

Supporting Information

Lewis Base-catalyzed Trifluoromethylsulfonylation of Alcohols and Phenols: Modular Synthesis of Trifluoromethanesulfinate Esters

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I. General information

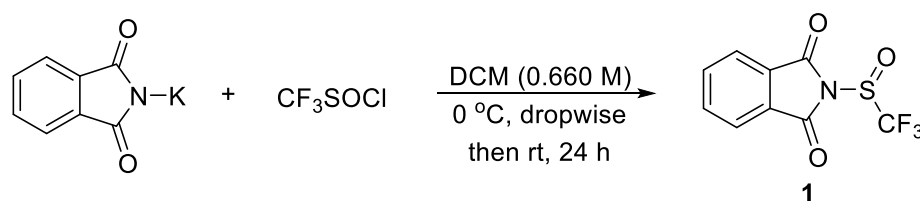
General procedures. General Information Unless specifically stated, all reagents were commercially obtained and where appropriate, purified prior to use. For example, dichloromethane (DCM) was freshly distilled from CaH₂; toluene, ether (Et₂O) was dried and distilled from metal sodium and benzophenone. Other commercially available reagents and solvents were used directly without purification. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash column chromatography was performed over silica (200 - 300 mesh). ¹H, ¹³C, ¹⁹F NMR spectra were recorded on a Bruker 400 MHz or 500 MHz spectrometer in CDCl₃ or THF-*d*₈ or CD₃COCD₃ or CD₃OD or C₆D₆. Multiplicities were given as: s (singlet); d (doublet); dd (doublets of doublet); t (triplet); q (quartet); td (triplet of doublets); tt (triplet of triplets) ddd (doublet of doublet of doublets) or m (multiplets). High resolution mass spectra (HRMS) of the products were obtained on a Bruker Daltonics micro TOF-spectrometer and on a Agilent Technologies micro Q-TOF-spectrometer.

Reagents. The following chemicals were used as received: 1-Adamantanol (Energy-Chemical), Benzaldehyde (Energy-Chemical), 1-Boc-3-azetidinone (Energy-Chemical), 3-Bromobenzaldehyde (Macklin), 1,4-Benzenedimethanol (Energy-Chemical), 3-Bromobenzyl alcohol (leyan.com), 4-Bromobenzyl Alcohol (Energy-Chemical), 4-Bromobenzaldehyde (leyan.com), 6-Bromo-1-hexanol (Energy-Chemical), 4-Bromo-1-indanone (Energy-Chemical), 5-Bromo-1-indanone (leyan.com), 4-Chlorobenzaldehyde (leyan.com), 4-Chlorobenzyl alcohol (Energy-Chemical), 6-Chloro-1-hexanol (Energy-Chemical), 5-Chloro-1-indanone (leyan.com), 6-Chloro-1-hexanol (Energy-Chemical), Cholesterol (Energy-Chemical), β-Citronellol (Adamas), 4-Cyanobenzaldehyde (leyan.com), Dehydroepiandrosterone (Macklin), Diacetone-beta-D-fructose (Adamas), Diethyl (ethoxyacetyl)phosphonate (Adamas), 3,5-Difluorobenzaldehyde (leyan.com), Diisobutylaluminiumhydrid (Energy-Chemical), 3,3-Dimethyl-1-indanone (leyan.com), 1,4-Dioxaspiro[4.5]decan-8-one (Energy-Chemical), 1,4-Dioxaspiro[4.5]decan-8-ol (Energy-Chemical), 1-(Diphenylmethyl)-3-hydroxyazetidine (Energy-Chemical), DL-menthol (Energy-Chemical), 2-Ethyl-1-indanone (leyan.com), Ethylmagnesium bromide (Energy-Chemical), Estrone (Adamas), 4-Fluorobenzaldehyde (leyan.com), 4-Fluorobenzyl alcohol (leyan.com), 5-Fluoro-1-indanone (leyan.com), Hept-6-yn-1-ol

(Energy-Chemical), 5-(2-Hydroxyethyl)-4-methylthiazole (leyan.com), Hydrogen peroxide (aladdin), 4-Hydroxymethylbiphenyl (Energy-Chemical), 1-Indanone (Energy-Chemical), 2-Indanone (leyan.com), 2-Indanol (Energy-Chemical), 4-Iodobenzyl Alcohol (leyan.com), 4-Iodobenzaldehyde (Adamas), Iodomethane (Energy-Chemical), Isopropenylmagnesium bromide (Energy-Chemical), Methyl 4-Formylbenzoate (Energy-Chemical), 2-Methylindan-1-one (Energy-Chemical), Methyl 4-(hydroxymethyl)benzoate (leyan.com), 5-Methyl-1-indanone (Energy-Chemical), 4-(Methylthio)benzaldehyde (leyan.com), 2-Naphthaldehyde (Adamas), 2-Nitrobenzaldehyde (Energy-Chemical), 3-Nitrobenzaldehyde (Energy-Chemical), 4-Nitrobenzaldehyde (Adamas), 4-Nitrobenzyl alcohol (Energy-Chemical), *N*-BOC-4-Hydroxypiperidine (Energy-Chemical), *N,N*-Diethylethanamin (Energy-Chemical), Palladium (Energy-Chemical), Potassium phthalimide (Energy-Chemical), *p*-phthalaldehyde (leyan.com), 3-Pyridinecarboxaldehyde (Energy-Chemical), Quinoline-3-carboxaldehyde (leyan.com), Ruthenium(III) chloride hydrate (Energy-Chemical), Sodium hydride (Energy-Chemical), Sodium periodate (Energy-Chemical), Sodium tungstate (Adamas), Stigmasterol (Energy-Chemical), *tert*-Butyl 2-oxo-7-azaspiro[3.5]nonane-7-carboxylate (Energy-Chemical), *tert*-Butyl *N*-(4-hydroxycyclohexyl)carbamate (leyan.com), 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (leyan.com), 3-Thiophenecarboxaldehyde (Energy-Chemical), 2-Tolualdehyde (Energy-Chemical), Trifluoromethanesulfinyl chloride (Energy-Chemical), 3-(Trifluoromethyl)benzaldehyde (Adamas), Tryptophol (leyan.com), 4-(Trifluoromethyl)benzaldehyde (Energy-Chemical), 4-(Trifluoromethyl)benzyl alcohol (Energy-Chemical), (Triphenylphosphoranylidene)acetaldehyde (leyan.com), Tryptophol (Energy-Chemical).

II. Synthesis of the starting materials

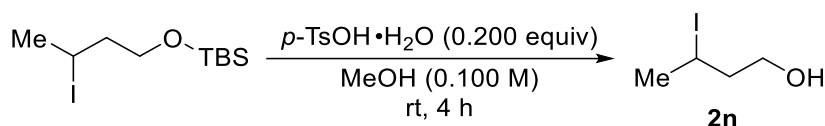
1. Synthesis of 2-((Trifluoromethyl)sulfinyl)isoindoline-1,3-dione **1**



A 120 °C oven-dried 200-mL glass, equipped with a stir bar, was charged with potassium

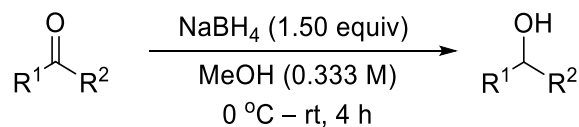
phthalimide (6.11 g, 33.0 mmol, 1.00 equiv), The mixture was evacuated and backfilled with nitrogen for three times. Then dry DCM (45.0 mL) was added under N₂ atmosphere. The mixture was cooled to 0 °C. A solution of trifluoromethanesulfinyl chloride (5.00 g, 33.0 mmol, 1.00 equiv) in DCM (5.00 mL) was added dropwise under N₂ atmosphere. Then the mixture was slowly warmed up to room temperature and stirred at room temperature for 24 h. The reaction mixture was filtered through a short pad of Celite and concentrated in vacuo. By repeated recrystallization from toluene at –20 °C. The product was white solid (4.46 g, 16.9 mmol, 51.4% yield). Spectra were consistent with literature data¹. **In particular, the purity of the substance will have an important effect on the efficiency of the subsequent reaction.**

2. Synthesis of alcohol 2n



A 120 °C oven-dried 100-mL round-bottom flask, equipped with a stir bar, was charged with 2-iodo-4-(*tert*-butyldimethylsilyloxy)butane (1.50 g, 4.77 mmol, 1.00 equiv) and MeOH (48.0 mL) were added under nitrogen. Then *p*-toluenesulfonic acid monohydrate (182 mg, 0.950 mmol, 0.2 equiv) was added to the mixture and the mixture was allowed to stir at room temperature for 4 h. After the completion of reaction, a saturated aqueous solution of NaHCO₃ was added and the mixture was extracted with Et₂O (50.0 mL × 3). The combined organic layers were washed with brine (10.0 mL), dried over Na₂SO₄ and filtrated. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography to provide the desired products as a colorless liquid (712 mg, 3.56 mmol, 74.6% yield). Spectra were consistent with literature data².

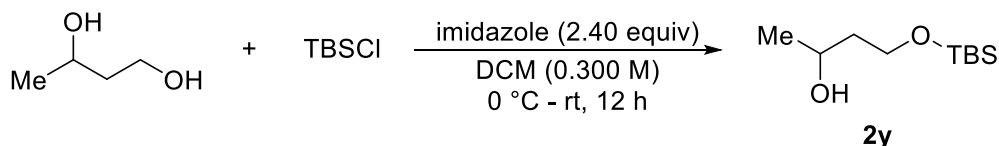
3. General Method A: Synthesis of alcohol 2r, 2v



A 120 °C oven-dried 100-mL glass, equipped with a stir bar, was charged with ketone (5.00 mmol, 1.00 equiv). The mixture was evacuated and backfilled with nitrogen for three

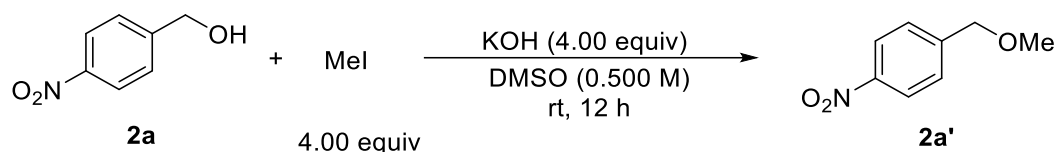
times. Then dry MeOH (15.0 mL) was added under N₂ atmosphere. The mixture was cooled to 0 °C. NaBH₄ (283.7 mg, 7.50 mmol, 1.50 equiv) was added under N₂ atmosphere. The mixture was warmed up to room temperature and stirred at room temperature for 1 h. After the completion of the reaction, the MeOH was removed by rotary evaporation, and H₂O (30.0 mL) was added, the aqueous solution was washed with EtOAc (20.0 mL × 3). The combined organic layers were washed with brine (30.0 mL × 3), dried over Na₂SO₄ and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography³. Compound **2r**: (prepared on 10.0 mmol scale, a colorless liquid, 0.961 g, 7.16 mmol, 71.6% yield), spectra were consistent with literature data⁴. Compound **2v**: a colorless liquid (0.897 g, 4.62 mmol, 92.3% yield), spectra were consistent with literature data⁵.

4. General Method B: Synthesis of alcohol **2y**



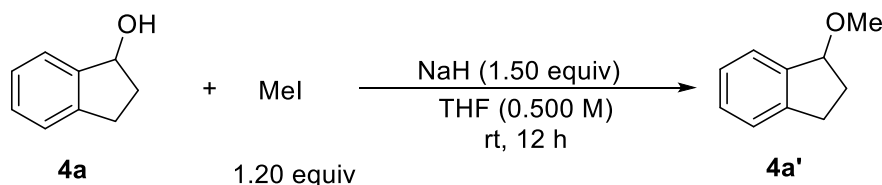
A 120 °C oven-dried 100-mL glass, equipped with a stir bar, and backfilled with nitrogen for three times. Then dry DCM (40.0 mL), imidazole (2.70 g, 39.6 mmol, 2.40 equiv) and butane-1,3-diol (1.48 g, 1.50 mL, 16.5 mmol, 1.00 equiv) were added under N₂ atmosphere. Then TBSCl (2.98 g, 19.8 mmol, 1.20 equiv) in dry DCM (15.0 mL) was added to the mixture under N₂ atmosphere at 0 °C. Then mixture was allowed to stirred at room temperature for 12 h. After the completion of the reaction, brine (30.0 mL × 3) was added to the mixture, and the aqueous phase was extracted with EtOAc (30.0 mL × 3). The combined organic phases was dried over Na₂SO₄ and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography. The product was isolated as a colorless liquid (2.94 g, 14.4 mmol, 87.2% yield). Spectra were consistent with literature data².

5. Synthesis of 1-(Methoxymethyl)-4-nitrobenzene **2a'**



A 120 °C oven-dried 100-mL glass, equipped with a stir bar, was charged with KOH (1.12 g, 20.0 mmol, 4.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then DMSO (10.0 mL) was added under N₂ atmosphere. Then a solution of **2a** (0.766 g, 5.00 mmol, 1.00 equiv) and MeI (2.84 g, 20.0 mmol, 4.00 equiv) in DMSO (2.50 mL) was added dropwise under N₂ atmosphere. The mixture was stirred at room temperature for 12 h. The reaction mixture was extracted with EtOAc (20.0 mL × 3). The combined organic layers were washed with 10% NaHSO₃ (30.0 mL) and water (20.0 mL), dried over Na₂SO₄ and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography. The product was yellow oil (0.558 g, 3.34 mmol, 66.7% yield). Spectra were consistent with literature data⁶.

6. Synthesis of 1-Methoxy-2,3-dihydro-1*H*-indene **6a'**

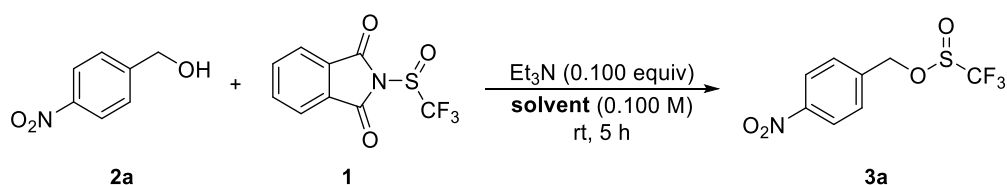


A 120 °C oven-dried 100-mL glass, equipped with a stir bar, was charged with NaH (60% disp. in mineral, 0.180 g, 4.50 mmol, 1.50 equiv) and **6a** (0.403 g, 3.00 mmol, 1.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then MeI (0.511 g, 3.60 mmol, 1.20 equiv) was added dropwise under N₂ atmosphere. The mixture was stirred at room temperature for 12 h. The reaction mixture was extracted with EtOAc (20.0 mL × 3). The combined organic layers were washed with brine (20.0 mL), dried over Na₂SO₄ and filtered. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography. The product was isolated as a colorless oil (0.258 g, 1.74 mmol, 58.0% yield). Spectra were consistent with literature data⁷.

III. Optimization of the reaction conditions

1. Optimization of reaction between 2a with reagent 1

Table S1. Evaluation of different solvents

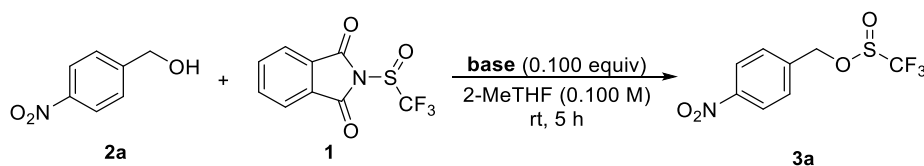


Entry	solvent	Yield of 3a (%) ^a
1	2-MeTHF	> 99
2	DCM	> 99
3	EtOAc	> 99
4	Ether	> 99
5	DMF	> 99
6	MeOH	trace
7	MeCN	> 99
8	NMP	53
9	DMSO	17
10	1,4-Dioxane	86

Reaction conditions: 2a (0.100 mmol), 1 (0.120 mmol), Et_3N (0.100 equiv), solvent (1.00 mL) at rt for 5 h.

^aYield was determined by ^{19}F NMR spectroscopy in the presence of PhCF_3 as an internal standard.

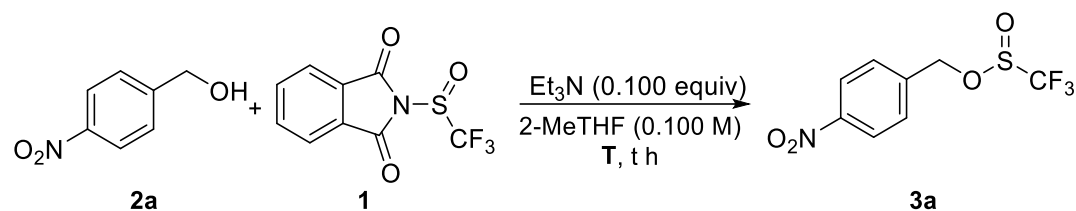
Table S2. Evaluation of different bases



Entry	base	Yield of 3a (%) ^a
1	Et_3N	> 99
2	none	no reaction
3	Cs_2CO_3	39
4	K_2CO_3	38
5	CsF	17
6	DMAP	> 99
7	K_3PO_4	trace
8	NaOAc	trace
9	DBU	> 99
10	$^t\text{BuOK}$	< 10
11	pyridine	75

Reaction conditions: 2a (0.100 mmol), 1 (0.120 mmol), base (0.0100 mmol), 2-MeTHF (1.00 mL) at rt for 5 h.

^aYield was determined by ^{19}F NMR spectroscopy in the presence of PhCF_3 as an internal standard.

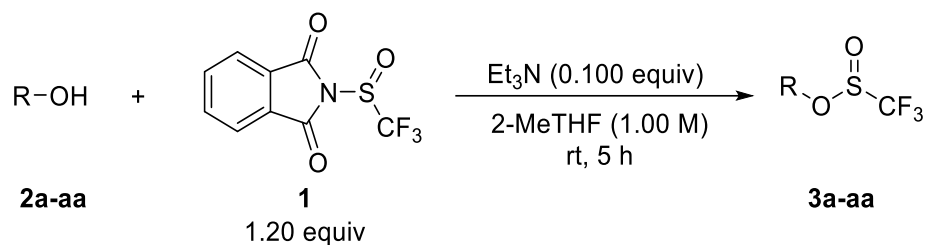
Table S3. Evaluation of different temperature and time

Entry	T (°C)	t (h)	Yield of 3a (%) ^a
1	60	5	76
2	rt	5	> 99
3	-40	5	98
4	rt	1	42
5	rt	3	94

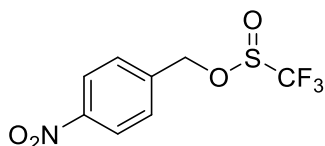
Reaction conditions: **2a** (0.100 mmol), **1** (0.120 mmol), Et_3N (0.0100 mmol), 2-MeTHF (1.00 mL) at T °C for t h. ^aYield was determined by ^{19}F NMR spectroscopy in the presence of PhCF_3 as an internal standard.

IV. Substrate scope

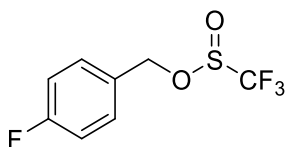
1. General Method C:



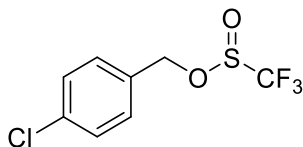
A 120 °C oven-dried 25-mL glass schlenk, equipped with a stir bar, was charged with 2-((trifluoromethyl)sulfonyl)isoindoline-1,3-dione (0.360 mmol, 1.20 equiv, 94.8 mg). The mixture was evacuated and backfilled with nitrogen for three times. Then dry 2-MeTHF (3.00 mL, 0.100 M), alcohol or benzyl alcohol (0.300 mmol, 1.00 equiv) and Et_3N (0.0300 mmol, 0.100 equiv, 3.00 mg) were added under N_2 atmosphere. The mixture was allowed to stir for 5 h at room temperature. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography.



4-Nitrobenzyl trifluoromethanesulfinate 3a: Prepared according to **General Method C** (Eluent: 100:1 to 5:1 petroleum ether:ethyl acetate) and the title compound was isolated as a colorless oil (60.1 mg, 0.223 mmol, 74.3% yield). **¹H NMR** (400 MHz, CDCl₃) δ 8.26 (d, $J = 8.7$ Hz, 2H), 7.57 (d, $J = 8.7$ Hz, 2H), 5.48 (1H, d, $J = 12.5$ Hz), 5.18 (1H, d, $J = 12.4$ Hz); **¹⁹F NMR** (471 MHz, CDCl₃) δ -77.8; **¹³C NMR** (101 MHz, CDCl₃) δ 148.4, 140.9, 129.1, 124.2, 123.0 (q, $J_{C-F} = 340.8$ Hz), 67.4. Spectra were consistent with literature data⁸.

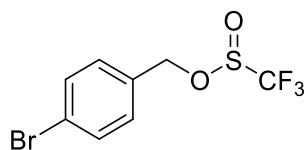


4-Fluorobenzyl trifluoromethanesulfinate 3b: Prepared according to **General Method C** (Eluent: 100:1 to 20:1 petroleum ether:ethyl acetate) and the title compound was isolated as a colorless oil (71.9 mg, 0.297 mmol, 99.0% yield). **IR** (thin film) 1605 (w), 1513 (m), 1185 (s), 1125 (s), 888 (m), 835 (m), 748 (m) cm⁻¹; **¹H NMR** (400 MHz, CDCl₃) δ 7.38 (2H, dd, $J = 3.3, 5.3$ Hz), 7.10 (2H, dd, $J = 8.6, 8.6$ Hz), 5.35 (1H, d, $J = 11.4$ Hz), 5.06 (1H, d, $J = 11.4$ Hz); **¹⁹F NMR** (471 MHz, CDCl₃) δ -78.0 (3F, s), -111.3 – -111.4 (1F, m); **¹³C NMR** (101 MHz, CDCl₃) δ 163.5 (d, $J_{C-F} = 249.9$ Hz), 131.2 (d, $J_{C-F} = 8.7$ Hz), 129.7 (d, $J_{C-F} = 3.1$ Hz), 123.1 (q, $J_{C-F} = 340.7$ Hz), 116.2 (d, $J_{C-F} = 22.0$ Hz), 69.0; **HRMS** (ESI) m/z : [M+H]⁺ Calcd for C₈H₇F₄O₂S 243.0103; Found 243.0117.

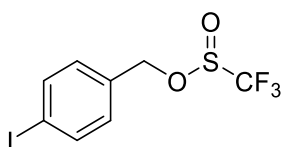


4-Chlorobenzyl trifluoromethanesulfinate 3c: Prepared according to **General Method C** (Eluent: 100:1 to 20:1 petroleum ether:ethyl acetate) and the title compound was isolated as a colorless oil (54.2 mg, 0.210 mmol, 70.0% yield). **¹H NMR** (400 MHz, CDCl₃) δ 7.38 (2H, d, $J = 8.4$ Hz), 7.32 (2H, d, $J = 8.4$ Hz), 5.34 (1H, d, $J = 11.6$ Hz), 5.05 (1H, d, $J = 11.6$ Hz); **¹⁹F NMR** (471 MHz, CDCl₃) δ -78.0; **¹³C NMR** (101 MHz, CDCl₃) δ 135.6,

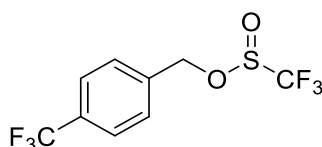
132.3, 130.3, 129.3, 123.1 (q, $J_{C-F} = 340.3$ Hz), 68.8. Spectra were consistent with literature data⁸.



4-Bromobenzyl trifluoromethanesulfinate 3d: Prepared according to **General Method C** (Eluent: 100:1 to 20:1 petroleum ether:ethyl acetate) and the title compound was isolated as a colorless oil (87.3 mg, 0.288 mmol, 96.0% yield). **¹H NMR** (400 MHz, CDCl₃) δ 7.45 (2H, d, $J = 8.4$ Hz), 7.17 (2H, d, $J = 8.4$ Hz), 5.23 (1H, d, $J = 11.6$ Hz), 4.95 (1H, d, $J = 11.6$ Hz); **¹⁹F NMR** (471 MHz, CDCl₃) δ -78.0; **¹³C NMR** (101 MHz, CDCl₃) δ 132.7, 132.2, 130.5, 123.8, 123.1 (q, $J_{C-F} = 340.2$ Hz), 68.8. Spectra were consistent with literature data⁸.

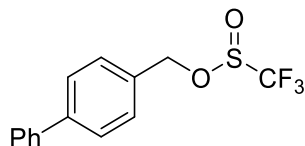


4-Iodobenzyl trifluoromethanesulfinate 3e: Prepared according to **General Method C** (Eluent: 100:1 to 20:1 petroleum ether:ethyl acetate) and the title compound was isolated as a colorless oil (101.7 mg, 0.290 mmol, 96.7% yield). **IR** (thin film) 1486 (w), 1182 (s), 1124 (s), 1059 (w), 1009 (w), 890 (m), 843 (m), 797 (m) cm⁻¹; **¹H NMR** (400 MHz, CDCl₃) δ 7.74 (2H, d, $J = 8.4$ Hz), 7.12 (2H, d, $J = 8.4$ Hz), 5.31 (1H, d, $J = 11.6$ Hz), 5.02 (1H, d, $J = 11.6$ Hz); **¹⁹F NMR** (471 MHz, CDCl₃) δ -78.0; **¹³C NMR** (101 MHz, CDCl₃) δ 138.2, 133.3, 130.6, 123.0 (q, $J_{C-F} = 340.3$ Hz), 95.6, 68.9; **HRMS** (ESI) m/z : [M+Na]⁺ Calcd for C₈H₆F₃INaO₂S 372.8978; Found 372.8979.

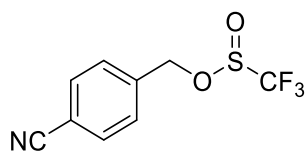


4-(Trifluoromethyl)benzyl trifluoromethanesulfinate 3f: Prepared according to **General Method C** (Eluent: 100:1 to 20:1 petroleum ether:ethyl acetate) and the title compound was isolated as a colorless oil (86.8 mg, 0.297 mmol, 99.0% yield). **IR** (thin film) 1324 (s), 1167 (s), 1121 (s), 1066 (s), 904 (m), 822 (m), 779 (m) cm⁻¹; **¹H NMR** (400 MHz, CDCl₃) δ 7.67 (2H, d, $J = 8.1$ Hz), 7.51 (2H, d, $J = 8.1$ Hz), 5.43 (1H, d, $J =$

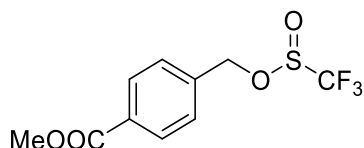
12.0 Hz), 5.14 (1H, d, $J = 12.0$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -62.9 (3F, s), -78.0 (3F, s); ^{13}C NMR (125 MHz, CDCl_3) δ 137.8, 131.7 (q, $J_{\text{C-F}} = 32.5$ Hz), 128.9, 126.1 (q, $J_{\text{C-F}} = 4.1$ Hz), 123.9 (q, $J_{\text{C-F}} = 270.3$ Hz), 123.1 (q, $J_{\text{C-F}} = 337.6$ Hz), 68.2; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_9\text{H}_7\text{F}_6\text{O}_2\text{S}$ 293.0065; Found 293.0061.



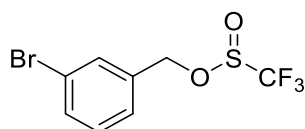
[1,1'-Biphenyl]-4-ylmethyl trifluoromethanesulfinate 3g: Prepared according to **General Method C** (Eluent: 100:1 to 20:1 petroleum ether:ethyl acetate) and the title compound was isolated as a colorless oil (66.1 mg, 0.220 mmol, 73.3% yield). IR (thin film) 1488 (w), 1185 (s), 1126 (s), 854 (s), 754 (m), 695 (s) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.67 – 7.61 (4H, m), 7.50 – 7.47 (4H, m), 7.42 – 7.38 (1H, m), 5.44 (1H, d, $J = 11.4$ Hz), 5.16 (1H, d, $J = 11.4$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -78.0; ^{13}C NMR (101 MHz, CDCl_3) δ 142.6, 140.3, 132.6, 129.5, 129.0, 127.9, 127.8, 127.3, 123.2 (q, $J_{\text{C-F}} = 340.3$ Hz), 69.7; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{14}\text{H}_{11}\text{F}_3\text{NaO}_2\text{S}$ 323.0324; Found 323.0332.



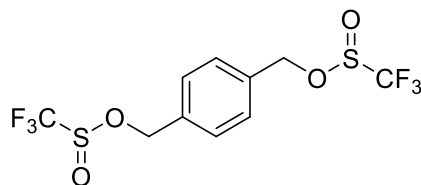
4-Cyanobenzyl trifluoromethanesulfinate 3h: Prepared according to **General Method C** (Eluent: 100:1 to 5:1 petroleum ether:ethyl acetate) and the title compound was isolated as a colorless oil (74.1 mg, 0.297 mmol, 99.1% yield). IR (thin film) 1185 (s), 1125 (s), 928 (m), 857 (m), 820 (m), 776 (m) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.71 (2H, d, $J = 8.1$ Hz), 7.50 (2H, d, $J = 8.0$ Hz), 5.43 (1H, d, $J = 12.3$ Hz), 5.12 (1H, d, $J = 12.3$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -77.8; ^{13}C NMR (101 MHz, CDCl_3) δ 138.9, 132.8, 128.9, 123.0 (q, $J_{\text{C-F}} = 340.3$ Hz), 118.3, 113.3, 67.7; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_9\text{H}_7\text{F}_3\text{NO}_2\text{S}$ 250.0144; Found 250.0146.



Methyl 4-(((trifluoromethyl)sulfinyl)oxy)methyl)benzoate 3i: Prepared according to **General Method C** (Eluent: 100:1 to 10:1 petroleum ether:ethyl acetate) and the title compound was isolated as a colorless oil (79.6 mg, 0.282 mmol, 94.0% yield). **IR** 1720 (s), 1437 (w), 1280 (s), 1180 (s), 1126 (s), 923 (m), 865 (m), 809 (m), 749 (s), 695 (m) cm^{-1} ; **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 8.06 (2H, d, $J = 8.1$ Hz), 7.43 (2H, d, $J = 8.1$ Hz), 5.40 (1H, d, $J = 12.0$ Hz), 5.12 (1H, d, $J = 12.0$ Hz), 3.91 (3H, s); **$^{19}\text{F NMR}$** (471 MHz, CDCl_3) δ -78.0; **$^{13}\text{C NMR}$** (101 MHz, CDCl_3) δ 166.5, 138.6, 131.1, 130.2, 128.4, 123.0 (q, $J_{\text{C-F}} = 340.8$ Hz), 68.6, 52.4; **MS** (FI): m/z (%) 69, 118, 149, 213, 282. **HRMS** (FI) Calcd for $\text{C}_{10}\text{H}_9\text{F}_3\text{O}_4\text{S}$ 282.0163; Found 282.0168.

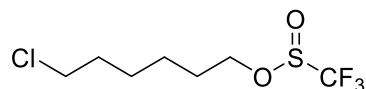


3-Bromobenzyl trifluoromethanesulfinate 3j: Prepared according to **General Method C** (Eluent: 100:1 to 20:1 petroleum ether:ethyl acetate) and the title compound was isolated as a colorless oil (65.0 mg, 0.214 mmol, 71.3% yield). **IR** (thin film) 1185 (s), 1125 (s), 886 (m), 789 (m), 685 (m) cm^{-1} ; **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.47 – 7.45 (2H, m), 7.26 – 7.20 (2H, m), 5.27 (1H, d, $J = 11.7$ Hz), 4.97 (1H, d, $J = 11.6$ Hz); **$^{19}\text{F NMR}$** (471 MHz, CDCl_3) δ -77.9; **$^{13}\text{C NMR}$** (101 MHz, CDCl_3) δ 136.0, 132.6, 131.7, 130.6, 127.3, 123.1 (q, $J_{\text{C-F}} = 342.7$ Hz), 123.0, 68.4; **MS** (FI): m/z (%) 69, 141, 169, 205, 233, 304. **HRMS** (FI) Calcd for $\text{C}_8\text{H}_6\text{F}_3\text{O}_2\text{BrS}$ 301.9216; Found 301.9218.

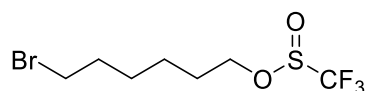


1,4-Phenylenebis(methylene) bis(trifluoromethanesulfinate) 3k: Prepared according to **General Method C** (reagent **1** 2.40 equiv, Et_3N 0.200 equiv) (Eluent: 50:1 to 10:1 petroleum ether:ethyl acetate) and the title compound was isolated as a colorless oil (107.0 mg, 0.289 mmol, 96.3% yield). **IR** (thin film) 1179 (s), 1123 (s), 893 (m),

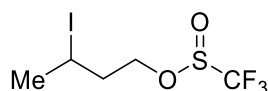
751 (m) cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.43 (4H, s), 5.39 (2H, d, $J = 11.6$ Hz), 5.10 (2H, d, $J = 11.6$ Hz); $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ -78.1; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 135.1, 129.3, 123.1 (q, $J_{\text{C-F}} = 340.7$ Hz), 69.0; **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{10}\text{H}_8\text{F}_6\text{NaO}_4\text{S}_2$ 392.9660; Found 392.9665.



6-Chlorohexyl trifluoromethanesulfinate 3l: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether:ethyl acetate) and the title compound was isolated as a colorless oil (60.6 mg, 0.240 mmol, 80.0% yield). **IR** (thin film) 1185 (s), 1127 (s), 894 (m), 724 (w) cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.39 – 4.11 (2H, m), 3.53 (2H, t, $J = 6.6$ Hz), 1.85 – 1.70 (4H, m), 1.52 – 1.39 (4H, m); $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ -78.6; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 123.0 (q, $J_{\text{C-F}} = 340.1$ Hz), 69.0, 44.9, 32.4, 29.7, 26.4, 24.8; **MS** (FI) $[\text{M}+\text{H}]^+$: m/z (%) 69, 83, 119, 183, 253. **HRMS** (FI) $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_7\text{H}_{13}\text{F}_3\text{O}_2\text{ClS}$ 253.0275; Found 253.0271.



6-Bromohexyl trifluoromethanesulfinate 3m: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether:ethyl acetate) and the title compound was isolated as a colorless oil (88.5 mg, 0.298 mmol, 99.3% yield). **IR** (thin film) 1185 (s), 1127 (s), 891 (m) cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.39 – 4.10 (2H, m), 3.40 (2H, t, $J = 6.7$ Hz), 1.86 (2H, p, $J = 6.7$ Hz), 1.76 (2H, p, $J = 6.4$ Hz), 1.52 – 1.38 (4H, m); $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ -78.6; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 122.9 (q, $J_{\text{C-F}} = 340.1$ Hz), 69.0, 33.6, 32.5, 29.6, 27.6, 24.7; **MS** (FI) $[\text{M}+\text{H}]^+$: m/z (%) 69, 165, 229, 297. **HRMS** (FI) $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_7\text{H}_{13}\text{F}_3\text{O}_2\text{BrS}$ 296.9769; Found 296.9766.

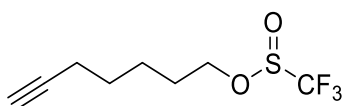


3-Iodobutyl trifluoromethanesulfinate 3n: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether:ethyl acetate) and the title compound was isolated as a colorless oil (82.1 mg, 0.260 mmol, 86.6% yield, dr = 1:1). **IR** (thin film) 1186 (s), 1125 (s), 925 (m), 868 (m), 751 (w) cm^{-1} ; **MS** (FI): m/z (%) 189, 247, 316. **HRMS** (FI)

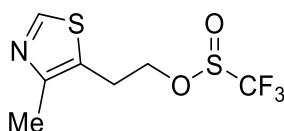
Calcd for C₅H₈F₃O₂IS 315.9239; Found 315.9236.

Isomer 1: ¹H NMR (400 MHz, CDCl₃) δ 4.57 – 4.17 (2H, m), 4.46 – 4.28 (1H, m), 2.24 – 2.15 (1H, m), 2.12 – 2.01 (1H, m), 1.98 (3H, d, *J* = 6.9 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ –78.3; ¹³C NMR (101 MHz, CDCl₃) δ 122.9 (q, *J*_{C-F} = 340.2 Hz), 68.7, 42.3, 28.9, 22.9;

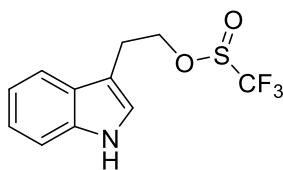
Isomer 2: ¹H NMR (400 MHz, CDCl₃) δ 4.57 – 4.17 (2H, m), 4.46 – 4.28 (1H, m), 2.24 – 2.15 (1H, m), 2.12 – 2.01 (1H, m), 1.98 (3H, d, *J* = 6.9 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ –78.5; ¹³C NMR (101 MHz, CDCl₃) δ 122.9 (q, *J*_{C-F} = 340.2 Hz), 69.2, 42.1, 28.9, 22.7.



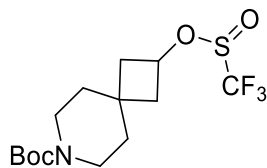
Hept-6-yn-1-yl trifluoromethanesulfinate 3o: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether:ethyl acetate) and the title compound was isolated as a colorless oil (56.9 mg, 0.249 mmol, 83.1% yield). **IR** (thin film) 1185 (s), 1127 (s), 882 (m), 633 (m) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.38 – 4.10 (2H, m), 2.25 – 2.15 (2H, m), 1.94 – 1.93 (1H, m), 1.77 (2H, p, *J* = 6.7 Hz), 1.59 – 1.47 (4H, m); ¹⁹F NMR (471 MHz, CDCl₃) δ –78.6; ¹³C NMR (101 MHz, CDCl₃) δ 123.0 (q, *J*_{C-F} = 340.1 Hz), 83.9, 68.9, 68.7, 29.3, 27.8, 24.5, 18.3; **HRMS** (ESI) *m/z*: [M+H]⁺ Calcd for C₈H₁₂F₃O₂S 229.0510; Found 229.0502.



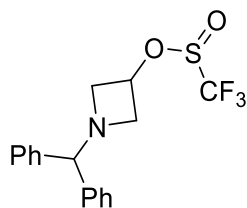
2-(4-Methylthiazol-5-yl)ethyl trifluoromethanesulfinate 3p: Prepared according to **General Method C** (Eluent: 50:1 to 3:1 petroleum ether:ethyl acetate) and the title compound was isolated as a colorless oil (76.6 mg, 0.295 mmol, 98.5% yield). **IR** (thin film) 1416 (w), 1185 (s), 1125 (s), 912 (m), 867 (m), 743 (w) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.59 (1H, s), 4.49 – 4.21 (2H, m), 3.19 (2H, t, *J* = 6.5 Hz), 2.38 (3H, s); ¹⁹F NMR (471 MHz, CDCl₃) δ –78.4; ¹³C NMR (101 MHz, CDCl₃) δ 150.7, 150.4, 125.0, 122.8 (q, *J*_{C-F} = 340.2 Hz), 67.6, 27.0, 14.9; **HRMS** (ESI) *m/z*: [M+H]⁺ Calcd for C₇H₉F₃NO₂S₂ 260.0021; Found 260.0029.



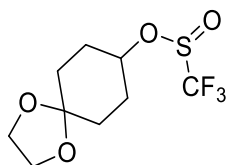
2-((1*H*-Indol-3-yl)ethyl) trifluoromethanesulfinate 3q: Prepared according to **General Method C** (Eluent: 50:1 to 5:1 petroleum ether:ethyl acetate) and the title compound was isolated as a yellow oil (41.9 mg, 0.151 mmol, 50.4% yield). **IR** (thin film) 3286 (w), 1489 (w), 1363 (w), 1153 (s), 1121 (s), 1062 (m), 992 (m), 743 (s) cm^{-1} ; **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 8.01 (1H, s), 7.48 (1H, d, $J = 7.9$ Hz), 7.26 (1H, d, $J = 8.0$ Hz), 7.13 (1H, dd, $J = 6.6, 8.2$ Hz), 7.06 (1H, dd, $J = 7.4, 7.4$ Hz), 6.94 (1H, s), 4.51 – 4.25 (2H, m), 3.12 (2H, t, $J = 7.0$ Hz); **$^{19}\text{F NMR}$** (471 MHz, CDCl_3) δ -78.6; **$^{13}\text{C NMR}$** (101 MHz, CDCl_3) δ 136.3, 127.1, 123.0 (q, $J_{\text{C-F}} = 340.0$ Hz), 122.9, 122.4, 119.8, 118.4, 111.5, 110.0, 69.1, 26.2; **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{11}\text{H}_{10}\text{F}_3\text{NNaO}_2\text{S}$ 300.0277; Found 300.0275.



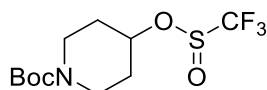
tert-Butyl 2-(((trifluoromethyl)sulfinyl)oxy)-7-azaspiro[3.5]nonane-7-carboxylate 3r: Prepared according to **General Method C** (Eluent: 100:1 to 15:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (99.6 mg, 0.280 mmol, 93.4% yield). **M.p.** = 63.4 – 64.5 $^{\circ}\text{C}$; **IR** (thin film) 1672 (m), 1416 (m), 1244 (m), 1186 (s), 1128 (s), 1000 (m), 881 (s), 817 (m), 771 (m) cm^{-1} ; **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 5.03 (1H, p, $J = 7.1$ Hz), 3.31 – 3.25 (4H, m), 2.40 – 2.33 (2H, m), 2.08 – 1.98 (2H, m), 1.55 – 1.52 (2H, m), 1.50 – 1.47 (2H, m), 1.39 (9H, s); **$^{19}\text{F NMR}$** (471 MHz, CDCl_3) δ -79.5; **$^{13}\text{C NMR}$** (101 MHz, CDCl_3) δ 154.8, 122.7 (q, $J_{\text{C-F}} = 338.9$ Hz), 79.5, 70.7, 40.7, 40.4, 39.0, 36.0, 31.8, 28.4; **MS** (FI): m/z (%) 57, 302, 357. **HRMS** (FI) Calcd for $\text{C}_{14}\text{H}_{22}\text{NF}_3\text{O}_4\text{S}$ 357.1221; Found 357.1216.



1-Benzhydrylazetididin-3-yl trifluoromethanesulfinate 3s: Prepared according to **General Method C** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (84.1 mg, 0.237 mmol, 78.9% yield). **IR** (thin film) 1453 (w), 1193 (s), 1127 (s), 854 (m), 795 (m), 744 (s), 702 (s), 636 (m) cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3) δ 7.37 (4H, d, $J = 7.8$ Hz), 7.25 (4H, dd, $J = 7.2, 7.7$ Hz), 7.18 – 7.14 (2H, m), 5.13 (1H, p, $J = 5.7$ Hz), 4.37 (1H, s), 3.59 – 3.54 (2H, m), 3.20 – 3.14 (2H, m); **^{19}F NMR** (471 MHz, CDCl_3) δ -79.1; **^{13}C NMR** (101 MHz, CDCl_3) δ 141.5, 128.7, 127.4, 122.8 (q, $J_{\text{C-F}} = 339.7$ Hz), 78.2, 67.8, 60.7, 60.5; **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{17}\text{F}_3\text{NO}_2\text{S}$ 356.0927; Found 356.0924.

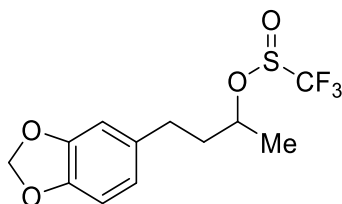


1,4-Dioxaspiro[4.5]decan-8-yl trifluoromethanesulfinate 3t: Prepared according to **General Method C** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (70.4 mg, 0.257 mmol, 85.6% yield). **IR** (thin film) 1379 (w), 1190 (s), 1125 (s), 1034 (m), 918 (s), 872 (m), 805 (m), 666 (w) cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3) δ 4.66 (1H, p, $J = 5.1$ Hz), 3.96 – 3.88 (4H, m), 2.02 – 1.92 (4H, m), 1.88 – 1.77 (2H, m), 1.64 – 1.58 (2H, m); **^{19}F NMR** (471 MHz, CDCl_3) δ -80.0; **^{13}C NMR** (101 MHz, CDCl_3) δ 122.8 (q, $J_{\text{C-F}} = 337.7$ Hz), 107.4, 79.3, 64.5, 30.8, 30.6, 30.0, 29.9; **MS** (FI): m/z (%) 69. **HRMS** (FI) Calcd for $\text{C}_9\text{H}_{13}\text{F}_3\text{O}_4\text{S}$ 274.0480; Found 274.0481.



tert-Butyl 4-(((trifluoromethyl)sulfinyl)oxy)piperidine-1-carboxylate 3u: Prepared according to **General Method C** (Eluent: 100:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (71.1 mg, 0.224 mmol, 74.7% yield). **IR**

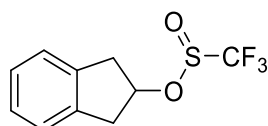
(thin film) 1691 (m), 1420 (m), 1366 (m), 1168 (s), 1126 (s), 1011 (m), 938 (m), 864 (m), 800 (m), 608 (w) cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.75 – 4.70 (1H, m), 3.70 – 3.61 (2H, m), 3.32 – 3.26 (2H, m), 1.97 – 1.88 (2H, m), 1.85 – 1.70 (2H, m), 1.42 (9H, s); $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ -79.8; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 154.6, 122.7 (q, $J_{\text{C-F}} = 337.8$ Hz), 80.1, 78.4, 39.9, 32.1 (d, $J_{\text{C-F}} = 17.7$ Hz), 28.4; **MS** (FI): m/z (%) 57, 149, 248, 260, 317. **HRMS** (FI) Calcd for $\text{C}_{11}\text{H}_{18}\text{F}_3\text{O}_4\text{S}$ 317.0905; Found 317.0903.



4-(Benzo[d][1,3]dioxol-5-yl)butan-2-yl trifluoromethanesulfinate 3v: Prepared according to **General Method C** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (91.1 mg, 0.294 mmol, 98.0% yield, dr = 1:1.5). **IR** (thin film) 1489 (m), 1443 (w), 1245 (m), 1185 (s), 1126 (s), 1037 (s), 926 (m), 857 (s), 809 (m) cm^{-1} ; **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{12}\text{H}_{13}\text{F}_3\text{NaO}_4\text{S}$ 333.0379; Found 333.0369.

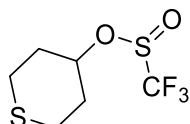
Isomer 1: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 6.74 (1H, s), 6.64 – 6.59 (2H, m), 5.92 (2H, s), 4.65 – 4.53 (1H, m), 2.75 – 2.68 (2H, m), 2.10 – 1.84 (2H, m), 1.48 (3H, d, $J = 6.3$ Hz); $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ -79.7; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 147.9, 146.1, 134.3, 122.8 (q, $J_{\text{C-F}} = 337.2$ Hz), 121.2, 108.8, 108.4, 101.0, 80.7, 39.2, 30.9, 21.8;

Isomer 2: $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 6.72 (1H, s), 6.69 – 6.65 (2H, m), 5.92 (2H, s), 4.65 – 4.53 (1H, m), 2.65 – 2.54 (2H, m), 2.10 – 1.84 (2H, m), 1.42 (3H, d, $J = 6.2$ Hz); $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ -80.2; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 147.9, 146.0, 134.3, 122.7 (q, $J_{\text{C-F}} = 336.5$ Hz), 121.4, 108.9, 108.4, 101.0, 80.4, 38.9, 30.9, 21.6.

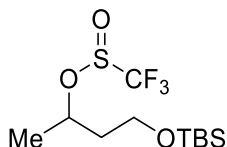


2,3-Dihydro-1H-inden-2-yl trifluoromethanesulfinate 3w: Prepared according to **General Method C** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (70.9 mg, 0.299 mmol, 99.6% yield). **IR** (thin

film) 1184 (s), 1125 (s), 995 (w), 853 (m), 739 (m) cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.27 – 7.18 (4H, m), 5.47 – 5.42 (1H, m), 3.41 – 3.33 (2H, m), 3.29 – 3.16 (2H, m); $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ -79.2; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 139.0 (d, $J_{\text{C-F}} = 17.8$ Hz), 127.4 (d, $J_{\text{C-F}} = 2.7$ Hz), 124.8 (d, $J_{\text{C-F}} = 5.1$ Hz), 122.8 (q, $J_{\text{C-F}} = 338.7$ Hz), 82.5, 40.6 (d, $J_{\text{C-F}} = 49.5$ Hz); **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{10}\text{H}_9\text{F}_3\text{NaO}_2\text{S}$ 273.0168; Found 273.0168.



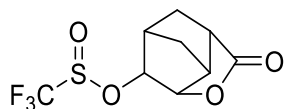
Tetrahydro-2H-thiopyran-4-yl trifluoromethanesulfinate 3x: Prepared according to **General Method C** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (65.4 mg, 0.279 mmol, 93.1% yield). **IR** (thin film) 1432 (w), 1183 (s), 1124 (s), 972 (m), 915 (m), 875 (m), 768 (m), 663 (w), 637 (m) cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.63 (1H, tt, $J = 7.6, 3.2$ Hz), 2.91 – 2.81 (2H, m), 2.59 – 2.53 (2H, m), 2.27 – 2.16 (2H, m), 2.10 – 1.99 (2H, m); $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ -79.8; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 122.6 (q, $J_{\text{C-F}} = 337.5$ Hz), 79.4, 33.8, 24.9; **MS** (FI): m/z (%) 101, 165, 234. **HRMS** (FI) Calcd for $\text{C}_6\text{H}_9\text{F}_3\text{O}_2\text{S}_2$ 233.9988; Found 233.9991.



4-((tert-Butyldimethylsilyloxy)butan-2-yl trifluoromethanesulfinate 3y: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (69.5 mg, 0.217 mmol, 72.3% yield, dr = 1:1). **IR** (thin film) 2931 (w), 1194 (s), 1131 (s), 1086 (m), 886 (m), 828 (s), 776 (s) cm^{-1} ; **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{11}\text{H}_{23}\text{F}_3\text{O}_3\text{SSi}$ 321.1162; Found 321.1168.

Isomer 1: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.88 – 4.77 (1H, m), 3.77 – 3.69 (2H, m), 1.97 – 1.87 (2H, m), 1.49 (3H, d, $J = 6.4$ Hz), 0.88 (9H, s), 0.06 (3H, s), 0.04 (3H, s); $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ -80.1; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 122.8 (q, $J_{\text{C-F}} = 336.6$ Hz), 79.0, 58.4, 40.1, 26.0, 22.2, 18.3, -5.4;

Isomer 2: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.88 – 4.77 (1H, m), 3.68 – 3.65 (2H, m), 1.87 – 1.77 (2H, m), 1.42 (3H, d, $J = 6.3$ Hz), 0.88 (9H, s), 0.05 (3H, s), 0.03 (3H, s); $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ –80.7; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 122.8 (q, $J_{\text{C-F}} = 336.6$ Hz), 79.0, 58.3, 39.9, 25.9, 21.8, 18.3, –5.5.

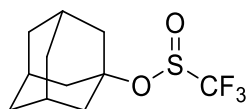


2-Oxo-2-(trifluoromethylsulfonyloxy)hexahydro-2H-3,5-methanocyclopenta[b]furan-6-yl trifluoromethanesulfinate

3z: Prepared according to **General Method C** (Eluent: 50:1 to 5:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (70.1 mg, 0.259 mmol, 86.4% yield, dr = 1: 1.6). **IR** (thin film) 1782 (s), 1175 (s), 1125 (s), 1037 (m), 1009 (m), 961 (s), 931 (s), 840 (m), 796 (s), 772.9 (s), 732 (m) cm^{-1} ; **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_9\text{H}_{10}\text{F}_3\text{O}_4\text{S}$ 271.0246; Found 271.0241.

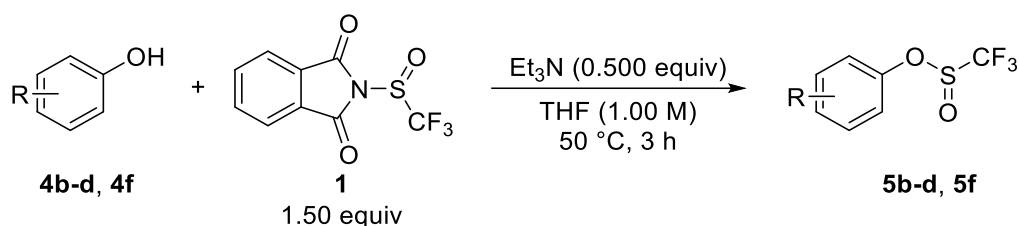
Isomer 1: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.62 (1H, d, $J = 5.0$ Hz), 4.43 (1H, s), 3.29 – 3.26 (1H, m), 2.73 (1H, d, $J = 2.8$ Hz), 2.61 – 2.57 (1H, m), 2.16 – 2.07 (2H, m), 1.76 – 1.71 (2H, m); $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ –79.4; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 178.9, 122.6 (q, $J_{\text{C-F}} = 337.9$ Hz), 85.0, 84.8, 44.9, 42.7, 37.6, 33.9, 31.3;

Isomer 2: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.72 (1H, d, $J = 5.0$ Hz), 4.50 (1H, s), 3.29 – 3.26 (1H, m), 2.61 – 2.57 (2H, m), 2.16 – 2.07 (2H, m), 1.76 – 1.71 (2H, m); $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ –79.2; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 178.9, 122.7 (q, $J_{\text{C-F}} = 338.8$ Hz), 84.6, 83.9, 44.9, 42.7, 37.6, 33.8, 31.3.



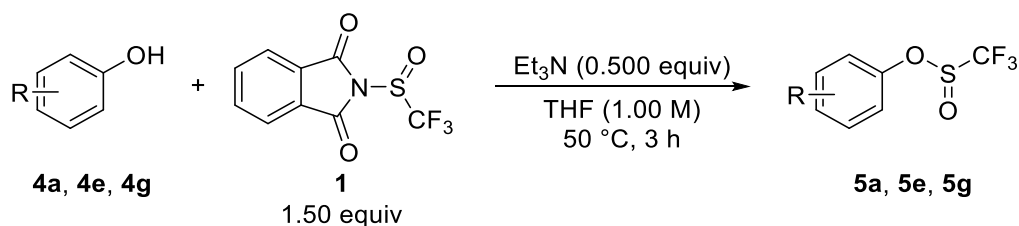
(3S,5S,7S)-Adamantan-1-yl trifluoromethanesulfinate 3aa: Prepared according to **General Method C** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (37.8 mg, 0.141 mmol, 47.0% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.28 (3H, s), 2.04 (6H, d, $J = 2.2$ Hz), 1.71 – 1.62 (6H, m); $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ –80.7; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 122.9 (q, $J_{\text{C-F}} = 335.0$ Hz), 86.7, 43.4, 35.5, 31.4. Spectra were consistent with literature data⁸.

2. General Method D:

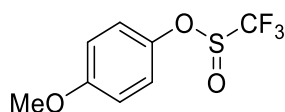


A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 2-((trifluoromethyl)sulfinyl)isoindoline-1,3-dione (0.750 mmol, 1.50 equiv, 197.4 mg), phenol (0.500 mmol, 1.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry THF (5.00 mL, 0.100 M) and Et₃N (0.250 mmol, 0.500 equiv, 25.2 mg) was added under N₂ atmosphere. The mixture was allowed to stir for 5 h at 50 °C. The solvent was removed by rotary evaporation and the residue was purified by silica gel chromatography.

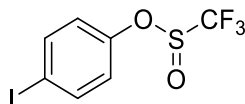
3. General Method E:



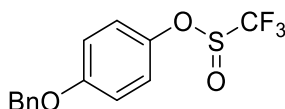
A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 2-((trifluoromethyl)sulfinyl)isoindoline-1,3-dione (1.50 mmol, 1.50 equiv, 394.8 mg), phenol (1.00 mmol, 1.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry THF (5.00 mL, 0.100 M) and Et₃N (0.500 mmol, 0.500 equiv, 50.1 mg) was added under N₂ atmosphere. The mixture was allowed to stir for 5 h at 50 °C. The solvent was removed by rotary evaporation and petroleum ether (20 mL) was added. The mixture was filtered and the solvent was removed by rotary evaporation to give the final product.



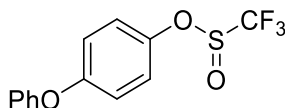
4-methoxyphenyl trifluoromethanesulfinate 5a: Prepared according to **General Method E** and the title compound was isolated as a colorless oil (195.0 mg, 0.812 mmol, 81.2% yield). **¹H NMR** (400 MHz, CDCl₃) δ 7.13 (2H, d, *J* = 9.0 Hz), 6.89 (2H, d, *J* = 9.0 Hz), 3.79 (3H, s); **¹⁹F NMR** (471 MHz, CDCl₃) δ -80.4; **¹³C NMR** (101 MHz, CDCl₃) δ 158.6, 145.3, 122.8 (q, *J*_{C-F} = 337.3 Hz), 122.3, 115.3, 55.7. Spectra were consistent with literature data⁹.



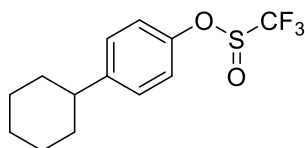
4-iodophenyl trifluoromethanesulfinate 5b: Prepared according to **General Method D** (Eluent: 100:0 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (107.2 mg, 0.319 mmol, 63.8% yield). **IR** (thin film) 2923 (w), 1478 (s), 1191 (s), 1155 (s), 1122 (s), 1055 (m), 1008 (s), 828 (s), 727 (s), 695 (s), 628 (m) cm⁻¹; **¹H NMR** (400 MHz, CDCl₃) δ 7.73 (2H, d, *J* = 8.8 Hz), 6.98 (6H, d, *J* = 8.8 Hz); **¹⁹F NMR** (471 MHz, CDCl₃) δ -79.9; **¹³C NMR** (101 MHz, CDCl₃) δ 151.8, 139.6, 123.0, 122.8 (q, *J*_{C-F} = 337.2 Hz), 91.6. **MS** (FI): *m/z* (%) 84, 220, 336. **HRMS** (FI) Calcd for C₇H₄F₃O₂SI 335.8929; Found 335.8922.



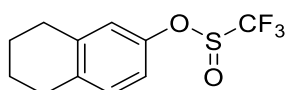
4-(benzyloxy)phenyl trifluoromethanesulfinate 5c: Prepared according to **General Method D** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (138.7 mg, 0.439 mmol, 87.7% yield). **M.p.** = 58.3 – 58.9 °C; **IR** (thin film) 3248 (w), 1503 (s), 1191 (s), 1155 (s), 1119 (s), 1007 (s), 833 (s), 795 (s), 751 (s), 695 (s), 621 (m) cm⁻¹; **¹H NMR** (500 MHz, CDCl₃) δ 7.48 – 7.35 (5H, m), 7.16 (2H, d, *J* = 9.1 Hz), 7.00 (2H, d, *J* = 9.1 Hz), 5.08 (2H, s); **¹⁹F NMR** (471 MHz, CDCl₃) δ -79.2; **¹³C NMR** (126 MHz, CDCl₃) δ 157.7, 145.5, 136.5, 128.8, 128.3, 127.6, 122.3, 122.8 (q, *J*_{C-F} = 336.6 Hz), 116.3, 70.6; **MS** (FI): *m/z* (%) 36, 99, 200, 316. **HRMS** (FI) Calcd for C₁₄H₁₁F₃O₃S 316.0381; Found 316.0376.



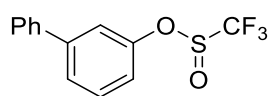
4-phenoxyphenyl trifluoromethanesulfinate 5d: Prepared according to **General Method D** (Eluent: 200:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (105.9 mg, 0.351 mmol, 70.1% yield). **IR** (thin film) 3047 (w), 1588 (m), 1487 (s), 1193 (s), 1163 (s), 1126 (s), 829 (s), 789 (s), 751 (s), 690 (s) cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3) δ 7.38 (3H, dd, $J = 7.8, 8.0$ Hz), 7.23 – 7.12 (3H, m), 7.03 (4H, d, $J = 8.8$ Hz); **^{19}F NMR** (471 MHz, CDCl_3) δ -79.1; **^{13}C NMR** (101 MHz, CDCl_3) δ 156.7, 156.4, 147.0, 130.1, 124.1, 122.8 (q, $J_{\text{C-F}} = 337.2$ Hz), 122.6, 120.1, 119.3; **MS** (FI): m/z (%) 186, 302. **HRMS** (FI) Calcd for $\text{C}_{13}\text{H}_9\text{F}_3\text{O}_3\text{S}$ 302.0224; Found 302.0219.



4-cyclohexylphenyl trifluoromethanesulfinate 5e: Prepared according to **General Method E** and the title compound was isolated as a colorless oil (243.2 mg, 0.832 mmol, 83.2% yield). **IR** (thin film) 2926 (m), 2853 (m), 1504 (m), 1191 (s), 1127 (s), 837 (s), 773 (s), 708 (m), 615 (m) cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3) δ 7.22 (2H, d, $J = 8.6$ Hz), 7.10 (2H, d, $J = 8.6$ Hz), 2.50 (1H, t, $J = 9.7$ Hz), 1.84 – 1.72 (5H, m), 1.43 – 1.22 (5H, m); **^{19}F NMR** (471 MHz, CDCl_3) δ -80.4; **^{13}C NMR** (101 MHz, CDCl_3) δ 150.0, 147.5, 128.7, 122.8 (q, $J_{\text{C-F}} = 336.8$ Hz), 120.7, 44.1, 34.6, 26.9, 26.1; **MS** (FI): m/z (%) 65, 82, 186, 248, 292. **HRMS** (FI) Calcd for $\text{C}_{13}\text{H}_{15}\text{F}_3\text{O}_2\text{S}$ 292.0745; Found 292.0739.

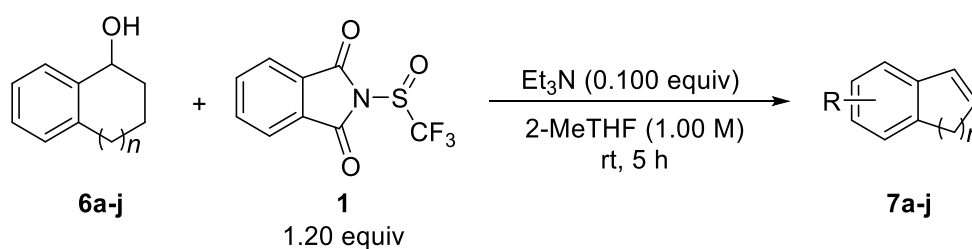


5,6,7,8-tetrahydronaphthalen-2-yl trifluoromethanesulfinate 5f: Prepared according to **General Method D** (Eluent: 100:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (65.7 mg, 0.249 mmol, 49.7% yield). **IR** (thin film) 2936 (w), 1493 (m), 1190 (s), 1126 (s), 916 (m), 774 (s), 689 (m) cm^{-1} ; **^1H NMR** (400 MHz, CDCl_3) δ 7.08 (1H, d, $J = 9.0$ Hz), 6.93 – 6.91 (2H, m), 2.76 (4H, d, $J = 4.4$ Hz), 1.80 (4H, p, $J = 3.3$ Hz); **^{19}F NMR** (471 MHz, CDCl_3) δ -80.5; **^{13}C NMR** (101 MHz, CDCl_3) δ 149.7, 139.8, 136.5, 130.9, 122.8 (q, $J_{\text{C-F}} = 337.1$ Hz), 121.1, 117.9, 29.6, 29.0, 23.0, 22.8; **MS** (FI): m/z (%) 131, 148, 195, 264. **HRMS** (FI) Calcd for $\text{C}_{11}\text{H}_{11}\text{F}_3\text{O}_2\text{S}$ 264.0432; Found 264.0426.

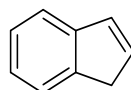


[1,1'-biphenyl]-3-yl trifluoromethanesulfinate 5g: Prepared according to **General Method E** and the title compound was isolated as a colorless oil (187.2 mg, 0.654 mmol, 65.4% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.40 – 7.34 (3H, m), 7.30 – 7.20 (5H, m), 7.01 (1H, d, $J = 7.3$ Hz); $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ -80.2; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 152.5, 144.0, 139.3, 130.7, 129.0, 128.2, 127.2, 125.9, 122.9 (q, $J_{\text{C-F}} = 337.0$ Hz), 119.4, 119.3. Spectra were consistent with literature data⁹.

3. General Method F:

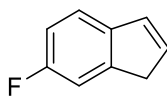


A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 2-((trifluoromethyl)sulfinyl)isoindoline-1,3-dione (0.360 mmol, 1.20 equiv, 94.8 mg), alcohol (0.300 mmol, 1.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry 2-MeTHF (3.00 mL, 0.100 M) and Et_3N (0.0300 mmol, 0.100 equiv, 3.00 mg) was added under N_2 atmosphere. The mixture was allowed to stir for 5 h at room temperature. The solvent was removed by rotary evaporation and the residue was purified by silica gel chromatography.

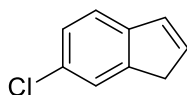


1H-indene 7a: Prepared according to **General Method F** (Eluent: 200 mL petroleum ether) and the title compound was isolated as a colorless oil (42.8 mg, 0.368 mmol, 73.7% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.45 (1H, d, $J = 7.4$ Hz), 7.38 (1H, d, $J = 7.5$ Hz), 7.23 (1H, d, $J = 9.0$ Hz), 7.18 – 7.14 (1H, m), 6.86 (1H, d, $J = 5.5$ Hz), 6.54 – 6.52 (1H, m), 3.37 (2H,

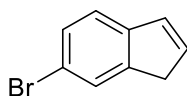
s); ^{13}C NMR (101 MHz, CDCl_3) δ 145.0, 143.8, 134.3, 132.2, 126.3, 124.7, 123.8, 121.1, 39.2. Spectra were consistent with literature data¹⁰.



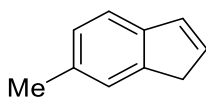
6-Fluoro-1H-indene 7b: Prepared according to **General Method F** (Eluent: 200 mL petroleum ether) and the title compound was isolated as a colorless oil (51.3 mg, 0.382 mmol, 76.5% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.32 (1H, dd, $J = 8.3, 5.1$ Hz), 7.21 – 7.19 (1H, m), 7.03 – 6.97 (1H, m), 6.86 (1H, d, $J = 5.5$ Hz), 6.55 – 6.52 (1H, m), 3.40 (2H, s); ^{13}C NMR (101 MHz, CDCl_3) δ 161.5 (d, $J_{\text{C-F}} = 243.2$ Hz), 145.8 (d, $J_{\text{C-F}} = 8.8$ Hz), 140.9 (d, $J_{\text{C-F}} = 2.6$ Hz), 133.9 (d, $J_{\text{C-F}} = 3.8$ Hz), 131.4, 121.4 (d, $J_{\text{C-F}} = 8.7$ Hz), 113.2 (d, $J_{\text{C-F}} = 22.8$ Hz), 111.5 (d, $J_{\text{C-F}} = 23.0$ Hz), 39.4 (d, $J_{\text{C-F}} = 2.3$ Hz). Spectra were consistent with literature data¹¹.



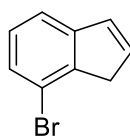
6-Chloro-1H-indene 7c: Prepared according to **General Method F** (Eluent: 200 mL petroleum ether) and the title compound was isolated as a colorless oil (49.0 mg, 0.325 mmol, 65.1% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.47 (1H, s), 7.33 (1H, d, $J = 8.0$ Hz), 7.27 (1H, d, $J = 8.2$ Hz), 6.86 (1H, d, $J = 5.5$ Hz), 6.59 – 6.57 (1H, m), 3.41 (2H, s); ^{13}C NMR (101 MHz, CDCl_3) δ 145.5, 143.4, 134.7, 131.5, 130.7, 126.6, 124.3, 121.7, 39.2. Spectra were consistent with literature data¹¹.



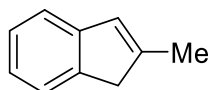
6-Bromo-1H-indene 7d: Prepared according to **General Method F** (Eluent: 200 mL petroleum ether) and the title compound was isolated as a colorless oil (49.1 mg, 0.252 mmol, 50.3% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.61 (1H, s), 7.41 (1H, dd, $J = 8.0, 1.6$ Hz), 7.26 (1H, d, $J = 8.0$ Hz), 6.84 (1H, d, $J = 5.5$ Hz), 6.57 – 6.54 (1H, m), 3.39 (2H, s); ^{13}C NMR (101 MHz, CDCl_3) δ 145.9, 143.8, 134.7, 131.6, 129.4, 127.1, 122.2, 118.8, 39.2. Spectra were consistent with literature data¹¹.



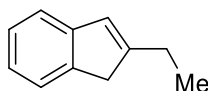
6-Methyl-1H-indene 7e: Prepared according to **General Method F** (Eluent: 200 mL petroleum ether) and the title compound was isolated as a colorless oil (41.9 mg, 0.322 mmol, 64.4% yield). **¹H NMR** (400 MHz, CDCl₃) δ 7.32 (2H, d, $J = 7.5$ Hz), 7.12 (1H, d, $J = 8.0$ Hz), 6.88 (1H, d, $J = 5.5$ Hz), 6.52 – 6.50 (1H, m), 3.39 (2H, s), 2.43 (3H, s); **¹³C NMR** (101 MHz, CDCl₃) δ 144.1, 142.3, 134.3, 133.3, 131.9, 127.1, 124.8, 120.7, 39.0, 21.6. Spectra were consistent with literature data¹¹.



7-Bromo-1H-indene 7f: Prepared according to **General Method F** (Eluent: 200 mL petroleum ether) and the title compound was isolated as a colorless oil (40.7 mg, 0.209 mmol, 41.7% yield). **¹H NMR** (400 MHz, CDCl₃) δ 7.34 (2H, dd, $J = 7.6, 5.2$ Hz), 7.17 (1H, dd, $J = 7.4, 5.0$ Hz), 6.93 – 6.91 (1H, m), 6.63 – 6.61 (1H, m), 3.40 (2H, t, $J = 1.6$ Hz); **¹³C NMR** (101 MHz, CDCl₃) δ 146.4, 143.9, 134.8, 132.2, 128.3, 127.9, 120.1, 119.0, 40.9. Spectra were consistent with literature data¹¹.

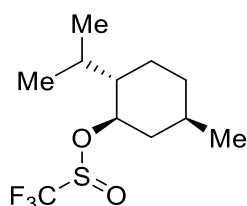


6-Methyl-1H-indene 7g: Prepared according to **General Method F** (Eluent: 200 mL petroleum ether) and the title compound was isolated as a colorless oil (45.8 mg, 0.352 mmol, 70.4% yield). **¹H NMR** (400 MHz, CDCl₃) δ 7.40 (1H, d, $J = 7.3$ Hz), 7.29 – 7.22 (2H, m), 7.12 (1H, dd, $J = 7.2, 7.2$ Hz), 6.51 (1H, s), 3.32 (2H, s), 2.18 (3H, s); **¹³C NMR** (101 MHz, CDCl₃) δ 146.2, 146.0, 143.5, 127.3, 126.3, 123.6, 123.4, 119.8, 42.8, 16.9. Spectra were consistent with literature data¹².



2-Ethyl-1H-indene 7h: Prepared according to **General Method F** (Eluent: 200 mL petroleum ether) and the title compound was isolated as a colorless oil (50.2 mg, 0.348 mmol, 69.6% yield). **¹H NMR** (400 MHz, CDCl₃) δ 7.43 (1H, d, $J = 7.4$ Hz), 7.33 (1H, d, $J = 7.3$ Hz), 7.27 (1H, dd, $J = 7.2, 7.2$ Hz), 7.17 – 7.13 (1H, m), 6.56 (1H, s), 3.36

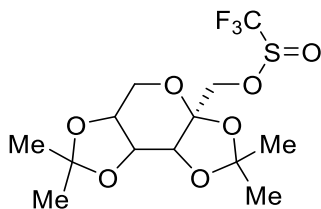
mixture was allowed to stir for 5 h at room temperature. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography.



(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl trifluoromethanesulfinate 9a: Prepared according to **General Method C** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (71.7 mg, 0.263 mmol, 87.8% yield, dr = 1: 1.5).

Isomer 1: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.26 (1H, dd, $J = 9.9, 4.5$ Hz), 2.20 – 2.00 (2H, m), 1.77 – 1.67 (2H, m), 1.54 – 1.42 (2H, m), 1.41 – 1.27 (2H, m), 1.10 – 0.98 (1H, m), 0.94 (3H, d, $J = 6.4$ Hz), 0.91 (3H, d, $J = 7.4$ Hz), 0.76 (3H, d, $J = 7.0$ Hz); $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ -80.0; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 122.8 (q, $J_{\text{C-F}} = 336.7$ Hz), 85.5, 48.1, 42.9, 33.7, 32.0, 25.3, 23.1, 21.9, 20.8, 15.4;

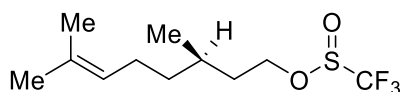
Isomer 2: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.21 (dd, $J = 10.7, 4.5$ Hz, 1H), 2.20 – 2.00 (2H, m), 1.77 – 1.67 (2H, m), 1.54 – 1.42 (2H, m), 1.26 – 1.20 (1H, m), 1.10 – 0.98 (1H, m), 0.94 (3H, d, $J = 6.5$ Hz), 0.92 (3H, d, $J = 7.1$ Hz), 0.87 – 0.83 (1H, m), 0.79 (3H, d, $J = 6.9$ Hz); $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ -80.6; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 122.7 (q, $J_{\text{C-F}} = 335.9$ Hz), 84.6, 47.9, 42.2, 33.7, 31.9, 25.5, 23.3, 21.9, 20.7, 15.6. Spectra were consistent with literature data⁸.



((3*aS*)-2,2,7,7-Tetramethyltetrahydro-3*aH*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3*a*-yl)methyl trifluoromethanesulfinate 9b: Prepared according to **General Method C** (Eluent: 100:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (103.4 mg, 0.275 mmol, 91.6% yield, dr = 1: 1.5).

Isomer 1: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.62 – 4.58 (1H, m), 4.29 (2H, dd, $J = 18.8$, 2.6 Hz), 4.23 – 4.17 (2H, m), 3.91 (1H, dd, $J = 5.7$, 1.8 Hz), 3.74 (1H, s), 1.52 (3H, s), 1.44 (3H, s), 1.37 (3H, s), 1.32 (3H, s); $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ -78.9; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 123.0 (q, $J_{\text{C-F}} = 340.2$ Hz), 109.8, 109.4, 100.8, 70.7, 70.1, 69.9, 68.5, 61.6, 26.6, 25.9, 25.3, 24.0;

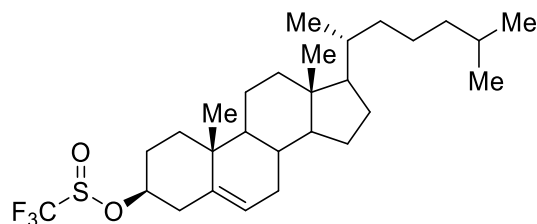
Isomer 2: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.62 – 4.58 (1H, m), 4.40 (1H, d, $J = 11.0$ Hz), 4.30 – 4.26 (1H, m), 4.23 – 4.17 (1H, m), 4.06 (1H, d, $J = 11.0$ Hz), 3.88 (1H, dd, $J = 5.7$, 1.8 Hz), 3.77 (1H, s), 1.52 (3H, s), 1.44 (3H, s), 1.36 (3H, s), 1.32 (3H, s); $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ -78.5; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 122.9 (q, $J_{\text{C-F}} = 340.0$ Hz), 109.8, 109.3, 100.8, 70.6, 70.4, 69.9, 67.2, 61.5, 26.5, 25.8, 25.1, 24.0. Spectra were consistent with literature data¹⁴.



(R)-3,7-Dimethyloct-6-en-1-yl trifluoromethanesulfinate 9c: Prepared according to **General Method C** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (68.3 mg, 0.251 mmol, 83.6% yield, dr = 1: 1).

Isomer 1: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.07 (1H, t, $J = 7.1$ Hz), 4.44 – 4.35 (1H, m), 4.22 – 4.13 (1H, m), 2.04 – 1.92 (2H, m), 1.83 – 1.75 (1H, m), 1.68 (3H, s), 1.64 – 1.61 (1H, m), 1.59 (3H, s), 1.57 – 1.49 (1H, m), 1.39 – 1.30 (1H, m), 1.24 – 1.15 (1H, m), 0.93 (3H, d, $J = 1.8$ Hz); $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ -78.6; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 131.8, 124.3, 123.0 (q, $J_{\text{C-F}} = 340.1$ Hz), 67.7, 36.9, 36.7, 29.0, 25.8, 25.4, 19.3, 17.7;

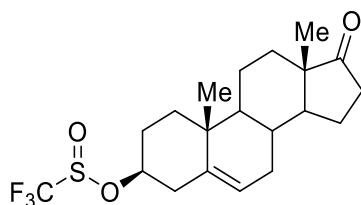
Isomer 2: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.07 (1H, t, $J = 7.1$ Hz), 4.44 – 4.35 (1H, m), 4.22 – 4.13 (1H, m), 2.04 – 1.92 (2H, m), 1.83 – 1.75 (1H, m), 1.68 (3H, s), 1.64 – 1.61 (1H, m), 1.59 (3H, s), 1.57 – 1.49 (1H, m), 1.39 – 1.30 (1H, m), 1.24 – 1.15 (1H, m), 0.91 (3H, d, $J = 1.8$ Hz); $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ -78.7; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 131.8, 124.3, 123.0 (q, $J_{\text{C-F}} = 340.1$ Hz), 67.6, 36.8, 36.6, 29.0, 25.8, 25.4, 19.2, 17.7. Spectra were consistent with literature data¹⁵.



(10R,13R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl trifluoromethanesulfinate 9d: Prepared according to **General Method C** (Eluent: 100:1 to 50:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless oil (141.7 mg, 0.282 mmol, 94.0% yield, dr = 1: 1).

Isomer 1: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.41 (1H, t, $J = 4.7$ Hz), 4.40 – 4.32 (1H, m), 2.62 – 2.38 (2H, m), 2.03 – 1.79 (6H, m), 1.63 – 1.43 (6H, m), 1.37 – 1.25 (4H, m), 1.20 – 1.05 (7H, m), 1.03 (3H, s), 1.00 – 0.94 (3H, m), 0.91 (3H, d, $J = 6.6$ Hz), 0.87 (3H, d, $J = 1.7$ Hz), 0.85 (3H, d, $J = 1.7$ Hz), 0.67 (3H, s); $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ -80.0; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 138.7, 124.0, 122.8 (q, $J_{\text{C-F}} = 337.2$ Hz), 83.2, 56.7, 56.3, 50.0, 42.4, 39.9, 39.8, 39.6, 37.1, 36.5, 36.3, 35.9, 32.0, 29.7, 28.3, 28.1, 27.0, 24.4, 24.0, 22.9, 22.7, 21.2, 19.3, 18.8, 11.9;

Isomer 2: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.41 (1H, t, $J = 4.7$ Hz), 4.40 – 4.32 (1H, m), 2.62 – 2.38 (2H, m), 2.03 – 1.78 (6H, m), 1.63 – 1.42 (6H, m), 1.37 – 1.25 (4H, m), 1.20 – 1.05 (7H, m), 1.03 (3H, s), 1.00 – 0.94 (3H, m), 0.91 (3H, d, $J = 6.6$ Hz), 0.87 (3H, d, $J = 1.7$ Hz), 0.85 (3H, d, $J = 1.7$ Hz), 0.67 (3H, s); $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ -80.1; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 138.6, 124.0, 122.8 (q, $J_{\text{C-F}} = 337.2$ Hz), 83.1, 56.7, 56.3, 50.0, 42.4, 39.9, 39.8, 39.6, 37.0, 36.5, 36.3, 35.9, 31.9, 29.5, 28.3, 28.1, 27.0, 24.4, 24.0, 22.9, 22.7, 21.2, 19.3, 18.8, 11.9. Spectra were consistent with literature data⁸.

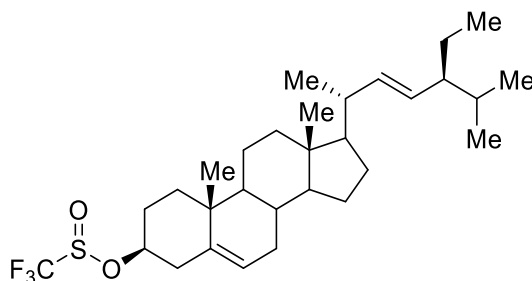


(10R,13S)-10,13-Dimethyl-17-oxo-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl trifluoromethanesulfinate 9e: Prepared according to **General Method C** (Eluent: 100:1 to 10:1 petroleum ether: ethyl acetate) and the title

compound was isolated as a white solid (108.0 mg, 0.267 mmol, 89.0% yield, dr = 1:1). **M.p.** = 114.8 – 115.3 °C; **IR** (thin film) 2935 (w), 1732 (m), 1190 (s), 1130 (s), 927 (m), 883 (m), 853 (m), 803 (s), 635 (w) cm⁻¹; **HRMS** (ESI) m/z: [M+H]⁺ Calcd for C₂₀H₂₈F₃O₃S 405.1706; Found 405.1700.

Isomer 1: ¹H NMR (400 MHz, CDCl₃) δ 5.43 (1H, t, *J* = 4.5 Hz), 4.40 – 4.31 (1H, m), 2.61 – 2.41 (3H, m), 2.16 – 1.76 (7H, m), 1.67 – 1.59 (3H, m), 1.56 – 1.42 (2H, m), 1.30 – 1.23 (2H, m), 1.17 – 1.09 (1H, m), 1.04 (3H, s), 1.02 – 0.93 (1H, m), 0.86 (3H, s); ¹⁹F NMR (471 MHz, CDCl₃) δ -79.9; ¹³C NMR (101 MHz, CDCl₃) δ 138.9, 123.2, 122.8 (q, *J*_{C-F} = 338.3 Hz), 82.8, 51.7, 50.1, 47.6, 39.8, 37.0, 36.6, 36.6, 35.9, 31.4, 31.4, 30.8, 29.5, 21.9, 20.4, 19.3, 13.6;

Isomer 2: ¹H NMR (500 MHz, CDCl₃) δ 5.43 (1H, t, *J* = 4.5 Hz), 4.40 – 4.31 (1H, m), 2.61 – 2.41 (3H, m), 2.16 – 1.76 (7H, m), 1.67 – 1.59 (3H, m), 1.56 – 1.42 (2H, m), 1.30 – 1.23 (2H, m), 1.17 – 1.09 (1H, m), 1.04 (3H, s), 1.02 – 0.93 (1H, m), 0.86 (3H, s); ¹⁹F NMR (471 MHz, CDCl₃) δ -80.0; ¹³C NMR (101 MHz, CDCl₃) δ 138.9, 123.2, 122.8 (q, *J*_{C-F} = 338.3 Hz), 82.7, 51.7, 50.1, 47.6, 39.7, 36.9, 36.6, 36.6, 35.9, 31.4, 31.4, 30.8, 29.4, 21.9, 20.4, 19.3, 13.6.

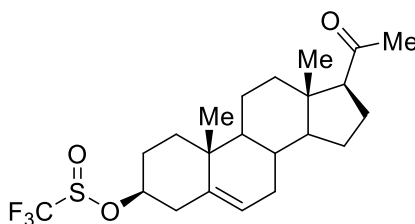


(10*R*,13*R*)-17-((2*R*,5*S*,*E*)-5-Ethyl-6-methylhept-3-en-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl trifluoromethanesulfinate 9f: Prepared according to **General Method C** (Eluent: 100:1 to 20:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (153.2 mg, 0.290 mmol, 96.6% yield, dr = 1:1). **M.p.** = 102.7 – 103.4 °C; **IR** (thin film) 2935 (w), 1464 (w), 1200 (s), 1131 (s), 971 (s), 910 (m), 856 (m), 791 (m) cm⁻¹; **MS** (FI): m/z (%) 528. **HRMS** (FI) Calcd for C₃₀H₄₇F₃O₂S 528.3250; Found 528.3243.

Isomer 1: ¹H NMR (400 MHz, CDCl₃) δ 5.42 (1H, t, *J* = 4.7 Hz), 5.17 – 4.98 (2H, m), 4.41 – 4.32 (1H, m), 2.62 – 2.38 (2H, m), 2.08 – 1.81 (6H, m), 1.74 – 1.66 (1H, m), 1.59 –

1.37 (9H, m), 1.22 – 1.06 (5H, m), 1.02 (6H, d, $J = 7.7$ Hz), 1.00 – 0.88 (2H, m), 0.84 (3H, d, $J = 6.4$ Hz), 0.80 (6H, dd, $J = 7.4, 6.8$ Hz), 0.70 (3H, s); ^{19}F NMR (471 MHz, CDCl_3) δ –80.0; ^{13}C NMR (101 MHz, CDCl_3) δ 138.7, 138.4, 124.0, 122.8 (q, $J_{\text{C-F}} = 337.2$ Hz), 83.2, 56.9, 56.0, 51.4, 50.1, 42.3, 40.7, 39.9, 39.7, 37.1, 36.6, 32.0, 32.0, 31.9, 29.9, 29.7, 29.0, 25.6, 24.5, 21.4, 21.2, 21.2, 19.3, 19.1, 12.4, 12.2;

Isomer 2: ^1H NMR (500 MHz, CDCl_3) δ 5.42 (1H, t, $J = 4.7$ Hz), 5.17 – 4.98 (2H, m), 4.41 – 4.32 (1H, m), 2.62 – 2.38 (2H, m), 2.08 – 1.81 (6H, m), 1.74 – 1.66 (1H, m), 1.59 – 1.37 (9H, m), 1.22 – 1.06 (5H, m), 1.02 (6H, d, $J = 7.7$ Hz), 1.00 – 0.88 (2H, m), 0.84 (3H, d, $J = 6.4$ Hz), 0.80 (6H, dd, $J = 7.4, 6.8$ Hz), 0.70 (3H, s); ^{19}F NMR (471 MHz, CDCl_3) δ –80.0; ^{13}C NMR (101 MHz, CDCl_3) δ 138.7, 138.4, 124.0, 122.8 (q, $J_{\text{C-F}} = 337.2$ Hz), 83.1, 56.9, 56.0, 51.4, 50.1, 42.3, 40.7, 39.8, 39.7, 37.1, 36.5, 32.0, 32.0, 31.9, 29.9, 29.6, 29.0, 25.6, 24.5, 21.4, 21.2, 21.2, 19.3, 19.1, 12.4, 12.2.

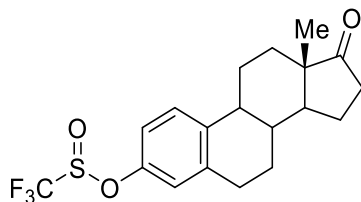


(10R,13S,17S)-17-Acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[*a*]phenanthren-3-yl trifluoromethanesulfinate 9g:

Prepared according to **General Method D** (Eluent: 100:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (106.2 mg, 0.246 mmol, 81.8% yield, dr = 1:1). **M.p.** = 88.1 – 88.9 °C; **IR** (thin film) 2945 (w), 1698 (m), 1361 (w), 1192 (s), 1126 (s), 930 (m), 852 (m), 801 (m) cm^{-1} ; **HRMS** (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{32}\text{F}_3\text{O}_3\text{S}$ 433.2019; Found 433.2021.

Isomer 1: ^1H NMR (400 MHz, CDCl_3) δ 5.38 (1H, s), 4.38 – 4.30 (1H, m), 2.58 – 2.47 (2H, m), 2.45 – 2.36 (1H, m), 2.20 – 2.13 (1H, m), 2.08 (3H, s), 2.03 – 1.78 (5H, m), 1.69 – 1.38 (7H, m), 1.33 – 1.08 (4H, m), 0.99 (3H, s), 0.59 (3H, s); ^{19}F NMR (471 MHz, CDCl_3) δ –80.0 (3F, d, $J = 3.6$ Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 209.5, 138.6, 123.7, 122.7 (q, $J_{\text{C-F}} = 337.7$ Hz), 82.9, 63.6, 56.8, 49.8, 44.0, 39.8, 38.7, 37.0, 36.5, 36.4, 31.8, 31.6, 29.5, 24.5, 22.8, 21.1, 19.2, 13.2;

Isomer 2: $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 5.38 (1H, s), 4.38 – 4.30 (1H, m), 2.58 – 2.47 (2H, m), 2.45 – 2.36 (1H, m), 2.20 – 2.13 (1H, m), 2.08 (3H, s), 2.03 – 1.78 (5H, m), 1.69 – 1.38 (7H, m), 1.33 – 1.08 (4H, m), 0.99 (3H, s), 0.59 (3H, s); $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ –80.1 (3F, d, $J = 3.7$ Hz); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 209.5, 138.6, 123.6, 122.7 (q, $J_{\text{C-F}} = 337.7$ Hz), 82.8, 63.6, 56.8, 49.8, 44.0, 39.6, 38.7, 36.9, 36.5, 36.4, 31.8, 31.6, 29.4, 24.5, 22.8, 21.1, 19.2, 13.2.

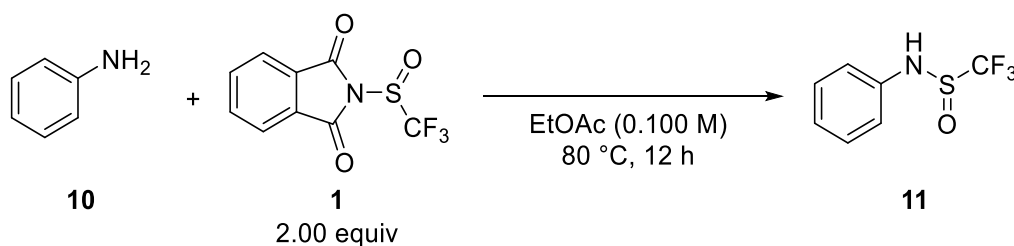


(13S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H

cyclopenta[a]phenanthren-3-yl trifluoromethanesulfinate 9h: Prepared according to **General Method D** (Eluent: 100:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (171.4 mg, 0.444 mmol, 88.7% yield, dr > 20:1).

M.p. = 116.7 – 117.5 °C; **IR** (thin film) 3448 (m), 2957 (w), 2828 (m), 2716 (w), 1603 (s), 1364 (s), 1070 (w), 770 (s) cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.30 (1H, d, $J = 8.5$ Hz), 7.00 – 6.90 (2H, m), 2.91 (2H, dd, $J = 8.8, 4.1$ Hz), 2.50 (1H, dd, $J = 19.0, 8.9$ Hz), 2.44 – 2.36 (1H, m), 2.29 – 2.24 (1H, m), 2.19 – 2.01 (3H, m), 1.98 – 1.94 (1H, m), 1.66 – 1.42 (6H, m), 0.91 (3H, s); $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ –80.4; $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 220.7, 149.9, 139.3, 139.1, 127.4, 122.7 (q, $J_{\text{C-F}} = 337.0$ Hz), 120.8, 117.9, 50.4, 47.9, 44.1, 37.9, 35.9, 31.5, 29.4, 26.2, 25.8, 21.6, 13.8; **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{21}\text{F}_3\text{O}_3\text{SNa}$ 409.1056; Found 409.1057.

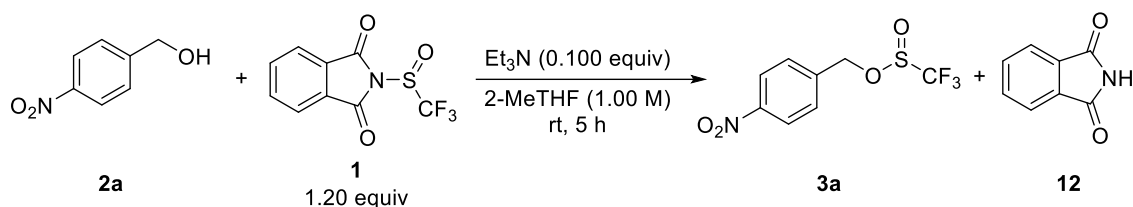
IV. Synthesis of trifluoromethanesulfinamide 11



A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 2-((trifluoromethyl)sulfinyl)isoindoline-1,3-dione **1** (263.2 mg, 1.00 mmol, 2.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry EtOAc (5.00 mL, 0.100 M), aniline (0.500 mmol, 1.00 equiv) was added under N₂ atmosphere. The mixture was allowed to stir for 12 h at 80 °C. The solvent was removed by rotary evaporation and the residue was purified by flash silica gel chromatography. (Eluent: 100:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (69.0 mg, 0.330 mmol, 66.0% yield).

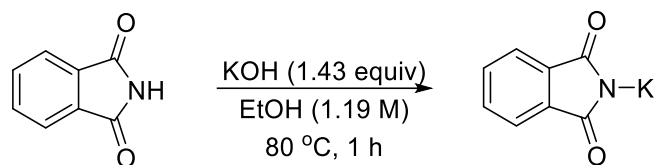
¹H NMR (400 MHz, CDCl₃) δ 7.35 (2H, dd, *J* = 7.7, 8.1 Hz), 7.18 (1H, dd, *J* = 7.4, 7.5 Hz), 7.10 (2H, dd, *J* = 7.6 Hz), 6.80 (1H, s); ¹⁹F NMR (471 MHz, CDCl₃) δ -77.8; ¹³C NMR (101 MHz, CDCl₃) δ 138.1, 130.0, 125.7, 120.5, 123.7 (q, *J*_{C-F} = 334.6 Hz). Spectra were consistent with literature data ¹⁶.

V. Scale-up reaction and sustainable utilization of phthalimide

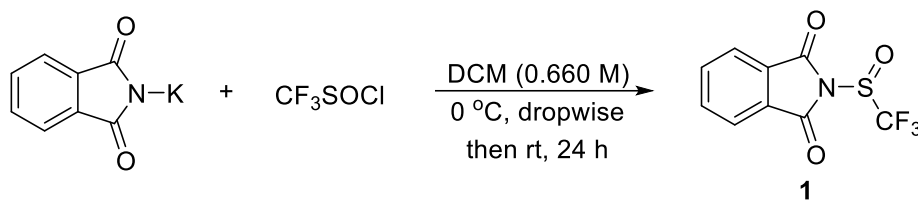


A 120 °C oven-dried 100-mL round bottom flask, equipped with a stir bar, was charged with 2-((trifluoromethyl)sulfinyl)isoindoline-1,3-dione (6.00 mmol, 1.20 equiv, 1.58 g). The mixture was evacuated and backfilled with nitrogen for three times. Then dry 2-MeTHF (50.0 mL, 0.100 M), (4-nitrophenyl)methanol (5.00 mmol, 1.00 equiv, 0.766 g) and Et₃N (0.500 mmol, 0.100 equiv, 50.6 mg) were added under N₂ atmosphere. The mixture was allowed to stir for 5 h at room temperature. The solvent was removed by rotary evaporation and petroleum ether (100 mL) was added to the mixture. The residue was filtered to give **12** (117.0 mg, 4.35 mmol, 86.9% yield) as a white solid and the solvent was removed by rotary evaporation to give **3a** (898 mg, 6.10 mmol, >99% yield) as a colorless

liquid.



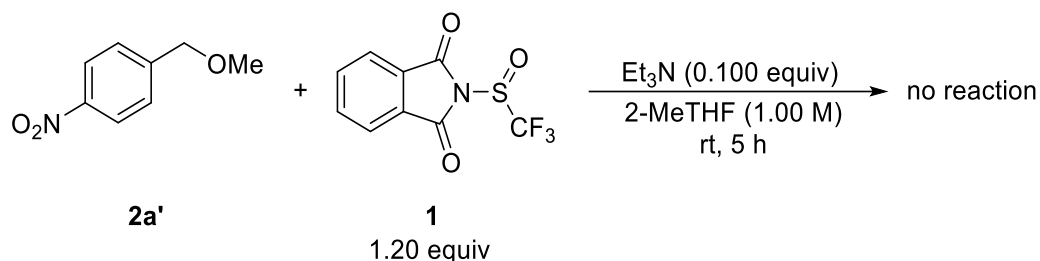
A 120 °C oven-dried 250-mL round bottom flask, equipped with a stir bar, was charged with KOH (169.7 mmol, 1.43 equiv, 9.52 g). The mixture was evacuated and backfilled with nitrogen for three times. Then dry EtOH (100 mL, 1.19 M) was added under N₂ atmosphere. When the solid completely dissolved, the isoindolin-1,3-dione (119 mmol, 1.00 equiv, 17.5 g) was added under N₂ atmosphere. The mixture was allowed to stir for 1 h at 80 °C. Cooled the mixture to room temperature. Filtered the mixture and washed the solid by absolute EtOH. Dry the mixture to give a white solid (21.7 g, 117 mmol, 98.4% yield). Spectra were consistent with literature data¹⁷.



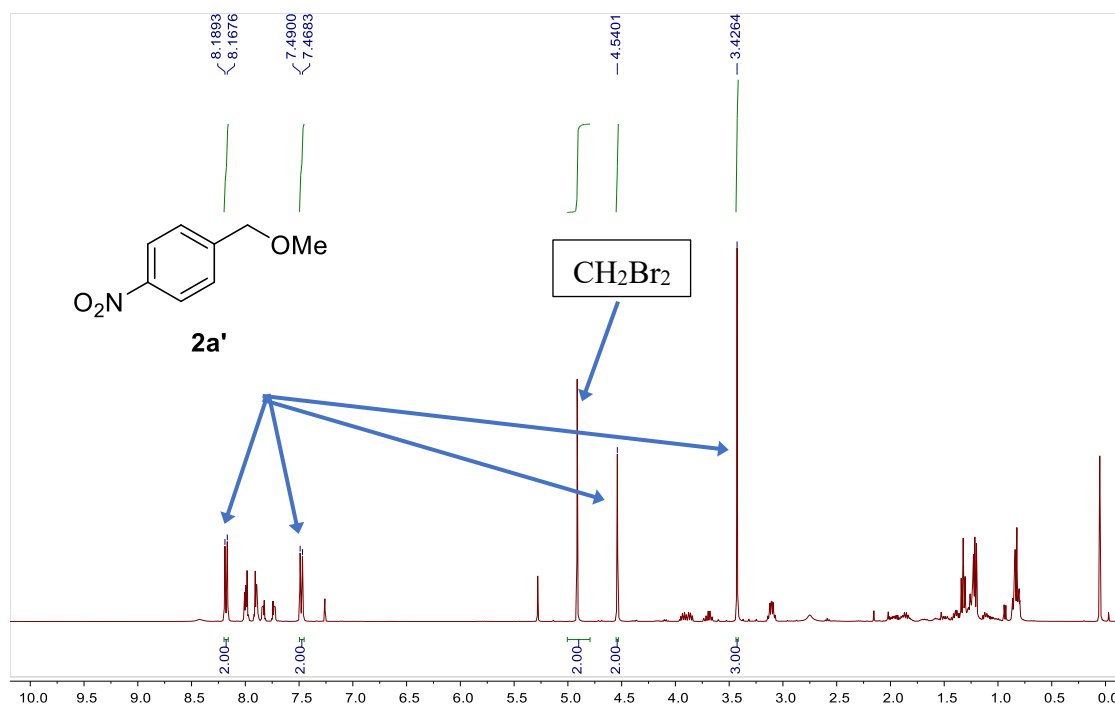
A 120 °C oven-dried 200-mL glass, equipped with a stir bar, was charged with potassium phthalimide (6.11 g, 33.0 mmol, 1.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry DCM (45.0 mL) was added under N₂ atmosphere. The mixture was cooled to 0 °C. A solution of trifluoromethanesulfinyl chloride (5.00 g, 33.0 mmol, 1.00 equiv) in DCM (5.00 mL) was added dropwise under N₂ atmosphere. Then the mixture was slowly warmed up to room temperature and stirred at room temperature for 24 h. The reaction mixture was filtered through a short pad of Celite and concentrated in vacuo. By repeated recrystallization from toluene at -20 °C. The product was white solid (4.01 g, 15.2 mmol, 46.2% yield). Spectra were consistent with literature data¹.

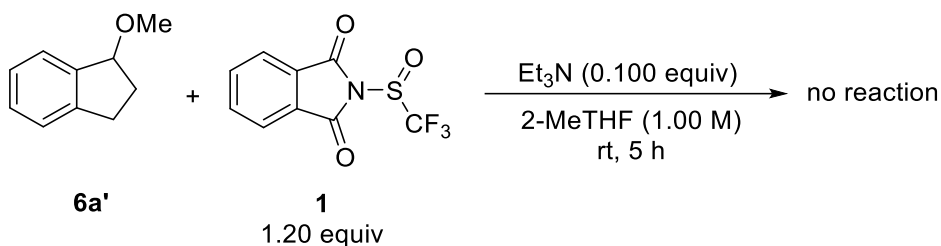
VI. Mechanistic studies

1. Control experiments: the effect of hydroxy group (-OH)

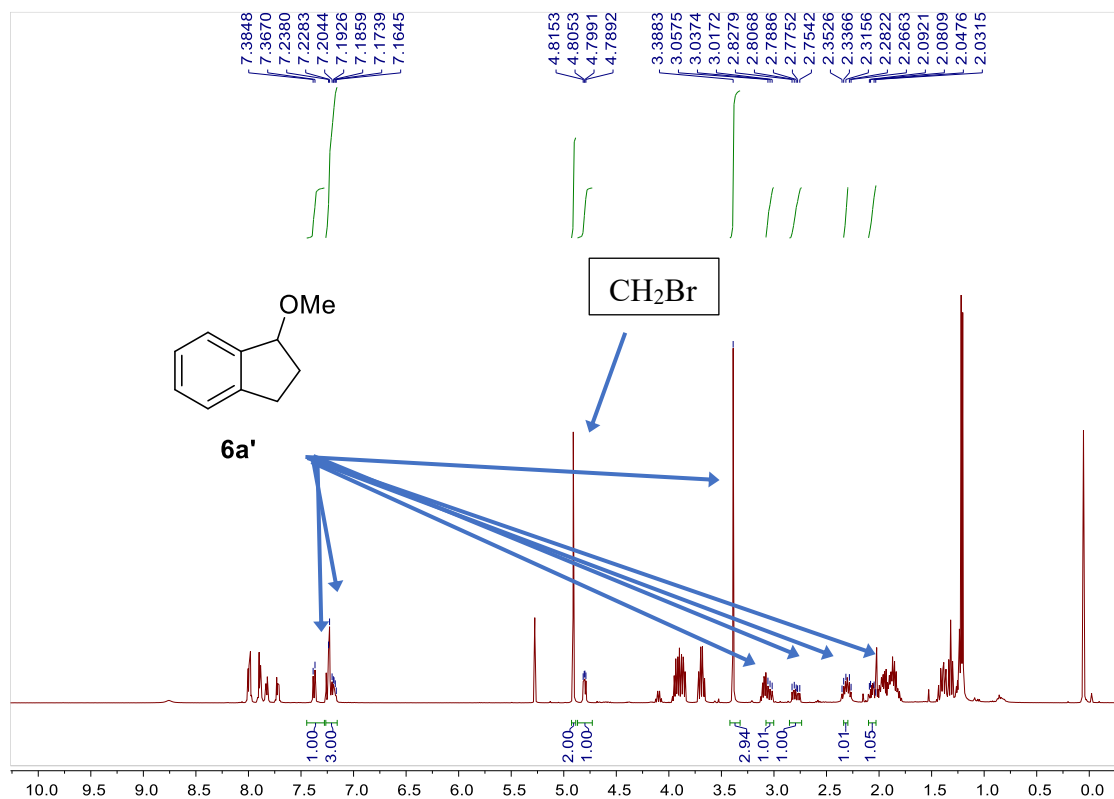


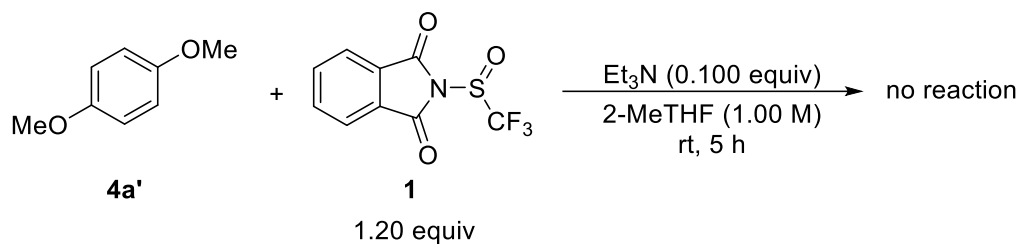
A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 2-((trifluoromethyl)sulfinyl)isoindoline-1,3-dione **1** (31.6 mg, 0.120 mmol, 1.20 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry 2-MeTHF (1.00 mL, 0.100 M), 1-(methoxymethyl)-4-nitrobenzene **2a'** (16.7 mg, 0.100 mmol, 1.00 equiv) and Et_3N (1.00 mg, 0.0100 mmol, 0.100 equiv) was added under N_2 atmosphere. The mixture was allowed to stir for 5 h at room temperature, then the reaction was monitored by TLC (5:1 petroleum etherhexanes: ethyl acetate), and no reaction occurred. The solvent was removed by rotary evaporation, the crude mixture was subjected to ^1H NMR spectroscopy in the presence of CH_2Br_2 (17.4 mg, 0.100 mmol).





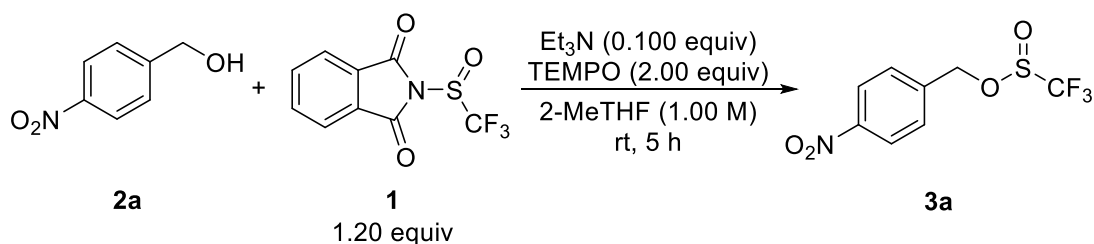
A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 2-((trifluoromethyl)sulfinyl)isoindoline-1,3-dione **1** (31.6 mg, 0.120 mmol, 1.20 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry 2-MeTHF (1.00 mL, 0.100 M), 1-methoxy-2,3-dihydro-1*H*-indene **6a'** (14.8 mg, 0.100 mmol, 1.00 equiv) and Et₃N (1.00 mg, 0.0100 mmol, 0.100 equiv) was added under N₂ atmosphere. The mixture was allowed to stir for 5 h at room temperature, then the reaction was monitored by TLC (5:1 petroleum etherhexanes: ethyl acetate), and no reaction occurred. The solvent was removed by rotary evaporation, the crude mixture was subjected to ¹H NMR spectroscopy in the presence of CH₂Br₂ (17.4 mg, 0.100 mmol).





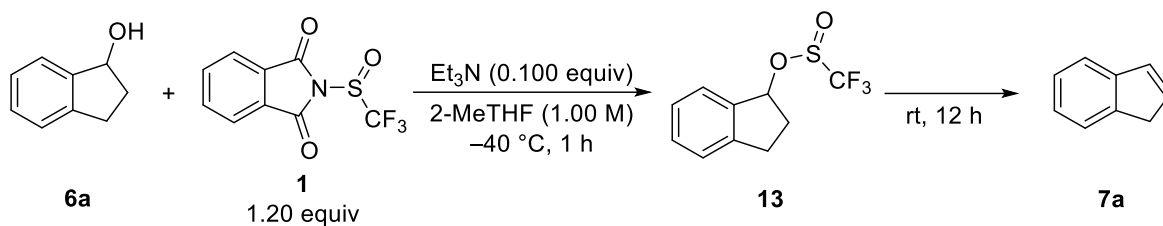
A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 2-((trifluoromethyl)sulfinyl)isoindoline-1,3-dione **1** (31.6 mg, 0.120 mmol, 1.20 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry 2-MeTHF (1.00 mL, 0.100 M), 1,4-dimethoxybenzene **4a'** (13.8 mg, 0.100 mmol, 1.00 equiv) and Et₃N (1.00 mg, 0.0100 mmol, 0.100 equiv) was added under N₂ atmosphere. The mixture was allowed to stir for 5 h at room temperature, then the reaction was monitored by TLC (5:1 petroleum etherhexanes: ethyl acetate), and no desired product was formed according to TLC. The solvent was removed by rotary evaporation, the crude mixture was subjected to ¹H NMR spectroscopy in the presence of CH₂Br₂ (17.4 mg, 0.100 mmol).

2. Radical trapping experiment: addition of radical scavenger

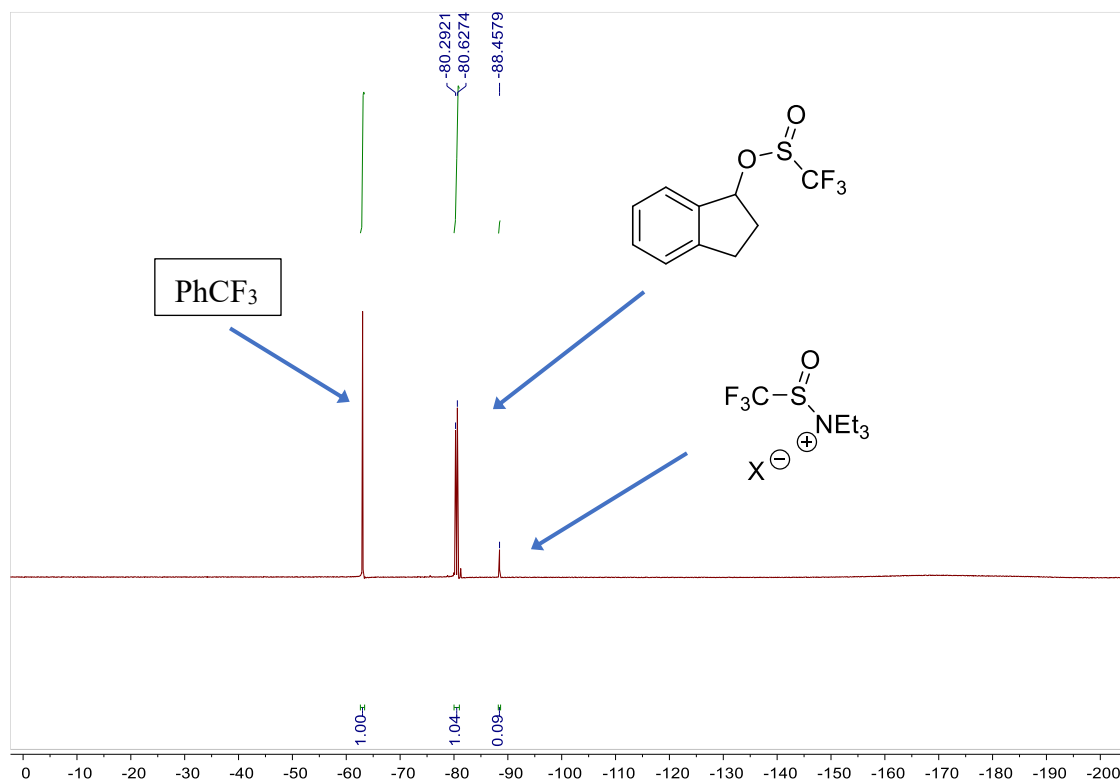


A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 4-nitrobenzyl alcohol **2a** (15.3 mg, 0.100 mmol, 1.00 equiv), TEMPO (31.2 mg, 0.200 mmol, 2.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then Et₃N (1.00 mg, 0.0100 mmol, 0.100 equiv) and dry 2-MeTHF (1.00 mL, 0.100 M), was added under N₂ atmosphere. The mixture was allowed to stir for 5 h at room temperature, then the reaction was monitored by TLC (5:1 petroleum etherhexanes: ethyl acetate), and desired product **3a** was formed in >99% yield according to ¹⁹F NMR.

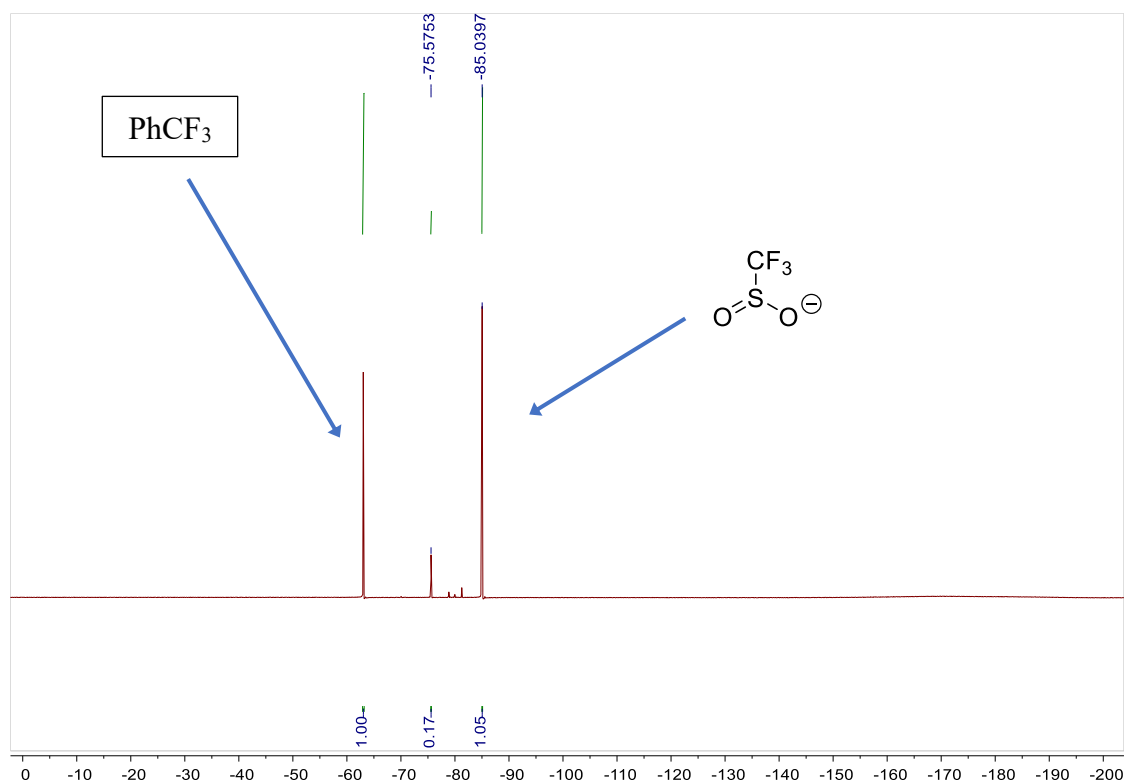
3. Evidence on the formation of O-(SO)CF₃ specie



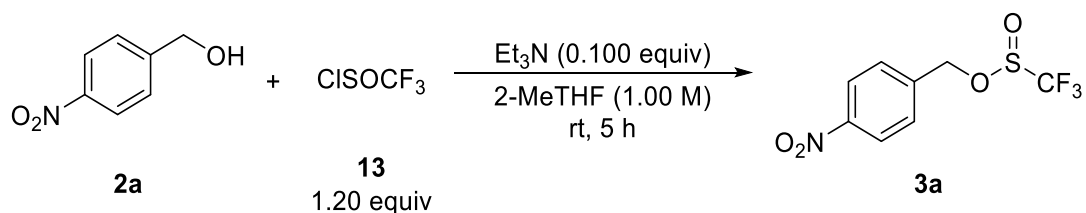
A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with 2-((trifluoromethyl)sulfinyl)isoindoline-1,3-dione (31.6 mg 0.120 mmol, 1.20 equiv), 2,3-dihydro-1H-inden-1-ol **6a** (13.4 mg, 0.300 mmol, 1.00 equiv). The mixture was evacuated and backfilled with nitrogen for three times. Then dry 2-MeTHF (1.00 mL, 0.100 M) and Et₃N (1.00 mg, 0.0100 mmol, 0.100 equiv) was added under N₂ atmosphere. The mixture was allowed to stir for 1 h at -40 °C. The crude mixture was subjected to ¹⁹F NMR spectroscopy in the presence of PhCF₃ (14.6 mg, 0.100 mmol). Then the mixture was allowed to stir for 12 h at room temperature, then the crude mixture was subjected to ¹⁹F NMR spectroscopy in the presence of PhCF₃ (14.6 mg, 0.100 mmol).



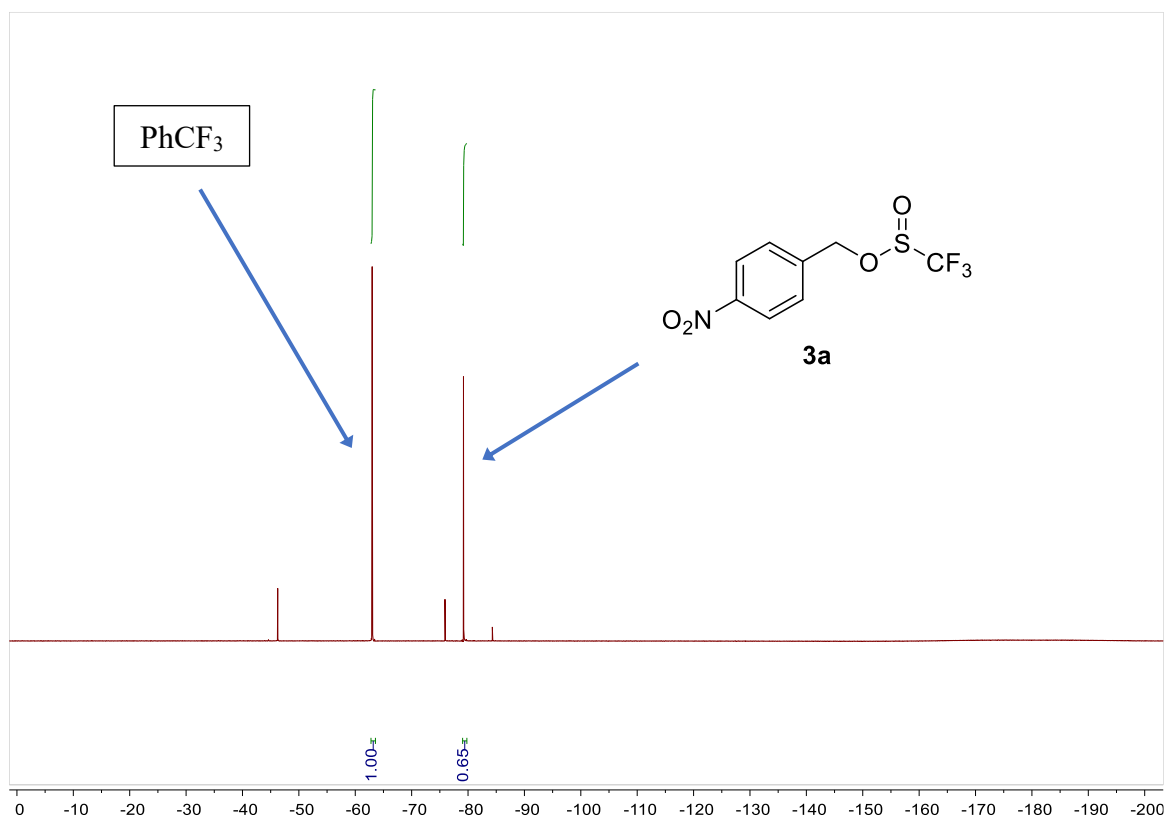
The NMR tube was then placed at room temperature for 12 h:



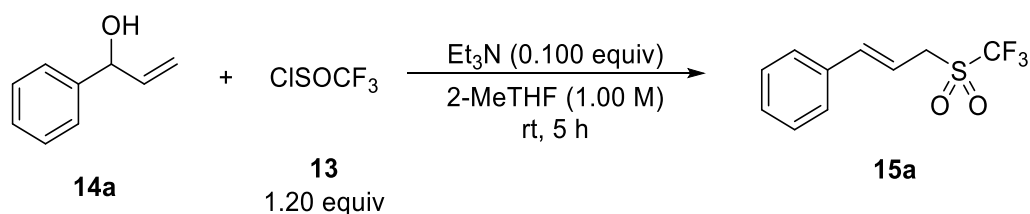
4. Effect of CF_3SOCl for O-S(O)CF_3 bond formation of (4-nitrophenyl)methanol



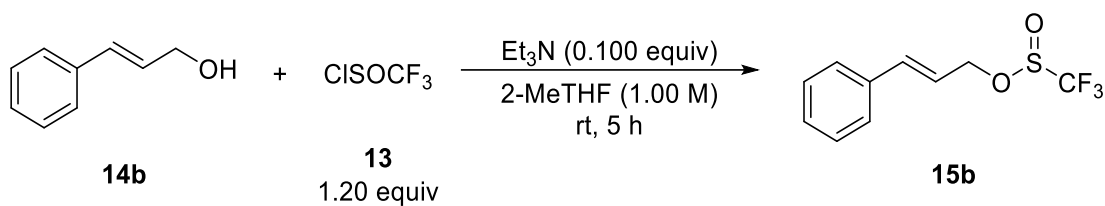
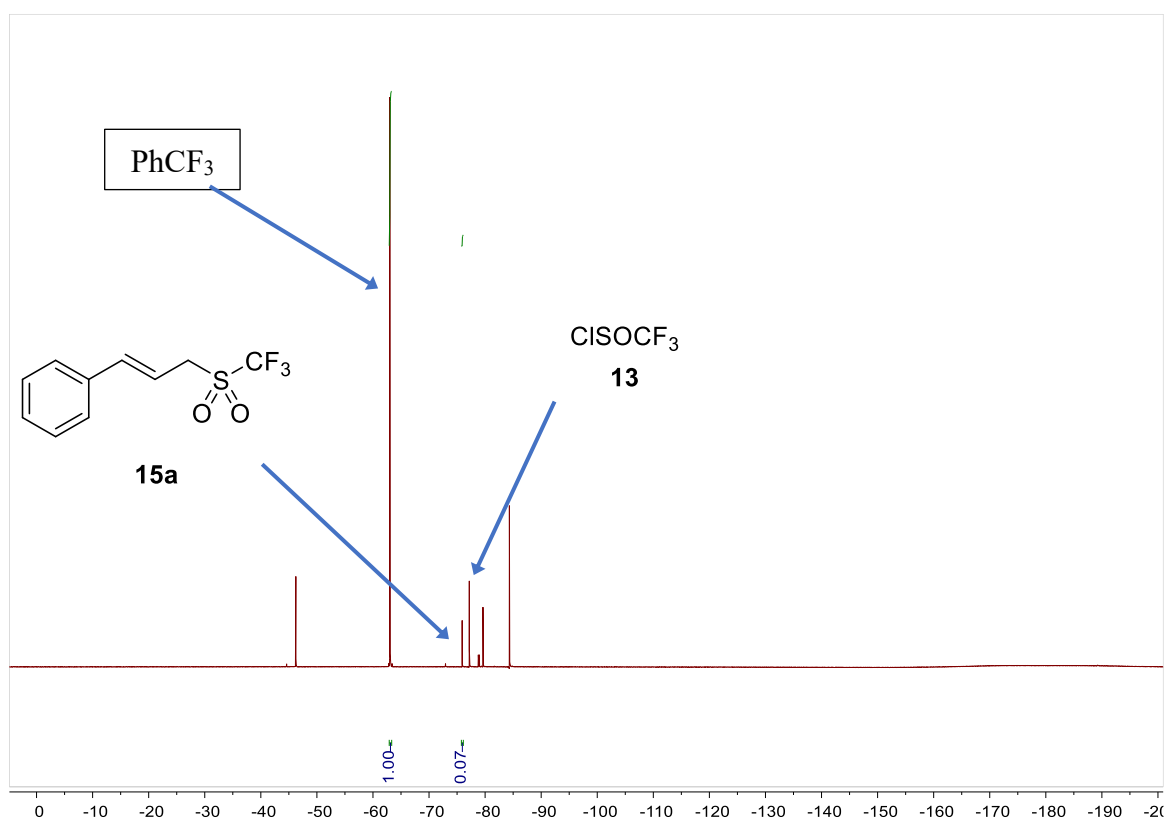
A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with Trifluoromethanesulfinic chloride (0.600 mmol, 1.20 equiv, 91.5 mg). The mixture was evacuated and backfilled with nitrogen for three times. Then dry 2-MeTHF (5.00 mL, 0.100 M), (4-nitrophenyl)methanol (0.500 mmol, 1.00 equiv, 76.6 mg) and Et_3N (0.0500 mmol, 0.100 equiv, 5.06 mg) were added under N_2 atmosphere. The mixture was allowed to stir for 5 h at room temperature. The crude mixture was subjected to ^{19}F NMR spectroscopy in the presence of PhCF_3 (73.1 mg, 0.500 mmol) as an internal standard. The **3a** ^{19}F NMR yield was 65% yield.



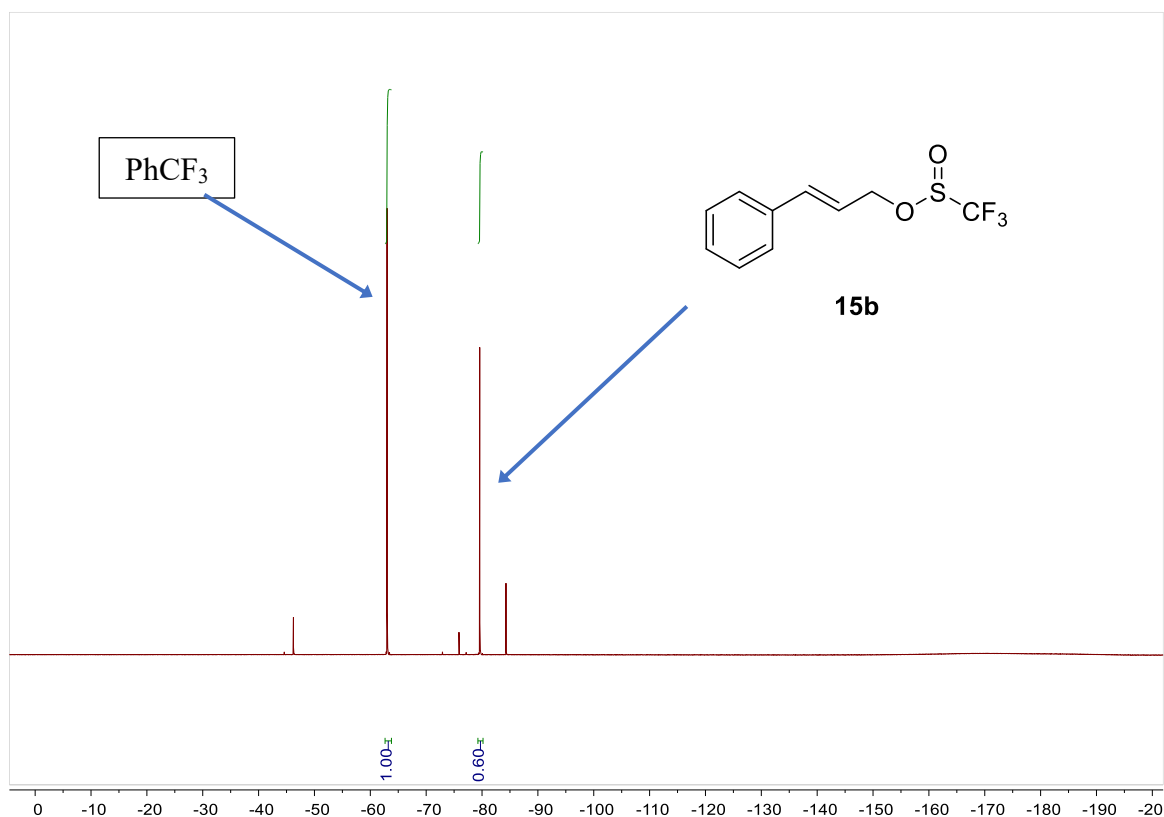
5. Effect of CF_3SOCl for O-S(O)CF_3 or SO_2CF_3 bond formation of Allylic Alcohols



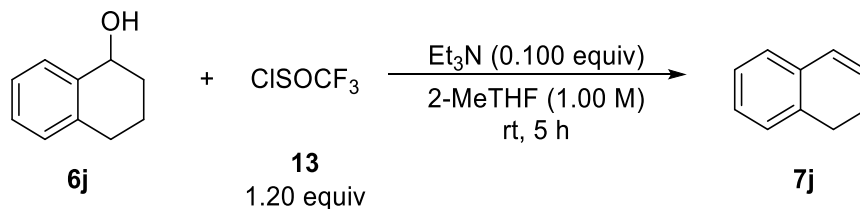
A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with Trifluoromethanesulfinic chloride (0.600 mmol, 1.20 equiv, 91.5 mg). The mixture was evacuated and backfilled with nitrogen for three times. Then dry 2-MeTHF (5.00 mL, 0.100 M), 1-phenylprop-2-en-1-ol (0.500 mmol, 1.00 equiv, 68.6 mg) and Et_3N (0.0500 mmol, 0.100 equiv, 5.06 mg) were added under N_2 atmosphere. The mixture was allowed to stir for 5 h at room temperature. The crude mixture was subjected to ^{19}F NMR spectroscopy in the presence of PhCF_3 (73.1 mg, 0.500 mmol) as an internal standard. The **15a** ^{19}F NMR yield was 7% yield.



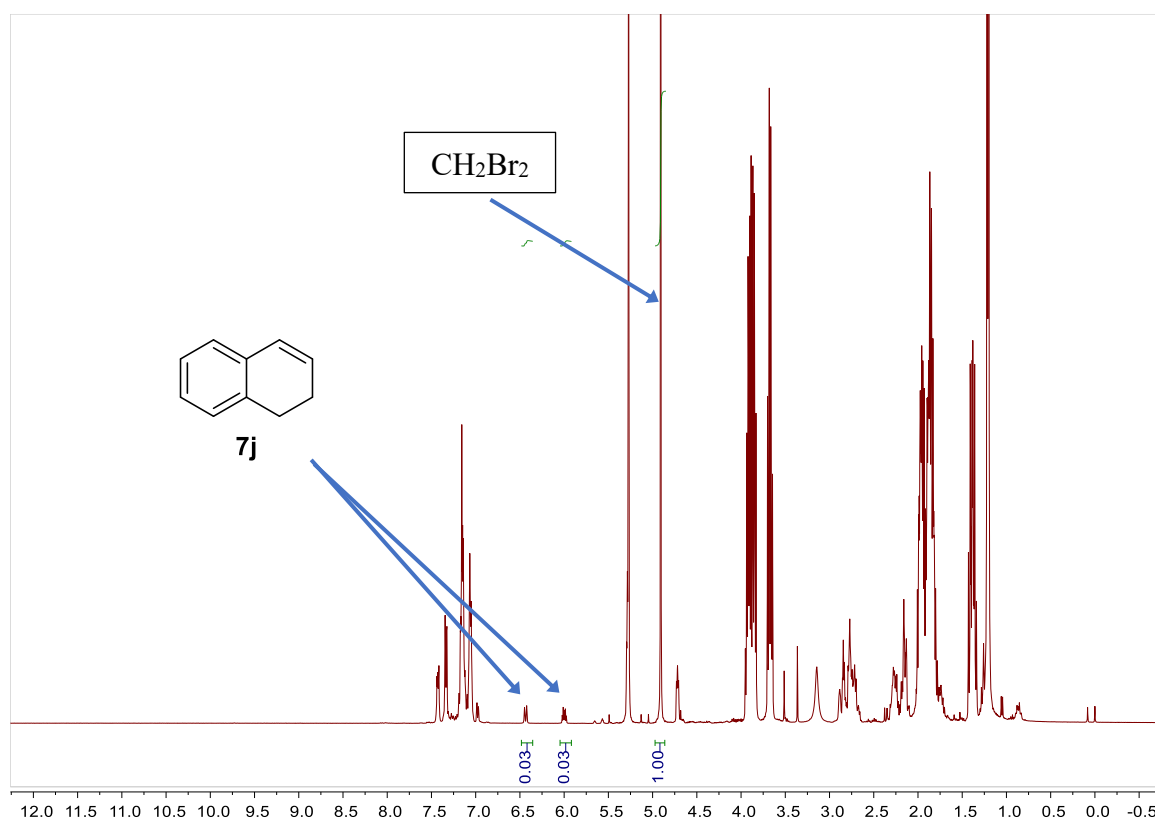
A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with Trifluoromethanesulfinic chloride (0.600 mmol, 1.20 equiv, 91.5 mg). The mixture was evacuated and backfilled with nitrogen for three times. Then dry 2-MeTHF (5.00 mL, 0.100 M), 3-phenylprop-2-en-1-ol (0.500 mmol, 1.00 equiv, 67.1 mg) and Et₃N (0.0500 mmol, 0.100 equiv, 5.06 mg) were added under N₂ atmosphere. The mixture was allowed to stir for 5 h at room temperature. The crude mixture was subjected to ¹⁹F NMR spectroscopy in the presence of PhCF₃ (73.1 mg, 0.500 mmol) as an internal standard. The **15b** ¹⁹F NMR yield was 60% yield.



6. Effect of CF_3SOCl for double bond formation of Allylic Alcohols



A 120 °C oven-dried 25-mL glass schlenck, equipped with a stir bar, was charged with Trifluoromethanesulfinic chloride (0.600 mmol, 1.20 equiv, 91.5 mg). The mixture was evacuated and backfilled with nitrogen for three times. Then dry 2-MeTHF (5.00 mL, 0.100 M), 1,2,3,4-tetrahydronaphthalen-1-ol (0.500 mmol, 1.00 equiv, 74.1 mg) and Et_3N (0.0500 mmol, 0.100 equiv, 5.06 mg) were added under N_2 atmosphere. The mixture was allowed to stir for 5 h at room temperature. The crude mixture was added 25.0 mL water, extracted by DCM (25.0 mL \times 3). The combined organic layers were extracted by brine (25.0 mL \times 2), dried over by Na_2SO_4 and filtered. The solvent was removed by rotary evaporation. The mixture was subjected to ^{19}F NMR spectroscopy in the presence of CH_2Br_2 (86.9 mg, 0.500 mmol) as an internal standard. The **7j** ^1H NMR yield was 6% yield.



VII. References

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VIII. DFT Calculation

All calculations were performed using Gaussian 16, Revision A.03 package.¹ All of the reactants, intermediates, transition states, products were optimized by the DFT with the M06-2X functional.² For geometry optimizations and frequency calculations, we employed 6-31G(d) basis sets for H, C, O, S, F, and N. All the stationary structures were characterized with no imaginary frequency and the transition state structures (TSs) were characterized with a single imaginary frequency. Intrinsic reaction coordinate (IRC) calculations were performed on the TSs. The solvent effect of Tetrahydrofuran was evaluated through the SMD method,³ in which a better basis system was used. We employed 6-311++G(d,p) basis sets for all atoms. All reported energies are free energies at a concentration of 1 M and a temperature of 298.15 K. Because no standard quantummechanics-based approach is available for accurate prediction of the entropy in solution, we adopted the approximate approach proposed by Martin et al.⁴

¹ Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**.

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³ A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B.*, **2009**, *113*, 6378.

⁴ R. L. Martin, P. J. Hay, L. R. Pratt, *J. Phys. Chem. A*, **1998**, *102*, 3565.

Cartesian coordinates of the optimized structures:

I

E = -1323.075672 a.u.

0 1

C	-2.26669100	1.92735400	2.79915200
C	-0.88342600	1.98492700	2.81442900
C	-0.20281300	3.19545000	2.78331600
C	-0.87167300	4.40705800	2.73518900
C	-2.26709200	4.36175400	2.71981100
C	-2.95266400	3.14270700	2.75121700
H	-2.78437800	0.97434200	2.82225000
H	-0.32623600	5.34436900	2.70915100
H	-2.83244900	5.28704400	2.68156600
H	-4.03763400	3.14448100	2.73690500
C	0.10266400	0.86635200	2.86353200
C	1.26050200	2.92532800	2.79846800
N	1.38056200	1.51014800	2.89449100
O	-0.09300800	-0.31434000	2.87936500
O	2.18170300	3.69409100	2.74242800
S	2.91853400	0.76915000	2.63309300
O	2.78595800	-0.34979400	1.68275700
C	2.97516300	0.00860800	4.33258100
F	4.15511200	-0.59305700	4.44167800
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F	2.01508900	-0.86756800	4.55003600

P

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C	-2.61272300	2.38590900	0.54136600
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C	-4.53037300	3.33451700	-0.60073800
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C	-3.17224300	0.30041300	2.00110700
C	-5.47258100	0.26055900	1.52532400
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H	-4.40971000	-1.23481600	2.89390700
H	-2.19030900	0.06486600	2.39588600

TS4-5

E = -1526.409606 a.u.

0 1

C	0.71853700	2.77299200	1.94498400
C	1.31333500	1.77948900	2.71431800
C	2.67010200	1.88037000	3.06198800
C	3.43673600	2.97871900	2.68107900
C	2.83628900	3.96732000	1.90754000
C	1.49088000	3.86201700	1.54006000
H	-0.33052900	2.70966500	1.66935500
H	4.47376600	3.06274100	2.99169100
H	3.41167900	4.83200100	1.59223400
H	1.03924600	4.64568100	0.93922100
C	3.03726400	0.68657800	3.82931100
O	3.10342200	1.71498900	5.69946500
C	0.74408300	0.50675400	3.27766600
H	0.16963000	0.73808000	4.19081500
H	0.09625800	-0.03331200	2.57487100
C	1.99708300	-0.23665700	3.72060600
H	1.93300000	-1.09925800	4.37906000
H	2.45388800	-0.83688300	2.42623400
H	4.04909600	0.44525300	4.12628300
S	2.06232900	1.33178600	6.74723600
O	0.68316400	1.18006000	6.18847000
C	2.55962100	-0.49752600	6.99369200
F	1.55971900	-1.34139800	6.71144200
F	3.61705800	-0.86754100	6.24949300
F	2.89791000	-0.68830400	8.27650000
N	2.72327900	-1.43109000	1.38561300
C	2.88188800	-0.33865200	0.38636900
H	2.08790900	0.38477300	0.59850300
H	3.82613800	0.16255300	0.62308900
C	1.54799600	-2.31548200	1.18445000
H	1.20983200	-2.59717000	2.18914500
H	0.76190100	-1.69132300	0.74847200
C	3.97703500	-2.11442400	1.79383700
H	4.50161000	-1.40248200	2.44289200
H	3.67836000	-2.95404900	2.42951000
C	2.81944500	-0.74716100	-1.08036600
H	2.97511300	0.14456200	-1.69357800

H	3.57967700	-1.48180800	-1.35292000
H	1.83662800	-1.15155100	-1.33857700
C	4.91528900	-2.57108800	0.68452400
H	5.29733900	-1.72277700	0.11048300
H	5.77451300	-3.06895700	1.14220600
H	4.44419900	-3.27548400	-0.00424300
C	1.77202300	-3.57005200	0.34961100
H	2.49568600	-4.24105400	0.82039000
H	0.82549800	-4.11220900	0.27436100
H	2.11339600	-3.34429100	-0.66301500

Int5

E = -1526.421065 a.u.

0 1

C	0.68623200	2.07823700	2.01267800
C	1.22232300	1.13902300	2.88456200
C	2.58861200	1.18077800	3.22514600
C	3.41886100	2.18432600	2.73072400
C	2.87619100	3.12001800	1.85082800
C	1.52778000	3.06259300	1.48522700
H	-0.37149300	2.06718700	1.76310100
H	4.44842800	2.25445600	3.06743100
H	3.50157000	3.91685400	1.45965300
H	1.12379600	3.80820200	0.80709300
C	2.88415300	0.02386900	4.08468600
O	3.69174700	1.84281900	5.90676200
C	0.57326800	0.03157500	3.66830200
H	0.08548100	0.52010900	4.53150800
H	-0.16103300	-0.57669100	3.12806800
C	1.75322100	-0.69235300	4.26341500
H	1.65578000	-1.54128700	4.92943900
H	2.66404000	-0.60614500	2.06387800
H	3.84162500	-0.14886100	4.55687400
S	2.39515100	1.97020100	6.66375000
O	1.17126300	1.95041100	5.78745500
C	2.28967500	0.19658400	7.39374700
F	1.09978000	-0.38738800	7.16615700
F	3.23188200	-0.64392200	6.92424700
F	2.45204000	0.24793500	8.72752300
N	2.85813700	-1.12479000	1.18640900
C	3.03952700	-0.03611000	0.15803800
H	2.30742200	0.73243400	0.42288800
H	4.02984600	0.38739100	0.34260500
C	1.62161900	-1.96529300	1.02054200

H	1. 34430300	-2. 25153200	2. 03992700
H	0. 85018000	-1. 28466800	0. 64874300
C	4. 10736600	-1. 88354400	1. 54532200
H	4. 69098900	-1. 18916500	2. 15716500
H	3. 78608800	-2. 69734600	2. 20112900
C	2. 85968500	-0. 45990900	-1. 28970300
H	3. 04473100	0. 41754400	-1. 91467300
H	3. 55028100	-1. 24516000	-1. 60269000
H	1. 83625200	-0. 78773700	-1. 48998700
C	4. 94568200	-2. 38193900	0. 38030100
H	5. 34222700	-1. 55401100	-0. 21245400
H	5. 79986700	-2. 92497100	0. 79287100
H	4. 40364000	-3. 06147900	-0. 27946200
C	1. 76332100	-3. 20322300	0. 15067700
H	2. 46466100	-3. 92070500	0. 58410600
H	0. 78683400	-3. 69220300	0. 10456500
H	2. 07349100	-2. 97731100	-0. 87080400

Int4

E = -1526.474977 a.u.

0 1

C	0. 56839800	2. 14597500	1. 73008900
C	1. 14696200	1. 40609700	2. 75708800
C	2. 47383000	1. 64194900	3. 11905100
C	3. 23456800	2. 62088200	2. 49160900
C	2. 65213200	3. 36422600	1. 46649300
C	1. 32958900	3. 12349400	1. 08793200
H	-0. 46201100	1. 96952400	1. 43394700
H	4. 26250300	2. 80118600	2. 79384400
H	3. 22829200	4. 12947400	0. 95619100
H	0. 88873700	3. 70448200	0. 28348800
C	2. 87406300	0. 74914900	4. 26162800
O	2. 98736600	1. 62001400	5. 44880100
C	0. 53900100	0. 33345000	3. 62639700
H	-0. 10256900	0. 78122500	4. 39440700
H	-0. 06184800	-0. 38276700	3. 05811800
C	1. 77010100	-0. 32249800	4. 27708600
H	1. 55991300	-0. 74714800	5. 25755200
H	2. 13669800	-1. 12124300	3. 62624600
H	3. 87309000	0. 31967500	4. 16304900
S	2. 20324000	1. 44751300	6. 84920700
O	0. 77660400	1. 12127600	6. 67551700
C	2. 97603700	-0. 20756100	7. 36755900
F	2. 03709400	-1. 13139400	7. 51316300

F	3. 89223900	-0. 64710800	6. 50809600
F	3. 56757500	-0. 00615200	8. 54414800
N	2. 84962500	-1. 21643000	1. 20633900
C	3. 31987000	-0. 14679200	0. 34434100
H	2. 65655100	0. 71636800	0. 48392300
H	4. 30415200	0. 16111600	0. 72106800
C	1. 53946400	-1. 76501700	0. 91838800
H	1. 07806900	-2. 07359300	1. 86983200
H	0. 92583600	-0. 93854200	0. 53530600
C	3. 84304600	-2. 12292800	1. 74845700
H	4. 47434900	-1. 56069300	2. 45438000
H	3. 30622300	-2. 87002500	2. 34821300
C	3. 40739300	-0. 43526300	-1. 16061400
H	3. 83148800	0. 43041900	-1. 68027200
H	4. 02796800	-1. 30735300	-1. 38439500
H	2. 41141800	-0. 61125600	-1. 57990500
C	4. 77171100	-2. 83832000	0. 75836100
H	5. 40593200	-2. 11926700	0. 23050900
H	5. 43136100	-3. 52893900	1. 29406300
H	4. 21057300	-3. 40742900	0. 01194700
C	1. 46531900	-2. 96154200	-0. 04008600
H	1. 97686700	-3. 83122900	0. 38517600
H	0. 42101400	-3. 24490200	-0. 20834500
H	1. 92198500	-2. 74070600	-1. 00852300

Int1

E = -1615.3143 a.u.

O 1

S	3. 06922900	0. 49098600	4. 75114100
O	2. 47024100	-0. 64991400	5. 45453500
C	4. 59468400	-0. 26563700	3. 95380200
F	5. 28933200	-0. 93010500	4. 86065000
F	4. 24414300	-1. 11939400	2. 99416200
F	5. 34535600	0. 69184100	3. 42432400
N	1. 64829900	0. 21910600	2. 69154100
C	1. 22388900	-1. 17522400	2. 53747600
H	2. 09664500	-1. 81248800	2. 70963300
H	0. 53178700	-1. 38399100	3. 36032800
C	2. 46959800	0. 79131200	1. 61903600
H	3. 15504400	1. 51707700	2. 08334100
H	3. 08882600	-0. 01824200	1. 22154600
C	0. 63645300	1. 11790200	3. 25305400
H	0. 50079200	0. 83203400	4. 30663200
H	1. 06894400	2. 12567100	3. 25507200

C	0.59544500	-1.56383900	1.19706400
H	0.30856400	-2.61958700	1.22447400
H	-0.29522600	-0.97500100	0.96459400
H	1.30979800	-1.43992500	0.37715200
C	-0.74649100	1.13162300	2.59808800
H	-1.23702600	0.15872500	2.69579100
H	-1.37577800	1.86810900	3.10705900
H	-0.70772700	1.39209600	1.53813700
C	1.74343100	1.49900500	0.47314700
H	1.20373700	2.38088300	0.82971500
H	2.48014200	1.84191100	-0.25959600
H	1.03462000	0.84181000	-0.03732000
C	5.96386400	5.47589200	7.04251300
C	5.33752900	4.47092900	6.33370000
C	5.20122900	3.19021800	6.85472500
C	5.68267400	2.84788300	8.10386200
C	6.32280500	3.85971900	8.83041500
C	6.46086300	5.14775100	8.31067900
H	6.06369100	6.47426100	6.62913600
H	5.57000700	1.84492500	8.50166000
H	6.71881000	3.63974000	9.81655100
H	6.96277200	5.90665900	8.90234400
C	4.68398700	4.44360500	4.97169600
C	4.47805000	2.43968700	5.79383300
N	4.18957800	3.12450000	4.73629900
O	4.58593500	5.36339500	4.20449600
O	4.18611000	1.16710900	5.98352800

TS2-3

E = -2039.320436 a.u.

0 1

S	2.08821500	0.84967900	4.58944000
O	2.02149700	-0.57190000	4.96675400
C	3.75311800	0.69513600	3.63138400
F	4.67841800	0.32301200	4.49384400
F	3.58834000	-0.31813200	2.76583400
F	4.17149800	1.74306200	2.95657100
N	0.89743300	0.82892100	2.76866800
C	0.64315600	-0.62006500	2.55560800
H	1.56330200	-1.15173000	2.80019000
H	-0.08603400	-0.92450700	3.31121800
C	1.59521500	1.55291000	1.66054700
H	2.09938800	2.39153100	2.15233400
H	2.34303900	0.86849600	1.25765400

C	-0.30018900	1.56839400	3.26037900
H	-0.40749100	1.33655400	4.32673700
H	-0.04978500	2.62735900	3.18839400
C	0.18445600	-1.03530800	1.16116900
H	0.05698500	-2.12144500	1.16279900
H	-0.76555600	-0.58507300	0.86822700
H	0.93504700	-0.79531500	0.40386100
C	-1.63098200	1.26586400	2.57735500
H	-1.93460100	0.22489000	2.71424000
H	-2.39305200	1.89225300	3.04979000
H	-1.62730700	1.49210500	1.51045500
C	0.71966800	2.10463400	0.53769600
H	0.04061200	2.88186500	0.89778800
H	1.38903600	2.57751400	-0.18690100
H	0.14050300	1.34419900	0.01060600
C	6.89545000	4.80721400	7.73532000
C	5.98547200	4.08765100	6.98379100
C	5.34149200	2.96869400	7.49528100
C	5.57585400	2.51542900	8.78049600
C	6.49452400	3.23424700	9.55105700
C	7.14267000	4.36121200	9.03731400
H	7.38424300	5.68562800	7.32644300
H	5.05883000	1.64412600	9.16923800
H	6.70781000	2.91676000	10.56693600
H	7.84731100	4.89869700	9.66425400
C	5.45981700	4.32203800	5.59576400
C	4.39802000	2.48632800	6.43947900
N	4.56459600	3.28244700	5.33723900
O	5.73860000	5.22864800	4.84738700
O	3.61086400	1.55105600	6.53621600
O	2.35935600	3.16422600	4.07819000
H	3.70315600	3.33107500	4.63955100
C	1.47006300	4.05734400	4.68065200
C	1.99151300	4.65297100	5.98588900
C	1.32778700	5.33362200	3.81665100
C	2.62601600	5.87138600	5.73362600
C	1.96032200	4.11820800	7.26775300
C	2.50615100	6.22267400	4.26710500
H	0.38387100	5.84379300	4.04578400
H	1.34923400	5.08684500	2.75051600
C	3.27390100	6.55117000	6.75947600
C	2.59727300	4.80642600	8.30235700
H	1.47356000	3.16482500	7.45806100
H	2.33443100	7.28936000	4.09438900

H	3.43323700	5.94413900	3.75035900
C	3.25678800	6.00933600	8.04632000
H	3.79177800	7.48603900	6.56281500
H	2.59135700	4.39918800	9.30917000
H	3.76220300	6.52742100	8.85609900
H	0.48920200	3.58160700	4.86808900

Int2

E = -2039.351682 a.u.

O 1

S	2.65462600	1.08140700	4.82211400
O	2.24489400	-0.24041300	5.30927600
C	4.12398700	0.72751700	3.66435600
F	5.27106500	0.59068000	4.31308500
F	3.87229900	-0.40981600	3.02438600
F	4.24029000	1.70739700	2.78046100
N	1.05554000	0.71701800	2.88225400
C	0.81687200	-0.73411400	2.84960600
H	1.78797200	-1.23133400	2.91637700
H	0.29309000	-0.98795200	3.77606200
C	1.56033700	1.31913900	1.63657100
H	2.12389800	2.21069800	1.92032900
H	2.26739100	0.60174300	1.20493200
C	-0.00122700	1.48379300	3.55219600
H	0.06852100	1.25639000	4.62695800
H	0.25989900	2.53959300	3.43195900
C	0.06619600	-1.29948200	1.64175100
H	-0.05057400	-2.37966500	1.77442000
H	-0.92842700	-0.86464100	1.51711300
H	0.62692900	-1.14301200	0.71544800
C	-1.45209500	1.22536400	3.13672100
H	-1.75045800	0.19696800	3.36032500
H	-2.10754400	1.88764700	3.71132900
H	-1.62936400	1.41166700	2.07564000
C	0.53426600	1.75375600	0.58624300
H	-0.07823900	2.57877100	0.96247000
H	1.07050700	2.12622500	-0.29219500
H	-0.12845500	0.94811000	0.26290000
C	6.77806100	4.86450600	7.70518200
C	5.92514600	4.17045600	6.87130000
C	5.30619000	2.99657700	7.27822400
C	5.50741000	2.45268800	8.53188000
C	6.37089000	3.14842000	9.38720600
C	6.99337100	4.33105400	8.98265000

H	7. 25423200	5. 78419500	7. 38078500
H	5. 01544800	1. 53583700	8. 83907100
H	6. 56044200	2. 76301000	10. 38385400
H	7. 65600400	4. 84355800	9. 67274900
C	5. 42446300	4. 45018800	5. 47782200
C	4. 45739500	2. 60328900	6. 12329600
N	4. 51765600	3. 41355600	5. 11054000
O	5. 72795100	5. 38025400	4. 77590800
O	3. 76706400	1. 49757200	6. 18025500
O	2. 20611800	3. 99797800	3. 36626500
H	3. 08038500	3. 92112300	3. 80125900
C	1. 42319800	4. 94987800	4. 07426200
C	1. 73724900	4. 90919600	5. 55479900
C	1. 75803500	6. 40595100	3. 69687600
C	2. 59494100	5. 95933700	5. 89116100
C	1. 40368400	3. 92940100	6. 48248500
C	2. 84501700	6. 85215300	4. 69710000
H	0. 86213200	7. 02216900	3. 83068900
H	2. 06902100	6. 47182200	2. 65212300
C	3. 14051000	6. 03001400	7. 17035400
C	1. 95005300	4. 00070600	7. 76457000
H	0. 73472300	3. 11585800	6. 21063900
H	2. 77932700	7. 91559400	4. 94599500
H	3. 85226300	6. 66804600	4. 30570400
C	2. 81580300	5. 04350100	8. 10188100
H	3. 82432600	6. 83198000	7. 43646200
H	1. 70863700	3. 23978300	8. 50062100
H	3. 25212800	5. 07874400	9. 09622700
H	0. 37921200	4. 70488800	3. 84843100

Int3

E = -2039.381289 a.u.

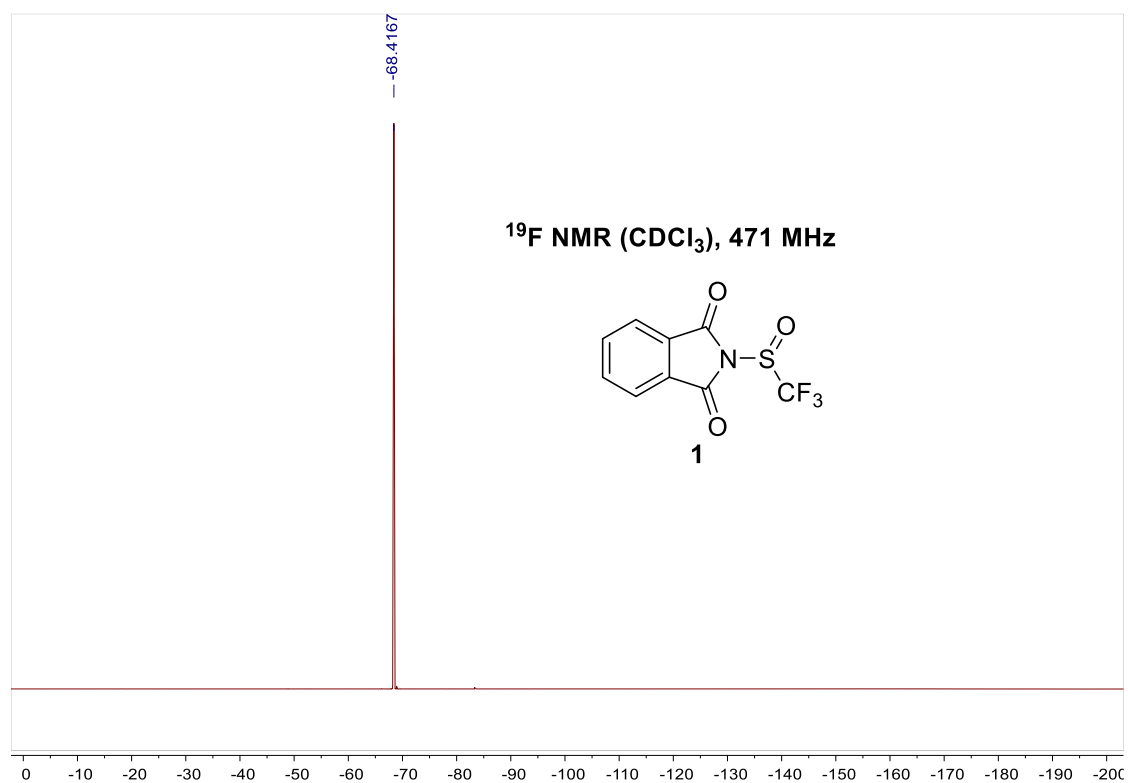
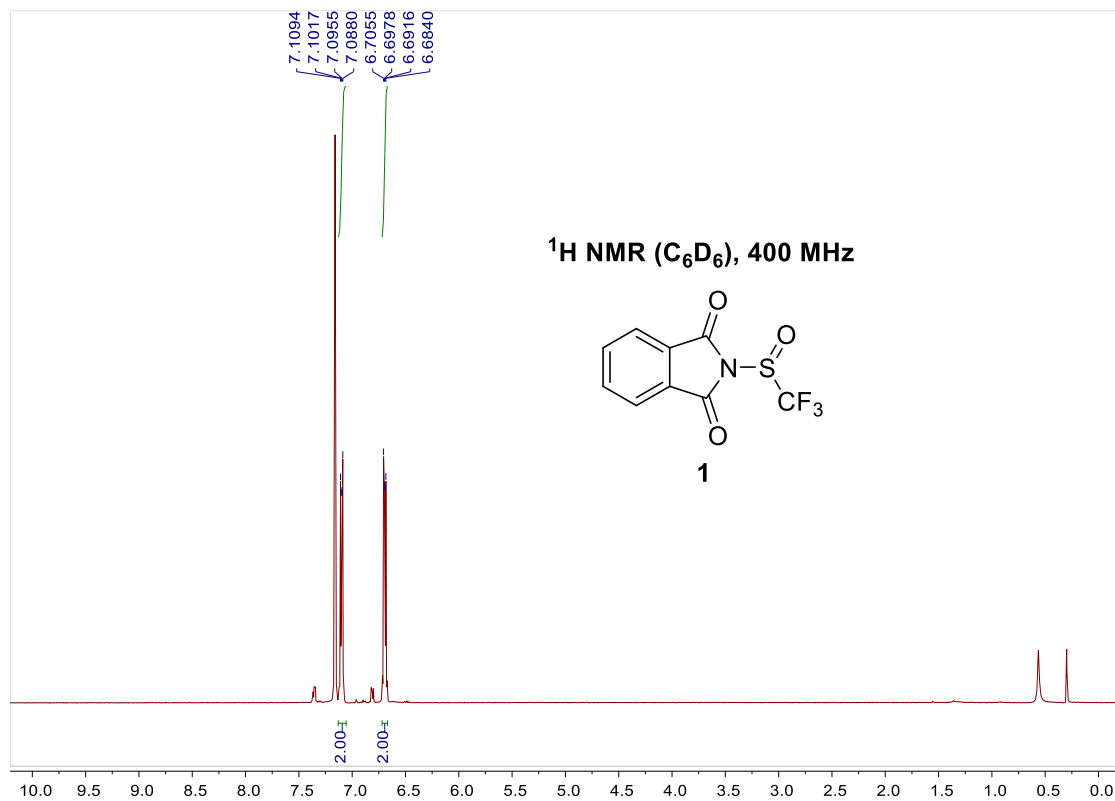
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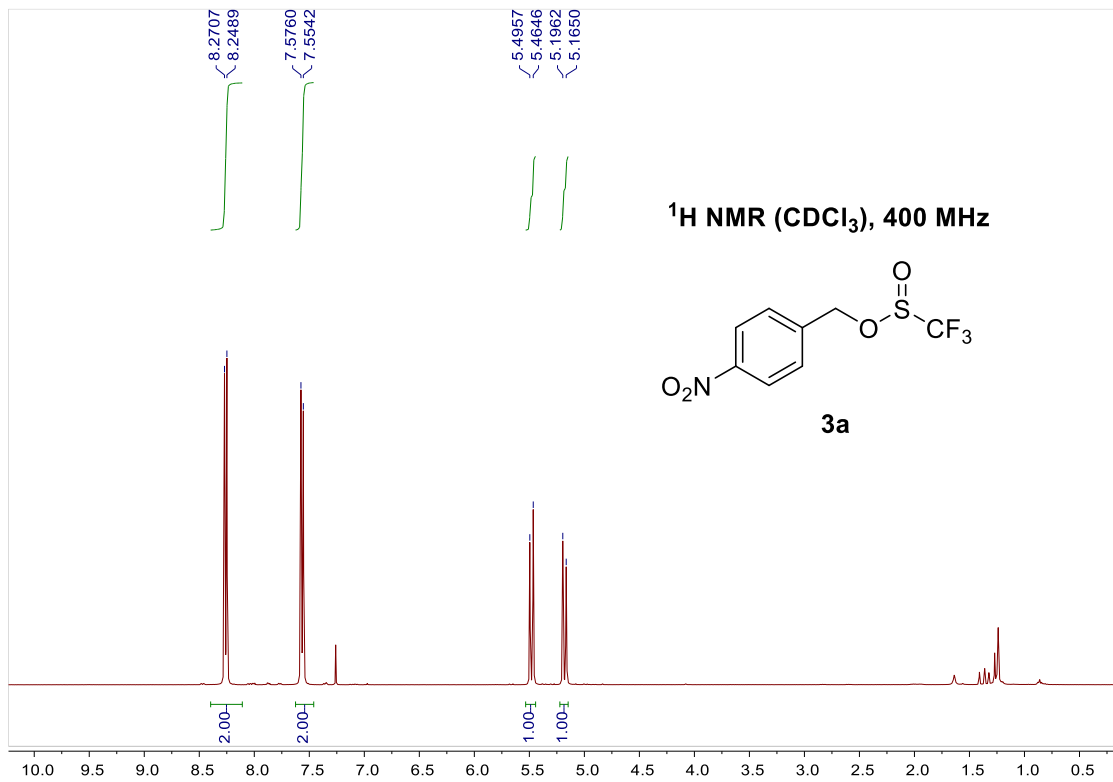
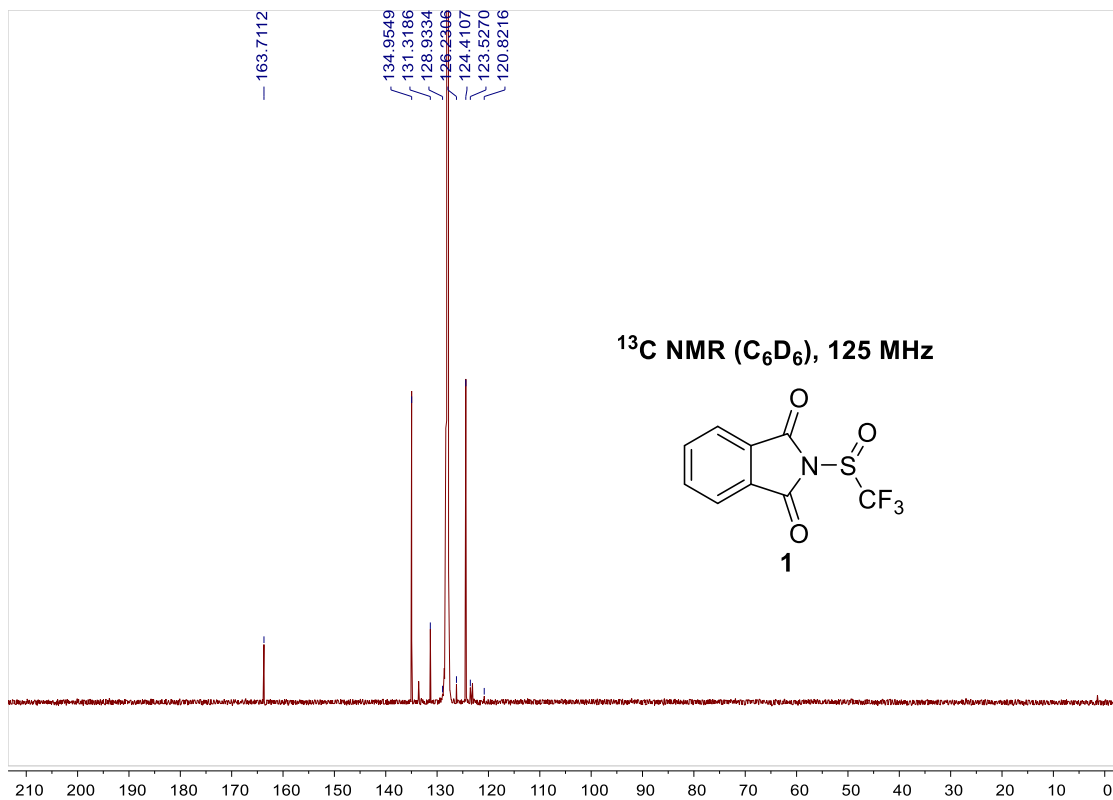
S	1. 75948100	0. 50145000	5. 41039900
O	0. 55058500	-0. 22253300	4. 98590900
C	3. 09566400	-0. 10181300	4. 22546800
F	3. 85582200	-0. 95709900	4. 90032400
F	2. 52273000	-0. 74180600	3. 22123600
F	3. 86604400	0. 86496100	3. 73256100
N	0. 26493400	0. 60713700	1. 93835700
C	0. 06320700	-0. 70549900	1. 36688200
H	0. 97902900	-1. 29464200	1. 51030700
H	-0. 71169900	-1. 20079600	1. 96462800
C	1. 28204300	1. 45188300	1. 35542500

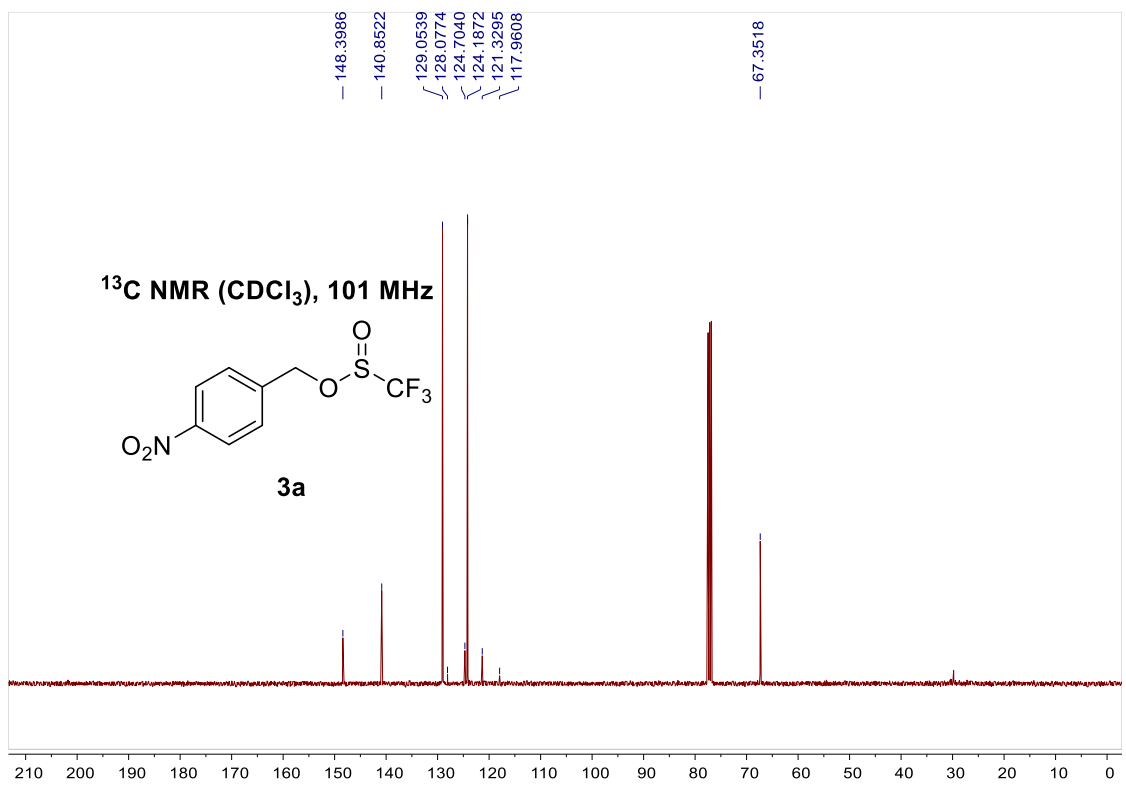
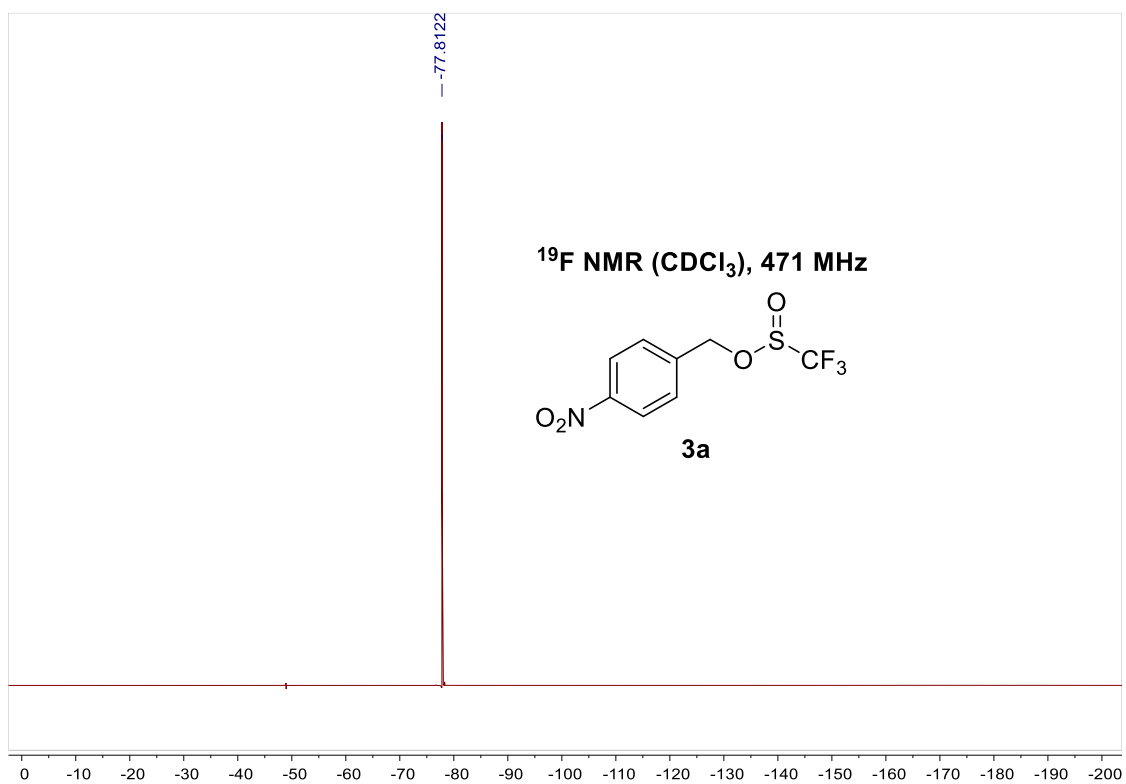
H	1. 78993100	1. 99677600	2. 16636300
H	2. 04006600	0. 79054200	0. 91677600
C	-0. 86915800	1. 23711300	2. 57640700
H	-1. 14490600	0. 63616500	3. 45310000
H	-0. 52440700	2. 20282100	2. 96640600
C	-0. 31049600	-0. 76108100	-0. 12132300
H	-0. 46891800	-1. 79804600	-0. 43686700
H	-1. 22070300	-0. 19339700	-0. 33554800
H	0. 49569600	-0. 34945200	-0. 73826400
C	-2. 12027300	1. 45793300	1. 71407400
H	-2. 54752200	0. 50045000	1. 39855200
H	-2. 88958500	1. 98642300	2. 28796000
H	-1. 89958300	2. 04112600	0. 81487600
C	0. 81972700	2. 47053400	0. 30492300
H	0. 12537600	3. 19492200	0. 74577200
H	1. 67459400	3. 03031100	-0. 08986900
H	0. 30855000	1. 98420400	-0. 53149000
C	6. 31457000	5. 52157000	7. 45765500
C	5. 66627700	4. 51465100	6. 76573500
C	5. 43478800	3. 26897400	7. 33441100
C	5. 84070200	2. 96961300	8. 62213400
C	6. 49814700	3. 97749400	9. 33245600
C	6. 73153900	5. 23195900	8. 75973000
H	6. 48104200	6. 49308300	7. 00379300
H	5. 64306600	1. 99509400	9. 05645300
H	6. 83346000	3. 78748100	10. 34698700
H	7. 24426800	5. 99239300	9. 34006600
C	5. 04313500	4. 53113800	5. 40591900
C	4. 66687000	2. 44514400	6. 35332300
N	4. 51329400	3. 25150000	5. 23082500
O	4. 97667800	5. 44388700	4. 61898300
O	4. 25312800	1. 31573600	6. 48659700
O	1. 79087700	2. 01319100	4. 70620200
H	3. 93199900	2. 97105100	4. 44835700
C	0. 87018100	2. 94419800	5. 34218800
C	1. 48242500	3. 56020200	6. 58111200
C	0. 68243700	4. 14178900	4. 39563300
C	1. 94135700	4. 85084100	6. 30450900
C	1. 65977200	2. 99299400	7. 83983000
C	1. 66718900	5. 23031200	4. 86995200
H	-0. 34691200	4. 49936600	4. 49690400
H	0. 83403100	3. 84504900	3. 35536400
C	2. 58831600	5. 59071700	7. 28973100
C	2. 30633800	3. 73719600	8. 82674100

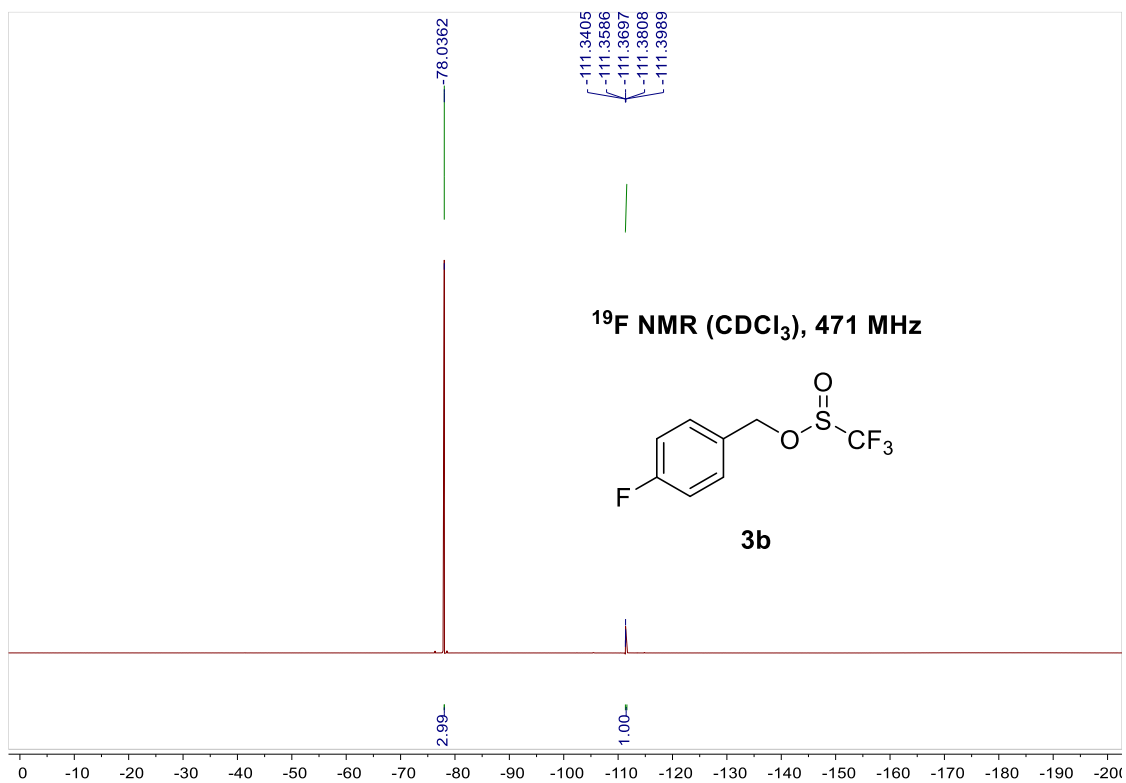
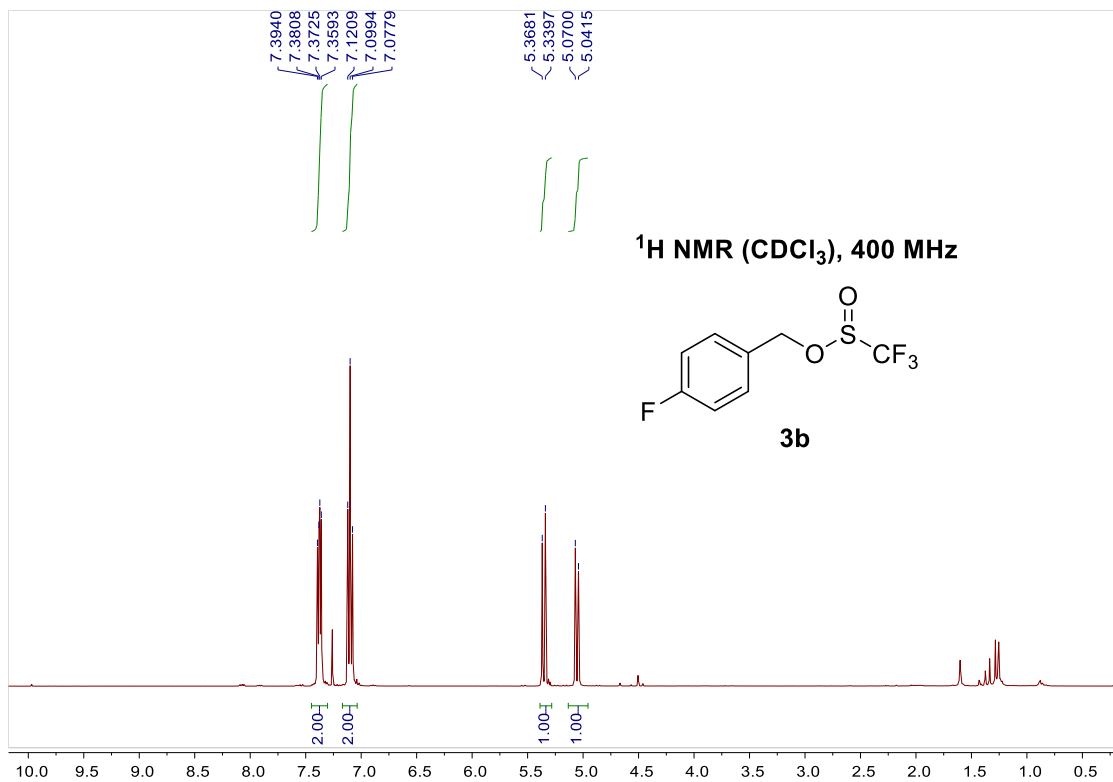
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C	2. 76519200	5. 02631800	8. 55297400
H	2. 95861700	6. 58950300	7. 07402800
H	2. 45534900	3. 31008900	9. 81341000
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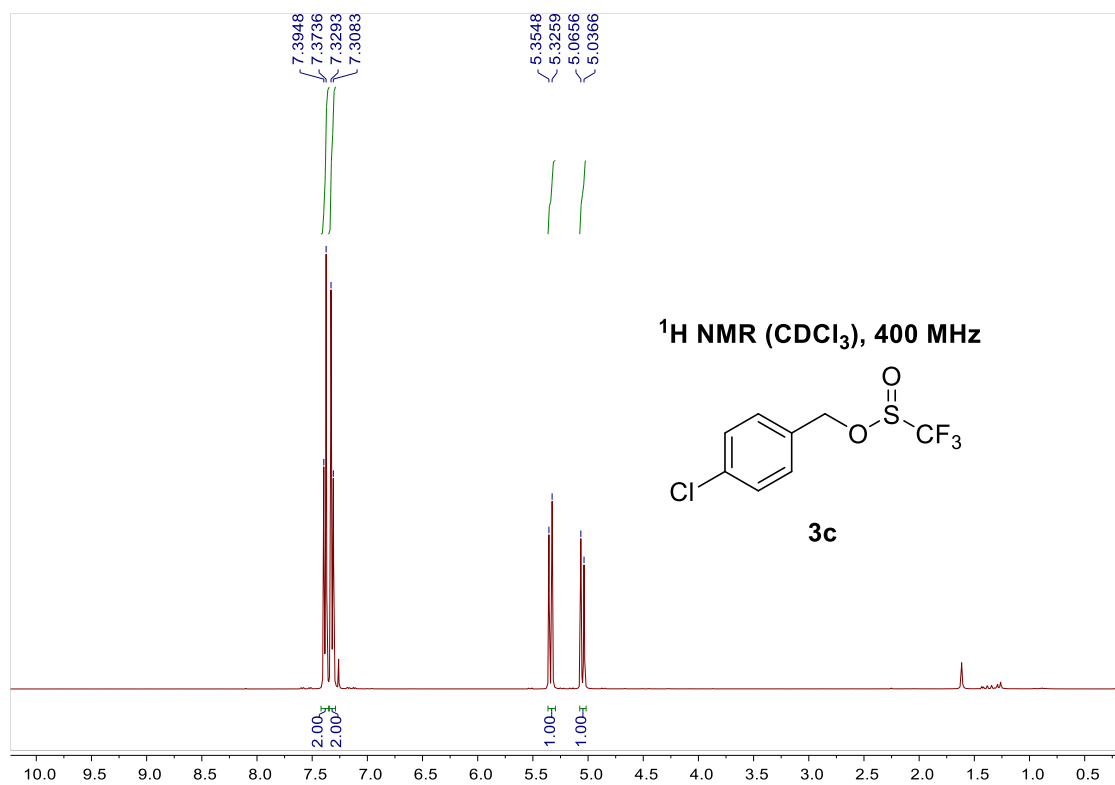
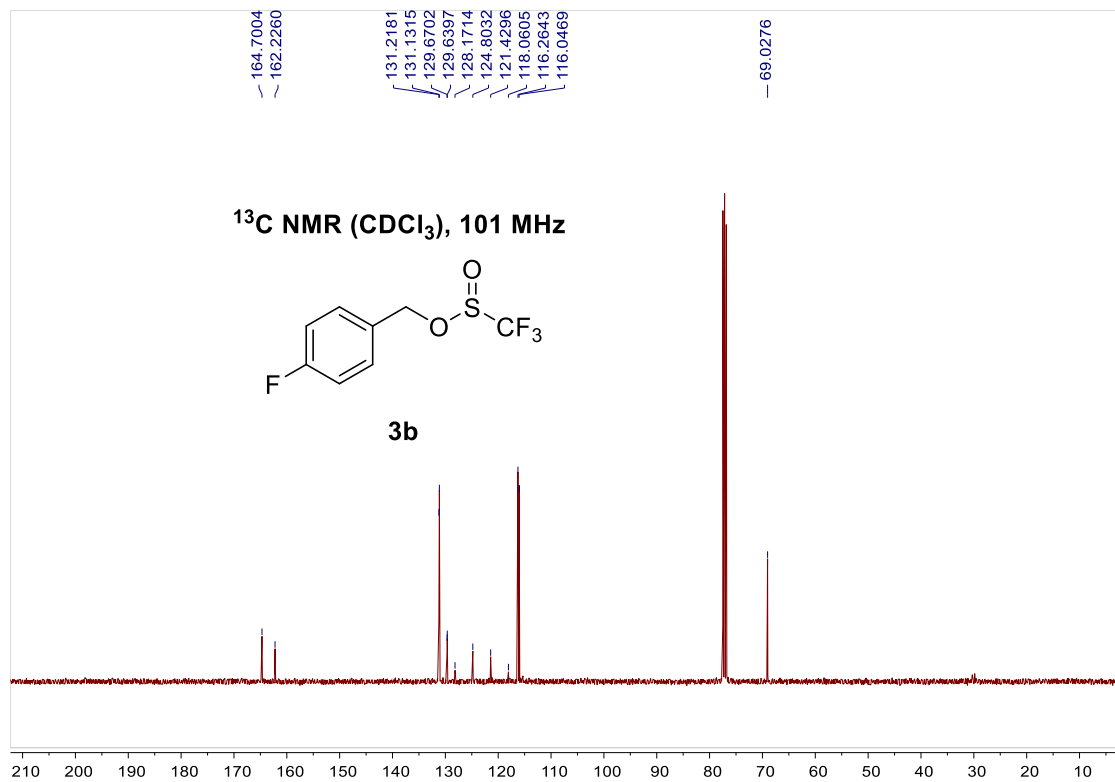
IX. NMR spectrum of the products

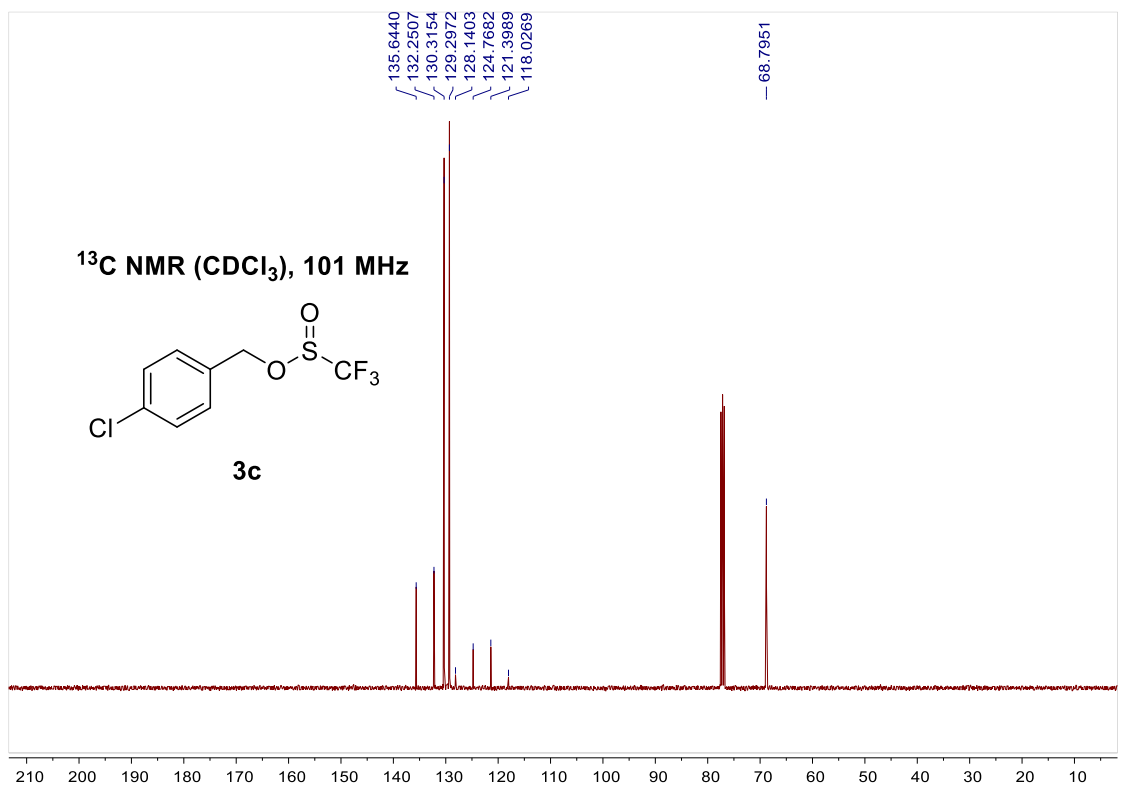
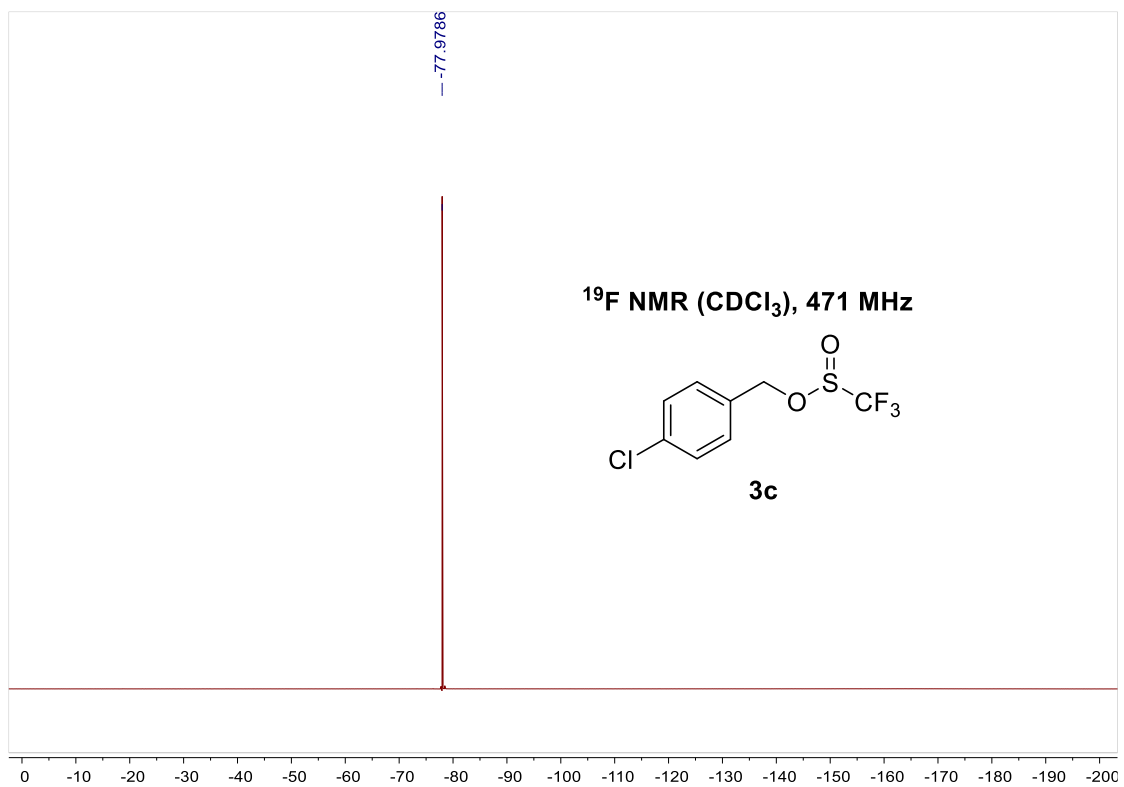


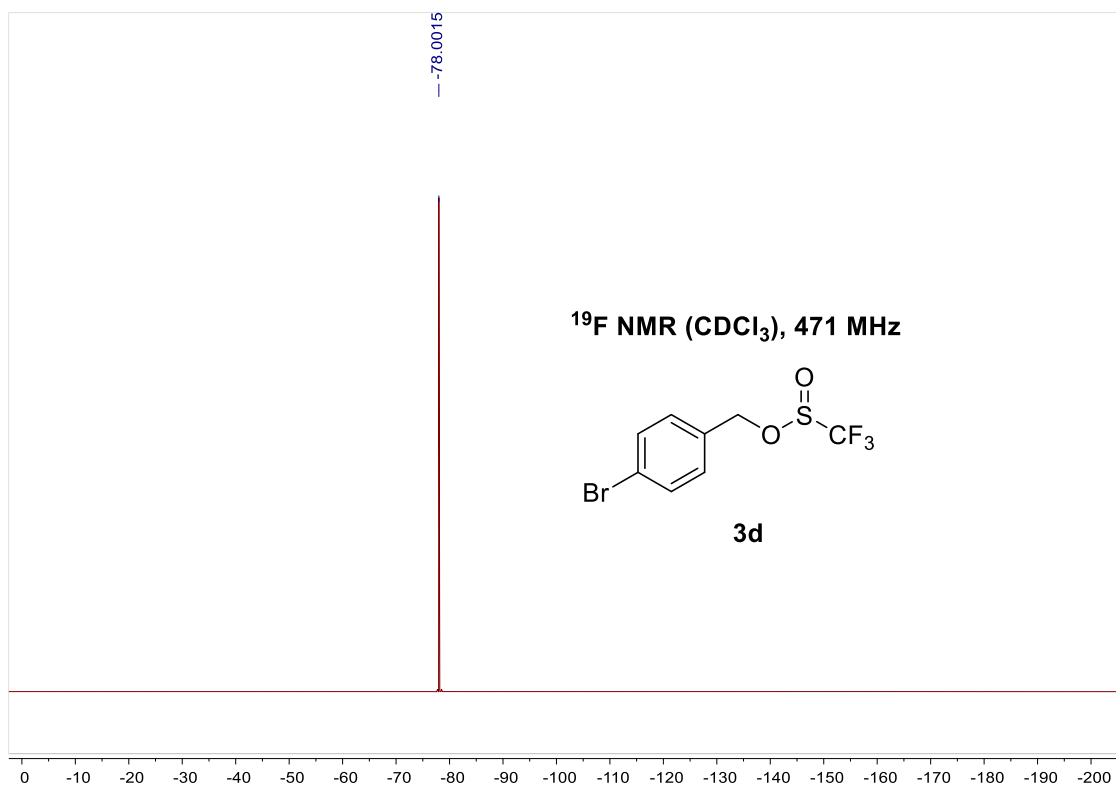
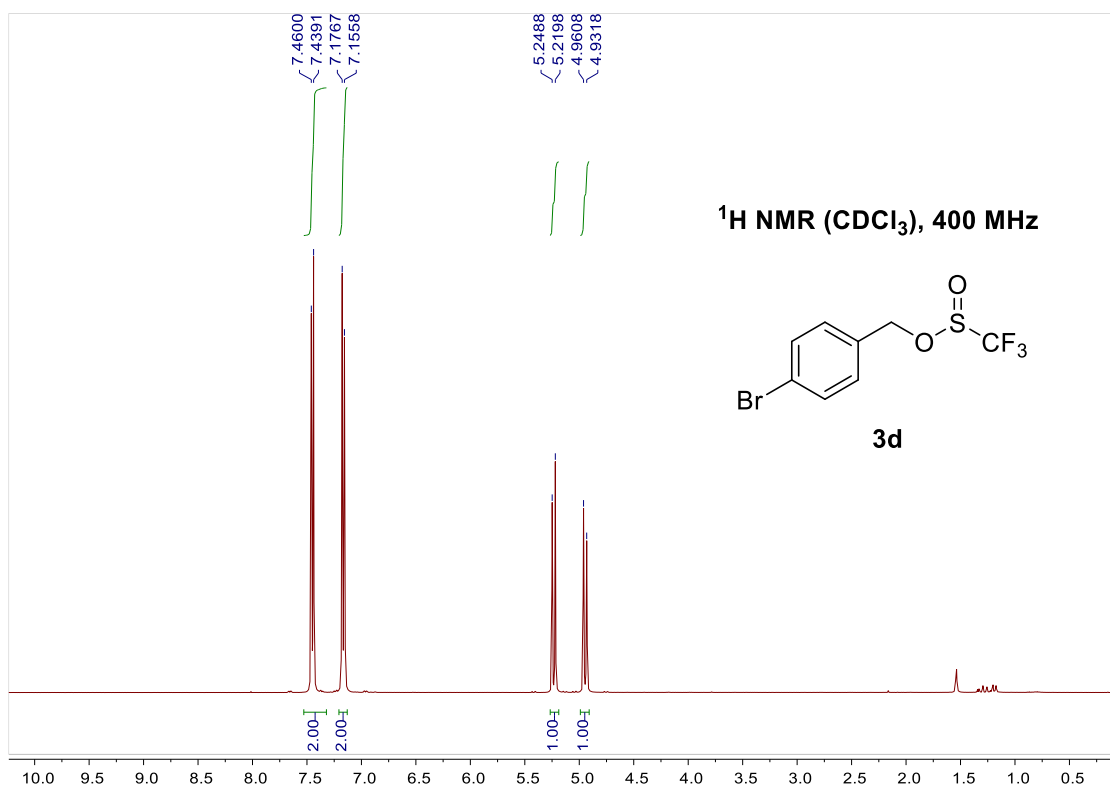


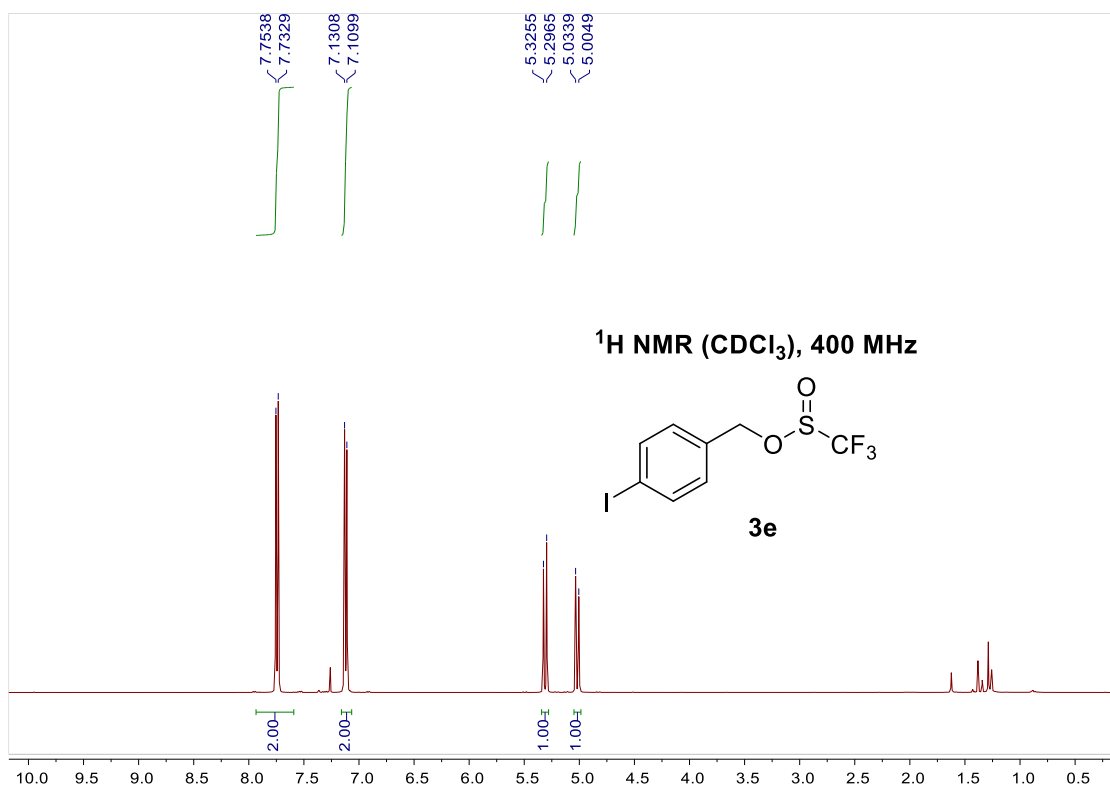
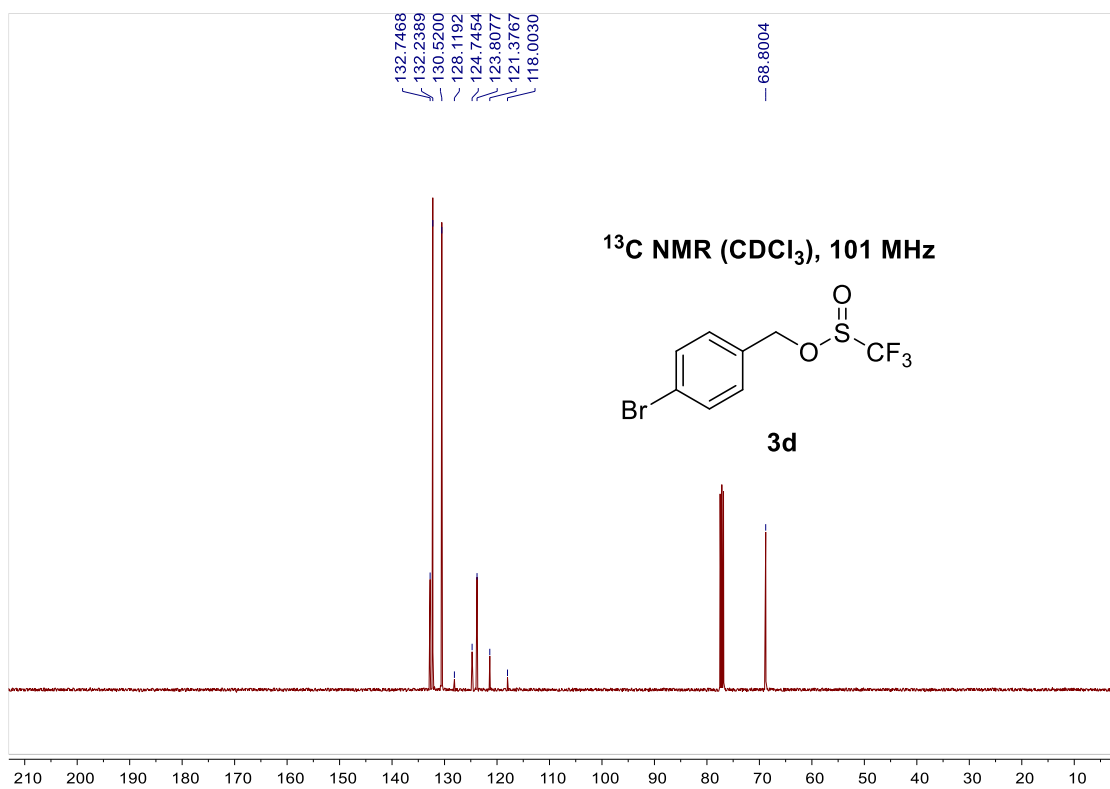


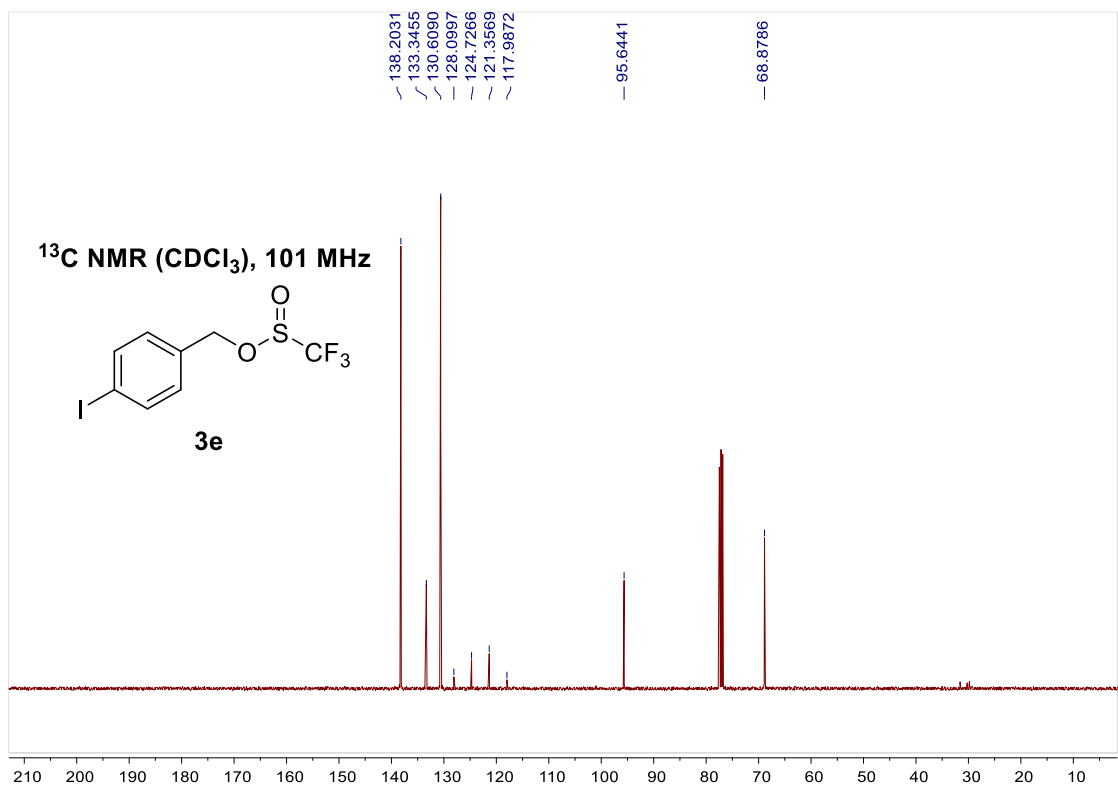
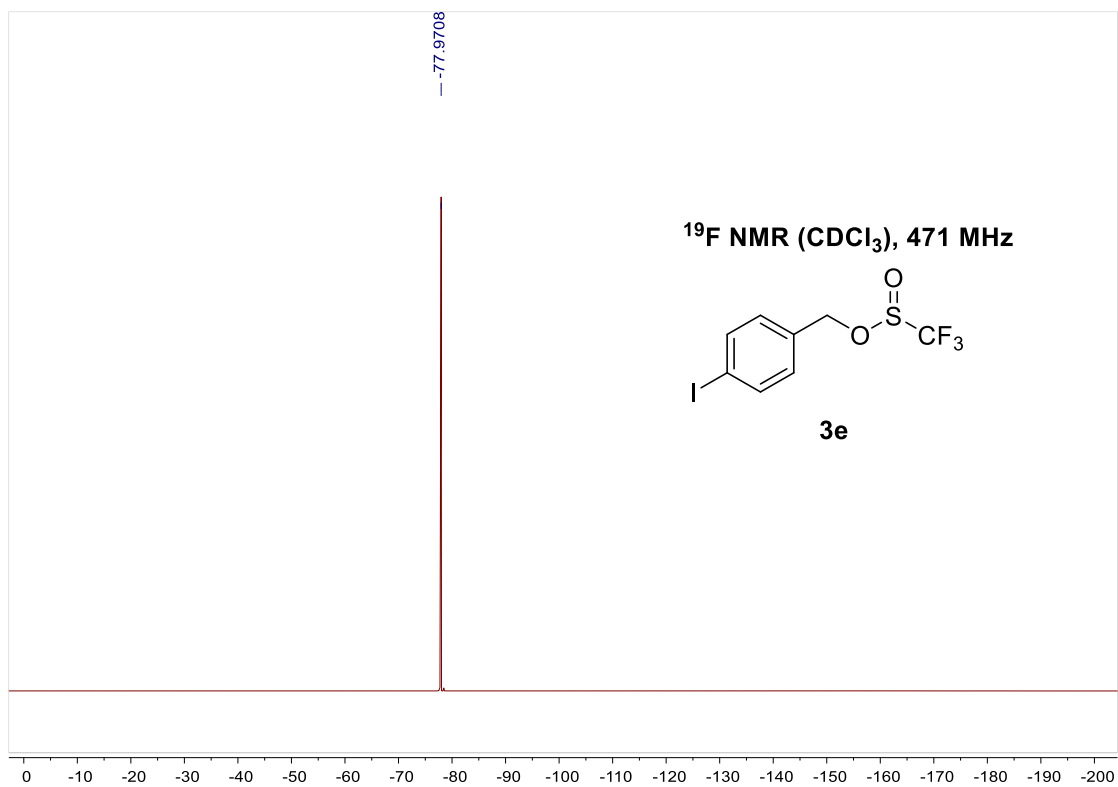


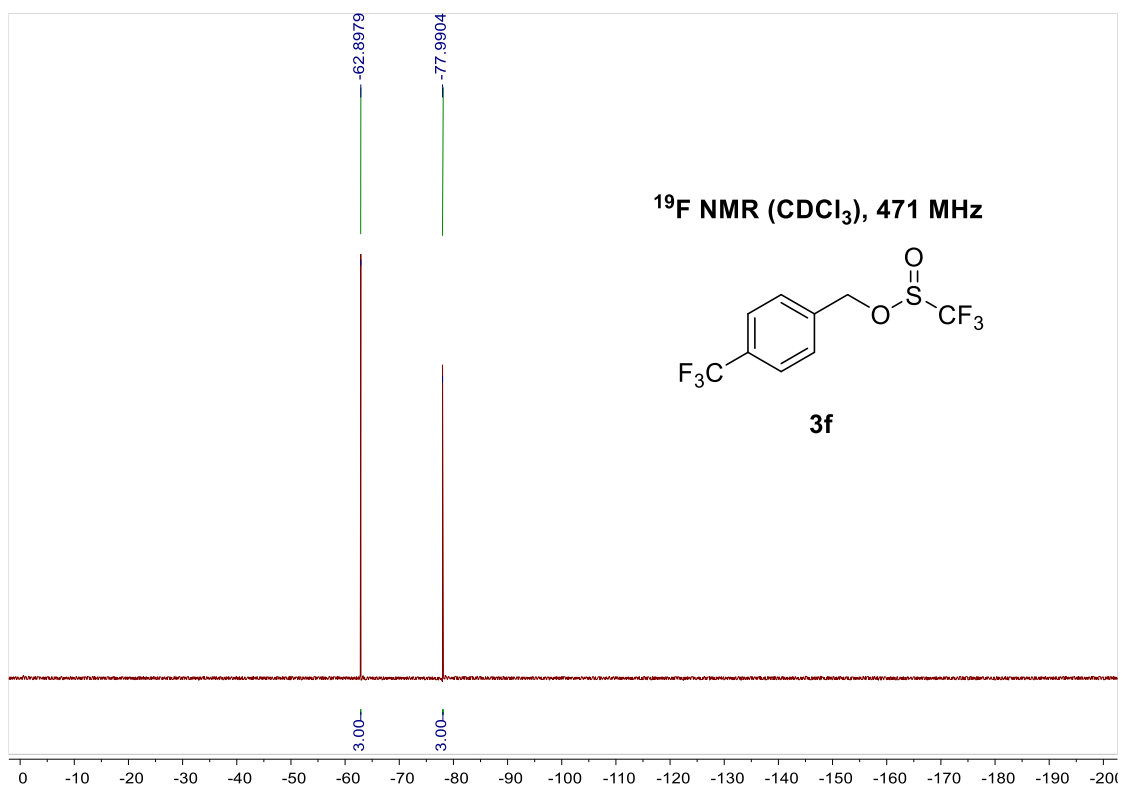
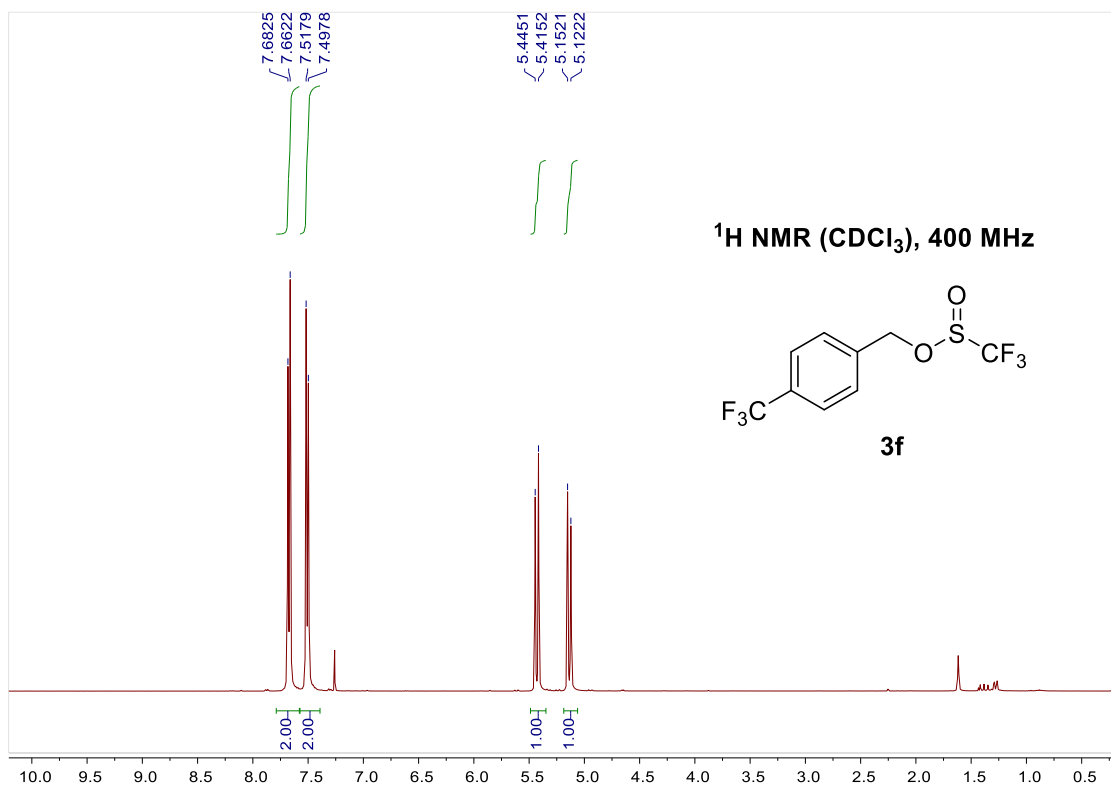


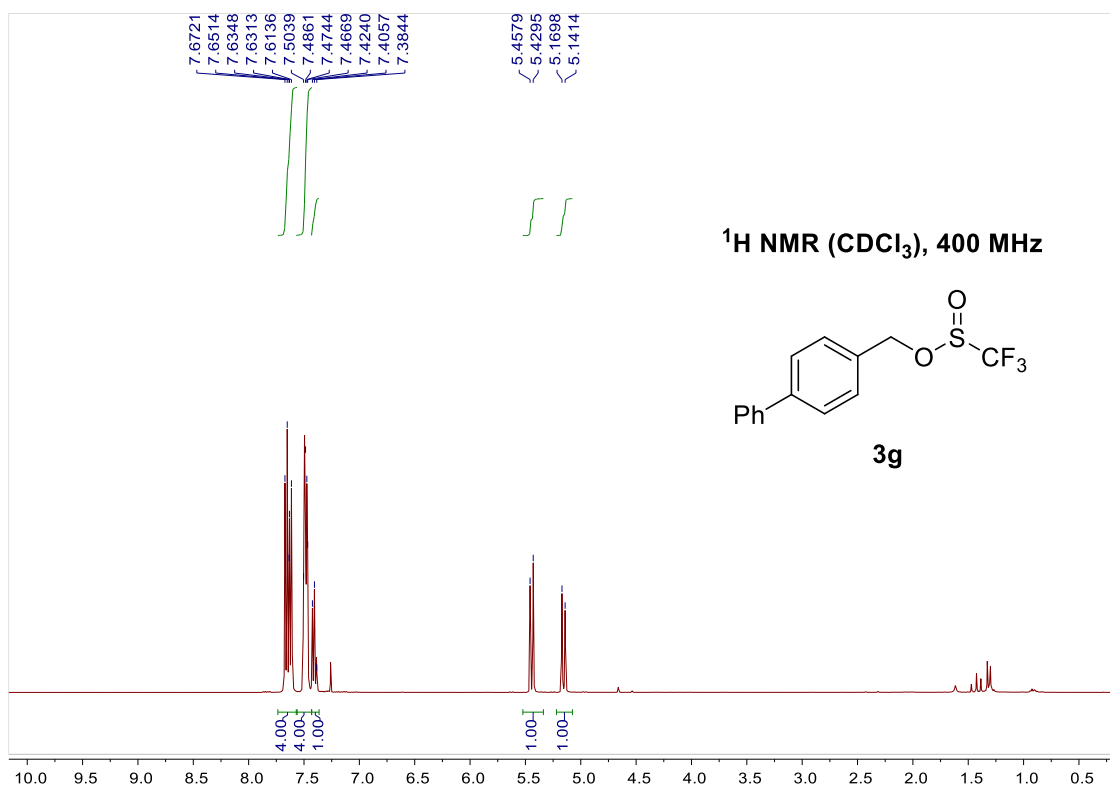
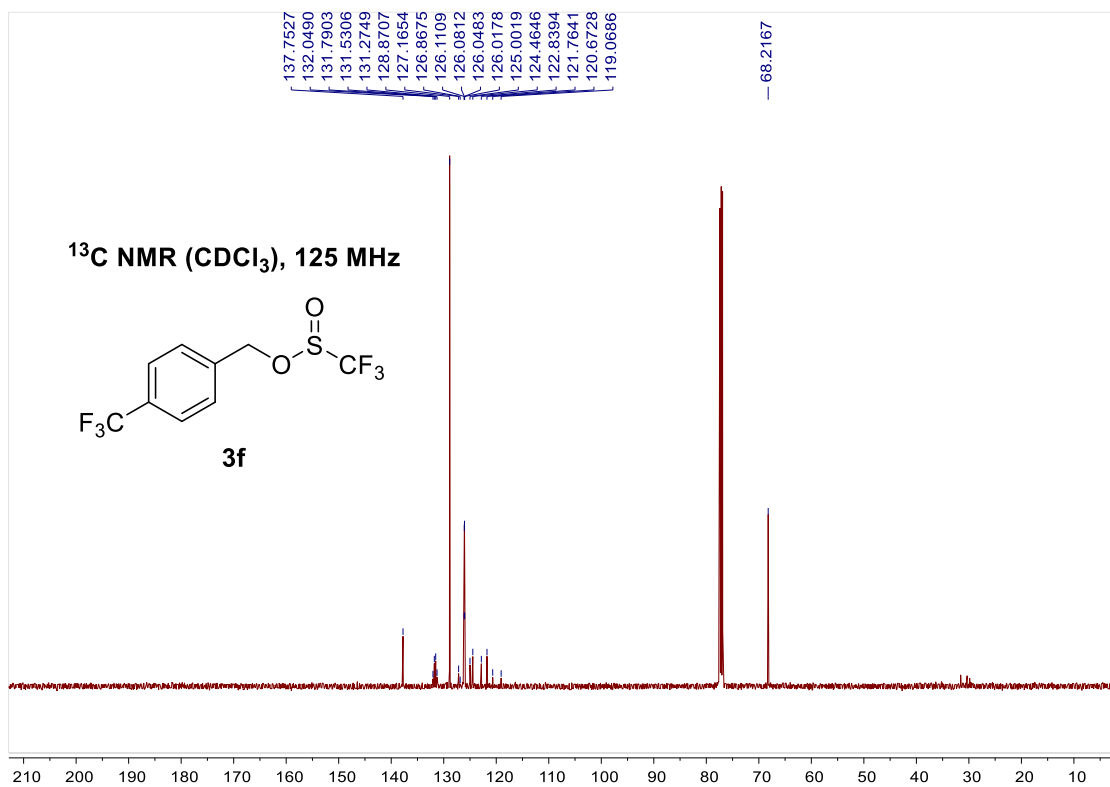


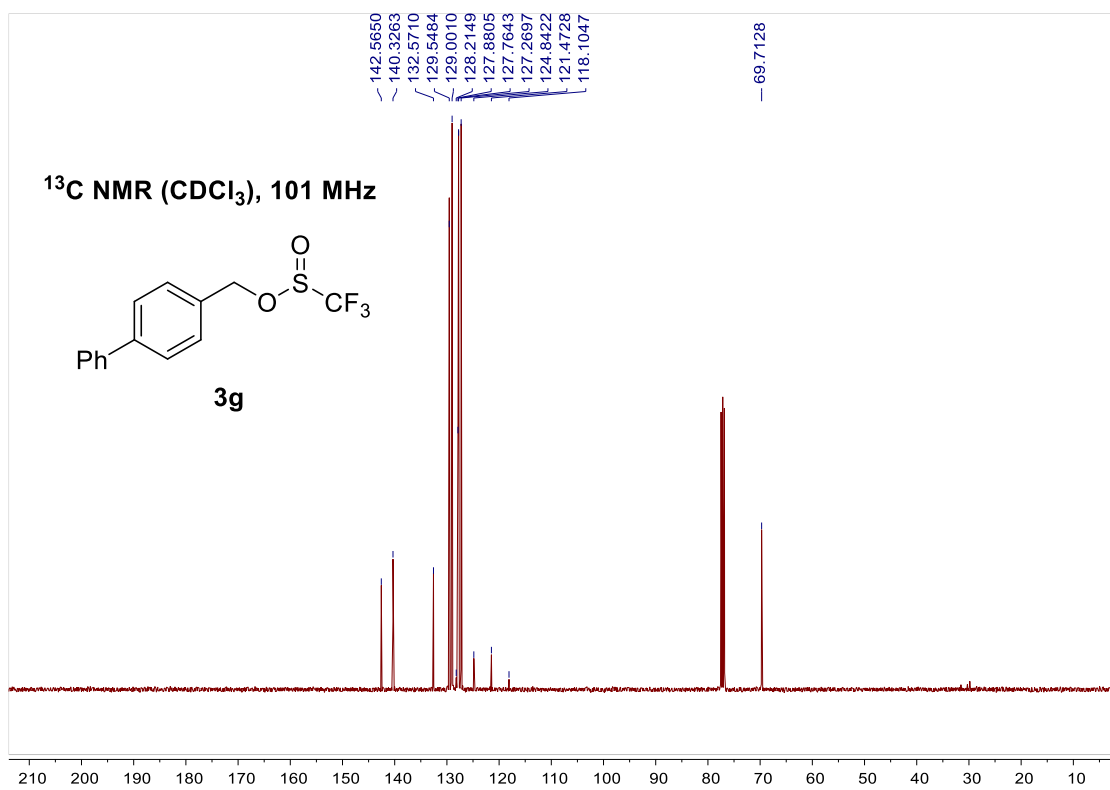
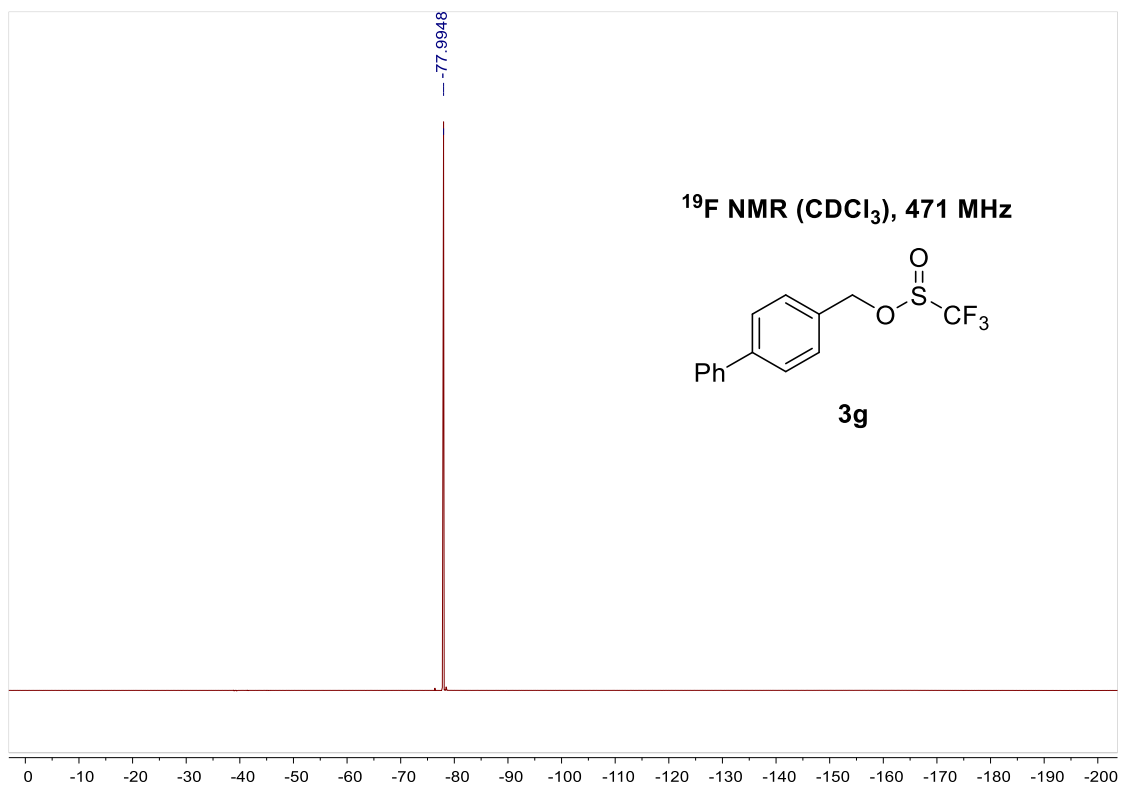


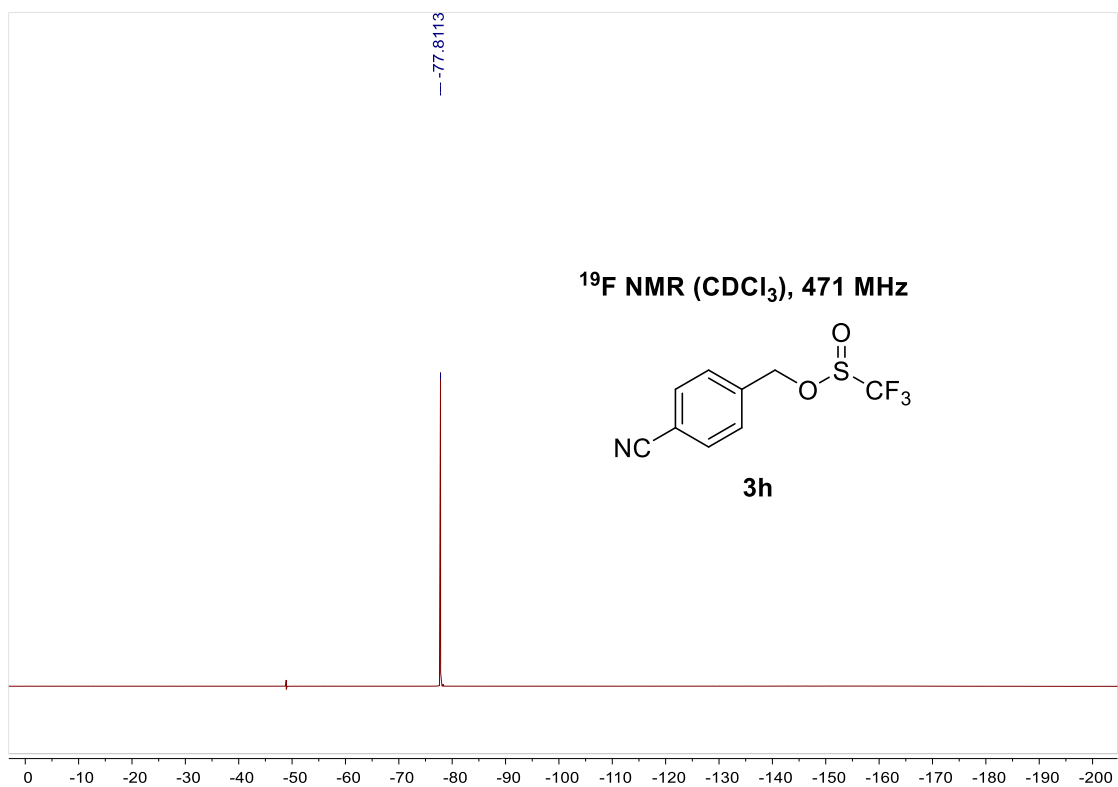
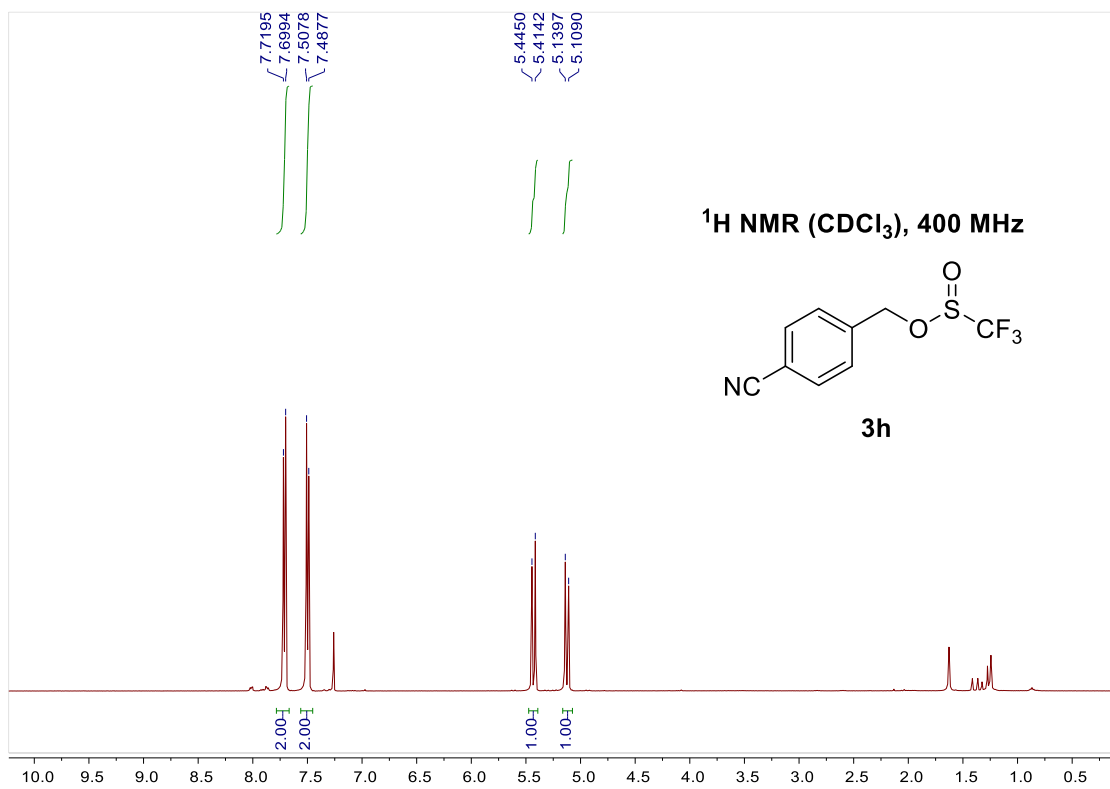


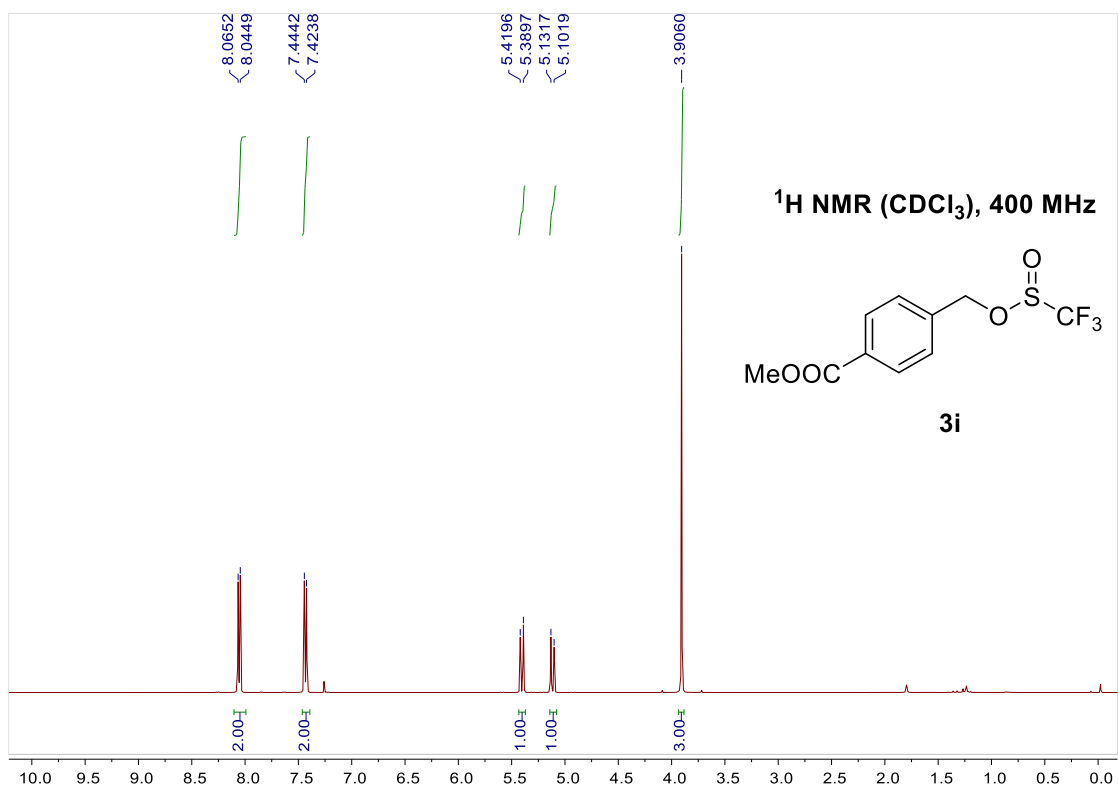
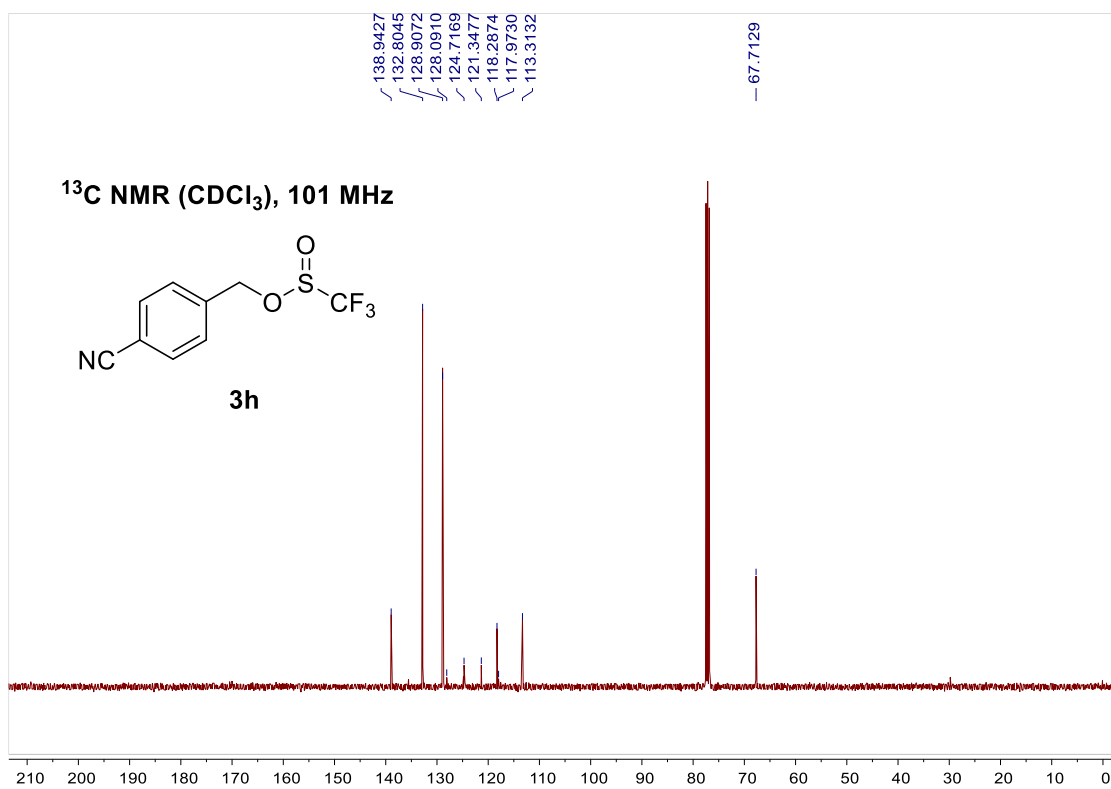


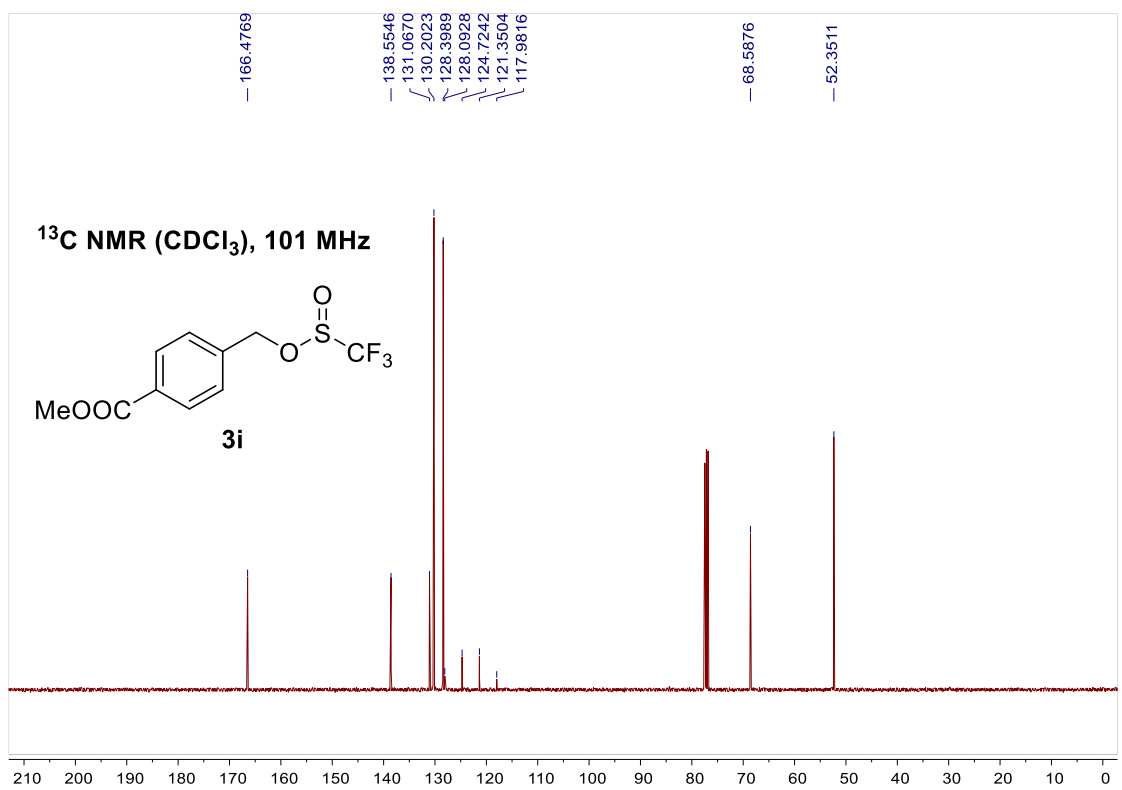
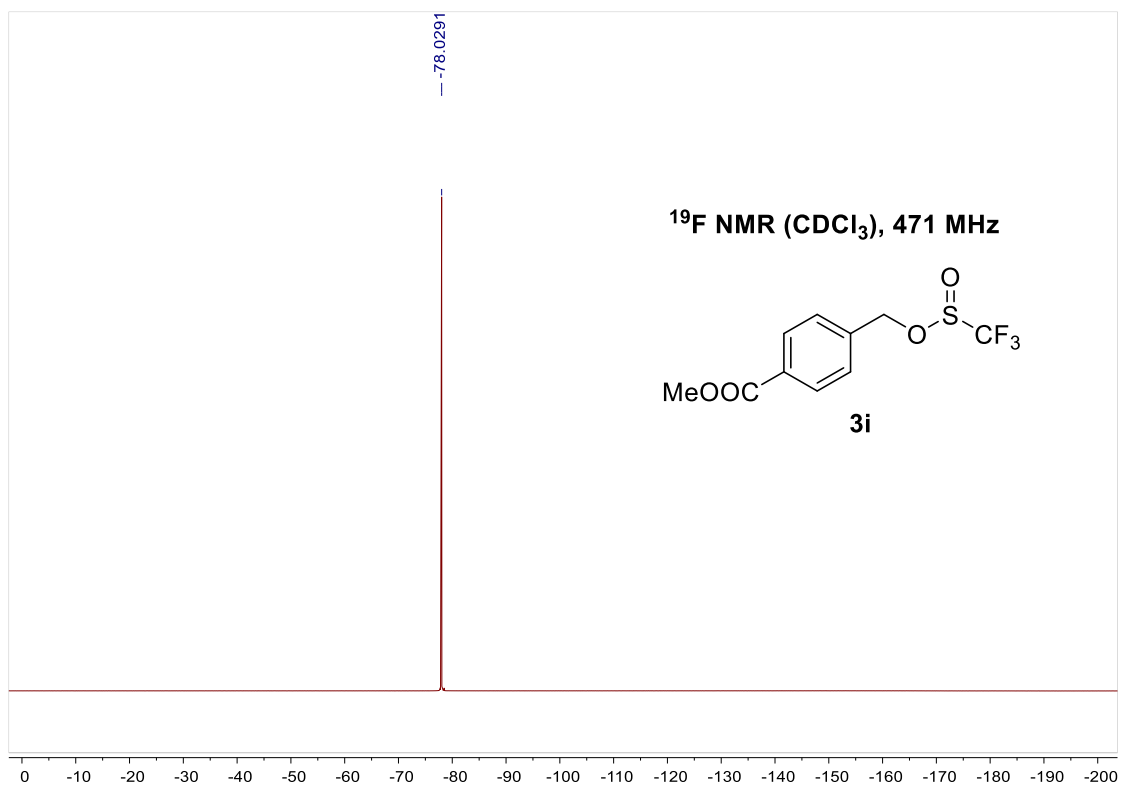


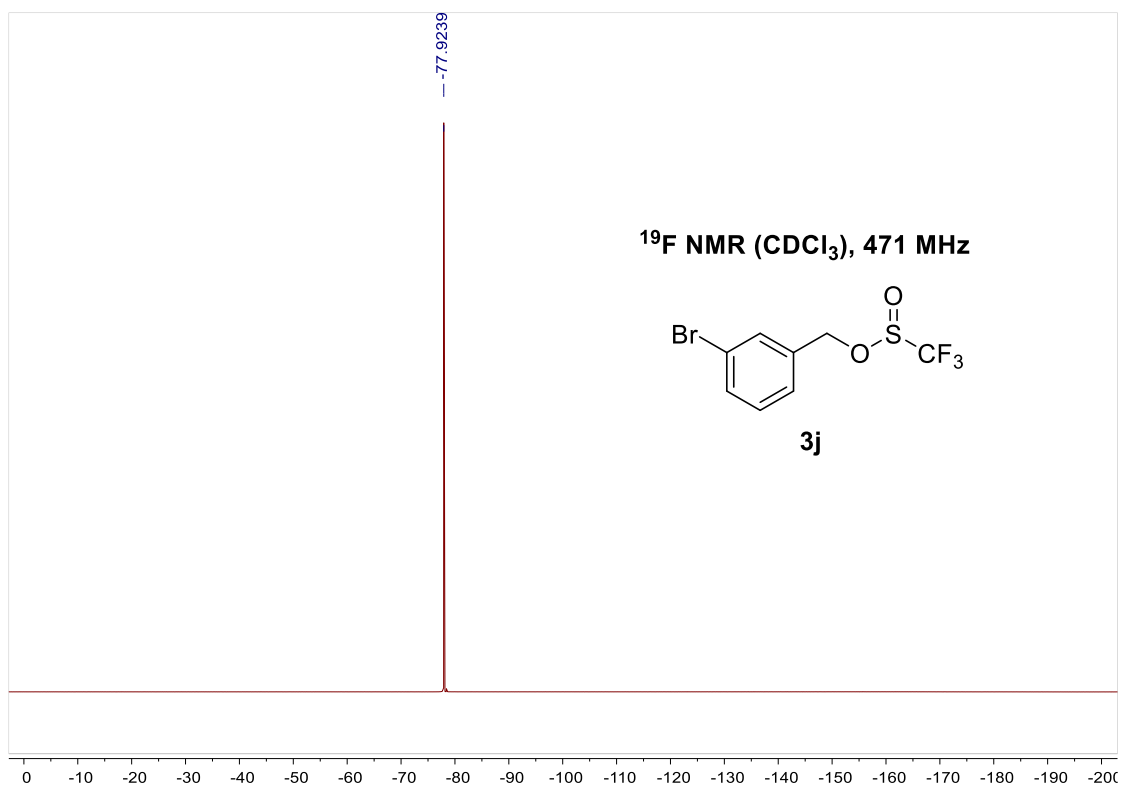
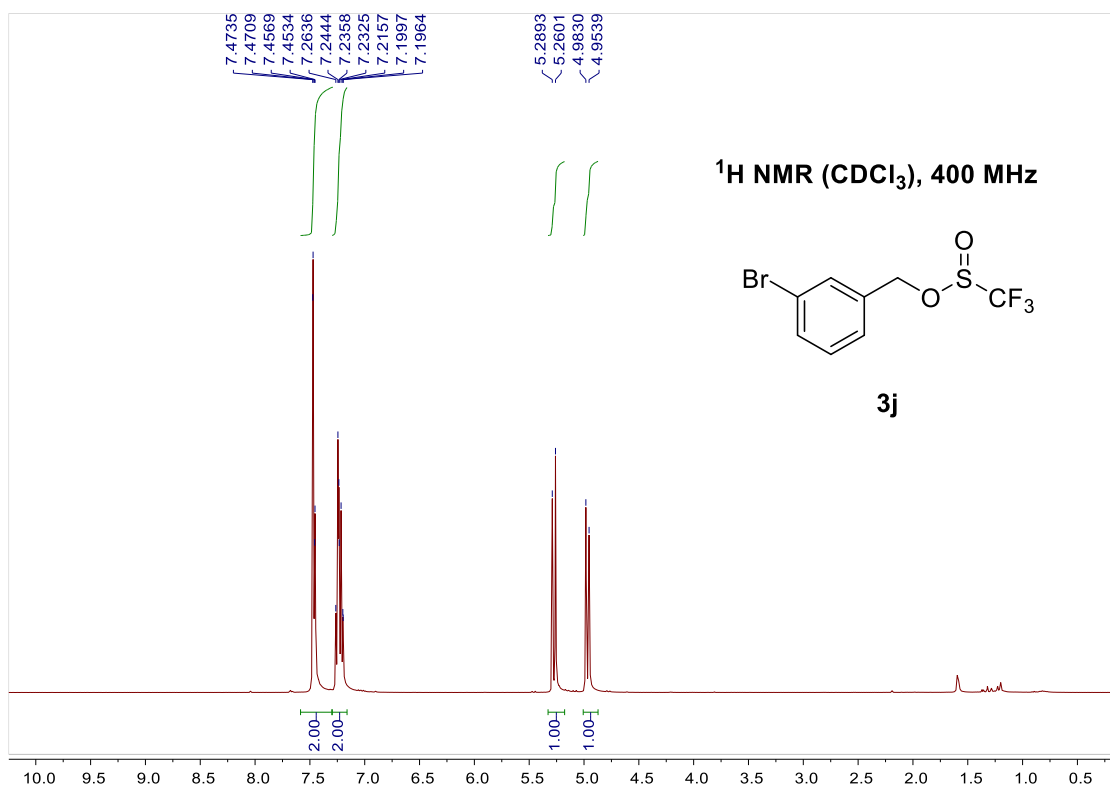


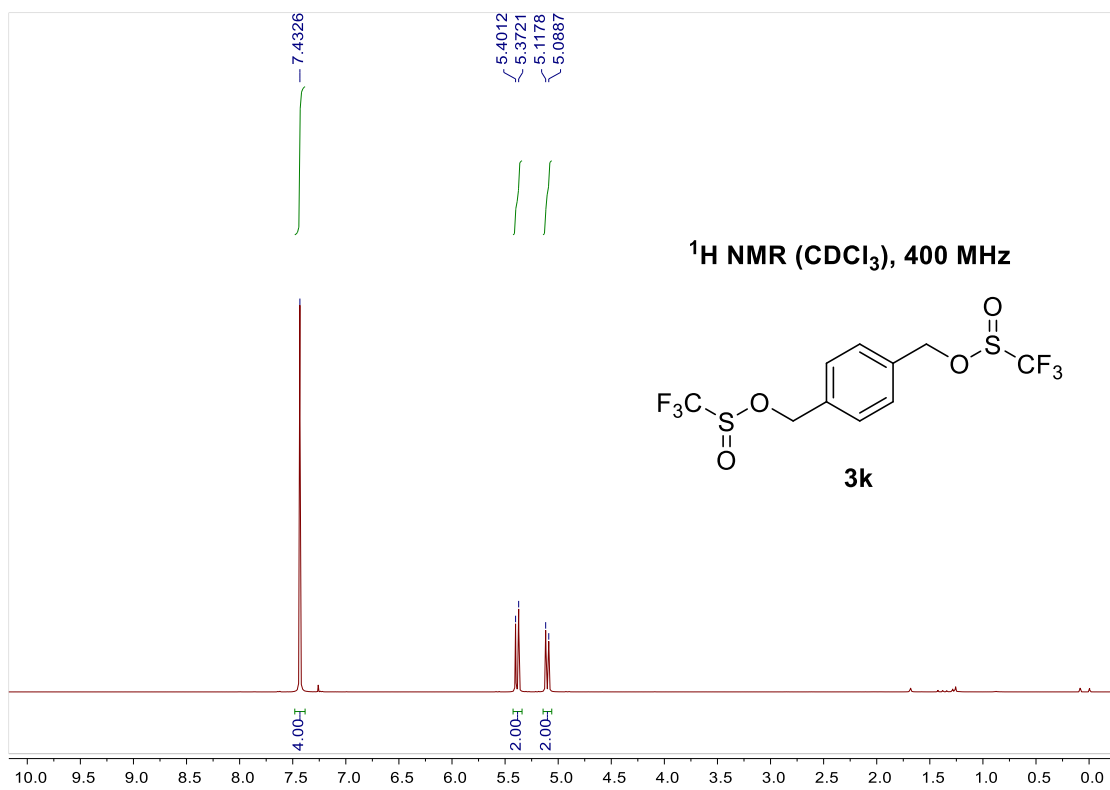
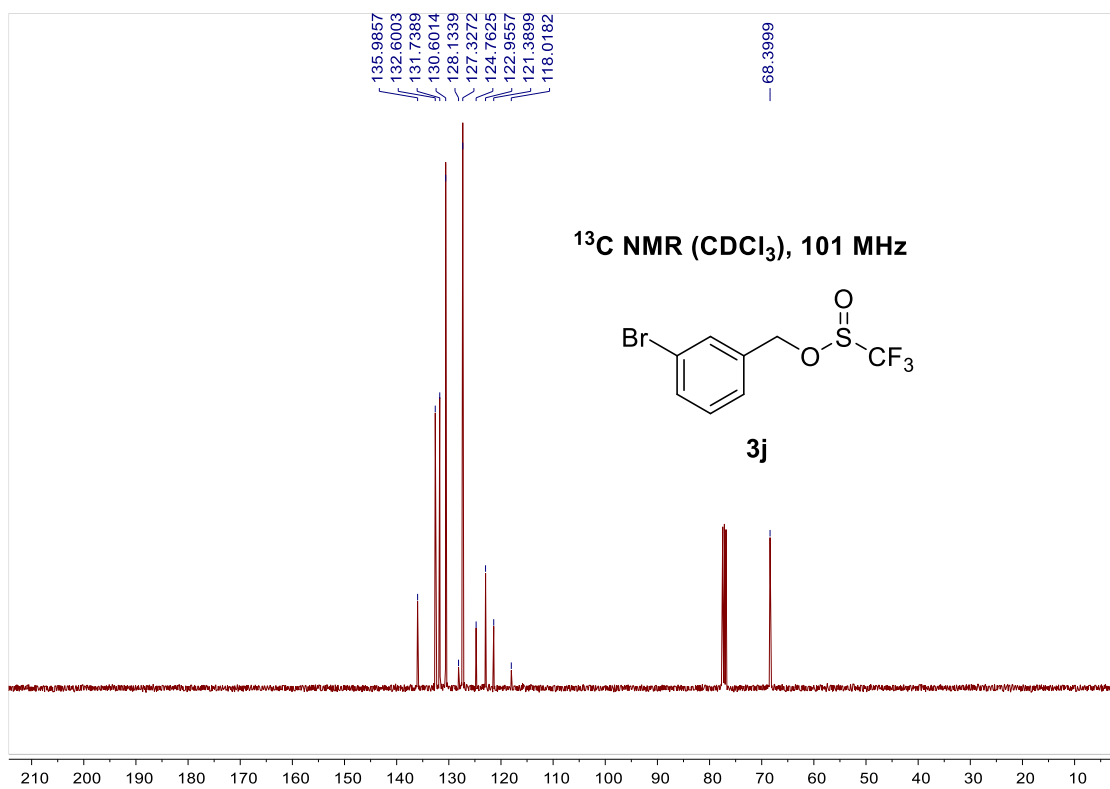


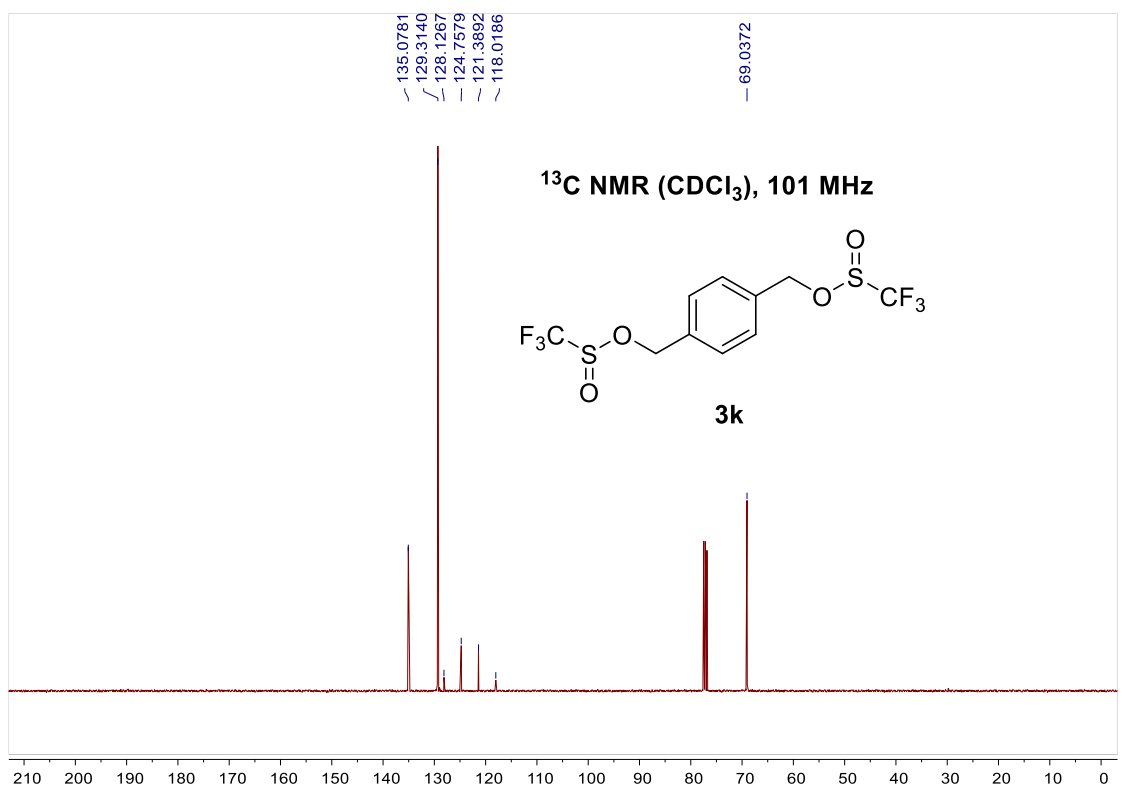
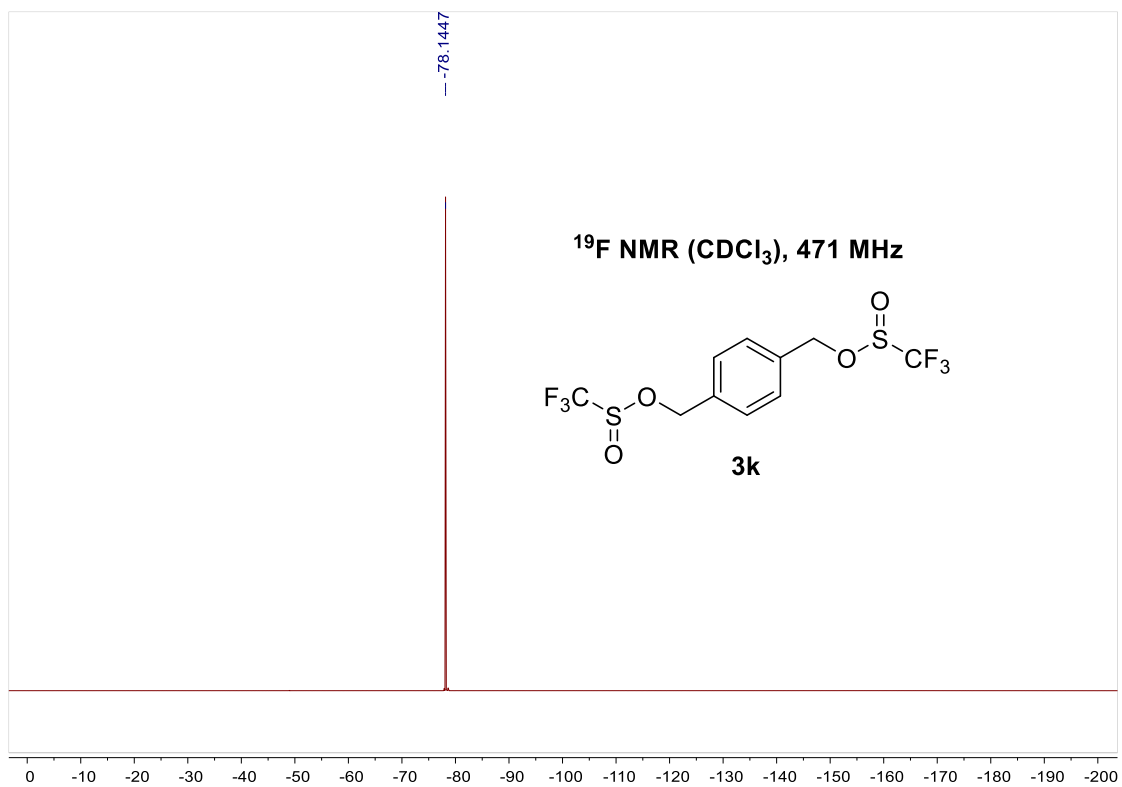


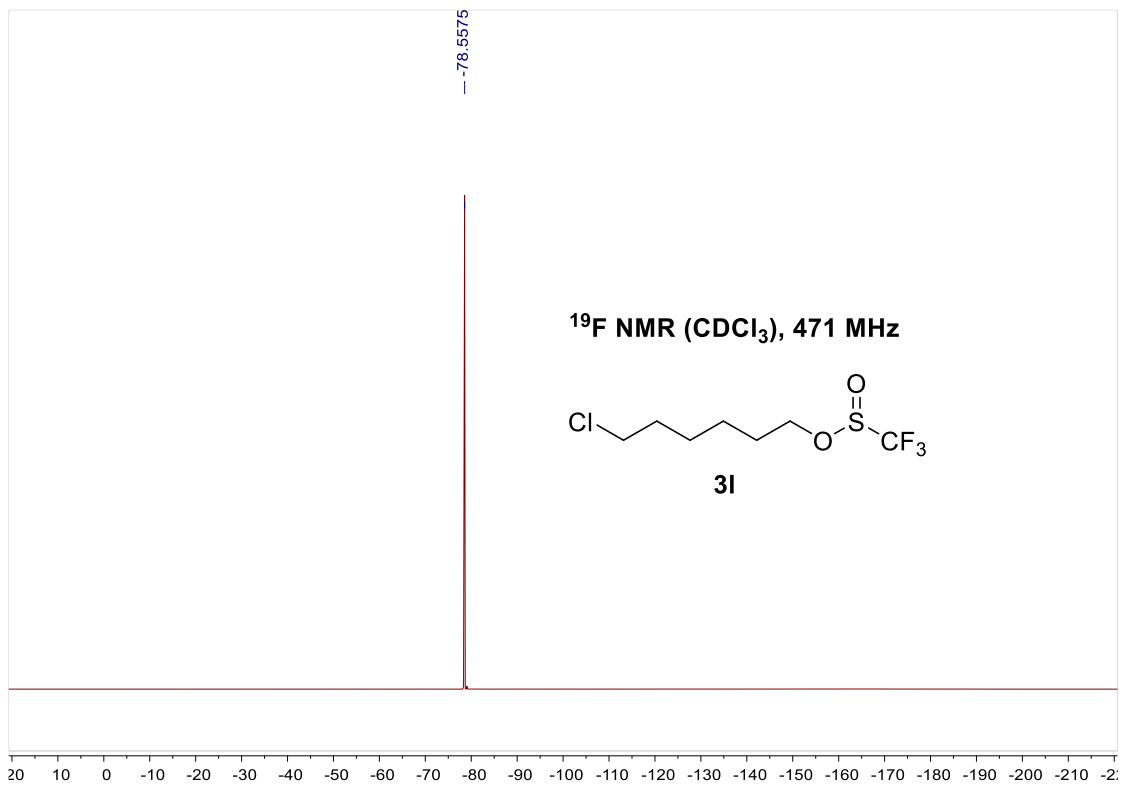
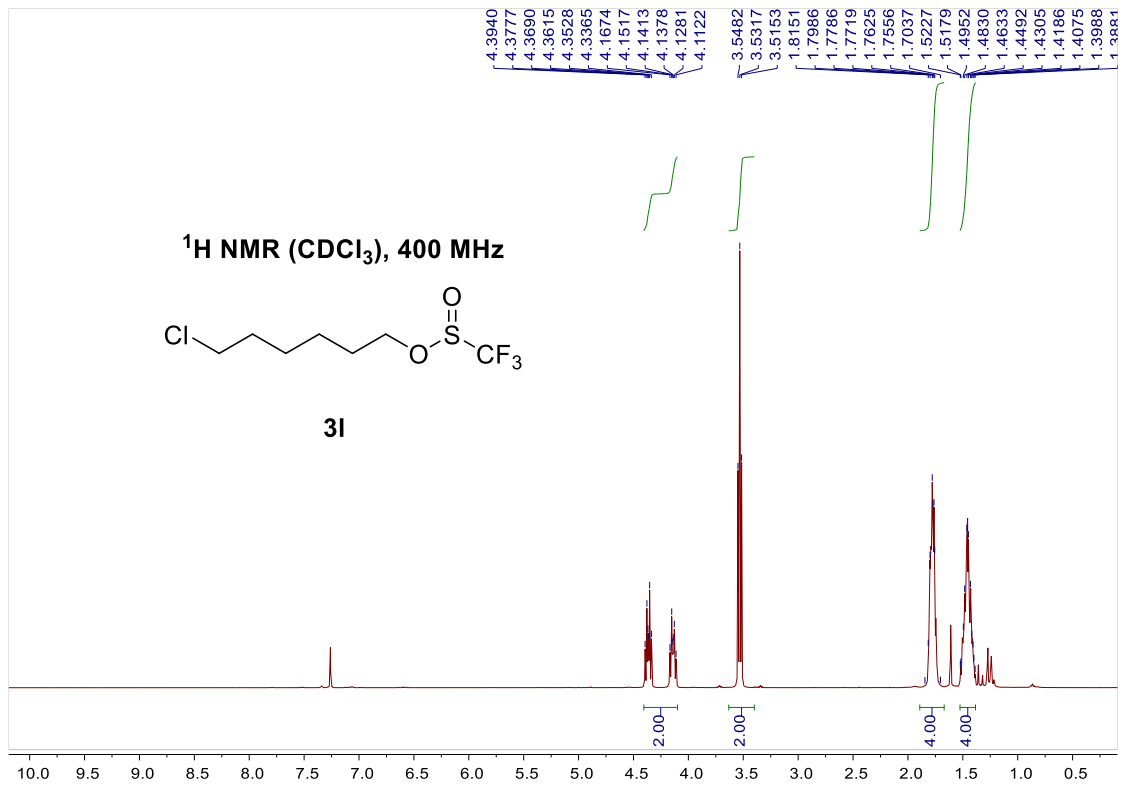


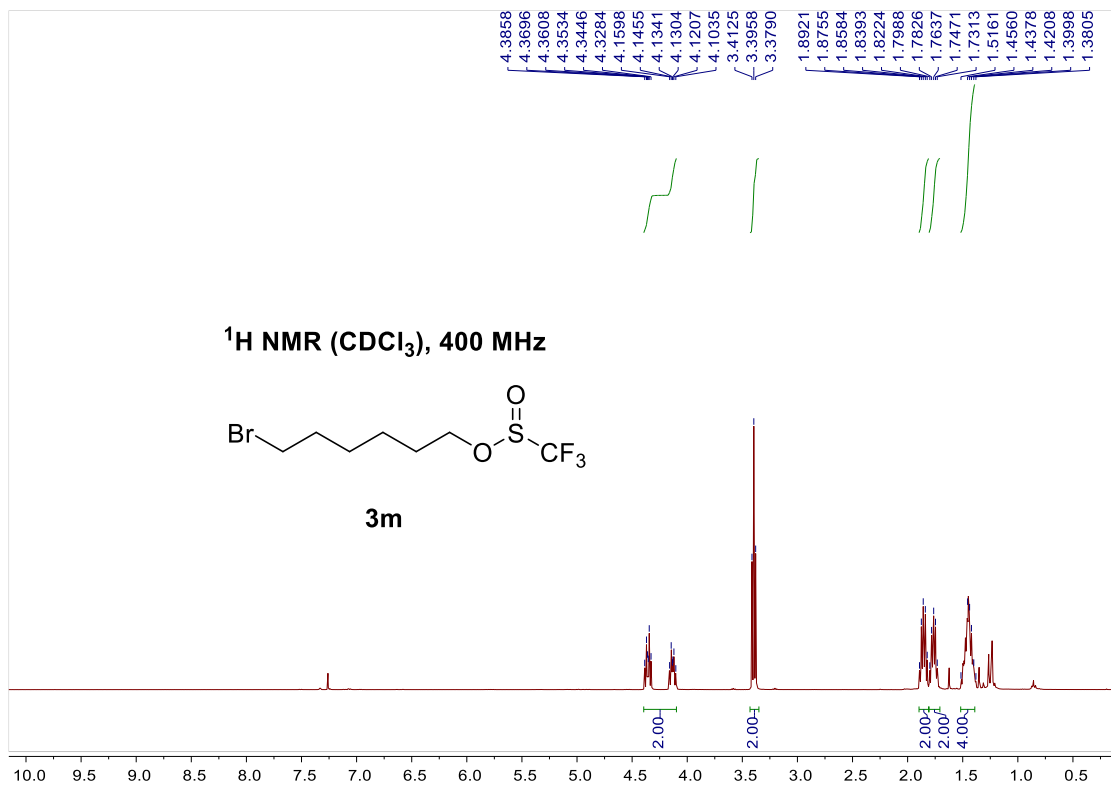
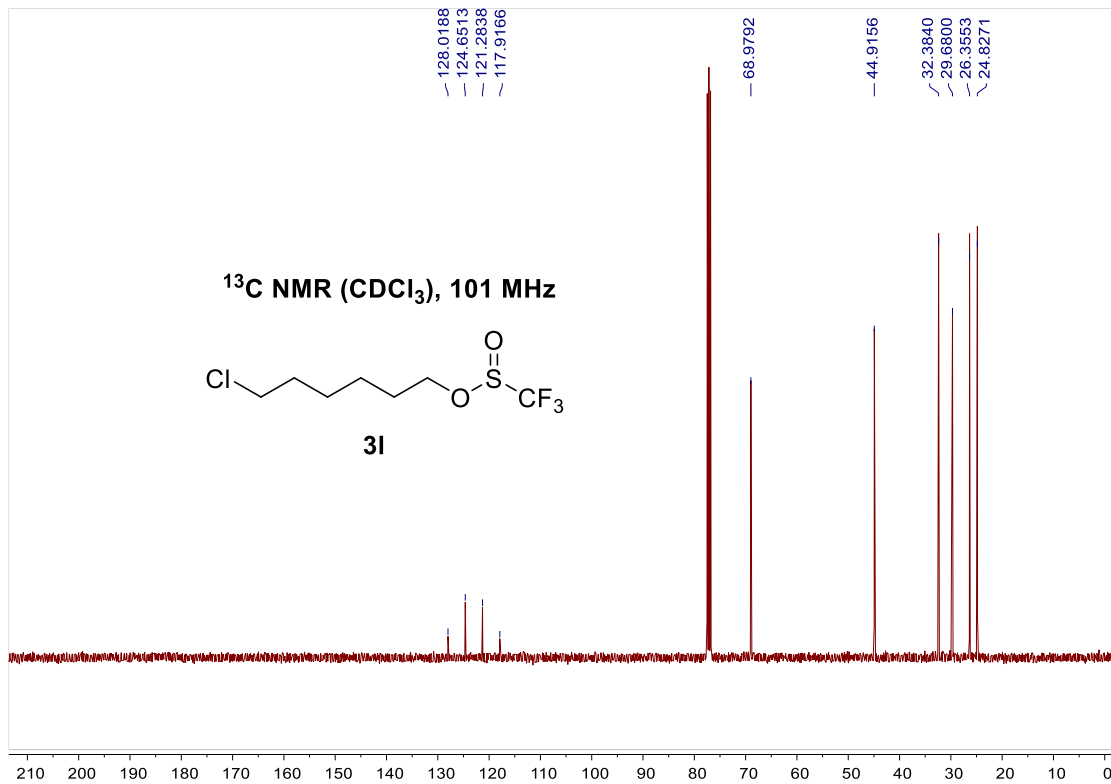


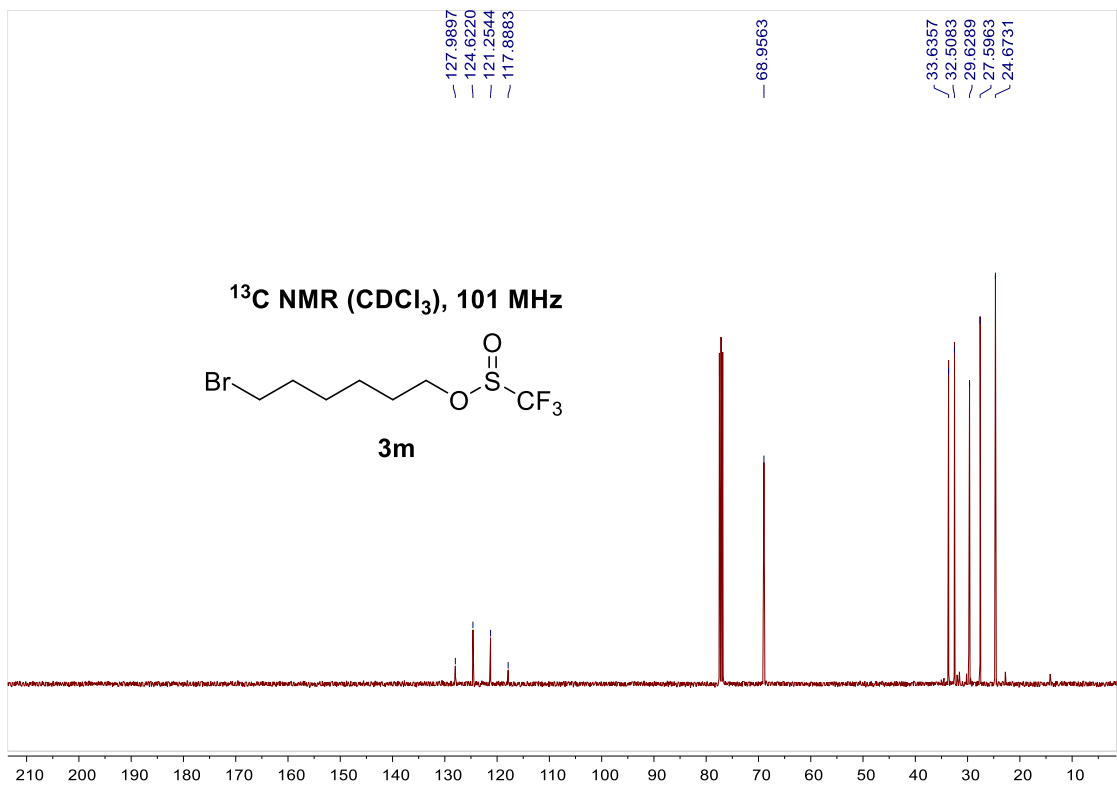
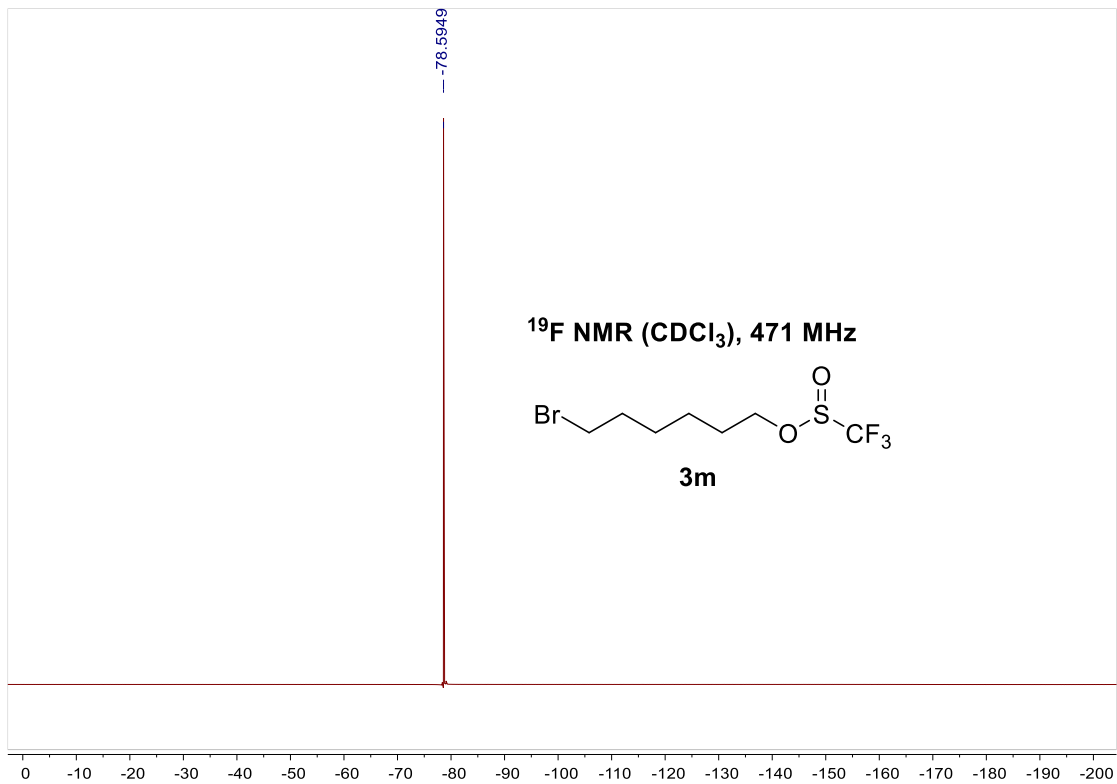


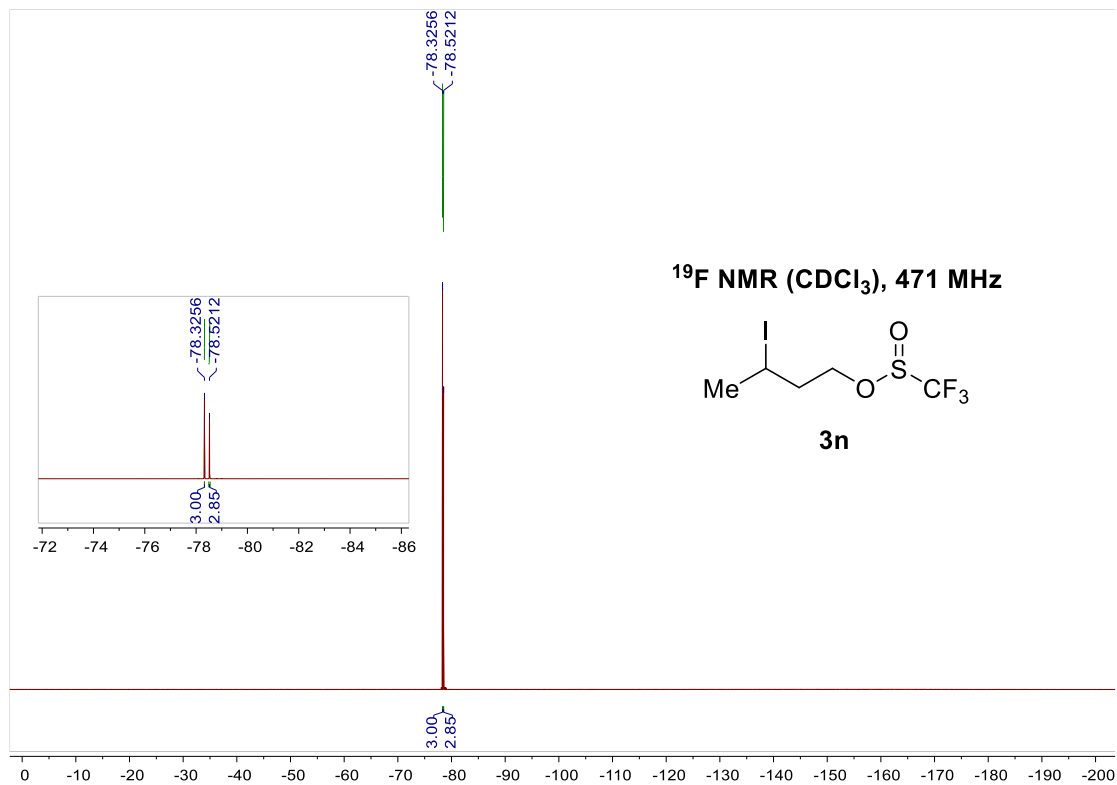
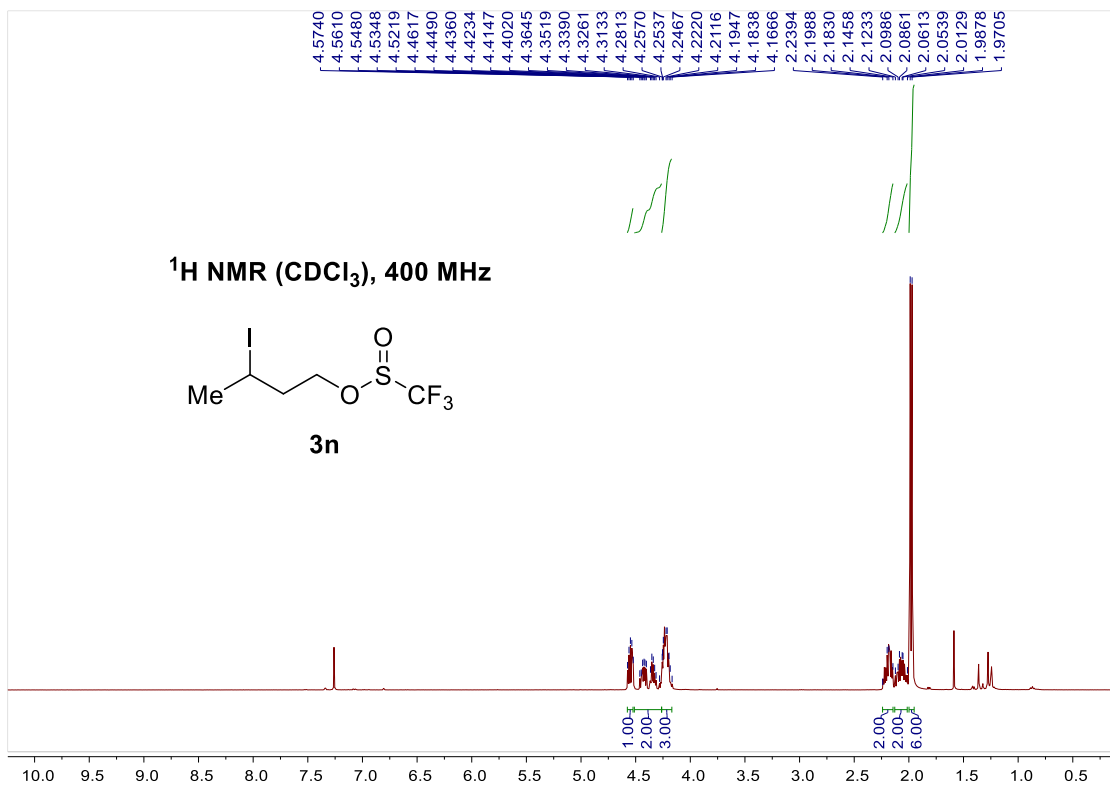


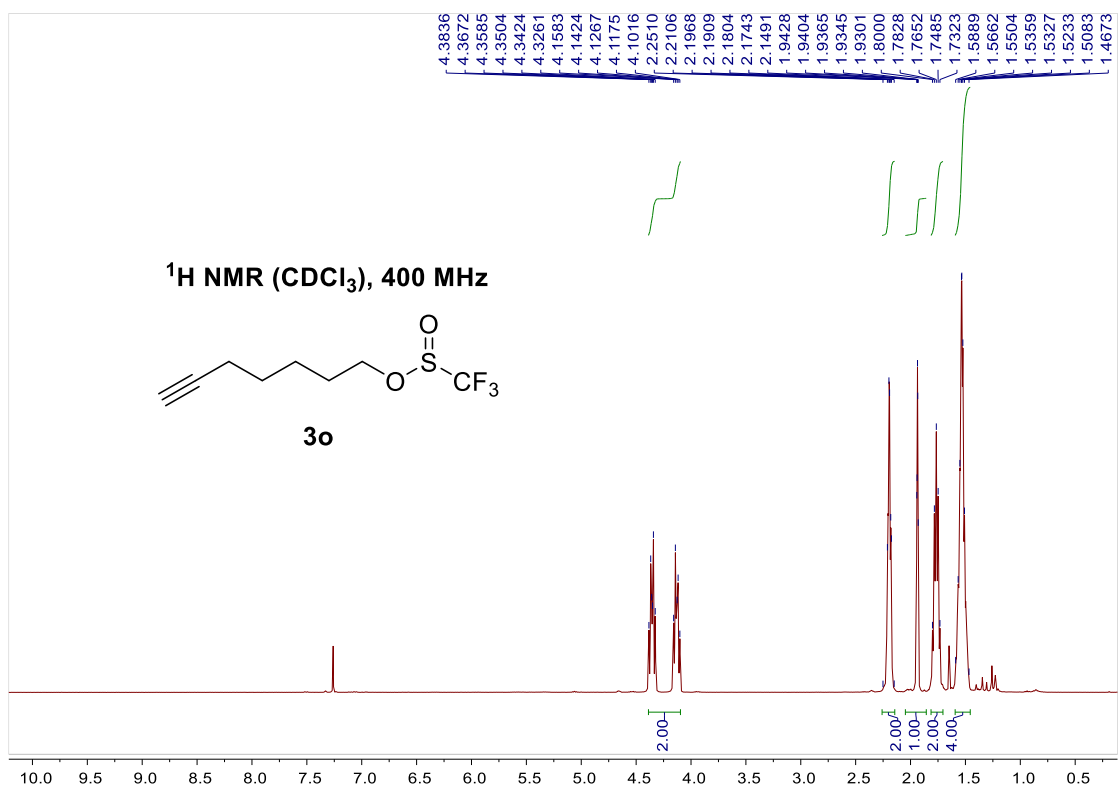
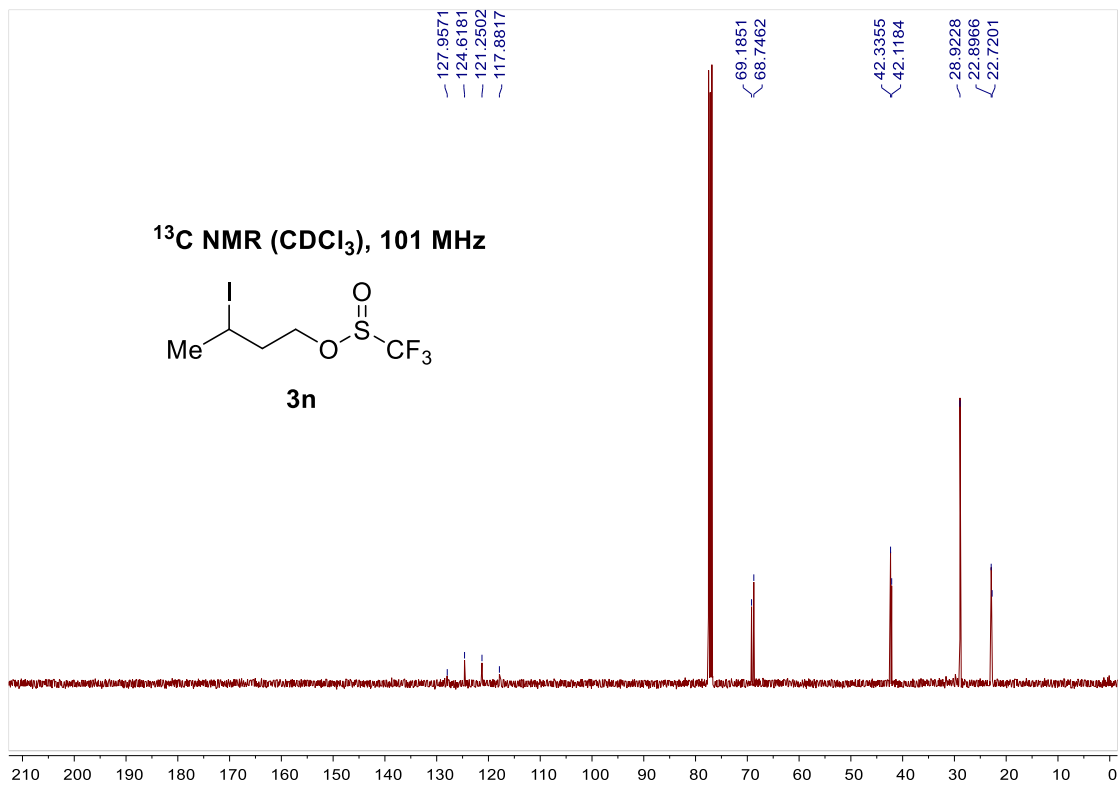


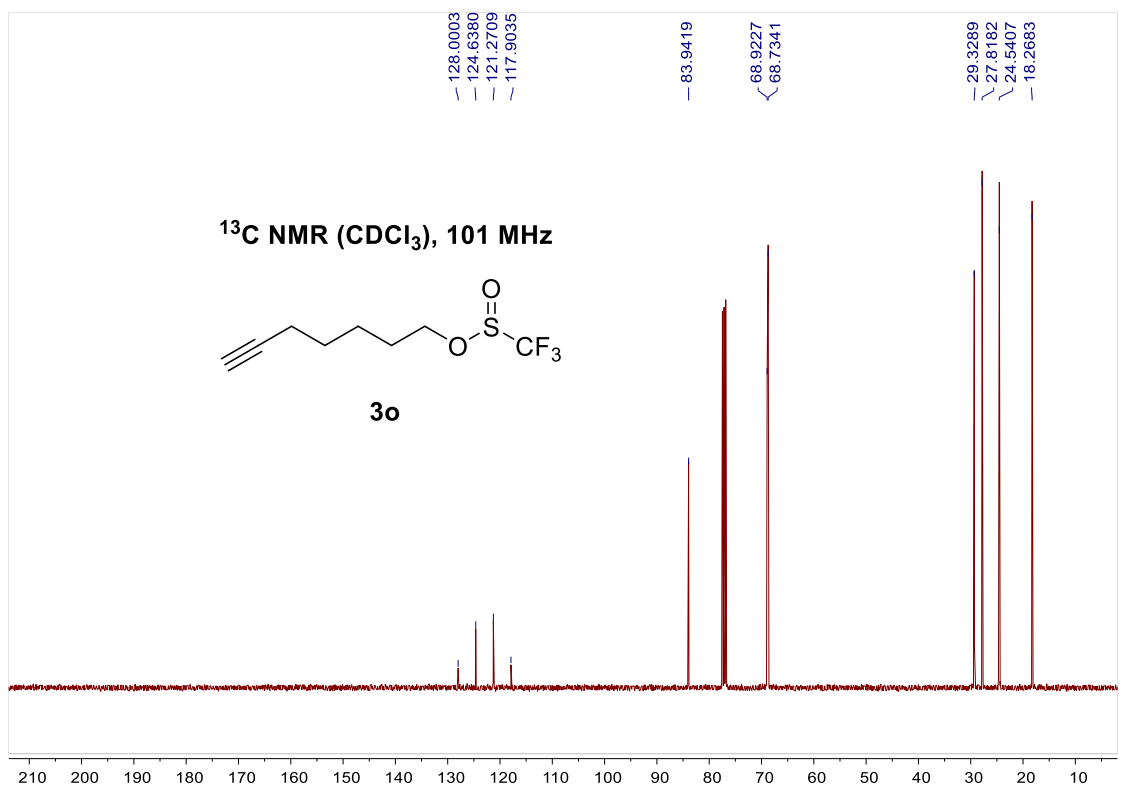
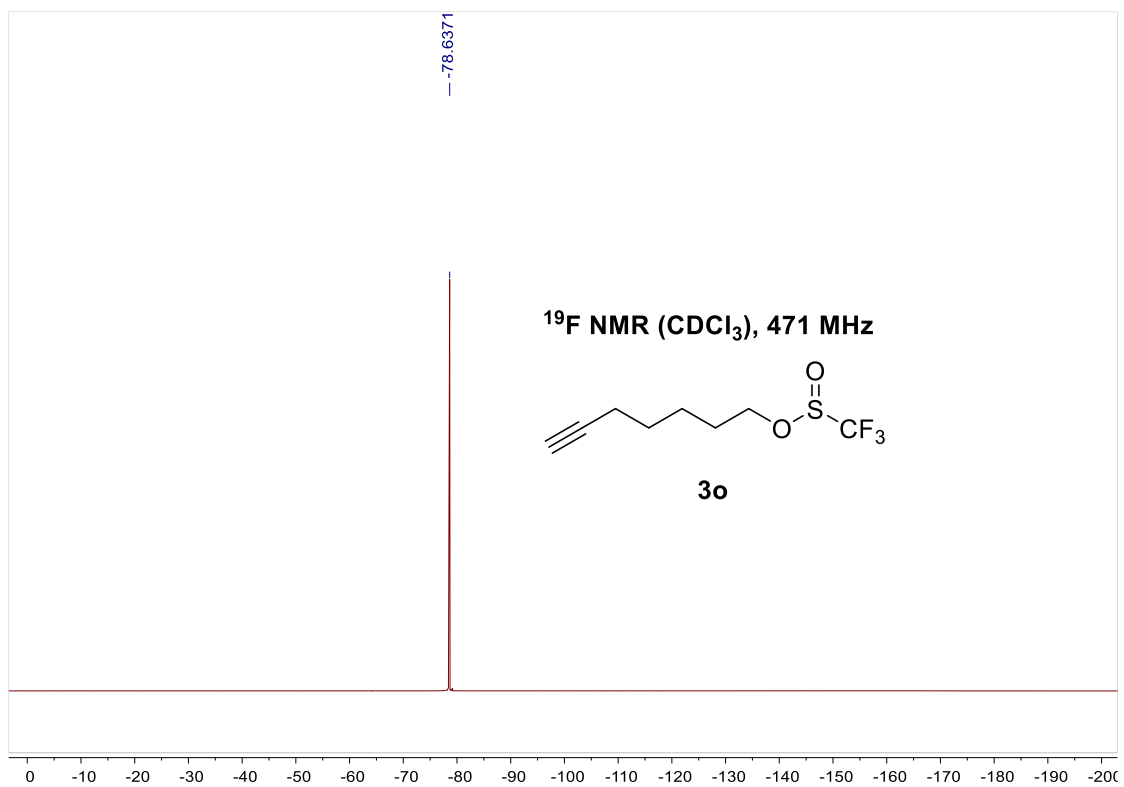


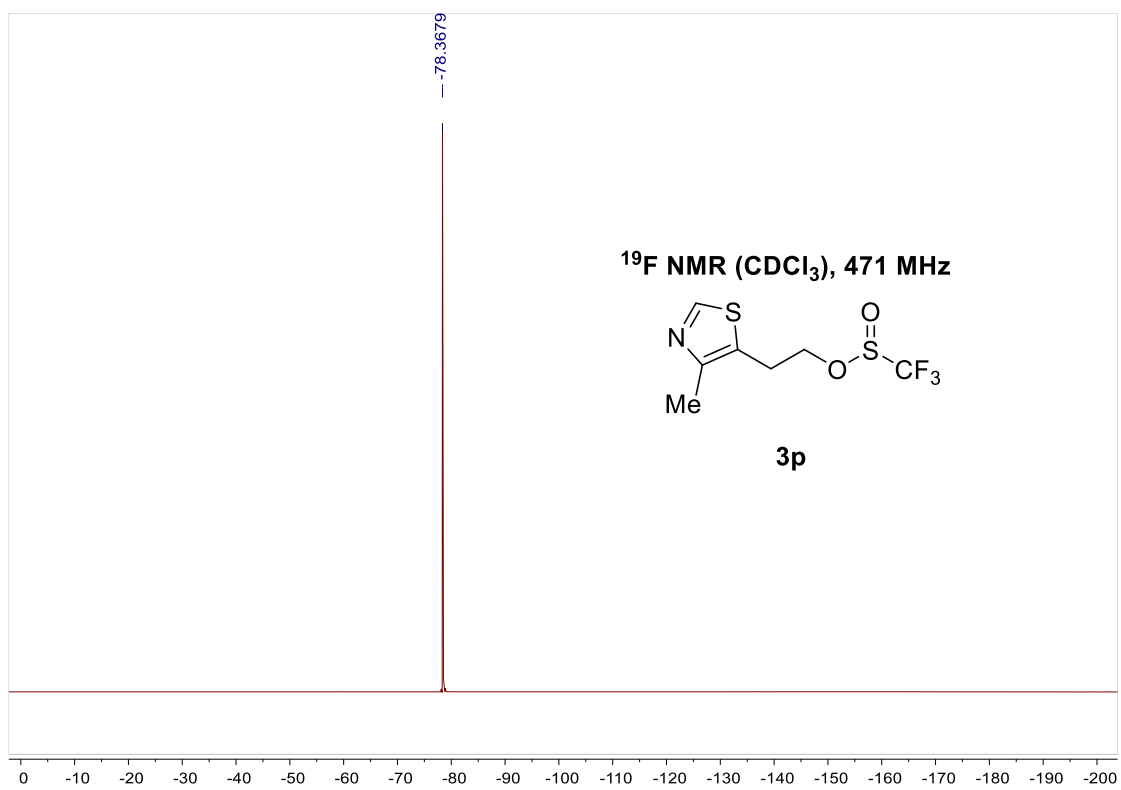
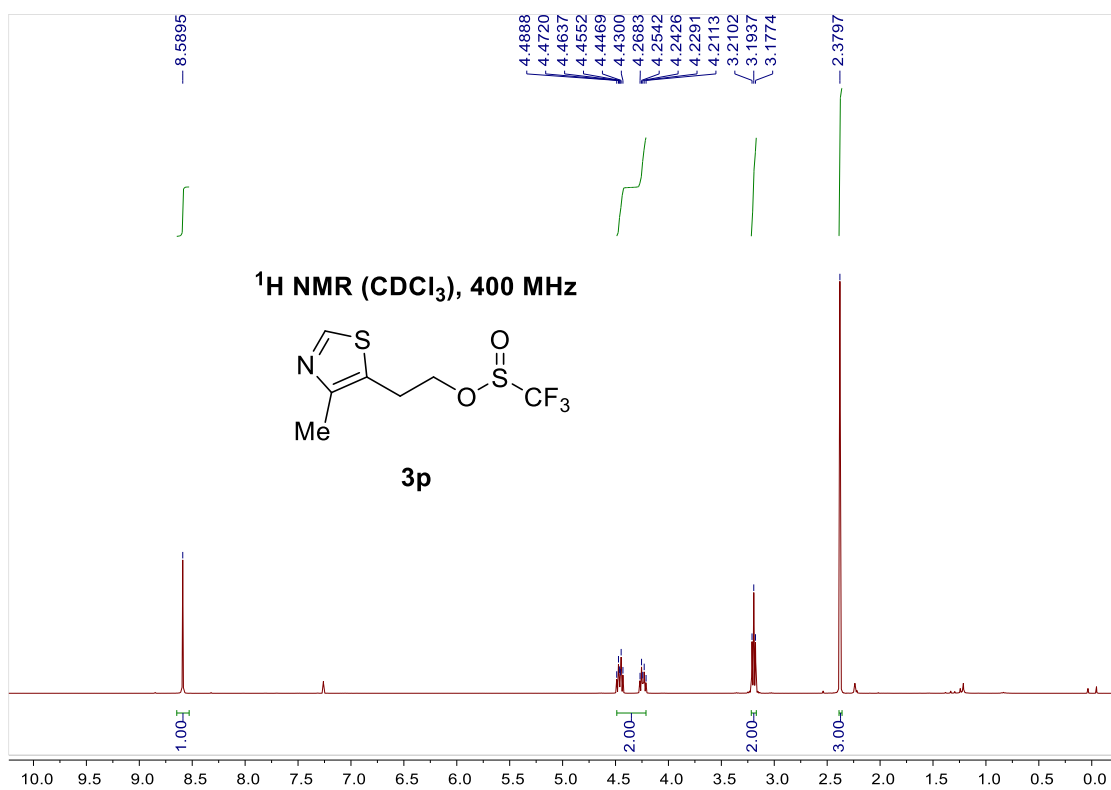


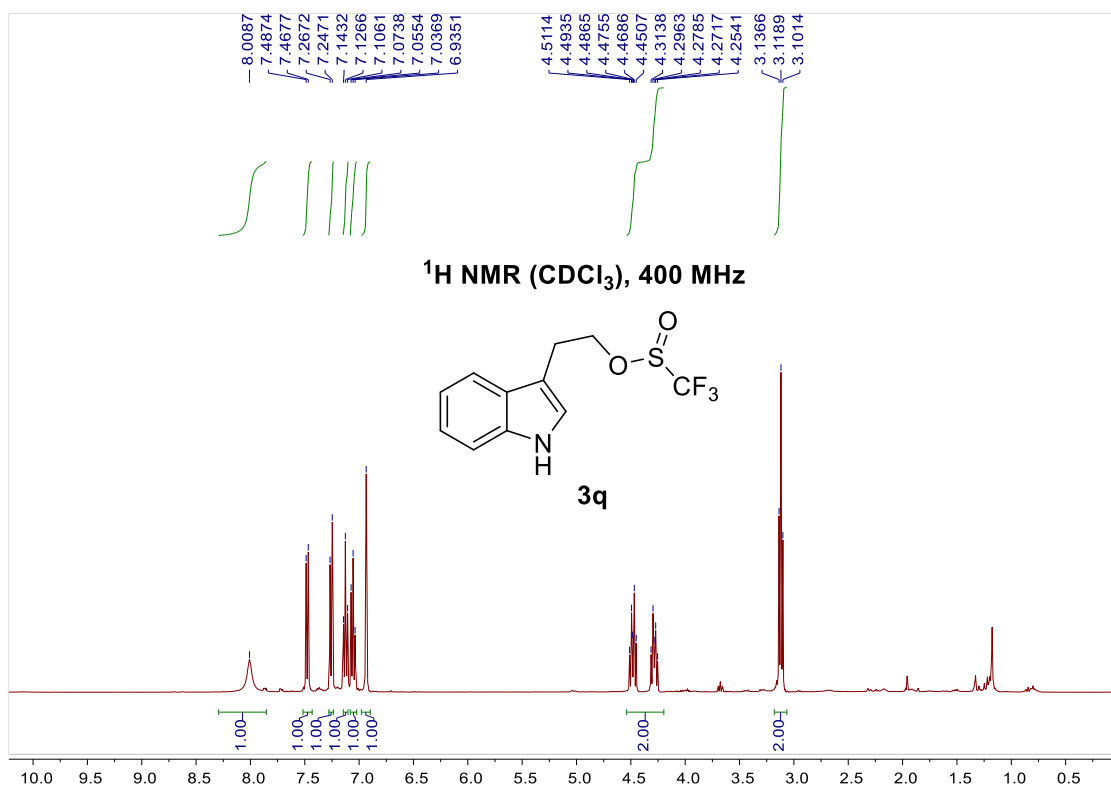
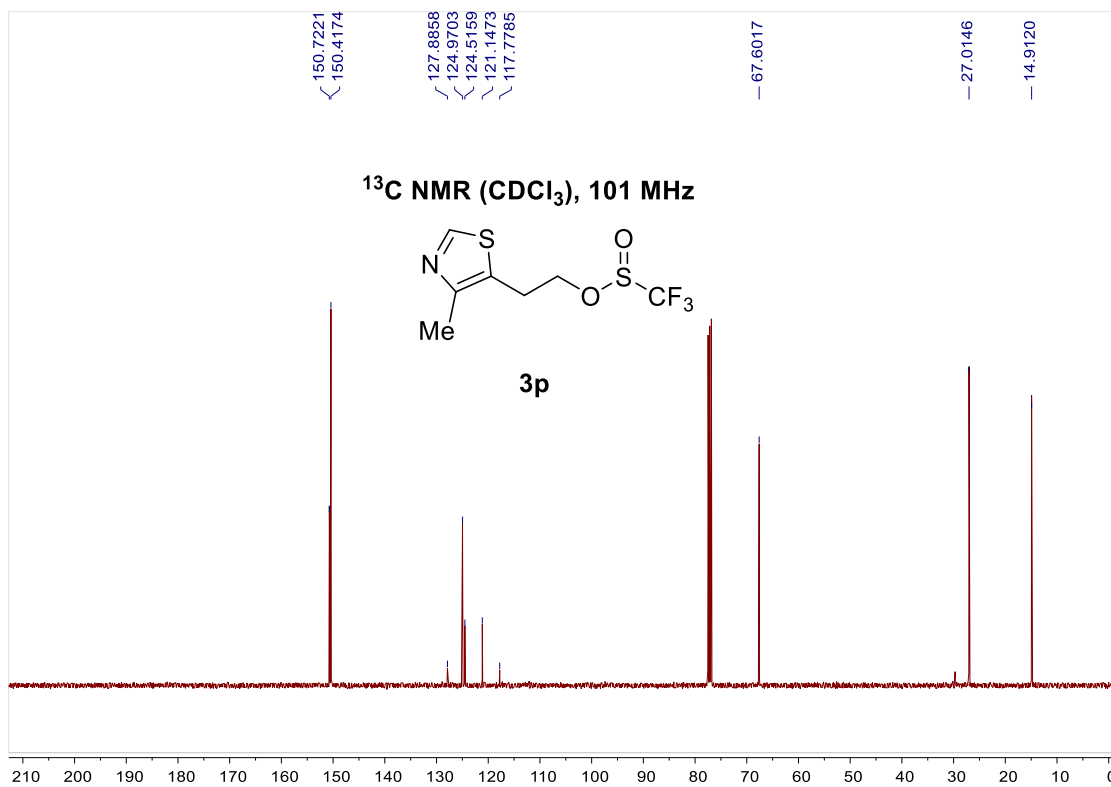


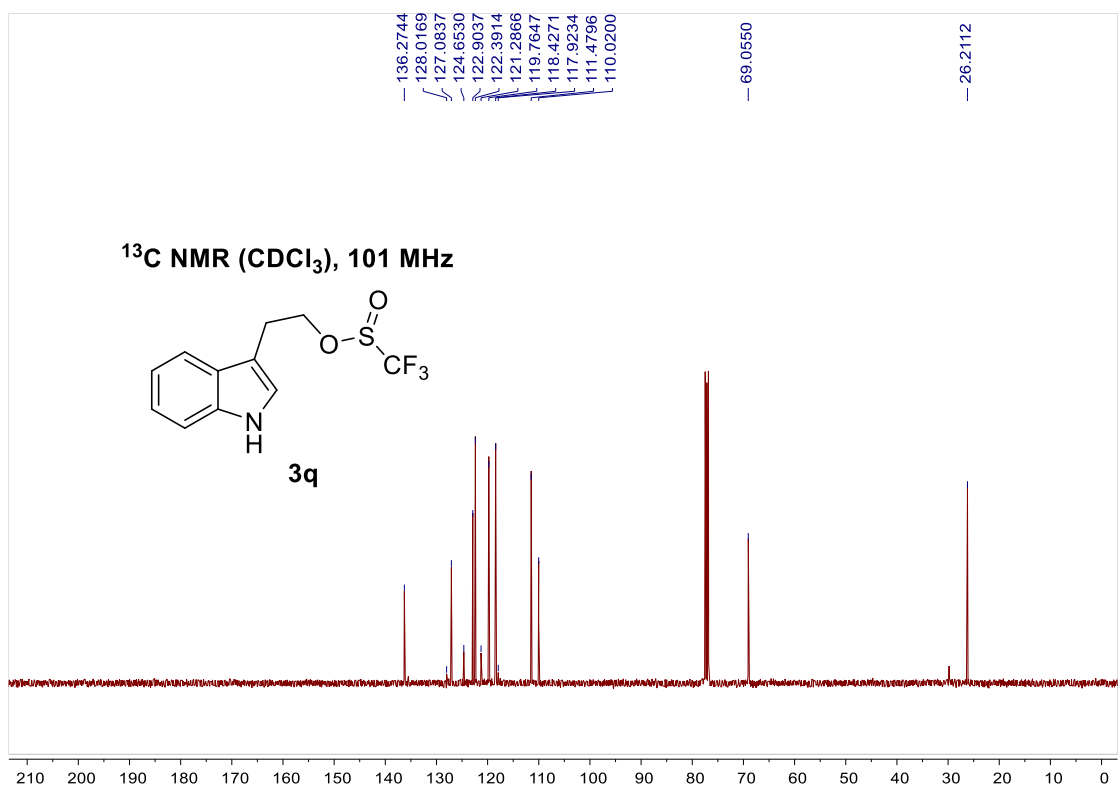
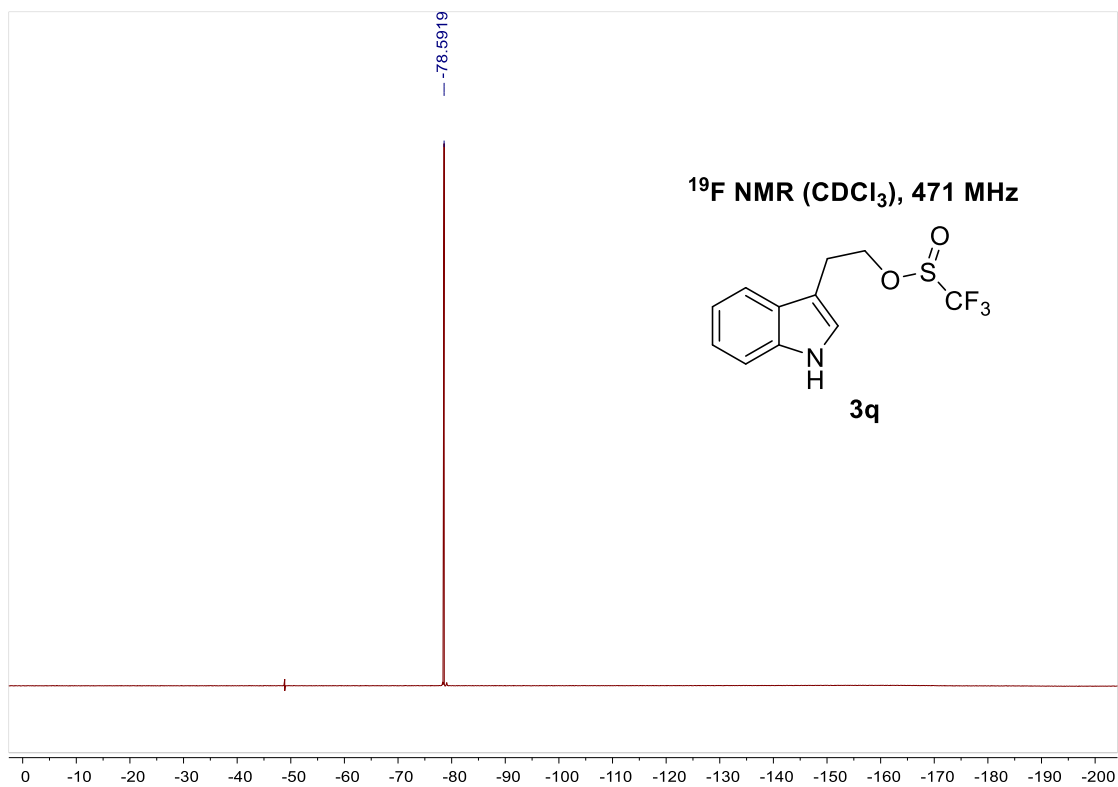


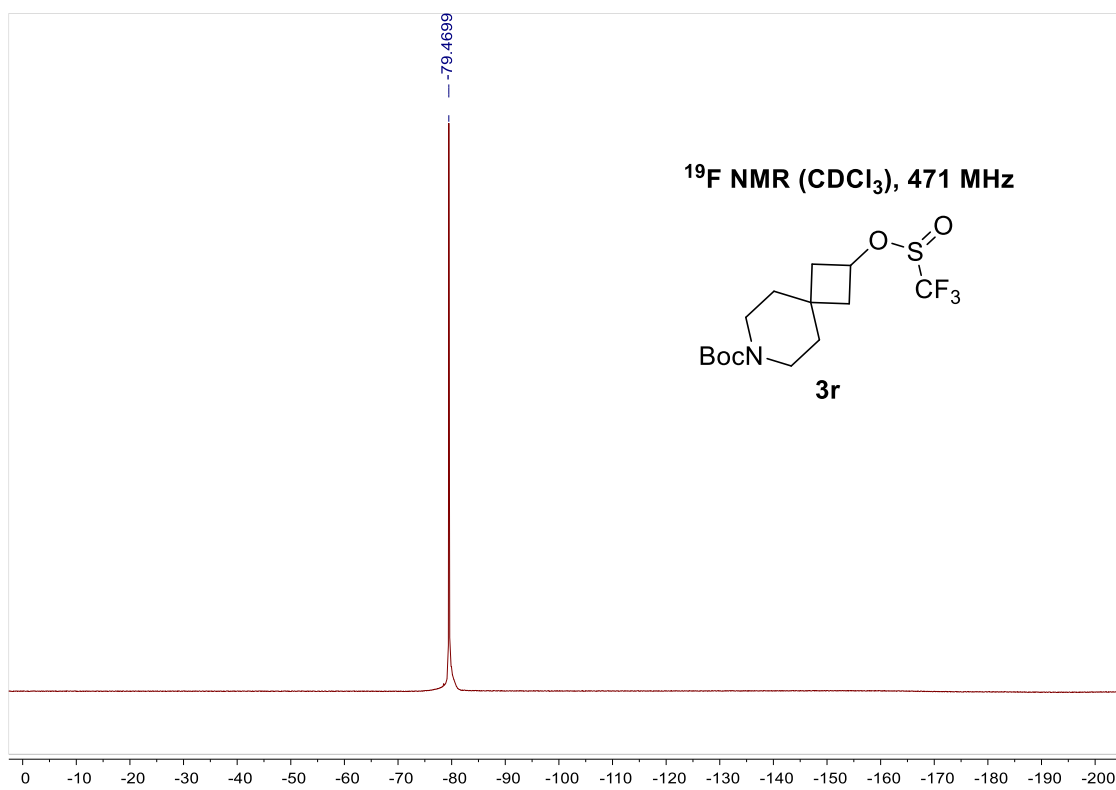
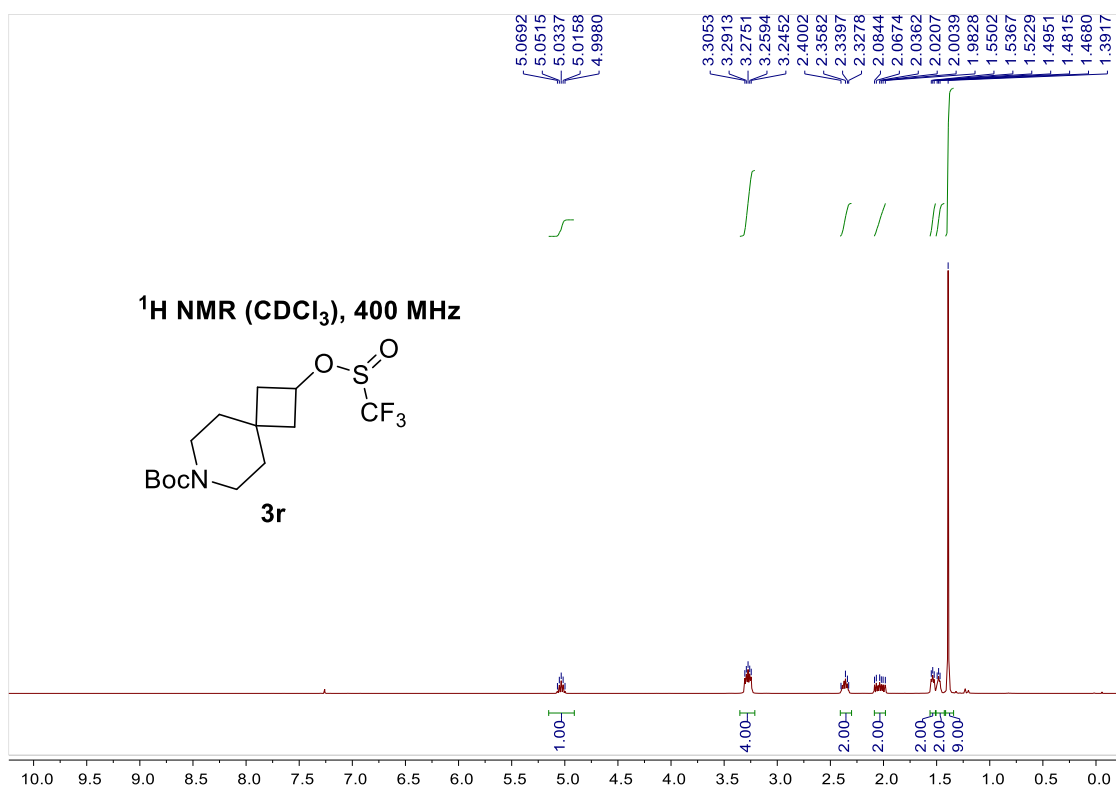


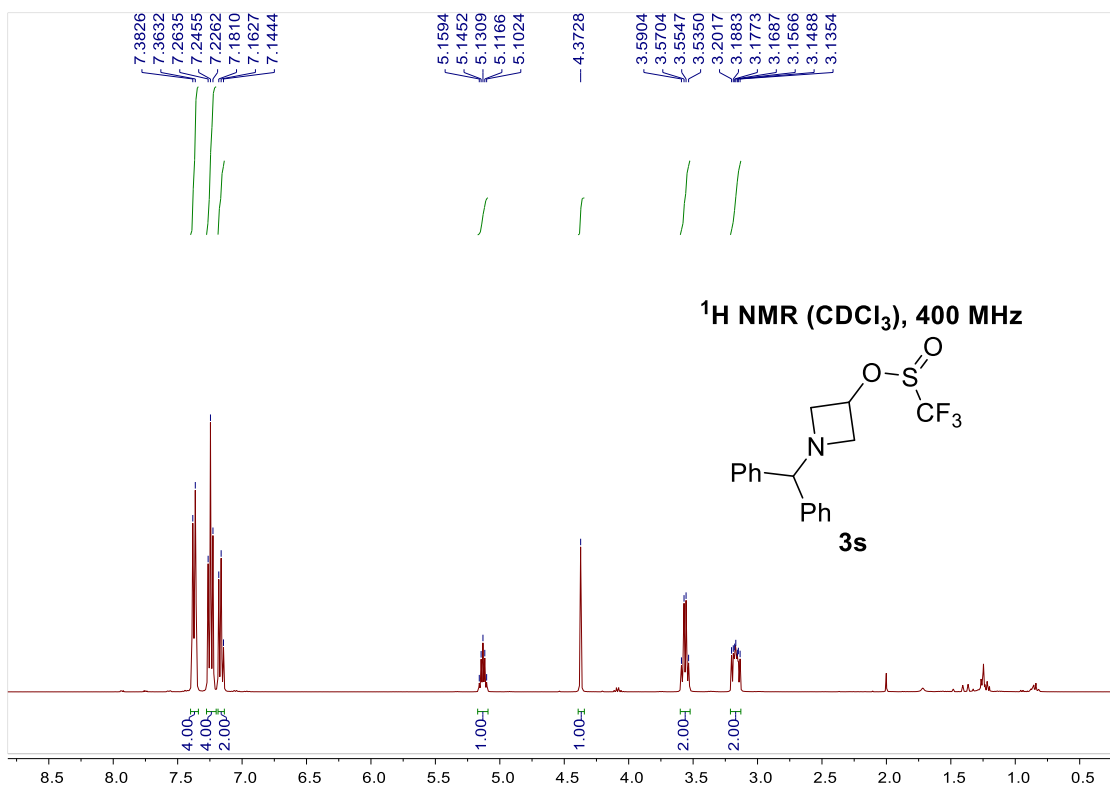
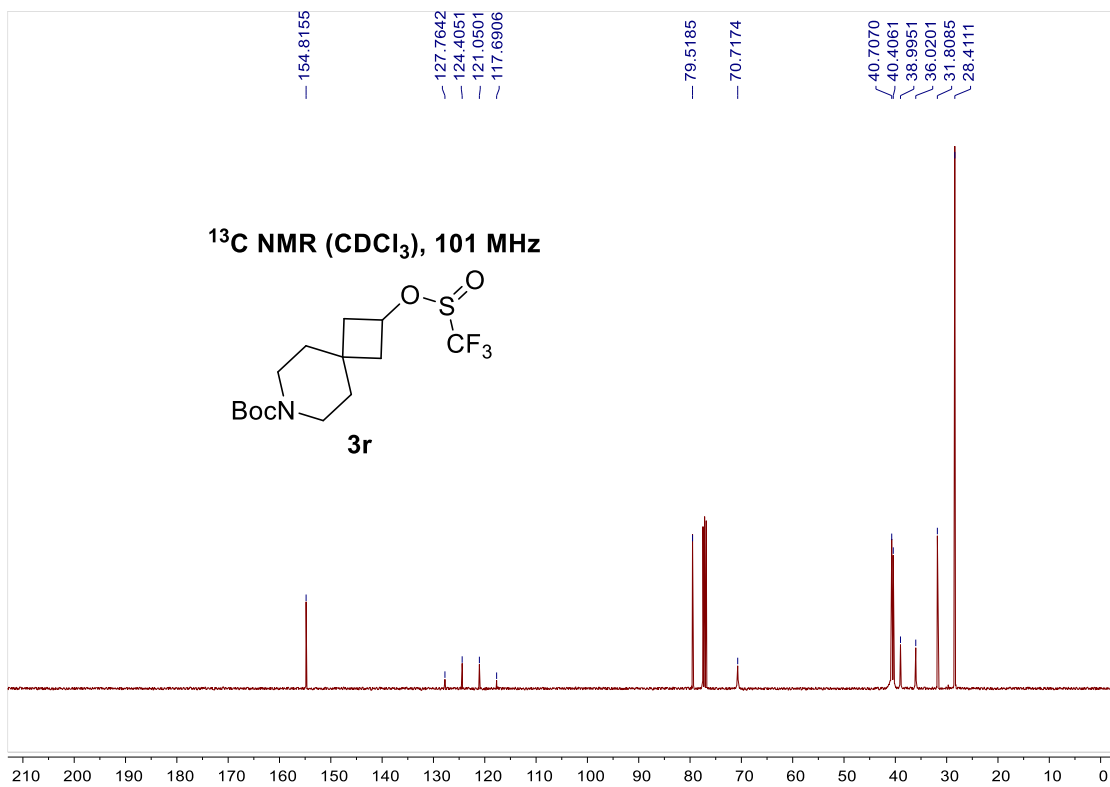


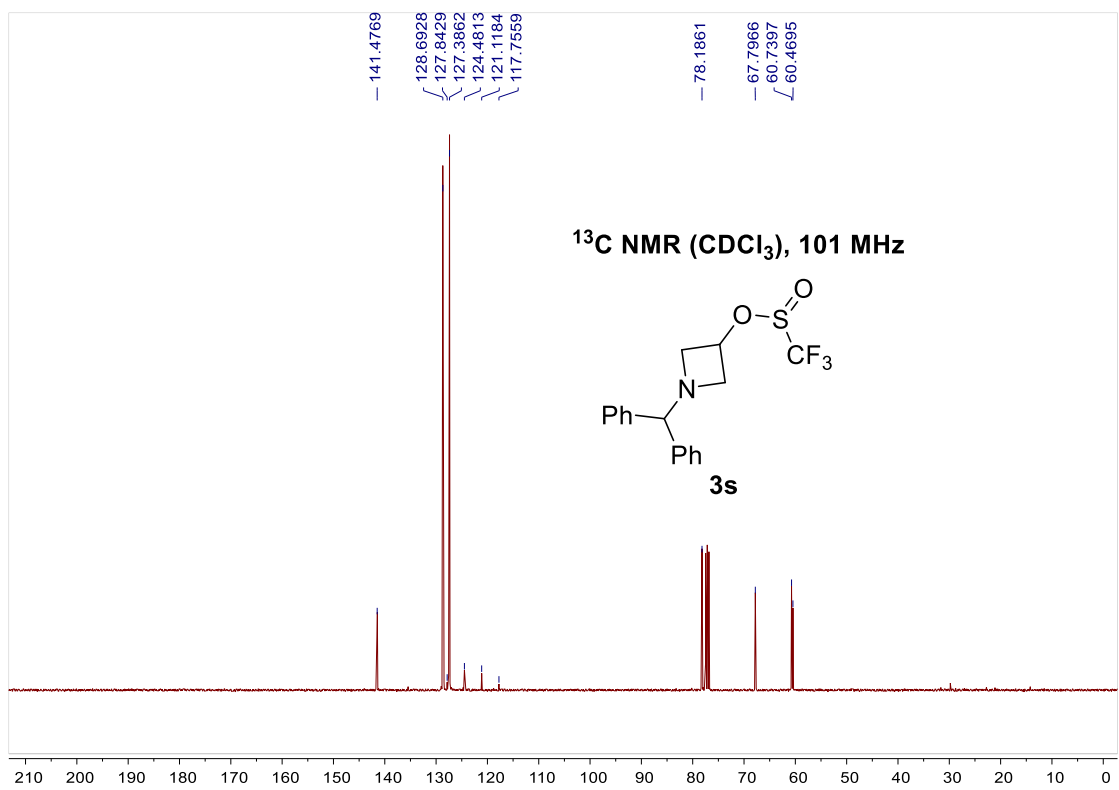
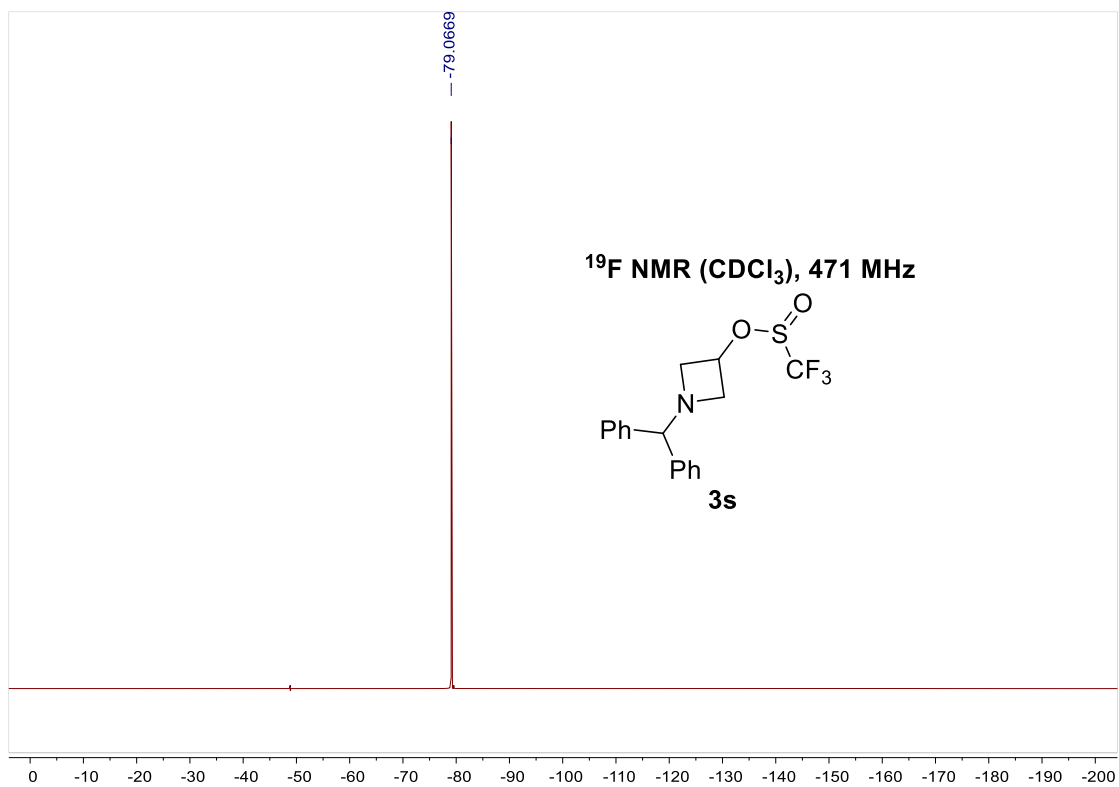


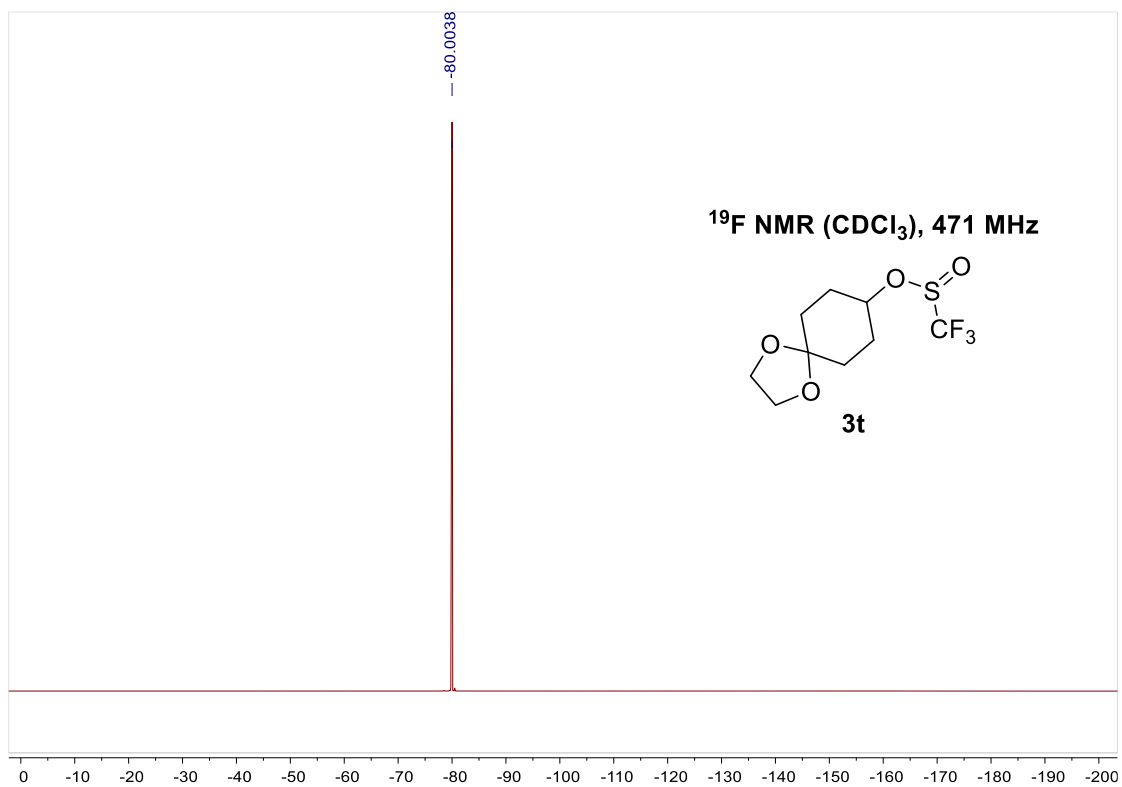
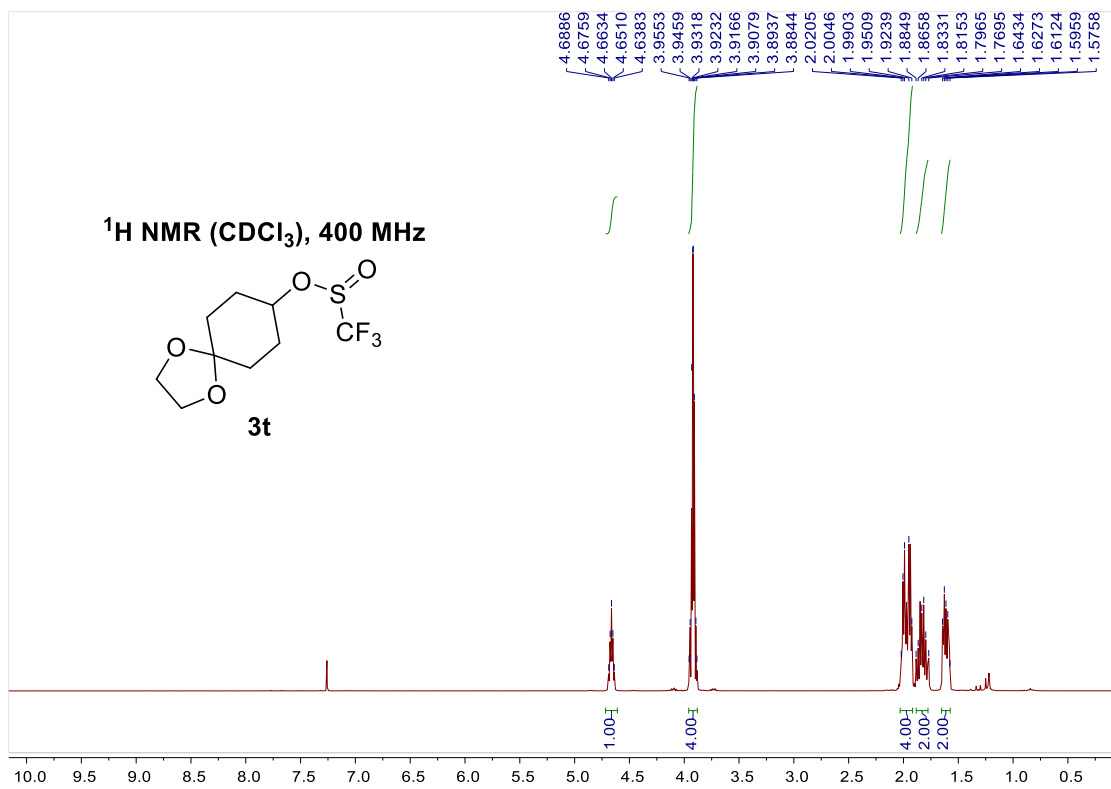


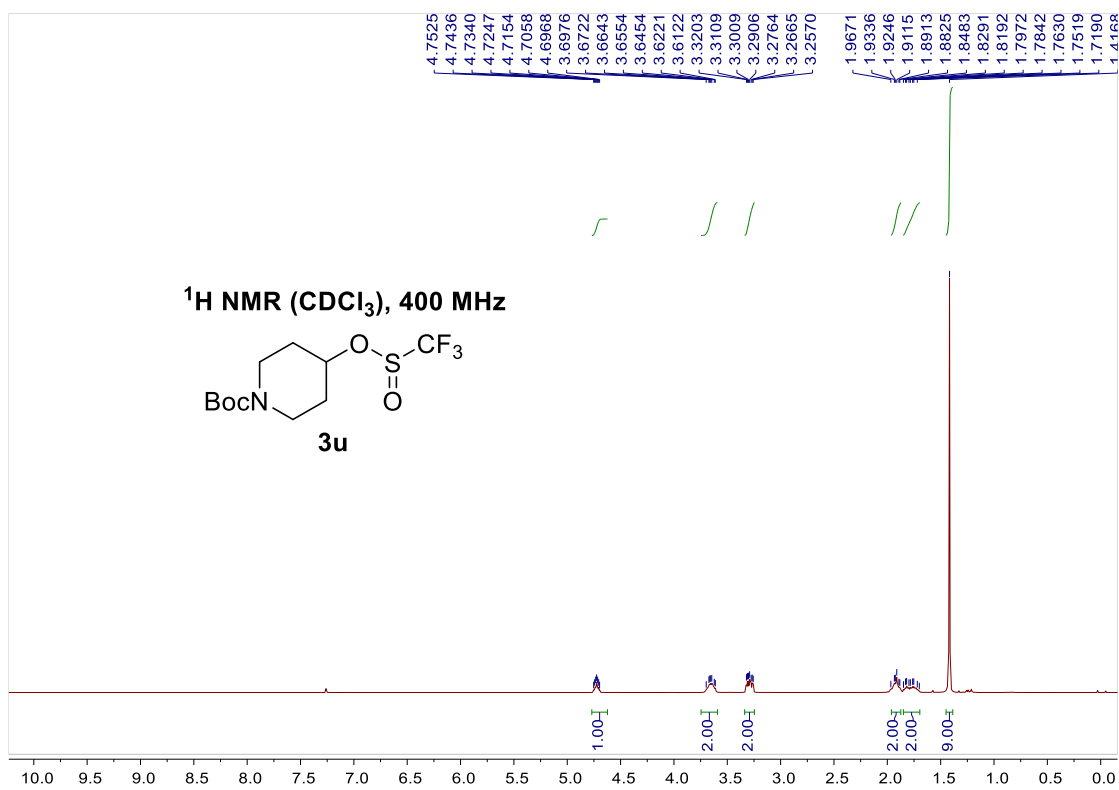
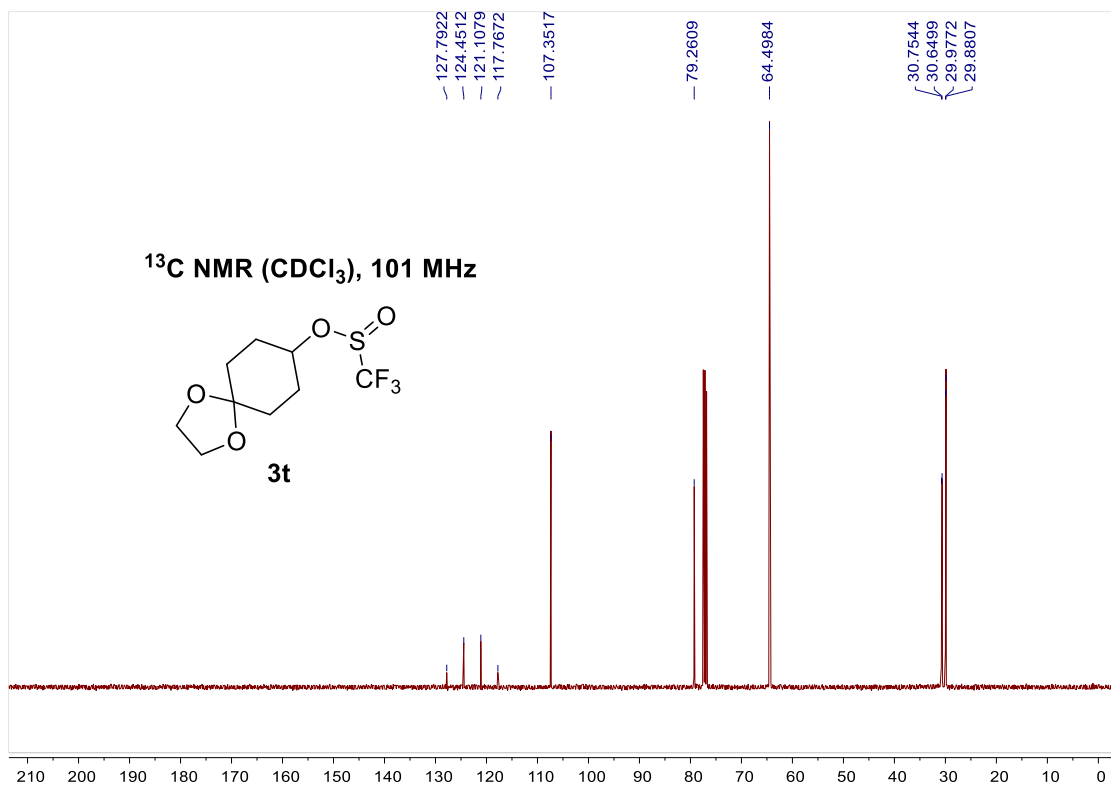


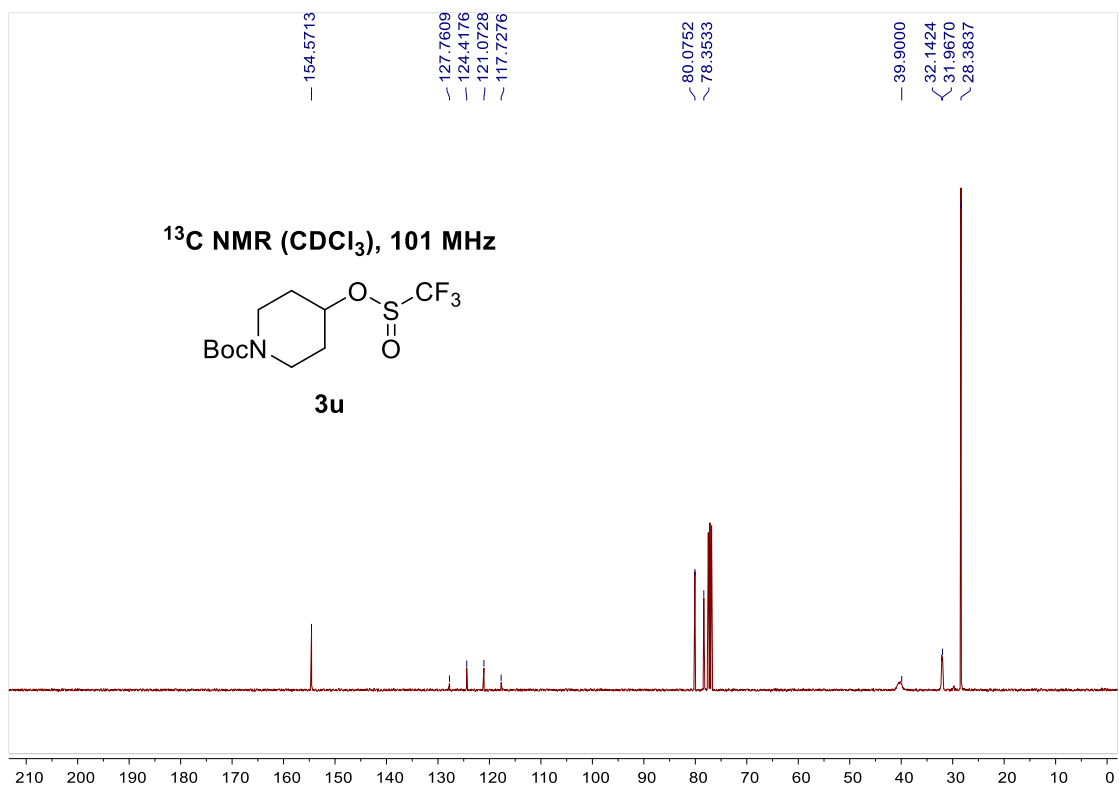
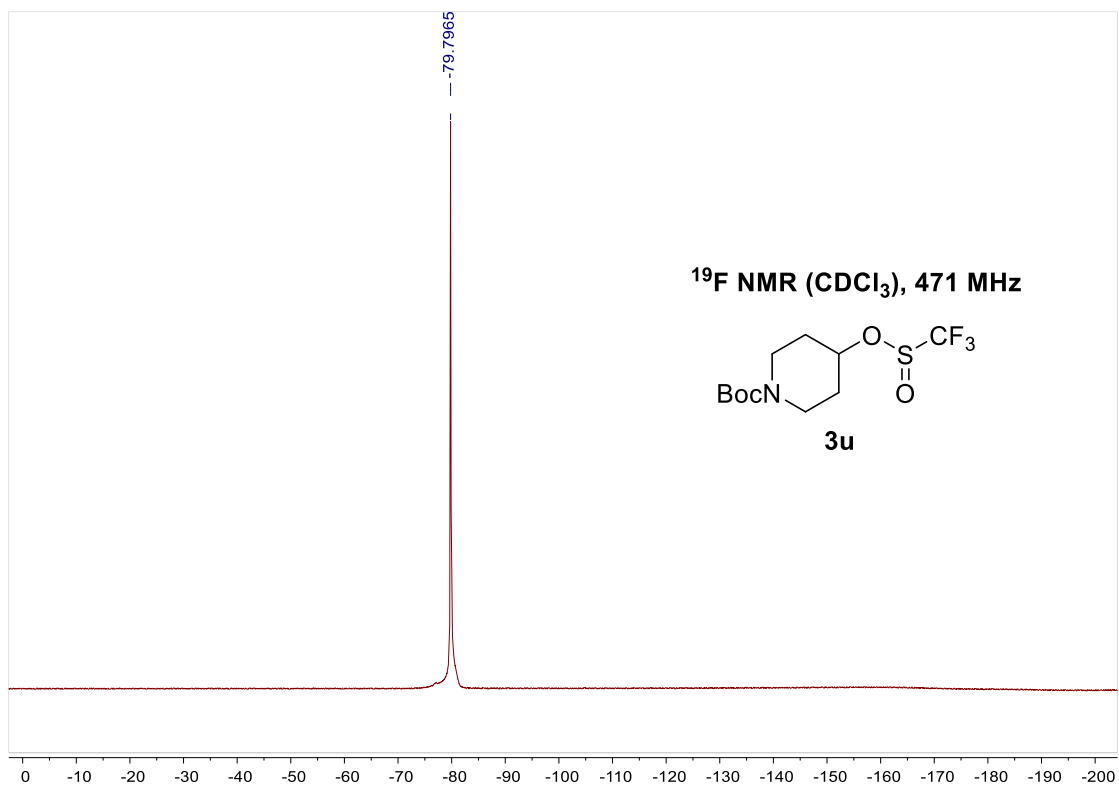


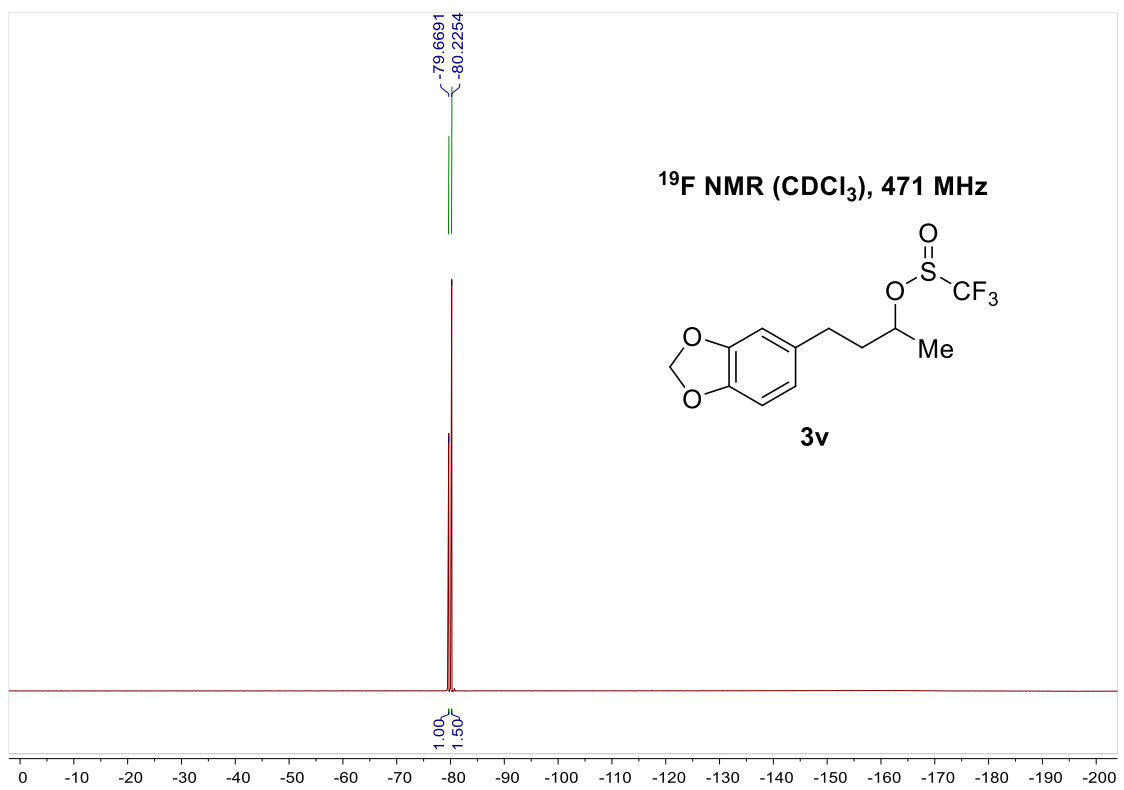
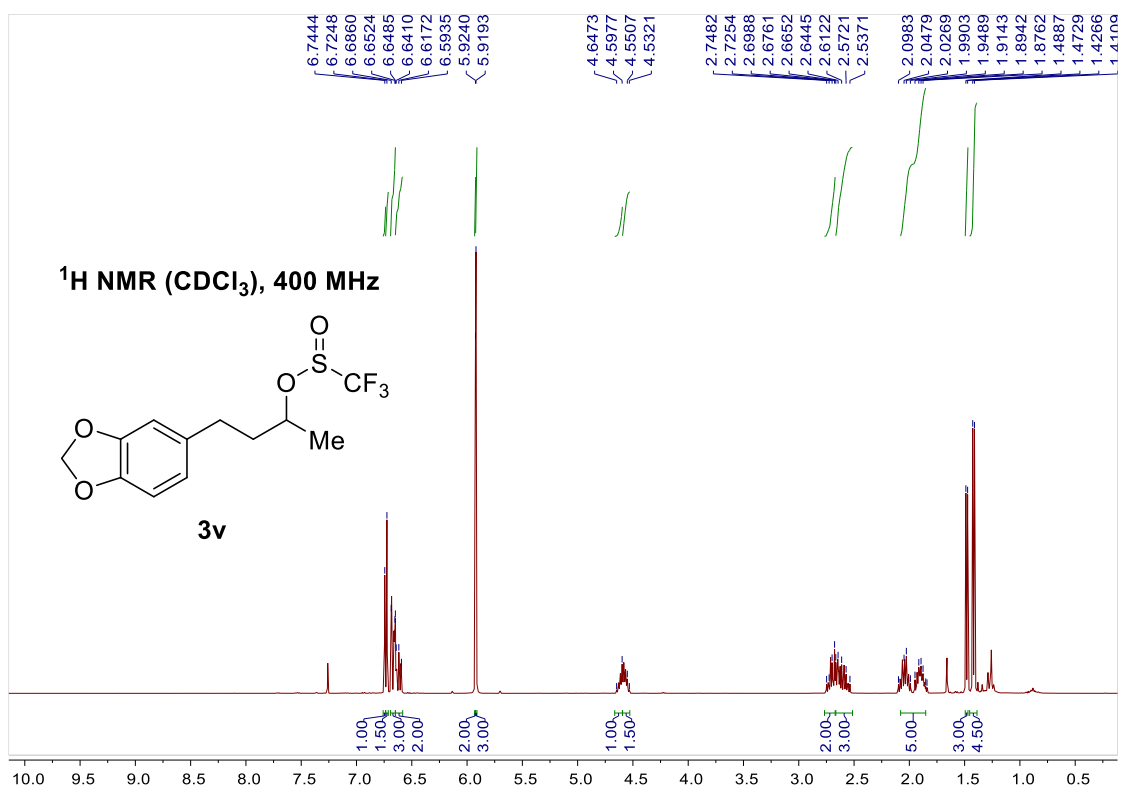


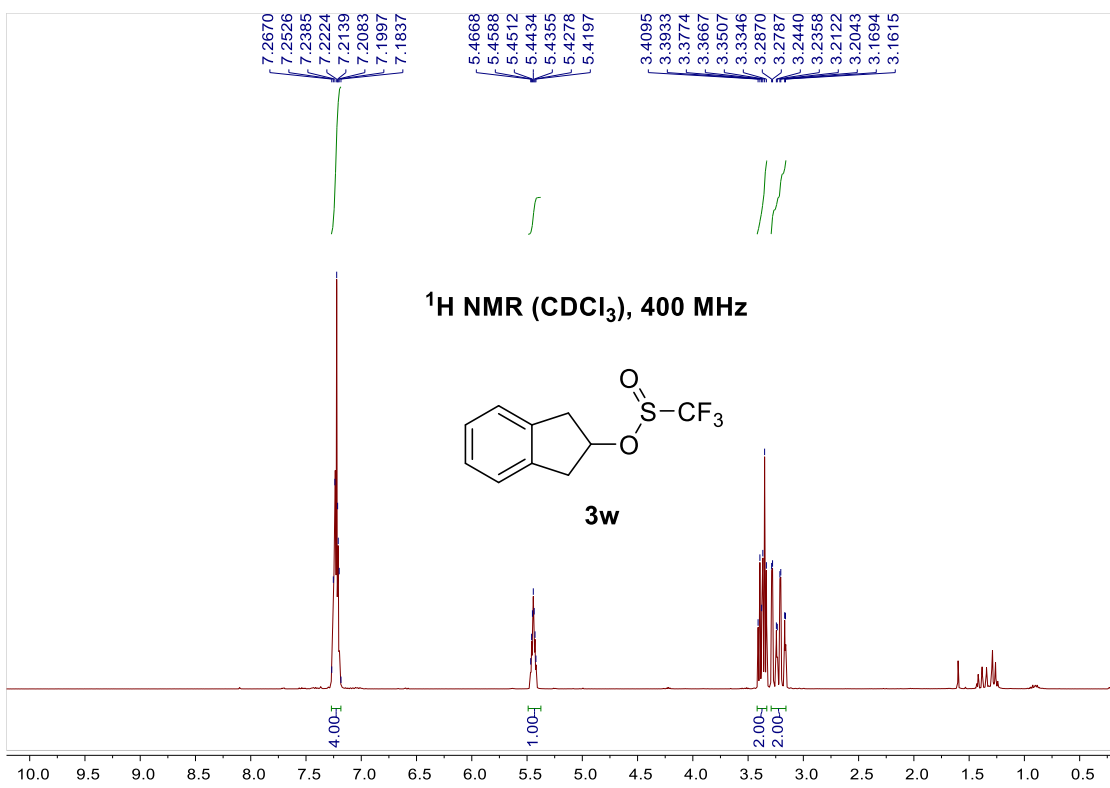
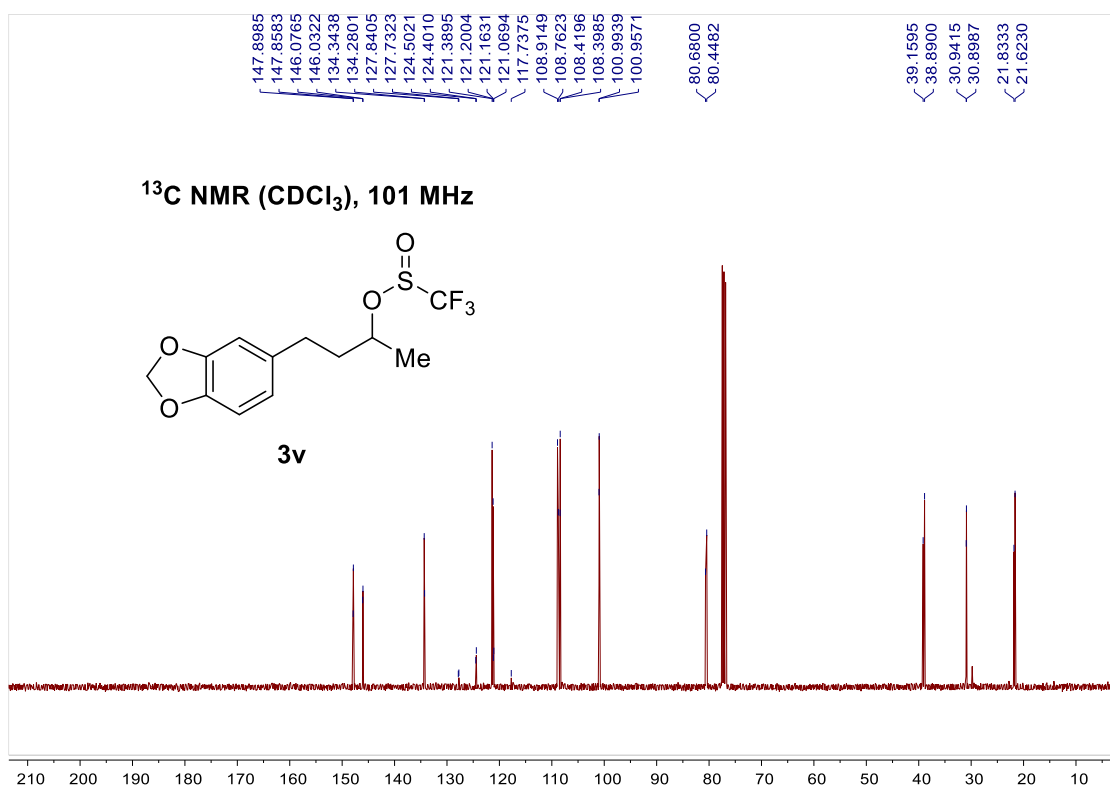


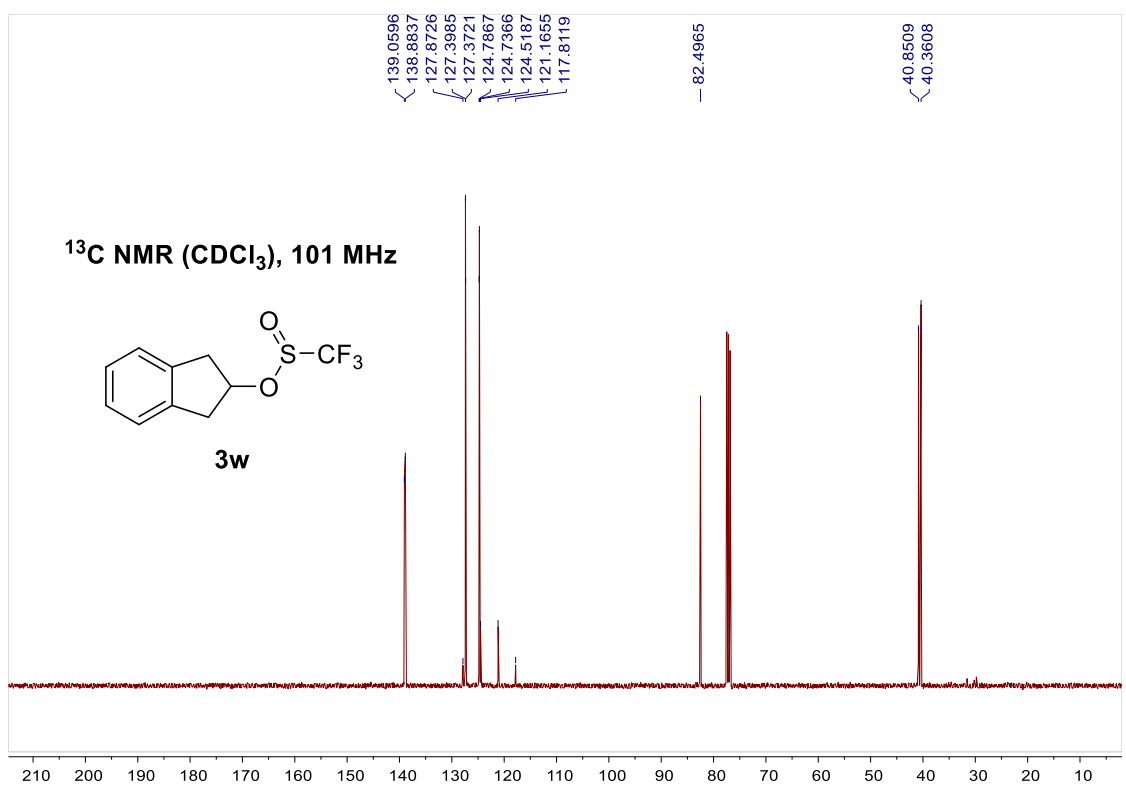
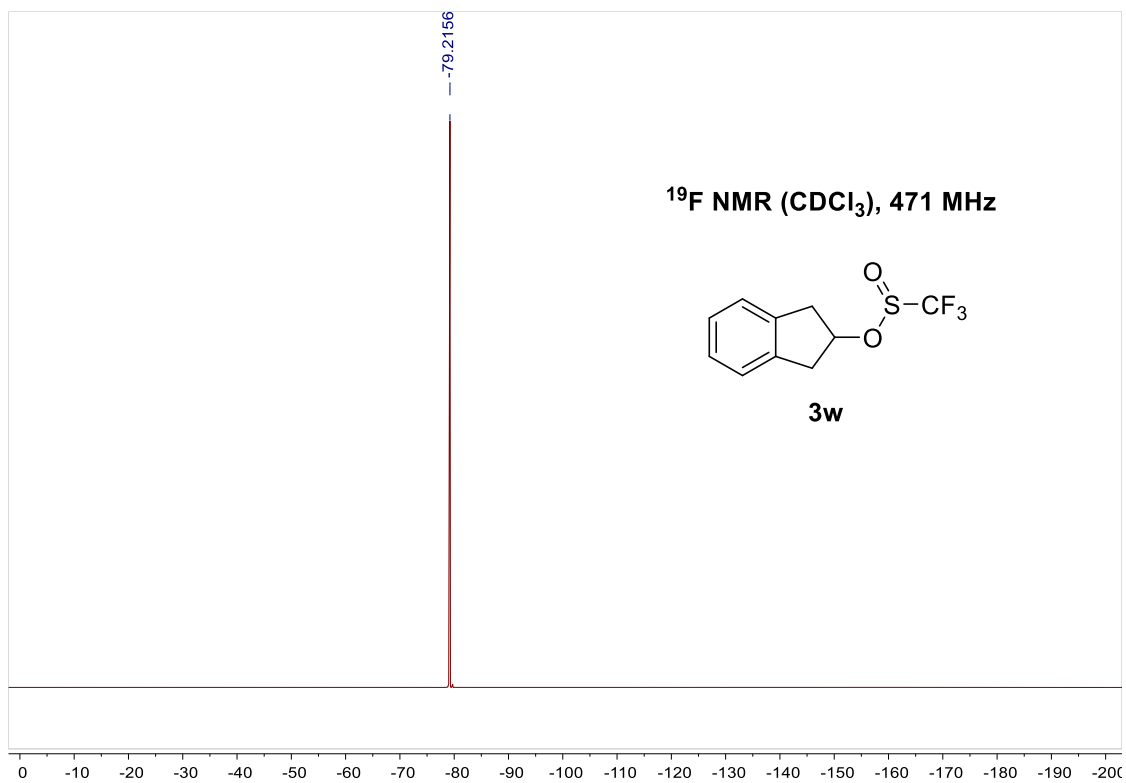


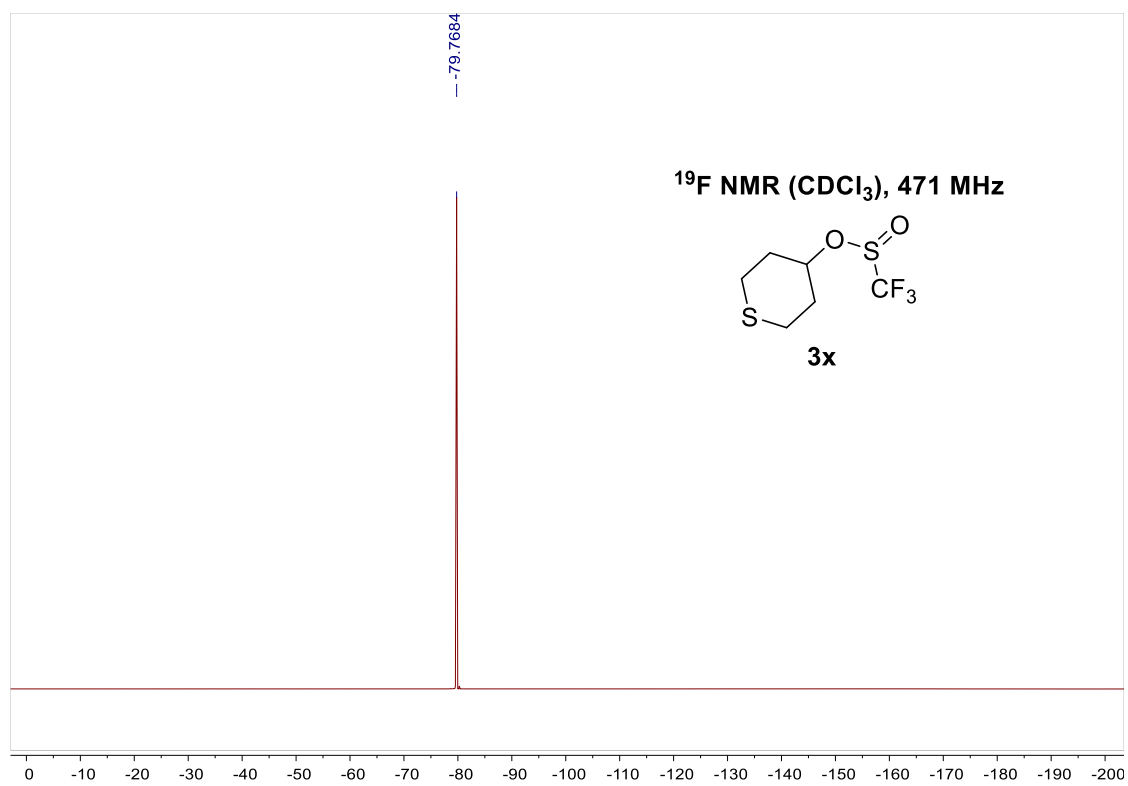
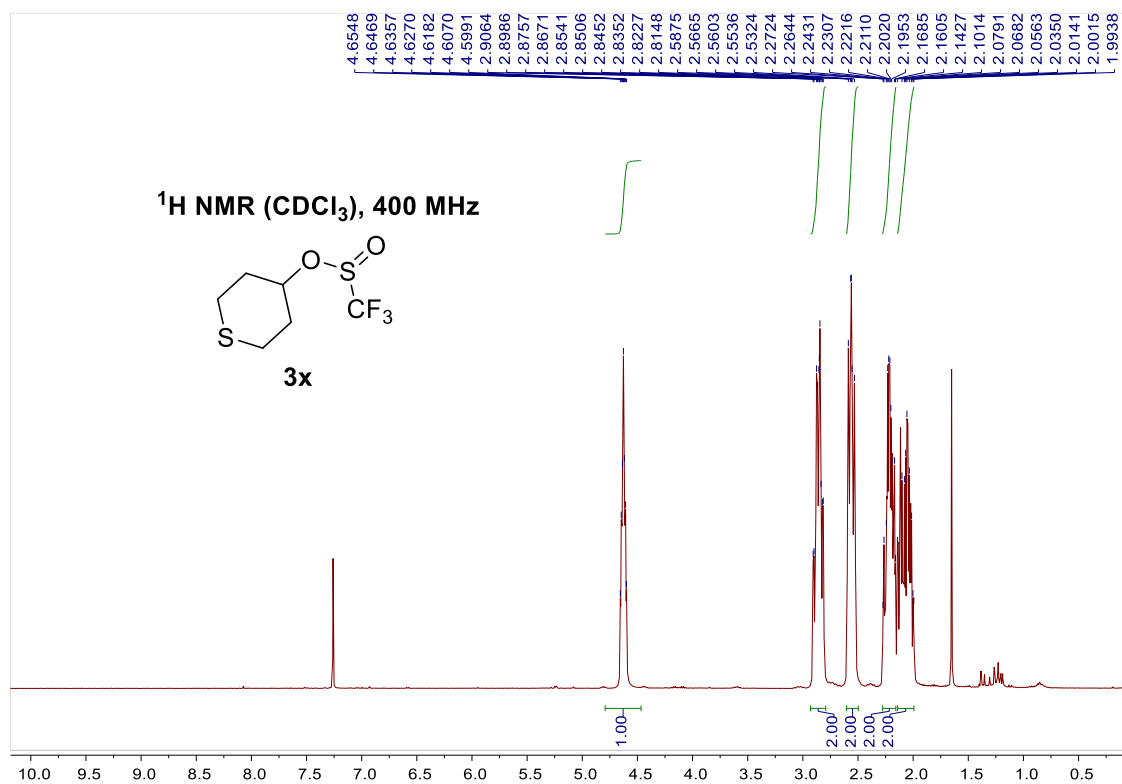


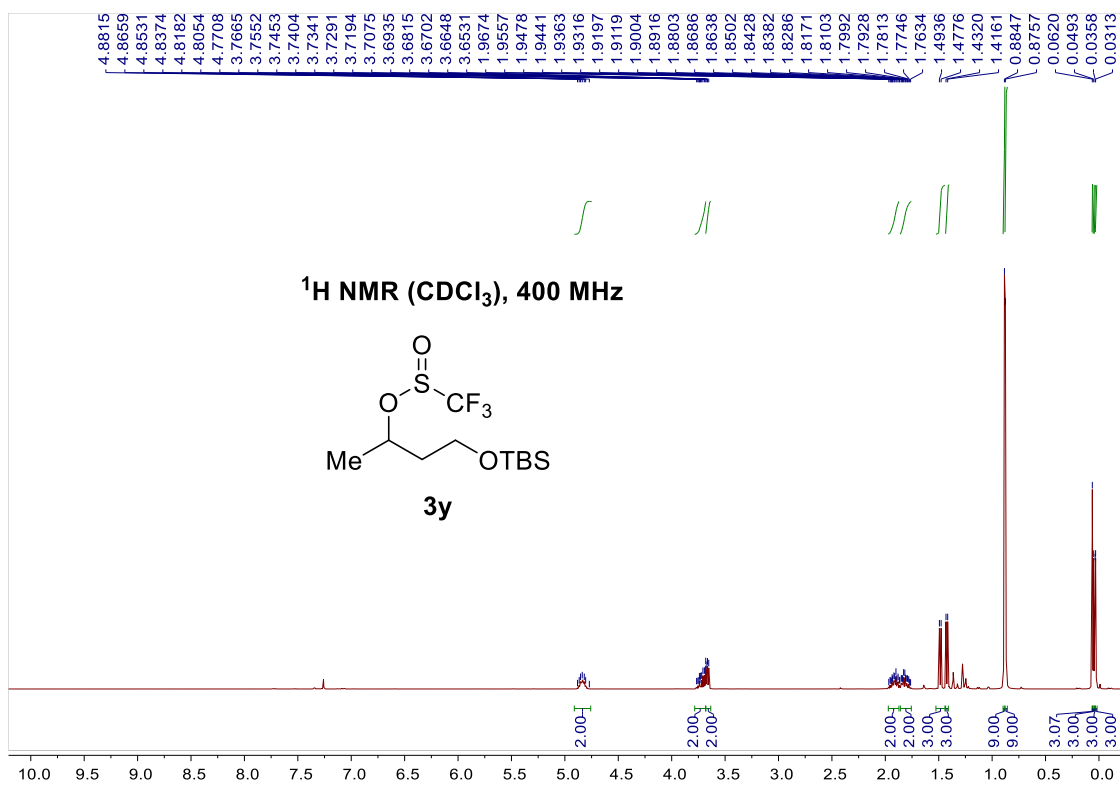
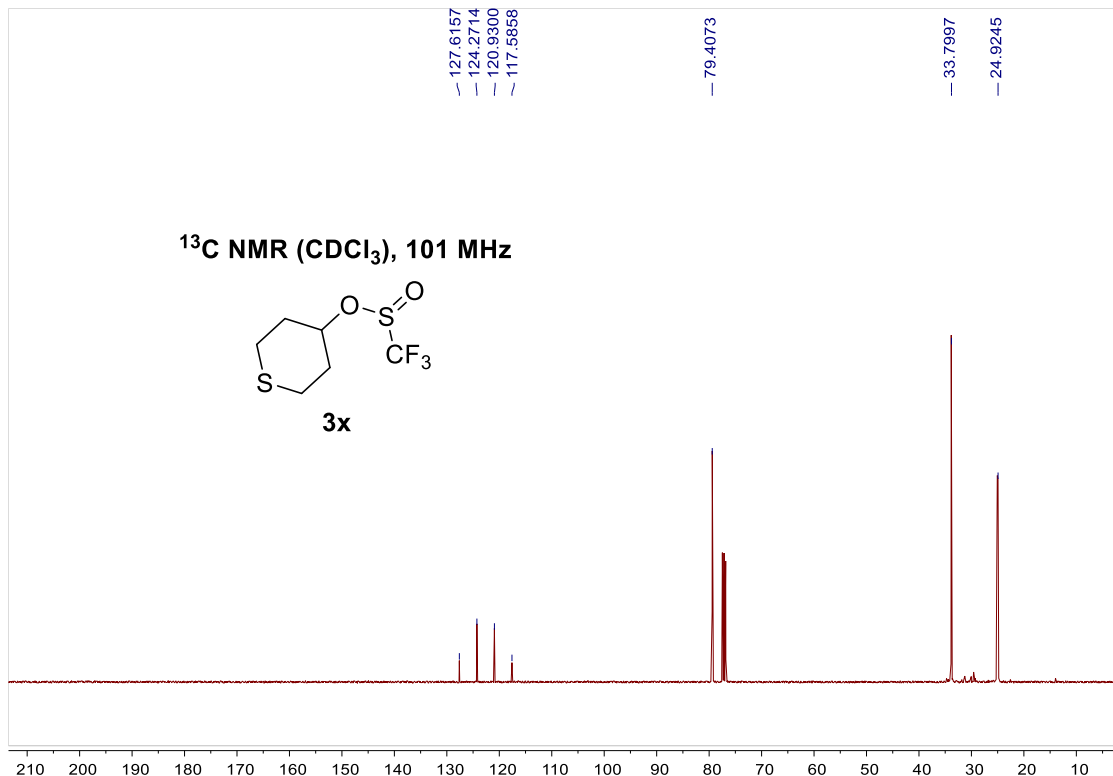


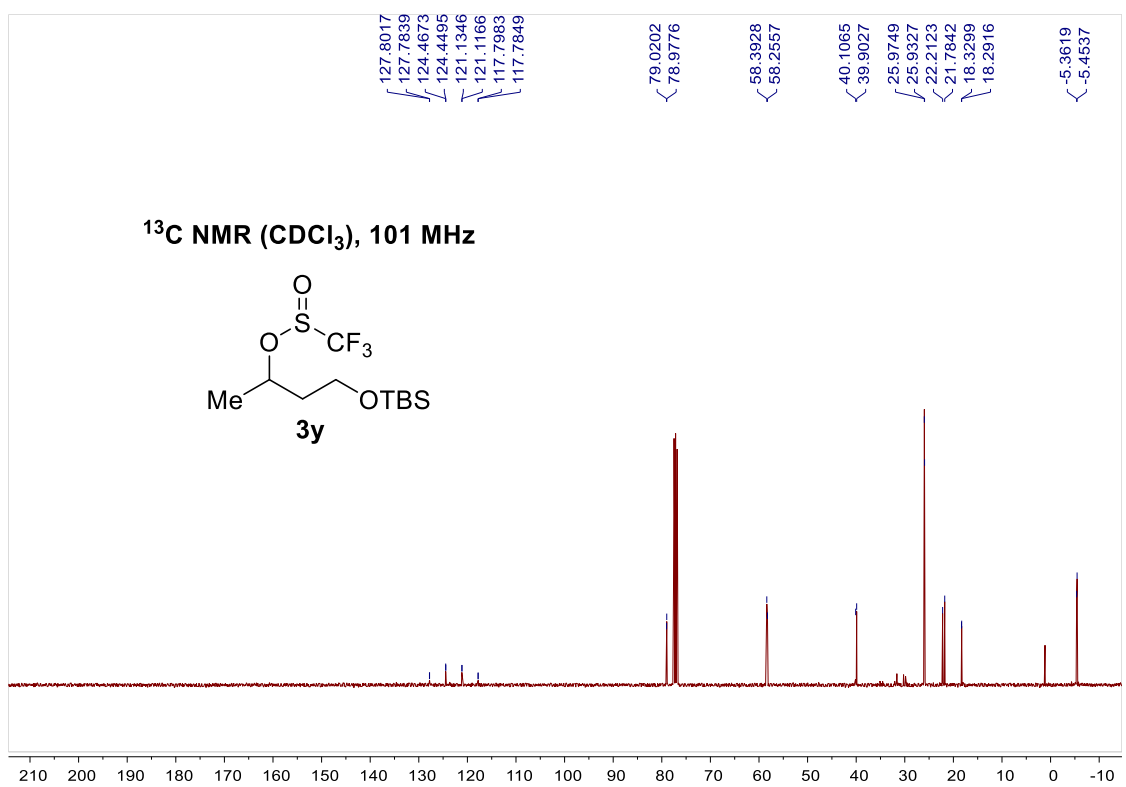
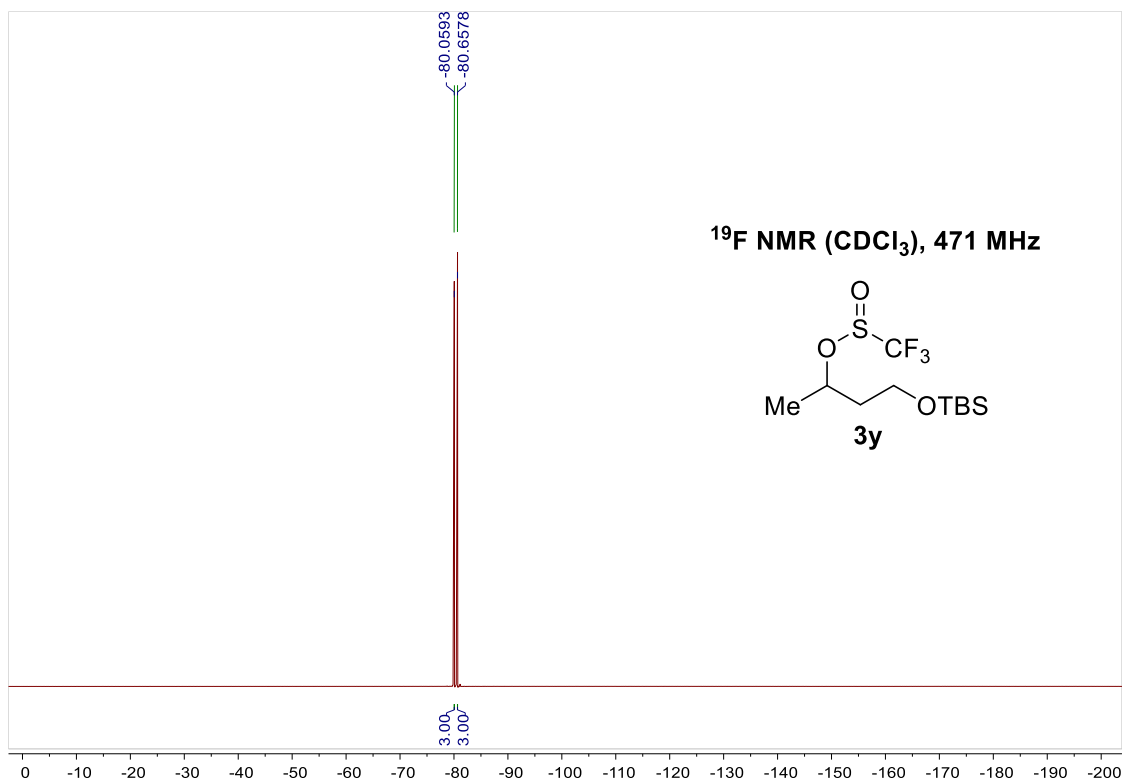


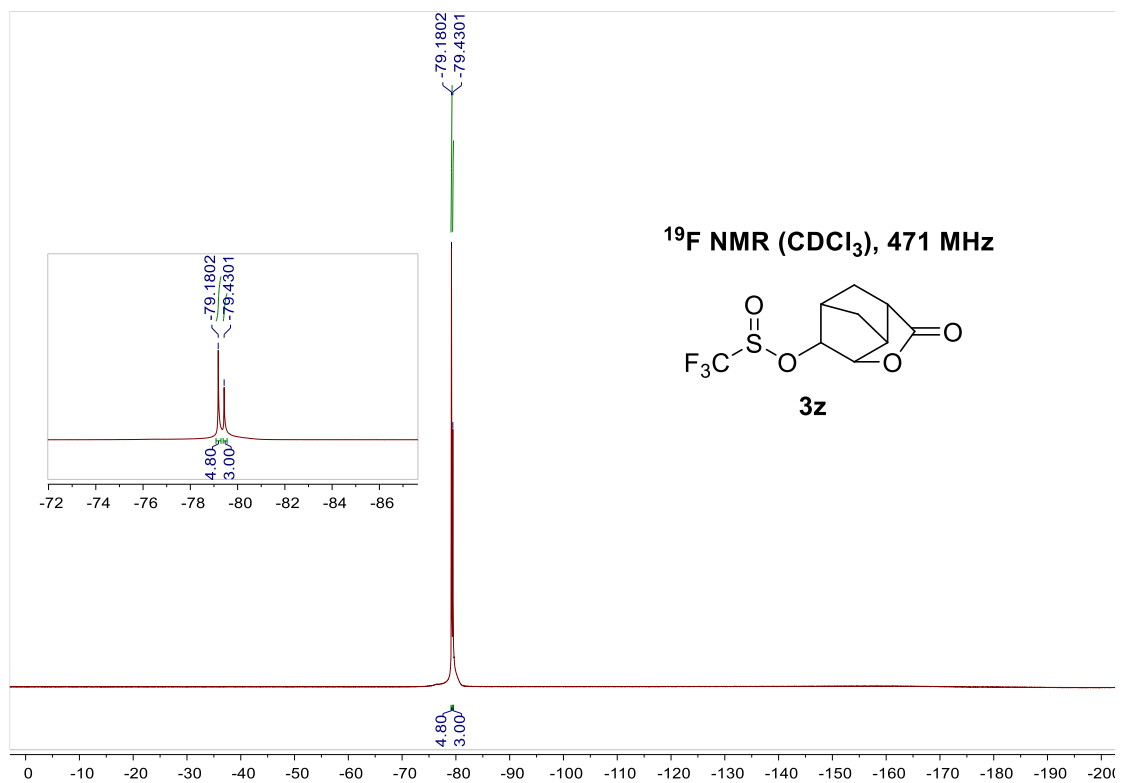
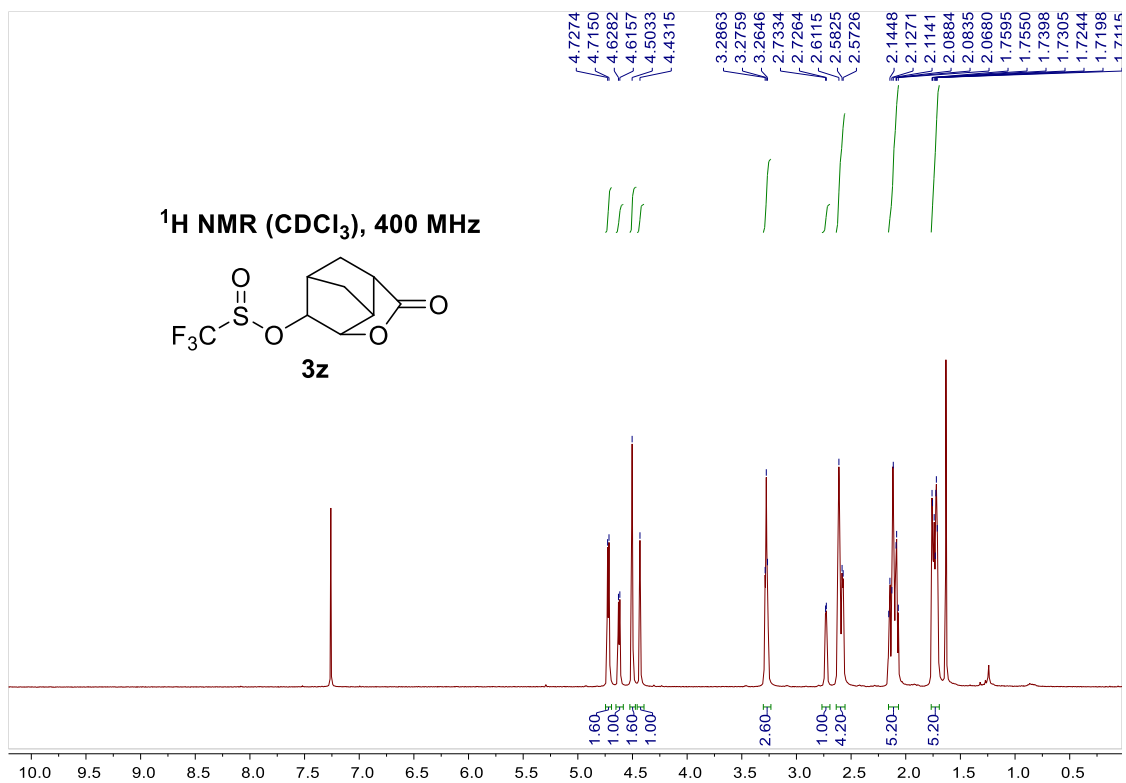


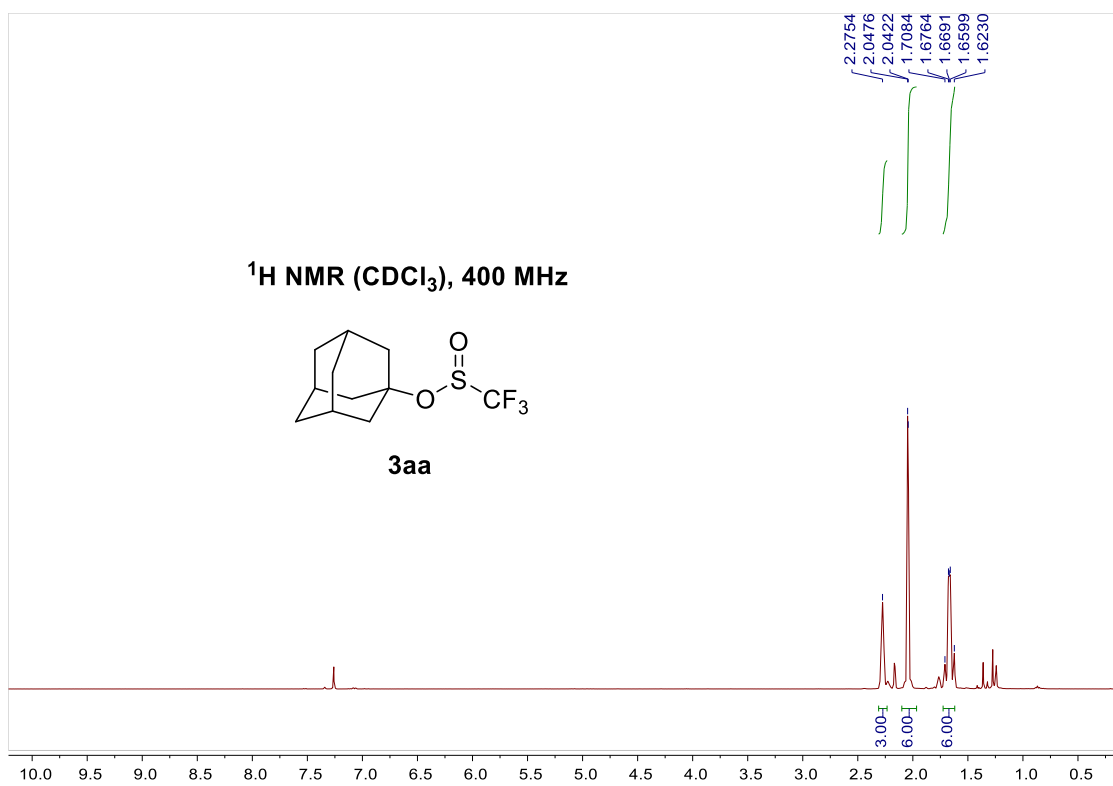
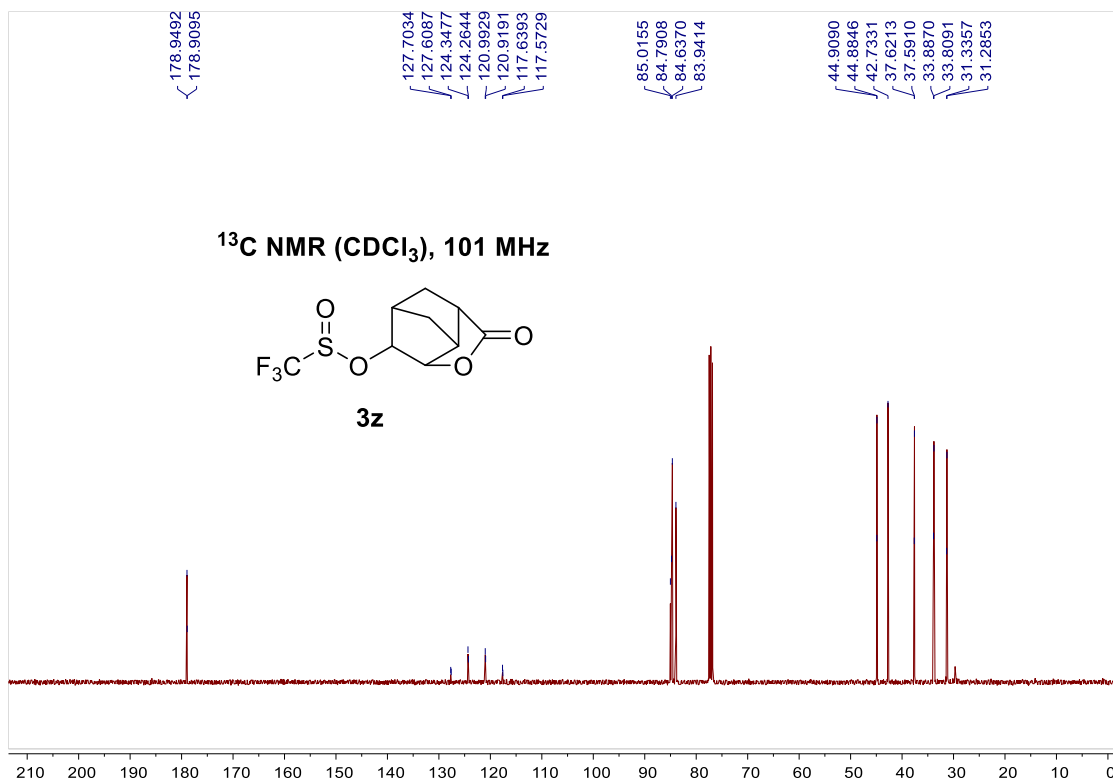


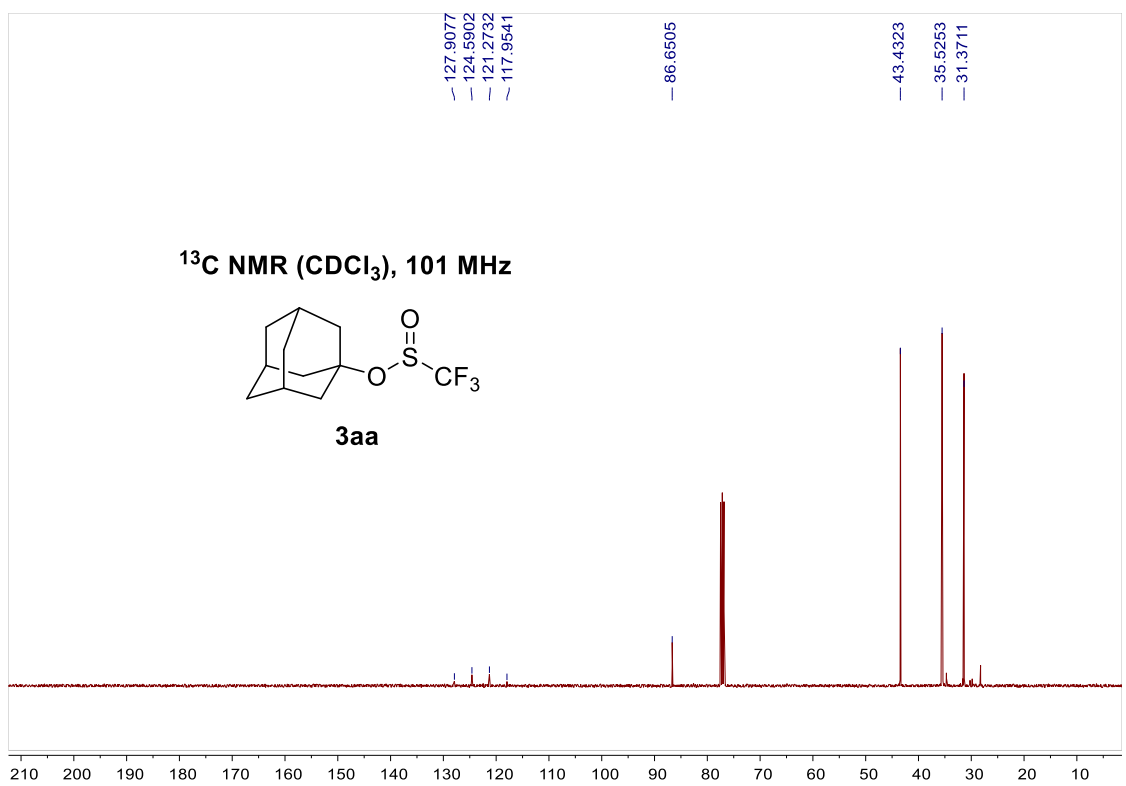
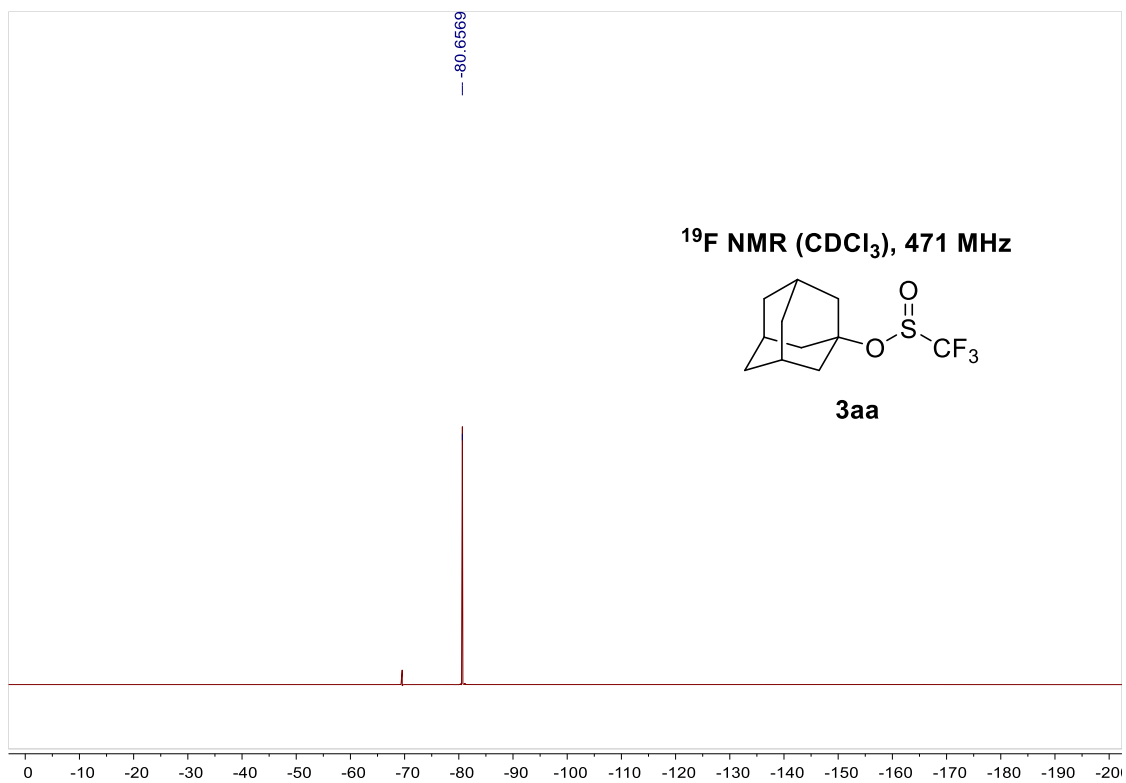


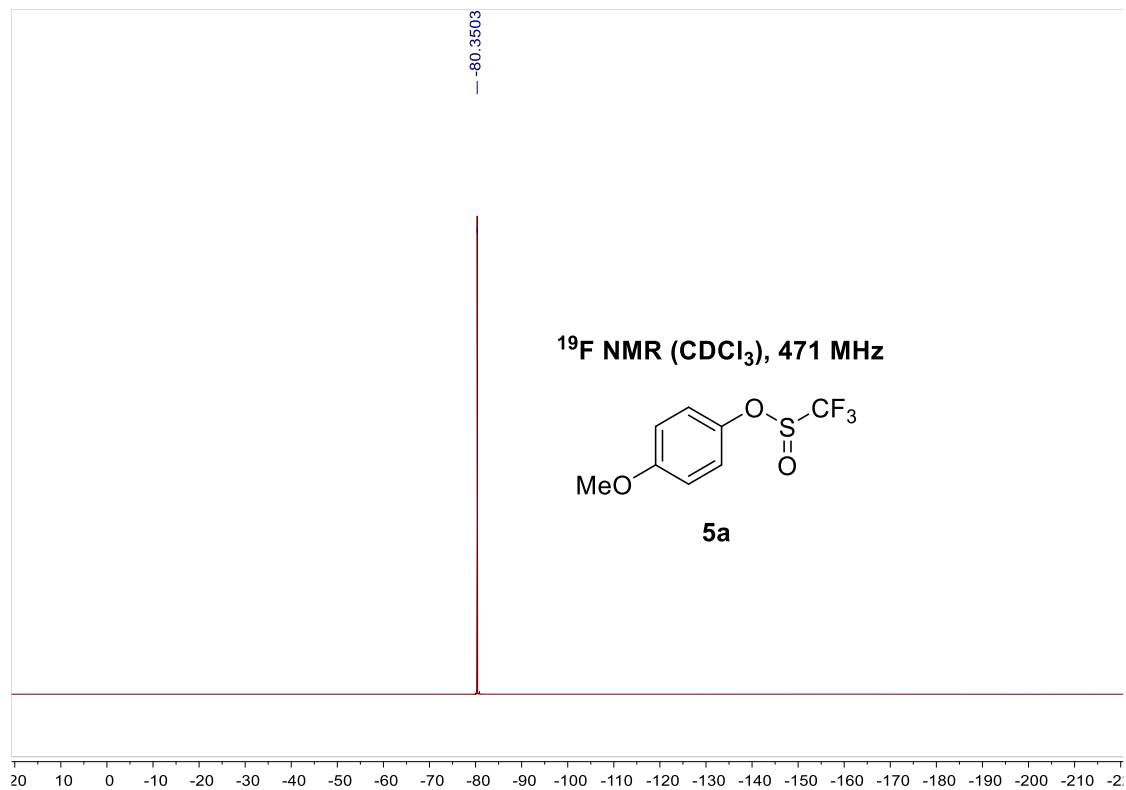
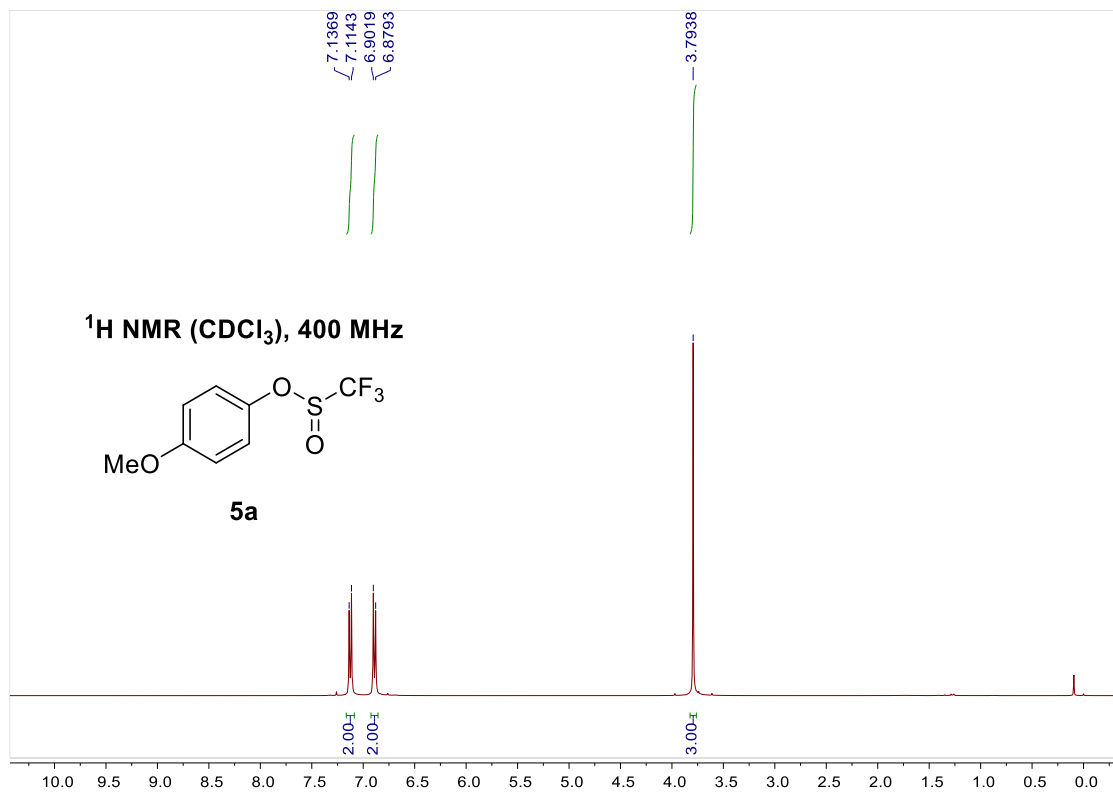


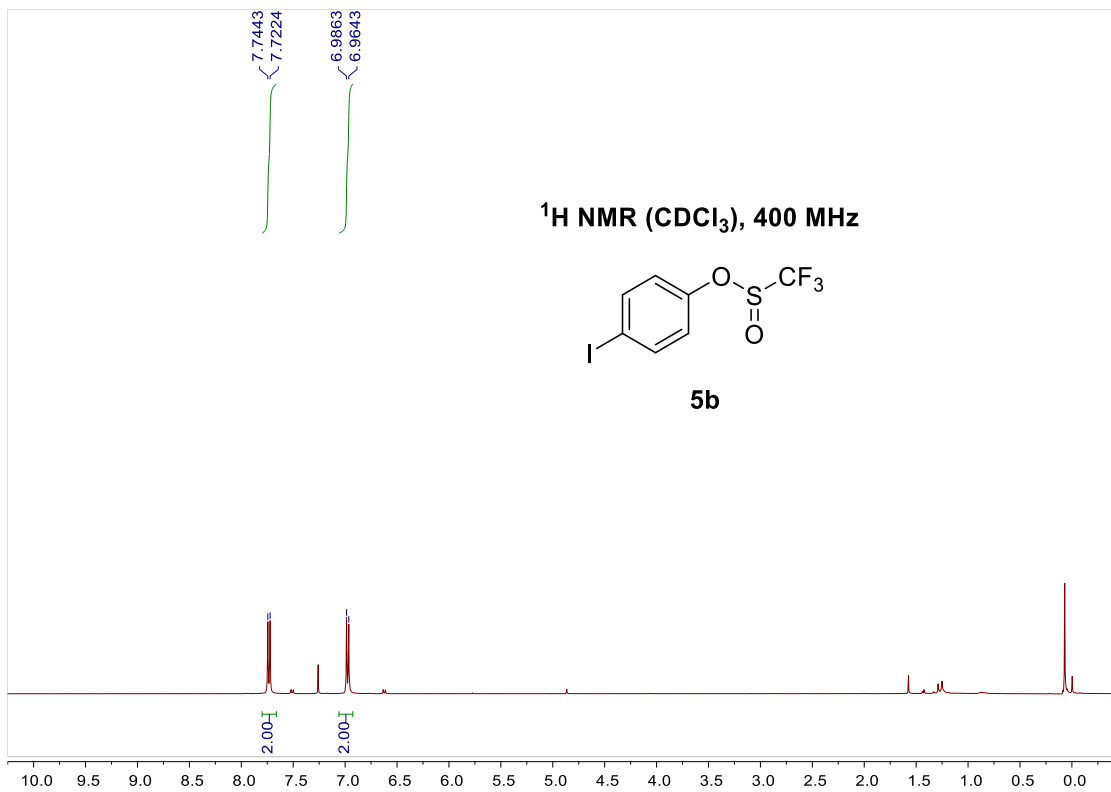
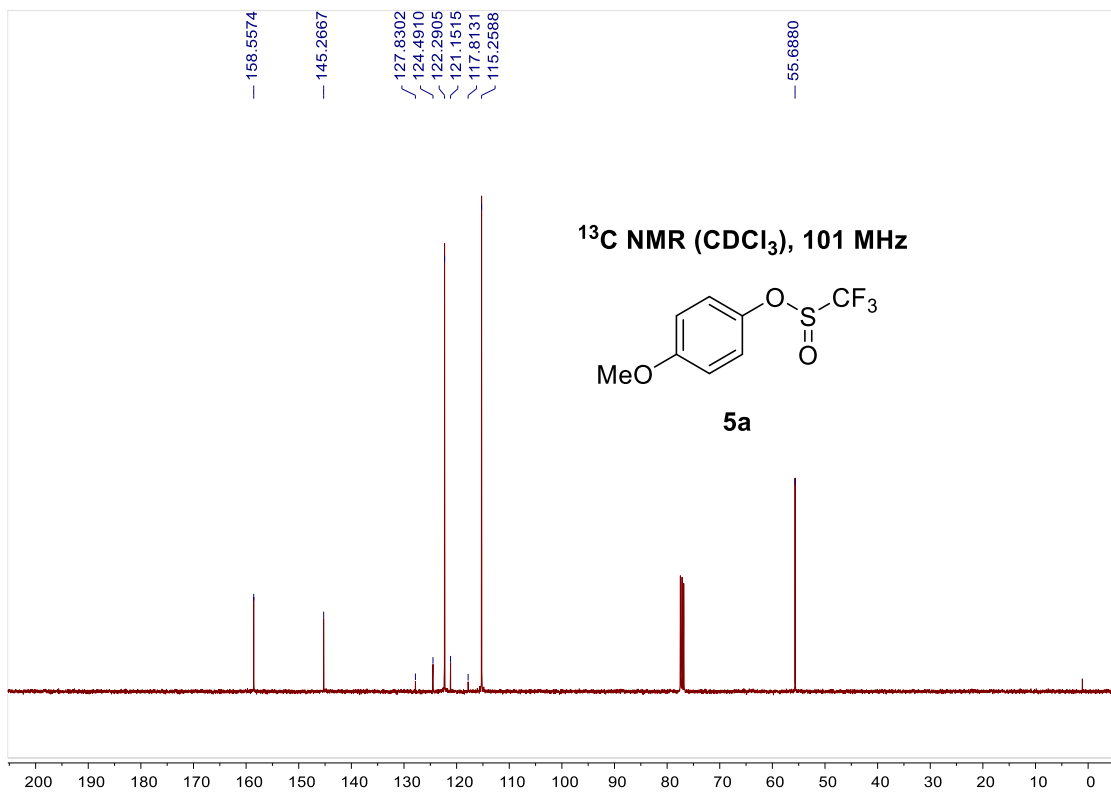


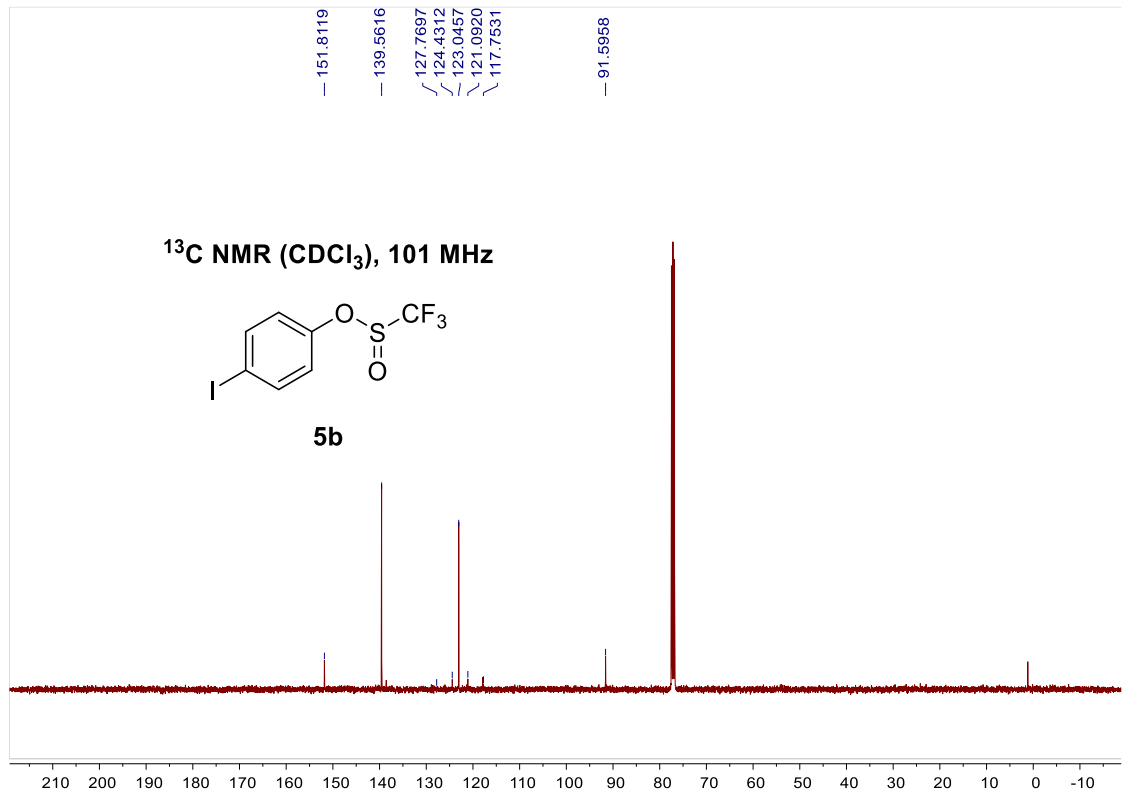
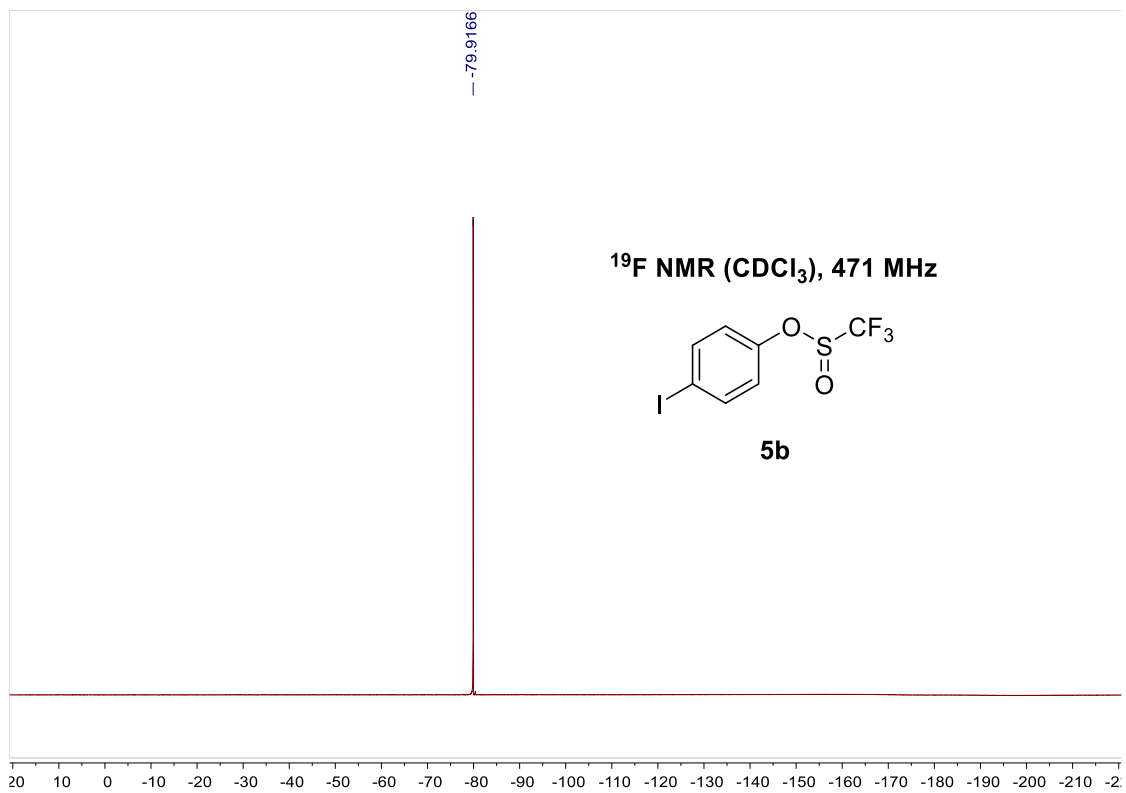


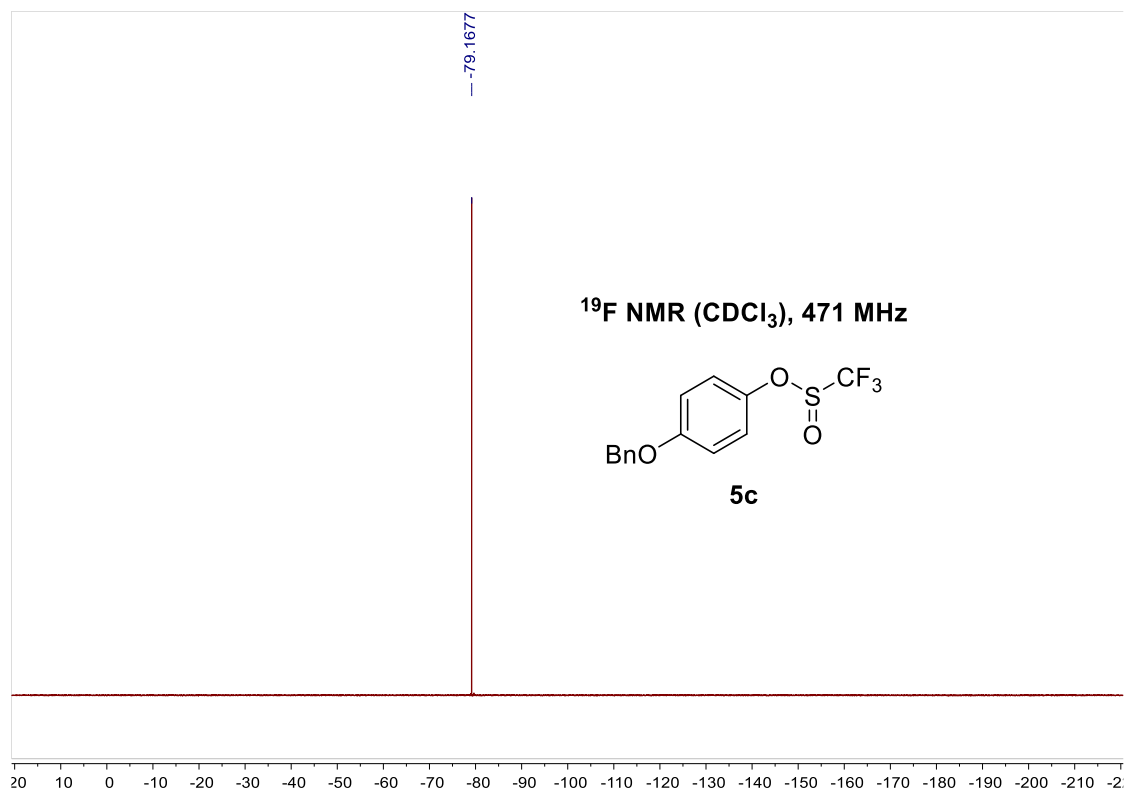
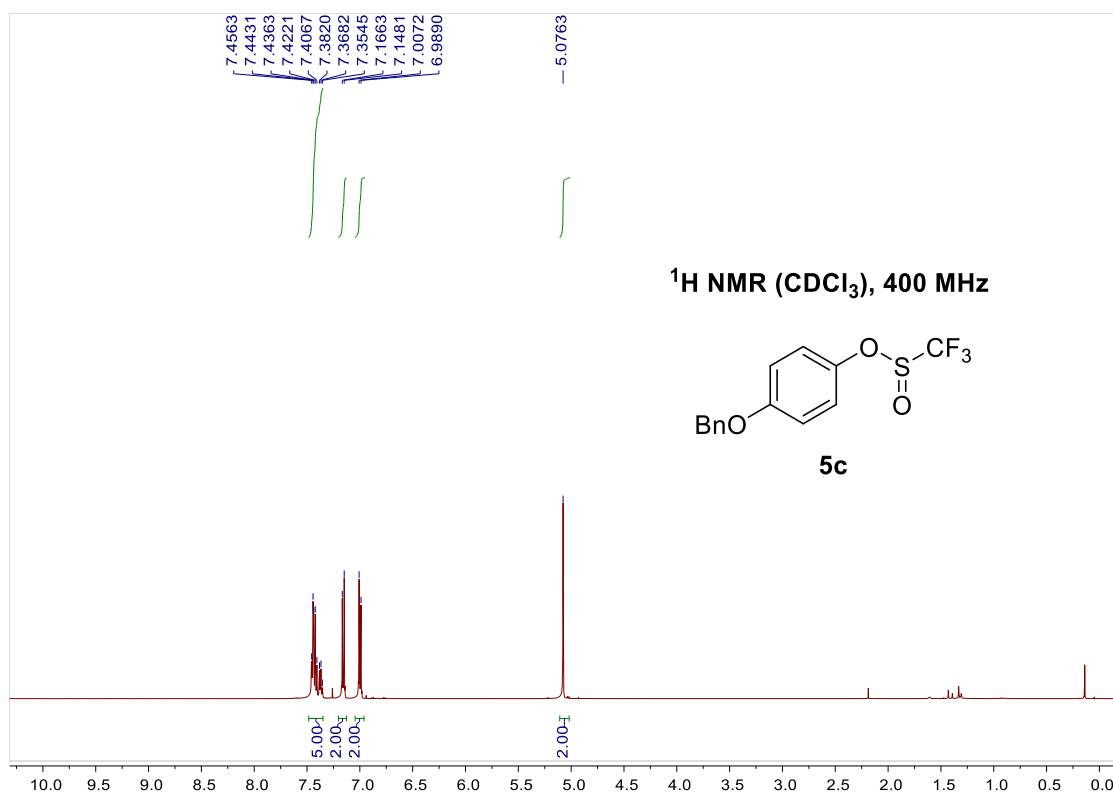


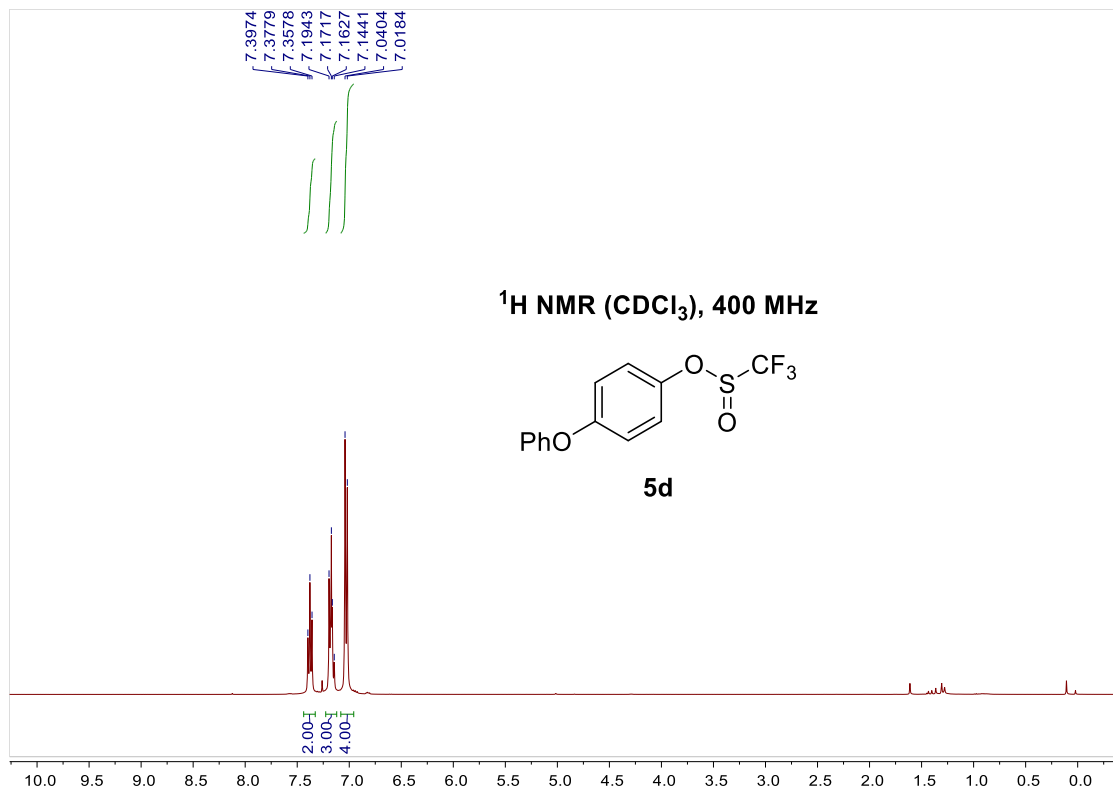
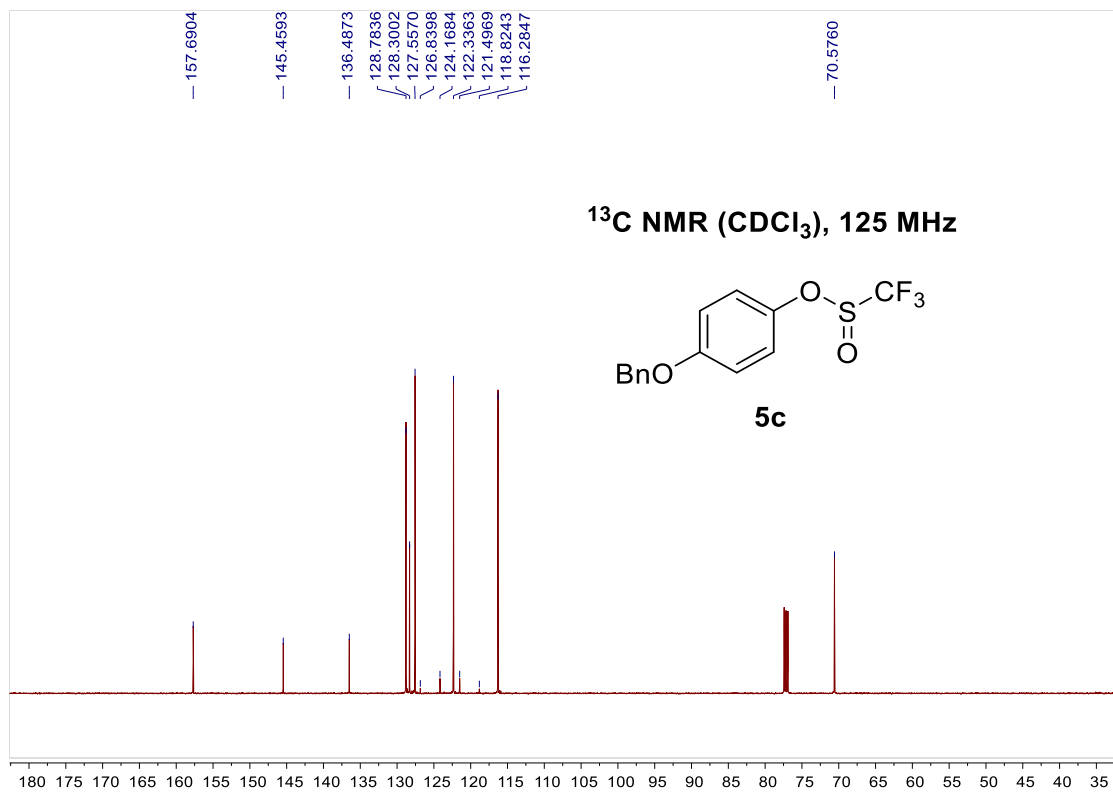


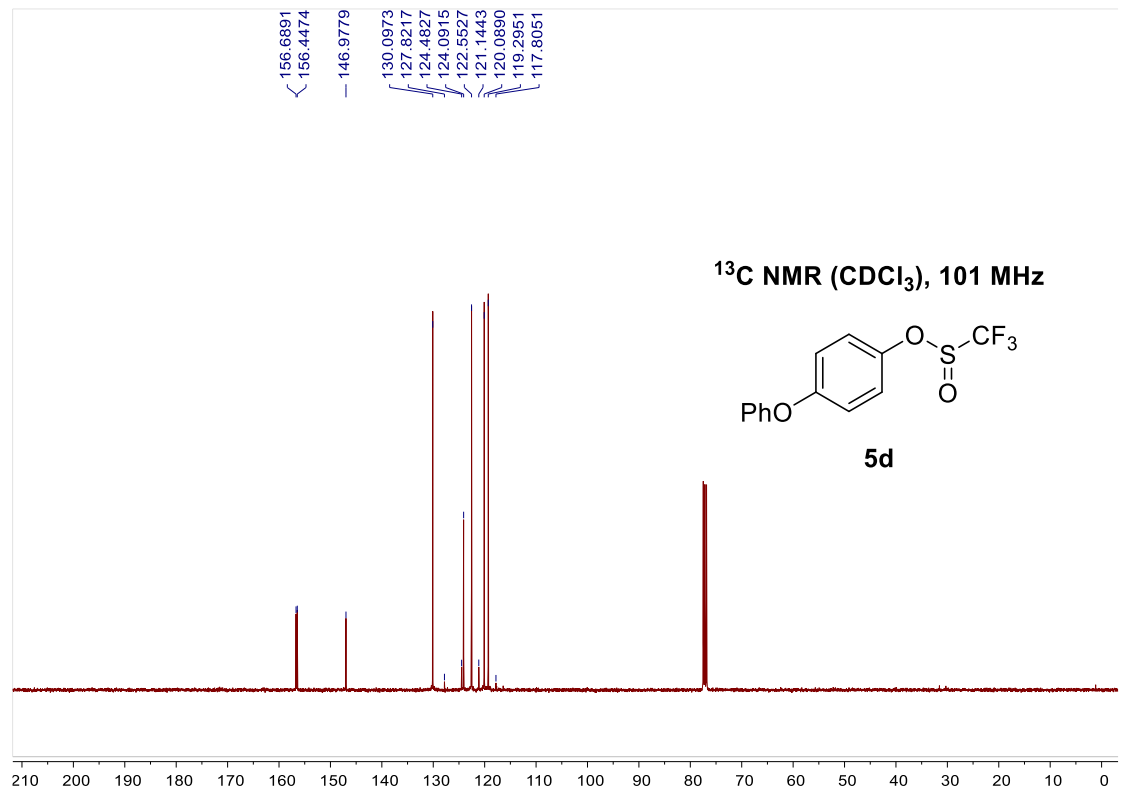
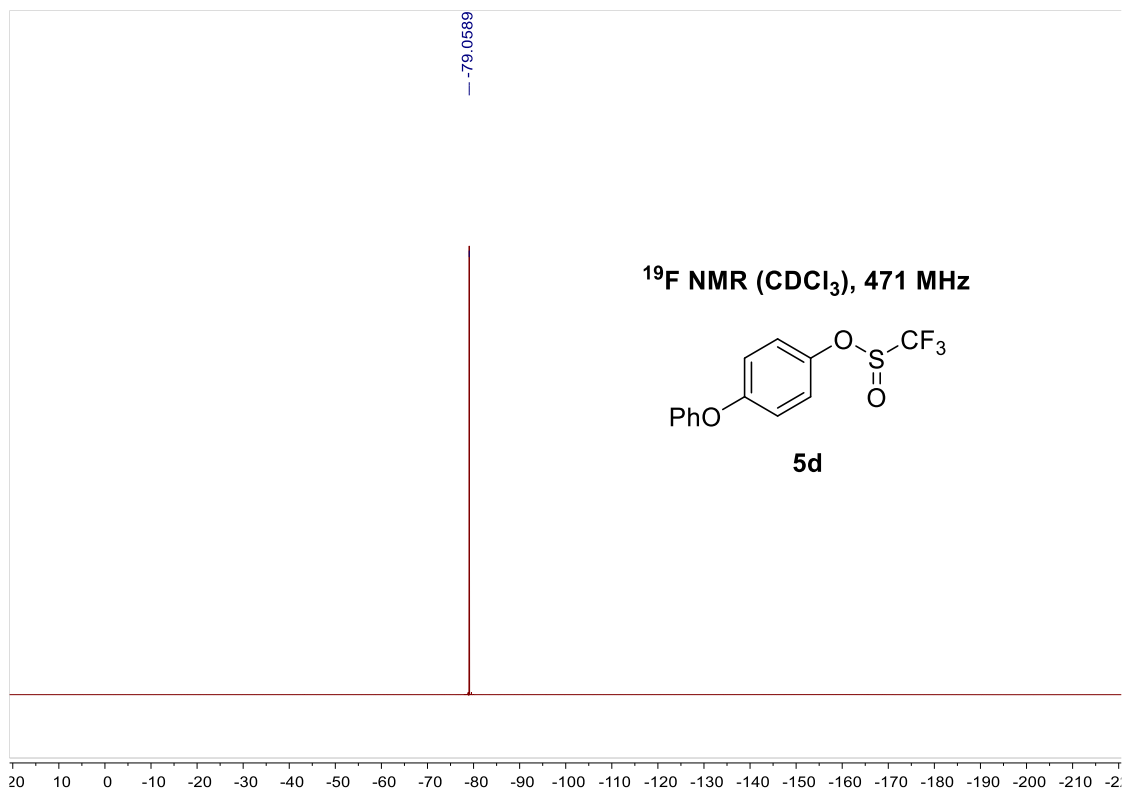


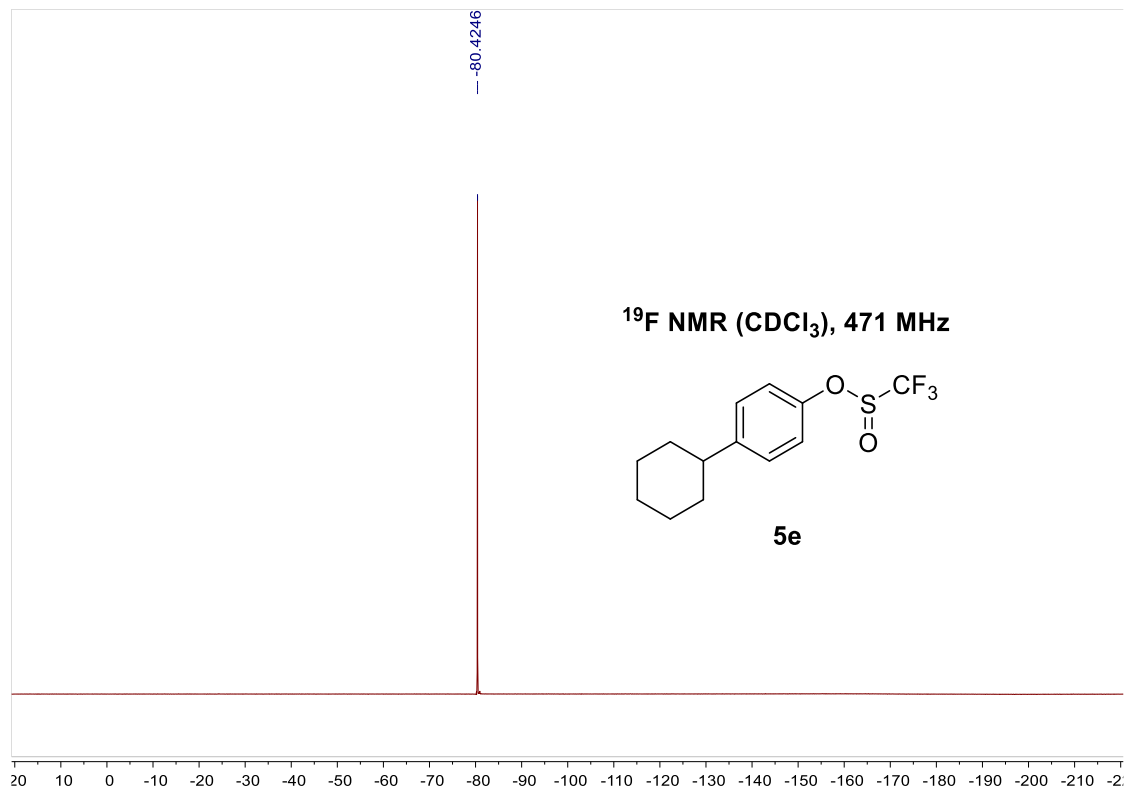
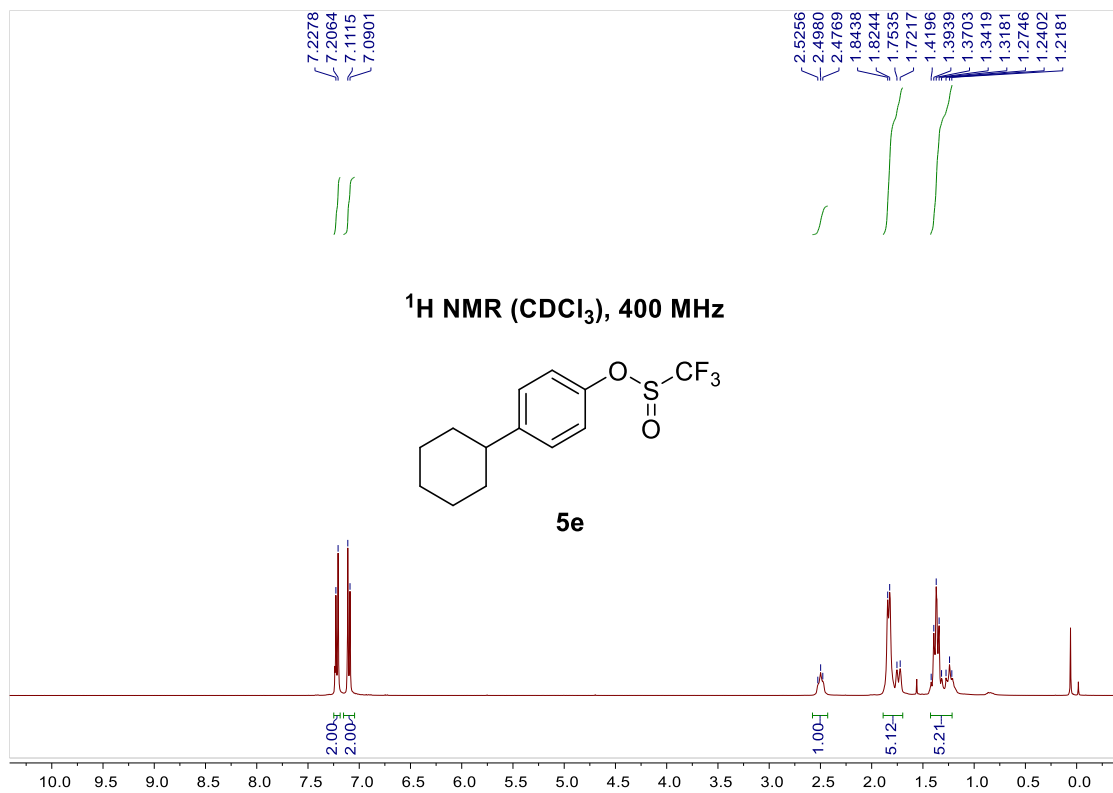


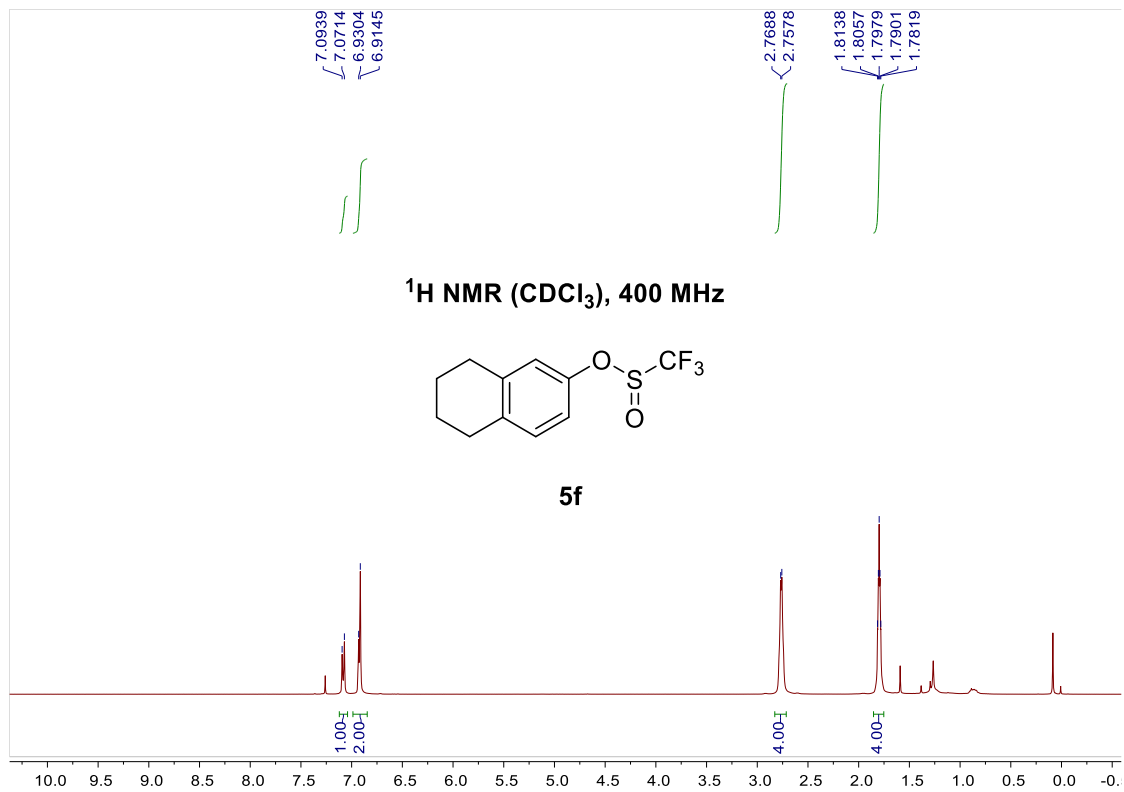
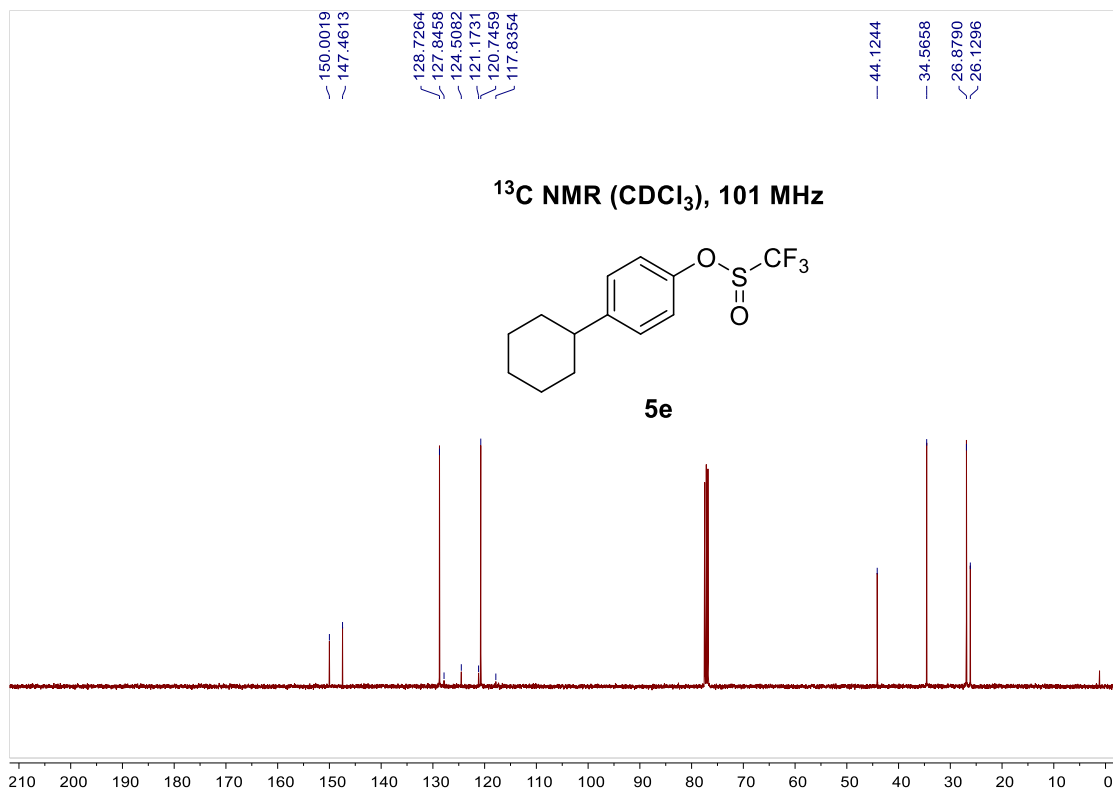


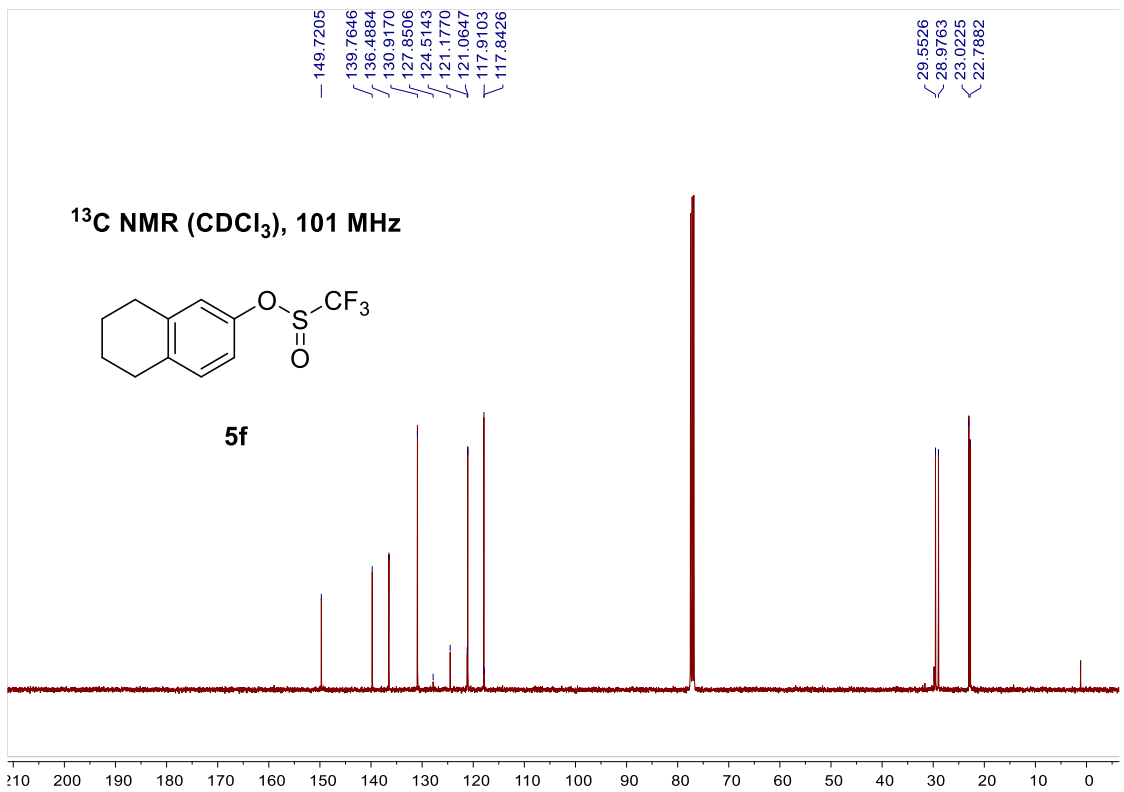
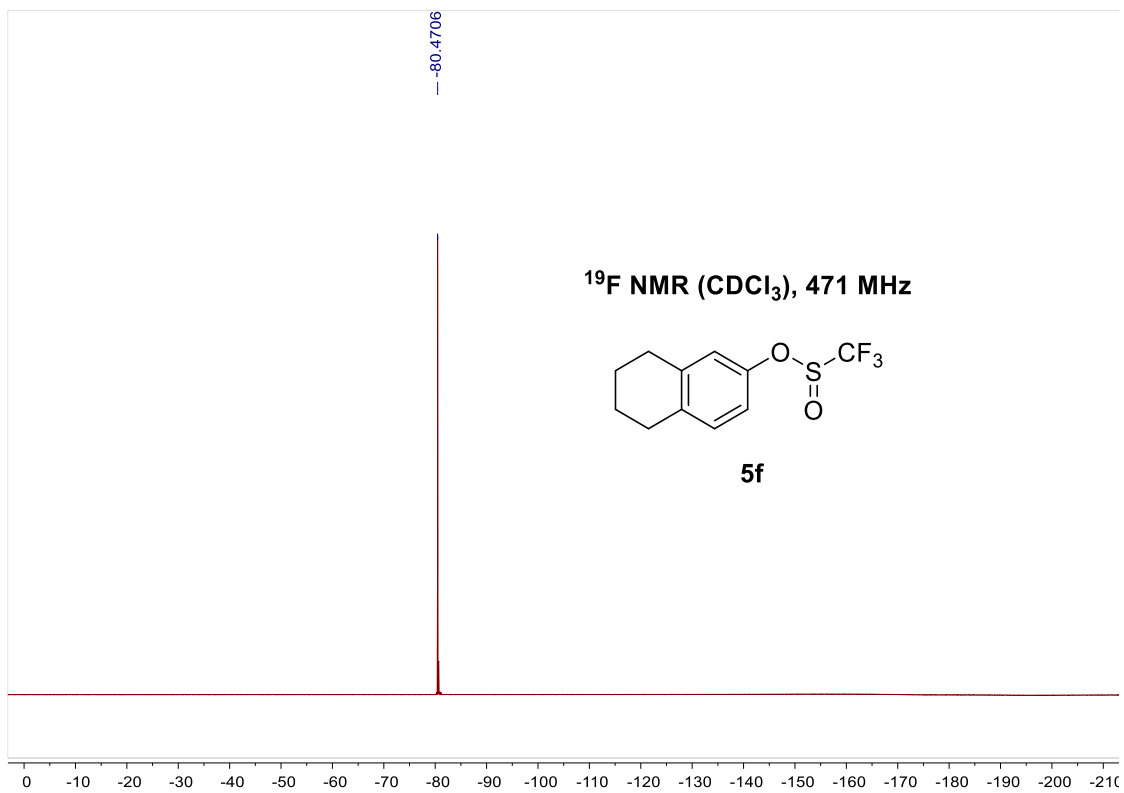




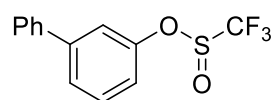








¹H NMR (CDCl₃), 400 MHz



5g

