Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

A highly stable and versatile heterobifunctional fluoroalkylation reagent for preparation of fluorinated organic compounds

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Content

1.General Information

Materials

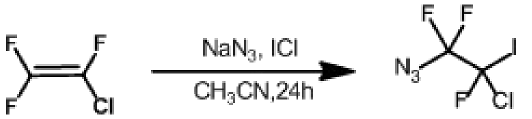
Chlorotrifluoroethylene (CTFE) was purchased from Zhejiang Juhua Co., Ltd, China. Sodium azide and Iodinemonochloride were purchased from Sinopharm Chemical Reagent Co., Ltd. copper(I)iodide, tetrabutylammonium acetate(TBAA) were purchased from Sigma-Aldrich. Unless otherwise stated, solvents were purchased Aladdin Industrial Corporation (Shanghai, China) in HPLC quality. The water was used after distillation.

Methods

^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker AM-300 spectrometer (300 MHz) with TMS as internal standard.^{19}F NMR spectra were taken on a Bruker AM-400(375 MHz) spectrometer using $PhCF_3$ as external standard.^{13}C NMR spectra were taken a Bruker AM-300(75 MHz) spectrometer. ^{1}H data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, hept = heptet, dd = doublet of doublet, m = multiplet, etc.), integration, and coupling constants (Hz). ^{13}C NMR data are reported in parts per million (ppm) on the δ scale. Infrared spectra were recorded on a JASCO FT/IR-4100 spectrometer. Elemental analysis C, H and N were obtained on Vario El III . High-resolution mass spectra (HRMS) were recorded on a BRUKER micrOTOF-QII spectrometer with ESI mode unless otherwise stated. Visible light irradiation was out using a 25 W, 240 V household light bulb that was positioned at about 10 cm from the reaction flask. Flash column chromatography was performed on silica gel (200–300 mesh) and thin layer chromatography (TLC) analyses were performed on commercial silica gel plates (60 F254).

2. Optimization conditions for CuAAC reaction between ACTI and phenylethyne

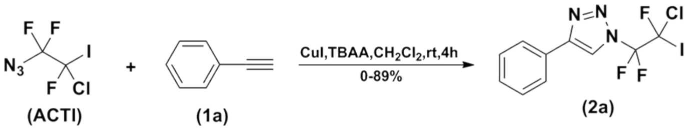
SI Table 1. Preparation of 2-Chloro-1,1,2-trifluoro-2-iodoethyl[a]



Entry	NaN_3 [equiv]	ICl [equiv]	CTFE [equiv]	T [℃]	Yield[b] [%]
1	1	1	6	rt	62
2	1.5	1	6	rt	65
3	1.1	1	3	-30	83

[a] Reaction conditions: ICl (5 mmol), NaN_3 (5.5 mmol) excess chlorotrifluoroethylene (CTFE) in 2 ml CH_3CN for 24 hours. [b] Yield was measured by weight base on ICl.

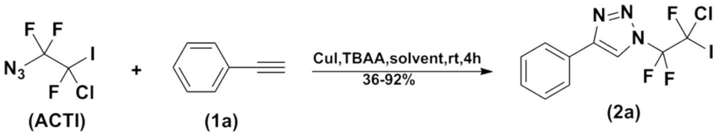
SI Table 2. Effects of the ratios of TBAA and CuI on CuAAC[a]



Entry	CuI [equiv]	TBAA [equiv]	Yield [%][b]
1	0.05	0	0
2	0.05	0.025	34
3	0.05	0.05	63
4	0.05	0.1	89
5	0.05	0.15	87
6	0.05	0.20	84
7	0.00	0.1	0
8	0.01	0.02	20
9	0.03	0.06	39
10	0.07	0.14	88
11	0.09	0.18	86

[a] The reaction was carried out using ACTI (1.5 mmol) and **1a** (1 mmol) in the presence of catalyst in 1 ml CH_2Cl_2 at room temperature under N_2 atmosphere for 4 hours. [b] Yields refer to isolation after chromatography.

SI Table 3. Effects of the solvent on CuAAC[a]



Entry	CuI [equiv]	TBAA [equiv]	Slovent	Yield [%][b]
1	0.05	0.1	C_6H_{12}	47
2	0.05	0.1	CH_2Cl_2	89
3	0.05	0.1	$PhCH_3$	92
4	0.05	0.1	EtOAc	87
5	0.05	0.1	THF	79
6	0.05	0.1	CH_3COCH_3	82
7	0.05	0.1	DMSO	73
8	0.05	0.1	EtOH	36
9	0.05	0.1	H_2O	55

[a] The reaction was carried out using **ACTI** (1.5 mmol) and **1a** (1 mmol) in the presence of catalyst in different solvents (1 ml) at room temperature under N_2 atmosphere for 4 hours. [b] Yields refer to isolation after chromatography.

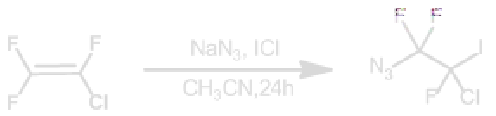
SI Table 4. Effects of the Cu and ammonium salts on CuAAC[a]

Entry	CuI [equiv]	Additive [equiv]	Time [h]	Yield [%][b]
1	Cu (0.05)	TBAA (0.1)	12	0
2	CuCl (0.05)	TBAA (0.1)	12	20
3	CuBr (0.05)	TBAA (0.1)	12	42
4	CuI (0.05)	TBAA (0.1)	4	92
5	$Cu(OAc)_2$(0.05)	TBAA (0.1)	12	0
6	CuI (0.05)	TBAI (0.1)	12	0
7	CuI (0.05)	TBAN (0.1)	12	0

[a] The reaction was carried out using **ACTI** (1.5 mmol) and **1a** (1 mmol) in the presence of different Cu and amine salts catalyst in 1ml toluene at room temperature under N_2 atmosphere. [b] Yields refer to isolation after chromatography.

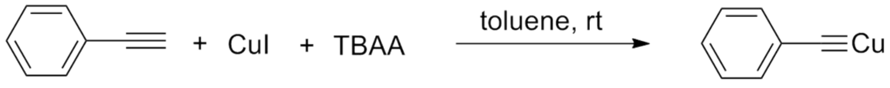
3. Experimental Procedures and Compound Characterization:

3.1 Synthesis of 1-azido-2-chloro-1,1,2-trifluoro-2-iodoethane (ACTI)

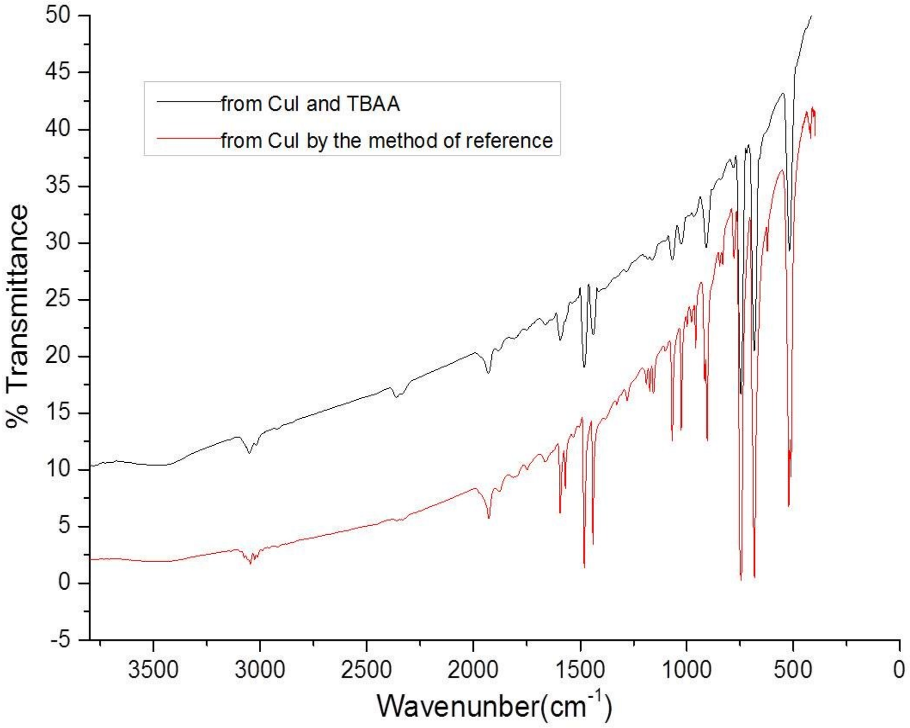


ICl (811 mg, 5 mmol, 1 eq) was added drop wise to a suspension of NaN$_3$ (357 mg, 5.5 mmol, 1.1eq) in 2 ml of CH$_3$CN for 15 minutes at -30℃ in a glass tube. Then the glass tube with resulting solution was transferred into a stainless steel autoclave equipped with a manometer, a safety inlet valve and a magnetic stirrer. Then the vessel was closed and immersed in the liquid nitrogen for 15 min. After several nitrogen–vacuum cycles to remove any traces of oxygen, a required quality of CTFE was condensed into the autoclave via a mass flow meter and the exact value was assessed by double weighing (the difference of weight before and after filling the autoclave with CTFE (1740 mg, 15mmol). After the reaction mixture was stirred at -30℃ for 24 h, all volatiles were removed under reduced pressure. The orange- brown product was poured into water (50 ml) and the mixture extracted with ether (3x50 ml). The ether extract was washed with 5% aqueous sodium thiosulphate solution and then water, and then dried by Na$_2$SO$_4$. Evaporation of the solvent afforded a light red oil product[1]: 1180 mg (4.15 mmol, 85%). ^{19}F NMR (376 MHz, CDCl$_3$) δ ppm -75.5 (t, J = 14.5 Hz), -86.0 (dd, J = 175.0, 14.4 Hz, 1F), -86.6 (dd, J = 174.9, 14.5 Hz, 1F). ^{13}C NMR (101 MHz, CDCl$_3$) δ ppm 116.6 (td, J = 274.2, 28.0 Hz), 71.3 (dt, J = 316.5, 43.1 Hz). Anal. Calcd for CCl$_2$F$_3$IN: C 8.42, N 14.72. Found: C 8.15, N 15.32.

3.2 Preparation of phenylethynylcopper(I) from phenylethyne and CuI/TBAA in toluene



To a suspension of CuI (2 mmol, 380 mg), TBAA (4 mmol, 1270 mg) in toluene (10 mL) was added phenylethyne (2 mmol, 204 mg) at room temperature without inert gas protection. On the moment after addition, large amount of yellow solid precipitated from the reaction system. After the reaction was stirred for 12 hours, it was cooled at 0℃for another 5minutes. The yellow solid was filtered and washed by ethanol (10 mL) and ether (10 mL). After it was dried on vacuum for 2 h, PhC≡CCu(I) was obtained (187 mg, 57%). IR (KBr): ν 1930, 1594, 1475, 1438, 889, 746 cm^{-1}. Anal. Calcd for C$_8$H$_5$Cu: C 58.35, H 3.06. Found: C 56.31, H 2.98.



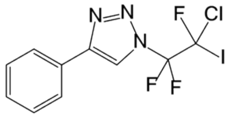
SI Figure 1. The IR spectra of PhC≡CCu for both our sample and comparing sample[2].

3.3 CuAAC reaction between ACTI and Alkynes

General procedure

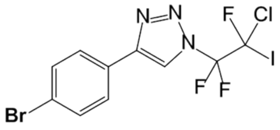
Alkyne (1 mmol, 1.0 equiv), CuI (0.05 mmol, 0.05 equiv), TBAA (0.1 mmol, 0.1 equiv) were placed in a 1 ml toluene under nitrogen.1-azido-2-chloro-1,1,2-trifluoro-2- iodoethane (1.5 mmol, 1.5 equiv) were added, the reaction was sealed at room temperature for 4 h whithout light. The reaction mixture was diluted with saturated aqueous NaCl (10 ml) and the resulting mixture extracted with ethyl acetate (3×20 ml). The combined ethyl acetate extracts were dryed ($NaSO_4$) and concentrated in vacuo. The residue purified by chromatography on silica gel.

1-(2-chloro-1,1,2-trifluoro-2-iodoethyl)-4-phenyl-1H-1,2,3-triazole (2a):



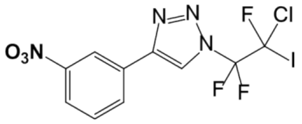
Purified by flash column chromatography (EtOAc/Petroleum ether, v/v 1/10). Colorless solid (356 mg, 92%). mp 89-90℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.82 (d, J = 7.8 Hz, 2H), 7.37 (dt, J = 26.2, 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.2 (s), 129.2 (s), 129.1 (s), 128.8 (s), 126.1 (s), 119.0 (s), 113.3 (td, J = 270.9, 27.6 Hz), 70.2 (dt, J = 317.1, 45.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -75.8 (t, J = 14.0 Hz, 1F), -87.8 (dd, J = 210.7, 14.3 Hz, 1F), -91.2 (dd, J = 210.4, 13.7 Hz, 1F). HRMS (ESI) *m/z* calcd for $C_{10}H_7F_3I^{35}ClN_3$, $C_{10}H_7F_3I^{37}ClN_3$ [M+H$^+$] 387.9320, 389.9290, found 387.9319, 389.9289.

4-(4-bromophenyl)-1-(2-chloro-1,1,2-trifluoro-2-iodoethyl)-1H-1,2,3-triazole(2b)



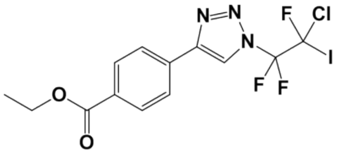
Purified by flash column chromatography (EtOAc/Petroleum ether, v/v 1/10). Colorless solid (285 mg, 61%). mp 120 - 121℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (s, 1H), 7.78 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.2 (s), 132.3 (s), 127.8 (s), 127.6 (s), 123.3 (s), 119.1 (s), 116.1 (s), 113.3 (d, *J* = 29.3 Hz), 110.6 (d, *J* = 29.0 Hz), 70.0 (dt, *J* = 95.6, 45.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -75.5 – -76.4 (m, 1F), -87.6 (dd, *J* = 210.6, 14.3 Hz, 1F), -91.0 (dd, *J* = 210.7, 13.6 Hz, 1F). HRMS (ESI) *m/z* calcd for $C_{10}H_6BrF_3I^{35}ClN_3$, $C_{10}H_6BrF_3I^{37}ClN_3$ [M+H$^+$] 465.8425, 467.8405, found 465.8423, 467.8401.

3-(1-(2-chloro-1,1,2-trifluoro-2-iodoethyl)-1H-1,2,3-triazol-4-yl)phenyl nitrate(2c)



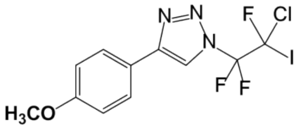
Purified by flash column chromatography (EtOAc/Petroleum ether, v/v 1/8). Yellow solid (315 mg, 73%). mp 139 – 140℃. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.71 (s, 1H), 8.48–8.14 (m, 2H), 7.71 (t, *J* = 8.0 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$): δ 148.8 (s), 146.0 (s), 131.9 (s), 130.6 (s), 130.3 (s), 123.8 (s), 121.0(s), 120.1 (s), 116.0 (d, *J* = 29.5 Hz), 113.3 (d, *J* = 29.5 Hz), 110.5(s), 69.7 (dt, *J* = 317.2, 44.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -76.1 (t, *J* = 14.0 Hz, 1F),-87.6 (dd, *J* = 210.7, 14.3 Hz, 1F), -91.0 (dd, *J* = 210.7, 13.6 Hz, 1F). HRMS (ESI) *m/z* calcd for $C_{10}H_5O_2F_3I^{35}ClN_4$ [M+H$^+$] 432.9098, found 432.9167.

ethyl4-(1-(2-chloro-1,1,2-trifluoro-2-iodoethyl)-1H-1,2,3-triazol-4-yl)benzoate (2d)



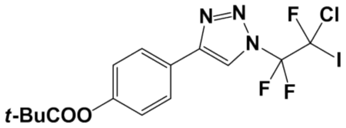
Purified by flash column chromatography (EtOAc/Petroleum ether, v/v 1/8). Colorless solid (340 mg,74%). mp 144 – 145℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (s, 1H), 8.15 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 8.4 Hz, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.1 (s), 147.9–146.0 (m), 132.9 (s), 131.0 (s), 130.6–129.9 (m), 126.4–125.4 (m), 120.4–119.2 (m), 117.1 (s), 113.3 (d, *J* = 29.7 Hz), 109.7(d, *J* = 29.2 Hz), 72.0 (t, *J* = 45.0 Hz), 67.5(d, *J* = 45.0 Hz), 61.2 (s), 14.3 (s). ^{19}F NMR (376 MHz, $CDCl_3$): δ -75.8 (t, *J* = 14.0 Hz, 1F), -87.8 (dd, *J* = 210.7, 14.3 Hz, 1F), -91.2 (dd, *J* = 210.4, 13.7 Hz, 1F). HRMS (ESI) *m/z* calcd for $C_{13}H_{11}O_2F_3I^{35}ClN_3$, $C_{13}H_{11}O_2F_3I^{37}ClN_3$ [M+H$^+$]459.9531, 461.9502, found 459.9530, 461.9500.

1-(2-chloro-1,1,2-trifluoro-2-iodoethyl)-4-(4-methoxyphenyl)-1H-1,2,3-triazole(2e)



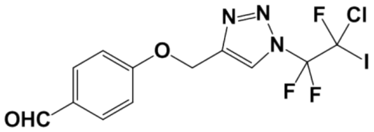
Purified by flash column chromatography (EtOAc/Petroleum ether, v/v 1/8). Colorless solid (358 mg, 86%). mp 103 – 104°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (s, 1H), 7.83 (d, *J* = 8.7 Hz, 2H), 7.01 (d, *J* = 8.7 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.4 (s), 148.0 (s), 127.5 (s), 121.4 (s), 118.0 (s), 116.0(d, *J* = 28.9 Hz), 114.5 (s), 113.3 (d, *J* = 29.0 Hz), 110.6 (d, *J* = 29.3 Hz), 70.3 (dt, *J* = 317.5, 45.5 Hz), 55.4 (s). ^{19}F NMR (376 MHz, $CDCl_3$): δ -76.0 (t, *J* = 13.8 Hz, 1F), -87.7 (d, *J* = 205.9 Hz, 1F), -91.1 (d, *J* = 213.3 Hz, 1F). HRMS (ESI) *m/z* calcd for $C_{11}H_9OF_3I^{35}ClN_3$, $C_{11}H_9OF_3I^{37}ClN_3$ [M+H$^+$] 417.9425, 417.9396, found 417.94232, 419.9394.

4-(1-(2-chloro-1,1,2-trifluoro-2-iodoethyl)-1H-1,2,3-triazol-4-yl)phenyl pivalate(2f)



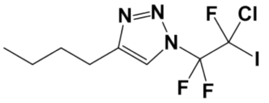
Purified by flash column chromatography (EtOAc/Petroleum ether, v/v 1/8). Yellow solid (409 mg, 84%). mp 124 – 125℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (s), 8.02–7.83 (m), 7.26–7.11 (m), 1.40 (s). ^{13}C NMR (101 MHz, $CDCl_3$): δ 176.9 (s), 151.8 (s), 147.5 (s), 127.2 (s), 126.3 (s), 122.3 (s), 119.0 (s), 113.3 (td, *J* = 270.9, 29.3 Hz), 70.1 (dt, *J* = 317.2, 45.2 Hz), 39.2 (s), 27.1 (s). ^{19}F NMR (376 MHz, $CDCl_3$): δ -75.9 (t, *J* = 14.0 Hz, 1F), -87.8 (dd, *J* = 210.8, 14.5 Hz, 1F), -91.1 (dd, *J* = 210.7, 13.6 Hz, 1F). HRMS (ESI) *m/z* calcd for $C_{15}H_{15}O_2F_3I^{35}ClN_3$, $C_{15}H_{15}O_2F_3I^{37}ClN_3$ [M+H$^+$]487.9844,489.9815, found 487.9842, 589.9812.

4-((1-(2-chloro-1,1,2-trifluoro-2-iodoethyl)-1H-1,2,3-triazol-4-yl)methoxy)benzaldehyde(2g)



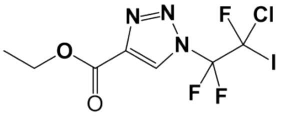
Purified by flash column chromatography (EtOAc/Petroleum ether, v/v 1/8). Colorless solid (347 mg, 78%). mp 134– 135℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.93 (s, 1H), 8.06 (s, 1H), 7.89 (d, *J* = 8.8 Hz, 2H), 7.13 (d, *J* = 8.7 Hz, 2H), 5.38 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 189.7 (s), 161.7 (s), 147.1–143.8 (m), 131.1 (s), 129.770 (s), 121.8 (s), 115.0 (d, *J* = 29.6 Hz), 114.0 (s), 112.3 (d, *J* = 29.1 Hz), 109.6 (d, *J* = 29.2 Hz), 68.8 (dt, *J* = 317.1, 45.0 Hz), 60.6 (s). ^{19}F NMR (376 MHz, $CDCl_3$): δ -76.2 (t, *J* = 13.9 Hz, 1F), -87.5 (dd, *J* = 210.7, 14.3 Hz, 1F), -90.9 (dd, *J* = 210.8, 13.5 Hz, 1F). HRMS (ESI) *m/z* calcd for $C_{12}H_9O_2F_3I^{35}ClN_3$, $C_{12}H_9O_2F_3I^{37}ClN_3$ [M+H$^+$] 445.9375, 447.9345, found 445.9378, 447.9358.

1-(2-chloro-1,1,2-trifluoro-2-iodoethyl)-4-pentyl-1H-1,2,3-triazole(2h)



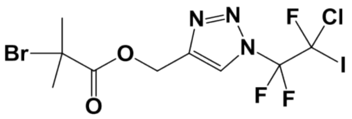
Purified by flash column chromatography (EtOAc/Petroleum ether, v/v 1/8). Yellow oil (330 mg, 90%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.62 (s, 1H), 2.95–2.55 (m, 2H), 1.67 (dt, *J* = 15.3, 7.5 Hz, 2H), 1.48–1.26 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz,, CDCl$_3$): δ 148.9 (s), 120.3 (s), 113.2 (td, *J* = 269.5, 28.9 Hz), 70.5 (dt, *J* = 317.6, 45.6 Hz), 31.1 (s), 25.0 (s), 22.2 (s), 13.7 (s). ^{19}F NMR (376 MHz, CDCl$_3$): δ -75.6 (d, *J* = 13.2 Hz, 1F), -87.9 (dd, *J* = 210.6, 14.3 Hz, 1F), -91.2 (dd, *J* = 210.7, 13.7 Hz, 1F). HRMS (ESI) *m/z* calcd for $C_8H_{11}F_3I^{35}ClN_3$, $C_8H_{11}F_3I^{37}ClN_3$ [M+H$^+$] 367.9633, 369.9603, found 367.9631, 369.9600.

ethyl 1-(2-chloro-1,1,2-trifluoro-2-iodoethyl)-1H-1,2,3-triazole-4-carboxylate(2i)



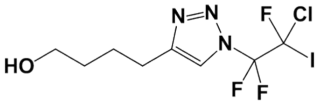
Purified by flash column chromatography (EtOAc/Petroleum ether, v/v 1/8). Yellow oil (325 mg, 85%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.48 (s, 1H), 4.49 (q, *J* = 7.1 Hz, 2H), 1.45 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 159.5 (s), 140.6 (s), 127.5 (s), 113.3 (td, *J* = 272.5, 29.8 Hz), 69.3 (dt, *J* = 316.9, 44.1 Hz), 62.1 (s), 14.3 (s). ^{19}F NMR (376 MHz, CDCl$_3$): δ -76.6 (t, *J* = 13.9 Hz, 1F), -87.6 (dd, *J* = 210.7, 14.3 Hz, 1F), -91.0 (dd, *J* = 210.8, 13.5 Hz, 1F). HRMS (ESI) *m/z* calcd for $C_7H_7O_2F_3I^{35}ClN_3$, $C_7H_7O_2F_3I^{37}ClN_3$ [M+H$^+$] 383.9218, 385.9189, found 383.9222, 385.9192.

(1-(2-chloro-1,1,2-trifluoro-2-iodoethyl)-1H-1,2,3-triazol-4-yl)methyl 2-bromo-2-methylpropanoate (2j)



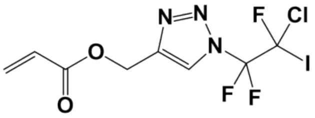
Purified by flash column chromatography (EtOAc/Petroleum ether, v/v 1/8). Yellow oil (367 mg, 75%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.01 (s, 1H), 5.37 (s, 2H), 1.90 (s, 6H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 171.4 (s), 142.9 (s), 123.7(s), 113.2 (td, *J* = 271.1, 29.2 Hz), 69.9 (dt, *J* = 317.4, 44.8 Hz), 58.4 (s), 55.2 (s), 30.6 (s). ^{19}F NMR (376 MHz, CDCl$_3$): δ -76.1 (t, *J* = 14.0 Hz, 1F), -87.8 (dd, *J* = 210.7, 14.3 Hz, 1F), -91.1 (dd, *J* = 210.5, 13.6 Hz, 1F). HRMS (ESI) *m/z* calcd for $C_9H_{10}O_2F_3I^{35}Cl^{79}BrN_3$, $C_9H_{10}O_2F_3I^{35}Cl^{81}BrN_3$, $C_9H_{10}O_2F_3I^{37}Cl^{81}BrN_3$ [M+H$^+$] 489.8636, 491.8616, 493.8586 found 489.8638, 491.8614, 493.8587.

4-(1-(2-chloro-1,1,2-trifluoro-2-iodoethyl)-1H-1,2,3-triazol-4-yl)butan-1-ol(2k)



Purified by flash column chromatography (EtOAc/Petroleum ether, v/v 1/8). Yellow oil (287 mg, 75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69 (s, 1H), 3.72 (t, *J* = 6.3 Hz, 2H), 2.85 (t, *J* = 7.6 Hz, 2H), 1.97–1.77 (m, 2H), 1.68 (tt, *J* = 13.2, 6.4 Hz, 2H), 1.58–1.42 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.5 (s), 124.0–119.0 (m), 113.2 (td, *J* = 270.0, 29.0 Hz), 70.4 (dt, *J* = 91.1, 45.0 Hz), 63.8–59.6 (m), 34.3–30.3 (m), 25.1 (d, *J* = 24.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -75.9 (s, 1F), -87.9 (d, *J* = 210.6 Hz, 1F), -90.18 – -92.2 (m, 1F). HRMS (ESI) *m/z* calcd for $C_8H_{11}OF_3I^{35}ClN_3$, $C_8H_{11}OF_3I^{37}ClN_3$ [M+H$^+$] 383.9582, 385.9552, found 383.9581, 385.9550.

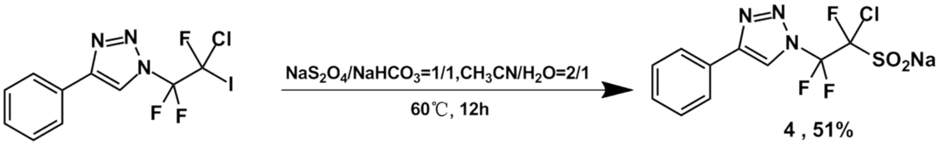
(1-(2-chloro-1,1,2-trifluoro-2-iodoethyl)-1H-1,2,3-triazol-4-yl)methyl acrylate(2l)



Purified by flash column chromatography (EtOAc/Petroleum ether, v/v 1/8). Yellow oil (355 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.00 (s, 1H), 6.44 (d, *J* = 17.3 Hz, 1H), 6.12 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.87 (d, *J* = 11.5 Hz, 1H), 5.34 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8 (s), 143.3 (s), 132.1 (s), 127.6 (s), 123.9 (s), 113.2 (td, *J* = 271.0, 29.4 Hz), 69.8 (dt, *J* = 317.5, 44.9 Hz), 57.0 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -75.9 (t, *J* = 14.0 Hz, 1F), -87.8 (dd, *J* = 210.6, 14.3 Hz, 1F), -91.2 (dd, *J* = 210.6, 13.7 Hz, 1F). HRMS (ESI) *m/z* calcd for $C_8H_7O2F_3I^{35}ClN_3$, $C_8H_7O2F_3I^{37}ClN_3$ [M+H$^+$] 395.9218, 397.9189, found 395.9212, 397.9182.

4. Representative fluoroalkylation reactions using 2a as a reagent

4.1 sodium 1-chloro-1,2,2-trifluoro-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethanesulfinate

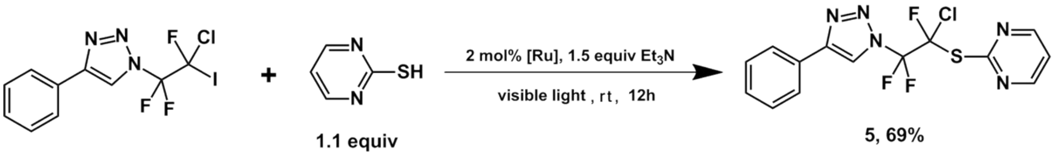


Compound **2a** (195 mg, 0.5 mmol) was added into deoxygenated aqueous acetonitrile solution (1 ml H_2O and 0.5 ml acetonitrile) containing $NaHCO_3$ (84 mg, 1 mmol) and $Na_2S_2O_4$ (174 g, 1 mmol) under nitrogen at room temperature. The mixture was heated at 60 °C for 12 h. The two-phase solution obtained was cooled to room temperature and ethyl acetate was added. The aqueous solution was extracted with a small amount of ethyl acetate several times. Finally, the ethyl acetate layer was dried over anhydrous Na_2SO_4. The solid obtained after removal of ethyl acetate. It was further purified by flash column chromatography (CH_2Cl_2/CH_3OH, v/v 3/1) to yield **5** as colorless solid (88mg, 51%).

^{1}H NMR (300 MHz, CD_3OD) δ ppm 8.79 (s, 1H), 7.92 (d, *J* = 7.5 Hz,2H), 7.62 – 7.26 (m, 3H). ^{13}C NMR (75 MHz, *d*-DMSO) δ ppm 146.6 – 146.2 (m), 129.4 – 128.9 (m), 128.6 (s), 125.8 – 125.4 (m), 121.1 –120.6 (m). ^{19}F NMR (376 MHz, CD_3OD) δ -91.9 (dd, *J* = 220.4, 7.3 Hz, 1F), -92.9 (dd, *J* = 220.3, 10.3 Hz, 1F), -135. 0 (t, *J* = 8.8 Hz, 1F).

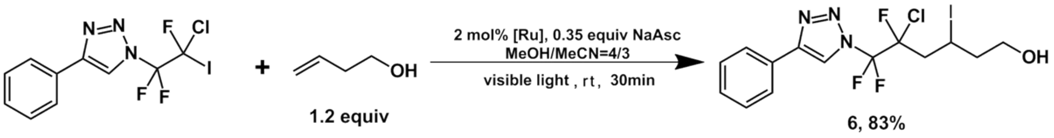
HRMS (ESI) *m/z* calcd for $C_{10}H_6O_2F_3I^{35}ClN_3SNa$, $C_{10}H_6O_2F_3I^{37}ClN_3SNa$ [M-Na$^+$] 323.9816, 325.9781, found 323.9812, 325.9780.

4.2 2-((1-chloro-1,2,2-trifluoro-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethyl)thio)pyrimidine



A 10 mL round bottom flask was equipped with a rubber septum and a magnetic stir bar and was charged with compound **2a** (195 mg, 0.5 mmol, 1 equiv), MeCN (2.0 mL), 2-Mercaptopyrimidine (62 mg, 0.55 mmol, 1.1 equiv), Et_3N (76mg, 0.75 mmol, 1.5 equiv), $Ru(bpy)_3Cl_2$ (6.4 mg, 0.001 mmol, 0.02 equiv). The mixture was then degassed by Ar sparging for 15 min. The mixture was then stirred under an Ar atmosphere and irradiated by 15W blue LEDs for 12 hours. After the reaction was complete, the reaction mixture was diluted with EtOAc and washed with water. The organic layer was then washed with brine and dried with sodium sulfate. The solid obtained after removal of ethyl acetate. It was further purified by flash column chromatography (EtOAc/Petroleum ether, v/v 1/2) to yield **6** as colorless solid (128mg, 69%). mp 112 – 113℃. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.52 (d, *J* = 4.9 Hz, 2H), 8.16 (s, 1H), 7.95–7.73 (m, 2H), 7.57–7.32 (m, 3H), 7.10 (t, *J* = 4.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.9 (d, *J* = 2.1 Hz), 157.9 (s), 148.1 (s), 129.0 (s), 126.0 (s), 119.4 (s), 115.8–109.0 (m). ^{19}F NMR (376 MHz, $CDCl_3$,): δ -90.9 (dd, *J* = 11.4, 5.7 Hz, 2F), -100.5 (t, *J* = 12.6 Hz, 1F). HRMS (ESI) *m/z* calcd for $C_{14}H_9F_3{}^{35}ClN_5S$, $C_{14}H_9F_3{}^{35}ClN_5S$ [M+H$^+$] 372.0292, 374.0265, found 372.0292, 374.0261.

4.3 5-chloro-5,6,6-trifluoro-3-iodo-6-(4-phenyl-1H-1,2,3-triazol-1-yl)hexan-1-ol

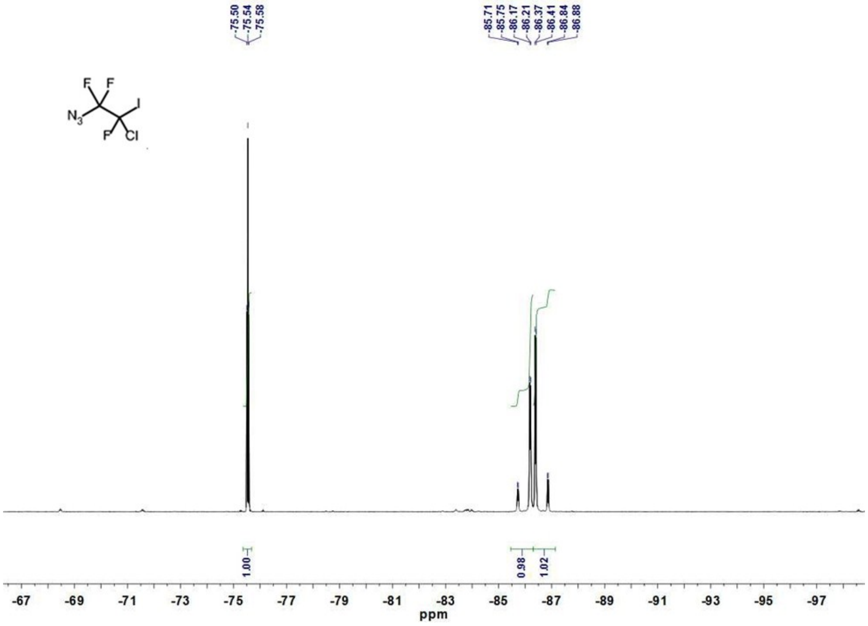


A 10 mL round bottom flask was equipped with a rubber septum and a magnetic stir bar and was charged with compound **3a** (195 mg, 0.5 mmol, 1 equiv), 3-Buten-1-ol(43mg, 0.6mmol, 1.2 equiv), MeCN (2.0 mL), MeOH (1.5 mL), sodium L-ascorbate (34mg, 0.175 mmol, 0.35 equiv.), $Ru(bpy)_3Cl_2$ (6.4 mg, 0.001 mmol, 0.02 equiv).The mixture was then degassed by Ar sparging for 15 min. The mixture was then stirred under an Ar atmosphere and irradiated by 25W blue LEDs for 30 min. After the reaction was complete, the reaction mixture was diluted with EtOAc and washed with water. The organic layer was then washed with brine and dried with sodium sulfate. After removal of ethyl acetate, it was purified by flash column chromatography (EtOAc/Petroleum ether, v/v 1/5) to yield diastereomeric **7** as yellow oil (190mg, 83%). The diastereomeric ratios is 0.54: 0.46 determinated by ^{1}H NMR.

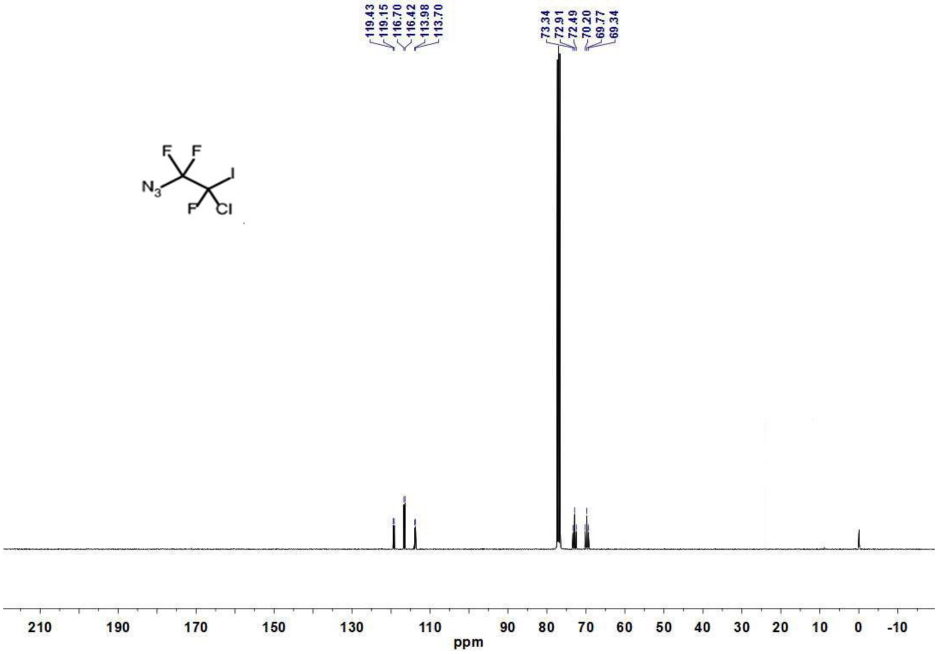
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 6.3 Hz, 1H), 8.00–7.78 (m, 2H), 7.44 (dt, *J* = 26.7, 7.2 Hz, 3H), 4.65 (dddd, *J* = 21.5, 13.3, 8.8, 4.4 Hz, 1H), 4.19–3.65 (m, 2H), 3.48–3.00 (m, 2H), 2.38–1.76 (m, 2H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 148.2 (d, J = 5.7 Hz), 129.2 (s), 129.1 (s), 128.79 (s), 126.1 (s), 118.9 (d, J = 4.5 Hz), 115.0 (dd, J = 41.8, 30.6 Hz), 112.5–110.3 (m), 109.9–107.5 (m), 62.4 (d, J = 88.8 Hz), 46.1 (dd, J = 53.7, 19.1 Hz), 43.2 (s), 41.7 (d, J = 3.1 Hz), 20.3 (s), 18.2 (s). ^{19}F NMR (376 MHz, CDCl$_3$): δ -93.70 (t, J = 8.1 Hz, 2F), -94.05 (dd, J = 24.2, 8.4 Hz, 2F), -119.55 (ddd, J = 33.6, 18.4, 7.4 Hz, 1F), -122.47 – -123.28 (m, 1F). HRMS (ESI) *m/z* calcd for $C_{14}H_{14}OF_3I^{35}ClN_3$, $C_{14}H_{14}OF_3I^{37}ClN_3$ [M+H$^+$] 459.9895, 461.9865, found 459.9898, 461.9872.

5. ^{1}H, ^{19}F, ^{13}C NMR Spectra of Corresponding Compunds

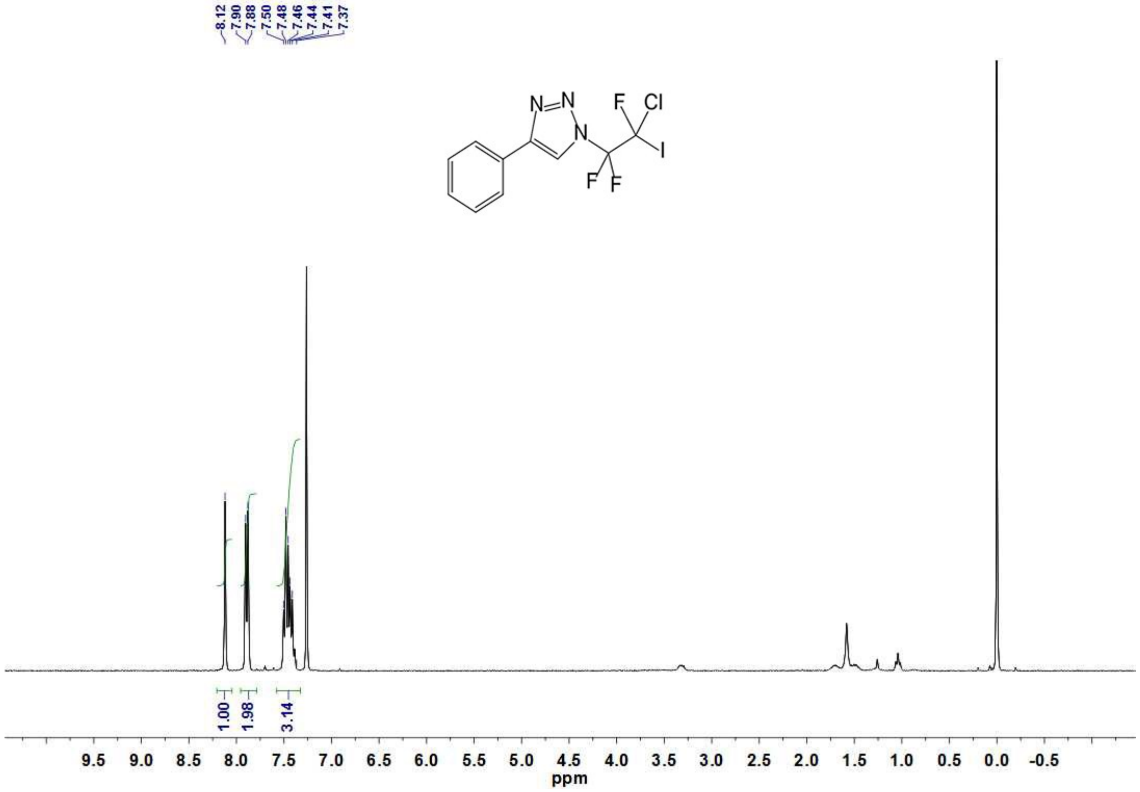
^{19}F NMR of Compound ACTI (376 MHz, CDCl$_3$)



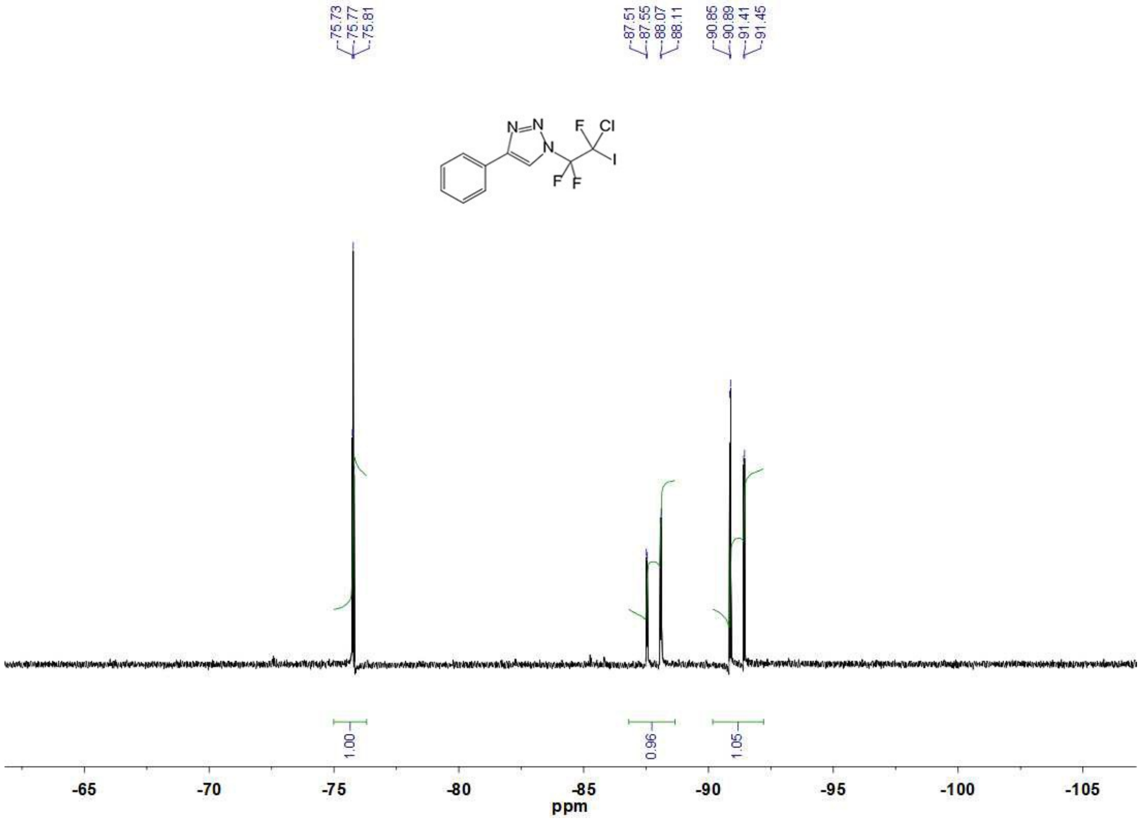
^{13}C NMR of Compound ACTI (101 MHz, CDCl$_3$)



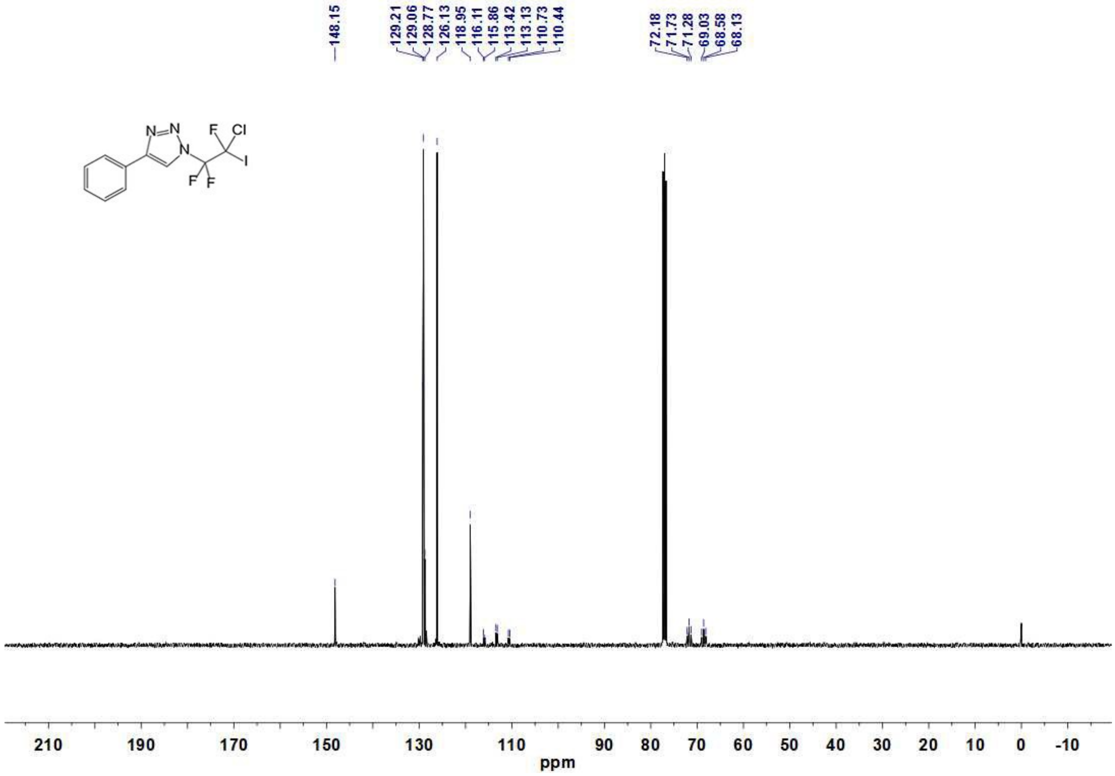
^{1}H NMR of 2a (400 MHz, CDCl$_3$)



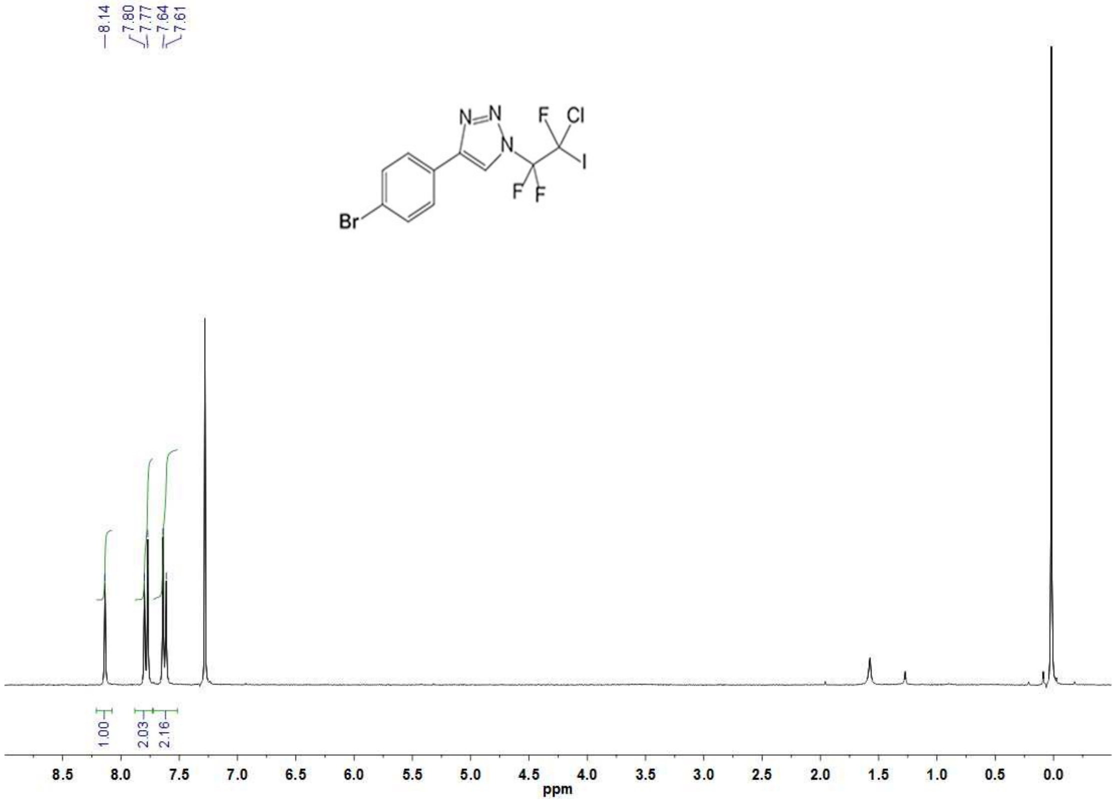
^{19}F NMR of 2a (376 MHz, CDCl$_3$)



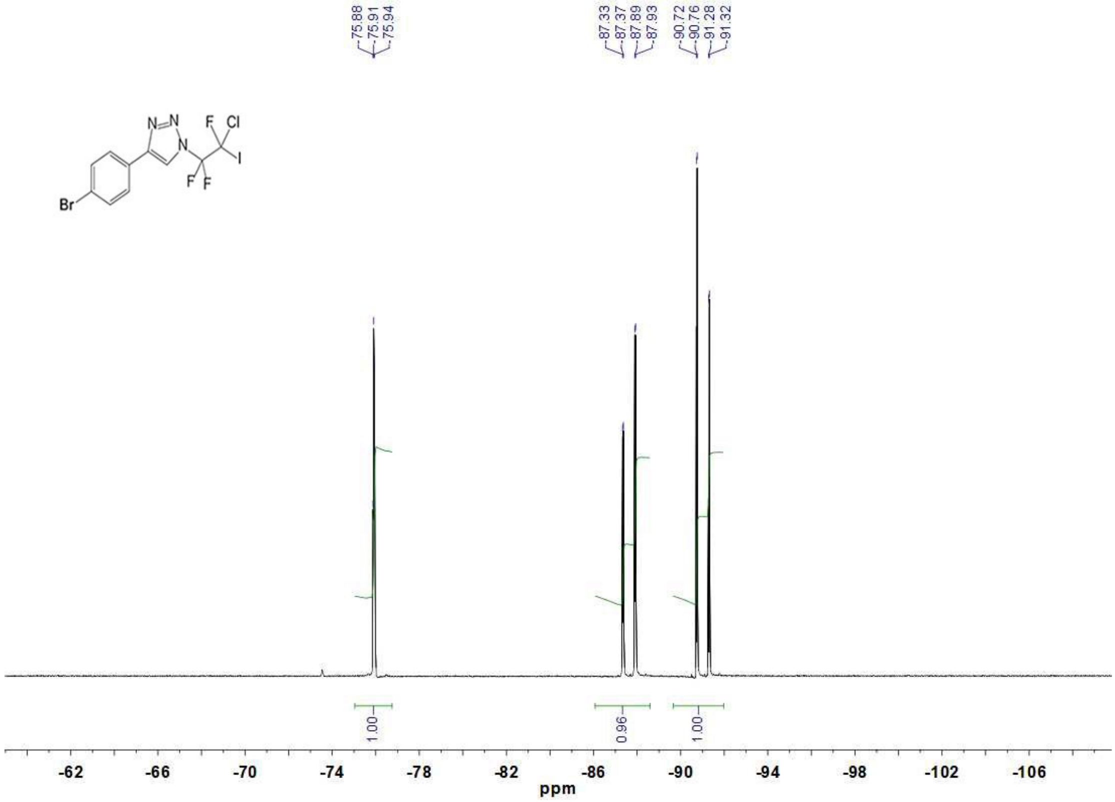
^{13}C NMR of 2a (101 MHz, CDCl$_3$)



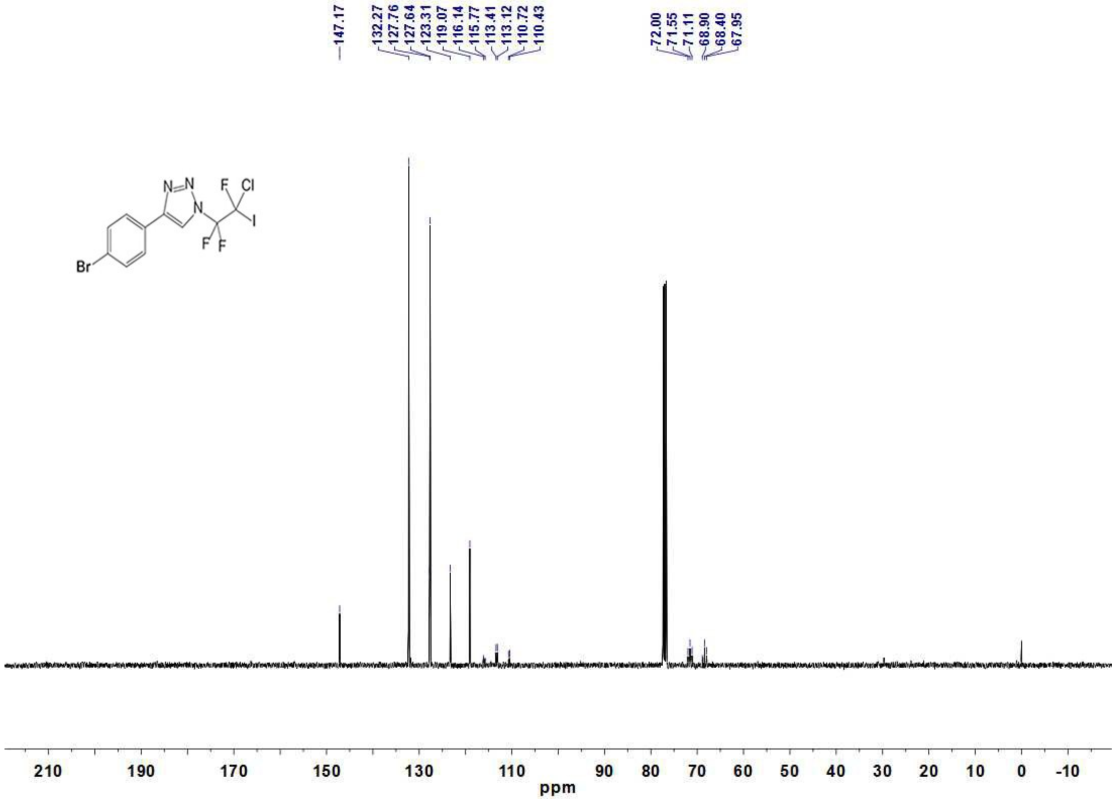
^{1}H NMR of 2b (400 MHz, CDCl$_3$)



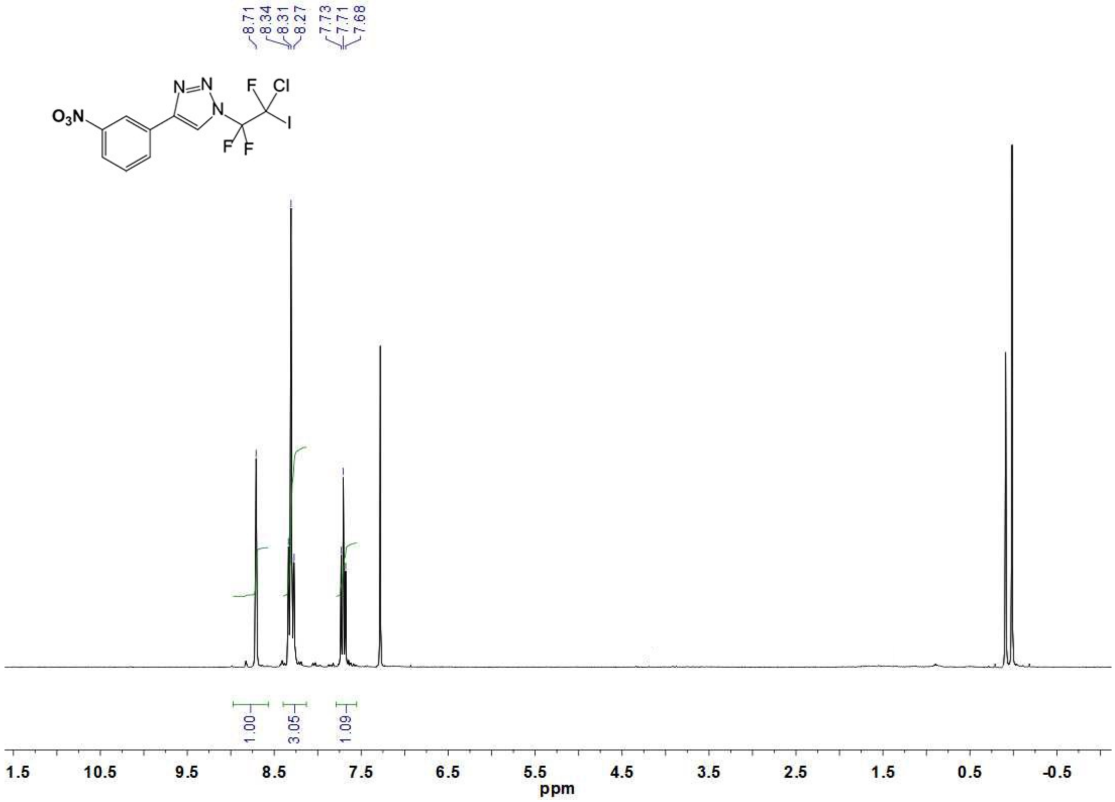
^{19}F NMR of 2b (376 MHz, CDCl$_3$)



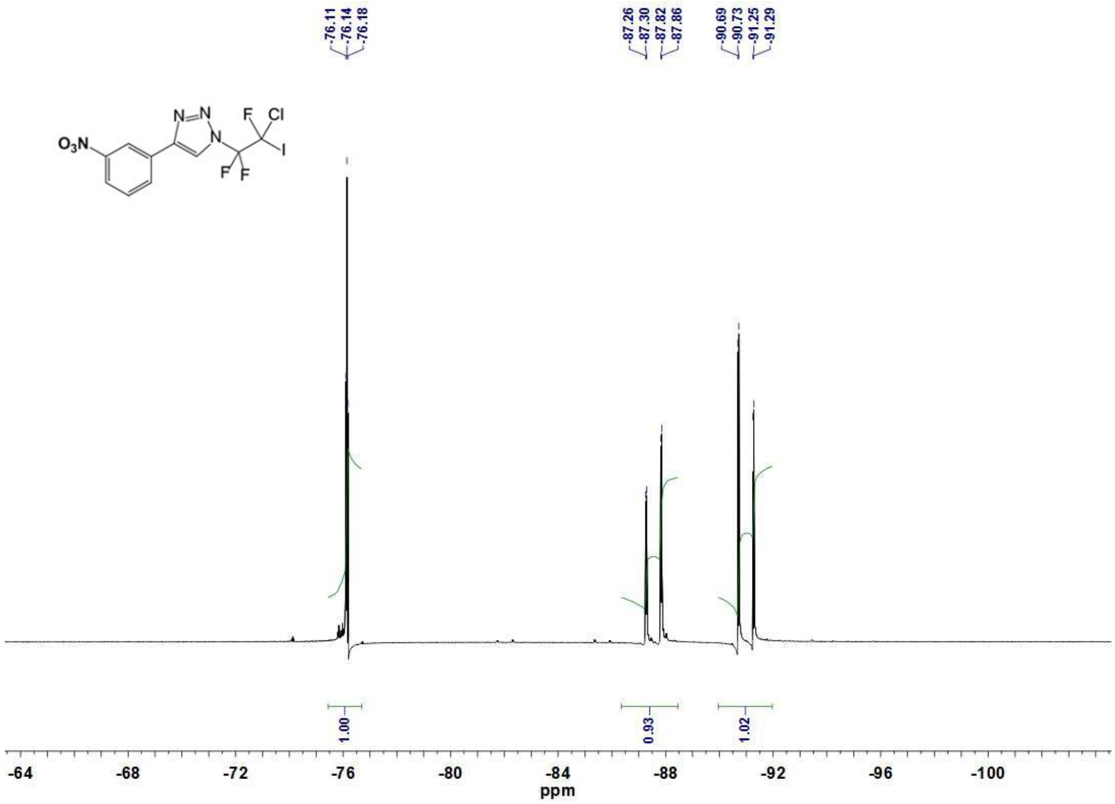
^{13}C NMR of 2b (101 MHz, CDCl$_3$)



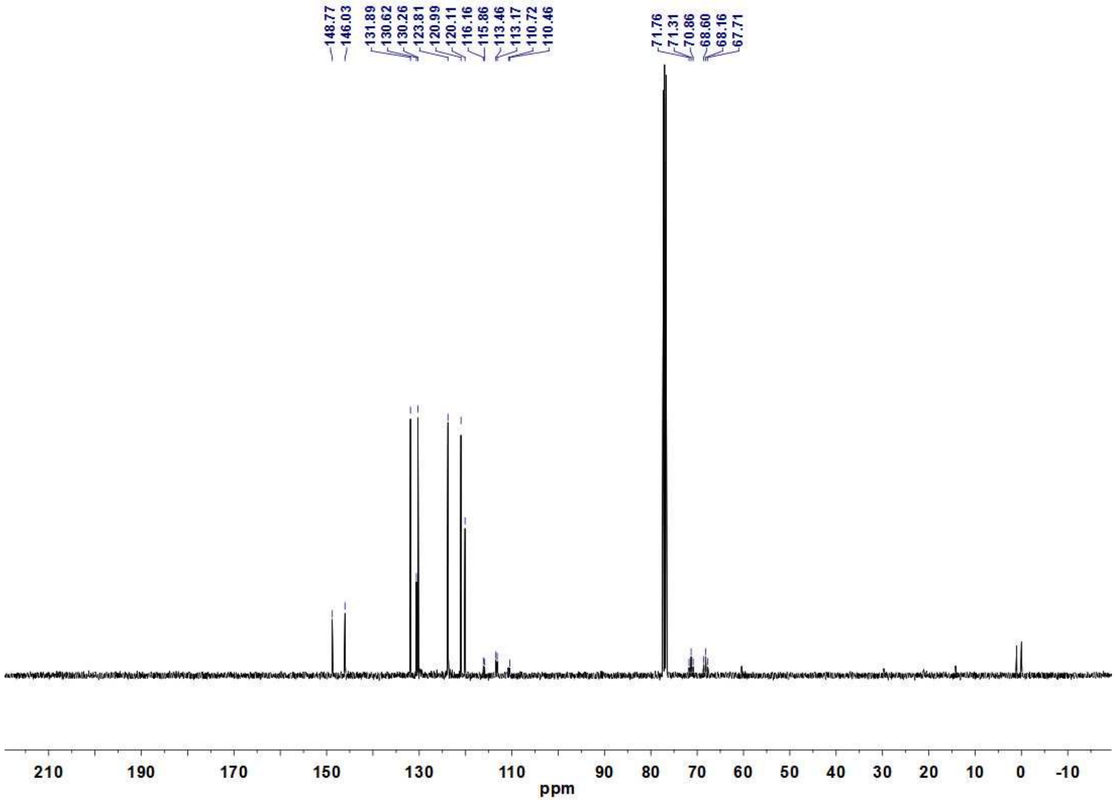
^{1}H NMR of 2c (400 MHz, CDCl$_3$)



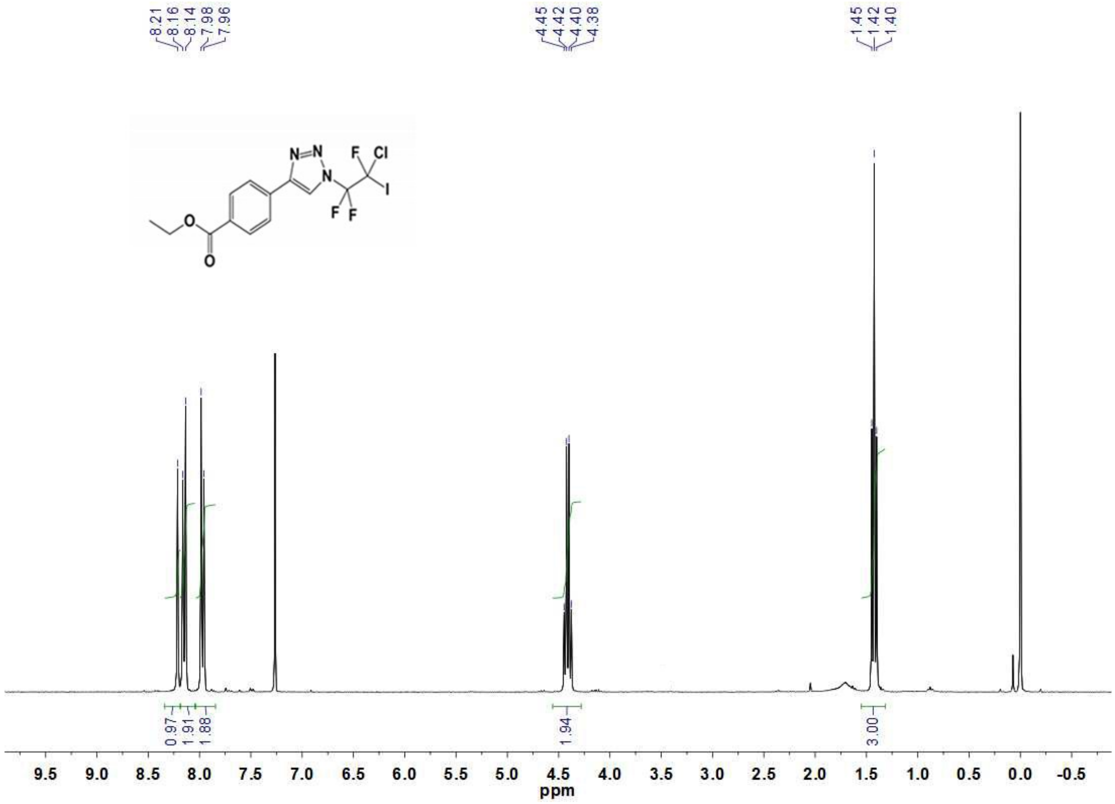
^{19}F NMR of 2c (376 MHz, CDCl$_3$)



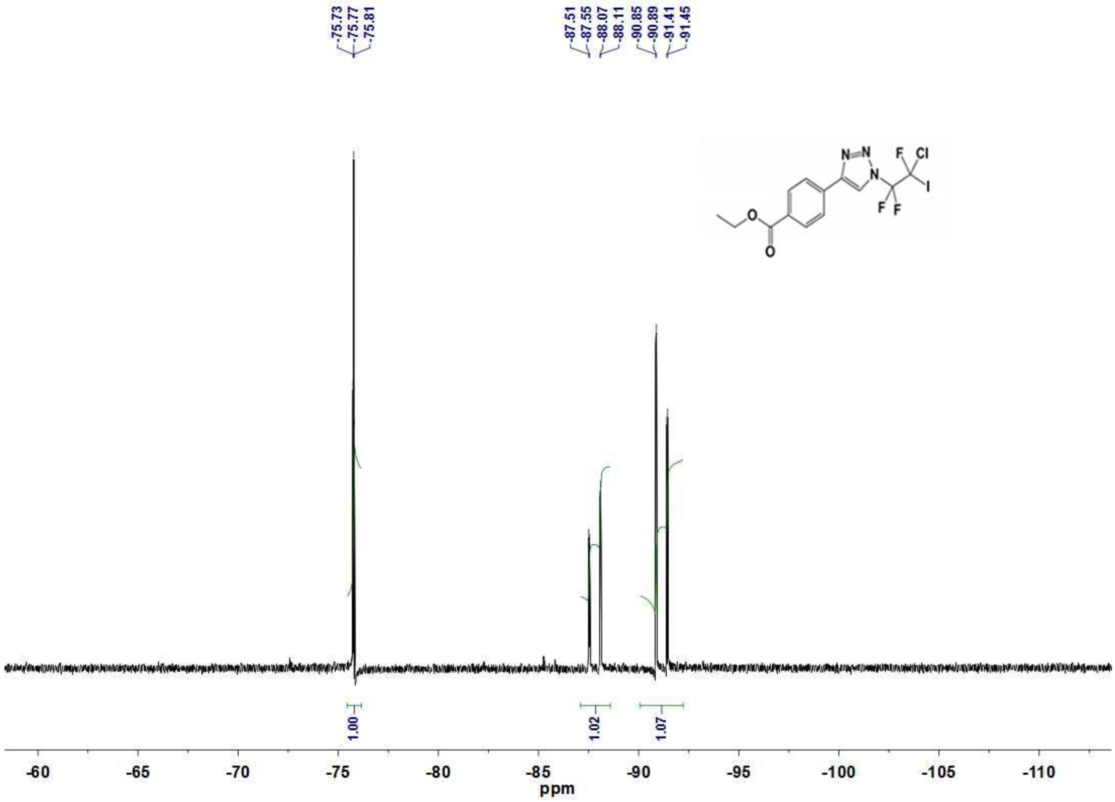
^{13}C NMR of 2c (101 MHz, CDCl$_3$)



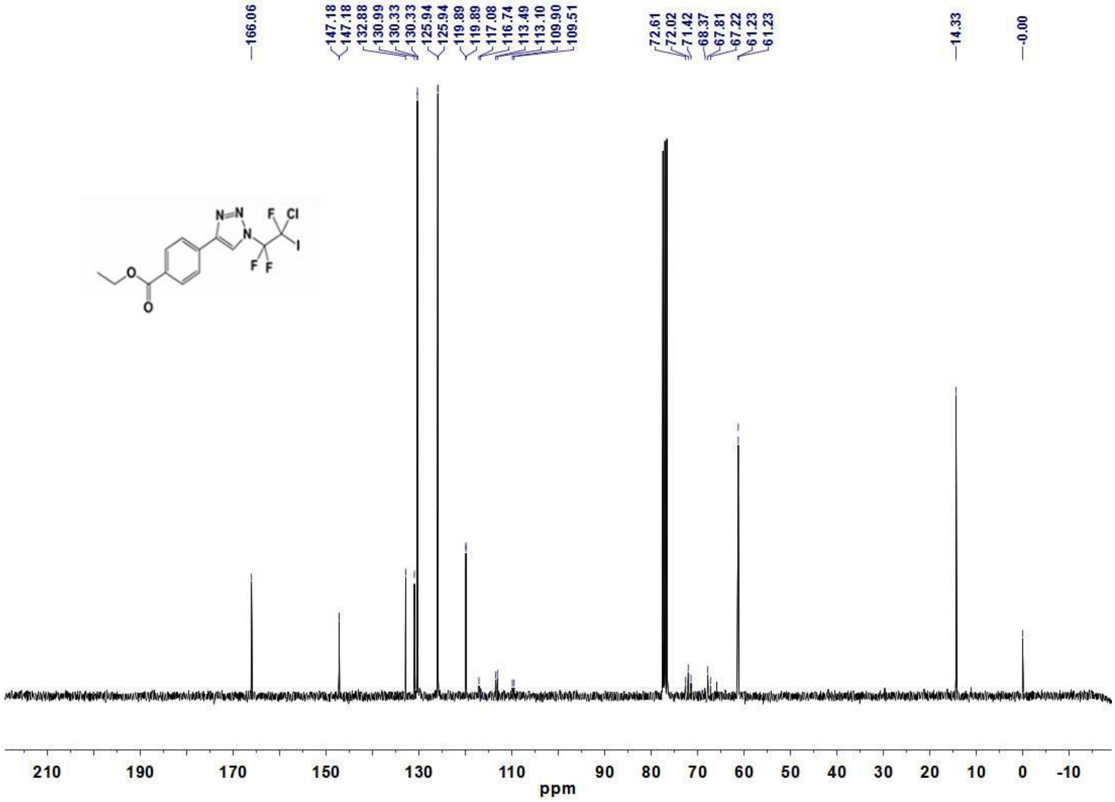
^{1}H NMR of 2d (400 MHz, CDCl$_3$)



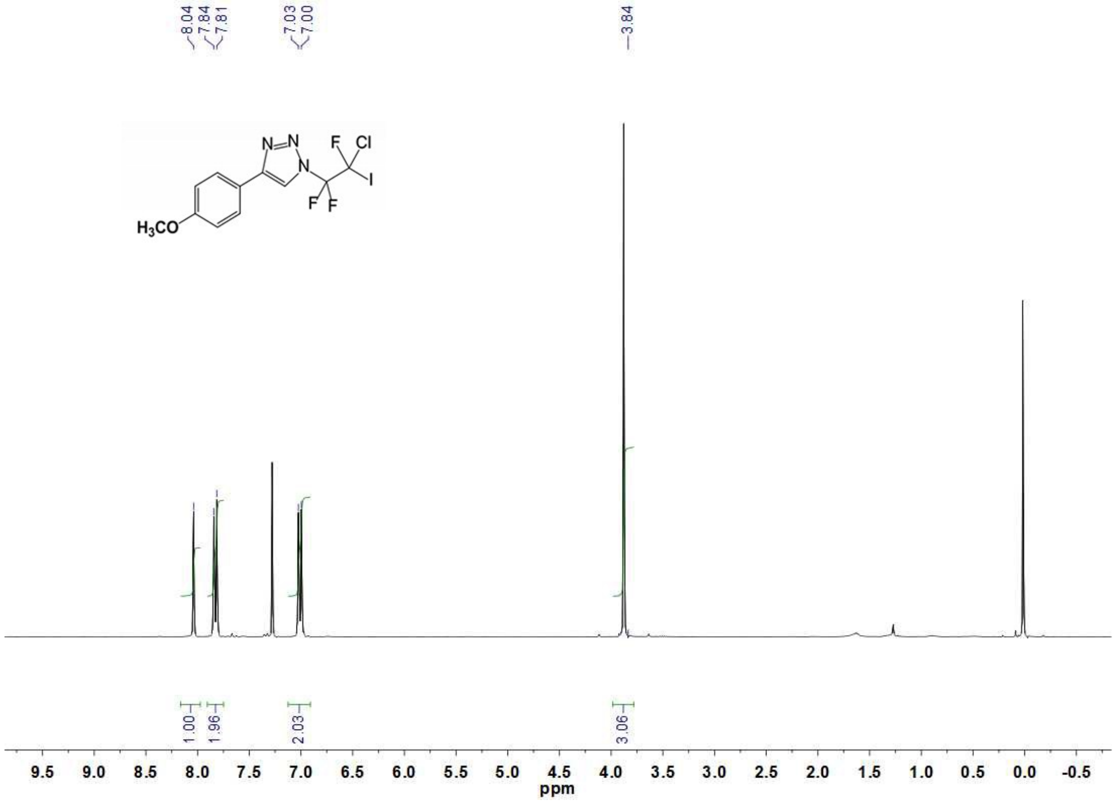
^{19}F NMR of 2d (376 MHz, CDCl$_3$)



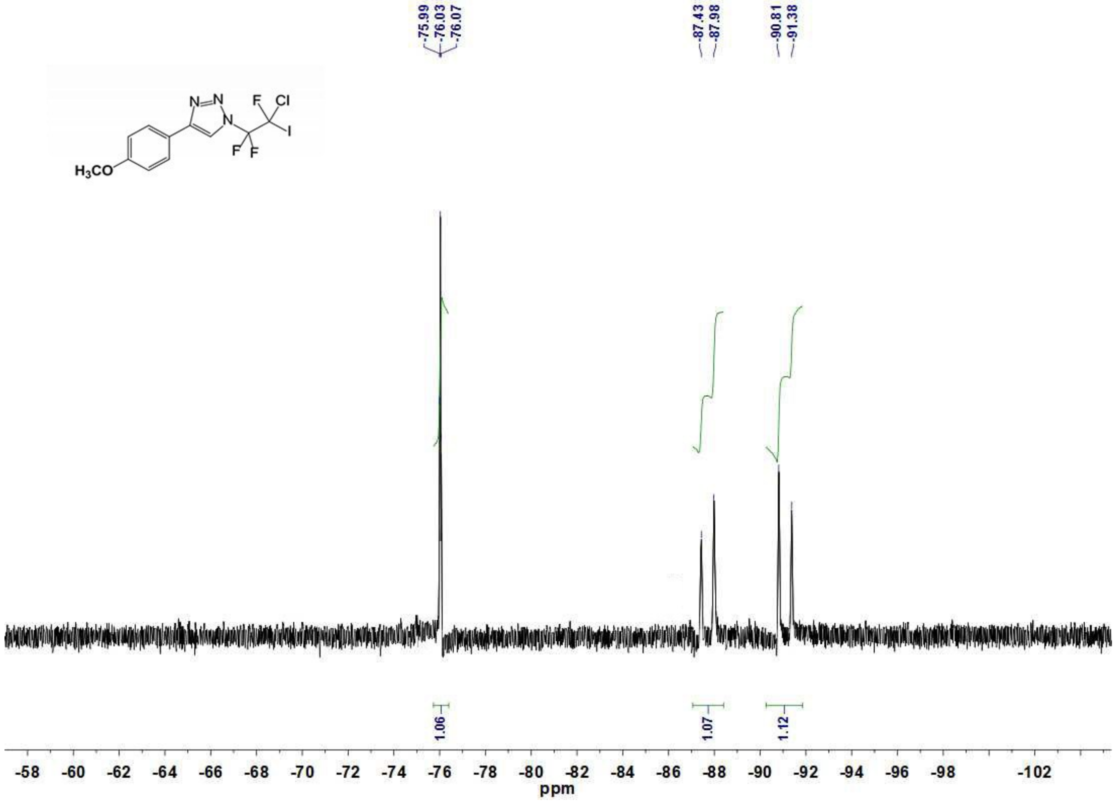
^{13}C NMR of 2d (101 MHz, CDCl$_3$)



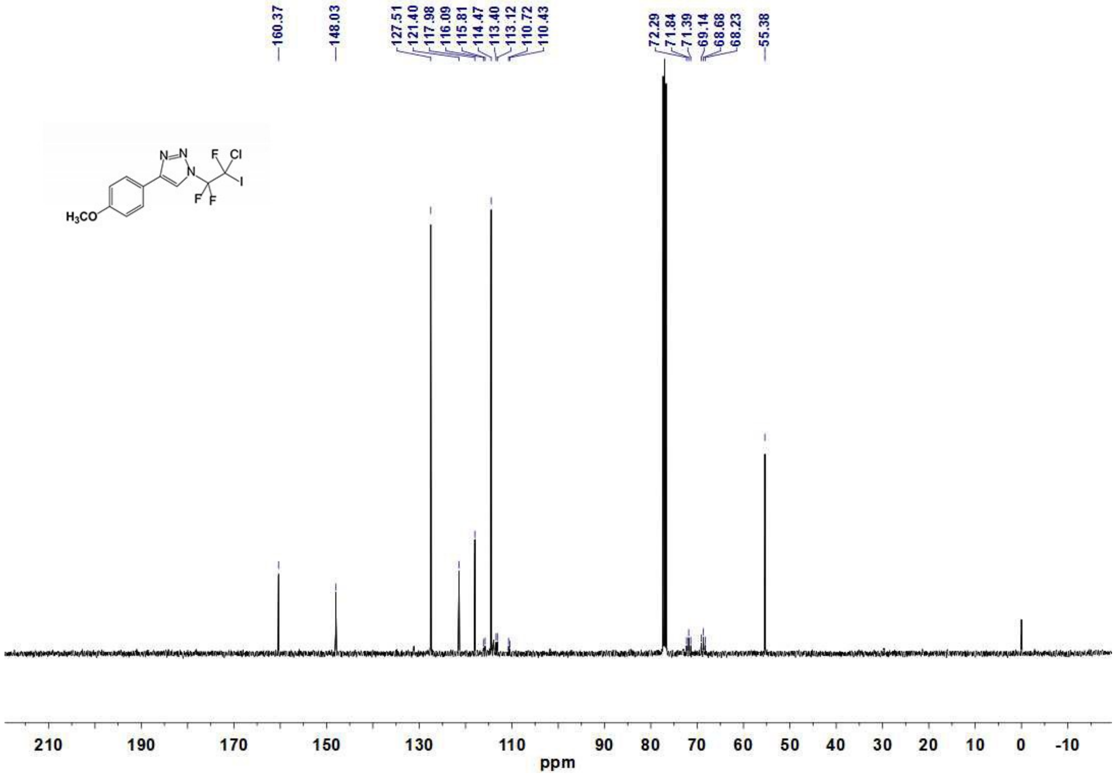
^{1}H NMR of 2e (400 MHz, $CDCl_3$)



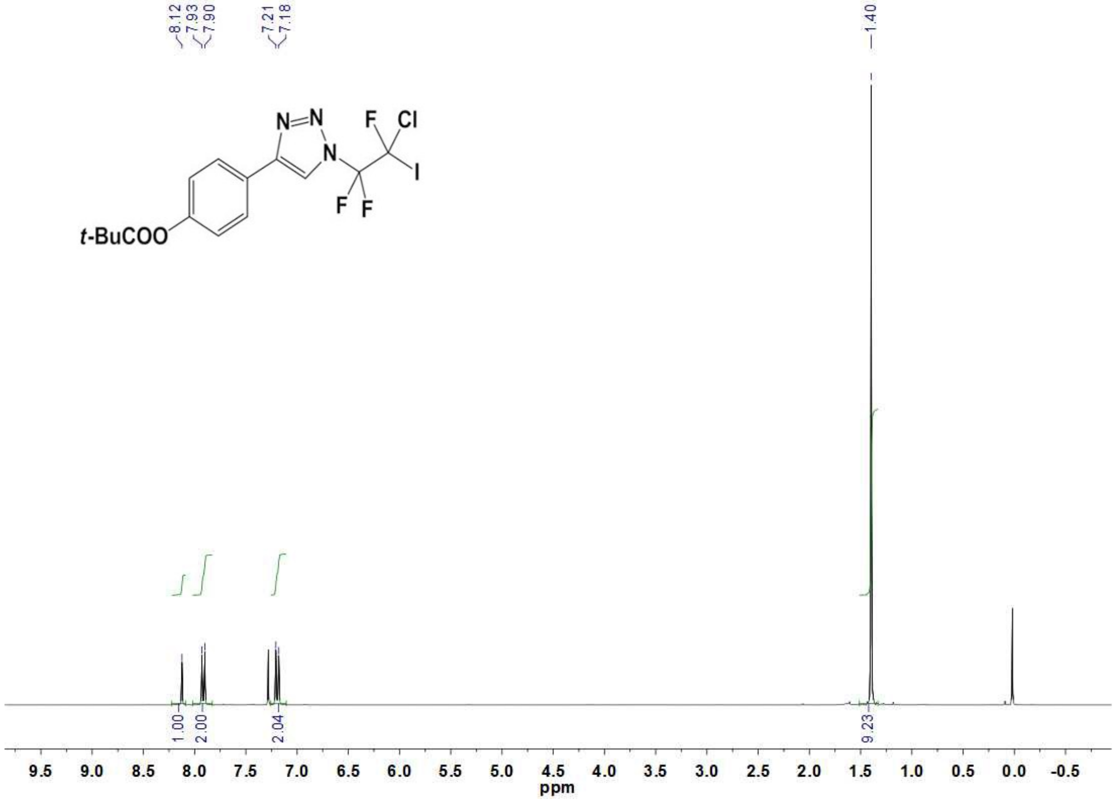
^{19}F NMR of 2e (376 MHz, $CDCl_3$)



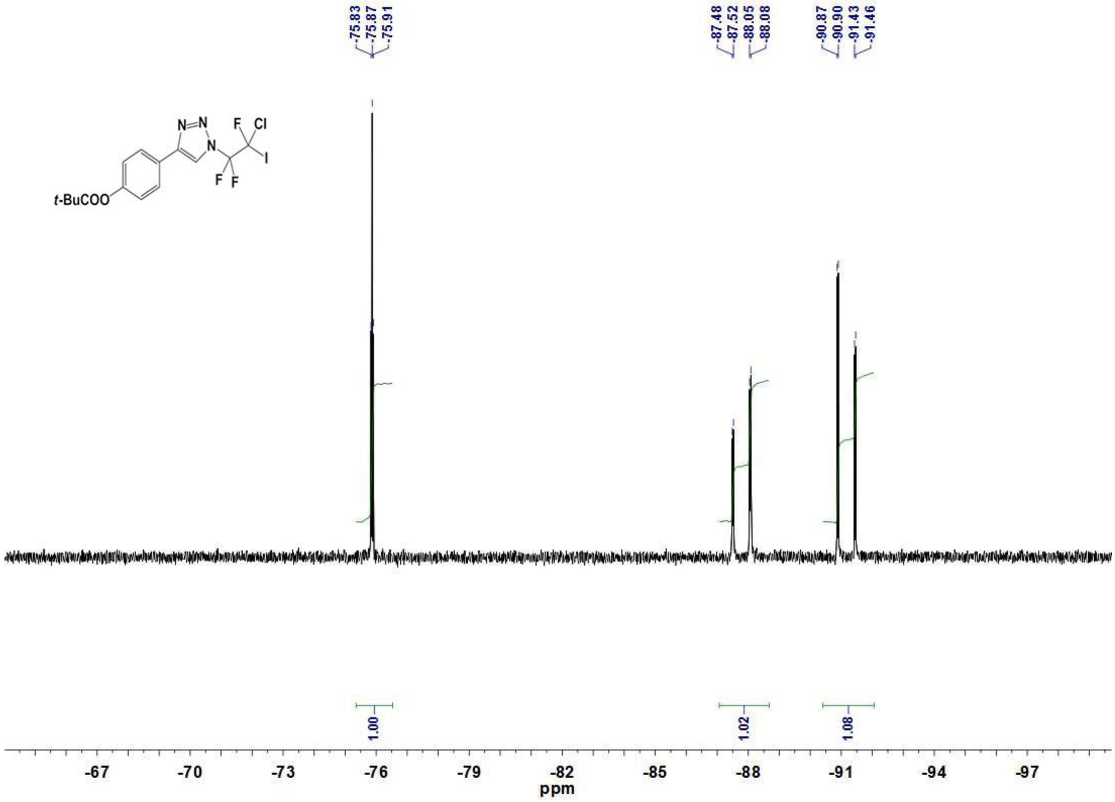
^{13}C NMR of 2e (101 MHz, CDCl$_3$)



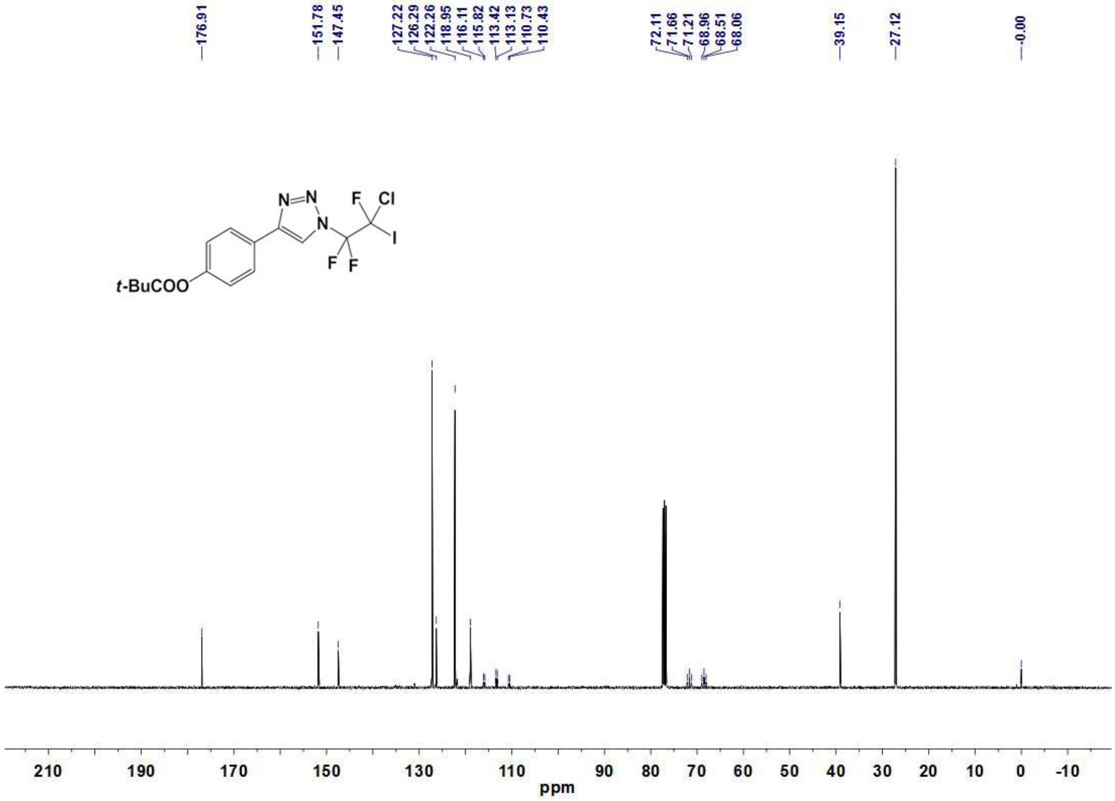
^{1}H NMR of 2f (400 MHz, CDCl$_3$)



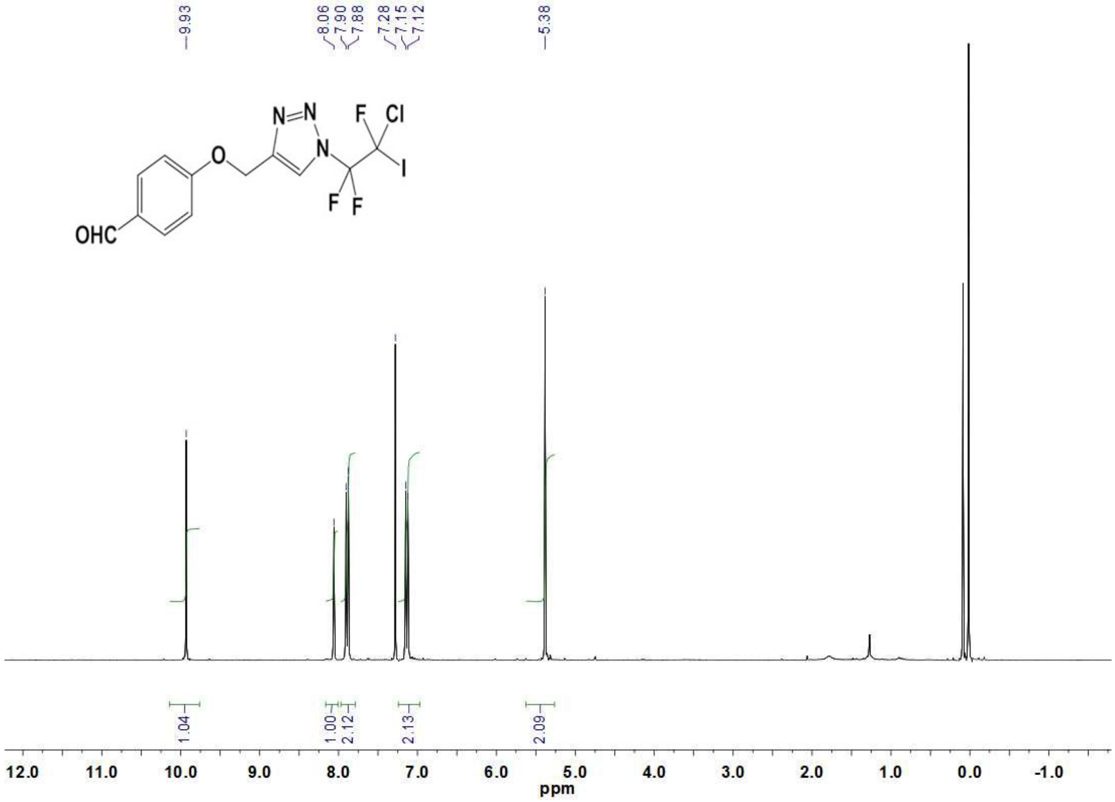
^{19}F NMR of 2f (376 MHz, CDCl$_3$)



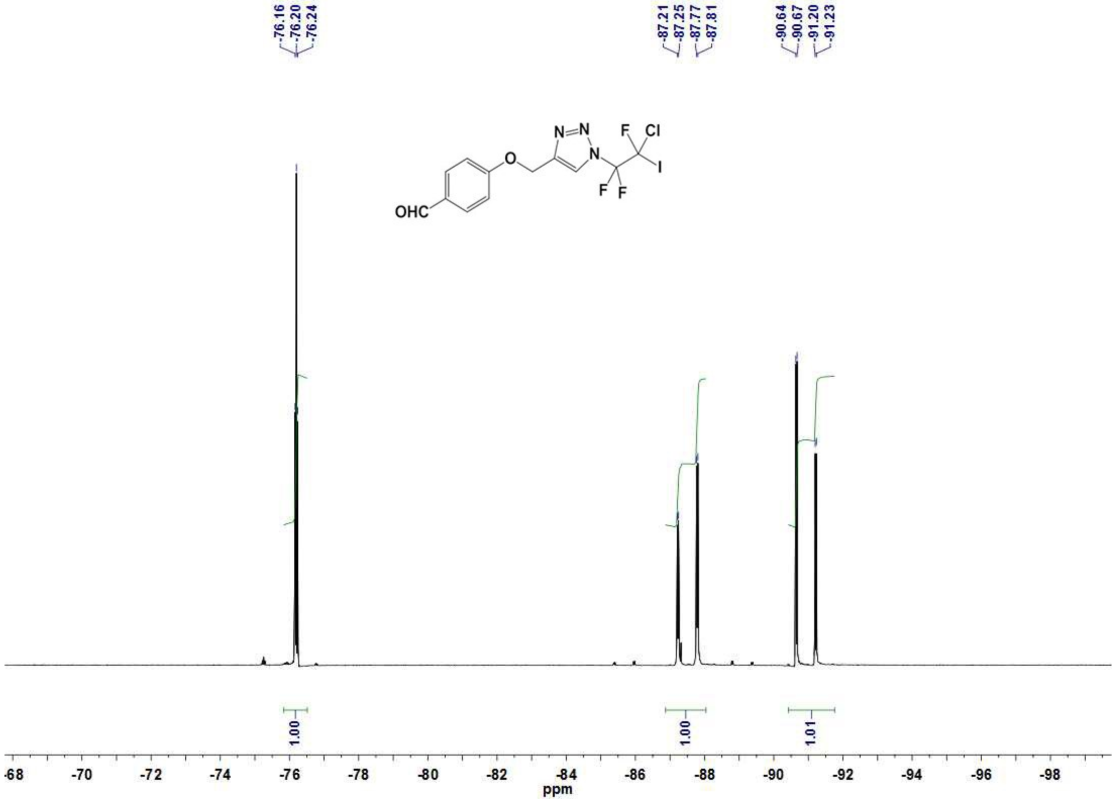
^{13}C NMR of 2f (101 MHz, CDCl$_3$)



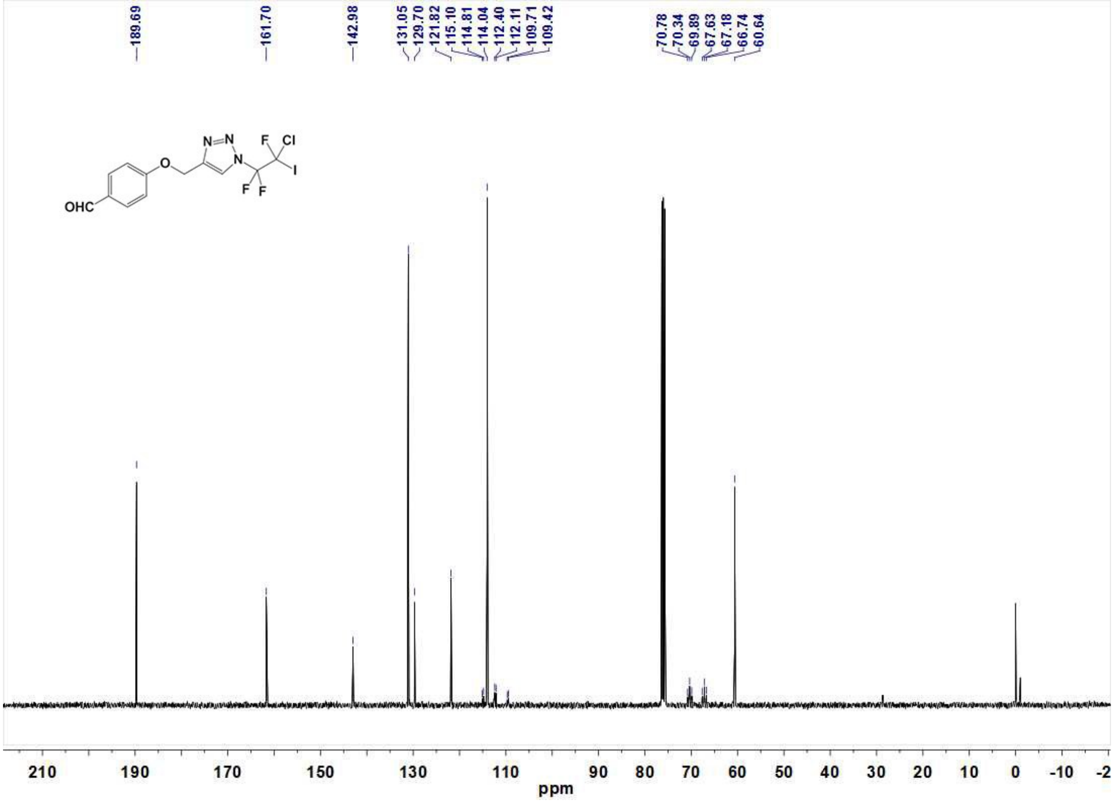
^{1}H NMR of 2g (400 MHz, $CDCl_3$)



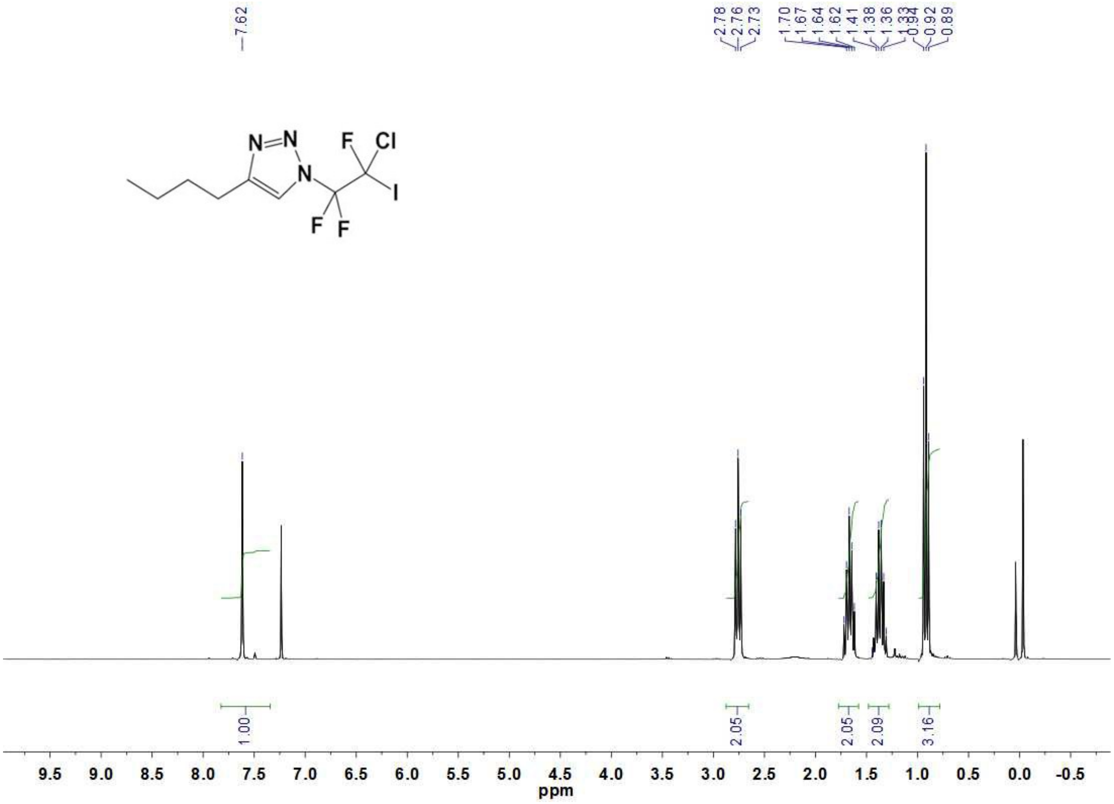
^{19}F NMR of 2g (376 MHz, $CDCl_3$)



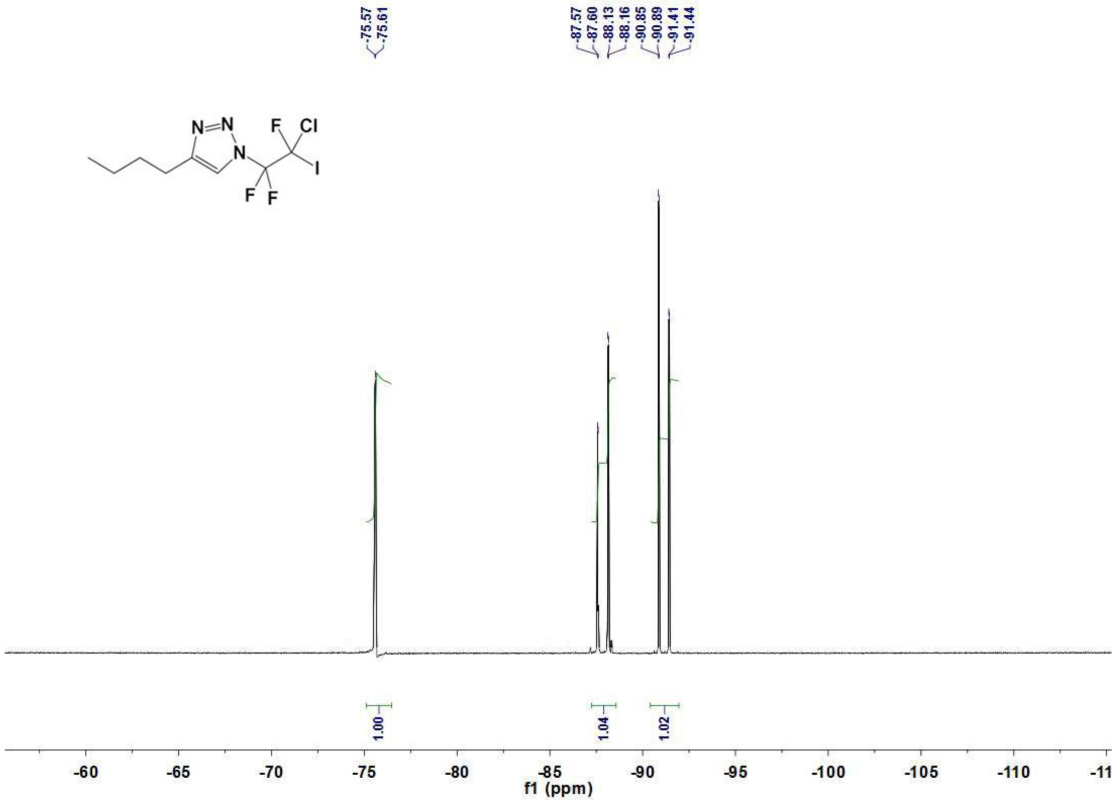
^{13}C NMR of 2g (101 MHz, CDCl$_3$)



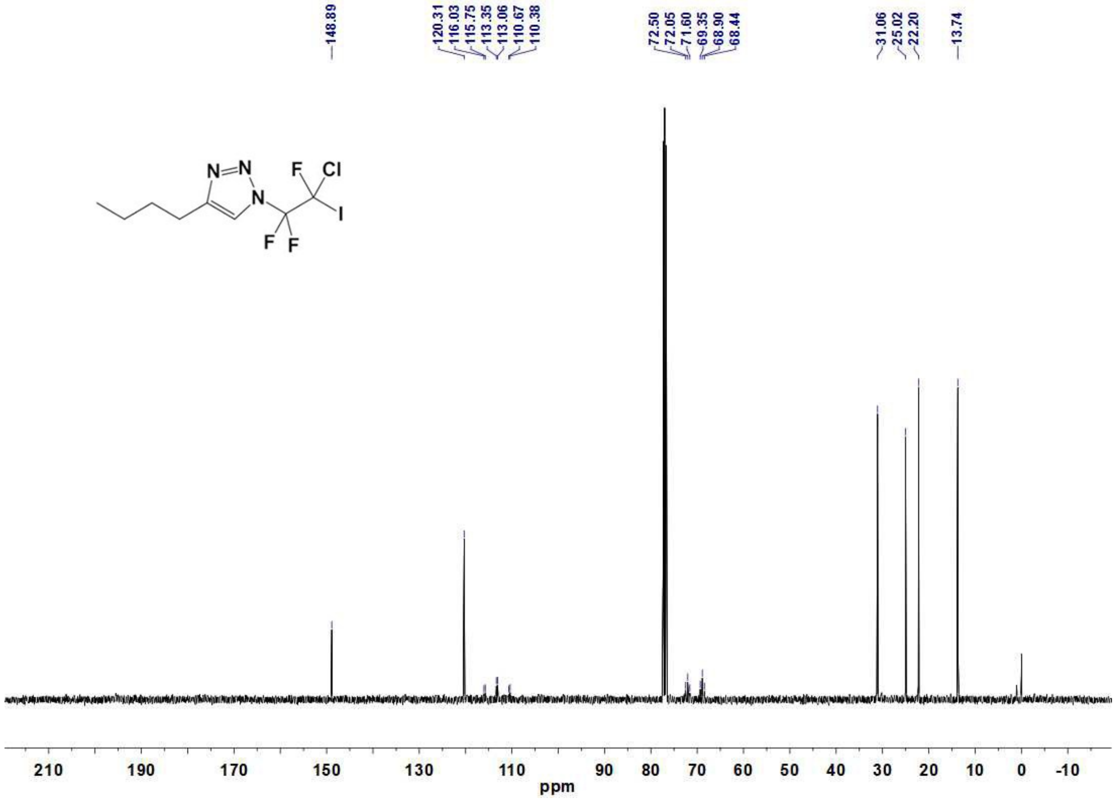
^{1}H NMR of 2h (400 MHz, CDCl$_3$)



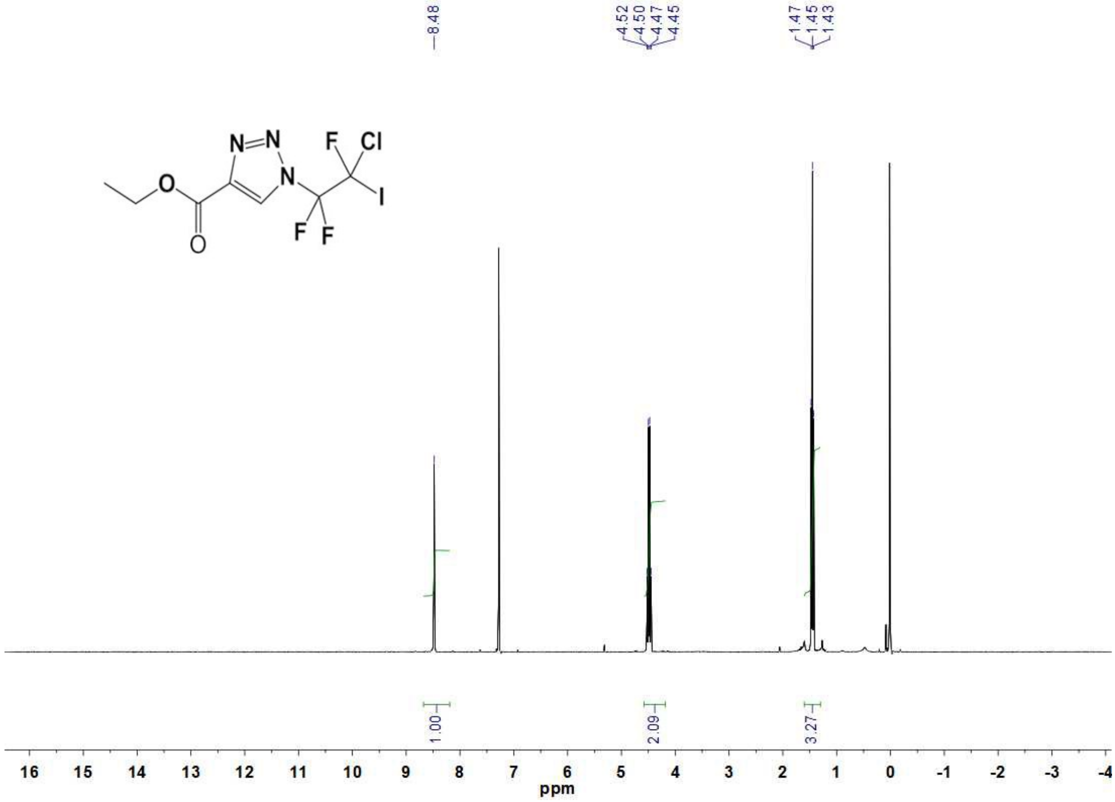
^{19}F NMR of 2h (376 MHz, $CDCl_3$)



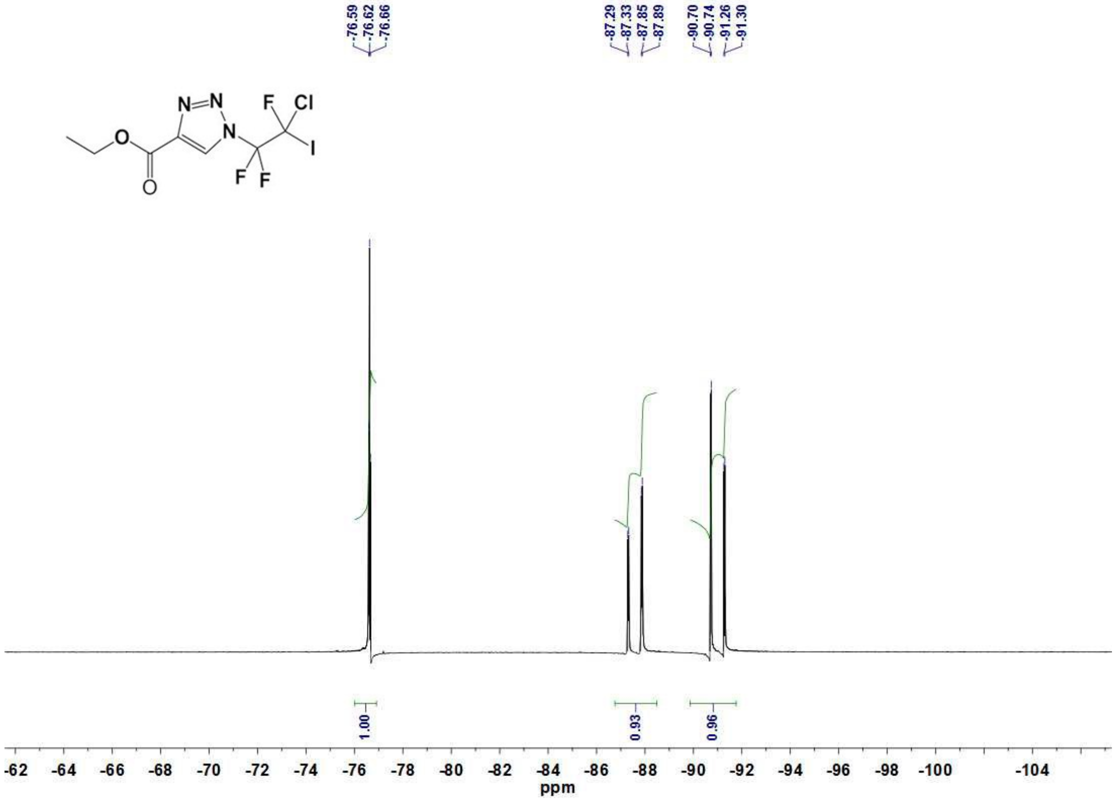
^{13}C NMR of 2h (101 MHz, $CDCl_3$)



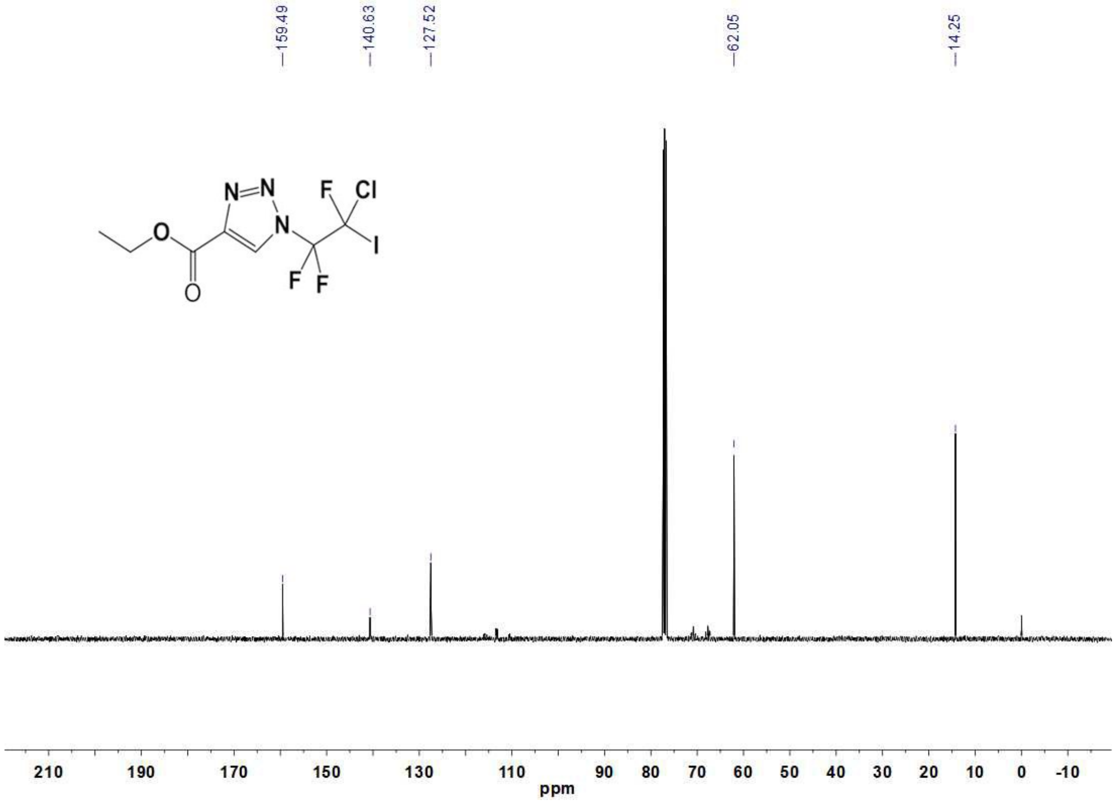
^{1}H NMR of 2i (400 MHz, $CDCl_3$)



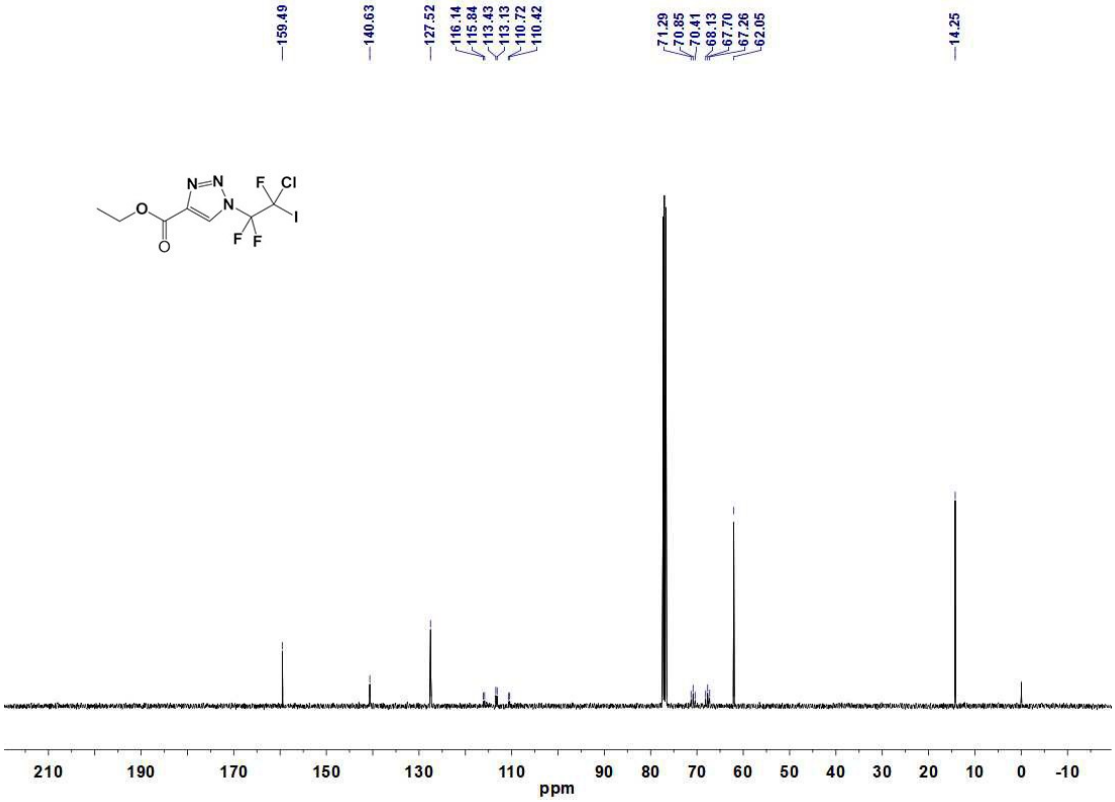
^{19}F NMR of 2i (376 MHz, $CDCl_3$)



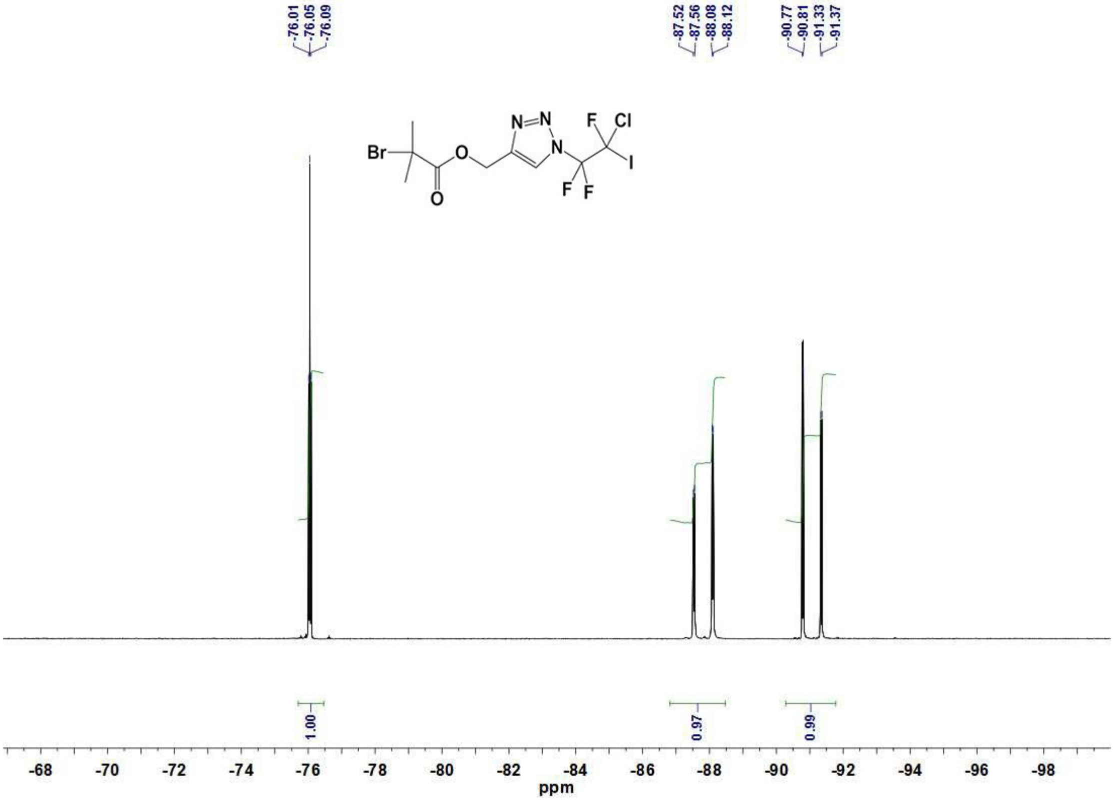
^{13}C NMR of 2i (101 MHz, CDCl$_3$)



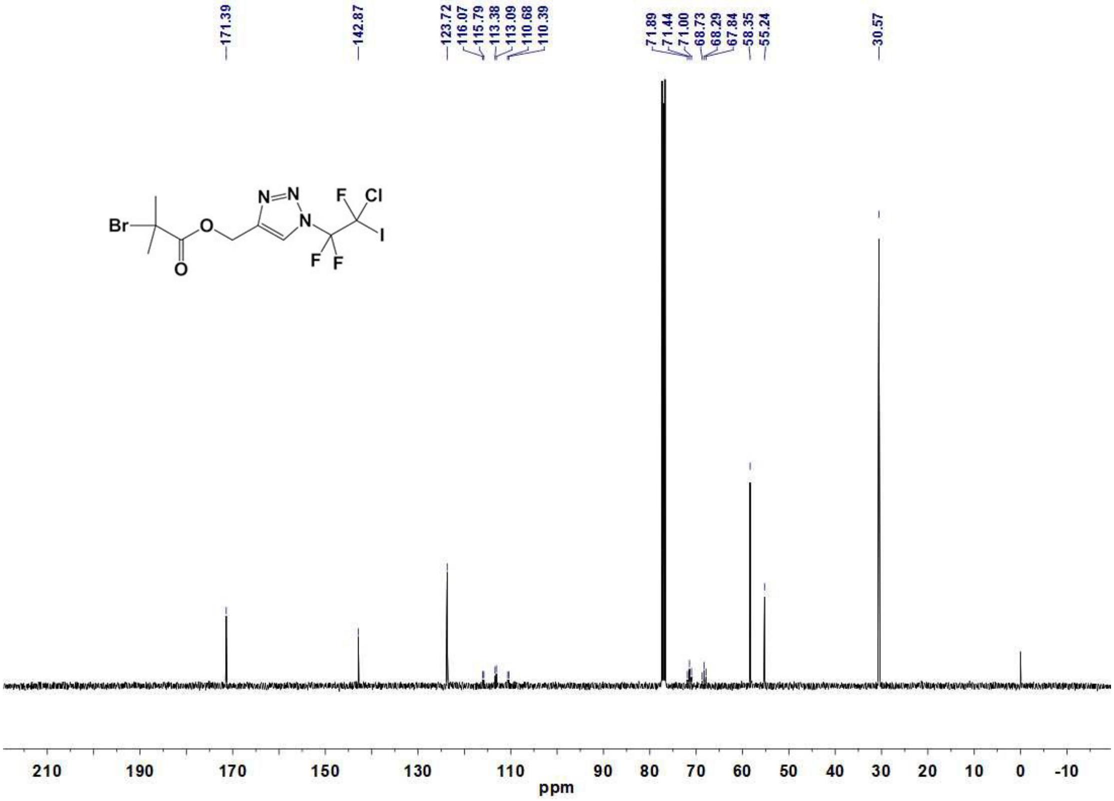
^{1}H NMR of 2j (400 MHz, CDCl$_3$)



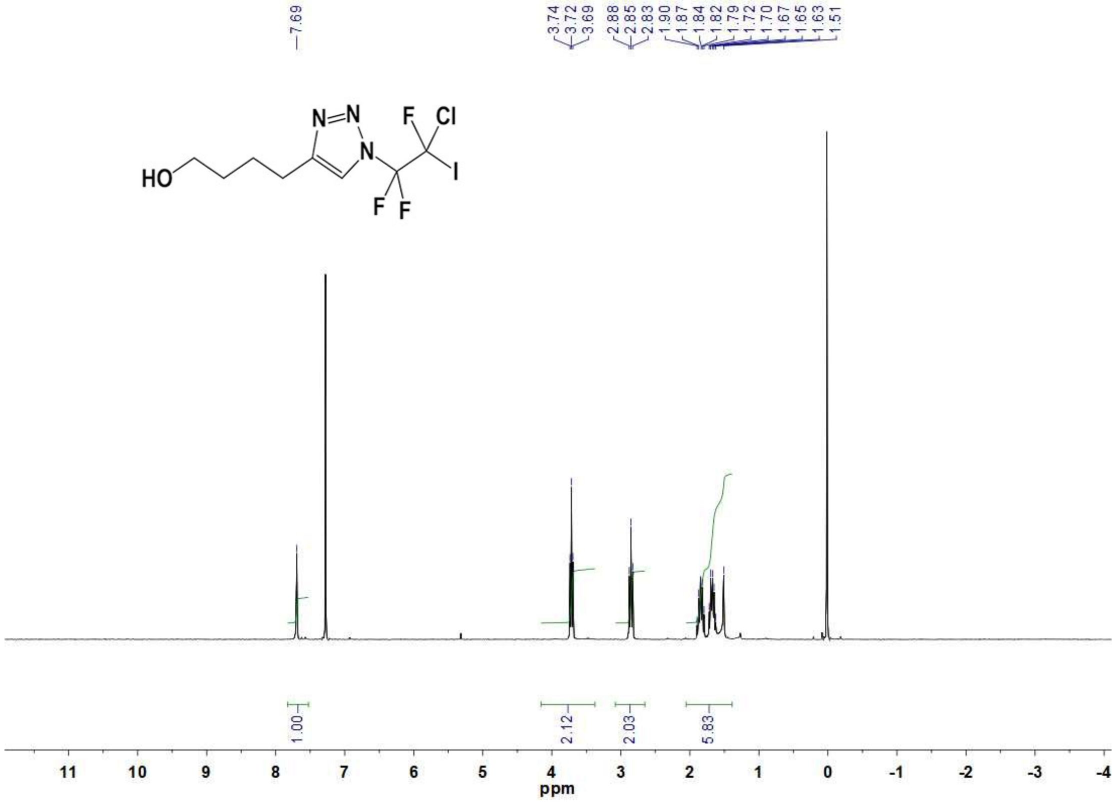
^{19}F NMR of 2j (376 MHz, $CDCl_3$)



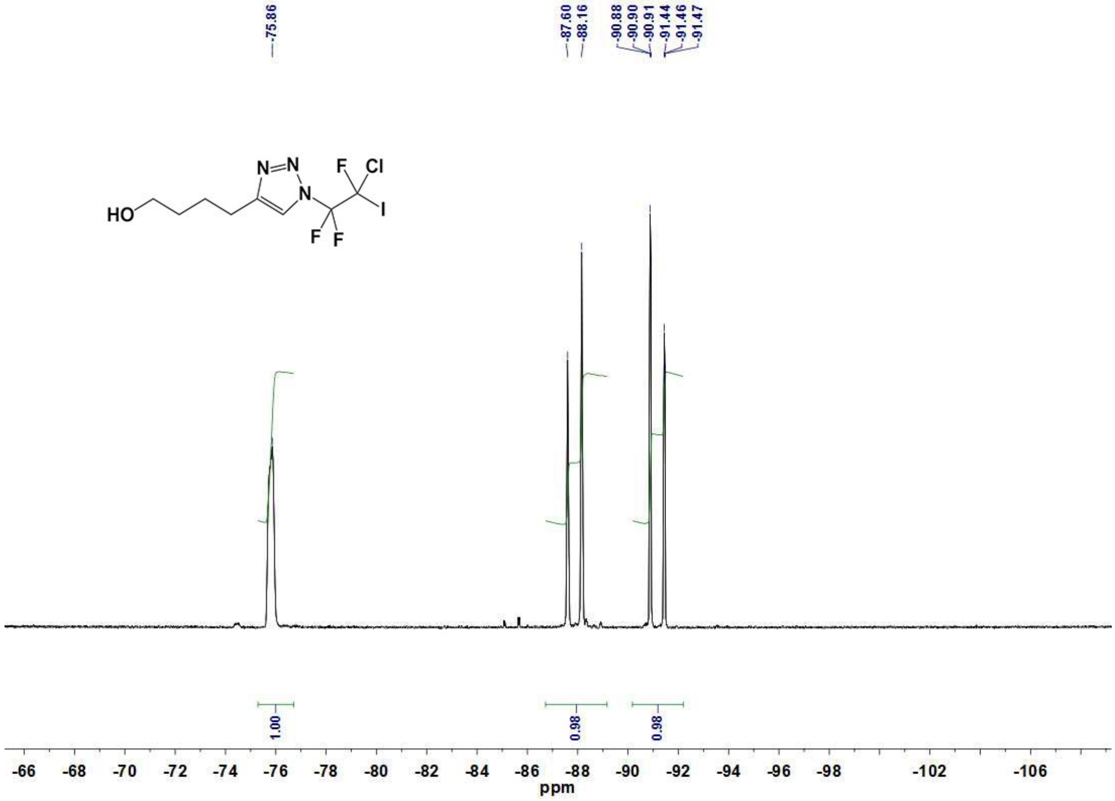
^{13}C NMR of 2j (101 MHz, $CDCl_3$)



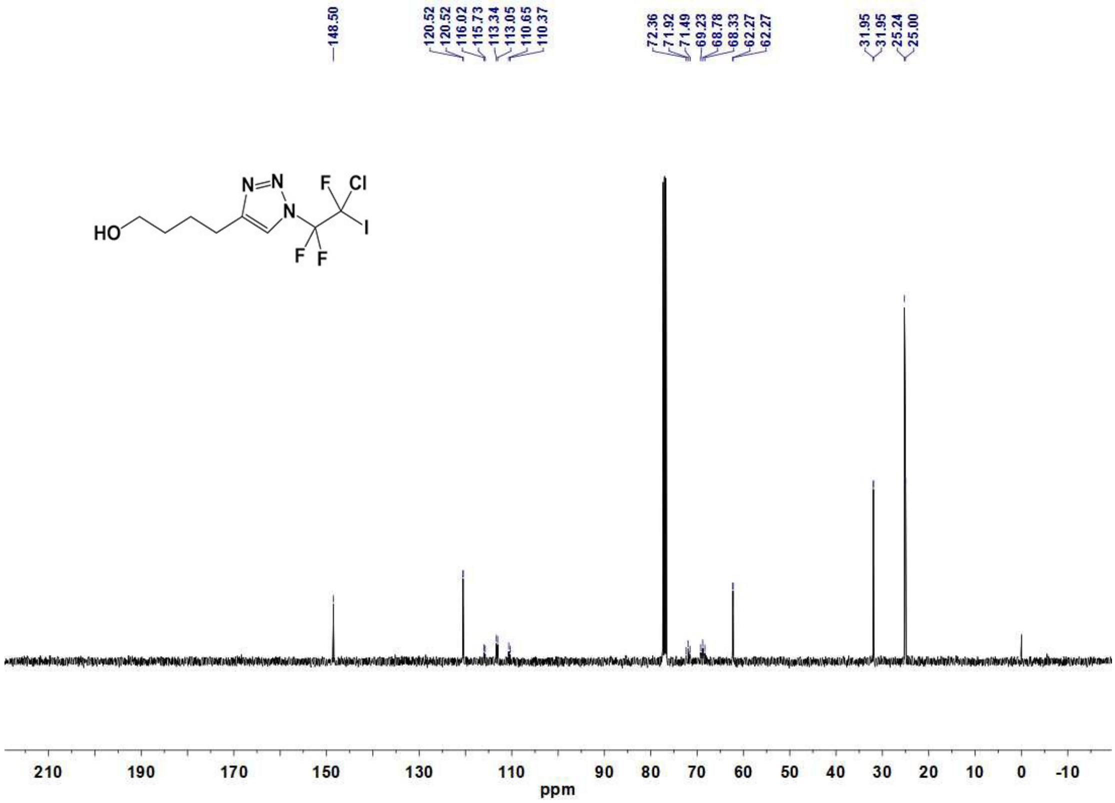
^{1}H NMR of 2k (400 MHz, CDCl$_3$)



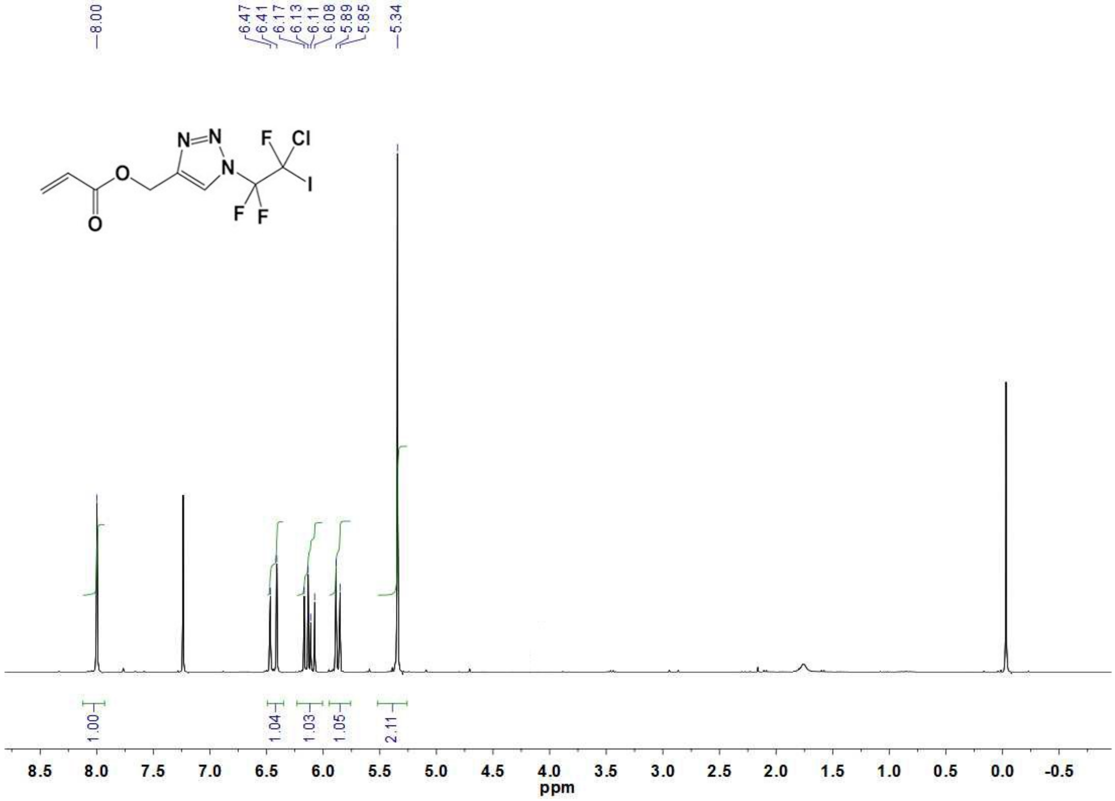
^{19}F NMR of 2k (376 MHz, CDCl$_3$)



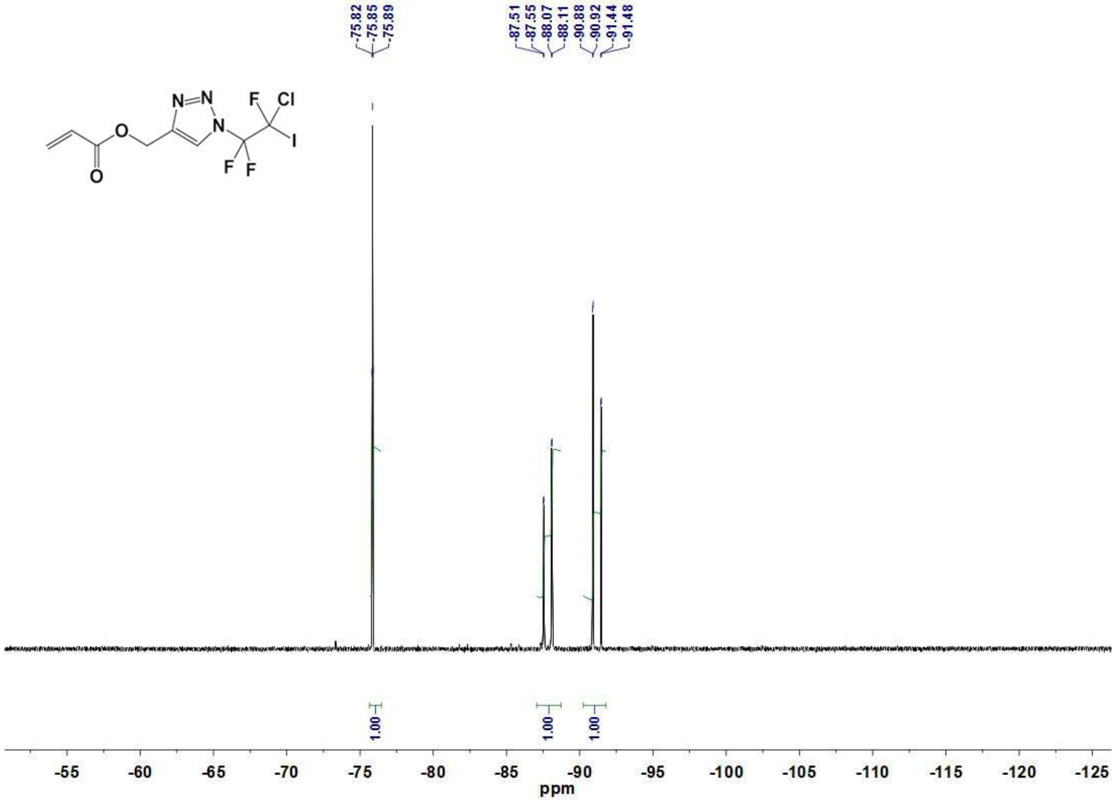
^{13}C NMR of 2k (101 MHz, $CDCl_3$)



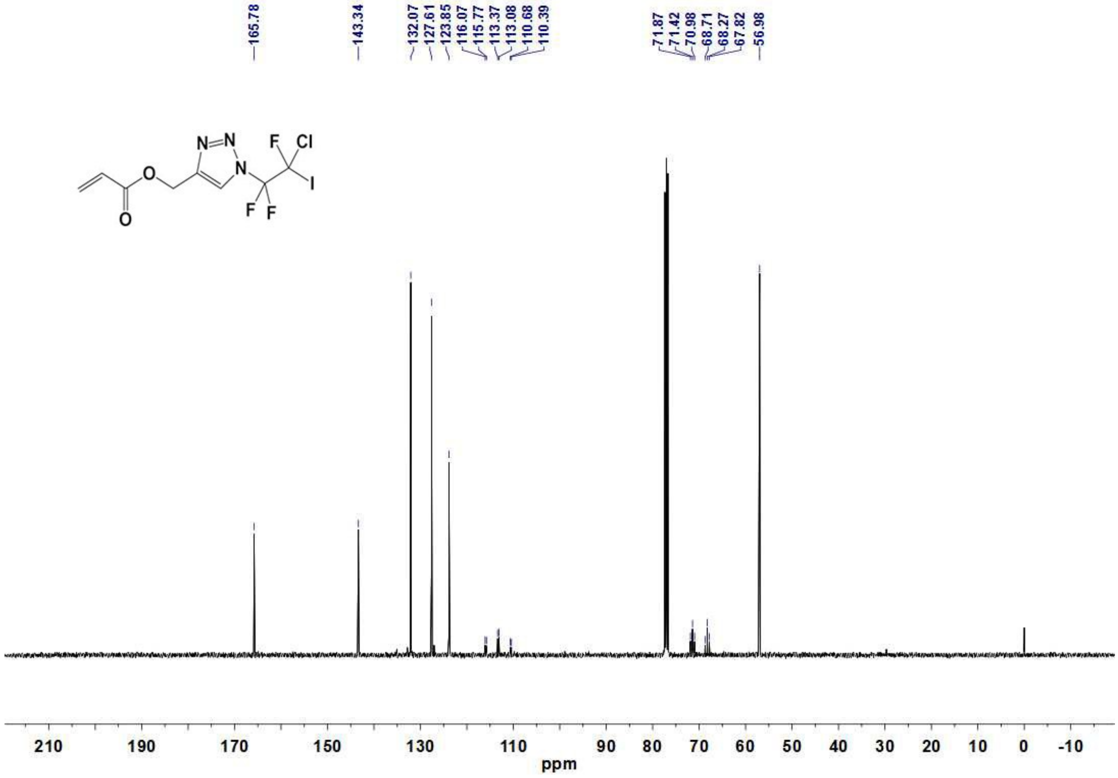
^{1}H NMR of 2l (400 MHz, $CDCl_3$)



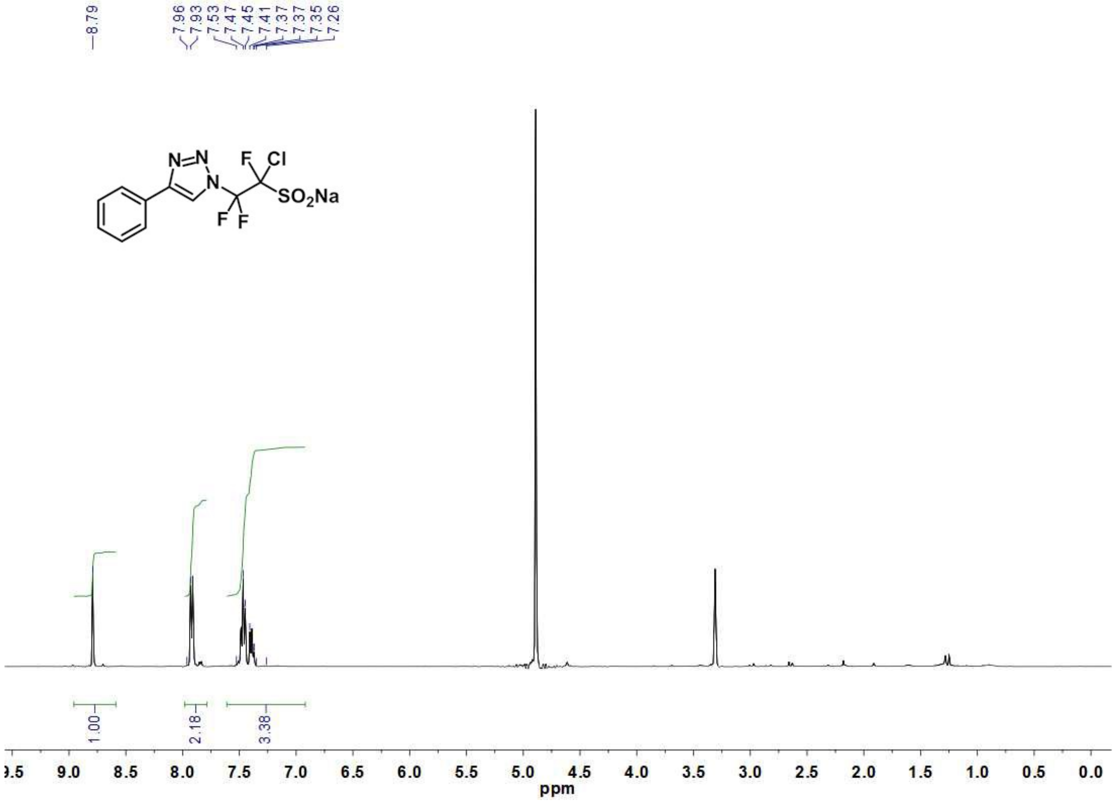
^{19}F NMR of 2l (376 MHz, CDCl$_3$)



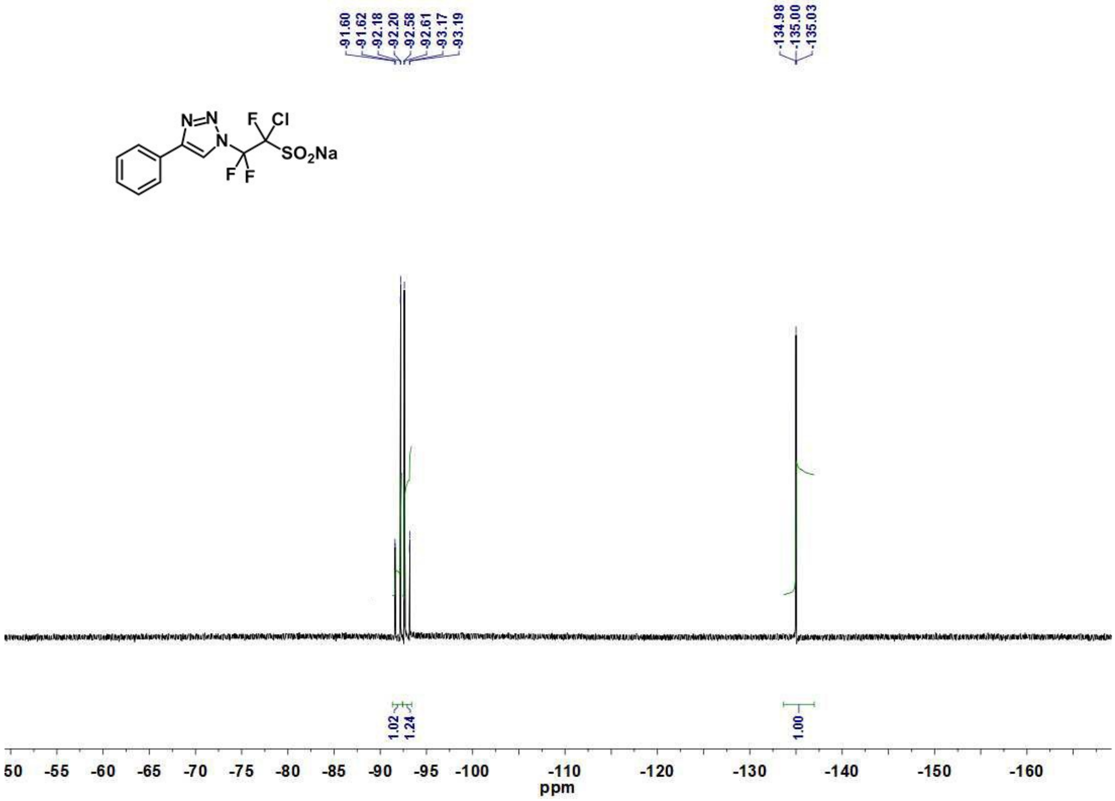
^{13}C NMR of 2l (101 MHz, CDCl$_3$)



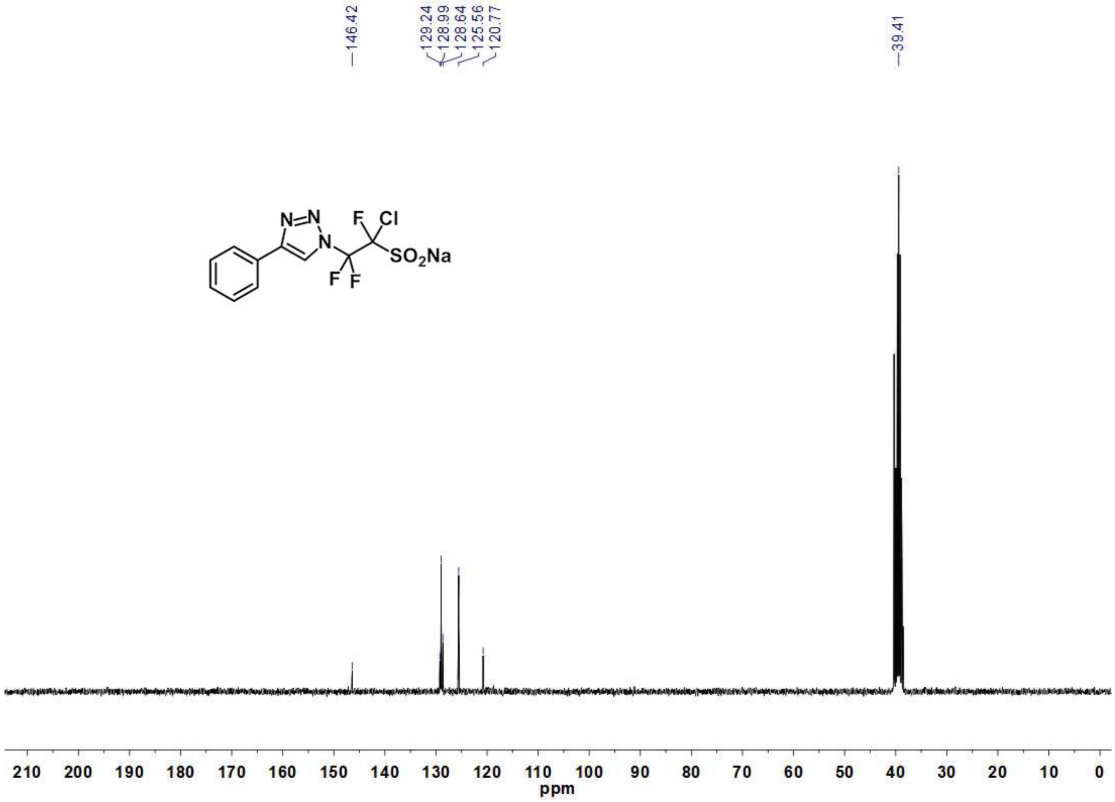
^{1}H NMR of 4 (300 MHz, CD_3OD)



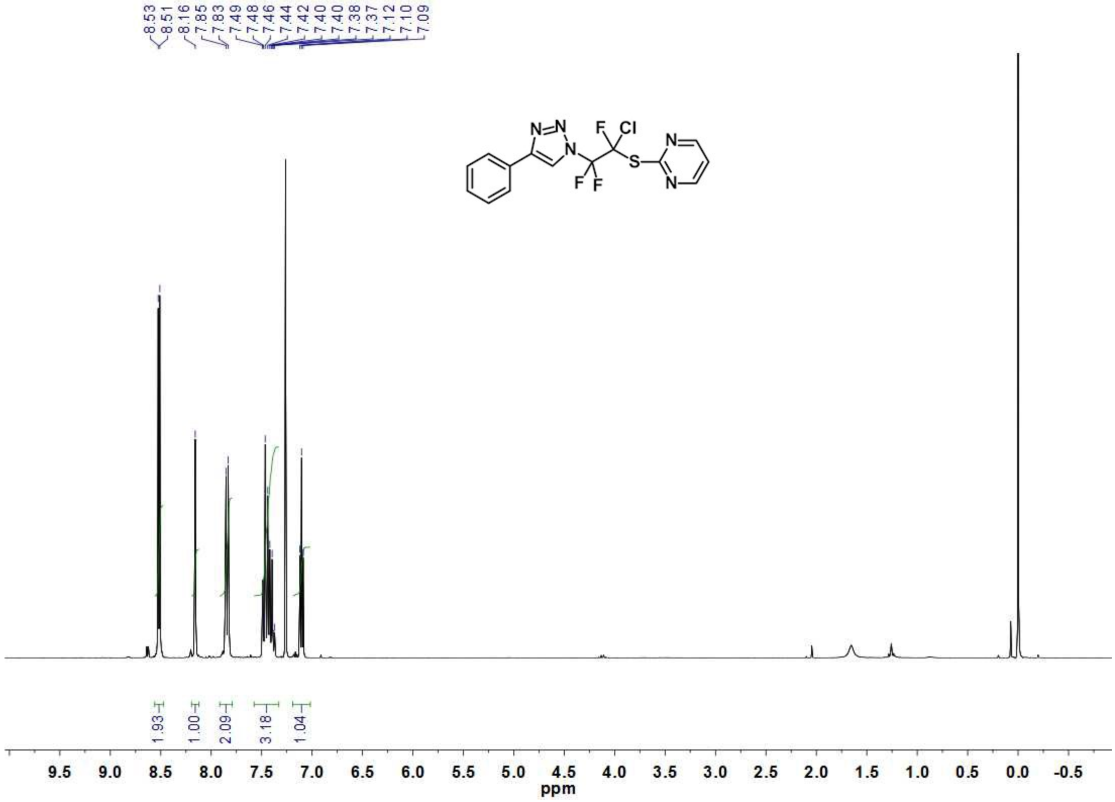
^{19}F NMR of 4 (376 MHz, CD_3OD)



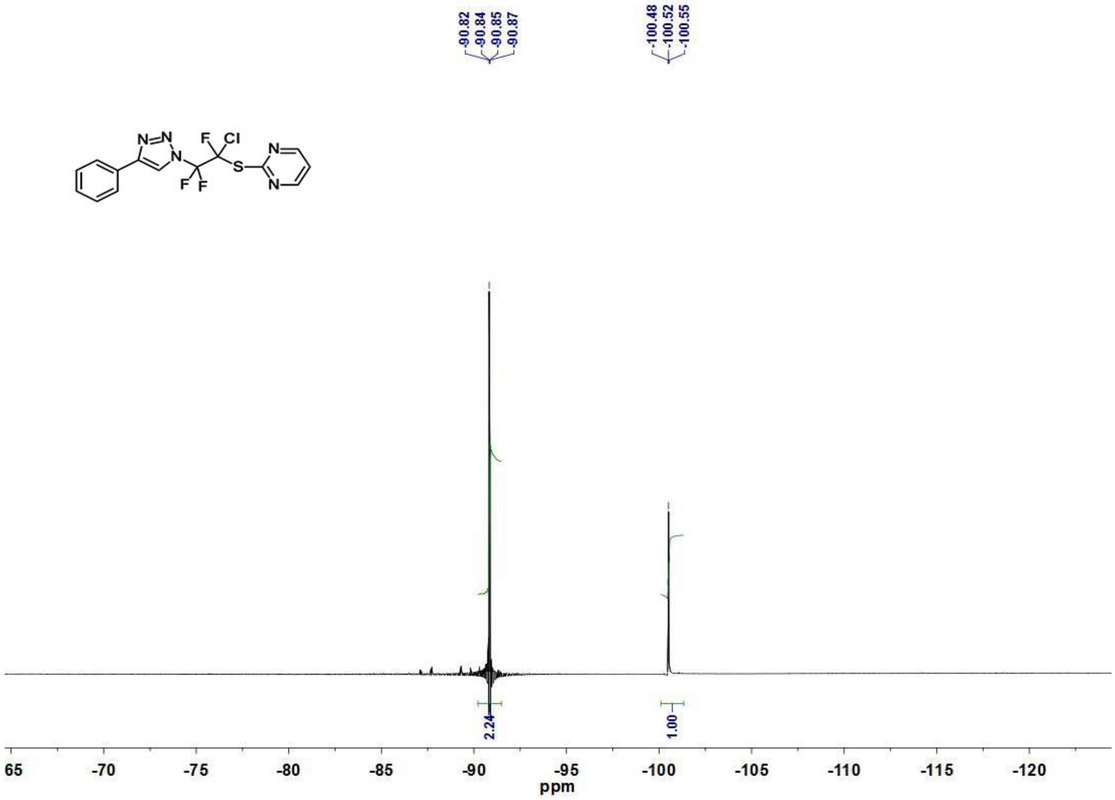
^{13}C NMR of 4 (75 MHz, *d*-DMSO)



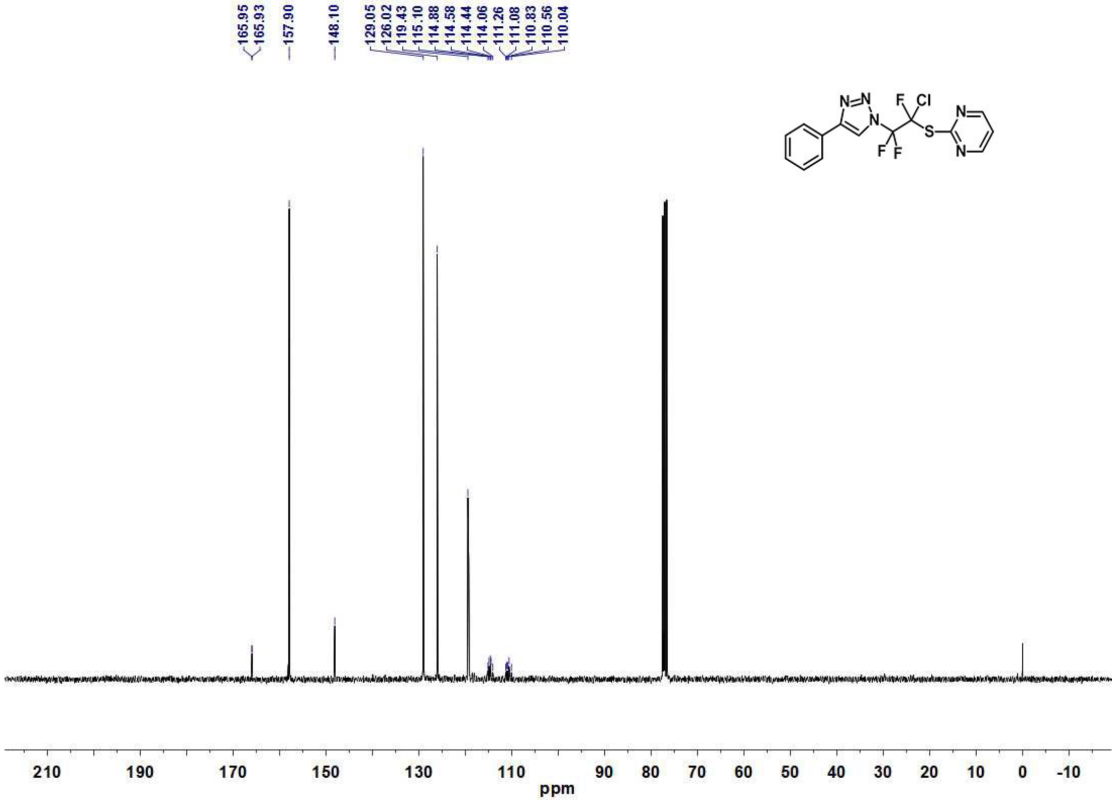
^{1}H NMR of 5 (300 MHz, CDCl$_3$)



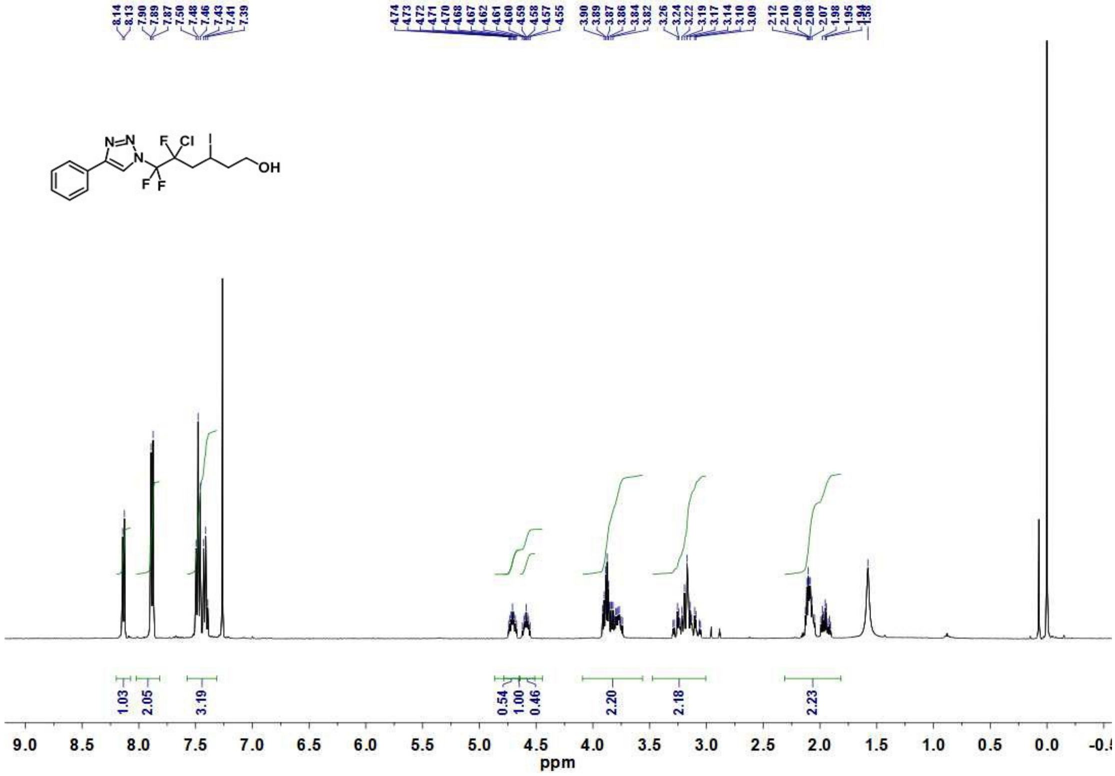
^{19}F NMR of 5 (376 MHz, CDCl$_3$)



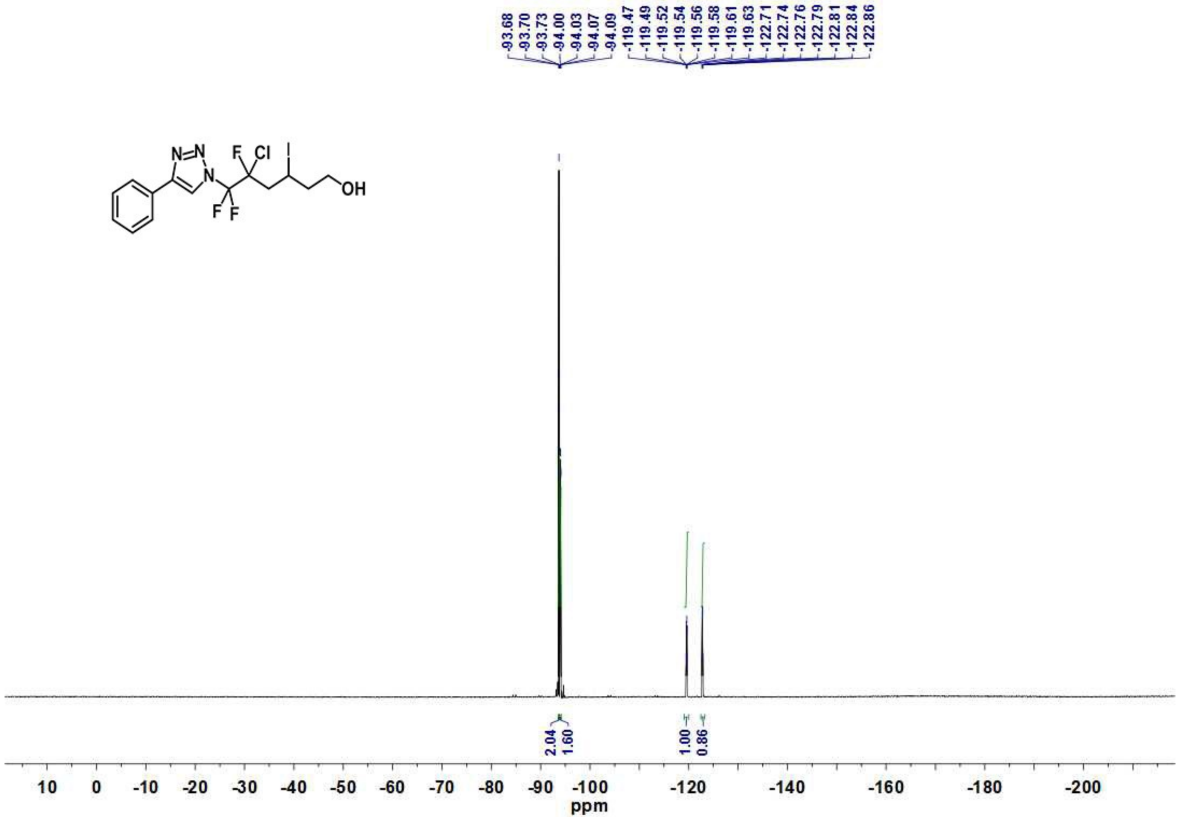
^{13}C NMR of 5 (75 MHz, CDCl$_3$)



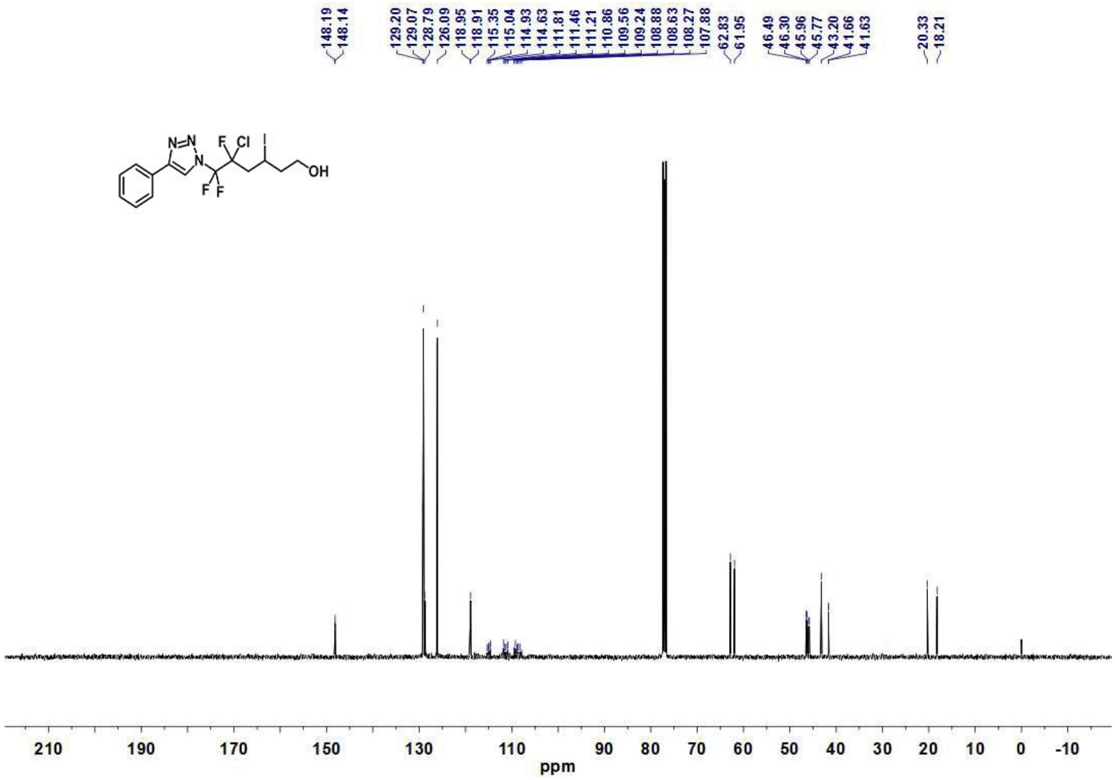
^{1}H NMR of 6 (400 MHz, CDCl$_3$)



^{19}F NMR of 6 (376 MHz, CDCl$_3$)



^{13}C NMR of 6 (101 MHz, CDCl$_3$)



6. References

[1] Banks , R. E.; McGlinchey, M. J. *J. Chem. Soc. C*, **1971**, *23*, 3971.

[2] Jouvin, K.; Heimburger, J.; Evano, G. *Chem. Sci.* **2012**, *3* , 756.