Supporting Information

Catalyst-free Geminal Aminofluorination of *ortho*-Sulfonamide-Tethered Alkylidenecyclopropanes *via* Wagner-Meerwein Rearrangement

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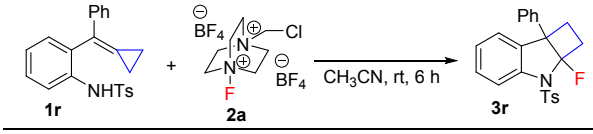
General Remarks

^{1}H and ^{13}C NMR spectra were recorded at 400 MHz, respectively. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad resonance. HRMS spectra were recorded by ESI method. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Mass spectra were recorded by ESI, and HRMS was measured on a HP-5989 instrument. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. X-ray structure was determined on a Bruker Smart-1000 X-ray Diffraction meter. The employed solvents were dried up by standard methods when necessary. Commercially obtained reagents such as “F” reagent 2a (Selectfluor et al.), S1 (anthranilic acid derivatives, 2-aminobenzophenone derivatives, 2-aminobenzonitrile derivatives), MeLi, RMgCl or RMgBr, nBuLi, AcOH et al. were used without further purification. All reactions were monitored by TLC with silica gel coated plates (Huanghai GF254). Flash column chromatography was performed by using 300-400 mesh silica gel eluting with ethyl acetate and petroleum ether at increased pressure. Abbreviations are reported as follows: EA = ethyl acetate, DCM = dichloromethane, DCE = 1,2-dichloroethane, MeOH = methanol, THF = tetrahydrofuran, DMF = N,N-dimethylformamide, Ns = 4-nitrobenzenesulfonyl, Ts = 4-methylbenzenesulfonyl, Ms = methanesulfonyl, Bz = Bznzoyl, Ac = Acetyl, TFA = trifluoroacetic acid, Tf = trifluoromethanesulfonyl, Nf = perfluoro-1-butanesulfonyl, NFSI = N-fluorobenzenesulfonimide.

Screen of reaction conditions

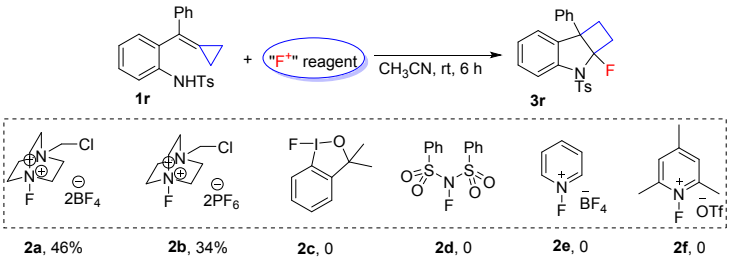
Table S1. Screen of reaction conditions on solvent.[a,b]



entry[a]	**2a** (equiv)	solvent	T/ °C	time/h	yield (%)[b]
1	1.0	MeCN	rt	8	trace
2	1.5	MeCN	rt	8	35
3	2.0	MeCN	rt	8	40
4	3.0	MeCN	rt	8	46
5	3.0	CH_3CH_2CN	rt	8	trace
6	3.0	PhCN	rt	8	trace
7	3.0	DMF	rt	8	trace
8	3.0	DMSO	rt	8	N.D.
9	3.0	MeOH	rt	8	<1%
10	3.0	^{t}BuOH	rt	8	<1%
11	3.0	$CHCl_3$	rt	8	<1%
12	3.0	acetone	rt	8	<5%
13	3.0	EA	rt	8	N.D.
14	3.0	THF	rt	8	N.D.
15	3.0	DCE	rt	8	N.D.
16	3.0	PhMe	rt	8	N.D.
17	3.0	MeCN	0	8	19
18	3.0	MeCN	60	8	N.D.

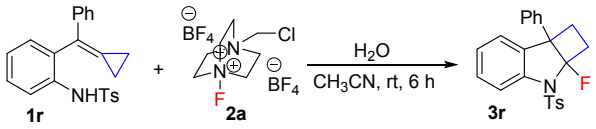
[a] All reactions were carried out with **1r** (0.1 mmol) and "F" source (0.3 mmol) in solvent (1.0 mL) at ambient temperature for 8 h. [b] ^{19}F NMR yields using 1-fluoronaphthalene as an internal standard.

Table S2. Screen of reaction conditions on "F" reagent.[a,b]



[a] All reactions were carried out with **1r** (0.1 mmol) and "F" source (0.3 mmol) in solvent (1.0 mL) at ambient temperature for 8 h. [b] ^{19}F NMR yields using 1-fluoronaphthalene as an internal standard.

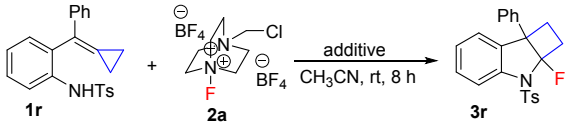
Table S3. Screen of reaction conditions on equivalent of water.[a,b]



entry[a]	H_2O (eq.)	solvent	T/ °C	time/h	yield (%)[b]
1	0.5	MeCN	R. T.	8	45
2	1.0	MeCN	R. T.	8	44
3	2.0	MeCN	R. T.	8	45
4	5.0	MeCN	R. T.	8	47
5	10	MeCN	R. T.	8	42
6	4Å MS	MeCN	R. T.	8	47

[a] All reactions were carried out with **1r** (0.1 mmol) and "F" source (0.3 mmol) in CH_3CN (1.0 mL) at ambient temperature for 8 h. [b] ^{19}F NMR yields using 1-fluoronaphthalene as an internal standard.

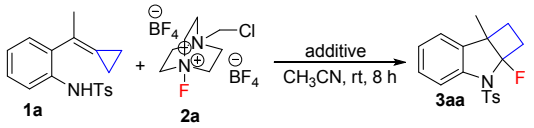
Table S4. Screen of reaction conditions on additives.[a,b]



entry[a]	additive	equiv	yield (%)[b]
1	InF_3	0.1	53
2	CuBr	0.2	N.R.
3	$Ce(OTf)_3$	0.2	N.R.
4	$Bi(OTf)_3$	0.2	N.R.
5	$PhI(OAc)_2$	3.0	52
6	$PhI(CO_2CF_3)_2$	0.2	58
7	SiO_2	3.0	45
8	TfOH	0.2	28
9	$Yb(OTf)_3$	0.2	35
10	$ZnCl_2$	0.2	39
11	Quinine	0.2	35
12	TsOH	0.2	16
13	$AgNO_3$	0.2	19
14	$Na_2S_2O_8$	3.0	45
15	^tBuOOH	3.0	27
16	NIS	3.0	N.R.
17	$BF_3 \cdot Et_2O$	3.0	N.R.
18	K_2CO_3	3.0	25
19	$AgNTf_2$	0.2	46
20	$MgSO_4$	3.0	41

[a] All reactions were carried out with **1r** (0.1 mmol) and "F" source (0.3 mmol) in CH_3CN (1.0 mL) at ambient temperature for 8 h. [b] ^{19}F NMR yields using 1-fluoronaphthalene as an internal standard.

Table S5. Screen of reaction conditions using **1a** as template substrate.[a,b,c]

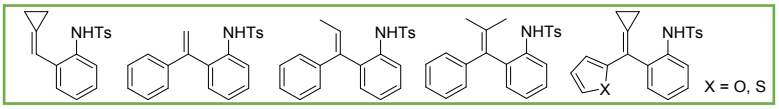


1a **2a** **3aa**

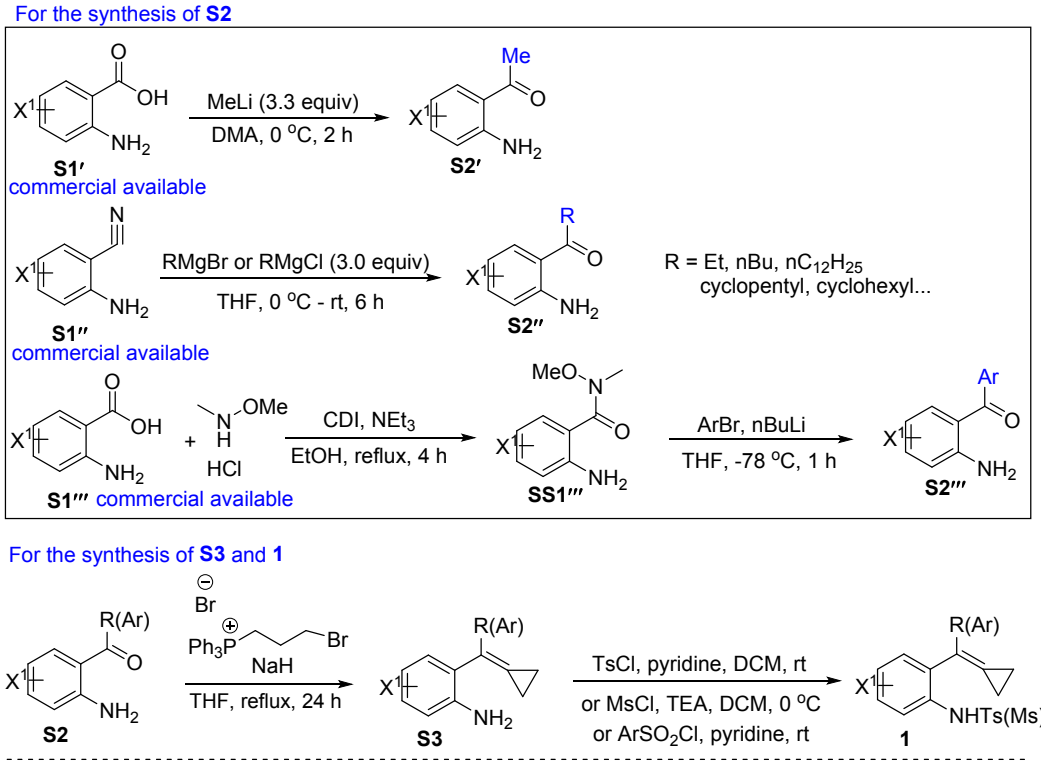
entry[a]	additive	equiv (x)	yield[b] (%)
1	AgF	2	30
2	InF_3	2	46
3	PivOH	2	68
4	PhCOCOOH	2	74
5	CH_3COOH	2	76
6	CF_3COOH	2	-
7	adipic acid	2	75
8	citric acid	2	66
9	2,6-lutidine	2	31
10	DABCO	2	17
11	phenol	2	46
12	-	-	70
13	$NaHCO_3$	2	36
14	CH_3COOH	0.5	76
15	CH_3COOH	1	80
16	CH_3COOH	5	82
17	CH_3COOH	10	85 (81[c])
18	CH_3COOH	100	65
19	PhCOOH	10	79 (73[c])

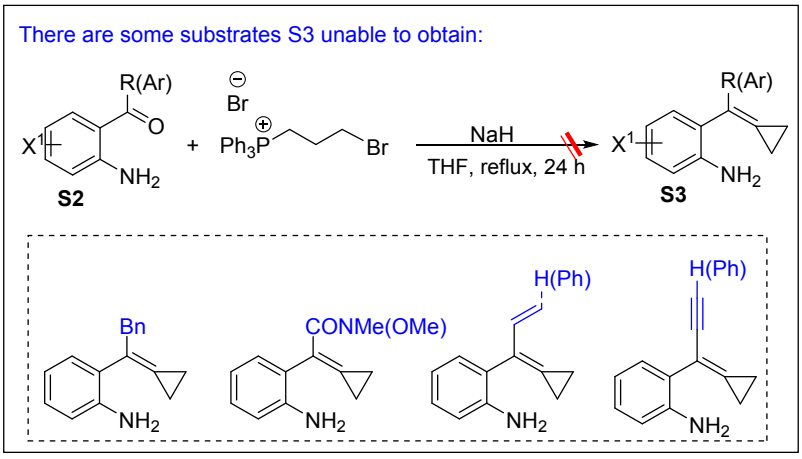
[a] All reactions were carried out with **1a** (0.1 mmol), "F" source (0.3 mmol) and additives in CH_3CN (1.0 mL) at ambient temperature for 6 h. [b] ^{19}F NMR yields using 1-fluoronaphthalene as an internal standard. [c] Isolated yields.

No reaction occurred for these substrates:



General procedure for the preparation of compounds 1a-1ac





Compounds **S2**,[1,2,3] **S3**[4] and several compounds **1**[5] were prepared according to the previous literature.

General procedure A: For the synthesis of **S2'**[1]:

To a solution of **S1'** (30 mmol, 1.0 equiv) in DMA (50 mL, superdry) was added MeLi (49.5 mL, 99 mmol, 3.3 equiv, 2.0 M) dropwise at 0 °C and then the mixture was stirred at 0 °C for 2 h, then 100 mL 1.0 N HCl was added for quenching the reaction. After separation, the resulting aqueous mixture was extracted with EA (3 x 30 mL), and the combined extracts were washed with brine,

dried over anhydrous Na_2SO_4. After the solution was filtered and the solvent was evaporated under vacuum, the residue was purified by a flash chromatograph on silica gel using PE/EA (30:1) as the eluent to yield the products **S2'**.

General procedure B: For the synthesis of **S2''**[2]:

To a solution of **S1''** (30 mmol, 1.0 equiv) in THF (50 mL, superdry) was added RMgBr or RMgCl (90 mmol, 3.0 equiv) dropwise at 0 °C and then the mixture was stirred at rt for 6 h, then 100 mL saturated NH_4Cl aqueous solution was added for quenching the reaction, after separation, the resulting aqueous mixture was extracted with EA (3 x 30 mL), and the combined extracts were washed with brine, dried over anhydrous Na_2SO_4. After the solution was filtered and the solvent was evaporated under vacuum, the residue was purified by a flash chromatograph on silica gel using PE/EA (30:1) as the eluent to yield the products **S2''**.

General procedure C: For the synthesis of **S2'''**[3]:

A solution of **S1'''** (30 mmol, 1.0 equiv) and CDI (30 mmol, 1.0 equiv) in dry THF (100 mL) was stirred at rt for 2 h, then, a solution of N,O-dimethylhydroxylamine hydrochloride (2.93 g, 30 mmol, 1.0 equiv) and NEt_3 (5 mL, 36 mmol, 1.2 equiv) in 50 mL dry THF was added and the mixture was stirred at rt overnight. The reaction mixture was then poured onto an equal volume of ice and saturated Na_2CO_3. The THF was then removed by rotary evaporation, and the resulting aqueous mixture was extracted with EA (3 x 30 mL), and the combined extracts were washed with water and brine, dried over anhydrous Na_2SO_4. After the solution was filtered and the solvent was evaporated under vacuum, the residue was purified by a flash chromatograph on silica gel using PE/EA (1:1) as the eluent to yield the products **SS1'''**.

Then, **n-BuLi** (2.0 equiv) was added slowly to a mixture of **SS1'''** and **ArBr** (1.0 equiv) in dry THF over 1.0 h in a flamed-dried 100 mL Schlenk tube at -78 °C under the protection of Ar atmosphere, and 1.0 N HCl (2.0 equiv) was added at -78 °C. The mixture was extracted with EA (3 x 20 mL), and the combined extracts were washed with saturated Na_2CO_3, dried over anhydrous Na_2SO_4. After the solution was filtered and the solvent was evaporated under vacuum, the residue was purified by a flash chromatograph on silica gel using PE/EA (30:1) as the eluent to yield the products **S2'''**.

General procedure D: For the synthesis of **S3**[4]:

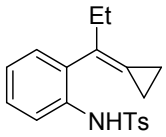
A solution of (4-bromobutyl)triphenylphosphonium bromide (1.3 equiv) and NaH (2.6 equiv) in THF (25 mL) was stirred at 75 °C under Ar atmosphere for 12 h. Afterwards, compound **S2** in THF

(10 mL) was added and the reaction solution was stirred at 75 °C until compound **S2** was consumed completely. The reaction mixture was cooled to room temperature, and the mixture was filtered through a celite pad. The filtrate was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (PE/EA (100:1-20:1) to afford the product **S3**.

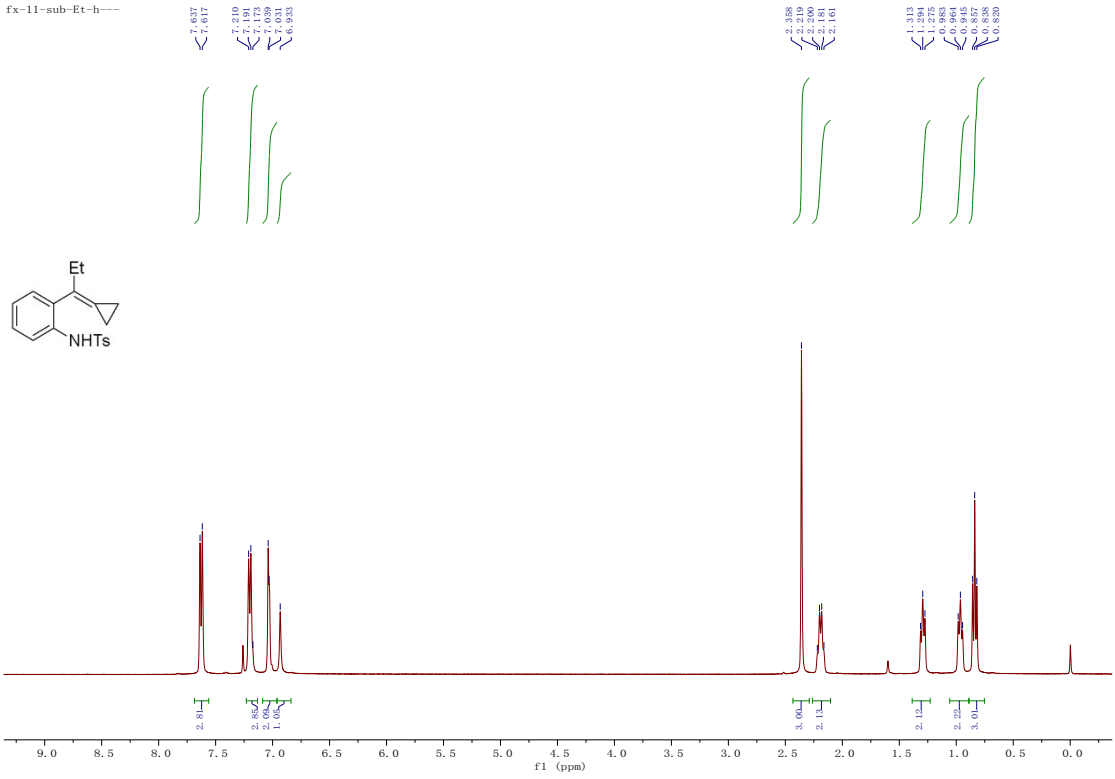
General procedure E: For the synthesis of **1**[5]:

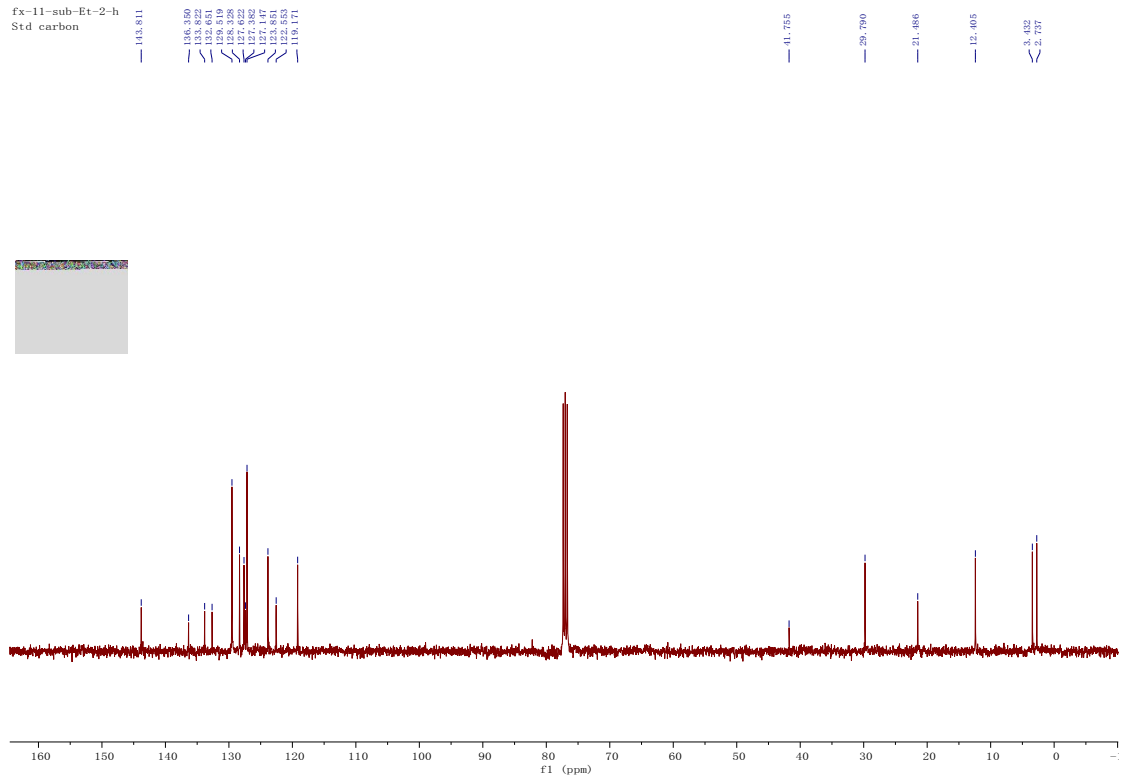
R(Ar)SO_2Cl (1.05-1.5 equiv) was added slowly to a solution of **S3** in dry DCM or pyridine at 0 °C followed the addition of NEt_3 or pyridine, and then the mixture was stirred at room temperature for 12 h (TsCl), and 0 °C for 2 h (MsCl), at rt for 6 h (BsCl, $PhSO_2Cl$). The reaction mixture was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (PE/EA (10:1) to afford the product **1**.

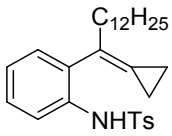
Spectroscopic data for products **1g-1y**



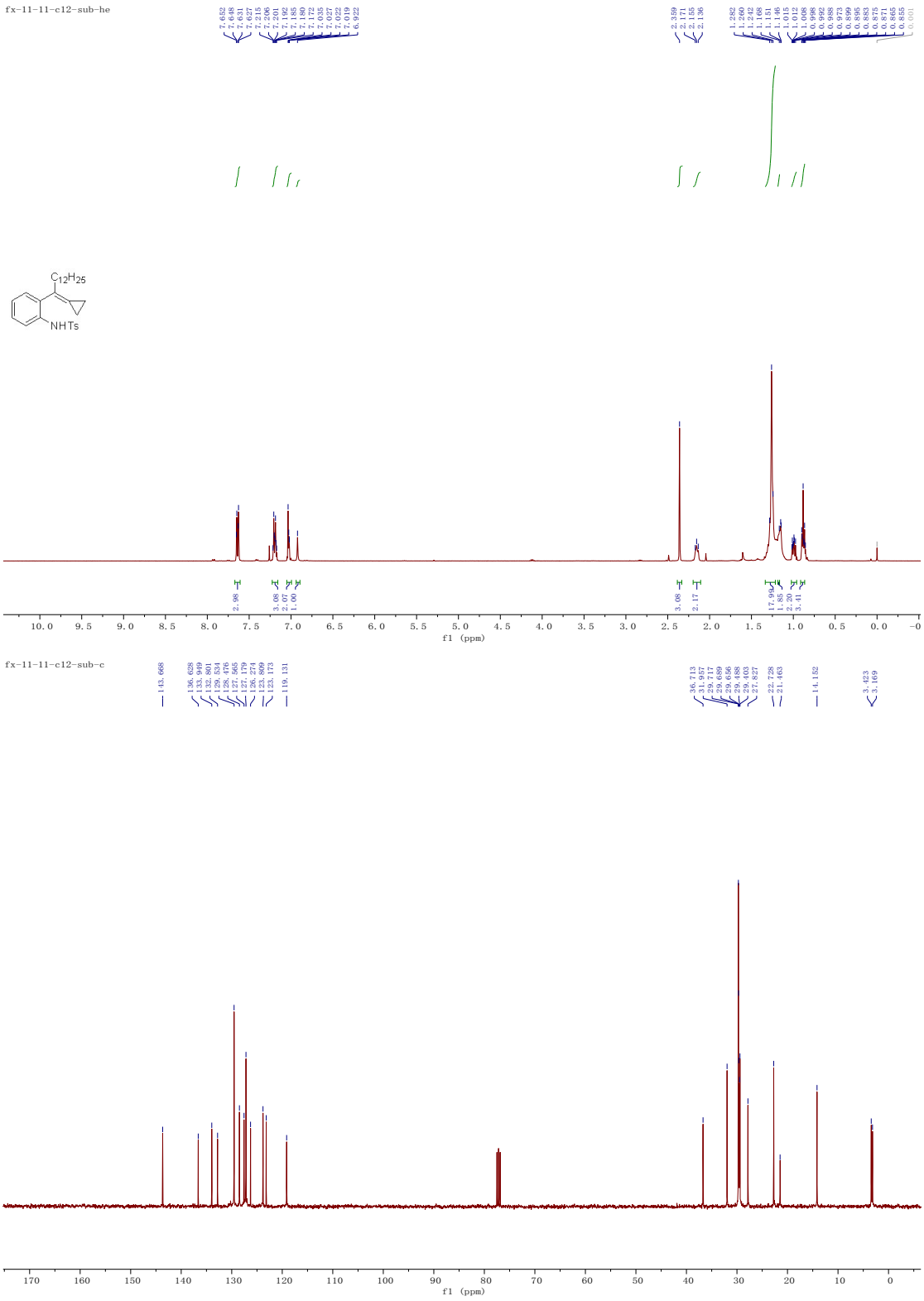
Compound 1g: A white solid (547.3 mg, 85%); M.p. 111-112 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 0.84 (t, *J* = 7.4 Hz, 3H), 0.96 (t, *J* = 7.7 Hz, 2H), 1.29 (t, *J* = 7.7 Hz, 2H), 2.19 (q, *J* = 7.7 Hz, 2H), 2.36 (s, 3H), 6.93 (s, 1H), 6.96 – 7.09 (m, 2H), 7.13 – 7.23 (m, 3H), 7.56 – 7.69 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 2.7, 3.4, 12.4, 21.5, 29.8, 41.8, 119.2, 122.6,A 123.9, 127.1, 127.4, 127.6, 128.3, 129.5, 132.7, 133.8, 136.4, 143.8. IR (neat) ν 3259, 1598, 1580, 1484, 1387, 1335, 1165, 1085, 934, 901, 814, 751, 679 cm^{-1}. HRMS (ESI) Calcd. for $C_{19}H_{25}N_2O_2S$ requires (M^++NH_4): 345.1631, Found: 345.1625.

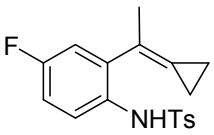






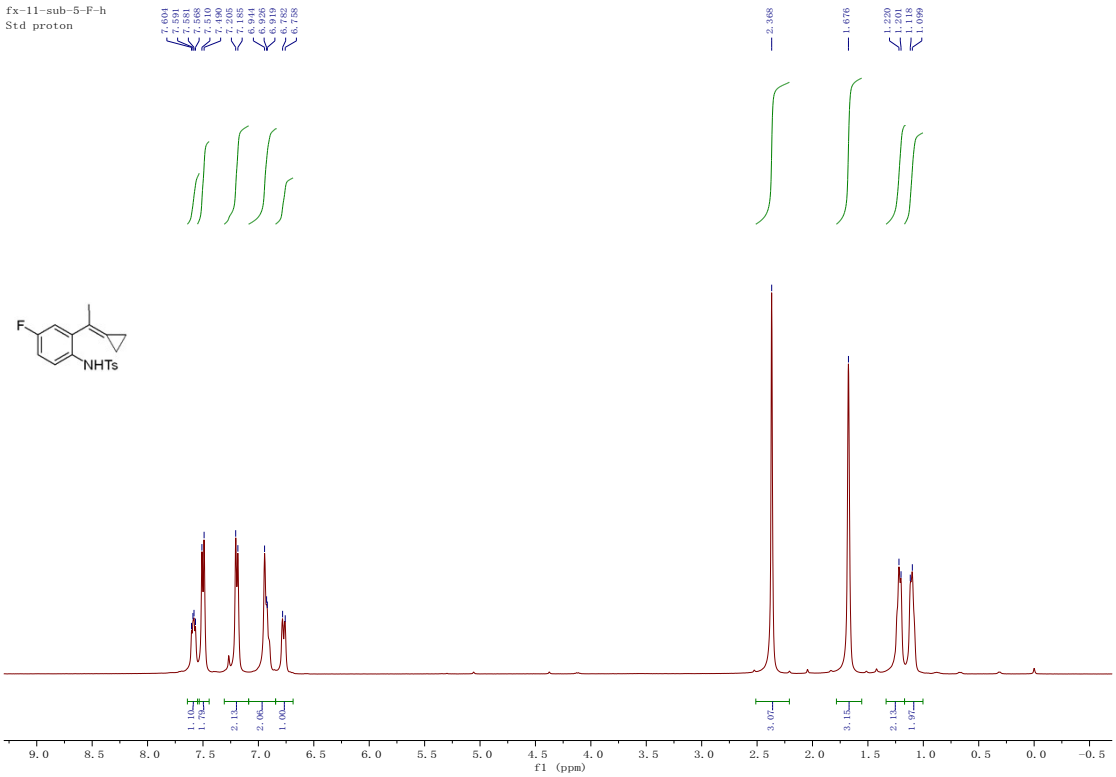
Compound 1i: A white solid (327.6 mg, 59%); M.p. 78-79 ^{o}C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 0.86 – 0.91 (m, 3H), 0.97 – 1.02 (m, 2H), 1.13 – 1.33 (m, 25H), 2.15 (t, *J* = 7.1 Hz, 2H), 2.36 (s, 3H), 6.92 (s, 1H), 7.00 – 7.05 (m, 2H), 7.17 – 7.22 (m, 3H), 7.60 – 7.67 (m, 3H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 3.2, 3.4, 14.2, 21.5, 22.7, 27.8, 29.4, 29.5, 29.66, 29.69, 29.72, 32.0, 36.7, 119.1, 123.2, 123.8, 126.3, 127.2, 127.6, 128.5, 129.5, 132.8, 133.9, 136.6, 143.7. IR (neat) ν 3267, 2977, 2954, 2922, 2850, 1600, 1571, 1487, 1459, 1378, 1340, 1166, 1093, 908, 813, 752, 723, 706, 683 cm^{-1}. HRMS (ESI) Calcd. for $C_{29}H_{45}N_2O_2S$ requires (M^++NH_4): 485.3196, Found: 485.3191.

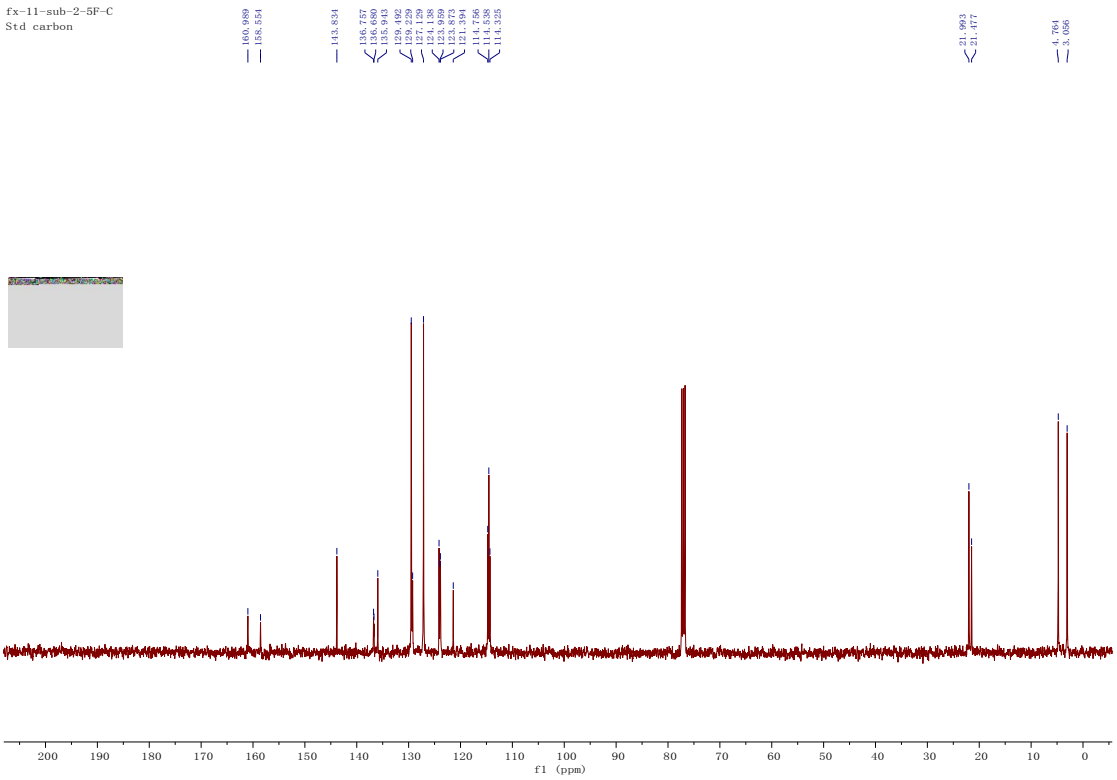


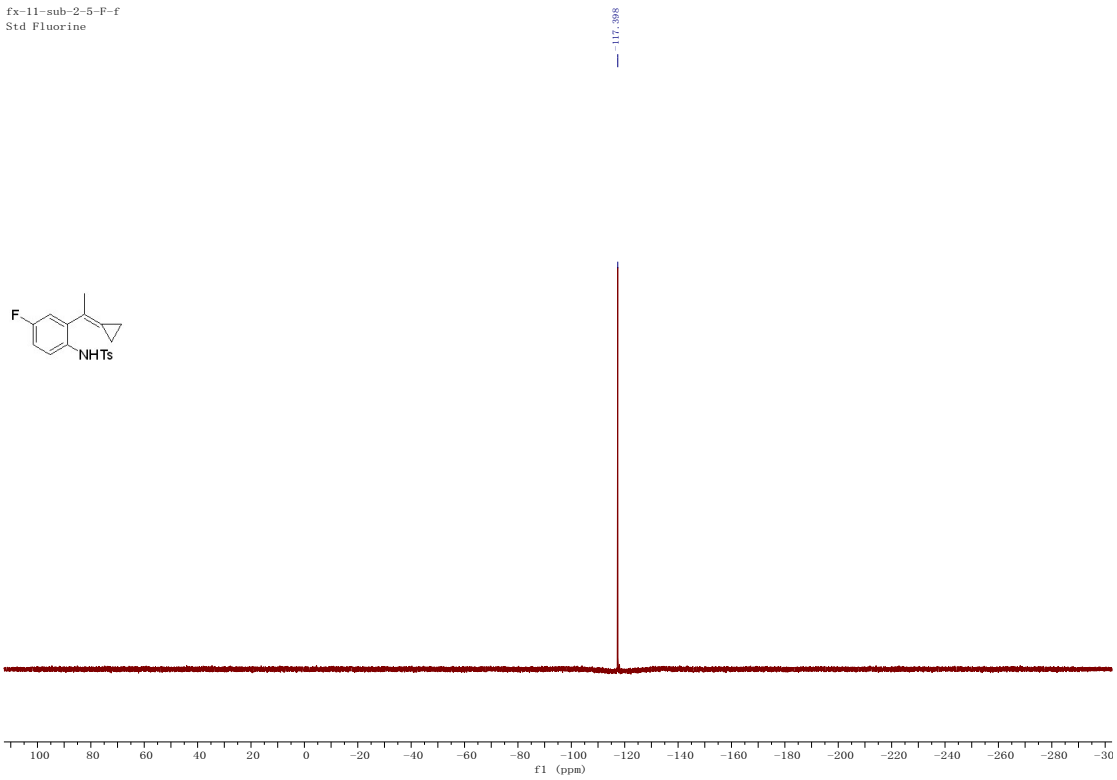


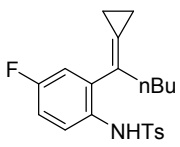
Compound 1j: A pale yellow solid (389.1 mg, 54%); M.p. 141-142 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.11 (d, *J* = 7.5 Hz, 2H), 1.21 (d, *J* = 7.5 Hz, 2H), 1.68 (s, 3H), 2.37 (s, 3H), 6.77

(d, J = 9.5 Hz, 1H), 6.84 – 7.09 (m, 2H), 7.09 – 7.31 (m, 2H), 7.44 – 7.55 (m, 2H), 7.59 (dd, J = 9.1, 5.3 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 3.1, 4.8, 21.5, 22.0, 114.3, 114.5, 114.8, 121.4, 123.9 (d, J = 8.6 Hz), 124.1, 127.1, 129.2, 129.5, 135.9, 136.7 (d, J = 7.7 Hz), 143.8, 159.8 (d, J = 244.9 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -117.4. IR (neat) ν 3255, 2978, 2919, 2845, 1609, 1598, 1494, 1378, 1329, 1162, 1091, 896, 874, 815, 676 cm^{-1}. HRMS (ESI) Calcd. for $C_{18}H_{22}FN_2O_2S$ requires (M^++NH_4): 349.1381, Found: 349.1376.



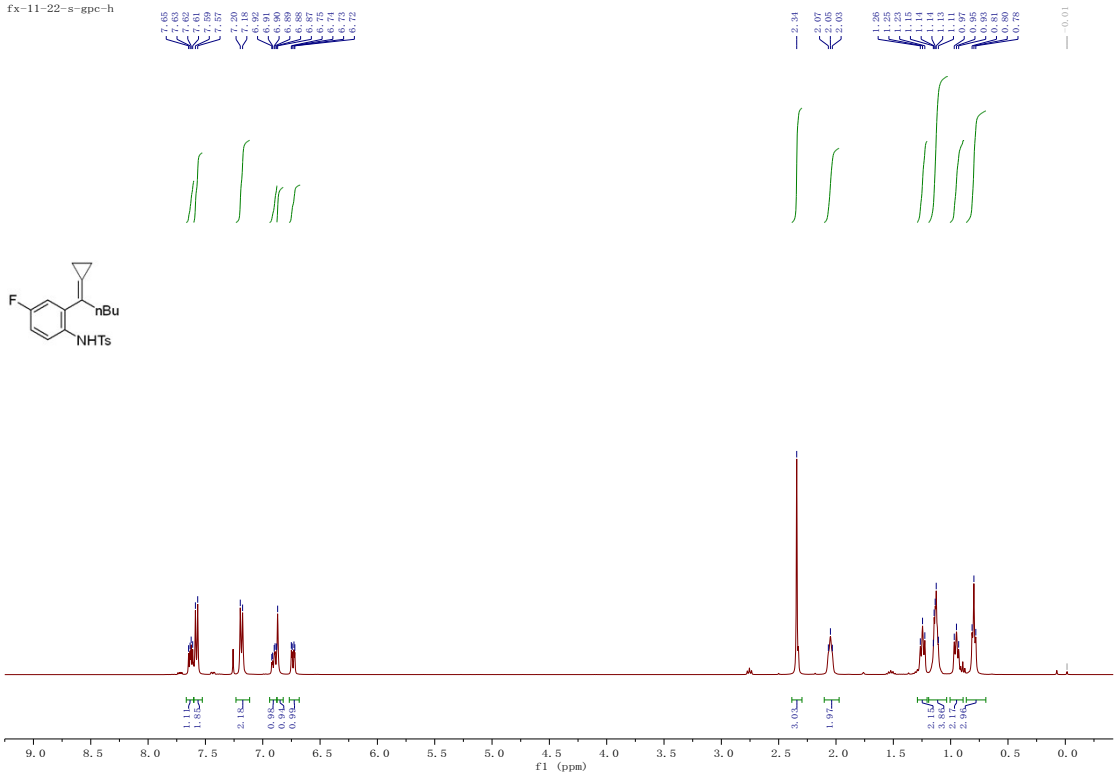


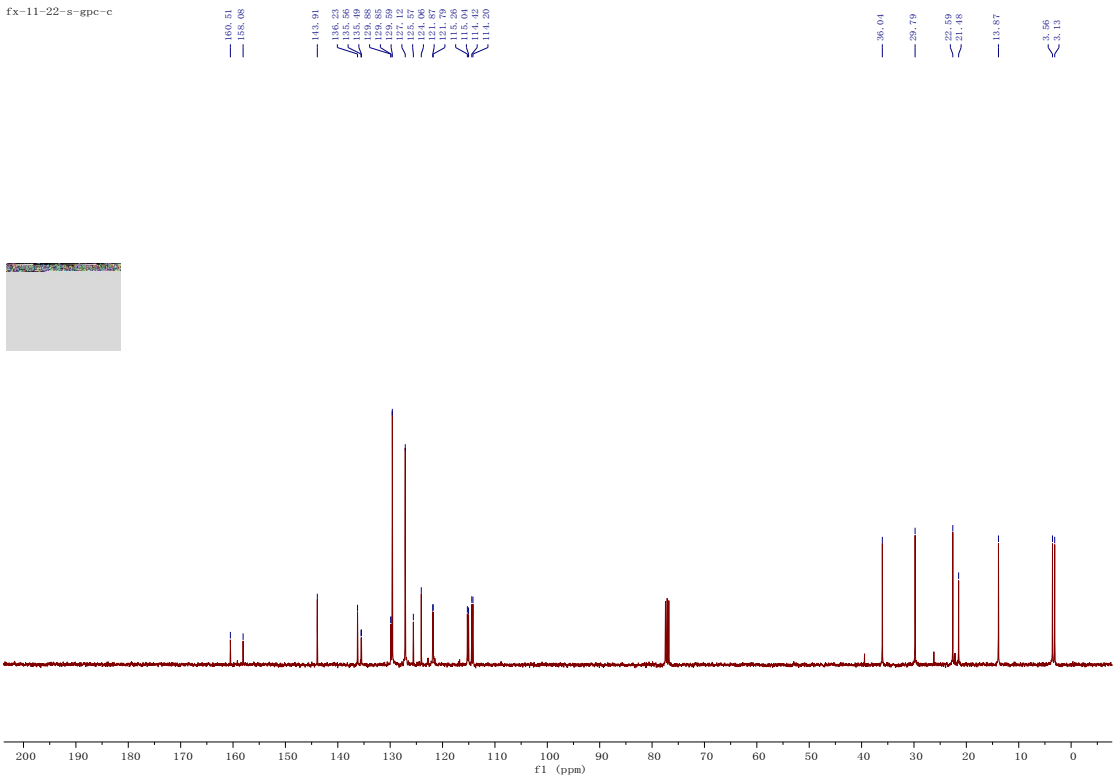


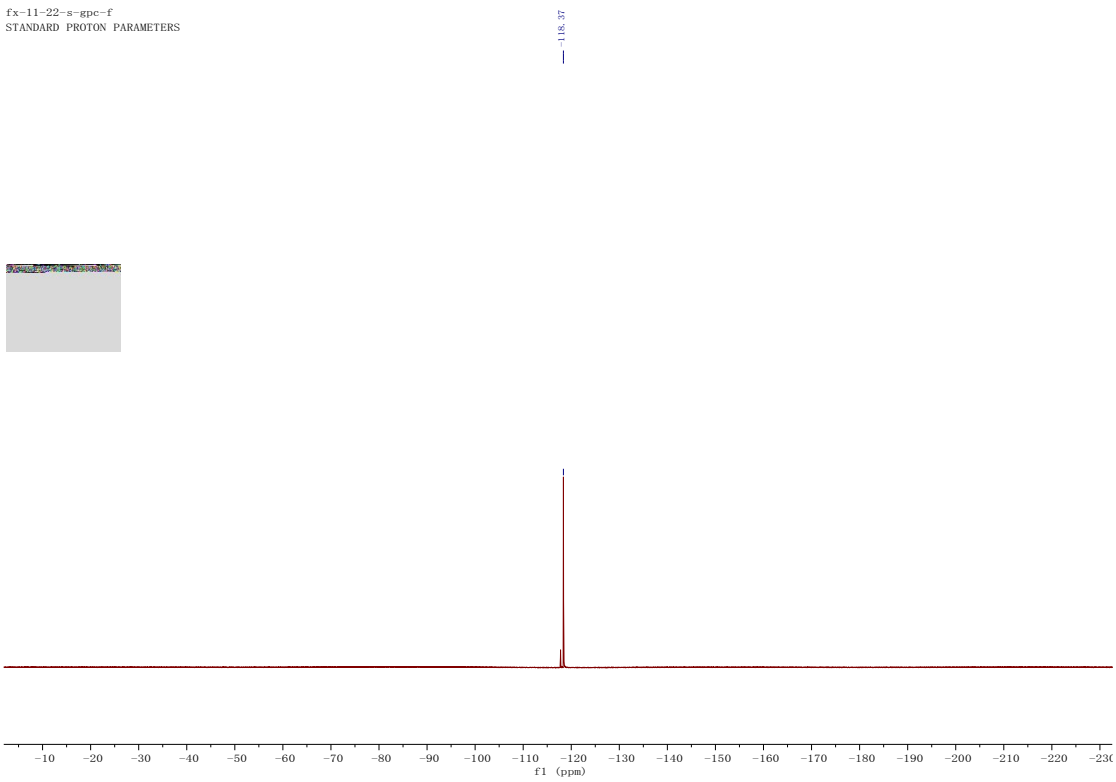


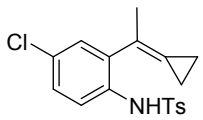
Compound 1k: A yellow solid (395.4 mg, 35%); M.p. 81-82 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 0.69 – 0.86 (m, 3H), 0.89 – 1.01 (m, 2H), 1.13 (h, *J* = 3.0 Hz, 4H), 1.25 (t, *J* = 7.9 Hz, 2H),

2.05 (t, J = 6.9 Hz, 2H), 2.34 (s, 3H), 6.74 (dd, J = 9.2, 3.0 Hz, 1H), 6.87 (s, 1H), 6.90 (ddd, J = 8.4, 4.2 Hz, 1H), 7.11 – 7.23 (m, 2H), 7.53 – 7.60 (m, 2H), 7.63 (dd, J = 9.0, 5.2 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 3.1, 3.6, 13.9, 21.5, 22.6, 29.8, 36.0, 114.2, 114.4, 115.0, 115.3, 121.8 (d, J = 8.3 Hz), 124.1, 125.6, 127.1, 129.6, 129.9 (d, J = 2.7 Hz), 135.5 (d, J = 7.6 Hz), 136.2, 143.9, 159.3 (d, J = 244.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, TMS) δ -118.4. IR (neat) ν 323254, 2977, 2941, 1657, 1592, 1478, 1376, 1332, 1166, 1091, 901, 814, 707, 682 cm^{-1}. HRMS (ESI) Calcd. for $C_{21}H_{28}FN_2O_2S$ requires (M^++NH_4): 391.1850, Found: 391.1842.



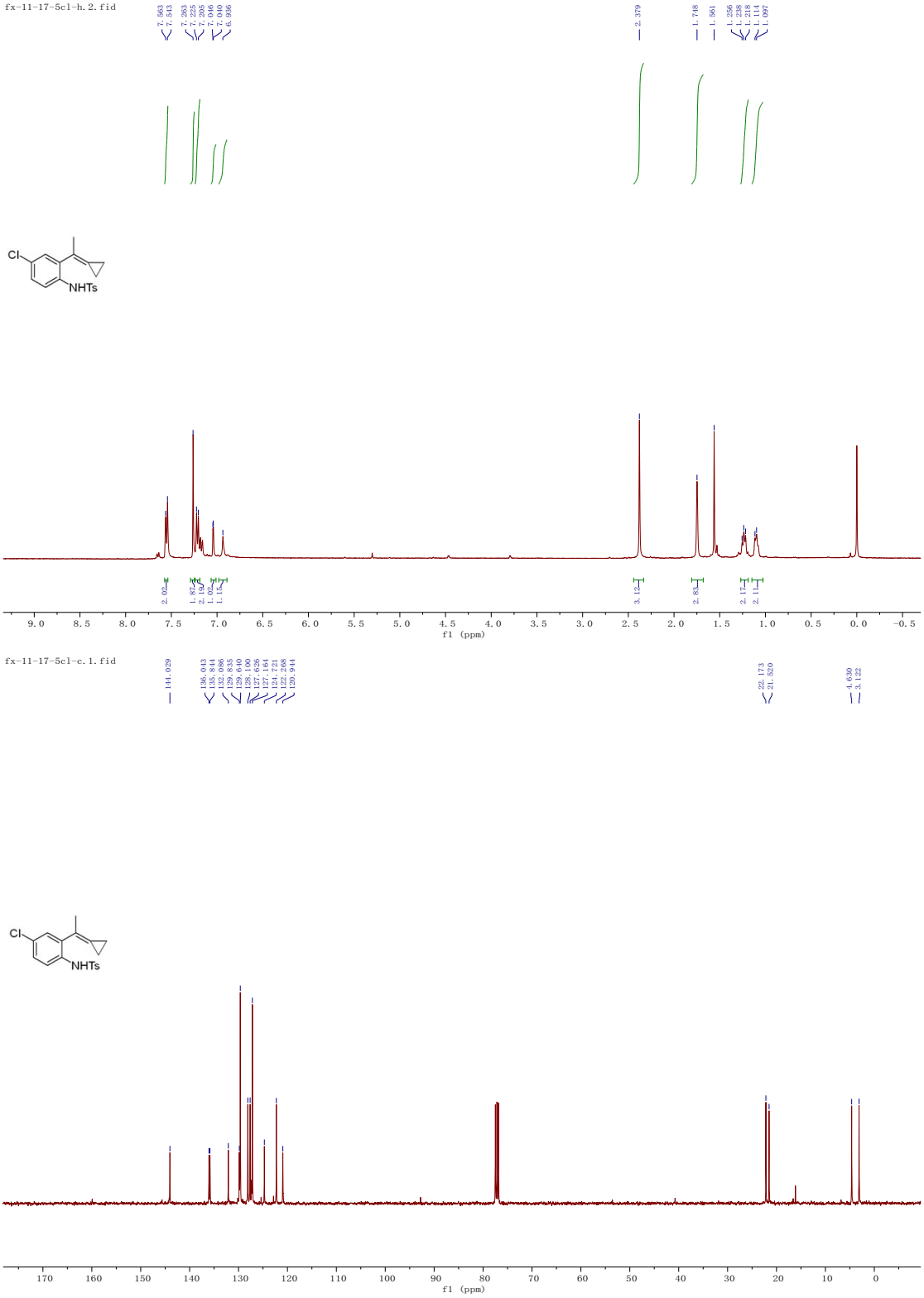


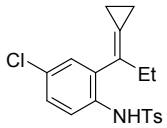




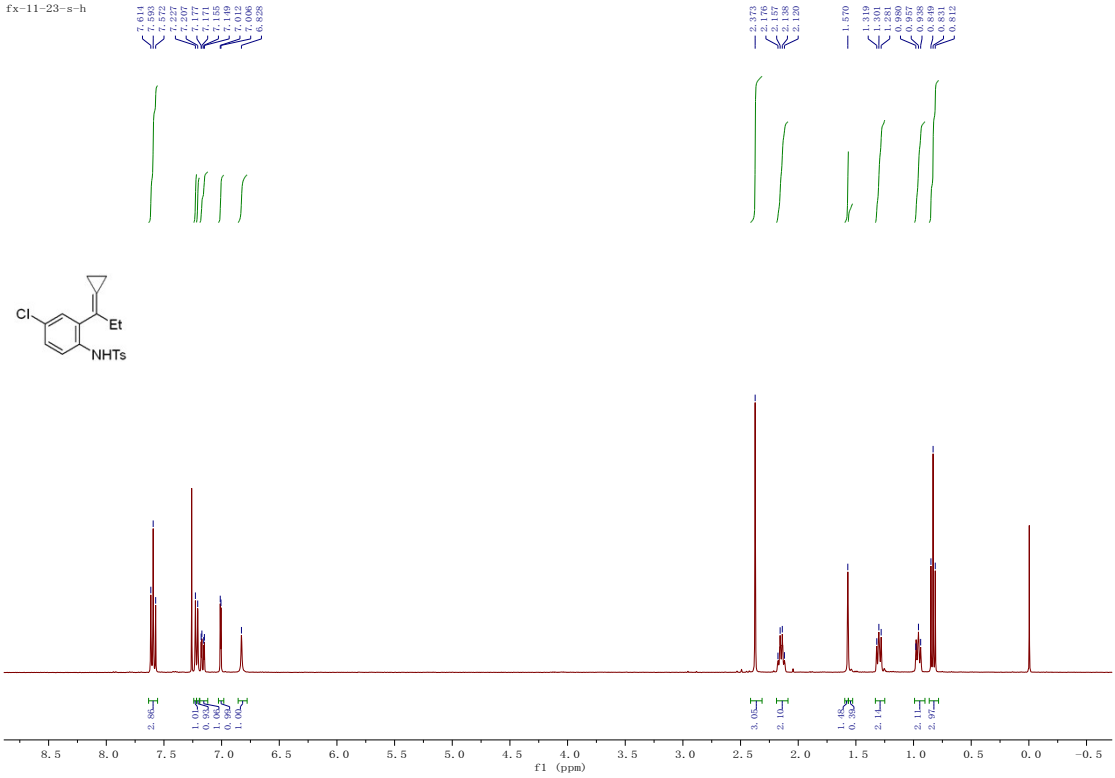
Compound 1l: A yellow solid (451.5 mg, 73%); M.p. 119-120 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.03 – 1.15 (m, 2H), 1.19 – 1.27 (m, 2H), 1.75 (s, 3H), 2.38 (s, 3H), 6.94 (s, 1H),

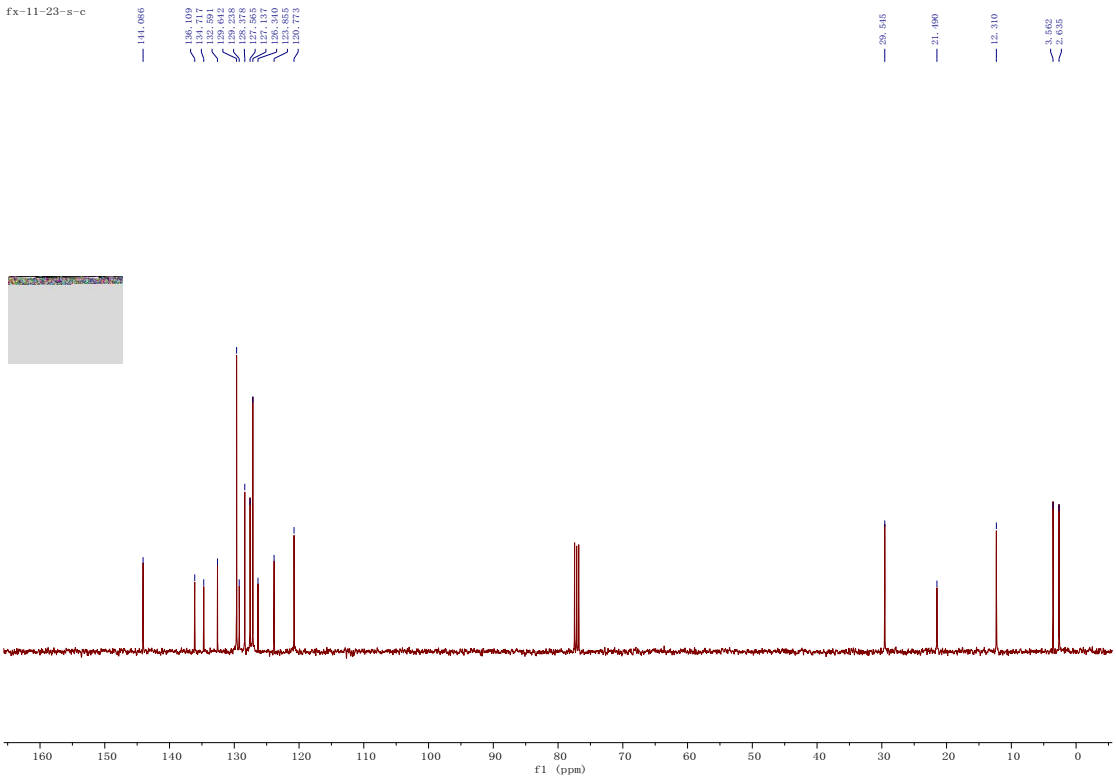
7.04 (d, *J* = 2.1 Hz, 1H), 7.19 – 7.24 (m, 2H), 7.26 (s, 2H), 7.54 – 7.57 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 3.1, 4.6, 21.5, 22.2, 120.9, 122.3, 124.7, 127.2, 127.6, 128.1, 129.6, 129.8, 132.1, 135.8, 136.0, 144.0. IR (neat) ν 3249, 2975, 2938, 1657, 1600, 1478, 1377, 1333, 1166, 1090, 901, 814, 707, 682 cm^{-1}. HRMS (ESI) Calcd. for $C_{18}H_{22}ClN_2O_2S$ requires (M^++NH_4): 365.1085, Found: 365.1085.

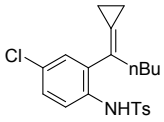




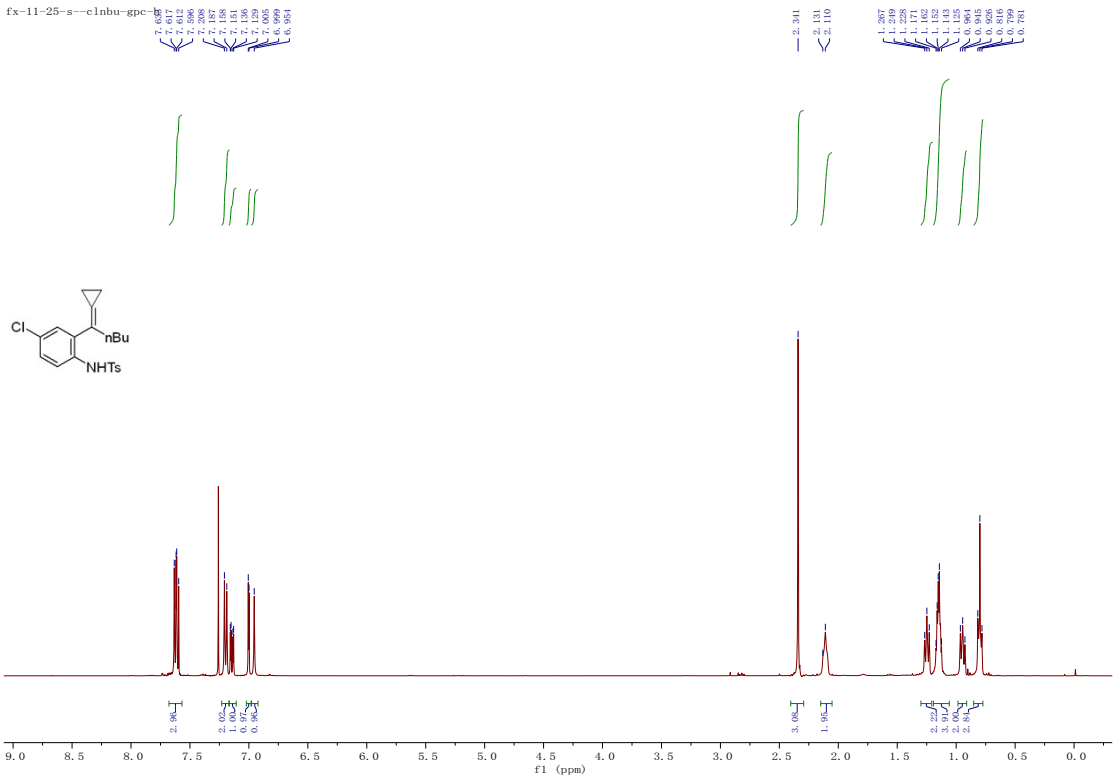
Compound 1m: A yellow solid (691.2 mg, 64%); M.p. 121-122 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 0.83 (t, *J* = 7.5 Hz, 3H), 0.96 (t, *J* = 8.4 Hz, 2H), 1.25 – 1.33 (m, 2H), 1.57 (s, 1H), 2.15 (q, *J* = 7.5 Hz, 2H), 2.37 (s, 3H), 6.83 (s, 1H), 7.01 (d, *J* = 2.5 Hz, 1H), 7.16 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.21 (s, 1H), 7.23 (s, 1H), 7.56 – 7.63 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 2.6, 3.6, 12.3, 21.5, 29.5, 120.8, 123.9, 126.3, 127.1, 127.6, 128.4, 129.2, 129.6, 132.6, 134.7, 136.1, 144.1. IR (neat) ν 3259, 2978, 2875, 1661, 1594, 1484, 1377, 1333, 1159, 1089, 904, 814, 708 cm^{-1}. HRMS (ESI) Calcd. for $C_{19}H_{24}ClN_2O_2S$ requires (M^++NH_4): 379.1242, Found: 379.1237.

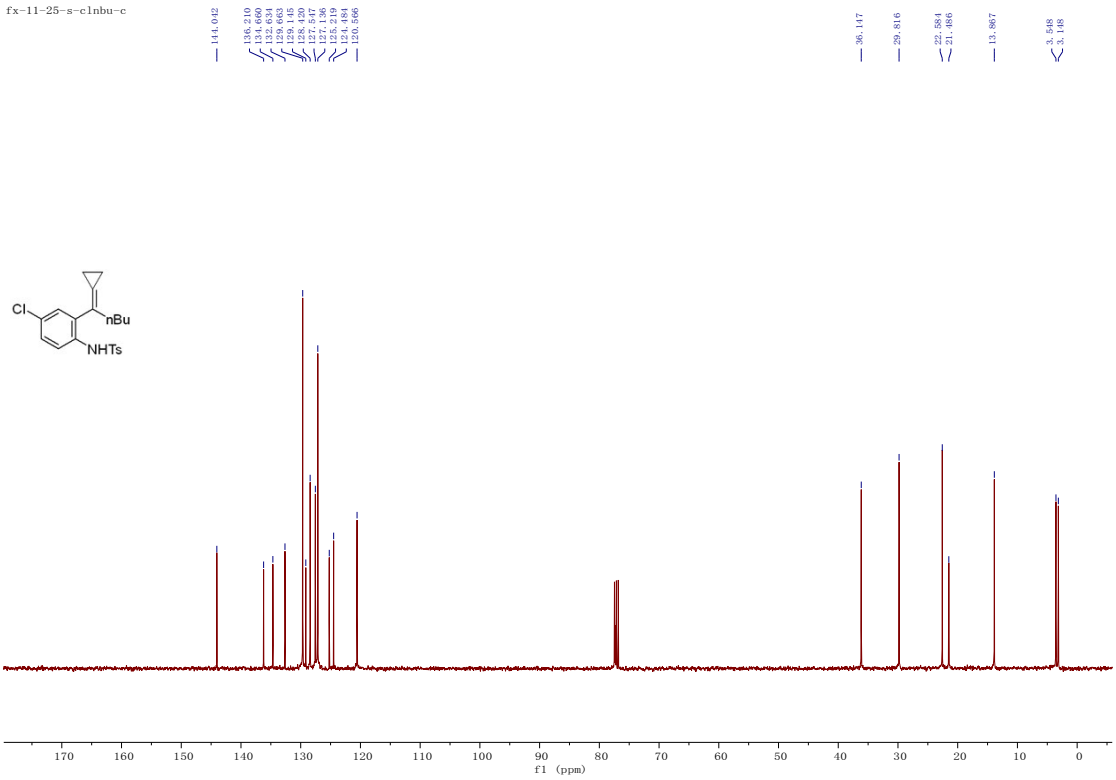


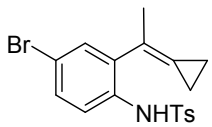




Compound 1n: A pale yellow solid (856.8 mg, 82%); M.p. 74-75 ^{o}C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 0.77 – 0.85 (m, 3H), 0.91 – 0.98 (m, 2H), 1.15 (q, *J* = 7.3, 5.5 Hz, 4H), 1.25 (t, *J* = 7.7 Hz, 2H), 2.12 (d, *J* = 8.6 Hz, 2H), 2.34 (s, 3H), 6.95 (s, 1H), 7.00 (d, *J* = 2.5 Hz, 1H), 7.14 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.17 – 7.23 (m, 2H), 7.57 – 7.68 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 3.1, 3.5, 13.9, 21.5, 22.6, 29.8, 36.1, 120.6, 124.5, 125.2, 127.1, 127.5, 128.4, 129.1, 129.7, 132.6, 134.7, 136.2, 144.0. IR (neat) ν 3266, 2956, 2922, 2860, 1598, 1481, 1377, 1331, 1166, 1090, 923, 860, 813, 669 cm^{-1}. HRMS (ESI) Calcd. for $C_{21}H_{28}ClN_2O_2S$ requires (M^++NH_4): 407.1555, Found: 407.1552.

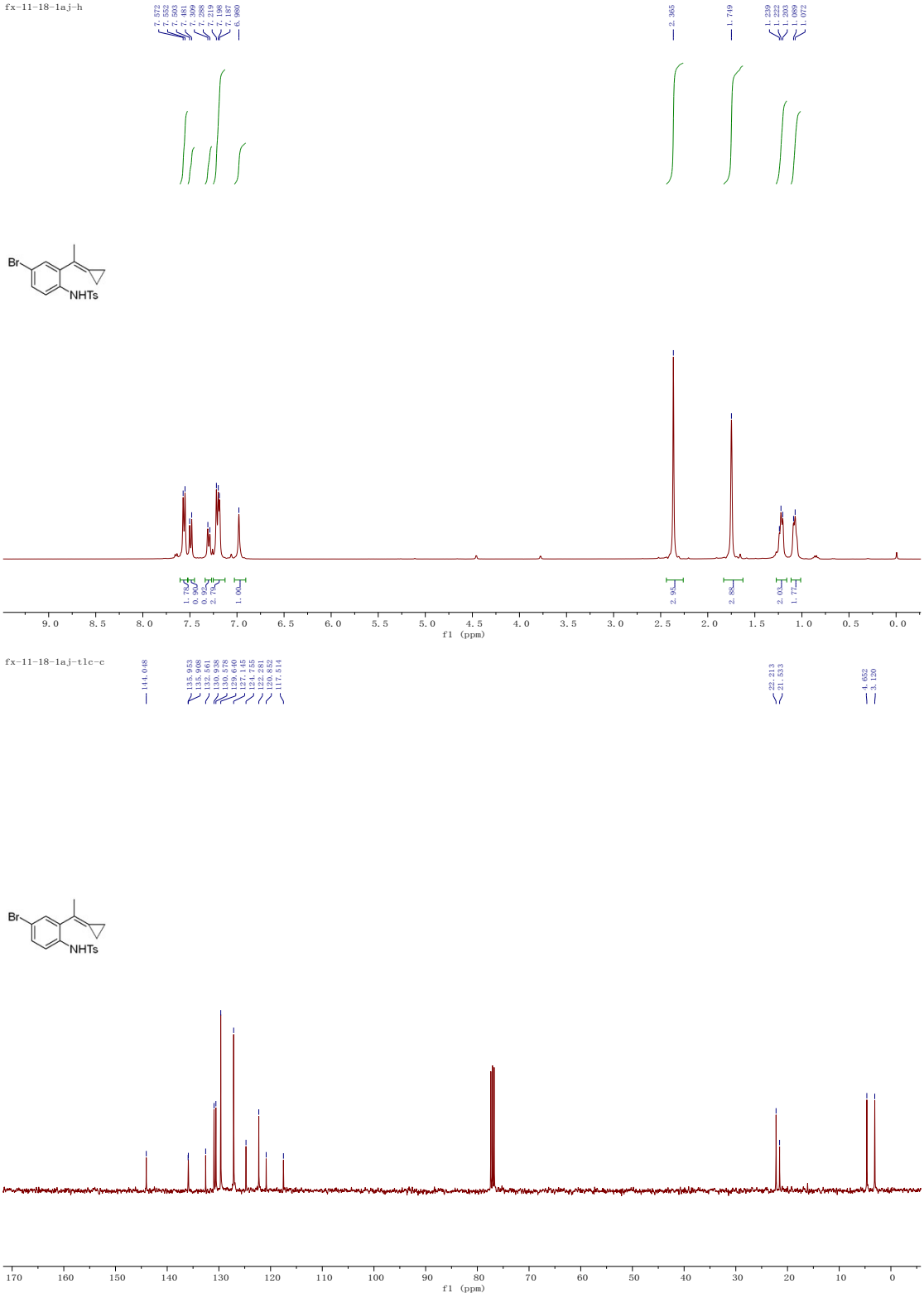


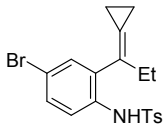




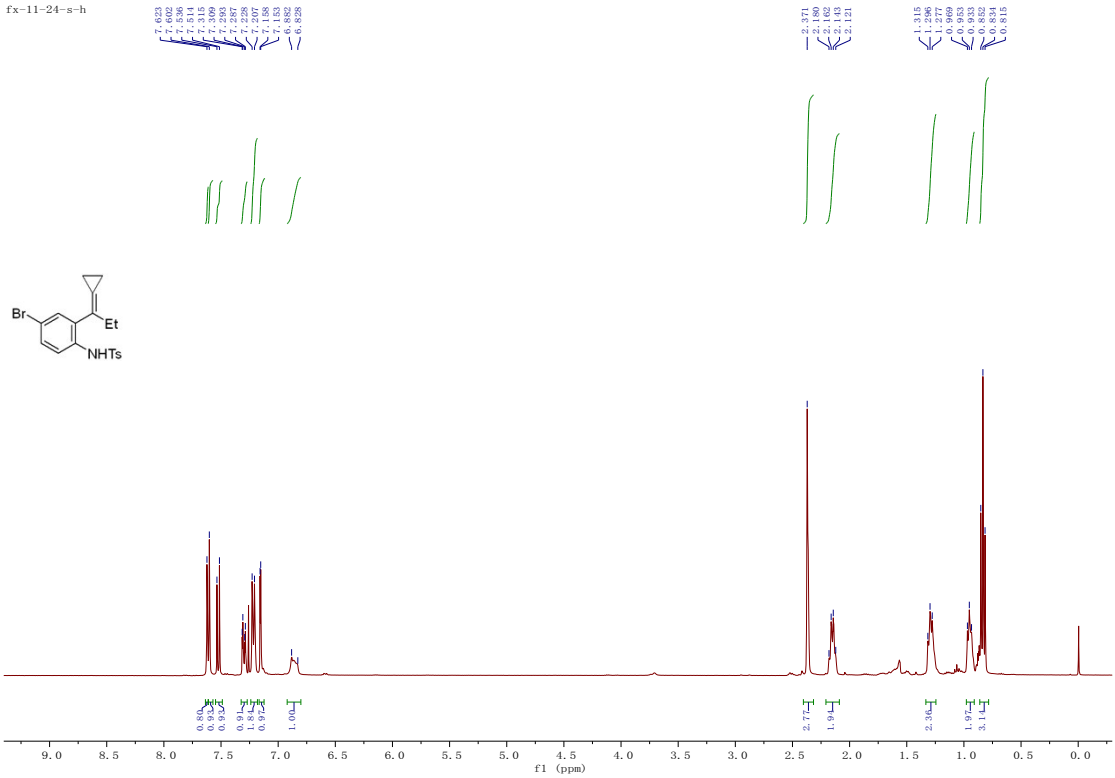
Compound 1o: A white solid (418.2 mg, 67%); M.p. 121-122 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.08 (d, *J* = 6.8 Hz, 2H), 1.16 – 1.27 (m, 2H), 1.75 (s, 3H), 2.37 (s, 3H), 6.98 (s,

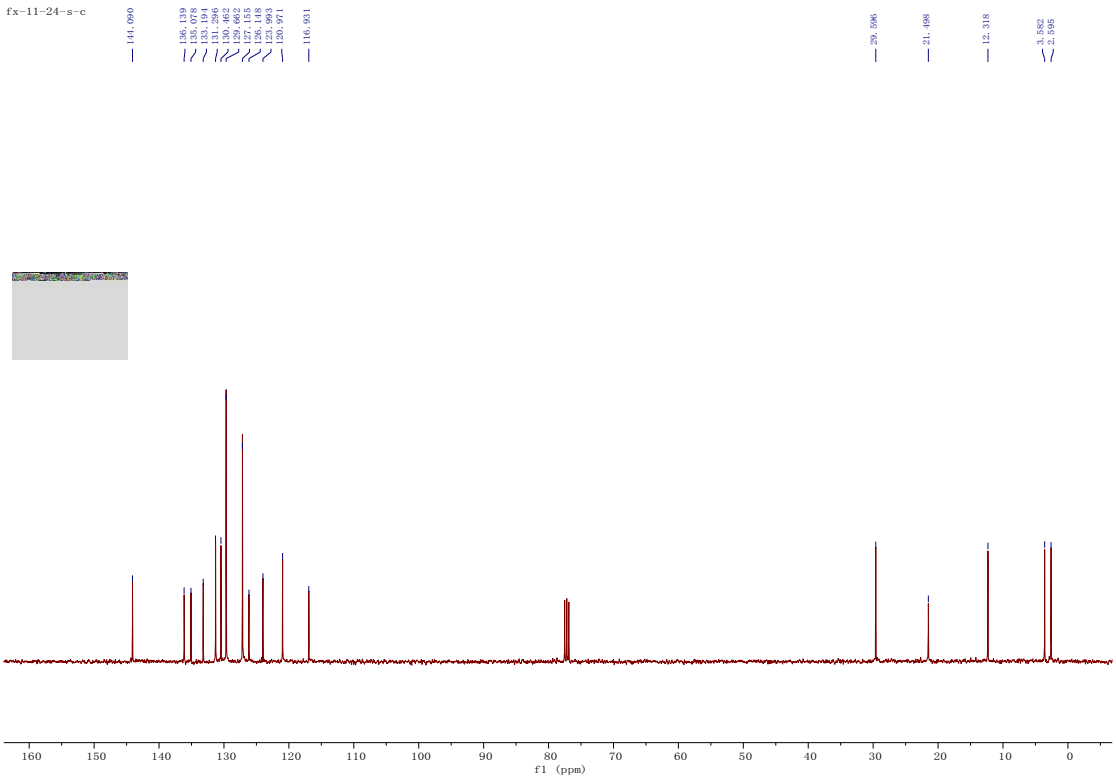
1H), 7.13 – 7.25 (m, 3H), 7.30 (d, *J* = 8.6 Hz, 1H), 7.49 (d, *J* = 8.7 Hz, 1H), 7.53 – 7.60 (m, 2H). ^{13}C NMR (100 Mhz, Chloroform-*d*) δ 3.1, 4.7, 21.5, 22.2, 117.5, 120.9, 122.3, 124.8, 127.1, 129.6, 130.6, 130.9, 132.6, 135.9, 136.0, 144.0. IR (neat) ν 3249, 1484, 1470, 1376, 1335, 1185, 1169, 1134, 1119, 1091, 1066, 908, 844, 816, 740, 705, 688, 673, 653 cm^{-1}. HRMS (ESI) Calcd. for $C_{18}H_{19}BrNO_2S$ requires (M^++H): 392.0314, Found: 392.0316.

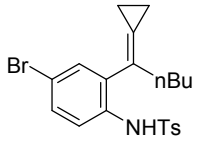




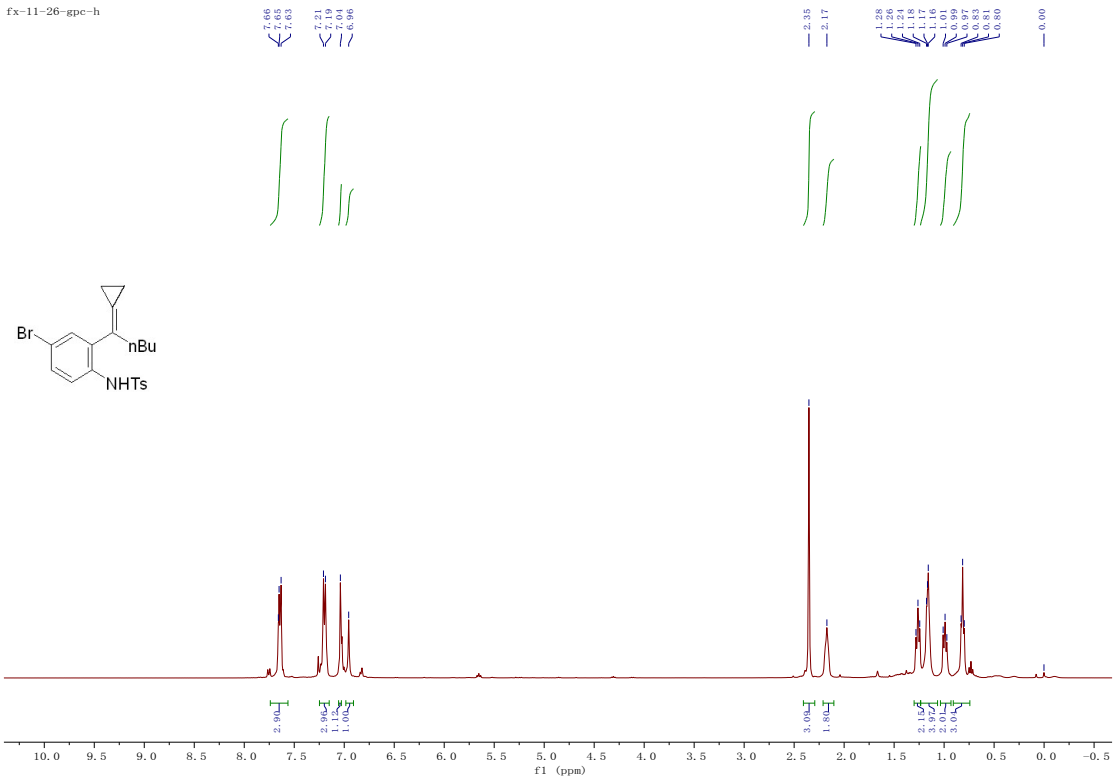
Compound 1p: A white solid (921.3 mg, 76%); M.p. 120-121 ^{o}C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 0.83 (t, *J* = 7.5 Hz, 3H), 0.91 – 0.98 (m, 2H), 1.24 – 1.33 (m, 2H), 2.15 (q, *J* = 8.7, 8.1 Hz, 2H), 2.37 (s, 3H), 6.86 (d, *J* = 21.8 Hz, 1H), 7.16 (d, *J* = 2.3 Hz, 1H), 7.18 – 7.24 (m, 2H), 7.30 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.60 (s, 1H), 7.62 (s, 1H). ^{13}C NMR (100 Mhz, Chloroform-*d*) δ 2.6, 3.6, 12.3, 21.5, 29.6, 116.9, 121.0, 124.0, 126.1, 127.2, 129.7, 130.5, 131.3, 133.2, 135.1, 136.1, 144.1. IR (neat) ν 3251, 2974, 1591, 1474, 1371, 1332, 1168, 1090, 900, 856, 814, 737, 706, 699, 676, 652 cm^{-1}. HRMS (ESI) Calcd. for $C_{19}H_{24}BrN_2O_2S$ requires (M^++NH_4): 423.0736, Found: 423.0732.

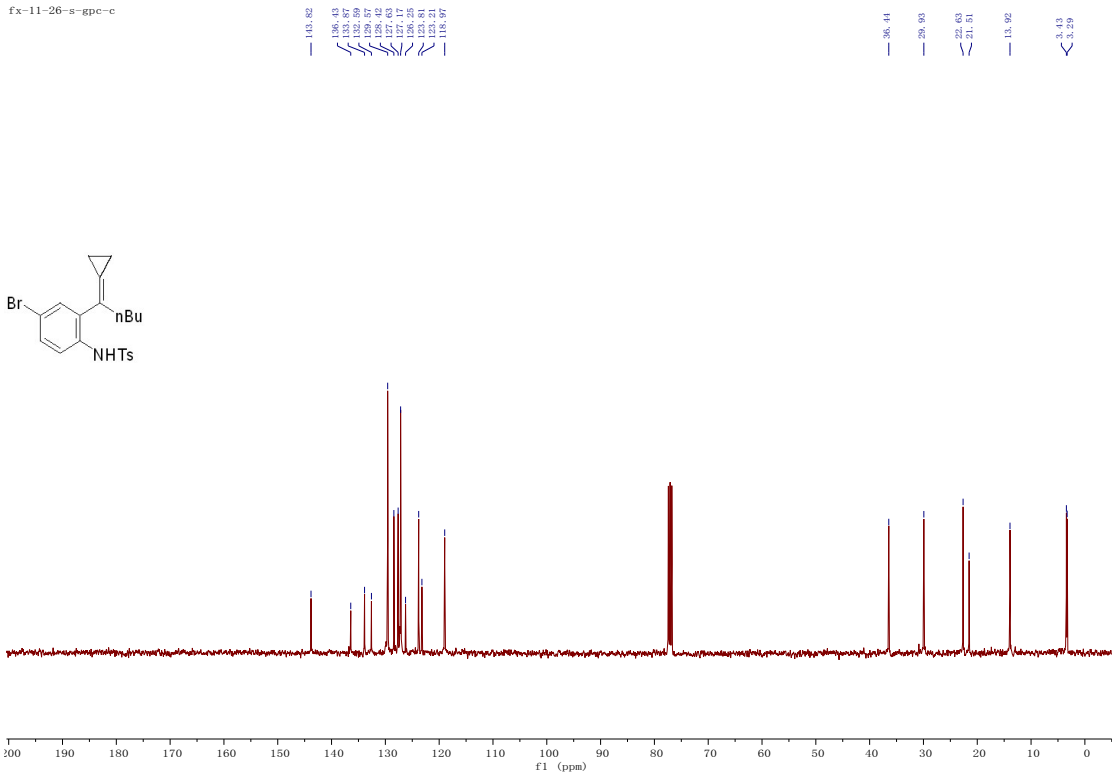


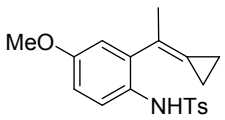




Compound 1q: A yellow oil (1051.4 mg, 81%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 0.81 (t, *J* = 6.3 Hz, 3H), 0.99 (d, *J* = 7.6 Hz, 2H), 1.07 – 1.24 (m, 4H), 1.26 (t, *J* = 7.5 Hz, 2H), 2.17 (d, *J* = 7.2 Hz, 2H), 2.35 (s, 3H), 6.96 (s, 1H), 7.04 (s, 1H), 7.15 – 7.25 (m, 3H), 7.56 – 7.74 (m, 3H). ^{13}C NMR (100 Mhz, Chloroform-*d*) δ 3.3, 3.4, 13.9, 21.5, 22.6, 29.9, 36.4, 119.0, 123.2, 123.8, 126.2, 127.2, 127.6, 128.4, 129.6, 132.6, 133.9, 136.4, 143.8. IR (neat) ν 3254, 2977, 2933, 1654, 1597, 1479, 1377, 1333, 1305, 1289, 1196, 1185, 1166, 1120, 1090, 1009, 902, 879, 842, 814, 741, 707, 682 cm^{-1}. HRMS (DART) Calcd. for $C_{21}H_{25}BrNO_2S$ requires (M^++H): 434.0784, Found: 434.0782.

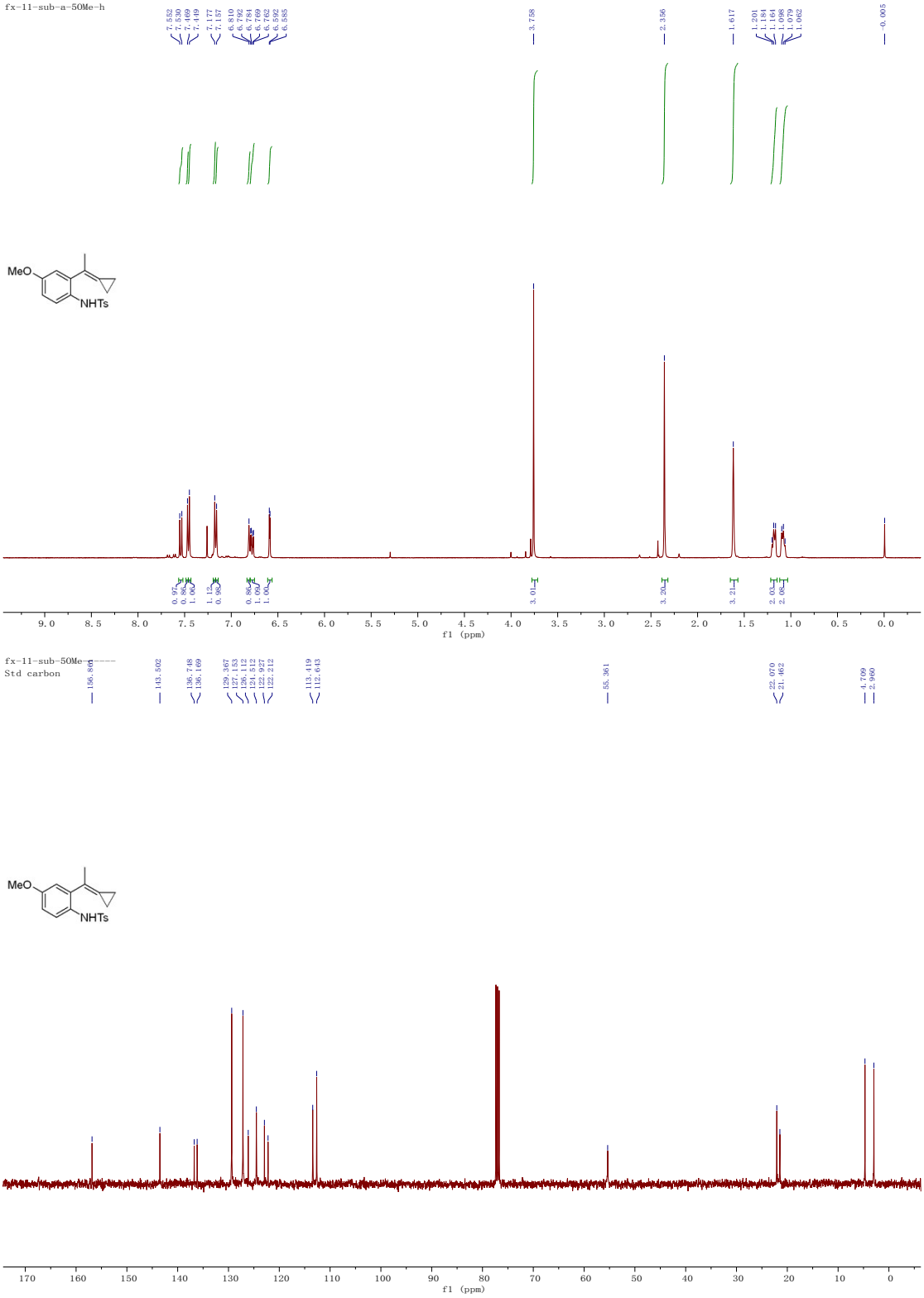


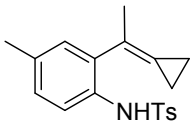




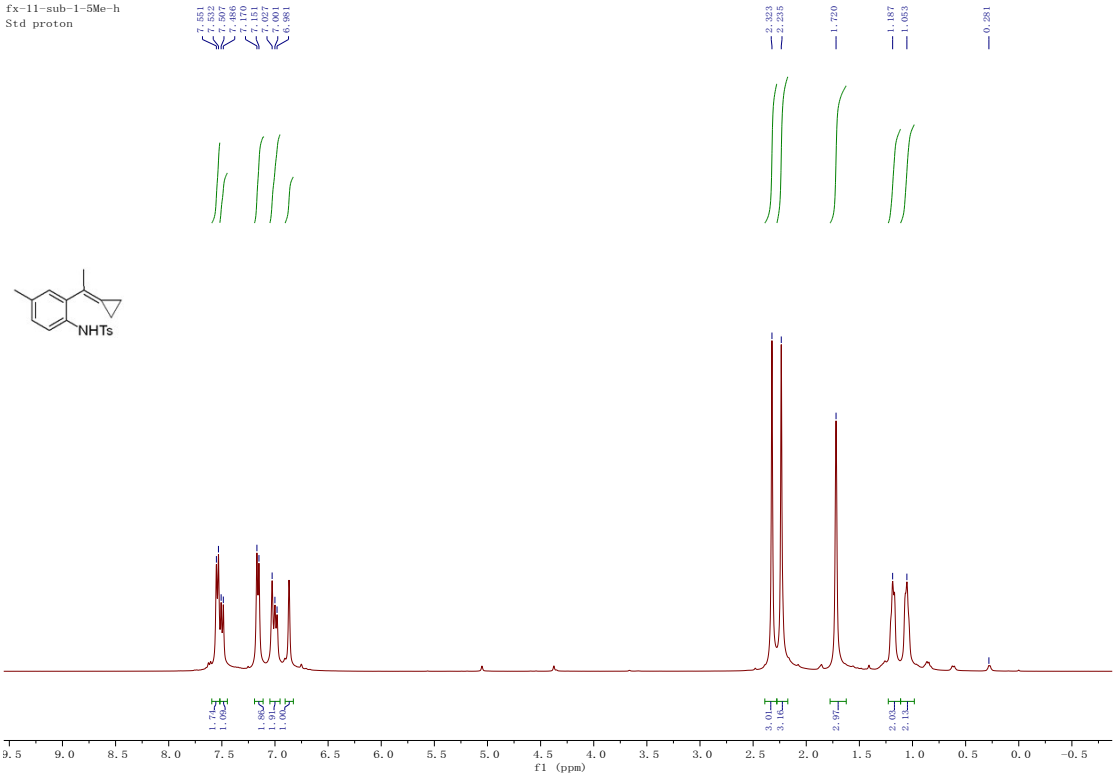
Compound 1u: A yellow solid (374.1 mg, 72%); M.p. 143-144 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.03 – 1.12 (m, 2H), 1.15 – 1.22 (m, 2H), 1.62 (s, 3H), 2.36 (s, 3H), 3.76 (s, 3H),

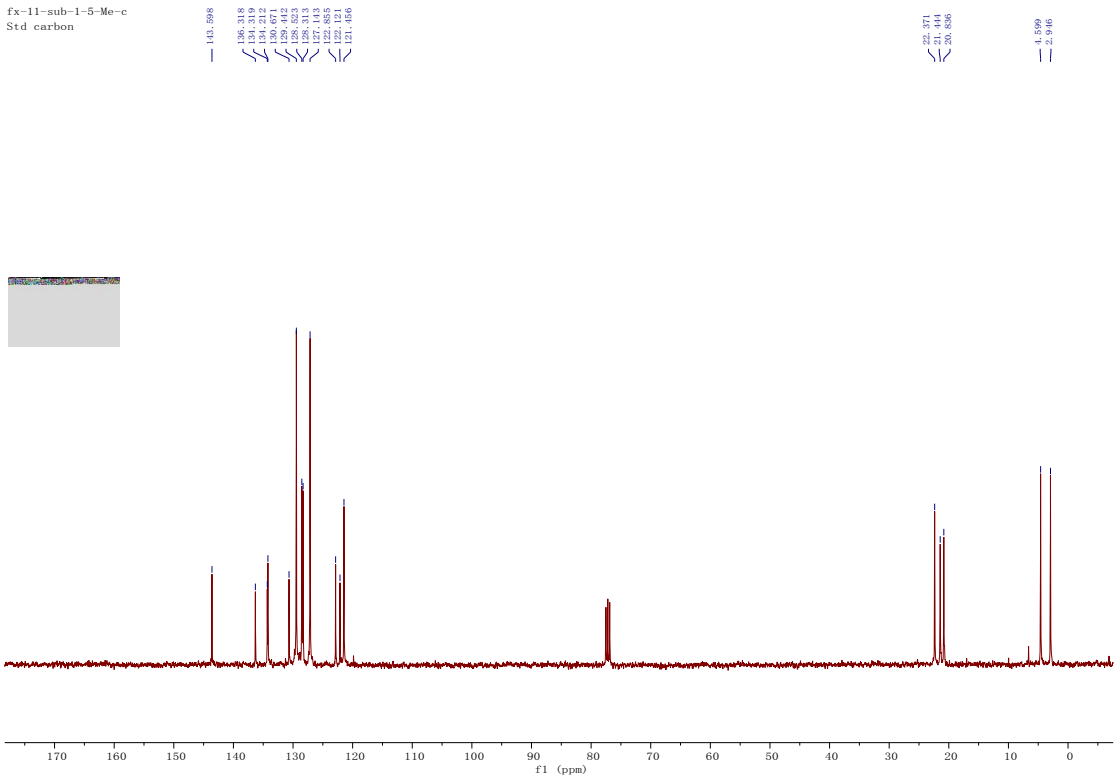
6.59 (d, *J* = 2.9 Hz, 1H), 6.78 (dd, *J* = 8.9, 2.9 Hz, 1H), 6.81 (s, 1H), 7.16 (s, 1H), 7.18 (s, 1H), 7.45 (s, 1H), 7.47 (s, 1H), 7.54 (d, *J* = 8.9 Hz, 1H). ^{13}C NMR (100 Mhz, Chloroform-*d*) δ 3.0, 4.7, 21.5, 22.1, 55.4, 112.6, 113.4, 122.2, 122.9, 124.5, 126.1, 127.2, 129.4, 136.2, 136.7, 143.5, 156.9. IR (neat) ν 3313, 1609, 1591, 1491, 1386, 1333, 1292, 1214, 1163, 1089, 1045, 1034, 895, 867, 817, 797, 666 cm^{-1}. HRMS (ESI) Calcd. for $C_{19}H_{22}NO_3S$ requires (M^++H): 344.1315, Found: 344.1312.

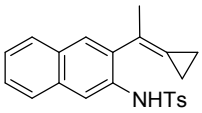




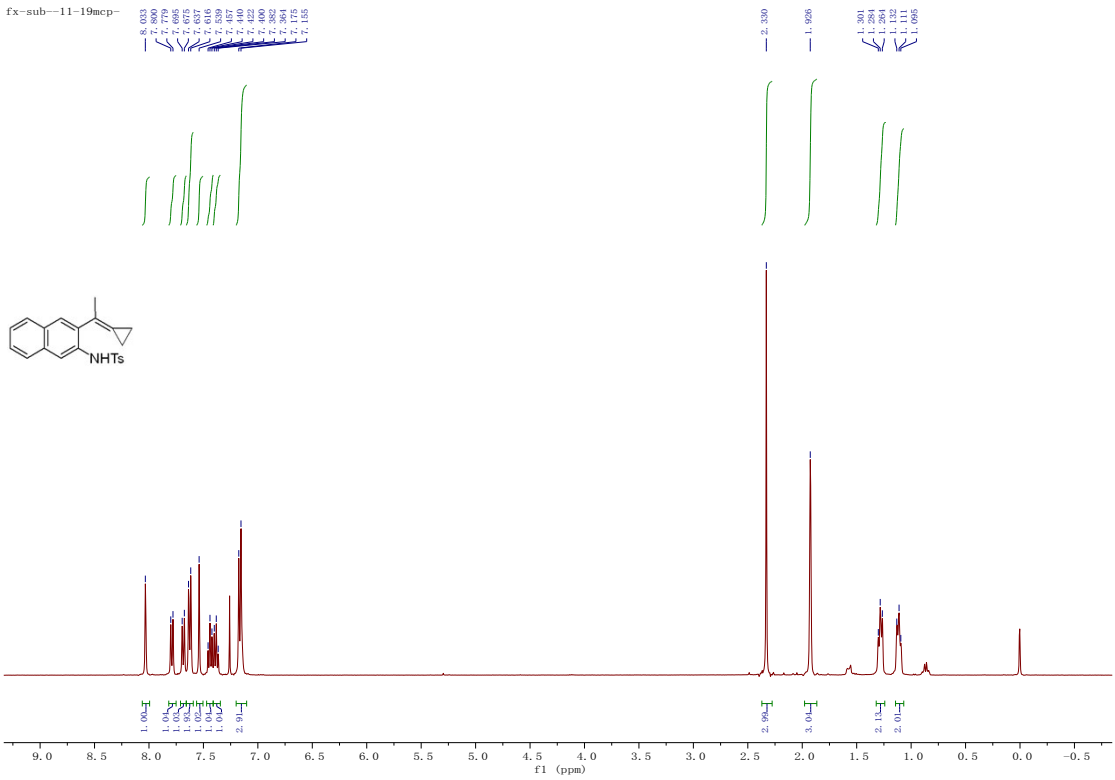
Compound 1v: A yellow solid (141.8 mg, 47%); M.p. 114-115 ^{o}C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.05 (s, 2H), 1.19 (s, 2H), 1.72 (s, 3H), 2.24 (s, 3H), 2.32 (s, 3H), 6.87 (s, 1H), 6.95 – 7.05 (m, 2H), 7.11 – 7.19 (m, 2H), 7.50 (d, *J* = 8.2 Hz, 1H), 7.52 – 7.59 (m, 2H). ^{13}C NMR (100 Mhz, Chloroform-*d*) δ 2.9, 4.6, 20.8, 21.4, 22.4, 121.5, 122.1, 122.9, 127.1, 128.3, 128.5, 129.4, 130.7, 134.2, 134.3, 136.3, 143.6. IR (neat) ν 3249, 2975, 2920, 1600, 1495, 1381, 1333, 1167, 1091, 912, 888, 813, 706, 677 cm^{-1}. HRMS (ESI) Calcd. for $C_{19}H_{25}N_2O_2S$ requires (M^++NH_4): 345.1631, Found: 345.1626.

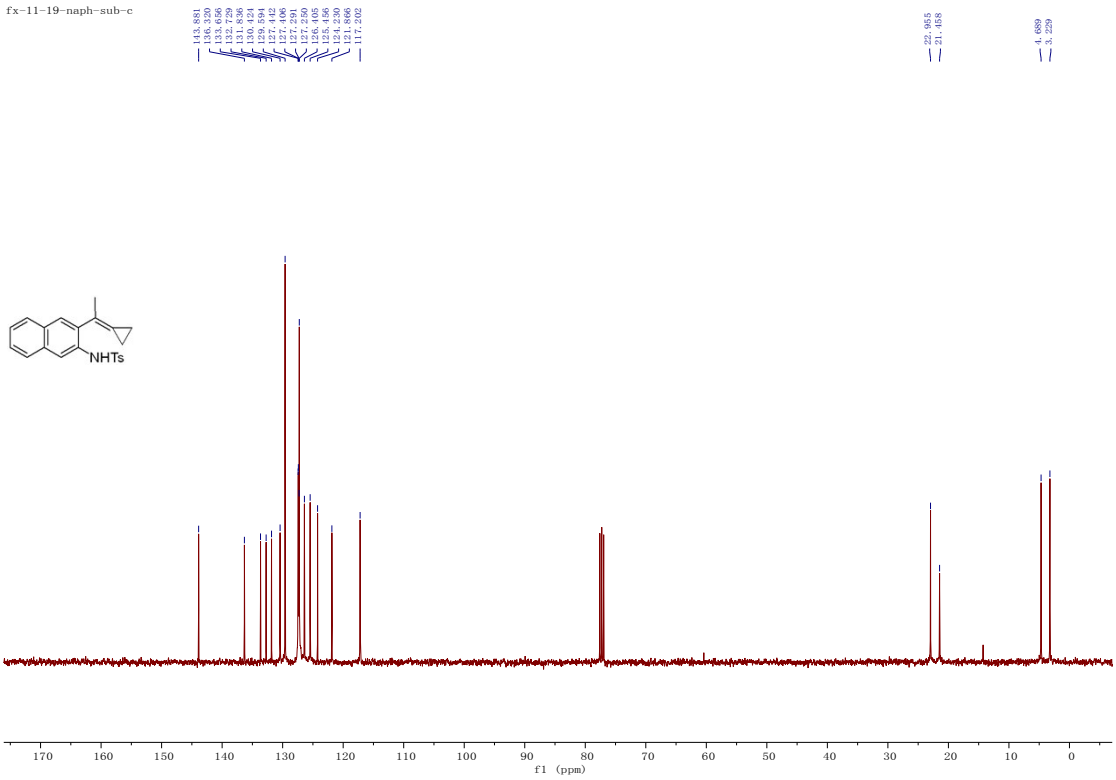


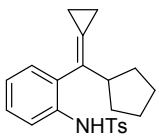




Compound 1w: A white solid (663.4 mg, 61%); M.p. 139-140 ^{o}C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.11 (t, *J* = 7.4 Hz, 2H), 1.24 – 1.32 (m, 2H), 1.93 (s, 3H), 2.33 (s, 3H), 7.10 – 7.20 (m, 3H), 7.38 (dd, *J* = 7.1 Hz, 1H), 7.44 (dd, *J* = 7.1 Hz, 1H), 7.54 (s, 1H), 7.59 – 7.66 (m, 2H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 8.03 (s, 1H). ^{13}C NMR (100 Mhz, Chloroform-*d*) δ 3.2, 4.7, 21.5, 23.0, 117.2, 121.9, 124.2, 125.5, 126.4, 127.25, 127.29, 127.41, 127.44, 129.6, 130.4, 131.8, 132.7, 133.7, 136.3, 143.9. IR (neat) ν 3262, 2974, 1590, 1506, 1402, 1346, 1319, 1154, 1092, 902, 811, 745 cm^{-1}. HRMS (ESI) Calcd. for $C_{22}H_{25}N_2O_2S$ requires (M^++NH_4): 381.1631, Found: 381.1630.

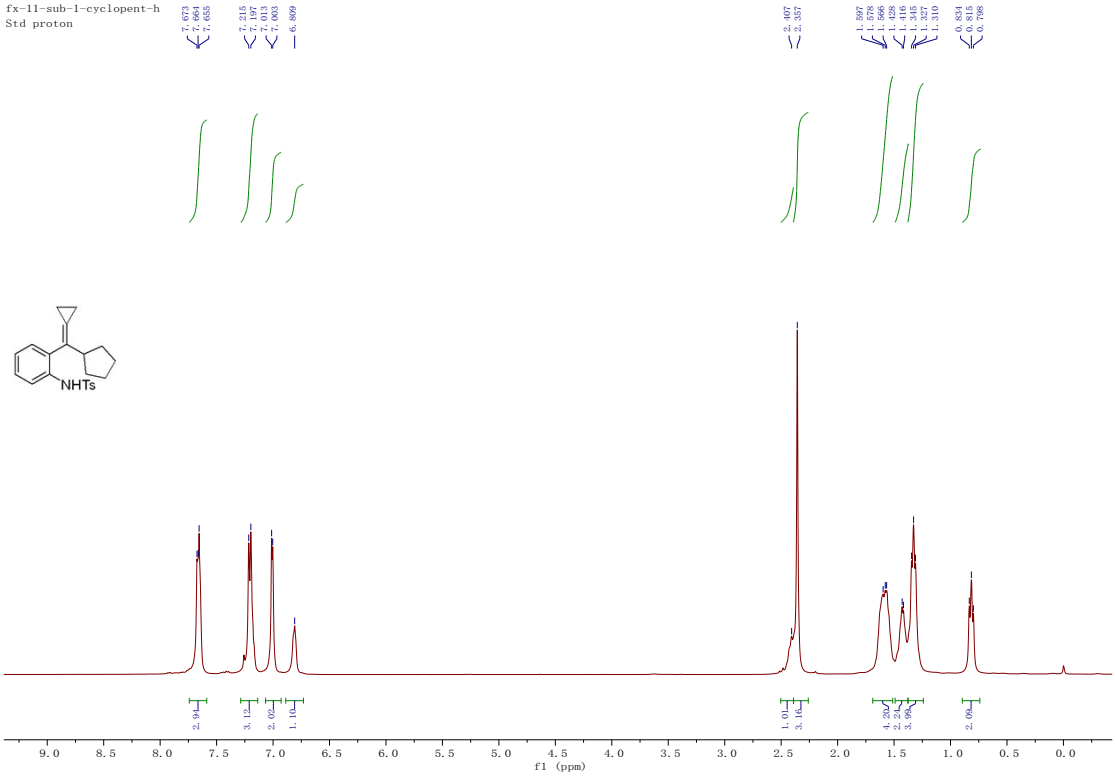


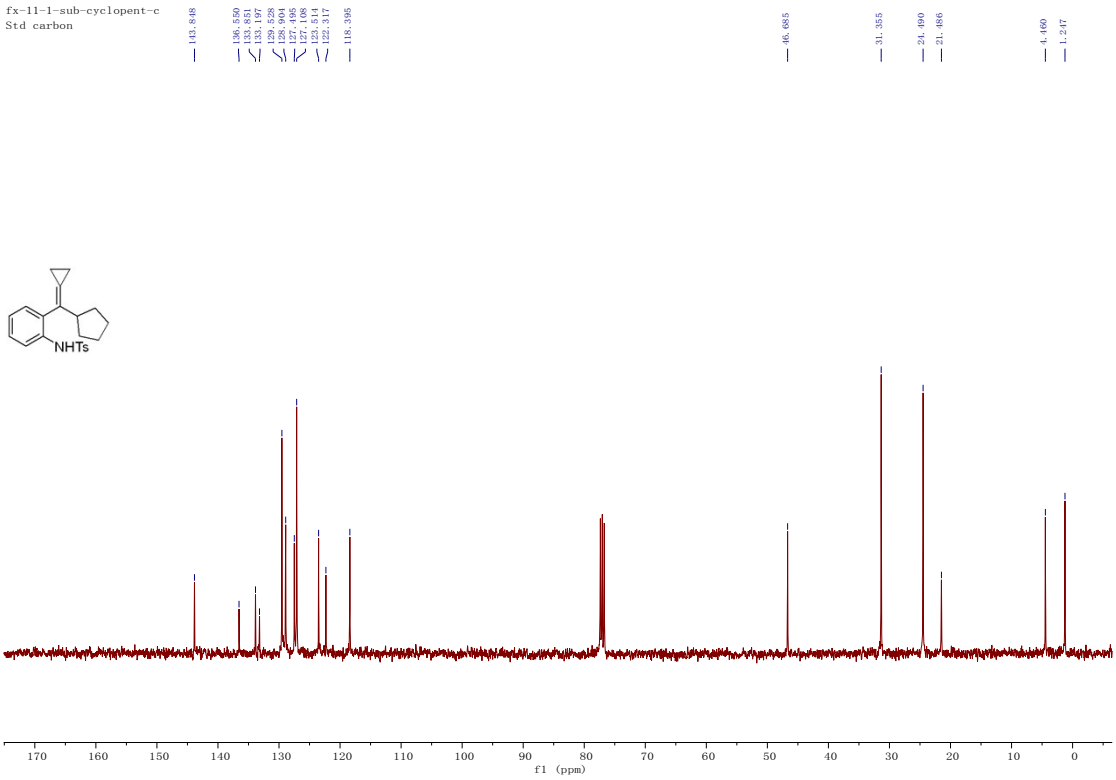


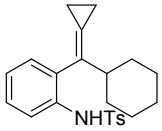


Compound 1x: A white solid (1250 mg, 49%); M.p. 116-117 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 0.74 – 0.90 (m, 2H), 1.24 – 1.38 (m, 4H), 1.37 – 1.49 (m, 2H), 1.51 – 1.69 (m, 4H), 2.36 (s,

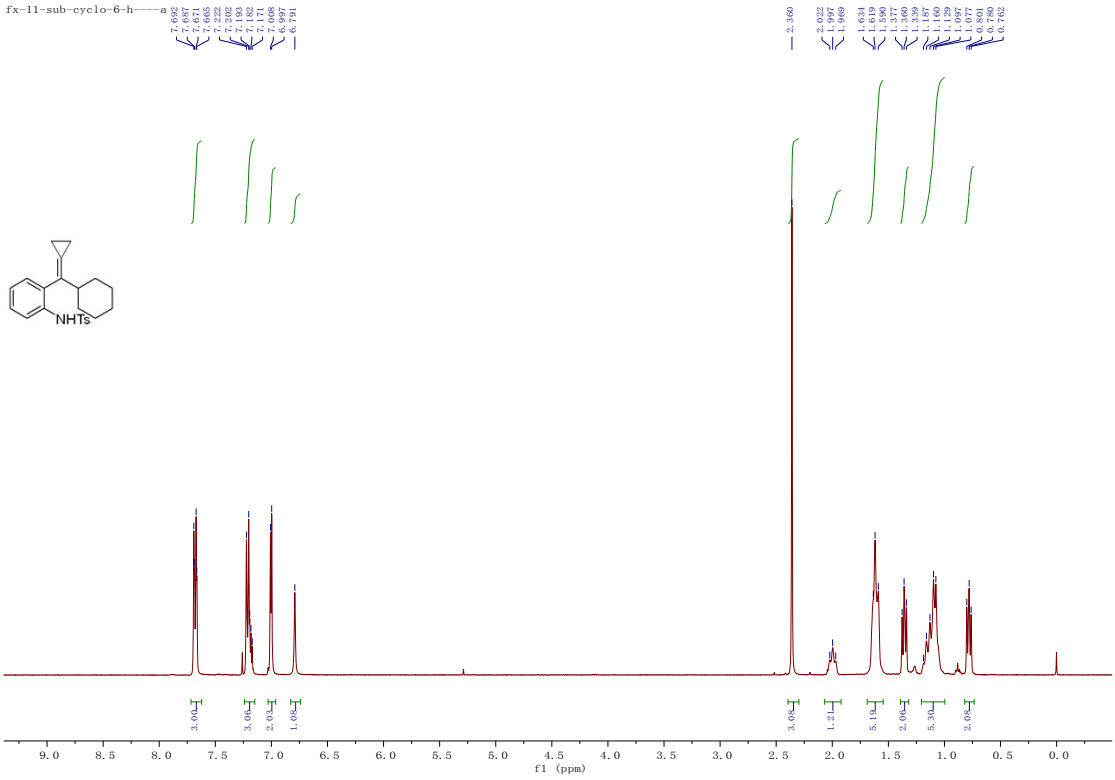
3H), 2.41 (s, 1H), 6.81 (s, 1H), 6.93 – 7.07 (m, 2H), 7.14 – 7.29 (m, 3H), 7.59 – 7.74 (m, 3H). ^{13}C NMR (100 Mhz, Chloroform-*d*) δ 1.2, 4.5, 21.5, 24.5, 31.4, 46.7, 118.4, 122.3, 123.5, 127.1, 127.5, 128.9, 129.5, 133.2, 133.9, 136.6, 143.8. IR (neat) ν 3262, 2971, 2856, 1598, 1572, 1491, 1380, 1338, 1167, 1093, 908, 815, 756, 708, 679 cm^{-1}. HRMS (ESI) Calcd. for $C_{22}H_{29}N_2O_2S$ requires (M^++NH_4): 385.1944, Found: 385.1939.

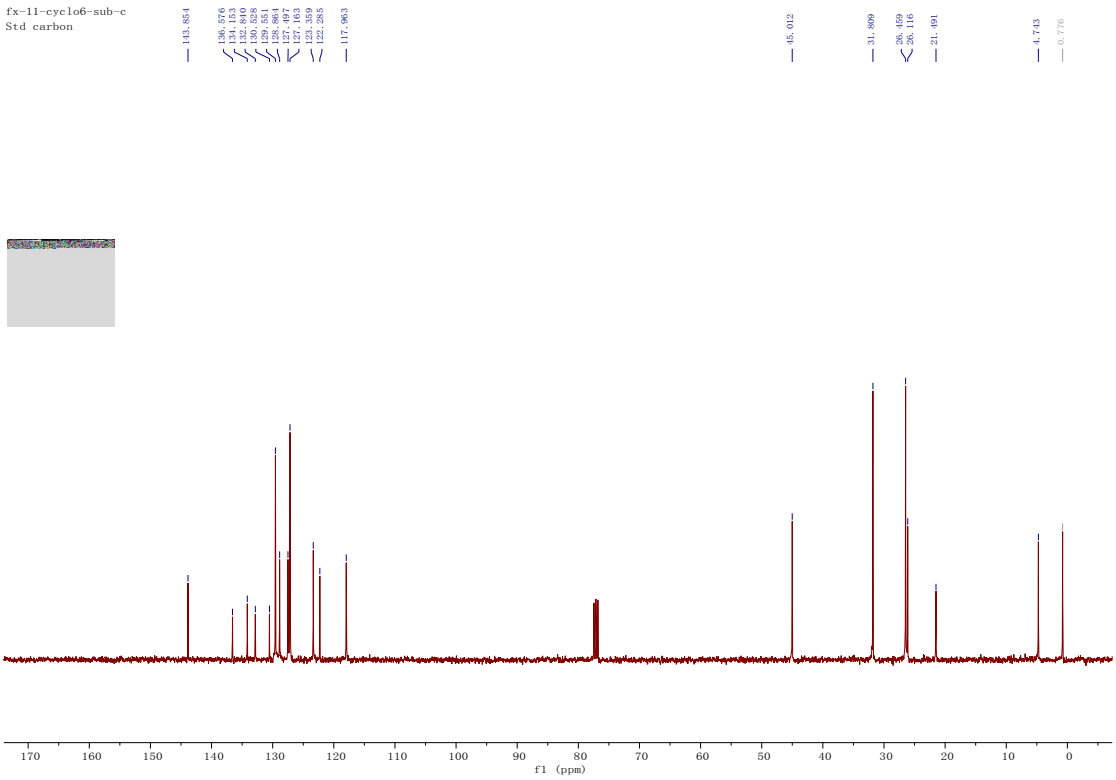






Compound 1y: A yellow solid (653.4 mg, 49%); M.p. 122-123 ^{o}C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 0.74 – 0.82 (m, 2H), 1.00 – 1.20 (m, 5H), 1.32 – 1.39 (m, 2H), 1.55 – 1.69 (m, 5H), 2.00 (t, *J* = 10.5 Hz, 1H), 2.36 (s, 3H), 6.79 (s, 1H), 6.96 – 7.03 (m, 2H), 7.15 – 7.24 (m, 3H), 7.62 – 7.72 (m, 3H). ^{13}C NMR (100 Mhz, Chloroform-*d*) δ 0.8, 4.7, 21.5, 26.1, 26.5, 31.8, 45.0, 118.0, 122.3, 123.4, 127.2, 127.5, 128.9, 129.6, 130.5, 132.8, 134.2, 136.6, 143.9. IR (neat) ν 3262, 2982, 2919, 2849, 1639, 1613, 1598, 1580, 1484, 1447, 1406, 1377, 1337, 1167, 1089, 898, 747, 706, 665 cm^{-1}. HRMS (ESI) Calcd. for $C_{23}H_{31}N_2O_2S$ requires (M^++NH_4): 399.2101, Found: 399.2096.

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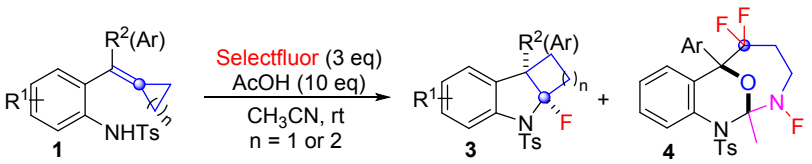
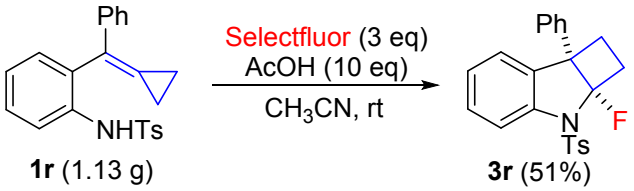
123.559
122.285
117.963
45.012
31.899
26.459
26.116
21.491
4.743
0.776
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

General procedure for the preparation of compounds 3a-4ac



General procedure F: For the synthesis of **3** and **4**:

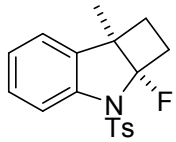
A solution of **1** (0.2 mmol, 1.0 eq) and **2a** (212.6 mg, 0.6 mmol, 3.0 eq) in 2 mL of CH_3CN, AcOH (0.1 mL, 2.0 mmol, 10 eq) was added by a syringe, and the mixture was stirred at room temperature for 6-8 h. The reaction mixture was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (PE/EA = 10:1 to 5:1) to afford the products **3** and **4**.



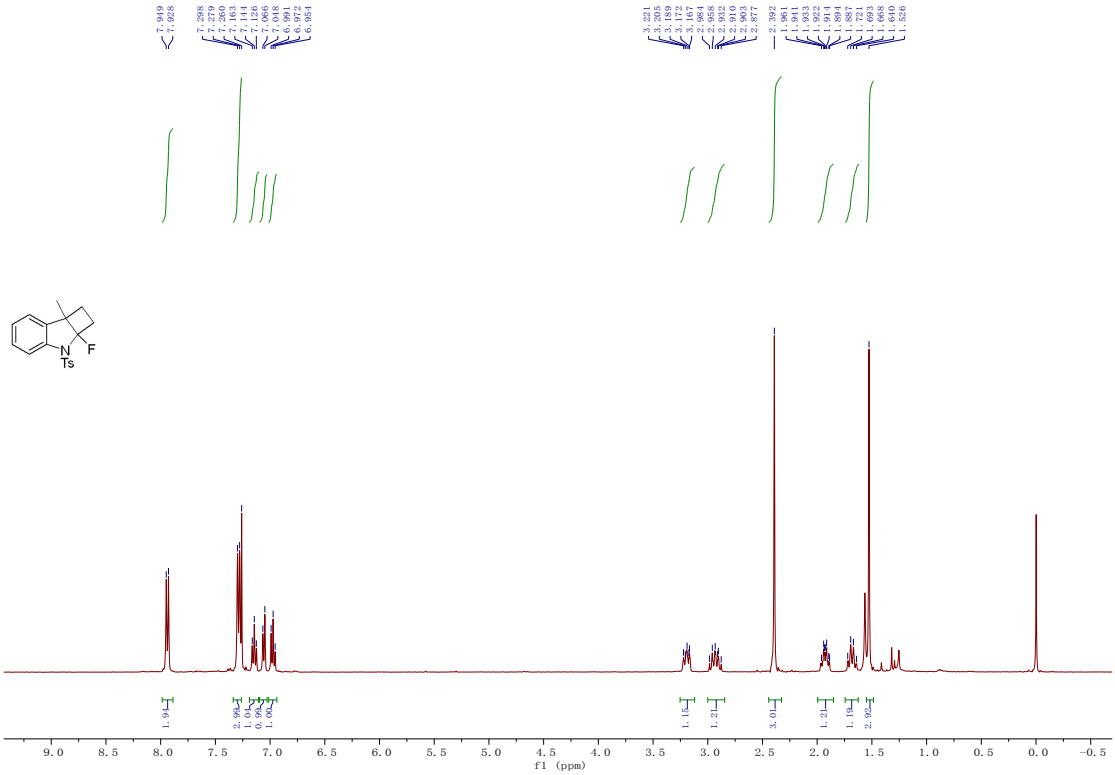
*Scale up experiment on 3.0 mmol of **1r**:*

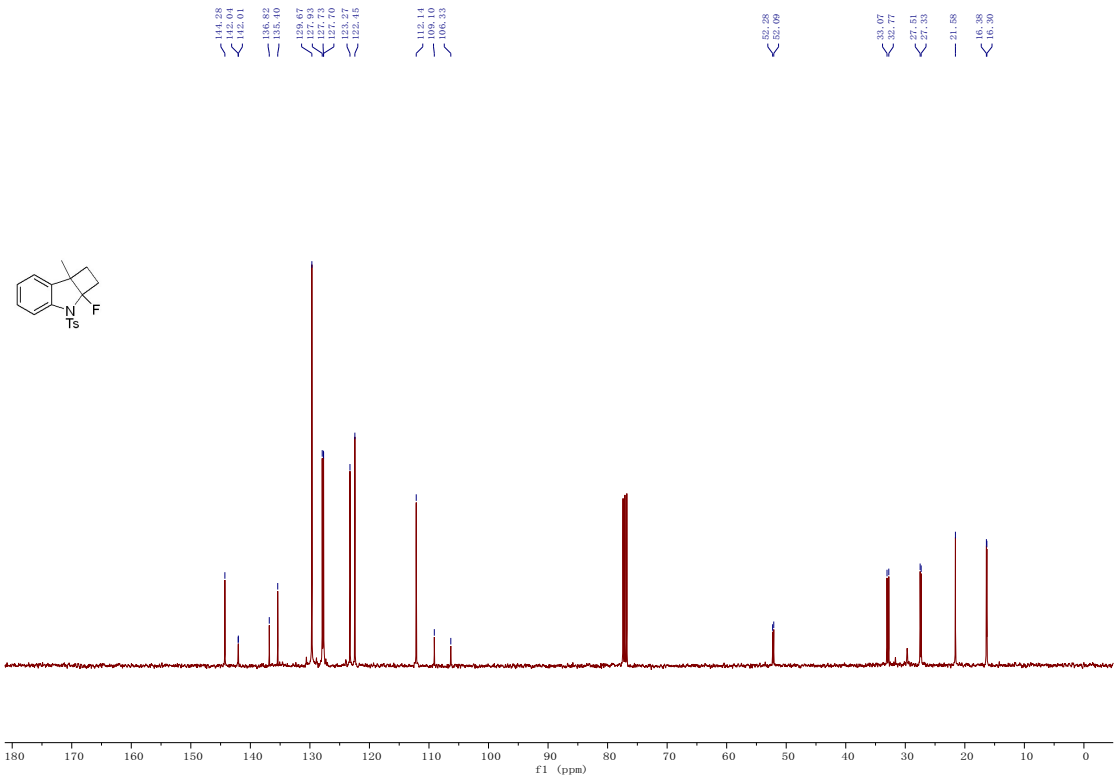
A solution of **1r** (1.13 g, 3 mmol, 1.0 eq) and **2a** (3.19 g, 9 mmol, 3.0 eq) in 30 mL of CH_3CN, AcOH (1.5 mL, 2.0 mmol, 10 eq) was added by a syringe, and the mixture was stirred at room temperature for 8 h. The reaction mixture was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (PE/EA = 10:1) to afford the product **3r** in 51% yield (605 mg).

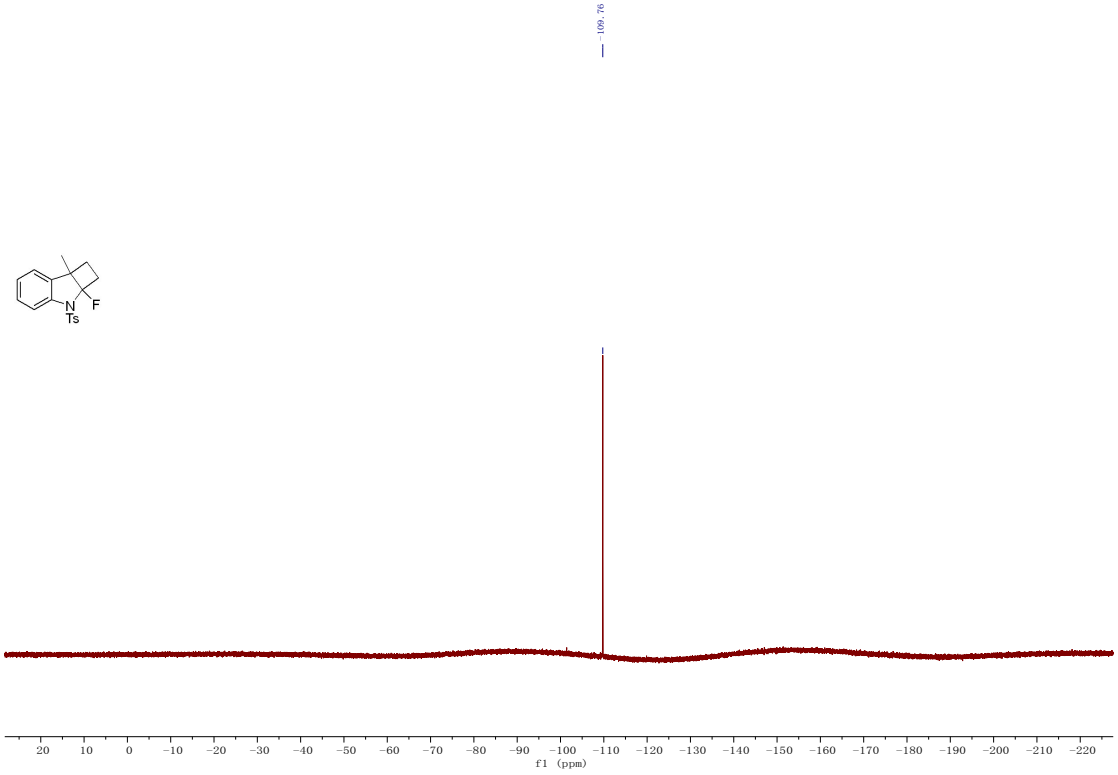
Spectroscopic data for products **3a-4ac** as following

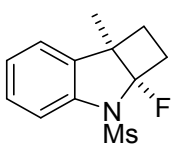


Compound 3a: A white solid (53.7 mg, 81%); M.p. 89-90 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.53 (s, 3H), 1.62 – 1.74 (m, 1H), 1.85 – 2.00 (m, 1H), 2.39 (s, 3H), 2.85 – 3.00 (m, 1H), 3.12 – 3.25 (m, 1H), 6.97 (dd, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 7.1 Hz, 1H), 7.14 (dd, *J* = 7.4 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 3H), 7.94 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 16.3 (d, *J* = 7.7 Hz), 21.6, 27.4 (d, *J* = 17.2 Hz), 32.9 (d, *J* = 30.2 Hz), 52.2 (d, *J* = 19.3 Hz), 107.7 (d, *J* = 278.4 Hz), 112.1, 122.4, 123.3, 127.7 (d, *J* = 3.0 Hz), 127.9, 129.7, 135.4, 136.8, 142.0, 144.3. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.8. IR (neat) ν 3050, 2975, 1670, 1595, 1491, 1444, 1431, 1314, 1286, 1249, 1151, 1116, 1042, 1022, 1015, 927, 904, 766, 753, 738, 692, 665 cm^{-1}. HRMS (ESI) Calcd. for $C_{18}H_{18}NO_2S$ requires (M^+-F): 312.1053, Found: 312.1055.



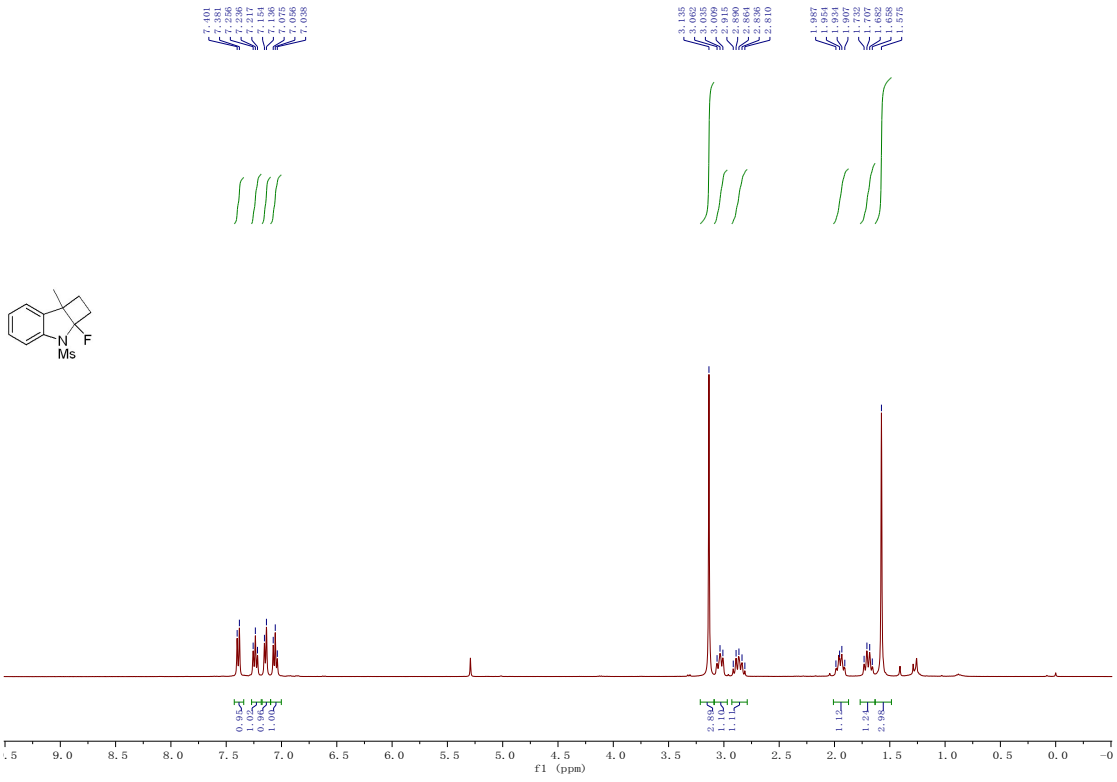


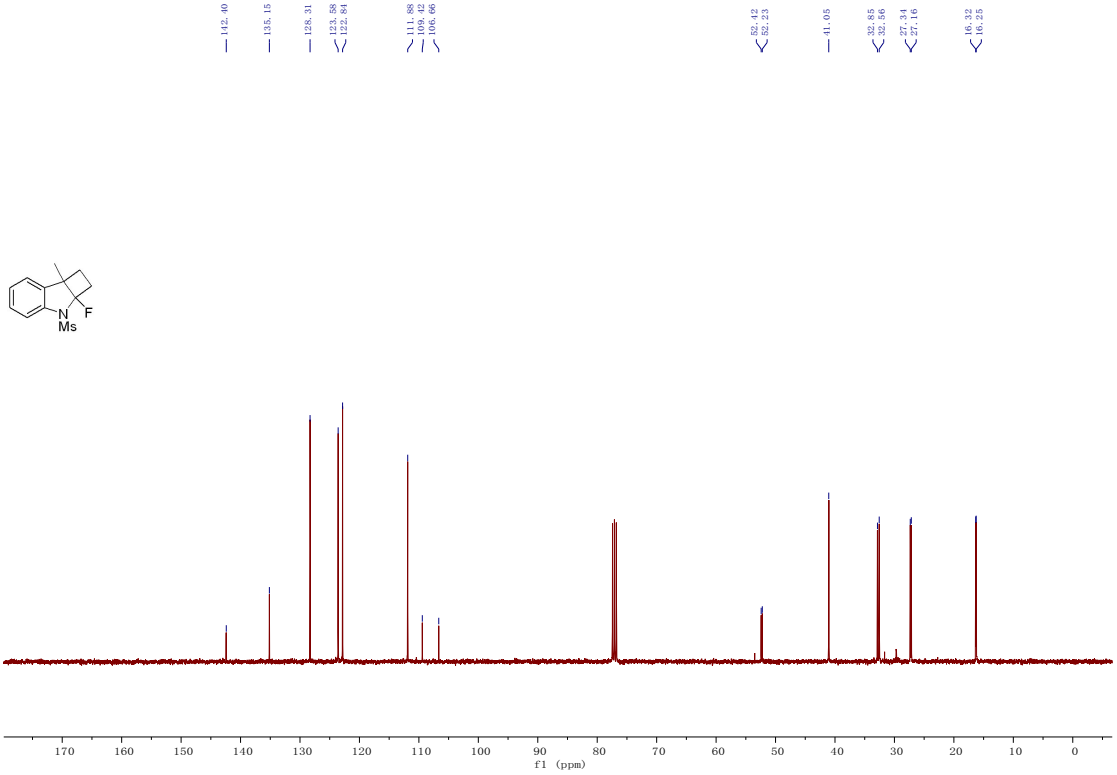


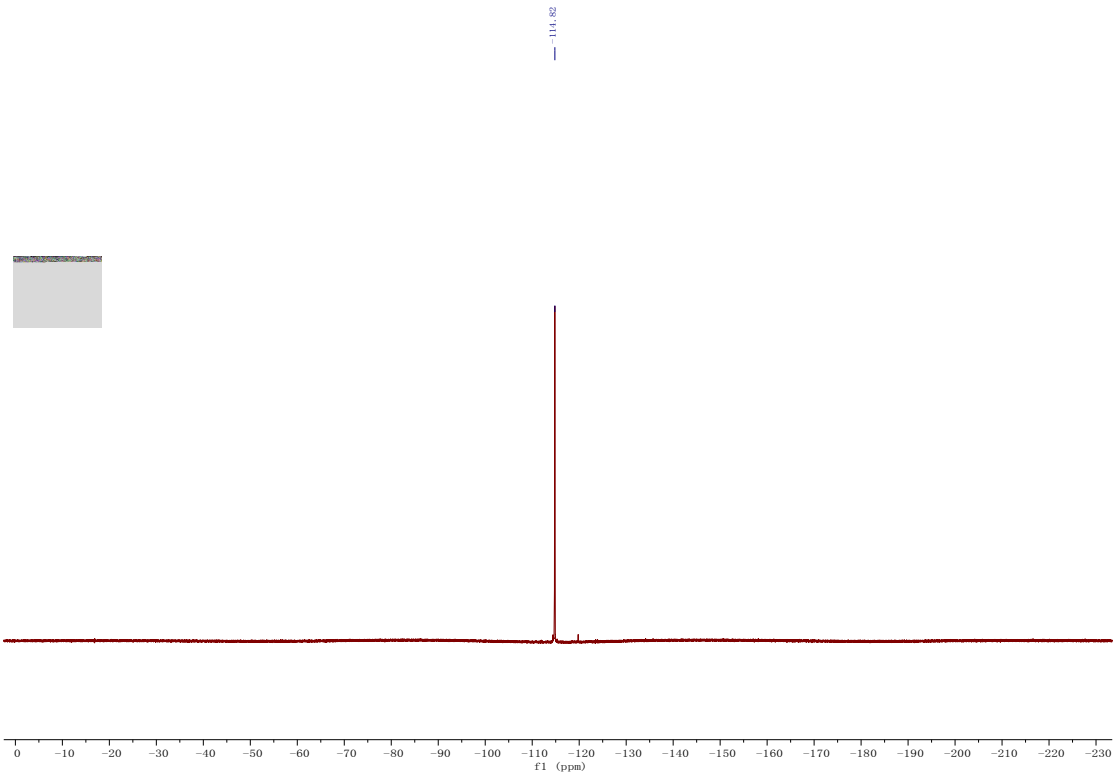


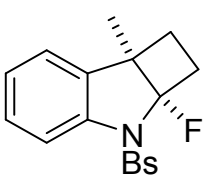
Compound 3b: A colorless oil (35.1 mg, 69%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.58 (s, 3H), 1.63 – 1.77 (m, 1H), 1.87 – 2.01 (m, 1H), 2.79 – 2.93 (m, 1H), 2.97 – 3.09 (m, 1H), 3.14 (s, 3H),

7.06 (dd, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 7.2 Hz, 1H), 7.24 (dd, *J* = 7.9 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 16.3 (d, *J* = 7.6 Hz), 27.2 (d, *J* = 17.7 Hz), 32.7 (d, *J* = 29.5 Hz), 41.0 (d, *J* = 1.5 Hz), 52.3 (d, *J* = 19.2 Hz), 108.0 (d, *J* = 278.5 Hz), 111.9, 122.8, 123.6, 128.3, 135.1, 142.4 (d, *J* = 3.0 Hz).^{19}F NMR (376 MHz, Chloroform-*d*) δ -114.8. IR (neat) ν 2964, 2927, 2867, 1604, 1479, 1453, 1354, 1247, 1185, 1168, 1154, 1095, 1017, 963, 943, 809, 767, 747 cm^{-1}. HRMS (ESI) Calcd. for $C_{12}H_{14}NO_2S$ requires (M^+-F): 236.0740, Found: 236.0741.

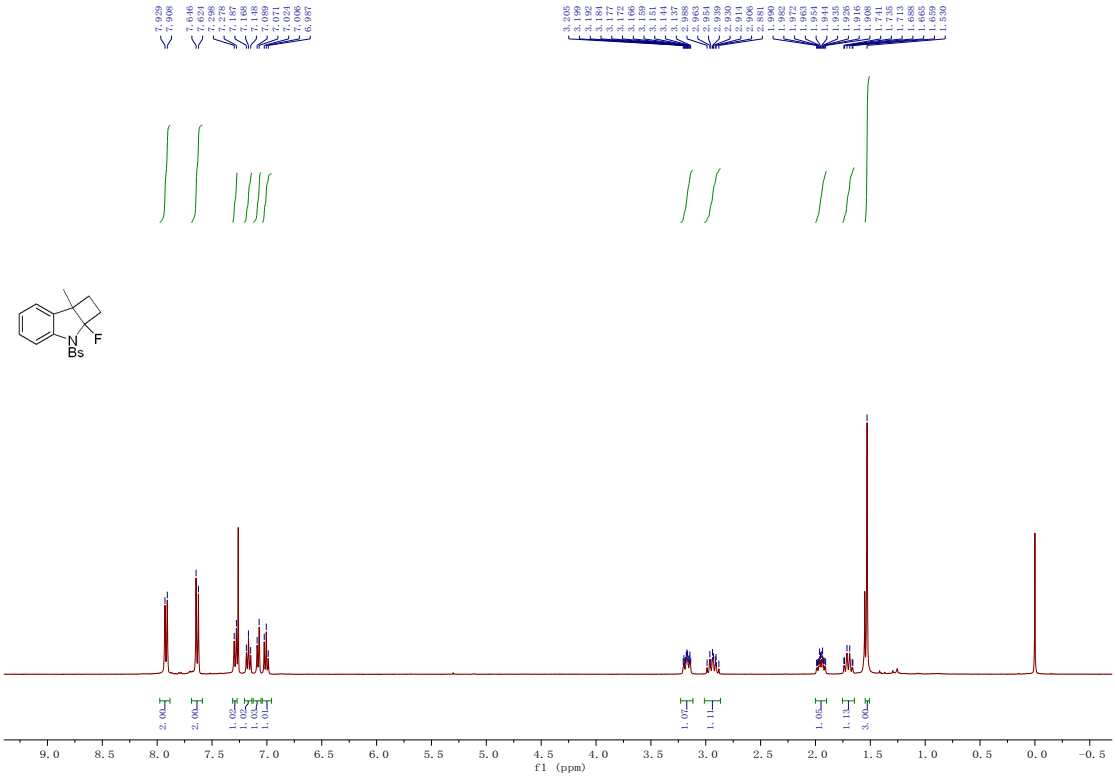


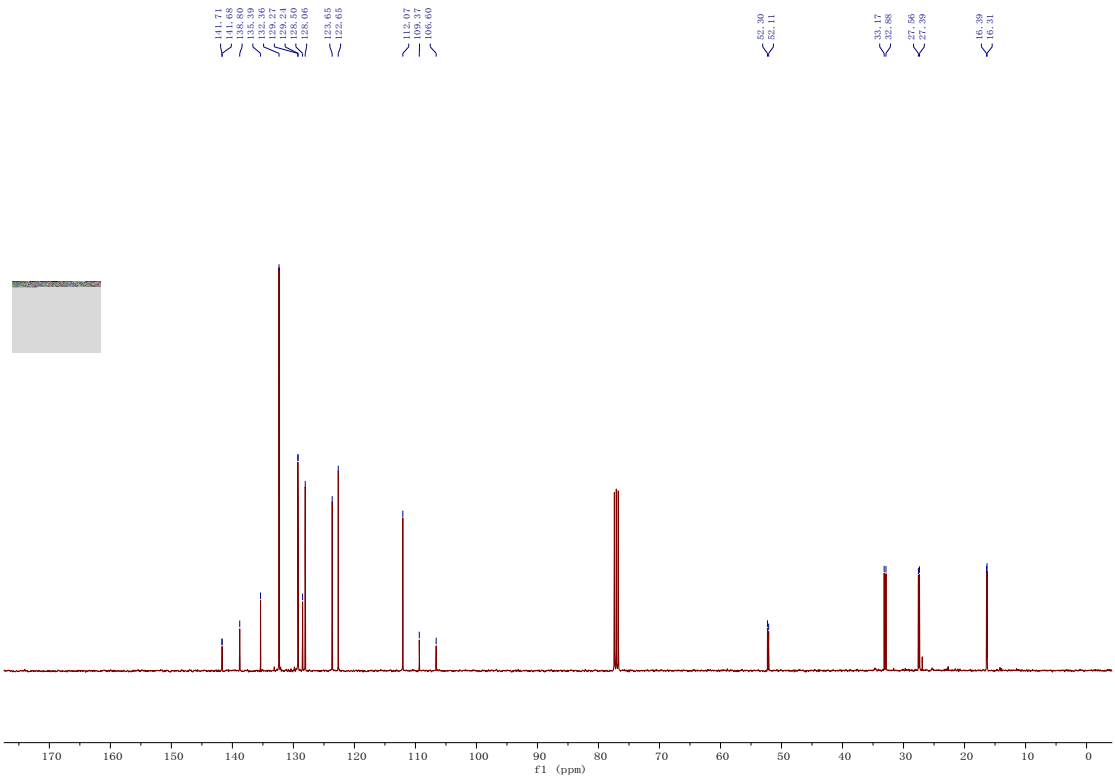

142.40
135.15
128.31
123.58
122.84
111.88
109.42
106.66
52.42
52.23
41.05
32.85
32.66
27.34
27.16
16.32
16.25
N
F
Ms
f1 (ppm)

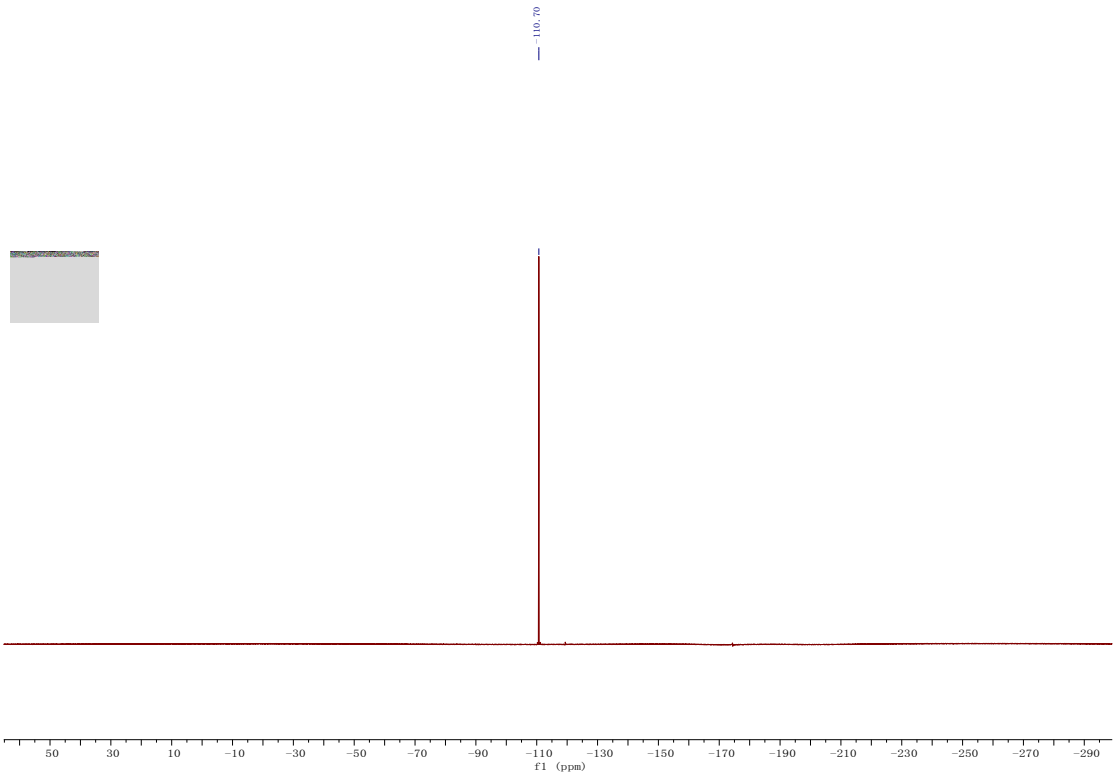

-114.82
f1 (ppm)

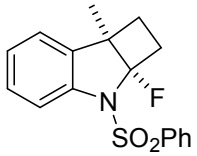

N
F
Bs

Compound 3c: A white solid (50.9 mg, 32%); M.p. 115-116 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.53 (s, 3H), 1.65 – 1.75 (m, 1H), 1.95 (tdd, *J* = 10.9, 7.2, 3.1 Hz, 1H), 2.93 (dq, *J* = 13.1, 10.1 Hz, 1H), 3.17 (ddt, *J* = 13.7, 8.7, 2.7 Hz, 1H), 7.01 (dd, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 7.3 Hz, 1H), 7.14 – 7.20 (m, 1H), 7.29 (d, *J* = 8.1 Hz, 1H), 7.59 – 7.69 (m, 2H), 7.88 – 7.98 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 16.4 (d, *J* = 7.7 Hz), 27.5 (d, *J* = 17.3 Hz), 33.0 (d, *J* = 29.7 Hz), 52.2 (d, *J* = 19.4 Hz), 108.0 (d, *J* = 278.7 Hz), 112.1, 122.6, 123.6, 128.1, 128.5, 129.3 (d, *J* = 3.5 Hz), 132.4, 135.4, 138.8, 141.7 (d, *J* = 2.7 Hz). ^{19}F NMR (377 MHz, Chloroform-*d*) -110.7. IR (neat) ν 2990， 2954， 2920， 2844， 1607， 1576， 1469， 1388， 1246， 1171， 1159， 1138， 1094， 1085， 1069， 1007， 937， 819， 812， 759， 750， 740 cm^{-1}. HRMS (ESI) Calcd. for $C_{17}H_{15}BrNO_2S$ requires (M^+-F): 376.0001, Found: 375.9999.



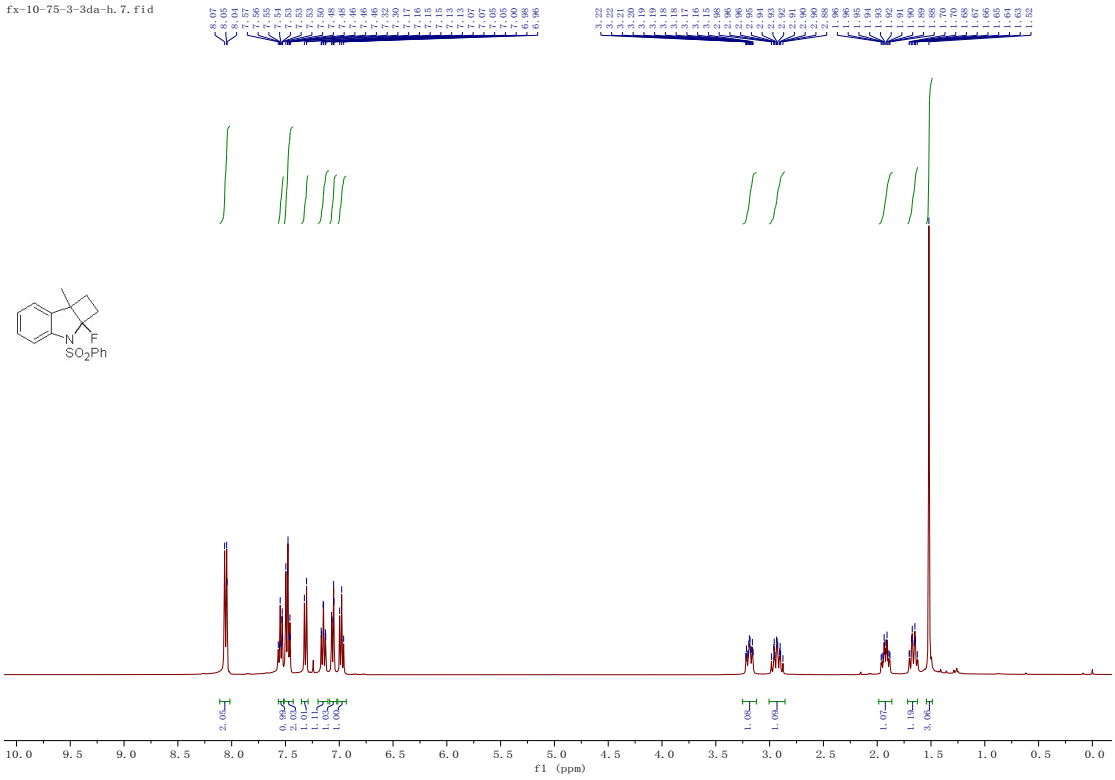


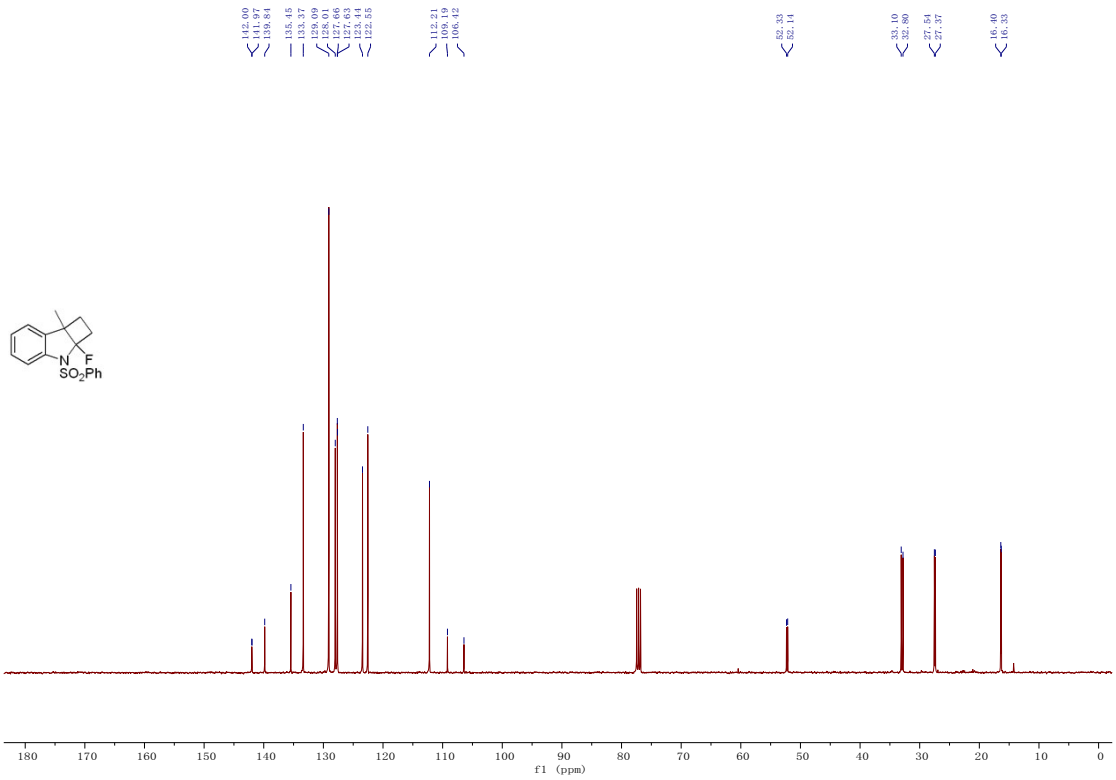


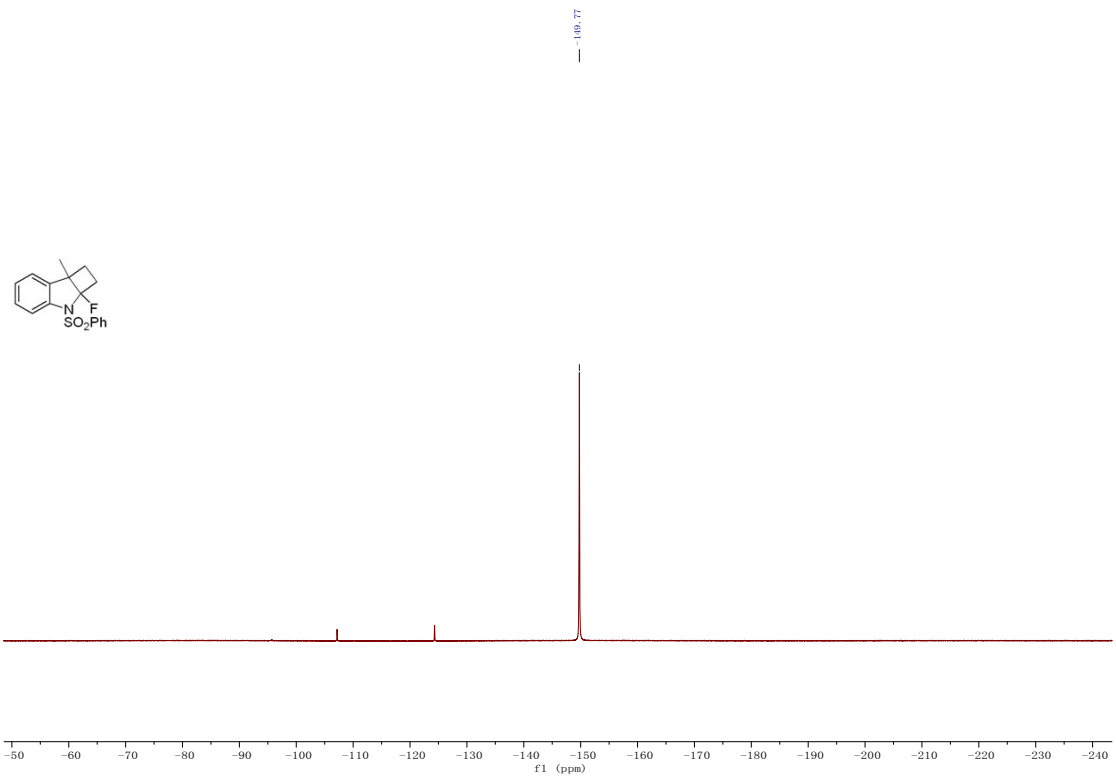


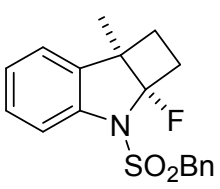
Compound 3d: A pale yellow oil (25.9 mg, 41%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.52 (s, 3H), 1.63 – 1.71 (m, 1H), 1.92 (tdd, *J* = 10.9, 7.2, 3.0 Hz, 1H), 2.93 (dq, *J* = 13.2, 10.4 Hz, 1H),

3.19 (ddt, *J* = 13.7, 8.7, 2.6 Hz, 1H), 6.98 (dd, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 7.3 Hz, 1H), 7.15 (ddd, *J* = 8.1, 7.8, 1.4 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.44 – 7.51 (m, 2H), 7.55 (dd, *J* = 7.3 Hz, 1H), 8.01 – 8.11 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 16.4 (d, *J* = 7.7 Hz), 27.5 (d, *J* = 17.1 Hz), 33.0 (d, *J* = 29.9 Hz), 52.2 (d, *J* = 19.5 Hz), 107.8 (d, *J* = 278.4 Hz), 112.2, 122.5, 123.4, 127.6 (d, *J* = 3.0 Hz), 128.0, 129.1, 133.4, 135.4, 139.8, 142.0 (d, *J* = 2.8 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -149.8. IR (neat) ν 3071, 2964, 2925, 2865, 1602, 1474, 1459, 447, 1360, 1248, 1185, 1157, 1141, 1118, 1097, 1086, 1013, 936, 809, 747, 732, 718, 686 cm^{-1}. HRMS (ESI) Calcd. for $C_{17}H_{16}NO_2S$ requires (M^+-F): 298.0896, Found: 298.0891.

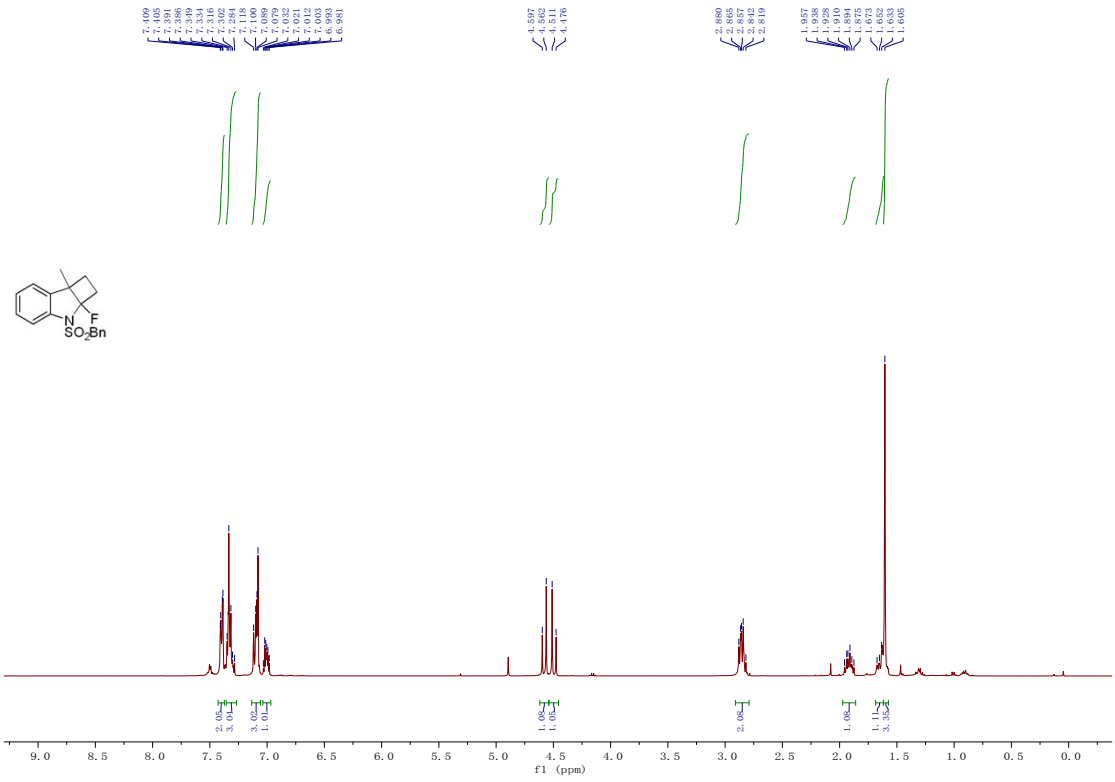


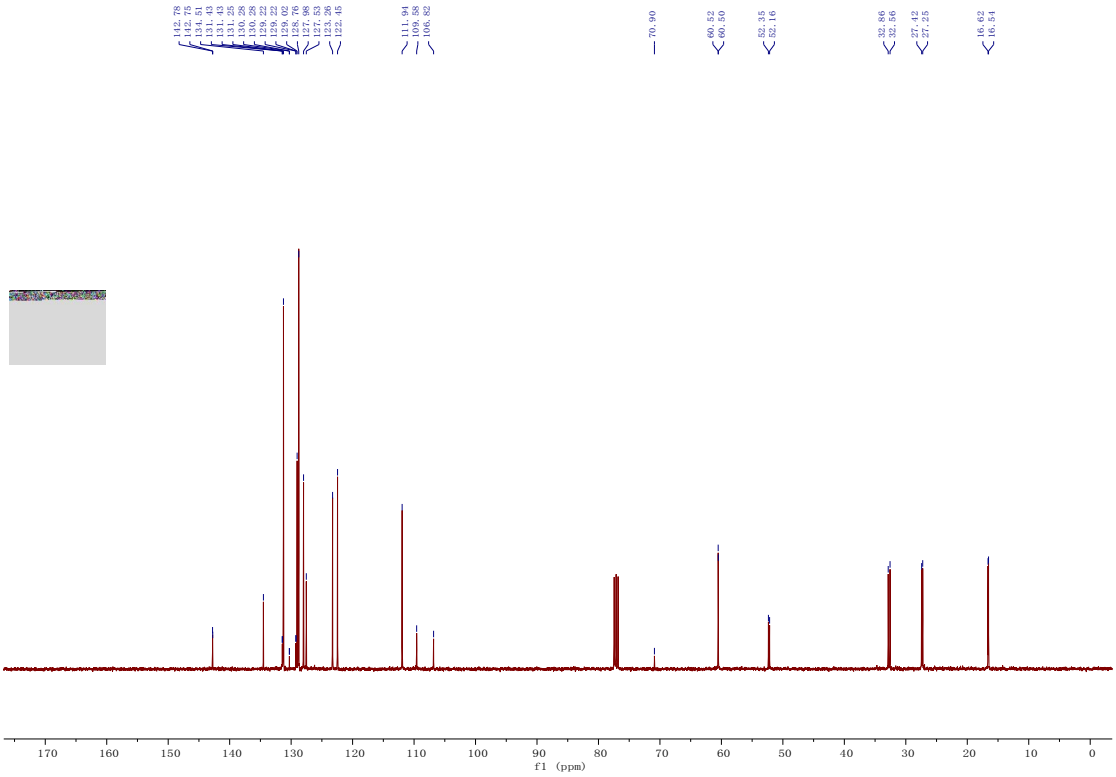

142.00
141.97
139.84
135.45
133.37
129.09
128.91
128.66
127.63
123.44
122.55
112.21
109.19
106.42
52.33
52.14
33.10
32.80
27.54
27.37
16.40
16.33
N
F
SO2Ph
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

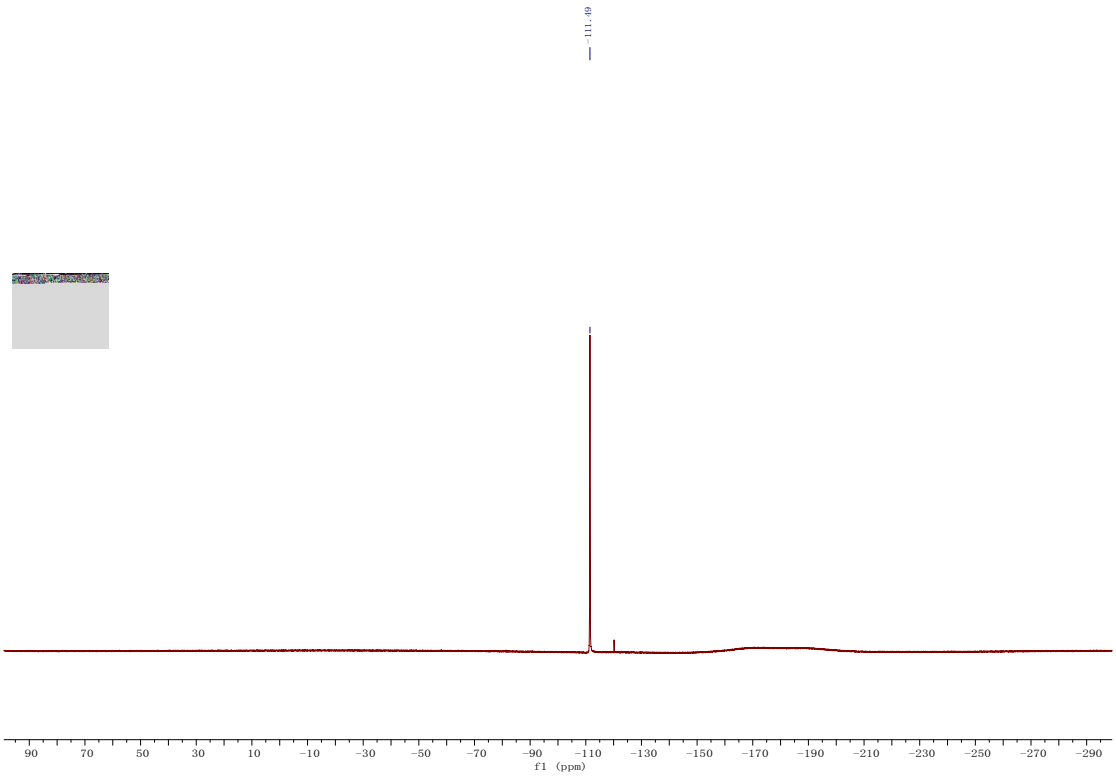

-149.77
N
F
SO2Ph
-50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

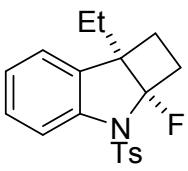

N
F
SO2Bn

Compound 3e: A colorless oil (31.3 mg, 47%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.61 (s, 3H), 1.62 – 1.69 (m, 1H), 1.92 (dq, *J* = 14.0, 7.5 Hz, 1H), 2.86 (dd, *J* = 9.2, 6.0 Hz, 2H), 4.49 (d, *J* = 13.8 Hz, 1H), 4.58 (d, *J* = 13.8 Hz, 1H), 7.01 (ddd, *J* = 8.6, 4.6, 4.6 Hz, 1H), 7.06 – 7.13 (m, 3H), 7.27 – 7.36 (m, 3H), 7.37 – 7.43 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ ^{13}C NMR (101 MHz, Chloroform-*d*) δ 16.6 (d, *J* = 8.0 Hz), 27.3 (d, *J* = 17.4 Hz), 32.7 (d, *J* = 30.0 Hz), 52.3 (d, *J* = 19.1 Hz), 60.5 (d, *J* = 2.3 Hz), 108.2 (d, *J* = 277.2 Hz), 111.9, 122.4, 123.3, 127.5, 128.0, 128.8, 129.0, 131.2, 134.5, 142.8 (d, *J* = 2.9 Hz). ^{19}F NMR (377 MHz, Chloroform-*d*) δ -111.5. IR (neat) ν 2959, 2923, 2849, 1686, 1594, 1477, 1451, 1358, 1247, 1188, 1180, 1158, 1141, 1097, 1086, 1022, 1014, 945, 833, 811, 690, 665 cm^{-1}. HRMS (ESI) Calcd. for $C_{18}H_{18}NO_2S$ requires (M^+-F): 312.1053, Found: 312.1049.

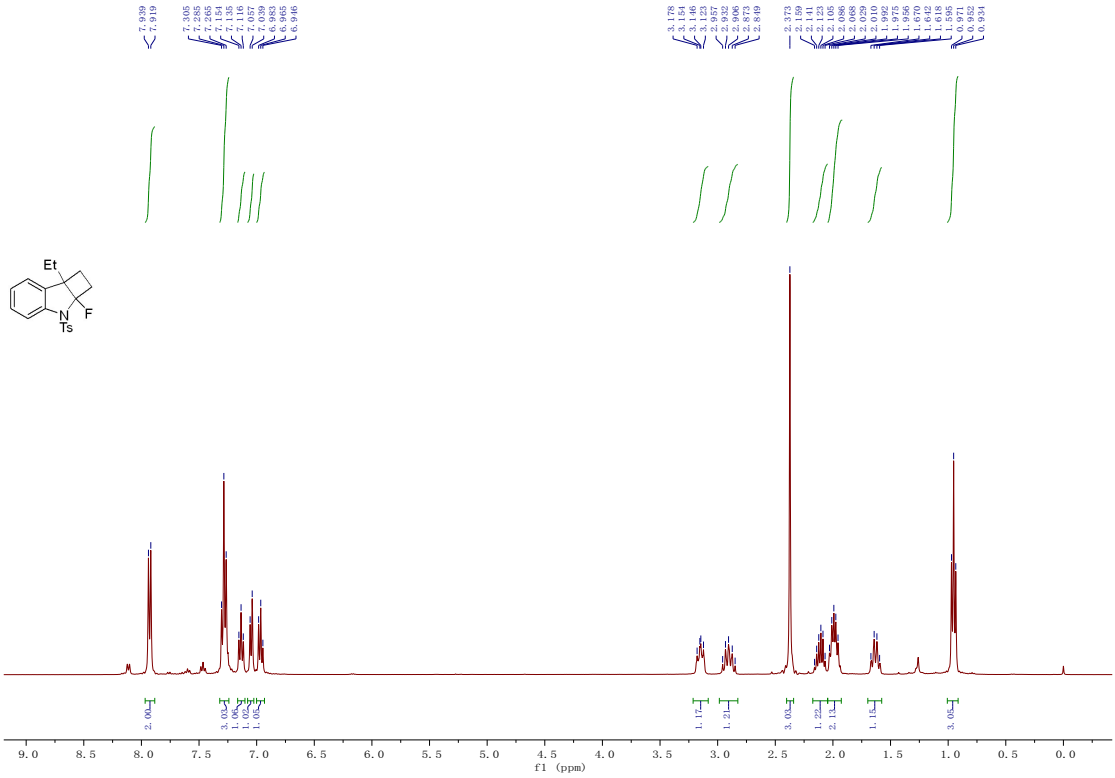


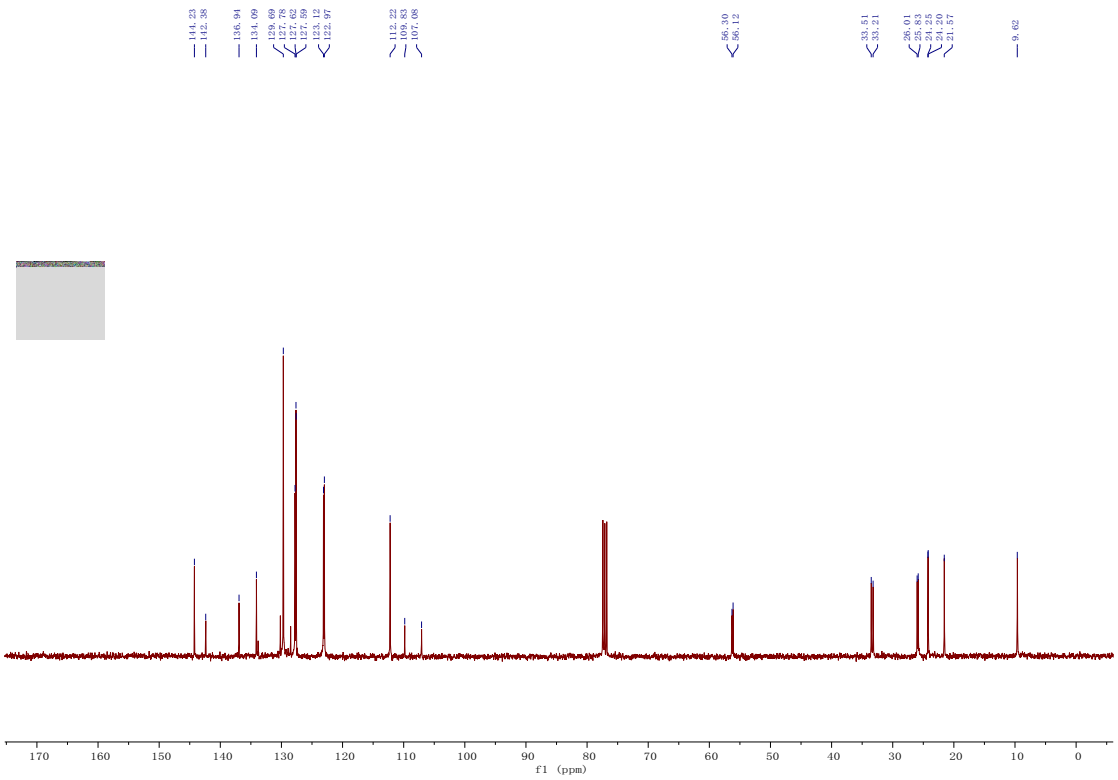

142.78
142.75
131.51
131.43
131.25
130.28
130.08
129.22
129.02
128.76
127.98
127.53
123.26
122.45
111.94
109.58
106.82
70.90
60.52
60.50
52.35
52.16
32.86
32.56
27.42
27.25
16.62
16.54
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-111.49
90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -270 -290
f1 (ppm)


Et
N
Ts
F

Compound 3g: A colorless oil (62.2 mg, 90%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 0.95 (t, *J* = 7.4 Hz, 3H), 1.63 (q, *J* = 10.3, 9.4 Hz, 1H), 1.99 (dt, *J* = 14.5, 7.7 Hz, 2H), 2.11 (dq, *J* = 14.6, 7.3 Hz, 1H), 2.37 (s, 3H), 2.82 – 2.99 (m, 1H), 3.15 (dd, *J* = 12.7, 9.5 Hz, 1H), 6.96 (dd, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 7.2 Hz, 1H), 7.14 (dd, *J* = 7.7 Hz, 1H), 7.24 – 7.32 (m, 3H), 7.88 – 7.97 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 9.6, 21.6, 24.2 (d, *J* = 5.3 Hz), 25.9 (d, *J* = 17.6 Hz), 33.4 (d, *J* = 30.5 Hz), 56.2 (d, *J* = 18.6 Hz), 108.5 (d, *J* = 277.0 Hz), 112.2, 123.0 (d, *J* = 14.6 Hz), 127.6 (d, *J* = 2.9 Hz), 127.8, 129.7, 134.1, 136.9, 142.4, 144.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -110.0. IR (neat) ν 2972, 2920, 1654, 1618, 1584, 1545, 1459, 1359, 1244, 1188, 1179, 1157, 1111, 1087, 993, 813, 748, 704, 654 cm^{-1}. HRMS (ESI) Calcd. for $C_{19}H_{20}NO_2S$ requires (M^+-F): 326.1209, Found: 326.1203.




144.23
142.38
136.94
134.09
129.69
127.78
127.62
127.59
123.12
122.97
112.22
109.83
107.08
56.30
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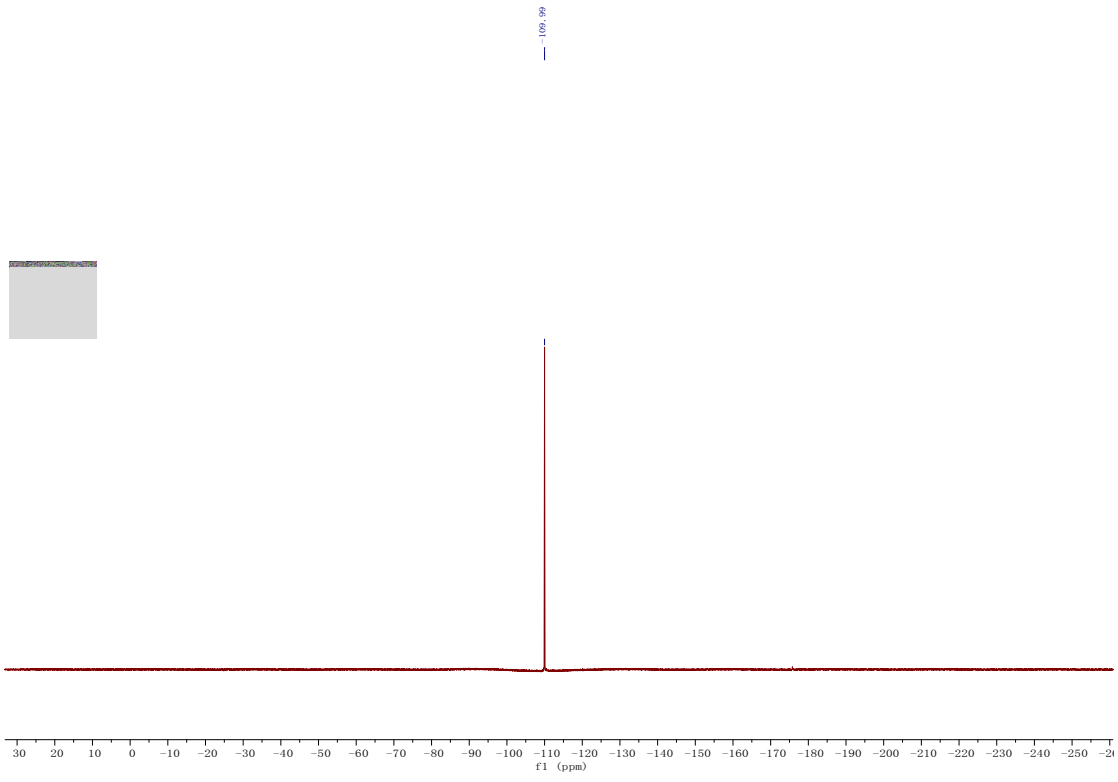
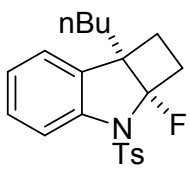
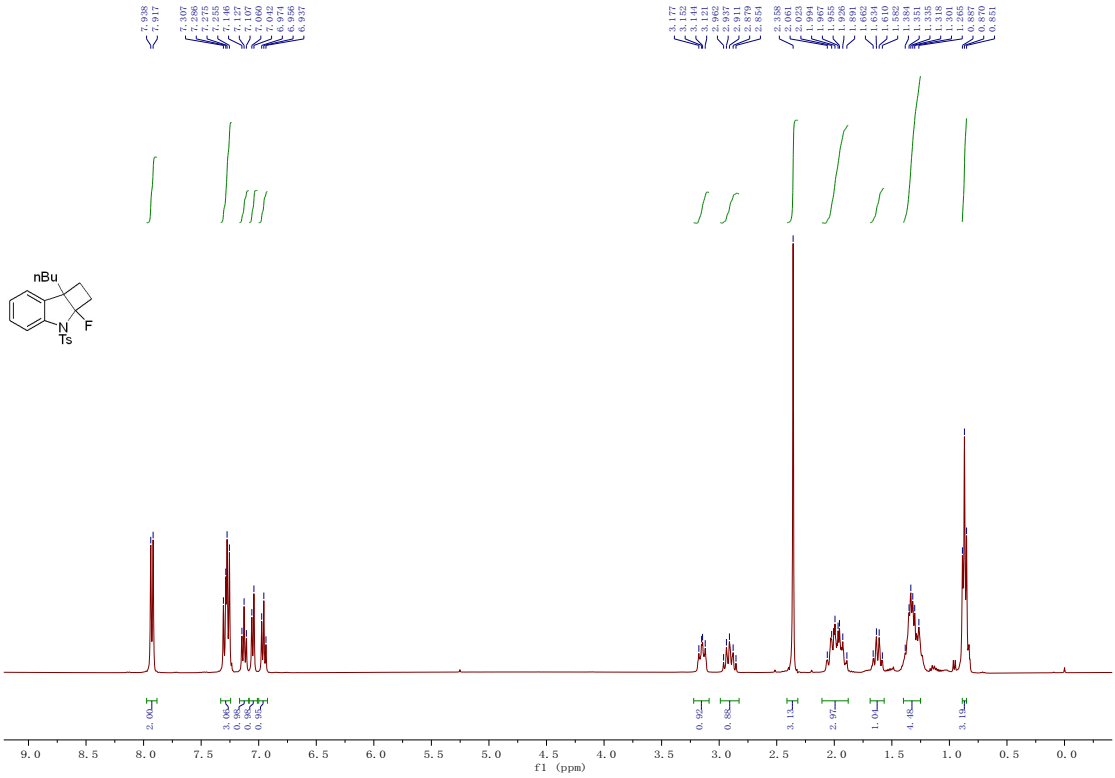
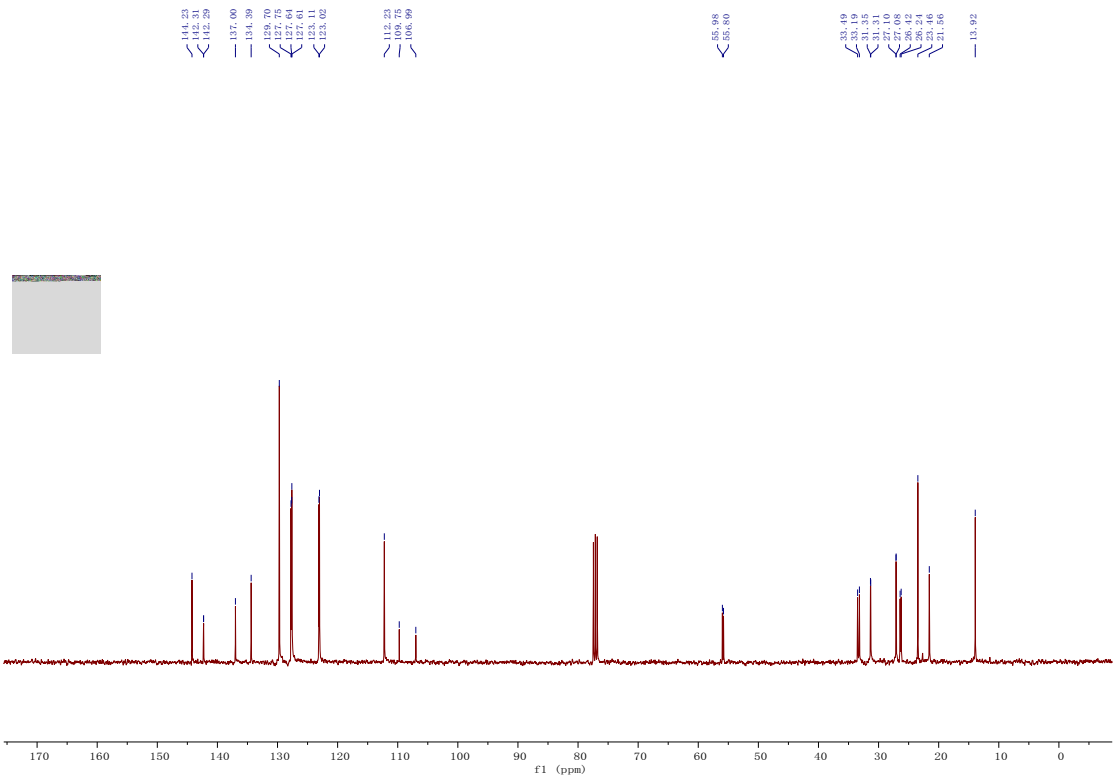
33.51
33.21
26.01
25.83
24.25
24.00
21.57
9.62
f1 (ppm)

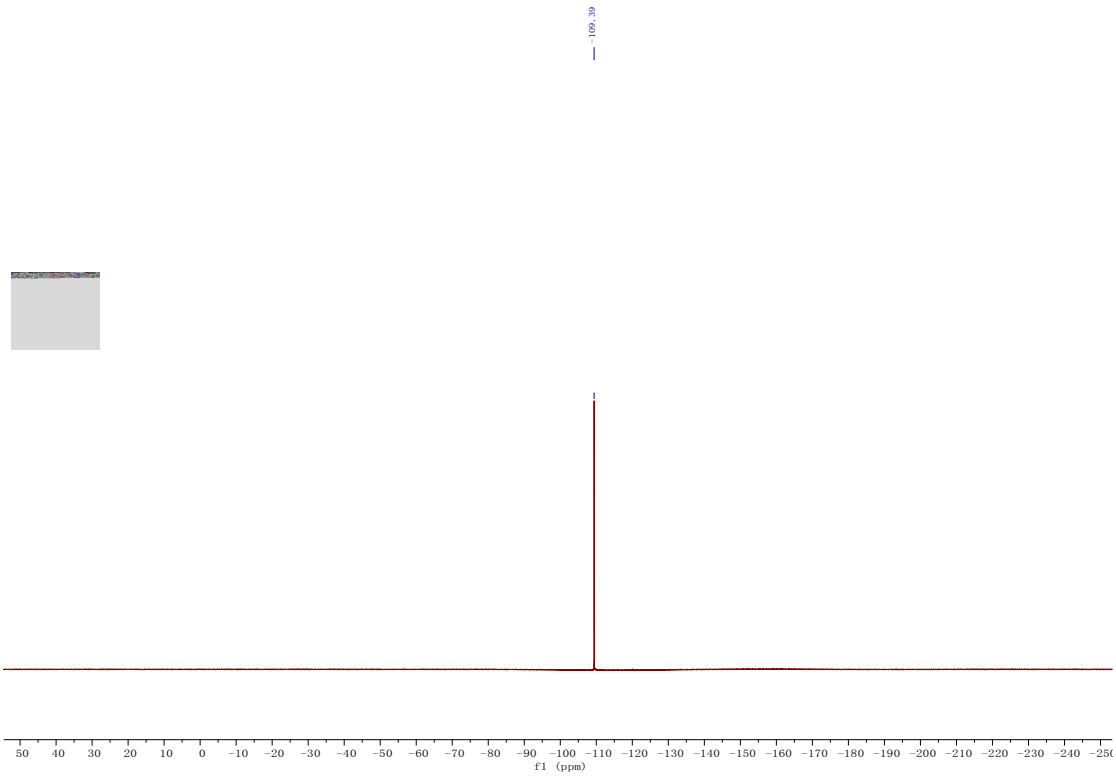

-109.99
f1 (ppm)

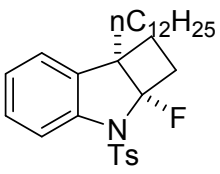

nBu
N
Ts
F

Compound 3h: A colorless oil (58.0 mg, 78%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 0.88 (d, *J* = 6.9 Hz, 3H), 1.31 (dt, *J* = 21.2, 10.3 Hz, 4H), 1.62 (q, *J* = 11.2 Hz, 1H), 1.88 – 2.11 (m, 3H), 2.36 (s, 3H), 2.83 – 2.99 (m, 1H), 3.09 – 3.22 (m, 1H), 6.96 (dd, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 7.2 Hz, 1H), 7.13 (dd, *J* = 7.7 Hz, 1H), 7.24 – 7.33 (m, 3H), 7.88 – 7.97 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 13.9, 21.6, 23.5, 26.3 (d, *J* = 17.6 Hz), 27.1 (d, *J* = 2.6 Hz), 31.3 (d, *J* = 4.5 Hz), 33.3 (d, *J* = 30.4 Hz), 55.9 (d, *J* = 18.6 Hz), 108.4 (d, *J* = 277.0 Hz), 112.2, 123.1 (d, *J* = 9.6 Hz), 127.6 (d, *J* = 2.8 Hz), 127.8, 129.7, 134.4, 137.0, 142.3, 144.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.4. IR (neat) ν 2956, 2920, 2873, 2849, 1644, 1594, 1479, 1463, 1365, 1257, 1188, 1170, 1114, 1089, 1042, 1032, 1012, 813, 749, 702, 679, 657 cm^{-1}. HRMS (ESI) Calcd. for $C_{21}H_{24}NO_2S$ requires (M^+-F): 354.1522, Found: 354.1514.

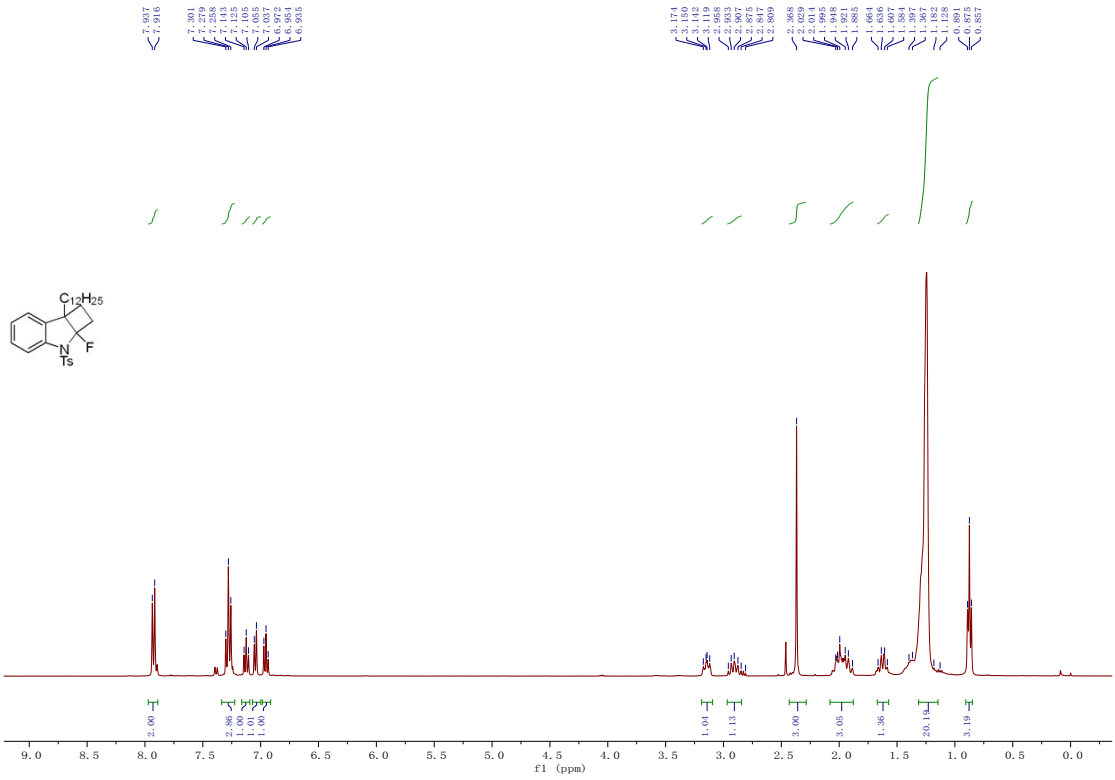


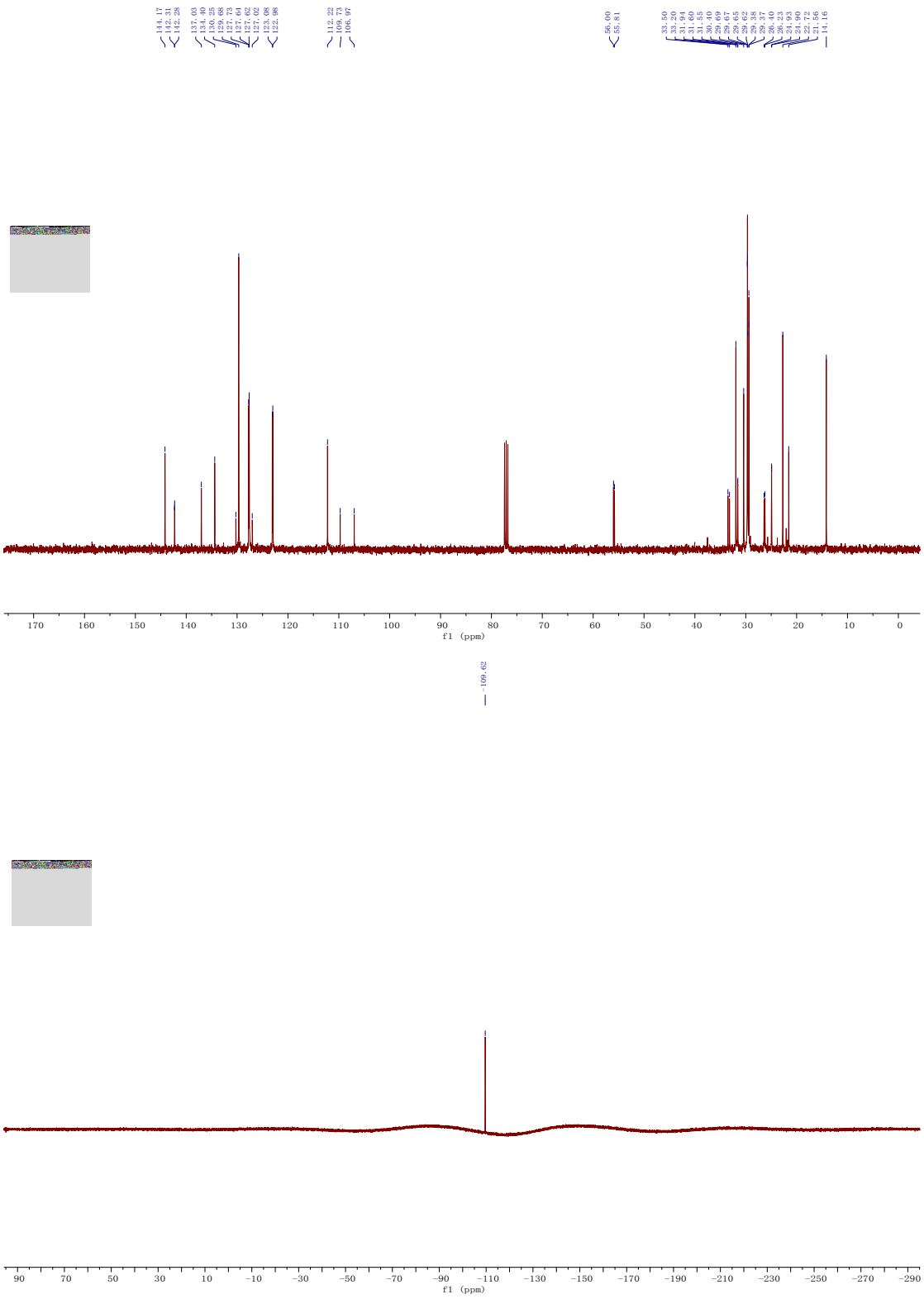

144.23
142.31
142.29
137.00
134.39
129.70
127.75
127.64
127.61
123.11
122.62
112.23
109.75
106.99
55.98
55.80
33.49
33.19
31.35
31.31
27.10
27.06
26.42
26.24
23.46
21.96
13.92
f1 (ppm)


-109.39
f1 (ppm)


nC12H25
F
N
Ts

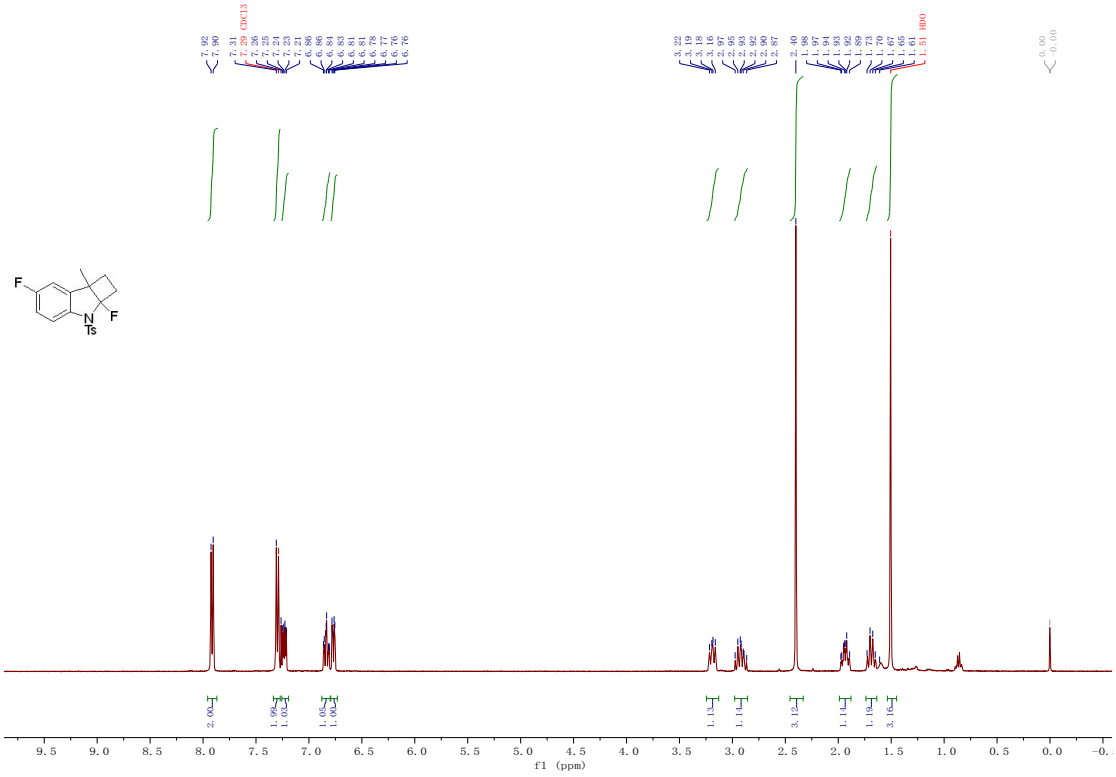
Compound 3i: A colorless oil (68.9 mg, 71%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 0.87 (t, *J* = 6.7 Hz, 3H), 1.18 (s, 20H), 1.62 (q, *J* = 10.3, 9.5 Hz, 1H), 1.88 – 2.08 (m, 3H), 2.37 (s, 3H), 2.84 – 2.97 (m, 1H), 3.15 (dd, *J* = 12.8, 9.4 Hz, 1H), 6.95 (dd, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 7.3 Hz, 1H), 7.12 (dd, *J* = 7.8 Hz, 1H), 7.22 – 7.34 (m, 3H), 7.89 – 7.97 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 14.2, 21.6, 22.7, 24.9 (d, *J* = 2.5 Hz), 26.3 (d, *J* = 17.6 Hz), 29.37, 29.38, 29.62, 29.65, 29.67, 29.69, 30.4, 31.6 (d, *J* = 4.5 Hz), 31.9, 33.3 (d, *J* = 30.3 Hz), 55.9 (d, *J* = 18.7 Hz), 108.4 (d, *J* = 277.2 Hz), 112.2, 123.0 (d, *J* = 9.8 Hz), 127.6 (d, *J* = 2.8 Hz), 127.7, 129.7, 134.4, 137.0, 142.3 (d, *J* = 2.4 Hz), 144.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.6. IR (neat) ν 2923, 2852, 1597, 1477, 1459, 1363, 1248, 1179, 1158, 1140, 1113, 1088, 1026, 1010, 932, 812, 747, 669, 684, 654 cm^{-1}. HRMS (ESI) Calcd. for $C_{29}H_{40}NO_2S$ requires (M^+-F): 466.2774, Found: 466.2767.

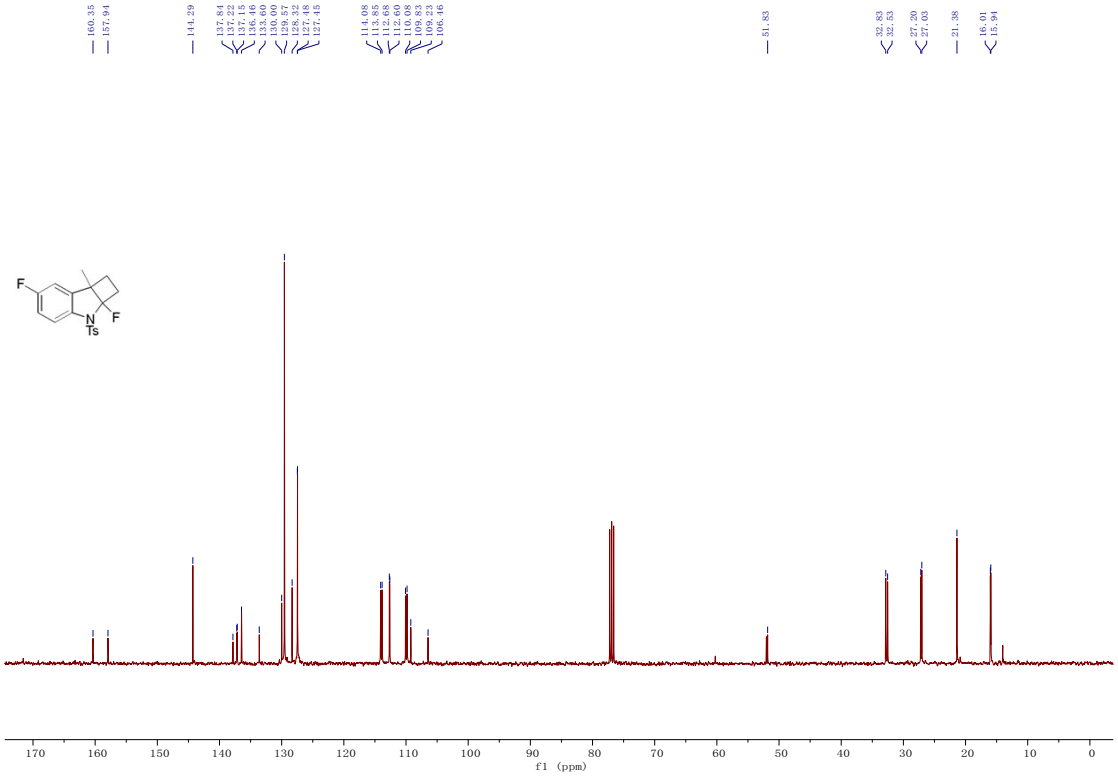


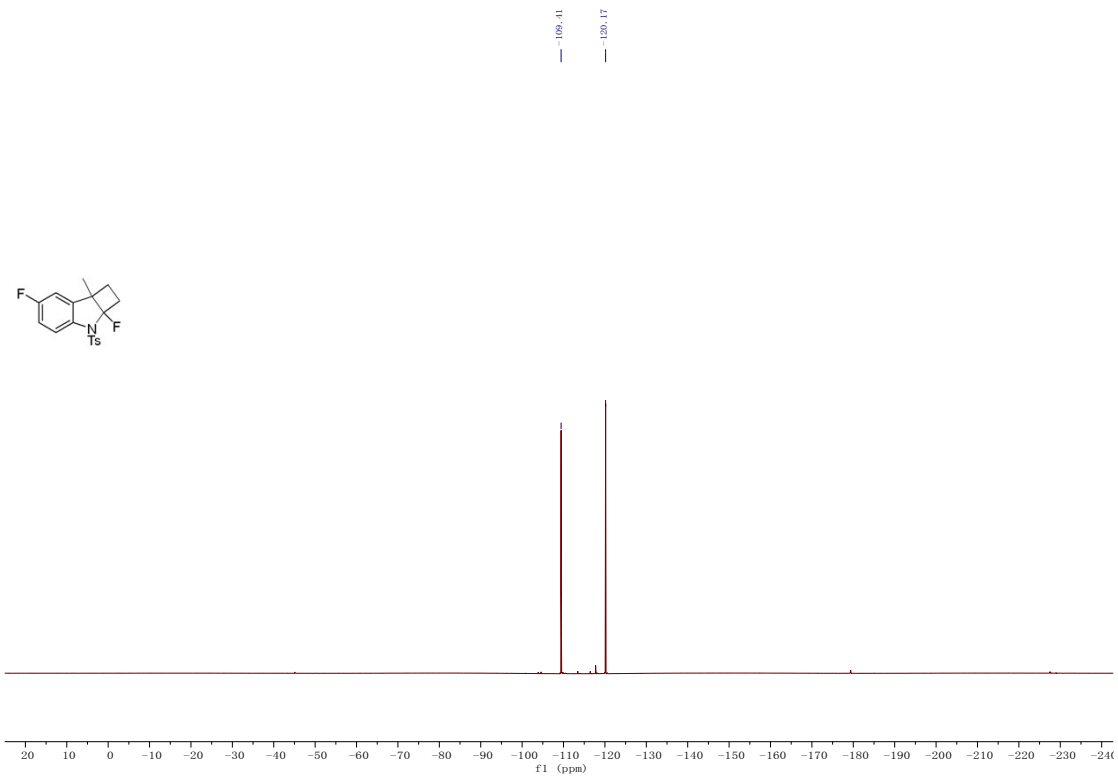


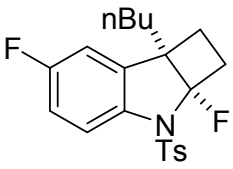
Compound 3j: A white solid (68.5 mg, 98%); M.p. 97-98 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.69 (q, *J* = 10.5, 9.7 Hz, 1H), 1.88 – 1.99 (m, 1H), 2.40 (s, 3H), 2.86 – 2.98 (m, 1H), 3.19 (dd, *J* =

13.1, 8.9 Hz, 1H), 6.77 (dd, *J* = 7.4, 3.3 Hz, 1H), 6.83 (ddd, *J* = 10.0, 9.9, 2.7 Hz, 1H), 7.23 (dd, *J* = 9.4, 4.9 Hz, 1H), 7.27 – 7.33 (m, 2H), 7.87 – 7.96 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 16.0 (d, *J* = 7.2 Hz), 21.4, 27.1 (d, *J* = 17.2 Hz), 32.7 (d, *J* = 30.1 Hz), 51.8, 107.8 (d, *J* = 278.9 Hz), 110.0 (d, *J* = 24.4 Hz), 112.6 (d, *J* = 8.4 Hz), 114.0 (d, *J* = 23.3 Hz), 127.5 (d, *J* = 3.1 Hz), 128.3, 129.6, 130.0, 133.6, 136.5, 137.2 (d, *J* = 7.6 Hz), 137.8, 144.3, 159.1 (d, *J* = 241.9 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -120.2, -109.4. IR (neat) ν 3056, 2975, 1670, 1595, 1495, 1469, 1448, 1430, 1314, 1287, 1249, 1151, 1114, 1023, 927, 803, 765, 753, 722, 654 cm^{-1}. HRMS (ESI) Calcd. for $C_{18}H_{17}F_2NaNO_2S$ requires (M^++Na): 372.0840, Found: 372.0840.

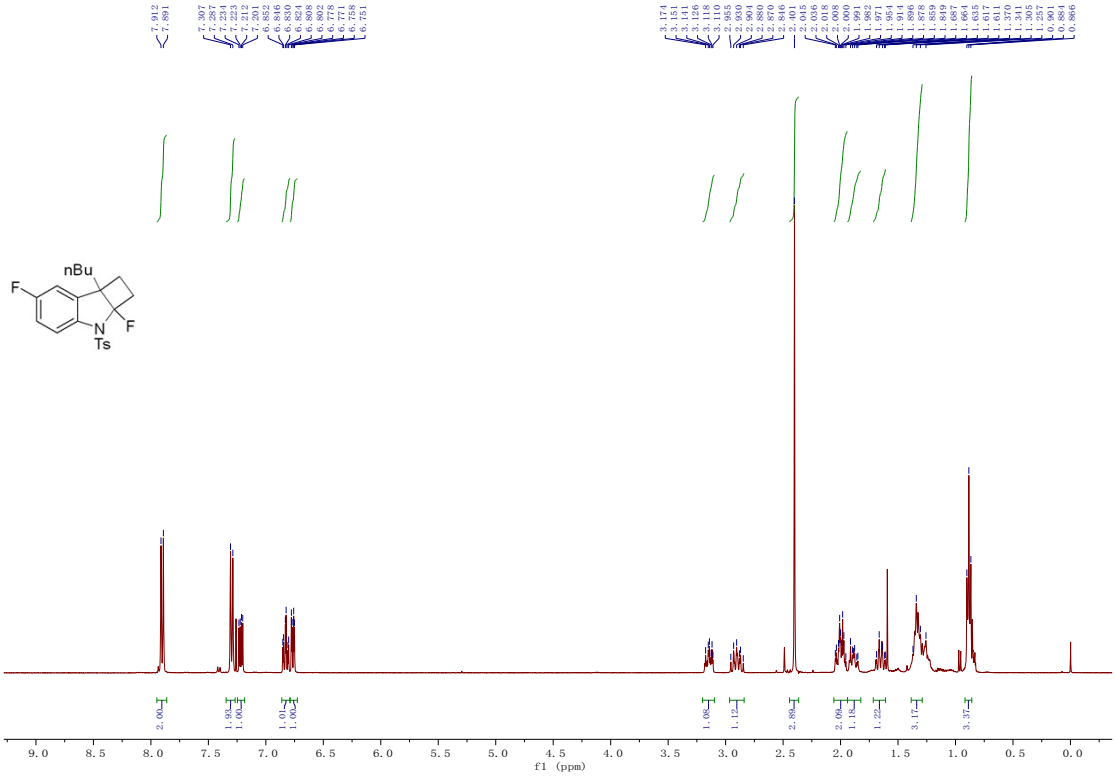


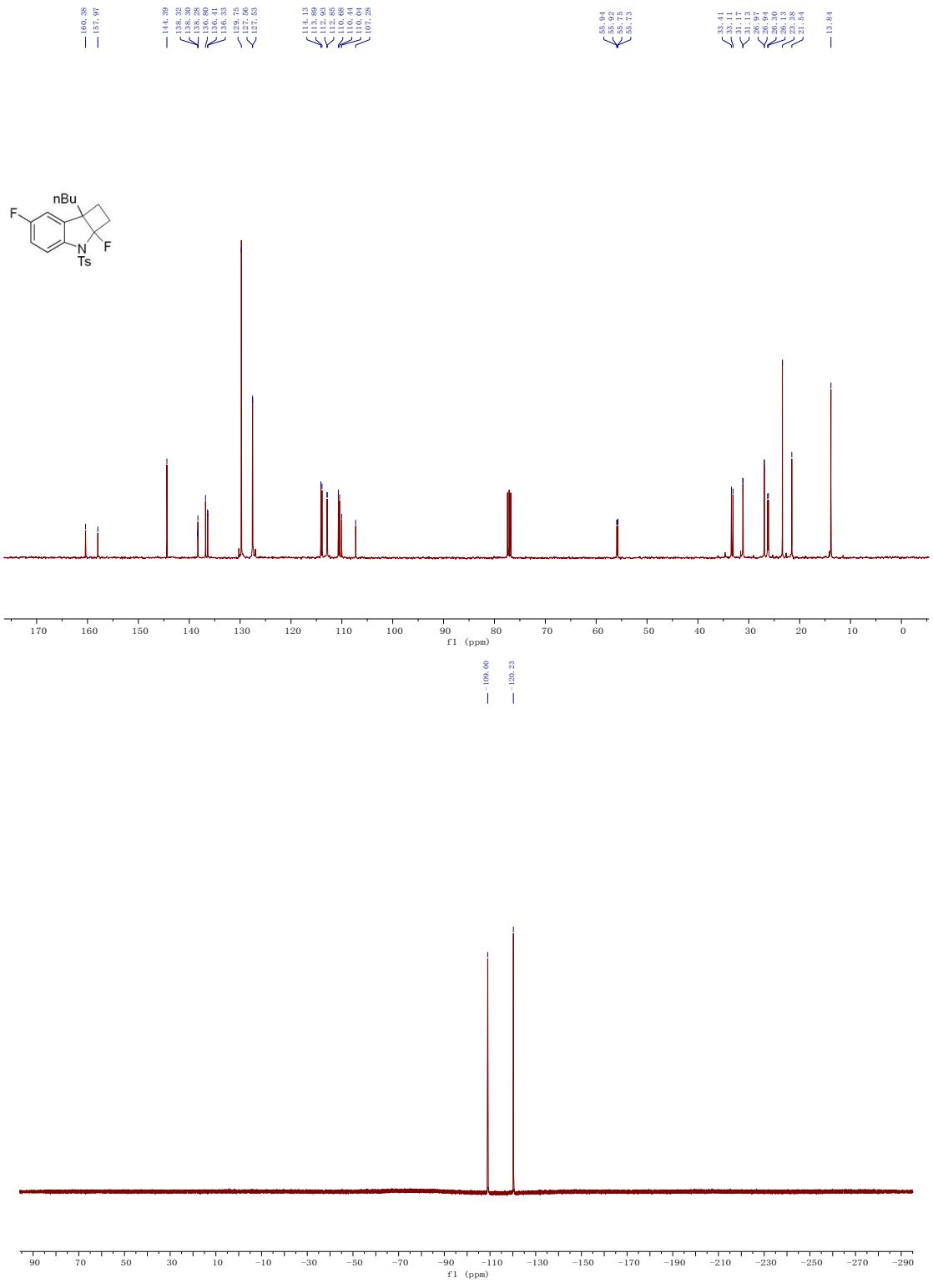

160.35
157.94
144.29
137.84
137.22
137.15
136.46
133.60
130.00
128.57
128.32
127.48
127.45
114.08
113.85
112.68
112.60
110.08
109.83
109.23
106.46
51.83
32.83
32.53
27.20
27.03
21.38
16.01
15.94
F
N
Ts
F
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

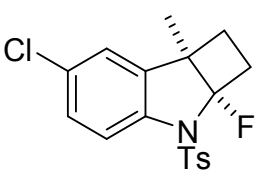

-109.41
-120.17
F
N
Ts
F
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)


nBu
F
N
Ts
F

Compound 3k: A pale yellow oil (51.1 mg, 65%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 0.88 (t, *J* = 6.9 Hz, 3H), 1.34 (t, *J* = 12.9 Hz, 3H), 1.61 – 1.72 (m, 1H), 1.82 – 1.94 (m, 1H), 1.94 – 2.06 (m, 2H), 2.40 (s, 3H), 2.84 – 2.97 (m, 1H), 3.10 – 3.20 (m, 1H), 6.76 (dd, *J* = 8.1, 2.6 Hz, 1H), 6.83 (ddd, *J* = 8.8, 8.8, 2.6 Hz, 1H), 7.22 (dd, *J* = 8.8, 4.3 Hz, 1H), 7.27 – 7.35 (m, 2H), 7.86 – 7.95 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 13.8, 21.5, 23.4, 26.2 (d, *J* = 17.4 Hz), 27.0 (d, *J* = 2.6 Hz), 31.2 (d, *J* = 4.3 Hz), 33.3 (d, *J* = 30.5 Hz), 55.8 (dd, *J* = 18.9, 1.8 Hz), 108.7 (d, *J* = 277.6 Hz), 110.6 (d, *J* = 24.2 Hz), 112.9 (d, *J* = 8.4 Hz), 114.0 (d, *J* = 23.5 Hz), 127.5 (d, *J* = 2.8 Hz), 129.8, 136.4 (d, *J* = 7.7 Hz), 136.8, 138.3 (dd, *J* = 2.3 Hz), 144.4, 159.2 (d, *J* = 241.7 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -120.2, -109.0. IR (neat) ν 3048, 2967, 1667, 1594, 1490, 1440, 1419, 1315, 1281, 1250, 1059, 1039, 1022, 1015, 906, 830, 766, 753, 723, 692, 665, 653 cm^{-1}. HRMS (ESI) Calcd. for $C_{21}H_{23}FNO_2S$ requires (M^+-F): 372.1428, Found: 372.1420.

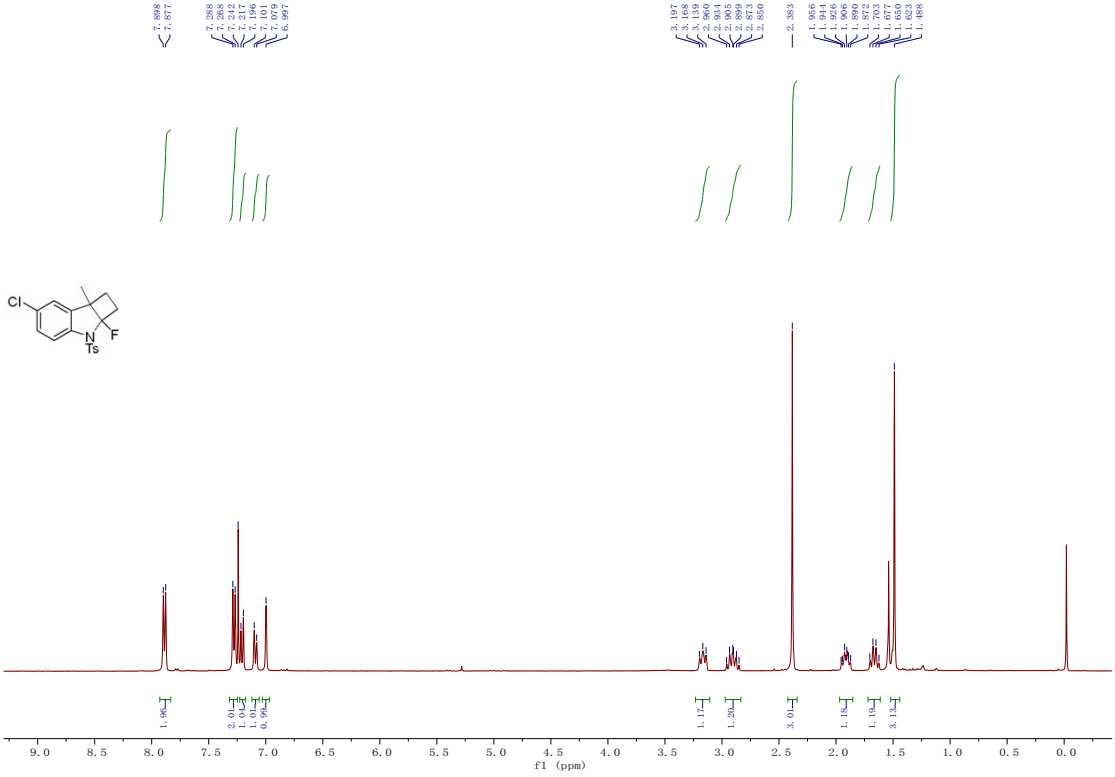


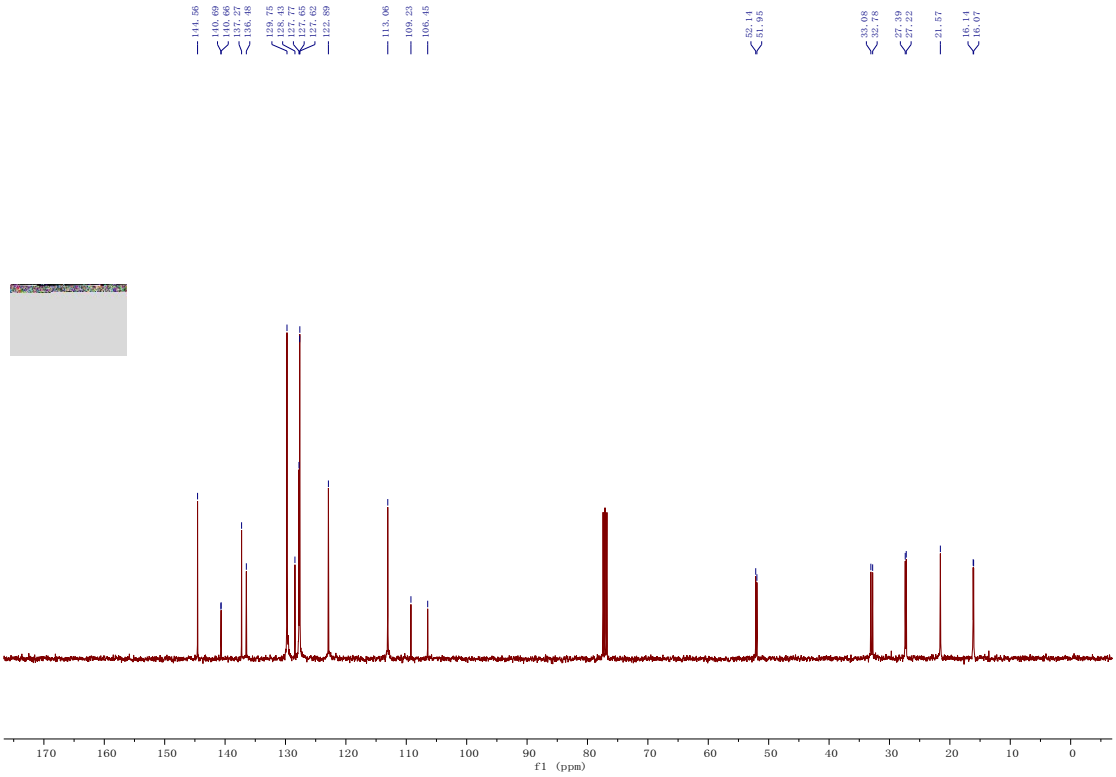


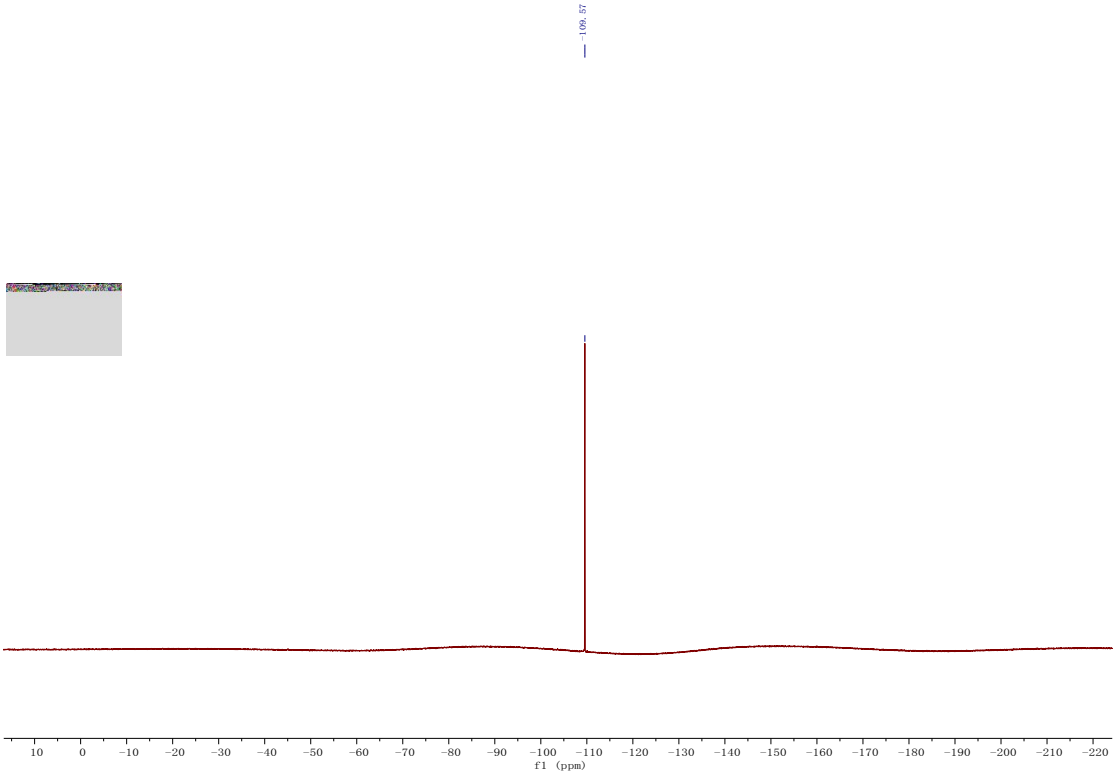


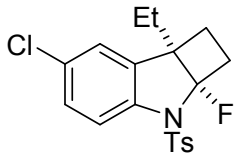
Compound 3l: A white solid (53.6 mg, 73%); M.p. 123-124 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.49 (s, 3H), 1.66 (q, *J* = 10.7 Hz, 1H), 1.85 – 1.97 (m, 1H), 2.38 (s, 3H), 2.83 – 2.97 (m, 1H),

3.11 – 3.23 (m, 1H), 7.00 (s, 1H), 7.09 (d, J = 8.6 Hz, 1H), 7.21 (d, J = 8.6 Hz, 1H), 7.25 – 7.32 (m, 2H), 7.83 – 7.93 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 16.1 (d, J = 7.5 Hz), 21.6, 27.3 (d, J = 17.0 Hz), 32.9 (d, J = 29.8 Hz), 52.0 (d, J = 19.6 Hz), 107.8 (d, J = 279.2 Hz), 113.1, 122.9, 127.6 (d, J = 2.9 Hz), 127.8, 128.4, 129.8, 136.5, 137.3, 140.7 (d, J = 2.8 Hz), 144.6. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.6. IR (neat) ν 2993, 2946, 2923, 2847, 1594, 1480, 1461, 1357, 1248, 1179, 1162, 1138, 1122, 1089, 1022, 931, 880, 866, 817, 809, 687, 664 cm^{-1}. HRMS (ESI) Calcd. for $C_{18}H_{17}ClNO_2S$ requires (M^+-F): 346.0663, Found: 346.0661.



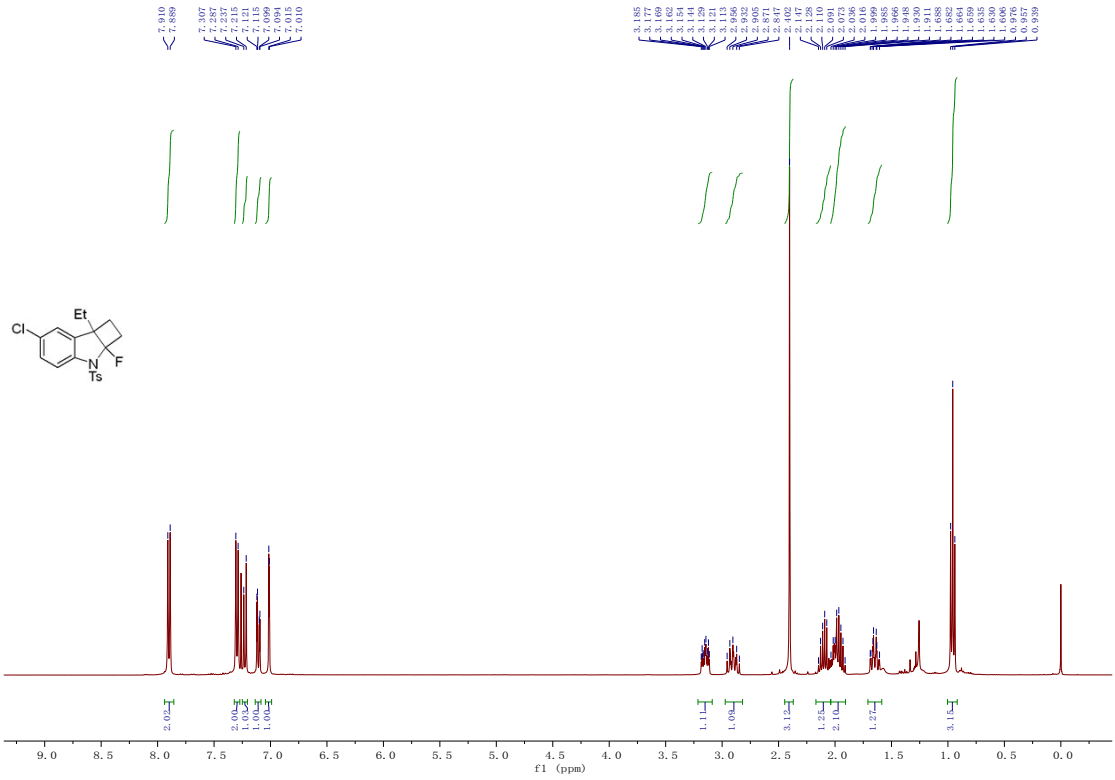


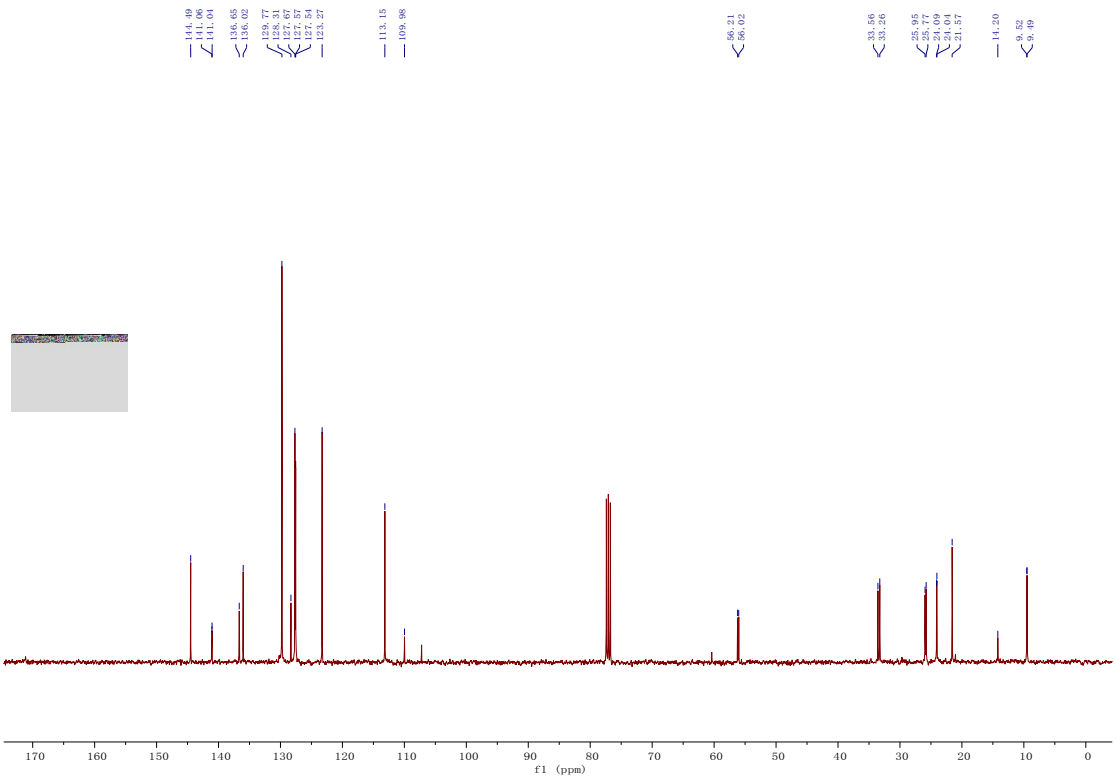


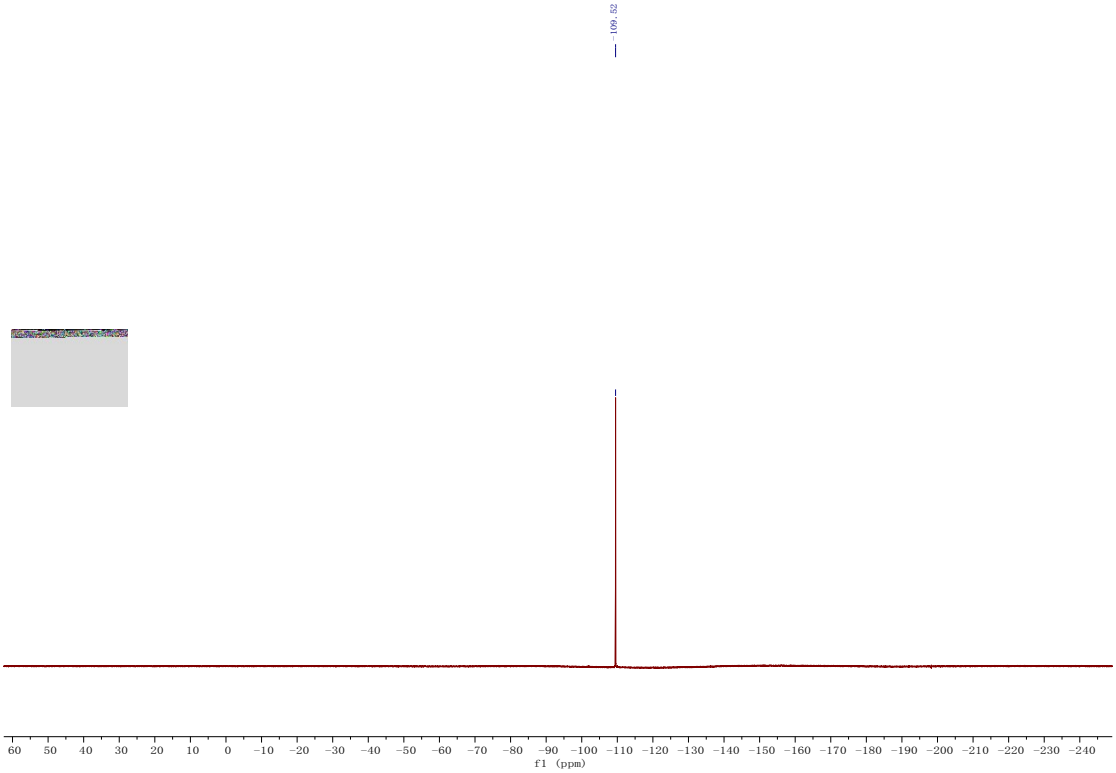


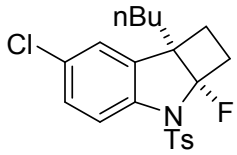
Compound 3m: A yellow solid (42.0 mg, 55%); M.p. 99-100 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 0.96 (t, *J* = 7.5 Hz, 3H), 1.59 – 1.71 (m, 1H), 1.97 (tq, *J* = 14.9, 7.7 Hz, 2H), 2.11 (dt, *J* = 14.7,

7.4 Hz, 1H), 2.40 (s, 3H), 2.82 – 2.97 (m, 1H), 3.09 – 3.21 (m, 1H), 7.01 (d, *J* = 2.1 Hz, 1H), 7.11 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.23 (d, *J* = 8.6 Hz, 1H), 7.27 – 7.32 (m, 2H), 7.86 – 7.94 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 9.5 (d, *J* = 3.0 Hz), 21.6, 24.1 (d, *J* = 5.0 Hz), 25.9 (d, *J* = 17.4 Hz), 33.4 (d, *J* = 30.3 Hz), 56.1 (d, *J* = 18.9 Hz), 108.6 (d, *J* = 277.8 Hz), 113.2, 123.3, 127.6 (d, *J* = 2.9 Hz), 127.7, 128.3, 129.8, 136.0, 136.7, 141.1 (d, *J* = 2.3 Hz), 144.5. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.5. IR (neat) ν 2959, 2922, 2852, 1600, 1464, 1356, 1242, 1176, 1157, 1141, 1119, 1089, 1029, 995, 979, 813, 687, 663 cm^{-1}. HRMS (ESI) Calcd. for $C_{19}H_{19}NClO_2S$ requires (M^+-F): 360.0820, Found: 360.0820.



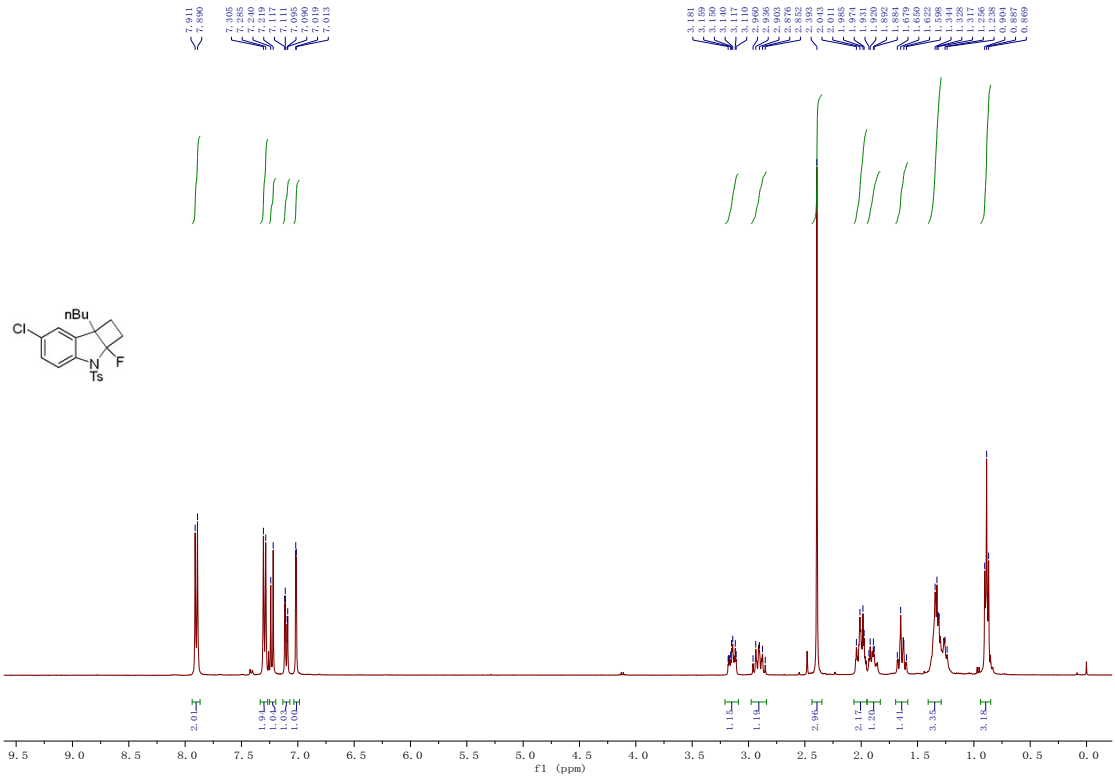


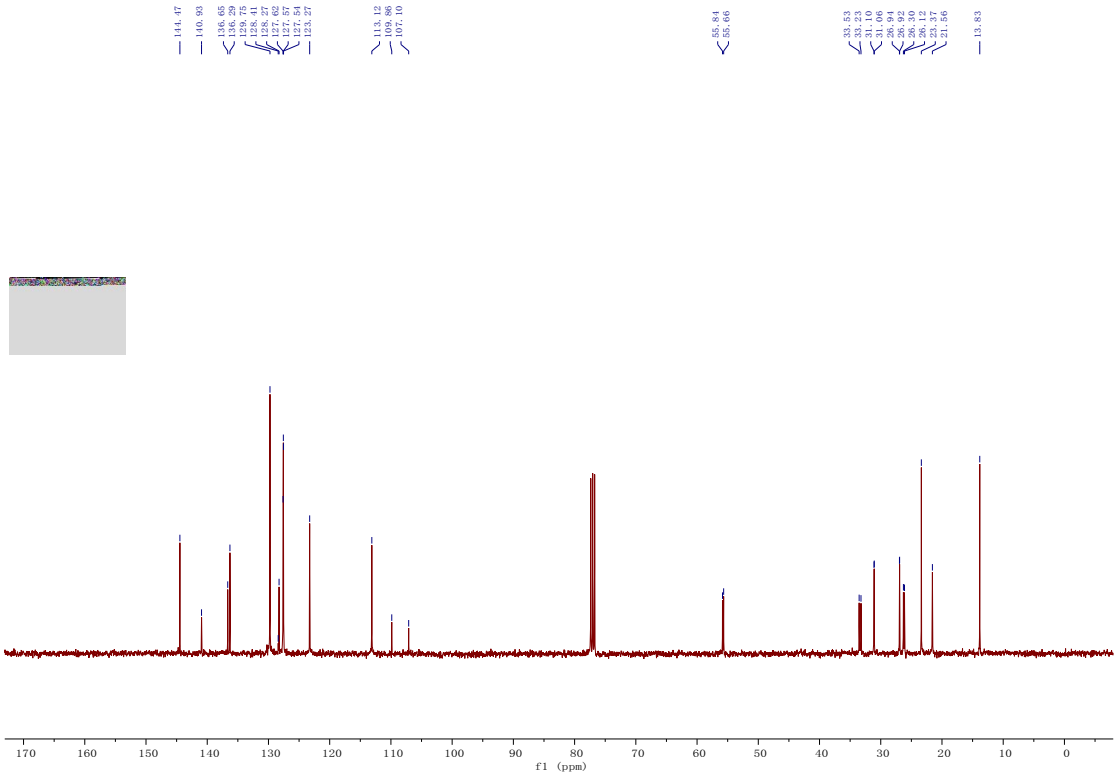


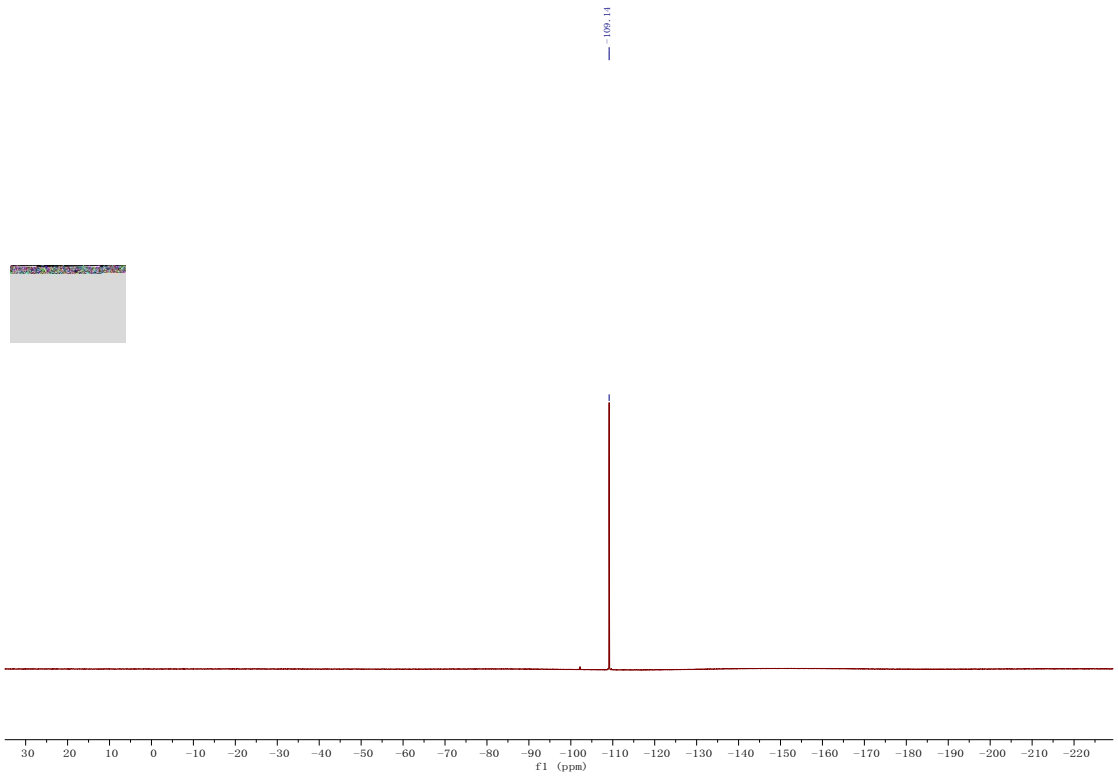


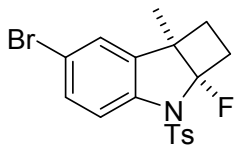
Compound 3n: A pale yellow oil (34.5 mg, 42%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 0.89 (t, *J* = 7.0 Hz, 3H), 1.29 – 1.41 (m, 3H), 1.64 (q, *J* = 10.7, 9.6 Hz, 1H), 1.83 – 1.95 (m, 1H), 1.95 – 2.06

(m, 2H), 2.39 (s, 3H), 2.91 (dt, *J* = 20.4, 9.7 Hz, 1H), 3.09 – 3.21 (m, 1H), 7.02 (d, *J* = 2.1 Hz, 1H), 7.10 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.23 (d, *J* = 8.6 Hz, 1H), 7.27 – 7.33 (m, 2H), 7.87 – 7.94 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 13.8, 21.6, 23.4, 26.2 (d, *J* = 17.4 Hz), 26.9 (d, *J* = 2.5 Hz), 31.1 (d, *J* = 4.5 Hz), 33.4 (d, *J* = 30.3 Hz), 55.8 (d, *J* = 18.7 Hz), 108.5 (d, *J* = 278.0 Hz), 113.1, 123.3, 127.6 (d, *J* = 2.8 Hz), 127.6, 128.3, 129.8, 136.3, 136.7, 140.9, 144.5. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.1. IR (neat) ν 2954, 2928, 2868, 1597, 1466, 1362, 1244, 1179, 1158, 1144, 1120, 1092, 1032, 1010, 933, 811, 705, 689, 664 cm^{-1}. HRMS (ESI) Calcd. for $C_{21}H_{23}ClNO_2S$ requires (M^+-F): 388.1133, Found: 388.1129.

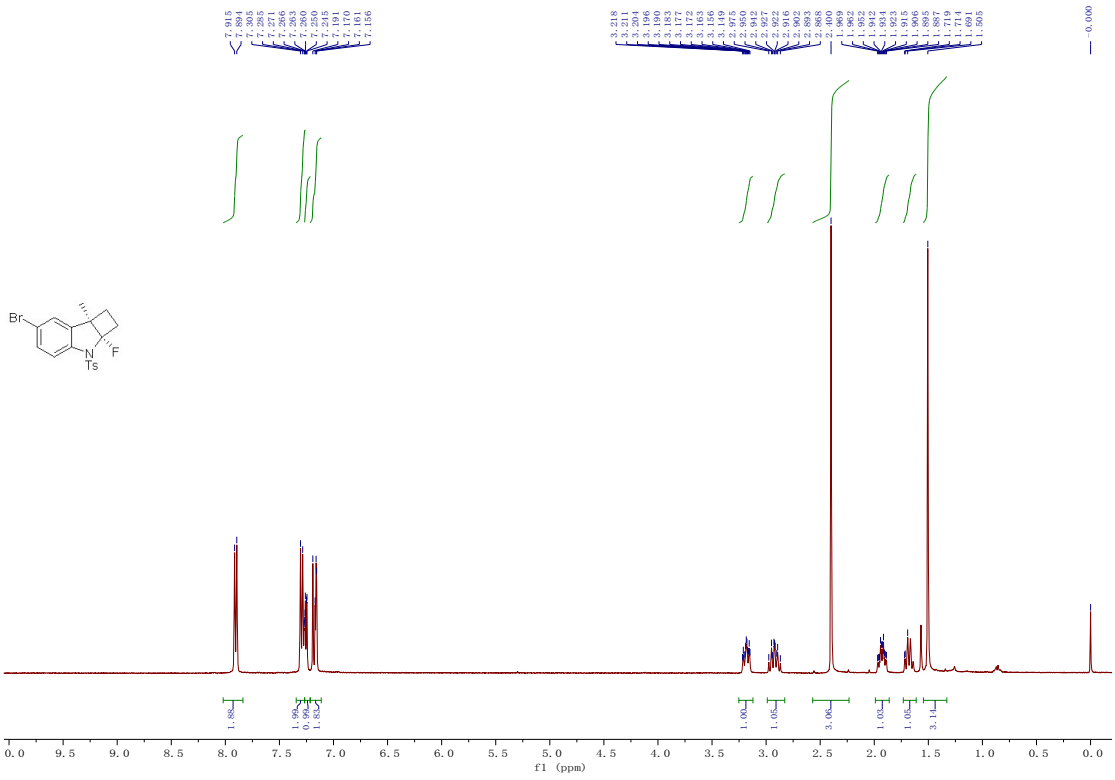


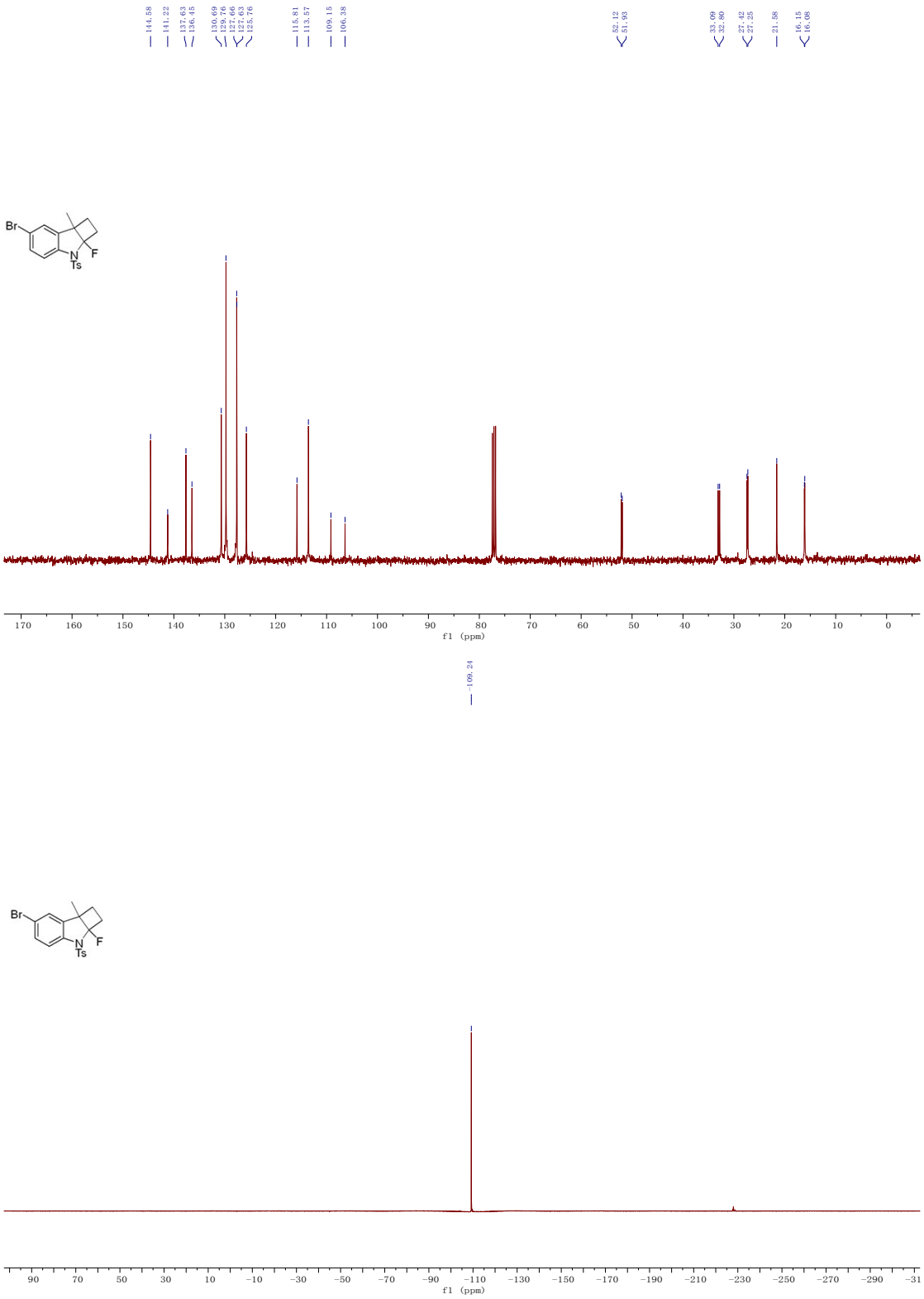

144.47
140.93
136.65
136.29
129.75
129.41
128.27
127.62
127.57
127.54
123.27
113.12
109.86
107.10
55.84
55.66
33.53
33.13
31.10
31.06
26.94
26.92
26.90
26.12
23.37
21.56
13.83
f1 (ppm)

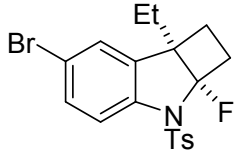

-109.14
f1 (ppm)


Br
N
Ts
F

Compound 3o: A white solid (56.2 mg, 68%); M.p. 170-171 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.49 (s, 3H), 1.66 (q, *J* = 11.0 Hz, 1H), 1.86 – 1.96 (m, 1H), 2.38 (s, 3H), 2.82 – 2.97 (m, 1H), 3.10 – 3.21 (m, 1H), 7.12 – 7.18 (m, 2H), 7.23 (d, *J* = 2.0 Hz, 1H), 7.26 – 7.31 (m, 2H), 7.85 – 7.92 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 16.1 (d, *J* = 7.4 Hz), 21.6, 27.3 (d, *J* = 16.9 Hz), 32.9 (d, *J* = 29.9 Hz), 52.0 (d, *J* = 19.8 Hz), 107.8 (d, *J* = 279.2 Hz), 113.6, 115.8, 125.8, 127.6 (d, *J* = 2.9 Hz), 129.8, 130.7, 136.4, 137.6, 141.2, 144.6. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.2. IR (neat) ν 3056, 2972, 1670, 1589, 1490, 1444, 1317, 1287, 1244, 1022, 1015, 927, 838, 766, 753, 723, 692, 665, 654 cm^{-1}. HRMS (ESI) Calcd. for $C_{18}H_{17}BrNO_2S$ requires (M^+-F): 390.0158, Found: 390.0157.

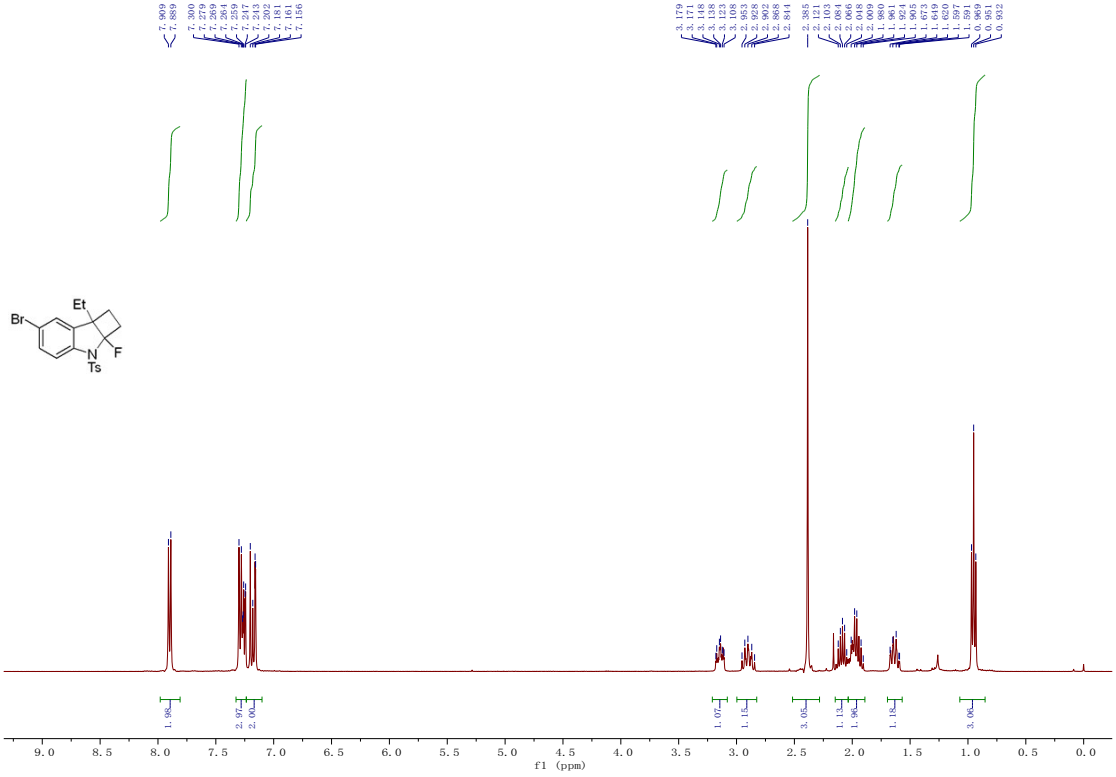


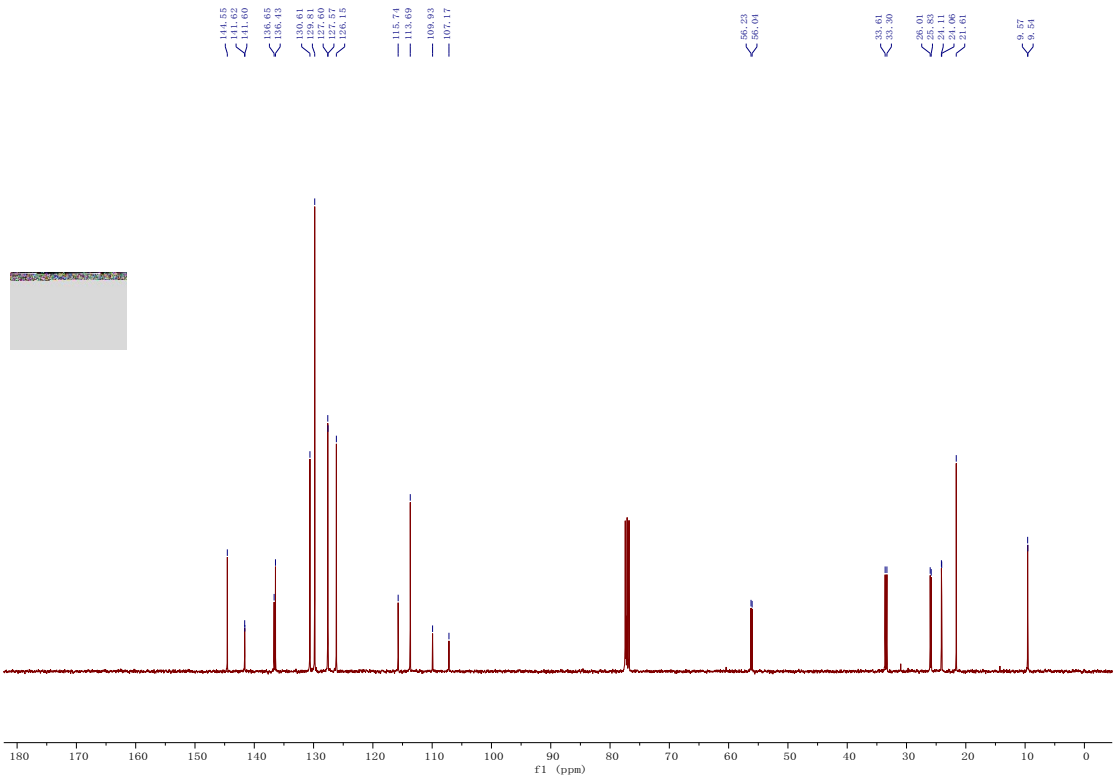


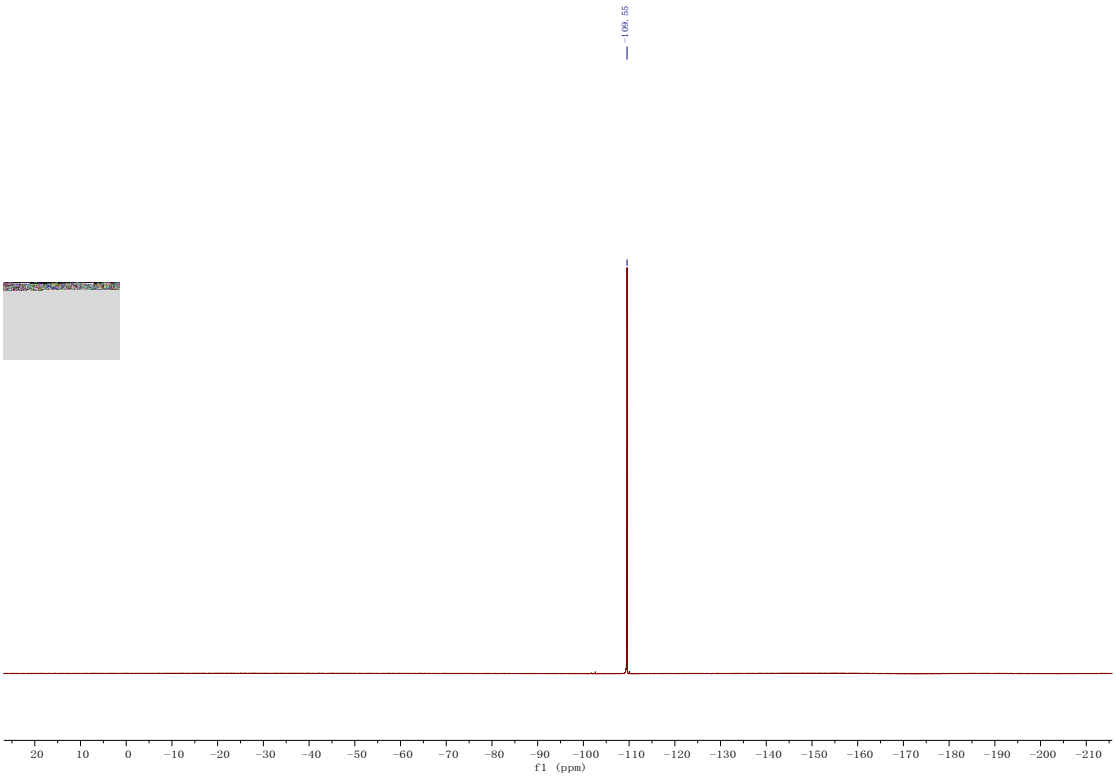


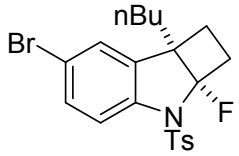
Compound 3p: A white solid (46.1 mg, 54%); M.p. 123-124 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 0.85 – 1.07 (m, 3H), 1.57 – 1.70 (m, 1H), 1.89 – 2.03 (m, 2H), 2.08 (dt, *J* = 14.7, 7.4 Hz, 1H),

2.39 (s, 3H), 2.83 – 3.00 (m, 1H), 3.14 (td, *J* = 12.1, 4.5 Hz, 1H), 7.10 – 7.24 (m, 2H), 7.24 – 7.33 (m, 3H), 7.81 – 7.98 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 9.6 (d, *J* = 2.9 Hz), 21.6, 24.1 (d, *J* = 5.0 Hz), 25.9 (d, *J* = 17.3 Hz), 33.5 (d, *J* = 30.2 Hz), 56.1 (d, *J* = 18.7 Hz), 108.5 (d, *J* = 277.9 Hz), 113.7, 115.7, 126.2, 127.6 (d, *J* = 2.9 Hz), 129.8, 130.6, 136.4, 136.7, 141.6 (d, *J* = 2.4 Hz), 144.5. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.6. IR (neat) ν 2969, 2925, 2857, 1594, 1465, 1358, 1242, 1187, 1178, 1159, 1142, 1119, 1089, 1027, 981, 874, 812, 775, 749, 688, 664 cm^{-1}. HRMS (ESI) Calcd. for $C_{19}H_{19}BrNO_2S$ requires (M^+-F): 404.0314, Found: 404.0314.



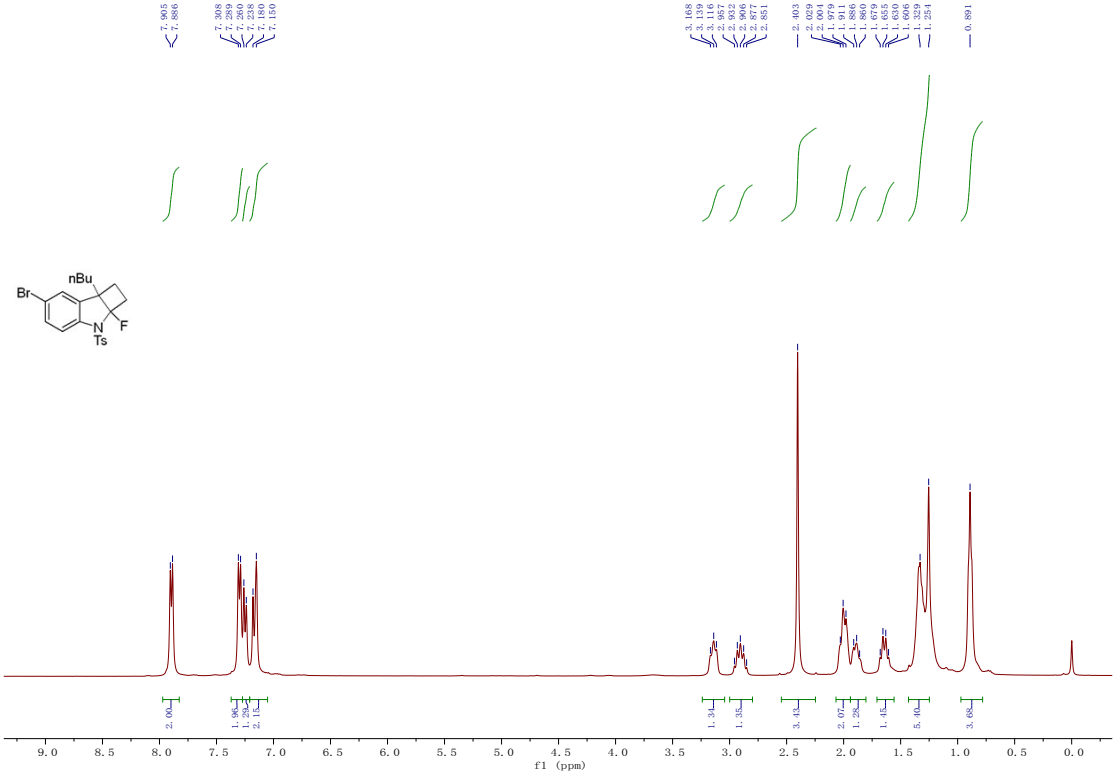


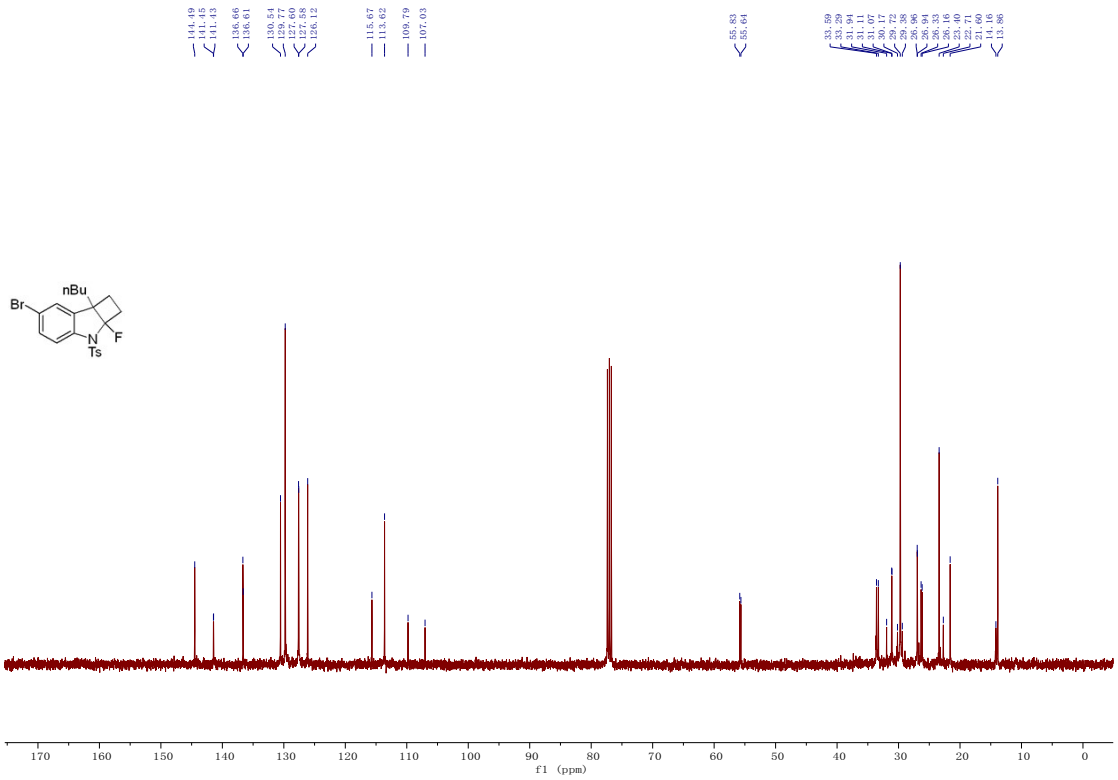


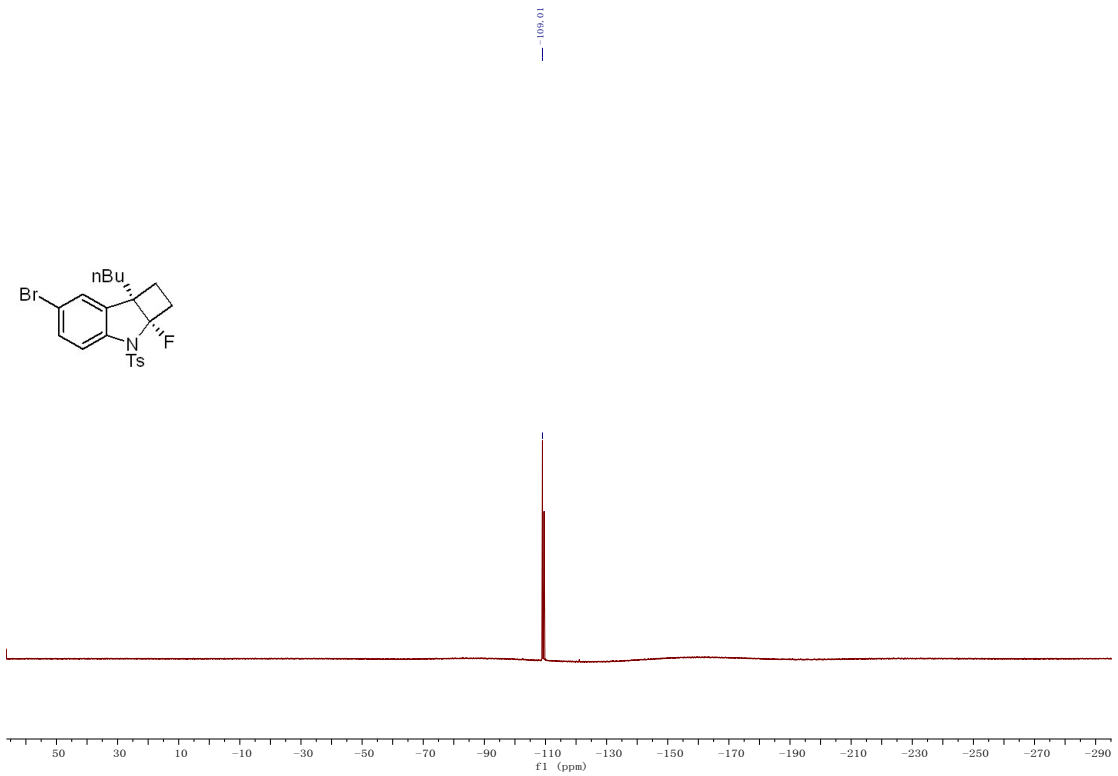


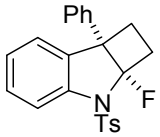
Compound 3q: A yellow oil (35.7 mg, 39%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 0.89 (s, 4H), 1.29 (d, *J* = 30.1 Hz, 5H), 1.64 (q, *J* = 9.6 Hz, 1H), 1.80 – 1.94 (m, 1H), 1.94 – 2.07 (m, 2H), 2.40

(s, 3H), 2.90 (dt, *J* = 22.0, 10.2 Hz, 1H), 3.04 – 3.24 (m, 1H), 7.05 – 7.21 (m, 2H), 7.25 (d, *J* = 8.6 Hz, 1H), 7.27 – 7.37 (m, 2H), 7.83 – 7.97 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 13.9, 21.6, 23.4, 26.2 (d, *J* = 17.4 Hz), 29.7, 31.1 (d, *J* = 4.3 Hz), 33.4 (d, *J* = 30.4 Hz), 55.7 (d, *J* = 18.8 Hz), 108.4 (d, *J* = 278.1 Hz), 113.6, 115.7, 126.1, 127.6 (d, *J* = 2.9 Hz), 129.8, 130.5, 136.6, 136.7, 141.4 (d, *J* = 2.3 Hz), 144.5. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.0. IR (neat) ν 2959, 2920, 2846, 1597, 1461, 1362, 1257, 1245, 1179, 1158, 1114, 1089, 1012, 934, 809, 749, 689, 663 cm^{-1}. HRMS (ESI) Calcd. for $C_{21}H_{23}BrNO_2S$ requires (M^+-F): 432.0627, Found: 432.0623.



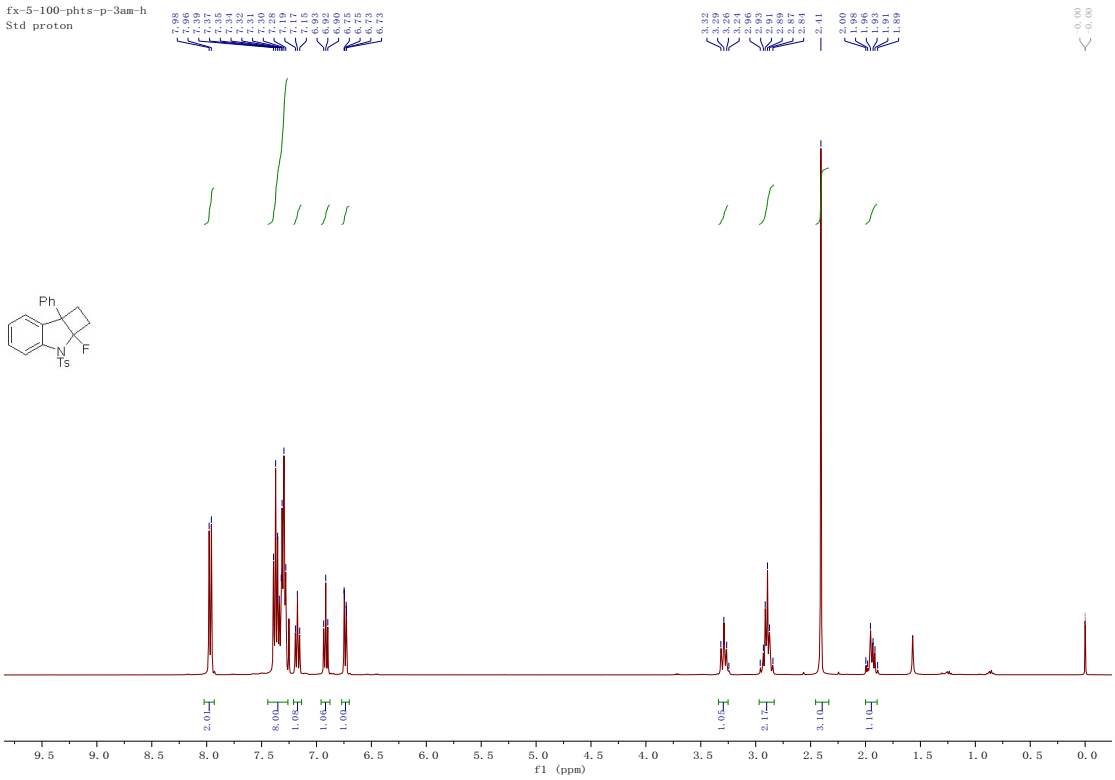


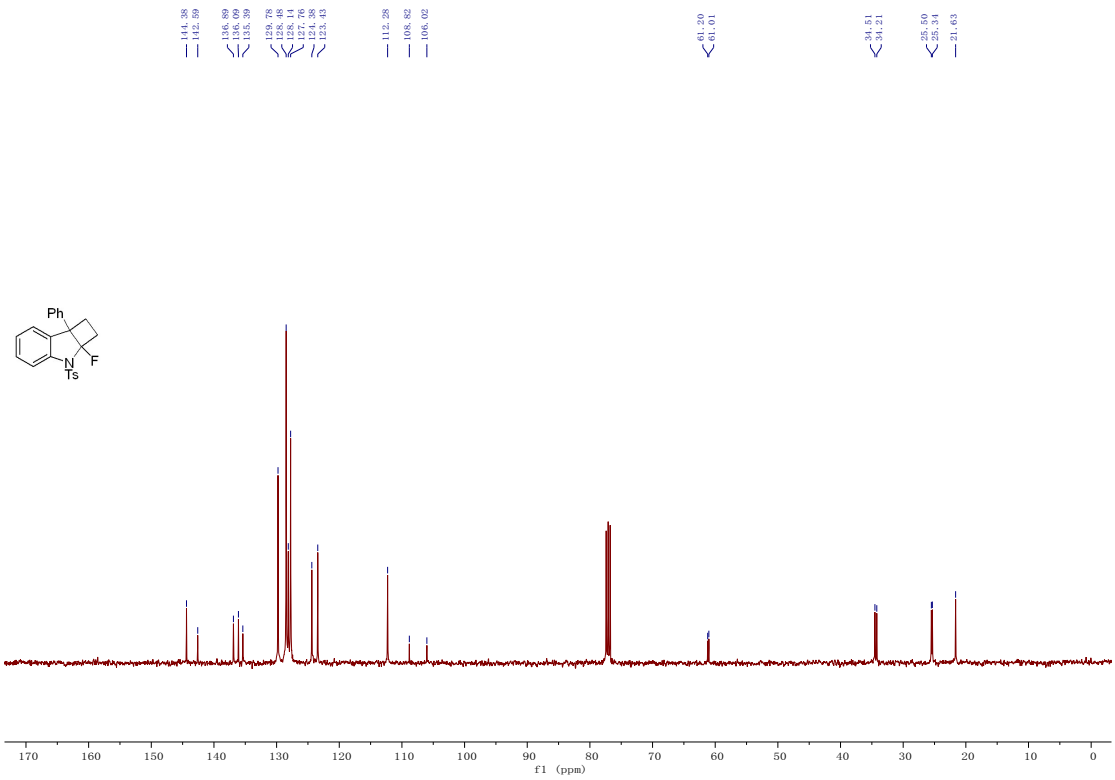


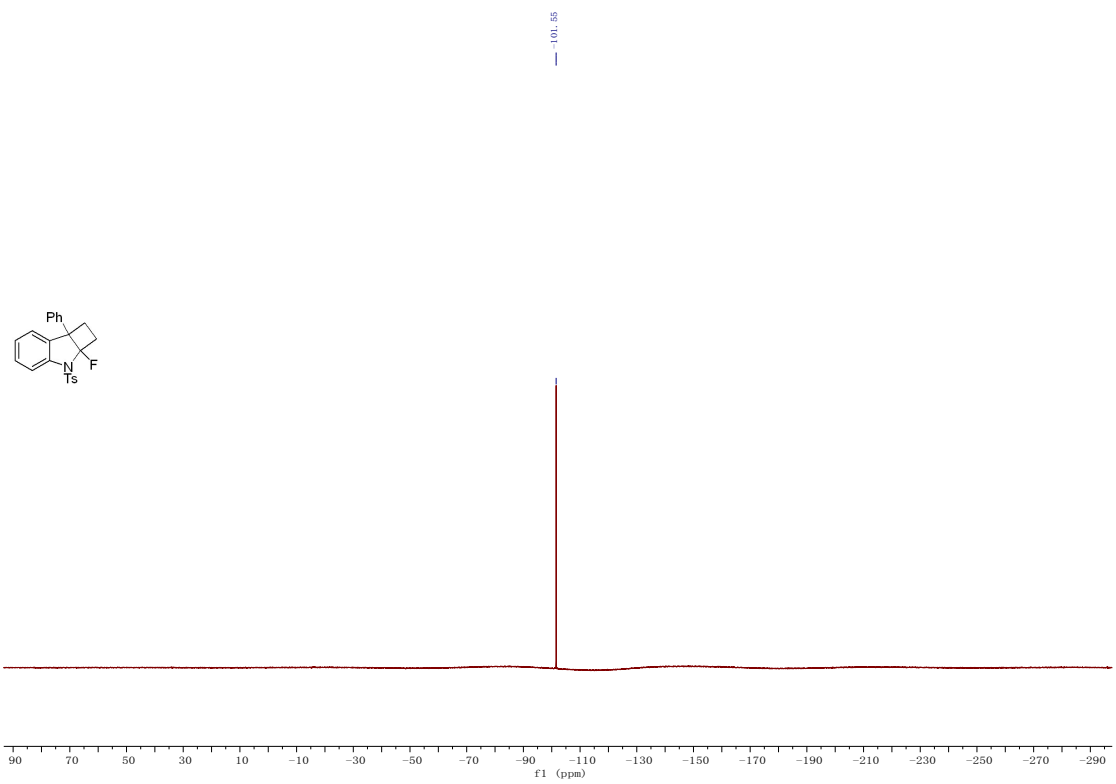


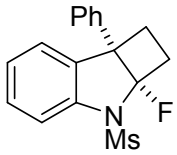
Compound 3r: A white solid (45.8 mg, 58%); M.p. 113-114 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.89 – 2.00 (m, 1H), 2.41 (s, 3H), 2.90 (q, *J* = 6.9 Hz, 2H), 3.29 (t, *J* = 10.6 Hz, 1H), 6.74 (dd,

J = 7.5, 1.3 Hz, 1H), 6.92 (dd, *J* = 7.5 Hz, 1H), 7.17 (dd, *J* = 7.8 Hz, 1H), 7.26 – 7.44 (m, 8H), 7.93 – 8.02 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 21.6, 25.4 (d, *J* = 16.0 Hz), 34.4 (d, *J* = 30.1 Hz), 61.1 (d, *J* = 18.6 Hz), 107.4 (d, *J* = 281.1 Hz), 112.3, 123.4, 124.4, 127.8, 128.1, 128.5, 129.8, 135.4, 136.1, 136.9, 142.6, 144.4. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -101.6. IR (neat) ν 3066, 3032, 2962, 2949, 1602, 1495, 1477, 1459, 1366, 1330, 1236, 1188, 1162, 1143, 1121, 1086, 1007, 955, 924, 807, 760, 693, 669, 652 cm^{-1}. HRMS (ESI) Calcd. for $C_{23}H_{20}NO_2S$ requires (M^+-F): 374.1209, Found: 374.1211.



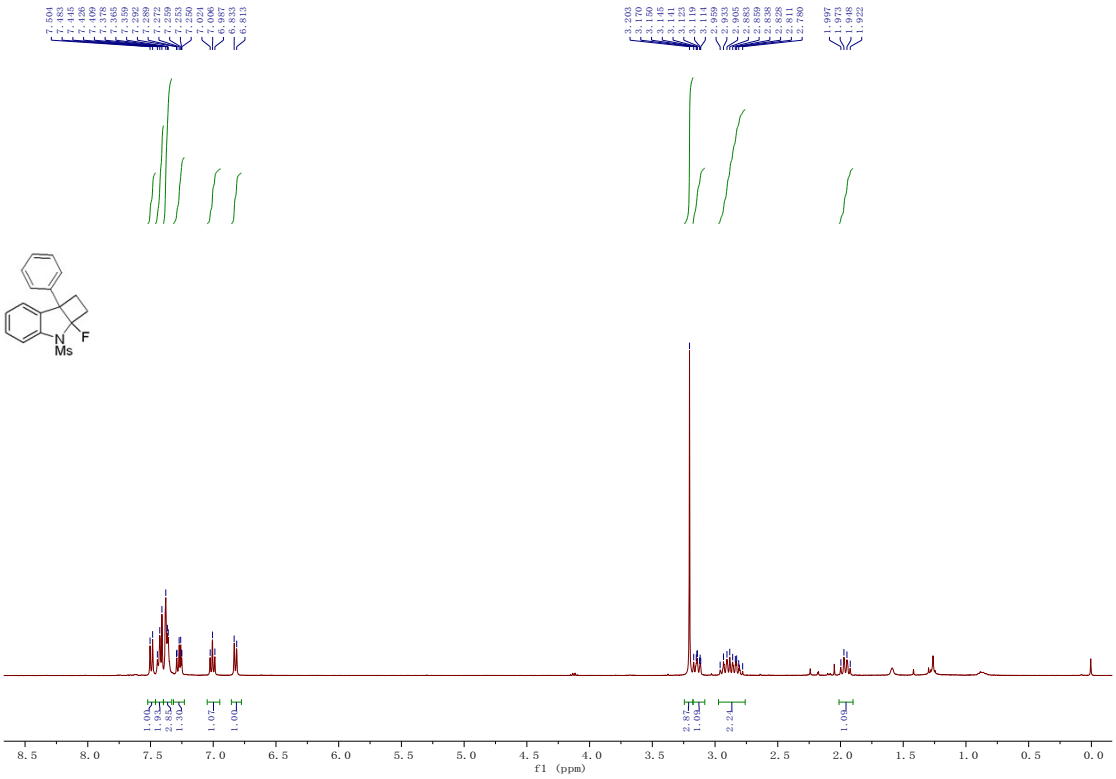


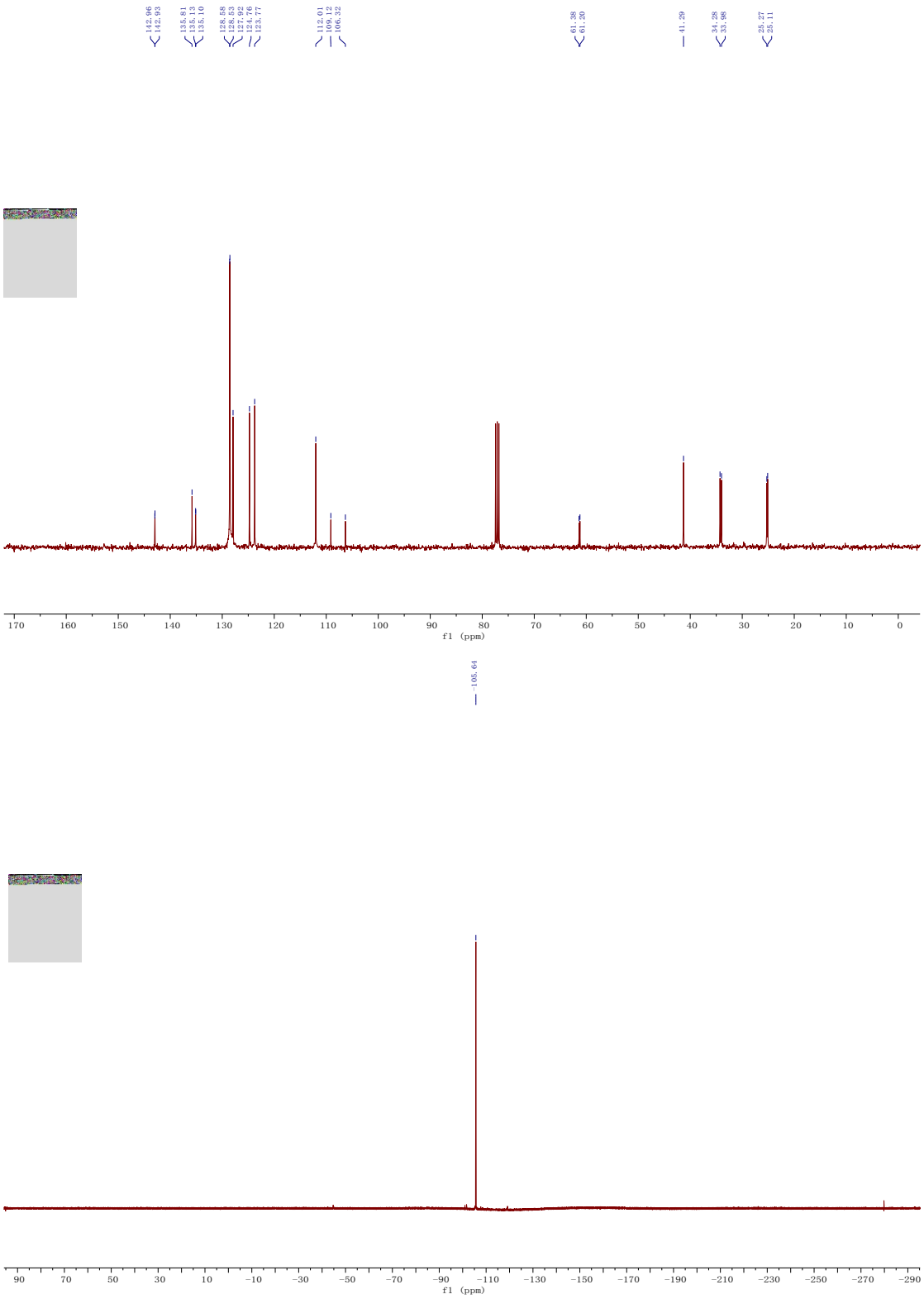


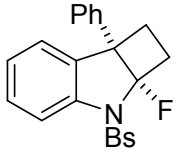


Compound 3s: A white solid (25.3 mg, 40%); M.p. 111-12 ^{o}C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.96 (q, *J* = 10.5, 10.1 Hz, 1H), 2.76 – 2.97 (m, 2H), 3.08 – 3.18 (m, 1H), 3.20 (s, 3H), 6.82 (d, *J*

= 8.2 Hz, 1H), 7.01 (dd, *J* = 7.5 Hz, 1H), 7.24 – 7.30 (m, 1H), 7.33 – 7.40 (m, 3H), 7.39 – 7.46 (m, 2H), 7.49 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 25.2 (d, *J* = 16.4 Hz), 34.1 (d, *J* = 29.8 Hz), 41.3, 61.3 (d, *J* = 17.9 Hz), 107.7 (d, *J* = 281.5 Hz), 112.0, 123.8, 124.8, 127.9, 128.5, 128.6, 135.1 (d, *J* = 3.1 Hz), 135.8, 142.9 (d, *J* = 3.1 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -105.6. IR (neat) ν 2959, 2925, 1602, 1474, 1360, 1448, 1352, 1234, 1183, 1155, 1136, 1012, 822, 766, 703 cm^{-1}. HRMS (ESI) Calcd. for $C_{17}H_{16}NO_2S$ requires (M^+-F): 298.0896, Found: 298.0893.

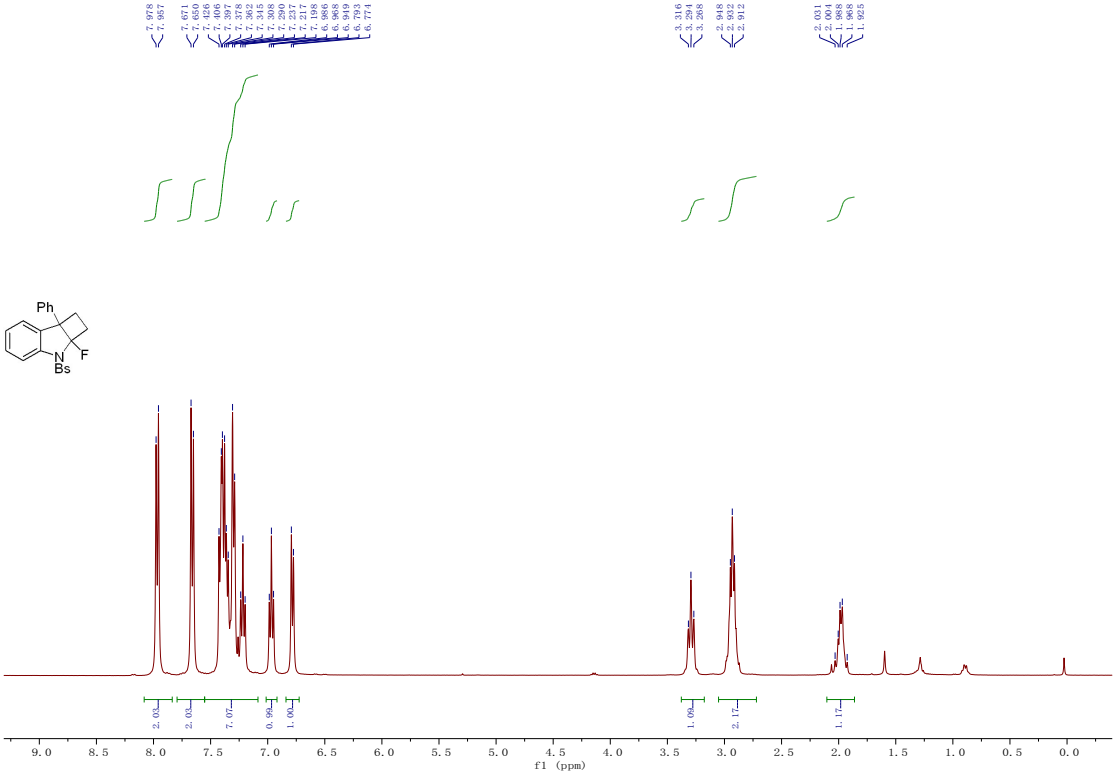


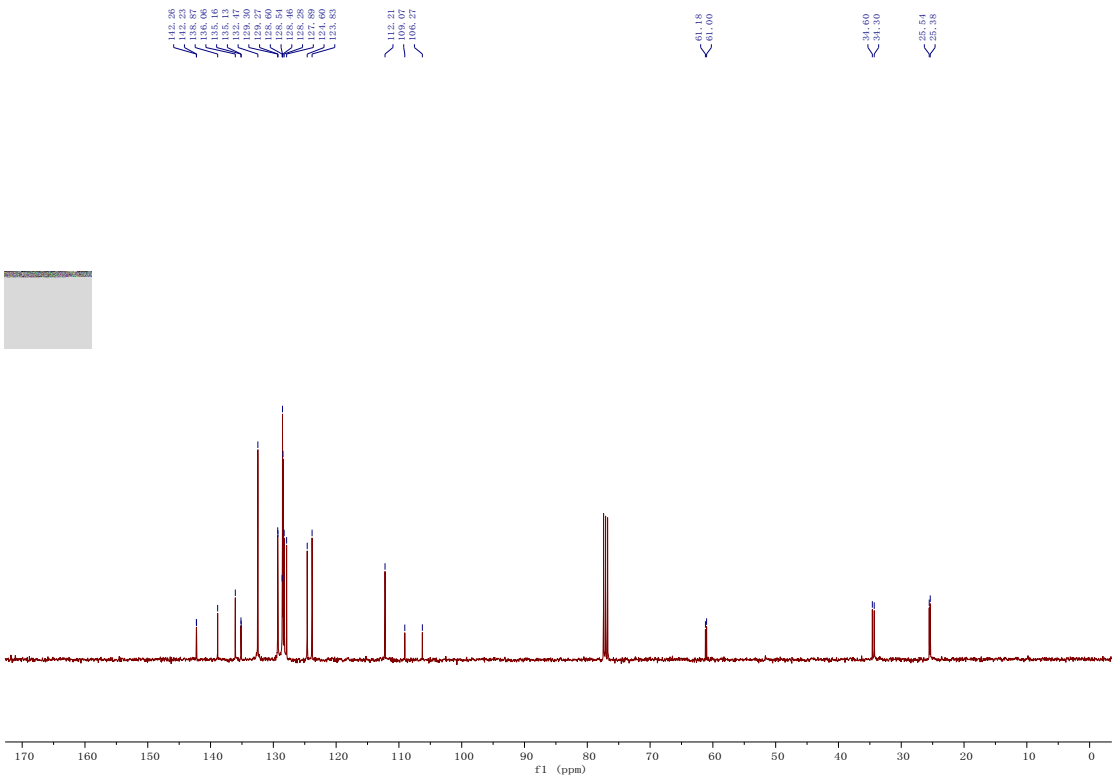


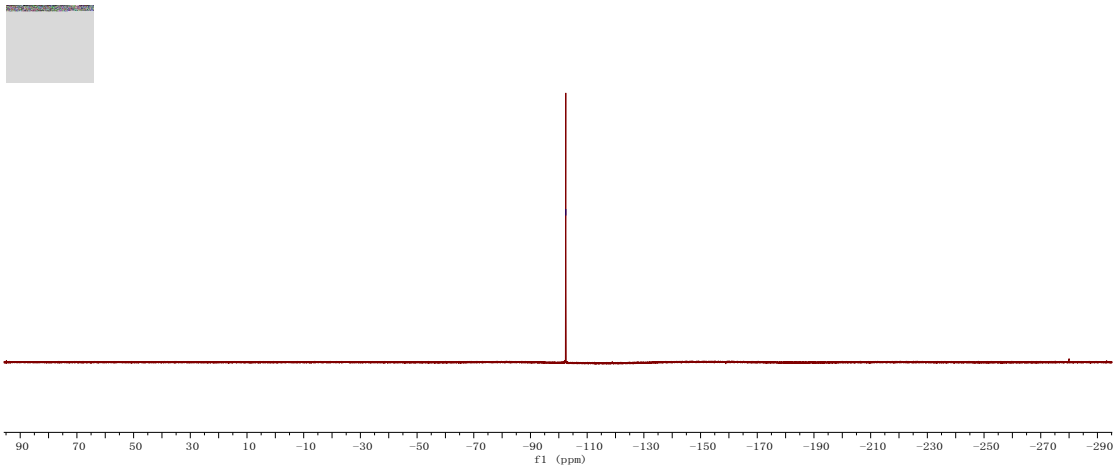


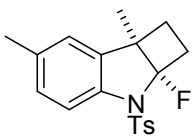
Compound 3t: A white solid (20.4 mg, 45%); M.p. 137-138 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.00 (dd, *J* = 15.8, 9.4 Hz, 1H), 2.84 – 3.03 (m, 2H), 3.29 (t, *J* = 9.5 Hz, 1H), 6.78 (d, *J* = 7.4

Hz, 1H), 6.97 (dd, J = 7.4 Hz, 1H), 7.12 – 7.54 (m, 7H), 7.56 – 7.77 (m, 2H), 7.86 – 8.08 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 25.5 (d, J = 16.0 Hz), 34.5 (d, J = 30.1 Hz), 61.1 (d, J = 18.3 Hz), 107.7 (d, J = 281.5 Hz), 112.2, 123.8, 124.6, 127.9, 128.3, 128.45, 128.53, 128.6, 129.3 (d, J = 3.4 Hz), 132.5, 135.1 (d, J = 3.1 Hz), 136.1, 138.9, 142.2 (d, J = 2.3 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -102.5. IR (neat) ν 3087, 3024, 2944, 1602, 1568, 1496, 1472, 1456, 1369, 1235, 1187, 1162, 1142, 1122, 1069, 1004, 958, 925, 820, 812, 758, 744, 692, 664 cm^{-1}. HRMS (ESI) Calcd. for $C_{22}H_{17}BrNO_2S$ requires (M^+-F): 438.0158, Found: 438.0159.



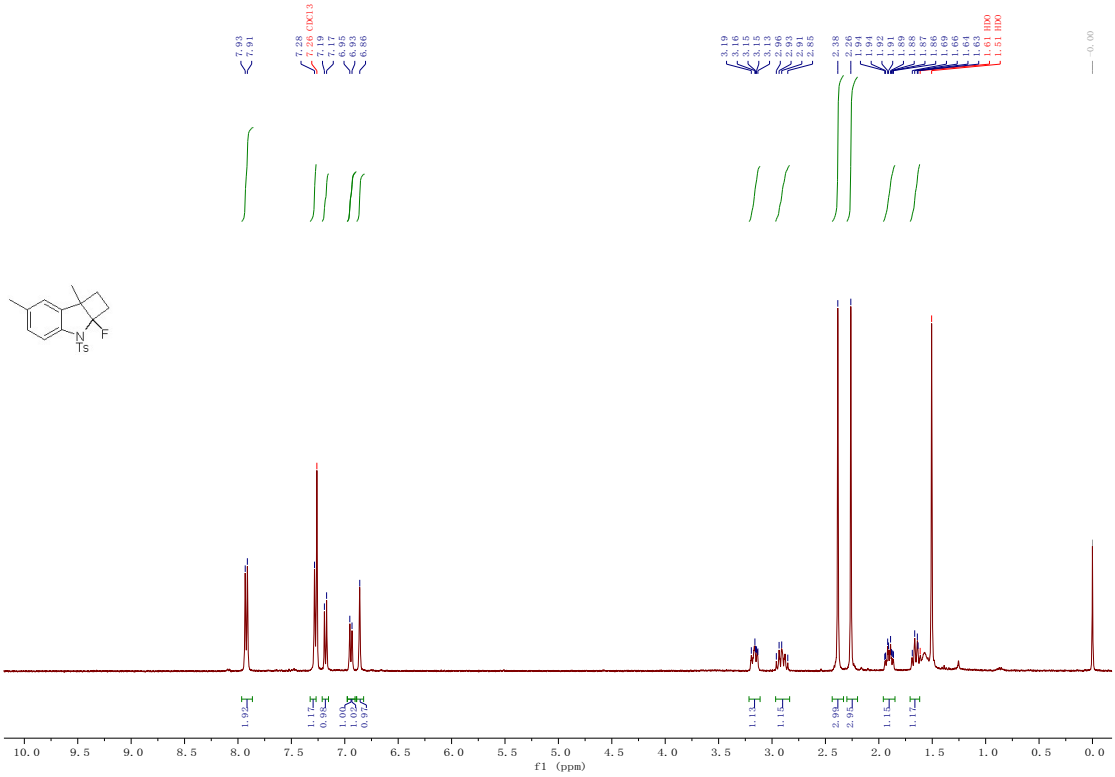


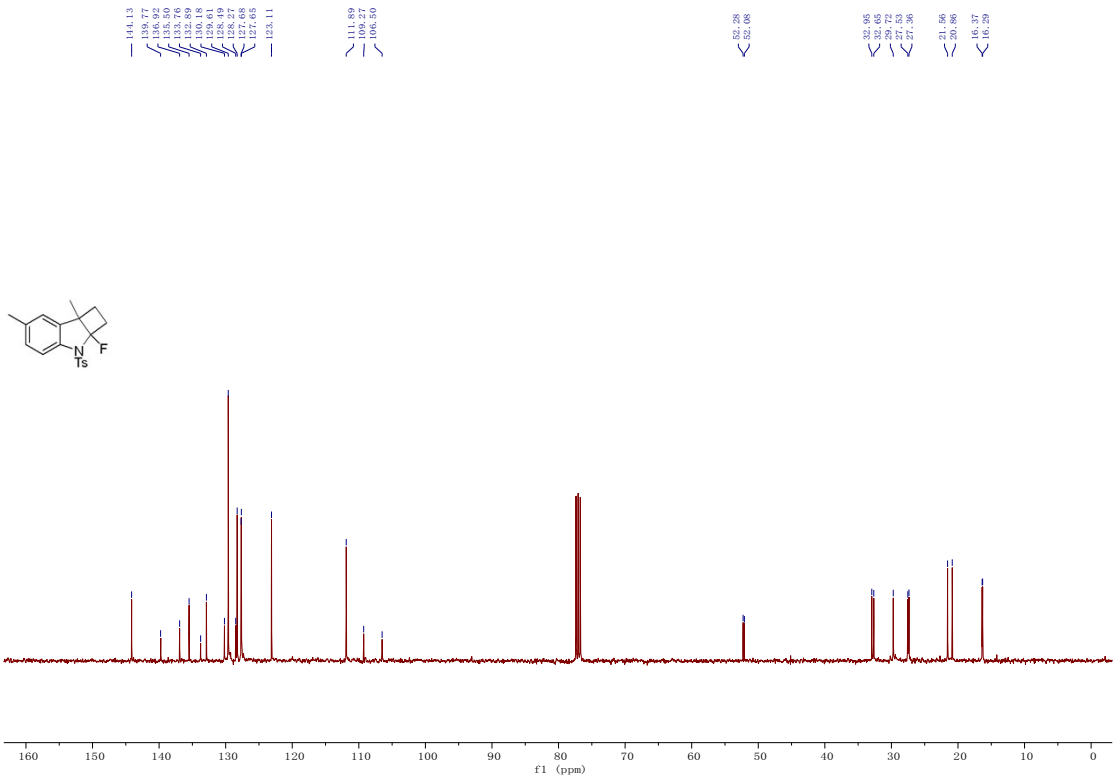


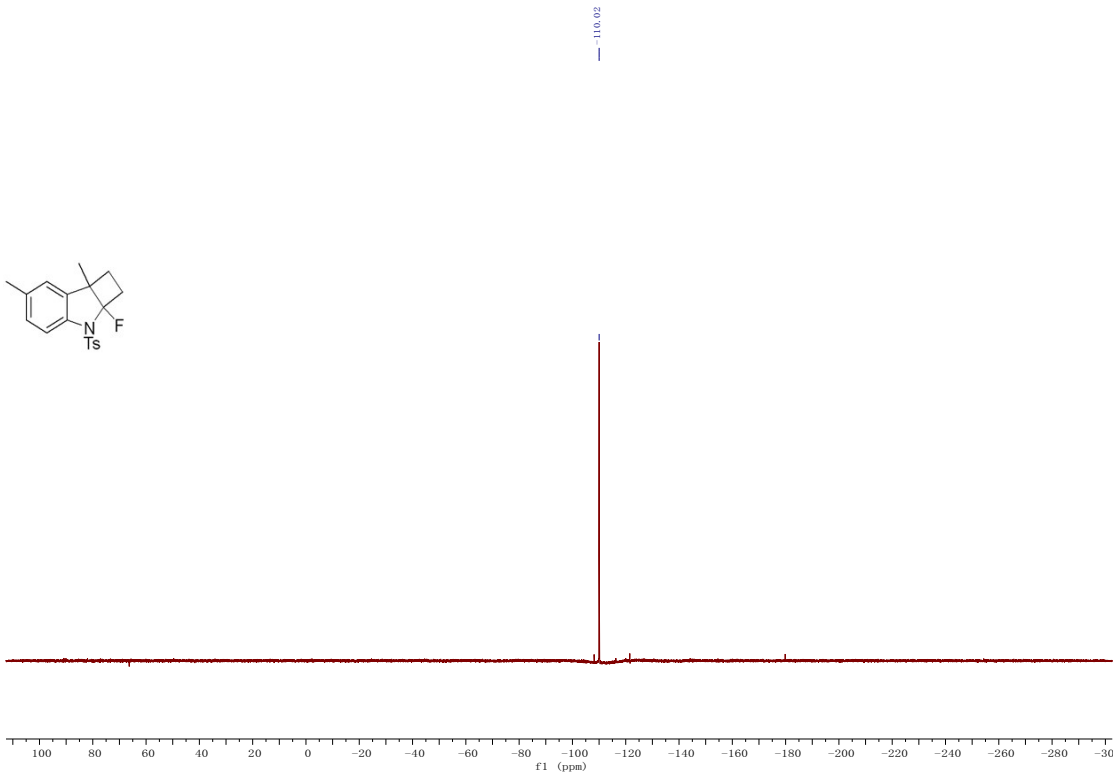


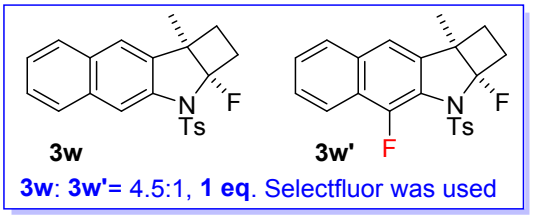
Compound 3v: A colorless oil (23.9 mg, 36%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.66 (dd, *J* = 9.5 Hz, 1H), 1.85 – 1.96 (m, 1H), 2.26 (s, 3H), 2.38 (s, 3H), 2.84 – 2.97 (m, 1H), 3.11 – 3.22 (m,

1H), 6.86 (s, 1H), 6.94 (d, J = 8.3 Hz, 1H), 7.18 (d, J = 8.2 Hz, 1H), 7.28 (s, 1H), 7.86 – 7.97 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 16.3 (d, J = 7.6 Hz), 21.2 (d, J = 70.5 Hz), 27.4 (d, J = 17.3 Hz), 29.7, 32.8 (d, J = 30.1 Hz), 52.2 (d, J = 19.5 Hz), 107.9 (d, J = 278.3 Hz), 111.9, 123.1, 127.7 (d, J = 3.0 Hz), 128.3, 128.5, 129.6, 130.2, 132.9, 133.8, 135.5, 136.9, 139.8 (d, J = 2.5 Hz), 144.1. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -110.0. IR (neat) ν 2975, 2920, 1600, 1494, 1381, 1167, 1091, 912, 813, 706, 677 cm^{-1}. HRMS (ESI) Calcd. for $C_{19}H_{20}FNNaO_2S$ requires (M^++Na): 368.1091, Found: 368.1090.





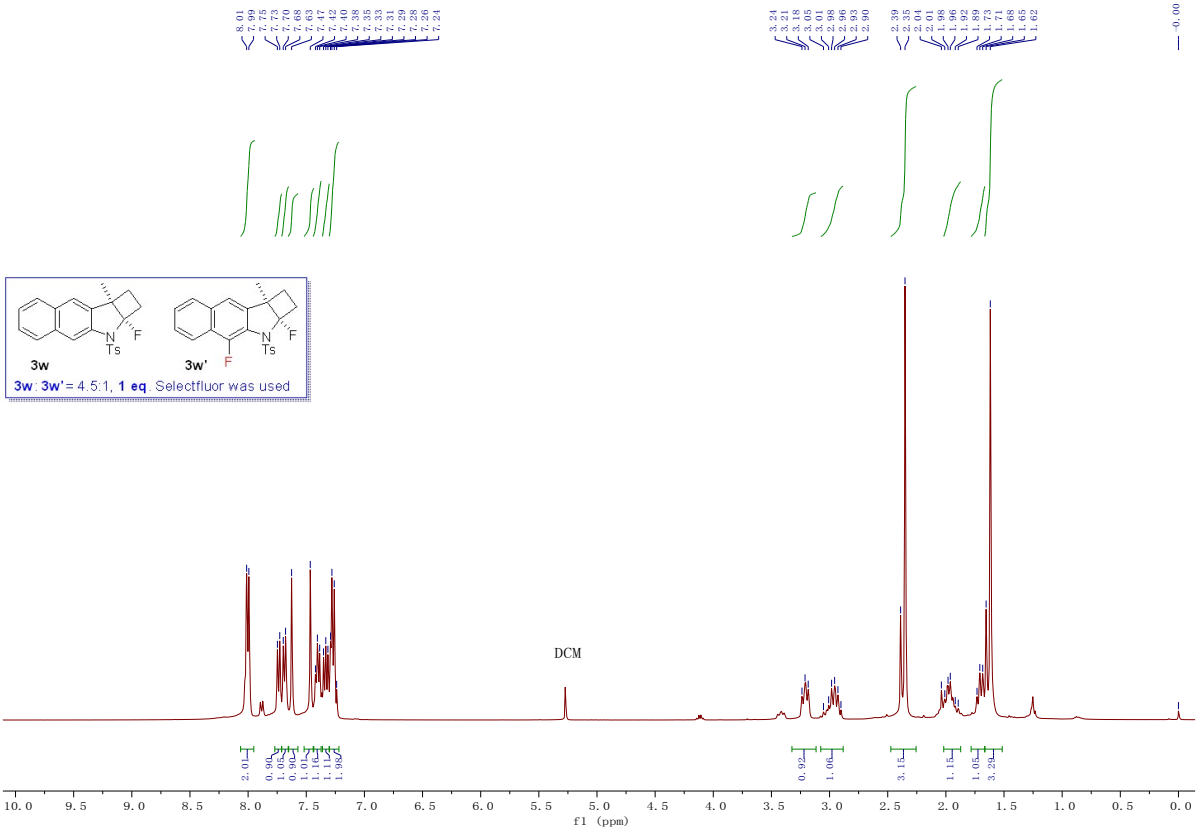


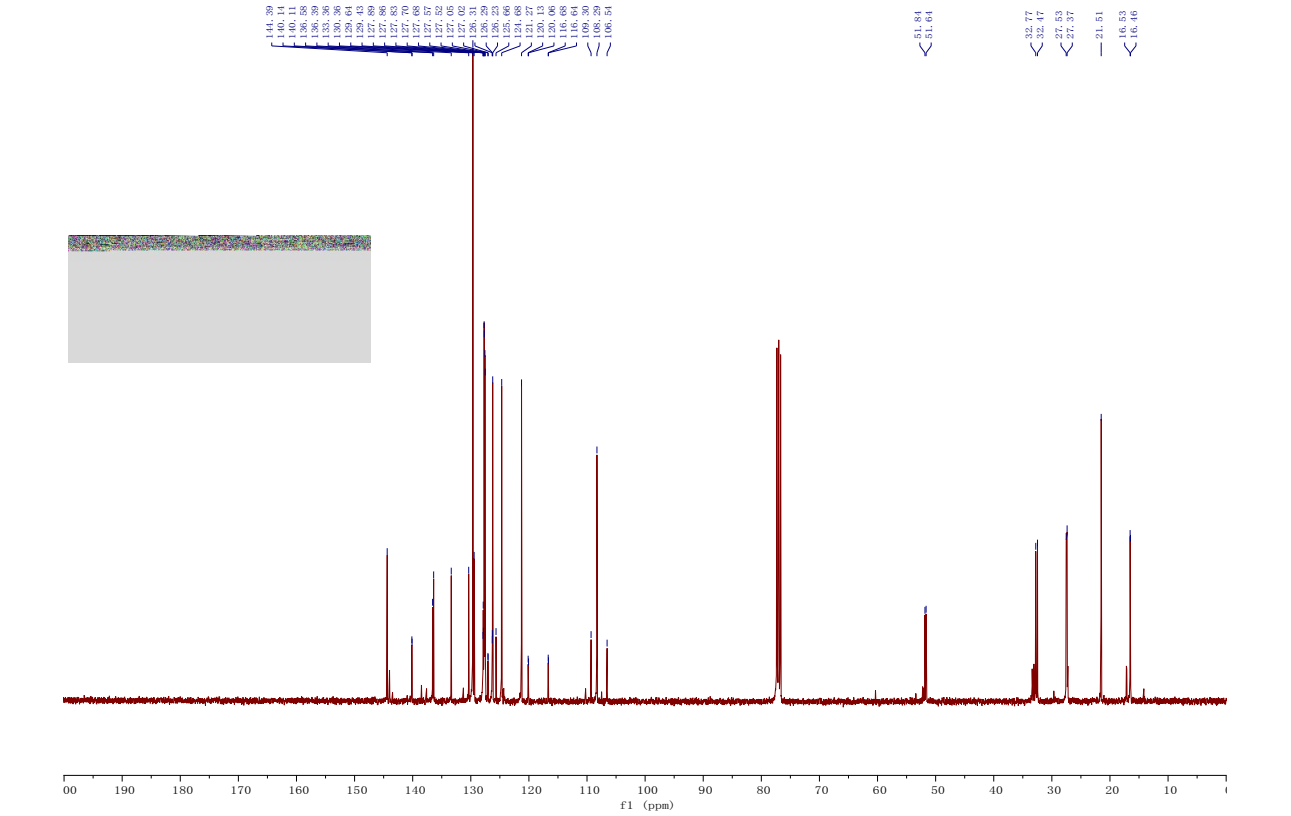


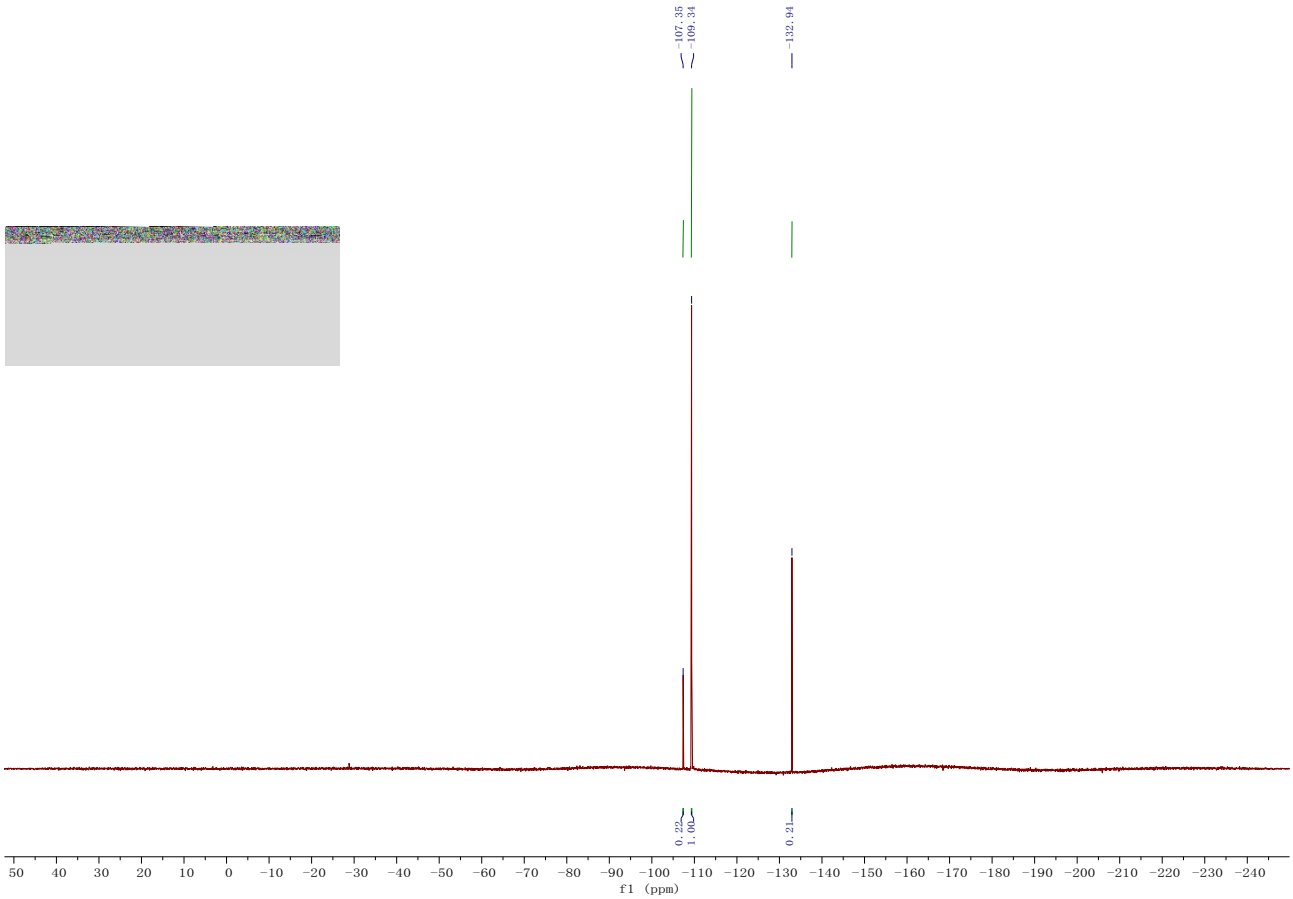
from

Compound 3w: A yellow oil (**3w**+**3w'** = 41.5 mg, **3w**:**3w'** = 4.5:1, it is an inseparable mixture). ^{1}H

NMR (400 MHz, Chloroform-*d*) δ 1.64 (s, 3H), 1.67 – 1.78 (m, 1H), 1.87 – 2.02 (m, 1H), 2.37 (s, 3H), 2.96 (dt, *J* = 21.7, 10.2 Hz, 1H), 3.12 – 3.32 (m, 1H), 7.27 (dd, *J* = 8.2, 6.5 Hz, 2H), 7.30 – 7.36 (m, 1H), 7.37 – 7.44 (m, 1H), 7.47 (s, 1H), 7.63 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.95 – 8.06 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 16.5 (d, *J* = 6.8 Hz), 21.5, 27.5 (d, *J* = 15.7 Hz), 32.6 (d, *J* = 29.9 Hz), 51.7 (d, *J* = 19.7 Hz), 107.9 (d, *J* = 277.4 Hz), 108.3, 120.1 (d, *J* = 6.5 Hz), 121.3, 124.7, 125.7, 126.2, 127.6 (d, *J* = 5.0 Hz), 127.7 (d, *J* = 2.9 Hz), 127.9, 129.6, 129.9 (d, *J* = 94.0 Hz), 133.4, 136.4, 136.6, 140.1 (d, *J* = 3.0 Hz), 144.4. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.3.




144.39
140.14
140.11
136.58
136.39
133.36
130.36
129.64
129.43
127.89
127.86
127.85
127.70
127.68
127.57
127.52
127.05
127.02
126.31
126.29
126.23
125.66
124.68
121.27
120.13
120.06
116.68
116.64
109.30
108.29
106.54
51.84
51.64
32.77
32.47
27.53
27.37
21.51
16.53
16.46
f1 (ppm)


-107.35
-109.34
-132.94
0.22
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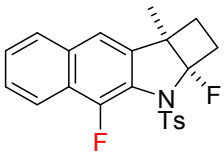
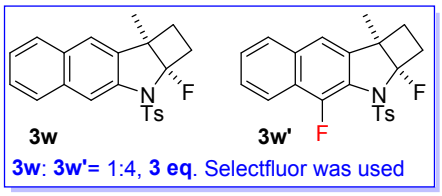
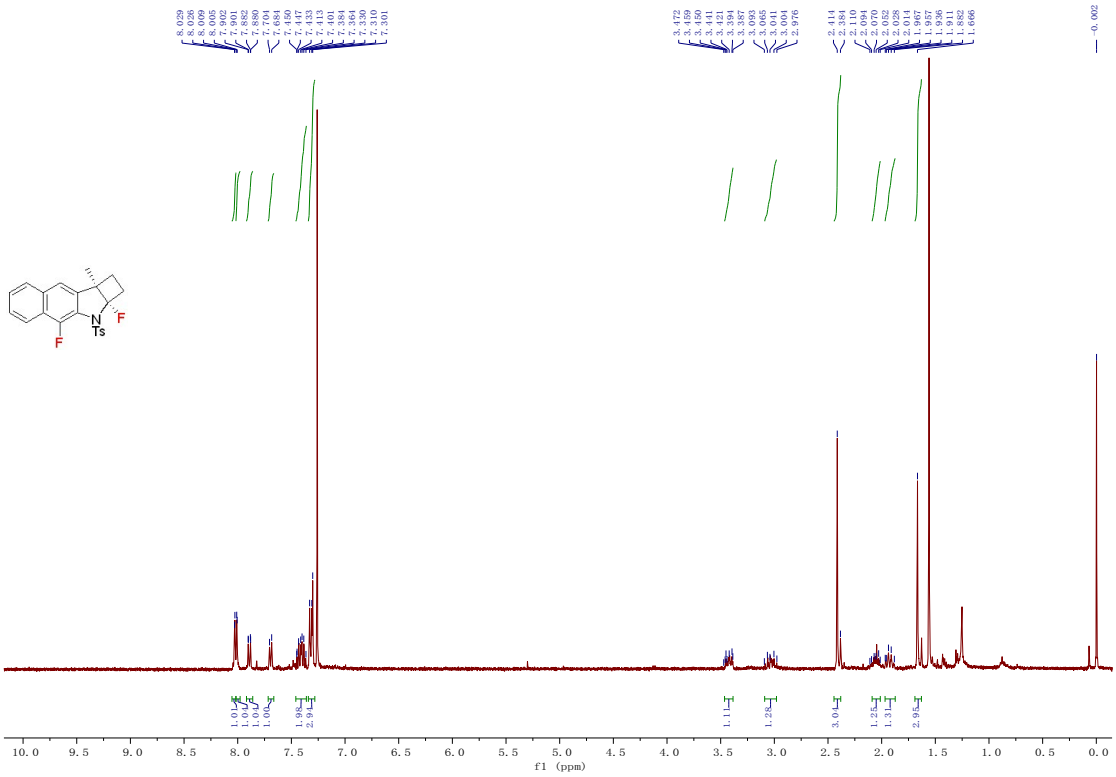
0.21
f1 (ppm)

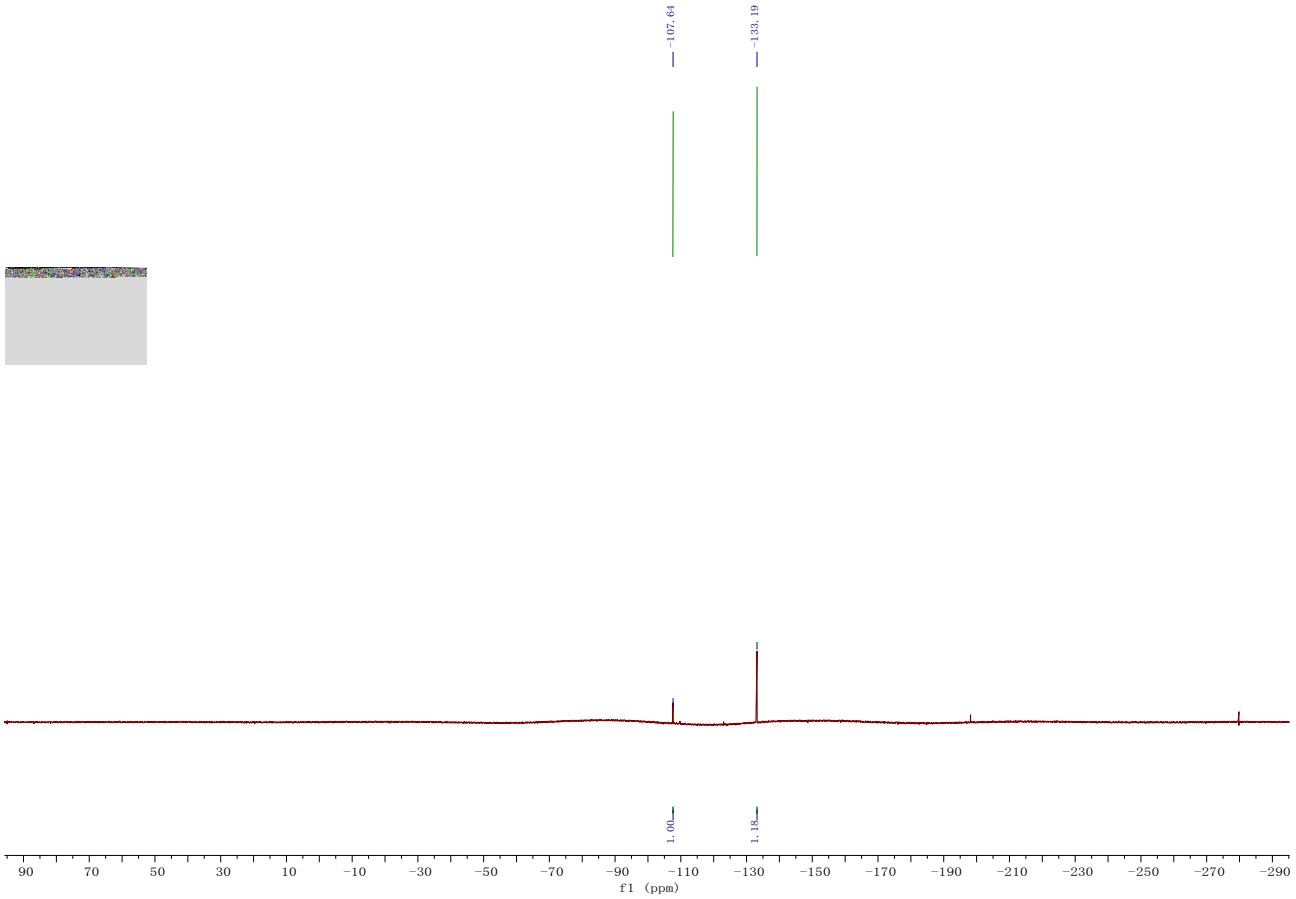


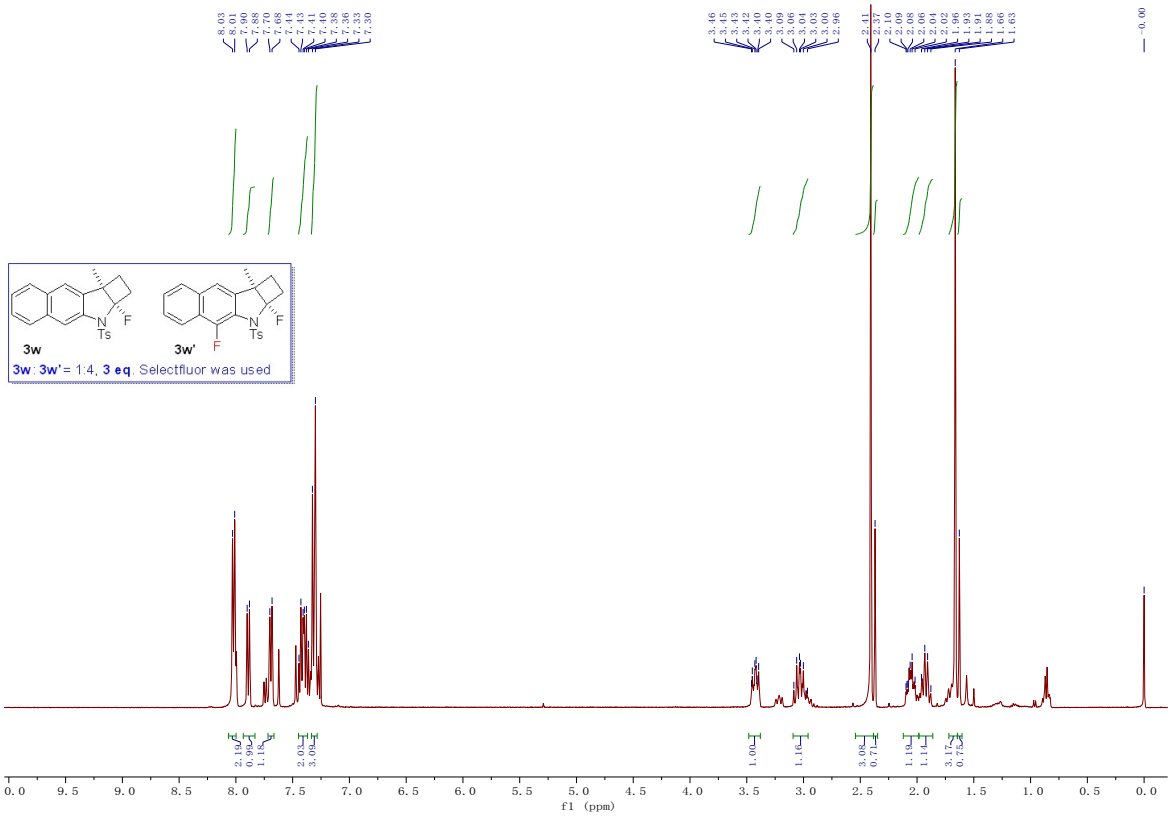
from 

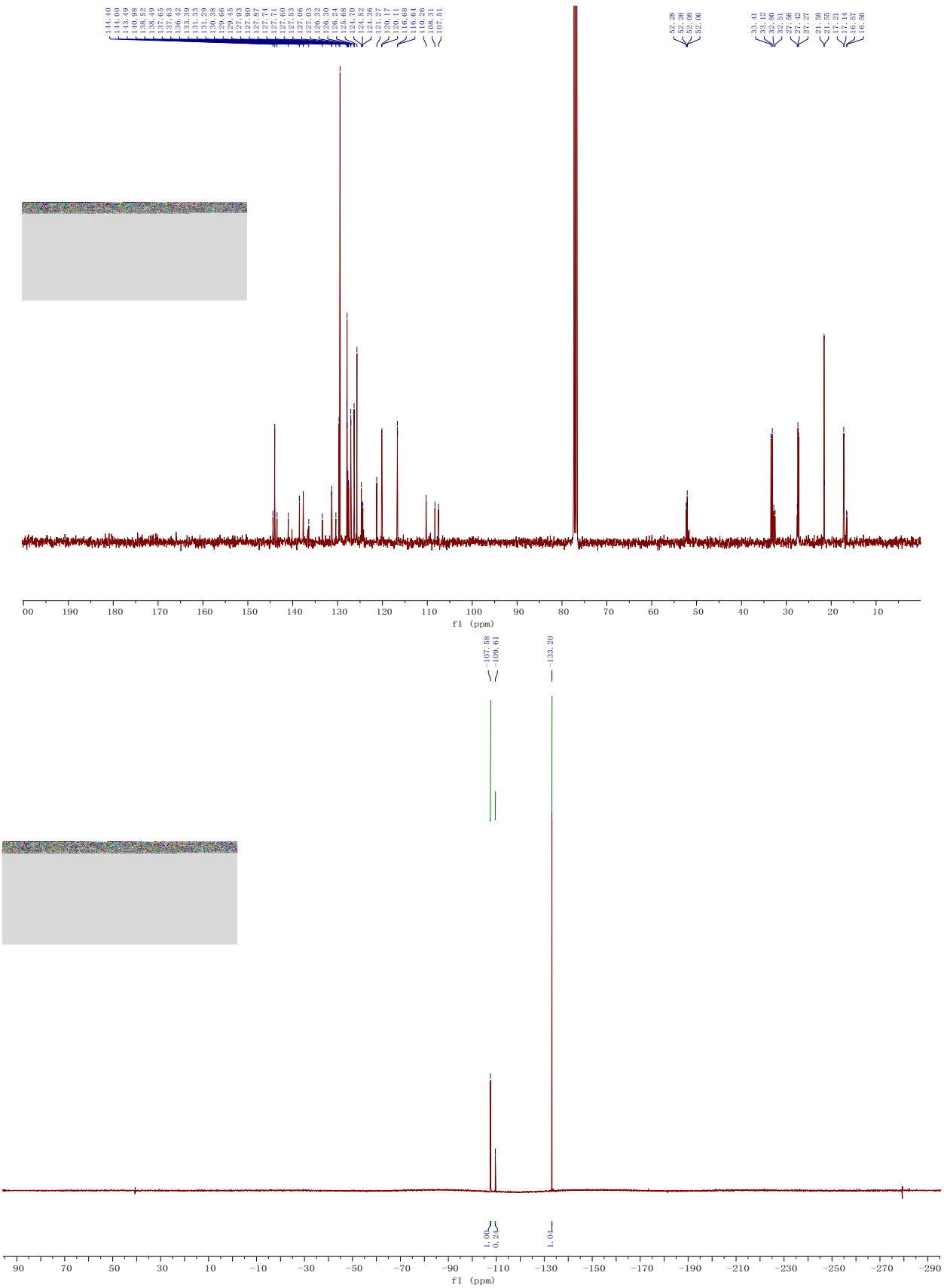
and prolonging the reaction time to 24 h

Compound 3w': A white solid (**3w**+**3w'** = 22.9 mg, **3w**:**3w'** = 1:4 in 6 h and **3w'** 7.1 mg, 9% in 24 h); M.p. 79-80 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.67 (s, 3H), 1.87 – 1.97 (m, 1H), 2.01 – 2.09 (m, 1H), 2.40 (s, 3H), 2.98 – 3.09 (m, 1H), 3.38 – 3.46 (m, 1H), 7.28 – 7.34 (m, 3H), 7.36 – 7.46 (m, 2H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.86 – 7.92 (m, 1H), 8.01 (d, *J* = 1.5 Hz, 1H), 8.02 – 8.05 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 17.17 (d, *J* = 7.2 Hz), 21.58, 27.34 (d, *J* = 14.9 Hz), 33.27 (d, *J* = 29.6 Hz), 52.17 (d, *J* = 18.3 Hz), 108.31, 108.89 (d, *J* = 277.2 Hz), 116.66 (d, *J* = 3.9 Hz), 120.14 (d, *J* = 6.5 Hz), 121.27, 125.68, 126.31 (d, *J* = 2.1 Hz), 127.06, 127.90, 129.45, 131.31 (d, *J* = 3.6 Hz), 137.64 (d, *J* = 2.5 Hz), 138.51 (d, *J* = 2.7 Hz), 143.95 (d, *J* = 92.0 Hz), 144.00. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -107.6, -133.2. IR (neat) ν 2974, 1591, 1506, 1402, 1346, 1319, 1154, 1092, 902, 811, 745 cm^{-1}. HRMS (ESI) Calcd. for $C_{22}H_{19}FNO_2S$ requires (M^+-F): 380.1115, Found: 380.1112.

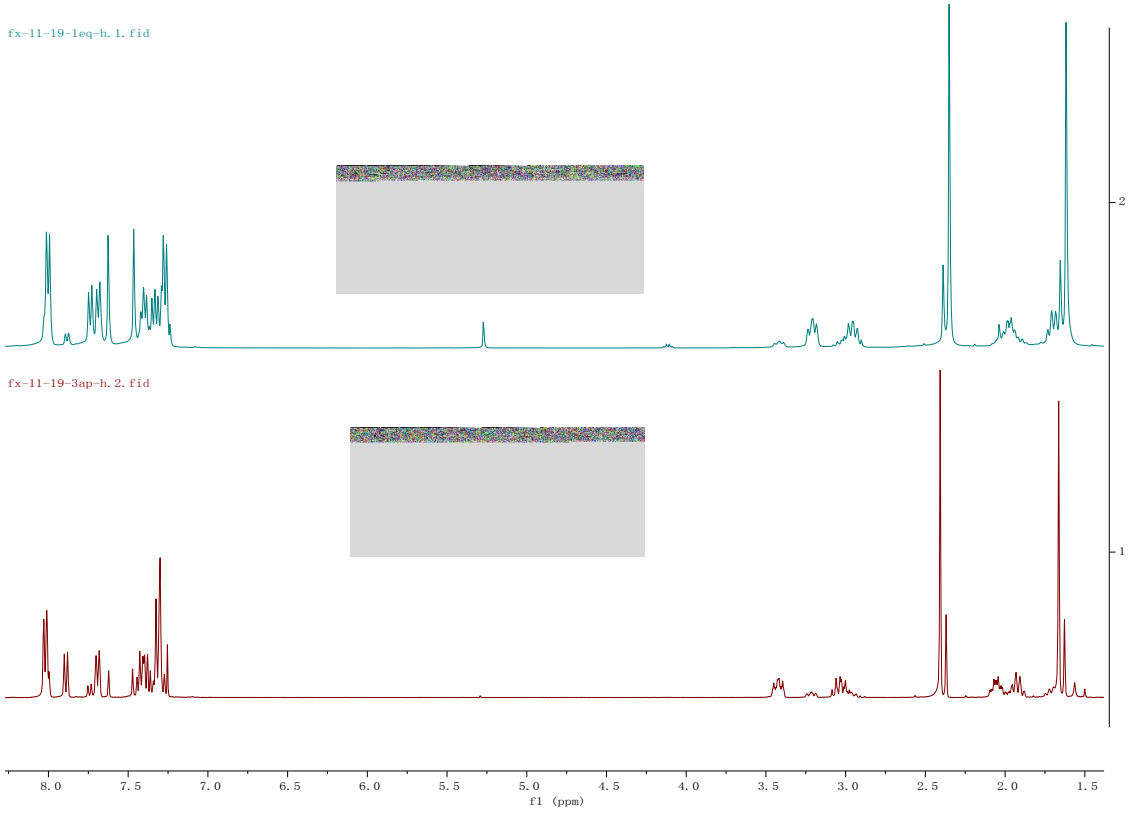


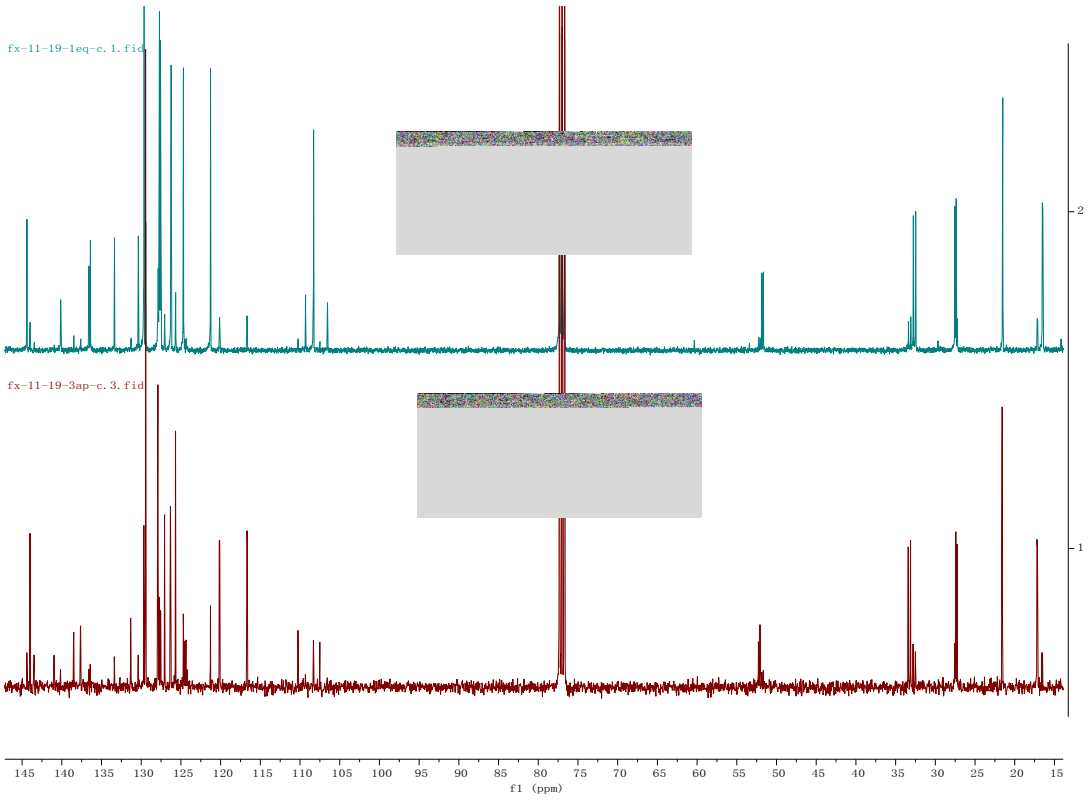

-107.64
-133.19
1.00
1.18
90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -270 -290
f1 (ppm)

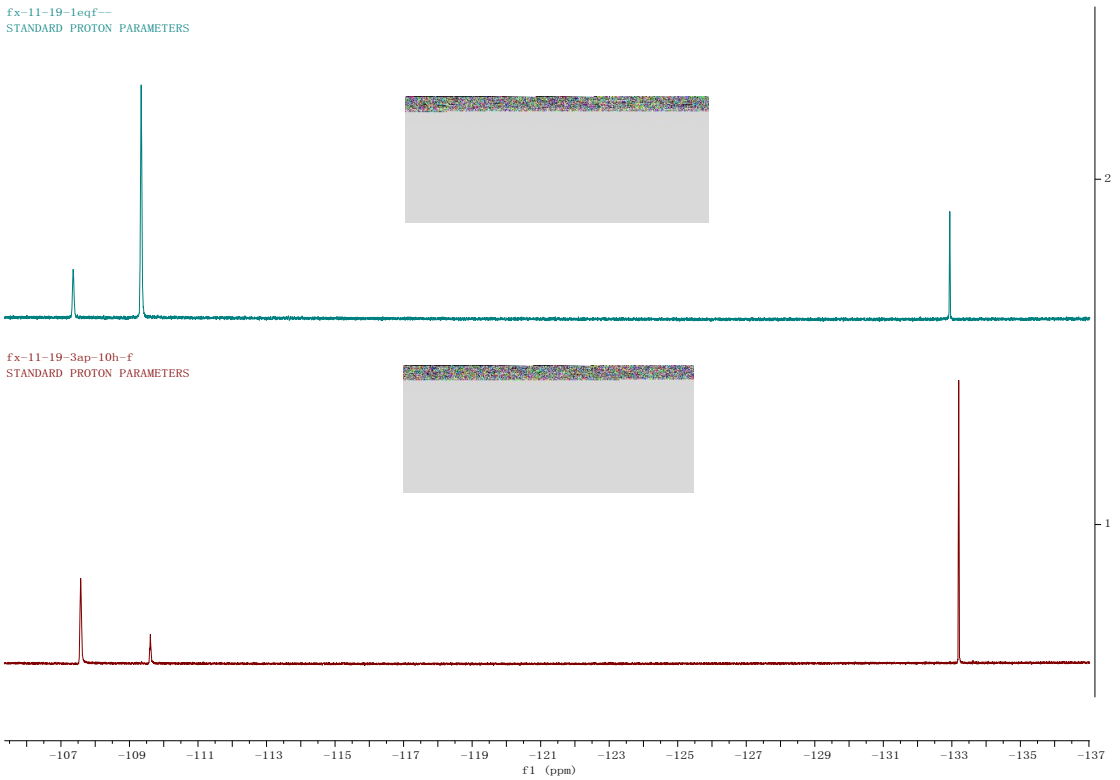

8.03
8.01
7.90
7.88
7.70
7.68
7.44
7.43
7.41
7.40
7.38
7.36
7.33
7.30
3.46
3.45
3.43
3.42
3.41
3.40
3.09
3.06
3.04
3.01
3.00
2.96
2.41
2.37
2.10
2.09
2.08
2.06
2.04
2.02
1.96
1.93
1.91
1.88
1.66
1.63
-0.00
3w
3w'
3w : 3w' = 1:4, 3 eq. Selectfluor was used
2.19
0.99
1.18
2.03
3.09
1.00
1.16
3.08
0.71
1.19
1.14
3.17
0.73
0.0 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)

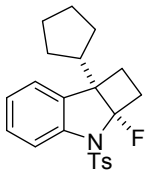


A slight difference between **3w** and **3w'** (comparison diagram)

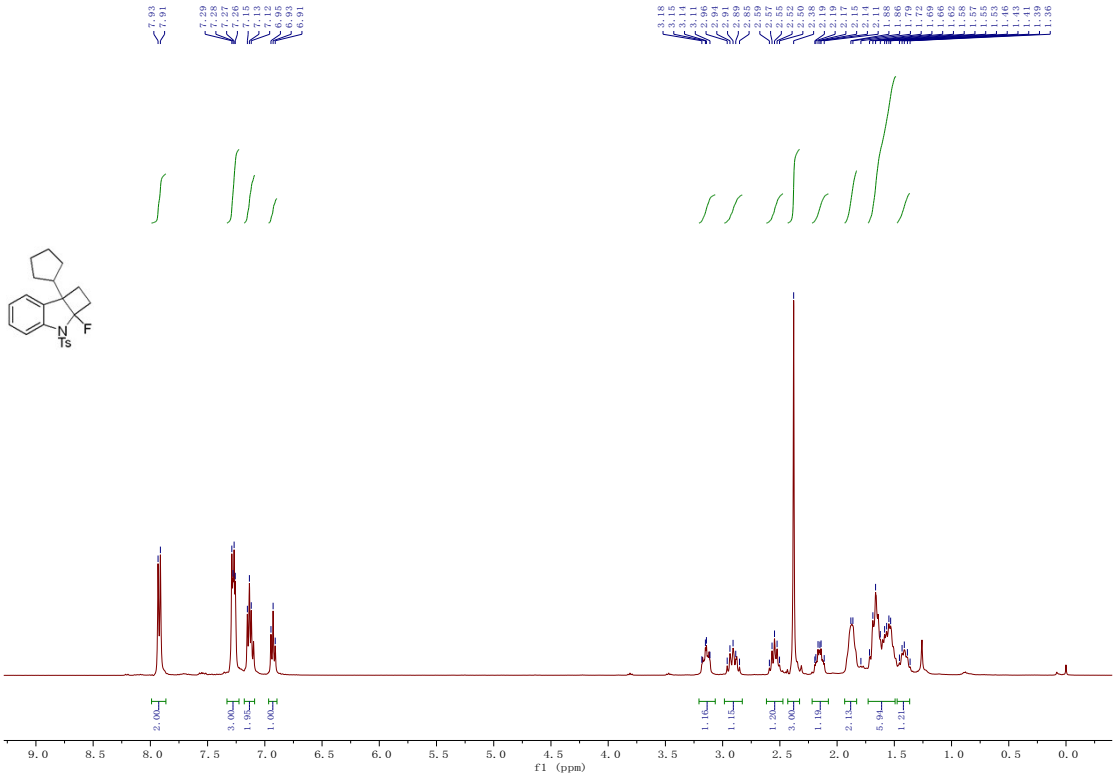

fx-11-19-1eq-h.1.fid
fx-11-19-3ap-h.2.fid
2
1
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

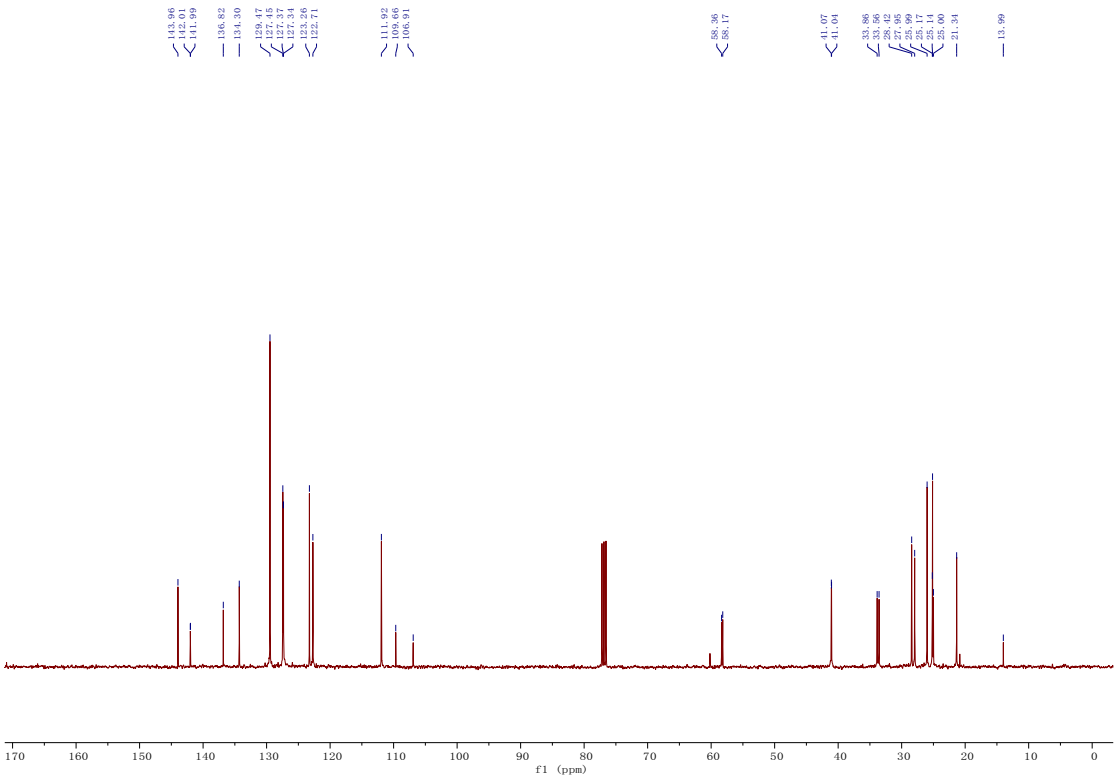

fx-11-19-1eq-c.1.fid
fx-11-19-3ap-c.3.fid
2
1
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
f1 (ppm)

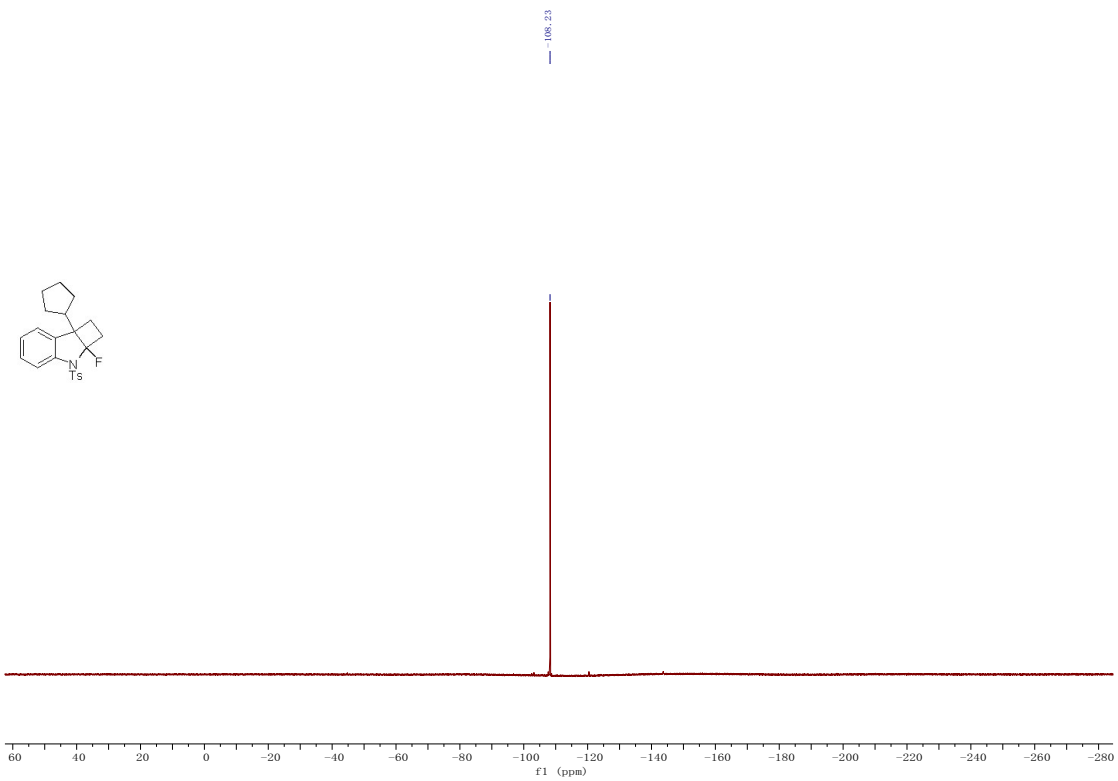

fx-11-19-1eqf--
STANDARD PROTON PARAMETERS
fx-11-19-3ap-10h-f
STANDARD PROTON PARAMETERS
2
1
−107 −109 −111 −113 −115 −117 −119 −121 −123 −125 −127 −129 −131 −133 −135 −137
f1 (ppm)

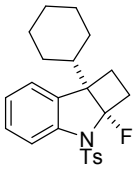

N
Ts
F

Compound 3x: A colorless oil (41.4 mg, 54%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.37 – 1.48 (m, 1H), 1.49 – 1.73 (m, 6H), 1.83 – 1.93 (m, 2H), 2.08 – 2.22 (m, 1H), 2.38 (s, 3H), 2.55 (p, *J* = 8.9 Hz, 1H), 2.91 (dt, *J* = 22.6, 11.4 Hz, 1H), 3.06 – 3.21 (m, 1H), 6.93 (dd, *J* = 7.5 Hz, 1H), 7.09 – 7.18 (m, 2H), 7.23 – 7.33 (m, 3H), 7.86 – 7.99 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 21.3, 25.1 (d, *J* = 17.2 Hz), 25.6 (d, *J* = 86.1 Hz), 28.1 (d, *J* = 47.0 Hz), 33.7 (d, *J* = 30.4 Hz), 41.1 (d, *J* = 3.3 Hz), 58.3 (d, *J* = 18.5 Hz), 108.3 (d, *J* = 276.3 Hz), 111.9, 122.7, 123.3, 127.4 (d, *J* = 3.0 Hz), 127.4, 129.5, 134.3, 136.8, 142.0 (d, *J* = 2.2 Hz), 144.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -108.2. IR (neat) ν 2971, 2856, 1598, 1572, 1491, 1380, 1338, 1167, 1092, 908, 815, 756, 679 cm^{-1}. HRMS (ESI) Calcd. for $C_{22}H_{24}FNNaO_2S$ requires (M^++Na): 408.1404, Found: 408.1403.

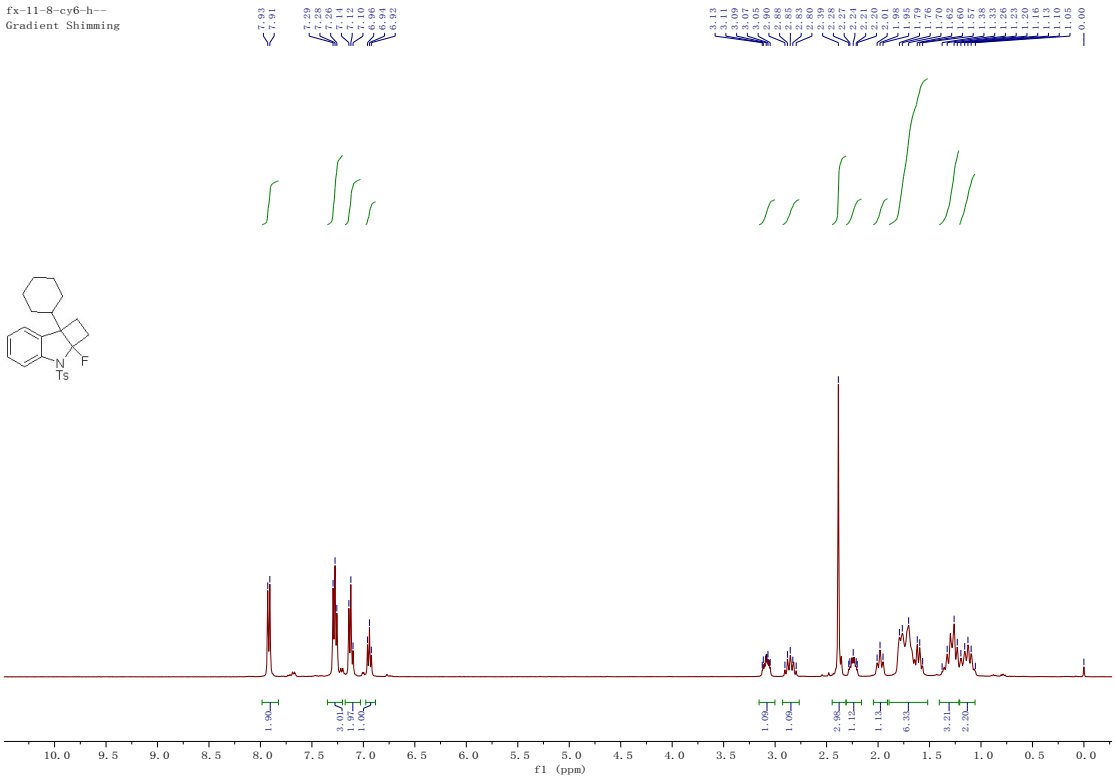


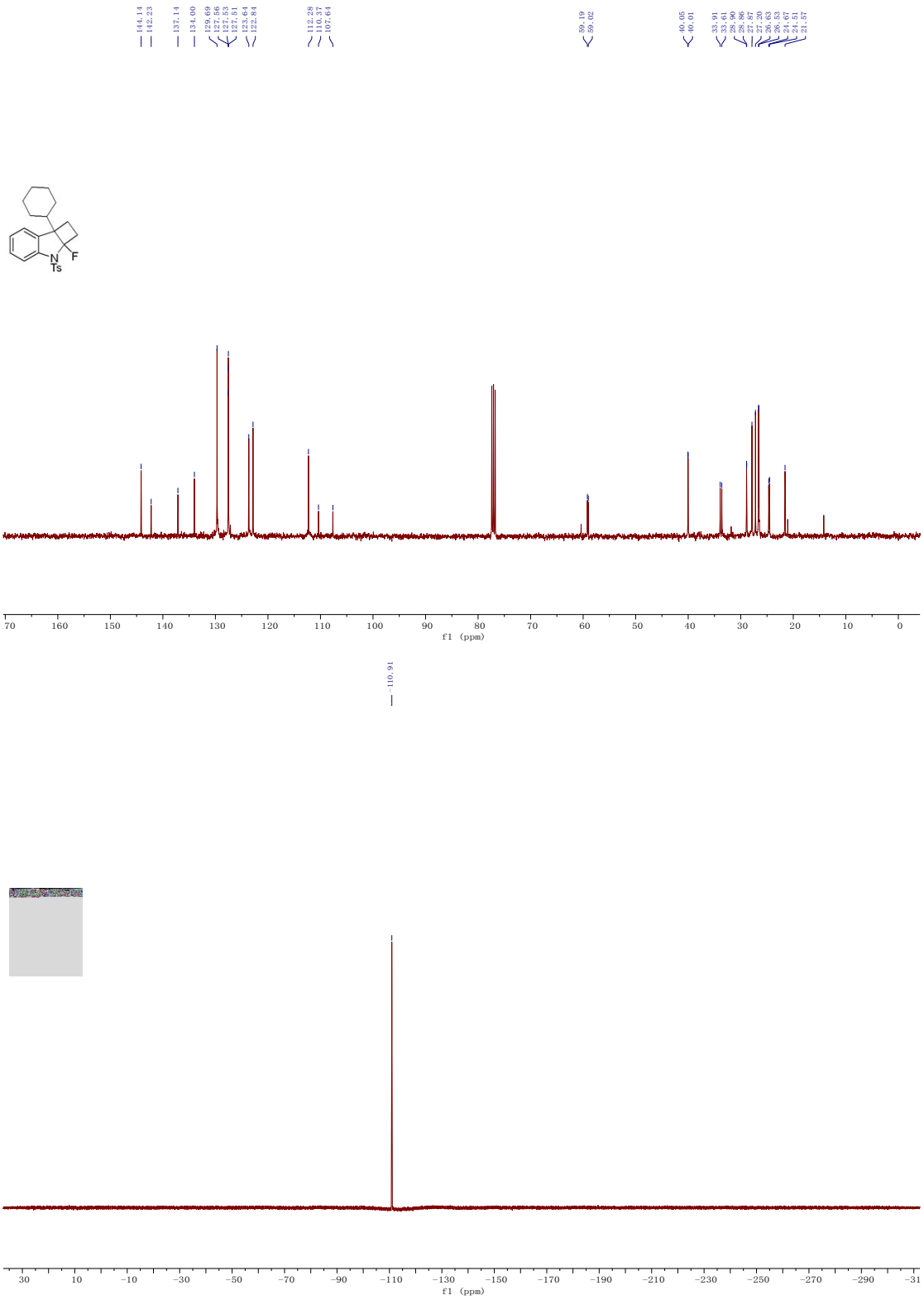

143.96
142.01
141.99
136.82
134.30
129.47
127.45
127.37
127.34
123.26
122.71
111.92
109.66
105.91
58.36
58.17
41.07
41.04
33.86
33.56
28.42
27.95
25.99
25.17
25.14
25.00
21.34
13.99
f1 (ppm)

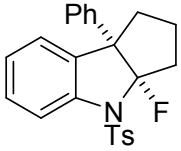

-108.23
f1 (ppm)


N
Ts
F

Compound 3y: A colorless oil (35.9 mg, 45%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.06 – 1.21 (m, 2H), 1.21 – 1.41 (m, 3H), 1.52 – 1.89 (m, 6H), 1.98 (t, *J* = 11.5 Hz, 1H), 2.16 – 2.31 (m, 1H), 2.39 (s, 3H), 2.85 (dt, *J* = 23.0, 11.5 Hz, 1H), 3.00 – 3.16 (m, 1H), 6.94 (dd, *J* = 7.4 Hz, 1H), 7.03 – 7.18 (m, 2H), 7.20 – 7.35 (m, 3H), 7.82 – 7.98 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 21.6, 24.6 (d, *J* = 16.1 Hz), 26.5, 26.6, 27.2, 27.9, 28.9 (d, *J* = 3.3 Hz), 33.8 (d, *J* = 31.0 Hz), 40.1 (d, *J* = 3.0 Hz), 59.1 (d, *J* = 17.7 Hz), 109.0 (d, *J* = 275.0 Hz), 112.3, 122.9, 123.7, 127.5 (d, *J* = 2.6 Hz), 127.6, 129.7, 134.0, 137.2, 142.3, 144.1. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -110.9. IR (neat) ν 2982, 2919, 2849, 1639, 1612, 1598, 1580, 1484, 1447, 1406, 1377, 1337, 1167, 1089, 898, 807, 747, 706, 689, 665 cm^{-1}. HRMS (ESI) Calcd. for $C_{23}H_{26}NO_2S$ requires (M^+-F): 380.1679, Found: 380.1673.

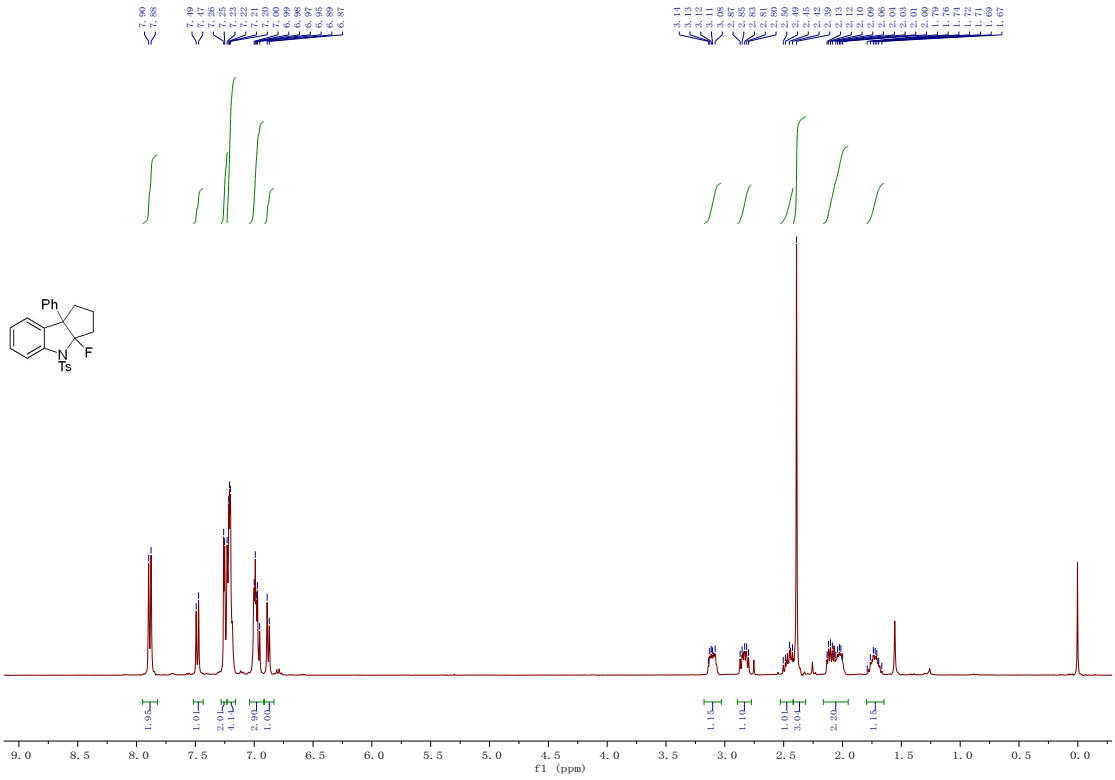


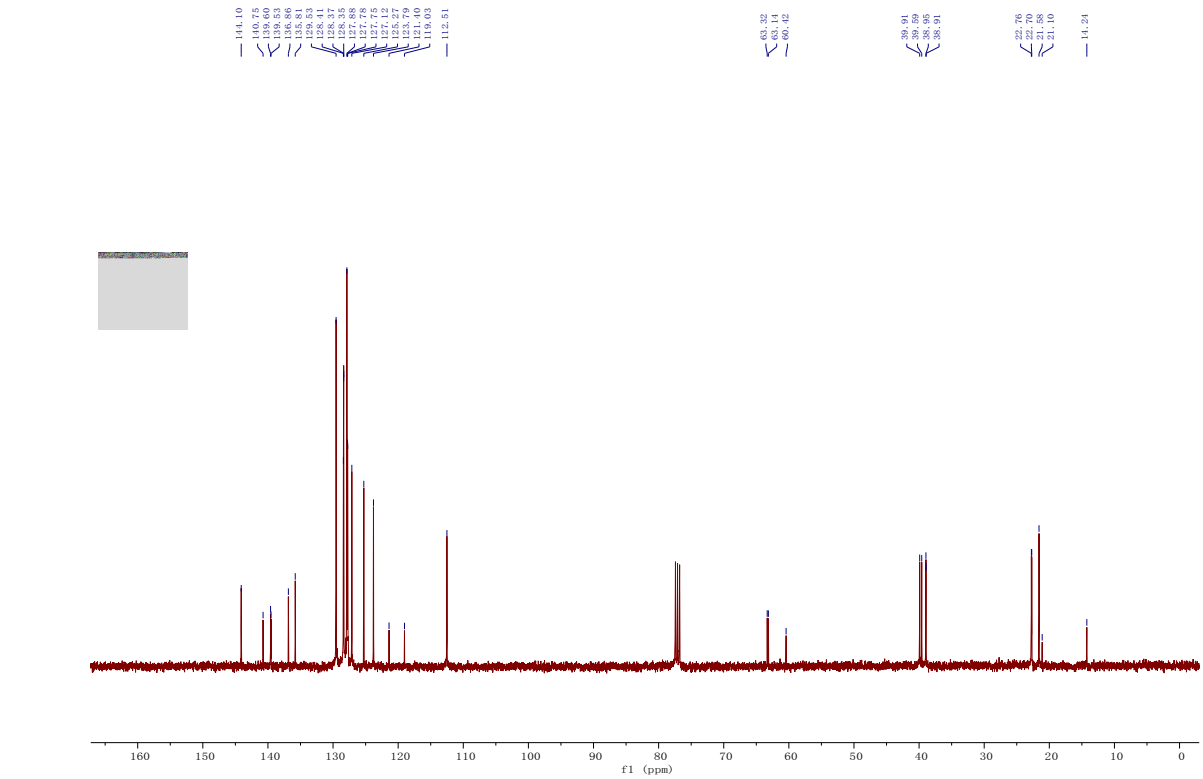


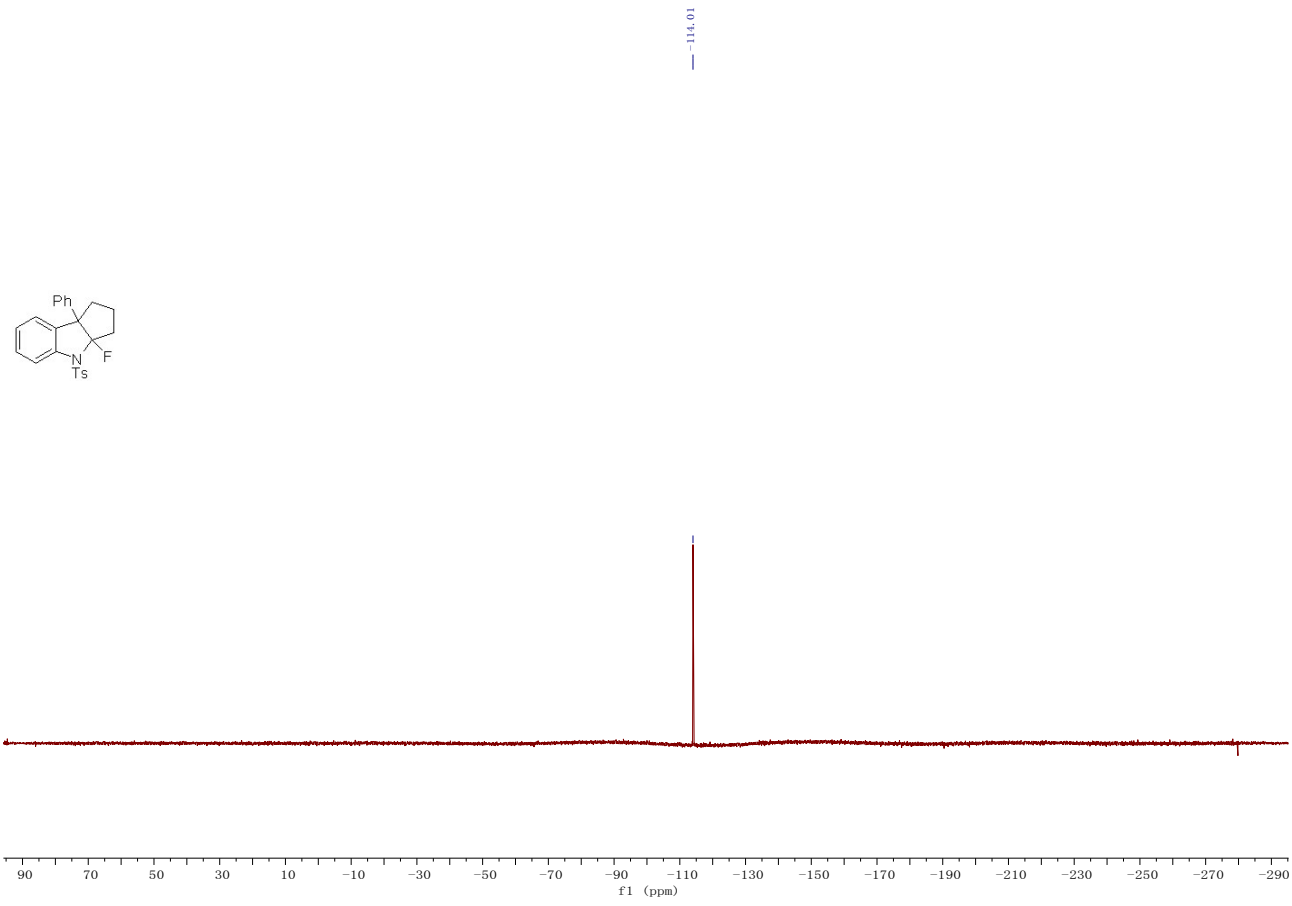


Compound 3z: A white solid (72.7 mg, 87%); M.p. 128-129 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.65 – 1.80 (m, 1H), 1.95 – 2.16 (m, 2H), 2.39 (s, 3H), 2.47 (dd, *J* = 22.7, 8.8 Hz, 1H), 2.77 –

2.89 (m, 1H), 3.11 (dt, *J* = 13.2, 6.8 Hz, 1H), 6.88 (d, *J* = 7.3 Hz, 1H), 6.92 – 7.04 (m, 3H), 7.16 – 7.23 (m, 4H), 7.23 – 7.28 (m, 2H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.82 – 7.95 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 21.6, 22.7 (d, *J* = 5.8 Hz), 38.9 (d, *J* = 3.5 Hz), 39.8 (d, *J* = 31.6 Hz), 60.4, 63.2 (d, *J* = 18.1 Hz), 112.5, 120.2 (d, *J* = 238.4 Hz), 123.8, 125.3, 127.1, 127.8 (d, *J* = 3.6 Hz), 127.9, 128.4 (d, *J* = 1.6 Hz), 128.4, 129.5, 135.8, 136.9, 139.6 (d, *J* = 7.1 Hz), 140.7, 144.1. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -114.0. IR (neat) ν 2969, 2927, 2870, 1597, 1456, 1360, 1234, 1187, 1168, 1155, 1131, 1091, 1007, 963, 912, 775, 756, 701, 677, 654 cm^{-1}. HRMS (ESI) Calcd. for $C_{24}H_{22}NO_2S$ requires (M^+-F): 388.1366, Found: 388.1360.




144.10
140.75
139.60
139.53
136.86
135.81
135.53
128.41
128.37
128.35
128.08
127.78
127.75
127.12
127.07
123.79
121.40
119.03
112.51
63.32
63.14
60.42
39.91
39.89
38.95
38.91
22.76
22.70
21.38
21.10
14.24
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-114.01
Ph
N
F
Ts
90
70
50
30
10
−10
−30
−50
−70
−90
−110
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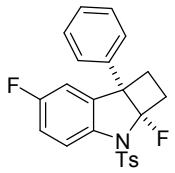
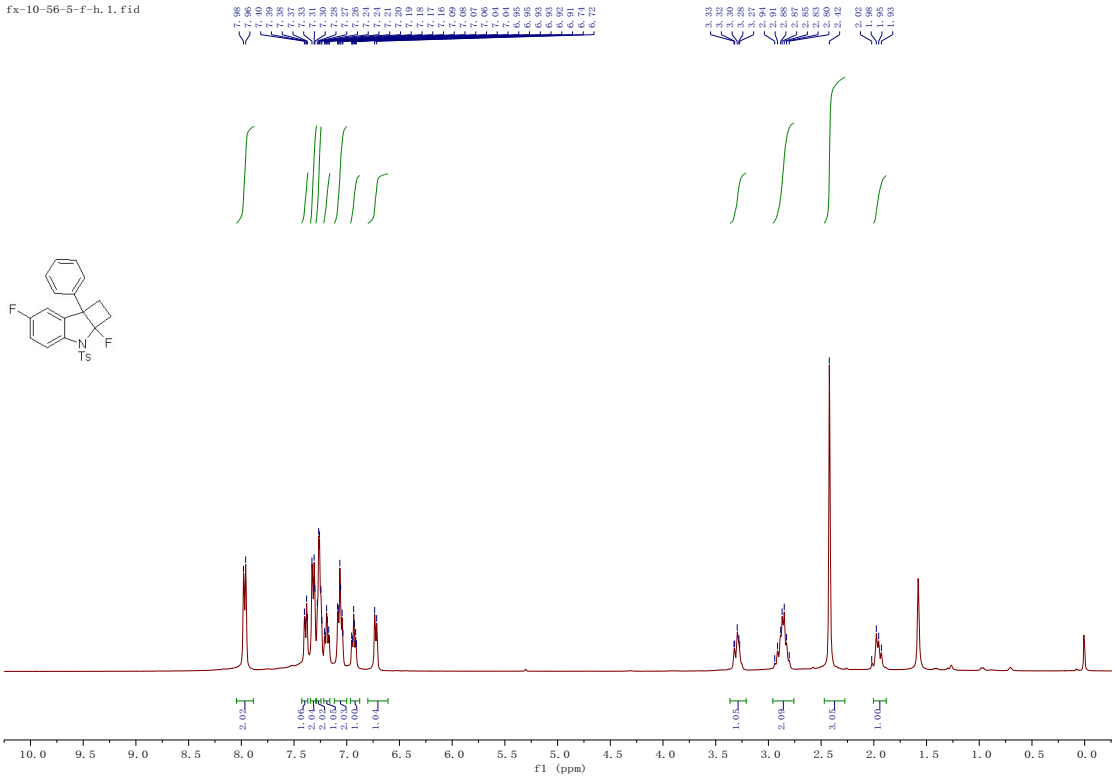
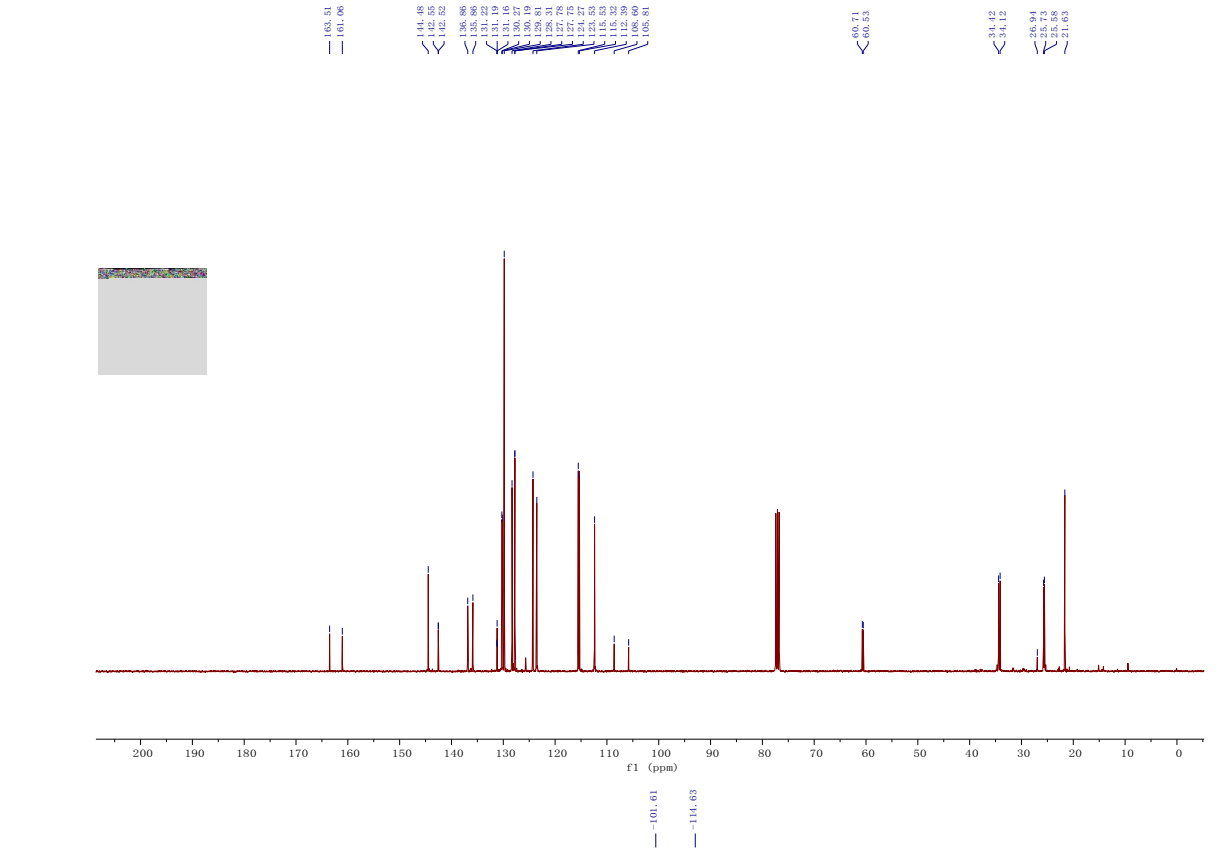
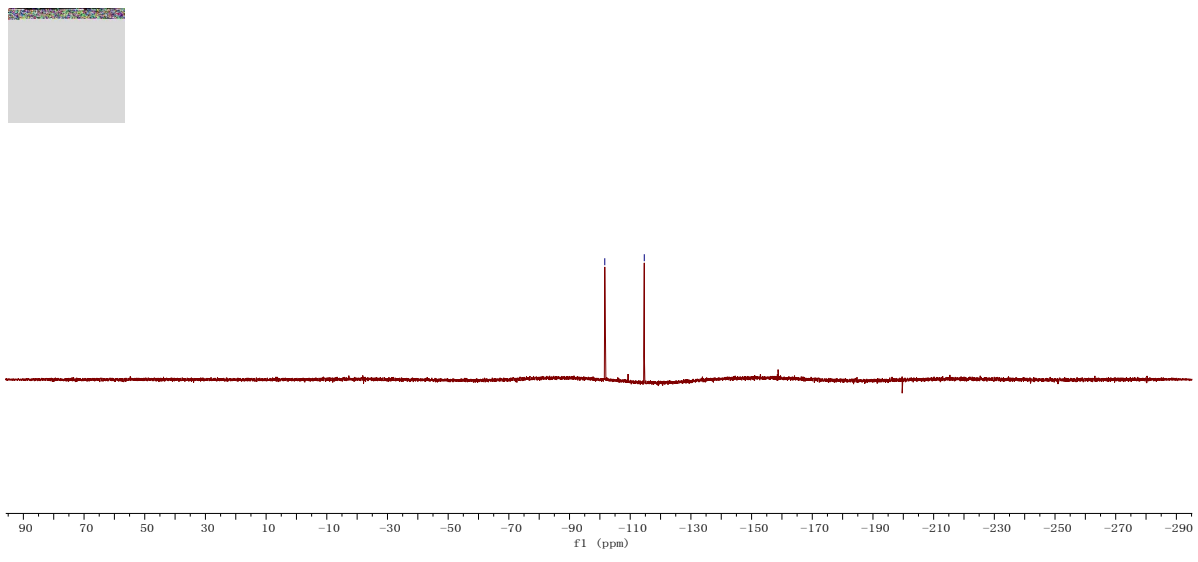
−150
−170
−190
−210
−230
−250
−270
−290
f1 (ppm)

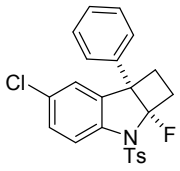


Compound 3aa: A white solid (30.4 mg, 39%); M.p. 182-183 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.88 – 2.00 (m, 1H), 2.42 (s, 3H), 2.87 (tt, *J* = 18.9, 10.4 Hz, 2H), 3.21 – 3.36 (m, 1H), 6.73 (d, *J* = 7.5 Hz, 1H), 6.93 (ddd, *J* = 7.6, 7.5, 2.9 Hz, 1H), 7.00 – 7.12 (m, 2H), 7.19 (ddd, *J* = 8.2, 7.9, 2.8 Hz, 1H), 7.24 – 7.29 (m, 2H), 7.29 – 7.35 (m, 2H), 7.39 (dd, *J* = 8.2, 2.9 Hz, 1H), 7.89 – 8.05 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 21.6, 25.7 (d, *J* = 15.9 Hz), 34.3 (d, *J* = 30.3 Hz), 60.6 (d, *J* = 18.1 Hz), 107.2 (d, *J* = 280.9 Hz), 112.4, 115.4 (d, *J* = 21.4 Hz), 123.5, 124.3, 127.8 (d, *J* = 3.0 Hz), 128.3, 129.8, 130.2 (d, *J* = 8.2 Hz), 131.2, 131.2 (d, *J* = 6.3 Hz), 136.4 (d, *J* = 100.2 Hz), 142.5 (d, *J* = 2.4 Hz), 144.5, 162.3 (d, *J* = 247.1 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -114.6, -101.6. IR (neat) ν 3022, 2962, 2949, 1597, 1510, 1463, 1366, 1232, 1189, 1160, 1143, 1123, 1093, 1006, 919, 831, 809, 766, 674, 667 cm^{-1}. HRMS (ESI) Calcd. for $C_{23}H_{19}FNO_2S$ requires (M^+-F): 392.1115, Found: 392.1112.

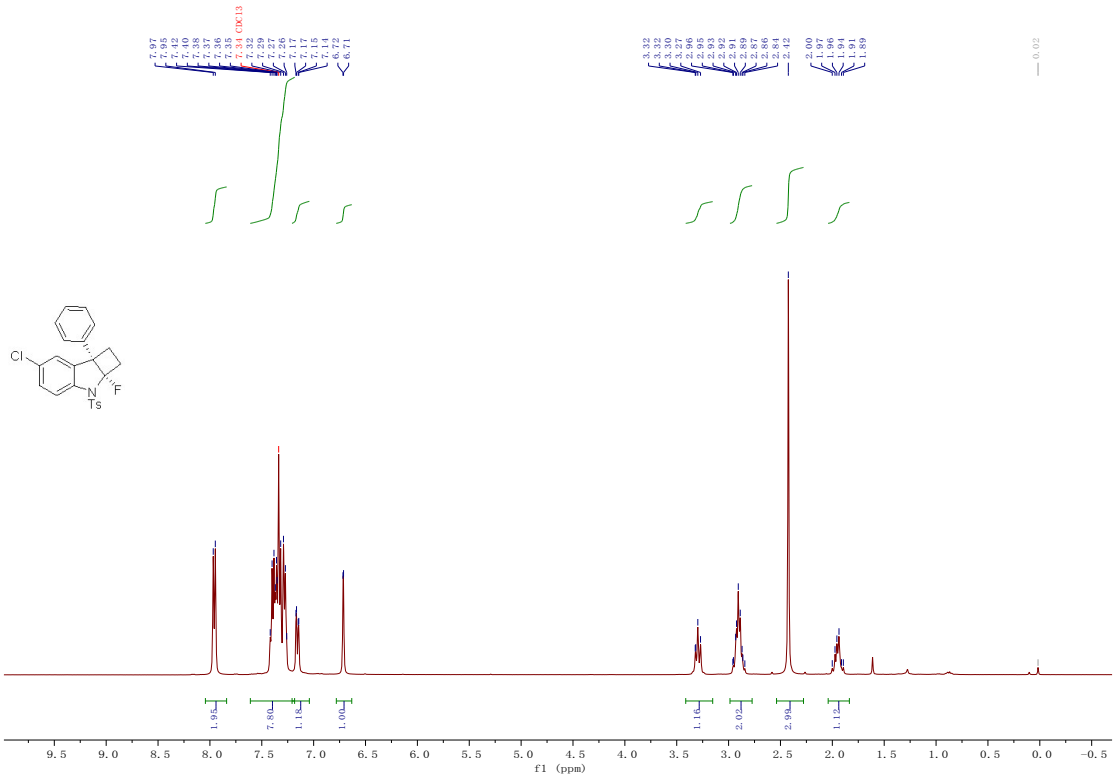


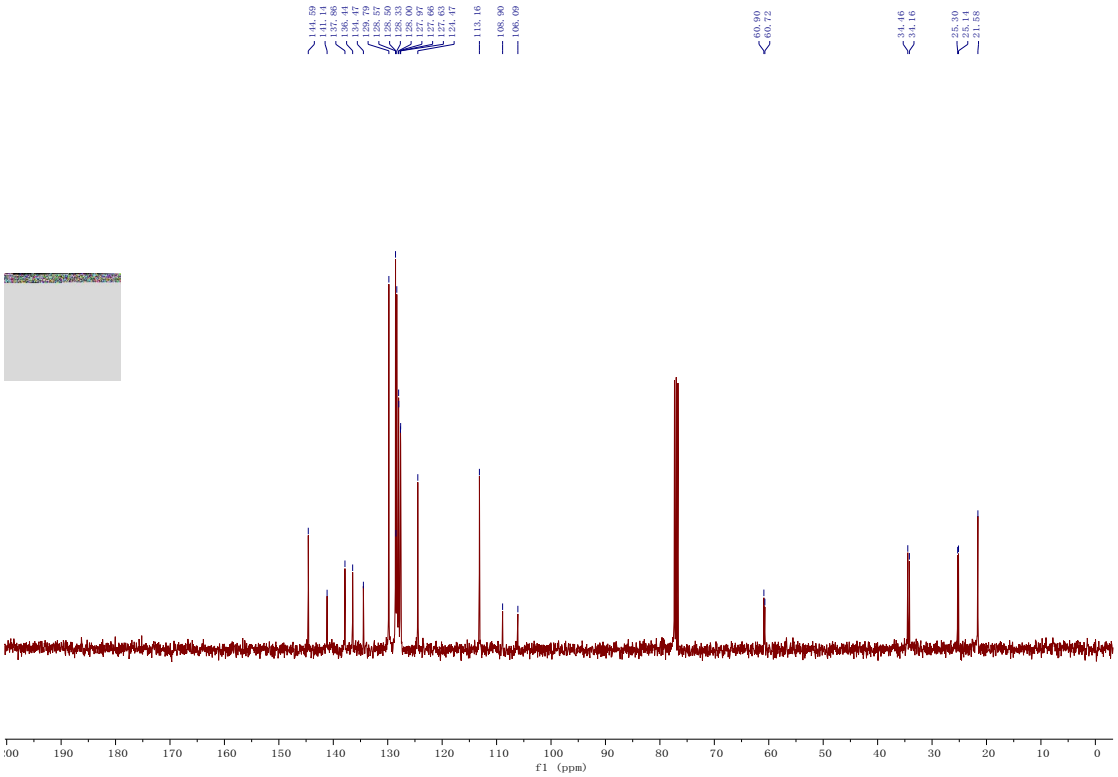

163.51
161.06
144.48
142.55
142.52
136.86
135.86
131.22
131.19
131.16
130.27
130.19
129.81
128.31
127.78
127.75
124.27
123.53
115.53
115.32
112.39
108.60
105.81
60.71
60.53
34.42
34.12
25.94
25.73
25.58
21.63
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

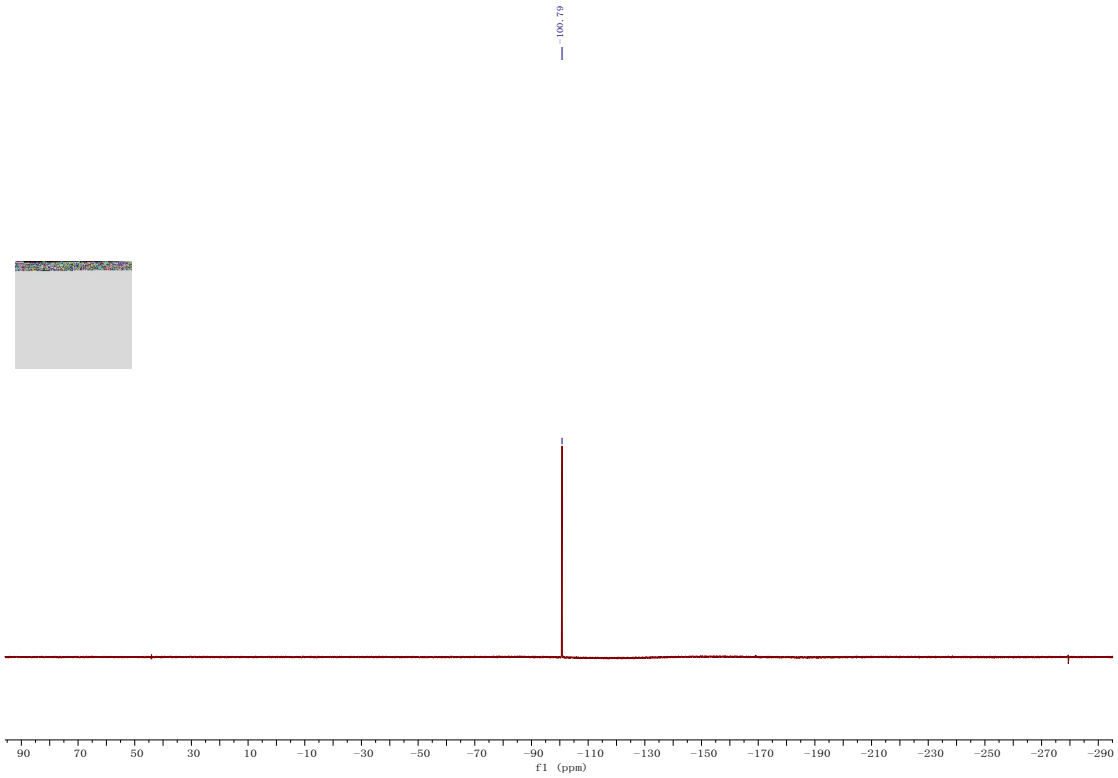

-101.61
-114.63
90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -270 -290
f1 (ppm)

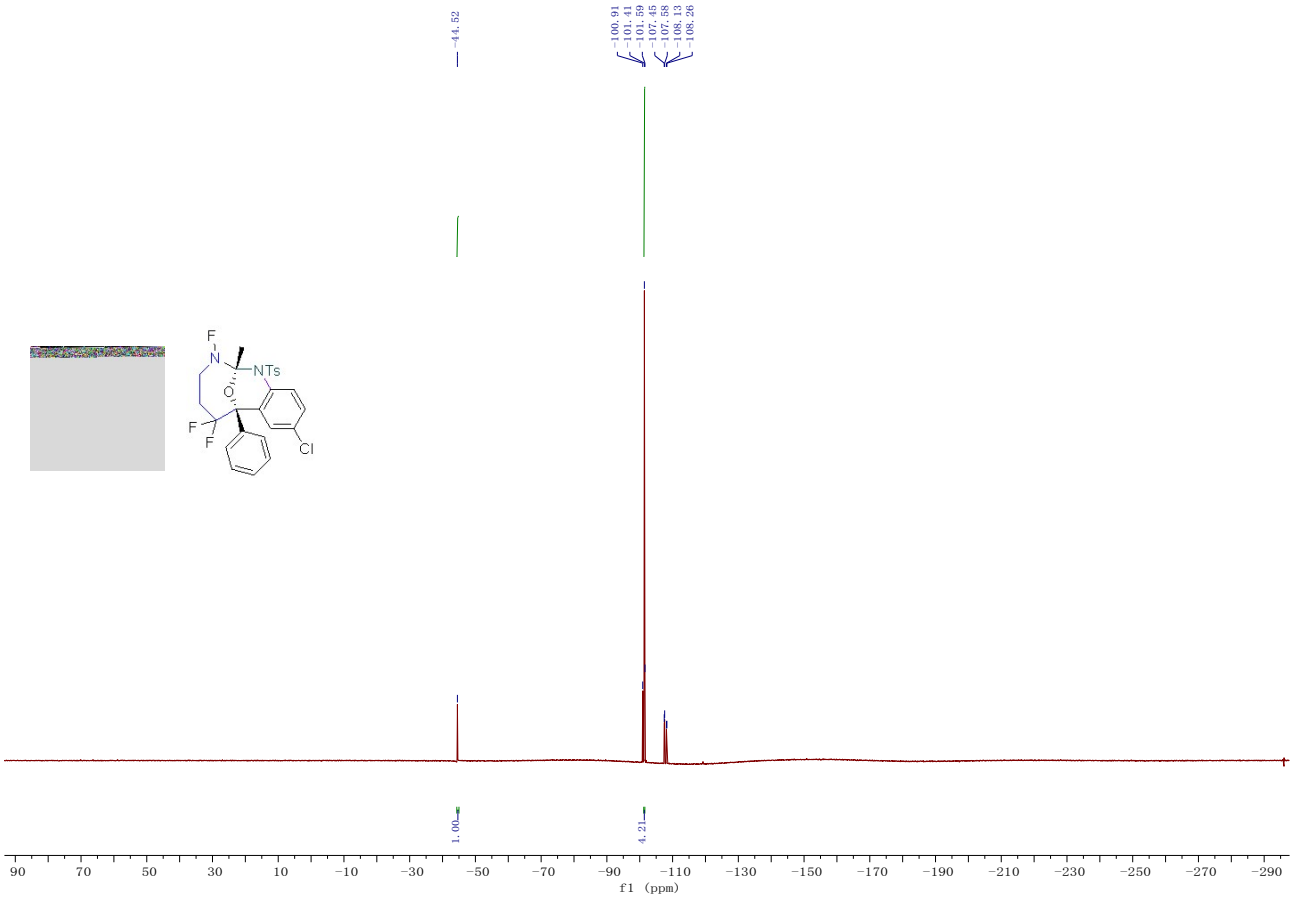

Cl
N
Ts
F

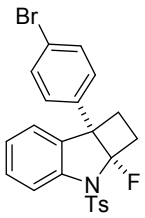
Compound 3ab: A white solid (36.0 mg, 45%); M.p. 194-195 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.84 – 2.04 (m, 1H), 2.42 (s, 3H), 2.91 (h, *J* = 7.7, 7.0 Hz, 2H), 3.30 (t, *J* = 10.2 Hz, 1H), 6.71 (d, *J* = 2.2 Hz, 1H), 7.16 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.18 – 7.61 (m, 8H), 7.84 – 8.04 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 21.6, 25.2 (d, *J* = 16.0 Hz), 34.3 (d, *J* = 30.0 Hz), 60.8 (d, *J* = 18.3 Hz), 107.5 (d, *J* = 282.0 Hz), 113.2, 124.5, 127.6 (d, *J* = 3.1 Hz), 128.0 (d, *J* = 2.7 Hz), 128.3, 128.5, 128.6, 129.8, 134.5 (d, *J* = 2.3 Hz), 136.4, 137.9, 141.12, 141.14, 144.6. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -100.8. IR (neat) ν 3008, 2967, 2920, 2849, 1597, 1460, 1357, 1247, 1231, 1177, 1160, 1133, 1121, 1085, 1040, 1012, 1001, 925, 818, 794, 754, 720, 705, 681 cm^{-1}. HRMS (ESI) Calcd. for $C_{23}H_{19}ClNO_2S$ requires (M^+-F): 408.0820, Found: 408.0819.



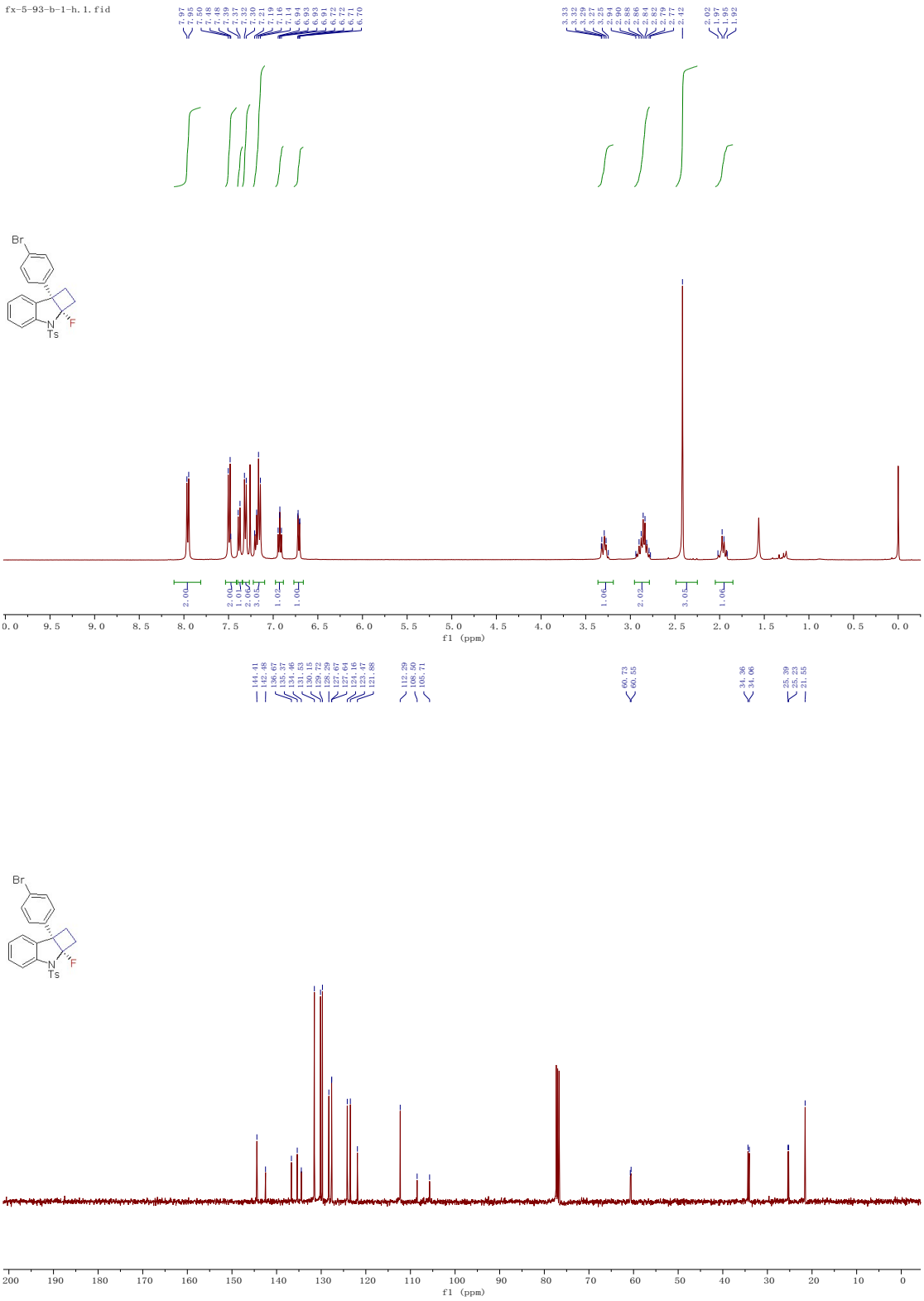

144.89
141.14
137.86
136.44
134.47
129.79
128.57
128.50
128.33
128.00
127.97
127.66
127.63
124.47
113.16
108.90
106.09
60.90
60.72
34.46
34.16
25.30
25.14
21.58
f1 (ppm)

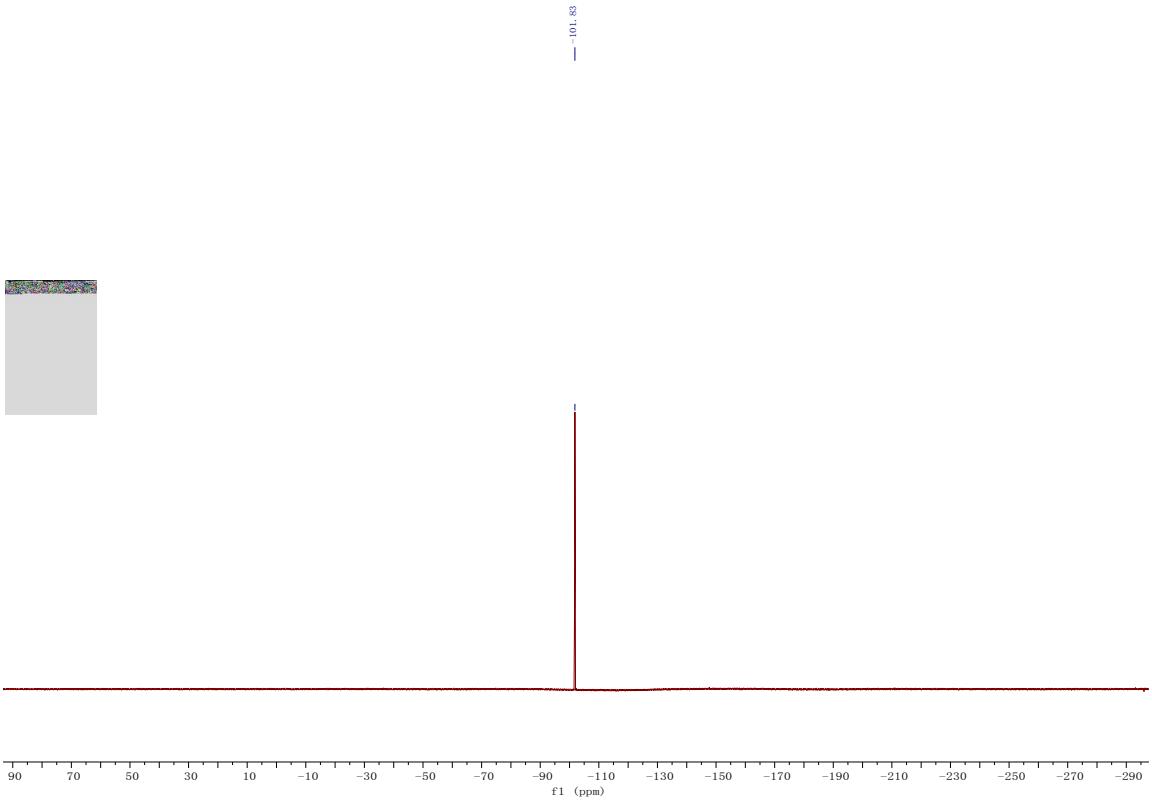

-100.79
f1 (ppm)

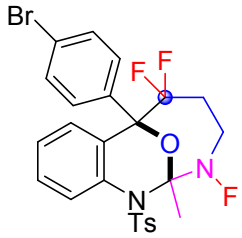




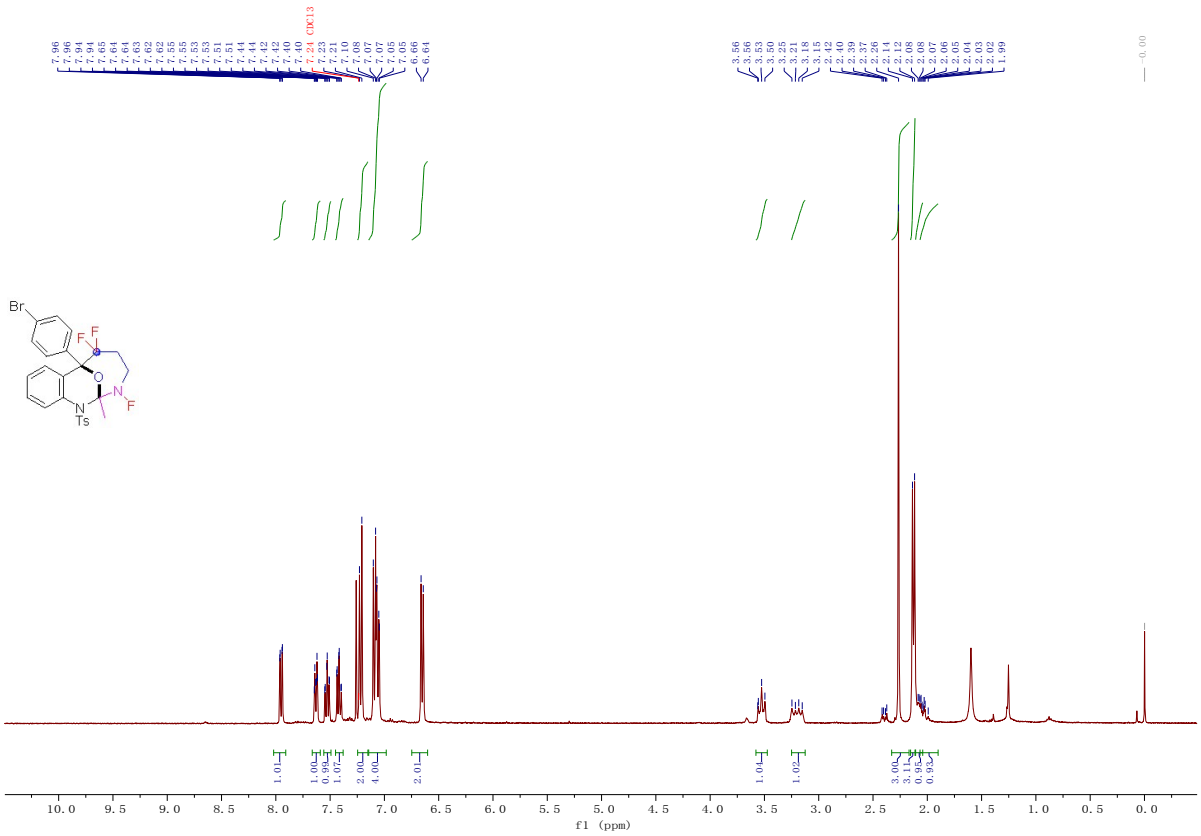
Compound 3ac: A white solid (36.4 mg, 39%); M.p. 218 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.96 (d, *J* = 8.0 Hz, 1H), 2.42 (s, 3H), 2.86 (dt, *J* = 15.5, 8.4 Hz, 2H), 3.19 – 3.36 (m, 1H), 6.71 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.89 – 6.97 (m, 1H), 7.10 – 7.22 (m, 3H), 7.27 – 7.35 (m, 2H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.41 – 7.53 (m, 2H), 7.81 – 8.11 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 21.5, 25.3 (d, *J* = 15.6 Hz), 34.2 (d, *J* = 30.1 Hz), 60.6 (d, *J* = 17.7 Hz), 107.1 (d, *J* = 280.8 Hz), 112.3, 121.9, 123.5, 124.2, 127.7 (d, *J* = 3.0 Hz), 128.3, 129.7, 130.2, 131.5, 134.5, 135.4, 136.7, 142.5, 144.4. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -101.8. IR (neat) ν 2069, 2927, 1602, 1492, 1469, 1561, 1363, 1257, 1243, 1187, 1179, 1161, 1143, 1121, 1090, 1005, 926, 822, 813, 751, 704, 687 cm^{-1}. HRMS (ESI) Calcd. for $C_{23}H_{19}BrNO_2S$ requires (M^+-F): 452.0314, Found: 452.0312.

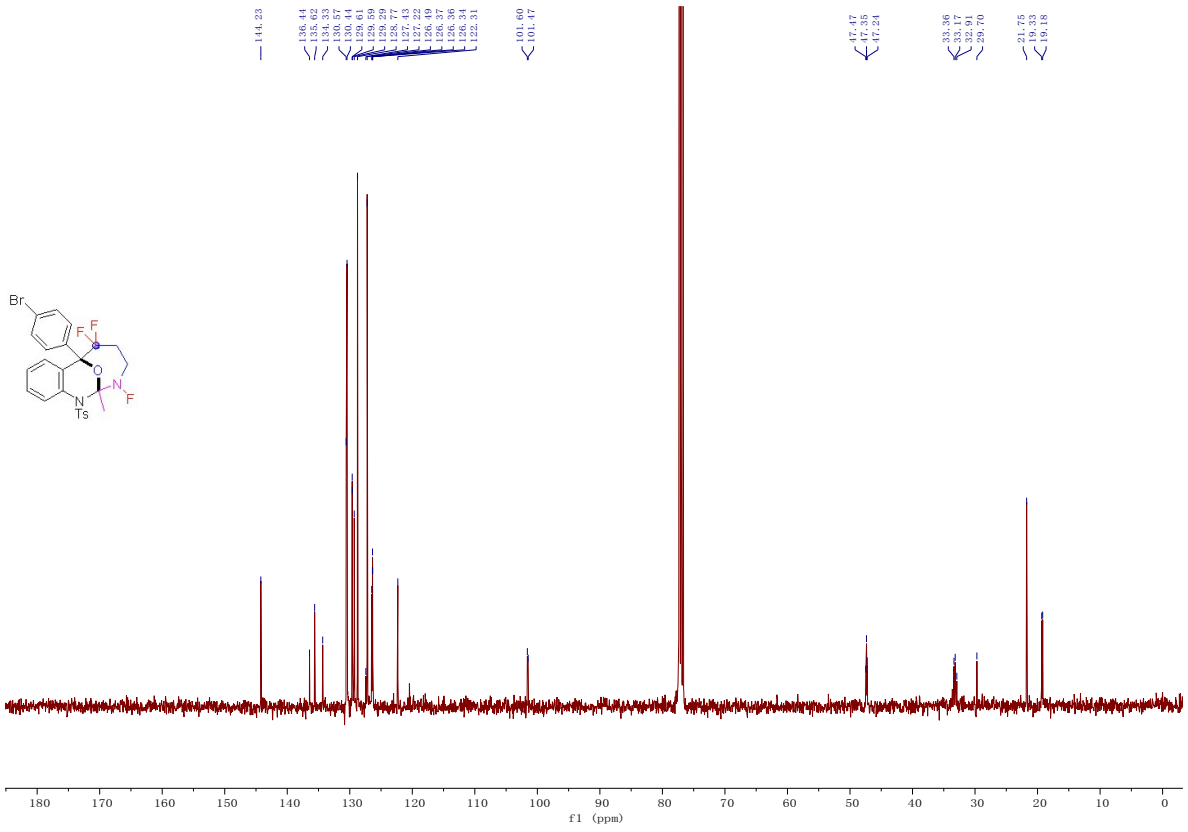

fx-5-93-b-1-h.1.fid
Br
N
Ts
F
f1 (ppm)
Br
N
Ts
F
f1 (ppm)

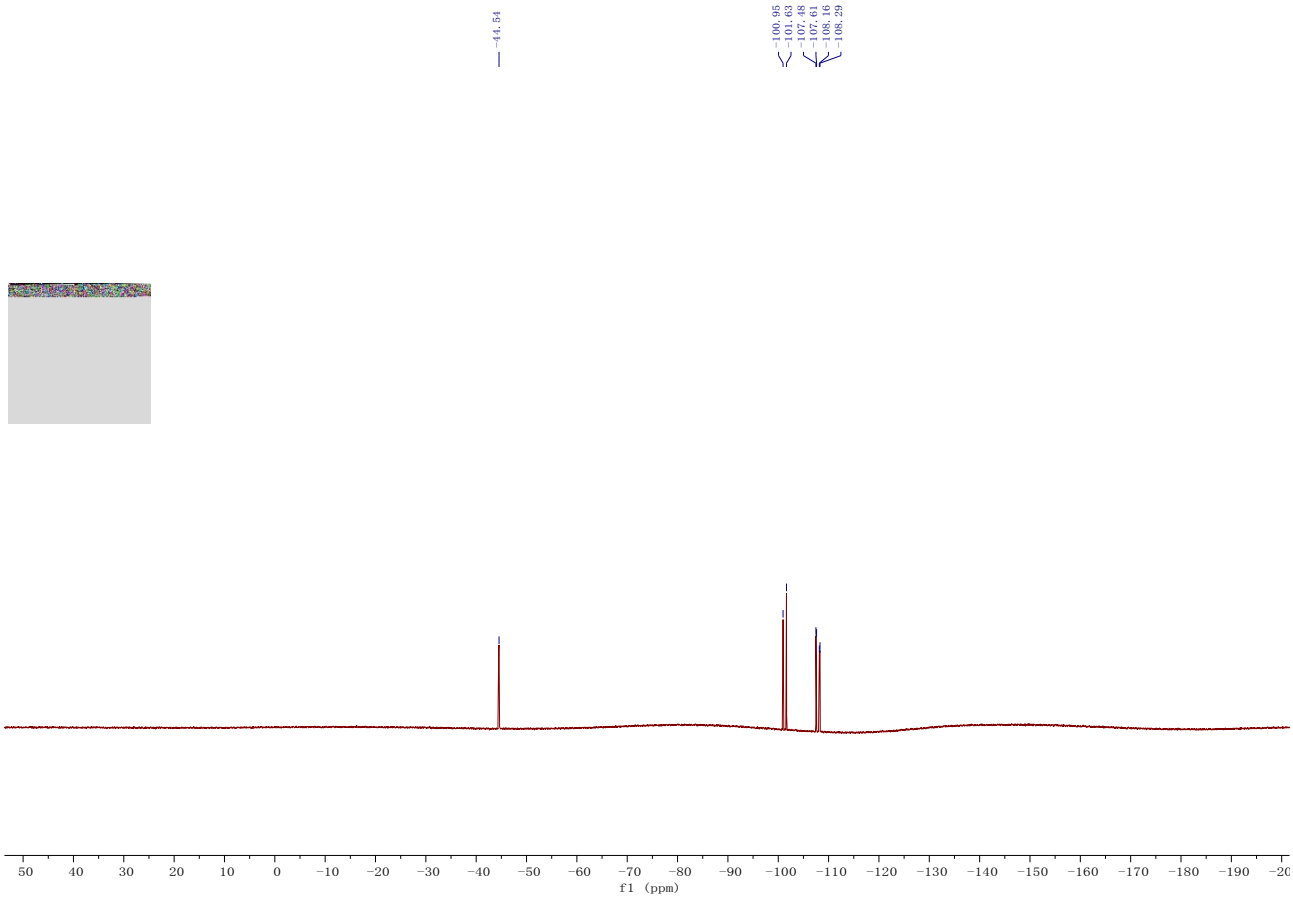


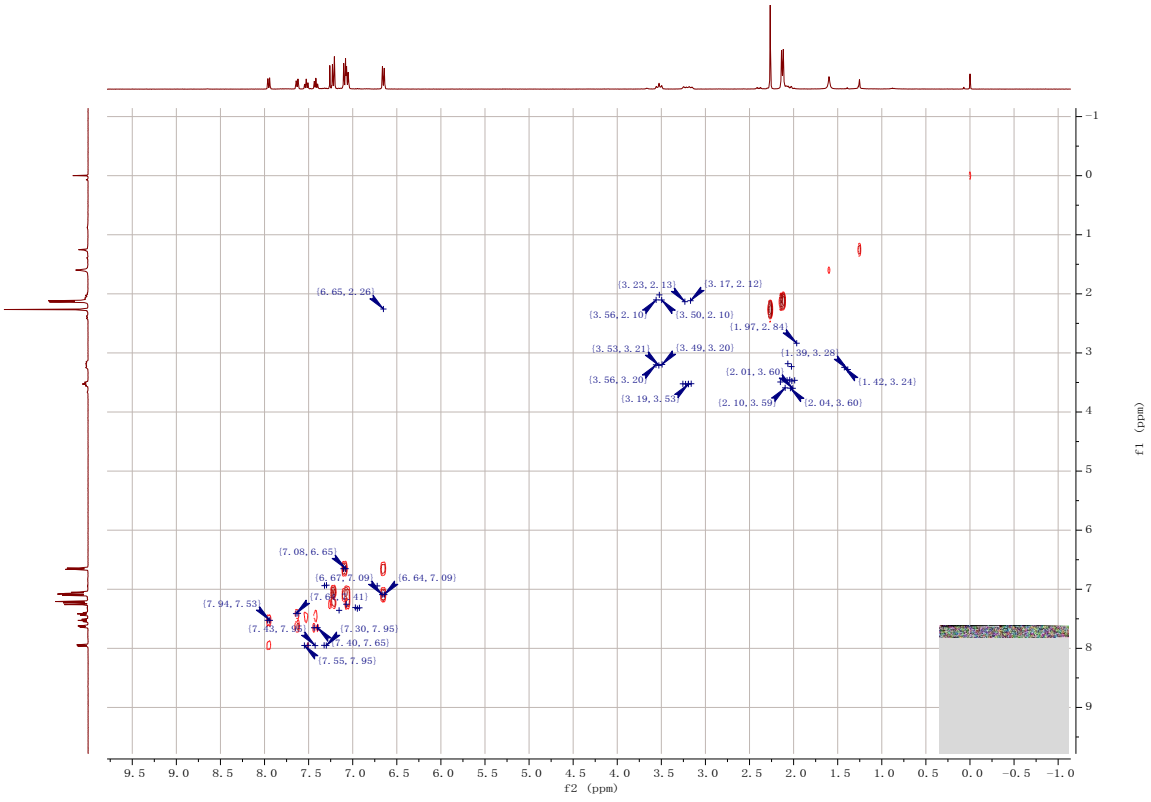


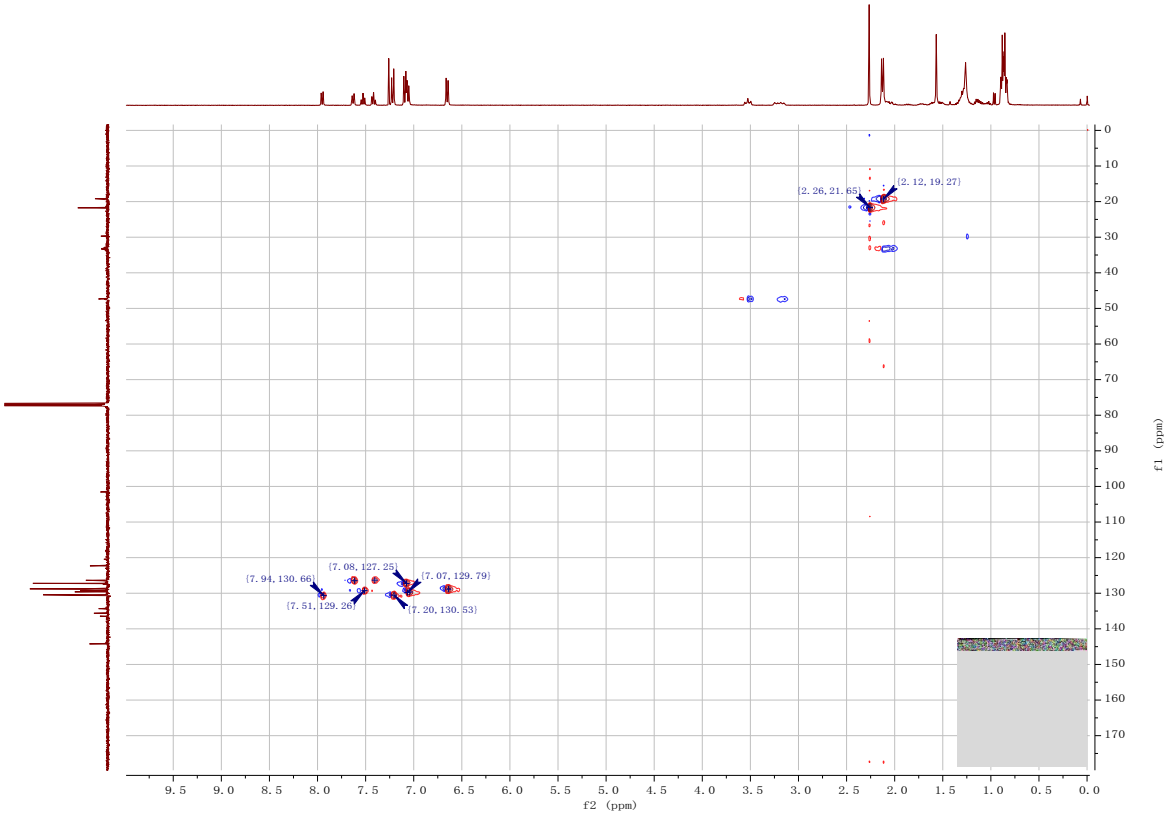
Compound 4ac: A white solid (9.8 mg, 9%); M.p. 172-173 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.90 – 2.07 (m, 1H), 2.07 (dt, *J* = 7.3, 5.4 Hz, 1H), 2.13 (d, *J* = 7.7 Hz, 3H), 2.26 (s, 3H), 3.20 (dd, *J* = 25.2, 12.8 Hz, 1H), 3.53 (t, *J* = 12.1 Hz, 1H), 6.60 – 6.75 (m, 2H), 6.98 – 7.14 (m, 4H), 7.15 – 7.25 (m, 2H), 7.42 (ddd, *J* = 7.7, 7.7, 1.4 Hz, 1H), 7.53 (ddd, *J* = 8.2, 7.8, 1.5 Hz, 1H), 7.63 (ddd, *J* = 8.0, 1.9, 1.9 Hz, 1H), 7.95 (dd, *J* = 8.2, 1.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 19.3 (d, *J* = 15.4 Hz), 21.7, 29.7, 33.3 (td, *J* = 26.3, 20.1 Hz), 47.4 (t, *J* = 11.6 Hz), 101.5 (d, *J* = 13.2 Hz), 122.3, 126.3 – 126.4 (m), 126.5, 127.2, 127.3 – 127.4 (m), 128.8, 129.3, 129.6 (d, *J* = 2.2 Hz), 130.4, 130.6, 134.3, 135.6, 136.4, 144.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -107.89 (d, *J* = 206.9 Hz, 1F), -101.29 (d, *J* = 255.2 Hz, 1F), -44.54 (s, 1F). IR (neat) ν 2959, 2923, 2854, 1600, 1490, 1446, 1396, 1363, 1176, 1108, 1091, 1066, 1007, 983, 807, 764, 745, 680, 656 cm^{-1}. HRMS (ESI) Calcd. for $C_{25}H_{23}BrF_3N_2O_3S$ requires (M^++H): 567.0559, Found: 567.0556.


Br
F
F
O
N
F
Ts
f1 (ppm)


Br
F
F
O
N
F
Ts
f1 (ppm)

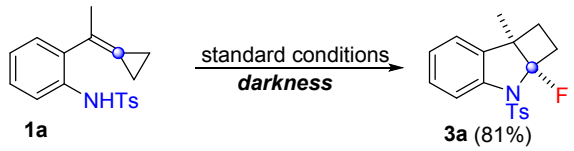

44.54
100.95
101.63
107.48
107.61
108.16
108.29
f1 (ppm)


{6.65, 2.26}
{3.23, 2.13}
{3.17, 2.12}
{3.56, 2.10}
{3.50, 2.10}
{1.97, 2.84}
{3.53, 3.21}
{3.49, 3.20}
{1.39, 3.28}
{3.56, 3.20}
{2.01, 3.60}
{1.42, 3.24}
{3.19, 3.53}
{2.10, 3.59}
{2.04, 3.60}
{7.08, 6.65}
{6.67, 7.09}
{6.64, 7.09}
{7.94, 7.53}
{7.30, 7.95}
{7.40, 7.65}
{7.55, 7.95}
f2 (ppm)
f1 (ppm)


{2.26, 21.65}
{2.12, 19.27}
{7.08, 127.25}
{7.94, 130.66}
{7.07, 129.79}
{7.51, 129.26}
{7.20, 130.53}
f2 (ppm)
f1 (ppm)

Control experiments

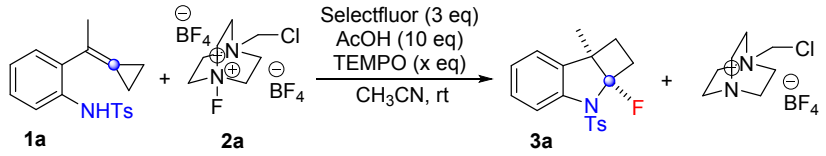
1. Darkness conditions:



1a **3a** (81%)

A solution of **1a** (62.6 mg, 0.2 mmol, 1.0 equiv) and **2a** (212.6 mg, 0.6 mmol, 3.0 equiv) in 2 mL CH_3CN at a vial encapsulated completely by aluminum foil, AcOH (0.1 mL, 2.0 mmol, 10 equiv) was added by a syringe, and the mixture was stirred at room temperature for 6 h. The reaction mixture was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (PE/EA = 10:1) to afford the product **3a** (62.6 mg) in the isolated yield of 81%.

2. Radical trapping experiments:

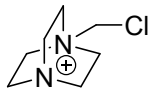


1a **2a** **3a**

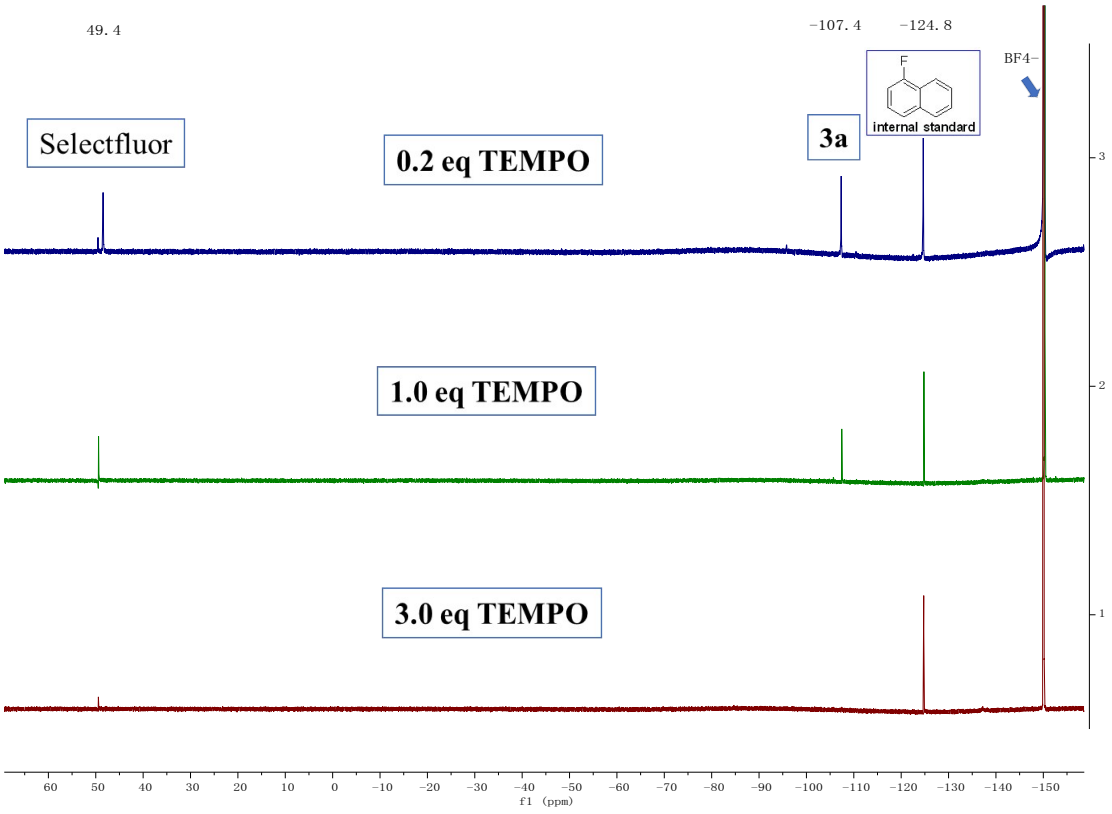
entry	x	**3a** (%)	**1a** (%)
A	0.2	77	15
B	1.0	53	32
C	3.0	0	95

A solution of **1a** (62.6 mg, 0.2 mmol, 1.0 equiv), **2a** (212.6 mg, 0.6 mmol, 3.0 equiv) and TEMPO (x equiv) (for entry A, 6.3 mg, 0.04 mmol, 0.2 equiv) (for entry B, 31.3 mg, 0.2 mmol, 1.0 equiv) (for entry C, 93.8 mg, 0.6 mmol, 3.0 equiv) in 2 mL CH_3CN at three vials, AcOH (0.1 mL, 2.0 mmol, 10 equiv) was added by a syringe, and the mixture was stirred at rt for 6 h. The reaction mixture was concentrated, and the residue was purified by a flash chromatograph on silica gel using PE/EA (10:1) as the eluent to yield the product **3a** in 77% yield along with the recovery of **1a** in 15% for entry A, and **3a** in 55% yield along with the recovery of **1a** in 32% for entry B, and the recovery of **1a** in 95% without product **3a** for entry C. In addition, the ^{19}F NMR signal of Selectfluor disappeared in entry C.

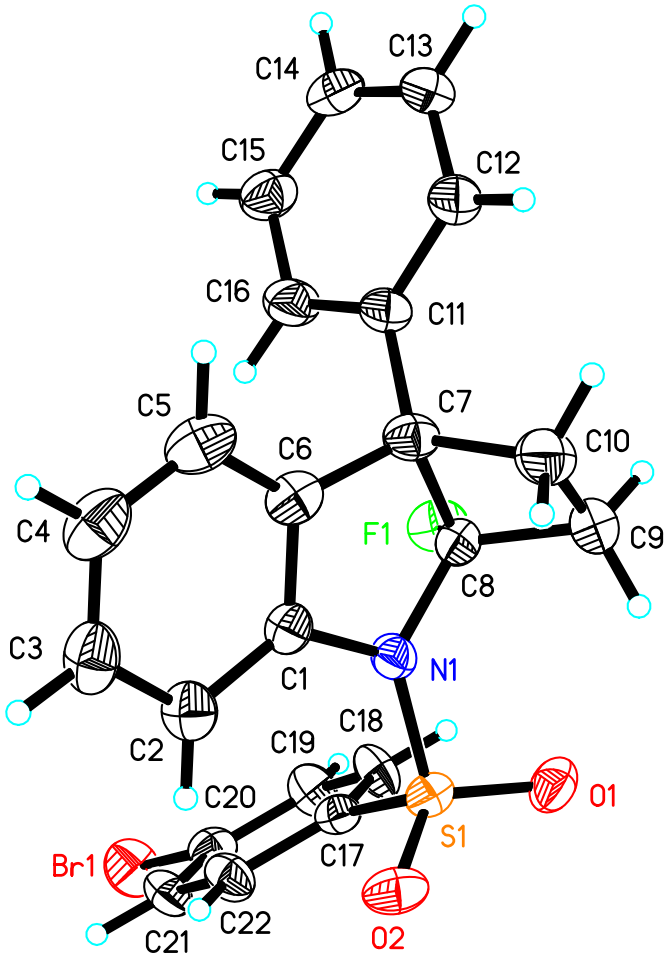
The decomposition of Selectfluor for the formation of compound **5a** has been confirmed by HRMS.



Compound **5a**: Its structure has been confirmed by HRMS (ESI) (Calcd. for $C_7H_{14}ClN_2$ requires (M^+): 161.0840, Found: 161.0840).

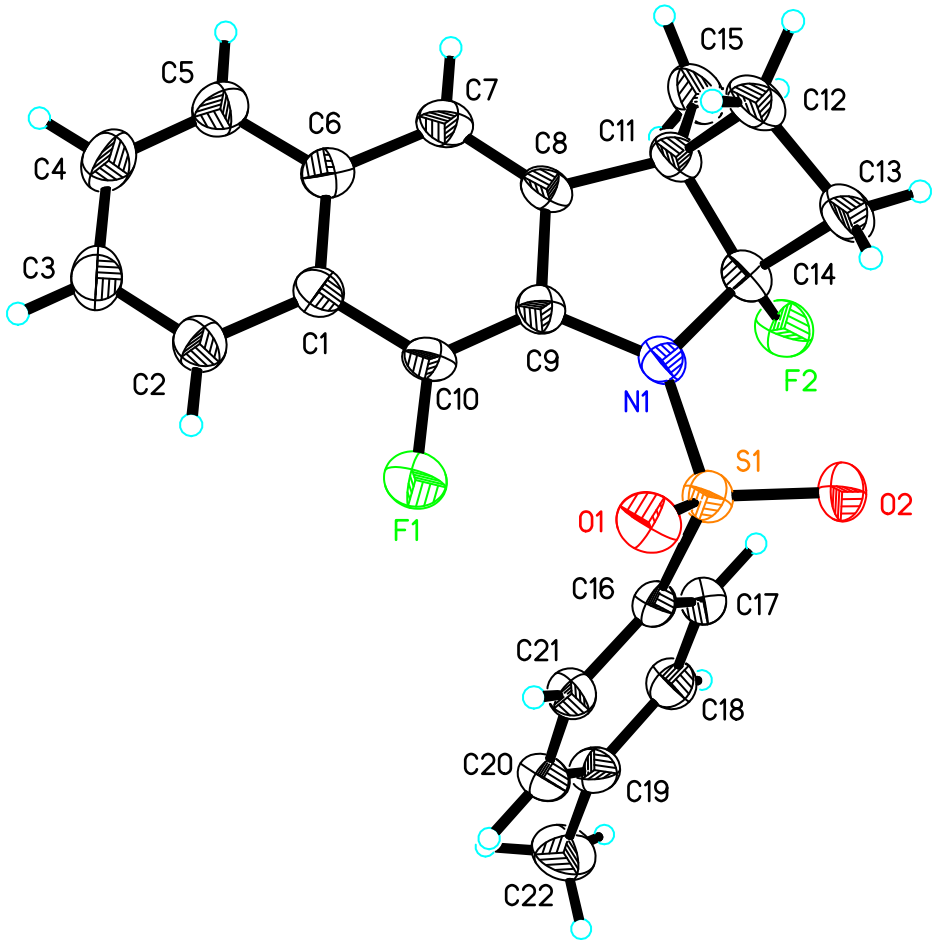


X-ray Crystal Data of Compound **3t**



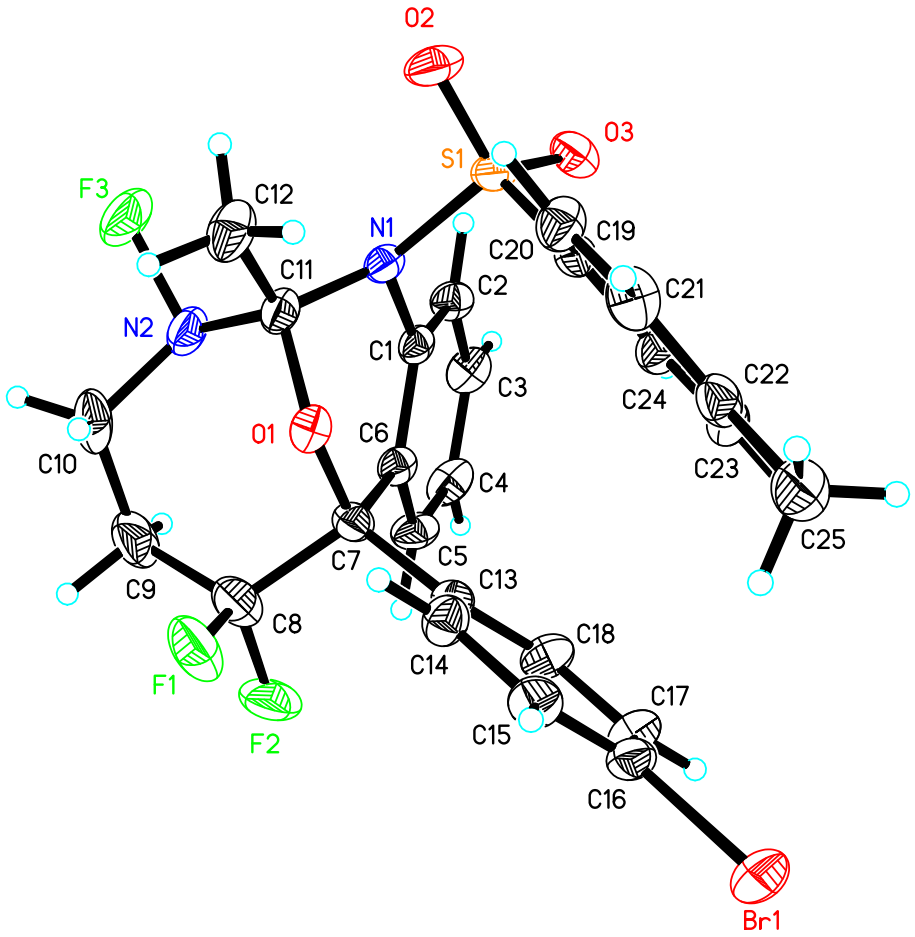
The crystal data of **3t** have been deposited in CCDC with number 1474587. Empirical Formula: $C_{22}H_{17}BrFNO_2S$; Formula Weight: 458.33; Crystal Dimensions: 0.210 x 0.170 x 0.130 mm^3; Crystal System: Orthorhombic; Lattice Parameters: a = 10.0581(11)Å, b = 11.3410(12)Å, c = 17.3605(19)Å, α = 90°, β = 90°, γ = 90°, V = 1980.3(4)$Å^3$; Space group: 21 21 21; Z = 4; D_{calc} = 1.537 g/cm^3; F_{000} = 928; Final R indices [I>2sigma(I)] R1 = 0.0399, wR2 = 0.0839.

X-ray Crystal Data of Compound **3w'**



The crystal data of **3w'** have been deposited in CCDC with number 1838252. Empirical Formula: $C_{22}H_{19}F_2NO_2S$; Formula Weight: 399.44; Crystal Dimensions: 0.200 x 0.160 x 0.130 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 14.943(3)Å, b = 11.511(2)Å, c = 11.392(2)Å, $\alpha = 90^o$, $\beta = 98.266(6)°$, $\gamma = 90^o$, V = 1939.0(6)$Å^3$; Space group: P 21/c; Z = 4; D_{calc} = 1.368 g/cm^3; F_{000} = 832; Final R indices [I>2sigma(I)] R1 = 0.0651, wR2 = 0.1539.

X-ray Crystal Data of Compound **4ac**



The crystal data of **4ac** have been deposited in CCDC with number 1504263. Empirical formula: $C_{25}H_{22}BrF_3N_2O_3S$, Formula weight: 567.41, Crystal system: Monoclinic, Space group: P 21/n, Unit cell dimensions: a = 14.399(2) Å, α = 90°; b = 9.6415(16) Å, β = 93.004(4)°; c = 17.024(3) Å, γ = 90°. Volume: 2360.2(7) $Å^3$, Z = 4, Density (calculated): 1.597 Mg/m^3, F(000) = 1152, Crystal size: 0.200 x 0.150 x 0.100 mm^3, Final R indices [I>2sigma(I)]: R1 = 0.0428, wR2 = 0.1007.

References

1 J. Malmquist and P. Ström, *J. Label Compd. Radiopharm* 2012, **55**, 387.

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3 (a) J. A. Stafford and J. E. McMurry, *Tetrahedron Lett.,* 1988, **29**, 2531; (b) K. Utimoto, M. Tamura and K. Sisido, *Tetrahedron*, 1973, **29**, 1169; (c) Y. Yan and Z. Wang, *Chem. Commun.*, 2011, **47**, 9513.

4 (a) K. Chen, Z. Zhang, Y. Wei and M. Shi, *Chem. Commun.*, 2012, **48**, 7696; (b) K. Chen, R. Sun, Q. Xu, Y. Wei and M. Shi, *Org. Biomol. Chem.*, 2013, **11**, 3949.