Electronic Supplementary Material (ESI) for ChemComm.

Regioselective synthesis of 4-fluoro-1,5-disubstituted-1,2,3-triazoles from synthetic surrogates of α-fluoroalkynes

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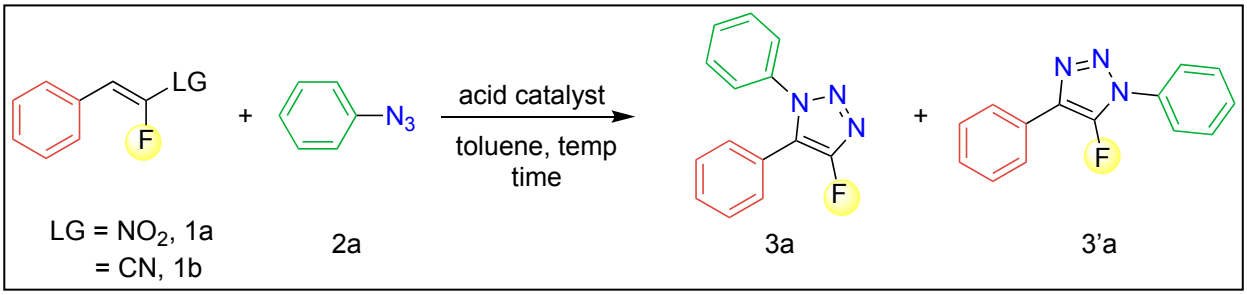
1. General Information:

Unless otherwise noted, all reactions were performed in a 1 dram chemglass reaction vials (CG-4912-01) with screw caps under an inert atmosphere. All reagents, anhydrous solvents, and starting materials were purchased from commercial vendors and were used without further purification. For TLC, Sorbtech silica XG TLC plates w/UV254 indicator was used and visualized under a UV lamp. Flash column chromatography was performed in Biotage Isolera One with Biotage SNAP 10g–50g cartridges. ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded on a Bruker Avance-500 (500 MHz) or Bruker Avance-400 (400 MHz) spectrometers, and the chemical shifts are reported in ppm using deuterated solvents for ^{1}H, ^{13}C NMR, and ^{19}F NMR. $CDCl_3$ (δ = 77.16 ppm) for ^{13}C NMR, $CFCl_3$ (δ = 0 ppm) for ^{19}F NMR, and TMS (δ = 0 ppm) or $CDCl_3$ (δ = 7.26 ppm) for ^{1}H NMR were used as internal standards. Data reported as: s = singlet, s_{br} = broad singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, b = broad, ap = apparent; coupling constants, *J*, in Hz. For HRMS, quadruple-TOF was used to obtain the data both in positive and negative modes. ATR-IR was taken using an Agilent Technologies Cary 600 series FTIR Spectrometer.

2. Optimization studies:

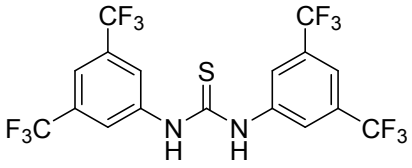


entry	LG	catalyst (equiv.)	solvent	temp (°C)	time (h)	yields(%)[a]	
						3a	3′a
1	NO_2	–	toluene	100	48	10	3
2	NO_2	$Cu(OTf)_2$ (0.2)	toluene	100	24	19	n.o.
3	NO_2	$Zn(OTf)_3$ (0.2)	toluene	100	24	16	n.o.
4	NO_2	$Sc(OTf)_2$ (0.2)	toluene	100	24	25	n.o.
5	NO_2	$Yb(OTf)_3$ (0.2)	toluene	100	24	11	n.o.
6	NO_2	$Fe(OTf)_3$ (0.2)	toluene	100	24	8	n.o.
7	NO_2	$Ce(OTf)_3$ (0.2)	toluene	100	24	22	n.o.
8	NO_2	$BF_3•(OEt)_2$ (0.3)	toluene	100	24	28	8
9	NO_2	AcOH (0.3)	toluene	100	48	42	10
10	NO_2	*p*TSA•H_2O (0.5)	toluene	100	48	31	<5
11	NO_2	10-CSA (0.5)	toluene	100	48	36	<5
12	NO_2	TFA (0.3)	toluene	100	48	60	n.o.
13	NO_2	TFA (0.5)	toluene	100	48	72	n.o.
14	NO_2	TFA (0.5)	toluene	110	48	78	n.o.
15	NO_2	TFA (0.8)	toluene	110	48	69	n.o.
16	NO_2	$MeSO_3H$ (0.5)	toluene	110	48	68	n.o.
17	NO_2	H_3PO_4 (0.5)	toluene	110	48	45	7
18	NO_2	NH_2SO_3 (0.5)	toluene	110	48	20	<5
19	NO_2	TFA (0.5)	DCE	110	24	56	n.o.
20	NO_2	TFA (0.5)	1,4-dioxane	110	24	53	n.o.
21	NO_2	TFA (0.5)	DMF	110	24	36	n.o.
22	NO_2	TFA (0.5)	DMSO	110	24	18	n.o.
23	NO_2	TFA (0.5)	ACN	110	24	53	n.o.
24	NO_2	TFA (0.5)	THF	110	24	45	n.o.
25	NO_2	TFA (0.5)	toluene	110	24	78	n.o.
26[b]	NO_2	Thiourea-I (0.2)	DCE	80	48	<5	<5
27[c]	NO_2	Thiourea-II (0.2)	DCE	80	48	n.o.	n.o.
28	Br	Et_3N (0.5)	DMF	90	48	n.o.	n.o.
29	Br	DBU (1)	DMF	100	24	n.o.	n.o.
30	Br	DIPEA (1)	DMF	100	48	n.o.	n.o.
31	Br	TMEDA (1)	DMF	100	48	n.o.	n.o.
32	Br	Ag_2CO_3 (1)	DMF	100	24	n.o.	n.o.
33	Br	$Pd(OAc)_2$ (0.5)	DMF	100	24	n.o.	n.o.
34	Br	$AgBF_4$ (1)	DMF	100	24	n.o.	n.o.
35	CN	TFA (0.5)	Toluene	110	72	n.o.	n.o.

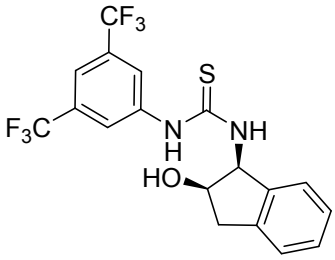
[a] Isolated yield

[b] For the preparation of Thiourea-I see the reference[1]

[c] For the preparation of Thiourea-II see the reference[2]
n.o.= not observed



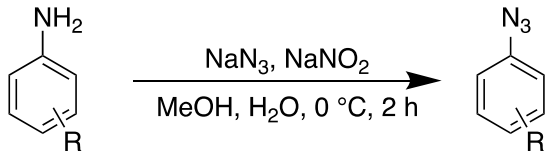
Thiourea-I



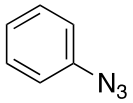
Thiourea-II

3. General procedure for the synthesis of azides:

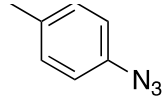
i. Procedure 1 (Amine to azide) (2a-2k):



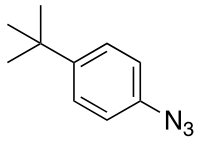
Appropriate aniline (10 mmol) was suspended in water (5 mL) and methanol (10 mL). Then, conc. HCl (3.9 mL) was added to the solution. After cooling the solution to 0 °C, $NaNO_2$ (12 mmol) in water (3 mL) was added dropwise for 10 minutes. The mixture was stirred at 0 °C for an additional 10 minutes, after which a solution of NaN_3 (12 mmol) in water was added dropwise at the same temperature over 15 minutes. After the addition, the whole reaction mixture was stirred for two hours at room temperature. The reaction mixture was extracted with Et_2O (x3) and the combined organic fractions were washed with a saturated $NaHCO_3$ solution followed by brine, dried over anhydrous Na_2SO_4, and concentrated in *vacuo* affording the corresponding azides (**2a–2k**).



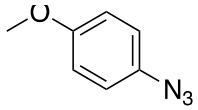
Azidobenzene (2a):
Aniline (1.00 g, 10.7 mmol), sodium nitrite (889 mg, 12.9 mmol), and sodium azide (837 mg, 12.9 mmol were used to afford **2a** in (925 mg) 72% yield as a yellow liquid after purification by column chromatography (using hexane as an eluent).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.8 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 7.9 Hz, 2H). Spectroscopic data for **2a** are consistent with previously reported data for this compound.[3]



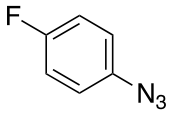
1-Azido-4-methylbenzene (2b):
p-Toluidine (1.00 g, 9.3 mmol), sodium nitrite (772 mg, 11.2 mmol), and sodium azide (728 mg, 11.2 mmol) were used to afford **2b** in (1000 mg) 80% yield as a yellow liquid after purification by column chromatography (using hexane as an eluent).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, *J* = 8.3 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 2.24 (s, 3H). Spectroscopic data for **2b** are consistent with previously reported data for this compound.[3]



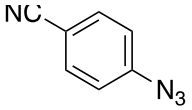
1-Azido-4-(tert-butyl)benzene (2c):
4-(*tert*-Butyl)aniline (1.00 g, 6.7 mmol), sodium nitrite (554 mg, 8 mmol), and sodium azide (522 mg, 8 mmol) were used to afford **2c** in (830 mg) 70% yield as a yellow liquid after purification by column chromatography (using hexane as an eluent).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.7 Hz, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 1.34 (s, 9H). Spectroscopic data for **2c** are consistent with previously reported data for this compound.[3-4]



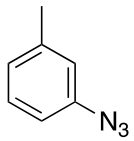
1-Azido-4-methoxybenzene (2d):
4-Methoxyaniline (1.00 g, 8.1mmol), sodium nitrite (672 mg, 9.7 mmol), and sodium azide (633 mg, 9.7 mmol) were used to afford **2d** in (1020 mg) 84% yield as an off-white solid after purification by column chromatography (using hexane as an eluent).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.85 (m, 2H), 7.84–7.79 (m, 2H), 4.72 (s, 3H). Spectroscopic data for **2d** are consistent with previously reported data for this compound.[3]



1-Azido-4-fluorobenzene (2e):
4-Fluoroaniline (1.00 g, 8.9 mmol), sodium nitrite (765 mg, 10.8 mmol), and sodium azide (702 mg, 10.8 mmol) were used to afford **2e** in (925 mg) 75% yield as a yellow liquid after purification by column chromatography (using hexane as an eluent).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (t, *J* = 8.5 Hz, 2H), 7.04–6.93 (m, 2H). Spectroscopic data for **2e** are consistent with previously reported data for this compound.[5]

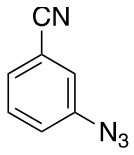


4-Azidobenzonitrile (2f):
4-Aminobenzonitrile (1.00 g, 8.4 mmol), sodium nitrite (700 mg, 10.1 mmol), and sodium azide (660 mg, 10.1 mmol) were used to afford **2f** in (1000 mg) 82% yield as an off-white solid after purification by column chromatography (using hexane as an eluent).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.7 Hz, 2H), 7.04 (d, *J* = 8.7 Hz, 2H). Spectroscopic data for **2f** are consistent with previously reported data for this compound.[6]

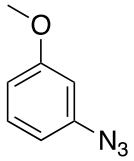


1-Azido-3-methylbenzene (2g):
m-Toluidine (1.00 g, 9 mmol), sodium nitrite (800 mg, 11.6 mmol), and sodium azide (700 mg, 10.8 mmol) were used to afford **2g** in (950 mg) 95% yield as a pale yellow liquid after purification by column chromatography (using hexane as an eluent).

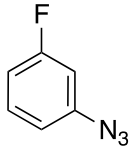
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.6 Hz,1H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.83 (s, 2H), 2.34 (s, 3H). Spectroscopic data for **2g** are consistent with previously reported data for this compound.[7]



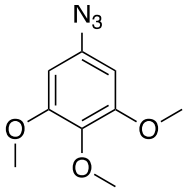
3-Azidobenzonitrile (2h):
3-Aminobenzonitrile (1.00 g, 8.5 mmol), sodium nitrite (700 mg, 10.2 mmol), and sodium azide (660 mg, 10.2 mmol) were used to afford **2h** in (1100 mg) 90% yield as an off-white solid after purification by column chromatography (using hexane as an eluent).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.33 (m, 2H), 7.25–7.16 (m, 2H). Spectroscopic data for **2h** are consistent with previously reported data for this compound.[8]



1-Azido-3-methoxybenzene (2i):
3-Methoxyaniline (1.00 g, 8.1 mmol), sodium nitrite (672 mg, 9.7 mmol), and sodium azide (633 mg, 9.7 mmol) were used to afford **2i** in (950 mg) 80% yield as an off-white solid after purification by column chromatography (using hexane as an eluent).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, *J* = 8.1 Hz, 1H), 6.61 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.56 (dd, *J* = 8.0, 2.1 Hz, 1H), 6.47 (t, *J* = 2.3 Hz, 1H), 3.72 (s, 3H). Spectroscopic data for **2i** are consistent with previously reported data for this compound.[5]



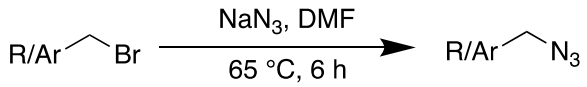
1-Azido-3-fluorobenzene (2j):
3-Fluoroaniline (1 g, 9.00 mmol), sodium nitrite (745.1 mg, 10.80 mmol), and sodium azide (702.1 mg, 1.2 Eq, 10.80 mmol) were used to afford **2j** in (940 mg) 76% yield as a colorless liquid after purification by column chromatography (using hexane as an eluent).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.29 (m, 1H), 6.88–6.81 (m, 2H), 6.78–6.71 (m, 1H). Spectroscopic data for **2j** are consistent with previously reported data for this compound.[5]



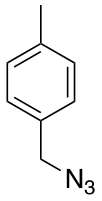
5-Azido-1,2,3-trimethoxybenzene (2k):

3,4,5-Trimethoxyaniline (1000 mg, 5.45 mmol), sodium nitrite (451.9 mg, 6.55 mmol), and sodium azide (451.9 mg, 6.55 mmol) were used to afford **2k** in (970 mg) 85% yield as an off-white solid after purification by column chromatography (using hexane as an eluent).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.18 (s, 2H), 3.78 (s, 6H), 3.74 (s, 3H). Spectroscopic data for **2k** are consistent with previously reported data for this compound.[5]

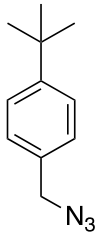
ii. Procedure 2 (bromo to azide) (2m–2z):



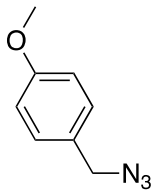
NaN_3 (1.2 equiv.) was added to a solution of appropriate bromide (1 equiv.) in DMF (0.8 M). The reaction mixture was then heated at 60 °C for 6 h. After the completion of the reaction, monitored by the consumption of the starting material (using TLC), the reaction mixture was quenched with water and extracted with DCM. The combined organic layer were dried over anhydrous Na_2SO_4 and concentrated in *vacuo* to afford the corresponding azides **(2m–2z)**.



1-(Azidomethyl)-4-methylbenzene (2m):
Sodium azide (412.7 mg, 6.3 mmol) was added to the solution of 1-(bromomethyl)-4-mehtyl benzene (1000 mg, 5 mmol) in DMF (5 mL). The reaction mixture was heated at 65 °C for 6 h. After the complete consumption of the starting material, the reaction mixture was quenched with water and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4 then dried in *vacuo.* to afford **2m** in (700 mg) 88% yield as a colorless liquid.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24–7.20 (m, 4H), 4.30 (s, 2H), 2.38 (s, 3H). Spectroscopic data for **2m** are consistent with previously reported data for this compound.[9]

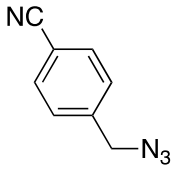


1-(Azidomethyl)-4-(*tert*-butyl)benzene (2n):
Sodium azide (300 mg, 5 mmol) was added to the solution of 1-(bromomethyl)-4-(tert-butyl)benzene (1000 mg, 4 mmol) in DMF (5 mL). The reaction mixture was heated at 65 °C for 6 h. After the completion of the reaction, the reaction mixture was quenched with water and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4 then dried in *vacuo.* to afford **2n** in (750 mg) 94% yield as a pale-yellow liquid.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45–7.39 (m, 2H), 7.29–7.23 (m, 2H), 4.32 (s, 2H), 1.34 (s, 9H). Spectroscopic data for **2n** are consistent with previously reported data for this compound. [5]

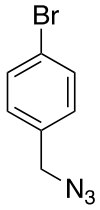


1-(Azidomethyl)-4-methoxybenzene (2o):

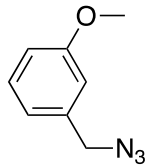
Sodium azide (539 mg, 8.3 mmol) was added to the solution of 1-(chloromethyl)-4-methoxybenzene (1000 mg, 6.4 mmol) in DMF (5 mL). The reaction mixture was heated at 65 °C for 6 h. After the completion of the reaction, the reaction mixture was quenched with water and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4 then dried in *vacuo.* to afford **2o** in (920 mg) 88% yield as an off-white liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 4.25 (s, 2H), 3.80 (s, 3H).
Spectroscopic data for **2o** are consistent with previously reported data for this compound.[10]



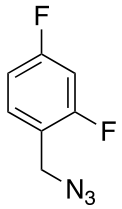
4-(Azidomethyl)benzonitrile (2p):
Sodium azide (257 mg, 3.9 mmol) was added to the solution of 4-(chloromethyl)benzonitrile (500 mg, 3.3 mmol) in DMF (3 mL). The reaction mixture was heated at 65 °C for 6 h. After the completion of the reaction, the reaction mixture was quenched with water and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4 then dried in *vacuo.* to afford **2p** in (450 mg) 86% yield as a pale-yellow liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 8.3 Hz, 2H), 4.45 (s, 2H).
Spectroscopic data for **2p** are consistent with previously reported data for this compound.[11]



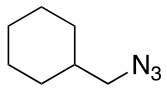
1-(Azidomethyl)-4-bromobenzene (2q):
Sodium azide (300 mg, 5 mmol) was added to the solution of 1-bromo-4-(bromomethyl)benzene (1000 mg, 4 mmol) in DMF (5 mL). The reaction mixture was heated at 65 °C for 6 h. After the completion of the reaction, the reaction mixture was quenched with water and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4 then dried in *vacuo.* to afford **2q** in (760 mg) 95% yield as an off-white solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 4.30 (s, 2H).
Spectroscopic data for **2q** are consistent with previously reported data for this compound. [12]



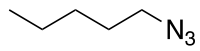
1-(Azidomethyl)-3-methoxybenzene (2r):
Sodium azide (400 mg, 6 mmol) was added to the solution of 1-(bromomethyl)-3-methoxybenzene (1000 mg, 5 mmol) in DMF (5 mL). The reaction mixture was heated at 65 °C for 6 h. After the completion of the reaction, the reaction mixture was quenched with water and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4 then dried in *vacuo.* to afford **2r** in (750 mg) 94% yield as a pale-yellow liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.8 Hz, 1H), 7.04–6.79 (m, 3H), 4.32 (s, 2H), 3.83 (s, 3H).
Spectroscopic data for **2r** are consistent with previously reported data for this compound.[9]



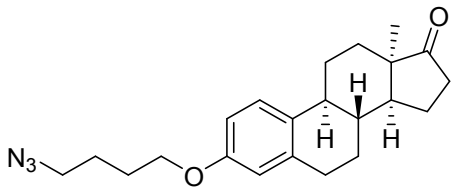
1-(Azidomethyl)-2,4-difluorobenzene (2s):
Sodium azide (400 mg, 6 mmol) was added to the solution of 1-(bromomethyl)-2,4-difluorobenzene (1000 mg, 5 mmol) in DMF (5 mL). The reaction mixture was heated at 65 °C for 6 h. After the completion of the reaction, the reaction mixture was quenched with water and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4 then dried in *vacuo.* to afford **2s** in (770 mg) 96% yield as a pale-yellow liquid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.27 (m, 1H), 6.96–6.72 (m, 2H), 4.37 (s, 2H). Spectroscopic data for **2s** are consistent with previously reported data for this compound.[13]



(azidomethyl)cyclohexane (2t):
Sodium azide (220 mg, 3.4 mmol) was added to the solution of (bromomethyl) cyclohexane (500 mg, 2.8 mmol) in DMF (3 mL). The reaction mixture was heated at 65 °C for 6 h. After the completion of the reaction, the reaction mixture was quenched with water and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4 then dried in *vacuo.* to afford **2t** in (286 mg) 73% yield as a colorless liquid.
^{1}H NMR (400 MHz, Chloroform-d) δ 3.11 (d, J = 6.7 Hz, 2H), 1.88–1.70 (m, 4H), 1.70–1.65 (m, 1H), 1.62–1.48 (m, 1H), 1.33–1.19 (m, 2H), 1.19–1.08 (m, 1H), 1.03–0.90 (m, 2H). Spectroscopic data for **2t** are consistent with previously reported data for this compound.[10]

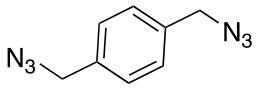


1-azidopentane (2u):
Sodium azide (258 mg, 3.9 mmol) was added to the solution of 1-bromopentane (500 mg, 3.3 mmol) in DMF (3 mL). The reaction mixture was heated at 65 °C for 6 h. After the completion of the reaction, the reaction mixture was quenched with water and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4 then dried in *vacuo.* to afford **2u** in (240 mg) 64% yield as a colorless liquid.
^{1}H NMR (400 MHz, Chloroform-d) δ 3.25 (t, *J* = 7.0 Hz, 2H), 1.80–1.46 (m, 2H), 1.48–1.18 (m, 4H), 1.08–0.69 (m, 3H). Spectroscopic data for **2u** are consistent with the previously reported data for this compound.[15]



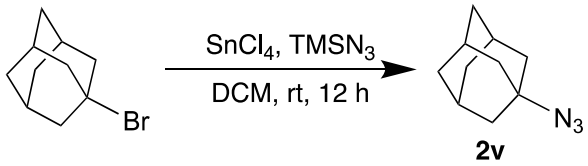
(13S)-3-(4-azidobutoxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (2y):
Sodium azide (125 mg, 1.92 mmol) was added to the solution of (13S)-3-(4-bromobutoxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (600 mg, 1.48 mmol) in DMF (4 mL). The reaction mixture was heated at 65 °C for 6 h. After the completion of the reaction, the reaction mixture was quenched with water and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4 then dried in *vacuo* to afford **2y** in (150 mg) 82% yield as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.6 Hz, 1H), 6.63 (d, *J* = 8.7 Hz, 1H), 6.56 (s, 1H), 3.89 (t, *J* = 5.7 Hz, 2H), 3.31–3.21 (m, 3H), 2.86–2.74 (m, 2H), 2.47–2.37 (m, 1H), 2.35–2.24 (m, 1H), 2.17 (t, *J* = 8.4 Hz, 1H), 2.11–2.03 (m, 1H), 2.02–1.85 (m, 3H), 1.82–1.74 (m, 2H), 1.74–1.66 (m, 2H), 1.53–1.33 (m, 5H), 0.83 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 220.9, 156.9, 137.9, 132.2, 126.4, 114.6, 112.2, 67.2, 51.0, 50.5, 48.1, 44.1, 38.5, 35.9, 31.7, 29.7, 26.6, 26.3, 26.0, 25.9, 21.7, 13.9. **HRMS**: $C_{22}H_{29}N_3O_2$ $[M]^+$; calculated: 368.2338, found: 368.2357. **IR** (v, cm^{-1}): 2092, 2328, 2677, 2861, 2925.



1,4-bis(azidomethyl)benzene (2z):
Sodium azide (600 mg, 9 mmol) was added to the solution of 1,4-bis(bromomethyl)benzene (1000 mg, 4 mmol) in DMF (5 mL). The reaction mixture was heated at 65 °C for 6 h. After the completion of the reaction, the reaction mixture was quenched with water and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4 then dried in *vacuo.* to afford **2z** in (600 mg) 80% yield as an off-white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.35 (s, 4H), 4.36 (s, 4H). Spectroscopic data for **2z** are consistent with previously reported data for this compound.[14]

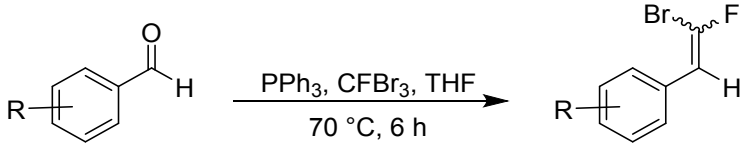
iii. Procedure 3: synthesis of adamentyl azide (2v):



2v

(3s,5s,7s)-1-azidoadamantane (2v):
A mixture of (3s,5s,7s)-1-bromoadamantane (1000 mg, 4.6 mmol), azidotrimethylsilane (660 mg, 5.5 mmol), and $SnCl_4$ (1200 mg, 4.6 mmol) in CH_2Cl_2 (8 mL) was refluxed under N_2 for 12 h. After all dibromide and mono-substituted intermediate were consumed, the mixture was poured into crushed ice and H_2O. The mixture was stirred for 30 min and then separated. The organic phase was washed with H_2O, aqueous $NaHCO_3$, and finally brine, dried over anhydrous $MgSO_4$, concentrated in *vacuo* to afford **2v** in (580 mg) 71% yield as a colorless solid. The crude was purified by column chromatography by hexane as eluent.
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.08 (s_{br}, 3H), 1.73 (s_{br}, 6H), 1.65–1.52 (m, 6H).
Spectroscopic data for **2v** are consistent with previously reported data for this compound.[16]

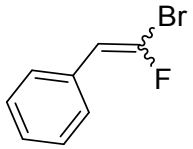
4. General procedure for the synthesis α-fluorobromoalkene:



An oven-dried screw-capped reaction tube was charged with PPh_3 (7 mmol) and $CFBr_3$ (6.13 mmol). The mixture was dissolved in THF (5 mL) and heated at 70 °C for 15 min. After that, the reaction mixture was cooled to room temperature and appropriate aldehyde (4.71 mmol) and remaining PPh_3 (7 mmol) were added to the reaction mixture. The reaction mixture was then heated at 70 °C for 6 h. After completion of the reaction, the crude reaction mixture was poured into cold water and extracted with petroleum ether (20 ml X 4). All organic fractions were then dried over anhydrous Na_2SO_4 and concentrated in *vacuo.* The crude reaction mixture was then purified by flash column chromatography using petroleum ether as eluent. The

product was obtained as a mixture of E and Z isomer (consistent with the literature report; the ratio was determined by ^{1}H NMR).

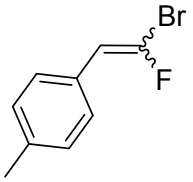
Caution: α-Fluorobromoalkenes are volatile compounds extra precaution should be taken while concentrating *in vacuo* to avoid losing the compounds.



(2-Bromo-2-fluorovinyl)benzene (1-SM):

Benzaldehyde (500 mg, 4.71 mmol), PPh_3 (3.71 g, 14.1 mmol), and $CFBr_3$ (0.6 mL, 6.13 mmol) were used to afford **1-SM** in (0.76 g, E/Z = 48:52) 80% yield as a colorless liquid after purification by column chromatography (using hexane as an eluent).

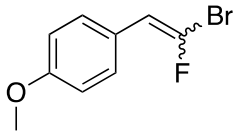
^{1}H NMR ($CDCl_3$) **(*Z*)-isomer** (full spectrum with all peaks) δ 7.55–7.47 (m, 1H), 7.45–7.28 (m, 4H), 6.68 (d, $^3J_{HF(cis)}$ = 15.1 Hz, 1H). ^{1}H NMR ($CDCl_3$) **(*E*)-isomer** (diagnostic vinyl peak only) 5.99 (d, $^3J_{HF(trans)}$ = 32.8 Hz, 1H); **^{19}F NMR** ($CDCl_3$) **(*E*)-isomer**: -68.3 (d, $^3J_{FH(trans)}$ = 32.9 Hz); **(*Z*)-isomer**: -65.9 (d, $^3J_{FH(cis)}$ = 15.1 Hz). Spectroscopic data for **1-SM** are consistent with previously reported data for this compound.[17]



(2-Bromo-2-fluorovinyl)-4-methylbenzene (1-SM-a):

4-Methylbenzaldehyde (500 mg, 4.16 mmol), PPh_3 (3.28 g, 12.5 mmol), and $CFBr_3$ (0.53 mL, 5.41 mmol) were used to afford **1-SM-a** in (0.8 g, E/Z = 50:50) 89% yield as an off-white solid after purification by column chromatography (using hexane as an eluent).

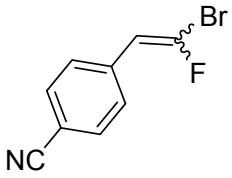
^{1}H NMR ($CDCl_3$) of **(Z)-isomer** (full spectrum with all peaks) δ 7.38 (d, *J* = 8.1 Hz, 2H), 7.21–7.16 (m, 2H), 6.64 (d, $^3J_{HF(cis)}$= 15.2 Hz, 1H), 2.36 (s, 3H)**;** ^{1}H NMR (CDCl3) **of (*E*)-isomer** (diagnostic vinyl peak only) 5.81 (d, $^3J_{HF(trans)}$ = 33.1 Hz, 1H) ppm; **^{19}F NMR** ($CDCl_3$) **(*E*)-isomer**: -69.3 (d, $^3J_{FH(trans)}$ = 30.9 Hz); **(*Z*)-isomer**: -66.9 (d, $^3J_{FH(cis)}$ = 15.5 Hz). Spectroscopic data for **1-SM-a** are consistent with previously reported data for this compound.[17]



(2-Bromo-2-fluorovinyl)-4-methoxybenzene (1-SM-b):

4-Methoxybenzaldehyde (500 mg, 3.67 mmol), PPh_3 (2.9 g, 11.02 mmol), and $CFBr_3$ (0.467 mL, 4.77 mmol) were used to afford **SM-b** in (0.77 g, E/Z = 85:15) 91% yield as a pale yellow solid after purification by column chromatography (using hexane as an eluent).

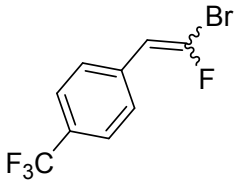
^{1}H NMR ($CDCl_3$) of **(*E*)-isomer** (full spectrum with all peaks) δ 7.35 (d, *J* = 9.0 Hz, 2H), 6.88 (d, *J* = 8.9 Hz, 2H), 5.91 (d, $^3J_{HF(trans)}$ = 33.2 Hz, 1H), 3.82 (s, 3H); ^{1}H NMR ($CDCl_3$**) (*Z*)-isomer** (diagnostic vinyl peak only) 6.62 (d, $^3J_{HF(cis)}$ = 15.3 Hz, 1H); **^{19}F NMR** ($CFCl_3$) **(*E*)-isomer**: -71.5 (d, $^3J_{FH(trans)}$ = 33.9 Hz); **(*Z*)-isomer**: -68.3 (d, $^3J_{FH(cis)}$ = 15.4 Hz). Spectroscopic data for **1-SM-b** are consistent with previously reported data for this compound.[17]



(2-Bromo-2-fluorovinyl)benzonitrile (1-SM-c):

4-Formylbenzonitrile (500 mg, 3.67 mmol), PPh3 (3 g, 11.44 mmol), and CFBr3 (0.485 mL, 4.96 mmol) were used to afford **1-SM-c** in (0.73 g, E/Z = 50:50) 85% yield as an off-white solid after purification by column chromatography (using hexane as an eluent).

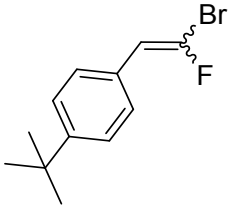
1H NMR (400 MHz, $CDCl_3$) of **(*E*)-isomer** (full spectrum with all peaks) δ 7.71–7.56 (m, 3H), 7.49 (m, *J* = 8.4 Hz, 1H), 6.04 (d, $^3J_{HF(trans)}$ = 31.9 Hz, 1H); ^{1}H NMR ($CDCl_3$) **(*Z*)-isomer** (diagnostic vinyl peak only) 6.68 (d, $^3J_{HF(cis)}$ = 14.5 Hz, 1H); **^{19}F NMR** ($CDCl_3$) **(*E*)-isomer**: -64.6 (d, $^3J_{FH(trans)}$ = 33.1 Hz); **(*Z*)-isomer**: -61.95 (d, $^3J_{FH(cis)}$ = 14.5 Hz). Spectroscopic data for **1-SM-c** are consistent with previously reported data for this compound.[18]



(2-Bromo-2-fluorovinyl)-4-(trifluoromethyl)benzene (1-SM-d):

4-(Trifluoromethyl)benzaldehyde (500 mg, 3.67 mmol), PPh_3 (2.26 g, 8.62 mmol), and $CFBr_3$ (0.37 mL, 3.74 mmol) were used to afford **SM-d** in (0.67 g, E/Z = 60:40) 87% yield as an off-white liquid after purification by column chromatography (using hexane as an eluent).

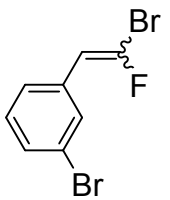
^{1}H NMR (400 MHz, $CDCl_3$) **(E)-isomer** (full spectrum with all peaks) δ 7.63–7.56 (m, 2H), 7.53–7.46 (m, 2H), 6.04 (d, $^3J_{HF(trans)}$ = 32.2 Hz, 1H); ^{1}H NMR ($CDCl_3$) **(*Z*)-isomer** (diagnostic vinyl peak only) 6.69 (d, $^3J_{HF(cis)}$ = 14.5 Hz, , 1H); **^{19}F NMR** ($CDCl_3$) **(*E*)-isomer**: -64.50 (d, $^3J_{FH(trans)}$ = 32.1 Hz); **(*Z*)-isomer**: -61.96 (d, $^3J_{FH(cis)}$ = 14.5 Hz). Spectroscopic data for **1-SM-d** are consistent with previously reported data for this compound.[17]



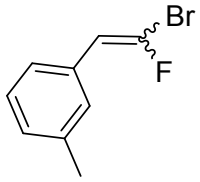
1-(2-Bromo-2-fluorovinyl)-4-(tert-butyl)benzene (1-SM-e):

4-(*tert*-Butyl)benzaldehyde (500 mg, 3.08 mmol), PPh_3 (2.43 g, 9.25 mmol), and $CFBr_3$ (0.39 mL, 4.01 mmol) were used to afford **SM-e** in (0.67 g, E/Z = 47:53) 84% yield as a colorless liquid after purification by column chromatography (using hexane as an eluent).

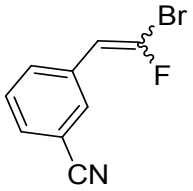
^{1}H NMR (400 MHz, $CDCl_3$) **(*Z*)-isomer** (full spectrum with all peaks) δ 7.48–7.16 (m, 4H), 6.54 (d, $^3J_{FH(cis)}$ = 15.3 Hz, 1H), 1.24 (s, 9H)**;** ^{1}H NMR ($CDCl_3$) **(*E*)-isomer** (diagnostic vinyl peak only) 5.86 (d, $^3J_{FH(trans)}$ = 33.1 Hz, 1H); **^{19}F NMR** ($CDCl_3$) **(*E*)-isomer** δ -69.32 (d, $J_{FH(trans)}$ = 33.0 Hz); **(*Z*)-isomer** -66.66 (d, $J_{FH(cis)}$= 15.2 Hz). Spectroscopic data for **1-SM-e** are consistent with previously reported data for this compound.[19]



1-Bromo-3-(2-bromo-2-fluorovinyl)benzene (1-SM-f):
3-Bromobenzaldehyde (500 mg, 2.70 mmol), PPh_3 (2.12 g, 8.10 mmol), and $CFBr_3$ (0.34 mL, 3.51 mmol) were used to afford **SM-f** in (0.70 g, E/Z = 60:40) 93% yield as a colorless oil after purification by column chromatography (using hexane as an eluent).
^{1}H NMR (400 MHz, $CDCl_3$) of **(*E*)-isomer** (full spectrum with all peaks) δ 7.55 (s, 1H), 7.47–7.13 (m, 3H), 5.93 (d, $^3J_{HF(trans)}$ = 32.2 Hz, 1H); ^{1}H NMR ($CDCl_3$) **(*Z*)-isomer** (diagnostic vinyl peak only) 6.60 (d, $^3J_{HF(cis)}$ = 14.7 Hz, 1H). **^{19}F NMR** ($CDCl_3$) **(*E*)-isomer**: -66.07 (d, $^3J_{FH(trans)}$ = 32.3 Hz); **(*Z*)-isomer**: -63.71 (d, $^3J_{FH(cis)}$ = 14.7 Hz). **^{13}C NMR** ($CDCl_3$) of the mixture of E and Z isomers: δ 136.06 (d, $^1J_{HF(cis)}$ = 317.0 Hz), 135.13 (d, $^1J_{HF(trans)}$ = 332.1 Hz), 134.45 (d, *J* = 4.8 Hz), 133.69 (d, *J* = 8.5 Hz), 131.29 (d, J = 3.3 Hz), 131.10, 130.97, 130.95, 130.87, 130.23, 130.01, 127.1 (d, *J* = 3.1 Hz), 126.64 (d, *J* = 7.3 Hz), 122.73 (d, *J* = 26.8 Hz), 111.97 (d, $^2J_{HF(trans)}$ = 6.2 Hz), 110.70 (d, $^2J_{HF(cis)}$ = 25.0 Hz) ppm. **IR** (v, cm^{-1}): 2841, 2928. **HRMS**: $C_8H_5Br_2F$ [M]$^-$; calculated: 276.86702, found: 276.86873.

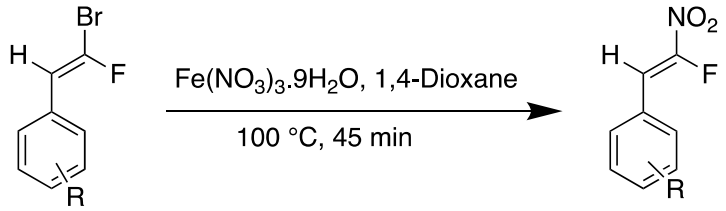


1-(2-Bromo-2-fluorovinyl)-3-methylbenzene (1-SM-g):
3-Methylbenzaldehyde (500 mg, 4.16 mmol), PPh_3 (3.27 g, 12.5 mmol), and $CFBr_3$ (0.53 mL, 5.41 mmol) were used to afford **1-SM-g** in (0.68 g, E/Z = 53:47) 76% yield as a colorless liquid after purification by column chromatography (using hexane as an eluent).
^{1}H NMR (400 MHz, $CDCl_3$) of **(*E*)-isomer** (full spectrum with all peaks) δ 7.18–6.91 (m, 4H), 5.77 (d, $^3J_{HF(trans)}$ = 33.0 Hz, 1H), 2.20 (s, 3H)); ^{1}H NMR ($CDCl_3$) **(*Z*)-isomer** (diagnostic vinyl peak only) δ 6.52 (d, $^3J_{HF(cis)}$ = 15.2 Hz, 1H).**^{19}F NMR** (376 MHz, $CDCl_3$-*d*) **(*Z*)-isomer**: -66.13 (d, $J_{FH(cis)}$= 15.3 Hz); **(*E*)-isomer**: -68.36 (d, $J_{FH(trans)}$ = 32.8 Hz). **^{13}C NMR** ($CDCl_3$) of the mixture of E and Z isomers: δ 138.25 (d, *J* = 20.5 Hz), 134.84 (d, $^1J_{HF(cis)}$ = 315.1.0 Hz), 133.77 (d, $^1J_{HF(trans)}$ = 330.9 Hz), 132.54 (d, *J* = 4.7 Hz), 131.45 (d, *J* = 8.1 Hz), 129.24 (d, *J* = 3.2 Hz), 128.91 (d, *J* = 1.4 Hz), 128.87, 128.82, 128.80, 128.67, 128.43, 125.51 (d, *J* = 3.1Hz), 125.30 (d, *J* = 7.3 Hz), 113.29 (d, $^2J_{HF(trans)}$ = 6.1 Hz), 111.81 (d, $^2J_{HF(cis)}$ = 23.6 Hz), 21.47, 21.45. **IR** (v, cm^{-1}): 2329, 2686, 2858, 2920, 3019. **HRMS**: C_9H_8BrF [M]$^-$; calculated: 212.9715, found: 212.9713.



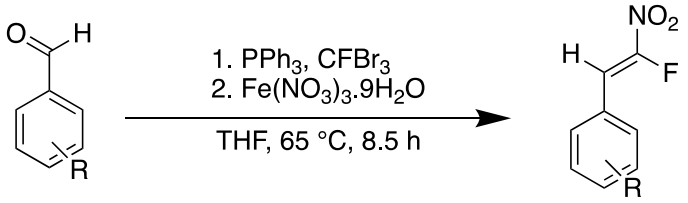
3-(2-Bromo-2-fluorovinyl)benzonitrile (1-SM-h):
3-Formylbenzonitrile (500 mg, 3.81 mmol), PPh_3 (3 g, 11.44 mmol), and $CFBr_3$ (0.485 mL, 4.95 mmol) were used to afford **1-SM-h** in (0.86 g, E/Z = 55:45, 90% yield) 90% yield as an off-white oil after purification by column chromatography (using hexane as an eluent).
^{1}H NMR (400 MHz, $CDCl_3$) of **(*E*)-isomer** (full spectrum with all peaks) δ 7.67 (d, *J* = 1.9 Hz, 1H), 7.62–7.38 (m, 3H), 5.99 (d, $^3J_{HF(trans)}$ = 31.8 Hz, 1H); ^{1}H NMR ($CDCl_3$) **(*Z*)-isomer** (diagnostic vinyl peak only) 6.64 (d, $^3J_{HF(cis)}$ = 14.1 Hz, 1H). **^{19}F NMR** ($CDCl_3$) **(*E*)-isomer**: -65.1 (d, $^3J_{FH(trans)}$ = 31.7 Hz); **(*Z*)-isomer**: -62.16 (d, $^3J_{FH(cis)}$ = 14.1 Hz). **^{13}C NMR** ($CDCl_3$) of the mixture of E and Z isomers: δ 143.08, 136.61 (d, $^1J_{HF(cis)}$ = 318.7 Hz), 135.90 (d, $^1J_{HF(trans)}$ = 332.4 Hz), 133.03, 133.47 (d, J = 4.6 Hz), 132.86 (d, *J* = 8.9 Hz), 132.63 (d, *J* = 3.2 Hz), 131.97 (d, *J* = 7.1 Hz), 131.53 (d, *J* = 3.3 Hz), 131.28, 131.15 (d, *J* = 7.9 Hz), 131.03 (d, *J* = 2.1 Hz), 129.42 (d, *J* = 22.0 Hz), 118.25, 112.79 (d, *J* = 22.9 Hz), 111.22 (d, $^2J_{HF(trans)}$ = 6.1 Hz), 110.10 (d, $^2J_{HF(cis)}$ = 25.6 Hz) ppm, 38.44. **IR** (v, cm^{-1}): 2855, 2921, 3064. **HRMS**: C_9H_5BrFN [M + H]$^+$; calculated: 225.9668, found: 225.9770.

5. General procedure for the synthesis α-fluoronitroalkenes:

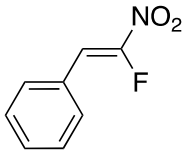


An oven-dried screw-capped pressure tube was charged with appropriate α-fluorobromoalkene (1 equiv.) and $Fe(NO_3)_3.9H_2O$ (3 equiv.). The mixture was dissolved in 1,4-dioxane (0.5 M) and heated at 100 °C for 45 min. After completion of the reaction, the crude reaction mixture was poured into water and extracted with petroleum ether (20 mL X 5). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. The product was obtained after purification by column chromatography (EtOAc/Petroleum Ether = 9:1 as eluent) on silica gel.

6. Alternative one-pot procedure for the synthesis α-fluoronitroalkenes:

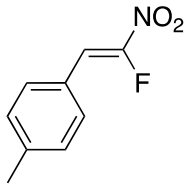


An oven-dried screw-capped pressure tube was charged with PPh_3 (1.5 equiv.). The vial was deggased and gassed with argon three times. PPh_3 was dissolved in THF (0.5 M), followed by the addition of benzaldehyde (1 equiv.) and $CFBr_3$ (1.3 equiv.). The reaction mixture was heated at 65 °C for 7 h and monitored by TLC. Then, under inert atmosphere, $Fe(NO_3)_3.9H_2O$ (1.5 equiv.) was quickly added and continued stirring for another 1.5 h at at 65 °C. After completion of the reaction, the crude reaction mixture was poured into water and extracted with petroleum ether (20 mL X 5). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. The product was obtained after purification by column chromatography (EtOAc/Petroleum Ether = 9:1 as eluent) on silica gel.

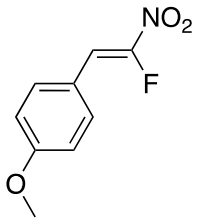


(*Z*)-(2-Fluoro-2-nitrovinyl)benzene (1):
(2-Bromo-2-fluorovinyl)benzene (500 mg, 2.49 mmol) and tris(nitrooxy)iron nonahydrate (2.7 g, 6.72 mmol) used to afford **1** (0. 37 g, 89% yield) as a light-yellow liquid after purification by column chromatography (EtOAc/Petroleum Ether = 9:1 as eluent).

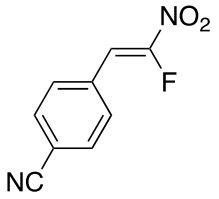
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77–7.59 (m, 2H), 7.57–7.49 (m, 3H), 7.44 (d, *J* = 26.4 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -111.98 (d, *J* = 26.3 Hz). Spectroscopic data for **1** are consistent with previously reported data for this compound.[17]



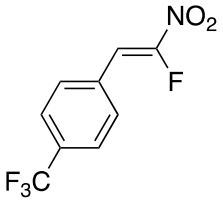
(*Z*)-1-(2-Fluoro-2-nitrovinyl)-4-methylbenzene (1a):
1-(2-Bromo-2-fluorovinyl)-4-methylbenzene (500 mg, 2.3 mmol) and tris(nitrooxy)iron nonahydrate (2.8 g, 6.9 mmol) used to afford **1a** (0. 37 g, 89% yield) as an off-white solid after purification by column chromatography (EtOAc/Petroleum Ether = 9:1 as eluent).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (m, 2H), 7.40 (d, *J* = 26.7 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 2H), 2.42 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.83 (d, *J* = 26.7 Hz). Spectroscopic data for **1a** are consistent with previously reported data for this compound.[17]



(*Z*)-1-(2-Fluoro-2-nitrovinyl)-4-methoxybenzene (1b):
1-(2-bromo-2-fluorovinyl)-4-methoxybenzene (500 mg, 2.1 mmol) and tris(nitrooxy)iron nonahydrate (2.6 g, 6.5 mmol) used to afford **1b** (0.19 g, 45% yield) as a bright yellow solid after purification by column chromatography (EtOAc/Petroleum Ether = 9:1 as eluent).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 26.8 Hz, 1H), 7.00 (m, 2H), 3.88 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.82 (d, *J* = 26.8 Hz). Spectroscopic data for **1b** are consistent with previously reported data for this compound.[17]



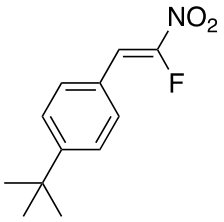
(*Z*)-4-(2-Fluoro-2-nitrovinyl)benzonitrile (1c):
4-(2-bromo-2-fluorovinyl)benzonitrile (500 mg, 2.2 mmol) and tris(nitrooxy)iron nonahydrate (2.6 g, 6.6 mmol) used to afford **1c** (0.38 g, 89% yield) as an off white solid after purification by column chromatography (EtOAc/Petroleum Ether = 9:1 as eluent).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.85–7.71 (m, 4H), 7.41 (d, *J* = 25.4 Hz, 1H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -108.08 (d, *J* = 25.1 Hz). Spectroscopic data for **1c** are consistent with previously reported data for this compound.[18]



(*Z*)-1-(2-Fluoro-2-nitrovinyl)-4-(trifluoromethyl)benzene (1d):

1-(2-Bromo-2-fluorovinyl)-4-(trifluoromethyl)benzene (500 mg, 1.8 mmol) and tris(nitrooxy)iron nonahydrate (2.2 g, 5.5 mmol) used to afford **1d** (0.38 g, 88% yield) as an off-white solid after purification by column chromatography (EtOAc/Petroleum Ether = 9:1 as eluent).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (s, 1H), 7.65–7.55 (m, 2H), 7.39–7.29 (m, 2H).**^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.73, -109.45 (d, *J* = 25.7 Hz). Spectroscopic data for **1d** are consistent with previously reported data for this compound.[3]

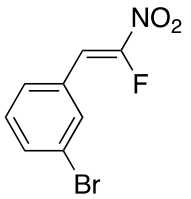


1-(2-bromo-2-fluorovinyl)-4-(tert-butyl)benzene (1e):

(*Z*)-1-(*tert*-Butyl)-4-(2-fluoro-2-nitrovinyl)benzene (500 mg, 1.56 mmol) and tris(nitrooxy)iron nonahydrate (1.89 g, 4.67 mmol) used to afford **1e** (245 mg, 71% yield) as a colorless liquid after purification by column chromatography (EtOAc/Petroleum Ether = 9:1 as eluent).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 26.7 Hz, 1H), 1.35 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.86 (d, *J* = 26.7 Hz).

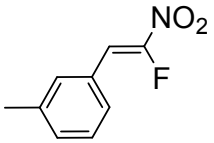
Spectroscopic data for **1e** are consistent with previously reported data for this compound.[19]



(*Z*)-1-Bromo-3-(2-fluoro-2-nitrovinyl)benzene (1f):

1-Bromo-3-(2-bromo-2-fluorovinyl)benzene (1g, 3.5 mmol) and tris(nitrooxy)iron nonahydrate (4.3g, 10.7 mmol) used to afford **1f** (0.77 g, 88% yield) as an off-white solid after purification by column chromatography (EtOAc/Petroleum Ether = 9:1 as eluent). **m.p.** 126–128 °C.

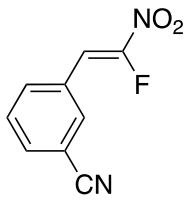
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66–7.56 (m, 2H), 7.59–7.44 (m, 2H), 7.47–7.33 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 152.73 (d, *J* = 293.3 Hz), 133.47, 132.76, 132.19, 132.13, 126.86 (d, *J* = 6.5 Hz), 126.31 (d, *J* = 3.9 Hz), 108.91 (d, *J* = 6.2 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.90 (d, *J* = 26.0 Hz). **IR (v, cm^{-1}):** 2106, 2344. **HRMS:** $C_8H_5BrFNO_2$ [M-H]$^-$; calculated: 243.9409, found: 243.9439.



(*Z*)-1-(2-fluoro-2-nitrovinyl)-3-methylbenzene (1g):

1-(2-bromo-2-fluorovinyl)-3-methylbenzene (0.4 g, 1.86 mmol) and tris(nitrooxy)iron nonahydrate (2.25 g, 5.58 mmol) used to afford **1g** (0.2 g, 61% yield) as an off-white oil after purification by column chromatography (EtOAc/Petroleum Ether = 9:1 as eluent).

^{1}H NMR (400 MHz, CDCl3) δ 7.47 (d, *J* = 7.4 Hz, 2H), 7.44–7.33 (m, 2H), 7.31 (d, *J* = 7.9 Hz, 1H), 2.41 (s, 3H).**^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.07 (d, *J* = 26.6 Hz, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.04 (d, *J* = 296.2 Hz), 139.27, 132.47 (d, *J* = 2.7 Hz), 131.56 (d, *J* = 7.4 Hz), 129.31, 128.14 (d, *J* = 7.8 Hz), 127.95 (d, *J* = 6.5 Hz), 110.16 (d, *J* = 6.2 Hz), 21.38. **IR** (v, cm^{-1}): 2330, 2852, 2922, 3078. **HRMS**: $C_9H_8FNO_2$ [M-H]$^-$; calculated: 180.0461, found: 195.0440

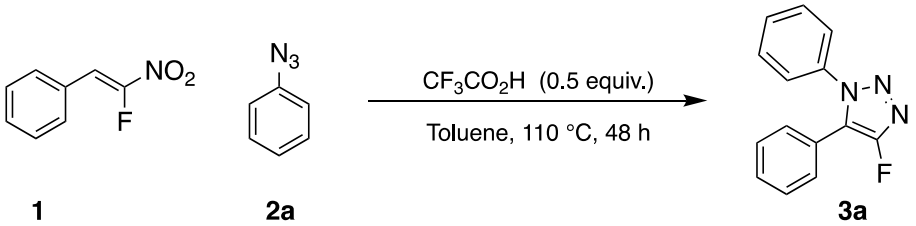


(*Z*)-3-(2-Fluoro-2-nitrovinyl)benzonitrile (1h):

3-(2-bromo-2-fluorovinyl)benzonitrile (1g, 4.4 mmol) and tris(nitrooxy)iron nonahydrate (5.3 g,13.2 mmol) used to afford **1h** (0.65 g, 88% yield) as an off-white solid after purification by column chromatography (EtOAc/Petroleum Ether = 9:1 as eluent). **m.p.** 81–82 °C.

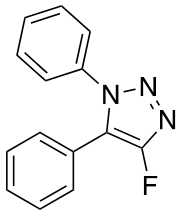
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.66 (t, *J* = 7.9 Hz, 1H), 7.43 (d, *J* = 25.4 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.04 (d, *J* = 296.2 Hz), 134.56 (d, *J* = 7.5 Hz), 134.39 (d, *J* = 2.6 Hz), 133.87 (d, *J* = 8.0 Hz), 130.38, 129.38 (d, *J* = 6.3 Hz), 117.67, 113.95, 107.46 (d, *J* = 6.1 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -109.11 (d, *J* = 25.3 Hz). **IR** (v, cm^{-1}): 2344, 2756, 2841, 2928, 3058, 3328. **HRMS:** $C_9H_5FN_2O_2$ $[M-H]^-$; calculated: 191.0257, found: 191.0276.

7. General Procedure for the Preparation of 1,5-disubstituted-4-fluoro-1,2,3-triazoles:



1 **2a** **3a**

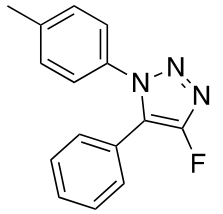
To an oven-dry screw-capped reaction tube with a magnetic stir bar was added α-fluoronitroalkene (1 equiv.) and corresponding azide (2 equiv.). The mixture was dissolved in toluene (0.4 mL) followed by TFA (0.5 equiv.) was added dropwise. The reaction mixture was purged with Ar and stirred at 110 °C for 48–96 h. After completion of the reaction (confirmed by TLC chromatography) the reaction mixture was quenched with saturated $NaHCO_3$ solution and extracted with DCM (20 mL X 3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The product was obtained after purification by column chromatography on silica gel by using DCM as eluent.



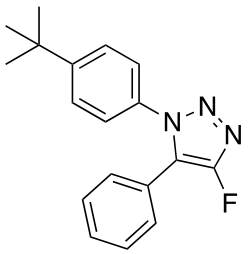
4-Fluoro-1,5-diphenyl-1H-1,2,3-triazole (3a):

α-Fluoronitroalkene (80 mg, 0.48 mmol), phenylazide (110 mg, 0.96 mmol), TFA (18 µL, 0.24 mmol) and toluene (0.4 mL) used to afford **3a** (85mg, 74% yield) as a pale-yellow oil after purification by column chromatography (DCM as eluent).

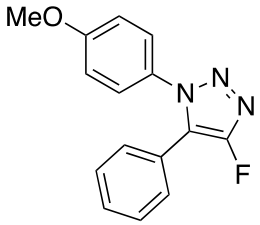
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.34 (m, 3H), 7.32–7.26 (m, 5H), 7.19–7.11 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -145.14. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.66 (d, *J* = 247.5 Hz), 136.78, 129.82, 129.58, 129.52, 129.03, 128.66 (d, *J* = 2.1 Hz), 125.02, 124.32 (d, *J* = 4.2 Hz), 119.70 (d, *J* = 28.3 Hz). **IR** (v, cm^{-1}): 2342, 2678, 2899. **HRMS**: $C_{14}H_{10}FN_3$ $[M]^-$; calculated: 239.0859, found: 239.0854.



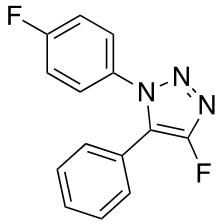
4-Fluoro-5-phenyl-1-(p-tolyl)-1H-1,2,3-triazole (3b):
α-Fluoronitroalkene (80 mg, 0.48 mmol), 1-azido-4-methylbenzene (130 mg, 0.96 mmol), TFA (18 µL, 0.24 mmol) and toluene (0.4 mL) used to afford **3b** (70mg, 58% yield) as an off-white oil after purification by column chromatography (DCM as eluent).
^{1}H NMR (400 MHz, MeOD-d4) δ 7.42–7.36 (m, 3H), 7.33–7.29 (m, 2H), 7.28–7.23 (m, 4H), 2.40 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -145.22. **^{13}C NMR** (101 MHz, $CDCl_3$) 158.68 (d, *J* = 247.2 Hz), 140.12, 134.43, 130.18, 129.47, 128.03, 128.69 (d, *J* = 2.1 Hz, 124.90, 124.52 (d, *J* = 4.2 Hz), 119.65 (d, *J* = 28.3z Hz), 21.32. **IR** (v, cm^{-1}): 2357, 3062. **HRMS**: $C_{15}H_{12}FN_3$ [M + Cs]$^+$; calculated: 386.0070, found: 386.0089.



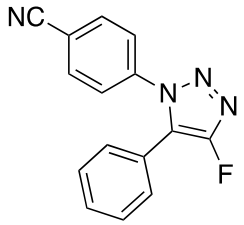
1-(4-(*tert*-Butyl)phenyl)-4-fluoro-5-phenyl-1H-1,2,3-triazole (3c):
α-Fluoronitroalkene (80 mg, 0.48 mmol), 1-azido-4-(tert-butyl)benzene (170 mg, 0.96 mmol), TFA (18 µL, 0.24 mmol) and toluene (0.4 mL) used to afford **3c** (74mg, 54% yield) as a pale-yellow oil after purification by column chromatography (DCM as eluent).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.7 Hz, 2H), 7.43–7.38 (m, 3H), 7.31 (d, *J* = 8.7 Hz, 2H), 7.29–7.26 (m, 2H), 1.37 (s, 9H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -145.19. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.73 (d, *J* = 247.3 Hz), 153.24, 134.35, 129.48, 129.07, 128.77 (d, *J* = 2.0 Hz), 126.56, 124.61 (d, *J* = 4.1 Hz), 124.57, 119.65 (d, *J* = 28.2 Hz), 35.02, 31.36. **IR** (v, cm^{-1}): 2867, 2959, 3060. **HRMS**: $C_{18}H_{18}FN_3$ [M + Cs]$^+$; calculated: 428.0539, found: 428.0539.



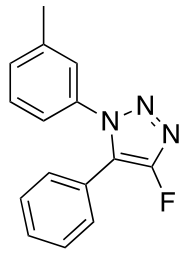
4-Fluoro-1-(4-methoxyphenyl)-5-phenyl-1H-1,2,3-triazole (3d):
α-Fluoronitroalkene (80 mg, 0.48 mmol), 1-azido-4-methoxybenzene (140 mg, 0.96 mmol), TFA (18 µL, 0.24 mmol) and toluene (0.4 mL) used to afford **3d** (66mg, 51% yield) as a pale-yellow oil after purification by column chromatography (DCM followed by DCM/EtOAc = 9:1 as eluent).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.37 (m, 3H), 7.31 (d, *J* = 8.9 Hz, 2H), 7.29–7.25 (m, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -145.13. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.55, 158.63 (d, *J* = 247.2 Hz), 129.89, 129.45, 129.06, 128.67 (d, *J* = 2.2 Hz), 126.56, 124.56 (d, *J* = 4.2 Hz), 119.7 (d, *J* = 28.2 Hz), 114.74, 55.72. **IR** (v, cm^{-1}): 2850, 2921, 3057. **HRMS**: $C_{15}H_{12}FN_3O$ [M + Cs]$^+$; calculated: 402.0019, found: 402.0018.



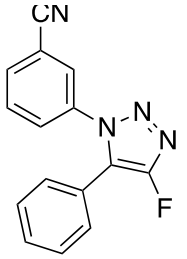
1-(4-(*tert*-Butyl)benzyl)-4-fluoro-5-phenyl-1H-1,2,3-triazole (3e):
α-Fluoronitroalkene (100 mg, 0.60 mmol), 1-azido-4-fluorobenzene (164 mg, 1.20 mmol), TFA (23 µL, 0.30 mmol) and toluene (0.4 mL) used to afford **3e** (73mg, 47% yield) as a pale-yellow oil after purification by column chromatography (DCM as eluent).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.38 (m, 3H), 7.38–7.35 (m, 2H), 7.25–7.20 (m, 2H), 7.18–7.11 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.69, -144.91. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.09 (d, *J* = 250.9 Hz), 158.71 (d, *J* = 247.9 Hz), 132.99 (d, *J* = 3.3 Hz), 129.76, 129.23, 128.75 (d, *J* = 2.1 Hz), 127.08 (d, *J* = 8.9 Hz), 124.20 (d, *J* = 4.1 Hz), 119.90 (d, *J* = 28.3 Hz), 116.78 (d, *J* = 23.3 Hz). **IR** (ν, cm^{-1}): 2852, 2920, 3020, 3060. **HRMS**: $C_{14}H_9F_2N_3$ $[M + H]^+$; calculated: 258.0843, found: 258.0849.



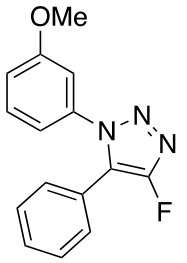
3-(4-Fluoro-5-phenyl-1H-1,2,3-triazol-1-yl)benzonitrile (3f):
α-Fluoronitroalkene (50 mg, 0.30 mmol), 1-azido-4-cyanobenzene (86 mg, 0.60 mmol), TFA (12 µL, 0.15 mmol) and toluene (0.4 mL) used to afford **3f** (29mg, 38% yield) as an off-white oil after purification by column chromatography (DCM followed by DCM/EtOAc = 9:1 as eluent).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.6 Hz, 2H), 7.54 (d, *J* = 8.7 Hz, 2H), 7.48–7.39 (m, 3H), 7.26–7.23 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -144.45. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.92 (d, *J* = 249.1 Hz), 139.97, 133.64, 130.26, 129.51, 128.92 (d, *J* = 1.8 Hz), 125.22, 123.74 (d, *J* = 4.0 Hz), 119.98 (d, *J* = 28.9 Hz), 117.59, 113.70. **IR** (ν, cm^{-1}): 2358, 2852, 2922. **HRMS**: $C_{15}H_9FN_4$ $[M + H]^+$; calculated: 265.0890, found: 265.0922.



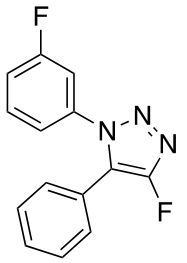
4-Fluoro-5-phenyl-1-(m-tolyl)-1H-1,2,3-triazole (3g):
α-Fluoronitroalkene (80 mg, 0.48 mmol), 1-azido-3-methylbenzene (130 mg, 0.96 mmol), TFA (18 µL, 0.24 mmol) and toluene (0.4 mL) used to afford **3g** (82mg, 68% yield) as an off-white oil after purification by column chromatography (DCM as eluent).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.36 (m, 3H), 7.33–7.29 (m, 2H), 7.28–7.24 (m, 3H), 7.08 (d, *J* = 7.0 Hz, 1H), 2.38 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -145.08. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.71 (d, *J* = 247.4 Hz), 140.02, 136.82, 130.64, 129.51, 129.30, 129.04, 128.69 (d, *J* = 2.2 Hz), 125.69, 124.52 (d, *J* = 4.2 Hz), 122.18, 119.70 (d, *J* = 28.2 Hz), 21.40. **IR** (ν, cm^{-1}): 2342, 2865, 2960, 3057. **HRMS**: $C_{15}H_{12}FN_3$ $[M + Cs]^+$; calculated: 386.0070, found: 386.0083.



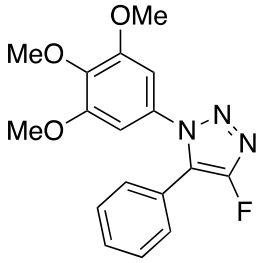
3-(4-Fluoro-5-phenyl-1H-1,2,3-triazol-1-yl)benzonitrile (3h):
α-Fluoronitroalkene (80 mg, 0.48 mmol), 1-azido-3-cyanobenzene (140 mg, 0.96 mmol), TFA (18 µL, 0.24 mmol) and toluene (0.4 mL) used to afford **3h** (40mg, 32% yield) as an pale-yellow oil after purification by column chromatography (DCM followed by DCM/EtOAc = 9:1 as eluent).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81–7.76 (m, 1H), 7.72 (d, *J* = 1.9 Hz, 1H), 7.66–7.59 (m, 2H), 7.48–7.40 (m, 3H), 7.27–7.19 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -144.49. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.65 (d, *J* = 248.8 Hz), 137.37, 133.20, 130.71, 130.20, 129.43, 128.98, 128.74 (d, *J* = 1.9 Hz), 128.02, 123.43 (d, *J* = 4.0 Hz), 119.97 (d, *J* = 29.1 Hz), 117.14, 113.94. **IR** (ν, cm^{-1}): 2358, 2852, 2922. **HRMS**: $C_{15}H_9FN_4$ $[M]^-$; calculated: 264.0811, found: 264.0827.



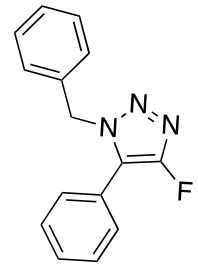
4-Fluoro-1-(3-methoxyphenyl)-5-phenyl-1H-1,2,3-triazole (3i):
α-Fluoronitroalkene (80 mg, 0.48 mmol), 1-azido-3-methoxybenzene (140 mg, 0.96 mmol), TFA (18 µL, 0.24 mmol) used to afford **3i** (61mg, 47% yield) as an off-white solid after purification by column chromatography (DCM followed by DCM/EtOAc = 9:1 as eluent). **m.p.** 85–86 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.36 (m, 3H), 7.32 (t, *J* = 8.1 Hz, 1H), 7.28–7.24 (m, 2H), 7.02–6.98 (m, 1H), 6.95 (t, *J* = 2.3 Hz, 1H), 6.89 (d, *J* = 7.9 Hz, 1H), 3.75 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -145.23. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.33, 158.65 (d, *J* = 247.4 Hz), 137.72, 130.30, 129.56, 129.04, 128.69 (d, *J* = 2.1 Hz), 124.36 (d, *J* = 4.1 Hz), 119.72 (d, *J* = 28.2 Hz), 117.11, 115.87, 110.55, 55.61. **IR** (ν, cm^{-1}): 2345, 2685, 2850, 2921. **HRMS**: $C_{15}H_{12}FN_3O$ $[M]^+$; calculated: 269.0964, found: 269.0994.



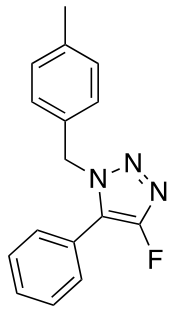
4-Fluoro-1-(3-fluorophenyl)-5-phenyl-1H-1,2,3-triazole (3j):
α-Fluoronitroalkene (80 mg, 0.48 mmol), 1-azido-3-cyanobenzene (130 mg, 0.96 mmol), TFA (18 µL, 0.24 mmol) used to afford **3j** (64mg, 52% yield) as an off-white oil following purification by column chromatography (DCM as eluent).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.37 (m, 5H), 7.24 (d, *J* = 3.6 Hz, 1H), 7.21–7.12 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.10, -145.00. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.75 (d, *J* = 249.5 Hz), 158.76 (d, *J* = 248.0 Hz), 137.99 (d, *J* = 9.9 Hz), 131.00 (d, *J* = 8.9 Hz), 129.89, 129.26, 128.81 (d, *J* = 1.9 Hz), 124.07 (d, *J* = 4.1 Hz), 120.71 (d, *J* = 3.5 Hz), 119.89 (d, *J* = 28.8 Hz), 116.98 (d, *J* = 21.0 Hz), 112.75 (d, *J* = 25.2 Hz). **IR** (ν, cm^{-1}): 2836, 2939, 2956, 3001, 3059. **HRMS**: $C_{14}H_9F_2N_3$ $[M + H]^+$; calculated: 258.08372, found: 258.0843.



4-Fluoro-5-phenyl-1-(3,4,5-trimethoxyphenyl)-1H-1,2,3-triazole (3k):
α-Fluoronitroalkene (80 mg, 0.48 mmol), 1-azido-3-cyanobenzene (200 mg, 0.96 mmol), TFA (18 µL, 0.24 mmol) used to afford **3k** (87mg, 55% yield) as an off-white oil after purification by column chromatography (DCM as eluent).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.37 (m, 3H), 7.32–7.23 (m, 2H), 6.58 (s, 2H), 3.88 (s, 3H), 3.71 (s, 6H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -144.88. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.61 (d, *J* = 247.7 Hz), 153.64, 138.92, 132.26, 129.63, 129.06, 128.77 (d, *J* = 2.1 Hz), 124.44 (d, *J* = 4.2 Hz), 119.68 (d, *J* = 28.5 Hz), 102.52, 61.13, 56.31. **IR** (v, cm^{-1}): 2336, 2830, 2934. **HRMS**:$C_{17}H_{16}FN_3O_3$ [M + Cs]$^{+}$; calculated: 462.0230, found: 462.0223.

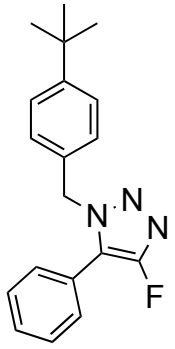


1-Benzyl-4-fluoro-5-phenyl-1H-1,2,3-triazole (3l):
α-Fluoronitroalkene (100 mg, 0.6 mmol), benzyl azide(159 mg, 1.20 mmol), TFA (23 µL, 0.3 mmol) and toluene (0.4 mL) used to afford **3l** (80mg, 53% yield) as an off-white oil following purification by column chromatography (DCM as eluent).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 5.1, 2.0 Hz, 3H), 7.32–7.21 (m, 5H), 7.14–6.93 (m, 2H), 5.49 (s, 2H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -145.68. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.56 (d, *J* = 246.1 Hz), 134.76, 129.92, 129.23, 129.05 (d, *J* = 1.8 Hz), 129.01, 128.53, 127.27, 124.34 (d, *J* = 3.9 Hz), 120.07 (d, *J* = 29.7 Hz), 53.52. **IR** (v, cm^{-1}): 2850, 2921. **HRMS**: $C_{15}H_{12}FN_3$ [M]$^{+}$; calculated: 254.1108, found: 254.1093.

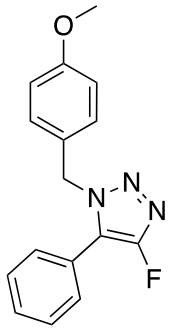


4-Fluoro-1-(4-methylbenzyl)-5-phenyl-1H-1,2,3-triazole (3m):
α-Fluoronitroalkene (80 mg, 0.48 mmol), 1-(azidomethyl)-4-methylbenzene (140 mg, 0.96 mmol), and TFA (18 µL, 0.24 mmol) used to afford **3m** (81mg, 63% yield) as a colorless oil after purification by column chromatography (DCM as eluent).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.40 (m, 3H), 7.31–7.24 (m, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 5.44 (s, 2H), 2.31 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -145.86. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.62 (d, *J* = 246.4 Hz), 138.42, 131.81, 129.90, 129.70, 129.24, 129.14 (d, *J* = 1.6 Hz), 127.31, 124.52

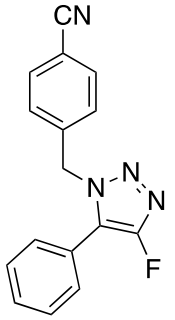
(d, *J* = 3.8 Hz), 119.99 (d, *J* = 29.8 Hz), 53.39, 21.24. **IR** (v, cm^{-1}): 2836, 2939, 2956, 3001. **HRMS**: $C_{16}H_{14}FN_3$ [M + Cs]+; calculated: 400.0225, found: 400.0226.



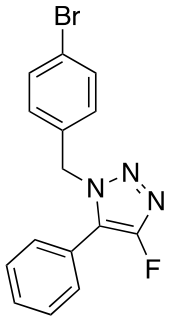
1-(4-(tert-butyl)benzyl)-4-fluoro-5-phenyl-1H-1,2,3-triazole (3n):
α-Fluoronitroalkene (80 mg, 0.48 mmol), 1-(azidomethyl)-4-(tert-butyl)benzene (180 mg, 0.96 mmol), and TFA (18 µL, 0.24 mmol) used to afford **3n** (74mg, 50% yield) as a pale-yellow oil after purification by column chromatography (DCM as eluent).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (t, *J* = 3.3 Hz, 3H), 7.39–7.25 (m, 4H), 7.11–6.97 (m, 2H), 5.46 (s, 2H), 1.29 (d, *J* = 1.5 Hz, 9H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -145.85. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.44 (d, *J* = 245.9 Hz), 151.50, 131.69, 129.77, 129.12, 129.02 (d, *J* = 1.5 Hz), 127.09, 125.80, 124.34, 119.91 (d, *J* = 29.7 Hz), 53.09, 34.54, 31.22. **IR** (v, cm^{-1}): 2342, 2865, 2960, 3057. **HRMS**: $C_{19}H_{20}FN_3$ [M + H]+ ; calculated: 310.1719, found: 310.1692.



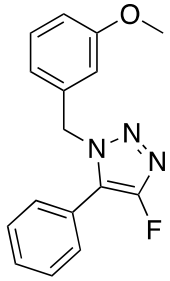
4-Fluoro-1-(4-methoxybenzyl)-5-phenyl-1H-1,2,3-triazole (3o):
α-Fluoronitroalkene (80 mg, 0.48 mmol), 1-(azidomethyl)-4-methoxybenzene (160 mg, 0.96 mmol), and TFA (18 µL, 0.24 mmol) used to afford **3o** (69mg, 51% yield) as a pale yellow oil after purification by column chromatography (DCM as eluent).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.44 (m, 3H), 7.30–7.23 (m, 2H), 7.02 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 5.43 (s, 2H), 3.77 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -145.80; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.74, 158.61 (d, *J* = 246.2 Hz), 129.91, 129.24, 129.18 (d, *J* = 1.5 Hz), 128.89, 126.76, 124.50 (d, *J* = 4.0 Hz), 119.88 (d, *J* = 29.8 Hz), 114.35, 55.40, 53.16. **IR** (v, cm^{-1}): 2922, 2852, 2358. **HRMS**: $C_{16}H_{14}FN_3O$ $[M + Cs]^+$; calculated: 416.0175, found: 416.0171.



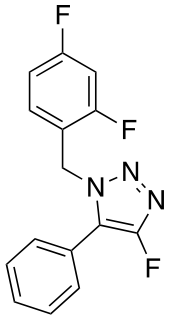
4-((4-Fluoro-5-phenyl-1H-1,2,3-triazol-1-yl)methyl)benzonitrile (3p):
α-Fluoronitroalkene (80 mg, 0.48 mmol), 4-(azidomethyl)benzonitrile (150 mg, 0.96 mmol), and TFA (18 µL, 0.24 mmol used to afford **3p** (68mg, 51% yield) as a pale yellow oil after purification by column chromatography (DCM as eluent).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.49–7.44 (m, 3H), 7.25–7.22 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -145.08. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.61 (d, *J* = 247.2 Hz), 139.74, 132.90, 130.33, 129.51, 128.95 (d, *J* = 1.5 Hz), 128.04, 123.94 (d, *J* = 3.8 Hz), 120.33 (d, *J* = 29.6 Hz), 118.22, 112.79, 52.91. **IR** (ν, cm^{-1}): 2336, 2830, 2934. **HRMS**: $C_{16}H_{11}FN_4$ [M + Cs]$^+$; calculated: 411.0020, found: 411.0022.



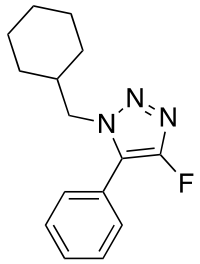
1-(4-Bromobenzyl)-4-fluoro-5-phenyl-1H-1,2,3-triazole (3q):
α-Fluoronitroalkene (80 mg, 0.48 mmol), 1-(azidomethyl)-4-bromobenzene (200 mg, 0.96 mmol), and TFA (18 µL, 0.24 mmol) used to afford **3q** (92mg, 58% yield) as a pale yellow oil after purification by column chromatography (DCM as eluent).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49–7.46 (m, 3H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.28–7.24 (m, 2H), 6.97 (d, *J* = 8.5 Hz, 2H), 5.46 (s, 2H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -145.22. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.59 (d, *J* = 246.7 Hz), 133.71, 132.22, 130.10, 129.36, 129.06, 129.04, 124.21 (d, *J* = 3.9 Hz), 122.76, 120.09 (d, *J* = 29.8 Hz), 52.90. **IR** (ν, cm^{-1}): 2854, 2922, 2951. **HRMS**: $C_{15}H_{11}BrFN_3$ [M + H]$^+$; calculated: 332.0023, found: 332.0018.



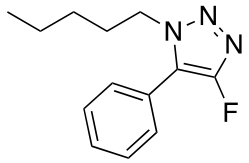
4-Fluoro-1-(3-methoxybenzyl)-5-phenyl-1H-1,2,3-triazole (3r):
α-Fluoronitroalkene (80 mg, 0.48 mmol), 1-(azidomethyl)-3-methoxybenzene (160 mg, 0.96 mmol), and TFA (18 µL, 0.24 mmol) used to afford **3r** (69mg, 51% yield) as a pale yellow oil after purification by column chromatography (DCM as eluent).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.40 (m, 3H), 7.31–7.25 (m, 2H), 7.20 (t, *J* = 7.9 Hz, 1H), 6.82 (dd, *J* = 8.2, 2.6 Hz, 1H), 6.68–6.57 (m, 2H), 5.46 (s, 2H), 3.72 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -145.73. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.12, 158.59 (d, *J* = 246.3 Hz), 136.29, 130.13, 129.94, 129.26, 129.11 (d, *J* = 1.7 Hz), 124.43 (d, *J* = 4.0 Hz), 120.10 (d, *J* = 29.7 Hz), 119.50, 114.22, 112.77, 55.36, 53.48. **IR** (ν, cm^{-1}): 2830, 2908., 2934. **HRMS**: $C_{16}H_{14}FN_3O$ [M + Cs]$^+$; calculated: 416.0175, found: 416.0160.



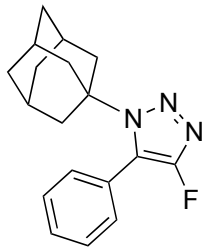
1-(2,4-Difluorobenzyl)-4-fluoro-5-phenyl-1H-1,2,3-triazole (3s):
α-Fluoronitroalkene (80 mg, 0.48 mmol), 1-(azidomethyl)-2,4-difluorobenzene (160 mg, 0.96 mmol), and TFA (18 µL, 0.24 mmol) used to afford **3s** (70mg, 51% yield) as a colorless oil after purification by column chromatography (DCM as eluent).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.46 (m, 3H), 7.31 (dd, *J* = 6.5, 3.0 Hz, 1H), 7.13–7.00 (m, 1H), 6.90–6.73 (m, 2H), 5.53 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -109.03, -113.95, -145.56. **^{13}C NMR** (101 MHz, CDCl3) δ 163.14 (dd, *J* = 251.0, 11.9 Hz), 160.09 (dd, *J* = 250.8, 12.1 Hz), 158.52(d, *J* = 246.6 Hz), 130.67 (dd, *J* = 9.9, 4.8 Hz), 130.12, 129.38, 128.93 (d, *J* = 1.5 Hz), 124.05 (d, *J* = 4.0 Hz), 120.21 (d, *J* = 29.8 Hz), 117.90 (dd, *J* = 14.4, 3.9 Hz), 112.11 (dd, *J* = 21.5, 3.8 Hz), 104.24 (t, *J* = 25.3 Hz), 46.57 (d, *J* = 4.2 Hz). **IR** (v, cm^{-1}): 2850, 2921. **HRMS**: $C_{15}H_{10}F_3N_3$ $[M]^-$; calculated: 289.0779, found: 289.0755.



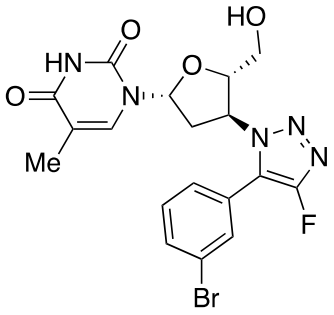
1-(Cyclohexylmethyl)-4-fluoro-5-phenyl-1H-1,2,3-triazole (3t):
α-Fluoronitroalkene (80 mg, 0.48 mmol), (azidomethyl)cyclohexane (130 mg, 0.96 mmol), and TFA (18 µL, 0.24 mmol). used to afford **3t** (65mg, 52% yield) as a colorless oil after purification by column chromatography (DCM as eluent).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.49 (m, 3H), 7.40–7.38 (m, 2H), 4.14 (d, *J* = 7.3 Hz, 2H), 1.90–1.73 (m, 1H), 1.72–1.58 (m, 3H), 1.56–1.51 (m, 2H), 1.19–1.07 (m, 3H), 0.92–0.82 (m, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -146.73. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.50 (d, *J* = 245.5 Hz), 129.80, 129.38, 129.07 (d, *J* = 1.5 Hz), 124.90 (d, *J* = 4.0 Hz), 120.03 (d, *J* = 29.6 Hz), 55.76, 38.22, 30.49, 26.10, 25.52. **IR** (v, cm^{-1}): 2358, 2852, 2922. **HRMS**: $C_{15}H_{18}FN_3$ $[M]^+$; calculated: 260.1563, found: 260.1577.



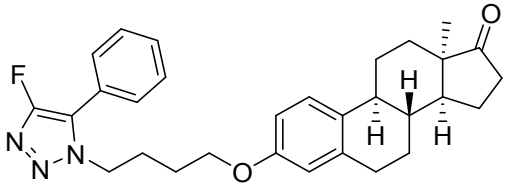
4-Fluoro-1-pentyl-5-phenyl-1H-1,2,3-triazole (3u):
α-Fluoronitroalkene (80 mg, 0.48 mmol), 1-azidopentane (110 mg, 0.96 mmol), and TFA (18 µL, 0.24 mmol) used to afford **3u** (55mg, 49% yield) as a colorless oil after purification by column chromatography (DCM as eluent).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.50 (m, 3H), 7.43–7.40 (m, 2H), 4.34–4.30 (m, 2H), 1.83 (t, *J* = 6.3 Hz, 2H), 1.27–1.24 (m, 4H), 0.85 (d, *J* = 5.2 Hz, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -146.54. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.52 (d, *J* = 245.7 Hz), 129.82, 129.39, 128.89 (d, *J* = 1.6 Hz), 124.79 (d, *J* = 4.0 Hz), 119.59 (d, *J* = 29.9 Hz), 49.95, 29.40, 28.53, 22.05, 13.83. **IR**(v, cm^{-1}): 2358, 2852, 2922. **HRMS:** $C_{13}H_{16}FN_3$ $[M]^+$; calculated: 234.1407, found: 234.1385.



1-((3s,5s,7s)-adamantan-1-yl)-4-fluoro-5-phenyl-1H-1,2,3-triazole (3v):
α-Fluoronitroalkene (80 mg, 0.48 mmol), (3s,5s,7s)-1-azidoadamantane (250 mg, 0.96 mmol), and TFA (18 µL, 0.24 mmol) used to afford **3v** (75mg, 49% yield) as an off-white solid after purification by column chromatography (DCM as eluent). **m.p.** 132–133 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 –7.45 (m, 3H), 7.38–7.33 (m, 2H), 2.23–2.17 (m, 5H), 2.13 (t, *J* = 3.2 Hz, 3H), 1.72–1.65 (m, 4H), 1.63–1.58 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -146.62. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.85 (d, *J* = 245.2 Hz), 131.20, 130.00, 128.70, 127.08 (d, *J* = 3.6 Hz), 119.31 (d, *J* = 31.6 Hz), 64.60, 42.56, 35.81, 29.67. **IR** (ν, cm^{-1}) 2342, 2678, 2899. **HRMS**: $C_{18}H_{20}FN_3$ [M + Cs]$^+$; calculated: 430.0695, found: 430.0678.



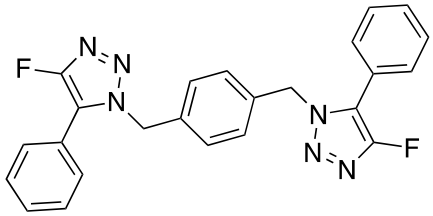
1-((2R,4S,5S)-4-(5-(3-Bromophenyl)-4-fluoro-1H-1,2,3-triazol-1-yl)-5-(hydroxymethyl)tetrahydrofuran-2-yl)-5-methylpyrimidine-2,4(1H,3H)-dione (3x):
(Z)-1-Bromo-3-(2-fluoro-2-nitrovinyl)benzene (138 mg, 0.56 mmol), 1-((2R,4S,5S)-4-azido-5-(hydroxymethyl) tetrahydrofuran-2-yl)-5-methylpyrimidine-2,4(1H,3H)-dione (100 mg, 0.37 mmol), and TFA (14.4 µL, 0.187 mmol) used to afford **3x** (43mg, 25% yield) as a white solid after purification by column chromatography (EtOAc as eluent). **m.p.** 124–126 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 7.68 – 7.63 (m, 1H), 7.57 (t, *J* = 1.8 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 1H), 7.37 – 7.32 (m, 1H), 7.27 (d, *J* = 1.4 Hz, 1H), 6.20 (t, *J* = 6.9 Hz, 1H), 5.35 – 5.28 (m, 1H), 4.58 (dt, *J* = 4.1, 2.0 Hz, 1H), 3.94 (dd, *J* = 12.5, 2.4 Hz, 1H), 3.58 (dd, *J* = 12.5, 2.4 Hz, 1H), 3.08 – 2.97 (m, 1H), 2.89 – 2.77 (m, 1H), 1.91 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -145.54. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.22, 158.57 (d, J = 248.4 Hz), 150.71, 138.33, 136.98, 133.49, 132.15, 131.18, 127.91, 123.59, 119.26 (d, *J* = 29.7 Hz), 111.43, 85.22, 84.71, 60.09, 58.92, 37.45, 12.57. Note: Even though the ^{1}H NMR and the HPLC trace of the product 3x looks clean, we found four extra peaks (89.75, 86.41, 61.97, 61.90) in the ^{13}C NMR despite our multiple attempts at purification. The peaks were assigned based on the starting material 1-((2R,4S,5S)-4-azido-5-(hydroxymethyl) tetrahydrofuran-2-yl)-5-methylpyrimidine-2,4(1H,3H)-dione. **IR**(ν, cm^{-1}): 2852, 2923, 3061, 3384. **HRMS**: $C_{18}H_{18}FN_5O_4$ [M]$^+$; calculated: 388.1421, found: 388.1397.



(8R,9S,13R,14S)-3-(4-(4-fluoro-5-phenyl-1H-1,2,3-triazol-1-yl)butoxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (3y):

α-Fluoronitroalkene (60 mg, 0.36 mmol), (13S)-3-(4-azidobutoxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (180 mg, 0.50 mmol), and TFA (14 µL, 0.18 mmol) used to afford **3y** (92mg, 53% yield) as a yellow oil after purification by column chromatography (DCM:EtOAc = 9:1 as eluent).

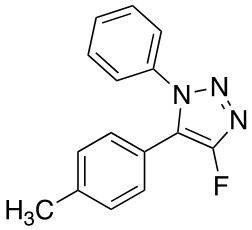
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47–7.38 (m, 3H), 7.33 (dd, *J* = 7.4, 2.2 Hz, 2H), 7.13–7.03 (m, 1H), 6.54 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.47 (d, *J* = 2.7 Hz, 1H), 4.34 (t, *J* = 7.3 Hz, 2H), 3.80 (t, *J* = 6.0 Hz, 2H), 2.89–2.65 (m, 2H), 2.42 (dd, *J* = 19.0, 8.7 Hz, 1H), 2.31 (dt, *J* = 9.0, 3.1 Hz, 1H), 2.21–2.13 (m, 1H), 2.06 (dt, *J* = 18.9, 8.8 Hz, 1H), 2.01–1.91 (m, 4H), 1.87 (dd, *J* = 9.1, 2.6 Hz, 1H), 1.67 (dt, *J* = 8.7, 6.1 Hz, 2H), 1.60–1.48 (m, 2H), 1.47–1.36 (m, 4H), 0.83 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -145.75. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 221.09, 158.52 (d, *J* = 246.0 Hz), 156.77, 137.89, 132.34, 129.89, 129.46, 128.89, 126.45, 124.61 (d, *J* = 4.1 Hz), 119.70 (d, *J* = 29.7 Hz), 114.56, 112.14, 66.75, 50.50, 49.61, 48.12, 44.07, 38.46, 35.98, 31.68, 29.74, 26.63, 26.59, 26.18, 26.03, 21.69, 13.96. **IR** (v, cm^{-1}): 2090, 2330, 2858, 2925, 3052. **HRMS**: $C_{30}H_{34}FN_3O_2$ $[M+H]^+$; calculated: 488.2713, found: 488.2708.



1,4-Bis((4-fluoro-5-phenyl-1H-1,2,3-triazol-1-yl)methyl)benzene (3z):

α-Fluoronitroalkene (231 mg, 1.38 mmol), 1,4-bis(azidomethyl)benzene (130 mg, 0.69 mmol), and TFA (26.6 µL, 0.345 mmol) used to afford **3z** (96mg, 32% yield) as an off-white oil after purification by column chromatography (DCM as eluent).

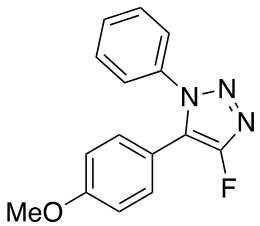
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.42 (m, 6H), 7.26–7.21 (m, 4H), 7.03 (s, 4H), 5.49 (s, 4H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -145.42. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.56 (d, *J* = 246.5 Hz), 135.14, 130.08, 129.33, 128.98 (d, *J* = 1.5 Hz), 127.91, 124.19 (d, *J* = 3.9 Hz), 120.11 (d, *J* = 29.6 Hz), 53.03. **IR** (v, cm^{-1}): 2856, 2924, 3055. **HRMS**: $C_{24}H_{18}F_2N_6$ $[M]^-$; calculated: 268.0858, found: 268.0886.



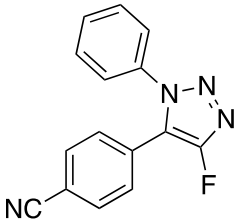
4-Fluoro-1-phenyl-5-(p-tolyl)-1H-1,2,3-triazole (4a):

(Z)-1-(2-Fluoro-2-nitrovinyl)-4-methylbenzene (100 mg, 0.55 mmol), azidobenzene (132 mg, 1.10 mmol), and TFA (21.3 µL, 0.28 mmol) used to afford **4a** (75mg, 54% yield) as a colorless solid after purification by column chromatography (DCM as eluent). **m.p.** 94-96 °C.

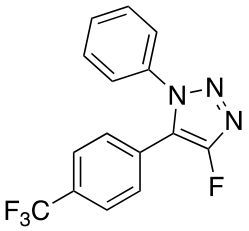
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.1 Hz, 3H), 7.37 (d, *J* = 5.7 Hz, 2H), 7.21–7.08 (m, 4H), 2.36 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -145.38. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.59 (d, *J* = 247.2 Hz), 139.79, 136.89, 129.79, 129.59, 128.57 (d, *J* = 2.0 Hz), 125.12, 125.06, 121.35 (d, *J* = 4.1 Hz), 119.85 (d, *J* = 28.3 Hz), 21.47. **IR** (v, cm^{-1}): 2923, 3016, 3367. **HRMS**: $C_{15}H_{12}FN_3$ $[M + Cs]^+$; calculated: 386.0070, found: 386.0051.



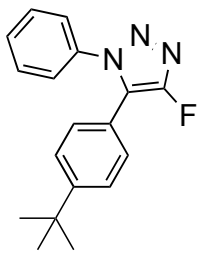
4-Fluoro-5-(4-methoxyphenyl)-1-phenyl-1H-1,2,3-triazole (4b):
(Z)-1-(2-Fluoro-2-nitrovinyl)-4-methoxybenzene (70 mg, 0.36 mmol), azidobenzene (85 mg, 0.71 mmol), and TFA (14 µL, 0.36 mmol) used to afford **4b** (70mg, 73% yield) as an off-white solid after purification by column chromatography (DCM as eluent). **m.p.** 76–78 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.45 (m, 3H), 7.44–7.36 (m, 2H), 7.16 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -145.82. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.39, 158.35 (d, *J* = 246.2 Hz), 136.84, 130.07 (d, *J* = 2.0 Hz), 129.72, 129.54, 125.00, 119.66 (d, *J* = 28.6 Hz), 116.34 (d, *J* = 4.2 Hz), 114.54, 55.35. **IR** (ν, cm^{-1}): 2923, 3016, 3367. **HRMS**: $C_{15}H_{12}FN_3O$ [M + Cs]$^+$; calculated: 561.0620, found: 561.0615.



4-(4-Fluoro-1-phenyl-1*H*-1,2,3-triazol-5-yl)benzonitrile (4c):
(Z)-4-(2-fluoro-2-nitrovinyl)benzonitrile (45 mg, 0.23 mmol), azidobenzene (56 mg, 0.47 mmol), TFA (9 µL, 0.12 mmol). The product was purified by column chromatography (DCM as eluent) affording **4c** (27 mg, 44% yield) as an off-white solid. **m.p.** 125–127 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 10.3 Hz, 3H), 7.35 (d, *J* = 8.4 Hz, 4H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -142.81. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.00 (d, *J* = 250.2 Hz), 136.36, 132.79, 130.48, 129.99, 129.02, 128.87 (d, *J* = 4.5 Hz), 125.15, 118.05 (d, *J* = 27.6 Hz), 117.94, 113.26. **IR** (ν, cm^{-1}): 2341, 2679, 2899. **HRMS:** $C_{15}H_9FN_4$ [M]+; calculated: 264.0811, found: 264.0845.

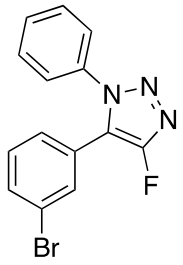


4-Fluoro-1-phenyl-5-(4-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazole (4d):
(Z)-1-(2-Fluoro-2-nitrovinyl)-4-(trifluoromethyl)benzene (101 mg, 0.425 mmol), azidobenzene (101 mg, 0.85 mmol), and TFA (16.4 µL, 0.21 mmol) used to afford **4d** (28mg, 46% yield) as a colorless oil after purification by column chromatography (DCM as eluent).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.57–7.47 (m, 3H), 7.42–7.34 (m, 4H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.54, -143.66. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.00 (d, *J* = 249.3 Hz), 136.53, 130.30, 129.91, 128.92 (d, *J* = 2.2 Hz), 126.09 (q, *J* = 3.7 Hz), 125.17, 125.10, 125.04, 122.34, 118.45 (d, *J* = 28.1 Hz). **IR** (ν, cm^{-1}): 2110, 2331, 2850, 2918, 3062. **HRMS:** $C_{15}H_9F_4N_3$ [M]$^-$; calculated: 307.0733, found: 307.0741.

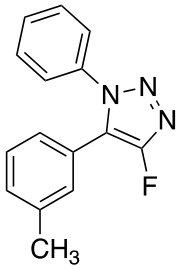


5-(3-(*tert*-Butyl)phenyl)-4-fluoro-1-phenyl-1H-1,2,3-triazole (4e):

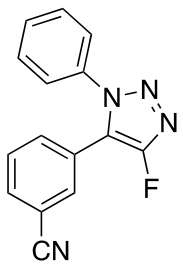
(Z)-1-(*tert*-Butyl)-4-(2-fluoro-2-nitrovinyl)benzene (50 mg, 0.22 mmol), azidobenzene (53 mg, 0.45 mmol), and TFA (8.6 µL, 0.11 mmol) used to afford **4e** (37mg, 56% yield) as a colorless oil after purification by column chromatography (DCM as eluent).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.45 (m, 3H), 7.43–7.35 (m, 5H), 7.21–7.11 (m, 1H), 1.31 (d, *J* = 1.9 Hz, 9H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -145.07. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.62 (d, *J* = 247.3 Hz), 152.74, 136.95, 129.72, 129.52, 128.20 (d, *J* = 2.2 Hz), 125.95, 125.10, 121.30 (d, *J* = 4.3 Hz), 119.69 (d, *J* = 28.2 Hz), 34.82, 31.14. **IR** (v, cm^{-1}): 2958, 3060. **HRMS**: $C_{18}H_{18}FN_3$ [M + Cs]$^+$; calculated: 428.0539, found: 428.0550.



5-(3-Bromophenyl)-4-fluoro-1-phenyl-1*H*-1,2,3-triazole (4f):
(Z)-1-Bromo-3-(2-fluoro-2-nitrovinyl)benzene (46 mg, 0.19 mmol), azidobenzene (45 mg, 0.37 mmol), and TFA (7.2 µL, 0.09 mmol) used to afford **4f** (27mg, 45% yield) as a pale yellow oil after purification by column chromatography (DCM as eluent).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.47 (m, 5H), 7.40–7.34 (m, 2H), 7.10 (d, *J* = 8.3 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -144.36.**^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.70 (d, *J* = 248.5 Hz), 136.60, 132.47, 130.16, 130.13, 130.11, 129.85, 125.12, 124.10, 123.34, 123.31, 118.81 (d, *J* = 28.2 Hz). **IR** (v, cm^{-1}): 2958, 3060. **HRMS**: $C_{14}H_9BrFN_3$ [M + Cs]$^+$; calculated: 449.9018, found: 449.9011.



4-Fluoro-1-phenyl-5-(m-tolyl)-1H-1,2,3-triazole (4g):
(Z)-1-(2-fluoro-2-nitrovinyl)-3-methylbenzene (50 mg, 0.28 mmol), azidobenzene (66 mg, 0.55 mmol), and TFA (11 µL, 0.14 mmol) used to afford **4g** (37mg, 53% yield) as a colorless oil after purification by column chromatography (DCM as eluent).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.37 (m, 5H), 7.32–7.16 (m, 2H), 7.11 (s, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 2.33 (s, 3H). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -145.20. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.61 (d, *J* = 247.2 Hz), 138.90, 136.82, 130.31, 129.75, 129.50, 129.23 (d, *J* = 2.2 Hz), 128.85, 125.78 (d, *J* = 1.9 Hz), 124.97, 124.18 (d, *J* = 4.2 Hz), 119.83 (d, *J* = 28.3 Hz), 21.36. **IR**(v, cm^{-1}): 2855, 2921, 3064. **HRMS**: $C_{15}H_{12}F_1N_3$ [M + Cs]$^+$; calculated: 386.0070, found: 386.0051.



3-(4-Fluoro-1-phenyl-1*H*-1,2,3-triazol-5-yl)benzonitrile (4h):

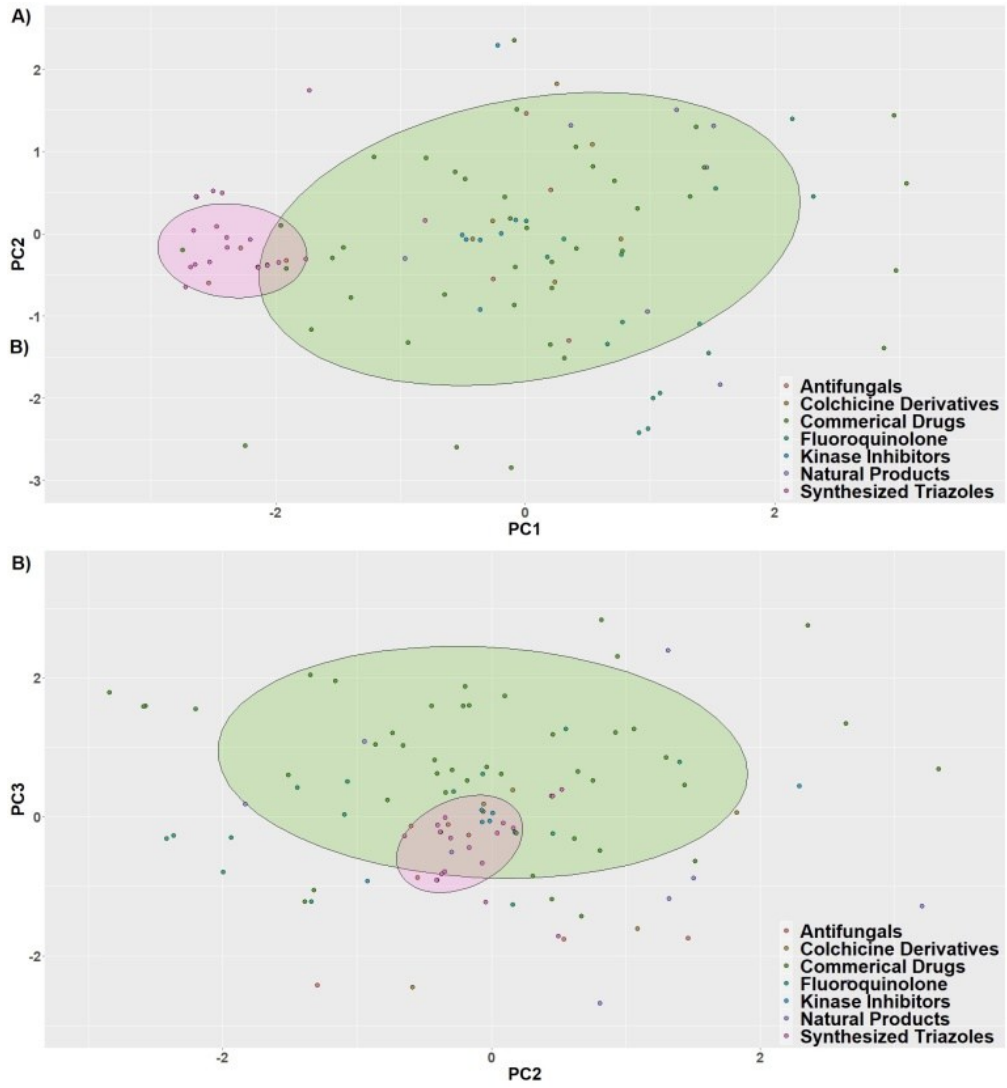
(Z)-3-(2-Fluoro-2-nitrovinyl)benzonitrile (100 mg, 0.52 mmol), azidobenzene (124 mg, 0.55 mmol), and TFA (20 µL, 0.26 mmol) used to afford **4h** (75mg, 55% yield) as a pale-yellow oil after purification by column chromatography (DCM as eluent).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.47 (m, 4H), 7.44–7.41 (m, 1H), 7.40–7.36 (m, 2H), 7.28–7.21 (m, 1H), 7.15–7.09 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -144.03. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.84 (d, *J* = 249.5 Hz), 136.14, 132.89, 132.64 (d, *J* = 2.3 Hz), 131.77 (d, *J* = 2.2 Hz), 130.50, 130.10, 129.98, 125.88 (d, *J* = 4.4 Hz), 125.04, 117.68 (d, *J* = 27.9 Hz), 117.66, 113.61. **IR** (ν, cm^{-1}): 2357, 2922, 3062. **HRMS**: $C_{15}H_9FN_4$ $[M + Cs]^+$; calculated: 396.9866, found: 396.9824.

8. Principal Component Analysis

In connection with our ongoing drug discovery efforts, we wanted to assess the chemical space and physicochemical properties of our library of 4-fluoro-1,5-disubstituted-1,2,3-triazoles relative to commercial drugs and triazole-containing pharmaceutical agents. To this end, we performed principal component analysis (PCA) on the library of synthesized triazoles adopting a modified protocol reported by Tan and Aubè.[20] The reference set included best-selling drugs, fluoroquinolones, triazole-containing kinase inhibitors, triazole antifungals, natural product-based drugs, and colchicine triazole derivatives and was chosen based on therapeutic value, similarities in the core triazole nucleus, and overall hybridization of the molecules. We used Swiss ADME[21] to calculate the 12 physicochemical properties of the synthesized triazoles and the reference set. The loadings, which are an estimation of the correlation between components and variables, demonstrate the influence of the 12 physicochemical properties and placement of the compounds in the PCA plots.

Examination of the eigenvector plots show that topological polar surface area (tPSA), number of oxygen atoms (O), and number of hydrogen bond donor/acceptor (HBD/HBA) have a strong positive impact on the PC1 axes. Whereas, calculated skin permeation rate (LogK) and calculated octanol/water partition coefficient (CLogP) have a strong negative impact on the PC1 axes. For PC2, molecular weight (MW), CLogP, and the number of rotatable bonds (RotB) have the largest impact and shift compounds in the positive direction. However, calculated aqueous solubility (AlogpS) has a significant negative effect on PC2 and shift compounds to the left along the PC2 axes. In PC3, the fraction of sp^3 hybridized carbons (Csp3), RotB, and O have a large positive influence along the PC3 axes, while the number of fluorine atoms (F) and the number of nitrogen atoms (N) have a large negative influence along the PC3 axes.

The orthogonal plots for the first 3 principal components (PC1—3, Supplementary Figure 1), show a slight overlap between PC1 and PC2 and a near complete overlap between PC2 and PC3. Together, the first 3 principal components account for over 75% of the total variation in the original dataset while the first 5 principal components account for over 90% of the variation. These analyses show, the fluorinated triazoles occupy a slight to near-complete overlapping chemical space as the reference set of commercial drugs and pharmaceutical agents and have a distinct set of physicochemical properties.



Supplementary Figure 1 PCA plots of 30 triazole library members, 8 antifungal compounds, 7 triazole kinase inhibitors, 7 triazole colchicine derivatives, 51 best-selling drugs, 12 natural products, and 15 fluoroquinolones. (A) Orthoganal plot of PC1 versus PC2 generated from 12 structural and physicochemical parameters. (B) Orthogonal plot for PC2 vs PC3 generated from 12 structural and physicochemical parameters. Note: the shaded regions in each plot show the t-distribution for commerically avaliable drugs (green) and the triazole synthesized in this work (pink) with a confidence interval of 80%.

In order to generate the plots shown in supplementary figure 1 of the manuscript, a modified version of the principal component analysis (PCA) method used by Tan et al.[20] A total of 130 compounds were chosen based on similarities in structure or function, arranged into 7 groups:

- 30 triazole compounds from this work
- 8 triazole antifungal compounds
- 7 triazole containing colchicine derivatives
- 7 triazole containing protein kinase inhibitors
- 12 natural product derived therapeutics
- 51 commercially available therapeutics
- 15 fluoroquinolones

For each compound, a set of 12 physiochemical properties were calculated using the free, online cheminformatic software SwissADME (http://www.swissadme.ch/) in addition to ChemDraw. The properties were chosen based on several criteria including: Lipinski parameters (MW ≤ 500, CLogP ≤ 5, HBA ≤ 10, HBD ≤ 5), Verber parameters (RotB ≤ 10, tSPA ≤ 140 Å^2), Tetko's calculated aqueous solubility (ALogpS), the fraction of sp_3 hybridized carbons (Csp_3), and calculated skin permeation rate (LogK). These criteria were chosen based on their general correlation with bioavailability, therapeutic value, and synthetic accessibility. Due to the general trend of synthetic compounds containing more nitrogen atoms and natural products containing more oxygen atoms, the total atom count for oxygen, nitrogen, and fluorine was included alongside the previously mentioned parameters.

Using Microsoft Excel, these data were compiled into a spreadsheet, where the average and standard deviation for each group of compounds as well as each parameter were calculated. Then, the open source statistical package "RStudio" was used to perform the PCA and compress the 12-dimensional vector for each compound into a 2-dimensional vector and plot each vector on an orthogonal biplot. This was performed by following a similar protocol to that published by Tan et al[1], and is described as follows:

1) In MS Excel, a "RAW DATA" worksheet was created with compounds and physicochemical descriptors in columns.
2) Mean values were calculated for individual categories (e.g., for "Imidazole Antifungals", "Drugs", etc.). Additionally, mean and standard deviation was calculated for each column (Note: The mean and standard deviation must not include the individual means previously calculated).
3) A "NORMALIZED DATA" worksheet was created and mean-centered, standardized values were generated for each column using the following formula:

$$normalized\ value = \frac{(Individual\ Value - Total\ Column\ Mean)}{Total\ Column\ Std\ Deviation}$$

4) The workbook was saved as "PCA_Datasheet.xlsx" and the workbook was closed.
5) In RStudio, the "Import Dataset" was used to import the "NORMALIZED DATA" worksheet into RStudio. Then the following commands were run:
6) R>prcomp(NormData)->Comps
7) R>summary(Comps)
8) R>view(Comps)
9) R>biplot(Comps, choices = c(1,2), col=c("gray","red"))
10) R>Comps$x->RotData
11) R>RotData[c(1:30,65:115),c(1:6)]->EllipseData
12) R>install.packages(ggplot2)
13) R>library(ggplot2)
14) R>ggplot(RotData,aes(PC1,PC2,col=Label,fill=Label)) + stat_ellipse(data=EllipseData, geom = "polygon", col = "black" , size = 0.05, alpha = 0.2,level=0.8,show.legend=FALSE) + geom_point(shape = 21, col="black", size=3) + xlim(-3.5,3.5) + ylim(-3,2.5) + theme(text=element_text(size=26,face="bold"),legend.position=c(0.88,0.15),legend.title=element_blank(),legend.text=element_text(size=28),legend.background = element_rect(fill="transparent"),legend.spacing.y=unit(1,'cm'))
    #Step 14 may be repeated for other principal components by replacing "PC1","PC2"
15) Once the plots were satisfactory, the "Export Plot" utility was used to generate image files of the corresponding PCA and Eigenvector biplots.

	Description	Method of Determination
MW	Molecular weight (g/mol)	ChemDraw Analysis
N	Number of nitrogen atoms	ChemDraw Analysis
O	Number of oxygen atoms	ChemDraw Analysis
F	Number of fluorine atoms	ChemDraw Analysis
CLogP	Calculated n-octanol/water partion coefficient (Consensus of 5 algorithms: iLOGP, XLOGP3,	http://www.swissadme.ch

	WLOGP, MLOGP, and SILICOS-IT)	
HBD	Number of hydrogen bond donors	http://www.swissadme.ch
HBA	Number of hydrogen bond acceptors	http://www.swissadme.ch
RotB	Number of rotatable bonds	http://www.swissadme.ch
tPSA	Calculated topological polar surface area	http://www.swissadme.ch
Csp3	Fraction of sp^3 hybridized carbons	http://www.swissadme.ch
ALogpS	Calculated aqueous solubility (Ali method)	http://www.swissadme.ch
LogK	Calculated cell permeation	http://www.swissadme.ch

Supplementary Table 1. Parameter descriptors for principal component analysis.

	Synthesized Triazoles	**Antifungal**	**Colchicine Derivatives**	**Kinase Inhibitors**	**Natural Products**	**Commercial Drugs**	**Fluoroquinolones**
MW	281.2	476.5	358.3	435.3	465.4	368.6	380.0
N	3.2	5.8	3.6	5.6	2.7	2.5	3.0
O	0.3	2.1	3.6	2.0	6.6	3.0	3.6
F	1.4	1.6	0.1	0.3	0.0	0.6	1.5
CLogP	3.5	3.1	2.7	3.1	1.3	2.8	1.7
HBD	0.0	0.8	0.1	2.3	3.8	1.5	1.8
HBA	3.9	7.1	5.7	5.6	7.3	5.1	6.1
RotB	2.8	7.1	5.6	5.7	9.7	7.4	3.1
tPSA	41.2	87.4	67.6	119.8	145.3	83.1	84.8
Csp3	0.1	0.3	0.2	0.1	0.5	0.4	0.4
ALogpS	-4.2	-4.6	-3.8	-6.0	-3.8	-3.9	-1.6
LogK	-5.3	-7.0	-6.5	-6.2	-8.3	-6.5	-8.4

Supplementary Table 2. Average values for each parameter within each group of compounds.

	PC1	**PC2**	**PC3**	**PC4**	**PC5**	**PC6**	**PC7**	**PC8**	**PC9**	**PC10**
Standard deviation	2.214	1.638	1.262	0.981	0.812	0.661	0.543	0.507	0.347	0.235
Proportion of Variance	0.408	0.223	0.132	0.080	0.055	0.036	0.025	0.021	0.010	0.005
Cumulative Proportion	0.408	0.631	0.763	0.843	0.898	0.934	0.959	0.980	0.990	0.995

Supplementary Table 3. Standard deviation and proportion of variance accounted by each principal component. The first 5 components account for 89.8% of all variance in the dataset.

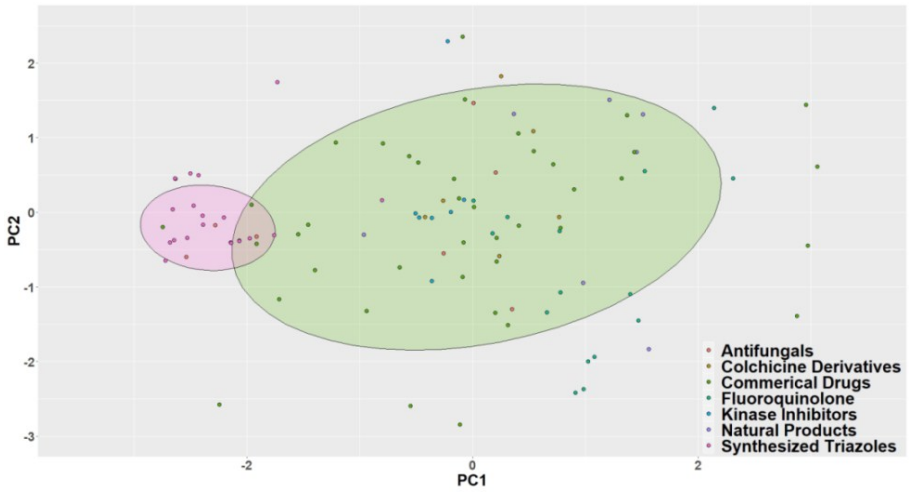
	PC1	**PC2**	**PC3**	**PC4**	**PC5**
MW	0.274	0.455	-0.039	0.019	-0.106
N	0.067	0.153	-0.622	-0.512	0.256
O	0.404	0.091	0.219	0.114	-0.232
F	-0.095	0.028	-0.496	0.696	0.109
CLogP	-0.268	0.454	0.121	0.155	-0.077
HBD	0.390	-0.051	0.022	-0.163	-0.115
HBA	0.351	0.148	-0.315	0.325	-0.079
RotB	0.167	0.304	0.238	0.027	0.850
tPSA	0.416	0.101	-0.116	-0.142	-0.162
Csp3	0.313	-0.116	0.334	0.235	0.158
AlogpS	0.067	-0.564	-0.066	0.066	0.225
LogK	-0.314	0.310	0.131	-0.052	-0.091

Supplementary Table 4. Loading values for each parameter by component. The values indicate the magnitude and direction of influence each parameter has in a component. The 4 largest contributors from the first five principal components are highlighted in yellow.

Analysis of these data indicates that 89.8% of all variance seen in the complete dataset can be attributed to the first five principal components (supplementary table 3). To simplify the interpretation of the data, the first 3 principal components (accounting for >75% of the variance) were used to generate the PCA plots shown in Figure 5a, b. Analysis of the component loadings scores as well as the eigenvector biplots produced (supplementary figure 1) indicates the following regarding the dataset:

1. The highest impact factors for PC1 are: the number of oxygen atoms (O), topological polar surface area (tPSA)—together moving compounds to the right along PC1 axes. As well as, the calculated octanol/water coefficient (CLogP), and calculated skin permeation rate—together moving compounds to the left along PC1 axes.
2. The highest impact factors for PC2 are: molecular weight (MW), calculated octanol/water coefficient (CLogP)—together moving compounds to the right along PC2 axes. As well as, fraction of sp3-hybridized carbons (Csp3) and calculated aqueous solubility (AlogpS)—together moving compounds to the left along PC2 axes.
3. The highest impact factors for PC3 are: the fraction of sp3-hybridized carbons (Csp3) and number of rotatable bonds (RotB)—together moving compounds to the right along PC3 axes. As well as, the number of nitrogen atoms (N) and the number of fluorine atoms (F)—together moving compounds to the left along PC3 axes.
4. The highest impact factors for PC4 are: the number of fluorine atoms (F) and number of hydrogen bond acceptors (HBA)—together moving compounds to the right along PC4 axes. As well as, the number of nitrogen atoms (N) and the number of hydrogen bond donors (HBD) together moving compounds to the left along PC4 axes.
5. The highest impact factors for PC5 are: the number of nitrogen atoms (N) and number of rotatable bonds (RotB)—together moving compounds to the right along PC5 axes. As well as, the number oxygen atoms (O) and the topological polar surface area (tPSA)—together moving compounds to the left along PC5 axes.

The biplots are shown below



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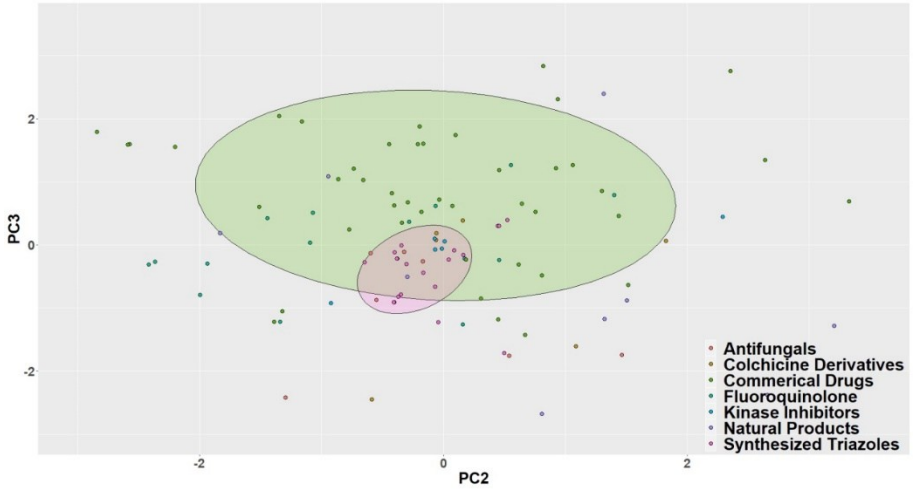

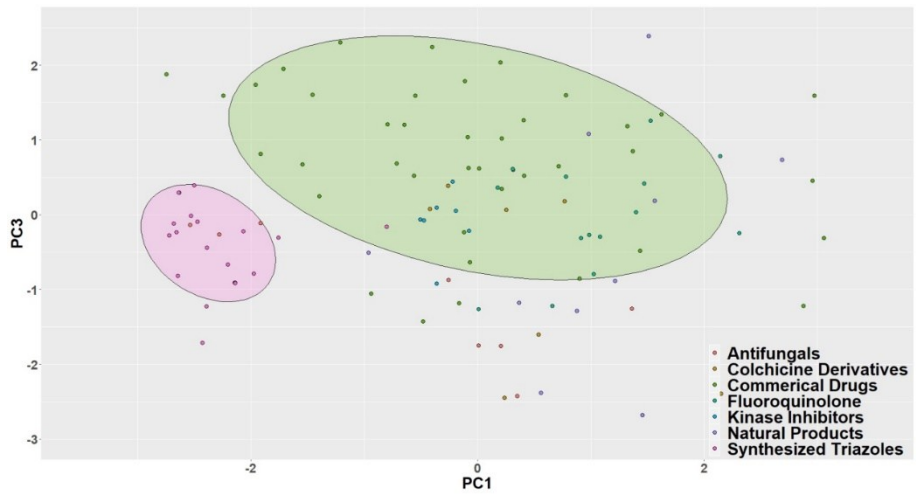

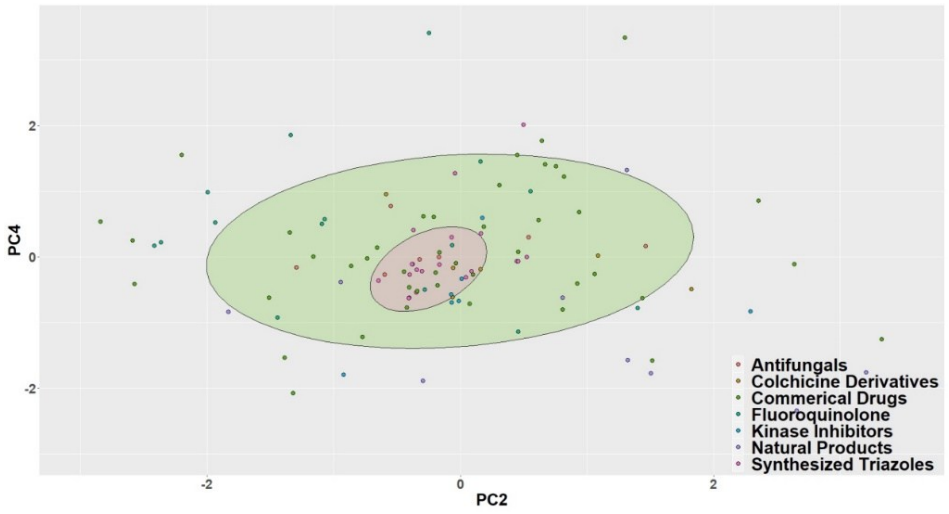
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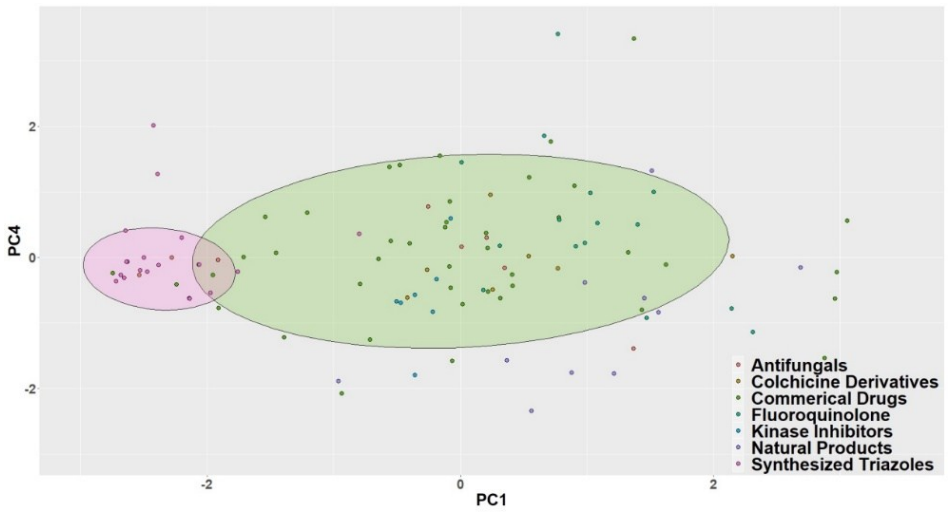
PC2
Antifungals
Colchicine Derivatives
Commerical Drugs
Fluoroquinolone
Kinase Inhibitors
Natural Products
Synthesized Triazoles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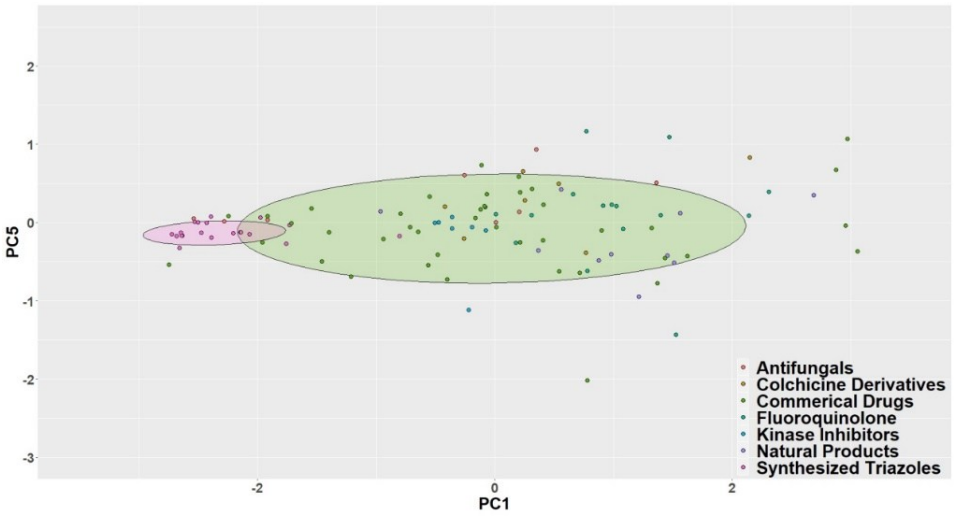
PC1
Antifungals
Colchicine Derivatives
Commerical Drugs
Fluoroquinolone
Kinase Inhibitors
Natural Products
Synthesized Triazoles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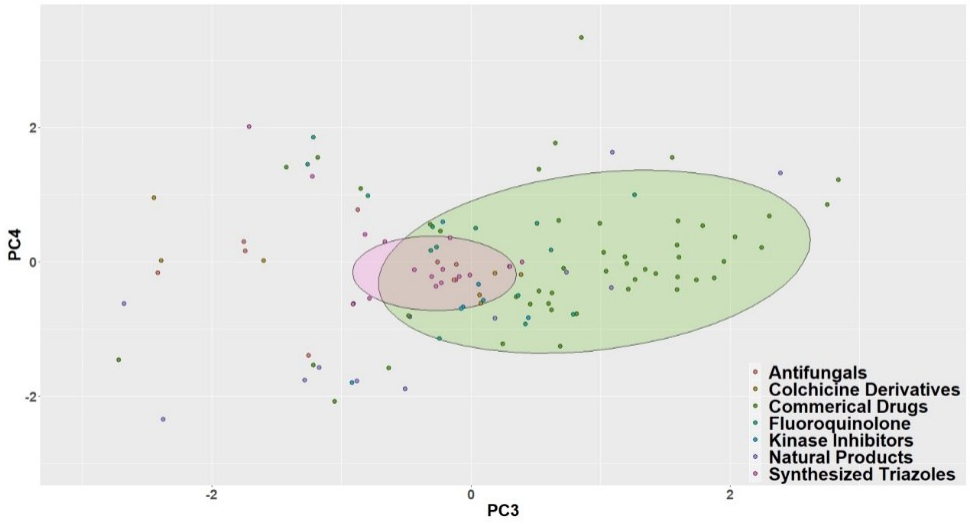
PC1
Antifungals
Colchicine Derivatives
Commerical Drugs
Fluoroquinolone
Kinase Inhibitors
Natural Products
Synthesized Triazoles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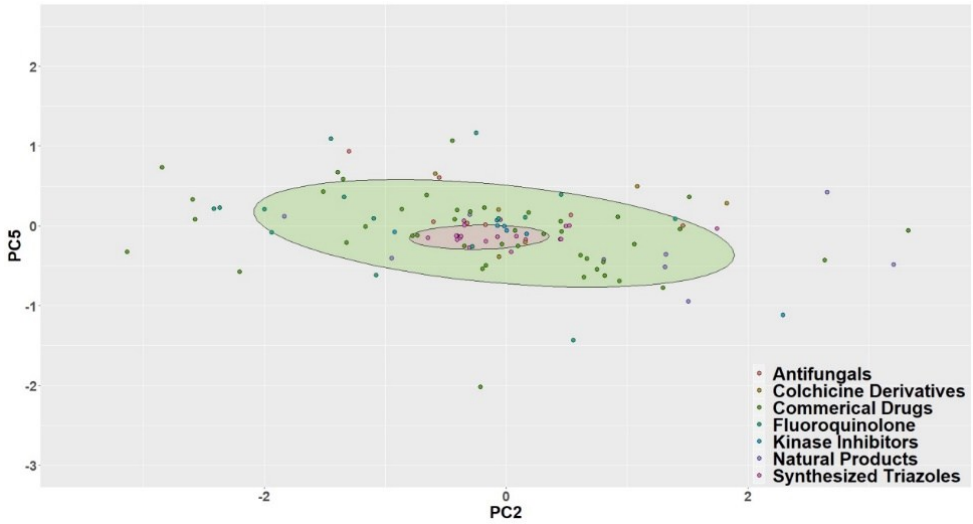
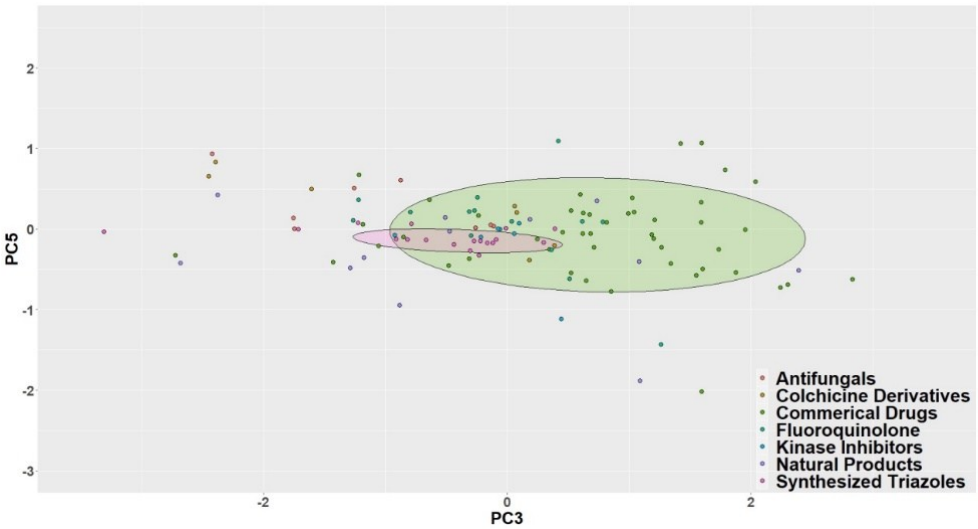
PC3
Antifungals
Colchicine Derivatives
Commerical Drugs
Fluoroquinolone
Kinase Inhibitors
Natural Products
Synthesized Triazoles


PC5
PC2
Antifungals
Colchicine Derivatives
Commerical Drugs
Fluoroquinolone
Kinase Inhibitors
Natural Products
Synthesized Triazoles


PC5
PC3
Antifungals
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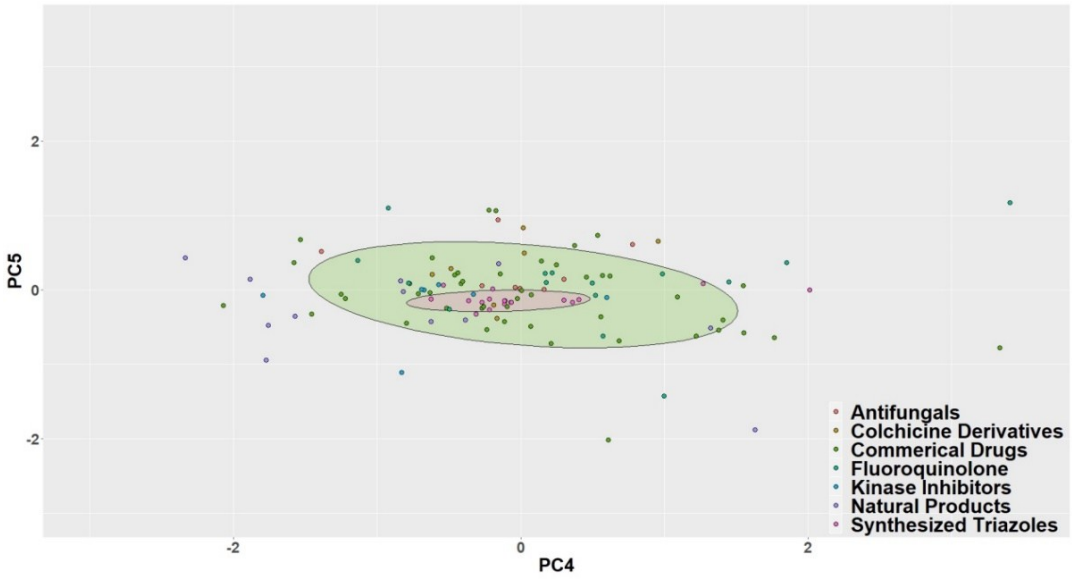
Commerical Drugs
Fluoroquinolone
Kinase Inhibitors
Natural Products
Synthesized Triazoles


PC5
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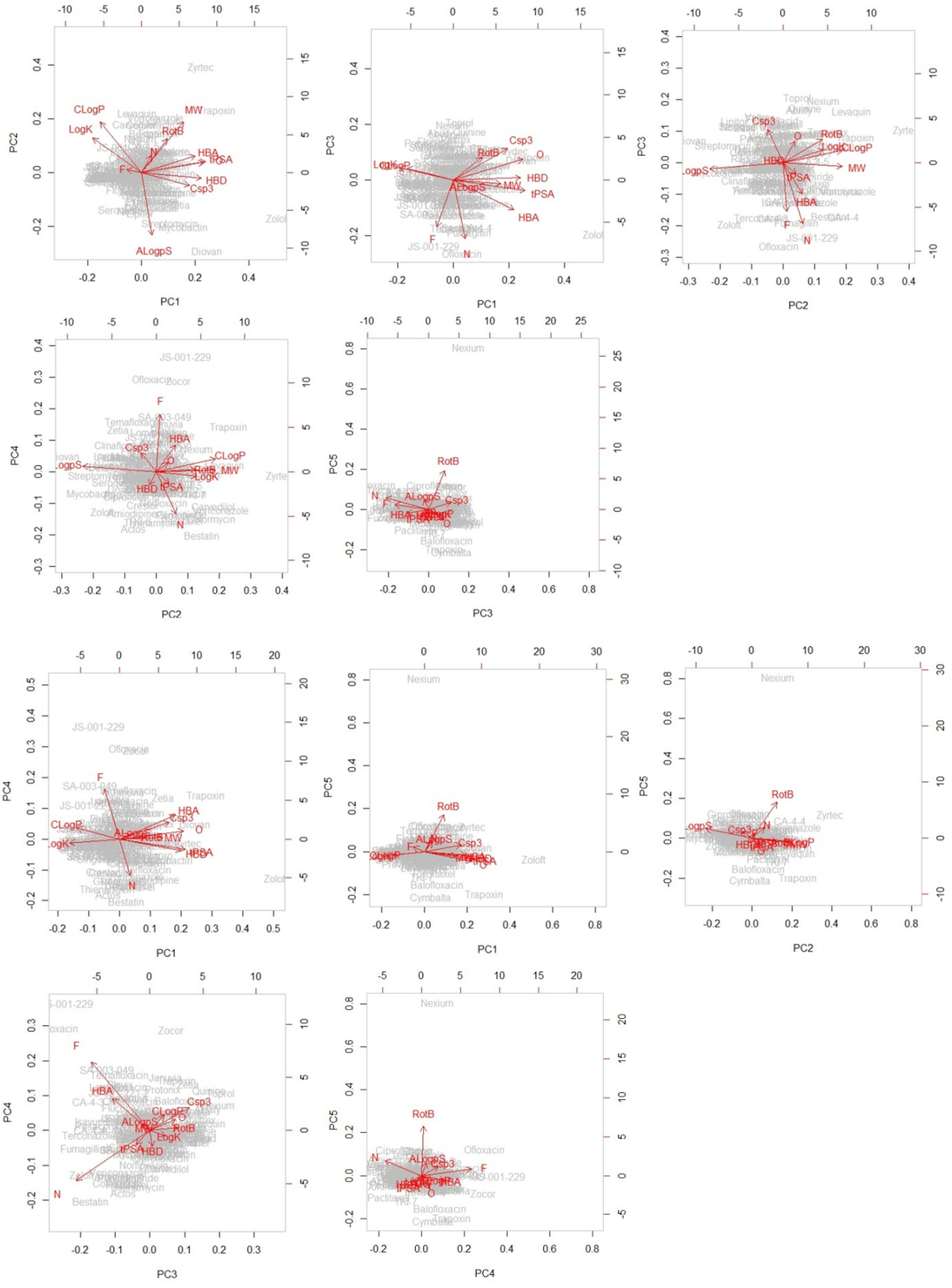
PC4
Antifungals
Colchicine Derivatives
Commerical Drugs
Fluoroquinolone
Kinase Inhibitors
Natural Products
Synthesized Triazoles


PC1
PC2
PC3
PC4
PC5
CLogP
MW
LogK
RotB
HBA
tPSA
HBD
Csp3
F
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ALogpS
Zyrtec
Zoloft
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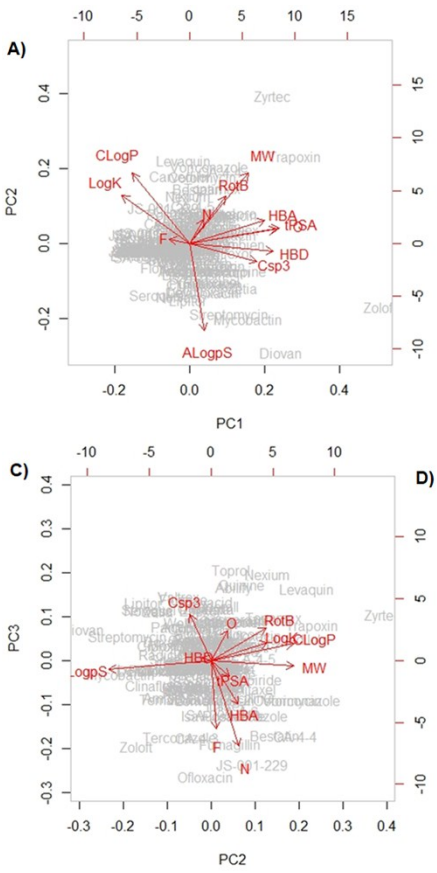


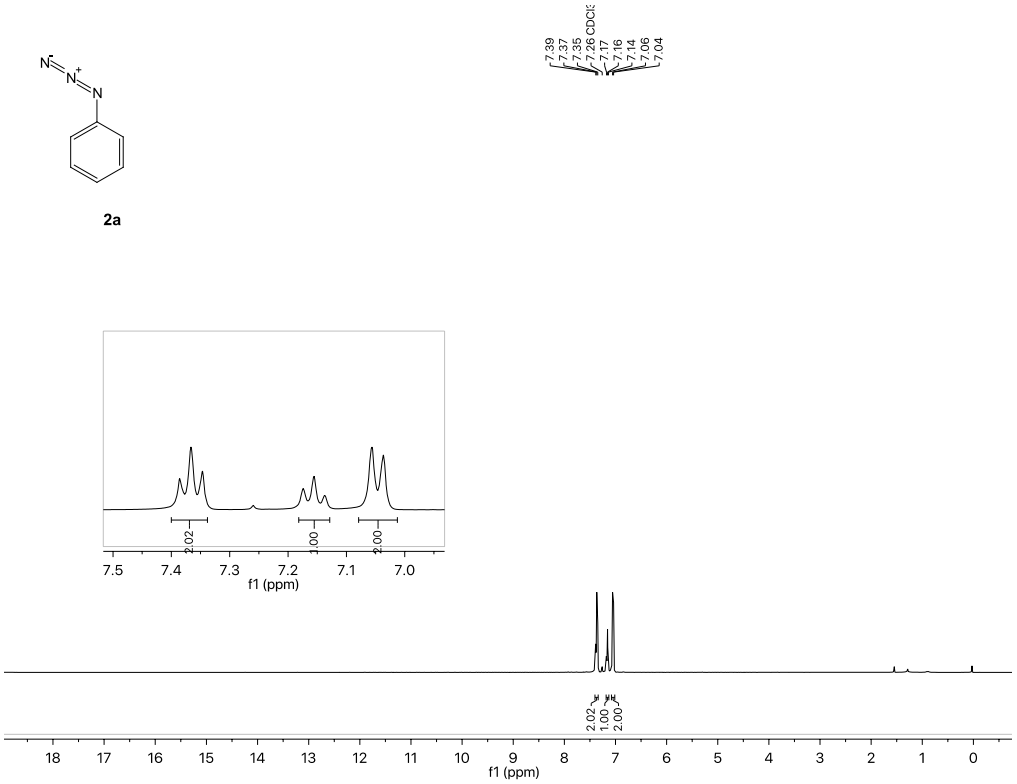
D)

	PC1	PC2	PC3
MW	0.274	0.455	-0.039
N	0.067	0.153	-0.622
O	0.404	0.091	0.219
F	-0.095	0.028	-0.496
CLogP	-0.268	0.454	0.121
HBD	0.390	-0.051	0.022
HBA	0.351	0.148	-0.315
RotB	0.167	0.304	0.238
tPSA	0.416	0.101	-0.116
Csp3	0.313	-0.116	0.334
AlogpS	0.067	-0.564	-0.066
LogK	-0.314	0.310	0.131

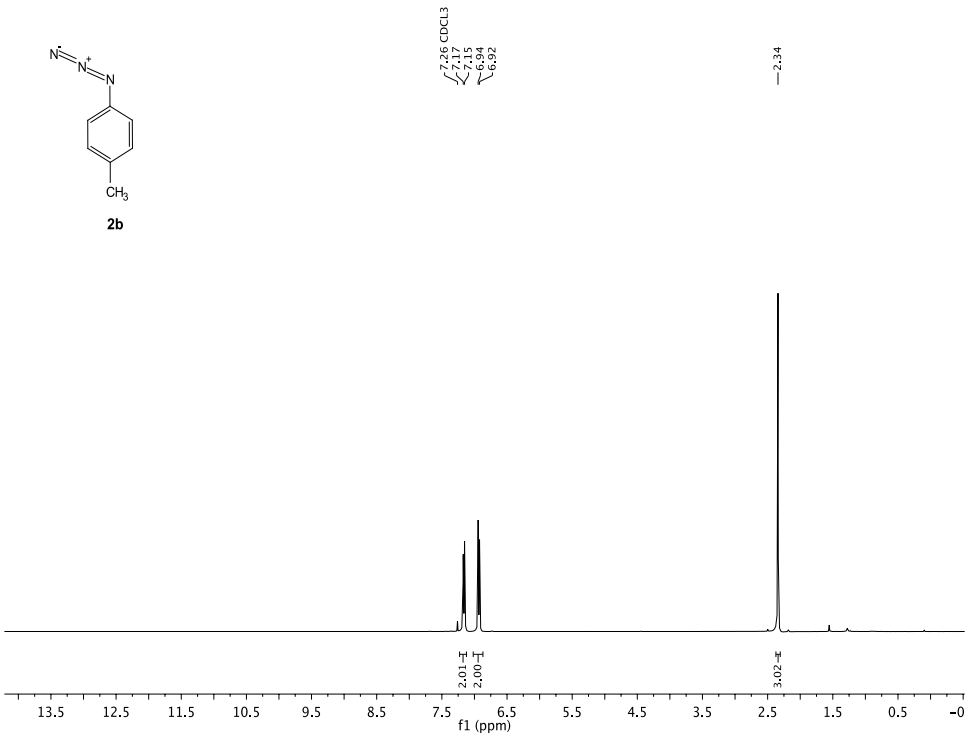
Supplementary Figure 3. Biplots and component loadings for the library of synthesized triazoles and reference sets. (A) Eigenvectors for PC1 vs. PC2. (B) Eigenvectors for PC1 vs. PC3. (C) Eigenvectors for PC2 vs. PC3. (D) Component loadings for the first 3 principal components (PC1—PC3). The 4 highest impact descriptors are highlighted in yellow.

9. ^{1}H, ^{19}F and ^{13}C NMR spectra:

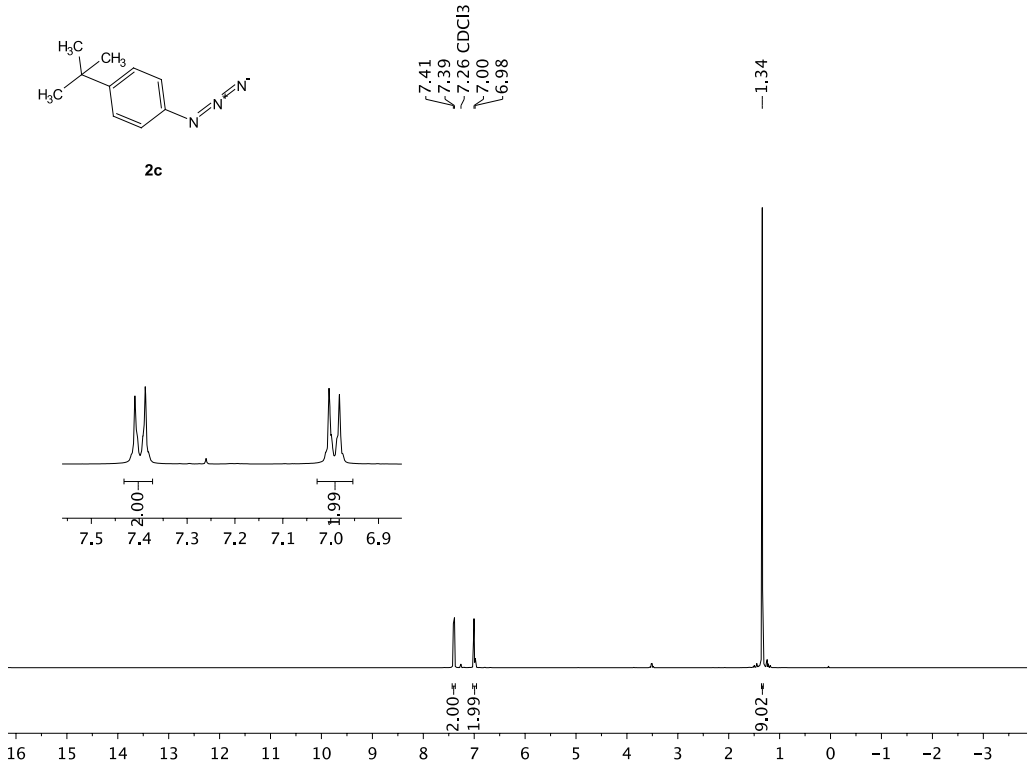
^{1}H NMR of **2a**



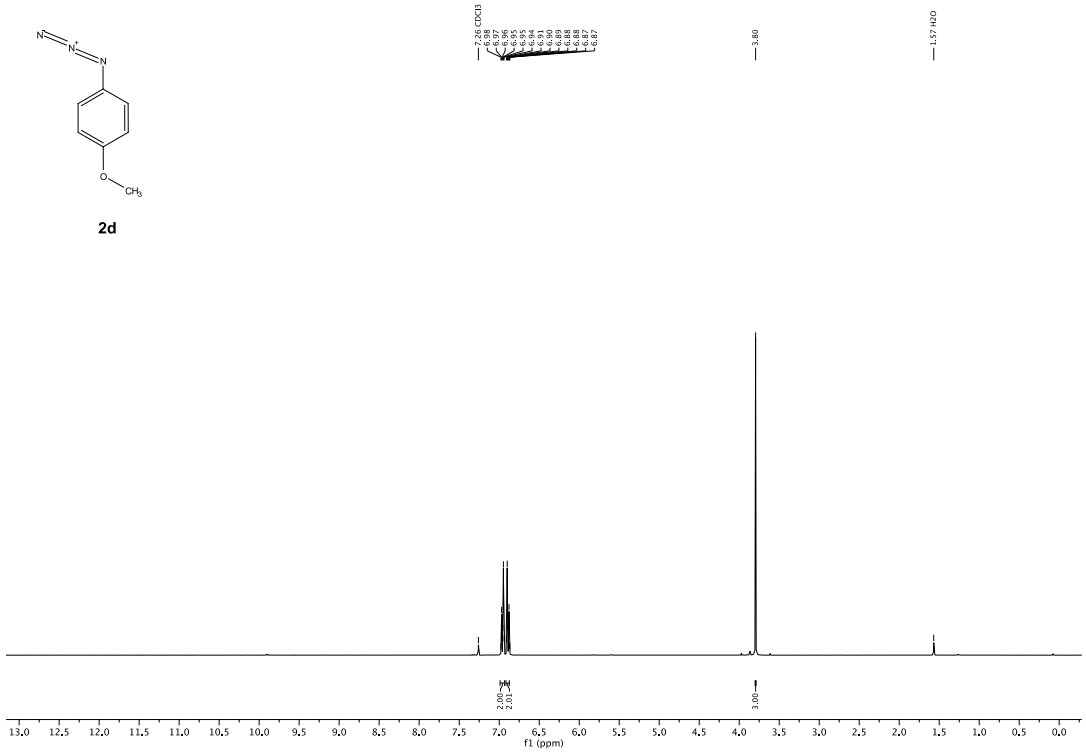
^{1}H NMR of **2b**



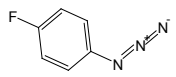
^{1}H NMR of **2c**



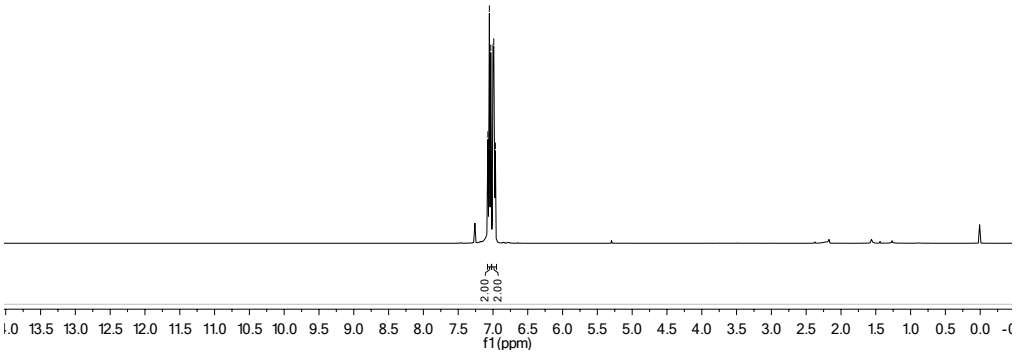
^{1}H NMR of **2d**



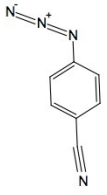
^{1}H NMR of **2e**



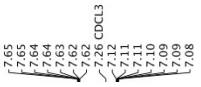
2e

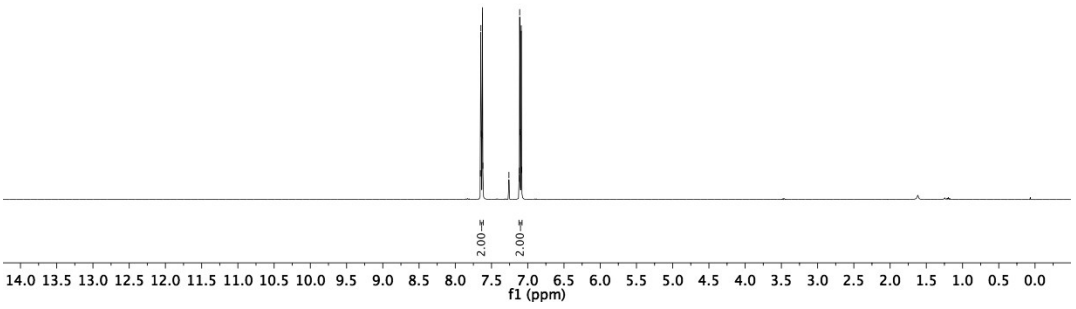


^{1}H NMR of **2f**

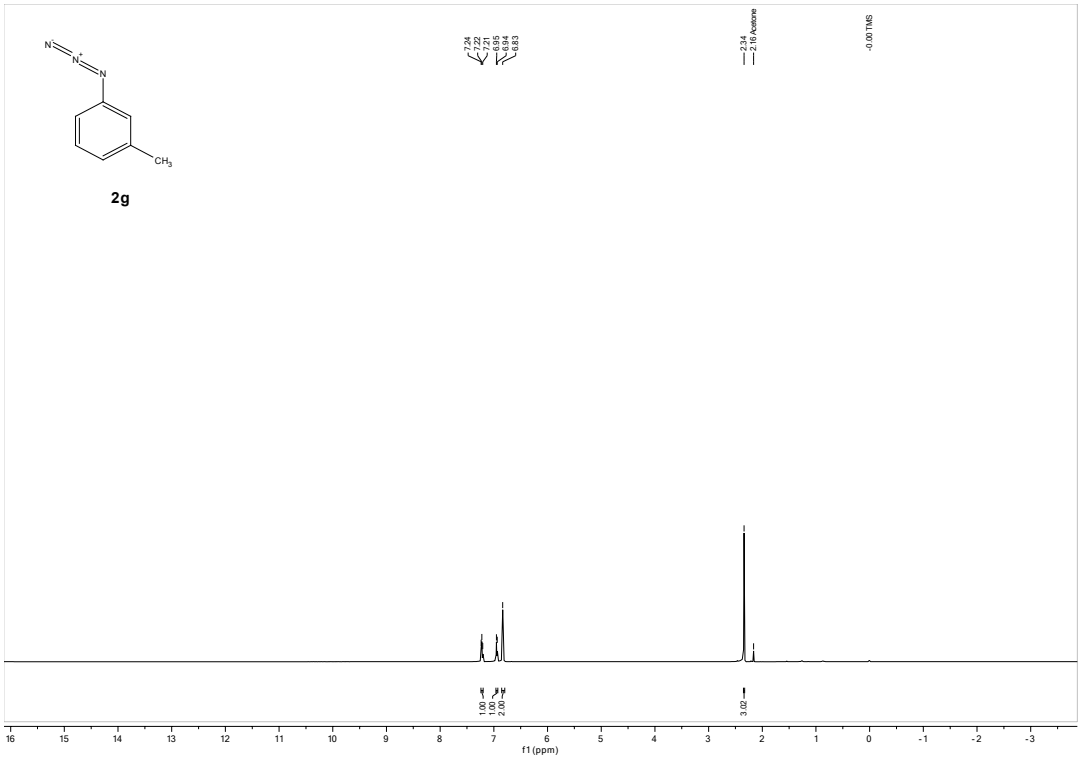


2f

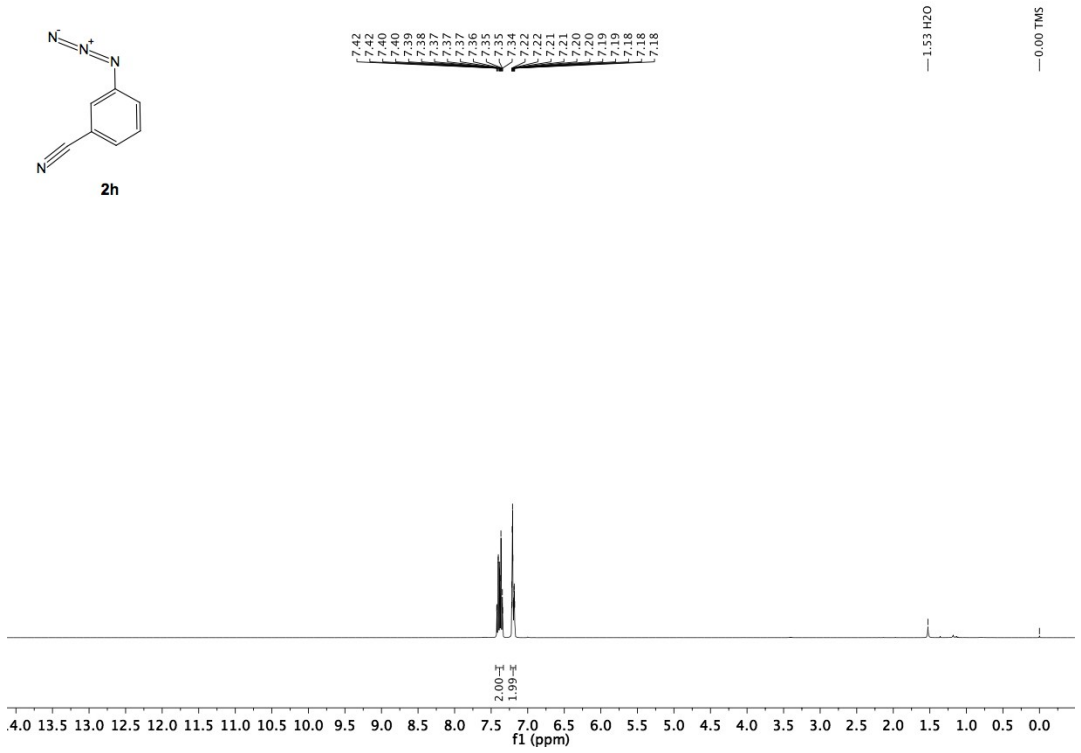




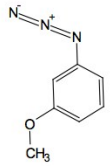
^{1}H NMR of **2g**



^{1}H NMR of **2h**

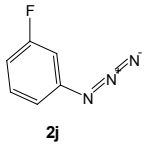


^{1}H NMR of **2i**



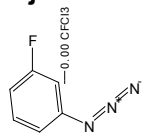
2i

^{1}H NMR of **2j**



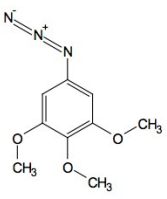
2j

^{19}F NMR of **2j**



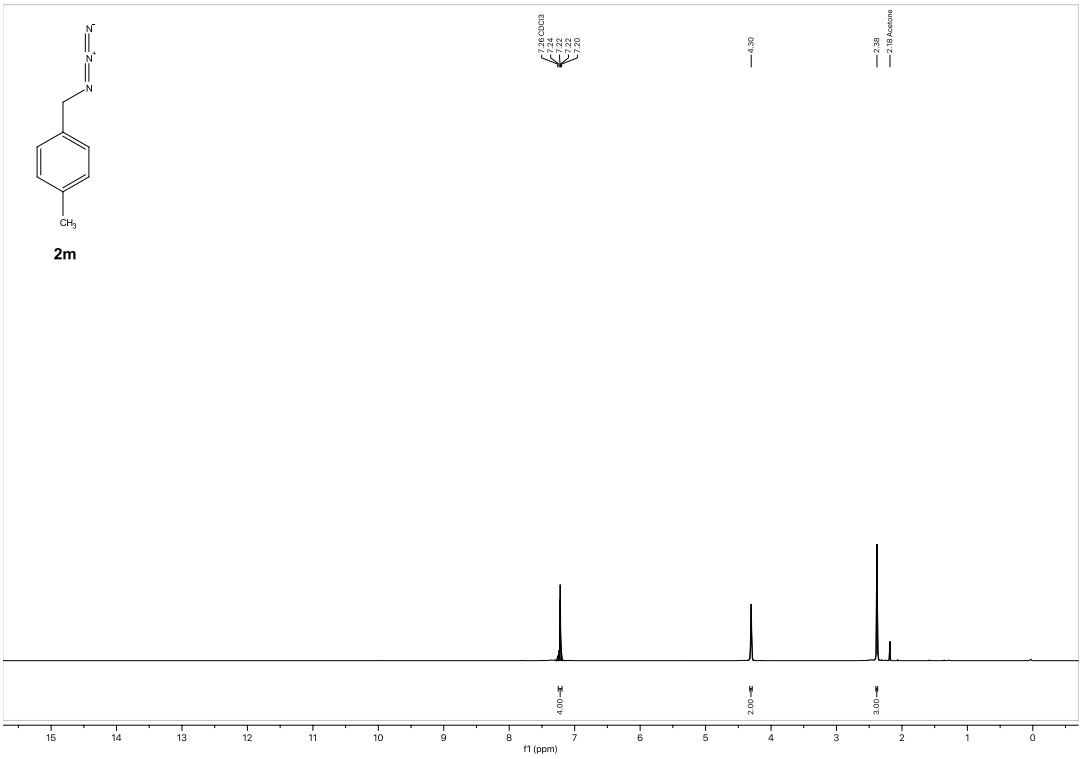
2j

^{1}H NMR of **2k**



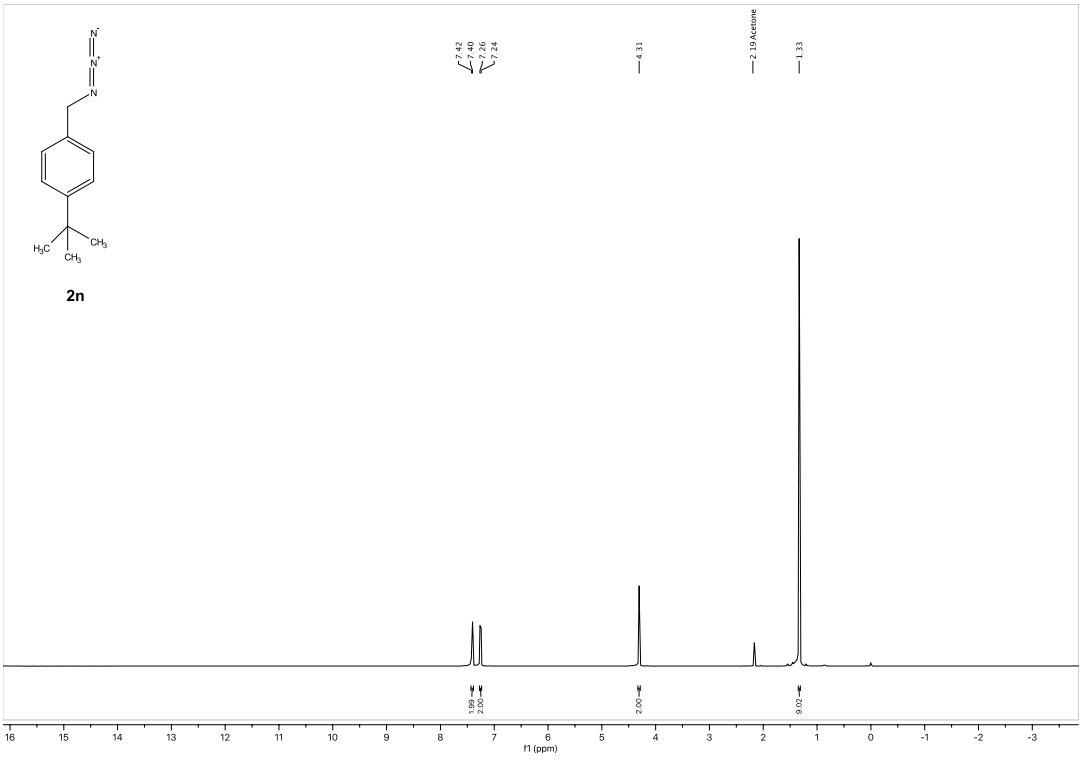
2k

^{1}H NMR of **2m**



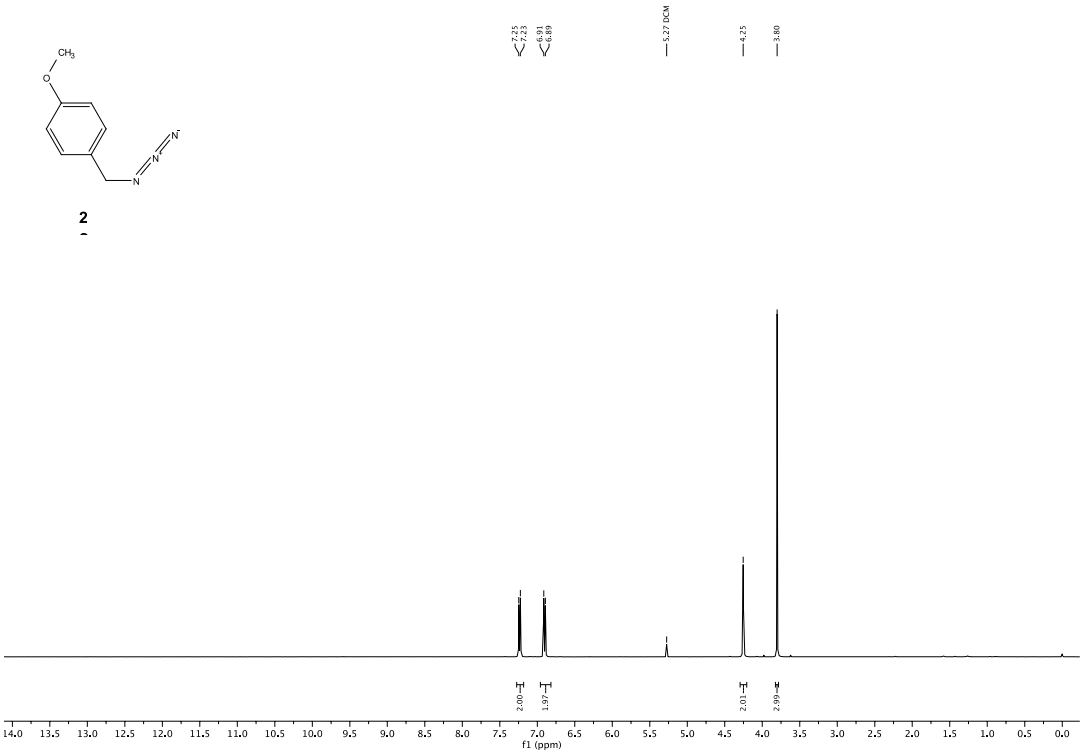
2m

^{1}H NMR of **2n**

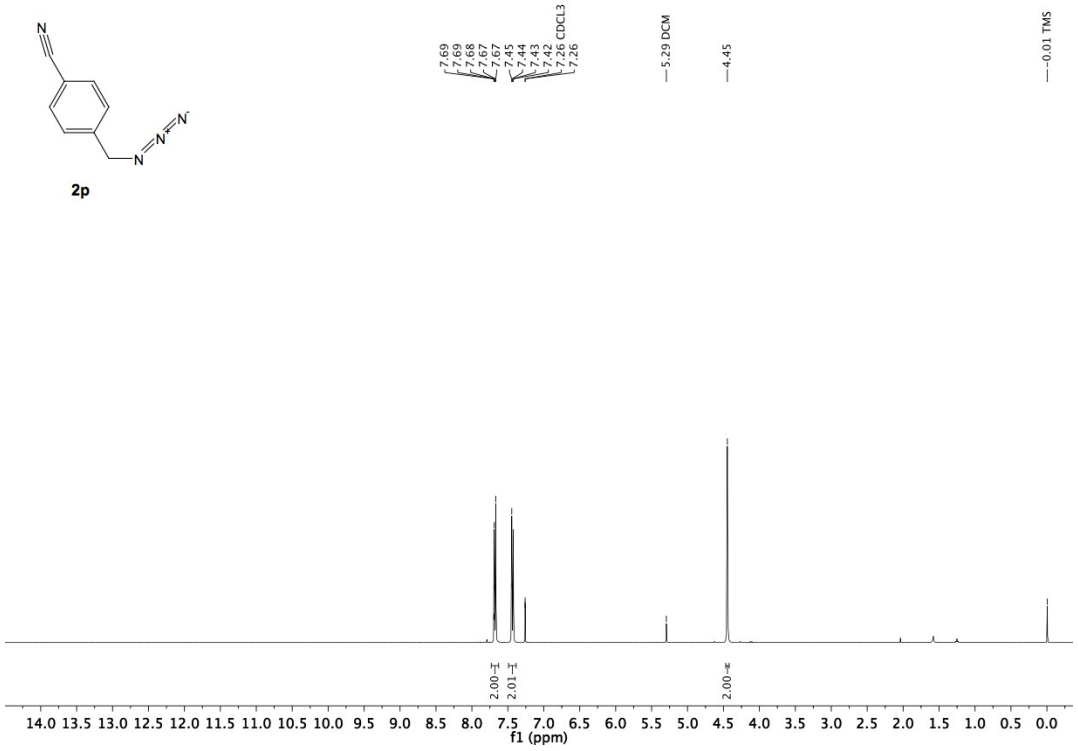


2n

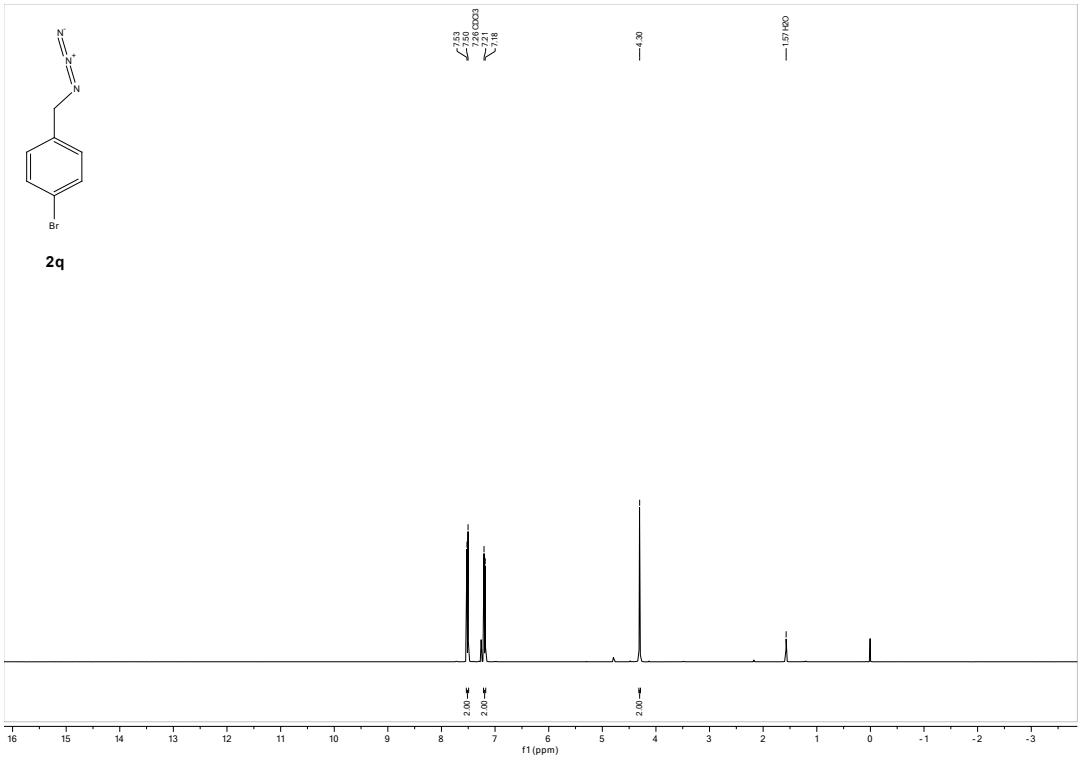
^{1}H NMR of **2o**



^{1}H NMR of **2p**

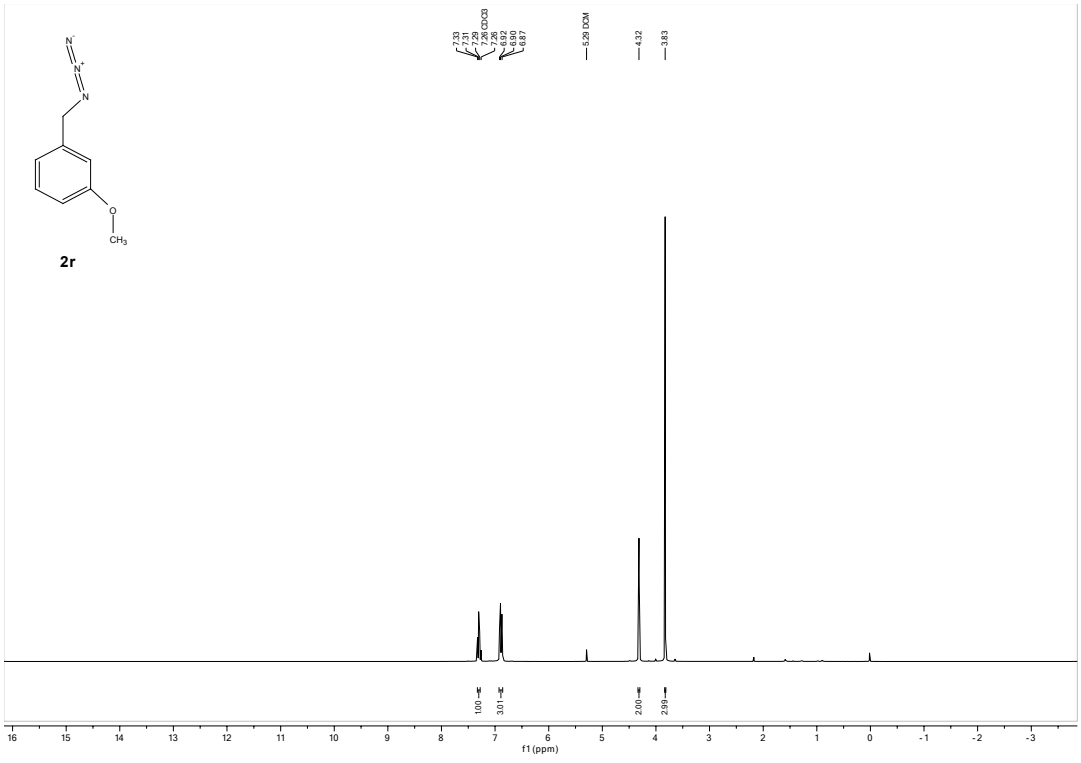


^{1}H NMR of **2q**



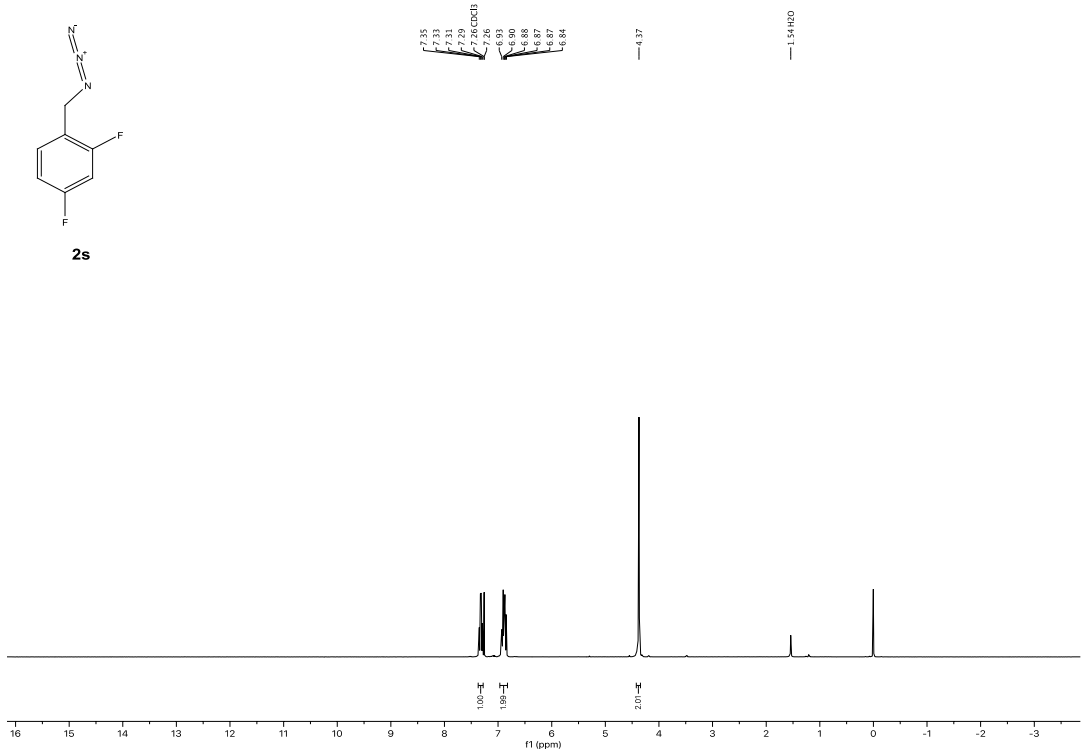
2q

^{1}H NMR of **2r**



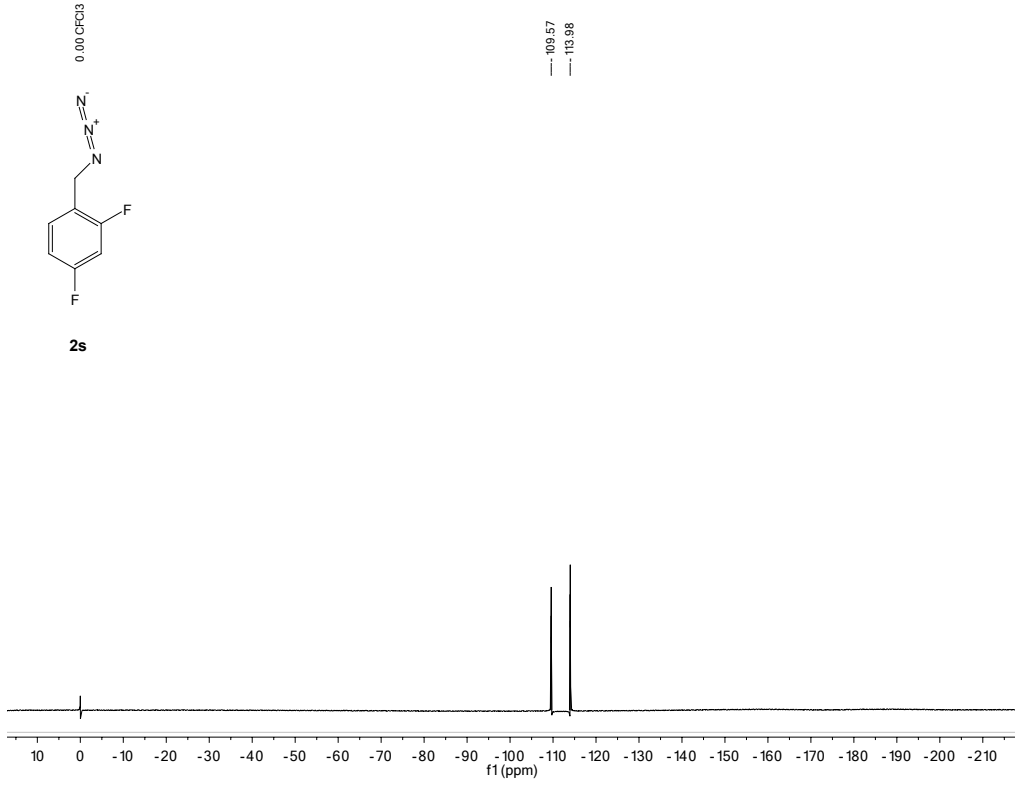
2r

^{1}H NMR of **2s**



2s

^{19}F NMR of **2s**



2s

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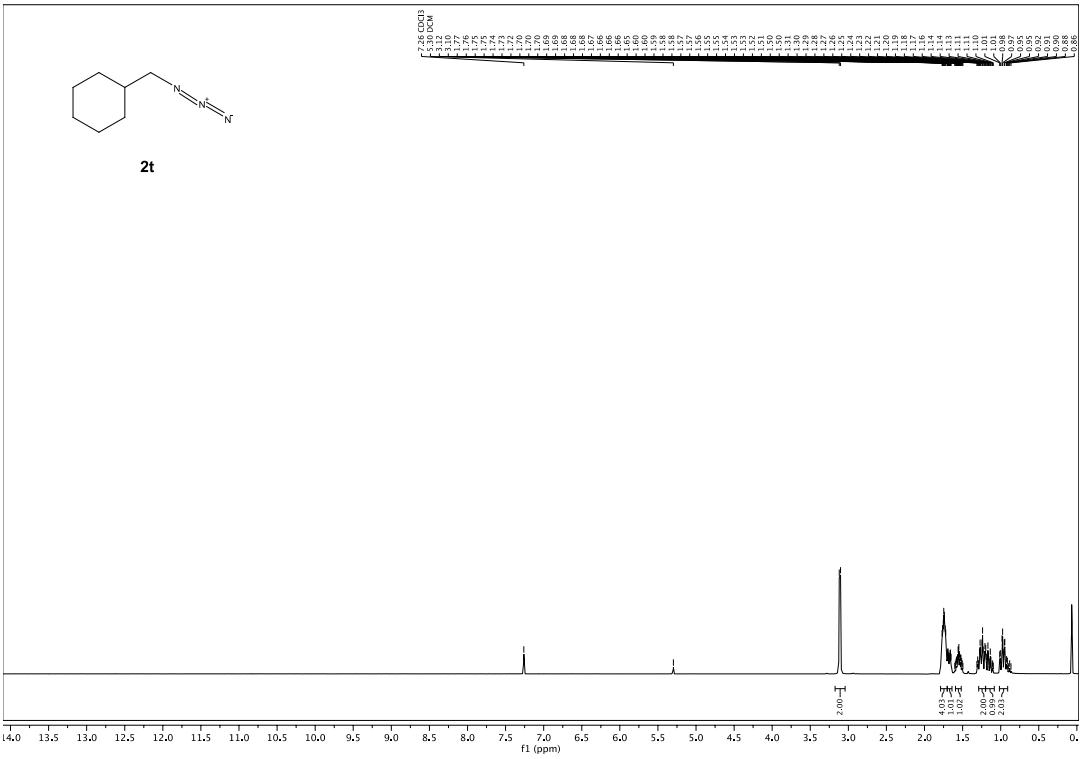
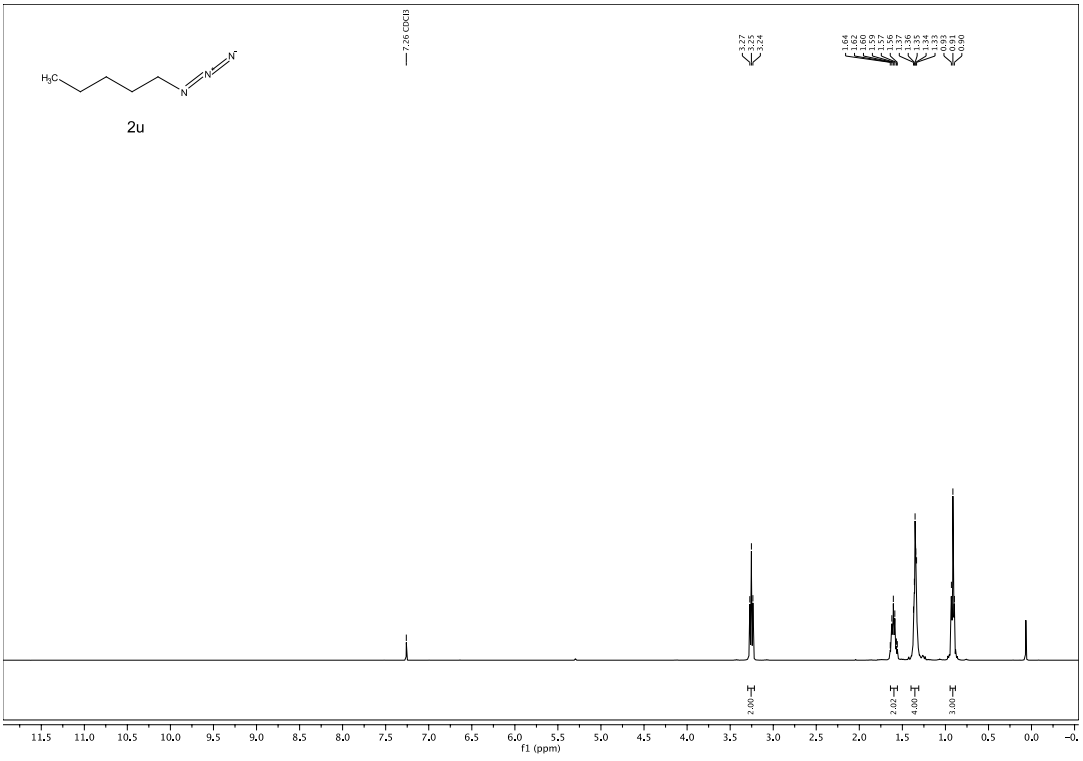
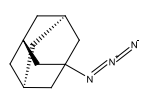


^{1}H NMR of **2u**

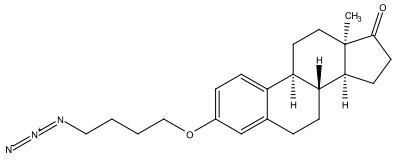


^{1}H NMR of **2v**



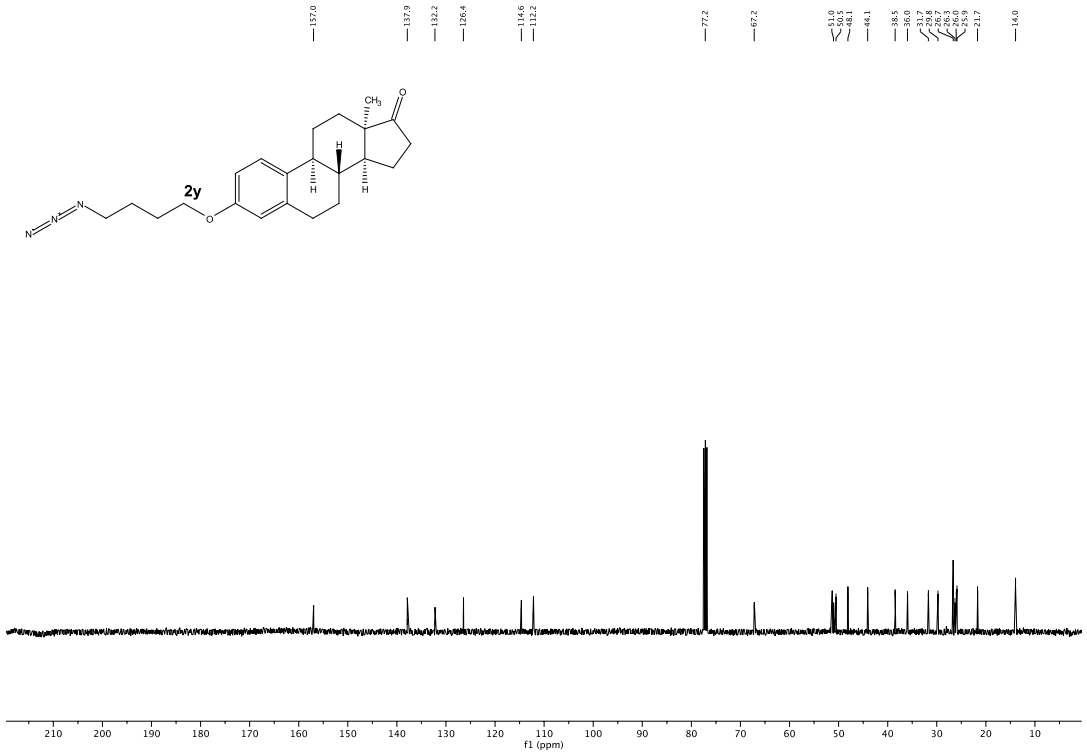
2v

^{1}H NMR of **2y**

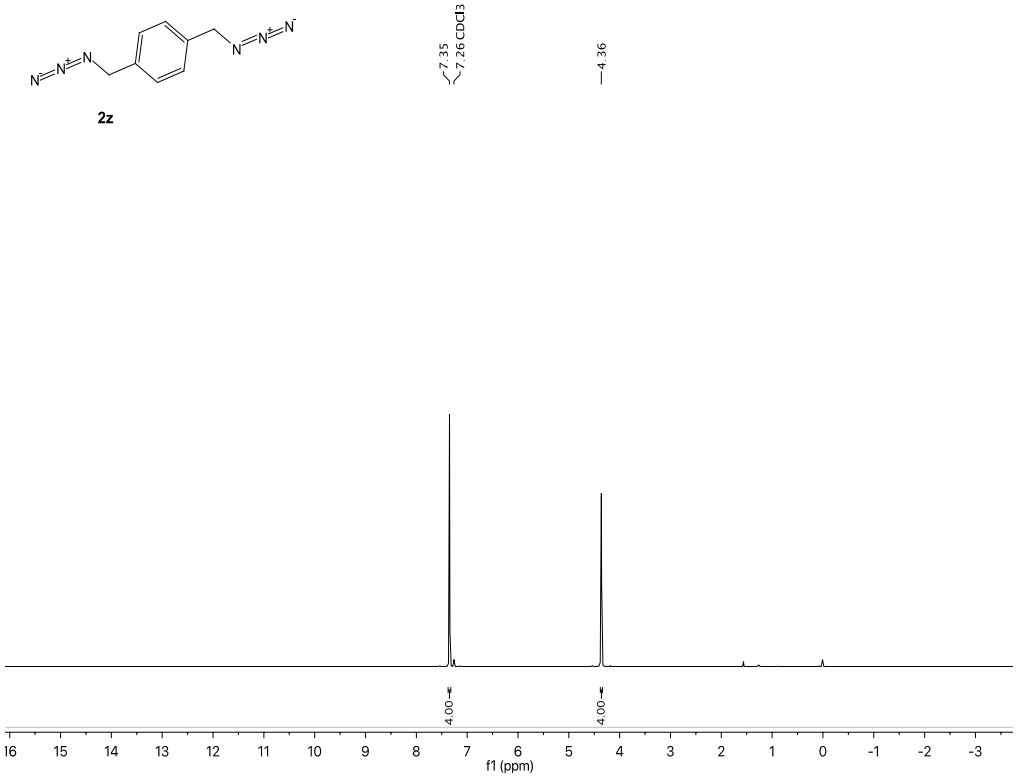


2y

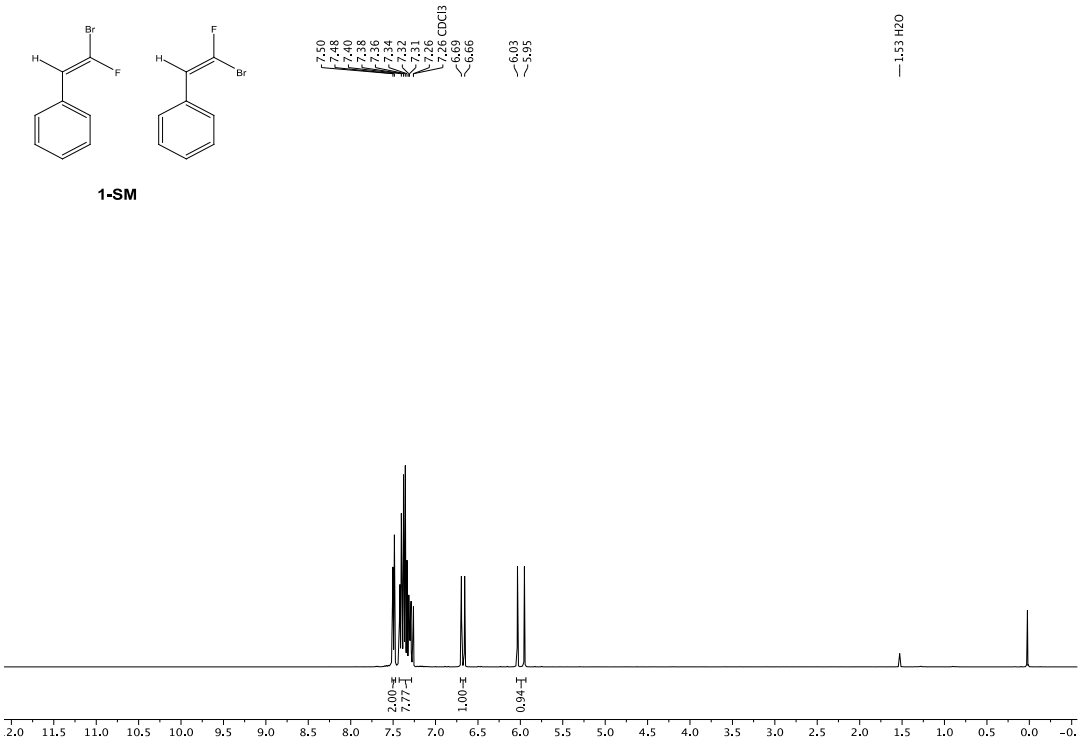
^{13}C NMR of **2y**



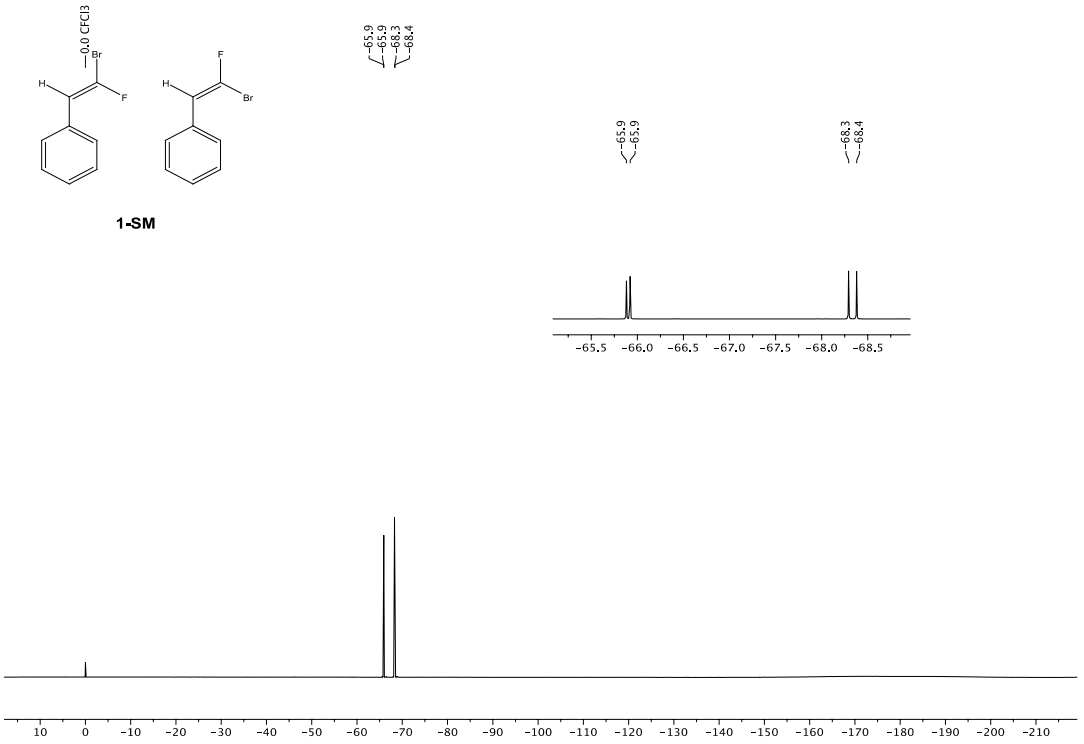
^{1}H NMR of **2z**



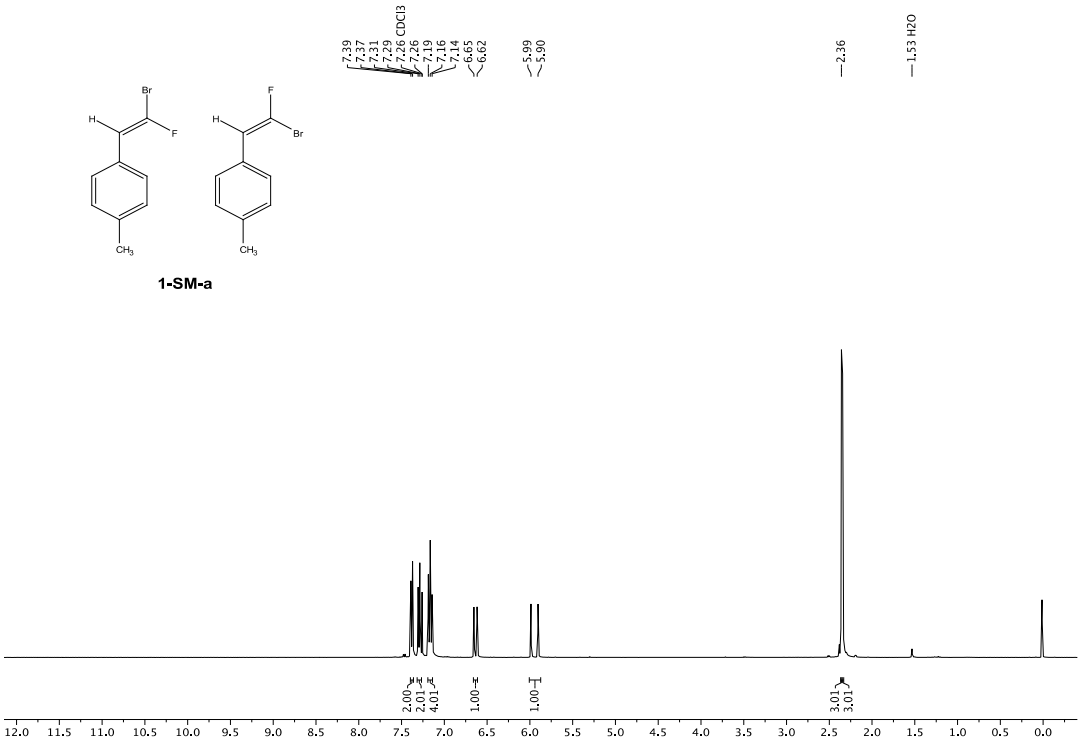
^{1}H NMR of **1-SM**



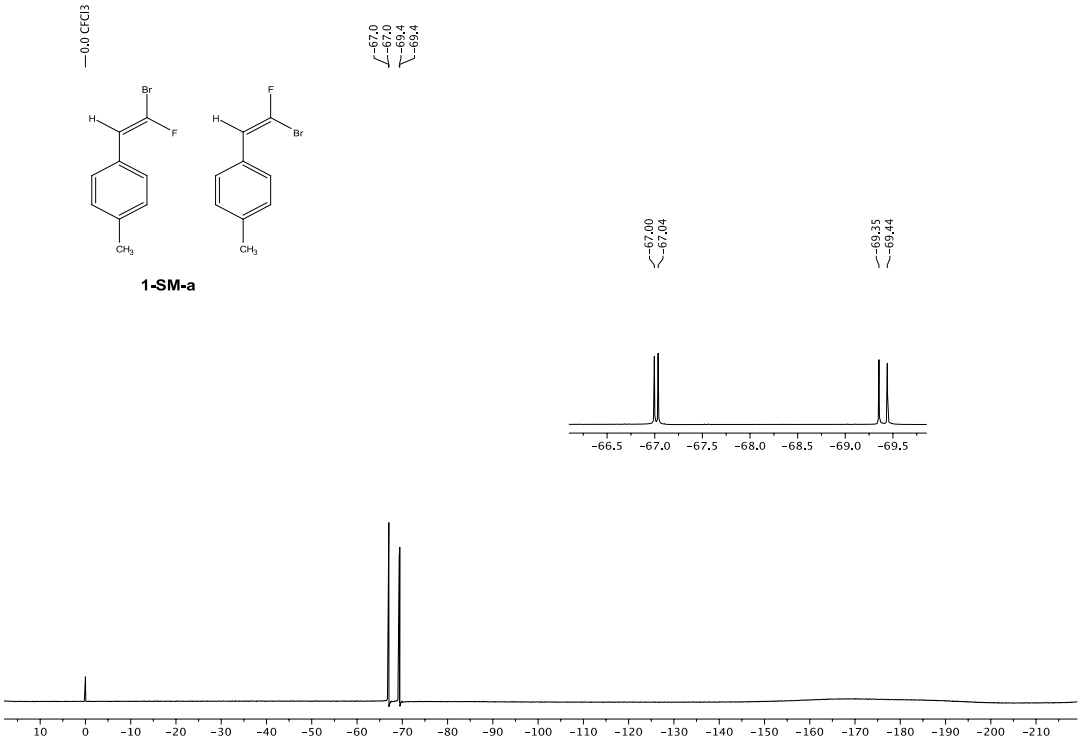
^{19}F NMR of **1-SM**



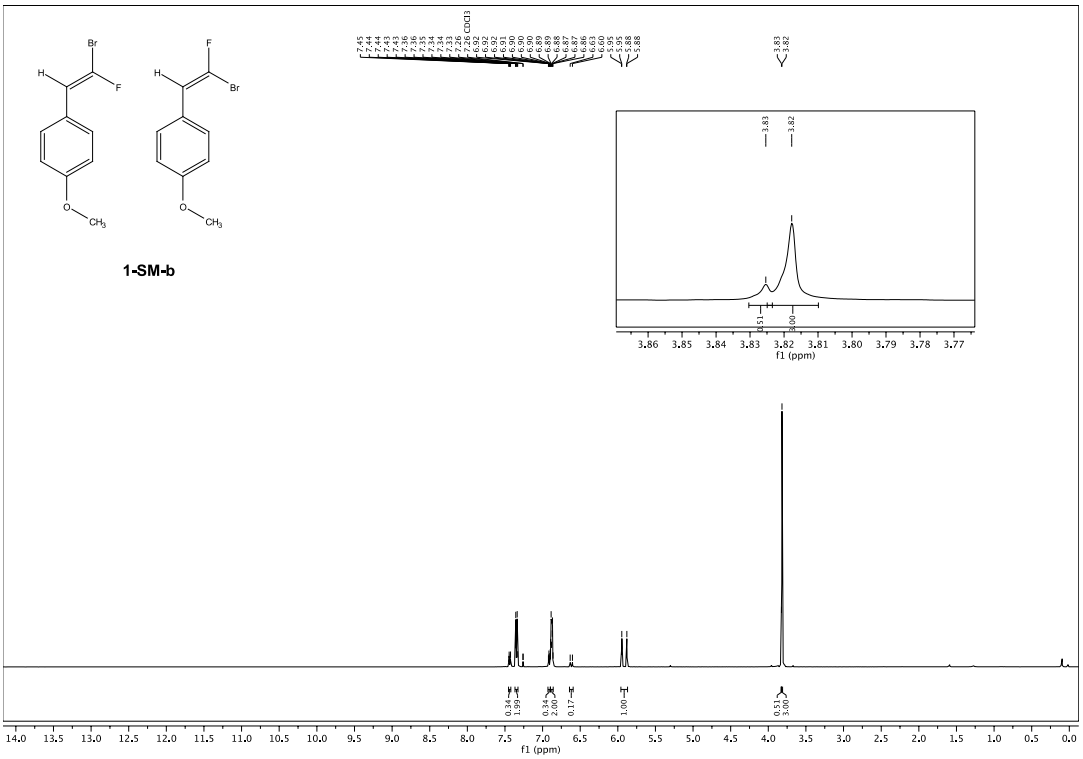
^{1}H NMR of **1-SM-a**



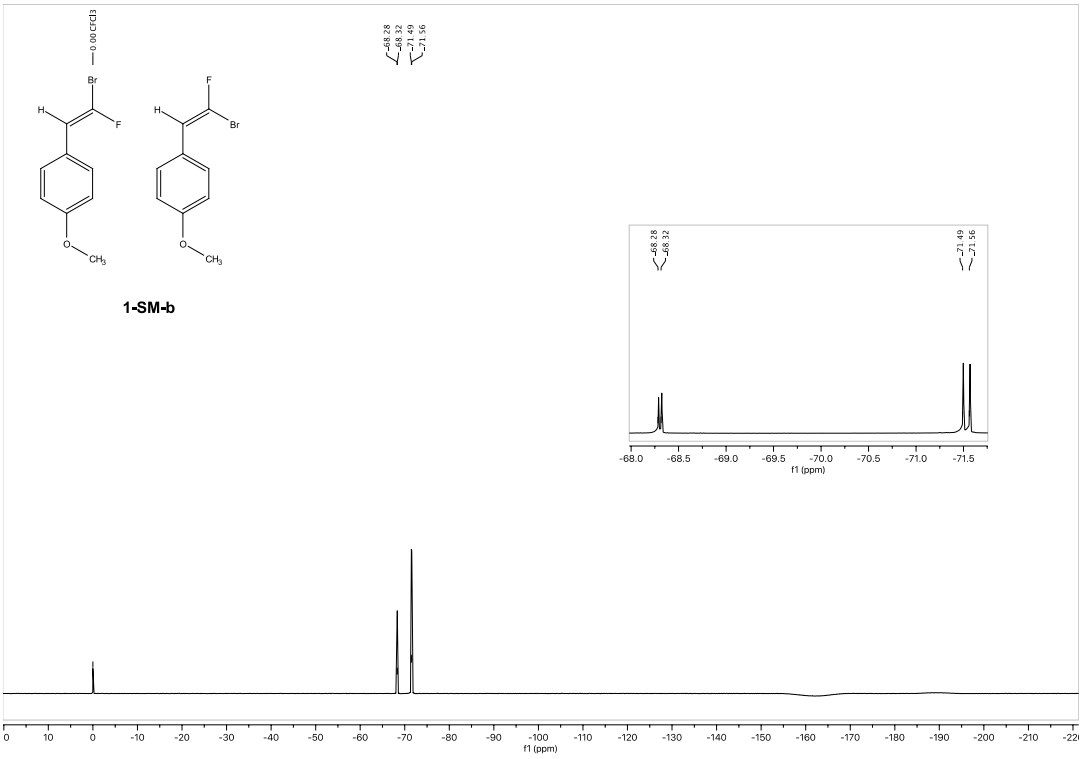
^{19}F NMR of **1-SM-a**



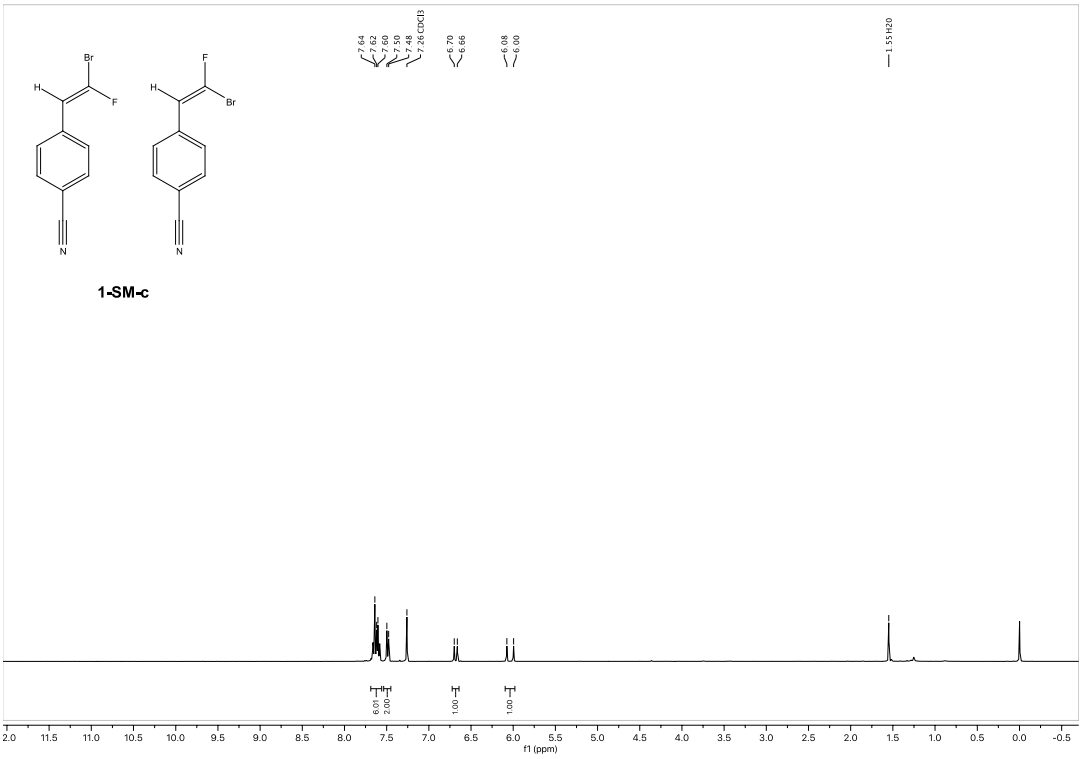
^{1}H NMR of **1-SM-b**



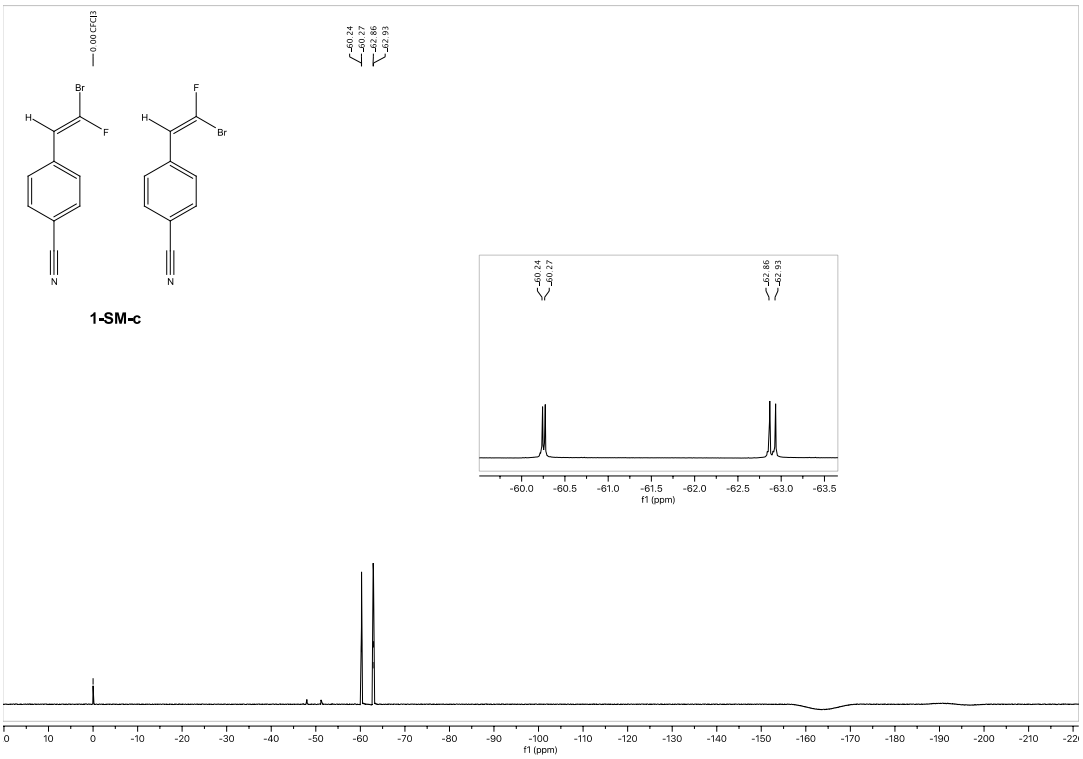
^{19}F NMR of **1-SM-b**



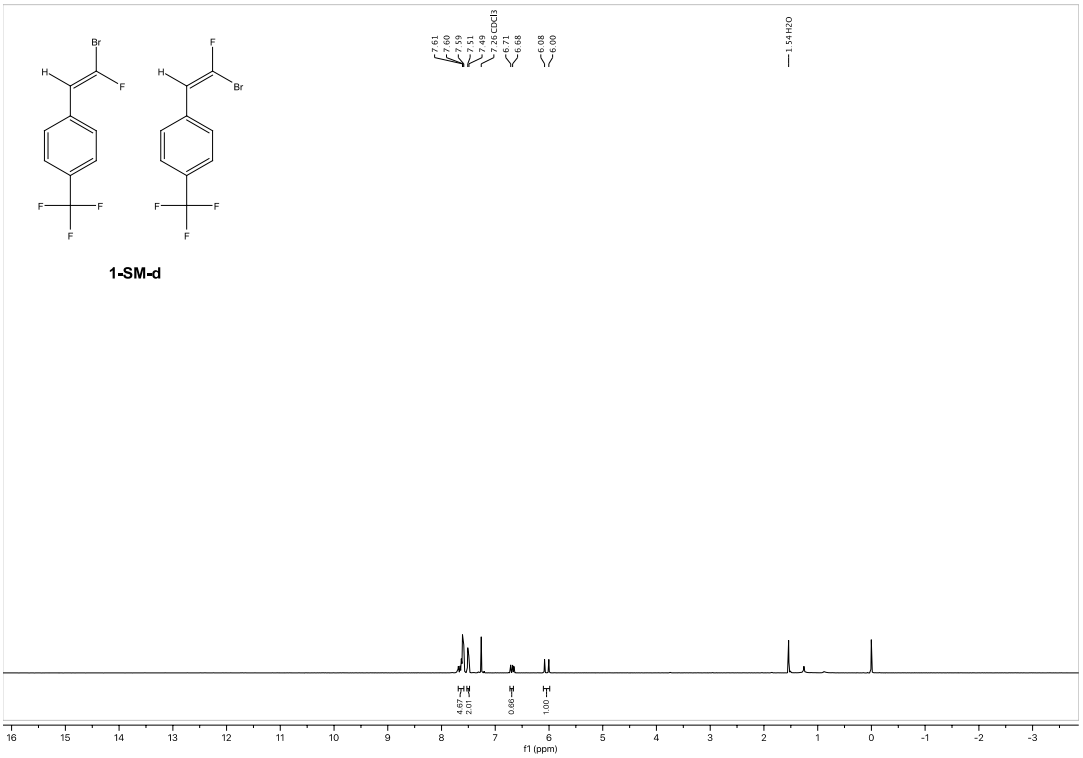
^{1}H NMR of **1-SM-c**



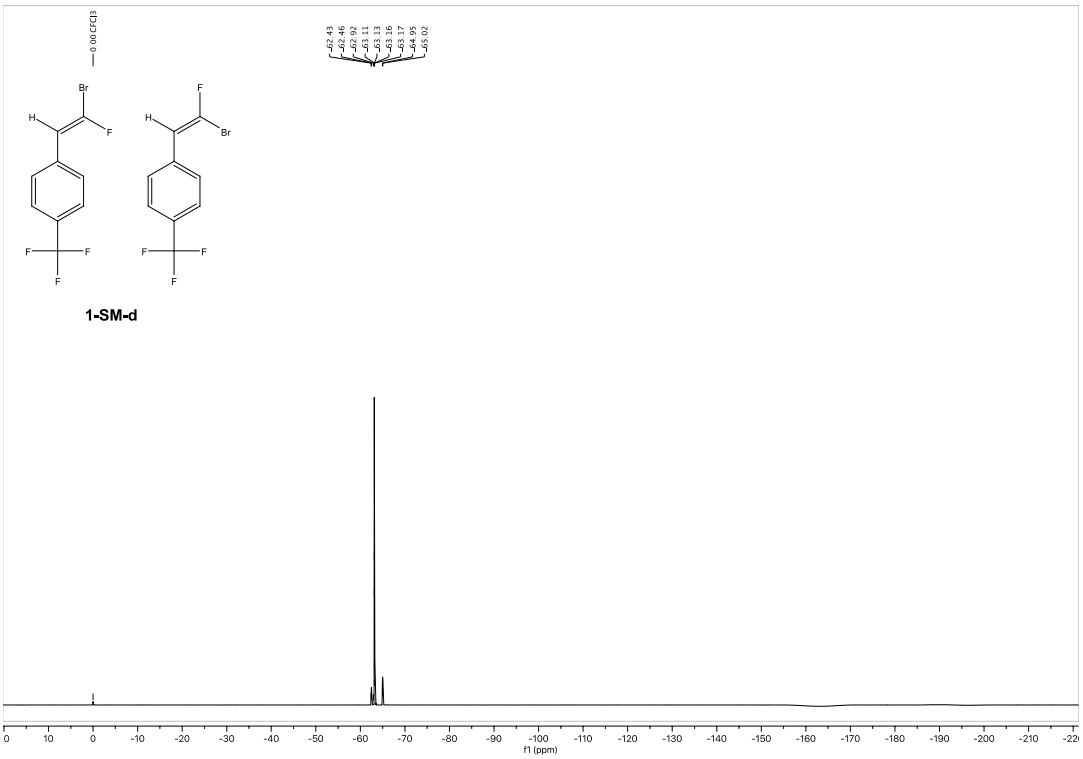
^{19}F NMR of **1-SM-c**



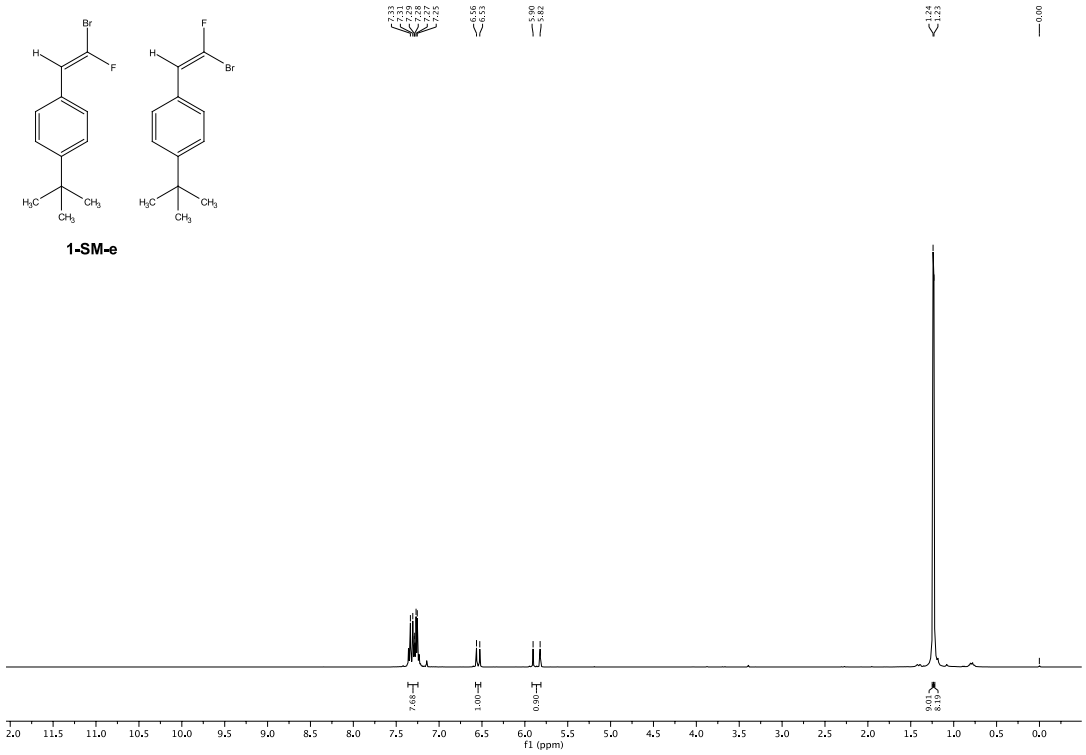
^{1}H NMR of **1-SM-d**



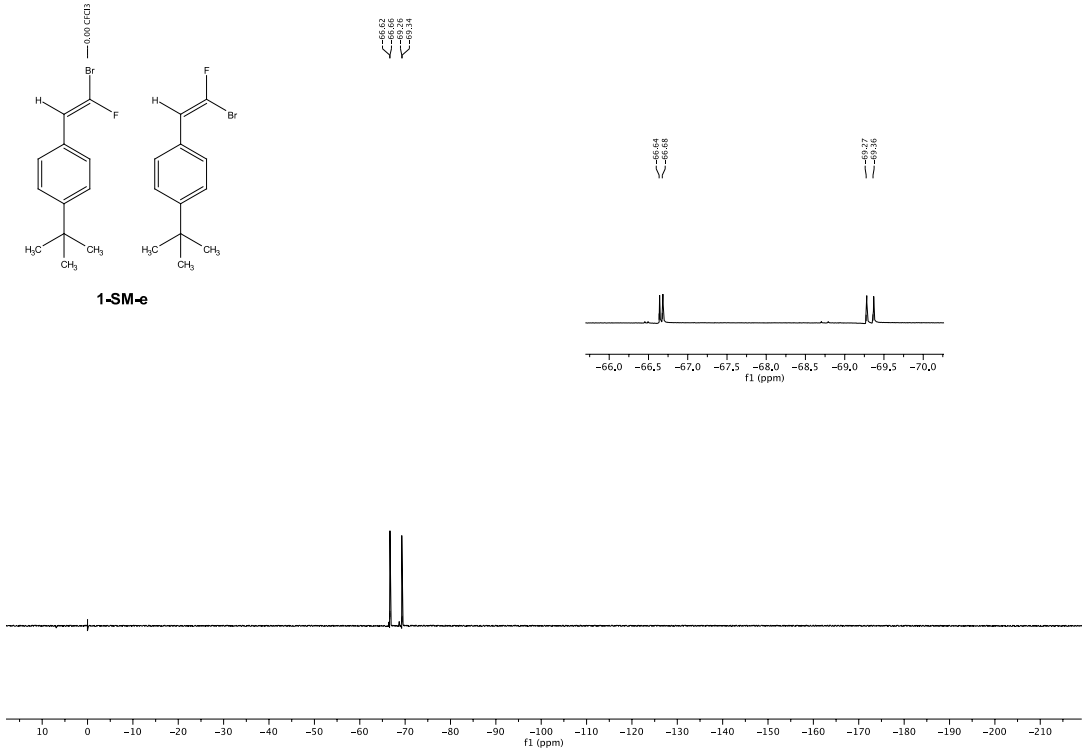
^{19}F NMR of **1-SM-d**



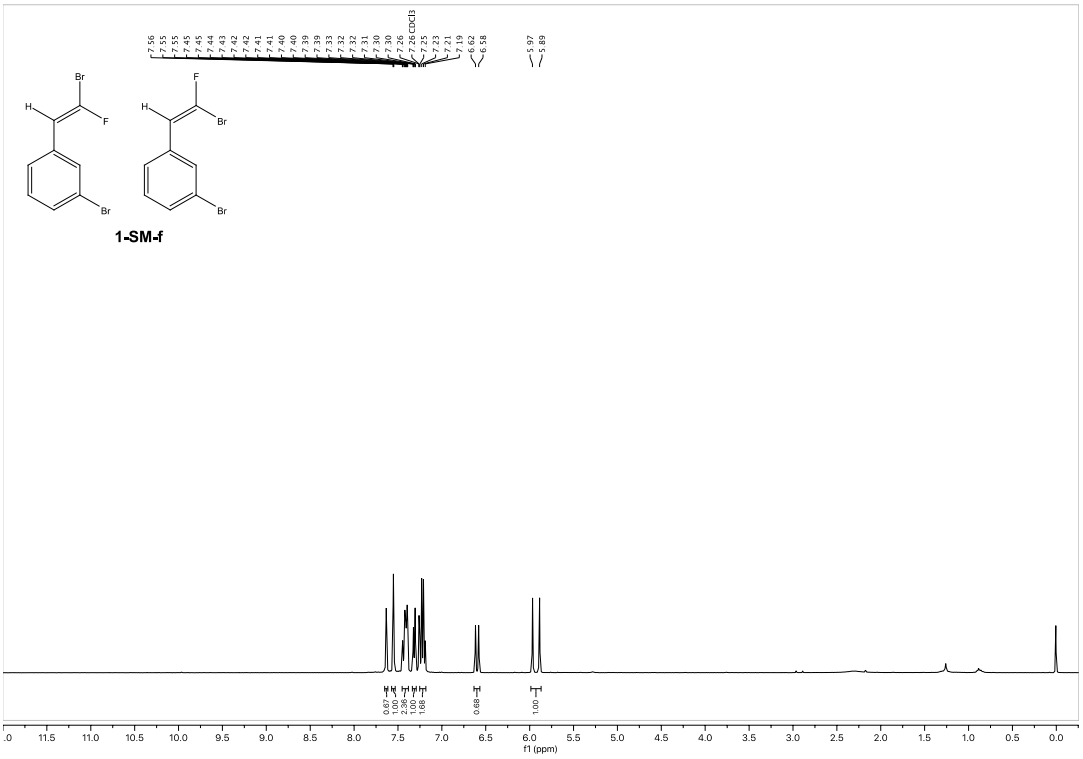
^{1}H NMR of **1-SM-e**



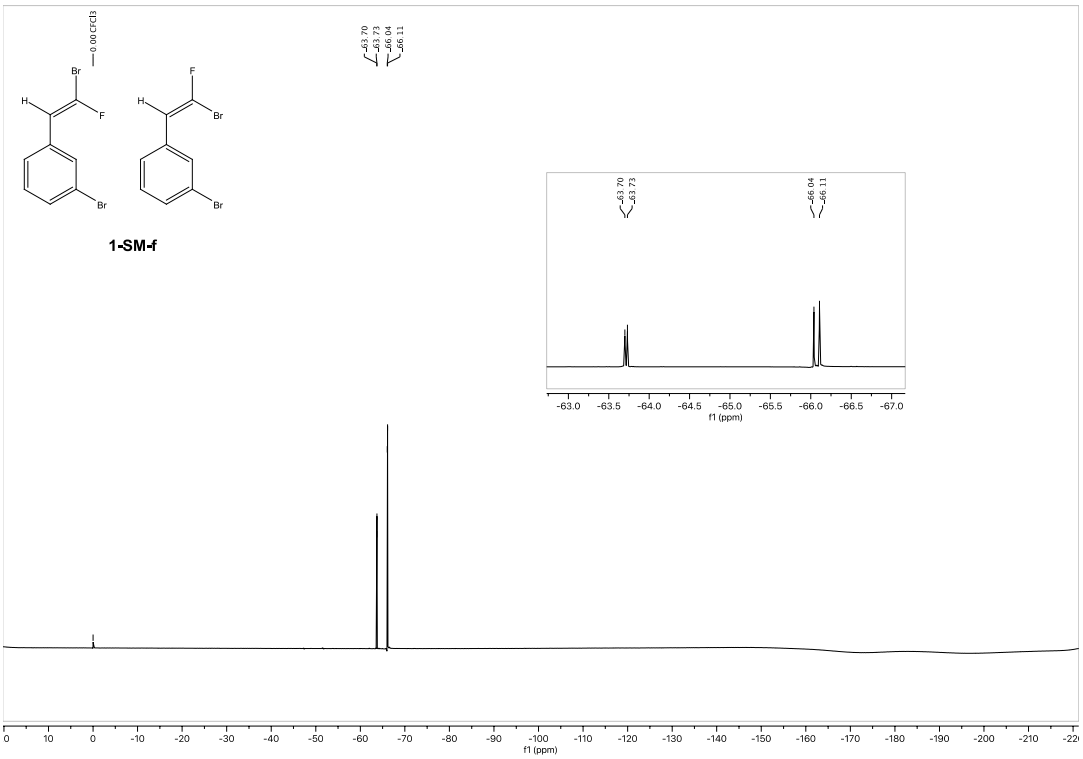
^{19}F NMR of **1-SM-e**



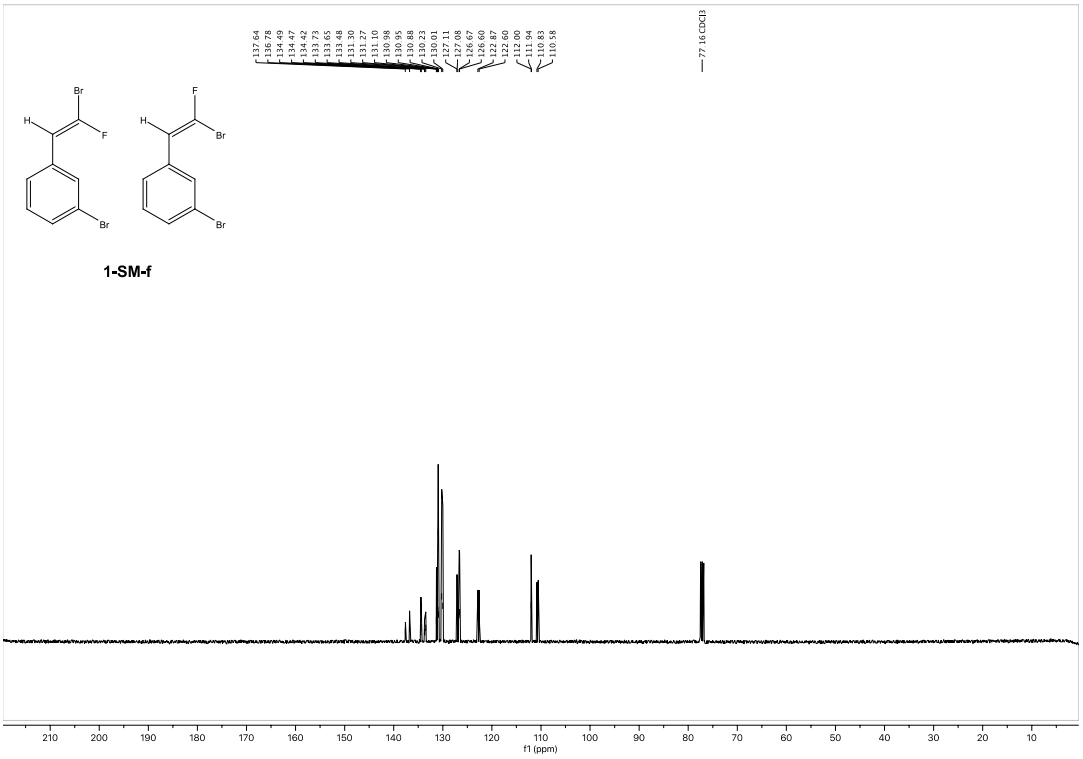
^{1}H NMR of **1-SM-f**



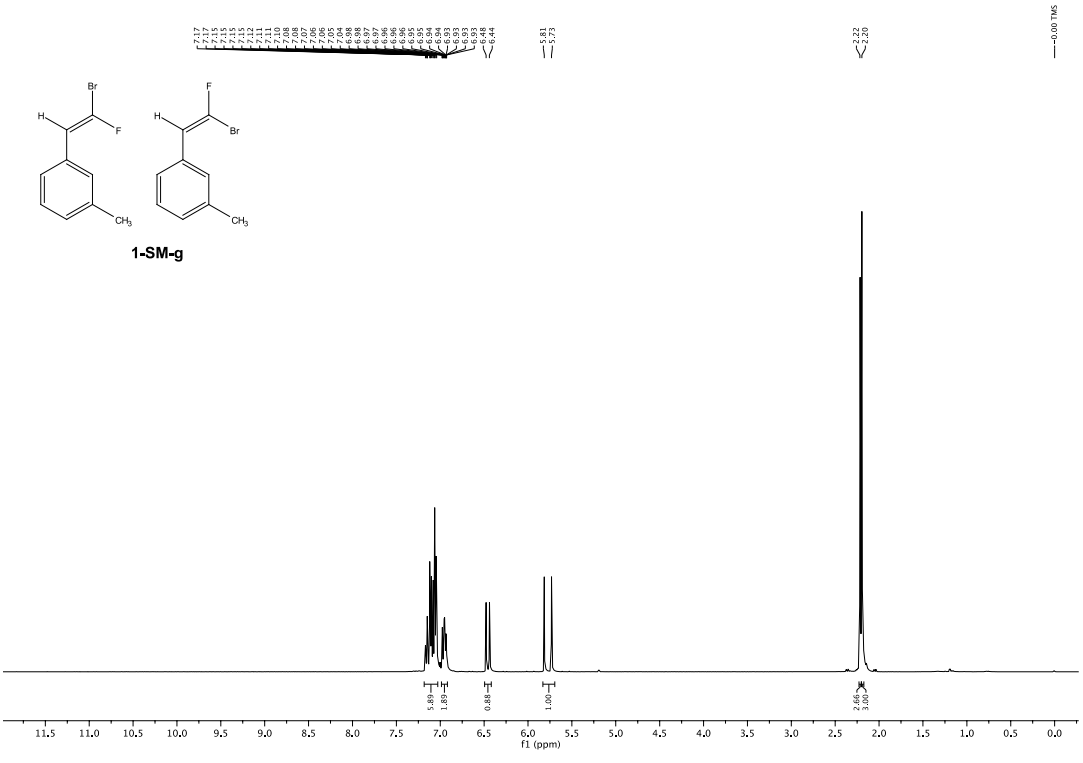
^{19}F NMR of **1-SM-f**



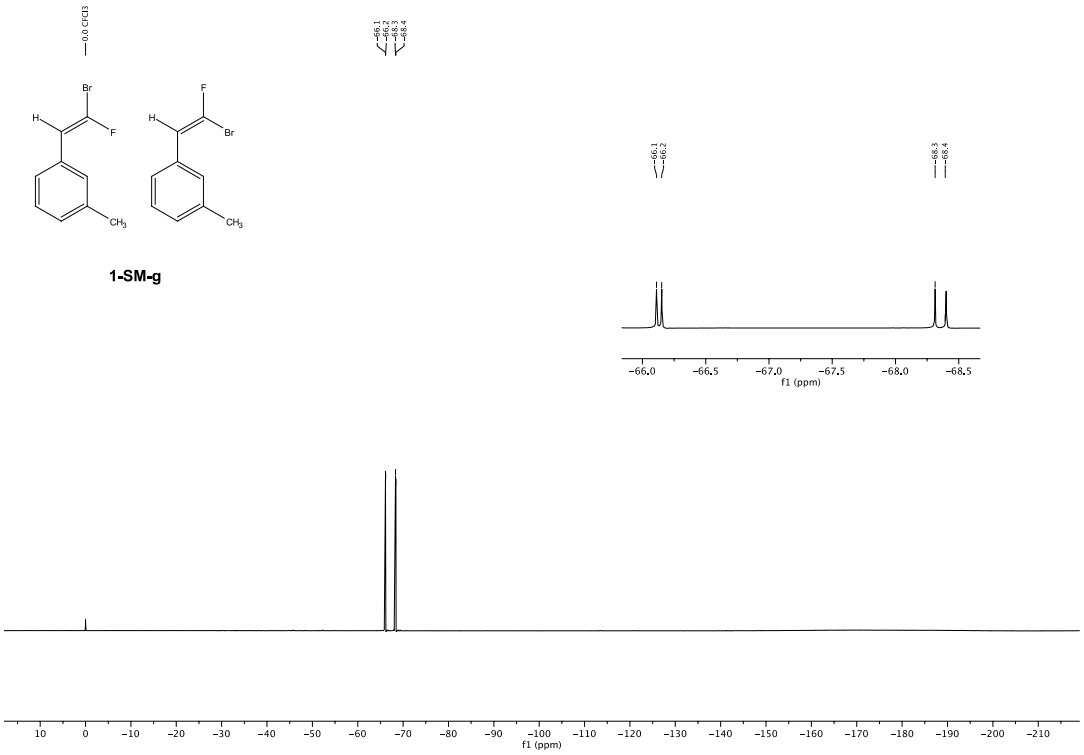
^{13}C NMR of **1-SM-f**



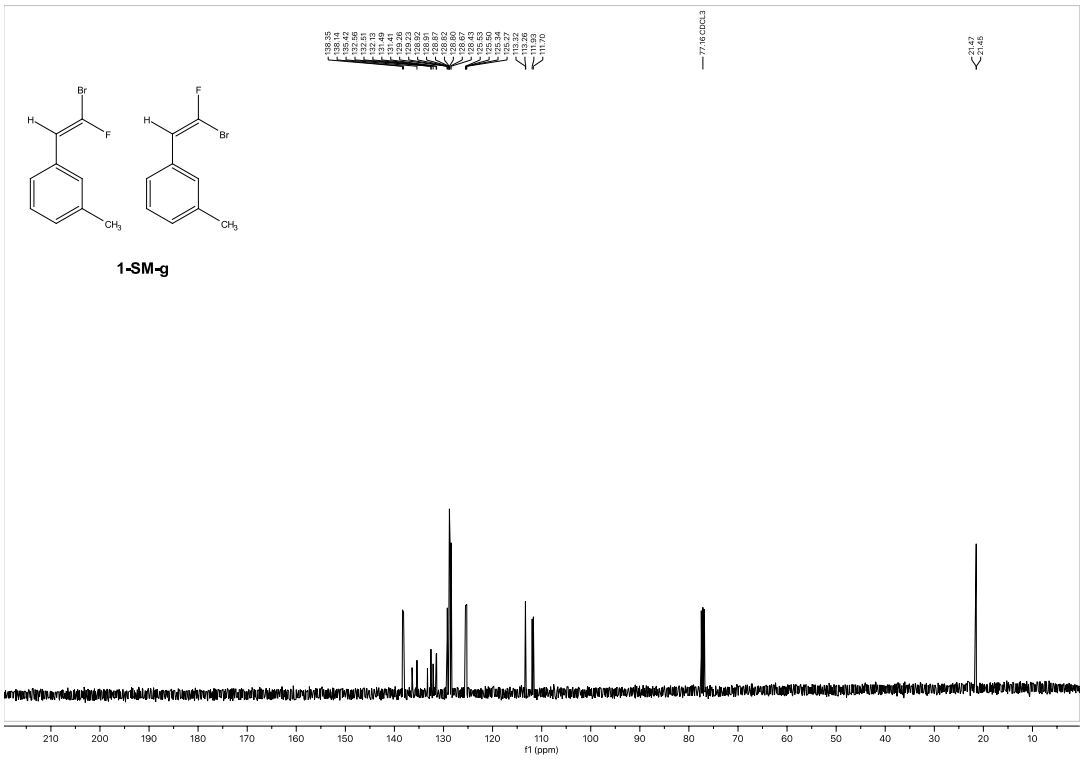
^{1}H NMR of **1-SM-g**



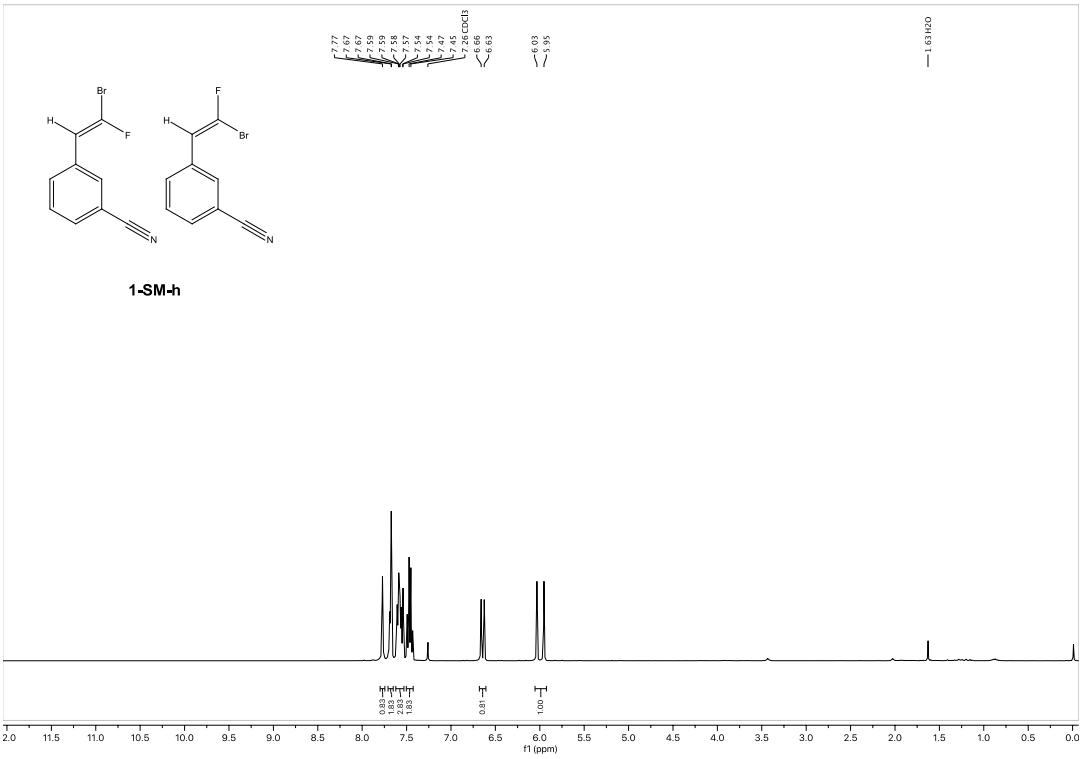
^{19}F NMR of **1-SM-g**



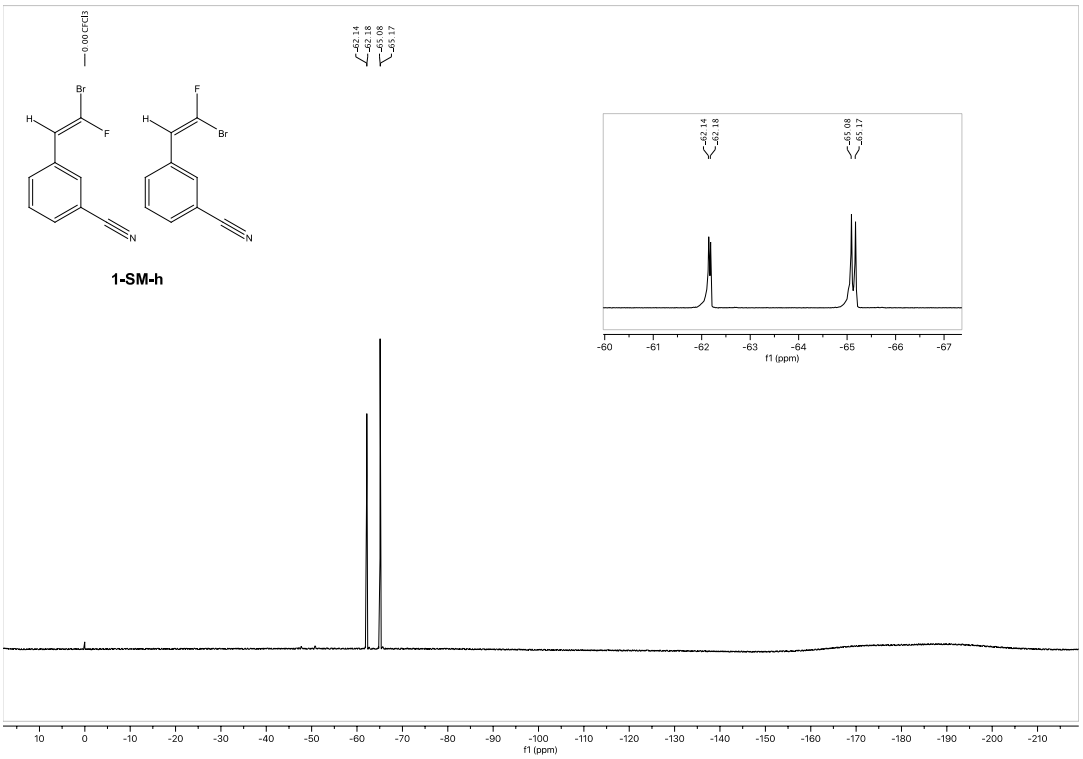
^{13}C NMR of **1-SM-g**



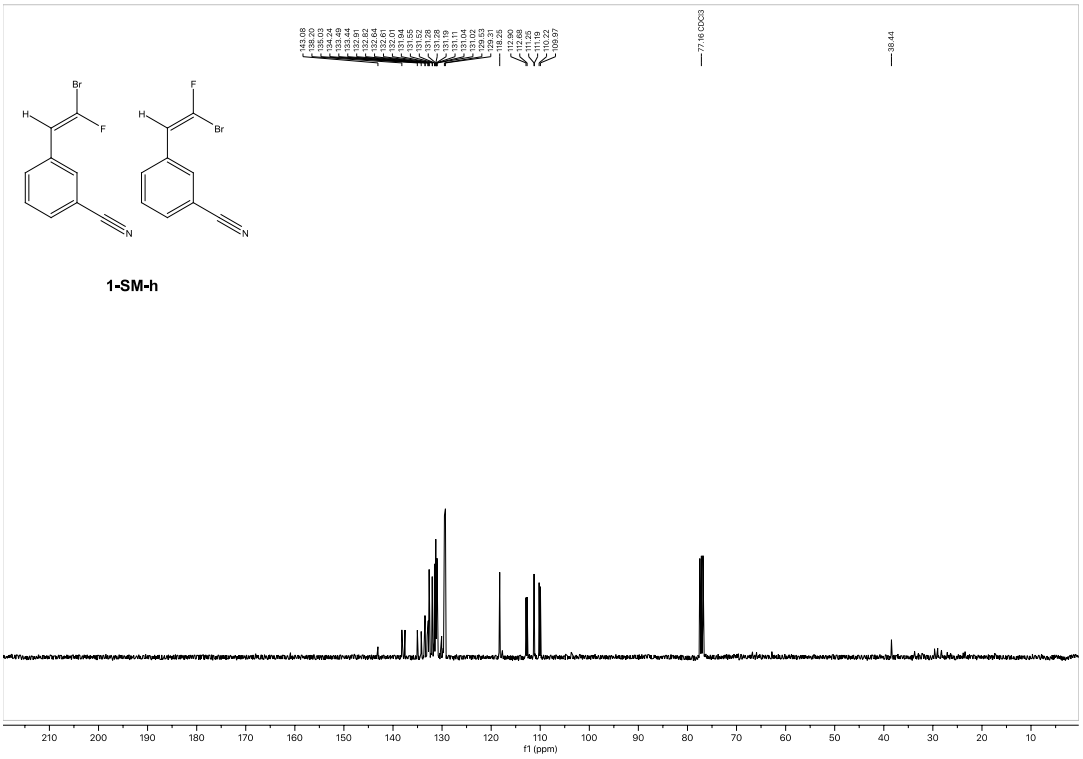
^{1}H NMR of **1-SM-h**



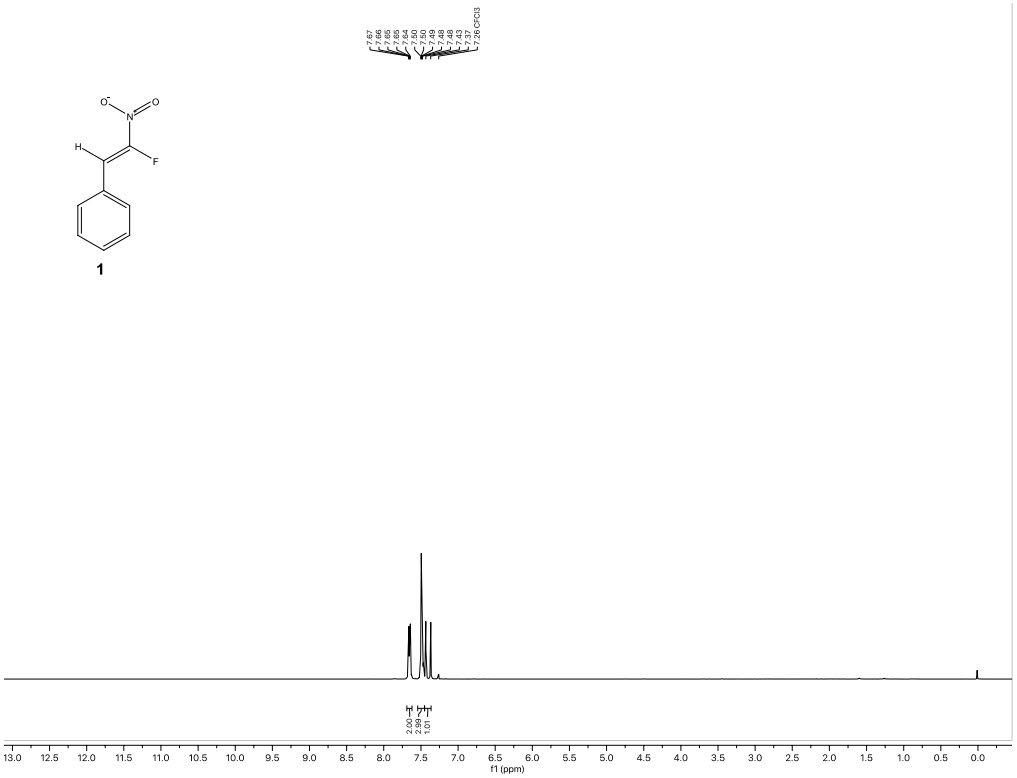
^{19}F NMR of **1-SM-h**



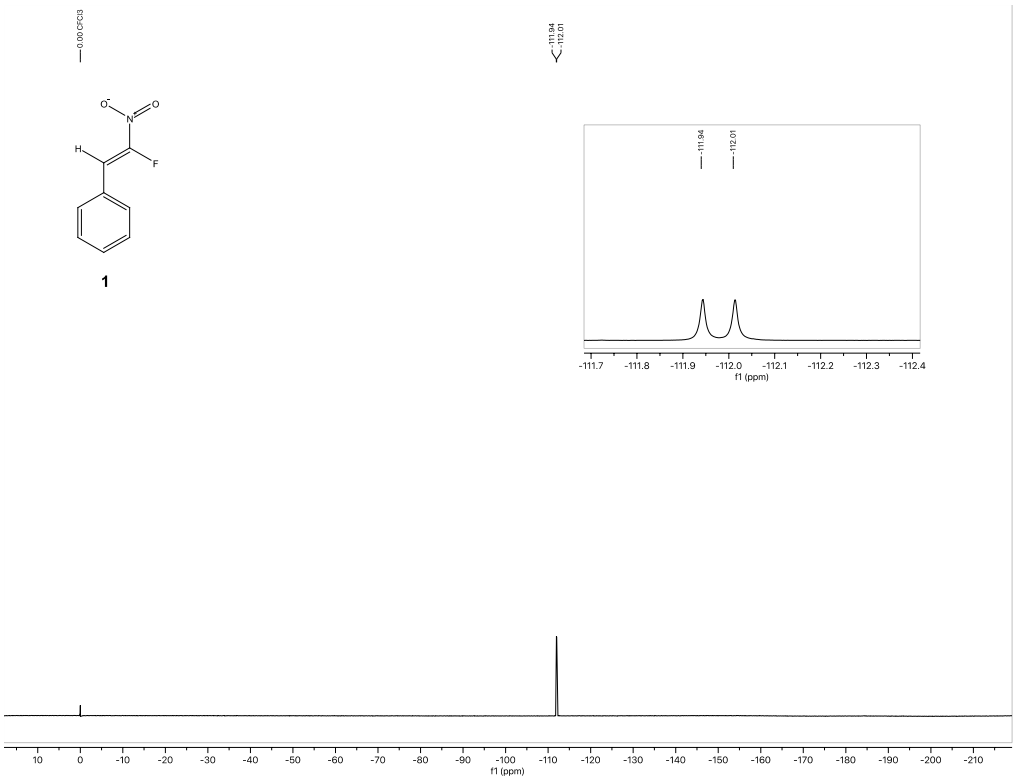
^{13}C NMR of **1-SM-h**



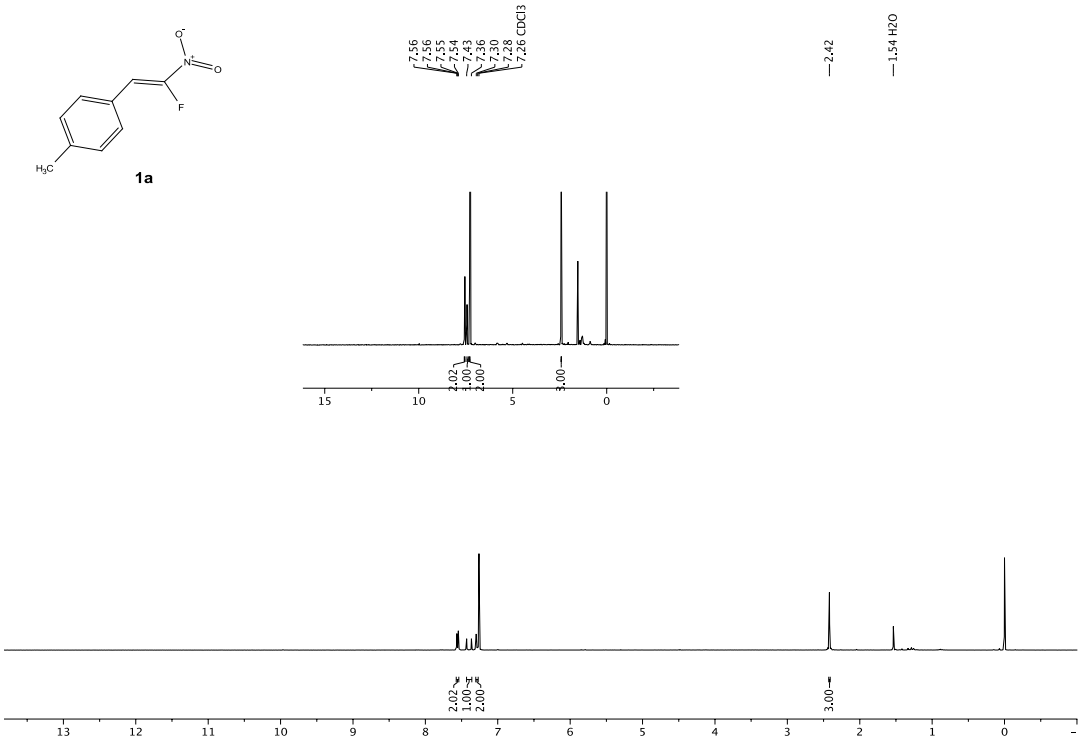
^{1}H NMR of **1**



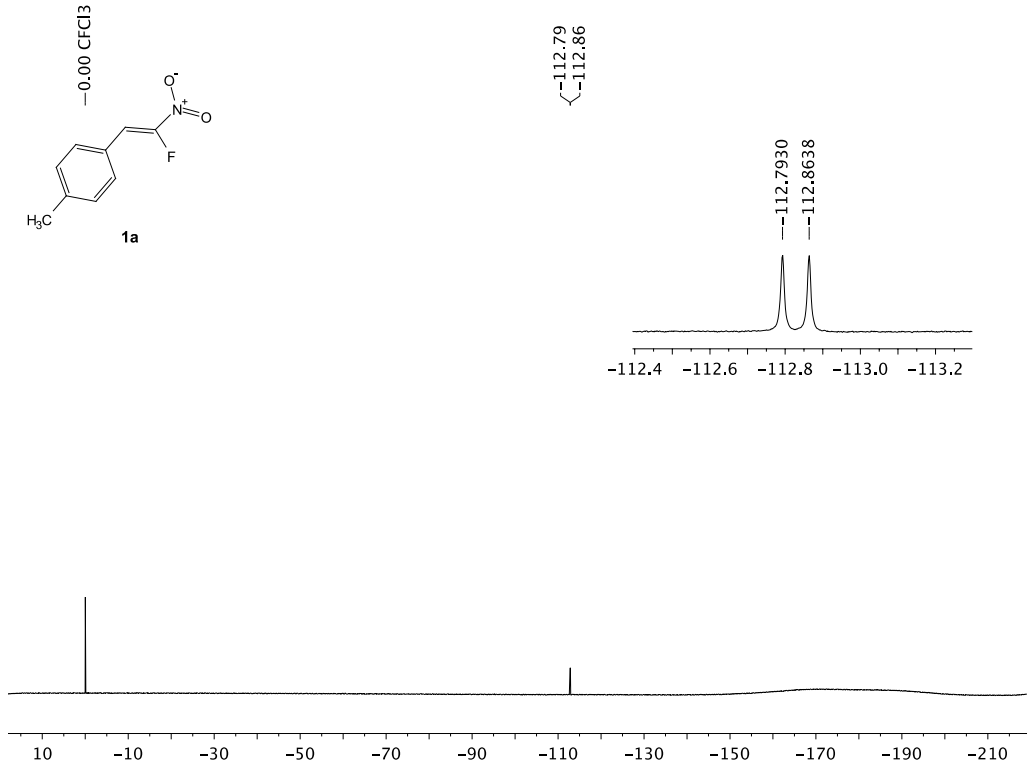
^{19}F NMR of **1**



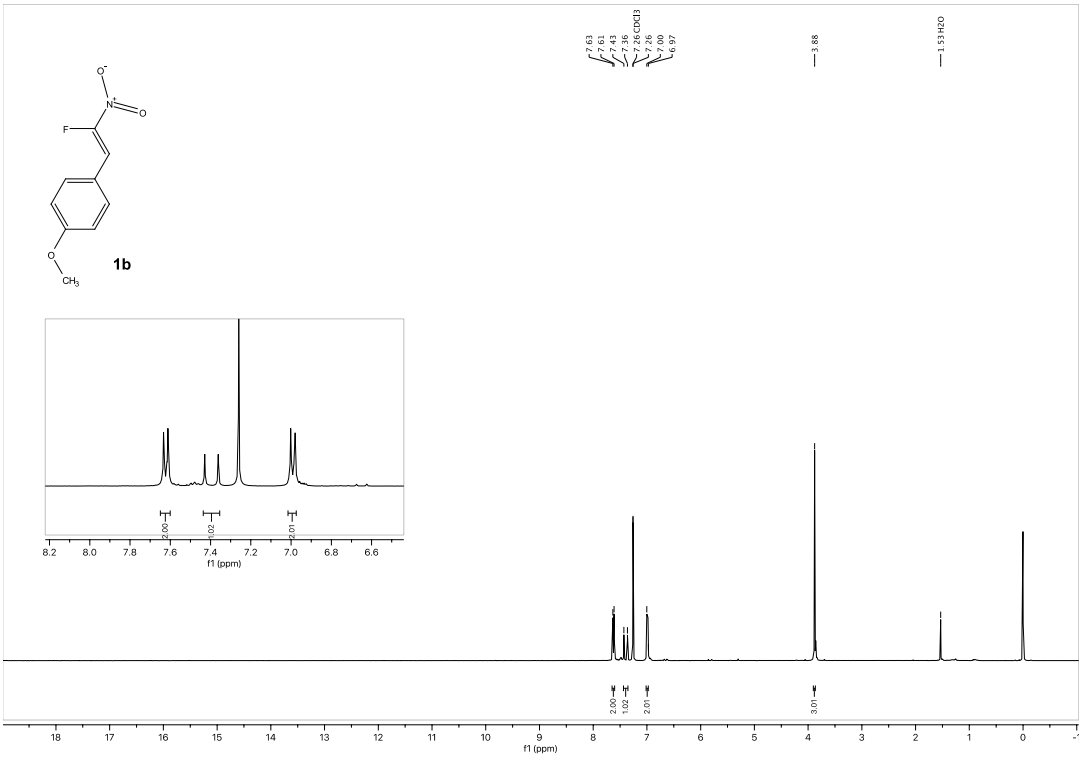
^{1}H NMR of **1a**



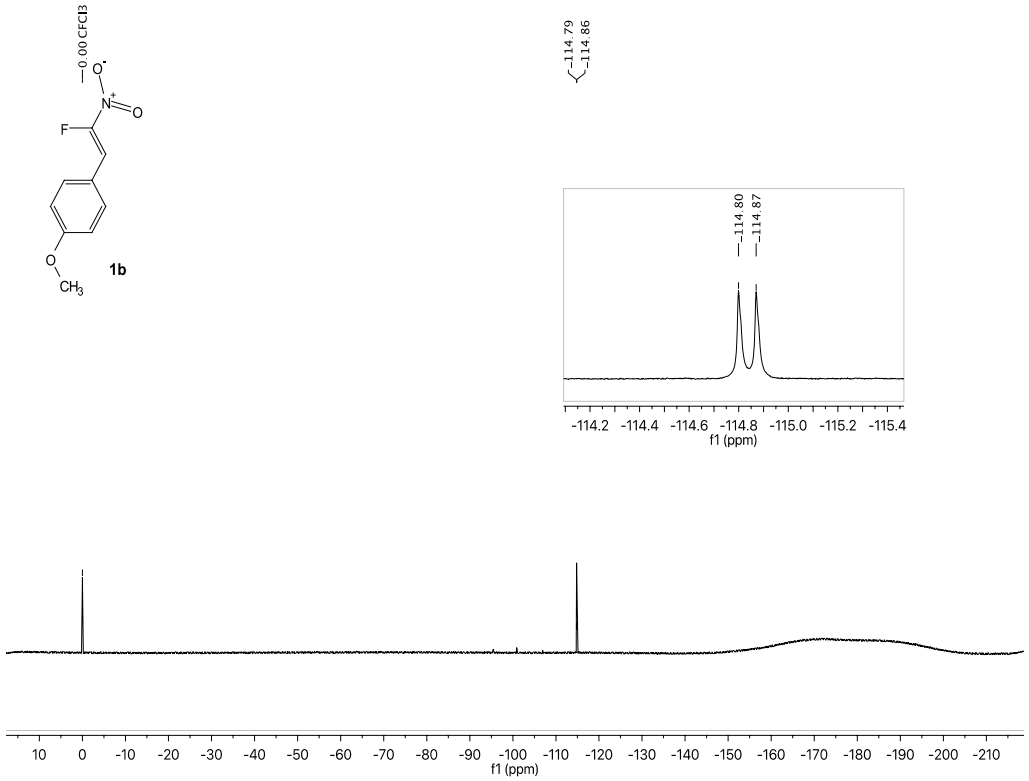
^{19}F NMR of **1a**



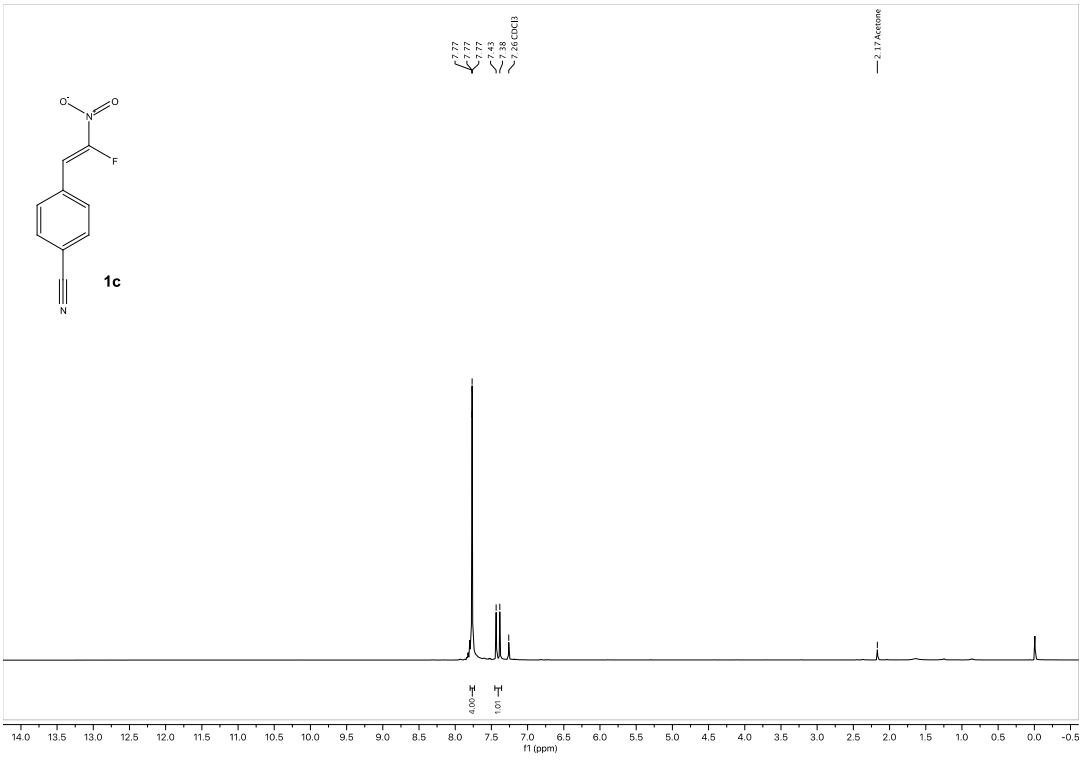
^{1}H NMR of **1b**



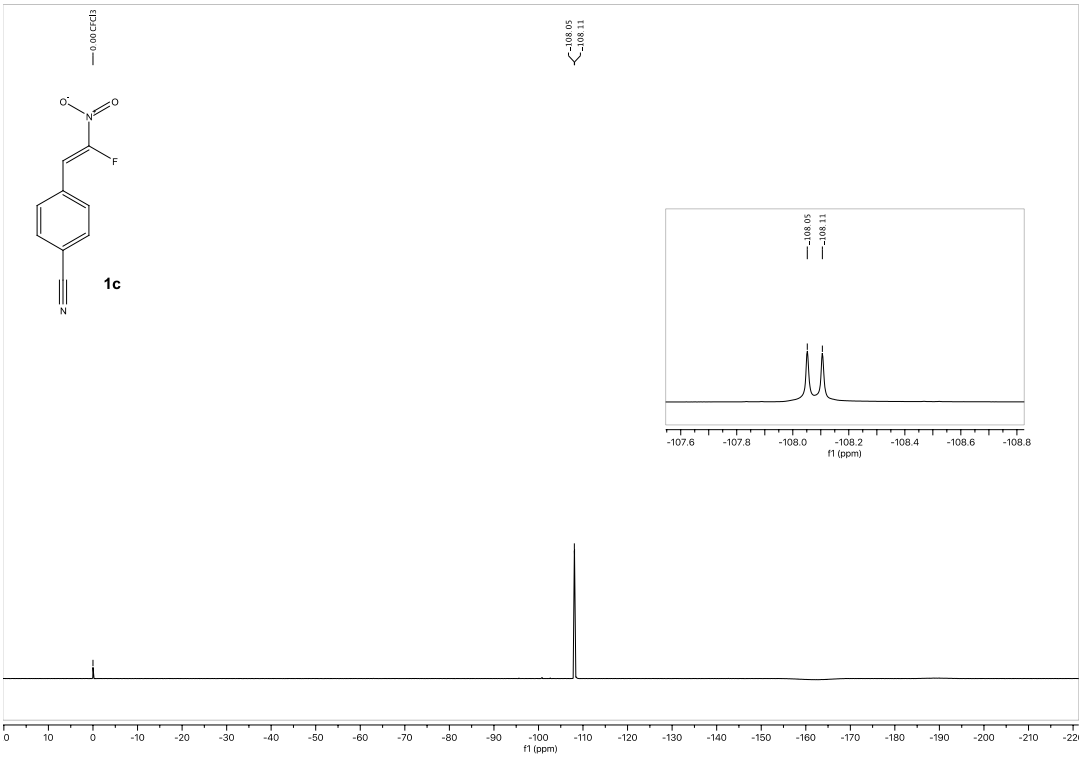
^{19}F NMR of **1b**



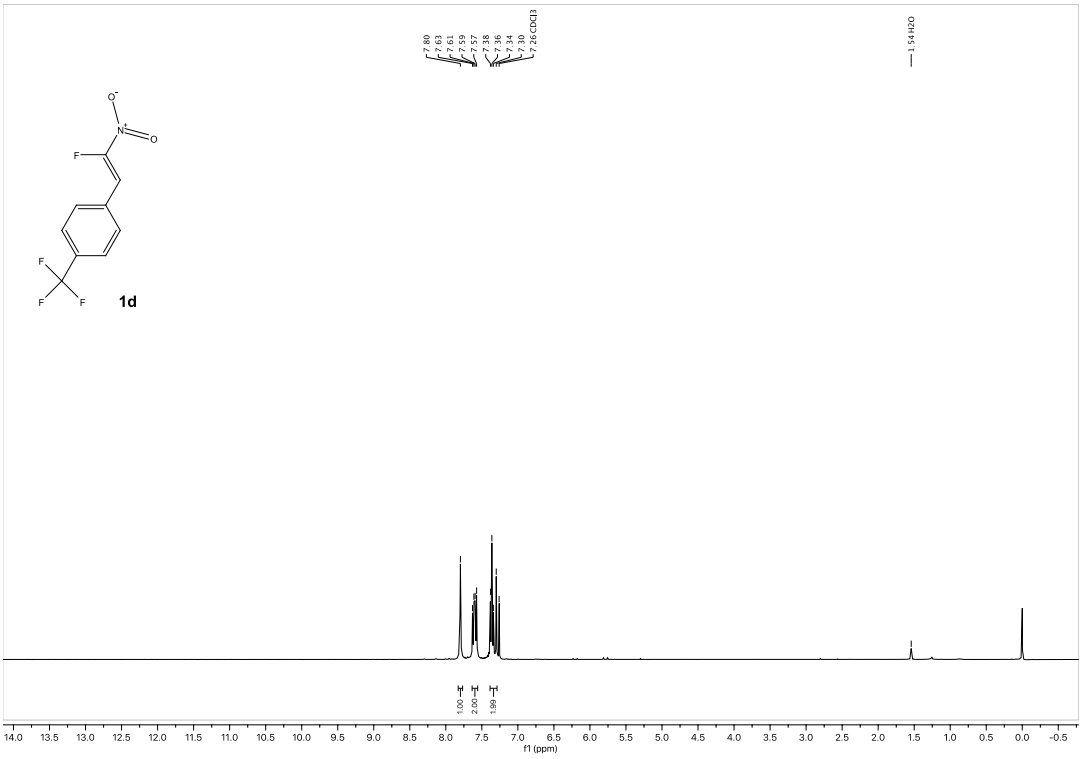
^{1}H NMR of **1c**



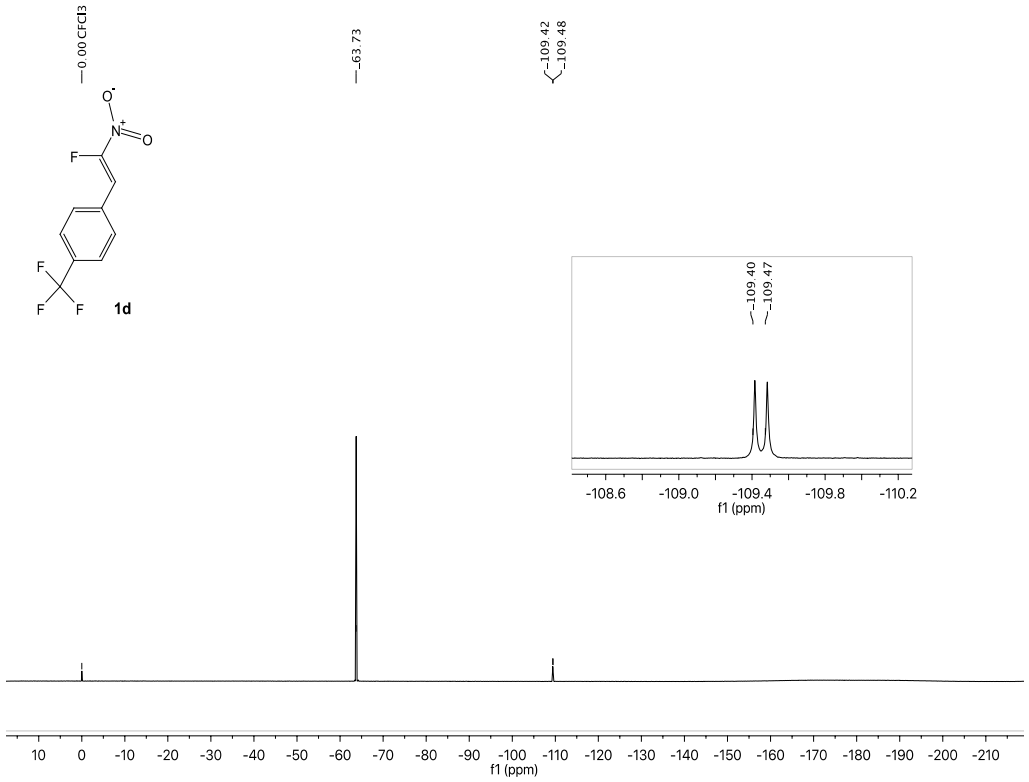
^{19}F NMR of **1c**



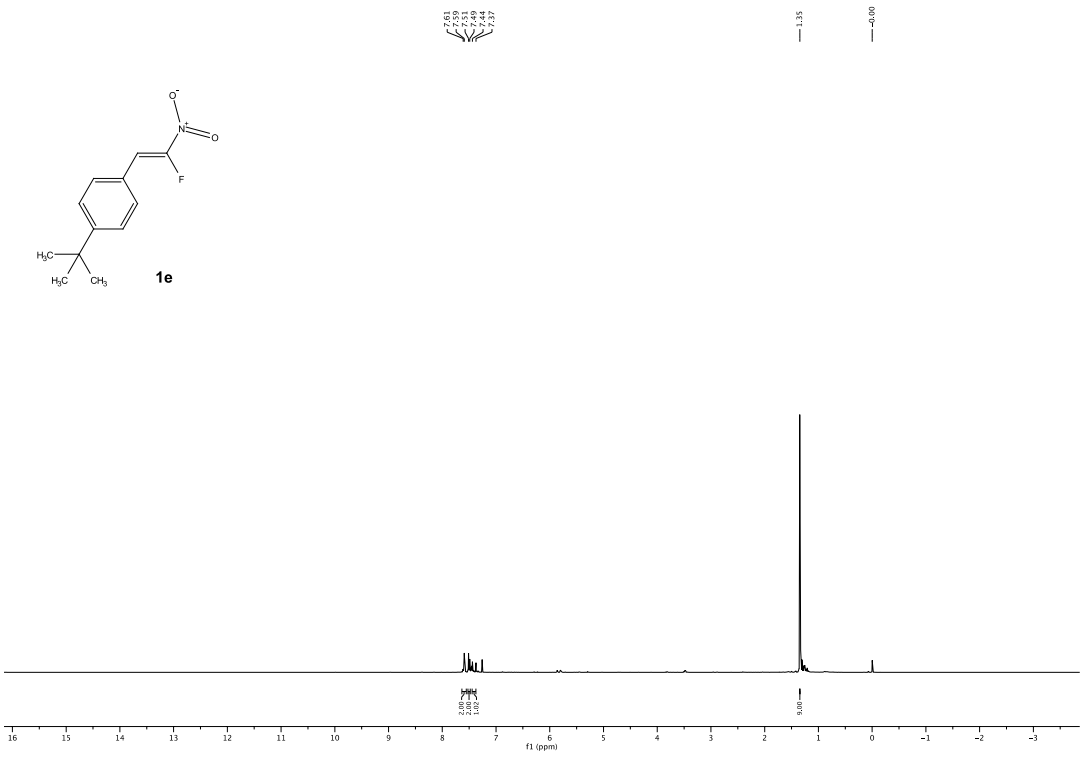
^{1}H NMR of **1d**



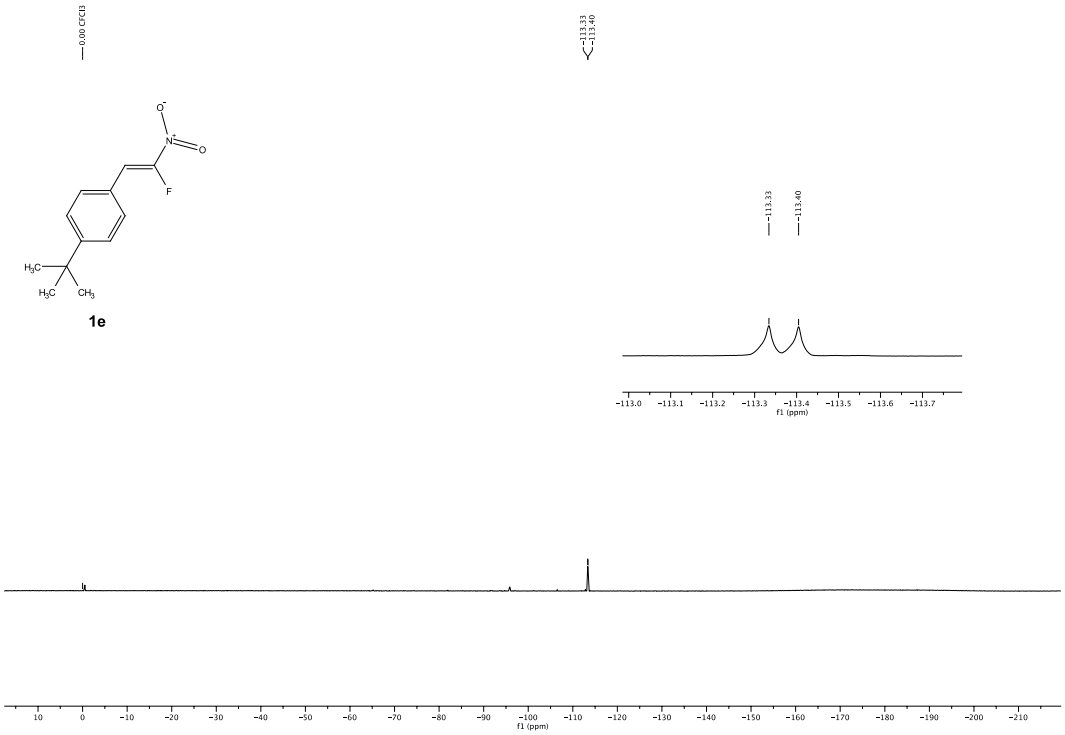
^{19}F NMR of **1d**



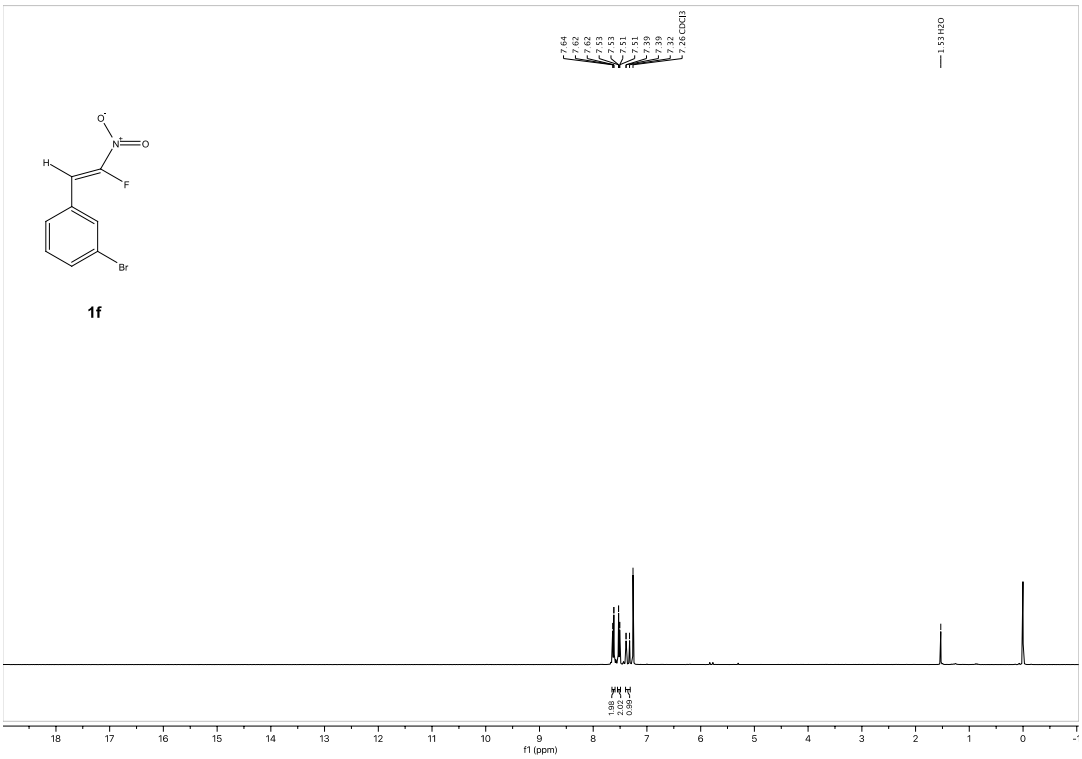
^{1}H NMR of **1e**



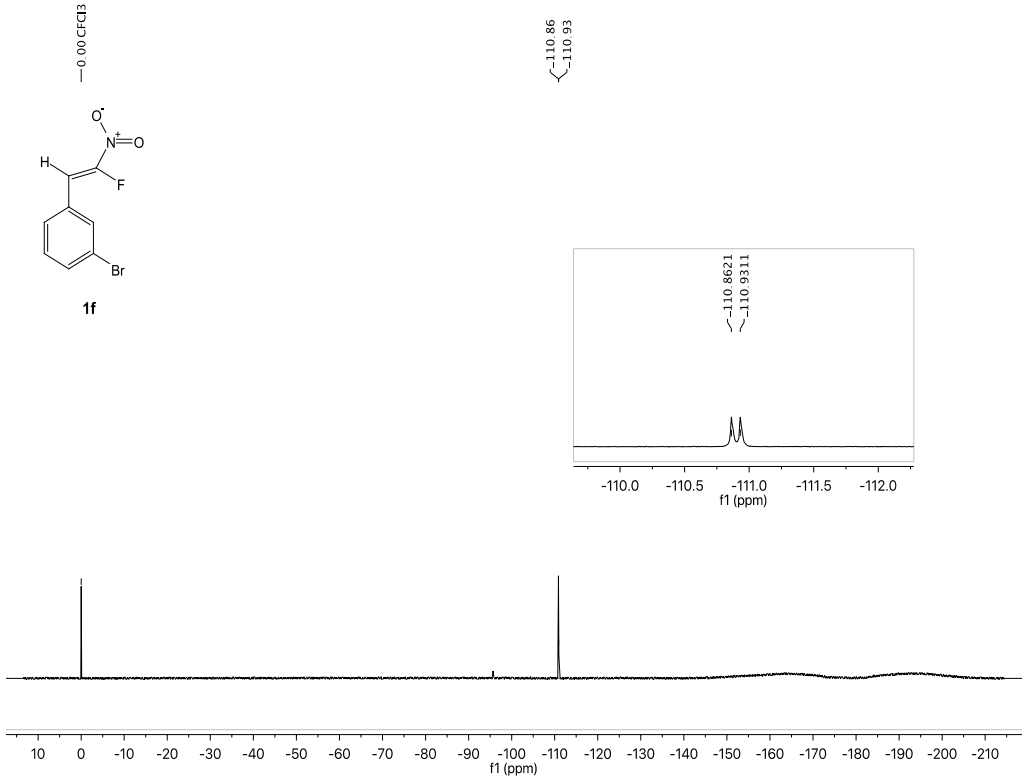
^{19}F NMR of **1e**



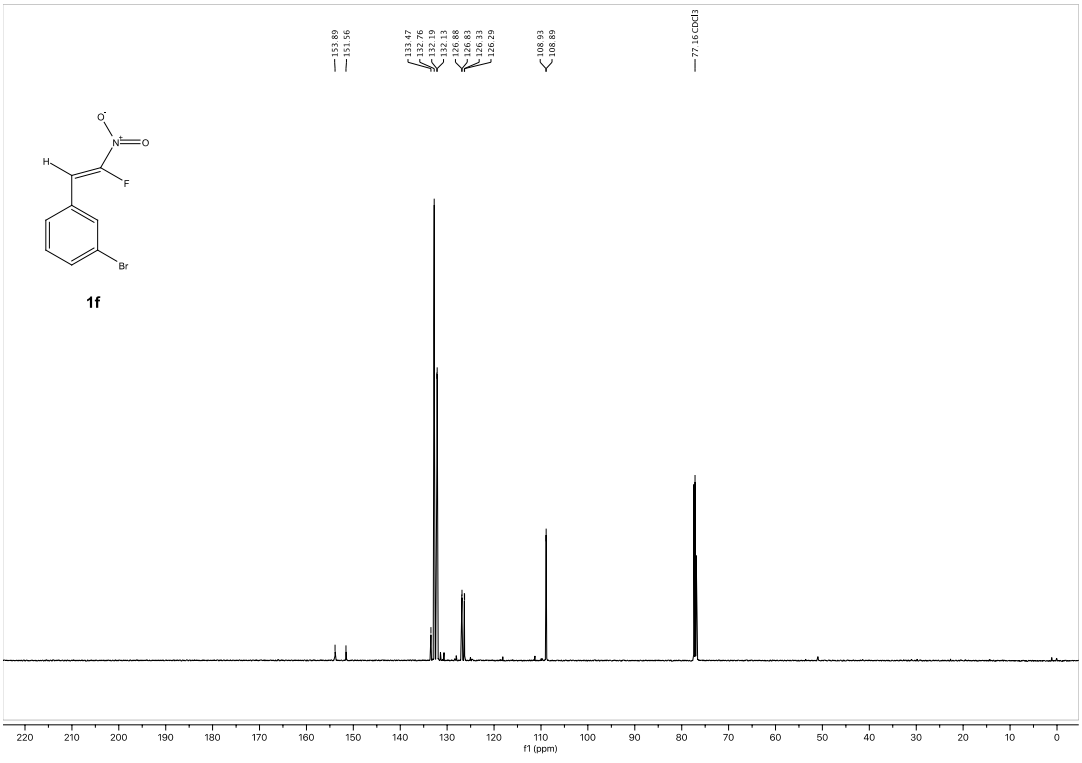
^{1}H NMR of **1f**



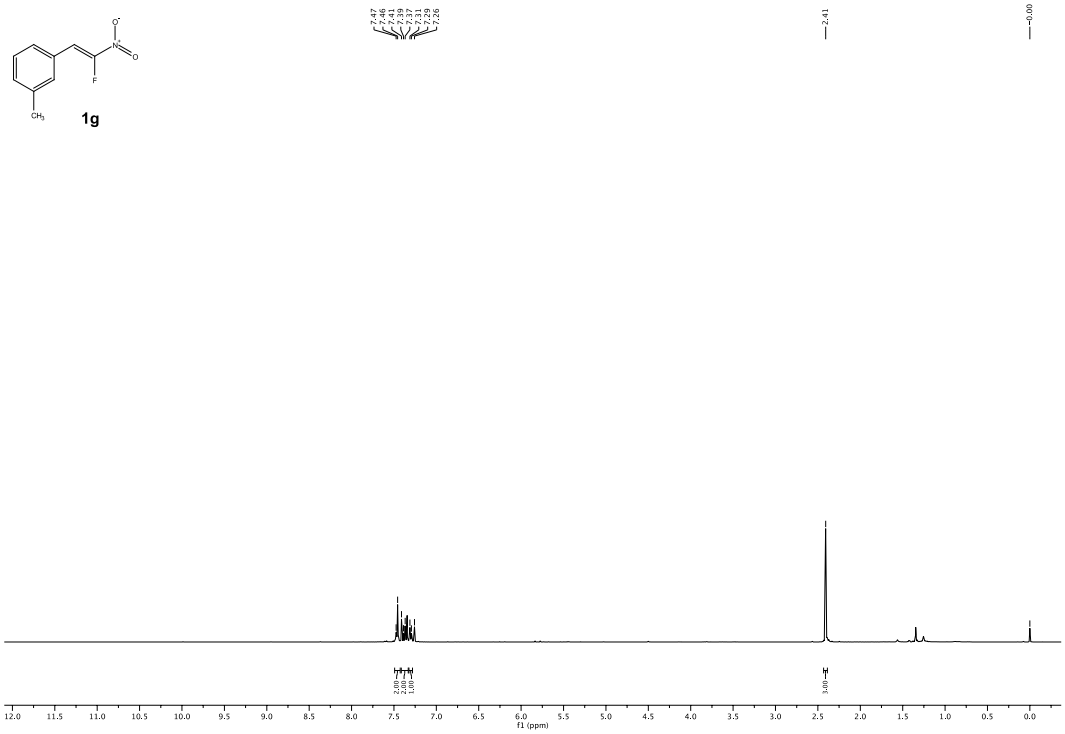
^{19}F NMR of **1f**



^{13}C NMR of **1f**

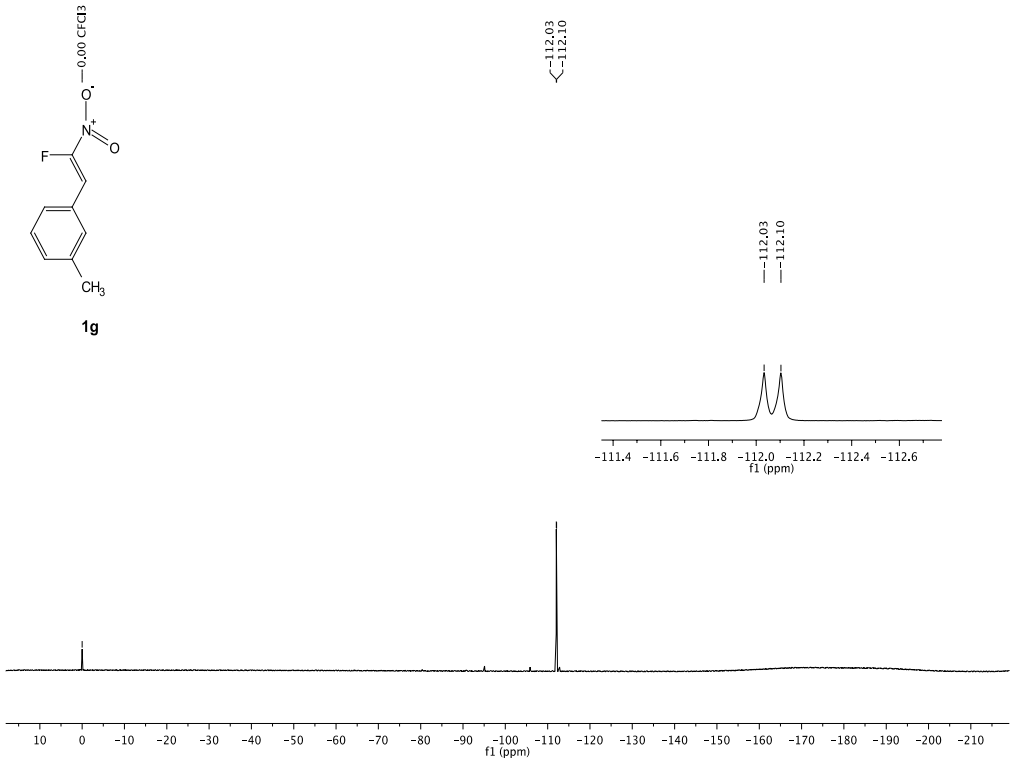


^{1}H NMR of **1g**



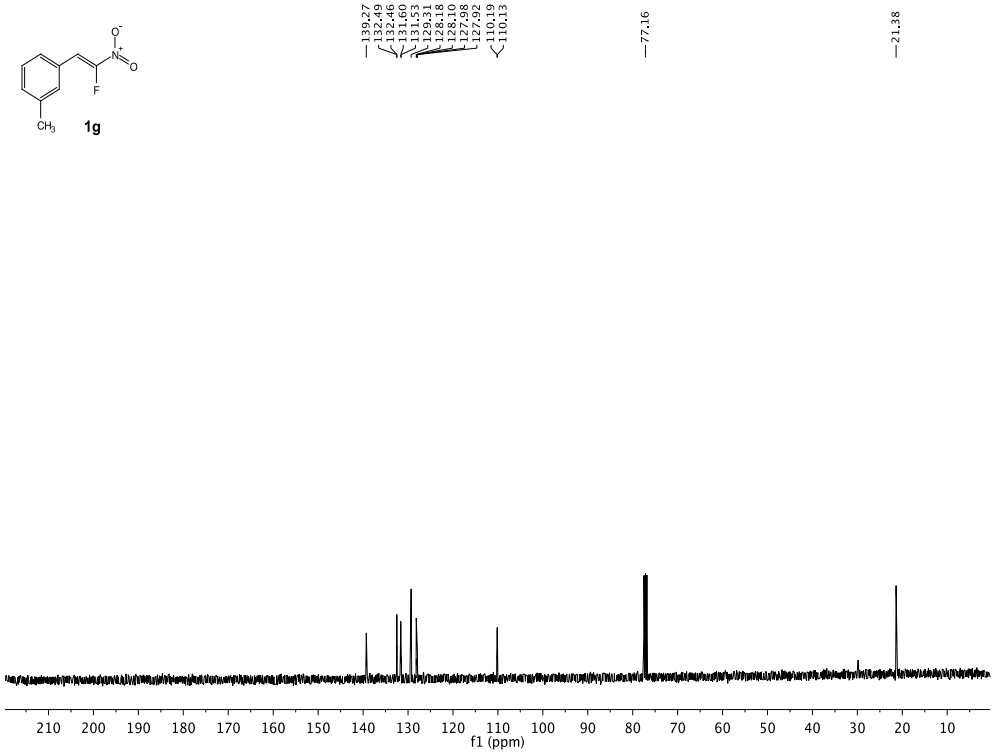
1g

^{19}F NMR of **1g**



1g

^{13}C NMR of **1g**



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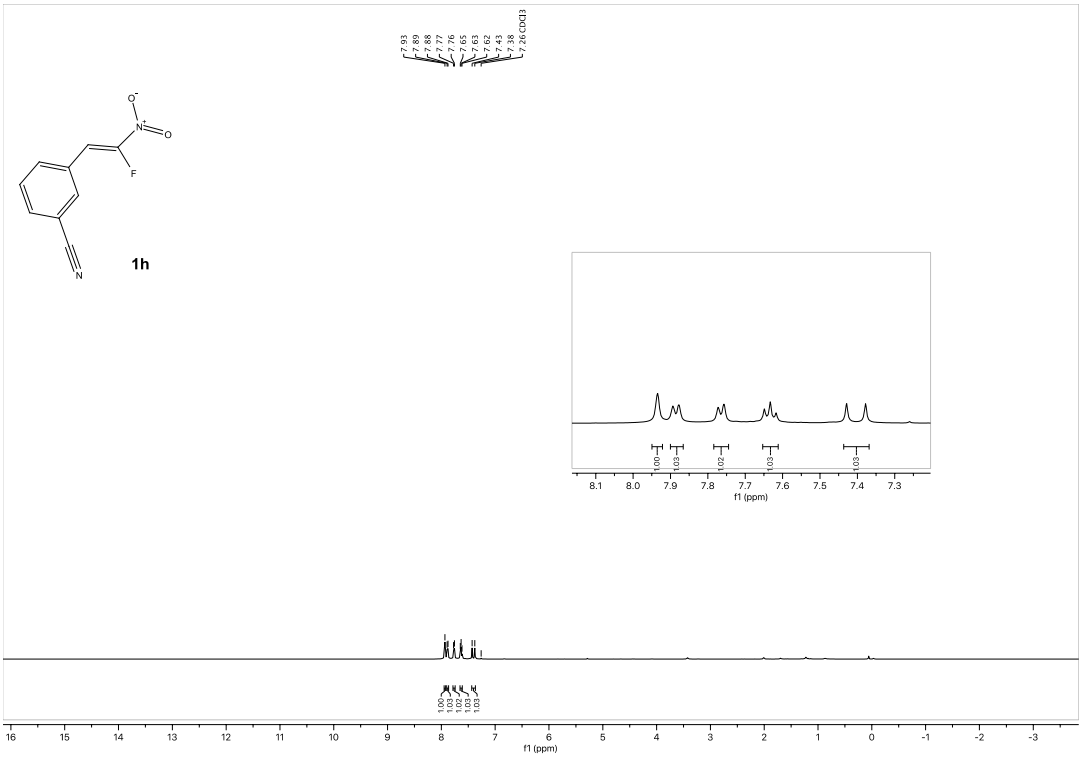
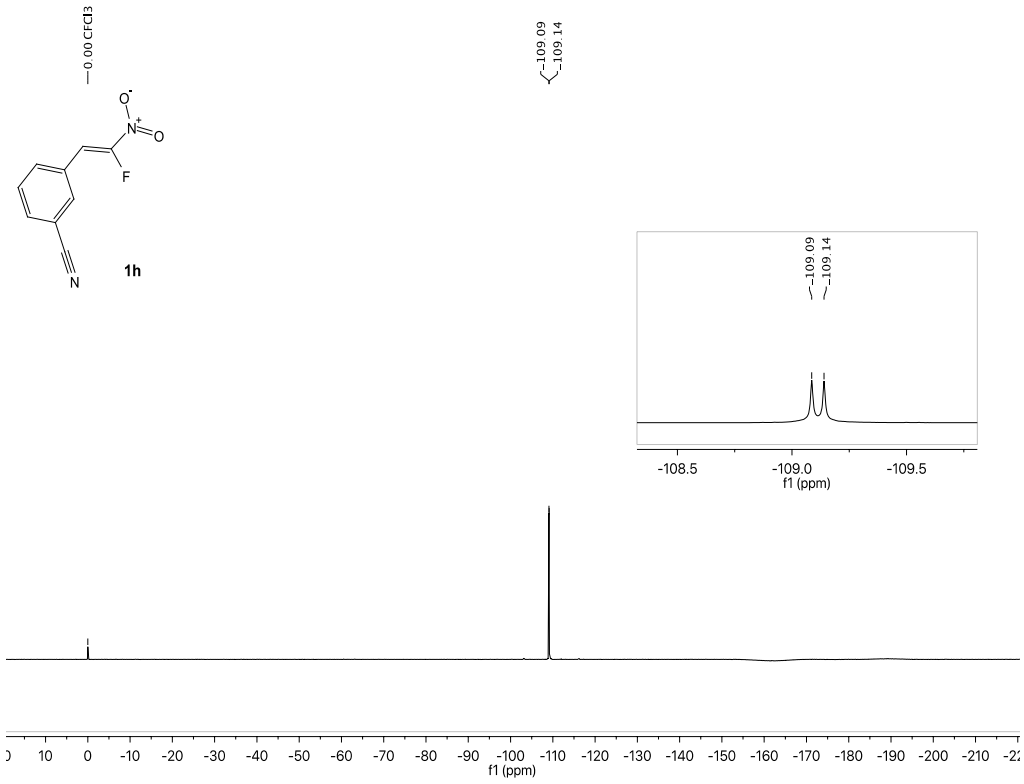


^{19}F NMR of **1h**



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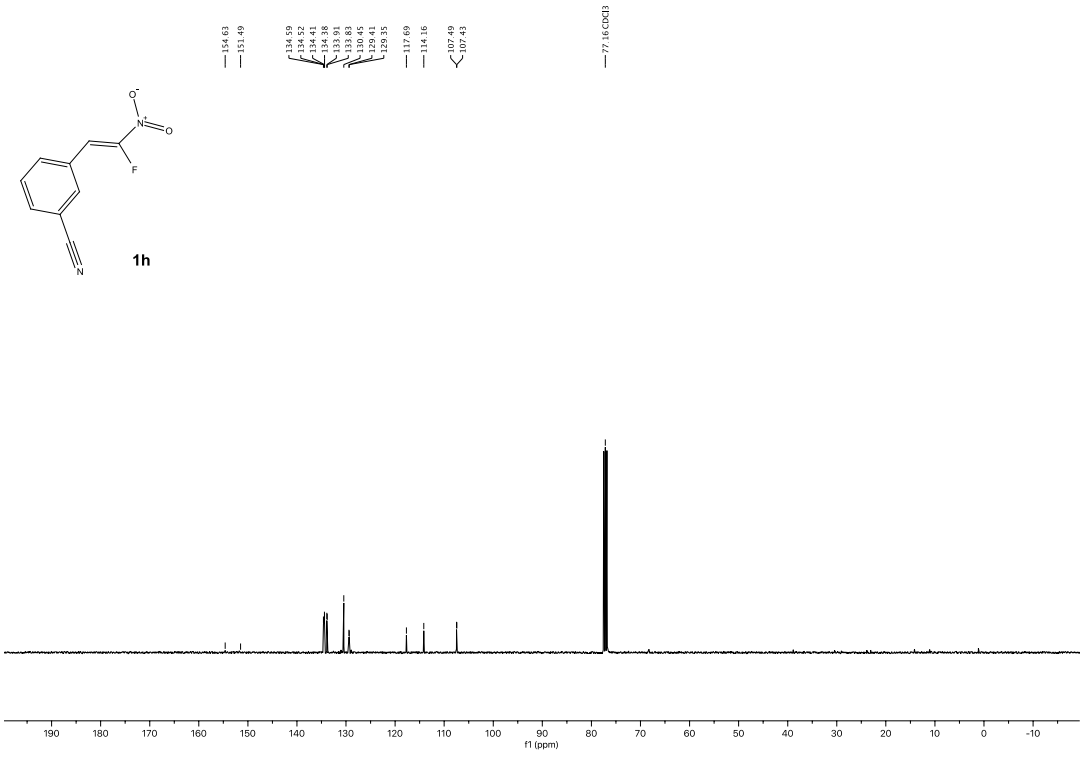
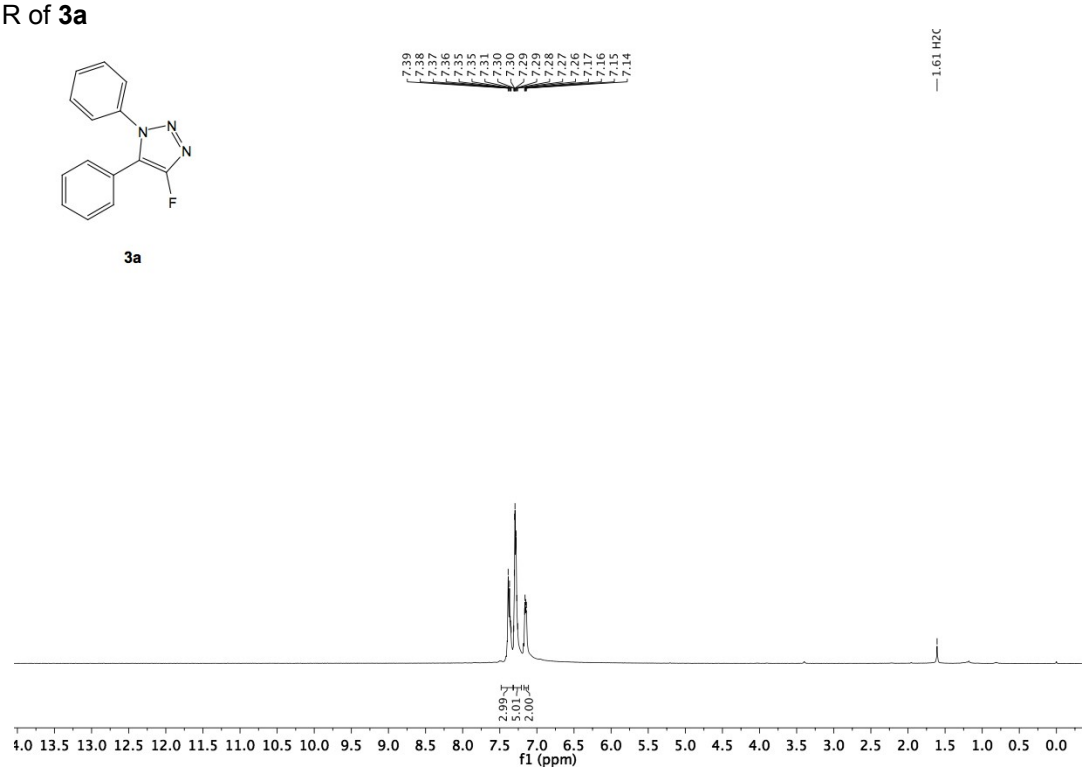
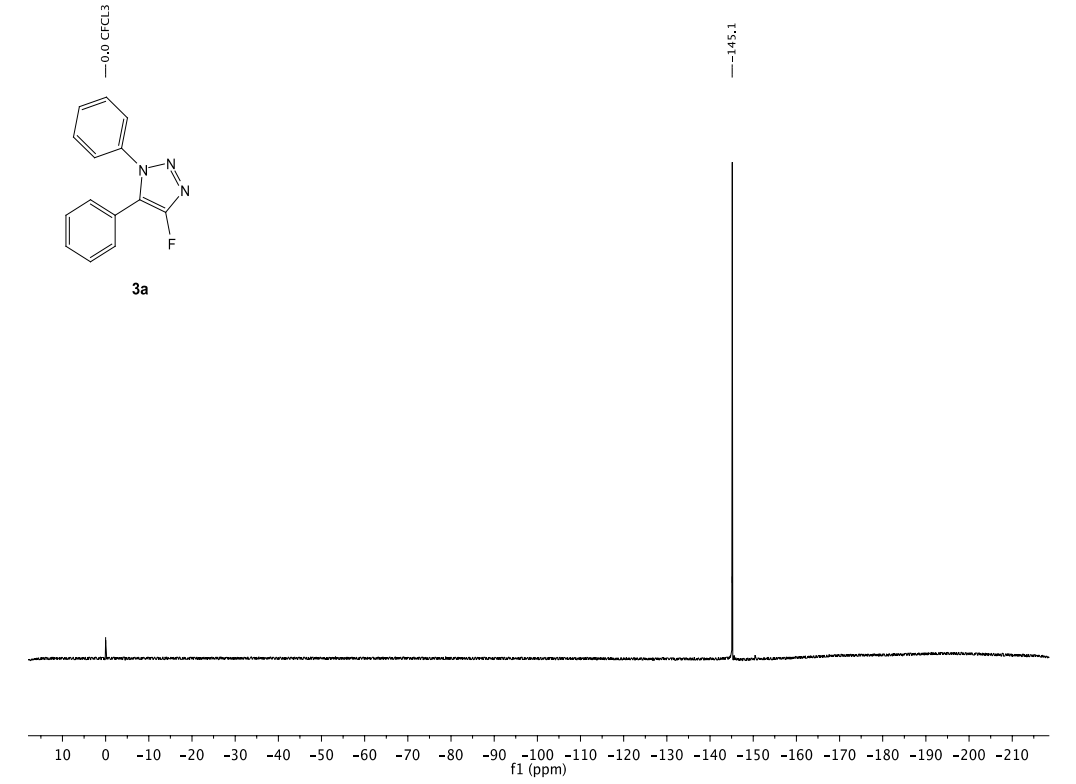


^{1}H NMR of **3a**



^{19}F NMR of **3a**



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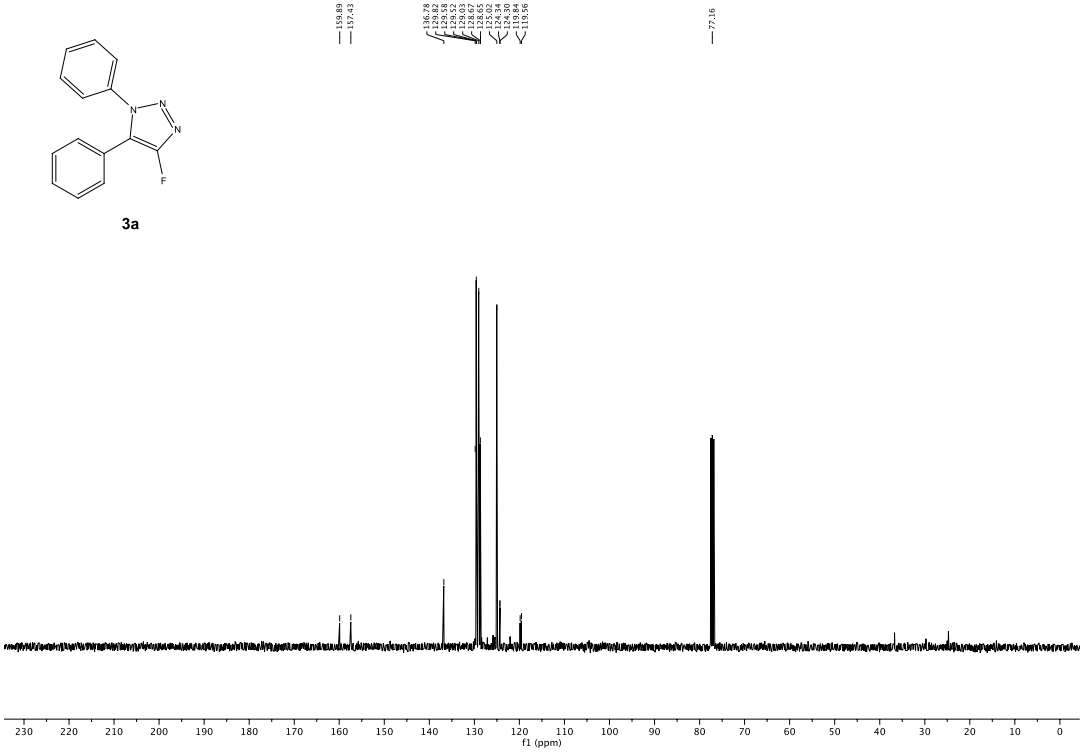

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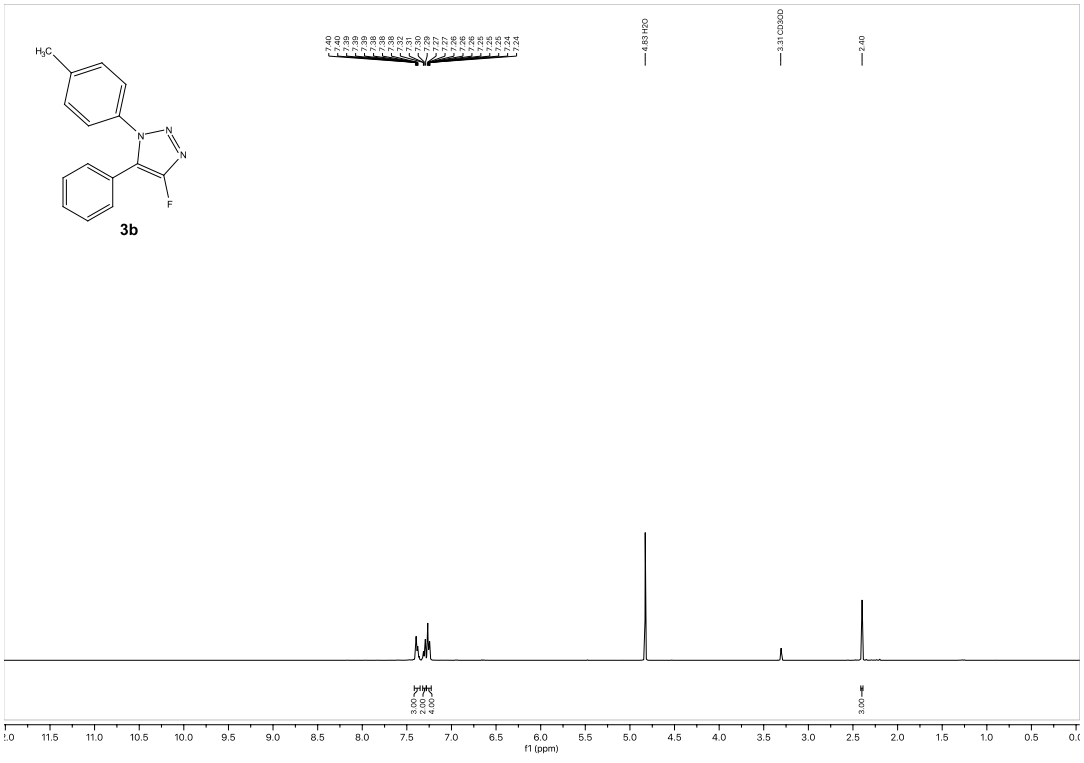

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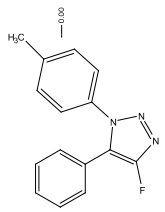
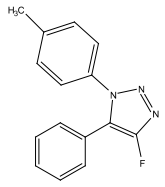
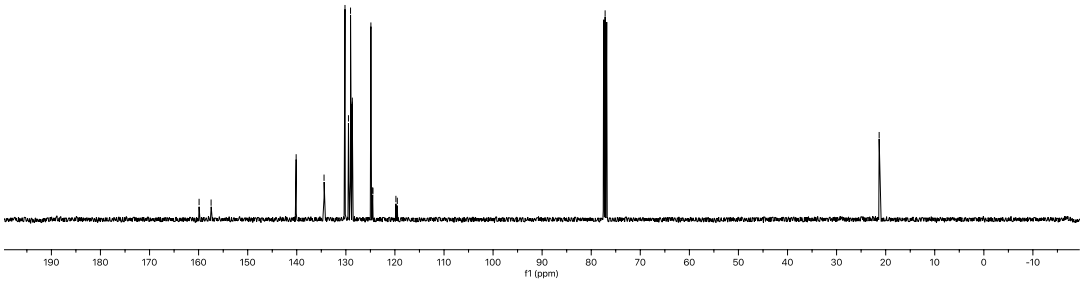


3b

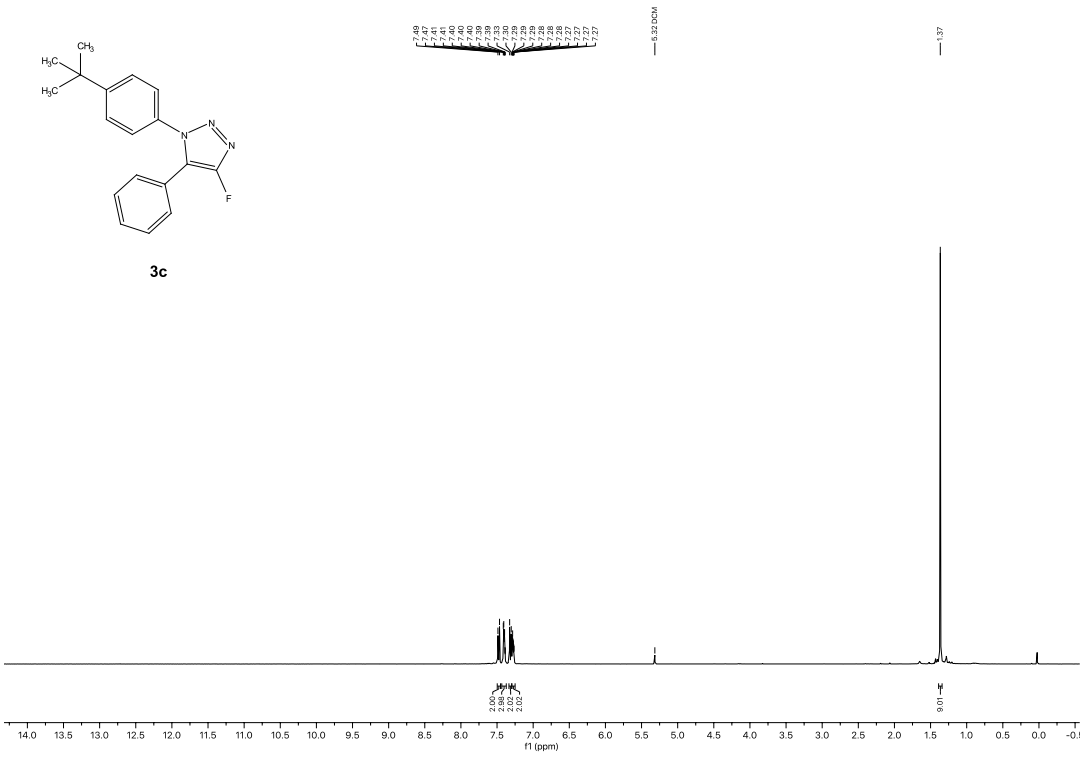
^{13}C NMR of **3b**



3b



^{1}H NMR of **3c**



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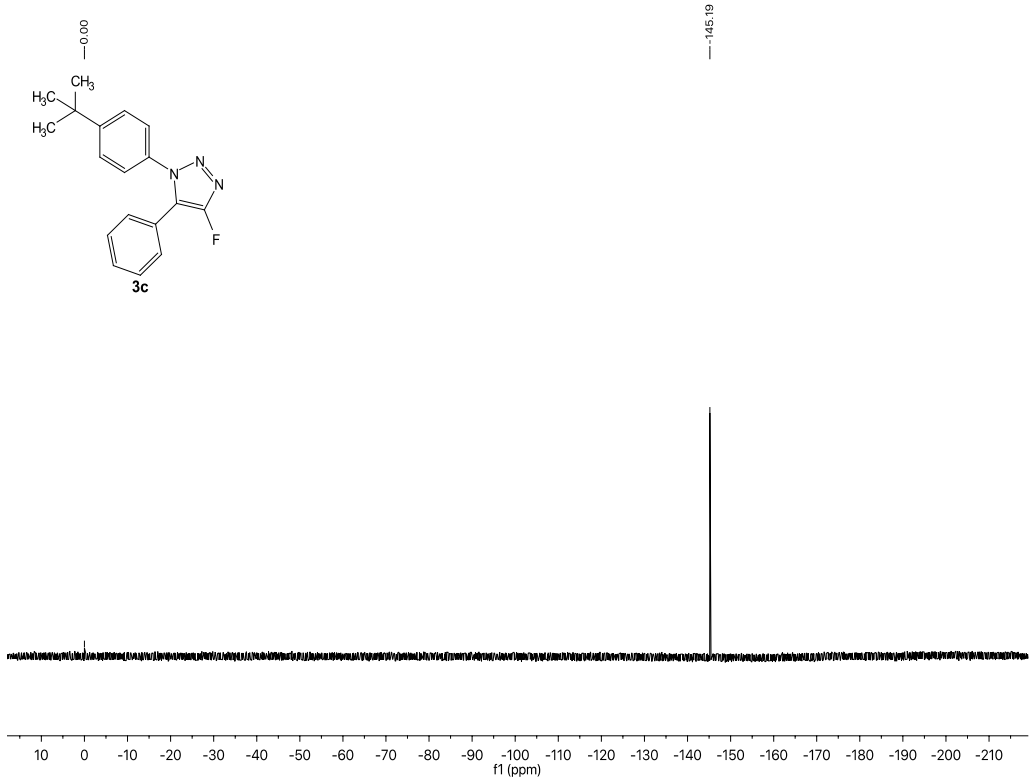

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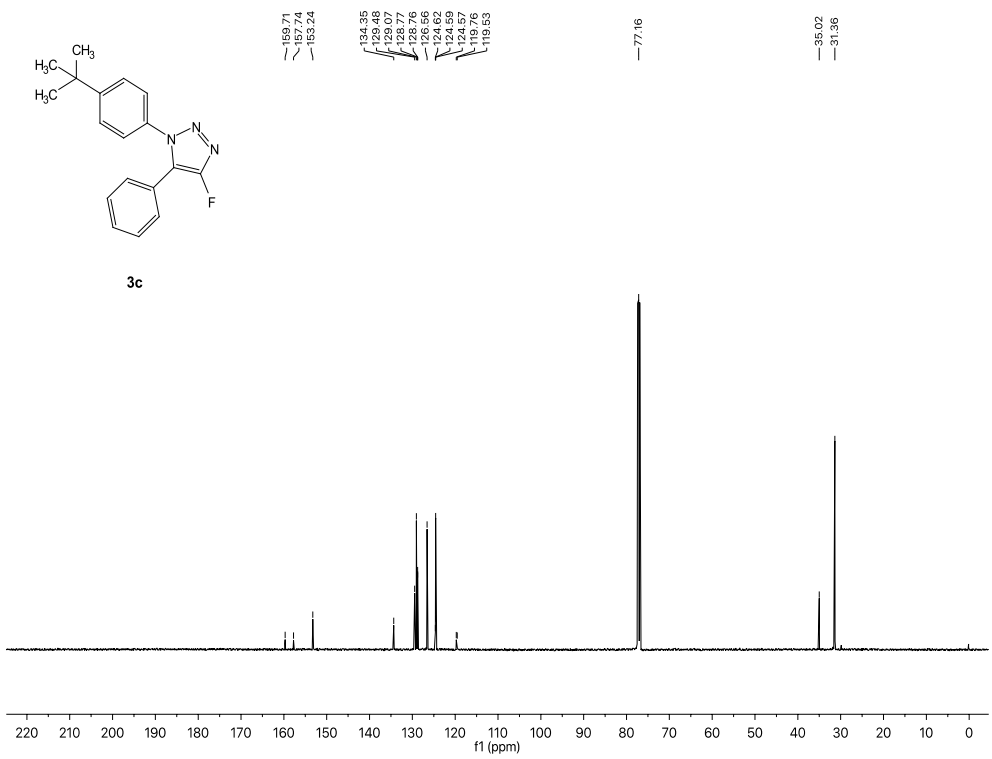
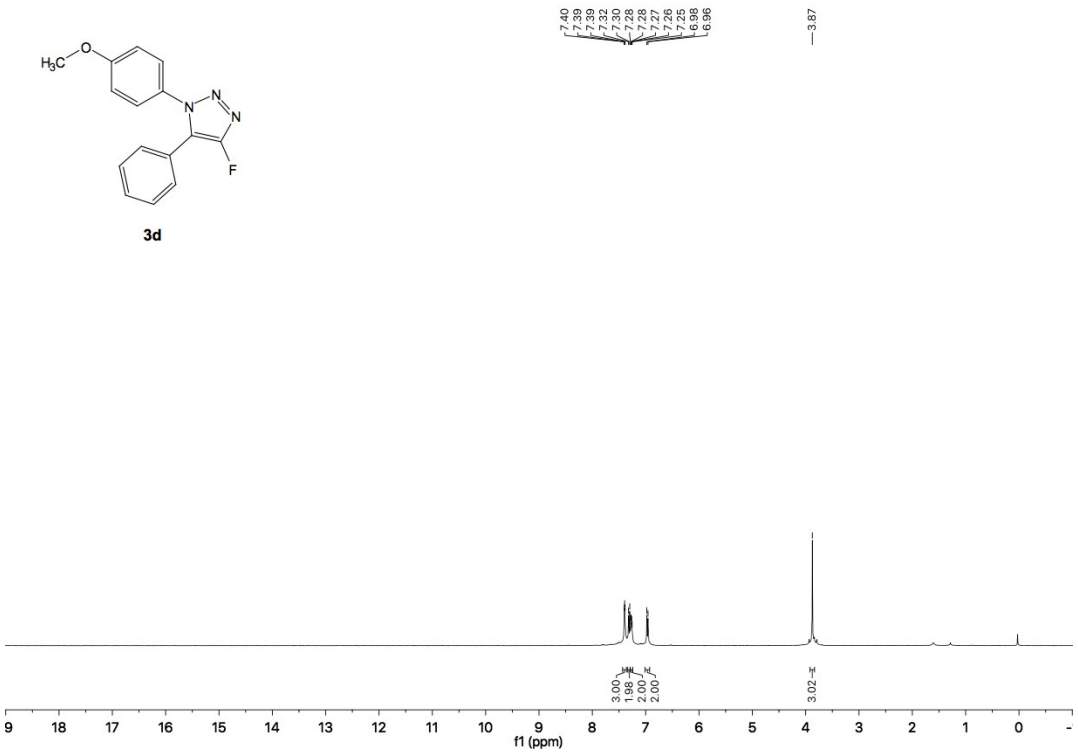


^{1}H NMR of **3d**



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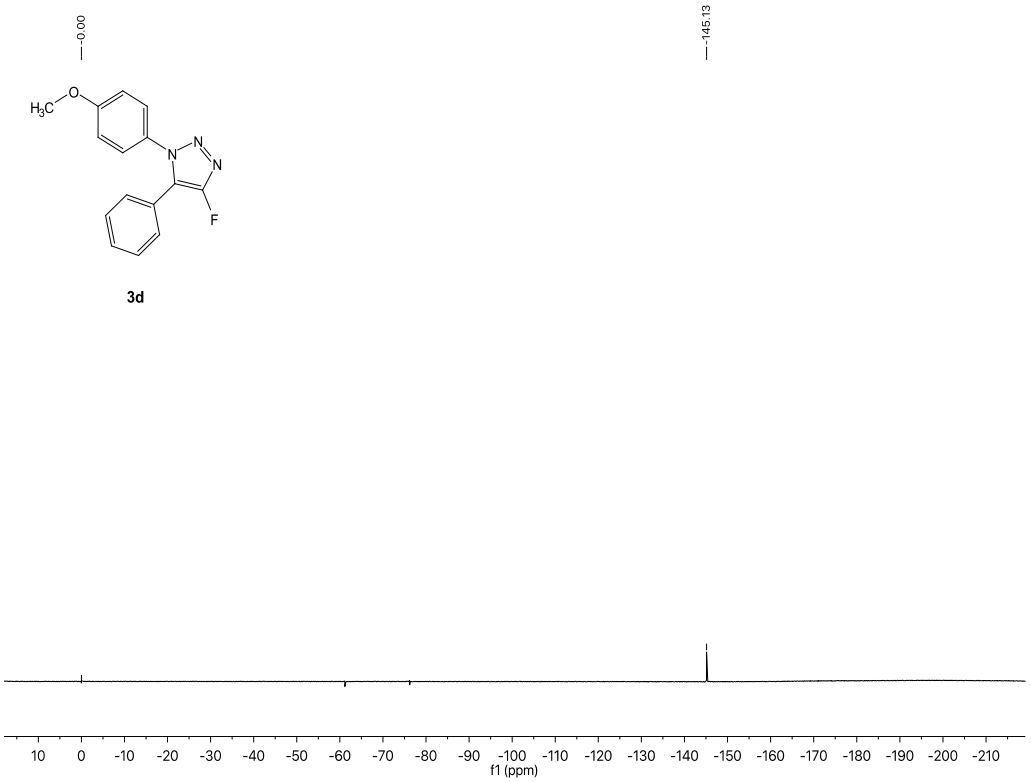

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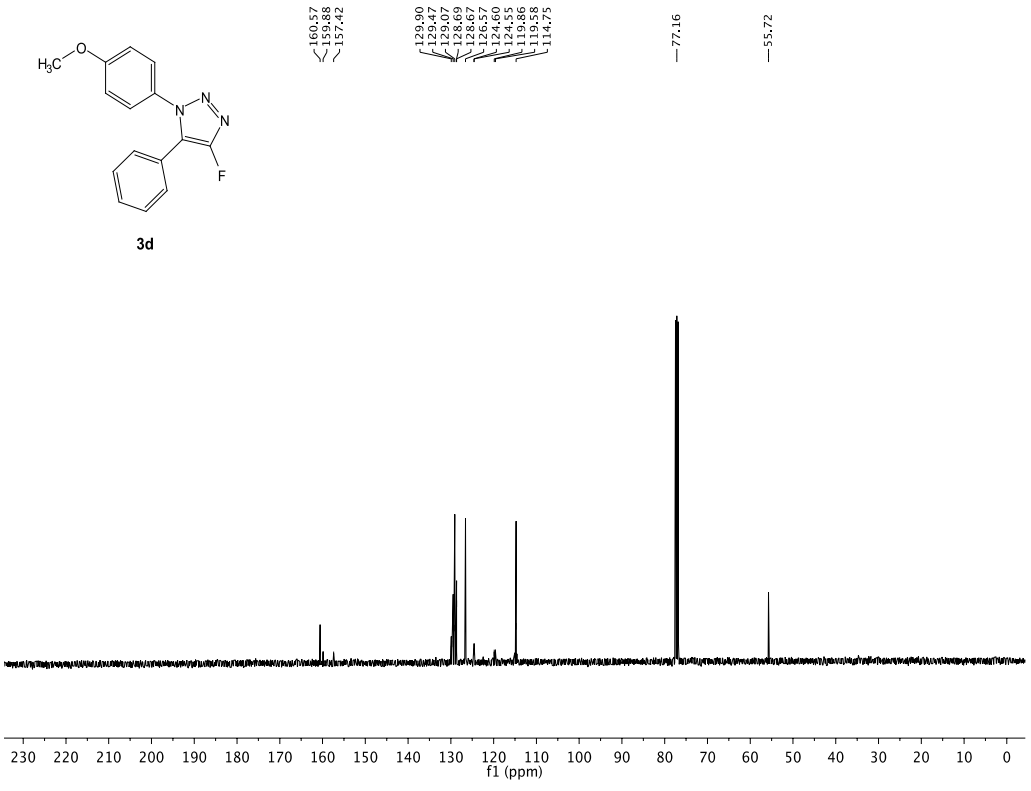
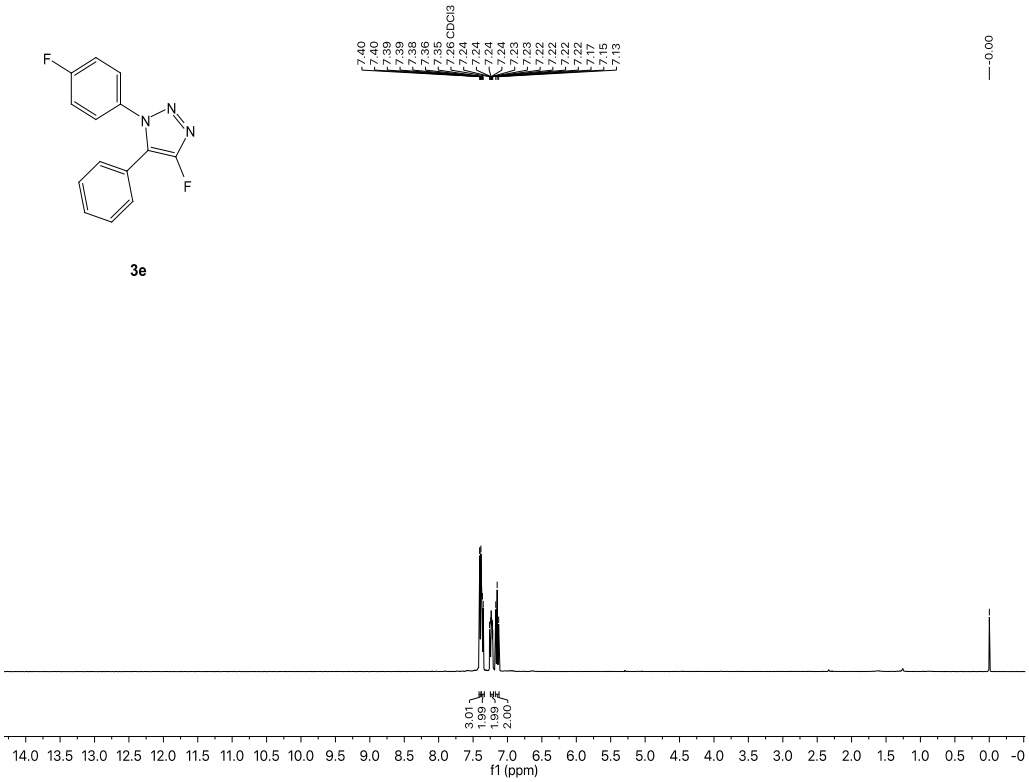


^{1}H NMR of **3e**



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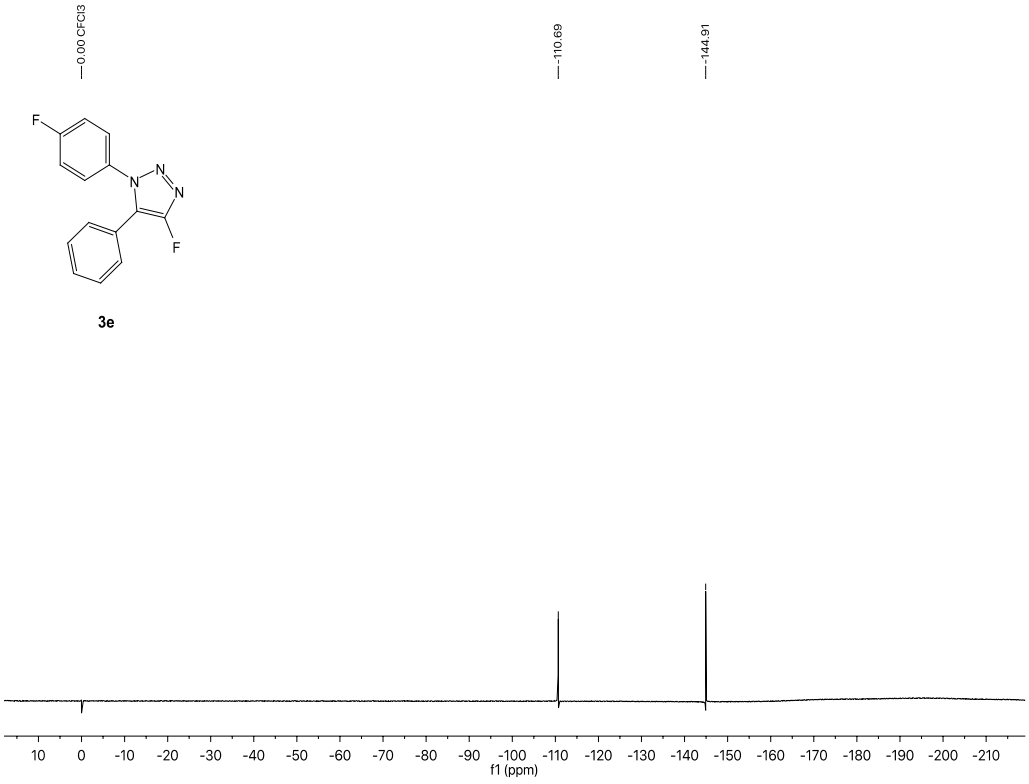

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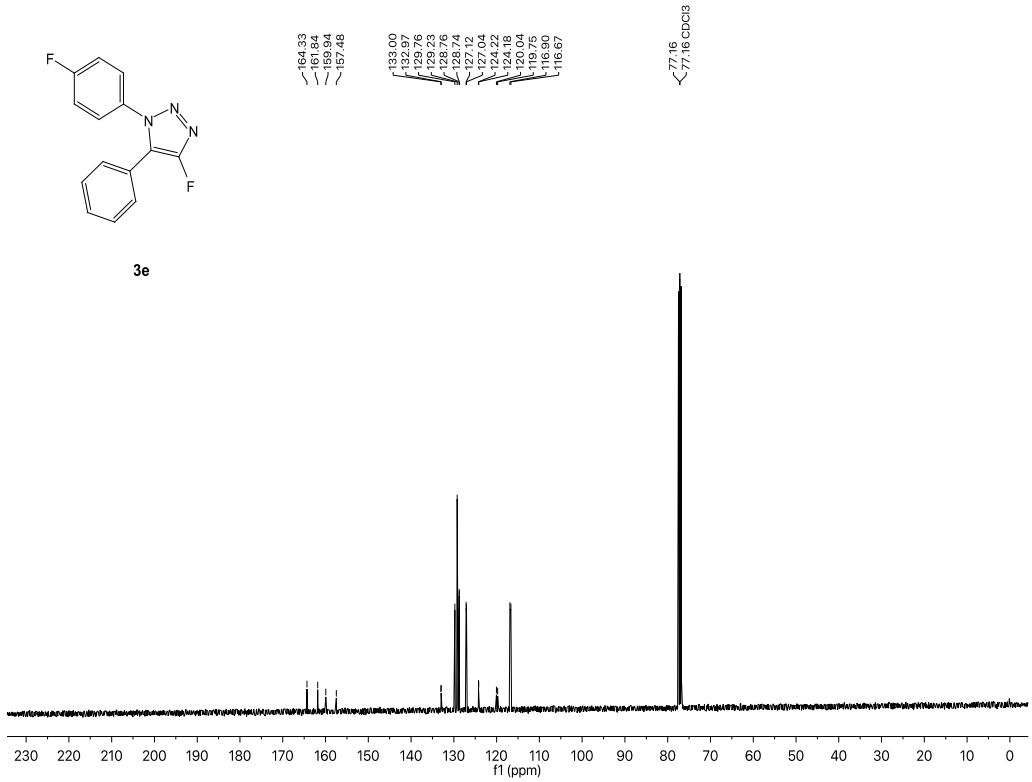

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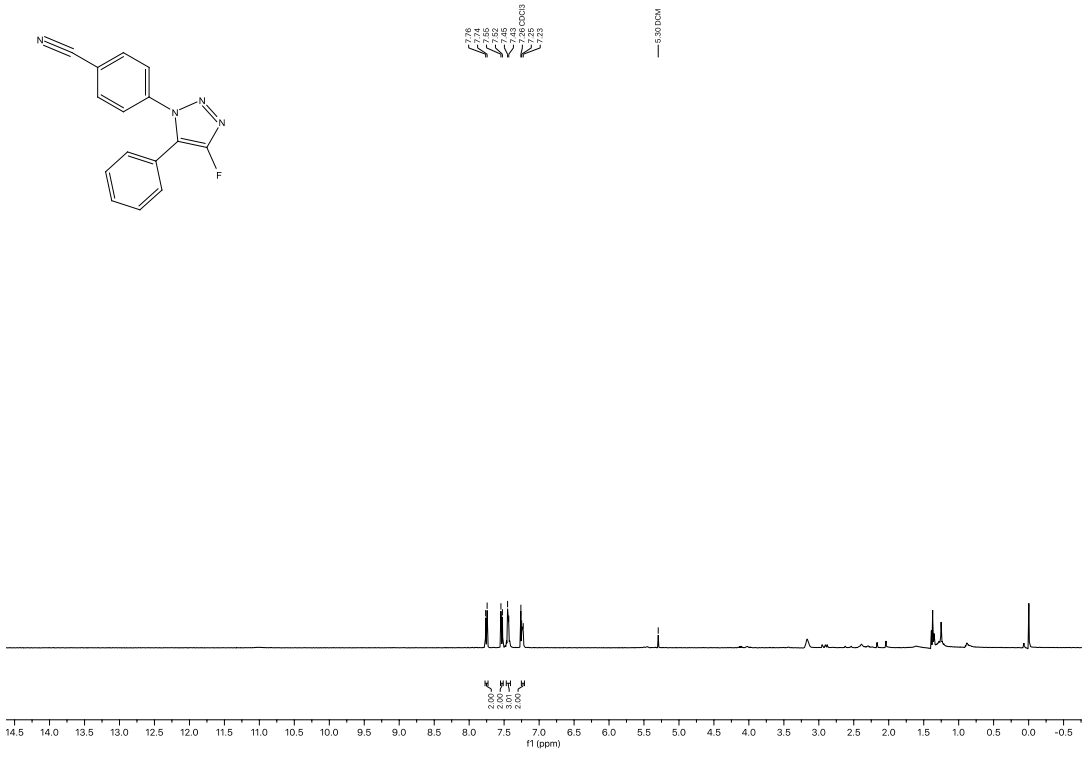
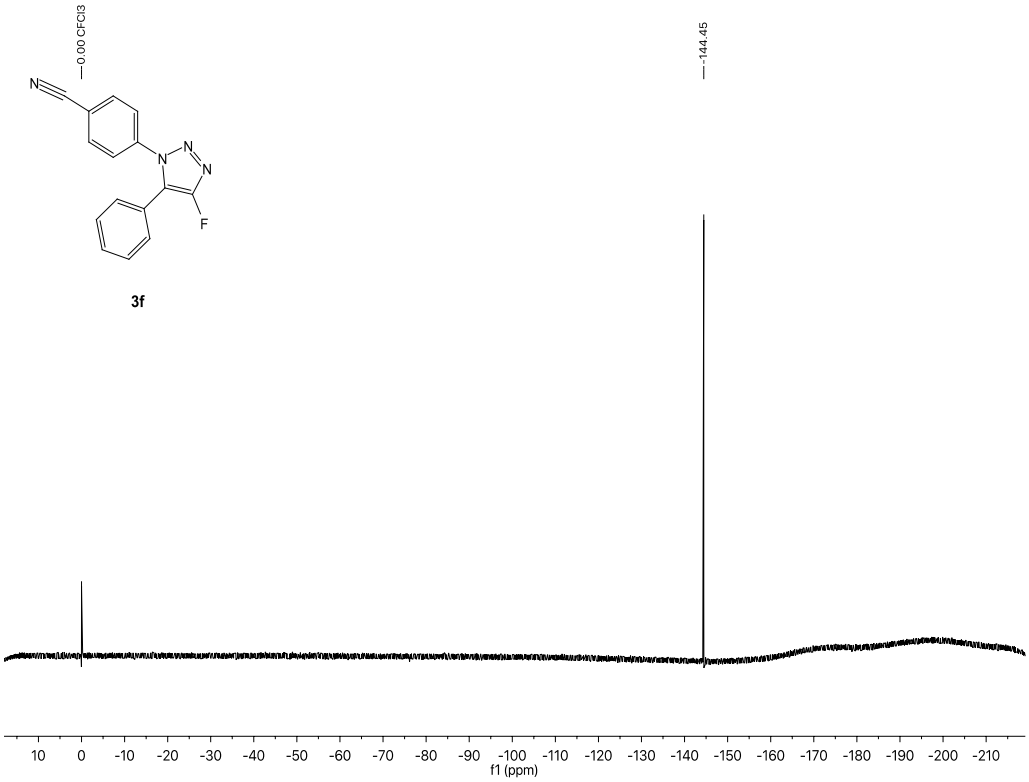


^{19}F NMR of **3f**



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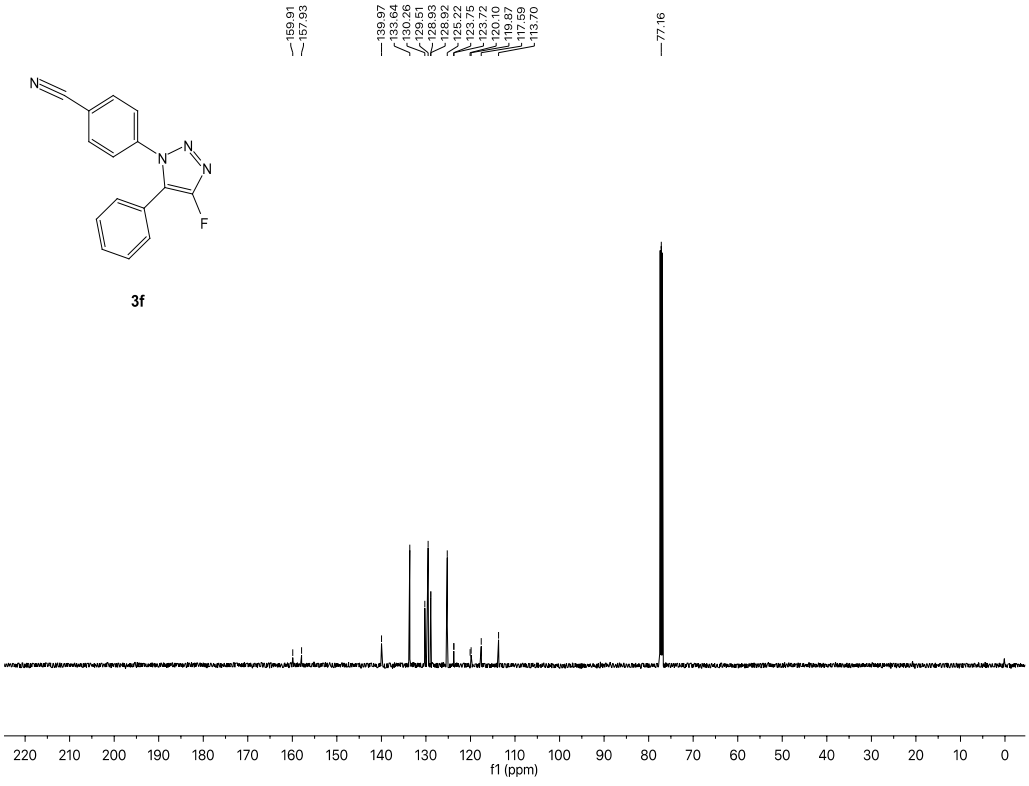
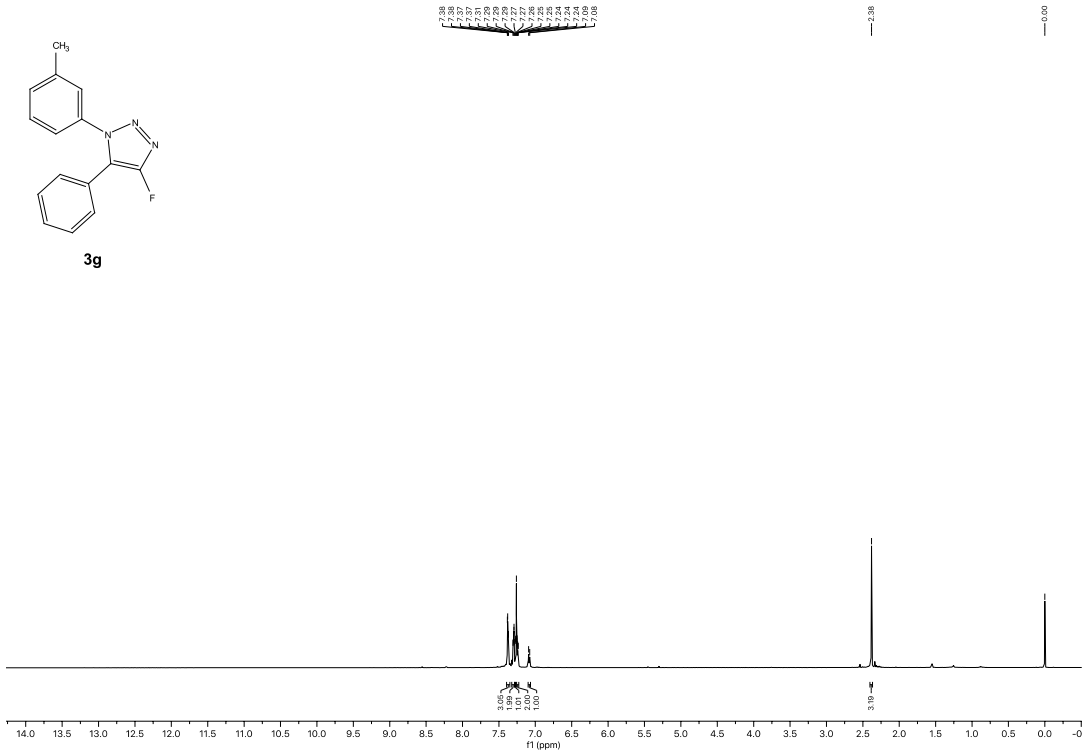
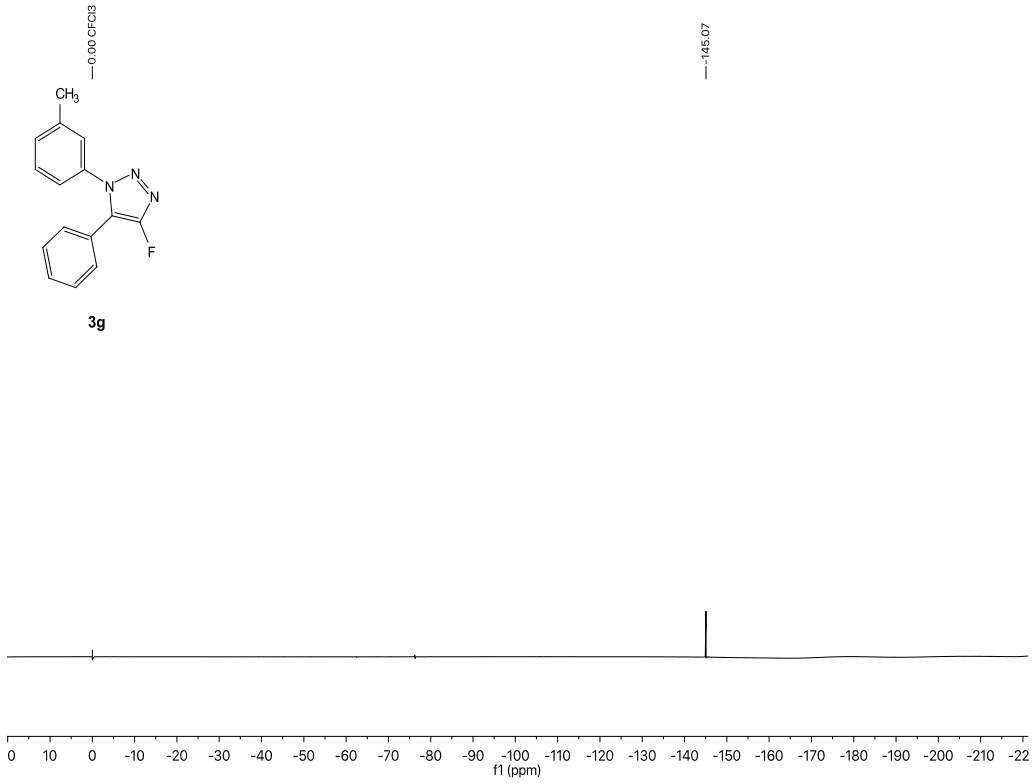


^{1}H NMR of **3g**



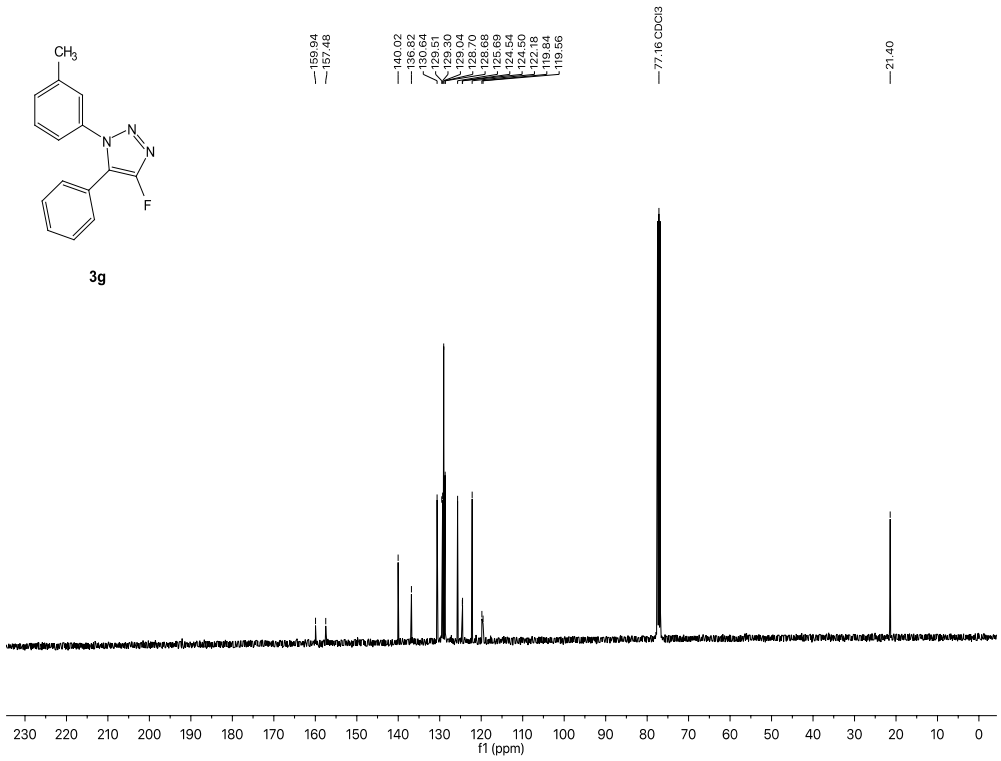
3g

^{19}F NMR of **3g**



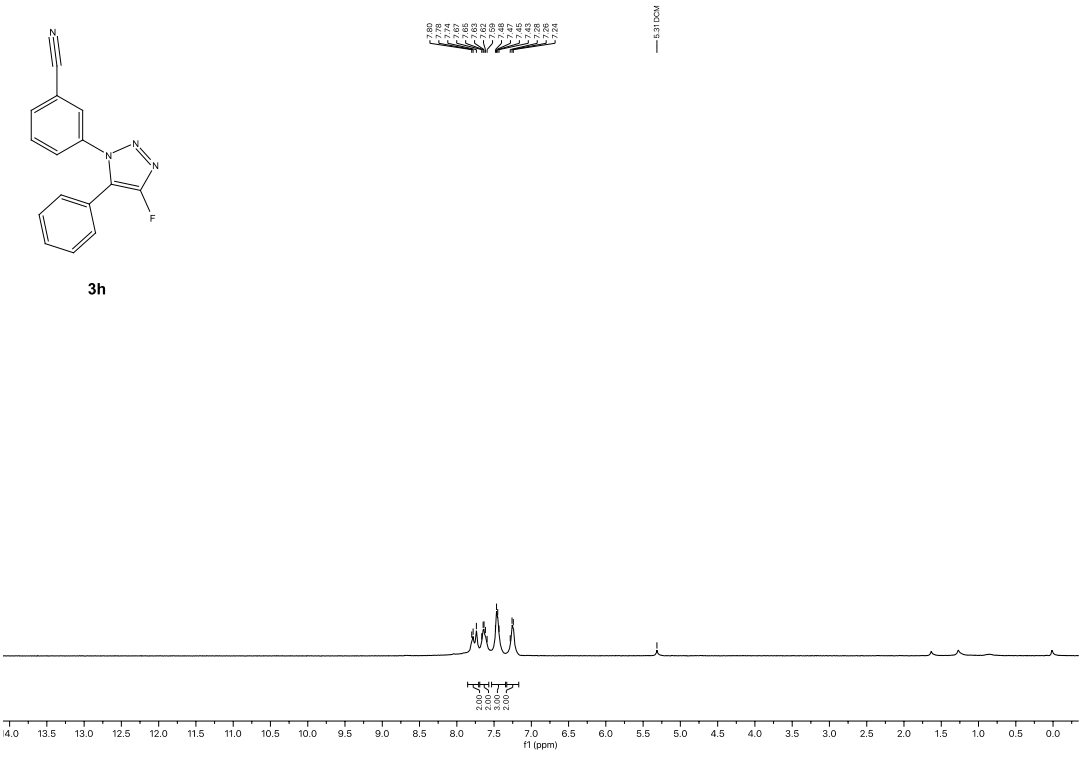
3g

^{13}C NMR of **3g**



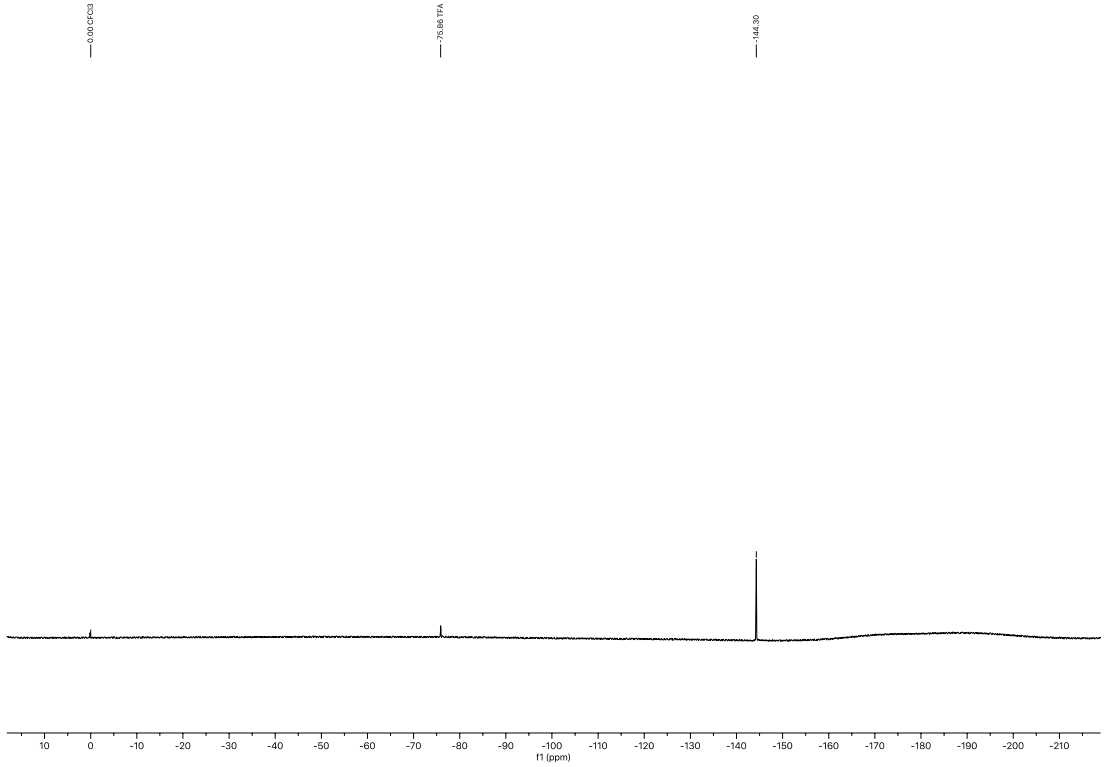
3g

^{1}H NMR of **3h**



3h

^{19}F NMR of **3h**



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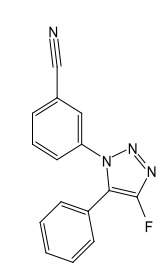
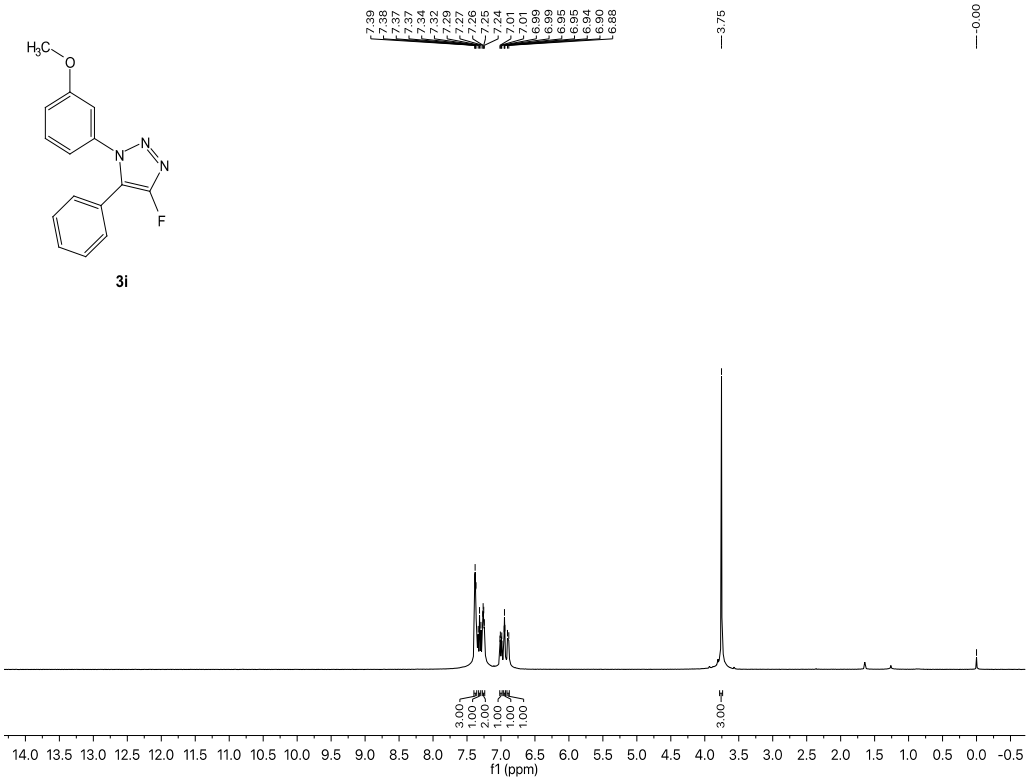


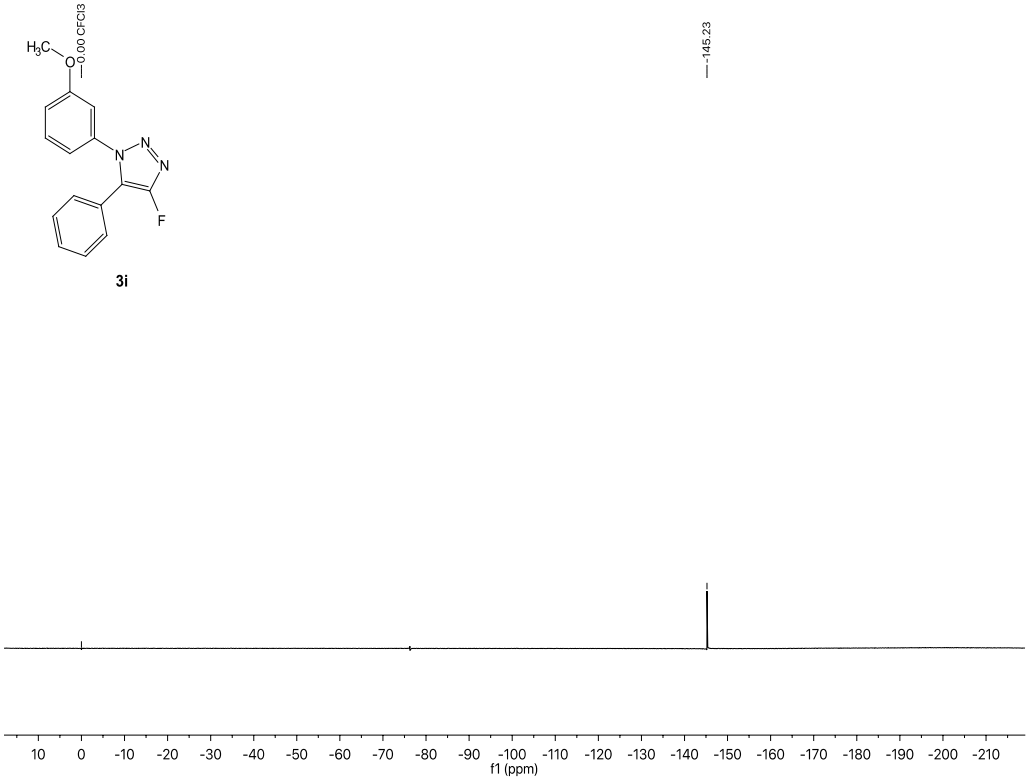
3h

^{1}H NMR of **3i**



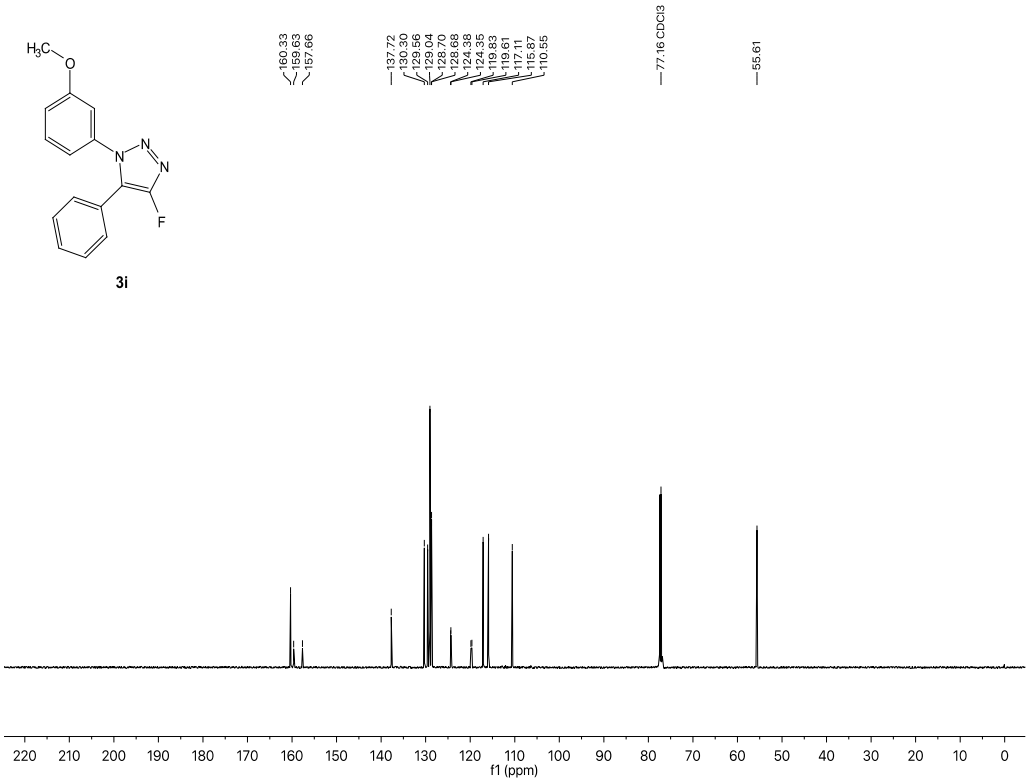
3i

^{19}F NMR of **3i**

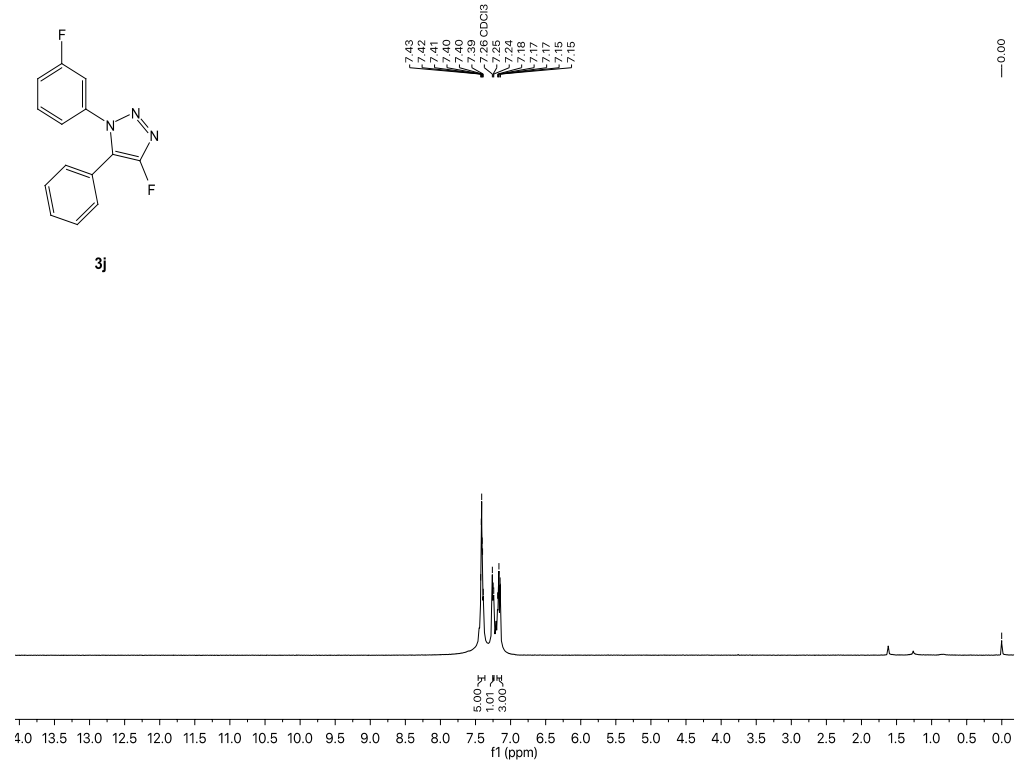


3i

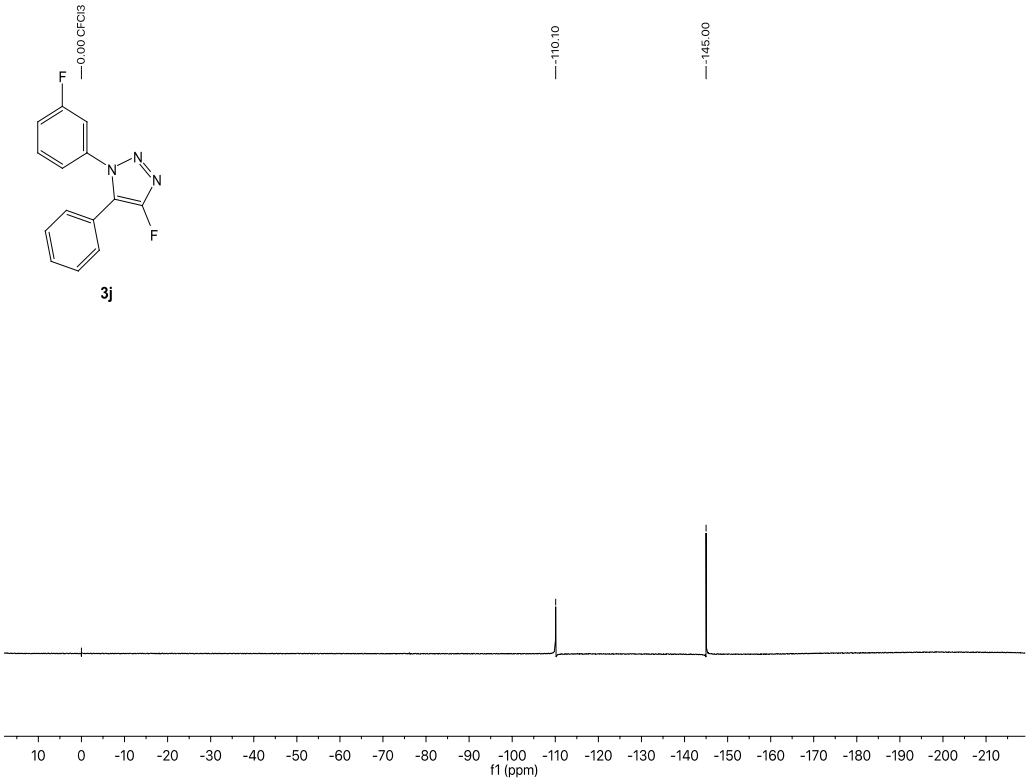
^{13}C NMR of **3i**



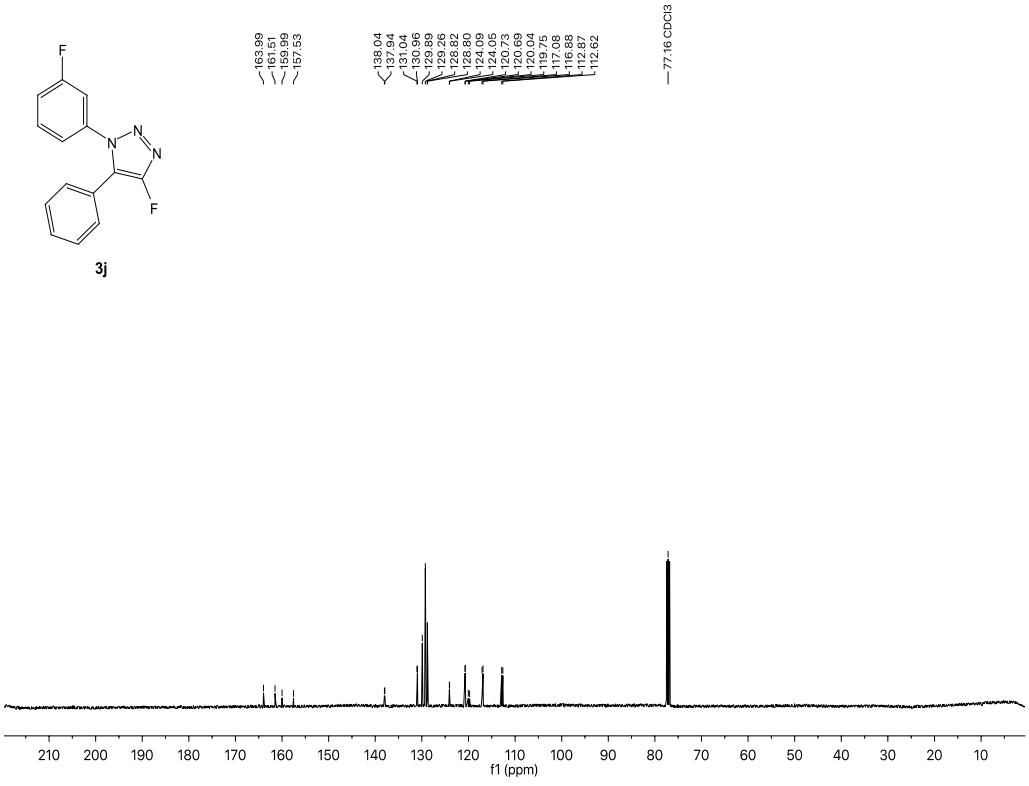
^{1}H NMR of **3j**



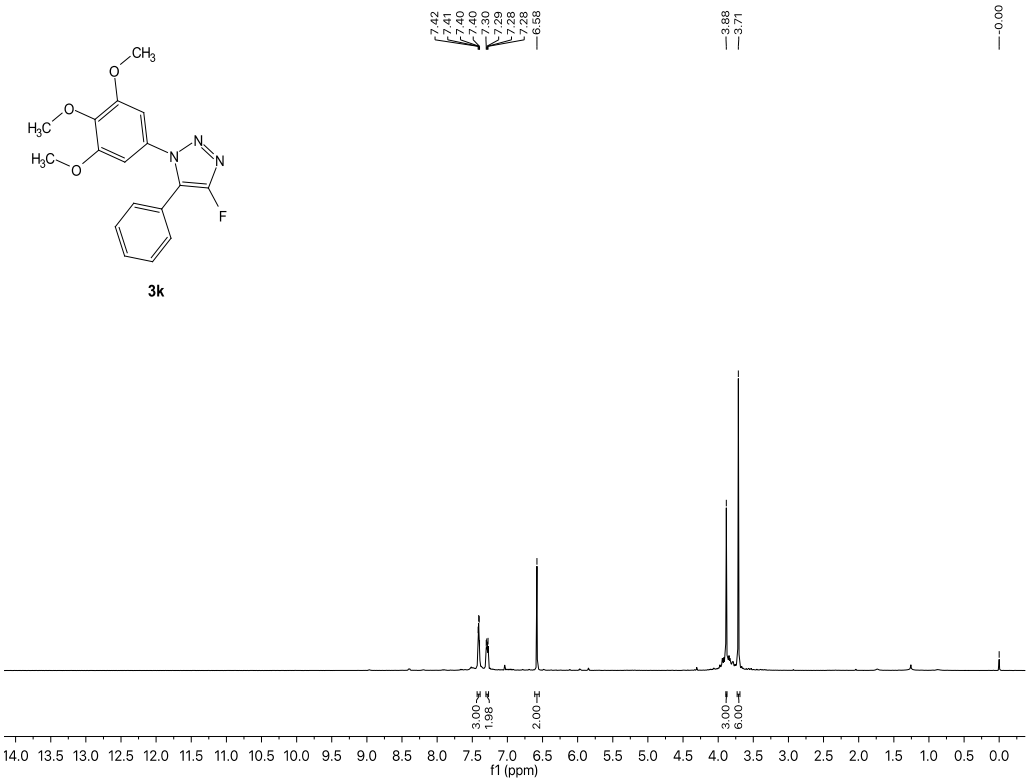
^{19}F NMR of **3j**



^{13}C NMR of **3j**

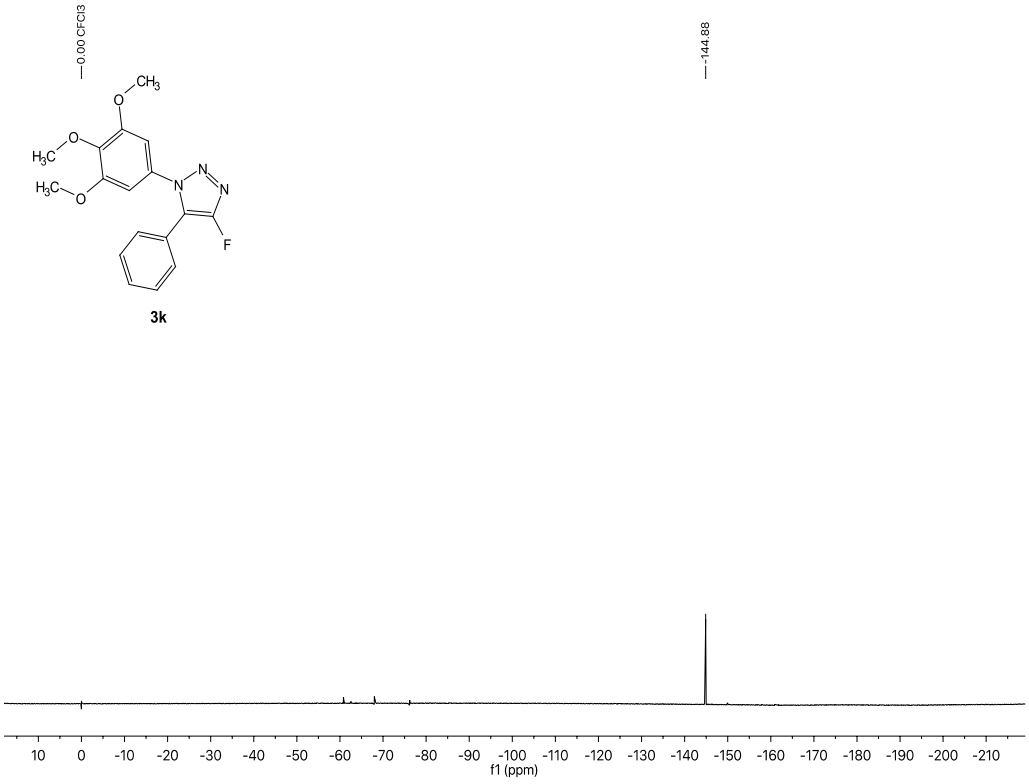


^{1}H NMR of **3k**



3k

^{19}F NMR of **3k**



3k

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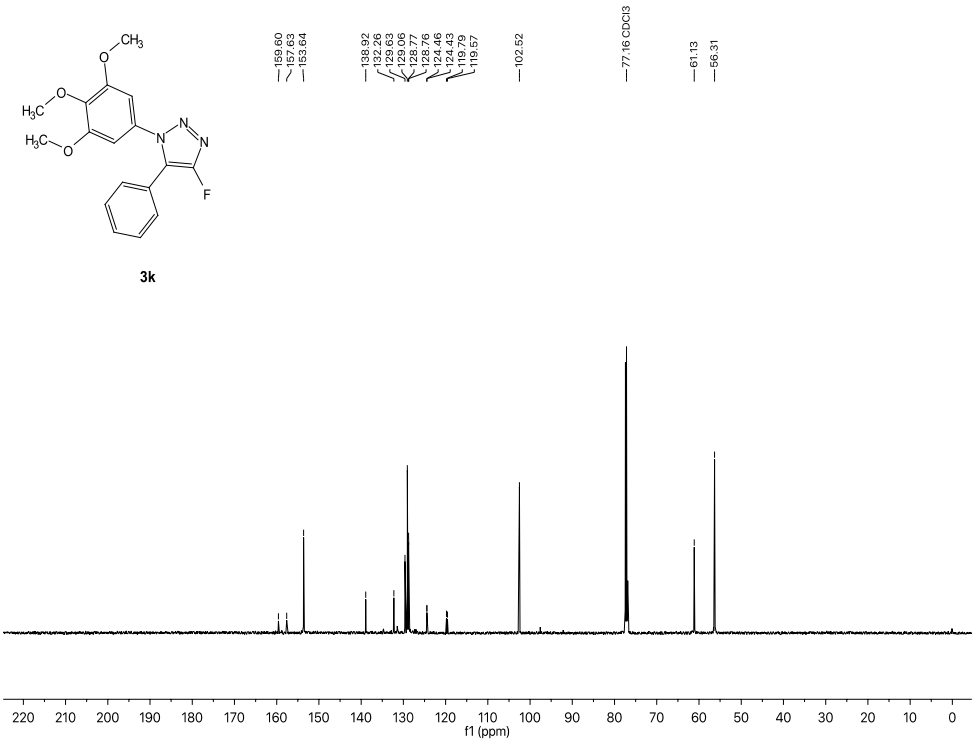

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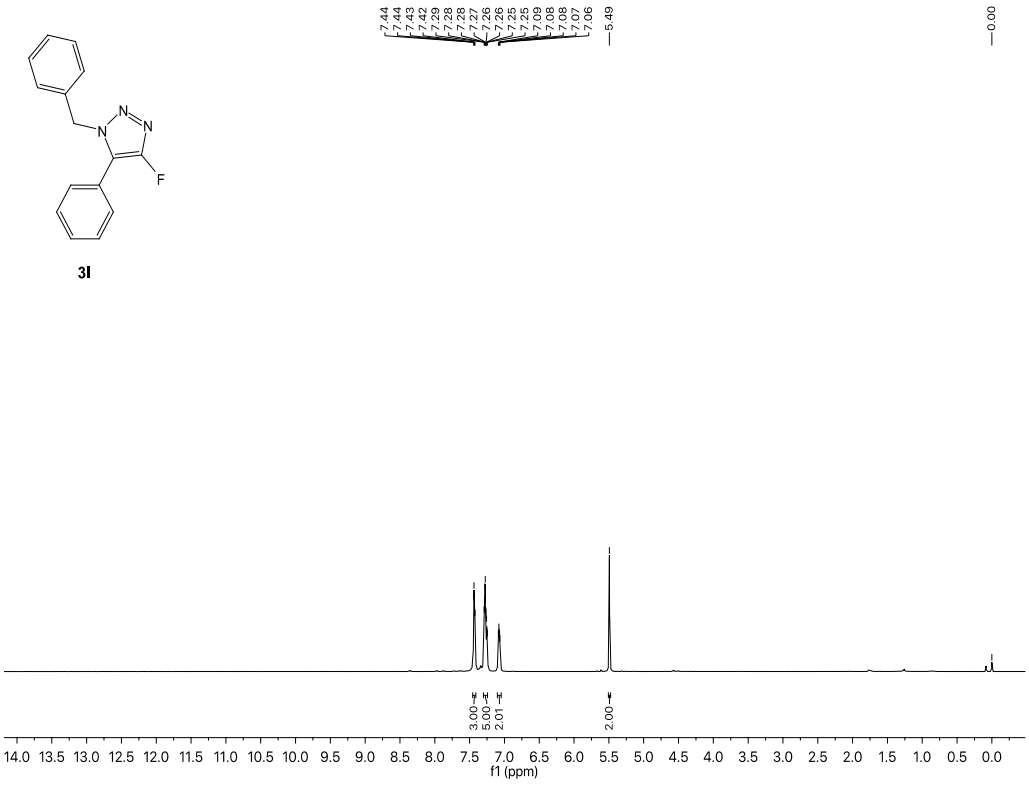

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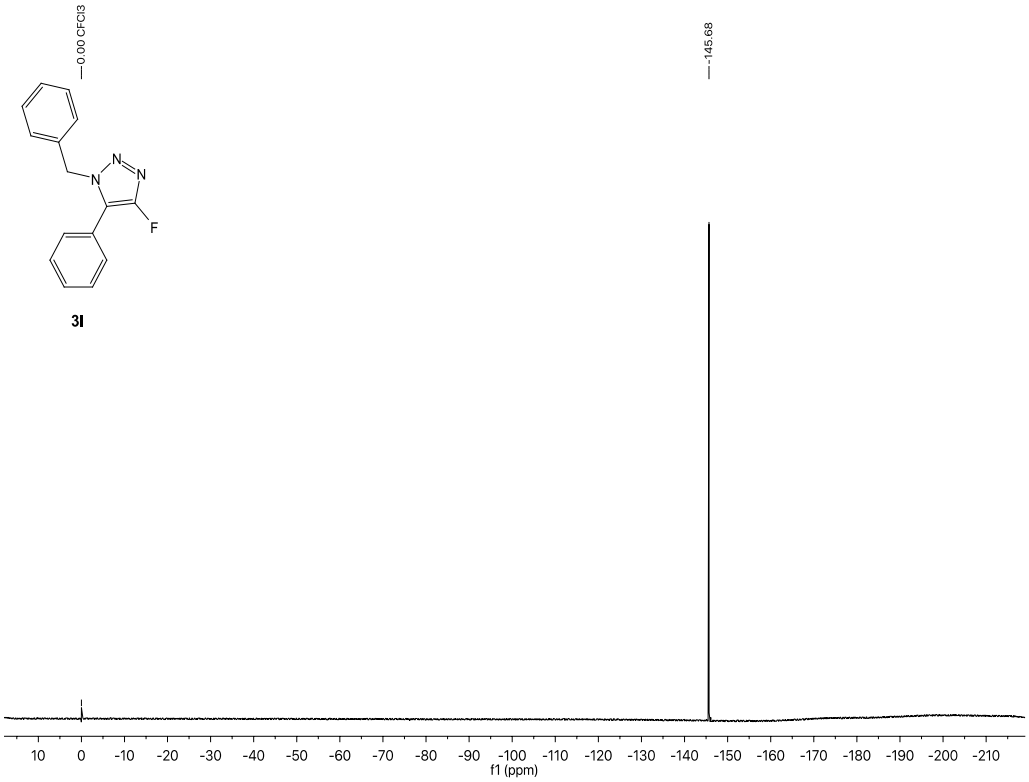

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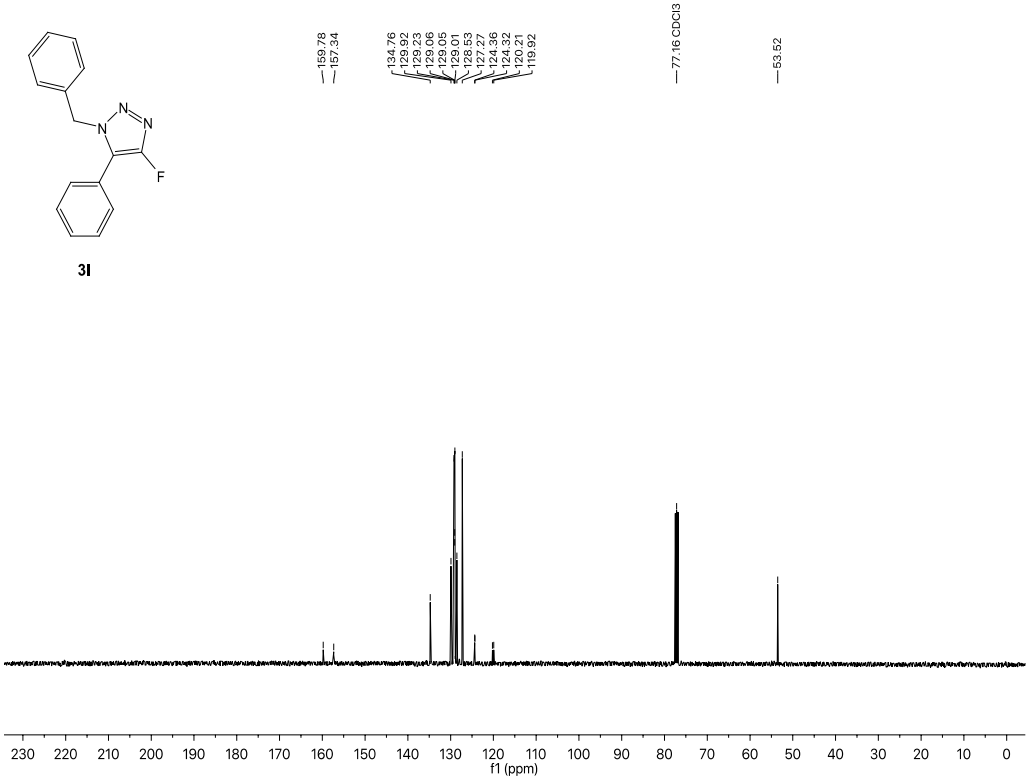

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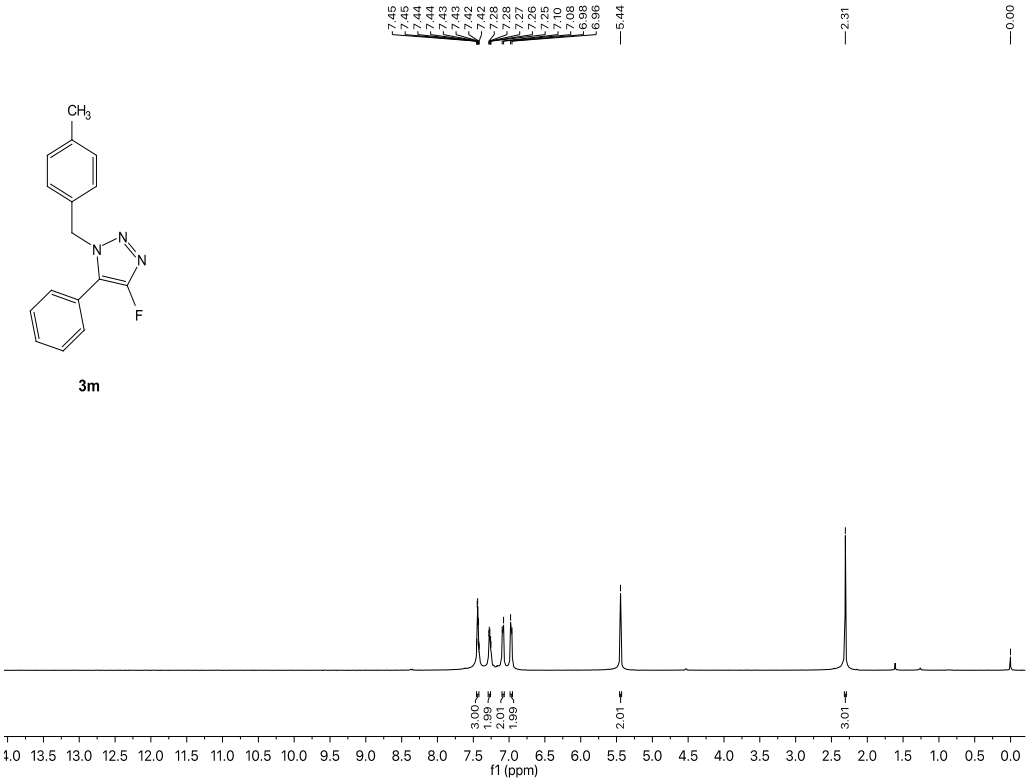
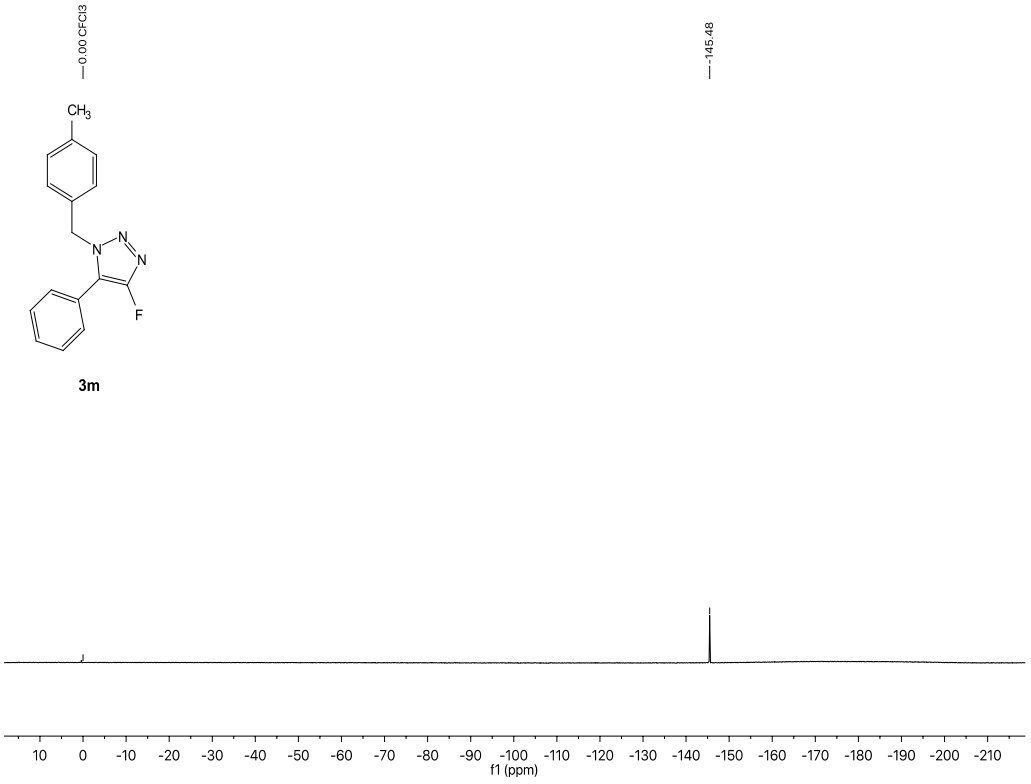


^{19}F NMR of **3m**



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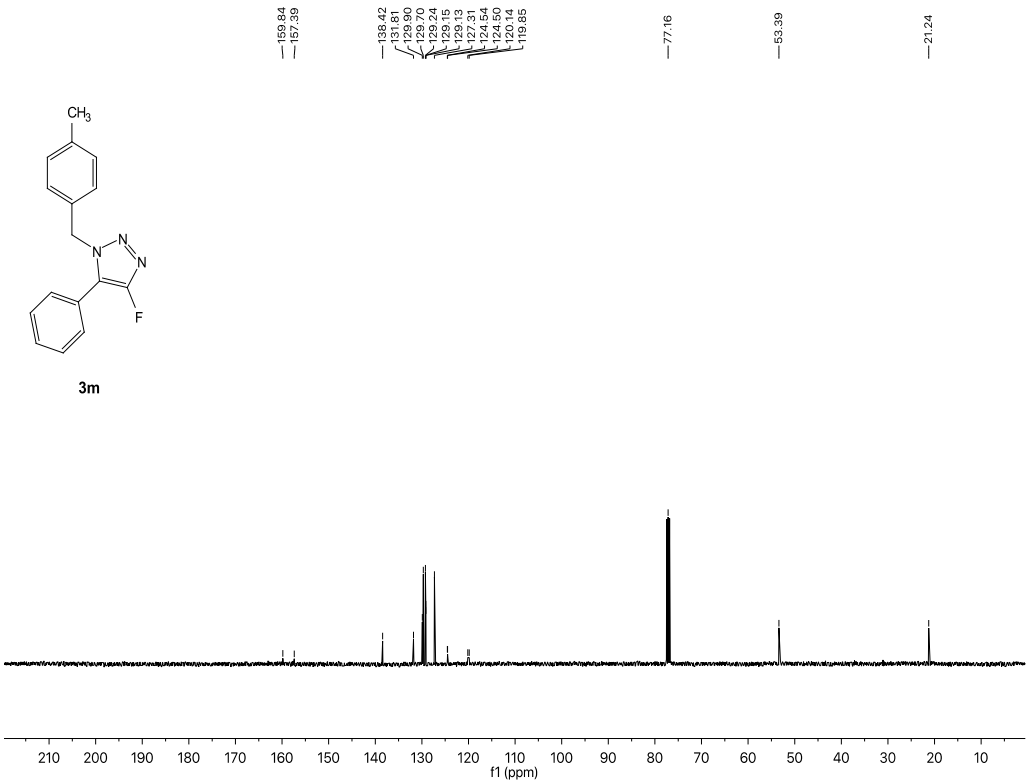

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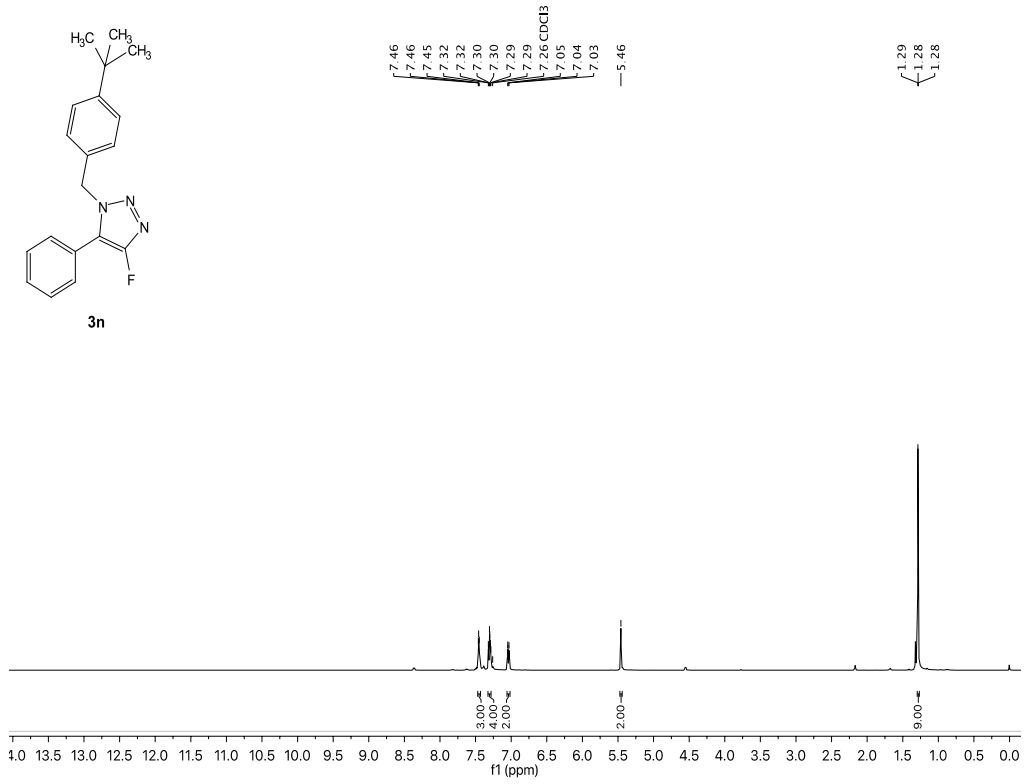

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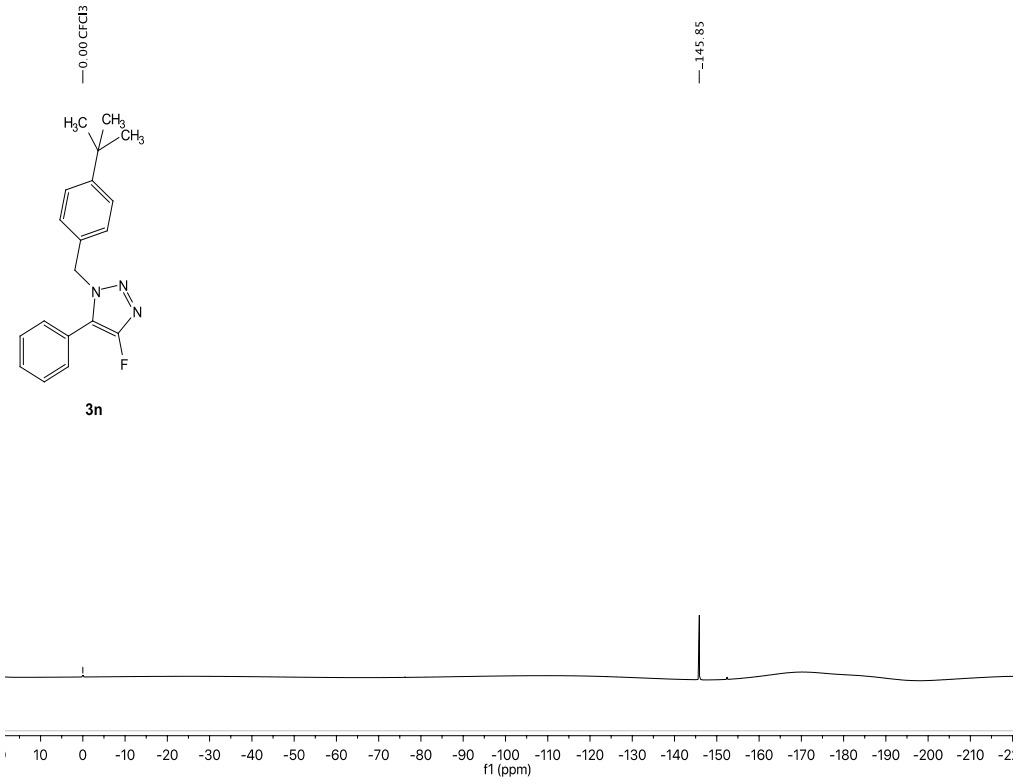

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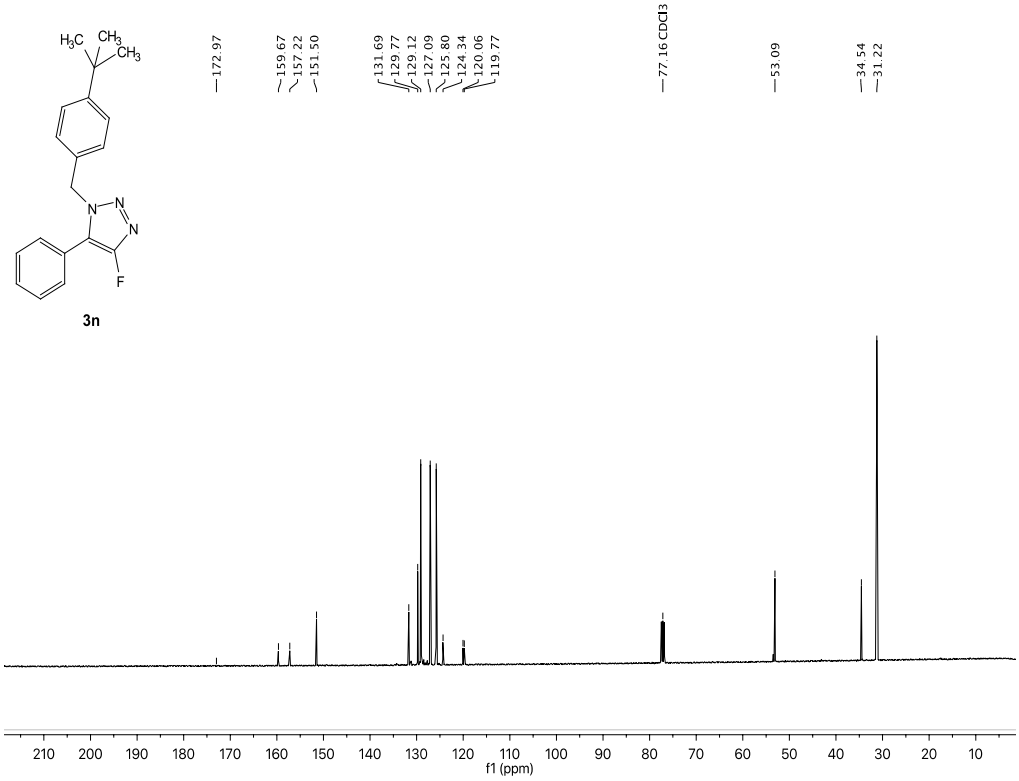

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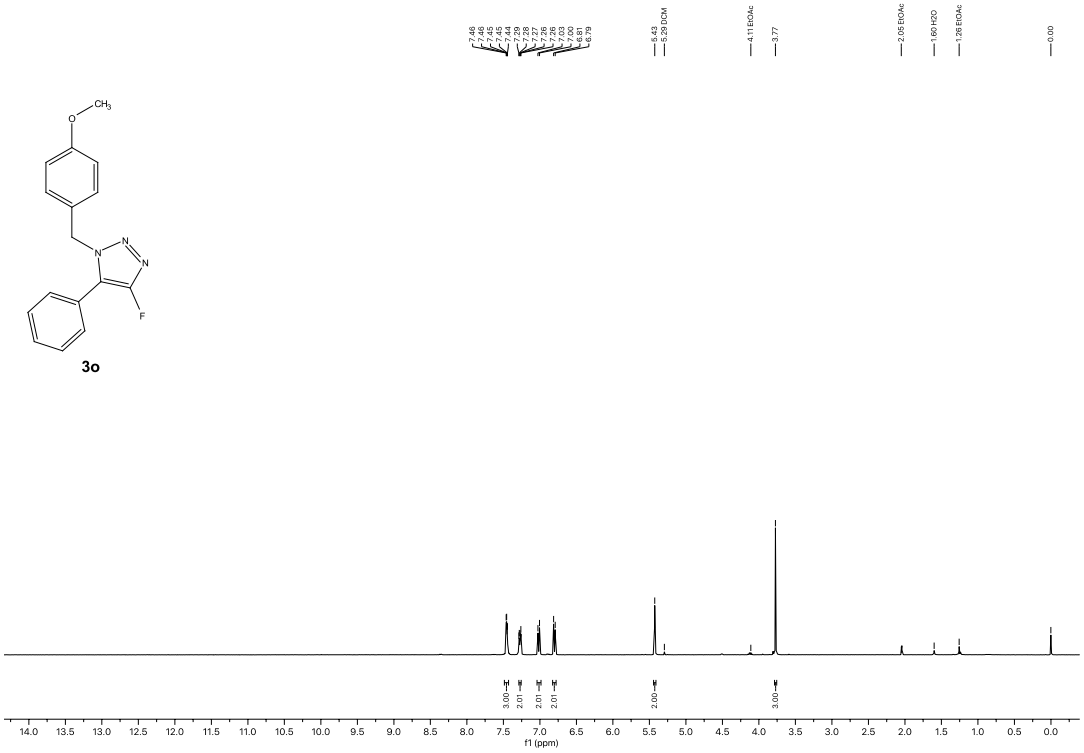

3o

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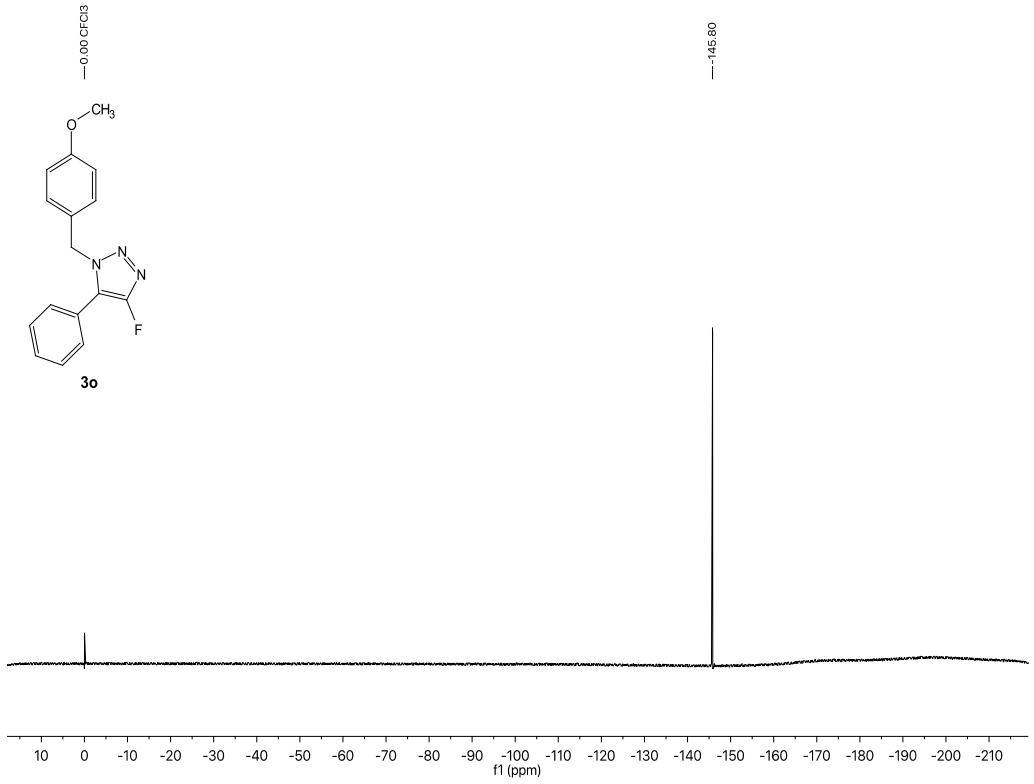
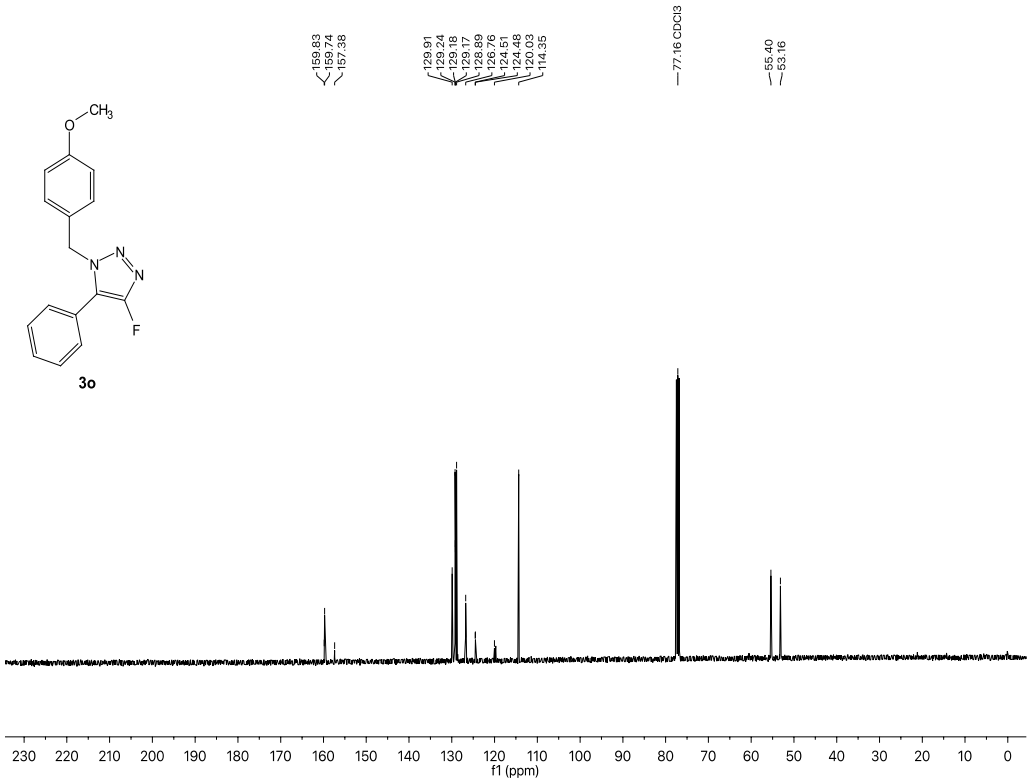


3o

^{13}C NMR of **3o**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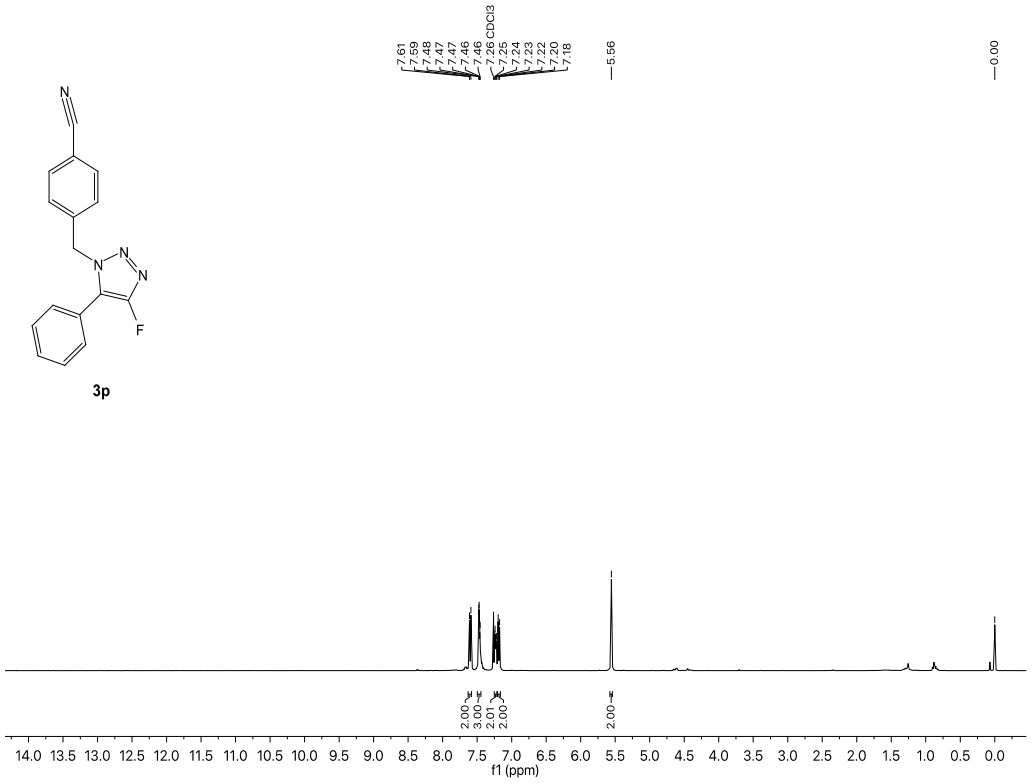
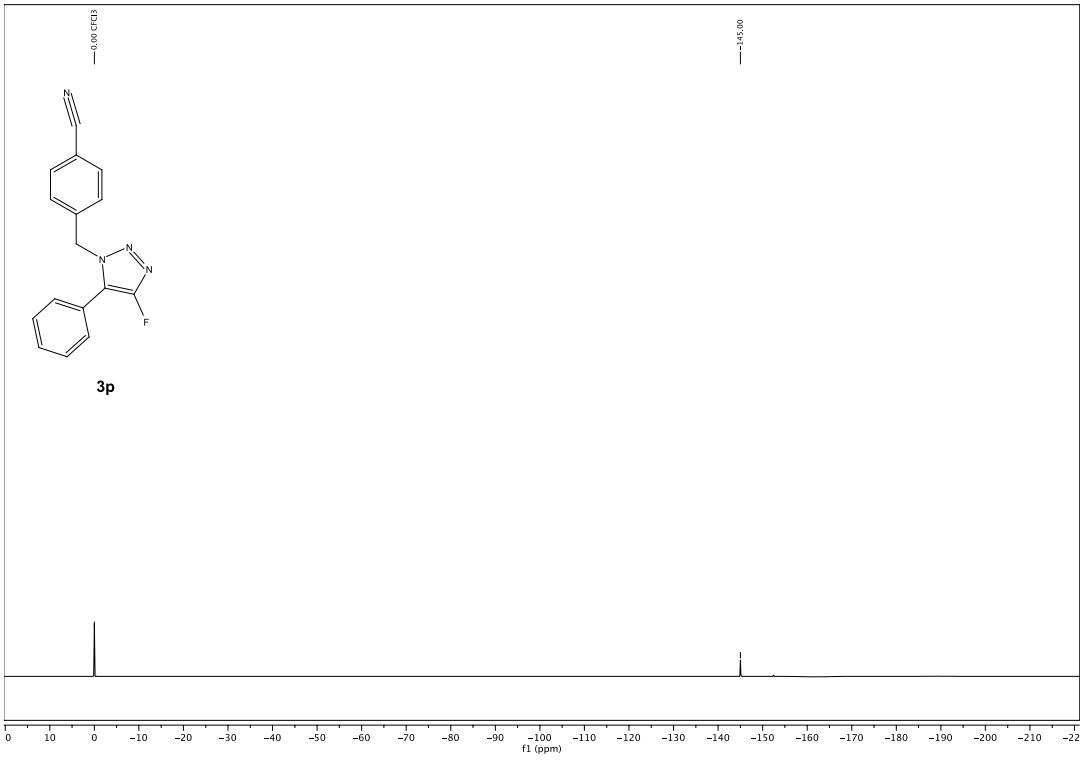
120.03
114.35
77.16 CDCl3
55.40
53.16
O
CH3
N
N
N
F
3o
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

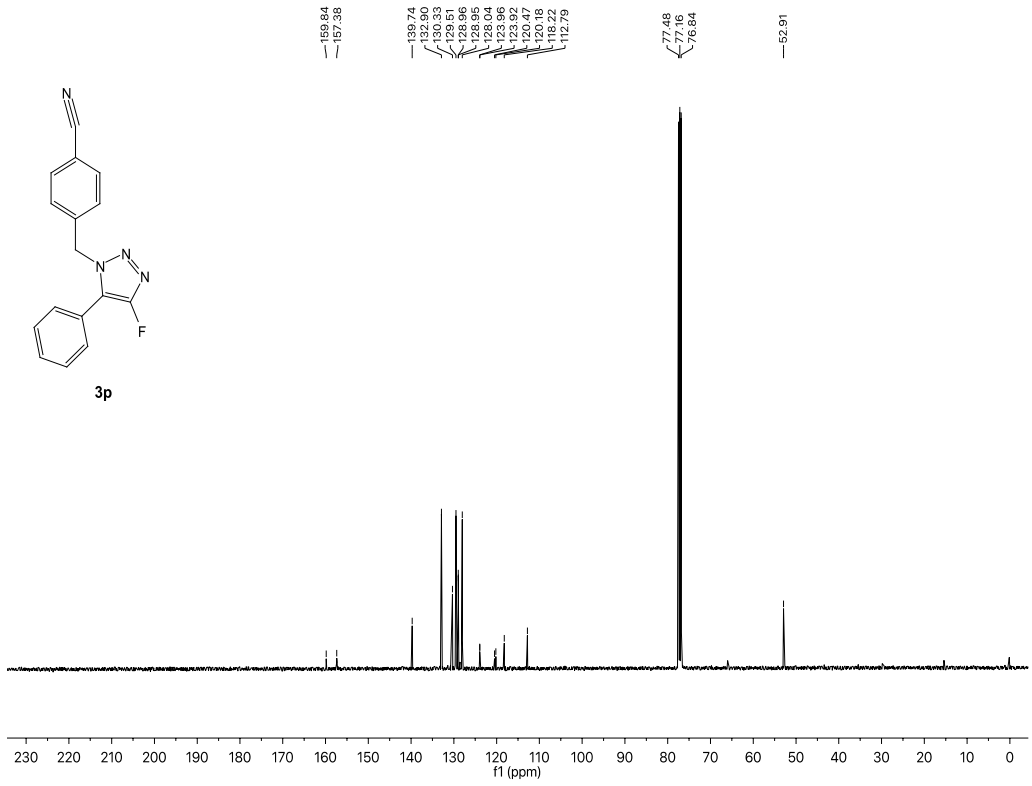
^{1}H NMR of **3p**


7.61
7.59
7.48
7.47
7.47
7.46
7.46
7.26 CDCl3
7.25
7.24
7.23
7.22
7.20
7.18
5.56
0.00
N
N
N
N
F
3p
2.00
3.00
2.01
2.00
2.00
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

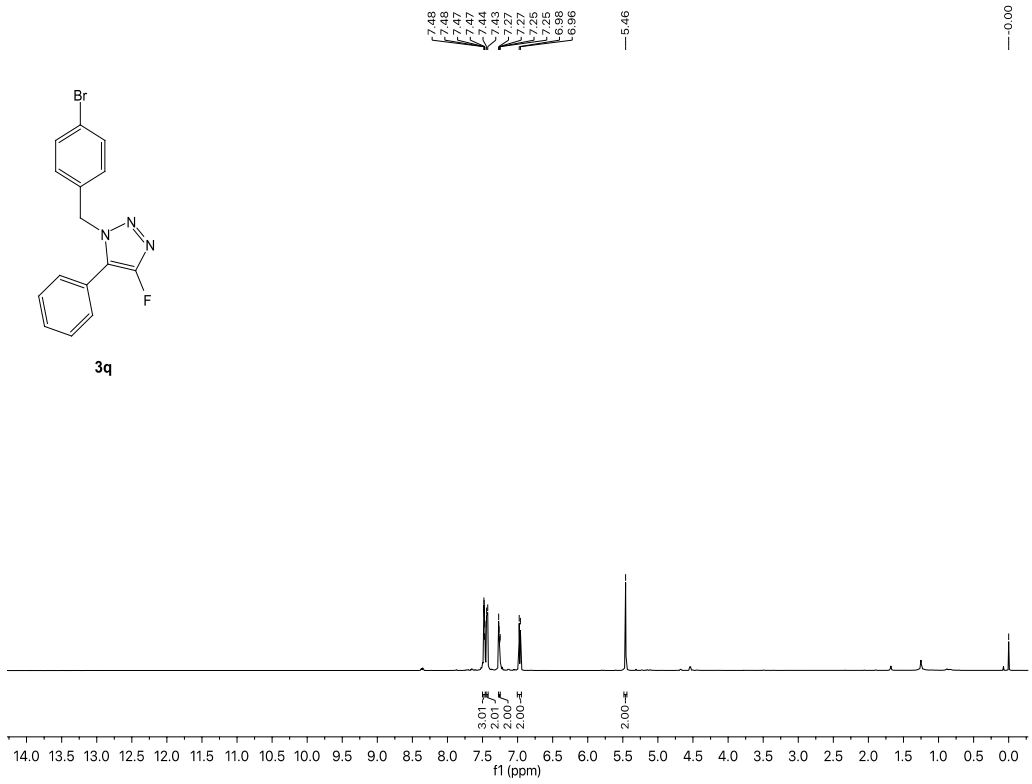
^{19}F NMR of **3p**



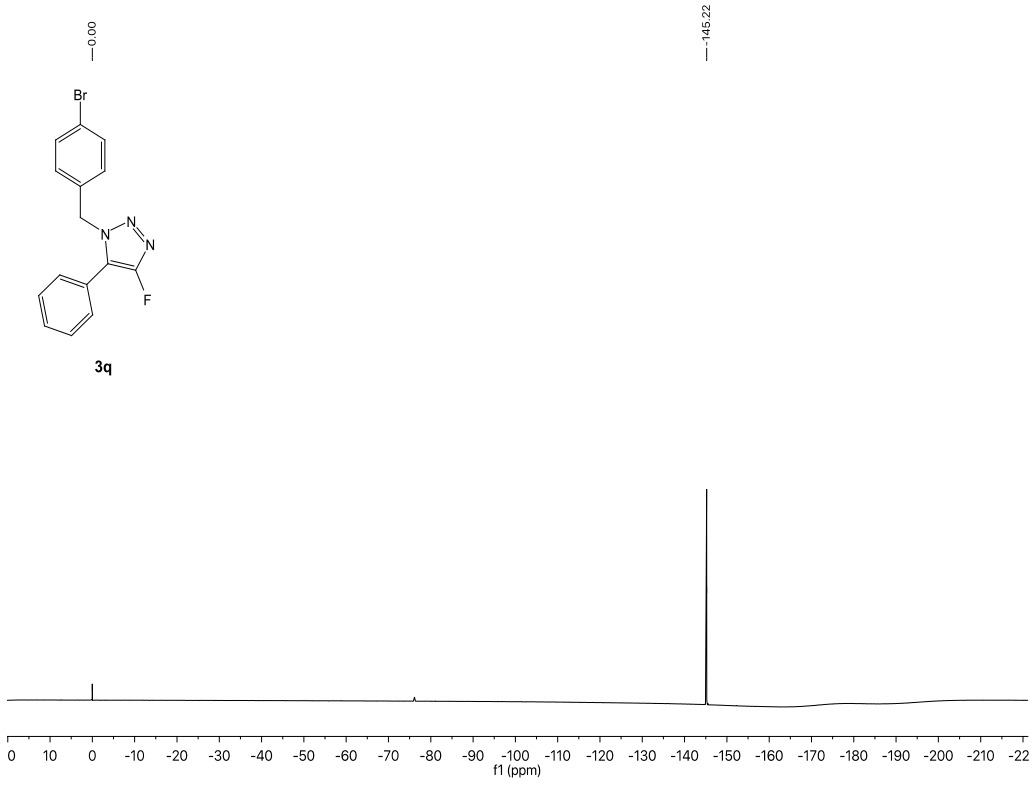
^{13}C NMR of **3p**



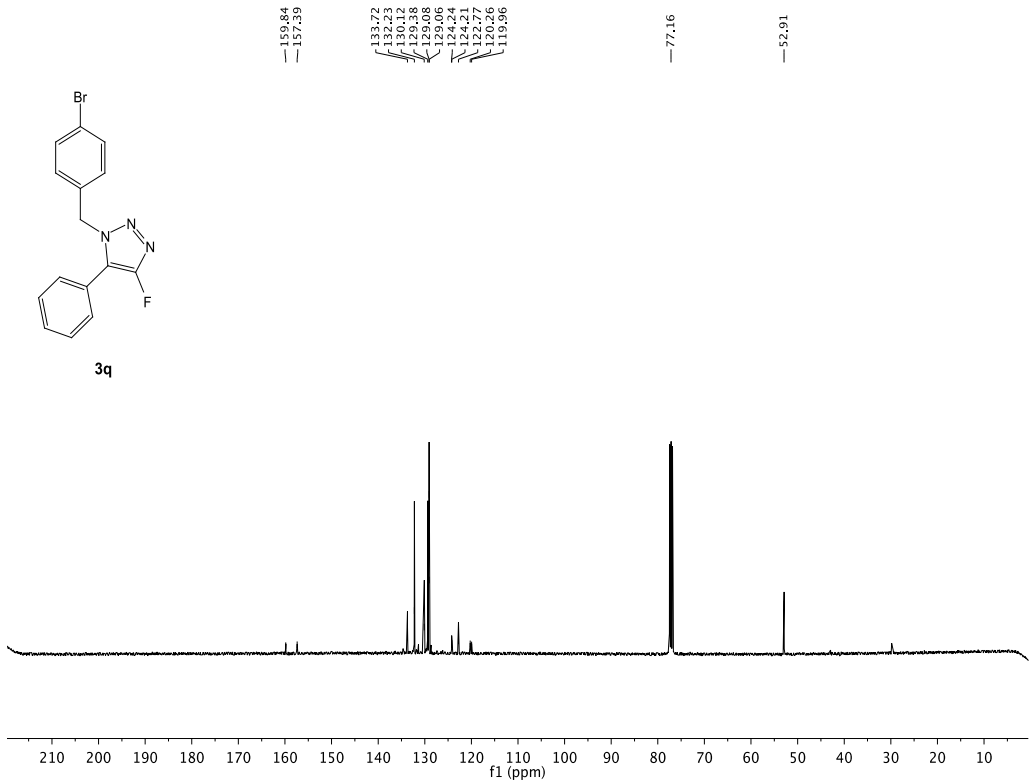
^{1}H NMR of **3q**


7.48
7.48
7.47
7.47
7.44
7.43
7.27
7.27
7.25
7.25
6.98
6.96
5.46
0.00
Br
N
N
N
F
3q
3.01
2.01
2.00
2.00
2.00
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

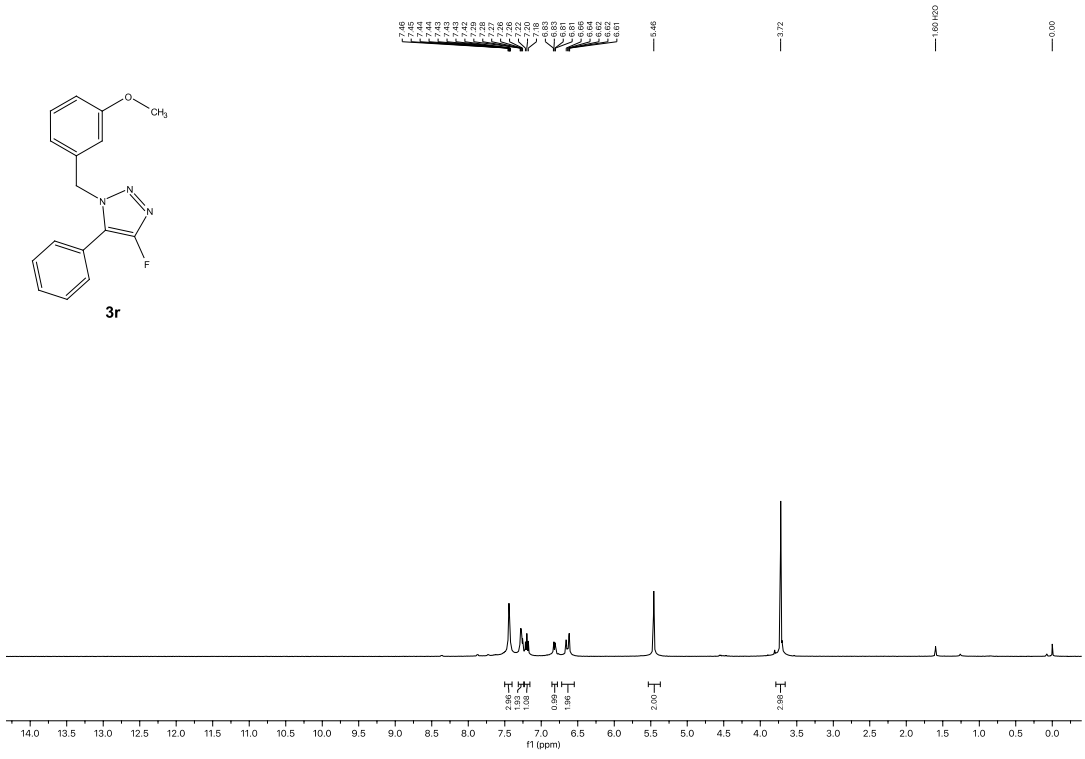
^{19}F NMR of **3q**


0.00
-145.22
Br
N
N
N
F
3q
0 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)

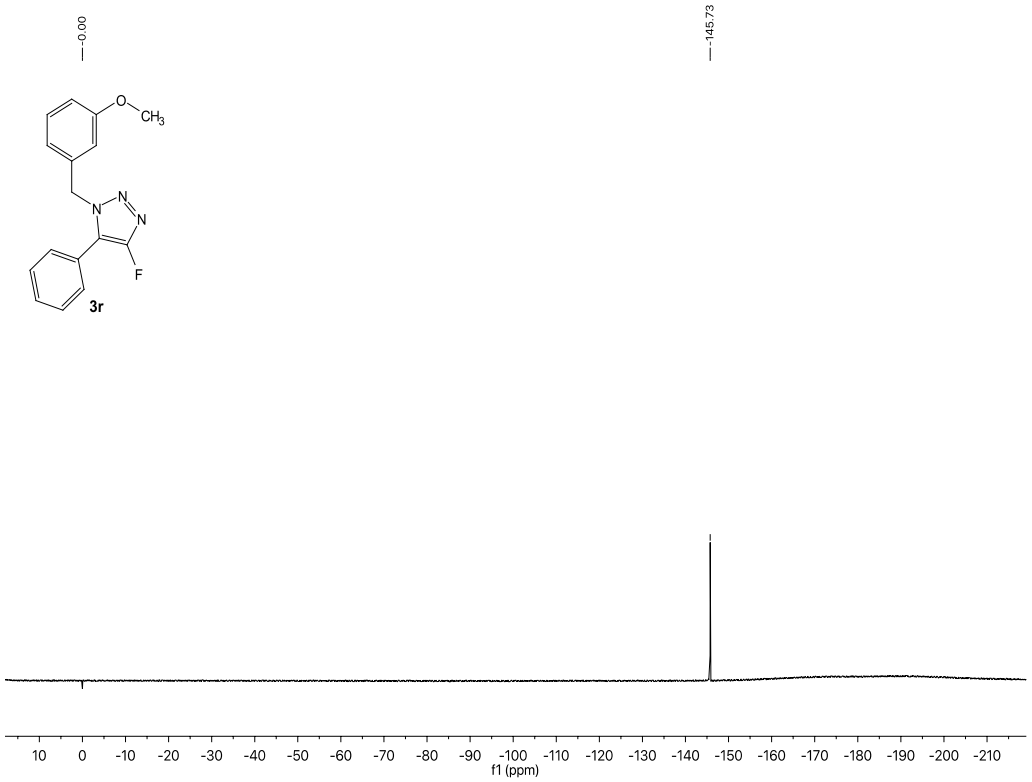
^{13}C NMR of **3q**



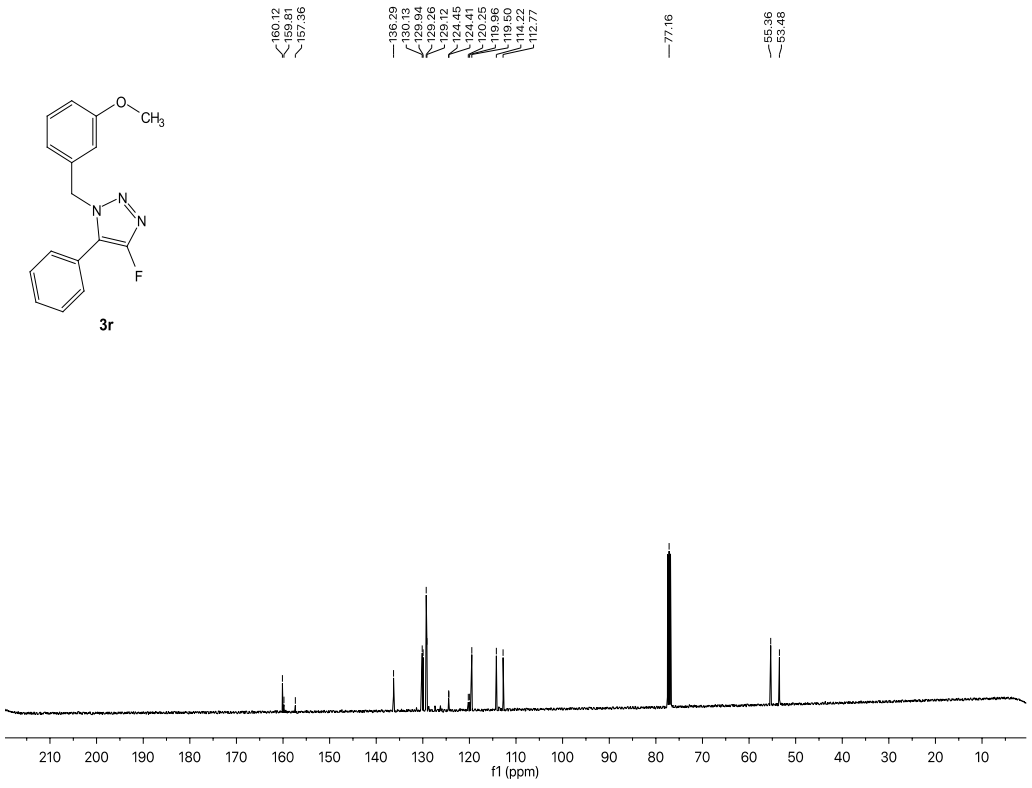
^{1}H NMR of **3r**



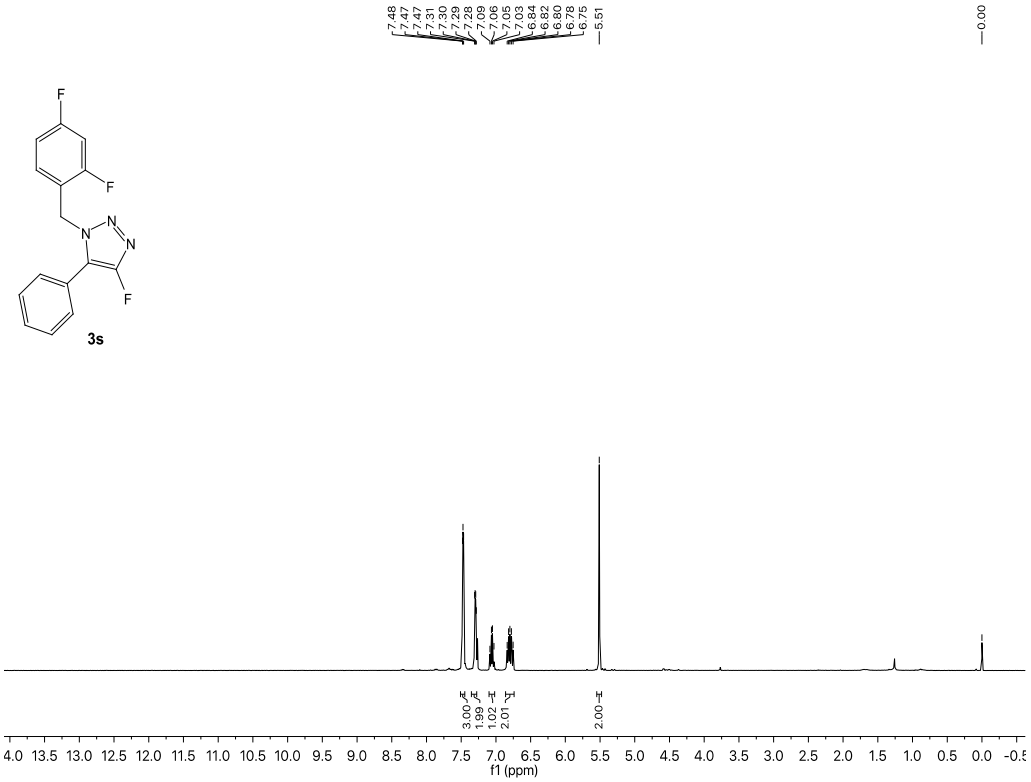
^{19}F NMR of **3r**



^{13}C NMR of **3r**

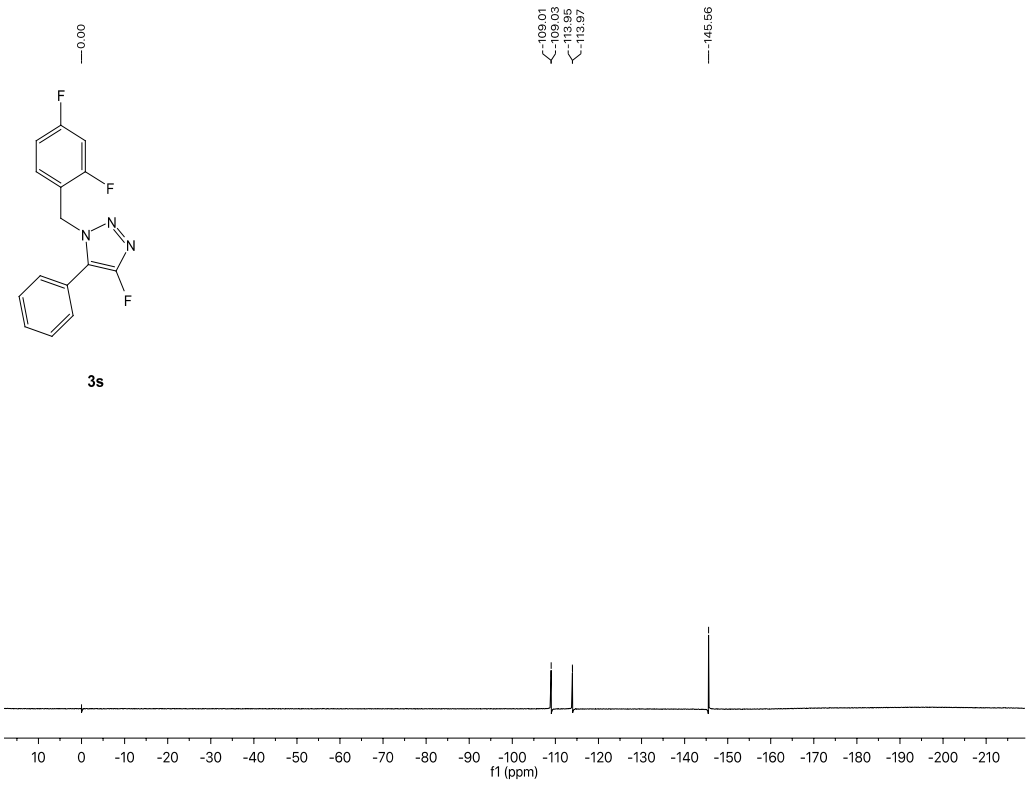


^{1}H NMR of **3s**



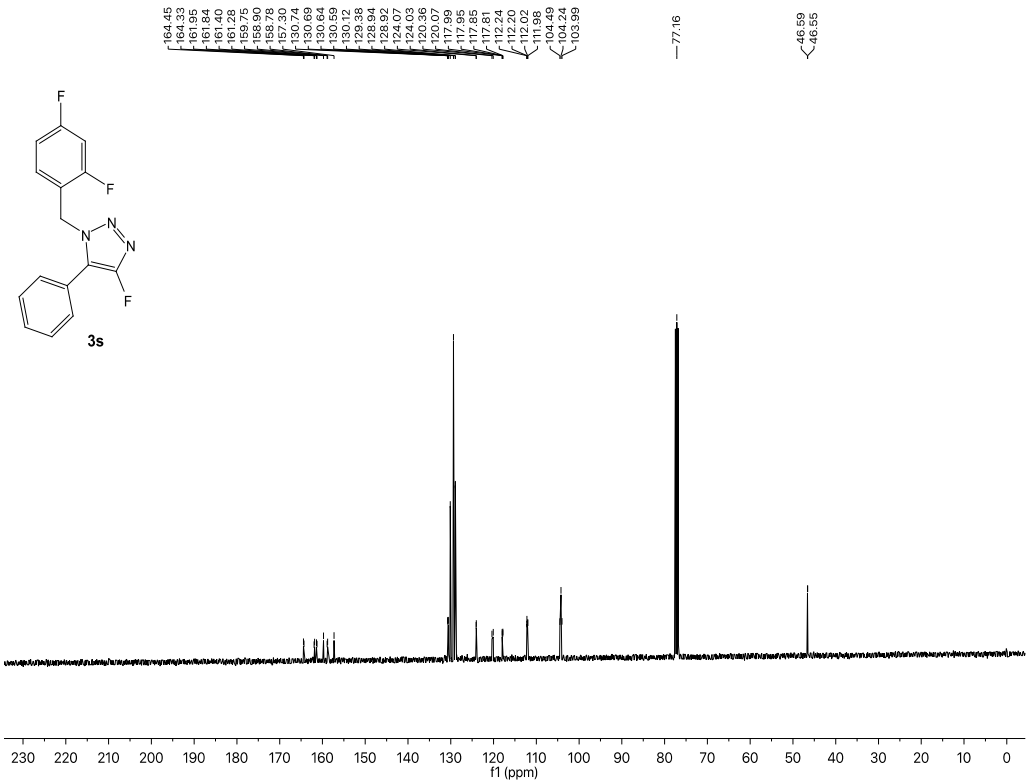
3s

^{19}F NMR of **3s**

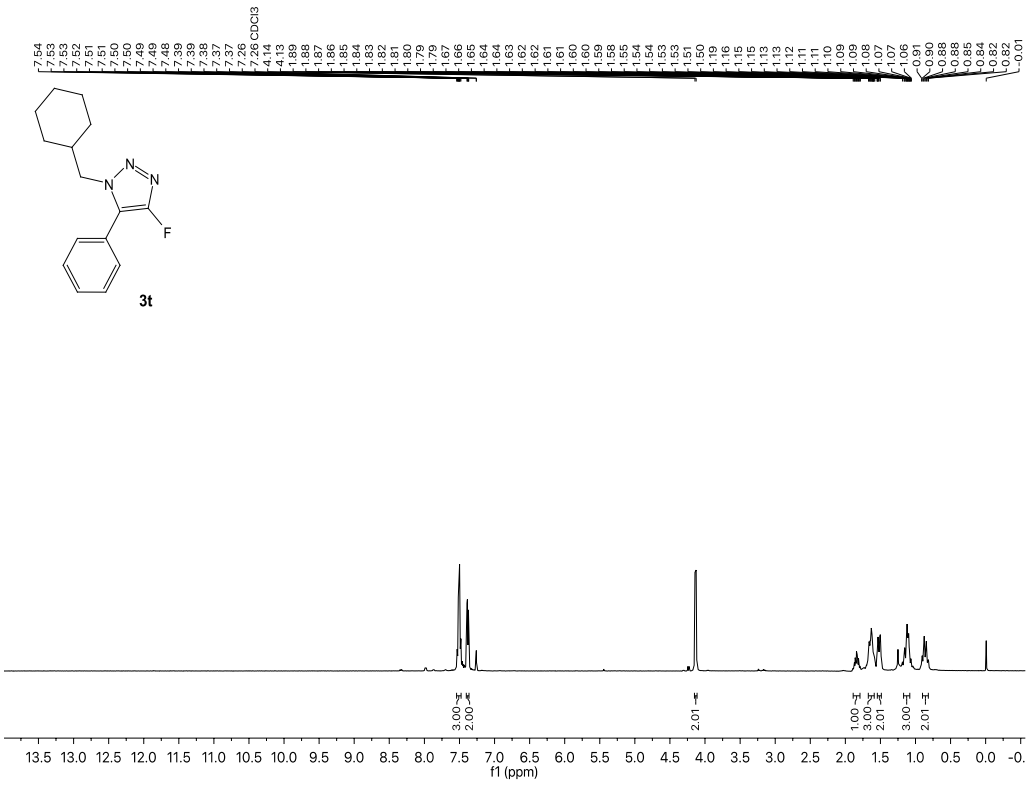


3s

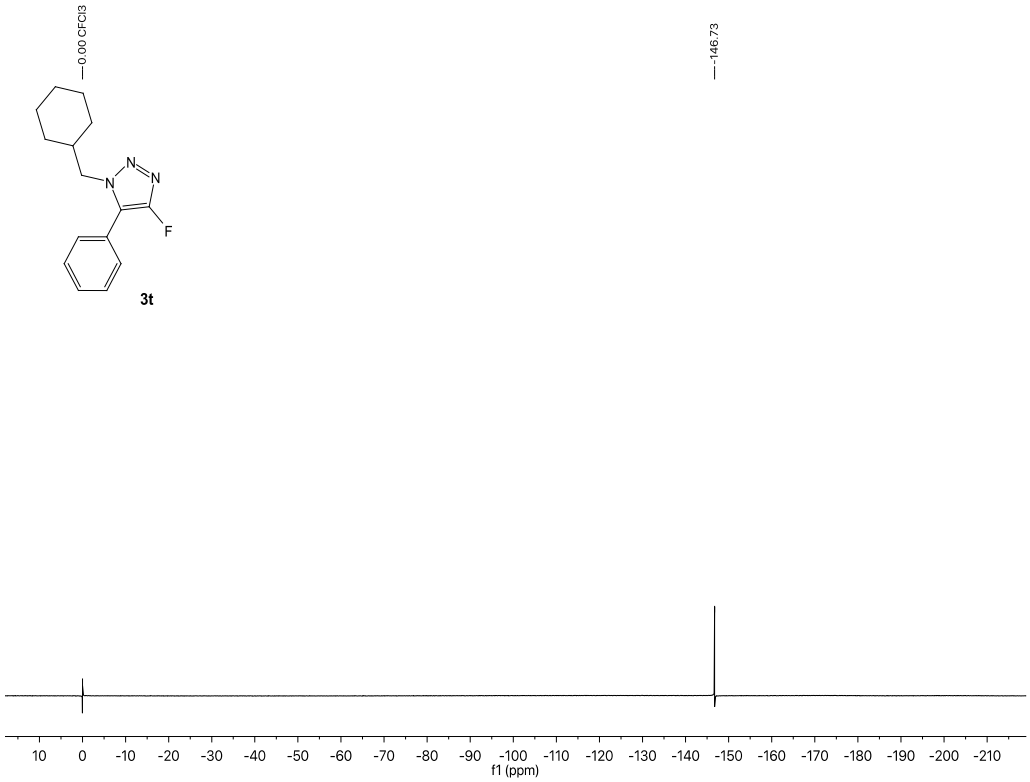
^{13}C NMR of **3s**



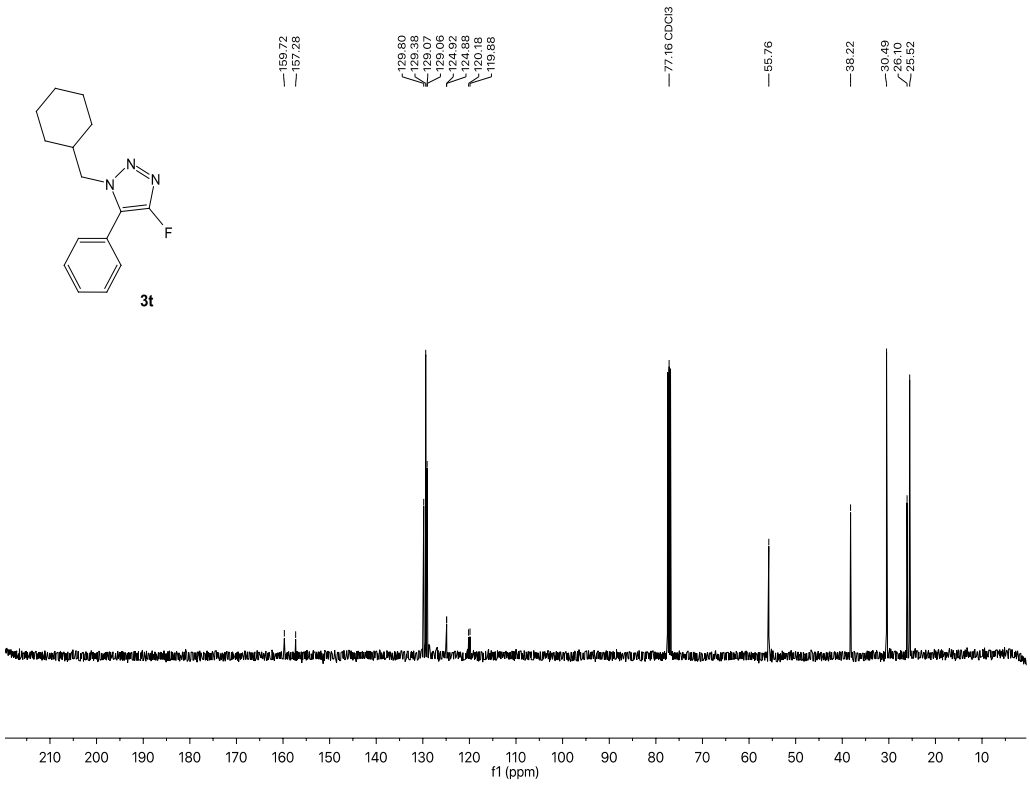
^{1}H NMR of **3t**



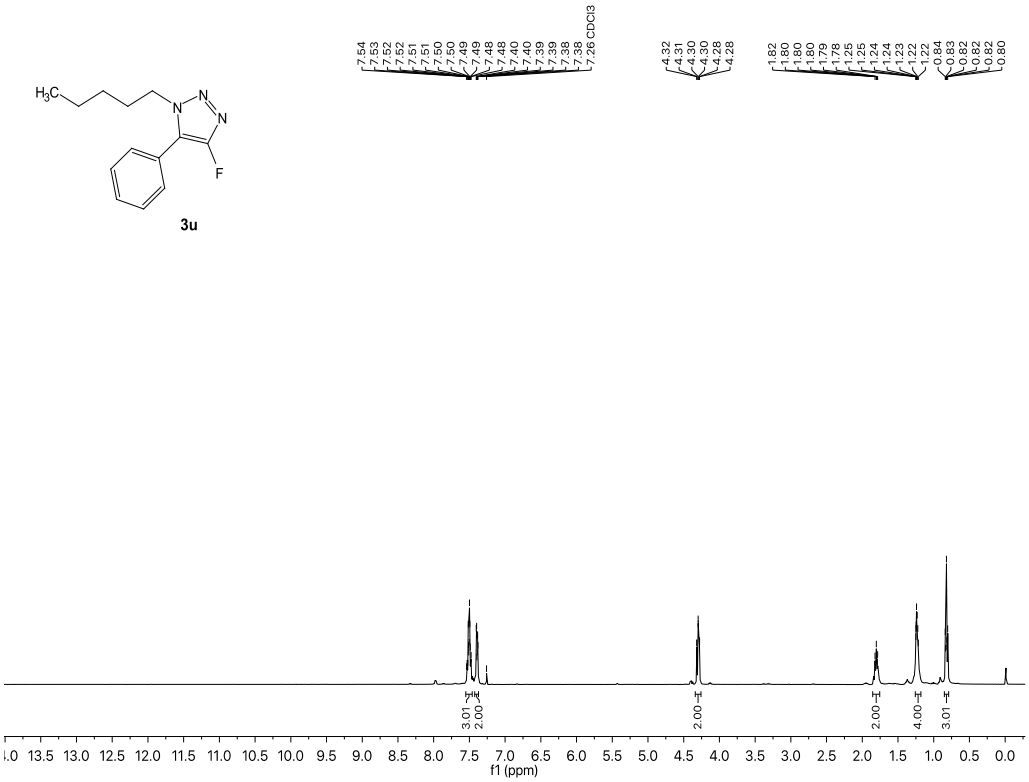
^{19}F NMR of **3t**



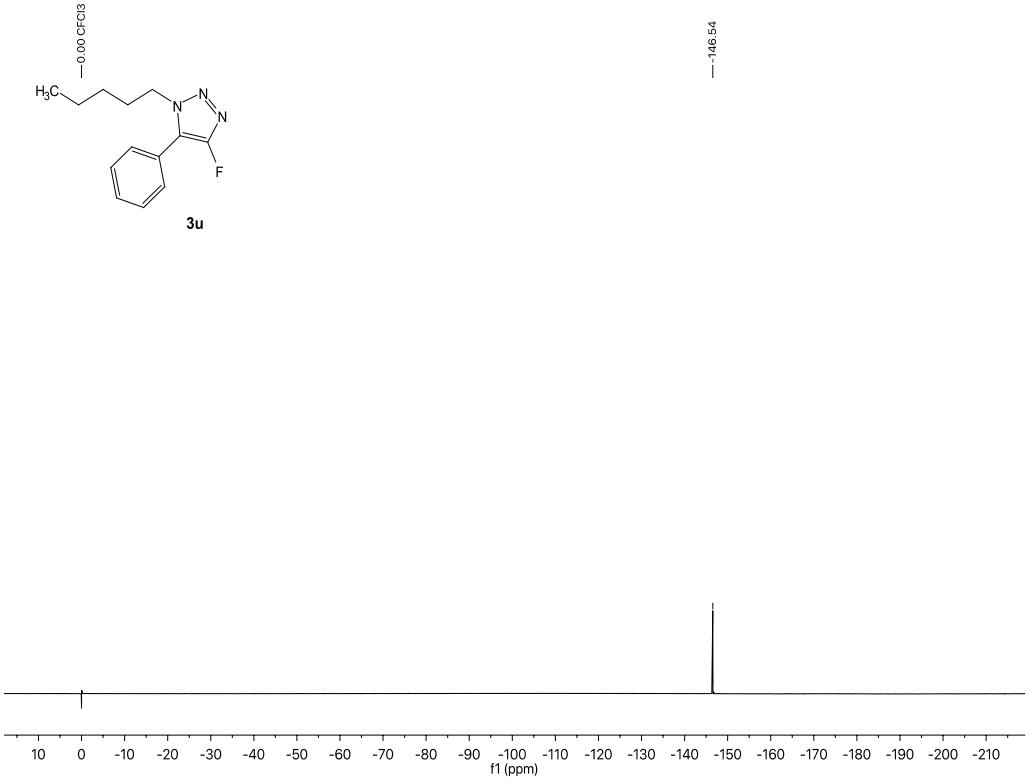
^{13}C NMR of **3t**



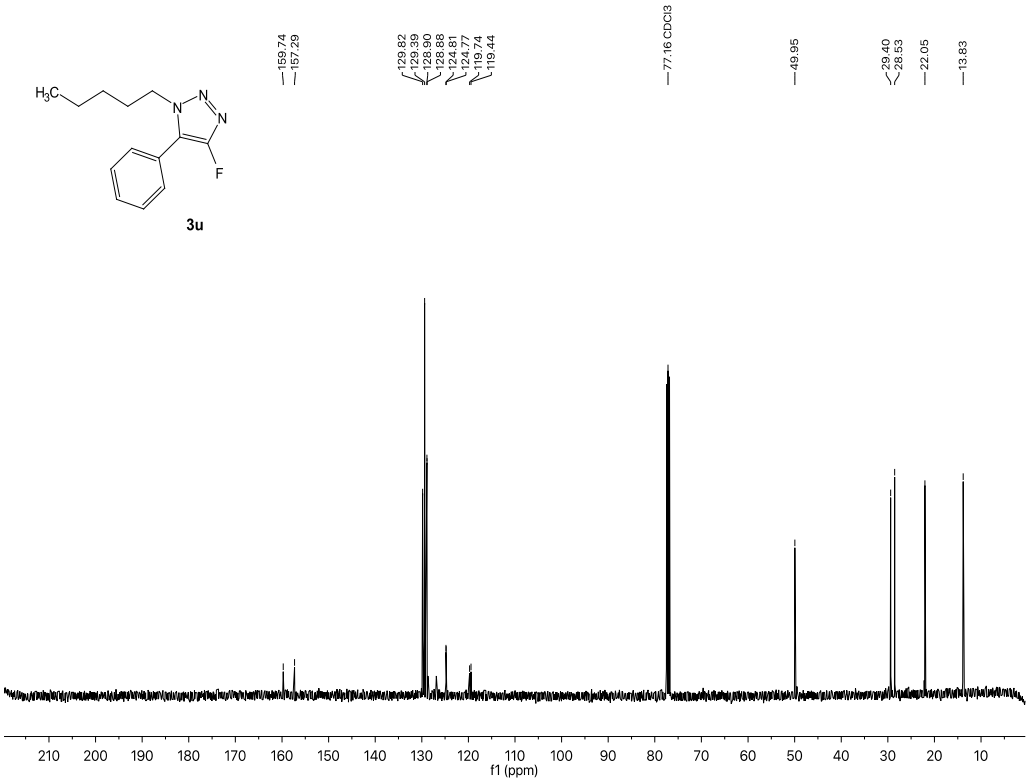
^{1}H NMR of **3u**



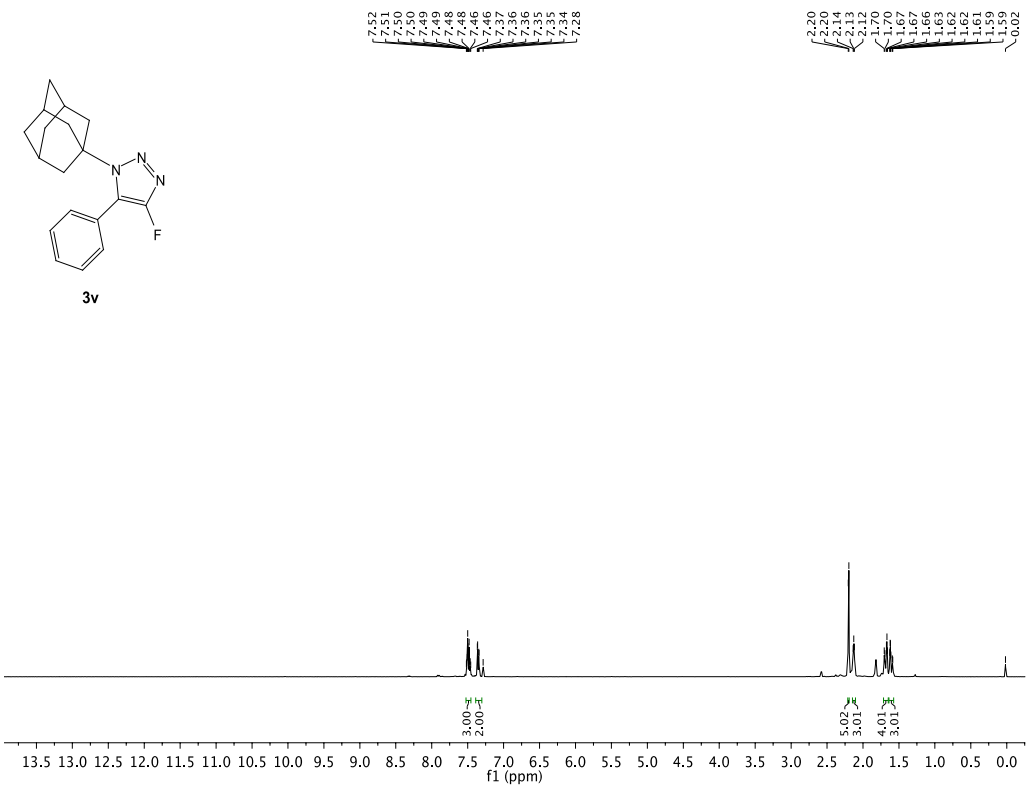
^{19}F NMR of **3u**



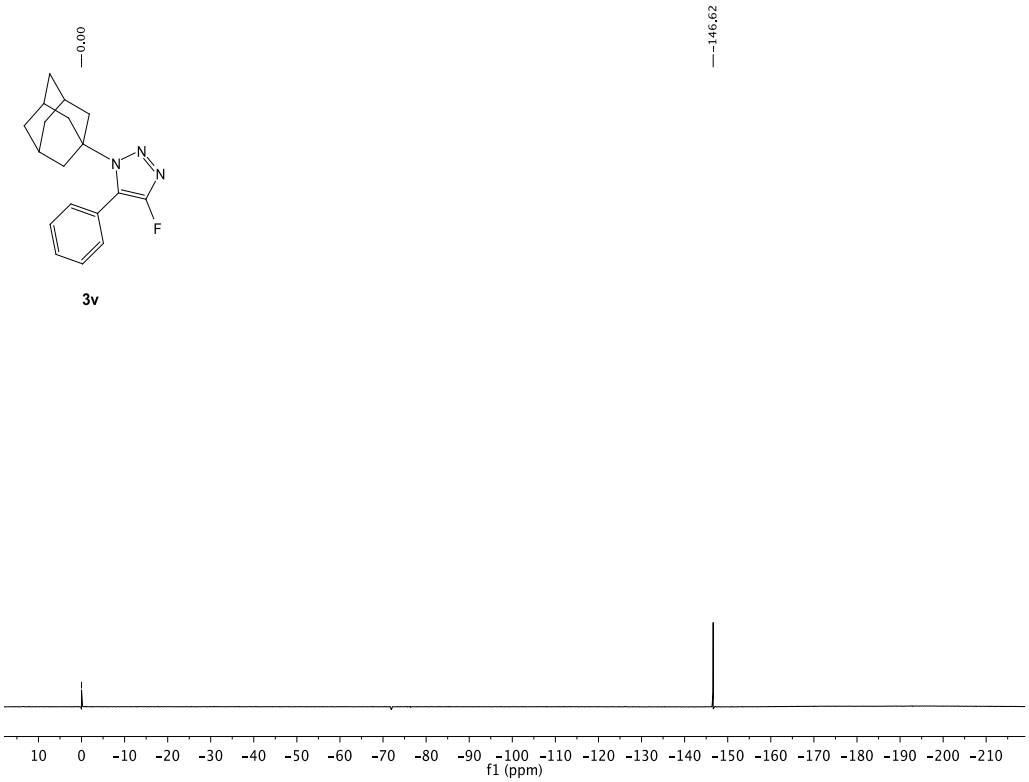
^{13}C NMR of **3u**



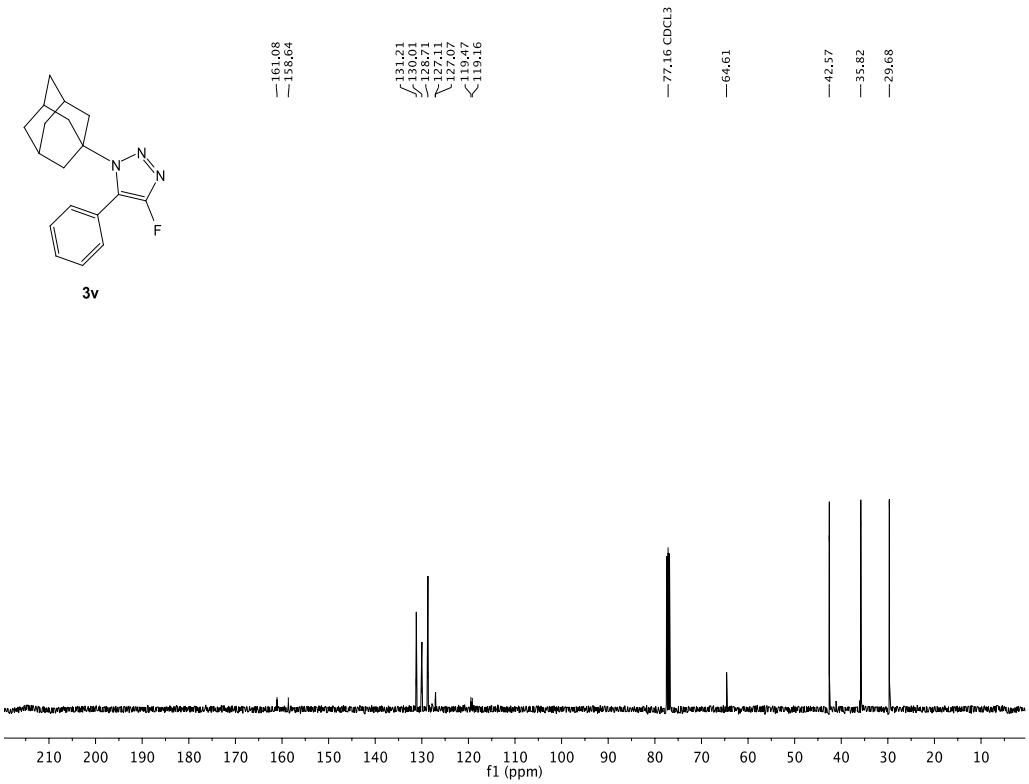
^{1}H NMR of **3v**



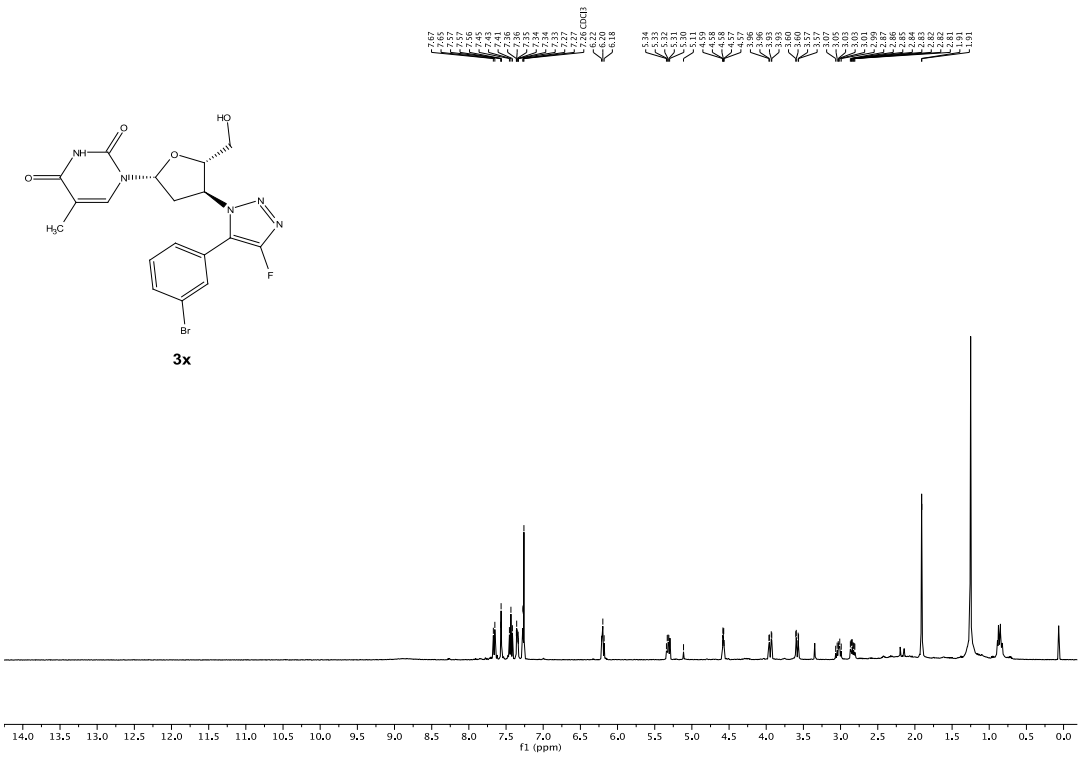
^{19}F NMR of **3v**



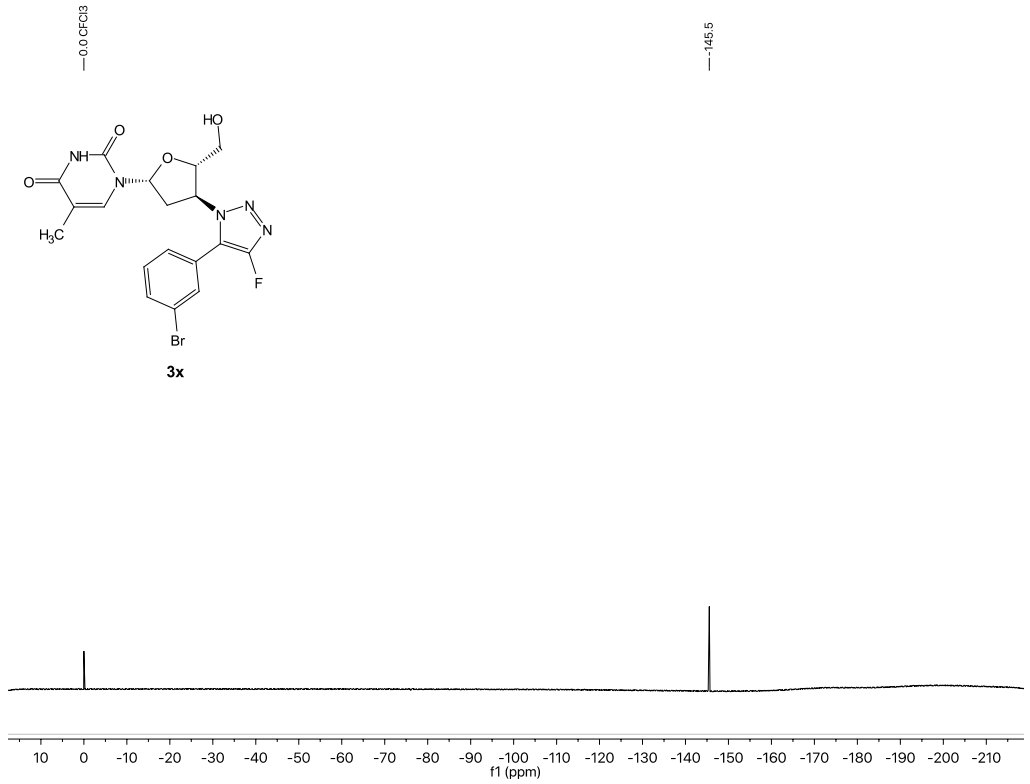
^{13}C NMR of **3v**



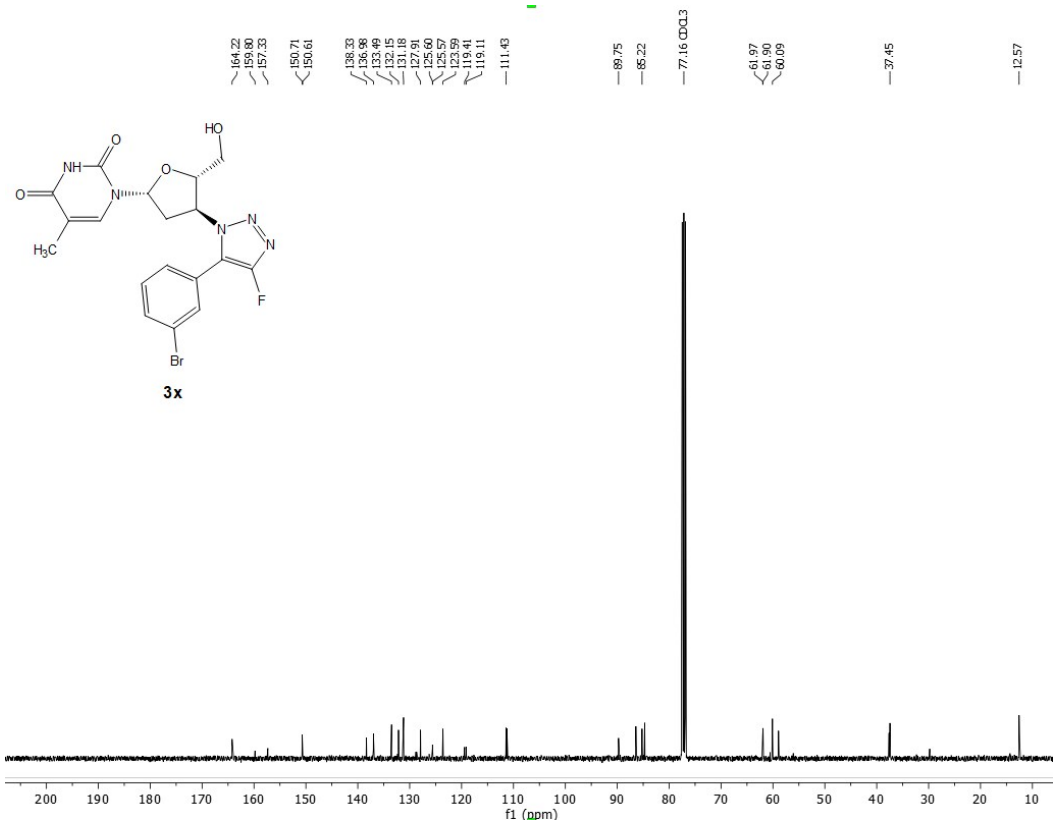
^{1}H NMR of **3x**



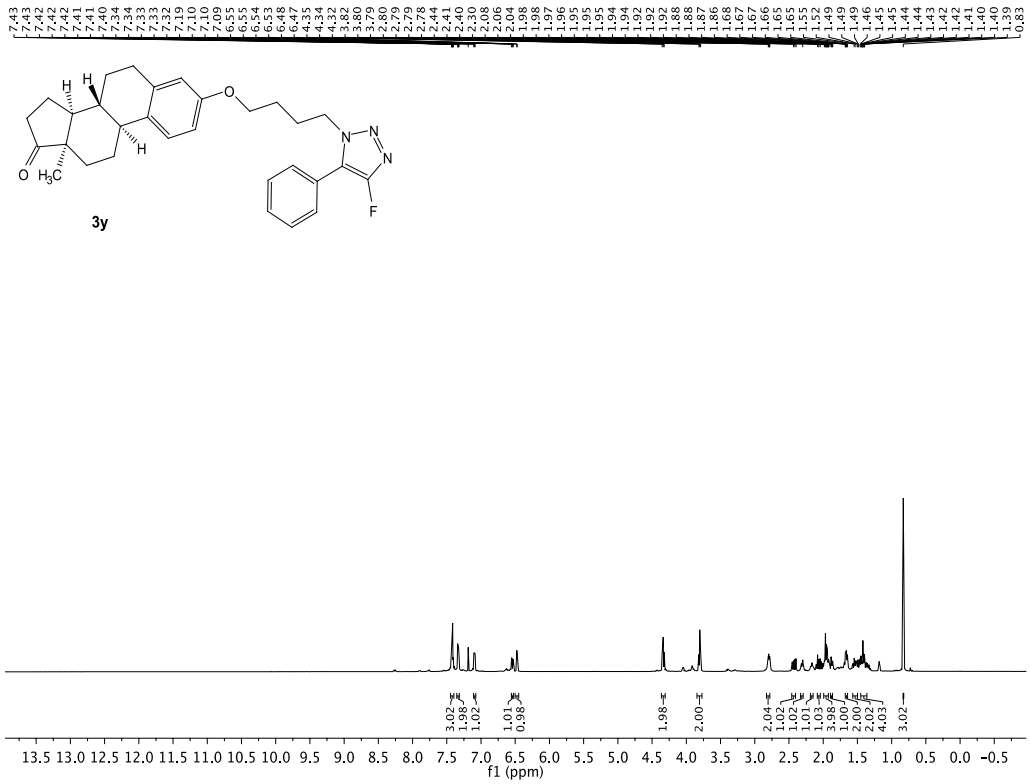
^{19}F NMR of **3x**



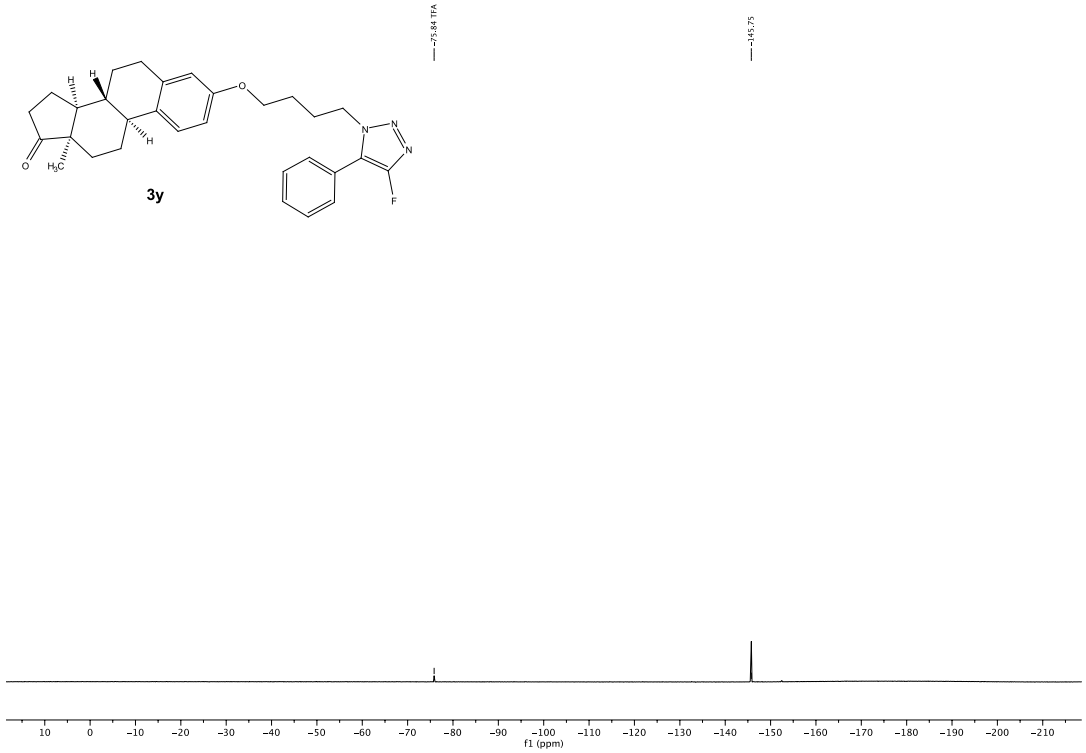
^{13}C NMR of **3x**


164.22
159.80
157.33
150.71
150.61
138.33
136.98
133.49
132.15
131.18
127.91
125.60
125.57
123.89
119.41
119.11
111.43
89.75
85.22
77.16 CDCl3
61.97
61.90
60.09
37.45
12.57
HO
O
NH
O
N
O
N
N
N
H3C
F
Br
3x
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

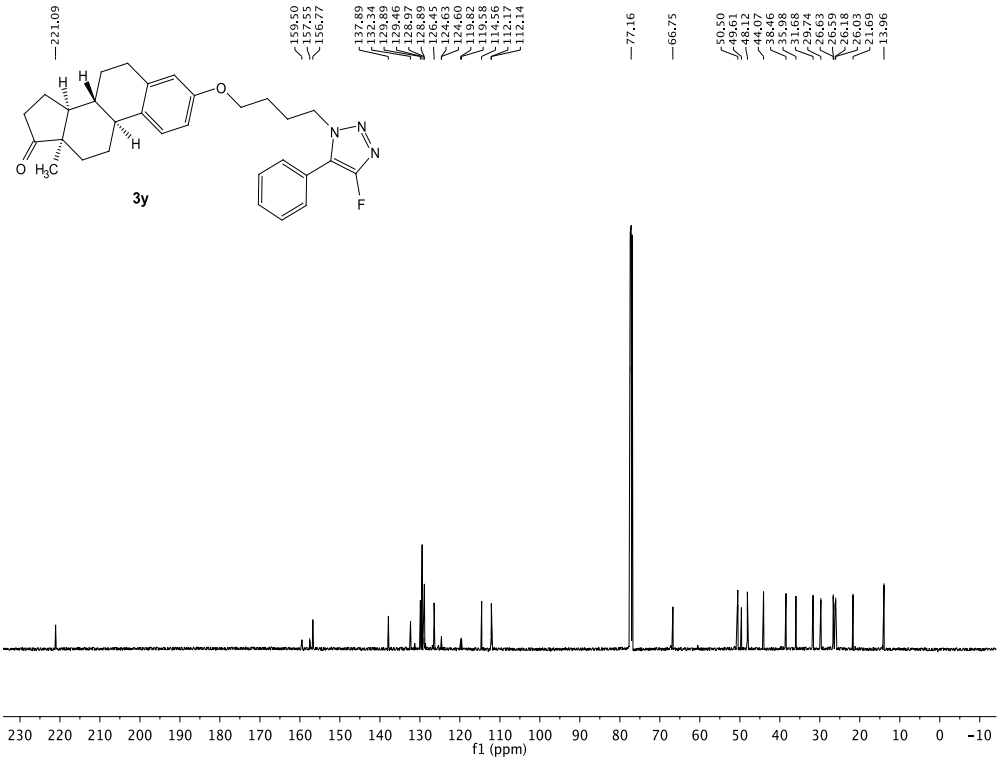
^{1}H NMR of **3y**


7.43
7.43
7.42
7.42
7.42
7.41
7.41
7.40
7.34
7.34
7.33
7.33
7.32
7.19
7.10
7.10
7.09
6.55
6.54
6.53
6.48
6.47
4.35
4.34
4.32
3.82
3.80
3.79
2.80
2.79
2.79
2.78
2.44
2.41
2.40
2.30
2.08
2.06
2.04
1.98
1.98
1.97
1.96
1.95
1.95
1.95
1.94
1.94
1.92
1.92
1.88
1.88
1.87
1.86
1.68
1.67
1.67
1.66
1.65
1.65
1.55
1.52
1.49
1.49
1.49
1.46
1.45
1.45
1.44
1.44
1.43
1.42
1.42
1.41
1.40
1.40
1.39
0.83
H
H
H
O
O
H3C
N
N
N
F
3y
3.02
1.98
1.02
1.01
0.98
1.98
2.00
2.04
1.02
1.02
1.01
3.98
1.00
2.00
2.02
4.03
3.02
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

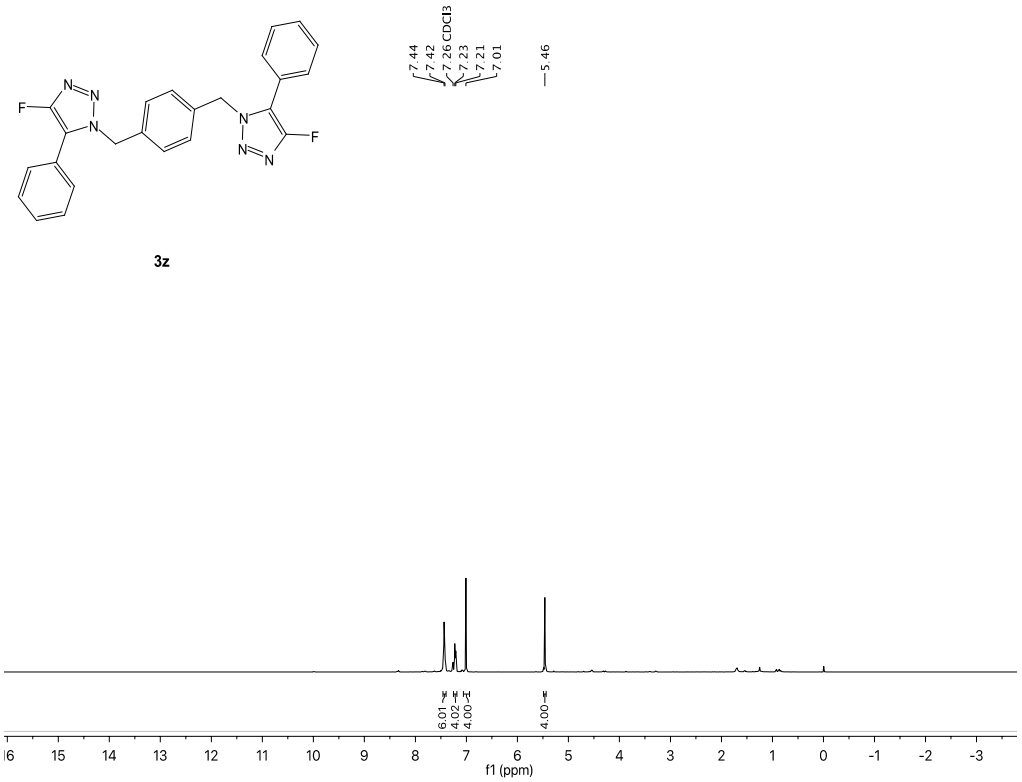
^{19}F NMR of **3y**



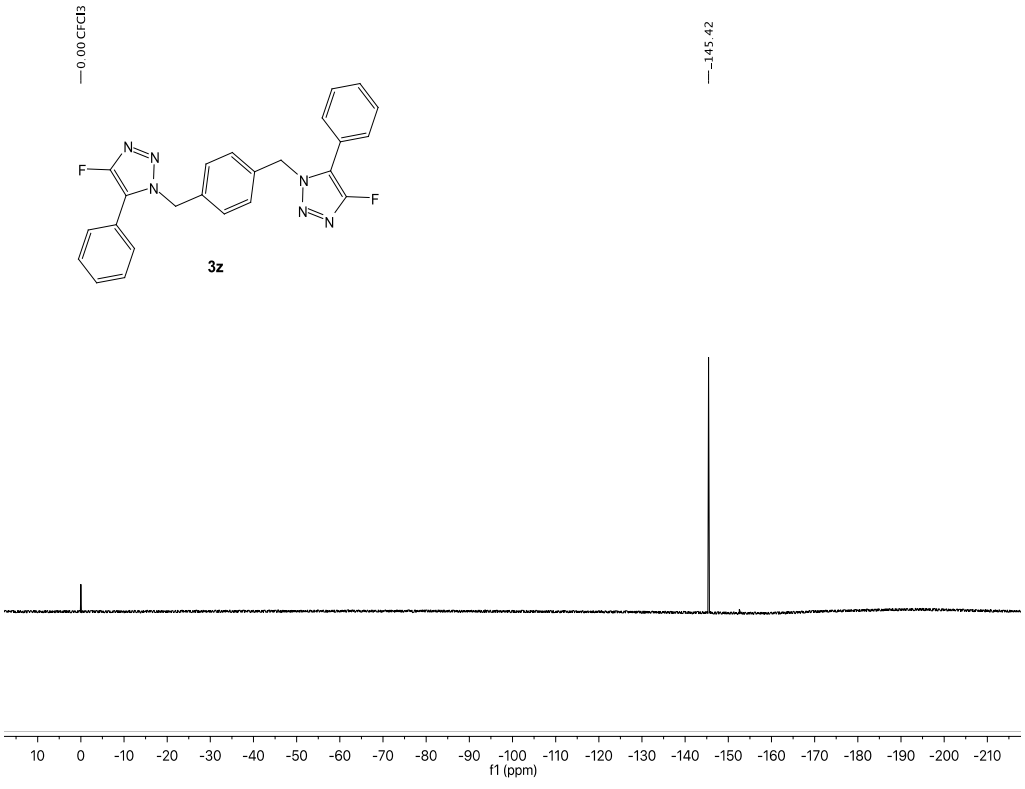
^{13}C NMR of **3y**



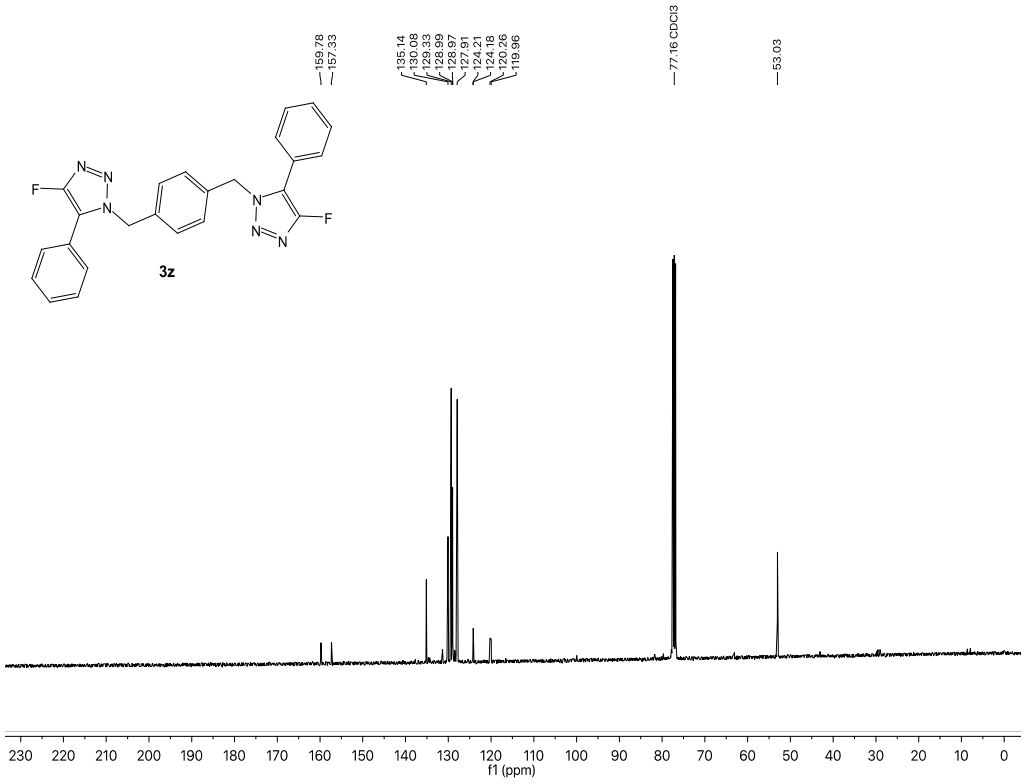
^{1}H NMR of **3z**


7.44
7.42
7.26 CDCl3
7.23
7.21
7.01
5.46
3z
6.01
4.02
4.00
4.00
f1 (ppm)

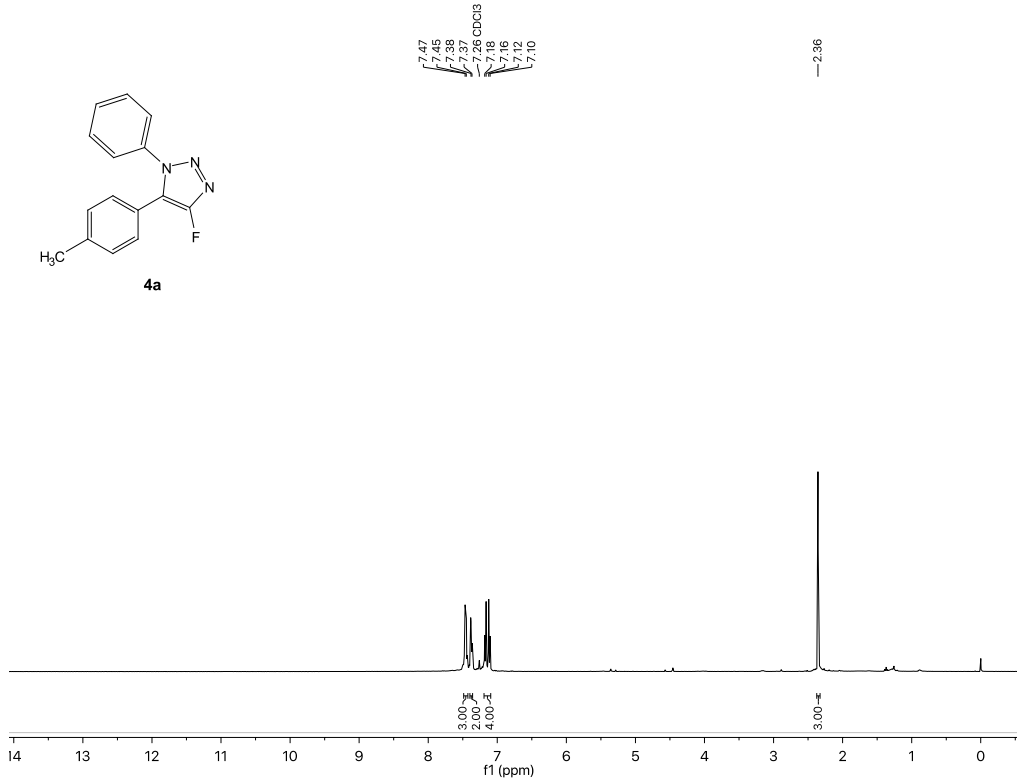
^{19}F NMR of **3z**


0.00 CFCl3
-145.42
3z
f1 (ppm)

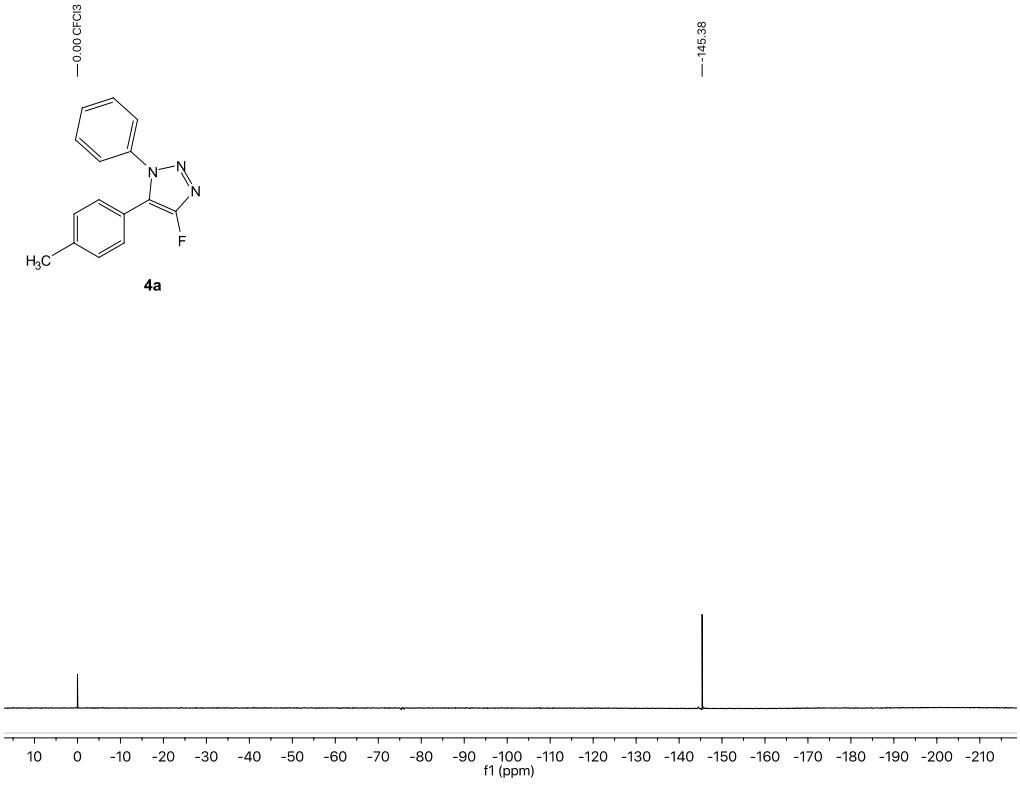
^{13}C NMR of **3z**



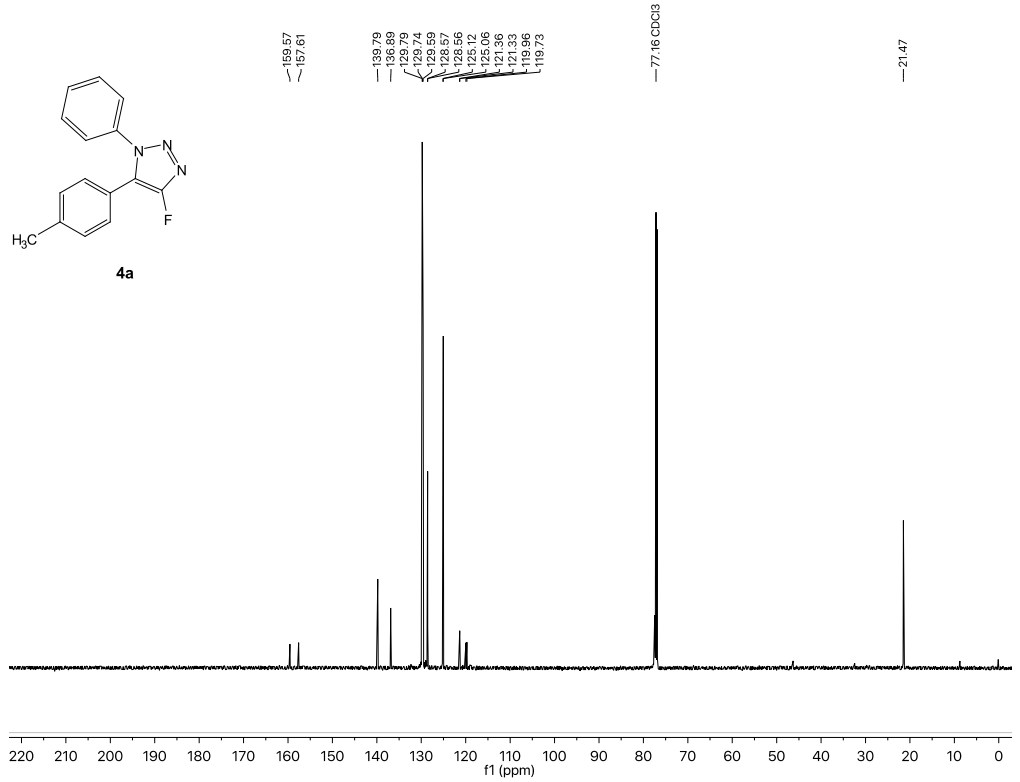
^{1}H NMR of **4a**



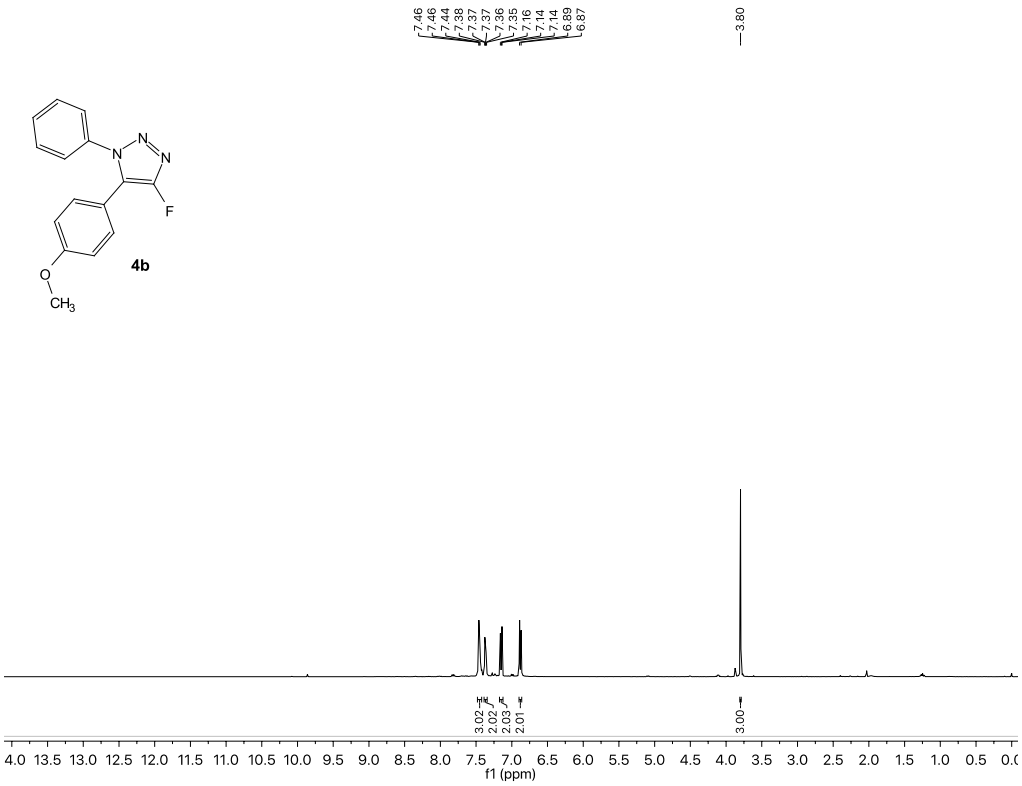
^{19}F NMR of **4a**



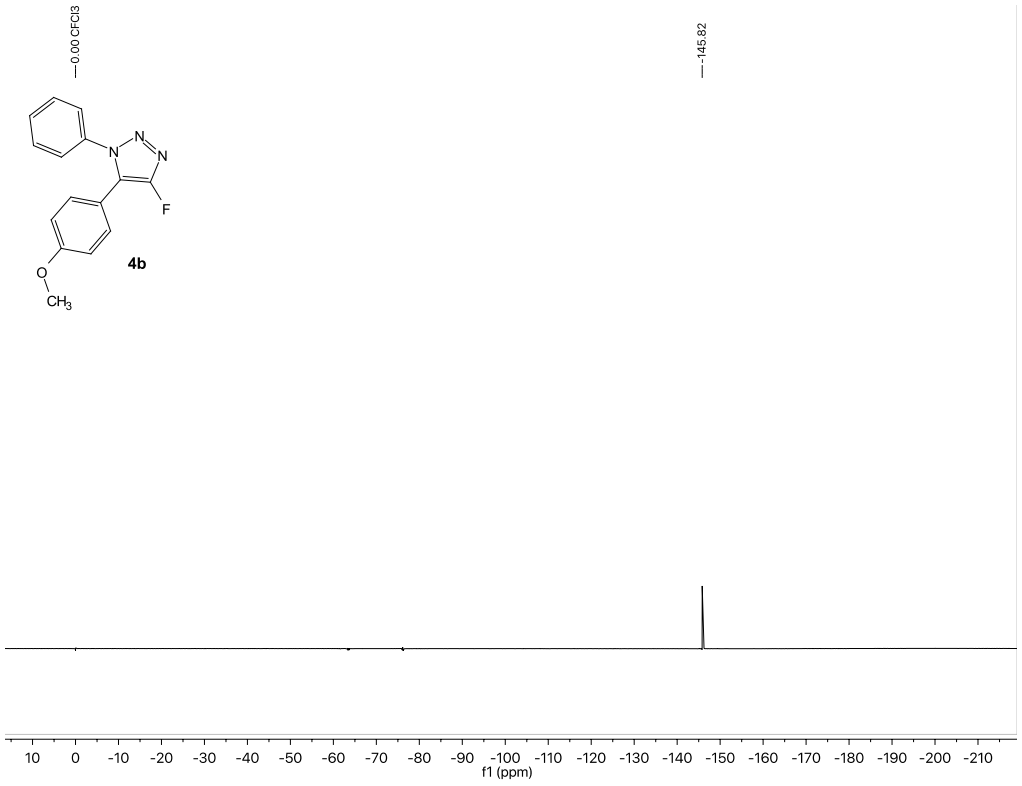
^{13}C NMR of **4a**



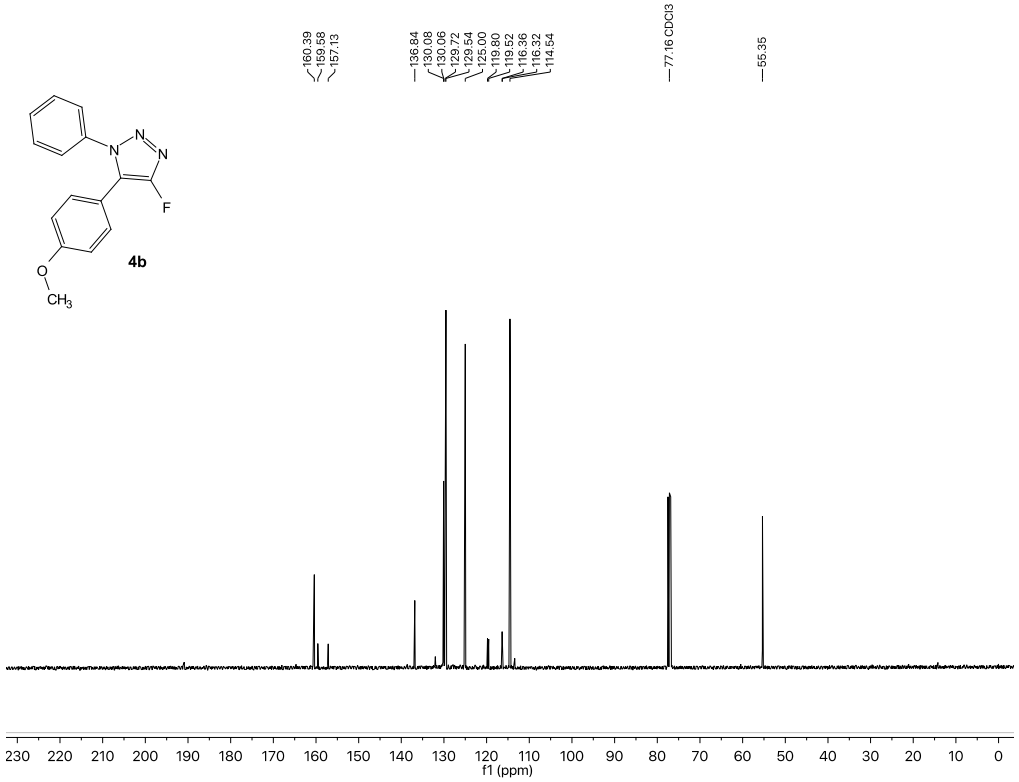
^{1}H NMR of **4b**



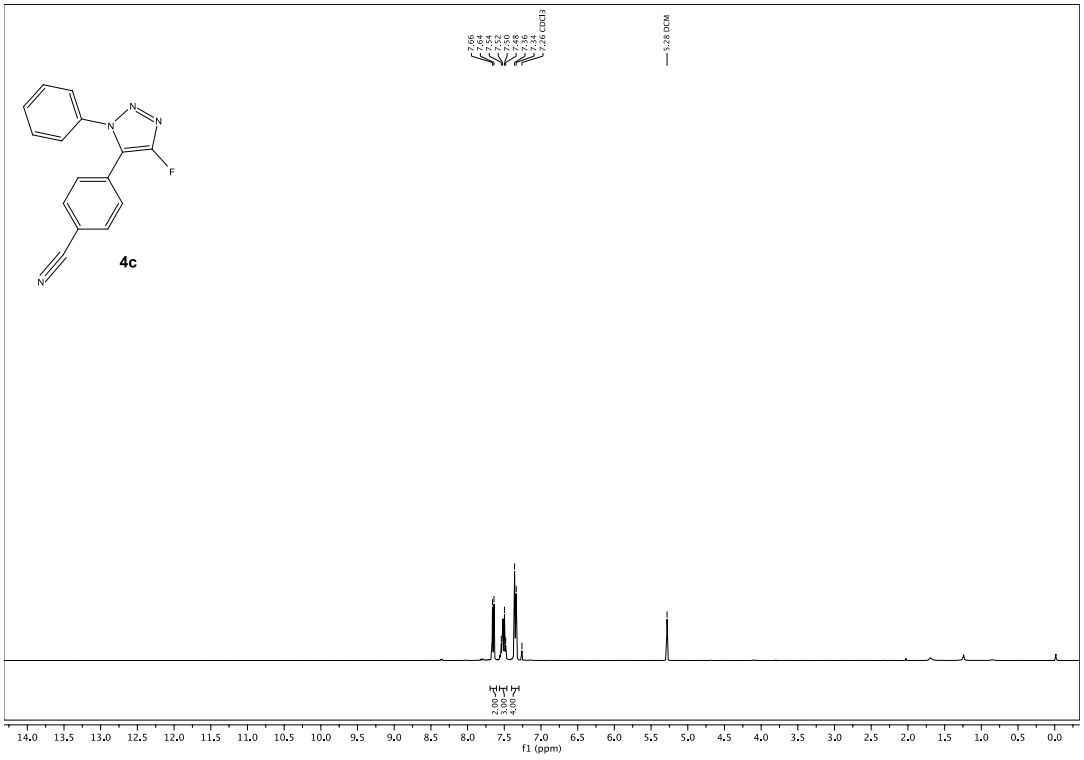
^{19}F NMR of **4b**



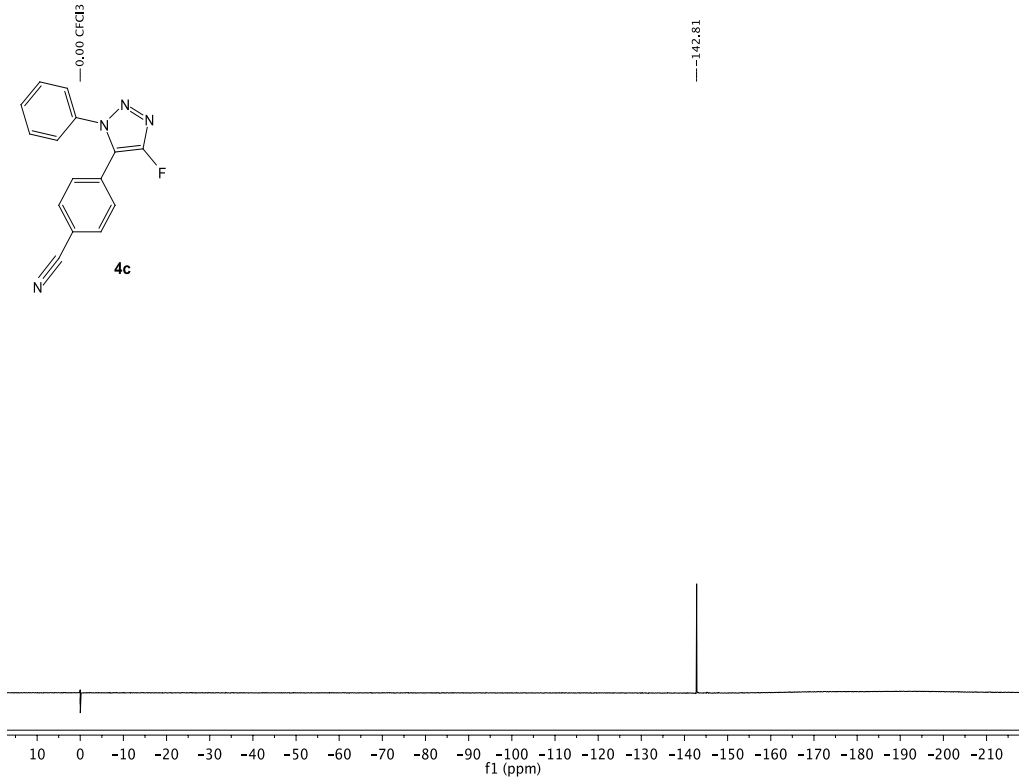
^{13}C NMR of **4b**



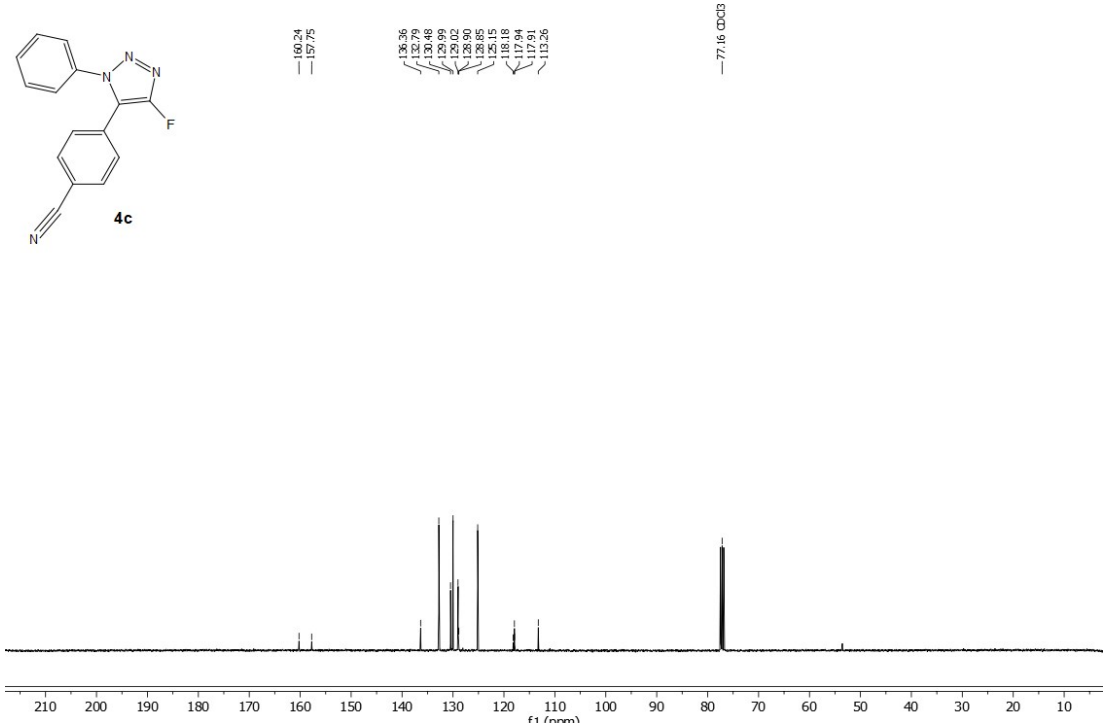
^{1}H NMR of **4c**



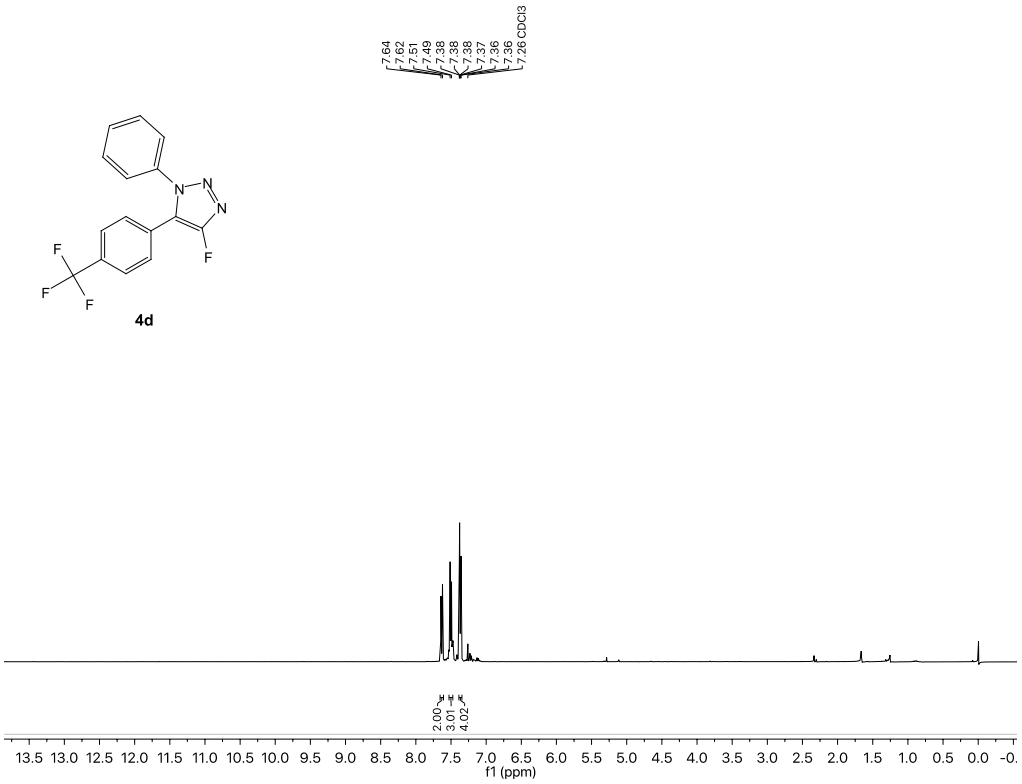
^{19}F NMR of **4c**



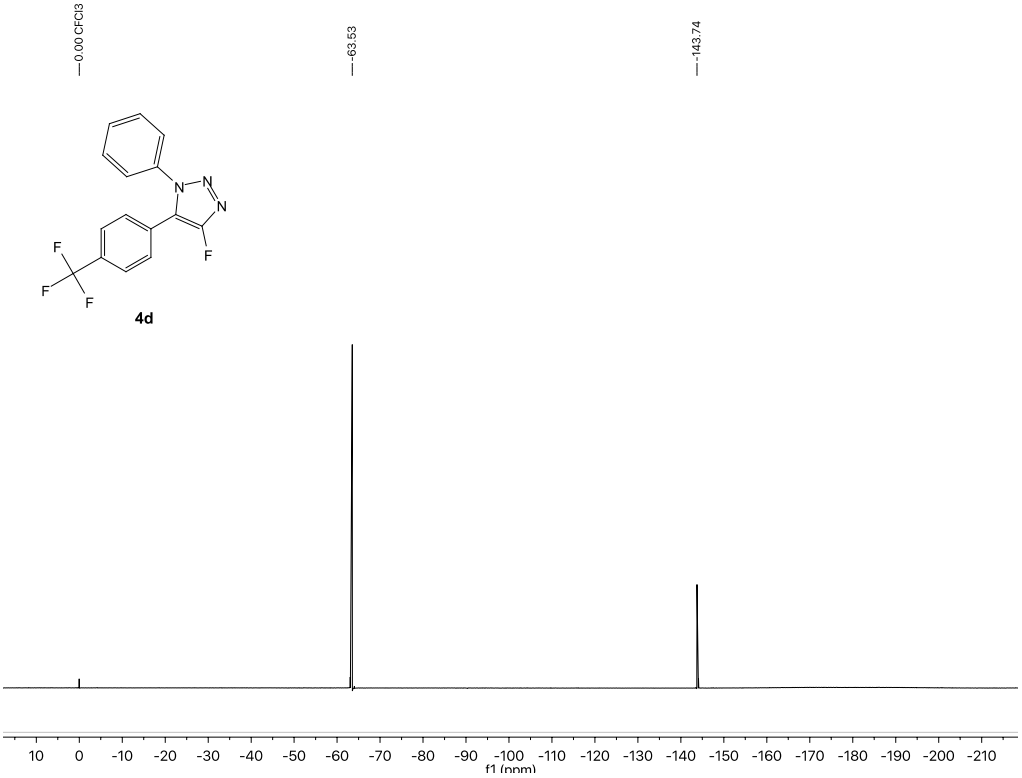
^{13}C NMR of **4c**



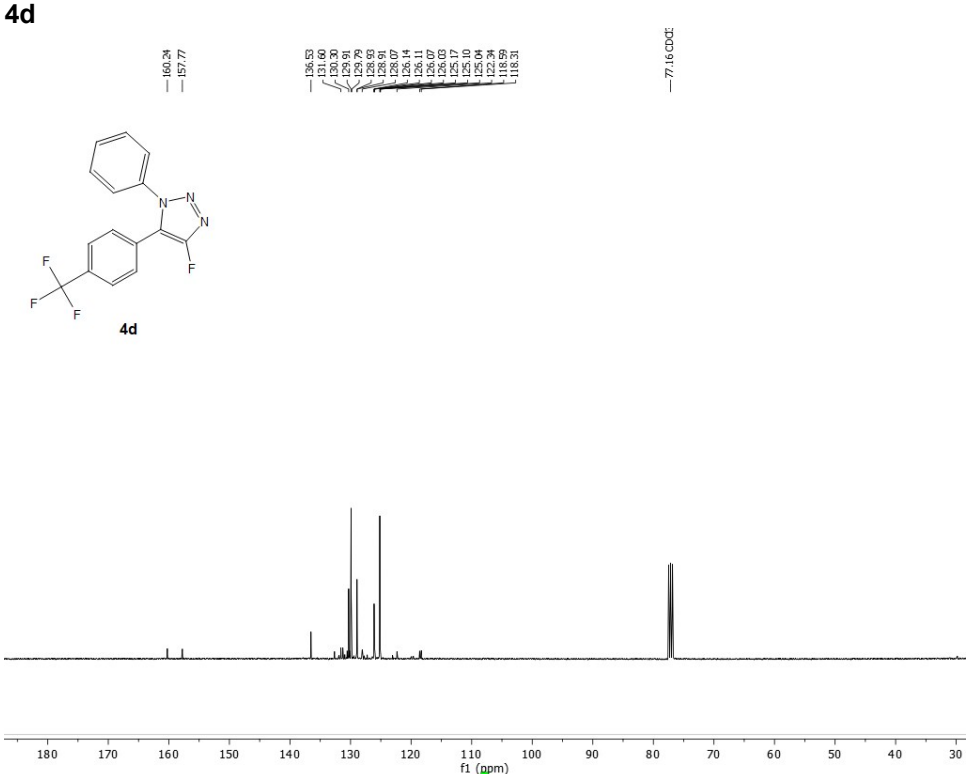
^{1}H NMR of **4d**



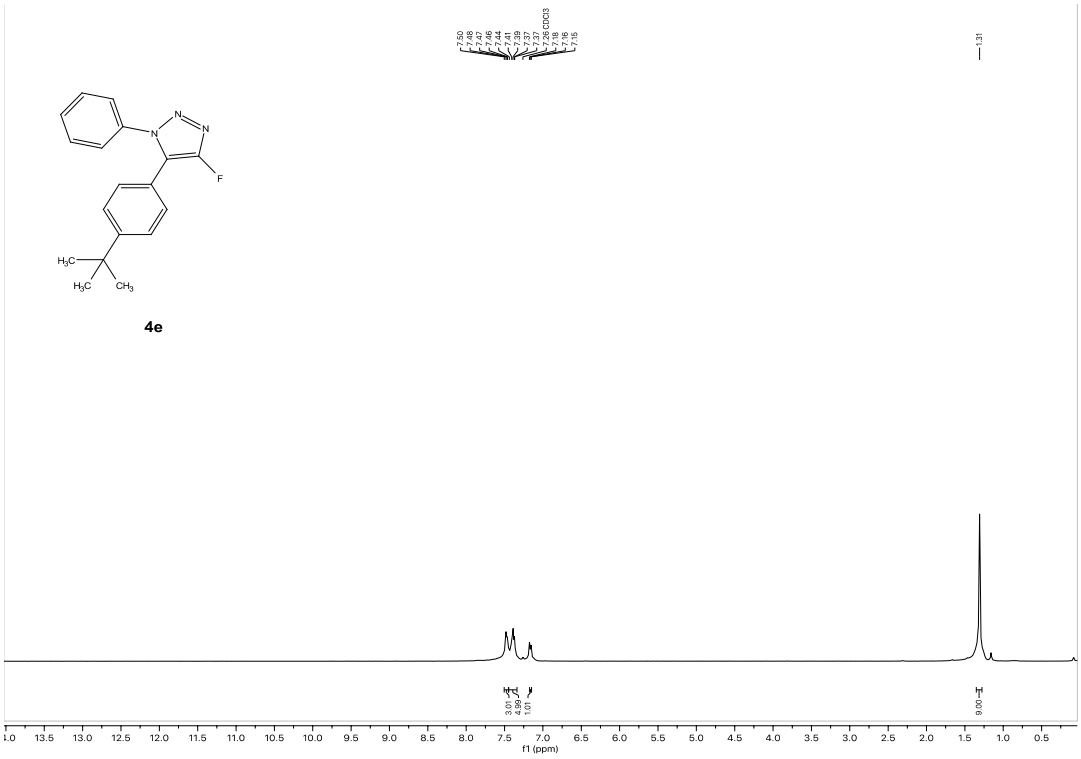
^{19}F NMR of **4d**



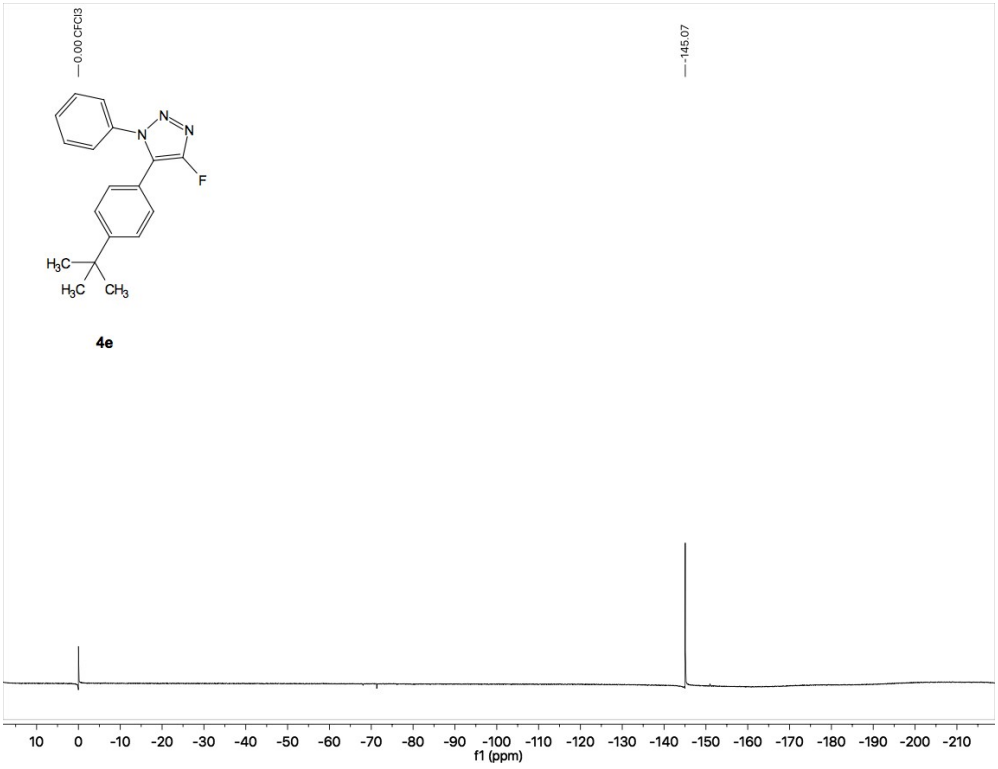
^{13}C NMR of **4d**



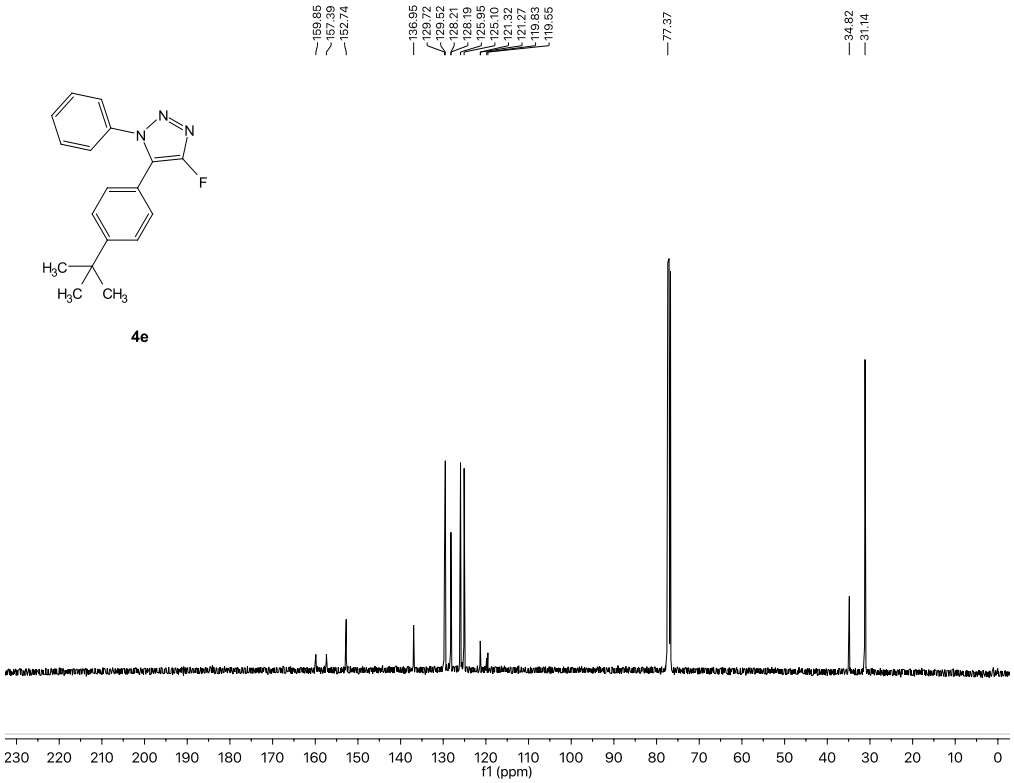
^{1}H NMR of **4e**



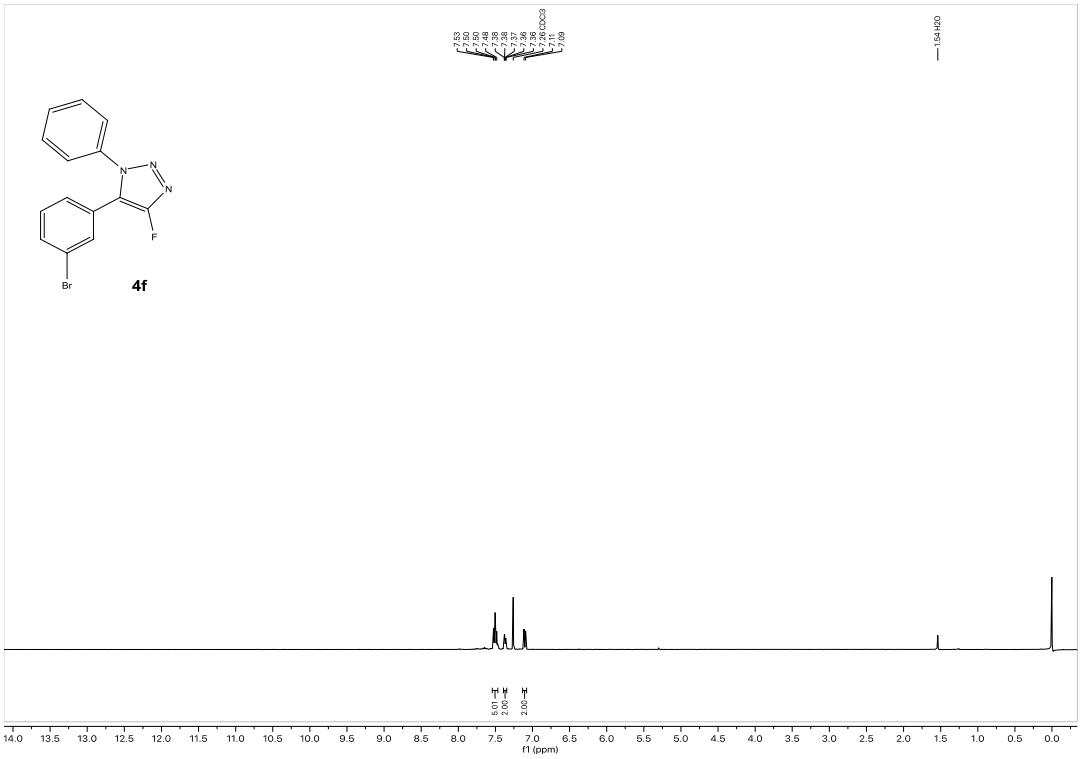
^{19}F NMR of **4e**



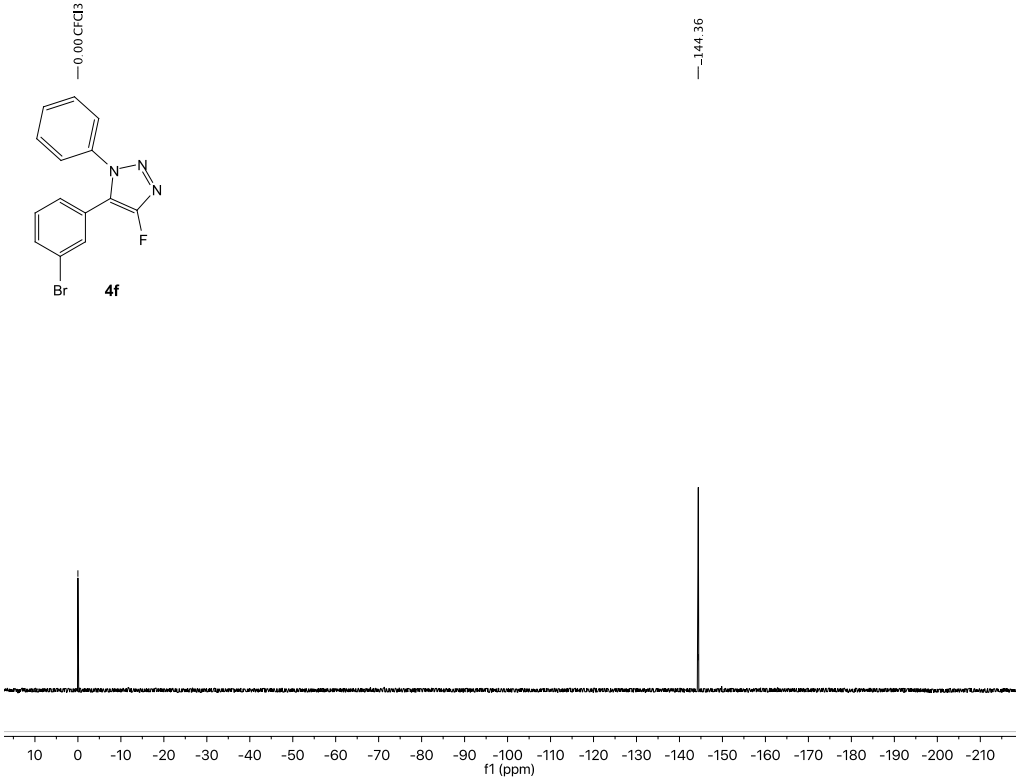
^{13}C NMR of **4e**



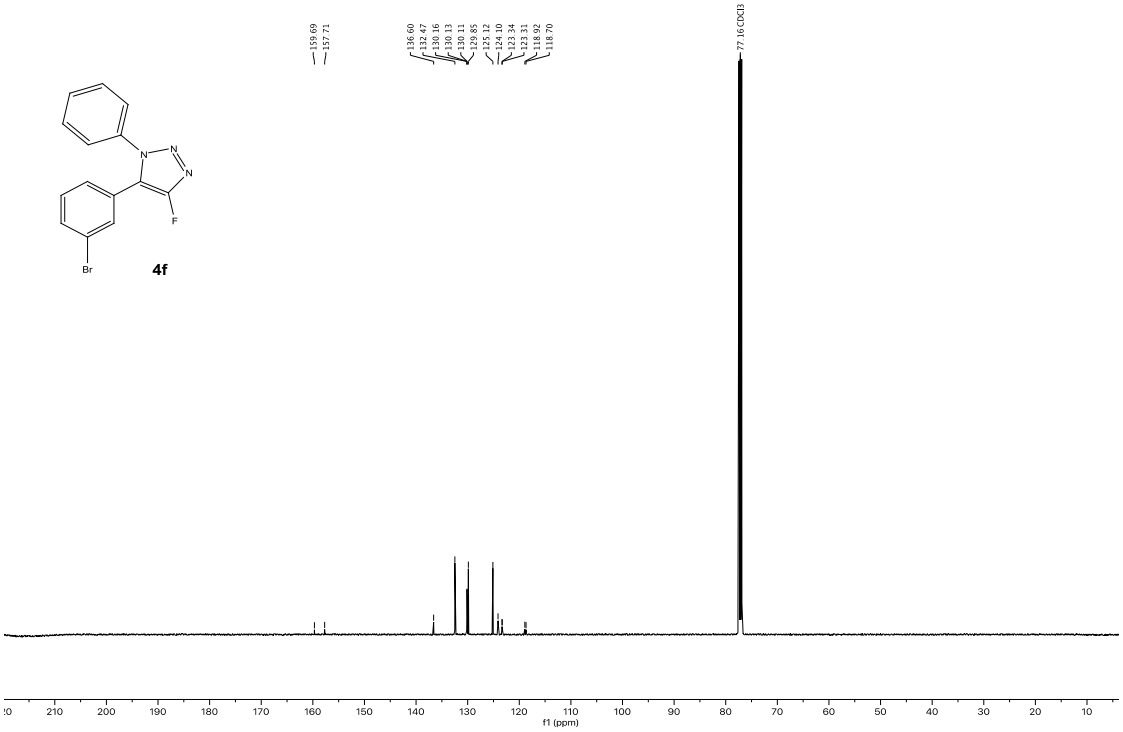
^{1}H NMR of **4f**



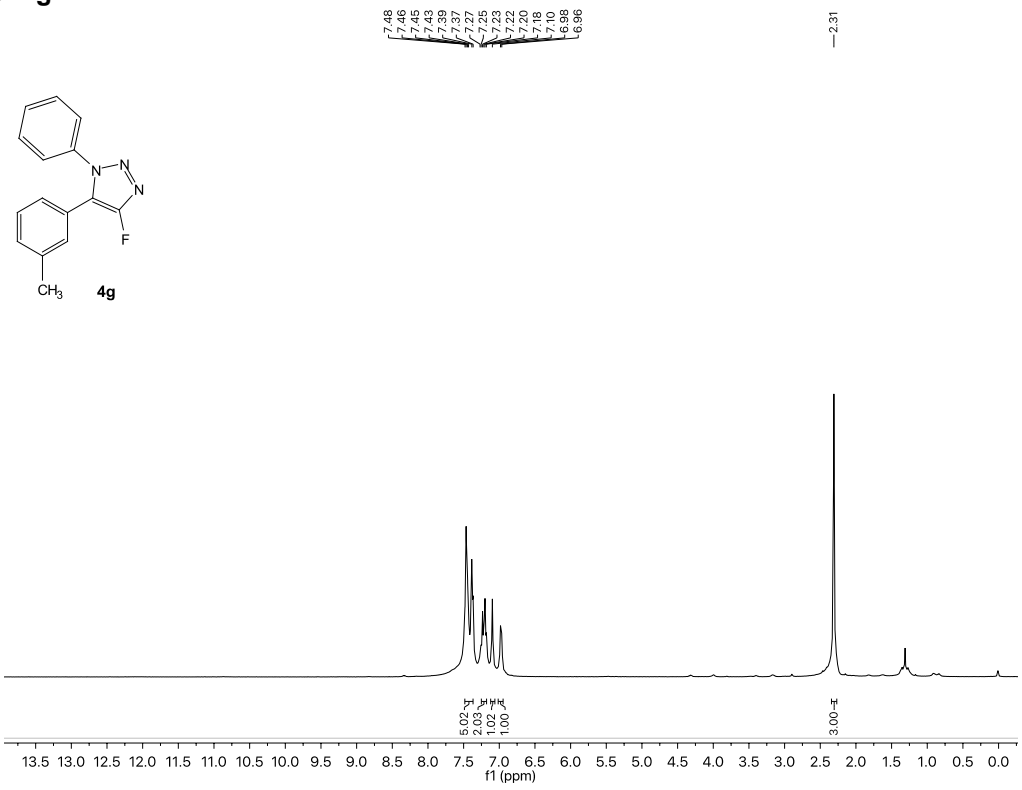
^{19}F NMR of **4f**



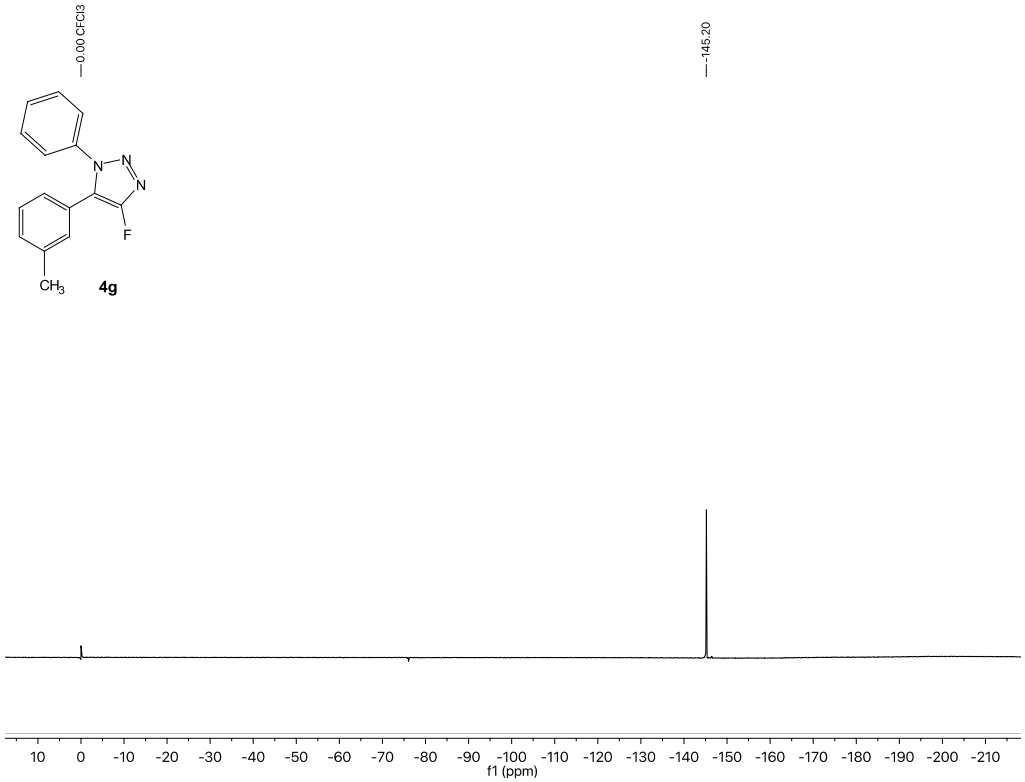
^{13}C NMR of **4f**



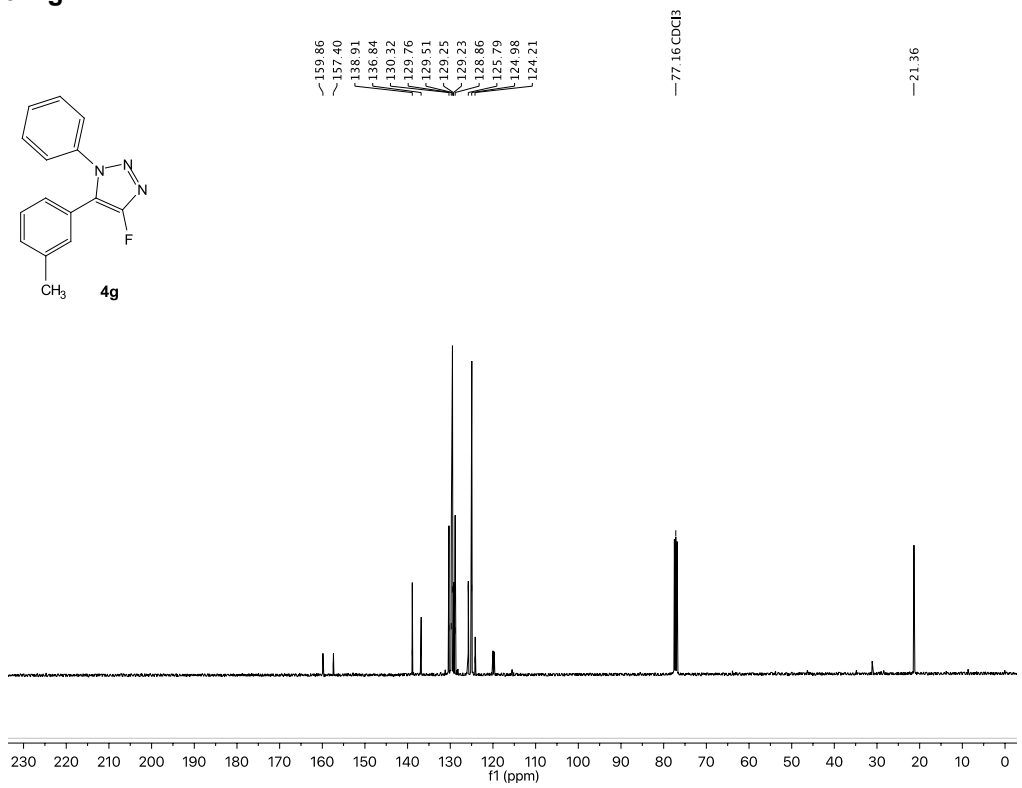
^{1}H NMR of **4g**



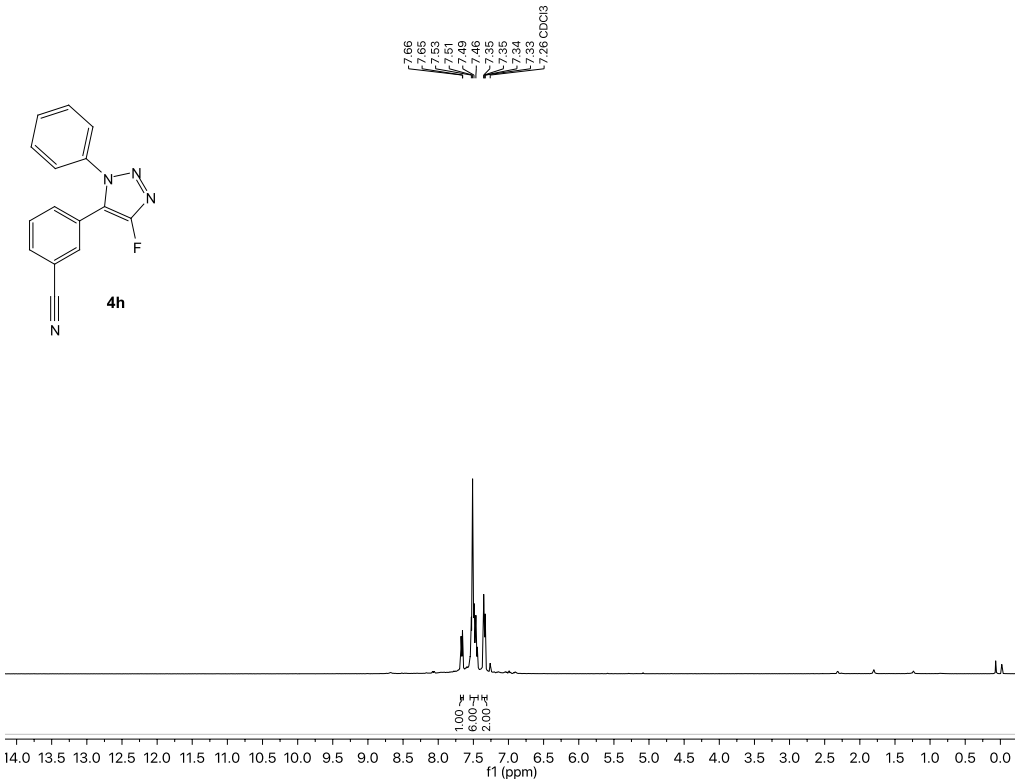
^{19}F NMR of **4g**



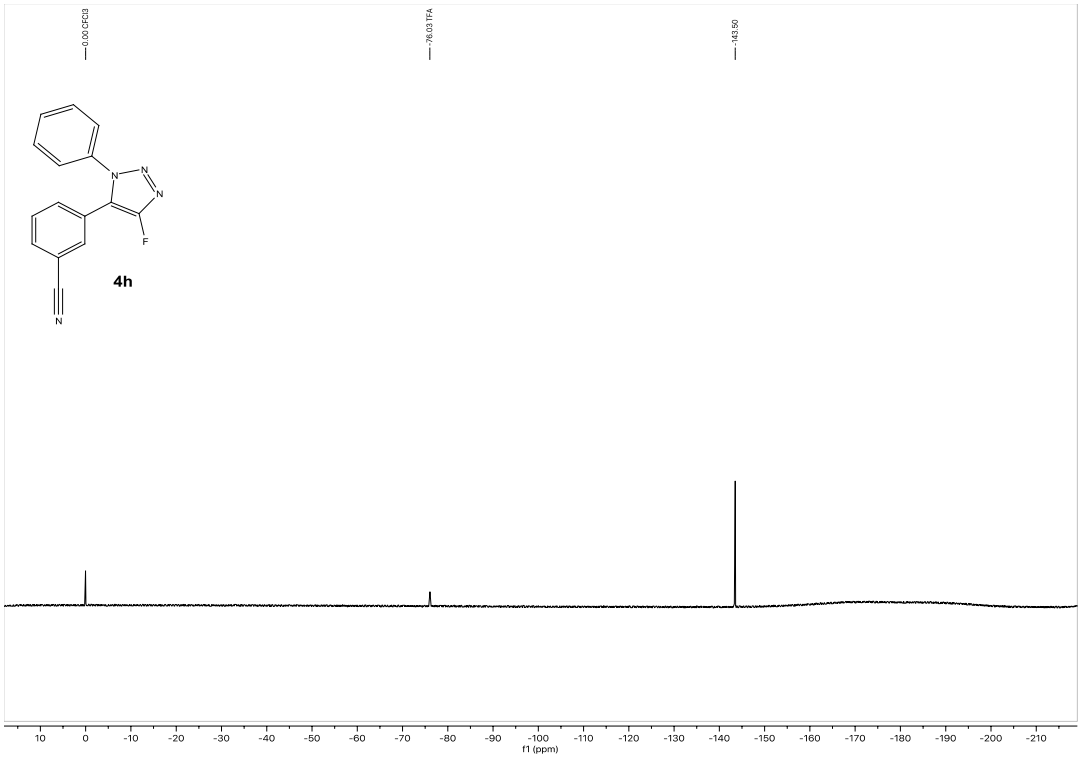
^{13}C NMR of **4g**



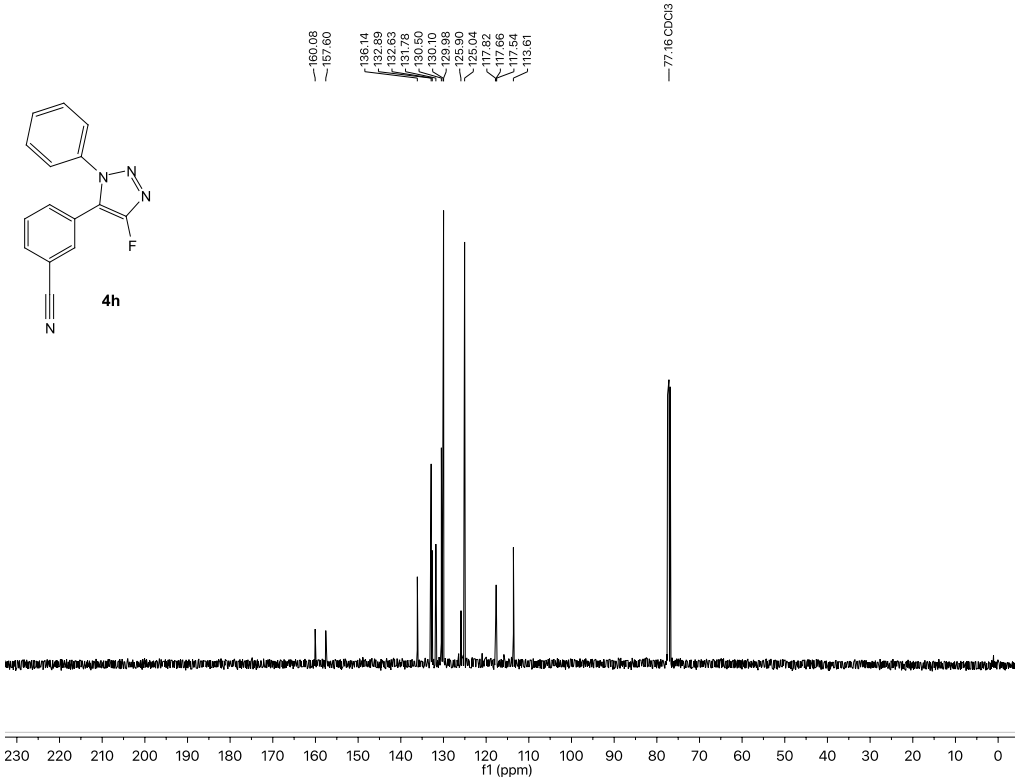
^{1}H NMR of **4h**



^{19}F NMR of **4h**



^{13}C NMR of **4h**


160.08
157.60
136.14
132.89
132.63
131.78
130.50
130.10
129.98
125.90
125.04
117.82
117.66
117.54
113.61
77.16 CDCl3
N
N
N
F
N
4h
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

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