Supporting Information

Ligand-free Nickel-Catalyzed Perfluoroalkylation of Arenes and Heteroarenes

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I. General specification

All reactions were performed using glovebox technique under a dry nitrogen atmosphere unless indicated otherwise. All chemicals unless noted otherwise were purchased from commercial suppliers (TCI, Sigma-Aldrich, CF-Plus chemicals and Nacalai Tesque) and used without purification. Anhydrous solvents were dispensed from an MBRAUN solvent purification system and degassed prior to use. Anhydrous deuterated solvents were purchased from Eurisotop and

stored over 4 Å molecular sieves. Metal precursor $Ni(MeCN)_2(C_2F_5)_2$ was prepared according to literature procedure[1].

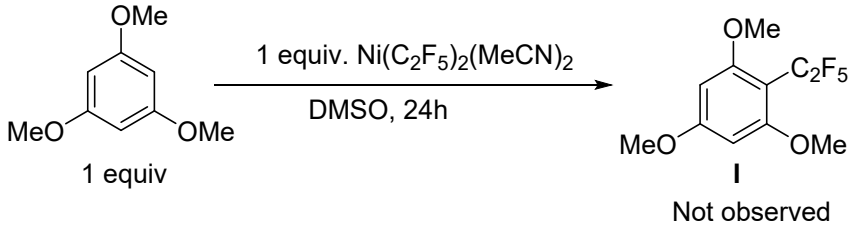
Instrumentation: NMR spectra were measured on JEOL ECZ600R 600MHz, JEOL ECZ400S 400 MHz and Bruker Avance III Neo 500 MHz (CryoProbe) spectrometers. The following abbreviations are used for describing NMR spectra: s (singlet), d (doublet), t (triplet), br. s (broad singlet), vd (virtual doublet), vt (virtual triplet), tq (triplet of quartets), qt (quartet of triplets), br (broad).

Electrospray Ionization High-Resolution Mass Spectrometry (ESI-HRMS) measurements were performed on a Thermo Scientific ETD apparatus.

Absorbance UV/vis spectra were collected using an Agilent Cary 60 instrument.

X-band EPR spectra were recorded using X-band JEOL JES-X330 instrument. For low temperature measurements, liquid nitrogen-cooled cryostat was used and the samples were measured in 5 mm diameter quartz tubes; for room temperature samples, 50 µL quartz capillary tubes were used. Simulation of the experimental spectrum were done using the Easyspin package [2] in Matlab R2016b. “Pepper” function was used for anisotropic spectra simulation, respectively.

II. Stoichiometric C-H perfluoro alkylation with Nickel precursor



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 1,3,5-Trimethoxybenzene (10.0 mg, 0.059 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (22.5 mg, 0.059 mmol), which were then dissolved in anhydrous DMSO (1 mL). Further, the reaction mixture was stirred at room temperature for 24 hours. After the completion of the reaction, α,α,α-trifluorotoluene (7.3 µL, 0.059 mmol) was added as an internal standard and the yield was determined by ^{19}F NMR spectroscopy.

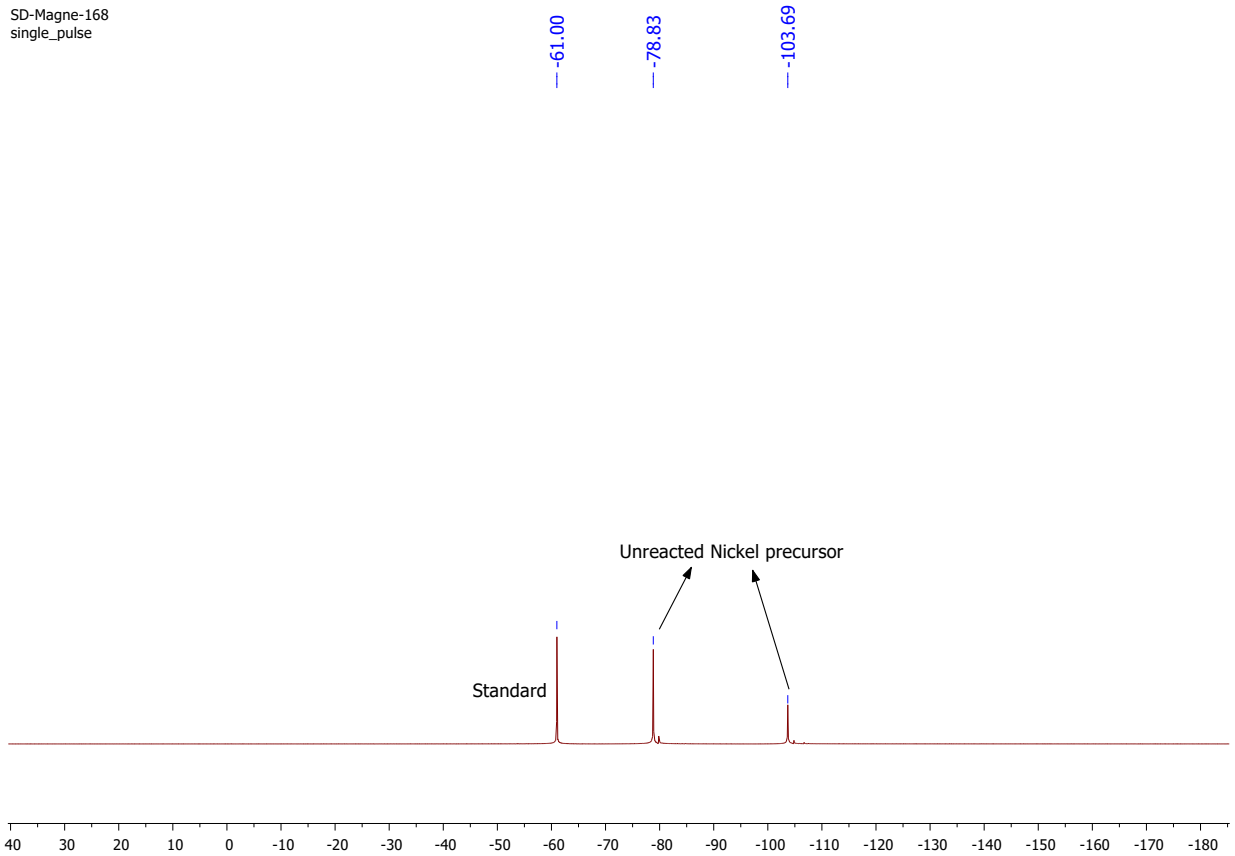
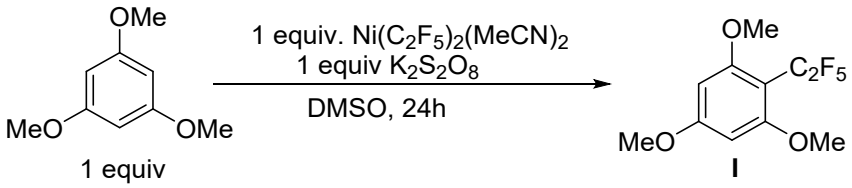


Figure S1. ^{19}F NMR spectrum showing unreacted nickel precursor in the absence of oxidant**.**



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 1,3,5-Trimethoxybenzene (10.0 mg, 0.059 mmol), potassium persulfate (16.0 mg, 0.059 mmol), and $Ni(C_2F_5)_2(MeCN)_2$ (22.5 mg, 0.059 mmol) that were all dissolved in anhydrous DMSO (1 mL). The reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (7.3 µL, 0.059 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy (75% yield).

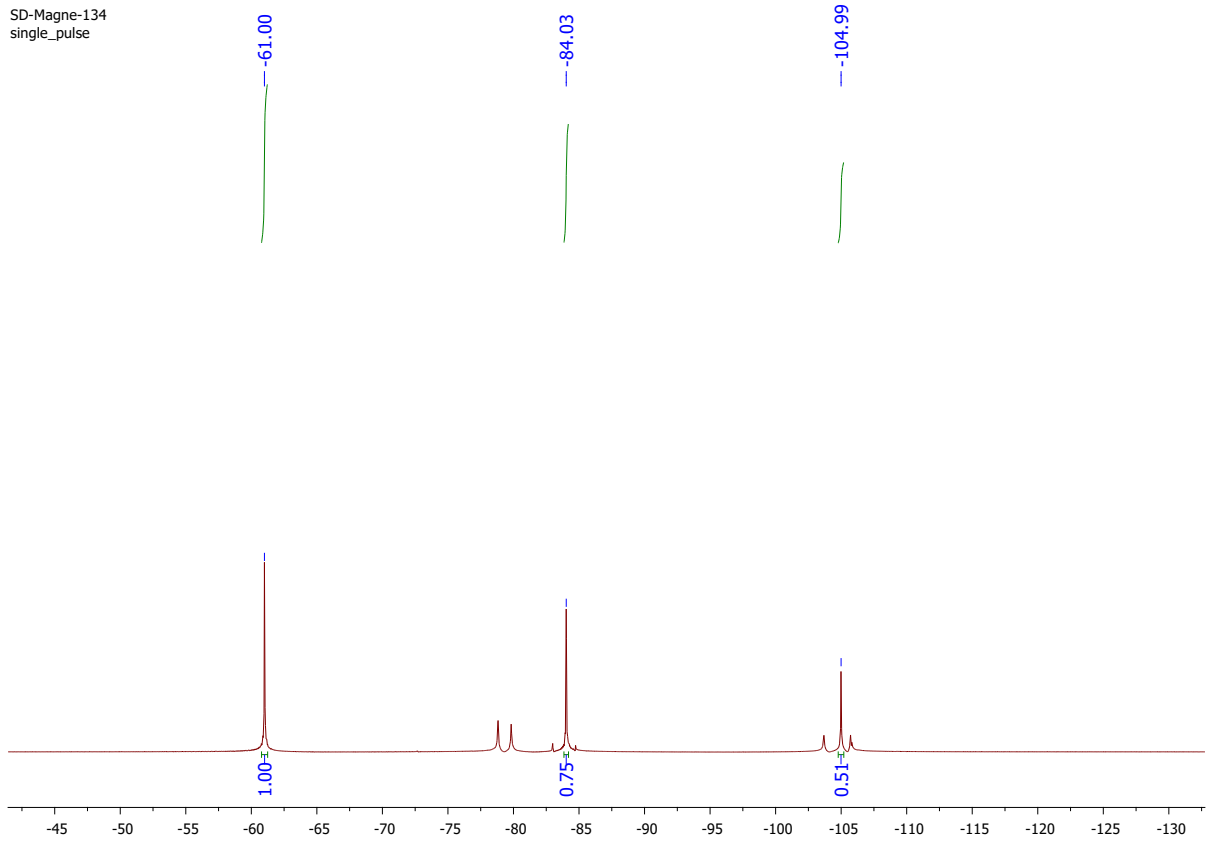
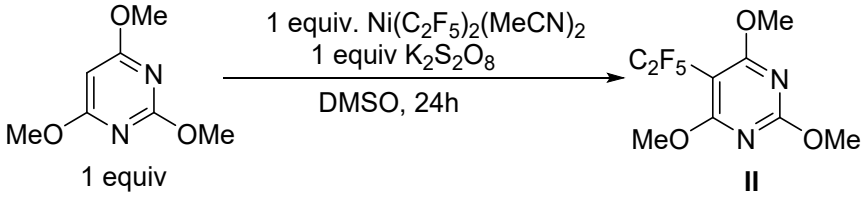


Figure S2. ^{19}F NMR spectrum showing formation of compound **I**.



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 2,4,6-Trimethoxypyrimidine (10.0 mg, 0.059 mmol), potassium persulfate (15.8 mg, 0.059 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (22.2 mg, 0.059 mmol) were dissolved in anhydrous DMSO (1 mL). The reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (7.2 µL, 0.059 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy (80% yield).

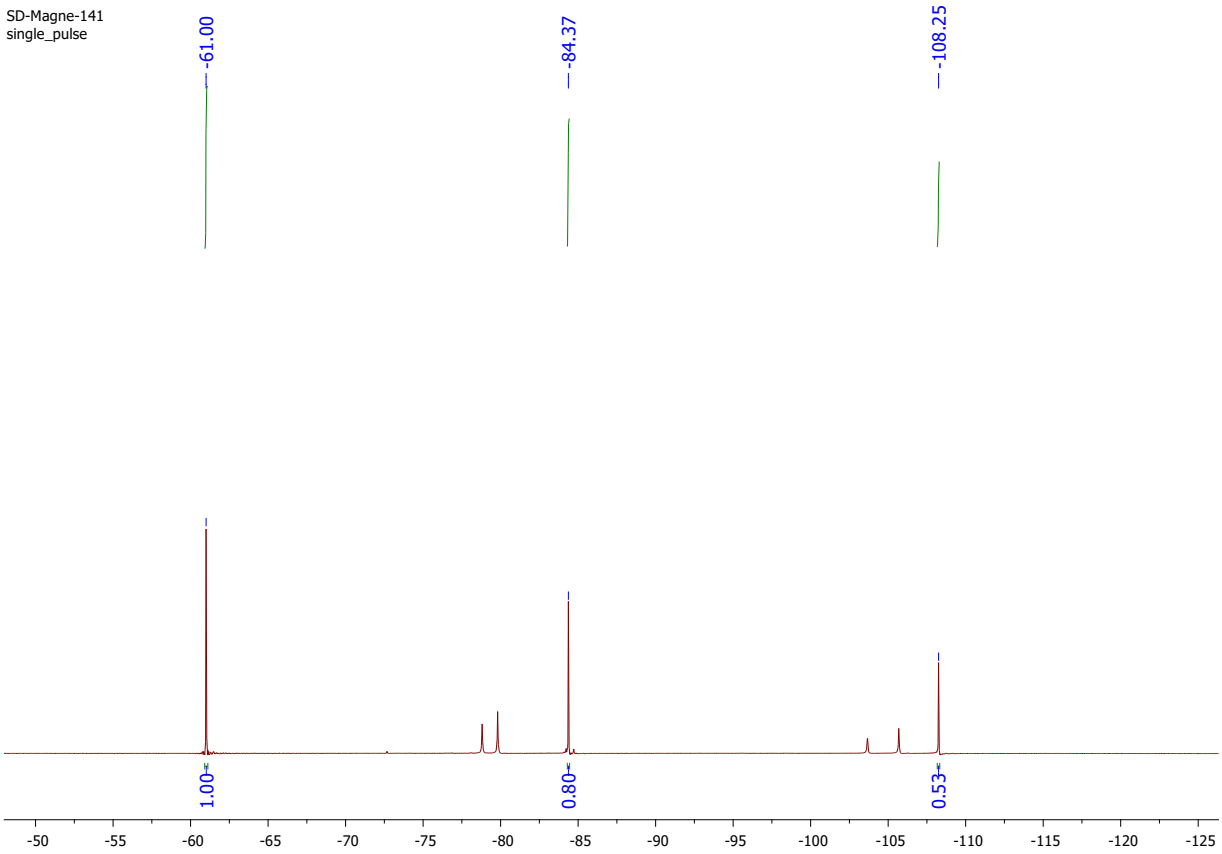
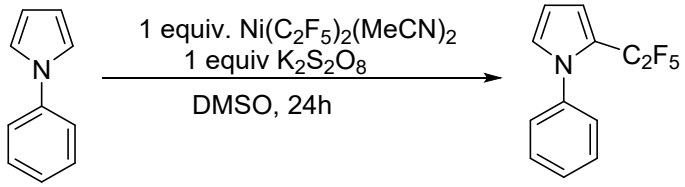


Figure S3. ^{19}F NMR spectrum showing formation of compound **II.**



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 1-phenylpyrrole (10 mg, 0.069 mmol), potassium persulfate (18.8 mg, 0.069 mmol), and $Ni(C_2F_5)_2(MeCN)_2$ (26.4 mg, 0.069 mmol), which were then dissolved in anhydrous DMSO (1 mL). The reaction mixture was stirred at room temperature for 24 hours. After the completion of the reaction, α,α,α-trifluorotoluene (8.5 µL, 0.069 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy (38% yield).

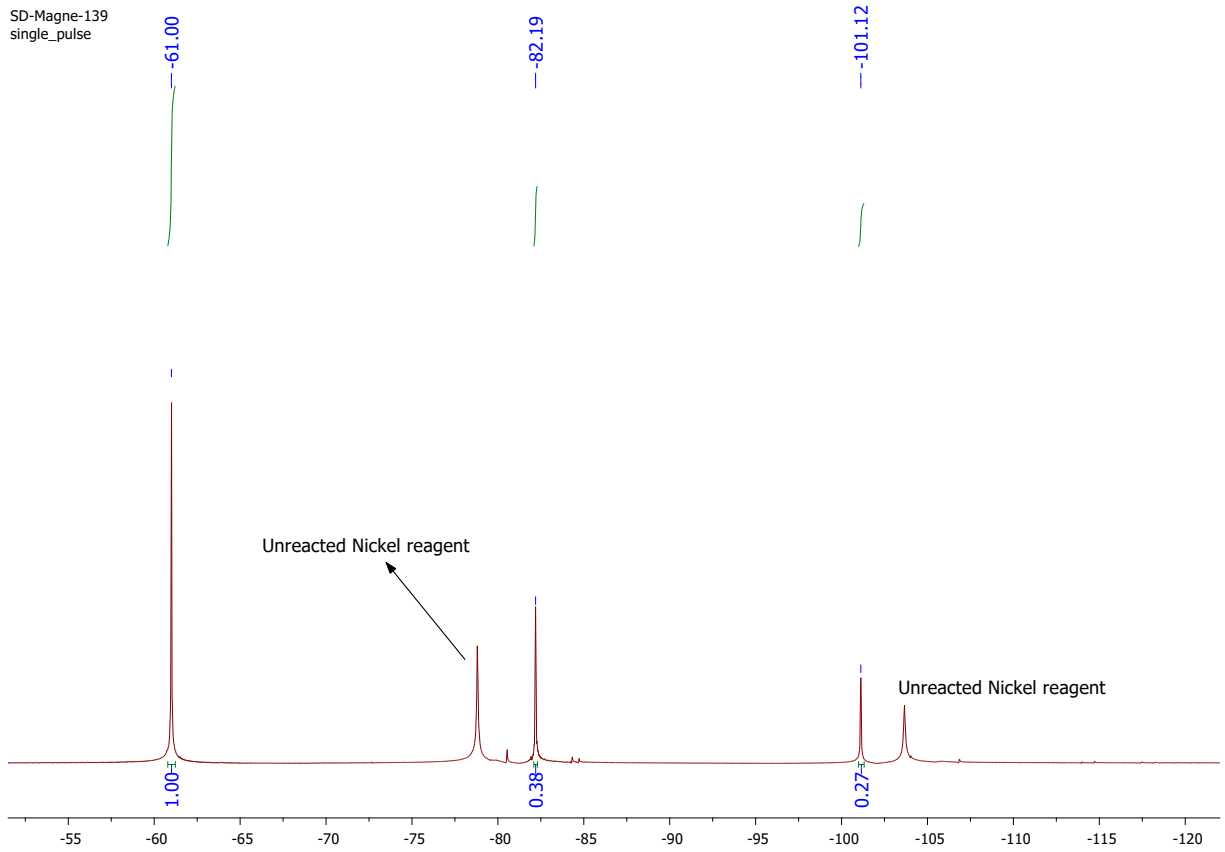
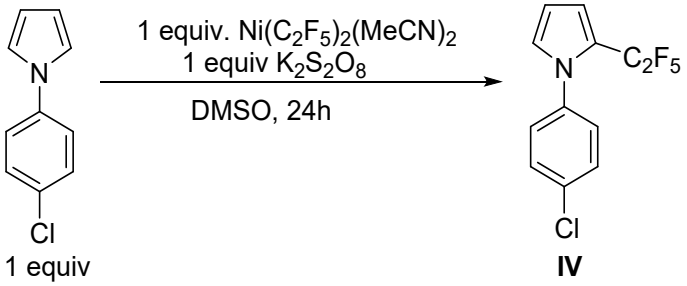


Figure S4. ^{19}F NMR spectrum showing formation of compound **III.**



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 1-(4-Chlorophenyl)-1H-pyrrole (10.0 mg, 0.056 mmol), potassium persulfate (15.2 mg, 0.056 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (21.3 mg, 0.056 mmol), which were dissolved in anhydrous DMSO (1 mL). The reaction mixture was stirred at room temperature for 24 hours. After the completion of the reaction, α,α,α-trifluorotoluene (6.9 µL, 0.056 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy (50% yield).

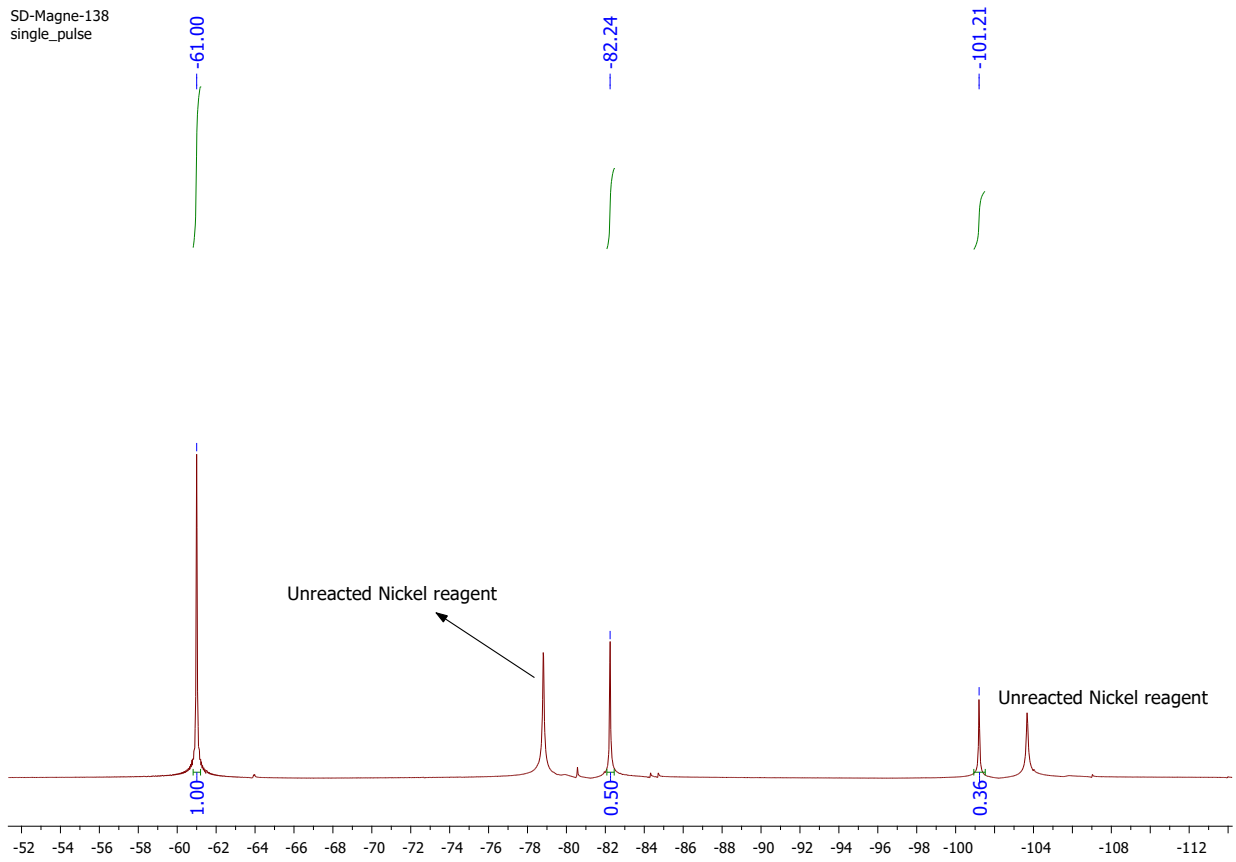
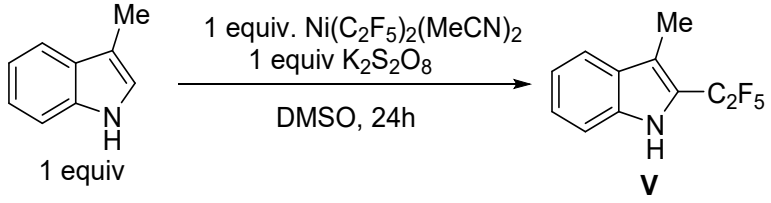


Figure S5. ^{19}F NMR spectrum showing formation of compound **IV.**



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 3-Methylindole (10.0 mg, 0.076 mmol), potassium persulfate (20.6 mg, 0.076 mmol) ,and $Ni(C_2F_5)_2(MeCN)_2$ (28.8 mg, 0.076 mmol), which were dissolved in anhydrous DMSO (1 mL). The reaction mixture was stirred at room temperature for 24 hours. After the completion of the reaction, α,α,α-trifluorotoluene (9.3 µL, 0.076 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy (37% yield).

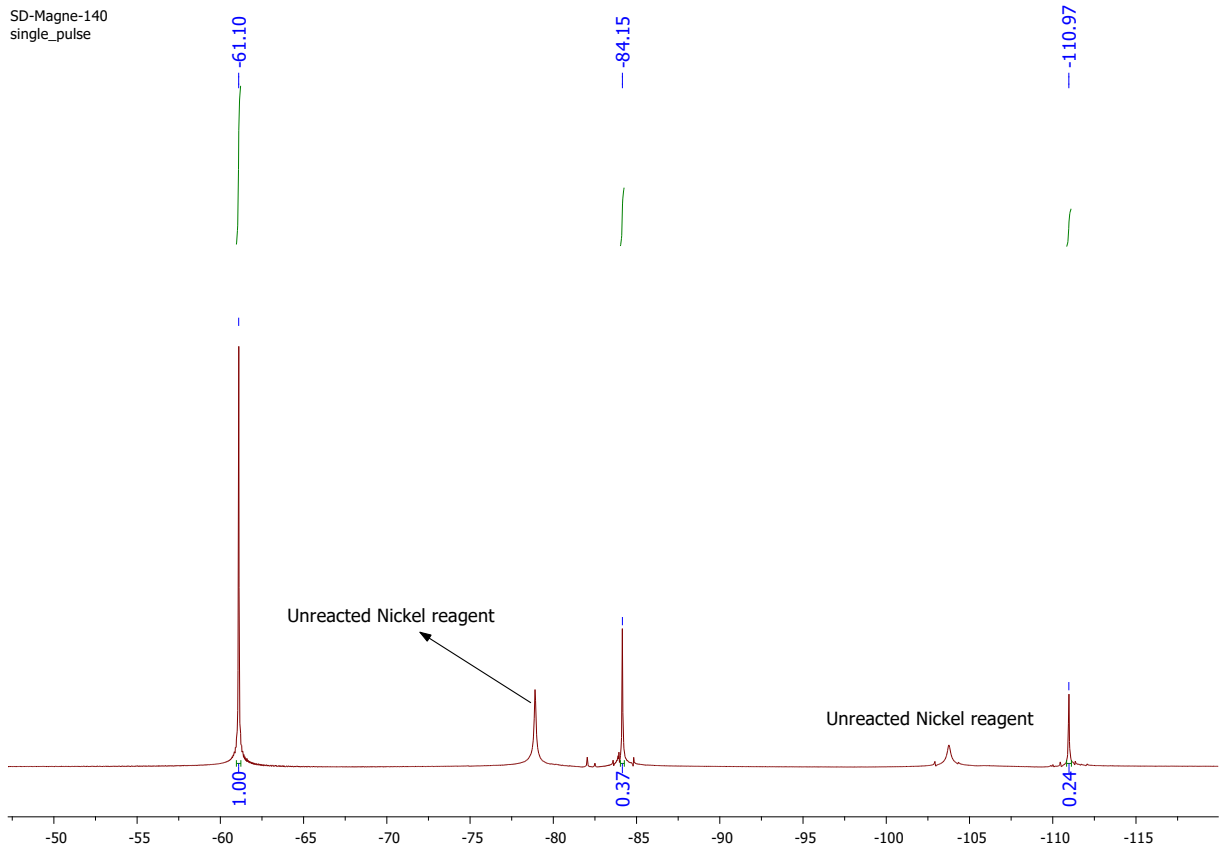
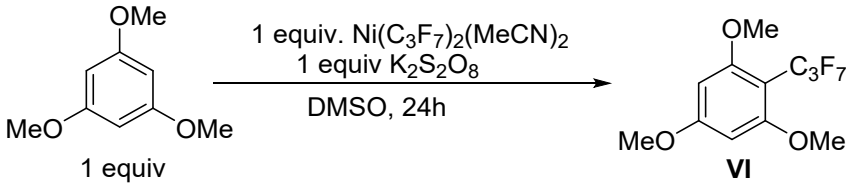


Figure S6. ^{19}F NMR spectrum showing formation of compound **V.**



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 1,3,5-Trimethoxybenzene (10.0 mg, 0.059 mmol), potassium persulfate (16.0 mg, 0.059 mmol) and $Ni(C_3F_7)_2(MeCN)_2$ (28.4 mg, 0.059 mmol) were dissolved in anhydrous DMSO (1 mL). The reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (7.3 µL, 0.059 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy (71% yield).

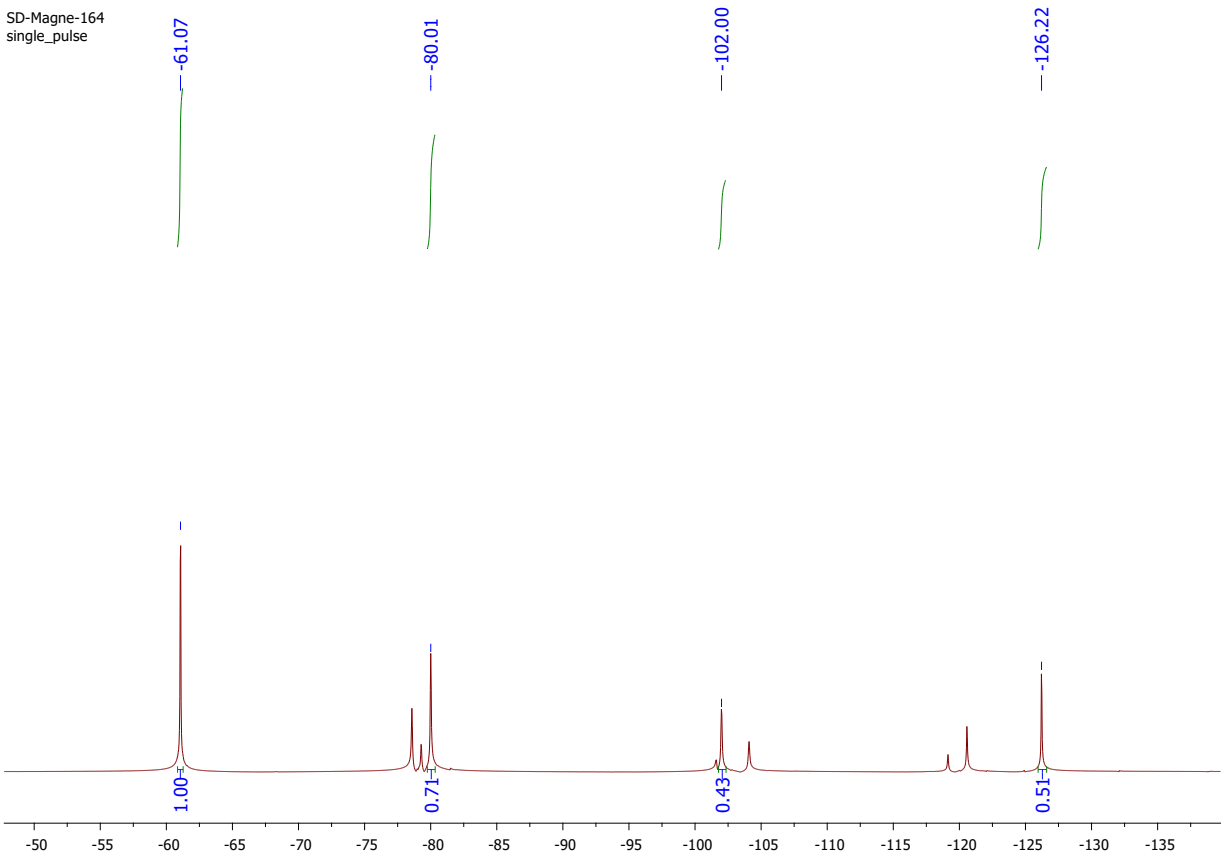


Figure S7. ^{19}F NMR spectrum showing formation of compound **VI.**

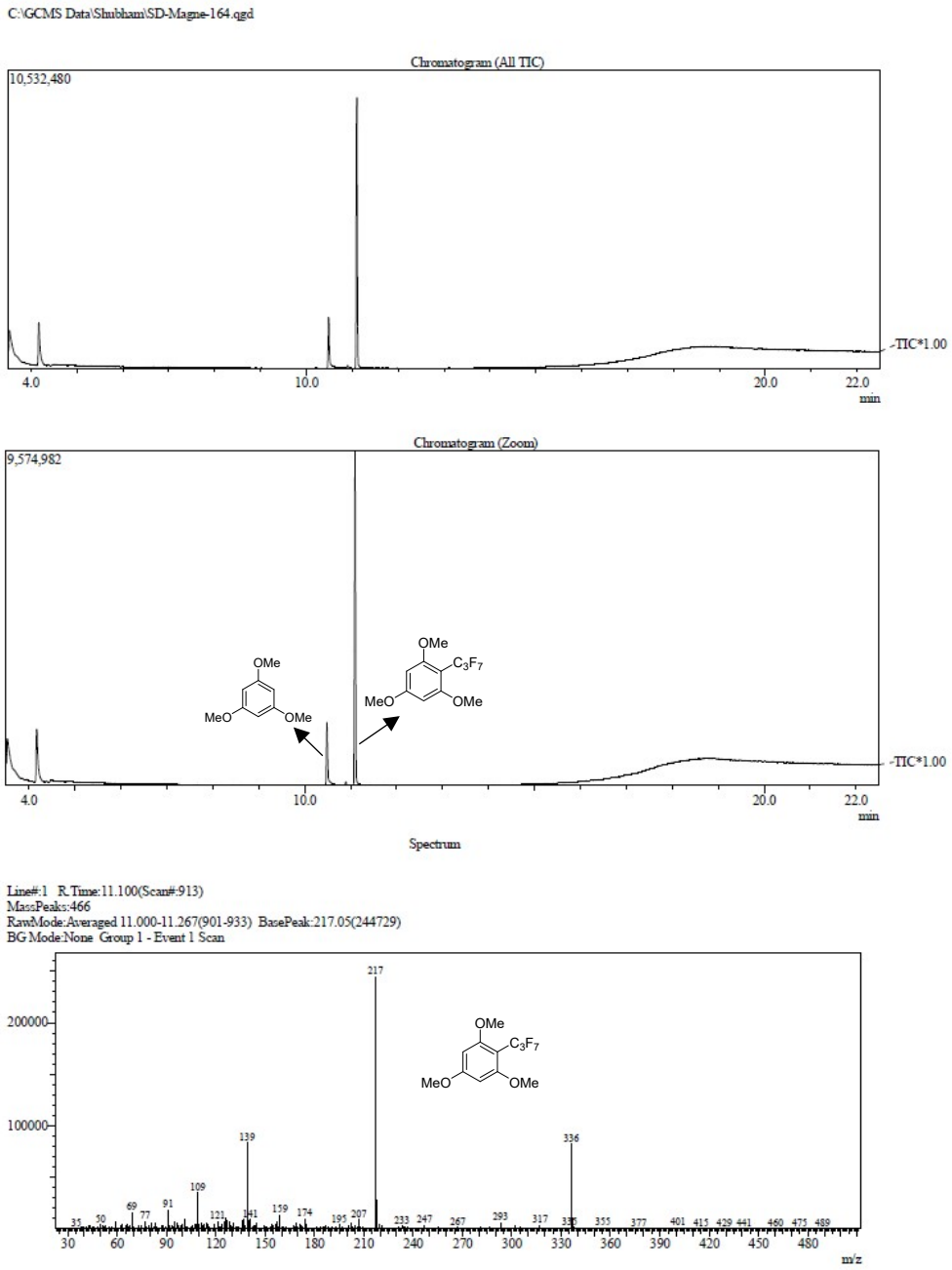
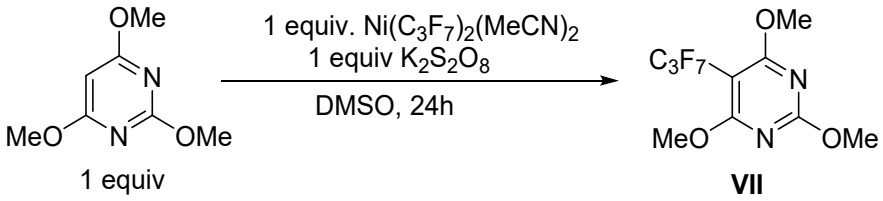


Figure S8. GC-MS data for products measured by GC-FID showing formation of compound **VI.**



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 2,4,6-Trimethoxypyrimidine (10.0 mg, 0.059 mmol), potassium persulfate (15.8 mg, 0.059 mmol) and $Ni(C_3F_7)_2(MeCN)_2$ (28.1 mg, 0.059 mmol), that were dissolved in anhydrous DMSO (1 mL). The reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (7.2 µL, 0.059 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy (63% yield).

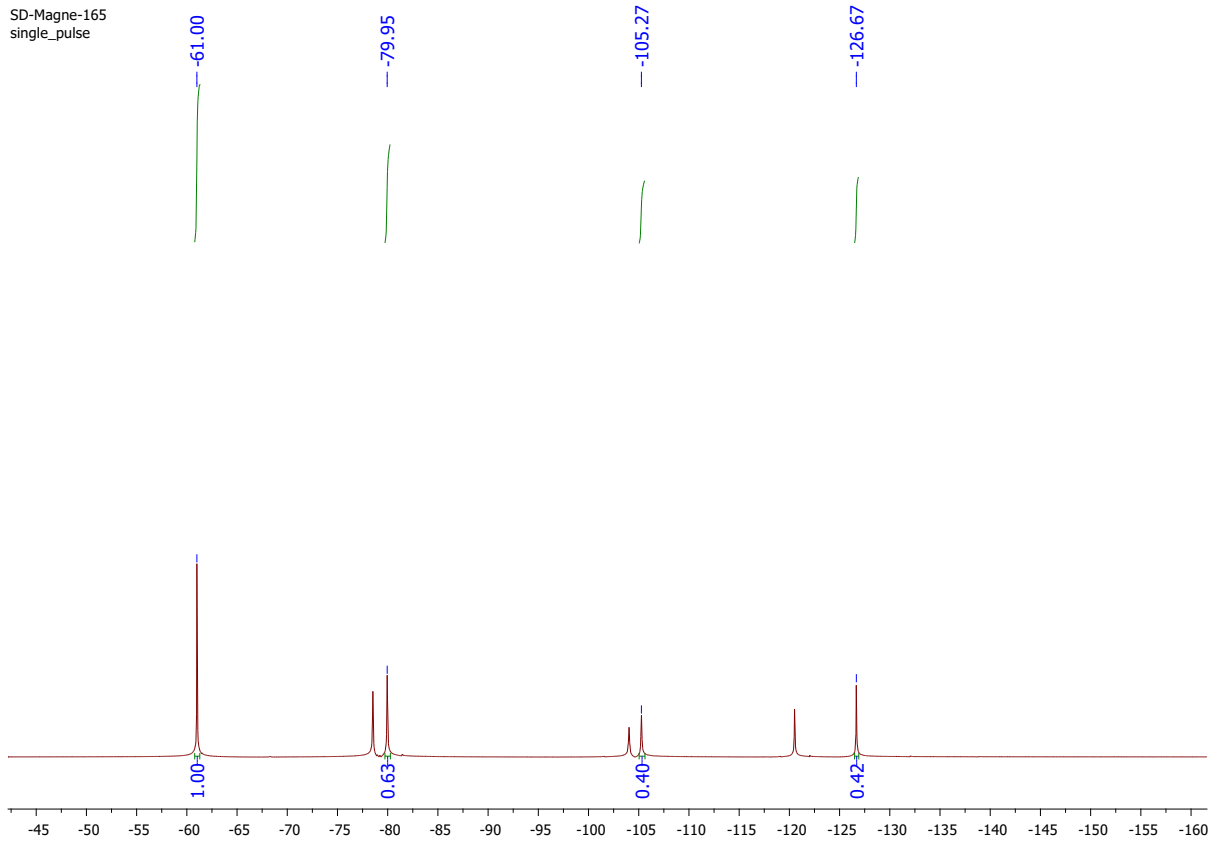


Figure S9. ^{19}F NMR spectrum showing formation of compound **VII.**

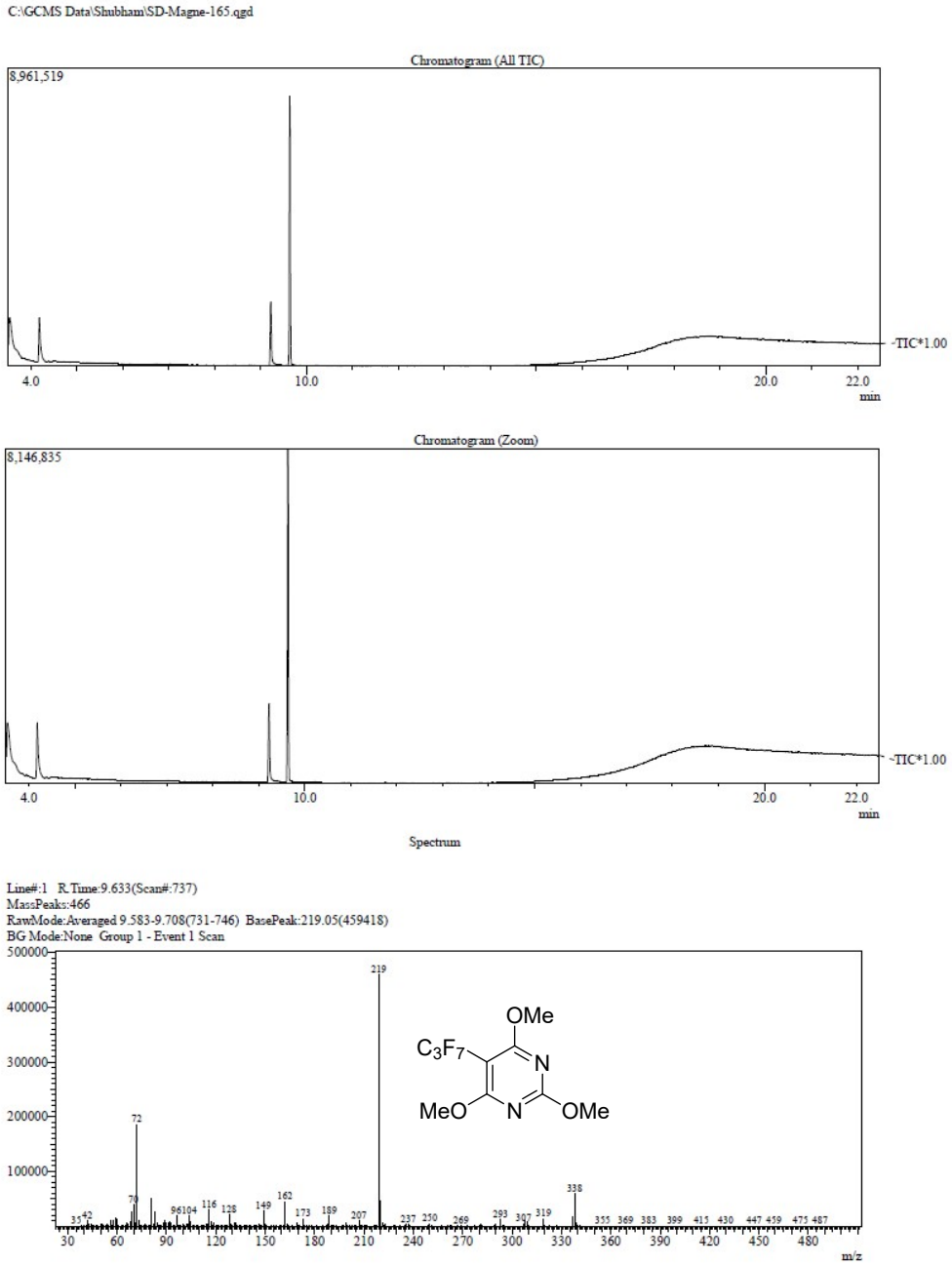
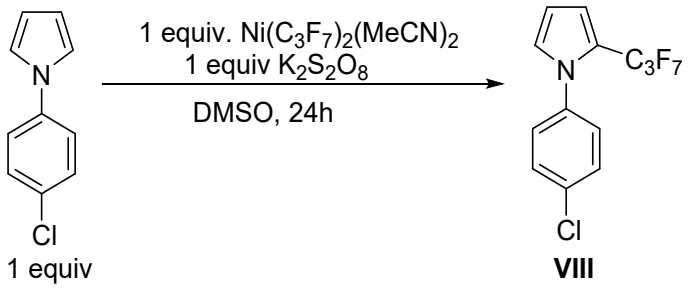


Figure S10. GC-MS data for products measured by GC-FID showing formation of compound **VII.**



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 1-(4-Chlorophenyl)-1H-pyrrole (10.0 mg, 0.056 mmol), potassium persulfate (15.2 mg, 0.056 mmol) and $Ni(C_3F_7)_2(MeCN)_2$ (26.9 mg, 0.056 mmol), that were dissolved in anhydrous DMSO (1 mL). The reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (6.9 µL, 0.056 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy (84% yield).

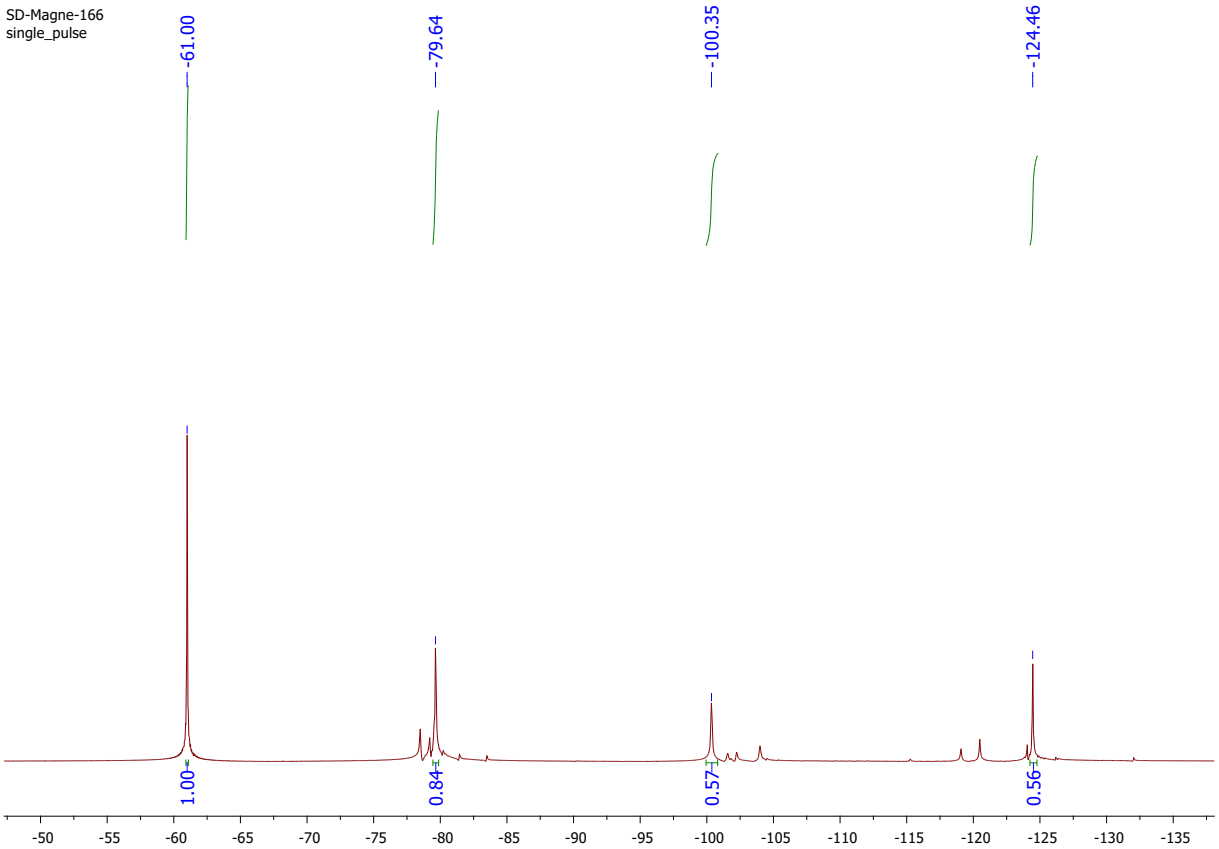


Figure S11. ^{19}F NMR spectrum showing formation of compound **VIII.**

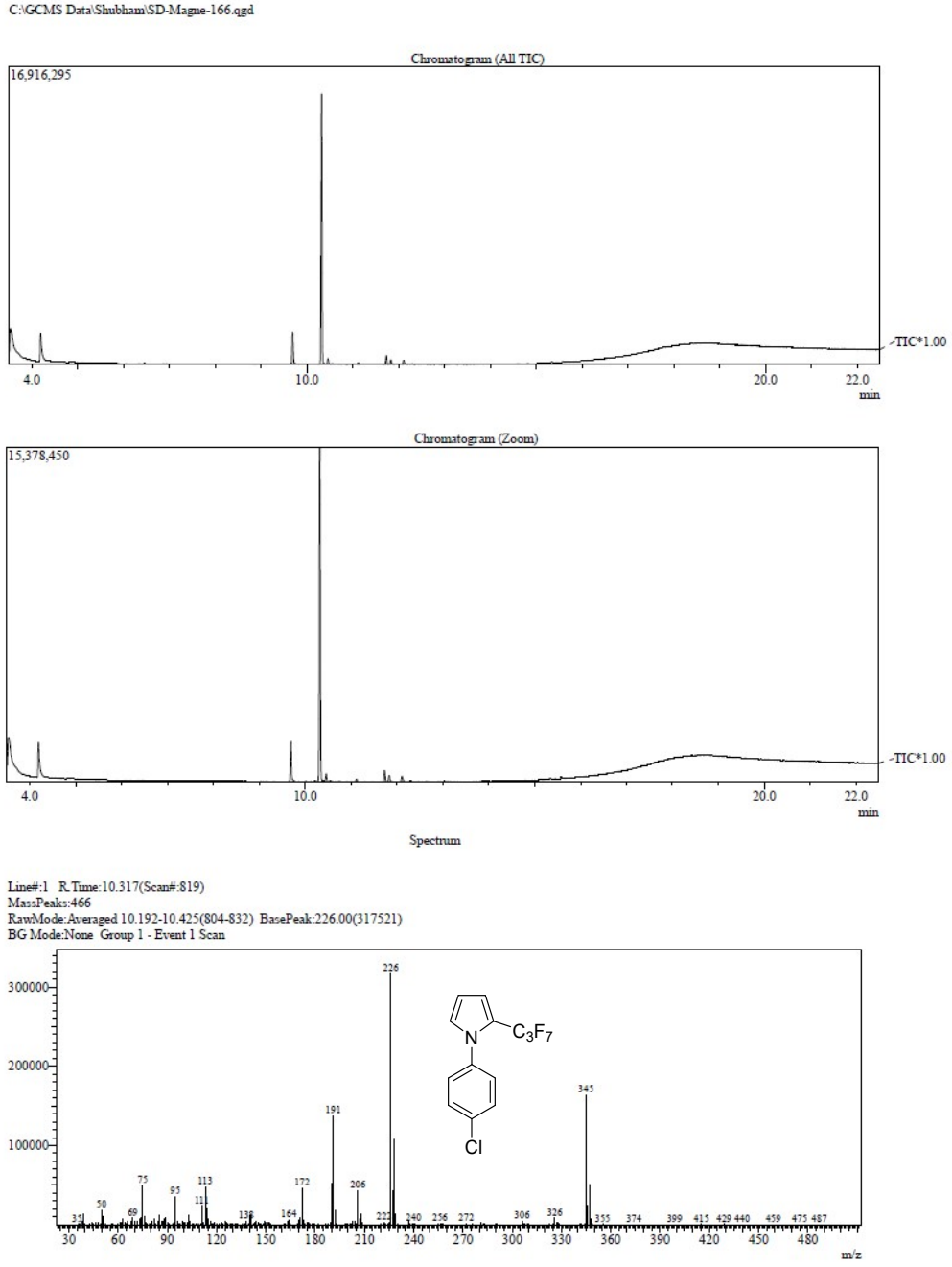
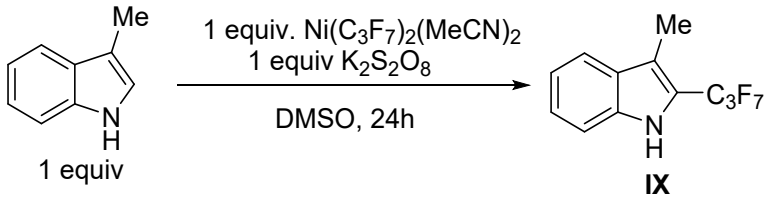


Figure S12. GC-MS data for products measured by GC-FID showing formation of compound **VIII.**



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 3-Methylindole (10.0 mg, 0.076 mmol), potassium persulfate (20.6 mg, 0.076 mmol) and $Ni(C_3F_7)_2(MeCN)_2$ (36.5 mg, 0.076 mmol), that were dissolved in anhydrous DMSO (1 mL). The reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (9.3 µL, 0.076 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy (42% yield).

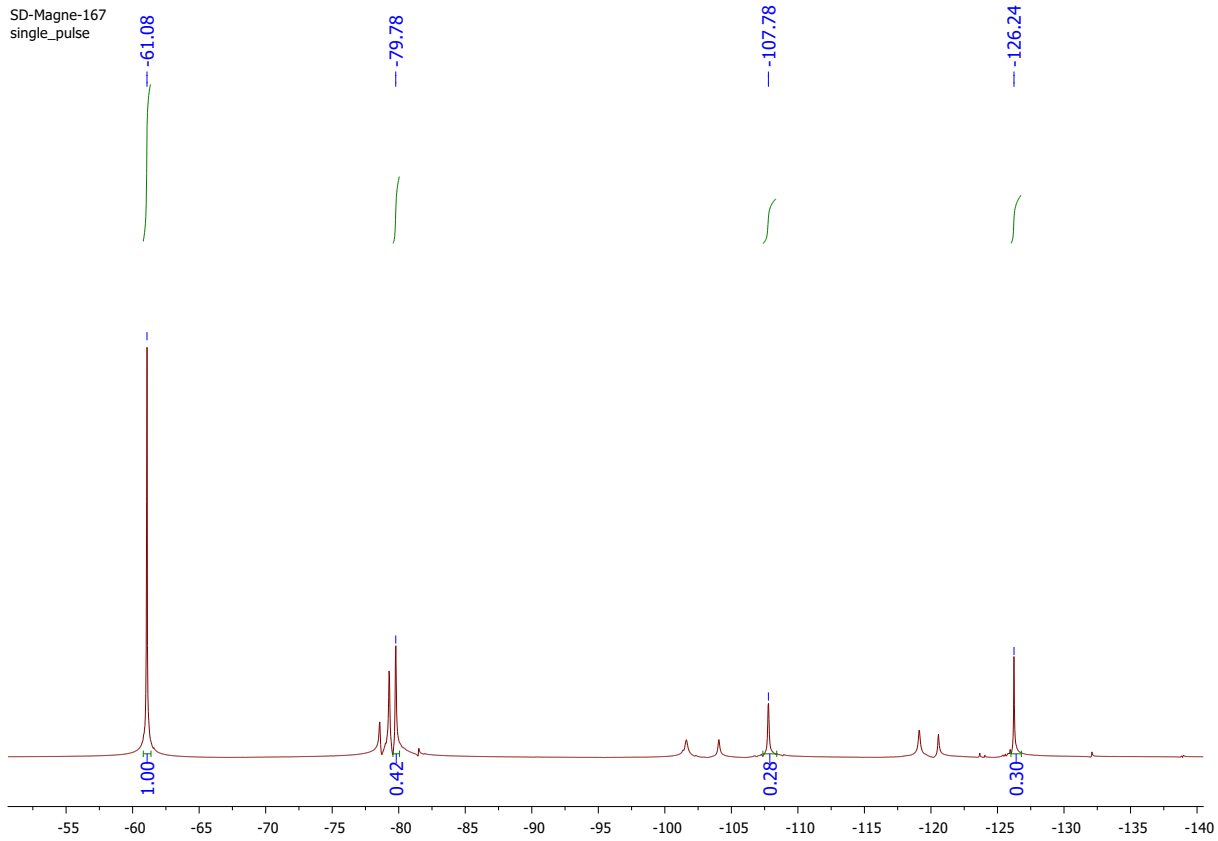


Figure S13. ^{19}F NMR spectrum showing formation of compound **IX.**

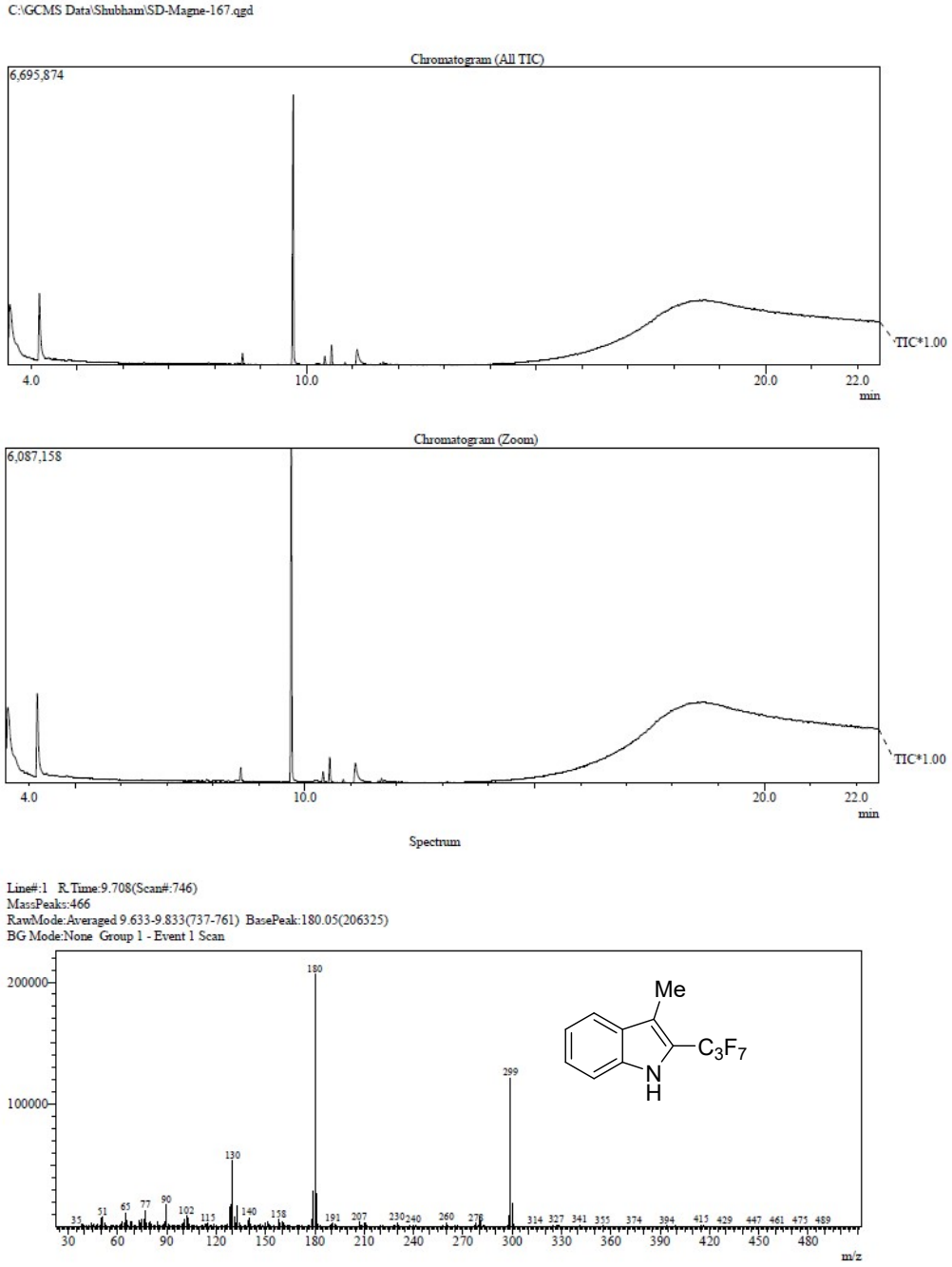
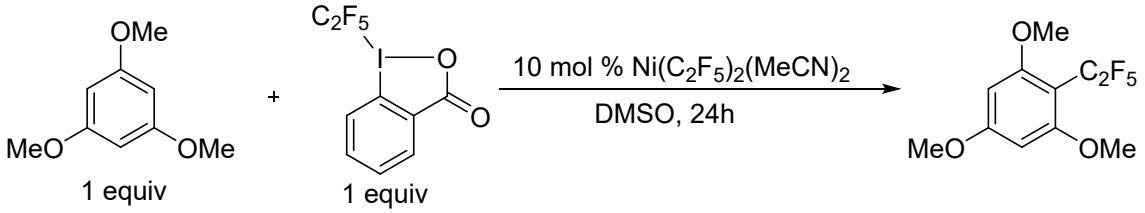


Figure S14. GC-MS data for products measured by GC-FID showing formation of compound **IX.**

III. Optimization Table for catalytic C-H perfluoro alkylation with Acid Togni II.



Typical procedure. Inside the glovebox to a 20 mL vial equipped with a magnetic stirring bar was charged with 1,3,5-Trimethoxybenzene (10.0 mg, 0.059 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (21.7 mg, 0.059 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (2.2 mg, 5.9 μmol) . Then anhydrous DMSO or other solvent (1 mL) was added. The reaction mixture was stirred vigorously at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (7.3 μL, 0.059 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy.

Table S1. Perfluoro alkylation of 1,3,5-Trimethoxybenzene in the presence of 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one: initial optimization.

Entry	Solvent (1 mL)	Additive (1 equiv)	Catalyst (mol%)	Atmosphere	Yield (%)
1	**DMSO**	None	(10)	Nitrogen	97
2	**MeOH**	None	(10)	Nitrogen	58
3	**MeCN**	None	(10)	Nitrogen	78
4	**THF**	None	(10)	Nitrogen	46
5	DMSO	None	(10)	**Air**	17
6	DMSO	None	**None**	Nitrogen	10
7	DMSO	**pyridine**	(10)	Nitrogen	95

Yields were determined by ^{19}F NMR spectroscopy using α,α,α-trifluorotoluene as an internal standard.

Table S2. Screening of different Nickel precursors.

Entry	Solvent (1 mL)	Catalyst (mol%)	Atmosphere	Yield (%)
1	DMSO	**$NiCl_2$-glyme** (10)	Nitrogen	0
2	DMSO	**$NiBr_2$-glyme** (10)	Nitrogen	0

Yields were determined by ^{19}F NMR spectroscopy using α,α,α-trifluorotoluene as an internal standard.

Table S3. Screening of different Perfluoro alkylation reagents.

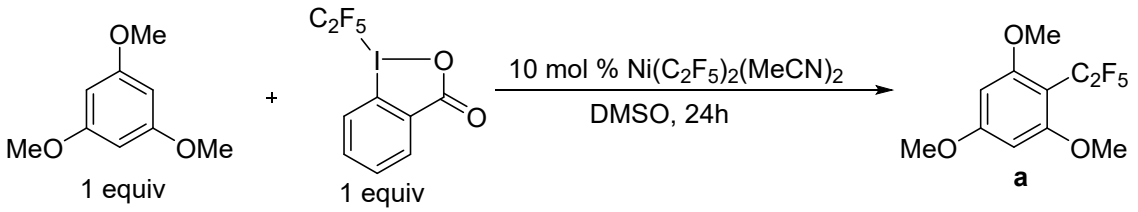
Entry	Solvent (1 mL)	C_2F_5 reagents (1 equiv)	Catalyst (mol%)	Atmosphere	Yield (%)
1	DMSO	**Pentafluoro propionic - anhydride**	(10)	Nitrogen	0
2	DMSO	**$TMSC_2F_5$**	(10)	Nitrogen	0

Yields were determined by ^{19}F NMR spectroscopy using α,α,α-trifluorotoluene as an internal standard.

Table S4. Screening of different silver salts to determine the effect of silver fluoride, which is present in the synthesis of the $Ni(C_2F_5)_2(MeCN)_2$ precursor, in catalysis. Silver bromide can be a byproduct of the synthesis, so it was screened as well.

Entry	Solvent (1 mL)	Substrate	Catalyst (mol%)	Atmosphere	Yield (%)
1	DMSO	1,3,5-Trimethoxy benzene	**Silver triflate** (10)	Nitrogen	0
2	DMSO	1,3,5-Trimethoxy benzene	**Silver fluoride** (10)	Nitrogen	26
3	DMSO	1,3,5-Trimethoxy benzene	**Silver fluoride** (100)	Nitrogen	56
4	DMSO	Para-chloro-N-phenylpyrrole	**Silver fluoride** (100)	Nitrogen	13
5	DMSO	1,3,5-Trimethoxy benzene	**Silver bromide** (10)	Nitrogen	0
6	DMSO	Para-chloro-N-phenylpyrrole	**Silver bromide** (10)	Nitrogen	0

IV. Substrate scope for catalytic C-H perfluoro alkylation with Acid Togni II.



Isolation procedure. Inside the glovebox, a 20 mL vial equipped with a stirring bar was charged with 1,3,5-Trimethoxybenzene (50.0 mg, 0.30 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-

one (108.8 mg, 0.30 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (11.2 mg, 0.030 mmol) dissolved in anhydrous DMSO (2.5 mL). The reaction mixture was vigorously stirred for 24 hours. After completion of the reaction, the yellow color reaction mixture was transferred to a separatory funnel outside the glovebox and mixed with ethyl acetate (30 mL) and saturated aqueous NaCl (10 mL). After the first extraction, the organic layer was separated, and remaining water layer was again extracted with ethyl acetate (20 mL). The organic layers were combined and dried over magnesium sulfate. Further the reaction mixture was concentrated under vacuum. The yellow color crude material was then purified by flash column chromatography on silica gel (mobile phase: hexane/ethyl acetate (95:5) as colorless solid (73.1 mg, 86% yield).

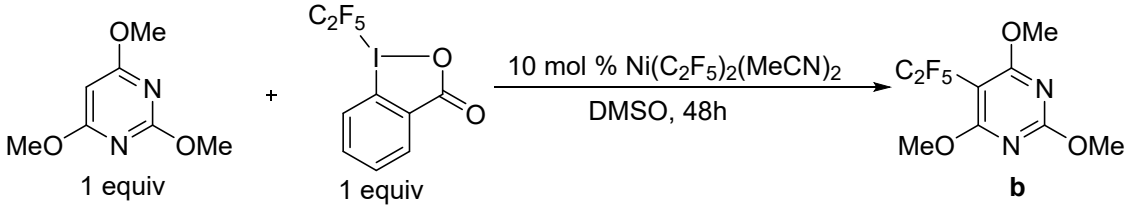
^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ 6.14 (s, 2H), 3.84 (s, 3H), 3.81 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$, 23 °C): δ 163.90, 161.69 (t, J = 2.1 Hz), 124.67-115.30 (qt, J = 288.1 Hz, 39.9 Hz), 117.57-111.26 (tq, J = 247.1 Hz, 40.5 Hz), 98.35 (t, J = 21.9 Hz), 91.84, 56.46, 55.48.

^{19}F NMR (376 MHz, $CDCl_3$, 23 °C): δ -84.96 (3F), -106.63 (2F).

HRMS (ESI) calculated for $[M^*H]^+$, $C_{11}H_{12}F_5$: m/z 287.0701; found, 287.0664.

The above analytical data is agreed with previously published data.[2]



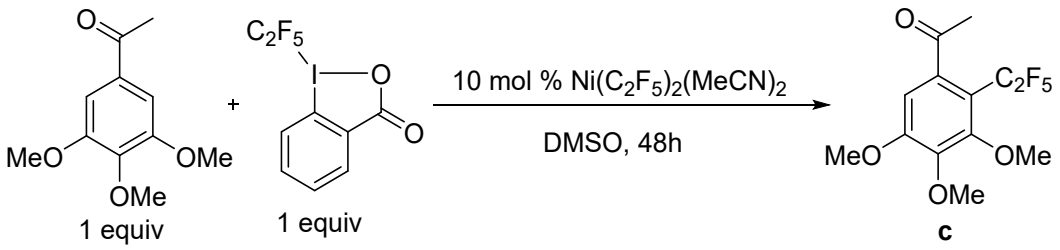
Isolation procedure. Inside the glovebox, a 20 mL vial equipped with a stirring bar was charged with 2,4,6-Trimethoxypyrimidine (50.0 mg, 0.29 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (107.5 mg, 0.29 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (11.1 mg, 0.029 mmol) dissolved in anhydrous DMSO (2.5 mL). The reaction mixture was vigorously stirred for 48 hours. After completion of the reaction, the yellow color reaction mixture was transferred to a separatory funnel outside the glovebox and mixed with ethyl acetate (25 mL), and saturated aqueous NaCl (10 mL). After the first extraction, the organic layer was separated, and remaining water layer was again extracted with ethyl acetate (15 mL). The organic layers were combined and dried over magnesium sulfate. Further the reaction mixture was concentrated under vacuum. The yellow color crude material was then purified by flash column chromatography on silica gel (mobile phase: hexane/ethyl acetate (95:5) to get a white solid (48.9 mg, 58% yield).

^{1}H NMR (600 MHz, $CDCl_3$, 23 °C): δ 4.01 (s, 3H), 3.99 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$, 23 °C): δ 170.82 (t, J = 1.6 Hz), 165.39, 122.83-116.59 (tq, J = 247.39 Hz, 39.9 Hz), 115.35-111.14 (qt, J = 288.19 Hz, 40.8 Hz), 86.92 (t, J = 25.6 Hz), 55.26, 55.03.

^{19}F NMR (565 MHz, $CDCl_3$, 23 °C): δ -85.16 (3F), -109.60 (2F).

HRMS (ESI) calculated for $[M^*H]^+$, $C_9H_9F_5N_2O_3$: m/z 289.0606; found, 289.0584.



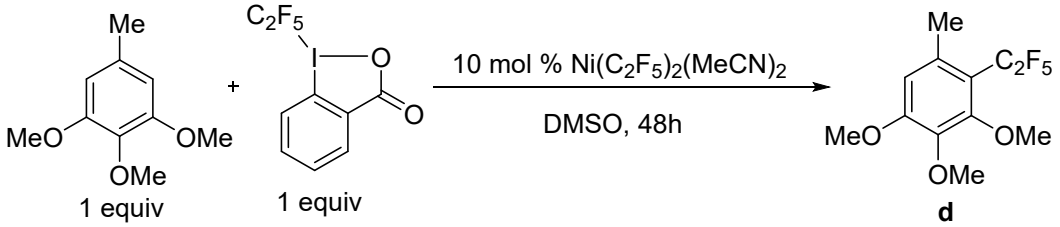
Isolation procedure. Inside the glovebox, a 20 mL vial equipped with a stirring bar was charged with 3,4,5 - Trimethoxyacetophenone (50.0 mg, 0.24 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (87.0 mg, 0.24 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (9.0 mg, 0.024 mmol) dissolved in anhydrous DMSO (2.5 mL). The reaction mixture was vigorously stirred for 48 hours. After completion of the reaction, the yellow color reaction mixture was transferred to a separatory funnel outside the glovebox and mixed with ethyl acetate (25 mL) and saturated aqueous NaCl (10 mL). After the first extraction, the organic layer was separated, and remaining water layer was again extracted with ethyl acetate (20 mL). The organic layers were combined and dried over magnesium sulfate. Further the reaction mixture was concentrated under vacuum. The yellow color crude material was then purified by flash column chromatography on silica gel (mobile phase: hexane/ethyl acetate (80:20) to get **c** as colorless solid (37.4 mg, 48% yield).

^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ 6.45 (s, 1H), 3.93 (s, 3H), 3.90 (s, 3H), 3.87 (s, 3H), 2.50 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$, 23 °C): δ 202.67, 156.56, 153.84 (t, J = 3.9 Hz), 143.21, 139.77 (t, J = 3.9 Hz), l22.95-115.47 (qt, J = 287.1 Hz, 39.2 Hz), 116.86-111.81 (tq, J = 253.1 Hz, 41.1 Hz), 110.83 (t, J = 22.9 Hz), 104.50, 62.04, 60.98, 56.37, 31.47.

^{19}F NMR (376 MHz, $CDCl_3$, 23 °C): δ -82.11 (3F), -103.23 (2F).

HRMS (ESI) calculated for $[M^*H]^+$, $C_{13}H_{13}F_5O_4$: m/z 329.0807; found, 329.0802.



Isolation procedure. Inside the glovebox, a 20 mL vial equipped with a stirring bar was charged with 3,4,5-Trimethoxytoluene (50.5 µL, 0.30 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (109.8 mg, 0.30 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (11.3 mg, 0.03 mmol) dissolved in anhydrous DMSO (2.5 mL). The reaction mixture was vigorously stirred for 48 hours. After completion of the reaction, the yellow color reaction mixture was transferred to a separatory funnel outside the glovebox and mixed with ethyl acetate (30 mL) and saturated aqueous NaCl (10 mL). After the first extraction, the organic layer was separated, the remaining water layer was again extracted

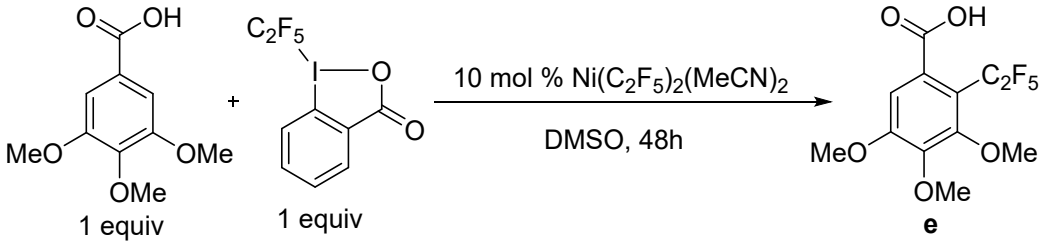
with ethyl acetate (30 mL). The organic layers were combined and dried over magnesium sulfate. The reaction mixture was concentrated under vacuum. The yellow color crude material was then purified by flash column chromatography on silica gel (mobile phase: hexane/ethyl acetate (95:5) to give **d** as a colorless oil (39.4 mg, 44 % yield).

^{1}H NMR (600 MHz, $CDCl_3$, 23 °C): δ 6.52 (s, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.83 (s, 3H), 2.41 (t, J = 4.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, 23 °C): δ 155.43, 154.64, 141.15, 135.06, 122.98-118.65 (qt, J = 285.1 Hz, 39.5 Hz), 117.28-113.36 (tq, J = 251.1 Hz, 40.1 Hz), 113.18 (t, J = 21.3 Hz), 111.29, 61.99, 60.83, 56.01, 22.09 (t, J = 6.7 Hz).

^{19}F NMR (565 MHz, $CDCl_3$, 23 °C): δ -84.29 (3F), -105.43 (2F).

HRMS (ESI) calculated for $[M^*H]^+$, $C_{12}H_{13}F_5O_3$: m/z 301.0858; found, 301.0848.



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 3,4,5-Trimethoxybenzoic acid (10.0 mg, 0.047 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (17.2 mg, 0.047 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (1.7 mg, 0.004 mmol) were dissolved in anhydrous DMSO (1 mL). Further the reaction mixture was stirred at room temperature for 48 hours. After the completion of reaction, α,α,α-trifluorotoluene (5.7 µL, 0.047 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy.

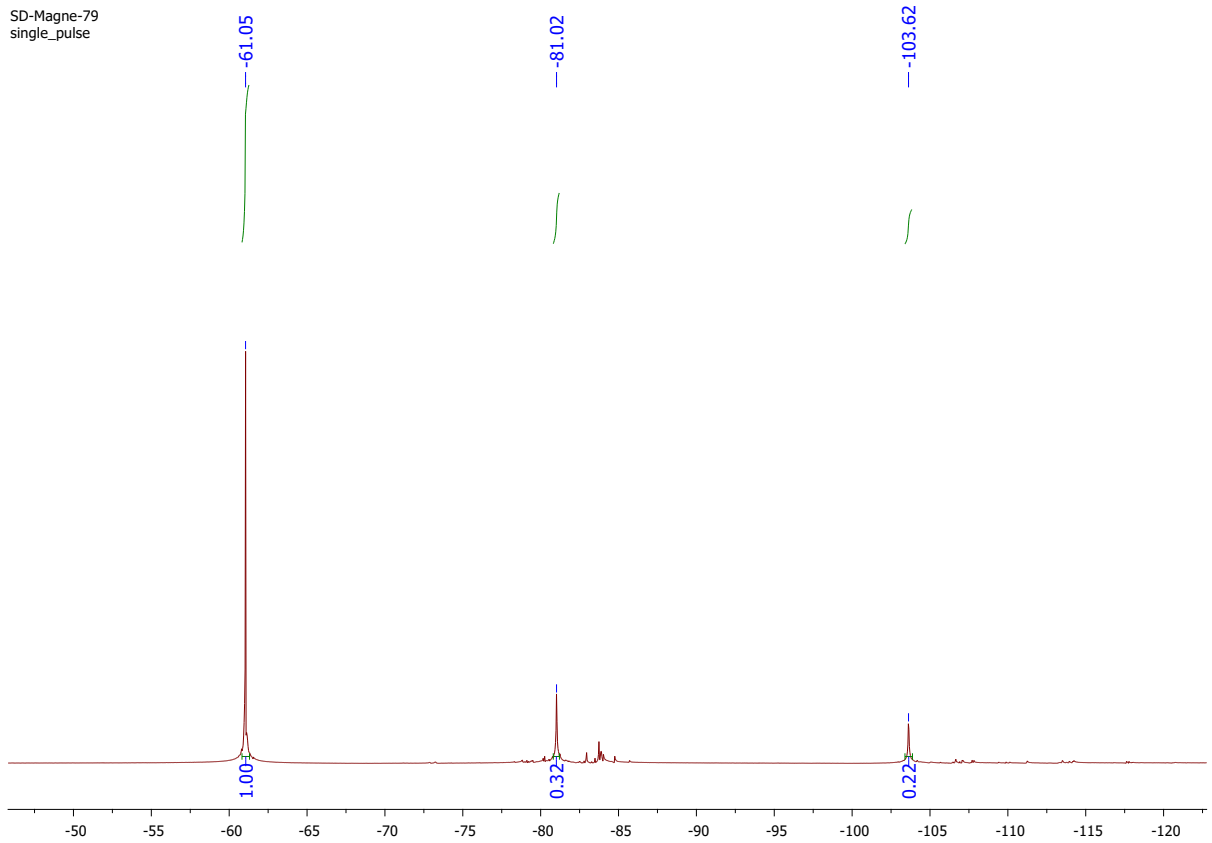
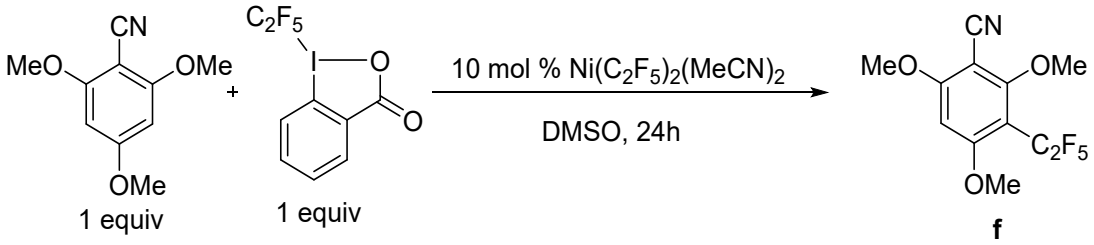


Figure S15. ^{19}F NMR spectrum showing formation of compound **e.**



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 2,4,6-Trimethoxybenzonitrile (10.0 mg, 0.052 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (18.9 mg, 0.052 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (1.9 mg, 0.0051 mmol) were dissolved in anhydrous DMSO (1 mL). The reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (6.3 µL, 0.052 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy.

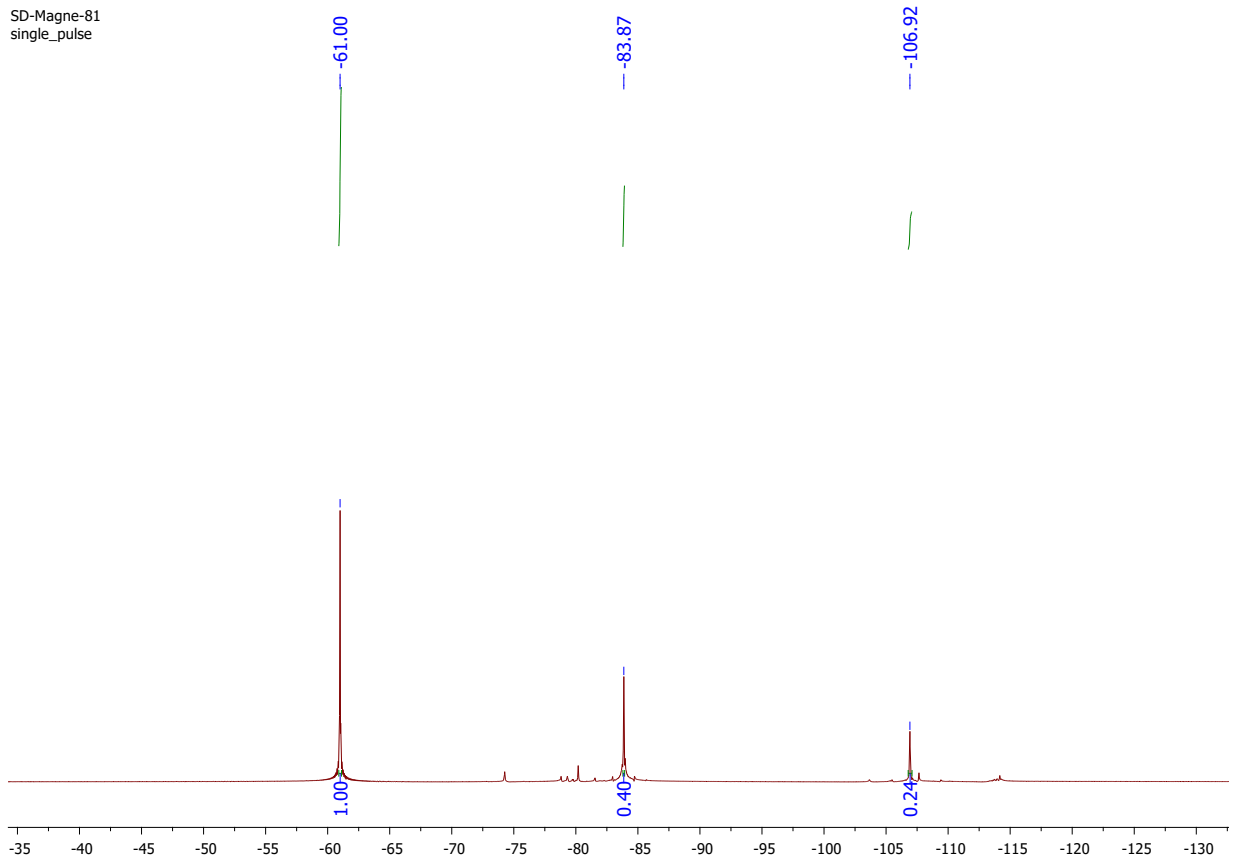
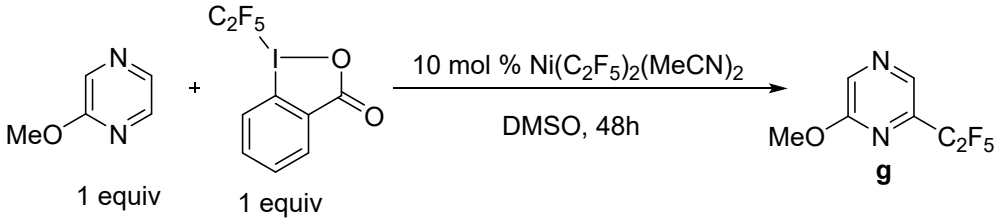


Figure S16. ^{19}F NMR spectrum showing formation of compound **f.**



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 2-Methoxypyrazine (4.8 µL, 0.050 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (18.3 mg, 0.050 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (1.8 mg, 0.005 mmol), and then dissolved in anhydrous DMSO (1 mL). The reaction mixture was stirred at room temperature for 48 hours. After the completion of reaction, α,α,α-trifluorotoluene (6.1 µL, 0.05 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy.

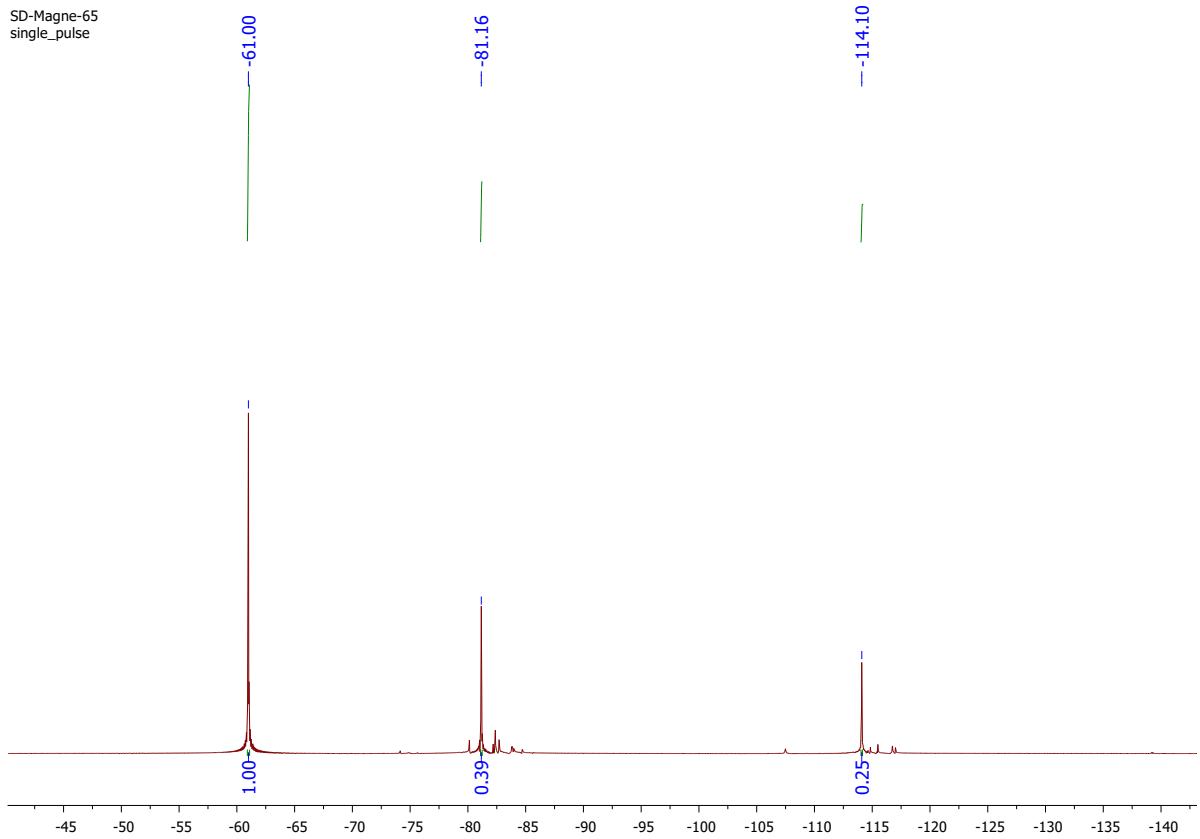
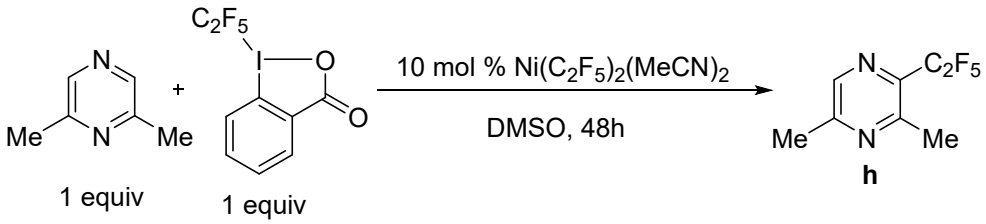


Figure S17. ^{19}F NMR spectrum showing formation of compound **g.**



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 2,6-Dimethylpyrazine (10.0 mg, 0.092 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (33.8 mg, 0.092 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (3.5 mg, 0.009 mmol), and then dissolved in anhydrous DMSO (1 mL). The reaction mixture was stirred at room temperature for 48 hours. After the completion of reaction, α,α,α-trifluorotoluene (11.3 µL, 0.092 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy.

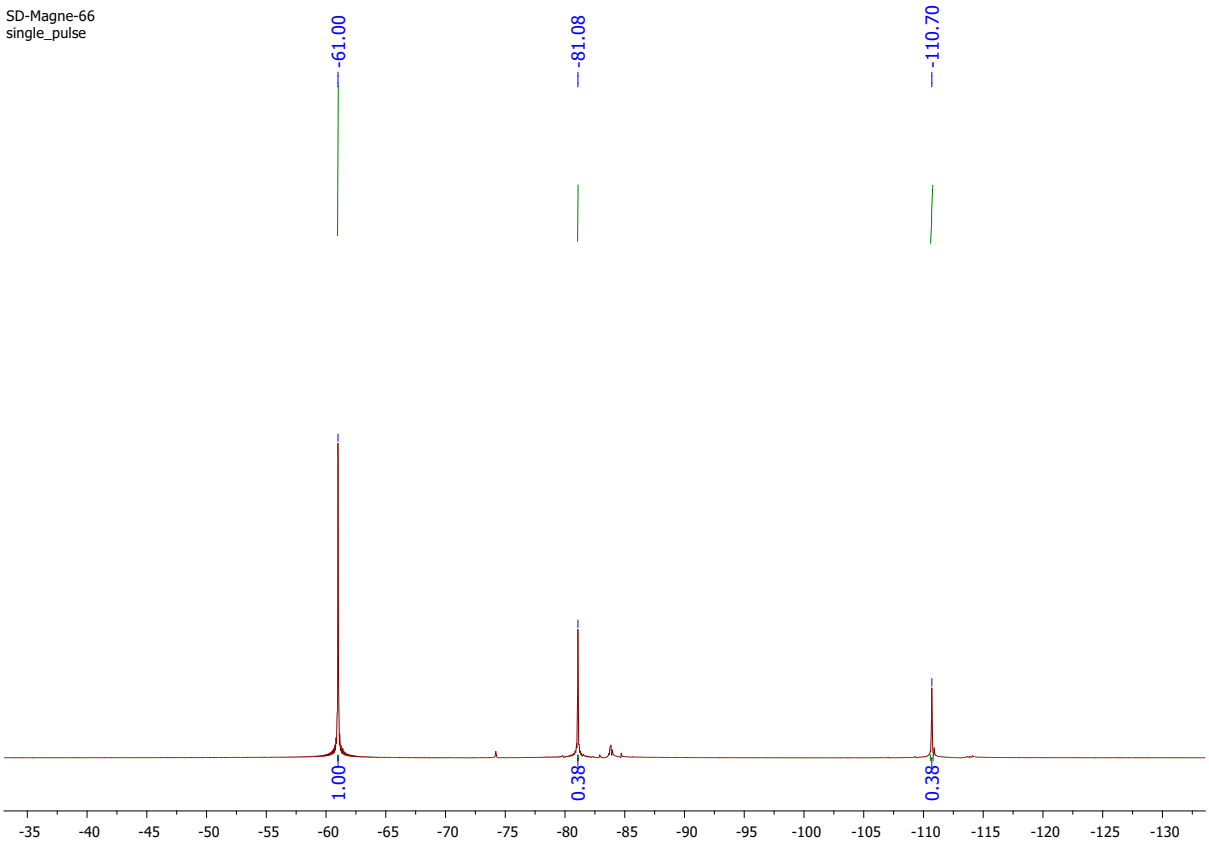
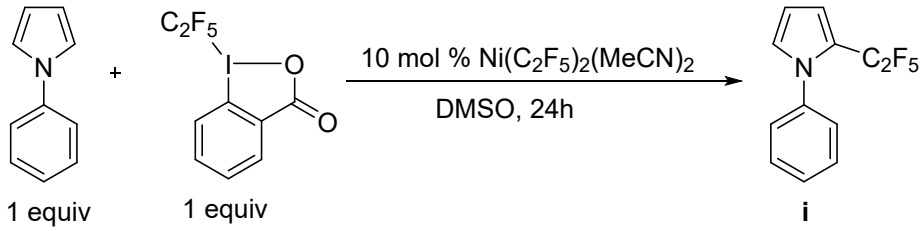


Figure S18. ^{19}F NMR spectrum showing formation of compound **h.**



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 1-phenylpyrrole (10.0 mg, 0.069 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (25.5 mg, 0.069 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (2.6 mg, 0.006 mmol), and then dissolved in anhydrous DMSO (1 mL). The reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (8.5 µL, 0.069 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy.

HRMS (ESI) calculated for $[M^*H]^+$, $C_{12}H_9F_5N_1$: m/z 262.0650; found, 262.0628.

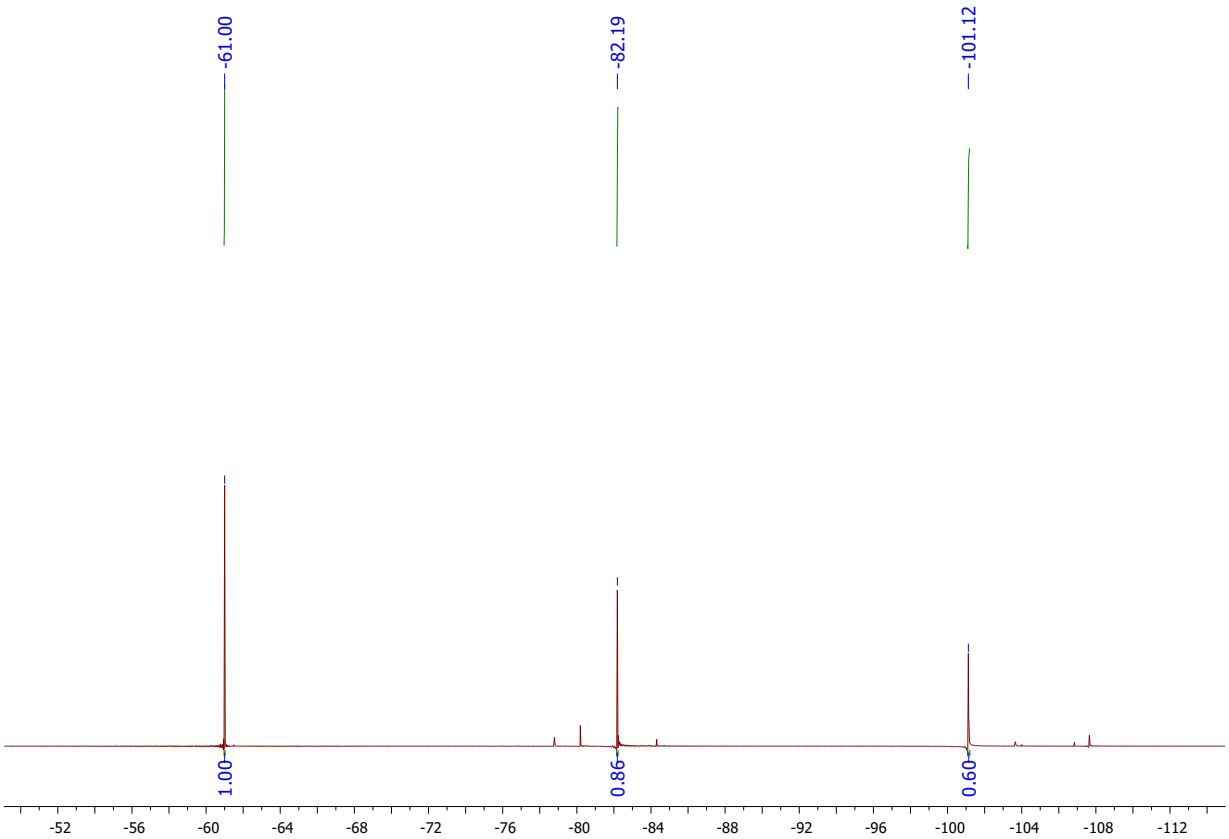


Figure S19. ^{19}F NMR spectrum showing formation of compound **i.**

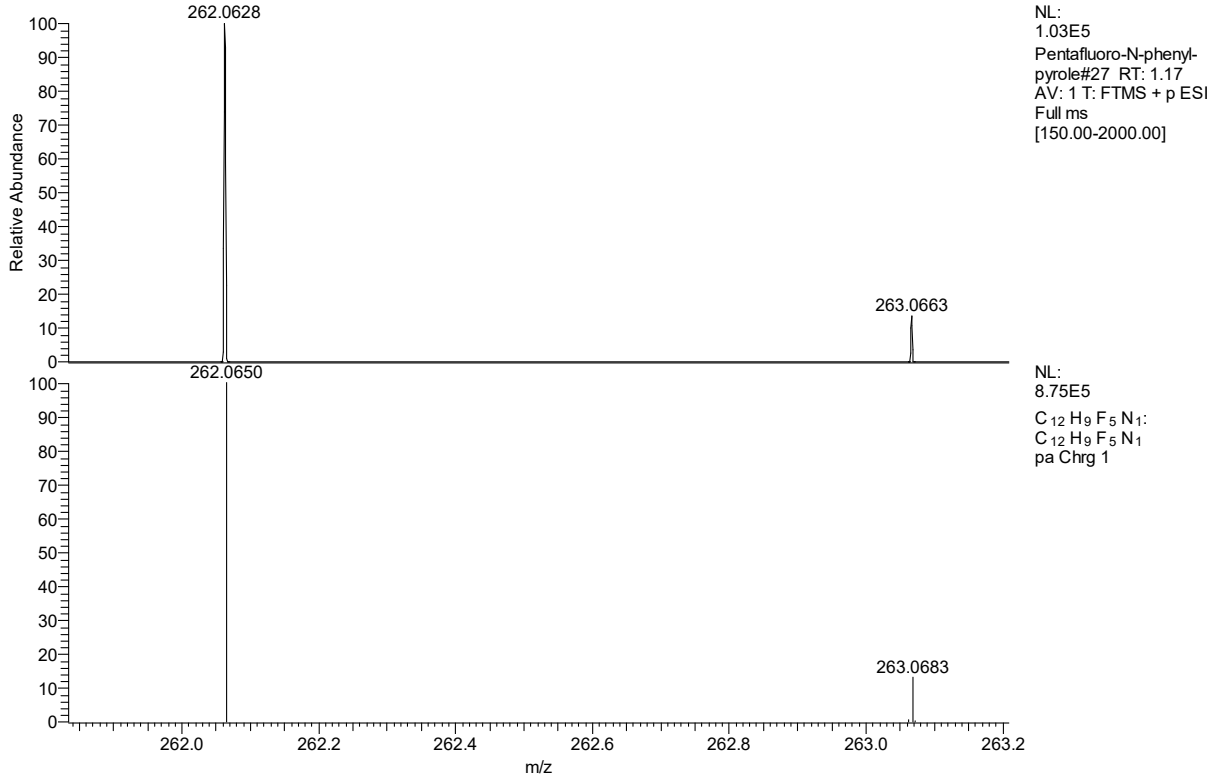
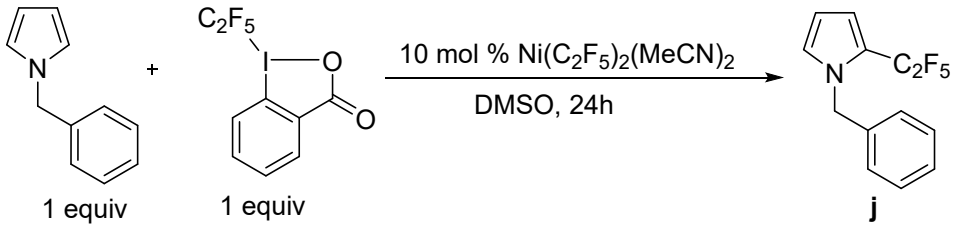


Figure S20. ESI-(HR)MS spectrum of a MeOH solution of **i.**

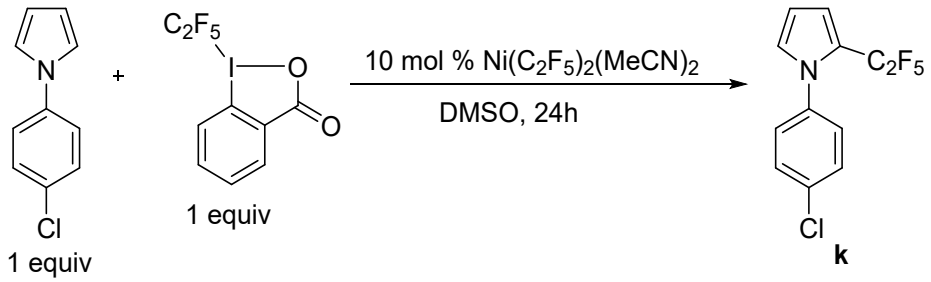


Isolation procedure. Inside the glovebox, to a 20 mL vial equipped with a stirring bar was charged with N-benzylpyrrole (31 μL, 0.20 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (73.2 mg, 0.20 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (7.5 mg, 0.02 mmol) dissolved in anhydrous DMSO (2.5 mL). The reaction mixture was vigorously stirred for 24 hours. After completion of the reaction, the light blue color reaction mixture was transferred to a separatory funnel outside the glovebox and mixed with ethyl acetate (20 mL) and saturated aqueous NaCl (10 mL). After the first extraction, the organic layer was separated, and remaining water layer was again reextracted with ethyl acetate (20 mL). The organic layers were combined and dried over magnesium sulfate, during this the crude color changed to colorless. Further the reaction mixture was concentrated under vacuum. The crude material was then purified by flash column chromatography on silica gel (mobile phase: hexane/ethyl acetate (95:5) to give **j** as a colorless oil (38.9 mg, 71% yield).

^{1}H NMR (600 MHz, $CDCl_3$, 23 °C): δ 7.42-7.39 (m, 3H), 7.32 (br.s, 2H), 7.30 (br.s, 1H), 6.86-6.84 (m, 1H), 6.74 (br.s, 1H), 6.33-6.31 (m, 1H), 5.30 (s,1H).

^{13}C NMR (151 MHz, $CDCl_3$, 23 °C): δ 138.18, 134.78, 130.06 (m), 129.12, 128.72, 128.63, 120.08 (qt, *J* = 288.2 Hz, 31 Hz), 117.99 (t, *J* = 38.3 Hz), 116.10 (t, *J* = 38.3Hz), 114.84, 111.18 (tq, *J* = 255.1.2 Hz, 38.3Hz), 109.14, 53.56.

^{19}F NMR (565 MHz, $CDCl_3$, 23 °C): δ -83.32 (3F), -102.75 (2F).



Isolation procedure. Inside the glovebox, to a 20 mL vial equipped with a stirring bar was charged with 1-(4-Chlorophenyl)-1H-pyrrole (50.0 mg, 0.281 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (103.0 mg, 0.281 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (10.6 mg, 0.028 mmol), which were then dissolved in anhydrous DMSO (2.5 mL). The reaction mixture was vigorously stirred for 24 hours. After completion of the reaction, the yellow color reaction mixture was transferred to a separatory funnel outside the glovebox and mixed with ethyl acetate (25 mL) and saturated aqueous NaCl (10 mL). After the first extraction, the organic layer was separated, and remaining water layer was again reextracted with ethyl acetate (20 mL). The organic layers were combined and dried over magnesium sulfate. The reaction mixture was concentrated under vacuum. The yellow color crude material was then purified by flash column chromatography on silica gel (mobile phase: hexane/ethyl acetate 60:40) to get **k** as a colorless solid (61.1 mg, 73% yield).

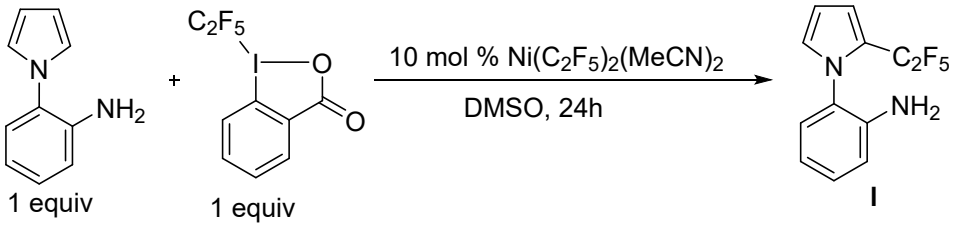
^{1}H NMR (600 MHz, $CDCl_3$, 23 °C): δ 7.42-7.39 (m, 2H), 7.32-7.29 (br.m, 2H), 6.86-6.84 (m, 1H), 6.74-6.71 (m, 1H), 6.32-6.30 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$, 23 °C): δ 138.19, 134.79, 130.07, 129.13, 128.72, 128.63, 122.53-117.73 (m), 114.84, 113.09-109.52 (m), 109.14.

^{19}F NMR (565 MHz, $CDCl_3$, 23 °C): δ -83 (3F), -102.65 (2F).

HRMS (ESI) calculated for $[M^*H]^+$, $C_{12}H_7F_5N_1Cl_1$: m/z 296.0260; found, 296.0237.

The above analytical data is agreed with previously published data.[3]



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 1-(2-Aminophenyl)pyrrole (10.0 mg, 0.063 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (23.1 mg, 0.063 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (2.3 mg, 0.006 mmol), which were dissolved in

anhydrous DMSO (1 mL). The reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (7.7 µL, 0.063 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy.

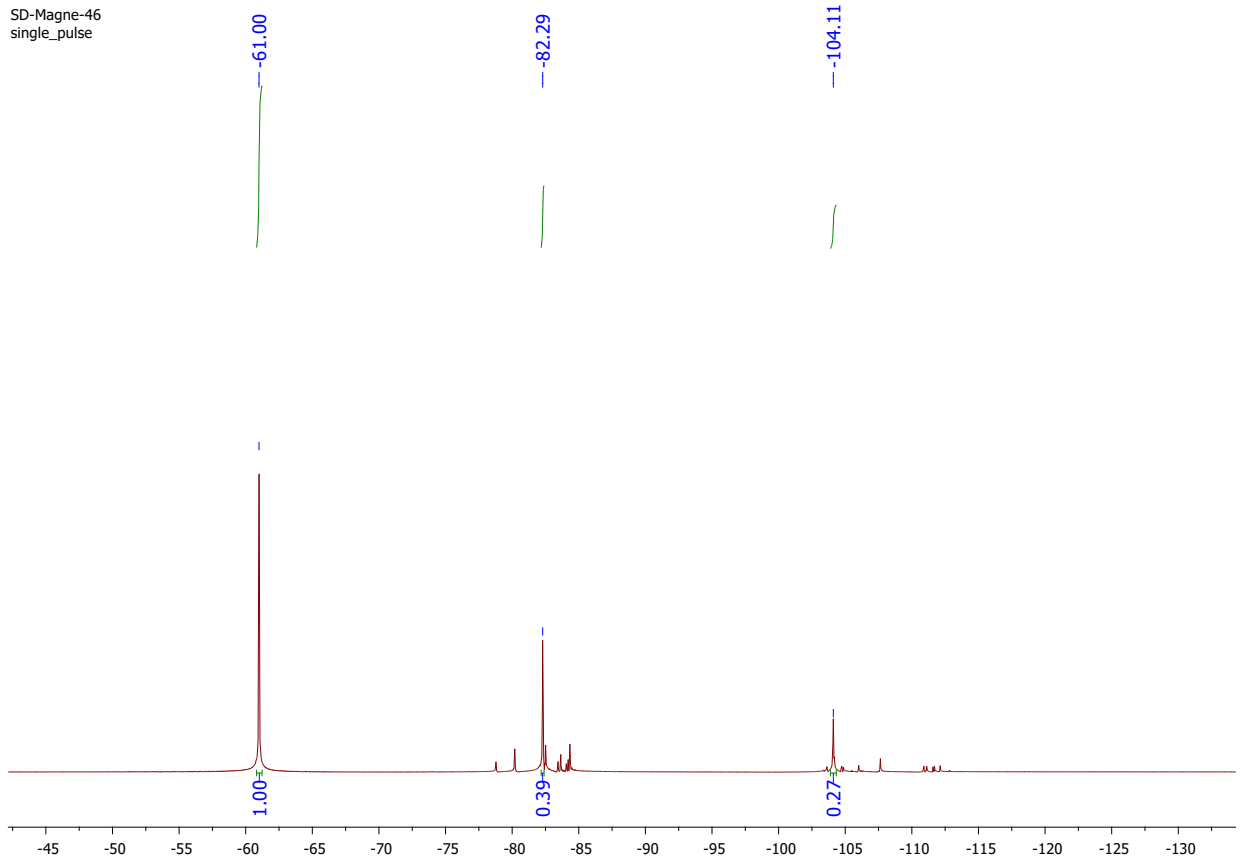
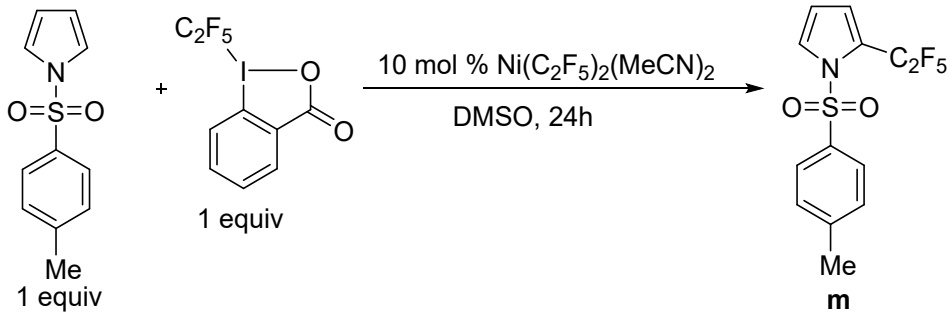


Figure S21. ^{19}F NMR spectrum showing formation of compound **l.**



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 1-(p-Tolylsulfonyl)pyrrole (16.5 mg, 0.045 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (23.1 mg, 0.045 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (1.7 mg, 0.005 mmol), which were dissolved in anhydrous DMSO (1 mL). The reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (5.5 µL, 0.0451 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy.

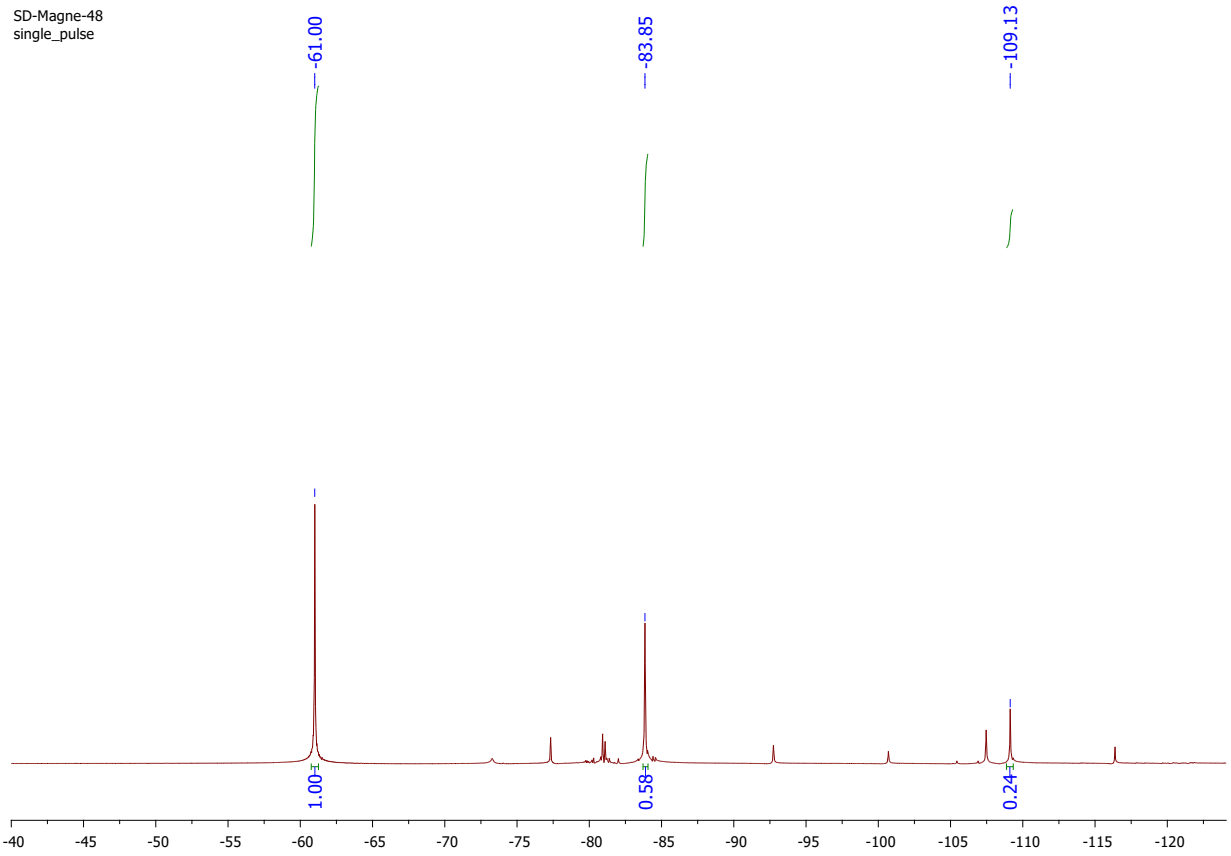
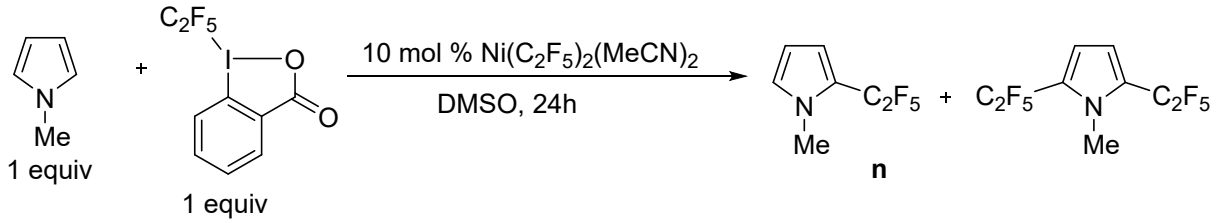


Figure S22. ^{19}F NMR spectrum showing formation of compound **m.**



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with N-Methyl pyrrole (8.8 µL, 0.10 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (36.6 mg, 0.10 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (3.7 mg, 0.01mmol) were dissolved in anhydrous DMSO (1 mL). Further the reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (12.2 µL, 0.1 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy.

HRMS (ESI) calculated for $[M^*H]^+$, $C_7H_6F_5N_1$: m/z 200.0493; found, 200.0479.

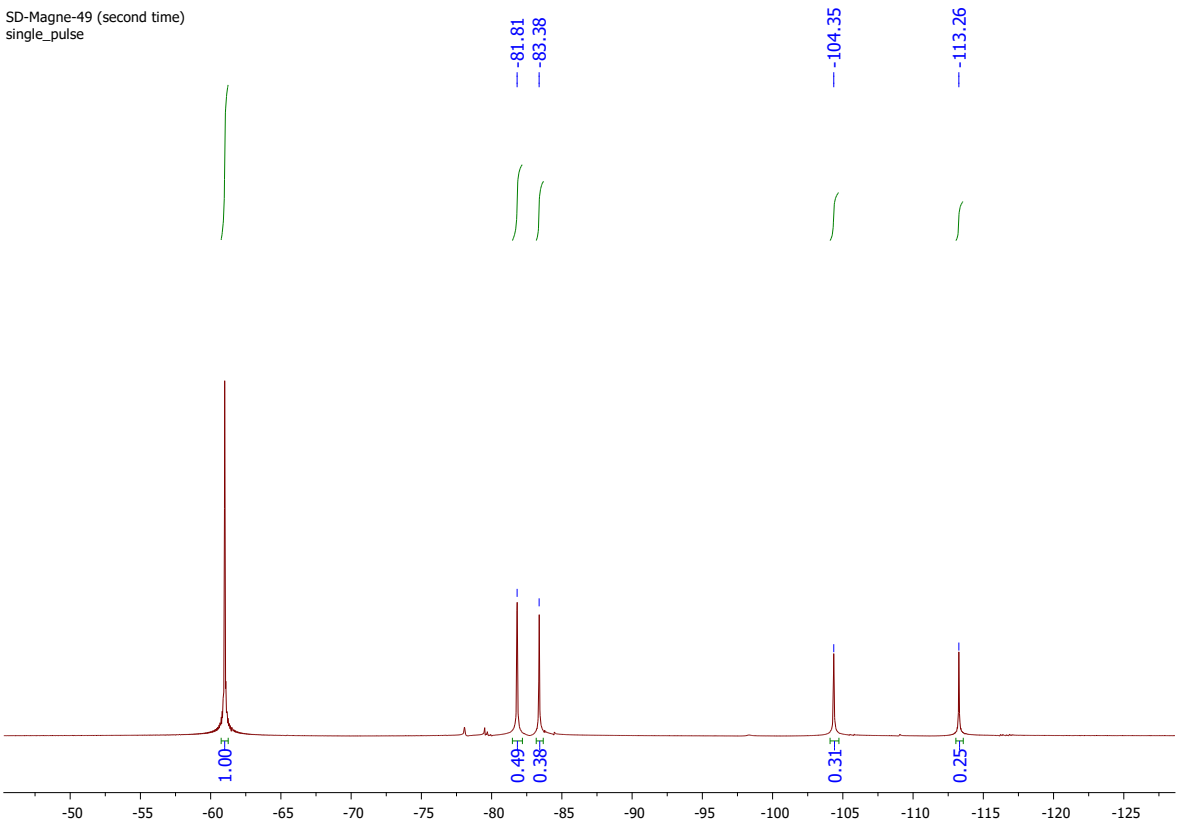


Figure S23. ^{19}F NMR spectrum showing formation of compound **n.**

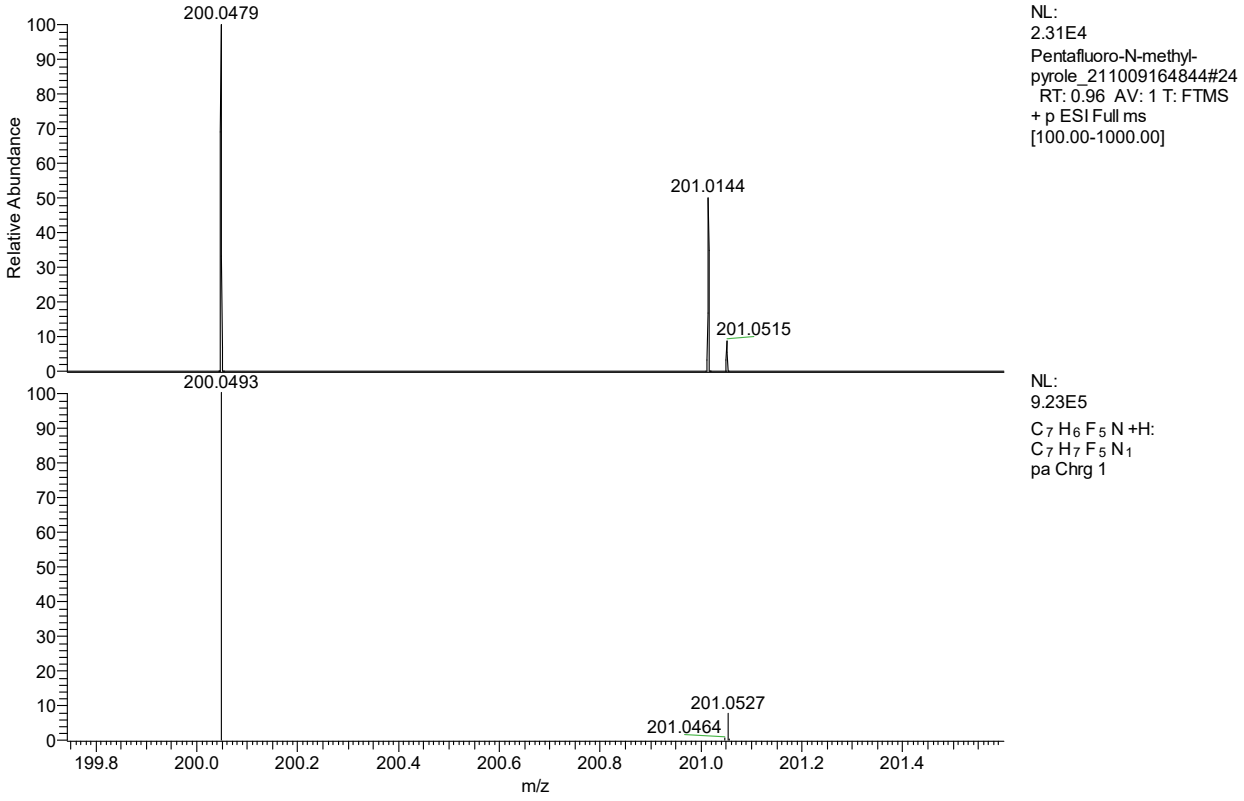
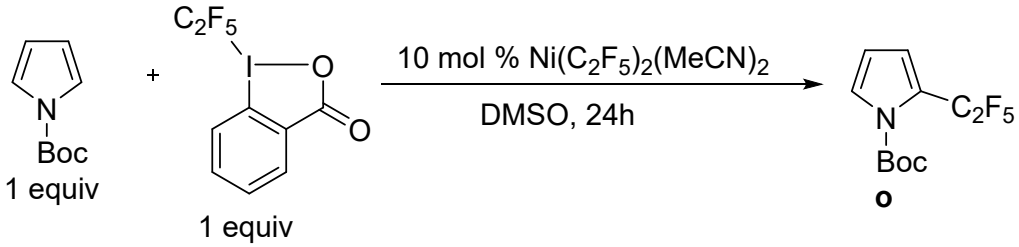


Figure S24. ESI-(HR)MS spectrum of a MeOH solution of **n.**



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with N-Boc pyrrole (16.7 μL, 0.10 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (36.6 mg, 0.10 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (3.7 mg, 0.01mmol), which were dissolved in anhydrous DMSO (1 mL). The reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (12.2 μL, 0.10 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy.

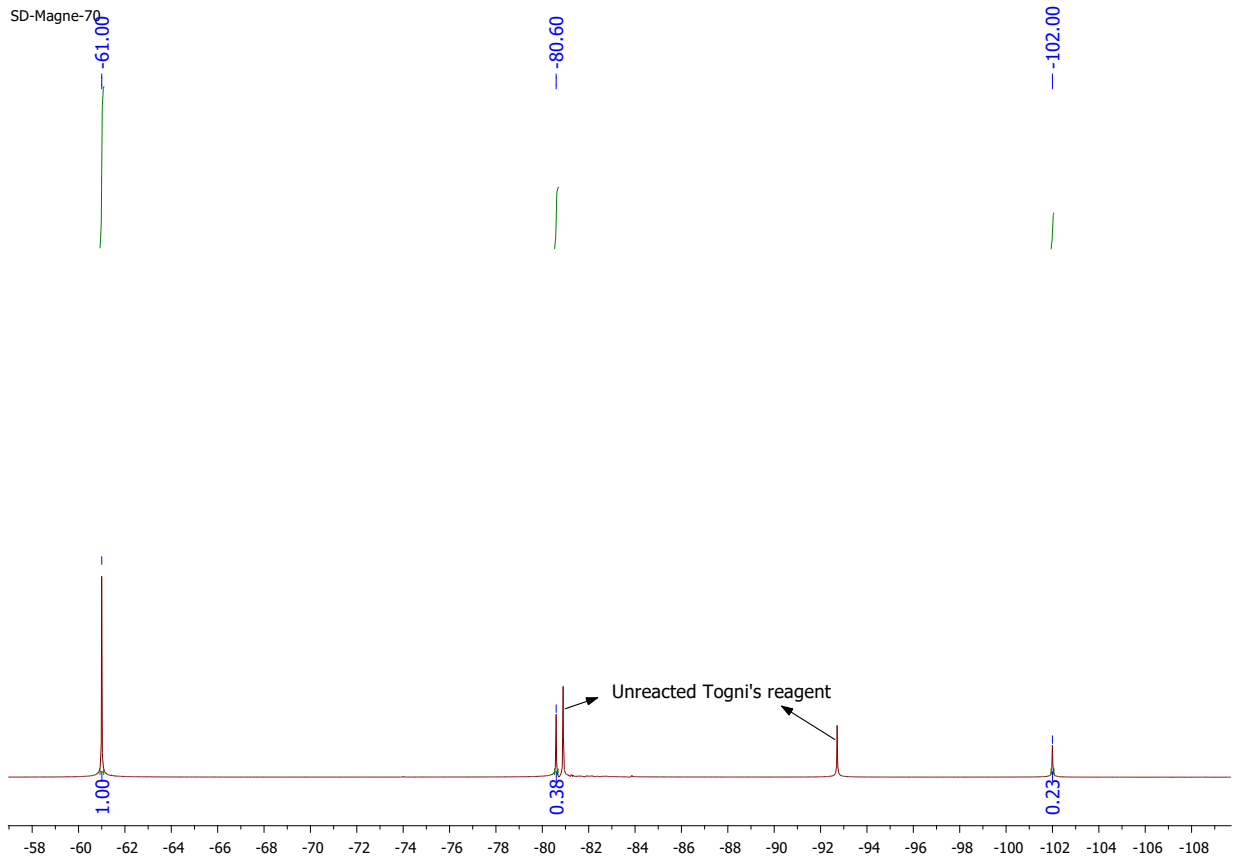
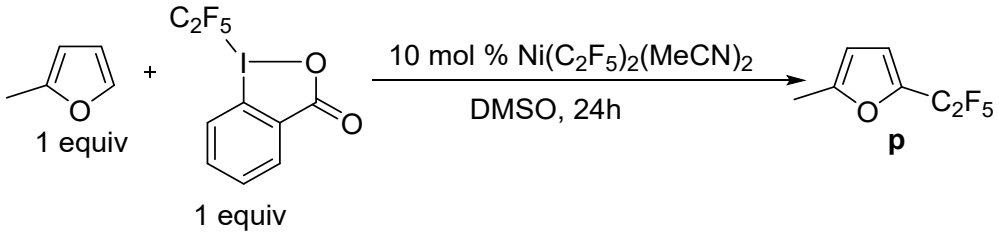


Figure S25. ^{19}F NMR spectrum showing formation of compound **o.**



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 2-Methylfuran (4.4 µL, 0.050 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (18.3 mg, 0.050 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (1.8 mg, 0.005 mmol), which were dissolved in anhydrous DMSO (1 mL). The reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (6.1 µL, 0.05 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy.

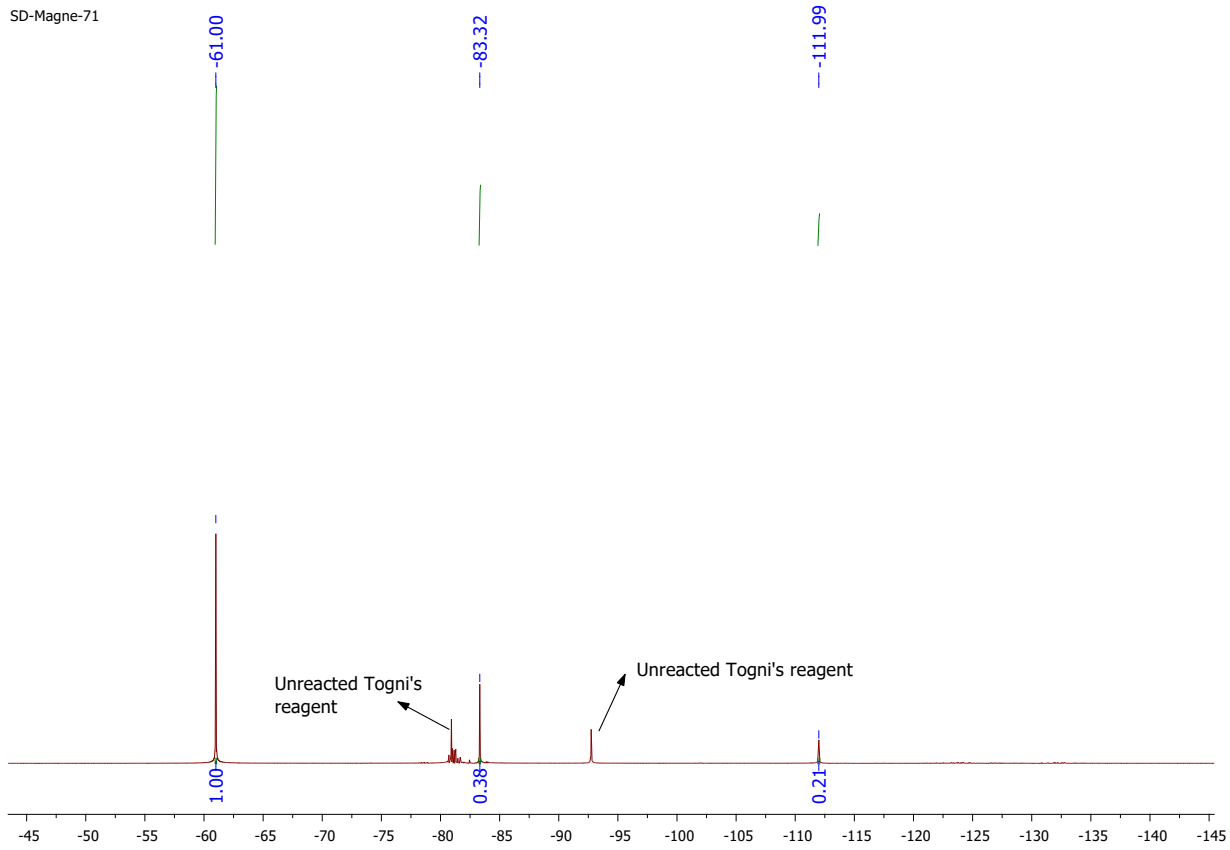
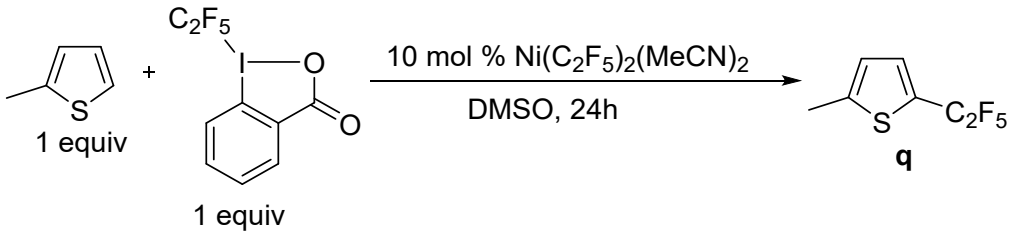


Figure S26. ^{19}F NMR spectrum showing formation of compound **p.**



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 2-Methylthiophene (9.7 µL, 0.10 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (36.6 mg, 0.10 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (3.7 mg, 0.01 mmol) were dissolved in anhydrous DMSO (1 mL). Further the reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (12.2 µL, 0.1 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy.

HRMS (ESI) calculated for $[M^*H]^+$, $C_7H_5F_5S_1$: m/z 217.0105; found, 217.0090.

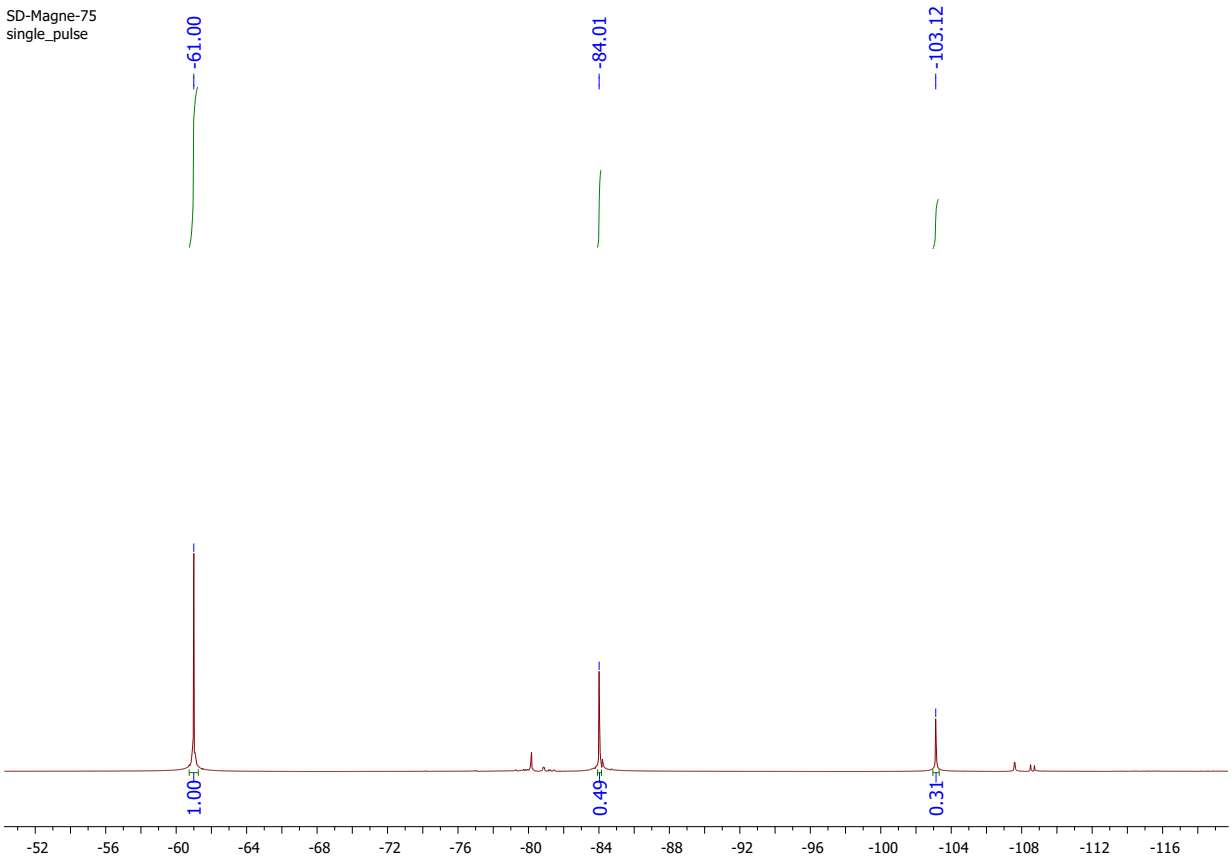


Figure S27. ^{19}F NMR spectrum showing formation of compound **q.**

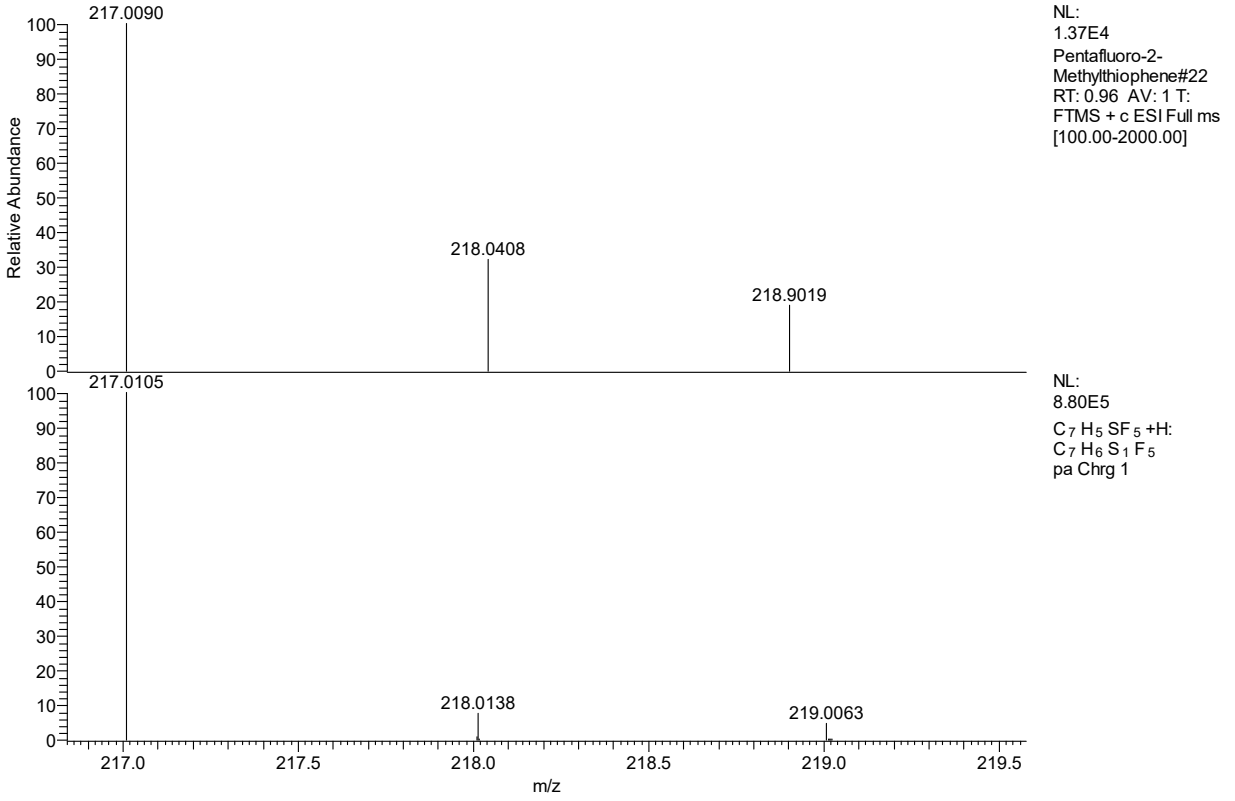
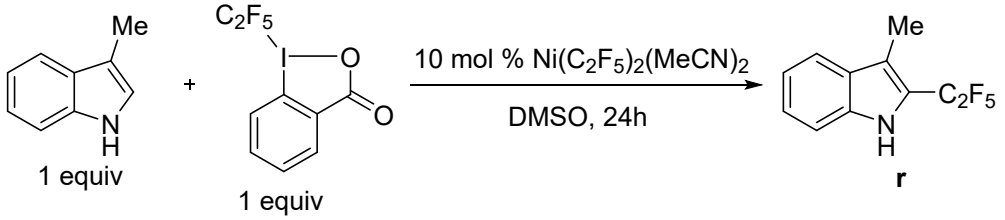


Figure S28. ESI-(HR)MS spectrum of a MeOH solution of **q.**



Isolation procedure. Inside the glovebox, to a 20 mL vial equipped with a stirring bar was charged with 3-methylindole (50.6 mg, 0.386 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (141.1 mg, 0.386 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (14.6 mg, 0.039 mmol), which were dissolved in anhydrous DMSO (2.5 mL). The reaction mixture was vigorously stirred for 24 hours. After completion of the reaction, the reaction mixture was transferred to a separatory funnel outside the glovebox and mixed with ethyl acetate (20 mL) and saturated aqueous NaCl (10 mL). After the first extraction, the organic layer was separated, and the remaining water layer was again extracted with ethyl acetate (20 mL). The organic layers were combined and dried over magnesium sulfate and concentrated under vacuum. The yellow color crude material was then purified by HPLC to get **r** as a yellow color oil (49.6 mg, 51% yield). The description of HPLC method: (A) MilliQ water and (B) Acetonitrile-Milli-Q water (90:10), both contained 0.1% formic acid. Gradient: 35% B for 0.0-1.0 min, 35-80% B for 1.0-6.0 min, hold 80% B for 6.0-9.0 min, equilibrate 80% B for 9.1-12.0 min

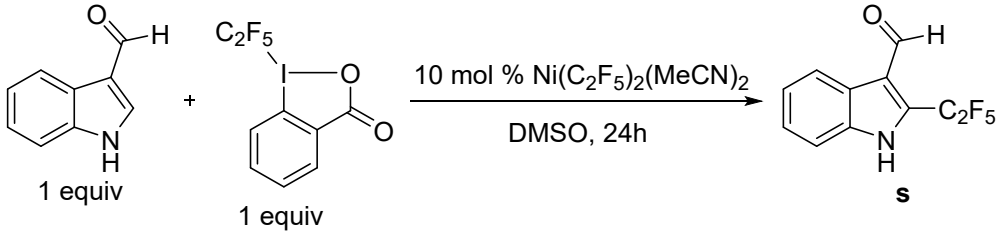
^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ 8.15 (br s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, 23 °C): δ 135.96, 128.50, 125.01, 121.22-117.57 (m), 120.53, 120.15, 116.32 (t, *J* = 3.2 Hz), 115.53-114.13 (m), 112.82-109.50 (m), 111.65, 8.61.

^{19}F NMR (376 MHz, $CDCl_3$, 23 °C): δ -84.67 (3F), -112.72 (2F).

HRMS (ESI) calculated for $[M^*H]^+$, $C_{11}H_9F_5N_1$: m/z 250.0650; found, 250.0642.

The above analytical data is agreed with previously published data.[4]



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with Indole-3-carboxaldeyde (10.0 mg, 0.069 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (25.2 mg, 0.069 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (2.6 mg, 0.007 mmol), which were dissolved in anhydrous DMSO (1 mL). The reaction mixture was stirred at room temperature for 24 hours. After the completion of the reaction, α,α,α-trifluorotoluene (8.4 μL, 0.069 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy.

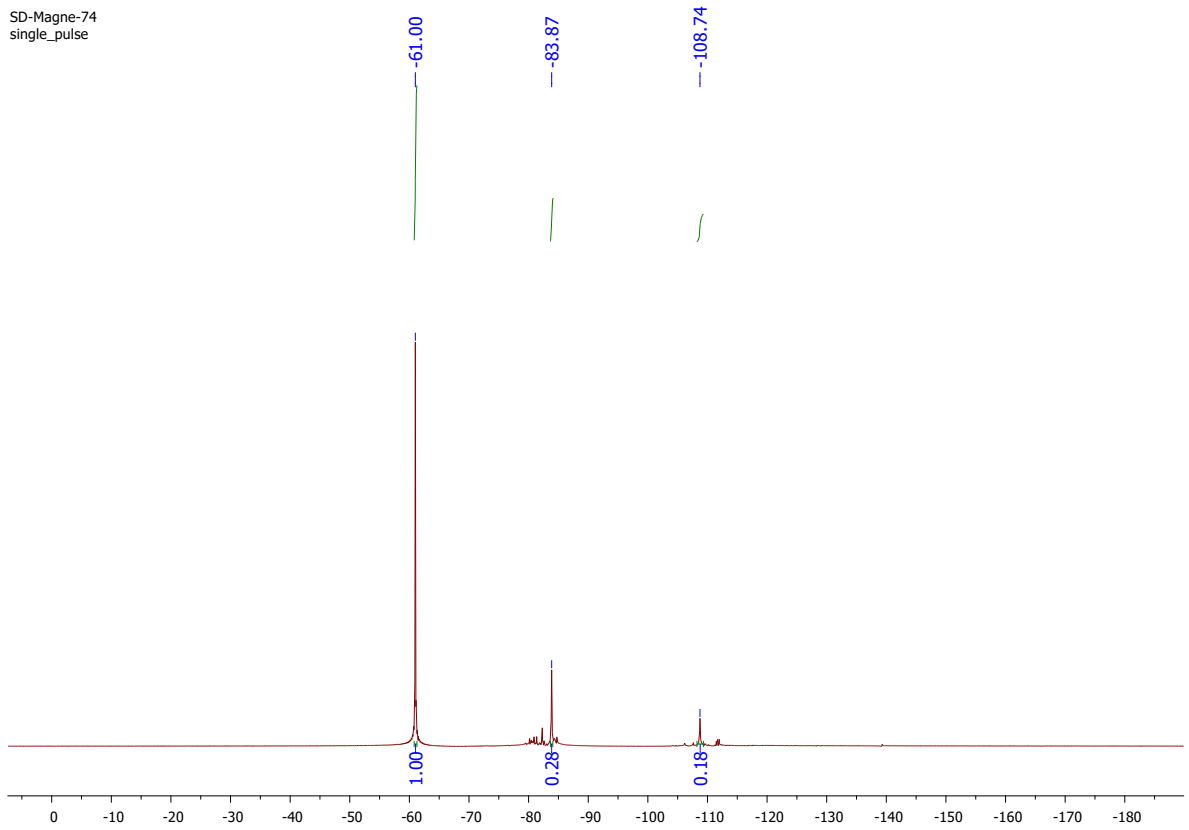
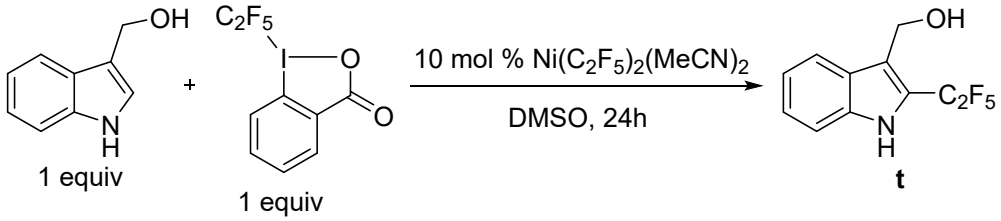


Figure S29. ^{19}F NMR spectrum showing formation of compound **s**.



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with Indole-3-carbinol (10.0 mg, 0.068 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (24.8 mg, 0.068 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (2.5 mg, 0.007 mmol) were dissolved in anhydrous DMSO (1 mL). Further the reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (8.3 µL, 0.068 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy.

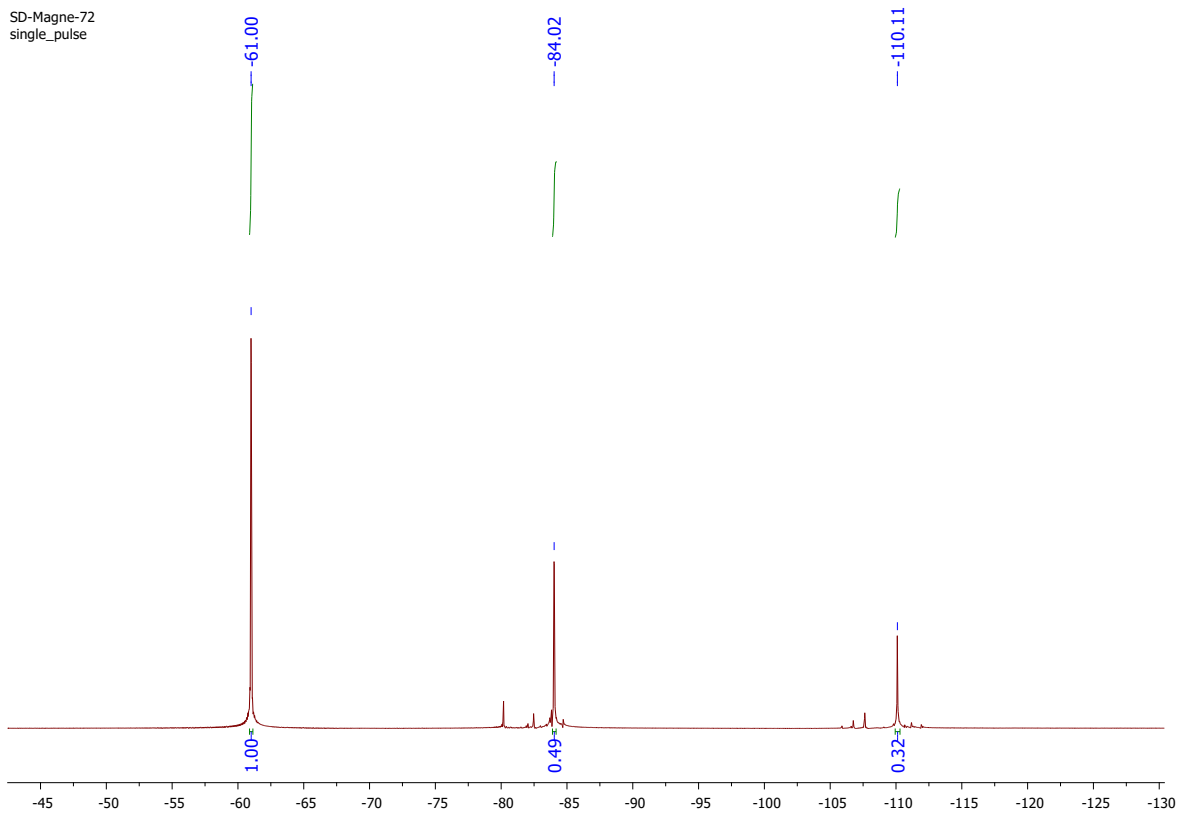
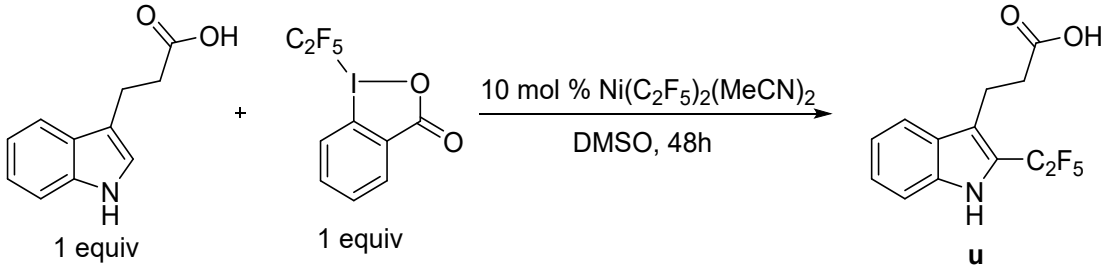


Figure S30. ^{19}F NMR spectrum showing formation of compound **t**.



Isolation procedure. Inside the glovebox, a 20 mL vial equipped with a stirring bar was charged with Indole-3-propionic acid (50.3 mg, 0.266 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (97.3 mg, 0.266 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (10.1 mg, 0.027 mmol) dissolved in anhydrous DMSO (2.5 mL). The reaction mixture was vigorously stirred for 48 hours. After completion of the reaction, the yellow color reaction mixture was transferred to a separatory funnel outside the glovebox and mixed with ethyl acetate (25 mL) and saturated aqueous NaCl (10 mL). After the first extraction, the organic layer was separated, and remaining water layer was again extracted with ethyl acetate (15 mL). The organic layers were combined and dried over magnesium sulfate. Further the reaction mixture was concentrated under vacuum. The reaction crude material was then purified by HPLC to give **u** as pale yellow solid (27.9 mg, 34% yield). The description of HPLC method: (A) MilliQ water and (B) Acetonitrile-Milli-Q water (90:10), both contained 0.1% formic acid. Gradient: 35% B for 0.0-1.0 min, 35-80% B for 1.0-6.0 min, hold 80% B for 6.0-9.0 min, equilibrate 80% B for 9.1-12.0 min

^{1}H NMR (600 MHz, $CDCl_3$, 23 °C): δ 8.30 (br.s, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 3.24 (m, 2H), 2.72 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$, 23 °C): δ 179.20, 136.59, 127.73, 125.74, 123.82 – 110.72 (overlap of signals consist of fluorine's splitting), 121.41, 120.55, 120.02 (t, *J* = 28.4 Hz), 119.17,112.41, 35.78, 19.82.

^{19}F NMR (565 MHz, $CDCl_3$, 23 °C): δ -84.61 (3F), -112.16 (2F).

HRMS (ESI) calculated for $[M^*Na]^+$, $C_{13}H_{10}F_5O_2N_1Na_1$: m/z 330.0524; found, 330.0529.

NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with Indole-3-acetamide (10.0 mg, 0.057 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (21.0 mg, 0.057 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (2.1 mg, 0.006 mmol), which were dissolved in anhydrous DMSO (1 mL). The reaction mixture was stirred at room temperature for 48 hours. After the completion of reaction, α,α,α-trifluorotoluene (7.0 μL, 0.057 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy.

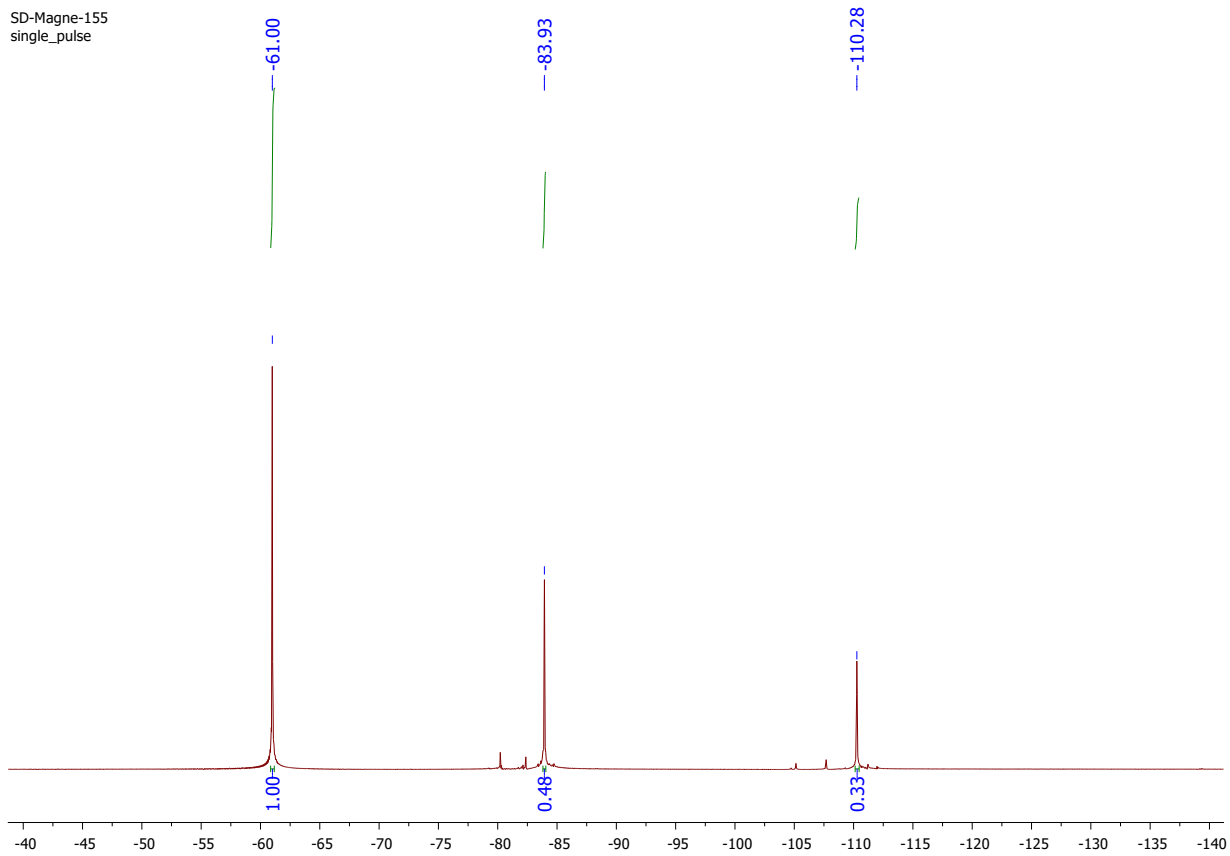
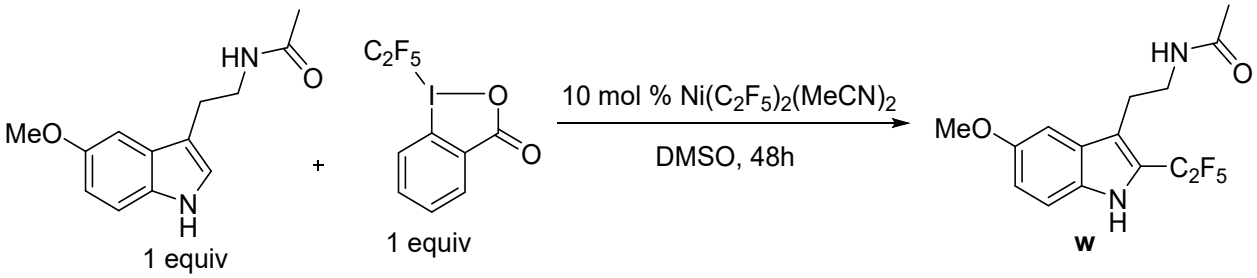


Figure S31. ^{19}F NMR spectrum showing formation of compound **v**.



Isolation procedure. Inside the glovebox, a 20 mL vial equipped with a stirring bar was charged with Melatonin (100.6 mg, 0.433 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (158.5 mg, 0.433 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (16.4 mg, 0.043 mmol), which were dissolved in anhydrous DMSO (4 mL). The reaction mixture was vigorously stirred for 48 hours. After completion of the reaction, the yellow color reaction mixture was transferred to a separatory funnel outside the glovebox and mixed with ethyl acetate (30 mL) and saturated aqueous NaCl (20 mL). After the first extraction, the organic layer was separated, and the remaining water layer was again extracted with ethyl acetate (30 mL). The organic layers were combined and dried over magnesium sulfate and concentrated under vacuum. The yellow color crude material was then purified by HPLC to give **w** as a yellow color oil (58.1 mg, 38% yield). The description of HPLC method: (A) MilliQ water and (B) Acetonitrile-Milli-Q water (90:10), both contained

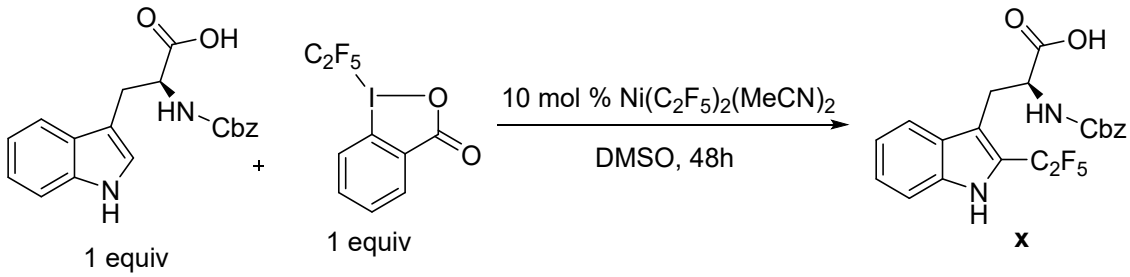
0.1% formic acid. Gradient: 35% B for 0.0-1.0 min, 35-80% B for 1.0-6.0 min, hold 80% B for 6.0-9.0 min, equilibrate 80% B for 9.1-12.0 min

^{1}H NMR (600 MHz, $CDCl_3$, 23 °C): δ 8.76 (br s, 1H), 7.31 (d, *J*= 8.9 Hz, 1H), 7.13 (d, *J*= 2.4 Hz, 1H), 6.99 (dd, *J*= 8.9, 2.3 Hz, 1H), 5.96 (m, 1H), 3.85 (s, 3H), 3.56 (m, 2H), 3.07 (t, *J*= 7.1 Hz, 2H), 1.98 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, 23 °C): δ 172.40, 155.67, 134.19-125.34 (m), 132.13, 128.81, 122.91-118.58 (m), 117.17 (m), 114.96-109.02 (m), 113.70, 111.49, 101.31, 56.60, 41.18, 24.87, 23.73.

^{19}F NMR (376 MHz, $CDCl_3$, 23 °C): δ -84.67 (3F), -112.74 (2F).

HRMS (ESI) calculated for $[M^*H]^+$, $C_{15}H_{16}F_5O_2N_2$: m/z 351.1126; found, 351.1149.



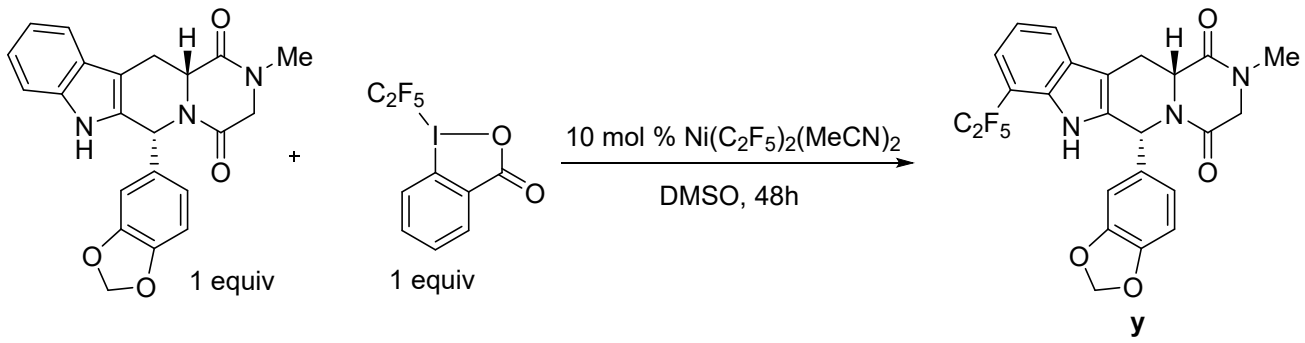
Isolation procedure. Inside the glovebox, a 20 mL vial equipped with a stirring bar was charged with N-Cbz-L-Tryptophan (110.8 mg, 0.327 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (119.8 mg, 0.327 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (12.4 mg, 0.032 mmol), which were dissolved in anhydrous DMSO (2.5 mL). The reaction mixture was vigorously stirred for 48 hours. After completion of the reaction, the reaction mixture was transferred to a separatory funnel outside the glovebox and mixed with ethyl acetate (30 mL) and saturated aqueous NaCl (15 mL). After the first extraction, the organic layer was separated, and the remaining water layer was again extracted with ethyl acetate (25 mL). The organic layers were combined and dried over magnesium sulfate. Further the reaction mixture was concentrated under vacuum. The yellow color crude material was then purified by HPLC to give **x** as a colorless solid (57.4 mg, 38% yield). The description of HPLC method: (A) MilliQ water and (B) Acetonitrile-Milli-Q water (90:10), both contained 0.1% formic acid. Gradient: 35% B for 0.0-1.0 min, 35-80% B for 1.0-6.0 min, hold 80% B for 6.0-9.0 min, equilibrate 80% B for 9.1-12.0 min

^{1}H NMR (400 MHz, CD_3OD, 23 °C): δ 11.31 (br.s, 1H), 7.65 (d, *J* = 8 Hz, 1H), 7.32 (d, *J* = 8 Hz, 1H), 7.18- 6.97 (m, 8H), 6.99 (t, *J* = 7.7 Hz, 1H), 4.40 (dd, *J* = 8.6, 5.8 Hz, 1H), 3.36 (dd, *J* = 14.3, 5.7 Hz, 1H), 3.26-3.18 (m, 1H), 3.14 (dd, *J* = 14.3, 8.9 Hz, 1H) Two proton overlaps with water peak confirm by COSY.

^{13}C NMR (101 MHz, CD_3OD, 23 °C): δ 174.95, 158.24, 138.09 (d, *J* = 7.5 Hz), 129.36, 128.97, 128.82, 128.56, 125.44, 122.43-110.57 (m, coupling constant could not be measured due to signal overlap), 121.23, 121.09, 116.04, 112.98, 67.47, 56.85, 28.05.

^{19}F NMR (376 MHz, CD_3OD, 23 °C): δ - δ -84.13 (3F), -112.39 (2F).

HRMS (ESI) calculated for $[M^*Na]^+$, $C_{21}H_{17}F_5O_4N_2Na_1$: m/z 479.1001; found, 479.0992.



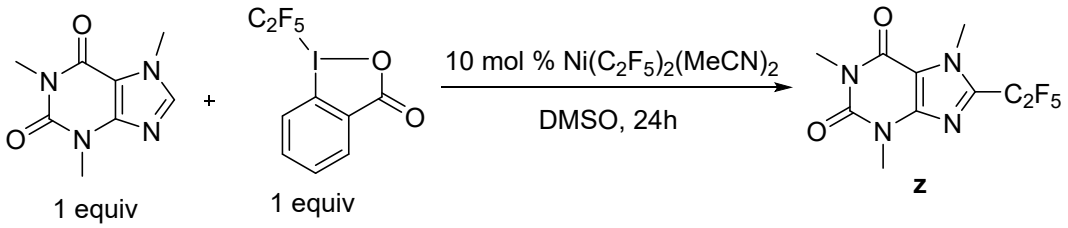
Isolation procedure. Inside the glovebox, a 20 mL vial equipped with a stirring bar was charged with Tadalafil (100.9 mg, 0.259 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (94.8 mg, 0.259 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (9.8 mg, 0.026 mmol), which were dissolved in anhydrous DMSO (4 mL). The reaction mixture was vigorously stirred for 48 hours. After completion of the reaction, the yellow color reaction mixture was transferred to a separatory funnel outside the glovebox and mixed with ethyl acetate (30 mL) and saturated aqueous NaCl (20 mL). After the first extraction, the organic layer was separated, and the remaining water layer was again extracted with ethyl acetate (30 mL). The organic layers were combined and dried over magnesium sulfate, and then concentrated under vacuum. The yellow color crude material was then purified by HPLC to give **y** as a yellow color oil (34.7 mg, 26% yield). The compound begins to solidify with time at room temperature. The description of HPLC method: (A) MilliQ water and (B) Acetonitrile-Milli-Q water (90:10), both contained 0.1% formic acid. Gradient: 35% B for 0.0-1.0 min, 35-80% B for 1.0-6.0 min, hold 80% B for 6.0-9.0 min, equilibrate 80% B for 9.1-12.0 min

^{1}H NMR (600 MHz, $(CD_3)_2SO$, 23 °C): δ 11.82 (s, 1H), 7.66 (d, J = 8 Hz, 1H), 7.33 (d, J = 7.5 Hz, 1H), 7.26 (t, J = 7.8 Hz, 1H), 6.88 (s, 1H), 6.78 (s, 2H), 6.19 (s, 1H), 5.92 (s, 2H), 4.37 (dd, J = 11.8, 3.6 Hz, 1H), 4.16 (dd, J = 17.1, 1.1 Hz, 1H), 3.94 (d, J = 25.9 Hz, 1H), 3.60 (m, 2H), 2.92 (s, 4H).

^{13}C NMR (126 MHz, $(CD_3)_2SO$, 23 °C): 166.80, 166.39, 147.25, 146.36, 137.56, 137.30, 136.40, 123.05- 117.85 (qt, J = 40.5 Hz, another coupling constant could not be measured due to overlap), 122.05, 120.64, 119.32, 117.05 (t, J = 24.3 Hz), 116.43, 115.19-112.29 (tq, J = 37.2 Hz, another coupling constant could not measure due to overlap), 108.26, 106.97, 103.96, 101.11, 55.69, 55.06, 51.48, 33.02, 25.09.

^{19}F NMR (376 MHz, $CDCl_3$, 23 °C): δ -83.30 (3F), -109.61 (2F).

HRMS (ESI) calculated for $[M^*Na]^+$, $C_{24}H_{18}F_5O_4N_3Na_1$: m/z 530.1110; found, 530.1071.



Isolation procedure. Inside the glovebox, to a 20 mL vial equipped with a stirring bar was charged with Caffeine (100.2 mg, 0.516 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (188.8 mg, 0.516 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (19.5 mg, 0.052 mmol) dissolved in anhydrous DMSO (4 mL). The reaction mixture was vigorously stirred for 24 hours. After completion of the reaction, the reaction mixture was transferred to a separatory funnel outside the glovebox and mixed with ethyl acetate (25 mL) and saturated aqueous NaCl (10 mL). After the first extraction, the organic layer was separated, and the remaining water layer was again extracted with ethyl acetate (25 mL). The organic layers were combined and dried over magnesium sulfate and then concentrated under vacuum. The yellow color crude material was then purified by HPLC to give **z** as colorless solid (63.8 mg, 39 % yield). The description of HPLC method: (A) MilliQ water and (B) Acetonitrile-Milli-Q water (90:10), both contained 0.1% formic acid. Gradient: 35% B for 0.0-1.0 min, 35-80% B for 1.0-6.0 min, hold 80% B for 6.0-9.0 min, equilibrate 80% B for 9.1-12.0 min

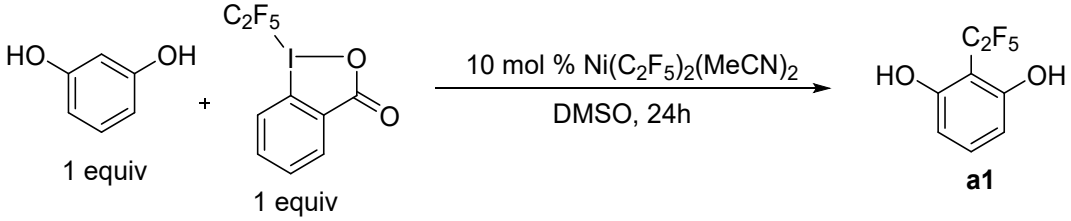
^{1}H NMR (500 MHz, $CDCl_3$, 23 °C): δ 4.19 (s, 3H), 3.58 (s, 3H), 3.41 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$, 23 °C): δ 155.67, 151.54, 147.10, 137.94 (t, J= 28.6 Hz), 118.35 (qt, J = 290.33 Hz, 36.8 Hz), 115.22-107.01 (tq, J = 254.33 Hz, 40.3 Hz), 110.28, 33.86, 30.15, 28.45.

^{19}F NMR (376 MHz, $CDCl_3$, 23 °C): δ -82.56 (3F), -111.40 (2F).

HRMS (ESI) calculated for $[M^*H]^+$, $C_{10}H_9F_5O_2N_4$: m/z 313.0718; found, 313.0707.

The above analytical data is agreed with previously published data.[5]



Isolation procedure. Inside the glovebox, a 20 mL vial equipped with a stirring bar was charged with Resorcinol (50.8 mg, 0.461 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (168.8 mg, 0.461 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (17.4 mg, 0.046 mmol), which were dissolved in anhydrous DMSO (2.5 mL). The reaction mixture was vigorously stirred for 24 hours. After completion of the reaction, the reaction mixture was transferred to a separatory funnel outside the glovebox and mixed with ethyl acetate (30 mL) and saturated aqueous NaCl (10 mL). After the first extraction, the organic layer was separated, and remaining water layer was again

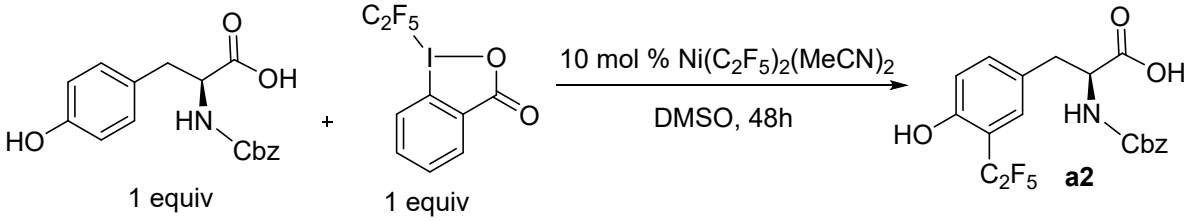
extracted with ethyl acetate (25 mL). The organic layers were combined and dried over magnesium sulfate and then concentrated under vacuum. The yellow color crude material was purified by HPLC to give **a1** as a yellow color oil (41 mg, 39% yield). The description of HPLC method: (A) MilliQ water and (B) Acetonitrile-Milli-Q water (90:10), both contained 0.1% formic acid. Gradient: 35% B for 0.0-1.0 min, 35-80% B for 1.0-6.0 min, hold 80% B for 6.0-9.0 min, equilibrate 80% B for 9.1-12.0 min

^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ 7.27 (d, J = 8.5 Hz, 1H), 6.51-6.44 (m, 2H), 5.80 (br.s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$, 23 °C): δ 160.13, 156.16, 130.01 (t, J = 7.7 Hz), 124.08-111.69 (overlap of two signals with fluorine splitting), 108.82, 106.31 (t, J = 22.5 Hz), 104.95.

^{19}F NMR (376 MHz, $CDCl_3$, 23 °C): δ -84.78 (3F), -111.16 (2F).

HRMS (ESI) calculated for $[M^*Na]^+$, $C_8H_5F_5O_2Na$: m/z 251.0102; found, 251.0065.



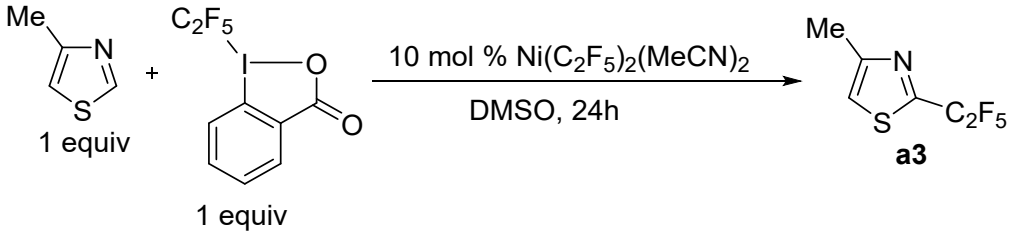
Isolation procedure. Inside the glovebox, a 20 mL vial equipped with a stirring bar was charged with N-Cbz-L-tyrosine (100.4 mg, 0.318 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (116.5 mg, 0.318 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (12.0 mg, 0.0318 mmol), which were dissolved in anhydrous DMSO (4 mL). The reaction mixture was vigorously stirred for 48 hours. After completion of the reaction, the reaction mixture was transferred to a separatory funnel outside the glovebox and mixed with ethyl acetate (35 mL) and saturated aqueous NaCl (15 mL). After the first extraction, the organic layer was separated, and remaining water layer was again extracted with ethyl acetate (25 mL). The organic layers were combined and dried over magnesium sulfate and then concentrated under vacuum. The yellow color crude material was purified by HPLC to give **a2** as a colorless oil which was dried under high vacuum for two days (42.5 mg, 31% yield). The description of HPLC method: (A) MilliQ water and (B) Acetonitrile-Milli-Q water (90:10), both contained 0.1% formic acid. Gradient: 35% B for 0.0-1.0 min, 35-80% B for 1.0-6.0 min, hold 80% B for 6.0-9.0 min, equilibrate 80% B for 9.1-12.0 min. Crystal structure of MeO modified **a2** (as methoxy ester), through which the carbofluorination position could be determined, was obtained by slow evaporation of methanol solvent.

^{1}H NMR (600 MHz, CD_3OD, 23 °C): δ 7.31-7.19 (m, 7H), 6.84-6.80 (m, 1H), 5.06-4.9 (m, 3H), 4.39-4.31 (m, 1H), 3.09 (dd, J = 14, 5.2 Hz, 1H), 2.86 (dd, J = 14, 9.5 Hz, 1H).

^{13}C NMR (126 MHz, CD_3OD, 23 °C): δ 173.73, 158.36, 156.87, 138.16, 135.36, 130.14 (t, J = 8.3 Hz), 129.43, 129.07, 128.94, 128.61, 124.75-119.57 (one triplet pattern overlaps with adjacent signals), 118.32, 117.92-112.79 (m), 115.14 (m), 67.57, 56.94, 37.53

^{19}F NMR (376 MHz, CD_3OD, 23 °C): δ -84.71 (3F), -111.14 (2F).

HRMS (ESI) calculated for $[M^*H]^+$, $C_{19}H_{16}F_5O_2N$: m/z 434.1021; found, 434.1007.



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 4-methylthiazole (10 mg, 0.10 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (36.9 mg, 0.10 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (3.8 mg, 0.01 mmol) were dissolved in anhydrous DMSO (1 mL). Further the reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (12.3 µL, 0.1 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy.

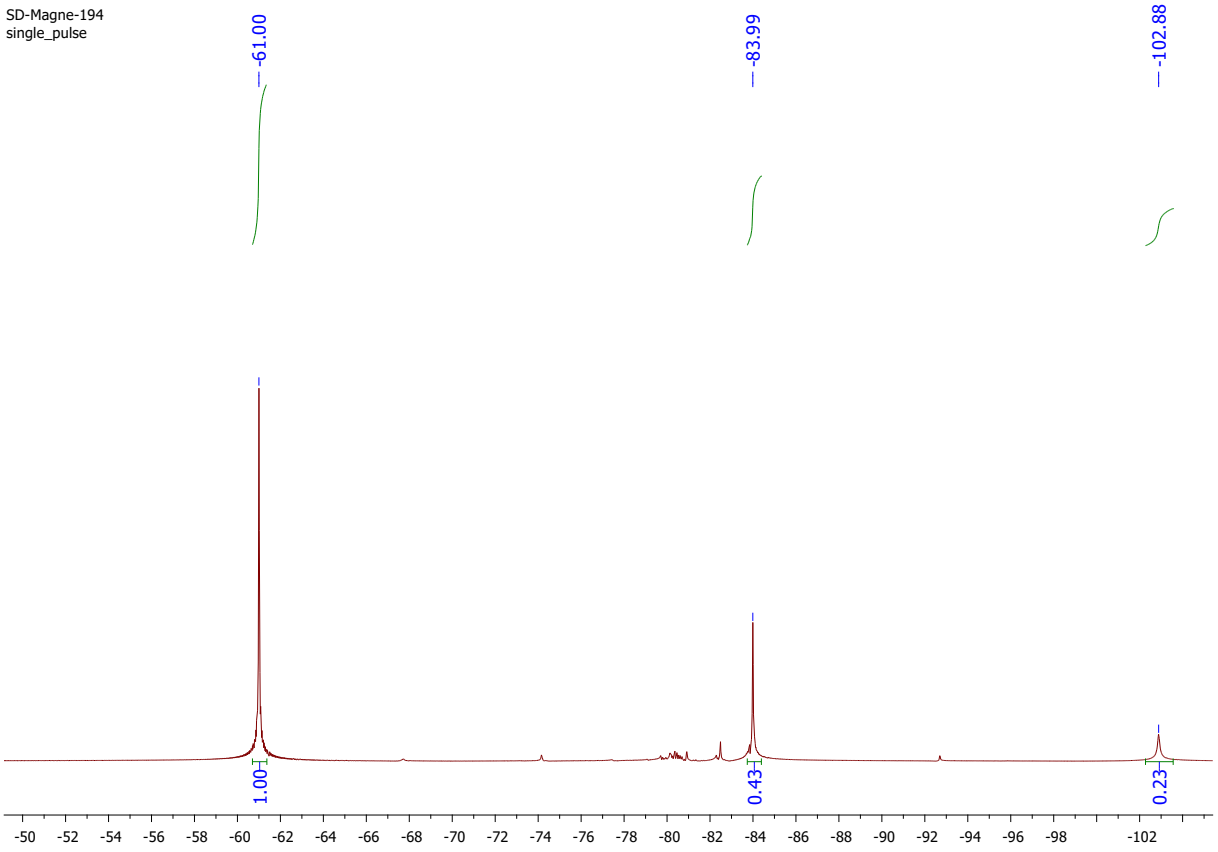
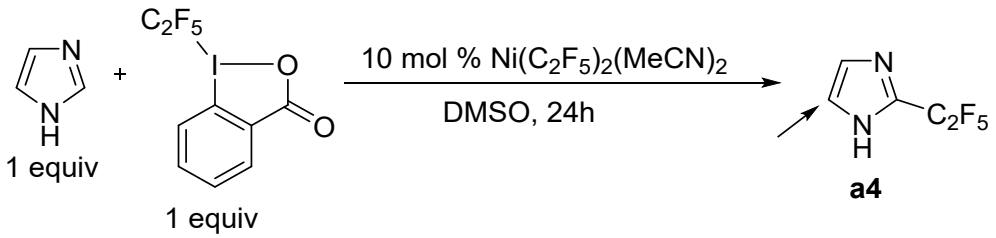


Figure S32. ^{19}F NMR spectrum showing formation of compound **a3.**



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with imidazole (10 mg, 0.14 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (53.7 mg, 0.14 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (5.5 mg, 0.014 mmol) were dissolved in anhydrous DMSO (1 mL). Further the reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (18 µL, 0.14 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy.

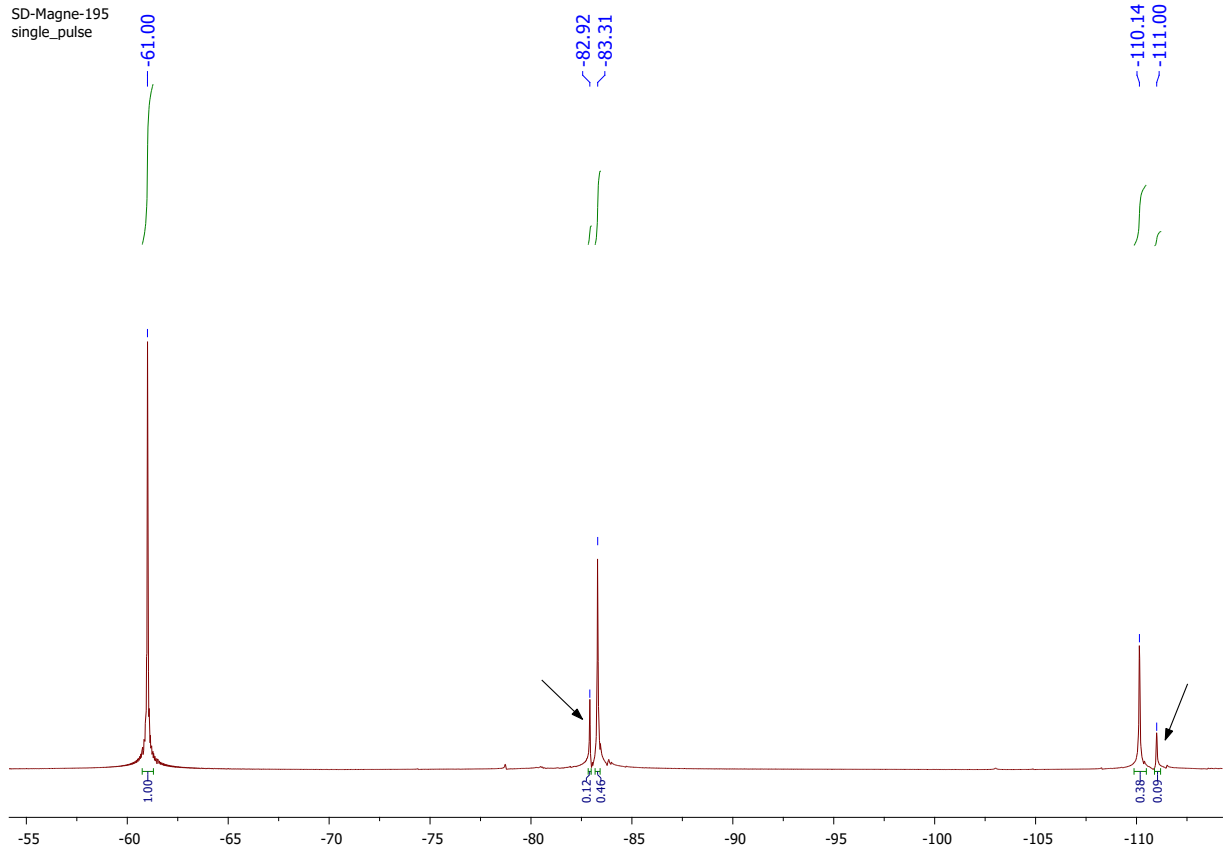
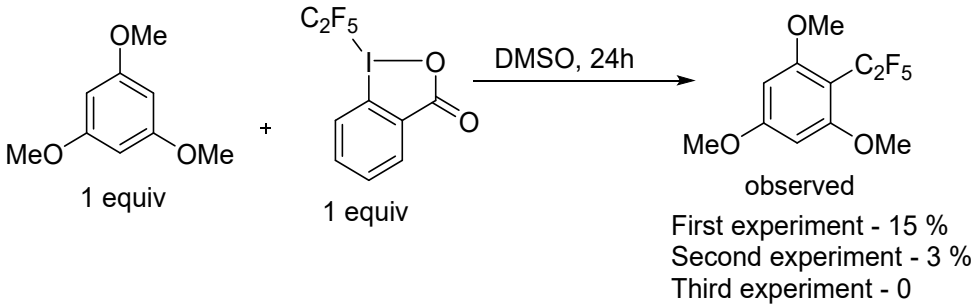


Figure S33. ^{19}F NMR spectrum showing formation of compound **a4**. Arrow indicates minor isomers.

Control Experiments with different substrates –



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with Trimethoxybenzene (10.0 mg, 0.059 mmol) and 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (21.7 mg, 0.059 mmol), which were dissolved in anhydrous DMSO (1 mL). Further the reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (7.3 µL, 0.059 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy.

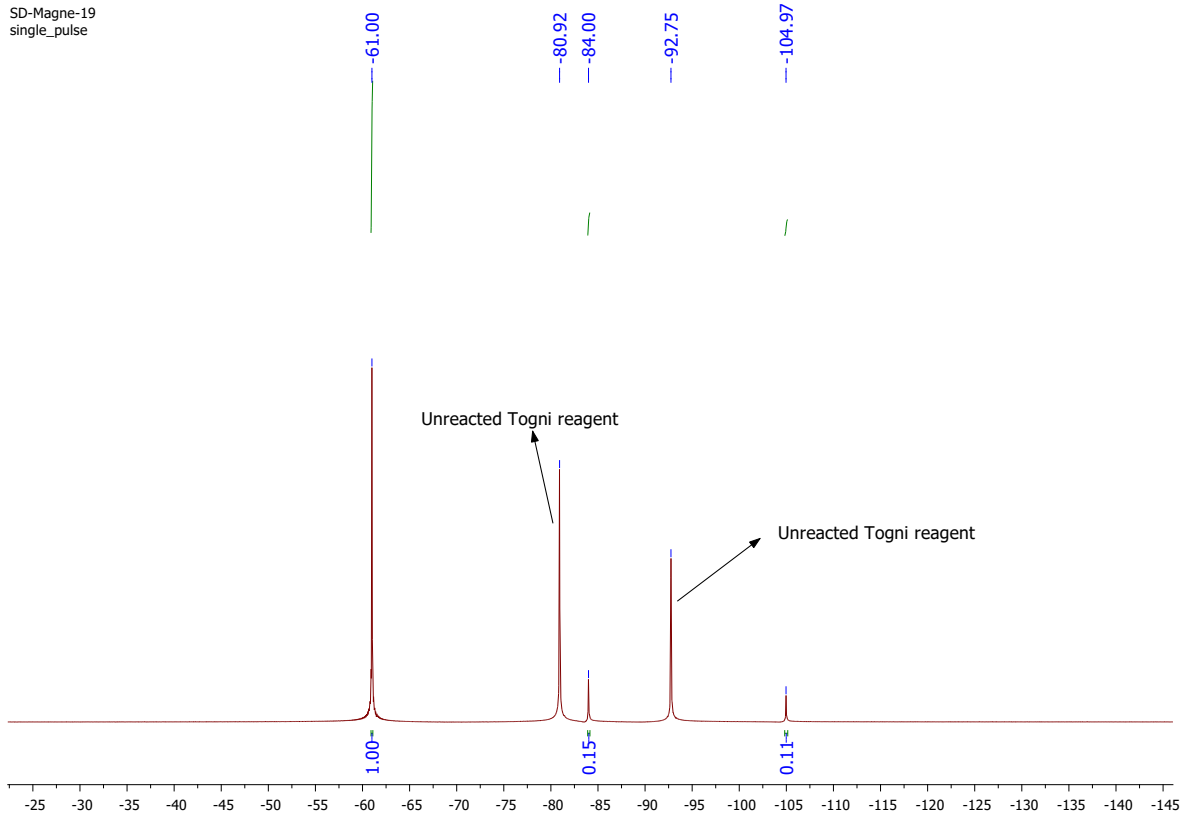


Figure S34. ^{19}F NMR spectrum in absence of catalyst.

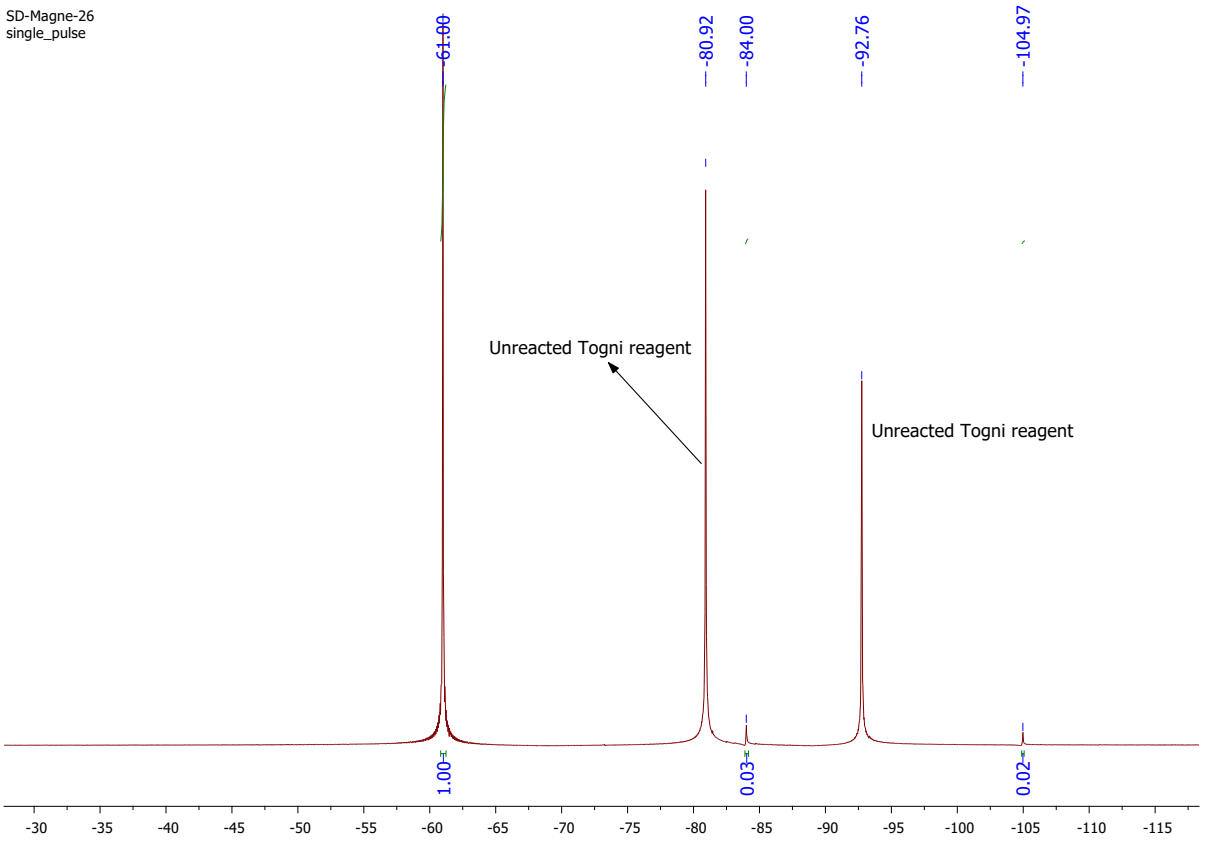


Figure S35. ^{19}F NMR spectrum in absence of catalyst. Second time the reaction was performed.

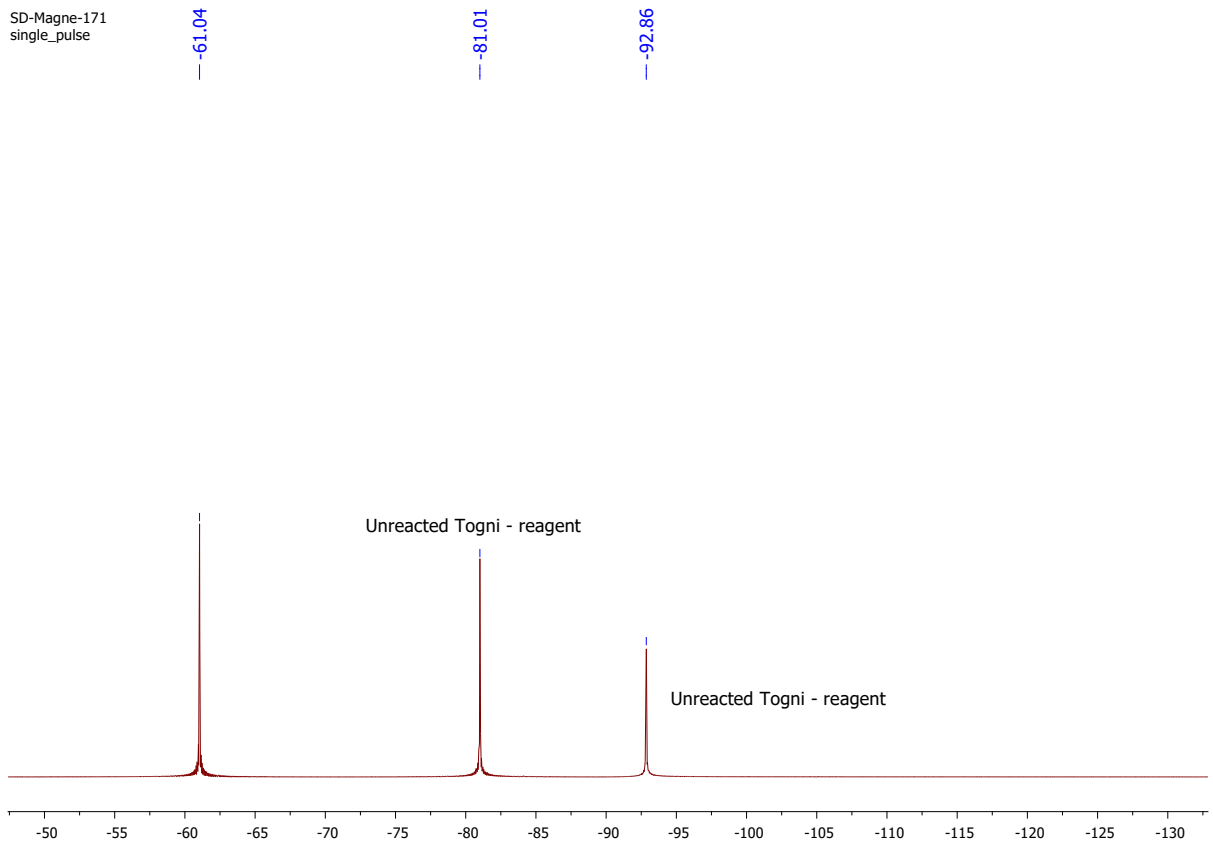
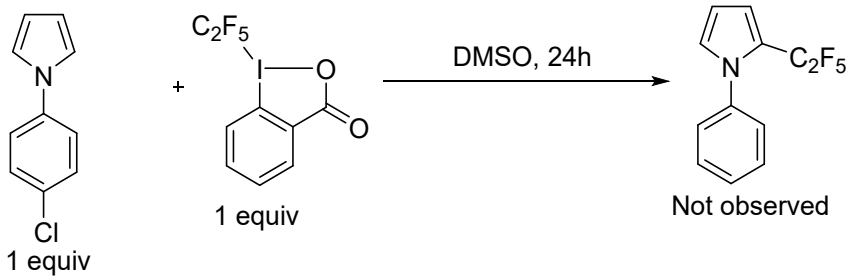


Figure S36. ^{19}F NMR spectrum in absence of catalyst. Third time the reaction was performed.



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 1-(4-Chlorophenyl)-1H-pyrrole (10.0 mg, 0.056 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (23.1 mg, 0.056 mmol) were dissolved in anhydrous DMSO (1 mL). Further the reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (6.9 µL, 0.056 mmol) was added as a standard. ^{19}F NMR spectroscopy showed no product formation.

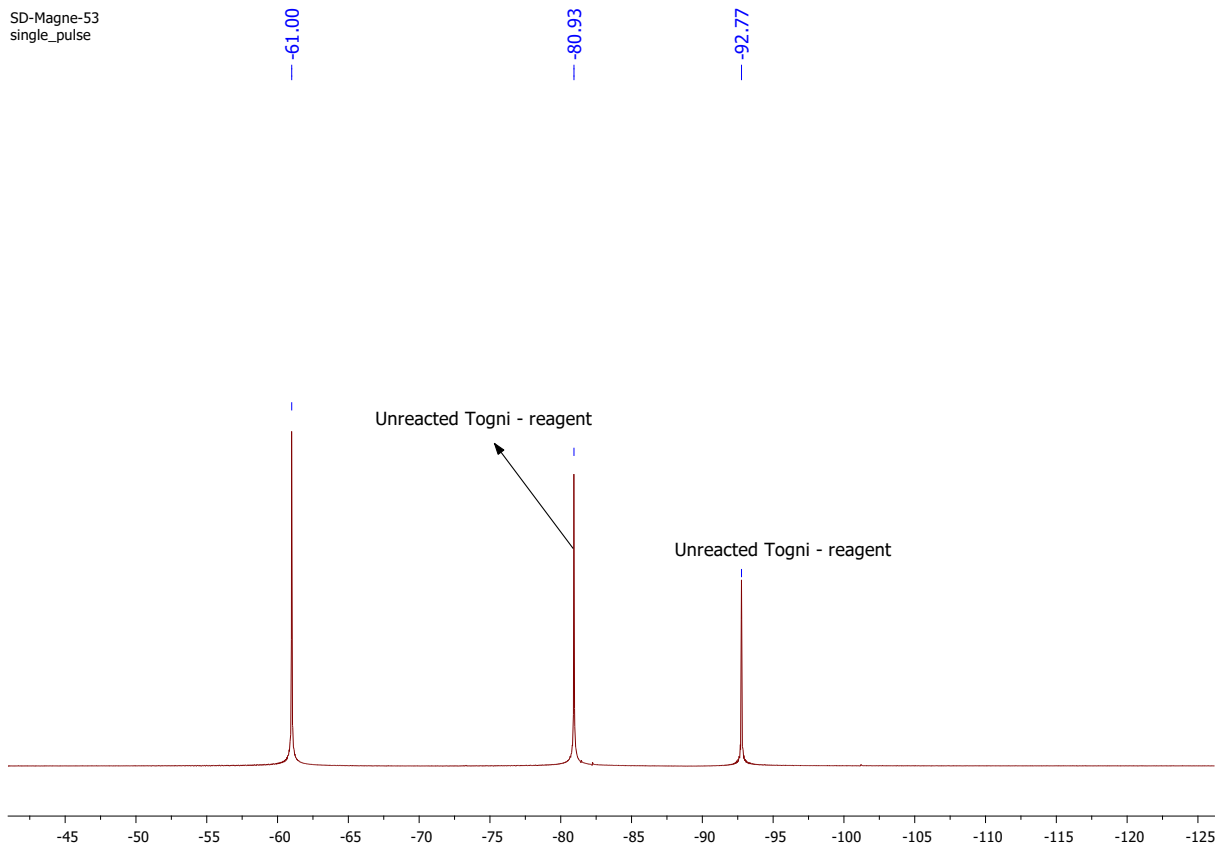
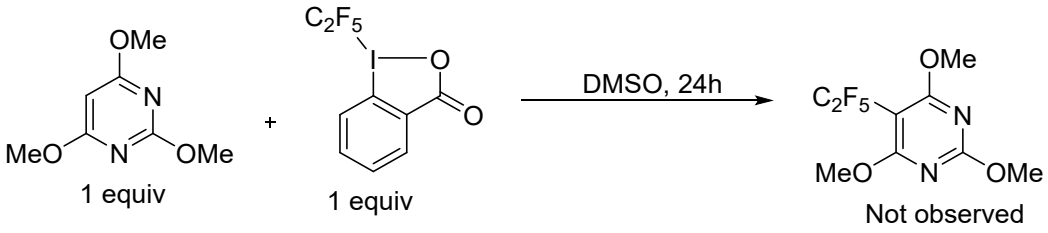


Figure S37. ^{19}F NMR spectrum in absence of catalyst.



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 2,4,6-Trimethoxypyrimidine (10.0 mg, 0.059 mmol) and 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (21.5 mg, 0.059 mmol) were dissolved in anhydrous DMSO (1 mL). Further the reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (7.2 µL, 0.059 mmol) was added as a standard. ^{19}F NMR spectroscopy showed no product formation.

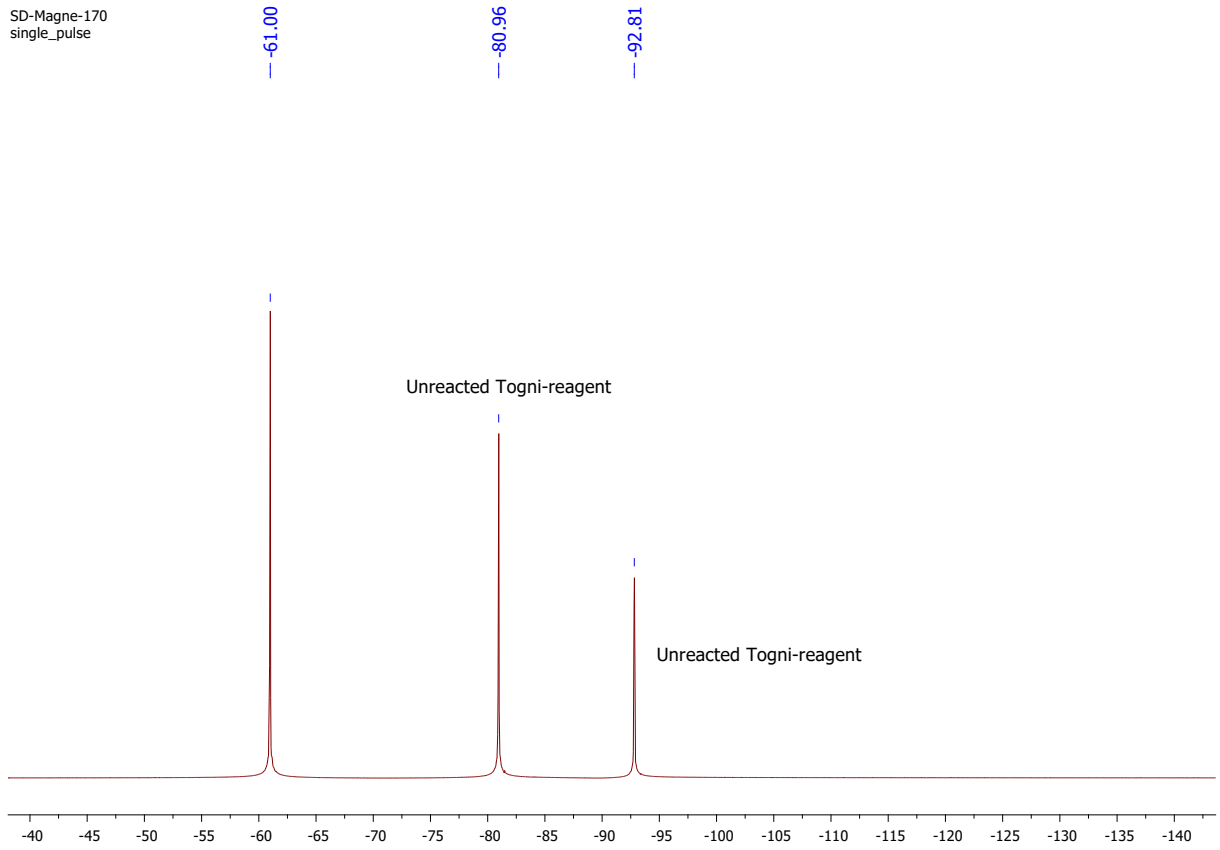
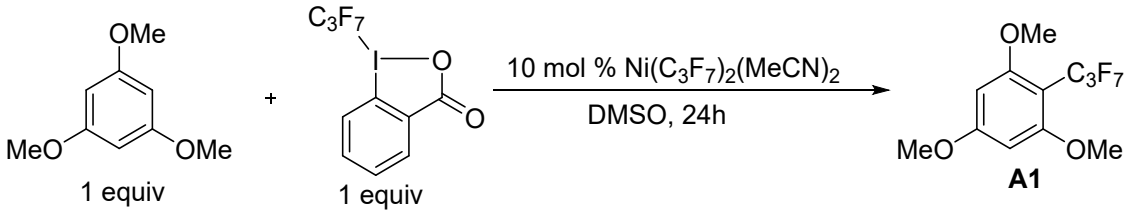


Figure S38. ^{19}F NMR spectrum in absence of catalyst.



Isolation procedure. Inside the glovebox, a 20 mL vial equipped with a stirring bar was charged with 1,3,5-Trimethoxybenzene (50.0 mg, 0.297 mmol), 1-heptafluoropropyl-1,2-benziodoxol-3(1H)-one (123.6 mg, 0.297 mmol) and $Ni(C_3F_7)_2(MeCN)_2$ (14.2 mg, 0.030 mmol), which were dissolved in anhydrous DMSO (2.5 mL). The reaction mixture was vigorously stirred for 24 hours. After completion of the reaction, the yellow color reaction mixture was transferred to a separatory funnel outside the glovebox and mixed with ethyl acetate (25 mL) and saturated aqueous NaCl (10 mL). After the first extraction, the organic layer was separated, and the remaining water layer was again extracted with ethyl acetate (20 mL). The organic layers were combined and dried over magnesium sulfate and then concentrated under vacuum. The reaction crude material was then purified by flash column chromatography on silica gel (mobile phase: hexane/ethyl acetate (95:5) as colorless solid (73.8 mg, 74% yield).

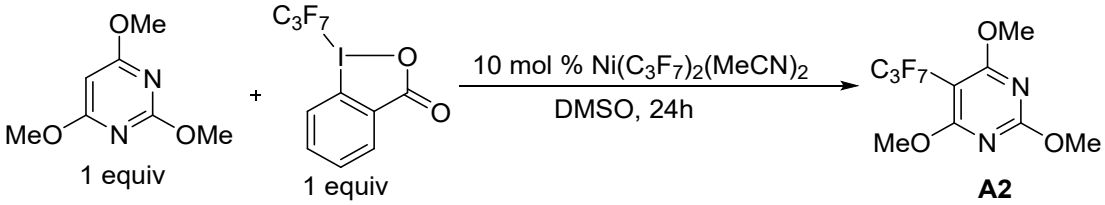
^1H NMR (400 MHz, $CDCl_3$, 23 °C): δ 6.14 (s, 2H), 3.84 (s, 3H), 3.80 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$, 23 °C): δ 164, 161.82(t, J = 2.1 Hz), 123.15 – 106.51 (m, fluorine splitting overlap), 98.48 (t, J = 21.9 Hz), 93.06, 91.82, 56.40, 55.45.

^{19}F NMR (376 MHz, $CDCl_3$, 23 °C): δ -80.54 (3F), -103.43 (2F), -126.78 (2F).

HRMS (ESI) calculated for $[M^*H]^+$, $C_{12}H_{11}F_7O_3$: m/z 337.0669; found, 337.0650.

The above analytical data is agreed with previously published data.[2]



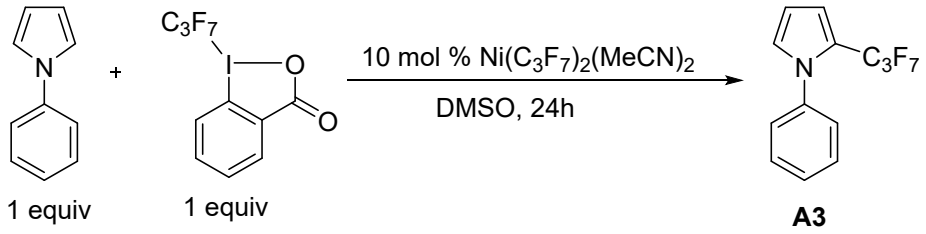
Isolation procedure. Inside the glovebox, a 20 mL vial equipped with a stirring bar was charged with 2,4,6-Trimethoxypyrimidine (50.0 mg, 0.294 mmol), 1-heptafluoropropyl-1,2-benziodoxol-3(1H)-one (122.2 mg, 0.294 mmol) and $Ni(C_3F_7)_2(MeCN)_2$ (14.0 mg, 0.029 mmol), which were dissolved in anhydrous DMSO (2.5 mL). The reaction mixture was vigorously stirred for 24 hours. After completion of the reaction, the yellow color reaction mixture was transferred to a separatory funnel outside the glovebox and mixed with ethyl acetate (20 mL) and saturated aqueous NaCl (10 mL). After the first extraction, the organic layer was separated, and the remaining water layer was again extracted with ethyl acetate (20 mL). The organic layers were combined and dried over magnesium sulfate and then concentrated under vacuum. The yellow color crude material was then purified by flash column chromatography on silica gel (mobile phase: hexane/ethyl acetate 97:3) to give **A2** as a colorless solid (56.3 mg, 56% yield).

^{1}H NMR (600 MHz, $CDCl_3$, 23 °C): δ 4.01 (s, 3H), 3.98 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$, 23 °C): δ 170.91, 165.43, 121.32-113.44 (m, fluorine splitting overlap), 109.52 (qt, J = 286.2, 41.9 Hz), 87.07 (t, J = 25.6 Hz), 55.27, 55.

^{19}F NMR (565 MHz, $CDCl_3$, 23 °C): δ -80.53 (3F), -106.49 (2F), -127.13 (2F).

HRMS (ESI) calculated for $[M^*H]^+$, $C_{10}H_9F_7O_3N_2$: m/z 339.0574; found, 339.0555.



Isolation procedure. Inside the glovebox, a 20 mL vial equipped with a stirring bar was charged with N-phenylpyrrole (50.0 mg, 0.349 mmol), 1-heptafluoropropyl-1,2-benziodoxol-3(1H)-one (145.2 mg, 0.349 mmol) and $Ni(C_3F_7)_2(MeCN)_2$ (16.7 mg, 0.035 mmol), which were dissolved in anhydrous DMSO (2.5 mL). The reaction mixture was vigorously stirred for 24 hours. After completion of the reaction, the yellow color reaction mixture was transferred to a separatory funnel outside the glovebox and mixed with ethyl acetate (30 mL) and saturated aqueous NaCl

(10 mL). After the first extraction, the organic layer was separated, and the remaining water layer was again extracted with ethyl acetate (20 mL). The organic layers were combined and dried over magnesium sulfate and then concentrated under vacuum. The yellow color crude material was then purified by HPLC to give **A3** as a yellow color oil (69.4 mg, 64% yield). The description of HPLC method: (A) MilliQ water and (B) Acetonitrile-Milli-Q water (90:10), both contained 0.1% formic acid. Gradient: 35% B for 0.0-1.0 min, 35-80% B for 1.0-6.0 min, hold 80% B for 6.0-9.0 min, equilibrate 80% B for 9.1-12.0 min

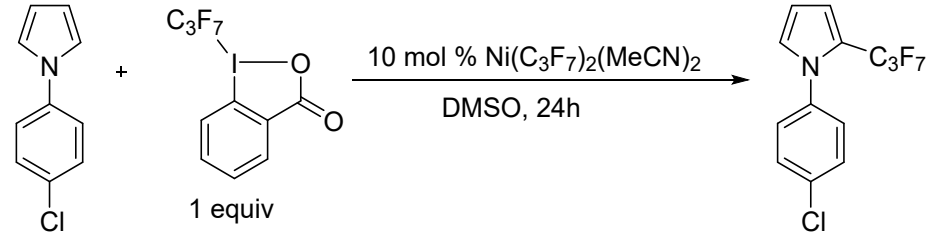
^{1}H NMR (500 MHz, $CDCl_3$, 23 °C): δ 7.34-7.29 (m, 3H), 7.27-7.23 (m, 2H), 6.78 (s, 1H), 6.65 (br.s, 1H), 6.23 (t, J = 2.6 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$, 23 °C): δ 139.80, 129.15, 128.78, 128.76, 127.51, 121.80-115.40 (m), 115.09 (m), 114.66-108.96, 108.83, 108.66-105.94 (m),

^{19}F NMR (565 MHz, $CDCl_3$, 23 °C): δ -80.19 (3F), -101.36 (2F), -124.81 (2F).

HRMS (ESI) calculated for $[M^*H]^+$, $C_{13}H_9F_7N_1$: m/z 312.0618; found, 312.0597.

The above analytical data is agreed with previously published data.[6]



1 equiv 1 equiv **A4**

NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 1-(4-Chlorophenyl)-1H-pyrrole (10.0 mg, 0.056 mmol), 1-heptafluoropropyl-1,2-benziodoxol-3(1H)-one (23.4 mg, 0.056 mmol) and $Ni(C_3F_7)_2(MeCN)_2$ (2.6 mg, 0.006 mmol), which were dissolved in anhydrous DMSO (1 mL). The reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (6.9 μL, 0.056 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy.

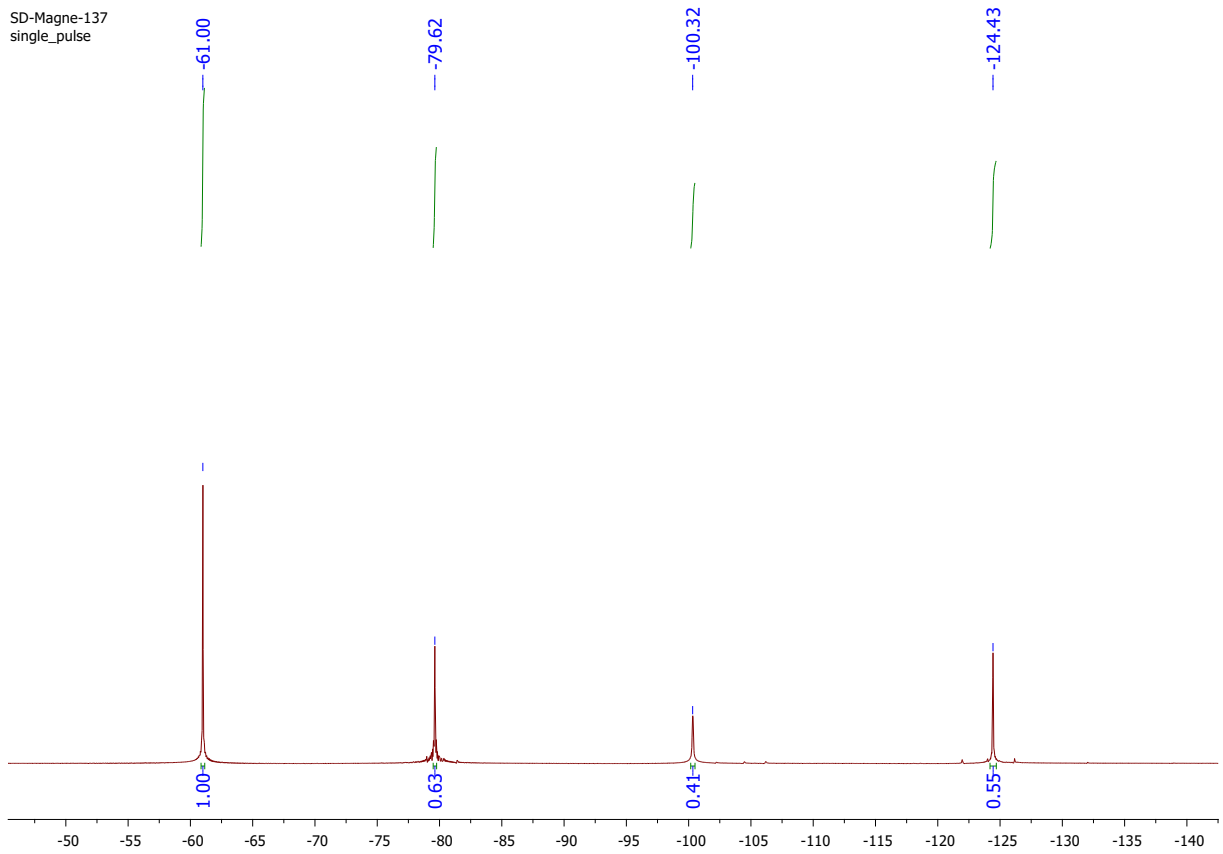
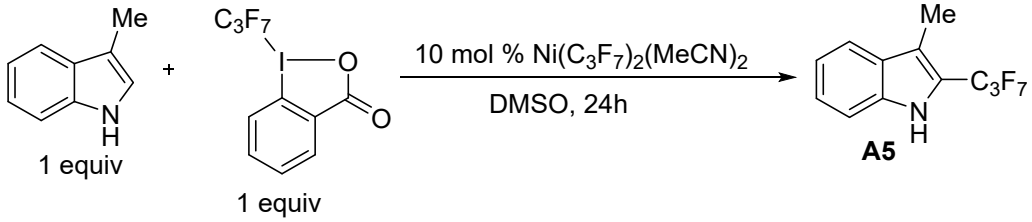


Figure S39. ^{19}F NMR spectrum showing formation of compound **A4**.



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 3-Methylindole (10.0 mg, 0.076 mmol), 1-heptafluoropropyl-1,2-benziodoxol-3(1H)-one (31.7 mg, 0.076 mmol) and $Ni(C_3F_7)_2(MeCN)_2$ (3.6 mg, 0.008 mmol), which were dissolved in anhydrous DMSO (1 mL). The reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (9.3 µL, 0.0762 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy.

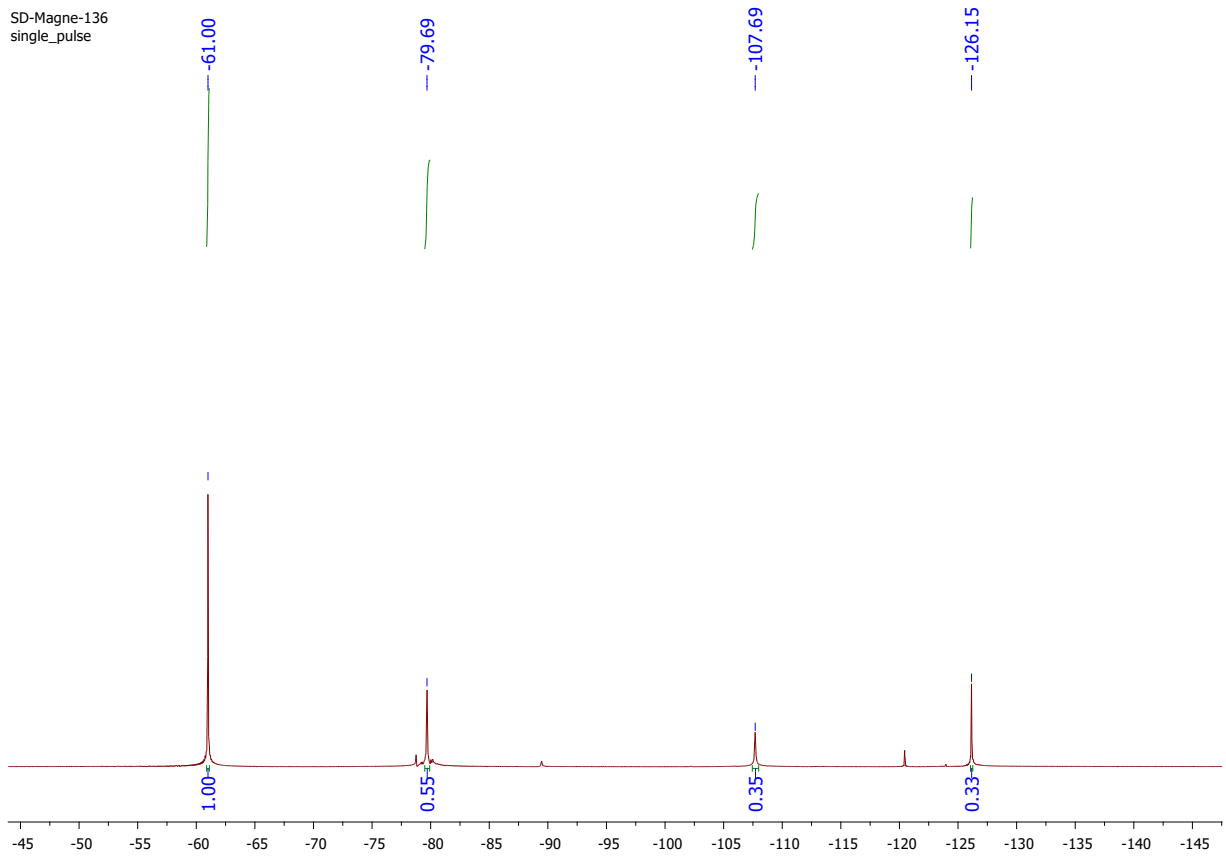
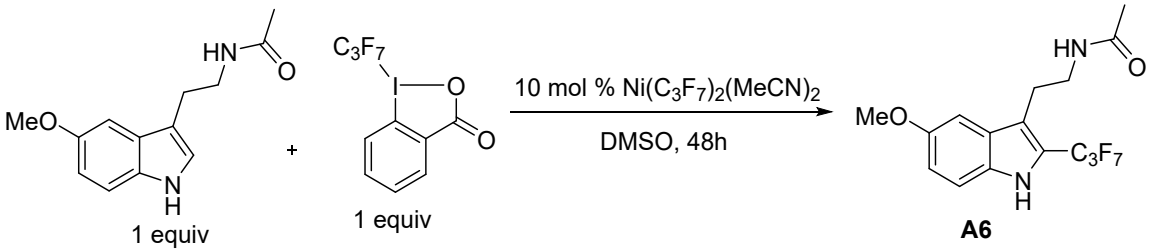


Figure S40. ^{19}F NMR spectrum showing formation of compound **A5**.



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with Melatonin (10.0 mg, 0.043 mmol), 1-heptafluoropropyl-1,2-benziodoxol-3(1H)-one (17.9 mg, 0.043 mmol) and $Ni(C_3F_7)_2(MeCN)_2$ (2.0 mg, 0.004 mmol) were dissolved in anhydrous DMSO (1 mL). Further the reaction mixture was stirred at room temperature for 48 hours. After the completion of reaction, α,α,α-trifluorotoluene (5.2 µL, 0.043 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy.

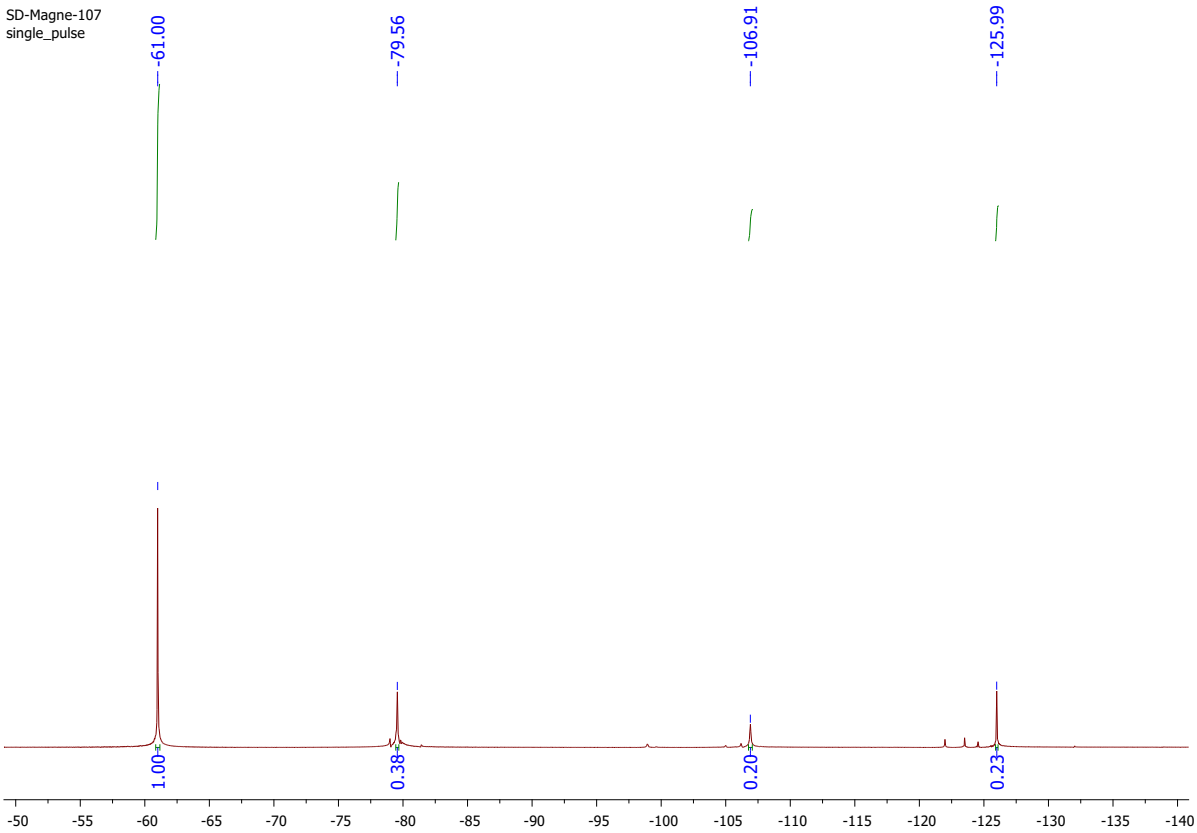
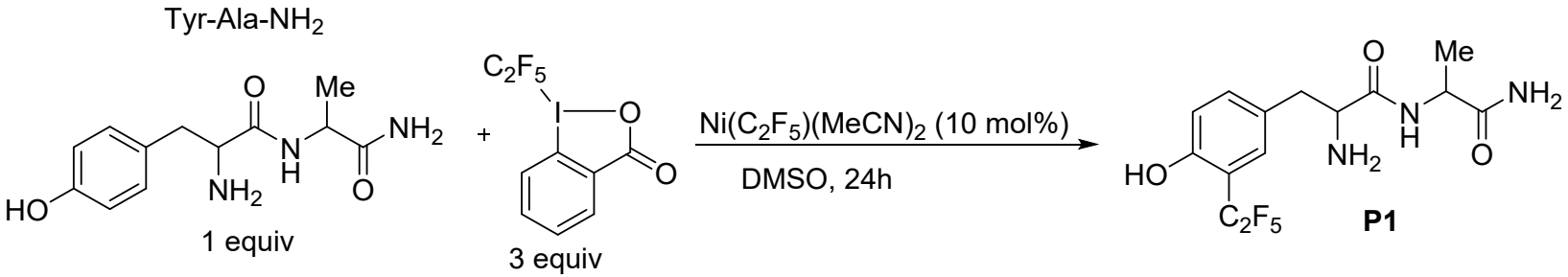


Figure S41. ^{19}F NMR spectrum showing formation of compound **A6**

V. Modification of Peptides

Synthesis of peptides were performed under the analogue condition reported by Saze and coworkers in Chapter 6, Plant Epigenetics and Epigenomics – https://link.springer.com/book/10.1007/978-1-0716-0179-2.



Reaction scale: A 5 mL vial equipped with a magnetic stirring bar was charged with peptide (Tyr-Ala-NH_2) (6.0 mg, 0.024 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (26.2 mg, 0.072 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (0.9 mg, 0.002 mmol) were dissolved in anhydrous DMSO (1 mL). Further the reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, the reaction mixture was analyzed by LC-MS.

Note: the nickel precursor was added to the reaction mixture by preparing a stock solution in DMSO.

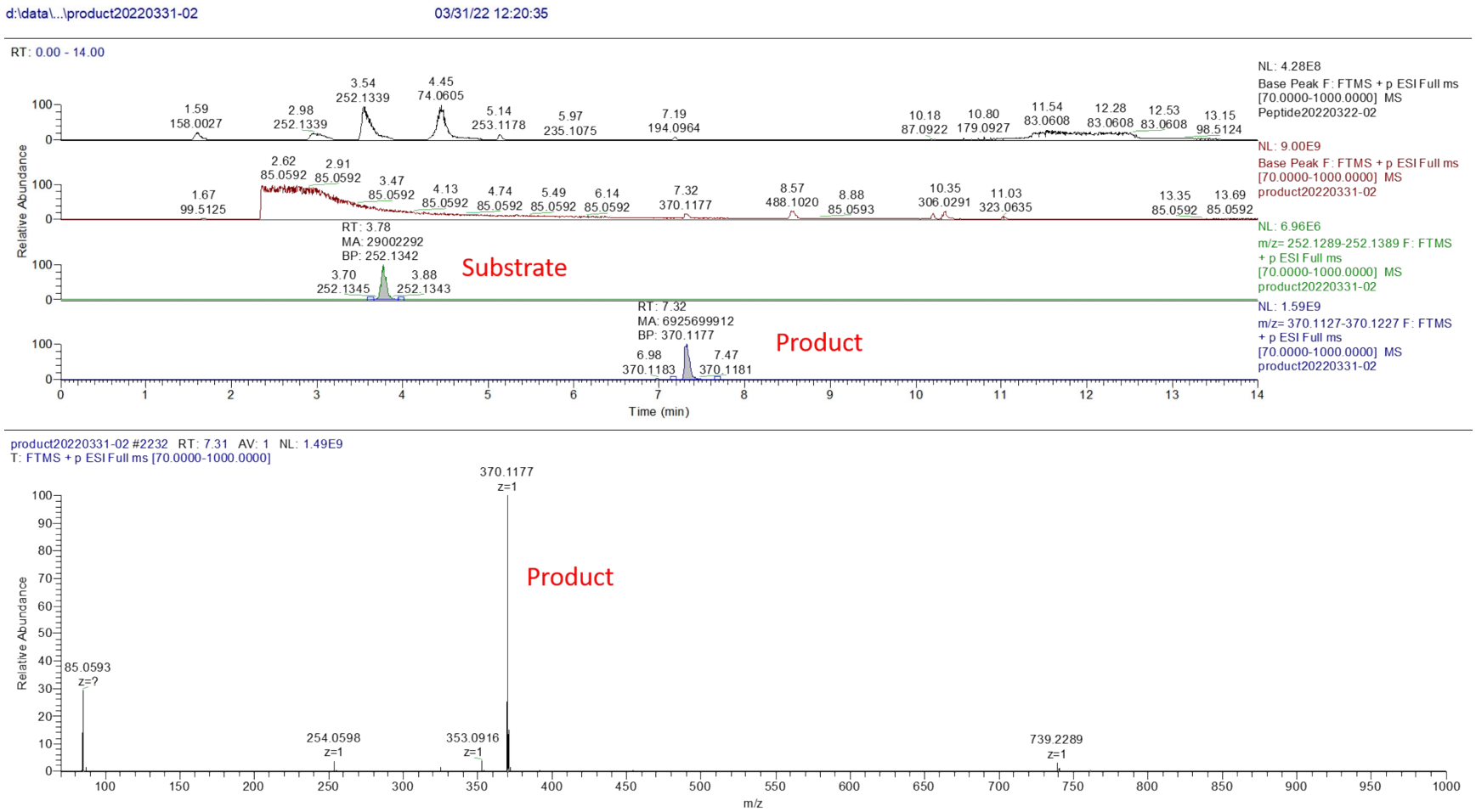


Figure S42. LC-MS spectrum showing the product formation **P1**(area under curve = 6925699912), with retention time (7.32 min) and substrate (area under curve = 29002292), with retention time (3.78 min).

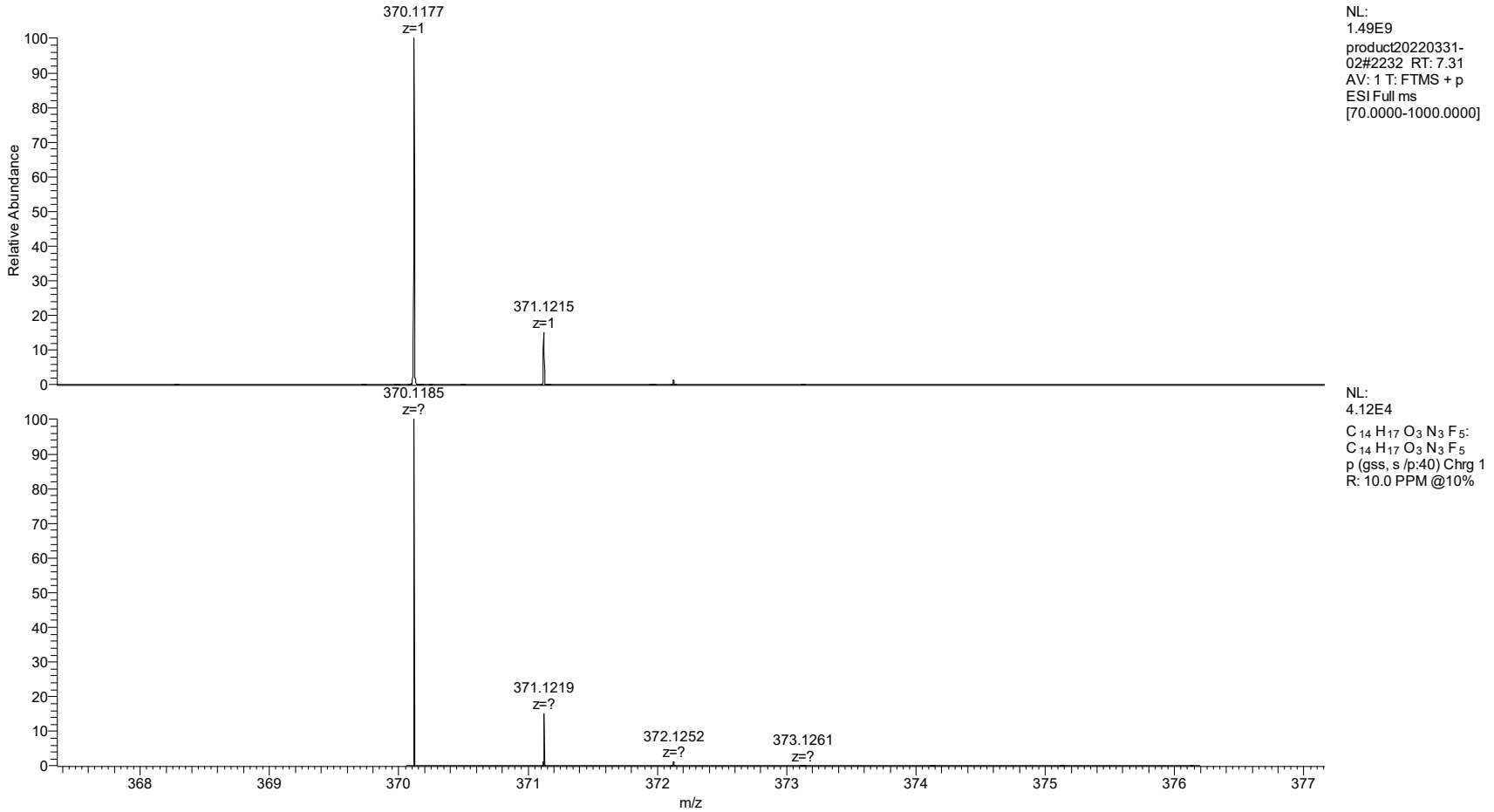
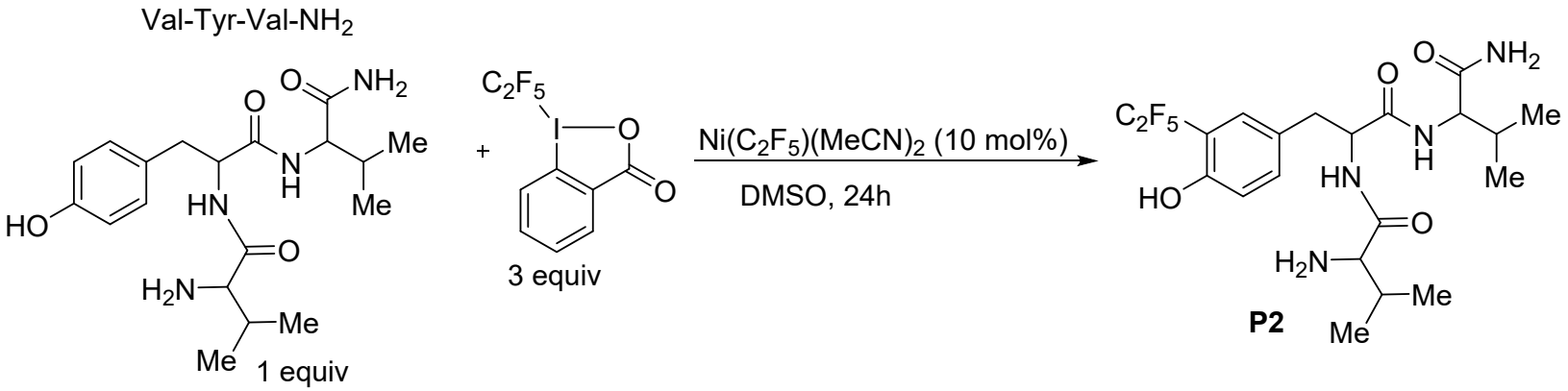


Figure S43. LC-MS spectrum of **P1**(top), with simulated spectrum (bottom).



Reaction scale: A 5 mL vial equipped with a magnetic stirring bar was charged with peptide (Val-Tyr-Val-NH_2) (6.2 mg, 0.016 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (17.9 mg, 0.049 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (0.6 mg, 0.002 mmol) were dissolved in anhydrous DMSO (1 mL). Further the reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, the reaction mixture was analyzed by LC-MS.

Note: the nickel precursor was added to the reaction mixture by preparing a stock solution in DMSO.

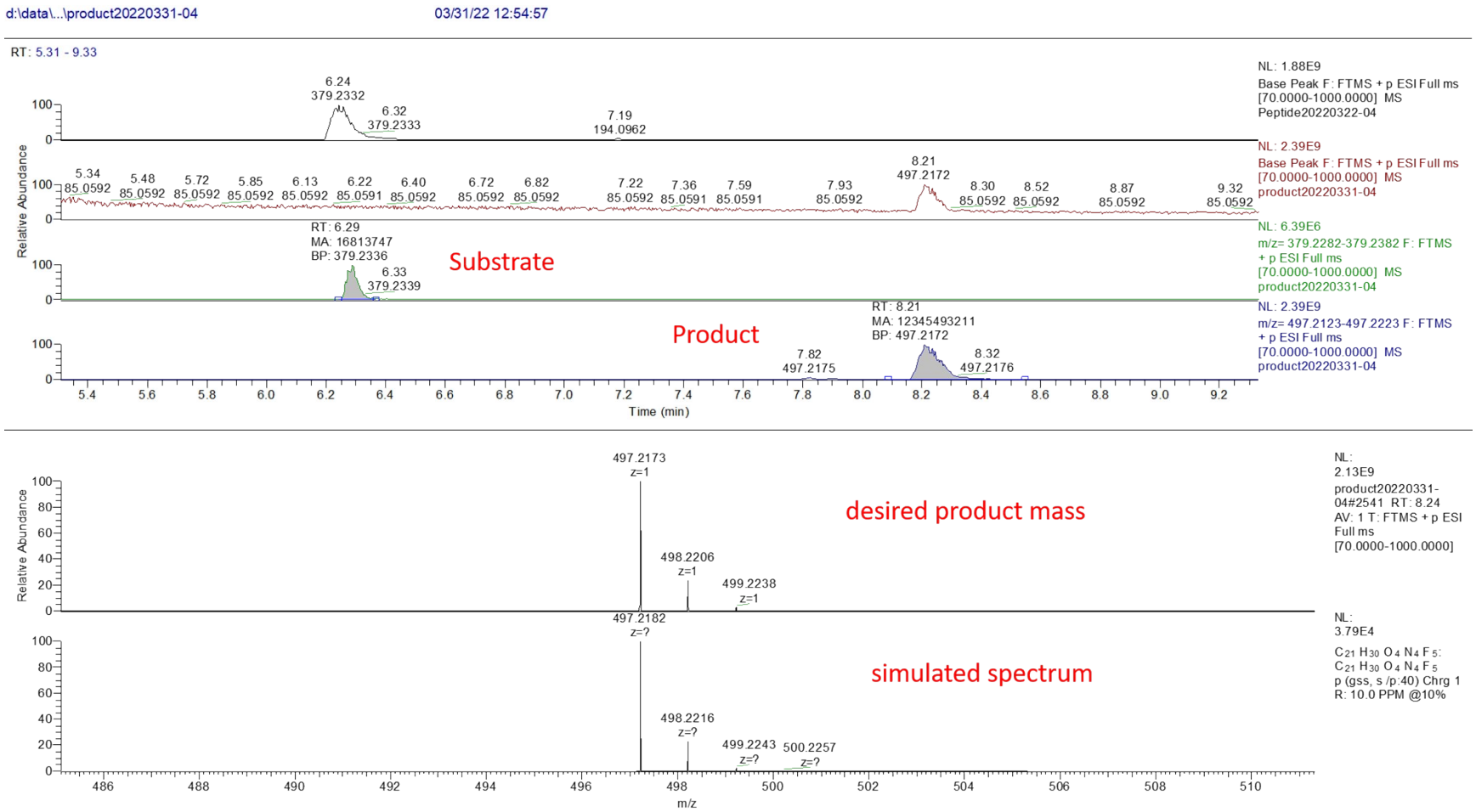
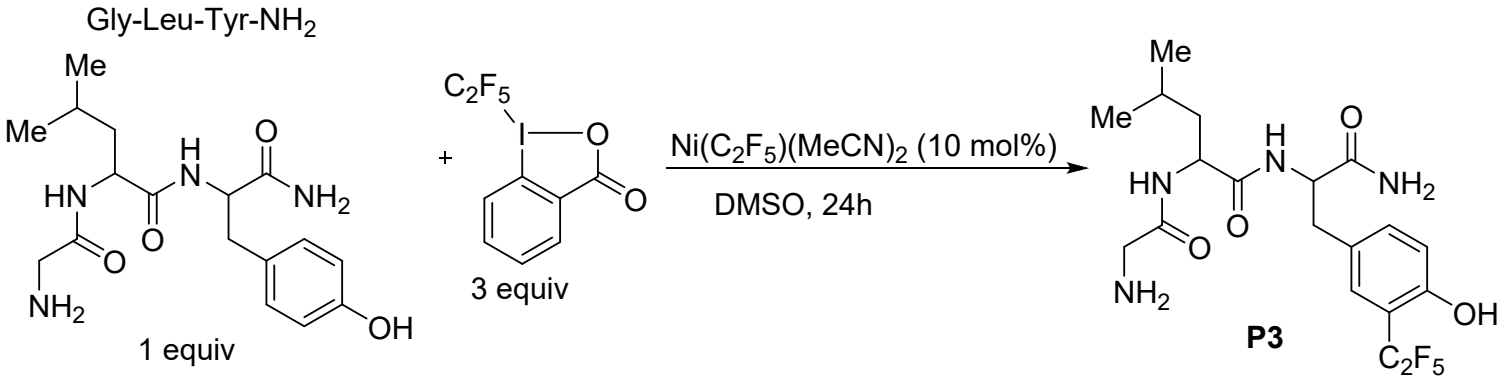


Figure S44. LC-MS spectrum showing the product formation **P2**(area under curve = 12345493211), with retention time (8.21 min) and substrate (area under curve = 16813747), with retention time (6.29 min).



Reaction scale: A 5 mL vial equipped with a magnetic stirring bar was charged with peptide (GLy-Leu-Tyr-NH_2) (7.9 mg, 0.023 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (24.7 mg, 0.068 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (0.8 mg, 0.002 mmol) were dissolved in anhydrous DMSO (1 mL). Further the reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, the reaction mixture was analyzed by LC-MS.

Note: the nickel precursor was added to the reaction mixture by preparing a stock solution in DMSO.

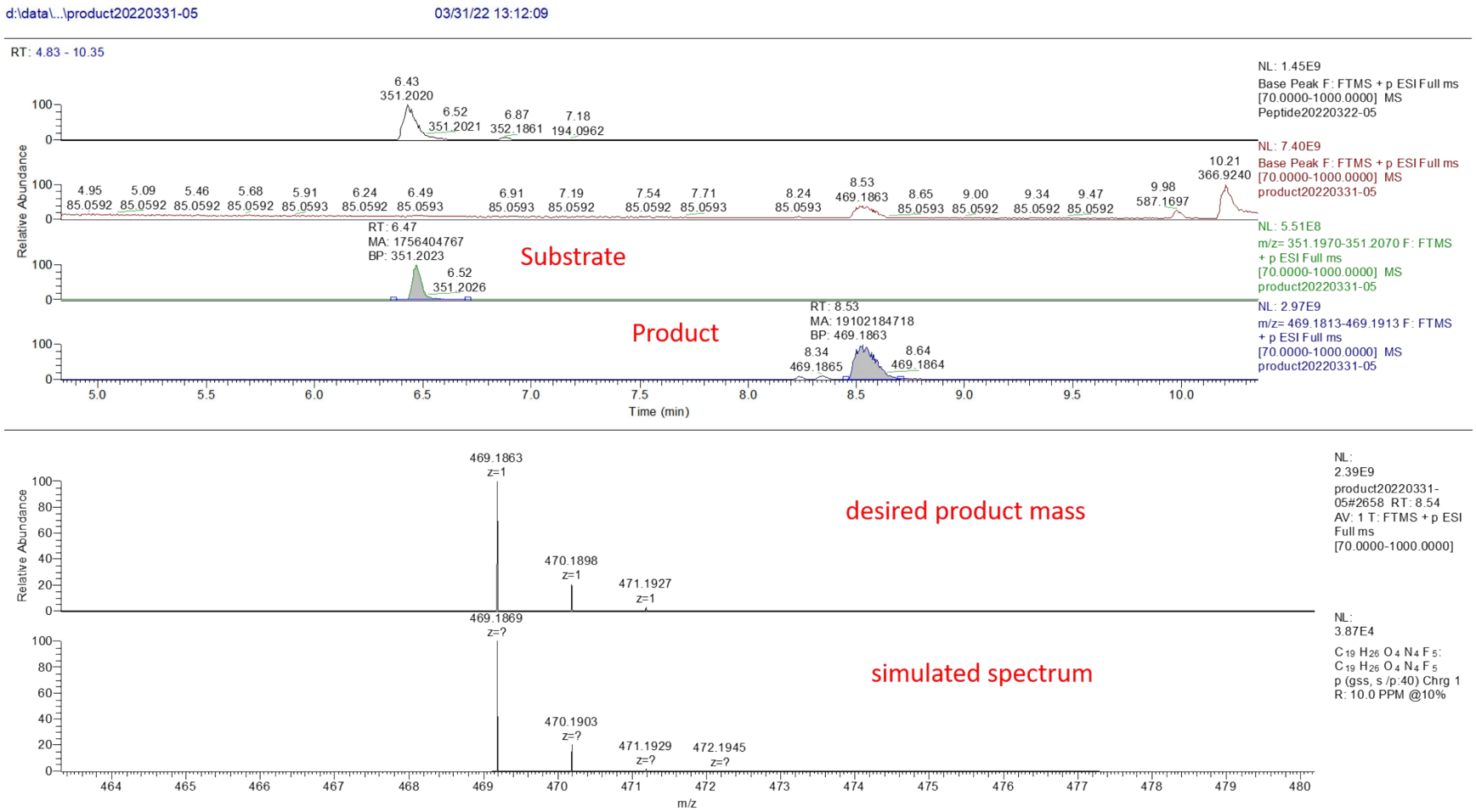
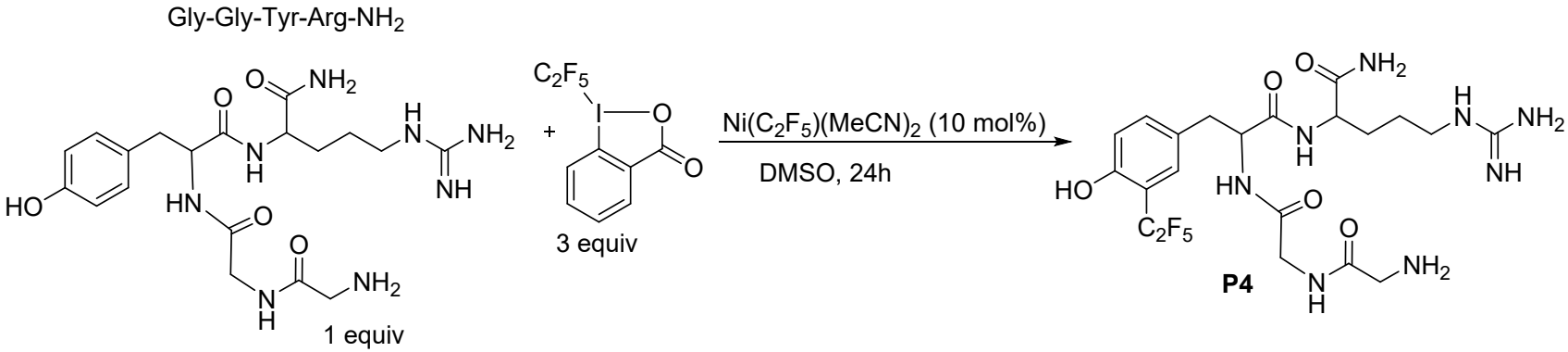


Figure S45. LC-MS spectrum showing the product formation **P3** (area under curve = 19102184718), with retention time (8.53 min) and substrate (area under curve = 1756404767), with retention time (6.47 min).



Reaction scale: A 5 mL vial equipped with a magnetic stirring bar was charged with peptide (Gly-Gly-Tyr-Arg-NH_2) (13.2 mg, 0.029 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (32.1 mg, 0.088 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (1.1 mg, 0.003 mmol) were dissolved in anhydrous DMSO (1 mL). Further the reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, the reaction mixture was analyzed by LC-MS.

Note: the nickel precursor was added to the reaction mixture by preparing a stock solution in DMSO.

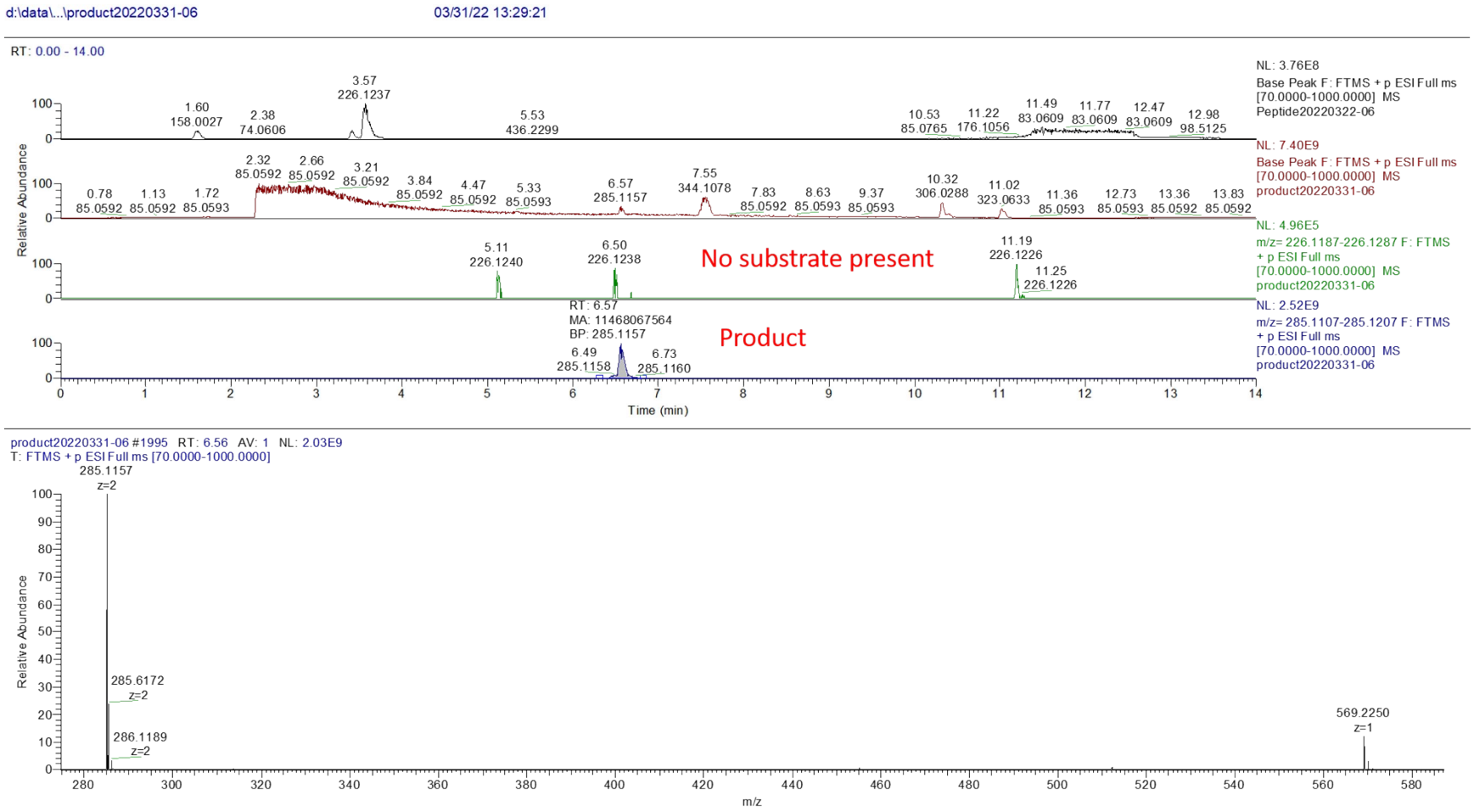


Figure S46. LC-MS spectrum showing the product formation **P4** (area under curve = 11468067564), with retention time (6.57 min) and substrate is not present.

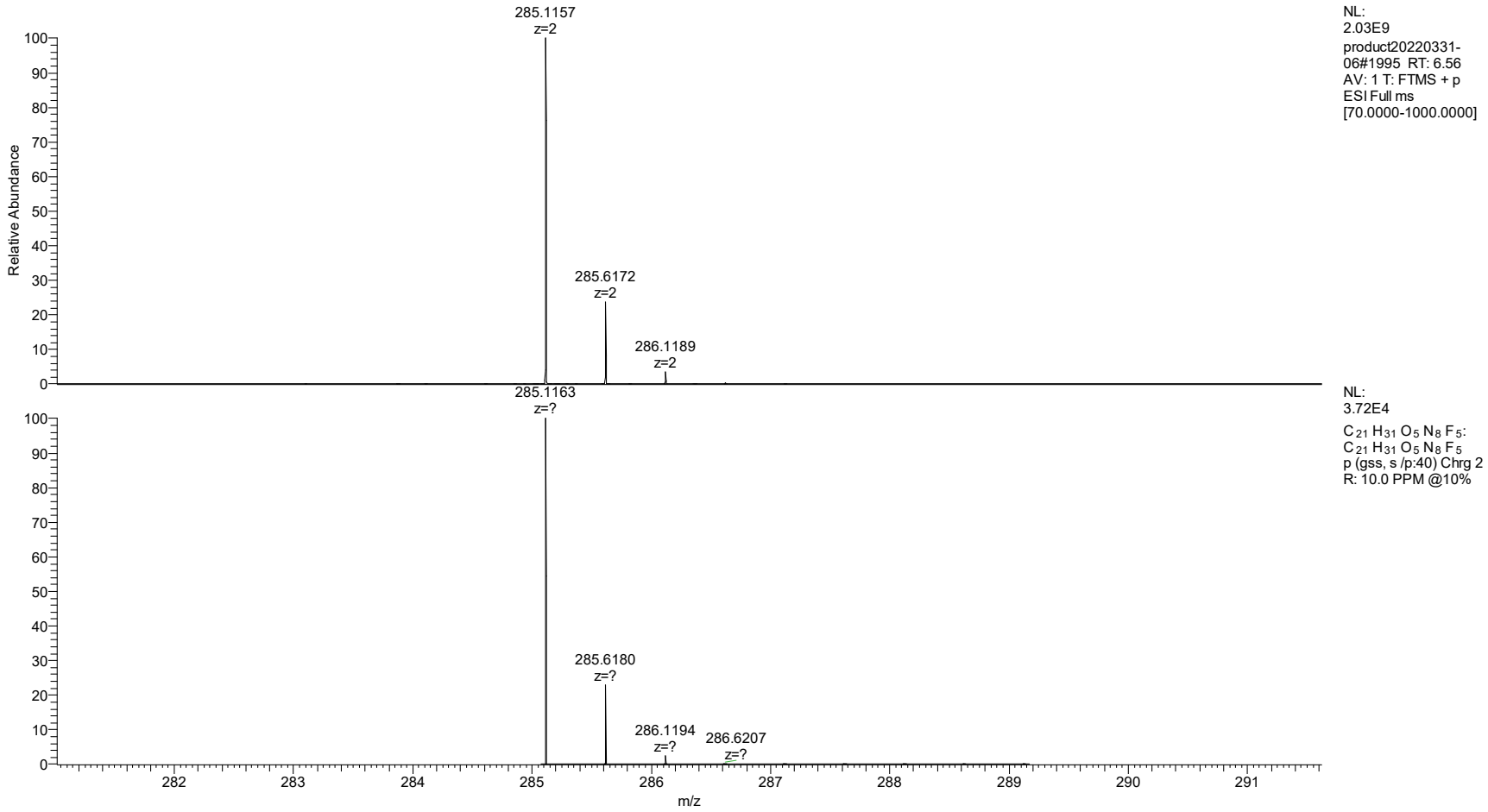


Figure S47. LC-MS spectrum of **P4**(top), with simulated spectrum (bottom). The M^{++} signal is observed.

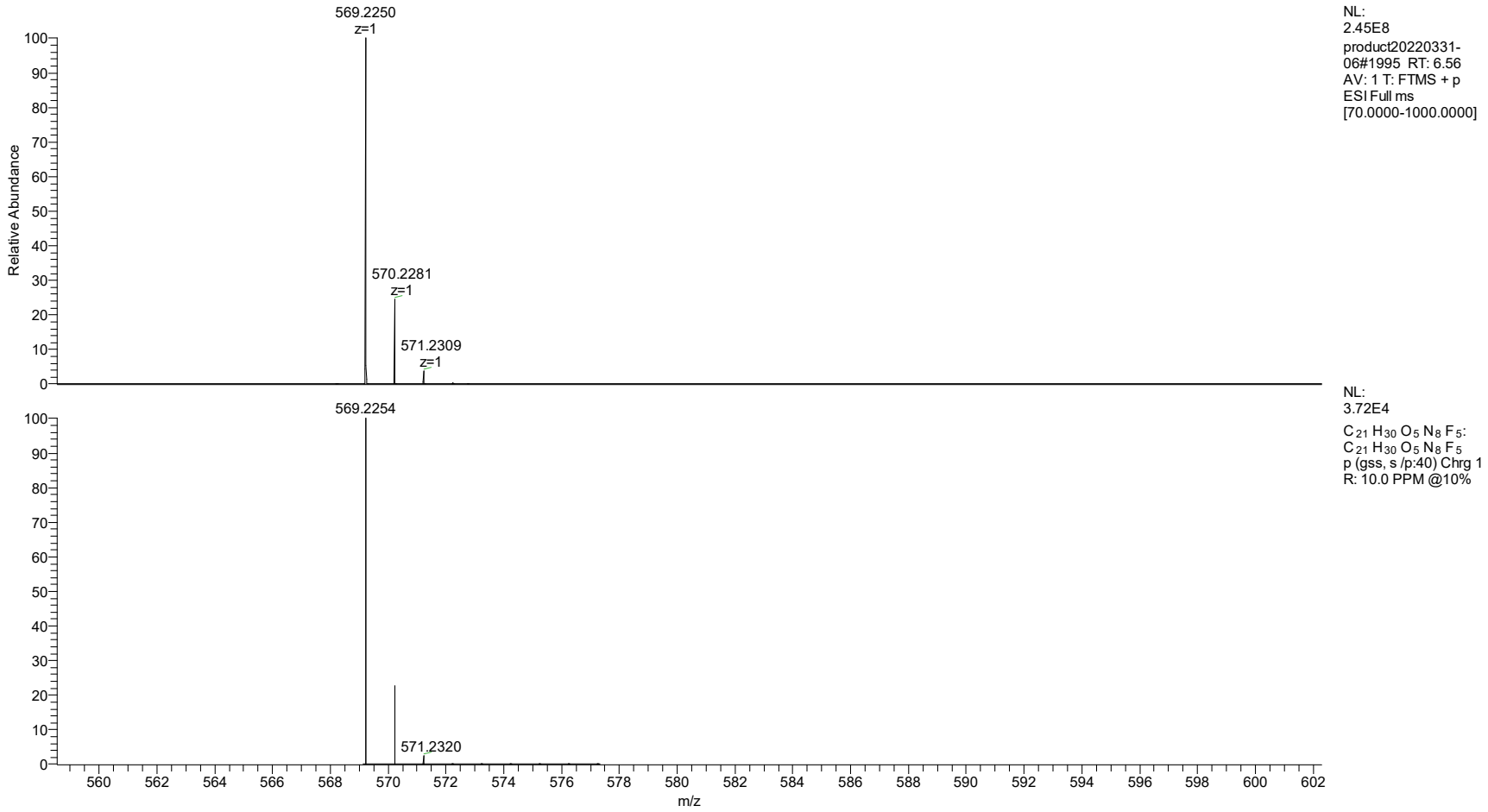
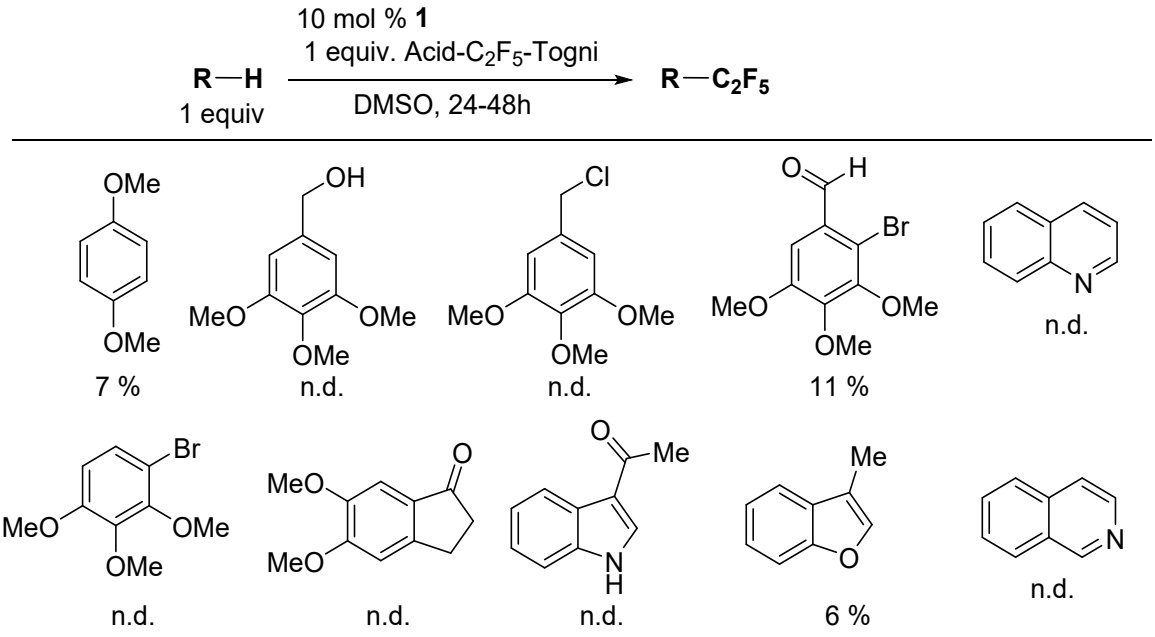


Figure S48. LC-MS spectrum of **P4**(top), with simulated spectrum (bottom).

VI. Screening of other substrates typical procedure

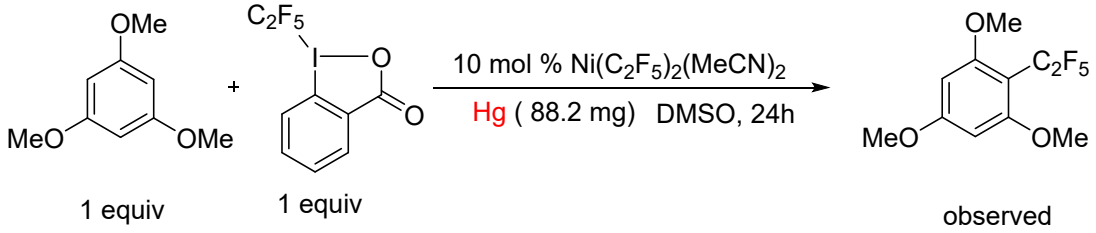
Inside the glovebox to a 20 mL glass vial equipped with a magnetic stirring bar was charged with a substrate, 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (1 equiv. relative to substrate) and **1** (10 mol%) in anhydrous DMSO (1 mL). The reaction mixture was stirred at room temperature, for 24-48 h (time depends on substrate). Then α,α,α-Trifluorotoluene was added as a standard (1 equiv) and the reaction mixtures were analyzed by ^{19}F NMR spectroscopy.



n.d. – not detected

Figure S49. Failed substrate scope for the typical procedure.

VII. Catalytic reaction in the presence of Mercury.



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 1,3,5-Trimethoxybenzene (10.0 mg, 0.059 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (21.7 mg, 0.059 mmol), mercury (88.2 mg) and $Ni(C_2F_5)_2(MeCN)_2$ (2.2 mg, 0.006 mmol), which were dissolved in anhydrous DMSO (1 mL). The reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (7.3 µL, 0.059

mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy. The presence of mercury did not affect the yield.

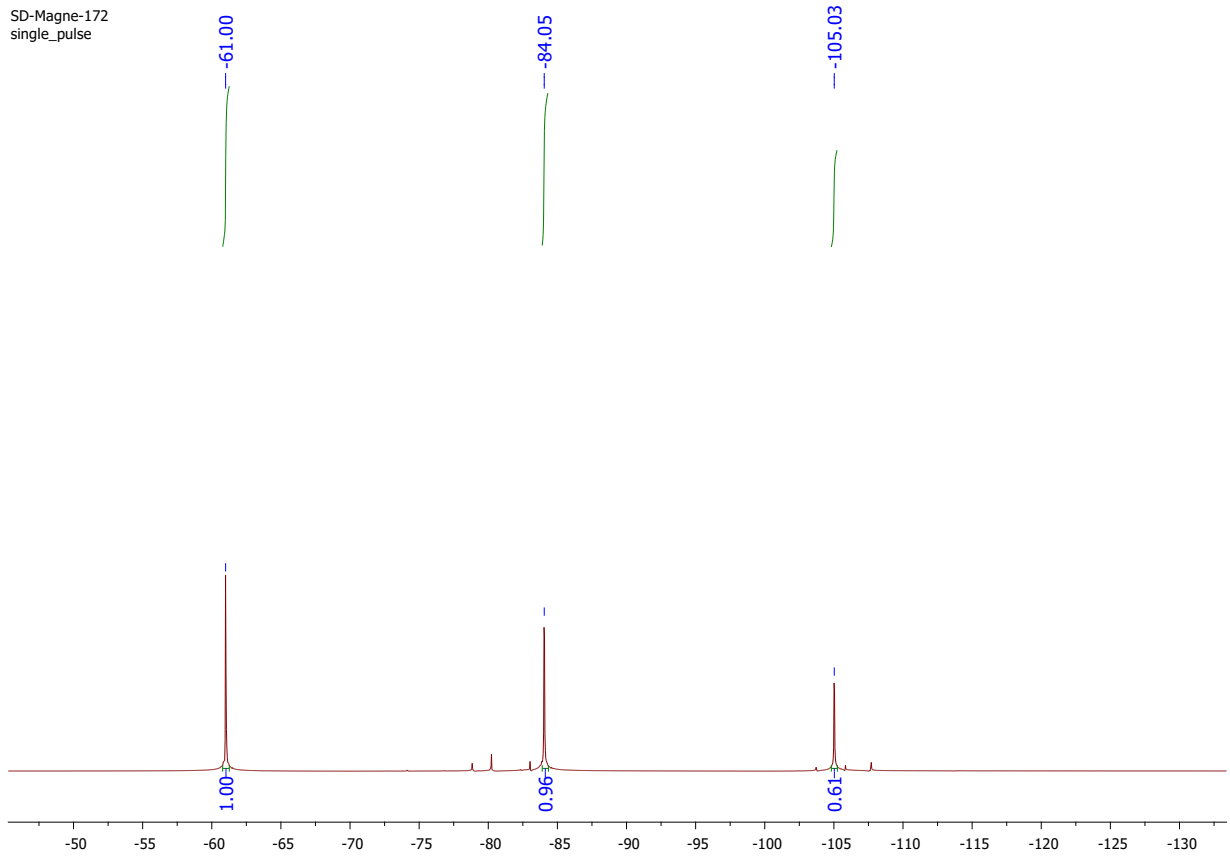
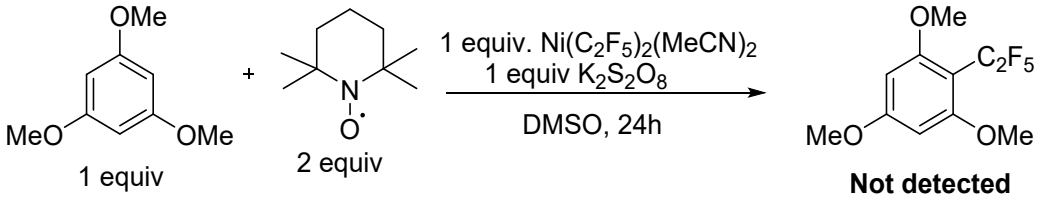


Figure S50. ^{19}F NMR spectrum showing formation of product in 96% yield.

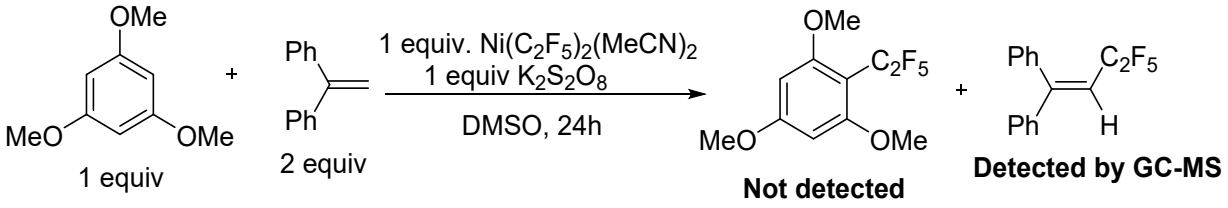
VIII. Radical trap experiments

Stoichiometric reaction of 1 in the presence of substrate, oxidant and TEMPO



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 1,3,5-Trimethoxybenzene (10.0 mg, 0.059 mmol), potassium persulfate (16.0 mg, 0.059 mmol), TEMPO (18.5 mg, 0.119 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (22.5 mg, 0.059 mmol) were dissolved in anhydrous DMSO (1 mL). Further the reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (7.3 µL, 0.059 mmol) was added as a standard. ^{19}F NMR spectroscopy showed no product formation.

Stoichiometric reaction of 1 in presence of substrate, oxidant and DPE



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 1,3,5-Trimethoxybenzene (10.0 mg, 0.059 mmol), potassium persulfate (16.0 mg, 0.059 mmol), 1,1-Diphenylethylene (20.8 µL, 0.119 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (22.5 mg, 0.059 mmol) were dissolved in anhydrous DMSO (1 mL). Further the reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (7.3 µL, 0.059 mmol) was added as a standard. ^{19}F NMR spectroscopy showed no product formation.

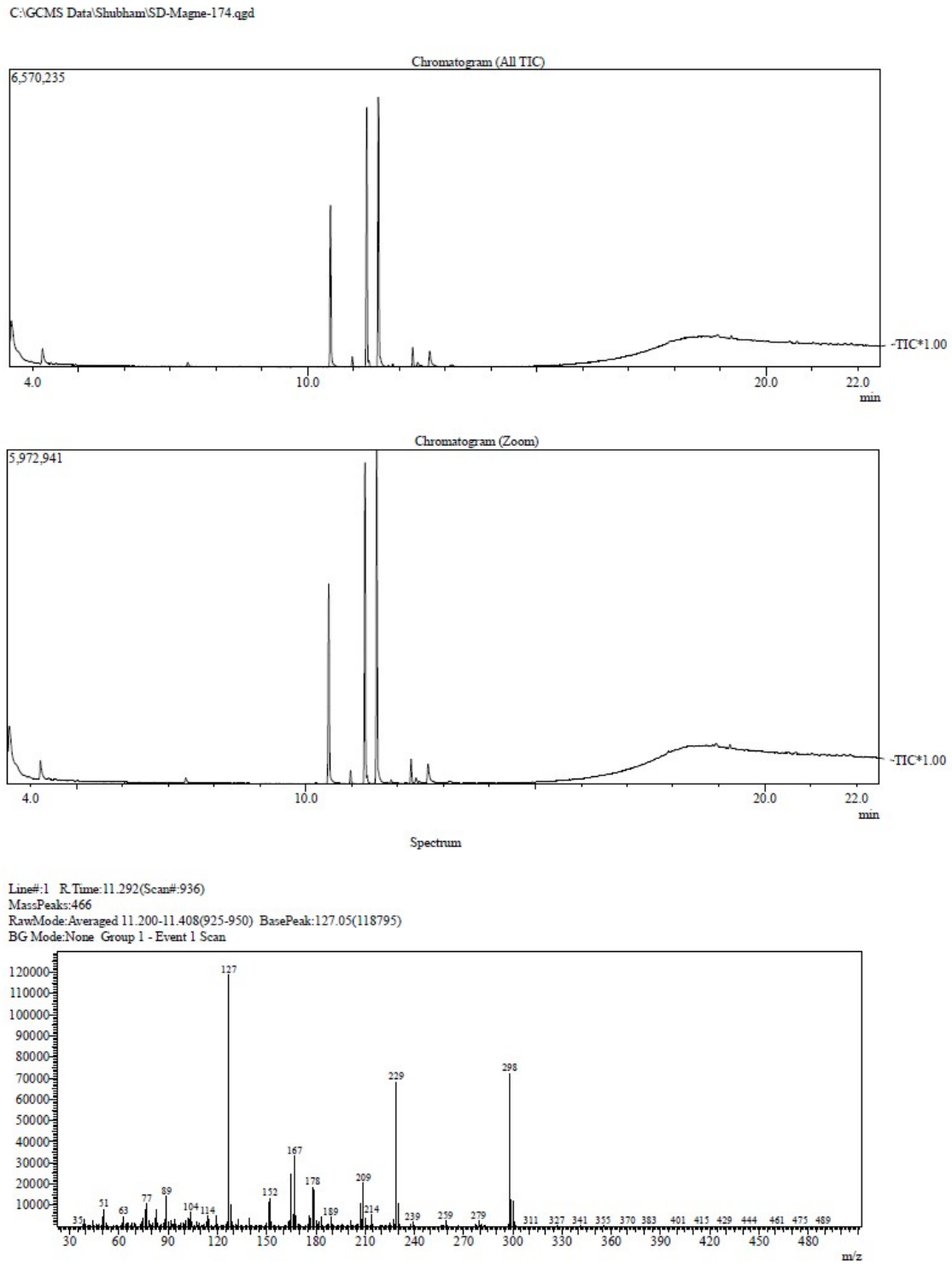
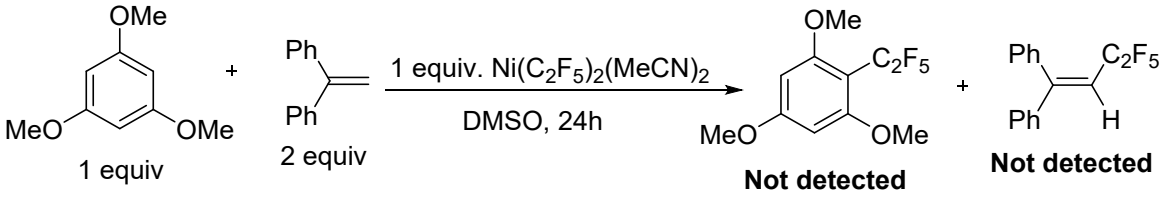


Figure S51. GC-MS data for products measured by GC-FID showing formation of compound **DPE-C_2F_5** adduct.

Stoichiometric reaction of 1 in presence of substrate, DPE and in the absence of oxidant



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 1,3,5-Trimethoxybenzene (10.0 mg, 0.059 mmol), potassium persulfate (16.0 mg, 0.059 mmol), 1,1-Diphenylethylene (20.8 µL, 0.119 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (22.5 mg, 0.059 mmol), which were dissolved in anhydrous DMSO (1 mL). The reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (7.3 µL, 0.059 mmol) was added as a standard. ^{19}F NMR spectroscopy showed no product formation.

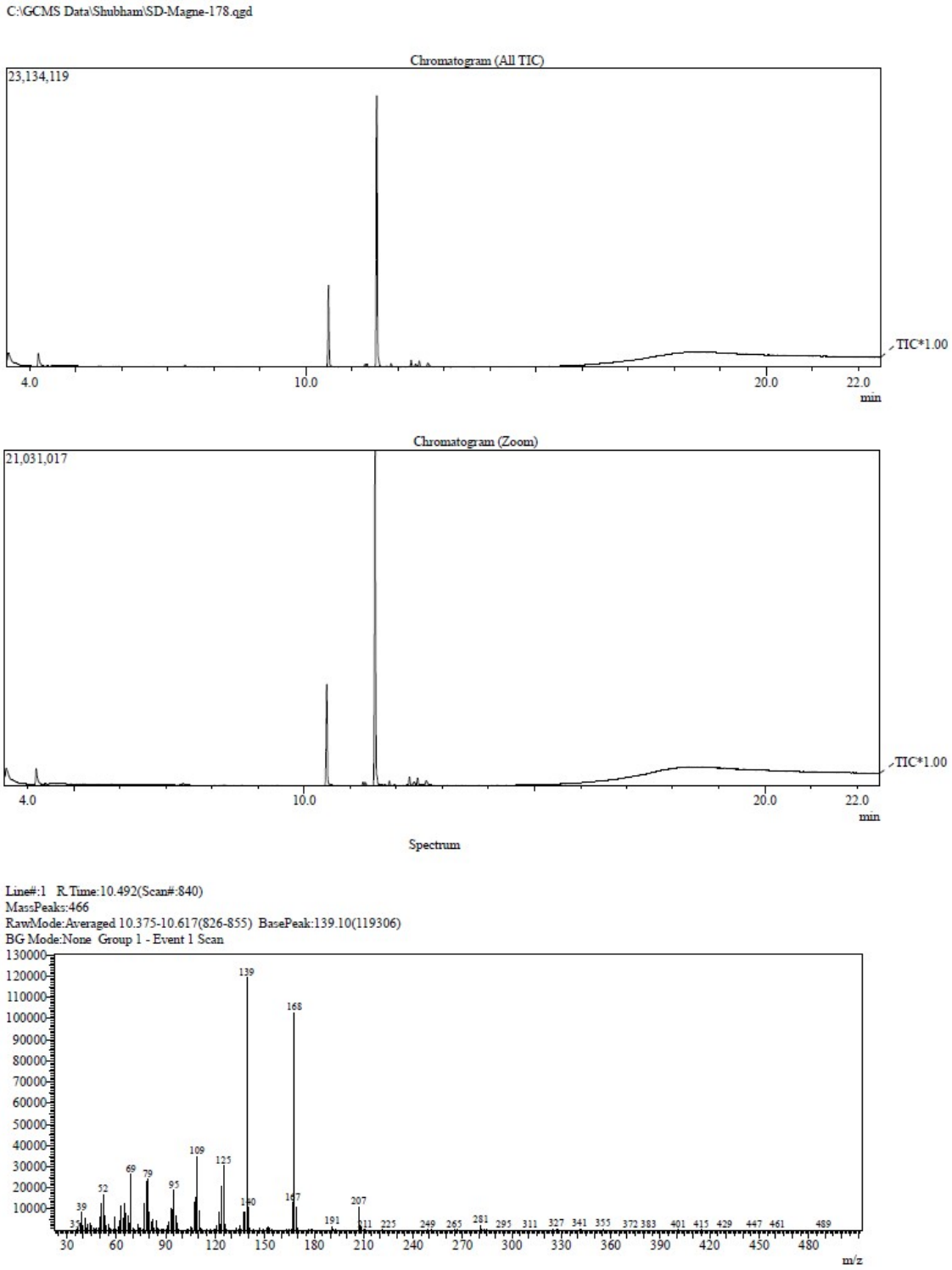
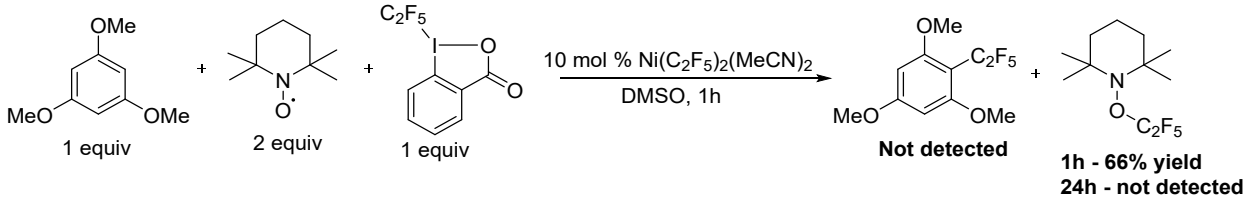


Figure S52. GC-MS data for products measured by GC-FID showing no formation of compound **DPE-C_2F_5** adduct.

Reaction in the presence of substrate, Togni reagent, catalytic 1 and TEMPO.



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 1,3,5-Trimethoxybenzene (10.0 mg, 0.059 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (21.7 mg, 0.059 mmol), TEMPO (18.5 mg, 0.119 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (2.2 mg, 0.006 mmol), which were dissolved in anhydrous DMSO (1 mL). The reaction mixture was stirred at room temperature for 1 hour. After the completion of reaction, α,α,α-trifluorotoluene (7.3 µL, 0.0594 mmol) was added as a standard. ^{19}F NMR spectroscopy showed the TEMPO-C_2F_5 adduct formed in 66% yield. The TEMPO-C_2F_5 adduct is unstable and could not be detected after 24 hours; there were no other products observed.

HRMS (ESI) calculated for $[M^*H]^+$, $C_{11}H_{19}F_5N_1O_1$: m/z 276.1381; found, 276.1380.

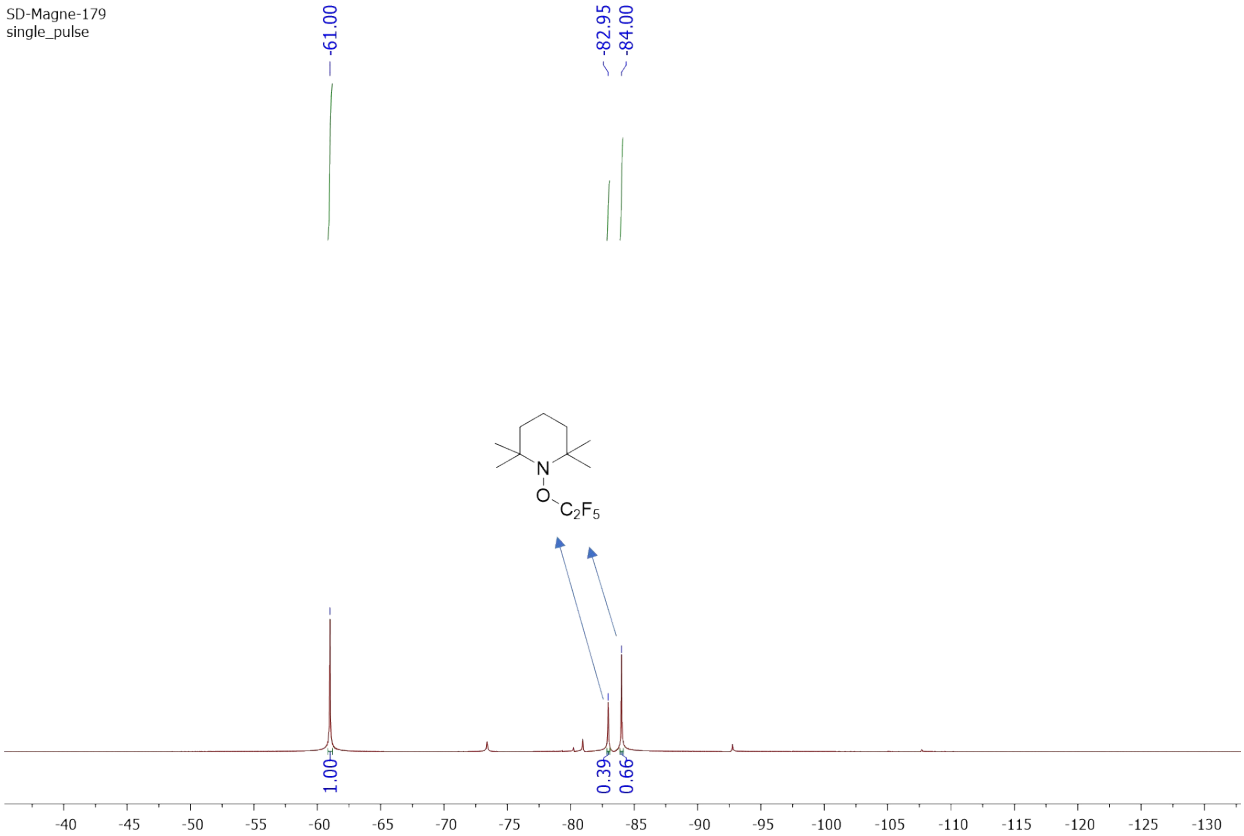


Figure S53. ^{19}F NMR spectrum of the reaction mixture containing **1**, substrate, TEMPO and Togni reagent after 1 hour.

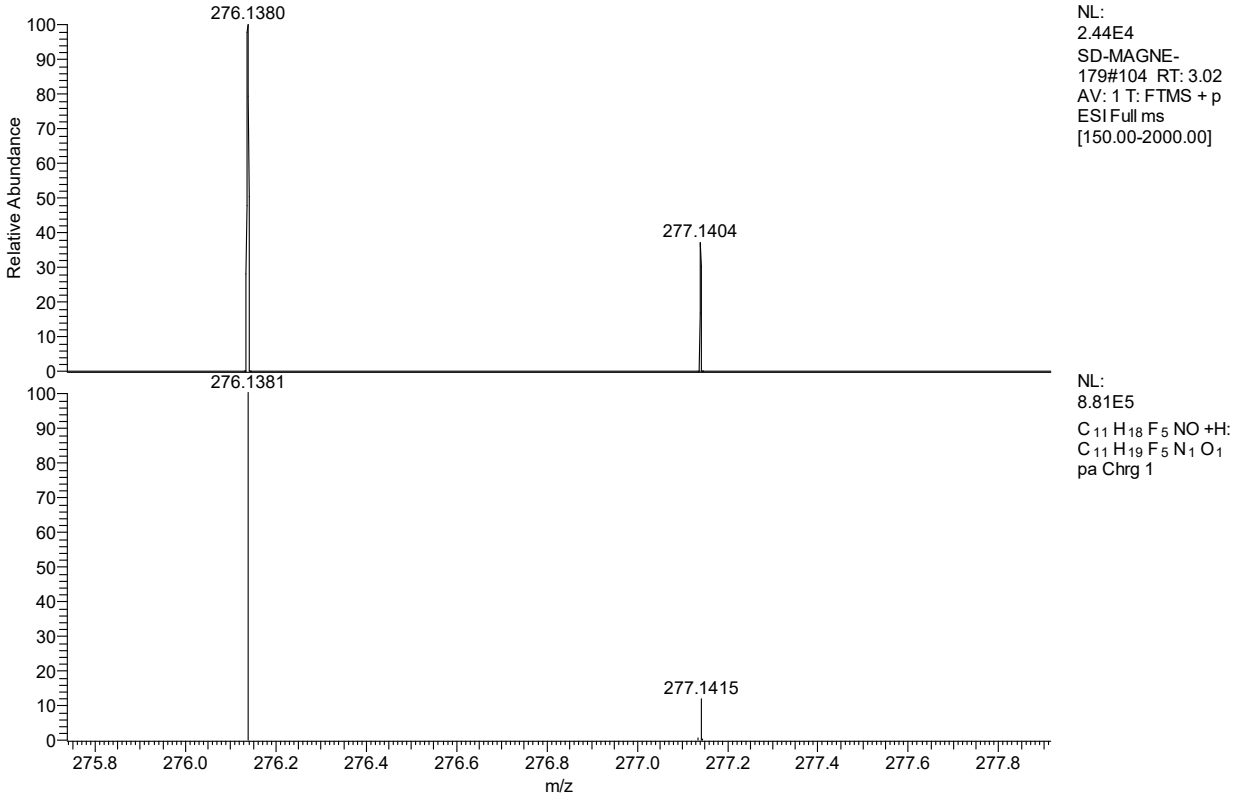
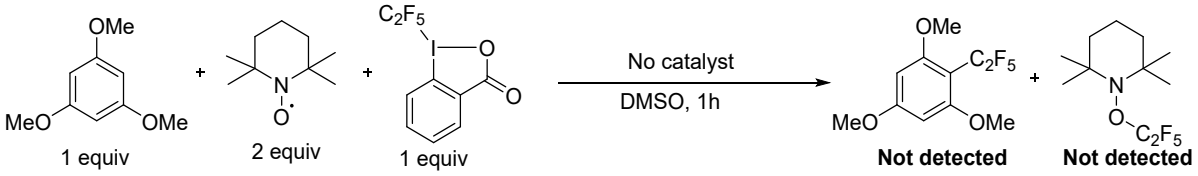


Figure S54. ESI-(HR)MS spectrum of a MeOH solution of TEMPO-C_2F_5 adduct.

Reaction in the presence of substrate, Togni reagent and TEMPO.



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 1,3,5-Trimethoxybenzene (10.0 mg, 0.059 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (21.7 mg, 0.059 mmol) and TEMPO (18.5 mg, 0.119 mmol), which were dissolved in anhydrous DMSO (1 mL). The reaction mixture was stirred at room temperature for 1 hour. After the completion of reaction, α,α,α-trifluorotoluene (7.3 μL, 0.059 mmol) was added as a standard. ^{19}F NMR spectroscopy showed no product formation and no TEMPO-C_2F_5 adduct was observed.

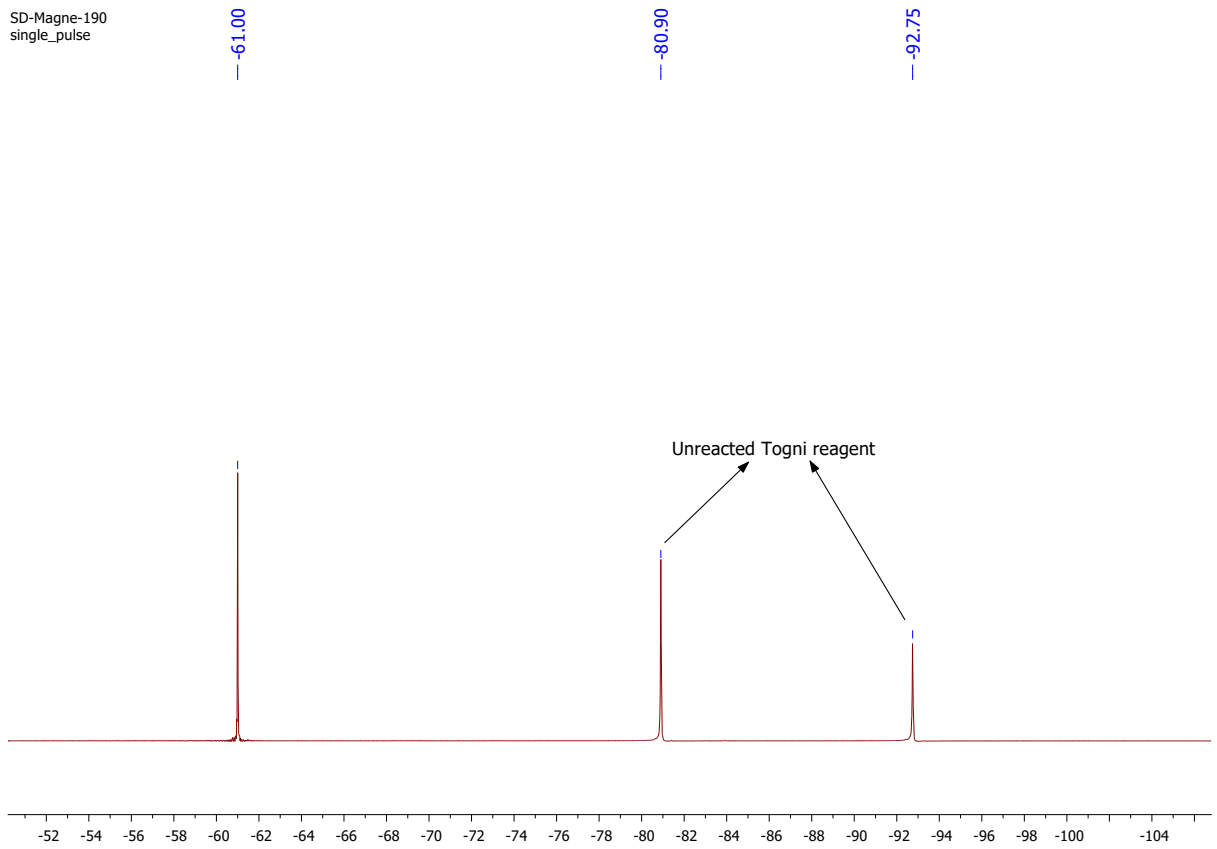
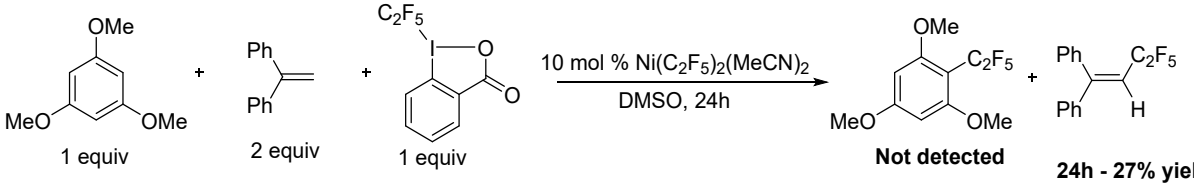


Figure S55. ^{19}F NMR spectrum of the reaction mixture containing substrate, TEMPO and Togni reagent after 1 hour.

Reaction in the presence of substrate, Togni reagent, catalytic 1 and DPE.



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 1,3,5-Trimethoxybenzene (10.0 mg, 0.059 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (21.7 mg, 0.059 mmol), 1,1-Diphenylethylene (20.8 µL, 0.119 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (2.2 mg, 0.0059 mmol), which were dissolved in anhydrous DMSO (1 mL). The reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (7.3 µL, 0.059 mmol) was added as a standard. ^{19}F NMR spectroscopy showed that the DPE-C_2F_5 adduct formed in 27% yield.

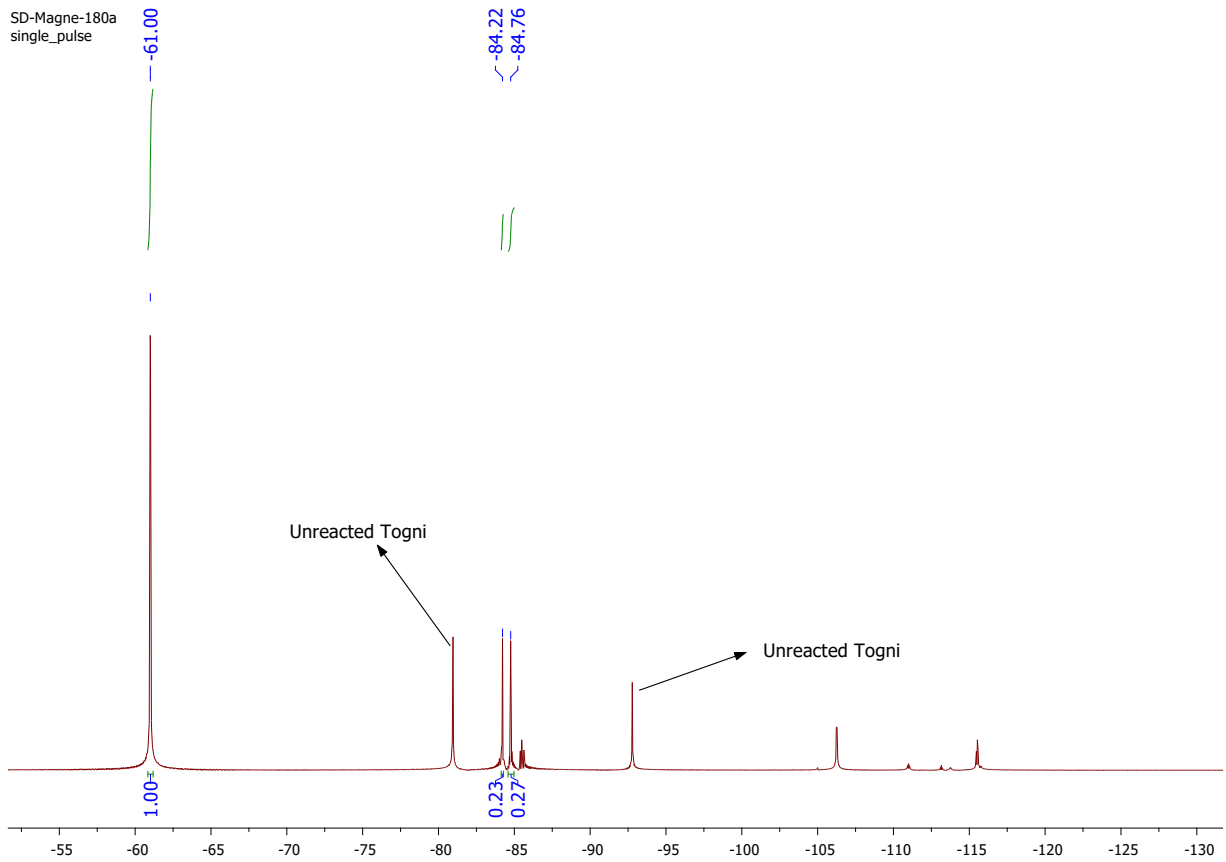
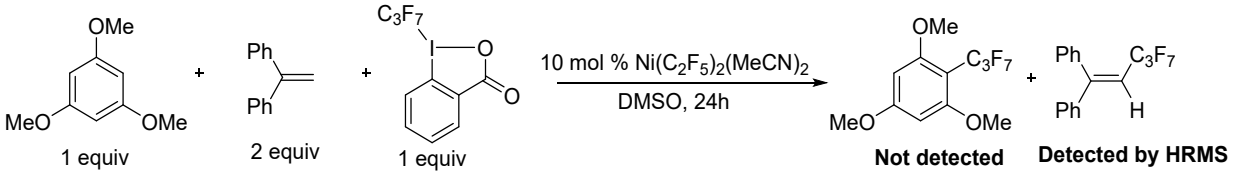


Figure S56. ^{19}F NMR spectrum of the reaction mixture containing **1**, substrate, DPE and Togni reagent after 24 hours.

Reaction in the presence of substrate, Togni reagent-C_3F_7, catalytic 1 and DPE.



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 1,3,5-Trimethoxybenzene (10.0 mg, 0.059 mmol), 1-heptafluoropropyl-1,2-benziodoxol-3(1H)-one (24.7 mg, 0.059 mmol), 1,1-Diphenylethylene (20.8 µL, 0.119 mmol) and $Ni(C_3F_7)_2(MeCN)_2$ (2.8 mg, 0.0059 mmol), which were dissolved in anhydrous DMSO (1 mL). The reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (7.3 µL, 0.059 mmol) was added as a standard. ^{19}F NMR spectroscopy shows no product formation and unreacted Togni reagent. The formation of DPE-C_3F_7 adduct could not be confirmed by ^{19}F NMR spectroscopy, however it could be detected with by HRMS/ESI$^+$.

HRMS (ESI) calculated for $[M^*H]^+$, $C_{17}H_{12}F_7$: m/z 349.0882; found, 349.0465.

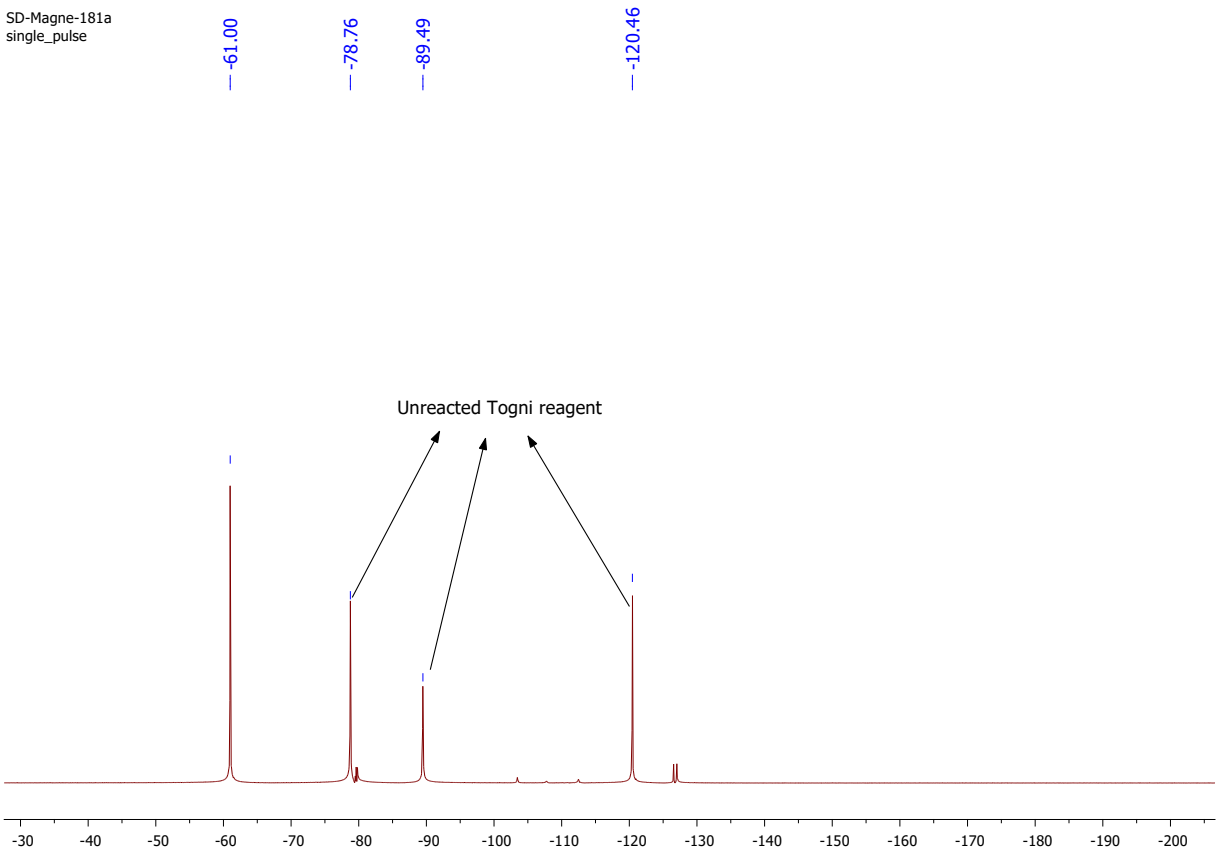


Figure S57. ^{19}F NMR spectrum of the reaction mixture containing **1**, substrate, DPE and Togni reagent after 24 hours.

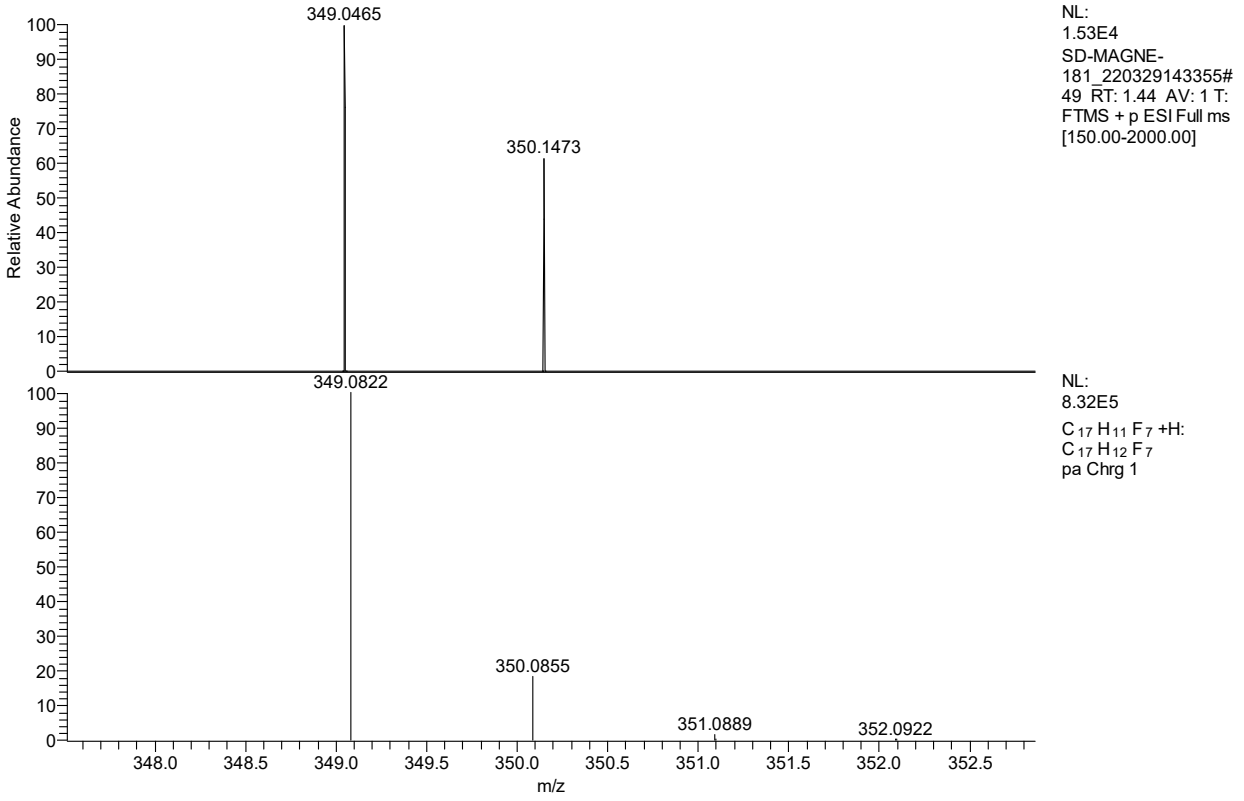
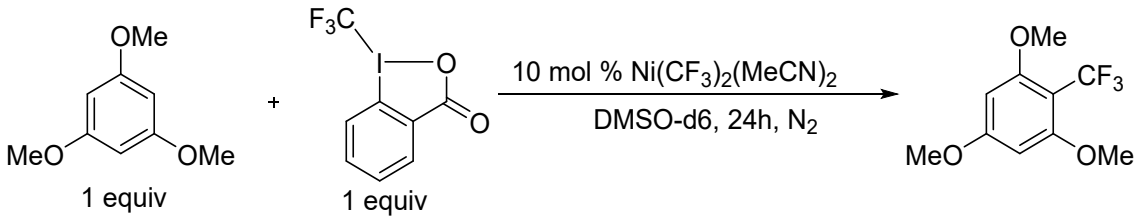


Figure S58. ESI-(HR)MS spectrum of a MeOH solution of DPE-C_3F_7 adduct.

IX. Optimization Table for catalytic trifluoromethylation with Acid Togni -CF_3.



Typical procedure. Inside the glovebox to a 20 mL vial equipped with a magnetic stirring bar was charged with 1,3,5-Trimethoxybenzene (10.0 mg, 0.059 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (18.7 mg, 0.059 mmol) and $Ni(CF_3)_2(MeCN)_2$ (1.6 mg, 5.9 μmol) . Then anhydrous deuterated DMSO or other solvent (1 mL) was added. The reaction mixture was stirred vigorously at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (7.3 μL, 0.059 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy.

Table S5. Trifluoromethylation of 1,3,5-Trimethoxybenzene in the presence of 1-trifluoromethyl-1,2-benziodoxol-3(1H)-one: initial optimization.

Entry	Solvent (1 mL)	Additive (1 equiv)	Catalyst (mol%)	Yield (%)
1	**DMSO-d6**	None	10	30
2	**MeOH-d4**	None	10	11
3	**MeCN-d3**	None	10	25
4	**DCM-d2**	None	10	20
5	**Acetone-d6**	None	10	10
6	DMSO-d6	**pyridine**	10	24

Yields were determined by ^{19}F NMR spectroscopy using α,α,α-trifluorotoluene as an internal standard.

Table S6. Effect of equivalent of 1-trifluoromethyl-1,2-benziodoxol-3(1H)-one.

Entry	Solvent (1 mL)	Togni-CF_3 (equiv)	Catalyst (mol%)	Yield (%)
1	DMSO-d6	**1 equiv**	10	30
2	DMSO-d6	**2 equiv**	10	43
3	DMSO-d6	**3 equiv**	10	73
4	DMSO-d6	**3 equiv**	0	8

Yields were determined by ^{19}F NMR spectroscopy using α,α,α-trifluorotoluene as an internal standard.

NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 1,3,5-Trimethoxybenzene (10.0 mg, 0.059 mmol), 1- trifluoromethyl -1,2-benziodoxol-3(1H)-one (56.3 mg, 0.1783 mmol) and $Ni(CF_3)_2(MeCN)_2$ (1.6 mg, 5.9 μmol) were dissolved in anhydrous DMSO (1 mL). Further the reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (7.3 μL, 0.059 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy.

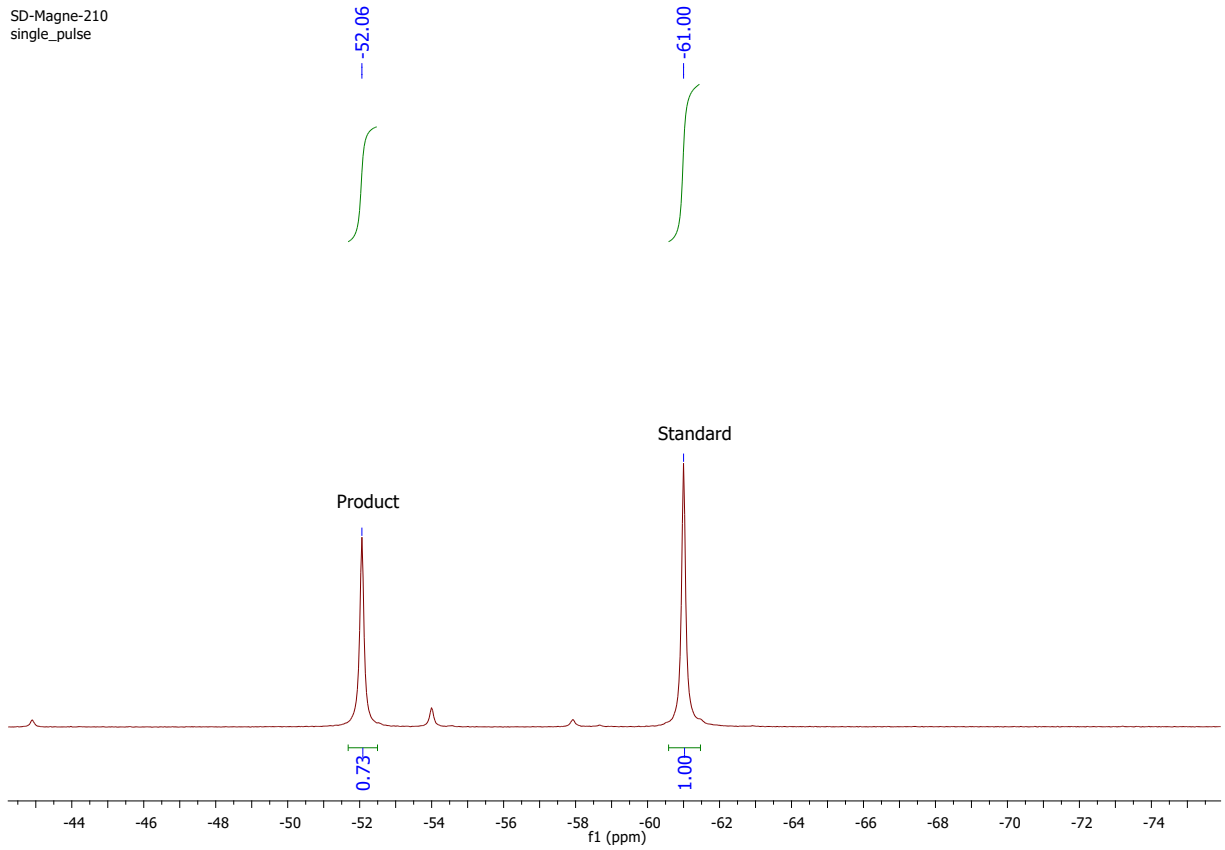
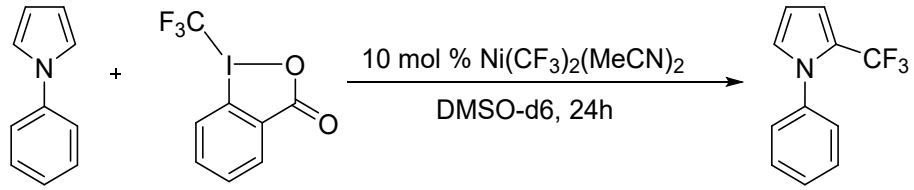


Figure S59. ^{19}F NMR spectrum showing formation of compound **B1**.



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with N-phenylpyrrole (10.0 mg, 0.070 mmol), 1-trifluoromethyl-1,2-benziodoxol-3(1H)-one (66.2 mg, 0.210 mmol) and $Ni(CF_3)_2(MeCN)_2$ (1.9 mg, 6.9 µmol) were dissolved in anhydrous DMSO (1 mL). Further the reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (8.5 µL, 0.070 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy.

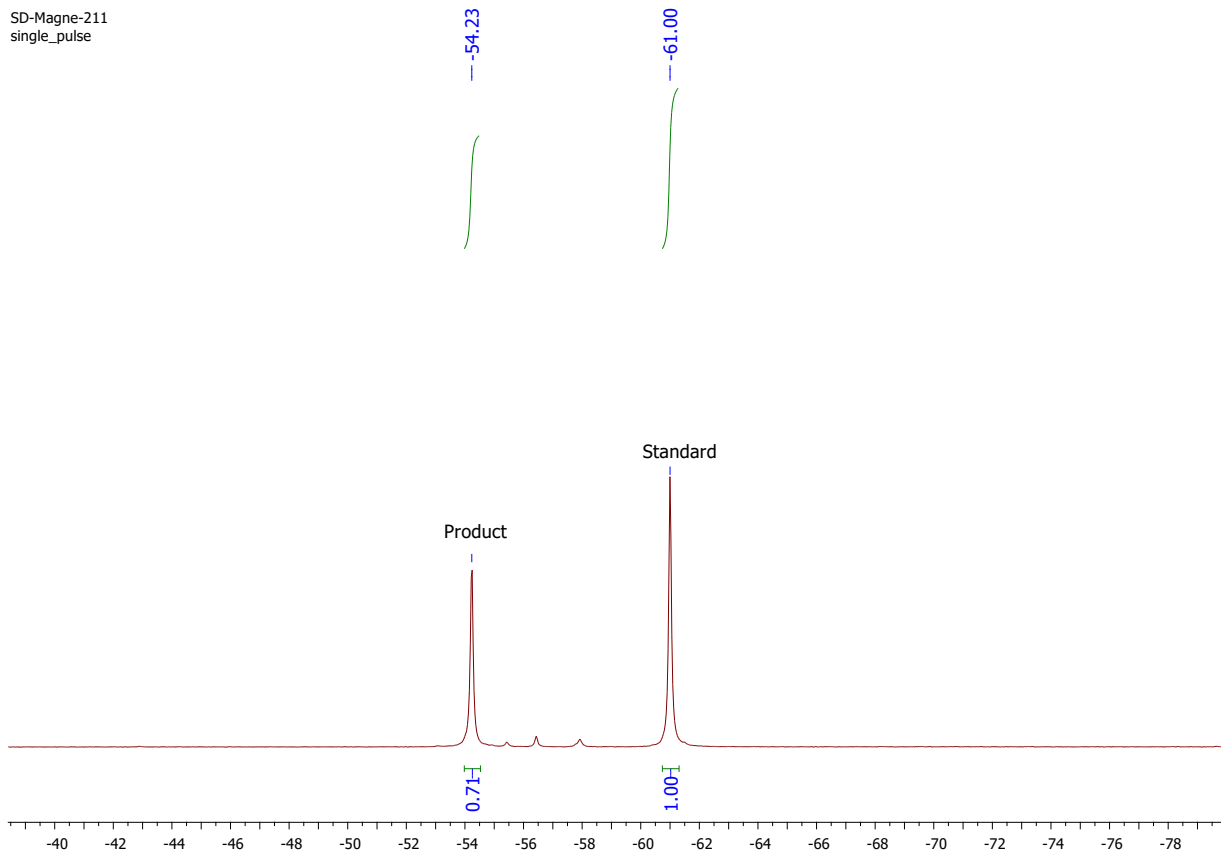
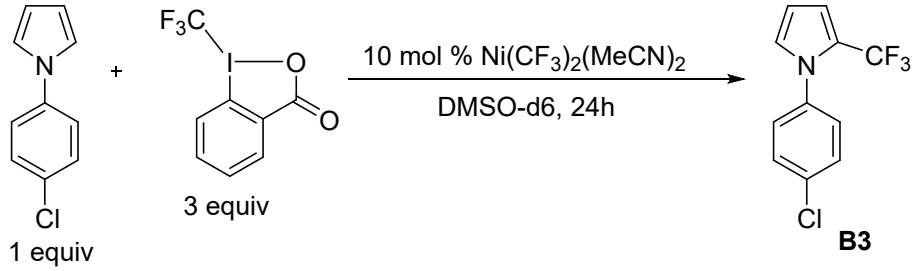


Figure S60. ^{19}F NMR spectrum showing formation of compound **B2**.



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 1-(4-Chlorophenyl)-1H-pyrrole (10.0 mg, 0.056 mmol), 1-trifluoromethyl-1,2-benziodoxol-3(1H)-one (53.3 mg, 0.169 mmol) and $Ni(CF_3)_2(MeCN)_2$ (1.5 mg, 5.6 μmol) were dissolved in anhydrous DMSO (1 mL). Further the reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (6.9 μL, 0.056 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy.

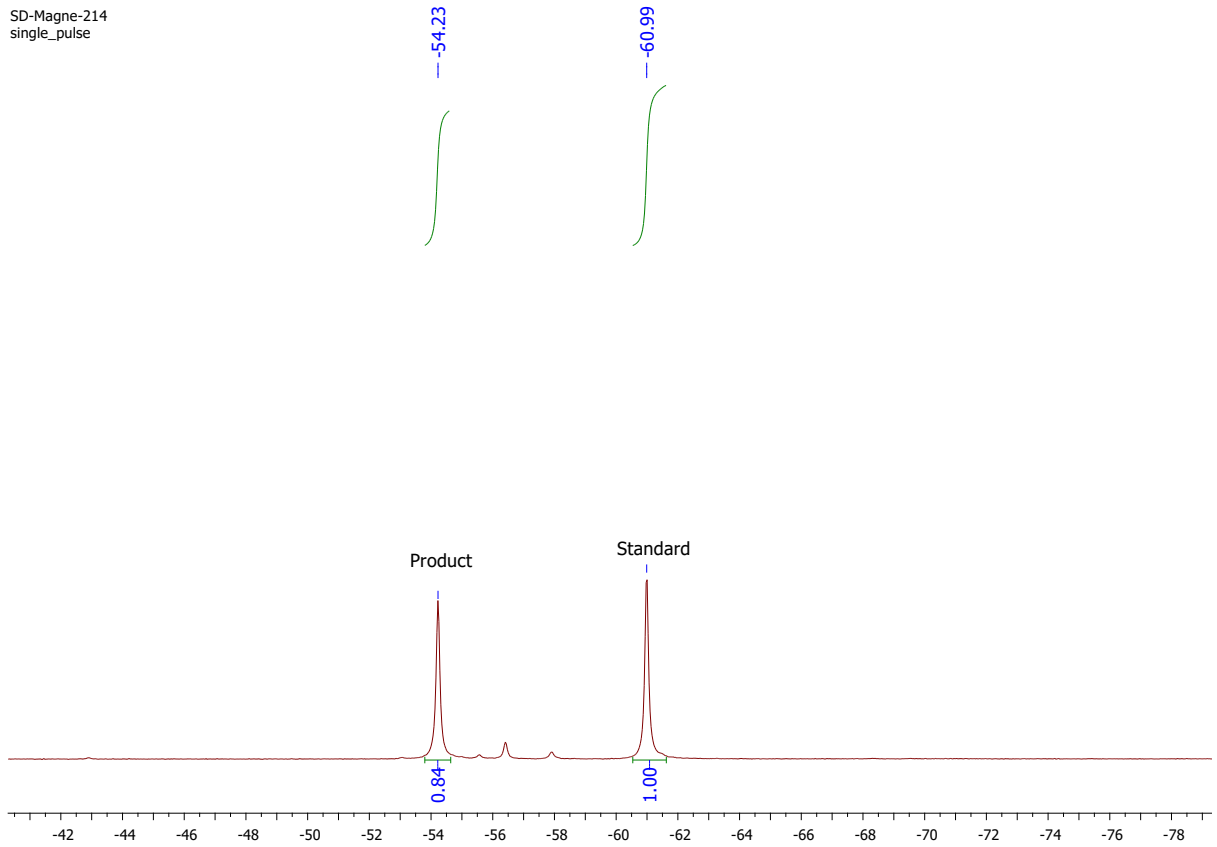
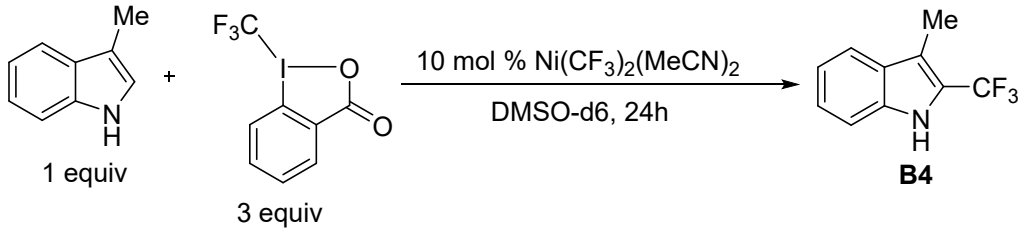


Figure S61. ^{19}F NMR spectrum showing formation of compound **B3**.



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 3-methylindole (10.0 mg, 0.076 mmol), 1-trifluoromethyl-1,2-benziodoxol-3(1H)-one (72.2 mg, 0.229 mmol) and $Ni(CF_3)_2(MeCN)_2$ (2.1 mg, 7.6 µmol) were dissolved in anhydrous DMSO (1 mL). Further the reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (9.3 µL, 0.076 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy.

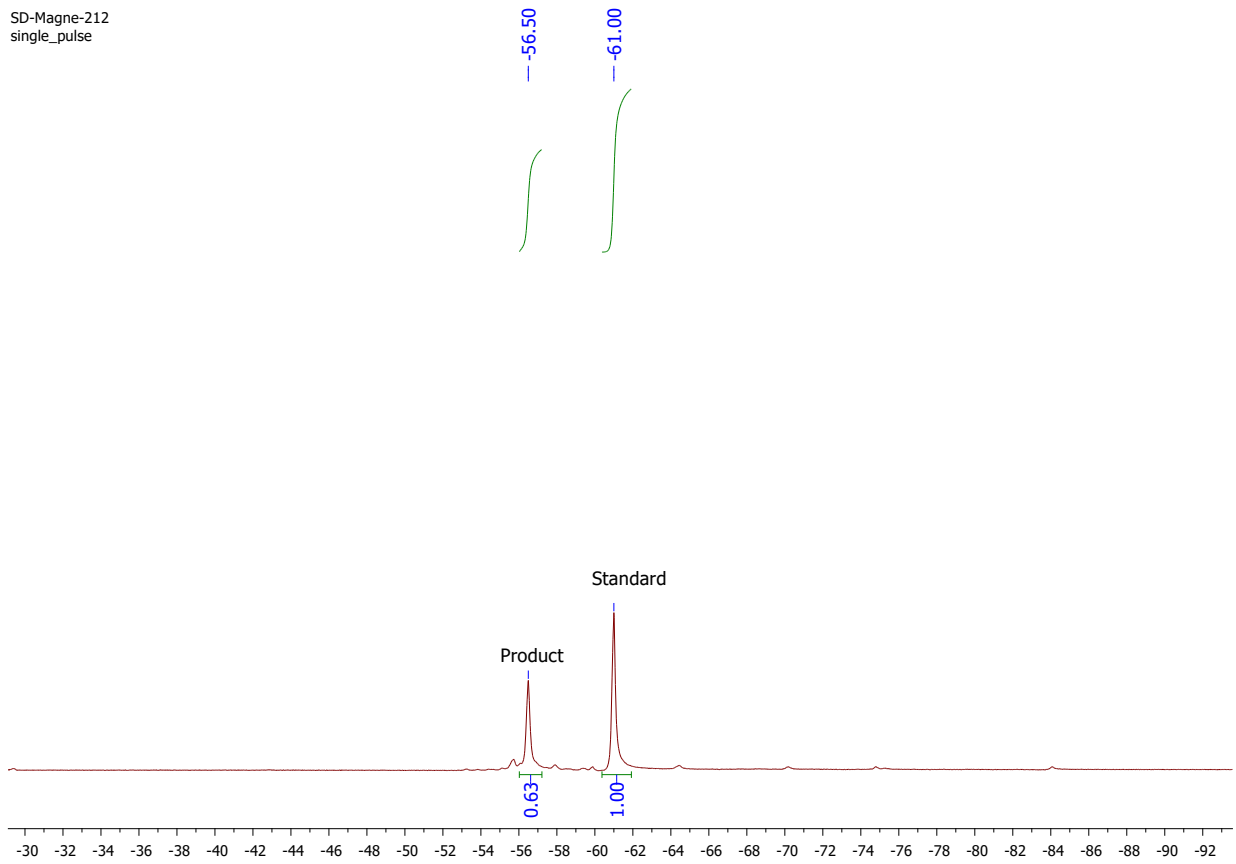
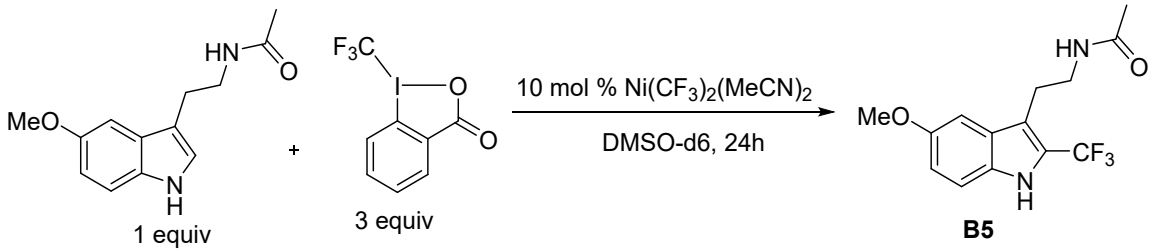


Figure S62. ^{19}F NMR spectrum showing formation of compound **B4**.



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with Melatonin (10.0 mg, 0.043 mmol), 1-trifluoromethyl-1,2-benziodoxol-3(1H)-one (40.8 mg, 0.129 mmol) and $Ni(CF_3)_2(MeCN)_2$ (1.2 mg, 4.3 µmol) were dissolved in anhydrous DMSO (1 mL). Further the reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (5.2 µL, 0.076 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy.

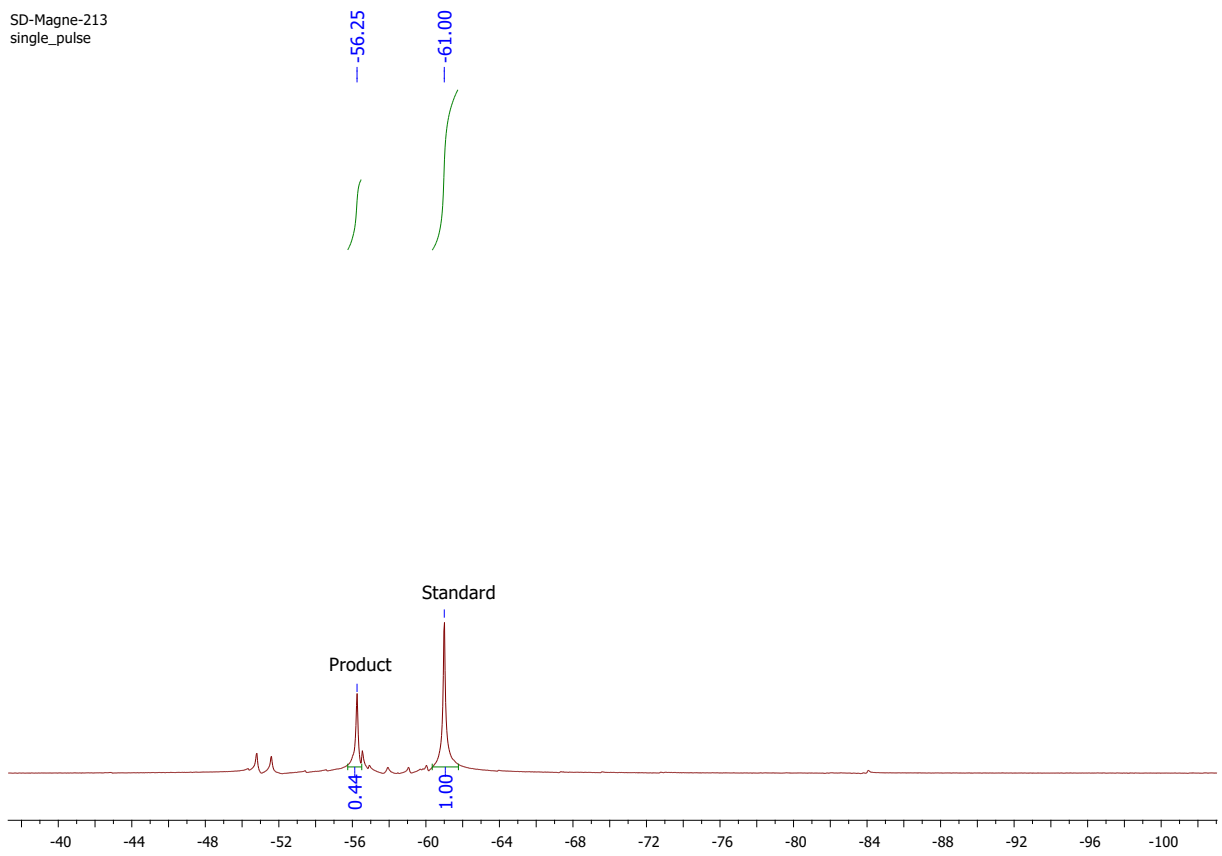
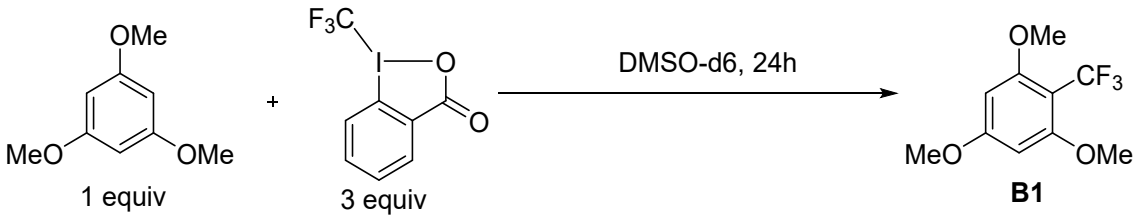


Figure S63. ^{19}F NMR spectrum showing formation of compound **B5**.

Control Experiment–



NMR scale: A 20 mL vial equipped with a magnetic stirring bar was charged with 1,3,5-Trimethoxybenzene (10.0 mg, 0.059 mmol) and 1- trifluoromethyl -1,2-benziodoxol-3(1H)-one (56.3 mg, 0.178 mmol) were dissolved in anhydrous DMSO (1 mL). Further the reaction mixture was stirred at room temperature for 24 hours. After the completion of reaction, α,α,α-trifluorotoluene (7.3 µL, 0.059 mmol) was added as a standard and the yield was determined by ^{19}F NMR spectroscopy.

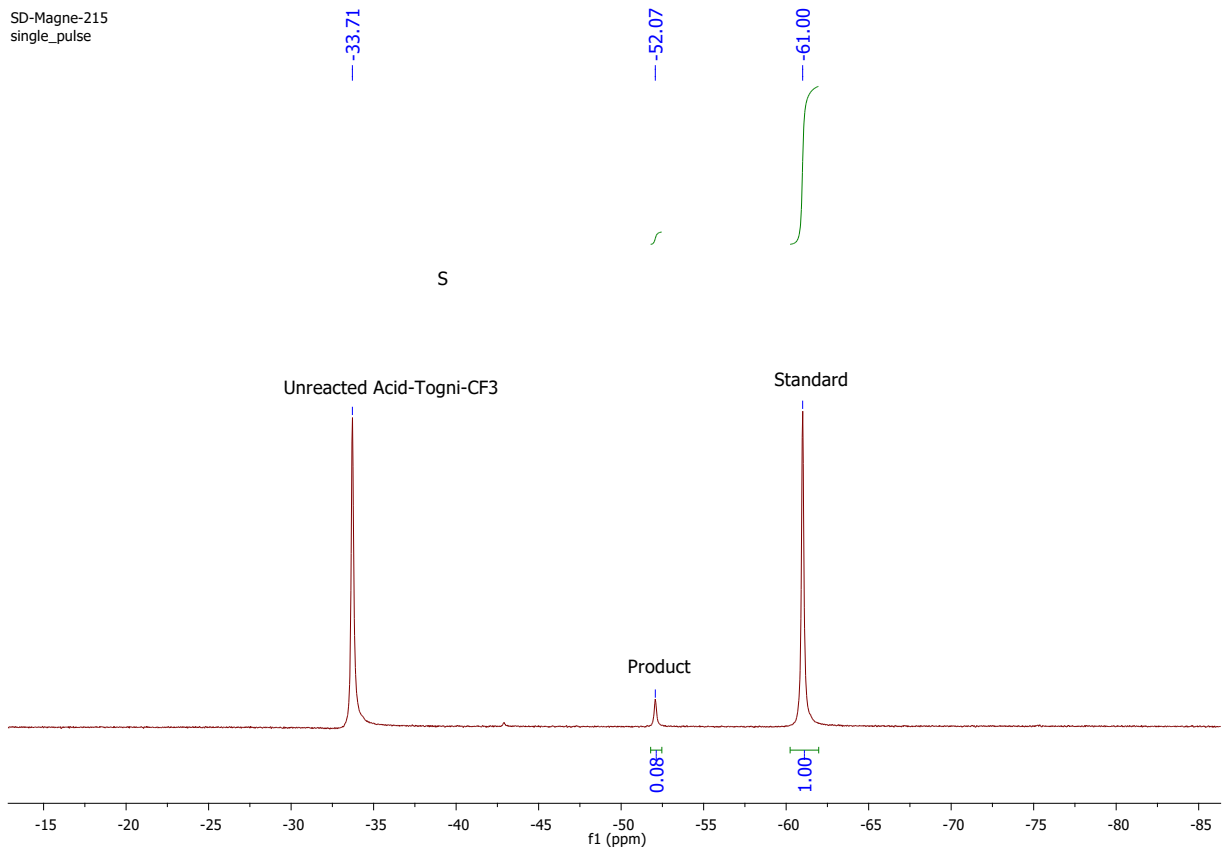


Figure S64. ^{19}F NMR spectrum showing formation of compound **B1** and unreacted Togni's reagent.

X. UV-Vis experiments.

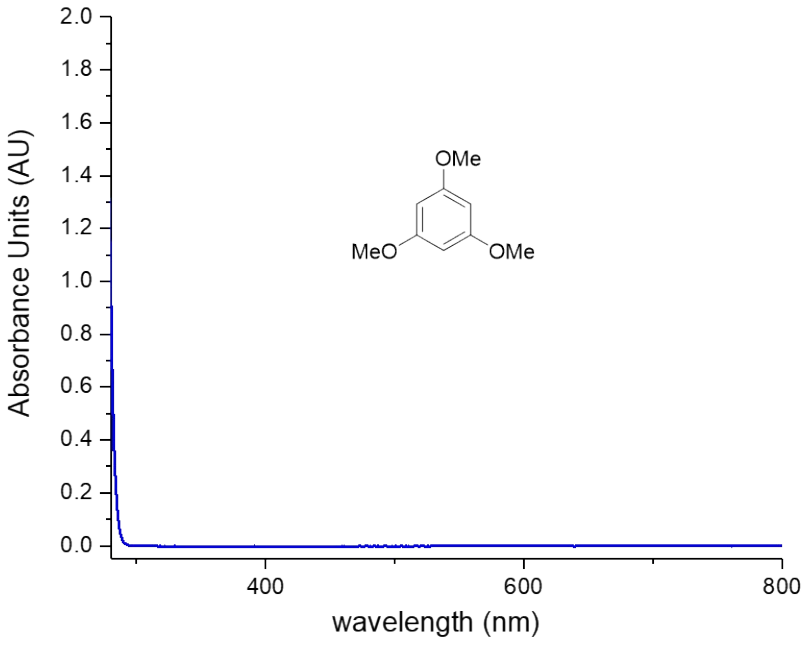


Figure S65. UV-Vis spectrum of 1,3,5-Trimethoxybenzene shows no absorption band in DMSO.

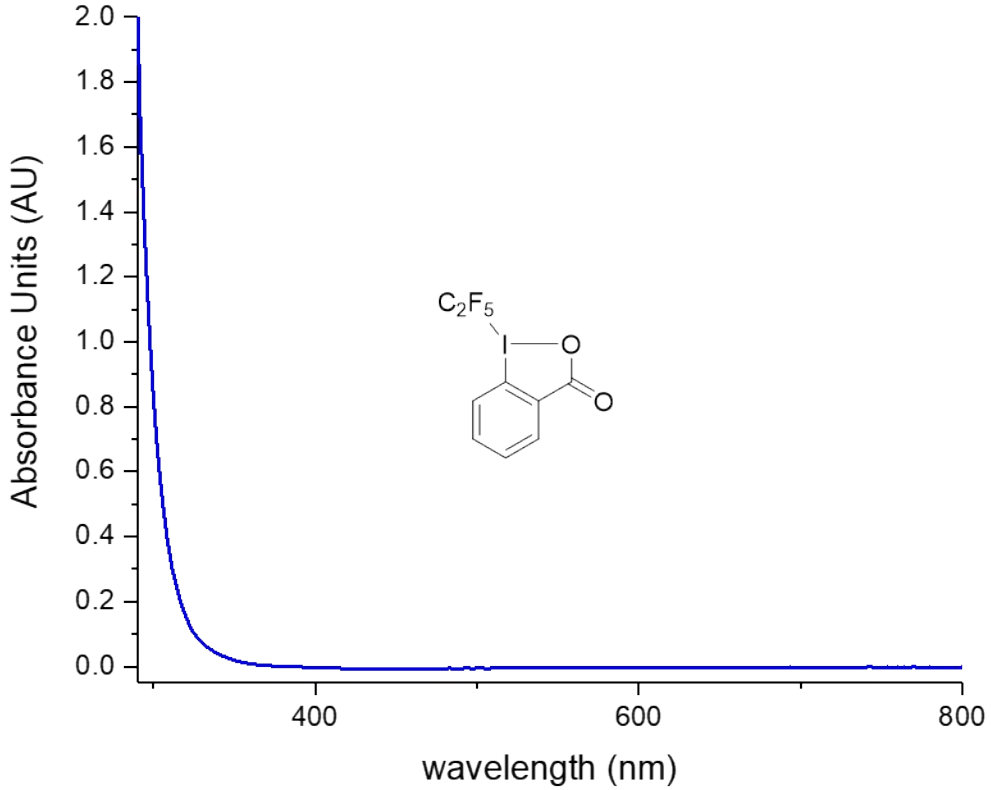


Figure S66. UV-Vis spectrum of Acid-C_2F_5 Togni reagent shows no absorption band in DMSO.

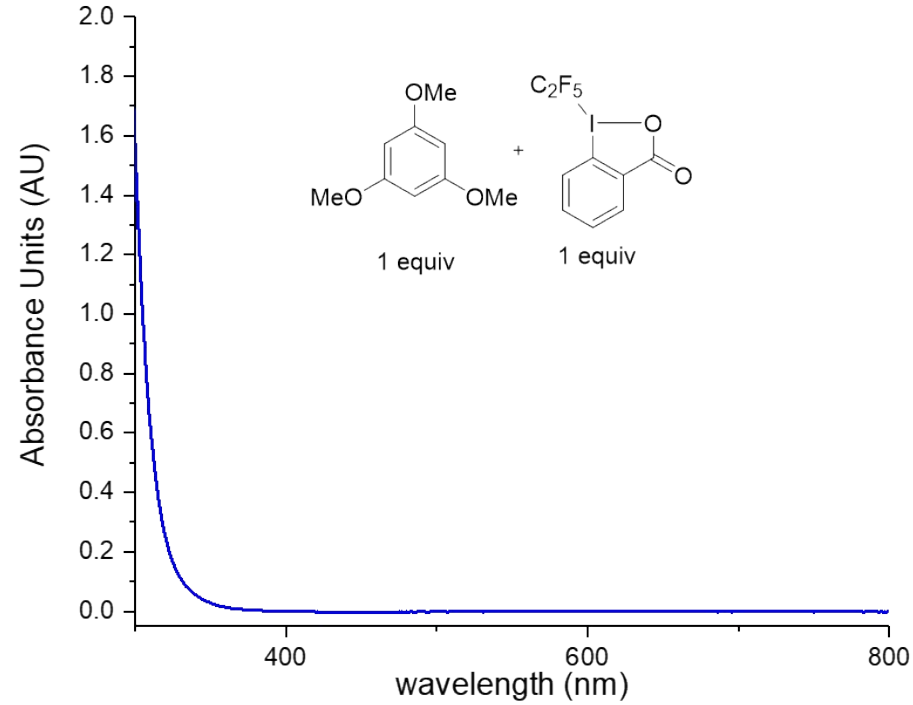


Figure S67. UV-Vis spectrum of a reaction mixture containing substrate and Acid-C_2F_5 Togni reagent shows no absorption band in DMSO.

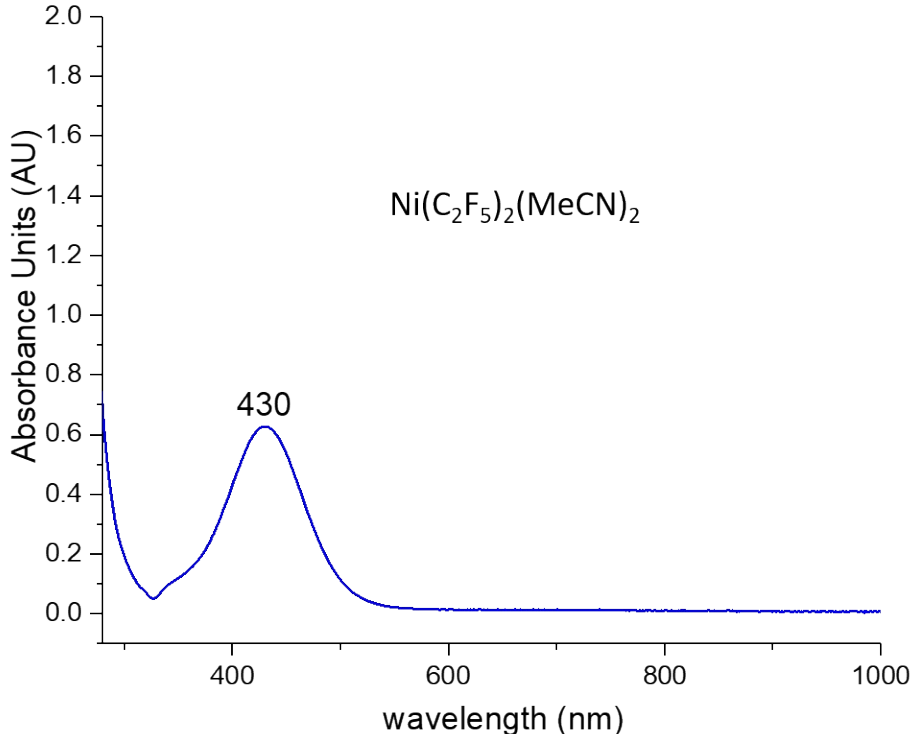


Figure S68. UV-Vis spectrum of $Ni(C_2F_5)_2(MeCN)_2$ precursor shows absorption band at 430 nm in DMSO.

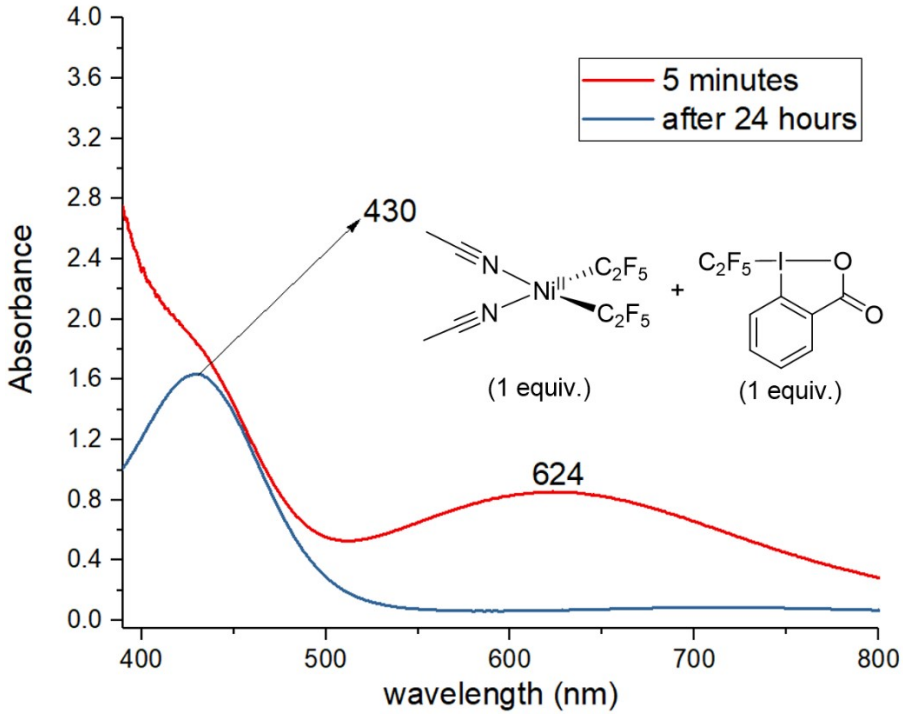


Figure S69. UV-Vis spectrum of a reaction mixture containing $Ni(C_2F_5)_2(MeCN)_2$ and Acid-C_2F_5 Togni reagent shows new absorption band at λ 624 nm after 5 minutes in DMSO.

Sample preparation: Inside the glovebox a 20 mL vial equipped with a magnetic stirring bar was charged with 1,3,5- Trimethoxybenzene (10.0 mg, 0.059 mmol), 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (21.7 mg, 0.059 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (2.2 mg, 0.006 mmol), which were dissolved in anhydrous DMSO (3 mL). The reaction mixture was transferred to cuvette and the reaction mixture was stirred for 5 minutes, then the first spectrum was recorded which shows the new band appears at 624 nm, consistent with previous experiments. Further the reaction mixture was stirred for 22 hours and then the last spectrum was recorded.

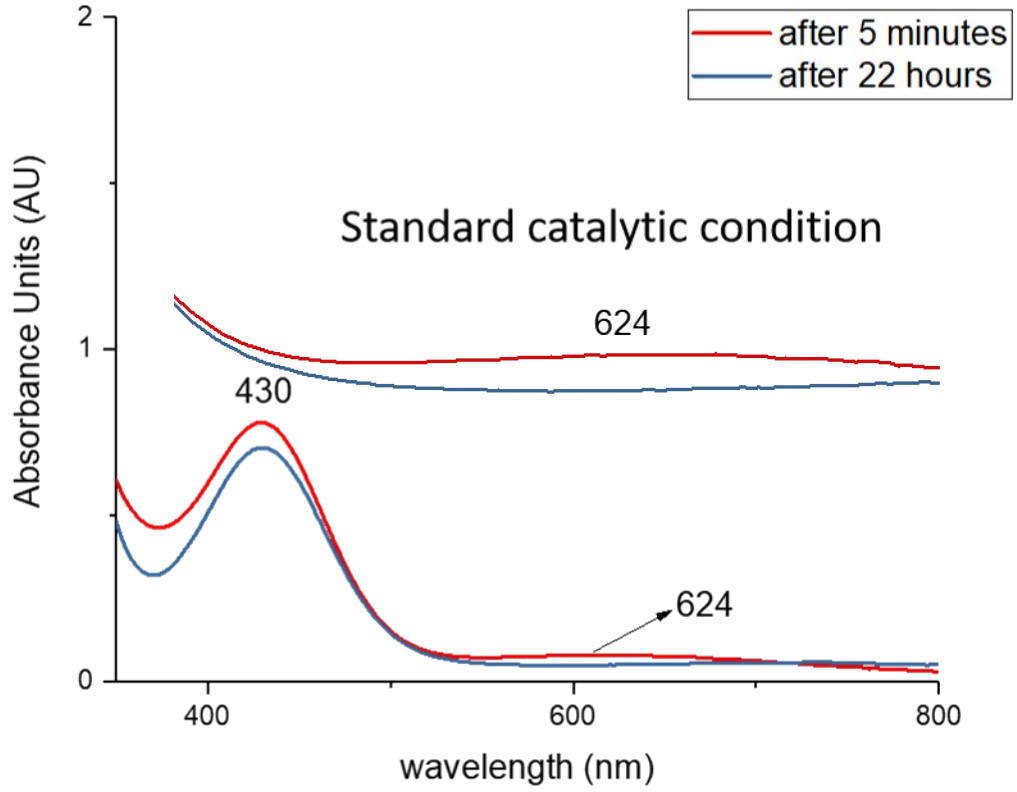


Figure S70. UV-Vis spectrum of a reaction mixture with standard catalytic condition in DMSO.

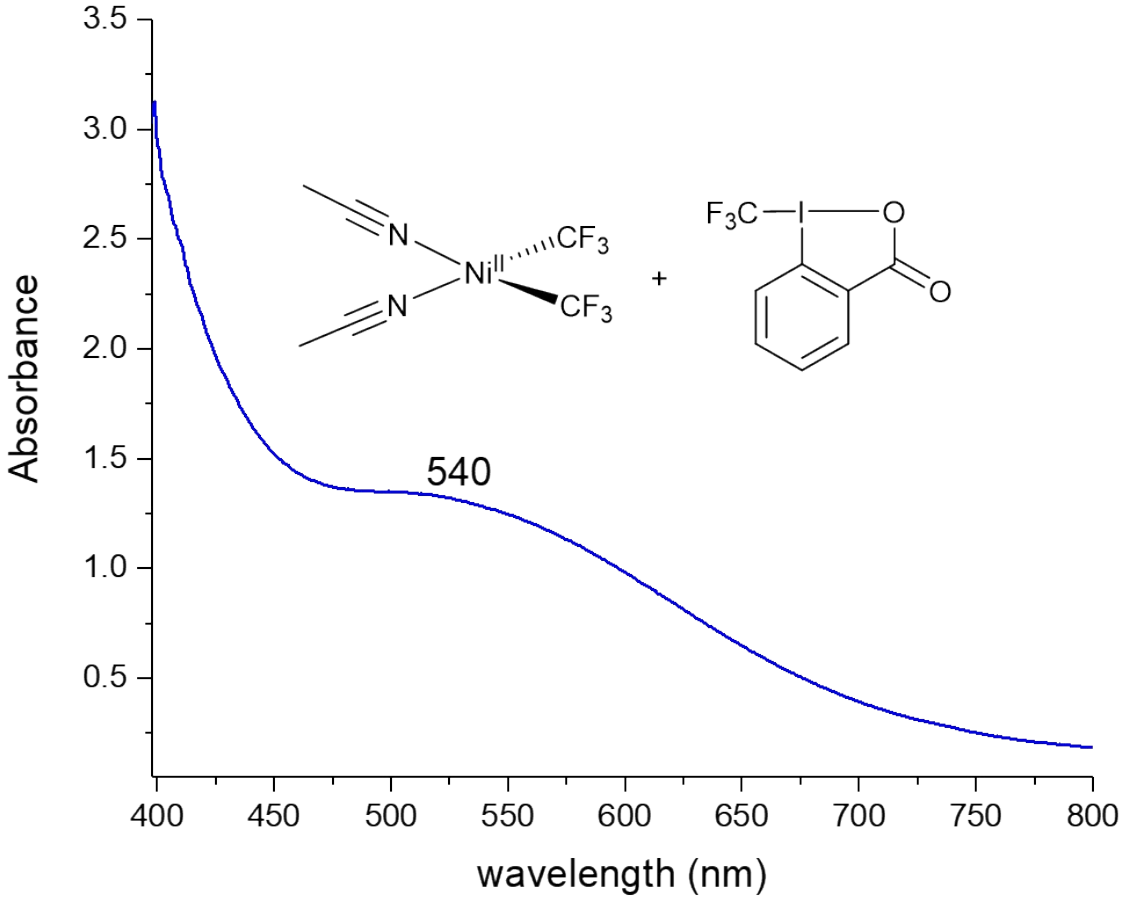
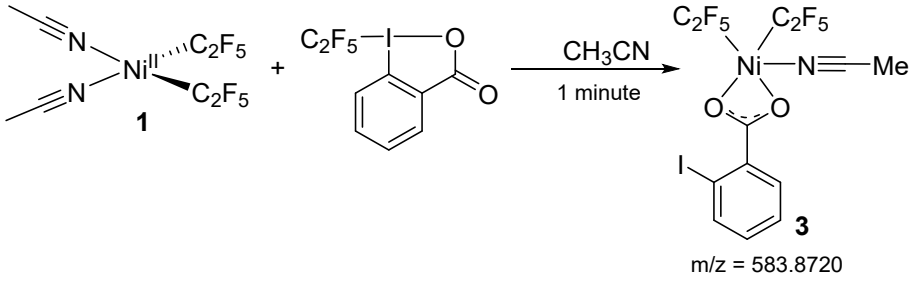


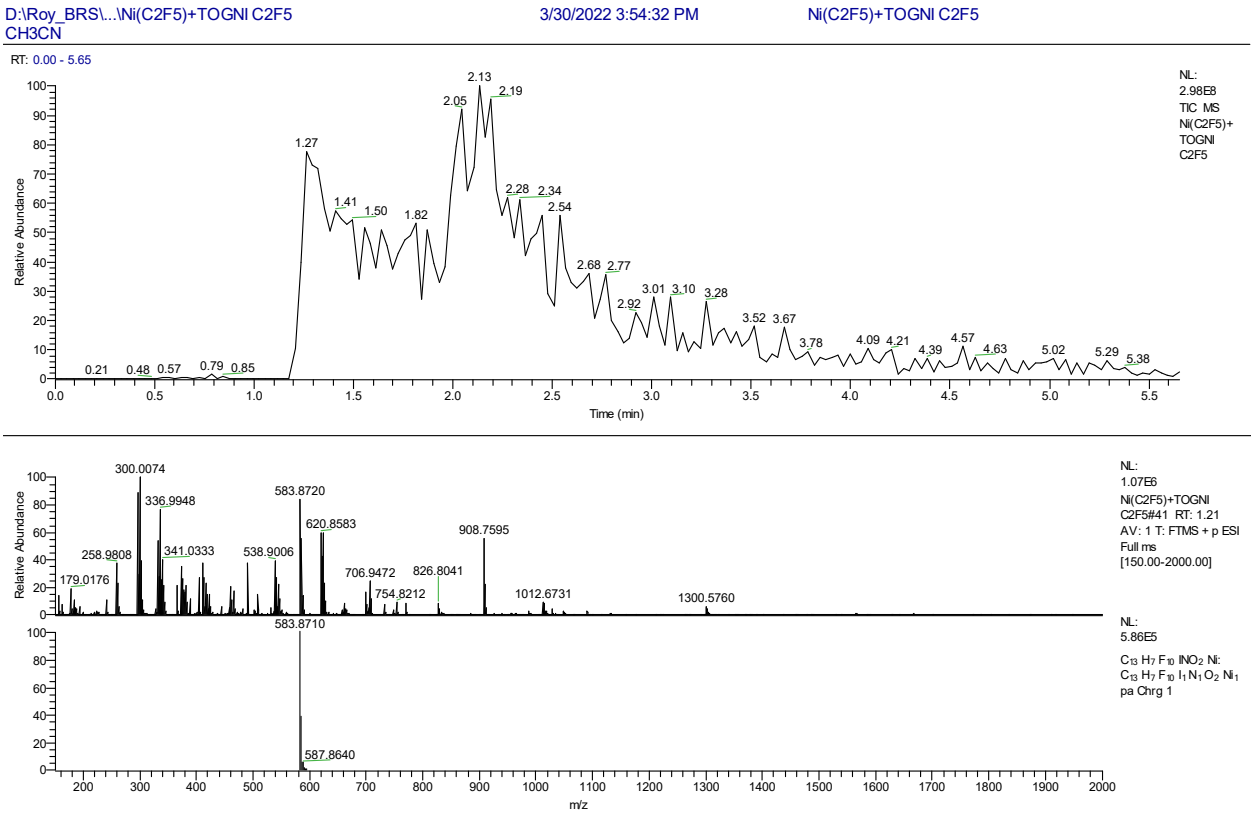
Figure S71. UV-Vis spectrum of a reaction mixture containing $Ni(CF_3)_2(MeCN)_2$ and Acid-CF_3 Togni reagent (3 equiv) shows new absorption band at λ 540 nm after 5 minutes in DMSO.

XI. HRMS experiments.



Sample Preparation: A septum vial was charged with 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (5.0 mg, 0.014 mmol), $Ni(C_2F_5)_2(MeCN)_2$ (5.2 mg, 0.014 mmol) and sealed with electric tape. Anhydrous acetonitrile (0.5 mL) was added with syringe and the vial was shaken for one-minute, resulting in a green color solution which was analyzed by HRMS.

HRMS (ESI) calculated for $C_{13}H_7F_{10}INO_2Ni$: m/z 583.8710; found, 583.8720.



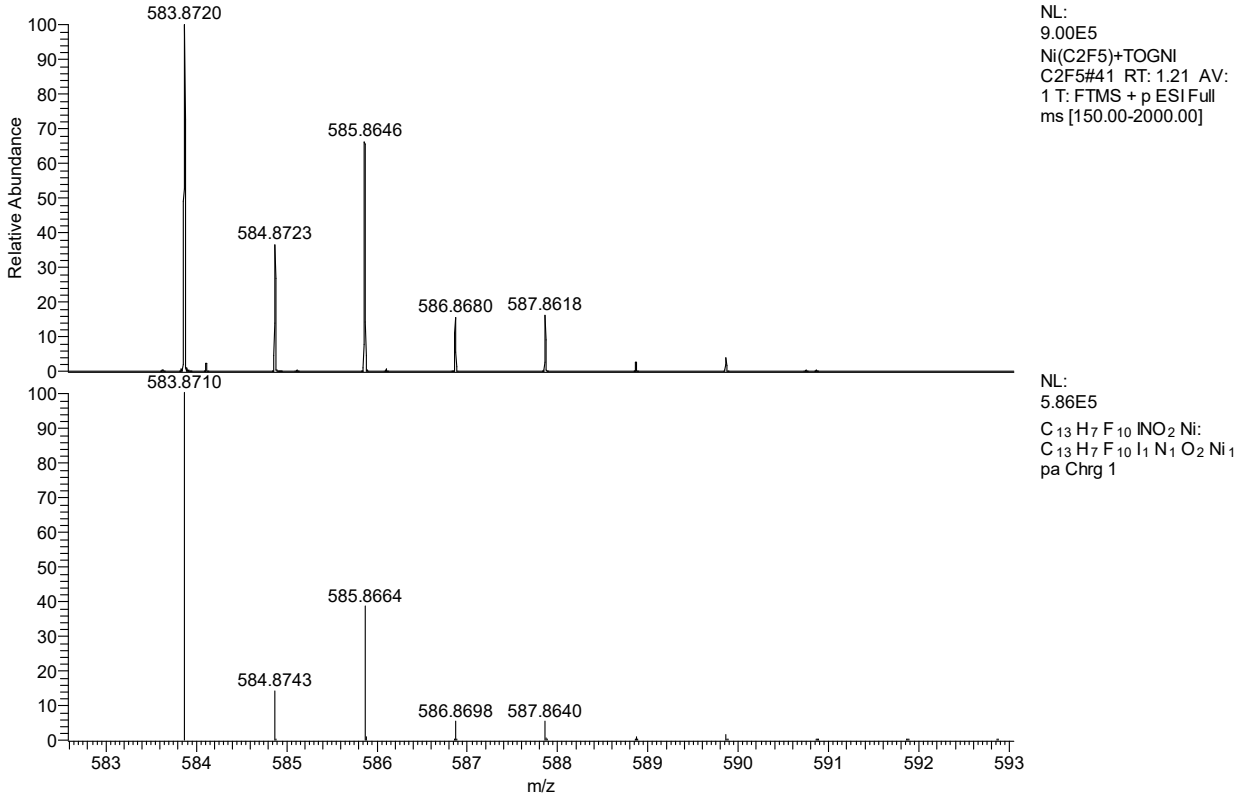
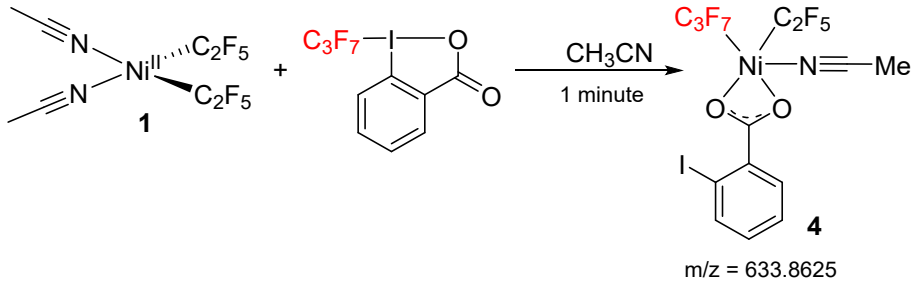


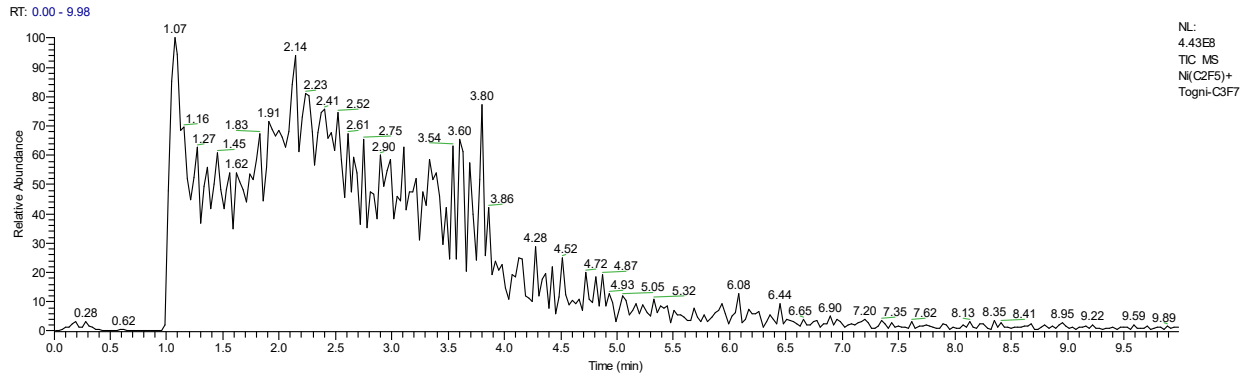
Figure S72. ESI-(HR)MS spectrum of a MeCN solution of **1** reacting with 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one.

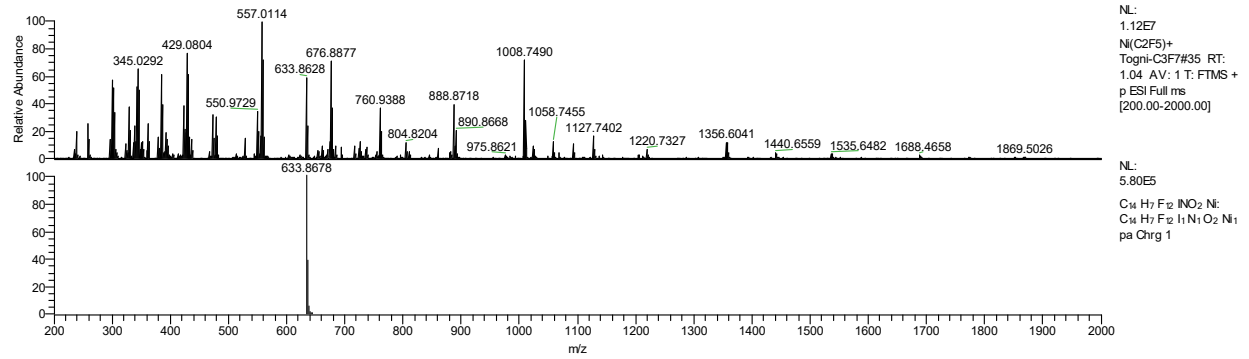


Sample Preparation: A septum vial was charged with 1-heptafluoropropyl-1,2-benziodoxol-3(1H)-one (6.6 mg, 0.016 mmol), $Ni(C_2F_5)_2(MeCN)_2$ (6.1 mg, 0.016 mmol) and sealed with electric tape. Further anhydrous acetonitrile (0.5 mL) was added via syringe and the vial was shaken for one-minute, resulting in a green color solution which was analyzed by HRMS.

HRMS (ESI) calculated for $C_{14}H_7F_{12}INO_2Ni$: m/z 633.8678; found, 633.8625.

D:\Roy_BRS\...\Ni(C2F5)+Togni-C3F7 3/31/2022 6:11:56 PM Ni(C2F5)+Togni-C3F7
MeCN





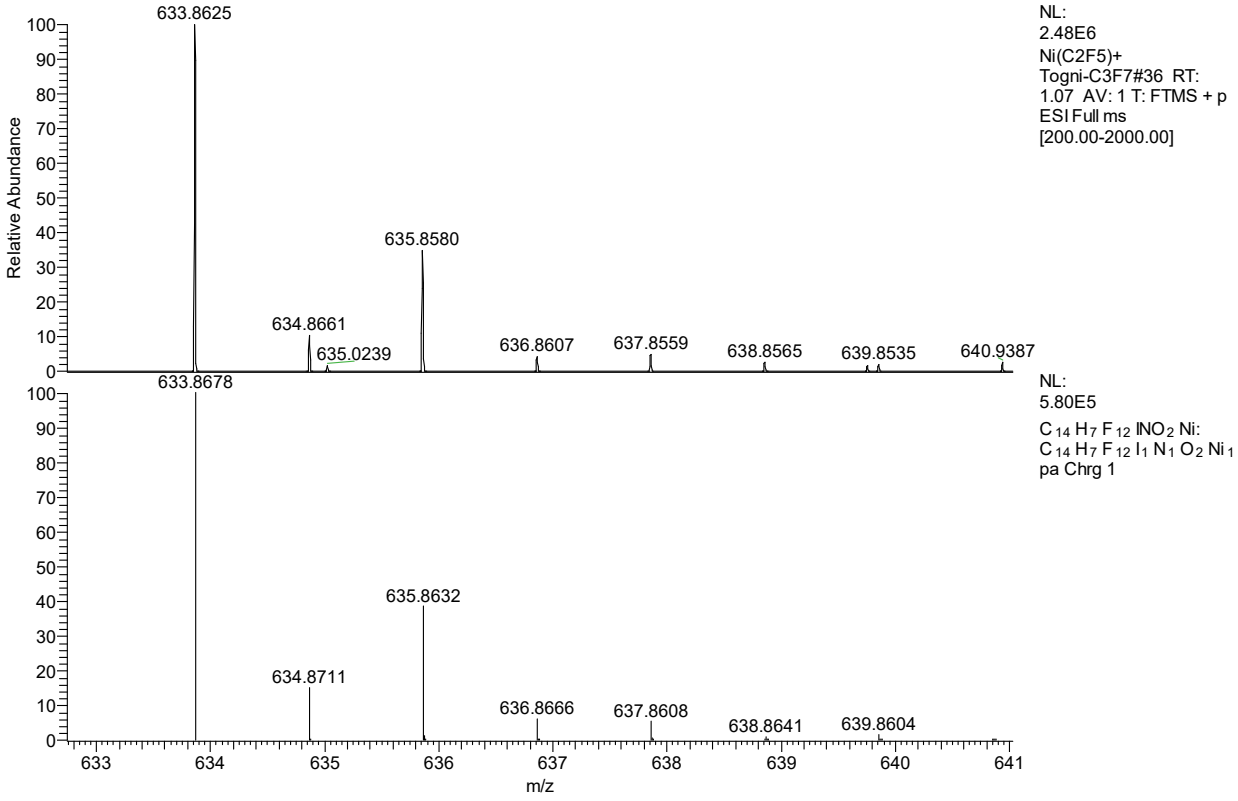
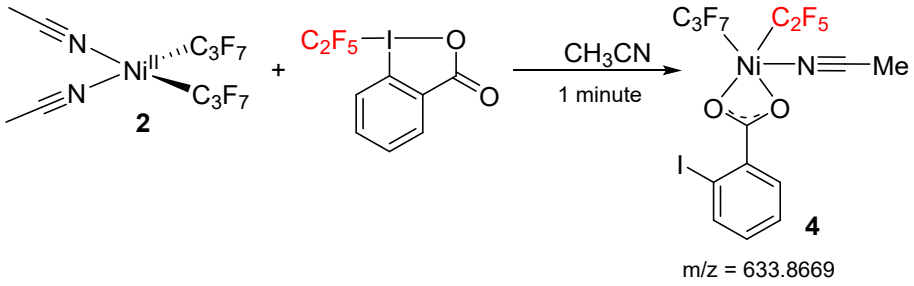


Figure S73. ESI-(HR)MS spectrum of a MeCN solution of **1** reacting with 1-heptafluoropropyl-1,2-benziodoxol-3(1H)-one.



Sample Preparation: A septum vial was charged with 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (3.6 mg, 0.01 mmol), $Ni(C_3F_7)_2(MeCN)_2$ (4.8 mg, 0.01 mmol) and sealed with electric tape. Further anhydrous acetonitrile (0.5 mL) was added via syringe and the vial was shaken for one-minute, resulting in a green color solution which was analyzed by HRMS.

HRMS (ESI) calculated for $C_{14}H_7F_{12}INO_2Ni$: m/z 633.8678; found, 633.8669.

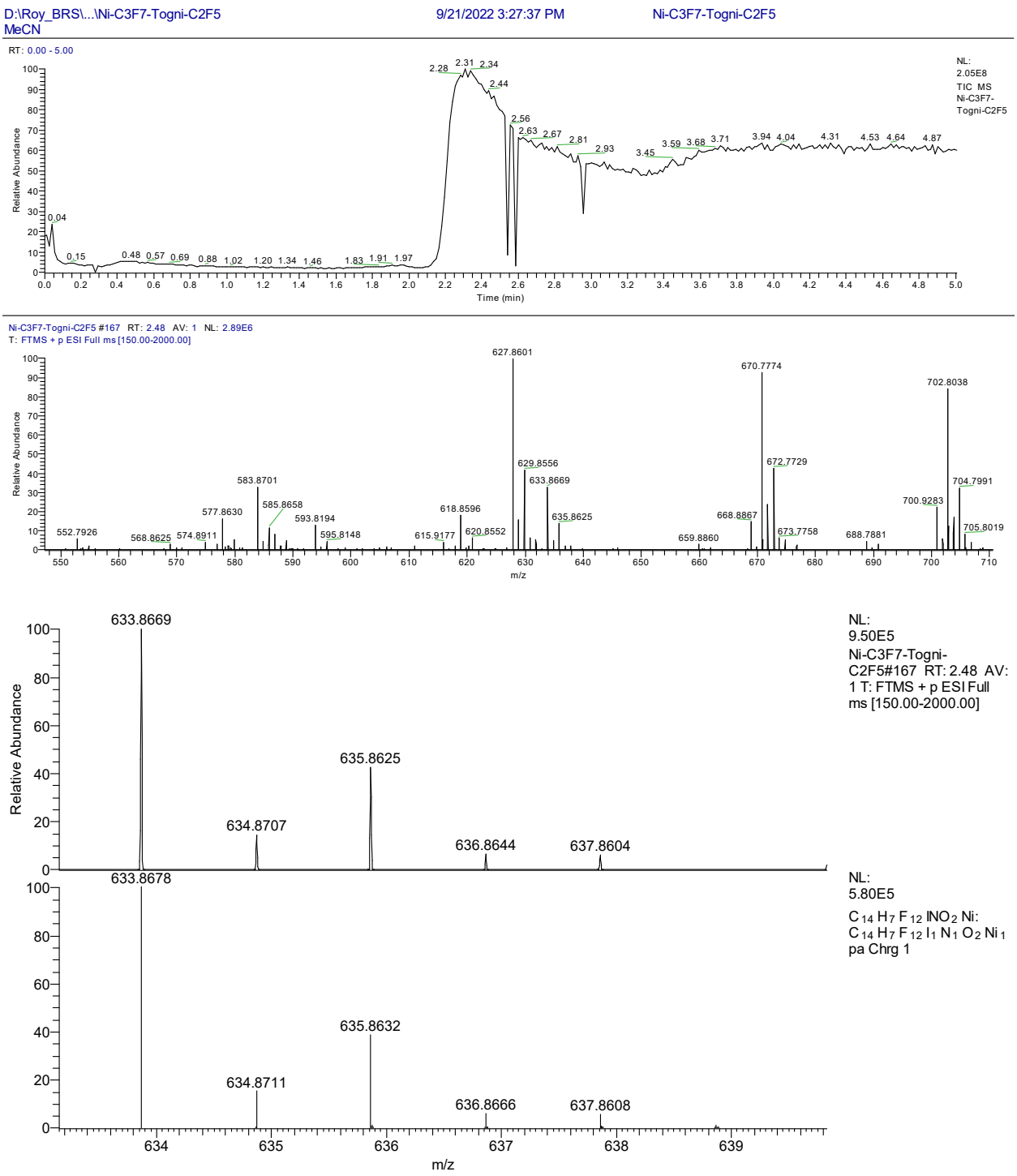
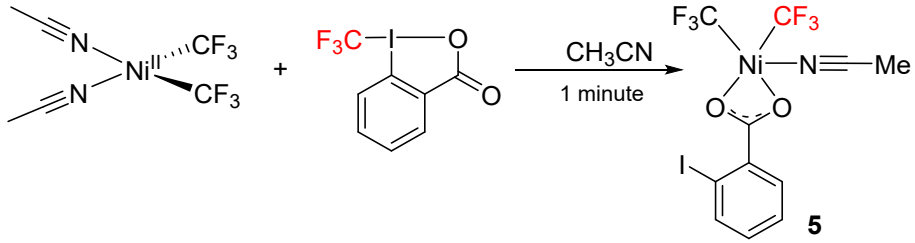


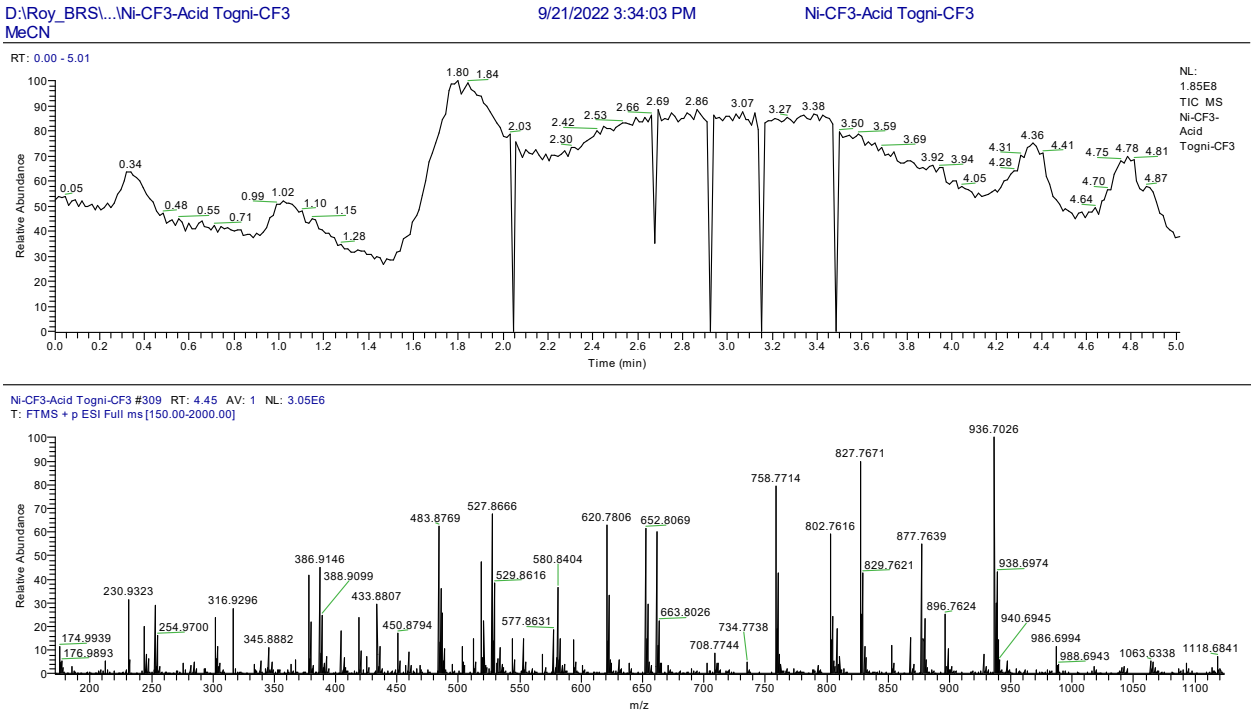
Figure S74. ESI-(HR)MS spectrum of a MeCN solution of **2** reacting with 1-heptafluoropropyl-1,2-benziodoxol-3(1H)-one.



m/z = 483.8770

Sample Preparation: A septum vial was charged with 1-trifluoromethyl-1,2-benziodoxol-3(1H)-one (19.7 mg, 0.0624 mmol), $Ni(CF_3)_2(MeCN)_2$ (5.8 mg, 0.0208 mmol) and sealed with electric tape. Further anhydrous acetonitrile (0.5 mL) was added via syringe and the vial was shaken for one-minute, resulting in a green color solution which was analyzed by HRMS.

HRMS (ESI) calculated for $C_{11}H_7F_6INO_2Ni$: m/z 483.8774; found, 483.8770.



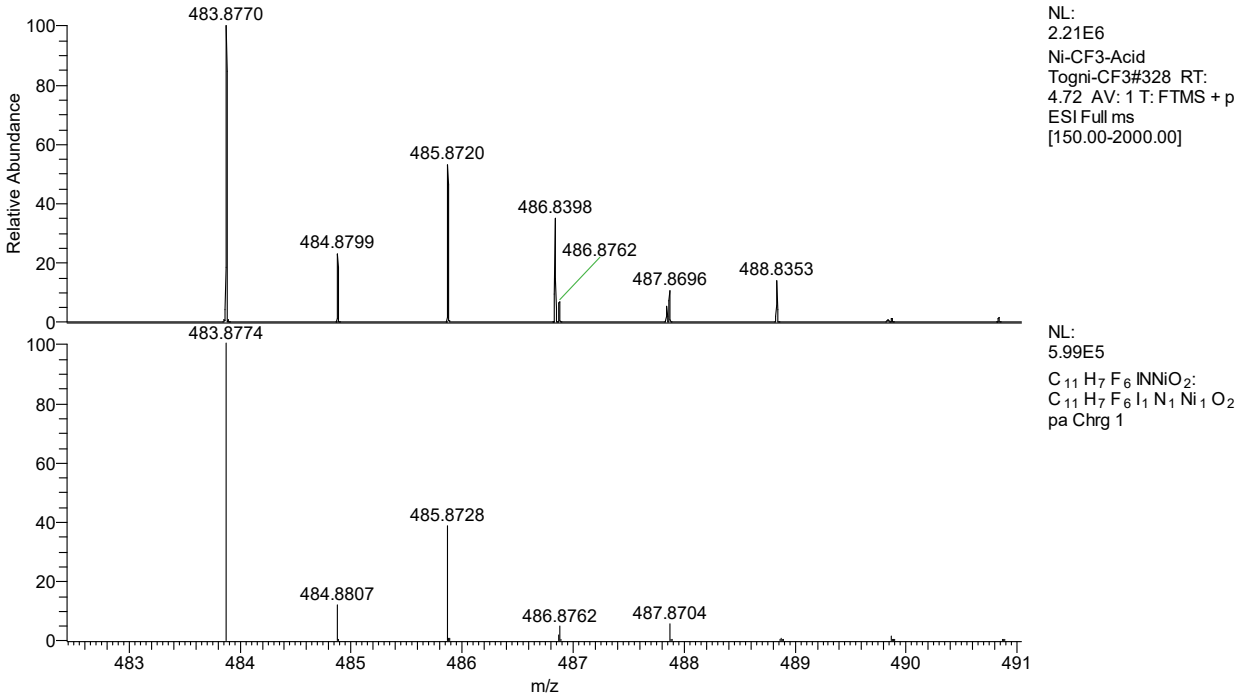


Figure S75. ESI-(HR)MS spectrum of a MeCN solution of $Ni(CF_3)_2(MeCN)_2$ reacting with 1-trifluoromethyl-1,2-benziodoxol-3(1H)-one.

XII. Stability in presence of 2-Iodobenzoic acid.

Inside the glovebox a 20 mL vial was charged with 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (Acid-C_2F_5 Togni reagent) (6.9 mg, 0.019 mmol) and $Ni(C_2F_5)_2(MeCN)_2$ (7.2 mg, 0.019 mmol), which dissolved in anhydrous DMSO (2.5 mL). The green color reaction mixture was transferred to a cuvette and a UV-vis spectrum was recorded before the addition of acid. Afterwards, 10 equivalents of 2-Iodobenzoic acid (47.1 mg, 0.190 mmol) were added. Under these conditions, the green color persists throughout the reaction, and the recorded UV-vis spectrum matches those obtained above.

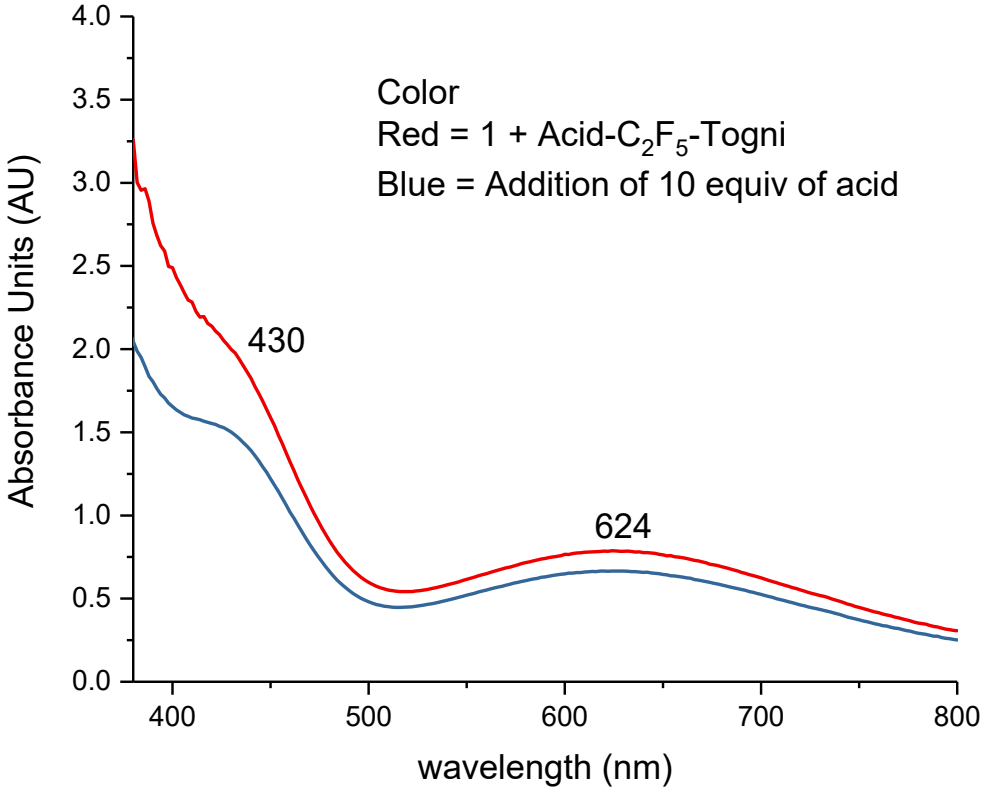


Figure S76. UV-Vis spectrum of a reaction mixture **1** with Acid-C_2F_5 Togni reagent in presence of 10 equivalents of 2-Iodobenzoic acid, measured in DMSO.

XIII. EPR data.

Inside the glovebox a septum vial was charged with 1-pentafluoroethyl-1,2-benziodoxol-3(1H)-one (5.0 mg, 0.014 mmol), $Ni(C_2F_5)_2(MeCN)_2$ (5.2 mg, 0.014 mmol) and sealed with electric tape. Further the anhydrous acetonitrile (0.50 mL) was added with syringe under ice bath, resulting in a green color solution. The reaction mixture was transferred to another vial and diluted (ca. 1:10) with glassing solvent mixture, PrCN:EtCN (1:1 v/v); the spectrum as recorded at 94 K.

The experimental EPR spectrum (Figure S77) could be satisfactorily simulated as a nearly axial signal with g values of 2.23, 2.185, 2.026 (g_{ave} = 2.147). Splitting along g_3 component could be simulated as a superhyperfine splitting from two equivalent F-atoms (A_F = 11.3 G) and one N-atom (A_N = 19.6 G), which gave most satisfactory fit to the experimental data (Figure S78). However, in the absence of direct structural information, an alternative explanation cannot be excluded with g_3 component showing superhyperfine splitting from two inequivalent N-atoms, with A_N of 10.7 G and 19.3 G; the resulting spectrum shows similar multiplicity, however,

comparison of line intensities was in less satisfactory agreement with experimental results (Figure S79). The splitting along g_1 and g_2 components was not simulated due to significant broadening which was not sufficiently resolved.

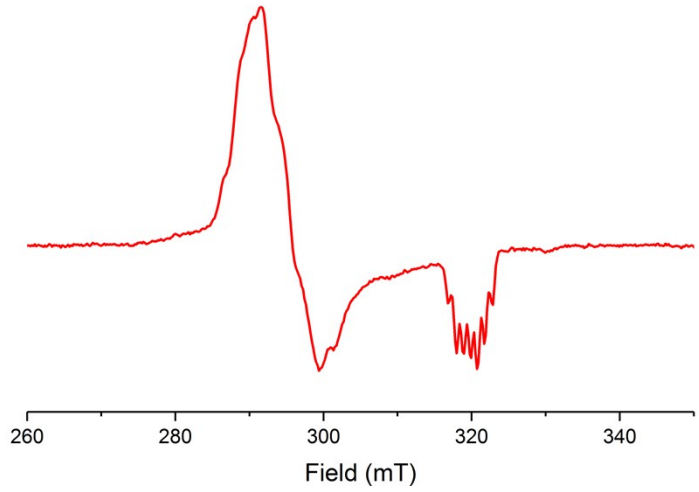


Figure S77. Experimental EPR spectrum of the sample of the reaction mixture containing **1** and Togni reagent

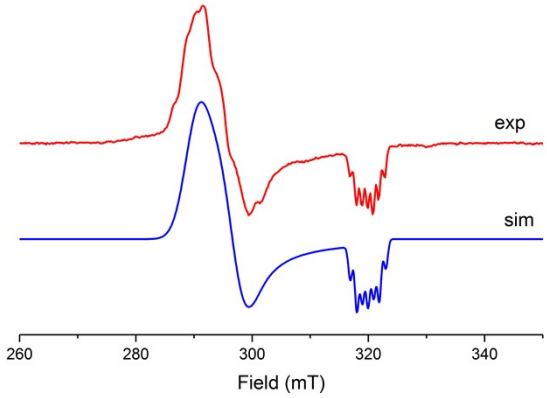


Figure S78. EPR spectrum of the sample of the reaction mixture containing **1** and Togni reagent (PrCN:EtCN glass, 94K, 9.07 GHz) (red) and simulated EPR spectrum with superhyperfine splitting from two F and one N atom (A_N = 19.6 H; A_F = 11.G G) (blue). (HStrain parametes: 160 for g_1 and g_2; 15 for g_3).

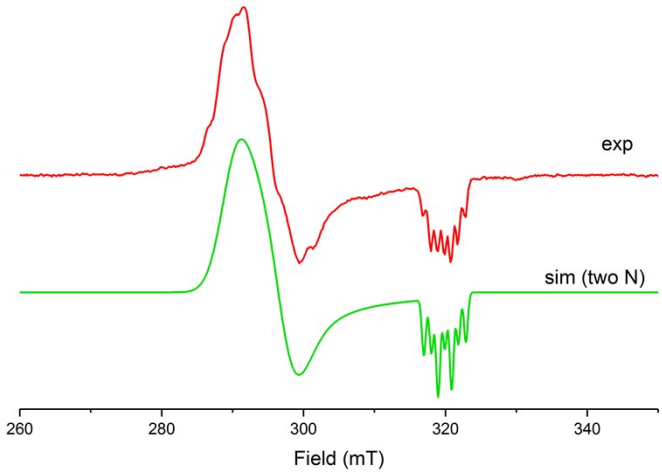


Figure S79. EPR spectrum of the sample of the reaction mixture containing **1** and Togni reagent (PrCN:EtCN glass, 94K, 9.07 GHz) (red); simulated EPR spectrum with superhyperfine splitting from two inequivalent N-atoms (A_N = 10.7; 19.3 G) (green). (HStrain parametes: 160 for g_1 and g_2; 15 for g_3).

XIV. NMR spectra of isolated compounds

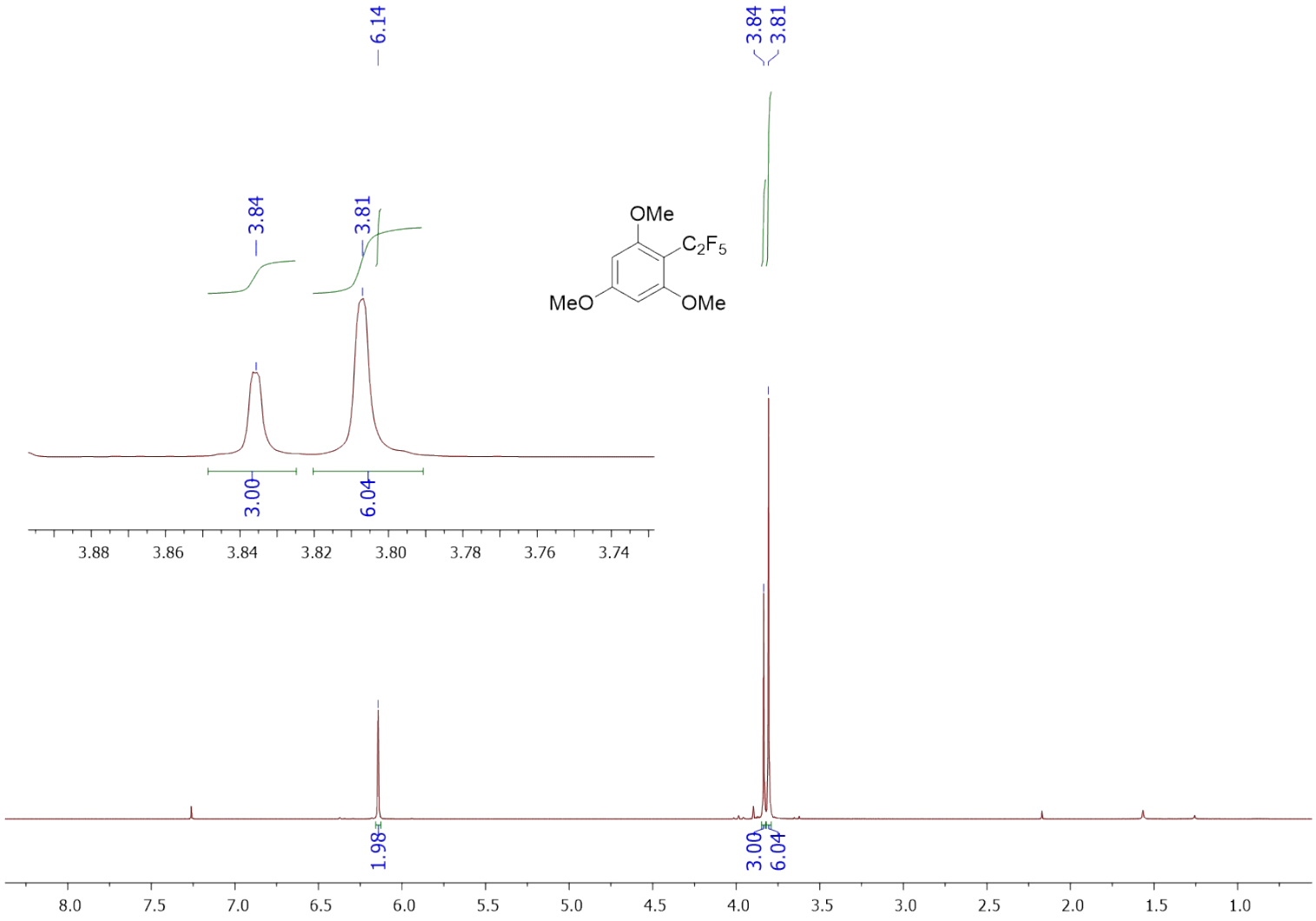


Figure S80. ^{1}H NMR spectrum of **a** in $CDCl_3$ at 23 °C.

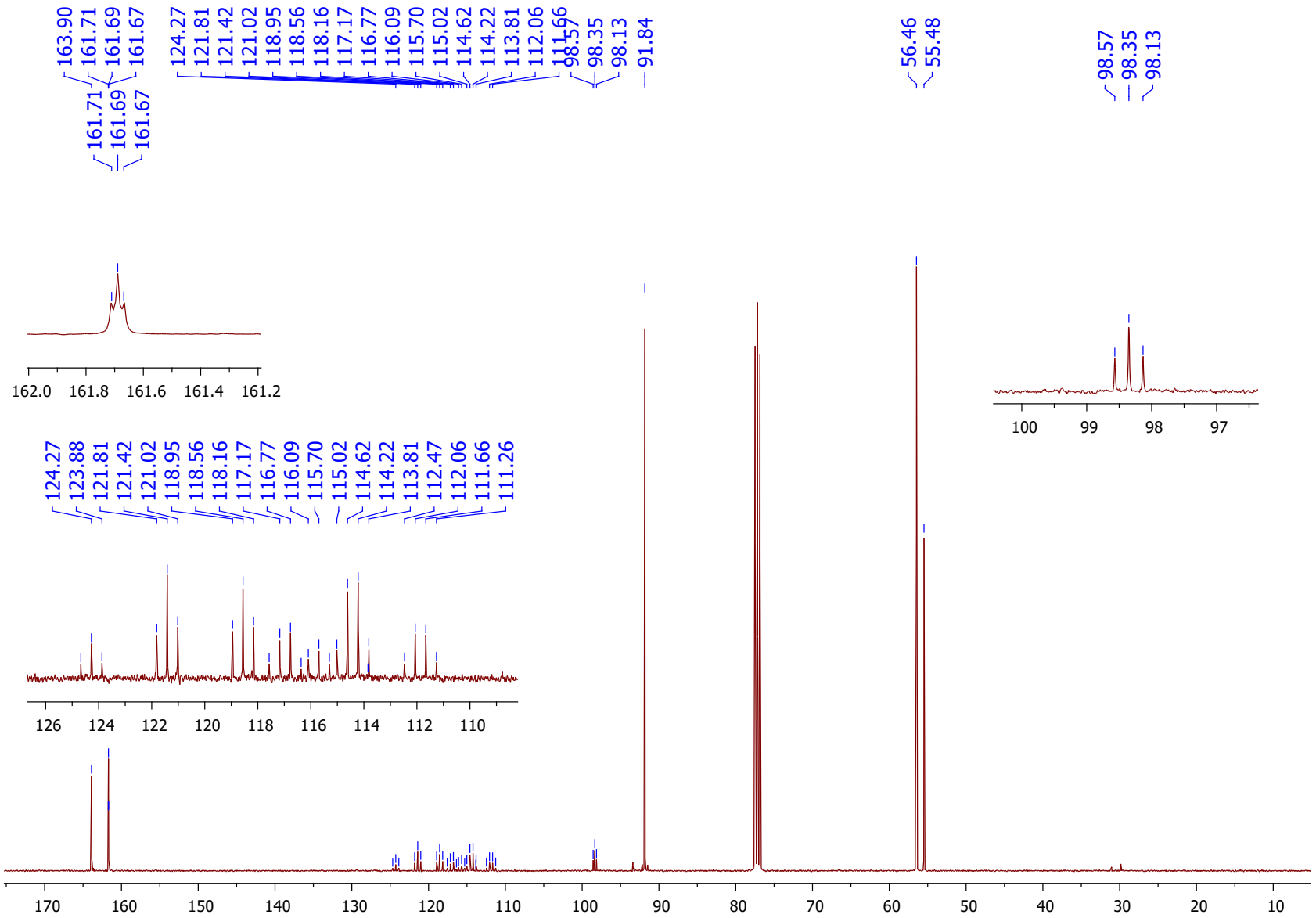


Figure S81. ^{13}C NMR spectrum of **a** in $CDCl_3$ at 23 °C.

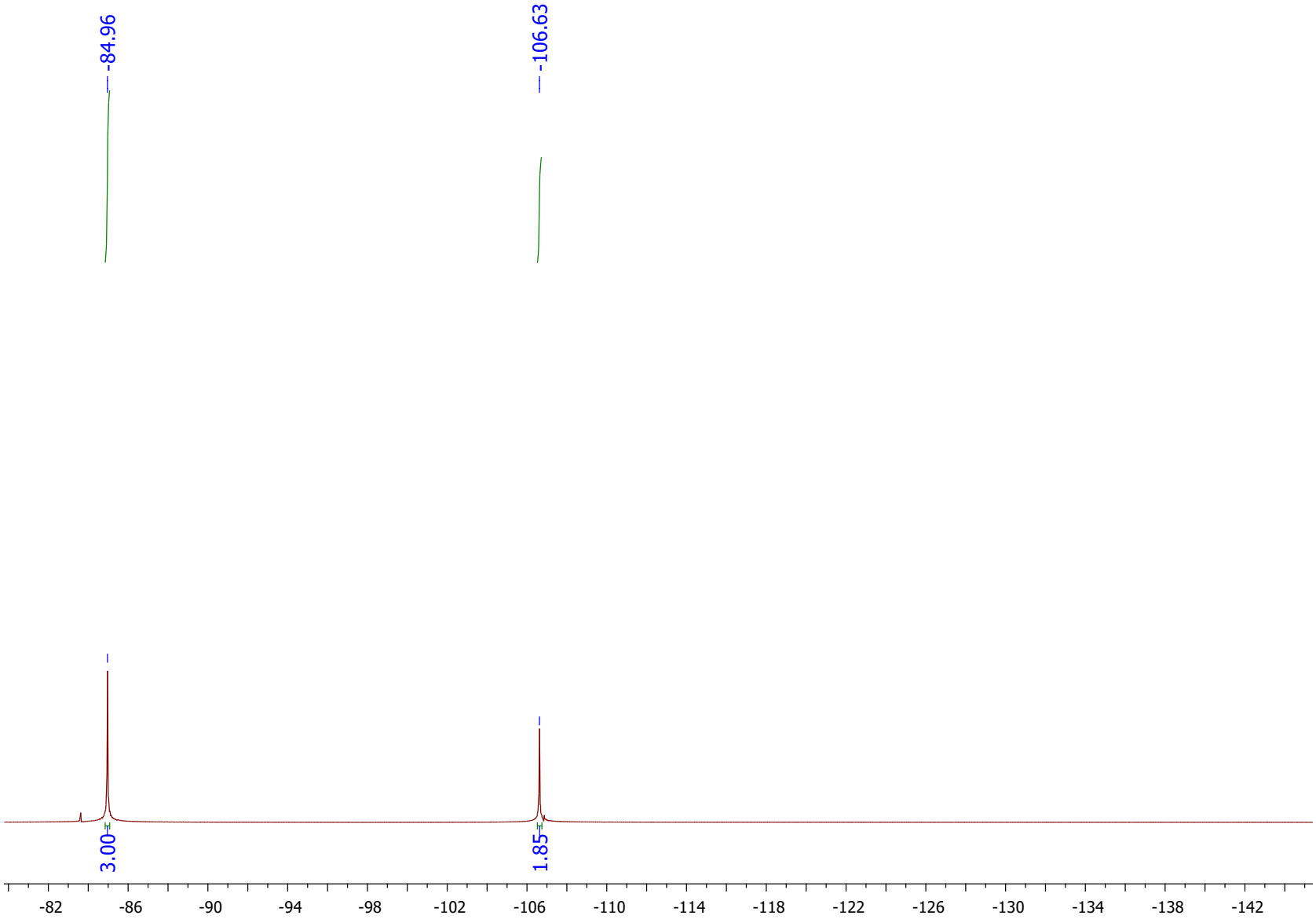


Figure S82. ^{19}F NMR spectrum of **a** in $CDCl_3$ at 23 °C.

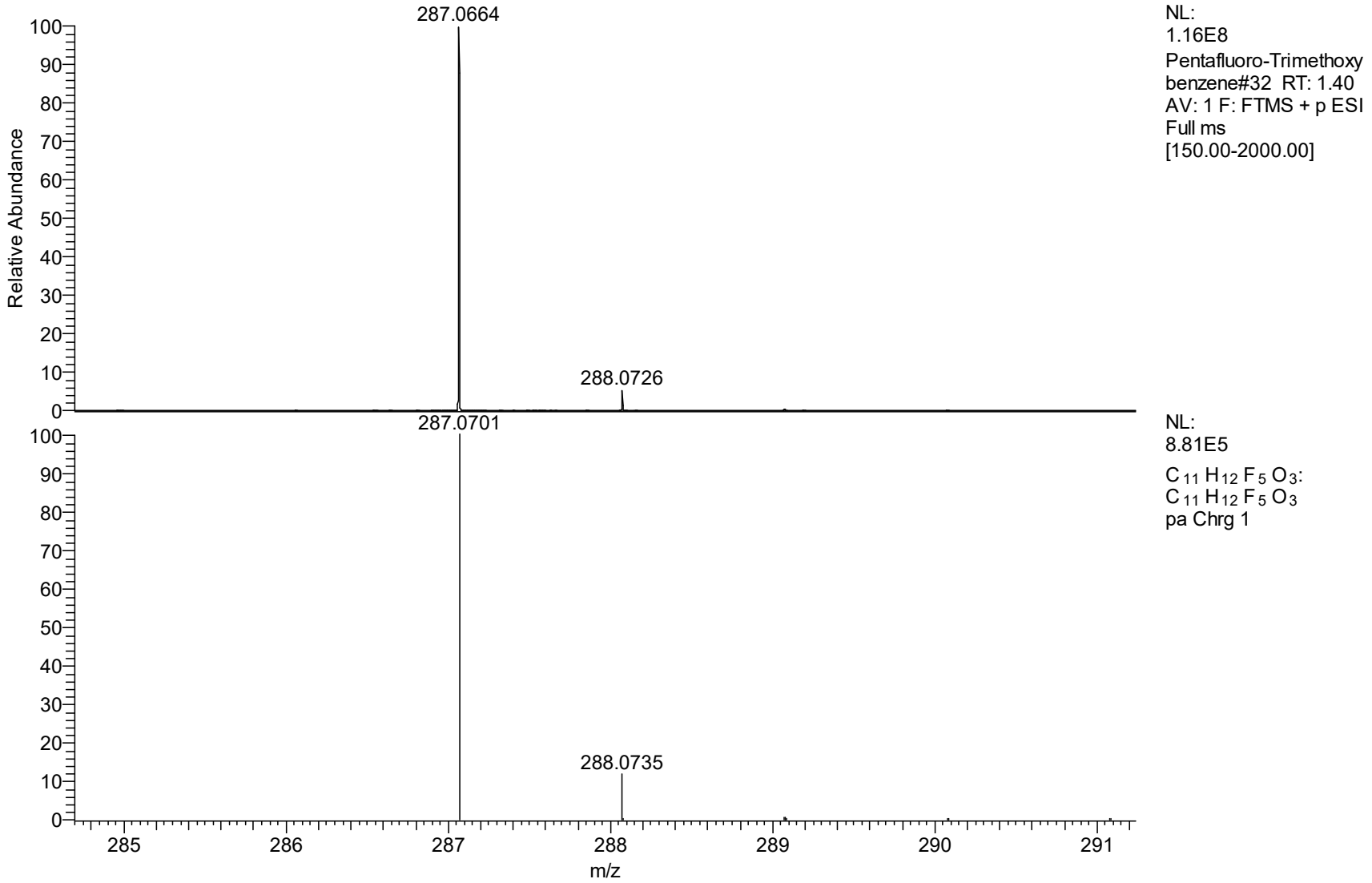


Figure S83. ESI-(HR)MS spectrum of a MeOH solution of **a**.

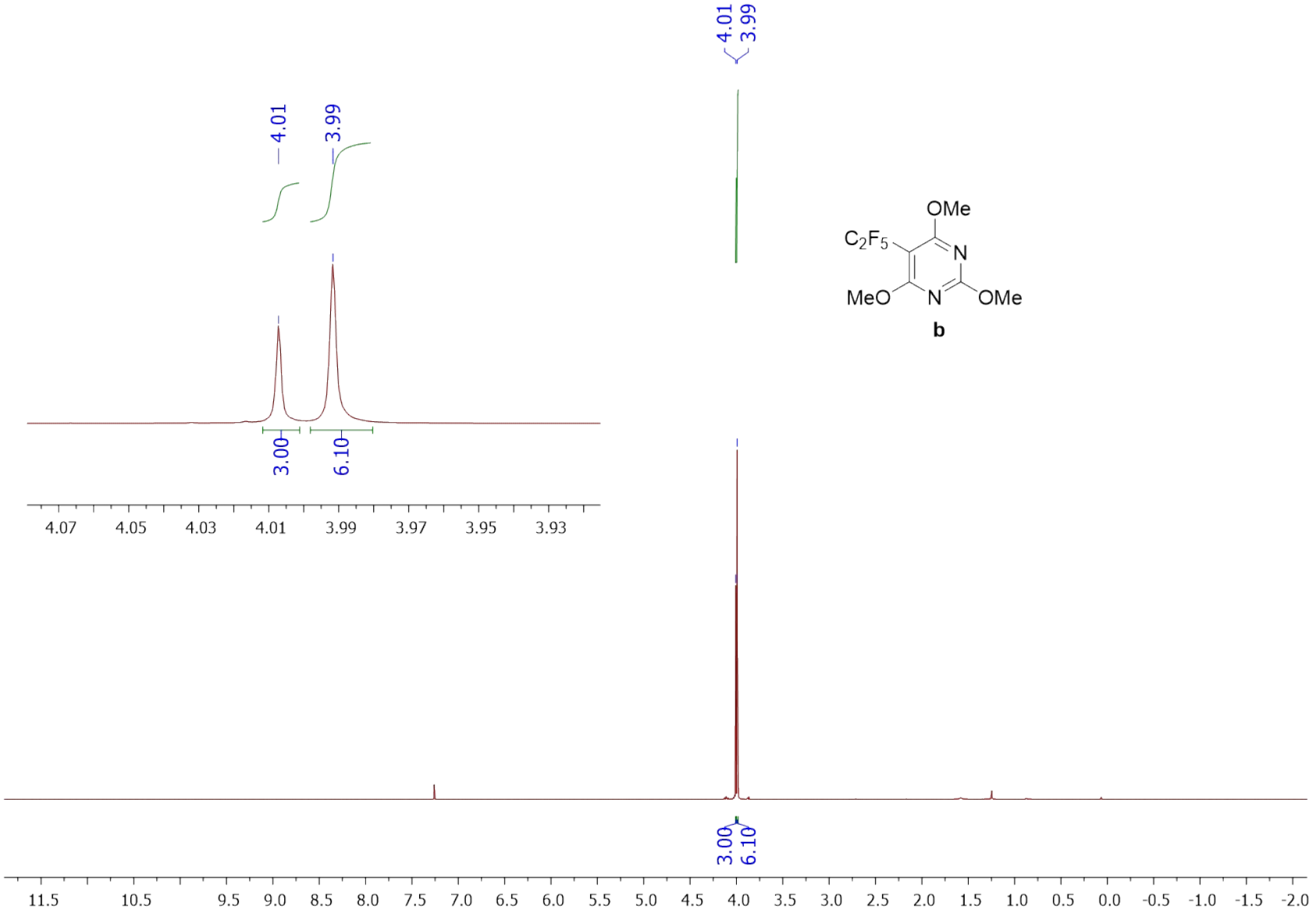


Figure S84. ^{1}H NMR spectrum of **b** in $CDCl_3$ at 23 °C.

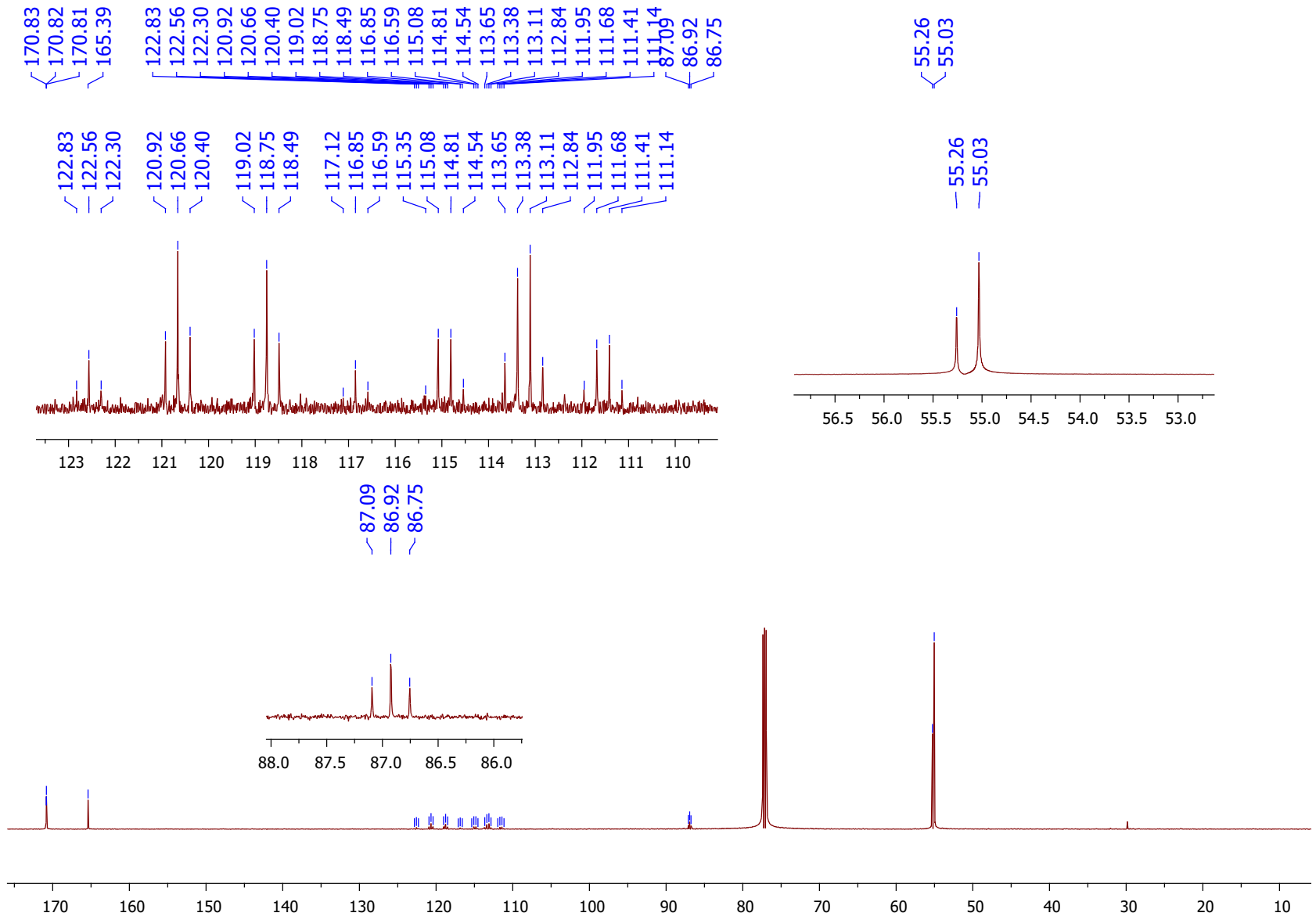


Figure S85. ^{13}C NMR spectrum of **b** in $CDCl_3$ at 23 °C.

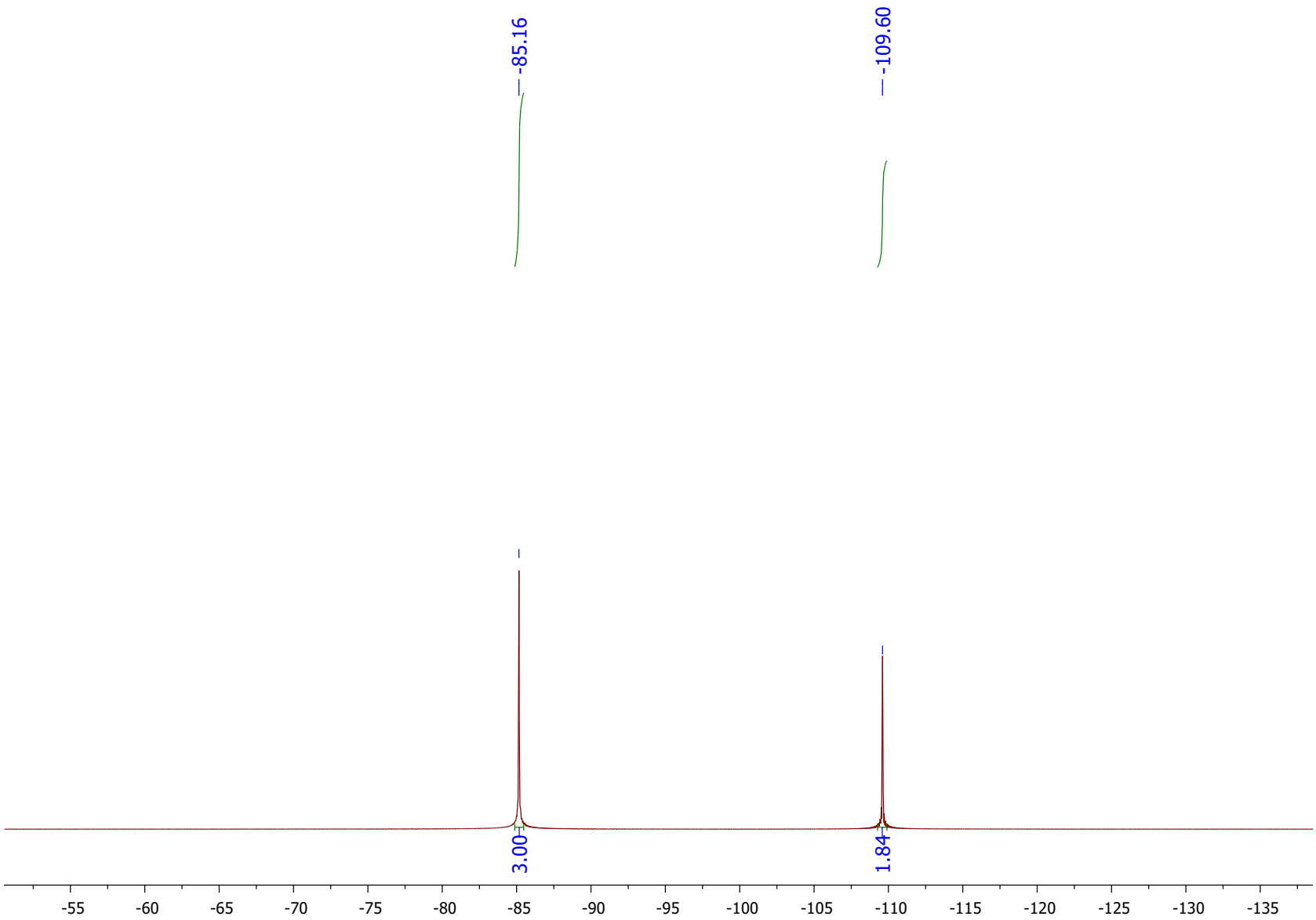


Figure S86. ^{19}F NMR spectrum of **b** in $CDCl_3$ at 23 °C.

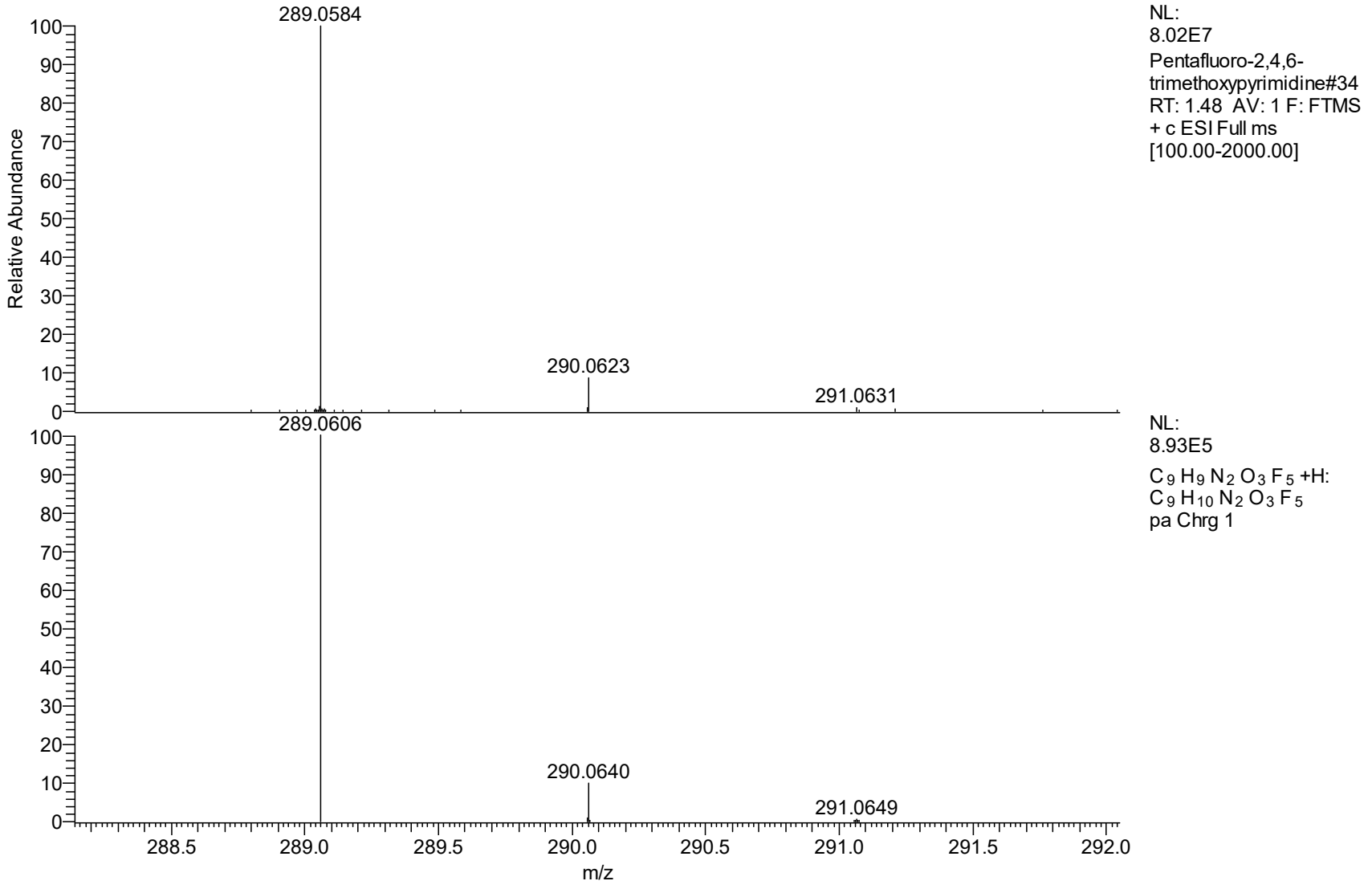


Figure S87. ESI-(HR)MS spectrum of a MeOH solution of **b**.

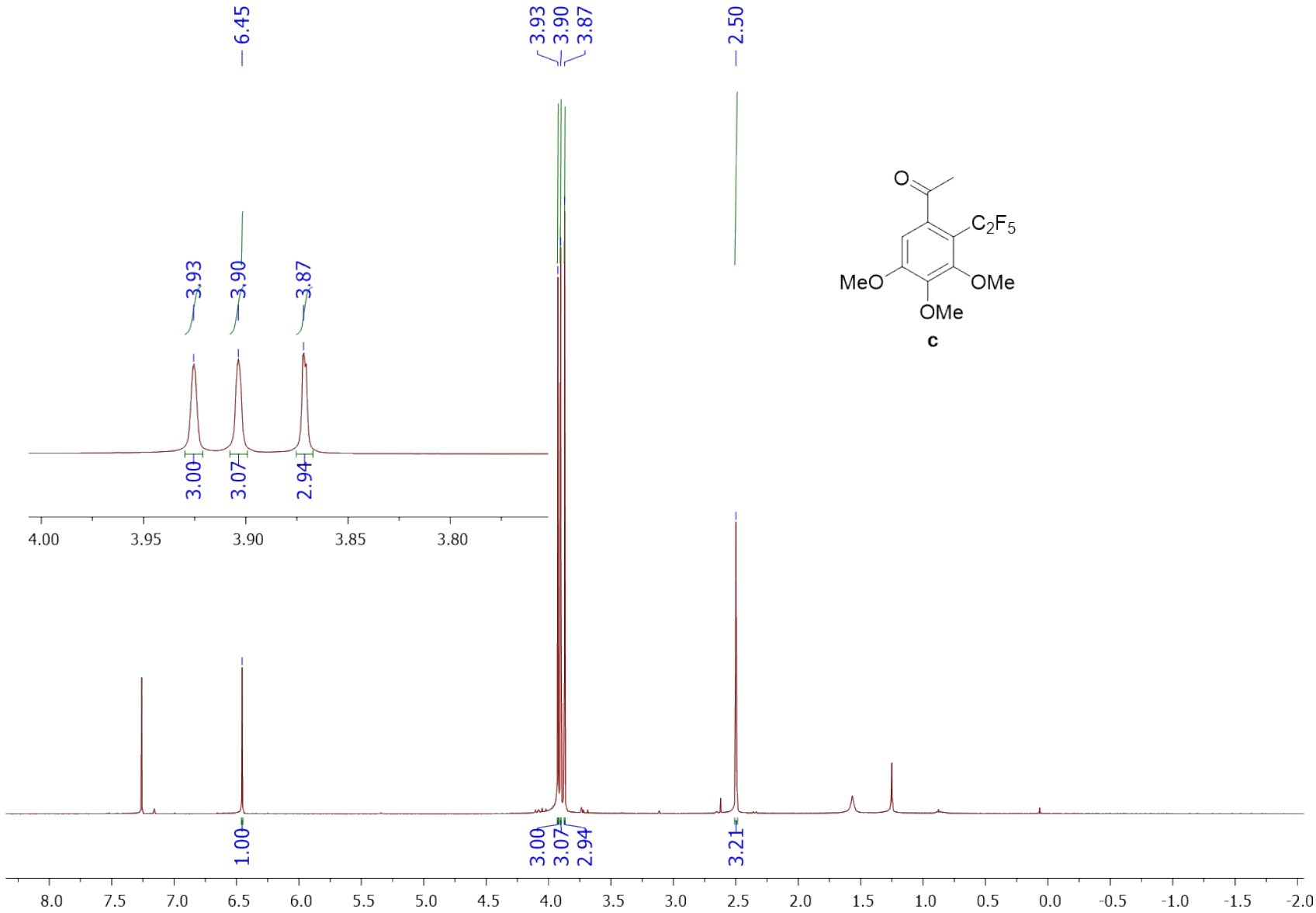


Figure S88. ^{1}H NMR spectrum of **c** in $CDCl_3$ at 23 °C.

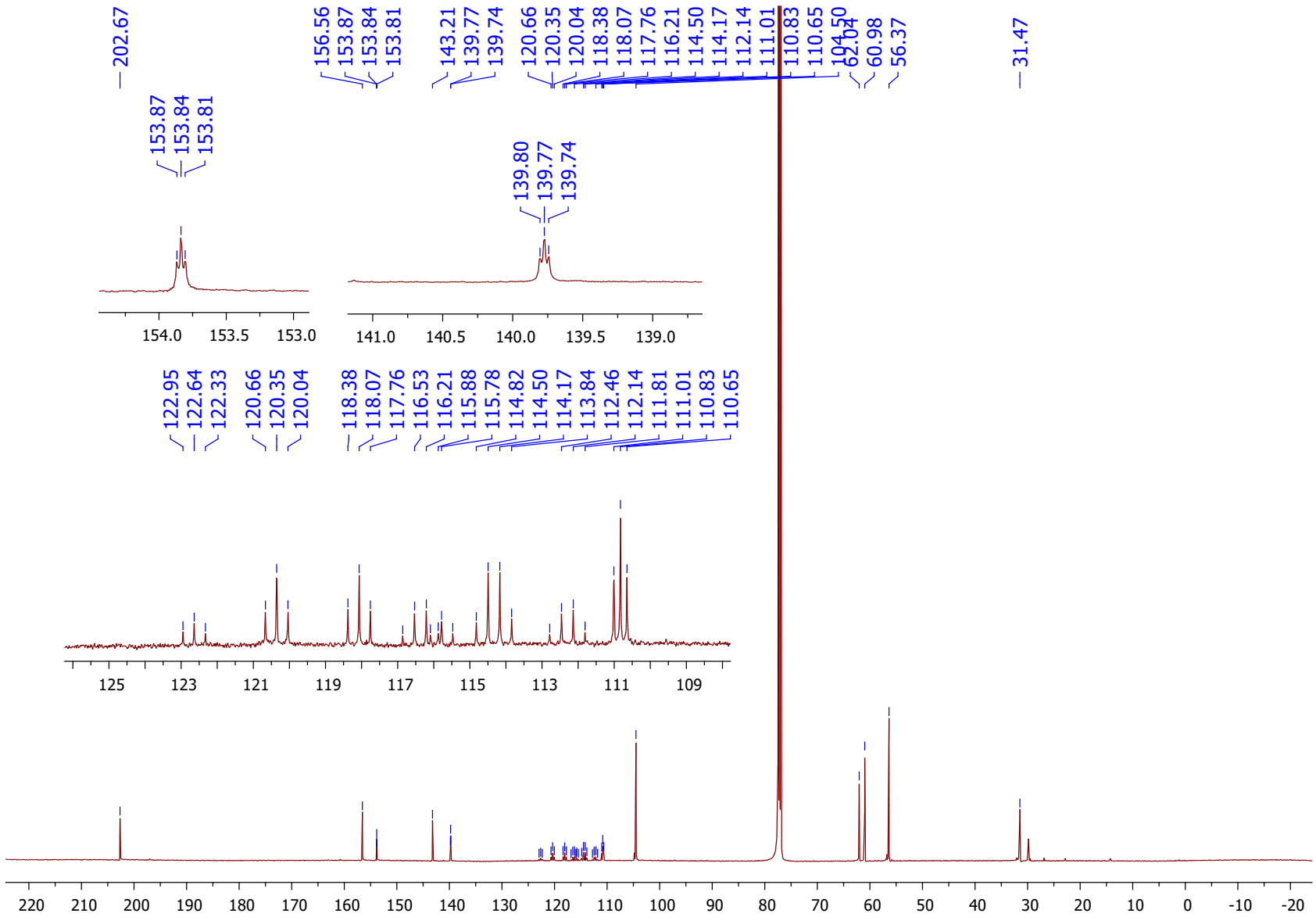


Figure S89. ^{13}C NMR spectrum of **c** in $CDCl_3$ at 23 °C.

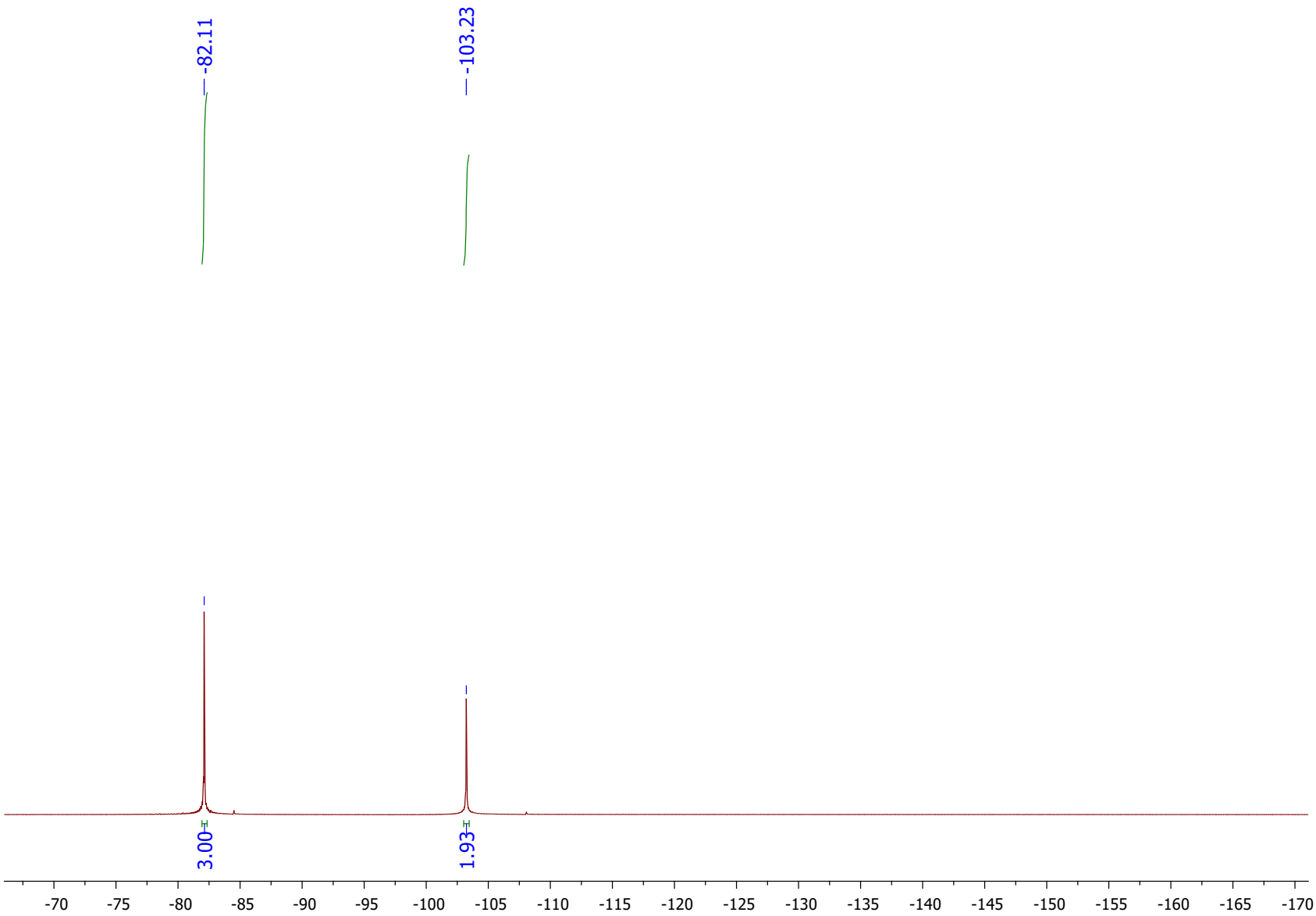


Figure S90. ^{19}F NMR spectrum of **c** in $CDCl_3$ at 23 °C.

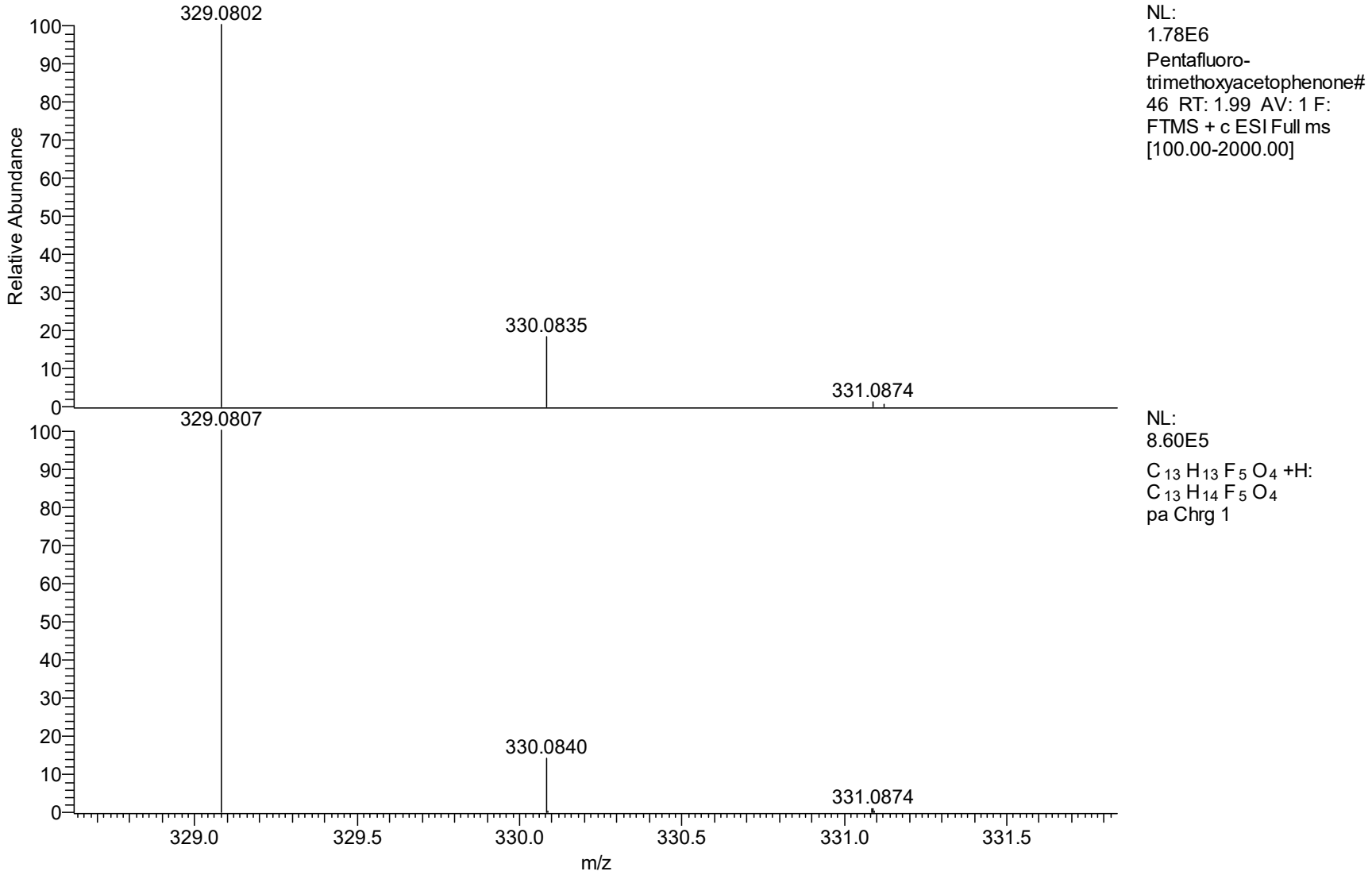


Figure S91. ESI-(HR)MS spectrum of a MeOH solution of **c**

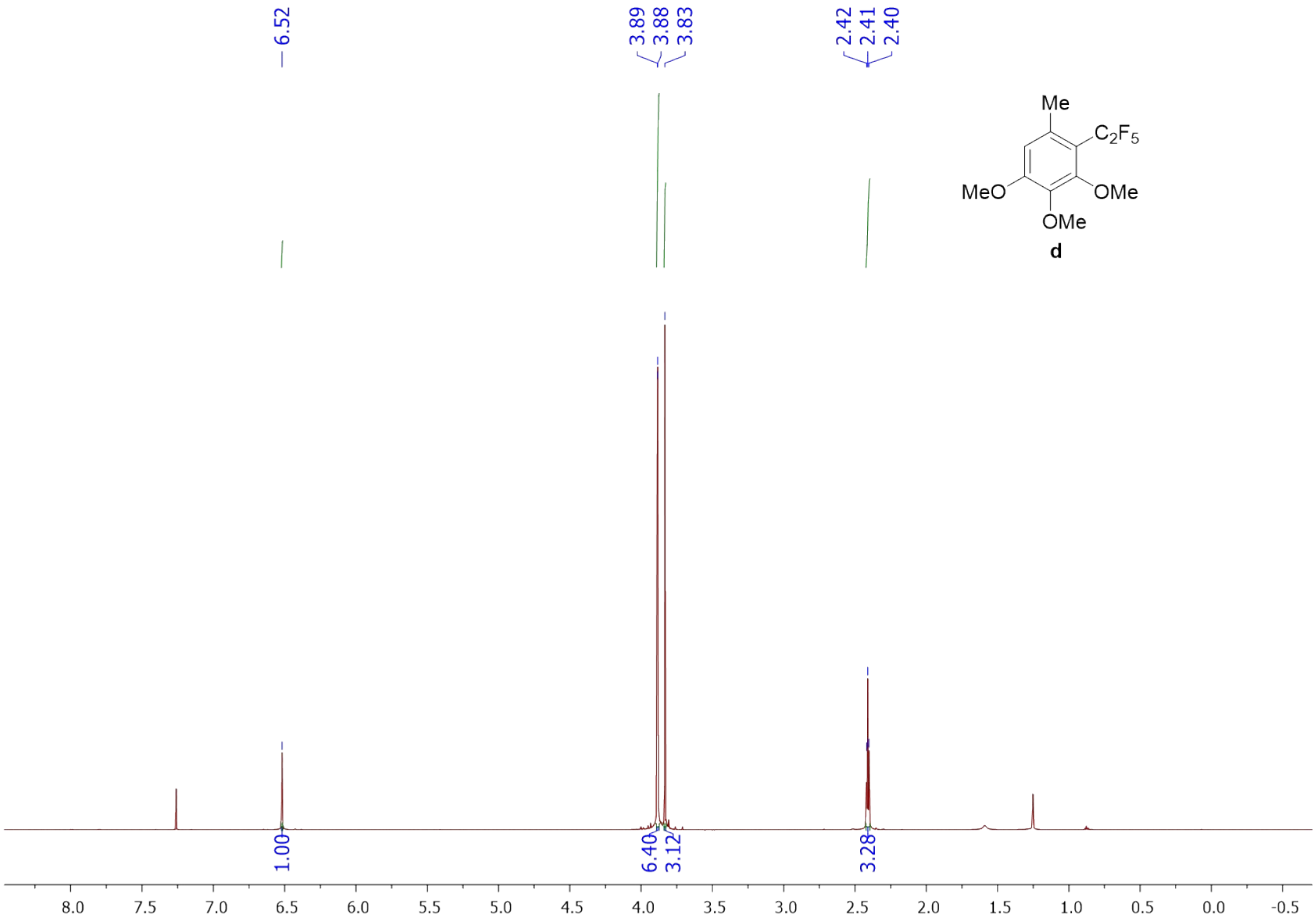


Figure S92. ^{1}H NMR spectrum of **d** in $CDCl_3$ at 23 °C.

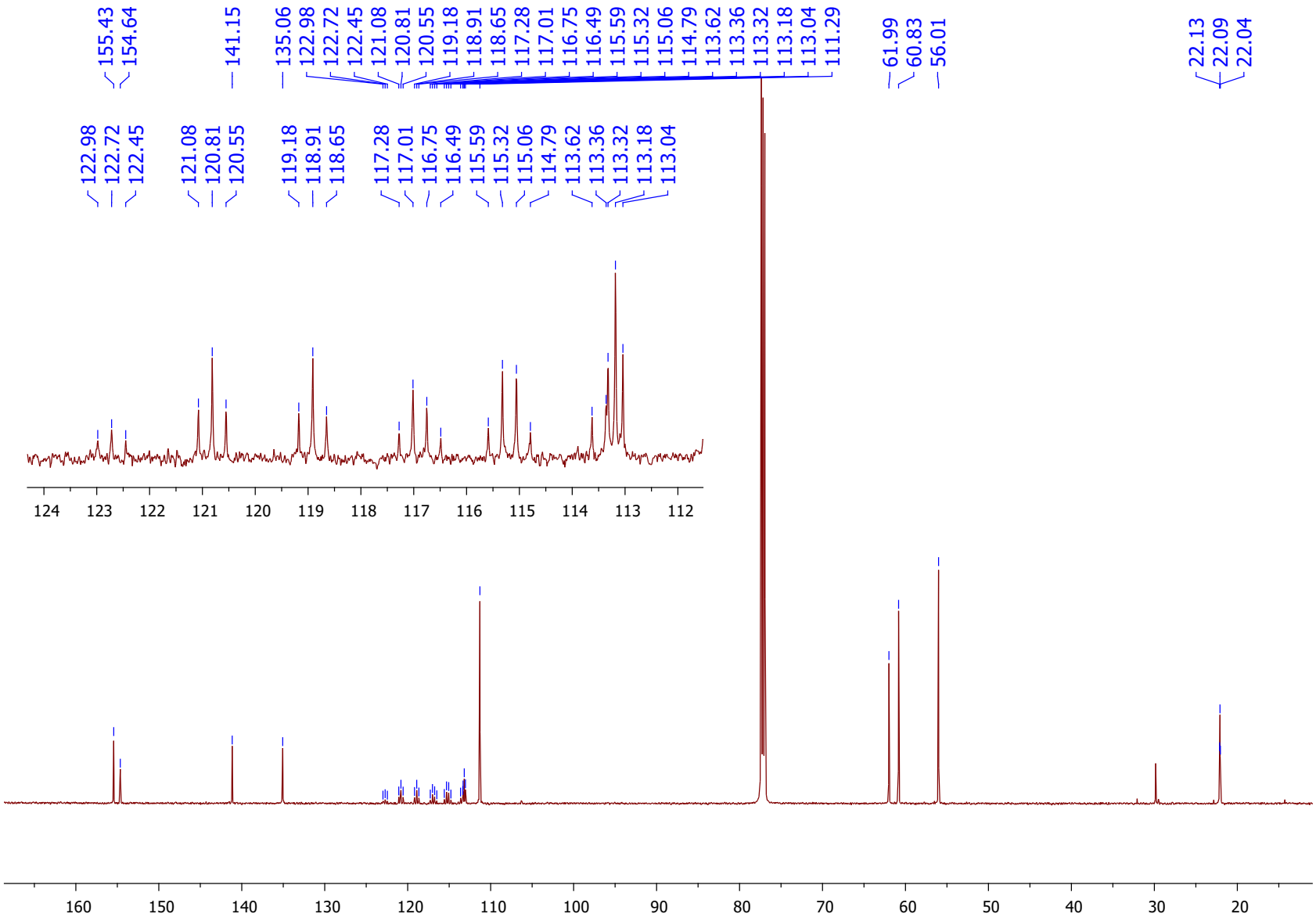


Figure S93. ^{13}C NMR spectrum of **d** in $CDCl_3$ at 23 °C.

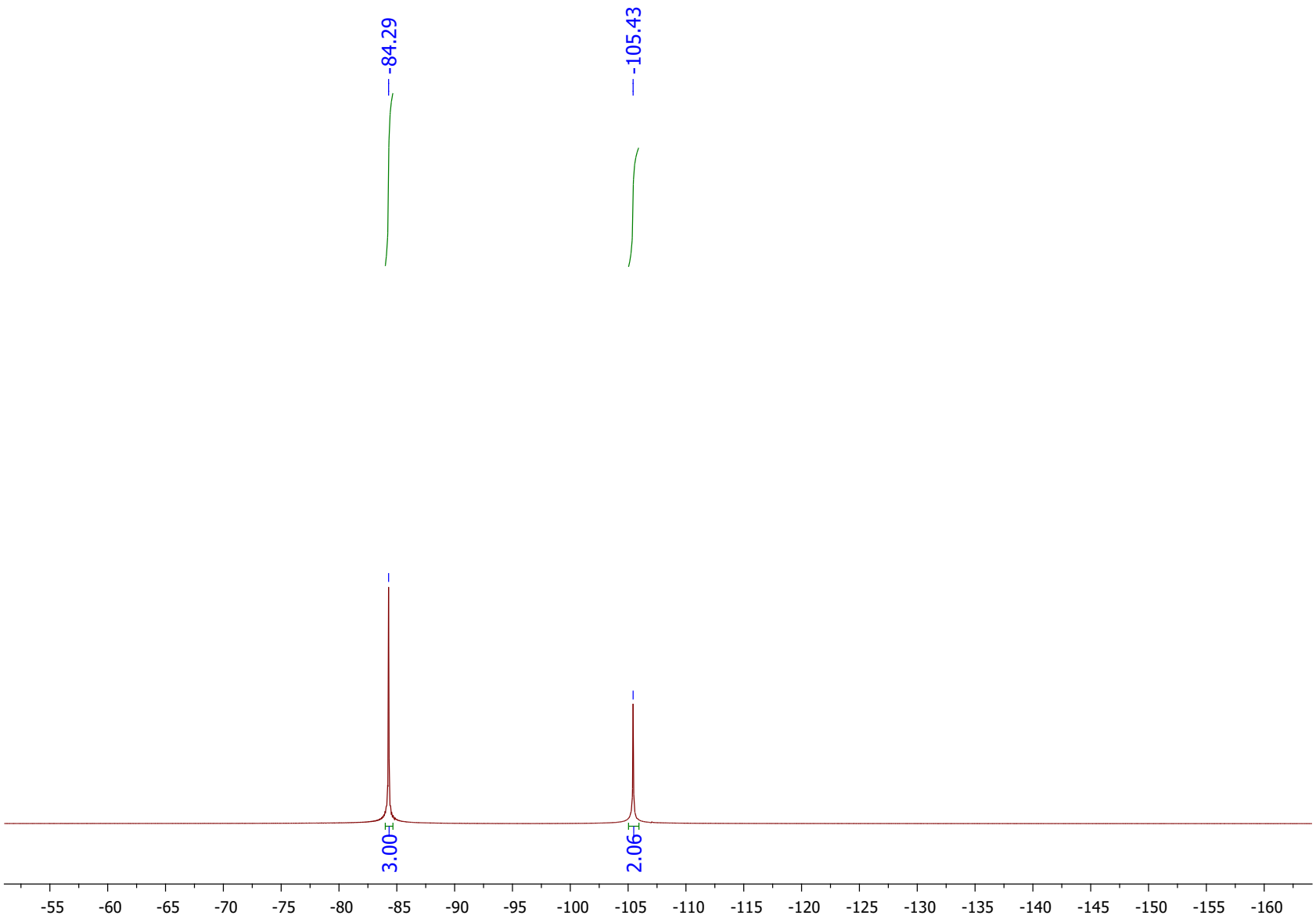


Figure S94. ^{19}F NMR spectrum of **d** in $CDCl_3$ at 23 °C.

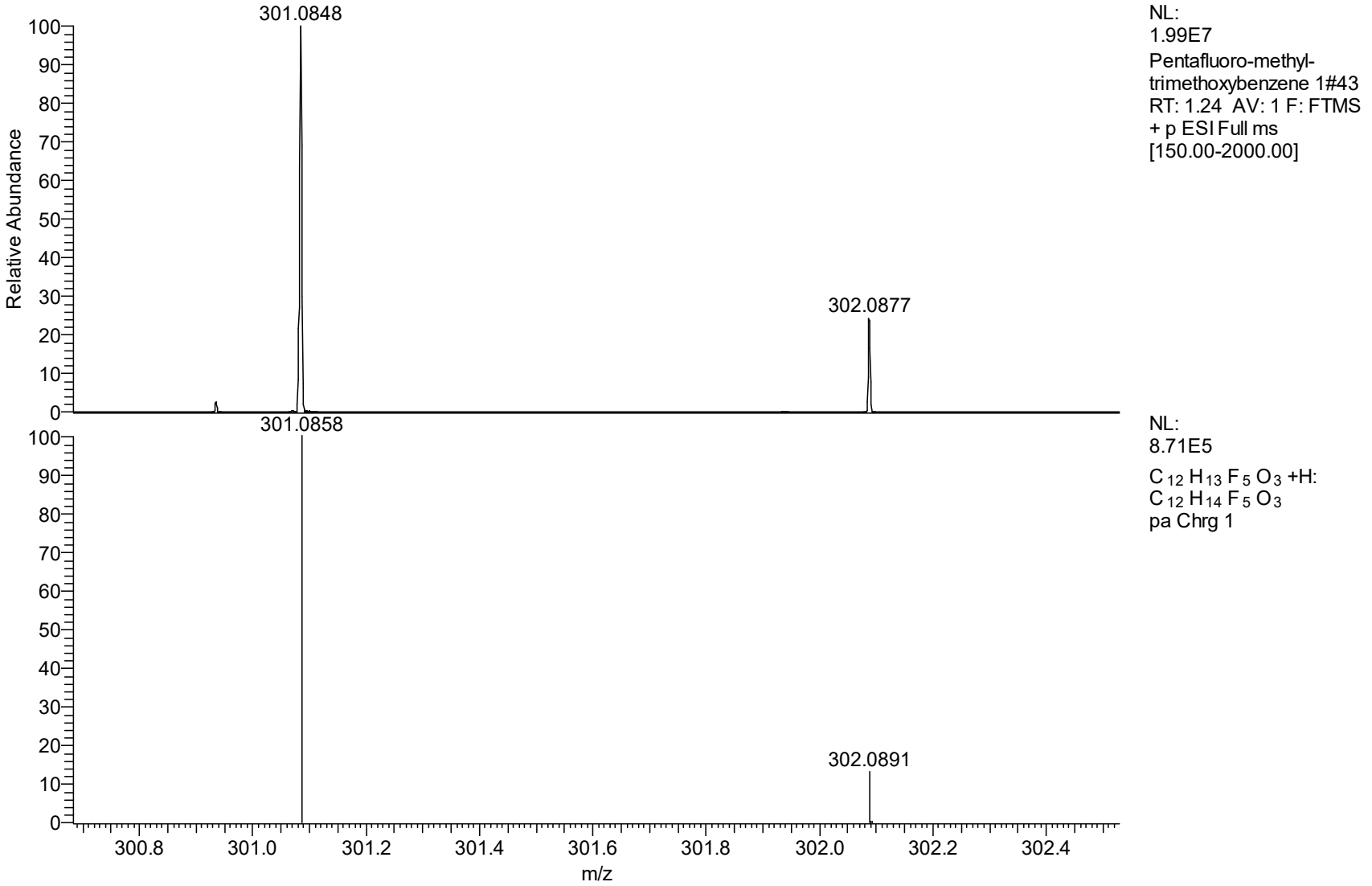


Figure S95. ESI-(HR)MS spectrum of a MeOH solution of **d.**

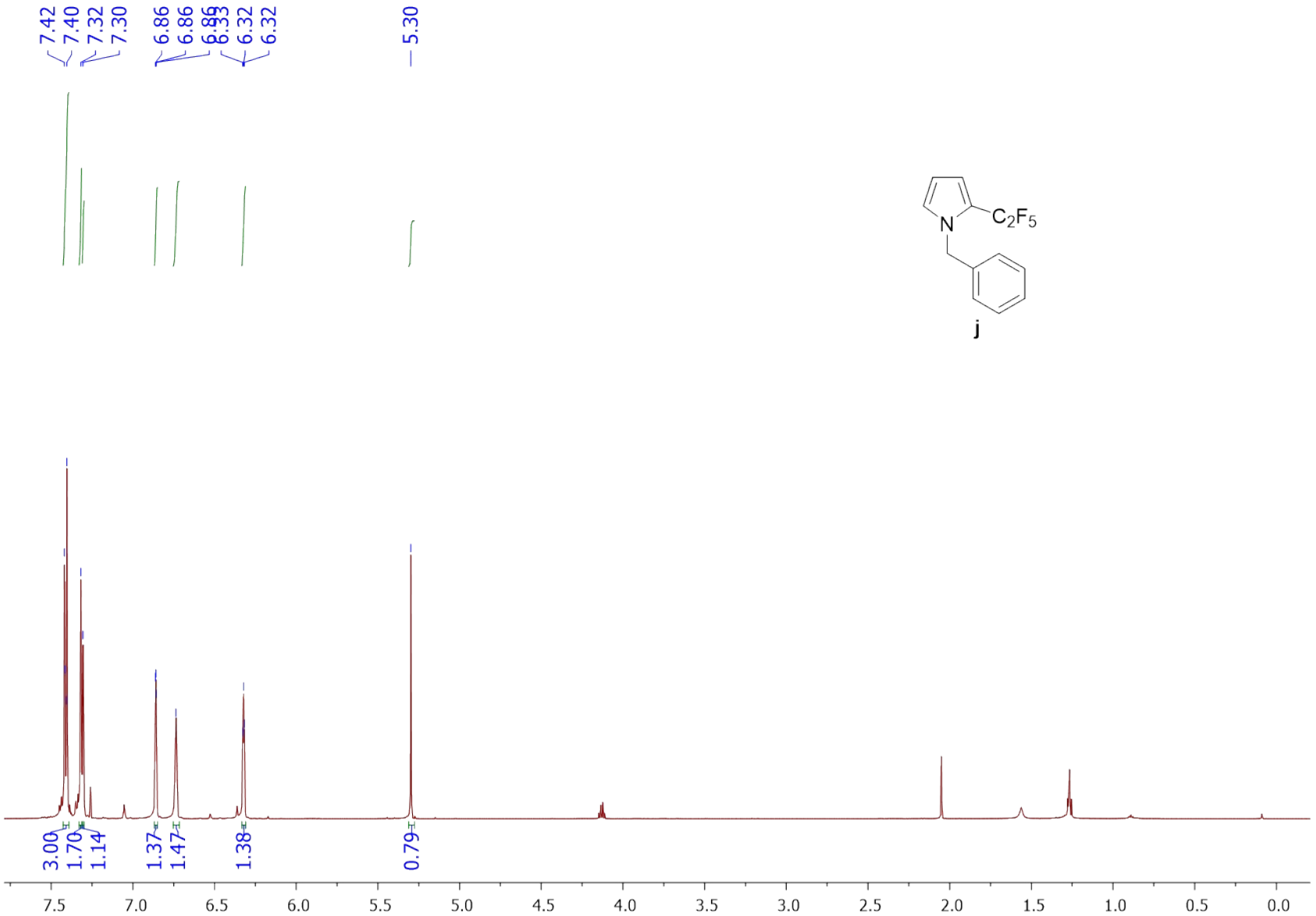


Figure S96. ^{1}H NMR spectrum of **j** in $CDCl_3$ at 23 °C. Remnant ethyl acetate solvent peaks at 1.26, 2.05, and 4.12.

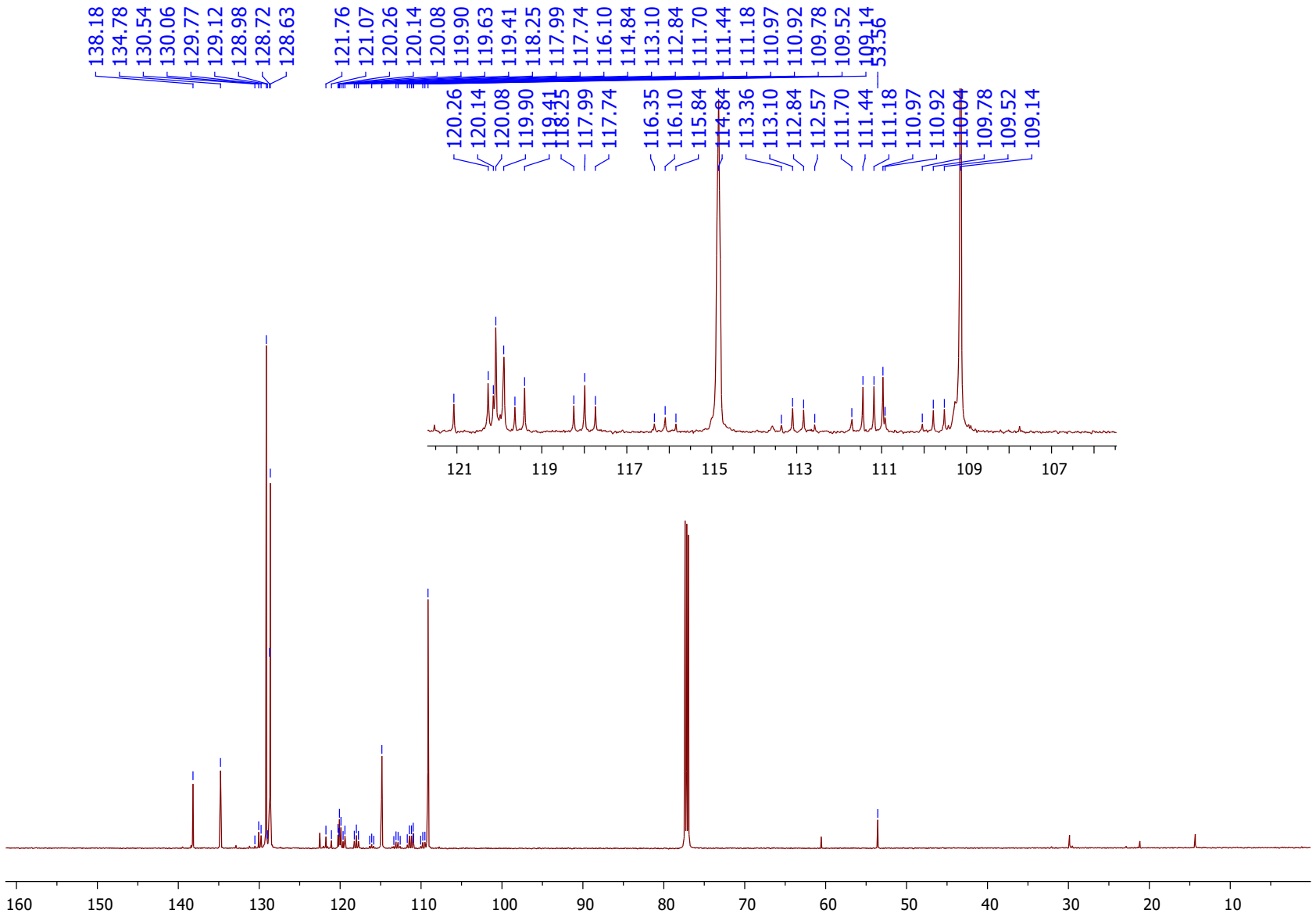


Figure S97. ^{13}C NMR spectrum of **j** in $CDCl_3$ at 23 °C. Remnant ethyl acetate solvent peaks at 14.2, 21.0, 60.5, and 171.4.

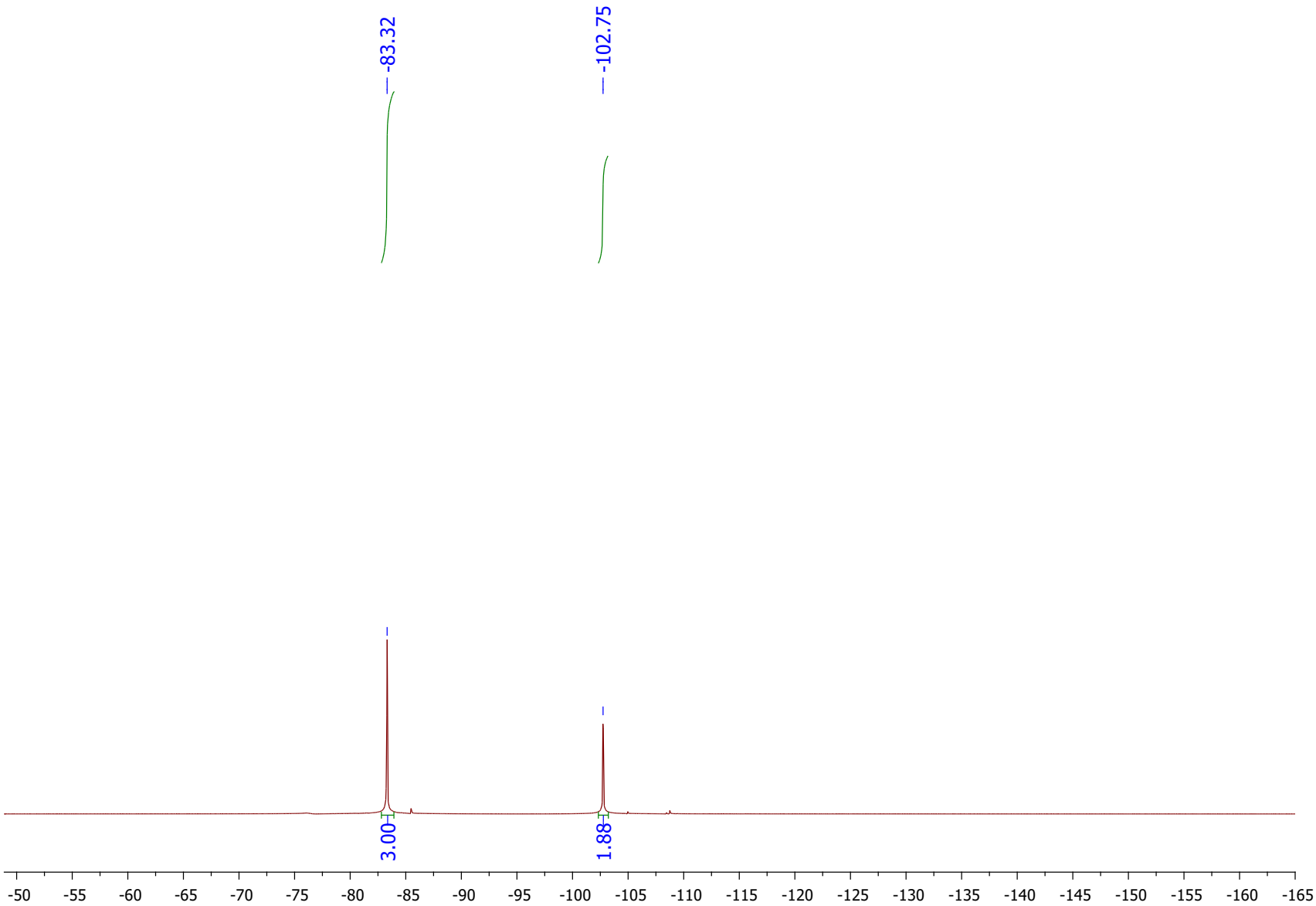


Figure S98. ^{19}F NMR spectrum of **j** in $CDCl_3$ at 23 °C.

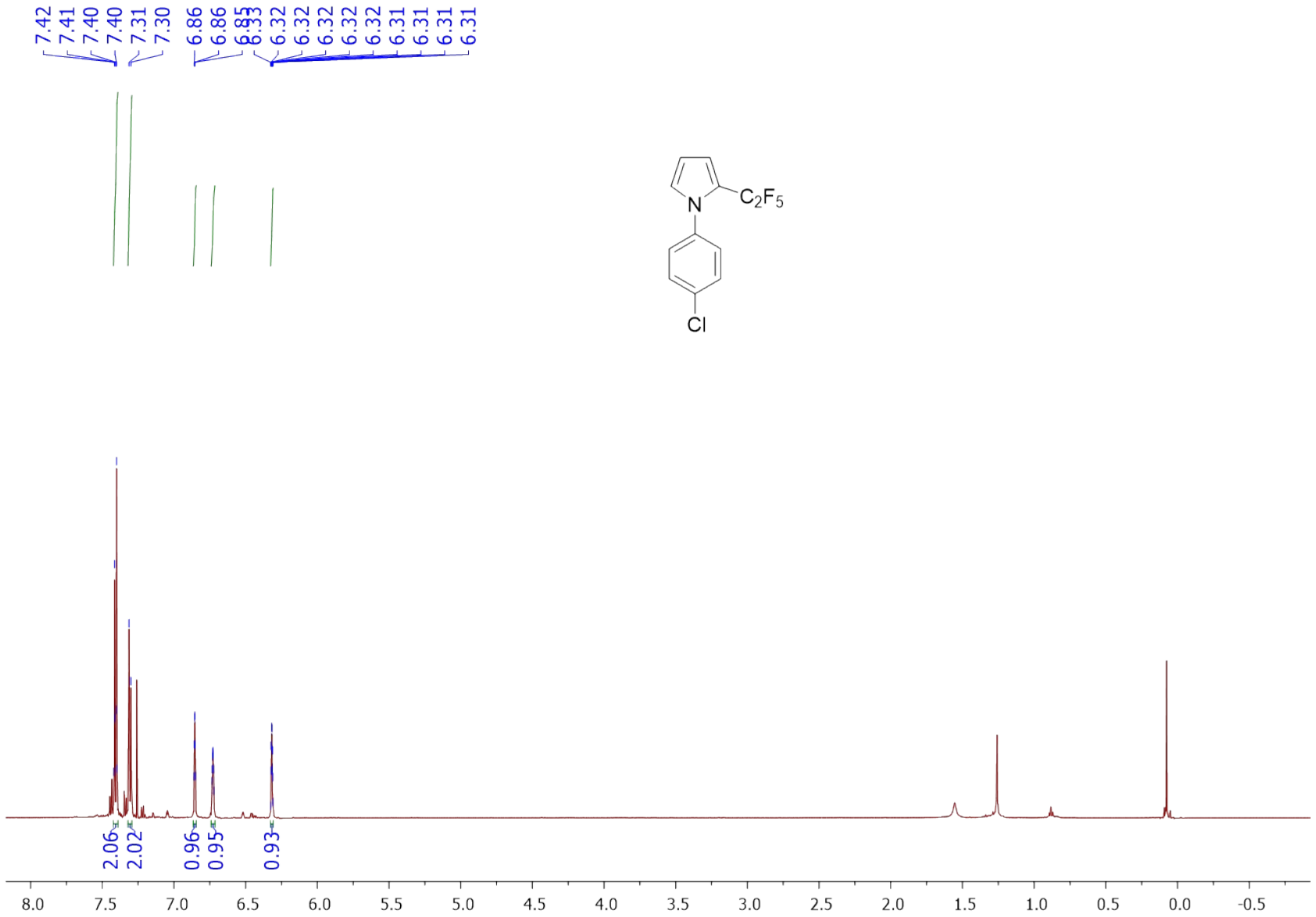


Figure S99. ^{1}H NMR spectrum of **k** in $CDCl_3$ at 23 °C.

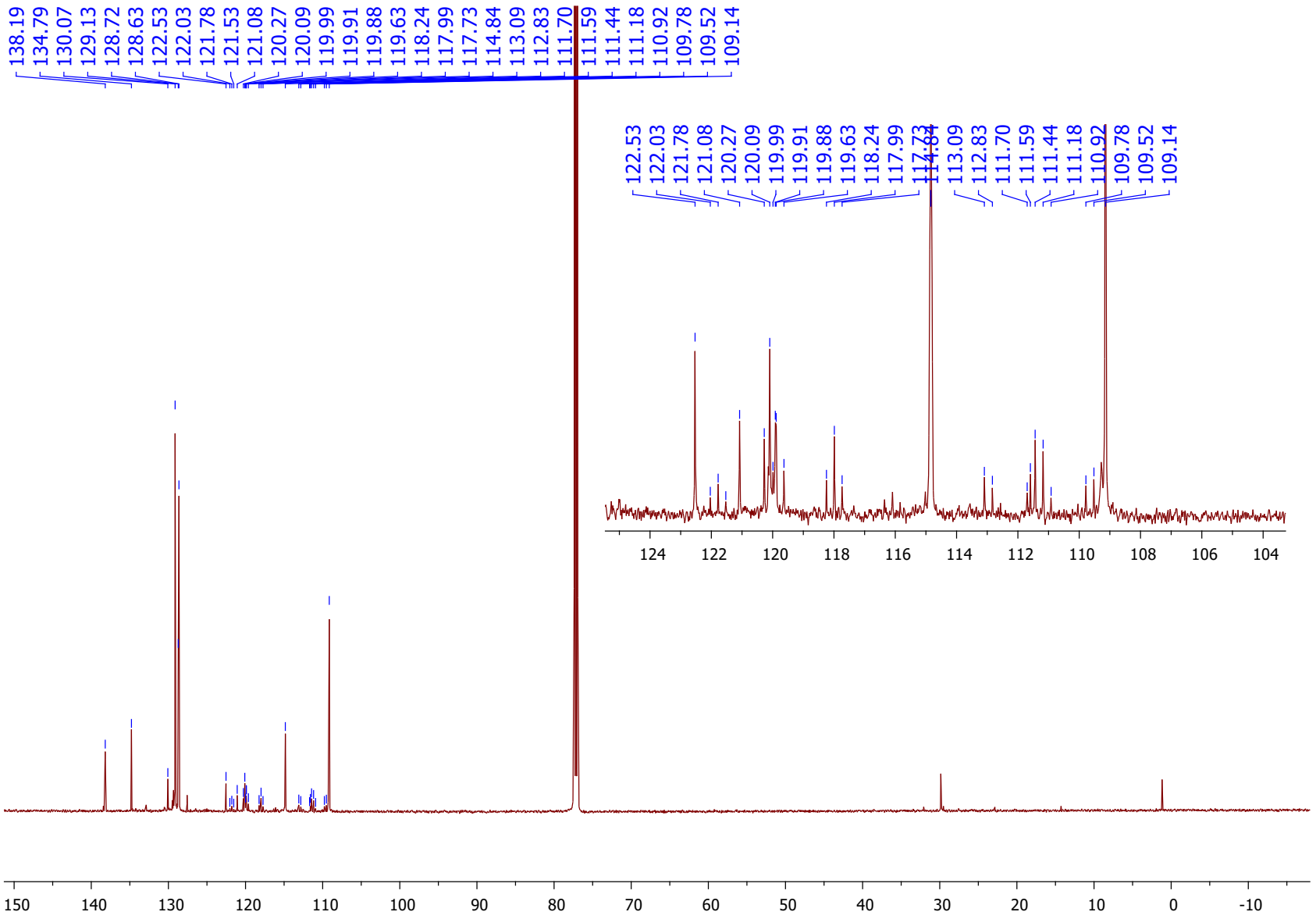


Figure S100. ^{13}C NMR spectrum of **k** in $CDCl_3$ at 23 °C.

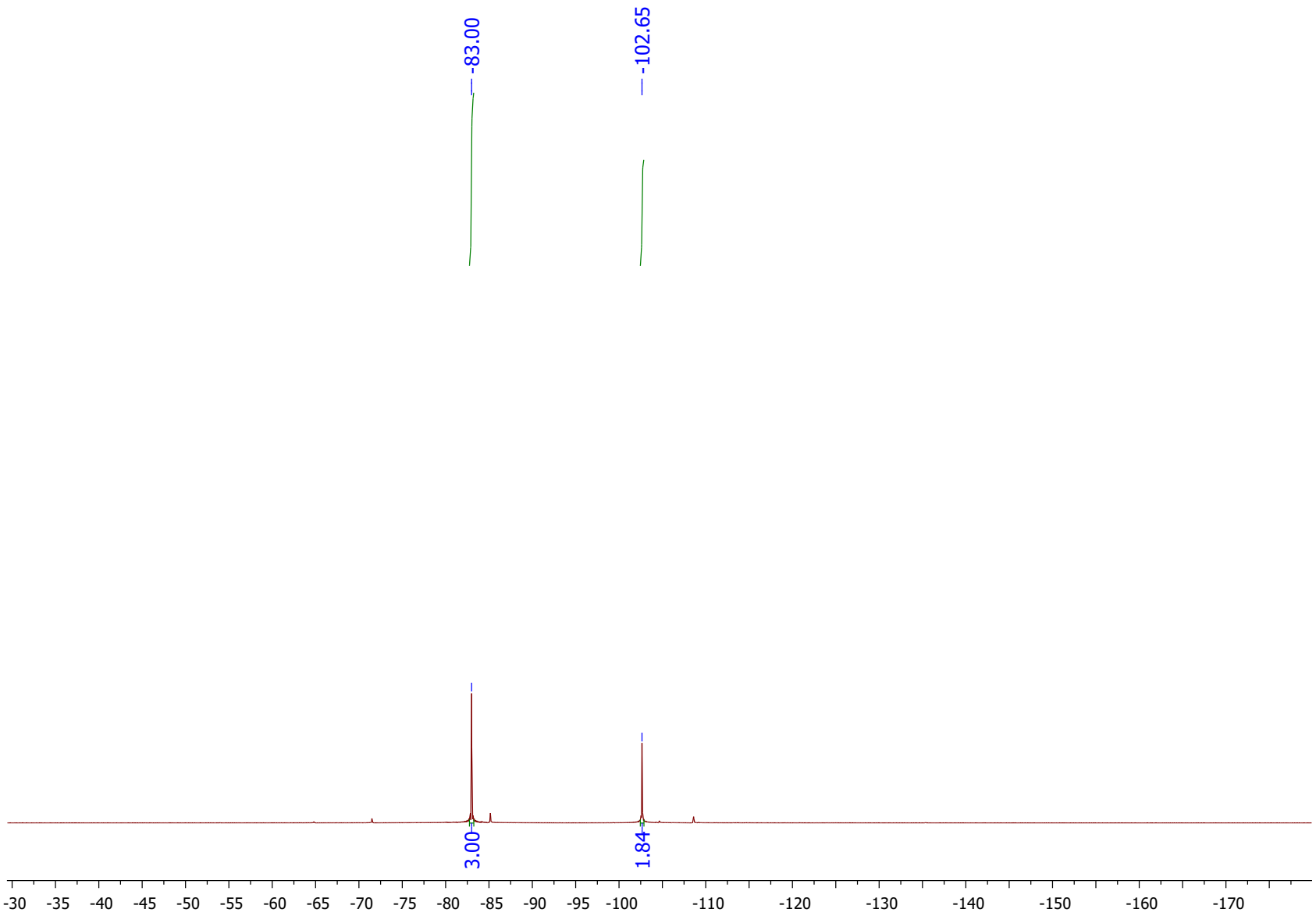


Figure S101. ^{19}F NMR spectrum of **k** in $CDCl_3$ at 23 °C.

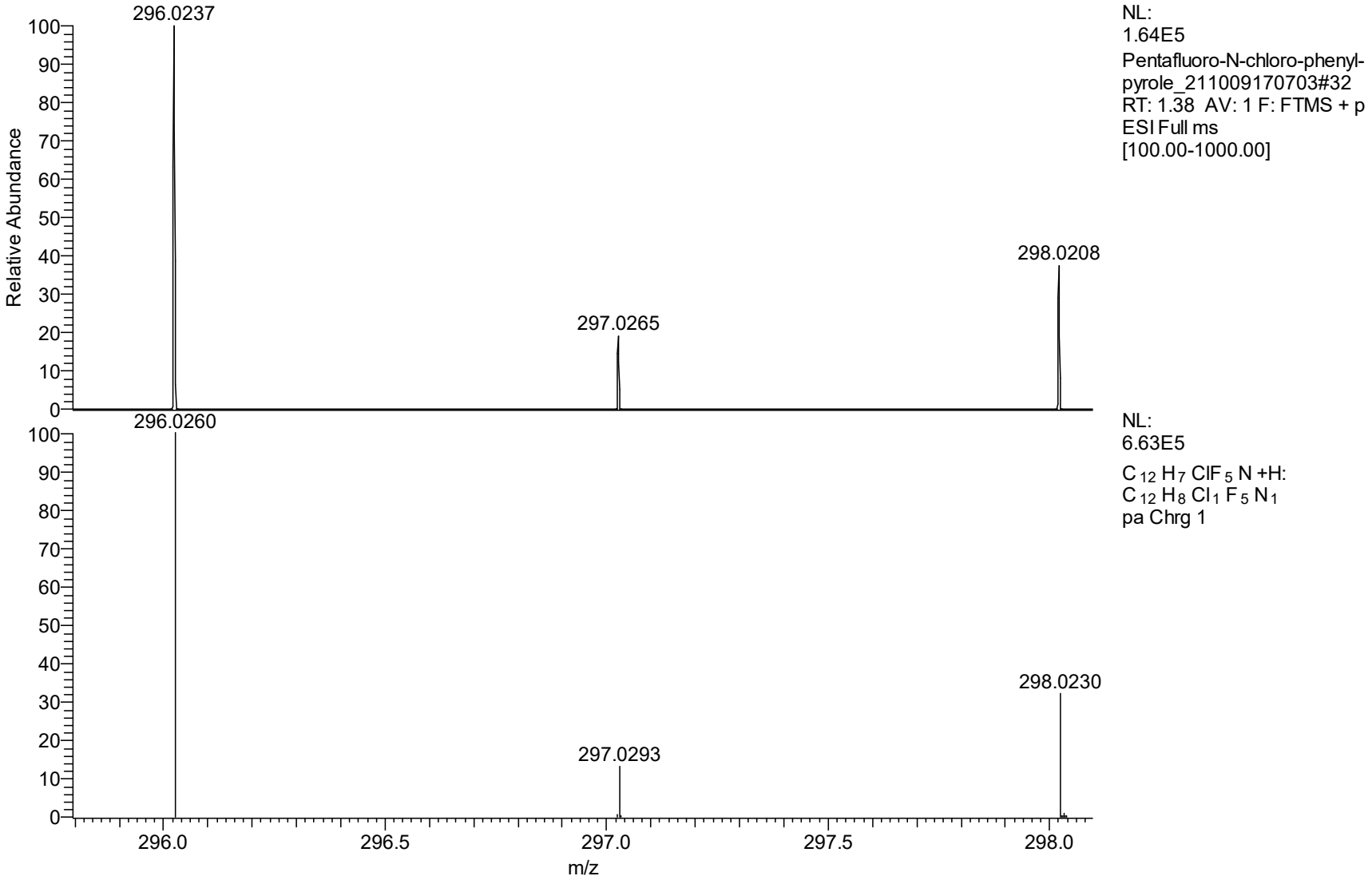


Figure S102. ESI-(HR)MS spectrum of a MeOH solution of **k.**

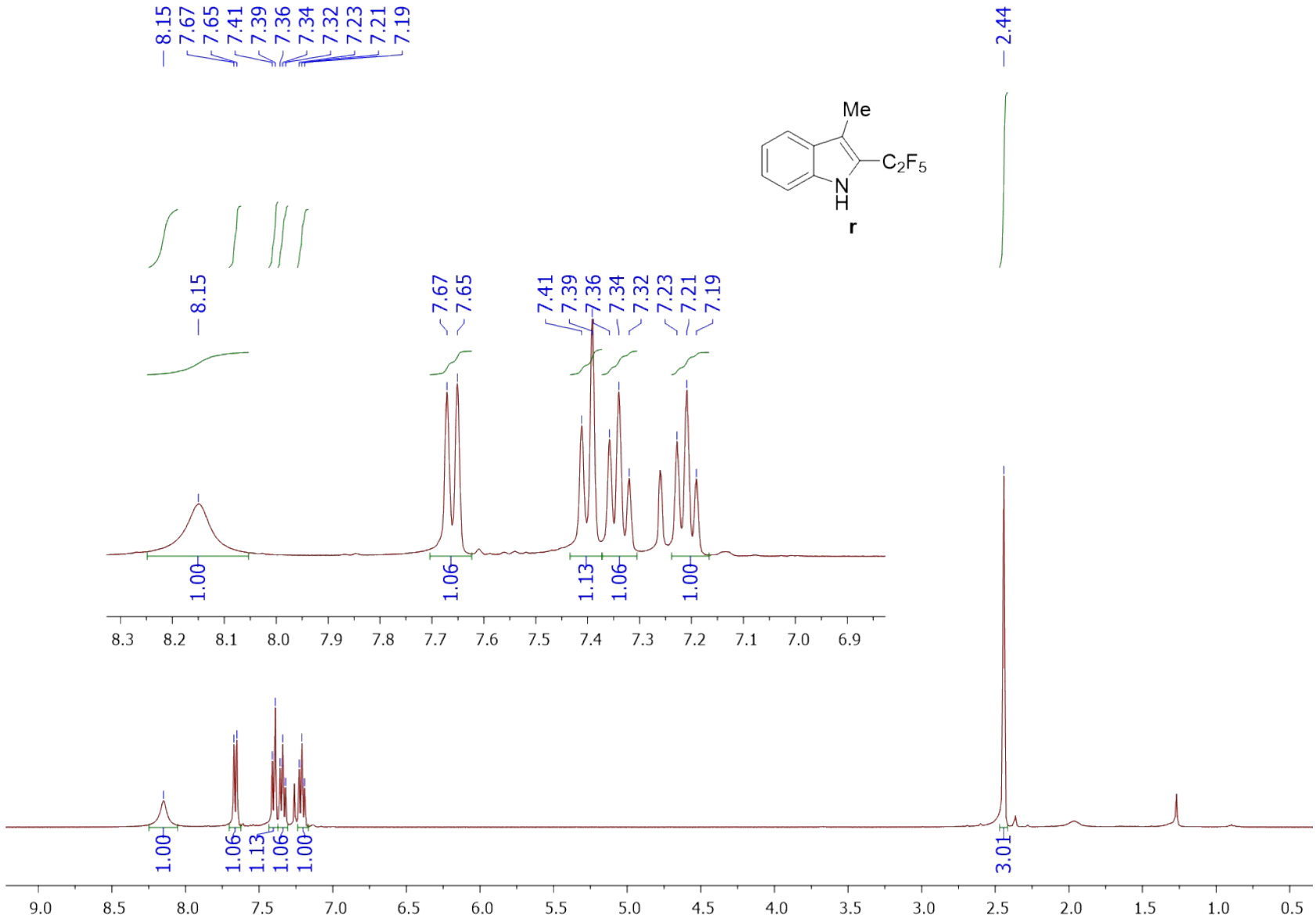


Figure S103. ^{1}H NMR spectrum of **r** in $CDCl_3$ at 23 °C.

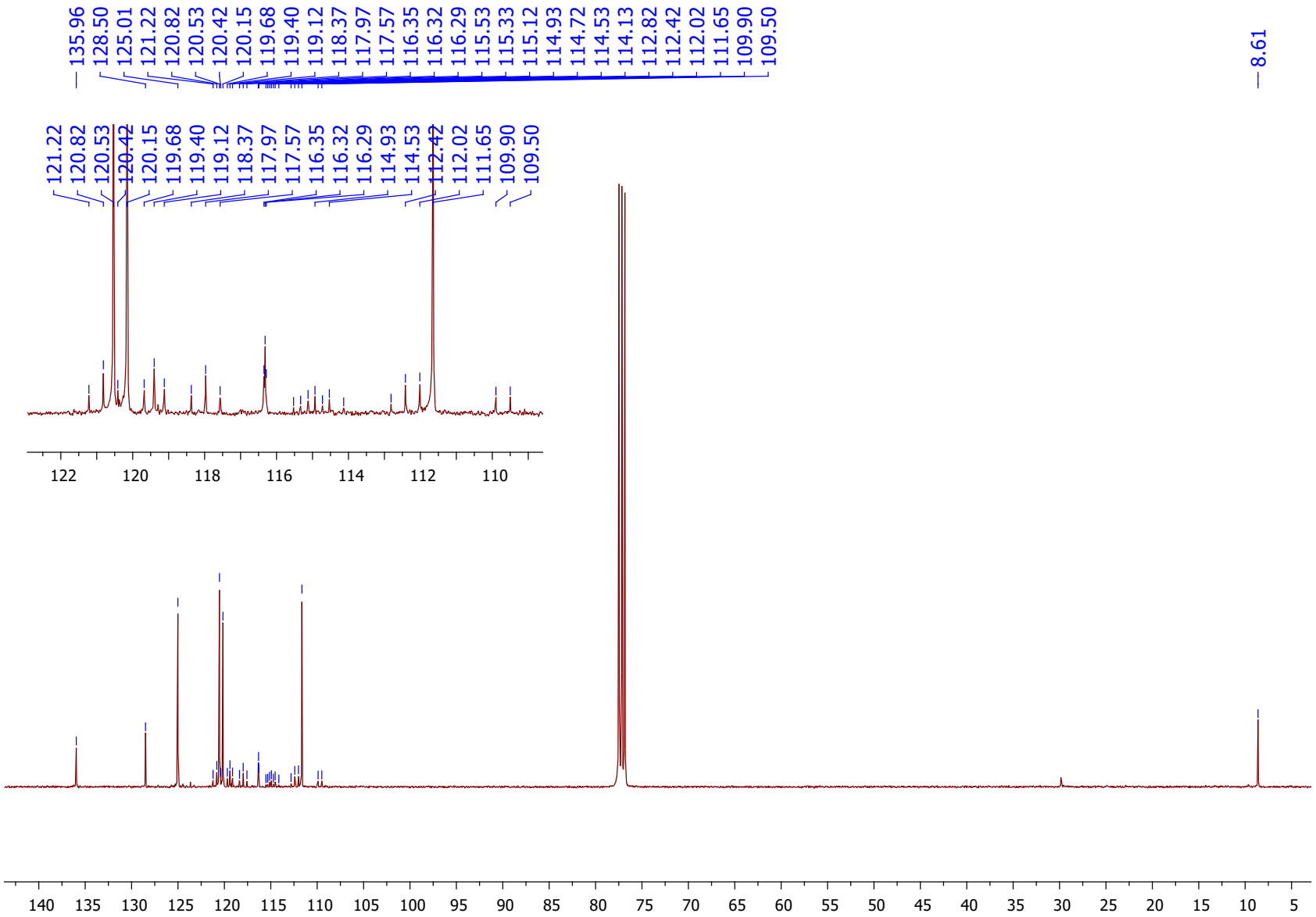


Figure S104. ^{13}C NMR spectrum of **r** in $CDCl_3$ at 23 °C.

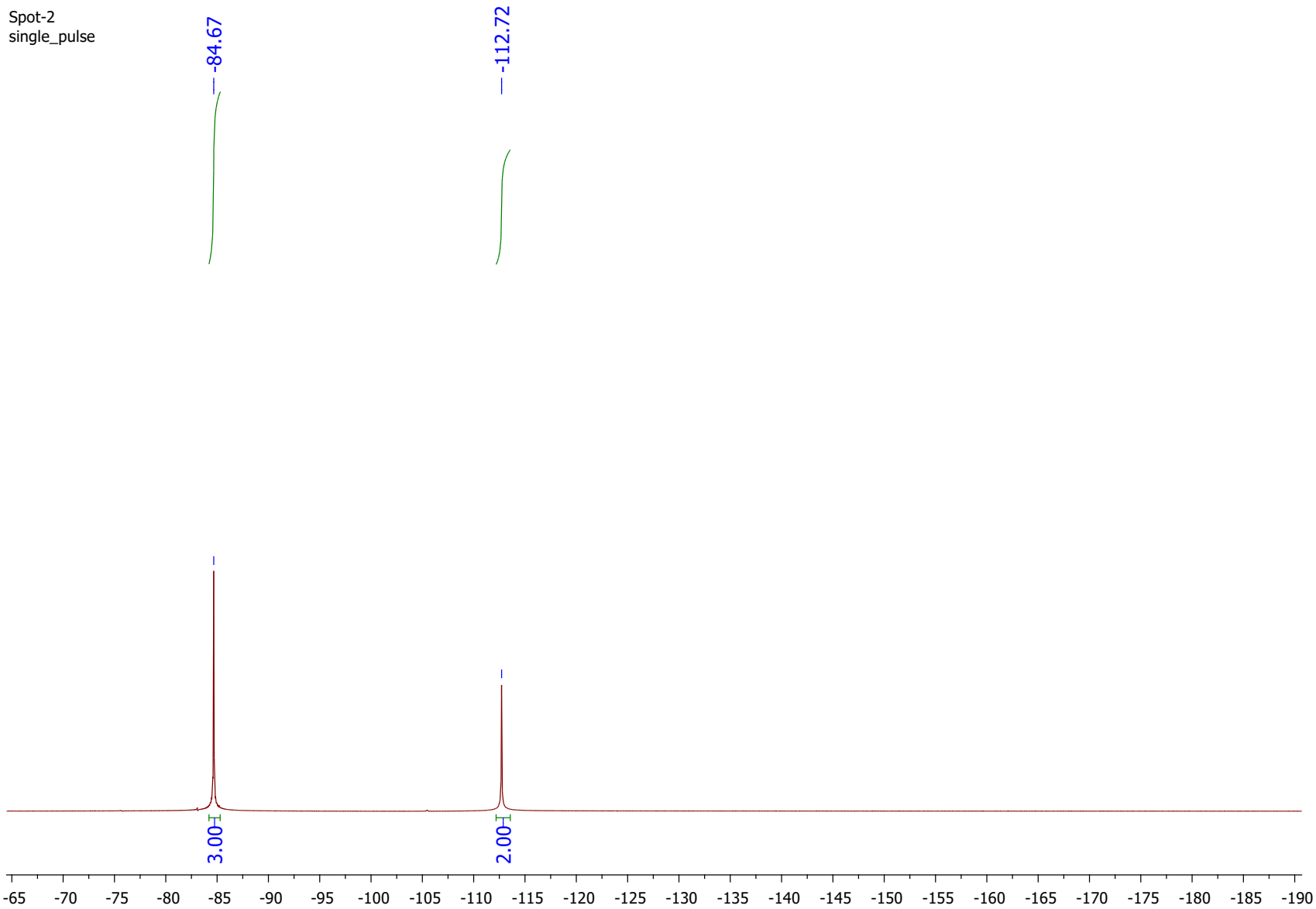


Figure S105. ^{19}F NMR spectrum of **r** in $CDCl_3$ at 23 °C.

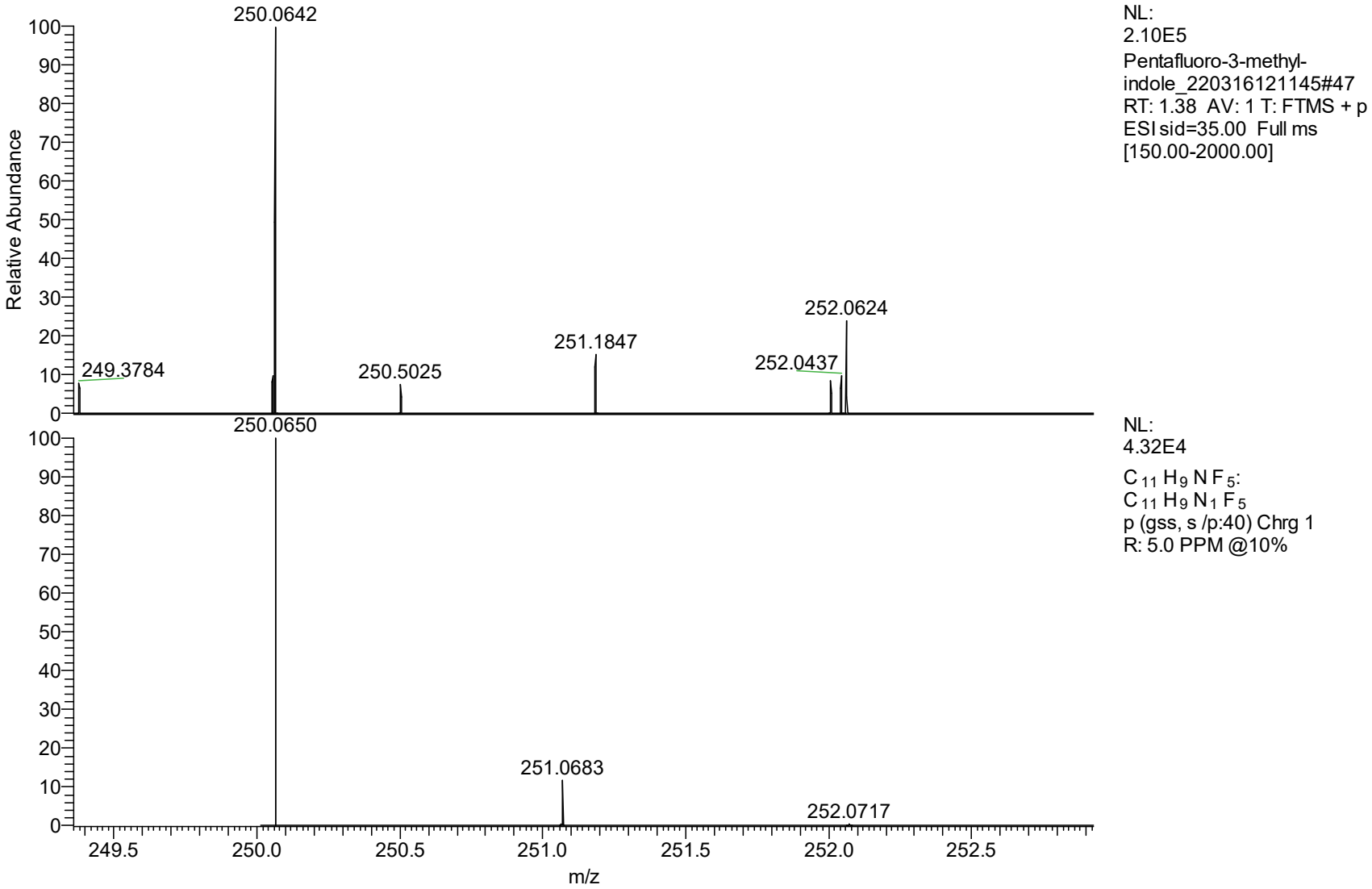


Figure S106. ESI-(HR)MS spectrum of a MeOH solution of **r.**

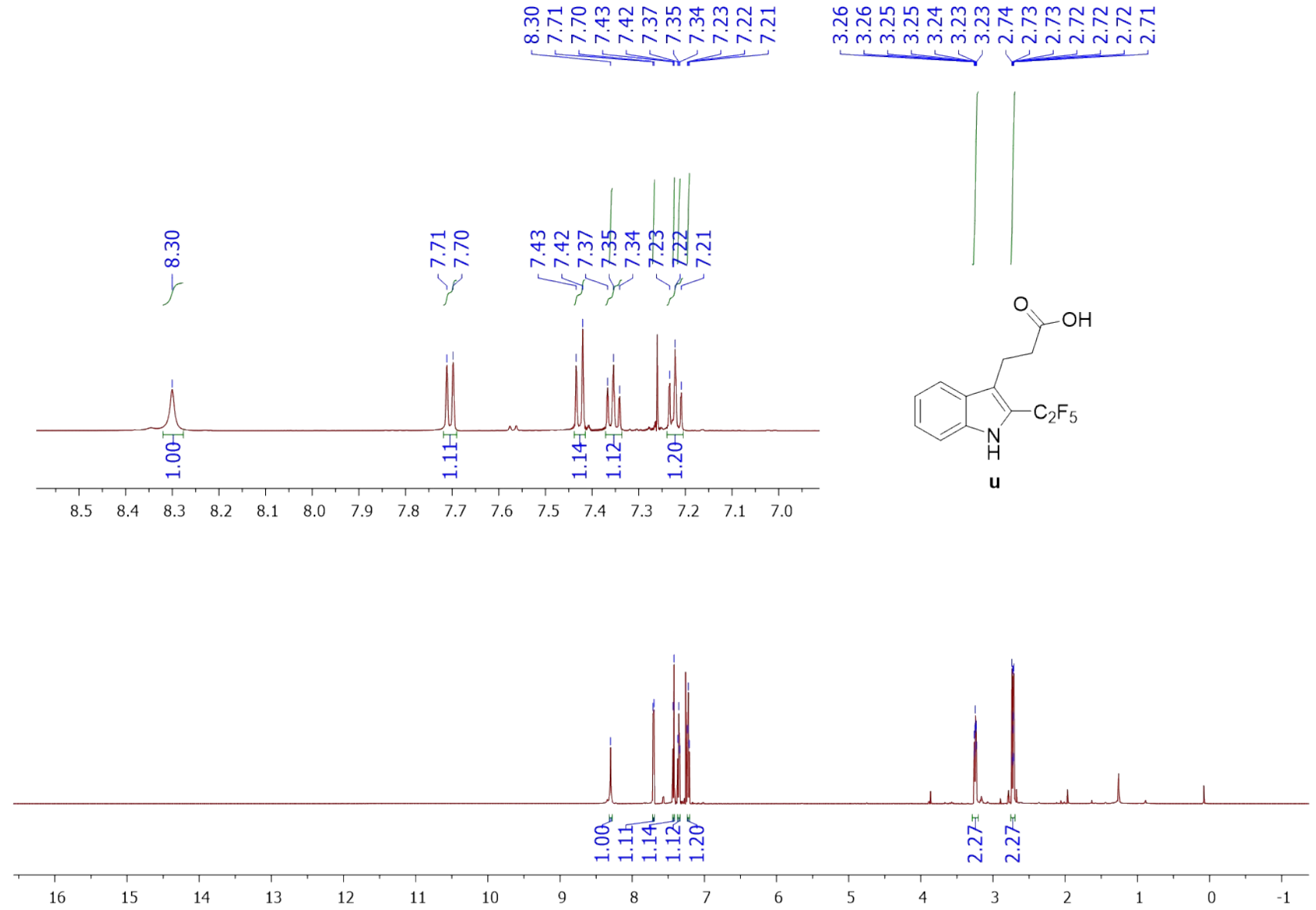


Figure S107. ^{1}H NMR spectrum of **u** in $CDCl_3$ at 23 °C.

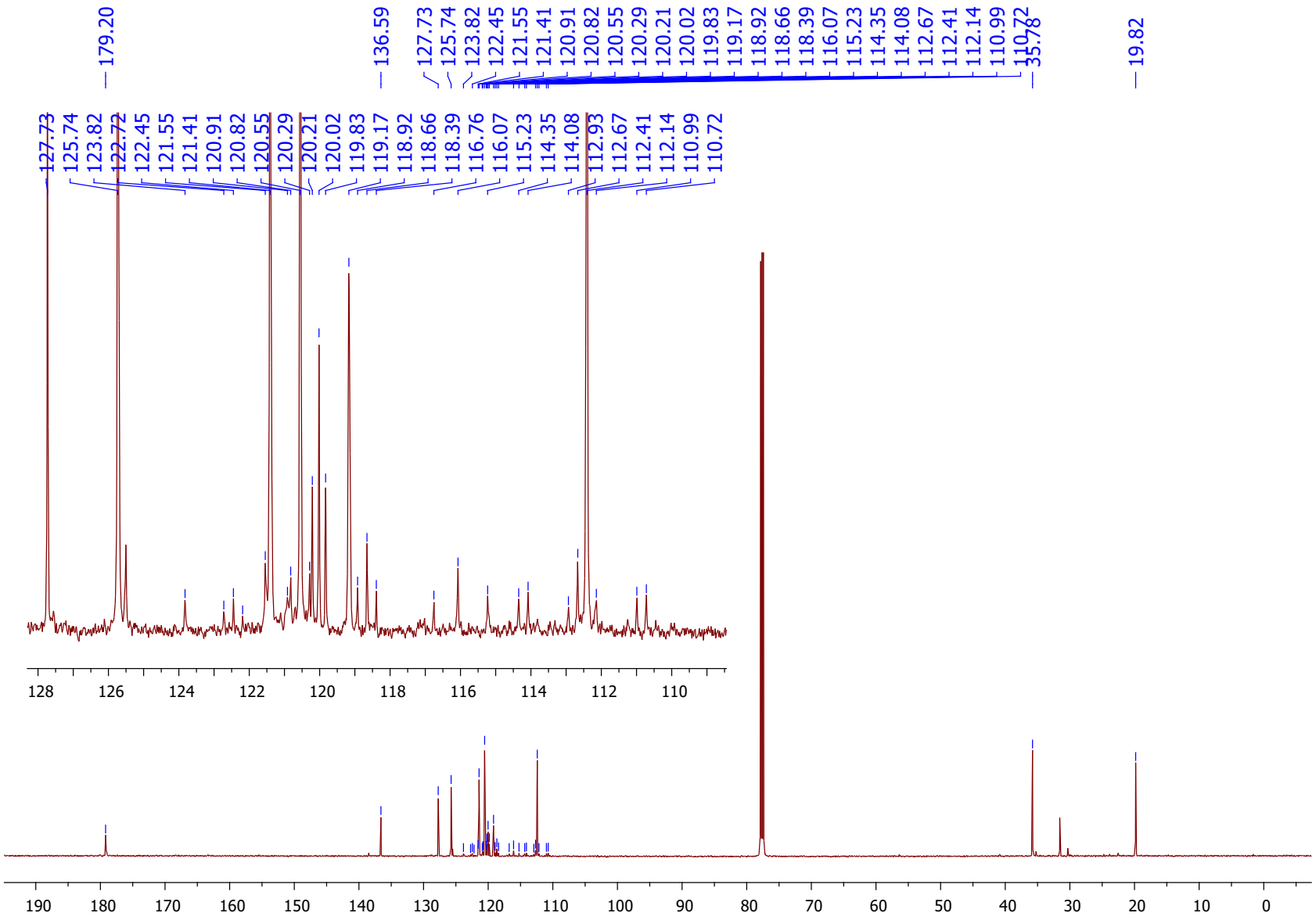


Figure S108. ^{13}C NMR spectrum of **u** in $CDCl_3$ at 23 °C.

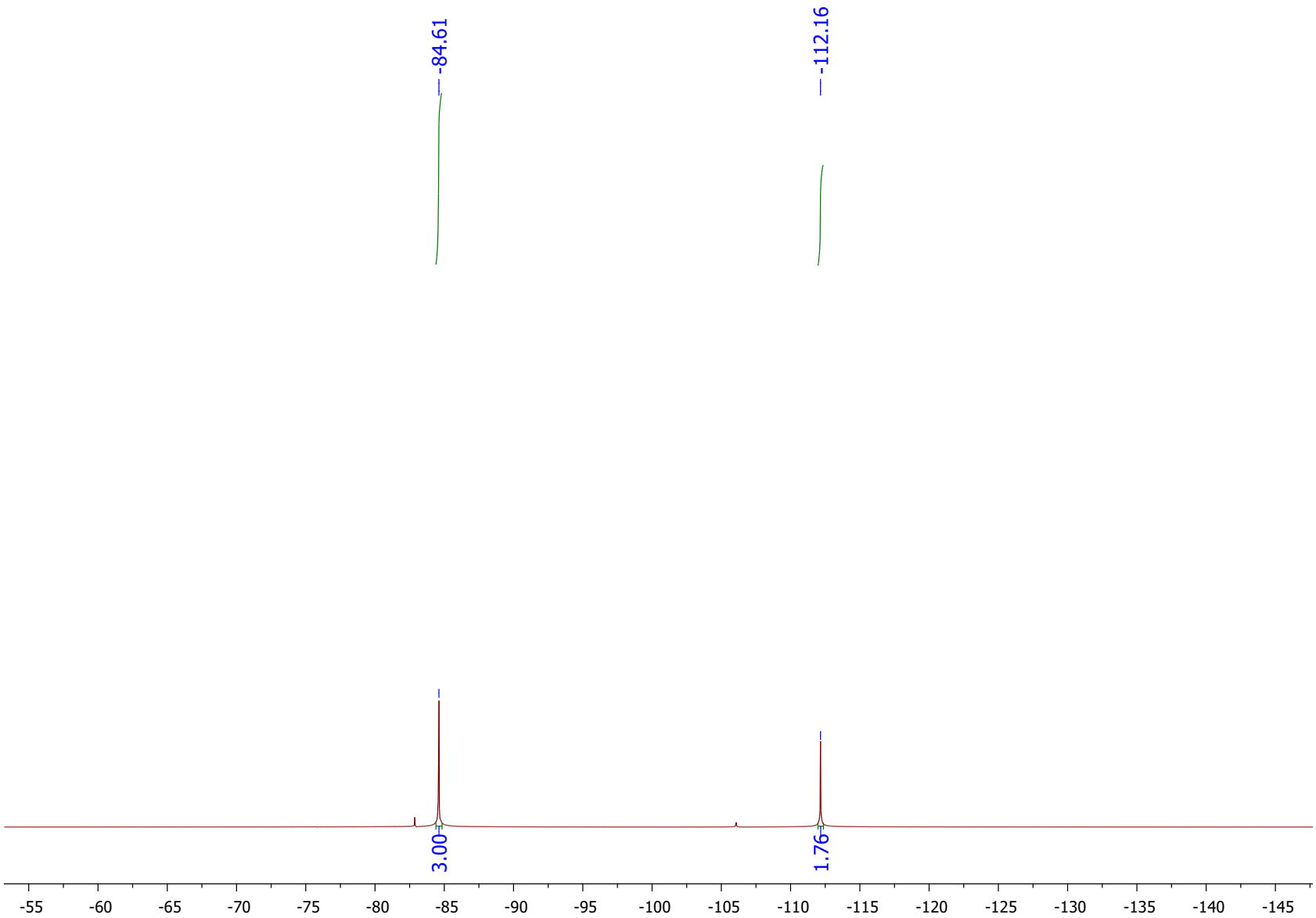


Figure S109. ^{19}F NMR spectrum of **u** in $CDCl_3$ at 23 °C.

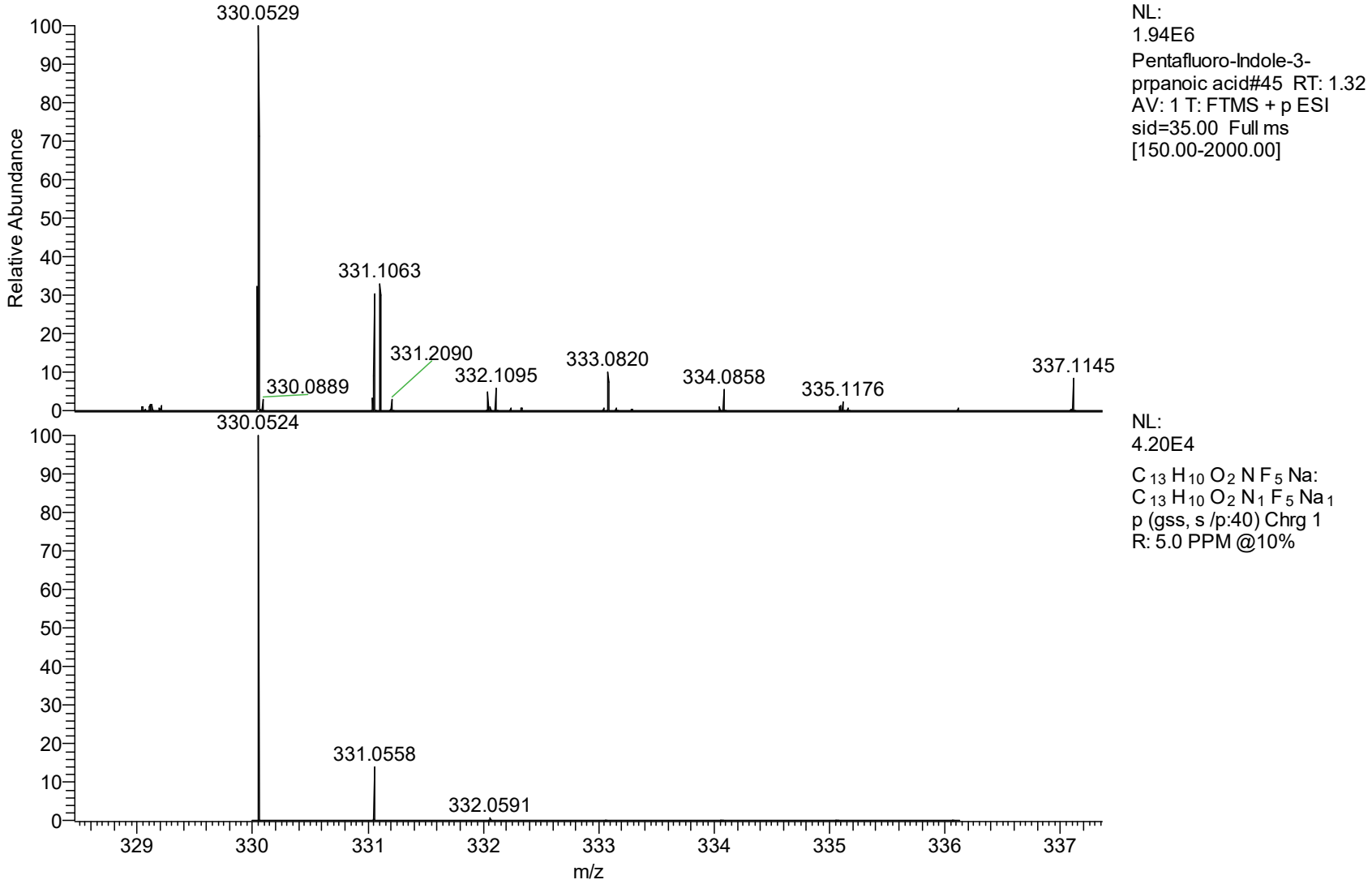


Figure S110. ESI-(HR)MS spectrum of a MeOH solution of **u.**

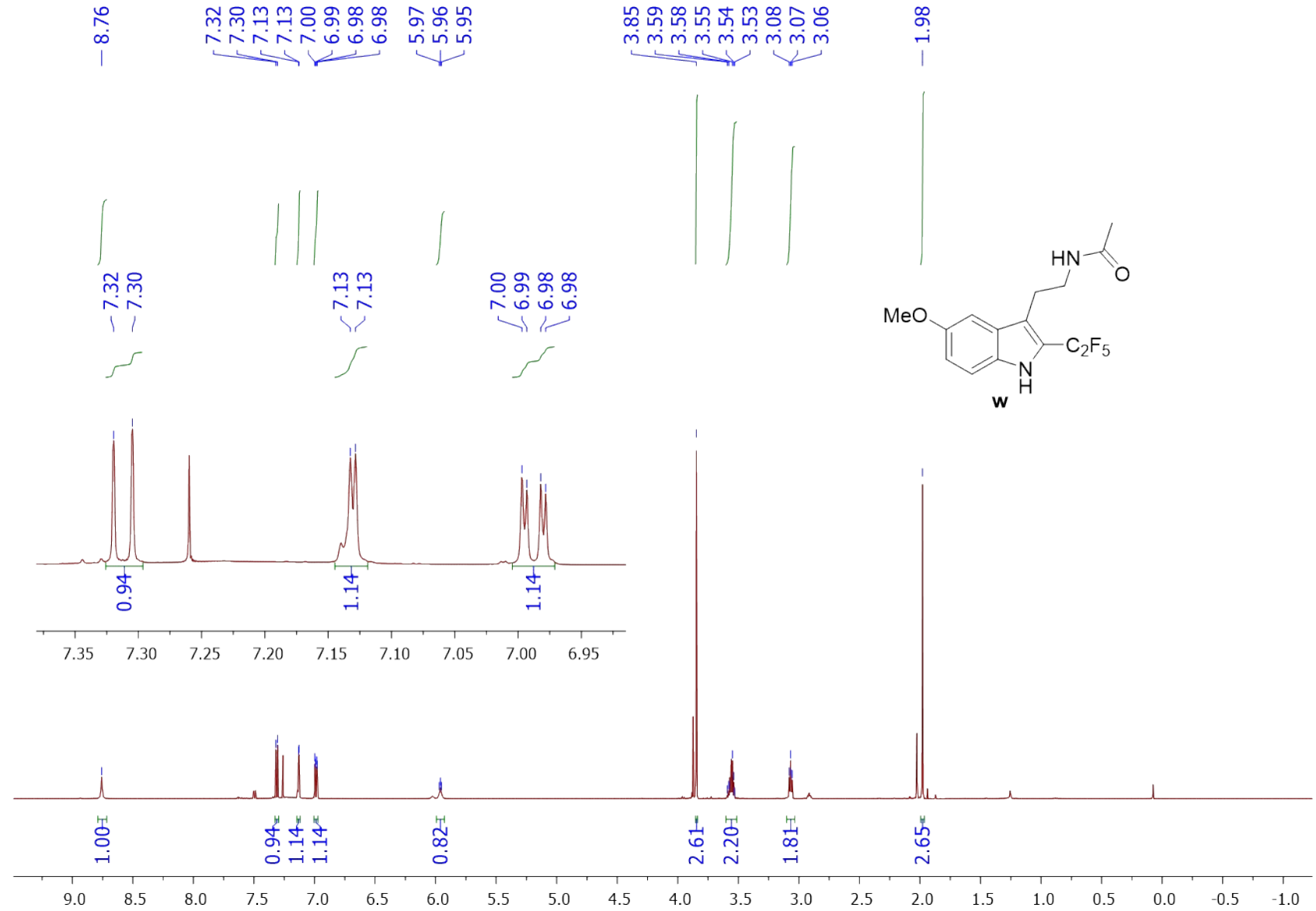


Figure S111. ^{1}H NMR spectrum of **w** in $CDCl_3$ at 23 °C.

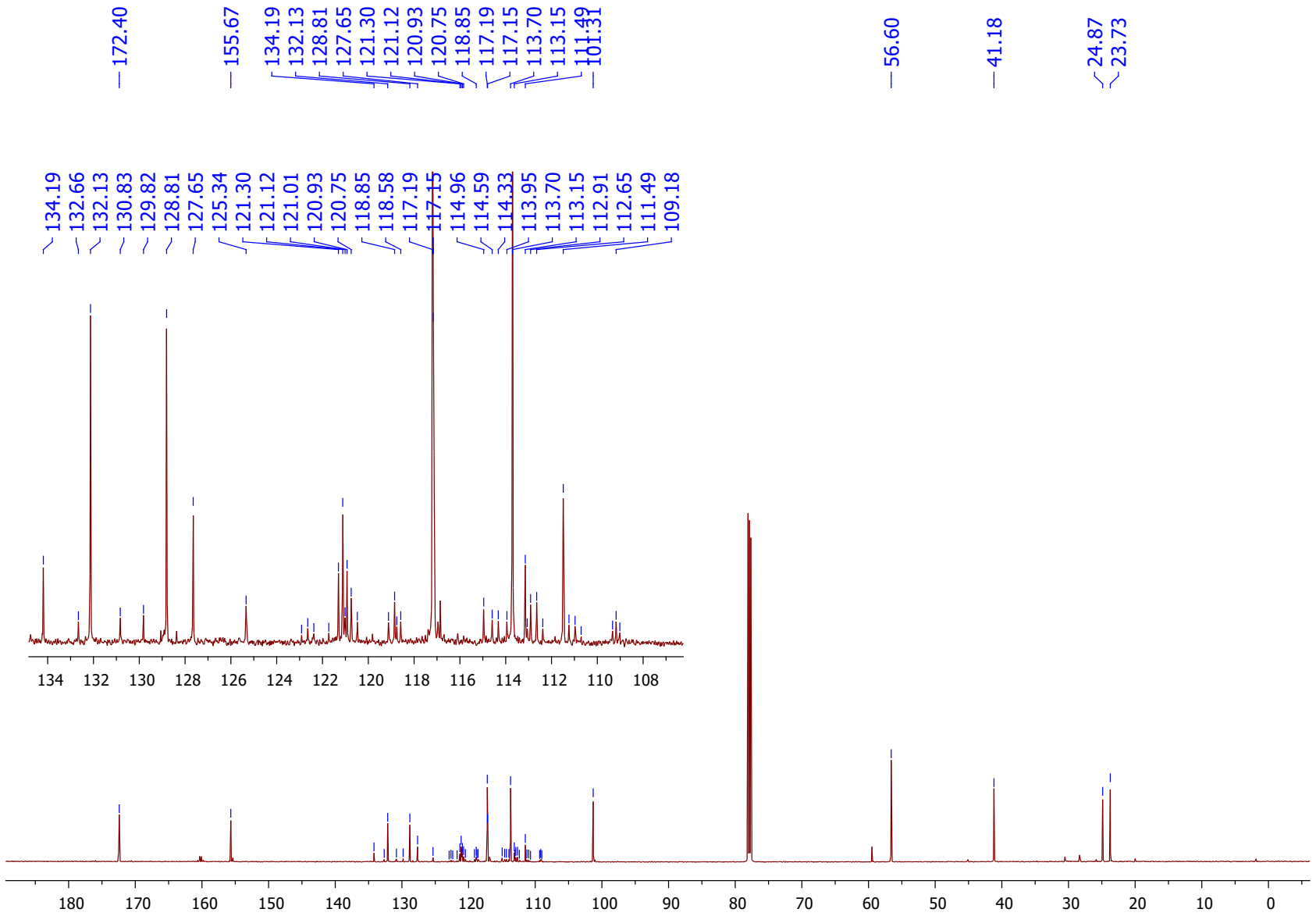


Figure S112. ^{13}C NMR spectrum of **w** in $CDCl_3$ at 23 °C.

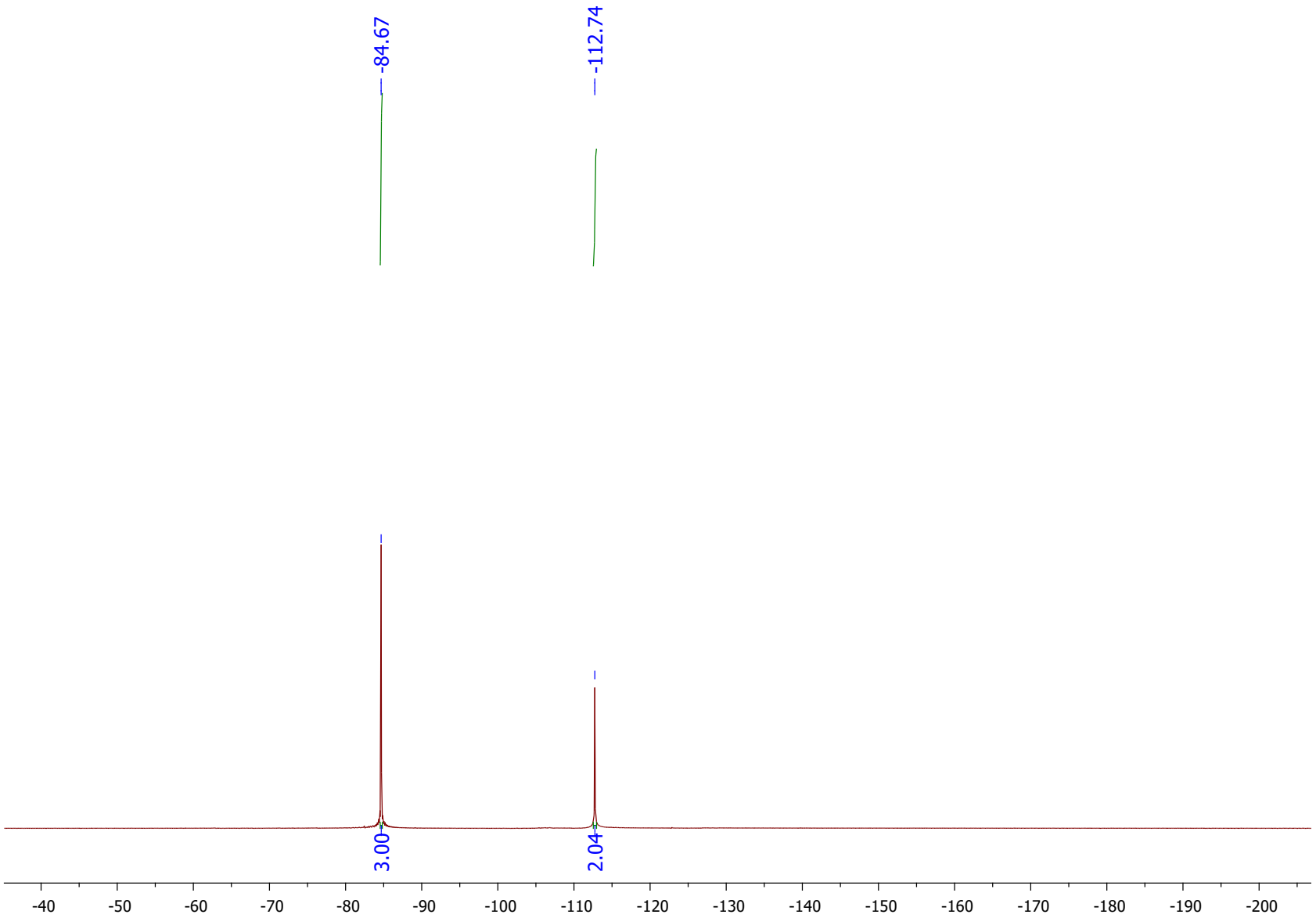


Figure S113. ^{19}F NMR spectrum of **w** in $CDCl_3$ at 23 °C.

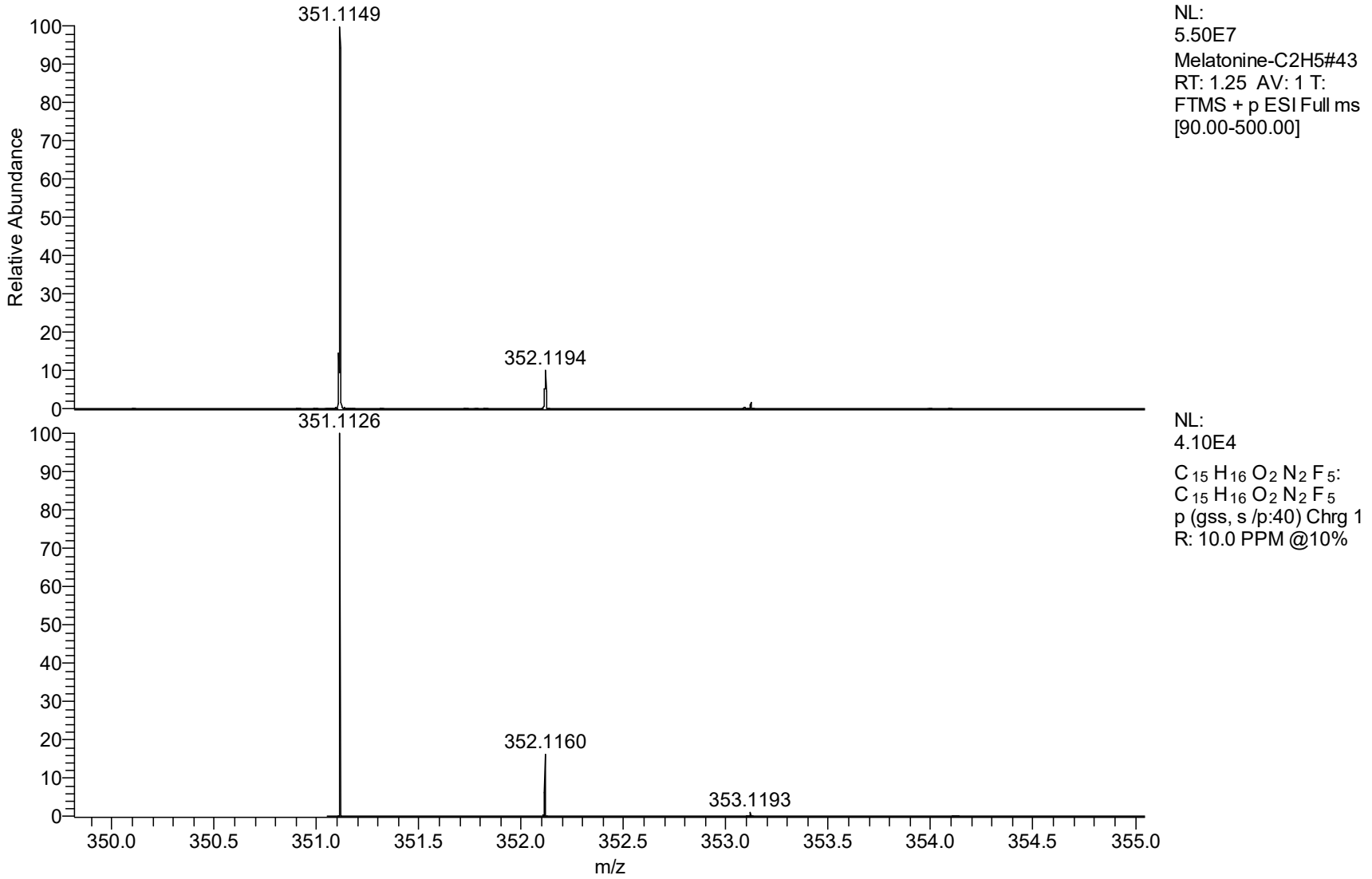


Figure S114. ESI-(HR)MS spectrum of a MeOH solution of **w.**

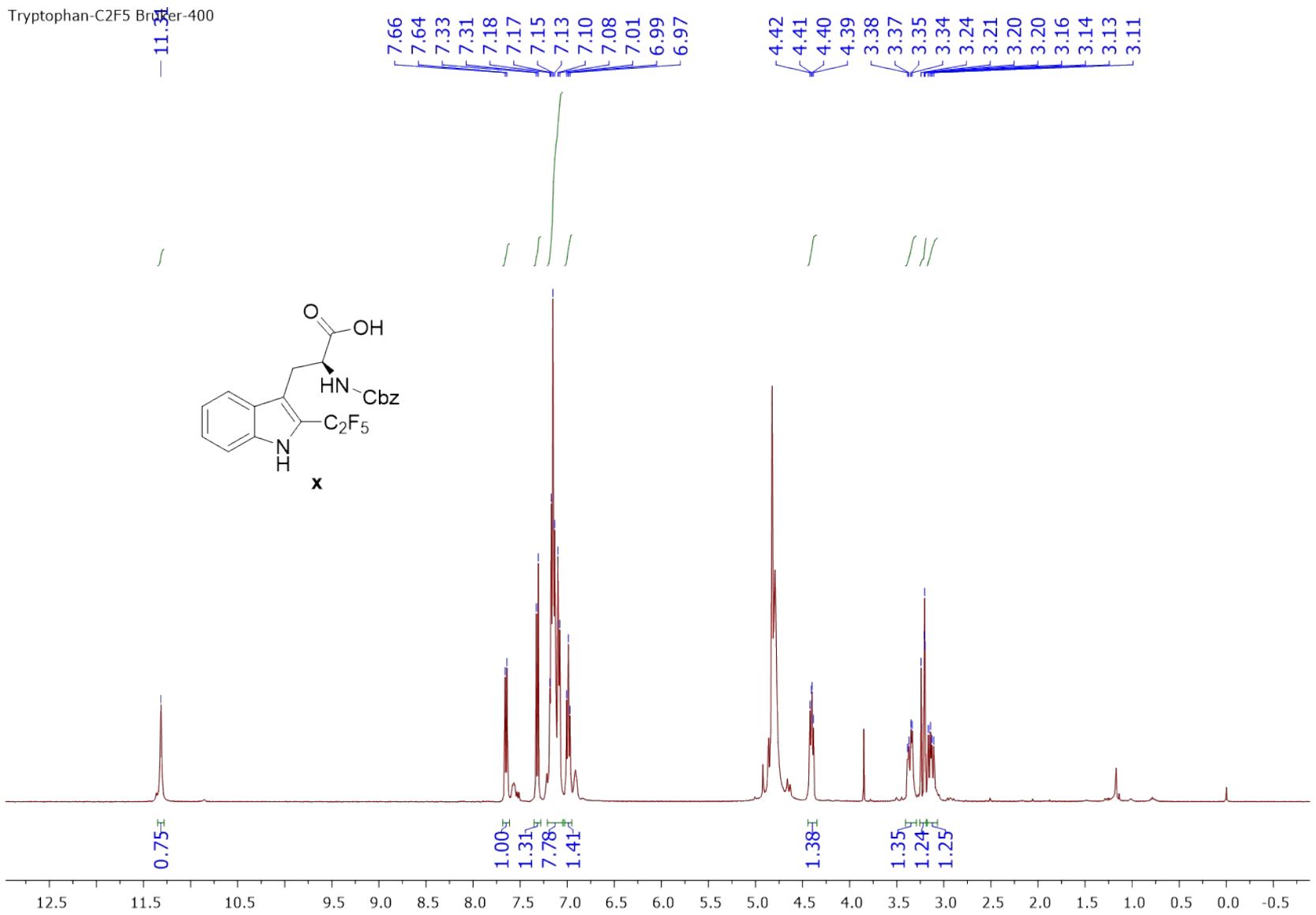


Figure S115. ^{1}H NMR spectrum of **x** in CD_3OD at 23 °C.

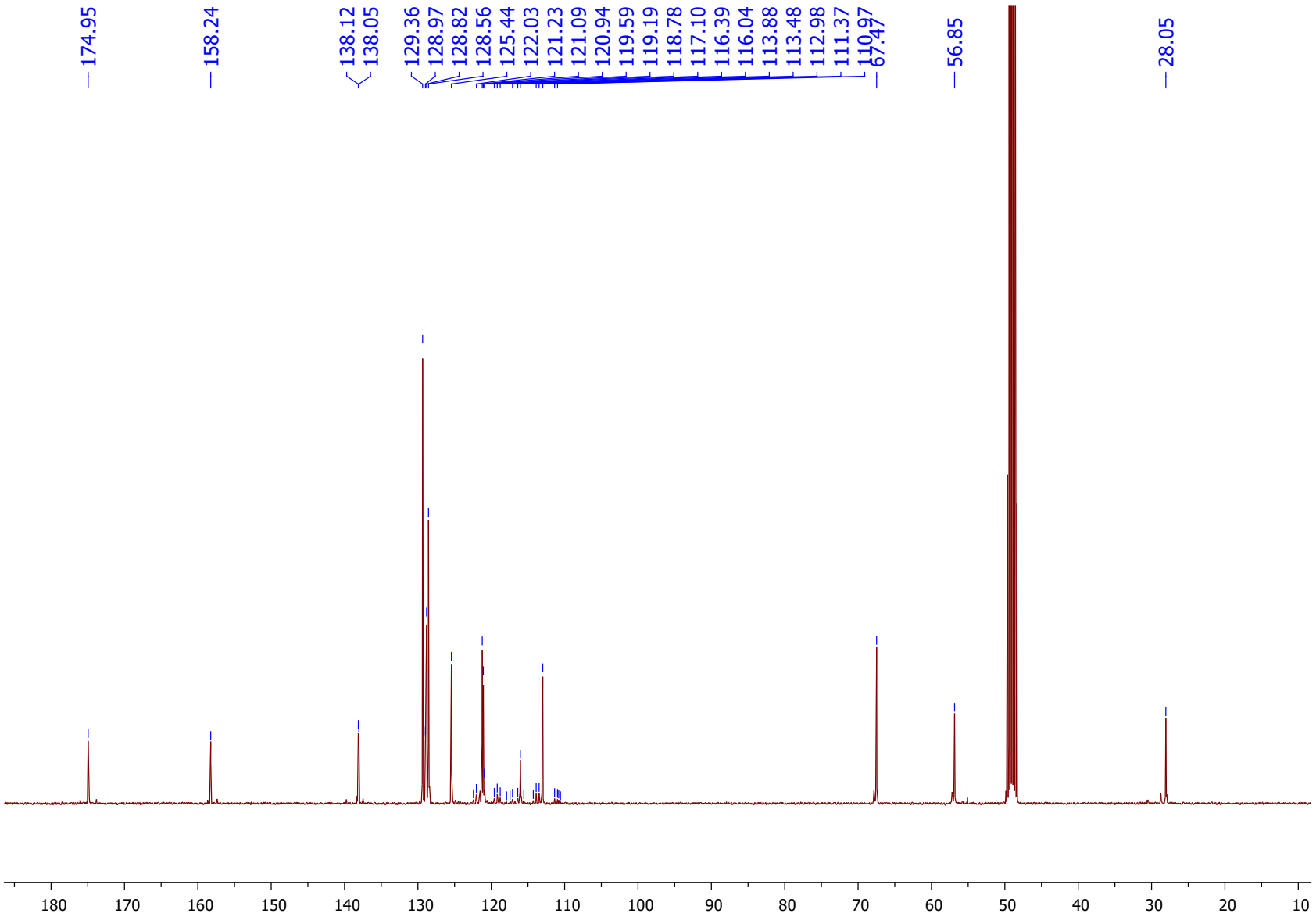


Figure S116. ^{13}C NMR spectrum of **x** in CD_3OD at 23 °C.

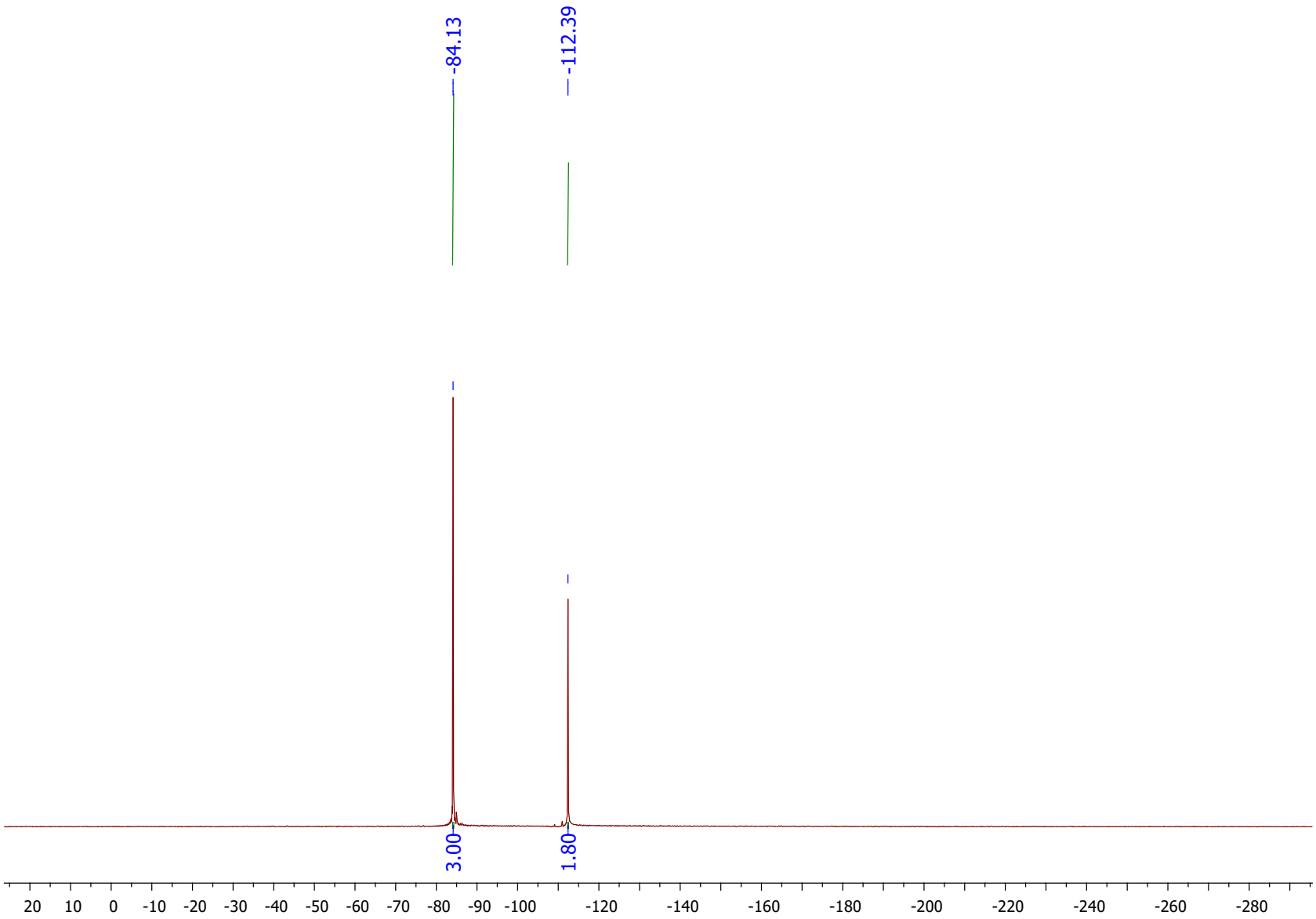


Figure S117. ^{19}F NMR spectrum of **x** in CD_3OD at 23 °C.

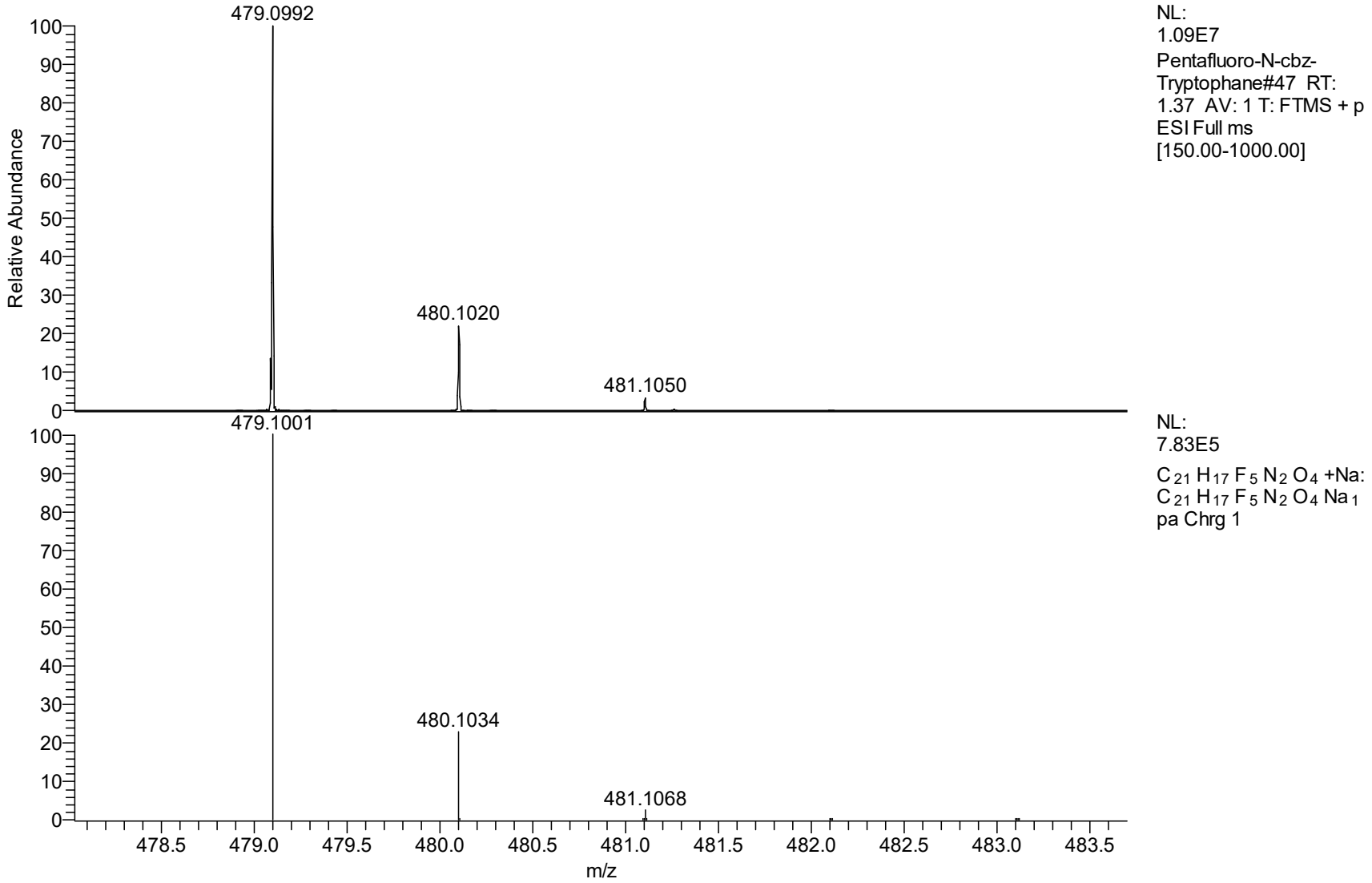


Figure S118. ESI-(HR)MS spectrum of a MeOH solution of **x**.

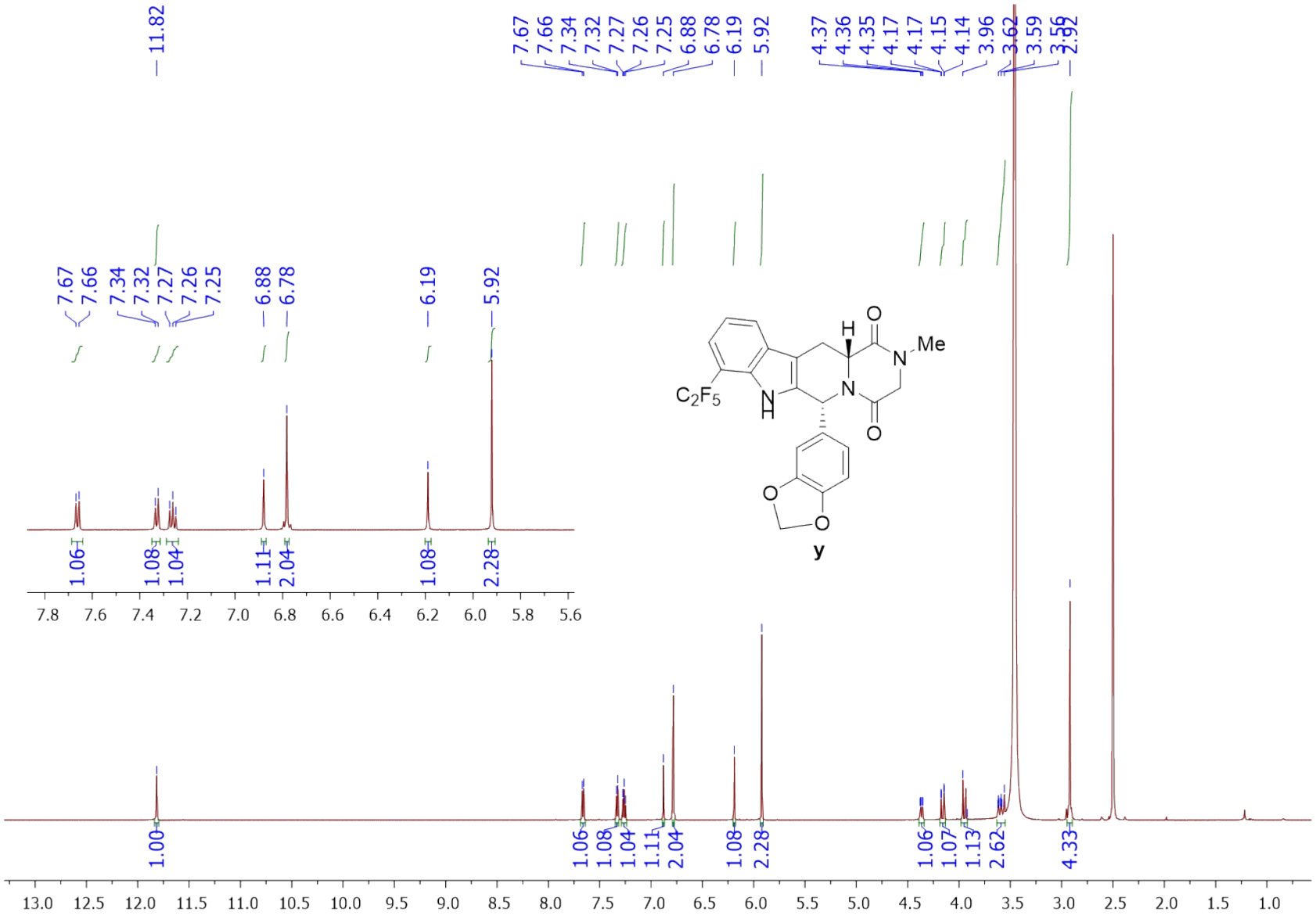


Figure S119. ^{1}H NMR spectrum of **y** in $(CD_3)_2SO$ at 23 °C.

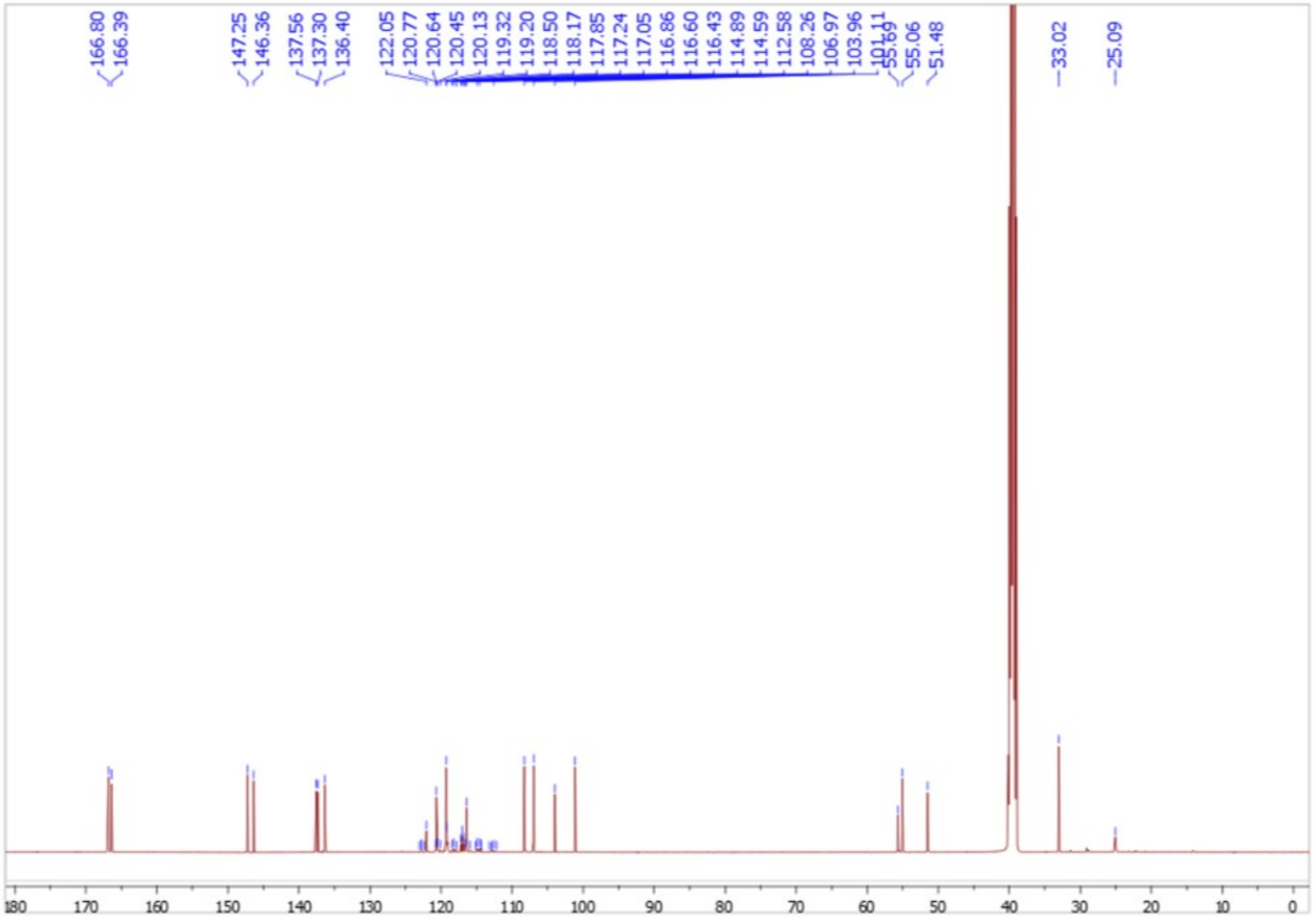


Figure S120. ^{13}C NMR spectrum of **y** in $(CD_3)_2SO$ at 23 °C.

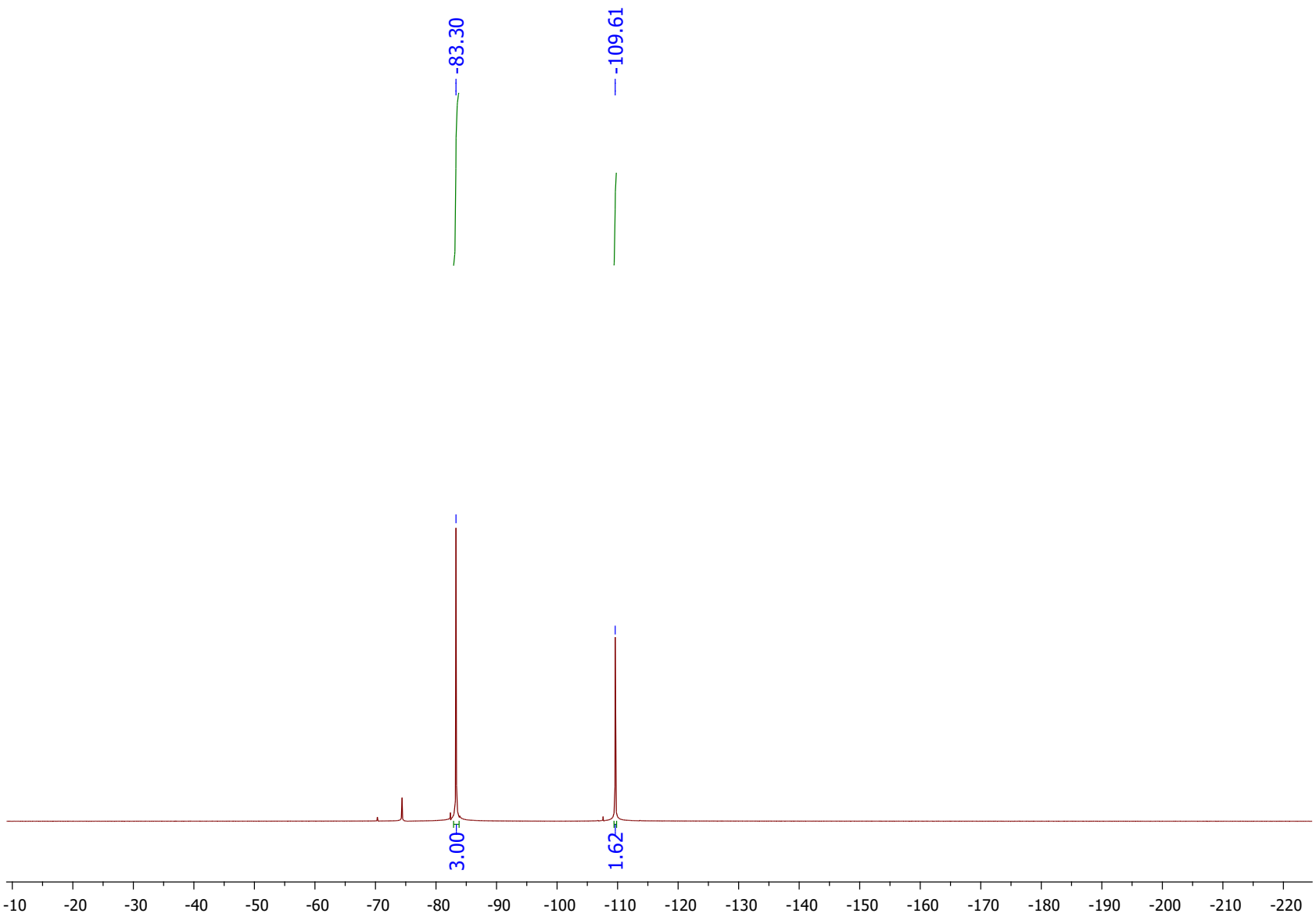


Figure S121. ^{19}F NMR spectrum of **y** in $(CD_3)_2SO$ at 23 °C.

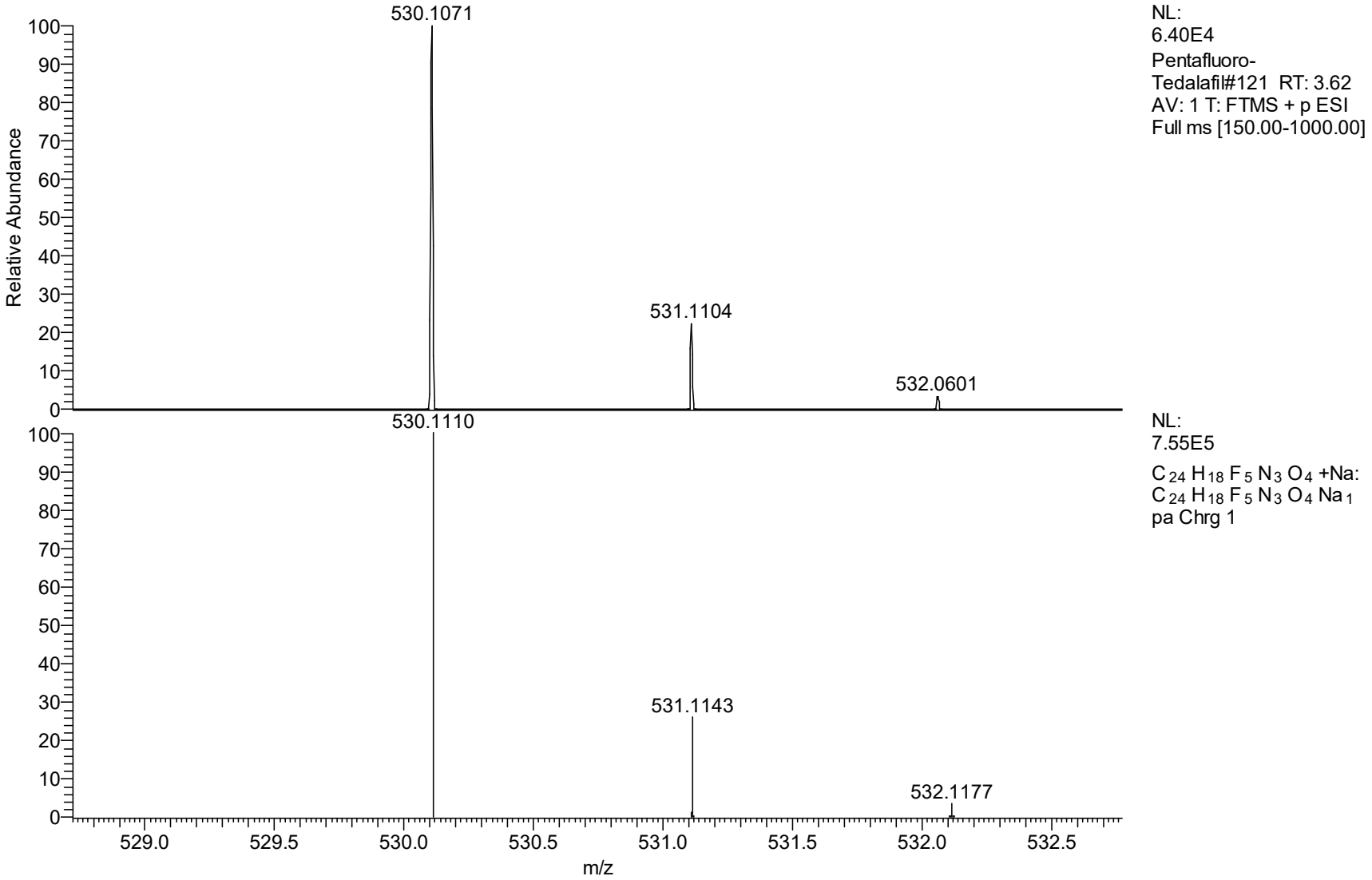


Figure S122. ESI-(HR)MS spectrum of a MeOH solution of **y**.

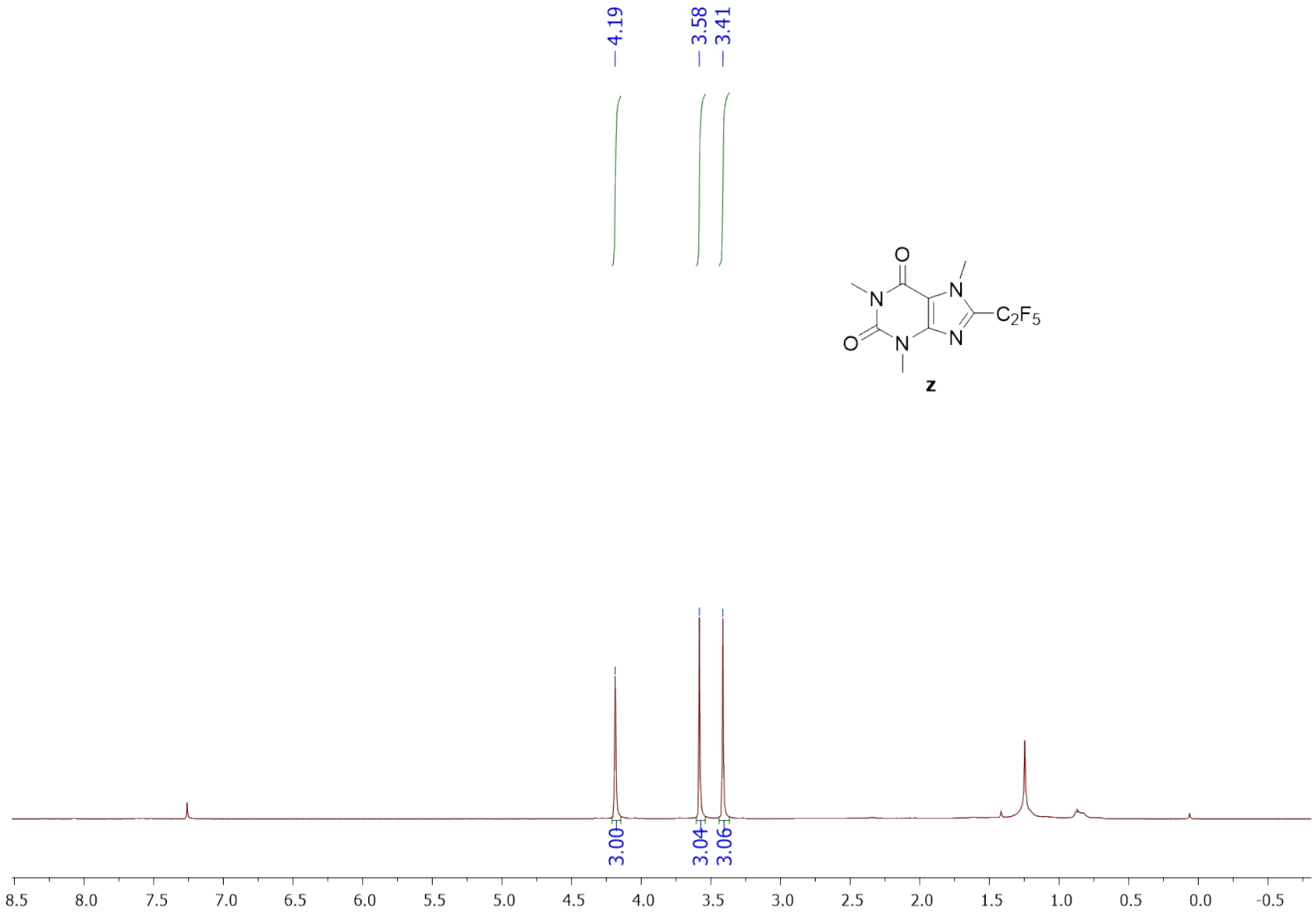


Figure S123. ^{1}H NMR spectrum of **z** in $CDCl_3$ at 23 °C.

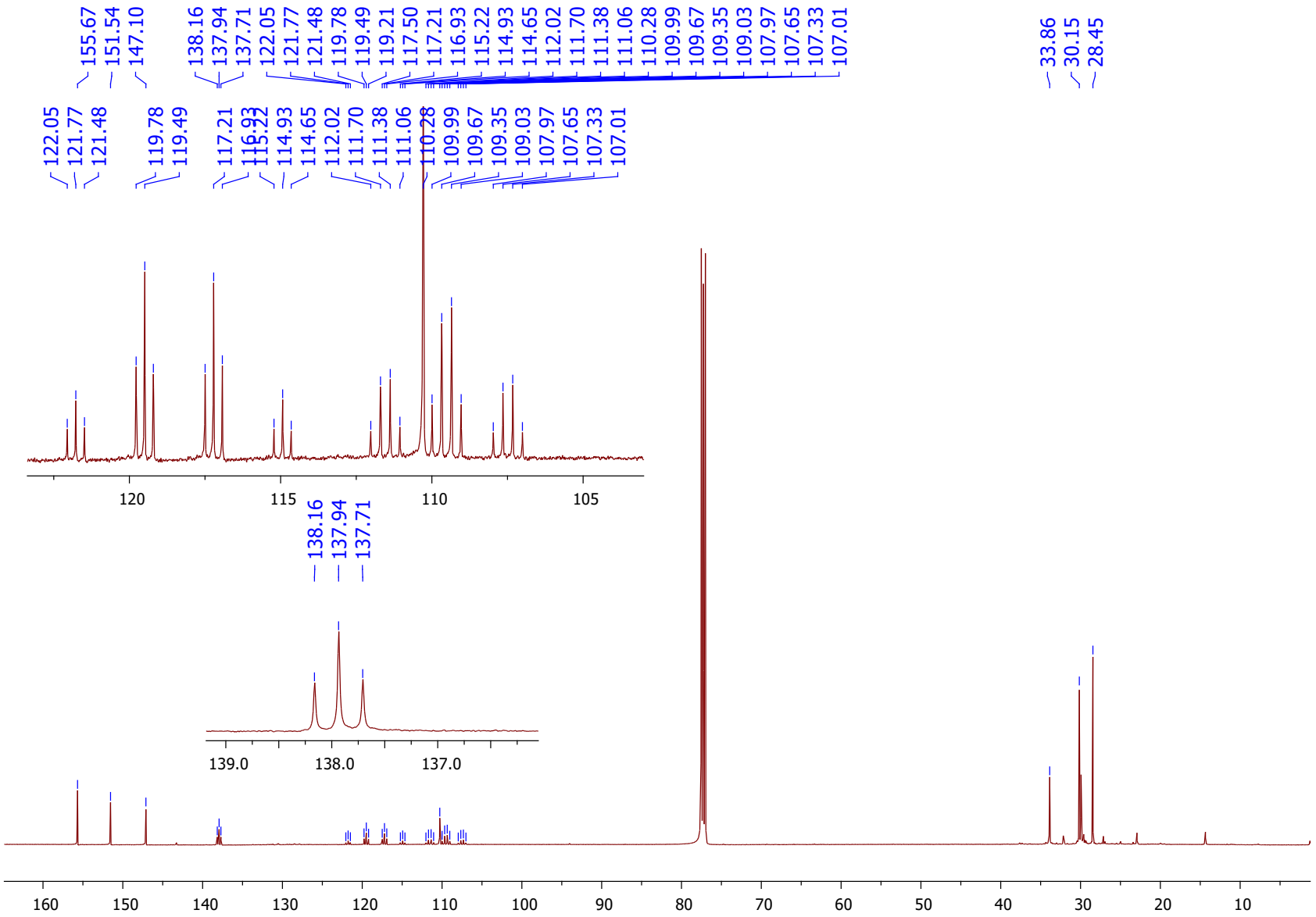


Figure S124. ^{13}C NMR spectrum of **z** in $CDCl_3$ at 23 °C.

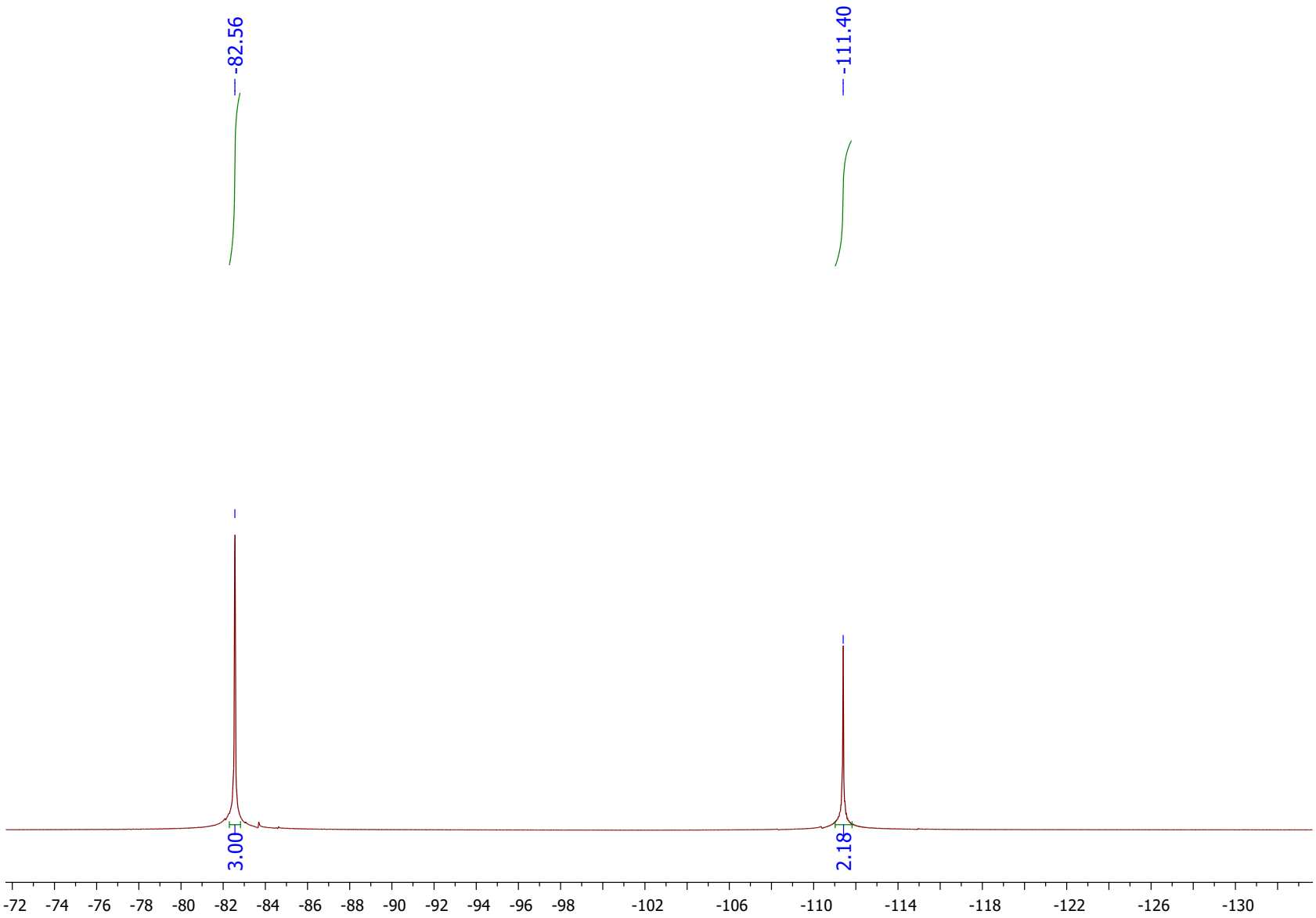


Figure S125. ^{19}F NMR spectrum of **z** in $CDCl_3$ at 23 °C.

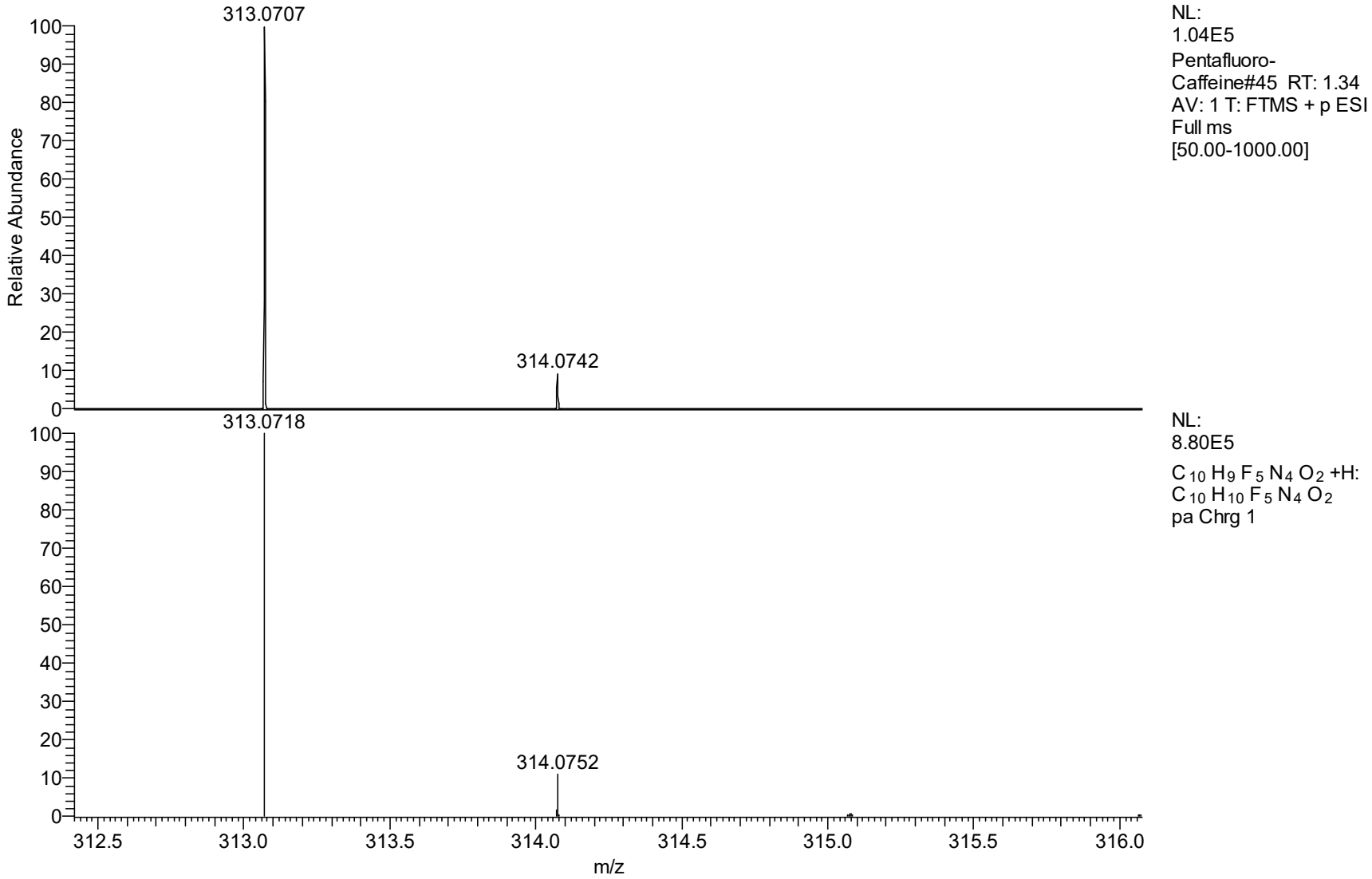
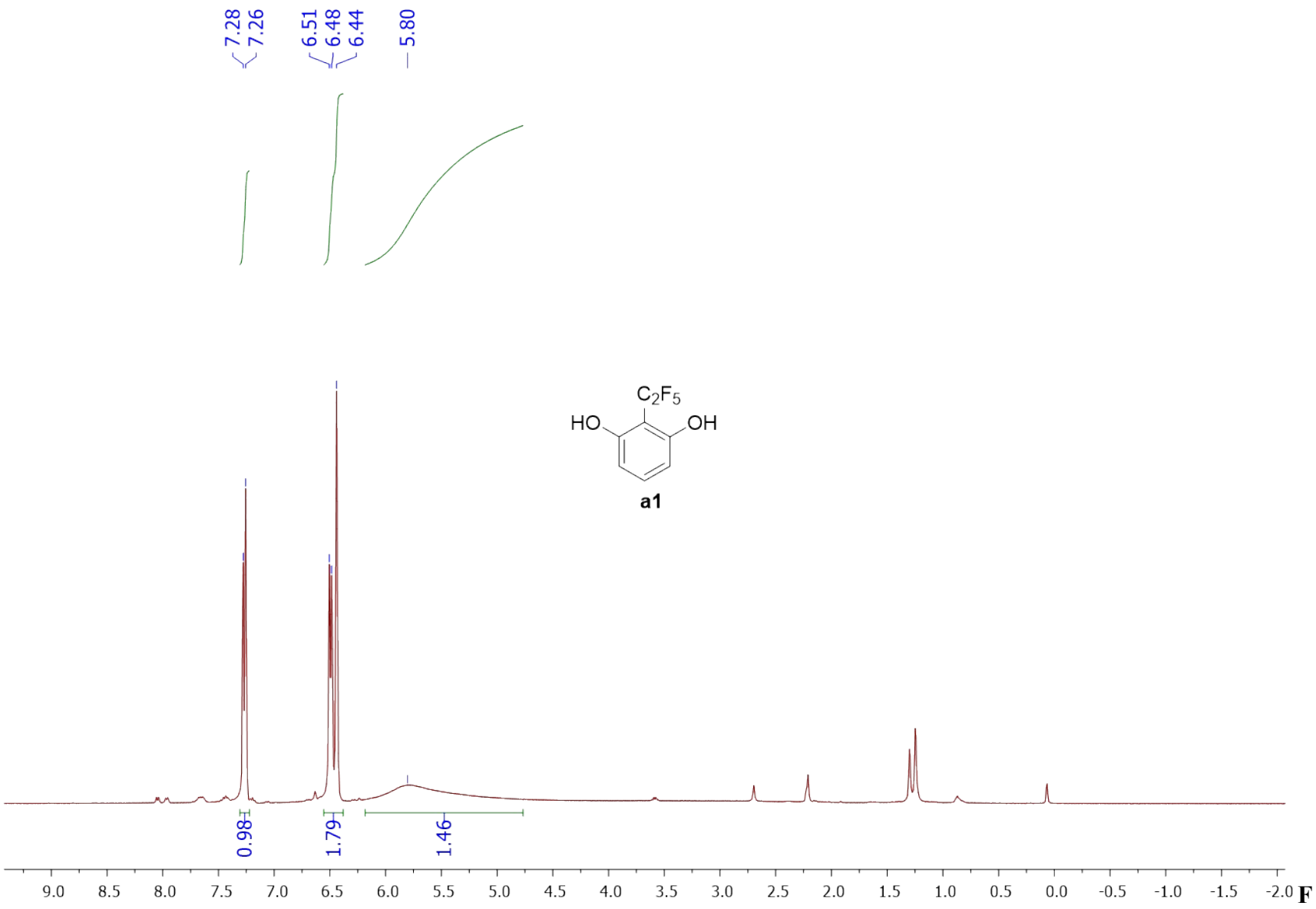


Figure S126. ESI-(HR)MS spectrum of a MeOH solution of **z**.


7.28
7.26
6.51
6.48
6.44
5.80
C2F5
HO
OH
a1
0.98
1.79
1.46
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
F

igure S127. ^{1}H NMR spectrum of **a1** in $CDCl_3$ at 23 °C.

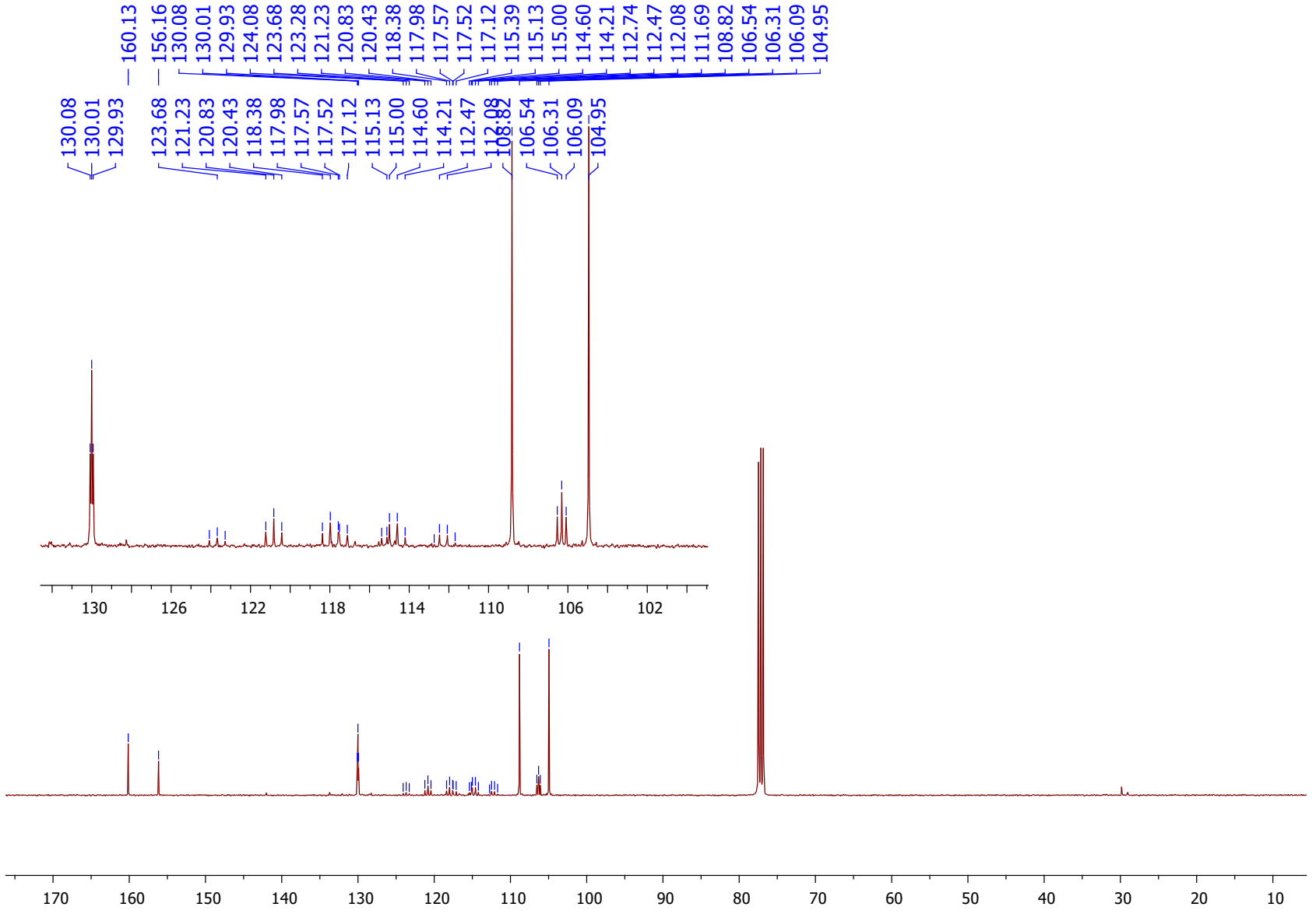


Figure S128. ^{13}C NMR spectrum of **a1** in $CDCl_3$ at 23 °C.

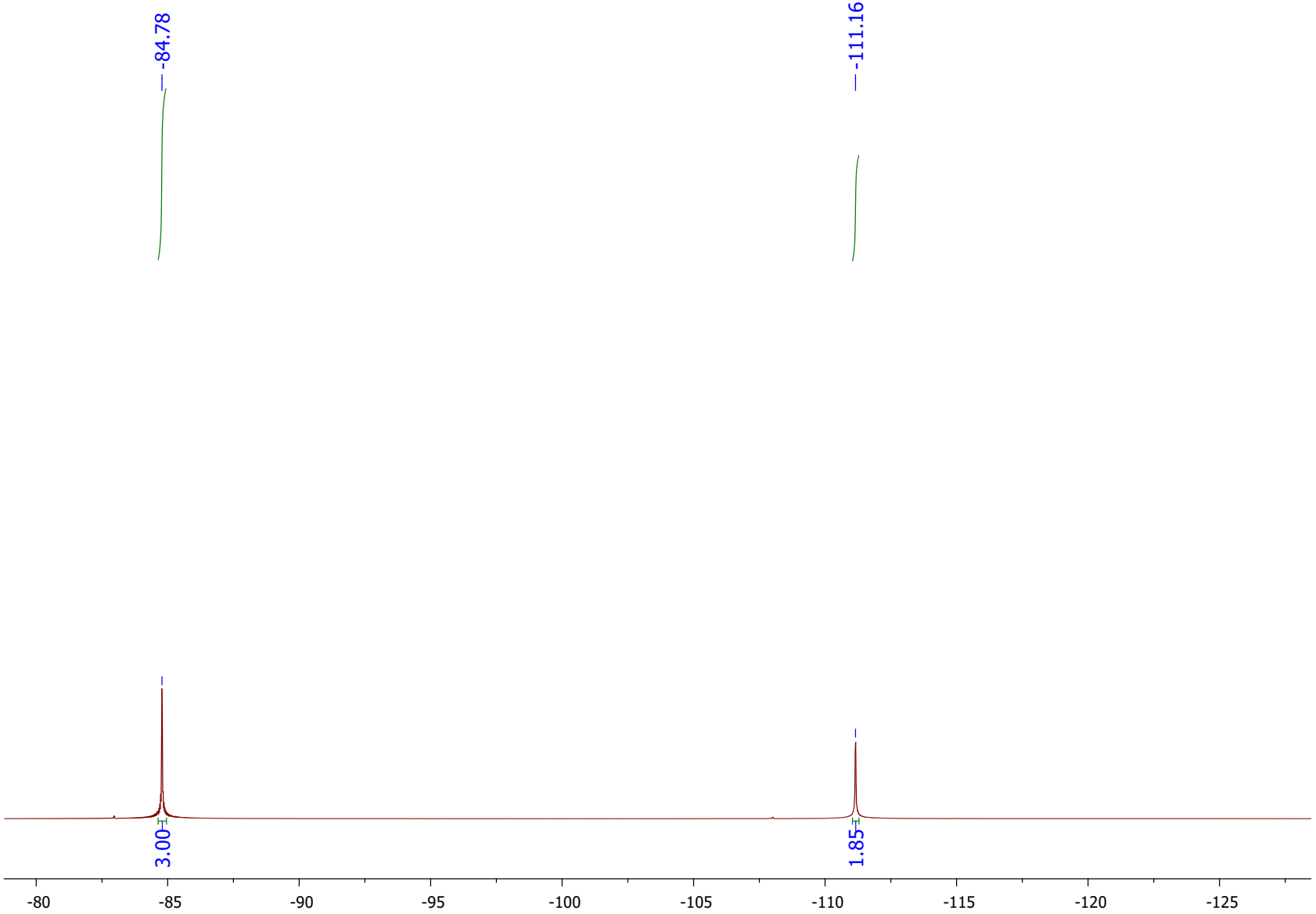


Figure S129. ^{19}F NMR spectrum of **a1** in $CDCl_3$ at 23 °C.

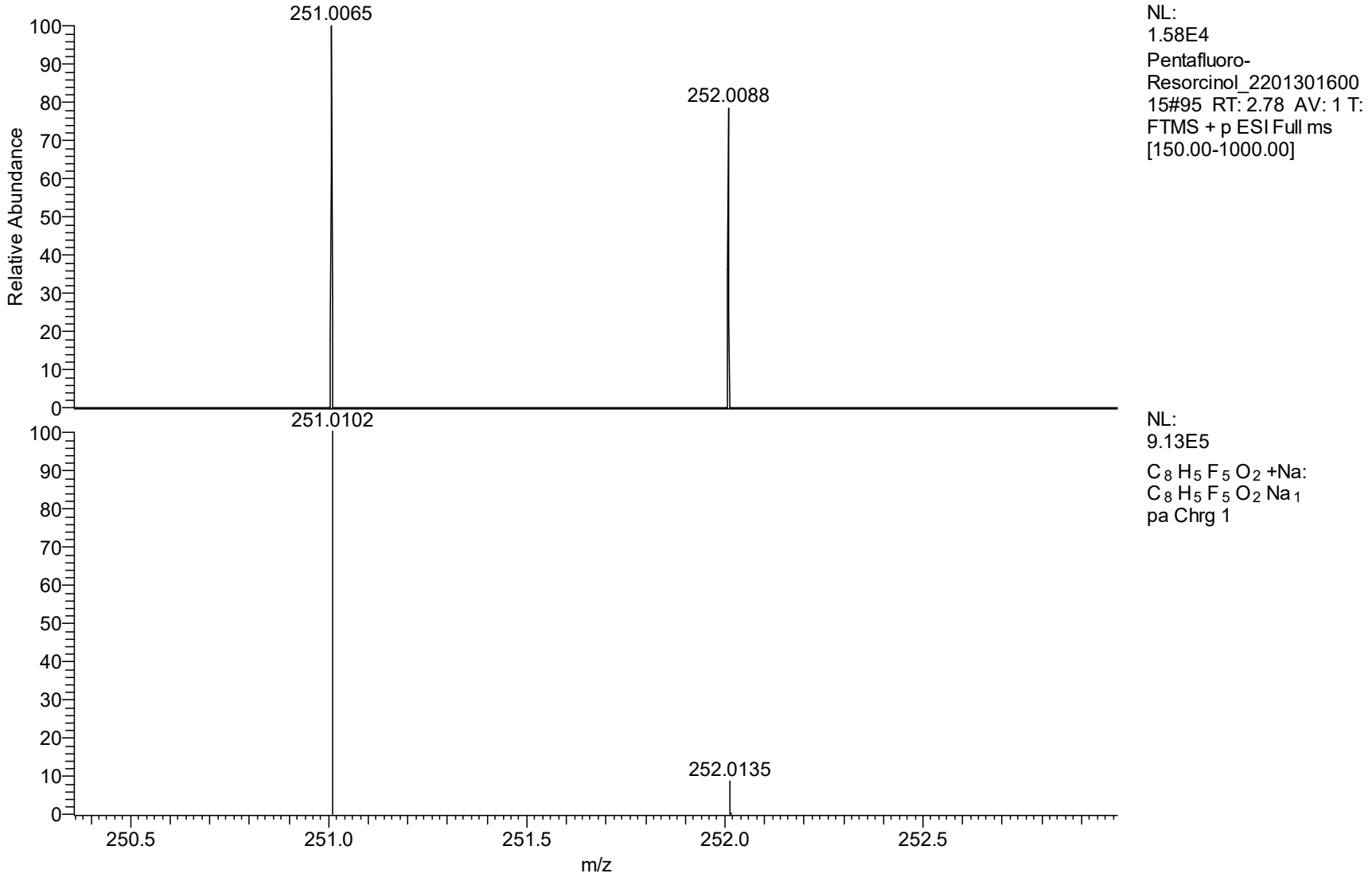


Figure S130. ESI-(HR)MS spectrum of a MeOH solution of **a1**.

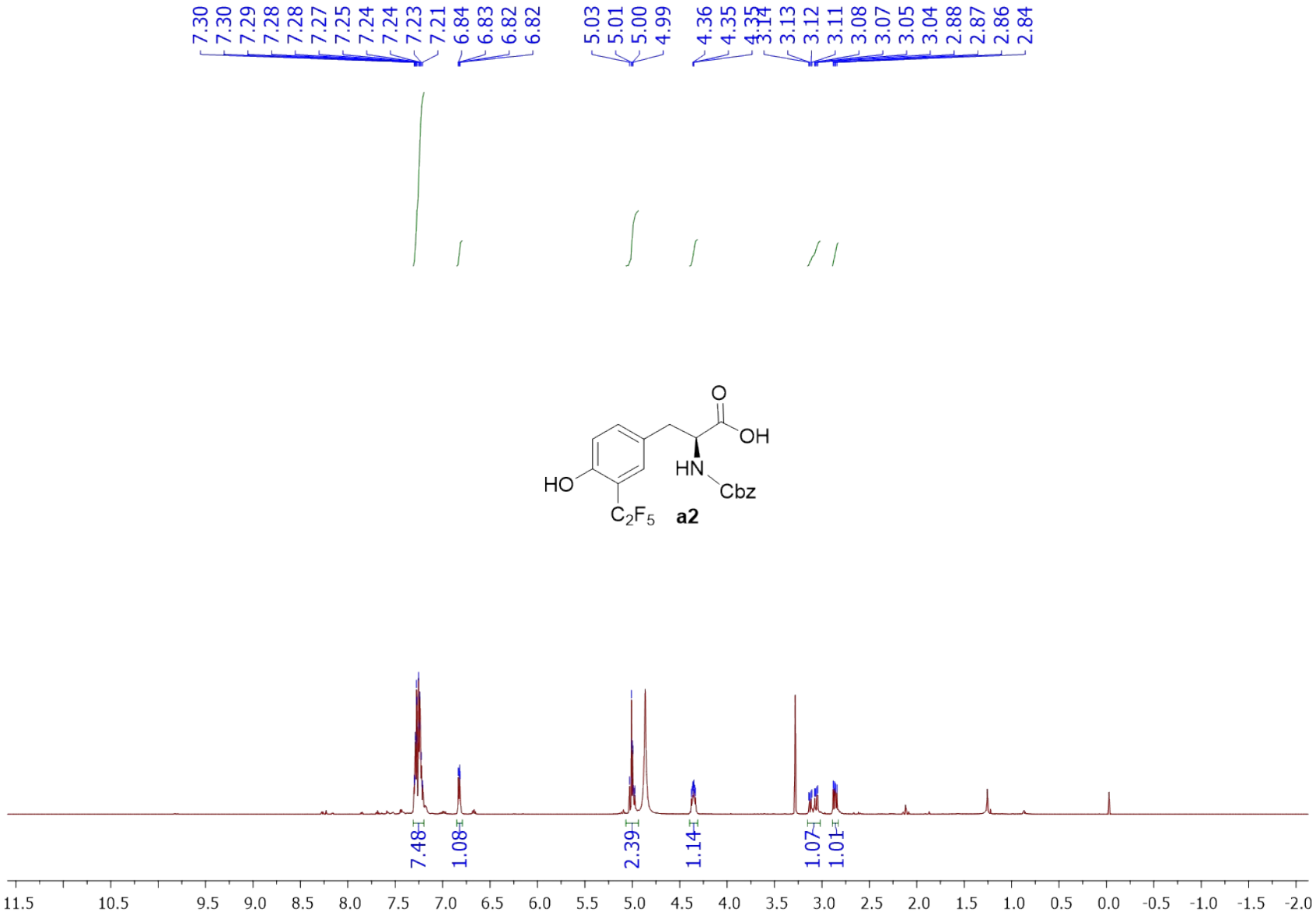
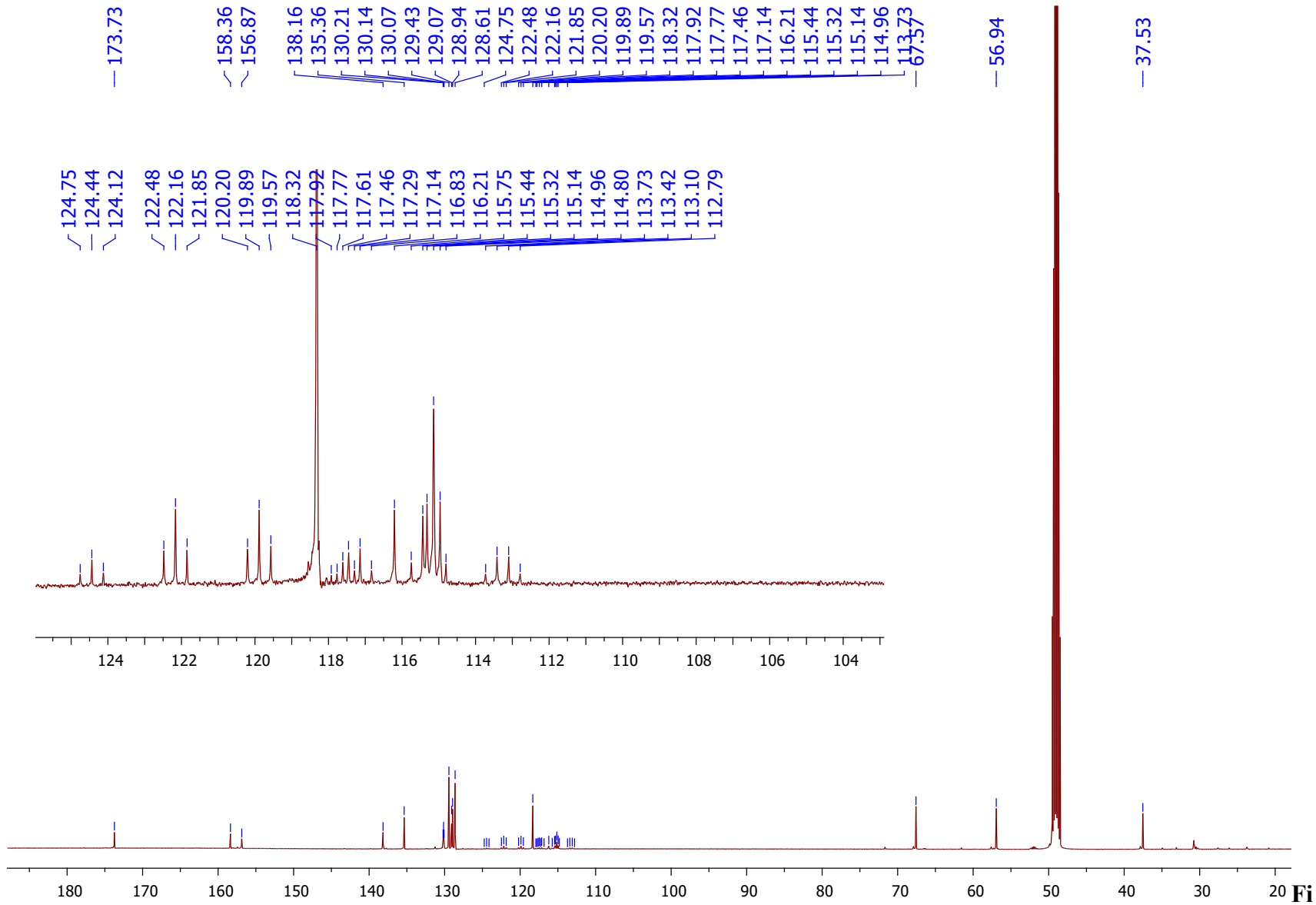


Figure S131. ^{1}H NMR spectrum of **a2** in CD_3OD at 23 °C.



gure S132. ^{13}C NMR spectrum of **a2** in CD_3OD at 23 °C.

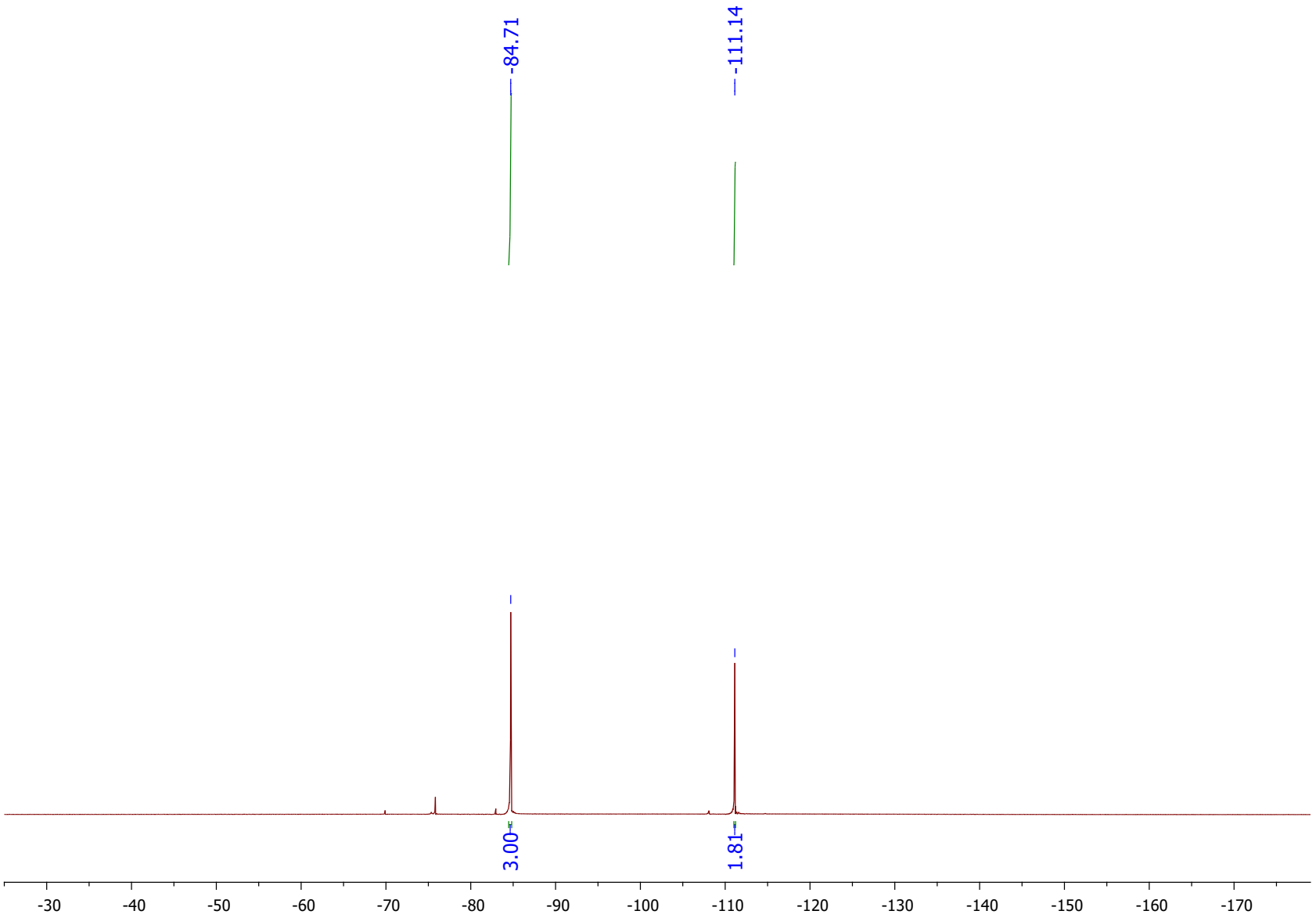


Figure S133. ^{19}F NMR spectrum of **a2** in CD_3OD at 23 °C.

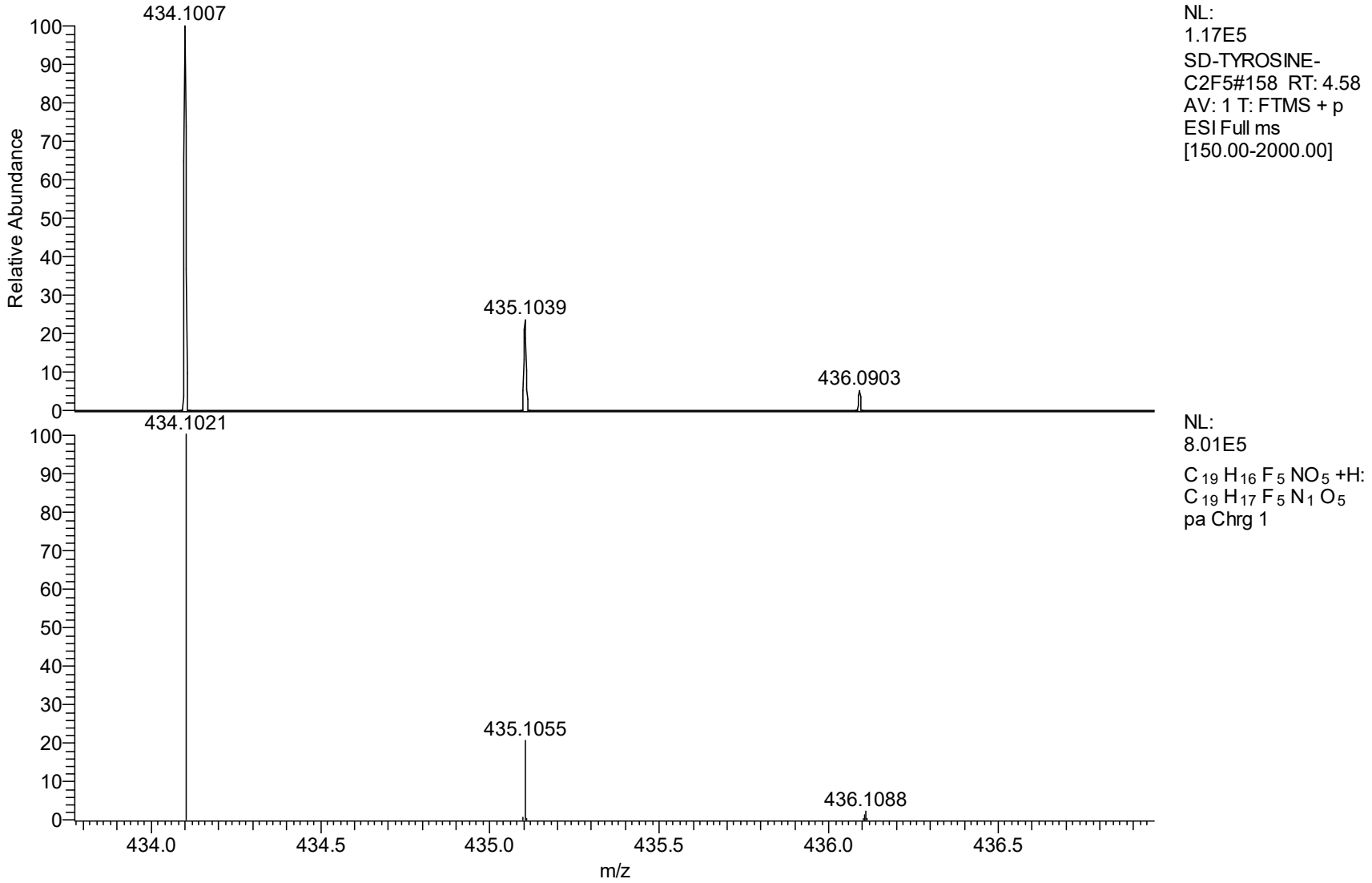


Figure S134. ESI-(HR)MS spectrum of a MeOH solution of **a2.**

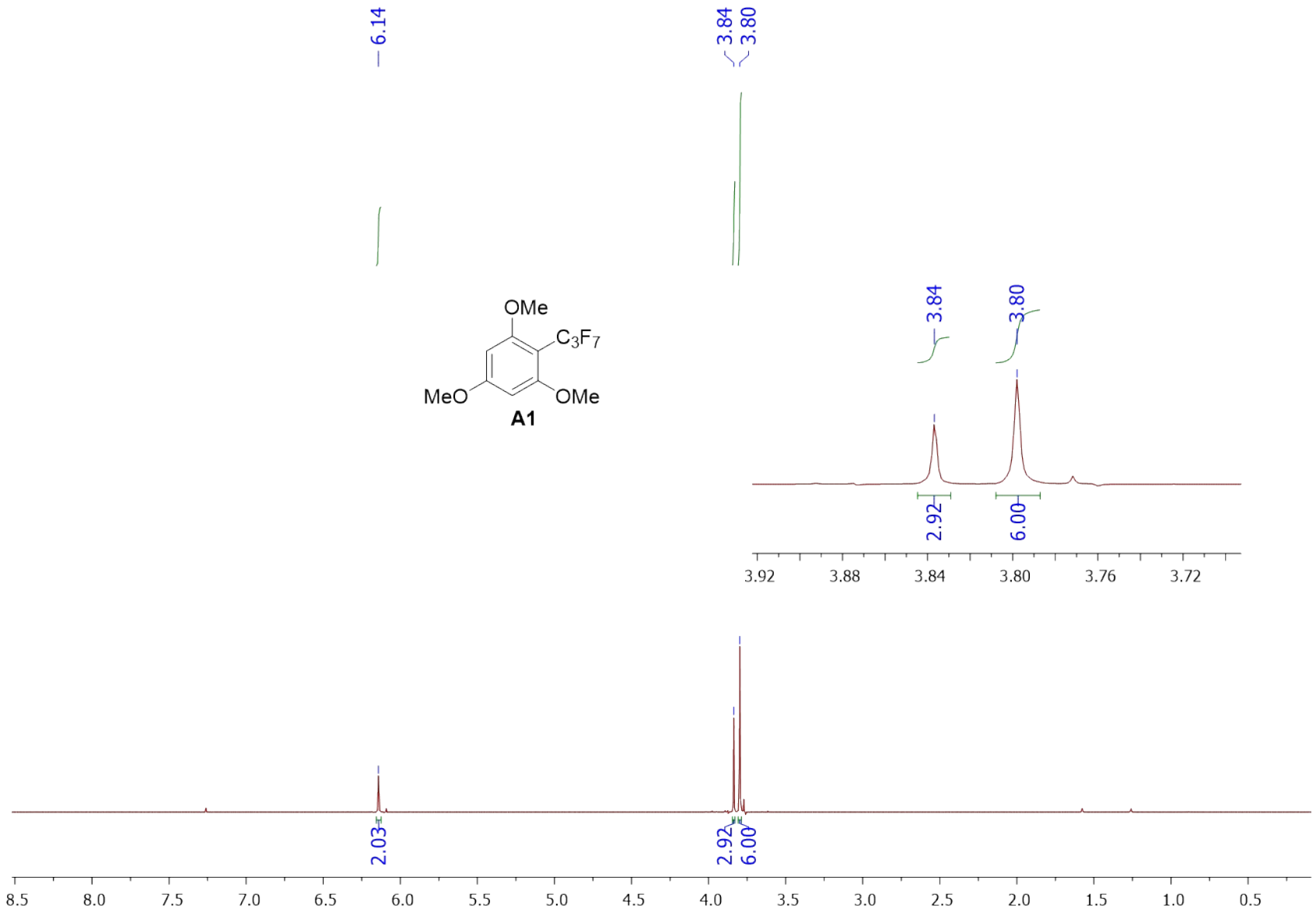


Figure S135. ^{1}H NMR spectrum of **A1** in $CDCl_3$ at 23 °C.

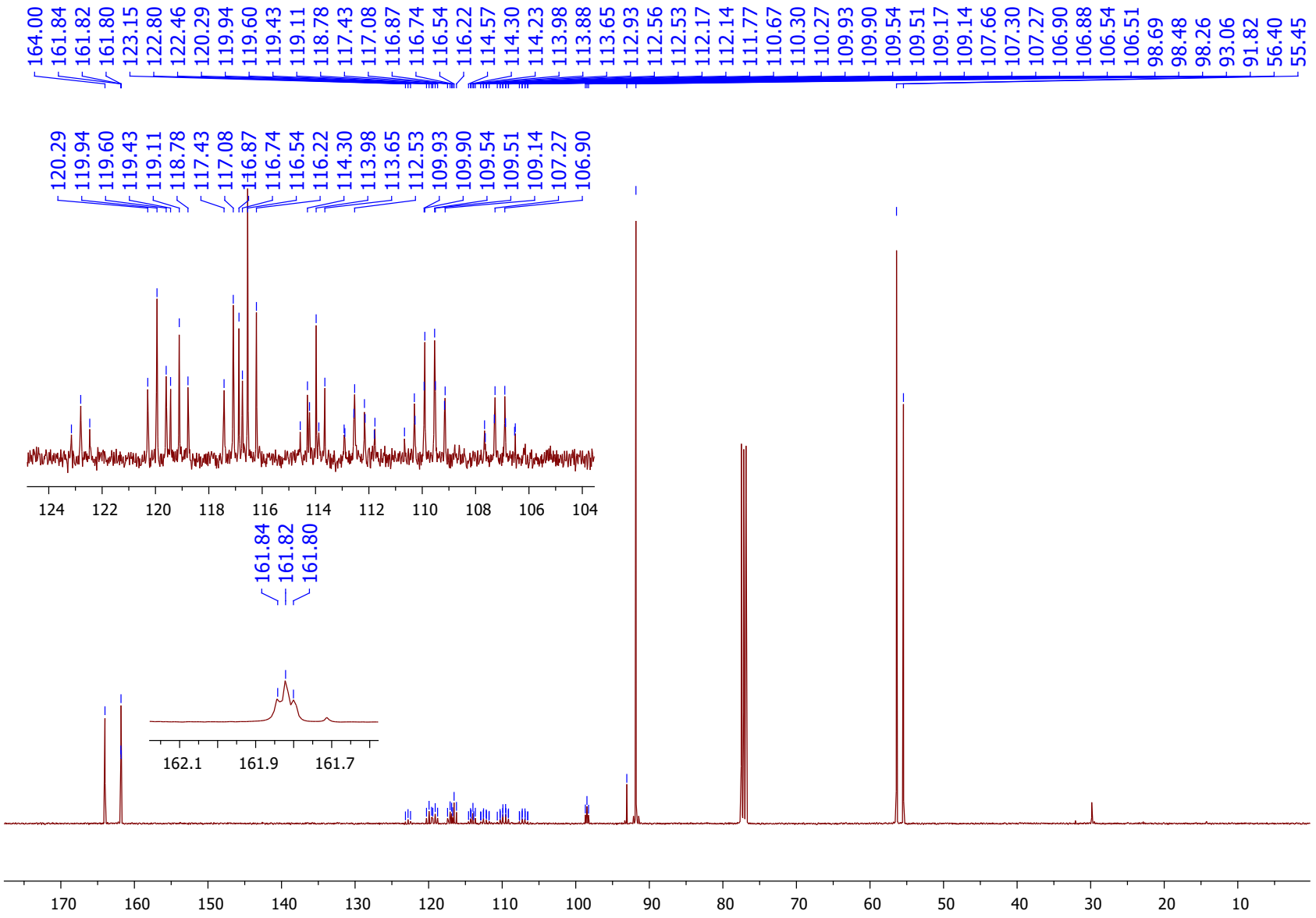


Figure S136. ^{13}C NMR spectrum of **A1** in $CDCl_3$ at 23 °C.

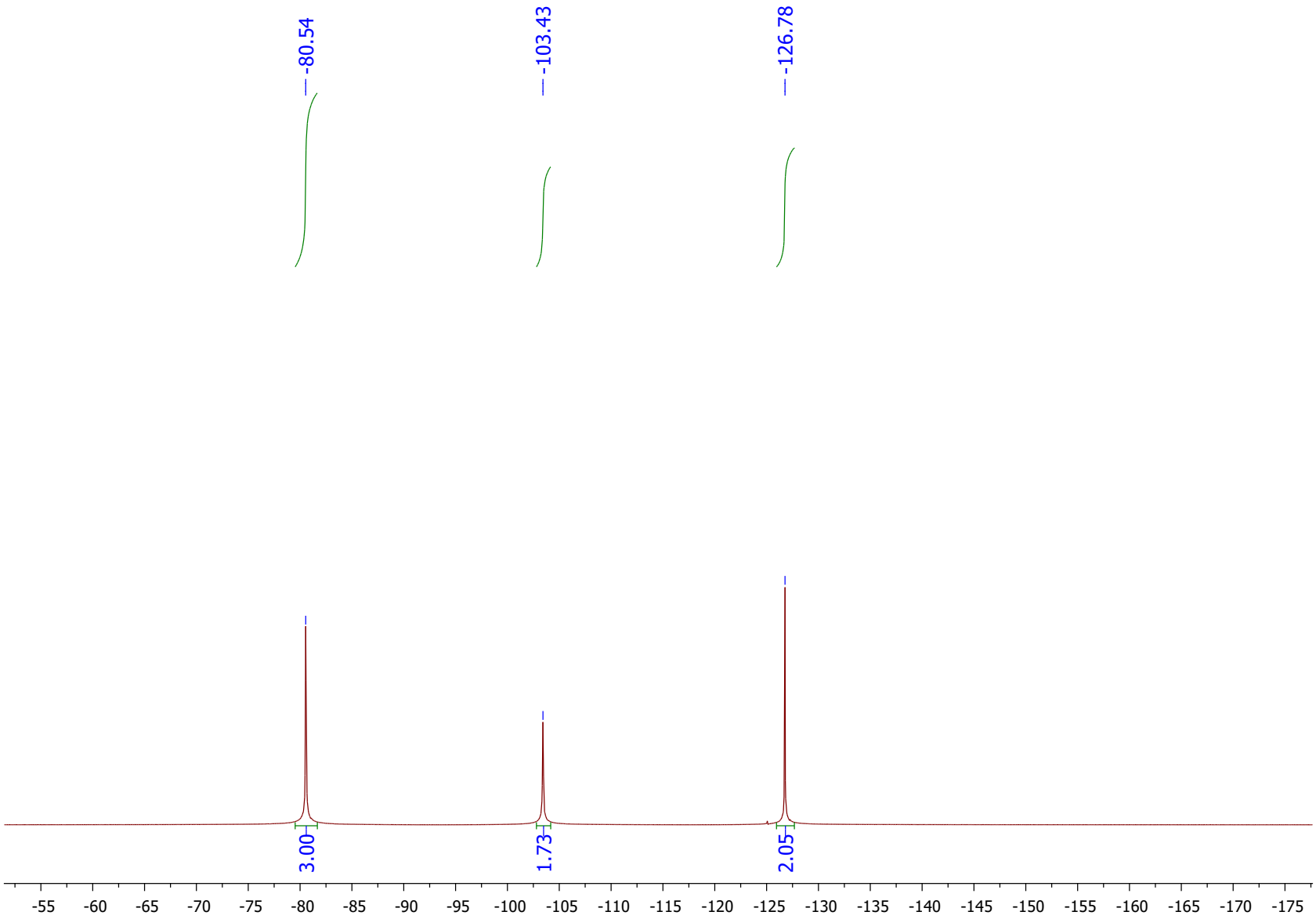


Figure S137. ^{19}F NMR spectrum of **A1** in $CDCl_3$ at 23 °C.

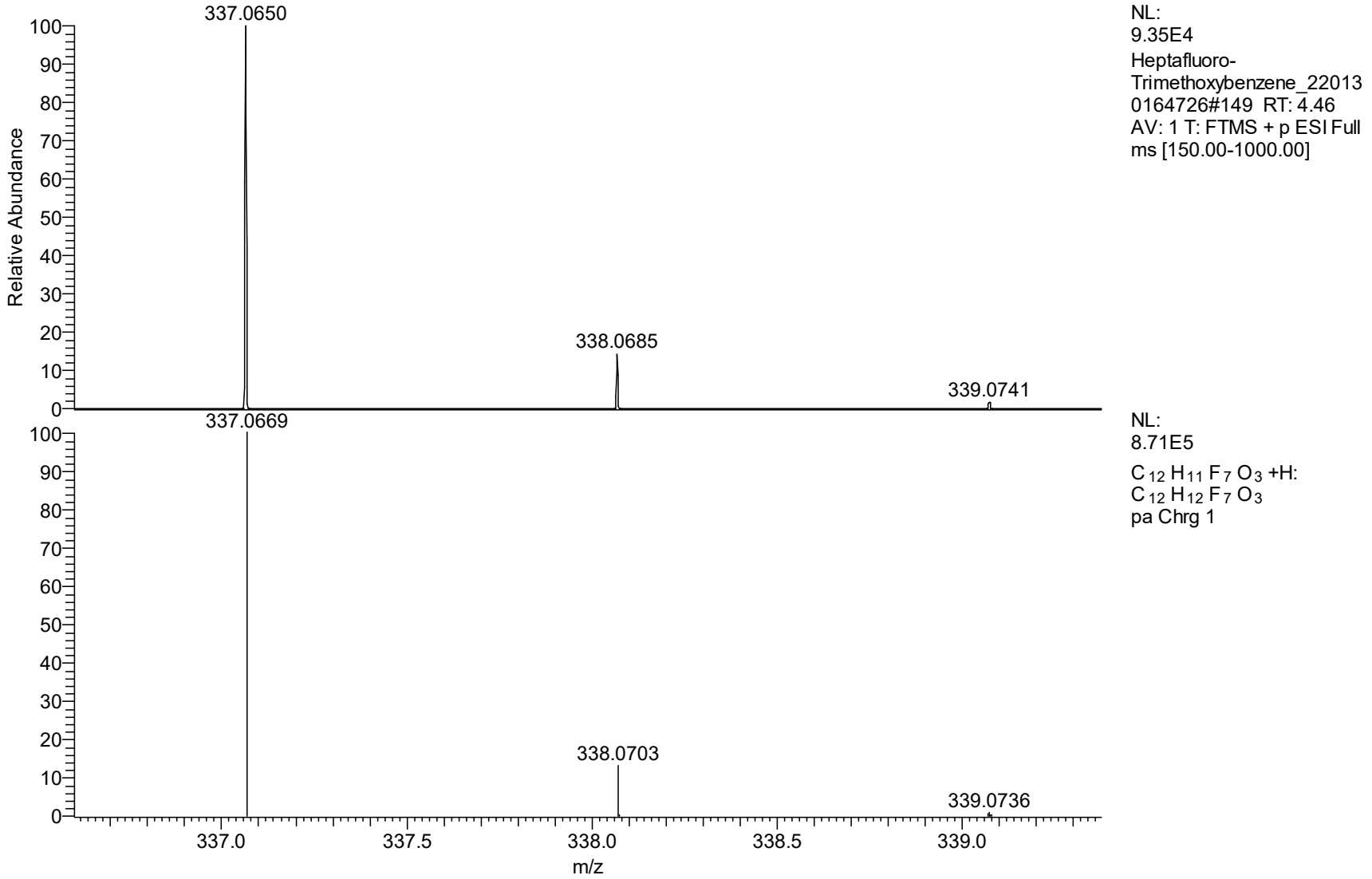


Figure S138. ESI-(HR)MS spectrum of a MeOH solution of **A1.**

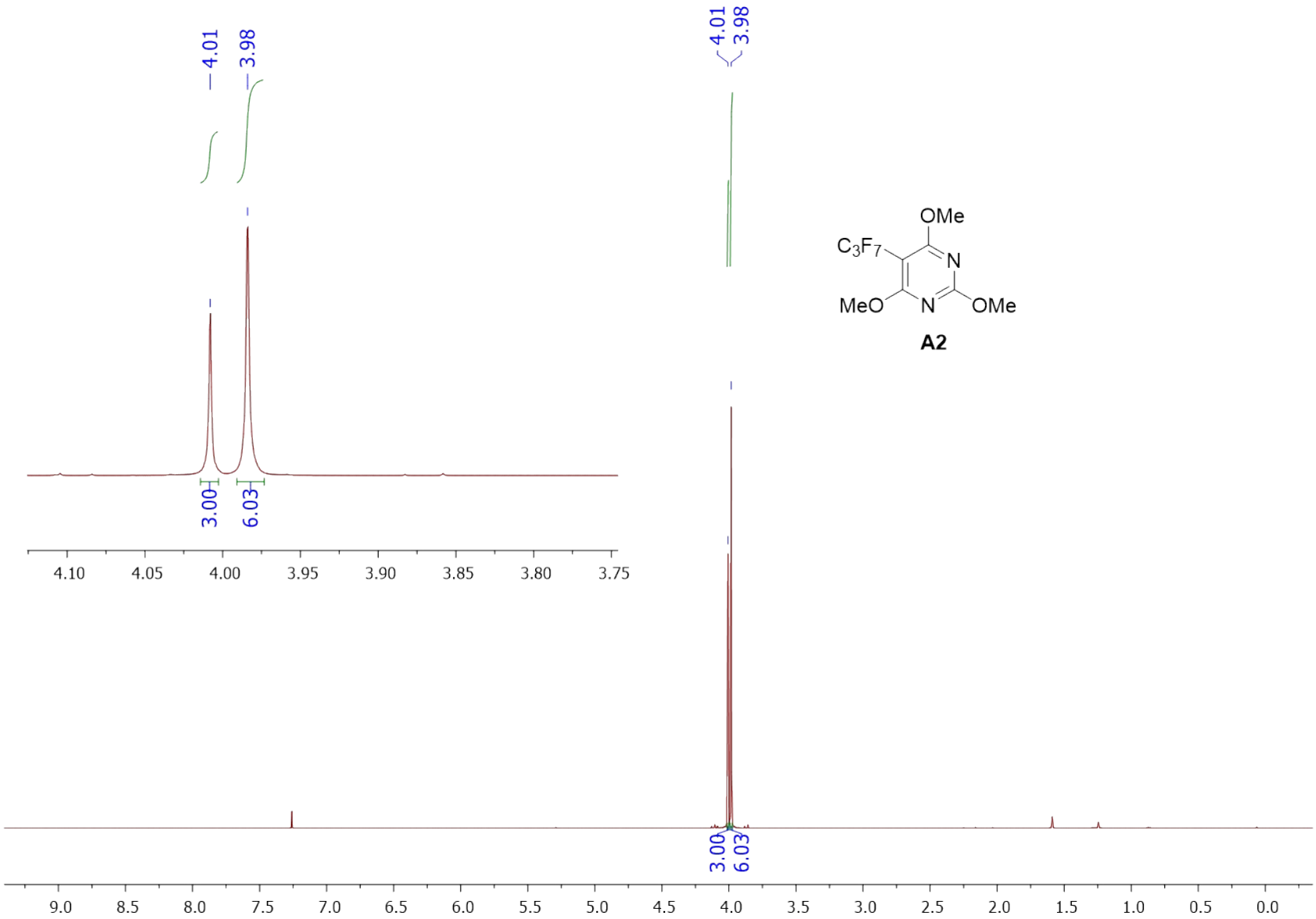


Figure S139. ^{1}H NMR spectrum of **A2** in $CDCl_3$ at 23 °C.

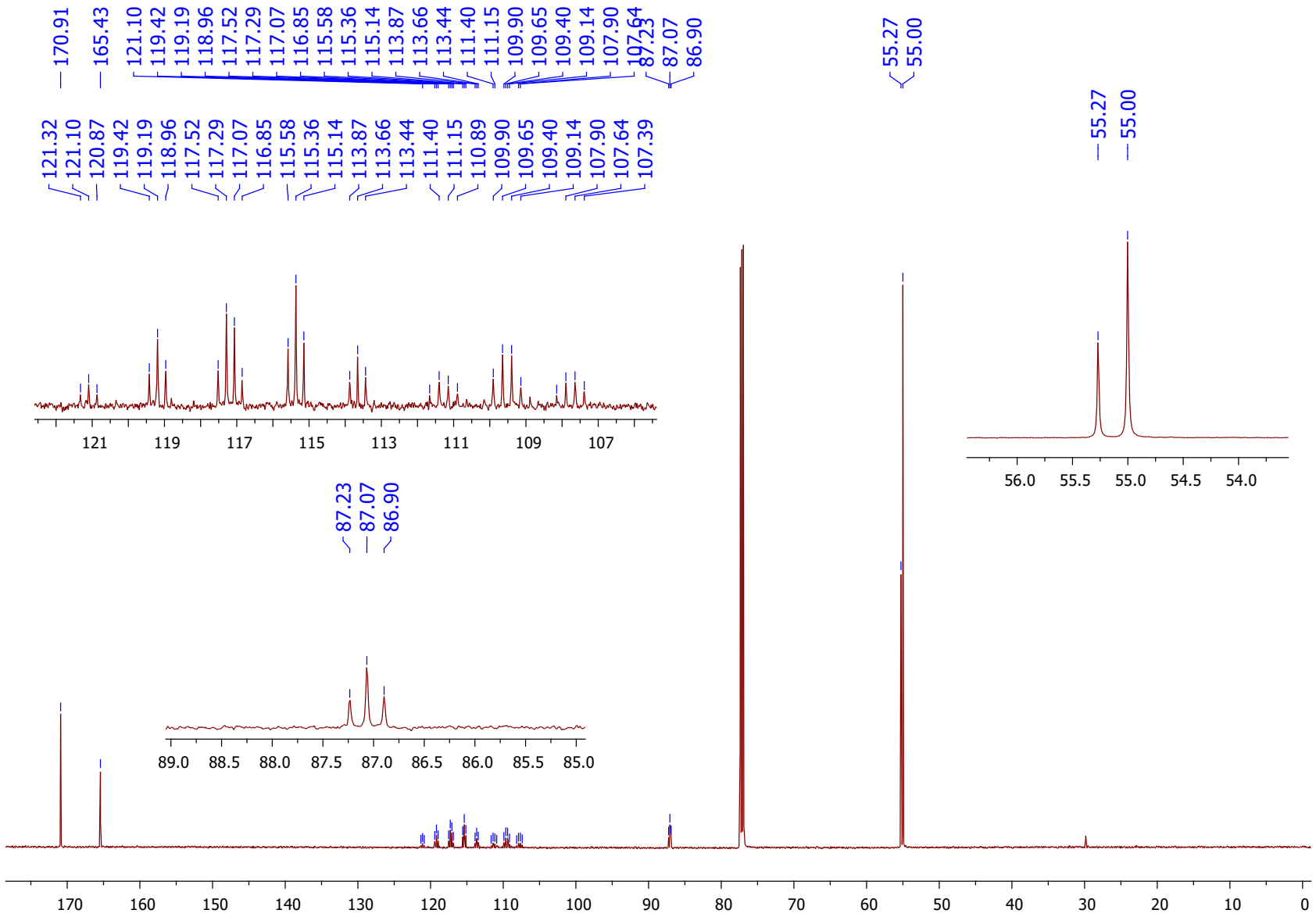


Figure S140. ^{13}C NMR spectrum of **A2** in $CDCl_3$ at 23 °C.

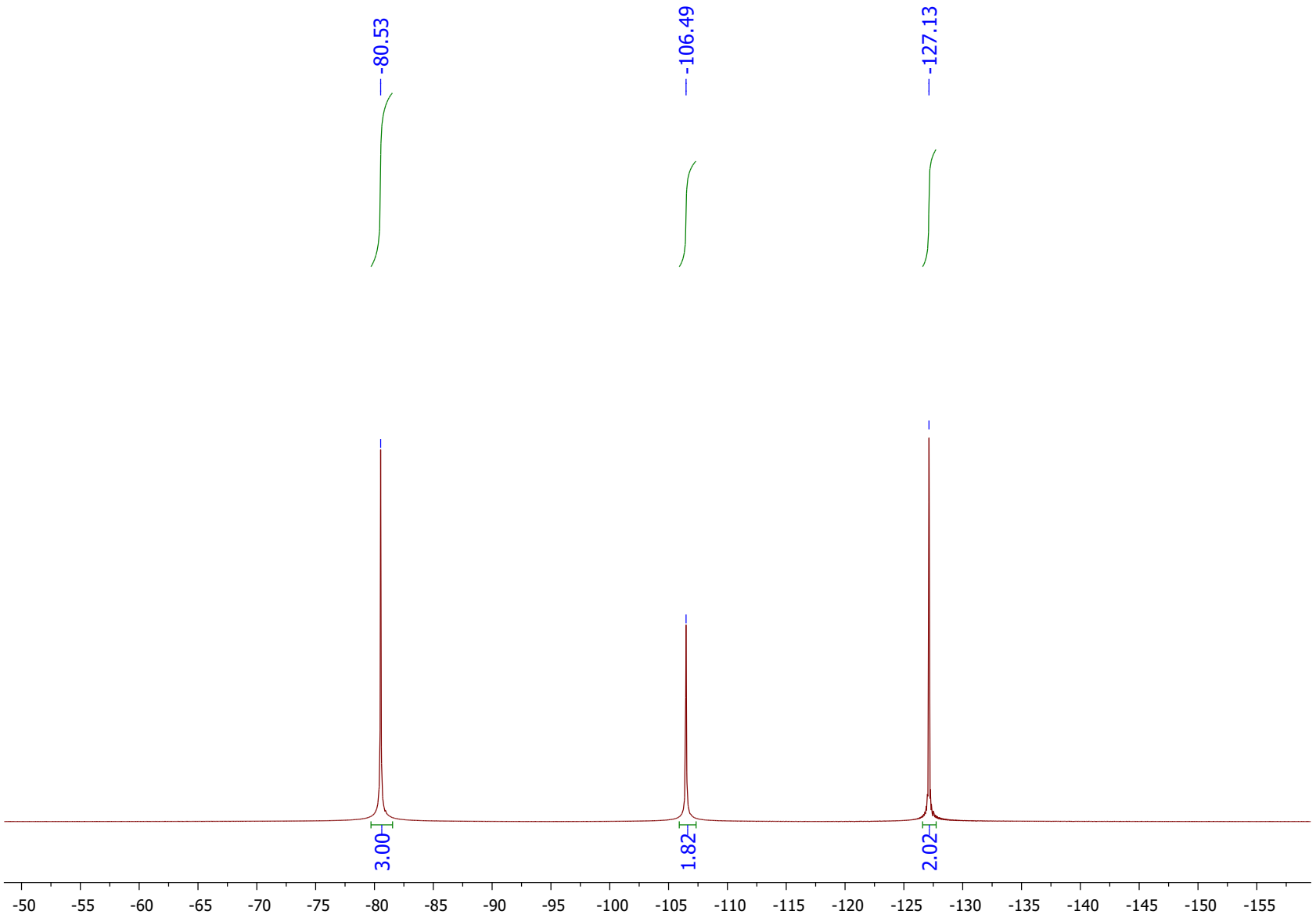


Figure S141. ^{19}F NMR spectrum of **A2** in $CDCl_3$ at 23 °C.

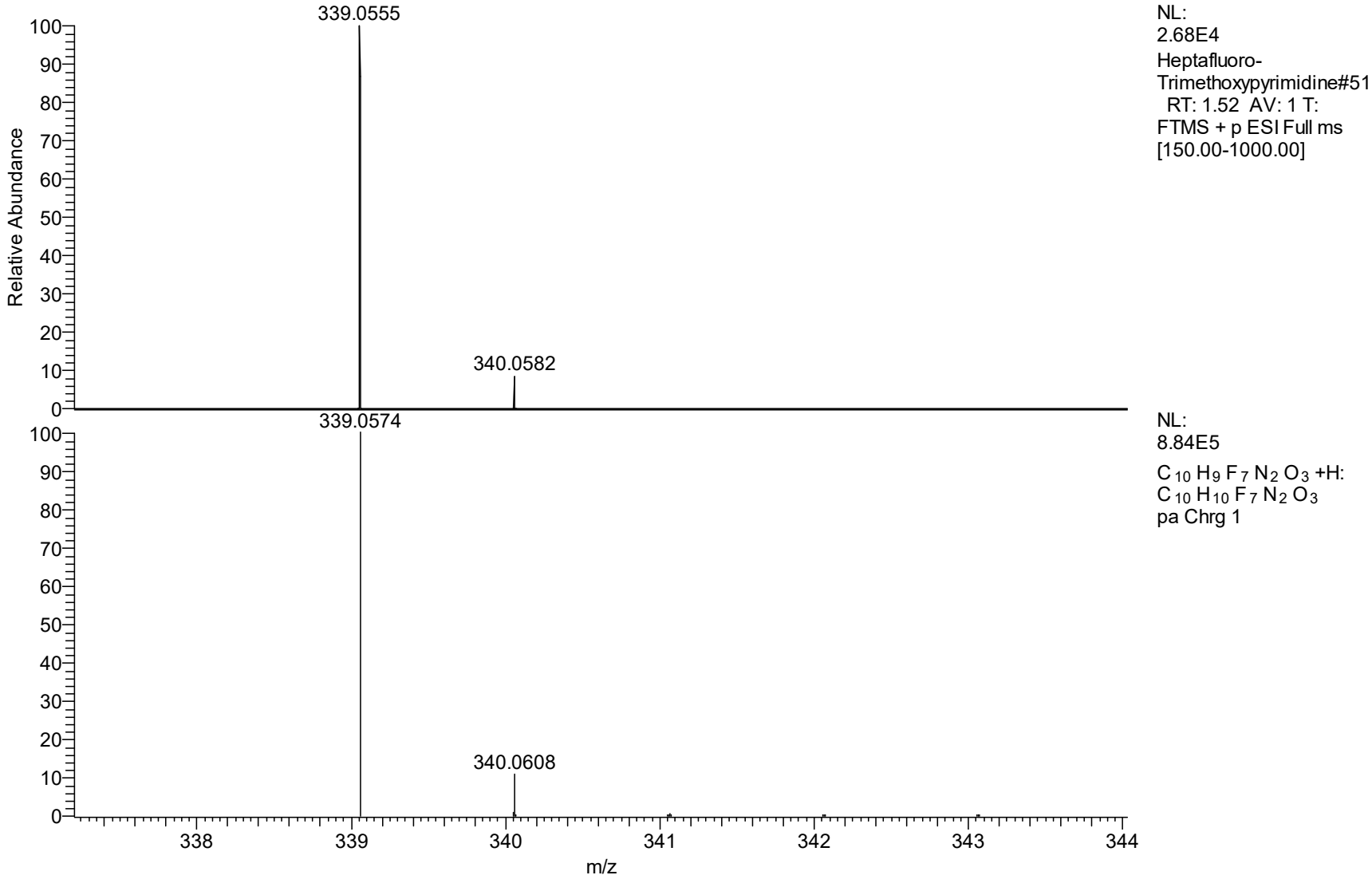


Figure S142. ESI-(HR)MS spectrum of a MeOH solution of **A2**.

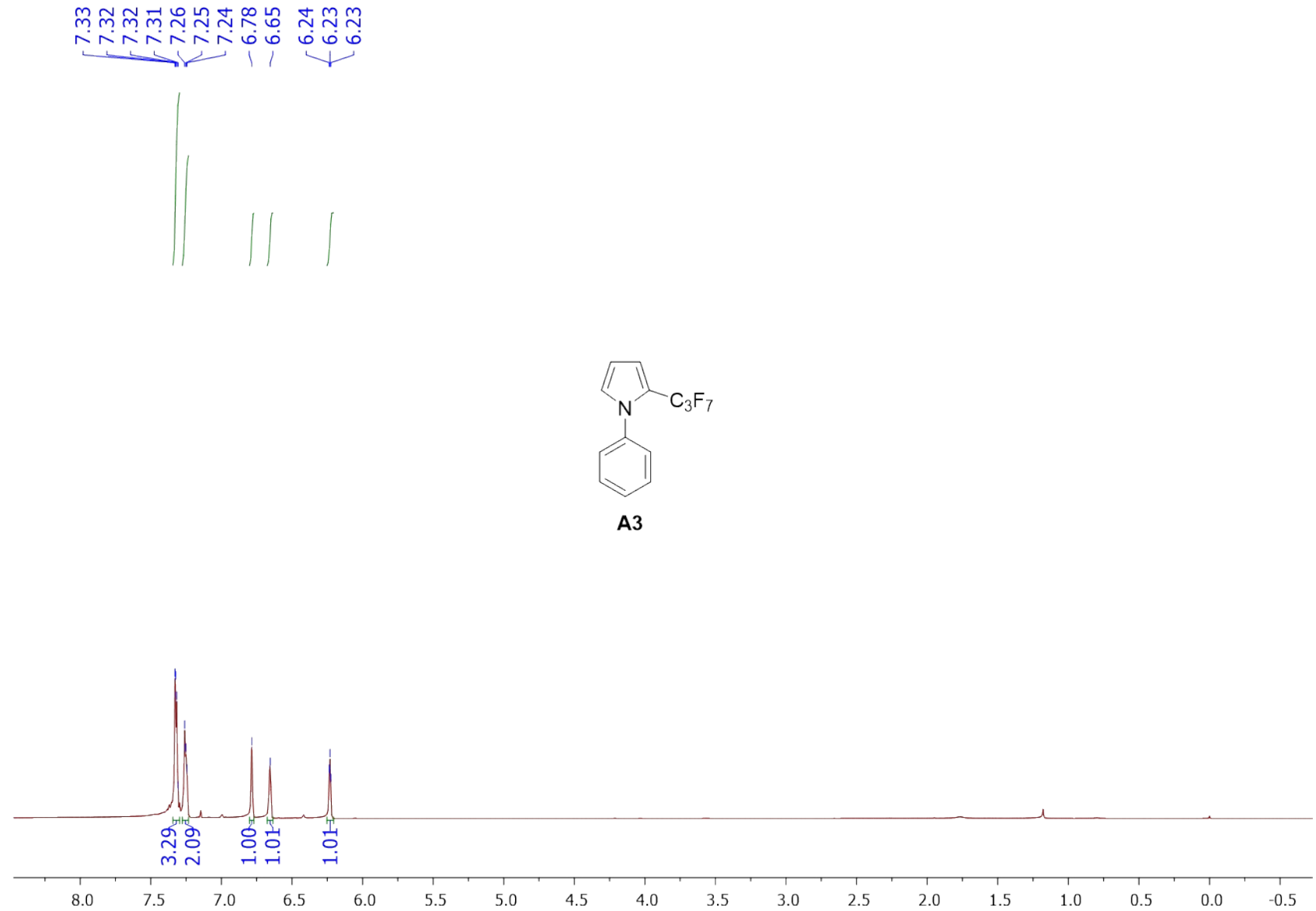


Figure S143. ^{1}H NMR spectrum of **A3** in $CDCl_3$ at 23 °C.

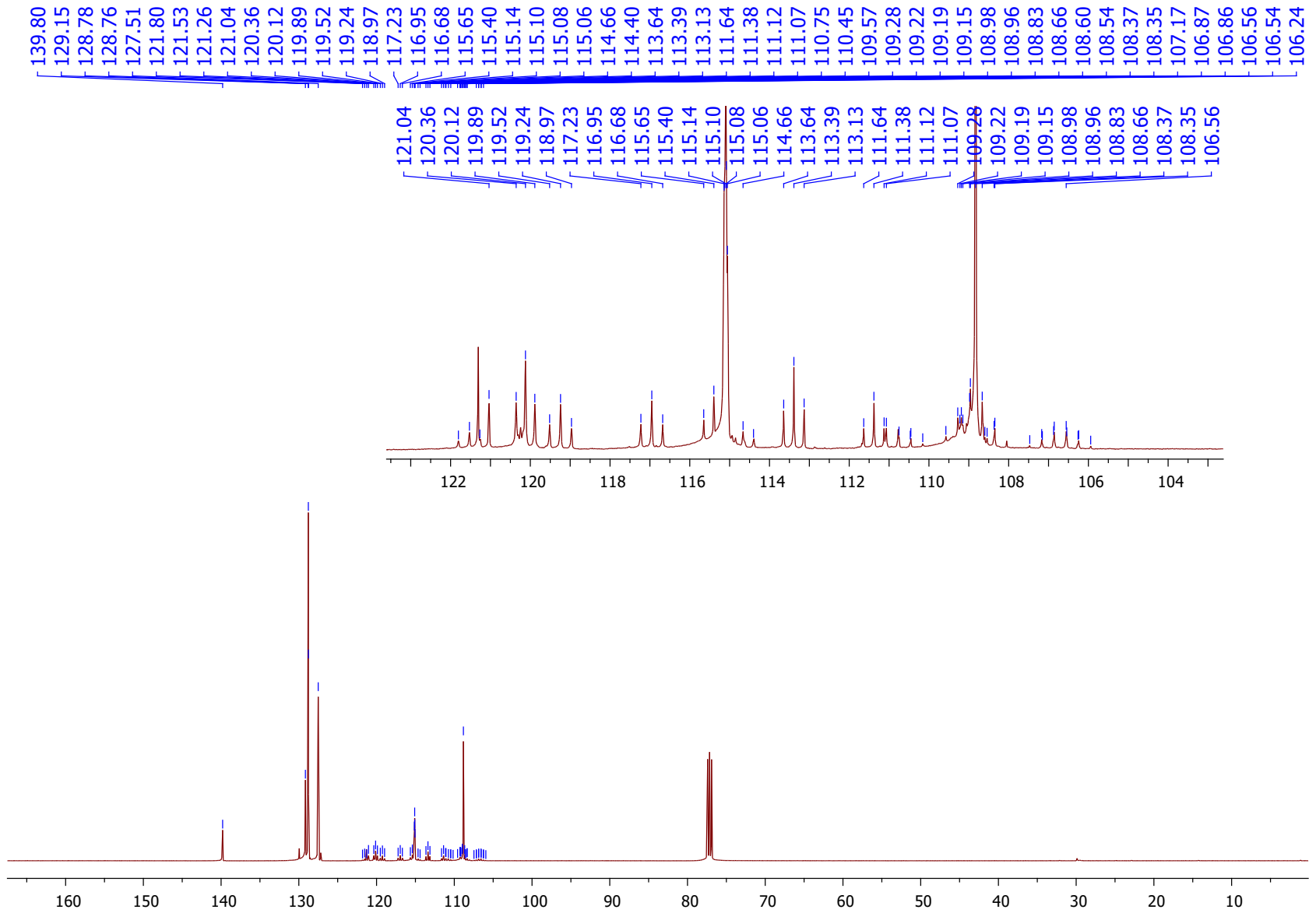


Figure S144. ^{13}C NMR spectrum of **A3** in $CDCl_3$ at 23 °C.

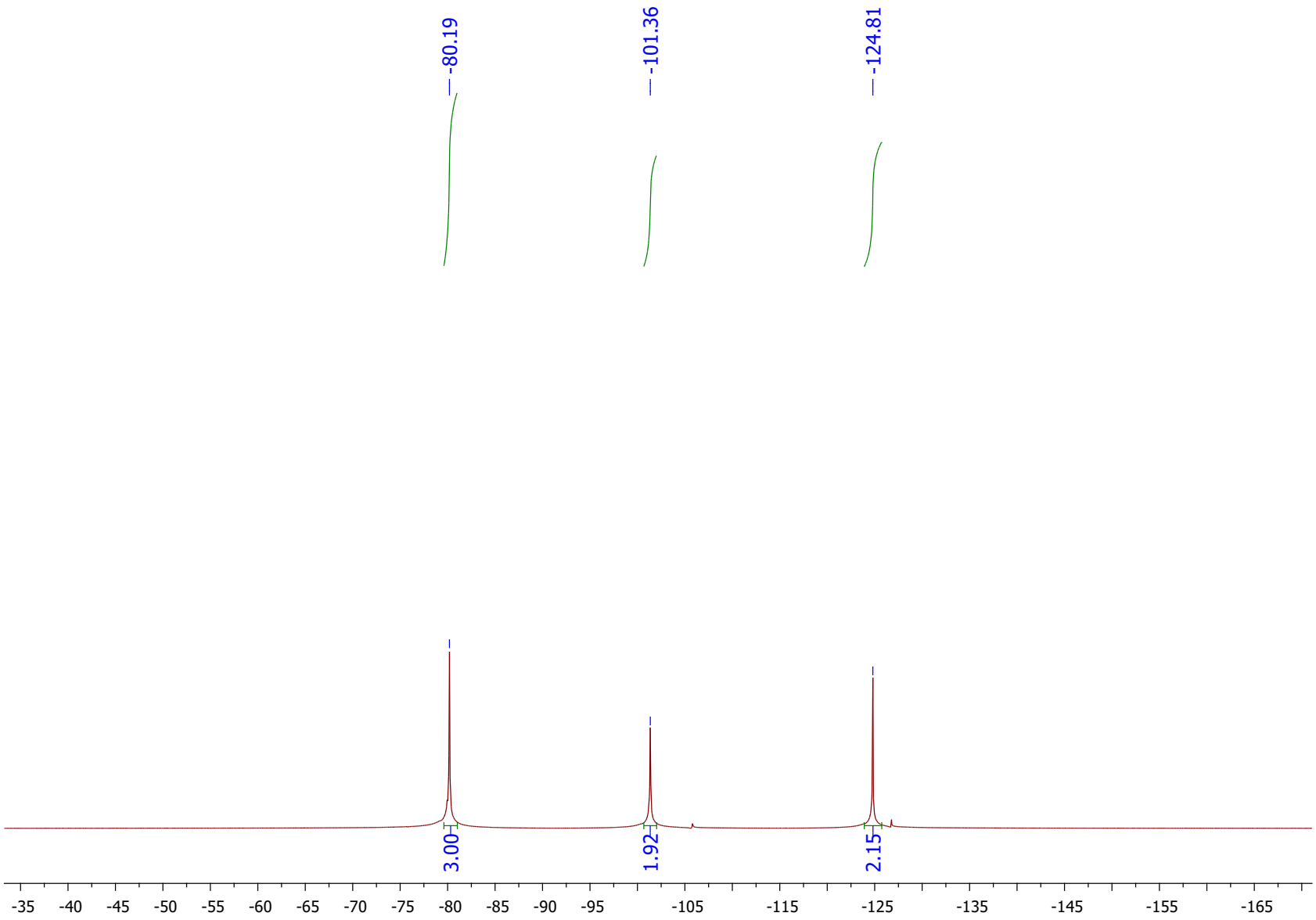


Figure S145. ^{19}F NMR spectrum of **A3** in $CDCl_3$ at 23 °C.

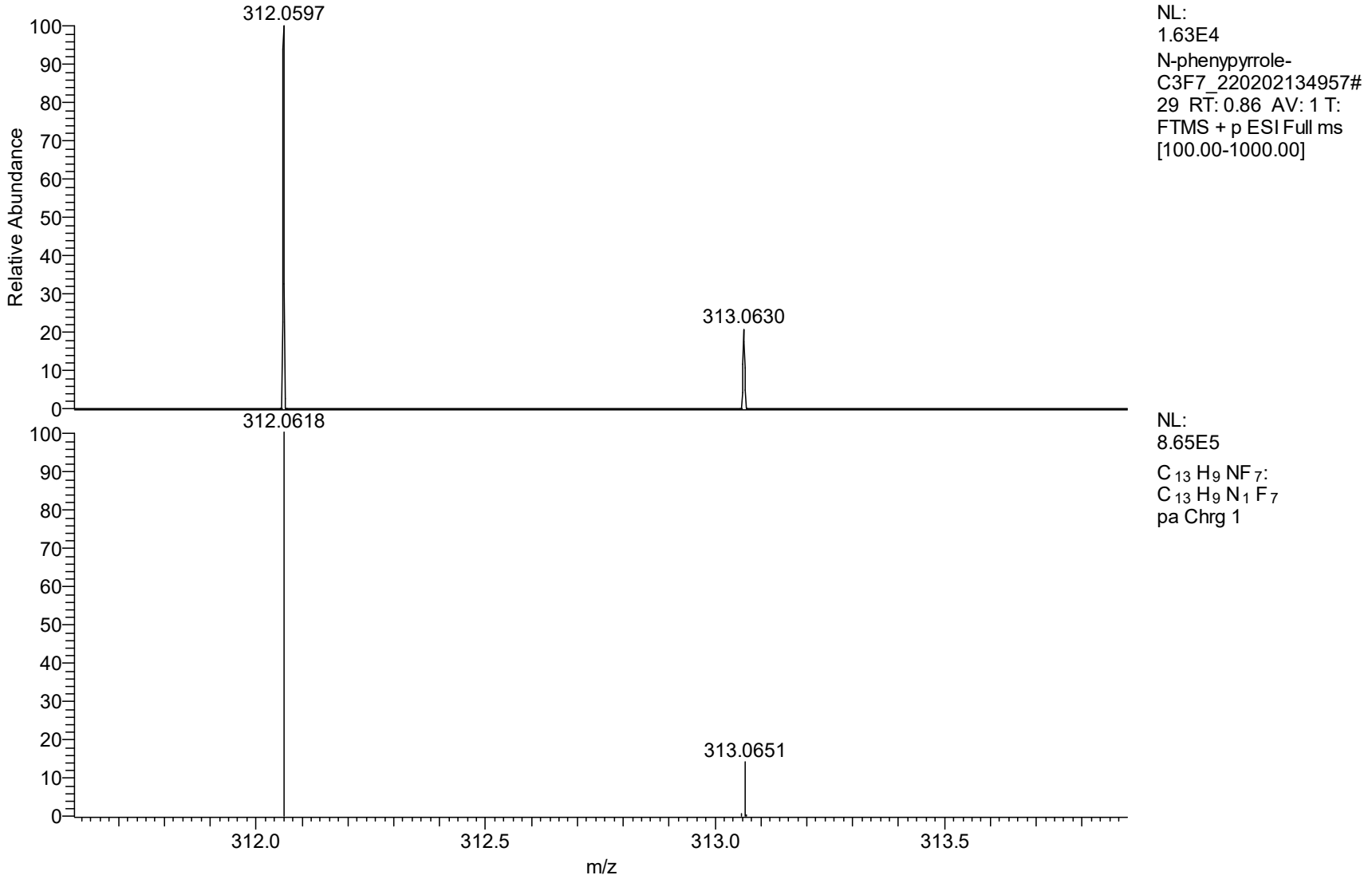


Figure S146. ESI-(HR)MS spectrum of a MeOH solution of **A3**.

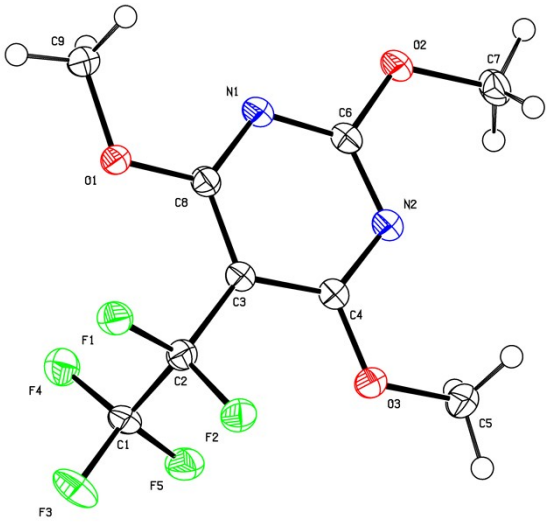
XV. X-ray structure determination details.

For compounds **r** and **A2**: data were collected using a Bruker SMART APEX2 area detector diffractometer operating at $T = 200.00$ K. Data were measured using w and f scans with Mo K_a radiation. The unit cell was refined using SAINT V8.40B (Bruker, 2016) Data reduction, scaling and absorption corrections were performed using SAINT V8.40B (Bruker, 2016). SADABS-2016/2 (Bruker, 2016/2) was used for absorption correction.

For compounds **b** and **a2**: Data were collected using a XtaLAB AFC12 (RINC): Kappa dual home/near diffractometer operating at $T = 100$ K. Data were measured using w scans with Cu K_a radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro 1.171.40.54a (Rigaku OD, 2019). Data reduction, scaling and absorption corrections were performed using CrysAlisPro 1.171.40.54a (Rigaku OD, 2019). A multi-scan absorption correction was performed using CrysAlisPro 1.171.40.54a (Rigaku Oxford Diffraction, 2019) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

The structures were solved, and the space group determined by the ShelXT 2018/2 (Sheldrick, 2018) structure solution program using iterative methods and refined by full matrix least squares minimization on F^2 using version 2016/6 of **ShelXL** 2016/6 (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Structures can be found by corresponding CCDC numbers: 2180252 -2180254, 2180257.

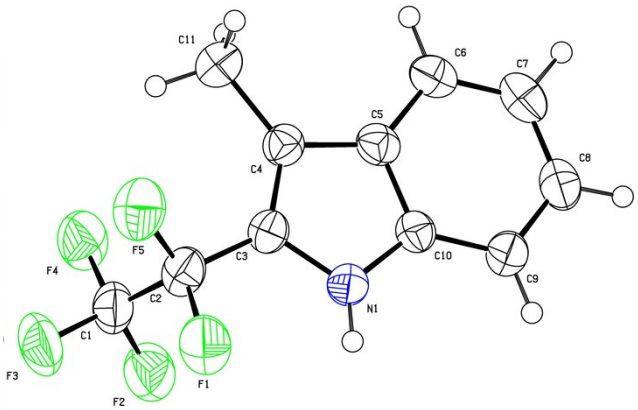
Compound **b**



Experimental. Single clear-light-colourless plate-shaped crystals of compound **b** were used as supplied. A suitable crystal with dimensions 0.13 × 0.12 × 0.08 mm^3 was selected and mounted on a XtaLAB AFC12 (RINC): Kappa dual home/near diffractometer. The crystal was kept at a steady T = 100 K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) solution program using dual methods and by using **Olex2** 1.5 (Dolomanov et al., 2009) as the graphical interface. The model was refined with **ShelXL** 2016/6 (Sheldrick, 2015) using full matrix least squares minimisation on $\boldsymbol{F^2}$.

Crystal Data. $C_9H_9F_5N_2O_3$, M_r = 288.18, triclinic, P-1 (No. 2), a = 7.9519(6) Å, b = 8.3267(6) Å, c = 9.1611(7) Å, a = 82.449(6)°, b = 72.420(7)°, g = 77.031(6)°, V = 562.18(8) Å^3, T = 100 K, Z = 2, Z' = 1, m(Cu K$_a$) = 1.623, 7514 reflections measured, 2353 unique (R_{int} = 0.0358) which were used in all calculations. The final wR_2 was 0.1326 (all data) and R_1 was 0.0438 (I≥2 s(I)).

Compound **r**

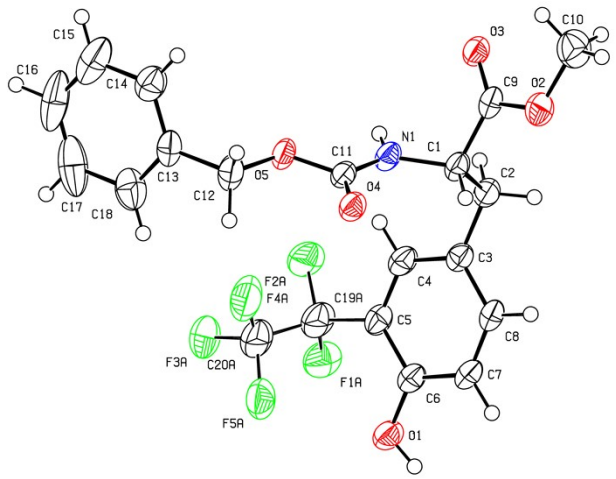


Experimental. Single clear-light-colorless block-shaped crystals of compound **r** were used as supplied. A suitable crystal with dimensions 0.26 × 0.25 × 0.23 mm^3 was selected and mounted on a Bruker SMART APEX2 area detector diffractometer. The crystal was kept at a steady T = 200.00(10) K during data collection. The structure was solved with the **ShelXT** 2018/2 (Sheldrick, 2018) solution program using iterative methods and by using **Olex2** 1.5 (Dolomanov et al., 2009) as the graphical interface. The model was refined with **ShelXL** 2016/6 (Sheldrick, 2015) using full matrix least-squares minimization on $\boldsymbol{F^2}$.

Crystal Data. $C_{11}H_8F_5N$, M_r = 249.18, monoclinic, $P2_1/n$ (No. 14), a = 7.8320(7) Å, b = 6.1313(5) Å, c = 22.4930(17) Å, b = 93.678(7)°, a = g = 90°, V = 1077.90(15) Å^3, T = 200.00(10) K, Z = 4, Z' = 1, m(Mo K$_a$) = 0.152, 9790 reflections measured, 2111 unique (R_{int} =

0.0797) which were used in all calculations. The final wR_2 was 0.1490 (all data) and R_1 was 0.0566 (I≥2 s(I)).

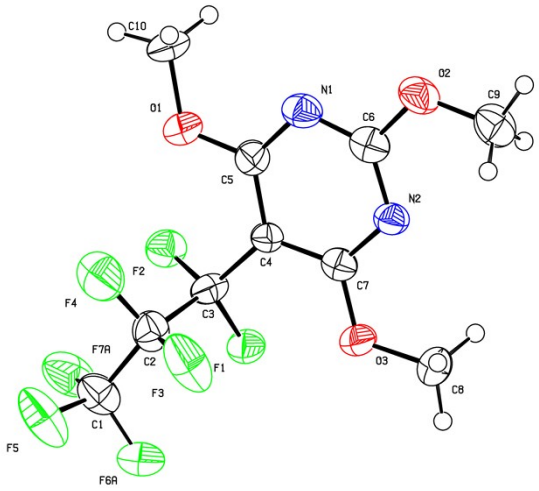
Compound **a2**



Experimental. Single clear-colorless plate-shaped crystals of compound **a2** were used as supplied. A suitable crystal with dimensions 0.12 × 0.09 × 0.01 mm^3 was selected and mounted on a XtaLAB AFC12 (RINC): Kappa dual home/near diffractometer. The crystal was kept at a steady T = 100 K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) solution program using dual methods and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with **ShelXL** (Sheldrick, 2015) using full matrix least squares minimisation on $\boldsymbol{F^2}$.

Crystal Data. $C_{20}H_{18}F_5NO_5$, M_r = 447.35, monoclinic, $I2$ (No. 5), a = 20.3374(7) Å, b = 7.1756(3) Å, c = 14.0098(7) Å, b = 92.999(4)°, a = g = 90°, V = 2041.69(15) Å^3, T = 100 K, Z = 4, Z' = 1, m(Cu K$_a$) = 1.174, 11116 reflections measured, 4292 unique (R_{int} = 0.0309) which were used in all calculations. The final wR_2 was 0.1549 (all data) and R_1 was 0.0567 (I≥2 s(I)).

Compound **A2**



Experimental. Single clear-light-colorless block-shaped crystals of compound **A2** were used as supplied. A suitable crystal with dimensions 0.05 × 0.03 × 0.03 mm^3 was selected and mounted on a Bruker SMART APEX2 area detector diffractometer. The crystal was kept at a steady T = 200.00(10) K during data collection. The structure was solved with the **ShelXT** 2018/2 (Sheldrick, 2018) solution program using iterative methods and by using **Olex2** 1.5 (Dolomanov et al., 2009) as the graphical interface. The model was refined with **ShelXL** 2016/6 (Sheldrick, 2015) using full matrix least squares minimisation on $\boldsymbol{F^2}$.

Crystal Data. $C_{10}H_9F_7N_2O_3$, M_r = 338.19, triclinic, P-1 (No. 2), a = 8.4543(9) Å, b = 8.9233(15) Å, c = 9.8274(14) Å, a = 111.704(14)°, b = 98.837(11)°, g = 101.362(11)°, V = 654.12(17) $Å^3$, T = 200.00(10) K, Z = 2, Z' = 1, m(Mo K_a) = 0.189, 7895 reflections measured, 2392 unique (R_{int} = 0.1175) which were used in all calculations. The final wR_2 was 0.1834 (all data) and R_1 was 0.0649 (I≥2 s(I)).

Compound	**b** (2180253)	**r** (2180254)	**a2** (2180257)	**A2** (2180252)
Formula	$C_9H_9F_5N_2O_3$	$C_{11}H_8F_5N$	$C_{20}H_{18}F_5NO_5$	$C_{10}H_9F_7N_2O_3$
Dcalc./ g cm-3	1.702	1.536	1.455	1.717
m/mm-1	1.623	0.152	1.174	0.189
Formula Weight	288.18	249.18	447.35	338.19
Colour	Clear-light-colourless	Clear-light-colourless	Clear-colourless	Clear-light-colourless
Size/mm3	0.13×0.12×0.08	0.26×0.25×0.23	0.12×0.09×0.01	0.05×0.03×0.03
T/K	100	200.00(10)	100	200.00(10)
Crystal System	triclinic	monoclinic	monoclinic	triclinic
Space Group	P-1	$P2_1/n$	$I2$	P-1
a/Å	7.9519(6)	7.8320(7)	20.3374(7)	8.4543(9)
b/Å	8.3267(6)	6.1313(5)	7.1756(3)	8.9233(15)
c/Å	9.1611(7)	22.4930(17)	14.0098(7)	9.8274(14)
a/°	82.449(6)	90	90	111.704(14)
b/°	72.420(7)	93.678(7)	92.999(4)	98.837(11)
g/°	77.031(6)	90	90	101.362(11)
V/Å3	562.18(8)	1077.90(15)	2041.69(15)	654.12(17)
Z	2	4	4	2
Radiation type	Cu Ka	Mo K_a	Cu K_a	Mo K_a
Qmin/°	5.076	3.445	3.742	2.303
Qmax/°	79.873	26.020	80.509	25.349
Measured Refl's.	7514	9790	11116	7895
Indep't Refl's	2353	2111	4292	2392
Refl's I≥2 s(I)	2051	1458	3939	1140
Rint	0.0358	0.0797	0.0309	0.1175
Parameters	175	160	353	222
Largest Peak	0.307	0.217	0.418	0.374
Deepest Hole	-0.365	-0.215	-0.413	-0.303
GooF	1.097	1.040	1.077	0.986
wR2 (all data)	0.1326	0.1490	0.1549	0.1834
wR2	0.1281	0.1280	0.1515	0.1367
R1 (all data)	0.0492	0.0867	0.0606	0.1604
R1	0.0438	0.0566	0.0567	0.0649

XVI. Preparation of Nickel precursor $[(CH_3CN)_2Ni(C_3F_7)]_2$

Inside the glovebox to a 50 mL vial, $TMSC_3F_7$ (0.5 mL, 2.430 mmol) and AgF (312.8 mg, 1.9441 mmol) were added into 30 mL of dry CH_3CN. The reaction mixture was stirred at room temperature for 2 hours. Then $NiBr_2$·DME (300 mg, 0.9720 mmol) was added. The reaction mixture was kept stirring for 2 days and filtered. The filtrate was evaporated on a vacuum line to give a yellow solid (83%) yield.

^{1}H NMR (CD_2Cl_2, 600 MHz, 23 °C): δ 2.16 (s, 6H).

^{13}C NMR (CD_2Cl_2, 151 MHz, 23 °C): δ 128-107 (complicated fluorine splitting), 2.95.

^{19}F NMR (CD_2Cl_2,565 MHz, 23 °C): δ -80.59 (3F), -98.33 (2F), -119.83 (2F).

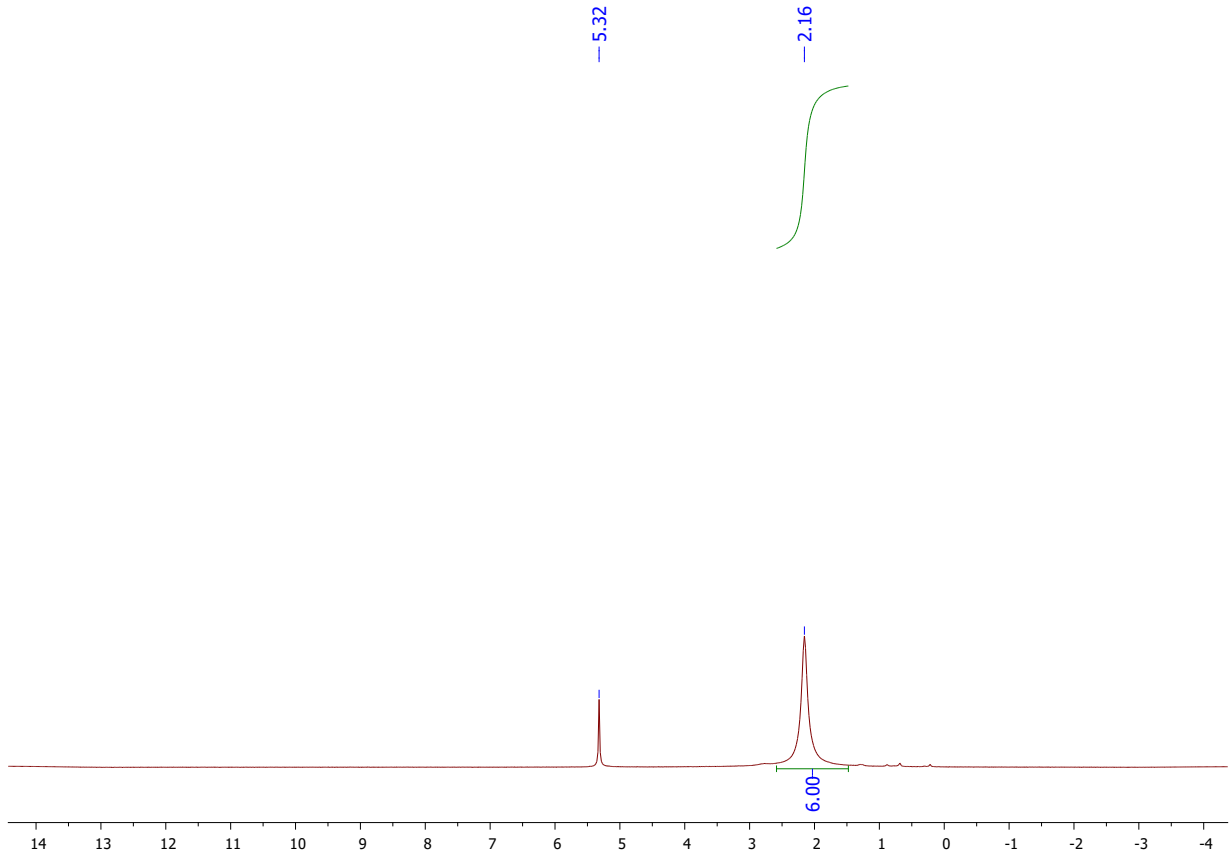


Figure S147. ^{1}H NMR spectrum of **2** in CD_2Cl_2 at 23 °C.

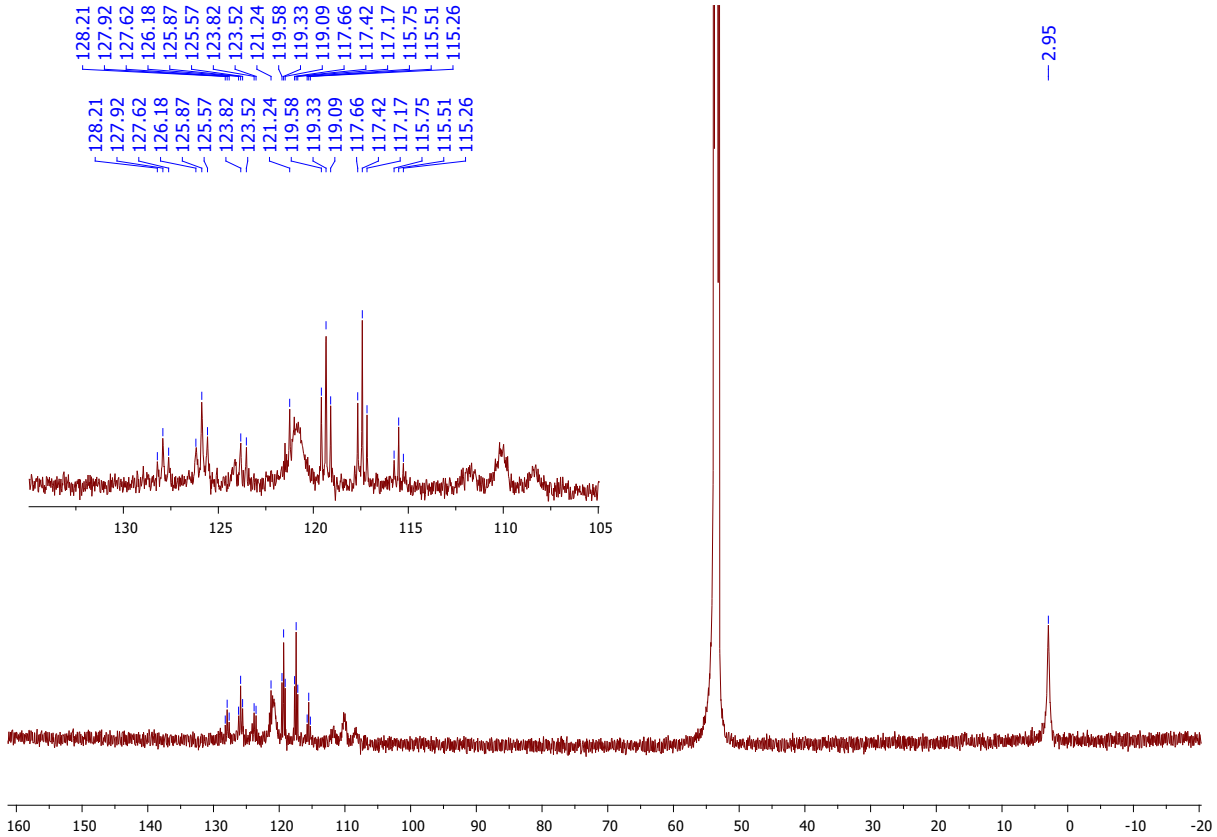


Figure S148. ^{13}C NMR spectrum of **2** in CD_2Cl_2 at 23 °C.

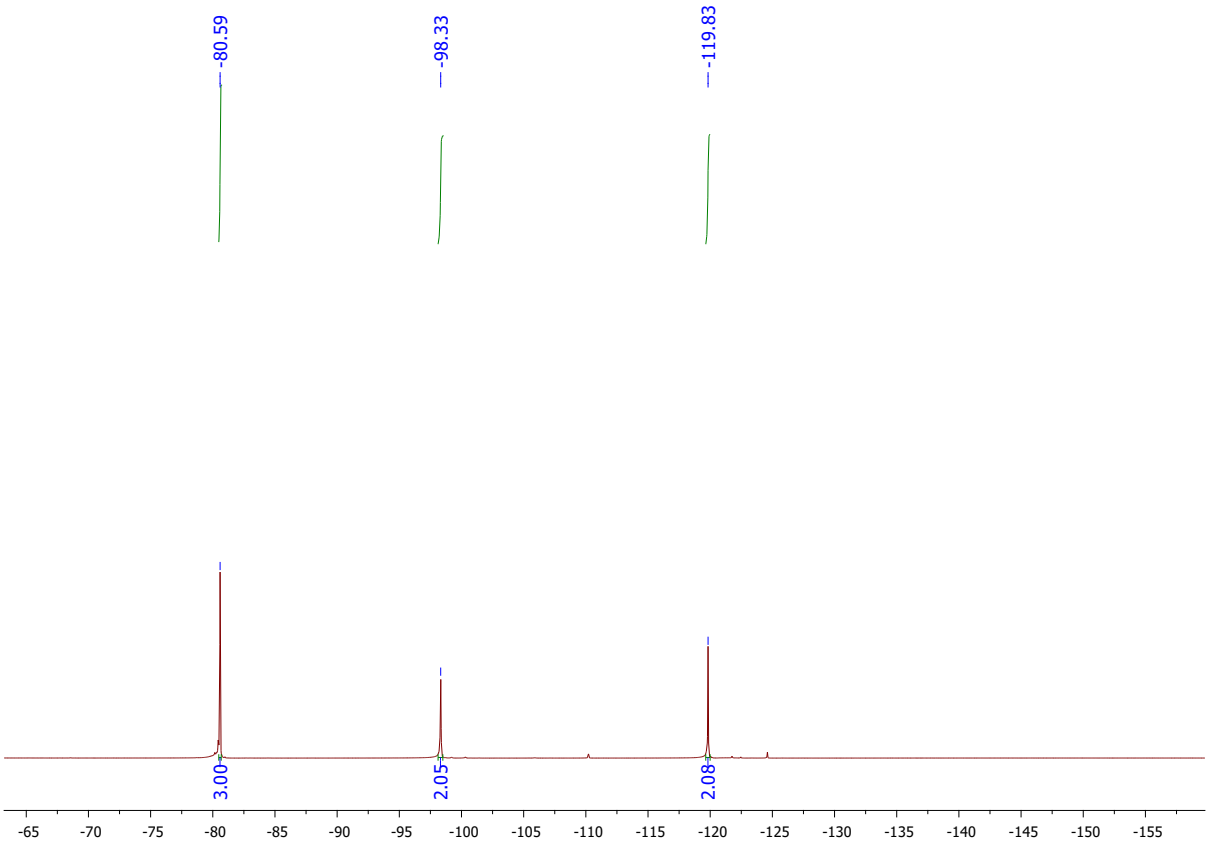


Figure S149. ^{19}F NMR spectrum of **2** in CD_2Cl_2 at 23 °C.

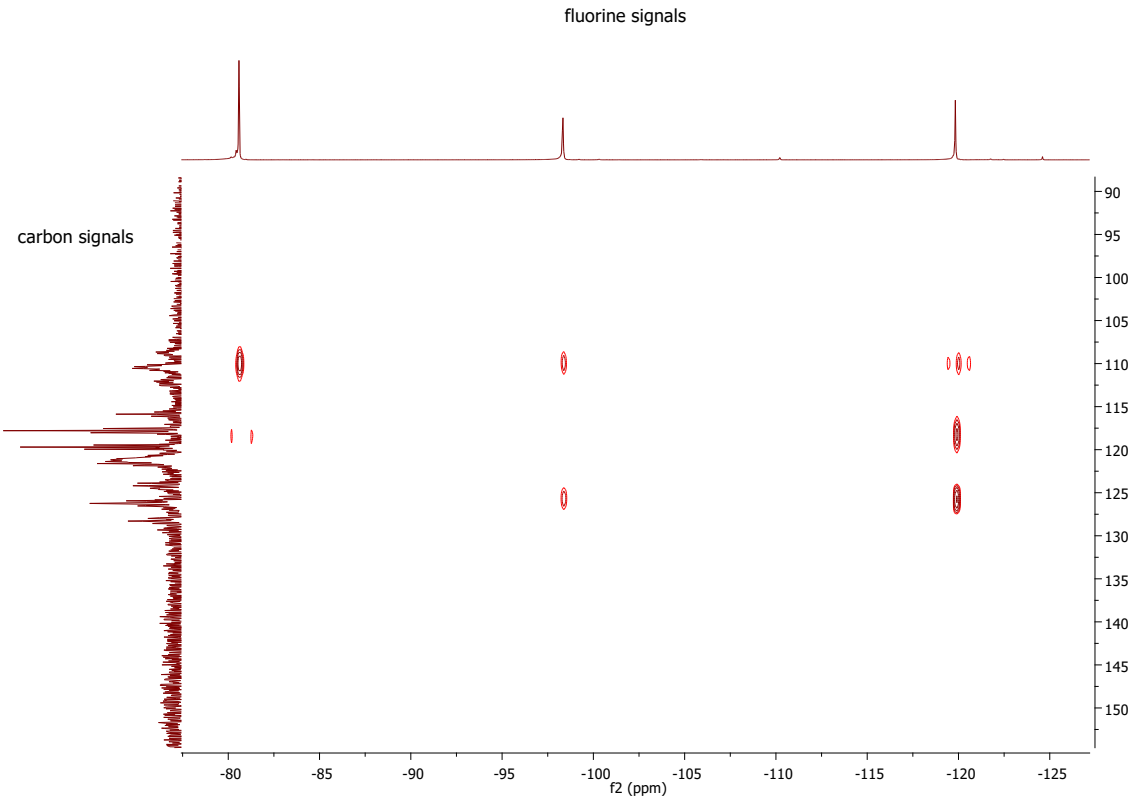


Figure S150. ^{19}F-^{13}C HMQC spectrum of **2** in CD_2Cl_2 at 23 °C.

XVII. References

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