From Boom to Bloom: Synthesis of Diazidodifluoromethane, its Stability and Applicability in the 'Click' Reaction

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Content

1. General information

All commercially available chemicals were purchased from Fisher Scientifics, Fluorochem or Sigma-Aldrich and, unless otherwise noted, used without any previous purification. All synthetic reactions were carried out in oven-dried vessels under a dry N_2 atmosphere. Solvents used for workup and purification procedures were of technical grade. THF was freshly distilled over Na/benzophenone prior to use. $CDCl_3$ and DMF were dried using molecular sieves (3 Å and 4 Å, respectively).

Microwave heating was performed using sealed flasks on a CEM Discovery System 908,010. Automated flash column chromatography was performed on a Teledyne ISCO CombiFlash Rf+ Lumen Automated Flash Chromatography System with UV/vis detection. Preparative HPLC isolation were performed on 1260 Infinity II (Agilent) equipped with YMC-Actus Triart C18 column (5 µm, 100 Å, 250 × 20.0 mm) using H_2O–MeCN gradients (20 mL/min flow rate) with formic acid (0.1%) as an additive.

^1H, ^{13}C, ^{19}F NMR spectra were measured on a 400 MHz spectrometer with a broad-band PRODIGY cryo probe (^1H at 400 MHz, ^{19}F at 337 MHz, ^{13}C at 101 MHz,) and 500 MHz spectrometer, operating at 500 MHz for ^1H, 470 MHz for ^{19}F and 126 MHz for ^{13}C. ^{15}N NMR spectra were recorded on a 500 MHz spectrometer, operating at 470.60 MHz for ^{19}F and 50.69 MHz for ^{15}N. Chemical shift values (δ) are reported in ppm relative to internal Me_4Si (0 ppm for ^1H and ^{13}C NMR) or residual solvents and internal $CFCl_3$ (0 ppm for ^{19}F NMR) and CH_3NO_2 (0 ppm for ^{15}N NMR).

FTIR spectra were recorded on Nicolet 6700 spectrometer (Thermo Scientific, USA) equipped with standard MIR source, KBr beamsplitter, and DTGS detector in transmission mode in the 4000–700 cm^{-1} spectral range with the following setup (256 scans, 2 cm^{-1} spectral resolution, Happ-Genzel apodization function).

High resolution MS spectra (HRMS) were recorded on an LTQ Orbitrap XL using electrospray (ESI) or APCI ionizations, on a Waters Micromass AutoSpec Ultima, or Agilent 7890A GC coupled with Waters GCT Premier orthogonal acceleration TOF detector using electron impact (EI) or chemical ionizations (CI). DSC was performed on a TA DSC250 differential scanning calorimeter (TA Instruments).

2. Safety precautions and synthesis of $N_3CF_2N_3$ solution

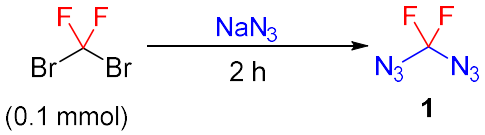
Safety Precautions*:* Diazidodifluoromethane (**1**) may exhibit a rapid decomposition or an explosive behaviour without discernible triggers. We recommend to handle **1** in solution (e.g. 0.1M solution in THF) rather than working with neat **1**. Neat **1** should not be heated and a solution of **1** in THF should not be heated above the boiling point of THF under normal pressure. In one instance we observed a violent decomposition of neat **1** on contact with a rough glass surface (crack or a quickfit joint).

Synthesis: Sodium dodecanethiolate (0.11 g, 0.1 mmol, 0.1 equiv.) together with sodium azide (1.08 g, 16.7 mmol, 3.5 equiv.) were placed in a 100 ml round bottom flask. The flask was cooled to –10 °C, backfilled with argon and dry DMF (47 ml) was added.

After 5 min of stirring bibromodifluorometane (1 g, 4.7 mmol, 1 equiv.) was added. The reaction mixture was heated to 60 °C during 130 min. Then the flask was cooled down to –30 °C. Cold dry THF (40 ml) was added and the product was distilled using 25–30 cm Vigreux column (heating bath 90 °C, ambient pressure) together with THF to a cooled (dry ice/acetone) receiving flask. The product was obtained as a solution in THF (approx. 30 ml of 0.1M solution of **1**) containing a small amount of unreacted bibromodifluorometane and traces of N_3CF_2H side-product. Yields of 67% ^{19}F NMR. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 121.3 (t, $^1J_{C\text{-}F}$ = 267 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –55.5 (s); HRMS (EI) *m/z* calcd for $[CHF_2N_6]^+$: 93.0139, found 93.0133; calcd for $[CF_2N]^+$: 63.9999, found 63.9995; calcd for $[CHF_2]^+$: 51.0041, found 51.0061; IR (KBr, cm^{-1}) 2151 (vs, $\nu_{as}(N_3)$), 1268 (s, $\nu_{as}(CF_2)$), 1241 (m, $\nu_{as}(CF_2)$), 1139 (m, $\nu_{ss}(CF_2)$), 1076 (s, $\nu_{ss}(CF_2)$).

3. Optimisation of the synthesis of 1

Table S1: Optimisation for the synthesis of **1**.



(0.1 mmol) **1**

Entry	Solvent	Eq. of NaN_3	T (°C)	Additive	^{19}F yield of **1**
1	DMF	2	55	None	0
2	NMP	3.5	60	None	2
3	Glyme	3	60	None	0
4	Water	3.5	60	None	0
5	THF	3.5	55	None	0
6	MeCN	3.5	55	None	0
7[a]	DMF	3.5	60	None	20
8[a]	NMP	3.5	60	None	17
9	DMF	2	60	BnSH (5 mol%)	0
10	DMF	3	60	EtSNa (5 mol%)	30
11	THF	2	60	BnSH (5 mol%)	3
12	THF	3	60	EtSNa (5 mol%)	20–30
13	NMP	2	60	BnSH (5 mol%)	0
14	NMP	3	60	EtSNa (5 mol%)	50
15	**DMF**	**3.5**	**60**	***n*-$C_{12}H_{25}$SNa (5 mol%)**	**65–77**
16	THF	2	60	*n*-$C_{12}H_{25}$SNa (5 mol%)	15
17	DMSO	3	60	*n*-$C_{12}H_{25}$SNa (5 mol%)	1–5
18	NMP	2	60	*n*-$C_{12}H_{25}$SNa (5 mol%)	0
19[a]	DMF	3.5	60	*n*-$C_{12}H_{25}$SNa (5 mol%)	39
20	NMP	3.5	60	*n*-$C_{12}H_{25}$SNa (5 mol%)	14
21	DMF	3.5	60	18-crown-6 (1 mol%)	2
22	NMP	3.5	60	18-crown-6 (1 mol%)	2
23	DMF	3.5	60	18-crown-6 (1 mol%) + *n*-$C_{12}H_{25}$SNa (5 mol%)	73
24	NMP	3.5	55	18-crown-6 (1 mol%) + *n*-$C_{12}H_{25}$SNa (5 mol%)	5

[a] Using tetrabutylammonium azide (3.5 equiv.) instead of sodium azide.

4. Control mechanistic experiment

Sodium dodecanethiolate (20 mg, 0.09 mmol, 0.1 equiv.), sodium azide (216 mg, 3.3 mmol, 3.5 equiv.), and styrene (104 mg, 1 mmol, 1 equiv.) were placed in a 5 mL pressure-resistant reaction tube. The tube was cooled to 0 °C, flushed with argon, and anhydrous DMF (3.5 mL) was added. After stirring for 5 minutes, dibromodifluoromethane (200 mg, 1 mmol, 1 equiv.) was added to the reaction mixture. The mixture was then heated to 60 °C and maintained at this temperature for 120 minutes. Then, the reaction mixture was cooled to 0 °C and the crude product mixture was analysed by ^{19}F NMR showing the formation of difluorocyclopropane side-product.[1]

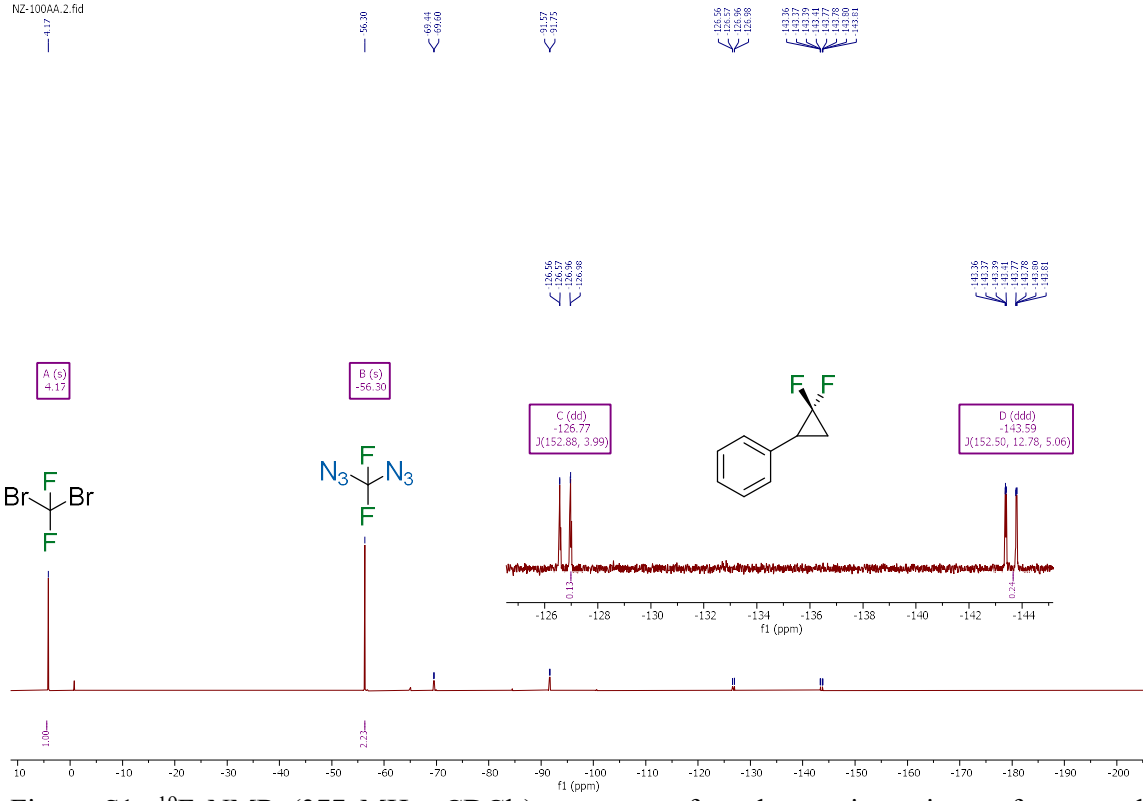


Figure S1: ^{19}F NMR (377 MHz, $CDCl_3$) spectrum of crude reaction mixture for control experiment with styrene.

5. General procedure for the synthesis of triazoles 2

Alkyne (1 mmol, 2.1 equiv.) was placed in a 25 ml screw-cap glass tube together with copper(I) 3-methylsalicylate (2.5 mg, 0.01 mmol, 2 mol%) and THF (5 mL). The air in the flask was exchanged for argon the flask was cooled down to –30 °C. A cold (–30 °C) solution of **1** (10 ml, 0.5 mmol, 1.0 equiv., ~0.05M in THF) was added via syringe. The flask was stirred at rt overnight (45 °C for **2f, 2h** and **2l**). The solvent was evaporated under reduced pressure and the

crude product was purified by column chromatography on silica gel or preparative HPLC (C_{18} column; H_2O–MeCN gradient with formic acid additive). For the synthesis of **2f′** 6.0 equiv. of **1** was used.

6. General procedure for the synthesis of imidazoles 3

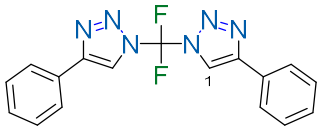
Triazole **2** (0.5 mmol, 1 equiv.) was dissolved in anhydrous DCE (4 ml) in a microwave tube. $Rh_2(Oct)_4$ (3.9 mg, 0.5 μmol, 1 mol%) and the corresponding nitrile (1.0 mmol, 2 equiv.) were added, the tube was closed, and briefly sonicated. The reaction mixture was heated at 160 °C for 1 h in a microwave reactor. The solvent was evaporated under reduced pressure and the crude product was purified by preparative HPLC (C_{18} column; H_2O–MeCN gradient with formic acid additive).

7. General procedure for the synthesis of isoquinoline 4

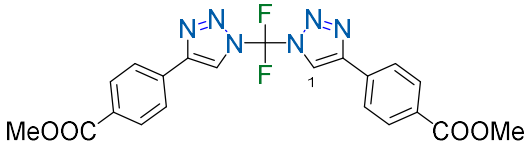
Triazole **2a** (0.5 mmol, 1 equiv.) was dissolved in anhydrous 1,1,2,2 tetrachloroethane-d_2 (4 ml) in a microwave tube. The tube was closed, and briefly sonicated. The reaction mixture was heated at 172 °C for 90 min in a microwave reactor. The solvent was evaporated under reduced pressure and the crude product was purified by preparative HPLC (C_{18} column; H_2O–MeCN gradient with formic acid additive).

8. Characterization data for compounds 2–4

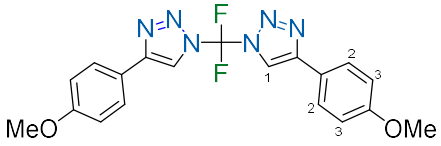
*Difluorobis(4-phenyl-1H-1,2,3-triazol-1-yl)methane (**2a**):* Yield 89%; 620 mg; pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 2H, H1), 7.90–7.86 (m, 4H, ArH), 7.49–45 (s, 4H, ArH), 7.43–7.40 (m, 2H, ArH); ^{19}F NMR (377 MHz, $CDCl_3$): δ –65.97 (s); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.9, 129.5, 129.2, 128.7, 126.4, 118.3, 113.7 (t, $^1J_{C\text{-}F}$ = 257 Hz); HRMS (ESI$^+$) *m/z* calcd for $C_{17}H_{12}F_2N_6Na^+$ [M+Na]$^+$: 361.0984, found 361.0985.



*Methyl 4-(1-((4-(4-acetoxyphenyl)-1H-1,2,3-triazol-1-yl)difluoromethyl)-1H-1,2,3-triazol-4-yl)benzoate (**2b**):* Yield 80%; 32 mg; pale yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (s, 2H, H1), 8.17–8.14 (m, 4H, ArH), 7.99–7.97 (m, 4H, ArH), 3.95 (s, 6H, Me); ^{19}F NMR (470 MHz, $CDCl_3$) δ –65.5 (s); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 166.5, 147.8, 132.7, 131.0, 130.4, 126.1, 119.1, 113.5 (t, $^1J_{C\text{-}F}$ = 262 Hz,), 52.3; HRMS (ESI$^+$) *m/z* calcd for $C_{21}H_{16}F_2N_6O_4Na^+$ [M+Na]$^+$: 477.1093, found 477.1095.

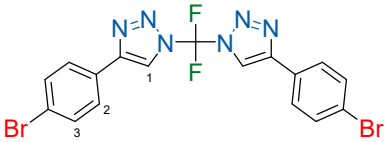


*Difluorobis(4-(4-methoxyphenyl)-1H-1,2,3-triazol-1-yl)methane (**2c**):* Yield 70%; 34 mg; white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (s, 2H, H1), 7.81 (d, J = 8.98 Hz, 4H, H2), 7.0 (d, J = 8.93 Hz, 4H, H3), 3.86 (s, 6H, Me); ^{19}F NMR (470 MHz, $CDCl_3$) δ –66 (s); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 160.5,

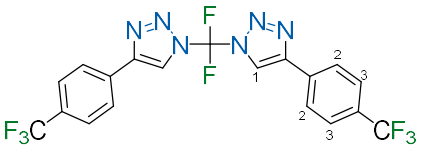


148.6, 127.6, 121.2, 117.2, 114.5, 113.5 (t, $^{1}J_{C\text{-}F}$ = 260 Hz), 55.4; HRMS (ESI^{+}) *m/z* calcd for $C_{19}H_{16}F_2N_6^{+}$ [M]$^{+}$: 361.0984, found 361.0985.

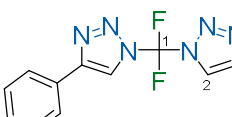
*Bis(4-(4-bromophenyl)-1H-1,2,3-triazol-1-yl)difluoromethane (**2d**):* Yield 90%; 230 mg; pale yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.34 (s, 2H, H1), 7.78–7.74 (m, 4H, H2), 7.63–7.60 (m, 4H, H3); ^{19}F NMR (470 MHz, $CDCl_3$) δ –65.49 (s); ^{13}C{^{1}H, ^{19}F} NMR (101 MHz, $CDCl_3$) δ 147.9, 132.4, 127.79, 127.56, 123.7, 118.4, 113.6; HRMS (ESI^{+}) *m/z* calcd for $C_{17}H_{10}F_2N_6Br_2Na^{+}$ [M+Na]$^{+}$: 516.9194, found 516.9182.



*Difluorobis(4-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazol-1-yl)methane (**2e**):* Yield 64%; 148 mg; white yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (s, 2H, H1), 8.02 (d, J = 8.11 Hz, 4H, H2), 7.75 (d, J = 8.59 Hz, 4H, H3); ^{19}F NMR (470 MHz, $CDCl_3$) δ –62.7 (s, 3F, CF_3), –65.5 (s, 2F, CF_2); ^{13}C{^{1}H, ^{19}F} NMR (126 MHz, $CDCl_3$) δ 147.6, 132.1, 126.6, 126.3, 124, 119.2, 113.7; HRMS (ESI^{+}) *m/z* calcd for $C_{19}H_{10}F_2N_8Na^{+}$ [M+Na]$^{+}$: 497.0731, found 497.0729

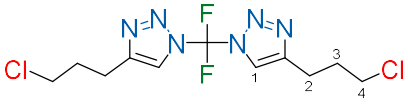


*Difluorobis(4-(pyridin-3-yl)-1H-1,2,3-triazol-1-yl)methane (**2f**):* Yield 80%; 103 mg; pale yellow solid; ^{1}H NMR (500 MHz, CD_3OD): δ 9.13 (br s, 2H, H5), 9.10 (s, 2H, H2), 8.60 (br s, 2H, H6), 8.38 (dd, J = 8.0, 1.8 Hz, 2H, H8), 7.58 (dd, J = 8.0, 4.7 Hz, 2H, H7); ^{19}F NMR (470 MHz, CD_3OD) δ –60.65 (s); ^{13}C{^{1}H} NMR (126 MHz, CD_3OD) δ 148.8, 146.0, 144.8, 134.0, 125.8, 124.5, 120.1, 116.9 (t, $^{1}J_{C\text{-}F}$ = 263 Hz); HRMS (ESI^{+}) *m/z* calcd for $C_{15}H_{11}F_2N_8^{+}$ [M]$^{+}$: 341.1069, found 341.1068.

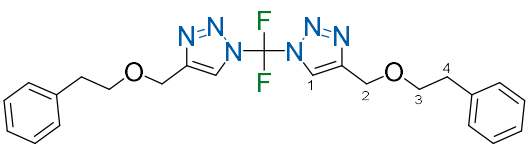


*3-(1-(Azidodifluoromethyl)-1H-1,2,3-triazol-4-yl)pyridine (**2f'**):* Yield 60%; 113 mg; yellow liquid; ^{1}H NMR (500 MHz, CD_3OD) δ 9.11 (br s, 1H, H5), 9.08 (s, 1H, H2), 8.59 (br s, 1H, H6), 8.36 (dt, J = 8.0, 1.8 Hz, 1H, H8), 7.56 (dd, J = 8.0, 4.7 Hz, 1H, H7); ^{19}F NMR (470 MHz, CD_3OD) δ –60.95 (s); ^{13}C{^{1}H} NMR (126 MHz, CD_3OD) δ 150.2, 147.3, 146.2, 135.4, 127.5, 125.9, 121.4, 118.2 (t, $^{1}J_{C\text{-}F}$ = 260 Hz); HRMS (ESI^{+}) *m/z* calcd for $C_8H_6F_2N_7^{+}$ [M]$^{+}$: 238.0647, found 238.0649.

*Bis(4-(3-chloropropyl)-1H-1,2,3-triazol-1-yl)difluoromethane (**2g**):* Yield 67%; 194 mg; white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (s, 2H, H1), 3.58 (t, J = 6.29 Hz, 4H, H4), 2.95 (t, J = 7.48 Hz, 4H, H2), 2.19 (m, 4H, H3); ^{19}F NMR (470 MHz, $CDCl_3$) δ –65.05 (s); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 147.5, 120.3, 113.4 (t, $^{1}J_{C\text{-}F}$ = 259.92 Hz, CF_2), 43.9 (C4), 31.4 (C2), 22.4 (C3); HRMS (ESI^{+}) *m/z* calcd for $C_{11}H_{15}F_2N_6Cl_2^{+}$ [M]$^{+}$: 339.0698, found 339.0700.



*Difluorobis(4-(phenethoxymethyl)-1H-1,2,3-triazol-1-yl)methane (**2h**):* Yield 82%; 145 mg; white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 2H, H1), 7.37–7.28 (m, 10H, ArH), 4.53 (s, 4H, H2), 3.79 (t, J = 6.24 Hz, 4H, H4), 3.11 (t, J = 5.83 Hz, 4H, H3); ^{19}F NMR (470 MHz, $CDCl_3$) δ –65.64 (s); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 146.5, 138.0, 128.6, 127.9, 127.9,



121.0, 113.5 (t, $^{1}J_{C\text{-}F}$ = 236.9.2 Hz), 73.2 (C3), 68.3 (C2), 26.4 (C4); HRMS (ESI^{+}) *m/z* calcd for $C_{23}H_{24}F_2N_6O_2Na^{+}$ [M+Na]$^{+}$: 477.1821, found 477.1812.

Bis(4-butyl-1H-1,2,3-triazol-1-yl)difluoromethane ***(2i)****:* Yield 71%; 154 mg; white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (s, 2H, H1), 2.72 (t, J = 7.34 Hz, 4H, H2), 1.67–1.60 (m, 4H, H3), 1.34 (dq, J = 14.7 Hz, 7.4 Hz, 4H, H4), 0.88 (t, J = 7.4 Hz, 6H, H5); ^{19}F NMR (470 MHz, $CDCl_3$) δ –65.03 (s); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 149.4, 119.6, 113.4 (t, $^{1}J_{C\text{-}F}$ = 260 Hz), 31.0, 25.0, 22.2, 13.7; HRMS (ESI^{+}) *m/z* calcd for $C_{13}H_{21}F_2N_6^{+}$ [M]$^{+}$: 299.1790, found 299.1791

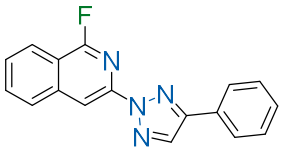
Bis(4-cyclohexyl-1H-1,2,3-triazol-1-yl)difluoromethane ***(2j)****:* Yield 73%; 127 mg; white needles; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 2H, H2), 2.85–2.79 (m, 2H, H1), 2.12–2.07 (m, 4H), 1.85–1.71 (m, 6H), 1.49–1.35 (m, 8H), 1.32–1.23 (m, 2H); ^{19}F NMR (377 MHz, $CDCl_3$) δ –65.01 (s); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.6, 118.4, 113.6 (t, $^{1}J_{C\text{-}F}$ = 257 Hz,), 35.1, 32.7, 26.06, 25.98; HRMS (ESI^{+}) *m/z* calcd for $C_{17}H_{24}F_2N_6Na^{+}$ [M+Na]$^{+}$: 373.1923, found 373.1922

Bis(2,4-diphenyl-1H-imidazol-1-yl)difluoromethane ***(3a)****:* Yield 90%; 221 mg; pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67–7.64 (m, 4H), 7.40–7.36 (m, 8H), 7.33–7.28 (m, 8H), 7.33 (s, 2H); ^{19}F NMR (377 MHz, $CDCl_3$) δ –50.07 (s); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.2, 141.3, 132.2, 130.0, 129.2, 129.0, 128.6, 128.2, 127.8, 125.4, 113.5, 113.5 (t, $^{1}J_{C\text{-}F}$ = 257 Hz); HRMS (EI^{+}) *m/z* calcd for $C_{31}H_{22}F_2N_6^{+}$ [M]$^{+}$: 488.1807, found 488.1805.

Difluorobis(2-isopropyl-4-phenyl-1H-imidazol-1-yl)methane ***(3b)****:* Yield 95%; 183 mg; pale yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78–7.75 (m, 4H, ArH), 7.40–7.36 (m, 4H, ArH), 7.30–7.27 (m, 2H, ArH), 6.99 (s, 2H), 3.08–3.02 (m, 2H), 1.39 (d, J = 6.80 Hz, 12H); ^{19}F NMR (470 MHz, $CDCl_3$) δ –55.09 (s); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.6, 141.3, 132.7, 128.8, 125.4, 113.9 (t, $^{1}J_{C\text{-}F}$ = 253 Hz, CF_2), 111.4, 27.9, 22.2; HRMS (EI^{+}) *m/z* calcd for $C_{25}H_{26}F_2N_4^{+}$ [M]$^{+}$: 420.2120, found 420.4122.

Bis(2-benzyl-4-phenyl-1H-imidazol-1-yl)difluoromethane ***(3c)****:* Yield 87%; 223 mg; yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73–7.69 (m, 4H, ArH), 7.42–7.33 (m, 4H, ArH), 7.33–7.28 (m, 2H, ArH), 7.25–7.20 (m, 4H, ArH), 7.18–7.11 (m, 6H, ArH), 6.89 (s, 2H, H2), 4.10 (s, 4H, H1); ^{19}F NMR (376 MHz, $CDCl_3$) δ –55.83 (s); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.4, 147.1, 147.0, 147.0, 141.4, 135.7, 132.2, 128.7, 128.5, 128.4, 127.0, 125.3, 113.6 (t, $^{1}J_{C\text{-}F}$ = 254 Hz, CF_2), 112.5, 34.6; HRMS (EI^{+}) *m/z* calcd for $C_{33}H_{26}F_2N_4^{+}$ [M]$^{+}$: 516.2120, found 516.2114.

*1-Fluoro-3-(4-phenyl-2H-1,2,3-triazol-2-yl)isoquinoline (**4**):* Yield 83%; 119 mg; white solid;



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.22 (dq, J = 8.32, 0.96 Hz, 1H), 8.18 (s, 1H), 8.00–7.96 (m, 3H), 7.88 (dd, J = 8.26, 6.95, 1.23 Hz, 1H), 7.69 (ddd, J = 8.14, 6.92, 1.07 Hz, 1H), 7.51-747 (m, 2H), 7.44-7.41 (m, 1H); ^{19}F NMR (377 MHz, $CDCl_3$) δ –68.32 (s); ^{13}C{^{1}H, ^{19}F} NMR (101 MHz, $CDCl_3$) δ 159.6, 150.1, 143.3, 141.1, 134.0, 132.7, 129.6, 129.3, 129.1, 129.0, 128.1, 127.2, 126.5, 123.7, 116.8, 107.0.; HRMS (ESI^{+}) *m/z* calcd for $C_{17}H_{12}F_1N_4^{+}$ $[M+H]^{+}$: 291.1041, found 291.1042.

9. FTIR spectrum of 1

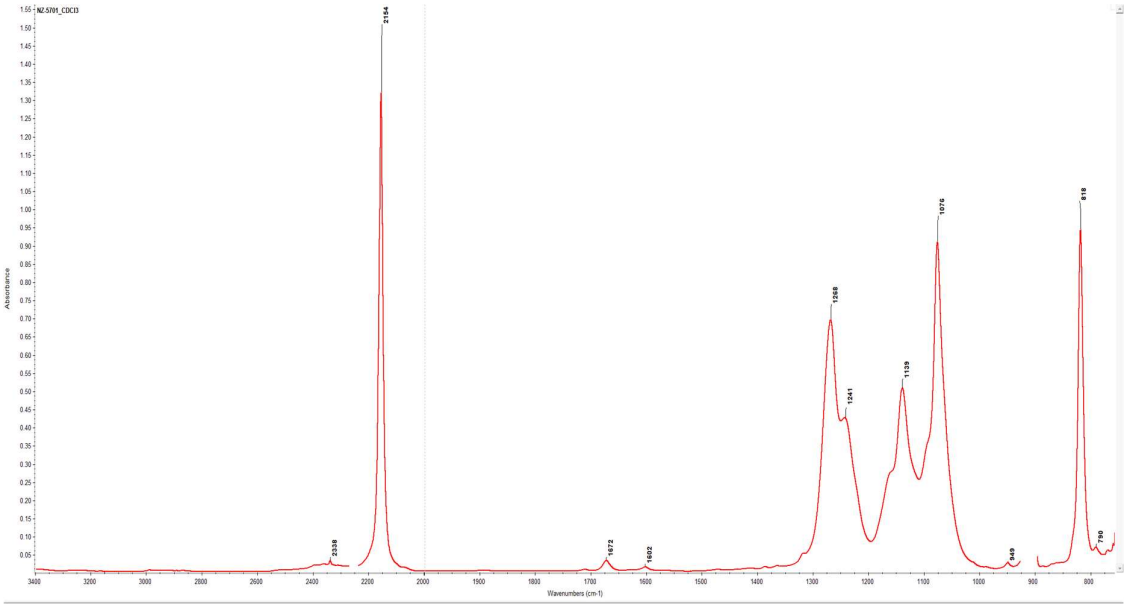


Figure S2: FTIR (KBr) spectrum of diazidodifluoromethane (**1**).

10.Sensitivity to impact measurement of 1

The Kast fallhammer apparatus BFH-12 produced by OZM Research (Hrochův Týnec, Czech Republic) was used for determining impact sensitivity with 5 kg and 10 kg hammers. Testing sets composed of steel guides BFH-SC and cylinders BFH-SR were acquired by OZM Research. The measuring apparatus, related supplies and measurement methodology were in compliance with the regulations: *Recommendation on the transport of dangerous goods, Manual of tests and criteria,* Union Nations, Chapter 13.4.2 Test 3 (a) (ii): BAM Fallhammer, New York 2015, pp. 85–92.

The measurement was started with 6 trials at an energy level of 10 J (20 cm/5 kg hammer) with the result "no reaction". The impact energy was gradually increased (20, 30, 40 J) to a final energy level of 50 J (50 cm/10 kg hammer) again with six trials at each level. In all cases the result was evaluated as "no reaction". The results of impact sensitivity measurement were

negative, indicating that diazidodifluoromethane (**1**) in the form of a 0.1 M solution in THF is insensitive to impact.

11.Calculated stabilities azides

Activation Gibbs free energies $\Delta G^{\#}$ and the corresponding rate constants k assuming all of the localized transition states leading to the loss of the N_2 molecule at 300 K and 473.15 K in the gas phase are presented in Table S1. These values were calculated at the DLPNO-CCSD(T)/aug-cc-pVQZ level with thermal corrections from the PBE0/6-31+g* calculations. Geometries were optimized at the PBE0/6-31+g* level.

Table S2: Calculated Gibbs free energies and rate constants of decomposition of azidomethanes.

		T=300 K		T=473.15 K	
Entry	Azide	$\Delta G^{\#}$/eV	k/s^{-1}	$\Delta G^{\#}$/eV	k/s^{-1}
1	CH_3N_3	1.58	$1.31\cdot10^{-14}$	1.55	$3.09\cdot10^{-4}$
2	CFH_2N_3	1.24	$5.91\cdot10^{-9}$	1.21	1.15
3	CF_2HN_3	1.35	$8.78\cdot10^{-11}$	1.32	$7.84\cdot10^{-2}$
4	CF_3N_3	2.16	$2.08\cdot10^{-24}$	2.10	$3.91\cdot10^{-10}$
5	CF_2N_6	1.35	$7.84\cdot10^{-11}$	1.33	$7.49\cdot10^{-2}$
6	$CFHN_6$	1.30	$6.18\cdot10^{-10}$	1.27	$2.63\cdot10^{-1}$
7	CH_2N_6	1.25	$4.19\cdot10^{-9}$	1.20	1.62
8	CFN_9	1.32	$3.15\cdot10^{-10}$	1.29	$1.66\cdot10^{-1}$
9	CHN_9	1.30	$6.20\cdot10^{-10}$	1.28	$2.41\cdot10^{-1}$
10	CN_{12}	1.31	$4.92\cdot10^{-10}$	1.28	$2.34\cdot10^{-1}$

12. Calculation of decomposition of azides

Geometry optimizations: All the geometries were optimized in the gas phase using the PBE0/6-31+g* method. ORCA 4.2.0 was used for all the calculations. For localization of transition states, the nudged elastic band (NEB-TS) method in its ZOOM-NEB-TS implementation was employed in many cases. Frequency calculations confirmed the character of each converged stationary point.

If more than one azide group was present in the molecule, transition states corresponding to all of the azide groups were localized. For each of $CHF(N_3)_2$ and $CF_2(N_3)_2$, three different transition states were found. Cartesian coordinates of all the found stationary states are listed below.

Gibbs free energy and rate constant calculations: Each Gibbs free energy value in the gas phase G_g for each geometry was evaluated as

$$G_g = E_{\mathrm{DLPNO-CCS\ (T),g}} + \mathrm{TC}_{\mathrm{PBE0,g}},$$

where $E_{\mathrm{DLPNO-CCS\ (T),g}}$ is energy calculated at the DLPNO-CCSD(T)/aug-cc-pVQZ level and $\mathrm{TC}_{\mathrm{PBE0,g}}$ is thermal correction from the PBE0/6-31+g* calculation.

In the cases of multiple transition states, the individual activation Gibbs free energies

$$\Delta G_i^{\#} = G_{\mathrm{g}}(\text{transition state } i) - G_{\mathrm{g}}(\text{minimum geometry})$$

were calculated and the total activation Gibbs free energy was obtained as

$$\Delta G_{\mathrm{tot}}^{\#} = -k_{\mathrm{B}} T \ln \sum_i e^{-\frac{\Delta G_i^{\#}}{k_{\mathrm{B}} T}},$$

where k_{B} is Boltzmann constant and T is temperature.

Rate constants were calculated using the Eyring–Polanyi equation

$$k = \frac{k_{\mathrm{B}} T}{h} e^{-\frac{\Delta G_{\mathrm{tot}}^{\#}}{k_{\mathrm{B}} T}},$$

where h is Planck constant. Lifetimes τ were then calculated as

$$\tau = \frac{1}{k}.$$

Gibbs free energies in solvent: Gibbs free energies in solvent (THF) were calculated as follows

$$G_{\mathrm{THF}} = G_{\mathrm{g}} + \Delta G_{\mathrm{solv}},$$

where ΔG_{solv} is the solvation Gibbs free energy calculated at the DLPNO-CCSD(T)/aug-cc-pVQZ level as

$$\Delta G_{\mathrm{solv}} = E_{\mathrm{DLPNO-CCSD(T),PCM}} - E_{\mathrm{DLPNO-CCSD(T),g}},$$

where $E_{\mathrm{DLPNO-CCSD(T),PCM}}$ is electronic energy calculated at the DLPNO-CCSD(T)/aug-cc-pVQZ level with the polarizable continuum model (PCM) of the solvent (THF).

Cartesian coordinates:

Ground state minima – optimized at the PBE0/6-31+g level*

CH_3N_3

7

C	-0.04876270683597	-0.00000000061259	0.03918769964190
N	0.17117192467744	-0.00000000521028	1.48544646492212
H	0.93683888513723	0.00000000323394	-0.42612243876707
H	-0.59419824560428	-0.89452616848227	-0.28763022641452
H	-0.59419825008090	0.89452616689289	-0.28763022247595
N	-0.84196006263545	0.00000000000051	2.17779854494257
N	-1.70269754465808	0.00000000417781	2.92328317815096

$CH_2(N_3)_2$

9

C	0.29433962129494	-0.16878993386884	-0.08882259267286
N	0.22497614166121	1.07373719505705	-0.85901227047664
N	-0.11575858028726	2.07771655454676	-0.22991503732840
N	-0.40010418936778	3.07504466372650	0.23347223070532
H	0.42226701686474	0.03752109593362	0.98358235504212

H	1.15988919095829	-0.71990661274968	-0.45331317096759
N	-0.84064845411120	-1.06037956046616	-0.31430448882176
N	-1.93944438880674	-0.62317081394325	0.03290220144317
N	-3.00408835820620	-0.33303958823601	0.30076777307664

FCH_2N_3

7

C	0.03641098216181	-0.04724746589783	-0.05403655245507
H	0.08895113755966	-0.02992932630747	1.03461363230414
H	1.03422333745856	-0.12015753869361	-0.50191629753836
F	-0.50602382112262	1.15620355814489	-0.47861077853672
N	-0.80847947249724	-1.15534525815015	-0.40991126830309
N	-0.87080870901373	-1.40522404772876	-1.62005989329526
N	-1.02742445454645	-1.73648992136707	-2.69181984217565

$CH(N_3)_3$

11

C	0.12688133095729	-0.00466565853099	-0.10995591332502
N	-0.51078383055536	1.25265730344884	-0.54088399253940
N	0.03466363190663	2.27410223230395	-0.11292652993659
N	0.45926113494672	3.27129301187221	0.21878030419358
H	0.37947399448759	0.04247799930922	0.95682561176641
N	1.38244652828763	-0.26616352811215	-0.77817786566595
N	-0.79571373629566	-1.09393433451360	-0.38671023456974
N	-1.95909443330134	-0.89791457594552	-0.02132484049330
N	-3.05262737402099	-0.83917449270385	0.26672655633865
N	1.27639527884526	-0.55111618412169	-1.98068192182526
N	1.32658647474224	-0.82378377300643	-3.07684017394337

$CHF(N_3)_2$

9

C	0.04983668361210	0.01196269085987	0.20900967310963
N	-0.61825853695471	1.28961964721561	0.09379091405563
N	0.13232718086569	2.24629325777225	-0.13000489011416
N	0.71362570634374	3.19532563448207	-0.33516404769677
H	0.82495501874176	0.00013797346908	0.97949715158601
F	0.68627973667530	-0.27156497605195	-0.99608288695883
N	-0.89071089266792	-1.00485616001589	0.53927543622823
N	-1.91545897362991	-1.01477140945735	-0.16210475015061
N	-2.89137392298606	-1.15072065827368	-0.71392460005911

HCF_2N_3

7

C	-0.05594951232002	-0.05929017025544	0.01440517238467
H	-0.17950334279972	-0.11565941071147	1.10188918540450
F	1.25087049722275	-0.01060328740587	-0.28369606997566
F	-0.62697338163908	1.10410499872917	-0.40695722608697
N	-0.59903939301538	-1.17899392331721	-0.69635363700827
N	-1.77390425921809	-1.44253789676148	-0.41777432168536

N	-2.83953760823046	-1.78829531027769	-0.25772110303291

$C(N_3)_4$

13

C	0.01819201523761	-0.12462007931364	-0.13225541665662
N	-0.95523564169162	-1.10919383604427	-0.58956607148827
N	-2.12844499857947	-0.84909162885496	-0.28877445785511
N	-3.23105173122755	-0.72638242623162	-0.07358034701930
N	-0.50103222038693	1.19671488996855	-0.46271860915267
N	0.11606058214369	2.13621536309478	0.05762358976861
N	0.59586989260351	3.07418042521246	0.46644225751361
N	0.24231117423035	-0.16340993703241	1.30782911735283
N	1.28776460470879	-0.42288560797885	-0.78464147297042
N	1.20011088217673	-0.64245929086882	-2.00064844057466
N	1.25043478215419	-0.85982538386337	-3.10848337996496
N	0.86742744310624	-1.15727809644287	1.70249144792672
N	1.42186321552446	-2.01598539164499	2.18452478312025

$CF(N_3)_3$

11

C	0.08742748326347	0.01231317051963	-0.13440966172807
N	-0.58291053030555	1.26735956595564	-0.42933458327309
N	0.06727019244649	2.27748033829439	-0.12416968365858
N	0.56169879731460	3.26693647822628	0.10528514025592
F	0.41690169741241	-0.00625883610789	1.19953521439631
N	1.34780719110503	-0.15432993942730	-0.81485772600310
N	-0.79334816720569	-1.07206383094986	-0.45799661057808
N	-1.96284808423922	-0.91982761163312	-0.07273352094768
N	-3.05218012640494	-0.91252929417057	0.22183032050247
N	1.25716106999169	-0.52858837839698	-1.99081927234519
N	1.32050947662171	-0.86671366231022	-3.06749861662091

$CF_2(N_3)_2$

9

C	0.06936583087824	-0.02541097784683	0.01368551634221
F	0.29496431979992	0.08635642392392	1.36052339390486
F	1.27385411562400	-0.27794579598050	-0.53537574028870
N	-0.75936394531593	-1.14379420613040	-0.27538091736190
N	-1.96535894908985	-0.96373848728639	-0.05399146473277
N	-3.08368188549046	-0.94822162342197	0.09865846601944
N	-0.50567737269246	1.18752361068085	-0.48951863843518
N	0.15418818700767	2.20770536462467	-0.23633655962221
N	0.65760969927886	3.20480869143666	-0.07689105582577

CF_3N_3

7

C	0.08508974589323	0.15708586671488	-0.11534511128774
F	-0.16108066809286	-0.58882958193400	0.95191493429073
F	1.38131519443012	0.51849523682919	-0.09735555842213

F	-0.63293280909067	1.29104719298281	-0.02252325292671
N	-0.25079622956569	-0.60702262004575	-1.26583877554887
N	-0.06374867638181	-0.01783855972446	-2.34136896769571
N	0.05469444280769	0.39006946517732	-3.38675626840956

difluorodiazirine

5

C	0.36488871022681	-0.09244757690197	-0.06839666827570
F	0.02791267476395	-0.15658610005795	1.21845165448508
F	1.68694624547957	-0.17383137889248	-0.20885785652074
N	-0.48734212494311	-0.60107636090533	-1.05358013674387
N	-0.40108750552721	0.65461041675774	-0.96889099294477

difluorocarbene

3

C	-0.01858398275078	0.00000000000000	-0.01311591907754
F	0.04071926868691	0.00000000000000	1.29210034612241
F	1.23180271406387	0.00000000000000	-0.39231342704487

tetrafluoroethylene

6

C	0.12996800374671	-0.00001497628612	-0.07383776565183
F	1.43069589371943	0.00000762113434	-0.28515070616681
F	-0.19235989604756	0.00000739726106	1.20384162229851
C	-0.76510486860200	-0.00001513743186	-1.04964733653980
F	-2.06584775610341	0.00000765740628	-0.83874387811816
F	-0.44242537671317	0.00000743791630	-2.32724893582191

N_2

2

N	0.00000000000000	0.00000000000000	-0.00107120023956
N	0.00000000000000	0.00000000000000	1.10107120023956

Transition states – optimized at the PBE0/6-31+g level*

CH_3N_3

7

C	-0.00023353088333	0.00066406896468	-0.00005196130394
N	0.00515676400338	-0.01122852911570	1.36368122787883
N	1.91586912233905	-0.01522473122509	2.05132334065226
N	2.56130628472961	0.01096092812539	2.94727147560016
H	-1.13060261620428	0.00851294766737	0.10205603708890
H	0.26687887241173	0.92294809776915	-0.55137861390943
H	0.25119810360382	-0.91663278218580	-0.56704150600678

$CH_2(N_3)_2$ – TS1

9

C	0.11355133091860	-0.12385057789680	0.08974294338390
N	-0.49823307458534	0.95743800011275	-0.57609615203039
N	0.45776031595799	2.53841651022949	-0.10262160191569
N	0.56381694797707	3.62676557237823	-0.27072718613519
H	0.02137042145314	-0.20796874411633	1.18604366121630
H	1.10342808533432	-0.46007457952401	-0.24924879589234
N	-0.88330137704372	-0.93211185310327	-0.64269471301276
N	-2.01060816125930	-0.94918934113690	-0.10093838574976
N	-3.06635648875275	-1.09069198694319	0.27189723013593

$CH_2(N_3)_2$ – TS2

9

C	0.10193584430066	0.03237250854649	-0.02938773548325
N	-0.15979090222591	1.26948880105290	-0.80261440558441
N	0.24934045332575	2.29965154586964	-0.26746273777635
N	0.58611294528744	3.29694868324268	0.16244709511364
H	0.35355055227045	0.27344902923009	1.02128495757571
H	1.00422739934875	-0.51523789462319	-0.46366085663096
N	-0.55349166888279	-1.09100748864256	-0.35265270424994
N	-2.37235984037761	-0.91457774247229	0.20588664776446
N	-3.40809678304674	-1.29235444220377	0.13151673927108

FCH_2N_3

7

C	0.00035271153728	0.00144356087307	0.00070300233906
F	-0.01021821671818	0.00996899784104	1.40832262843922
N	1.14875073498610	0.00241638520838	-0.65705599769265
N	1.89113685945317	-1.76620100038778	-0.61329292846938
N	2.75978905214409	-2.42159962687060	-0.80147285535024
H	-0.14858310990034	1.06412325788803	-0.36416416947324
H	-0.86871403150212	-0.60164457455213	-0.29752967979277

$CH(N_3)_3$ – TS1

11

C	0.03770920710998	-0.12965277198861	-0.10724552091992
N	-0.60697097569285	0.99705053250752	-0.61320797613098
N	0.45887494071563	2.45287469855898	-0.16506593836544
N	0.59970529470328	3.54920532331043	-0.20772657947700
H	0.13401517804080	-0.27757397705299	0.97638767049158
N	1.28374725140577	-0.61307753923855	-0.66796901059150
N	-1.13918075190596	-0.86437976312403	-0.69238099558126
N	-2.11086473973140	-0.95077713714105	0.08359934728039
N	-3.04653953410729	-1.11306723402838	0.69403325532059
N	1.41274655545360	-0.41045484070112	-1.88335604401268
N	1.64424657400847	-0.27636929110223	-2.98223720801376

$CH(N_3)_3$ – TS2

11

C	0.15032863995095	0.04363555854570	-0.11291544655608

N	-0.21760556388300	1.30004544733342	-0.77681035584121
N	0.13506667733454	2.32244454403186	-0.17992678177488
N	0.39817619285295	3.31622602773060	0.29974462336017
H	0.45310511345888	0.22568511475162	0.93020569895457
N	1.27563655634631	-0.69019917092231	-0.75758133440965
N	-0.59953251932349	-1.07513421629813	-0.42923182128432
N	-2.30845979242939	-0.77498649386977	0.24195904621296
N	-3.34073836596605	-1.15837219348563	0.34512019292786
N	1.28140483526994	-0.58705832057379	-2.00505115803405
N	1.44010722638839	-0.55850829724359	-3.12068166355533

$CH(N_3)_3$ – TS3

11

C	0.04245618418377	-0.06359331082604	-0.04316728883200
N	-0.69862707334701	1.21154630402408	-0.16524442817024
N	0.02515239305959	2.20864362894662	-0.20049429188200
N	0.62257781602855	3.16963978530963	-0.24235226358082
H	0.56804226811179	-0.12919350295633	0.98505702689804
N	1.29967624772168	-0.23169826126573	-0.46654323927808
N	-0.90364053727349	-1.14995151277259	-0.20207757387728
N	-2.08602022903068	-0.89576195706139	0.06189319560366
N	-3.19601809642719	-0.80703127818491	0.26535050109148
N	1.23332077348271	-0.36039298637292	-2.30666405112397
N	1.76056925349029	-0.58842890884044	-3.25092658684876

$CHF(N_3)_2$ – TS1

9

C	0.04988183567886	0.05566143552662	0.21724487505230
N	-0.46012190847371	1.39488375372442	0.34952384065652
N	0.24830098604747	2.29202897714782	-0.13053338569198
N	0.78996663807961	3.20321934841141	-0.52353129332194
H	0.72712659755244	-0.27441902883277	1.08935043360346
F	0.82993283499428	-0.00737593759473	-0.95122978199085
N	-0.65907868388297	-0.98127430105913	0.61040247534067
N	-2.22876123364512	-0.97348212398536	-0.45192887976679
N	-3.20602606635085	-1.40781712333829	-0.72500528388140

$CHF(N_3)_2$ – TS2

9

C	0.06267713790015	-0.05087456500708	0.21398638747477
N	-0.64897690517636	1.11065657998037	0.29594525476104
N	0.54191601137942	2.48124516007606	-0.16845374979489
N	0.68428447537075	3.56451685373986	-0.33547075353586
H	0.91784354514763	-0.26121812967148	0.86443141635298
F	0.42916159190303	-0.50407454823092	-1.05627481661618
N	-1.13503878292793	-0.73465863796583	0.72098799288376
N	-1.97003745393670	-0.98512152968042	-0.17757010530587
N	-2.79060861965997	-1.31904618324059	-0.87328862621973

$CHF(N_3)_2$ – TS3

9

C	0.48674451757543	-0.30660388098417	0.27473755606164
N	-0.02540102513261	1.03262443138160	0.39954190481069
N	0.67511020438422	1.92688739142646	-0.09713269087680
N	1.21297397846069	2.83576024129555	-0.50056670469676
H	1.16540367353096	-0.62871532516186	1.14888571012812
F	1.26523290141208	-0.37611467712628	-0.89413909921015
N	-0.21914124355914	-1.34238489511013	0.67632897731817
N	-1.79128946886973	-1.34806516708555	-0.37836009618748
N	-2.76963353780190	-1.79338811863561	-0.62929555734743

HCF_2N_3

7

C	-0.00016061927504	-0.00146246679261	0.00118818579915
N	-0.00373476033558	-0.00618716920879	1.31340890585910
F	1.14580816038115	-0.00352729288429	-0.73726102455170
F	-0.88278182285787	0.72557368925796	-0.73951241313308
N	0.61485509305982	1.73411681597798	1.85891034959155
N	0.87489246881314	2.47837062385908	2.63031834879482
H	-0.38521751978563	-1.07815920020933	0.16020064764016

$C(N_3)_4$ – TS1

13

C	0.10673105177897	-0.13117298806173	-0.15858642704396
N	-0.67828550712498	-1.17772640744444	-0.59229401539078
N	-2.34709886567873	-0.84506165515063	0.08461924084612
N	-3.41468211900488	-1.13154776723062	0.11848490615552
N	-0.23536123401952	1.18533838714718	-0.64649728530614
N	0.26238649996080	2.14576911041563	-0.03863174439261
N	0.62595502311190	3.10862309874012	0.42861777459160
N	0.52341569642915	-0.01060333813222	1.23374795075058
N	1.20639605527810	-0.83101931317709	-0.94609917331433
N	1.21346413816099	-0.53176907693449	-2.15793056188832
N	1.33820781449564	-0.32230804212884	-3.25881258254303
N	0.70065172166427	-1.09392531497802	1.80138393228688
N	0.88248972494830	-2.02861769306487	2.41024098524847

$C(N_3)_4$ – TS2

13

C	-0.02818859805912	-0.20715715355172	-0.16103043265155
N	-1.21896300032867	-0.86322000024446	-0.84750432638149
N	-2.24578704683394	-0.88963367082376	-0.13826299172599
N	-3.22489085774259	-0.99653283318772	0.41073061338909
N	-0.58234996958744	0.96543052101469	-0.62712287446469
N	0.51125517740226	2.29723607869929	-0.00692077130333
N	0.67643586022426	3.38199919680650	0.13063801230043
N	0.00992872467065	-0.38552431106933	1.27267344964589
N	1.20238782765451	-0.75133909655019	-0.72317780667529
N	1.35115589339822	-0.52028143832892	-1.92815383587862

N	1.58032023903896	-0.36373067829958	-3.02374330466082
N	0.75726887839316	-1.28042538673736	1.69714643612378
N	1.39569687176975	-2.05084222772743	2.22297083228261

$C(N_3)_4$ – TS3

13

C	-0.02898200848918	-0.05016364151519	-0.17589345323670
N	-0.98942480211320	-0.90262527059422	-0.86723127921228
N	-2.05936813375172	-1.04577899923529	-0.26538646275521
N	-3.06682693189019	-1.24445690338982	0.20675733631115
N	-0.60429326770449	1.35526067697351	-0.06520362338192
N	0.26939225838184	2.24412488327397	0.00195454364125
N	0.95877576213094	3.13555166144798	0.04255762387550
N	0.02604012077781	0.01398069791362	1.19969962523779
N	1.23339853658961	-0.12749967707963	-0.87561208854897
N	1.18584093467026	-0.48564545411608	-2.06260573612518
N	1.29494708957855	-0.80717644692345	-3.14073431424120
N	0.76904251521375	-1.57311000949955	1.72861966346159
N	1.19572792660601	-2.17648251725583	2.55132116497420

$C(N_3)_4$ – TS4

13

C	0.00701562286623	-0.12153043925833	-0.04138523802338
N	-0.94758457898565	-1.18034593715722	-0.27850563404757
N	-2.14380808644850	-0.88993895549875	-0.12246356551237
N	-3.26317856336911	-0.76885559434226	-0.02279717656241
N	-0.68013751206103	1.15649371348371	-0.18781361401530
N	0.06900400259834	2.13846014155099	-0.14003258252752
N	0.66742018290392	3.09694334167690	-0.11587902470580
N	0.67788169122910	-0.17079527061215	1.32498109634398
N	1.28431198622309	-0.31694653049823	-0.52058200123740
N	1.11287223599636	-0.38669988024876	-2.34213291252542
N	1.59730227706686	-0.57022697586447	-3.31915745255335
N	0.82067250567264	-1.33005220310318	1.76498069531901
N	0.98249823630776	-2.32052641012824	2.27903041004757

$CF(N_3)_3$ – TS1

11

C	0.10411972030784	0.01066342326519	-0.12850254326545
N	-0.33423521942564	1.25674006737294	-0.70986423840271
N	0.15621228761027	2.28305301204443	-0.21190203016438
N	0.51616831021152	3.28894054738378	0.15518121197181
F	0.49189918949339	0.24219230703550	1.17915257132234
N	1.26878337289822	-0.66338092094812	-0.77690388107304
N	-0.59353676335645	-1.11616940373265	-0.41741622964437
N	-2.32694008516956	-0.78614166936297	0.20090422853456
N	-3.36176489678008	-1.16070562160873	0.29772960604054
N	1.29418010459714	-0.52276385881591	-2.01992057883805
N	1.45260297961337	-0.46864988263348	-3.13362711648123

$CF(N_3)_3$ – TS2

11

C	-0.01203374383865	-0.04306832127301	-0.02092110349418
N	-0.70247687334656	1.19448573067544	-0.17476434802383
N	0.03995435028528	2.18997265580640	-0.20550470075957
N	0.61646314372415	3.15667388024293	-0.24764931226588
F	0.67254685434652	-0.06572731531439	1.34732090683818
N	1.31479656765227	-0.22453911199378	-0.33014577160034
N	-0.89378636549116	-1.13074161857362	-0.14296619049143
N	-2.10405549076748	-0.88596395893213	0.02692666661208
N	-3.22361919440448	-0.82675531811914	0.14451825456520
N	1.21626596972880	-0.38086932468505	-2.51188214571521
N	1.74343378211134	-0.61968929783366	-3.45010125566499

$CF(N_3)_3$ – TS3

11

C	-0.00431114703739	-0.10398373033784	-0.18010005241580
N	-0.63592954793430	1.01630304629590	-0.64073278370360
N	0.50020244180007	2.41409837787415	-0.22532105491621
N	0.66699781782138	3.50628842166001	-0.19848992834356
F	0.12014826942638	-0.27320257870671	1.17849817938373
N	1.25261772257630	-0.57822363498421	-0.69697312801004
N	-1.16915510554220	-0.86280231886444	-0.72141359100544
N	-2.11166653385075	-0.95846788634899	0.09489682290610
N	-3.01793142342255	-1.13887017615581	0.73863269458563
N	1.40507623569223	-0.38127891064659	-1.90919208113326
N	1.66144027047084	-0.27608260978551	-3.00497407734752

$CF_2(N_3)_2$ – TS1

9

C	0.05578848813133	-0.04564470548126	-0.00318011035419
F	-0.01059064851098	-0.10908258319235	1.36407338916268
F	1.30607180650152	-0.45861441647697	-0.30305919377831
N	-0.92375066547818	-0.90925017787275	-0.67310813783339
N	-2.00027404898607	-1.01555877544322	-0.03978680188633
N	-3.00974429693423	-1.21372741100086	0.41460362658868
N	-0.50518907811149	0.99655761704236	-0.65562788268438
N	0.53019438528605	2.49619537333689	-0.11855730274769
N	0.69339505810209	3.58640807908811	-0.17998458646707

$CF_2(N_3)_2$ – TS2

9

C	0.99214782523040	-0.54173471075629	-0.03066809081197
F	1.34681309431379	-0.14931093373744	1.24613902404753
F	2.09810192649210	-1.14690501070554	-0.53314192155022
N	-0.01521085377547	-1.47847695142006	-0.13615890883272
N	-1.97095092039413	-0.52181857766026	0.01662385754856
N	-3.01811247630001	-0.84567072378268	0.13909760161610
N	0.66559150610678	0.62518048862516	-0.81389555729992

N	0.18570990274780	1.56844090602877	-0.17095966243286
N	-0.28409000442124	2.49029551340834	0.28296365771549

$CF_2(N_3)_2$ – TS3

9

N	-2.91740362575700	-1.35043378711741	0.75416933211437
N	-2.00034544707976	-0.84506711790385	0.40914643546508
N	0.25517983982940	-1.18807287926672	0.14428844290006
C	0.93211429658540	-0.04263980422499	0.50837859052670
F	2.20549535482239	-0.27250970535971	0.03475701177073
F	1.08182693267588	0.22644808847453	1.83029411561755
N	0.30259298186252	1.13106402868355	-0.03417127508936
N	0.16099280034784	1.10640582641844	-1.27092971985983
N	-0.02045313328667	1.23480535029616	-2.37593293344529

CF_3N_3

7

C	0.000000	0.000000	0.000000
N	0.000000	0.000000	1.360192
F	1.398058	0.000000	0.165941
F	-0.371628	-1.066991	-0.701278
F	-0.371974	1.066963	-0.701060
N	-3.464767	0.002454	-0.411204
N	-4.353862	0.002922	-1.062177

difluorodiazirine to difluorocarbene

5

C	0.23812879305266	-0.40663959690771	0.28185919294597
F	-0.17755814026560	0.03140341196689	1.45483365323294
F	1.46524307035908	0.01430369261976	0.04180533512199
N	-0.81076382248318	-0.40042201008343	-0.93767610179324
N	-0.71504990066296	0.76135450240449	-0.84082207950766

13. DSC experiment

Sample analysis was performed on a TA DSC250 differential scanning calorimeter (TA Instruments). Nitrogen was used as purge gas, with a flow rate of 50 ml/min. The samples were weighed into aluminum pans. Sample **2a** (1.68 mg) was analyzed in the temperature range from 25 ℃ to 350 ℃, with a heating rate of 10 ℃/min (Figure S1).

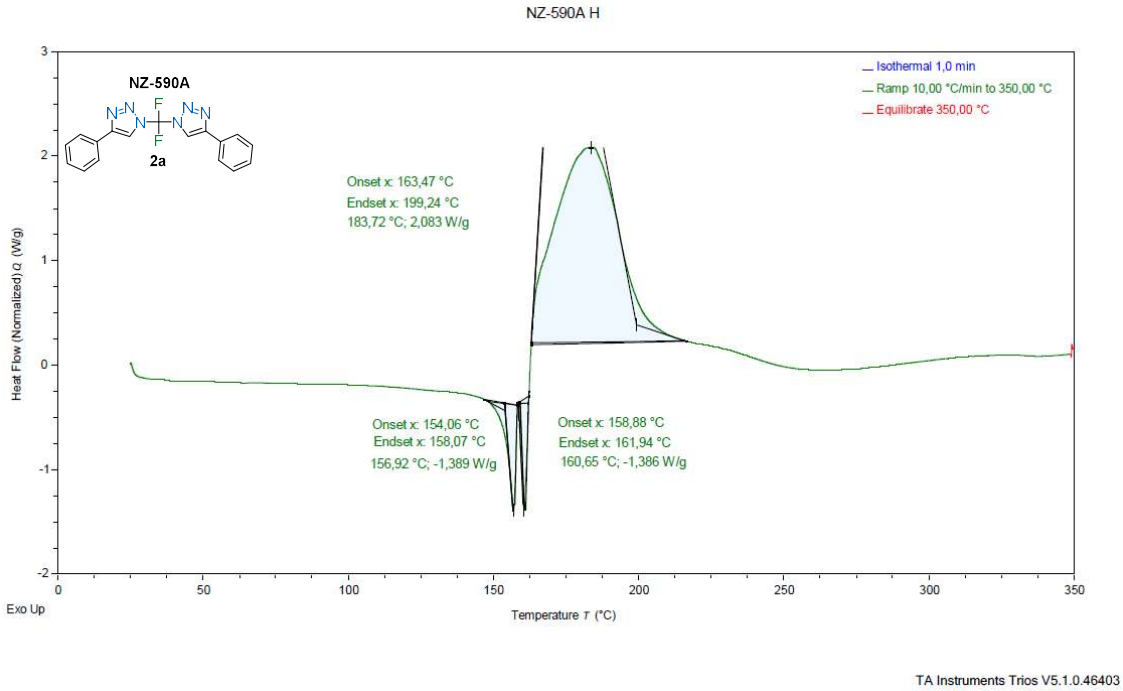


Figure S3: DSC of **2a**.

14. Copies of NMR spectra

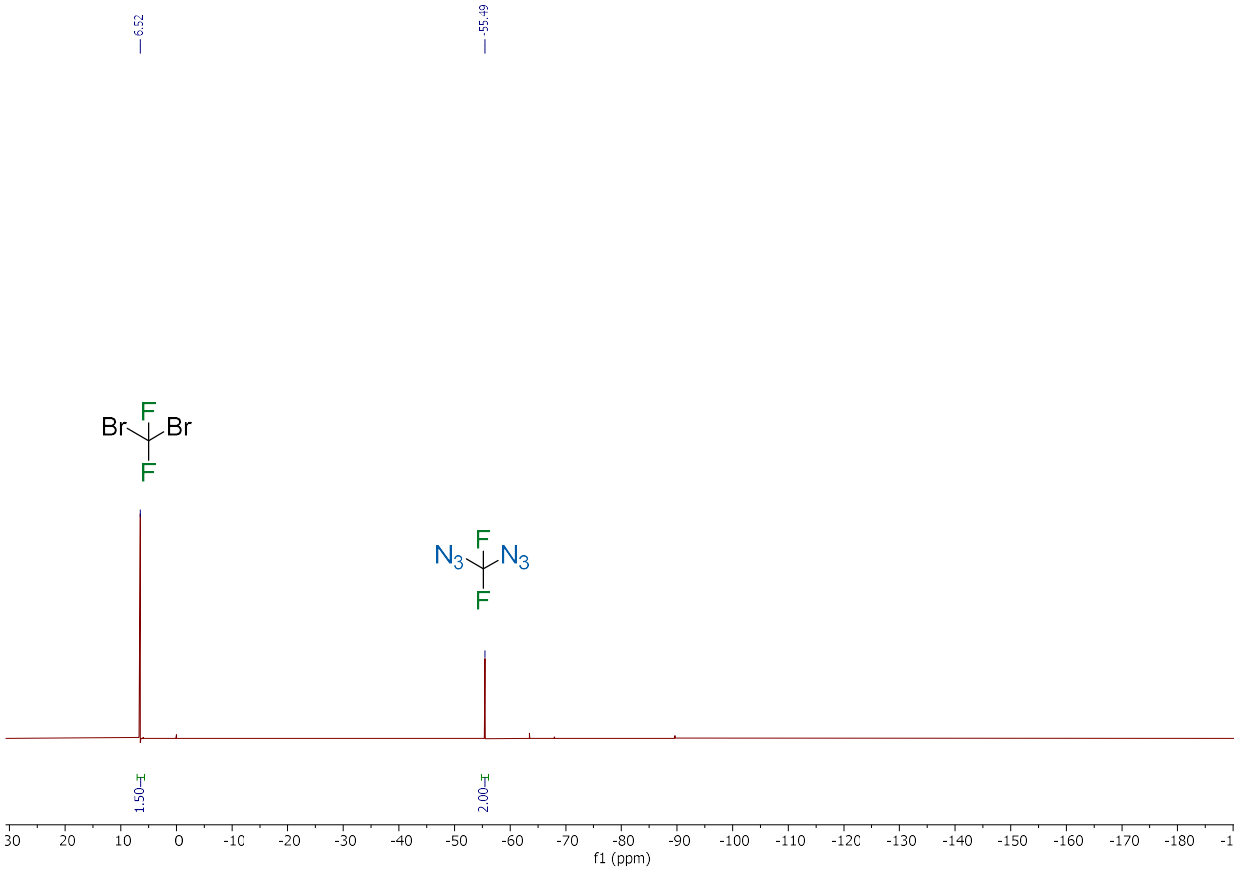


Figure S4: ^{19}F NMR spectrum of neat **1** (376 MHz, $CDCl_3$)

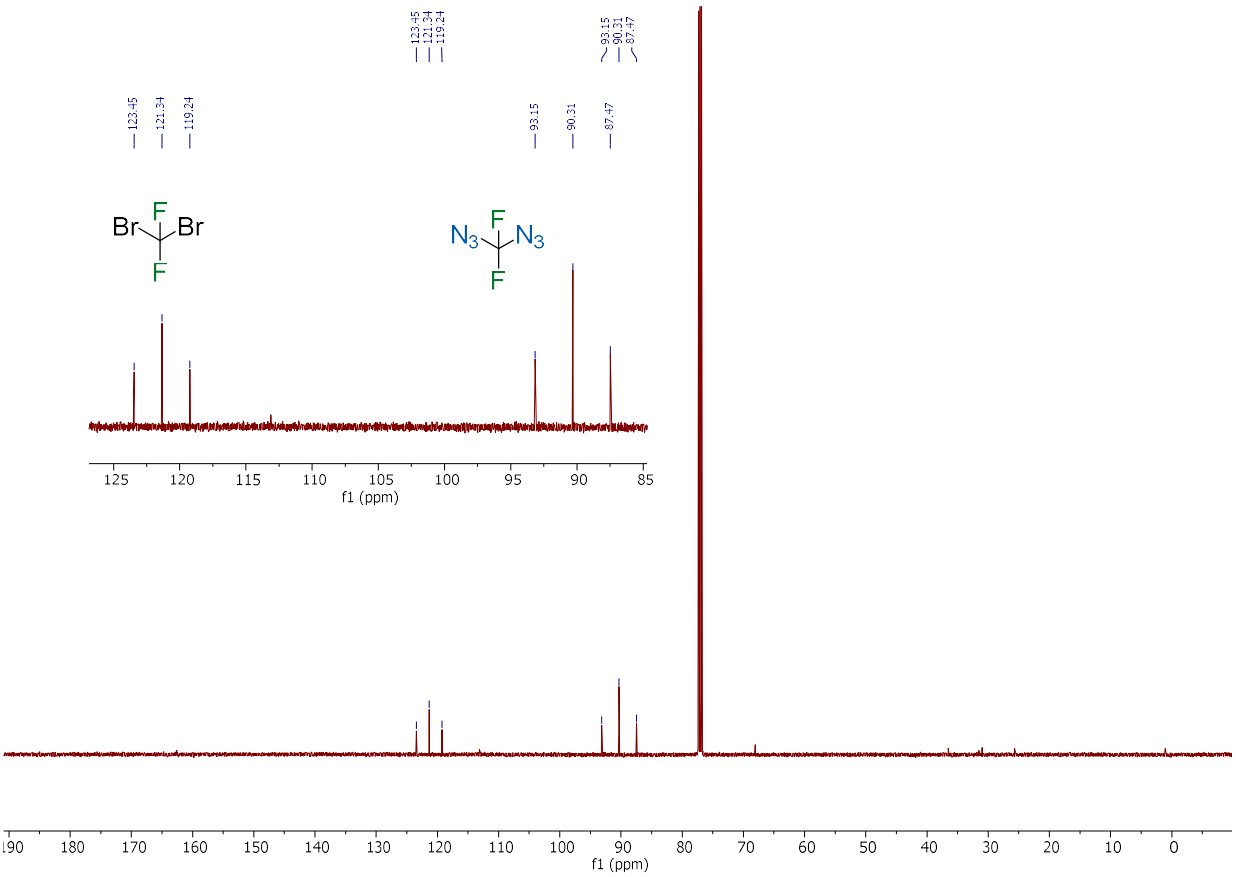


Figure S5: ^{13}C NMR spectrum of neat **1** (101 MHz, $CDCl_3$)

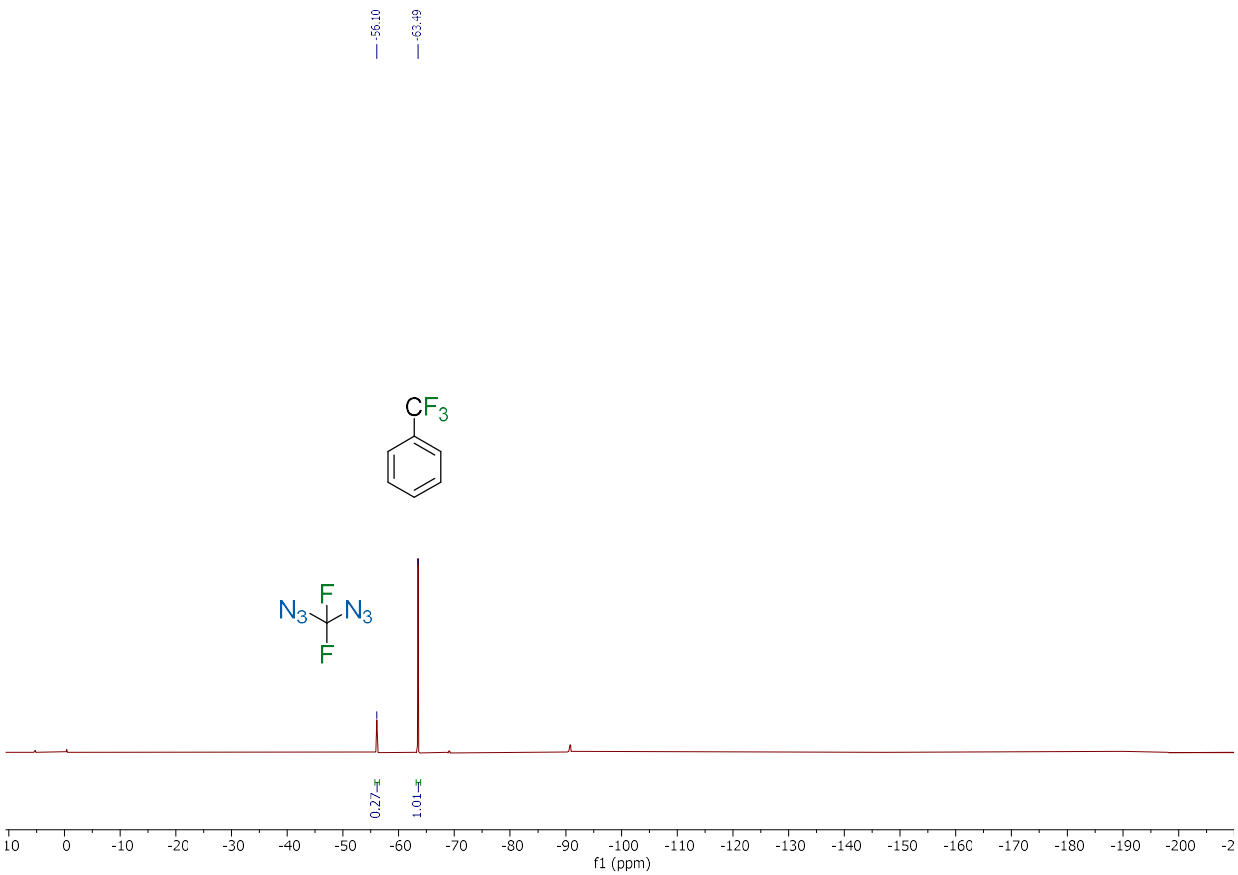


Figure S6: ^{19}F NMR spectrum of 0.1M solution **1** in THF with $PhCF_3$ as a standard (376 MHz, $CDCl_3$)

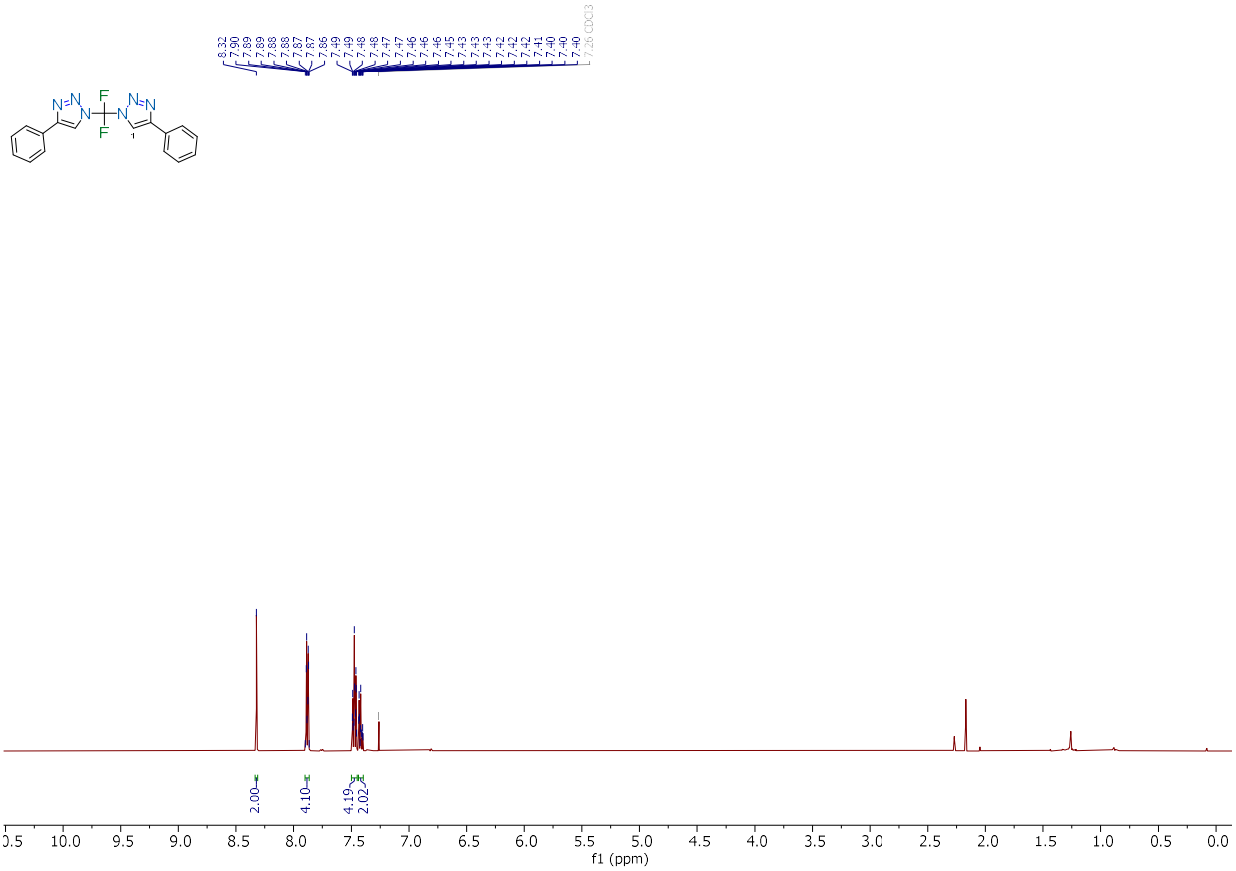


Figure S7: ^{1}H NMR spectrum of **2a** (400 MHz, $CDCl_3$)

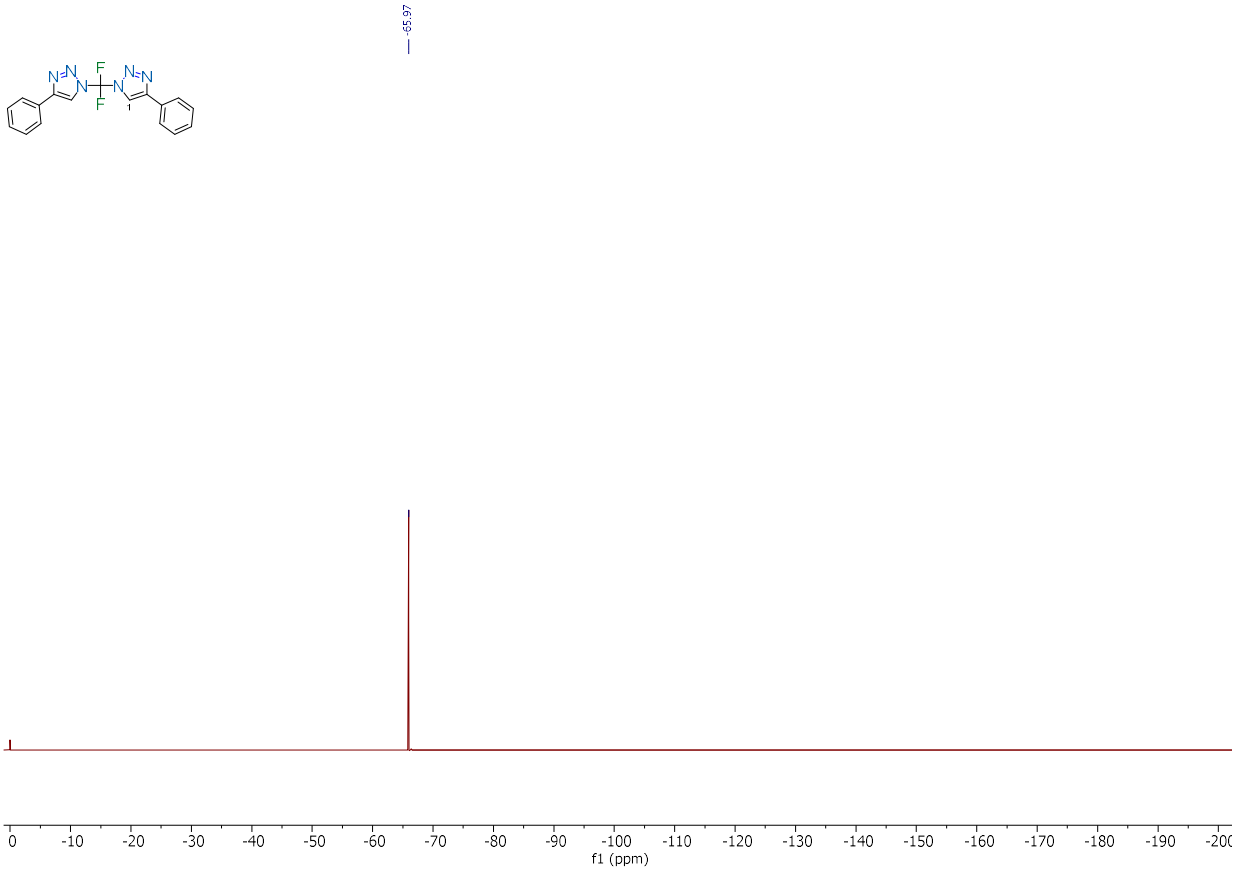


Figure S8: ^{19}F NMR spectrum of **2a** (377 MHz, $CDCl_3$)

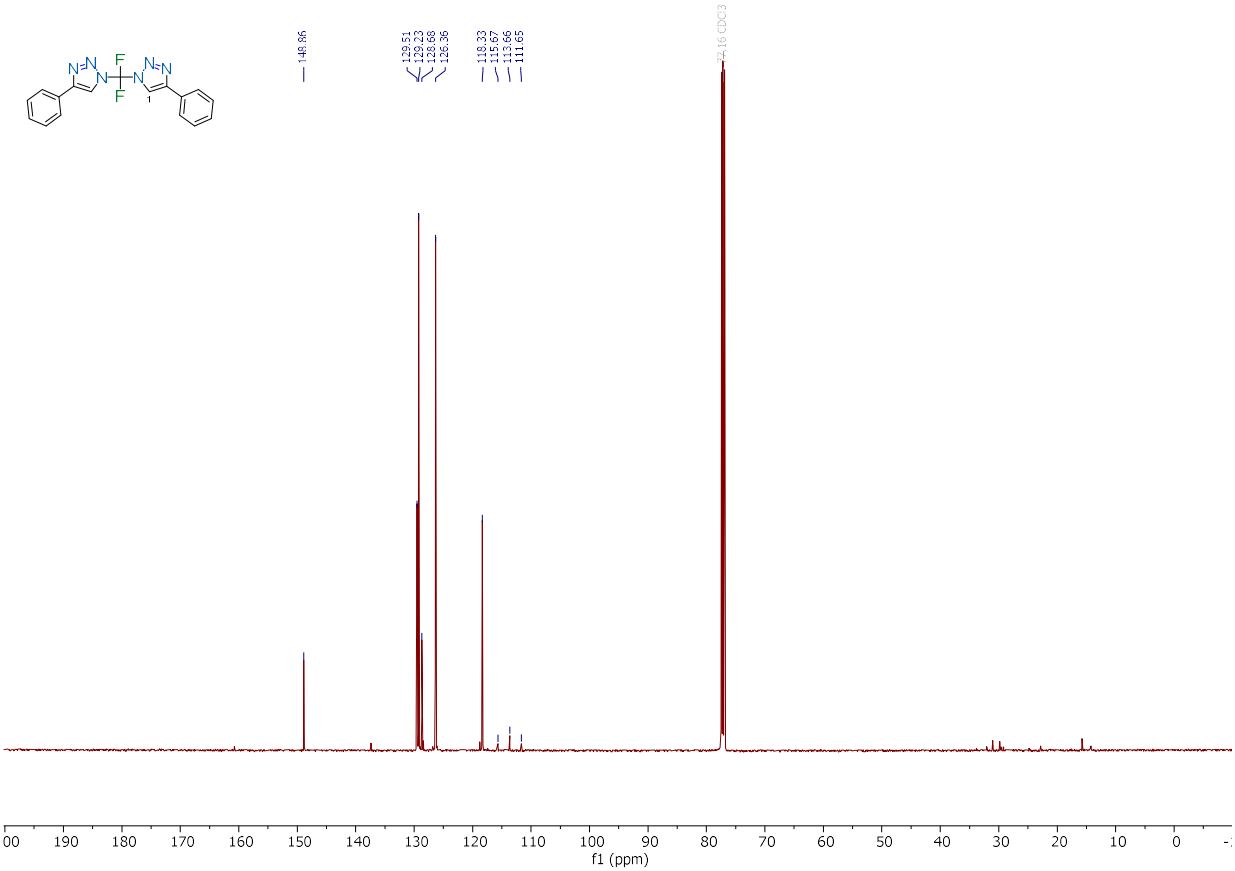


Figure S9: $^{13}C\{^{1}H\}$ NMR spectrum of **2a** (101 MHz, $CDCl_3$)

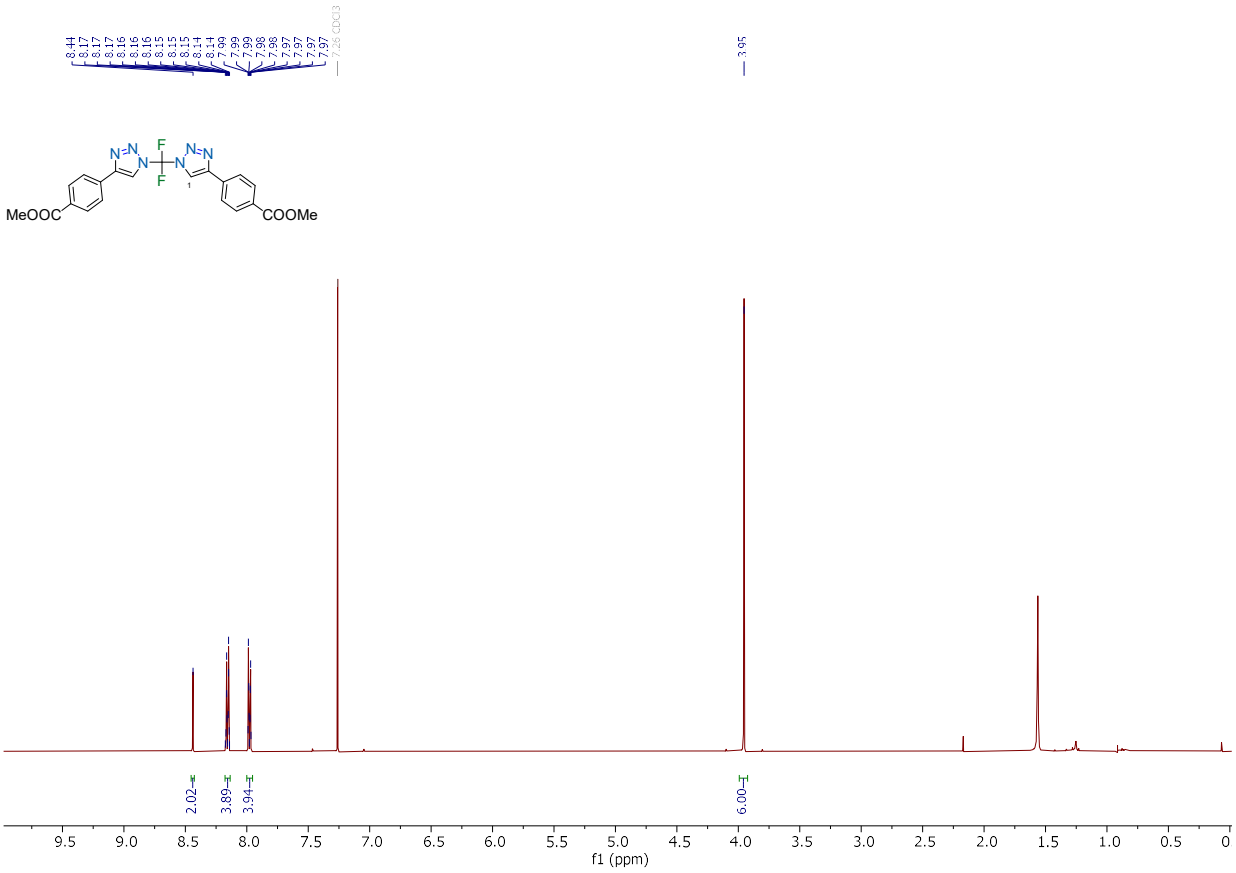


Figure S10: ^{1}H NMR spectrum of **2b** (500 MHz, $CDCl_3$)

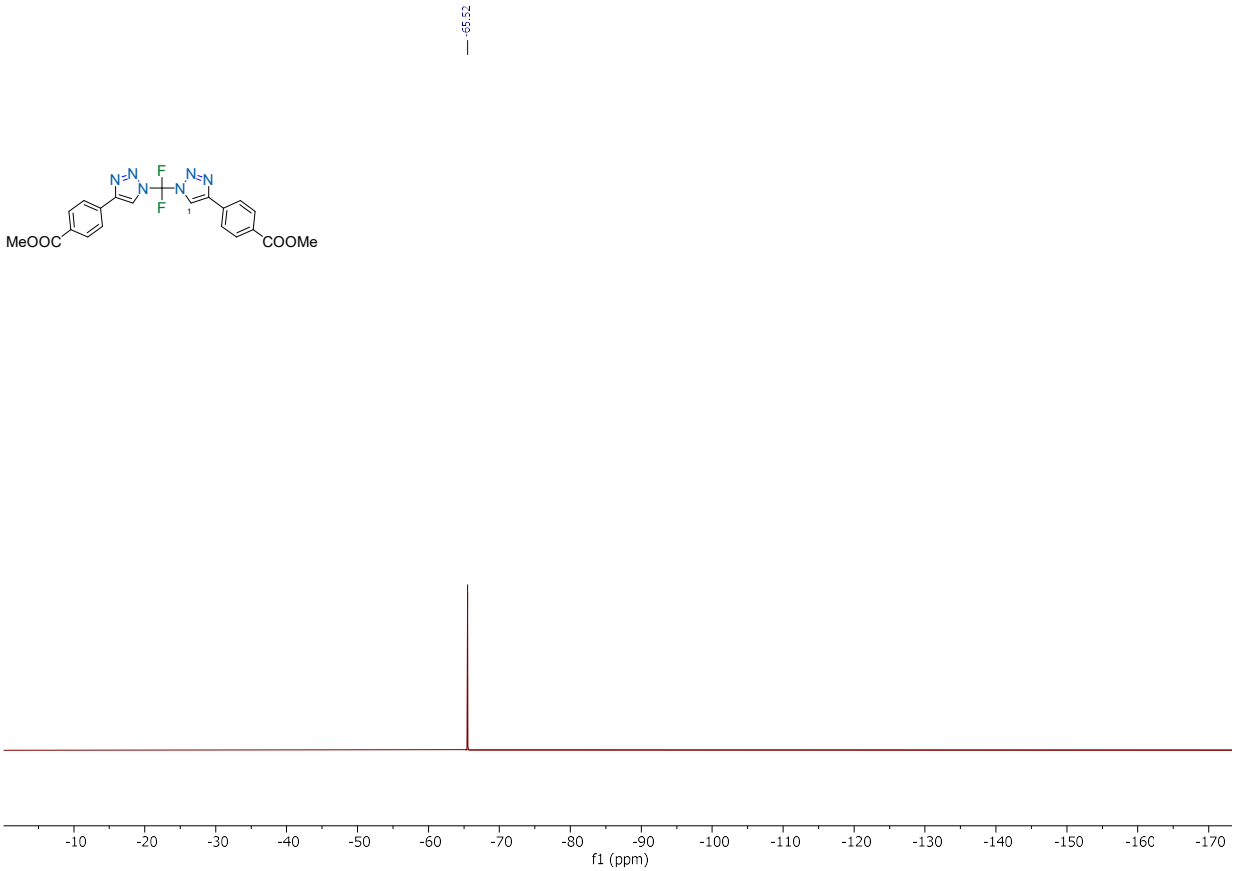


Figure S11: ^{19}F NMR spectrum of **2b** (470 MHz, $CDCl_3$)

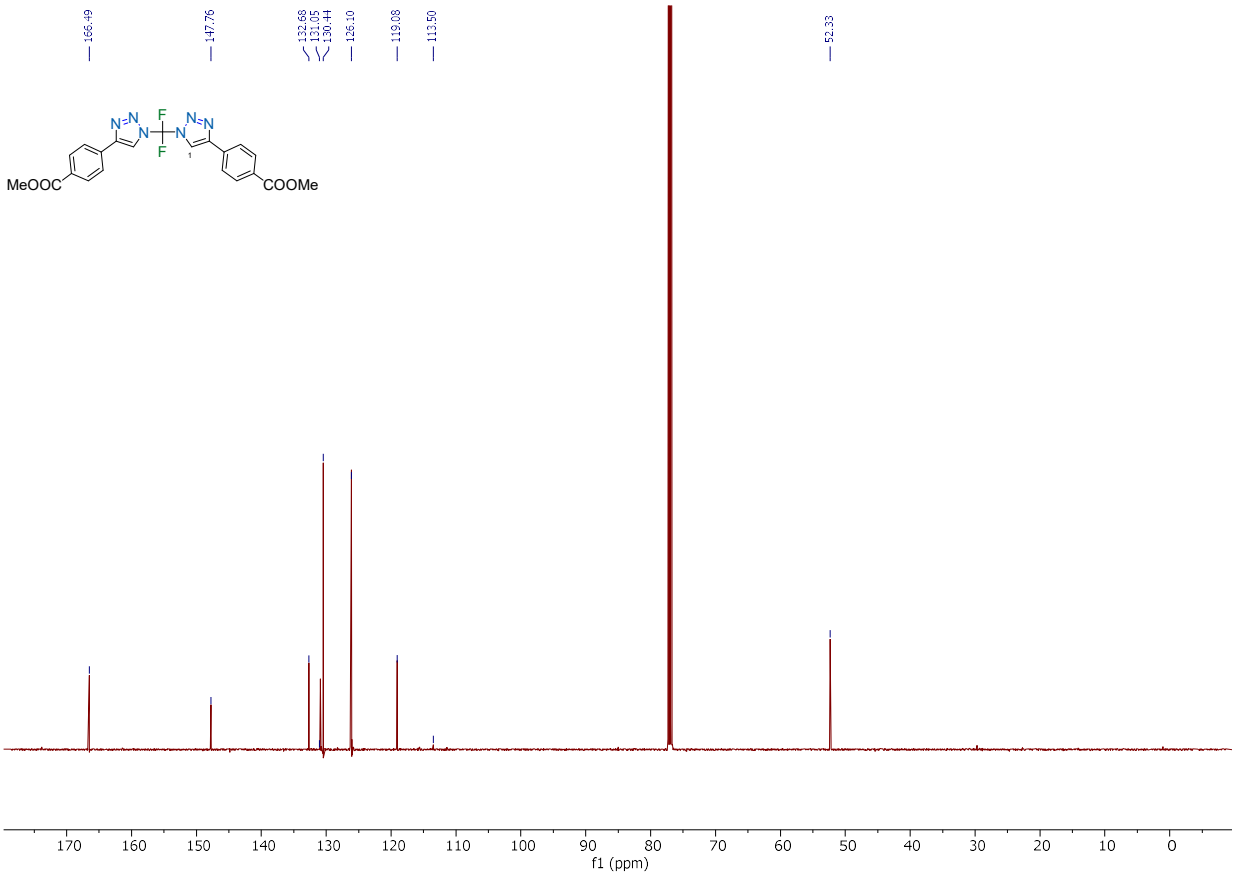


Figure S12: $^{13}C\{^{1}H\}$ NMR spectrum of **2b** (126 MHz, $CDCl_3$)

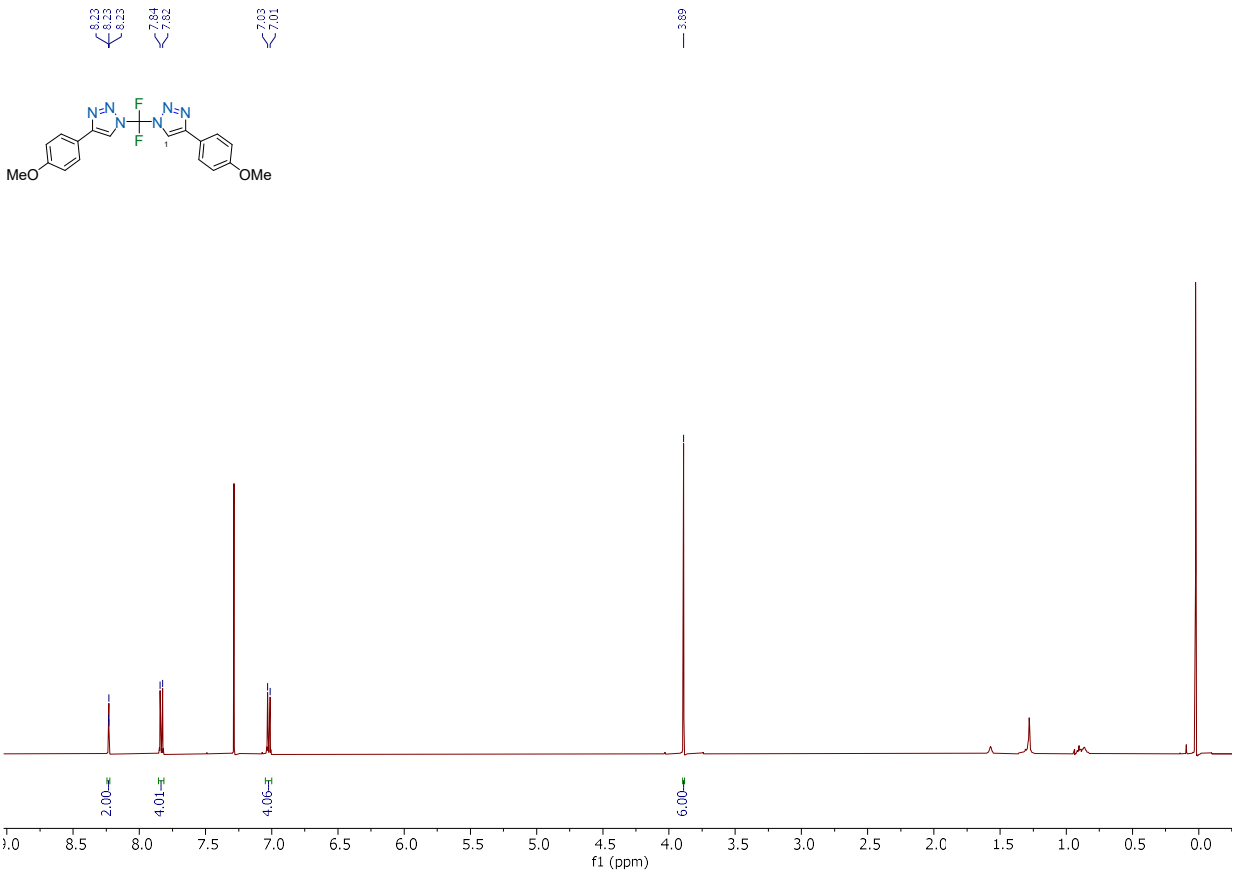


Figure S13: ^{1}H NMR spectrum of **2c** (500 MHz, $CDCl_3$)

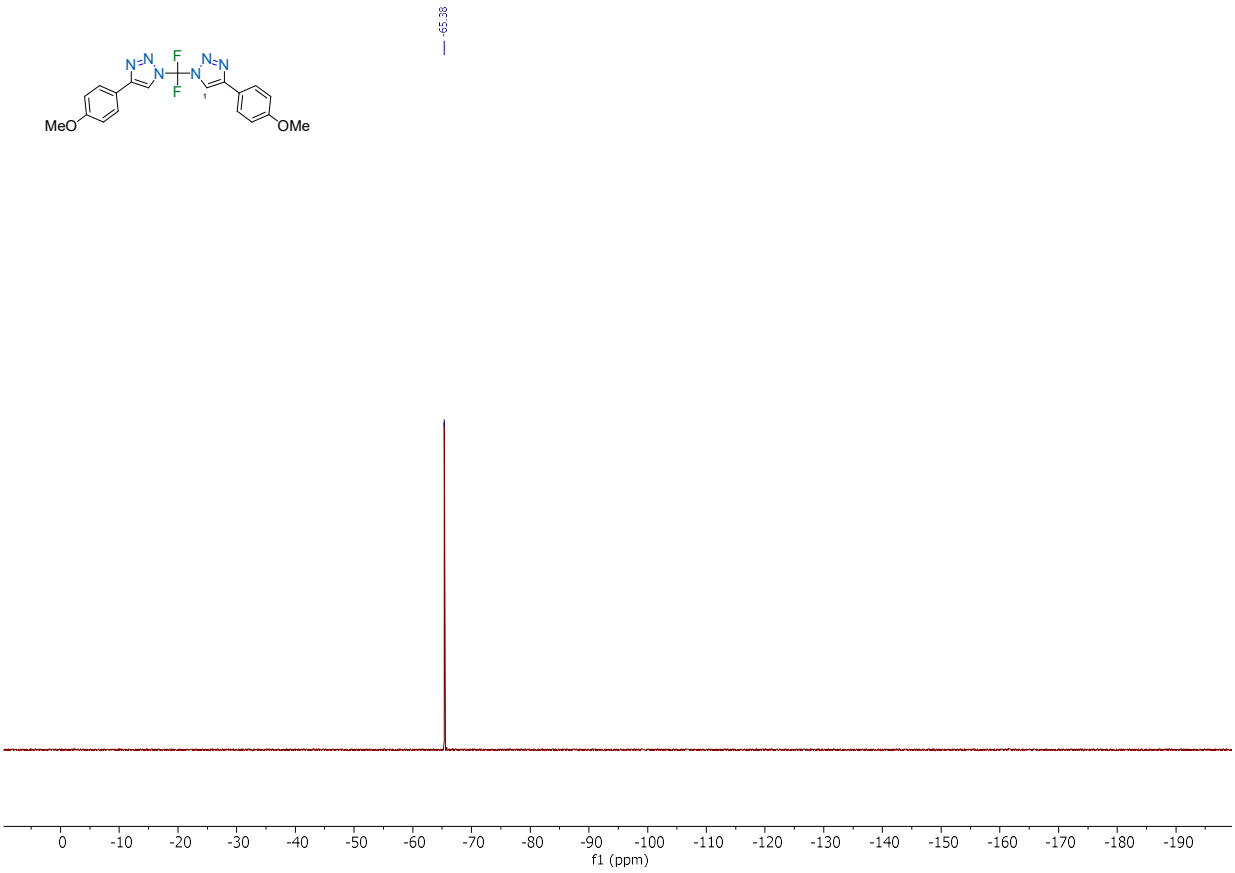


Figure S14: ^{19}F NMR spectrum of **2c** (470 MHz, $CDCl_3$)

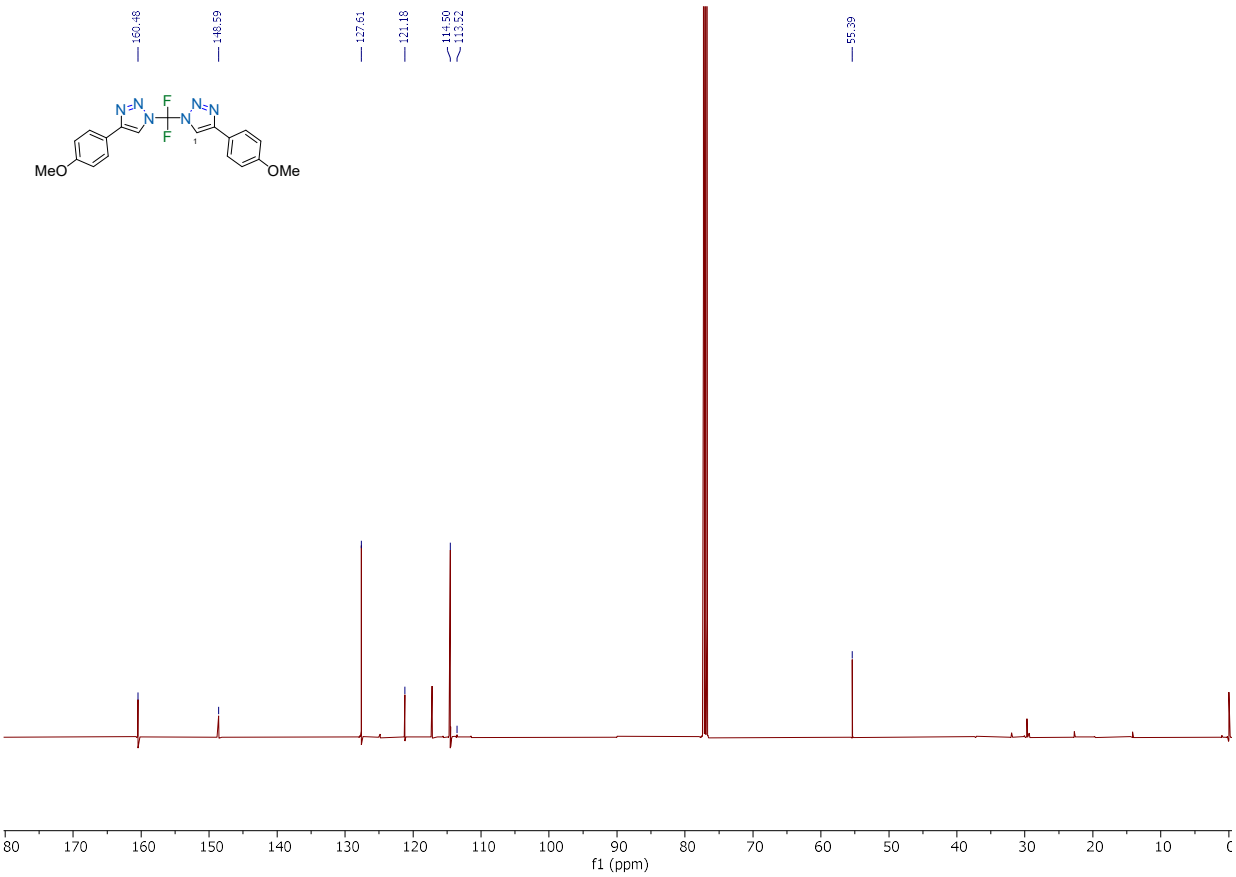


Figure S15: $^{13}C\{^{1}H\}$ NMR spectrum of **2c** (126 MHz, $CDCl_3$)

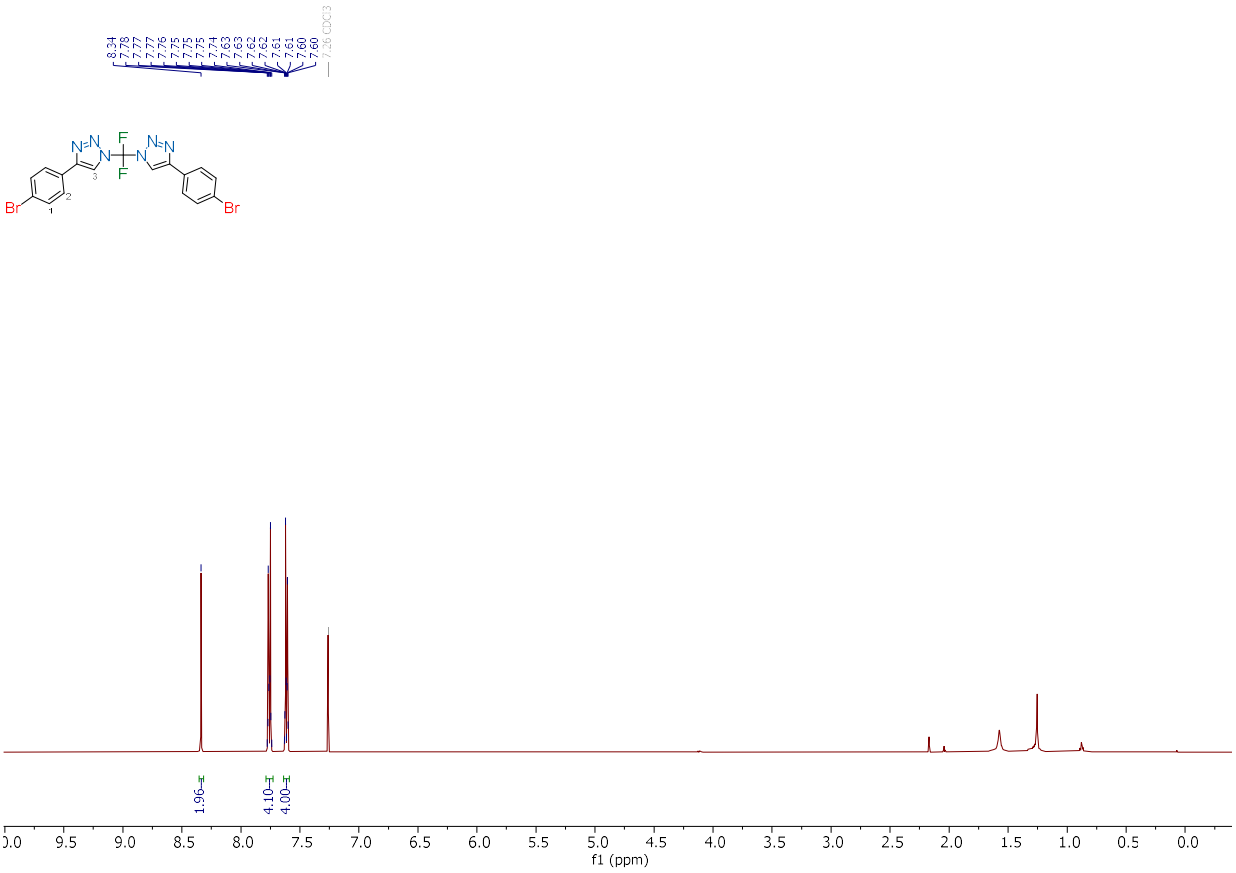


Figure S16: ^{1}H NMR spectrum of **2d** (500 MHz, $CDCl_3$)

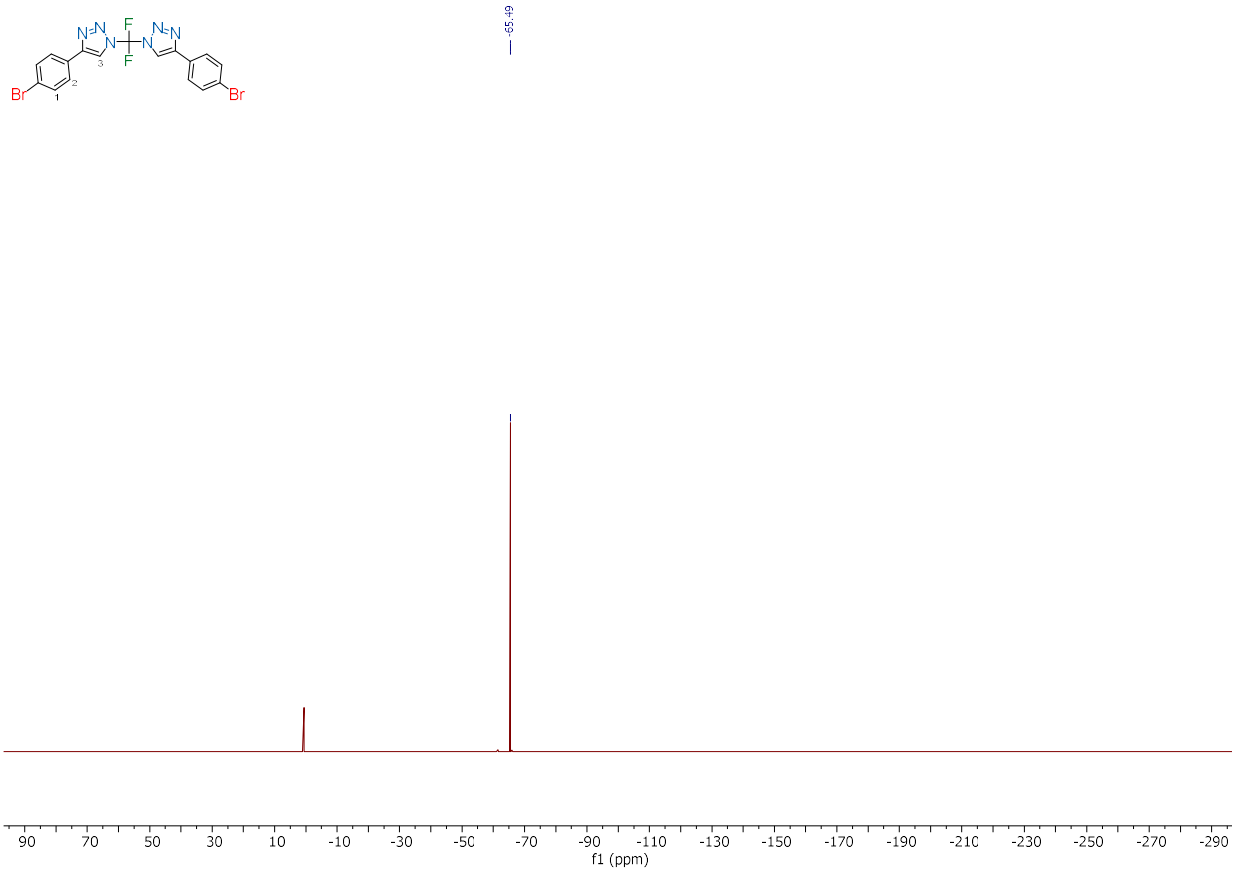


Figure S17: ^{19}F NMR spectrum of **2d** (470 MHz, $CDCl_3$)

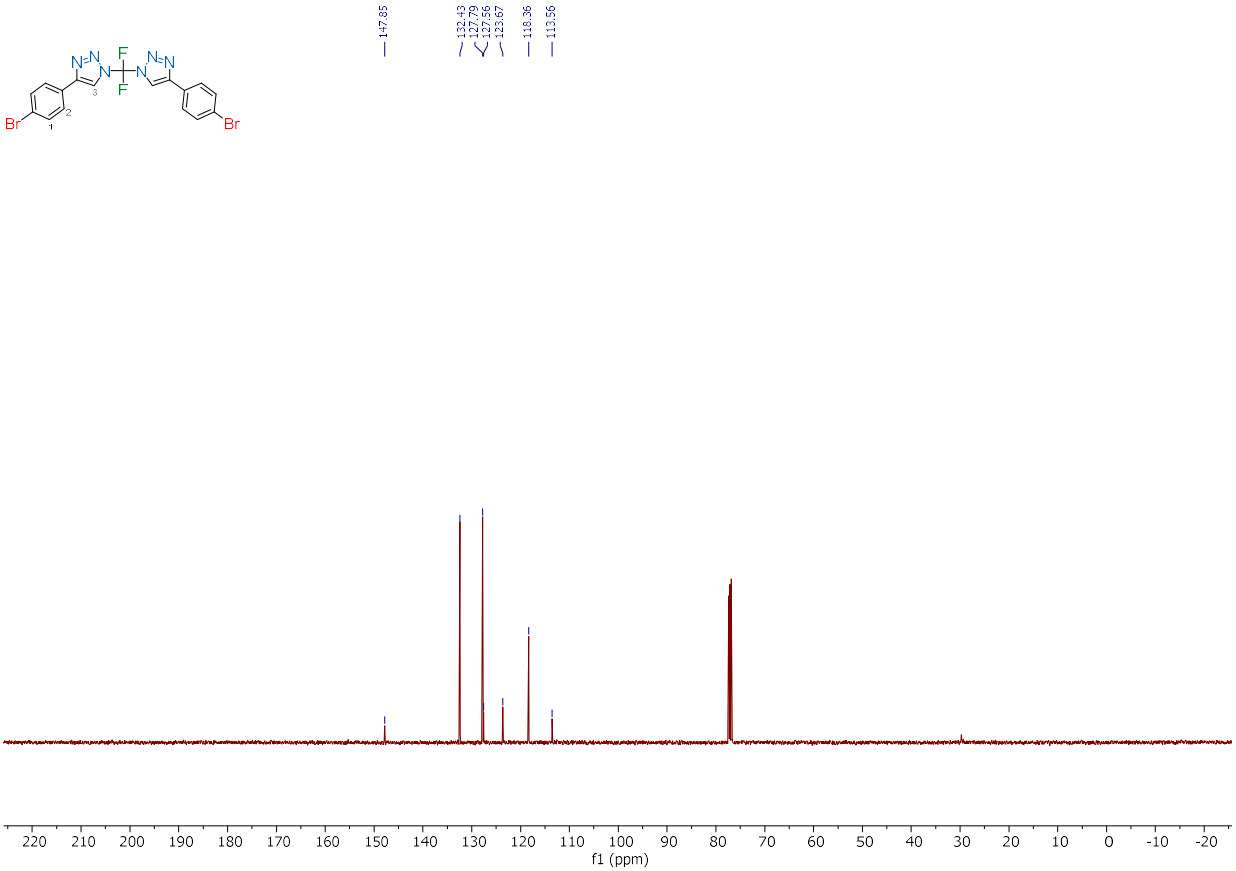


Figure S18: $^{13}C\{^{1}H, ^{19}F\}$ NMR spectrum of **2d** (126 MHz, $CDCl_3$)

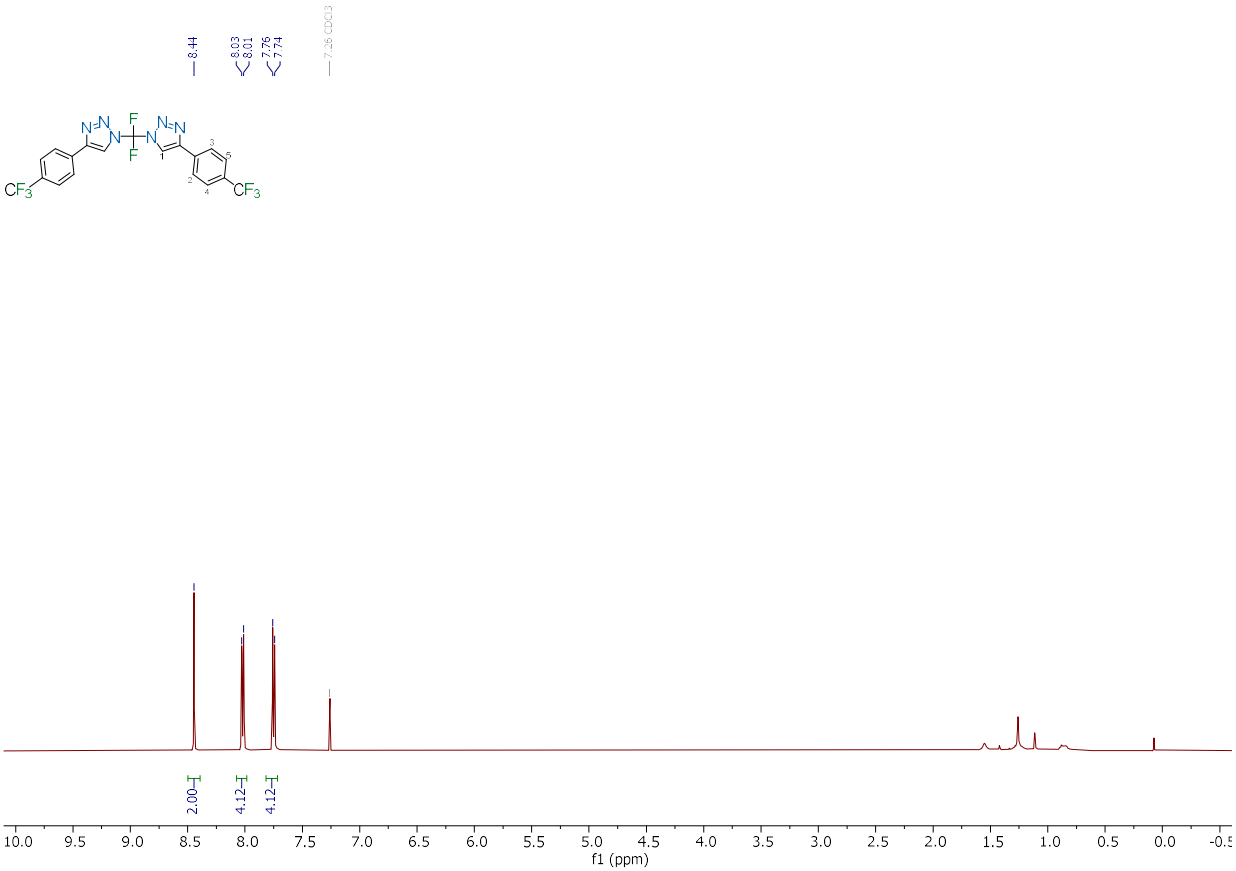


Figure S19: ^{1}H NMR spectrum of **2e** (500 MHz, $CDCl_3$)

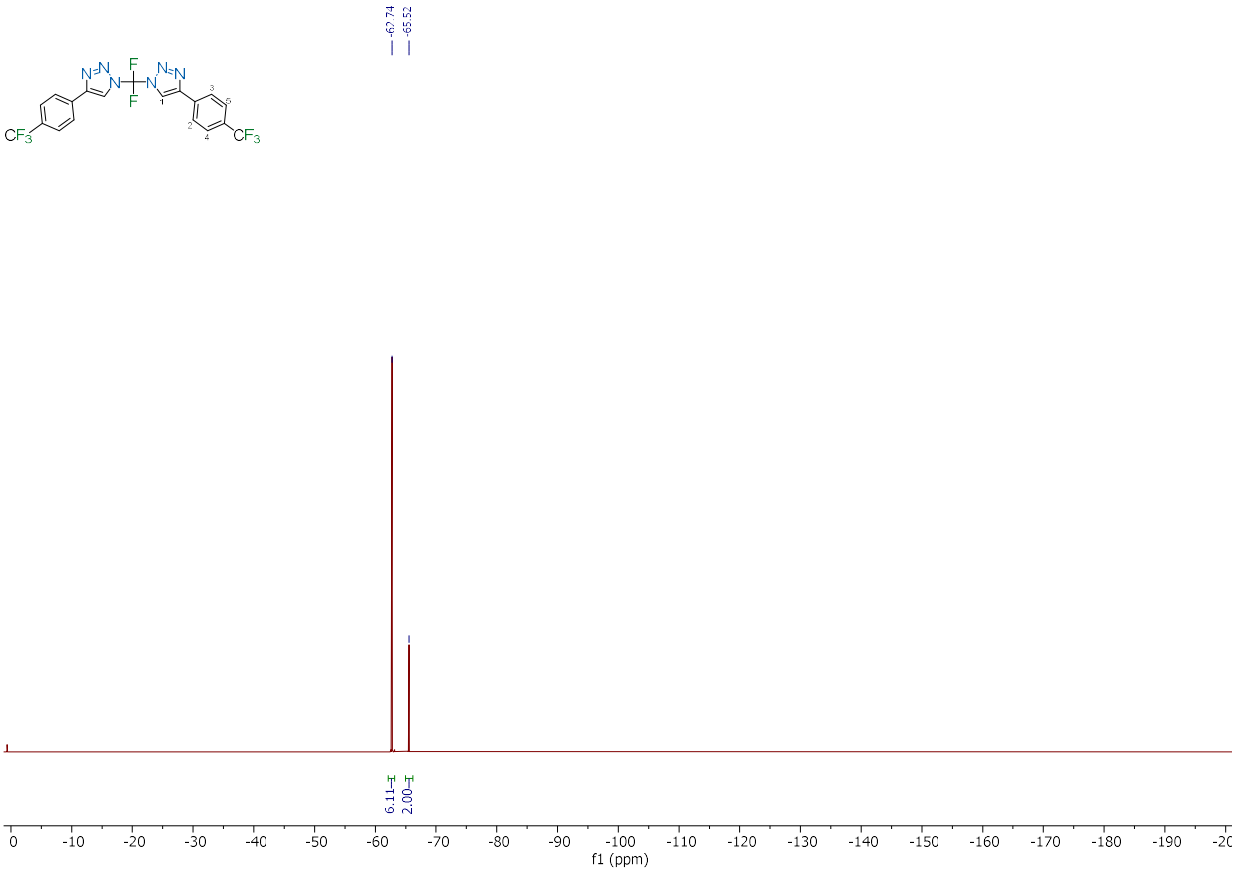


Figure S20: ^{19}F NMR spectrum of **2e** (470 MHz, $CDCl_3$)

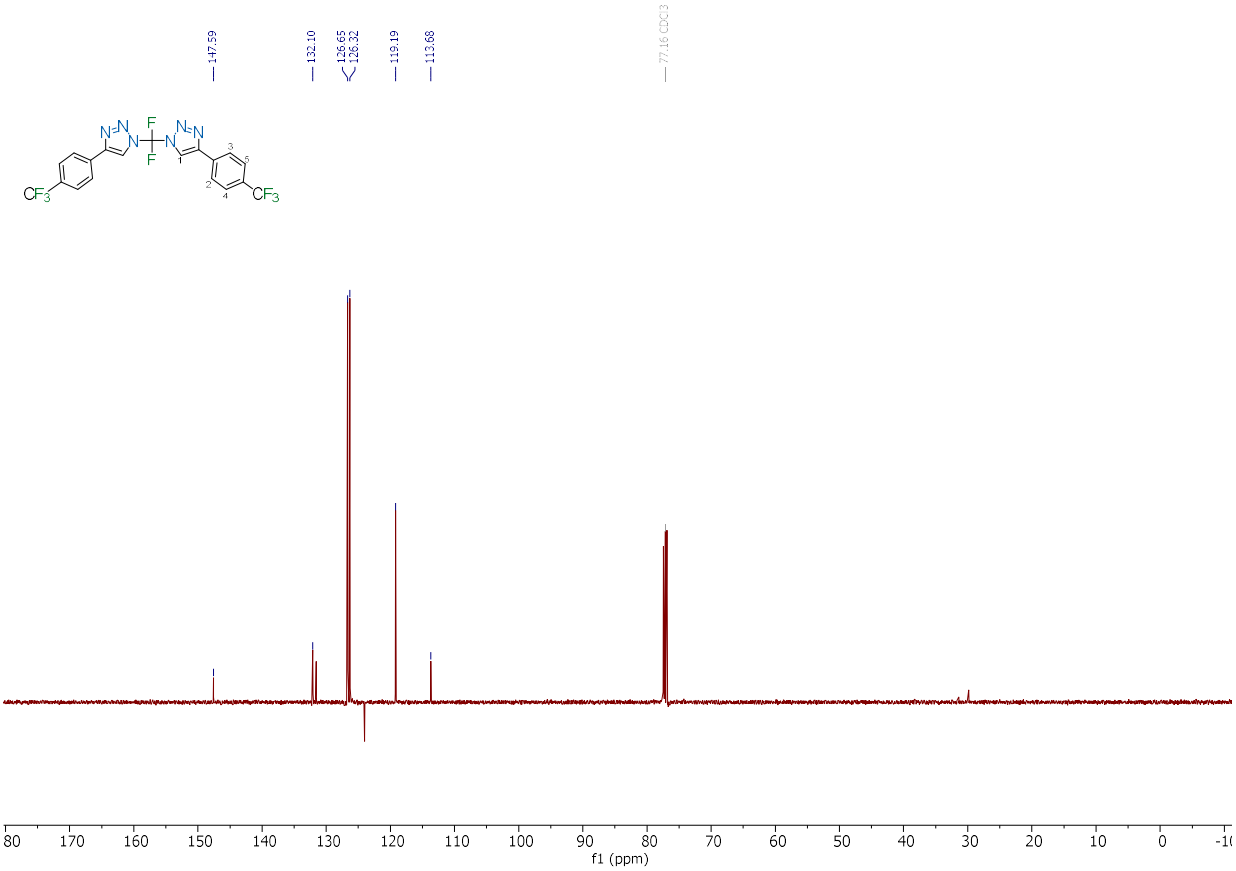


Figure S21: $^{13}C\{^{1}H, ^{19}F\}$ NMR spectrum of **2e** (126 MHz, $CDCl_3$)

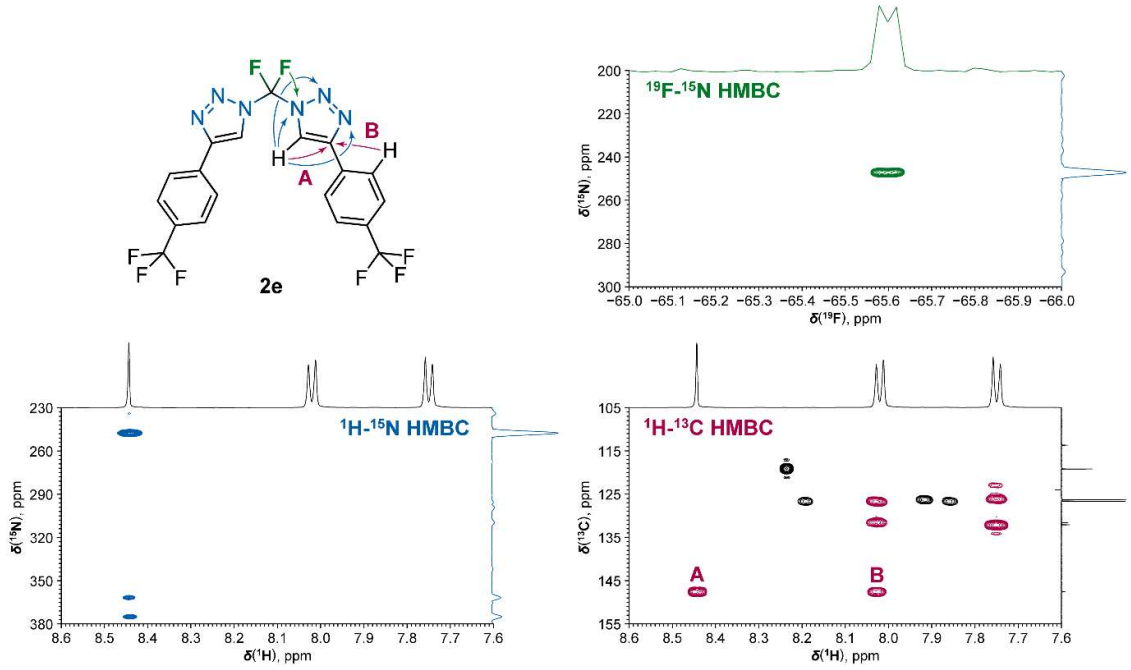


Figure S22: HMBC and HSQS spectrums of **2e**

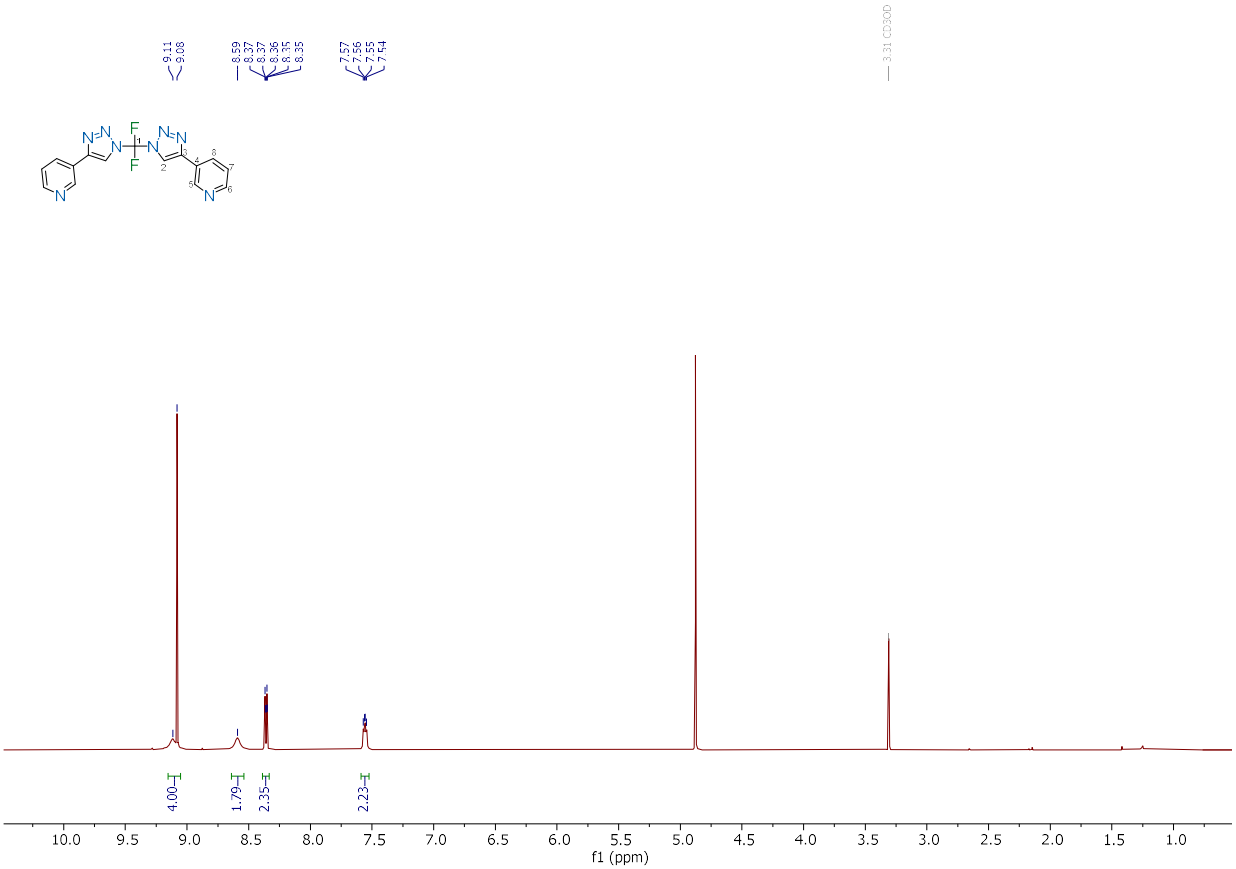


Figure S23: ^{1}H NMR spectrum of **2f** (500 MHz, Methanol-d_4)

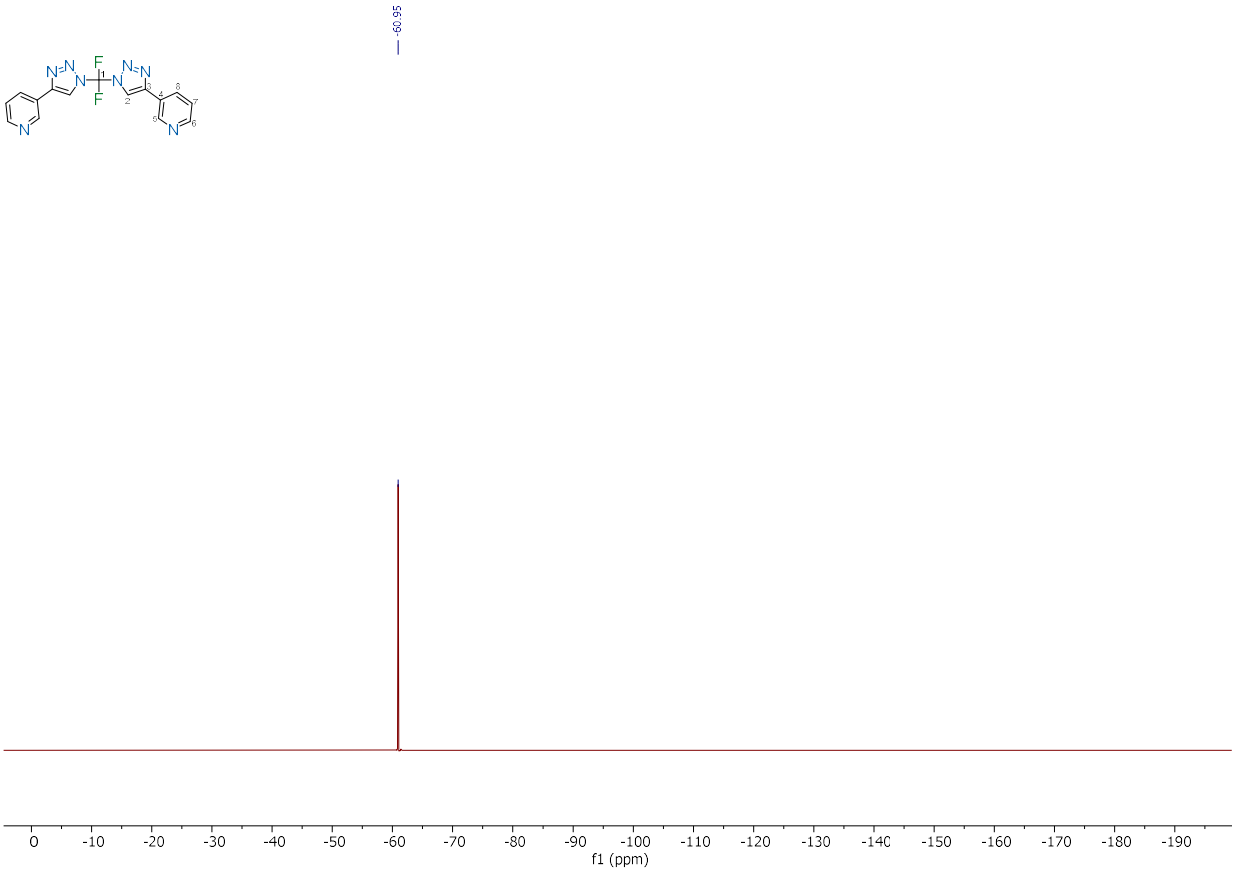


Figure S24: ^{19}F NMR spectrum of **2f** (470 MHz, Methanol-d_4)

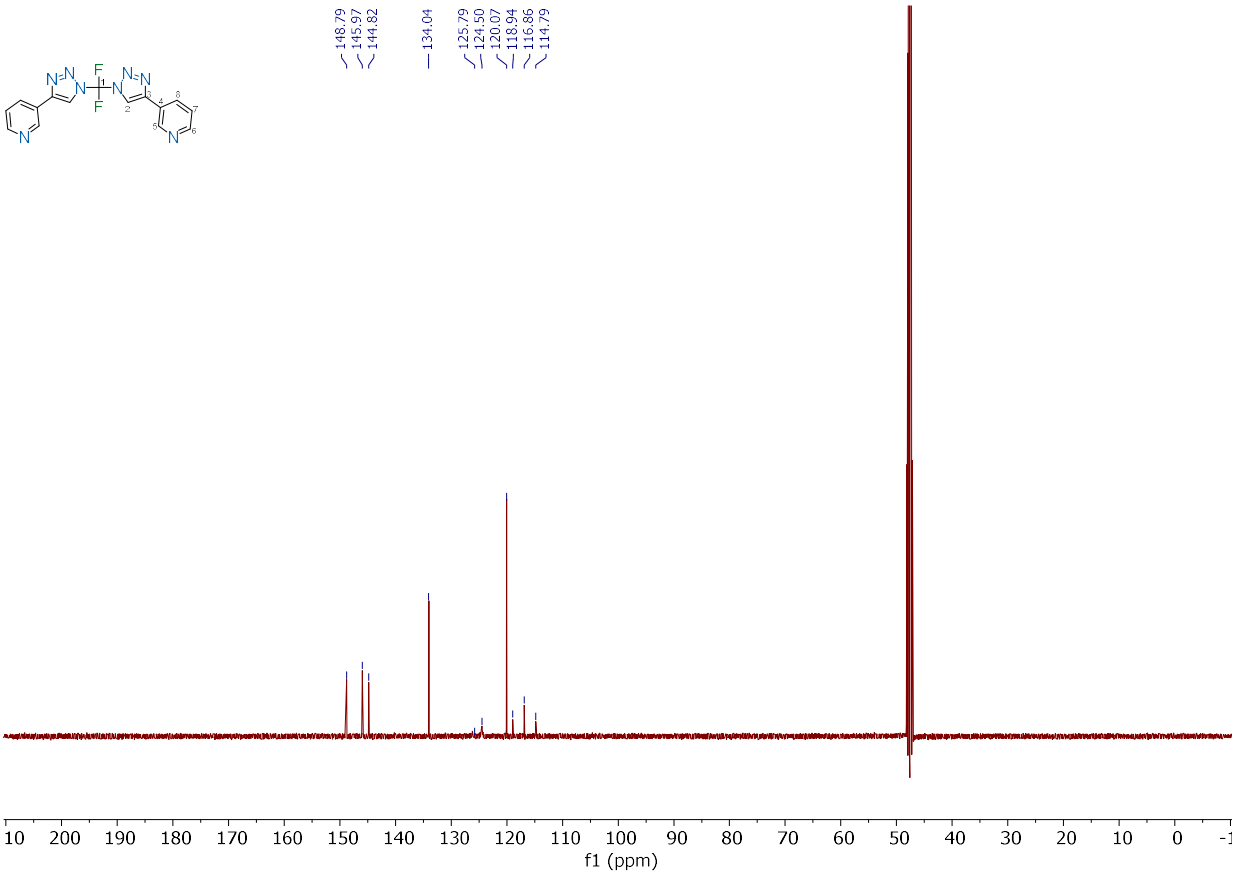


Figure S25: $^{13}C\{^{1}H\}$ NMR spectrum of **2f** (126 MHz, Methanol-d_4)

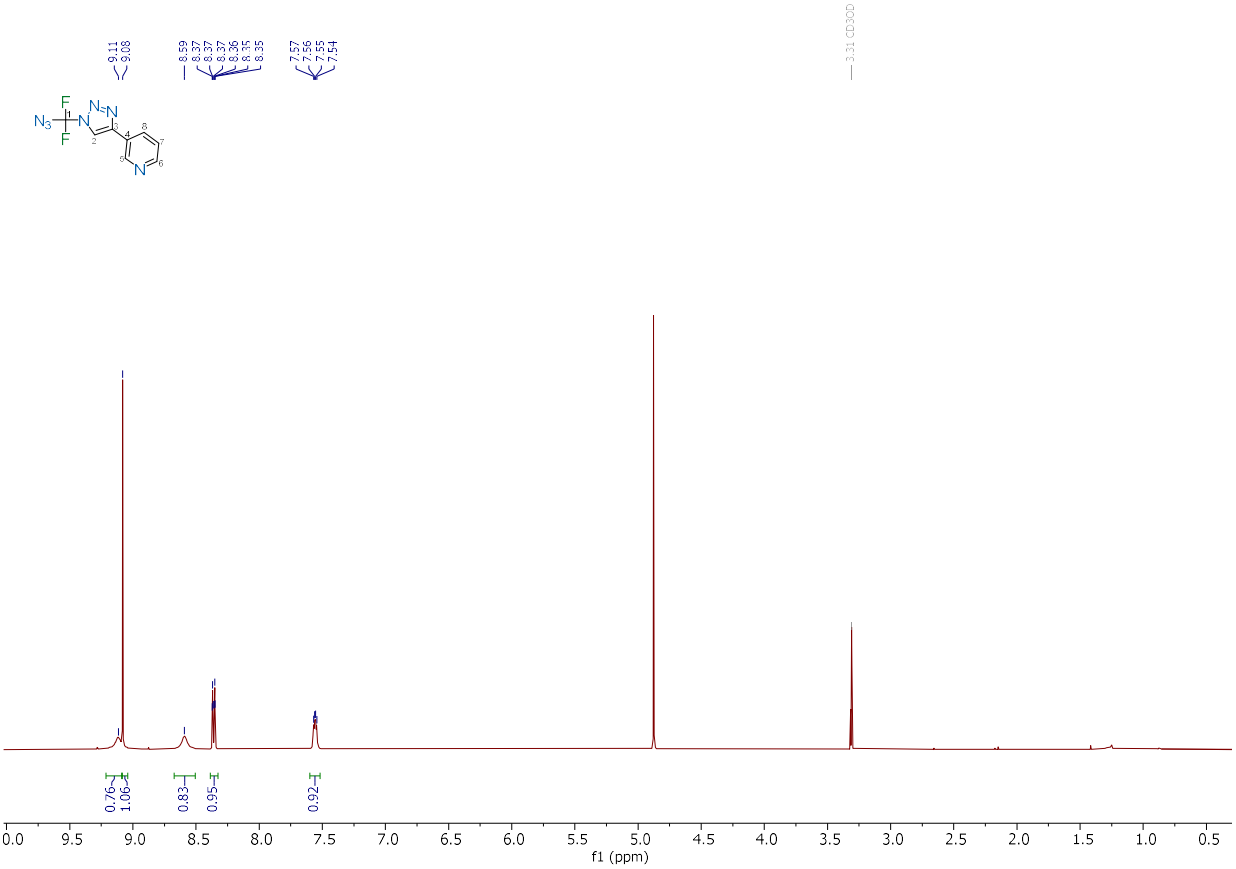


Figure S26: ^{1}H NMR spectrum of **2f`** (500 MHz, Methanol-d_4)

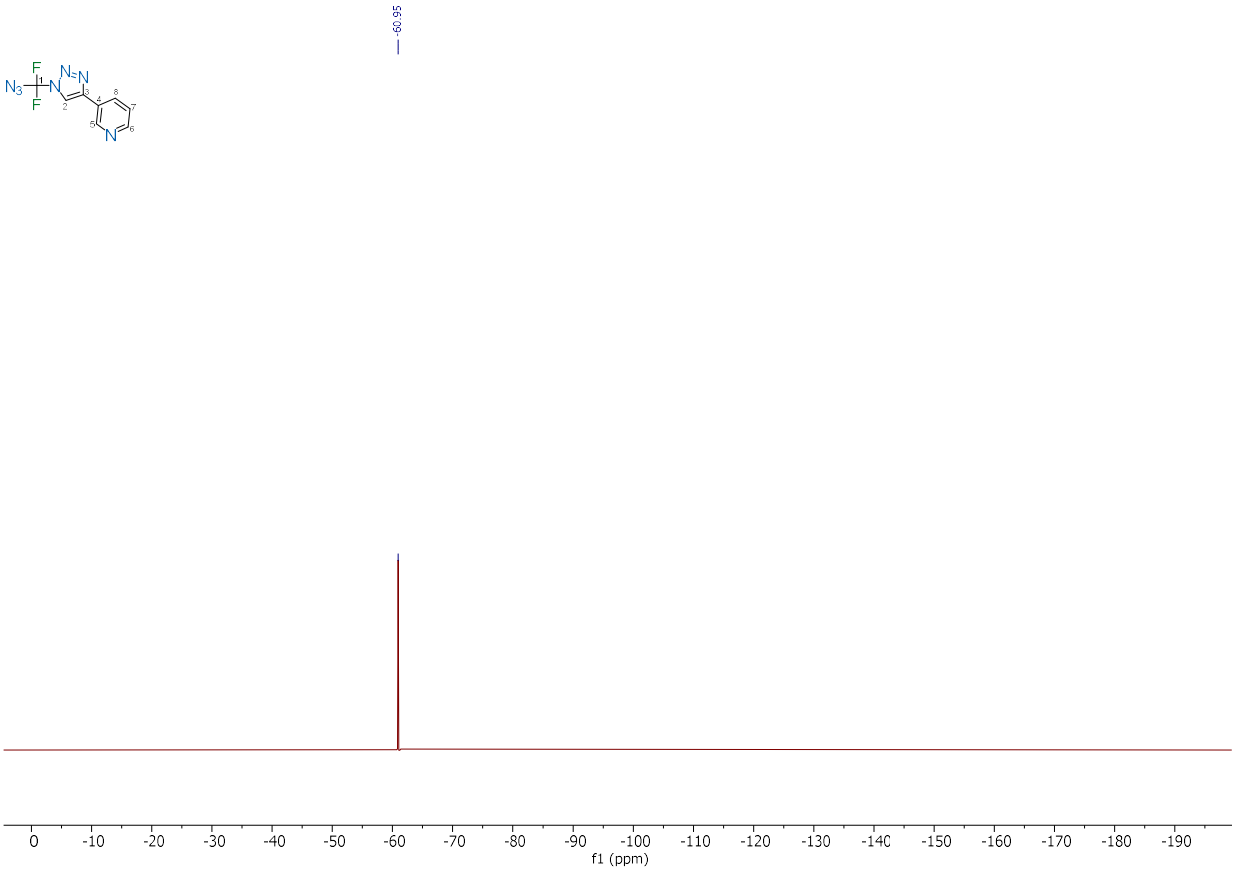


Figure S27: ^{19}F NMR spectrum of **2f`** (470 MHz, Methanol-d_4)

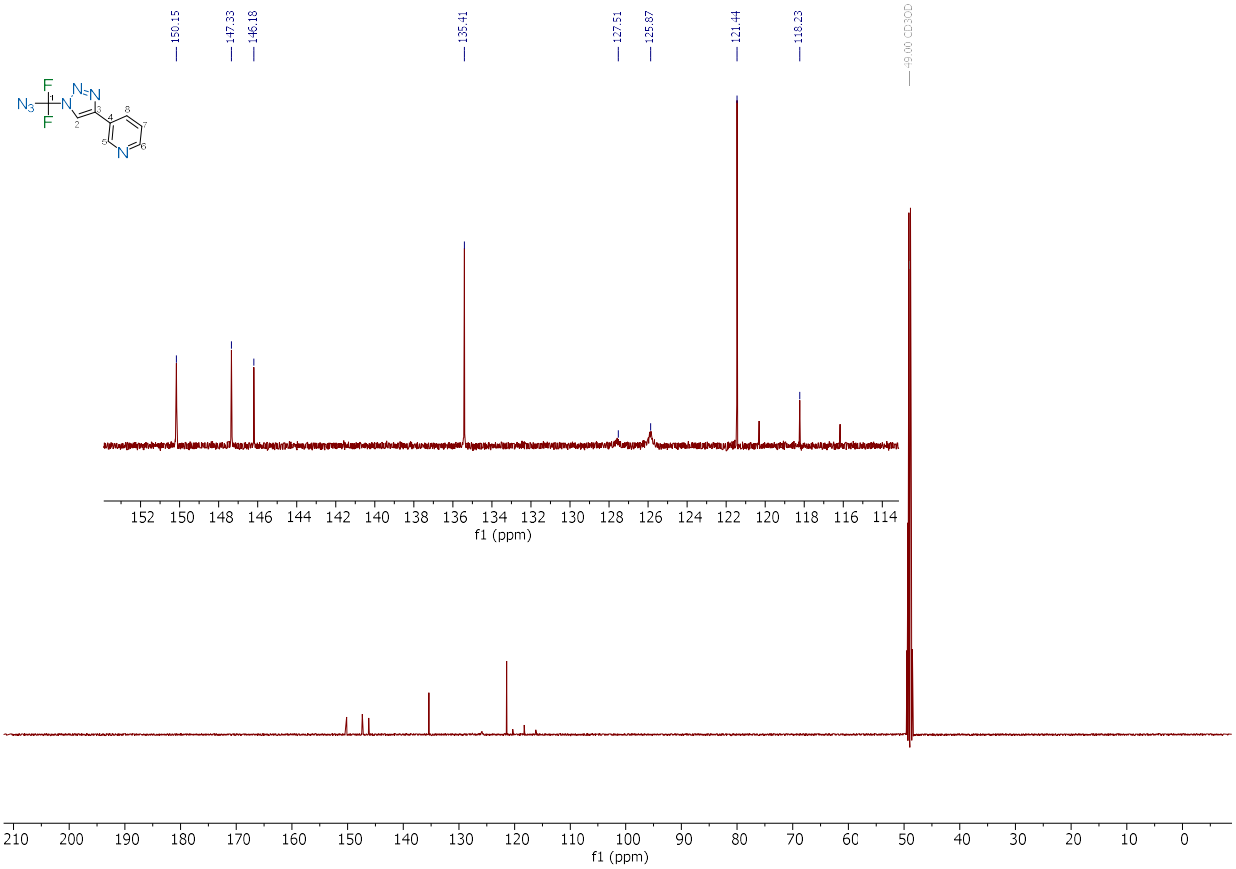


Figure S28: $^{13}C\{^{1}H\}$ NMR spectrum of **2f'** (126 MHz, Methanol-*d*$_4$)

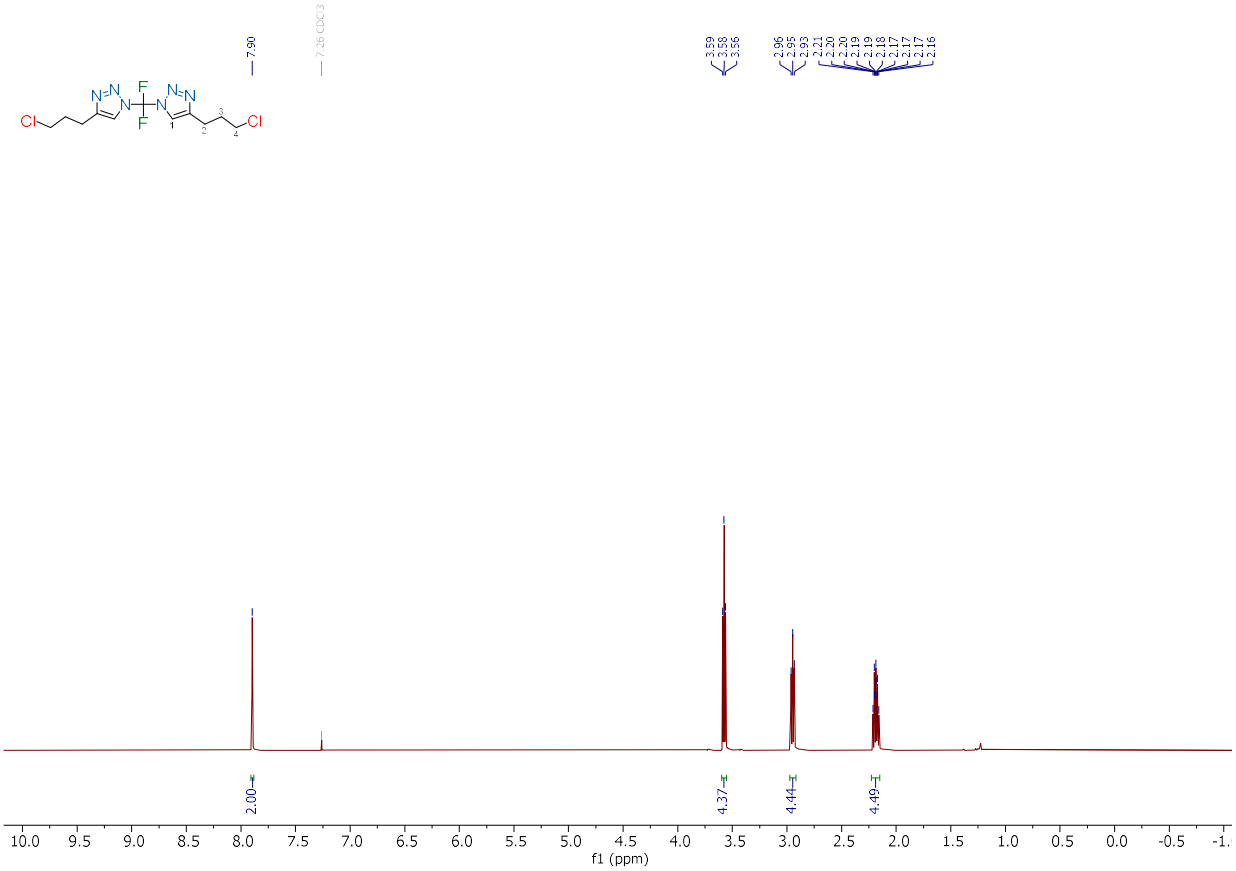


Figure S29: ^{1}H NMR spectrum of **2g** (500 MHz, $CDCl_3$)

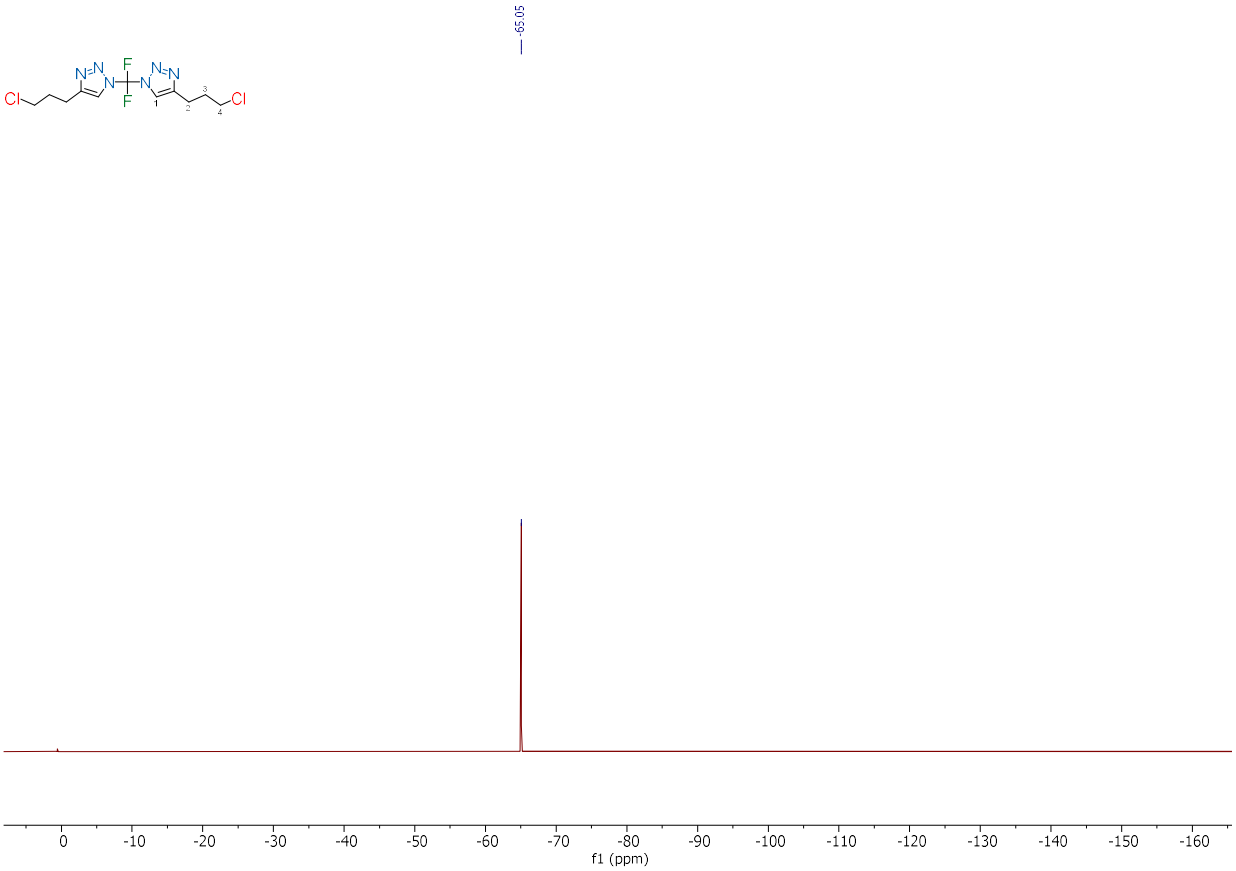


Figure S30: ^{19}F NMR spectrum of **2g** (470 MHz, $CDCl_3$)

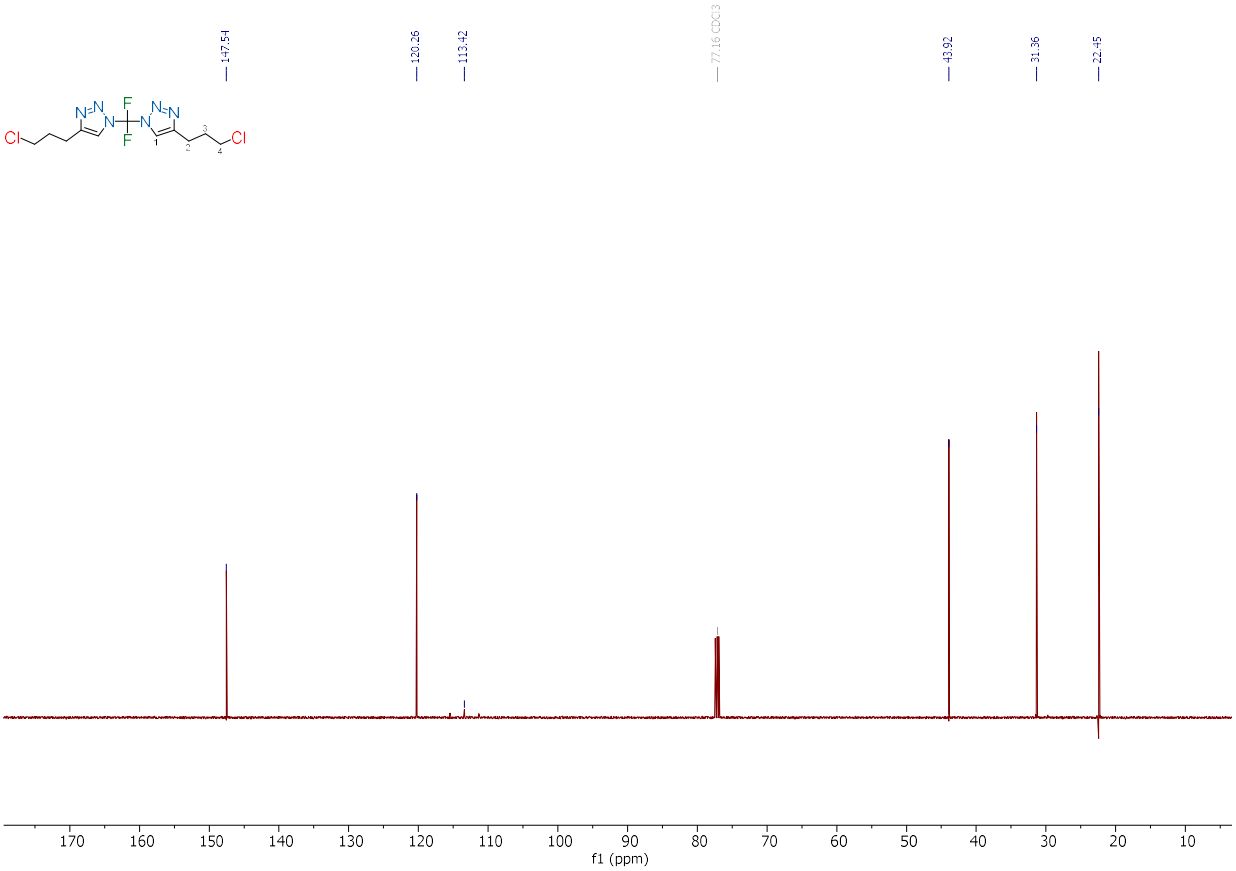


Figure S31: $^{13}C\{^{1}H\}$ NMR spectrum of **2g** (126 MHz, $CDCl_3$)

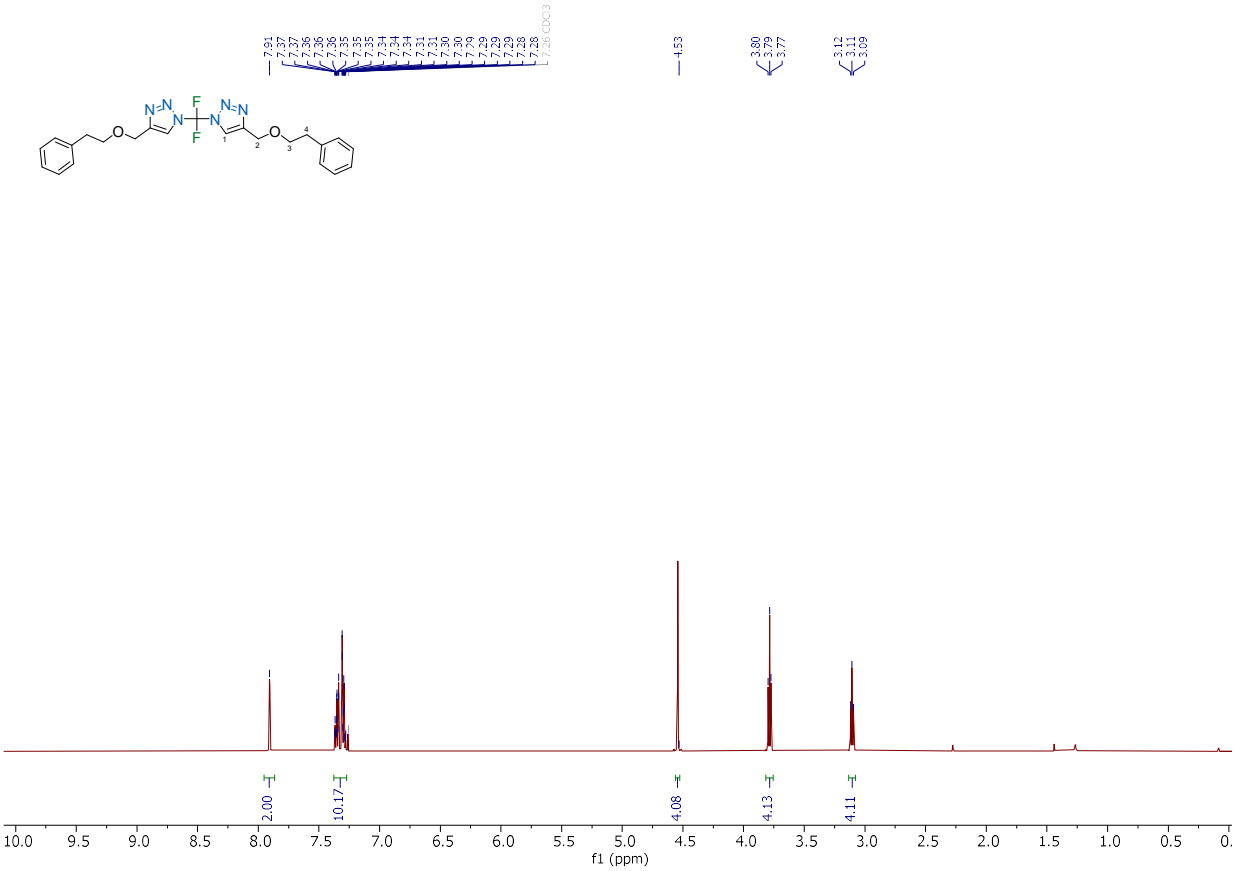


Figure S32: ^{1}H NMR spectrum of **2h** (500 MHz, $CDCl_3$)

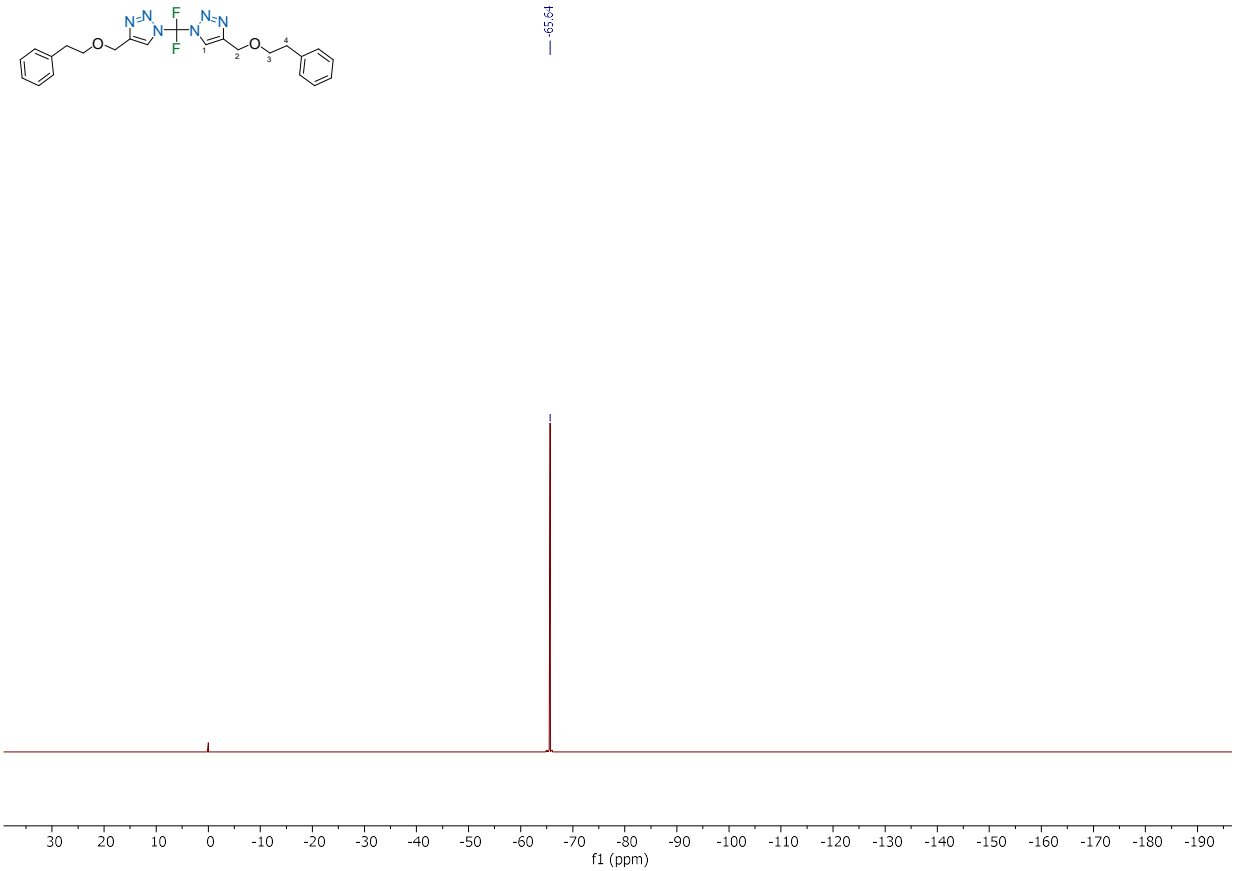


Figure S33: ^{19}F NMR spectrum of **2h** (470 MHz, $CDCl_3$)

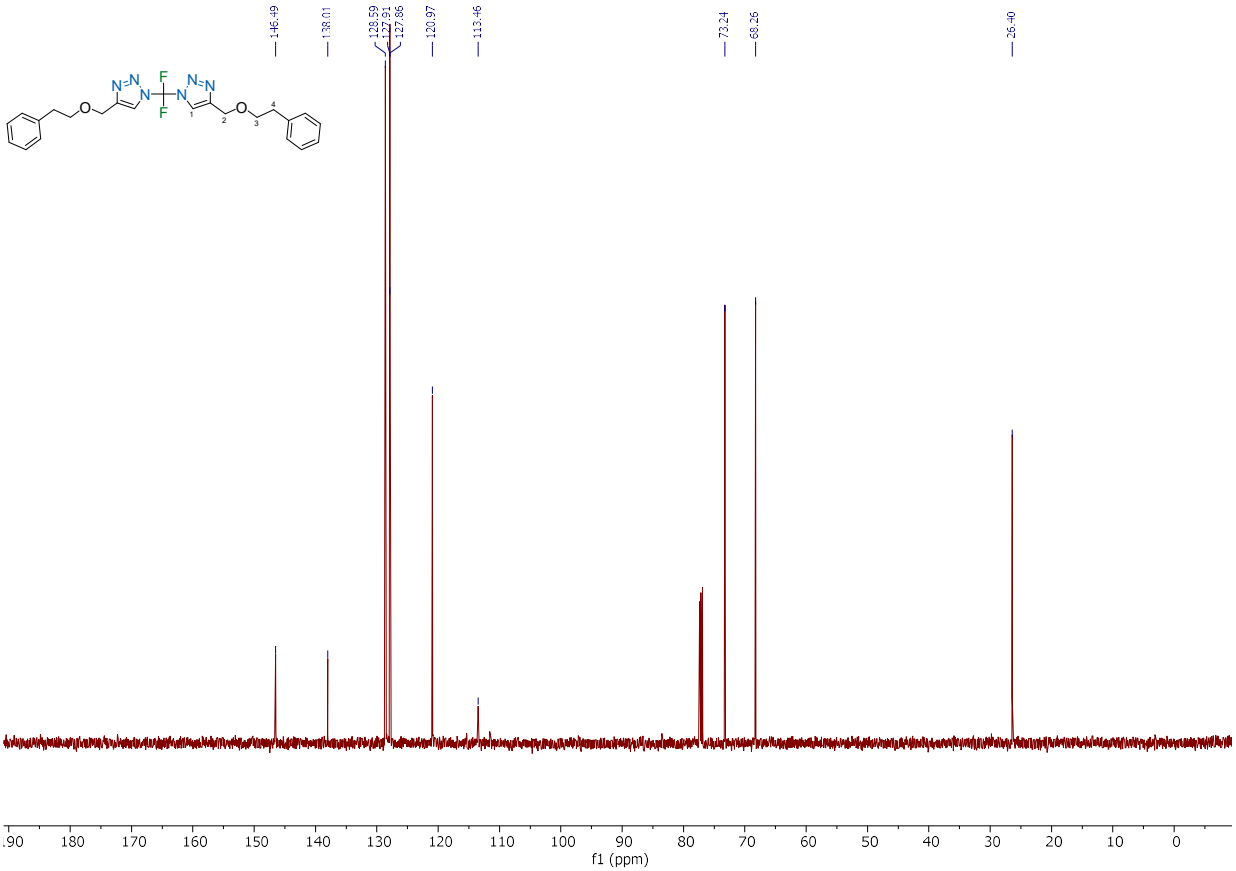


Figure S34: $^{13}C\{^{1}H\}$ NMR spectrum of **2h** (126 MHz, $CDCl_3$)

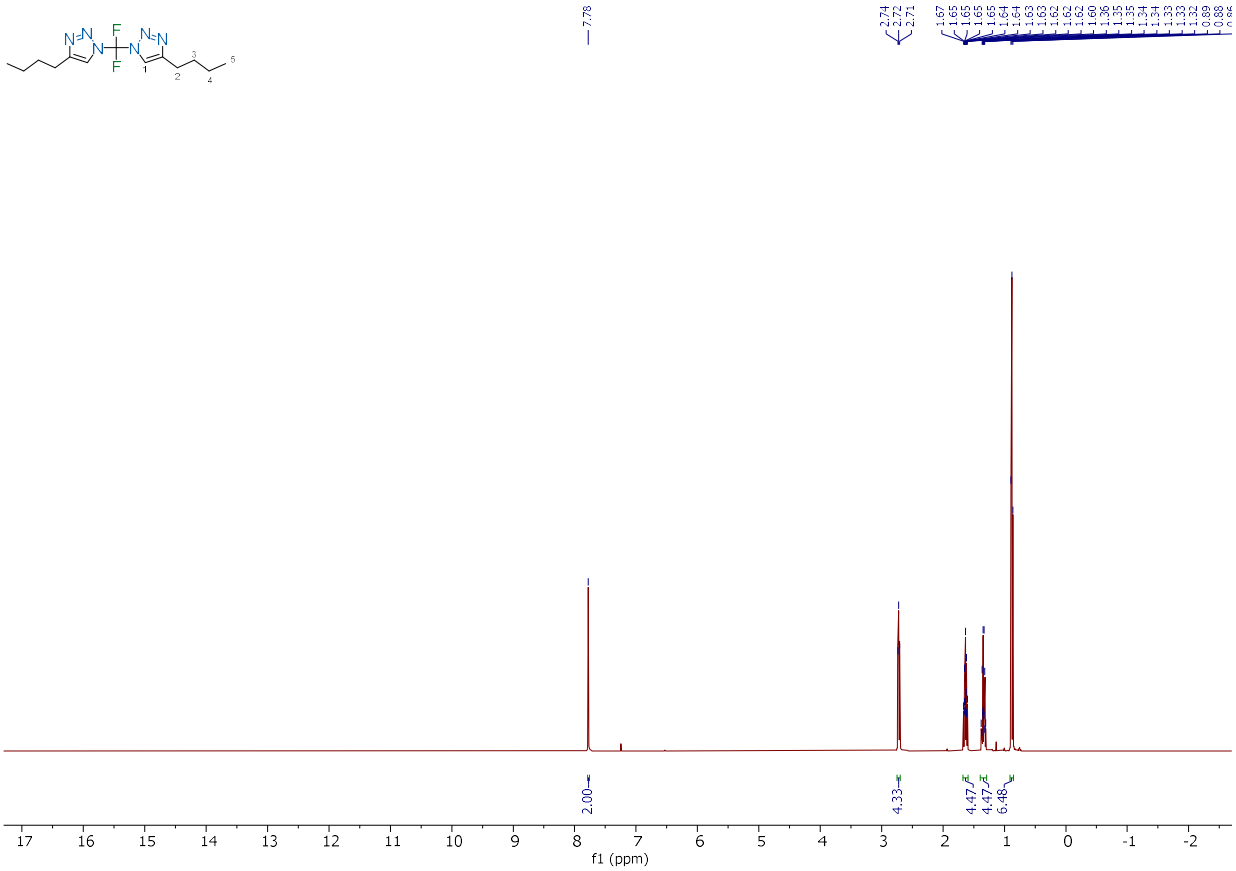


Figure S35: ^{1}H NMR spectrum of **2i** (500 MHz, $CDCl_3$)

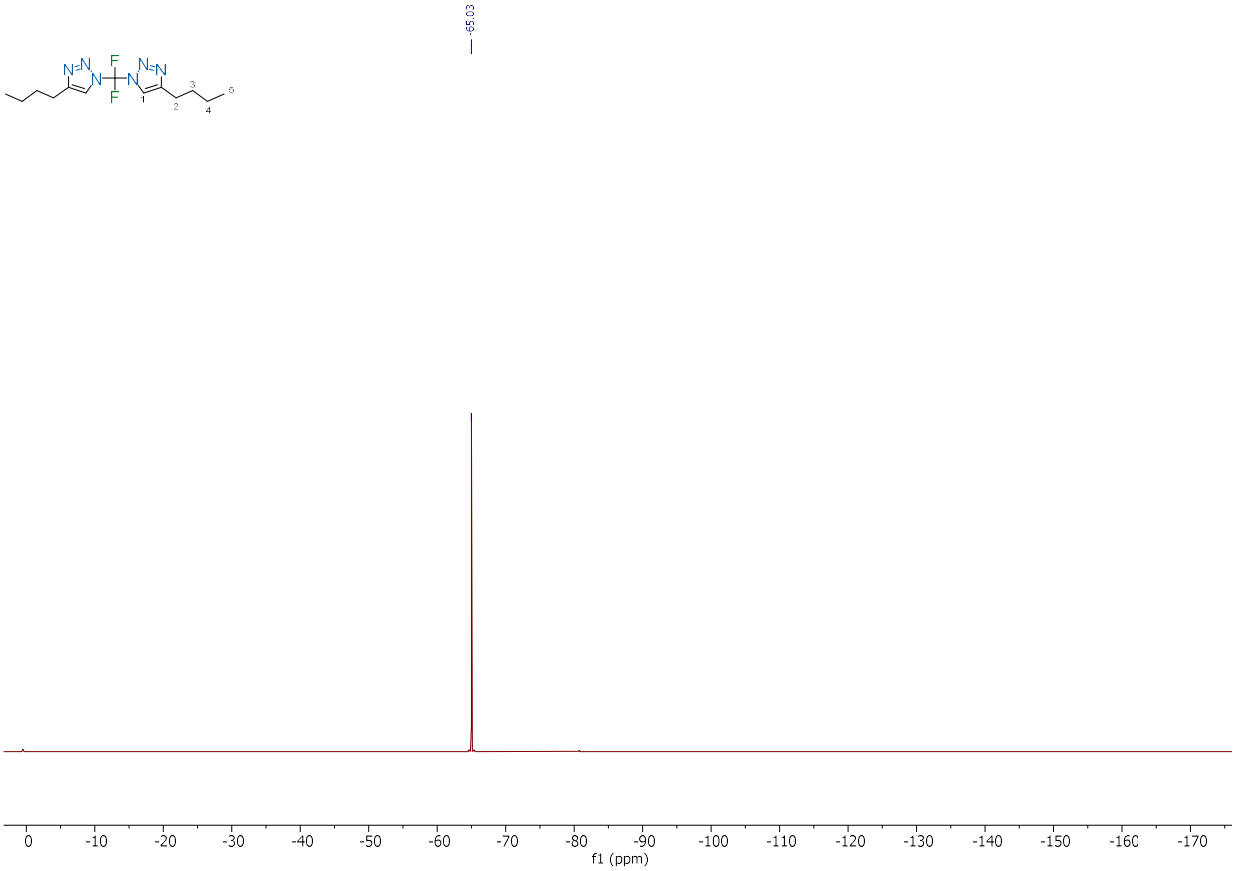


Figure S36: ^{19}F NMR spectrum of **2i** (470 MHz, $CDCl_3$)

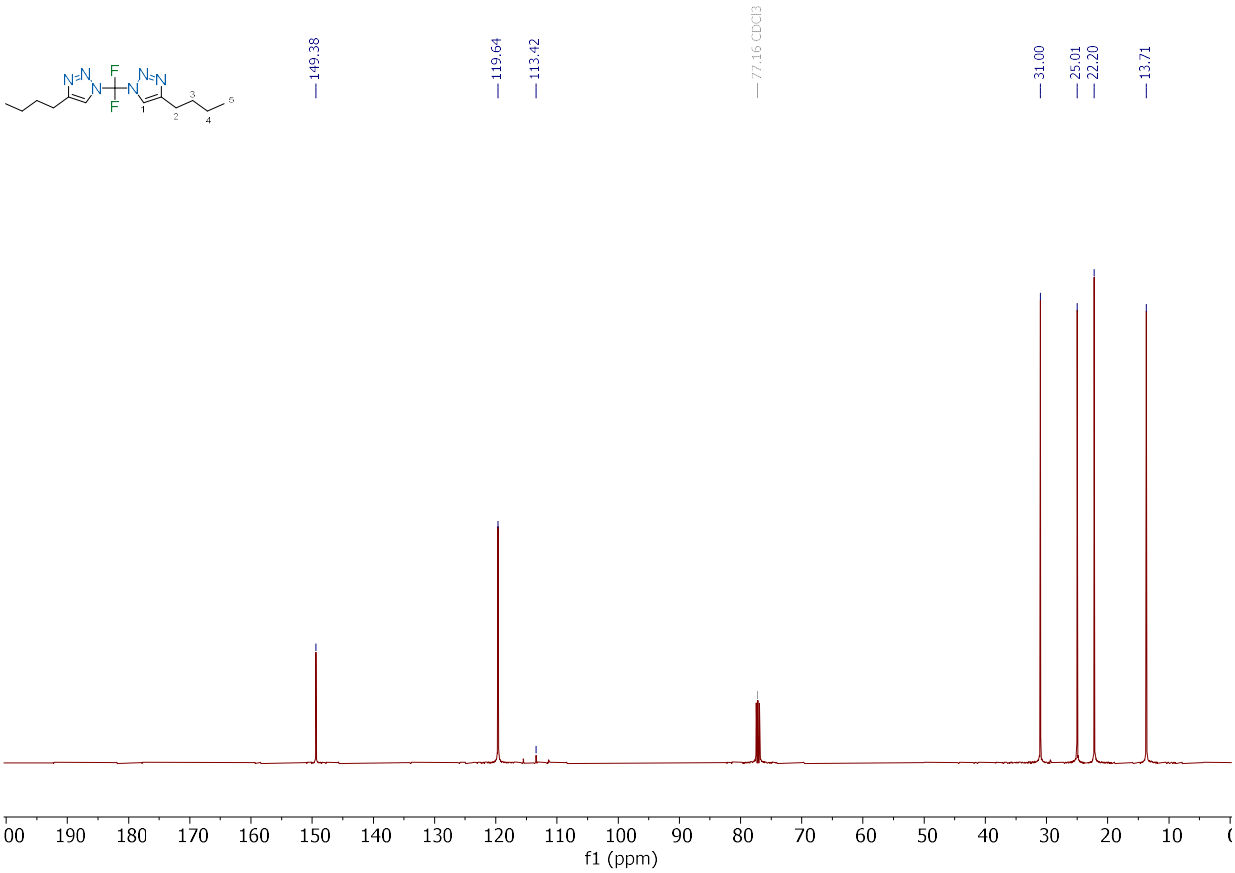


Figure S37: $^{13}C\{^{1}H\}$ NMR spectrum of **2i** (126 MHz, $CDCl_3$)

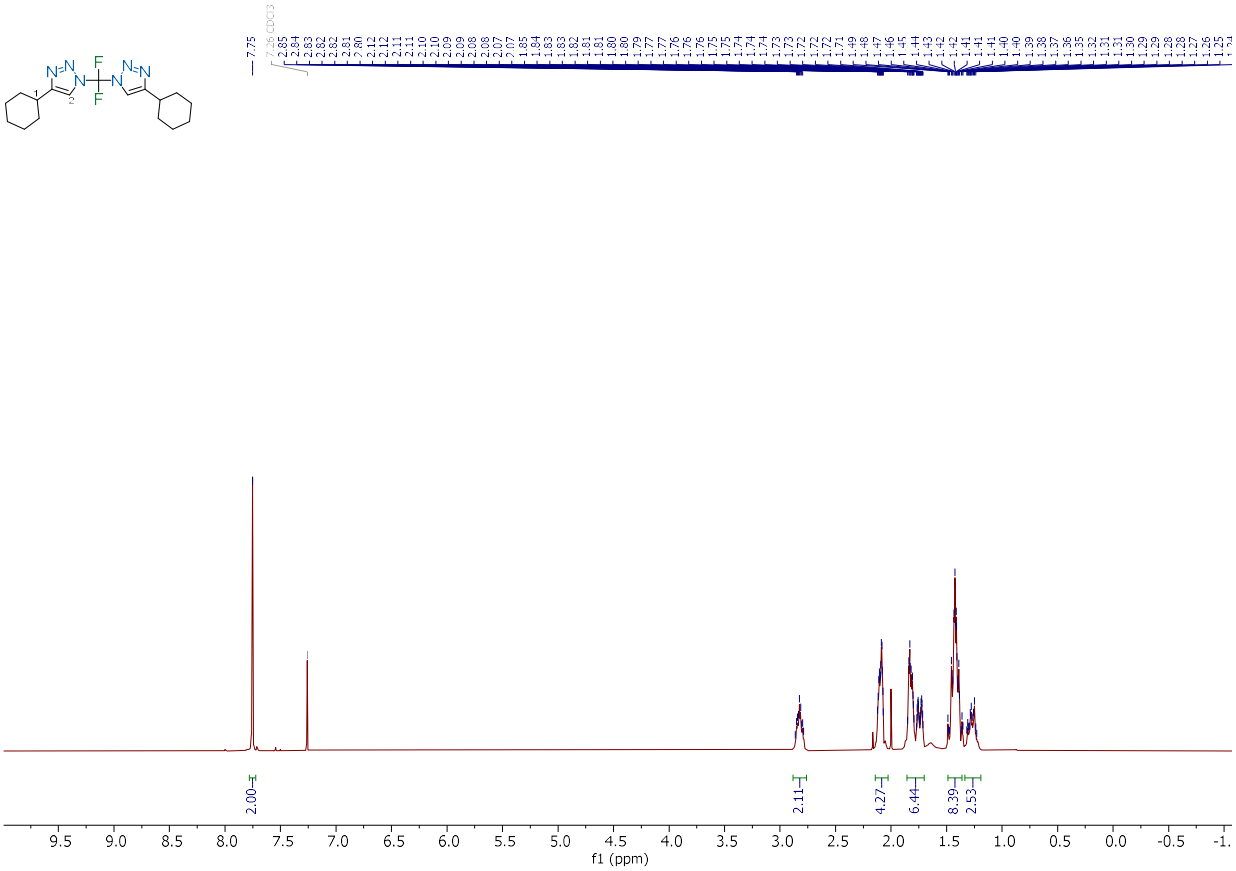


Figure S38: ^{1}H NMR spectrum of **2j** (400 MHz, $CDCl_3$)

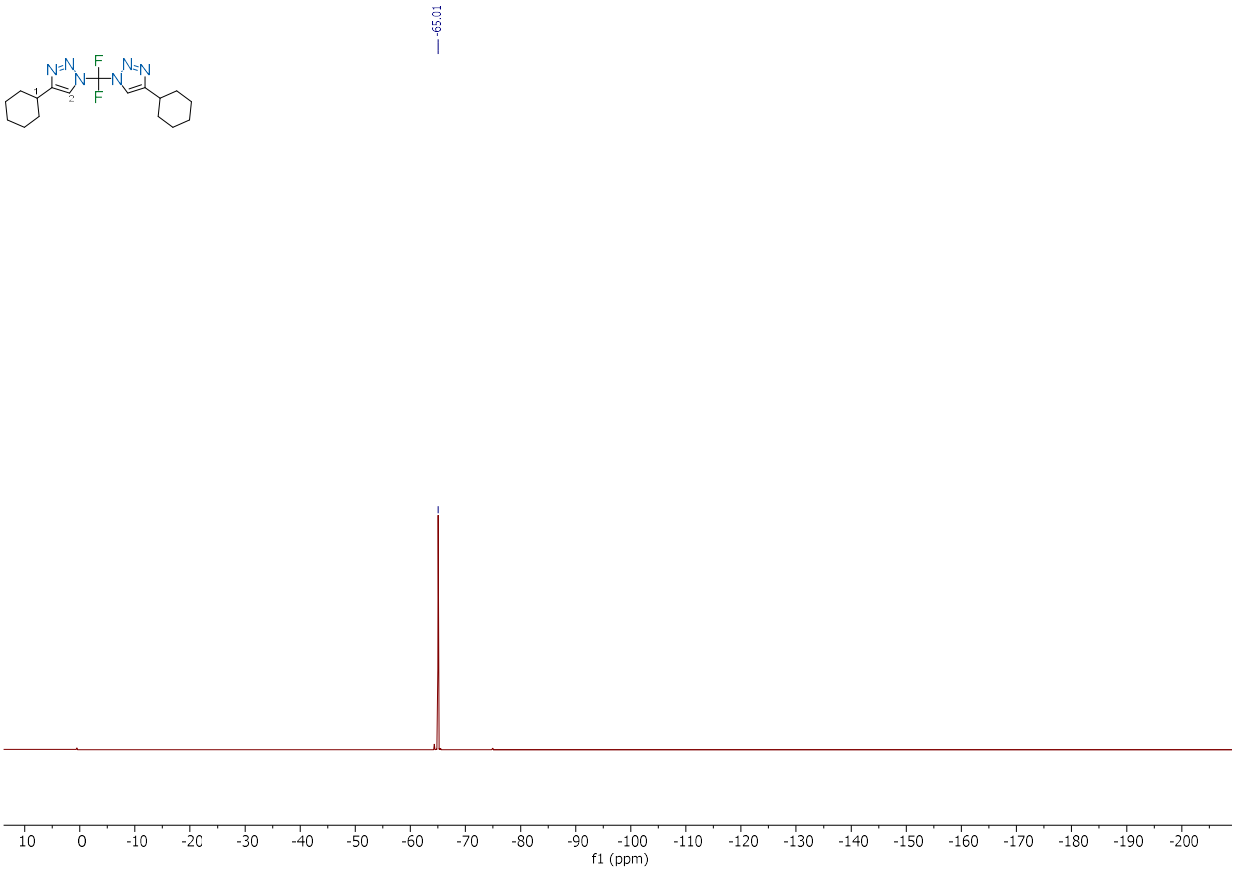


Figure S39: ^{19}F NMR spectrum of **2j** (377 MHz, $CDCl_3$)

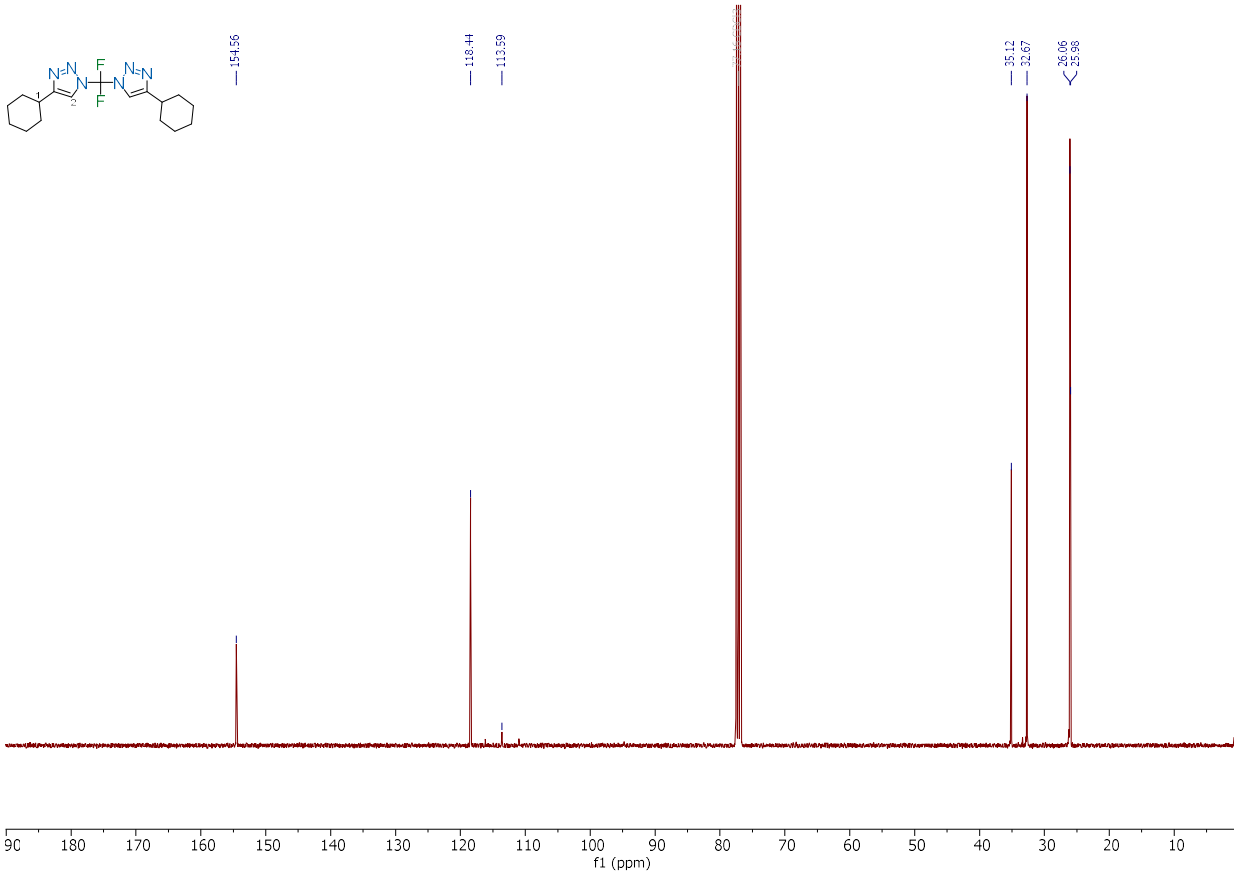


Figure S40: $^{13}C\{^{1}H\}$ NMR spectrum of **2j** (101 MHz, $CDCl_3$)

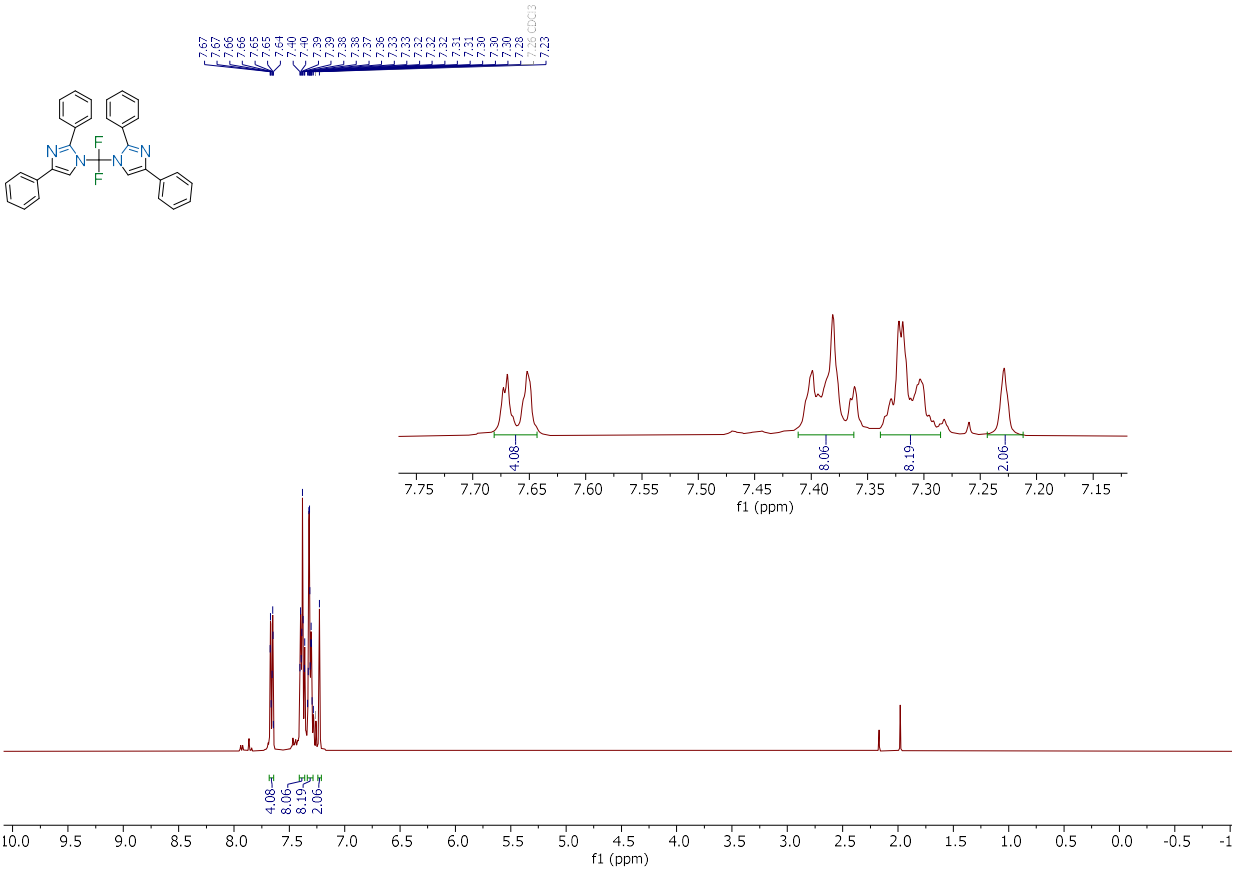


Figure S41: ^{1}H NMR spectrum of **3a** (400 MHz, $CDCl_3$)

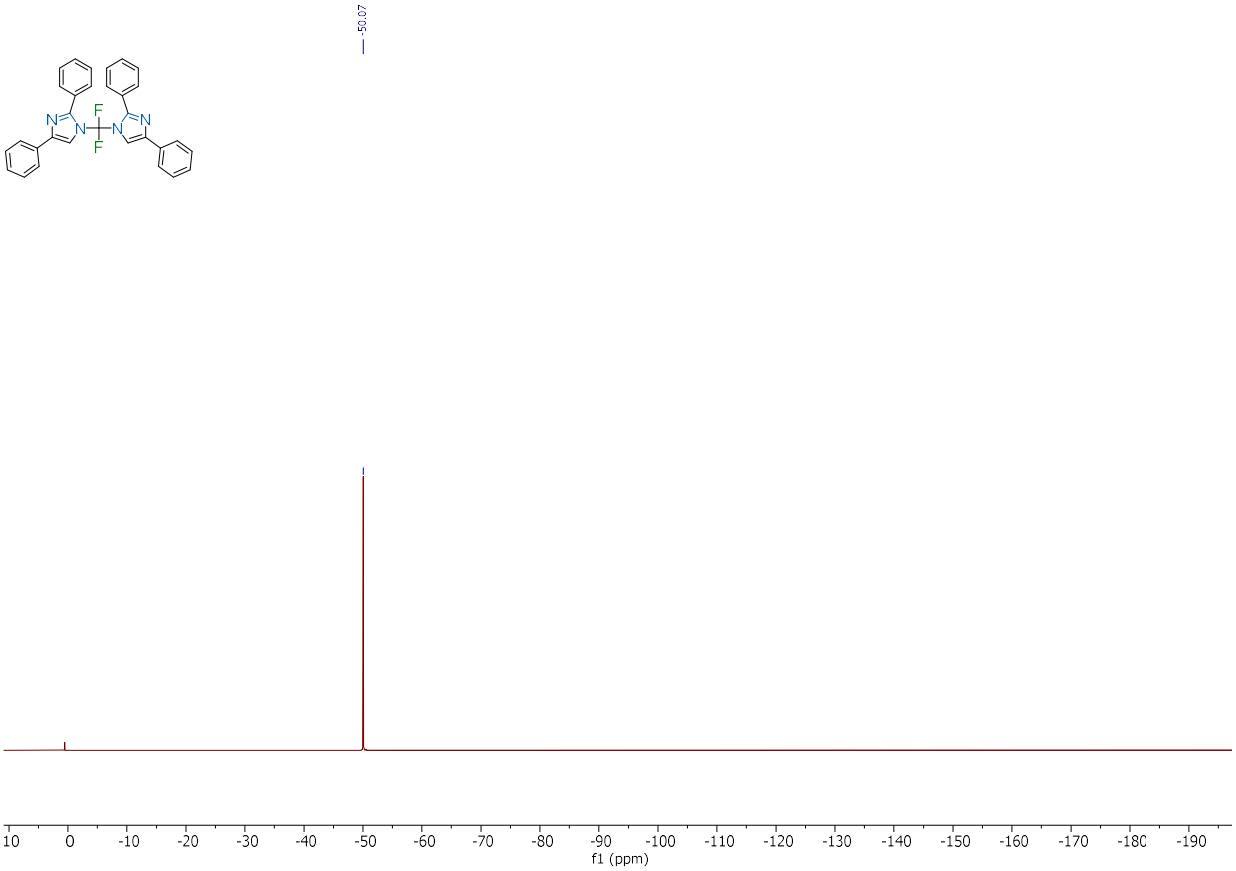


Figure S42: ^{19}F NMR spectrum of **3a** (377 MHz, $CDCl_3$)

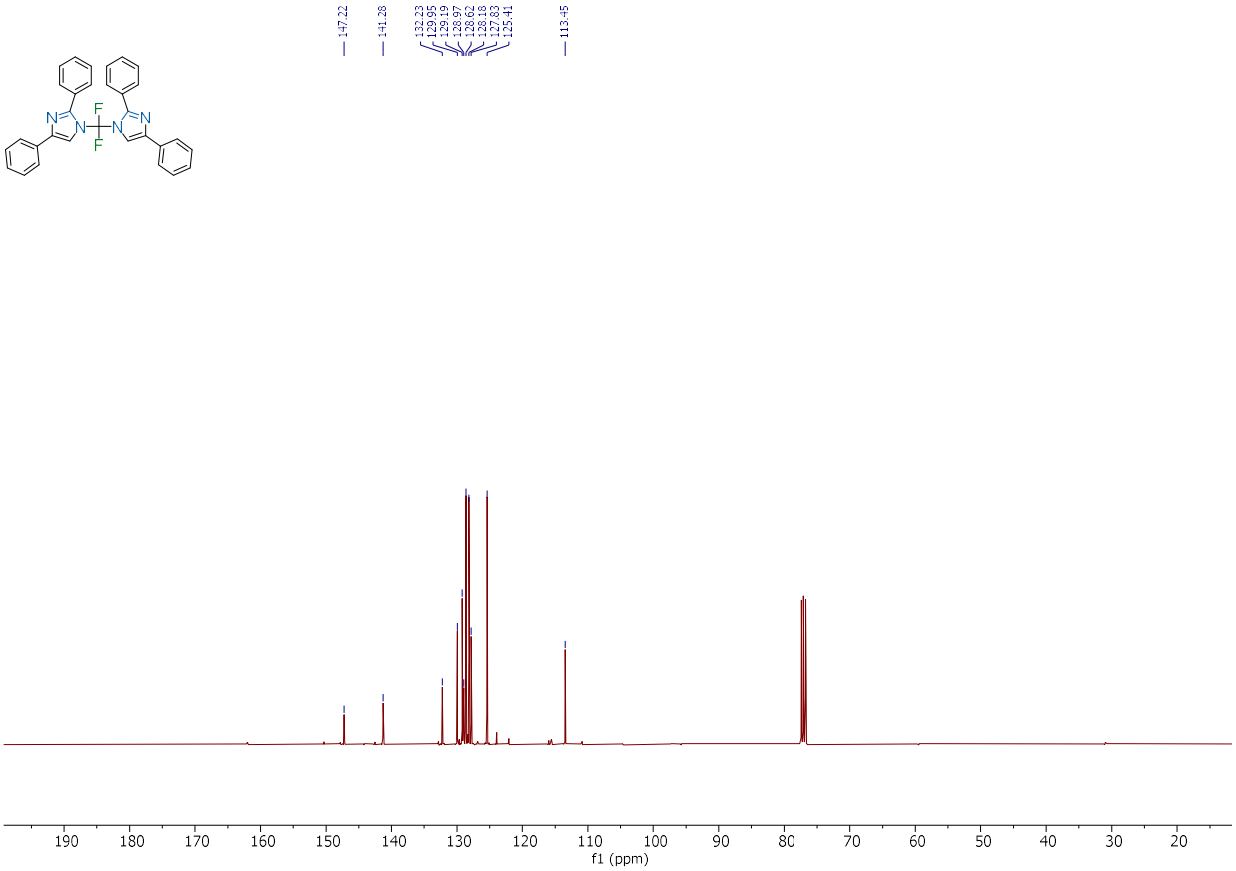


Figure S43: $^{13}C\{^{1}H\}$ NMR spectrum of **3a** (101 MHz, $CDCl_3$)

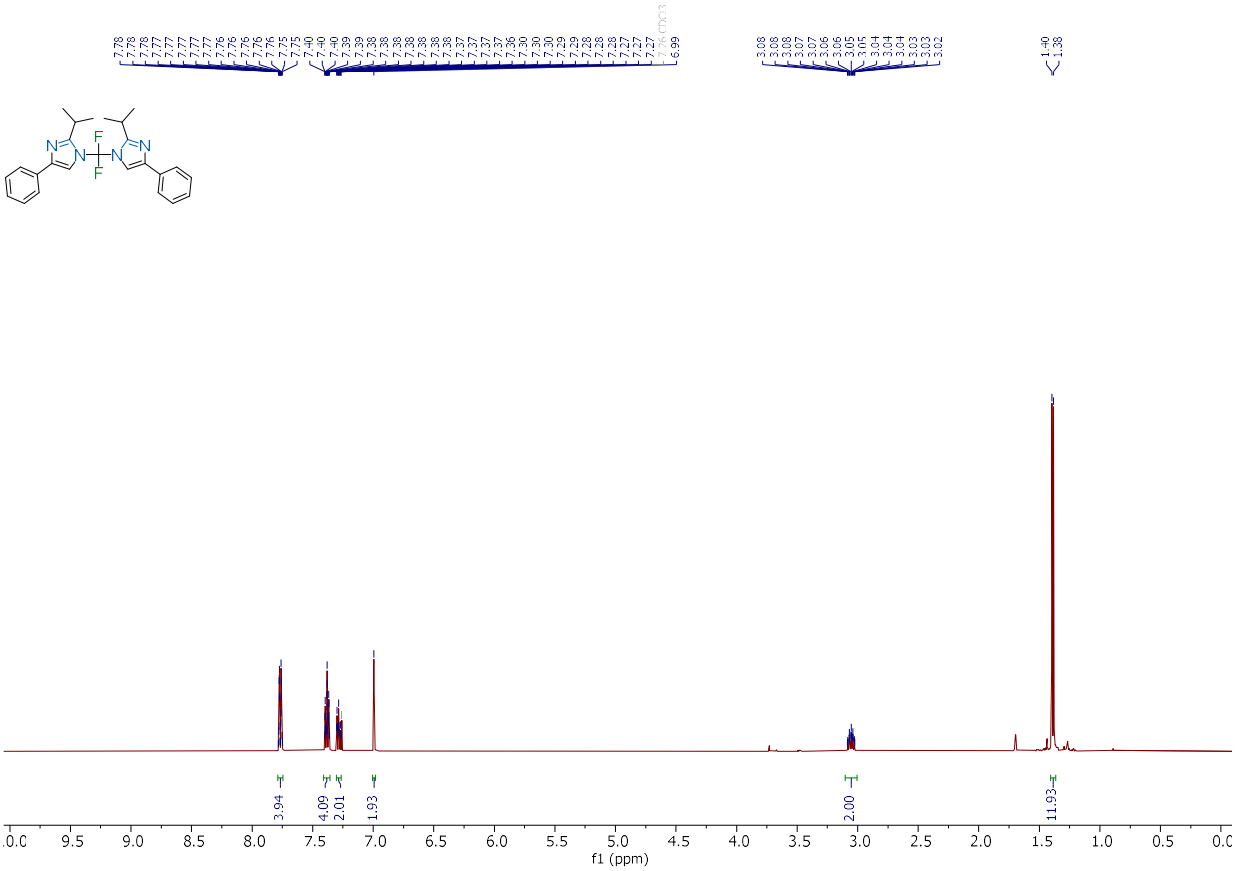


Figure S44: ^{1}H NMR spectrum of **3b** (500 MHz, $CDCl_3$)

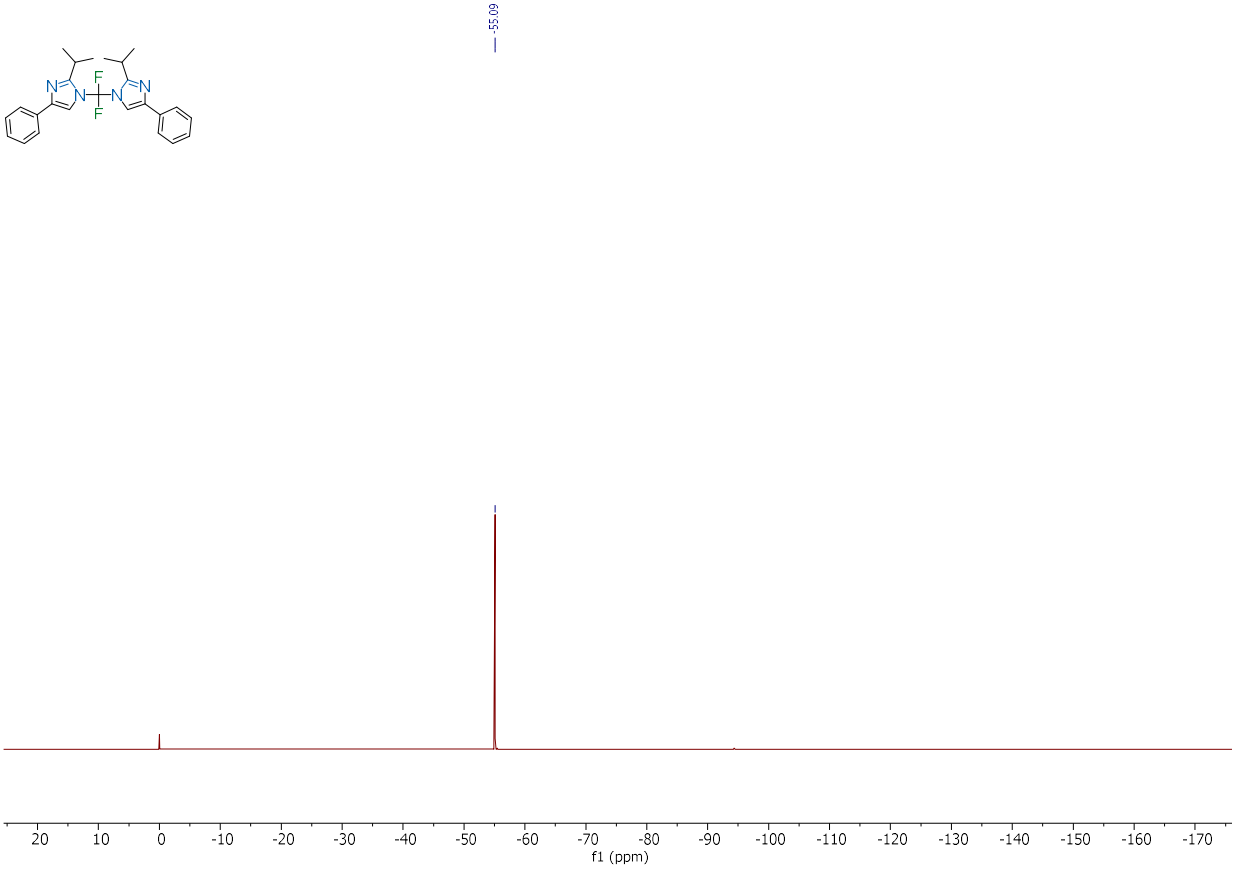


Figure S45: ^{19}F NMR spectrum of **3b** (470 MHz, $CDCl_3$)

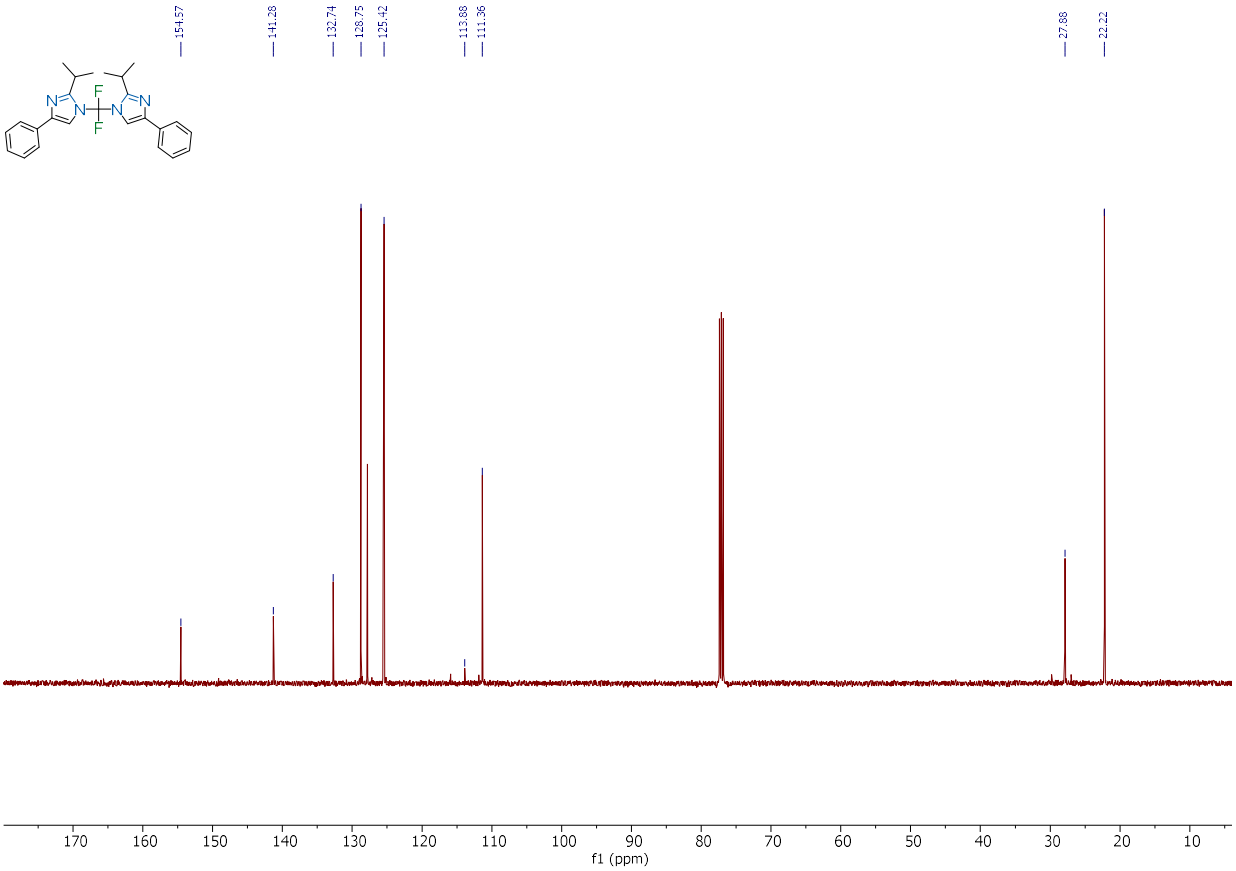


Figure S46: $^{13}C\{^{1}H\}$ NMR spectrum of **3b** (126 MHz, $CDCl_3$)

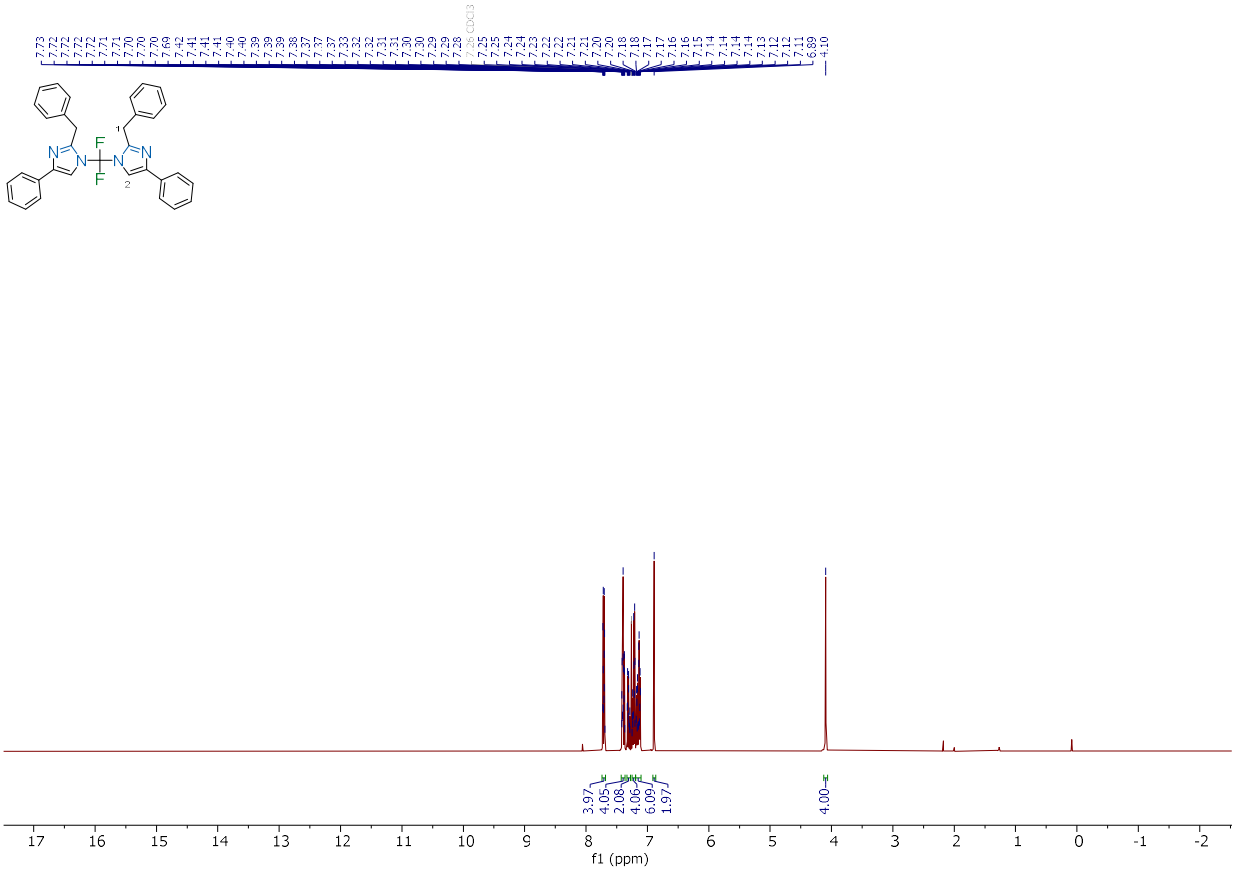


Figure S47: ^{1}H NMR spectrum of **3c** (400 MHz, $CDCl_3$)

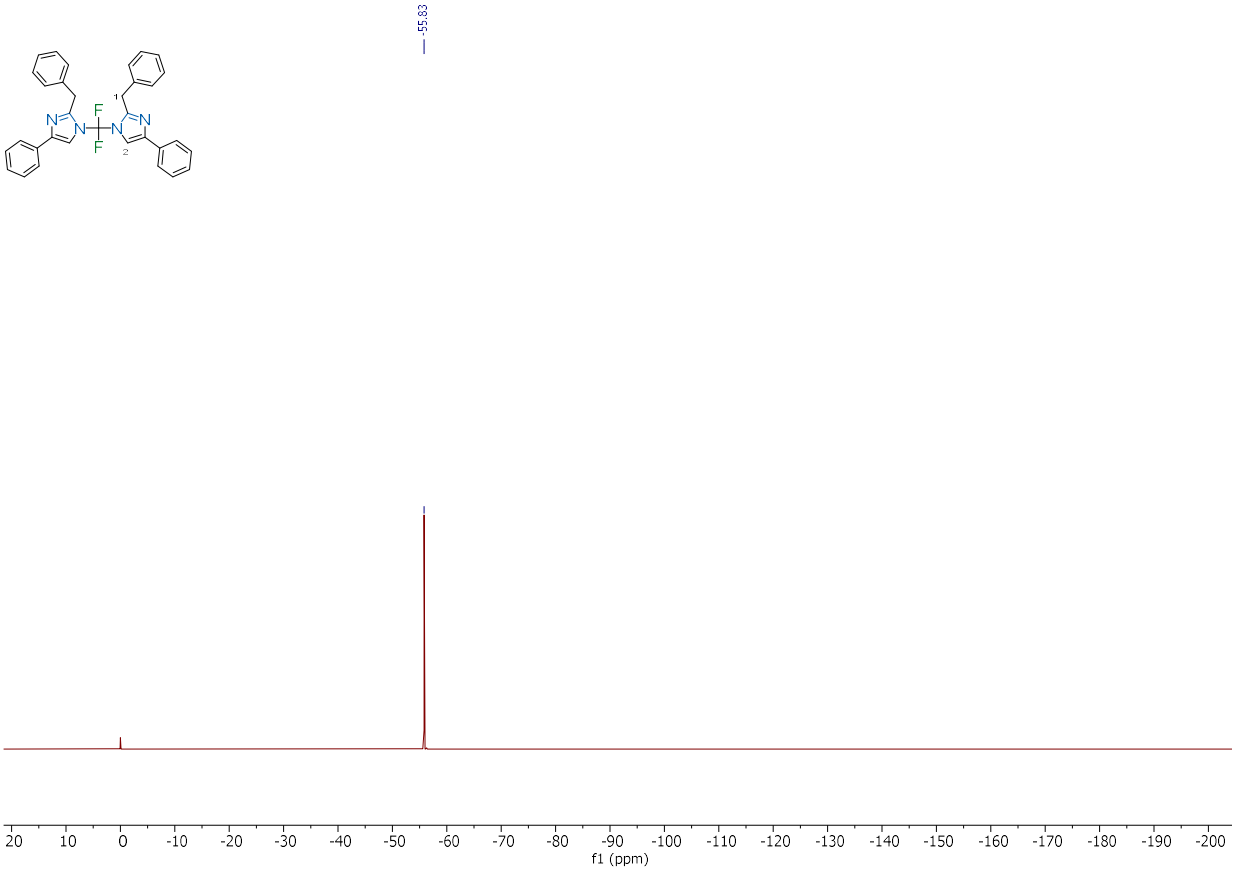


Figure S48: ^{19}F NMR spectrum of **3c** (376 MHz, $CDCl_3$)

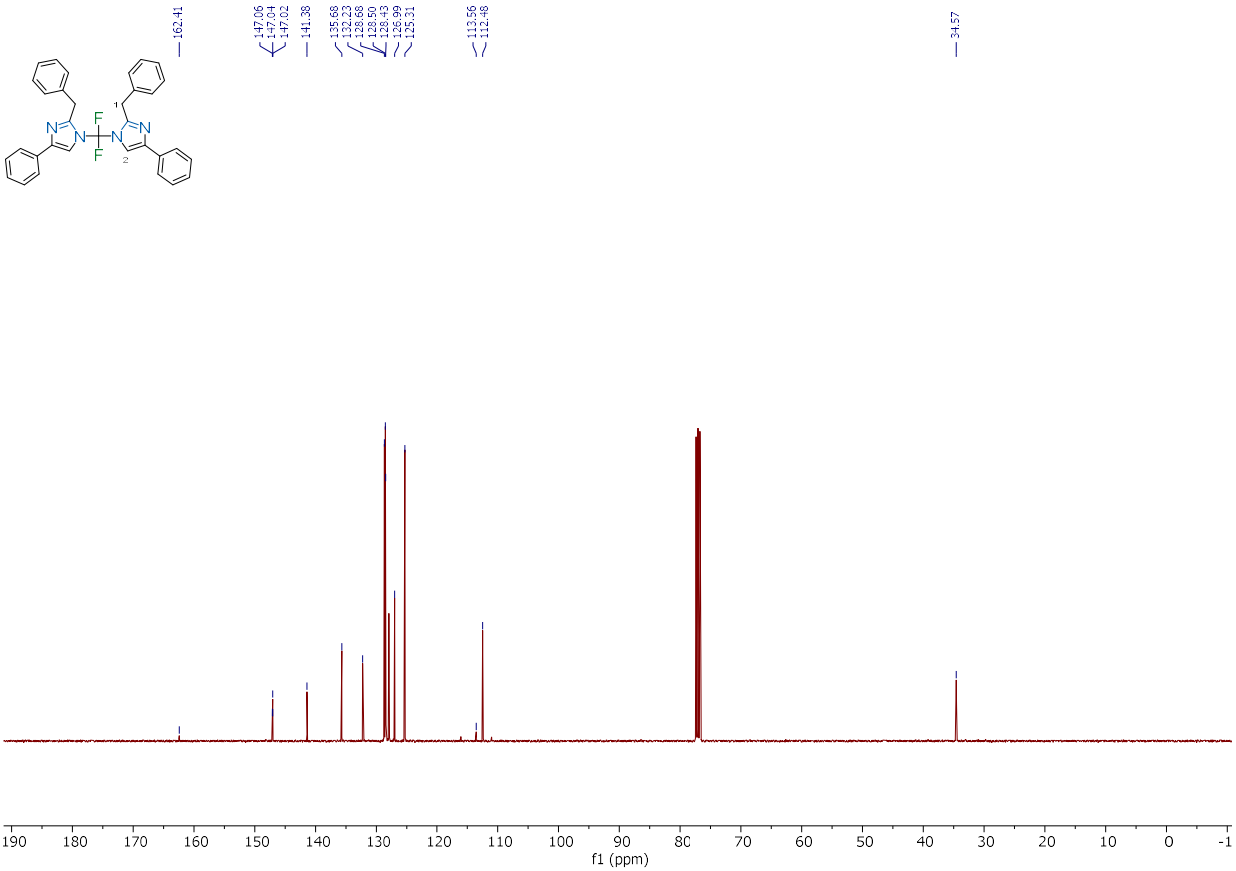


Figure S49: $^{13}C\{^{1}H\}$ NMR spectrum of **3c** (126 MHz, $CDCl_3$)

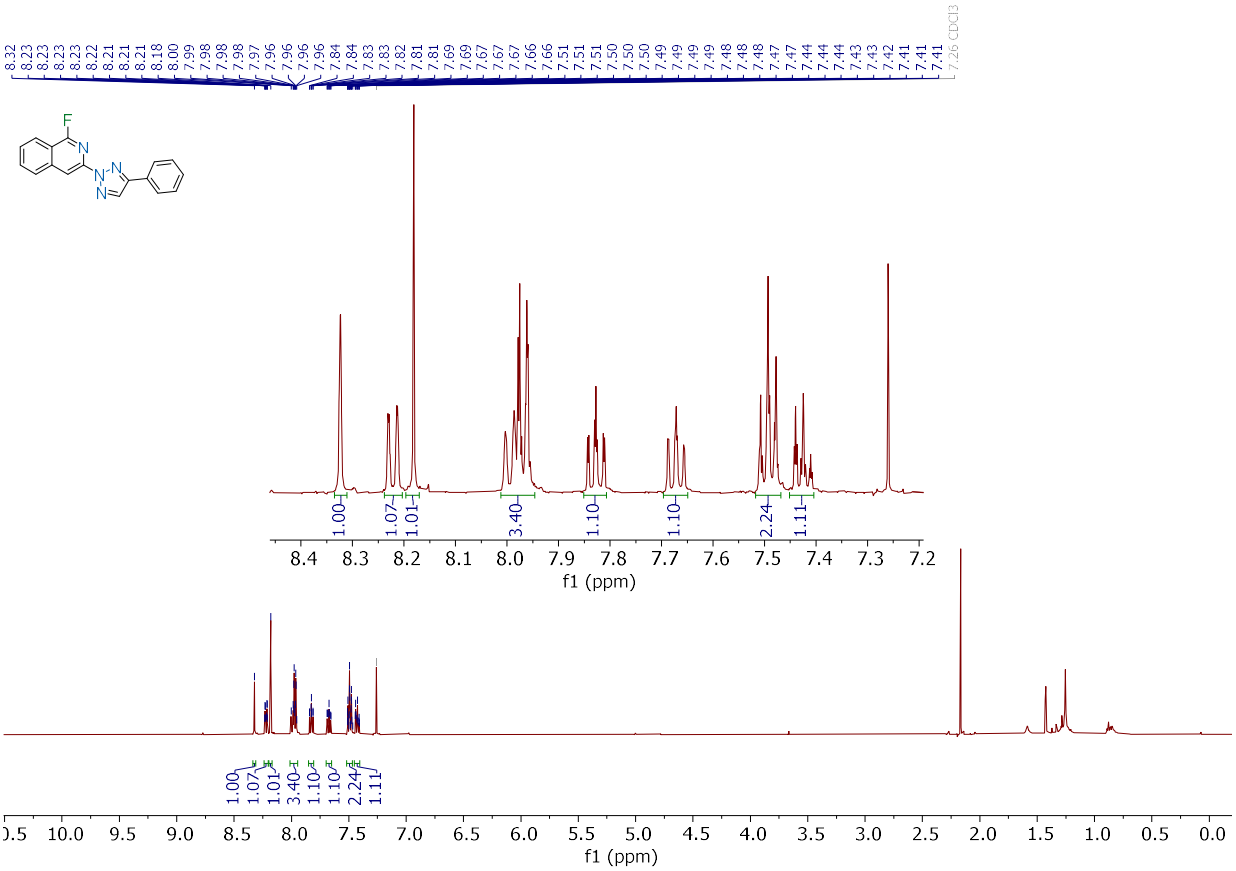


Figure S50: ^{1}H NMR spectrum of **4** (500 MHz, $CDCl_3$)

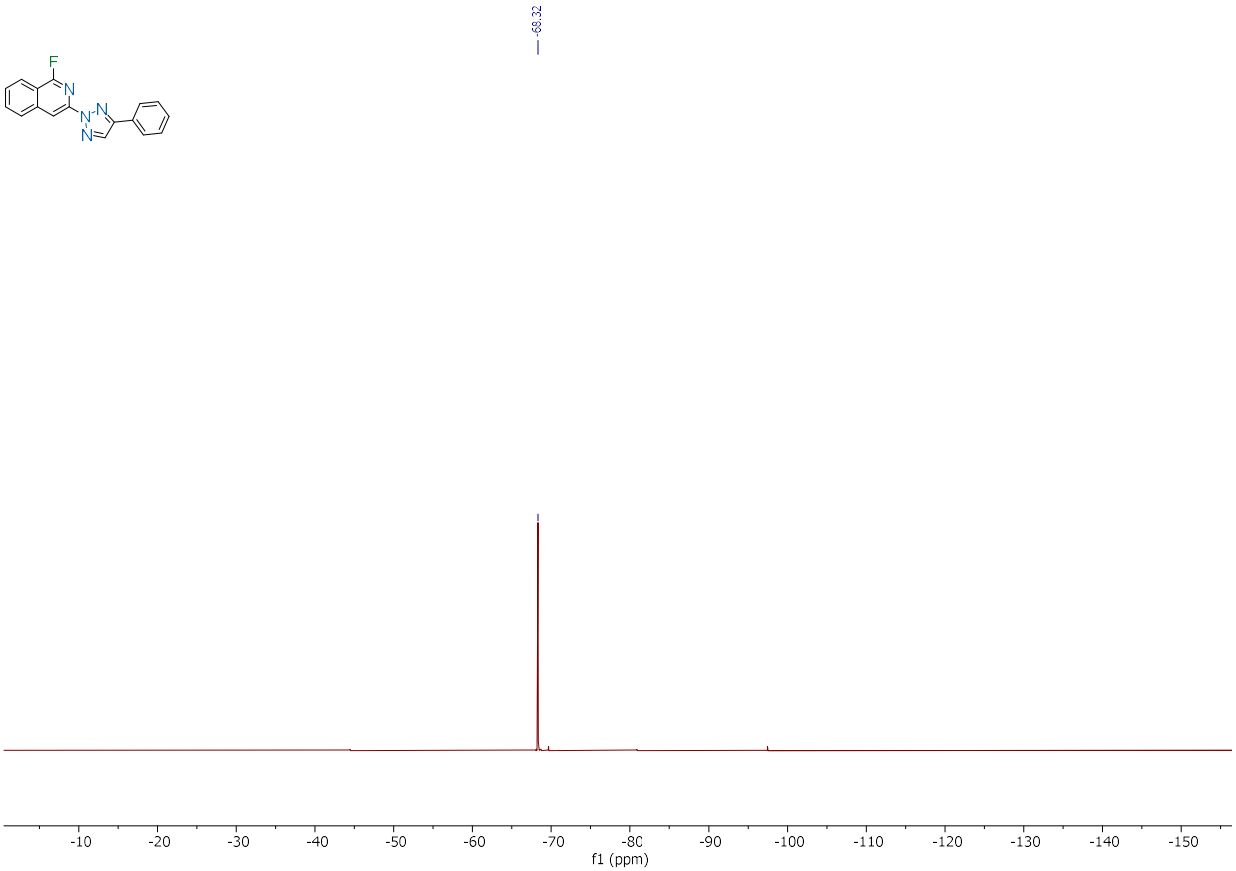


Figure S51: ^{19}F NMR spectrum of **4** (377 MHz, $CDCl_3$)

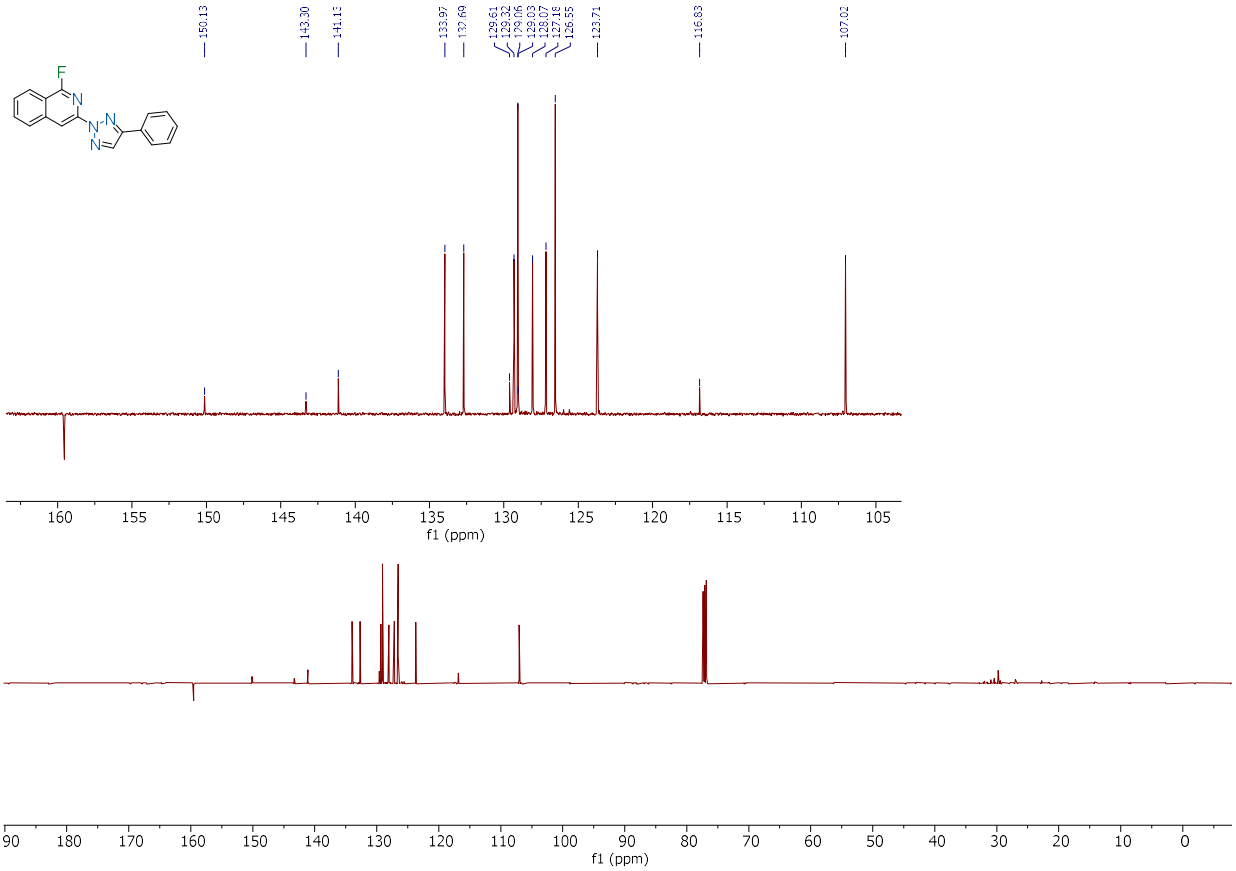


Figure S52: $^{13}C\{^{1}H, ^{19}F\}$ NMR spectrum of **4** (126 MHz, $CDCl_3$)

15. X-ray structures and data for compounds 2d and 4

The single-crystal data of **2d** and **4** were collected at 180 K using Bruker D8 VENTURE system equipped with a Photon 100 CMOS detector, a multilayer monochromator, and a CuKα (**2d**) or Mo-Kα (**4**) Incoatec microfocus sealed tube (λ = 1.54178 Å and 0.71073 Å respectively). The data reduction and absorption correction were performed with Apex3[2] software. The structure was solved by direct methods with SIR92[3] and refined by full-matrix least-squares on F^2 with CRYSTALS.[4] The positional and anisotropic thermal parameters of non-hydrogen atoms were refined. The positional and anisotropic thermal parameters of all non-hydrogen atoms were refined. All hydrogen atoms were found from a Fourier difference map and then recalculated into idealized positions and refined with riding constraints.

Crystal data for 2d (colorless, 0.149 x 0.175 x 392 mm):

$C_{17}H_{10}Br_2F_2N_6$, monoclinic, space group $P2_1/m$, a = 4.6371(10) Å, b = 33.771(7) Å, c = 5.6015(12) Å, β = 96.286(6)°, V = 871.9(3) Å^3, Z = 2, M = 496.11, 12951 reflections measured, 1637 independent reflections. Final R = 0.0610, wR = 0.1571, GoF = 1.0839 for 1491 reflections with I > 2σ(I) and 127 parameters. CCDC 2382300.

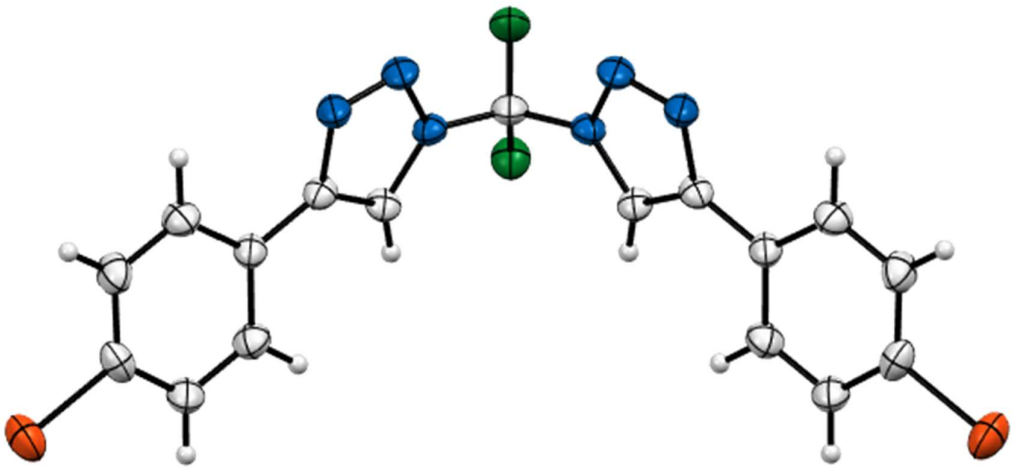


Figure S53: ORTEP[5] diagram of **2d**.

Crystal data 4 (colorless, 0.037 x 0.092 x 0.255 mm):

$C_{17}H_{11}F_1N_4$, monoclinic, space group $P2_1/c$, a = 13.7560(3) Å, b = 6.4533(2) Å, c = 16.5581(4) Å, β = 113.5808(7)°, V = 1347.15(6) Å^3, Z = 4, M = 290.30, 37999 reflections measured, 3093 independent reflections. Final R = 0.0457, wR = 0.1123, GoF = 1.0381 for 2282 reflections with I > 2σ(I) and 200 parameters. CCDC 2382301.

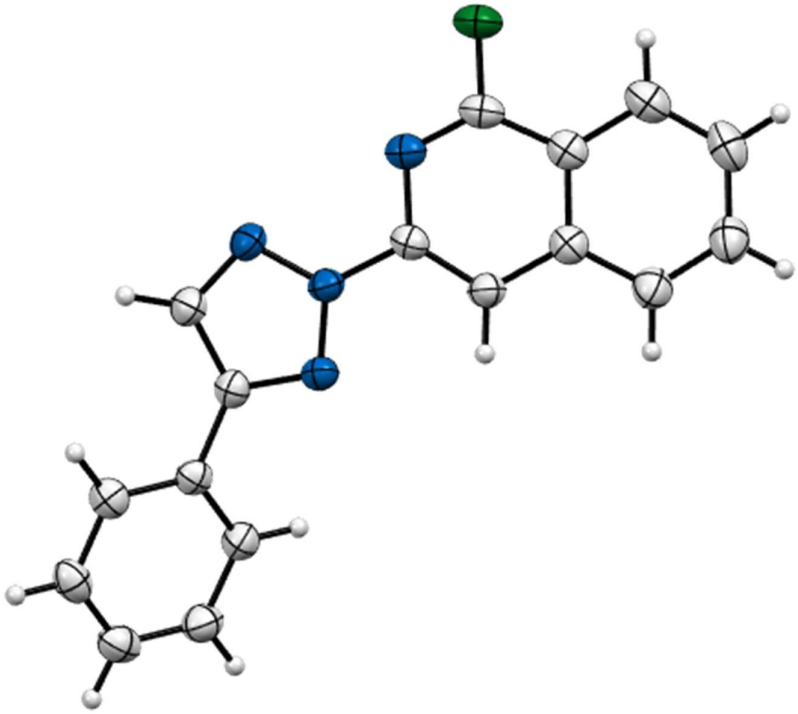


Figure S54: ORTEP diagram of **4**.

16. References

(1) Xu, J.; Ahmed, E.-A.; Xiao, B.; Lu, Q.-Q.; Wang, Y.-L.; Yu, C.-G.; Fu, Y. *Angew. Chem. Int. Ed*. **2015**, *54*, 8231.

(2) SAINT. Bruker AXS Inc., Madison, Wisconsin, USA, 2015.

(3) Altomare, A.; Cascarano, G.; Giacovazzo G.; Guagliardi A.; Burla M. C.; Polidori, G.; Camalli, M. *J. Appl. Cryst.* **1994,** *27*, 435.

(4) Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K., Watkin, D. J. *J. Appl. Cryst.* **2003**, *36*, 1487.

(5) Farrugia, L. J. WinGX and ORTEP for Windows: An Update. *J. Appl. Crystal.* **2012**, *45*, 849.