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Electro-oxidative intermolecular C_{SP}^2-H amination of heteroarenes via proton-coupled electron transfer

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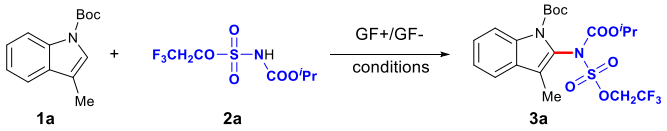
Supporting Information

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. Additional optimization of electrochemical amination reaction

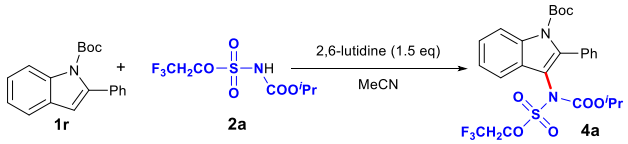
2.1 The optimization of different concentration of 2,6-lutidine [a]



Entry	Base	Solvent	Yield (%)
1	2,6-lutidine (0.1 eq)	MeCN	trace
2	2,6-lutidine (0.2 eq)	MeCN	trace
3	2,6-lutidine (0.5 eq)	MeCN	33%
4	2,6-lutidine (1.0 eq)	MeCN	68%
5	2,6-lutidine (1.5 eq)	MeCN	76%
6	2,6-lutidine (2.0 eq)	MeCN	72%

[a] Reaction conditions: **1a** (0.24 mmol), **2a** (0.2 mmol), 2,6-lutidine, MeCN (3.0 mL), rt, GF+ / GF-, 6.5 V cell voltage, 4 h.

2.2 The electrode optimization of product 4a[a]



Entry	Anode +	Cathode -	Yield (%)
1	Graphite felt	Graphite felt	35
2	platina	platina	71
3	nickel foam	platina	58
4	Graphite	platina	55
5	platina	Graphite felt	65

[a] Reaction conditions: **1r** (0.24 mmol), **2a** (0.2 mmol), 2,6-lutidine (1.5 eq), MeCN (3.0 mL), rt, Anode+ / Cathode-, 6.5 V cell voltage, 4 h.

3. General procedures for electrochemical reactions

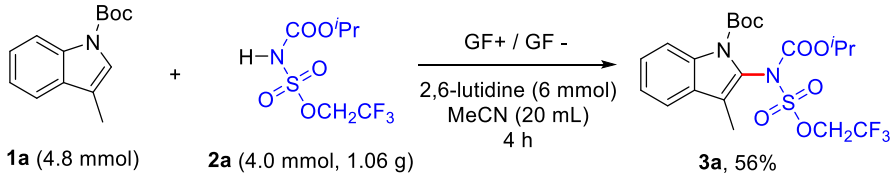
3.1 General procedure A:

According to our previous work (*CCS Chem*. **2022**, *4*, 693–703), 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 stir bar. The flask was equipped with a rubber stopper, graphite felt (1.5 cm x 1 cm x 0.3 cm, produced by Inner Mongolia Wanxing Carbon Company) as anode and cathode, Two electrodes were separated with a teflon film. 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. 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 General procedure B:

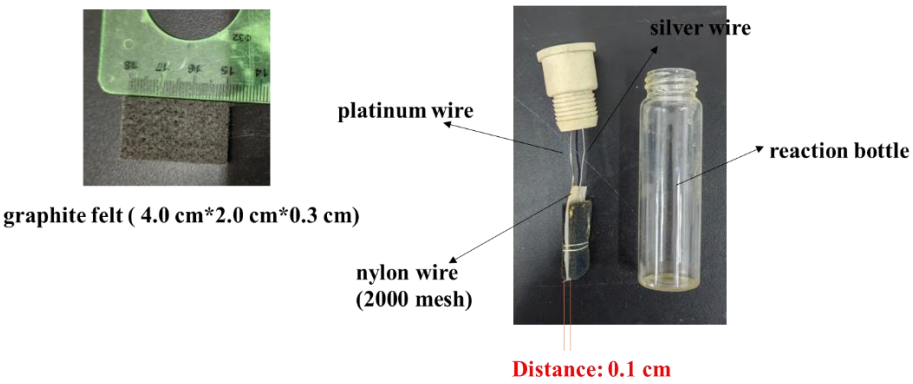
According to our previous work (*CCS Chem.* **2022**, *4*, 693–703), a 10 mL three-necked heart-shaped flask was charged with the substrate **1** (0.24 mmol), **2** (0.2 mmol), 2.6-lutidine (0.3 mmol) and a magnetic stir bar. The flask was equipped with a rubber stopper, Pt plate (15 mm x 10 mm x 0.1 mm) as anode and Pt plate (15 mm x 10 mm x 0.1 mm) as cathode. The flask was evacuated and backfilled with nitrogen for three times, then a nitrogen balloon was connected to this flask via a needle. Next, 3 mL of anhydrous MeCN was added via syringe. The electrolysis with constant cell potential was carried out at room temperature. After the completion of reaction 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**.

3.3 Gram scale reaction:



1a (4.8 mmol) **2a** (4.0 mmol, 1.06 g) **3a**, 56%

A 40 mL reaction bottle was charged with the substrate **1a** (4.8 mmol, 1.11 g), **2a** (4.0 mmol, 1.06 g), 2.6-lutidine (6.0 mmol, 0.64 g) and a magnetic stir bar. The flask was equipped with a rubber stopper, graphite felt (4.0 cm x 2.0 cm x 0.3 cm, produced by Inner Mongolia Wanxing Carbon Company) as both anode and cathode, two electrodes were separated with a nylon wire (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 8.5 V cell voltage was carried out at room temperature. After 4 hours, the reaction was 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 **3a** (56%, 1.10 g).



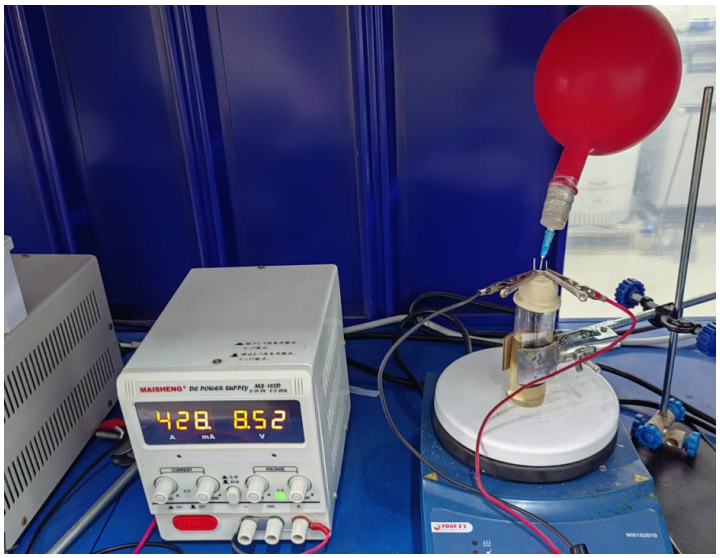


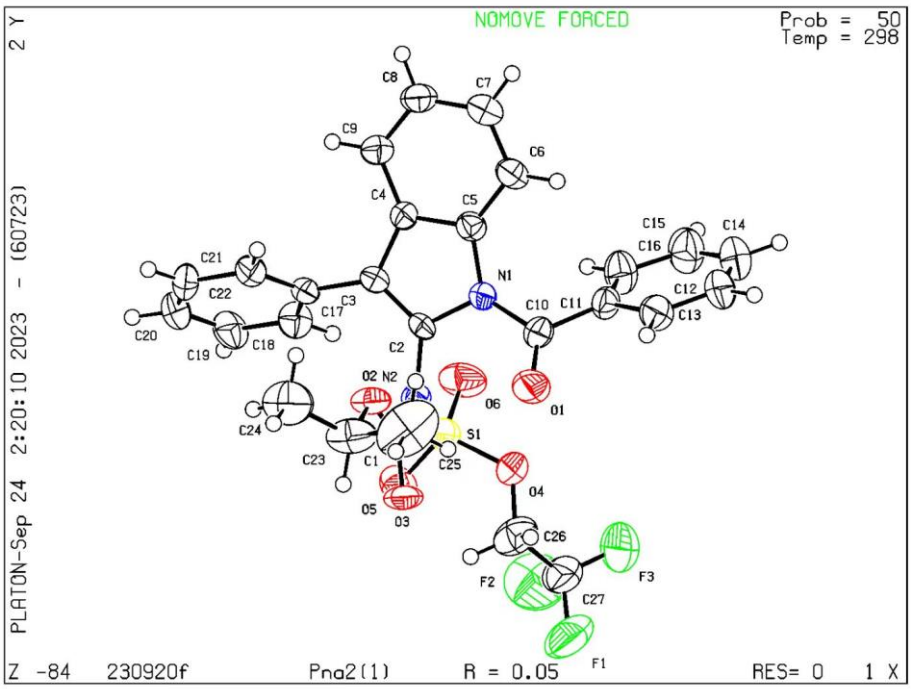
Figure 1. Electrolysis setup

4. The thermal ellipsoid plot of 3o and 8

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

Table 1 Crystal data and structure refinement for 3o

Identification code	3o
CCDC	2320450
Empirical formula	$C_{27}H_{23}F_3N_2O_6S$
Formula weight	560.53
Temperature/K	298(2)
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	15.0600(14)
b/Å	17.7122(16)
c/Å	9.6717(9)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	2579.9(4)
Z	4
ρ_{calc}g/cm^3	1.443
μ/mm^{-1}	0.193
F(000)	1160.0
Crystal size/mm^3	0.28 × 0.23 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	44.6 to 50.04
Index ranges	$-17 \le h \le 16$, $-21 \le k \le 21$, $-11 \le l \le 8$
Reflections collected	12126
Independent reflections	4035 [R_{int} = 0.0607, R_{sigma} = 0.0786]
Data/restraints/parameters	4035/1/354
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0550, wR_2 = 0.1200
Final R indexes [all data]	R_1 = 0.0863, wR_2 = 0.1370
Largest diff. peak/hole / e Å^{-3}	0.34/-0.31

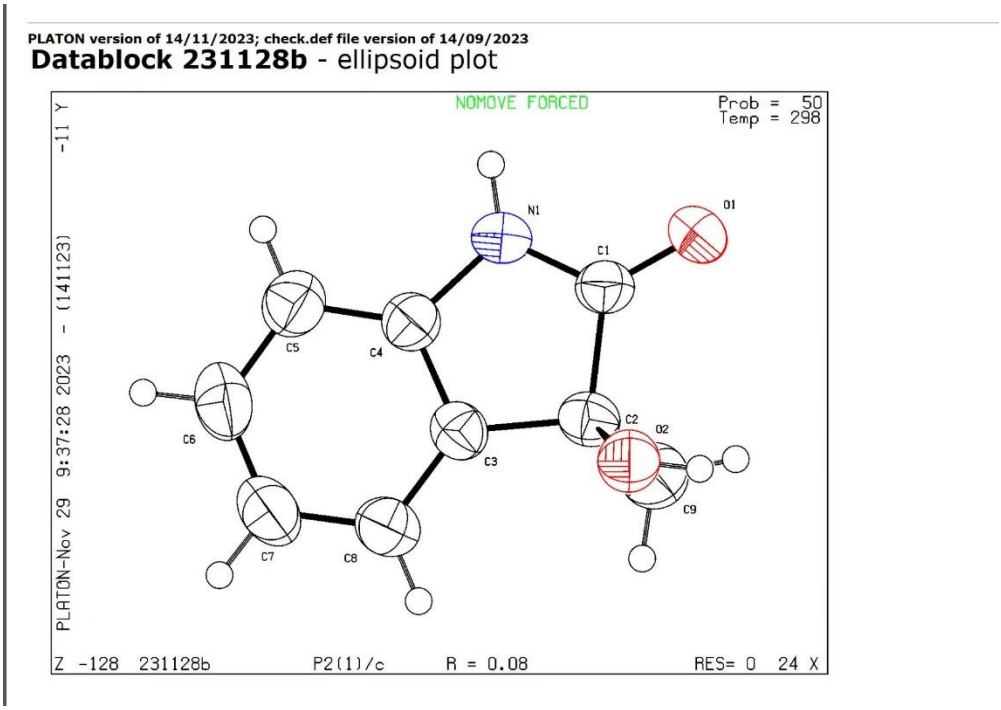


Add 100 mg of **8** to a 25 mL beaker, completely dissolve it with EtOAc. A single crystal 8 was obtained by slowly evaporating at room temperature under the air conditions.

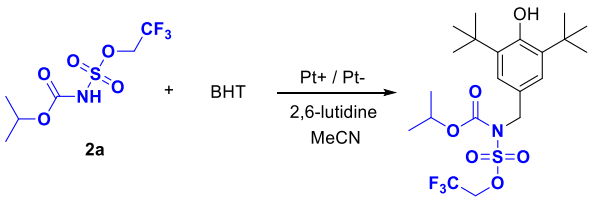
Table 2 Crystal data and structure refinement for 8

Identification code	8
CCDC	2311019
Empirical formula	$C_9H_9NO_2$
Formula weight	163.17
Temperature/K	298(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.2336(8)
b/Å	10.6828(11)
c/Å	10.9368(12)
α/°	90.00
β/°	101.791(4)
γ/°	90.00
Volume/Å^3	827.31(15)
Z	4
ρ_{calc}g/cm^3	1.310
μ/mm^{-1}	0.094
F(000)	344.0
Crystal size/mm^3	0.35 × 0.16 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.38 to 50.04
Index ranges	-8 ≤ h ≤ 8, -12 ≤ k ≤ 12, -4 ≤ l ≤ 12
Reflections collected	1442
Independent reflections	1442 [R_{int} = 0.0000, R_{sigma} = 0.0748]
Data/restraints/parameters	1442/0/112

Goodness-of-fit on F^2	1.095
Final R indexes [I>=2σ (I)]	R_1 = 0.0795, wR_2 = 0.1824
Final R indexes [all data]	R_1 = 0.1081, wR_2 = 0.1982
Largest diff. peak/hole / e Å^{-3}	0.29/-0.24

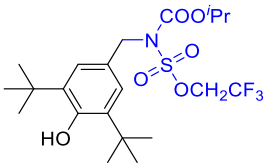


5. The capture of Carbonyl sulfonyl substituted *N*-radical species

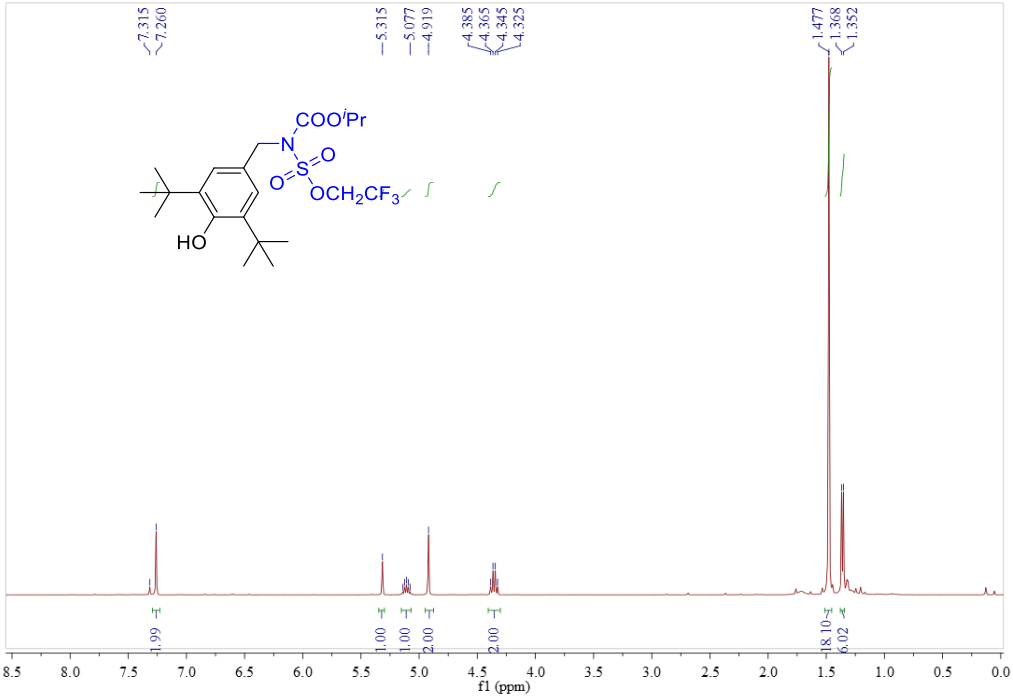


Following the general **procedure B**, a 10 mL three-necked heart-shaped flask was charged with the 2,6-di-*tert*-butyl-4-methylphenol (0.3 mmol, 0.066 g), **2a** (0.2 mmol, 0.053 g), 2.6-lutidine (0.3 mmol, 0.032 g) and a magnetic stir bar. The flask was equipped with a rubber stopper, Pt plate (15 mm x 10 mm x 0.1 mm) as anode, and Pt plate (15 mm x 10 mm x 0.1 mm) as cathode. The flask was evacuated and backfilled with nitrogen for three times, then a nitrogen balloon was connected to this flask via a needle. Next, 3 mL of anhydrous MeCN was added via syringe. The electrolysis with constant cell potential was carried out at room temperature. After the completion of reaction monitored with TLC, the mixture was concentrated under reduced pressure. The residue was purified by chromatography on silica gel to afford the yellow oil **9** (0.048g, 50%).

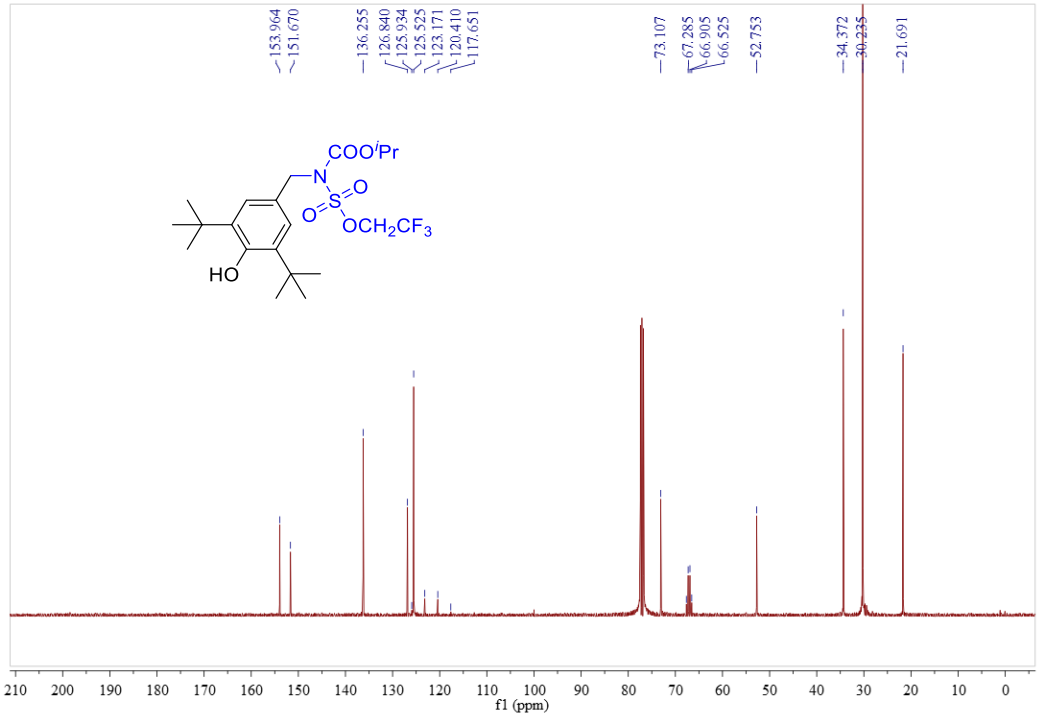
2,2,2-trifluoroethyl (isopropoxycarbonyl)(3-methyl-1H-indol-2-yl)sulfamate (9)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (s, 2H), 5.31 (s, 1H), 5.11 (dt, *J* = 12.5, 6.2 Hz, 1H), 4.92 (s, 2H), 4.35 (q, *J* = 8.0 Hz, 2H), 1.48 (s, 118H), 1.36 (d, *J* = 6.3 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 154.0, 151.7, 136.3, 126.8, 125.5, 121.8 (q, *J* = 276.1 Hz), 73.1, 67.1 (q, *J* = 38.2 Hz), 52.8, 34.4, 30.2, 21.7. **HRMS m/z (ESI)** calcd. for $C_{21}H_{32}F_3NNaO_6S^+$ (M + Na)$^+$ 506.1800, found 506.1805.



^{1}H NMR of **9** (100 MHz, $CDCl_3$)



^{13}C NMR of **9** (100 MHz, $CDCl_3$)

6. Cyclic voltammetry experiments of reactants

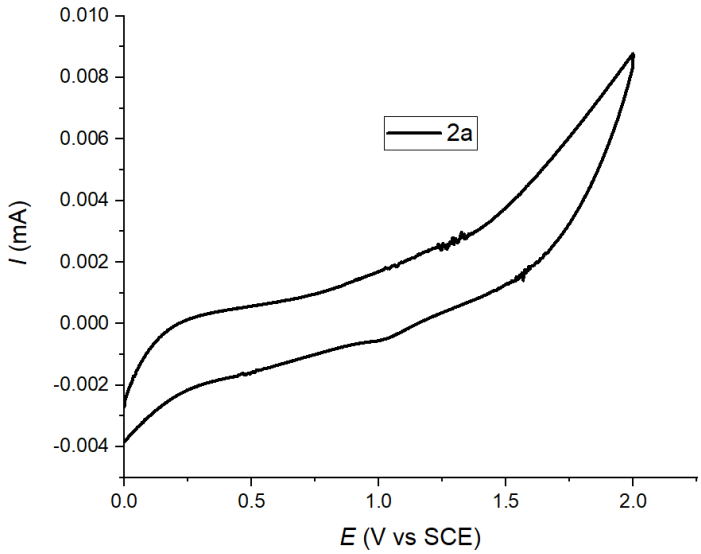


Figure 2. 2a in MeCN

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 $^{n}Bu_4NClO_4$ (0.03 M in MeCN). Potential sweep rate was 50 mV/s.

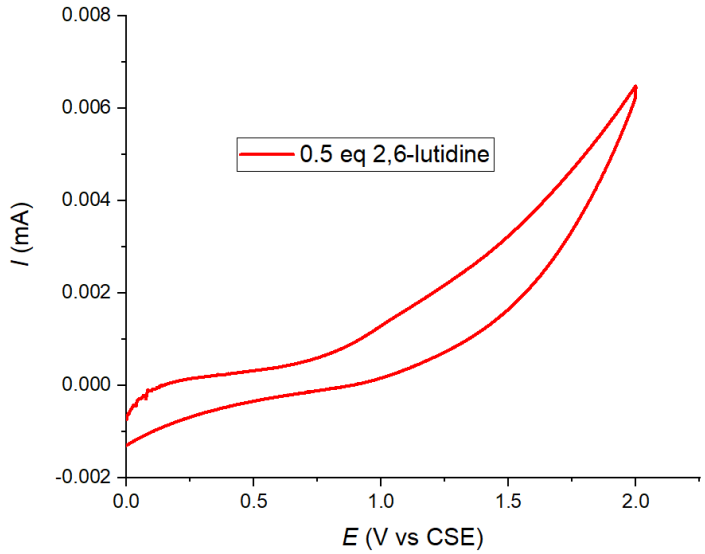


Figure 3. 2,6-lutidine in MeCN

A solution of **2,6-lutidine** (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 $^{n}Bu_4NClO_4$ (0.03 M in MeCN). Potential sweep rate was 50 mV/s.

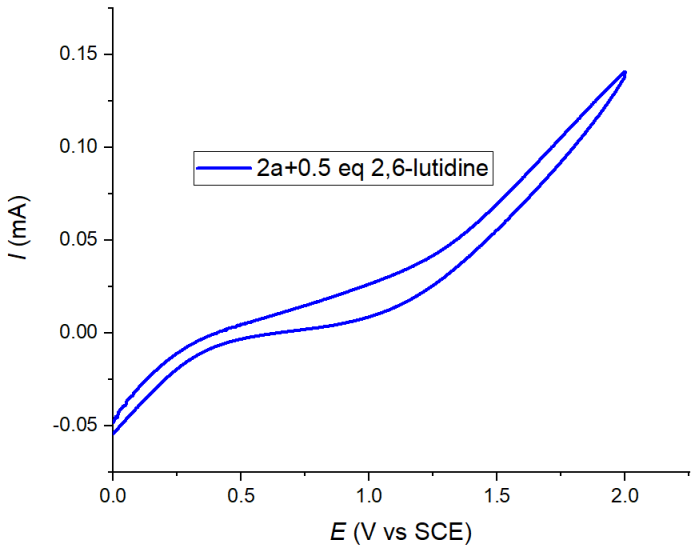


Figure 4. 2a and 2,6-lutidine (0.5 eq) in MeCN

A solution of **2a** (0.1 mmol), **2,6-lutidine** (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 $^{n}Bu_4NClO_4$ (0.03 M in MeCN). Potential sweep rate was 50 mV/s.

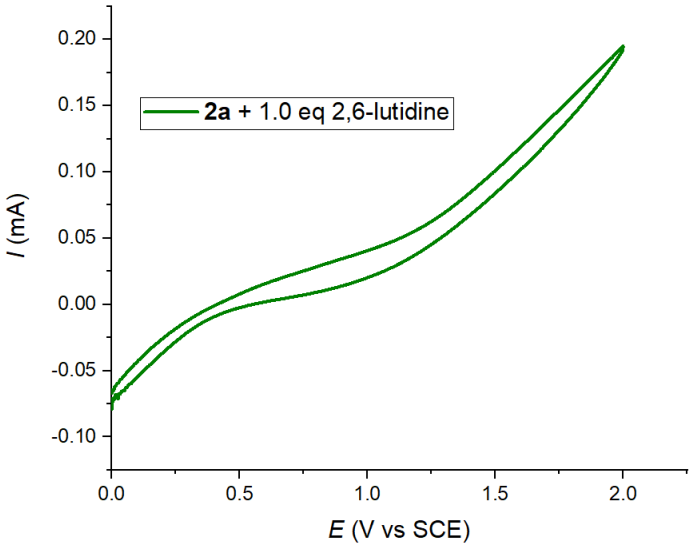


Figure 5. 2a and 2,6-lutidine (1.0 eq) in MeCN

A solution of **2a** (0.1 mmol), **2,6-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 $^{n}Bu_4NClO_4$ (0.03 M in MeCN). Potential sweep rate was 50 mV/s.

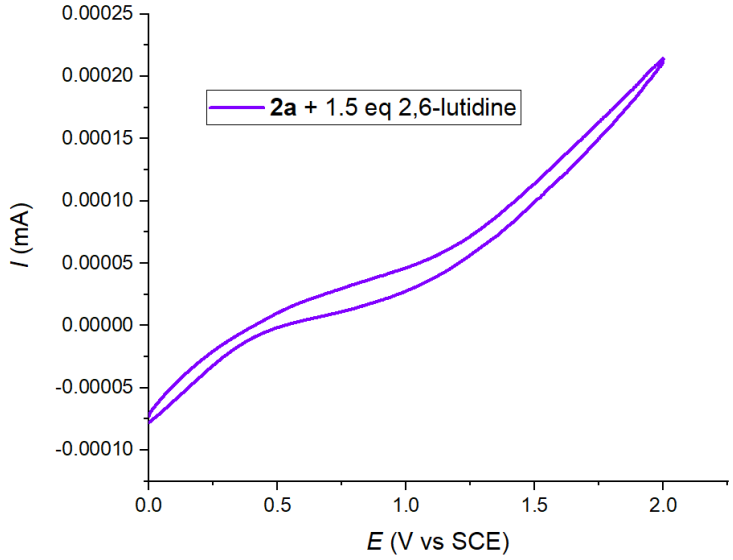


Figure 6. 2a and 2,6-lutidine (1.5 eq) in MeCN

A solution of **2a** (0.1 mmol), **2,6-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 $^{n}Bu_4NClO_4$ (0.03 M in MeCN). Potential sweep rate was 50 mV/s.

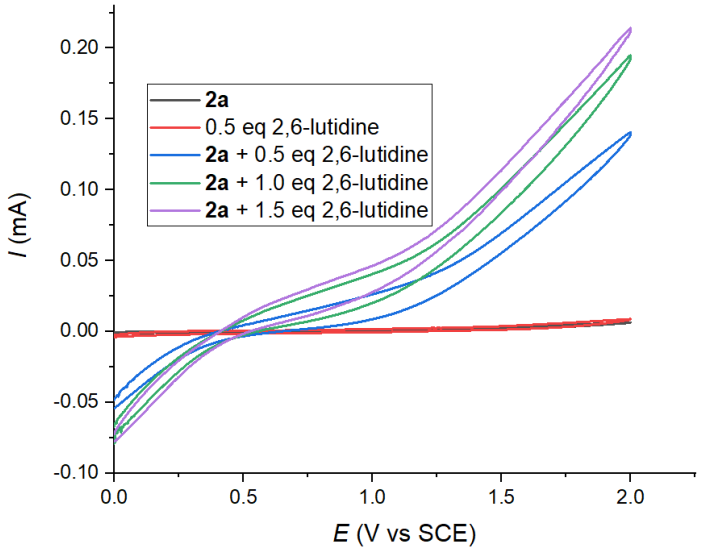
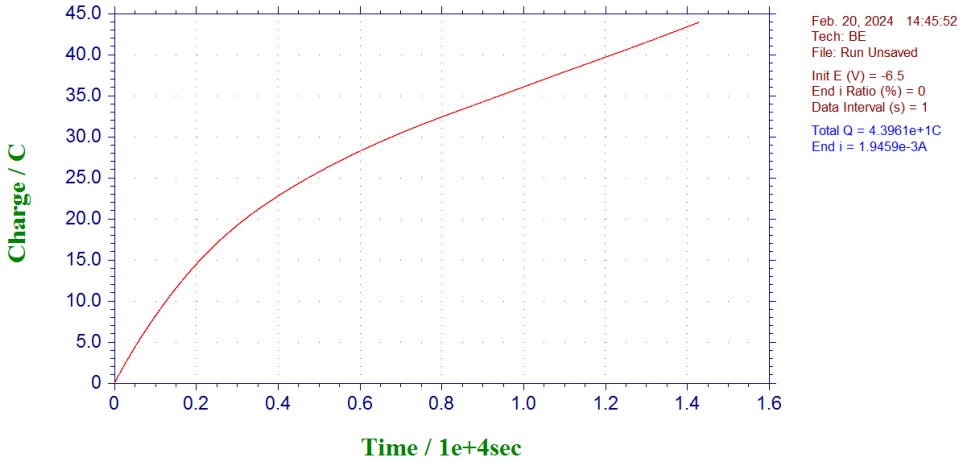


Figure 7. Overlapped CV results in MeCN

7. Measurement of faraday of electrons per mole of substrate

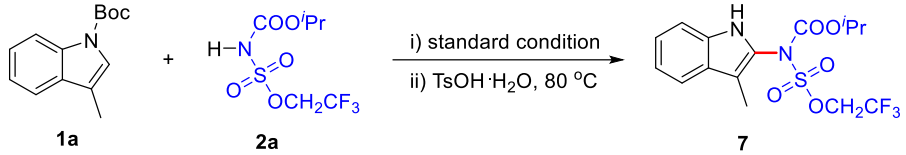
The reaction was setup under standard electrochemical reaction condition（constant potential condition: **1a** (0.24 mmol), **2a** (0.2 mmol), 2, 6-lutidine (0.3 mmol), MeCN (3.0 mL), 6.5 V cell voltage, rt.）using CHI 730E bipotentiostat as power source with bulk electrolysis method (BE).

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 = 43.961/(96485*0.0002) F/mol = 2.3 F/mol.

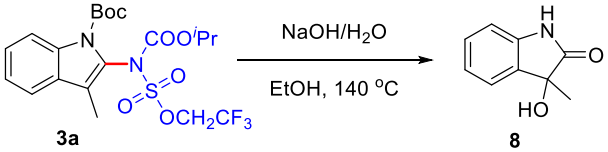
8. Transformation of 3a



1a **2a** **7**

Following the general **procedure A**, a 10 mL two-necked heart-shaped flask was charged with the substrate **1a** (0.24 mmol, 55.4 mg), **2a** (0.2 mmol, 53.0 mg), 2.6-lutidine (0.3 mmol, 32.1 mg) and a magnetic stir bar. The flask was equipped with a rubber stopper, graphite felt (1.5 cm x 1 cm x 0.3 cm, produced by Inner Mongolia Wanxing Carbon Company) as both anode and cathode, Two electrodes were separated with a teflon film. 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. 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.

Then, the previous mixture, TsOH·H_2O (38 mg, 0.2 mmol) and DCE (2.0 mL) was added to a 25 mL reaction tube. The tube was sealed with a teflon cap with screw and the mixture was heated at 80 °C for 3 h. After cooling to room time, the reaction mixture was alkalized to pH 12 with 2 M NaOH and extracted with ethyl acetate 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 the achromic oil **7** (49.6 mg, 63%).

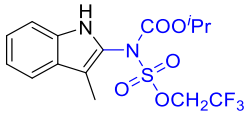


3a **8**

A mixture of *tert*-butyl-2-((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)-3-methyl-

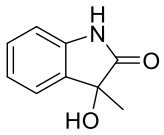
1H-indole-1-carboxylate (**3a**) (0.1 mmol, 49.4 mg,), NaOH (20 mg, 0.5 mmol), H_2O (0.1 mL) and EtOH (2.0 mL) was added to a 25 mL reaction tube. The tube was sealed with a teflon cap with screw and the mixture was heated at 140 °C for 12 h. After cooling to room time, the reaction mixture was extracted 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 the white solid **8** (12.5 mg, 76%).

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

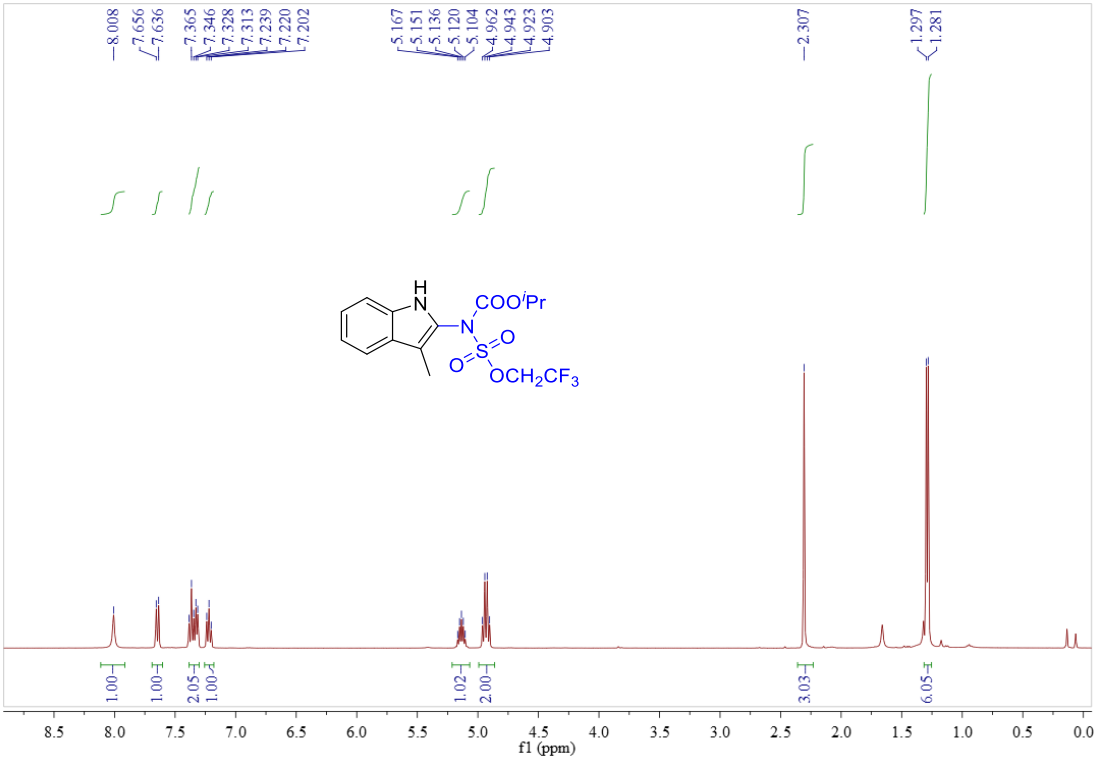


^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (s, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.38 – 7.30 (m, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 5.14 (dt, *J* = 12.5, 6.2 Hz, 1H), 4.93 (q, *J* = 7.9 Hz, 2H), 2.31 (s, 3H), 1.29 (d, *J* = 6.2 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 151.2, 134.3, 127.3, 123.9, 121.8 (q, *J* = 275.9 Hz), 120.0, 119.8, 111.4, 111.0, 73.9, 68.9 (q, *J* = 38.2 Hz), 21.5, 7.9.

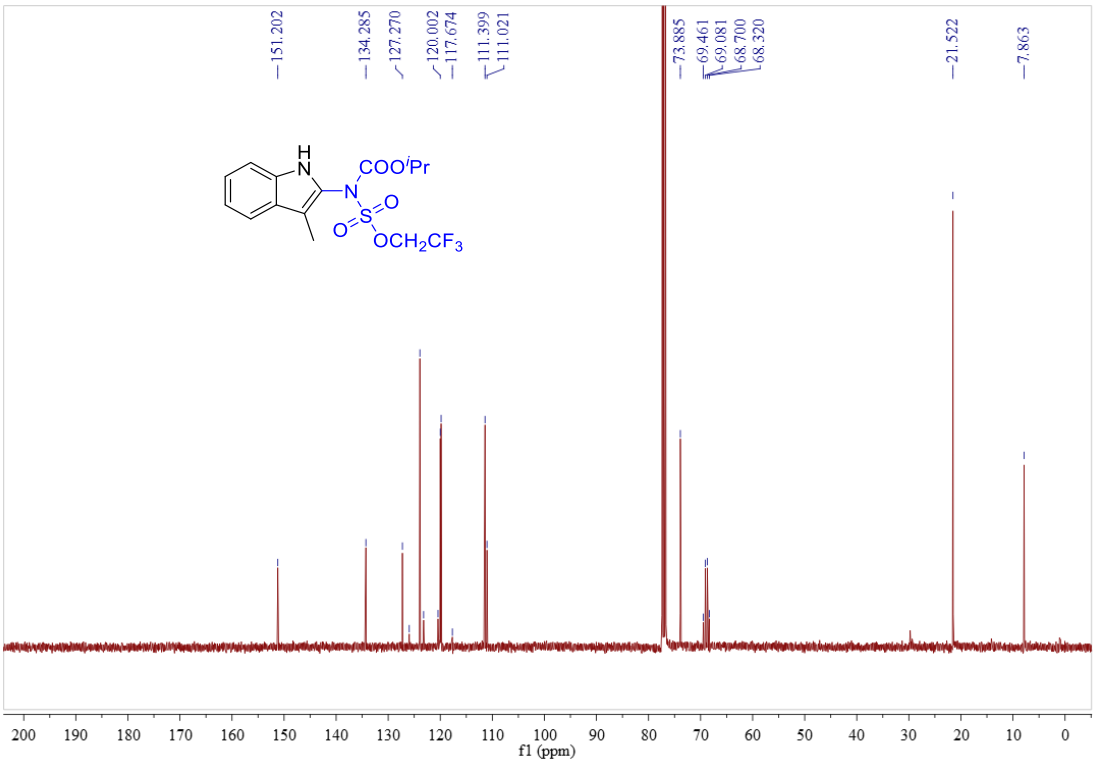
3-hydroxy-3-methylindolin-2-one (8)



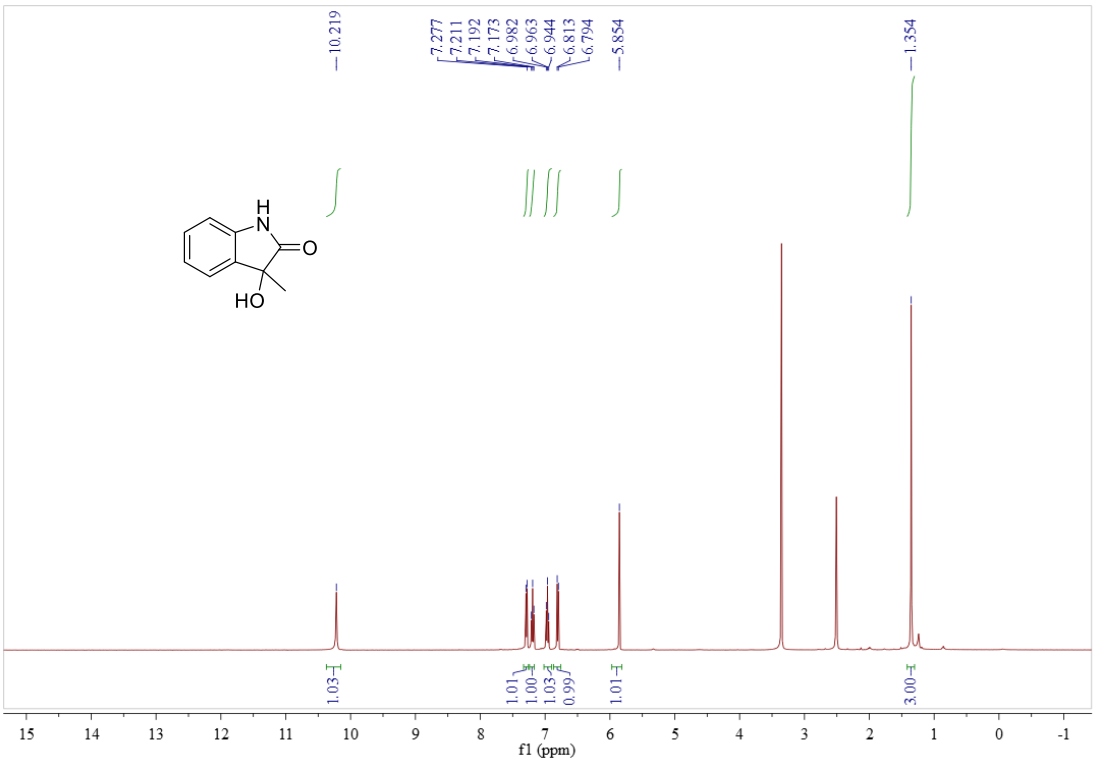
mp 165.1– 166.1 °C. **^{1}H NMR (400 MHz, DMSO-*d*)** δ 10.22 (s, 1H), 7.29 (d, *J* = 7.3 Hz, 1H), 7.19 (t, *J* = 7.7 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 7.7 Hz, 1H), 5.85 (s, 1H), 1.35 (s, 3H). **^{13}C NMR (100 MHz, DMSO-*d*)** δ 1180.2, 141.6, 134.1, 129.3, 123.9, 122.1, 110.1, 73.1, 25.0.



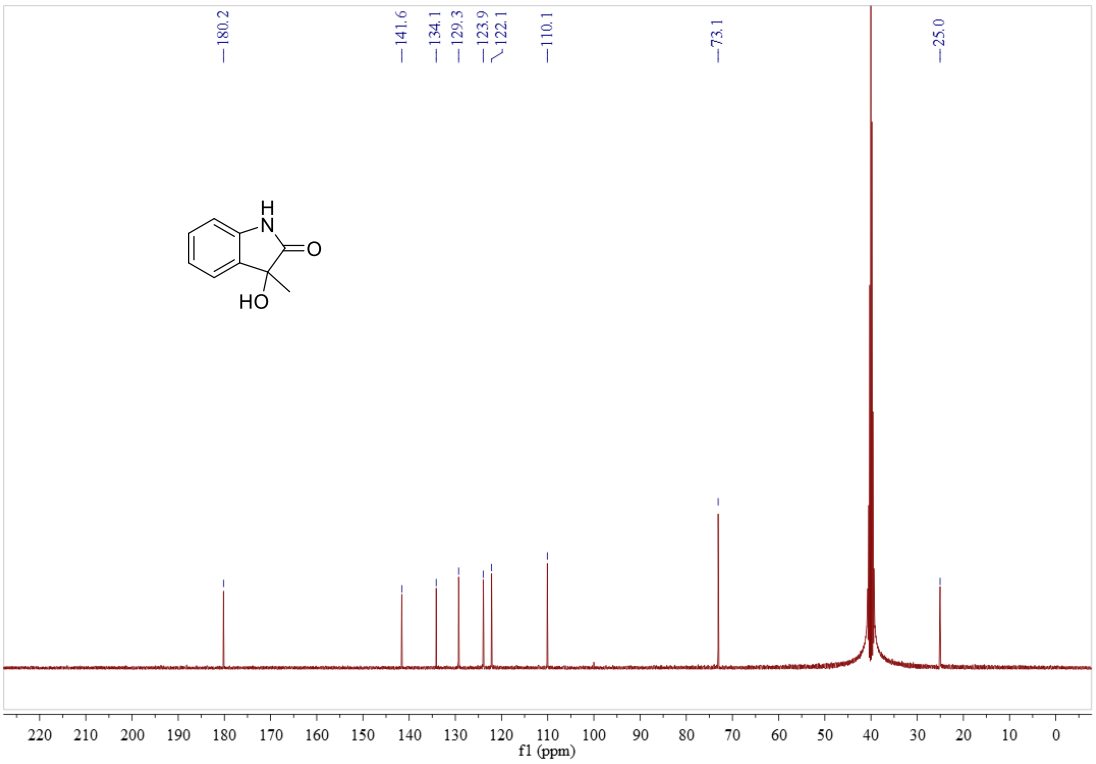
^{1}H NMR of **7** (100 MHz, $CDCl_3$)



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



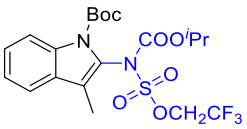
^{1}H NMR of **8** (100 MHz, DMSO-d_6)



^{13}C NMR of **8** (100 MHz, DMSO-d_6)

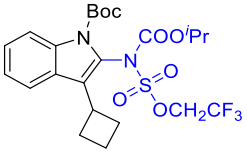
9. Characterization of products

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



Following the general **procedure A** on 0.1 mmol scale with 6.5 V cell potential, the substrate **3a** was obtained as a white solid in 77% yield (38.0 mg). mp 106.3 – 107.3 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.12 (d, J = 8.4 Hz, 1H), 7.59 (d, J = 7.7 Hz, 1H), 7.49 – 7.23 (m, 2H), 5.29 – 4.81 (m, 3H), 2.28 (s, 3H), 1.69 (s, 9H), 1.25 (dd, J = 6.1, 3.2 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 151.1, 149.2, 134.6, 127.7, 126.1, 124.7, 122.9, 121.9 (q, *J* = 275.6 Hz), 119.7, 119.1, 115.9, 84.7, 73.2, 68.8 (q, *J* = 38.0 Hz), 28.1, 21.6, 21.5, 8.0. **HRMS m/z (ESI)** calcd. for $C_{20}H_{25}F_3N_2NaO_7S^+$ (M + Na)$^+$ 517.1232, found 517.1234.

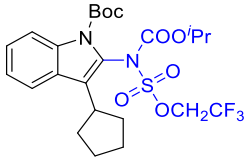
tert-butyl-3-cyclobutyl-2-((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)-1H-indole-1-carboxylate (3b)



Following the general **procedure A** on 0.2 mmol scale with 6.5 V cell potential, the substrate **3b** was obtained as a white solid in 62% yield (66.2 mg). mp 171.6 – 172.6 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.11 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.29 (dd, *J* = 10.2, 4.7 Hz, 1H), 5.22 – 4.96 (m, 2H), 4.87 (dq, *J* = 12.3, 8.0 Hz, 1H), 3.88 – 3.69 (m, 1H), 2.65 – 2.37 (m, 4H), 2.26 – 2.10 (m, 1H), 1.99 (dd, *J* = 18.8, 8.5 Hz, 1H), 1.68 (s, 9H), 1.25 (dd, *J* = 9.6, 6.3 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δδ 151.2, 149.2, 134.8, 126.8, 125.7, 123.4, 122.7,

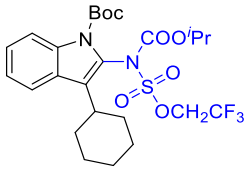
121.9 (q, *J* = 275.9 Hz), 120.8, 116.1, 84.7, 73.0, 68.9 (q, *J* = 38.0 Hz), 32.0, 28.5, 28.1, 27.8, 21.6, 21.5, 19.5. **HRMS m/z (ESI)** calcd. for $C_{23}H_{29}F_3N_2NaO_7S^+$ (M + Na)$^+$ 557.1545, found 557.1551.

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



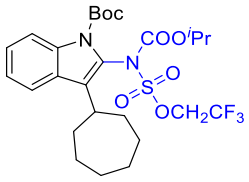
Following the general **procedure A** on 0.2 mmol scale with 6.5 V cell potential, the substrate **3c** was obtained as a white solid in 60% yield (65.7 mg). mp 108.9 – 109.9 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.17 (d, *J* = 8.5 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.28 (t, *J* = 3.9 Hz, 1H), 5.16 – 5.01 (m, 2H), 4.86 (dq, *J* = 12.3, 8.0 Hz, 1H), 3.28 – 3.13 (m, 1H), 2.14 – 1.76 (m, 8H), 1.68 (s, 9H), 1.23 (d, *J* = 6.3 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ151.3, 149.1, 135.3, 126.2, 125.8, 125.6, 123.9, 122.5, 122.2 (q, *J* = 275.7 Hz), 120.9, 116.3, 84.7, 73.0, 68.9 (q, *J* = 38.4 Hz), 36.3, 31.9, 31.3, 28.1, 26.5, 21.6, 21.5. **HRMS m/z (ESI)** calcd. for $C_{24}H_{31}F_3N_2NaO_7S^+$ (M + Na)$^+$ 571.1702, found 571.1709.

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



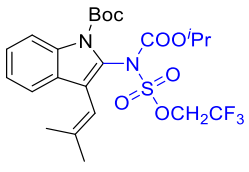
Following the general **procedure A** on 0.1 mmol scale with 6.5 V cell potential, the substrate **3d** was obtained as a white solid in 61% yield (68.5 mg). mp 118.5 – 119.5 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.17 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 5.20 – 5.02 (m, 2H), 4.87 (dq, *J* = 12.3, 7.9 Hz, 1H), 2.79 (dd, *J* = 15.2, 7.7 Hz, 1H), 2.00 – 1.73 (m, 7H), 1.68 (s, 9H), 1.47 – 1.32 (m, 3H), 1.24 (d, *J* = 6.2 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ151.3, 149.1, 135.3, 127.2, 126.2, 125.6, 123.2, 122.5, 121.9 (q, *J* = 275.8 Hz) 121.4, 116.2, 84.7, 73.0, 69.0 (q, *J* = 38.2 Hz), 36.3, 31.7, 30.7, 28.1, 26.8, 26.6, 26.2, 21.6, 21.5. **HRMS m/z (ESI)** calcd. for $C_{25}H_{33}F_3N_2NaO_7S^+$ (M + Na)$^+$ 585.1858, found 585.1866.

tert-butyl 3-cycloheptyl-2-((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)-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 50% yield (57.6 mg). mp 148.4 – 149.4 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.17 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 3.6 Hz, 1H), 5.17 – 5.03 (m, 2H), 4.87 (dq, *J* = 12.3, 7.9 Hz, 1H), 2.92 (tt, *J* = 10.7, 3.6 Hz, 1H), 2.07 – 1.98 (m, 2H), 1.91 – 1.51 (m, 19H), 1.23 (d, *J* = 6.3 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ151.3, 149.2, 135.4, 129.0, 125.9, 125.6, 122.5, 122.2, 121.9 (q, *J* = 275.8 Hz)， 121.5, 116.2, 84.6, 730, 69.0 (q, *J* = 38.9 Hz), 37.7, 33.9, 33.0, 28.3, 28.1, 27.9, 27.8, 27.7, 21.5. **HRMS m/z (ESI)** calcd. for $C_{26}H_{35}F_3N_2NaO_7S^+$ (M + Na)$^+$ 599.2015, found 599.2024.

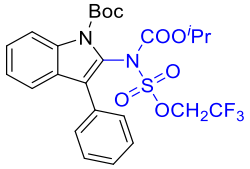
tert-butyl 2-((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)-3-(2-methylprop-1-en-1-yl)-1*H*-indole-1-carboxylate (3f)



Following the general **procedure A** on 0.2 mmol scale with 6.5 V cell potential, the substrate **3f** was obtained as a white solid in 51% yield (54.5 mg). mp 71.9 – 72.9 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.16 (d, *J* =

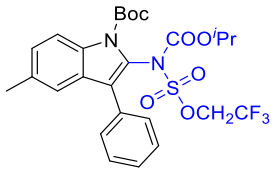
8.4 Hz, 1H), 7.49 – 7.38 (m, 2H), 7.29 (dd, *J* = 9.4, 5.6 Hz, 1H), 6.00 (s, 1H), 4.96 (dddd, *J* = 20.1, 12.2, 10.3, 5.3 Hz, 3H), 1.98 (s, 3H), 1.67 (d, *J* = 10.1 Hz, 12H), 1.23 (dd, *J* = 9.0, 6.3 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 150.9, 149.1, 142.3, 134.6, 127.0, 125.9, 124.4, 122.9, 121.9 (q, *J* = 275.7 Hz), 121.1, 121.0, 116.0, 112.4, 84.9, 73.1, 68.5 (q, *J* = 38.0 Hz), 28.1, 25.5, 21.6, 21.5, 20.5. **HRMS m/z (ESI)** calcd. for $C_{23}H_{29}F_3N_2NaO_7S^+$ (M + Na)$^+$ 557.1545, found 557.1554.

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



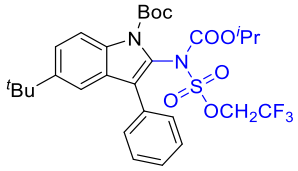
Following the general **procedure A** on 0.1 mmol scale with 6.5 V cell potential, the substrate **3g** was obtained as a white solid in 86% yield (47.8 mg). mp 129.1 – 130.1 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.25 (d, *J* = 8.5 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.55 – 7.41 (m, 6H), 7.32 (t, *J* = 7.5 Hz, 1H), 5.16 (dt, *J* = 12.5, 6.3 Hz, 1H), 4.33 – 4.15 (m, 2H), 1.71 (s, 9H), 1.31 (d, *J* = 6.3 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 150.5, 148.3, 134.1, 130.20, 128.5, 128.1, 127.7, 126.1, 125.7, 123.2, 122.6, 120.9 (q, *J* = 275.7 Hz), 119.8, 115.3, 84.6, 72.6, 67.0 (q, *J* = 38.7 Hz), 27.3, 20.9. **HRMS m/z (ESI)** calcd. for $C_{25}H_{28}F_3N_2O_7S^+$ (M + H)$^+$ 557.1569, found 557.1559.

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



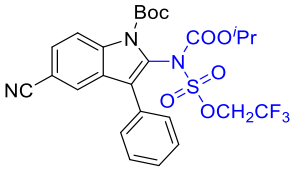
Following the general **procedure A** on 0.1 mmol scale with 6.5 V cell potential, the substrate **3h** was obtained as a white solid in 82% yield (46.7 mg). mp 140.9 – 141.9 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.12 (d, *J* = 8.6 Hz, 1H), 7.54 – 7.44 (m, 5H), 7.36 (s, 1H), 7.32 – 7.29 (m, 1H), 5.15 (dt, *J* = 12.5, 6.3 Hz, 1H), 4.40 – 4.18 (m, 2H), 2.45 (s, 3H), 1.71 (s, 9H), 1.30 (dd, *J* = 6.2, 2.1 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ151.2, 149.1, 133.1, 133.0, 131.1, 129.3, 128.8, 128.3, 127.9, 127.0, 124.0, 123.7, 121.5 (q, *J* = 275.6 Hz), 120.2, 115.8, 85.1, 73.3, 67.7 (q, *J* = 38.6 Hz), 28.1, 21.6, 21.2. **HRMS m/z (ESI)** calcd. for $C_{26}H_{29}F_3N_2NaO_7S^+$ (M + Na)$^+$ 593.1545, found 593.1561.

tert-butyl 5-(tert-butyl)-2-((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)-3-phenyl-1H-indole-1-carboxylate (3i)



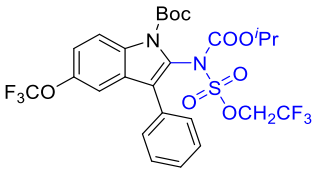
Following the general **procedure A** on 0.1 mmol scale with 6.5 V cell potential, the substrate **3i** was obtained as a white oil in 80% yield (49.0 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.16 (d, *J* = 9.5 Hz, 1H), 7.64 – 4.40 (m, 7H), 5.17 (dt, *J* = 12.5, 6.2 Hz, 1H), 4.47– 4.12 (m, 2H), 1.71 (s, 9H), 1.38 (s, 9H), 1.33 – 1.23 (m, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 151.3, 149.1, 146.6, 132.9, 131.2, 129.3, 128.9, 128.3, 126.6, 124.6, 124.2, 121.6 (q, *J* = 275.9 Hz), 120.2, 116.3, 115.7, 85.1, 73.3, 67.8 (q, *J* = 37.6 Hz), 34.7, 31.6, 28.1, 21.6. **HRMS m/z (ESI)** calcd. for $C_{29}H_{35}F_3N_2NaO_7S^+$ (M + Na)$^+$ 635.2015, found 635.2032.

tert-butyl 5-cyano-2-((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)-3-phenyl-1H-indole-1-carboxylate (3j)



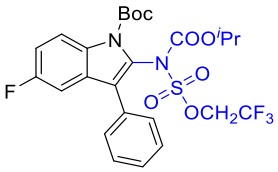
Following the general **procedure A** on 0.1 mmol scale with 6.5 V cell potential, the substrate **3j** was obtained as a white solid in 63% yield (36.5 mg). mp 68.6 – 69.6 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.36 (d, *J* = 8.8 Hz, 1H), 7.92 (s, 1H), 7.71 (d, *J* = 8.7 Hz, 1H), 7.61–7.49 (m, 3H), 7.44 (d, *J* = 7.0 Hz, 2H), 5.15 (dt, *J* = 12.4, 6.2 Hz, 1H), 4.50– 4.18 (m, 2H), 1.72 (s, 9H), 1.31 (d, *J* = 4.4 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 150.8, 148.4, 136.6, 129.6, 129.2(9), 129.2(6), 129.1, 129.0, 126.9, 126.1, 125.6, 123.5, 121.4 (q, *J* = 276.0 Hz), 119.1, 117.1, 107.1, 86.8, 73.8, 68.0 (q, *J* = 38.8 Hz), 28.0, 21.6(9), 21.6(5). **HRMS m/z (ESI)** calcd. for $C_{26}H_{26}F_3N_3NaO_7S^+$ (M + Na)$^+$ 604.1341, found 604.1348.

tert-butyl 2-((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)-3-phenyl-5-(trifluoromethoxy)-1H-indole-1-carboxylate (3k)



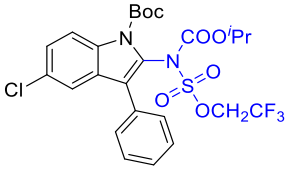
Following the general **procedure A** on 0.1 mmol scale with 6.5 V cell potential, the substrate **3k** was obtained as a white solid in 55% yield (35.2 mg). mp 122.8 – 123.8 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.28 (d, *J* = 9.2 Hz, 1H), 7.62 – 7.37 (m, 6H), 7.35 (d, *J* = 9.2 Hz, 1H), 5.16 (dt, *J* = 12.5, 6.3 Hz, 1H), 4.30 (dd, *J* = 17.1, 8.8 Hz, 2H), 1.71 (s, 9H), 1.31 (d, *J* = 6.3 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 151.0, 148.7, 145.4, 133.0, 130.2, 129.2, 129.0, 128.7, 127.4, 125.5, 123.7, 121.5 (q, *J* = 276.0 Hz), 120.6 (q, *J* = 255.0 Hz), 120.0, 117.4, 112.9, 86.0, 73.6, 67.9 (q, *J* = 38.1 Hz), 28.0, 21.6(9), 21.6(8). **HRMS m/z (ESI)** calcd. for $C_{26}H_{26}F_6N_2NaO_8S^+$ (M + Na)$^+$ 663.1212, found 663.1219.

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



Following the general **procedure A** on 0.1 mmol scale with 6.5 V cell potential, the substrate **3l** was obtained as a white solid in 70% yield (40.2 mg). mp 155.3 – 156.3 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.23 (dd, *J* = 9.1, 4.5 Hz, 1H), 7.58 – 7.41 (m, 5H), 7.28 – 7.15 (m, 2H), 5.16 (hept, *J* = 6.3 Hz, 1H), 4.43 – 4.18 (m, 2H), 1.71 (s, 9H), 1.32 (d, *J* = 6.3 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 159.5 (d, *J* = 241.1 Hz), 151.0, 148.8, 131.2, 130.5, 129.2, 129.0, 128.6, 127.7 (d, *J* = 9.8 Hz), 125.2, 123.6 (d, *J* = 4.1 Hz), 121.5 (d, *J* = 275.9 Hz), 117.5 (d, *J* = 8.7 Hz), 114.6 (d, *J* = 24.9 Hz), 105.9 (d, *J* = 24.2 Hz), 85.7, 73.5, 67.8 (q, *J* = 38.4 Hz), 28.0, 21.6, 21.6. **HRMS m/z (ESI)** calcd. for $C_{25}H_{26}F_4N_2NaO_7S^+$ (M + Na)$^+$ 597.1295, found 597.1305.

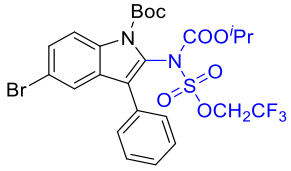
tert-butyl 5-chloro-2-((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)-3-phenyl-1H-indole-1-carboxylate (3m)



Following the general **procedure A** on 0.1 mmol scale with 6.5 V cell potential, the substrate **3m** was obtained as a white solid in 62% yield (36.6 mg). mp 154.3 – 155.3 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.20 (d, *J* = 9.0 Hz, 1H), 7.57 – 7.42 (m, 7H), 5.15 (dq, *J* = 12.5, 6.2 Hz, 1H), 4.30 (dd, *J* = 16.0, 7.9 Hz, 2H), 1.71 (s, 9H), 1.31 (d, *J* = 6.3 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 151.0, 148.7, 133.2, 130.3, 129.3, 129.2, 129.0, 128.7, 128.0, 126.8, 123.2, 121.5 (d, *J* = 275.7 Hz), 120.0, 117.4, 85.9, 73.6, 67.8 (d, *J* = 38.4 Hz), 28.0,

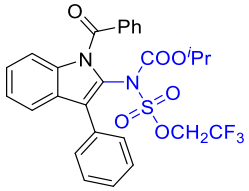
21.6(0), 21.6(9). **HRMS m/z (ESI)** calcd. for $C_{25}H_{26}ClF_3N_2NaO_7S^+$ (M + Na)$^+$ 613.0999, found 613.1010.

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



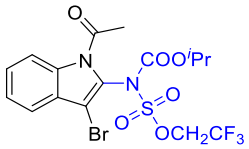
Following the general **procedure A** on 0.1 mmol scale with 6.5 V cell potential, the substrate **3n** was obtained as a white solid in 63% yield (40.0 mg). mp 138.1 – 139.1 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.14 (d, *J* = 9.0 Hz, 1H), 7.70 (d, *J* = 1.8 Hz, 1H), 7.52 – 7.43 (m, 6H), 5.15 (dt, *J* = 12.5, 6.3 Hz, 1H), 4.44 – 4.12 (m, 2H), 1.70 (s, 9H), 1.31 (d, *J* = 6.3 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 151.0, 148.7, 133.5, 130.3, 129.4, 129.2, 129.0, 128.7, 128.5, 124.9, 123.1, 121.5 (d, *J* = 275.8 Hz), 117.7, 116.8, 85.9, 67.9 (q, *J* = 38.2 Hz), 28.0, 21.6(0), 21.6(8). **HRMS m/z (ESI)** calcd. for $C_{25}H_{26}BrF_3N_2NaO_7S^+$ (M + Na)$^+$ 657.0494, found 657.0502.

2,2,2-trifluoroethyl (1-benzoyl-3-phenyl-1H-indol-2-yl)(isopropoxycarbonyl)sulfamate (3o)



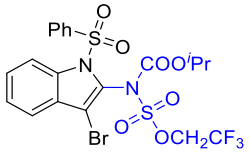
Following the general **procedure A** on 0.1 mmol scale with 6.5 V cell potential, the substrate **3o** was obtained as a white solid in 63% yield (35.3 mg). mp 173.6 – 174.6 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.86 (d, *J* = 7.5 Hz, 2H), 7.72 (dd, *J* = 18.4, 7.9 Hz, 2H), 7.60 (m, 6H), 7.53 – 7.49 (m, 1H), 7.28 (t, *J* = 7.5 Hz, 2H), 6.71 (d, *J* = 8.4 Hz, 1H), 5.18 (dt, *J* = 12.5, 6.3 Hz, 1H), 4.59 (td, *J* = 16.0, 7.9 Hz, 1H), 4.40 – 4.29 (m, 1H), 1.32 (dd, *J* = 11.0, 6.3 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 151.3, 149.4, 136.9, 135.2, 135.1, 130.8, 129.9, 128.4, 125.9, 125.7, 124.1, 121.7 (q, *J* = 276.4 Hz) 117.4, 116.9, 115.9, 84.8, 73.5, 68.4 (q, *J* = 38.3 Hz), 27.6, 21.5(9), 21.5(6). **HRMS m/z (ESI)** calcd. for $C_{27}H_{23}F_3N_2NaO_6S^+$ (M + Na)$^+$ 583.1127, found 583.1134.

2,2,2-trifluoroethyl (1-acetyl-3-bromo-1H-indol-2-yl)(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 53% yield (52.9 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.22 (d, *J* = 8.5 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.9 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 5.19 (dt, *J* = 12.4, 6.2 Hz, 1H), 5.02 (dd, *J* = 13.6, 7.0 Hz, 2H), 2.78 (s, 3H), 1.33 – 1.30 (m, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 168.1, 150.3, 134.3, 128.0, 126.4, 126.3, 124.5, 121.7 (q, *J* = 276.2 Hz), 120.7, 116.2, 104.4, 74.6, 69.5 (q, *J* = 38.5 Hz), 26.1, 21.6(2), 21.6(9). **HRMS m/z (ESI)** calcd. for $C_{16}H_{16}BrF_3N_2NaO_6S^+$ (M + Na)$^+$ 522.9762, found 522.9771.

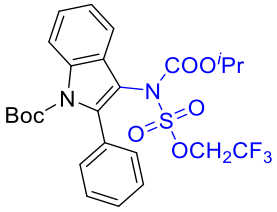
2,2,2-trifluoroethyl (3-bromo-1-(phenylsulfonyl)-1H-indol-2-yl)(isopropoxycarbonyl)sulfamate (3q)



Following the general **procedure A** on 0.1 mmol scale with 6.5 V cell potential, the substrate **3q** was obtained as a white solid in 40% yield (24.0 mg). mp 160.9 – 161.9 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 88.02 (dd, *J* = 18.2, 8.2 Hz, 3H), 7.64 (t, *J* = 6.7 Hz, 2H), 7.51 (dd, *J* = 17.9, 8.4 Hz, 3H), 7.42 (t, *J* = 7.5 Hz, 1H), 5.21 – 4.97 (m, 3H), 1.33 (dd, *J* = 9.4, 6.5 Hz, 6H). **^{13}C NMR (100 MHz,**

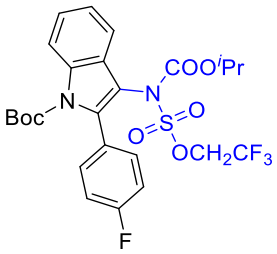
Chloroform-*d*) δ 150.4, 138.5, 134.2, 134.0, 129.4, 127.6, 127.4, 126.68, 126.4, 124.4, 121.9 (q, *J* = 276.2 Hz), 121.0, 114.4, 74.6, 69.5 (q, *J* = 38.1 Hz), 21.7, 21.4. **HRMS m/z (ESI)** calcd. for $C_{20}H_{18}BrF_3N_2NaO_7S_2^+$ (M + Na)$^+$ 620.9589, found 620.9590.

tert-butyl 3-((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)-2-phenyl-1H-indole-1-carboxylate (4a)



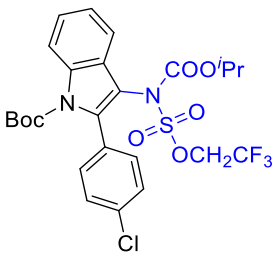
Following the general **procedure B** on 0.1 mmol scale with 6.5 V cell potential, the substrate **4a** was obtained as a white solid in 71% yield (39.5 mg). mp 145.7 – 146.7 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.32 (d, *J* = 8.3 Hz, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.48 – 7.35 (m, 7H), 5.01 (hept, *J* = 6.2 Hz, 1H), 4.32 (dq, *J* = 12.1, 7.9 Hz, 1H), 4.15 (dq, *J* = 12.1, 7.9 Hz, 1H), 1.28 (s, 9H), 1.19 (dd, *J* = 12.7, 6.3 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 151.3, 149.5, 138.0, 135.1, 131.5, 129.4, 128.8, 128.1, 125.8, 125.5, 123.9, 121.6 (q, *J* = 275.8 Hz), 117.3, 116.5, 115.7, 84.3, 73.3, 67.7 (q, *J* = 38.3 Hz), 27.4, 21.4(7), 21.4(5). **HRMS m/z (ESI)** calcd. for $C_{25}H_{27}F_3N_2NaO_7S^+$ (M + Na)$^+$ 579.1389, found 579.1396.

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



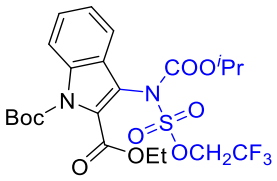
Following the general **procedure B** on 0.1 mmol scale with 6.5 V cell potential, the substrate **4b** was obtained as a white solid in 66% yield (37.9 mg). mp 139.3 – 140.3 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ8.34 (d, *J* = 8.3 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.44 (dq, *J* = 15.3, 7.6 Hz, 4H), 7.20 (t, *J* = 8.3 Hz, 2H), 5.08– 4.96 (m, 1H), 4.63 – 4.44 (m, 2H), 1.36 (s, 9H), 1.20 (dd, *J* = 14.4, 6.2 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 163.2 (d, *J* = 249.3 Hz), 151.3, 149.5, 137.1, 135.1, 131.3 (d, *J* = 8.6 Hz), 127.5 (d, *J* = 3.7 Hz), 125.8, 125.7, 124.1, 121.7 (d, *J* =276.1 Hz), 117.4, 116.9, 115.9, 115.3 (d, *J* = 21.8 Hz), 84.6, 73.4, 68.3 (q, *J* = 38.3 Hz), 27.6, 21.5(9), 21.5(6). **HRMS m/z (ESI)** calcd. for $C_{25}H_{26}F_4N_2NaO_7S^+$ (M + Na)$^+$ 597.1295, found 597.1303.

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



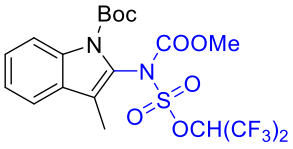
Following the general **procedure B** on 0.1 mmol scale with 6.5 V cell potential, the substrate **4c** was obtained as a white solid in 65% yield (38.4 mg). mp 144.1 – 145.1 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.33 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.43 (dt, *J* = 19.0, 8.2 Hz, 6H), 5.02 (dt, *J* = 12.4, 6.2 Hz, 1H), 4.54 (m, 2H), 1.37 (s, 9H), 1.20 (dd, *J* = 12.7, 6.2 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 168.4, 151.3, 135.1, 134.3, 133.6, 130.8, 130.1, 129.1, 129.0, 128.6, 127.0, 125.6, 125.4, 124.2, 123.2, 121.6 (d, *J* = 276.1 Hz), 121.1, 114.6, 73.9, 68.3 (d, *J* = 38.1 Hz), 21.6(3), 21.6(1). **HRMS m/z (ESI)** calcd. for $C_{25}H_{26}ClF_3N_2NaO_7S^+$ (M + Na)$^+$ 613.0999, found 613.1002.

1-(tert-butyl) 2-ethyl 3-((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)-1H-indole-1,2-dicarboxylate (4d)



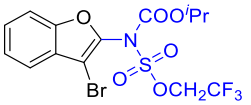
Following the general **procedure B** on 0.1 mmol scale with 6.5 V cell potential, the substrate **4d** was obtained as a colorless oil in 50% yield (31.7 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.16 (d, *J* = 8.5 Hz, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 5.13 – 5.02 (m, 2H), 4.89 (dq, *J* = 15.8, 7.8 Hz, 1H), 4.52 – 4.40 (m, 2H), 1.70 (s, 9H), 1.43 (t, *J* = 7.1 Hz, 3H), 1.28 (d, *J* = 6.2 Hz, 3H), 1.22 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 160.2, 151.0, 148.6, 135.2, 128.0, 127.6, 125.1, 124.3, 121.9 (q, *J* = 275.9), 120.3, 118.5, 115.2, 85.7, 73.7, 68.8 (q, *J* = 38.2 Hz), 62.1, 27.9, 21.5, 21.4, 14.0. **HRMS m/z (ESI)** calcd. for $C_{22}H_{27}F_3N_2NaO_9S^+$ (M + Na)$^+$ 575.1287, found 575.1296.

tert-butyl 2-((((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)sulfonyl)(methoxycarbonyl)amino)-3-methyl-1H-indole-1-carboxylate (4e)



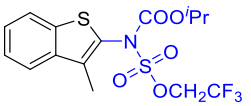
Following the general **procedure A** on 0.1 mmol scale with 6.5 V cell potential, the substrate **4e** was obtained as a white solid in 61% yield (32.5 mg). mp 131.4 – 132.4 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.19 (d, *J* = 8.4 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 5.86 (dt, *J* = 10.9, 5.5 Hz, 1H), 3.86 (s, 3H), 2.28 (s, 3H), 1.68 (s, 9H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 151.5, 148.9, 134.8, 127.5, 126.5, 123.7, 123.0, 120.0 (q, *J* = 282.1 Hz), 119.8 (q, *J* = 282.7 Hz), 119.7, 119.2, 116.0, 85.1, 75.2 (m, *J* = 38.0 Hz), 74.5, 55.2, 28.1, 7.7. **HRMS m/z (ESI)** calcd. for $C_{19}H_{20}F_6N_2NaO_7S^+$ (M + Na)$^+$ 557.0793, found 557.0800.

2,2,2-trifluoroethyl (3-bromobenzofuran-2-yl)(isopropoxycarbonyl)sulfamate (6a)



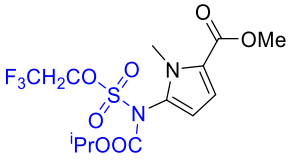
Following the general **procedure A** on 0.1 mmol scale with 6.5 V cell potential, the substrate **6a** was obtained as a colorless oil in 41% yield (18.8 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.64 (d, *J* = 7.7 Hz, 1H), 7.59 – 7.49 (m, 2H), 7.43 (t, *J* = 7.4 Hz, 1H), 5.17 (dt, *J* = 12.4, 6.2 Hz, 1H), 4.93 (q, *J* = 7.7 Hz, 2H), 1.34 (d, *J* = 6.2 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 152.1, 149.3, 140.0, 127.3, 127.2, 124.2, 121.6 (q, *J* = 275.9 Hz), 120.7, 112.14, 98.5, 74.8, 68.7 (q, *J* = 38.5 Hz), 21.5. **HRMS m/z (ESI)** calcd. for $C_{14}H_{13}BrF_3NNaO_6S^+$ (M + Na)$^+$ 481.9497, found 481.9500.

2,2,2-trifluoroethyl (isopropoxycarbonyl)(3-methylbenzo[b]thiophen-2-yl)sulfamate (6b)



Following the general **procedure A** on 0.1 mmol scale with 6.5 V cell potential, the substrate **6b** was obtained as a white solid in 64% yield (26.3 mg). mp 69.7 – 70.7 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.87– 7.75 (m, 2H), 7.52 – 7.46 (m, 2H), 5.14 (dt, *J* = 12.4, 6.2 Hz, 1H), 4.93 (dd, *J* = 14.6, 7.1 Hz, 2H), 2.41 (s, 3H), 1.31 (d, *J* = 6.2 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 150.2, 137.5, 136.8, 132.7, 129.3, 125.3, 123.8, 122.3, 121.9, 121.0 (q, *J* = 276.6 Hz), 73.1, 68.0 (q, *J* = 38.4 Hz), 20.7, 10.3. **HRMS m/z (ESI)** calcd. for $C_{15}H_{16}F_3NNaO_5S_2^+$ (M + Na)$^+$ 434.0320, found 434.0327.

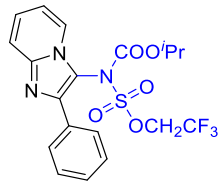
methyl 5-((isopropoxycarbonyl)((2,2,2-trifluoroethoxy)sulfonyl)amino)-1-methyl-1H-pyrrole-2-carboxylate (6c)



Following the general **procedure B** on 0.1 mmol scale with 6.5 V cell potential, the substrate **6c** was obtained as a white oil in 61% yield (24.5 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.99 (d, *J* = 4.2 Hz,

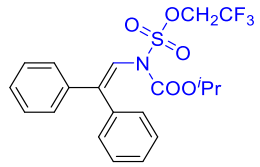
1H), 6.25 (d, *J* = 4.2 Hz, 1H), 5.14 – 5.08 (m, 1H), 4.91 (td, *J* = 13.0, 7.6 Hz, 2H), 3.89 (s, 3H), 3.85 (s, 3H), 1.32 (d, *J* = 6.3 Hz, 3H), 1.28 (d, *J* = 6.1 Hz, 3H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 161.3, 150.9, 127.6, 122.6, 121.7 (q, *J* =275.7 Hz), 116.3, 108.0, 74.1, 68.8 (q, *J* = 38.1 Hz), 51.4, 31.6, 21.5, 21.4. **HRMS m/z (ESI)** calcd. for $C_{13}H_{18}F_3N_2O_7S^+$ (M + H) $^+$ 403.0787, found 403.0784.

2,2,2-trifluoroethyl (isopropoxycarbonyl)(2-phenylimidazo[1,2-a]pyridin-3-yl)sulfamate (6d)



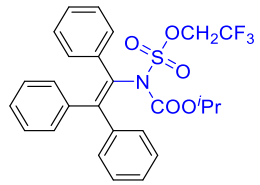
Following the general **procedure A** on 0.1 mmol scale with 6.5 V cell potential, the substrate **6d** was obtained as a colorless oil in 55% yield (25.1 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.01 (d, *J* = 6.8 Hz, 1H), 7.91 (d, *J* = 7.3 Hz, 2H), 7.75 (d, *J* = 9.1 Hz, 1H), 7.56 – 7.38 (m, 4H), 7.04 (t, *J* = 6.8 Hz, 1H), 5.05 (dt, *J* = 12.5, 6.2 Hz, 1H), 4.89 – 4.67 (m, 2H), 1.18 (d, *J* = 6.3 Hz, 3H), 1.04 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 150.9, 144.0, 142.9, 132.2, 129.0, 128.9, 127.5, 126.4, 122.2, 121.7 (q, *J* = 276.2 Hz), 118.2, 113.8, 74.5, 69.1 (q, *J* = 38.6 Hz), 21.4, 21.1. **HRMS m/z (ESI)** calcd. for $C_{19}H_{19}F_3N_3O_5S^+$ (M + H) $^+$ 458.0998, found 458.1007.

2,2,2-trifluoroethyl (2,2-diphenylvinyl)(isopropoxycarbonyl)sulfamate (6e)



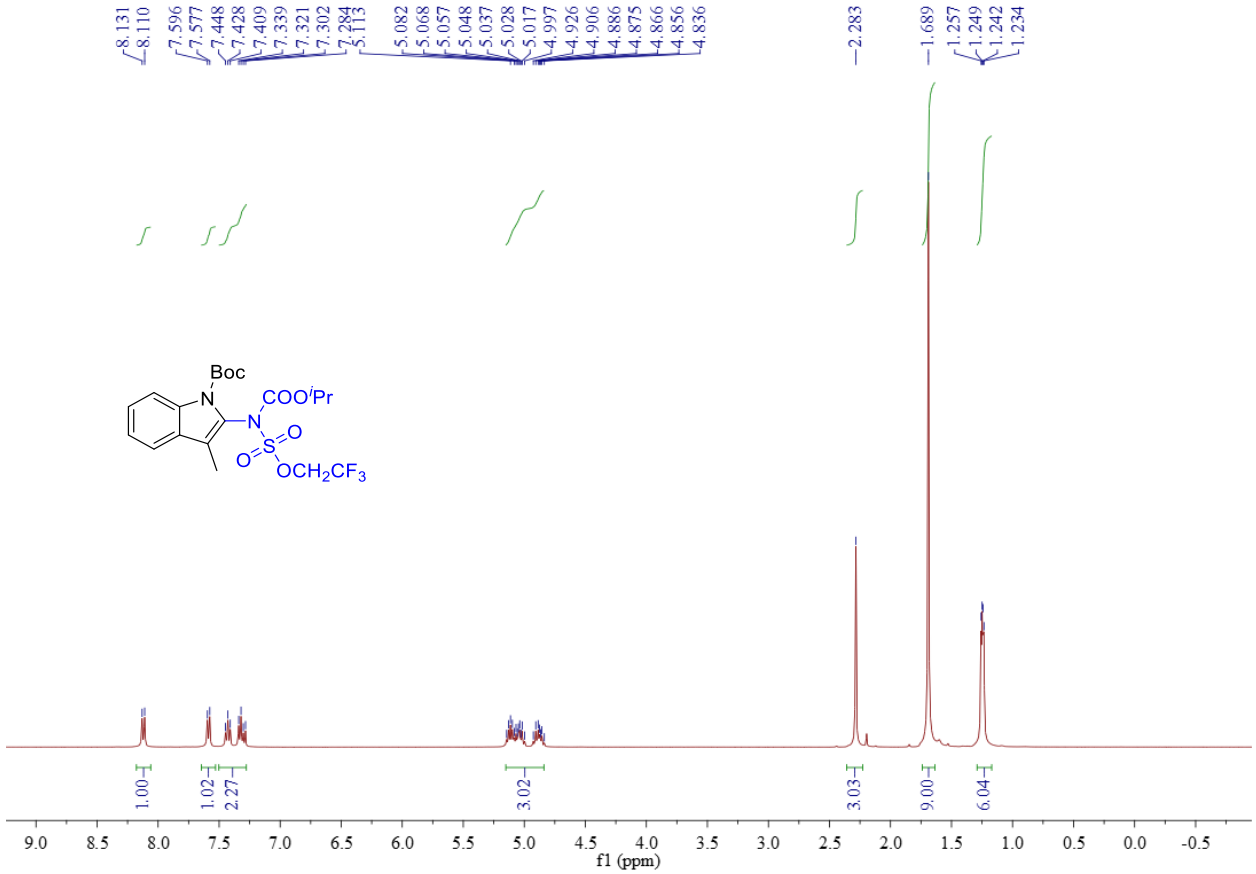
Following the general **procedure B** on 0.1 mmol scale with 6.5 V cell potential, the substrate **6e** was obtained as a colorless oil in 50% yield (22.2 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.42 (t, *J* = 8.4 Hz, 5H), 7.32 (dd, *J* = 14.8, 7.0 Hz, 5H), 6.52 (s, 1H), 4.94 (dt, *J* = 12.4, 6.2 Hz, 11H), 4.40 (q, *J* = 7.9 Hz, 2H), 1.25 (d, *J* = 6.2 Hz, 6H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 150.2, 146.7, 138.1, 136.0, 128.6, 128.3, 127.8, 127.7, 127.60, 120.9 (q, *J* = 276.1 Hz), 117.5, 72.4, 67.0 (q, *J* = 38.2 Hz), 20.7. **HRMS m/z (ESI)** calcd. for $C_{20}H_{20}F_3NNaO_5S^+$ (M + Na) $^+$ 466.0912, found 466.0918.

2,2,2-trifluoroethyl (isopropoxycarbonyl)(1,2,2-triphenylvinyl)sulfamate (6f)

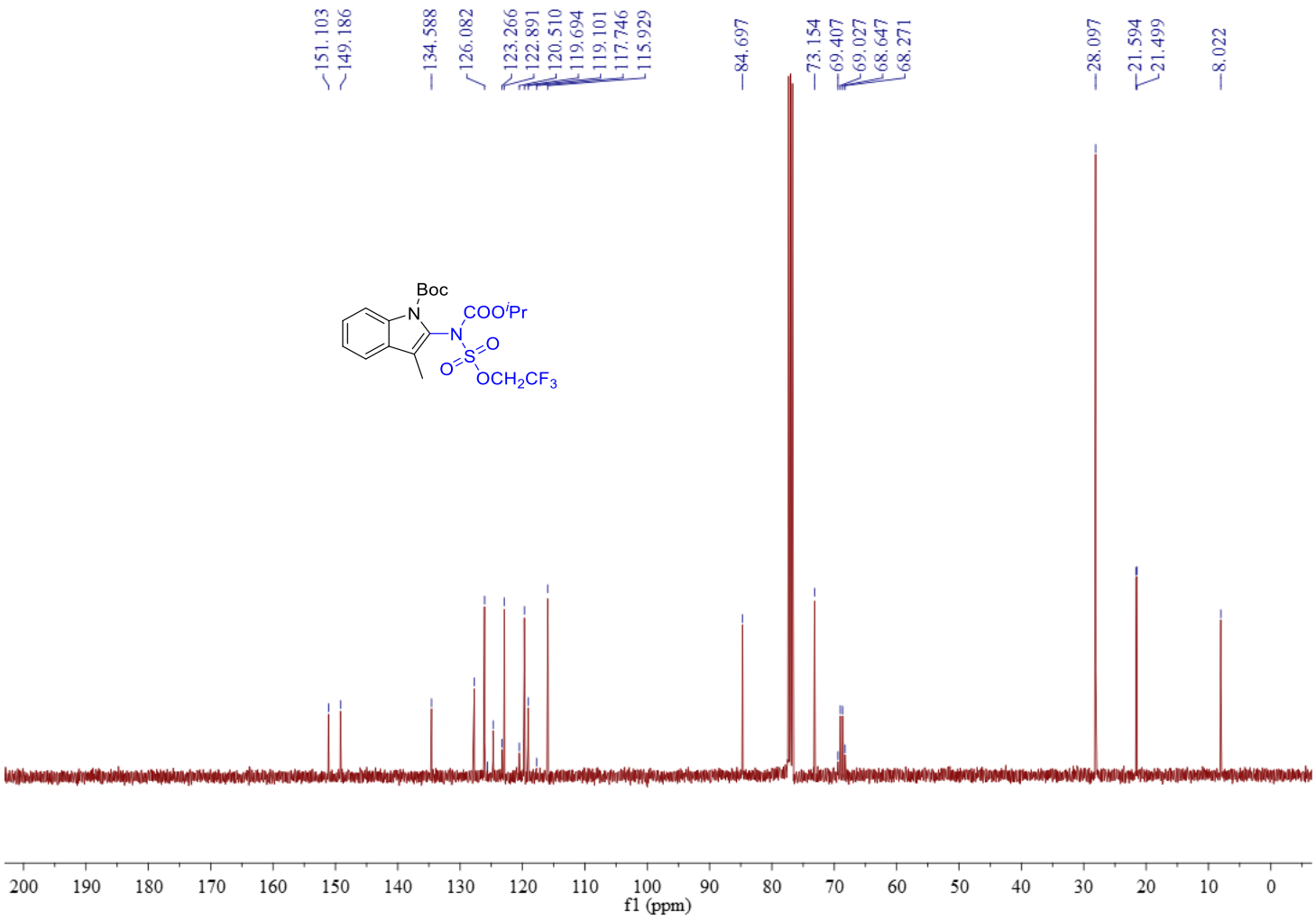


Following the general **procedure B** on 0.1 mmol scale with 6.5 V cell potential, the substrate **3a** was obtained as a colorless oil in 54% yield (28.0 mg). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ7.44 – 7.31 (m, 7H), 7.23 (dd, *J* = 14.7, 4.1 Hz, 6H), 7.13 (d, *J* = 6.5 Hz, 2H), 4.99 (dt, *J* = 12.4, 6.2 Hz, 1H), 4.45 (dd, *J* = 14.0, 6.9 Hz, 2H), 1.34 (d, *J* = 6.1 Hz, 3H), 1.15 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR (100 MHz, Chloroform-*d*)** δ 150.5, 144.8, 139.8, 139.7, 136.4, 130.5, 129.9, 129.0, 128.4, 127.5, 127.3, 127.0, 121.0 (q, *J* = 277.7 Hz), 72.1, 67.4 (q, *J* = 38.2 Hz), 20.9, 20.6. **HRMS m/z (ESI)** calcd. for $C_{26}H_{24}F_3NNaO_5S^+$ (M + Na) $^+$ 542.1225, found 542,1228.

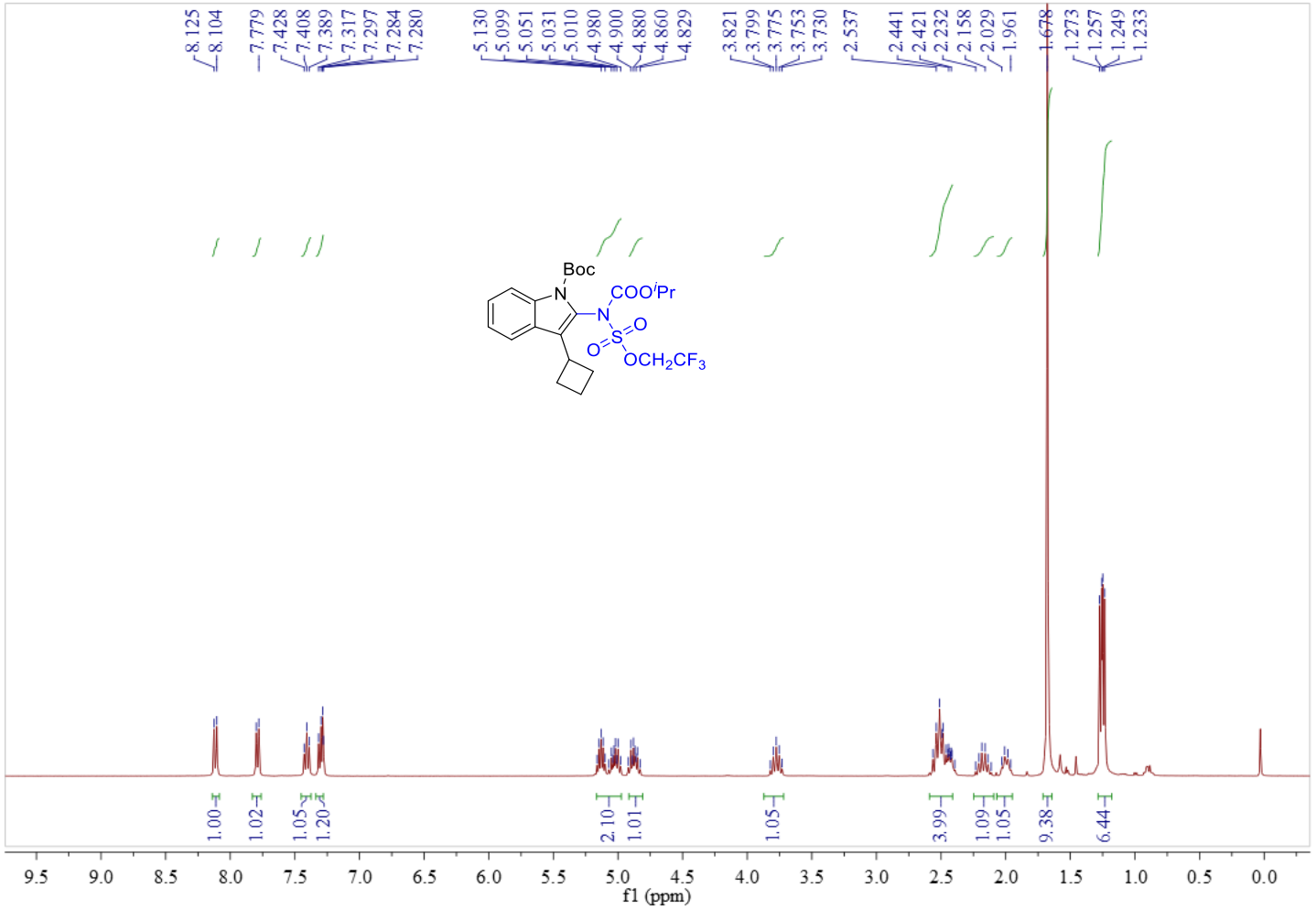
10. NMR spectra



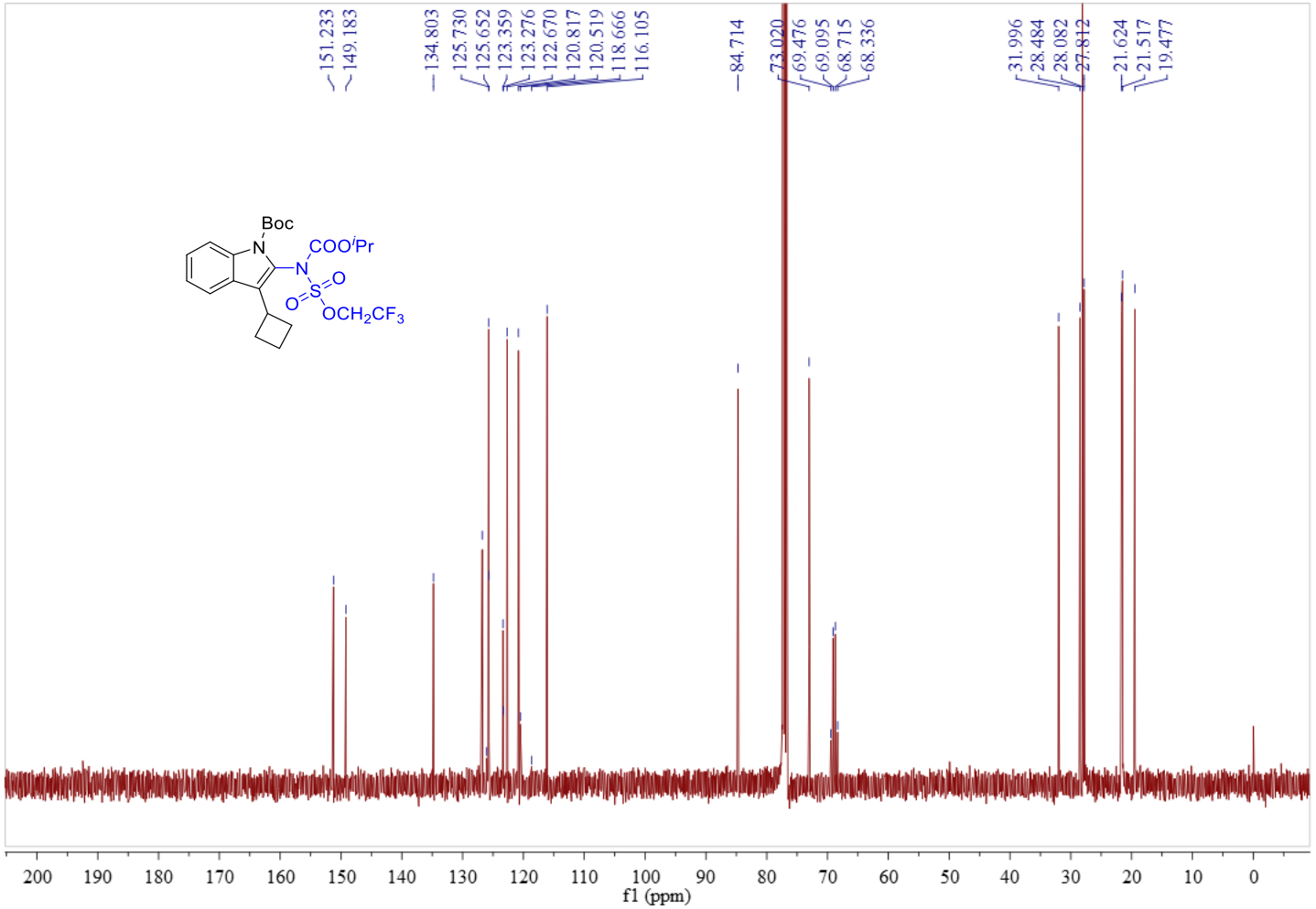
^{1}H NMR of **3a** (100 MHz, $CDCl_3$)



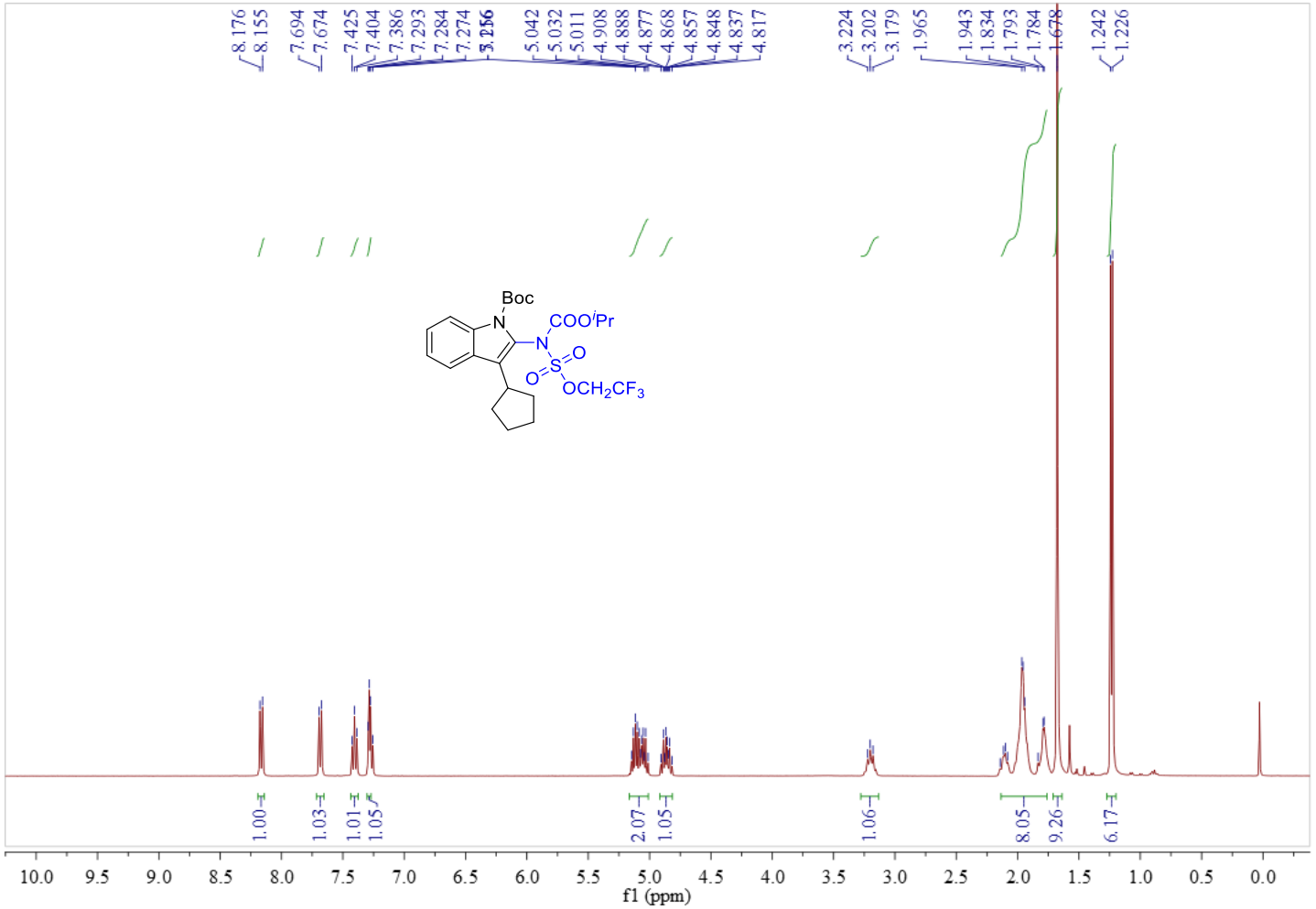
^{13}C NMR of **3a** (100 MHz, $CDCl_3$)



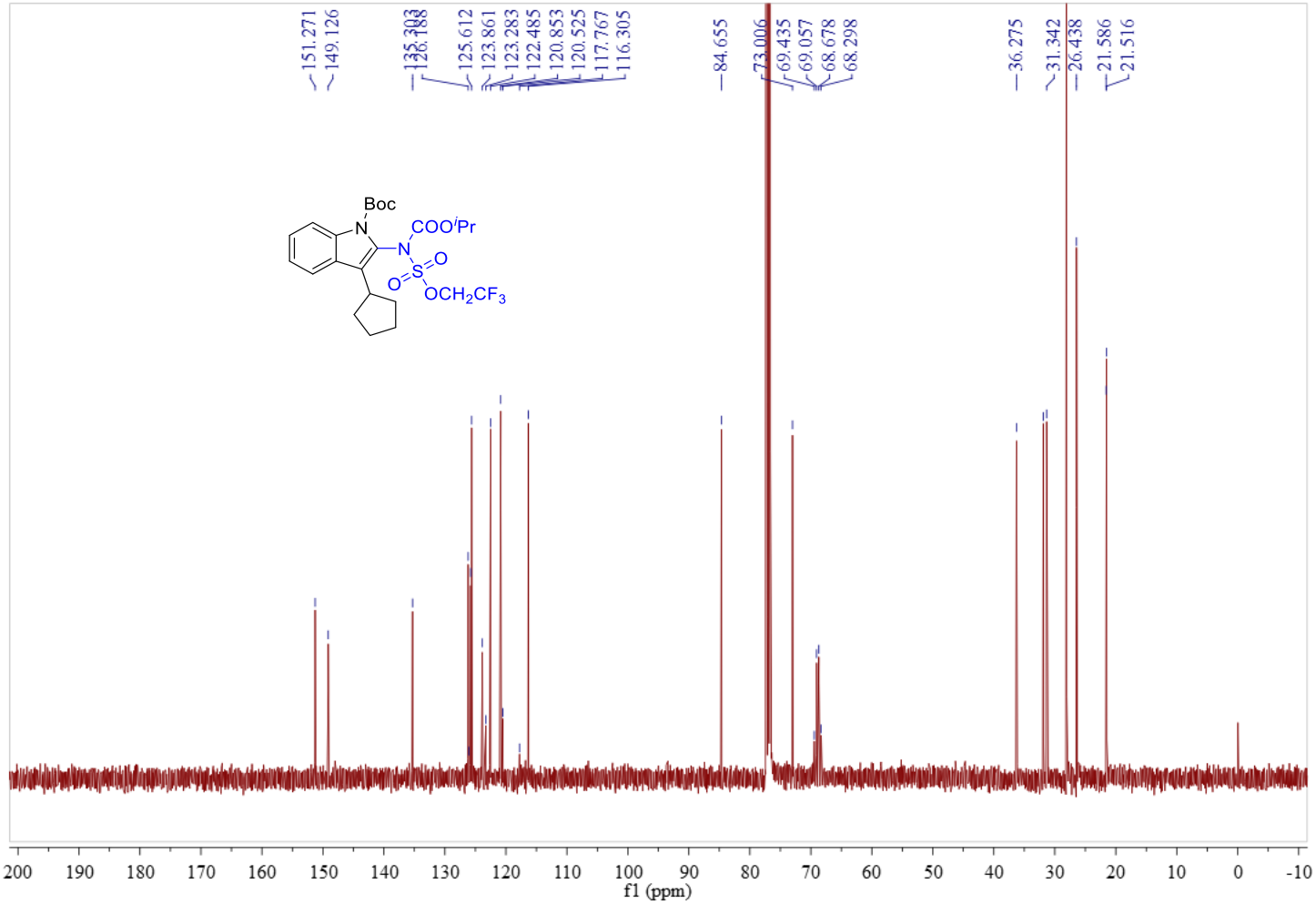
^{1}H NMR of **3b** (100 MHz, $CDCl_3$)



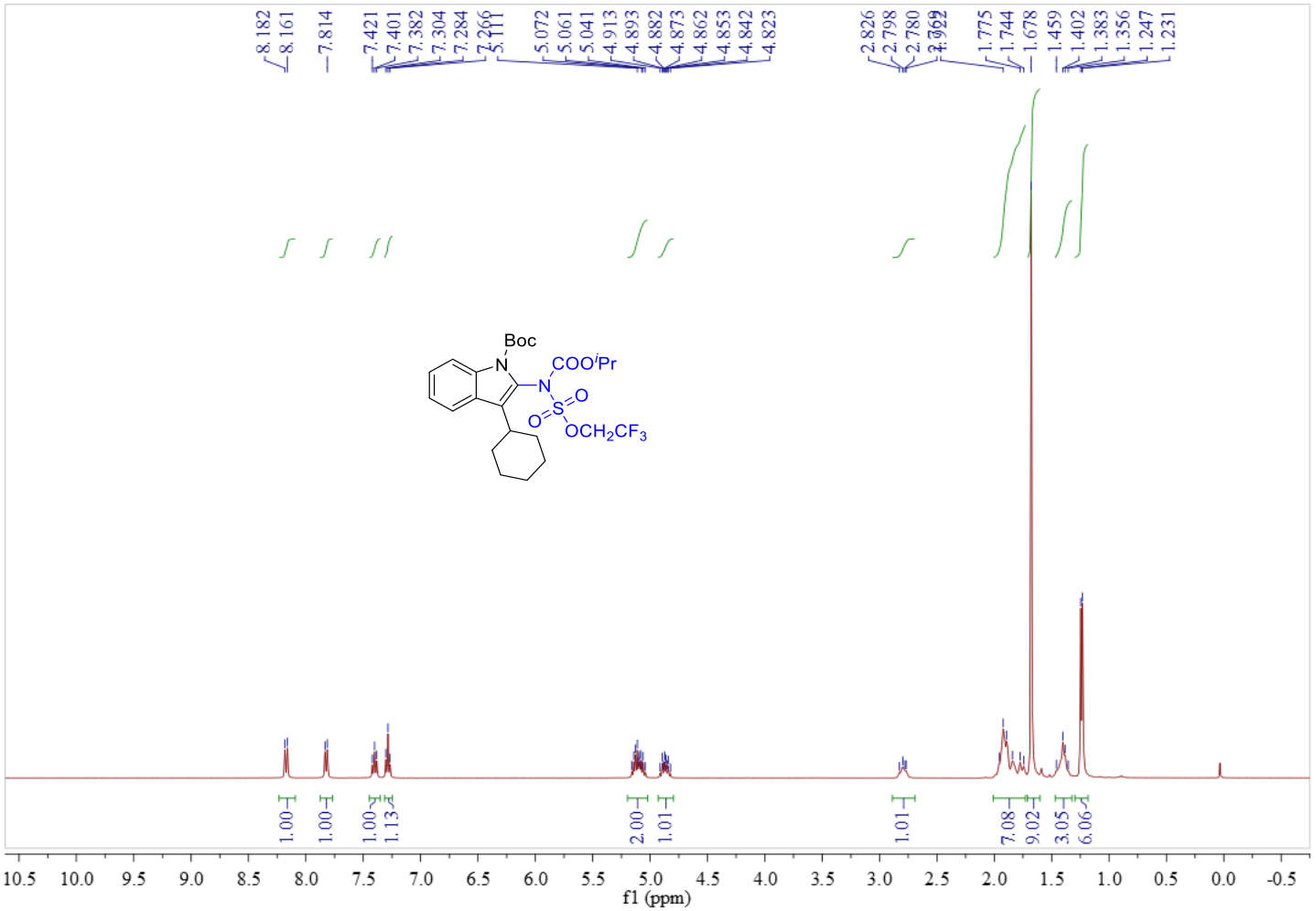
^{13}C NMR of **3b** (100 MHz, $CDCl_3$)



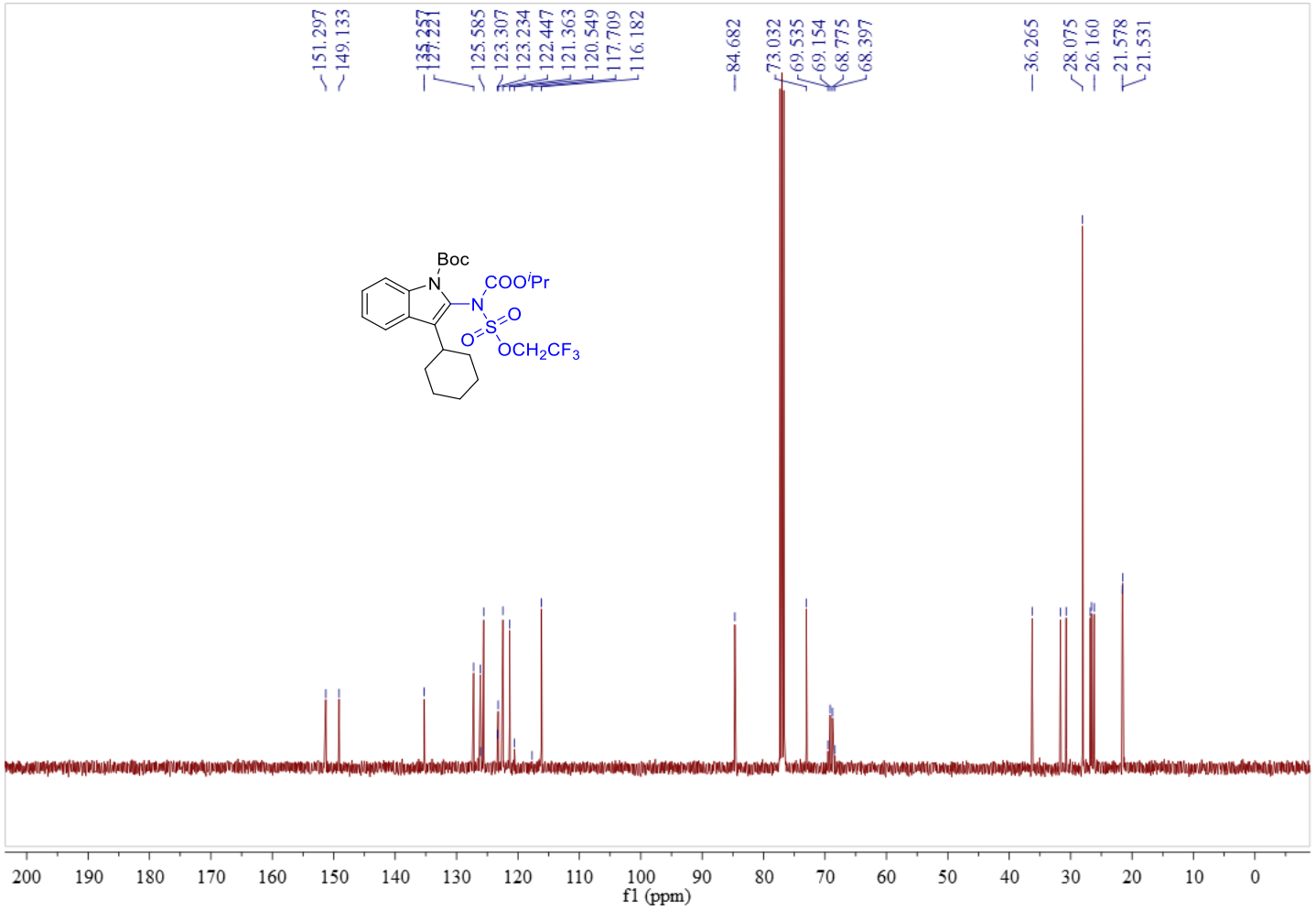
^{1}H NMR of **3c** (100 MHz, $CDCl_3$)



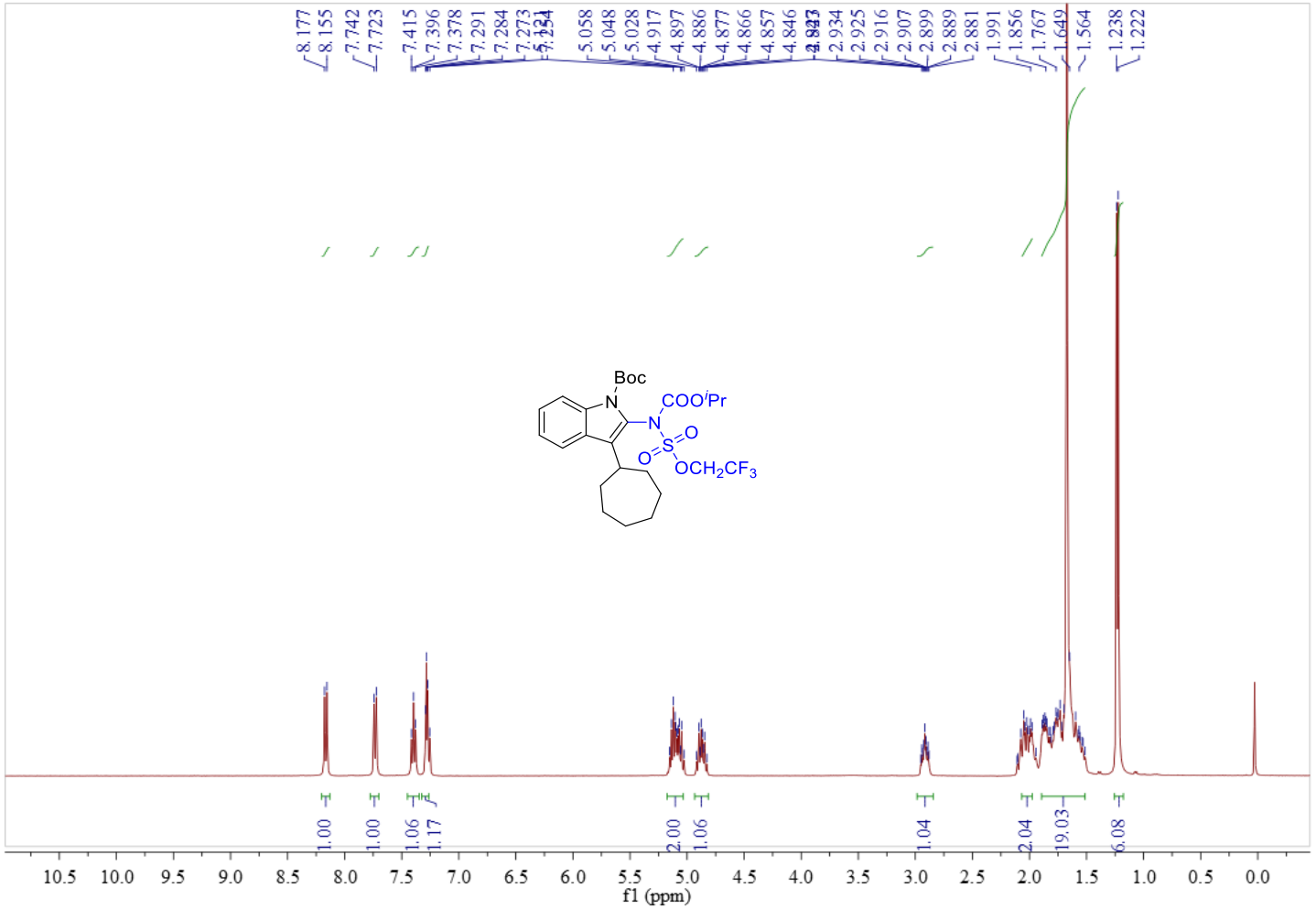
^{13}C NMR of **3c** (100 MHz, $CDCl_3$)



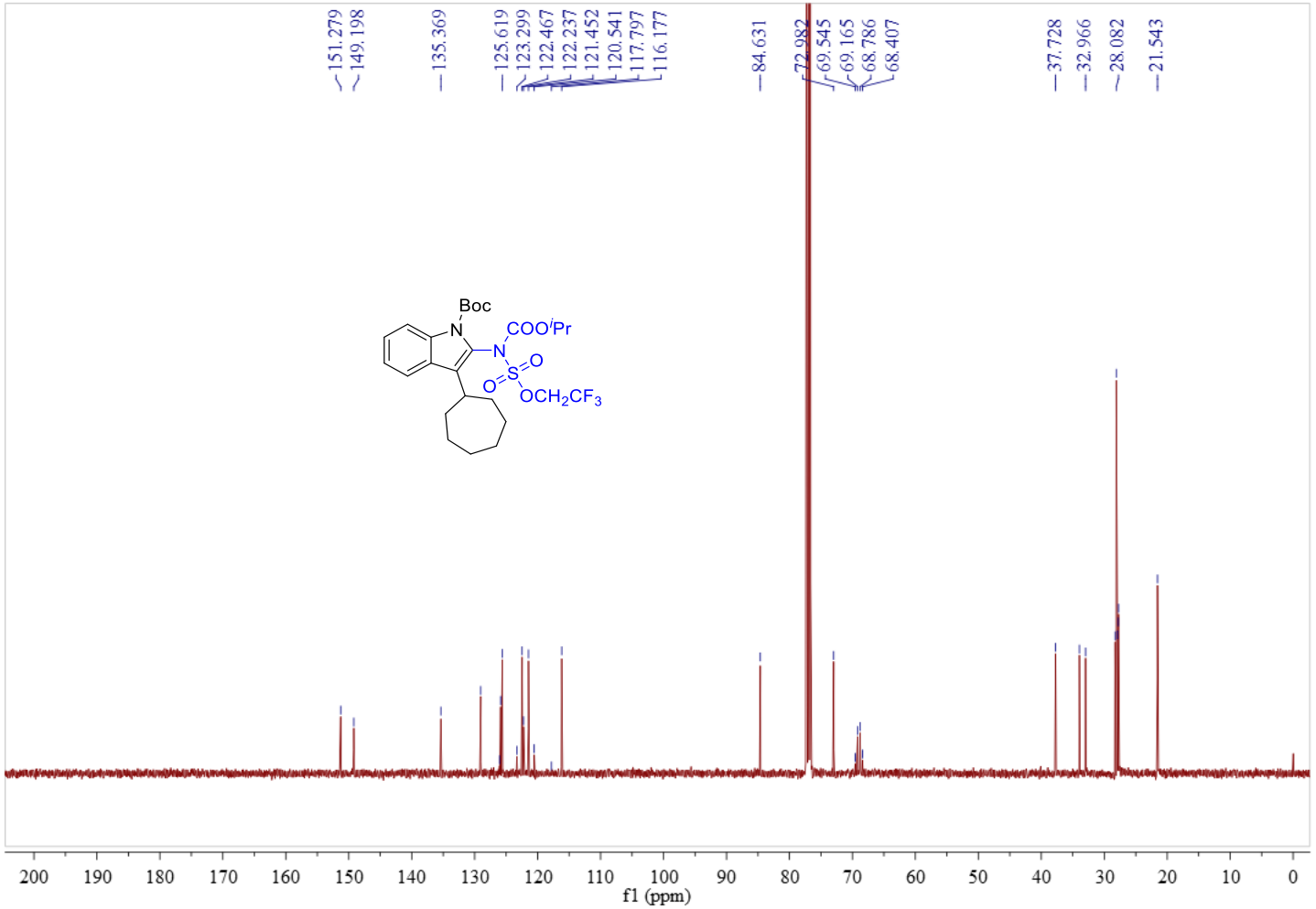
^{1}H NMR of **3d** (100 MHz, $CDCl_3$)



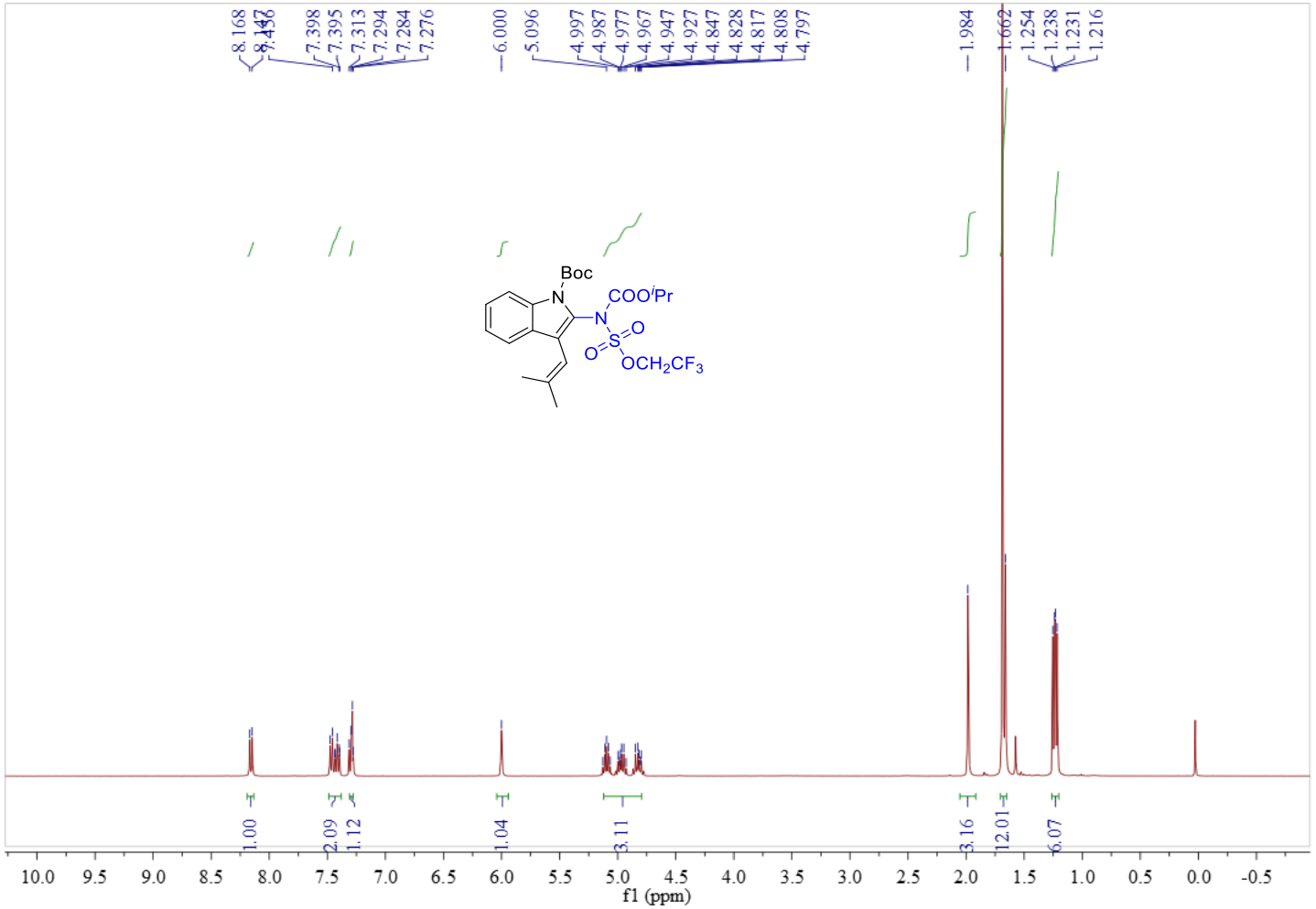
^{13}C NMR of **3d** (100 MHz, $CDCl_3$)



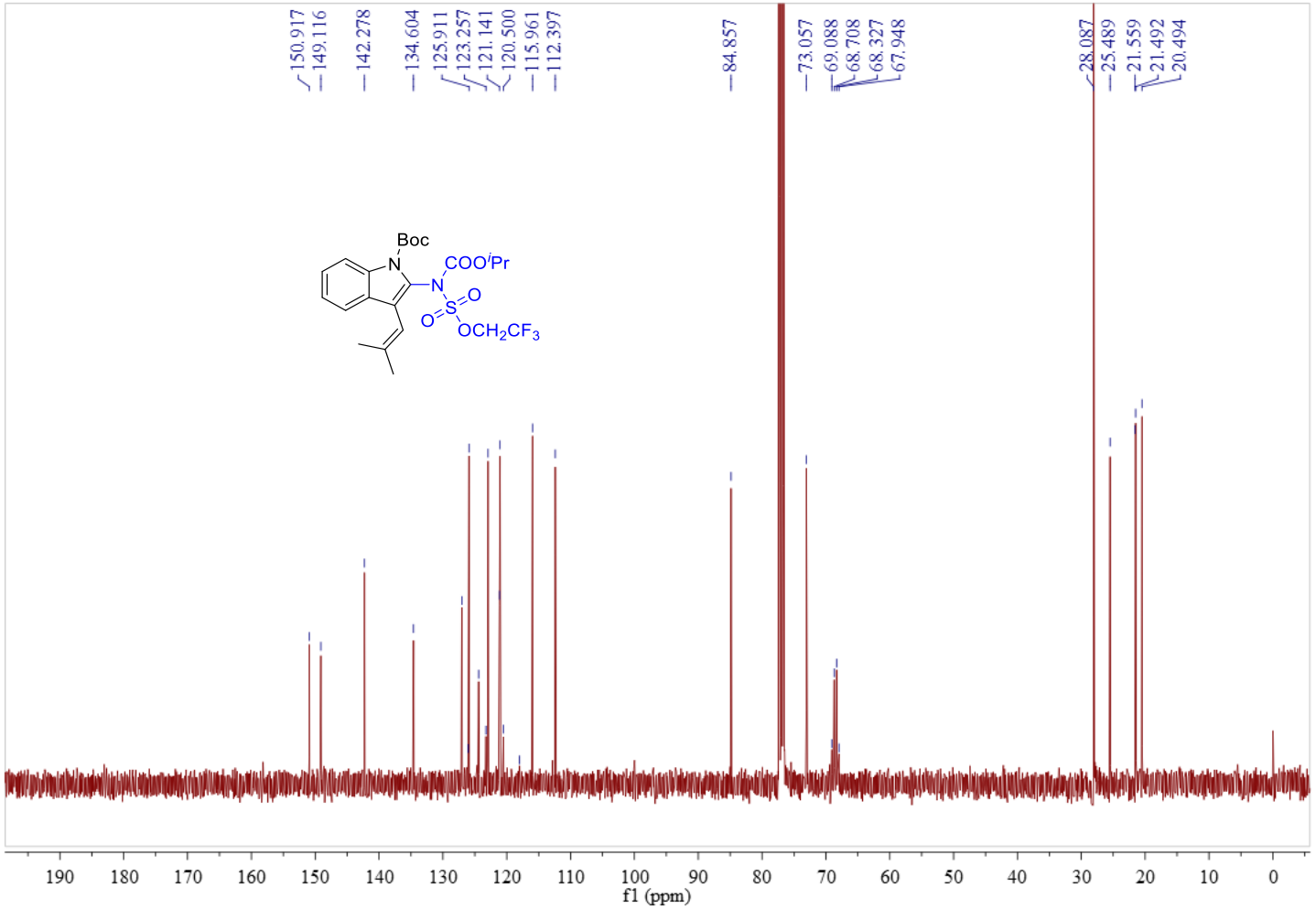
^{1}H NMR of **3e** (100 MHz, $CDCl_3$)



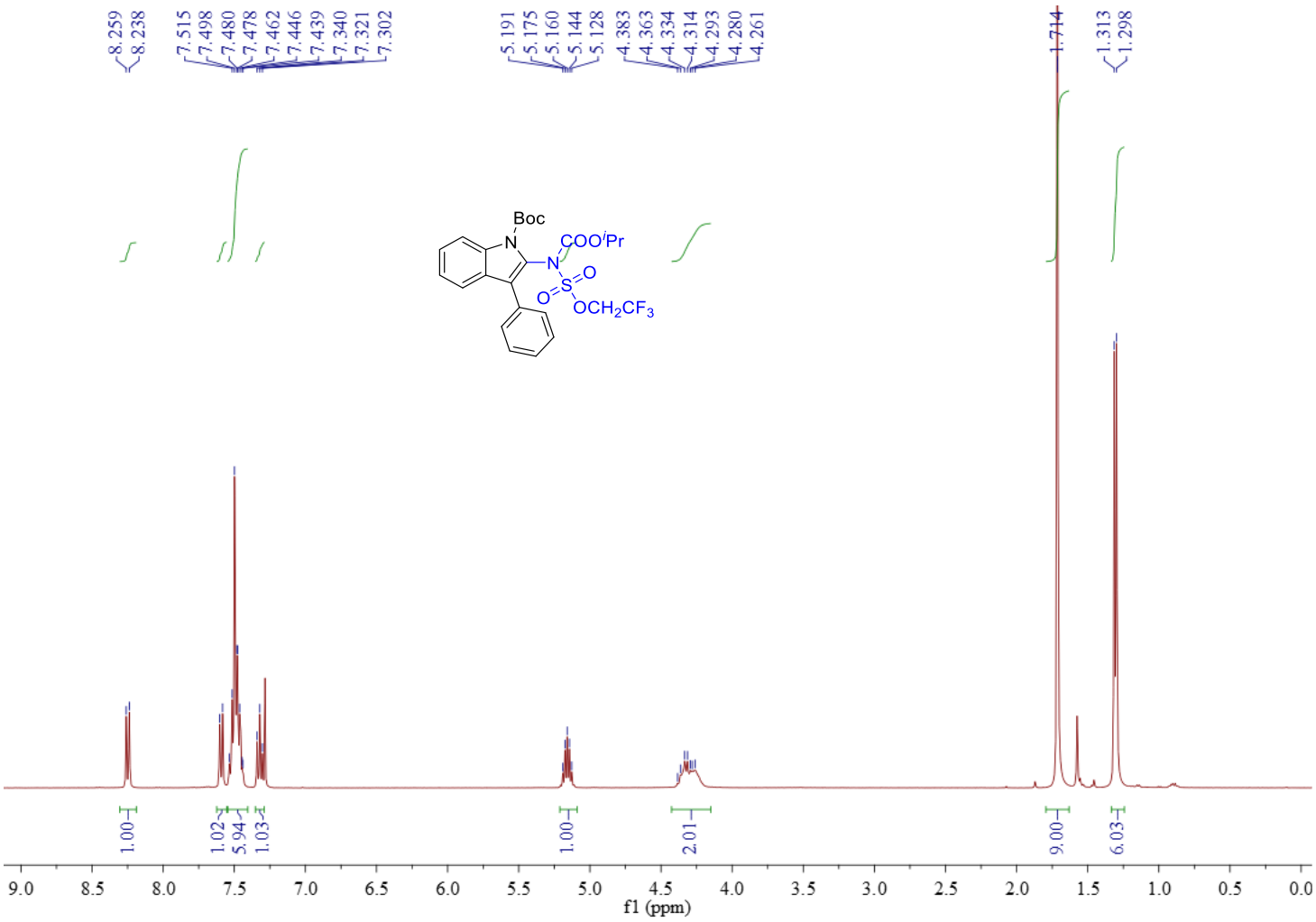
^{13}C NMR of **3e** (100 MHz, $CDCl_3$)



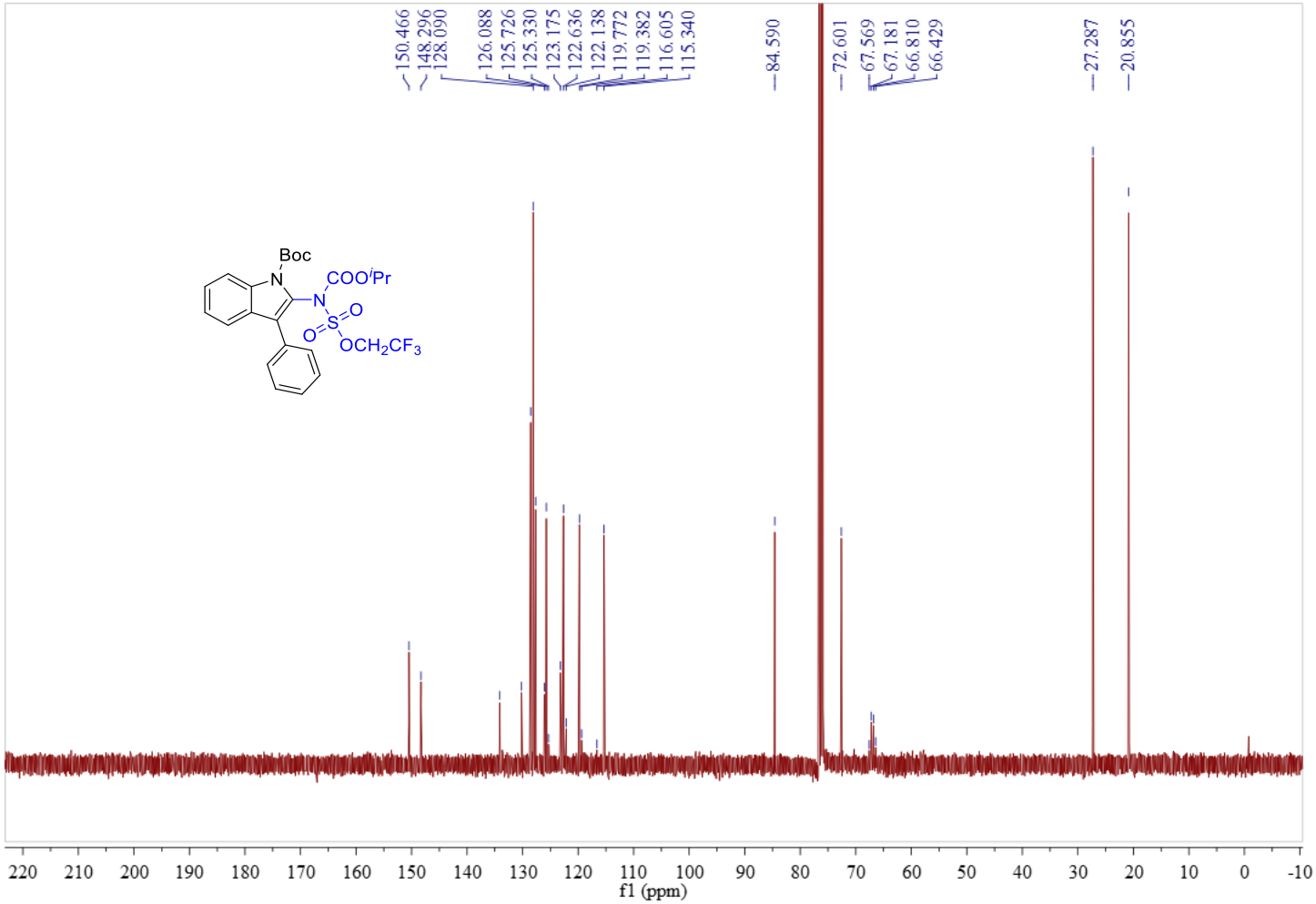
^{1}H NMR of **3f** (100 MHz, $CDCl_3$)



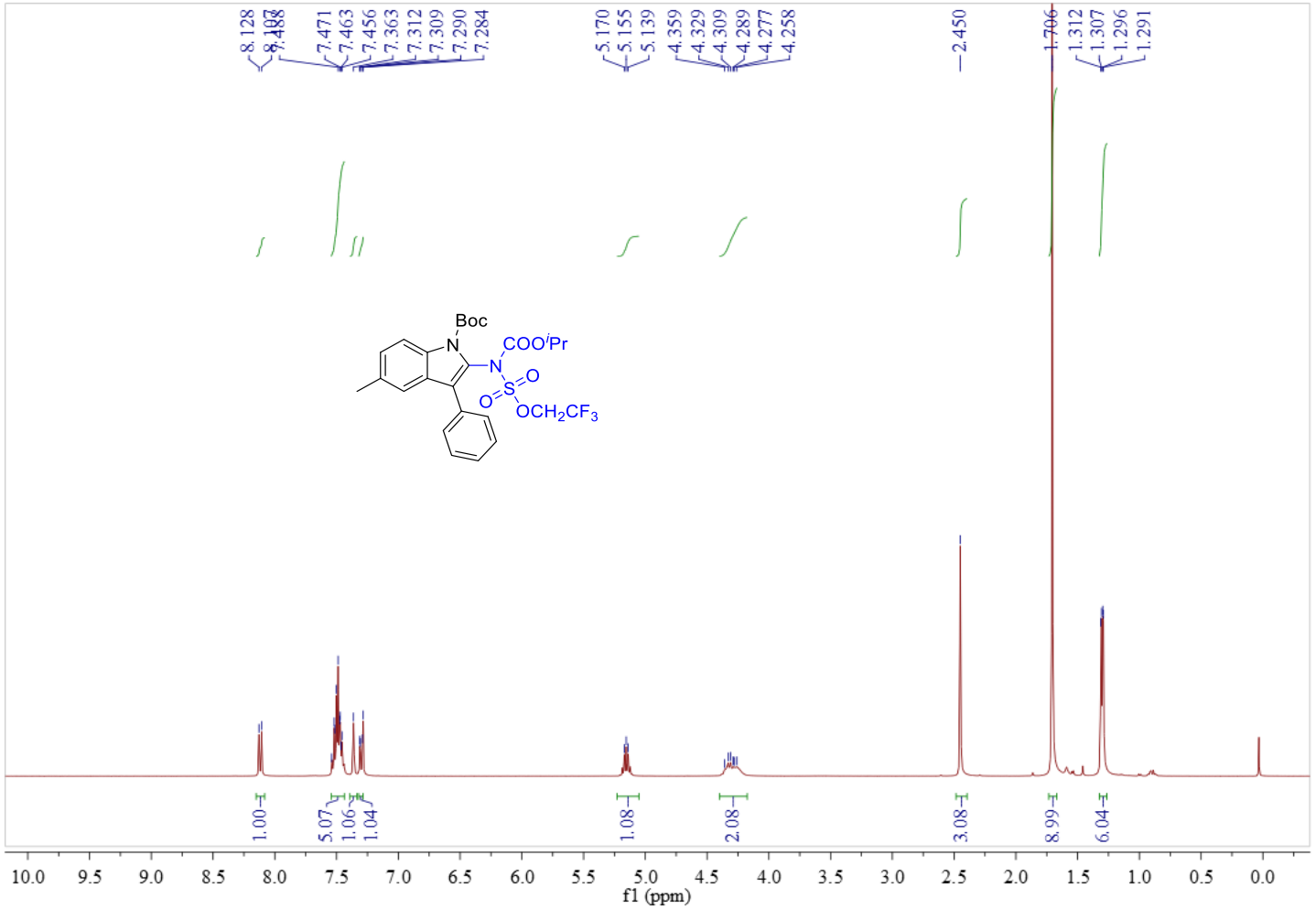
^{13}C NMR of **3f** (100 MHz, $CDCl_3$)



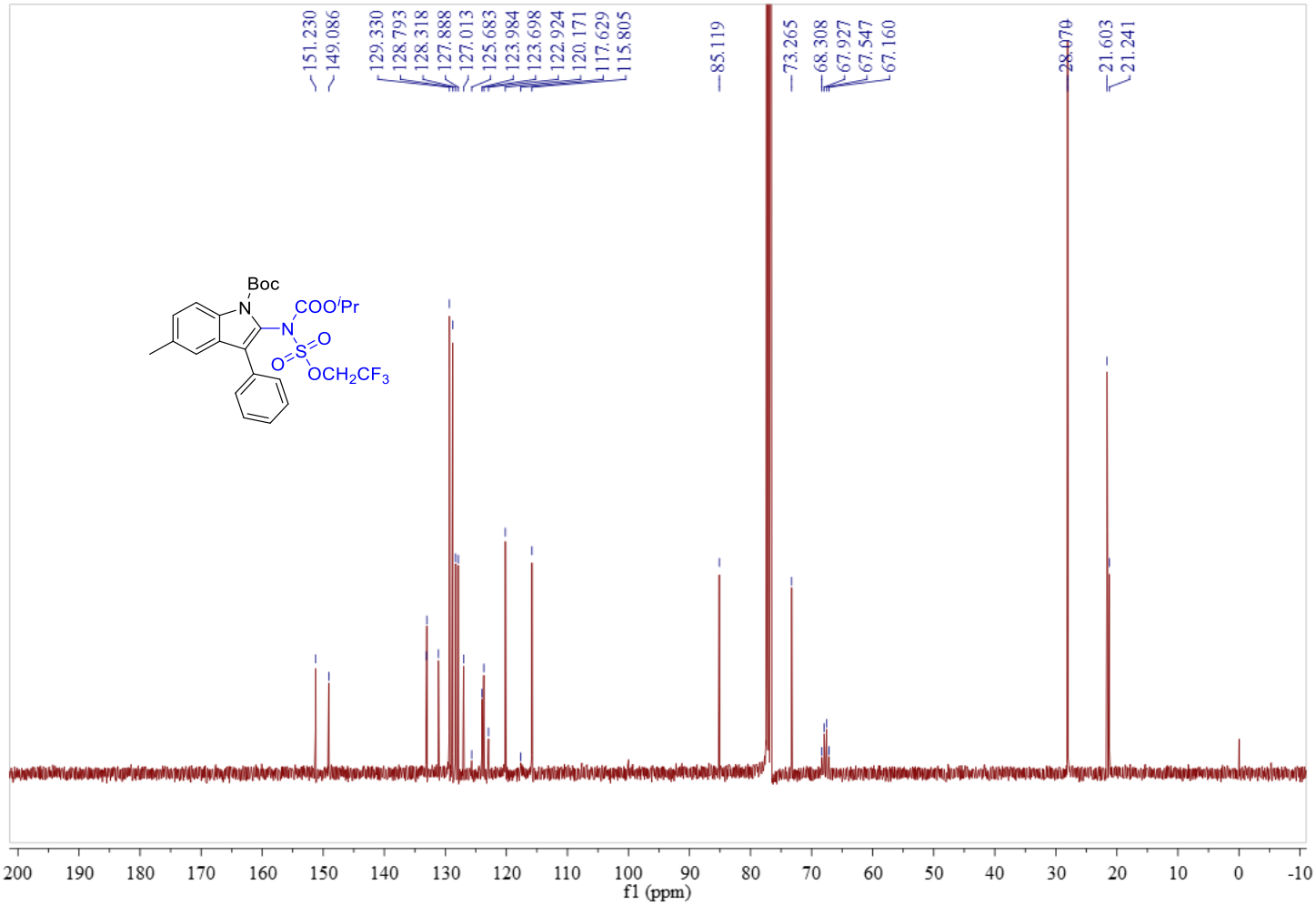
^{1}H NMR of **3g** (100 MHz, $CDCl_3$)



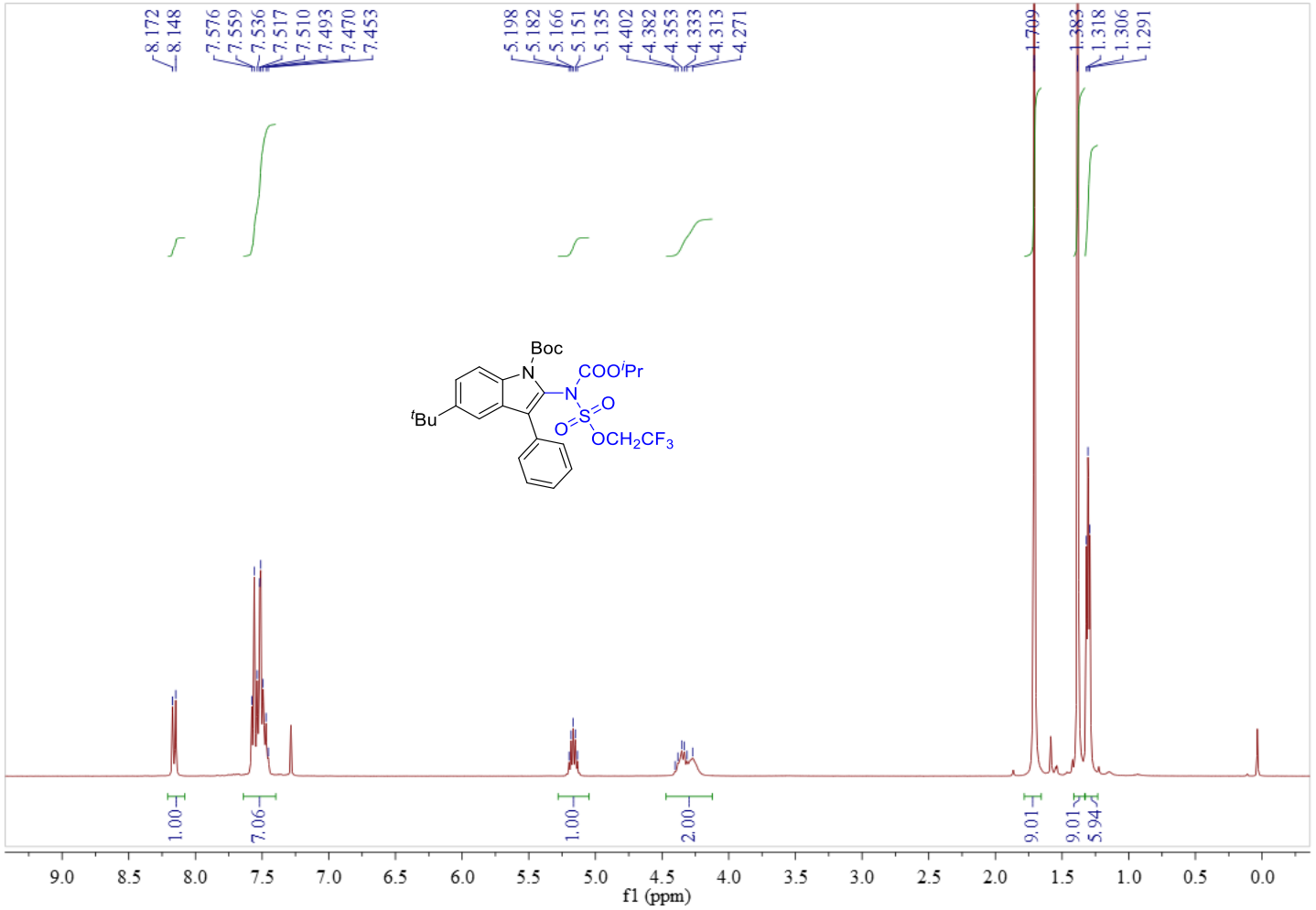
^{13}C NMR of **3g** (100 MHz, $CDCl_3$)



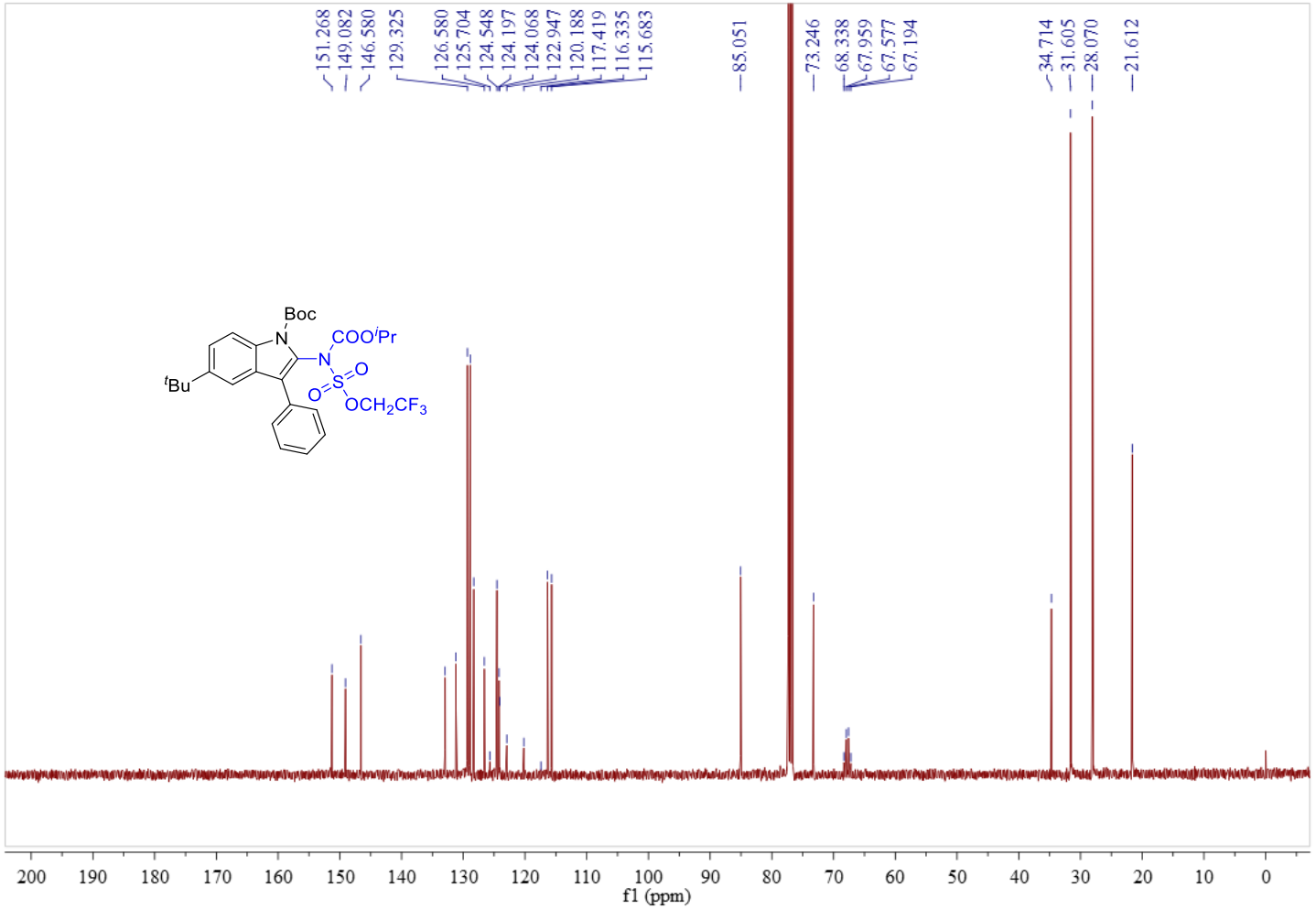
^{1}H NMR of **3h** (100 MHz, $CDCl_3$)



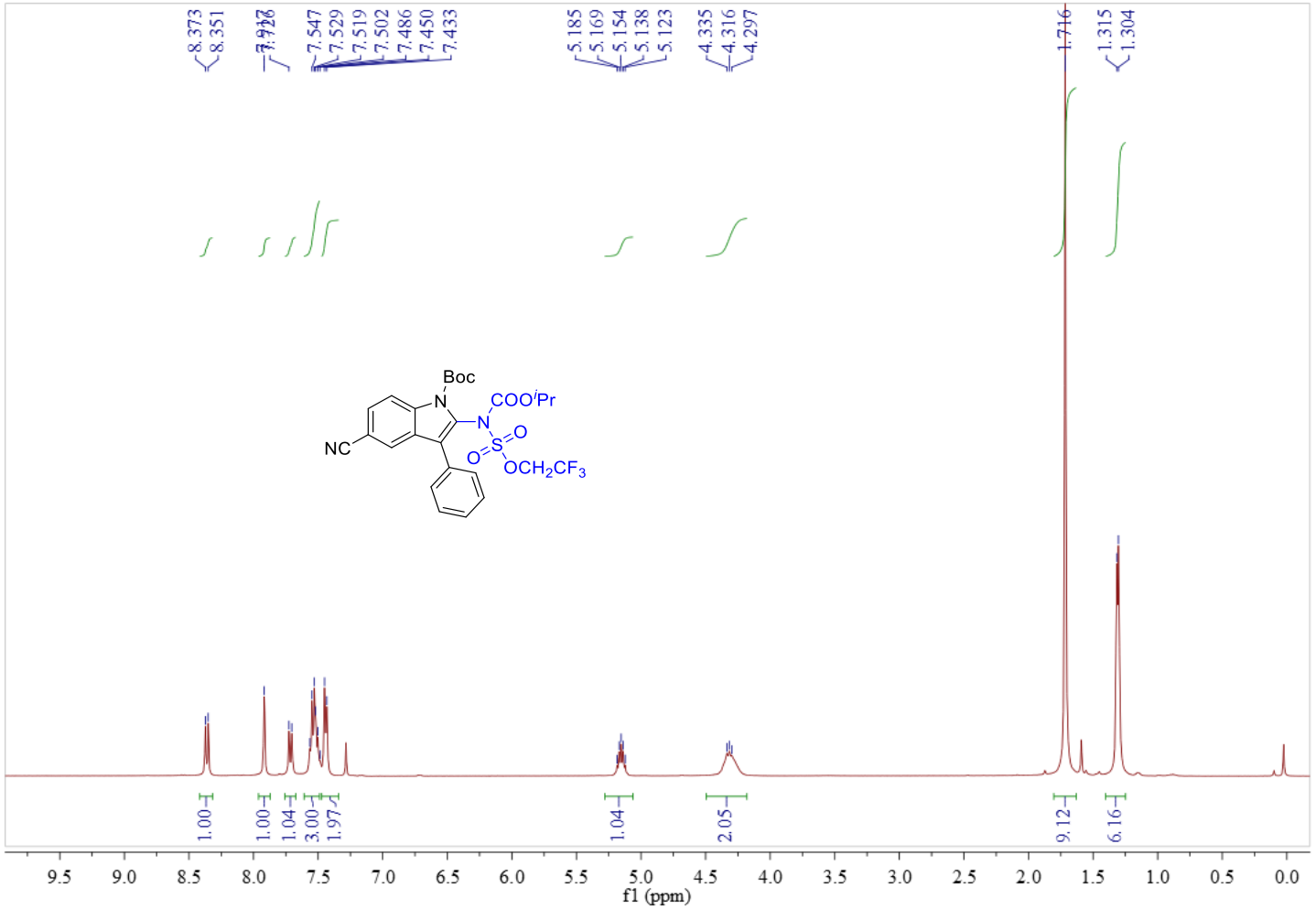
^{13}C NMR of **3h** (100 MHz, $CDCl_3$)



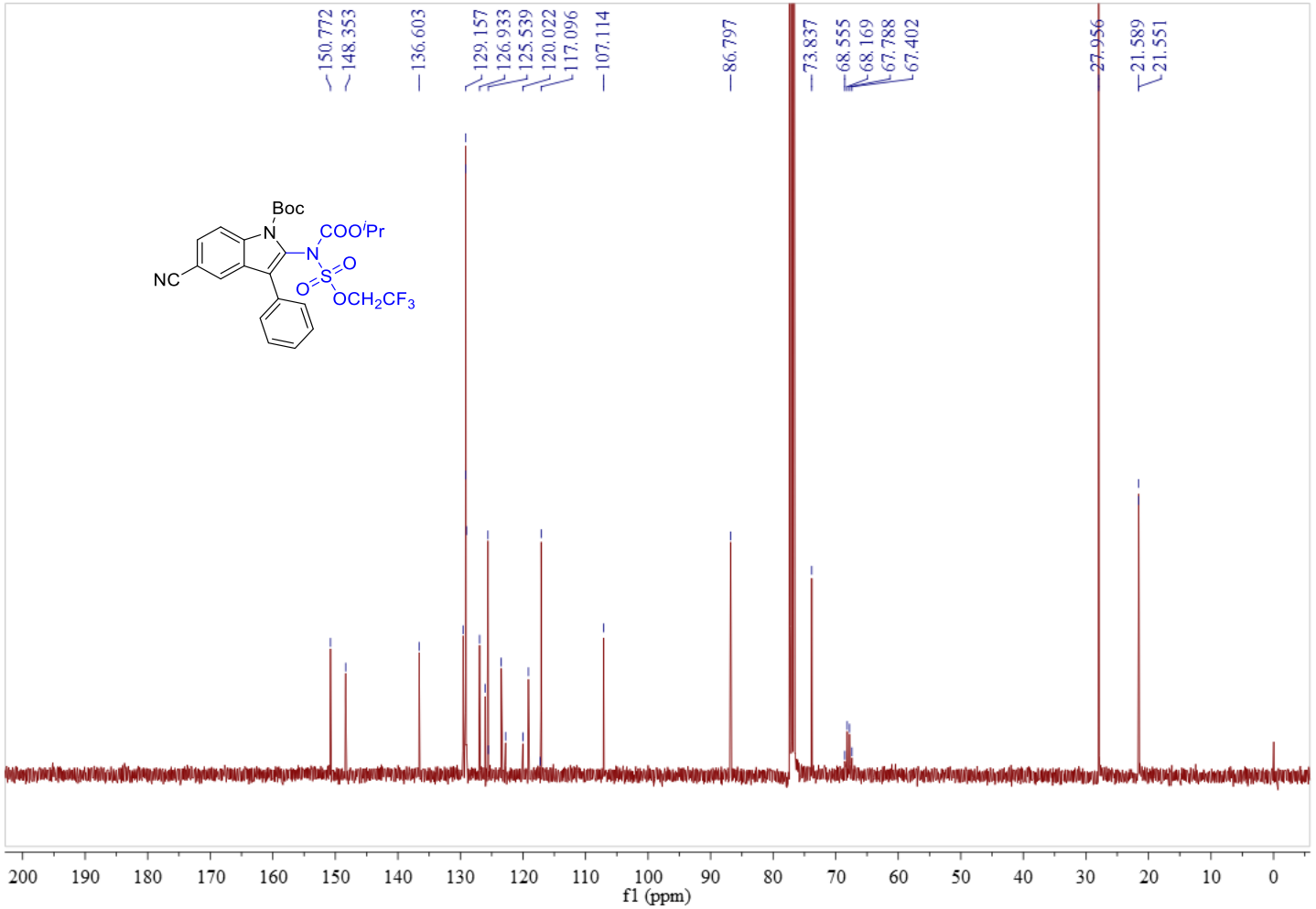
^{1}H NMR of **3i** (100 MHz, $CDCl_3$)



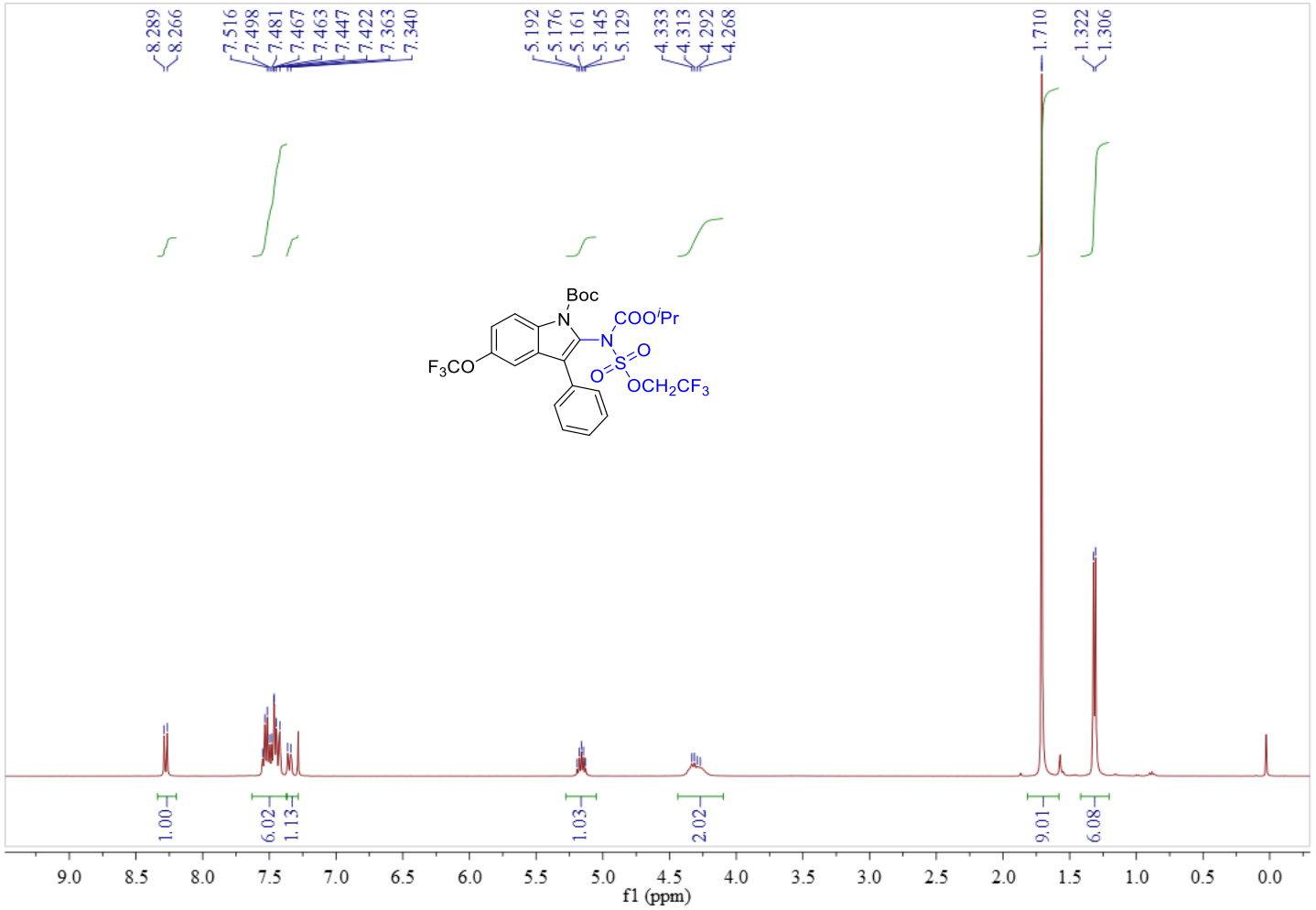
^{13}C NMR of **3i** (100 MHz, $CDCl_3$)



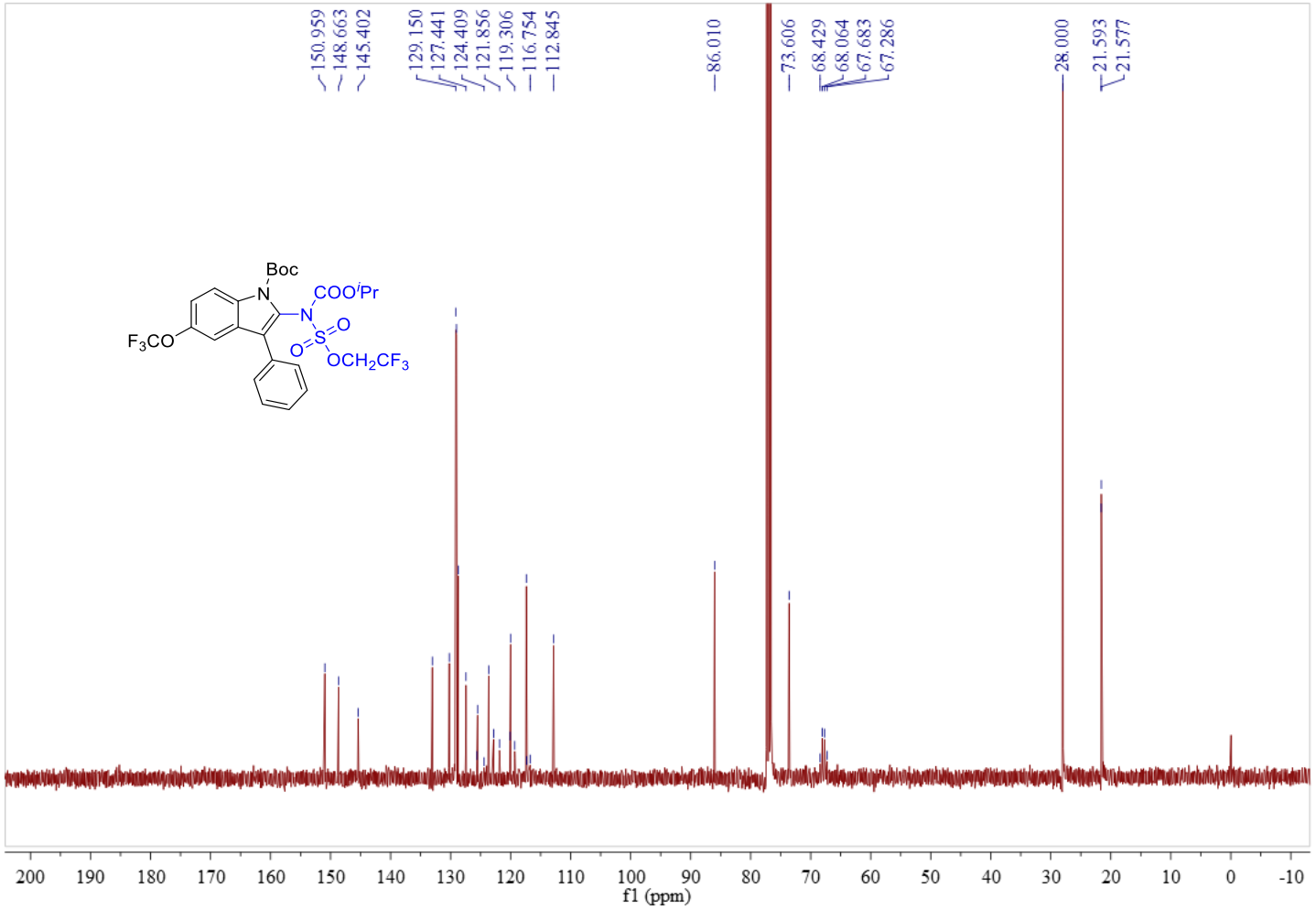
^{1}H NMR of **3j** (100 MHz, $CDCl_3$)



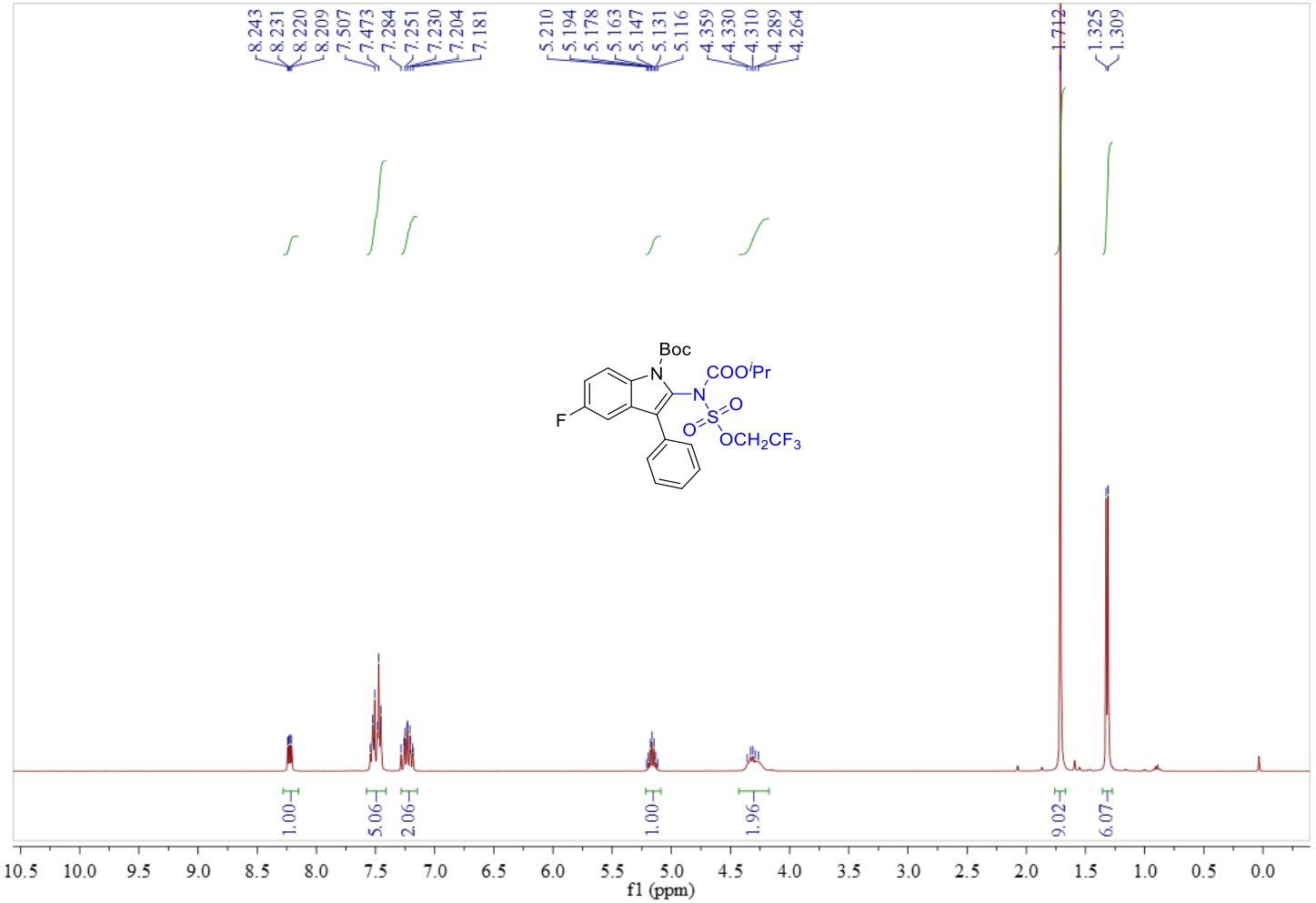
^{13}C NMR of **3j** (100 MHz, $CDCl_3$)



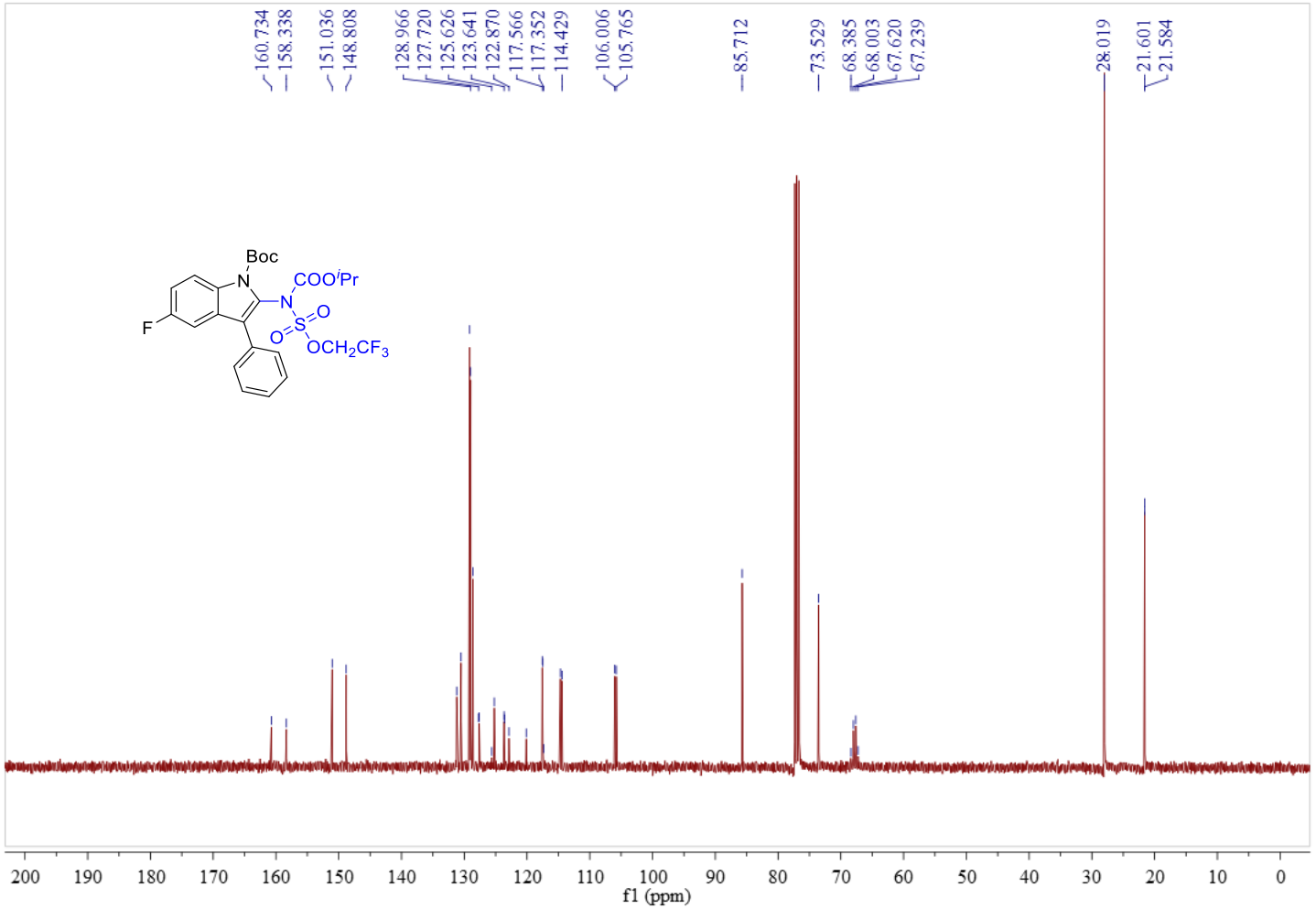
^{1}H NMR of **3k** (100 MHz, $CDCl_3$)



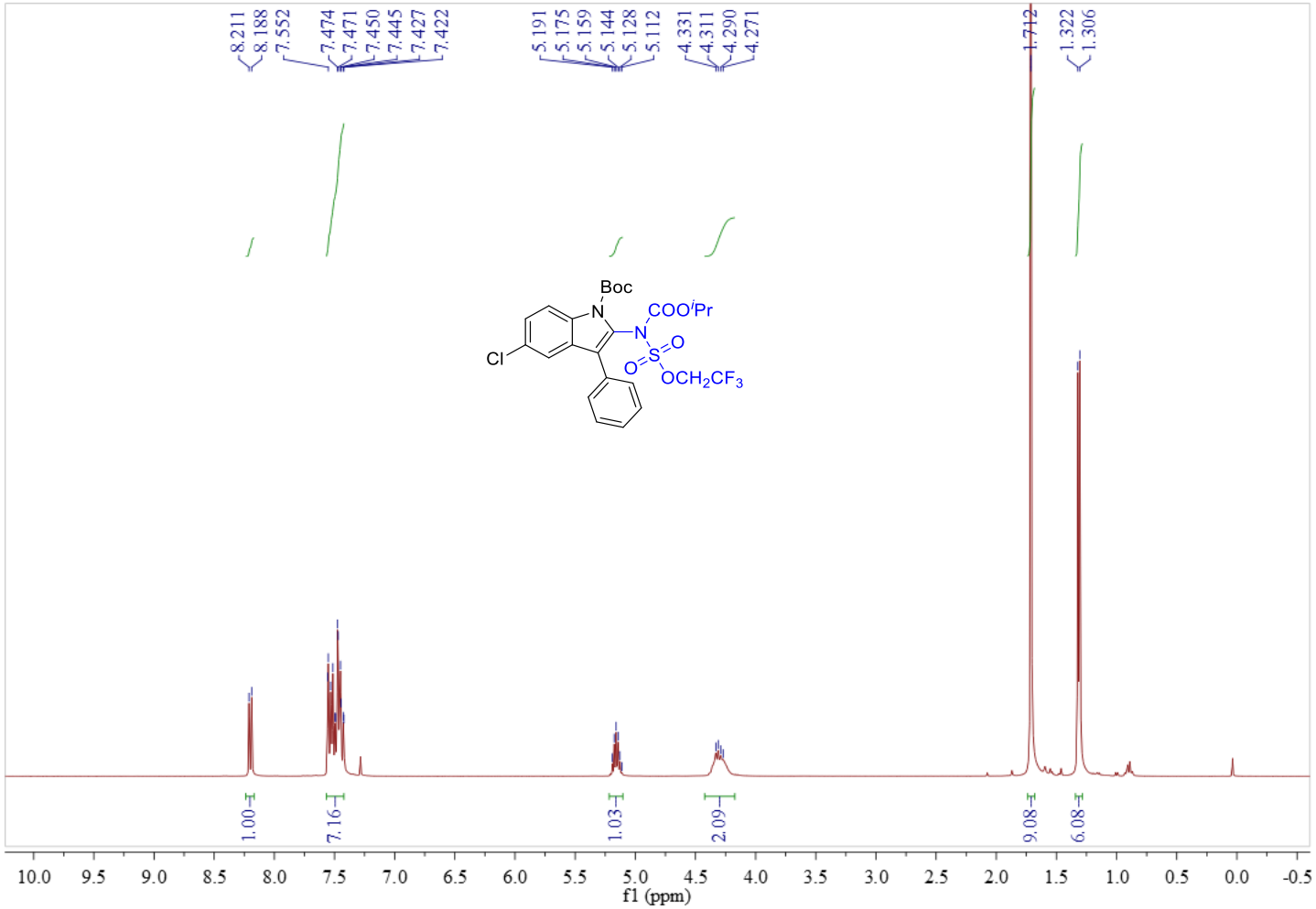
^{13}C NMR of **3k** (100 MHz, $CDCl_3$)



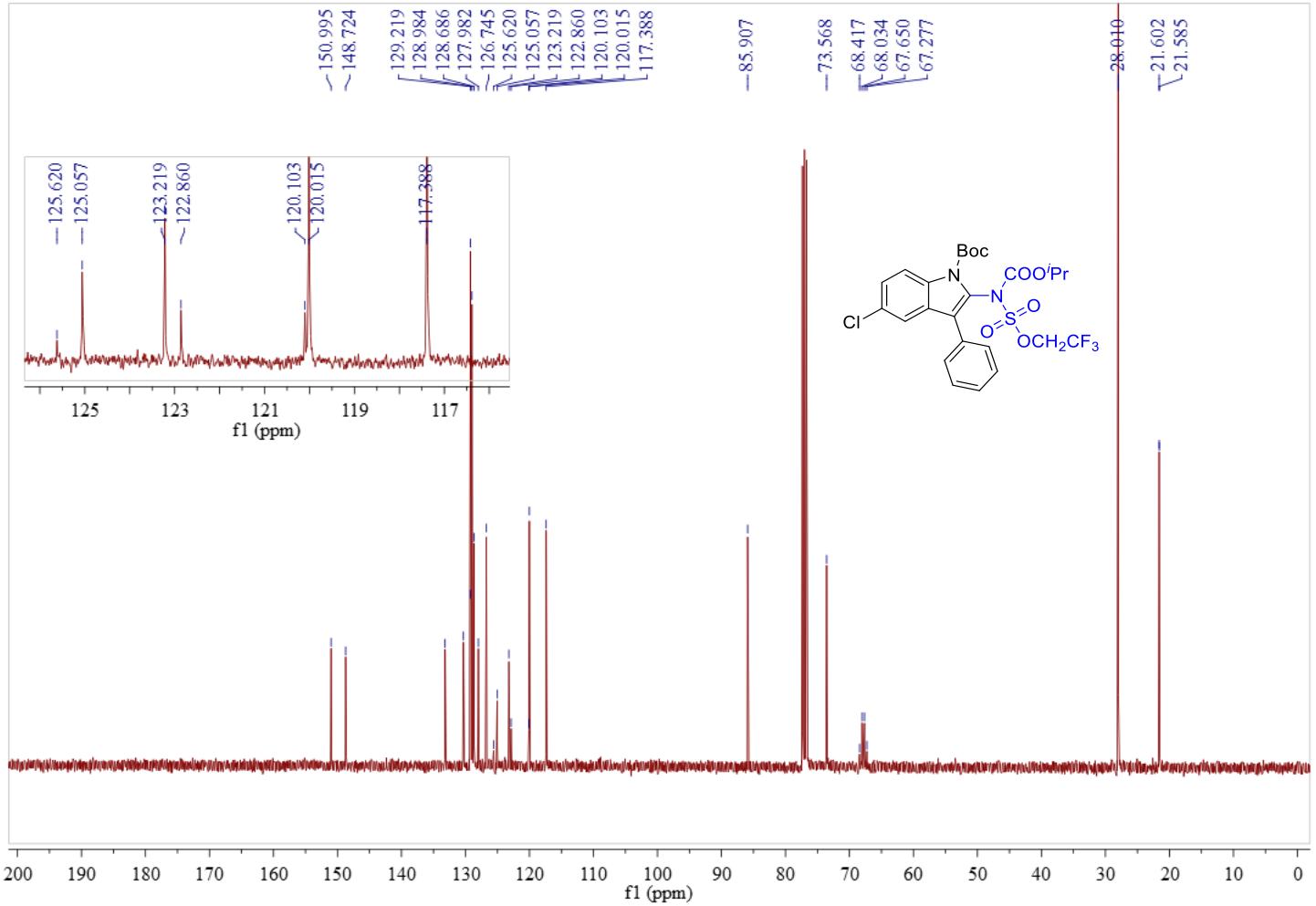
^{1}H NMR of **3l** (100 MHz, $CDCl_3$)



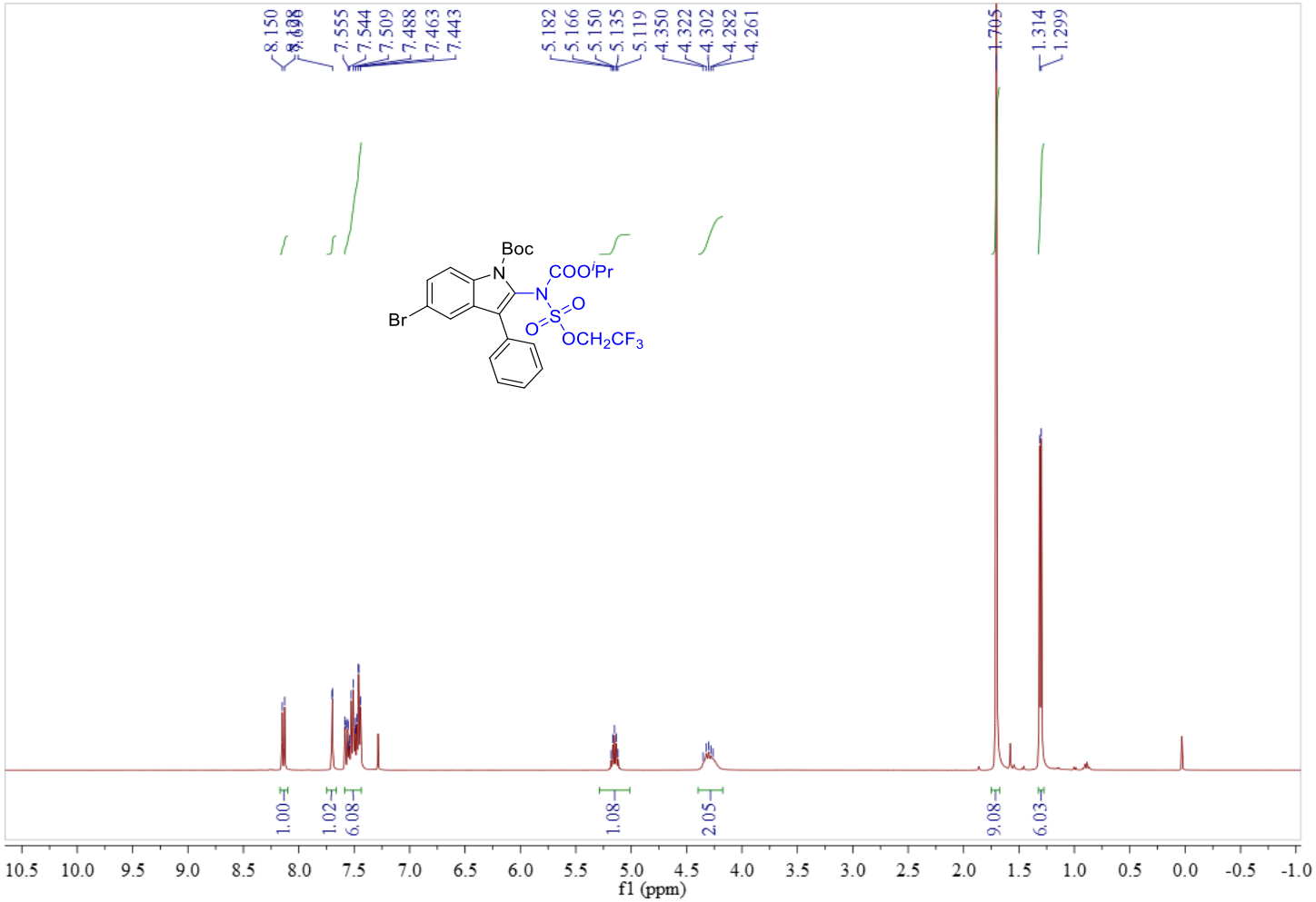
^{13}C NMR of **3l** (100 MHz, $CDCl_3$)



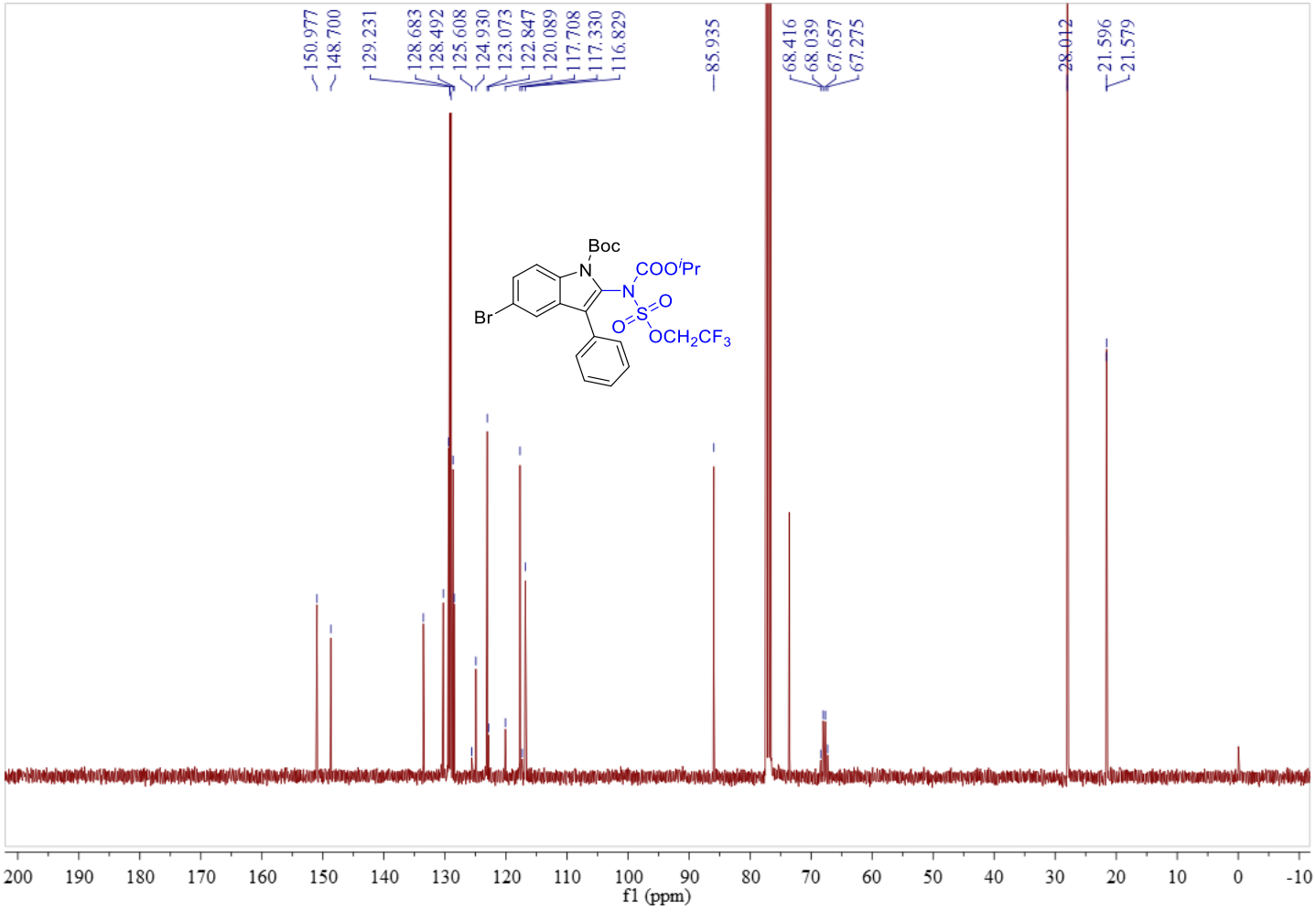
^{1}H NMR of **3m** (100 MHz, $CDCl_3$)



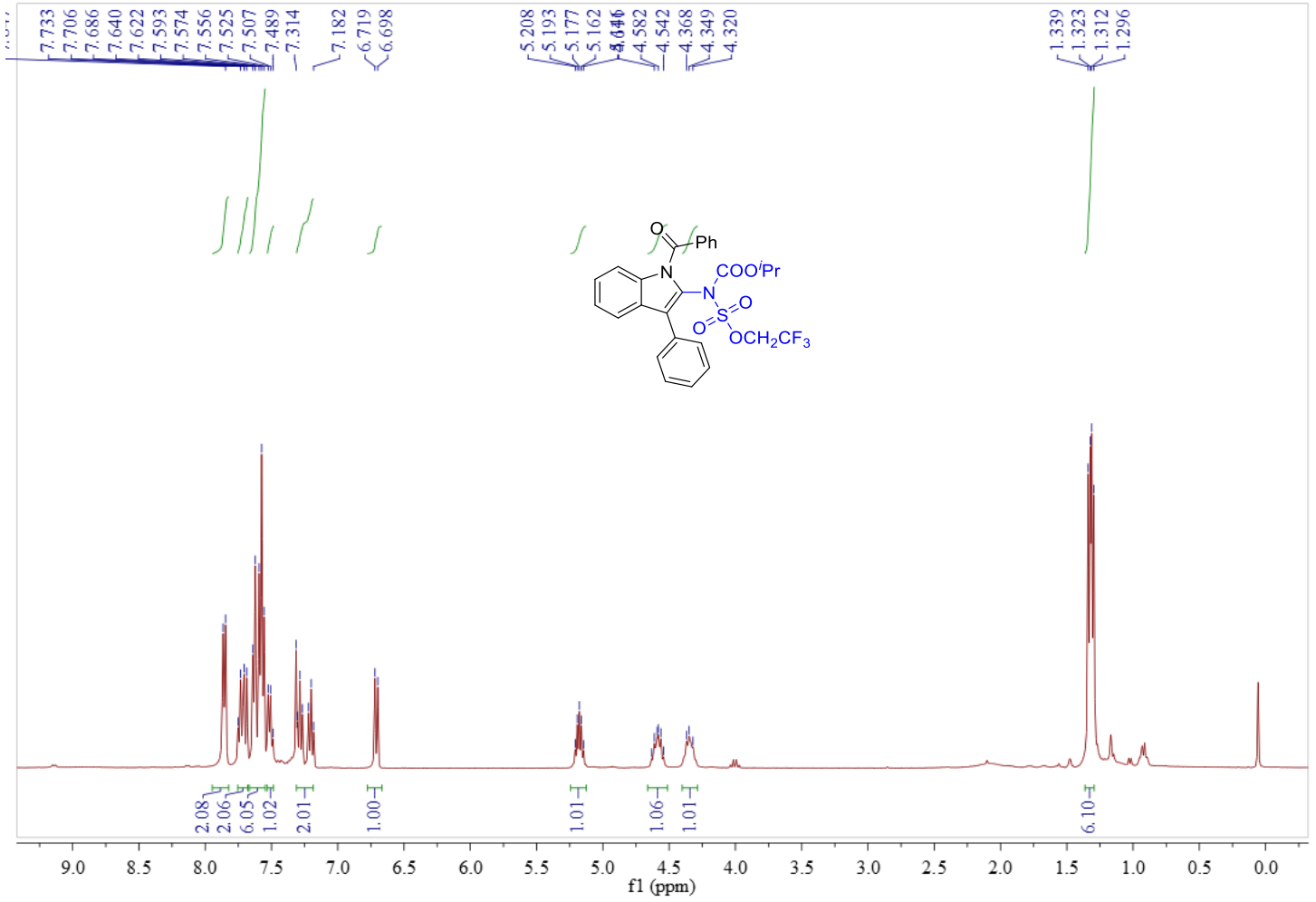
^{13}C NMR of **3m** (100 MHz, $CDCl_3$)



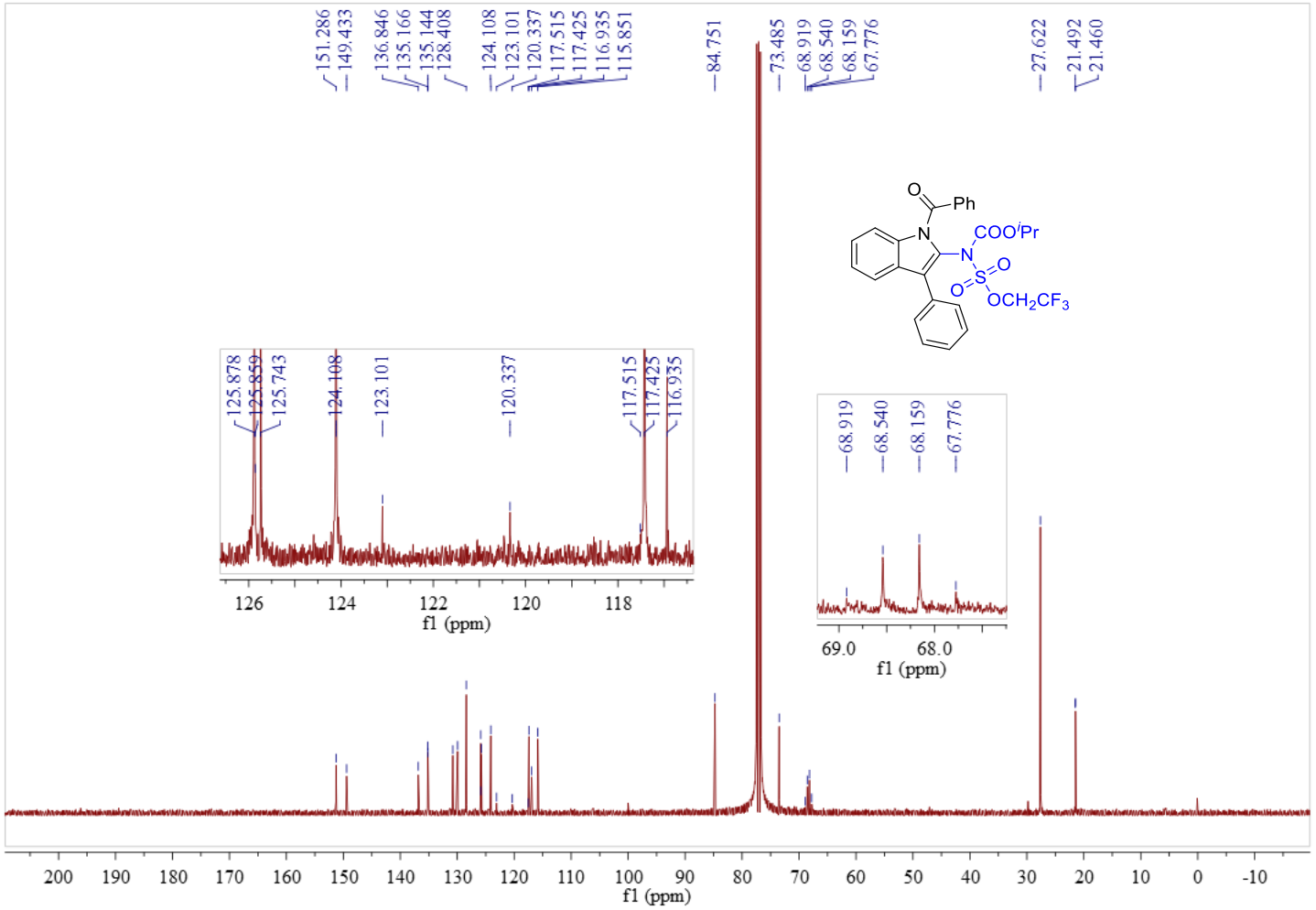
^{1}H NMR of **3n** (100 MHz, $CDCl_3$)



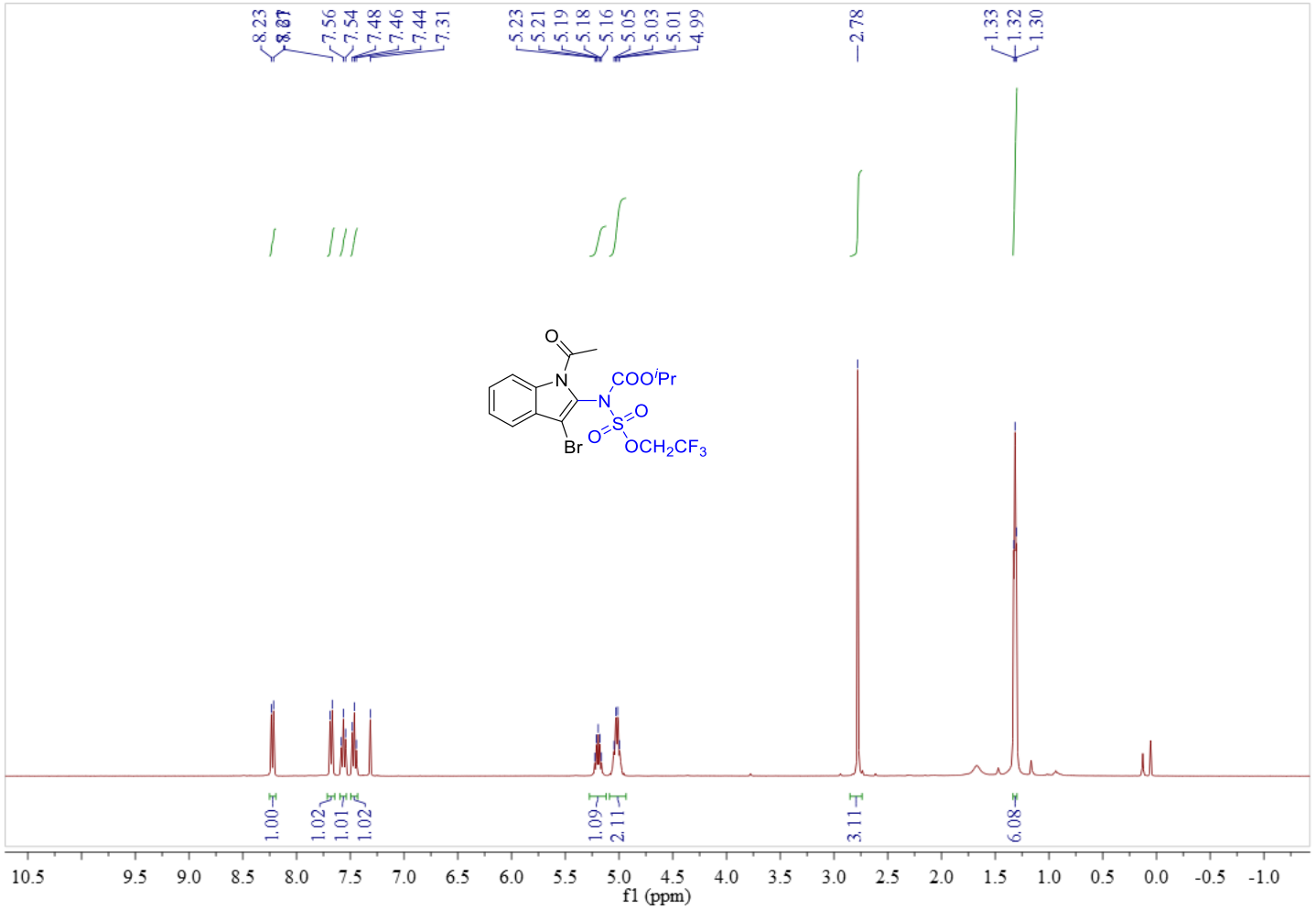
^{13}C NMR of **3n** (100 MHz, $CDCl_3$)



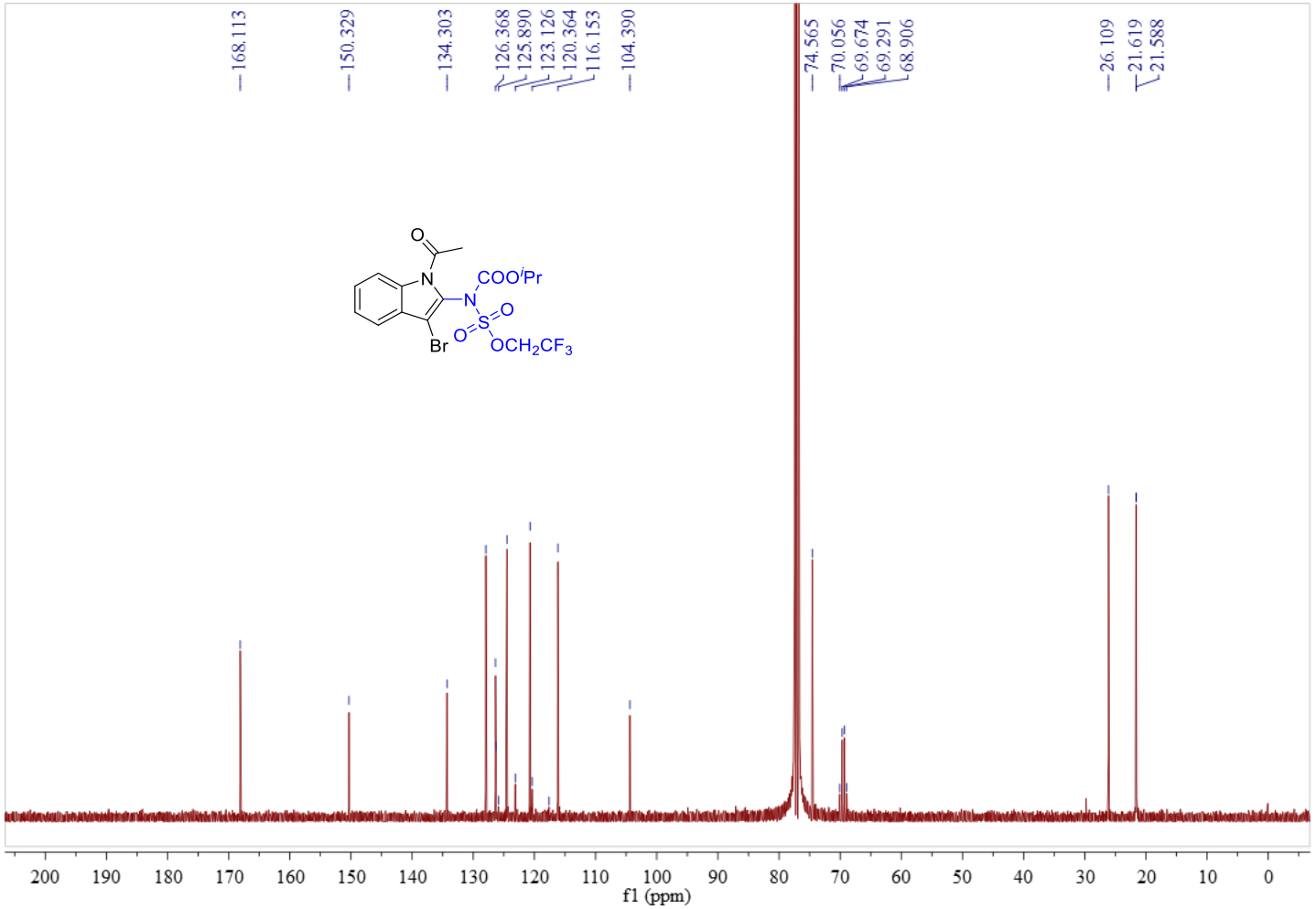
^{1}H NMR of **3o** (100 MHz, $CDCl_3$)



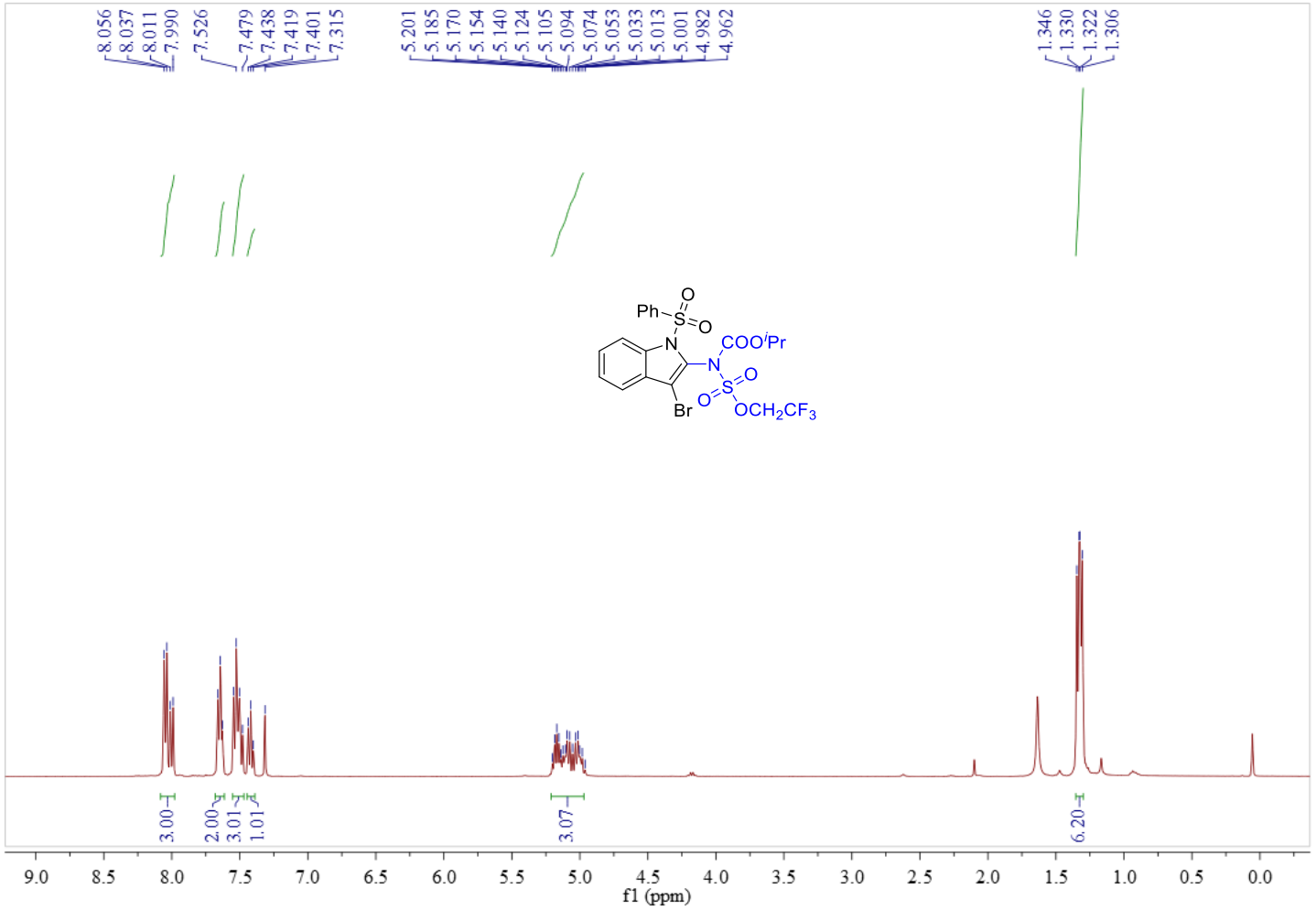
^{13}C NMR of **3o** (100 MHz, $CDCl_3$)



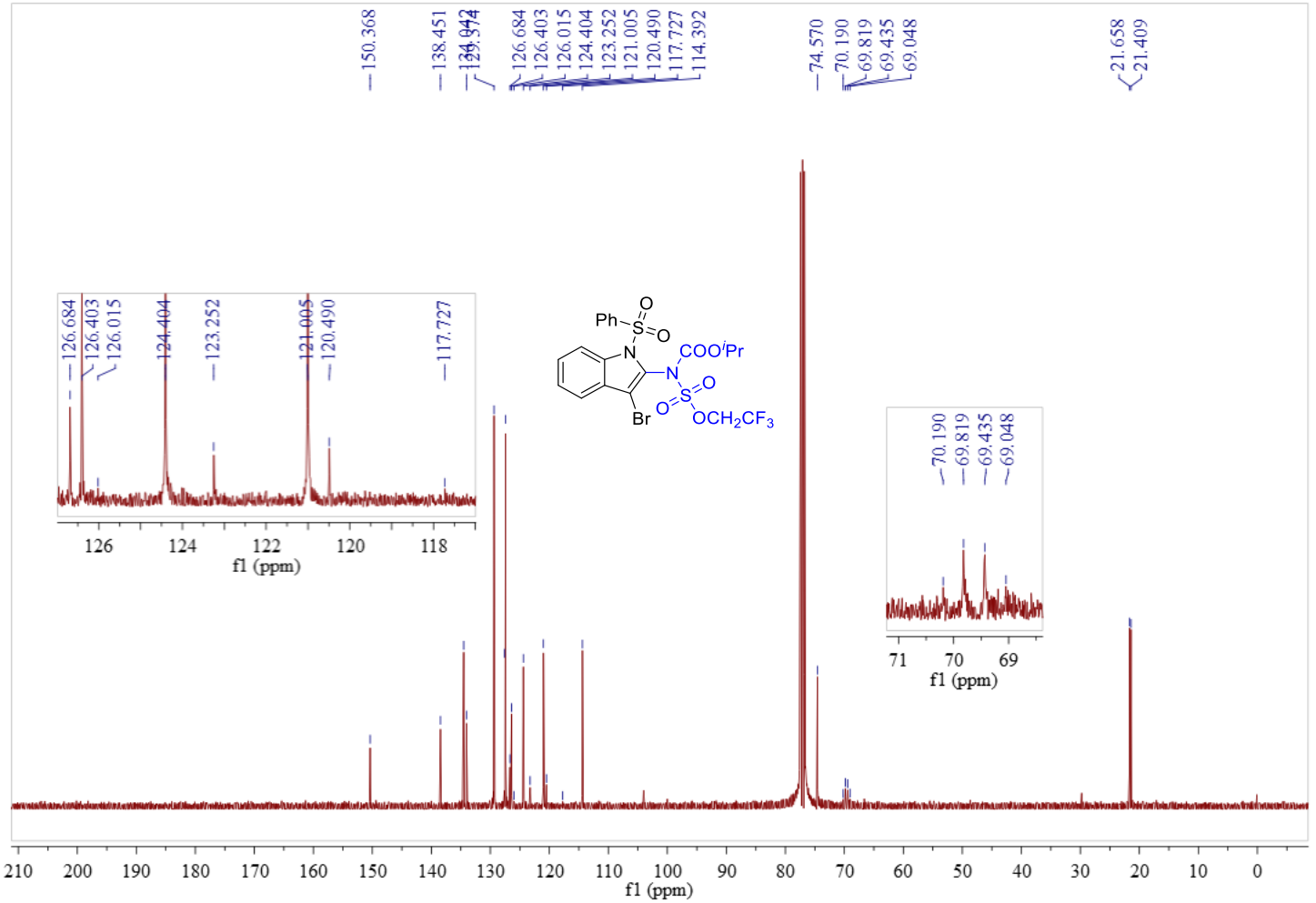
^{1}H NMR of **3p** (100 MHz, $CDCl_3$)



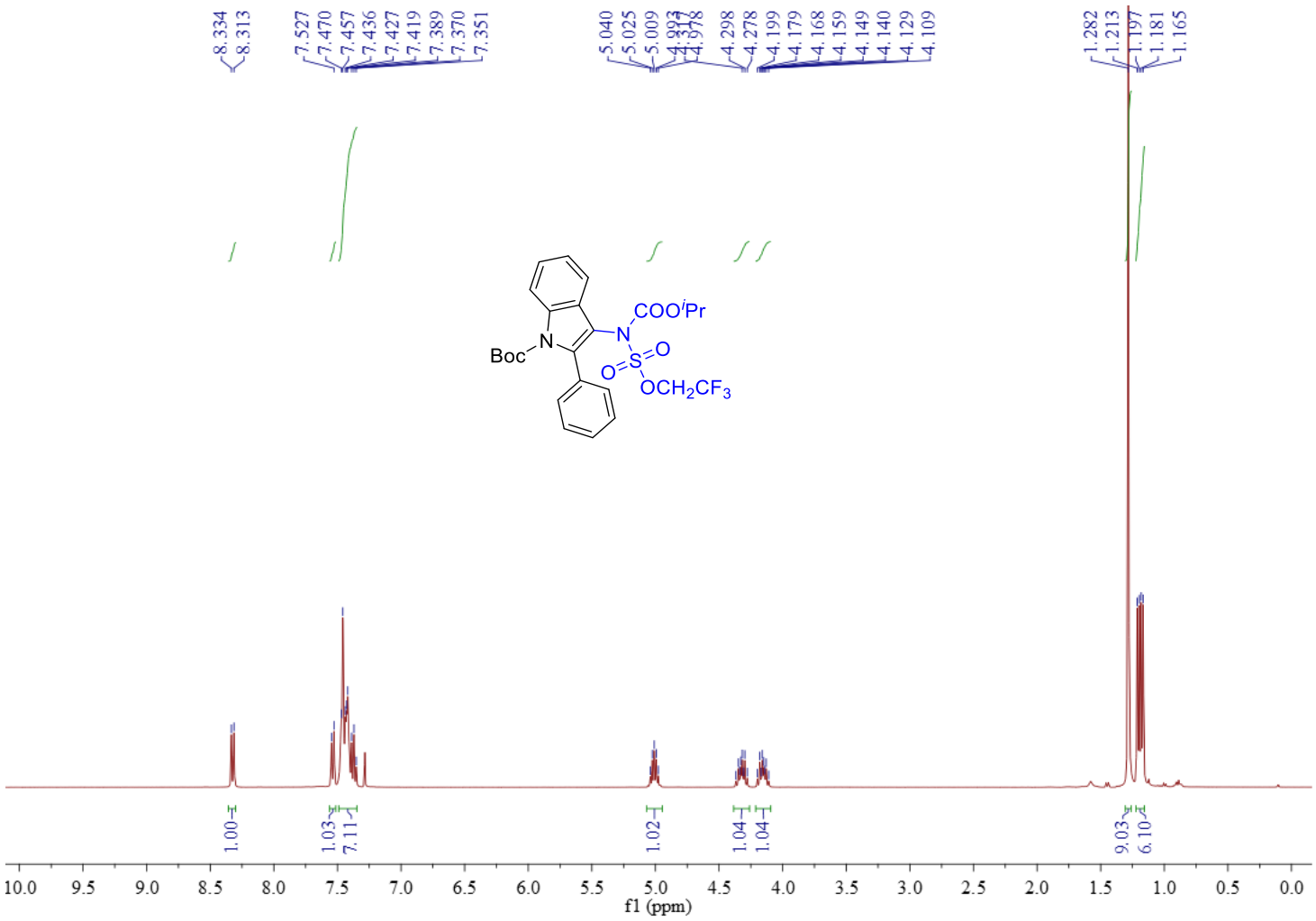
^{13}C NMR of **3p** (100 MHz, $CDCl_3$)



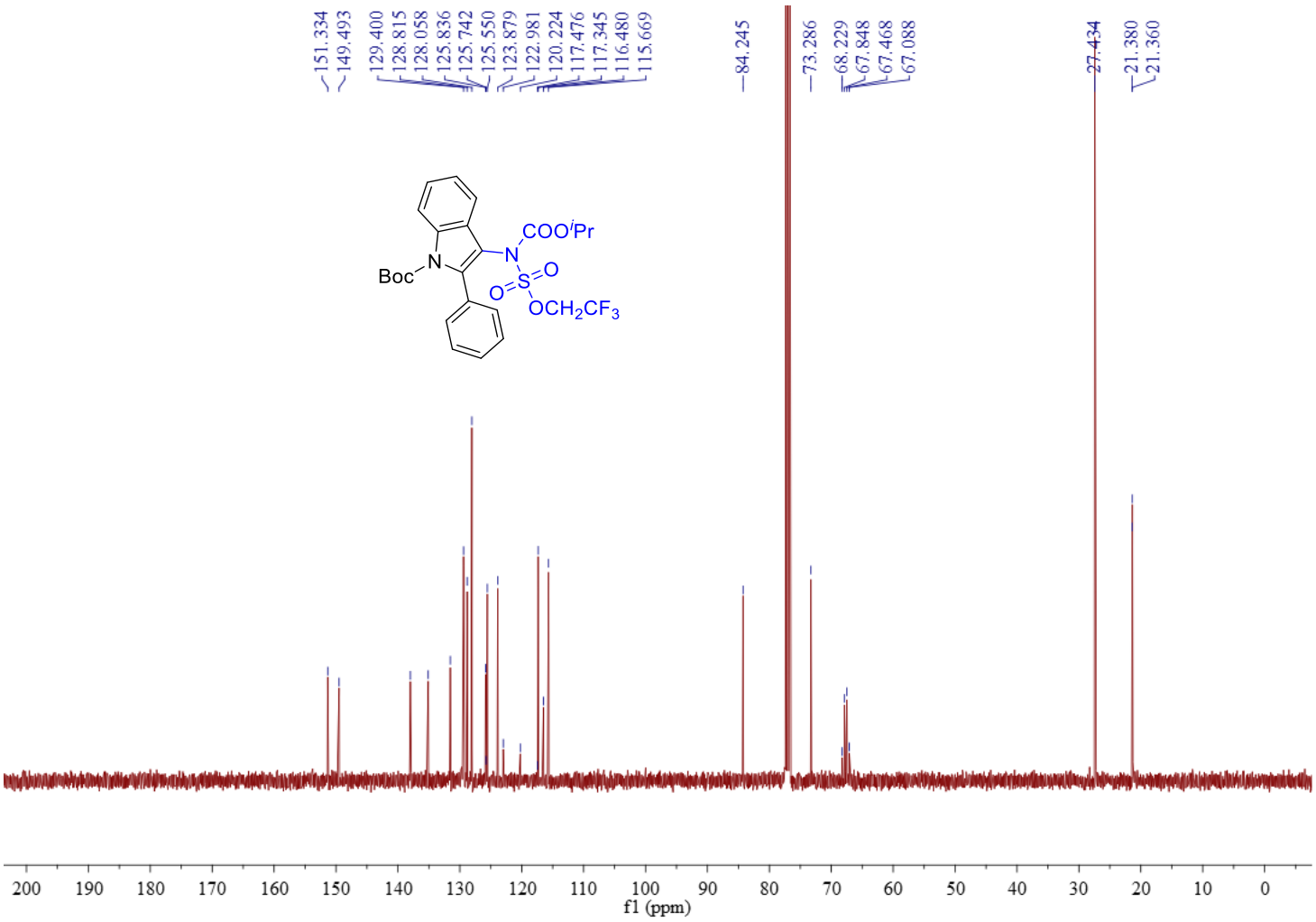
^{1}H NMR of **3q** (100 MHz, $CDCl_3$)



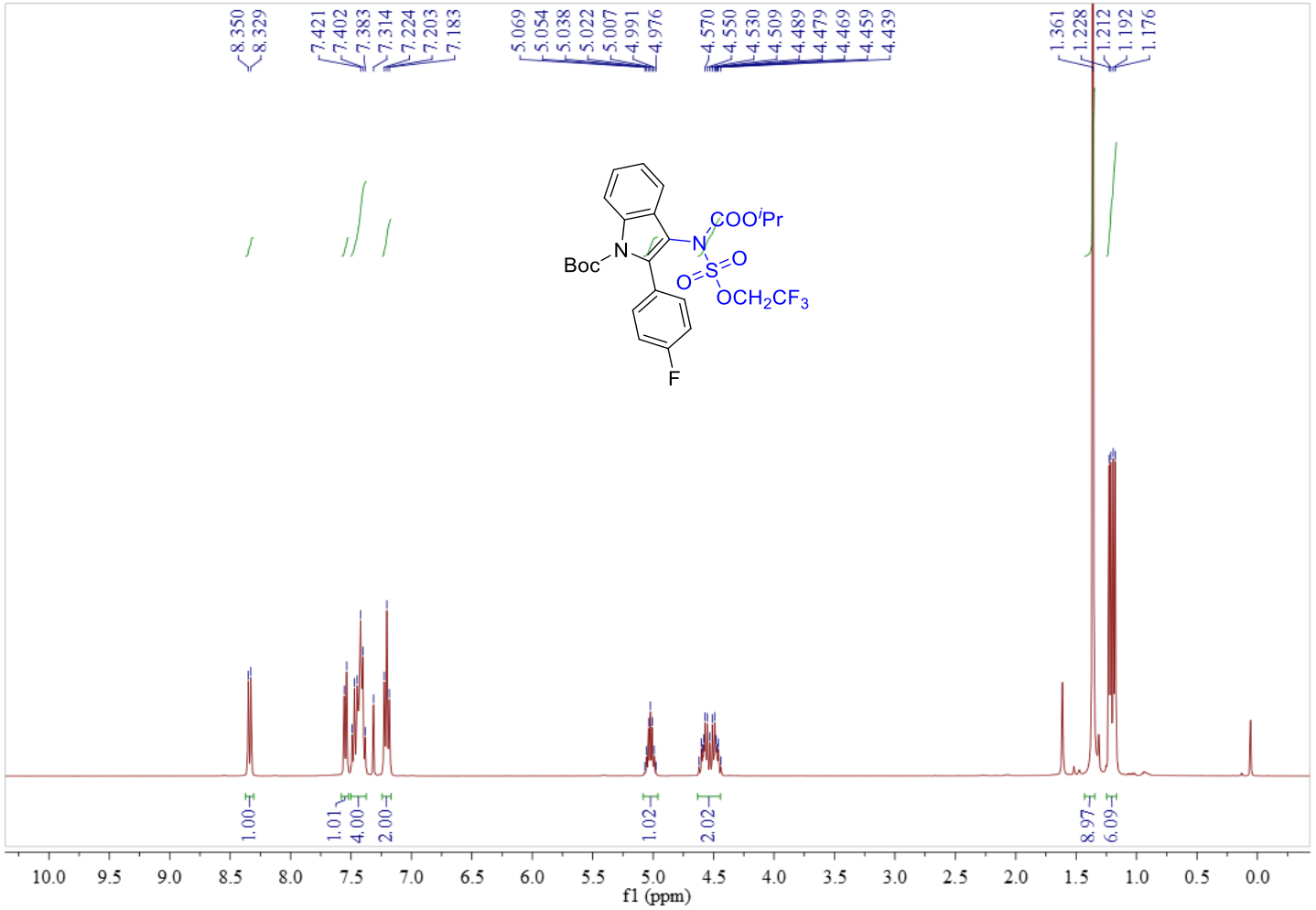
^{13}C NMR of **3q** (100 MHz, $CDCl_3$)



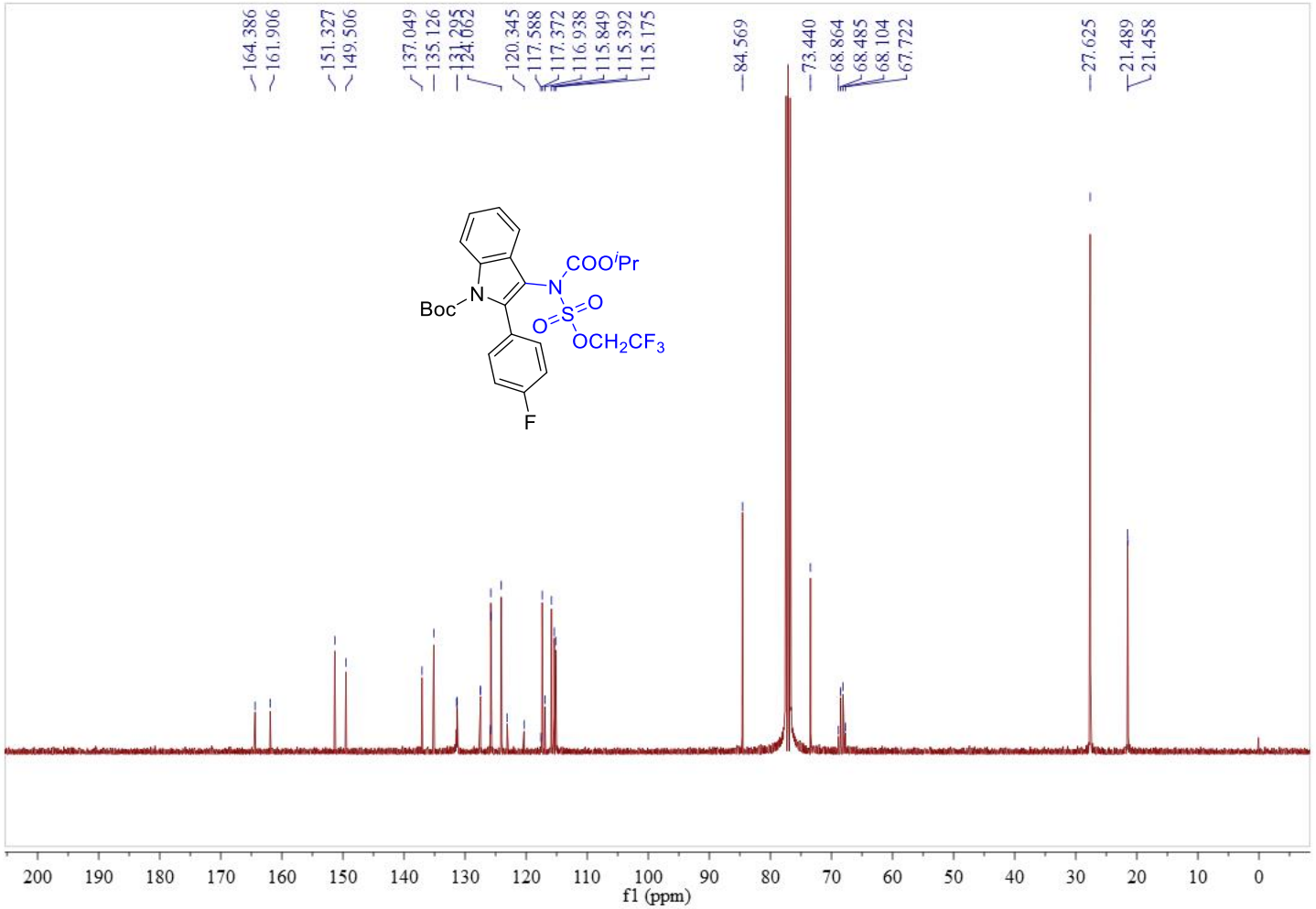
^{1}H NMR of **4a** (100 MHz, $CDCl_3$)



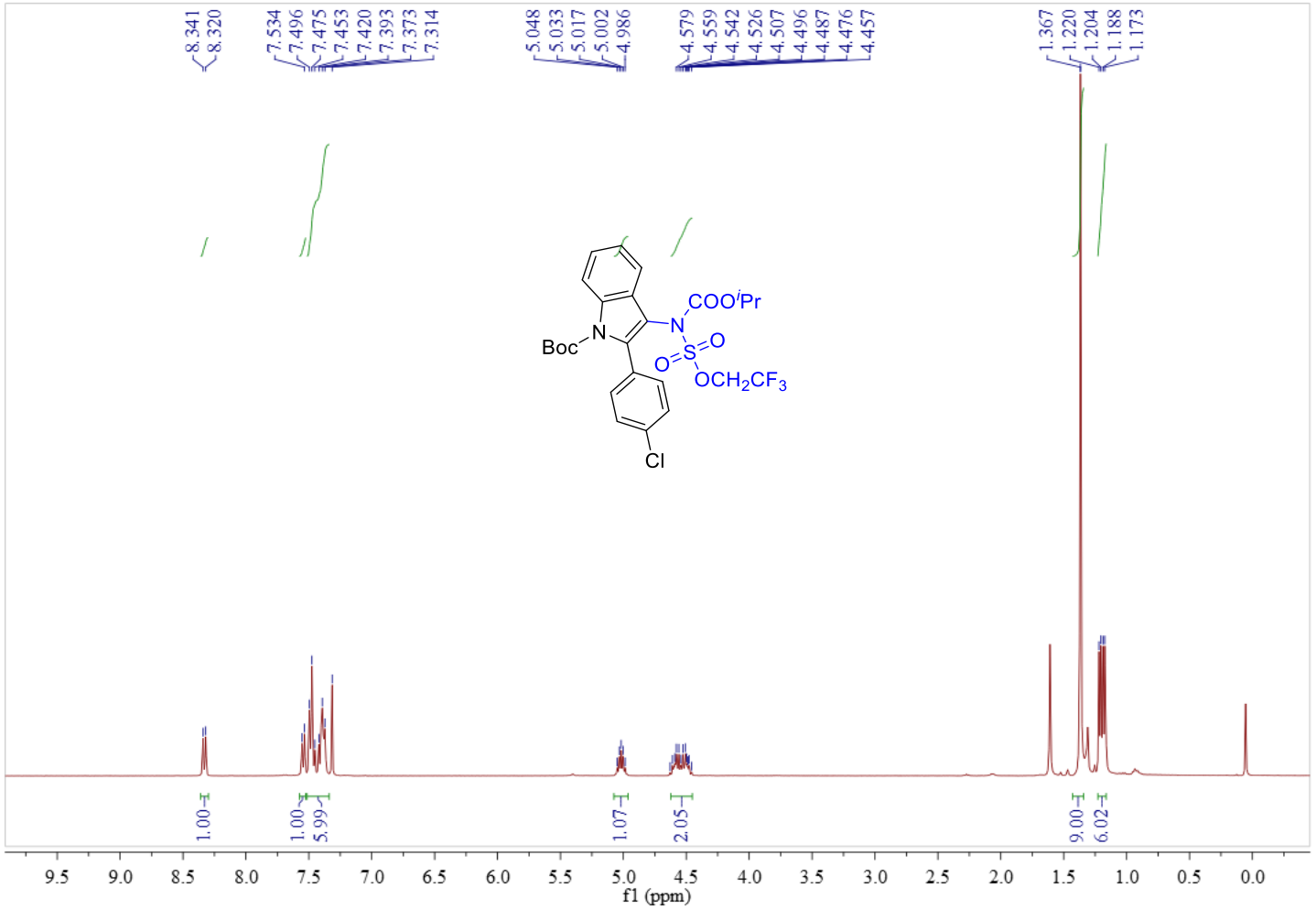
^{13}C NMR of **4a** (100 MHz, $CDCl_3$)



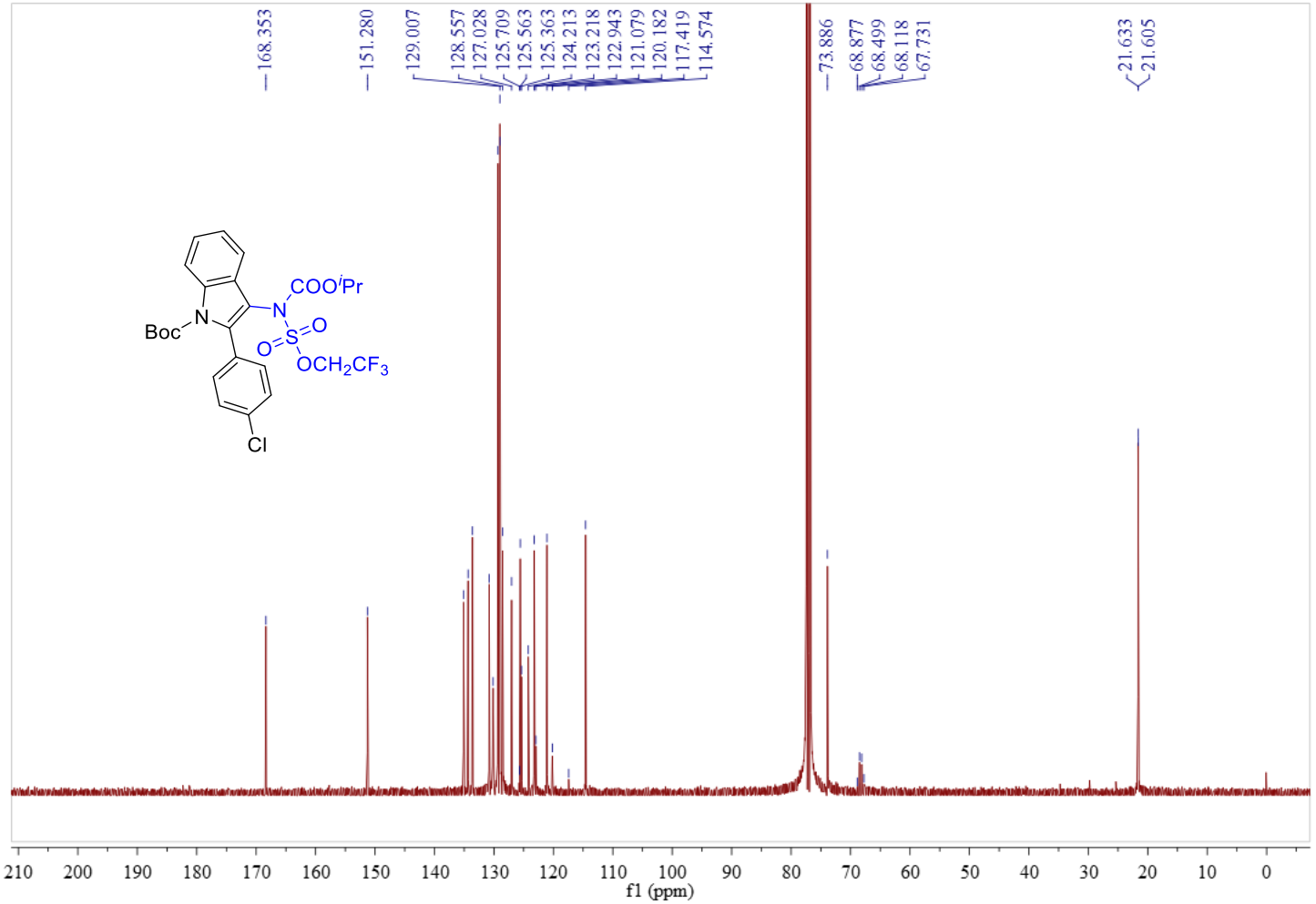
^{1}H NMR of **4b** (100 MHz, $CDCl_3$)



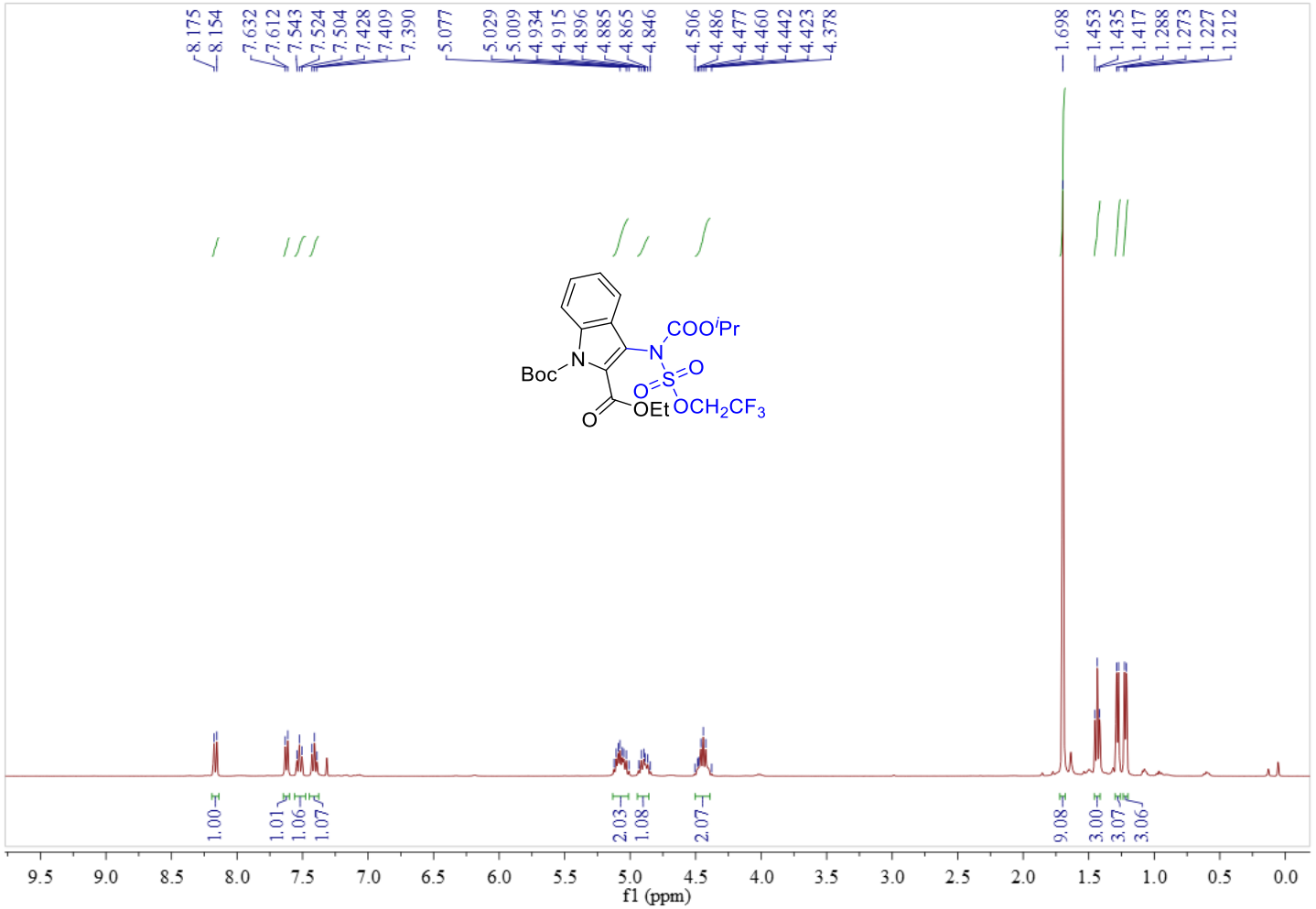
^{13}C NMR of **4b** (100 MHz, $CDCl_3$)



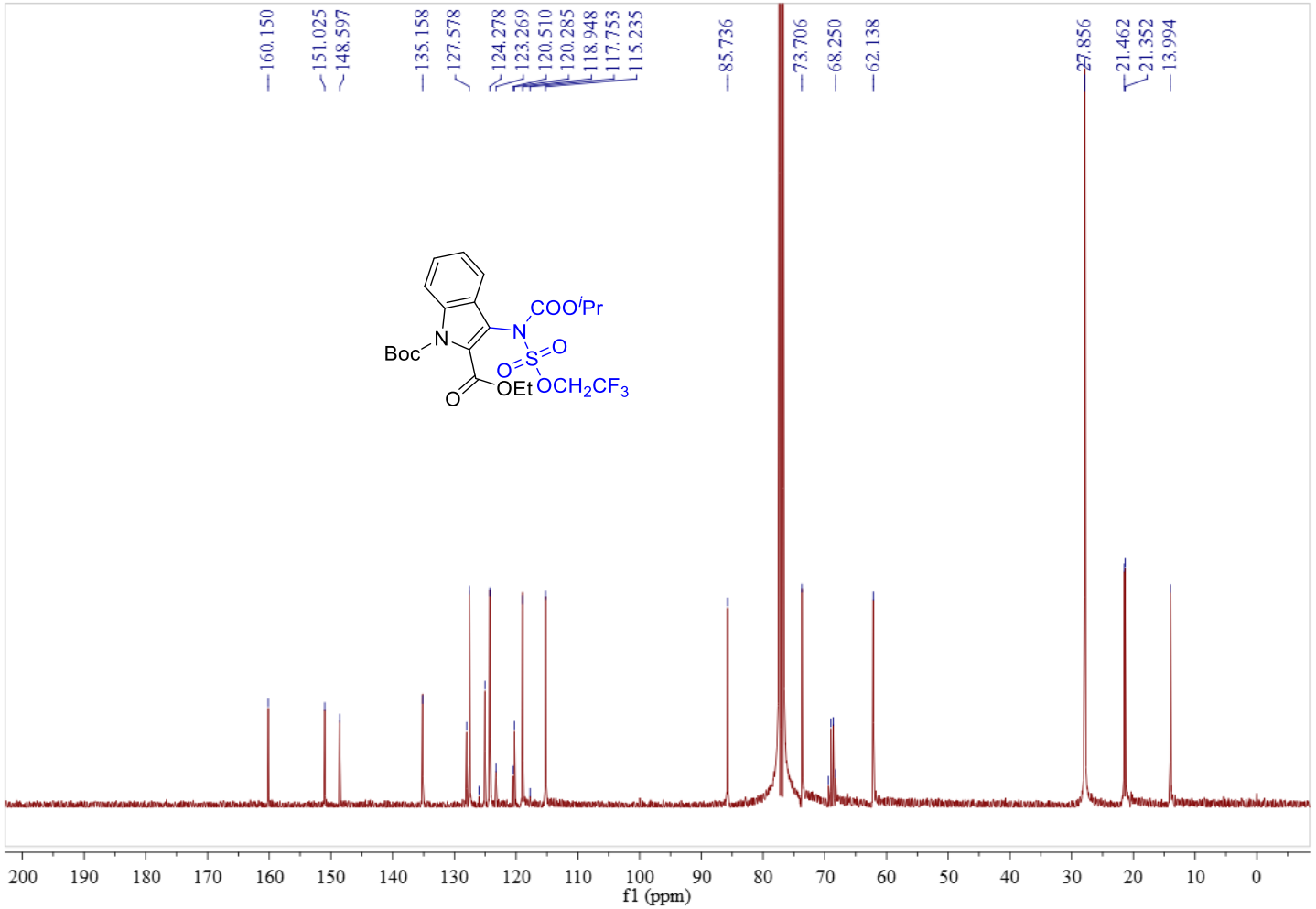
^{1}H NMR of **4c** (100 MHz, $CDCl_3$)



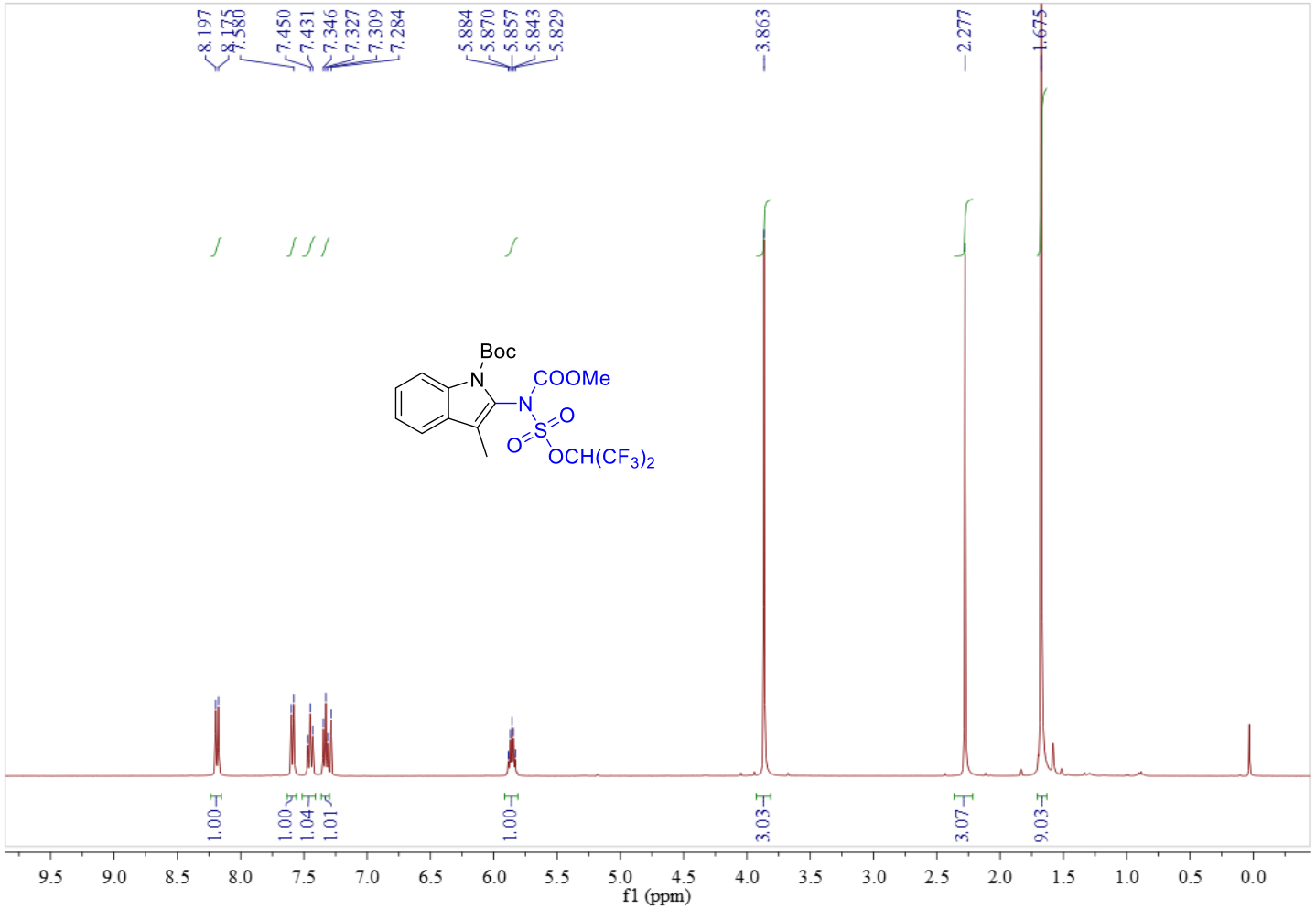
^{13}C NMR of **4c** (100 MHz, $CDCl_3$)



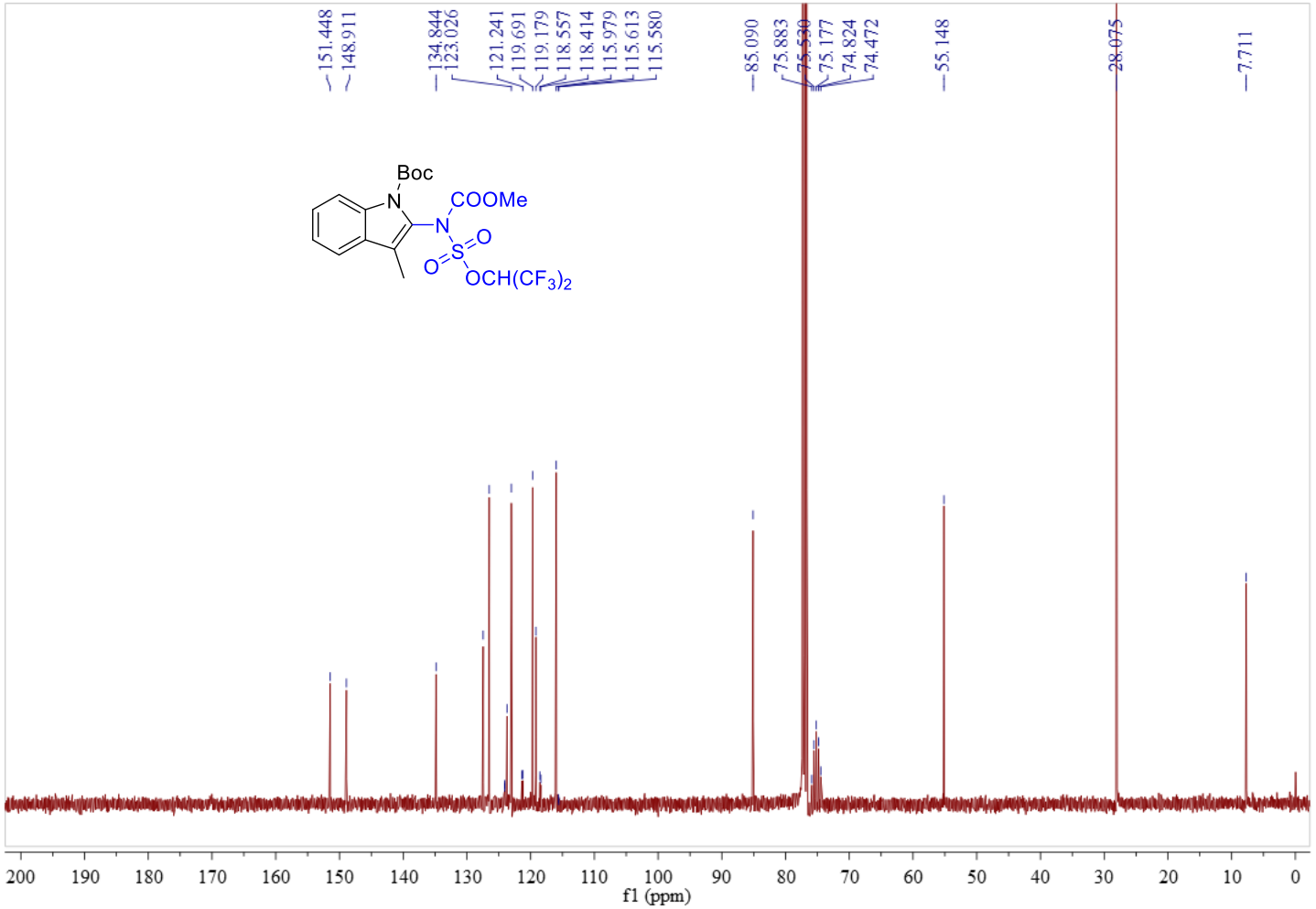
^{1}H NMR of **4d** (100 MHz, $CDCl_3$)



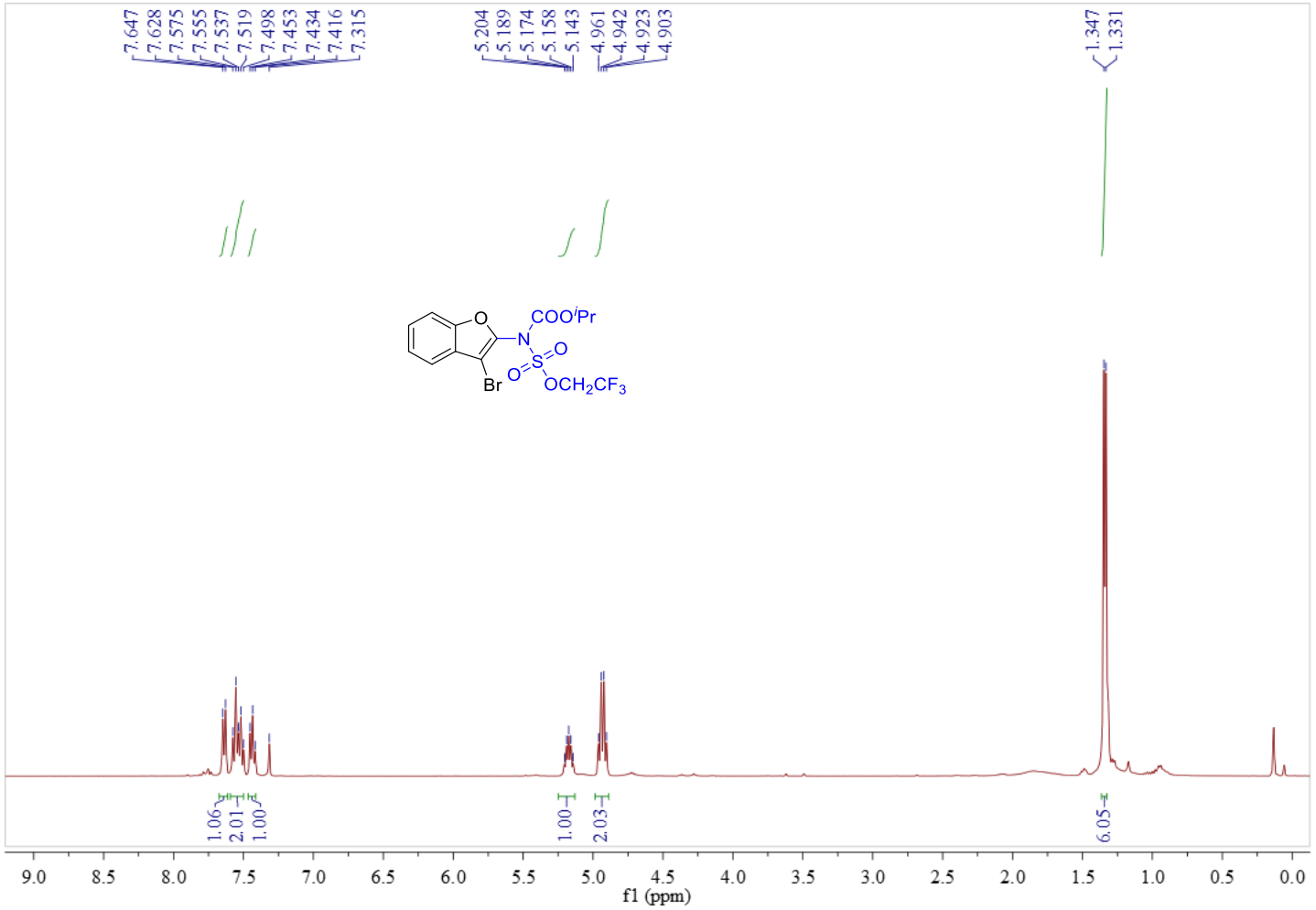
^{13}C NMR of **4d** (100 MHz, $CDCl_3$)



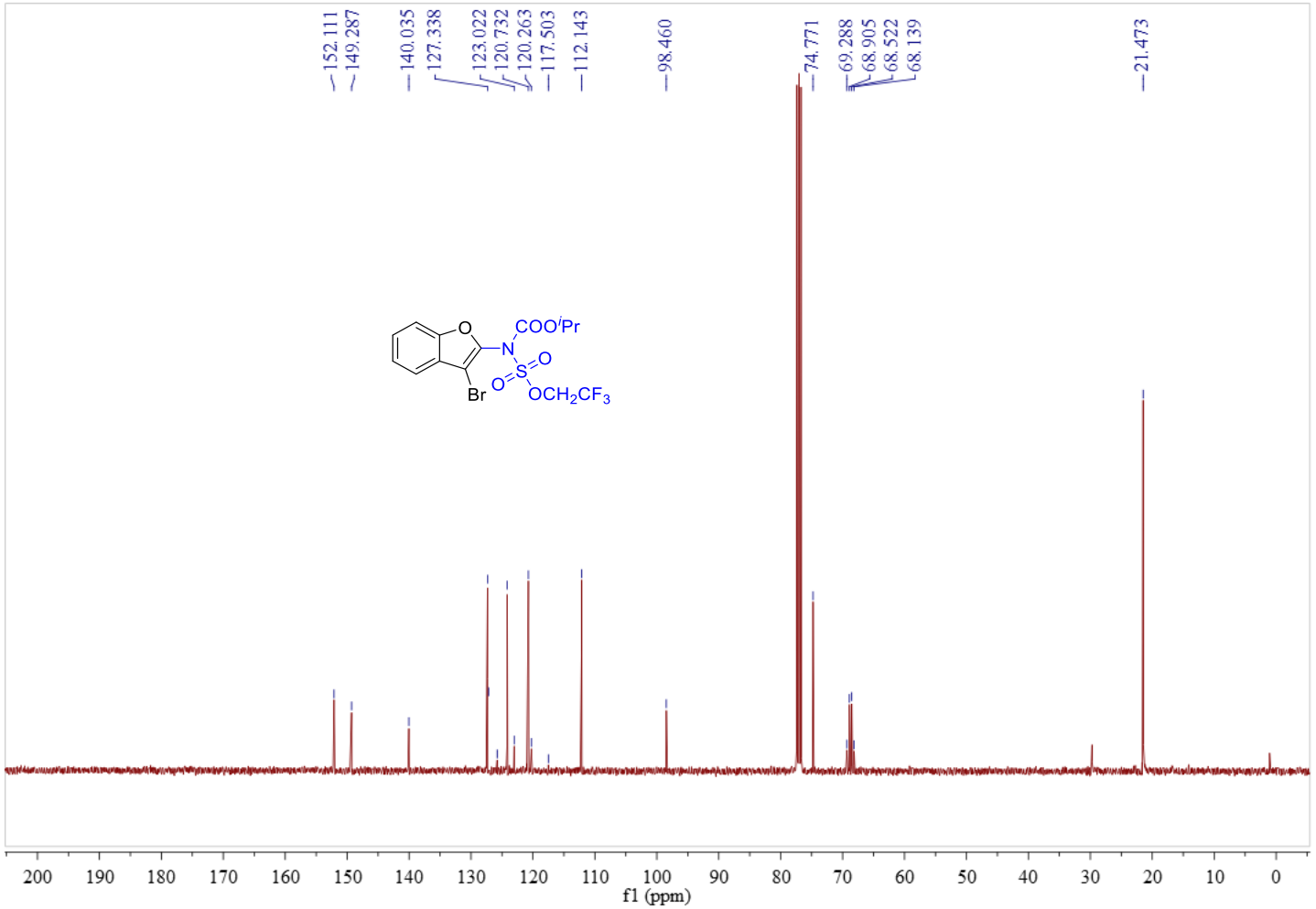
^{1}H NMR of **4e** (100 MHz, $CDCl_3$)



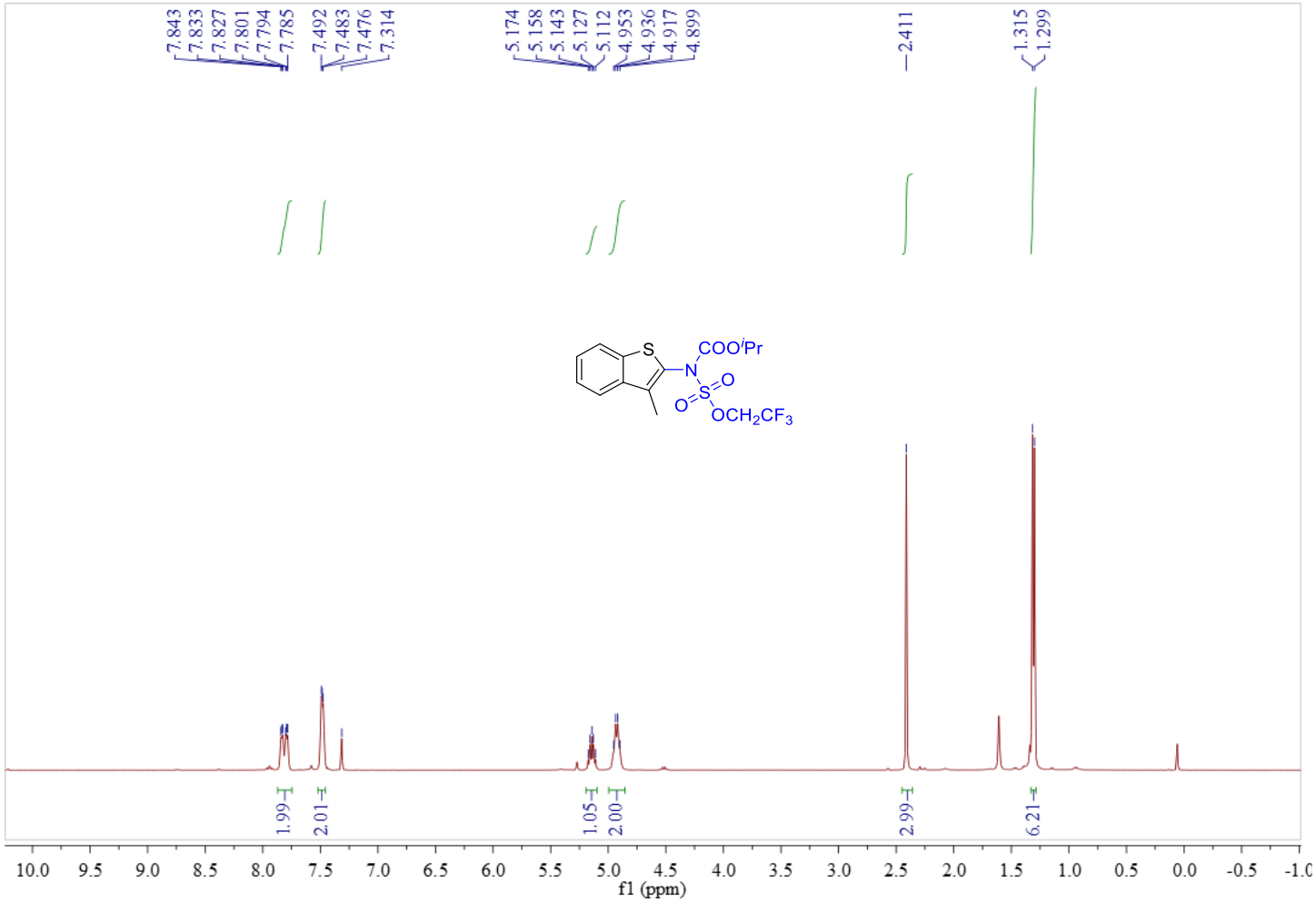
^{13}C NMR of **4e** (100 MHz, $CDCl_3$)



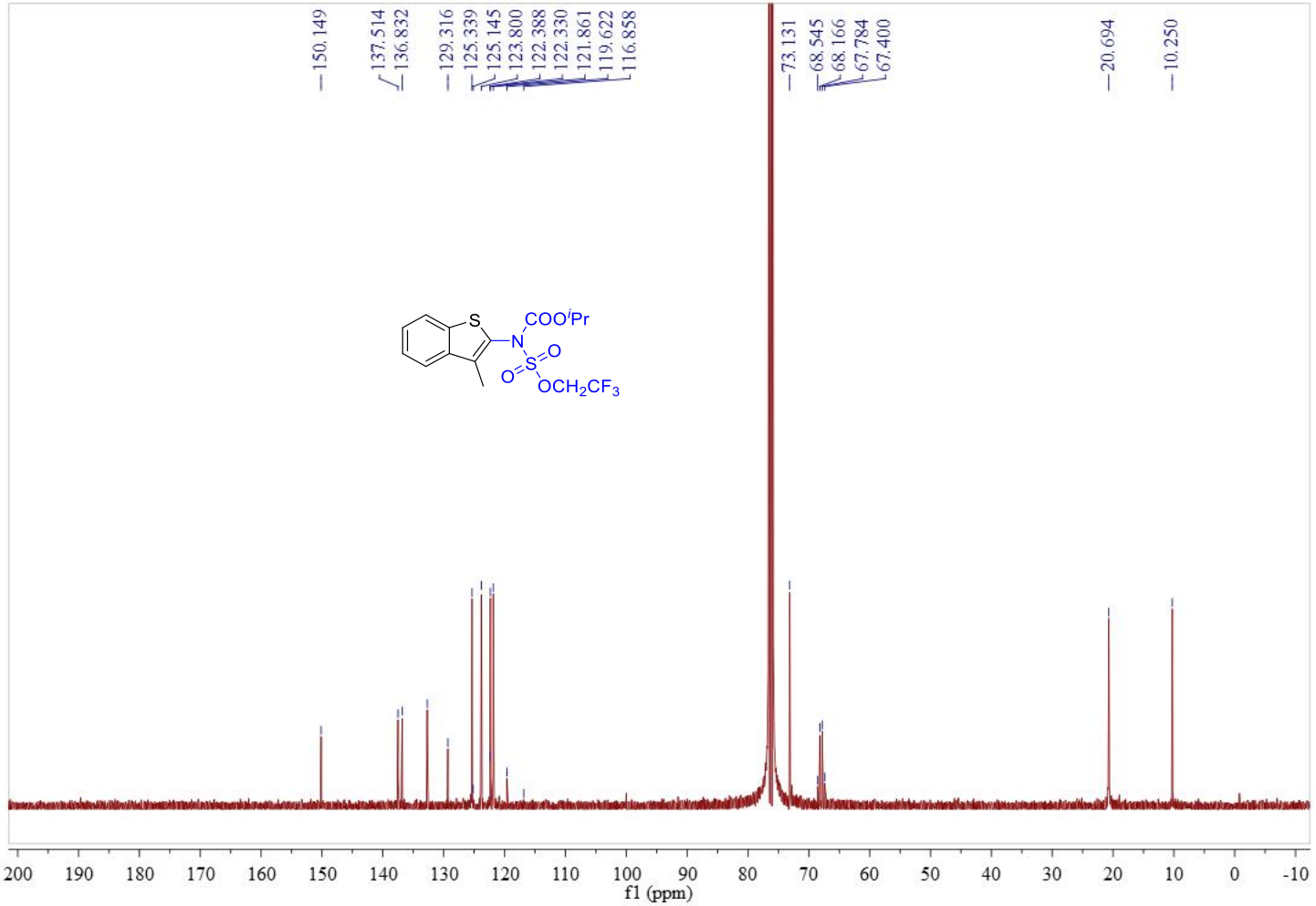
^{1}H NMR of **6a** (100 MHz, $CDCl_3$)



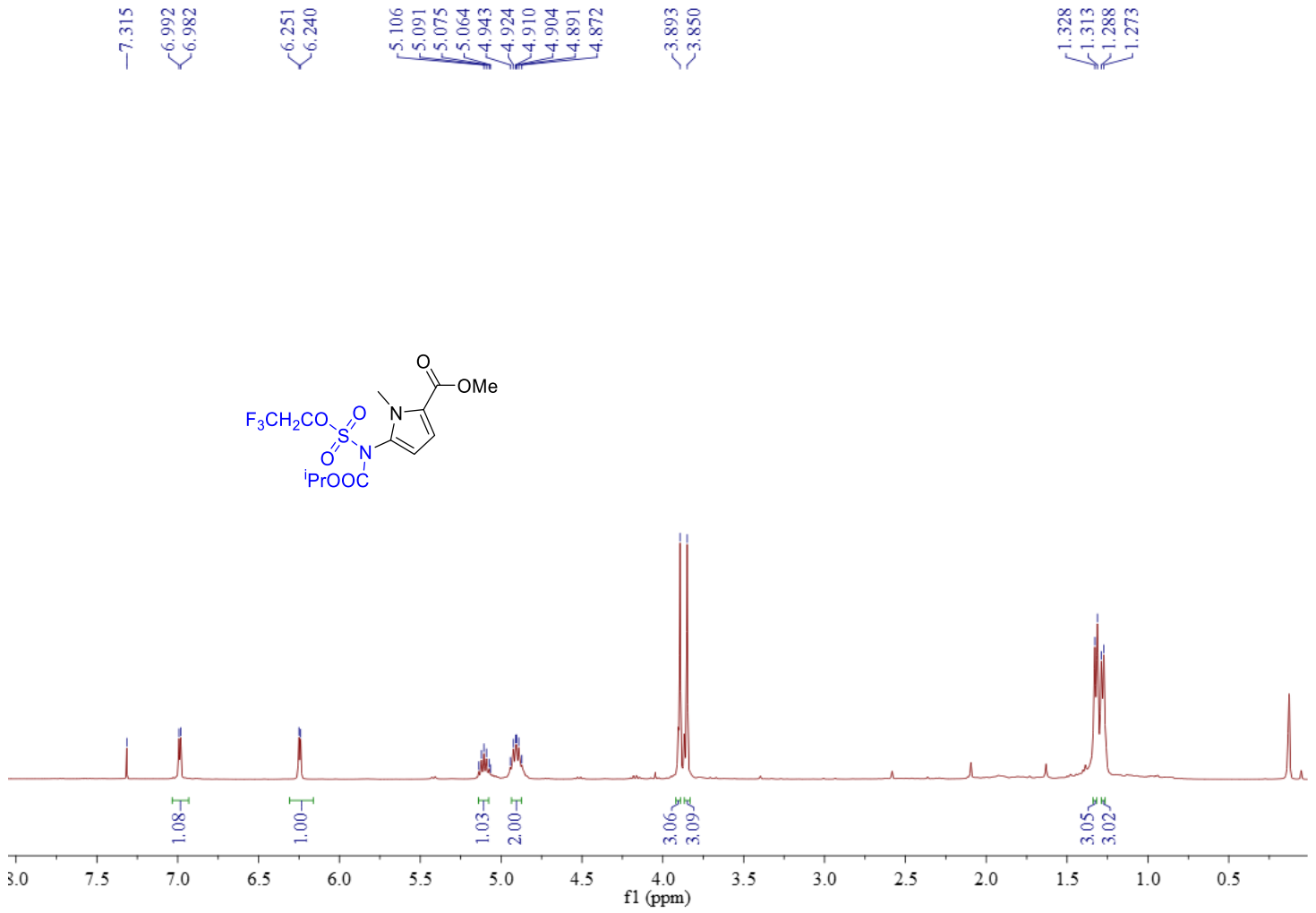
^{13}C NMR of **6a** (100 MHz, $CDCl_3$)



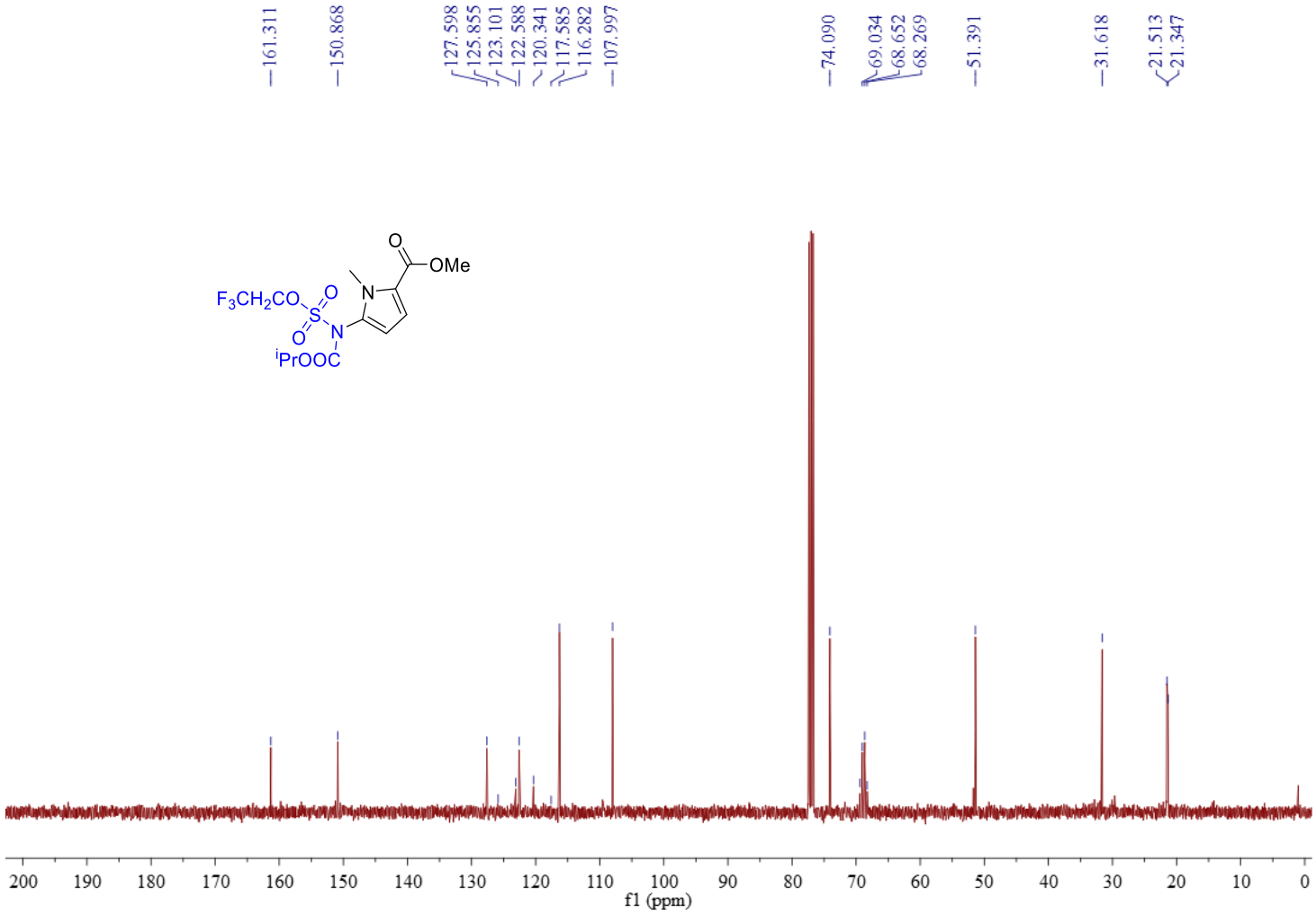
^{1}H NMR of **6b** (100 MHz, $CDCl_3$)



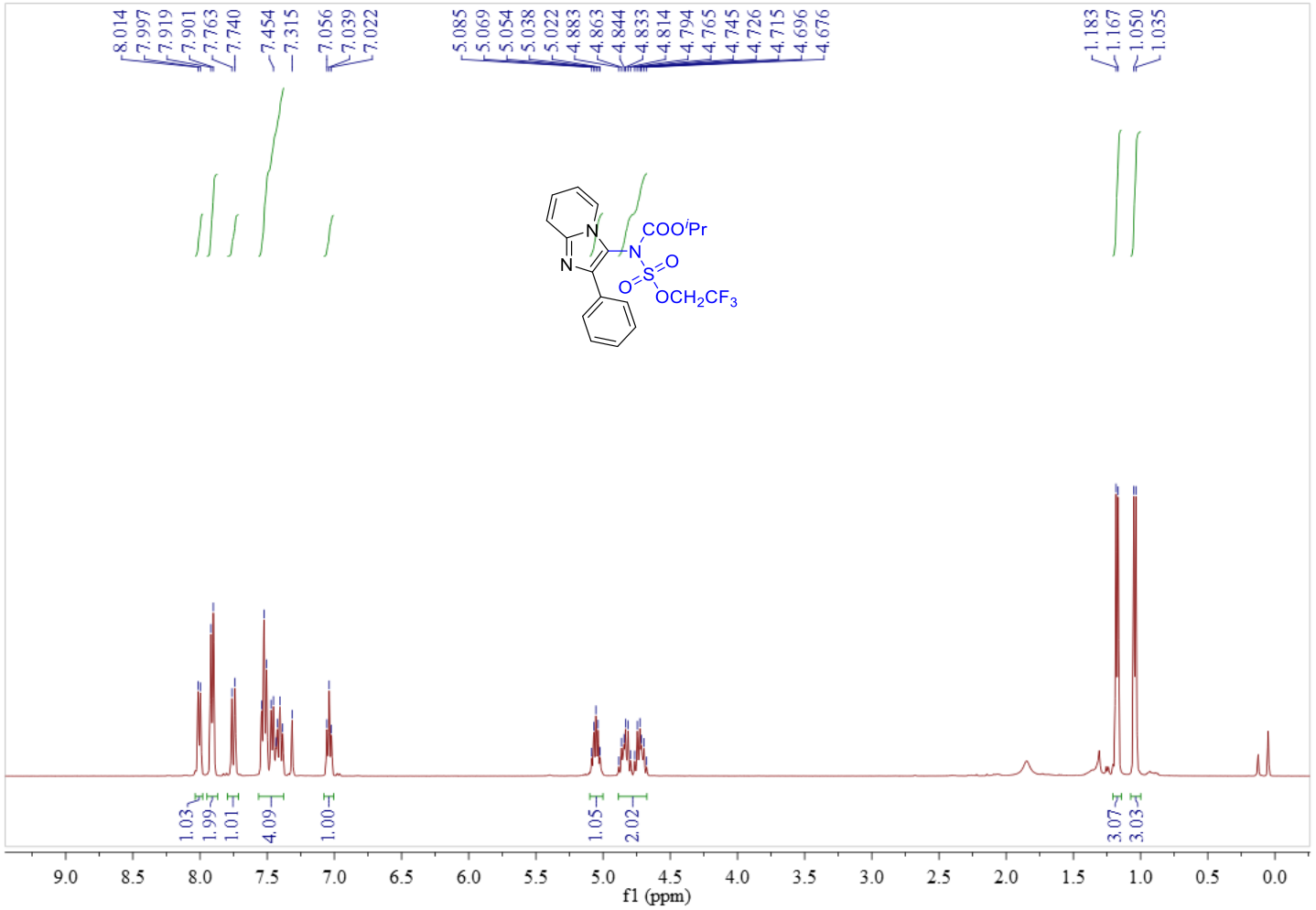
^{13}C NMR of **6b** (100 MHz, $CDCl_3$)



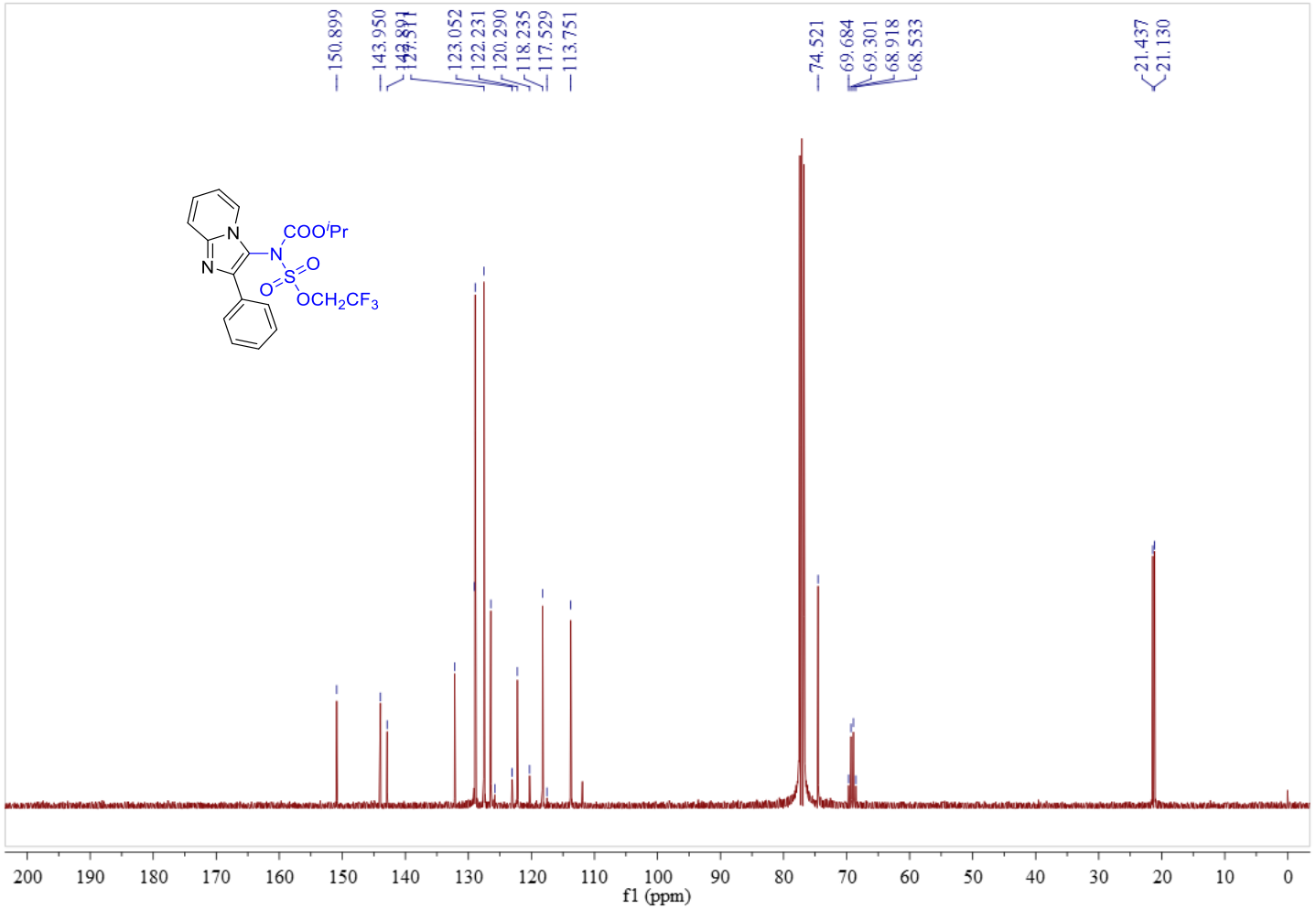
^{1}H NMR of **6c** (100 MHz, $CDCl_3$)



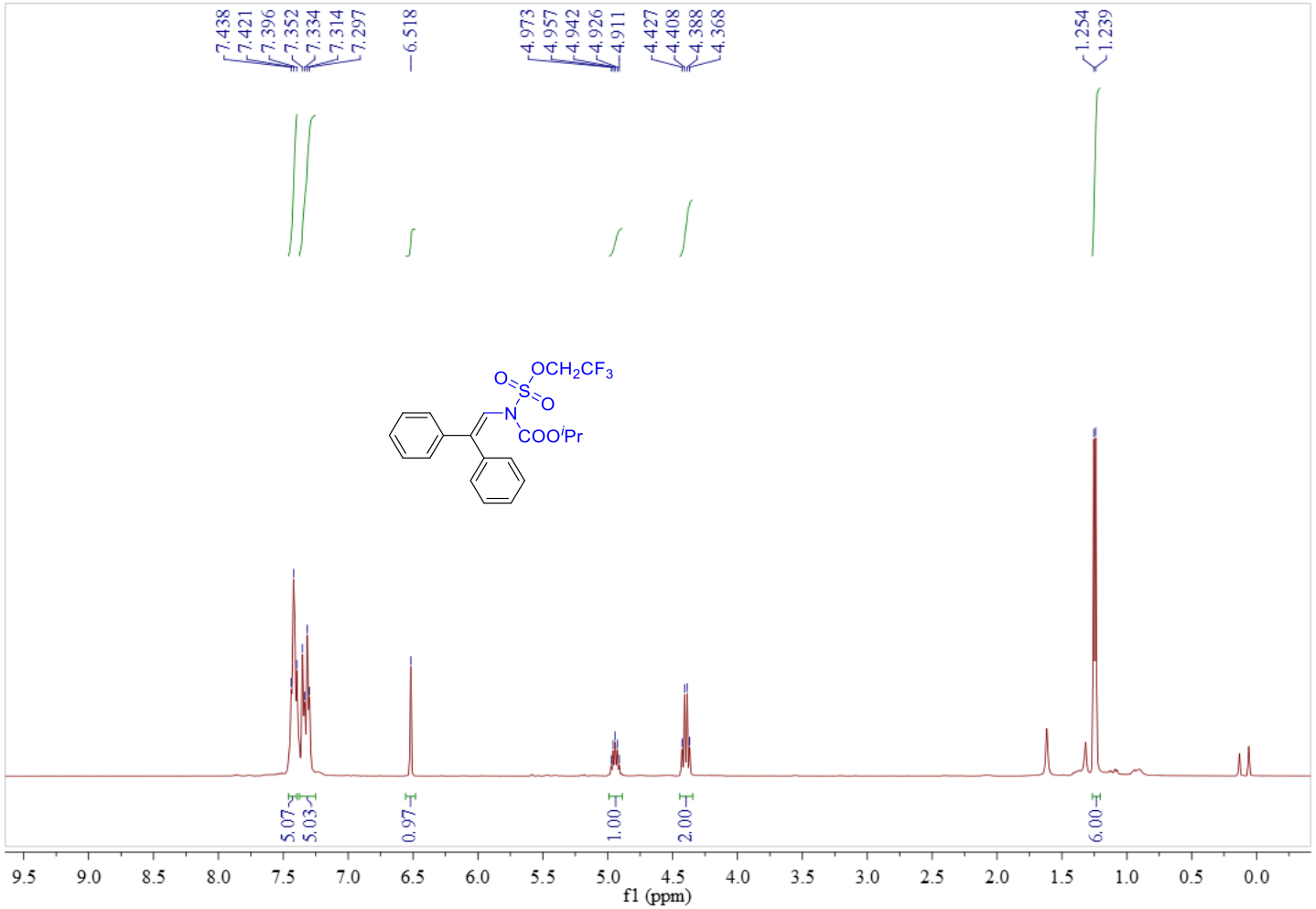
^{13}C NMR of **6c** (100 MHz, $CDCl_3$)



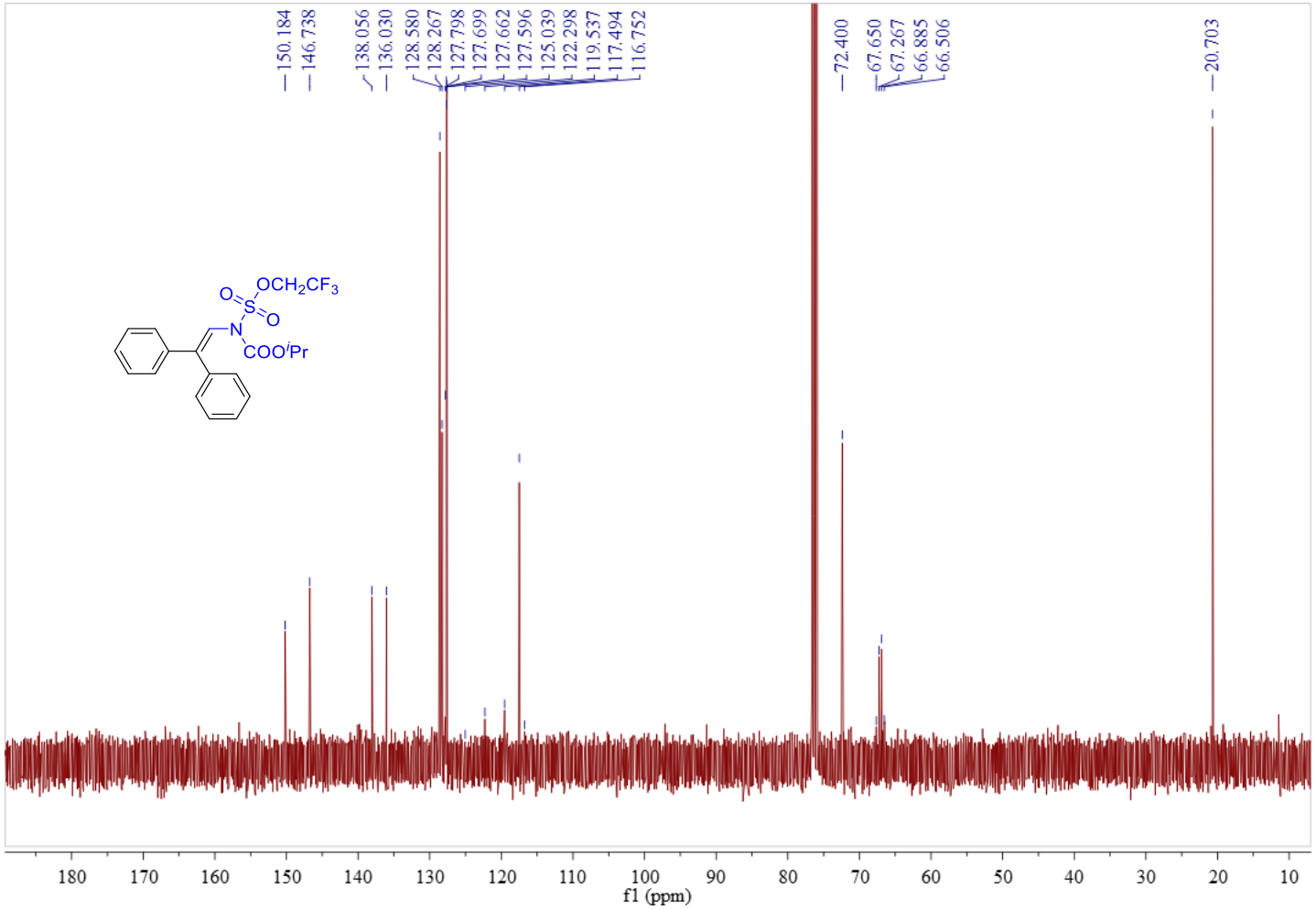
^{1}H NMR of **6d** (100 MHz, $CDCl_3$)



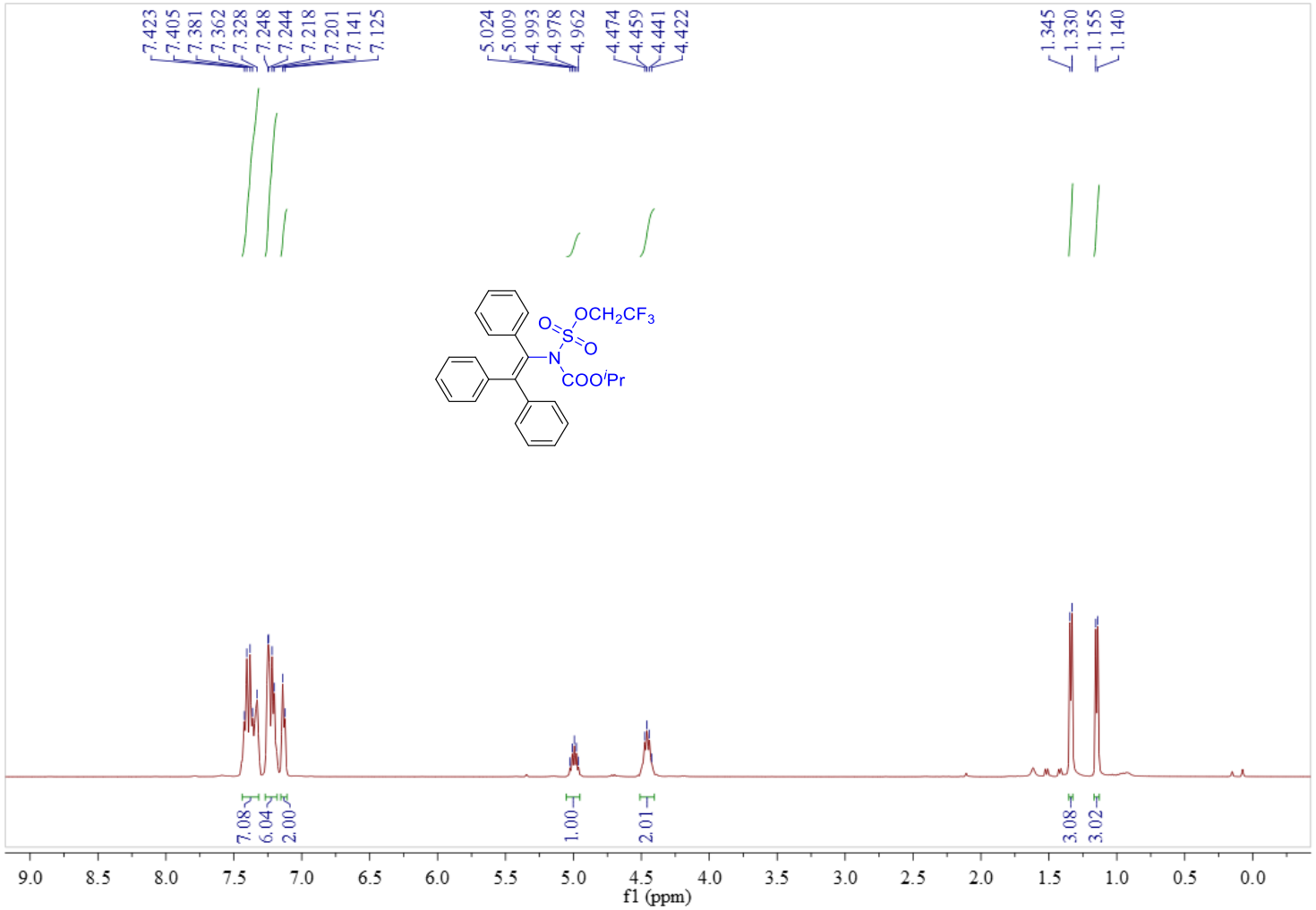
^{13}C NMR of **6d** (100 MHz, $CDCl_3$)



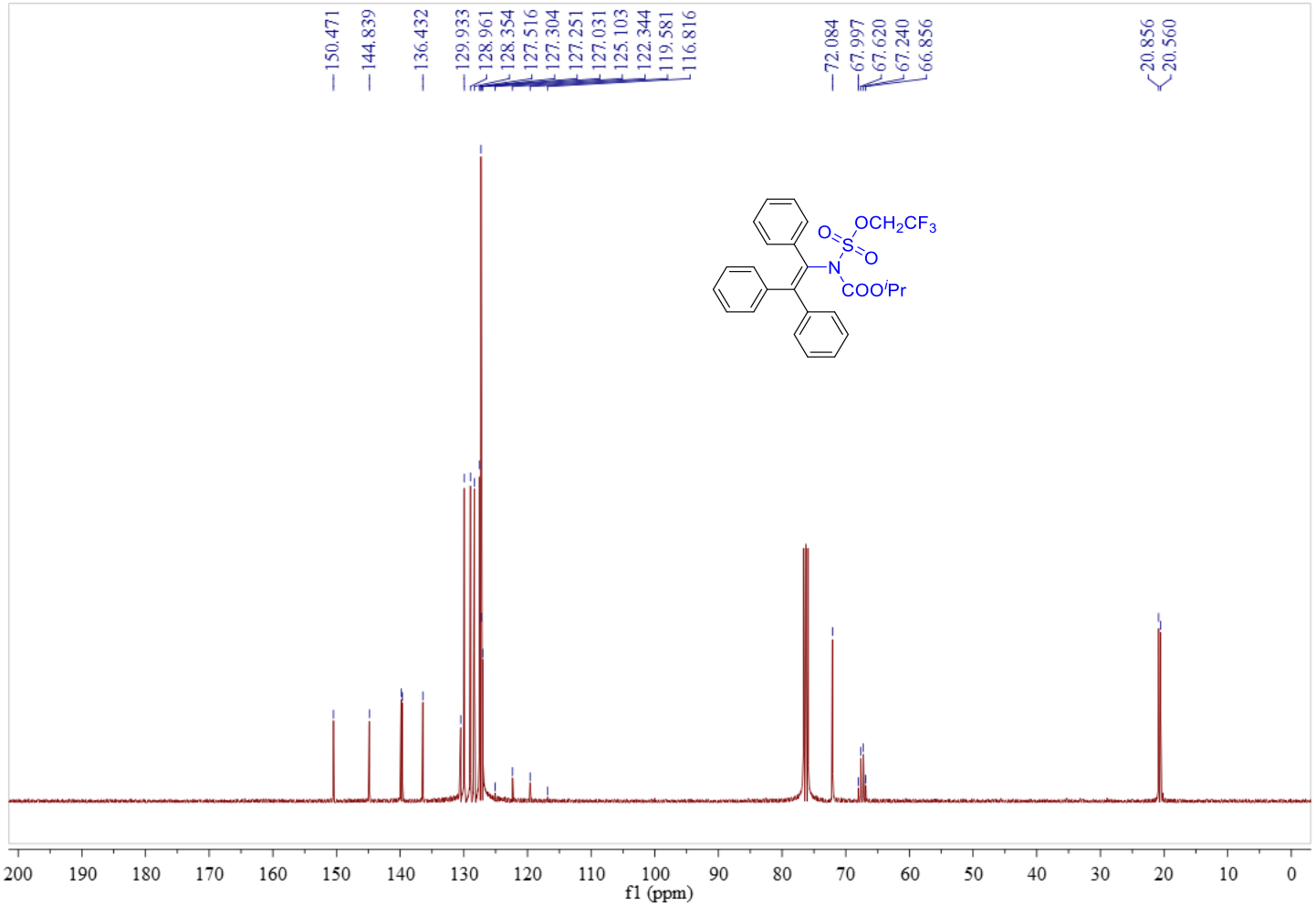
^{1}H NMR of **6e** (100 MHz, $CDCl_3$)



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



^{1}H NMR of **6f** (100 MHz, $CDCl_3$)



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

11. Indoles that failed to produce amination products under standard condition