Electrochemical Site-Selective C(sp^3)–H Amination of Alkyl Substituted Indoles and Pyrroles

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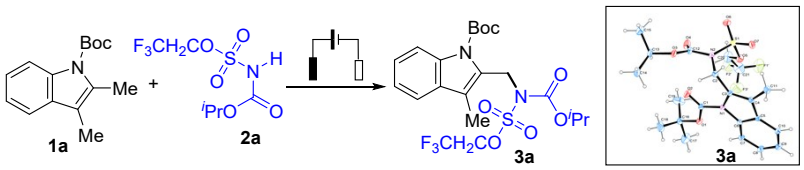
1. General information

All reactions that required anhydrous conditions were carried with standard procedures under nitrogen atmosphere. The solvents and chemicals were obtained from commercial sources, and were used without further purification. Column chromatography was generally performed on silica gel (300-400 mesh) and reactions were monitored by thin-layer chromatography (TLC) using 254 nm UV light. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were measured on Bruker Avance III 400 spectrometer. Chemical shifts are expressed in parts per million (ppm) with respect to tetramethylsilane. Coupling constants were reported as Hertz (Hz), signal shapes and splitting patterns were indicated as follows: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet. High-resolution mass spectra (HRMS) were recorded on Agilent mass spectrometer equipped with the APCI source and a Q-TOF detector. The X-ray analysis of crystal structure was carried out on Bruker SMART 1000 CCD.

2. Optimization of Electrochemical Reaction Conditions

Table S1. Optimization of electrochemical reaction of **1a** and **2a**



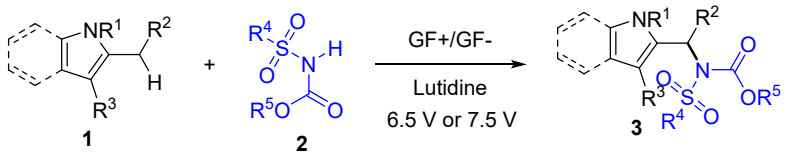
Entry[a]	Base	Solvent	Electrodes	Yield[d] (%)
1[b]	2,6-lutidine	MeCN	GF+ / GF-	72
2	2,6-lutidine	MeCN	GF+ / GF-	76(72[e])
3	2,6-lutidine	DMF	GF+ / GF-	50
4	2,6-lutidine	MeOH	GF+ / GF-	Trace
5	2,6-lutidine	DMSO	GF+ / GF-	Trace
6	2,6-lutidine	MeCN	Pt+ / GF-	75
7	2,6-lutidine	MeCN	C+ / GF-	72
8	2,6-lutidine	MeCN	GF+ / Pt-	76
9	--	MeCN	GF+ / GF-	N. R.
10[c]	2,6-lutidine (0.1 eq)	MeCN	GF+ / GF-	N. D.
11	2,6-dimethoxypyridine	MeCN	GF+ / GF-	N. R.
12	Pyridine	MeCN	GF+ / GF-	33
13	2,6-di-*tert*-butylpyridine	MeCN	GF+ / GF-	Trace
14	KOAc	MeCN	GF+ / GF-	55[e]
15	K_2CO_3	MeCN	GF+ / GF-	18[e]

[a] Reaction conditions: **1a** (0.24 mmol), **2a** (0.2 mmol), base (0.3 mmol), solvent (3.0 mL), rt, GF+ / GF-, 6.5 V cell voltage, 4 h. [b] Reaction conditions: **1a** (0.24 mmol), **2a** (0.2 mmol), base (0.3 mmol), $LiBF_4$ (0.1 mmol), solvent (3.0 mL), rt, GF+ / GF-, 6.5 V cell

voltage, 3 h. [c] Reaction conditions: **1a** (0.24 mmol), **2a** (0.2 mmol), base (0.02 mmol), $LiBF_4$ (0.1 mmol), solvent (3.0 mL), rt, GF+ / GF-, 6.5 V cell voltage, 3 h. [d] ^1H NMR yield. [e] Isolated yield. Graphite felt = GF, Platinum = Pt.

3. General procedures for electrochemical reactions

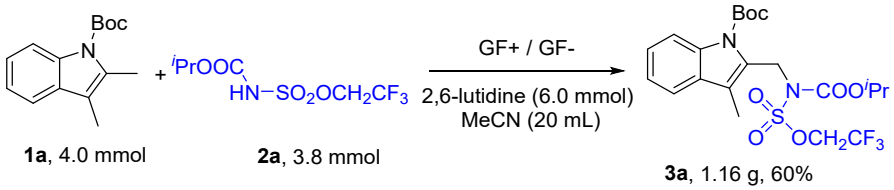
3.1 General procedure A:



Scheme S1. General procedure of C(sp^3)-H amination

A 10 mL two-necked heart-shaped flask was charged with the substrate **1** (0.24 mmol), **2** (0.2 mmol), 2.6-lutidine (0.3 mmol) and a magnetic stirrer. The graphite felt (1.0 cm x 1.0 cm x 0.3 cm, produced by Inner Mongolia Wanxing Carbon Company) as both the anode and cathode. The electrochemical reaction unit was installed according to our previous work (*Org. Biomol. Chem.* **2024**, *22*, 2549-2553). The flask was backfilled with nitrogen and 3 mL of anhydrous MeCN was added via syringe. The controlled potential electrolysis was carried out at room temperature. After the reaction completed as monitored with TLC, the mixture was concentrated under reduced pressure. The residue was purified by chromatography on silica gel to afford the desired product **3**.

3.2 Gram scale reaction:



Scheme S2. Gram scale reaction of electrochemical C(sp^3)-H amination

A 40 mL reaction bottle was charged with the substrate **1a** (4.0 mmol, 1.0 g), **2a** (3.8 mmol, 1.0 g), 2.6-lutidine (6.0 mmol, 0.64 g) and a magnetic stirrer. The flask was equipped with a rubber stopper and two graphite felts (4.0 cm x 2.0 cm x 0.3 cm, produced by Inner Mongolia Wanxing Carbon Company), which were used as both the anode and cathode and separated with a nylon cloth (2000 mesh). The graphite felt anode attached to a platinum wire and cathode attached to a silver wire. A teflon wire tied around two electrodes. The flask was evacuated and backfilled with nitrogen for three times, then a nitrogen balloon was connected to this flask via a needle. 15 mL of anhydrous MeCN was added via syringe. The electrolysis under 8.0 V cell voltage was carried out at room temperature. After 2 hours, the cell voltage increased to 10.0 V. The reaction was completed after 4 hours as monitored with TLC, and the mixture was concentrated under reduced pressure. The residue was purified by chromatography on silica gel to afford the desired product **3a** (60%, 1.16 g).

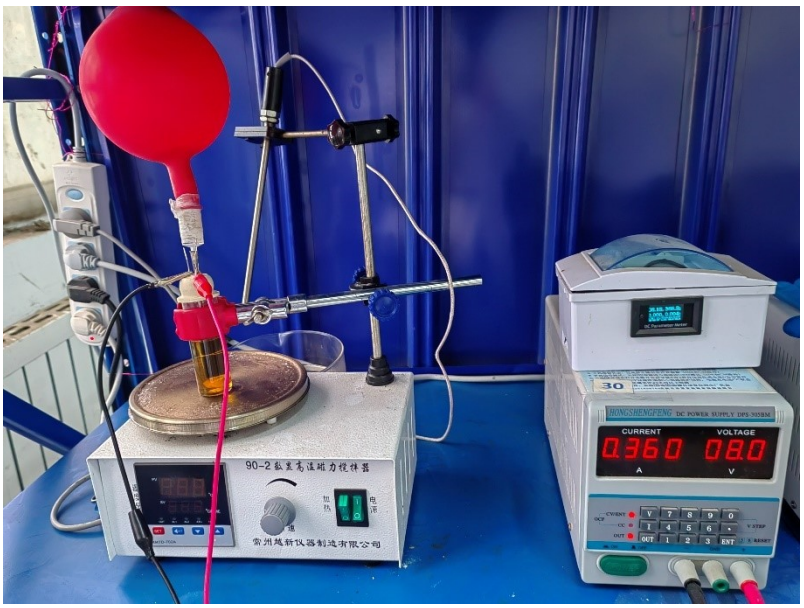


Figure S1. Electrolysis setup

4. DFT computation study of reaction pathway

4.1 Computational details:

Density functional theory (DFT) calculations were carried out using Gaussian 16 programs C01 [4] on Cluster of High Performance Computer Center, Nanjing University throughout this manuscript. Geometric optimizations of the reactants, transition states, and products were performed using B3LYP hybrid functional[5] with Grimme's dispersion correction of D3 version (Becke-Johnson damping)[6]. The standard 6-311G^{++} (d, p) basis set[7,8] for all atoms was used. Harmonic vibration frequency calculations were performed for all stationary points to confirm them as a local minima (zero imaginary frequencies). The thermochemical corrections for the Gibbs free energies were derived at 298.15 K. The intrinsic reaction coordinate (IRC) scheme[10,11] was applied for the calculations of the reaction coordinates to confirm whether or not the transition states were directly connected to the reactants and products. The single point energy (SP) calculations were performed on the optimized geometries with the larger def2-TZVPP basis set[12-14]. Approximate solvent effects were taken into consideration based on the SMD continuum solvation model[15] in all SP calculations. The Gibbs free energy of a solute in solution is given as

$$G_{soln} = E_{SP} + G_{corr}^{298.15K} + \Delta G_{1atm\rightarrow 1M}^{298.15K}$$

references

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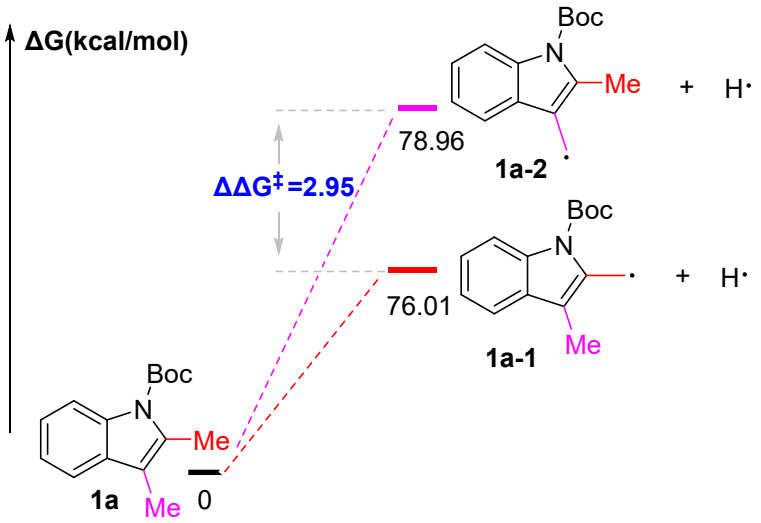
4.2 Summary of the energy of transition states:

Table S2. Summary of the energy of transition states of **1a**

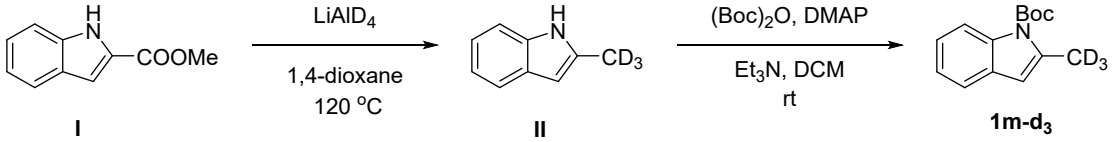


(All Values Are in Hartrees)

Species	E_sp	G_corr	1atm 1M	G
1a	-788.604233	0.264278	0.003019	-788.336936
1a-1	-787.959998	0.250551	0.003019	-787.706428
1a-2	-787.955404	0.250658	0.003019	-787.701727
H·	-0.501741	-0.010654	0.003019	-0.509376

5. Kinetic isotope effect study

5.1 The preparation of 1m-d_3



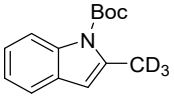
I II **1m-d_3**

Scheme S3. preparation of **1m-d_3**

Methyl 1*H*-indole-2-carboxylate (0.7 g, 4.0 mmol) and $LiAlD_4$ (0.336 g, 8 mmol, 2.0 equiv) were dissolved in 1,4-dioxane (10 ml). The solution was stirred at 120 °C for 12 h under nitrogen. The reaction mixture was quenched with water and extracted with ethyl acetate for three times. The combined organic layers were dried ($MgSO_4$), filtered, and concentrated. The residue was purified by flash column chromatography to afford the white solid **II** (0.24 g, 45%).

A mixture of 2-(methyl-d_3)-1*H*-indole (0.134 g, 1.0 mmol), $(Boc)_2O$ (0.327 g, 1.5 mmol), DMAP (12.2 mg, 0.1 mmol) and Et_3N (0.152 g, 1.5 mmol) were dissolved in DCM (10 ml) in a 25 mL reaction flask. Then, the reaction was stirred at room temperature for 12 h under nitrogen. The mixture was concentrated, and extracted with DCM/H_2O for three times. The combined organic layers were dried ($MgSO_4$), filtered, and concentrated. The residue was purified by flash column chromatography to afford the target product **1m-d_3** (0.21 g, 90%).

tert-butyl 2-(methyl-d3)-1*H*-indole-1-carboxylate (1m-d_3)



A colorless oil. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.18 (d, *J* = 8.1 Hz, 1H), 7.50 (d, *J* = 7.4 Hz, 1H), 7.32-7.24 (m, 2H), 6.38 (s, 1H), 2.63 (s, 0.03H), 1.75 (s, 9H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 150.8, 136.6, 129.5, 123.2, 122.7, 119.6, 115.6, 108.0, 83.7, 28.4.

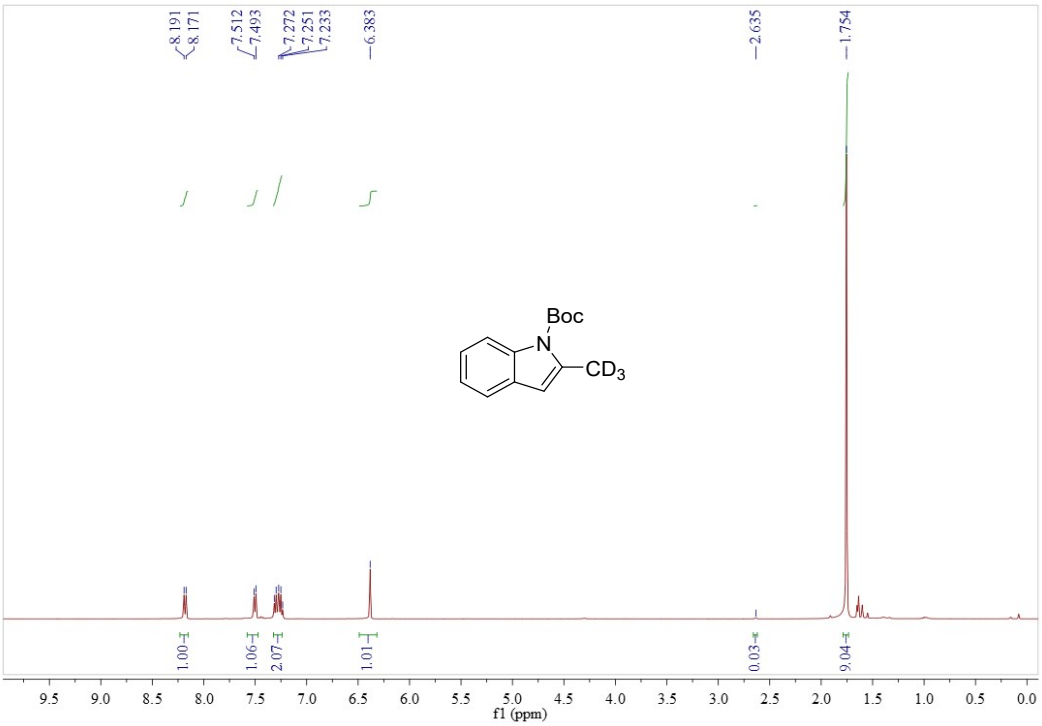


Figure S2. ^{1}H NMR (400 MHz, Chloroform-*d*) of **1m-d_3**

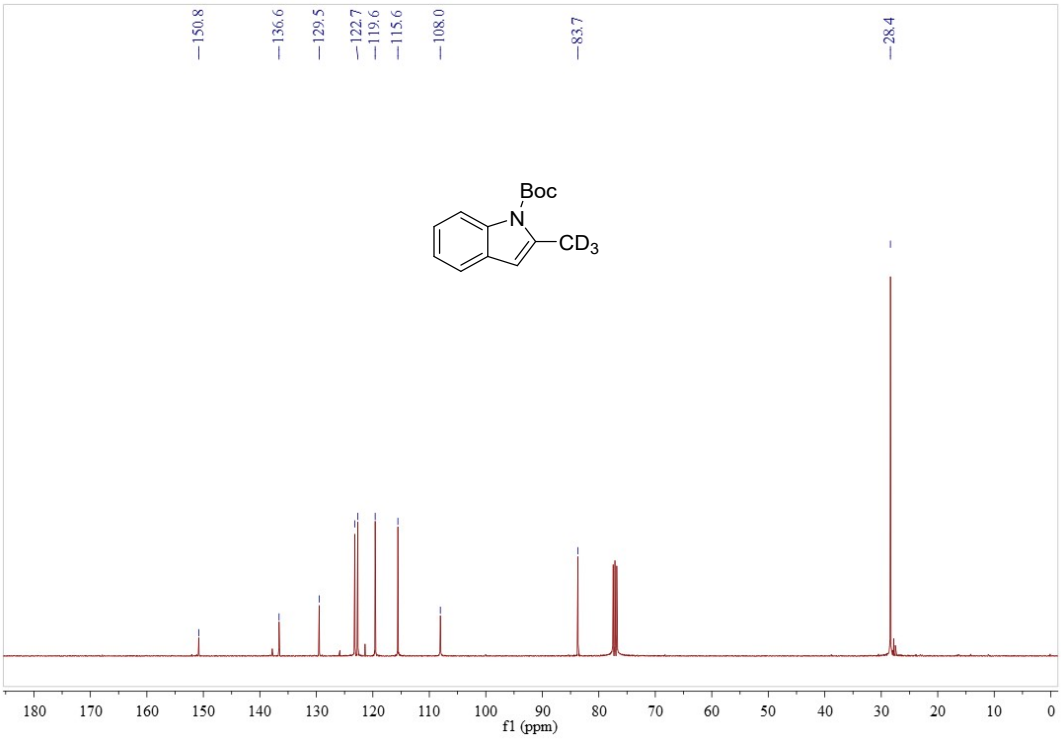
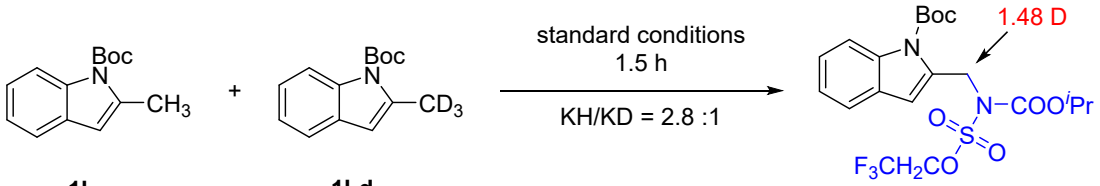


Figure S3. ^{13}C NMR (100 MHz, Chloroform-*d*) of **1m-d$_3$**

5.2 The electrochemical reaction of 1l and 1l-d$_3$



1l **1l-d$_3$** **3l/3l-d**, 15%

Scheme S4. Electrochemical reaction of **1l** and **1l-d$_3$**

The electrochemical reaction employing **1l** (0.1 mmol) and **1l-d$_3$** (0.1 mmol) as the raw material following the **general procedure A**. After 1.5 hours, the mixture was concentrated under reduced pressure. The residue was purified by chromatography on silica gel to afford the mixture of **3l** and **3l-d$_3$**.

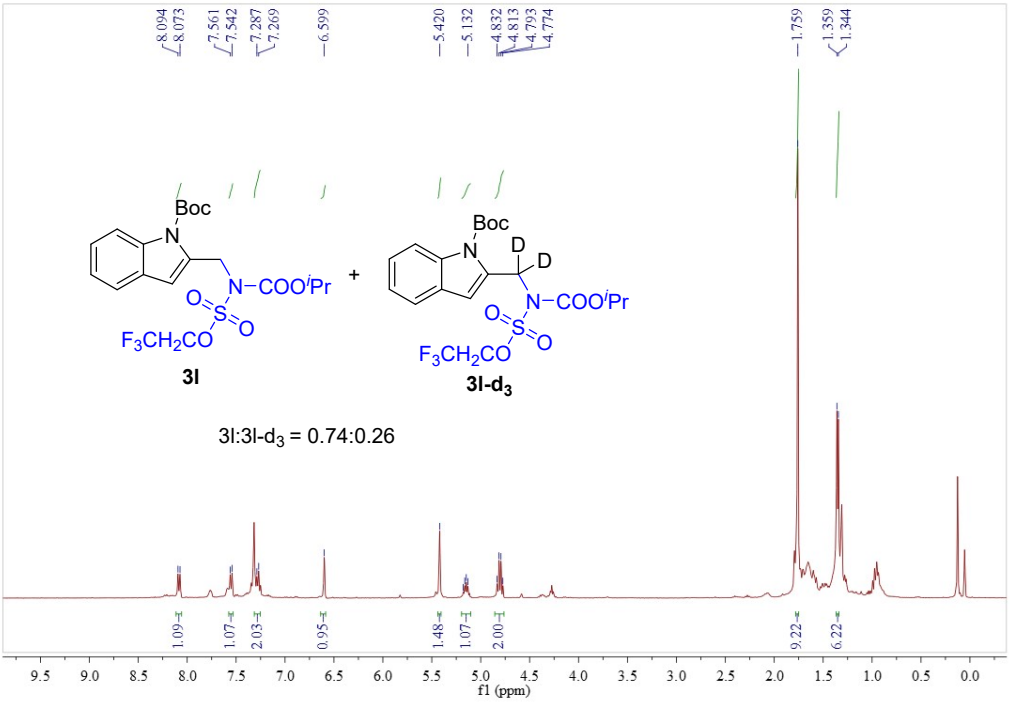
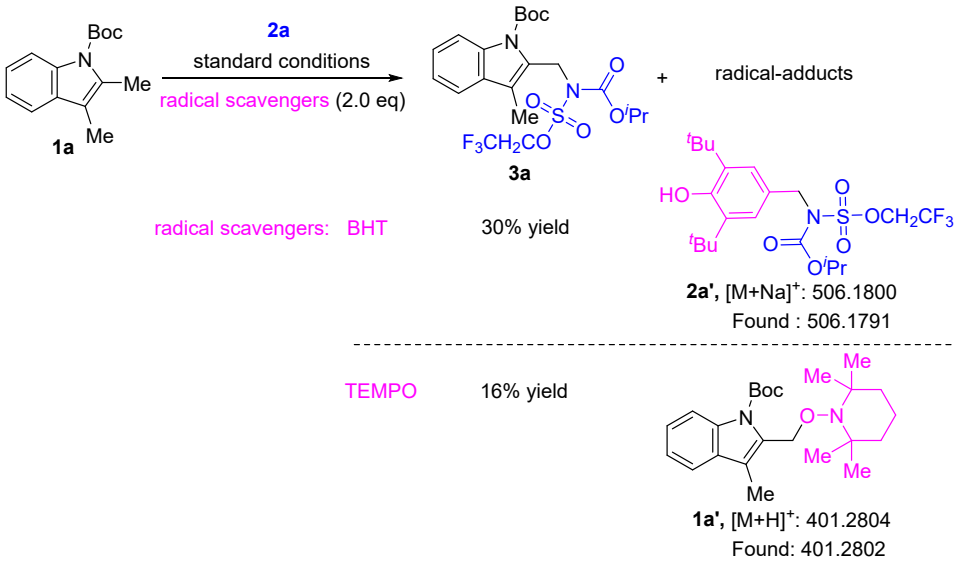


Figure S4. ^{1}H NMR (400 MHz, Chloroform-*d*) of **3l** and **3l-d$_3$**

6. Detection and analysis of radical adduct 2a' and 1a'



Scheme S5. Suppression effect of radical scavengers

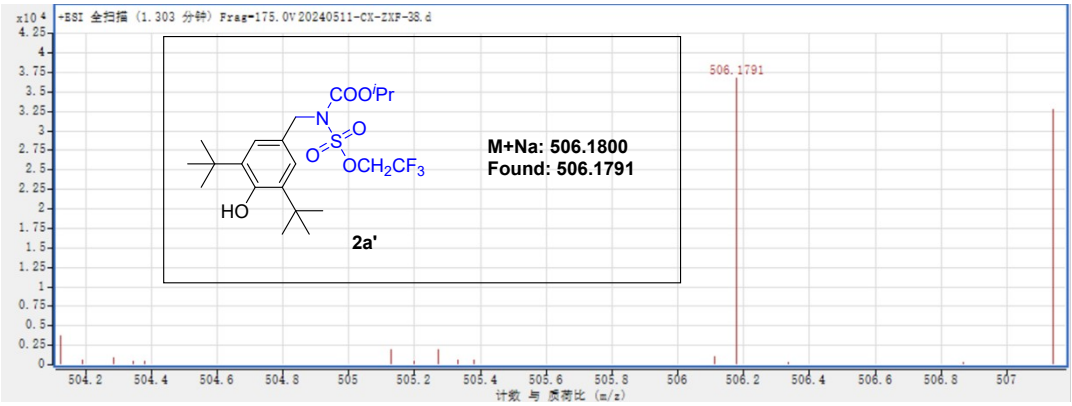


Figure S5. The HMRS analysis of radical adduct **2a'**

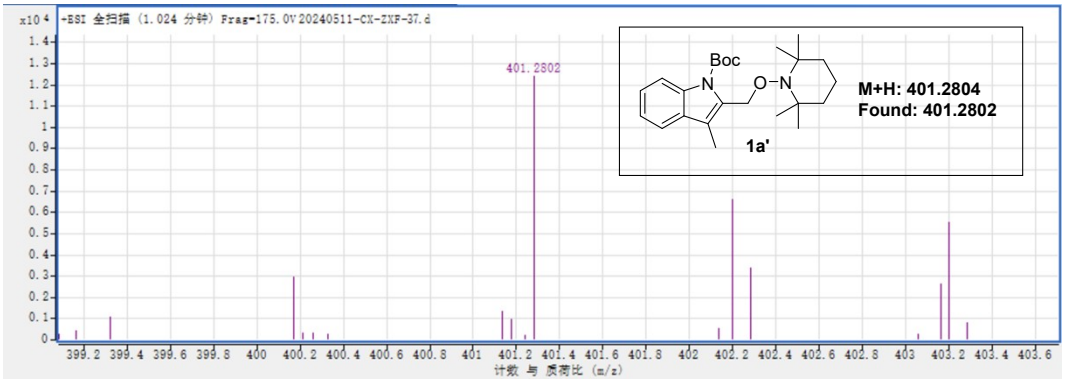
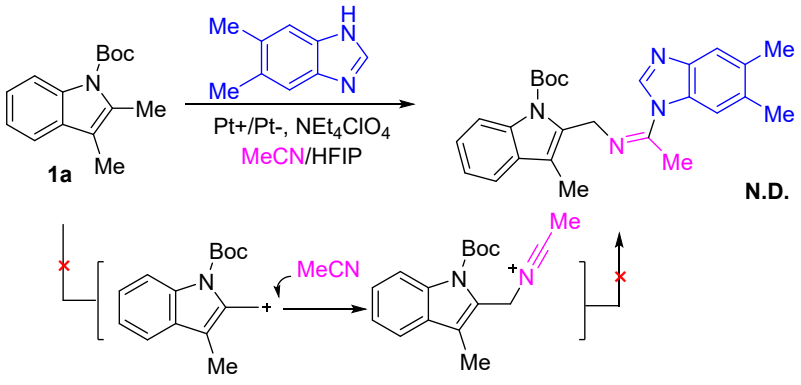


Figure S6. The HMRS analysis of radical adduct **1a'**

7. Reaction intermediate investigation



Scheme S6. Electrochemical reaction of compound **1a** under the conditions reported by Zhang and Li' s group (*Chem Catal.,* 2023, **3**, 100582)

8. Measurement of faraday of electrons per mole of 3a

The reaction was setup under standard electrochemical reaction condition（constant potential condition: **1a** (0.24 mmol), **2a** (0.2 mmol), 2, 6-lutidine (0.3 mmol), MeCN (3.0 mL), 6.5 V cell voltage, rt.）using CHI 730E bipotentiostat as power source with bulk electrolysis method (BE). The reaction was stopped after 4 hours. Q was read from the experiment as item "Total Q", and F was Faraday's constant: 96485. Faraday of electrons per mole = 64.526/(96485*0.0002) F/mol = 3.3 F/mol.

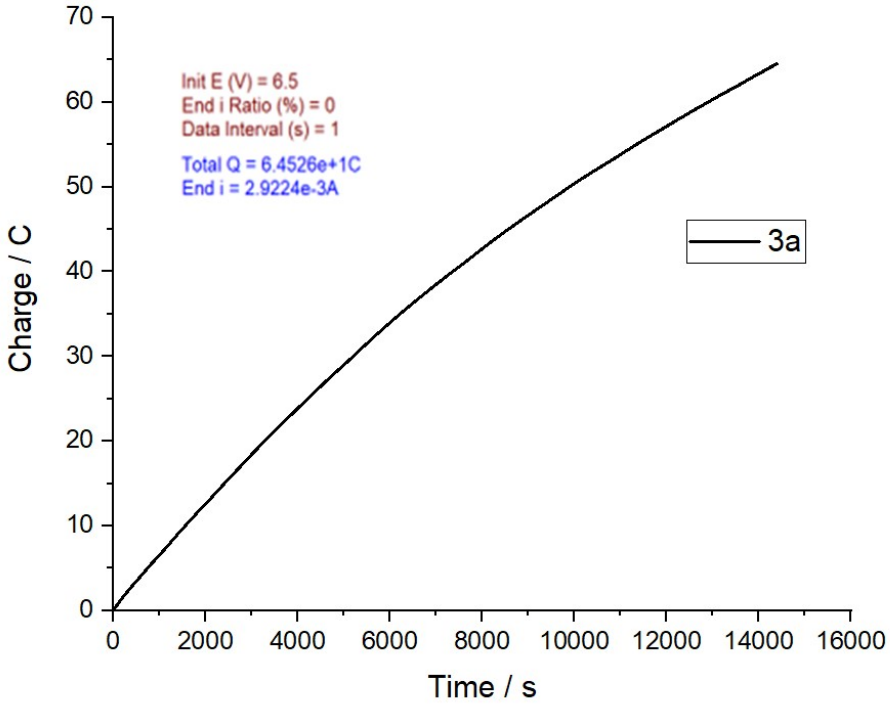


Figure S7. The bulk electrolysis of standard reaction of **3a**

9. Cyclic voltammetry experiments of reactants

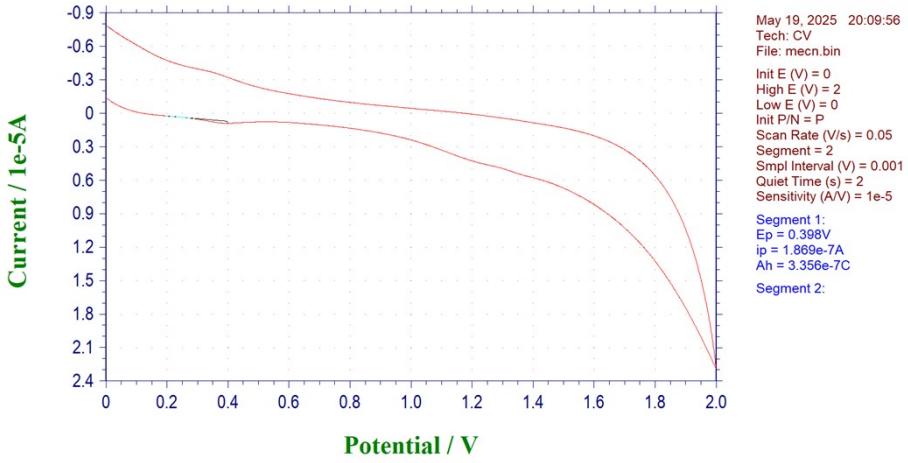


Figure S8. Cyclic voltammograms of $LiBF_4$ in MeCN

A solution of $LiBF_4$ (0.1 mmol) in 3 mL MeCN was subject to the cyclic voltammetry experiment. Electrodes included a platinum disc (diameter, 4.0 mm) working electrode, a gauze platinum counter electrode and a saturated calomel reference electrode (SCE) via a salt bridge charged with a solution of $LiBF_4$ (0.033 M in MeCN). Potential sweep rate was 50 mV/s.

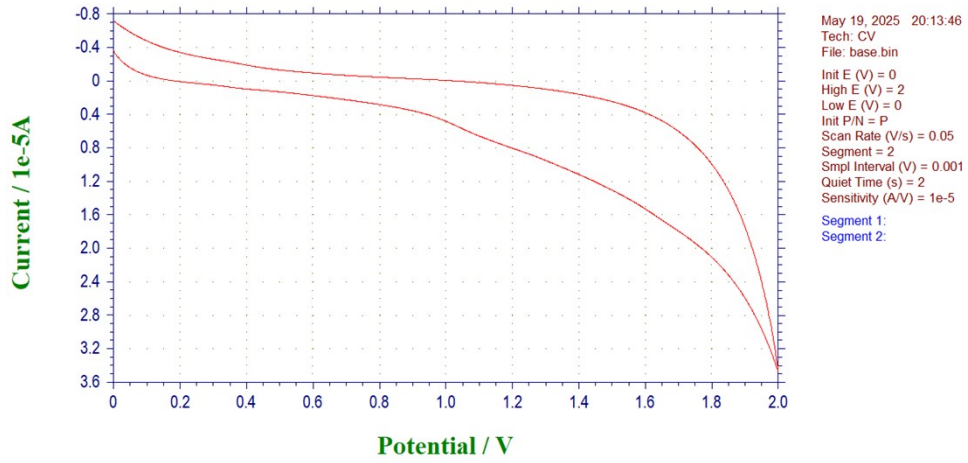


Figure S9. Cyclic voltammograms of $LiBF_4$ and lutidine in MeCN

A solution of $LiBF_4$ (0.1 mmol) and lutidine (0.1 mmol) in 3 mL MeCN was subject to the cyclic voltammetry experiment. Electrodes included a platinum disc (diameter, 4.0 mm) working electrode, a gauze platinum counter electrode and a saturated calomel reference electrode (SCE) via a salt bridge charged with a solution of $LiBF_4$ (0.033 M in MeCN). Potential sweep rate was 50 mV/s.

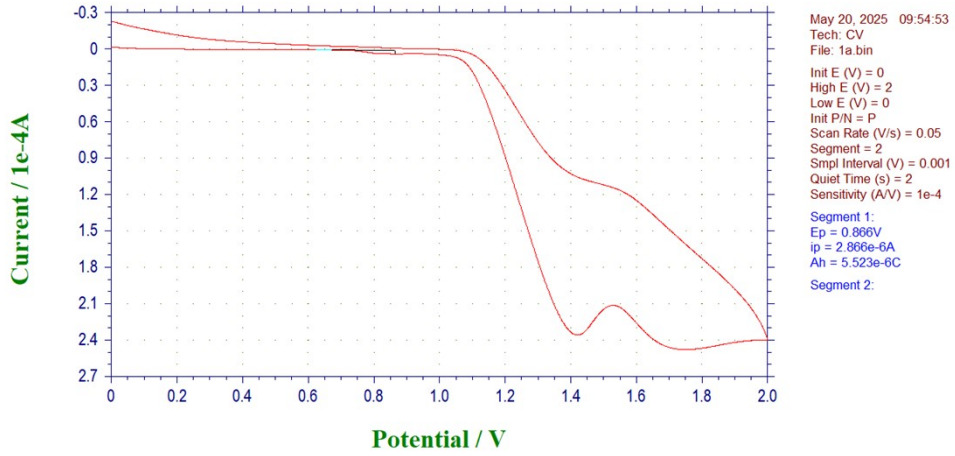


Figure S10. Cyclic voltammograms of $LiBF_4$ and **1a** in MeCN

A solution of $LiBF_4$ (0.1 mmol) and **1a** (0.1 mmol) in 3 mL MeCN was subject to the cyclic voltammetry experiment. Electrodes included a platinum disc (diameter, 4.0 mm) working electrode, a gauze platinum counter electrode and a saturated calomel reference electrode (SCE) via a salt bridge charged with a solution of $LiBF_4$ (0.033 M in MeCN). Potential sweep rate was 50 mV/s.

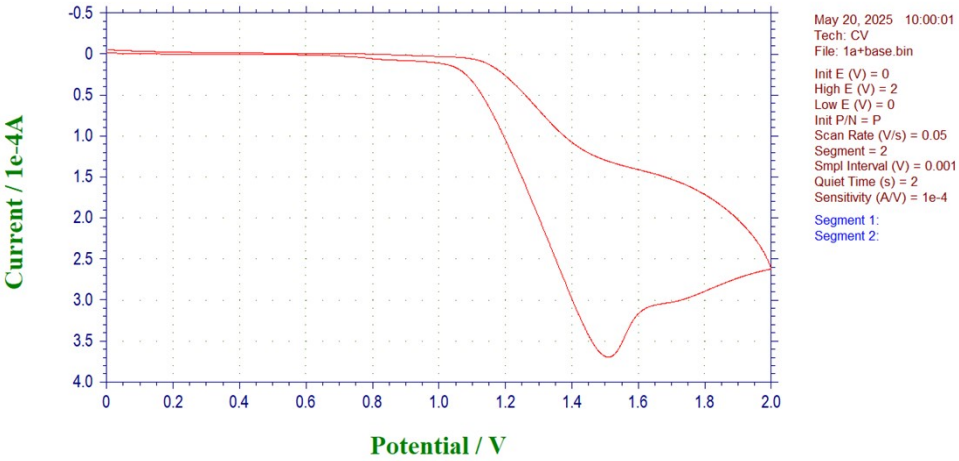


Figure S11. Cyclic voltammograms of $LiBF_4$, **1a** and lutidine in MeCN

A solution of $LiBF_4$ (0.1 mmol), **1a** (0.1 mmol) and lutidine (0.15 mmol) in 3 mL MeCN was subject to the cyclic voltammetry experiment. Electrodes included a platinum disc (diameter, 4.0 mm) working electrode, a gauze platinum counter electrode and a saturated calomel reference electrode (SCE) via a salt bridge charged with a solution of $LiBF_4$ (0.033 M in MeCN). Potential sweep rate was 50 mV/s.

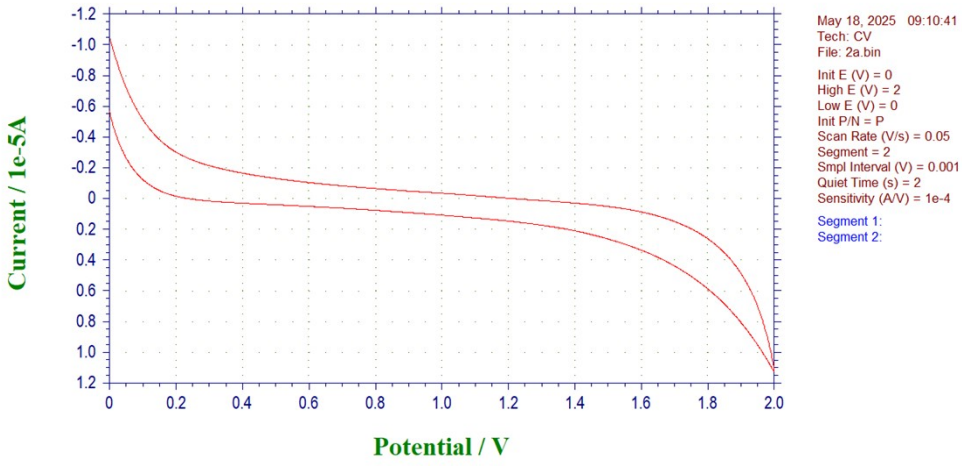


Figure S12. Cyclic voltammograms of $LiBF_4$ and **2a** in MeCN

A solution of $LiBF_4$ (0.1 mmol) and **2a** (0.1 mmol) in 3 mL MeCN was subject to the cyclic voltammetry experiment. Electrodes included a platinum disc (diameter, 4.0 mm) working electrode, a gauze platinum counter electrode and a saturated calomel reference electrode (SCE) via a salt bridge charged with a solution of $LiBF_4$ (0.033 M in MeCN). Potential sweep rate was 50 mV/s.

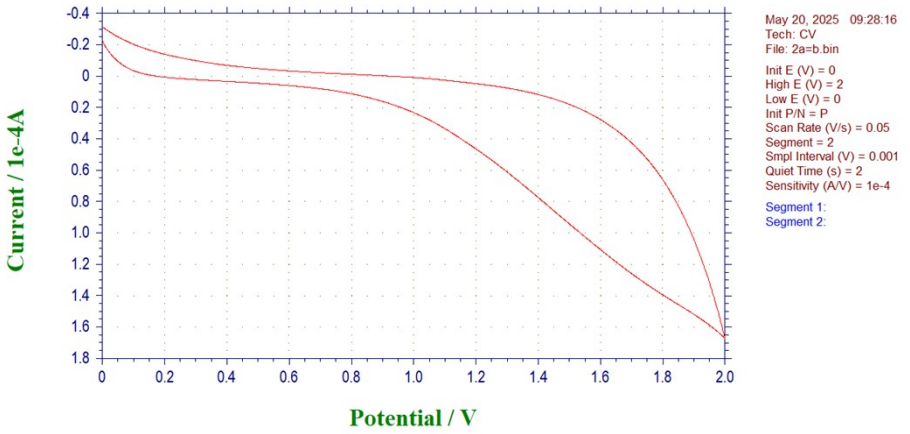


Figure S13. Cyclic voltammograms of $LiBF_4$, **2a** and lutidine in MeCN

A solution of $LiBF_4$ (0.1 mmol), **2a** (0.1 mmol) and lutidine (0.15 mmol) in 3 mL MeCN was subject to the cyclic voltammetry experiment. Electrodes included a platinum disc (diameter, 4.0 mm) working electrode, a gauze platinum counter electrode and a saturated calomel reference electrode (SCE) via a salt bridge charged with a solution of $LiBF_4$ (0.033 M in MeCN). Potential sweep rate was 50 mV/s.

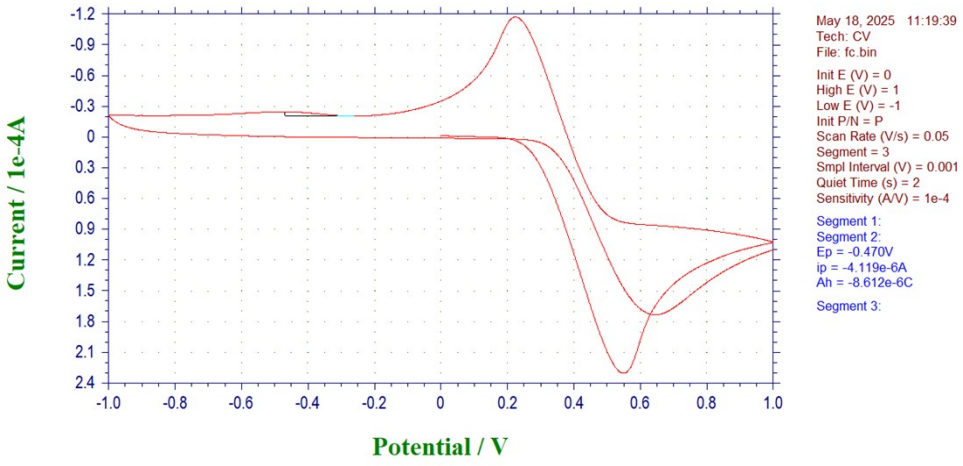


Figure S14. Cyclic voltammograms of $LiBF_4$ and ferrocene (Fc) in MeCN

A solution of $LiBF_4$ (0.1 mmol) and ferrocene (0.05 mmol) in 3 mL MeCN was subject to the cyclic voltammetry experiment. Electrodes included a platinum disc (diameter, 4.0 mm) working electrode, a gauze platinum counter electrode and a saturated calomel reference electrode (SCE) via a salt bridge charged with a solution of $LiBF_4$ (0.033 M in MeCN). Potential sweep rate was 50 mV/s.

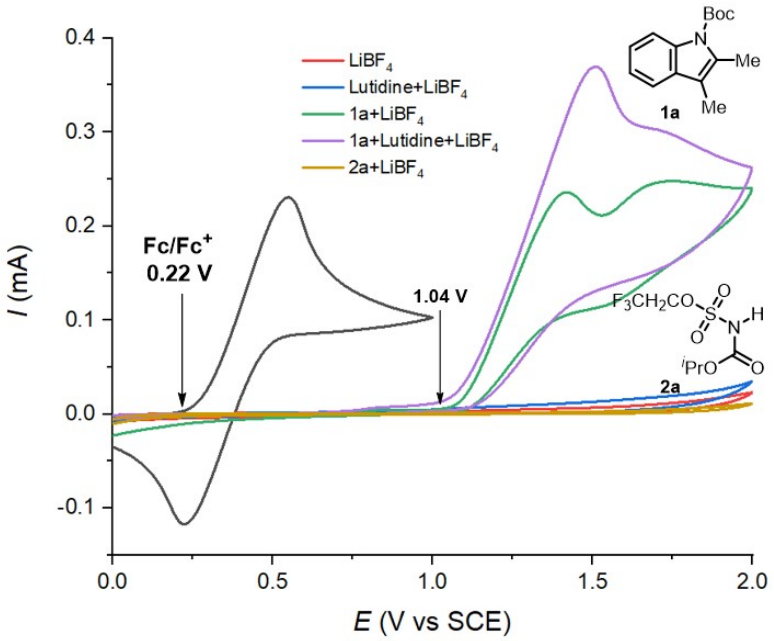


Figure S15. Overlapped CV results of $LiBF_4$, **1a**, lutidine, and their mixture in MeCN

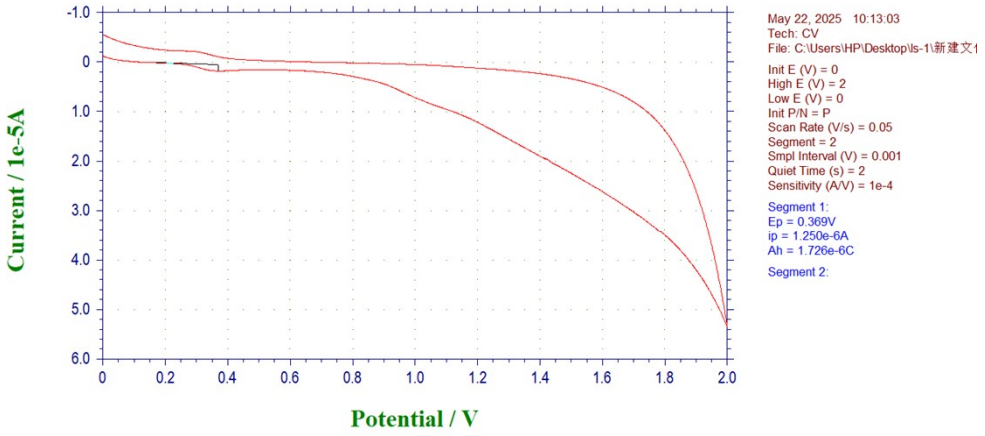


Figure S16. Cyclic voltammograms of **2a** and lutidine in MeCN

A solution of **2a** (0.1 mmol) and lutidine (0.15 mmol) in 3 mL MeCN was subject to the cyclic voltammetry experiment. Electrodes included a platinum disc (diameter, 4.0 mm) working electrode, a gauze platinum counter electrode and a saturated calomel reference electrode (SCE) via a salt bridge charged with a solution of $LiBF_4$ (0.033 M in MeCN). Potential sweep rate was 50 mV/s.

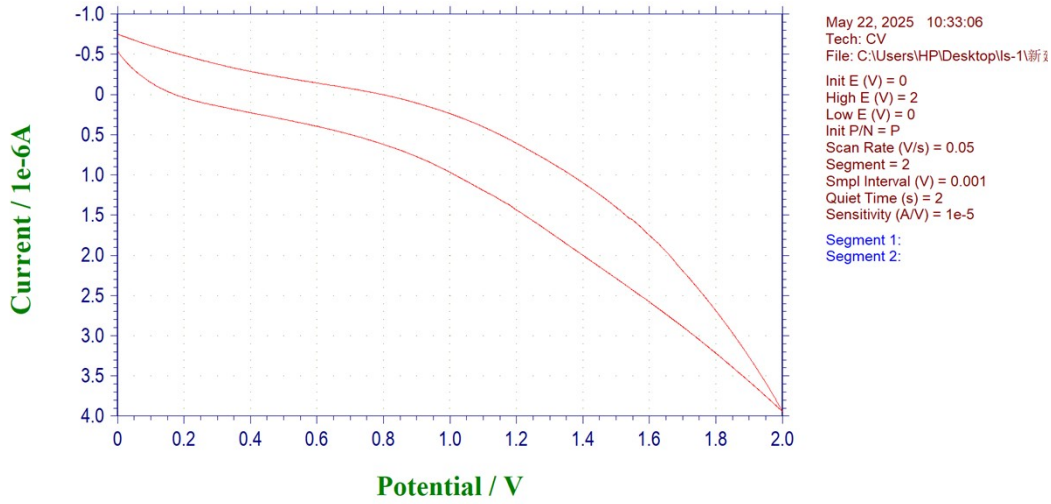


Figure S17. Cyclic voltammograms of lutidine in MeCN

A solution of lutidine (0.1 mmol) in 3 mL MeCN was subject to the cyclic voltammetry experiment. Electrodes included a platinum disc (diameter, 4.0 mm) working electrode, a gauze platinum counter electrode and a saturated calomel reference electrode (SCE) via a salt bridge charged with a solution of $LiBF_4$ (0.033 M in MeCN). Potential sweep rate was 50 mV/s.

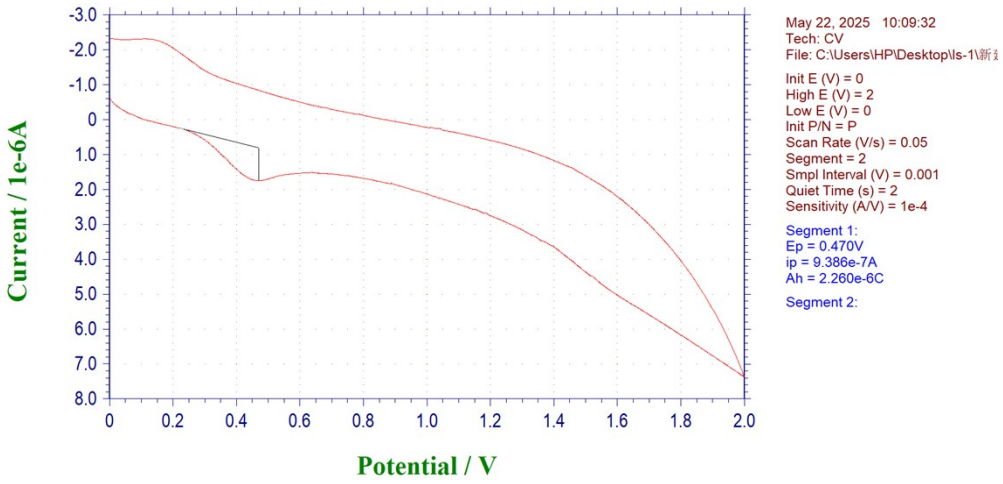


Figure S18. Cyclic voltammograms of **2a** in MeCN

A solution of **2a** (0.1 mmol) in 3 mL MeCN was subject to the cyclic voltammetry experiment. Electrodes included a platinum disc (diameter, 4.0 mm) working electrode, a gauze platinum counter electrode and a saturated calomel reference electrode (SCE) via a salt bridge charged with a solution of $LiBF_4$ (0.033 M in MeCN). Potential sweep rate was 50 mV/s.

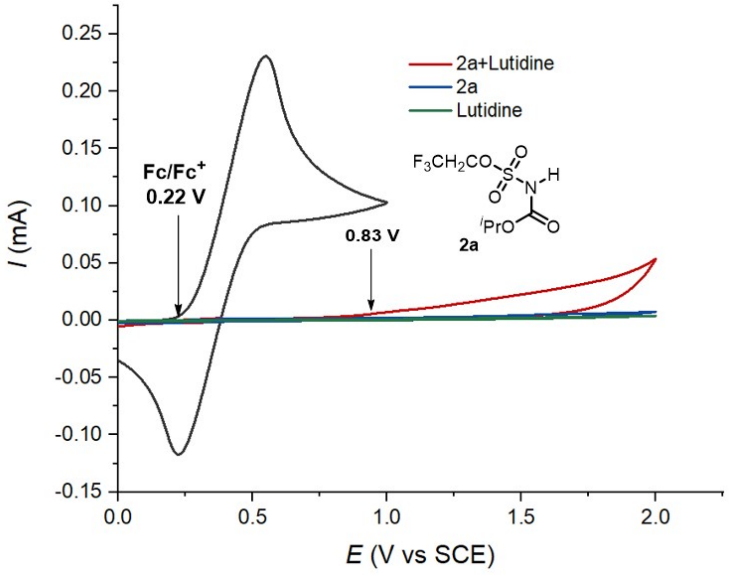


Figure S19. Overlapped CV results of **2a**, lutidine, and their mixture in MeCN

10. The thermal ellipsoid plot of 3a

Add 100 mg of **3a** to a 25 mL beaker, completely dissolve it with EtOH. A single crystal **3a** was obtained by slowly evaporating at room temperature under the air conditions.

Table S3 Crystal data and structure refinement for **3a**

Identification code	3a
CCDC	2295559
Empirical formula	$C_{21}H_{27}F_3N_2O_7S$
Formula weight	508.51
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.6415(8)
b/Å	10.1608(9)
c/Å	24.945(2)
α/°	90.00
β/°	95.477 (3)
γ/°	90.00
Volume/Å^3	2432.6 (4)
Z	4
ρ_{calc}g/cm^3	1.388
μ/mm^{-1}	0.199
F(000)	1064.0
Crystal size/mm^3	0.33 × 0.12 × 0.13
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.34 to 50.04
Index ranges	$-11 \le h \le 7$, $-12 \le k \le 11$, $-28 \le l \le 29$
Reflections collected	14423
Independent reflections	4274 [R_{int} = 0.0639, R_{sigma} = 0.0855]
Data/restraints/parameters	4274/135/324
Goodness-of-fit on F^2	1.087
Final R indexes [I>=2σ (I)]	R_1 = 0.0751, wR_2 = 0.1967
Final R indexes [all data]	R_1 = 0.1232, wR_2 = 0.2200
Largest diff. peak/hole / e Å^{-3}	0.43/-0.27

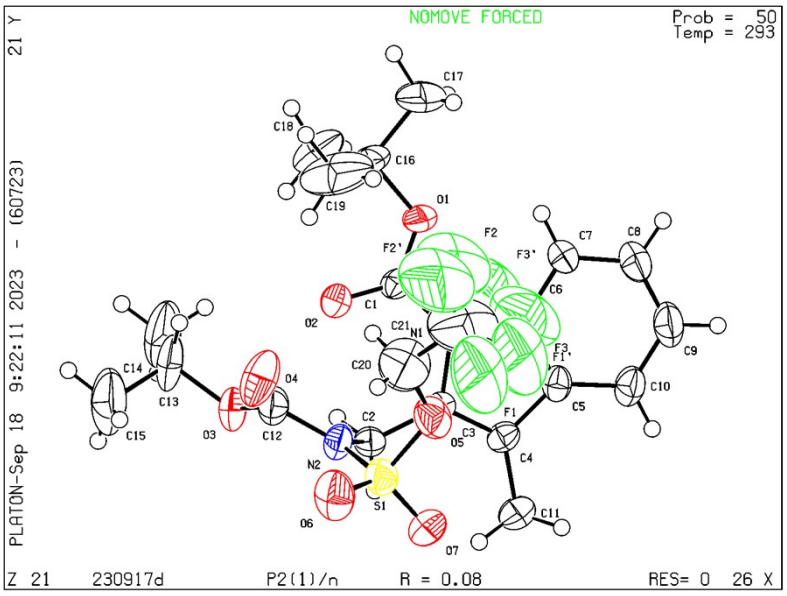
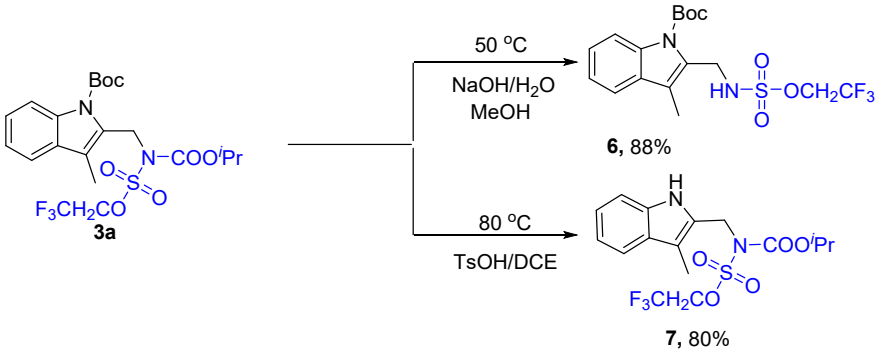


Figure S20. The thermal ellipsoid plot of **3a**

11. Further transformations of 3a



Scheme S7. Preparation of **6** and **7**

A mixture of *tert*-butyl 2-(((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl) amino)methyl)-3-methyl-1*H*-indole-1-carboxylate **3a** (0.1 mmol, 50.8 mg,), NaOH (0.5 mmol, 20 mg), H_2O (0.1 mL) and MeOH (2.0 mL) was added to a 25 mL reaction tube, which was heated at 50 °C. After the reaction completed as monitored with TLC, the reaction mixture was extracted with ethyl acetate and water for three times. The combined organic layers were dried over Na_2SO_4, filtered and evaporated under reduced pressure. Then, the residue was purified by chromatography on silica gel to afford a colorless oil **6** (37.1 mg, 88%).

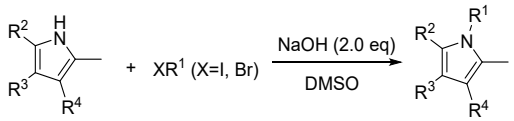
A mixture of *tert*-butyl 2-(((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl) amino)methyl)-3-methyl-1H-indole-1-carboxylate **3a** (0.1 mmol, 50.8 mg,), TsOH·H_2O (0.2 mmol, 38 mg) and DCE (2.0 mL) was added to a 25 mL reaction tube, which was heated at 80 °C. After the reaction completed as monitored with TLC, the reaction mixture was extracted with ethyl acetate and Na_2CO_3 saturated solution for three times. The combined organic layers were dried over Na_2SO_4, filtered and evaporated under reduced pressure. Then, the residue was purified by chromatography on silica gel to afford a

colorless oil **7** (32.6 mg, 80%).

12. Synthetic and analytical data of indole and pyrrole derivatives

1a-1m were prepared according to the known procedure (*Org. Lett*. 2019, **21**, 14−17). **4a-4e** and **4g-4p** were prepared according to the following procedure B. **4f** and **4r** were purchased from company of Innochem. **4q** was prepared according to the following procedure C.

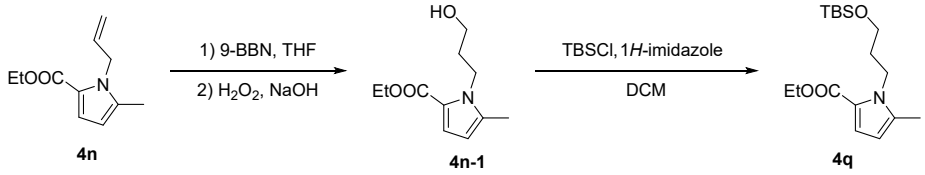
11.1 General procedure B



Scheme S8. Preparation of **4a-4e** and **4g-4p**

2-methyl-1*H*-pyrrole derivatives (2.0 mmol), NaOH (4.0 mmol, 0.16 g) and halogenated hydrocarbon (2.4 mmol) were dissolved in DMSO (10 ml). The reaction mixture was stirred overnight at room temperature. The mixture was concentrated, and extracted with ethyl acetate and water for three times. The combined organic layers were dried ($MgSO_4$), filtered, and concentrated. The residue was purified by flash column chromatography to afford the target products.

11.2 General procedure C

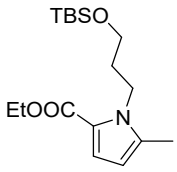


Scheme S9. Preparation of **4q**

To a flask charged with ethyl 1-allyl-5-methyl-1*H*-pyrrole-2-carboxylate **4n** (0.775 g, 4 mmol) in anhydrous THF (10 mL) was added 9-BBN (20 mL, 0.5 M in THF, 10 mmol, 2.5 equiv) at 0 °C under nitrogen. The reaction was allowed to warm to 50 °C spontaneously, and then was stirred for 2.0 h. H_2O_2 (4.0 mL) and NaOH (2 M, 4.0 mL) were added dropwise at 0 °C. After completion of addition, the reaction was allowed to being stirred overnight at room temperature. Then the mixture was extracted with ethyl acetate and water for three times. The combined organic layers were dried ($MgSO_4$), filtered, and concentrated. The residue was purified with flash chromatography to afford the desired product **4n-1** (0.5 g, 59%).

A solution of ethyl 1-(3-hydroxypropyl)-5-methyl-1*H*-pyrrole-2-carboxylate **4n-1** (0.422 g, 2.0 mmol), *tert*-butylchlorodimethylsilane (0.450 g, 3.0 mmol), 1*H*-imidazole (0.204 g, 3.0 mmol) in DCM (10 mL) was stirred at room temperature overnight. The reaction mixture was then quenched with saturated aqueous $NaHCO_3$ solution and extracted with DCM for three times. The organic layer was dried ($MgSO_4$), filtered, and concentrated. The residue was purified by flash chromatography on silica gel to afford the desired product **4q** (0.585 g, 90%).

ethyl 1-(3-((tert-butyldimethylsilyl)oxy)propyl)-5-methyl-1*H*-pyrrole-2-carboxylate (4q)



A colorless oil. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.96 (s, 1H), 5.94 (s, 1H), 4.40 (t, *J* = 7.3 Hz, 2H), 4.30 (q, *J* = 6.9 Hz, 2H), 3.68 (t, *J* = 5.4 Hz, 2H), 2.33 (s, 3H), 2.04-1.91 (m, 2H), 1.38 (t, *J* = 7.0 Hz, 3H), 0.96 (s, 9H), 0.11 (s, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 161.1, 136.8, 121.2, 117.8, 107.7, 60.2, 59.5, 42.3, 34.3, 26.0, 18.3, 14.6, 12.6, -5.3. **HRMS m/z (ESI)** calcd. for $C_{17}H_{31}NNaO_3Si^+$ (M + Na)$^+$ 348.1971, found 348.1969.

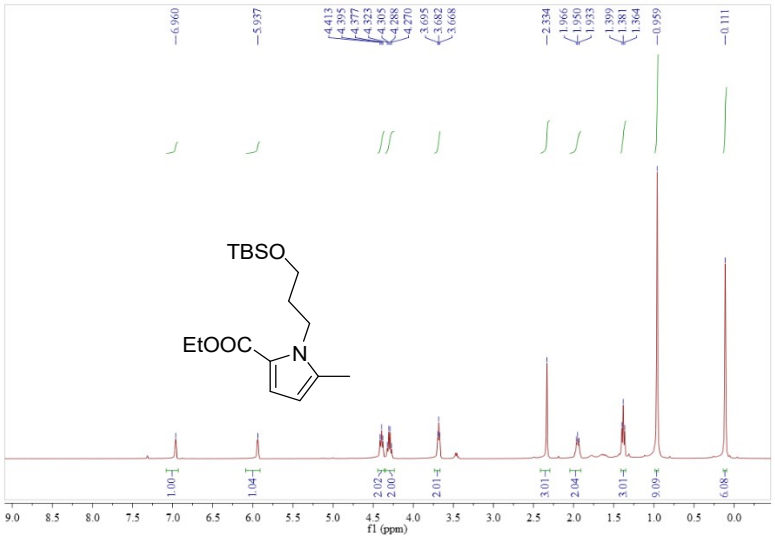


Figure S21. ^{1}H NMR (400 MHz, Chloroform-*d*) of **4q**

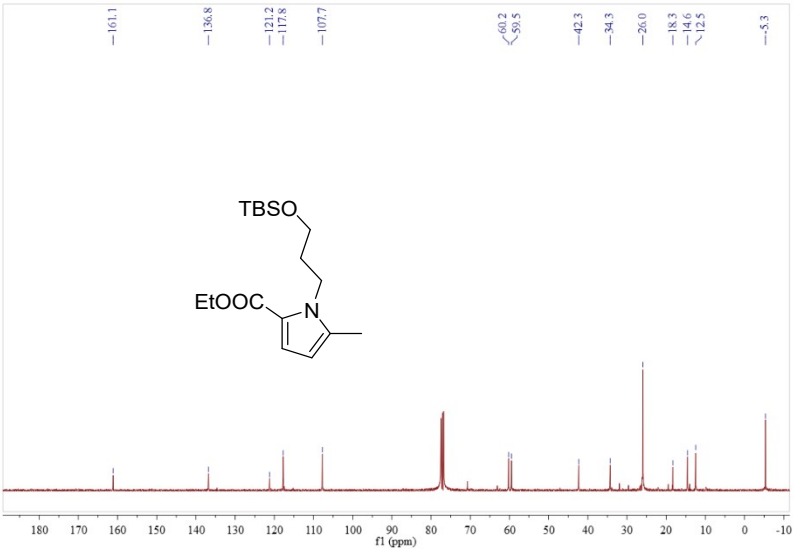
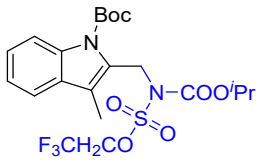


Figure S22. ^{13}C NMR (100 MHz, Chloroform-*d*) of **4q**

13. Experimental data

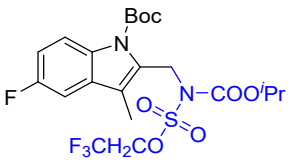
tert-butyl 2-(((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)methyl)-3-methyl-1H-indole-1-carboxylate (3a)



Following the general procedure A on 0.2 mmol scale with 6.5 V cell potential, the substrate **3a** was obtained as a white solid in 72% yield (73.2

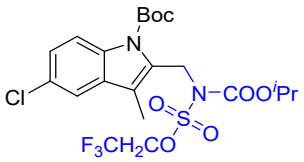
mg). mp 143.2 – 144.2 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.01 (d, *J* = 8.3 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.34 (dt, *J* = 25.3, 7.4 Hz, 2H), 5.43 (s, 2H), 5.15 (dt, *J* = 12.3, 6.2 Hz, 1H), 4.45 (q, *J* = 7.9 Hz, 2H), 2.37 (s, 3H), 1.74 (s, 9H), 1.40 (d, *J* = 6.2 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 152.2, 150.7, 135.6, 130.1, 128.8, 125.2, 122.7, 121.7 (q, *J* = 276.2 Hz), 120.6, 119.1, 115.6, 84.3, 73.2, 66.9 (q, *J* = 38.2 Hz), 45.0, 28.2, 21.6, 9.0. **HRMS m/z (ESI)** calcd. for $C_{21}H_{27}F_3N_2NaO_7S^+$ (M + Na)$^+$ 531.1389, found 531.1385.

tert-butyl 5-fluoro-2-(((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)methyl)-3-methyl-1H-indole-1-carboxylate (3c)



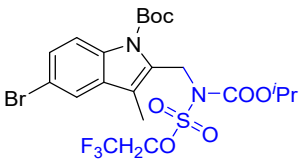
Following the general procedure A on 0.2 mmol scale with 6.5 V cell potential, the substrate **3c** was obtained as a white solid in 68% yield (71.5 mg). mp 154.4 – 155.4 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.94 (dd, *J* = 8.9, 4.3 Hz, 1H), 7.20 (d, *J* = 8.3 Hz, 1H), 7.08 (t, *J* = 8.9 Hz, 1H), 5.41 (s, 2H), 5.14 (dt, *J* = 12.4, 6.2 Hz, 1H), 4.48 (q, *J* = 7.9 Hz, 2H), 2.31 (s, 3H), 1.72 (s, 9H), 1.39 (d, *J* = 6.2 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 158.4 (d, *J* = 239.8), 151.2, 149.5, 131.0, 130.2 (d, *J* = 9.4 Hz), 129.6, 120.9 (q, *J* = 276.0 Hz), 119.3(d, *J* = 4.1 Hz), 115.8 (d, *J* = 8.9 Hz), 112.0 (d, *J* = 24.8 Hz), 103.7 (d, *J* = 23.5 Hz), 83.8, 72.5, 66.1 (q, *J* = 38.2 Hz), 44.2, 27.4, 20.8, 8.1. **HRMS m/z (ESI)** calcd. for $C_{21}H_{26}F_4N_2NaO_7S^+$ (M + Na)$^+$ 549.1295, found 549.1283.

tert-butyl 5-chloro-2-(((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)methyl)-3-methyl-1H-indole-1-carboxylate (3d)



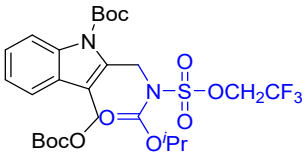
Following the general procedure A on 0.2 mmol scale with 6.5 V cell potential, the substrate **3d** was obtained as a white solid in 63% yield (68.3 mg). mp 175.9 – 176.9 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.91 (d, *J* = 8.9 Hz, 1H), 7.52 (s, 1H), 7.31 (d, *J* = 8.6 Hz, 1H), 5.40 (s, 2H), 5.14 (dt, *J* = 12.4, 6.2 Hz, 1H), 4.49 (q, *J* = 7.9 Hz, 2H), 2.32 (s, 3H), 1.72 (s, 9H), 1.39 (d, *J* = 6.2 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 152.1, 150.3, 133.9, 131.3, 130.2, 128.5, 125.2, 121.7 (q, *J* = 276.0 Hz), 119.8, 118.8, 116.7, 84.8, 73.3, 67.0 (q, *J* = 38.2 Hz), 44.9, 28.2, 21.6, 8.9. **HRMS m/z (ESI)** calcd. for $C_{21}H_{26}ClF_3N_2NaO_7S^+$ (M + Na)$^+$ 565.0999, found 565.1003.

tert-butyl 5-bromo-2-(((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)methyl)-3-methyl-1H-indole-1-carboxylate (3e)



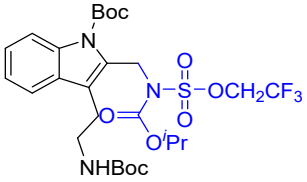
Following the general procedure A on 0.2 mmol scale with 6.5 V cell potential, the substrate **3e** was obtained as a white solid in 66% yield (77.4 mg). mp 122.3 – 123.3 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.86 (d, *J* = 8.8 Hz, 1H), 7.68 (s, 1H), 7.44 (d, *J* = 8.9 Hz, 1H), 5.40 (s, 2H), 5.20 – 5.10 (m, 1H), 4.49 (q, *J* = 7.8 Hz, 2H), 2.32 (s, 3H), 1.72 (s, 9H), 1.39 (d, *J* = 6.2 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 152.0, 150.3, 134.2, 131.8, 130.1, 127.9, 121.8, 121.6 (q, *J* = 275.8 Hz), 119.6, 117.0, 116.1, 84.8, 73.3, 66.9 (q, *J* = 38.0 Hz), 44.8, 28.2, 21.6, 8.9. **HRMS m/z (ESI)** calcd. for $C_{21}H_{26}BrF_3N_2NaO_7S^+$ (M + Na)$^+$ 609. 0494, found 609.0486.

tert-butyl 3-(((tert-butoxycarbonyl)oxy)methyl)-2-(((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)methyl)-1H-indole-1-carboxylate (3f)



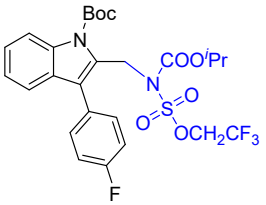
Following the general procedure A on 0.2 mmol scale with 6.5 V cell potential, the substrate **3f** was obtained as a colorless oil in 51% yield (63.6 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.01 (d, *J* = 8.3 Hz, 1H), 7.76 (d, *J* = 7.7 Hz, 1H), 7.43 – 7.22 (m, 2H), 5.53 (s, 2H), 5.43 (s, 2H), 5.16 (dt, *J* = 12.3, 6.1 Hz, 1H), 4.45 (q, *J* = 7.9 Hz, 2H), 1.73 (s, 9H), 1.51 (s, 9H), 1.42 (d, *J* = 6.3 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 152.7, 151.2, 149.6, 134.8, 131.5, 127.5, 124.6, 122.4, 120.8 (q, *J* = 276.5 Hz), 118.8, 118.2, 114.8, 84.2, 81.5, 72.6, 66.03 (q, *J* = 38.1 Hz), 58.2, 43.4, 27.3, 27.0, 20.8. **HRMS m/z (ESI)** calcd. for $C_{26}H_{35}F_3N_2NaO_{10}S^+$ (M + Na)$^+$ 647.1862, found 647.1858.

tert-butyl 3-(2-((tert-butoxycarbonyl)amino)ethyl)-2-(((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)methyl)-1H-indole-1-carboxylate (3g)



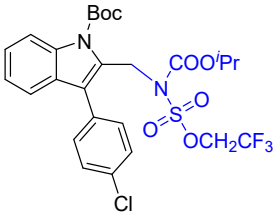
Following the general procedure A on 0.2 mmol scale with 6.5 V cell potential, the substrate **3g** was obtained as a white solid in 70% yield (89.2 mg). mp 111.9 – 112.9 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.00 (d, *J* = 8.3 Hz, 1H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 11.5 Hz, 1H), 5.39 (s, 2H), 5.13 (dt, *J* = 12.3, 6.2 Hz, 1H), 4.72 (s, 1H), 4.49 (q, *J* = 7.9 Hz, 2H), 3.41 (d, *J* = 6.3 Hz, 2H), 3.07 (t, *J* = 6.9 Hz, 2H), 1.73 (s, 9H), 1.50 (s, 9H), 1.38 (d, *J* = 6.1 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 155.9, 152.0, 150.6, 135.6, 129.6, 129.2, 125.2, 122.9, 121.8, 121.7 (q, *J* = 275.7 Hz), 119.4, 115.7, 84.5, 79.3, 73.2, 67.0 (q, *J* = 38.0 Hz), 44.6, 40.5, 28.4, 28.2, 24.8, 21.6. **HRMS m/z (ESI)** calcd. for $C_{27}H_{38}F_3N_3NaO_9S^+$ (M + Na)$^+$ 660.2179, found 660.2178.

tert-butyl 3-(4-fluorophenyl)-2-(((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)methyl)-1H-indole-1-carboxylate (3h)



Following the general procedure A on 0.2 mmol scale with 6.5 V cell potential, the substrate **3h** was obtained as a colorless oil in 61% yield (71.7 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.08 (d, *J* = 8.6 Hz, 1H), 7.47 – 7.34 (m, 4H), 7.34 – 7.09 (m, 3H), 5.46 (s, 2H), 5.03 (dt, *J* = 12.4, 6.2 Hz, 1H), 4.48 (q, *J* = 7.9 Hz, 2H), 1.77 (s, 9H), 1.32 (d, *J* = 6.2 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 162.6 (d, *J* = 247.0 Hz), 151.8, 150.7, 135.5, 132.1 (d, *J* = 8.1 Hz), 129.7, 129.5, 128.5 (d, *J* = 3.5 Hz), 125.4, 124.9, 123.2, 121.8 (d, *J* =276.1 Hz), 119.7, 115.7, 115.6 (d, *J* = 9.9 Hz), 84.9, 73.2, 67.27 (q, *J* = 38.2 Hz), 45.5, 28.3, 21.6. **HRMS m/z (ESI)** calcd. for $C_{26}H_{28}F_4N_2NaO_7S^+$ (M + Na)$^+$ 611.1451, found 611.1443.

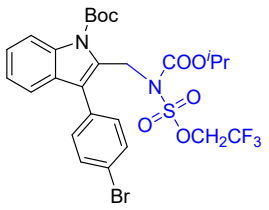
tert-butyl 3-(4-chlorophenyl)-2-(((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)methyl)-1H-indole-1-carboxylate (3i)



Following the general procedure A on 0.2 mmol scale with 6.5 V cell potential, the substrate **3i** was obtained as a white solid in 60% yield (72.3 mg). mp 90.1 – 91.1 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.08 (d, *J* = 8.6 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 2H), 7.40 (d, *J* = 6.9 Hz, 4H), 7.29 (dd, *J* = 13.8, 6.4 Hz, 1H), 5.46 (s, 2H), 5.02 (dq, *J* = 12.4, 6.2

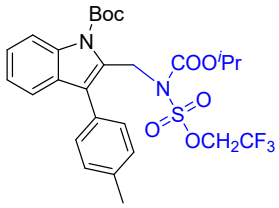
Hz, 1H), 4.48 (q, *J* = 7.9 Hz, 2H), 1.77 (s, 9H), 1.32 (d, *J* = 6.0 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 151.7, 150.6, 135.6, 133.9, 131.8, 131.1, 129.8, 129.3, 128.8, 125.4, 124.7, 123.3, 121.8 (q, *J* = 276.2 Hz), 119.7, 115.6, 85.0, 73.3, 67.3, 45.5, 28.3, 21.6. **HRMS m/z (ESI)** calcd. for $C_{26}H_{28}ClF_3N_2NaO_7S^+$ $(M + Na)^+$ 627.1156, found 627.1147.

tert-butyl 3-(4-bromophenyl)-2-(((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)methyl)-1H-indole-1-carboxylate (3j)



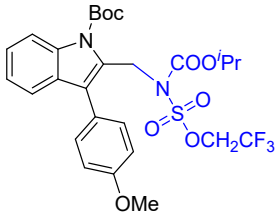
Following the general procedure A on 0.2 mmol scale with 6.5 V cell potential, the substrate **3j** was obtained as a white solid in 68% yield (88.1 mg). mp 107.5 – 107.6 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.07 (d, *J* = 8.6 Hz, 1H), 7.66 (d, *J* = 7.7 Hz, 2H), 7.40 (d, *J* = 7.5 Hz, 2H), 7.37 – 7.31 (m, 2H), 7.28 (t, *J* = 7.5 Hz, 1H), 5.46 (s, 2H), 5.10 – 4.96 (m, 1H), 4.47 (q, *J* = 7.9 Hz, 2H), 1.77 (s, 9H), 1.32 (d, *J* = 6.1 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 150.9, 149.8, 134.7, 131.2, 130.9, 130.7, 128.9, 128.3, 124.5, 123.8, 122.4, 121.2, 120.9 (q, *J* = 276.1 Hz) 119.5, 118.8, 114.8, 84.1, 72.4, 66.4 (q, *J* = 38.2 Hz), 44.6, 27.4, 20.7. **HRMS m/z (ESI)** calcd. for $C_{26}H_{28}BrF_2N_2NaO_7S^+$ $(M + Na)^+$ 671.0650, found 671.0642.

tert-butyl 2-(((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)methyl)-3-(p-tolyl)-1H-indole-1-carboxylate (3k)



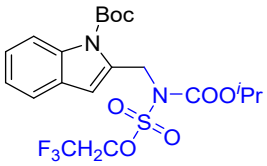
Following the general procedure A on 0.2 mmol scale with 6.5 V cell potential, the substrate **3k** was obtained as a colorless oil in 63% yield (73.6 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.43 – 7.33 (m, 5H), 7.29 (dd, *J* = 13.9, 6.5 Hz, 1H), 5.51 (d, *J* = 17.4 Hz, 2H), 5.02 (dt, *J* = 12.2, 6.1 Hz, 1H), 4.57 – 4.27 (m, 2H), 2.49 (s, 3H), 1.78 (s, 9H), 1.30 (d, *J* = 6.2 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 151.8, 150.7, 137.6, 135.7, 130.3, 129.6, 129.5, 129.3, 126.0,125.2, 123.1, 120.0, 115.6, 84.7, 73.1, 67.2 (q, *J* = 38.1 Hz), 45.6, 28.3, 21.5, 21.4. **HRMS m/z (ESI)** calcd. for $C_{27}H_{31}F_3N_2NaO_7S^+$ $(M + Na)^+$ 607.1702, found 607.1698.

tert-butyl 2-(((isopropoxycarbonyl) ((2,2,2-trifluoroethoxy) sulfonyl)amino)methyl) -3-(4-methoxyphenyl)-1H-indole-1-carboxylate (3l)



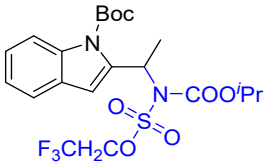
Following the general procedure A on 0.2 mmol scale with 6.5 V cell potential, the substrate **3l** was obtained as a colorless oil in 63% yield (75.6 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 7.1 Hz, 3H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 7.9 Hz, 2H), 5.50 (s, 2H), 5.04 (dt, *J* = 12.4, 6.2 Hz, 1H), 4.49 (q, *J* = 7.9 Hz, 2H), 3.93 (s, 3H), 1.79 (s, 9H), 1.32 (d, *J* = 6.3 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 159.3, 151.8, 150.7, 135.6, 131.5, 129. 7, 129.2, 125.7, 125.2, 124.7, 123.1, 121.8 (q, J = 275.9 Hz), 120.0, 117.67, 115.5, 114.1, 84.7, 73.0, 67.2 (q, *J* = 38.1 Hz), 55.3, 45.6, 28.2, 21.5. **HRMS m/z (ESI)** calcd. for $C_{27}H_{31}F_3N_2NaO_8S^+$ $(M + Na)^+$ 623.1651, found 623.1643.

tert-butyl 2-(((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)methyl)-1H-indole-1-carboxylate (3m)



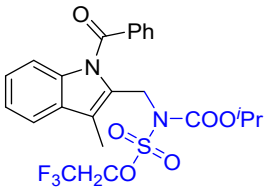
Following the general procedure A on 0.2 mmol scale with 6.5 V cell potential, the substrate **3m** was obtained as a colorless oil in 50% yield (49.5 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.09 (d, *J* = 8.2 Hz, 1H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.30 (dt, *J* = 23.1, 7.2 Hz, 2H), 6.61 (s, 1H), 5.43 (s, 2H), 5.15 (dt, *J* = 12.4, 6.2 Hz, 1H), 4.81 (q, *J* = 7.9 Hz, 2H), 1.76 (s, 9H), 1.36 (d, *J* = 6.2 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 151.4, 150.6, 136.5, 136.3, 129.0, 124.2, 123.1, 121.9 (q, *J* = 276.1 Hz), 120.6, 115.6, 107.1, 84.9, 73.6, 68.2 (q, *J* = 38.3 Hz), 48.9, 28.3, 21.6. **HRMS m/z (ESI)** calcd. for $C_{20}H_{25}F_3N_2NaO_7S^+$ $(M + Na)^+$ 517.1232, found 517.1231.

tert-butyl 2-(1-((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)ethyl)-1H-indole-1-carboxylate (3n)



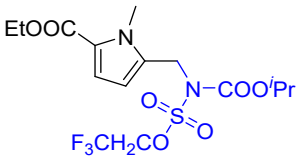
Following the general procedure A on 0.2 mmol scale with 6.5 V cell potential, the substrate **3n** was obtained as a colorless oil in 66% yield (67.1 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.00 (d, *J* = 8.3 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.32 (m, 2H), 6.86 (s, 1H), 6.25 (q, *J* = 6.8 Hz, 1H), 5.15 (dt, *J* = 12.3, 6.1 Hz, 1H), 4.50 (m, 2H), 1.99 (d, *J* = 6.8 Hz, 3H), 1.74 (s, 9H), 1.42 (d, *J* = 6.1 Hz, 3H), 1.35 (d, *J* = 6.1 Hz, 3H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 152.3, 150.6, 137.4, 136.3, 128.4, 124.8, 123.0, 121.8 (q, *J* = 275.8 Hz), 121.0, 115.8, 112.1, 84.6, 72.9, 67.1 (q, *J* = 38.0 Hz), 54.8, 28.1, 21.7, 21.5, 19.1. **HRMS m/z (ESI)** calcd. for $C_{21}H_{27}F_3N_2NaO_7S^+$ $(M + Na)^+$ 531.1389, found 531.1388.

2,2,2-trifluoroethyl ((1-benzoyl-3-methyl-1H-indol-2-yl)methyl)(isopropoxycarbonyl)sulfamate (3p)



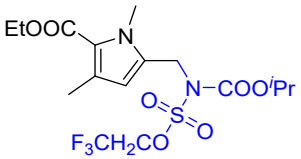
Following the general procedure A on 0.2 mmol scale with 6.5 V cell potential, the substrate **3p** was obtained as a colorless oil in 65% yield (66.6 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.76 (m, 2H), 7.65 (m, 1H), 7.50 (ddd, *J* = 13.7, 6.4, 1.2 Hz, 3H), 7.17 (td, *J* = 7.6, 0.8 Hz, 1H), 7.01 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 6.60 (d, *J* = 8.4 Hz, 1H), 5.38 (s, 2H), 5.05 (dt, *J* = 12.6, 6.3 Hz, 1H), 4.42 (q, *J* = 8.0 Hz, 2H), 2.35 (s, 3H), 1.29 (d, *J* = 6.3 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 169.8, 151.5, 136.7, 135.3, 133.3, 130.9, 130.3, 130.1, 128.9, 124.3, 122.5, 121.7 (q, *J* = 276.3 Hz), 120.5, 119.2, 114.1, 73.6, 67.5 (q, *J* = 38.0 Hz), 44.3, 21.6, 8.9. **HRMS m/z (ESI)** calcd. for $C_{23}H_{23}F_3N_2NaO_6S^+$ $(M + Na)^+$ 535.1127, found 535.1119.

ethyl 5-(((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)methyl)-1-methyl-1H-pyrrole-2-carboxylate (5a)



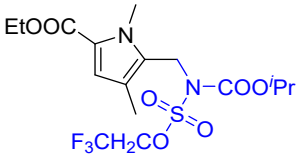
Following the general procedure A on 0.2 mmol scale with 7.5 V cell potential, the substrate **5a** was obtained as a colorless oil in 61% yield (52.5 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.97 (d, *J* = 3.0 Hz, 1H), 6.27 (d, *J* = 3.3 Hz, 1H), 5.13 (dt, *J* = 12.4, 6.0 Hz, 1H), 5.02 (s, 2H), 4.53 (q, *J* = 7.8 Hz, 2H), 4.32 (q, *J* = 6.7 Hz, 2H), 3.99 (s, 3H), 1.41 – 1.35 (m, 9H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 161.4, 151.2, 134.1, 123.7, 121.7 (q, *J* = 276.1 Hz), 117.3, 109.7, 73.9, 67.6 (q, *J* = 38.3 Hz), 60.0, 44.3, 32.7, 21.6, 14.5. **HRMS m/z (ESI)** calcd. for $C_{15}H_{21}F_3N_2NaO_7S^+$ $(M + Na)^+$ 453.0919, found 453.0912.

ethyl 5-(((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)methyl)-1,3-dimethyl-1H-pyrrole-2-carboxylate (5b)



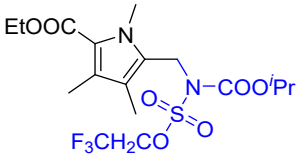
Following the general procedure A on 0.2 mmol scale with 7.5 V cell potential, the substrate **5b** was obtained as a white solid in 54% yield (48.0 mg). mp 83.5 – 84.5 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.10 (s, 1H), 5.13 (dt, *J* = 12.3, 6.1 Hz, 1H), 4.98 (s, 2H), 4.53 (q, *J* = 7.8 Hz, 2H), 4.34 (q, *J* = 7.0 Hz, 2H), 3.91 (s, 3H), 2.32 (s, 3H), 1.45 – 1.32 (m, 9H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 162.2, 151.2, 132.7, 129.2, 121.7 (q, *J* = 275.9 Hz), 120.8, 112.1, 73.8, 67.5 (q, *J* = 38.2 Hz), 59.8, 44.3, 33.1, 21.6, 14.5, 14.4. **HRMS m/z (ESI)** calcd. for $C_{16}H_{23}F_3N_2NaO_7S^+$ (M + Na)$^+$ 467.1076, found 467.1067.

ethyl 5-(((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)methyl)-1,4-dimethyl-1H-pyrrole-2-carboxylate (5c)



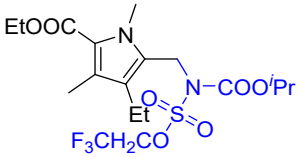
Following the general procedure A on 0.2 mmol scale with 7.5 V cell potential, the substrate **5b** was obtained as a white solid in 70% yield (62.2 mg). mp 75.4 – 76.4 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.10 (s, 1H), 5.13 (dt, *J* = 12.3, 6.1 Hz, 1H), 4.98 (s, 2H), 4.53 (q, *J* = 7.8 Hz, 2H), 4.34 (q, *J* = 7.0 Hz, 2H), 3.91 (s, 3H), 2.32 (s, 3H), 1.41 – 1.34 (m, 9H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 161.3, 151.5, 130.1, 122.7, 121.7 (q, *J* = 276.3 Hz), 120.0, 118.3, 73.8, 67.1 (q, *J* = 38.2 Hz), 59.9, 42.9, 32.7, 21.6, 14.4, 11.3. **HRMS m/z (ESI)** calcd. for $C_{16}H_{23}F_3N_2NaO_7S^+$ (M + Na)$^+$ 467.1068, found 467.1068.

ethyl 5-(((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)methyl)-1,3,4-trimethyl-1H-pyrrole-2-carboxylate (5d)



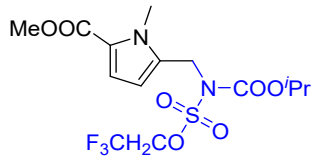
Following the general procedure A on 0.2 mmol scale with 7.5 V cell potential, the substrate **5d** was obtained as a white solid in 84% yield (77.0 mg). mp 81.6 – 82.6 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 5.14 (dt, *J* = 12.3, 6.1 Hz, 1H), 5.04 (s, 2H), 4.40 – 4.26 (m, 4H), 3.84 (d, *J* = 21.3 Hz, 3H), 2.26 (s, 3H), 2.04 (s, 3H), 1.41 (t, *J* = 7.0 Hz, 3H), 1.36 (d, *J* = 6.0 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 162.2, 151.5, 129.2, 127.4, 121.7 (q, *J* = 276.0 Hz), 120.8, 119.8, 73.7, 66.9 (q, *J* = 38.4 Hz), 59.8, 42.9, 33.1, 21.5, 14.5, 11.4, 9.2. **HRMS m/z (ESI)** calcd. for $C_{17}H_{25}F_3N_2NaO_7S^+$ (M + Na)$^+$ 481.1232, found 481.1238.

ethyl 4-ethyl-5-(((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)methyl)-1,3-dimethyl-1H-pyrrole-2-carboxylate (5e)



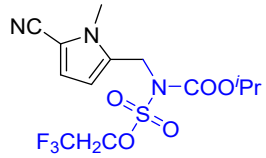
Following the general procedure A on 0.2 mmol scale with 7.5 V cell potential, the substrate **5e** was obtained as a colorless oil in 70% yield (66.1 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 5.13 (dq, *J* = 12.4, 6.0 Hz, 1H), 5.03 (s, 2H), 4.44 – 4.32 (m, 4H), 3.87 (s, 3H), 2.57 – 2.48 (m, 2H), 2.29 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.34 (d, *J* = 6.2 Hz, 6H), 1.07 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 162.3, 151.5, 128.6, 126.9, 126.4, 121.7 (q, *J* = 276.1 Hz), 121.1, 73.8, 67.2 (q, *J* = 38.3 Hz), 59.8, 42.8, 33.2, 21.5, 17.3, 15.8, 14.5, 11.3. **HRMS m/z (ESI)** calcd. for $C_{18}H_{27}F_3N_2NaO_7S^+$ (M + Na)$^+$ 495.1389, found 495.1387.

methyl 5-(((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)methyl)-1-methyl-1H-pyrrole-2-carboxylate (5f)



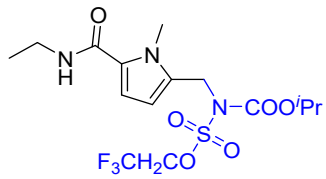
Following the general procedure A on 0.2 mmol scale with 7.5 V cell potential, the substrate **5f** was obtained as a white solid in 60% yield (50.0 mg). mp 81.1 – 82.1 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.96 (d, *J* = 3.8 Hz, 1H), 6.27 (d, *J* = 3.8 Hz, 1H), 5.21 – 5.09 (m, 1H), 5.02 (s, 2H), 4.54 (d, *J* = 7.9 Hz, 2H), 3.99 (s, 3H), 3.86 (s, 3H), 1.37 (d, *J* = 6.2 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 161.7, 151.1, 134.2, 123.3, 121.7 (q, *J* = 277.7 Hz) 117.4, 109.7, 73.8, 67.6 (q, *J* = 38.3 Hz), 51.2, 44.2, 32.7, 21.6. **HRMS m/z (ESI)** calcd. for $C_{14}H_{19}F_3N_2NaO_7S^+$ (M + Na)$^+$ 439.0763, found 439.0770.

2,2,2-trifluoroethyl ((5-cyano-1-methyl-1H-pyrrol-2-yl)methyl)(isopropoxycarbonyl)sulfamate (5g)



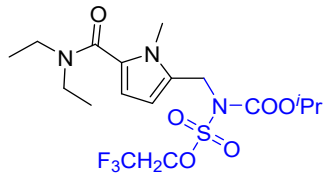
Following the general procedure A on 0.2 mmol scale with 7.5 V cell potential, the substrate **5g** was obtained as a colorless oil in 73% yield (56.0 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.80 (d, *J* = 3.7 Hz, 1H), 6.32 (d, *J* = 3.7 Hz, 1H), 5.21 – 5.07 (m, 1H), 4.99 (s, 2H), 4.59 (q, *J* = 7.8 Hz, 2H), 3.80 (d, *J* = 19.0 Hz, 3H), 1.38 (d, *J* = 6.2 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 151.1, 133.11, 121.7 (q, *J* = 276.2 Hz), 119.2, 113.6, 111.1, 105.8, 74.5, 67.8 (q, *J* = 38.4 Hz), 43.8, 32.9, 21.7. **HRMS m/z (ESI)** calcd. for $C_{13}H_{16}F_3N_3NaO_5S^+$ (M + Na)$^+$ 406.0660, found 406.0666.

2,2,2-trifluoroethyl ((5-(ethylcarbamoyl)-1-methyl-1H-pyrrol-2-yl)methyl)(isopropoxycarbonyl)sulfamate (5h)



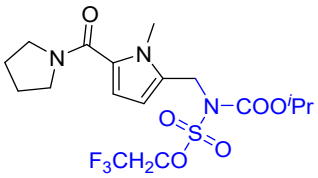
Following the general procedure A on 0.2 mmol scale with 7.5 V cell potential, the substrate **5h** was obtained as a colorless oil in 62% yield (53.2 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.51 (s, 1H), 6.23 (s, 1H), 5.93 (s, 1H), 5.12 (dt, *J* = 12.4, 6.1 Hz, 1H), 5.01 (s, 2H), 4.51 (q, *J* = 7.8 Hz, 2H), 3.97 (s, 3H), 3.45 (p, *J* = 6.4 Hz, 2H), 1.36 (d, *J* = 6.1 Hz, 6H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 162.0, 151.3, 132.3, 127.4, 121.7 (q, *J* = 276.2 Hz), 110.8, 109.2, 73.8, 67.5 (q, *J* = 38.3 Hz), 44.3, 34.3, 32.6, 21.6, 15.1. **HRMS m/z (ESI)** calcd. for $C_{15}H_{22}F_3N_3NaO_6S^+$ (M + Na)$^+$ 452.1079, found 452.1074.

2,2,2-trifluoroethyl ((5-(diethylcarbamoyl)-1-methyl-1H-pyrrol-2-yl)methyl)(isopropoxycarbonyl)sulfamate (5i)



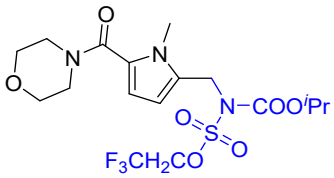
Following the general procedure A on 0.2 mmol scale with 7.5 V cell potential, the substrate **5i** was obtained as a colorless oil in 70% yield (64.0 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.26 (d, *J* = 24.8 Hz, 2H), 5.13 (dt, *J* = 12.3, 6.1 Hz, 1H), 5.01 (s, 2H), 4.47 (q, *J* = 7.8 Hz, 2H), 3.73 (s, 3H), 3.54 (q, *J* = 7.0 Hz, 4H), 1.37 (d, *J* = 6.1 Hz, 6H), 1.24 (t, *J* = 6.8 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 163.9, 151.3, 130.1, 127.9, 121.8 (q, *J* = 277.7 Hz), 109.9, 109.2, 73.7, 67.3 (q, *J* = 38.2 Hz), 44.2, 42.1, 32.3, 21.6, 13.8. **HRMS m/z (ESI)** calcd. for $C_{17}H_{26}F_3N_3NaO_6S^+$ (M + Na)$^+$ 480.1392, found 480.1398.

2,2,2-trifluoroethyl (isopropoxycarbonyl)((1-methyl-5-(pyrrolidine-1-carbonyl)-1H-pyrrol-2-yl)methyl)sulfamate (5j)



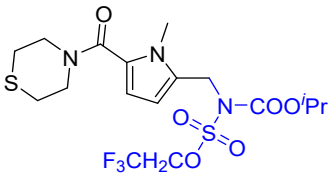
Following the general procedure A on 0.2 mmol scale with 7.5 V cell potential, the substrate **5j** was obtained as a colorless oil in 72% yield (65.5 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.47 (s, 1H), 6.24 (s, 1H), 5.12 (dt, *J* = 11.8, 6.0 Hz, 1H), 5.01 (s, 2H), 4.48 (q, *J* = 7.6 Hz, 2H), 3.85 (s, 3H), 3.65 (s, 4H), 1.96 (s, 4H), 1.36 (d, *J* = 6.1 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 162.0, 151.3, 131.0, 127.8, 121.8 (q, *J* = 276.2 Hz), 112.5, 108.9, 73.7, 67.4 (q, *J* = 38.0 Hz), 49.7, 46.3, 44.3, 32.7, 26.6, 24.2, 21.6. **HRMS m/z (ESI)** calcd. for $C_{17}H_{24}F_3N_3NaO_6S^+$ (M + Na)$^+$ 478.1236, found 478.1229.

2,2,2-trifluoroethyl (isopropoxycarbonyl)((1-methyl-5-(morpholine-4-carbonyl)-1H-pyrrol-2-yl)methyl)sulfamate (5k)



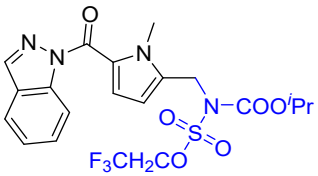
Following the general procedure A on 0.2 mmol scale with 7.5 V cell potential, the substrate **5k** was obtained as a white solid in 71% yield (66.9 mg). mp 76.4 – 77.4 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.26 (dd, *J* = 20.4, 3.5 Hz, 2H), 5.12 (dt, *J* = 12.4, 6.2 Hz, 1H), 5.00 (s, 2H), 4.50 (q, *J* = 7.9 Hz, 2H), 3.75 (d, *J* = 9.0 Hz, 11H), 1.36 (d, *J* = 6.2 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 162.9, 151.2, 131.2, 126.1, 121.7 (q, *J* = 275.9 Hz), 112.0, 109.2, 73.8, 67.4 (q, *J* = 38.0 Hz), 67.0, 45.7, 44.2, 32.3, 21.6. **HRMS m/z (ESI)** calcd. for $C_{17}H_{24}F_3N_3NaO_7S^+$ (M + Na)$^+$ 494.1185, found 494.1176.

2,2,2-trifluoroethyl (isopropoxycarbonyl)((1-methyl-5-(thiomorpholine-4-carbonyl)-1H-pyrrol-2-yl)methyl)sulfamate (5l)



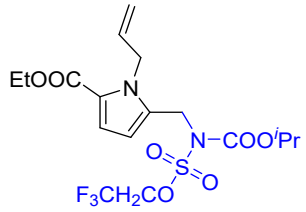
Following the general procedure A on 0.2 mmol scale with 7.5 V cell potential, the substrate **5l** was obtained as a white solid in 63% yield (61.4 mg). mp 80.1 – 81.1 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.26 (d, *J* = 12.3 Hz, 2H), 5.12 (dt, *J* = 12.2, 6.1 Hz, 1H), 5.00 (s, 2H), 4.51 (q, *J* = 7.8 Hz, 2H), 4.00 (s, 4H), 3.74 (s, 3H), 2.70 (s, 4H), 1.37 (d, *J* = 6.2 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 163.3, 151.2, 131.1, 121.7 (q, *J* = 275.9 Hz), 126.5, 111.5, 109.2, 73.8, 67.4 (q, *J* = 37.9 Hz), 47.9, 44.2, 32.3, 27.9, 21.6. **HRMS m/z (ESI)** calcd. for $C_{17}H_{24}F_3N_3NaO_6S_2^+$ (M + Na)$^+$ 510.0956, found 510.0947.

2,2,2-trifluoroethyl ((5-(1H-indazole-1-carbonyl)-1-methyl-1H-pyrrol-2-yl)methyl)(isopropoxycarbonyl)sulfamate (5m)



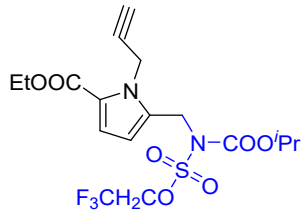
Following the general procedure A on 0.2 mmol scale with 7.5 V cell potential, the substrate **5m** was obtained as a white solid in 68% yield (68.3 mg). mp 97.5 – 98.5 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.55 (d, *J* = 8.4 Hz, 1H), 8.24 (s, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.43 (dd, *J* = 13.2, 5.7 Hz, 2H), 6.41 (d, *J* = 4.0 Hz, 1H), 5.26 – 4.98 (m, 3H), 4.62 (q, *J* = 7.9 Hz, 2H), 4.06 (s, 3H), 1.39 (d, *J* = 6.2 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 160.1, 151.1, 140.3, 139.4, 135.7, 129.1, 126.0, 125.0, 124.3, 122.5, 121.7 (q, *J* = 275.9 Hz), 121.0, 115.6, 110.2, 73.9, 67.8 (q, *J* = 38.0 Hz), 44.4, 33.4, 21.6. **HRMS m/z (ESI)** calcd. for $C_{20}H_{21}F_3N_4NaO_6S^+$ (M + Na)$^+$ 525.1032, found 525.1029.

ethyl 1-allyl-5-(((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)methyl)-1H-pyrrole-2-carboxylate (5n)



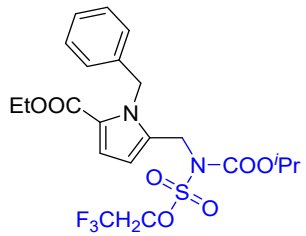
Following the general procedure A on 0.2 mmol scale with 7.5 V cell potential, the substrate **5n** was obtained as a colorless oil in 64% yield (58.4 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.02 (d, *J* = 3.7 Hz, 1H), 6.29 (d, *J* = 3.6 Hz, 1H), 6.05 – 5.95 (m, 1H), 5.13 (dd, *J* = 16.0, 9.0 Hz, 4H), 4.97 (s, 2H), 4.74 (d, *J* = 17.1 Hz, 1H), 4.60 (q, *J* = 7.8 Hz, 2H), 4.31 (q, *J* = 6.9 Hz, 2H), 1.42 – 1.33 (m, 9H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 161.0, 151.2, 134.4, 134.3, 123.0, 121.7 (q, *J* = 266.4 Hz), 117.7, 115.3, 109.3, 100.0, 73.8, 67.8 (q, *J* = 38.2 Hz), 60.0, 47.0, 44.4, 21.6, 14.4. **HRMS m/z (ESI)** calcd. for $C_{17}H_{23}F_3N_2NaO_7S^+$ (M + Na)$^+$ 479.1076, found 479.1082.

ethyl 5-(((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)methyl)-1-(prop-2-yn-1-yl)-1H-pyrrole-2-carboxylate (5o)



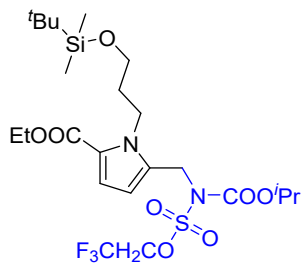
Following the general procedure A on 0.2 mmol scale with 7.5 V cell potential, the substrate **5o** was obtained as a colorless oil in 75% yield (68.1 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.00 (d, *J* = 3.2 Hz, 1H), 6.32 (d, *J* = 3.3 Hz, 1H), 5.42 (s, 2H), 5.24 – 5.05 (m, 3H), 4.51 (q, *J* = 7.8 Hz, 2H), 4.34 (q, *J* = 7.0 Hz, 2H), 2.35 (s, 1H), 1.39 (dd, *J* = 13.4, 6.6 Hz, 9H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 160.3, 150.5, 133.5, 122.0, 120.9 (q, *J* = 276.1Hz), 117.3, 109.8, 78.0, 73.2, 71.9, 66.8 (q, *J* = 38.1Hz), 59.5, 43.3, 33.6, 20.9, 13.6. **HRMS m/z (ESI)** calcd. for $C_{17}H_{21}F_3N_2NaO_7S^+$ (M + Na)$^+$ 477.0919, found 477.0922.

ethyl 1-benzyl-5-(((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)methyl)-1H-pyrrole-2-carboxylate (5p)



Following the general procedure A on 0.2 mmol scale with 7.5 V cell potential, the substrate **5p** was obtained as a colorless oil in 82% yield (83.0 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.30 (td, *J* = 14.4, 7.4 Hz, 3H), 7.09 (d, *J* = 2.8 Hz, 1H), 6.95 (d, *J* = 7.5 Hz, 2H), 6.35 (d, *J* = 3.1 Hz, 1H), 5.83 (s, 2H), 5.11 – 5.01 (m, 1H), 4.88 (s, 2H), 4.57 (q, *J* = 7.5 Hz, 2H), 4.28 (dt, *J* = 13.4, 6.7 Hz, 2H), 1.36 – 1.29 (m, 9H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 161.0, 151.1, 138.1, 134.6, 128.8, 127.2, 125.5, 123.5, 121.7 (q, *J* = 276.0Hz), 118.0, 109.6, 73.8, 67.8 (q, *J* = 38.0Hz), 60.0, 48.1, 44.5, 21.6, 14.3. **HRMS m/z (ESI)** calcd. for $C_{21}H_{25}F_3N_2NaO_7S^+$ (M + Na)$^+$ 529.1232, found 529.1236.

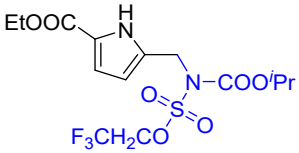
ethyl 1-(3-((tert-butyldimethylsilyl)oxy)propyl)-5-(((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)methyl)-1H-pyrrole-2-carboxylate (5q)



Following the general procedure A on 0.2 mmol scale with 7.5 V cell potential, the substrate **5p** was obtained as a colorless oil in 50% yield (58.8 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.00 (d, *J* = 3.7 Hz, 1H), 6.21 (d, *J* = 3.5 Hz, 1H), 5.15 – 5.06 (m, 3H), 4.61 (q, *J* = 7.8 Hz, 2H), 4.52 (t, *J* = 6.9 Hz, 2H), 4.31 (q, *J* = 7.0 Hz, 2H), 3.63 (t, *J* = 5.2

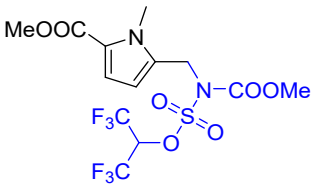
Hz, 2H), 1.98 – 1.9 (m, 2H), 1.40 – 1.33 (m, 9H), 0.96 (s, 9H), 0.12 (s, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 161.0, 151.3, 134.7, 122.6, 121.8 (q, *J* = 276.2Hz), 118.1, 108.1, 73.7, 67.8 (q, *J* = 38.0 Hz), 59.9, 59.7, 44.7, 42.2, 34.5, 26.0, 21.6, 18.3, 14.5, -5.3. **HRMS m/z (ESI)** calcd. for $C_{23}H_{39}F_3N_2NaO_8SSi^+$ (M + Na)$^+$ 611.2046, found 611.2044.

ethyl 5-(((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)methyl)-1H-pyrrole-2-carboxylate (5r)



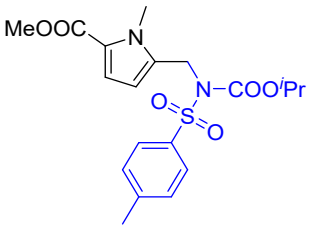
Following the general procedure A on 0.2 mmol scale with 7.5 V cell potential, the substrate **5r** was obtained as a white solid in 46% yield (38.3 mg). mp 78.7 – 79.7 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 9.36 (s, 1H), 6.87 (s, 1H), 6.33 (s, 1H), 5.18 (dd, *J* = 12.5, 6.2 Hz, 1H), 4.94 (s, 2H), 4.47 – 4.35 (m, 4H), 1.41 (dd, *J* = 12.4, 6.6 Hz, 9H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 160.7, 151.5, 130.5, 123.9, 121.6 (q, *J* = 276.0Hz), 115.1, 111.6, 74.1, 67.2 (q, *J* = 38.2Hz), 60.5, 45.0, 21.7, 14.4. **HRMS m/z (ESI)** calcd. for $C_{14}H_{19}F_3N_2NaO_7S^+$ (M + Na)$^+$ 439.0763, found 439.0761.

methyl 5-(((((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)sulfonyl)(methoxycarbonyl)amino)methyl)-1-methyl-1H-pyrrole-2-carboxylate (5s)



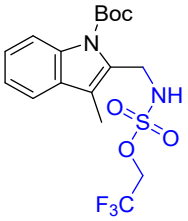
Following the general procedure A on 0.2 mmol scale with 7.5 V cell potential and $LiBF_4$ (0.1 mmol, 10 mg) as the electrolyte, the substrate **5s** was obtained as a colorless oil in 53% yield (48.3 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.97 (d, *J* = 3.5 Hz, 1H), 6.31 (d, *J* = 3.6 Hz, 1H), 5.27 (dt, *J* = 10.8, 5.3 Hz, 1H), 5.08 (s, 2H), 3.97 (d, *J* = 6.3 Hz, 6H), 3.86 (s, 3H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 161.6, 151.6, 133.2, 123.8, 119.6 (q, *J* = 278.9Hz), 117.3, 110.3, 74.0 (q, *J* = 35.4Hz), 55.4, 51.2, 44.8, 32.7. **HRMS m/z (ESI)** calcd. for $C_{13}H_{14}F_6N_2NaO_7S^+$ (M + Na)$^+$ 479.0324, found 479.0317.

methyl 5-(((N-(isopropoxycarbonyl)-4-methylphenyl)sulfonamido)methyl)-1-methyl-1H-pyrrole-2-carboxylate (5t)



Following the general procedure **A** on 0.2 mmol scale with 7.5 V cell potential, the substrate **5t** was obtained as a colorless oil in 40% yield (32.6 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.60 (d, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 7.7 Hz, 2H), 6.97 (d, *J* = 3.1 Hz, 1H), 6.22 (d, *J* = 3.2 Hz, 1H), 5.12 (s, 2H), 4.97 (dt, *J* = 12.4, 6.2 Hz, 1H), 3.98 (s, 3H), 3.87 (s, 3H), 2.46 (s, 3H), 1.19 (d, *J* = 6.0 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ161.9, 151.9, 144.7, 136.6, 135.6, 129.2, 128.5, 122.8, 117.4, 110.0, 72.4, 51.1, 41.7, 32.7, 21.7, 21.6. **HRMS m/z (ESI)** calcd. for $C_{19}H_{24}N_2NaO_6S^+$ (M + Na)$^+$ 431.1253, found 431.1260.

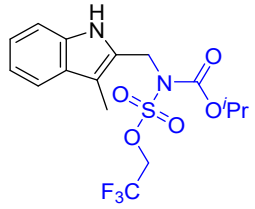
tert-butyl 3-methyl-2-((((2,2,2-trifluoroethoxy)sulfonyl)amino)methyl)-1H-indole-1-carboxylate (6)



A colorless oil, **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.00 (d, *J* = 8.2 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.36 (dt, *J* = 23.4, 7.0 Hz, 2H), 6.25 (t, *J* = 5.9 Hz, 1H), 4.65 (d, *J* = 6.4 Hz, 2H), 4.32 (q, *J* = 7.9 Hz, 2H), 2.38 (s, 3H), 1.78 (s, 9H). **^{13}C**

NMR (100 MHz, Chloroform-*d*) δ 150.9, 134.4, 129.4(0), 129.4(8), 124.5, 122.3, 121.3 (q, *J* = 276.2 Hz), 118.6, 118.1, 114.8, 84.5, 64.1 (q, *J* = 37.5 Hz), 38.6, 27.6, 7.8.**HRMS m/z (ESI)** calcd. for $C_{17}H_{21}F_3N_2NaO_5S^+$ $(M + Na)^+$ 445.1021, found 445.1024.

2,2,2-trifluoroethyl (isopropoxycarbonyl)((3-methyl-1H-indol-2-yl)methyl)sulfamate (7)



A colorless oil, **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.53 (s, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 5.28 – 5.09 (m, 3H), 4.42 (q, *J* = 7.8 Hz, 2H), 2.42 (s, 3H), 1.43 (d, *J* = 6.2 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 141.6, 128.7, 122.5, 122.5, 118.5, 117.3 (q, *J* = 221.1 Hz), 115.6, 115.5, 109.3, 108.9, 79.3, 73.7 (q, *J* = 30.4 Hz), 55.3, 37.4, 26.9. **HRMS m/z (ESI)** calcd. for $C_{16}H_{19}F_3N_2NaO_5S^+$ $(M + Na)^+$ 431.0864, found 431.0853.

14. NMR spectra

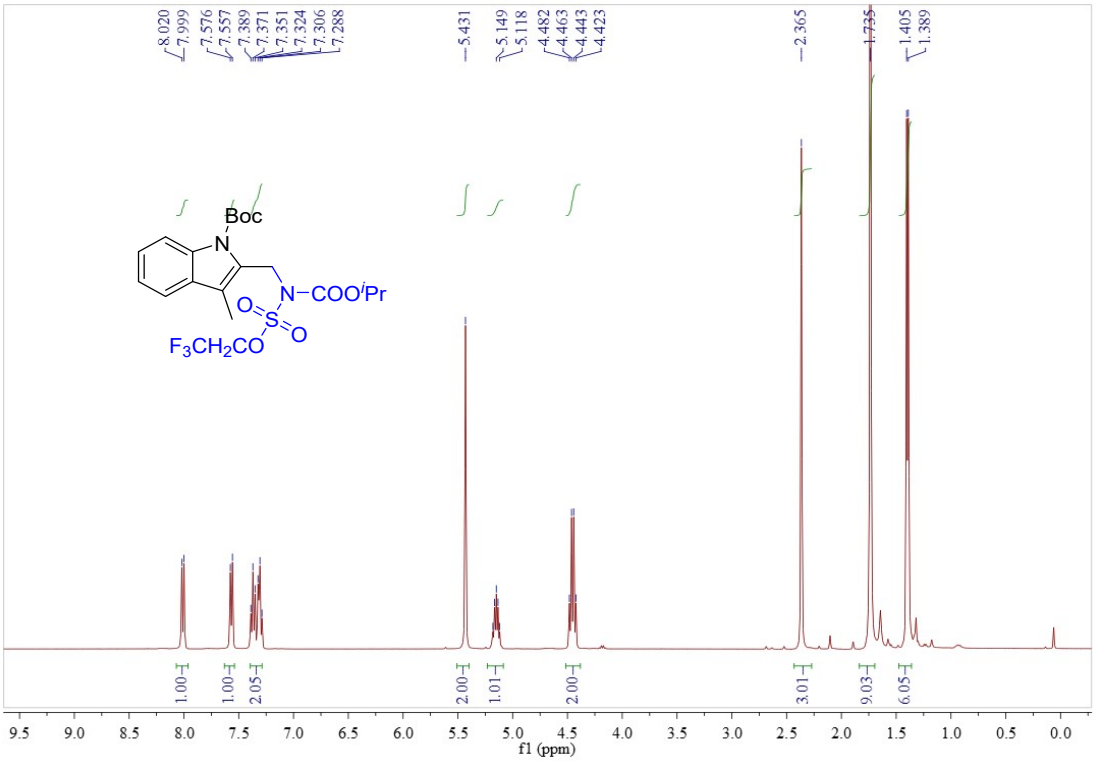


Figure S23. ^{1}H NMR of **3a** (400 MHz, $CDCl_3$)

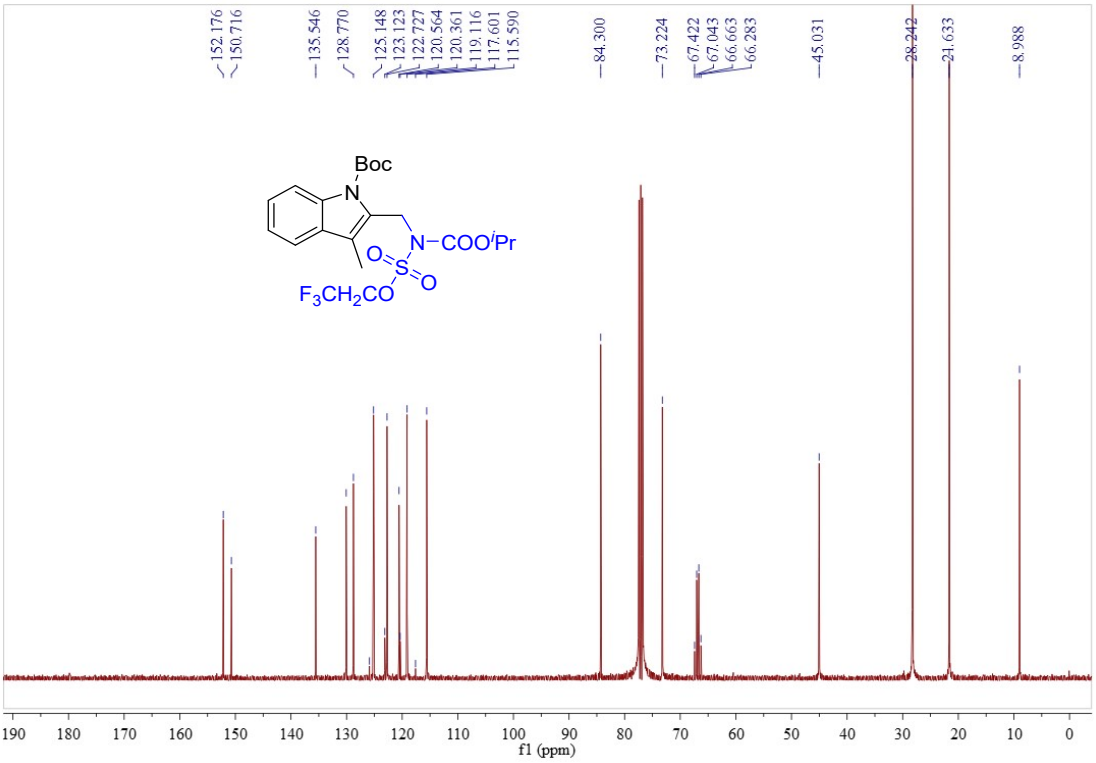


Figure S24. ^{13}C NMR of **3a** (100 MHz, $CDCl_3$)

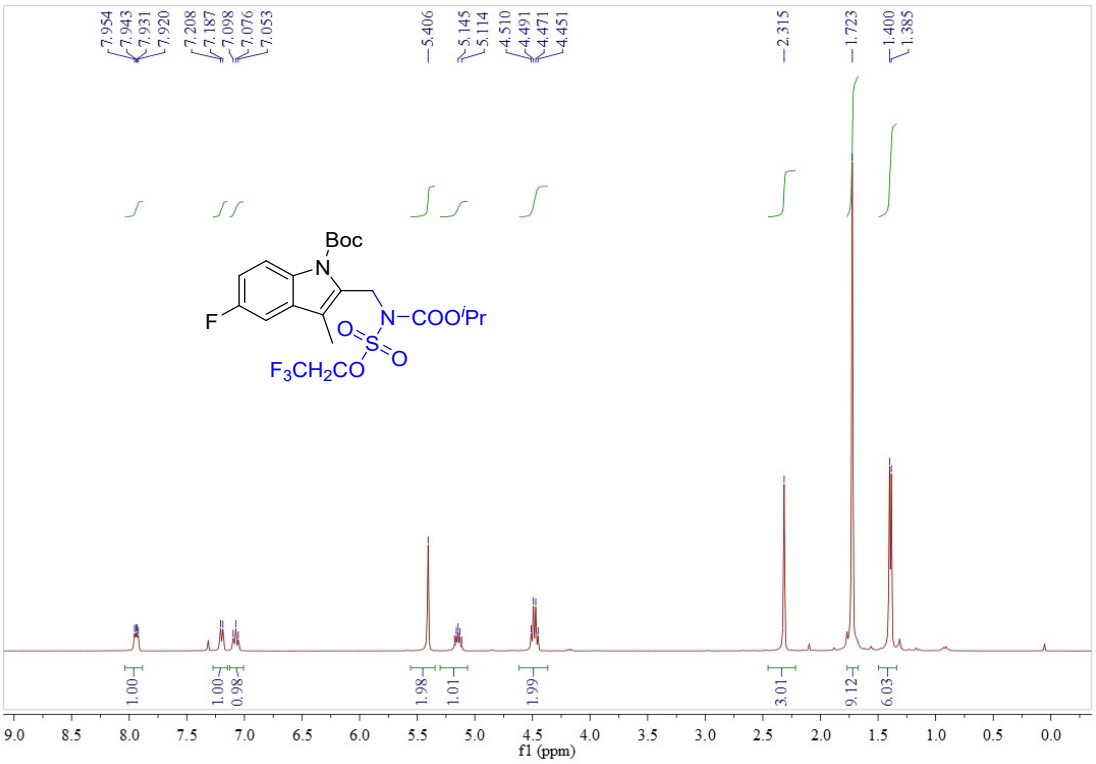


Figure S25. ^{1}H NMR of **3c** (400 MHz, $CDCl_3$)

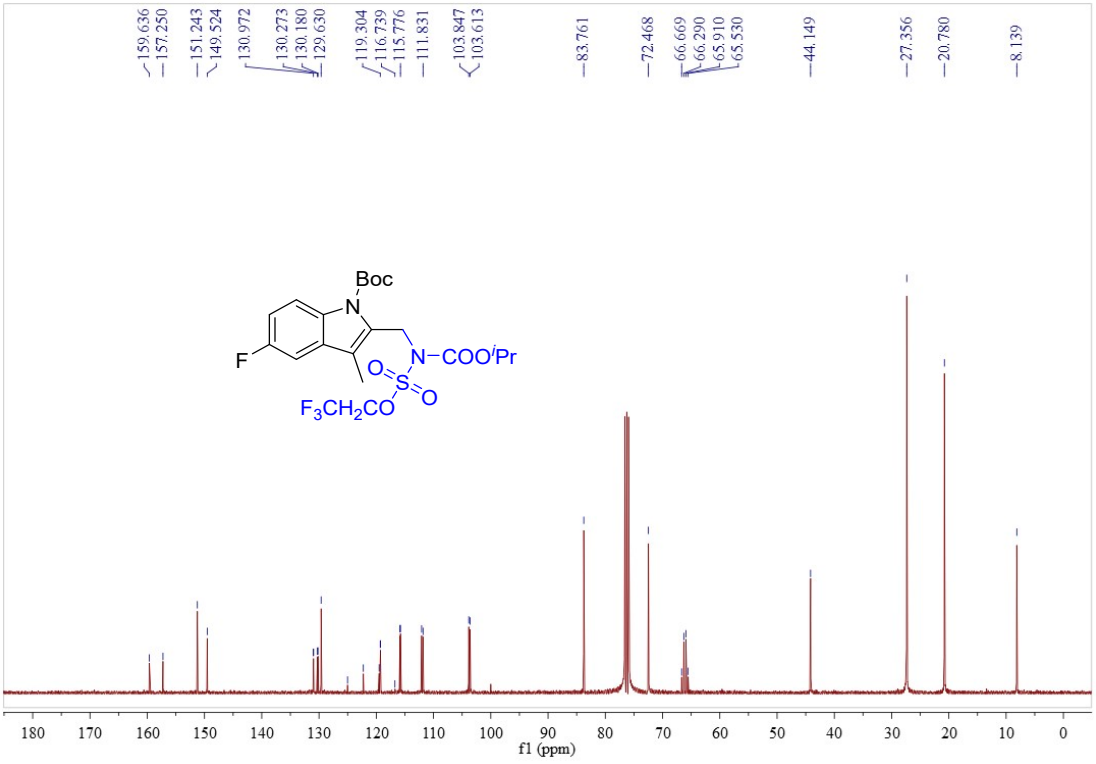


Figure S26. ^{13}C NMR of **3c** (100 MHz, $CDCl_3$)

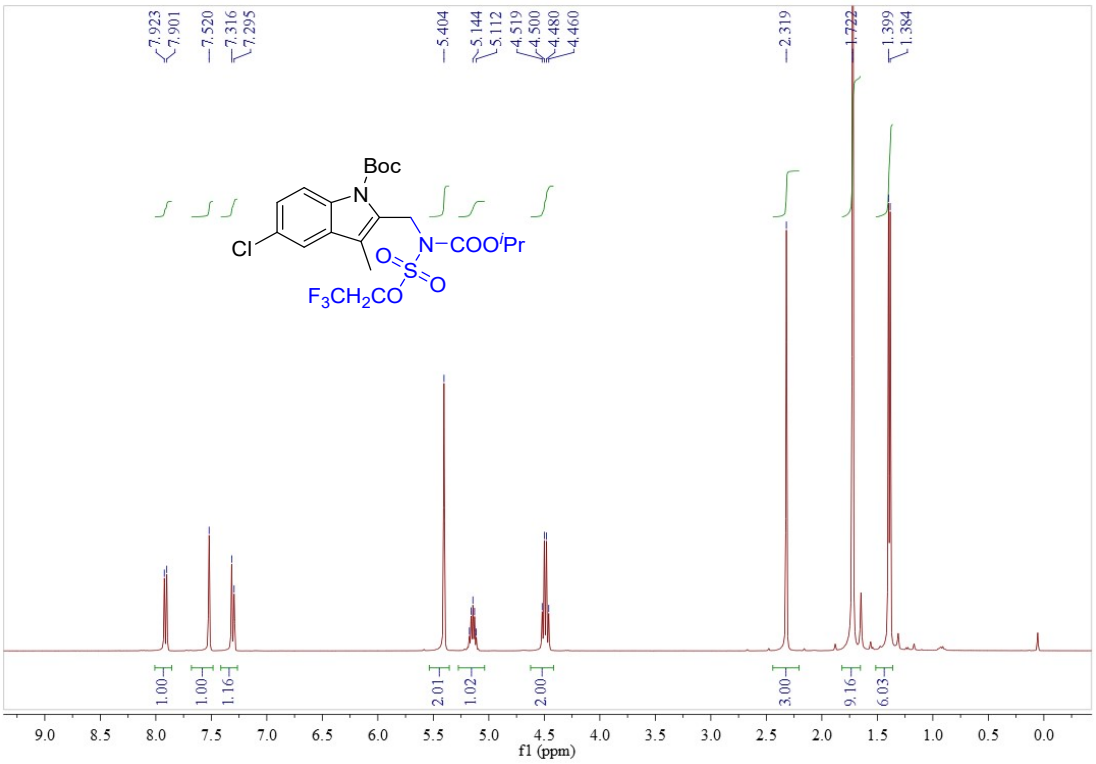


Figure S27. ^{1}H NMR of **3d** (400 MHz, $CDCl_3$)

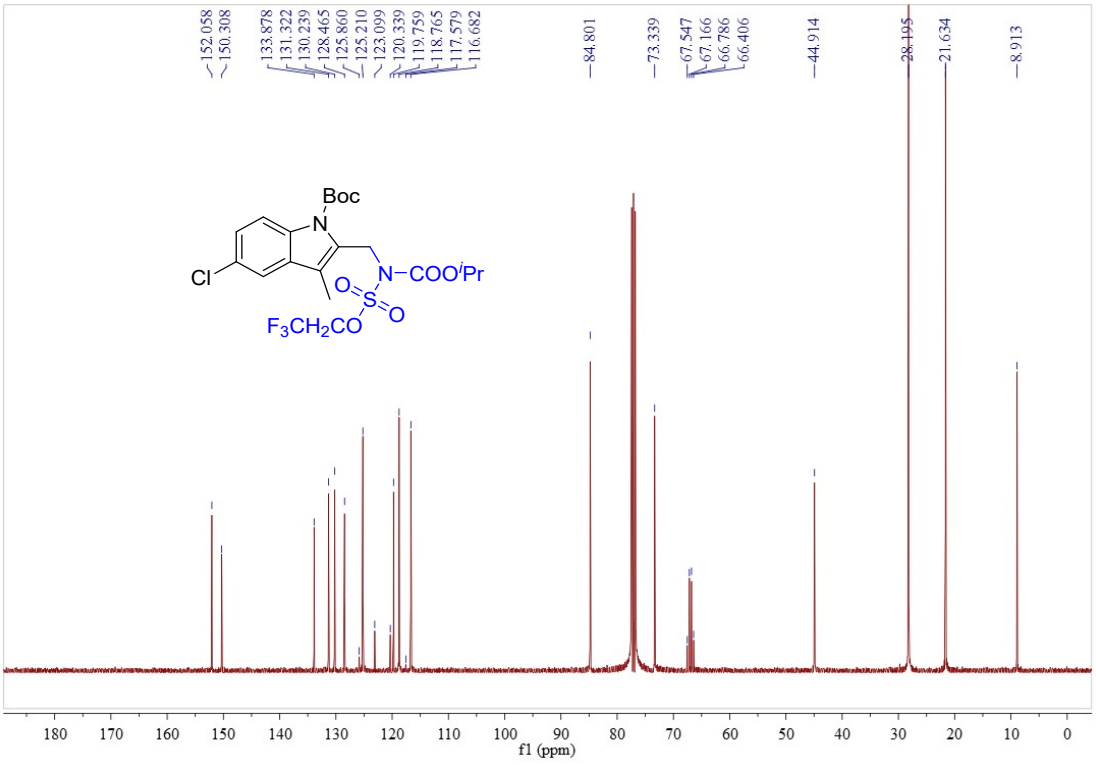


Figure S28. ^{13}C NMR of **3d** (100 MHz, $CDCl_3$)

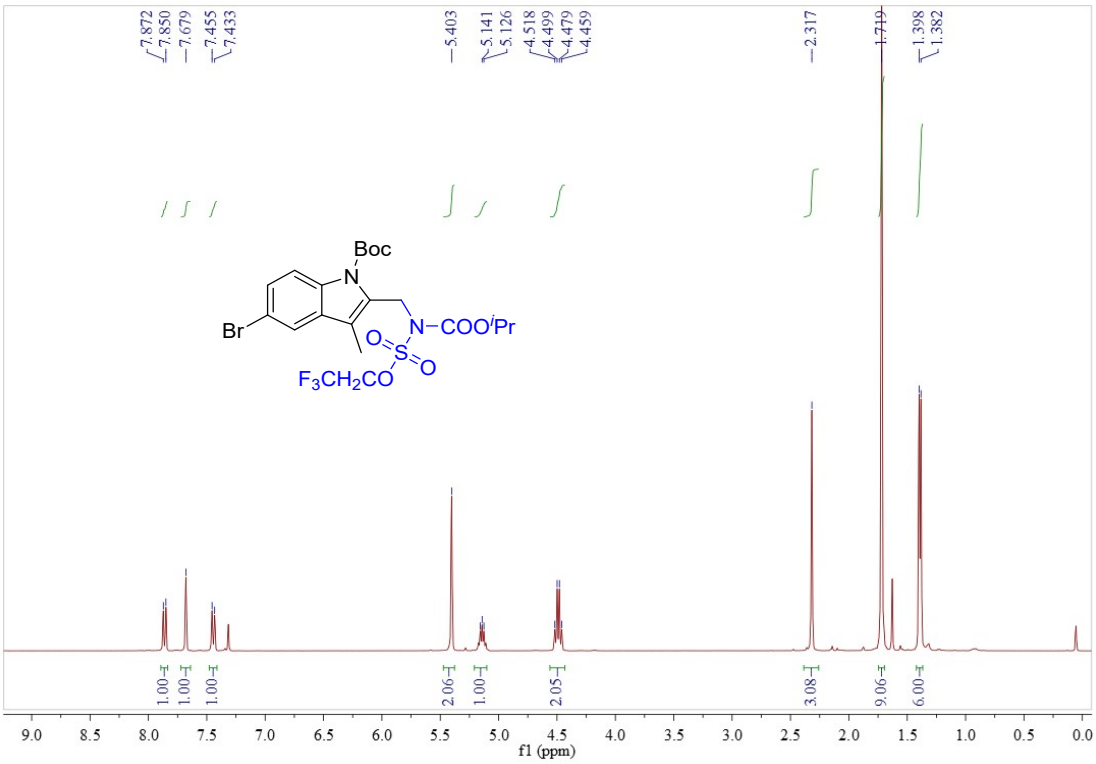


Figure S29. ^{1}H NMR of **3e** (400 MHz, $CDCl_3$)

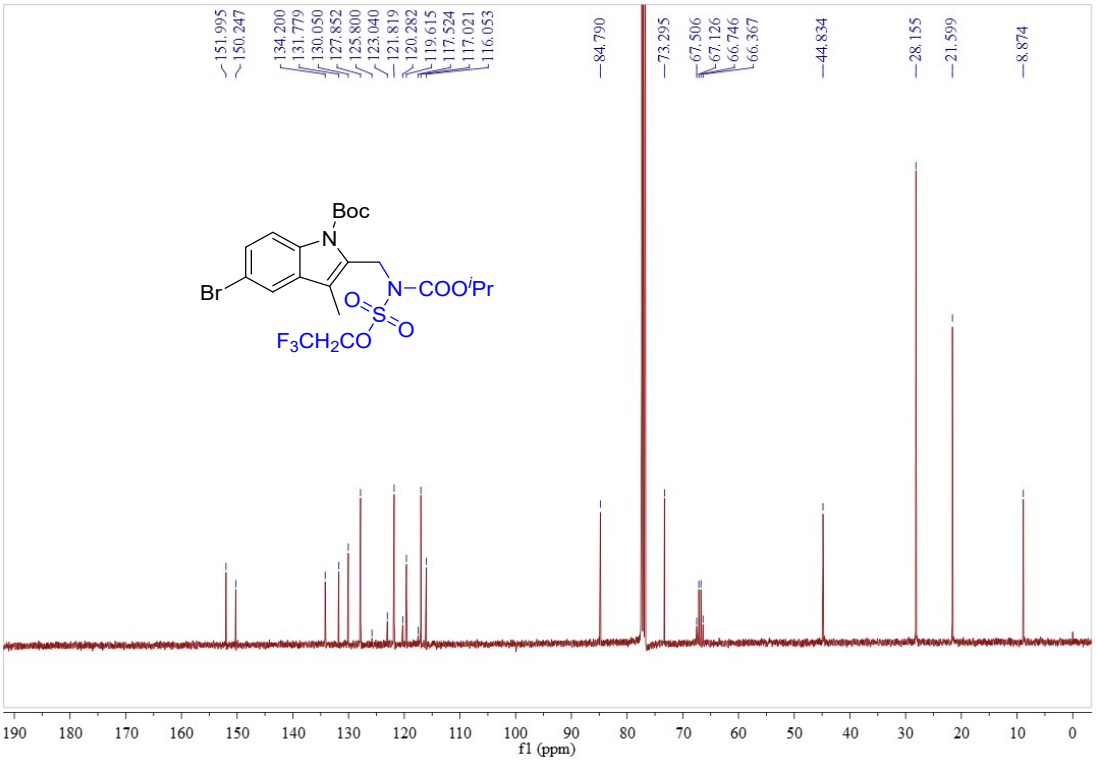


Figure S30. ^{13}C NMR of **3e** (100 MHz, $CDCl_3$)

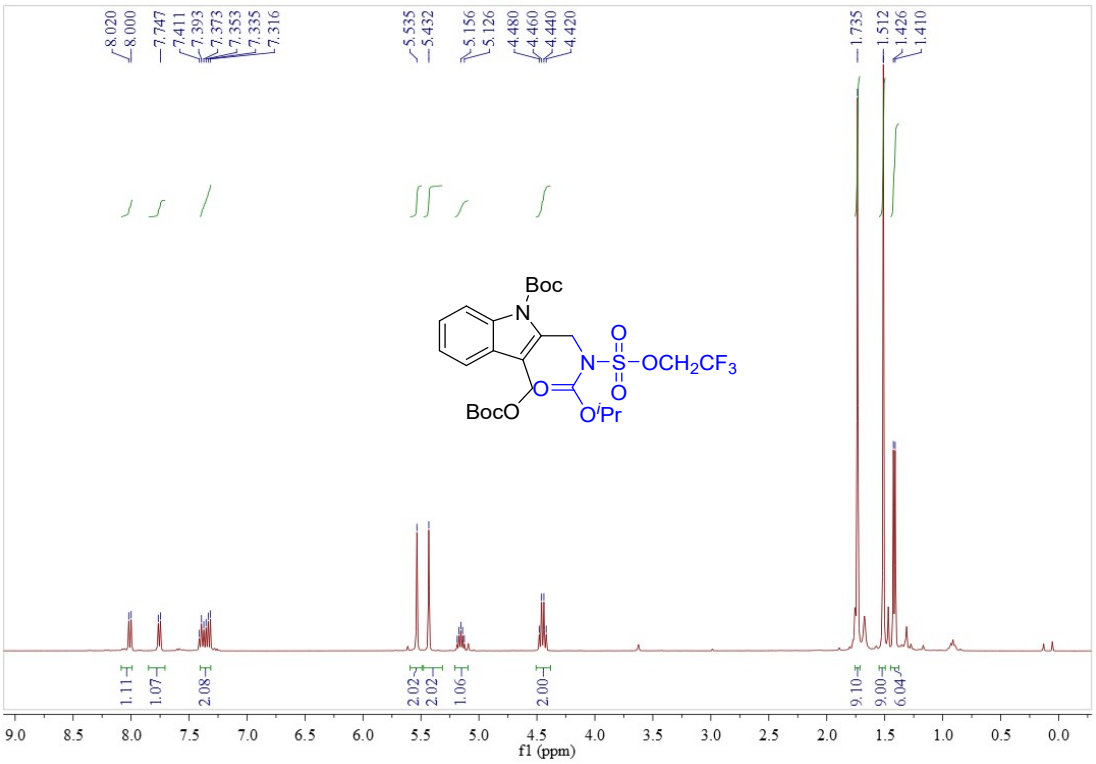


Figure S31. ^{1}H NMR of **3f** (400 MHz, $CDCl_3$)

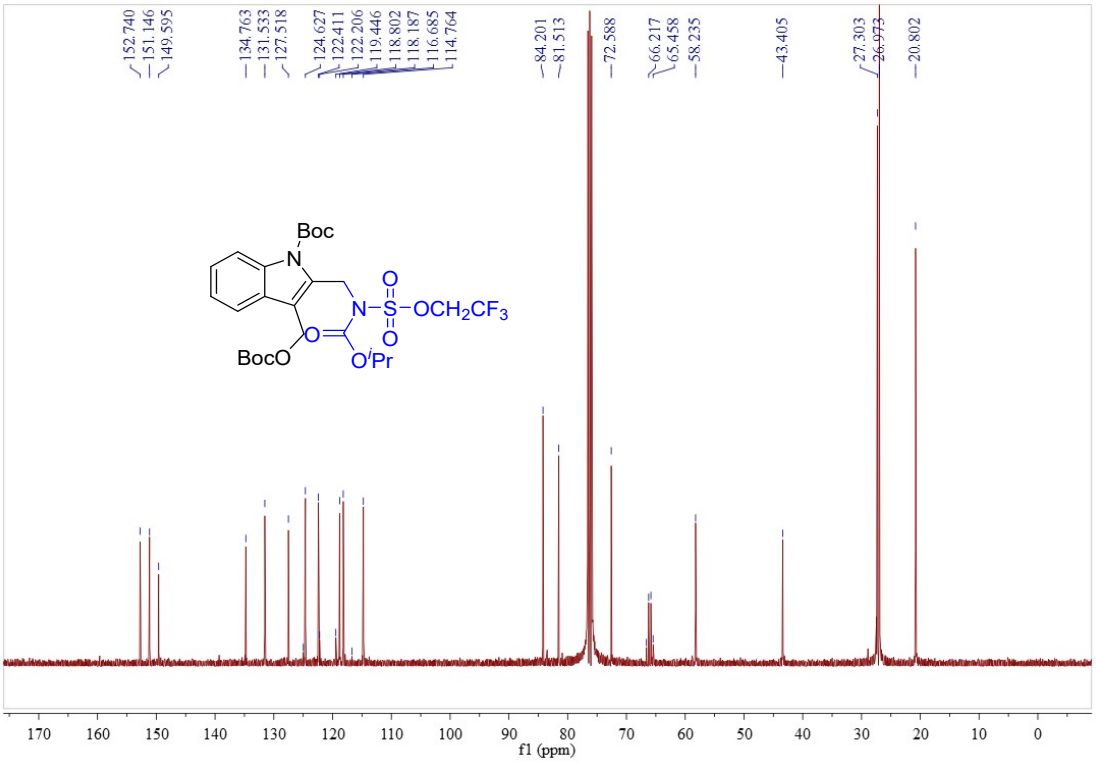


Figure S32. ^{13}C NMR of **3f** (100 MHz, $CDCl_3$)

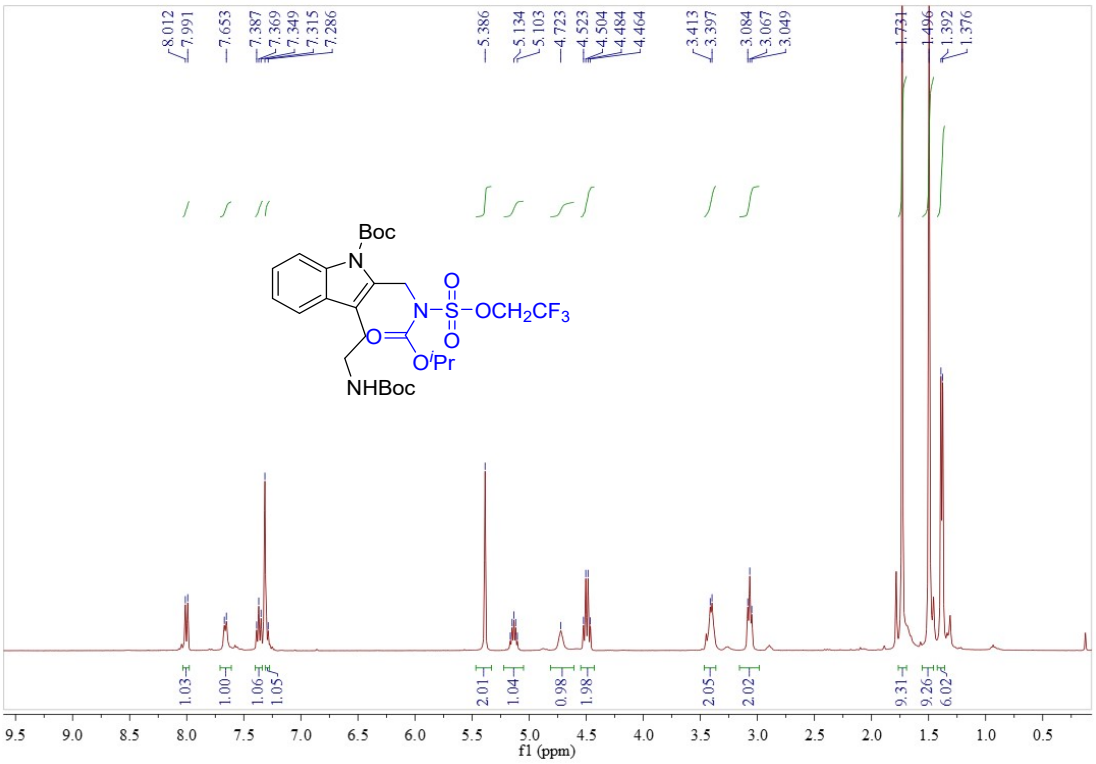


Figure S33. ^{1}H NMR of **3g** (400 MHz, $CDCl_3$)

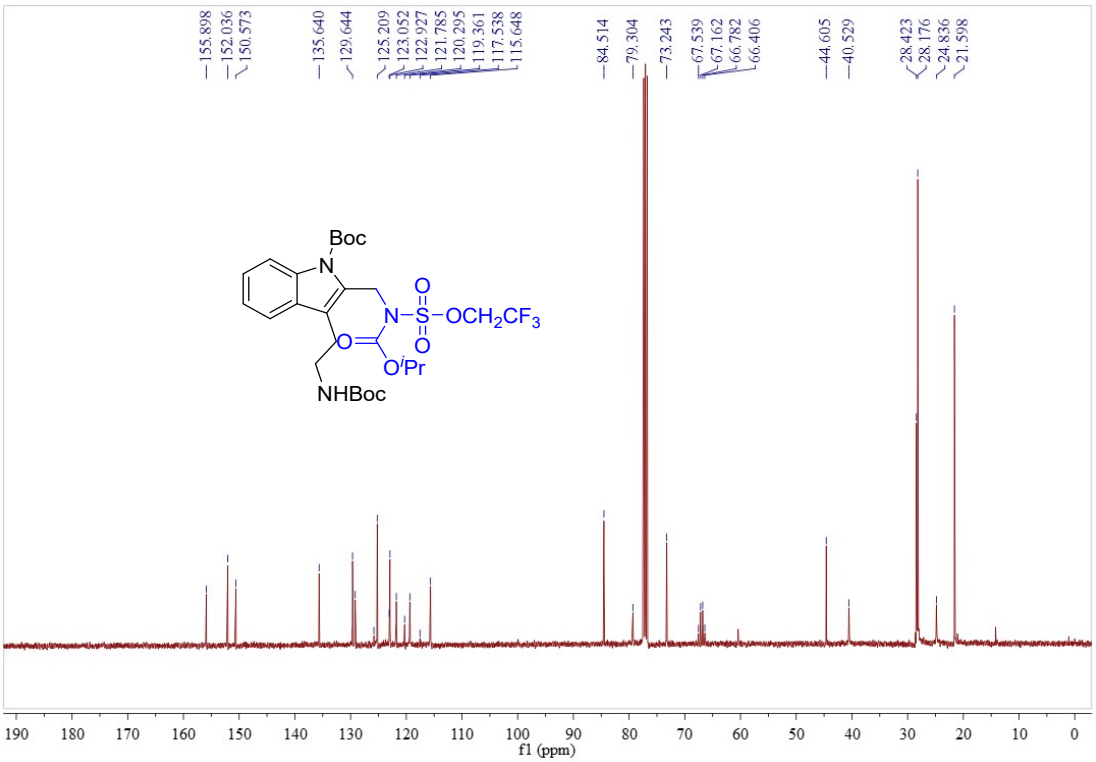


Figure S34. ^{13}C NMR of **3g** (100 MHz, $CDCl_3$)

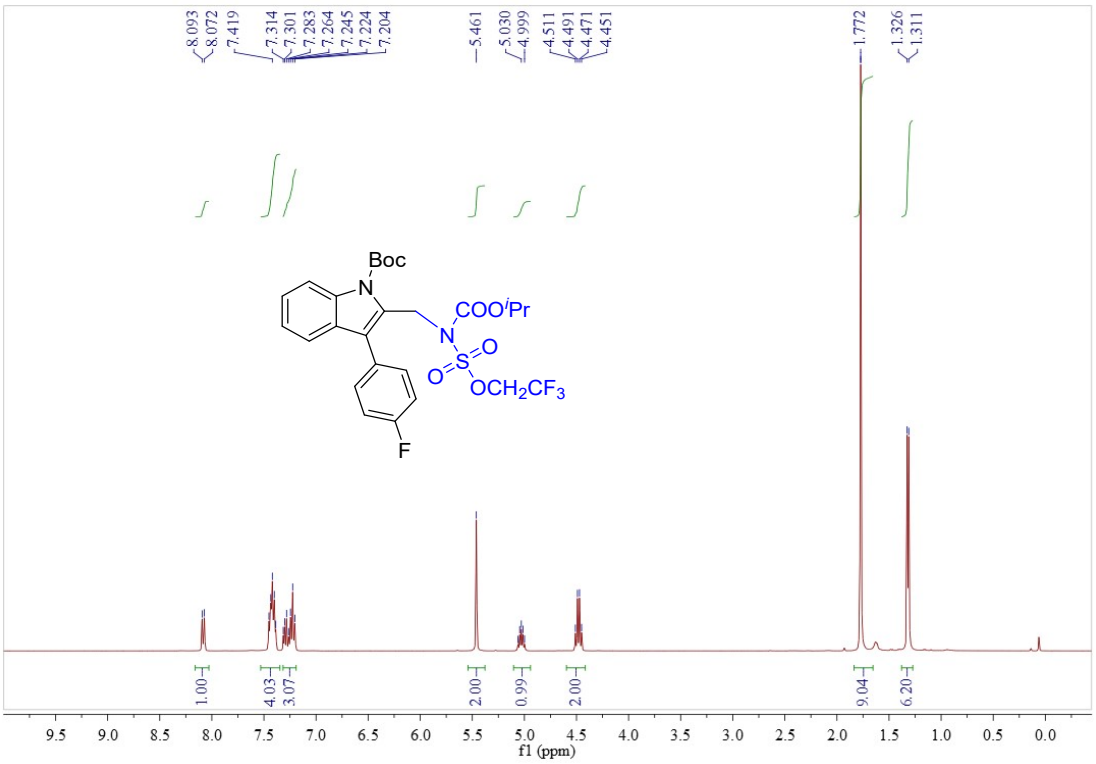


Figure S35. ^{1}H NMR of **3h** (400 MHz, $CDCl_3$)

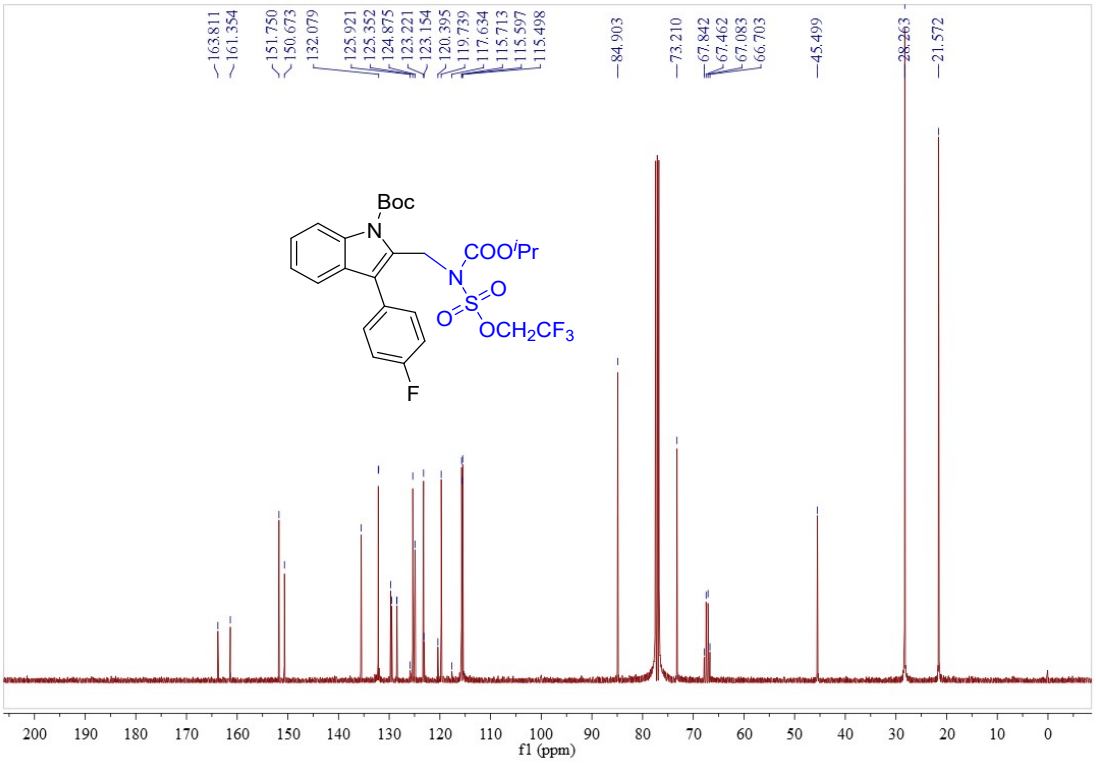


Figure S36. ^{13}C NMR of **3h** (100 MHz, $CDCl_3$)

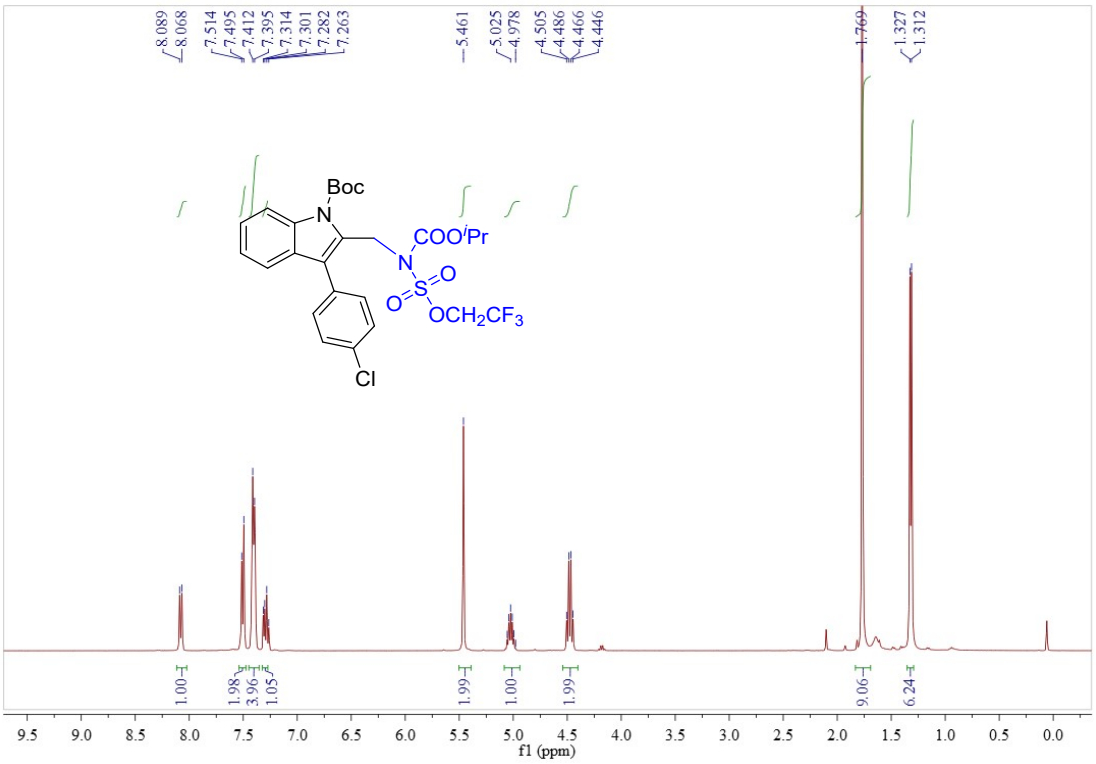


Figure S37. ^{1}H NMR of **3i** (400 MHz, $CDCl_3$)

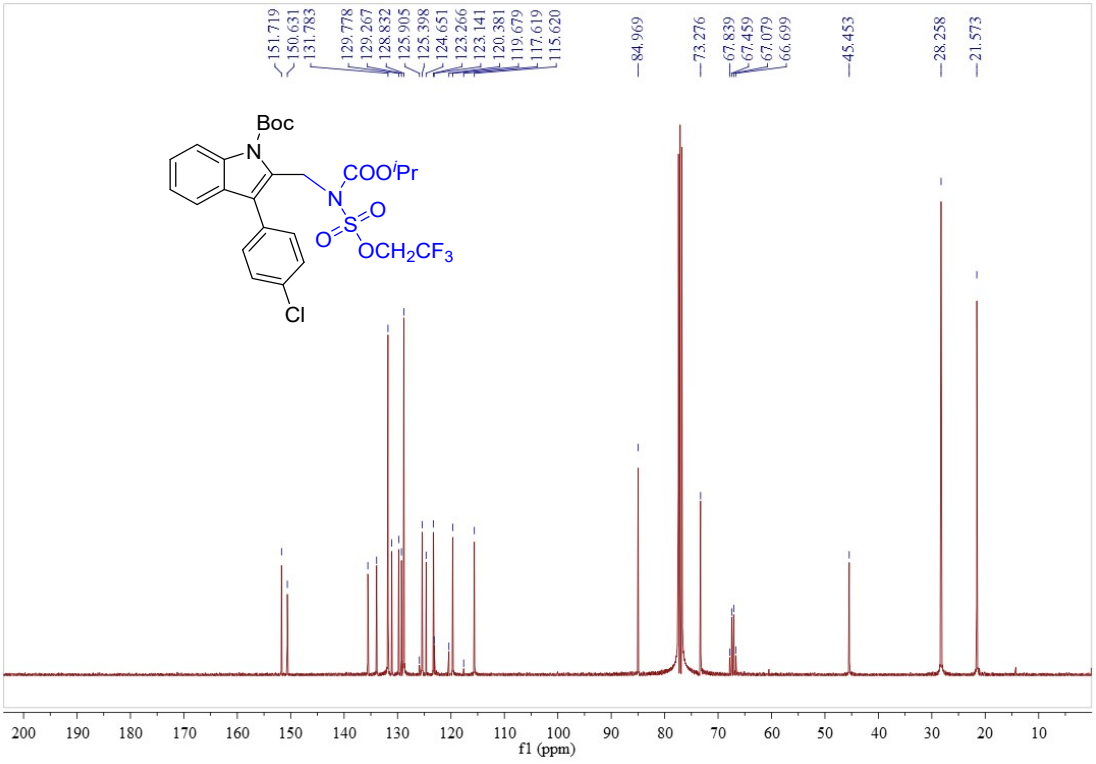


Figure S38. ^{13}C NMR of **3i** (100 MHz, $CDCl_3$)

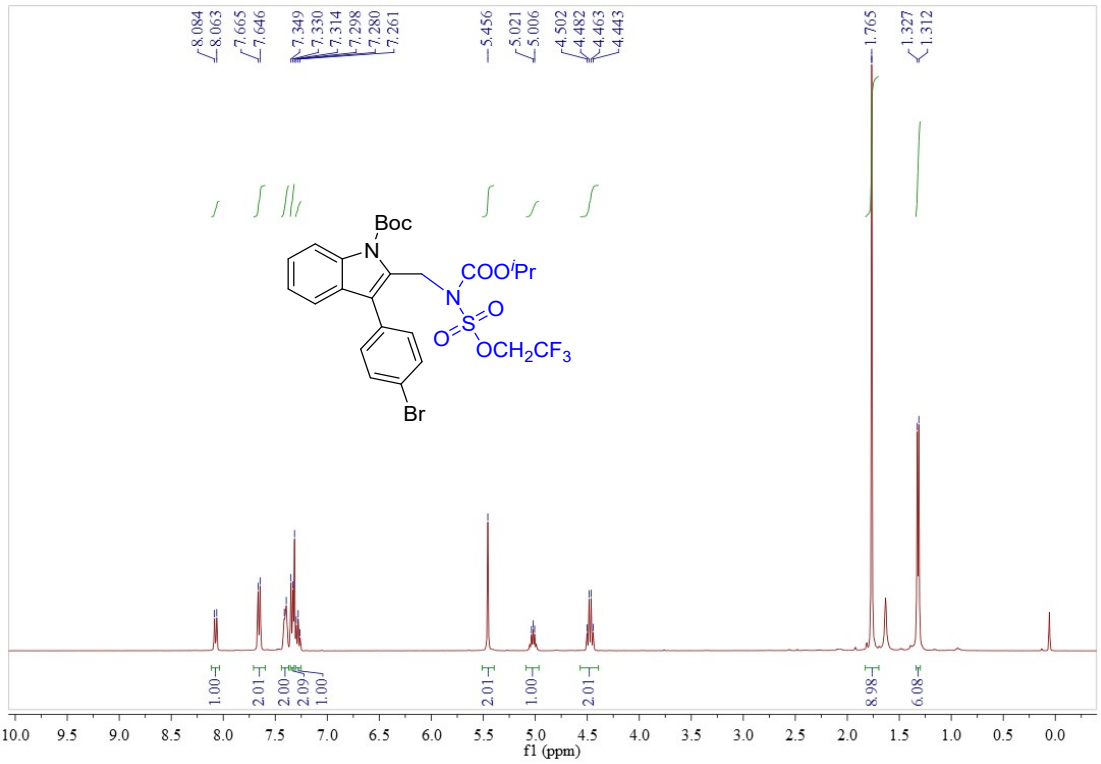


Figure S39. ^{1}H NMR of **3j** (400 MHz, $CDCl_3$)

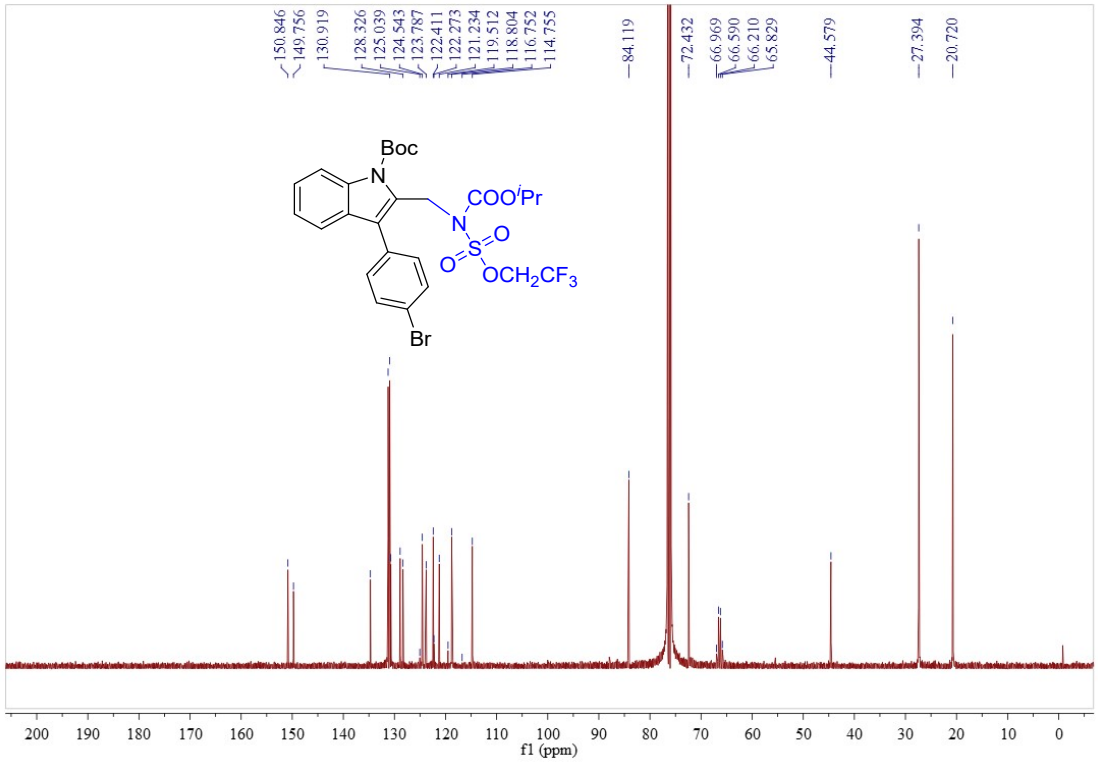


Figure S40. ^{13}C NMR of **3j** (100 MHz, $CDCl_3$)

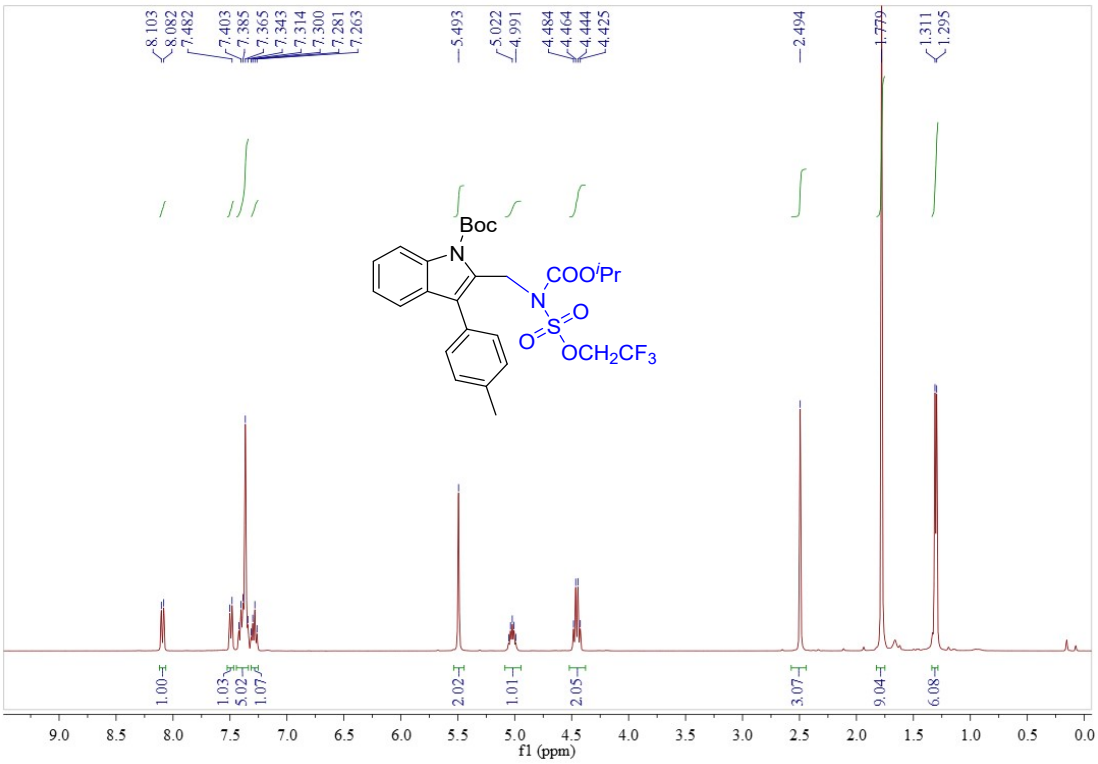


Figure S41. ^{1}H NMR of **3k** (400 MHz, $CDCl_3$)

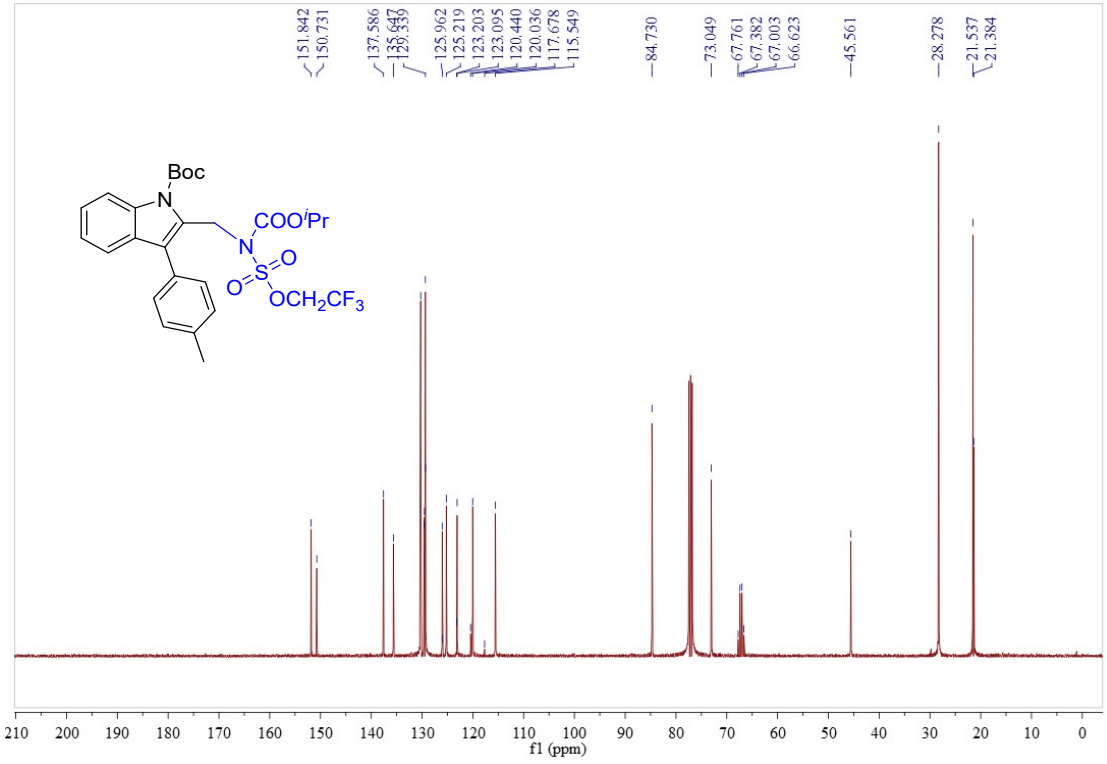


Figure S42. ^{13}C NMR of **3k** (100 MHz, $CDCl_3$)

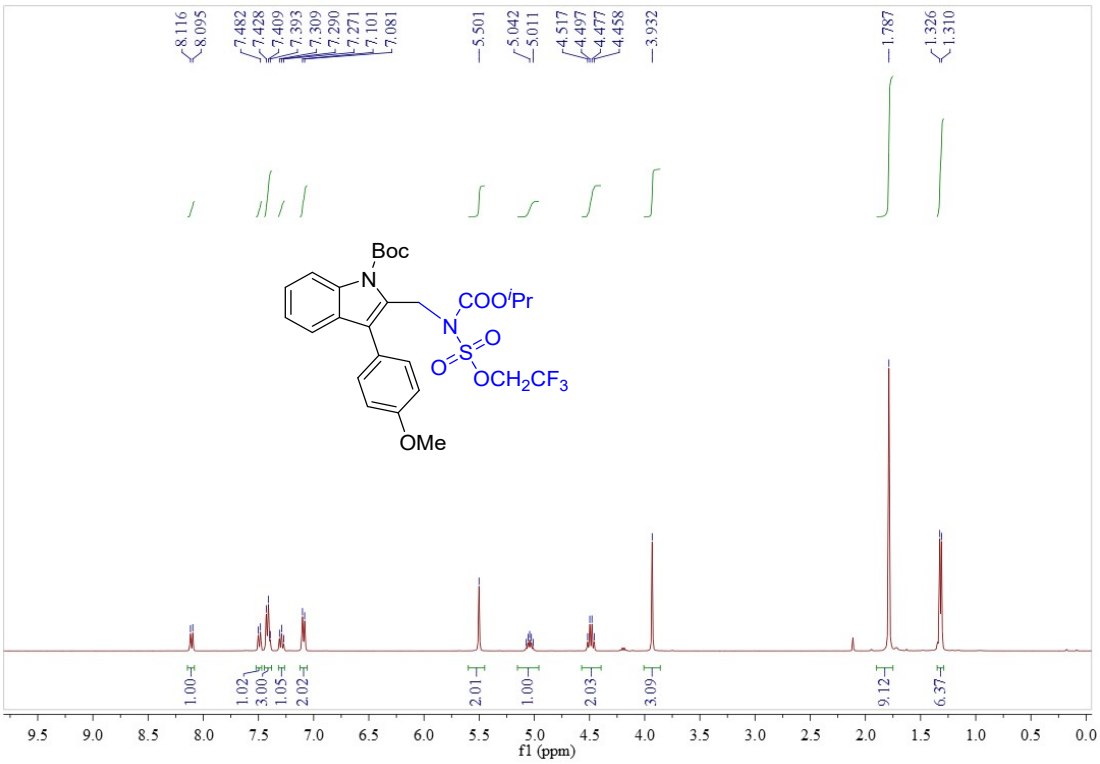


Figure S43. ^{1}H NMR of **3l** (400 MHz, $CDCl_3$)

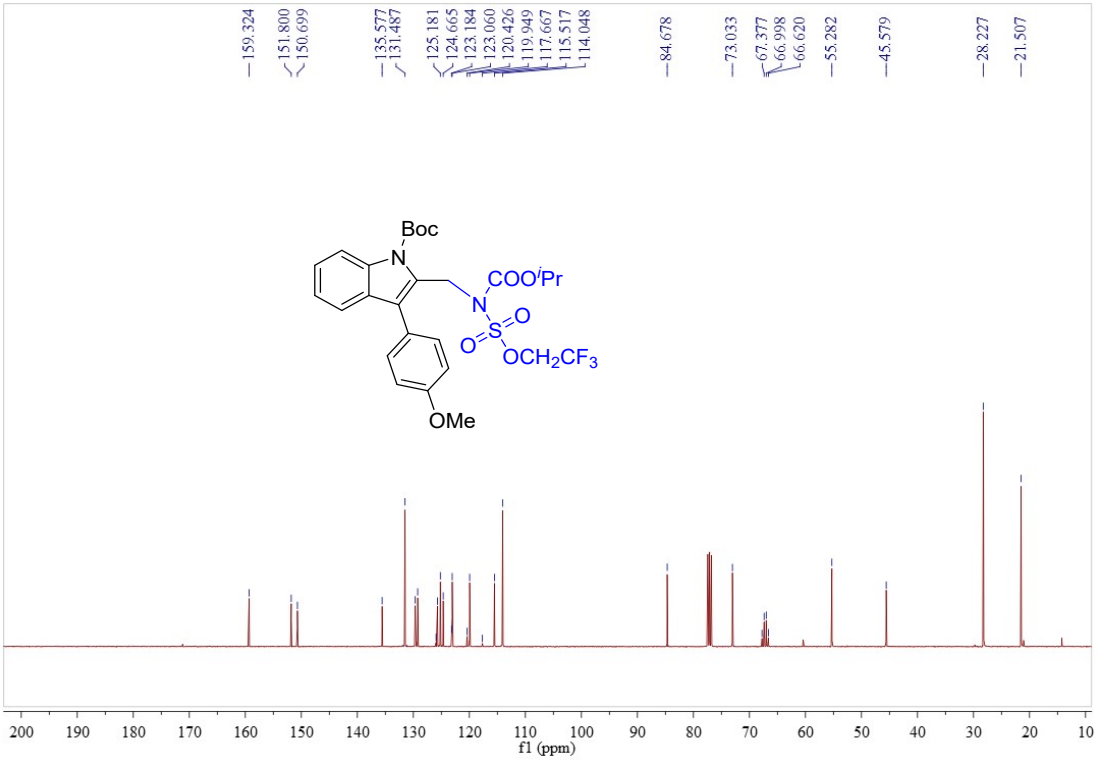


Figure S44. ^{13}C NMR of **3l** (100 MHz, $CDCl_3$)

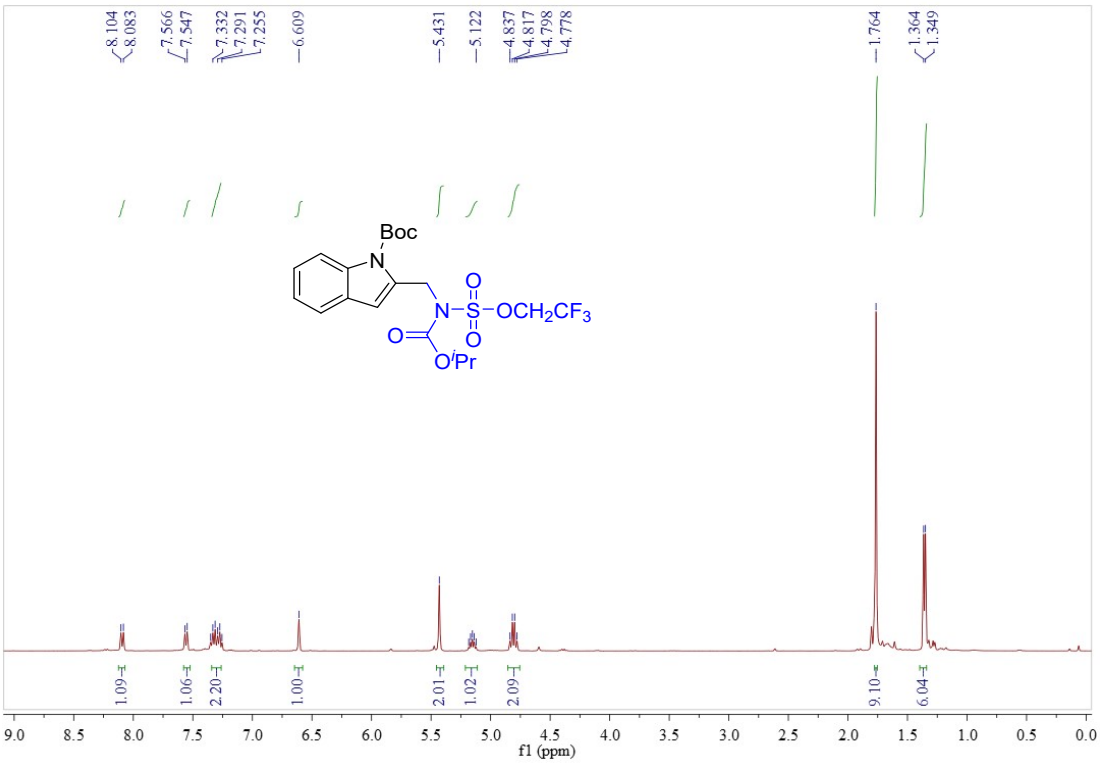


Figure S45. ^{1}H NMR of **3m** (400 MHz, $CDCl_3$)

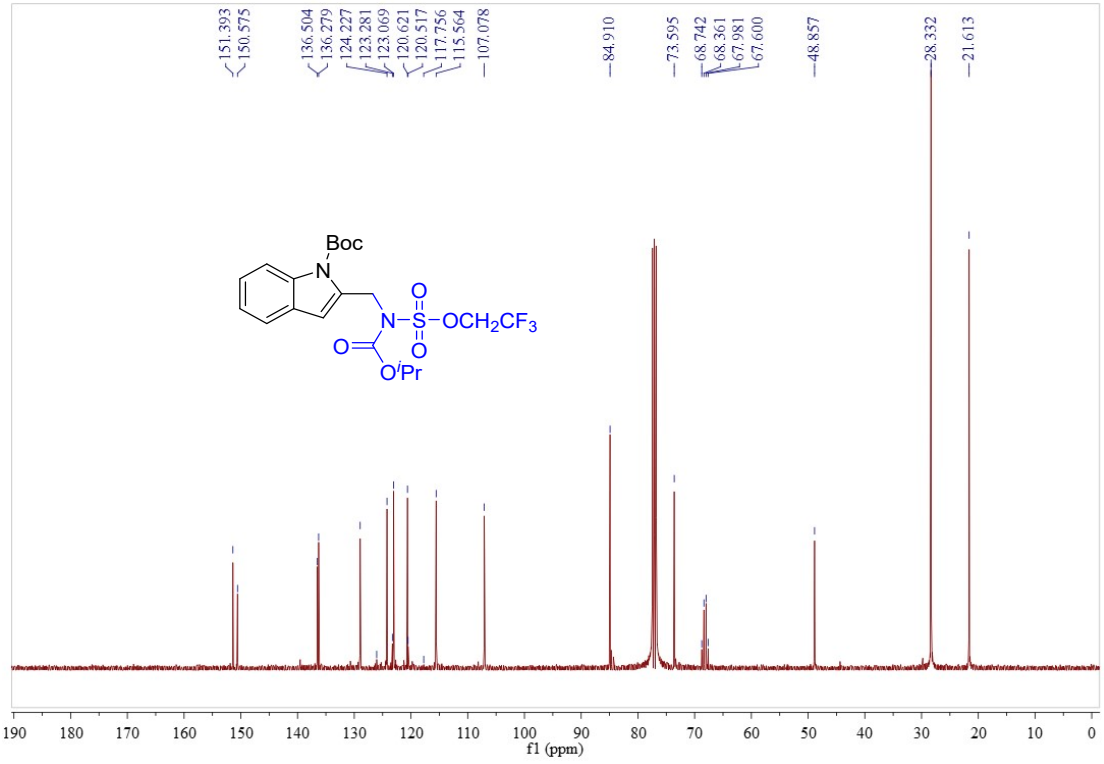


Figure S46. ^{13}C NMR of **3m** (100 MHz, $CDCl_3$)

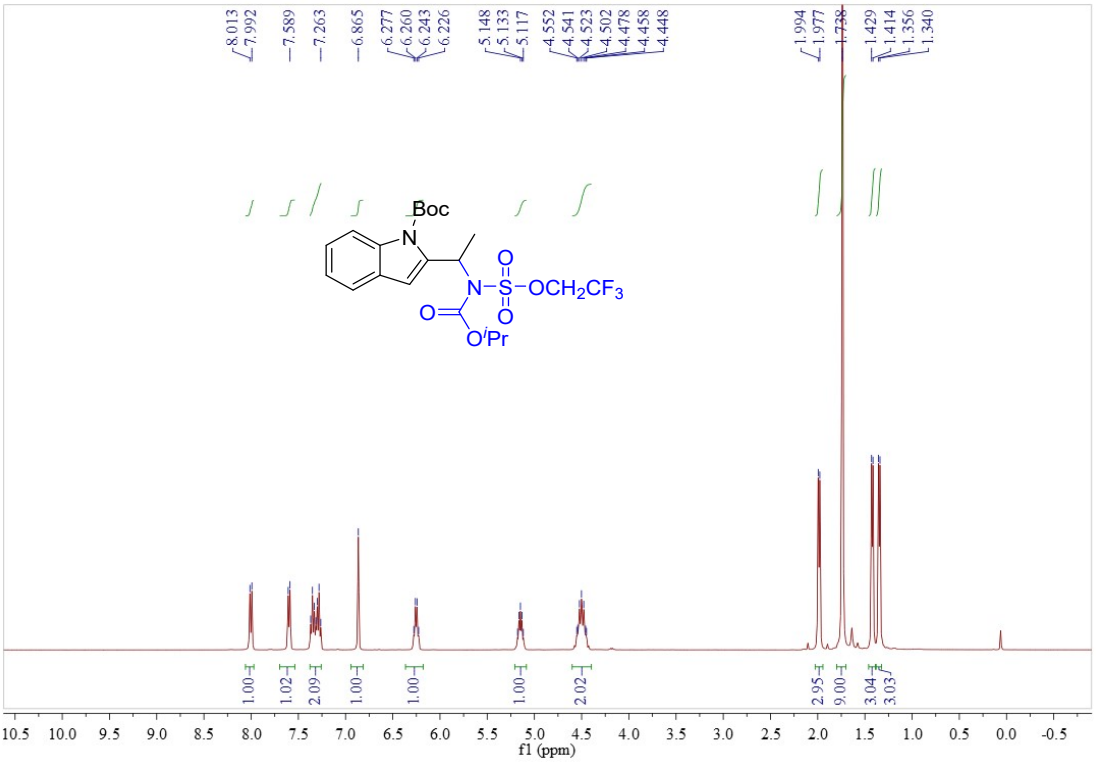


Figure S47. ^{1}H NMR of **3n** (400 MHz, $CDCl_3$)

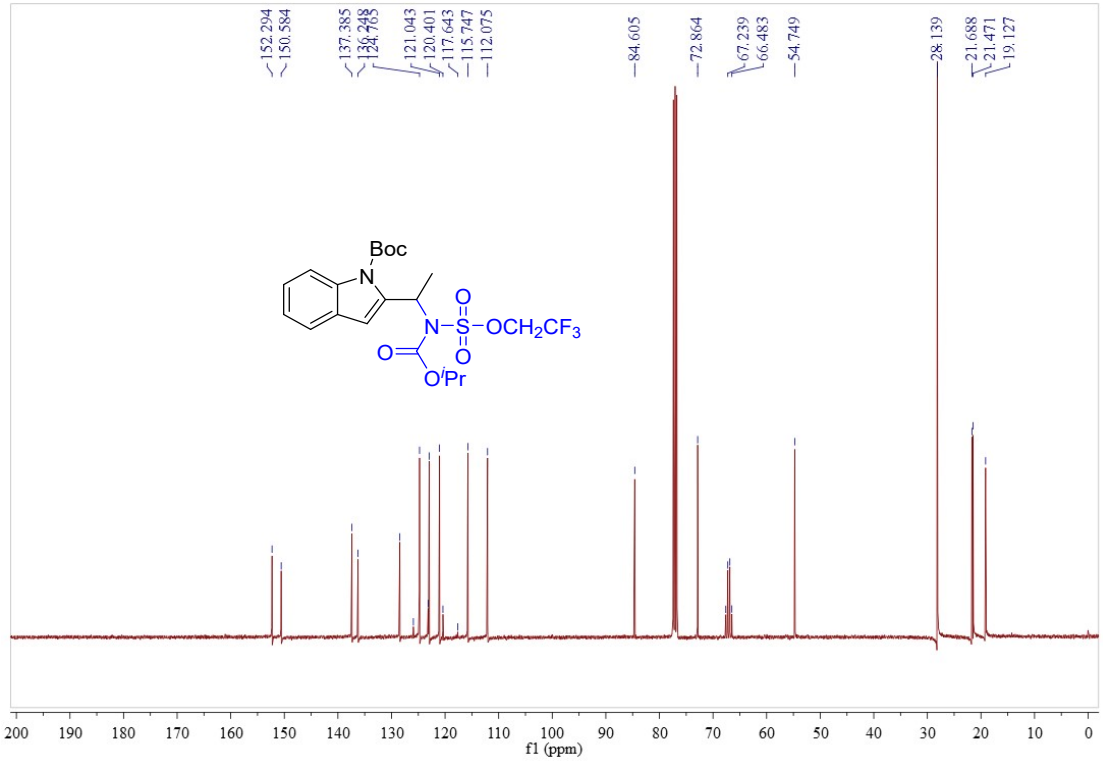


Figure S48. ^{13}C NMR of **3n** (100 MHz, $CDCl_3$)

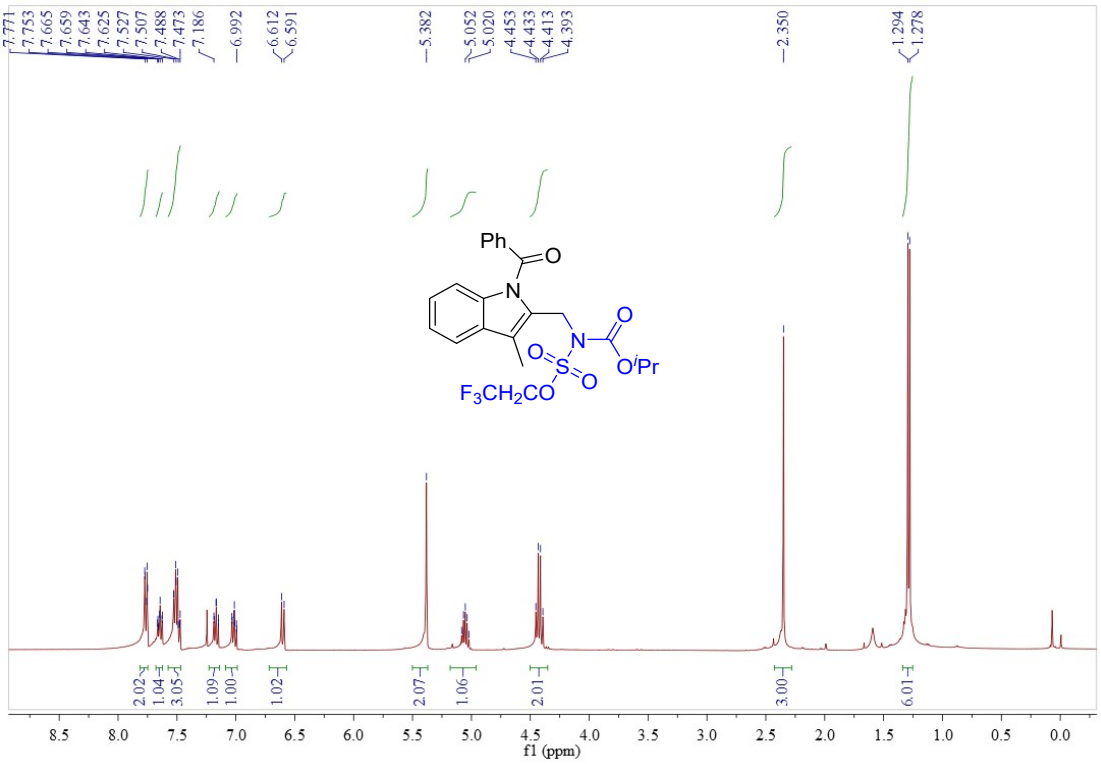


Figure S49. ^{1}H NMR of **3p** (400 MHz, $CDCl_3$)

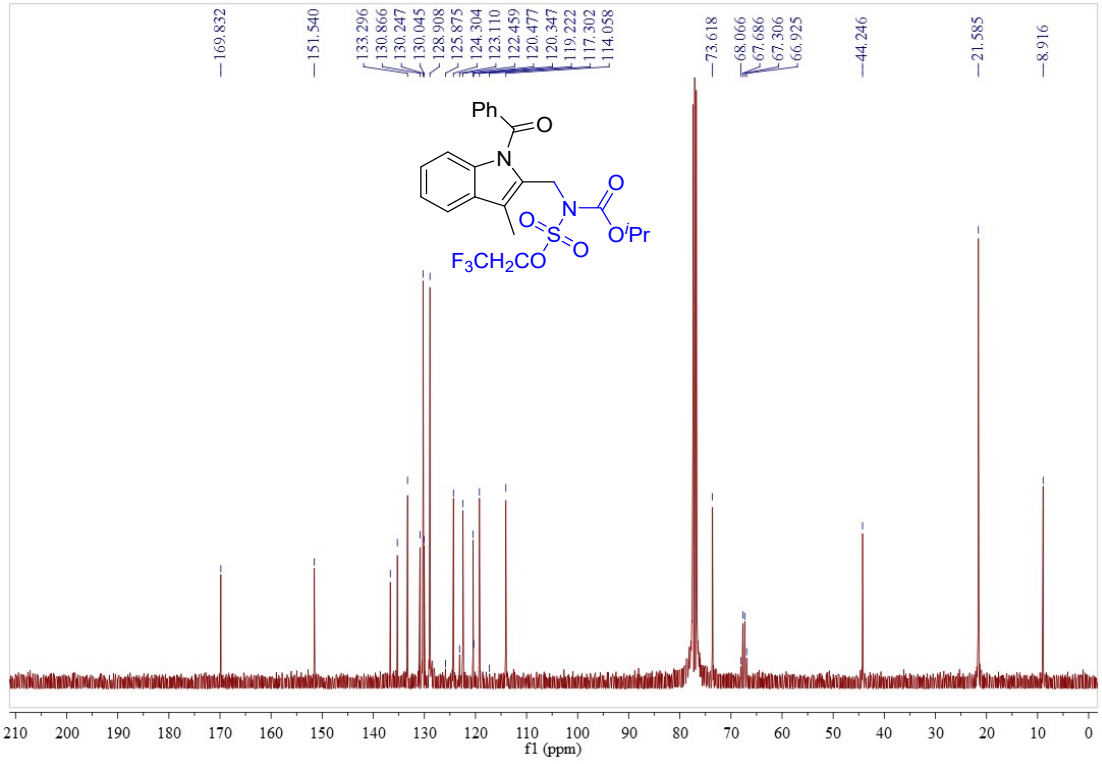


Figure S50. ^{13}C NMR of **3p** (100 MHz, $CDCl_3$)

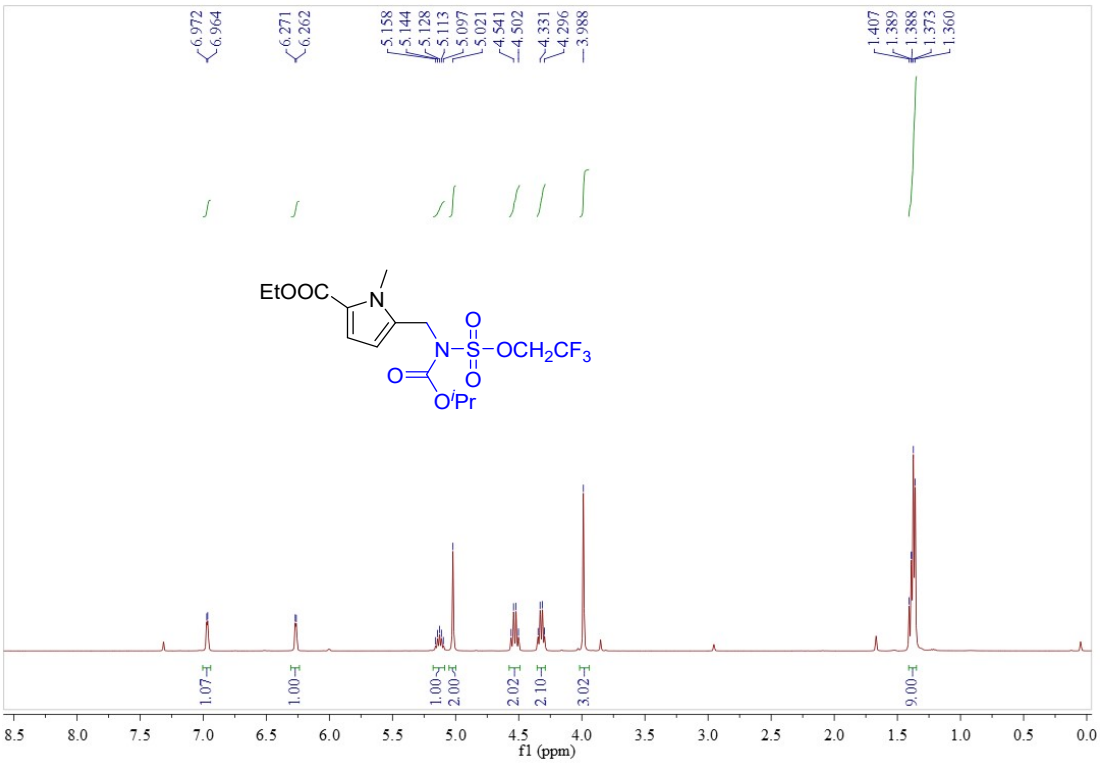


Figure S51. ^{1}H NMR of **5a** (400 MHz, $CDCl_3$)

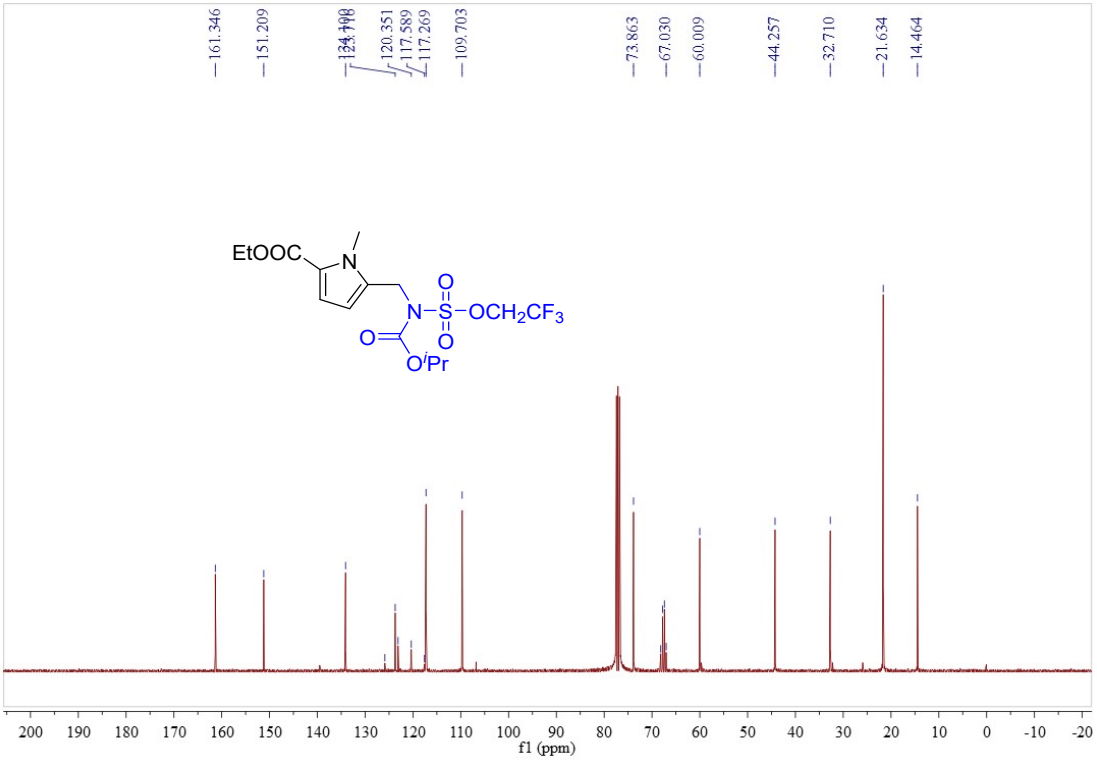


Figure S52. ^{13}C NMR of **5a** (100 MHz, $CDCl_3$)

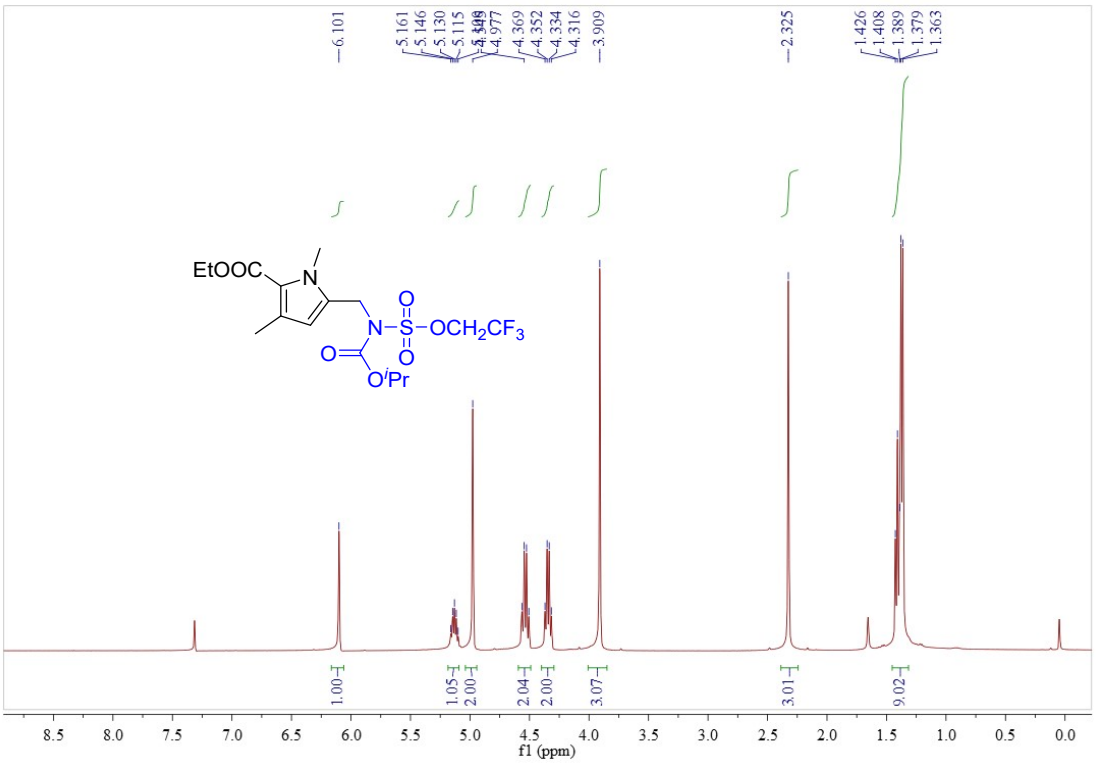


Figure S53. ^{1}H NMR of **5b** (400 MHz, $CDCl_3$)

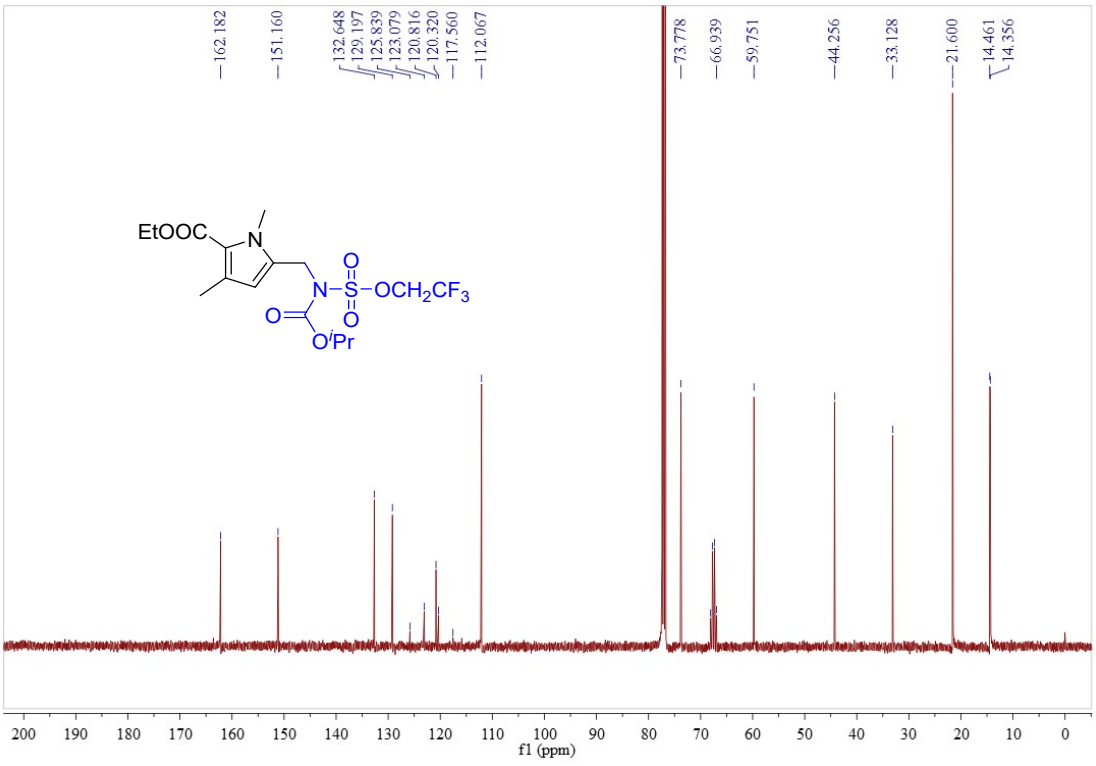


Figure S54. ^{13}C NMR of **5b** (100 MHz, $CDCl_3$)

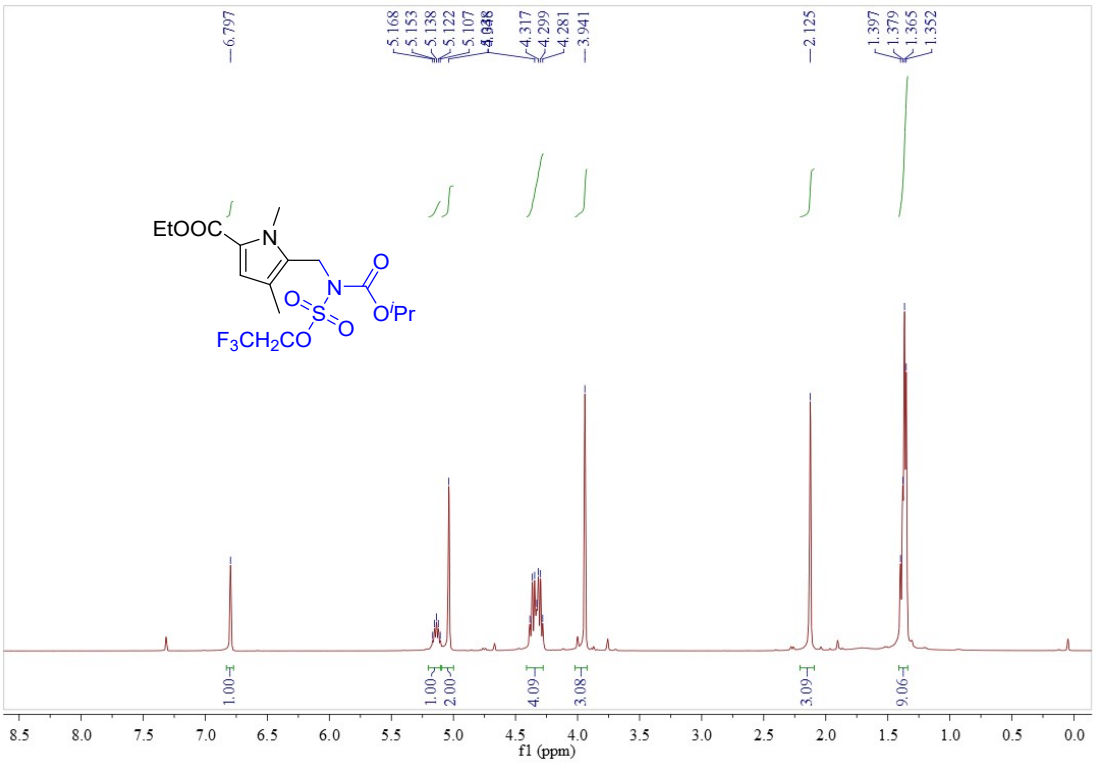


Figure S55. ^{1}H NMR of **5c** (400 MHz, $CDCl_3$)

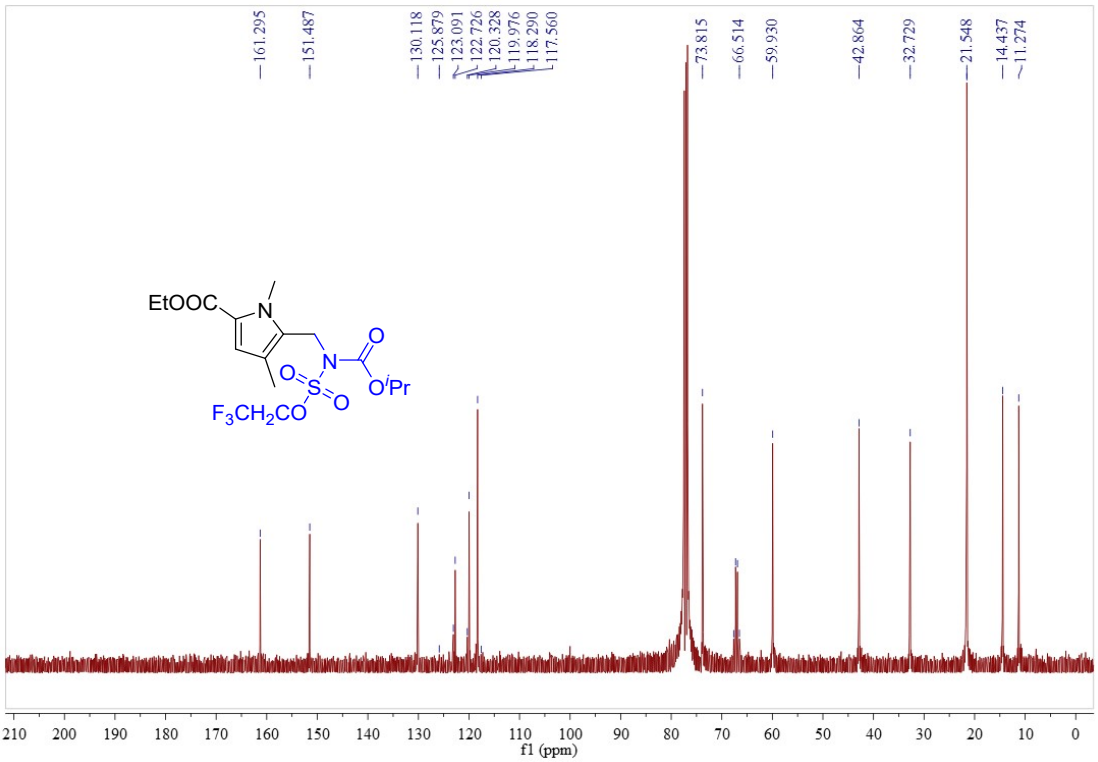


Figure S56. ^{13}C NMR of **5c** (100 MHz, $CDCl_3$)

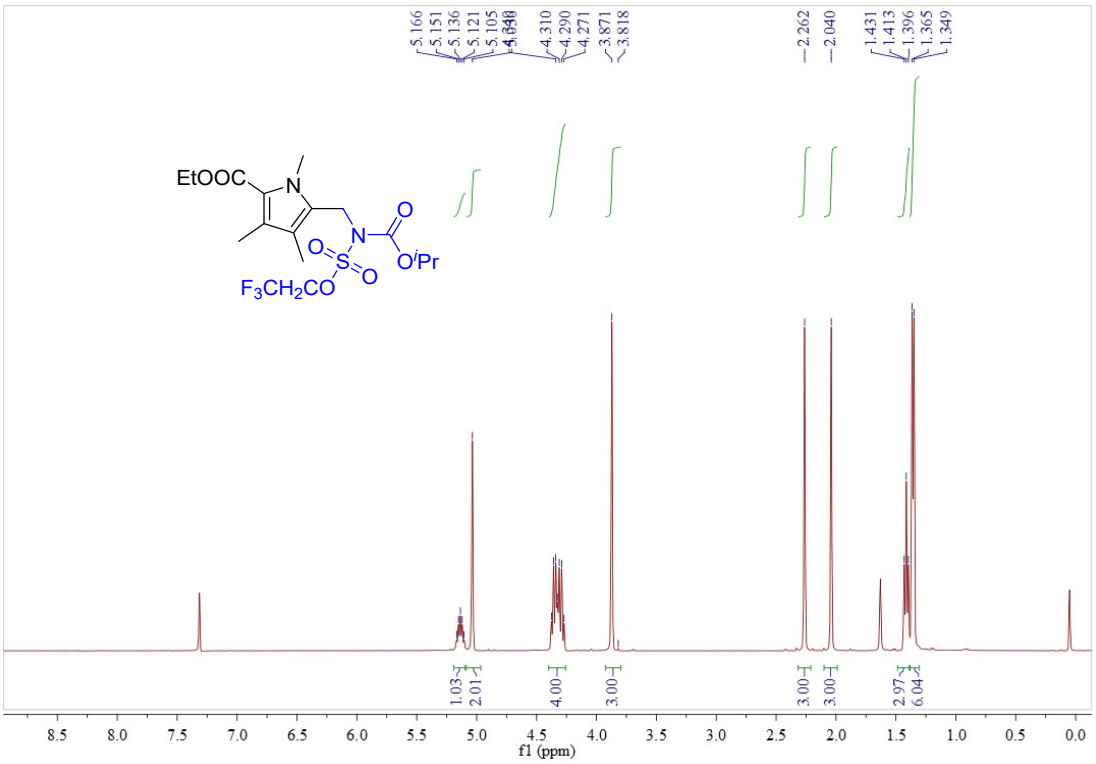


Figure S57. ^{1}H NMR of **5d** (400 MHz, $CDCl_3$)

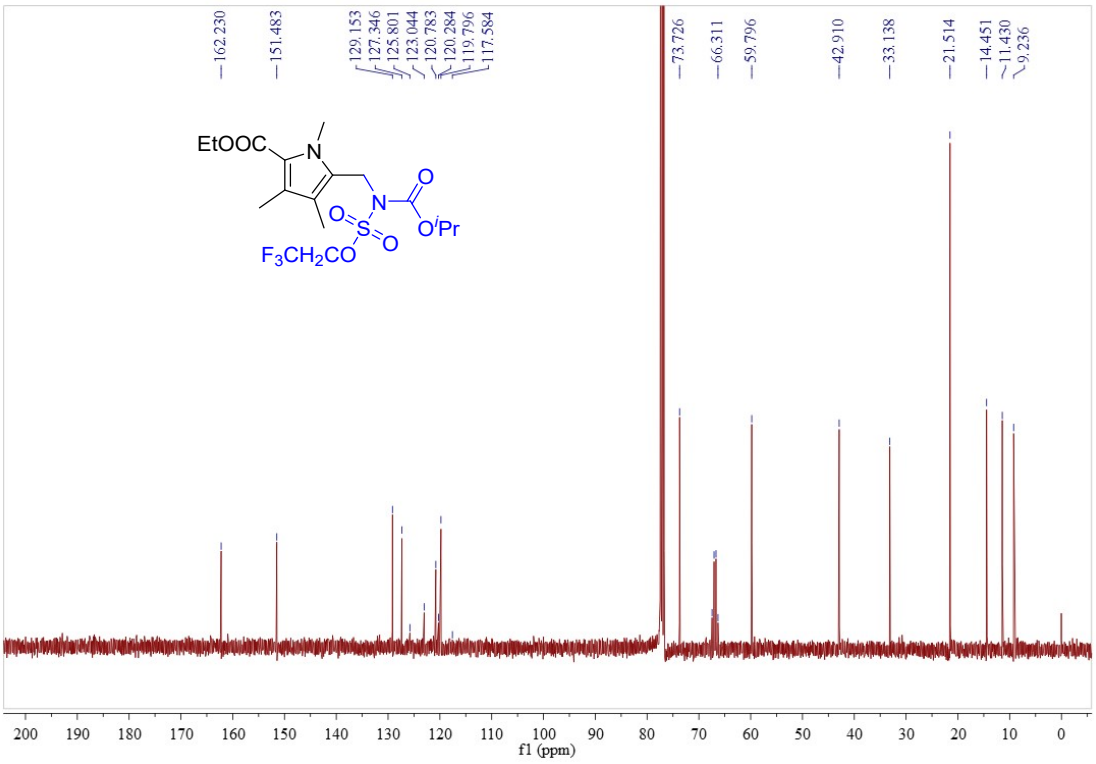


Figure S58. ^{13}C NMR of **5d** (100 MHz, $CDCl_3$)

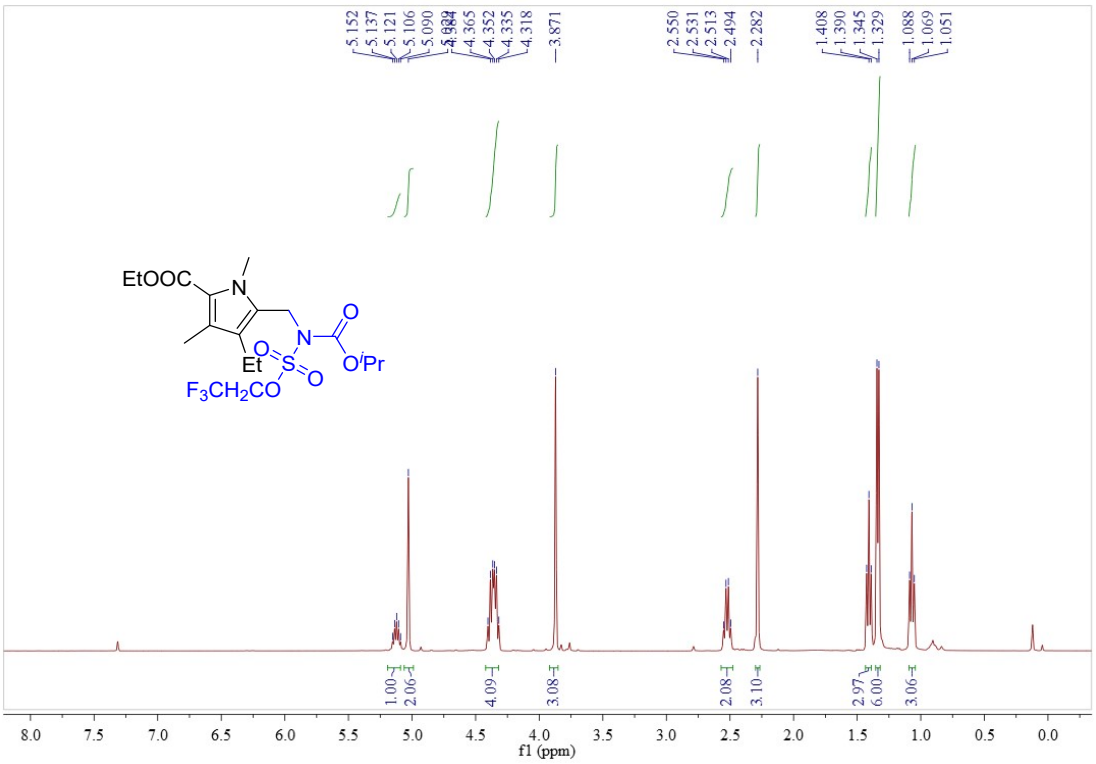


Figure S59. ^{1}H NMR of **5e** (400 MHz, $CDCl_3$)

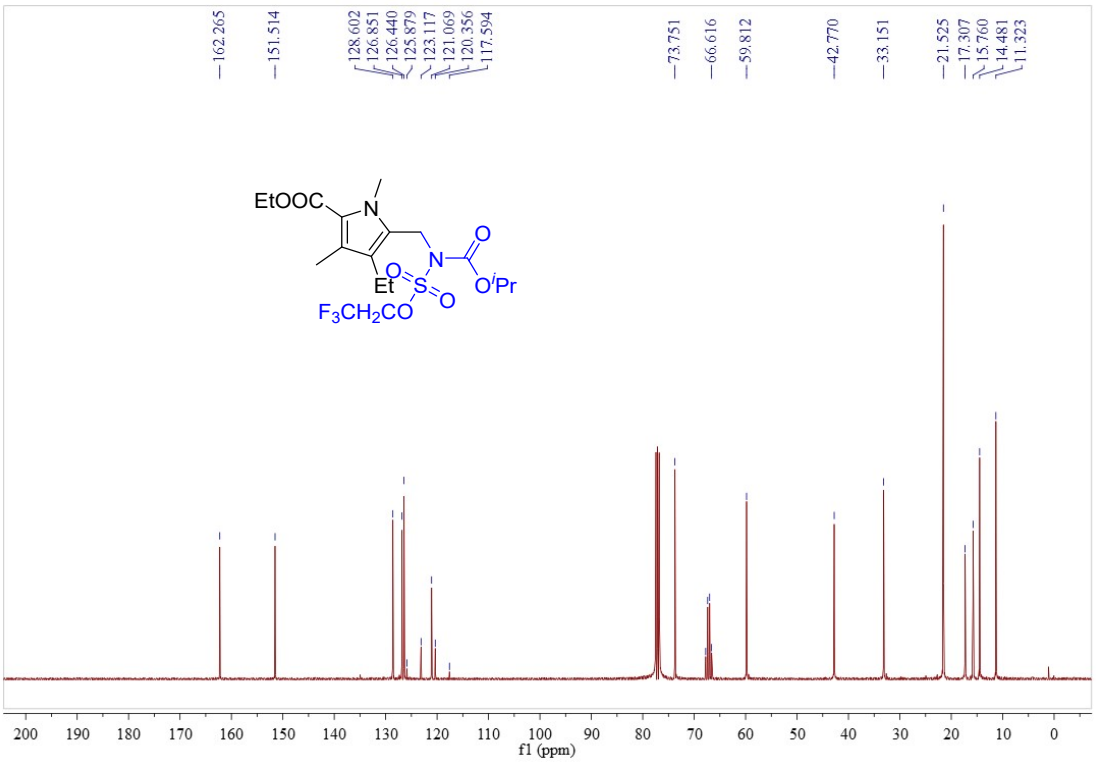


Figure S60. ^{13}C NMR of **5e** (100 MHz, $CDCl_3$)

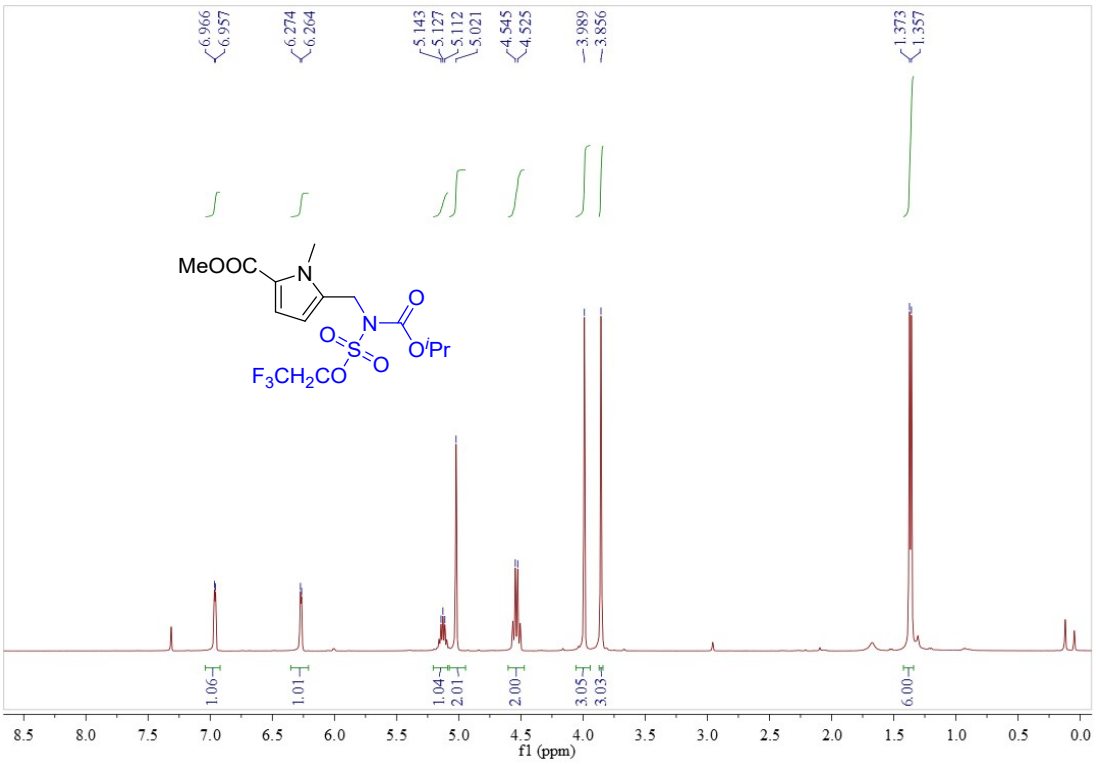


Figure S61. ^{1}H NMR of **5f** (400 MHz, $CDCl_3$)

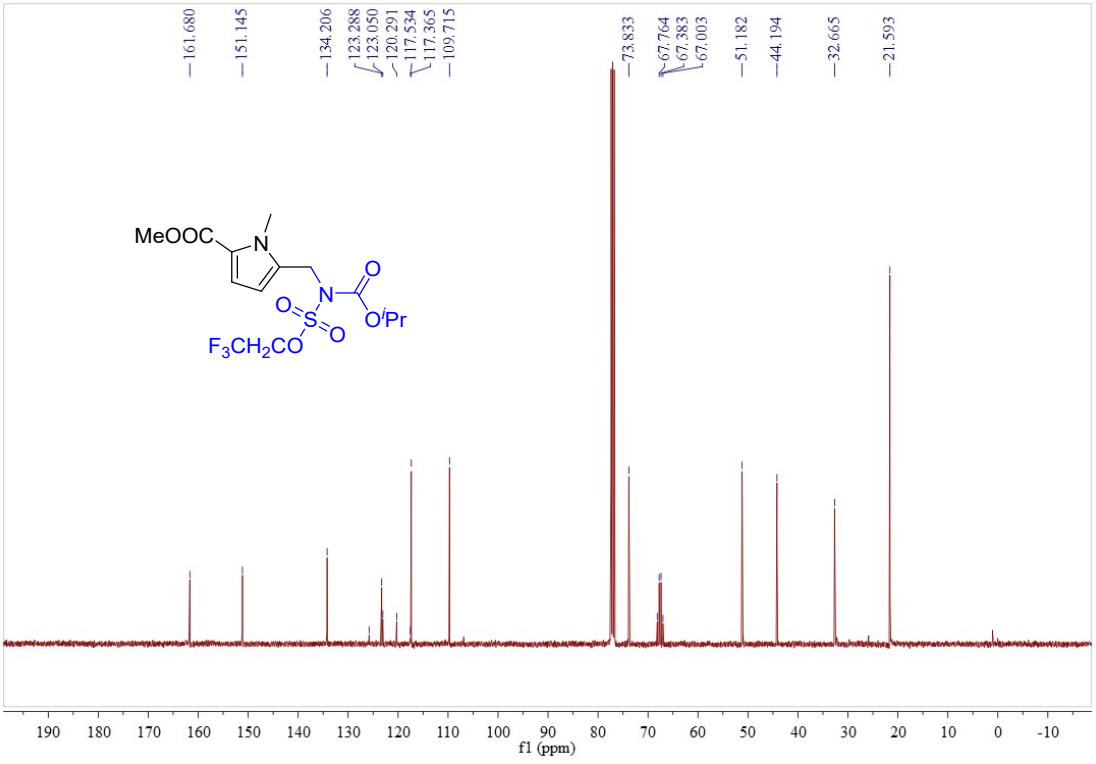


Figure S62. ^{13}C NMR of **5f** (100 MHz, $CDCl_3$)

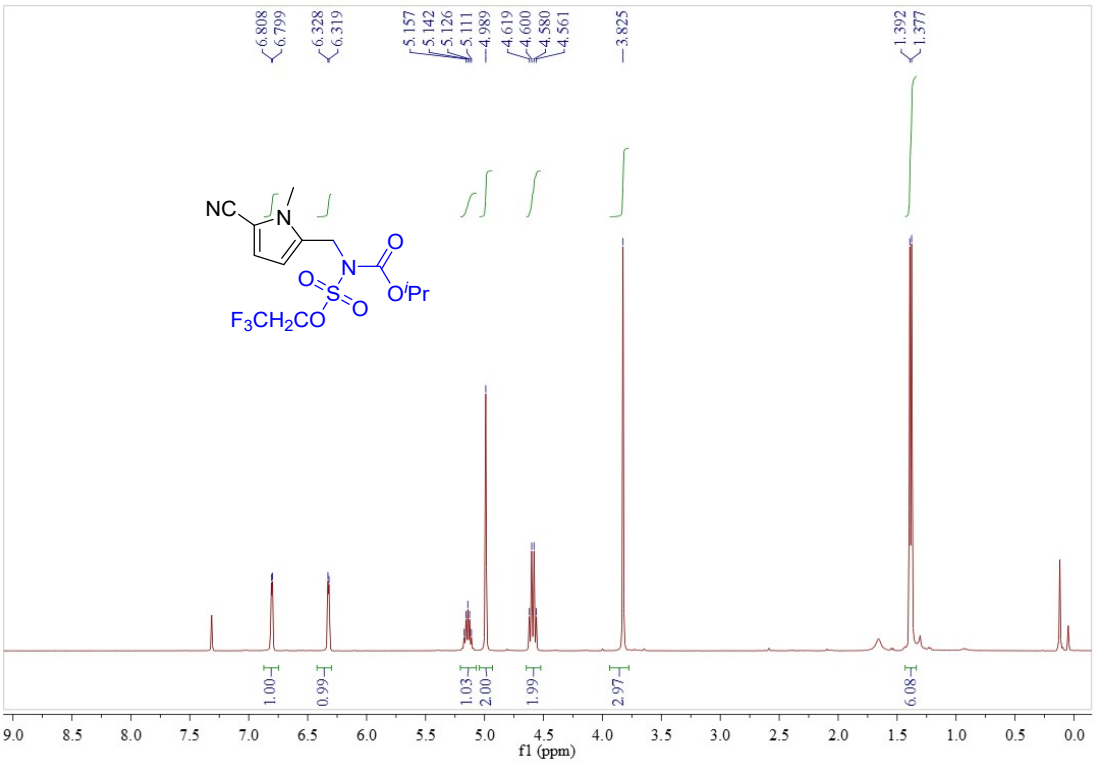


Figure S63. ^{1}H NMR of **5g** (400 MHz, $CDCl_3$)

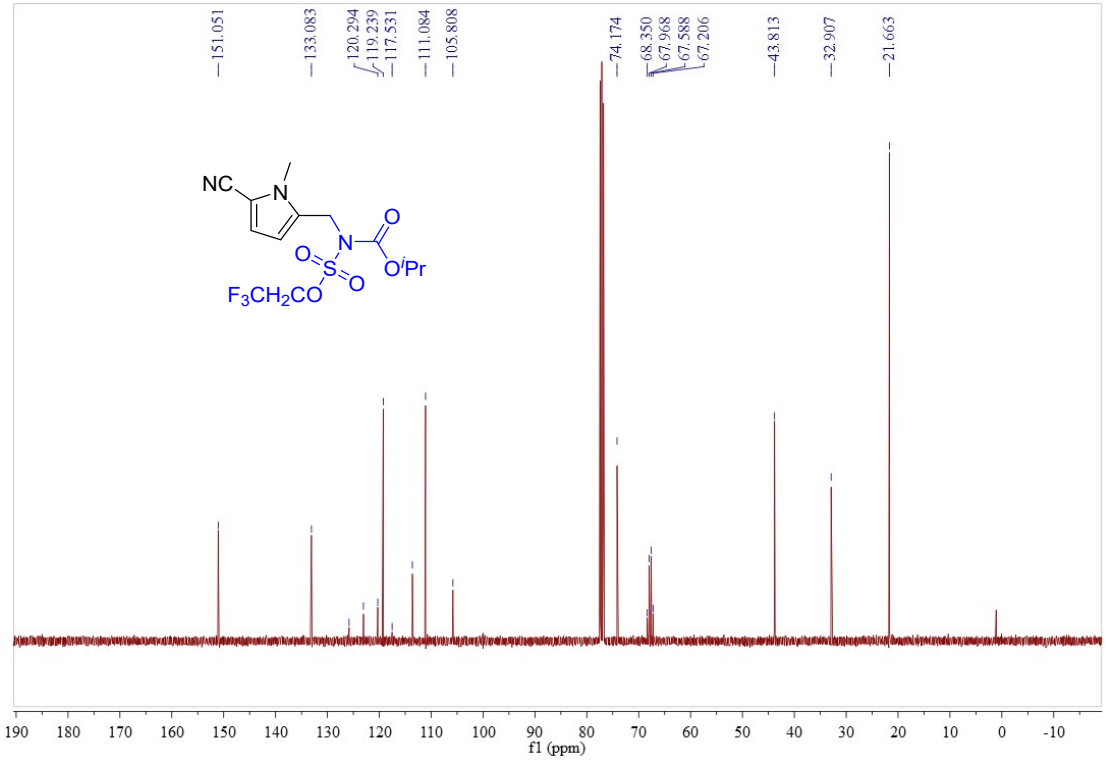


Figure S64. ^{13}C NMR of **5g** (100 MHz, $CDCl_3$)

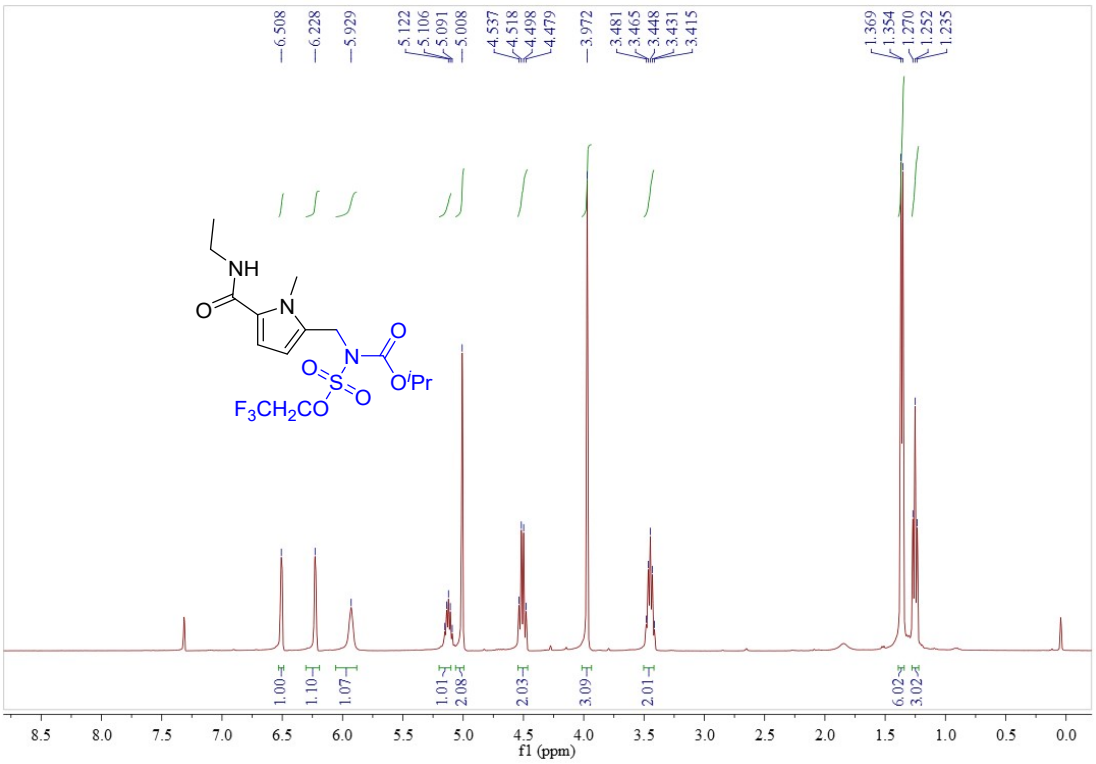


Figure S65. ^{1}H NMR of **5h** (400 MHz, $CDCl_3$)

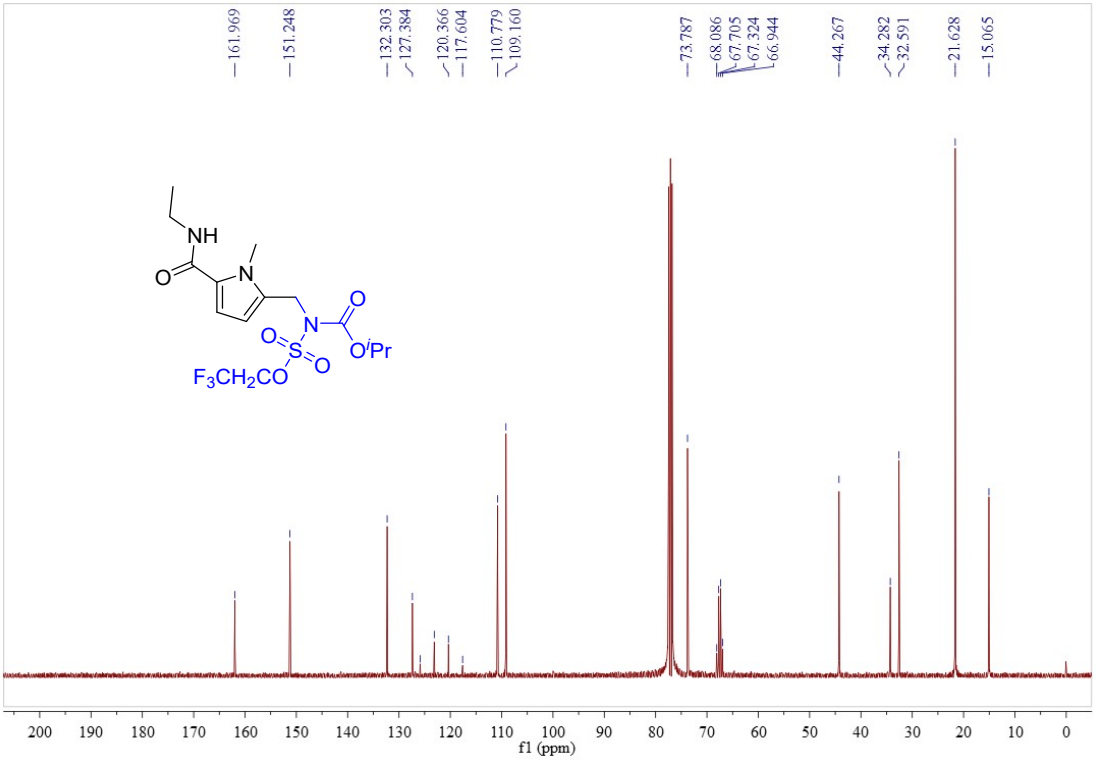


Figure S66. ^{13}C NMR of **5h** (100 MHz, $CDCl_3$)

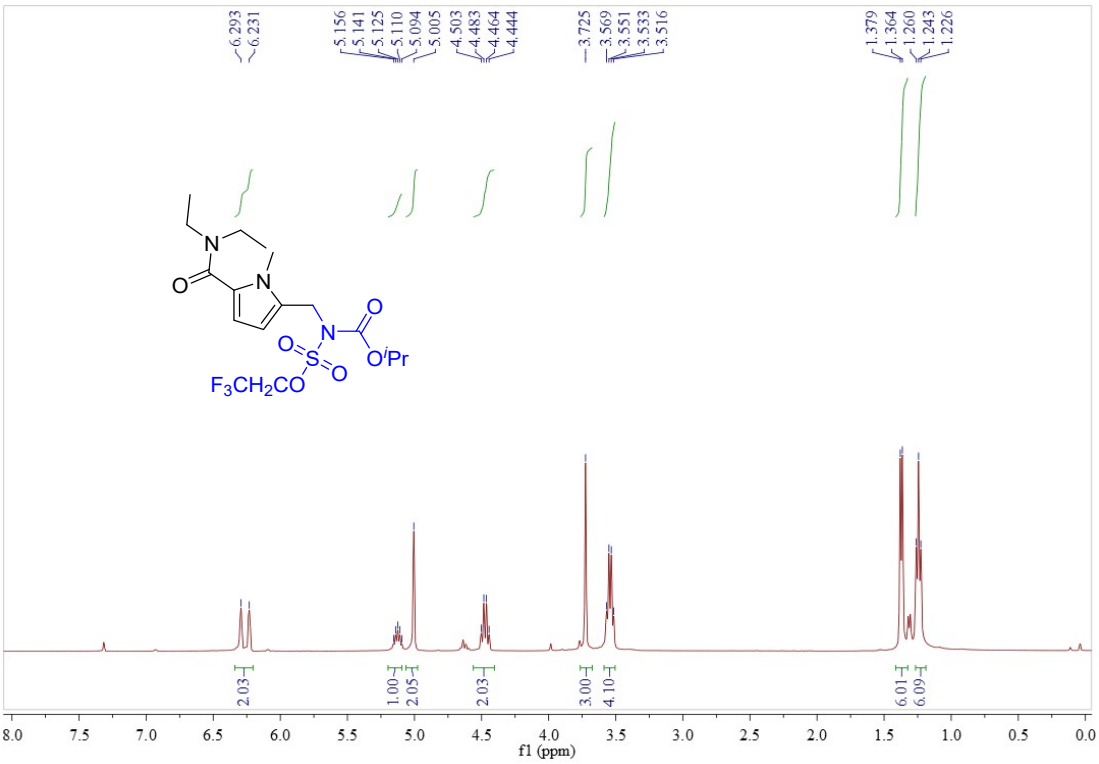


Figure S67. ^{1}H NMR of **5i** (400 MHz, $CDCl_3$)

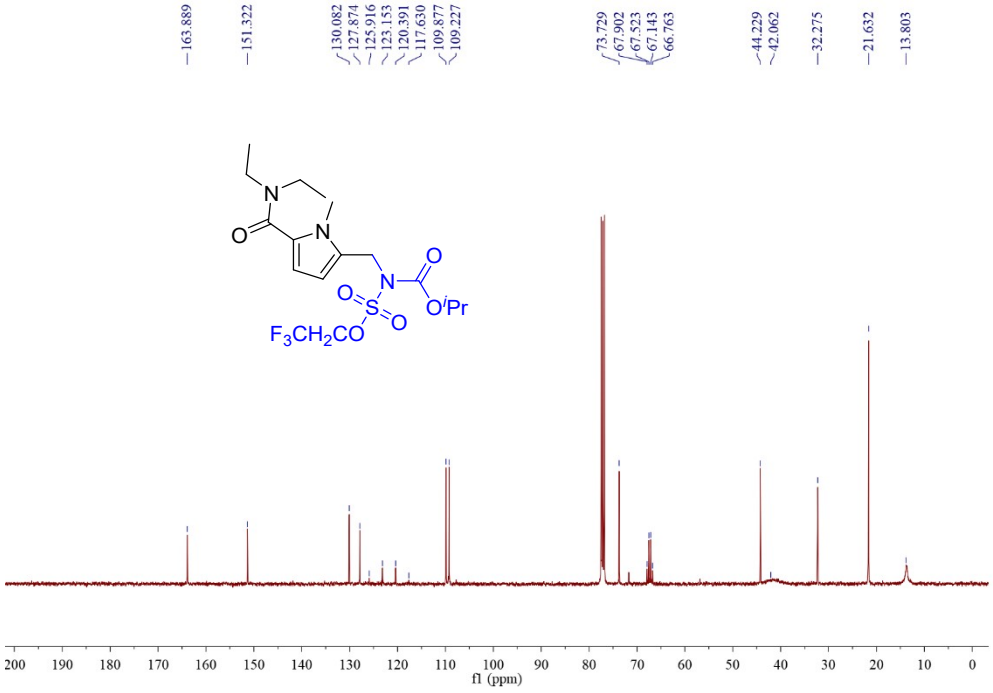


Figure S68. ^{13}C NMR of **5i** (100 MHz, $CDCl_3$)

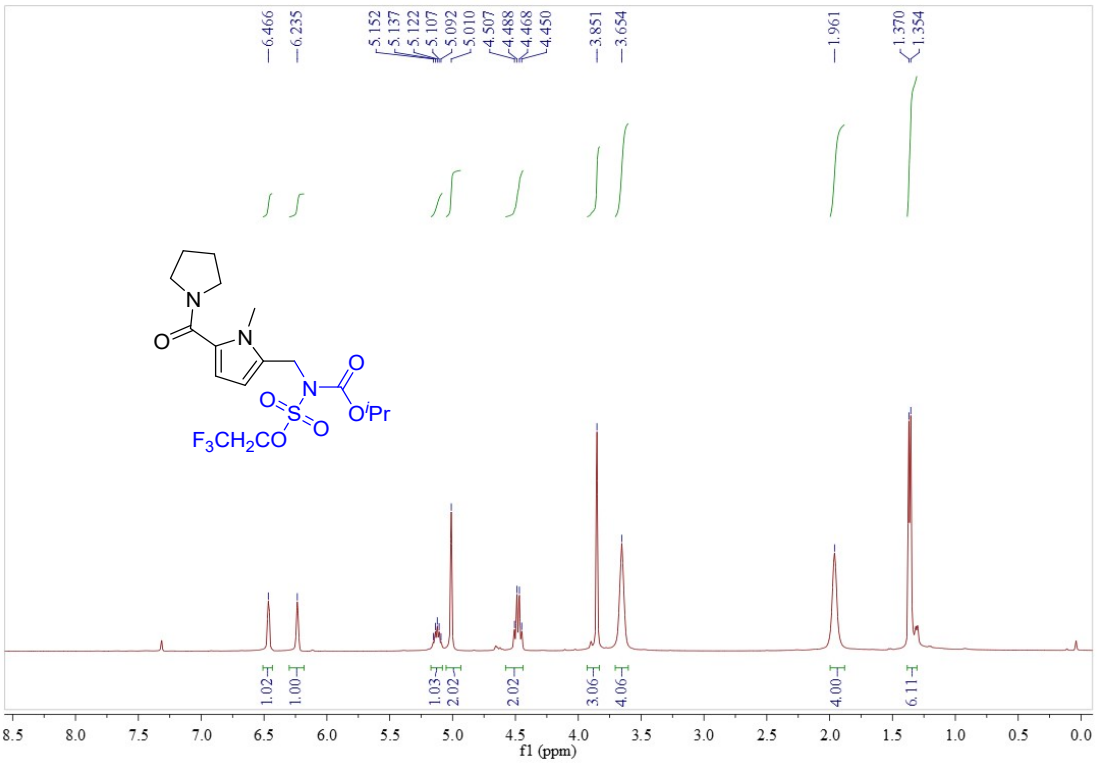


Figure S69. ^{1}H NMR of **5j** (400 MHz, $CDCl_3$)

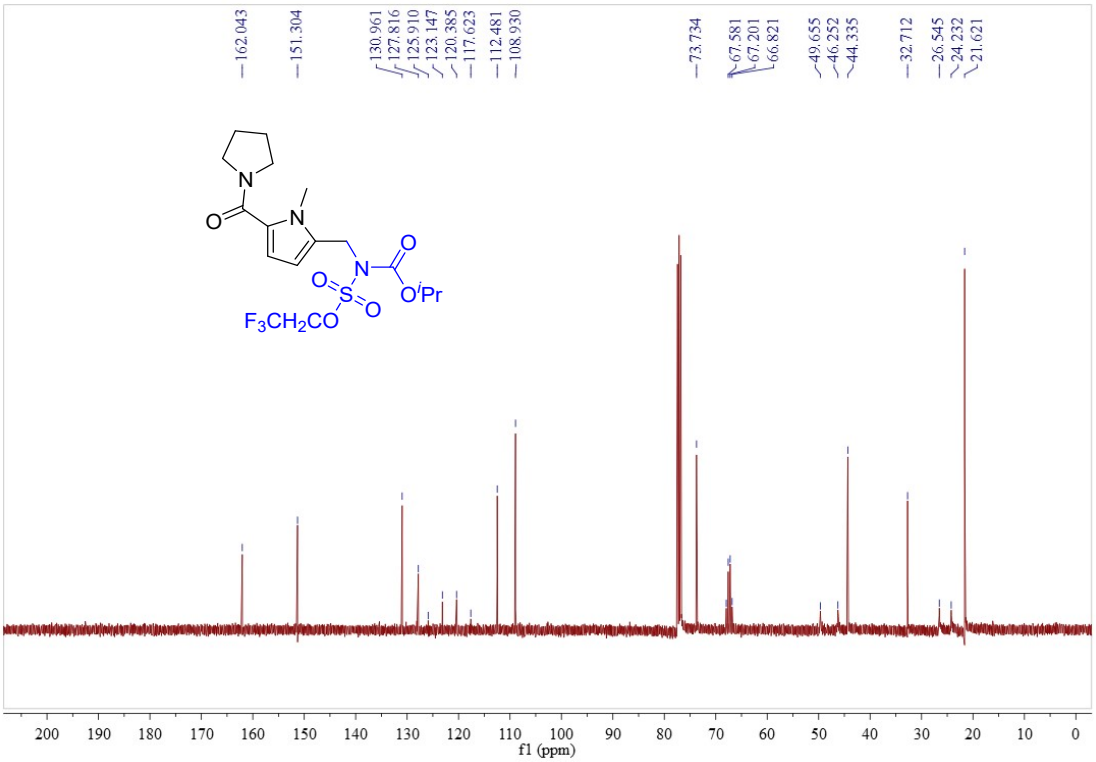


Figure S70. ^{13}C NMR of **5j** (100 MHz, $CDCl_3$)

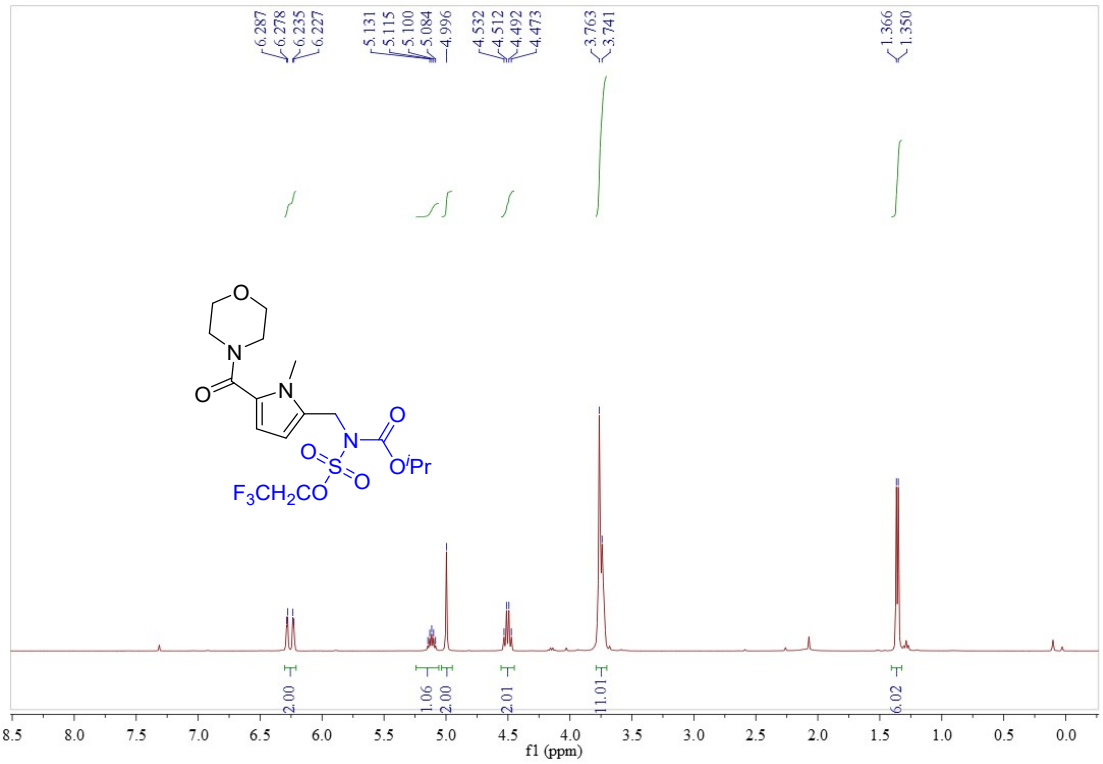


Figure S71. ^{1}H NMR of **5k** (400 MHz, $CDCl_3$)

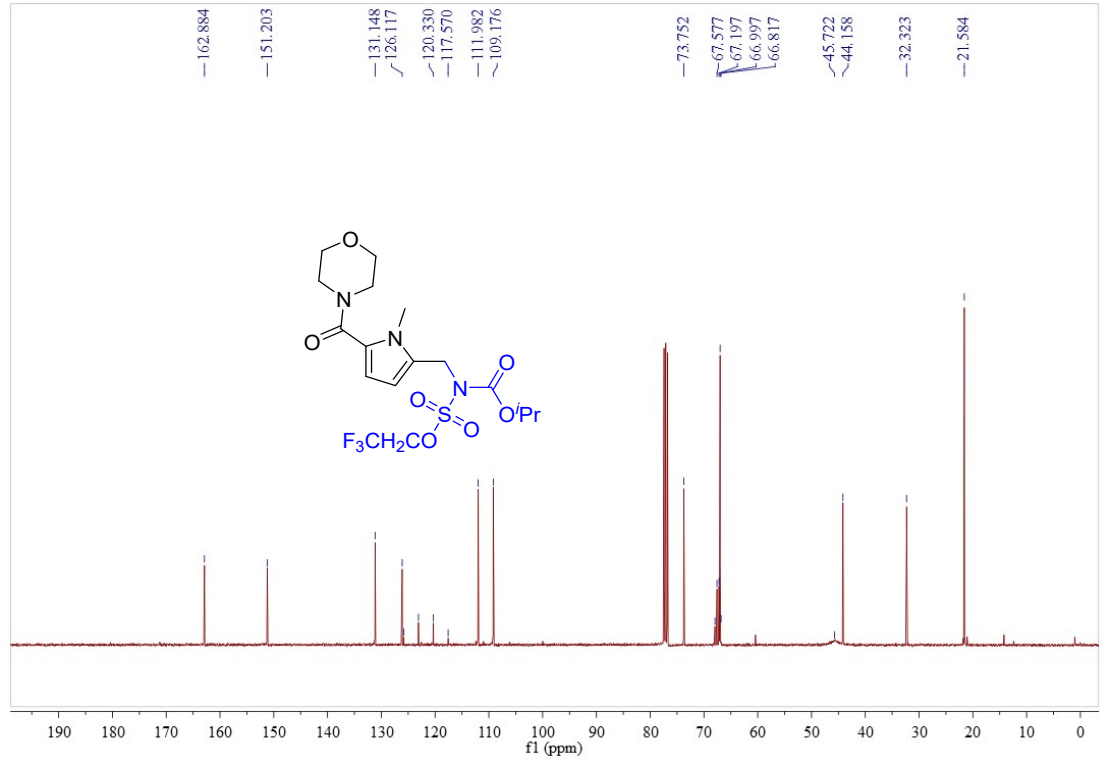


Figure S72. ^{13}C NMR of **5k** (100 MHz, $CDCl_3$)

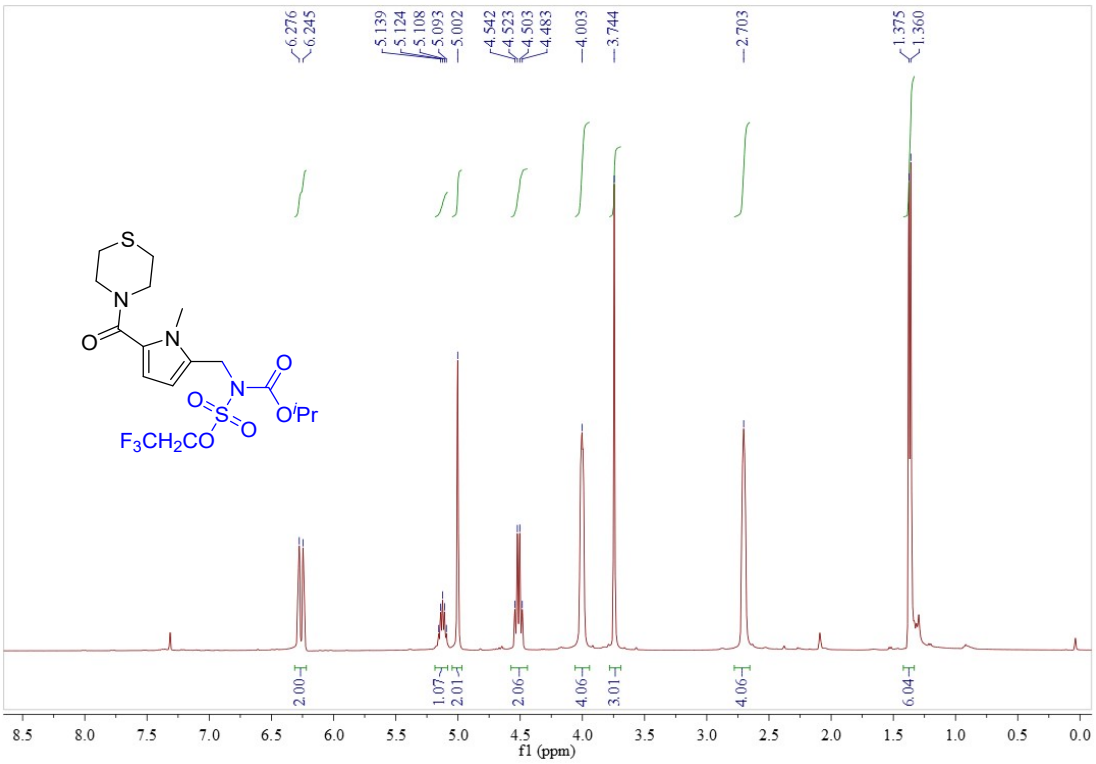


Figure S73. ^{1}H NMR of **5l** (400 MHz, $CDCl_3$)

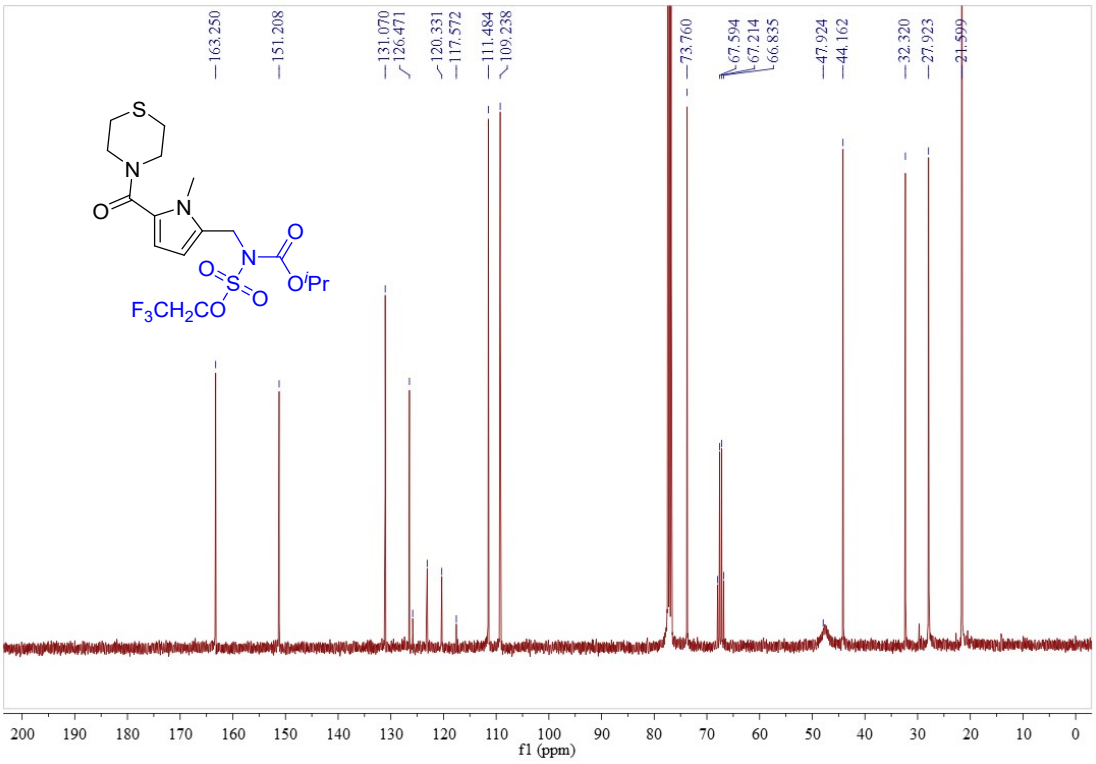


Figure S74. ^{13}C NMR of **5l** (100 MHz, $CDCl_3$)

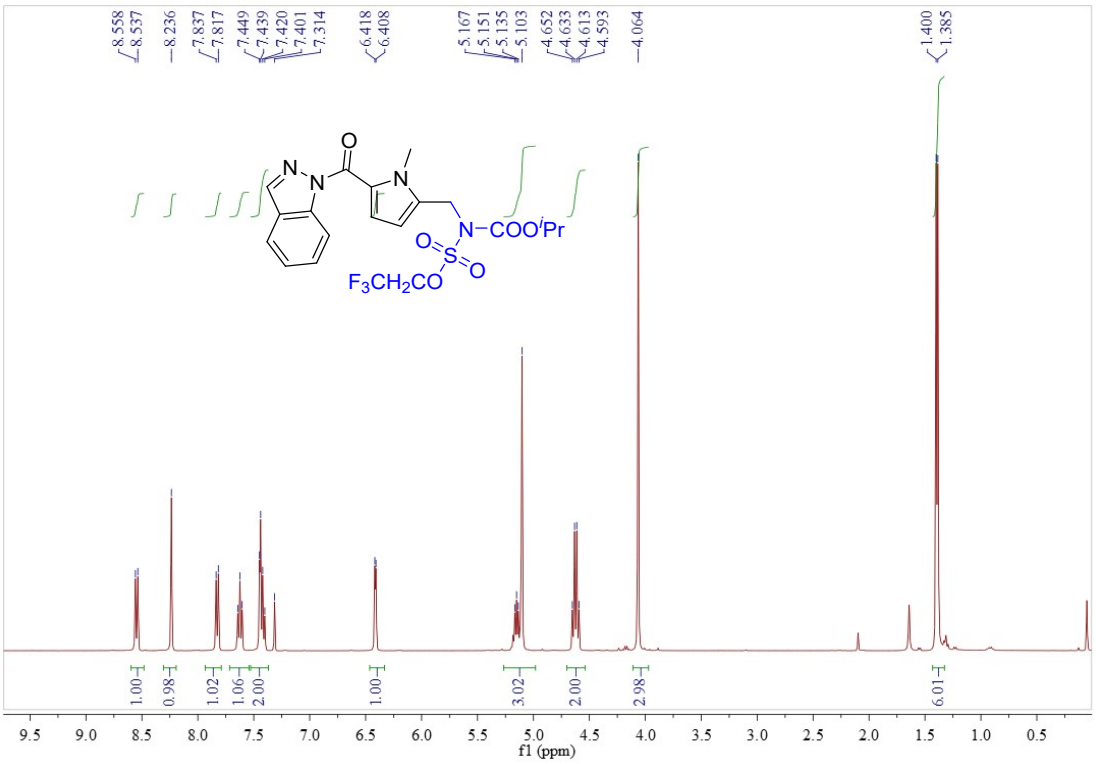


Figure S75. ^{1}H NMR of **5m** (400 MHz, $CDCl_3$)

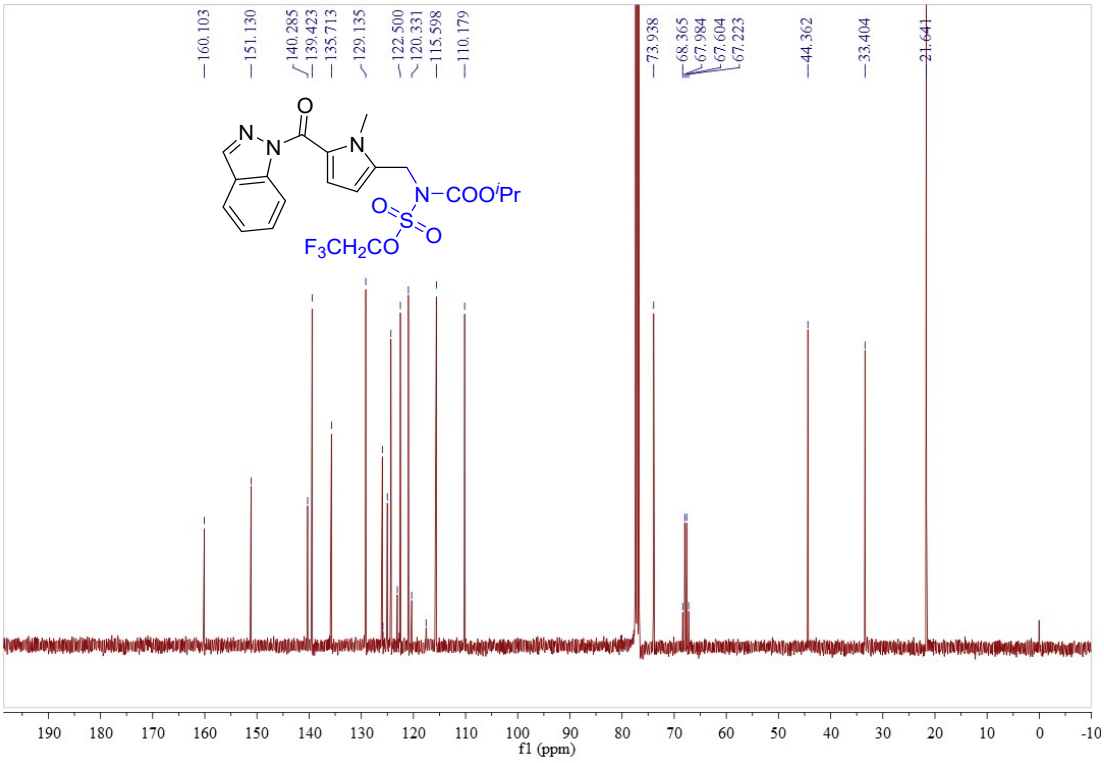


Figure S76. ^{13}C NMR of **5m** (100 MHz, $CDCl_3$)

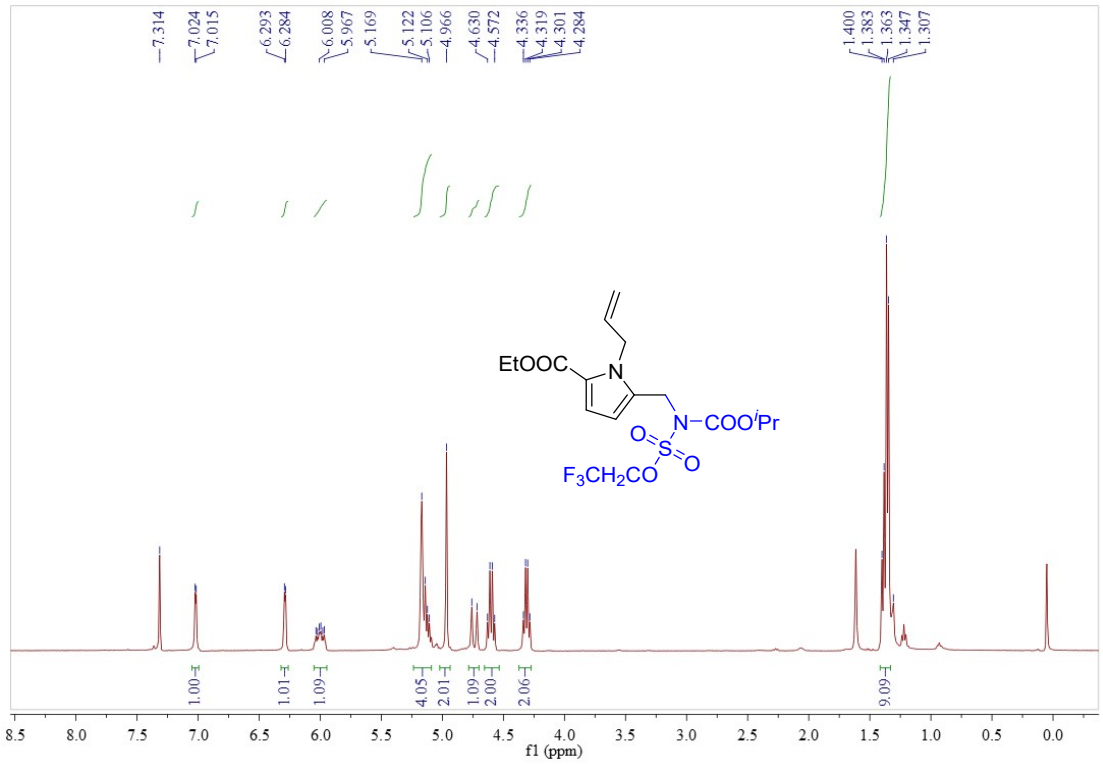


Figure S77. ^{1}H NMR of **5n** (400 MHz, $CDCl_3$)

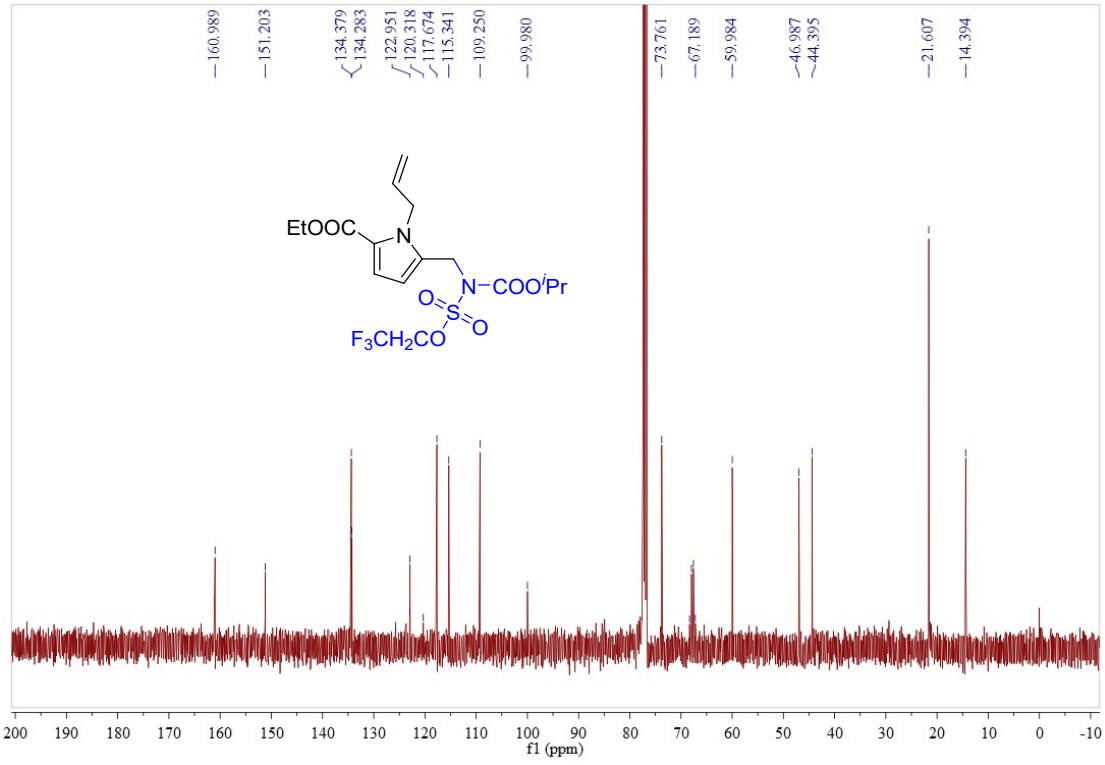


Figure S78. ^{13}C NMR of **5n** (100 MHz, $CDCl_3$)

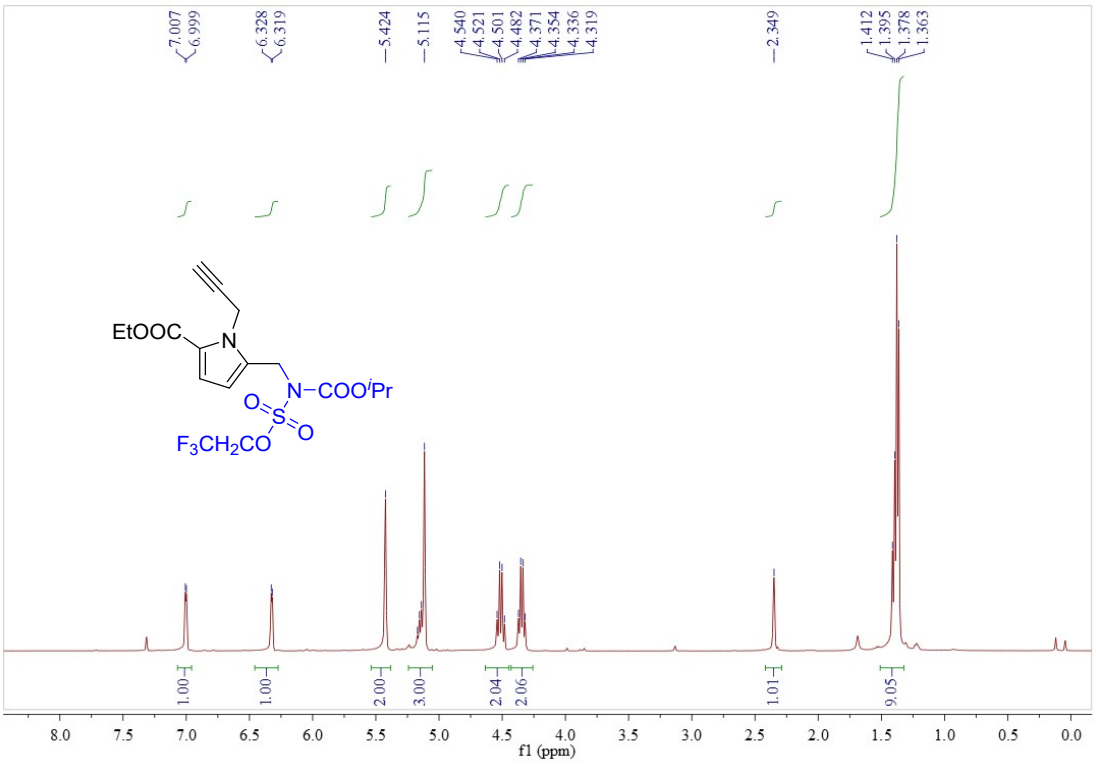


Figure S79. ^{1}H NMR of **5o** (400 MHz, $CDCl_3$)

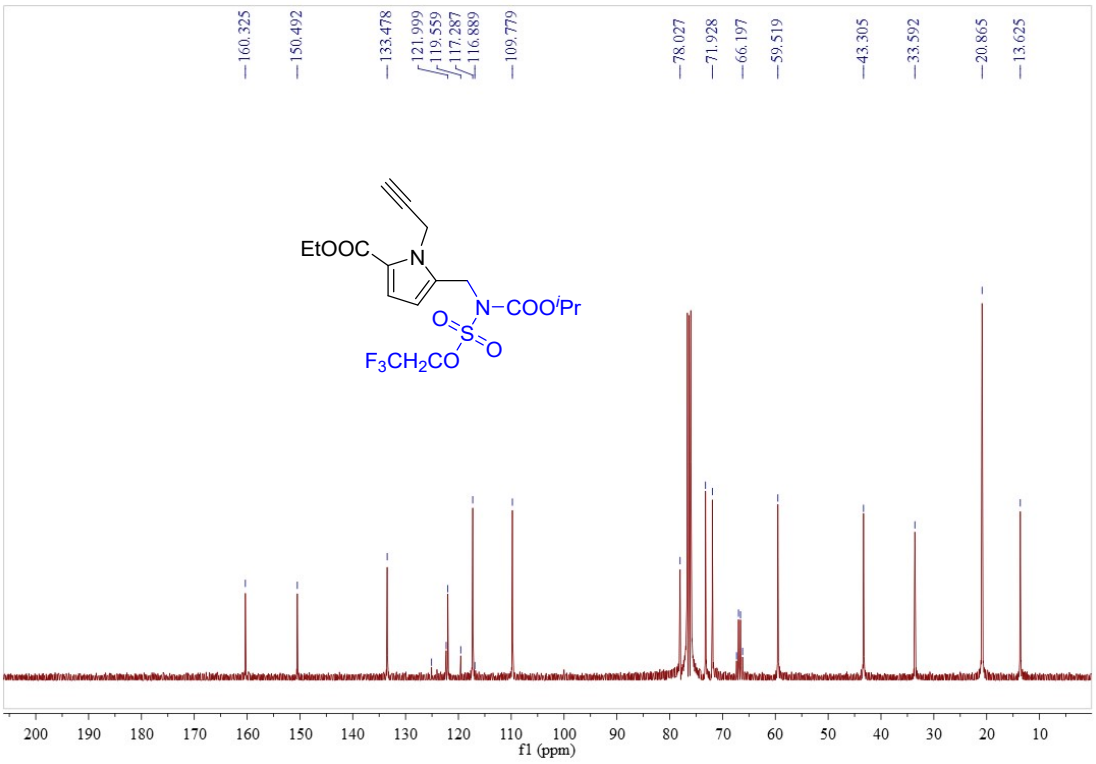


Figure S80. ^{13}C NMR of **5o** (100 MHz, $CDCl_3$)

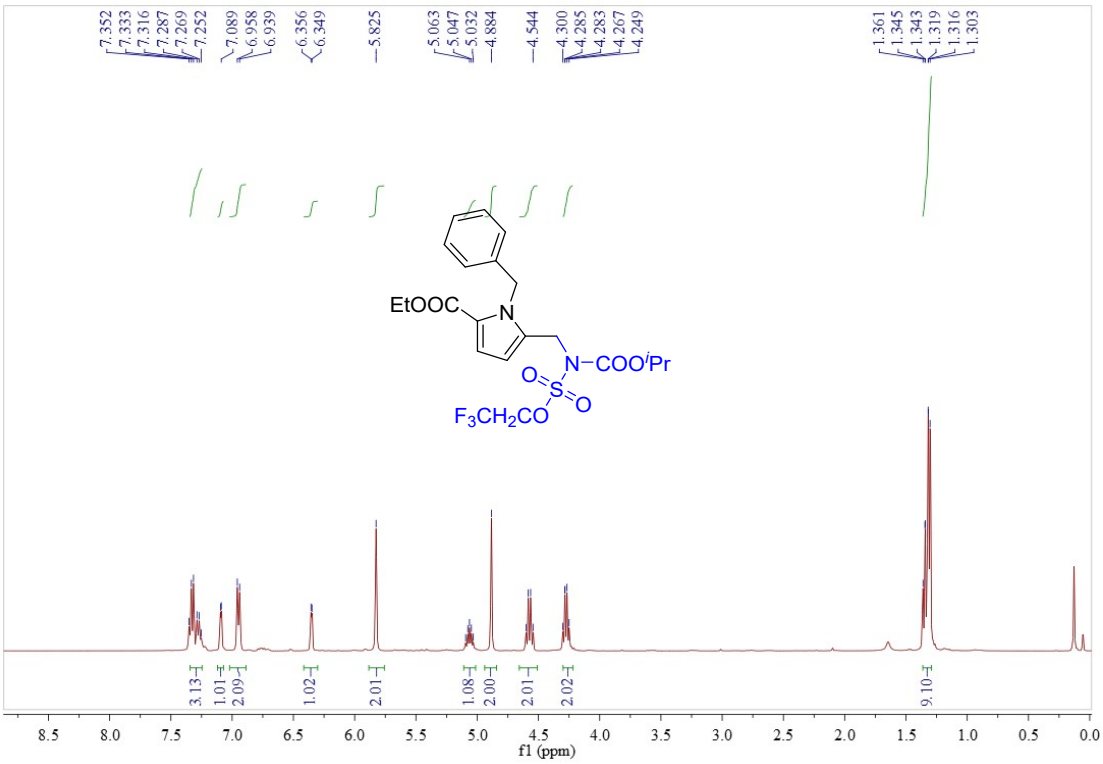


Figure S81. ^{1}H NMR of **5p** (400 MHz, $CDCl_3$)

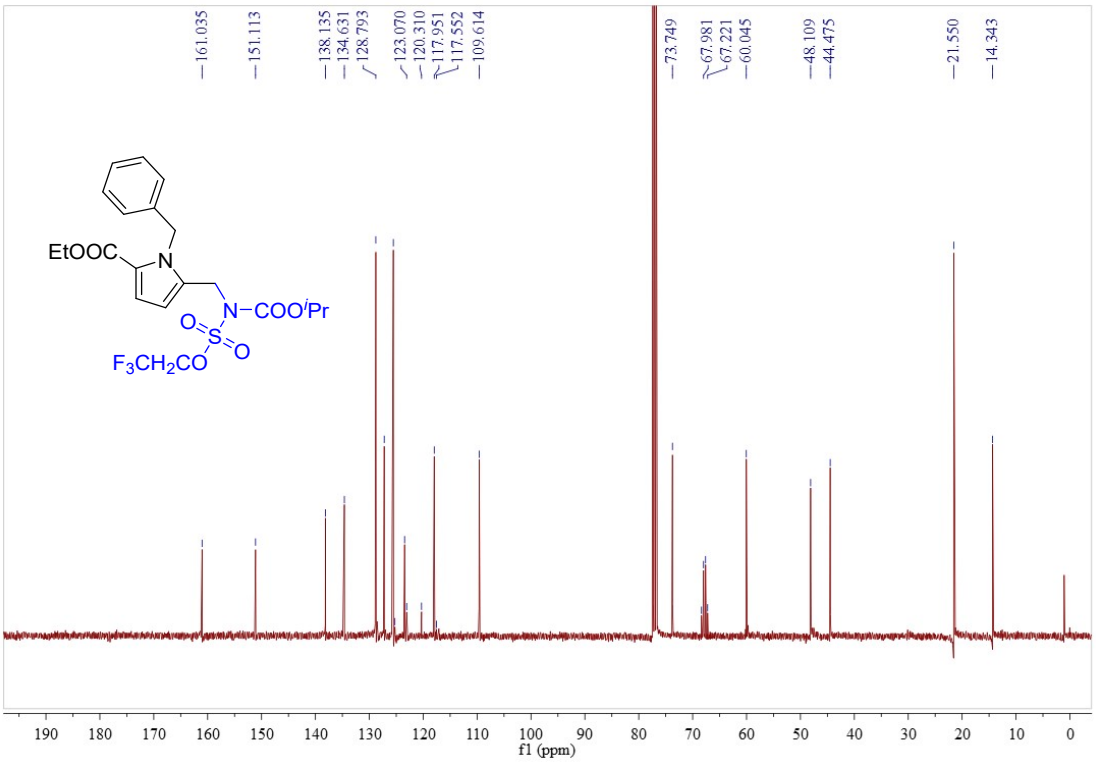


Figure S82. ^{13}C NMR of **5p** (100 MHz, $CDCl_3$)

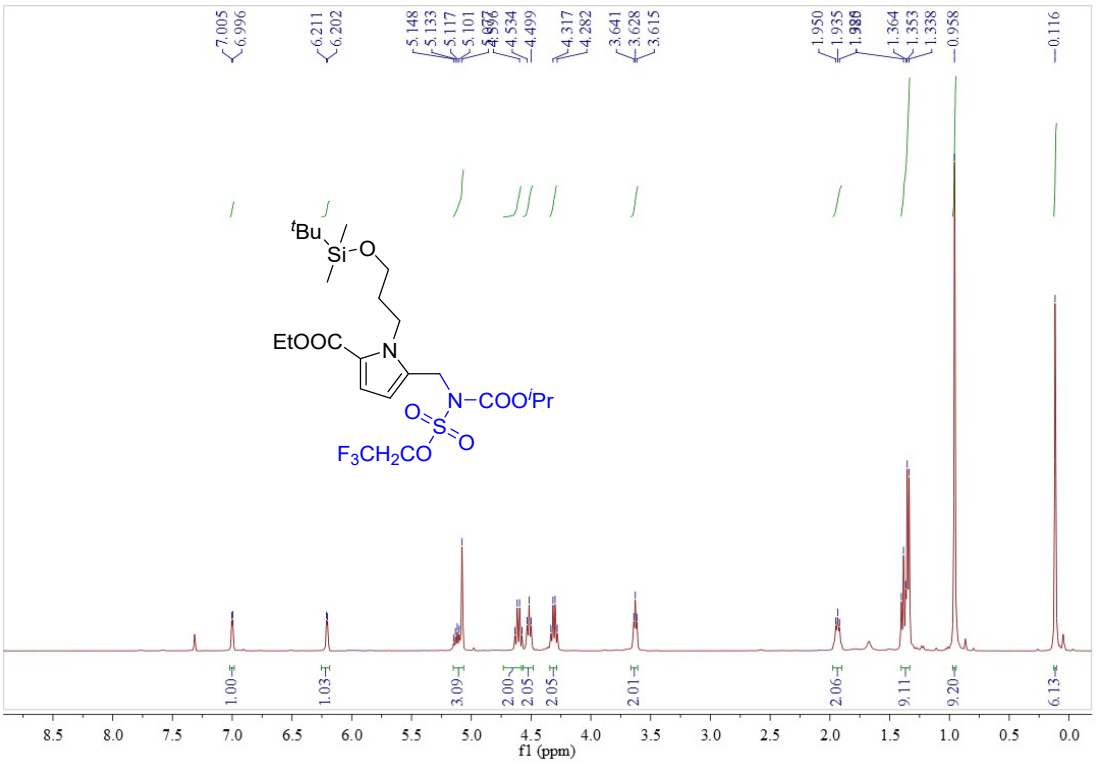


Figure S83. ^{1}H NMR of **5q** (400 MHz, $CDCl_3$)

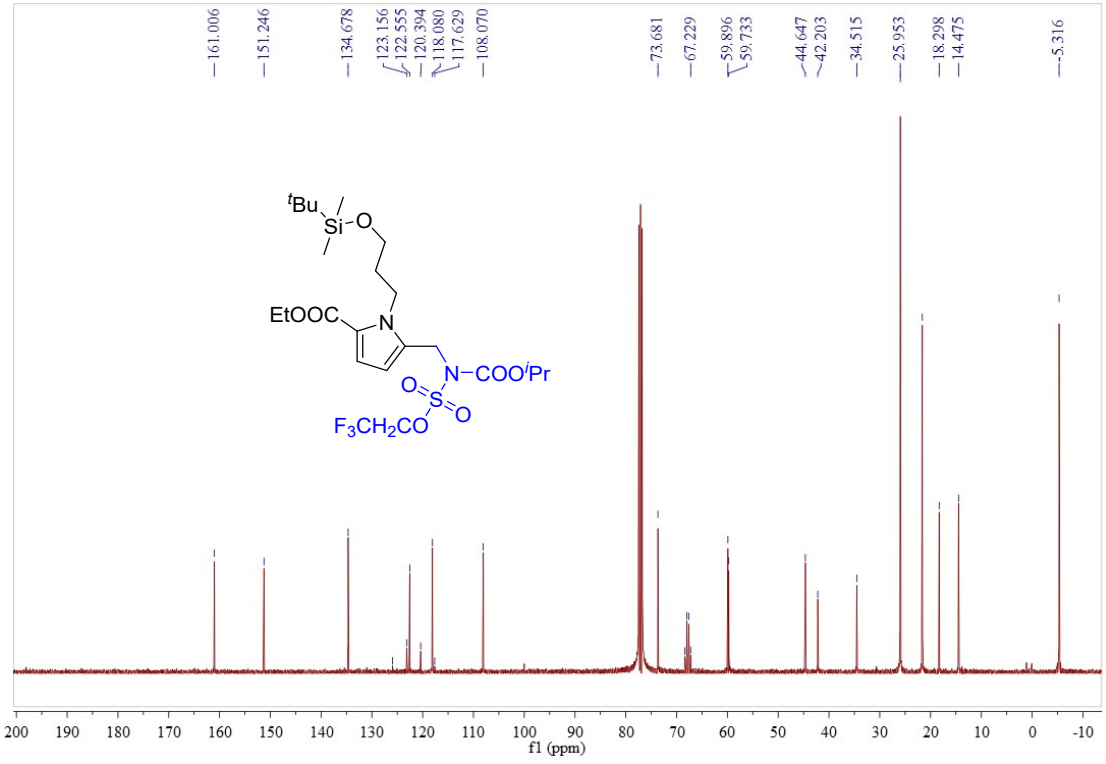


Figure S84. ^{13}C NMR of **5q** (100 MHz, $CDCl_3$)

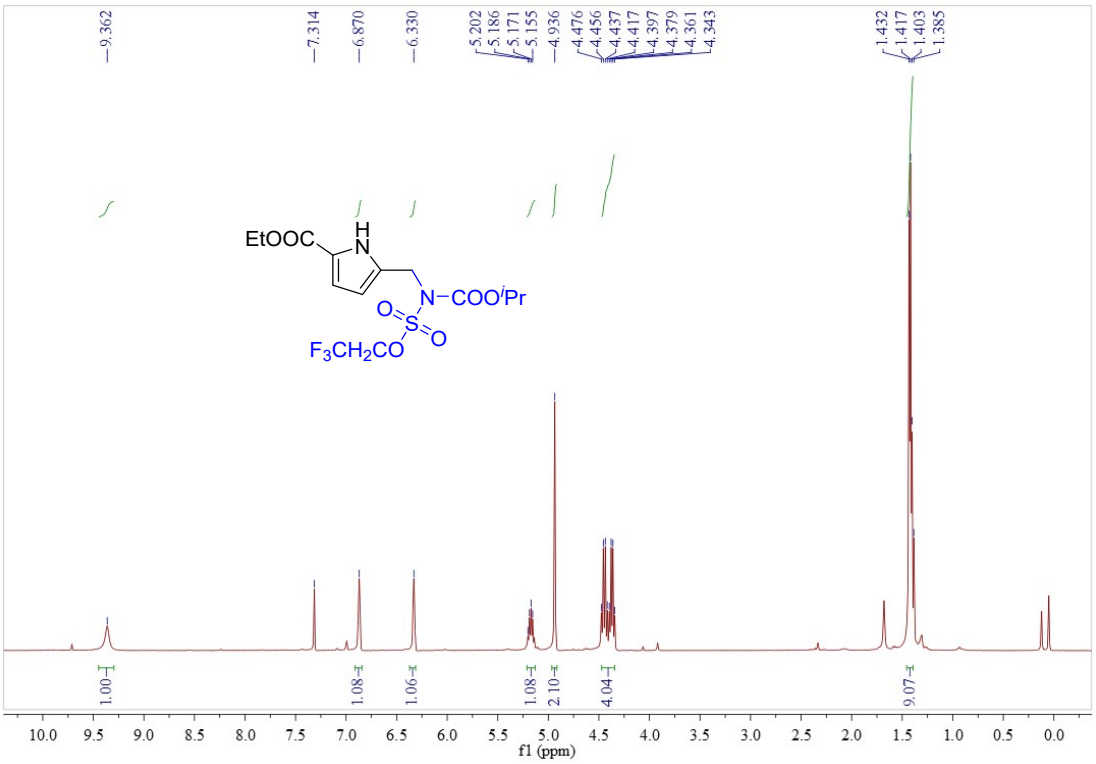


Figure S85. ^{1}H NMR of **5r** (400 MHz, $CDCl_3$)

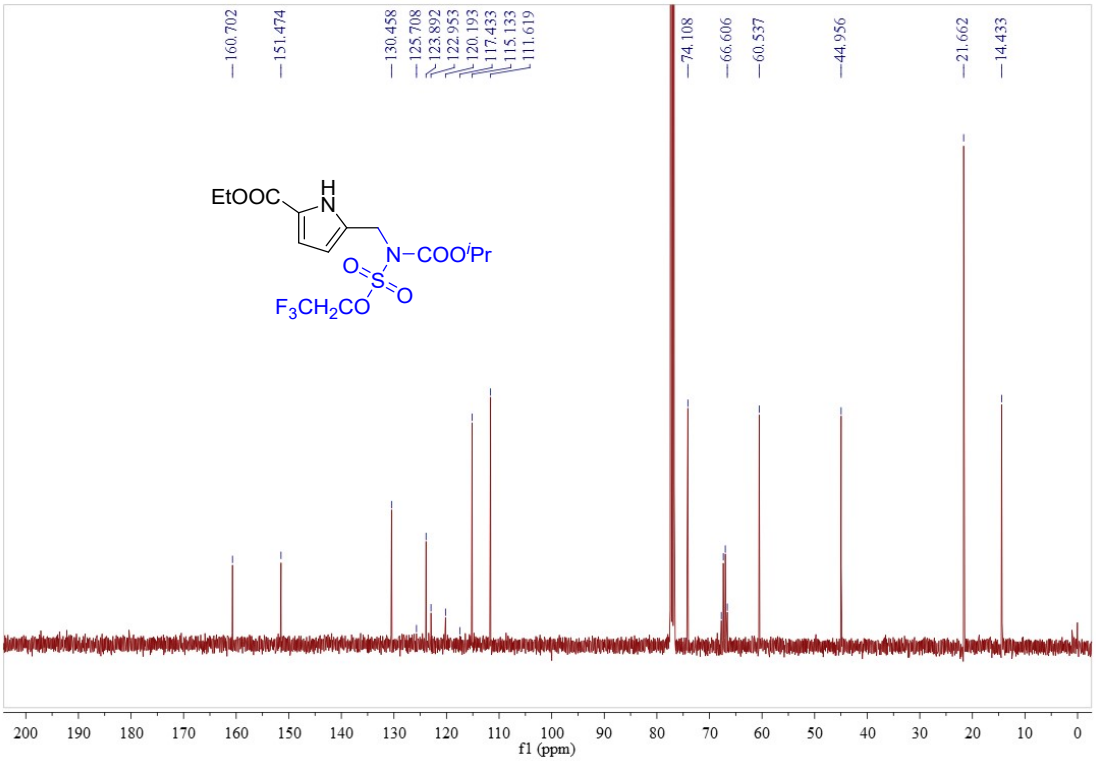


Figure S86. ^{13}C NMR of **5r** (100 MHz, $CDCl_3$)

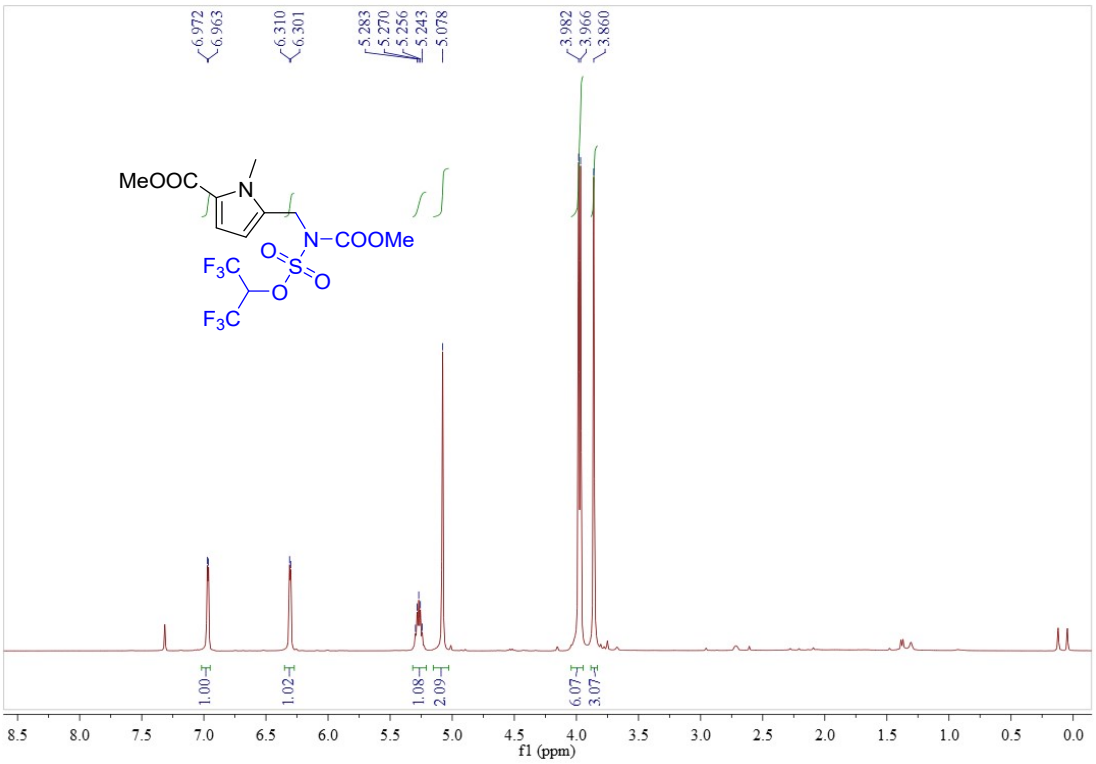


Figure S87. ^{1}H NMR of **5s** (400 MHz, $CDCl_3$)

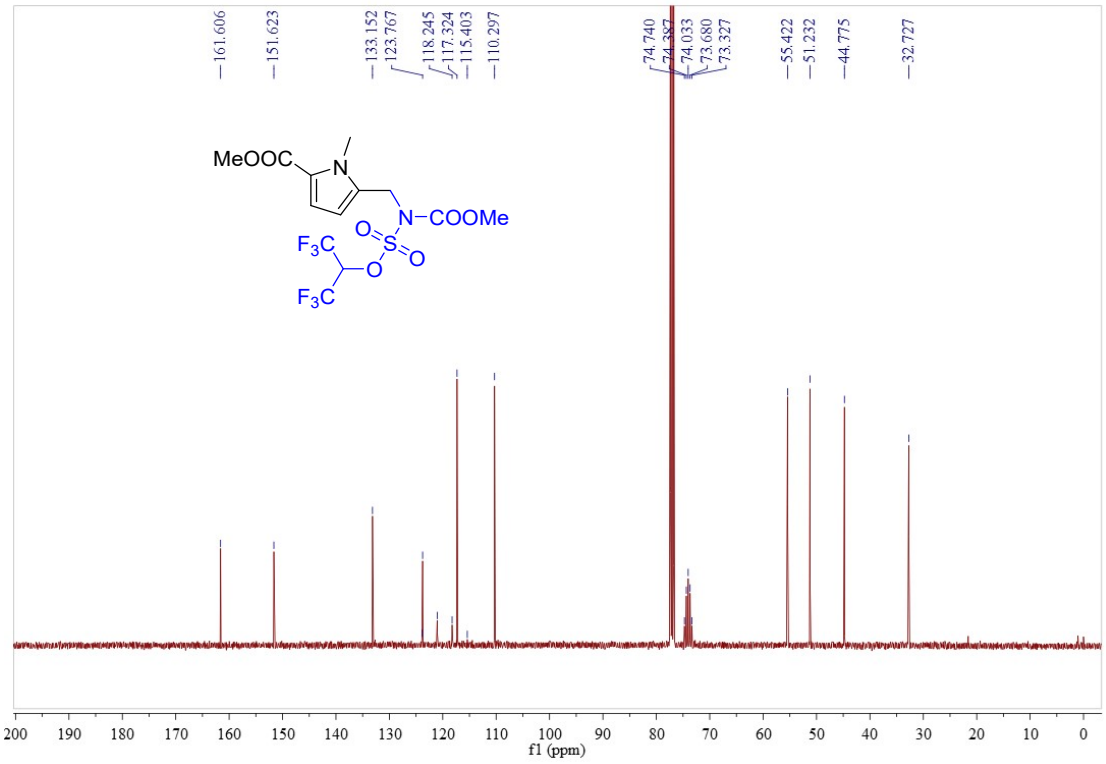


Figure S88. ^{13}C NMR of **5s** (100 MHz, $CDCl_3$)

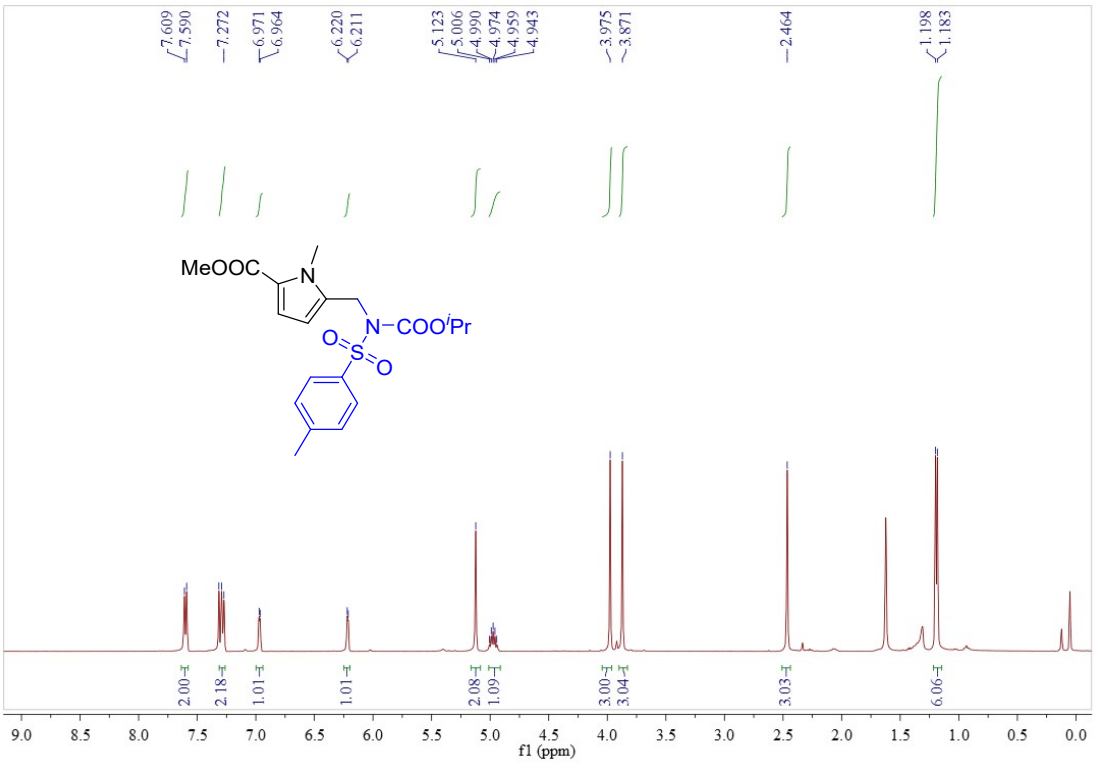


Figure S89. ^{1}H NMR of **5t** (400 MHz, $CDCl_3$)

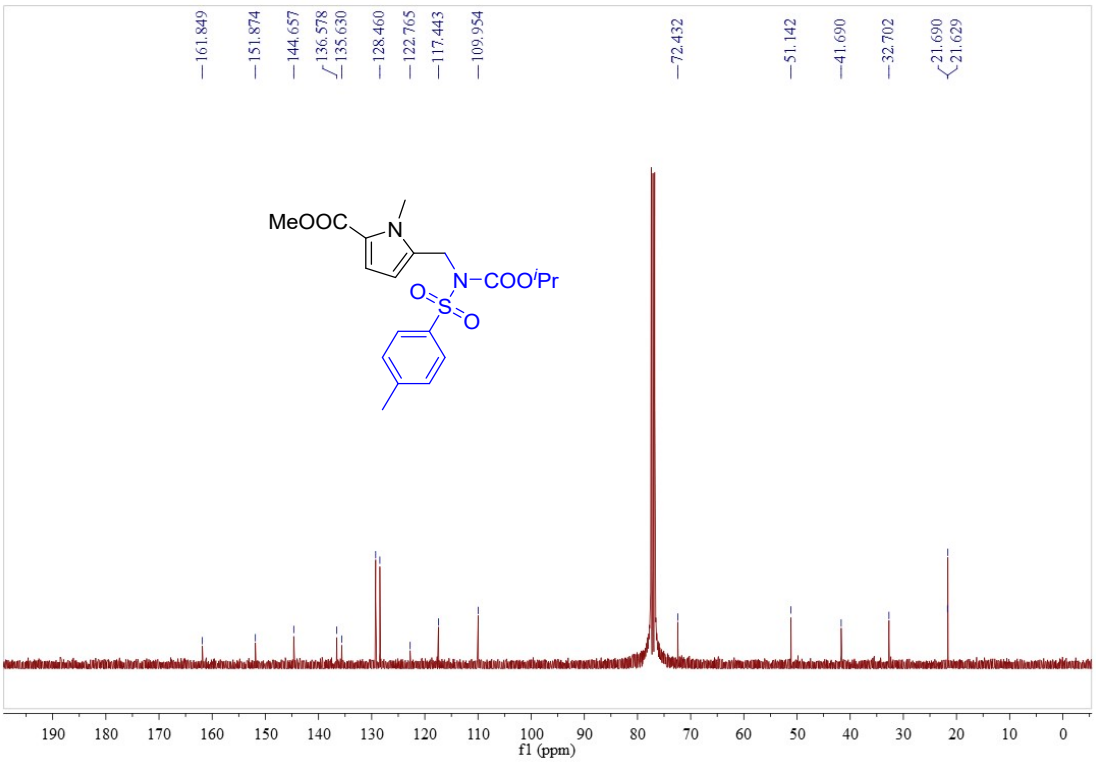


Figure S90. ^{13}C NMR of **5t** (100 MHz, $CDCl_3$)

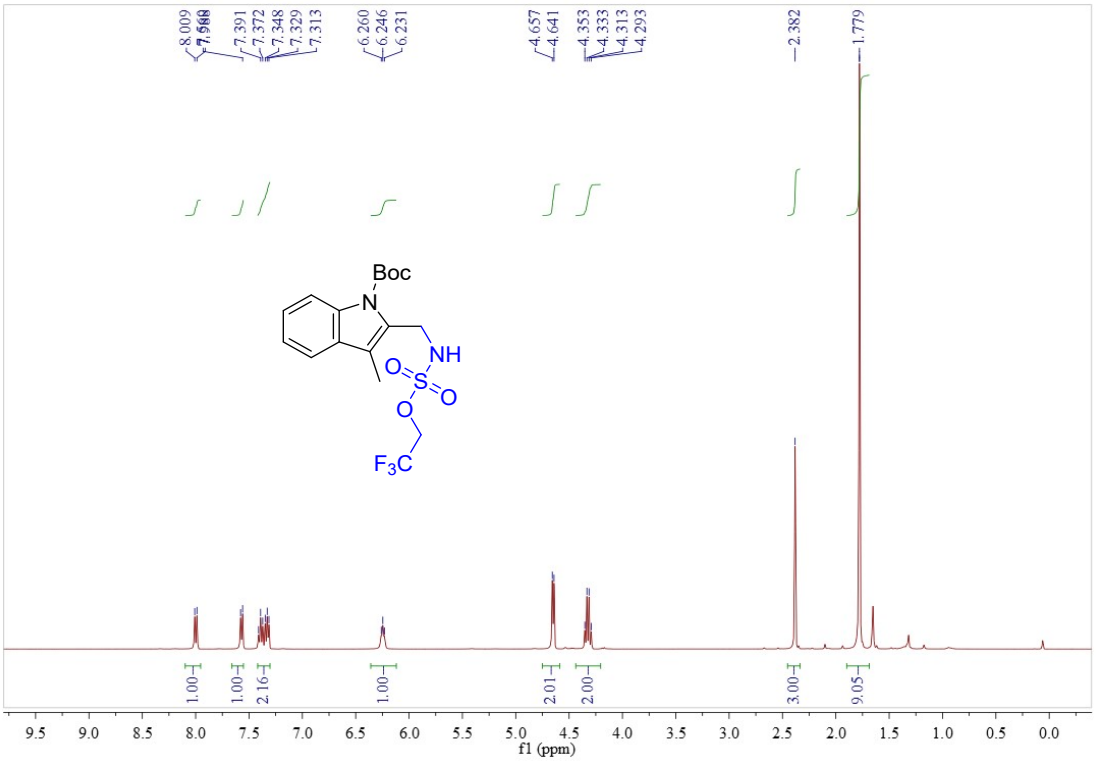


Figure S91. ^{1}H NMR of **6** (400 MHz, $CDCl_3$)

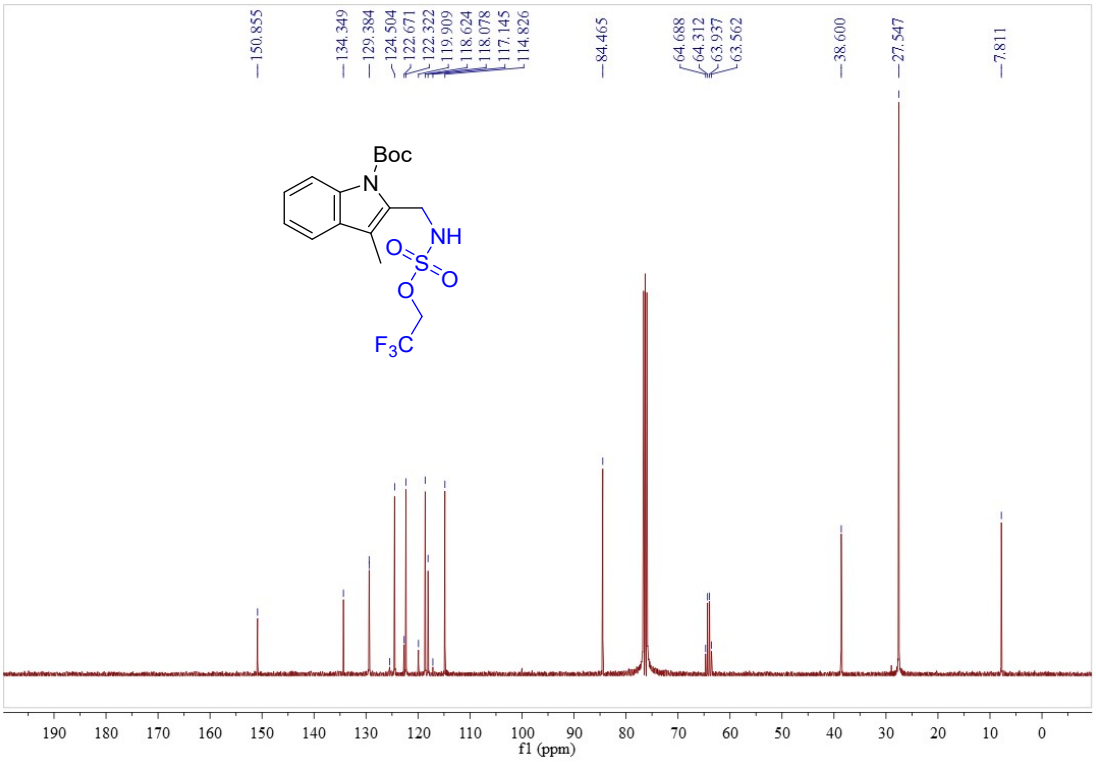


Figure S92. ^{13}C NMR of **6** (100 MHz, $CDCl_3$)

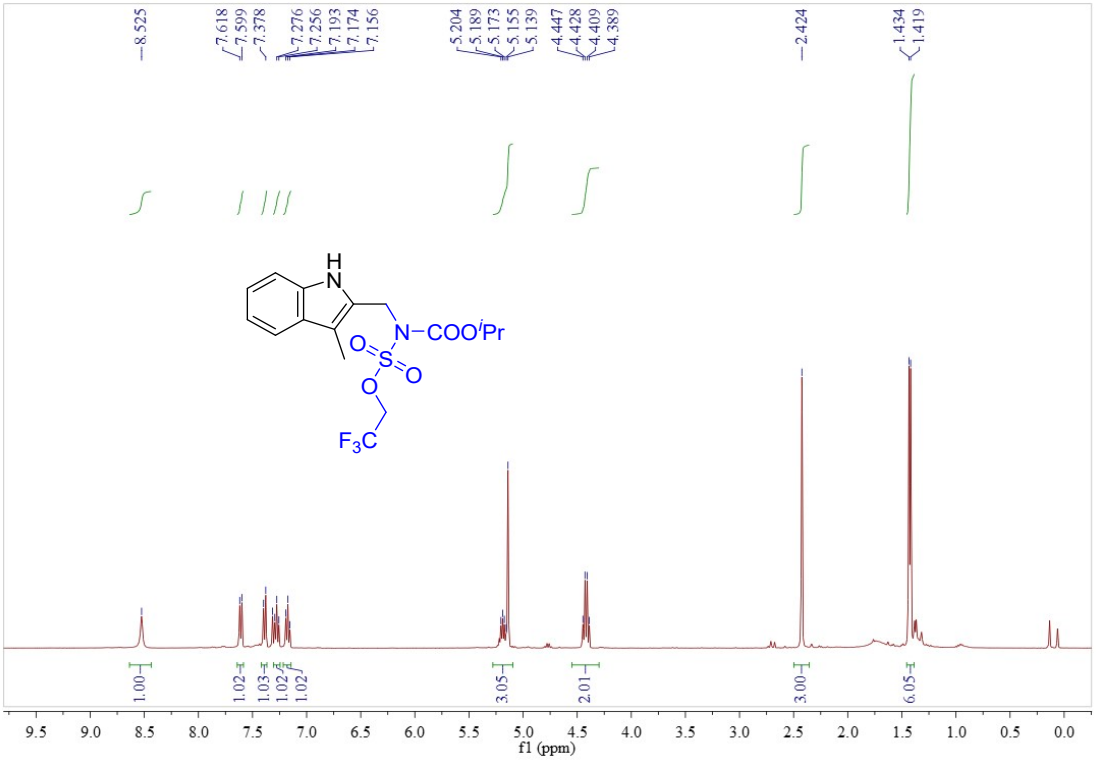


Figure S93. ^{1}H NMR of **7** (400 MHz, $CDCl_3$)

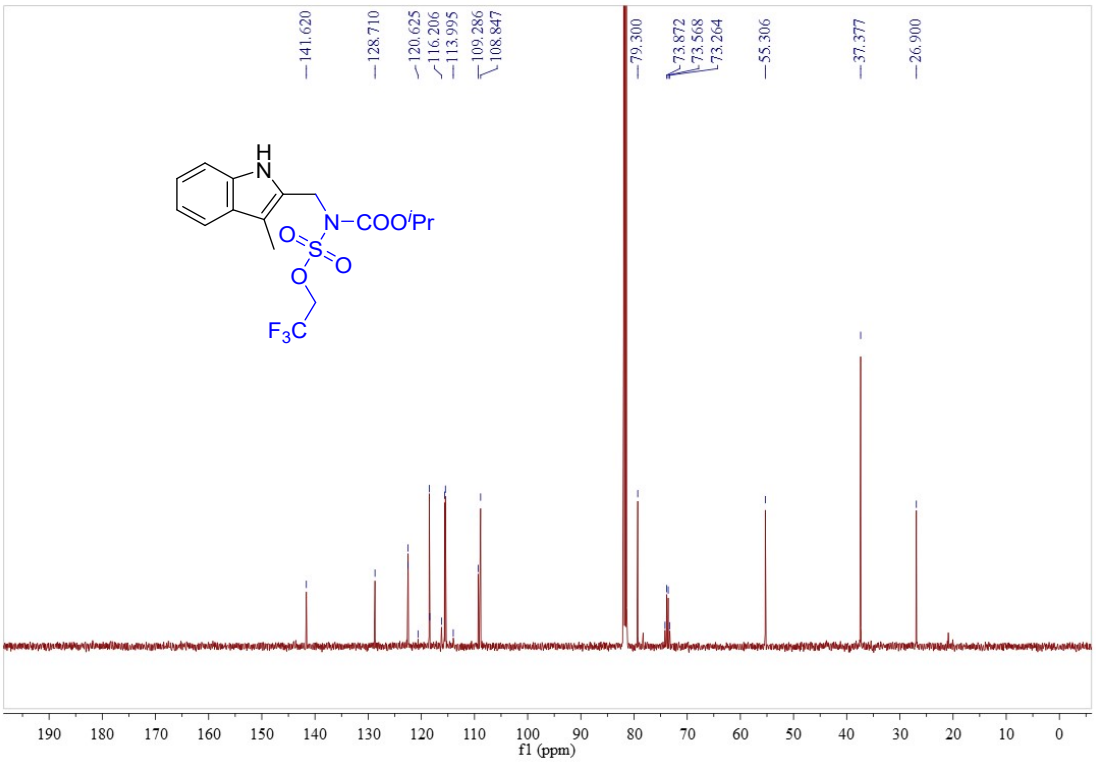


Figure S94. ^{13}C NMR of **7** (100 MHz, $CDCl_3$)