45 ppm.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{27}H_{24}F_3N_4O_4S$ 557.1465; Found 557.1459.

IR (neat): ν = 2360, 1489, 1350, 1244, 1164, 1039, 804 cm^{-1}

Compound **10** ethyl (*E*)-3-amino-4-((*N*-benzyl-4-methylphenyl)sulfonamido)but-3-enoate



$C_{20}H_{24}N_2O_4S$
MW: 388.48 g.mol^{-1}
Colorless oil
87%

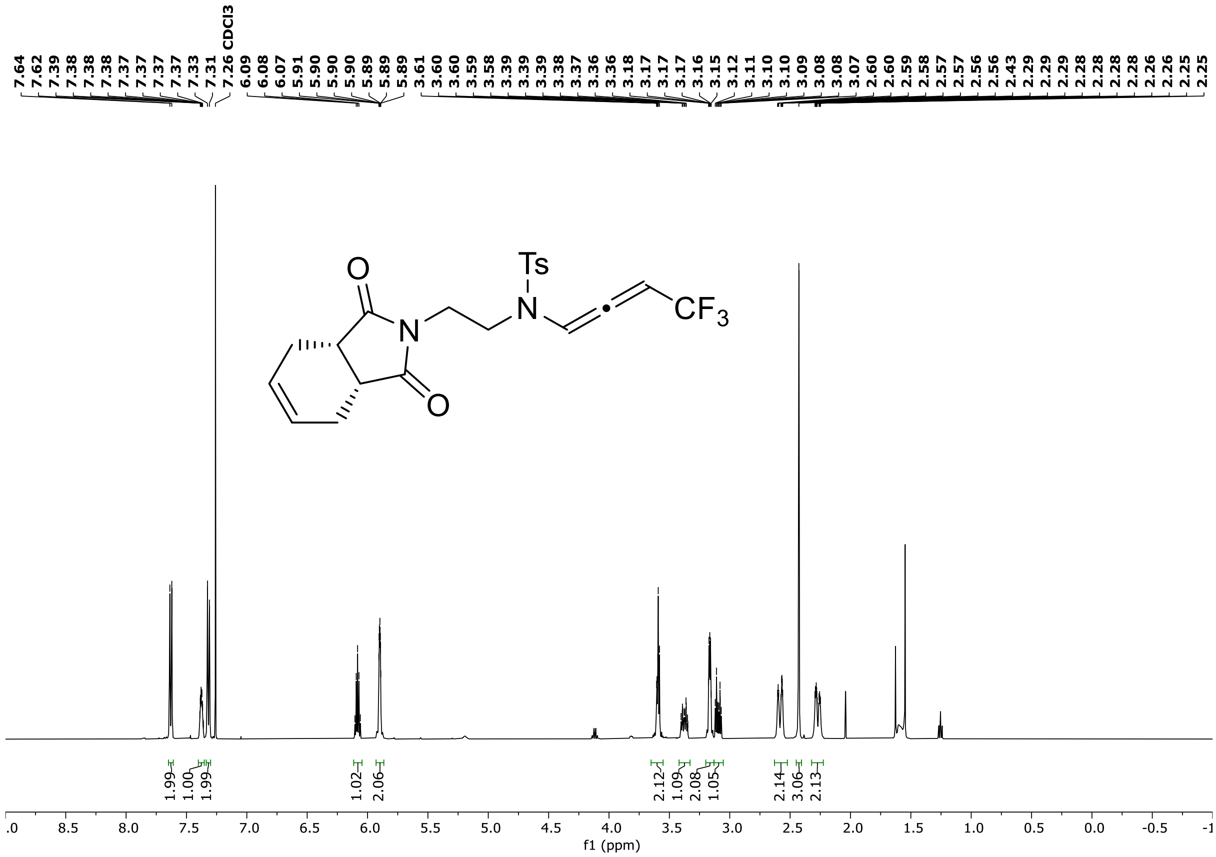
^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.72 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.28 – 7.26 (m, 3H), 7.19 – 7.12 (m, 2H), 4.40 (s, 2H), 4.31 (s, 1H), 4.09 (d, *J* = 7.1 Hz, 2H), 3.67 (s, 2H), 2.45 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ = 169.6, 156.4, 144.1, 136.5, 135.1, 130.1, 128.9, 128.7, 128.2, 127.3, 85.0, 58.9, 51.7, 50.6, 21.7, 14.6 ppm.

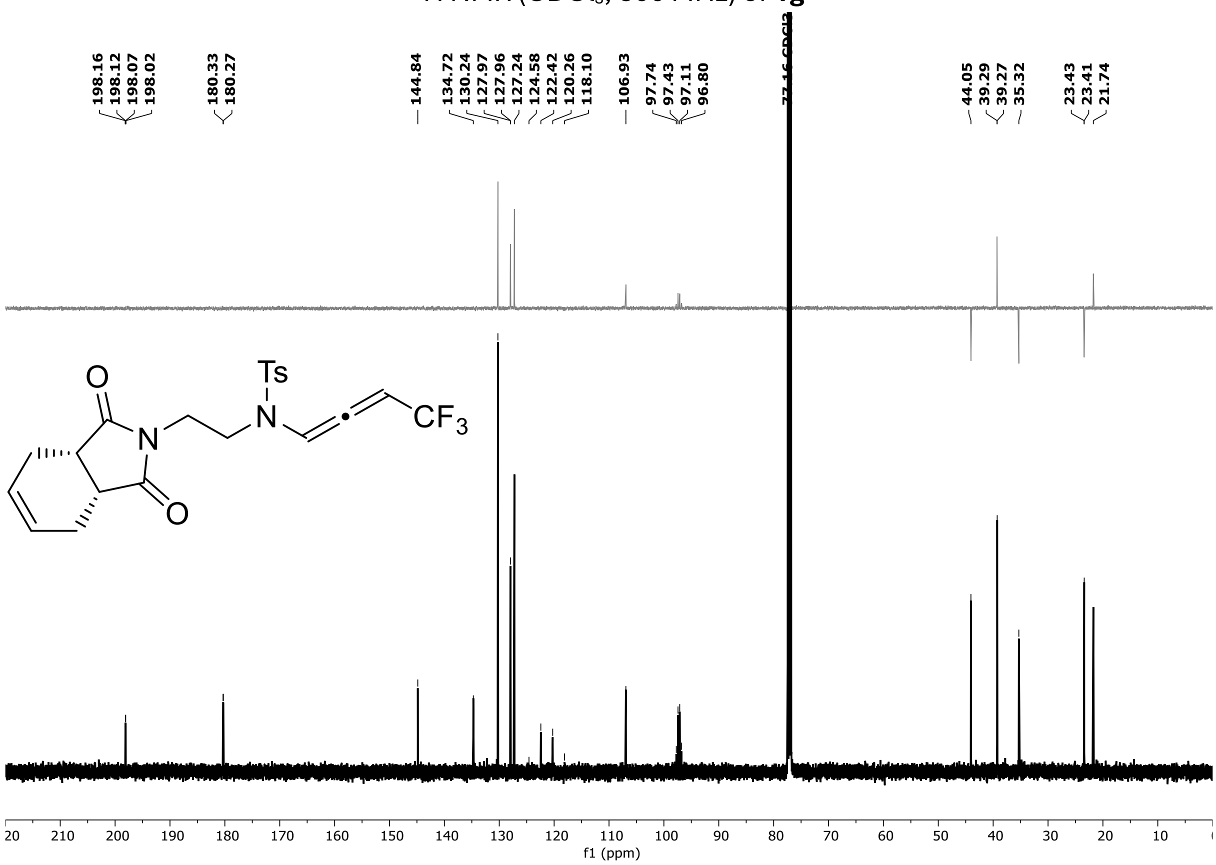
HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{20}H_{24}N_2NaO_4S$ 411.1349; Found 411.1346.

IR (neat): ν = 3462, 3340, 2978, 1668, 1619, 1562, 1278, 1154, 1091 cm^{-1}

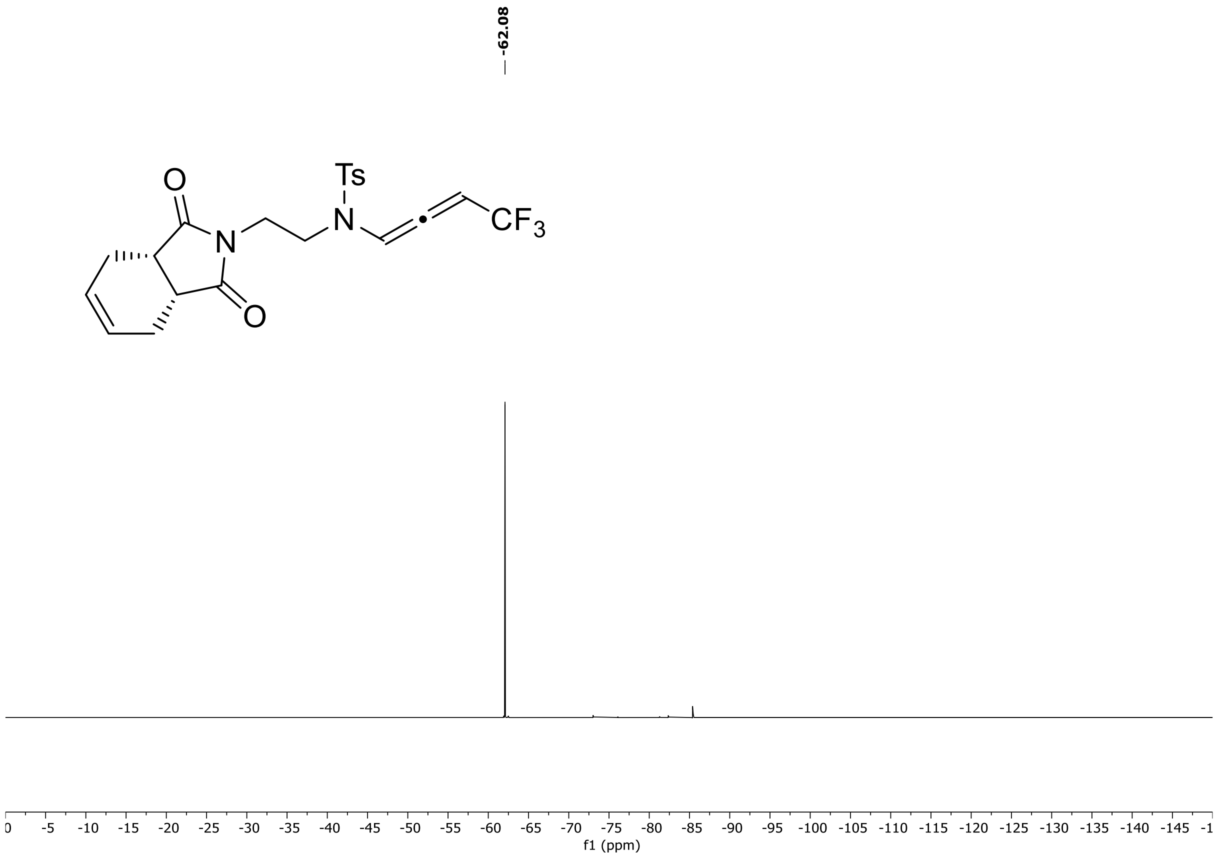
NMR spectra



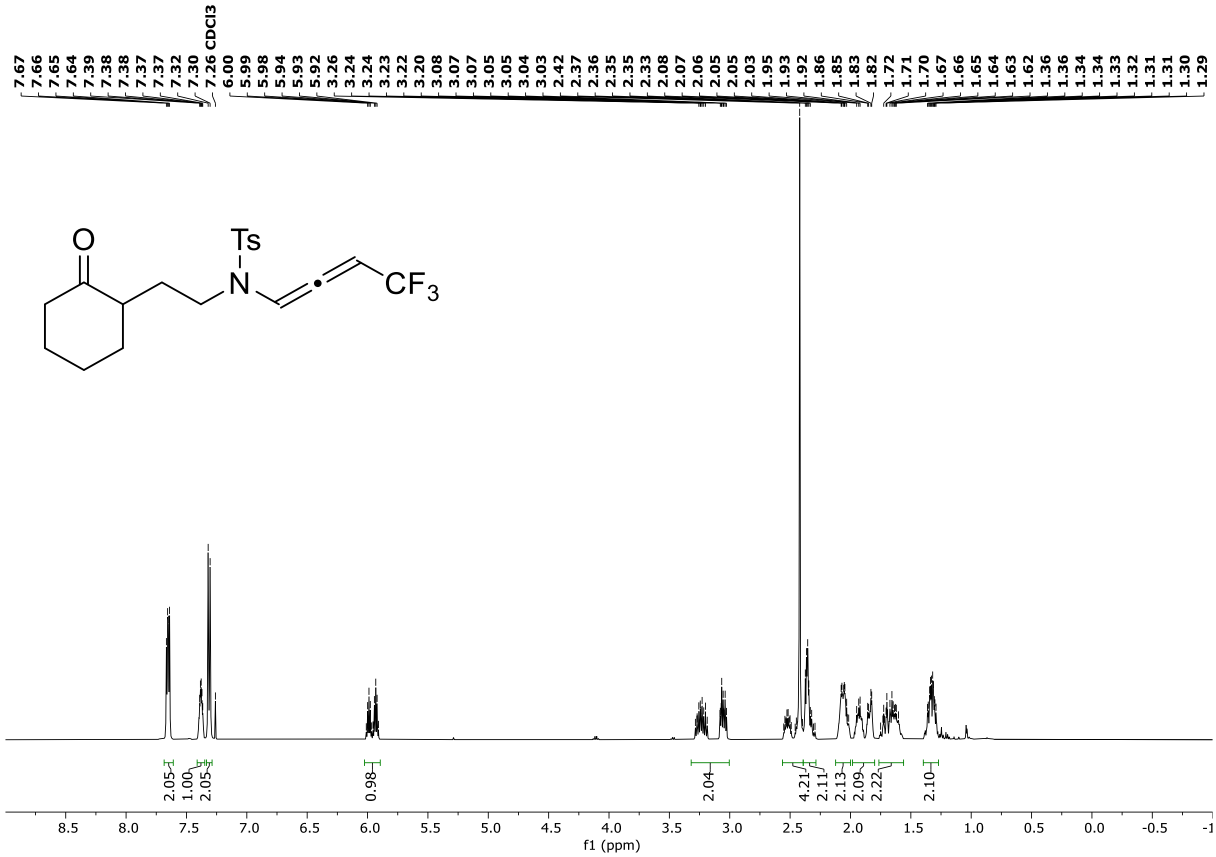
^{1}H NMR ($CDCl_3$, 500 MHz) of **1g**



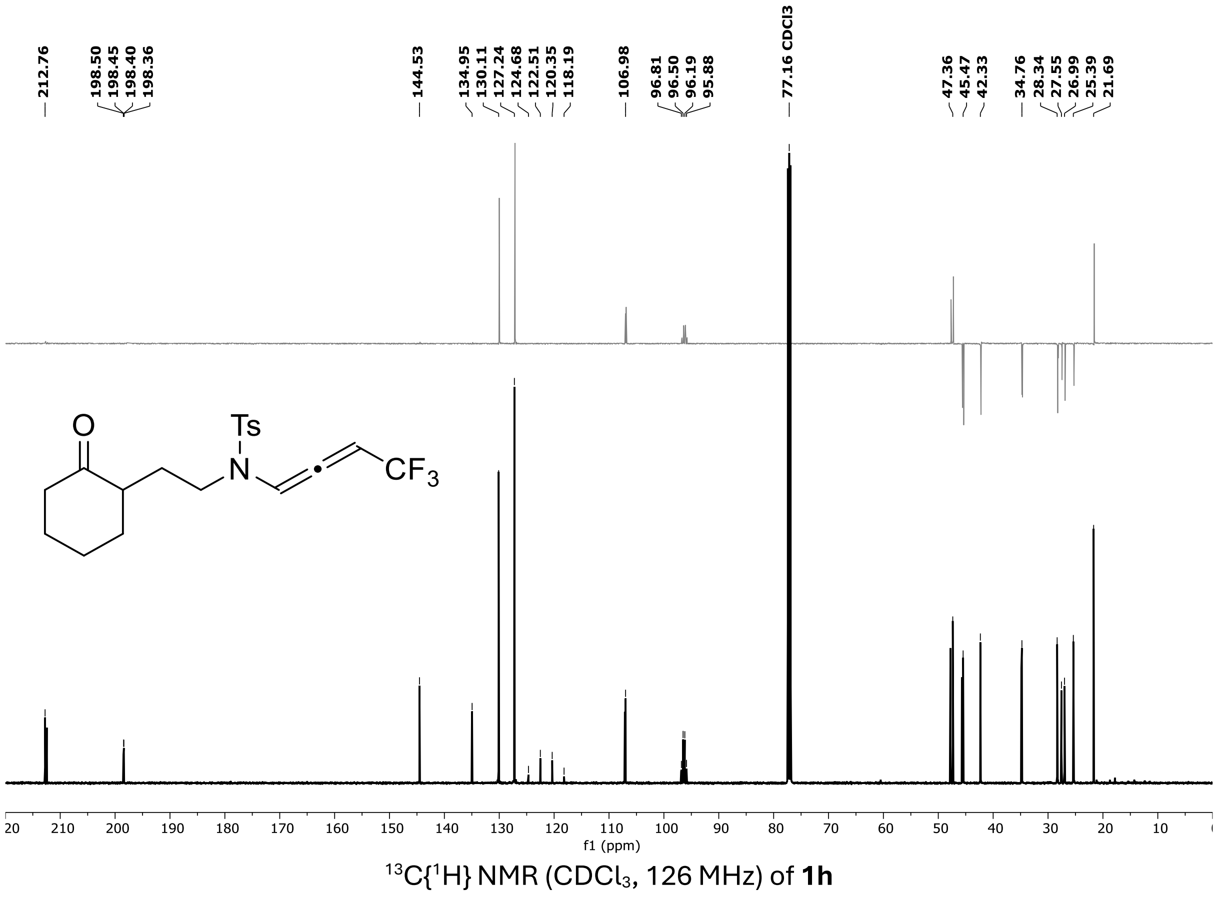
$^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) of **1g**



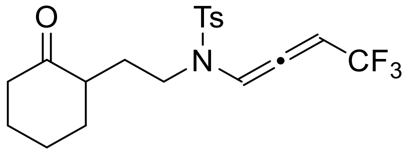
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 471 MHz) of **1g**

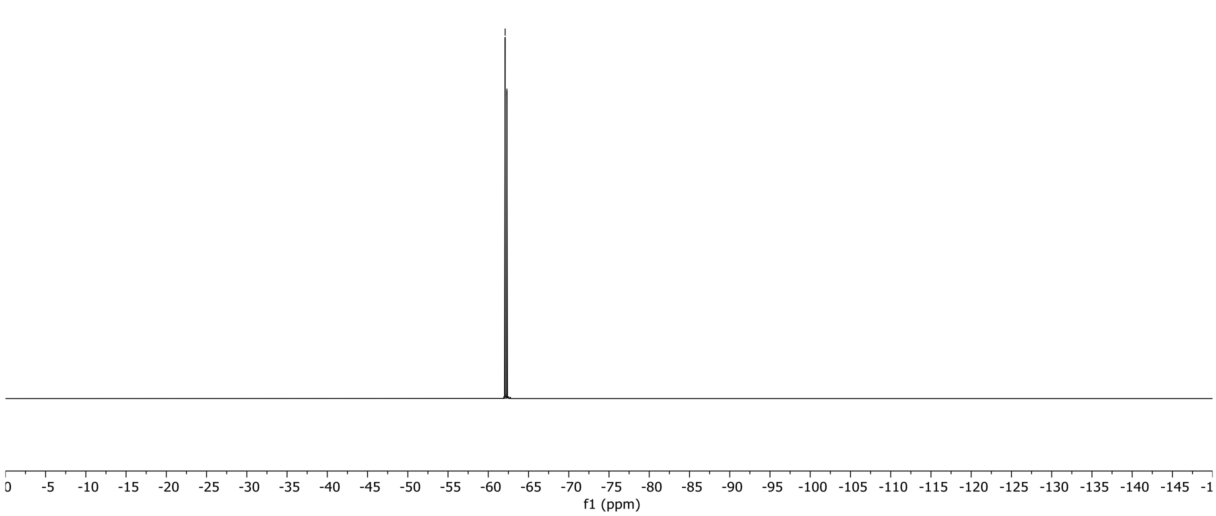


^1H NMR ($CDCl_3$, 500 MHz) of **1h**

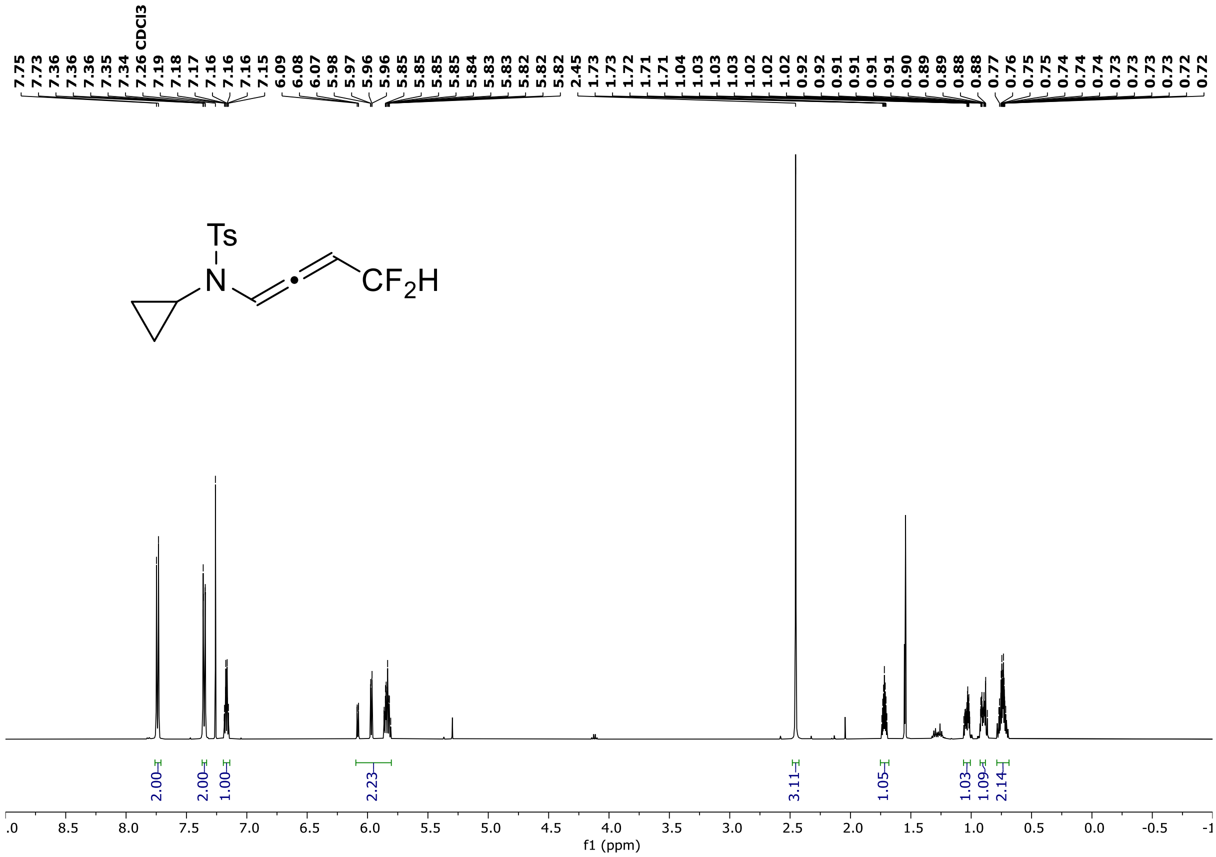


$^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) of **1h**

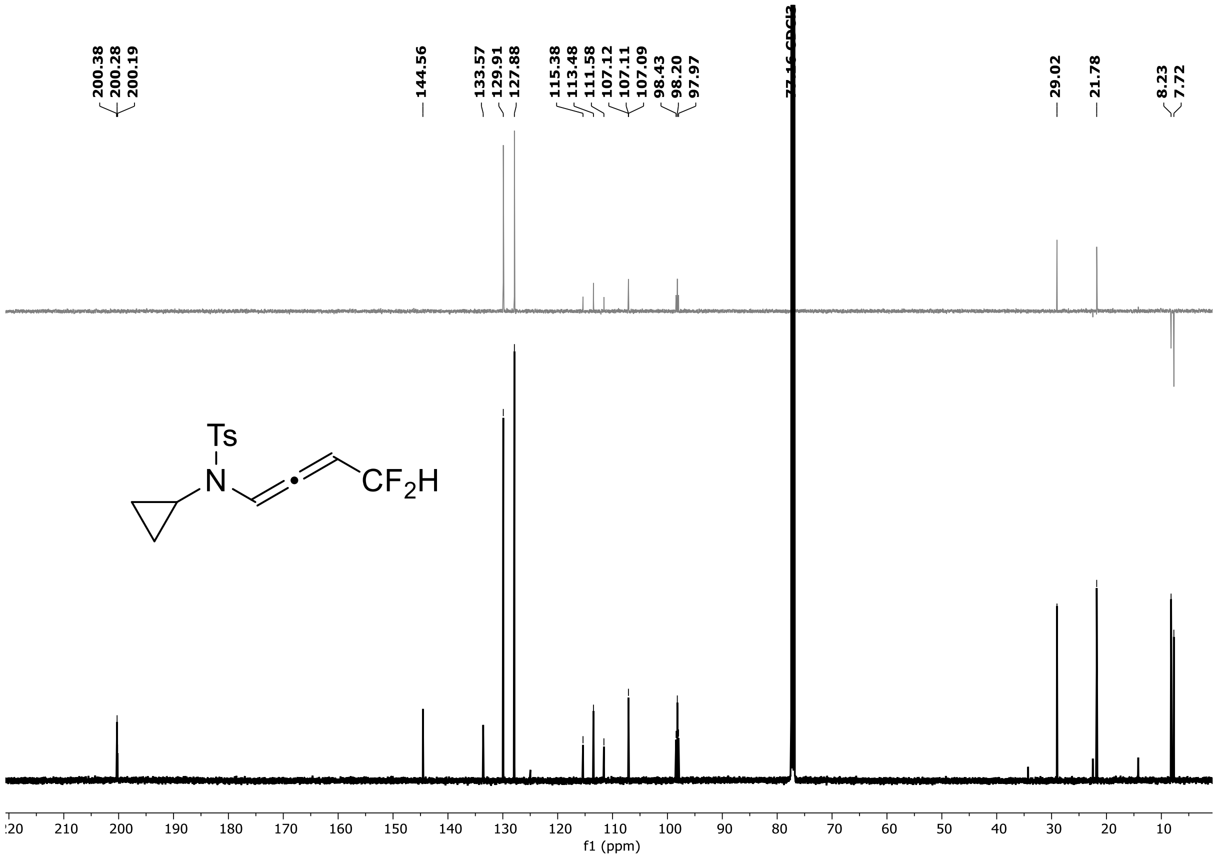




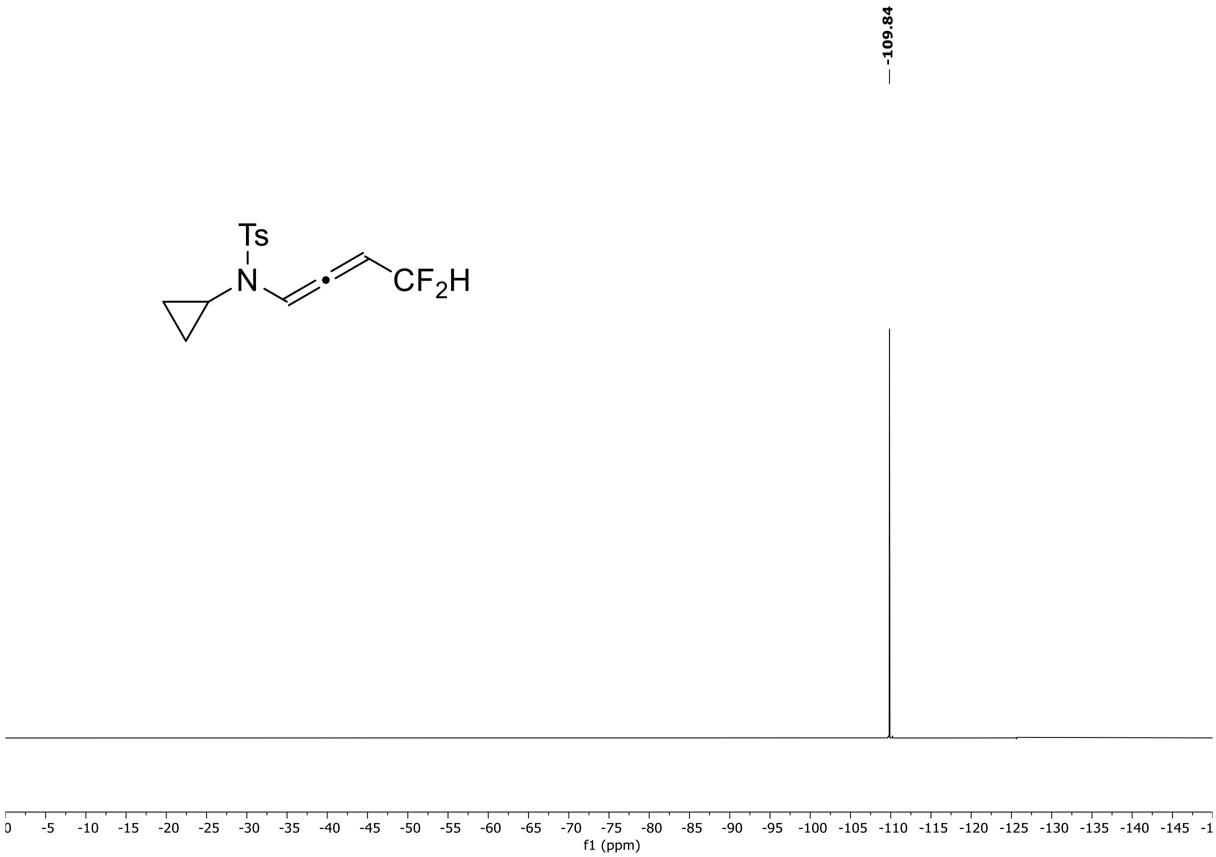
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 471 MHz) of **1h**



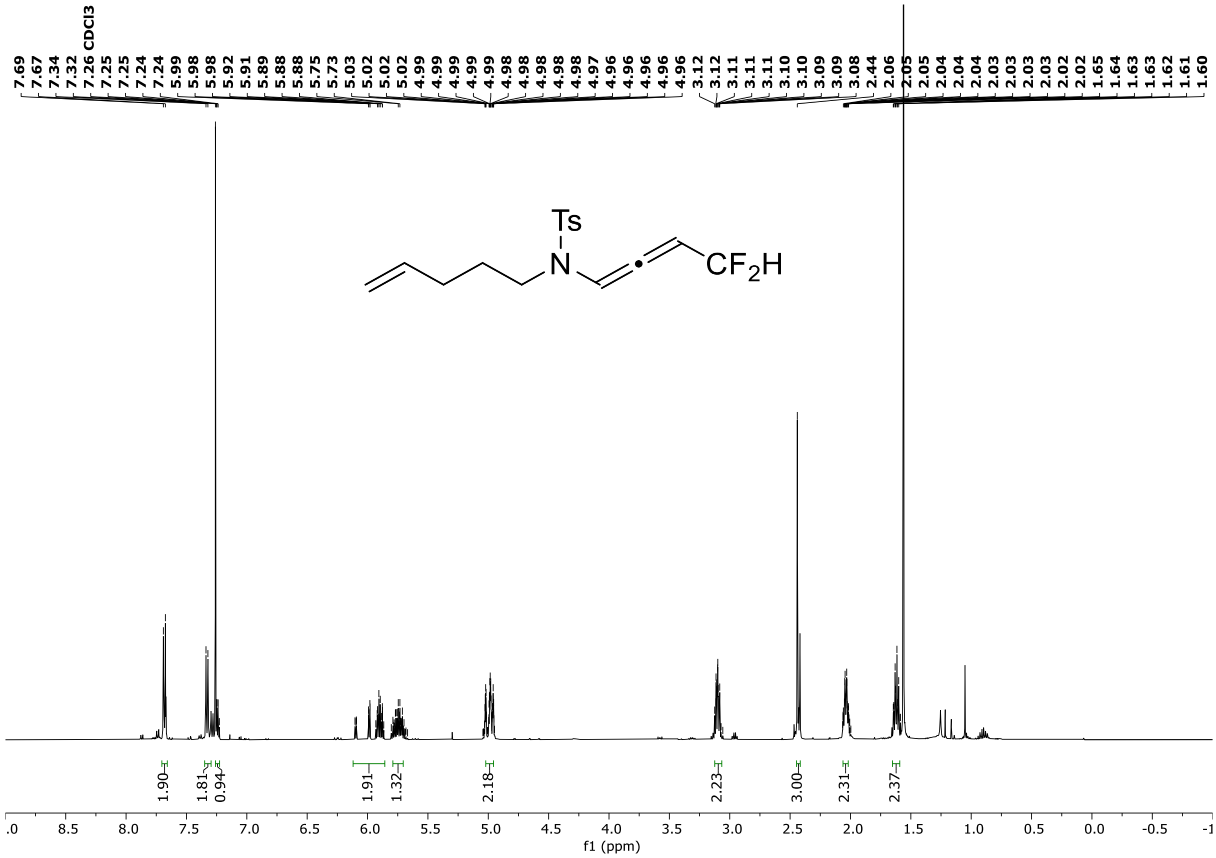
^1H NMR ($CDCl_3$, 500 MHz) of **1s**



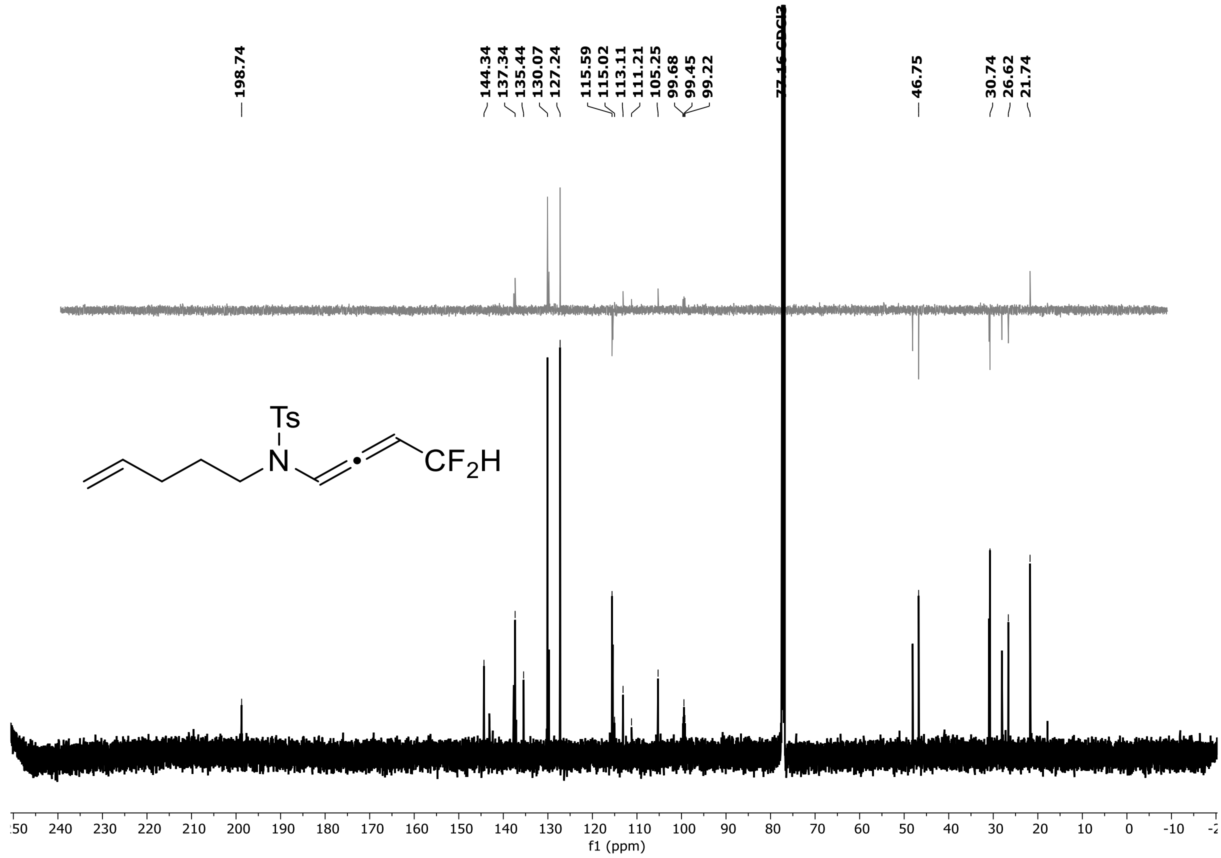
$^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) of **1s**



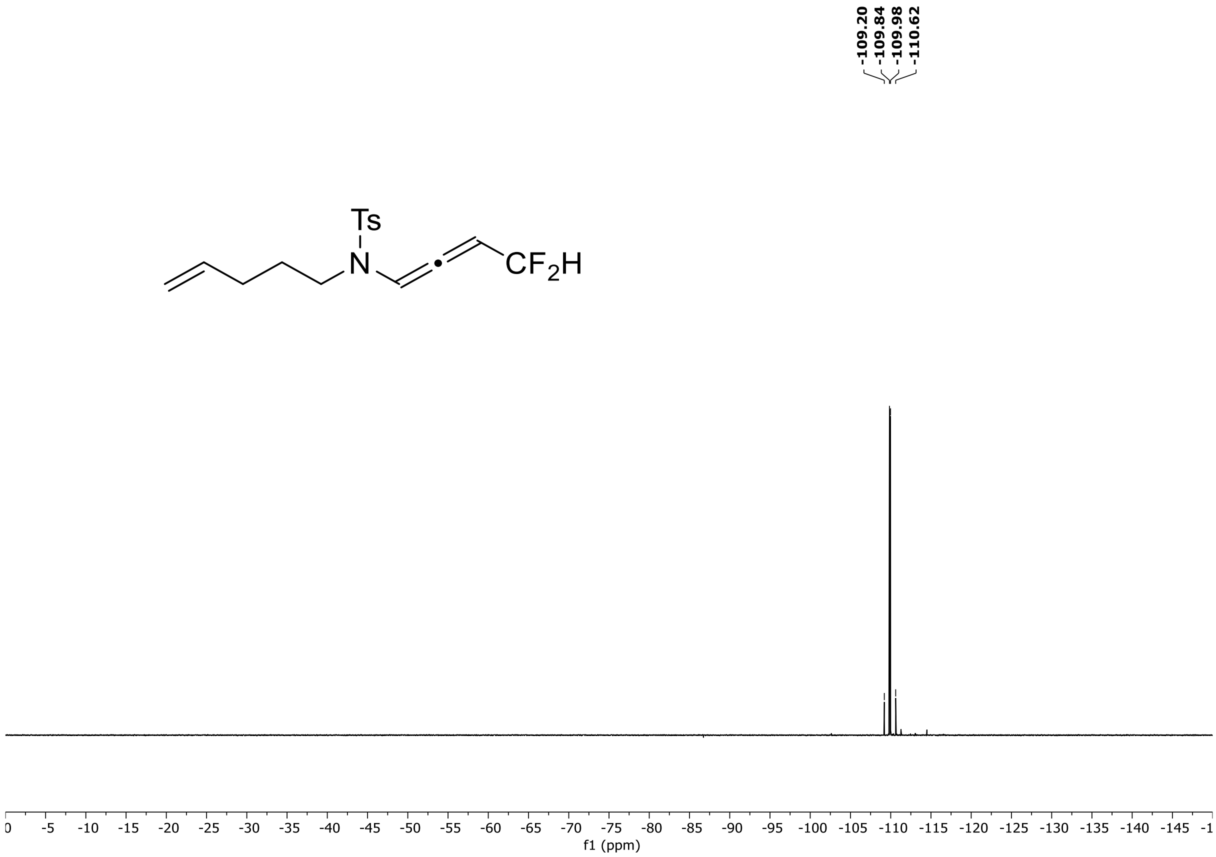
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 471 MHz) of **1s**



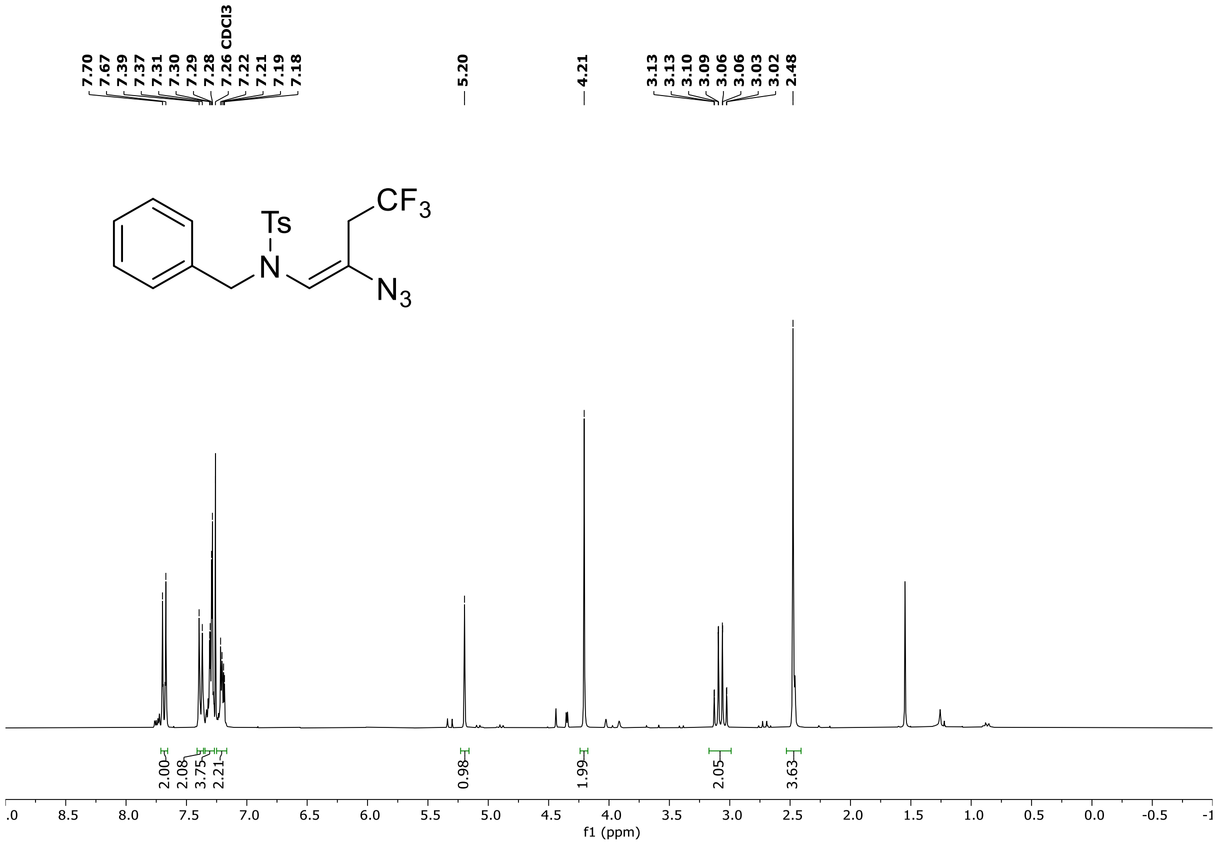
^{1}H NMR ($CDCl_3$, 500 MHz) of **1t**



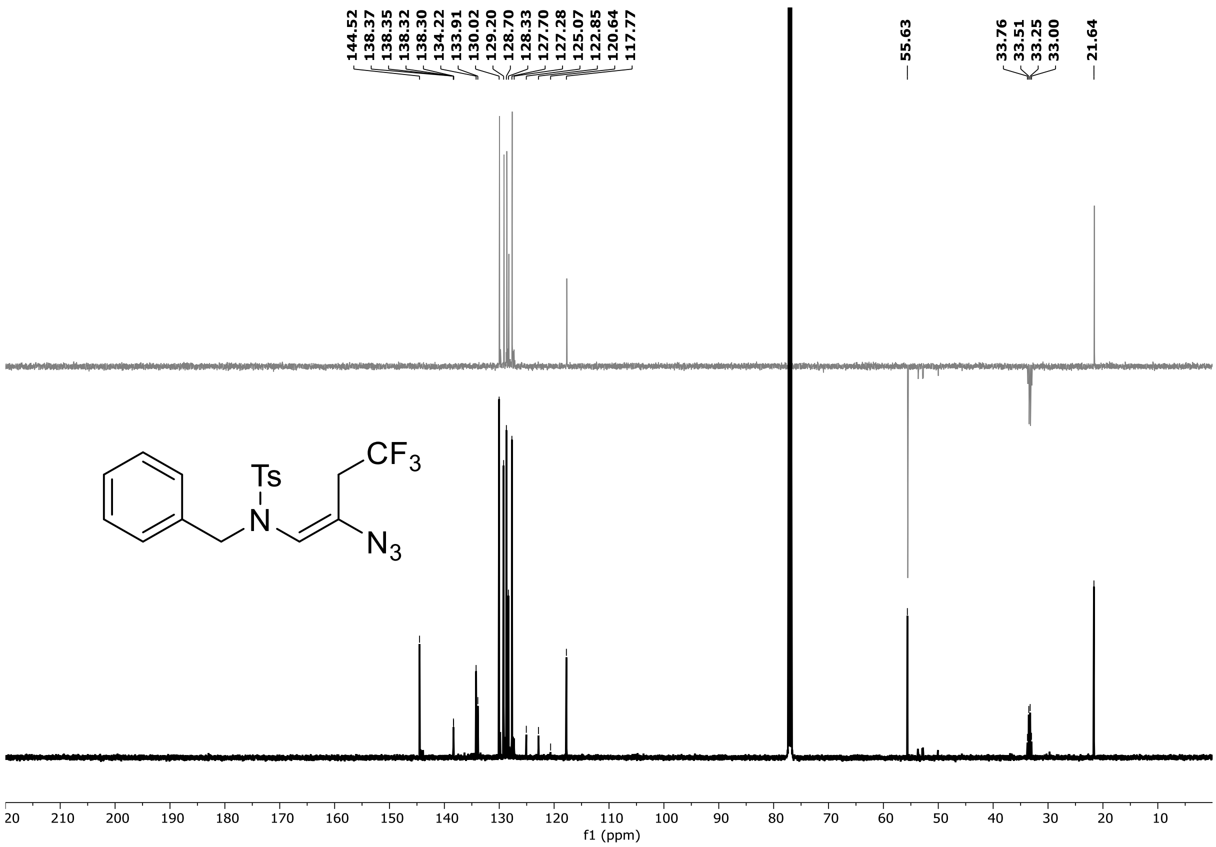
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) of **1t**



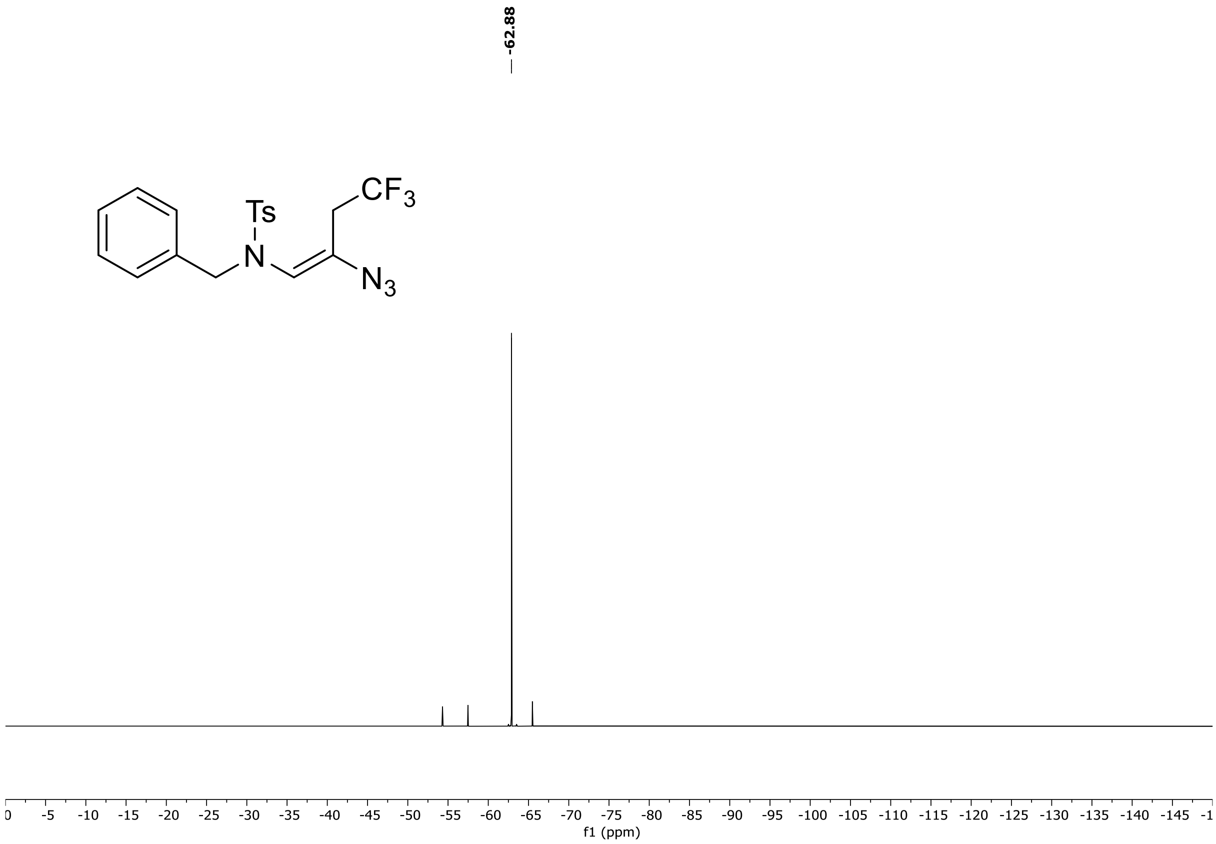
^{19}F{^{1}H} NMR ($CDCl_3$, 471 MHz) of **1t**



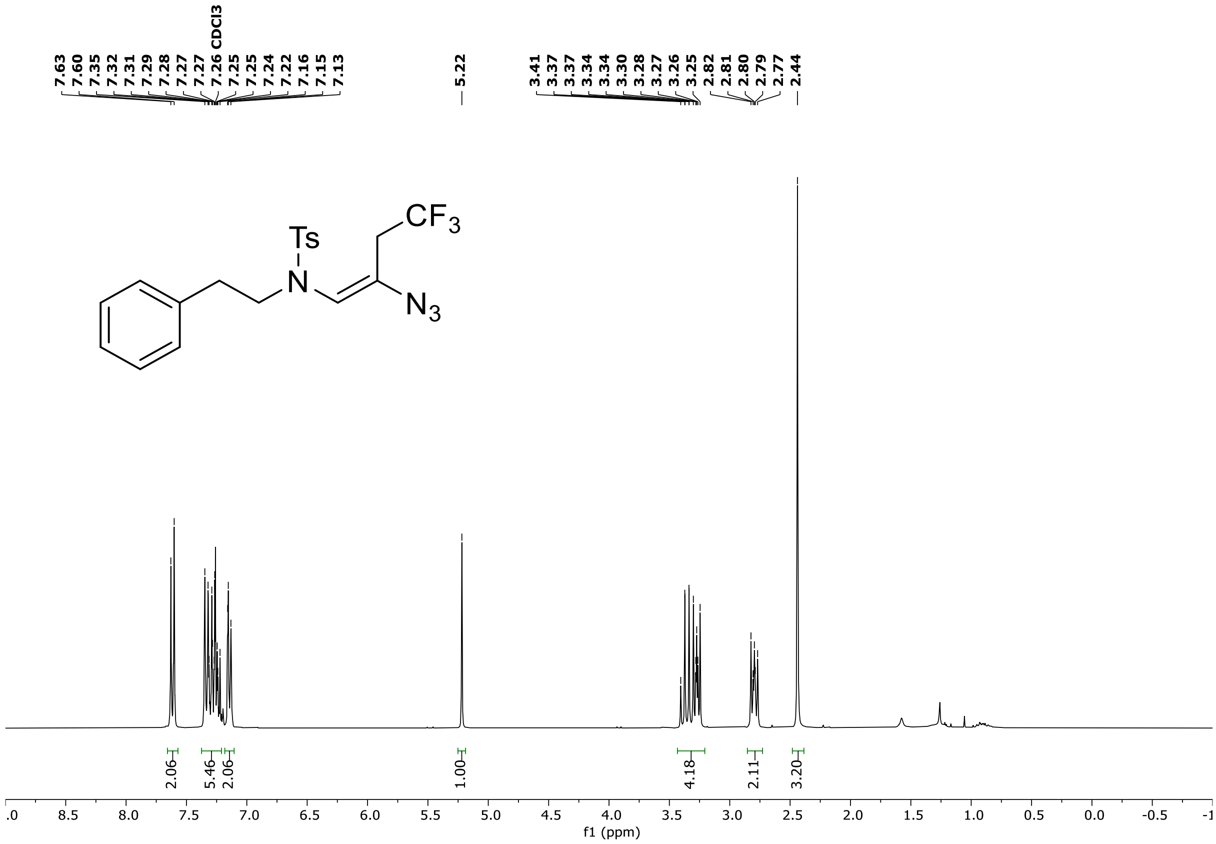
^{1}H NMR ($CDCl_3$, 300 MHz) of **2a**



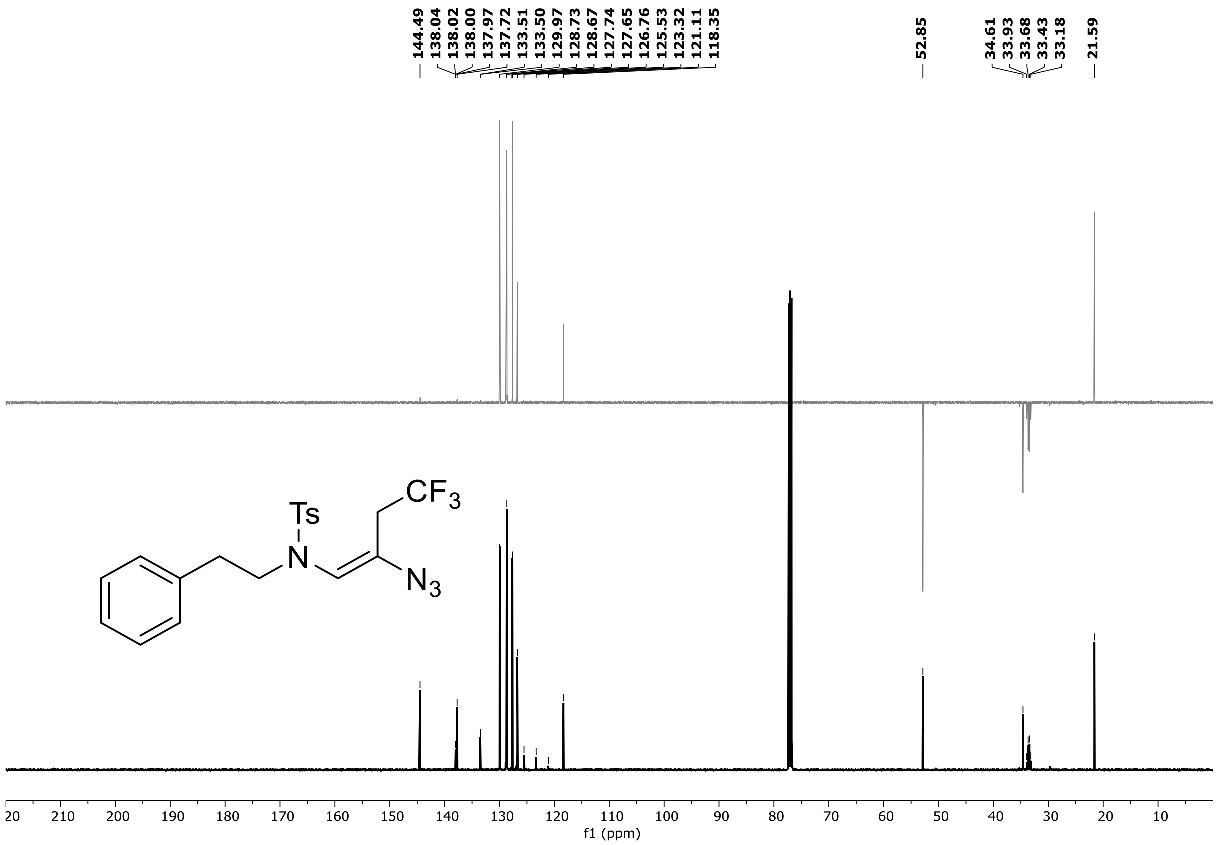
^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) of **2a**



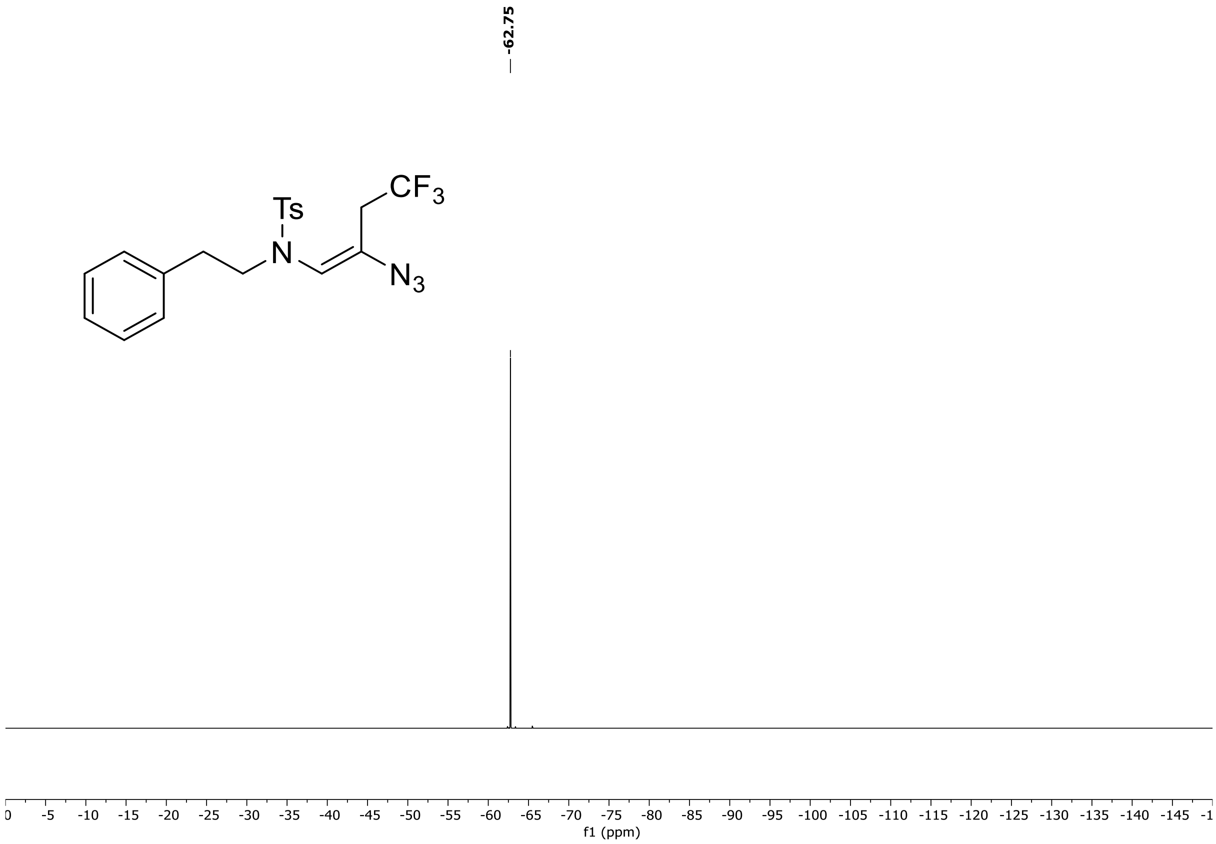
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 282 MHz) of **2a**



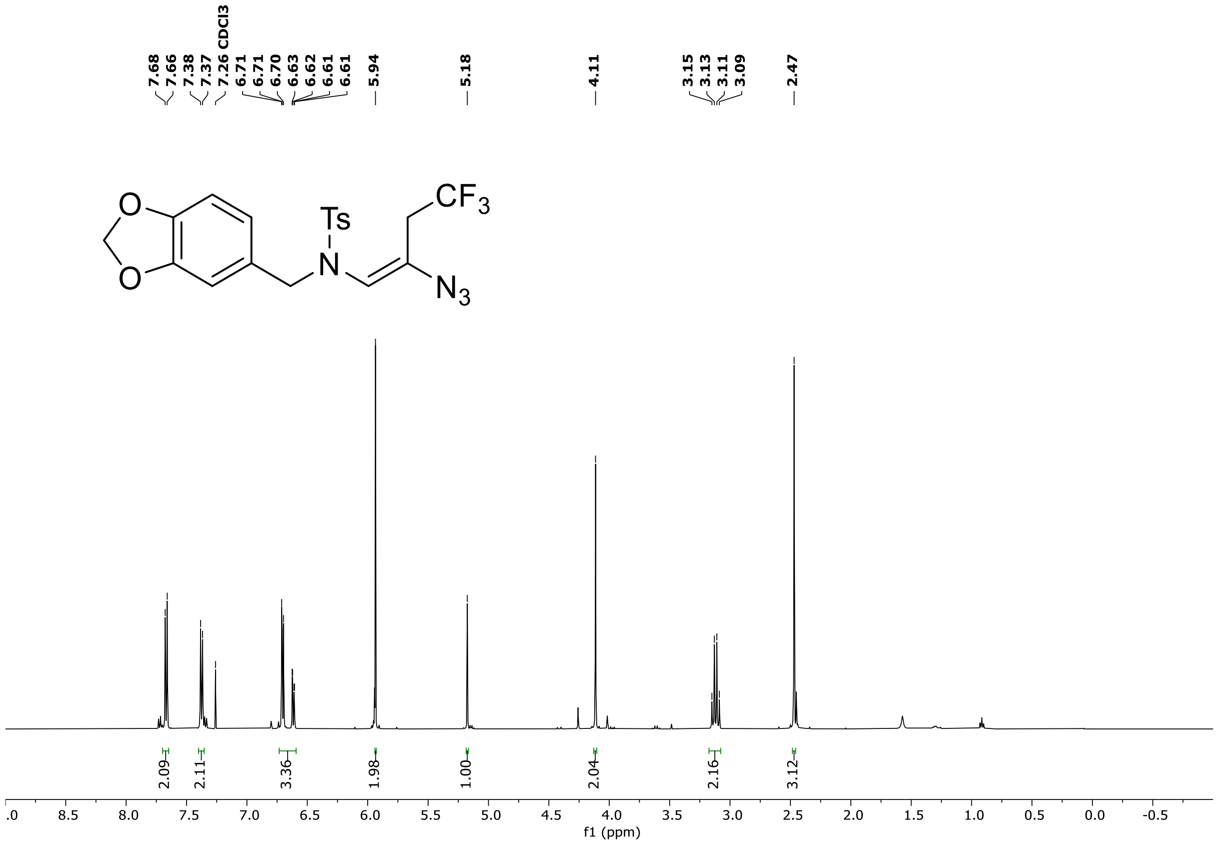
^{1}H NMR ($CDCl_3$, 300 MHz) of **2b**



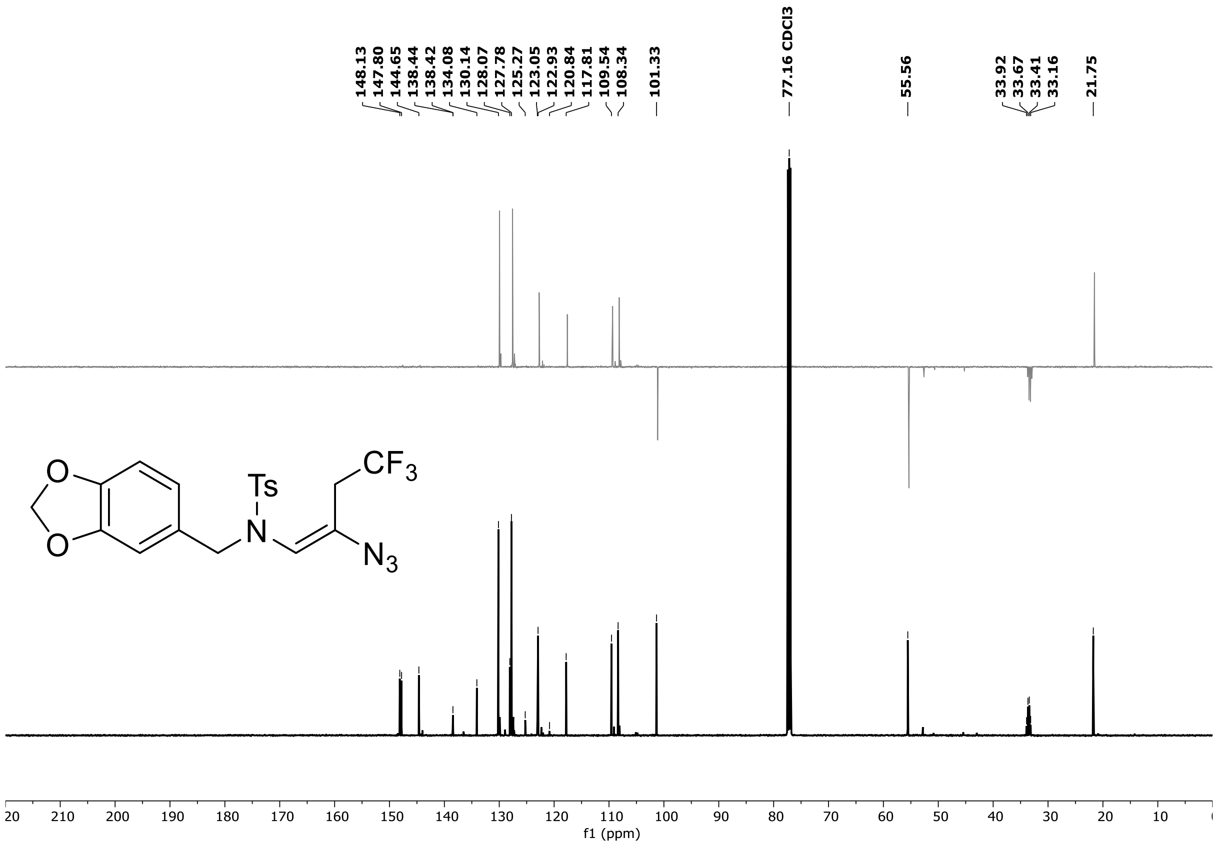
^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) of **2b**



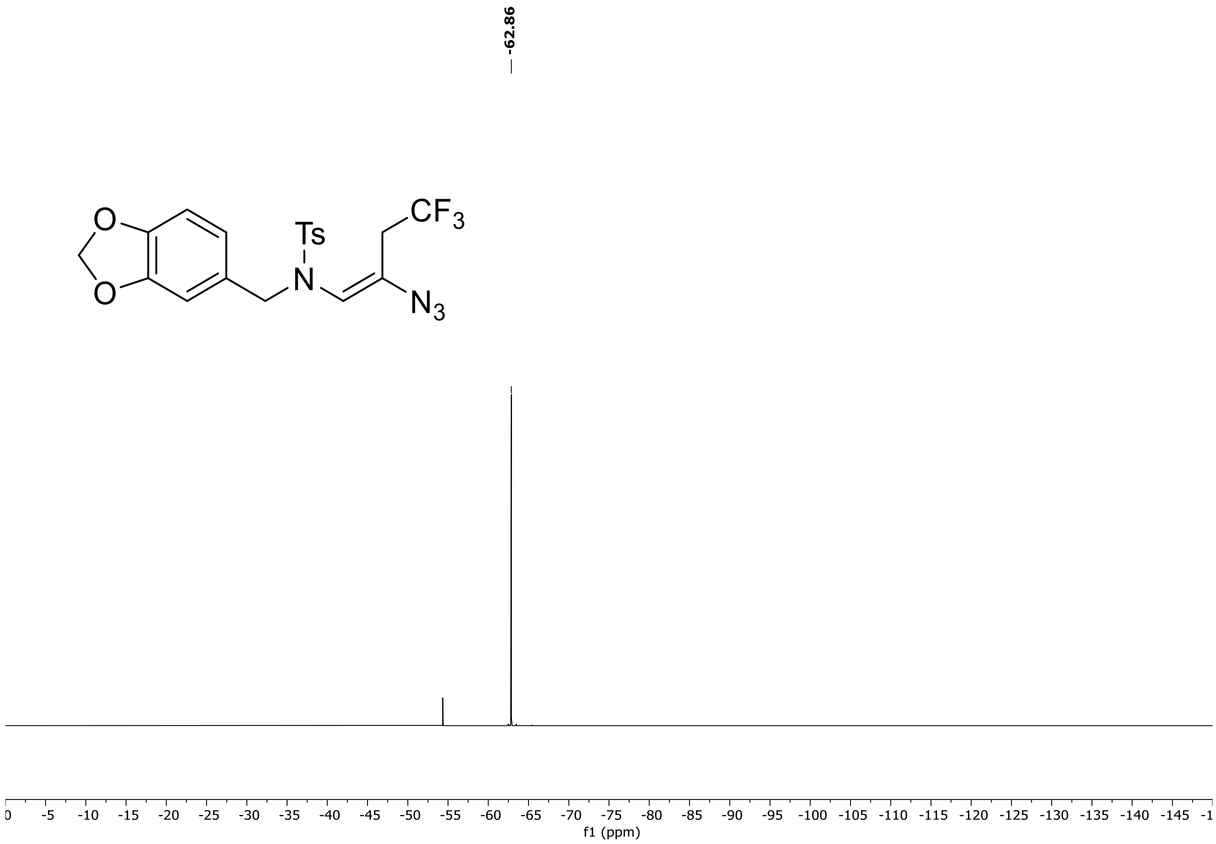
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 282 MHz) of **2b**



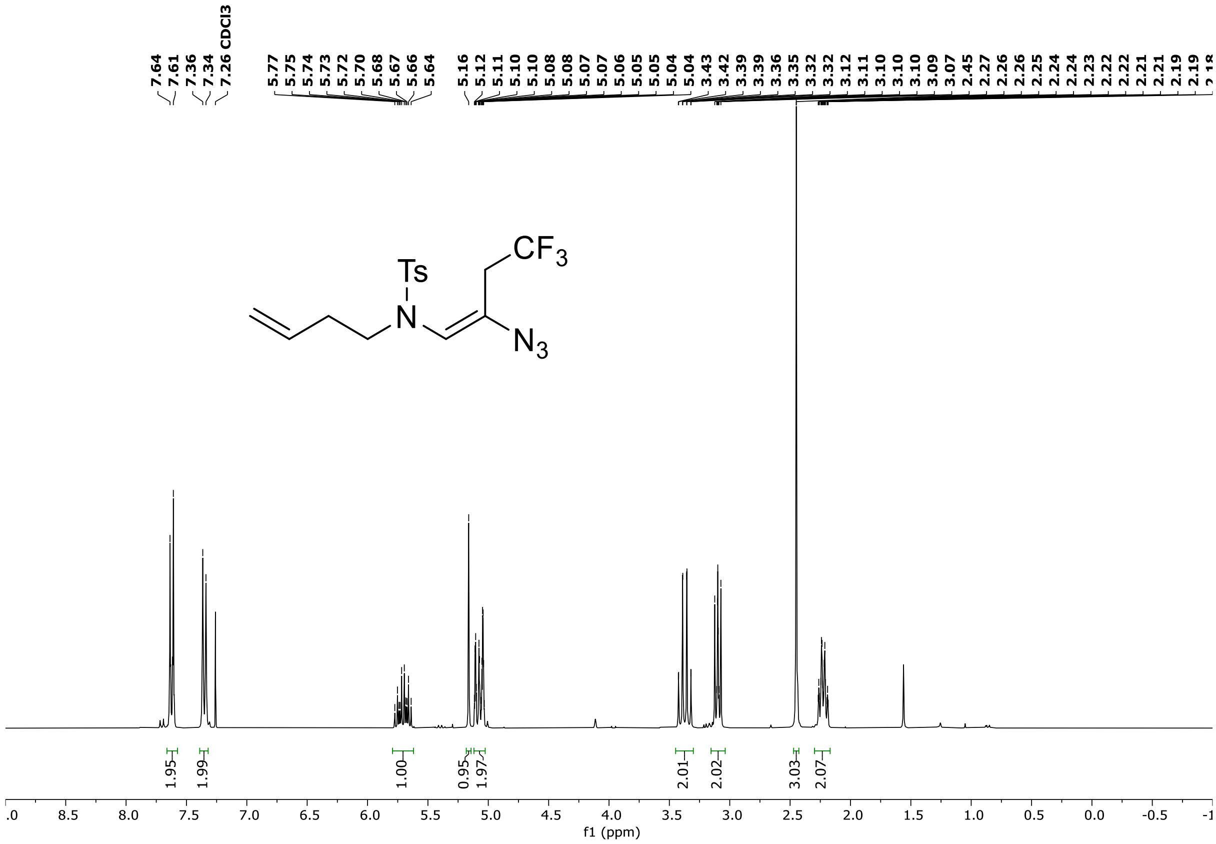
^{1}H NMR ($CDCl_3$, 500 MHz) of **2c**



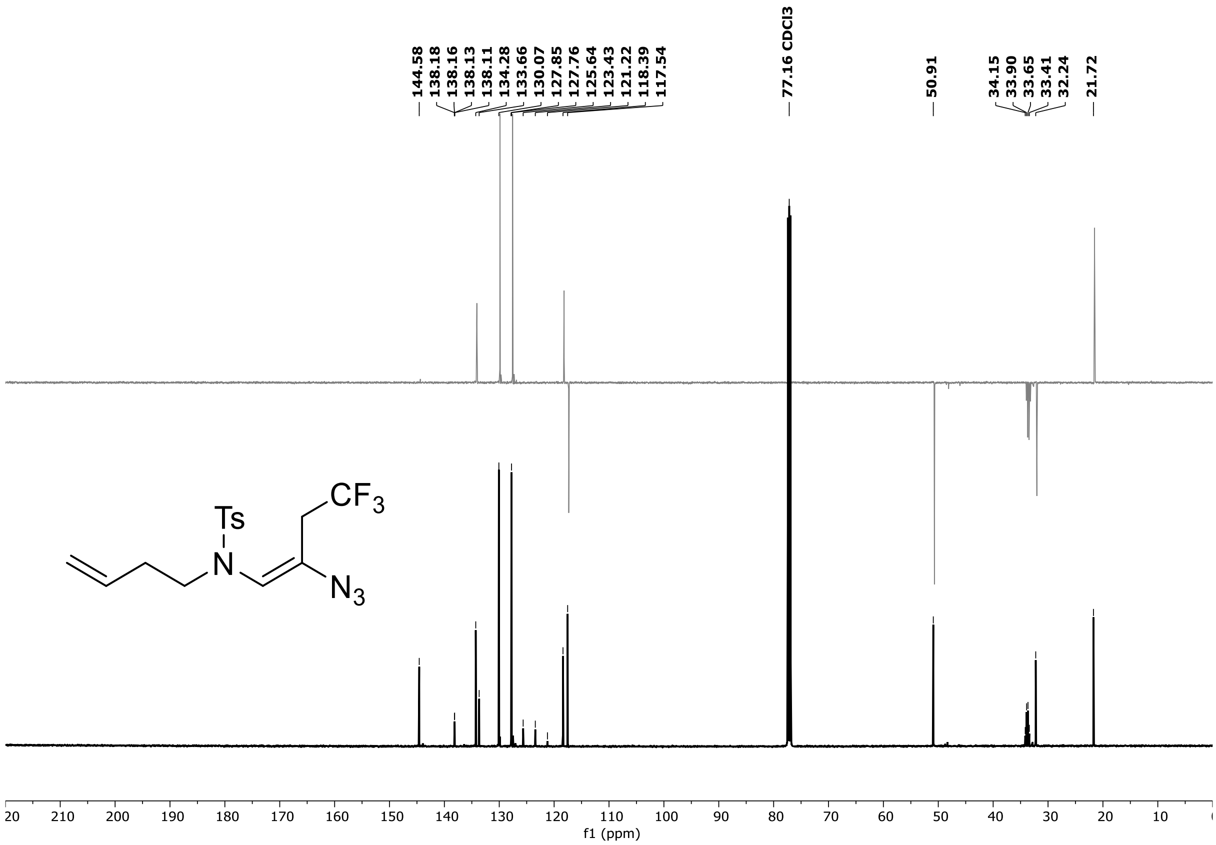
^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) of **2c**



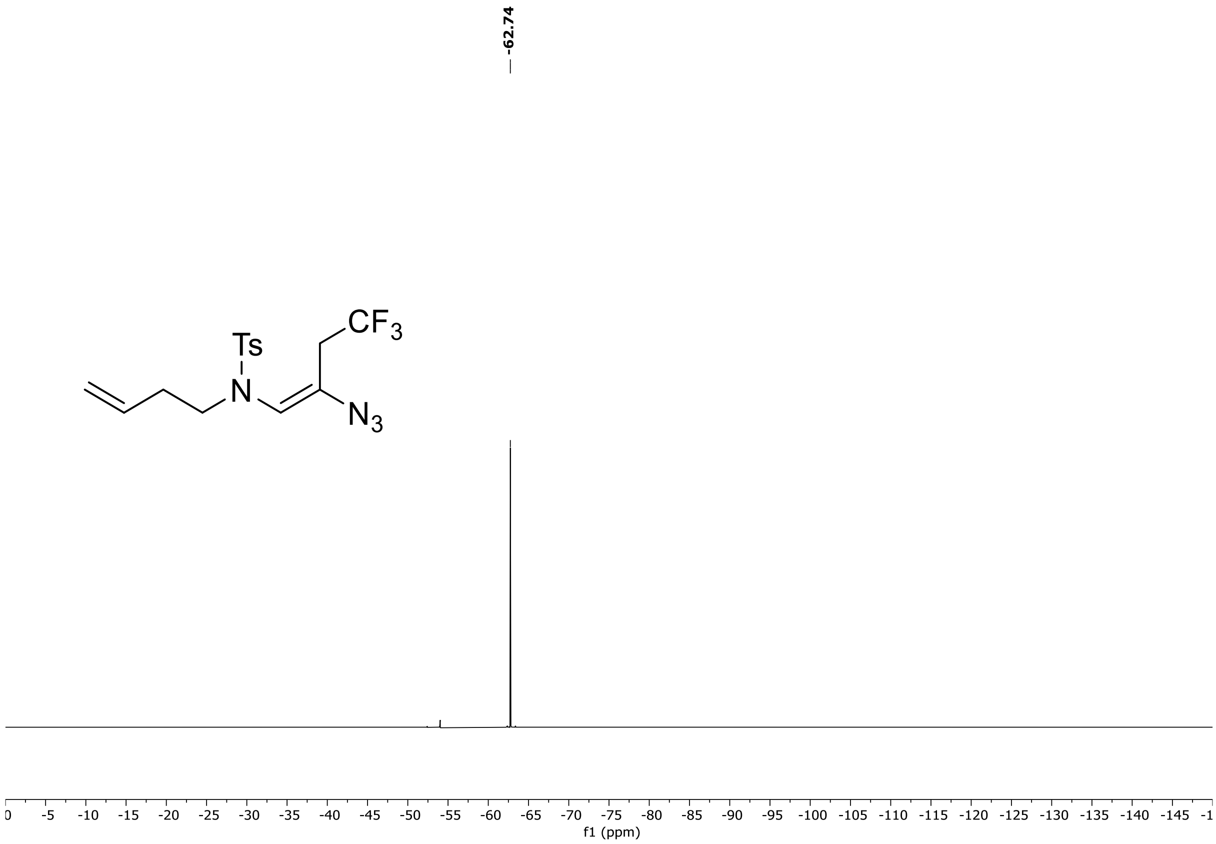
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 282 MHz) of **2c**



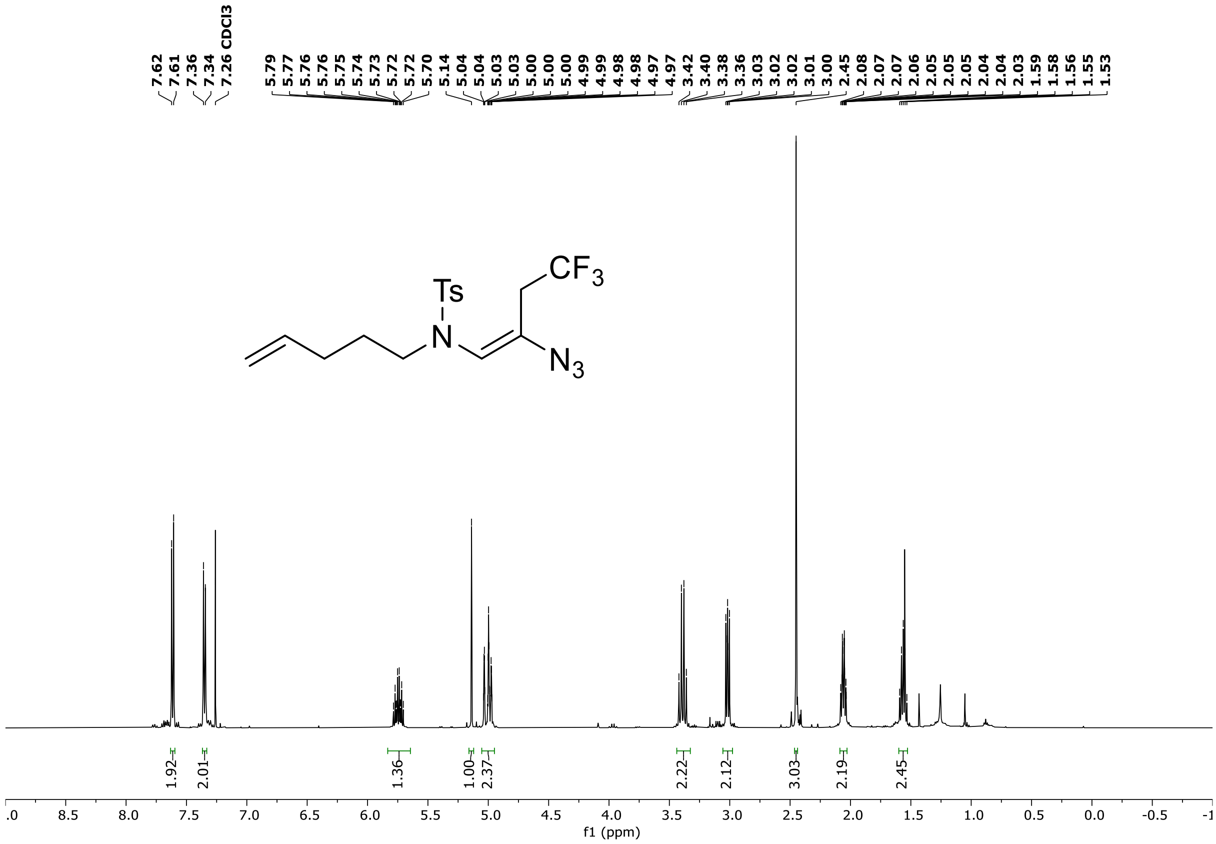
^{1}H NMR ($CDCl_3$, 300 MHz) of **2d**



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



$^{19}F\{^1H\}$ NMR ($CDCl_3$, 282 MHz) of **2d**



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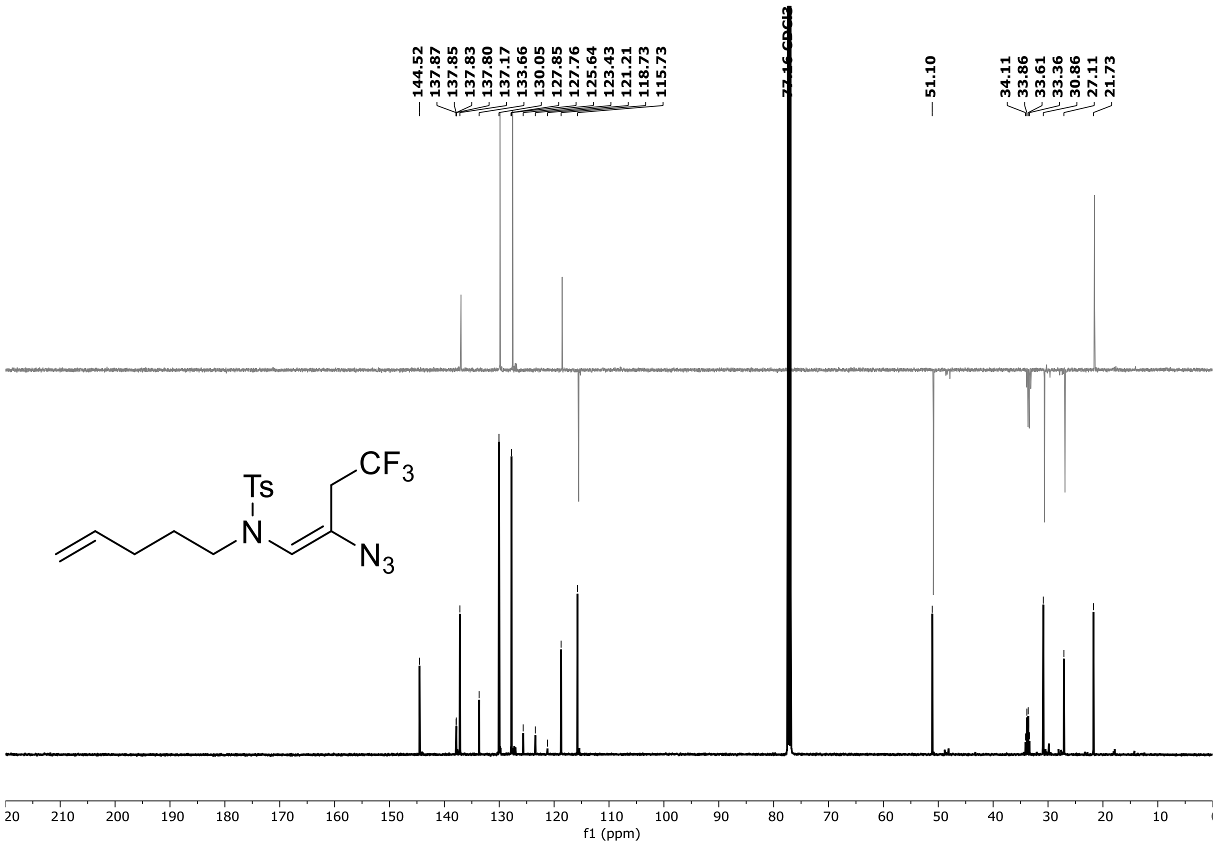
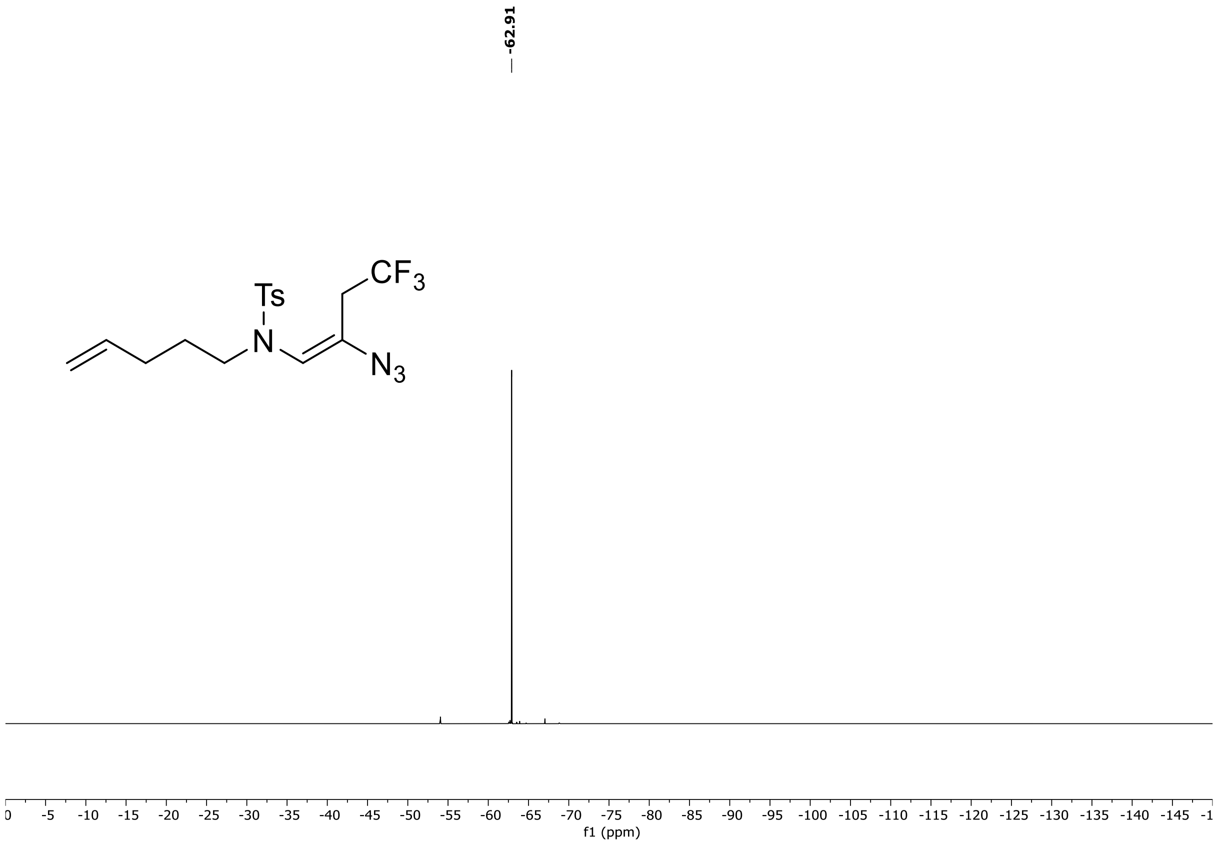
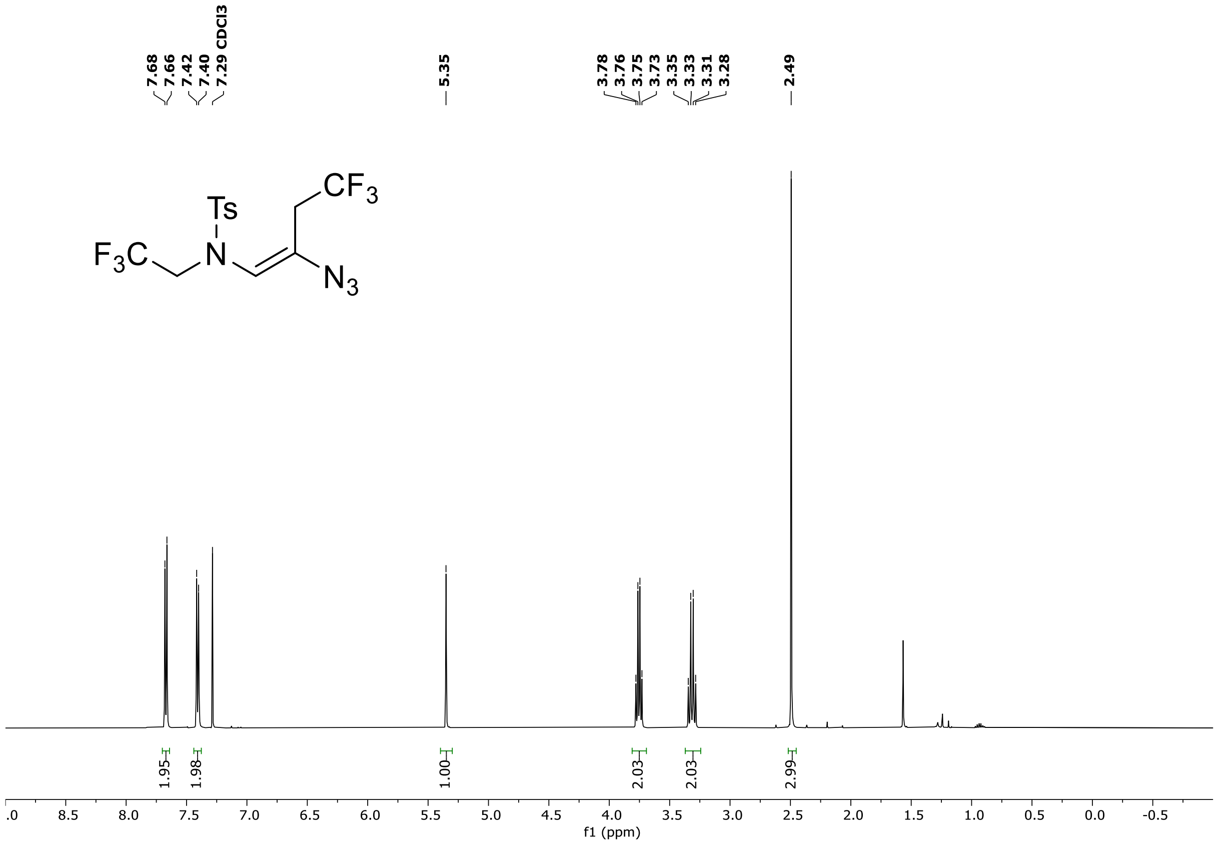


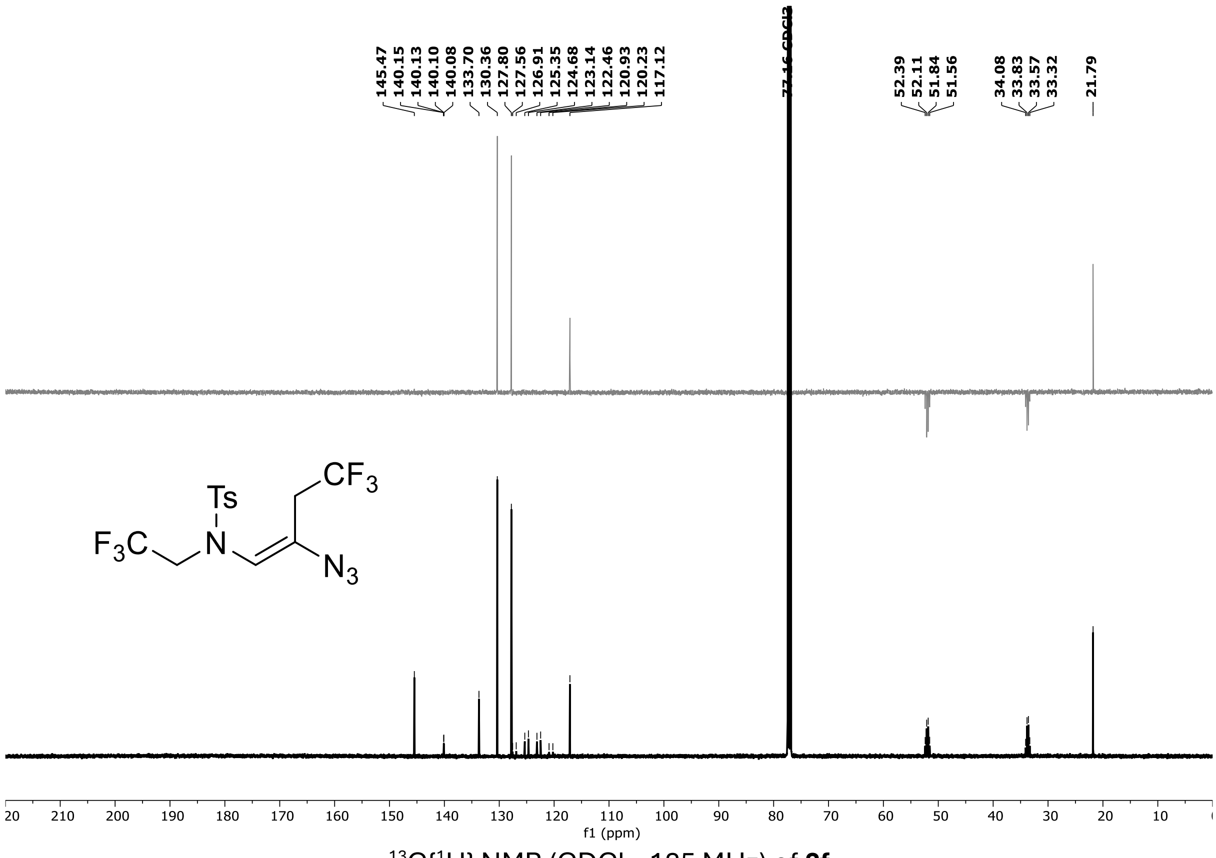
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) of **2e**



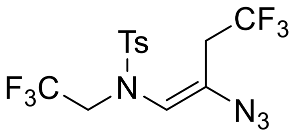
$^{19}F\{^1H\}$ NMR ($CDCl_3$, 282 MHz) of **2e**

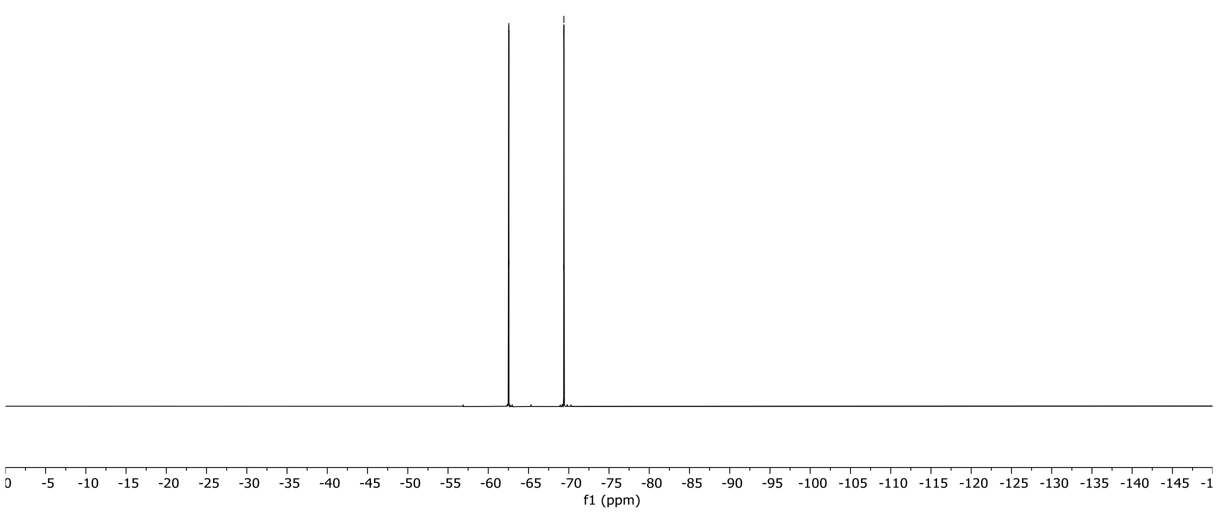


^{1}H NMR ($CDCl_3$, 500 MHz) of **2f**

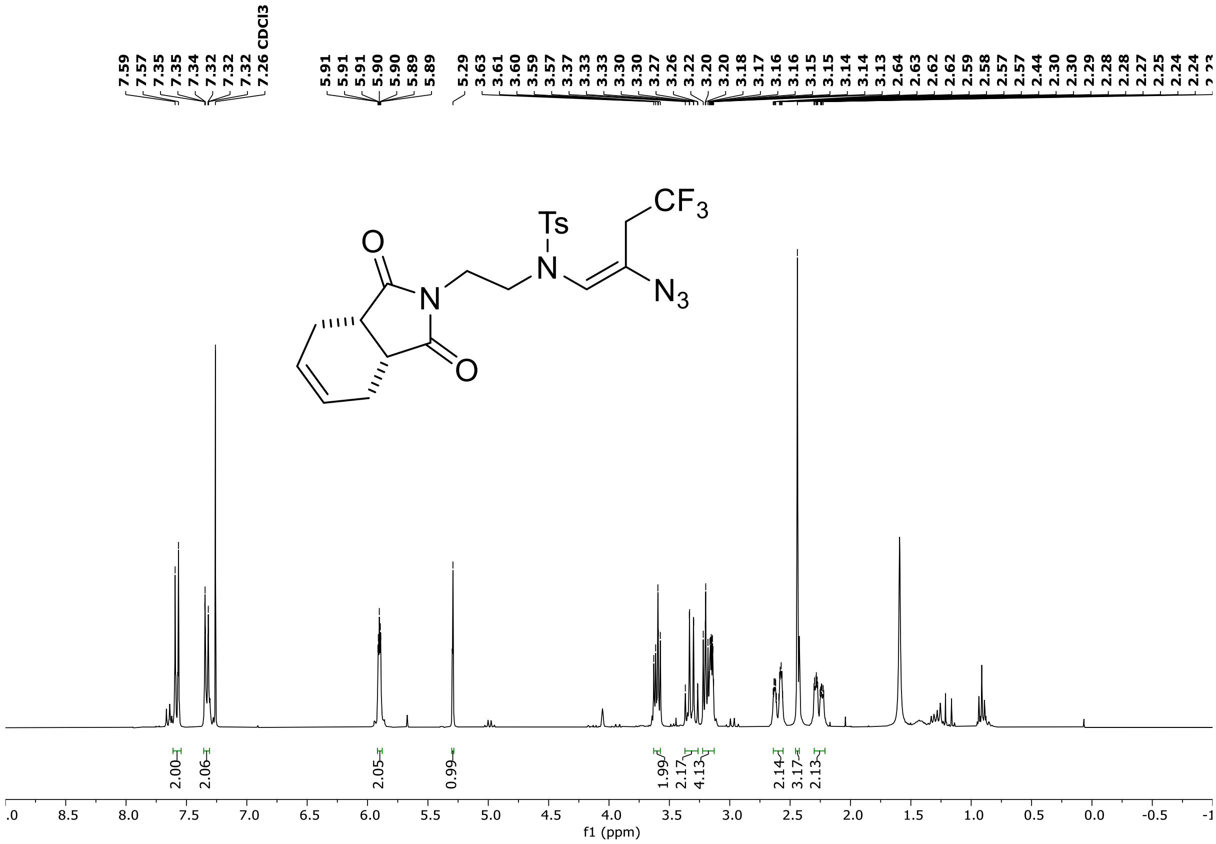


$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) of **2f**

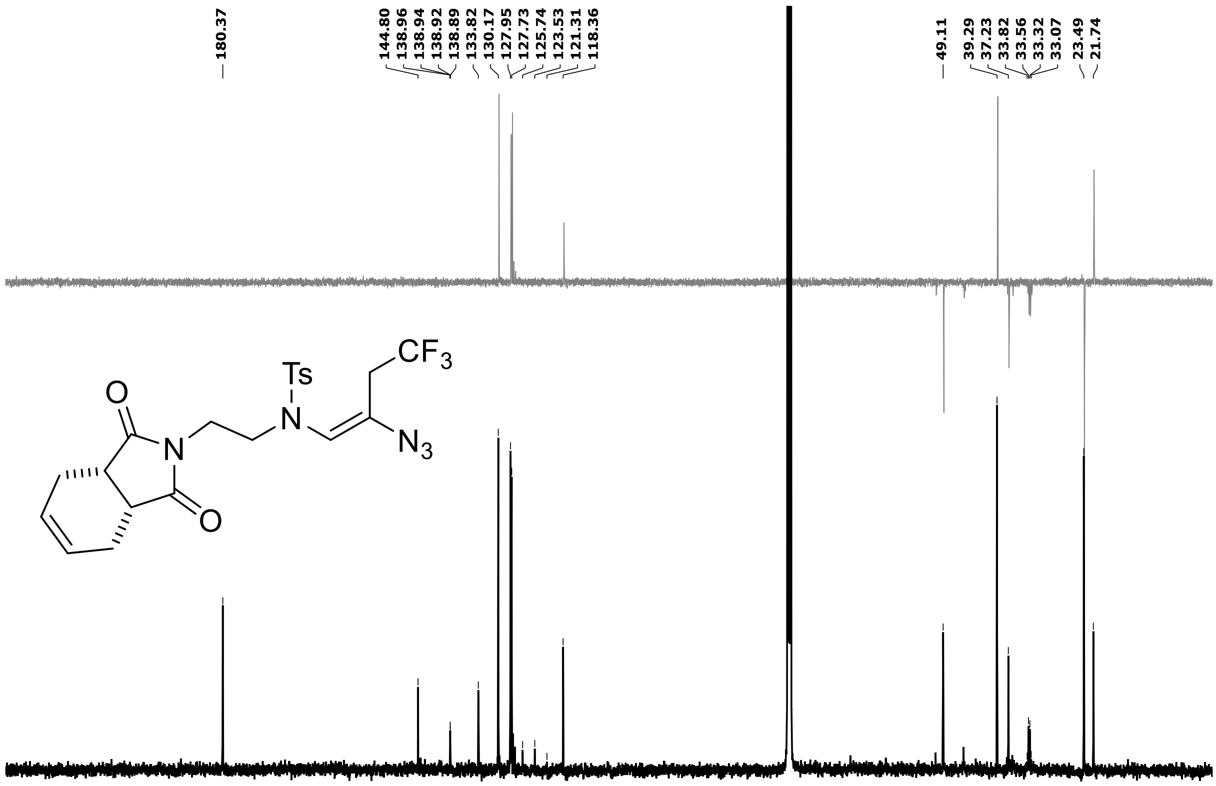




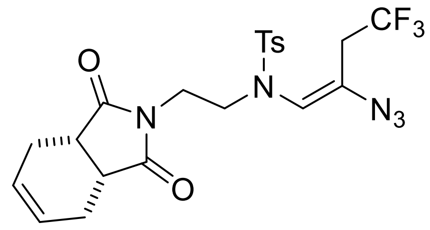
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 282 MHz) of **2f**

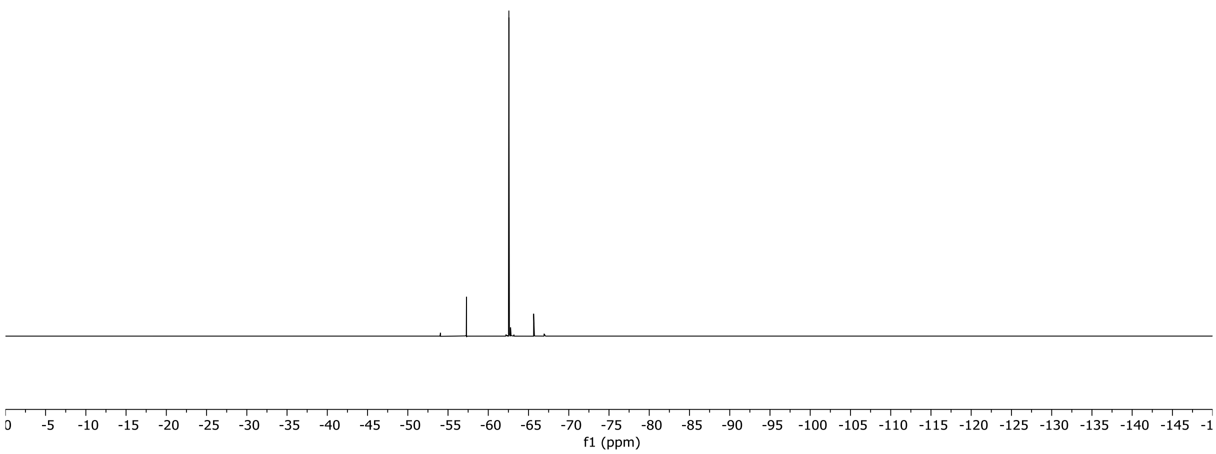


^{1}H NMR ($CDCl_3$, 300 MHz) of **2g**

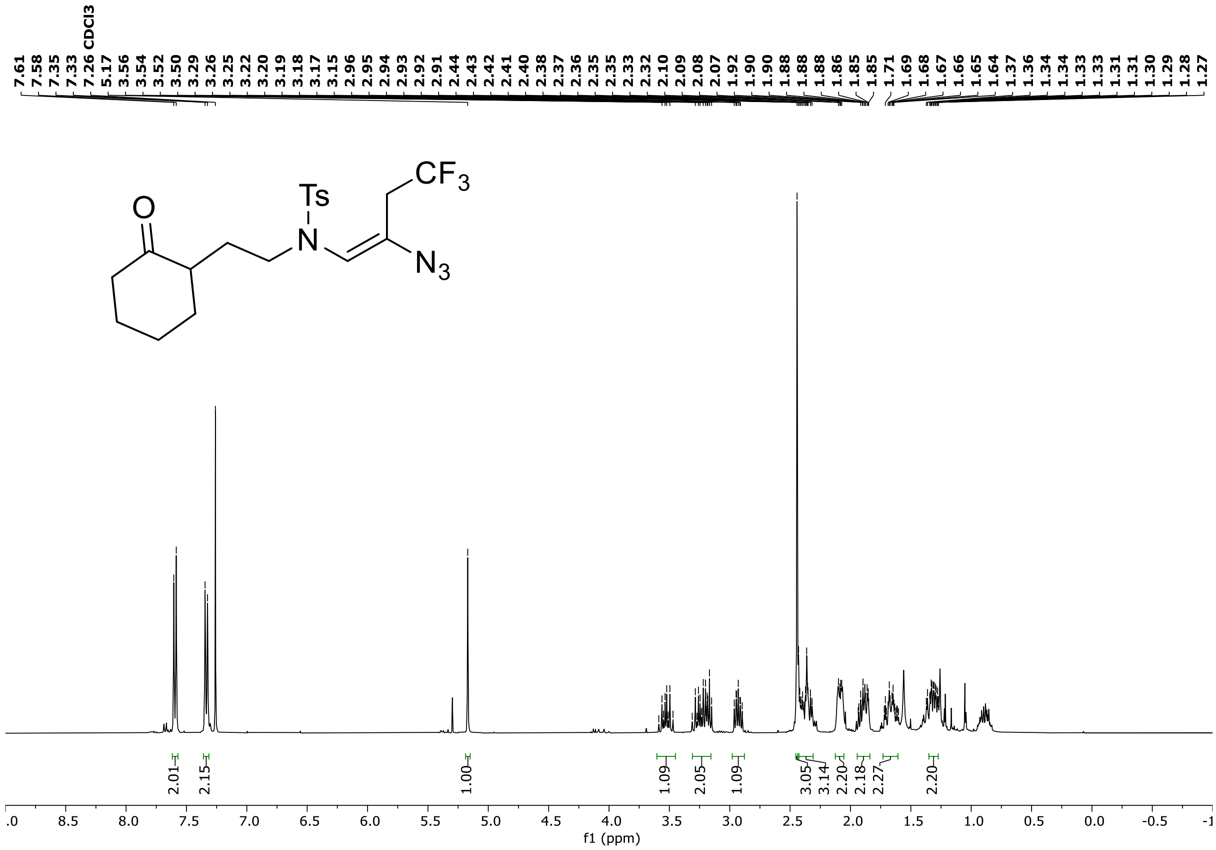


^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) of **2g**

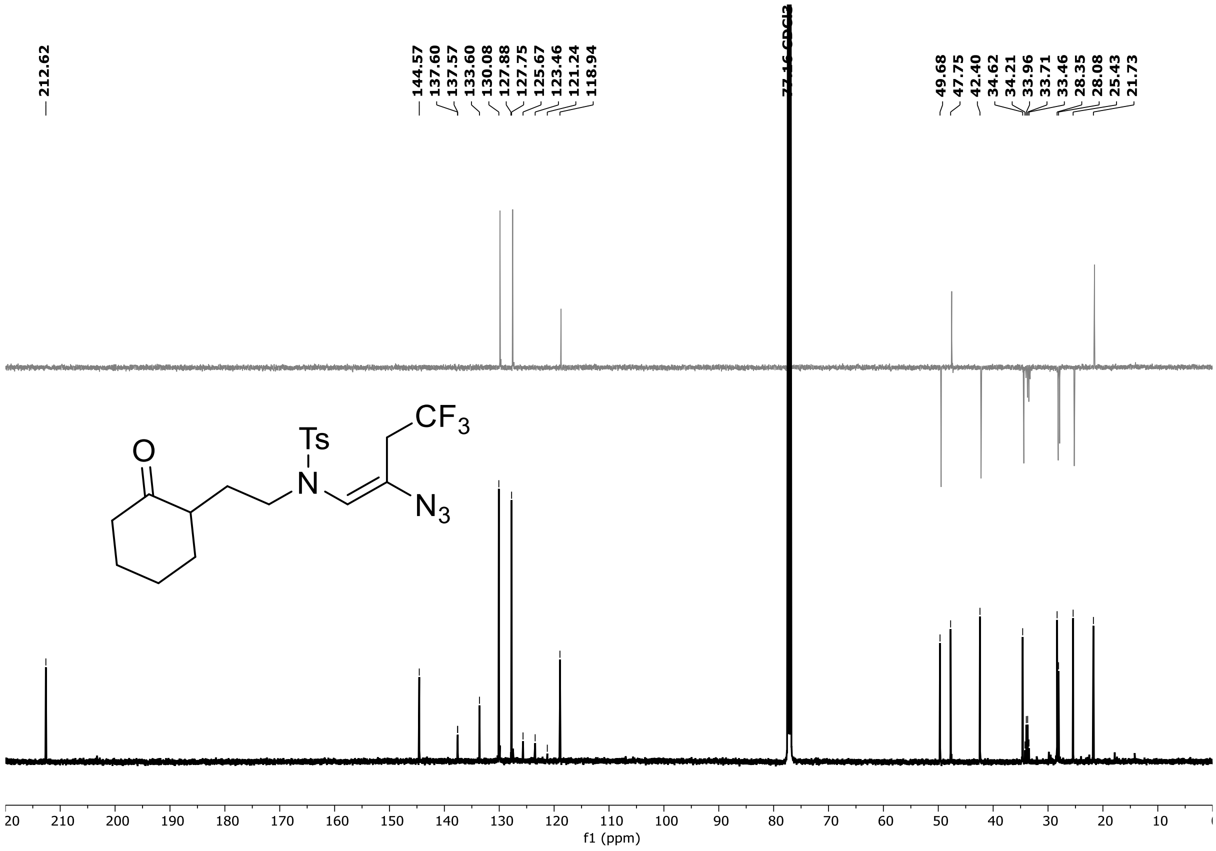




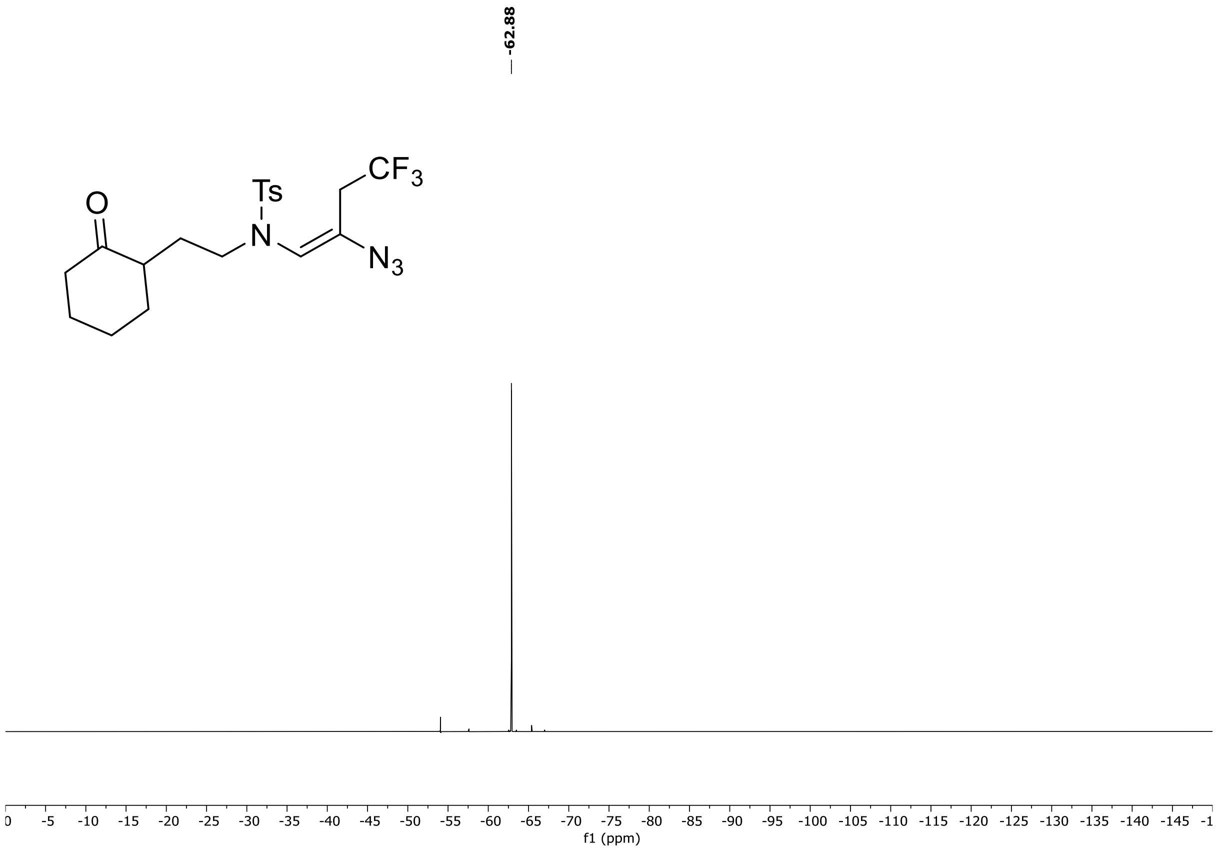
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 282 MHz) of **2g**



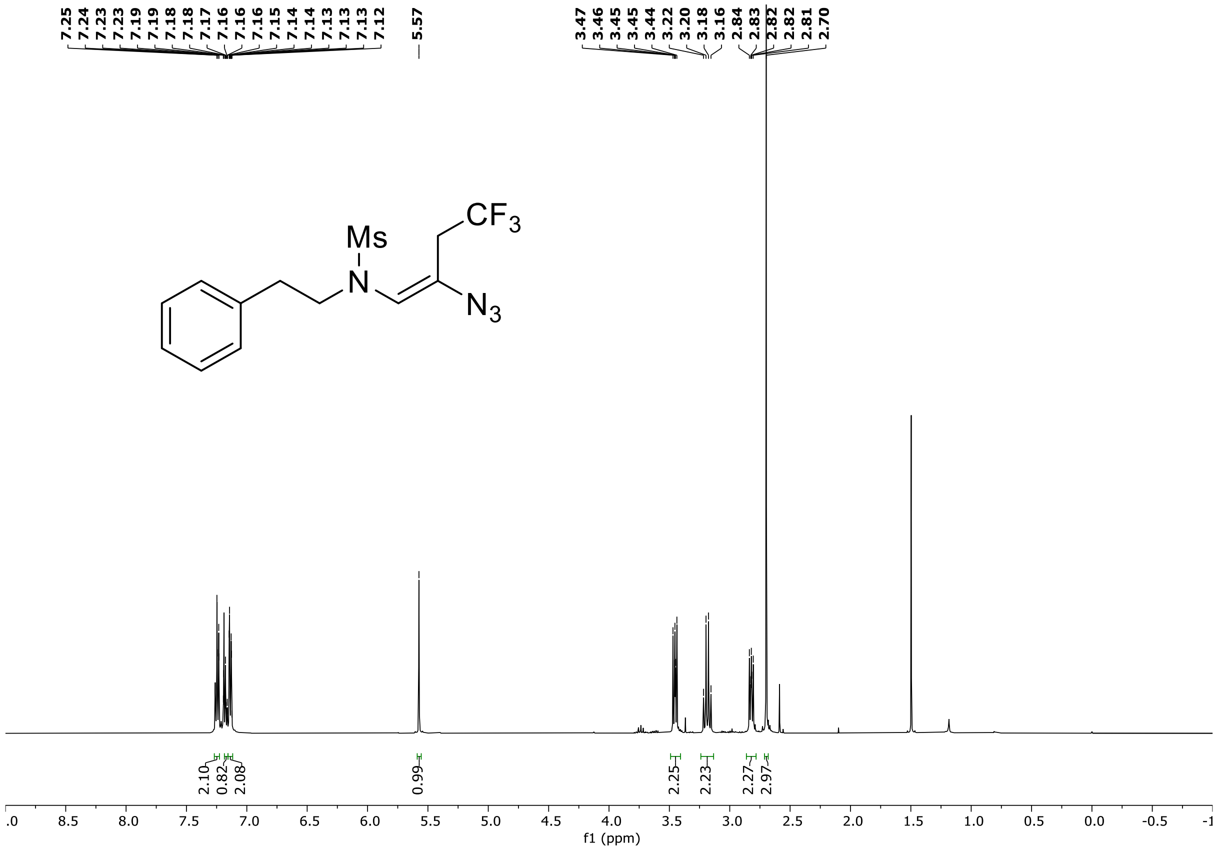
^{1}H NMR ($CDCl_3$, 400 MHz) of **2h**



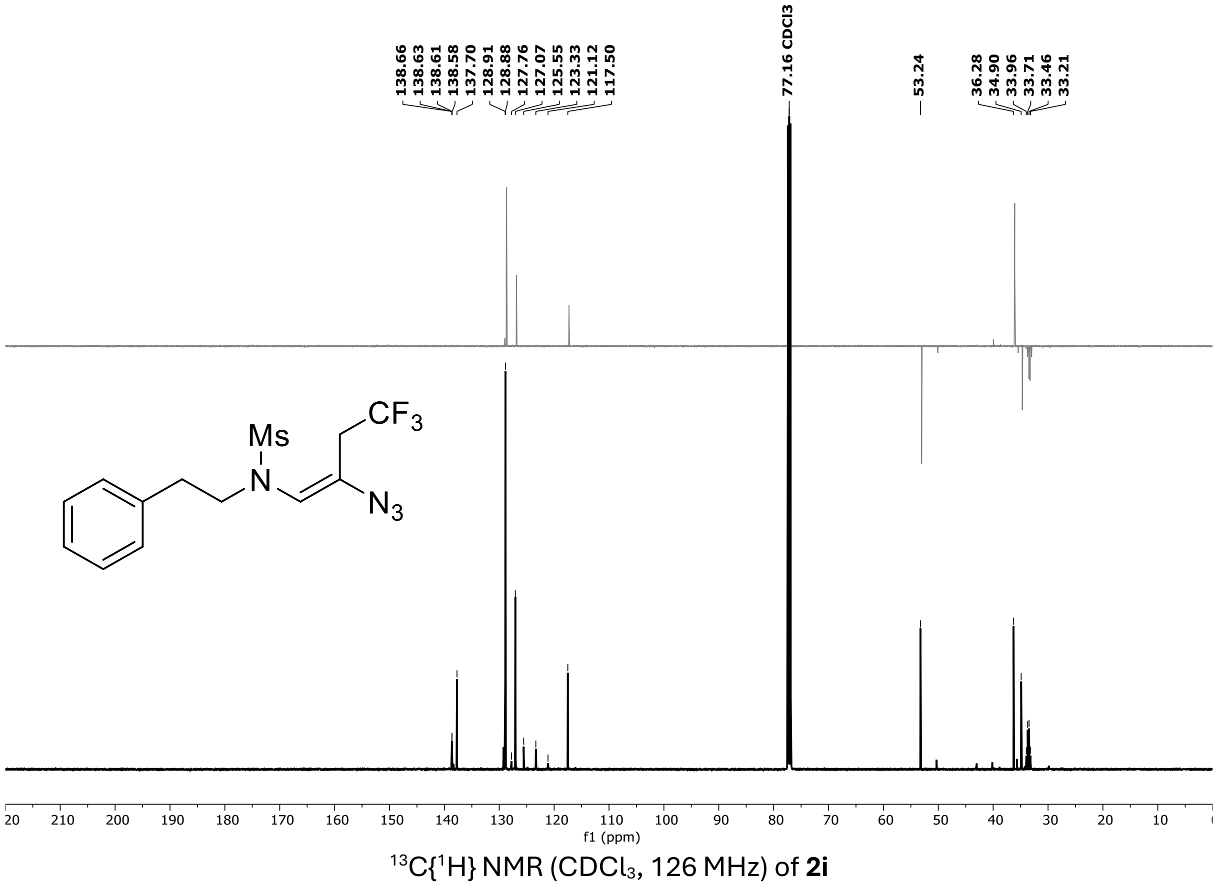
^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) of **2h**



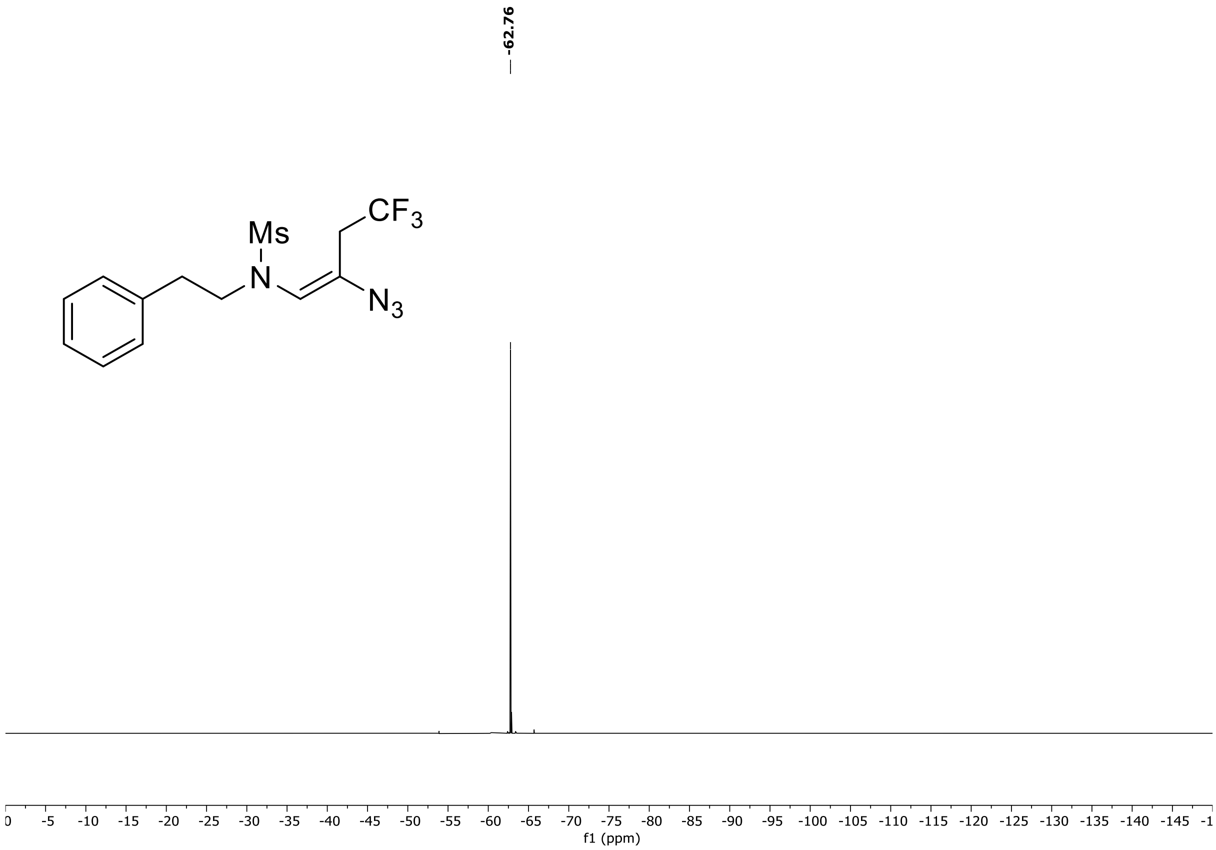
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 282 MHz) of **2h**



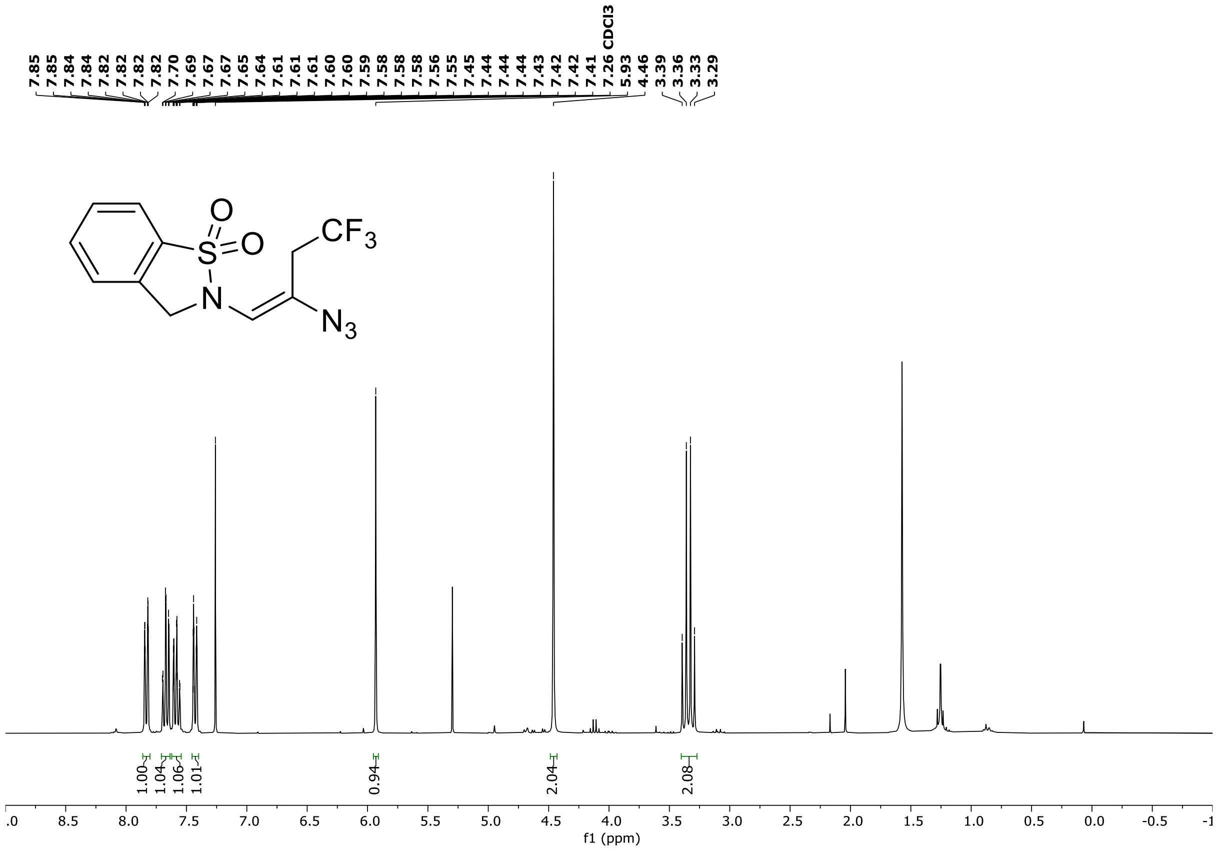
^{1}H NMR ($CDCl_3$, 300 MHz) of **2i**



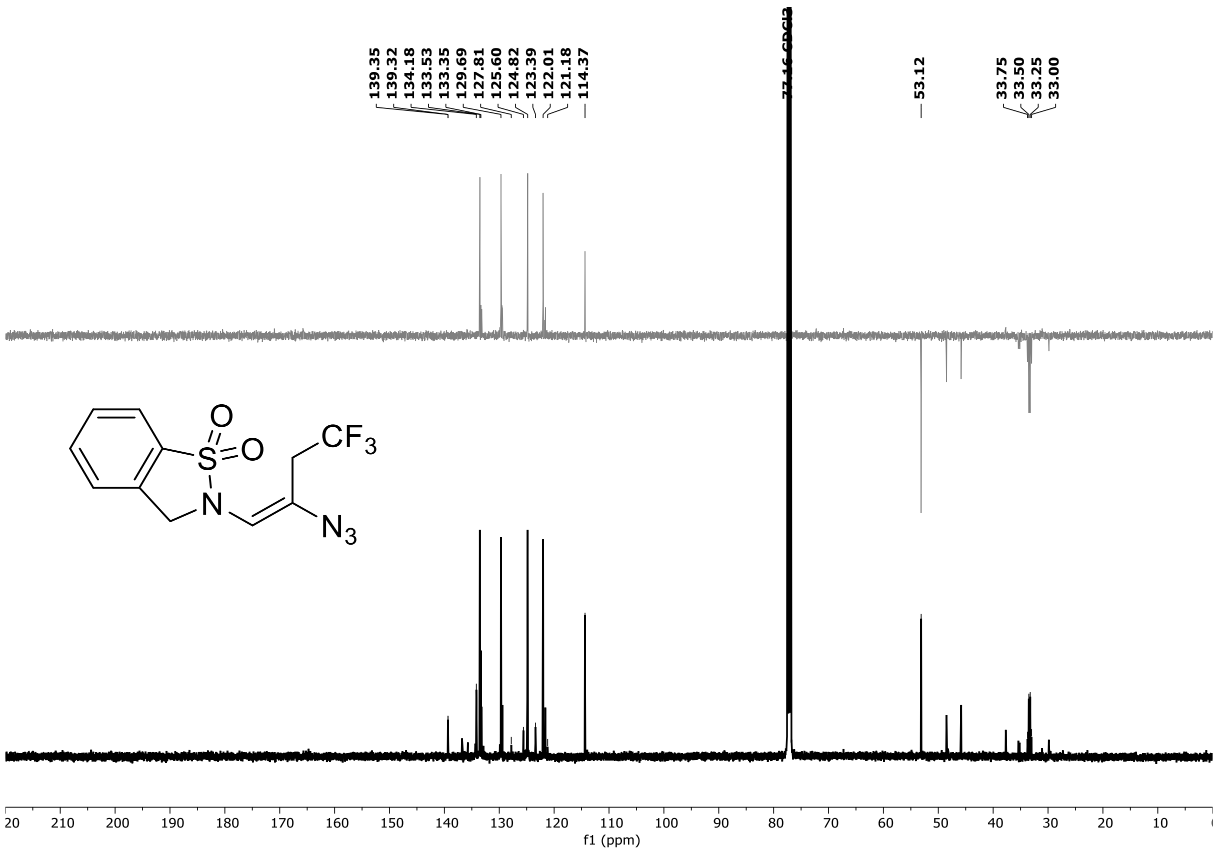
^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) of **2i**



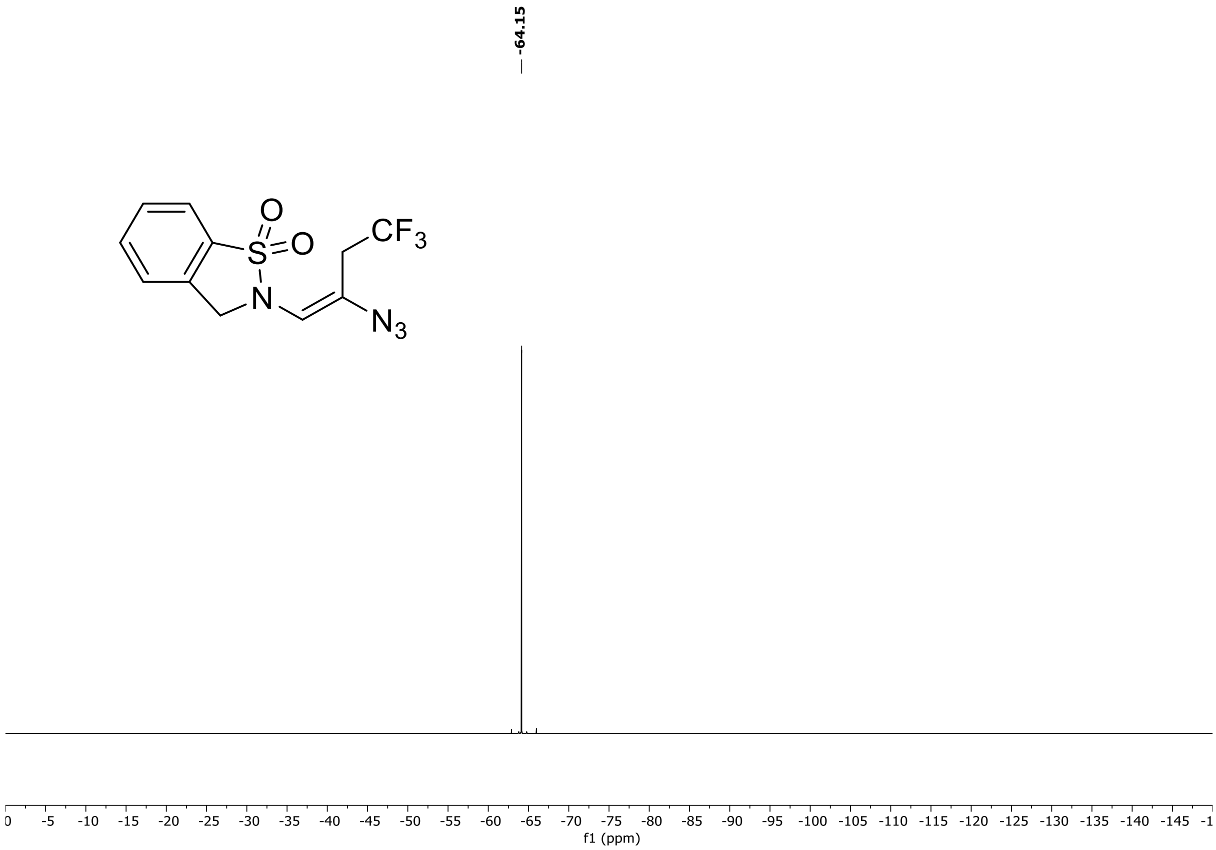
$^{19}F\{^1H\}$ NMR ($CDCl_3$, 282 MHz) of **2i**



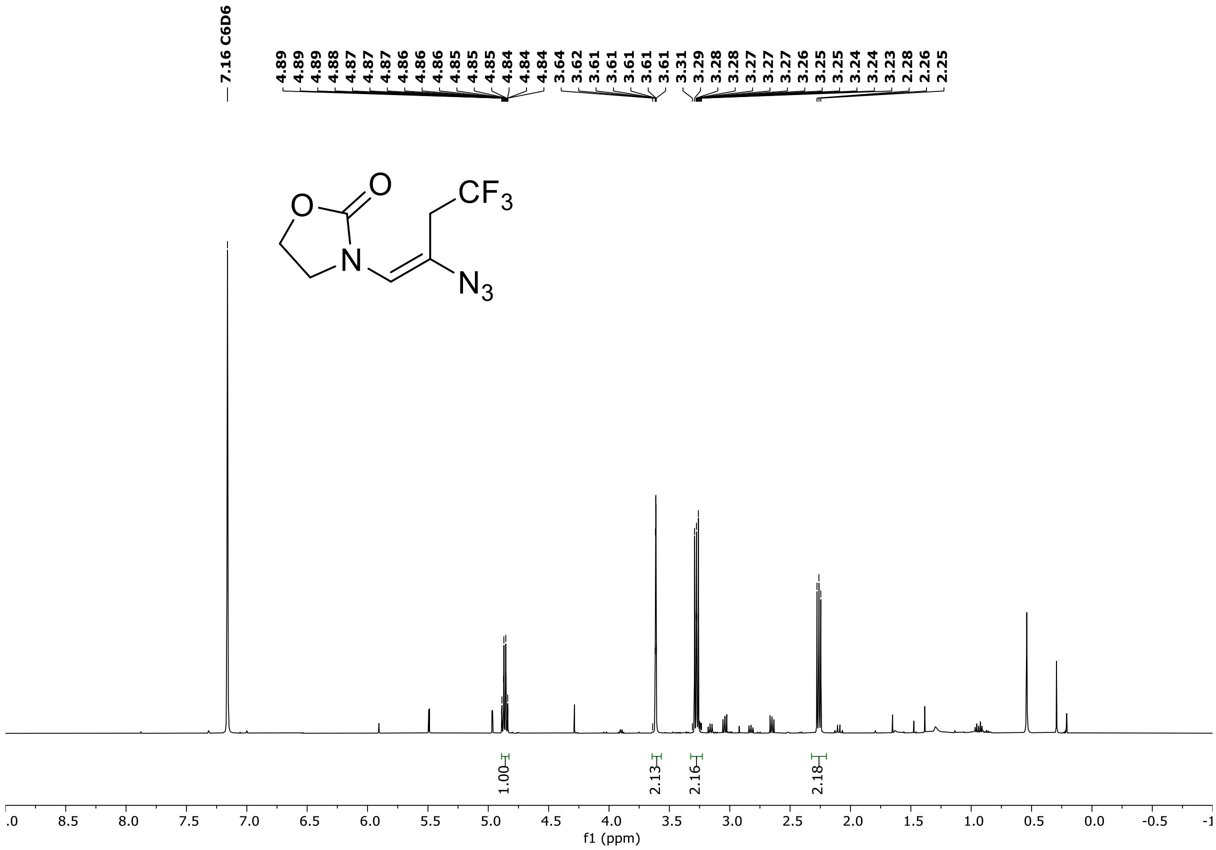
^{1}H NMR (CDCl$_3$, 300 MHz) of **2j**



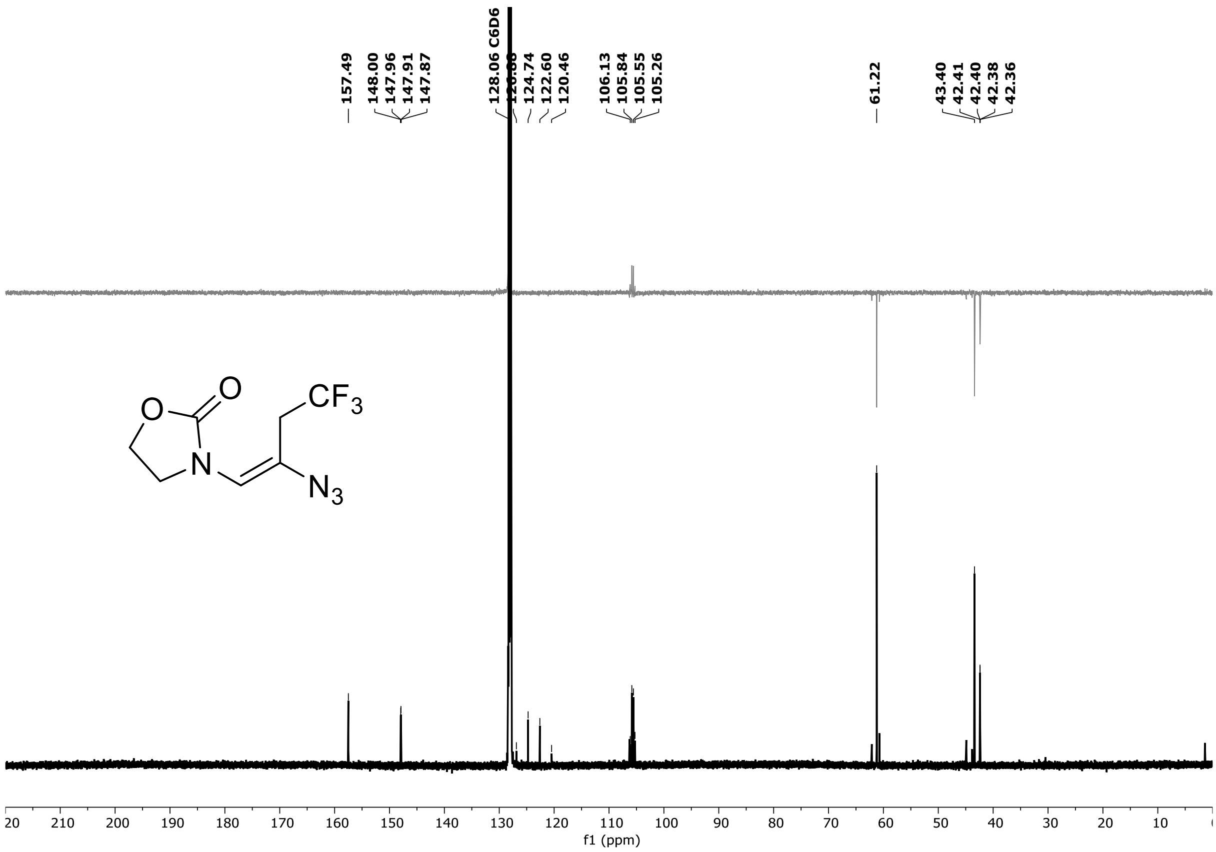
^{13}C{^{1}H} NMR (CDCl$_3$, 126 MHz) of **2j**



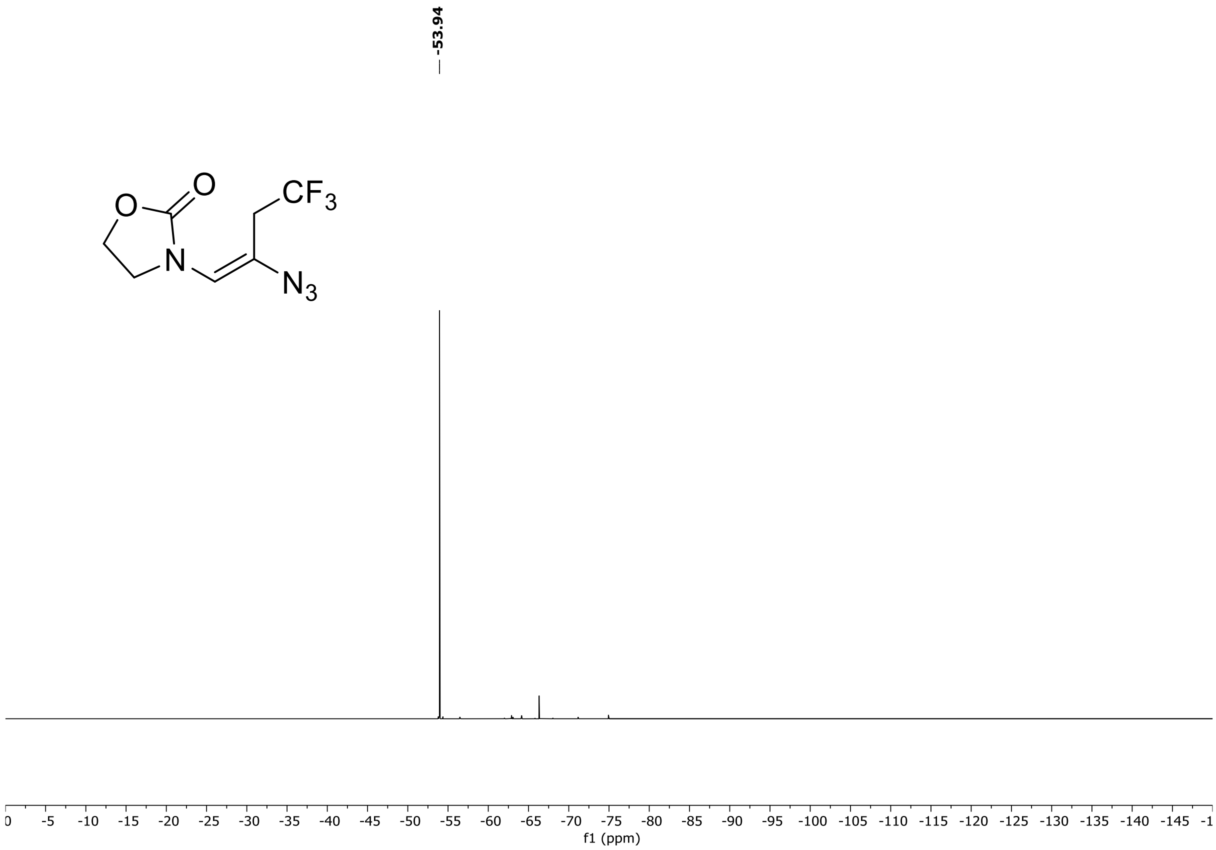
^{9}F{^{1}H} NMR ($CDCl_3$, 282 MHz) of **2j**



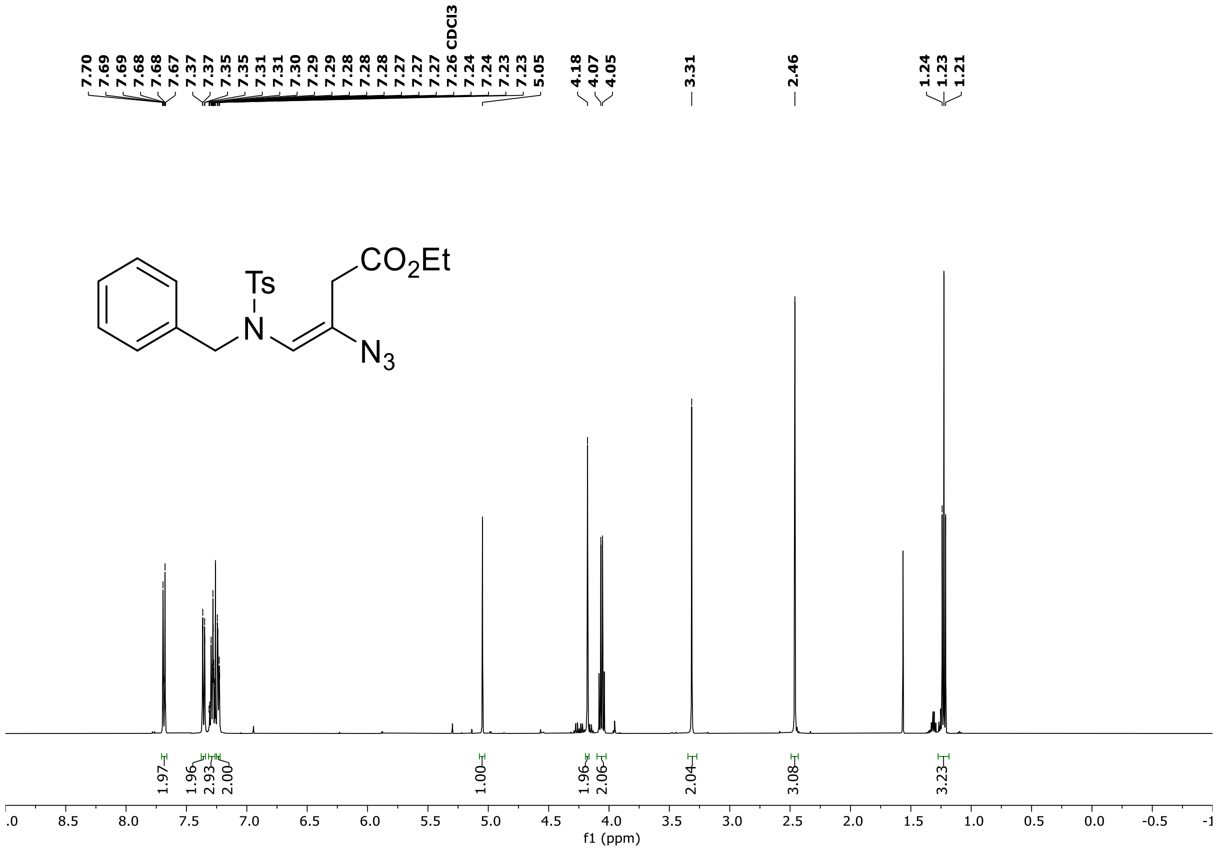
^1H NMR (C_6D_6, 500 MHz) of **2k**



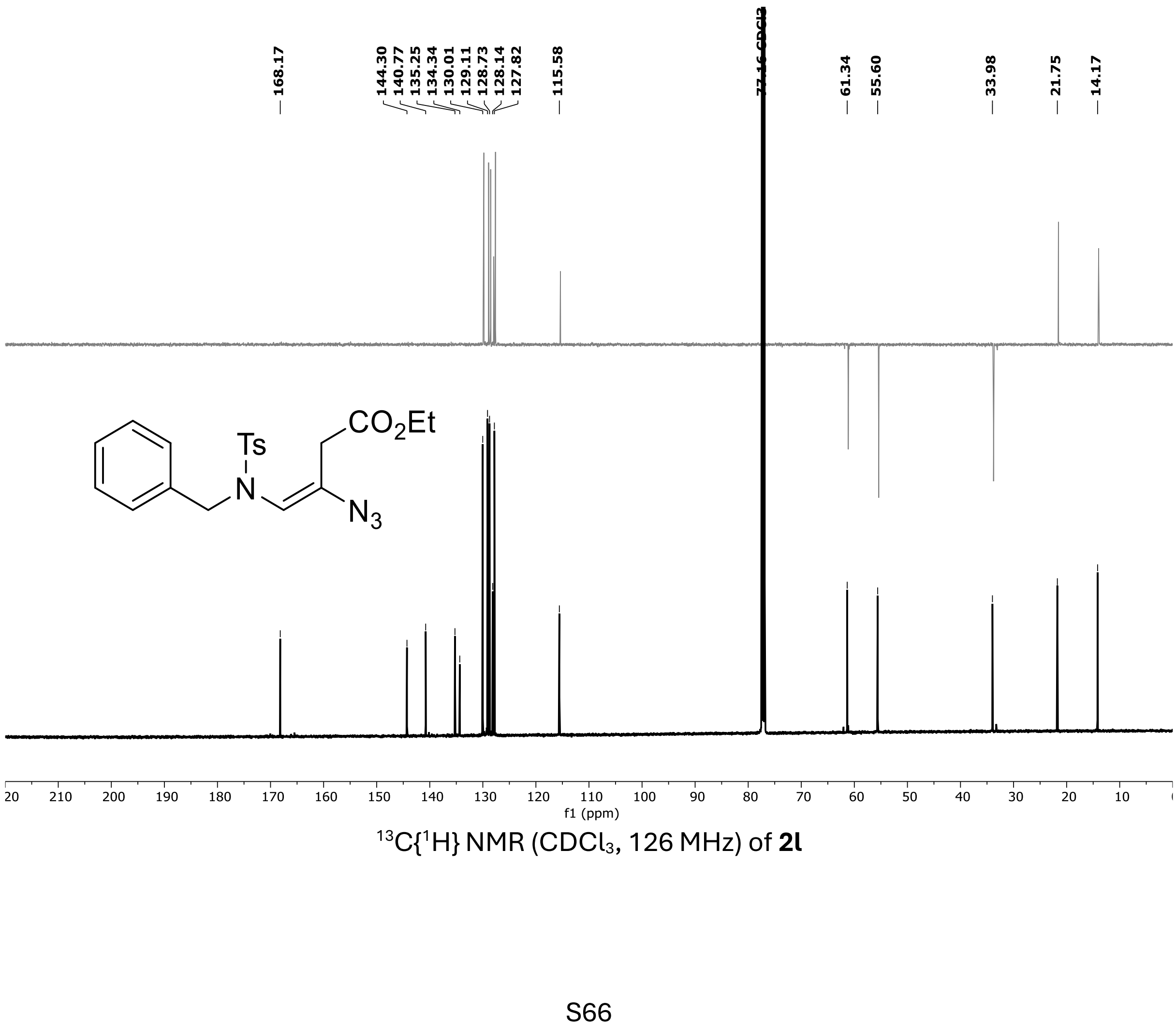
$^{13}C\{^1H\}$ NMR (C_6D_6, 126 MHz) of **2k**



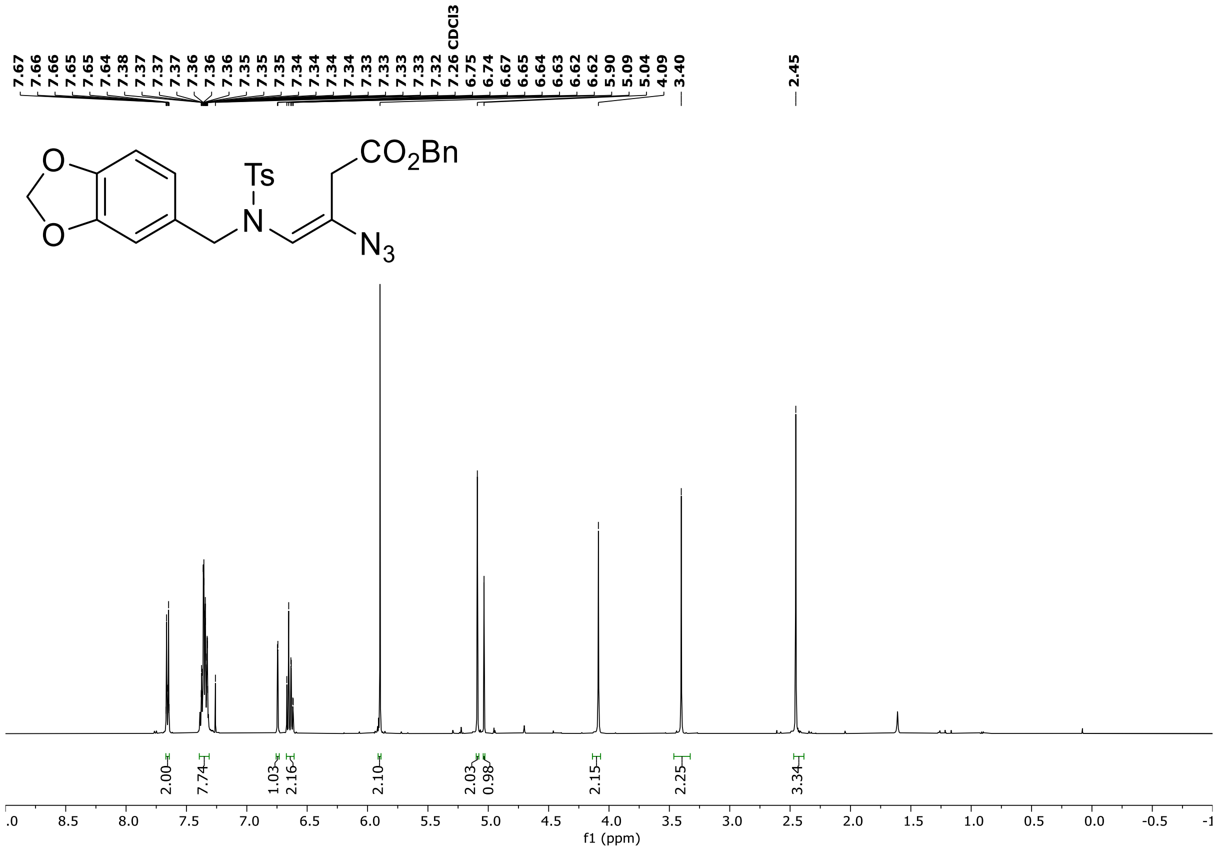
$^{19}F\{^{1}H\}$ NMR (C_6D_6, 471 MHz) of **2k**



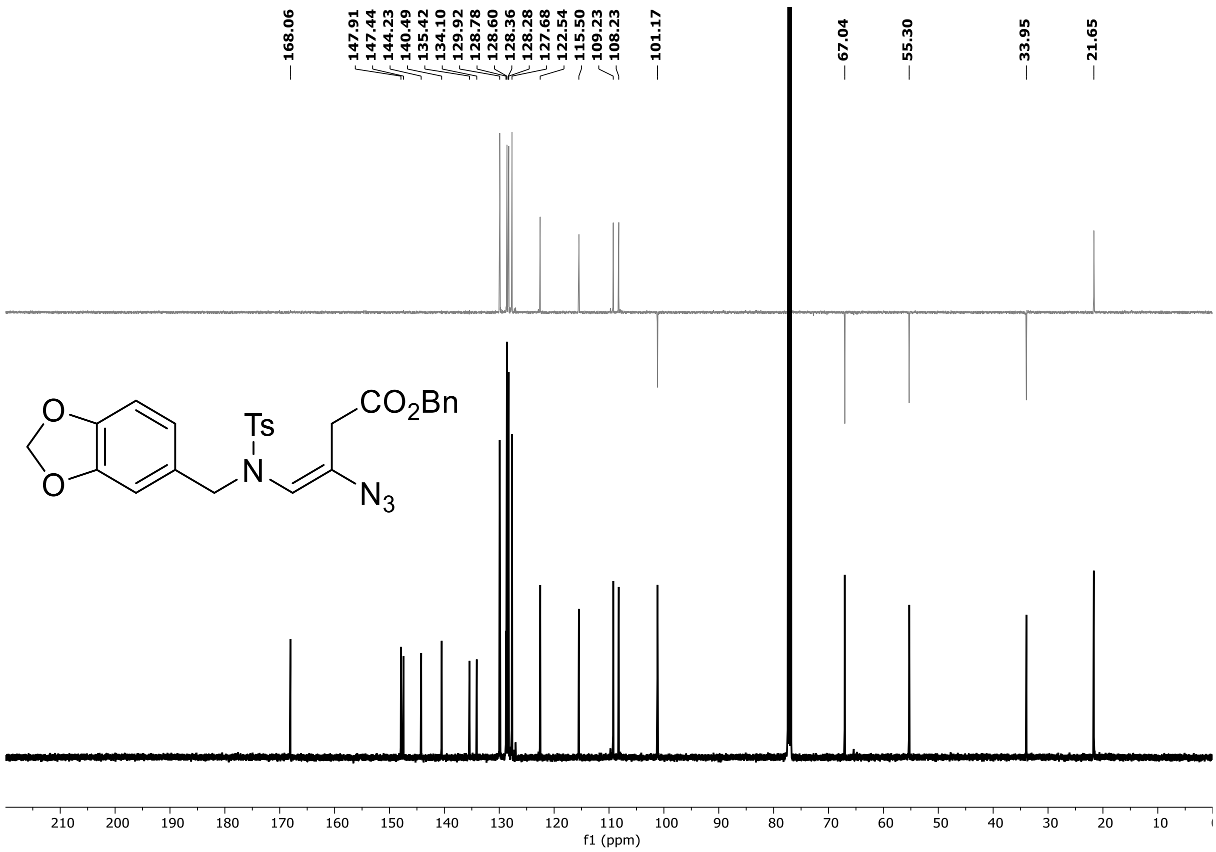
^{1}H NMR ($CDCl_3$, 500 MHz) of **2l**



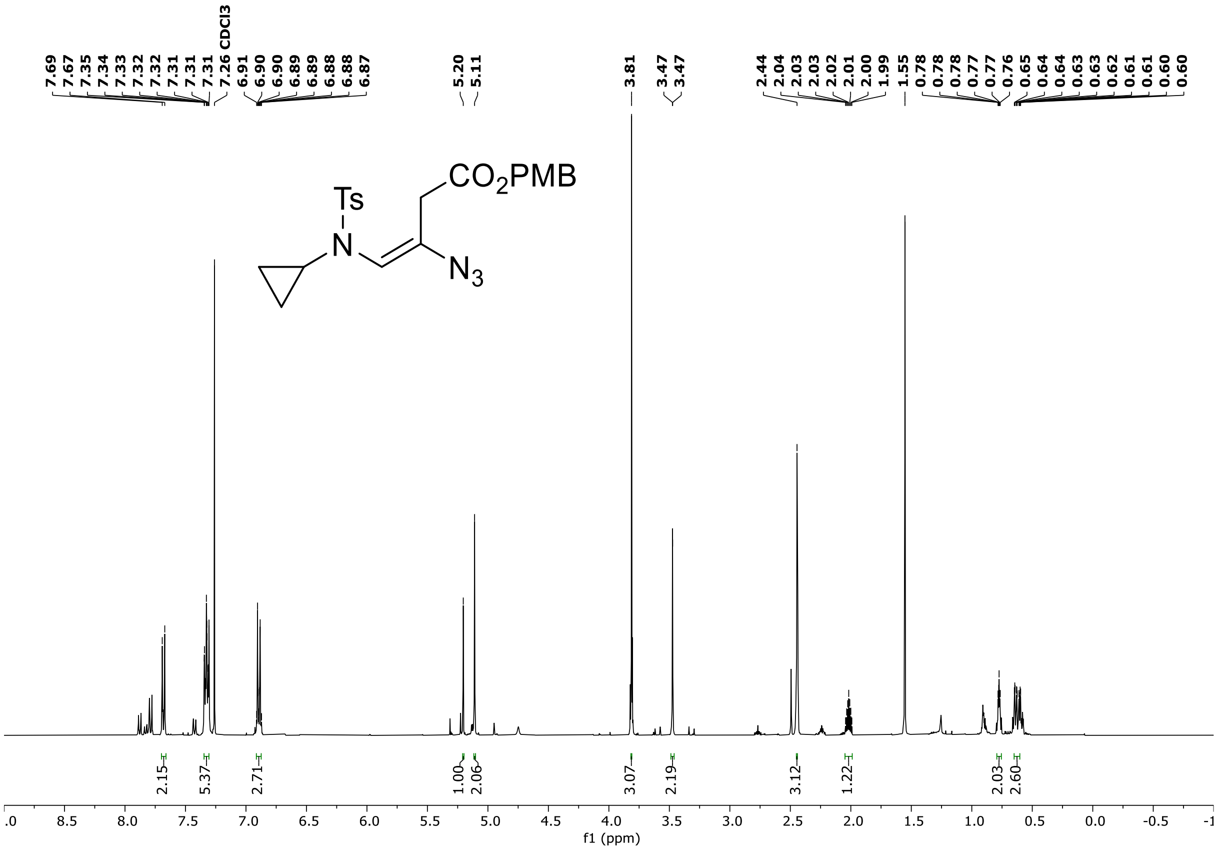
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) of **2l**



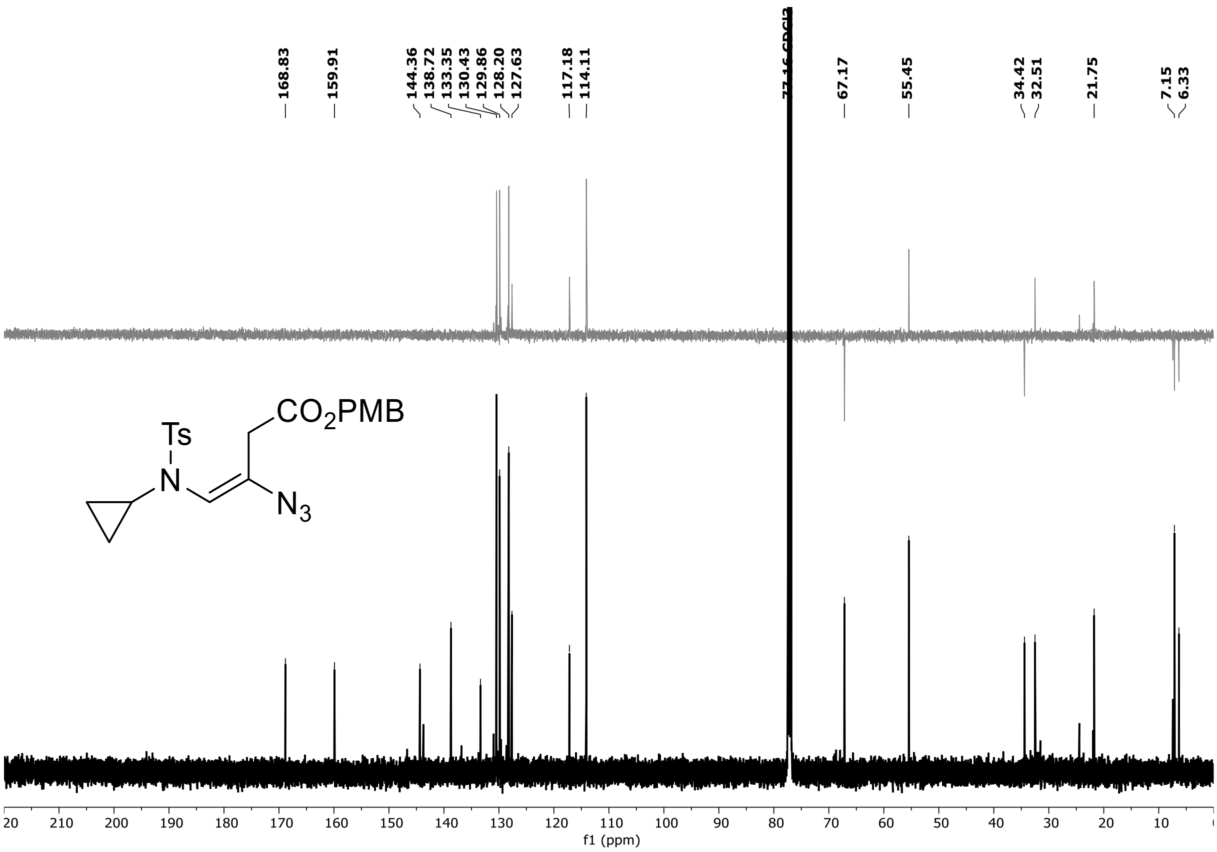
^{1}H NMR ($CDCl_3$, 500 MHz) of **2m**



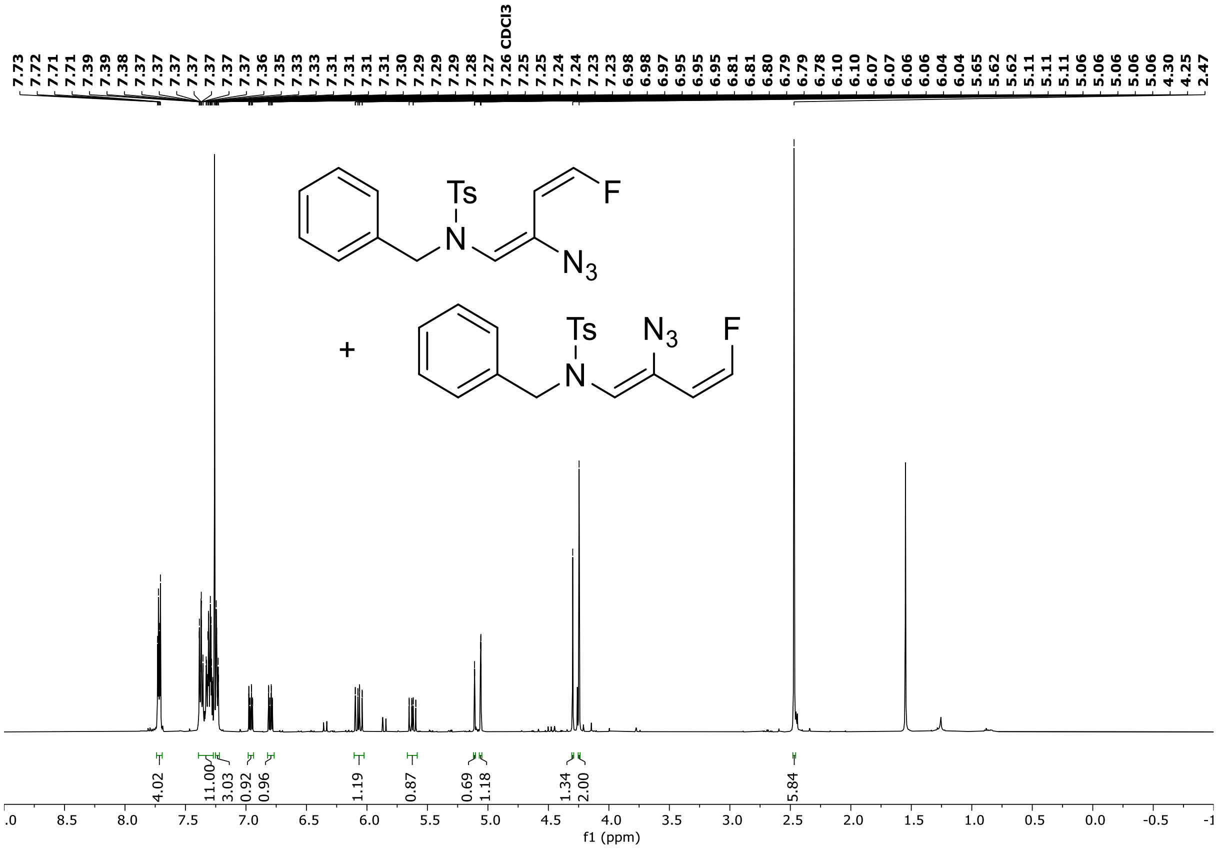
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) of **2m**



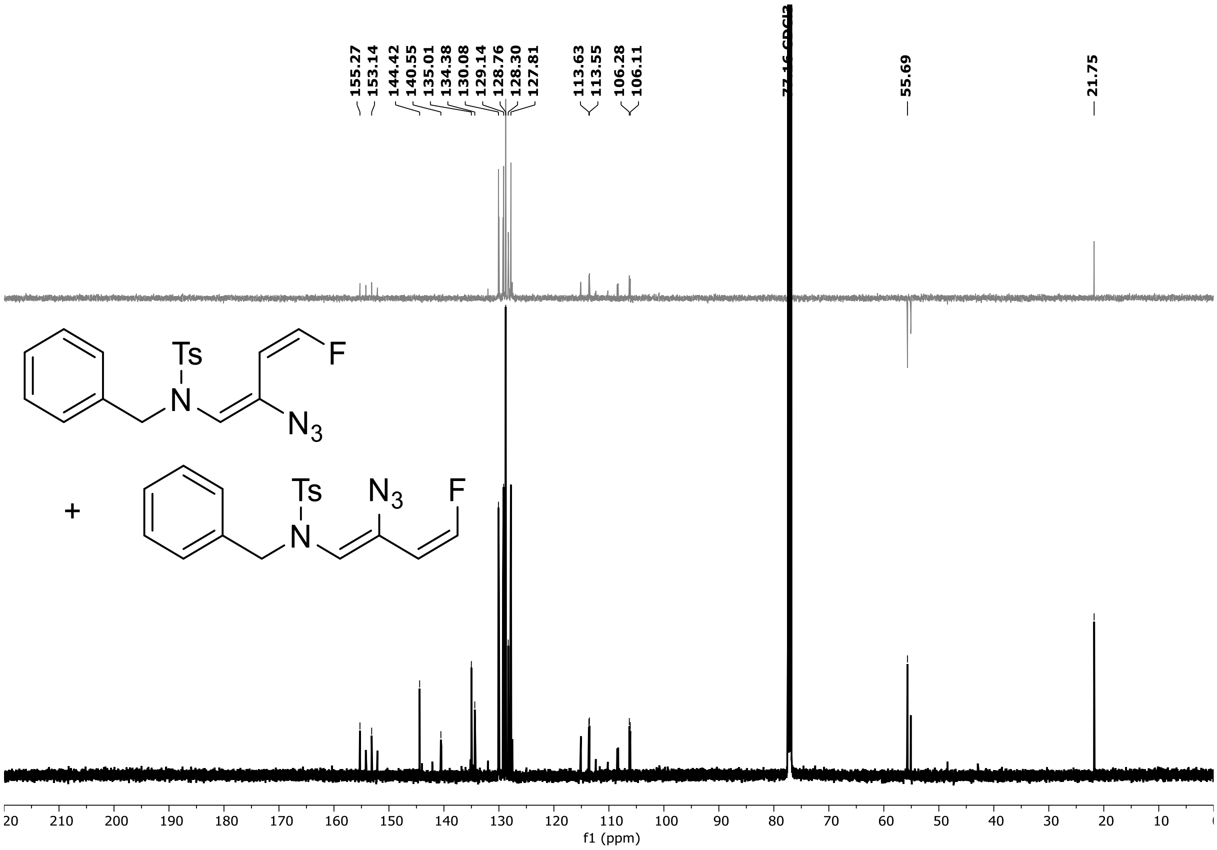
^{1}H NMR ($CDCl_3$, 400 MHz) of **2n**



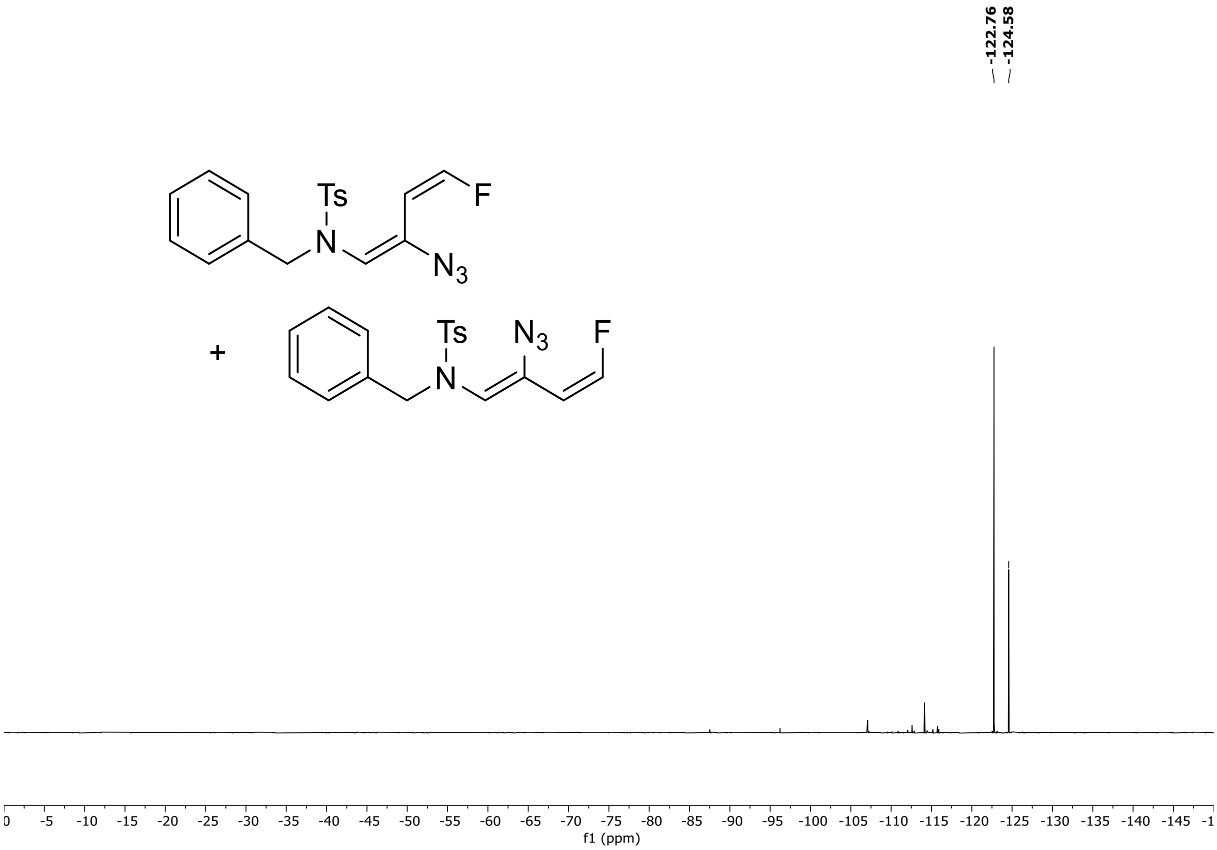
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) of **2n**



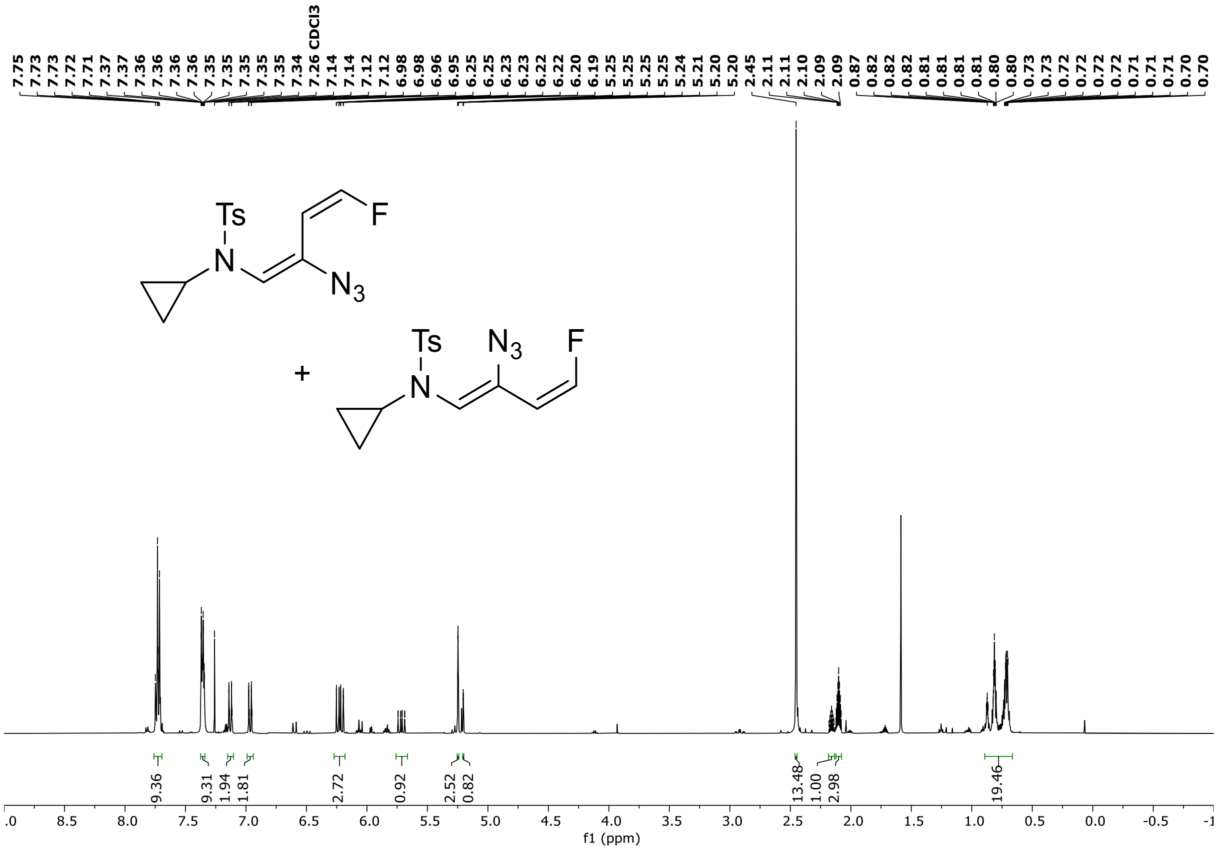
^{1}H NMR ($CDCl_3$, 500 MHz) of **2o**



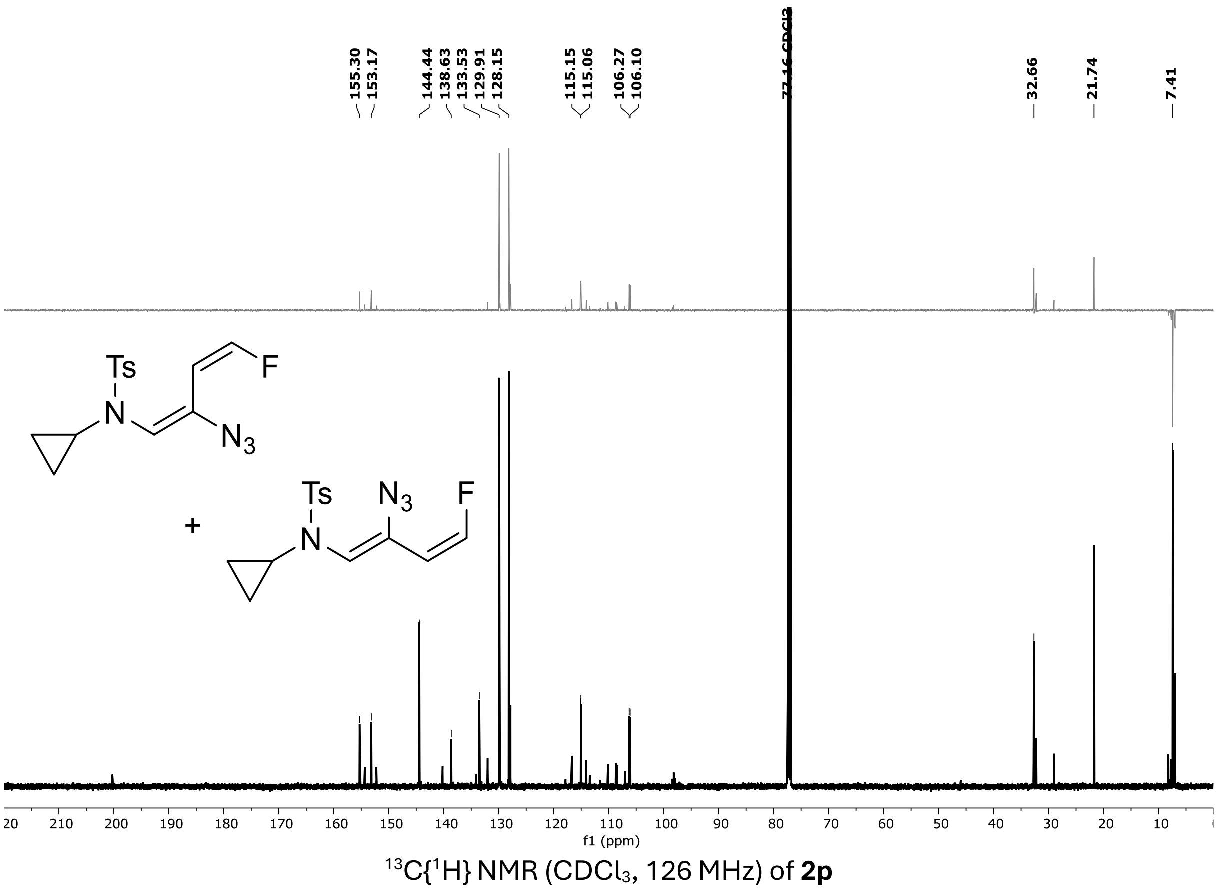
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) of **2o**



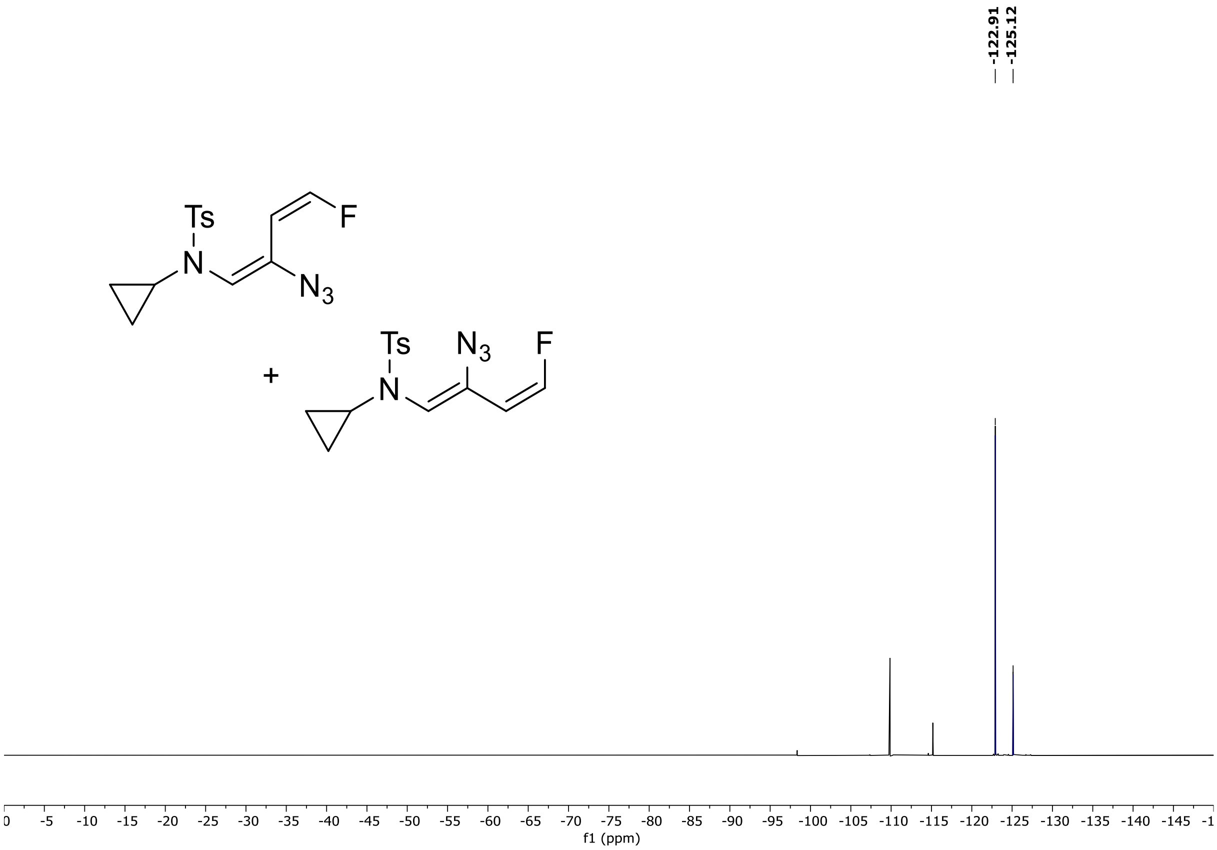
$^{19}F\{^1H\}$ NMR ($CDCl_3$, 471 MHz) of **2o**



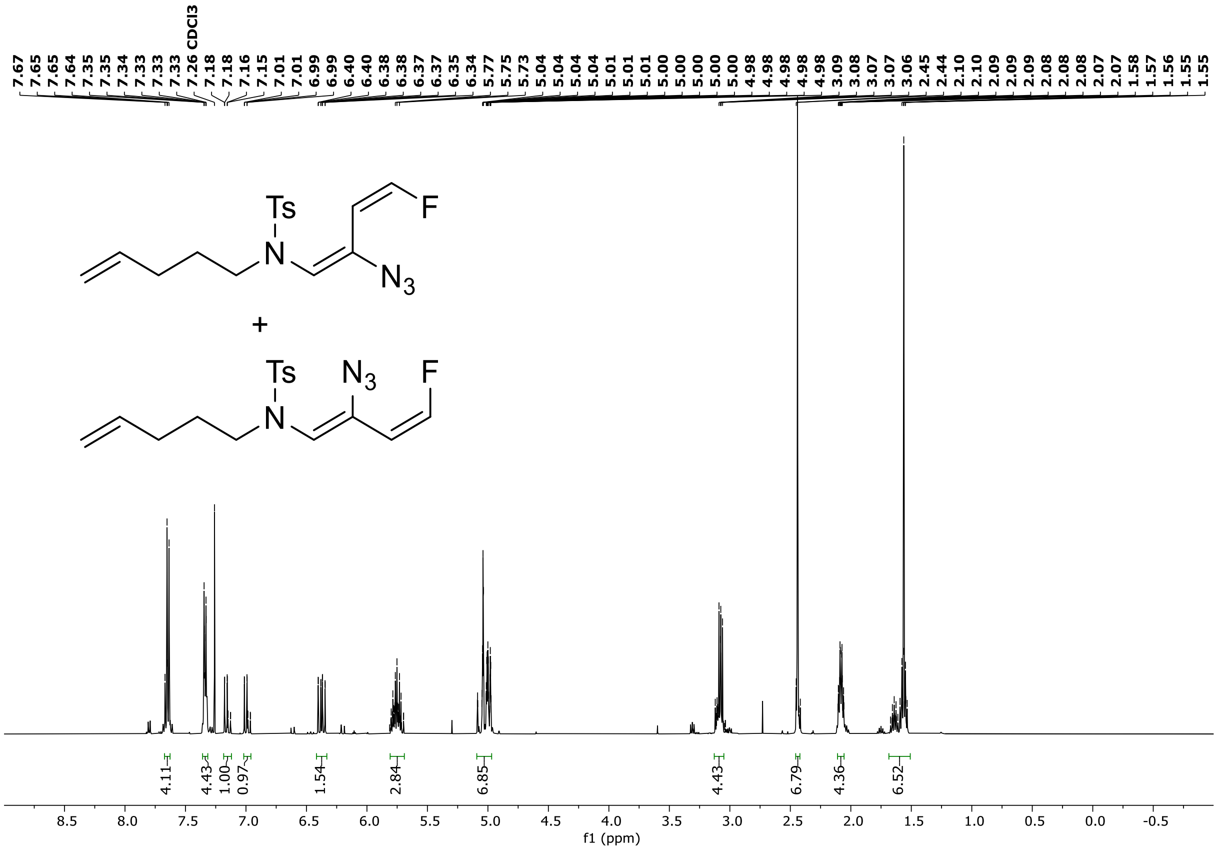
^{1}H NMR ($CDCl_3$, 500 MHz) of **2p**



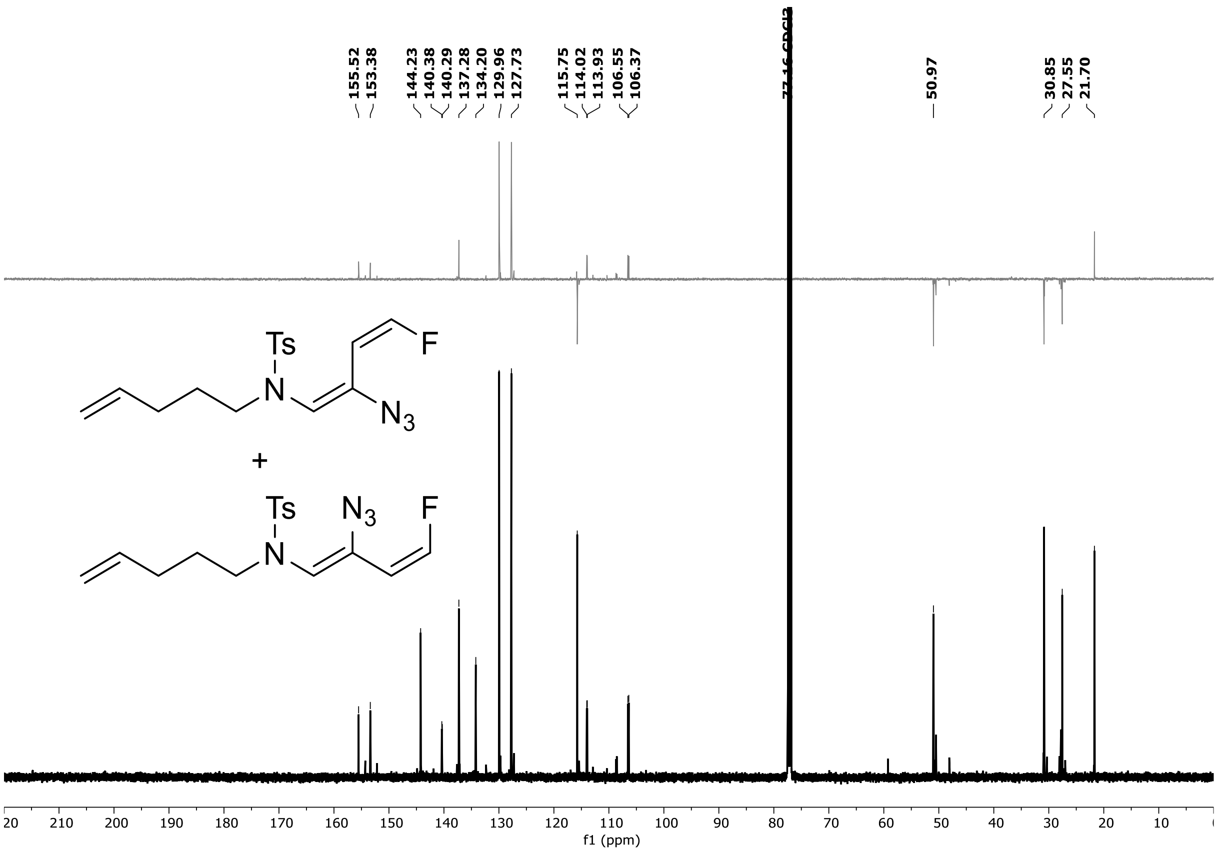
^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) of **2p**



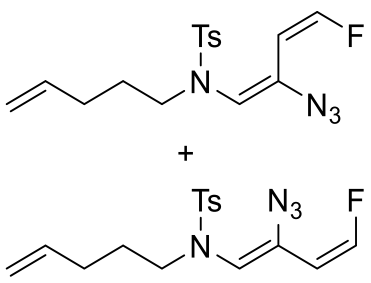
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 471 MHz) of **2p**

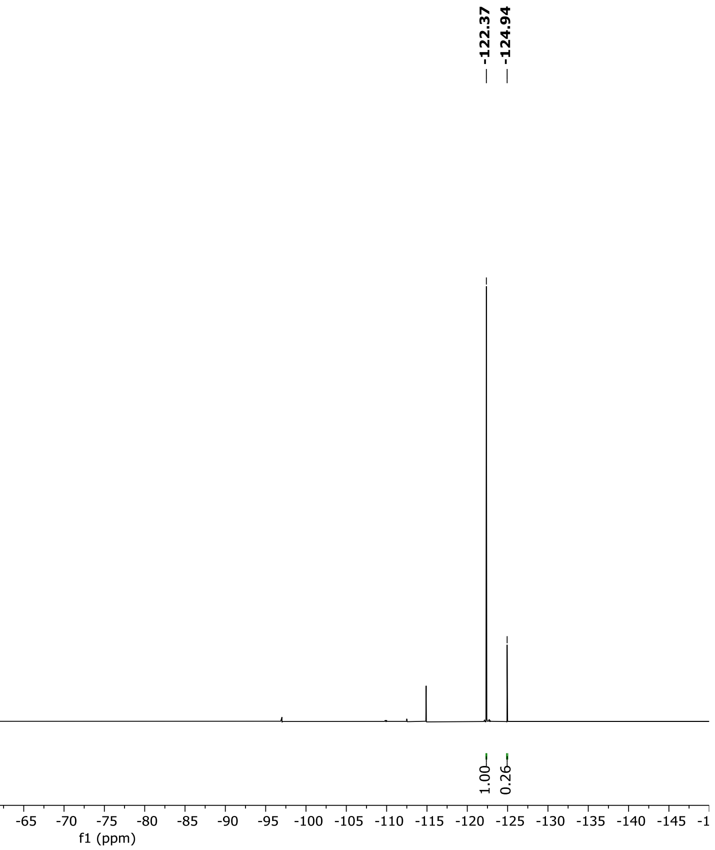


^{1}H NMR ($CDCl_3$, 500 MHz) of **2q**

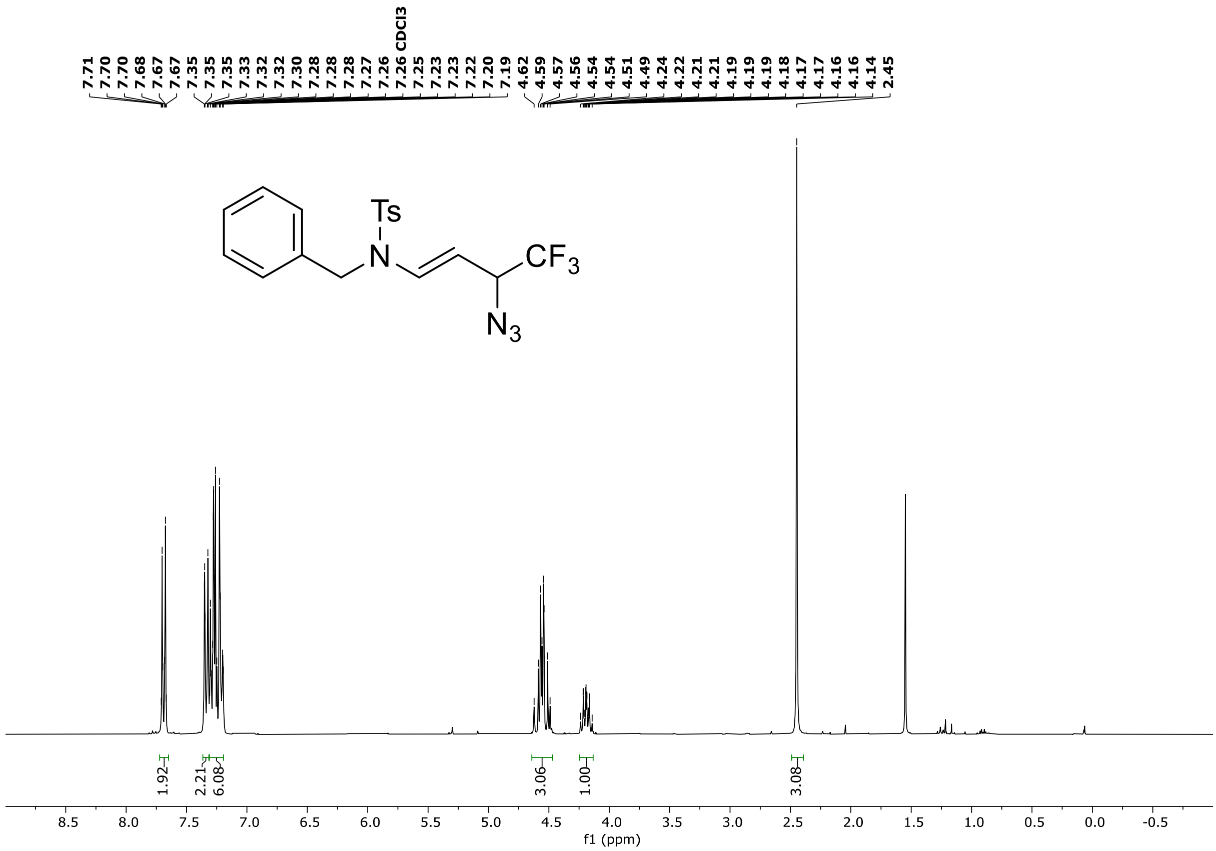


$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) of **2q**

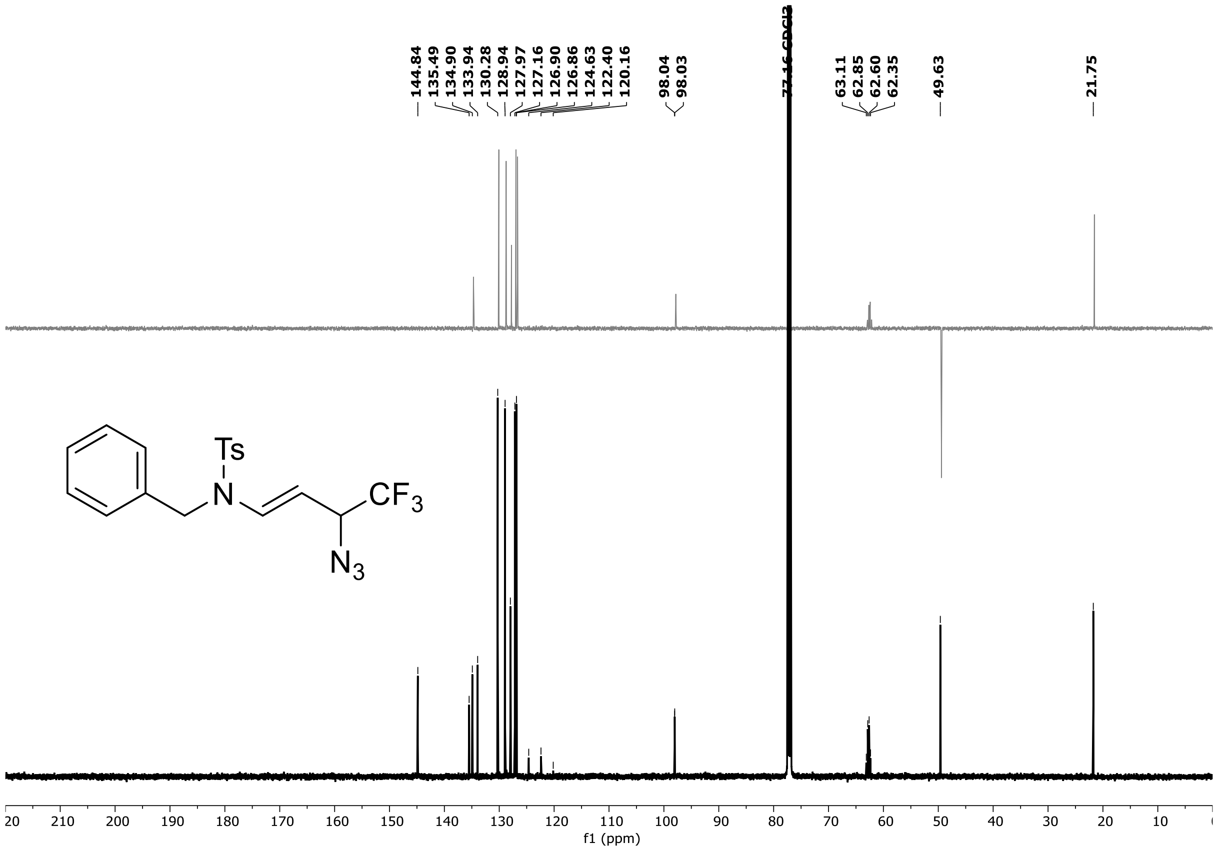




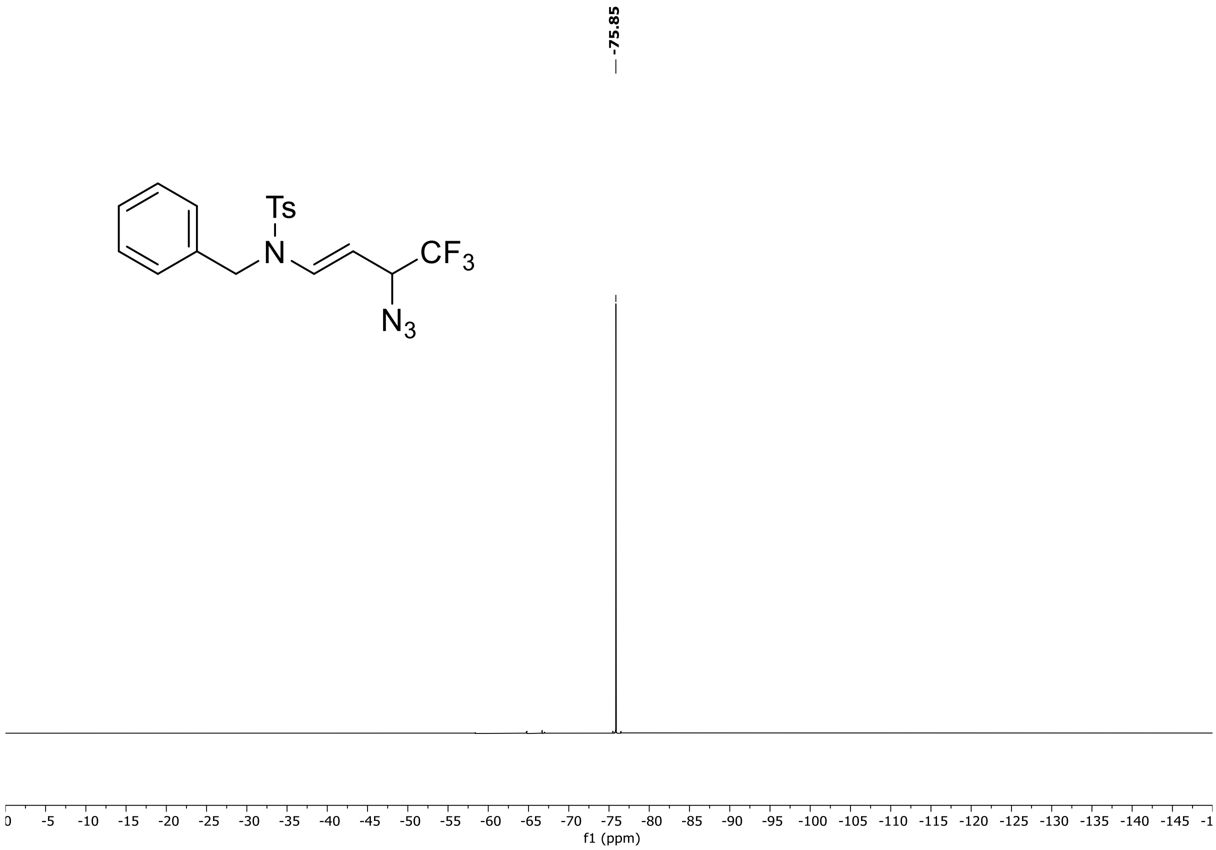
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 471 MHz) of **2q**



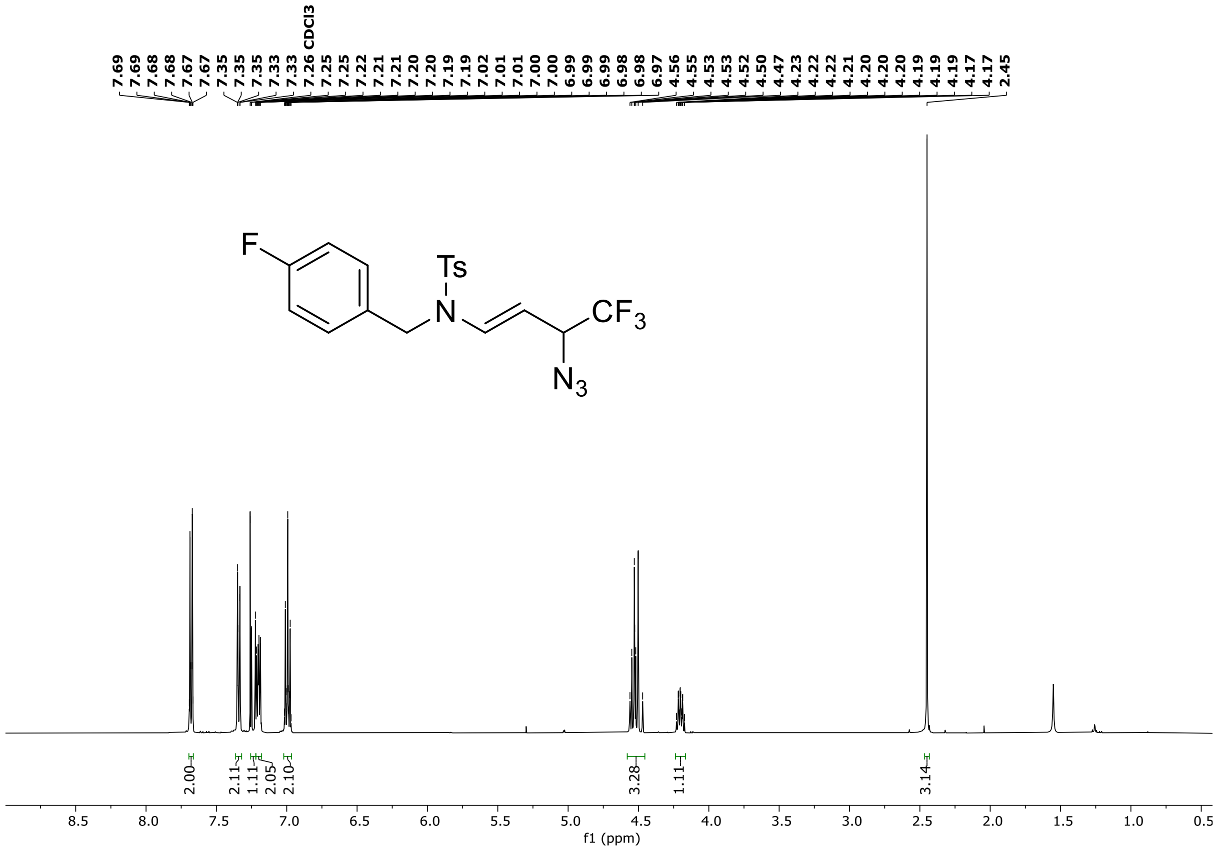
^{1}H NMR ($CDCl_3$, 300 MHz) of **3a**



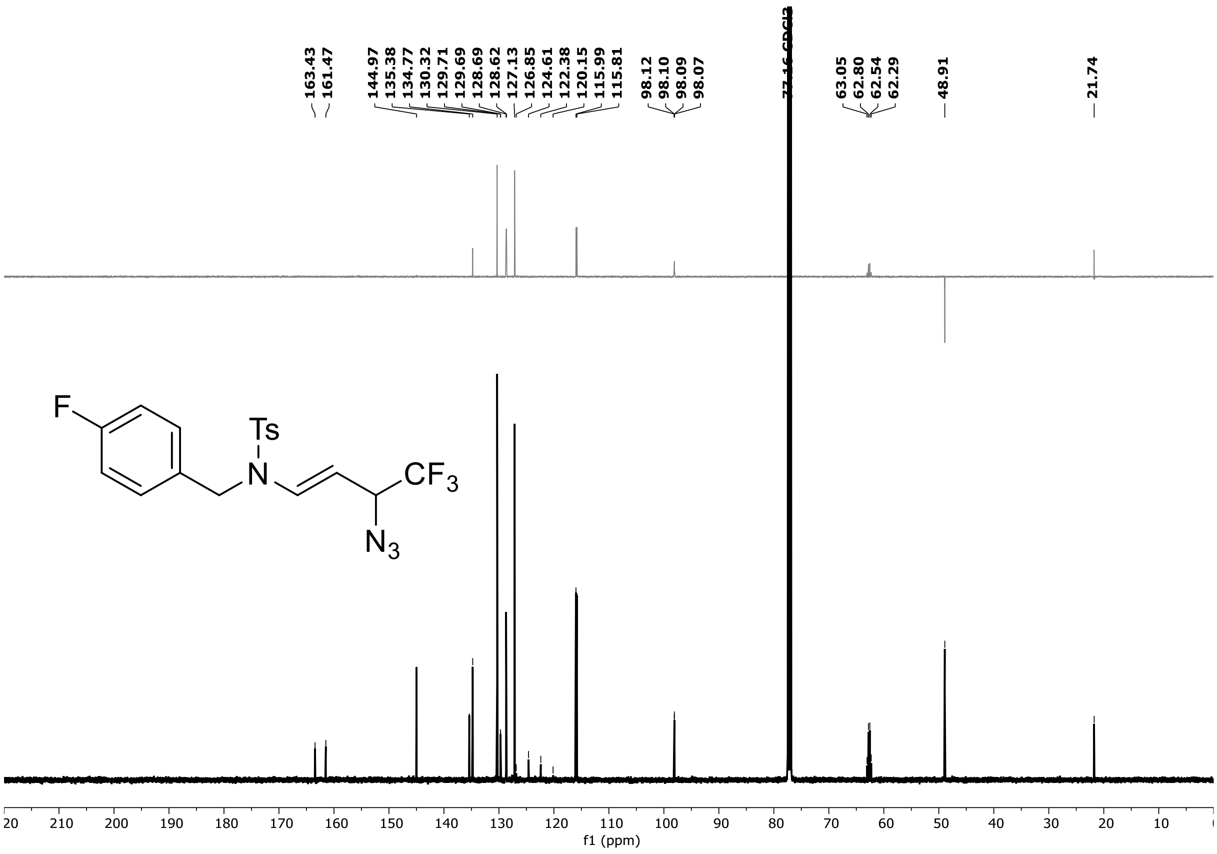
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) of **3a**



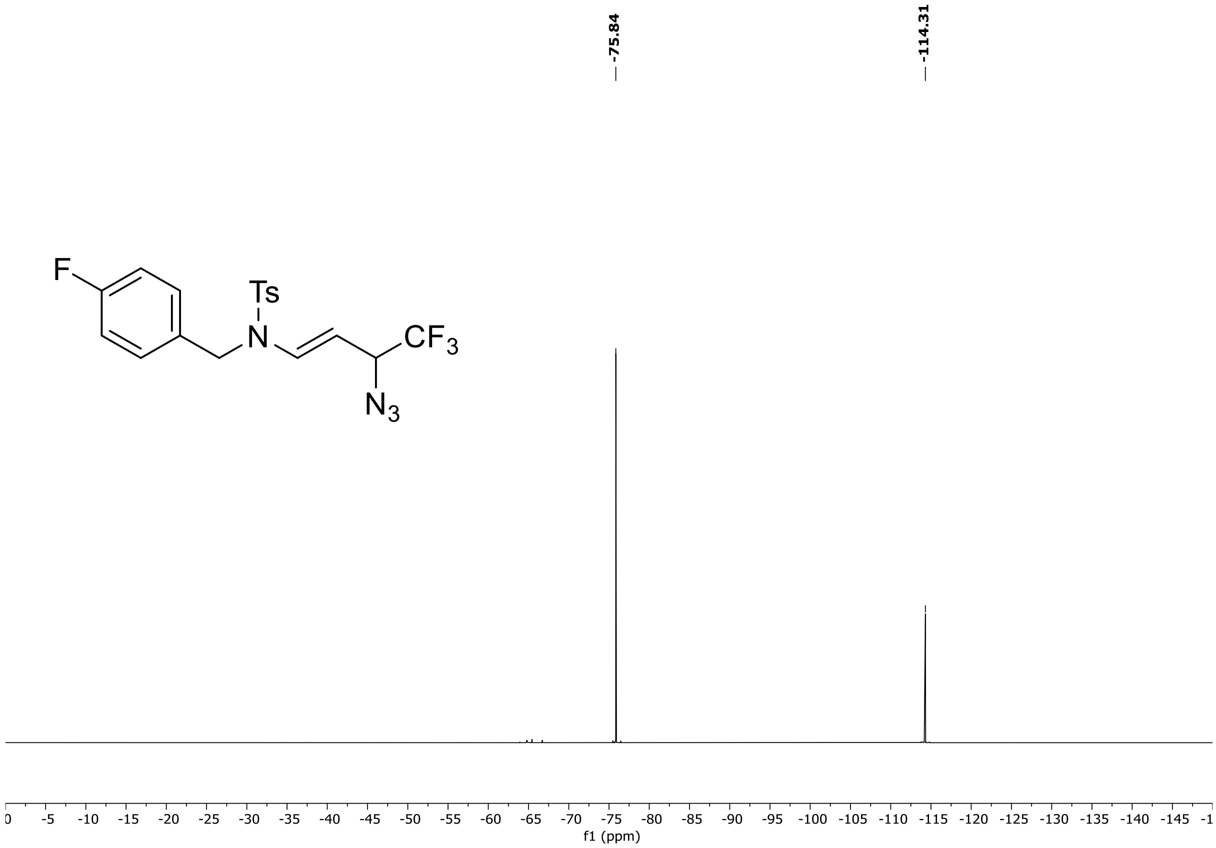
$^{19}F\{^1H\}$ NMR ($CDCl_3$, 282 MHz) of **3a**



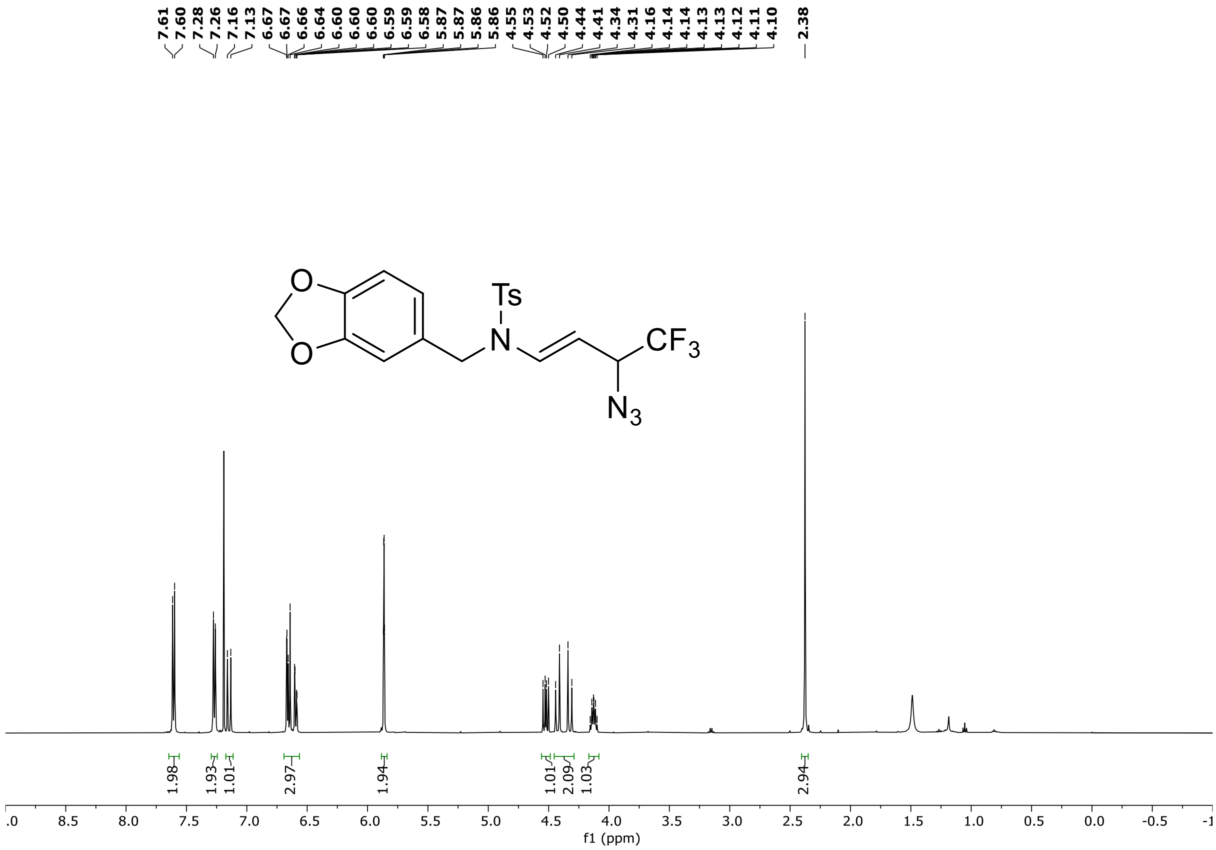
^{1}H NMR ($CDCl_3$, 500 MHz) of **3b**



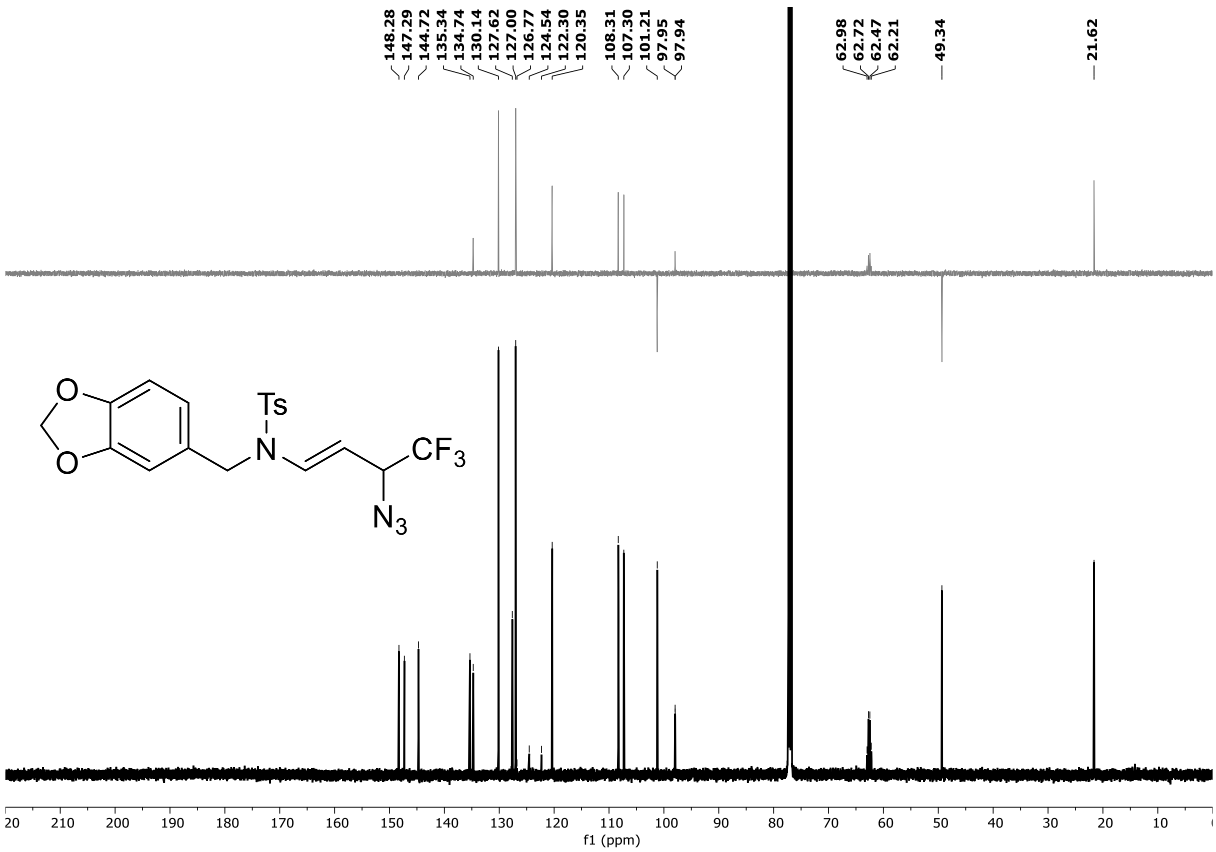
$^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) of **3b**



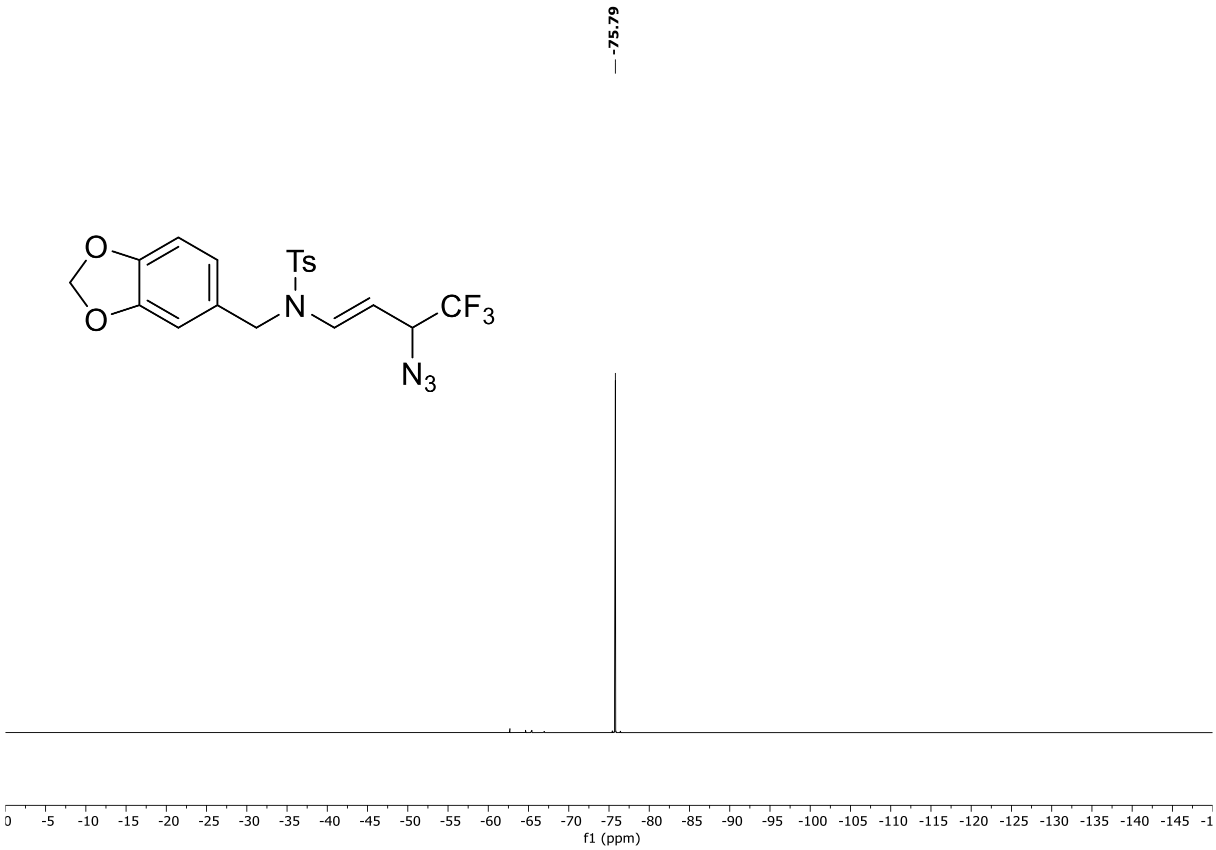
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 282 MHz) of **3b**



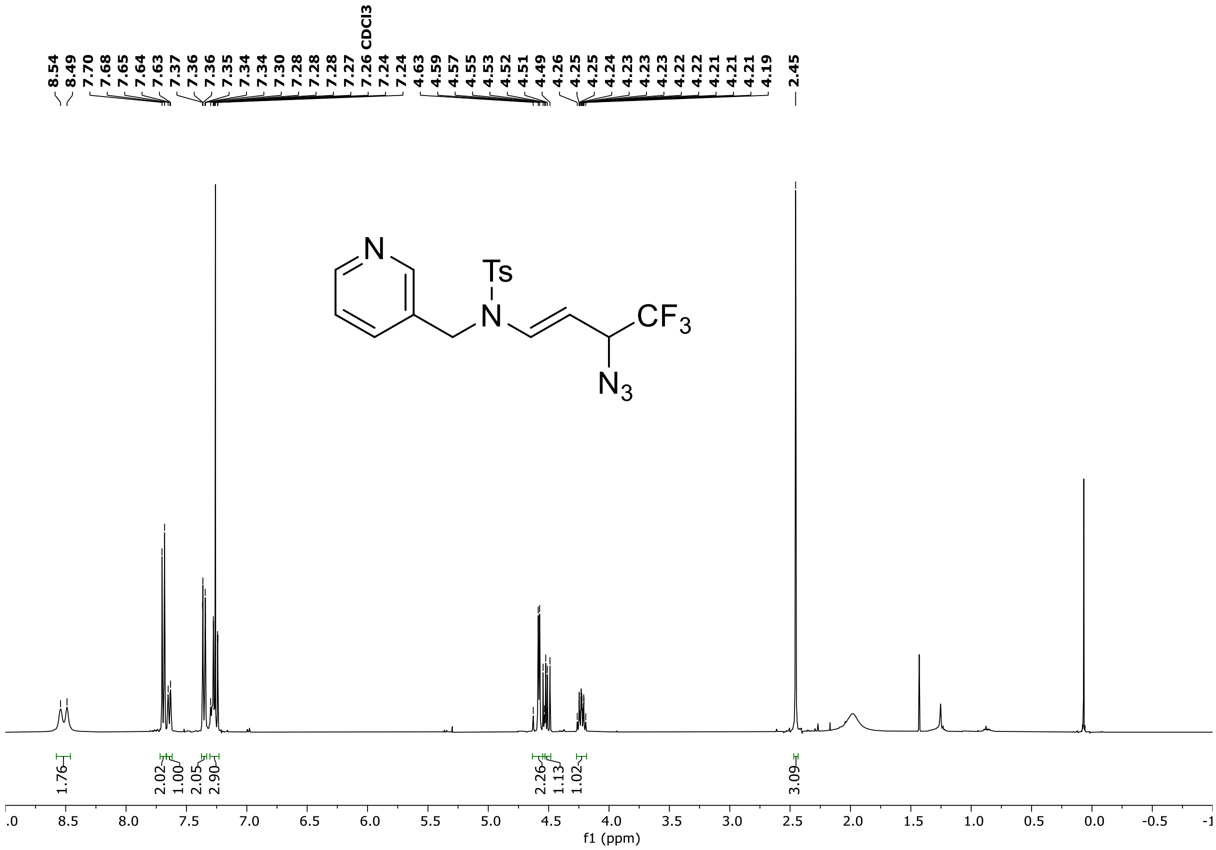
^{1}H NMR ($CDCl_3$, 500 MHz) of **3c**



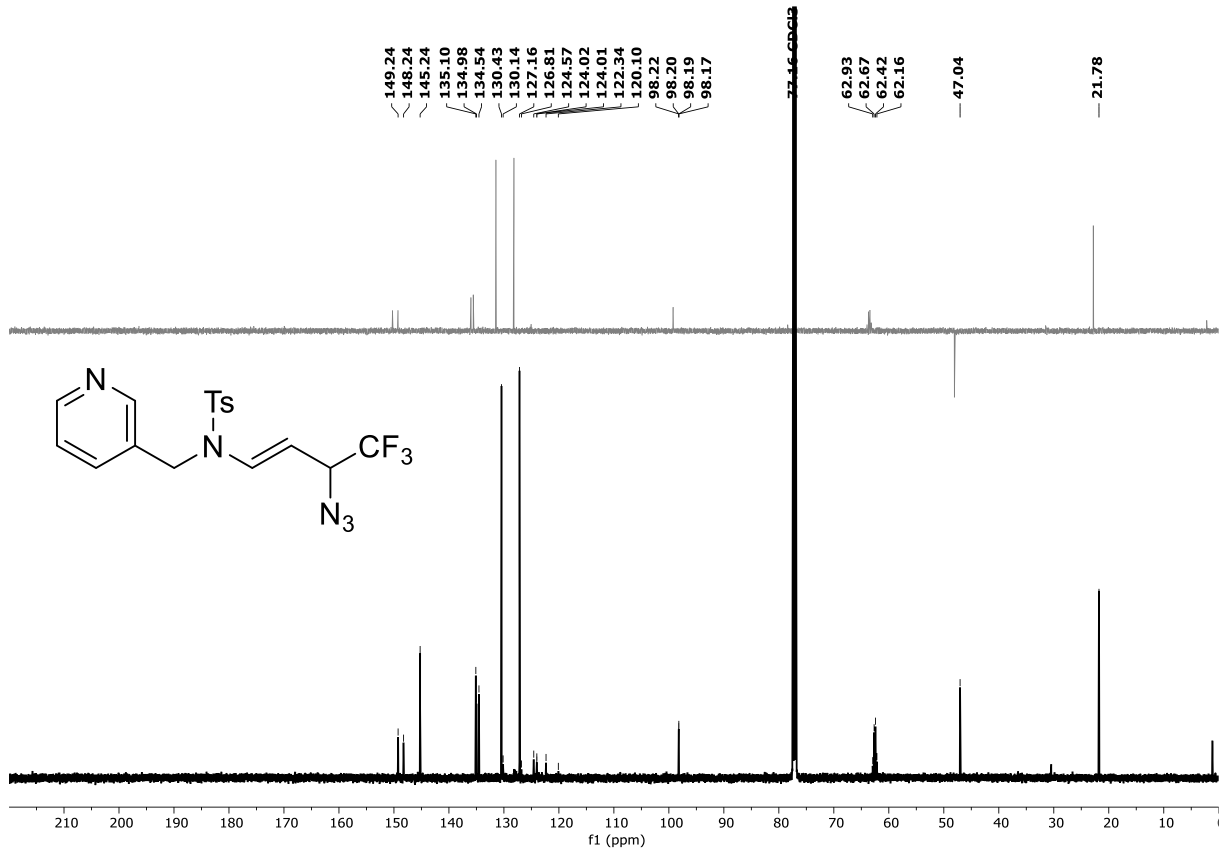
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) of **3c**



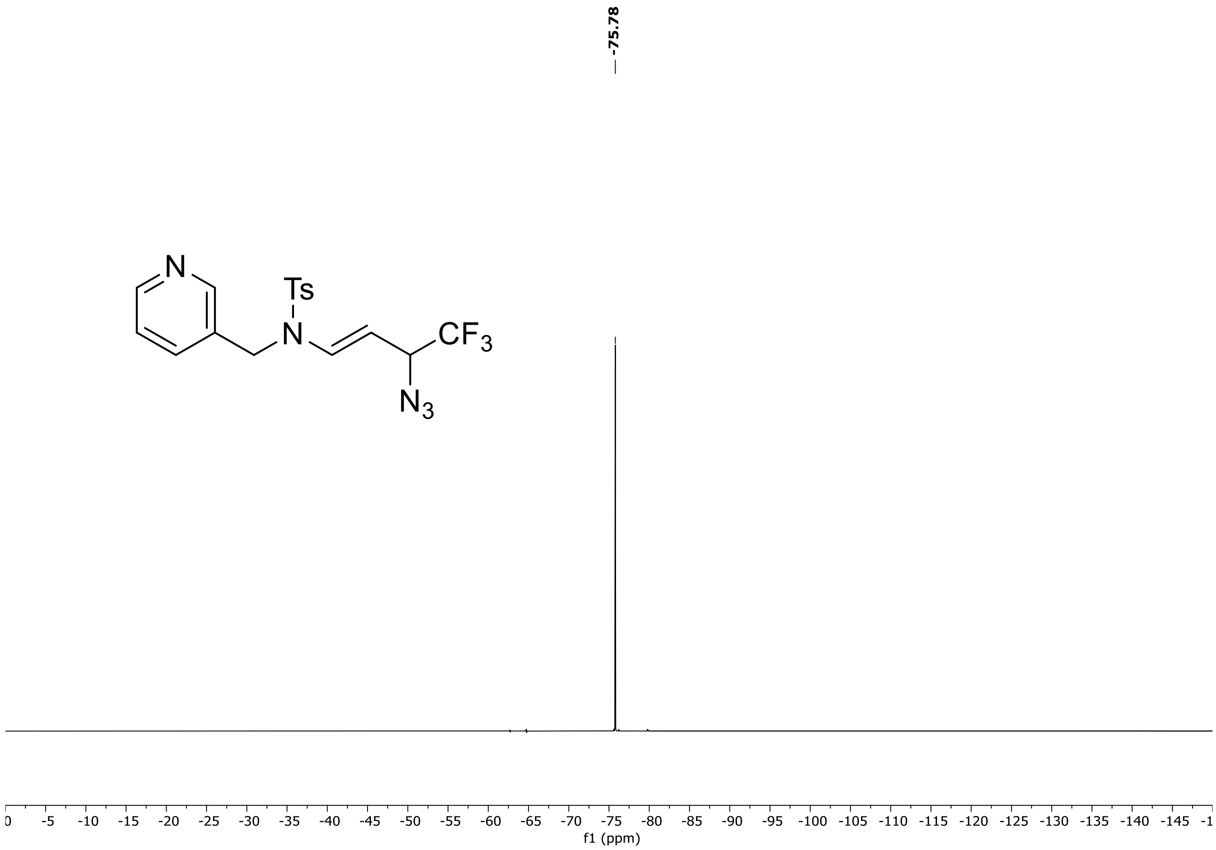
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 282 MHz) of **3c**



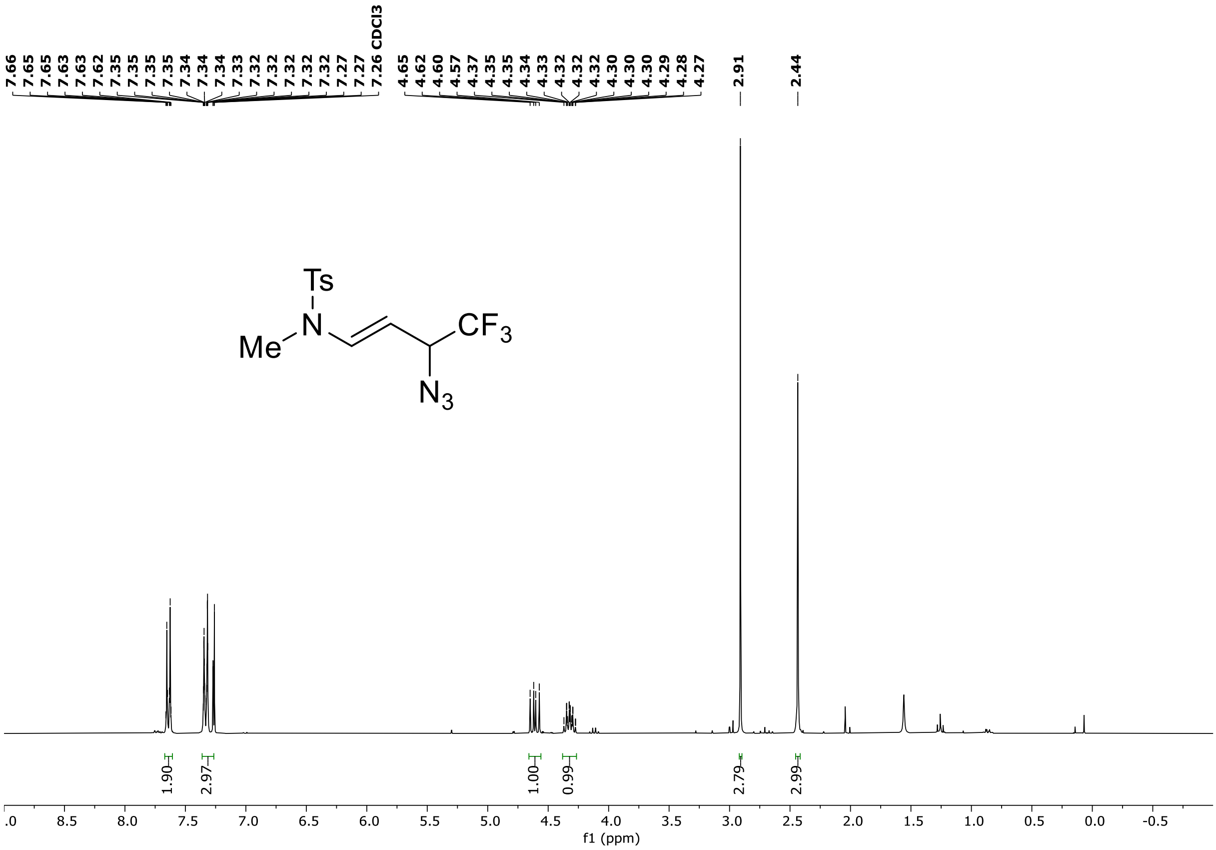
^{1}H NMR ($CDCl_3$, 400 MHz) of **3d**



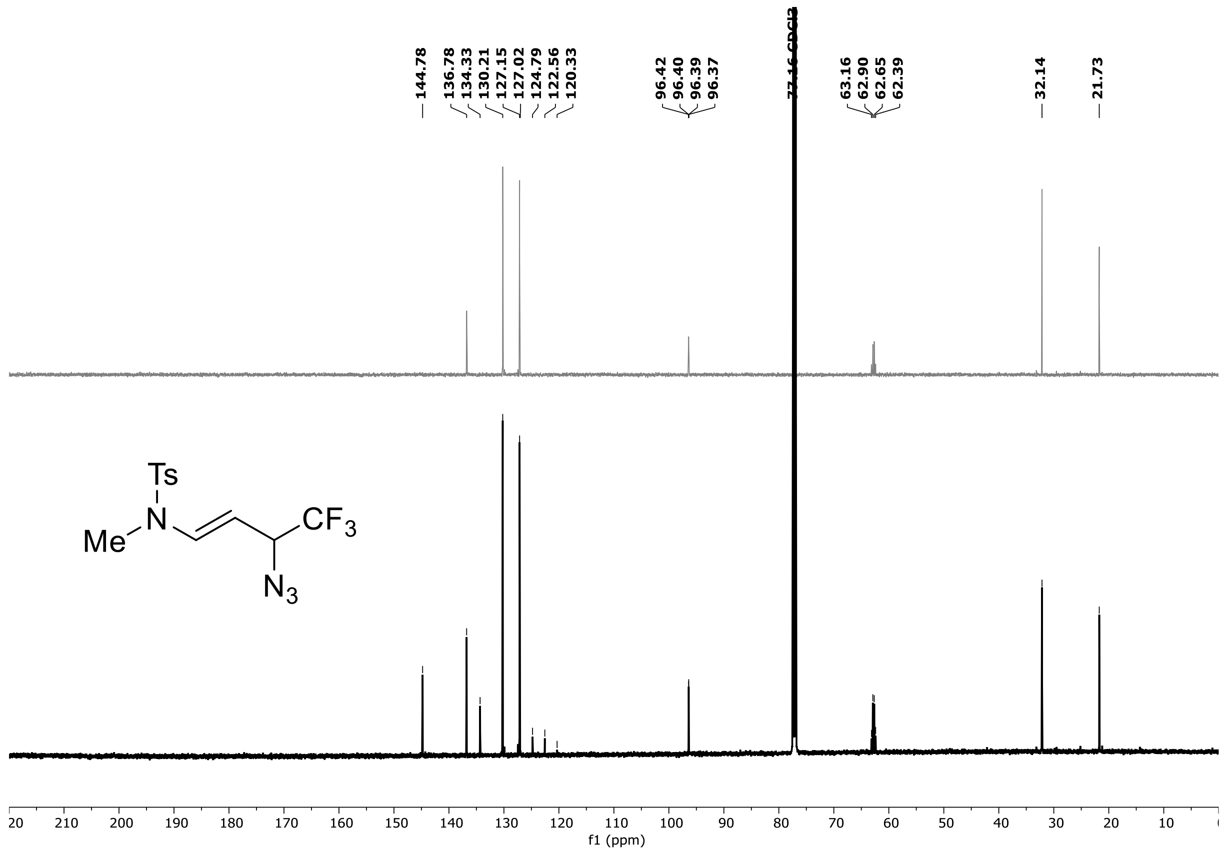
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) of **3d**



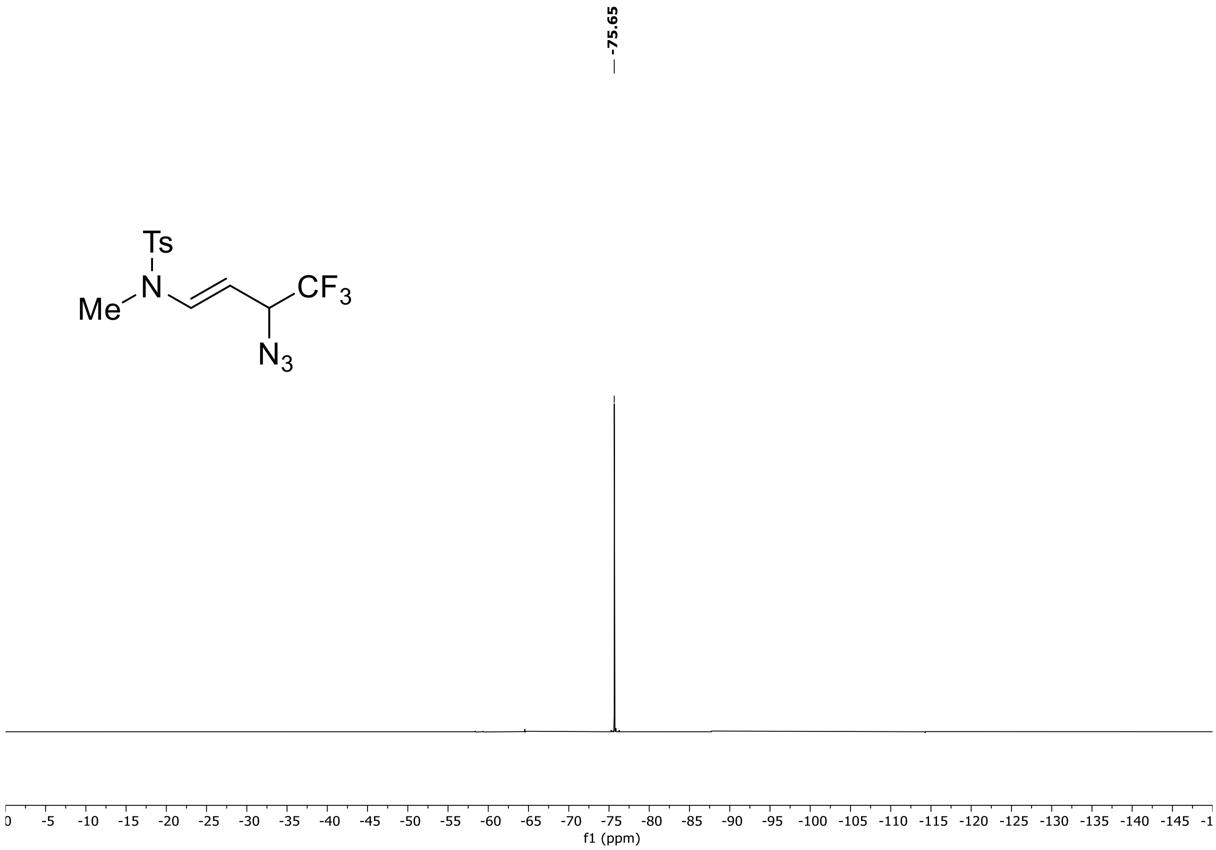
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 471 MHz) of **3d**



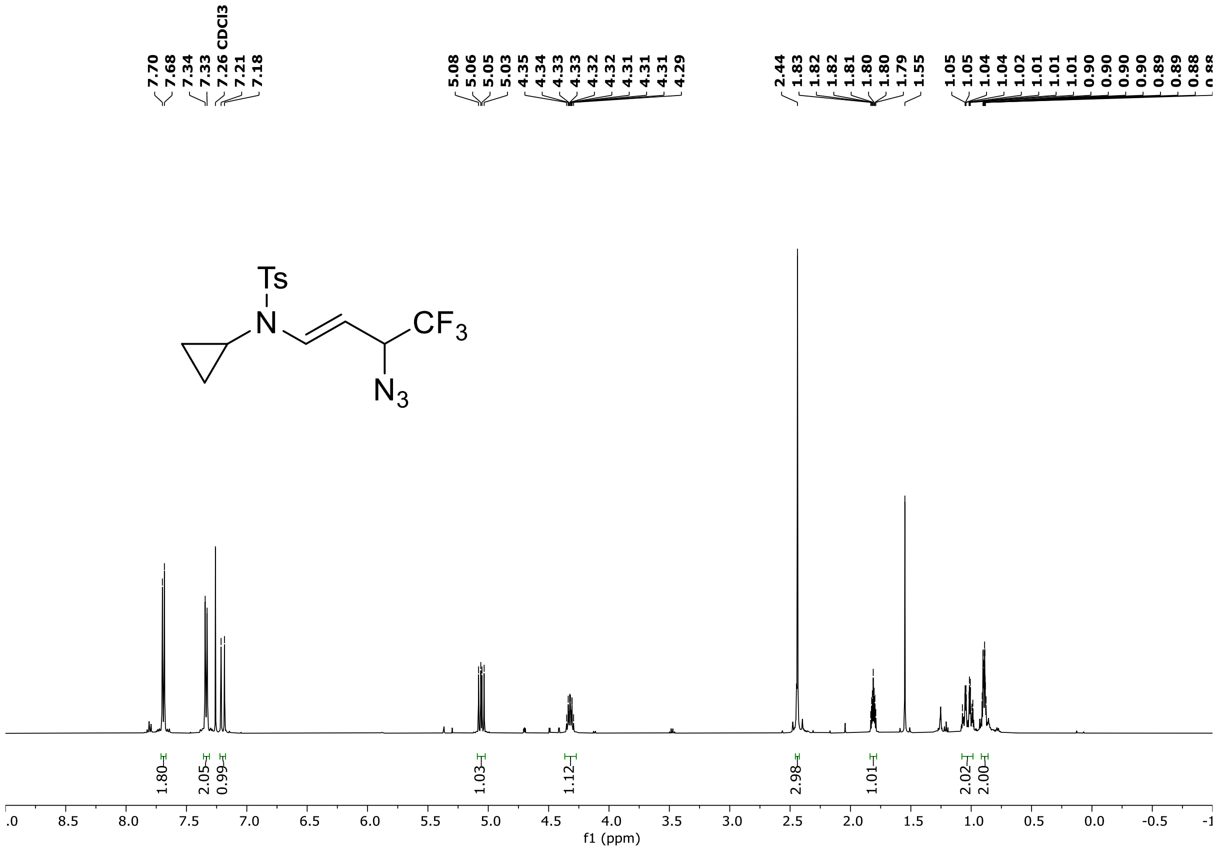
^{1}H NMR ($CDCl_3$, 300 MHz) of **3e**



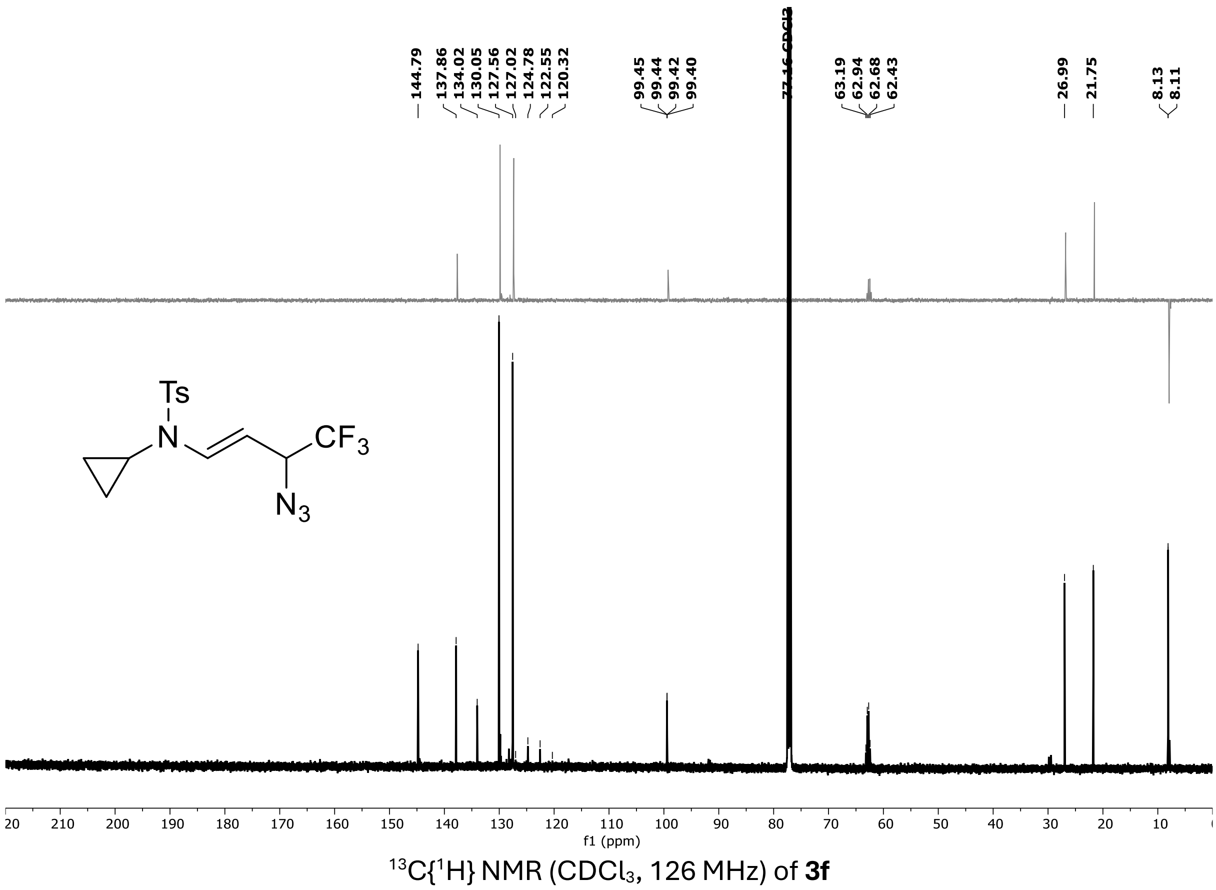
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) of **3e**



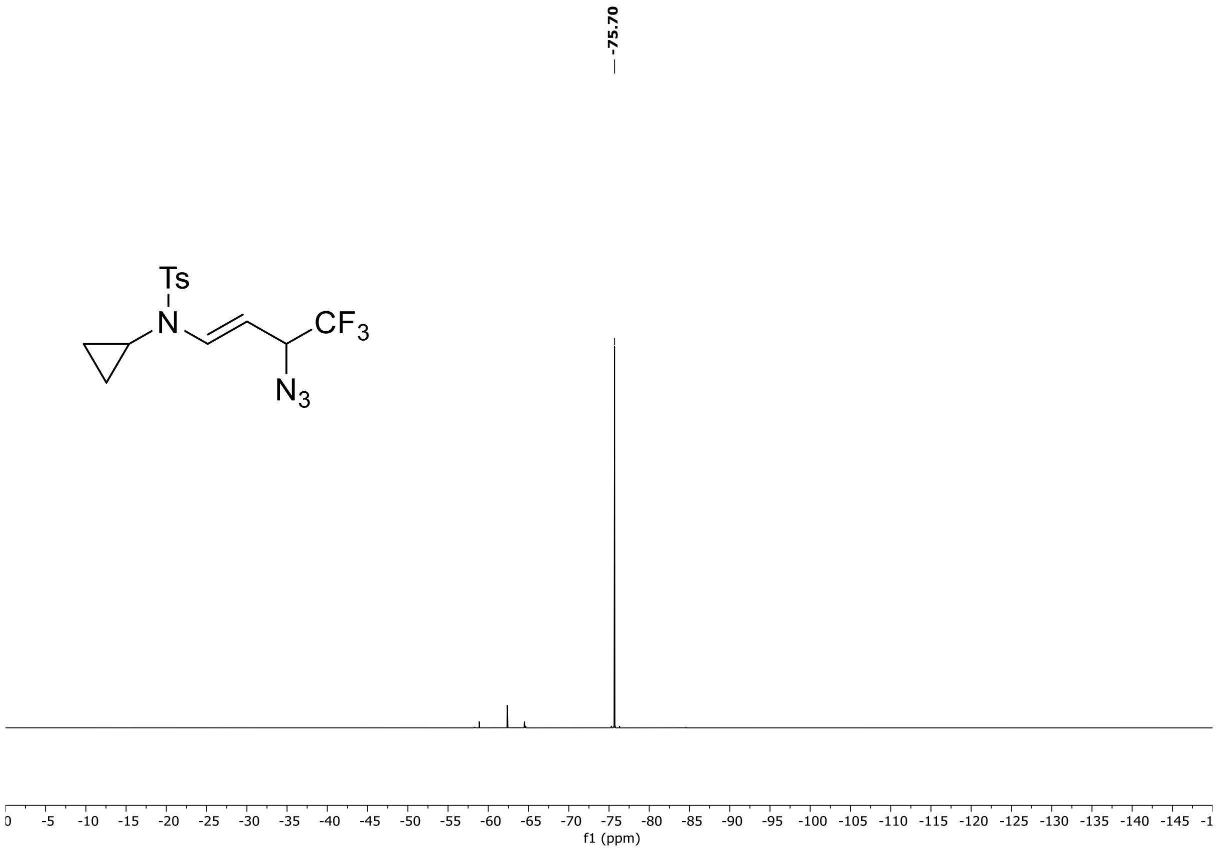
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 282 MHz) of **3e**



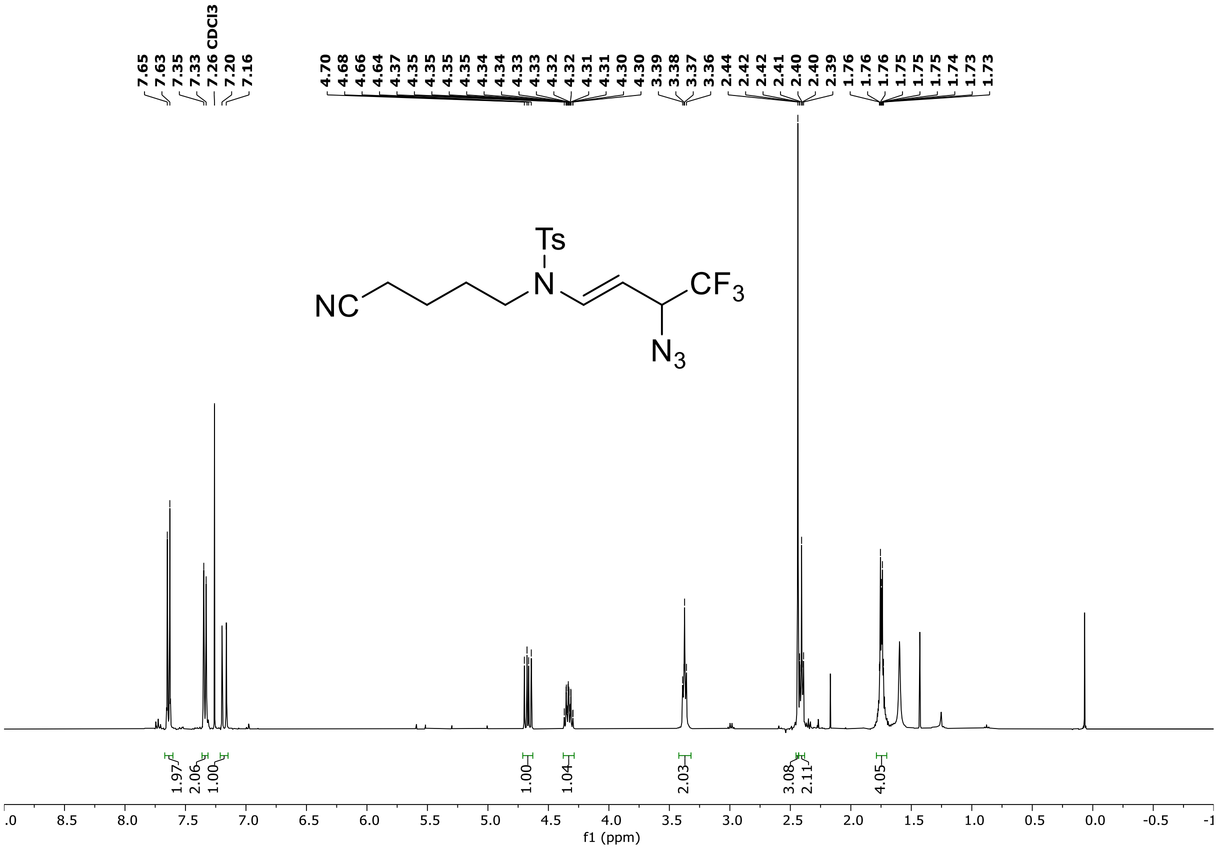
^1H NMR ($CDCl_3$, 500 MHz) of **3f**



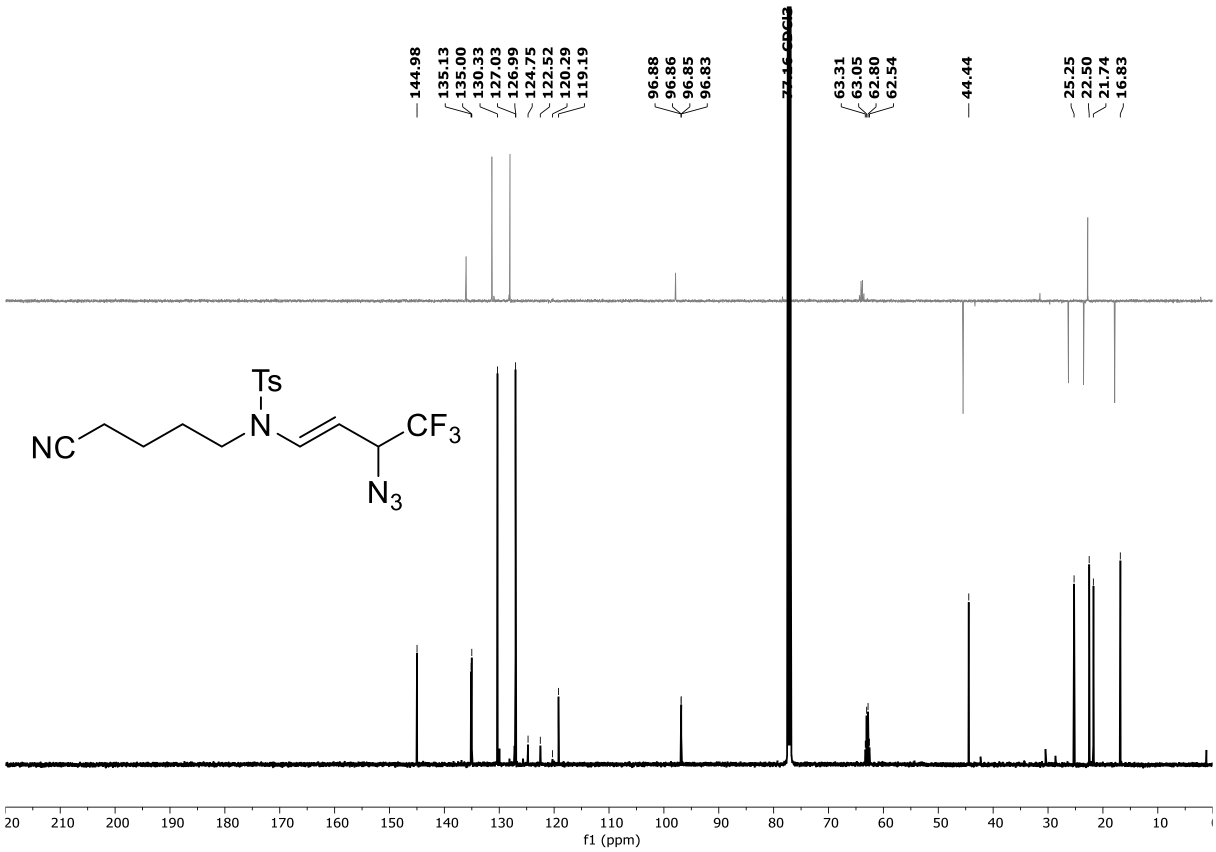
$^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) of **3f**



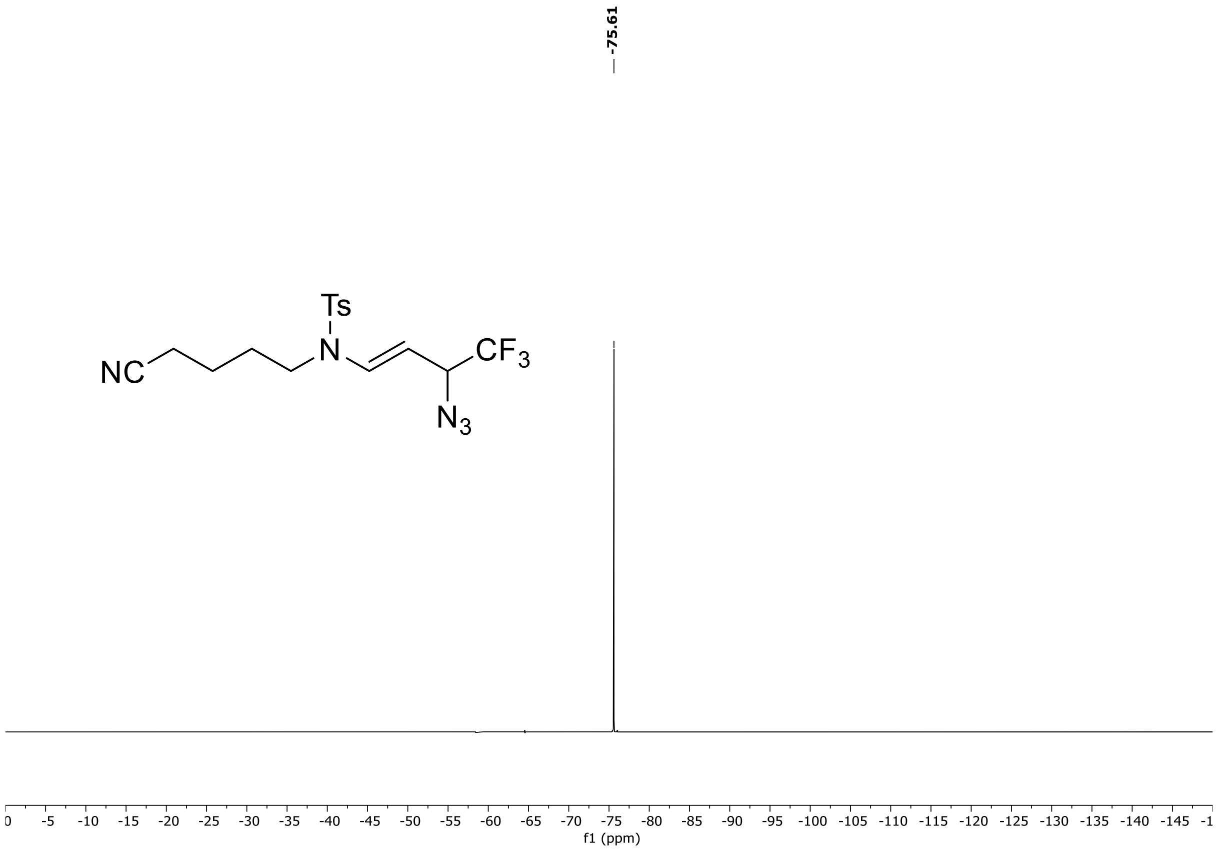
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 282 MHz) of **3f**



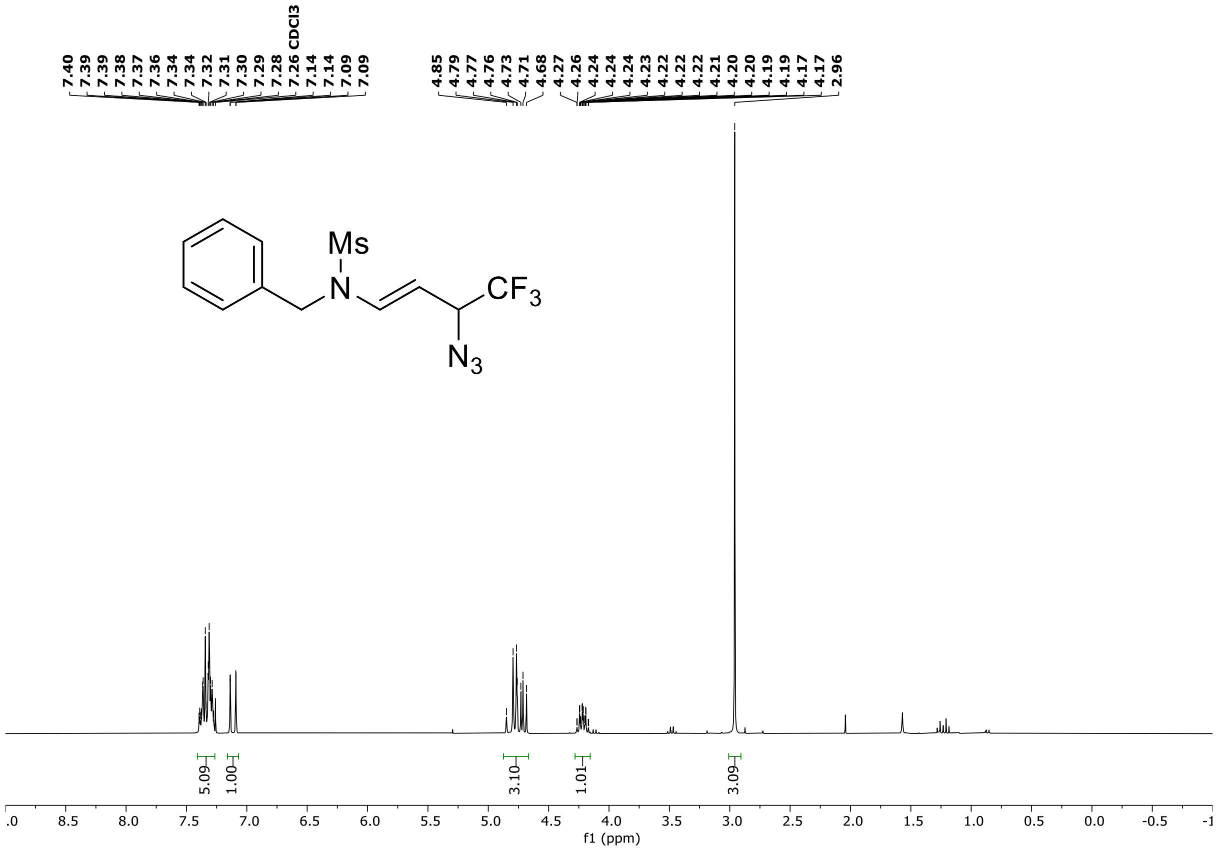
^{1}H NMR (CDCl$_3$, 400 MHz) of **3g**



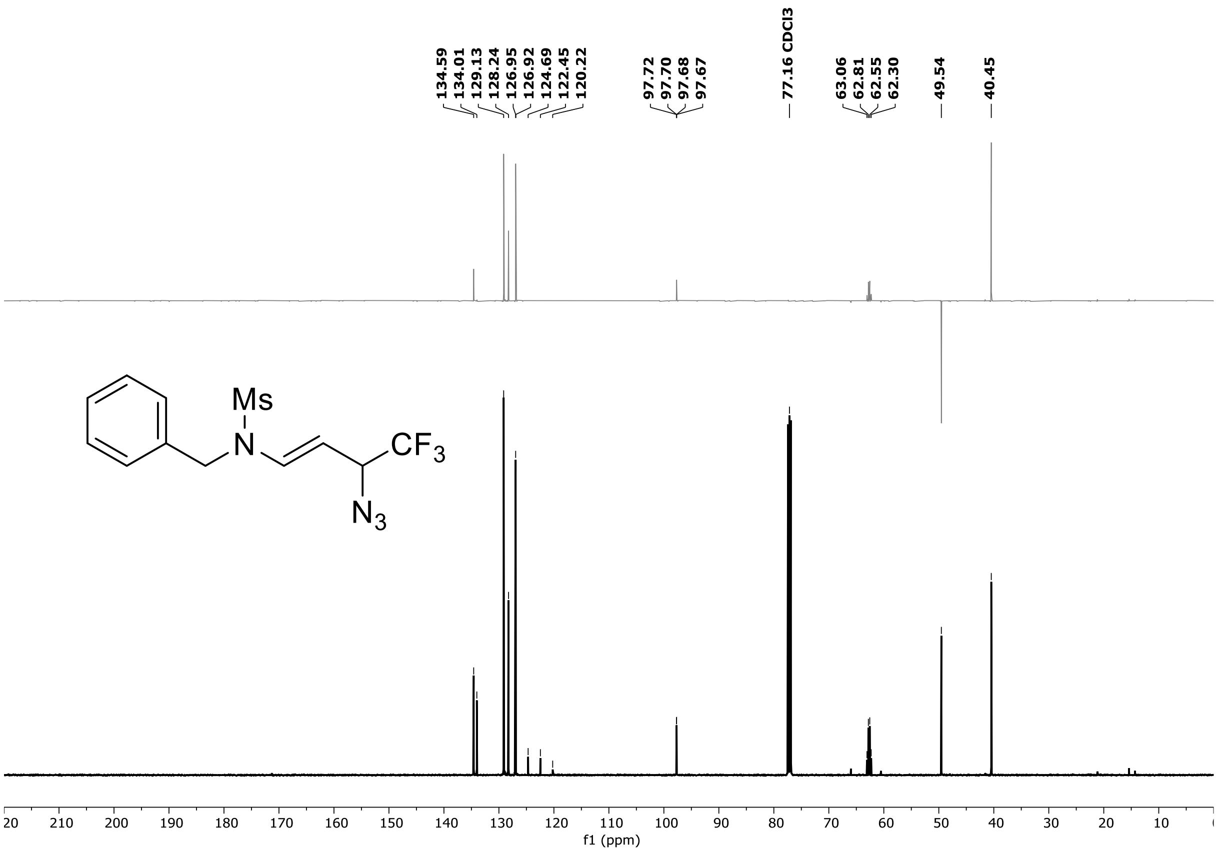
^{13}C{^{1}H} NMR (CDCl$_3$, 126 MHz) of **3g**



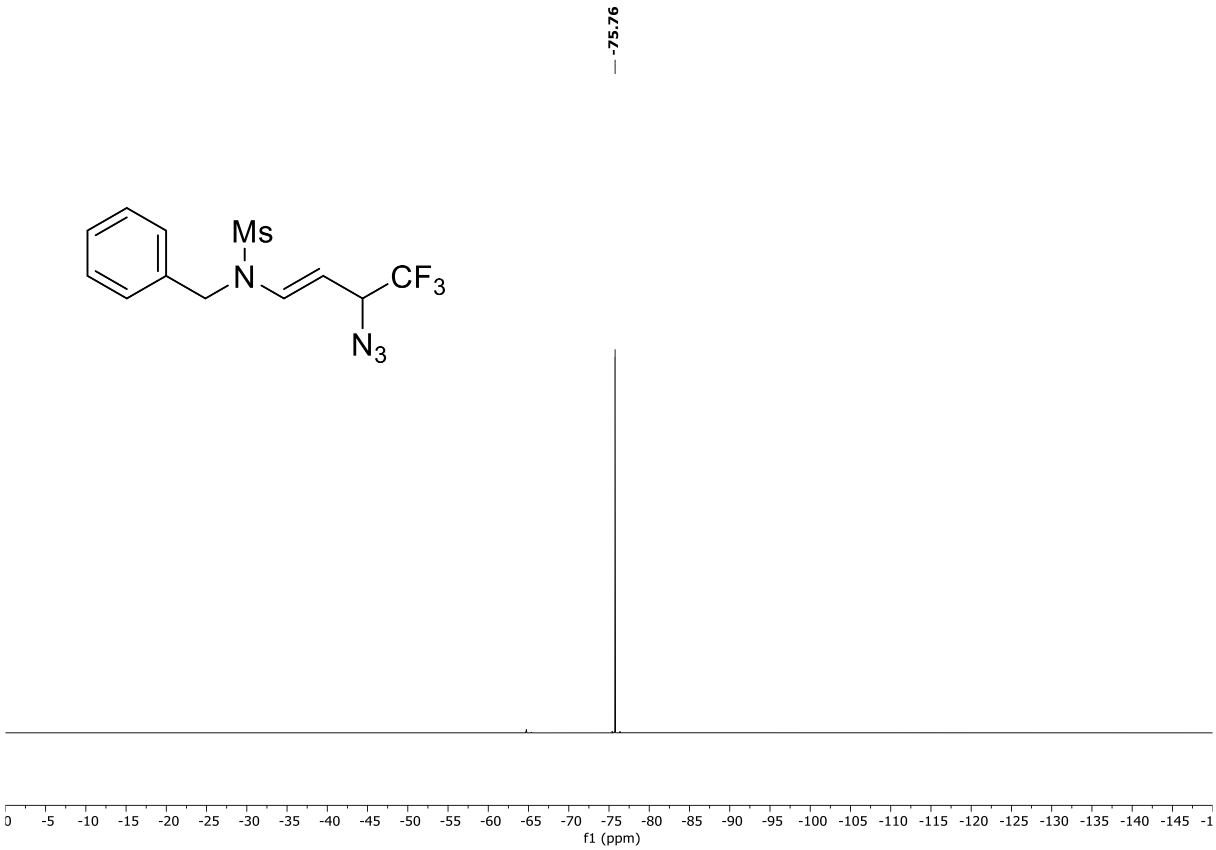
$^{19}F\{^1H\}$ NMR ($CDCl_3$, 471 MHz) of **3g**



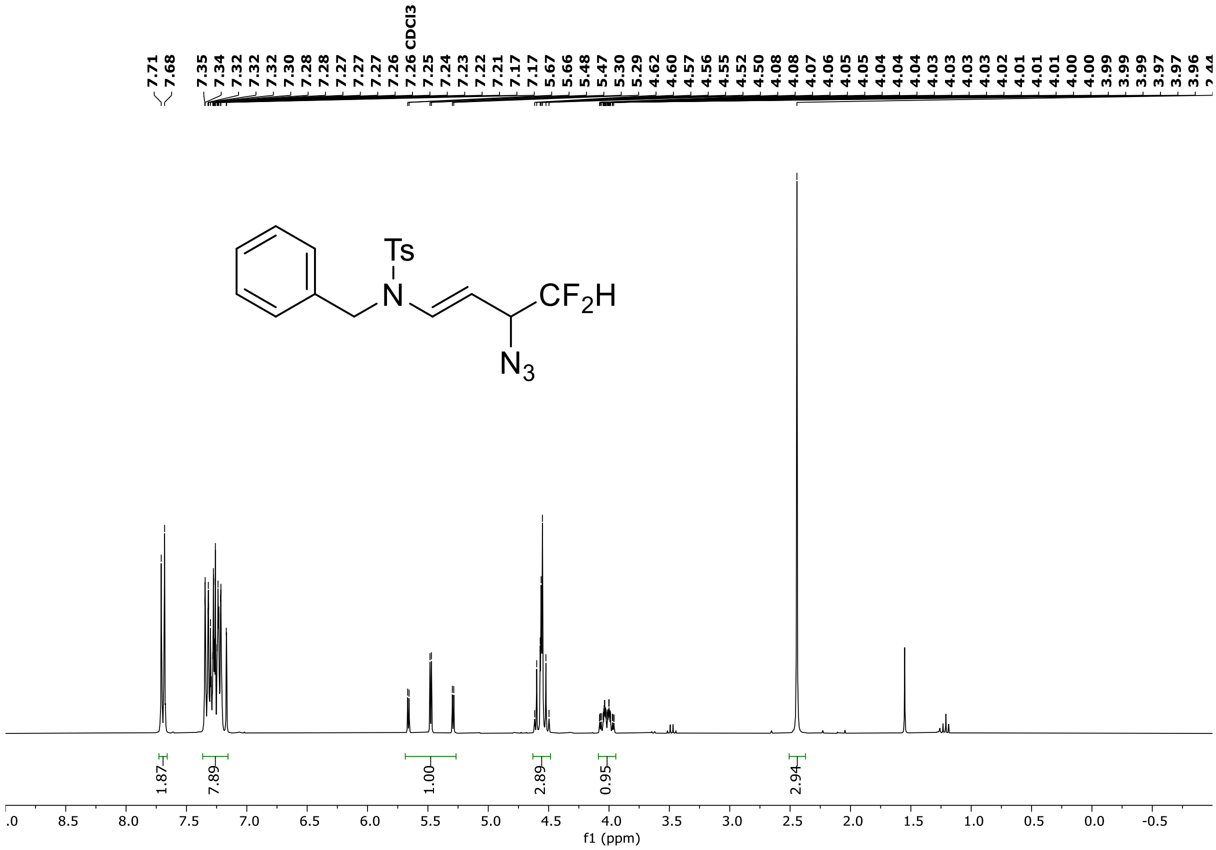
^{1}H NMR ($CDCl_3$, 300 MHz) of **3h**



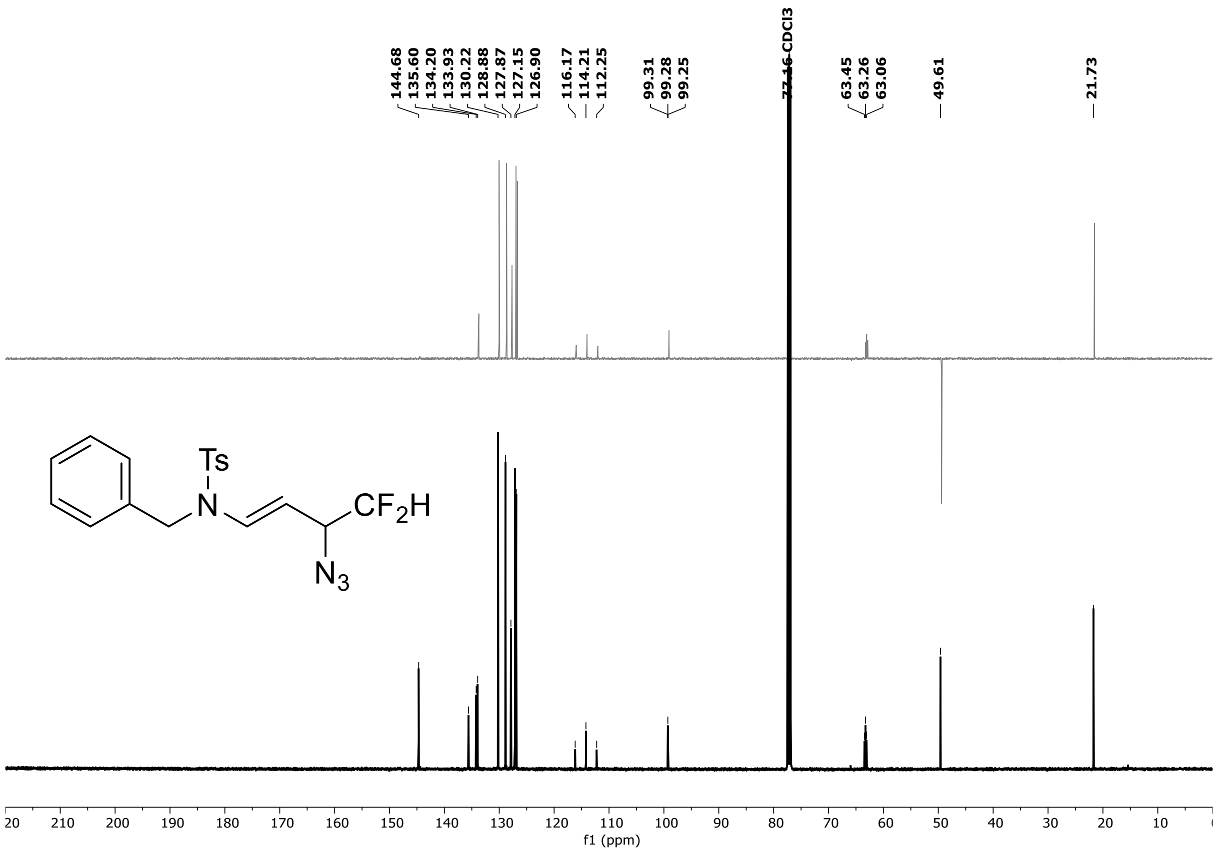
$^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) of **3h**



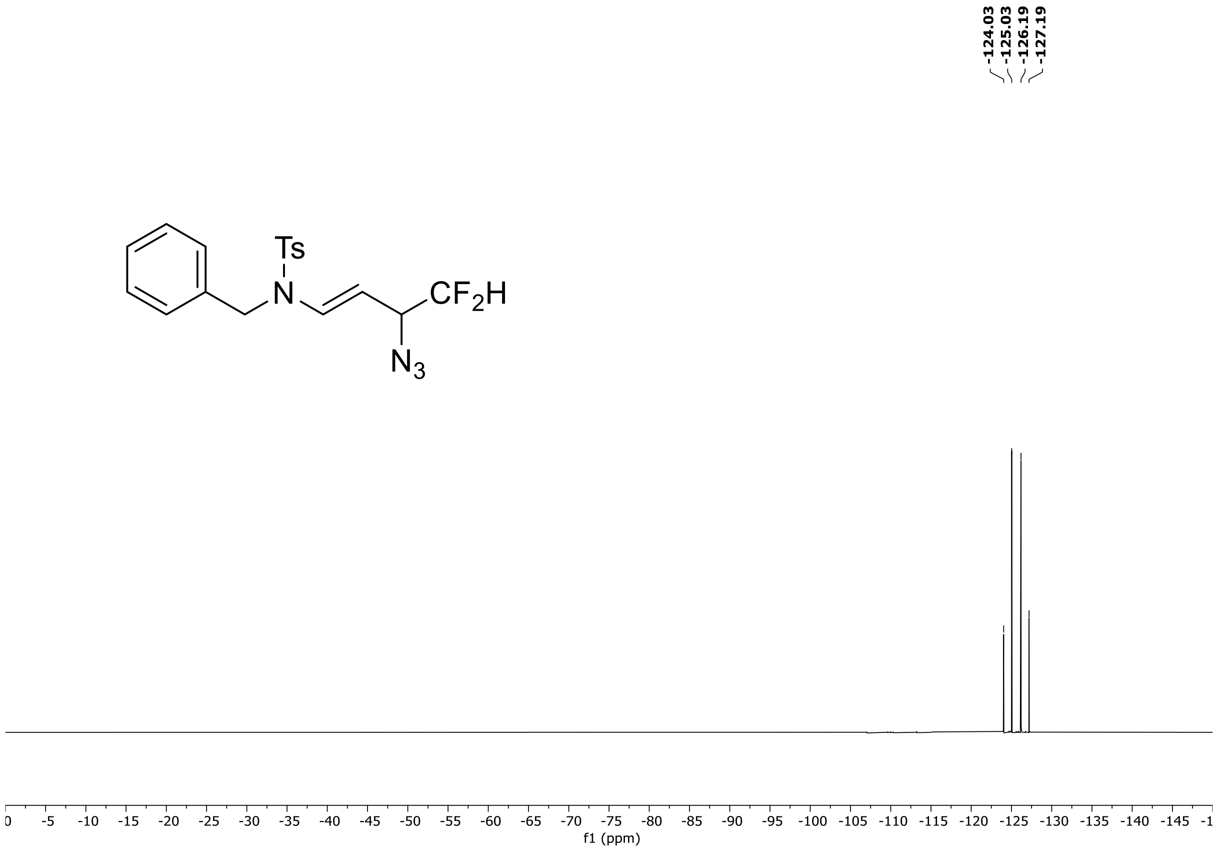
$^{19}F\{^1H\}$ NMR ($CDCl_3$, 282 MHz) of **3h**



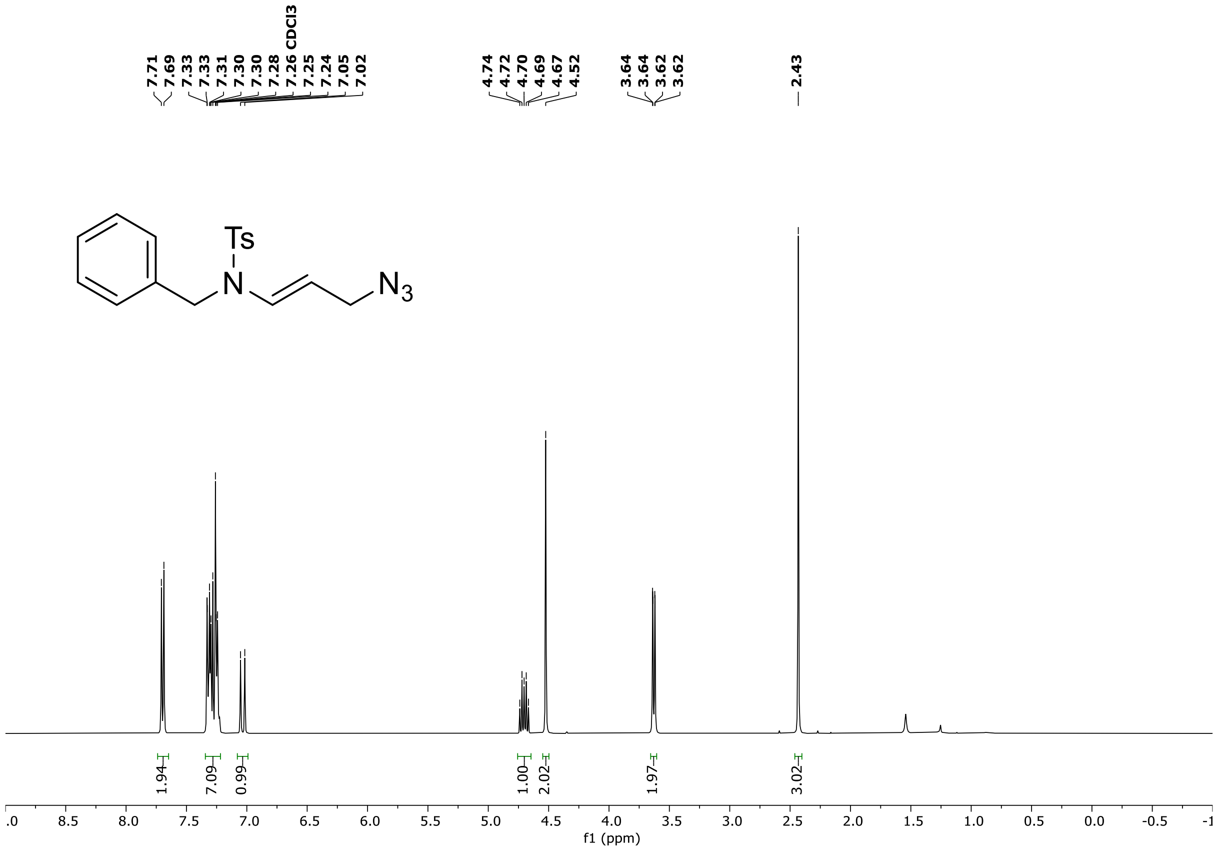
^{1}H NMR ($CDCl_3$, 300 MHz) of **3i**



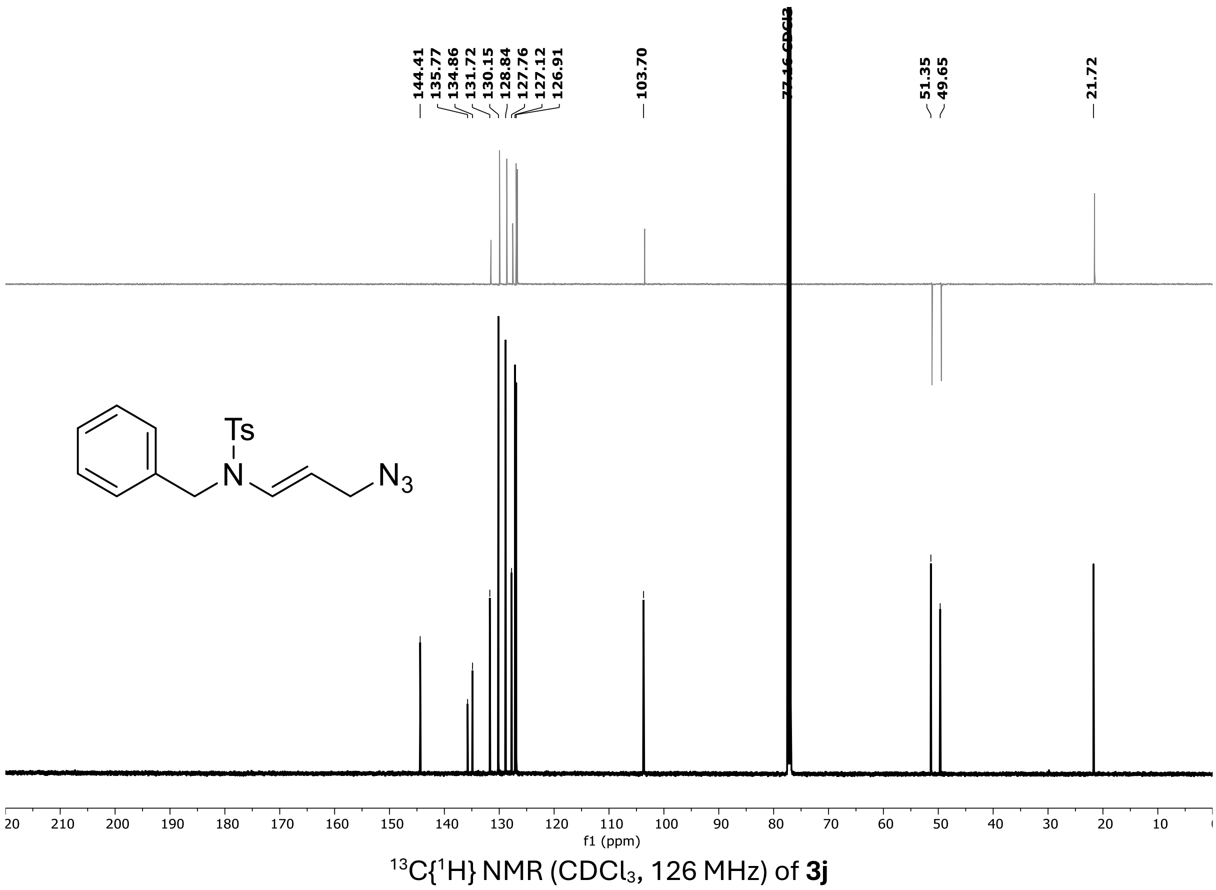
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) of **3i**



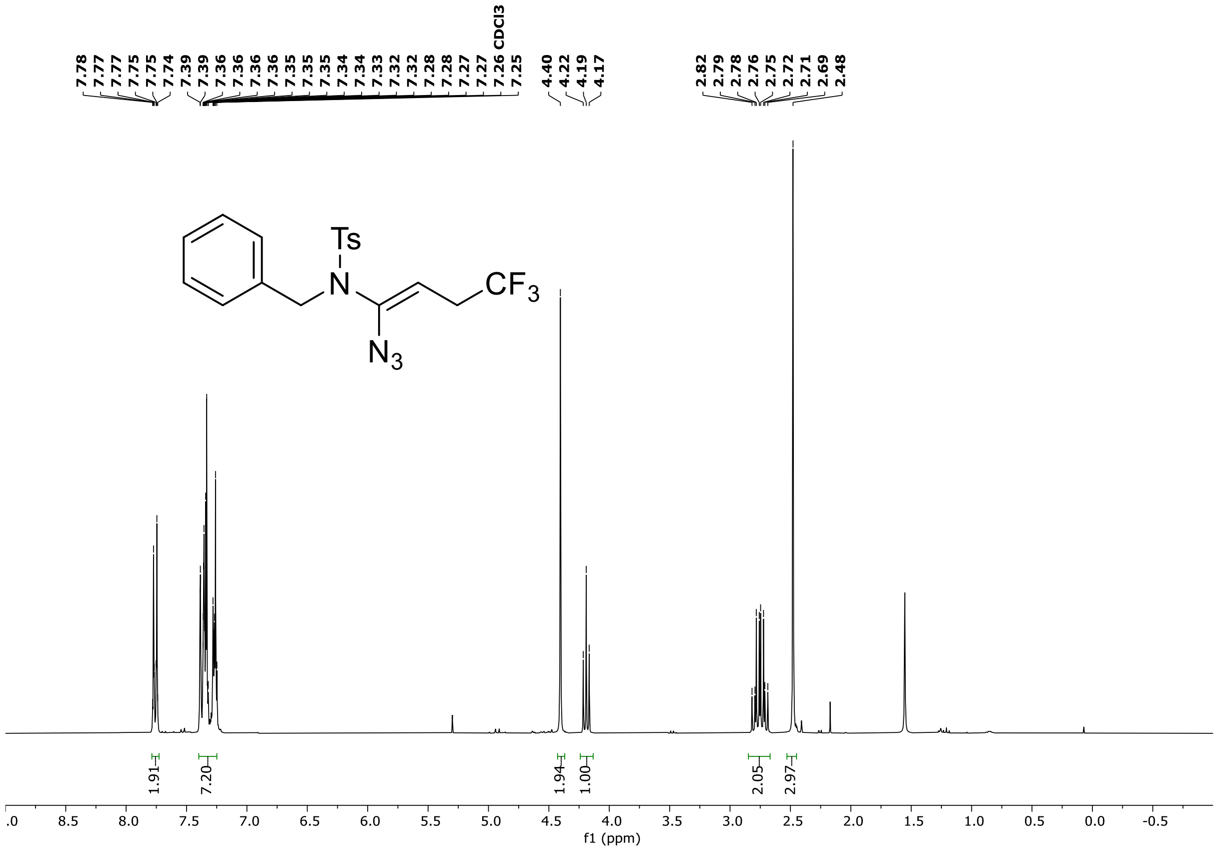
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 282 MHz) of **3i**



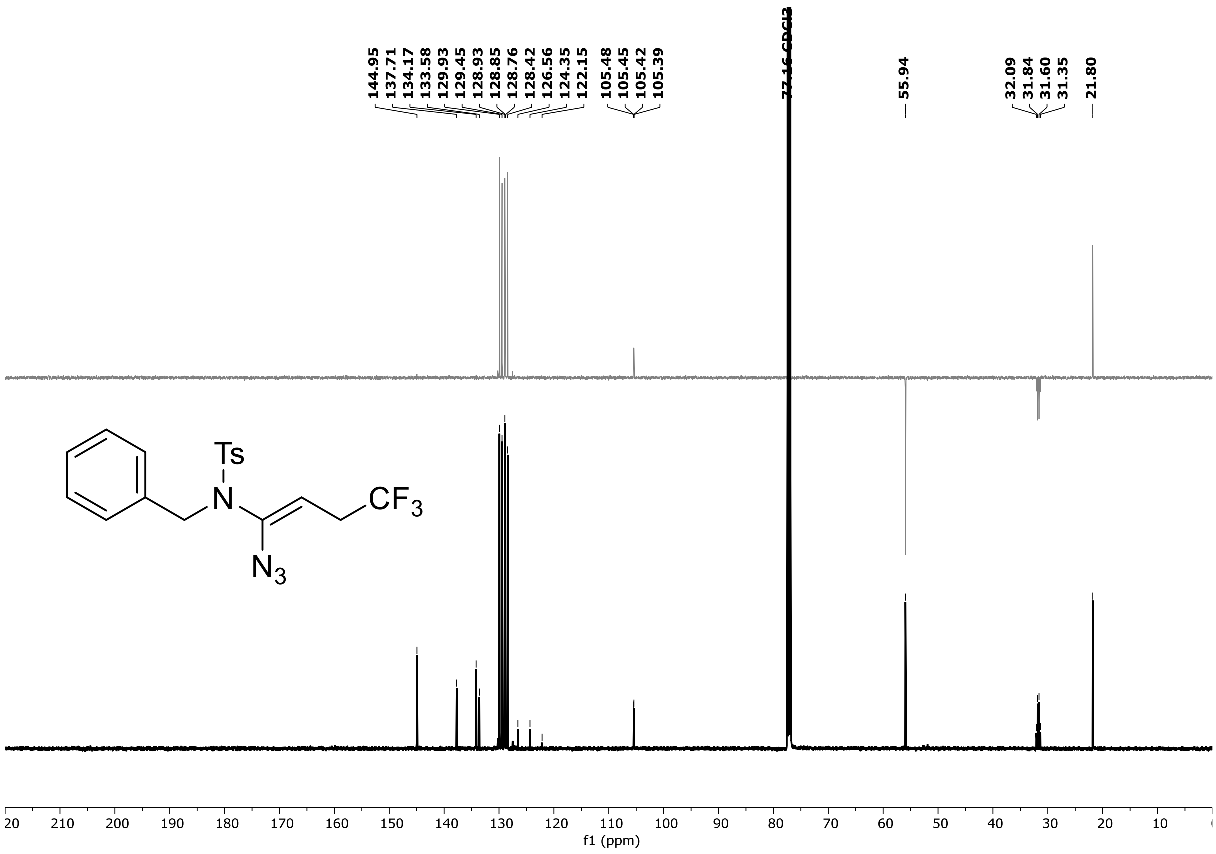
^{1}H NMR ($CDCl_3$, 400 MHz) of **3j**



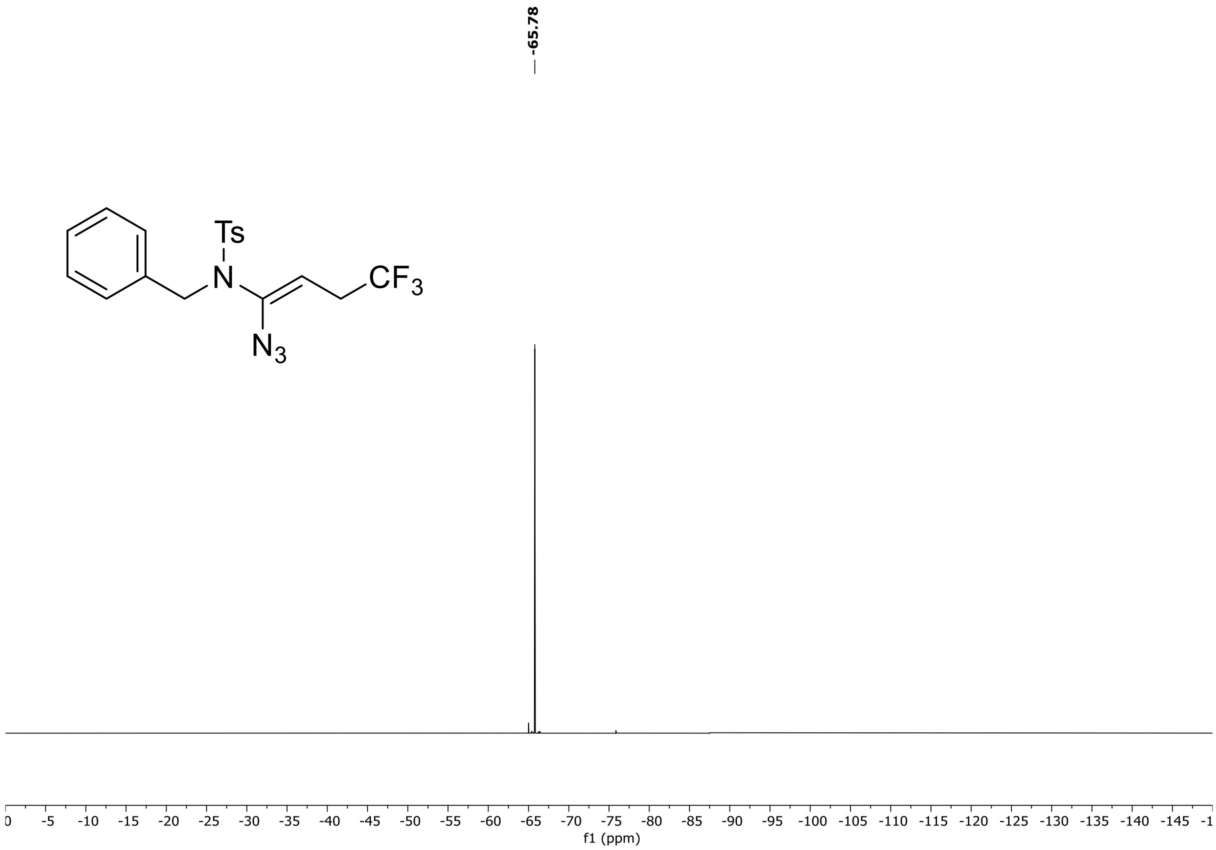
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) of **3j**



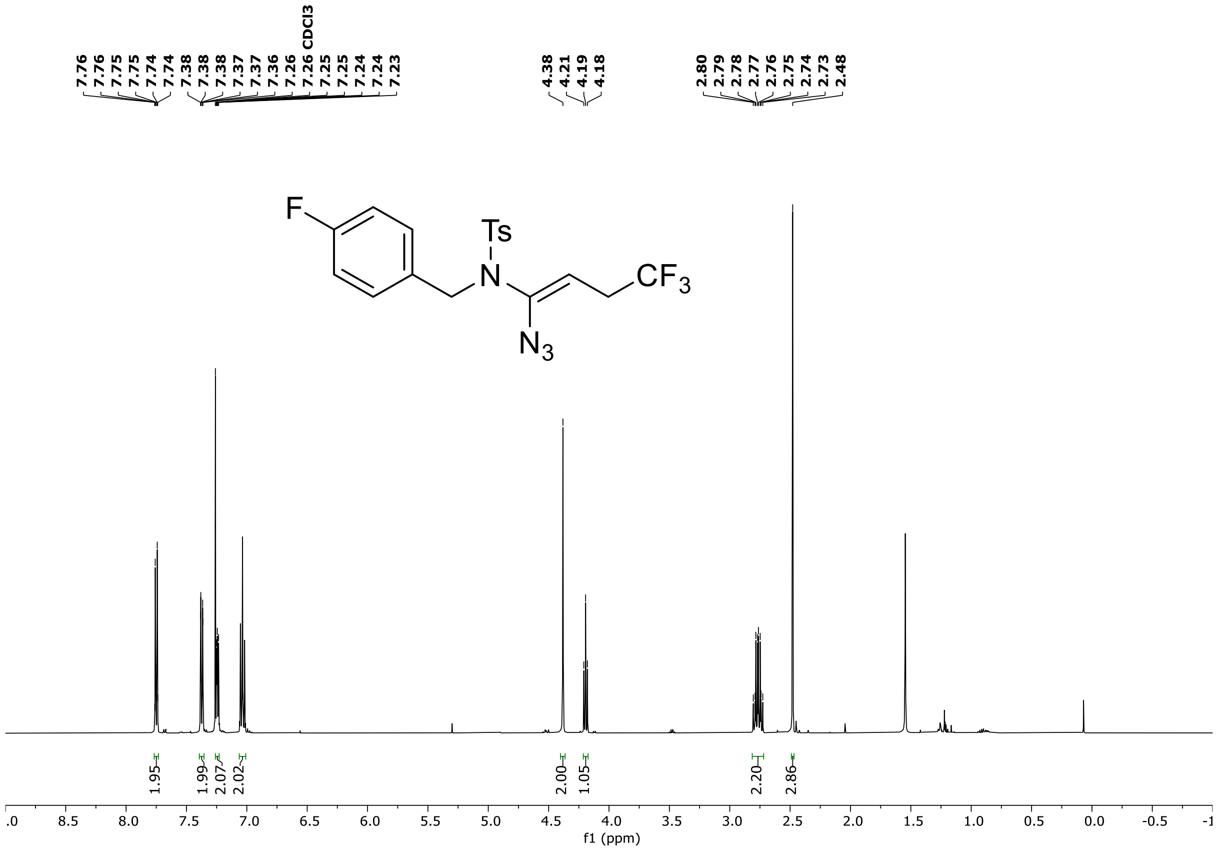
^{1}H NMR ($CDCl_3$, 300 MHz) of **4a**



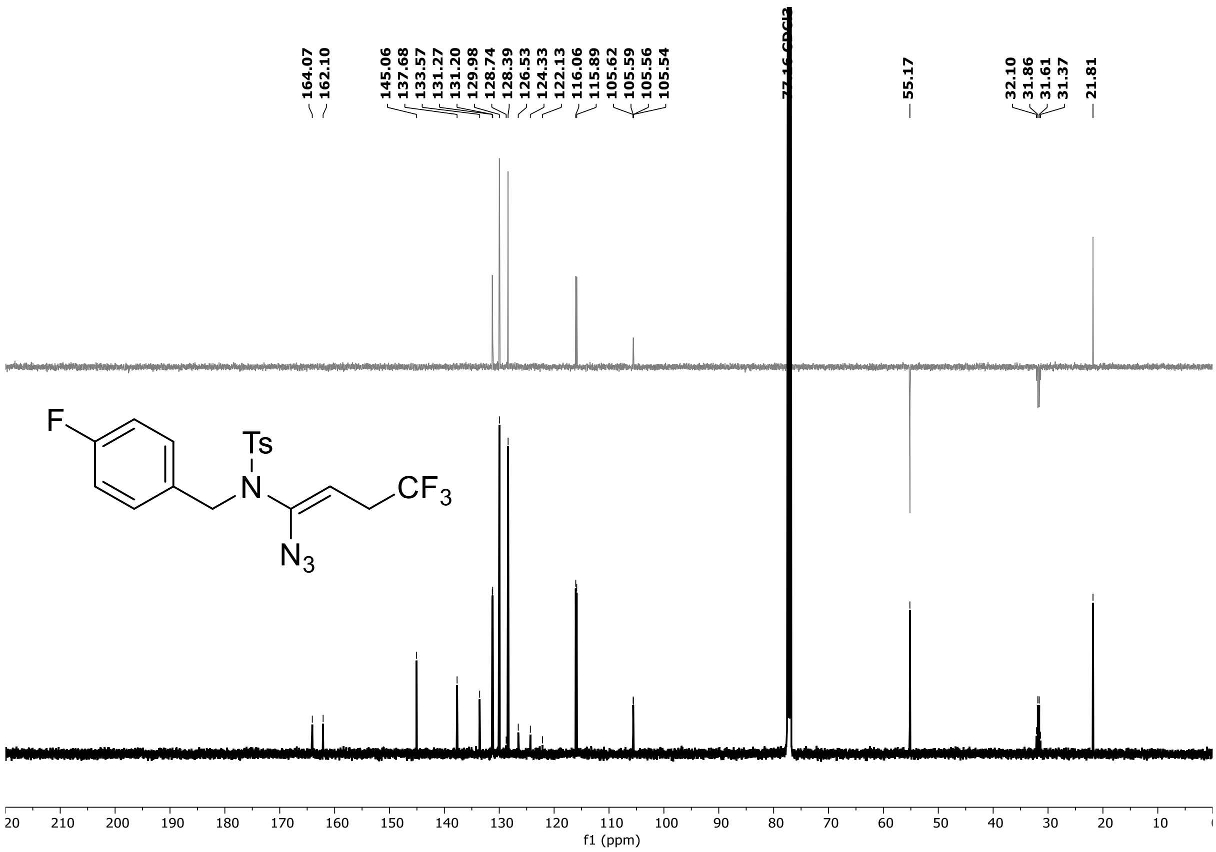
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) of **4a**



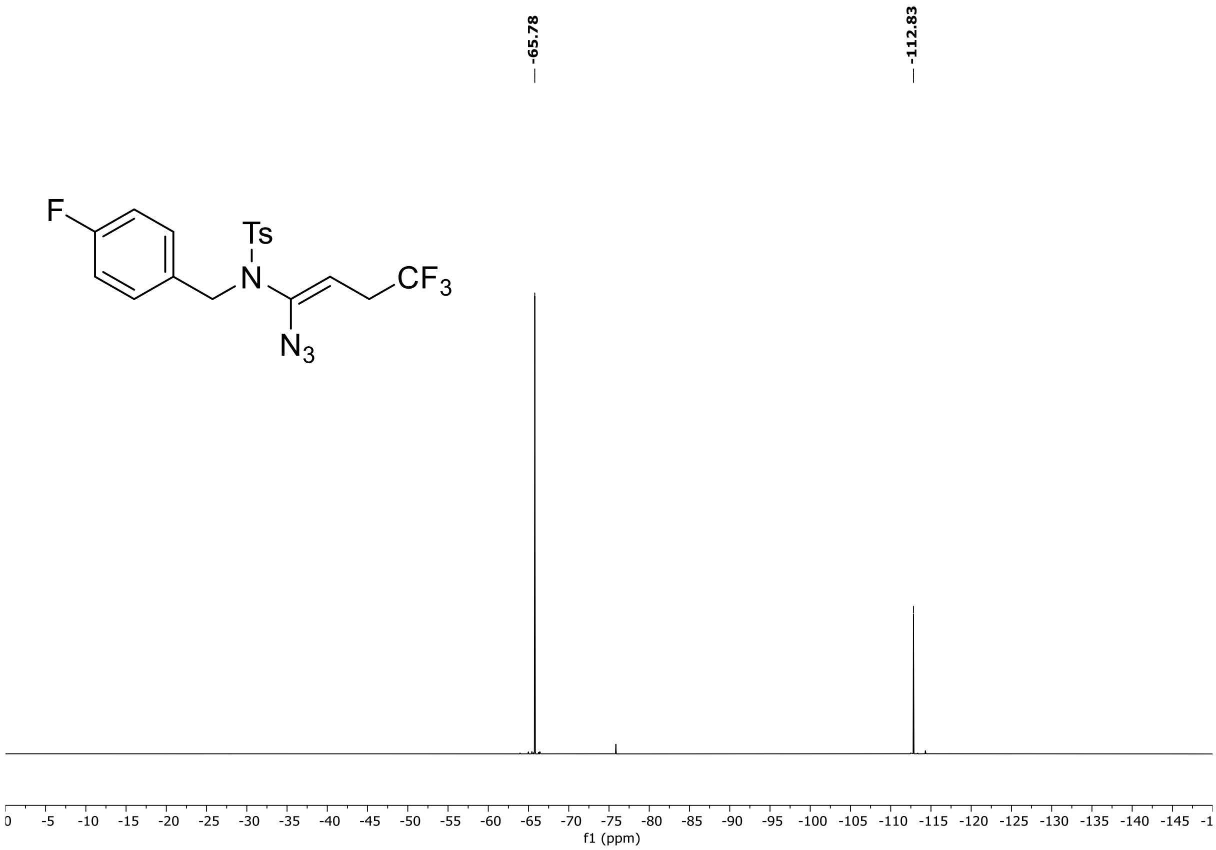
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 282 MHz) of **4a**



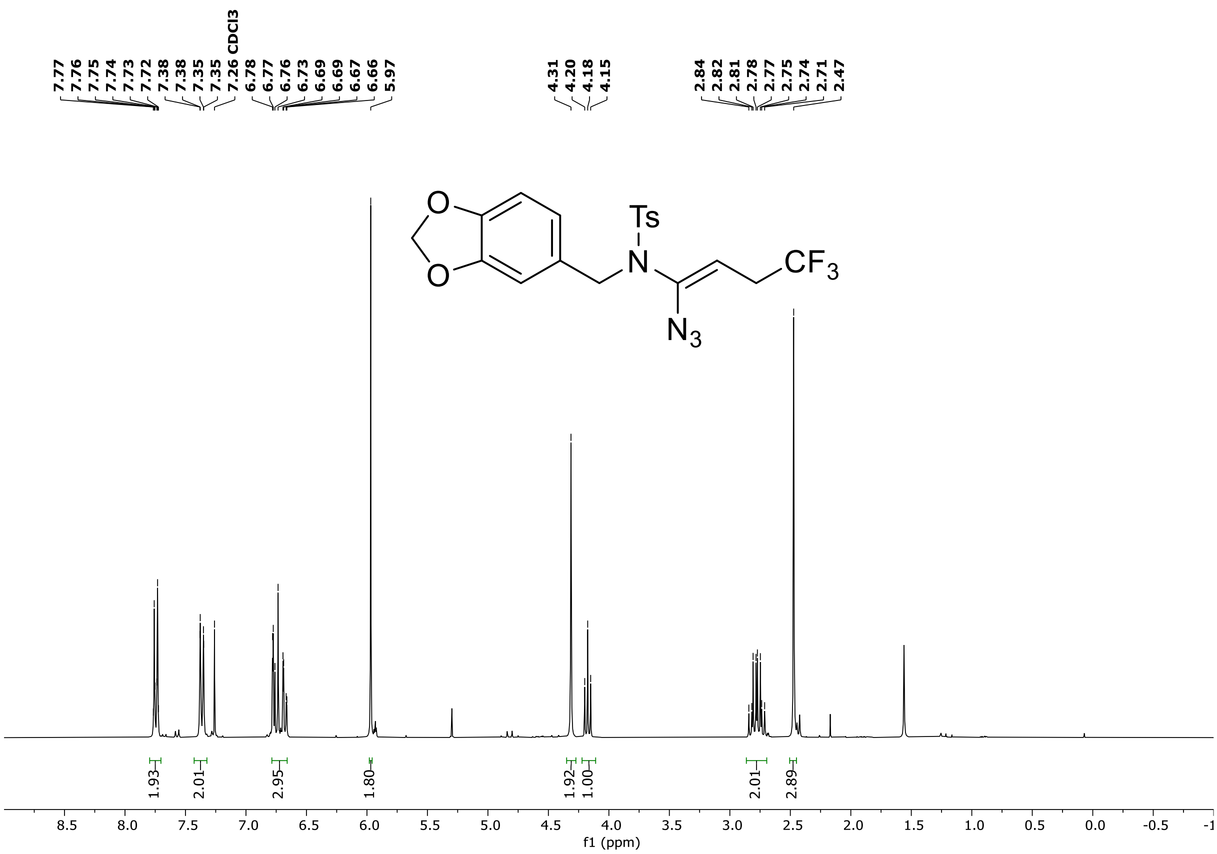
^{1}H NMR ($CDCl_3$, 500 MHz) of **4b**



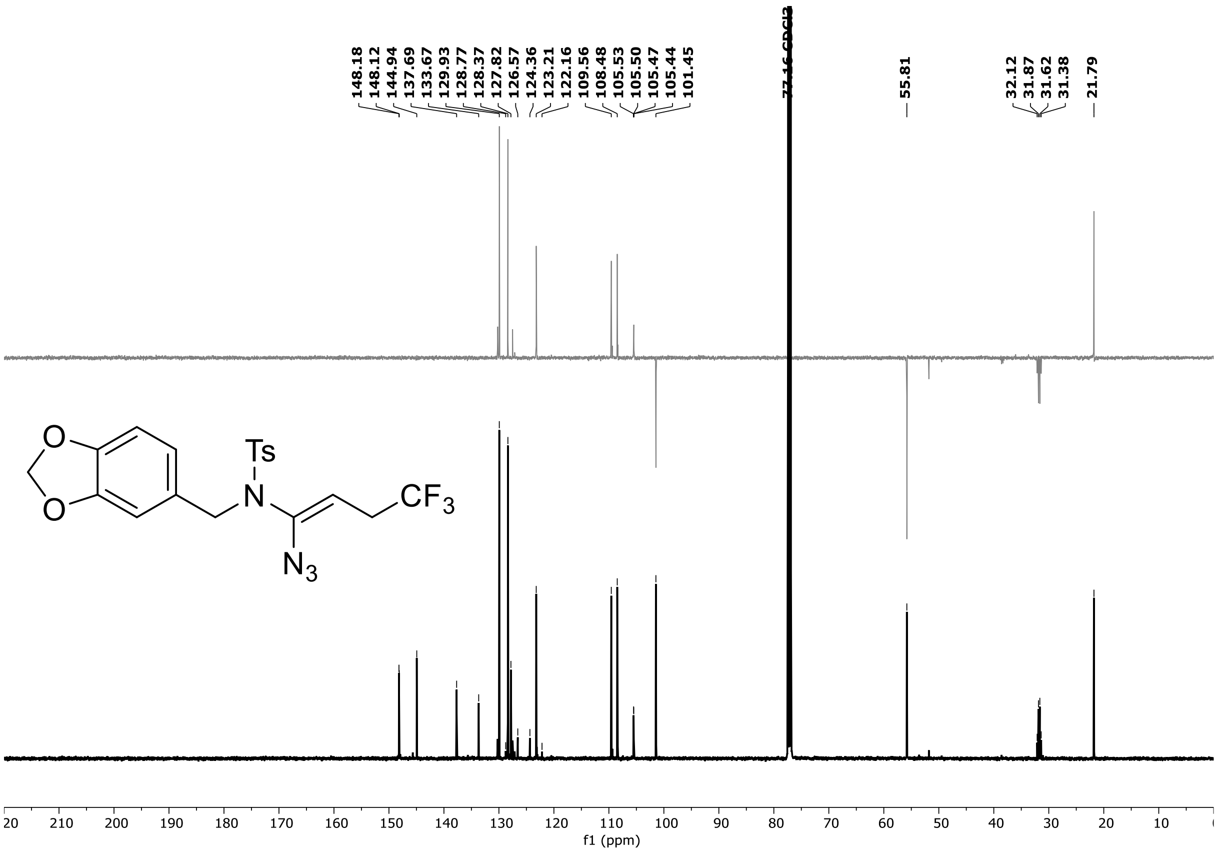
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) of **4b**



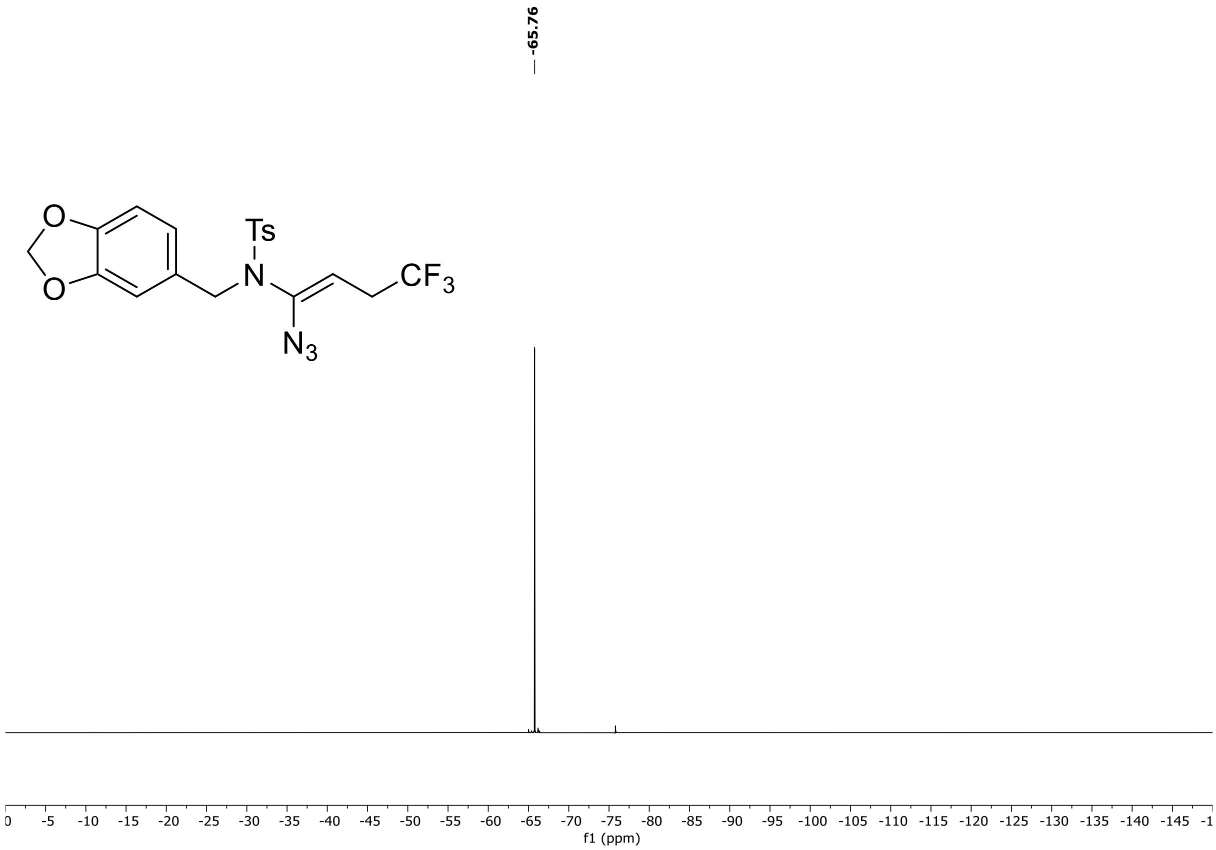
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 282 MHz) of **4b**



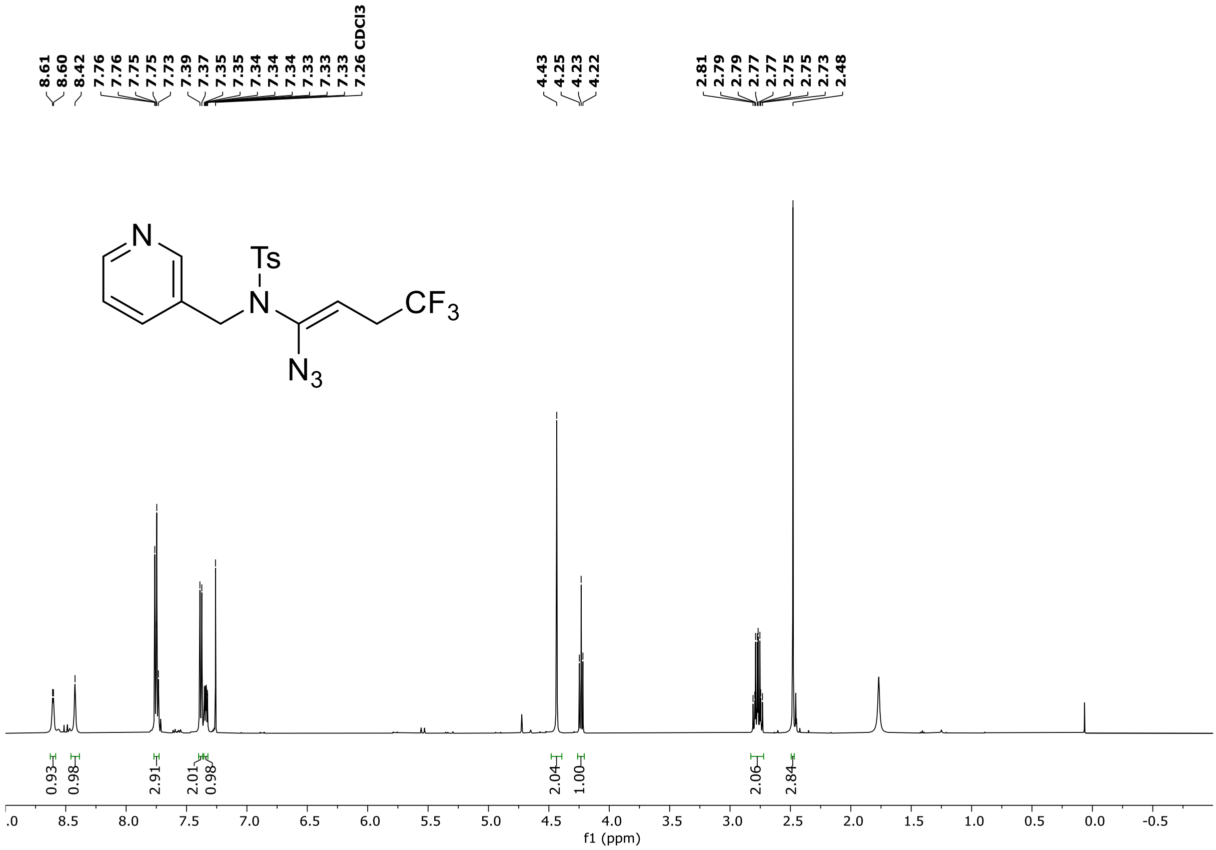
^{1}H NMR ($CDCl_3$, 300 MHz) of **4c**



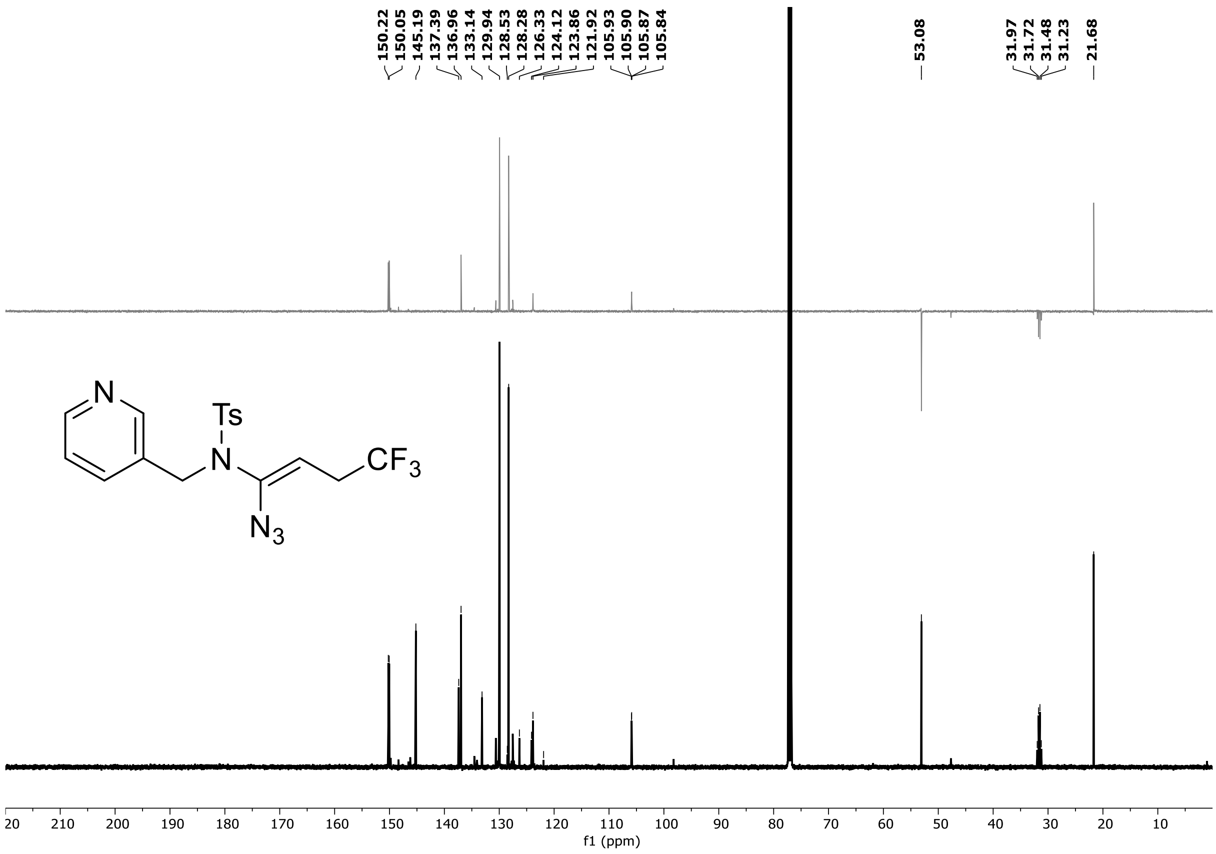
$^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) of **4c**



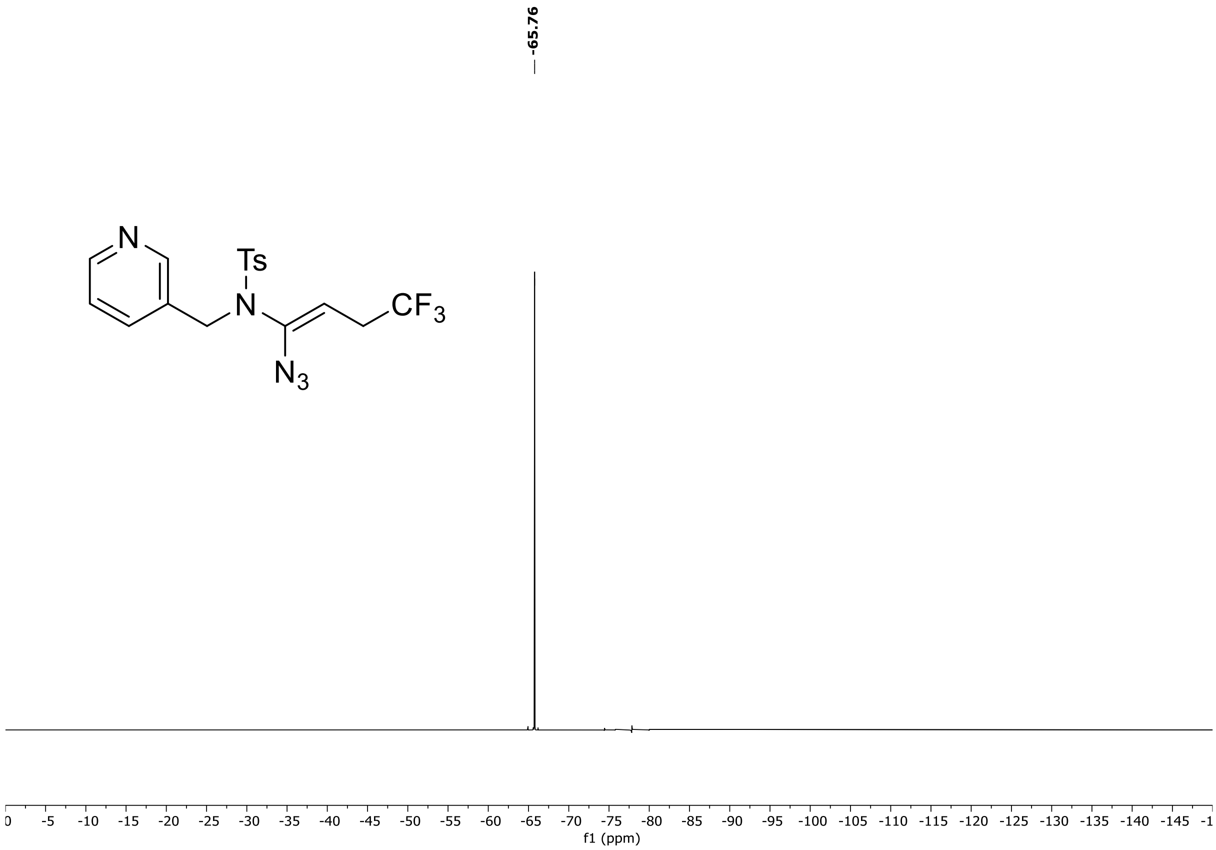
$^{19}F\{^1H\}$ NMR ($CDCl_3$, 282 MHz) of **4c**



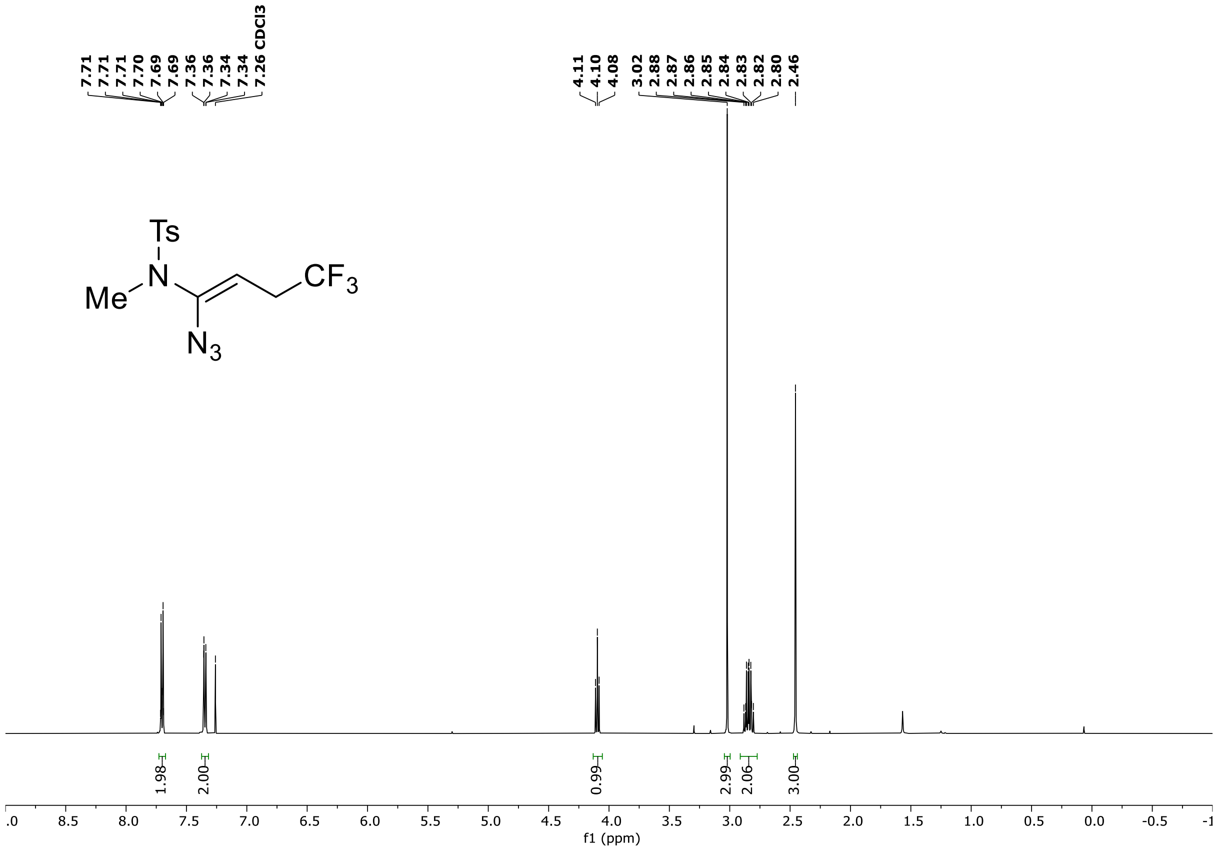
^{1}H NMR ($CDCl_3$, 500 MHz) of **4d**



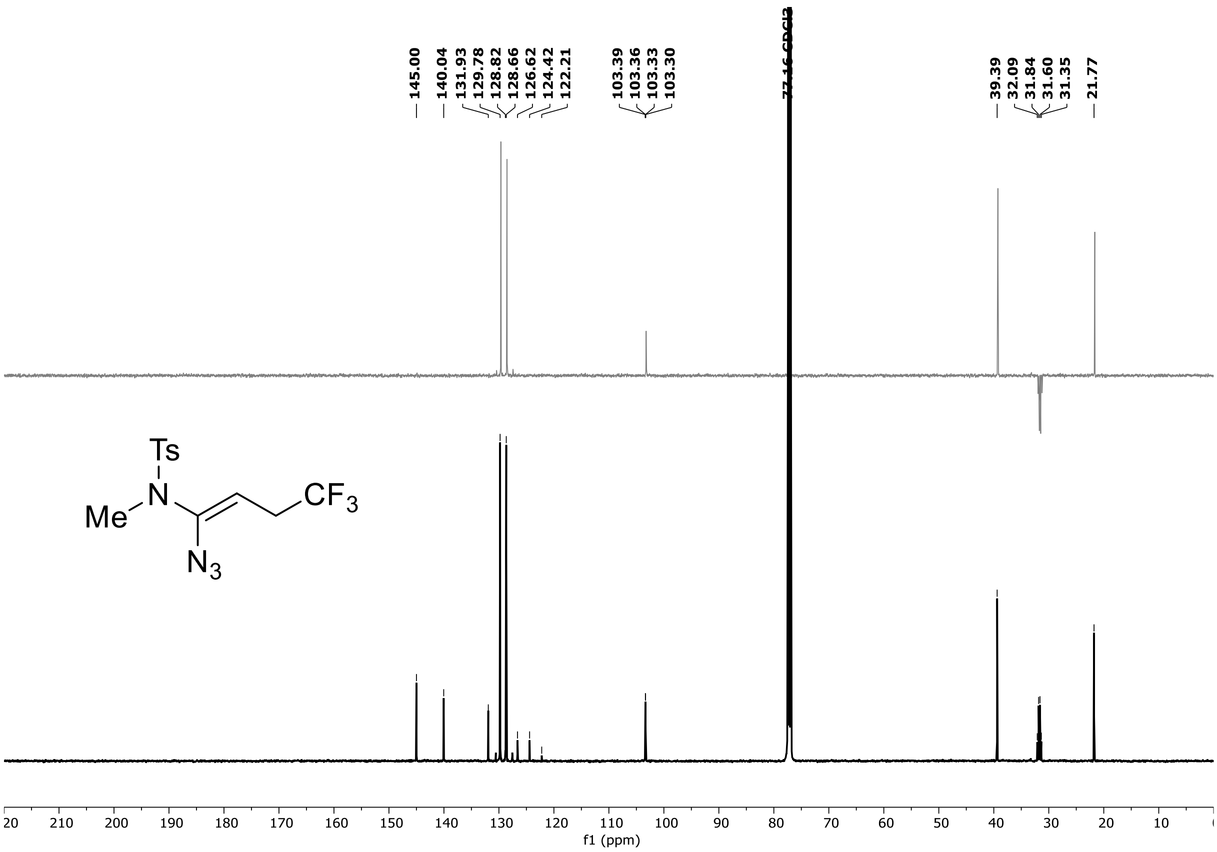
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) of **4d**



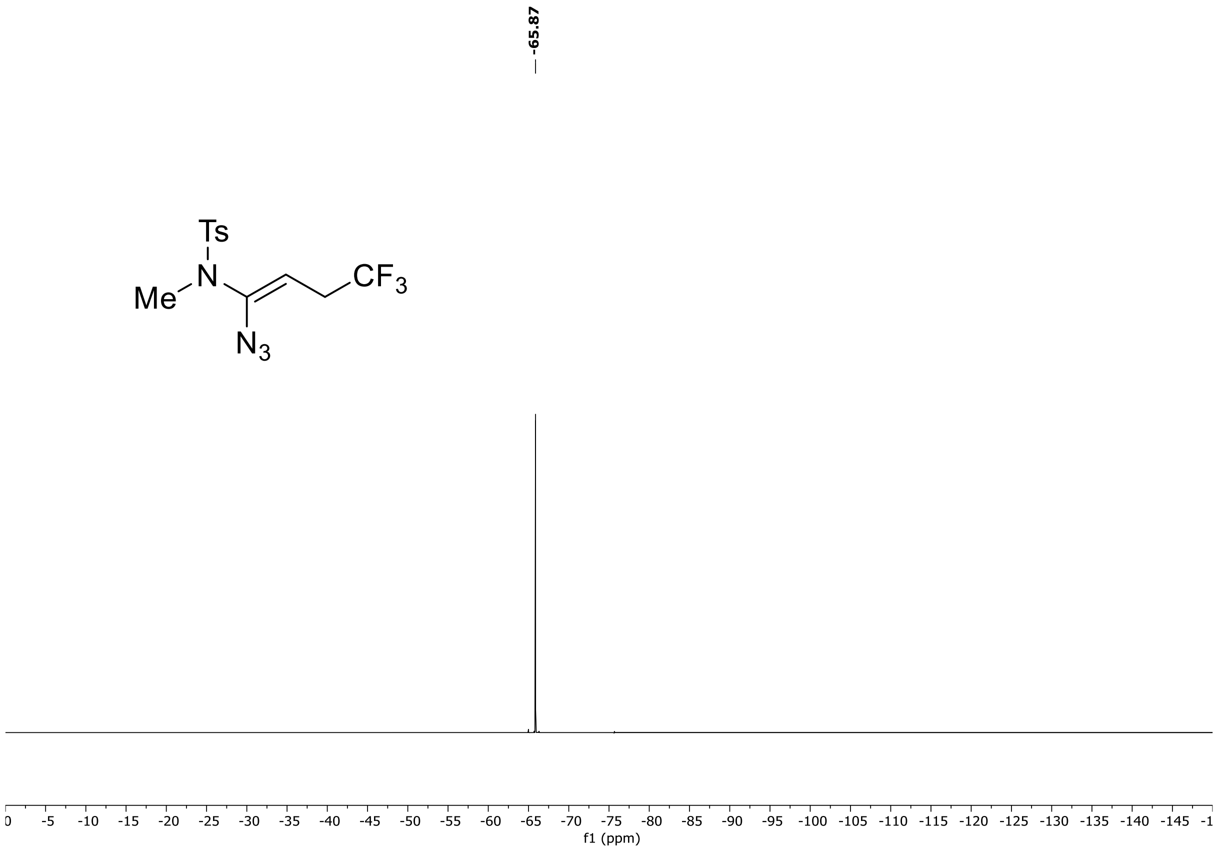
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 471 MHz) of **4d**



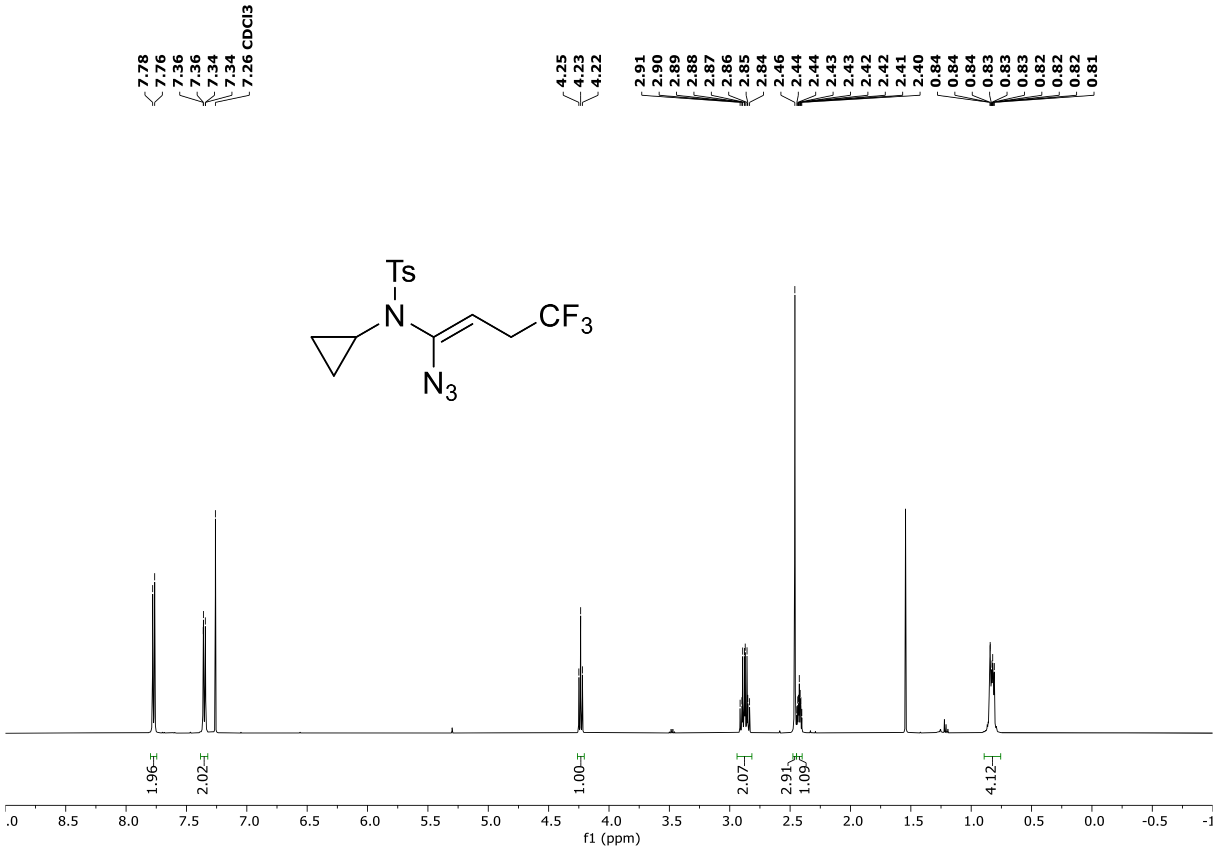
^{1}H NMR ($CDCl_3$, 500 MHz) of **4e**



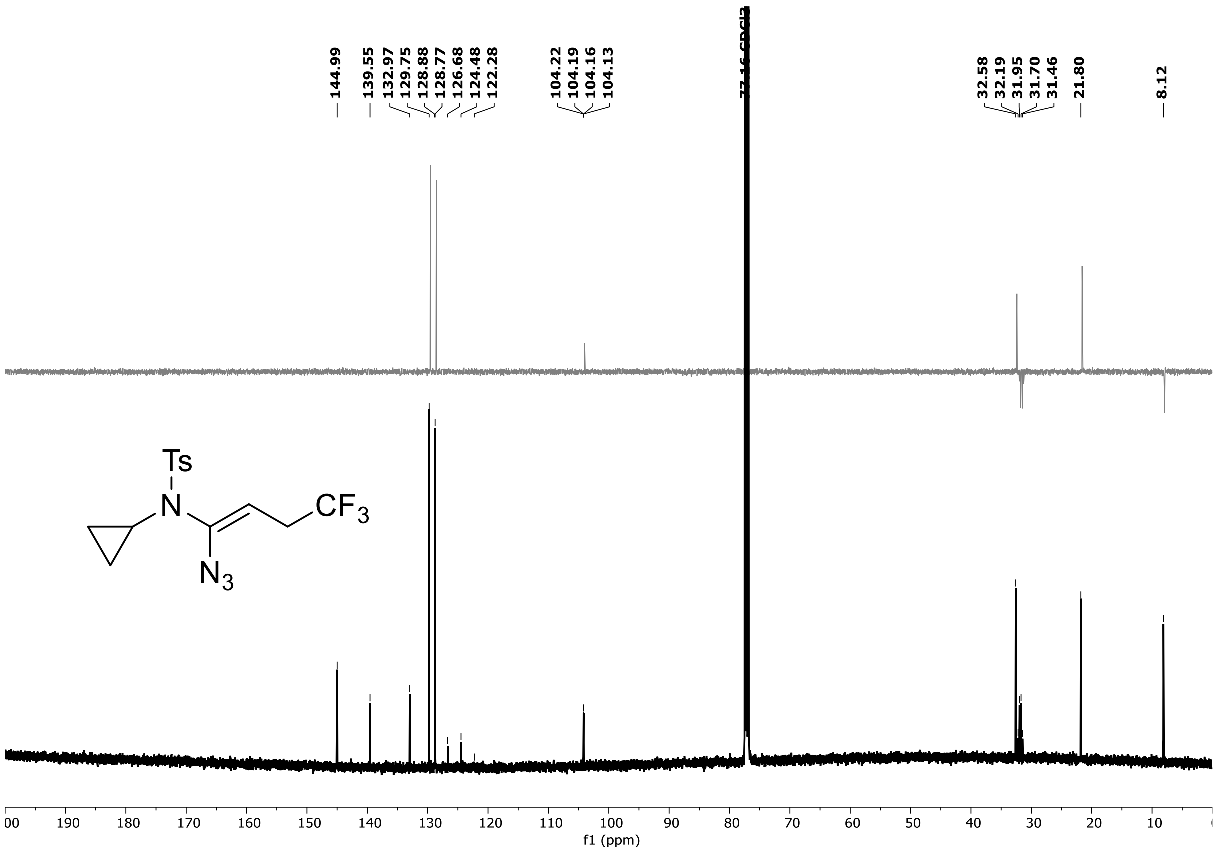
^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) of **4e**



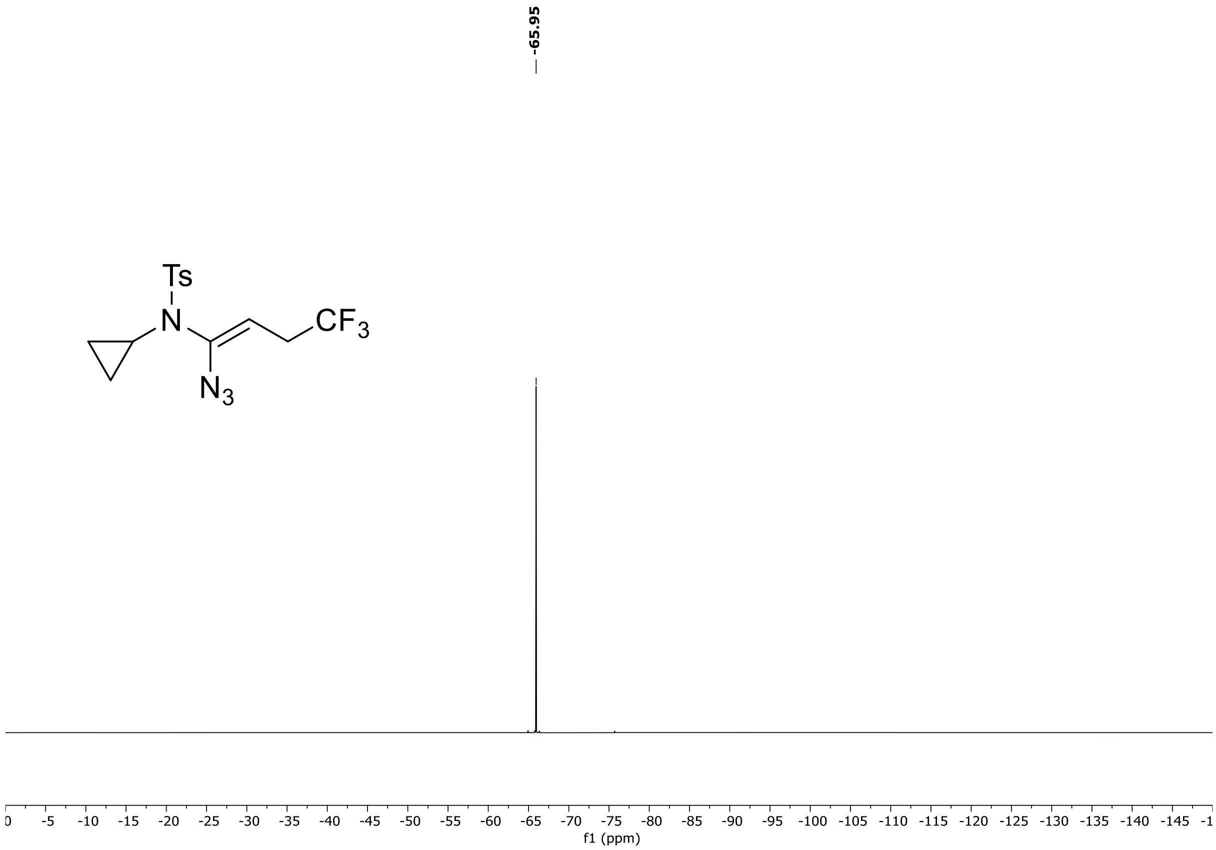
$^{19}F\{^1H\}$ NMR ($CDCl_3$, 471 MHz) of **4e**



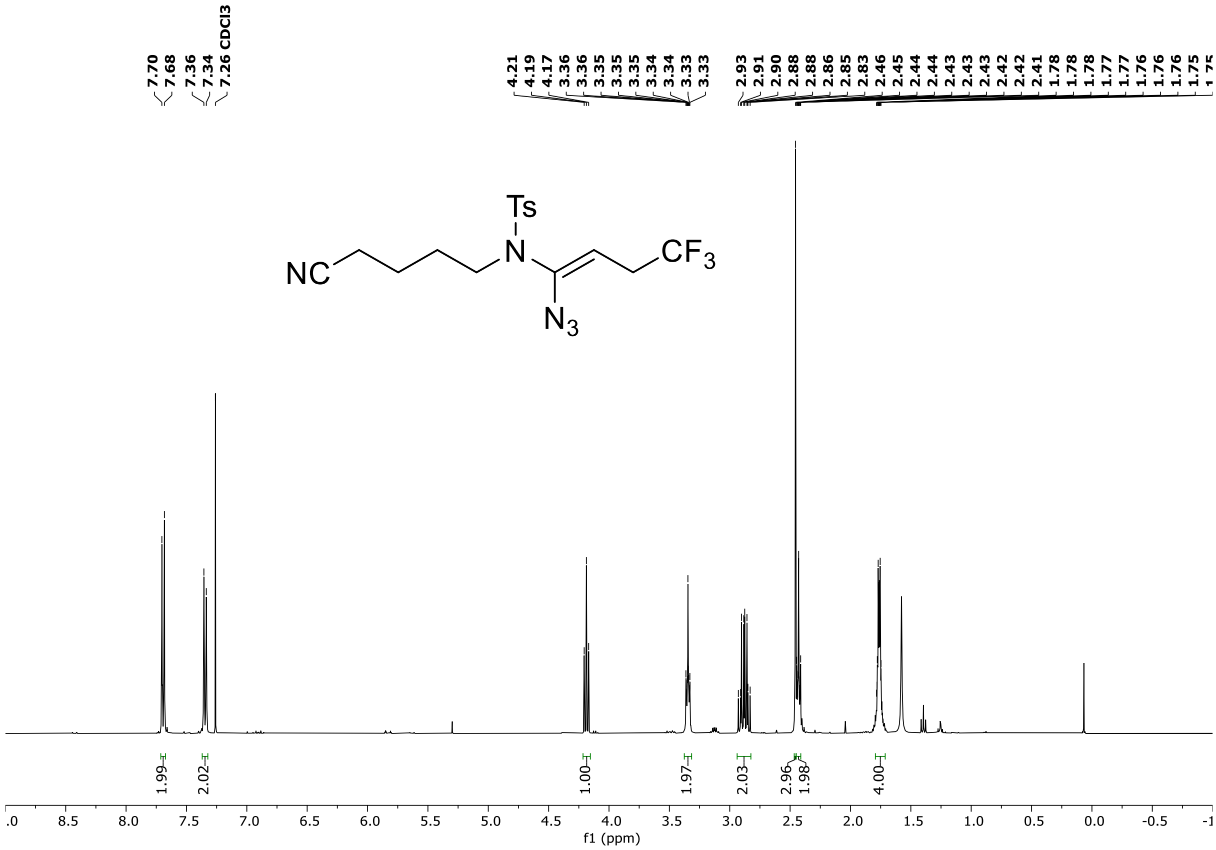
^{1}H NMR (CDCl$_3$, 500 MHz) of **4f**



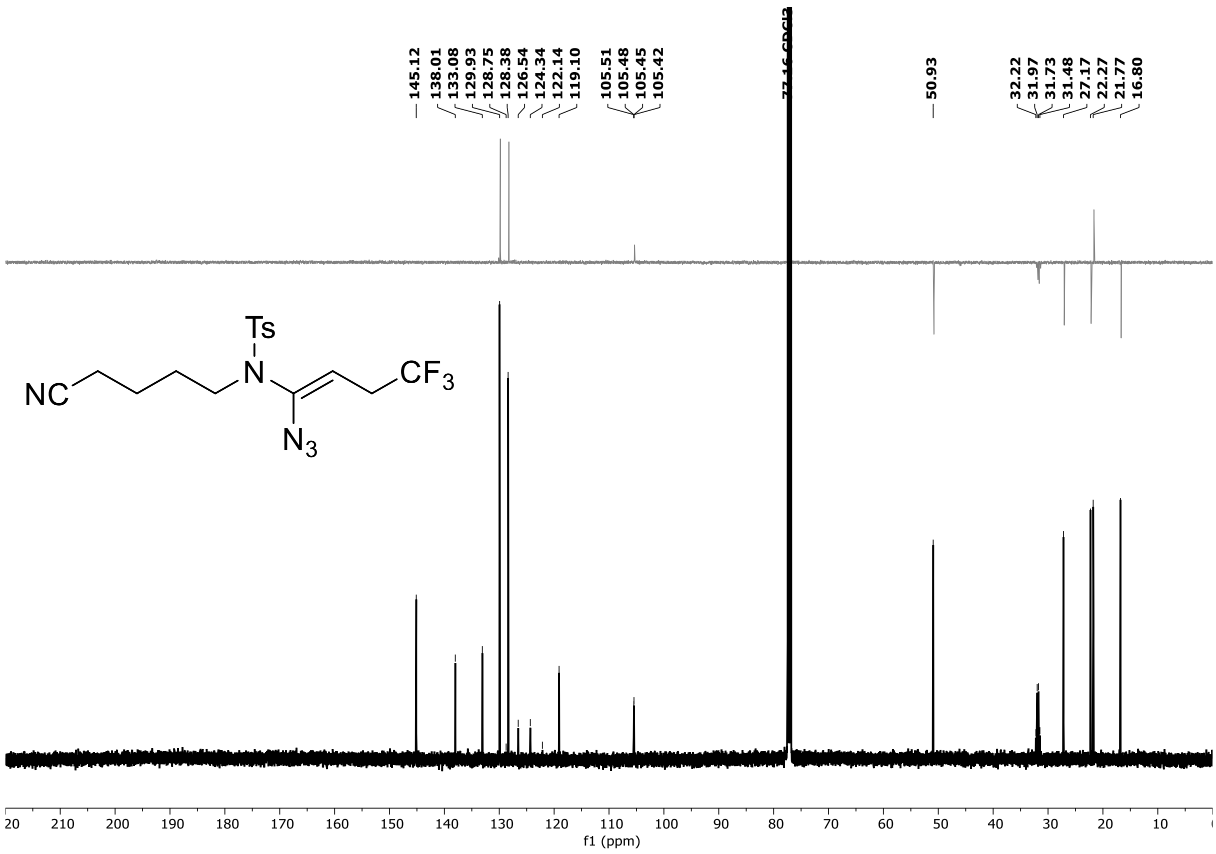
^{13}C{^{1}H} NMR (CDCl$_3$, 126 MHz) of **4f**



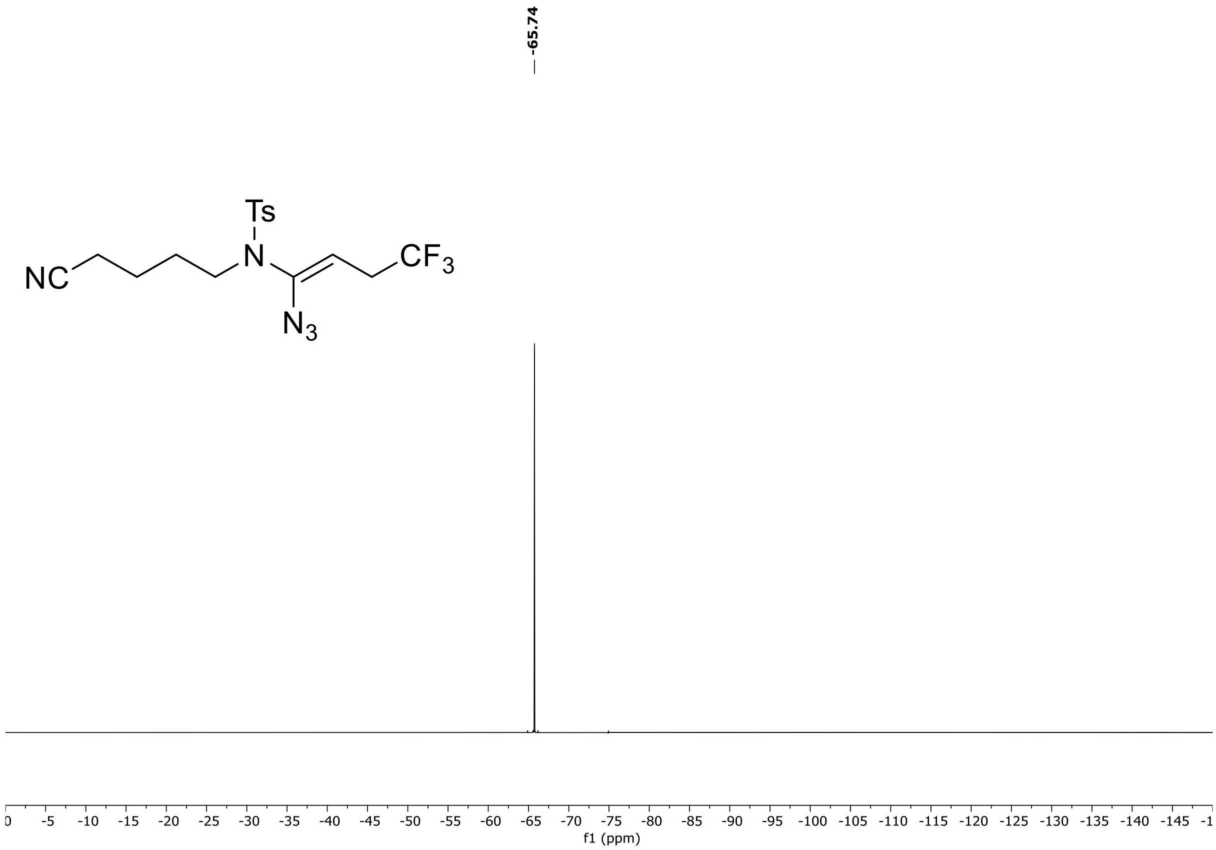
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 471 MHz) of **4f**



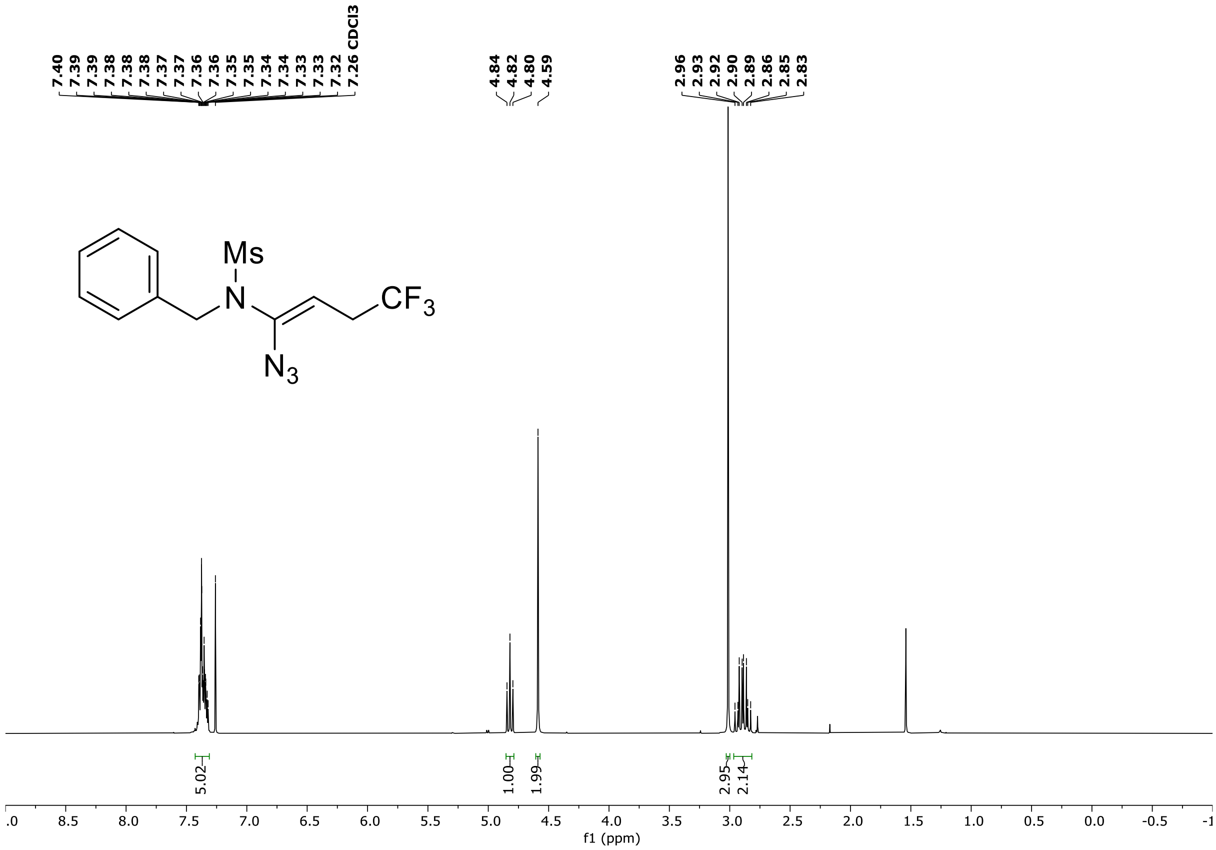
^{1}H NMR ($CDCl_3$, 400 MHz) of **4g**



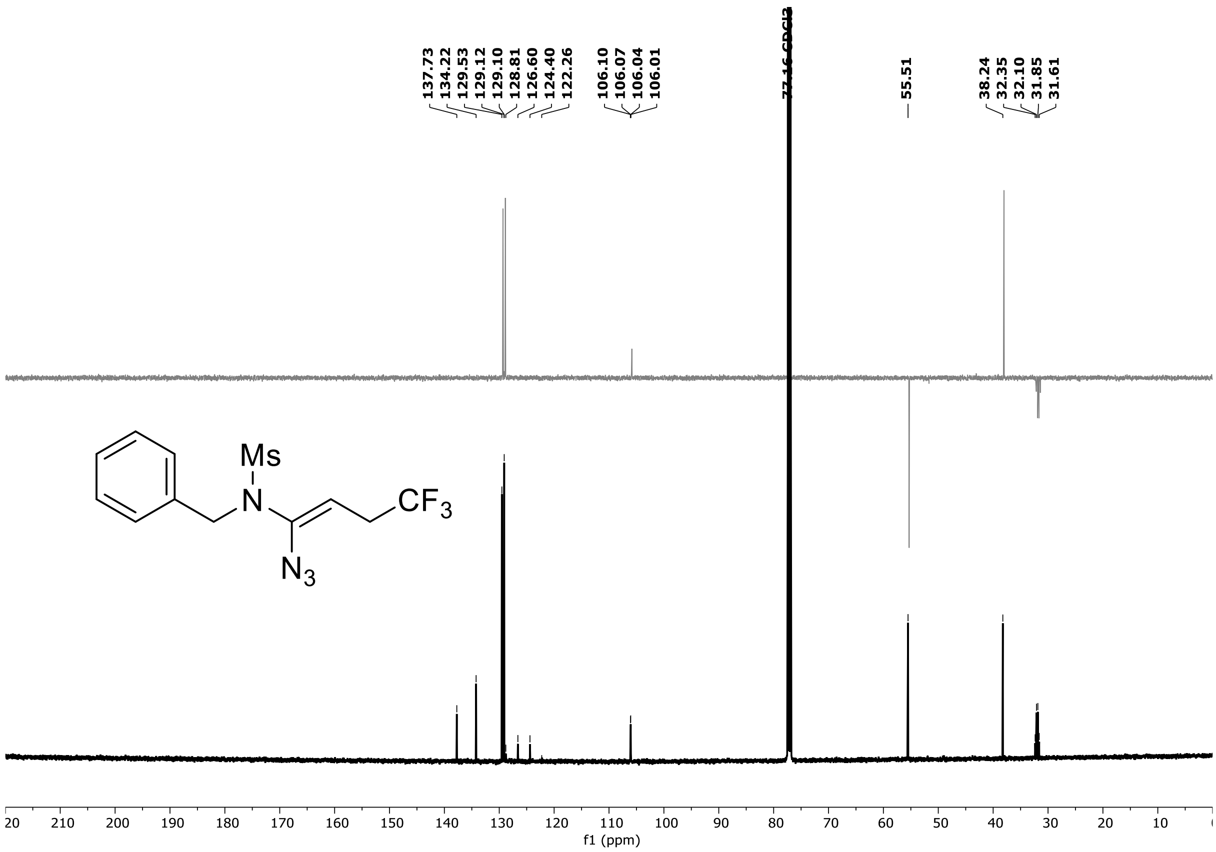
$^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) of **4g**



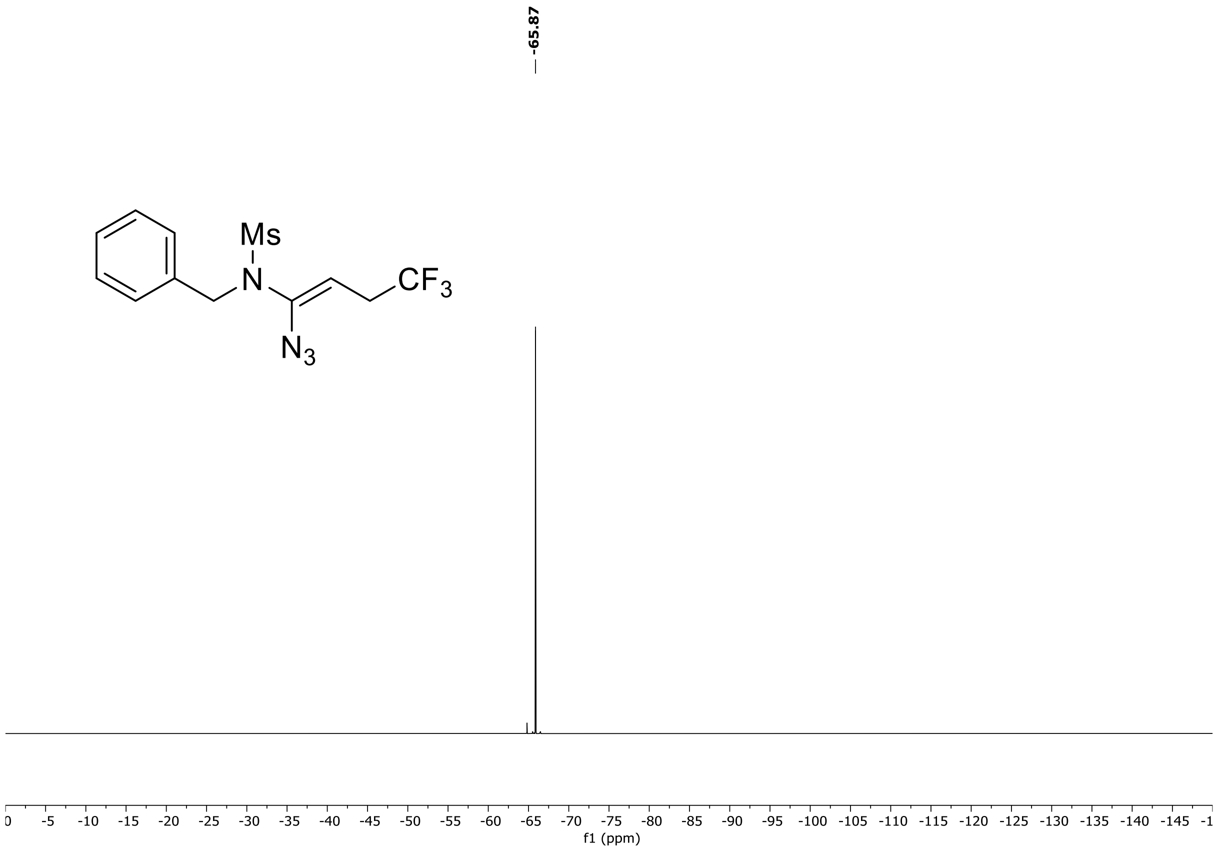
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 471 MHz) of **4g**



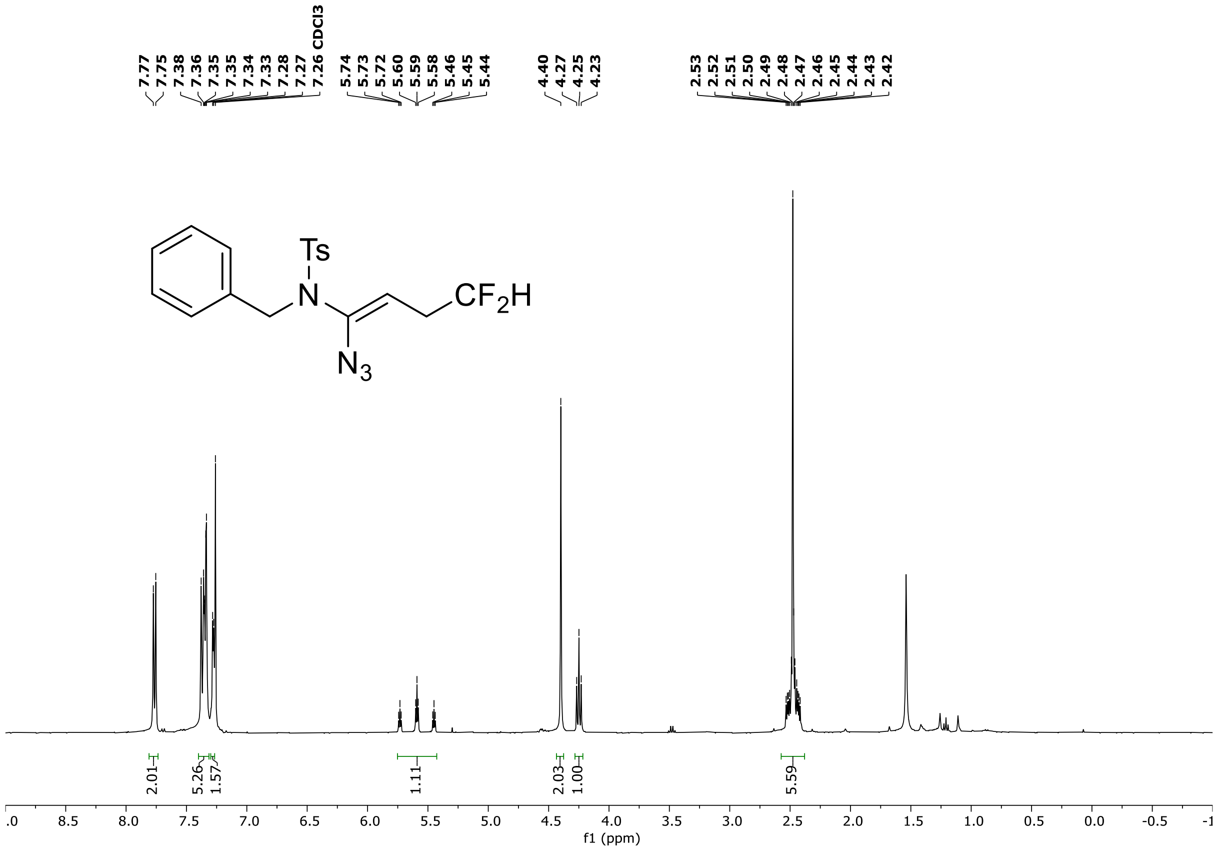
^{1}H NMR ($CDCl_3$, 300 MHz) of **4h**



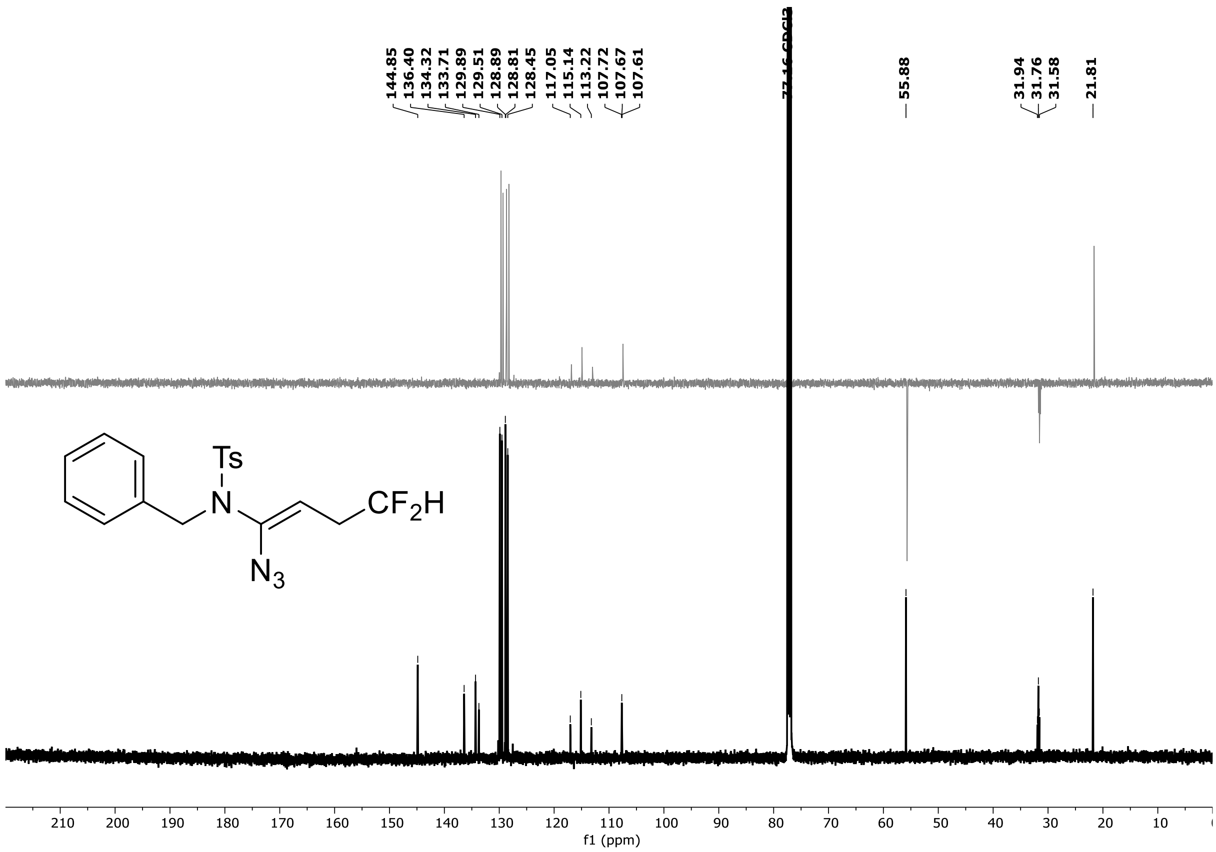
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) of **4h**



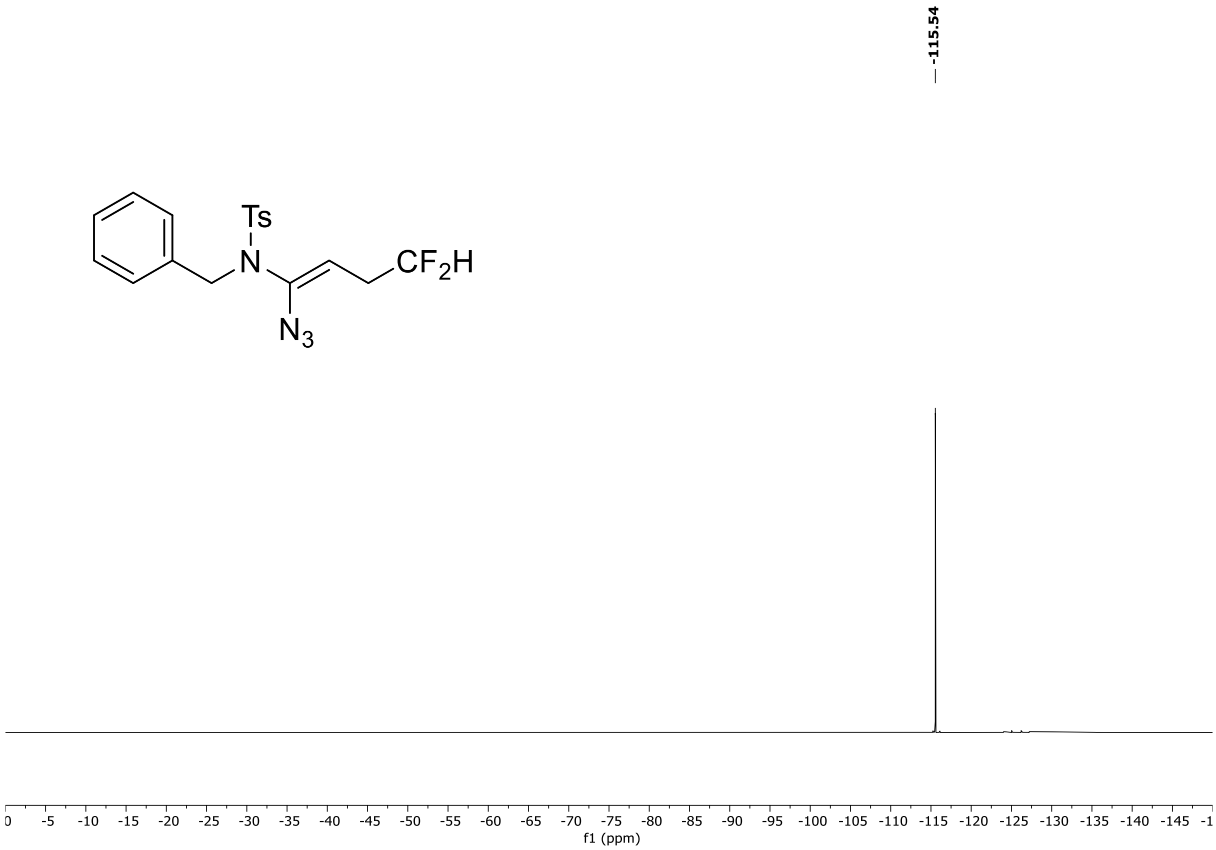
$^{19}F\{^1H\}$ NMR ($CDCl_3$, 282 MHz) of **4h**



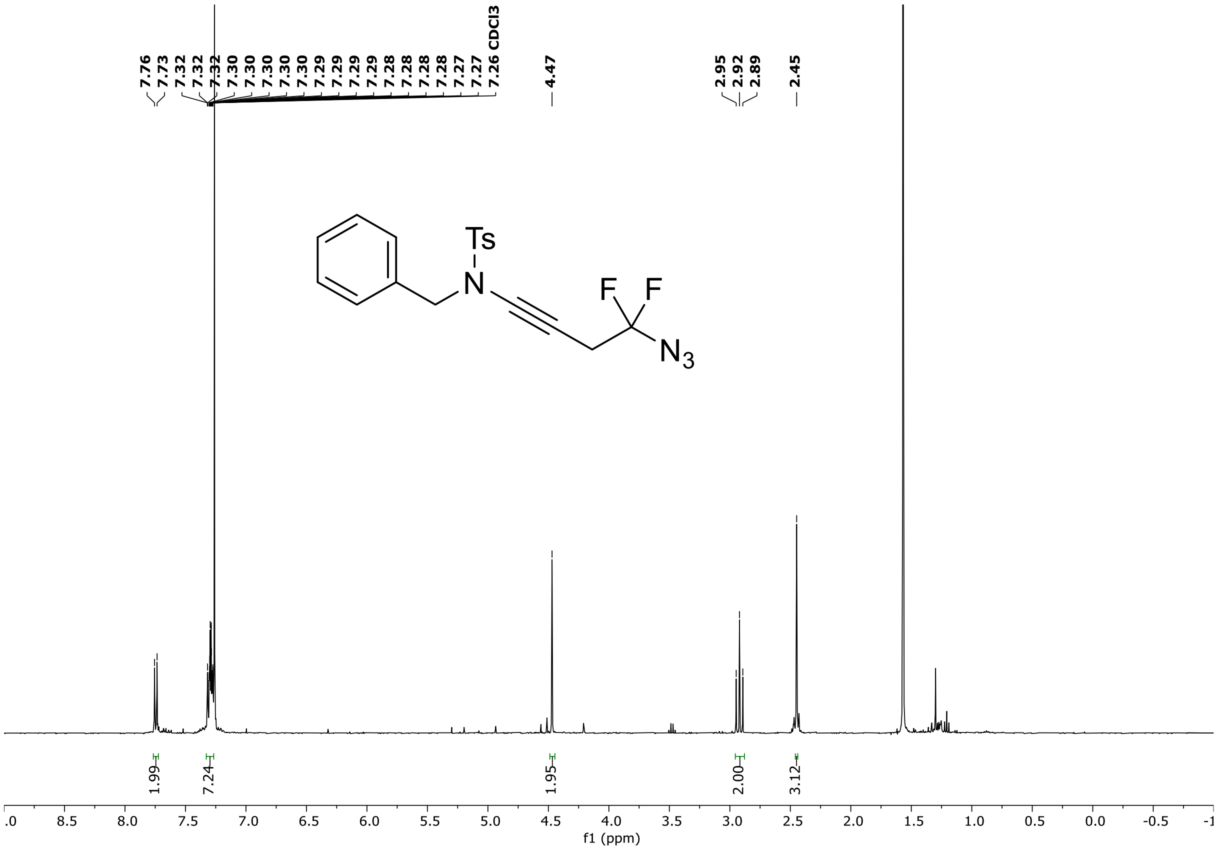
^{1}H NMR ($CDCl_3$, 400 MHz) of **4i**



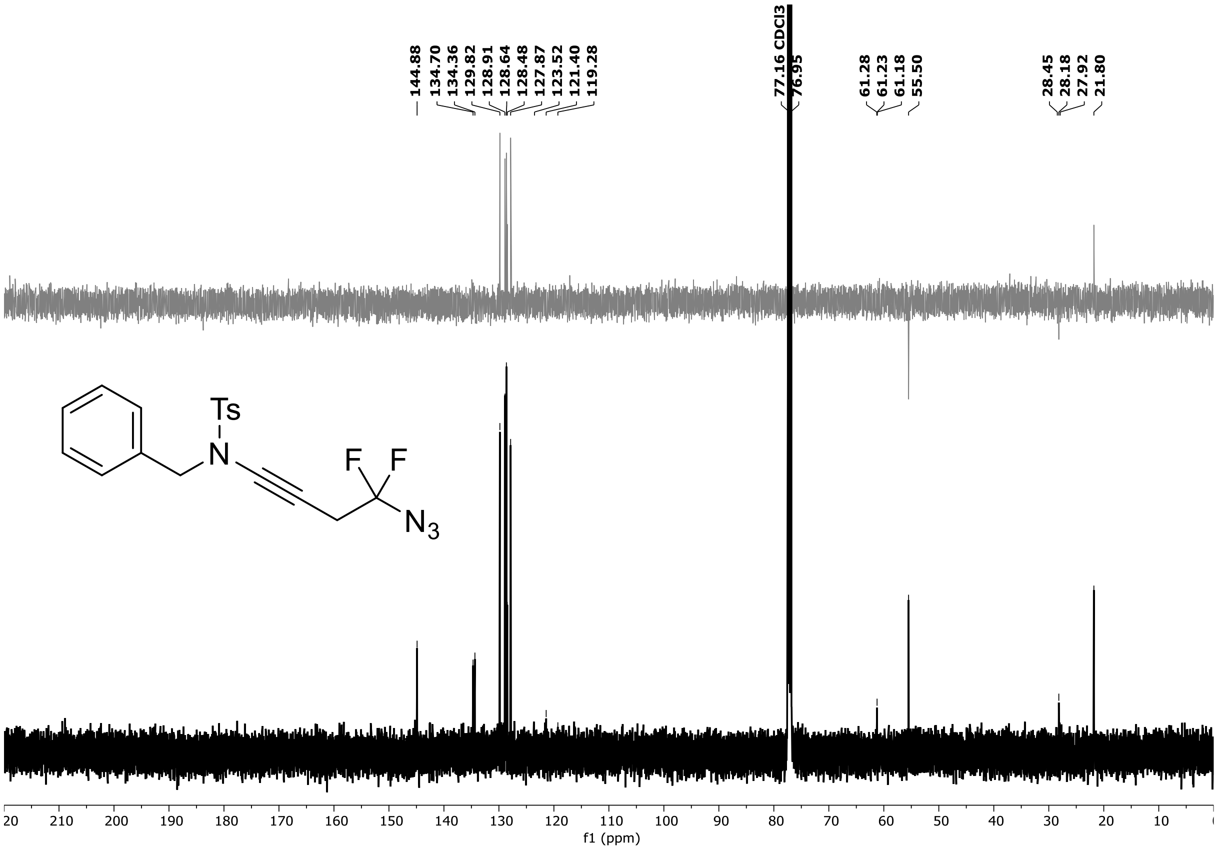
$^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) of **4i**



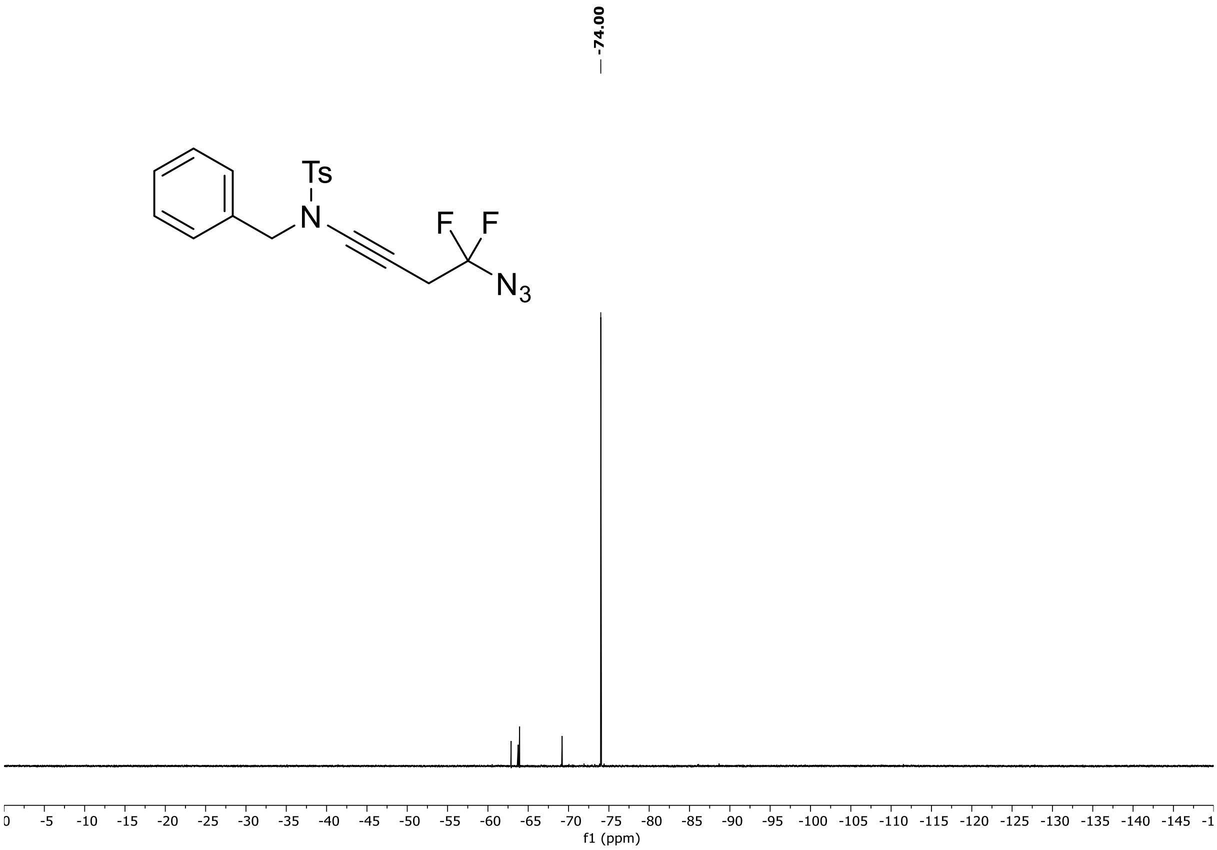
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 282 MHz) of **4i**



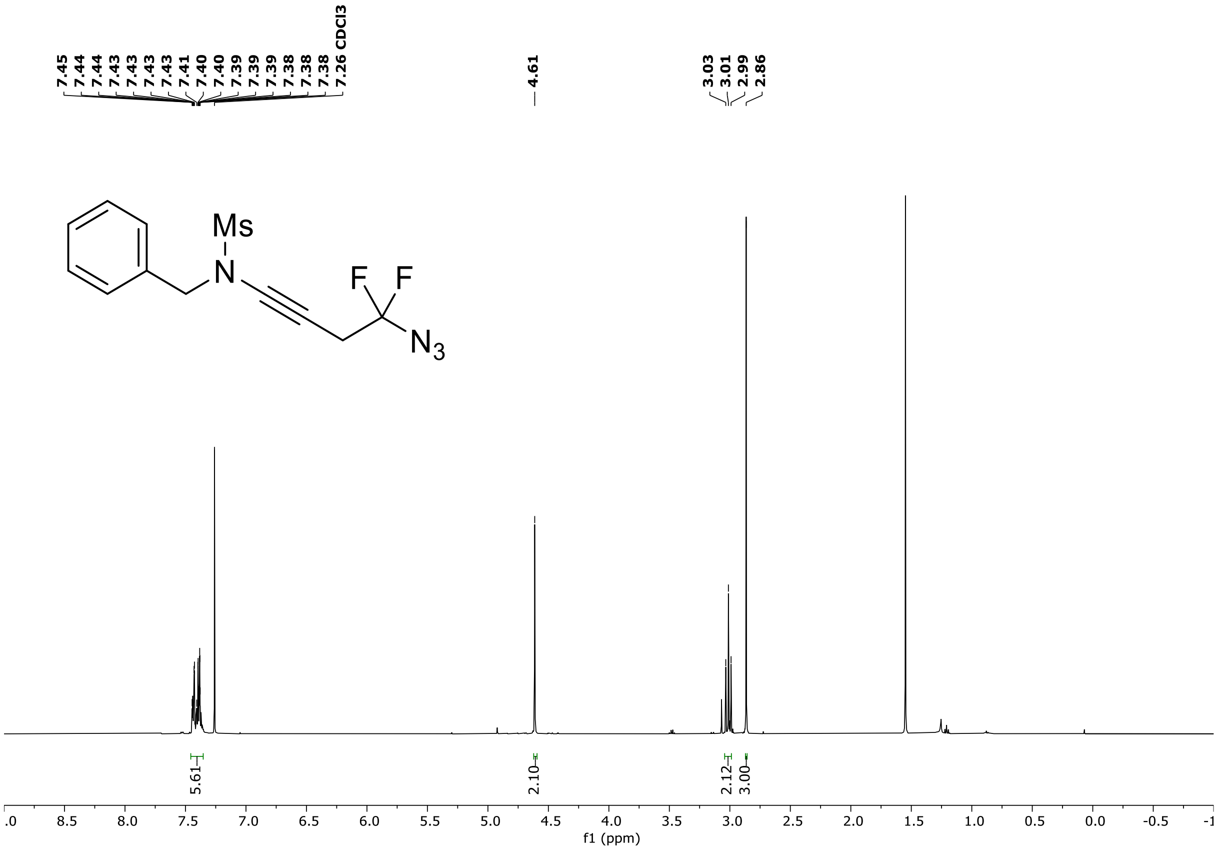
^{1}H NMR ($CDCl_3$, 400 MHz) of **6a**



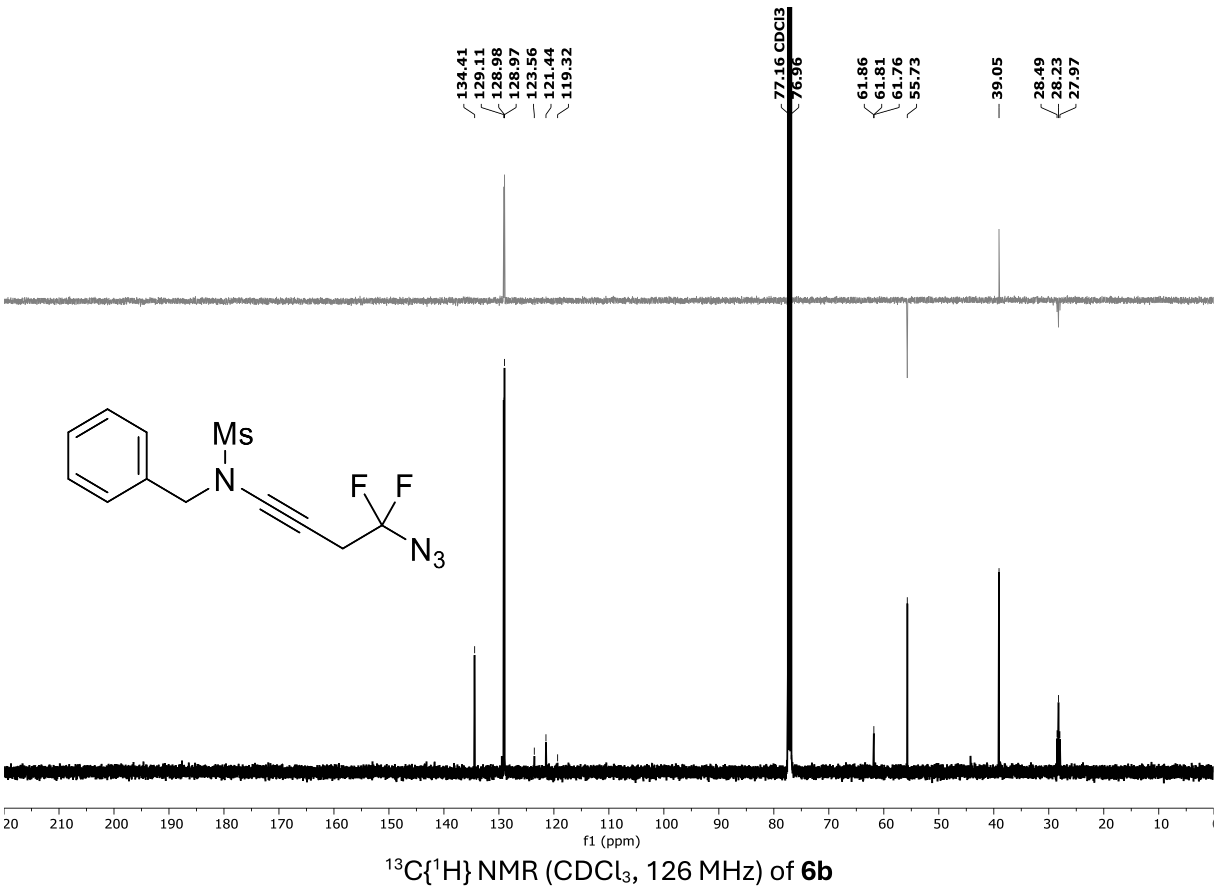
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) of **6a**



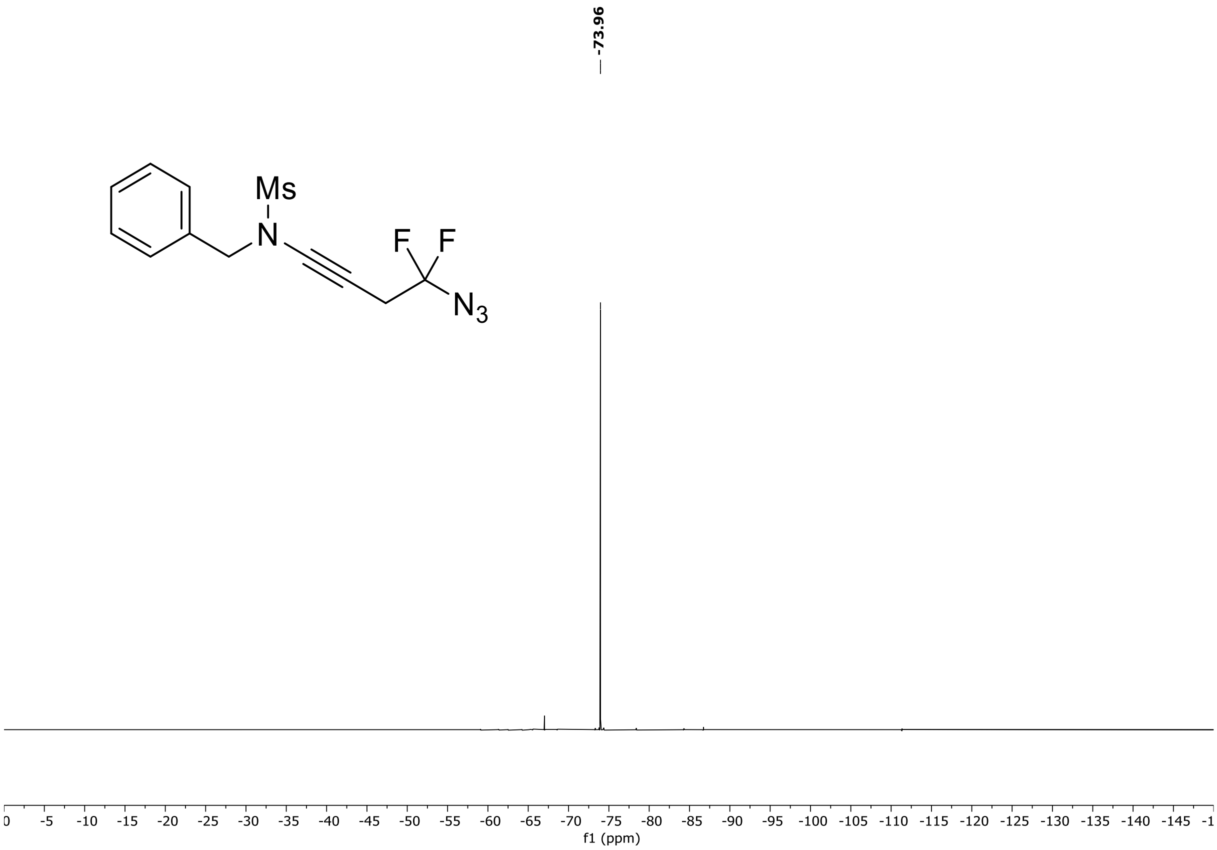
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 471 MHz) of **6a**



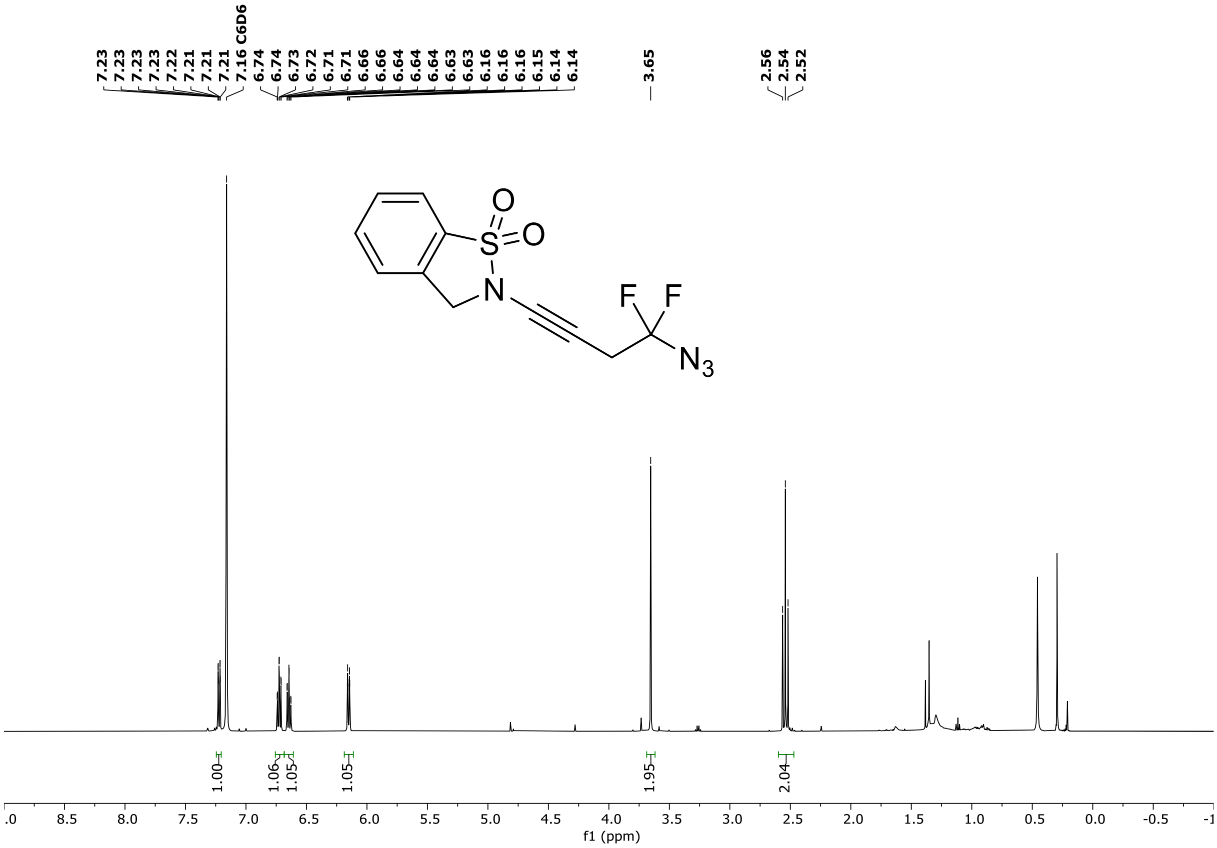
^{1}H NMR ($CDCl_3$, 500 MHz) of **6b**



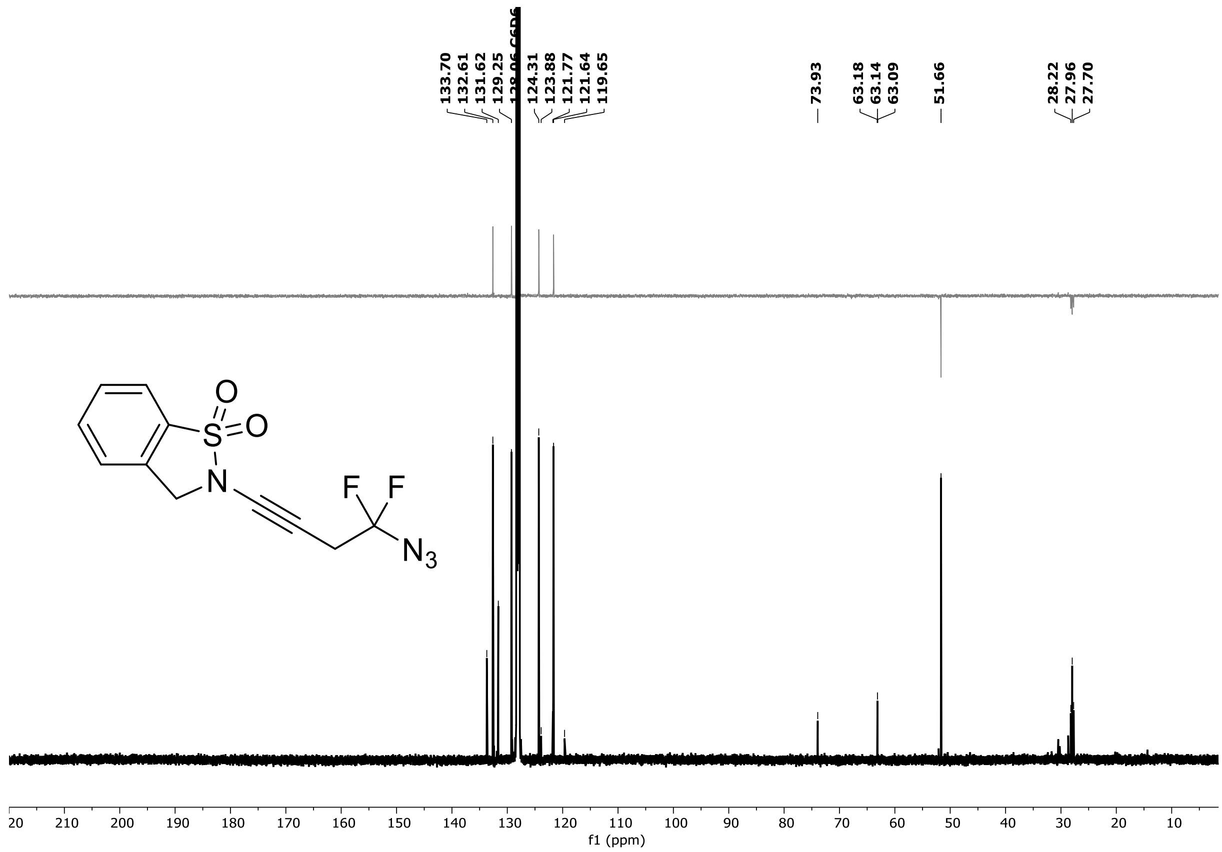
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) of **6b**



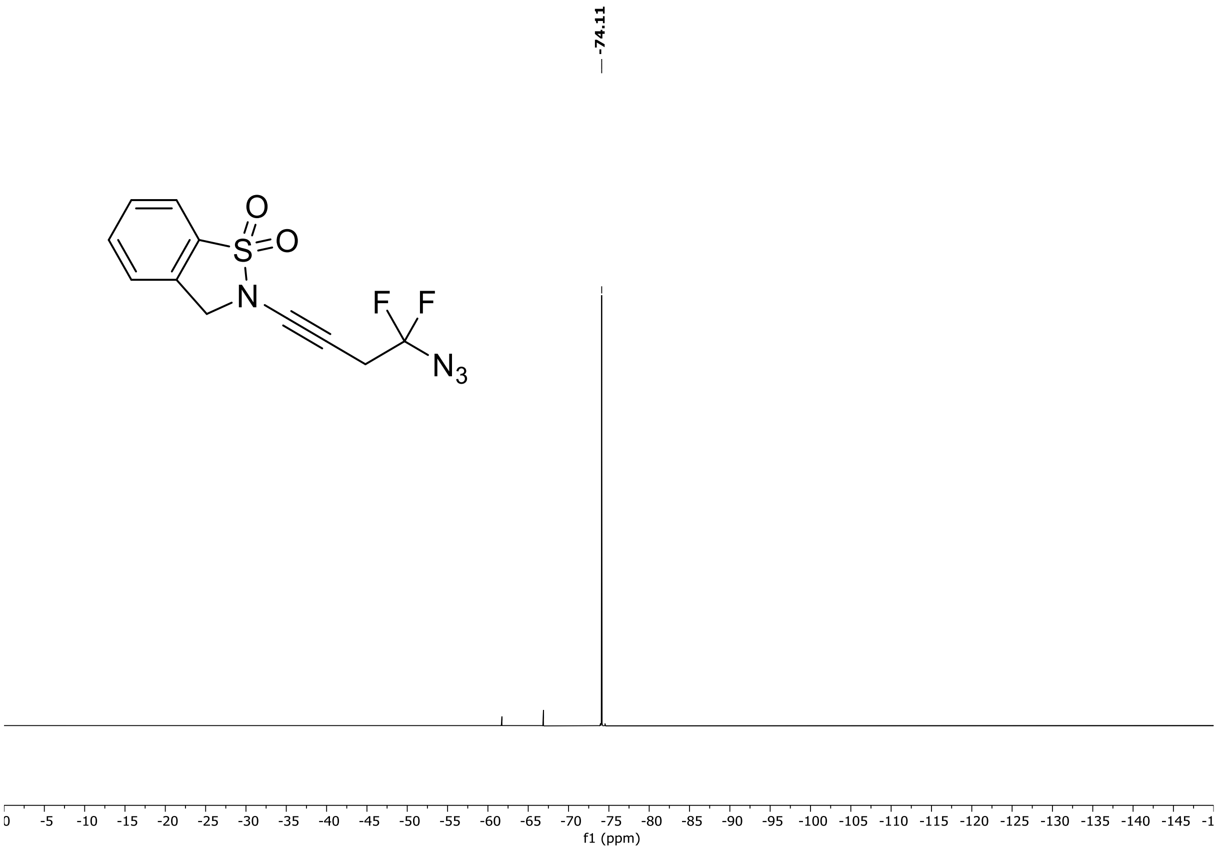
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 471 MHz) of **6b**



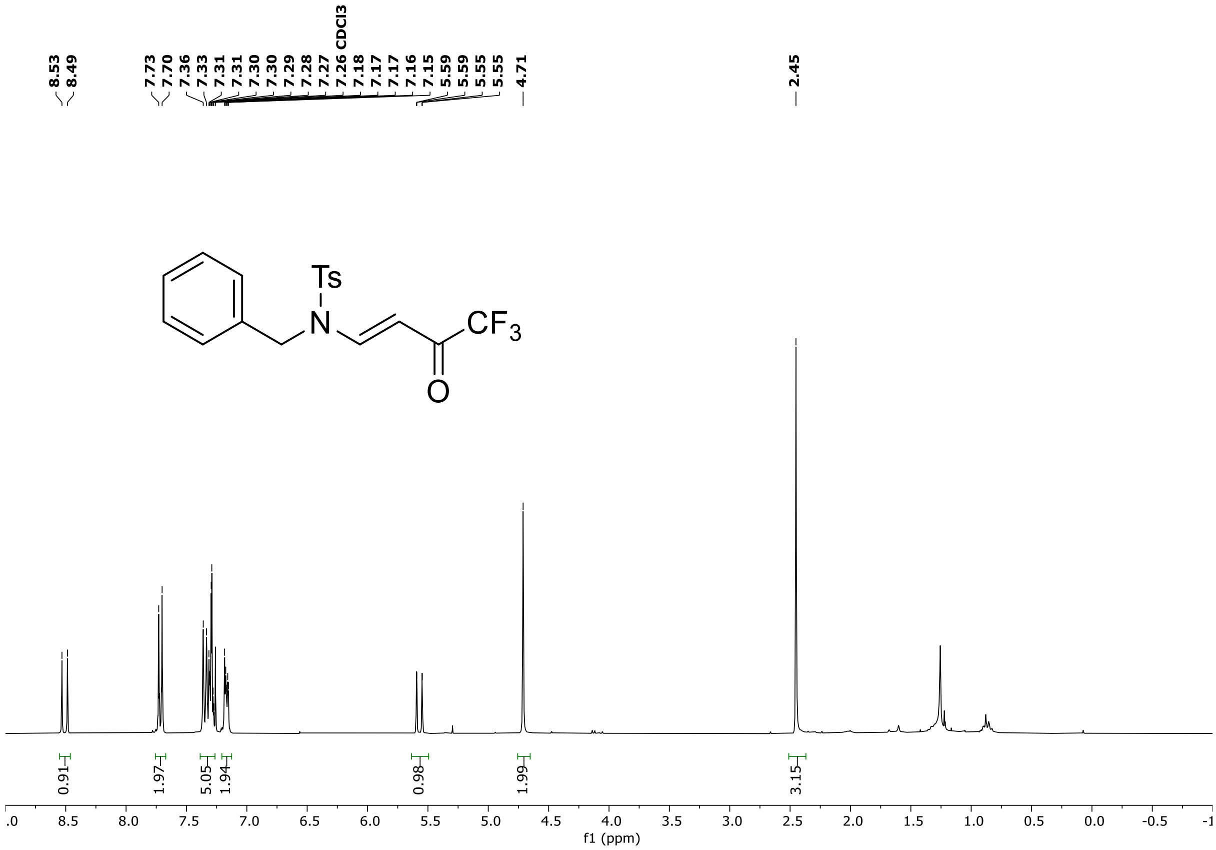
^1H NMR (C_6D_6, 500 MHz) of **6c**



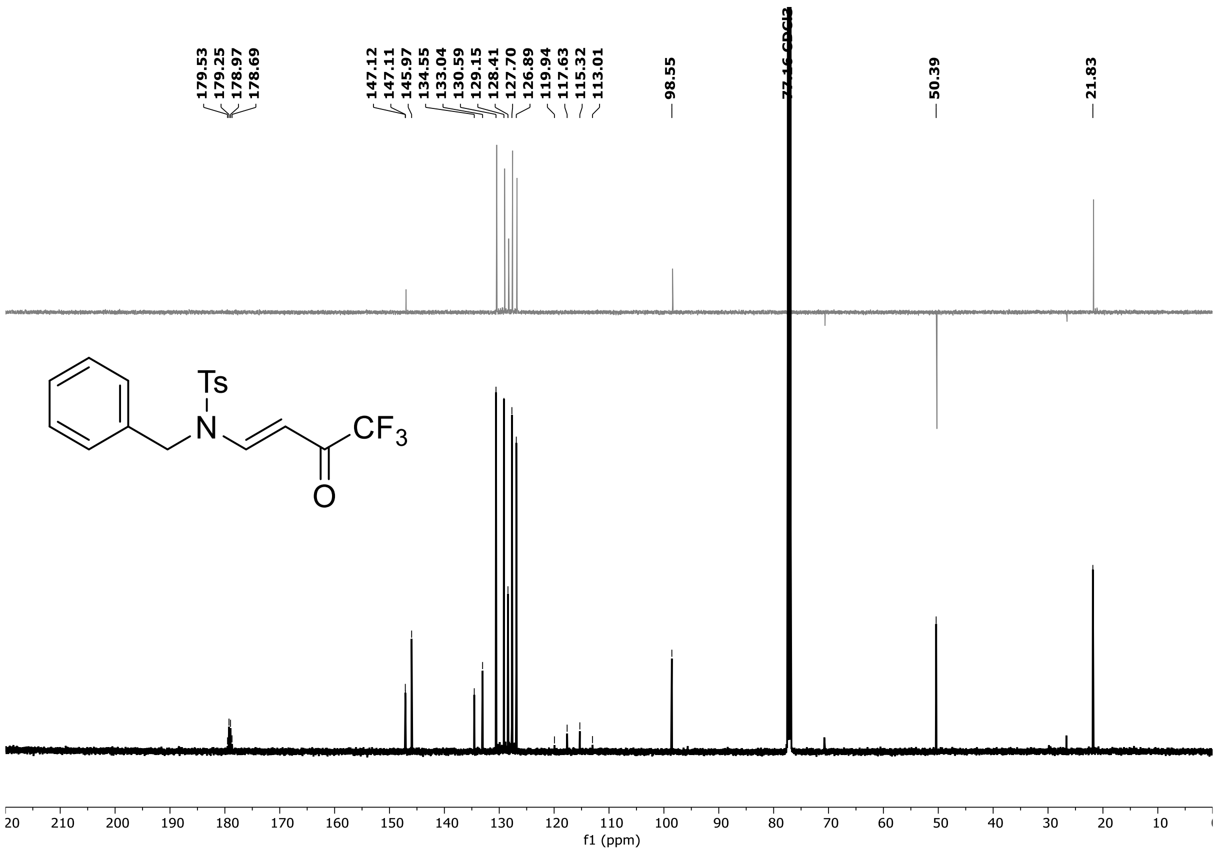
$^{13}C\{^1H\}$ NMR (C_6D_6, 126 MHz) of **6c**



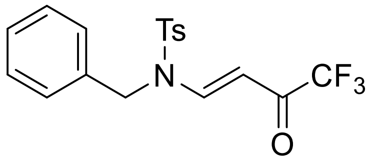
$^{19}F\{^{1}H\}$ NMR (C_6D_6, 471 MHz) of **6c**

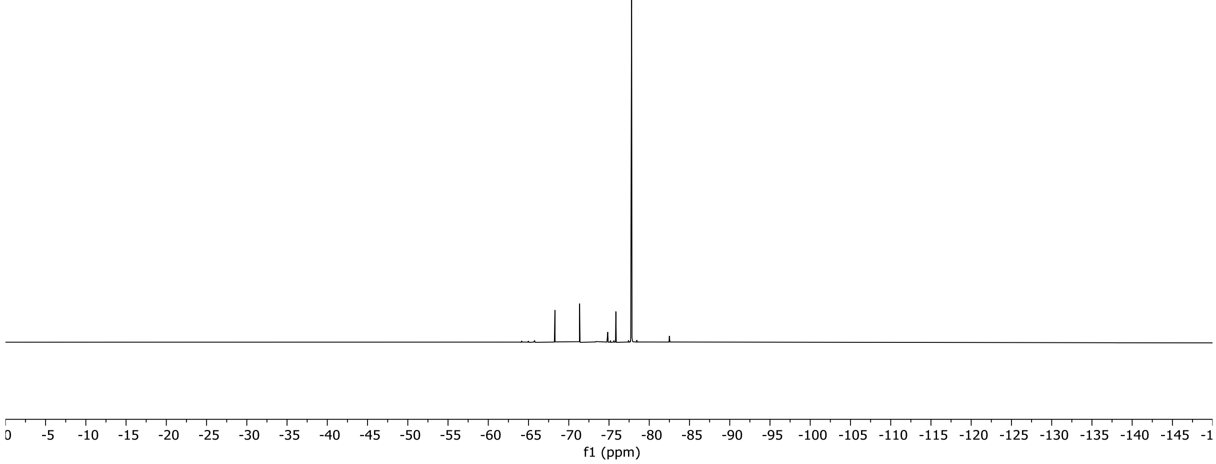


^{1}H NMR ($CDCl_3$, 300 MHz) of **7**

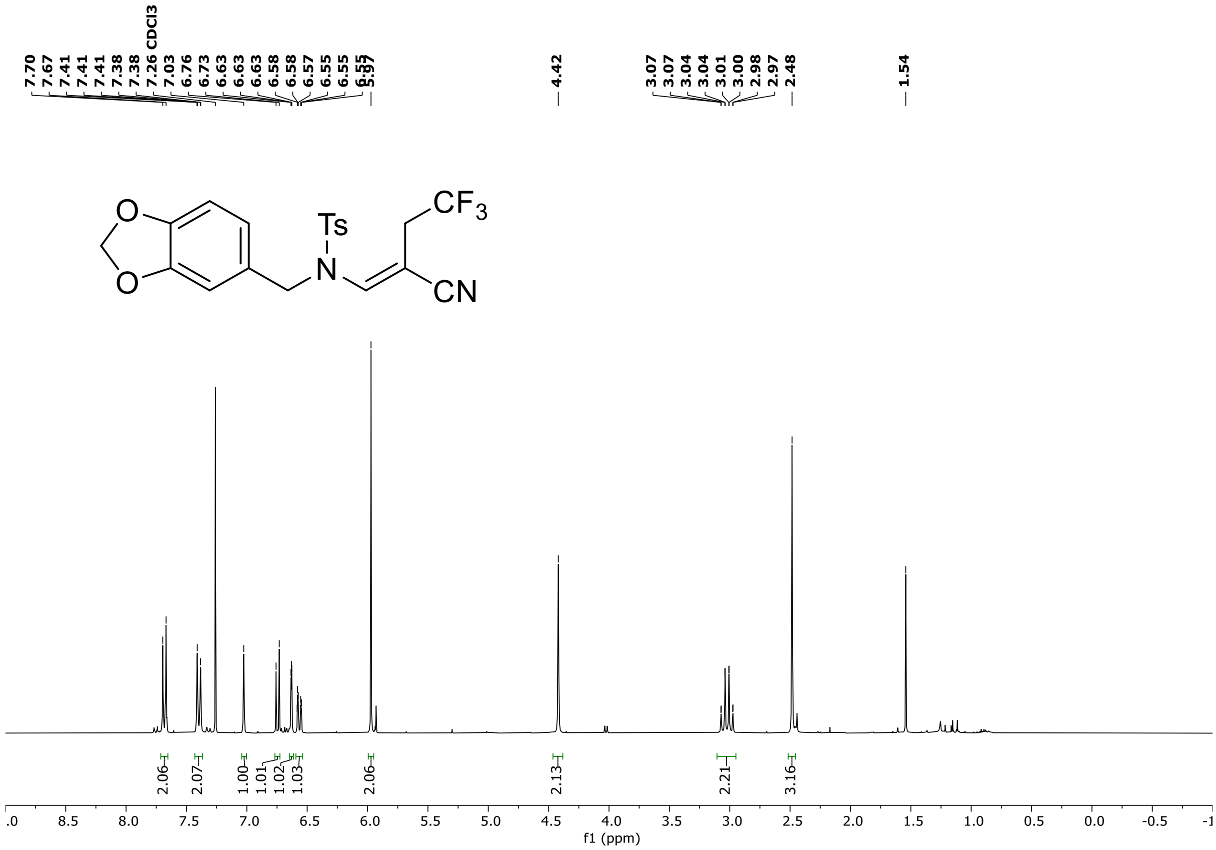


$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) of **7**

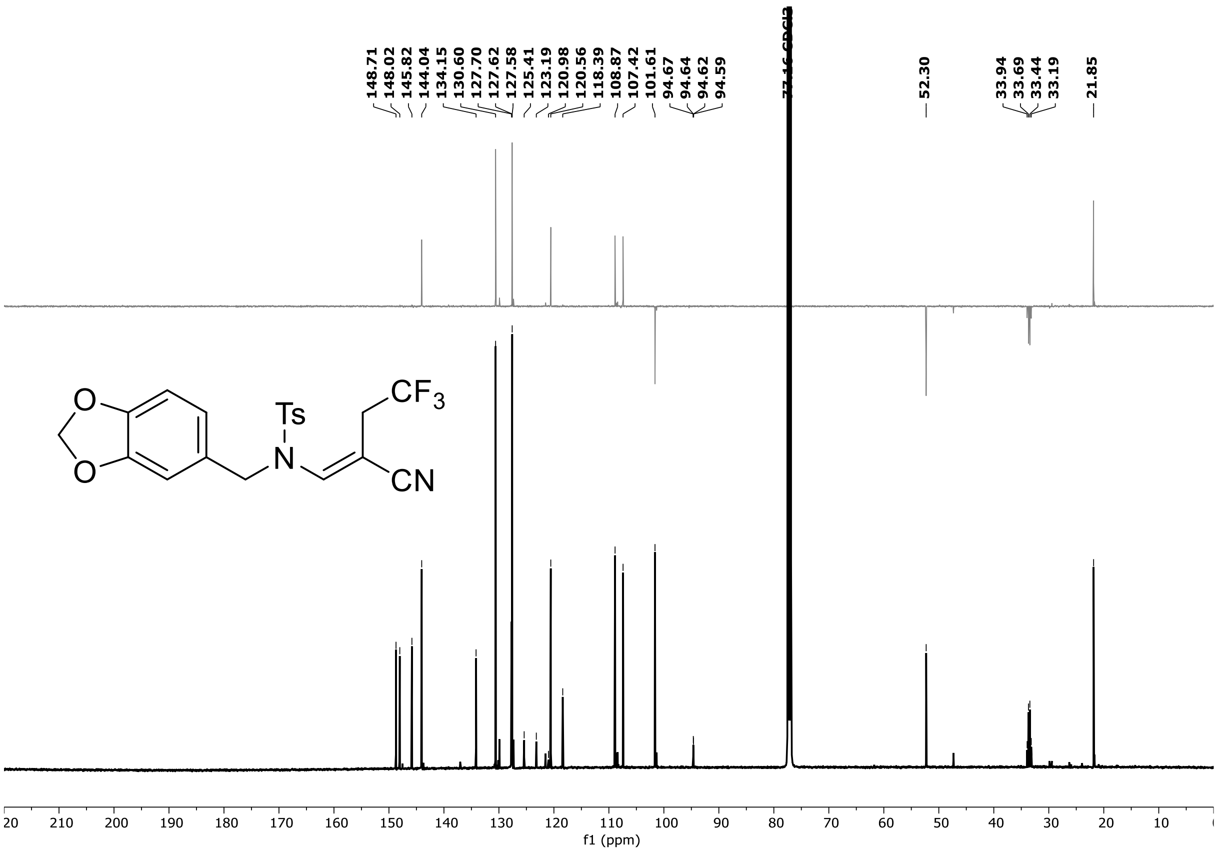




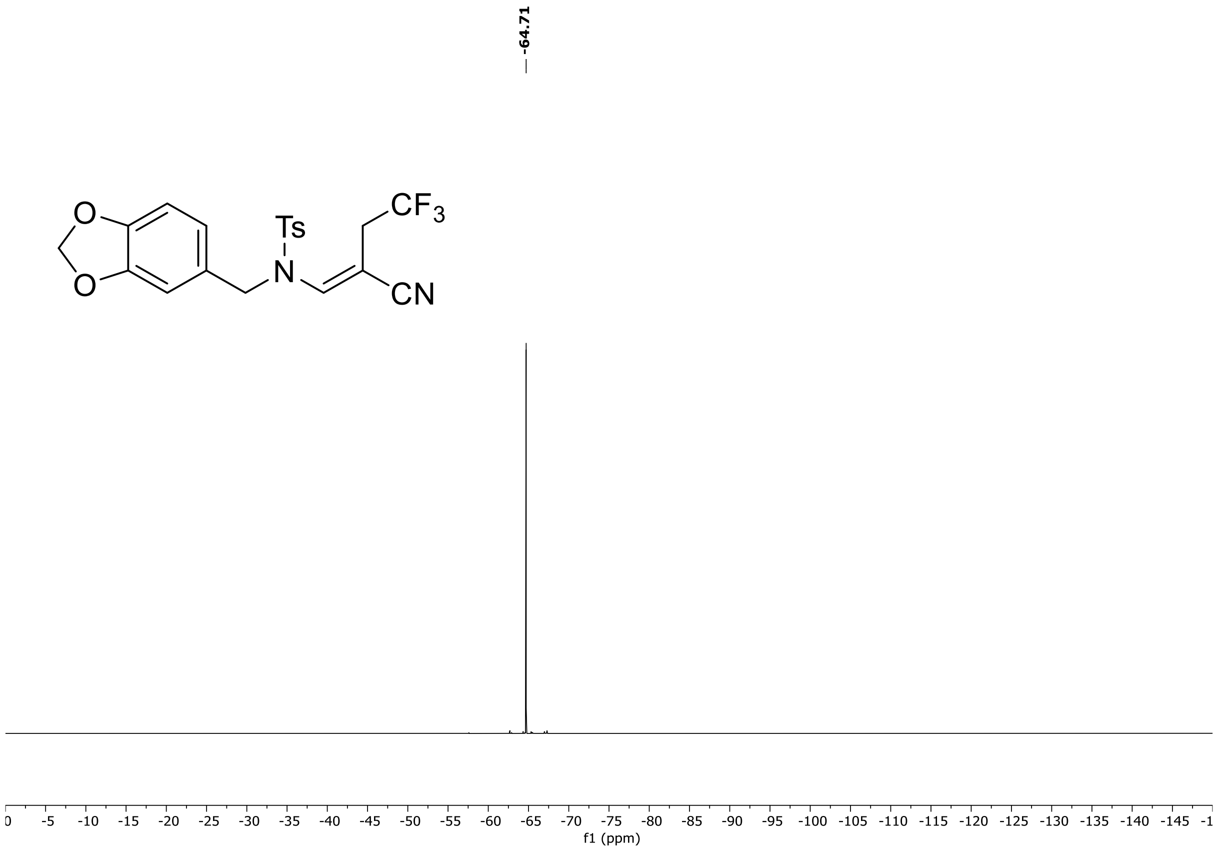
$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 282 MHz) of **7**



^{1}H NMR ($CDCl_3$, 300 MHz) of **8**

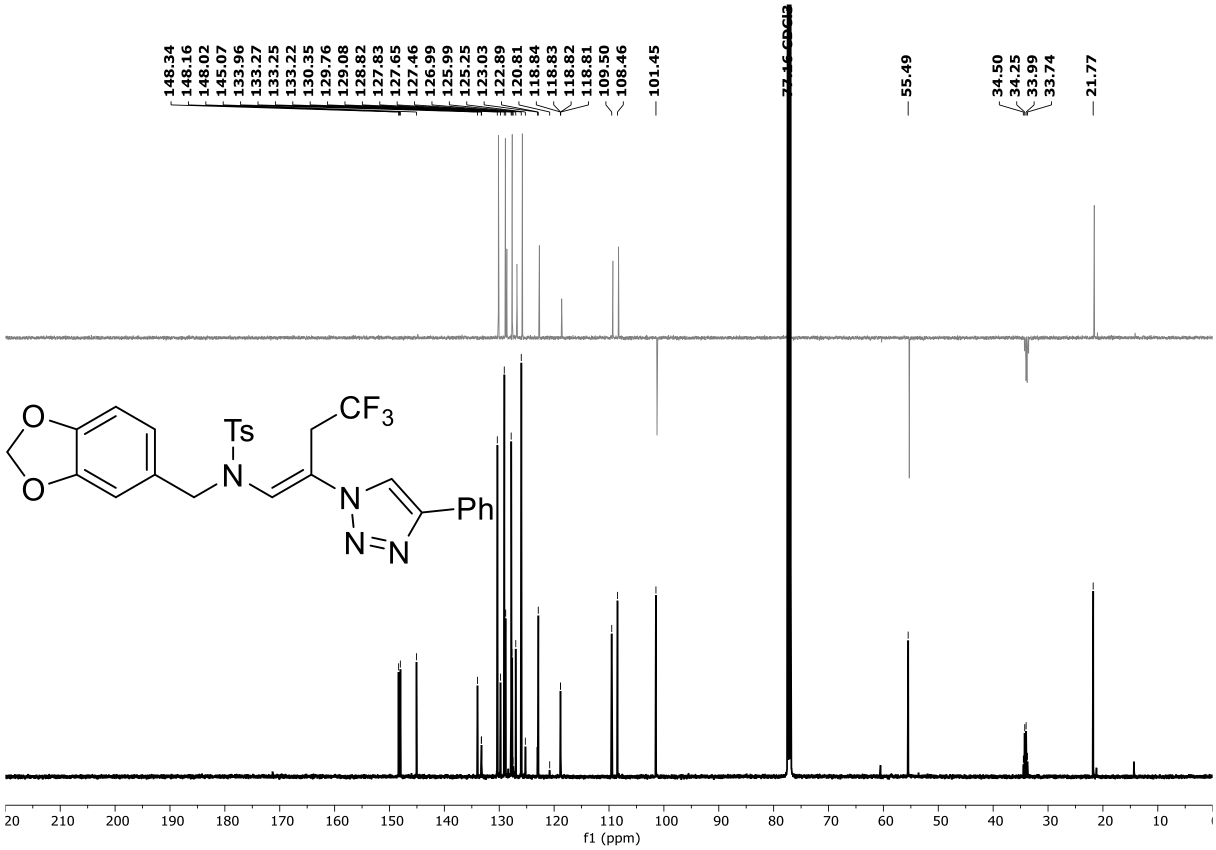


^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz) of **8**

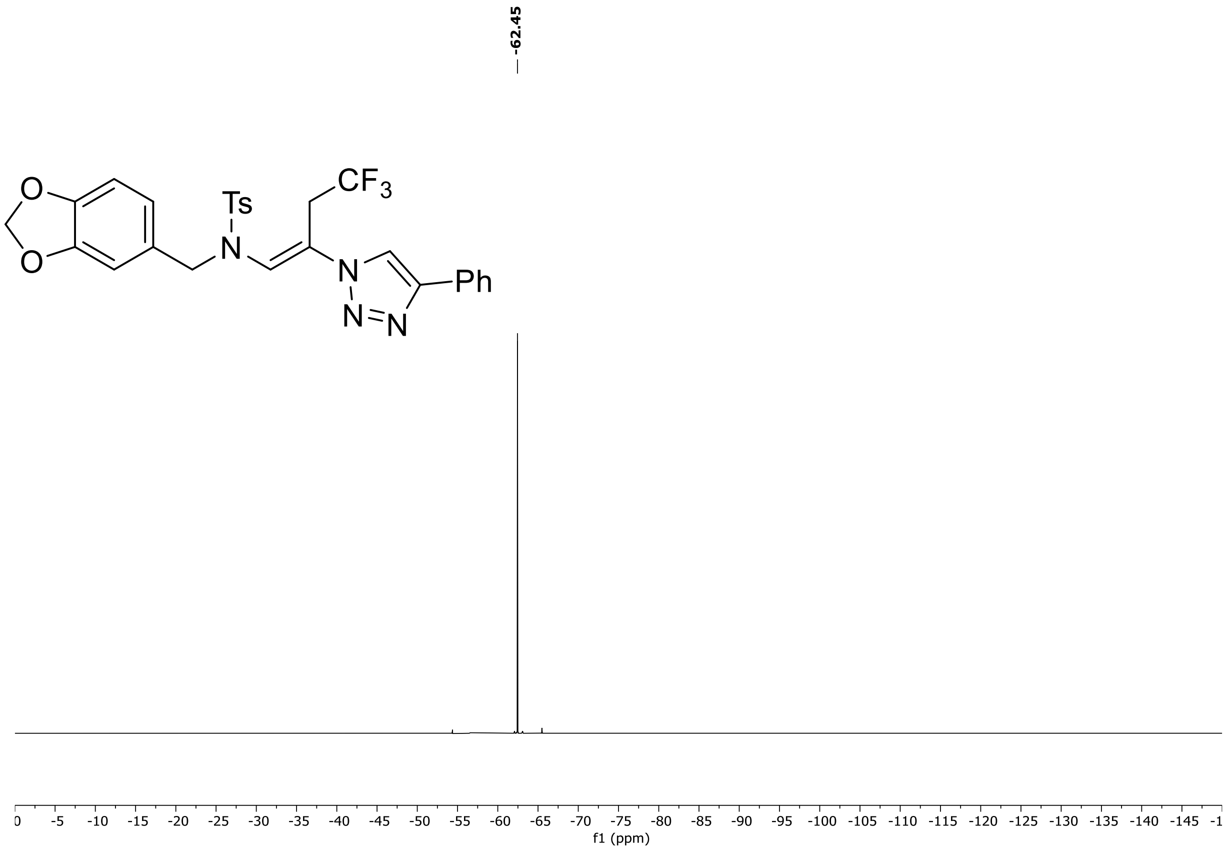


$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 282 MHz) of **8**

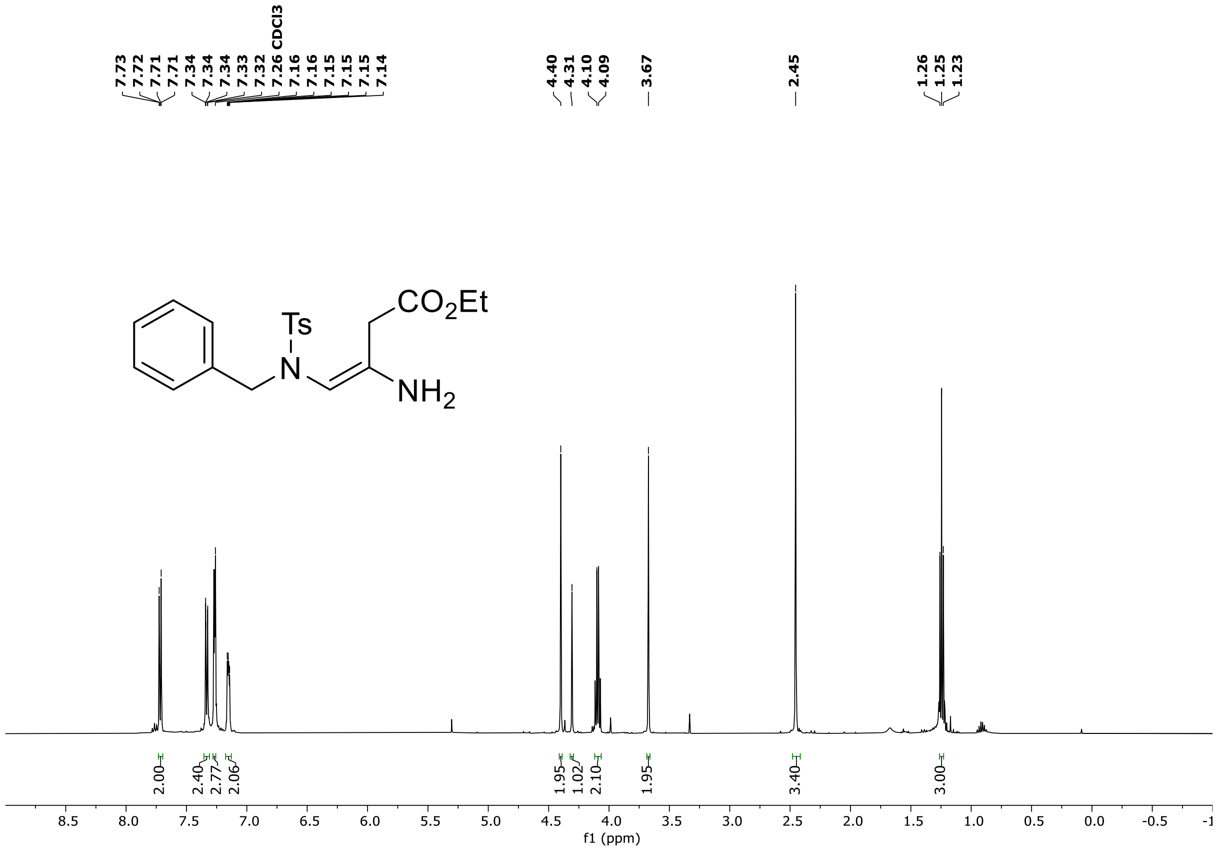
^{1}H NMR ($CDCl_3$, 500 MHz) of **9**



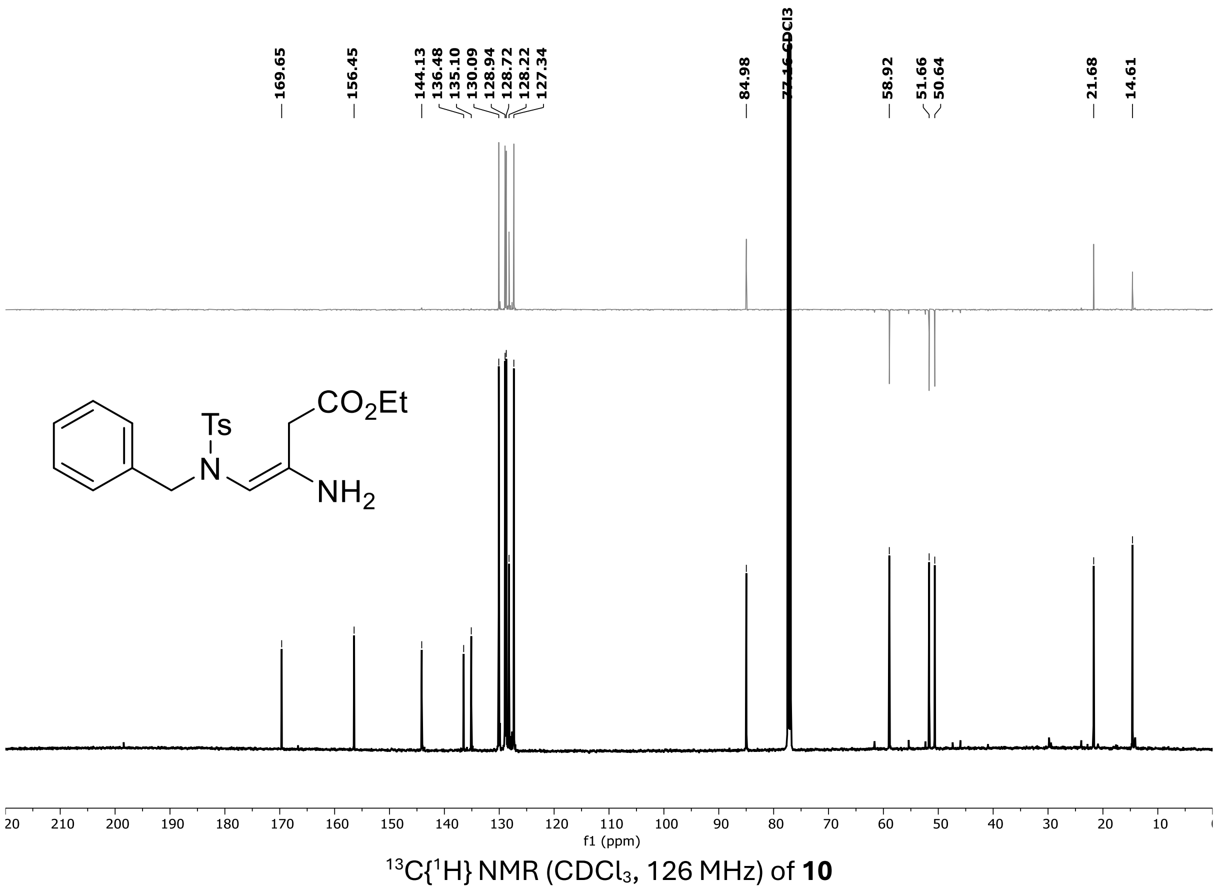
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz) of **9**



$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 282 MHz) of **9**



^1H NMR ($CDCl_3$, 500 MHz) of **10**



$^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz) of **10**

X-Ray Cristallography data

CCDC **2384608** (**2c**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge crystallographic Data Centre. Compound **2c** was dissolved in a 0.5 mL CH_2Cl_2, and *n*-hexane 2 mL were added. The sample was maintained at 4 °C for several days. Crystals were obtained through diffusion.

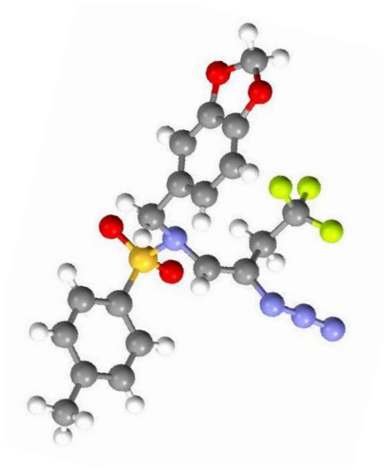
CCDC **2384809** (**2l**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge crystallographic Data Centre. Compound **2l** was dissolved in a 0.5 mL CH_2Cl_2, and *n*-hexane 2 mL were added. The sample was maintained at 4 °C for several days. Crystals were obtained through diffusion.

CCDC **2384604** (**4a**) 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 CH_2Cl_2, 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 MoKα radiation (λ = 0.71073 Å). The diffraction data were corrected for absorption using the SADABS program.[12] The structures were solved using SHELXS97[13] and refined by full matrix least squares 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).[14]

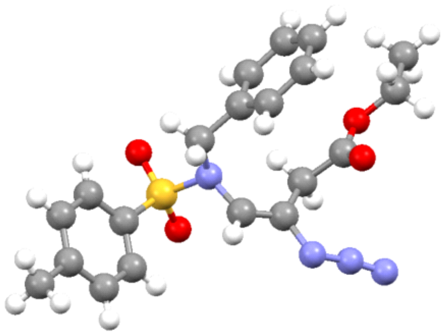
[12] Bruker. SADABS. Bruker AXS Inc.: Madison, Wisconsin, USA 2001.
[13] M. Sheldrick, *Acta Crystallogr. Sect. A Found. Crystallogr*. 2008, **64**, 112–122
[14] G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem*. 2015, **71**, 3-8

Crystallography data of **2c**



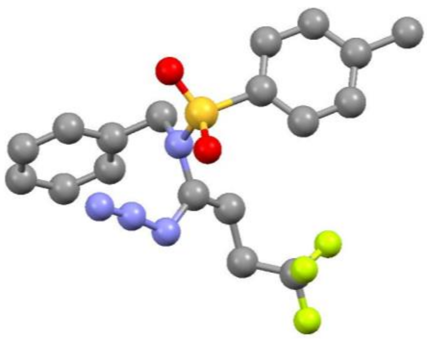
Structure of **2c**: ellipsoid contour probability: 50%

Crystallography data of **2l**



Structure of **2l**: ellipsoid contour probability: 50%

Crystallography data of **4a**



Structure of **4a**: ellipsoid contour probability: 50%

Crystal Structure Report for **2c** (CCDC **2384608**)

Table 1. Crystal data and structure refinement for **2c** (CCDC **2384608**)

Identification code	2384608
Empirical formula	C19 H17 F3 N4 O4 S,solvent
Formula weight	454.42
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 5.5258(4) A alpha = 90 deg.
	b = 19.0765(13) A beta = 94.338(3) deg.
	c = 21.2903(18) A gamma = 90 deg.
Volume	2237.8(3) A^3
Z, Calculated density	4, 1.349 Mg/m^3
Absorption coefficient	0.201 mm^-1
F(000)	936
Crystal size	0.160 x 0.150 x 0.140 mm
Theta range for data collection	1.435 to 27.921 deg.

Limiting indices -7<=h<=7, -25<=k<=24, -27<=l<=28

Reflections collected / unique 44897 / 5345 [R(int) = 0.0557]

Completeness to theta = 25.242 99.8 %

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 0.7456 and 0.7138

Refinement method Full-matrix least-squares on F^2

Data / restraints / parameters 5345 / 0 / 281

Goodness-of-fit on F^2 1.024

Final R indices [I>2sigma(I)] R1 = 0.0446, wR2 = 0.1104

R indices (all data) R1 = 0.0741, wR2 = 0.1245

Extinction coefficient n/a

Largest diff. peak and hole 0.317 and -0.218 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for elmmh_a_sq. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
N(1)	8271(3)	4230(1)	3532(1)	28(1)
S(1)	10064(1)	3907(1)	4126(1)	29(1)
O(1)	11547(2)	3392(1)	3854(1)	36(1)
O(2)	11188(2)	4496(1)	4446(1)	40(1)
C(1)	8130(3)	3483(1)	4621(1)	29(1)
C(2)	7528(4)	2780(1)	4515(1)	36(1)
C(3)	5866(4)	2470(1)	4878(1)	43(1)
C(4)	4751(4)	2838(1)	5336(1)	40(1)
C(5)	5382(4)	3537(1)	5430(1)	43(1)
C(6)	7060(4)	3863(1)	5081(1)	35(1)
C(7)	2891(4)	2491(1)	5720(1)	59(1)
C(8)	6872(3)	3700(1)	3190(1)	31(1)
C(9)	7638(3)	3357(1)	2703(1)	33(1)
N(2)	6030(3)	2823(1)	2445(1)	46(1)
N(3)	6908(3)	2380(1)	2099(1)	42(1)
N(4)	7470(4)	1950(1)	1782(1)	57(1)
C(10)	9965(4)	3493(1)	2406(1)	40(1)
C(11)	9605(5)	3857(1)	1783(1)	50(1)
F(004)	8345(3)	3481(1)	1344(1)	70(1)
F(005)	8469(3)	4469(1)	1830(1)	72(1)
F(006)	11730(3)	3997(1)	1552(1)	72(1)

C(12)	6793(3)	4856(1)	3696(1)	34(1)
C(13)	6163(3)	5290(1)	3117(1)	32(1)
C(14)	3993(4)	5197(1)	2763(1)	40(1)
C(15)	3412(4)	5568(1)	2209(1)	45(1)
C(16)	5080(4)	6038(1)	2034(1)	41(1)
O(3)	4920(3)	6482(1)	1519(1)	57(1)
C(17)	7226(5)	6810(1)	1528(1)	65(1)
O(4)	8515(3)	6683(1)	2122(1)	57(1)
C(18)	7227(4)	6154(1)	2391(1)	39(1)
C(19)	7835(3)	5789(1)	2934(1)	37(1)

Table 3. Selected bond lengths [A] and angles [deg] for elmmh_a_sq.

Symmetry transformations used to generate equivalent atoms:

Table 4. Bond lengths [A] and angles [deg] for elmmh_a_sq.

N(1)-C(8)	1.437(2)
N(1)-C(12)	1.502(2)
N(1)-S(1)	1.6659(16)
S(1)-O(2)	1.4301(14)
S(1)-O(1)	1.4301(13)
S(1)-C(1)	1.7529(18)
C(1)-C(6)	1.387(3)
C(1)-C(2)	1.397(3)
C(2)-C(3)	1.376(3)
C(2)-H(2)	0.9500
C(3)-C(4)	1.385(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.387(3)
C(4)-C(7)	1.514(3)
C(5)-C(6)	1.380(3)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-C(9)	1.322(3)
C(8)-H(8)	0.9500
C(9)-N(2)	1.433(3)
C(9)-C(10)	1.498(3)
N(2)-N(3)	1.243(2)
N(3)-N(4)	1.122(2)
C(10)-C(11)	1.497(3)
C(10)-H(10A)	0.9900

C(10)-H(10B)	0.9900
C(11)-F(004)	1.332(3)
C(11)-F(005)	1.333(3)
C(11)-F(006)	1.334(3)
C(12)-C(13)	1.505(3)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-C(14)	1.378(3)
C(13)-C(19)	1.402(3)
C(14)-C(15)	1.394(3)
C(14)-H(14)	0.9500
C(15)-C(16)	1.358(3)
C(15)-H(15)	0.9500
C(16)-C(18)	1.378(3)
C(16)-O(3)	1.382(2)
O(3)-C(17)	1.418(3)
C(17)-O(4)	1.426(3)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
O(4)-C(18)	1.383(2)
C(18)-C(19)	1.368(3)
C(19)-H(19)	0.9500
C(8)-N(1)-C(12)	113.34(14)
C(8)-N(1)-S(1)	112.97(12)
C(12)-N(1)-S(1)	114.80(13)
O(2)-S(1)-O(1)	119.36(8)
O(2)-S(1)-N(1)	106.45(8)
O(1)-S(1)-N(1)	105.78(8)
O(2)-S(1)-C(1)	109.84(9)
O(1)-S(1)-C(1)	108.70(8)

N(1)-S(1)-C(1)	105.80(8)
C(6)-C(1)-C(2)	120.43(18)
C(6)-C(1)-S(1)	119.67(14)
C(2)-C(1)-S(1)	119.70(15)
C(3)-C(2)-C(1)	118.88(19)
C(3)-C(2)-H(2)	120.6
C(1)-C(2)-H(2)	120.6
C(2)-C(3)-C(4)	121.94(19)
C(2)-C(3)-H(3)	119.0
C(4)-C(3)-H(3)	119.0
C(3)-C(4)-C(5)	117.90(18)
C(3)-C(4)-C(7)	121.0(2)
C(5)-C(4)-C(7)	121.1(2)
C(6)-C(5)-C(4)	121.84(19)
C(6)-C(5)-H(5)	119.1
C(4)-C(5)-H(5)	119.1
C(5)-C(6)-C(1)	119.00(18)
C(5)-C(6)-H(6)	120.5
C(1)-C(6)-H(6)	120.5
C(4)-C(7)-H(7A)	109.5
C(4)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(4)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(9)-C(8)-N(1)	123.60(17)
C(9)-C(8)-H(8)	118.2
N(1)-C(8)-H(8)	118.2
C(8)-C(9)-N(2)	115.24(17)
C(8)-C(9)-C(10)	125.56(18)
N(2)-C(9)-C(10)	119.19(17)

N(3)-N(2)-C(9)	116.82(17)
N(4)-N(3)-N(2)	172.8(2)
C(11)-C(10)-C(9)	113.21(18)
C(11)-C(10)-H(10A)	108.9
C(9)-C(10)-H(10A)	108.9
C(11)-C(10)-H(10B)	108.9
C(9)-C(10)-H(10B)	108.9
H(10A)-C(10)-H(10B)	107.7
F(004)-C(11)-F(005)	107.5(2)
F(004)-C(11)-F(006)	106.06(18)
F(005)-C(11)-F(006)	106.60(19)
F(004)-C(11)-C(10)	113.46(19)
F(005)-C(11)-C(10)	111.83(19)
F(006)-C(11)-C(10)	111.0(2)
N(1)-C(12)-C(13)	110.04(15)
N(1)-C(12)-H(12A)	109.7
C(13)-C(12)-H(12A)	109.7
N(1)-C(12)-H(12B)	109.7
C(13)-C(12)-H(12B)	109.7
H(12A)-C(12)-H(12B)	108.2
C(14)-C(13)-C(19)	120.04(19)
C(14)-C(13)-C(12)	120.93(17)
C(19)-C(13)-C(12)	119.02(18)
C(13)-C(14)-C(15)	122.16(19)
C(13)-C(14)-H(14)	118.9
C(15)-C(14)-H(14)	118.9
C(16)-C(15)-C(14)	116.7(2)
C(16)-C(15)-H(15)	121.6
C(14)-C(15)-H(15)	121.6
C(15)-C(16)-C(18)	121.9(2)
C(15)-C(16)-O(3)	128.2(2)

C(18)-C(16)-O(3)	109.84(18)
C(16)-O(3)-C(17)	104.89(18)
O(3)-C(17)-O(4)	108.93(19)
O(3)-C(17)-H(17A)	109.9
O(4)-C(17)-H(17A)	109.9
O(3)-C(17)-H(17B)	109.9
O(4)-C(17)-H(17B)	109.9
H(17A)-C(17)-H(17B)	108.3
C(18)-O(4)-C(17)	104.65(17)
C(19)-C(18)-C(16)	122.01(19)
C(19)-C(18)-O(4)	128.25(19)
C(16)-C(18)-O(4)	109.73(18)
C(18)-C(19)-C(13)	117.07(19)
C(18)-C(19)-H(19)	121.5
C(13)-C(19)-H(19)	121.5

Symmetry transformations used to generate equivalent atoms:

Table 5. Anisotropic displacement parameters (A^2 x 10^3) for elmmh_a_sq.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
N(1)	30(1)	24(1)	32(1)	0(1)	9(1)	2(1)
S(1)	26(1)	25(1)	36(1)	-3(1)	5(1)	0(1)
O(1)	29(1)	35(1)	46(1)	-5(1)	8(1)	7(1)
O(2)	35(1)	35(1)	50(1)	-9(1)	3(1)	-7(1)
C(1)	31(1)	27(1)	29(1)	0(1)	1(1)	-1(1)
C(2)	44(1)	28(1)	37(1)	-3(1)	2(1)	-3(1)
C(3)	51(1)	34(1)	42(1)	4(1)	-3(1)	-12(1)
C(4)	38(1)	49(1)	34(1)	13(1)	1(1)	-3(1)
C(5)	49(1)	47(1)	33(1)	4(1)	12(1)	7(1)
C(6)	44(1)	29(1)	33(1)	-1(1)	5(1)	2(1)
C(7)	51(1)	76(2)	51(2)	21(1)	6(1)	-15(1)
C(8)	26(1)	31(1)	38(1)	2(1)	4(1)	2(1)
C(9)	29(1)	34(1)	37(1)	-4(1)	2(1)	1(1)
N(2)	39(1)	47(1)	52(1)	-15(1)	4(1)	-6(1)
N(3)	44(1)	37(1)	43(1)	-6(1)	-7(1)	0(1)
N(4)	67(1)	46(1)	55(1)	-15(1)	-10(1)	6(1)
C(10)	34(1)	42(1)	43(1)	-10(1)	8(1)	-2(1)
C(11)	57(1)	44(1)	51(1)	-10(1)	20(1)	-6(1)
F(004)	89(1)	76(1)	43(1)	-5(1)	1(1)	-20(1)
F(005)	96(1)	52(1)	71(1)	9(1)	31(1)	13(1)
F(006)	79(1)	77(1)	65(1)	-13(1)	41(1)	-18(1)
C(12)	34(1)	27(1)	42(1)	0(1)	15(1)	6(1)

C(13)	30(1)	24(1)	44(1)	2(1)	10(1)	5(1)
C(14)	34(1)	31(1)	56(1)	6(1)	8(1)	-3(1)
C(15)	36(1)	37(1)	62(2)	4(1)	-6(1)	0(1)
C(16)	46(1)	29(1)	47(1)	8(1)	2(1)	3(1)
O(3)	61(1)	46(1)	61(1)	22(1)	-8(1)	-3(1)
C(17)	72(2)	55(2)	66(2)	26(1)	1(1)	-14(1)
O(4)	50(1)	47(1)	72(1)	29(1)	0(1)	-12(1)
C(18)	36(1)	29(1)	54(1)	9(1)	8(1)	0(1)
C(19)	29(1)	31(1)	52(1)	6(1)	4(1)	2(1)

Table 6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for elmmh_a_sq.

	x	y	z	U(eq)
H(2)	8254	2519	4199	43
H(3)	5473	1990	4811	51
H(5)	4639	3797	5743	51
H(6)	7476	4341	5155	42
H(7A)	3553	2050	5896	89
H(7B)	1415	2394	5449	89
H(7C)	2501	2803	6064	89
H(8)	5312	3589	3322	38
H(10A)	11034	3783	2695	48
H(10B)	10797	3040	2347	48
H(12A)	7727	5143	4016	41
H(12B)	5286	4698	3876	41
H(14)	2856	4869	2903	48
H(15)	1921	5495	1964	55
H(17A)	7023	7321	1460	77
H(17B)	8149	6619	1186	77
H(19)	9325	5870	3175	45

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

Symmetry transformations used to generate equivalent atoms:

Table 8. Torsion angles [deg] for elmmh_a_sq.

C(8)-N(1)-S(1)-O(2)	-175.82(12)
C(12)-N(1)-S(1)-O(2)	-43.76(14)
C(8)-N(1)-S(1)-O(1)	56.24(13)
C(12)-N(1)-S(1)-O(1)	-171.69(12)
C(8)-N(1)-S(1)-C(1)	-58.98(14)
C(12)-N(1)-S(1)-C(1)	73.08(14)
O(2)-S(1)-C(1)-C(6)	28.05(18)
O(1)-S(1)-C(1)-C(6)	160.31(15)
N(1)-S(1)-C(1)-C(6)	-86.47(16)
O(2)-S(1)-C(1)-C(2)	-156.99(15)
O(1)-S(1)-C(1)-C(2)	-24.73(18)
N(1)-S(1)-C(1)-C(2)	88.49(16)
C(6)-C(1)-C(2)-C(3)	-0.3(3)
S(1)-C(1)-C(2)-C(3)	-175.17(16)
C(1)-C(2)-C(3)-C(4)	0.9(3)
C(2)-C(3)-C(4)-C(5)	-0.9(3)
C(2)-C(3)-C(4)-C(7)	178.8(2)
C(3)-C(4)-C(5)-C(6)	0.2(3)
C(7)-C(4)-C(5)-C(6)	-179.5(2)
C(4)-C(5)-C(6)-C(1)	0.5(3)
C(2)-C(1)-C(6)-C(5)	-0.4(3)
S(1)-C(1)-C(6)-C(5)	174.49(16)
C(12)-N(1)-C(8)-C(9)	137.99(19)
S(1)-N(1)-C(8)-C(9)	-89.2(2)
N(1)-C(8)-C(9)-N(2)	177.10(17)
N(1)-C(8)-C(9)-C(10)	-4.2(3)
C(8)-C(9)-N(2)-N(3)	-162.64(19)
C(10)-C(9)-N(2)-N(3)	18.6(3)

C(8)-C(9)-C(10)-C(11)	-106.0(2)
N(2)-C(9)-C(10)-C(11)	72.6(2)
C(9)-C(10)-C(11)-F(004)	-63.7(2)
C(9)-C(10)-C(11)-F(005)	58.1(2)
C(9)-C(10)-C(11)-F(006)	176.99(17)
C(8)-N(1)-C(12)-C(13)	-73.51(19)
S(1)-N(1)-C(12)-C(13)	154.61(13)
N(1)-C(12)-C(13)-C(14)	94.3(2)
N(1)-C(12)-C(13)-C(19)	-84.9(2)
C(19)-C(13)-C(14)-C(15)	2.3(3)
C(12)-C(13)-C(14)-C(15)	-176.88(18)
C(13)-C(14)-C(15)-C(16)	-0.9(3)
C(14)-C(15)-C(16)-C(18)	-1.1(3)
C(14)-C(15)-C(16)-O(3)	-178.0(2)
C(15)-C(16)-O(3)-C(17)	-174.8(2)
C(18)-C(16)-O(3)-C(17)	8.0(3)
C(16)-O(3)-C(17)-O(4)	-13.6(3)
O(3)-C(17)-O(4)-C(18)	13.9(3)
C(15)-C(16)-C(18)-C(19)	1.9(3)
O(3)-C(16)-C(18)-C(19)	179.27(19)
C(15)-C(16)-C(18)-O(4)	-176.79(19)
O(3)-C(16)-C(18)-O(4)	0.6(3)
C(17)-O(4)-C(18)-C(19)	172.6(2)
C(17)-O(4)-C(18)-C(16)	-8.9(2)
C(16)-C(18)-C(19)-C(13)	-0.5(3)
O(4)-C(18)-C(19)-C(13)	177.9(2)
C(14)-C(13)-C(19)-C(18)	-1.5(3)
C(12)-C(13)-C(19)-C(18)	177.66(17)

Symmetry transformations used to generate equivalent atoms:

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

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

Crystal Structure Report for **2l** (CCDC **2384809**)

Table 1. Crystal data and structure refinement for **2l** (CCDC **2384809)**

Identification code	2384809
Empirical formula	C20 H22 N4 O4 S
Formula weight	414.47
Temperature	120(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P 1
Unit cell dimensions	a = 5.9999(8) A alpha = 86.813(5) deg.
	b = 8.0325(11) A beta = 82.243(5) deg.
	c = 10.7268(15) A gamma = 86.551(5) deg.
Volume	510.72(12) A^3
Z, Calculated density	1, 1.348 Mg/m^3
Absorption coefficient	0.193 mm^-1
F(000)	218

Crystal size 0.200 x 0.160 x 0.100 mm

Theta range for data collection 1.918 to 27.958 deg.

Limiting indices -7<=h<=7, -10<=k<=10, -14<=l<=14

Reflections collected / unique 18622 / 4435 [R(int) = 0.0373]

Completeness to theta = 25.242 99.7 %

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 0.7456 and 0.6954

Refinement method Full-matrix least-squares on F^2

Data / restraints / parameters 4435 / 3 / 264

Goodness-of-fit on F^2 1.051

Final R indices [I>2sigma(I)] R1 = 0.0329, wR2 = 0.0750

R indices (all data) R1 = 0.0360, wR2 = 0.0777

Absolute structure parameter 0.02(2)

Extinction coefficient n/a

Largest diff. peak and hole 0.310 and -0.184 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for elmds_a.

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

	x	y	z	U(eq)
S(1)	7087(1)	5310(1)	2877(1)	20(1)
O(1)	6866(3)	3918(2)	2129(2)	28(1)
O(2)	9275(3)	5788(3)	3062(2)	33(1)
C(1)	5660(4)	7083(3)	2260(2)	19(1)
C(2)	3746(4)	6891(3)	1695(2)	21(1)
C(3)	2533(5)	8297(4)	1289(3)	26(1)
C(4)	3192(5)	9898(3)	1443(2)	26(1)
C(5)	5131(5)	10066(3)	2000(2)	26(1)
C(6)	6371(4)	8676(3)	2412(2)	22(1)
C(7)	1824(6)	11410(4)	1027(3)	40(1)
N(1)	5737(4)	4861(3)	4296(2)	20(1)
C(8)	3629(4)	4086(3)	4311(2)	23(1)
C(9)	3422(4)	2489(3)	4692(2)	23(1)
C(10)	5244(5)	1376(3)	5191(2)	24(1)
C(11)	4700(5)	890(3)	6582(2)	24(1)
O(3)	2930(3)	1245(3)	7226(2)	35(1)
O(4)	6424(3)	16(2)	7000(2)	29(1)
C(12)	6115(6)	-490(4)	8332(3)	32(1)
C(13)	8257(6)	-1418(5)	8625(3)	41(1)
N(2)	1287(4)	1829(3)	4622(2)	30(1)
N(3)	1124(4)	302(3)	4853(3)	33(1)

N(4)	711(5)	-1056(4)	5022(3)	48(1)
C(14)	5708(5)	6174(3)	5225(2)	28(1)
C(15)	5832(5)	5395(3)	6531(2)	24(1)
C(16)	4021(5)	5576(4)	7482(3)	31(1)
C(17)	4203(6)	4911(4)	8685(3)	38(1)
C(18)	6168(6)	4064(4)	8957(3)	38(1)
C(19)	7957(6)	3848(4)	8008(3)	33(1)
C(20)	7801(5)	4516(4)	6799(3)	28(1)

Table 3. Selected bond lengths [A] and angles [deg] for elmds_a.

Symmetry transformations used to generate equivalent atoms:

Table 4. Bond lengths [A] and angles [deg] for elmds_a.

S(1)-O(2)	1.432(2)
S(1)-O(1)	1.435(2)
S(1)-N(1)	1.656(2)
S(1)-C(1)	1.762(2)
C(1)-C(2)	1.389(4)
C(1)-C(6)	1.398(4)
C(2)-C(3)	1.389(4)
C(2)-H(2)	0.9500
C(3)-C(4)	1.393(4)
C(3)-H(3)	0.9500
C(4)-C(5)	1.394(4)
C(4)-C(7)	1.506(4)
C(5)-C(6)	1.389(4)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
N(1)-C(8)	1.441(4)
N(1)-C(14)	1.488(3)
C(8)-C(9)	1.333(4)
C(8)-H(8)	0.9500
C(9)-N(2)	1.428(4)
C(9)-C(10)	1.506(4)
C(10)-C(11)	1.518(4)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-O(3)	1.214(3)

C(11)-O(4)	1.330(3)
O(4)-C(12)	1.454(3)
C(12)-C(13)	1.507(4)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
N(2)-N(3)	1.245(4)
N(3)-N(4)	1.132(4)
C(14)-C(15)	1.512(4)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-C(16)	1.393(4)
C(15)-C(20)	1.395(4)
C(16)-C(17)	1.384(4)
C(16)-H(16)	0.9500
C(17)-C(18)	1.383(5)
C(17)-H(17)	0.9500
C(18)-C(19)	1.387(5)
C(18)-H(18)	0.9500
C(19)-C(20)	1.388(4)
C(19)-H(19)	0.9500
C(20)-H(20)	0.9500
O(2)-S(1)-O(1)	120.11(13)
O(2)-S(1)-N(1)	106.44(12)
O(1)-S(1)-N(1)	106.42(11)
O(2)-S(1)-C(1)	107.40(12)
O(1)-S(1)-C(1)	108.89(12)
N(1)-S(1)-C(1)	106.88(11)

C(2)-C(1)-C(6)	120.5(2)
C(2)-C(1)-S(1)	119.5(2)
C(6)-C(1)-S(1)	119.9(2)
C(3)-C(2)-C(1)	119.4(3)
C(3)-C(2)-H(2)	120.3
C(1)-C(2)-H(2)	120.3
C(2)-C(3)-C(4)	121.2(3)
C(2)-C(3)-H(3)	119.4
C(4)-C(3)-H(3)	119.4
C(3)-C(4)-C(5)	118.5(2)
C(3)-C(4)-C(7)	120.5(3)
C(5)-C(4)-C(7)	120.9(3)
C(6)-C(5)-C(4)	121.2(3)
C(6)-C(5)-H(5)	119.4
C(4)-C(5)-H(5)	119.4
C(5)-C(6)-C(1)	119.2(2)
C(5)-C(6)-H(6)	120.4
C(1)-C(6)-H(6)	120.4
C(4)-C(7)-H(7A)	109.5
C(4)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(4)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(8)-N(1)-C(14)	114.8(2)
C(8)-N(1)-S(1)	115.23(16)
C(14)-N(1)-S(1)	115.38(18)
C(9)-C(8)-N(1)	120.7(2)
C(9)-C(8)-H(8)	119.7
N(1)-C(8)-H(8)	119.7
C(8)-C(9)-N(2)	116.0(2)

C(8)-C(9)-C(10)	124.8(3)
N(2)-C(9)-C(10)	119.2(2)
C(9)-C(10)-C(11)	113.0(2)
C(9)-C(10)-H(10A)	109.0
C(11)-C(10)-H(10A)	109.0
C(9)-C(10)-H(10B)	109.0
C(11)-C(10)-H(10B)	109.0
H(10A)-C(10)-H(10B)	107.8
O(3)-C(11)-O(4)	124.5(2)
O(3)-C(11)-C(10)	124.8(2)
O(4)-C(11)-C(10)	110.8(2)
C(11)-O(4)-C(12)	115.8(2)
O(4)-C(12)-C(13)	107.6(2)
O(4)-C(12)-H(12A)	110.2
C(13)-C(12)-H(12A)	110.2
O(4)-C(12)-H(12B)	110.2
C(13)-C(12)-H(12B)	110.2
H(12A)-C(12)-H(12B)	108.5
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
N(3)-N(2)-C(9)	117.1(2)
N(4)-N(3)-N(2)	171.3(3)
N(1)-C(14)-C(15)	110.7(2)
N(1)-C(14)-H(14A)	109.5
C(15)-C(14)-H(14A)	109.5
N(1)-C(14)-H(14B)	109.5
C(15)-C(14)-H(14B)	109.5

H(14A)-C(14)-H(14B)	108.1
C(16)-C(15)-C(20)	119.4(2)
C(16)-C(15)-C(14)	120.9(3)
C(20)-C(15)-C(14)	119.7(3)
C(17)-C(16)-C(15)	120.0(3)
C(17)-C(16)-H(16)	120.0
C(15)-C(16)-H(16)	120.0
C(18)-C(17)-C(16)	120.7(3)
C(18)-C(17)-H(17)	119.6
C(16)-C(17)-H(17)	119.6
C(17)-C(18)-C(19)	119.6(3)
C(17)-C(18)-H(18)	120.2
C(19)-C(18)-H(18)	120.2
C(20)-C(19)-C(18)	120.2(3)
C(20)-C(19)-H(19)	119.9
C(18)-C(19)-H(19)	119.9
C(19)-C(20)-C(15)	120.1(3)
C(19)-C(20)-H(20)	119.9
C(15)-C(20)-H(20)	119.9

Symmetry transformations used to generate equivalent atoms:

Table 5. Anisotropic displacement parameters (A^2 x 10^3) for elmds_a.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
S(1)	18(1)	20(1)	22(1)	4(1)	-1(1)	1(1)
O(1)	35(1)	21(1)	24(1)	-2(1)	3(1)	6(1)
O(2)	19(1)	33(1)	45(1)	14(1)	-7(1)	-4(1)
C(1)	20(1)	19(1)	16(1)	2(1)	0(1)	0(1)
C(2)	22(1)	20(1)	20(1)	2(1)	-2(1)	-4(1)
C(3)	21(1)	31(2)	24(1)	5(1)	-4(1)	0(1)
C(4)	25(1)	24(1)	24(1)	5(1)	5(1)	5(1)
C(5)	34(2)	17(1)	24(1)	0(1)	3(1)	-2(1)
C(6)	23(1)	22(1)	20(1)	-2(1)	-1(1)	-5(1)
C(7)	38(2)	30(2)	46(2)	13(1)	3(1)	13(1)
N(1)	23(1)	20(1)	16(1)	2(1)	-3(1)	-3(1)
C(8)	17(1)	27(1)	23(1)	5(1)	-3(1)	1(1)
C(9)	17(1)	27(1)	26(1)	1(1)	-1(1)	-2(1)
C(10)	23(1)	23(1)	26(1)	0(1)	-2(1)	0(1)
C(11)	26(1)	21(1)	25(1)	1(1)	-4(1)	-2(1)
O(3)	29(1)	45(1)	29(1)	2(1)	4(1)	5(1)
O(4)	31(1)	28(1)	26(1)	4(1)	-6(1)	4(1)
C(12)	40(2)	32(2)	24(1)	2(1)	-5(1)	-2(1)
C(13)	44(2)	43(2)	36(2)	9(1)	-16(1)	2(2)
N(2)	23(1)	29(1)	39(1)	2(1)	-6(1)	-3(1)
N(3)	21(1)	32(1)	47(2)	-3(1)	-4(1)	-4(1)
N(4)	31(2)	29(2)	84(2)	-6(1)	-2(1)	-9(1)

C(14)	41(2)	20(1)	24(1)	0(1)	-8(1)	-2(1)
C(15)	33(2)	20(1)	20(1)	-2(1)	-6(1)	-3(1)
C(16)	32(2)	31(2)	29(1)	-7(1)	-3(1)	2(1)
C(17)	48(2)	41(2)	24(1)	-5(1)	4(1)	-8(2)
C(18)	60(2)	36(2)	19(1)	2(1)	-10(1)	-11(2)
C(19)	40(2)	31(2)	32(2)	2(1)	-15(1)	-4(1)
C(20)	30(2)	28(1)	25(1)	0(1)	-4(1)	-2(1)

Table 6. Hydrogen coordinates (x 10^4) and isotropic

displacement parameters (A^2 x 10^3) for elmds_a.

	x	y	z	U(eq)
H(2)	3272	5807	1587	25
H(3)	1229	8165	898	31
H(5)	5612	11151	2100	31
H(6)	7687	8807	2792	26
H(7A)	2192	12386	1452	60
H(7B)	216	11220	1244	60
H(7C)	2171	11607	113	60
H(8)	2373	4720	4046	27
H(10A)	6671	1959	5055	29
H(10B)	5476	350	4709	29
H(12A)	4830	-1221	8525	38
H(12B)	5800	503	8847	38
H(13A)	8548	-2400	8113	61
H(13B)	8100	-1773	9520	61
H(13C)	9516	-682	8432	61
H(14A)	4308	6893	5227	34
H(14B)	7003	6883	4977	34
H(16)	2663	6154	7306	37
H(17)	2964	5039	9331	46
H(18)	6291	3633	9790	45
H(19)	9295	3240	8185	40
H(20)	9037	4374	6153	33

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

Symmetry transformations used to generate equivalent atoms:

Table 8. Torsion angles [deg] for elmds_a.

O(2)-S(1)-C(1)-C(2)	163.7(2)
O(1)-S(1)-C(1)-C(2)	32.2(2)
N(1)-S(1)-C(1)-C(2)	-82.4(2)
O(2)-S(1)-C(1)-C(6)	-20.3(2)
O(1)-S(1)-C(1)-C(6)	-151.82(19)
N(1)-S(1)-C(1)-C(6)	93.6(2)
C(6)-C(1)-C(2)-C(3)	-0.5(4)
S(1)-C(1)-C(2)-C(3)	175.5(2)
C(1)-C(2)-C(3)-C(4)	-0.3(4)
C(2)-C(3)-C(4)-C(5)	1.0(4)
C(2)-C(3)-C(4)-C(7)	-178.4(3)
C(3)-C(4)-C(5)-C(6)	-0.9(4)
C(7)-C(4)-C(5)-C(6)	178.5(3)
C(4)-C(5)-C(6)-C(1)	0.2(4)
C(2)-C(1)-C(6)-C(5)	0.5(4)
S(1)-C(1)-C(6)-C(5)	-175.40(19)
O(2)-S(1)-N(1)-C(8)	-170.21(18)
O(1)-S(1)-N(1)-C(8)	-41.0(2)
C(1)-S(1)-N(1)-C(8)	75.2(2)
O(2)-S(1)-N(1)-C(14)	52.3(2)
O(1)-S(1)-N(1)-C(14)	-178.53(19)
C(1)-S(1)-N(1)-C(14)	-62.3(2)
C(14)-N(1)-C(8)-C(9)	-112.4(3)
S(1)-N(1)-C(8)-C(9)	109.9(2)
N(1)-C(8)-C(9)-N(2)	-177.6(2)
N(1)-C(8)-C(9)-C(10)	3.1(4)
C(8)-C(9)-C(10)-C(11)	111.9(3)
N(2)-C(9)-C(10)-C(11)	-67.4(3)

C(9)-C(10)-C(11)-O(3)	4.9(4)
C(9)-C(10)-C(11)-O(4)	-175.3(2)
O(3)-C(11)-O(4)-C(12)	-1.5(4)
C(10)-C(11)-O(4)-C(12)	178.7(2)
C(11)-O(4)-C(12)-C(13)	-178.5(3)
C(8)-C(9)-N(2)-N(3)	173.0(3)
C(10)-C(9)-N(2)-N(3)	-7.6(4)
C(8)-N(1)-C(14)-C(15)	77.6(3)
S(1)-N(1)-C(14)-C(15)	-144.7(2)
N(1)-C(14)-C(15)-C(16)	-113.5(3)
N(1)-C(14)-C(15)-C(20)	68.0(4)
C(20)-C(15)-C(16)-C(17)	1.2(4)
C(14)-C(15)-C(16)-C(17)	-177.4(3)
C(15)-C(16)-C(17)-C(18)	-0.1(5)
C(16)-C(17)-C(18)-C(19)	-1.4(5)
C(17)-C(18)-C(19)-C(20)	1.7(5)
C(18)-C(19)-C(20)-C(15)	-0.6(5)
C(16)-C(15)-C(20)-C(19)	-0.8(4)
C(14)-C(15)-C(20)-C(19)	177.7(3)

Symmetry transformations used to generate equivalent atoms:

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

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

Crystal Structure Report for **4a** (CCDC **2384604**)

Table 1. Crystal data and structure refinement for **4a** (CCDC **2384604**)

Identification code	2384604
Empirical formula	C18 H17 F3 N4 O2 S
Formula weight	410.42
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 7.1393(12) A alpha = 87.980(7) deg.
	b = 10.5980(18) A beta = 88.779(6) deg.
	c = 13.216(2) A gamma = 76.119(6) deg.
Volume	970.1(3) A^3
Z, Calculated density	2, 1.405 Mg/m^3
Absorption coefficient	0.216 mm^-1

F(000) 424

Crystal size 0.180 x 0.160 x 0.140 mm

Theta range for data collection 1.542 to 27.907 deg.

Limiting indices -9<=h<=9, -13<=k<=13, -17<=l<=14

Reflections collected / unique 17075 / 4609 [R(int) = 0.0288]

Completeness to theta = 25.242 100.0 %

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 0.7456 and 0.6918

Refinement method Full-matrix least-squares on F^2

Data / restraints / parameters 4609 / 30 / 276

Goodness-of-fit on F^2 1.056

Final R indices [I>2sigma(I)] R1 = 0.0384, wR2 = 0.0953

R indices (all data) R1 = 0.0568, wR2 = 0.1060

Extinction coefficient n/a

Largest diff. peak and hole 0.324 and -0.291 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for elmds_a.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
N(1)	6582(2)	2212(1)	6487(1)	31(1)
S(1)	8606(1)	1755(1)	7120(1)	34(1)
O(1)	9826(2)	749(1)	6562(1)	51(1)
O(2)	9196(2)	2924(1)	7304(1)	46(1)
C(1)	8086(2)	1076(2)	8298(1)	30(1)
C(2)	8345(2)	-260(2)	8408(1)	34(1)
C(3)	7995(2)	-794(2)	9346(1)	36(1)
C(4)	7389(2)	-16(2)	10173(1)	33(1)
C(5)	7121(2)	1321(2)	10037(1)	37(1)
C(6)	7470(2)	1876(2)	9111(1)	35(1)
C(7)	7039(2)	-618(2)	11187(1)	44(1)
C(8)	5331(2)	3444(1)	6694(1)	29(1)
N(2)	5716(2)	4545(1)	6169(1)	40(1)
N(3)	7128(2)	4334(1)	5584(1)	40(1)
N(4)	8369(2)	4271(2)	5037(1)	55(1)
C(9)	3790(2)	3577(2)	7295(1)	34(1)
C(10)	2349(2)	4827(2)	7462(1)	43(1)
C(11)	2224(4)	5216(2)	8532(2)	69(1)
F(1)	2080(40)	4296(12)	9237(12)	98(3)
F(2)	3883(14)	5548(14)	8762(12)	77(2)
F(3)	760(20)	6263(11)	8632(11)	100(3)

F(1A)	990(20)	6358(11)	8713(14)	104(4)
F(2A)	1490(30)	4327(12)	9080(14)	89(3)
F(3A)	3862(18)	5270(20)	8980(16)	104(3)
C(12)	5703(2)	1220(1)	6043(1)	35(1)
C(13)	5056(2)	1650(1)	4983(1)	31(1)
C(14)	6408(3)	1589(2)	4205(1)	41(1)
C(15)	5833(3)	2000(2)	3235(1)	53(1)
C(16)	3913(4)	2476(2)	3026(1)	58(1)
C(17)	2553(3)	2546(2)	3784(2)	53(1)
C(18)	3115(2)	2130(2)	4767(1)	40(1)

Table 3. Selected bond lengths [A] and angles [deg] for elmds_a.

Symmetry transformations used to generate equivalent atoms:

Table 4. Bond lengths [A] and angles [deg] for elmds_a.

N(1)-C(8)	1.4262(18)
N(1)-C(12)	1.4892(19)
N(1)-S(1)	1.6460(12)
S(1)-O(1)	1.4221(13)
S(1)-O(2)	1.4313(13)
S(1)-C(1)	1.7615(15)
C(1)-C(2)	1.386(2)
C(1)-C(6)	1.390(2)
C(2)-C(3)	1.388(2)
C(2)-H(2)	0.9500
C(3)-C(4)	1.390(2)
C(3)-H(3)	0.9500
C(4)-C(5)	1.389(2)
C(4)-C(7)	1.506(2)
C(5)-C(6)	1.384(2)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-C(9)	1.325(2)
C(8)-N(2)	1.4162(19)
N(2)-N(3)	1.2389(19)
N(3)-N(4)	1.1223(19)
C(9)-C(10)	1.490(2)
C(9)-H(9)	0.9500
C(10)-C(11)	1.481(3)
C(10)-H(10A)	0.9900

C(10)-H(10B)	0.9900
C(11)-F(3A)	1.337(10)
C(11)-F(3)	1.339(8)
C(11)-F(1A)	1.340(10)
C(11)-F(1)	1.345(10)
C(11)-F(2)	1.357(9)
C(11)-F(2A)	1.362(10)
C(12)-C(13)	1.506(2)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-C(14)	1.387(2)
C(13)-C(18)	1.389(2)
C(14)-C(15)	1.377(3)
C(14)-H(14)	0.9500
C(15)-C(16)	1.373(3)
C(15)-H(15)	0.9500
C(16)-C(17)	1.372(3)
C(16)-H(16)	0.9500
C(17)-C(18)	1.392(3)
C(17)-H(17)	0.9500
C(18)-H(18)	0.9500

C(8)-N(1)-C(12)	117.29(12)
C(8)-N(1)-S(1)	118.25(9)
C(12)-N(1)-S(1)	120.13(10)
O(1)-S(1)-O(2)	120.28(8)
O(1)-S(1)-N(1)	106.41(7)
O(2)-S(1)-N(1)	105.78(7)
O(1)-S(1)-C(1)	107.75(7)
O(2)-S(1)-C(1)	107.99(7)
N(1)-S(1)-C(1)	108.12(7)

C(2)-C(1)-C(6)	120.73(14)
C(2)-C(1)-S(1)	119.28(12)
C(6)-C(1)-S(1)	119.97(12)
C(1)-C(2)-C(3)	119.07(14)
C(1)-C(2)-H(2)	120.5
C(3)-C(2)-H(2)	120.5
C(2)-C(3)-C(4)	121.33(15)
C(2)-C(3)-H(3)	119.3
C(4)-C(3)-H(3)	119.3
C(5)-C(4)-C(3)	118.35(14)
C(5)-C(4)-C(7)	121.20(15)
C(3)-C(4)-C(7)	120.45(15)
C(6)-C(5)-C(4)	121.39(15)
C(6)-C(5)-H(5)	119.3
C(4)-C(5)-H(5)	119.3
C(5)-C(6)-C(1)	119.12(15)
C(5)-C(6)-H(6)	120.4
C(1)-C(6)-H(6)	120.4
C(4)-C(7)-H(7A)	109.5
C(4)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(4)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(9)-C(8)-N(2)	120.00(14)
C(9)-C(8)-N(1)	122.82(14)
N(2)-C(8)-N(1)	117.04(13)
N(3)-N(2)-C(8)	116.19(13)
N(4)-N(3)-N(2)	173.15(17)
C(8)-C(9)-C(10)	124.72(15)
C(8)-C(9)-H(9)	117.6

C(10)-C(9)-H(9)	117.6
C(11)-C(10)-C(9)	112.93(17)
C(11)-C(10)-H(10A)	109.0
C(9)-C(10)-H(10A)	109.0
C(11)-C(10)-H(10B)	109.0
C(9)-C(10)-H(10B)	109.0
H(10A)-C(10)-H(10B)	107.8
F(3A)-C(11)-F(1A)	105.1(8)
F(3)-C(11)-F(1)	110.2(9)
F(3)-C(11)-F(2)	108.4(8)
F(1)-C(11)-F(2)	104.0(8)
F(3A)-C(11)-F(2A)	106.5(7)
F(1A)-C(11)-F(2A)	104.4(8)
F(3A)-C(11)-C(10)	117.6(9)
F(3)-C(11)-C(10)	108.7(7)
F(1A)-C(11)-C(10)	115.0(8)
F(1)-C(11)-C(10)	116.7(8)
F(2)-C(11)-C(10)	108.5(6)
F(2A)-C(11)-C(10)	107.2(8)
N(1)-C(12)-C(13)	109.50(12)
N(1)-C(12)-H(12A)	109.8
C(13)-C(12)-H(12A)	109.8
N(1)-C(12)-H(12B)	109.8
C(13)-C(12)-H(12B)	109.8
H(12A)-C(12)-H(12B)	108.2
C(14)-C(13)-C(18)	118.88(15)
C(14)-C(13)-C(12)	120.06(14)
C(18)-C(13)-C(12)	121.05(14)
C(15)-C(14)-C(13)	120.51(17)
C(15)-C(14)-H(14)	119.7
C(13)-C(14)-H(14)	119.7

C(16)-C(15)-C(14)	120.37(18)
C(16)-C(15)-H(15)	119.8
C(14)-C(15)-H(15)	119.8
C(17)-C(16)-C(15)	120.09(17)
C(17)-C(16)-H(16)	120.0
C(15)-C(16)-H(16)	120.0
C(16)-C(17)-C(18)	120.09(18)
C(16)-C(17)-H(17)	120.0
C(18)-C(17)-H(17)	120.0
C(13)-C(18)-C(17)	120.07(17)
C(13)-C(18)-H(18)	120.0
C(17)-C(18)-H(18)	120.0

Symmetry transformations used to generate equivalent atoms:

Table 5. Anisotropic displacement parameters (A^2 x 10^3) for elmds_a.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
N(1)	33(1)	24(1)	34(1)	0(1)	-7(1)	-5(1)
S(1)	27(1)	40(1)	34(1)	7(1)	-2(1)	-5(1)
O(1)	40(1)	59(1)	41(1)	9(1)	9(1)	10(1)
O(2)	42(1)	56(1)	48(1)	15(1)	-13(1)	-27(1)
C(1)	22(1)	35(1)	32(1)	3(1)	-4(1)	-6(1)
C(2)	30(1)	33(1)	37(1)	-2(1)	-1(1)	-4(1)
C(3)	32(1)	31(1)	44(1)	6(1)	-4(1)	-7(1)
C(4)	23(1)	43(1)	33(1)	7(1)	-7(1)	-10(1)
C(5)	35(1)	41(1)	34(1)	-4(1)	-3(1)	-9(1)
C(6)	36(1)	31(1)	37(1)	0(1)	-5(1)	-9(1)
C(7)	34(1)	60(1)	38(1)	14(1)	-6(1)	-15(1)
C(8)	32(1)	24(1)	32(1)	1(1)	-6(1)	-7(1)
N(2)	40(1)	31(1)	48(1)	6(1)	5(1)	-9(1)
N(3)	40(1)	31(1)	48(1)	6(1)	5(1)	-9(1)
N(4)	44(1)	62(1)	59(1)	14(1)	9(1)	-14(1)
C(9)	38(1)	29(1)	37(1)	1(1)	0(1)	-10(1)
C(10)	39(1)	37(1)	50(1)	-5(1)	8(1)	-6(1)
C(11)	92(2)	48(1)	61(1)	-12(1)	23(1)	-8(1)
F(1)	158(8)	78(3)	55(4)	-2(2)	38(5)	-24(4)
F(2)	115(4)	61(4)	60(4)	-13(3)	-22(2)	-27(2)
F(3)	124(6)	63(4)	84(4)	-24(4)	34(4)	31(5)
F(1A)	115(5)	73(5)	124(8)	-55(5)	48(4)	-21(5)

F(2A)	117(7)	89(4)	52(4)	-4(3)	40(4)	-10(3)
F(3A)	151(5)	87(6)	70(5)	-17(4)	-31(4)	-16(4)
C(12)	45(1)	24(1)	37(1)	0(1)	-8(1)	-9(1)
C(13)	39(1)	21(1)	33(1)	-5(1)	-2(1)	-7(1)
C(14)	43(1)	38(1)	44(1)	-12(1)	4(1)	-12(1)
C(15)	79(1)	50(1)	36(1)	-11(1)	9(1)	-28(1)
C(16)	100(2)	42(1)	36(1)	1(1)	-17(1)	-21(1)
C(17)	58(1)	41(1)	57(1)	-4(1)	-23(1)	-2(1)
C(18)	37(1)	36(1)	44(1)	-8(1)	-2(1)	-4(1)

Table 6. Hydrogen coordinates (x 10^4) and isotropic

displacement parameters (A^2 x 10^3) for elmds_a.

	x	y	z	U(eq)
H(2)	8756	-802	7849	41
H(3)	8173	-1709	9425	43
H(5)	6689	1866	10593	44
H(6)	7291	2791	9032	41
H(7A)	5671	-620	11259	65
H(7B)	7395	-111	11726	65
H(7C)	7824	-1513	11236	65
H(9)	3590	2820	7643	41
H(10A)	2702	5520	7032	51
H(10B)	1065	4742	7249	51
H(12A)	4585	1112	6464	42
H(12B)	6659	372	6032	42
H(14)	7740	1262	4342	49
H(15)	6771	1953	2708	63
H(16)	3526	2759	2356	70
H(17)	1225	2878	3638	64
H(18)	2170	2176	5290	47

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

Symmetry transformations used to generate equivalent atoms:

Table 8. Torsion angles [deg] for elmds_a.

C(8)-N(1)-S(1)-O(1)	-161.54(11)
C(12)-N(1)-S(1)-O(1)	42.48(13)
C(8)-N(1)-S(1)-O(2)	-32.53(13)
C(12)-N(1)-S(1)-O(2)	171.49(11)
C(8)-N(1)-S(1)-C(1)	82.95(12)
C(12)-N(1)-S(1)-C(1)	-73.04(13)
O(1)-S(1)-C(1)-C(2)	-19.22(14)
O(2)-S(1)-C(1)-C(2)	-150.57(12)
N(1)-S(1)-C(1)-C(2)	95.41(12)
O(1)-S(1)-C(1)-C(6)	159.16(12)
O(2)-S(1)-C(1)-C(6)	27.82(14)
N(1)-S(1)-C(1)-C(6)	-86.20(13)
C(6)-C(1)-C(2)-C(3)	-0.5(2)
S(1)-C(1)-C(2)-C(3)	177.89(11)
C(1)-C(2)-C(3)-C(4)	0.1(2)
C(2)-C(3)-C(4)-C(5)	0.6(2)
C(2)-C(3)-C(4)-C(7)	-179.29(14)
C(3)-C(4)-C(5)-C(6)	-0.9(2)
C(7)-C(4)-C(5)-C(6)	178.94(14)
C(4)-C(5)-C(6)-C(1)	0.6(2)
C(2)-C(1)-C(6)-C(5)	0.2(2)
S(1)-C(1)-C(6)-C(5)	-178.20(11)
C(12)-N(1)-C(8)-C(9)	57.35(19)
S(1)-N(1)-C(8)-C(9)	-99.32(15)
C(12)-N(1)-C(8)-N(2)	-118.21(14)
S(1)-N(1)-C(8)-N(2)	85.12(15)
C(9)-C(8)-N(2)-N(3)	-176.57(14)
N(1)-C(8)-N(2)-N(3)	-0.9(2)

N(2)-C(8)-C(9)-C(10)	1.0(2)
N(1)-C(8)-C(9)-C(10)	-174.40(14)
C(8)-C(9)-C(10)-C(11)	-118.8(2)
C(9)-C(10)-C(11)-F(3A)	53.2(12)
C(9)-C(10)-C(11)-F(3)	-173.2(8)
C(9)-C(10)-C(11)-F(1A)	177.8(8)
C(9)-C(10)-C(11)-F(1)	-47.8(13)
C(9)-C(10)-C(11)-F(2)	69.2(7)
C(9)-C(10)-C(11)-F(2A)	-66.6(9)
C(8)-N(1)-C(12)-C(13)	68.02(17)
S(1)-N(1)-C(12)-C(13)	-135.77(12)
N(1)-C(12)-C(13)-C(14)	73.66(17)
N(1)-C(12)-C(13)-C(18)	-105.25(16)
C(18)-C(13)-C(14)-C(15)	0.0(2)
C(12)-C(13)-C(14)-C(15)	-178.92(15)
C(13)-C(14)-C(15)-C(16)	0.1(3)
C(14)-C(15)-C(16)-C(17)	-0.1(3)
C(15)-C(16)-C(17)-C(18)	-0.1(3)
C(14)-C(13)-C(18)-C(17)	-0.2(2)
C(12)-C(13)-C(18)-C(17)	178.73(15)
C(16)-C(17)-C(18)-C(13)	0.3(3)

Symmetry transformations used to generate equivalent atoms:

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

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