Supporting Information

for

Ceramic boron carbonitrides for unlocking organic halides with visible light

Tao Yuan[a], Meifang Zheng*[,a], Markus Antonietti[b], and Xinchen Wang*[,a]

[a]State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou 350116, China.

[b]Max-Planck Institute of Colloids and Interfaces, Department of Colloid Chemistry, Research Campus Golm, 14424 Potsdam, Germany.

Email: mfzheng@fzu.edu.cn; xcwang@fzu.edu.cn

Supplementary text

Figures S1 to S31

Tables S1 to S5

SI References

General Information

Unless otherwise noted, reagents and solvents were used as commercially available without further treatment. X-ray diffraction (XRD) measurements were performed on a Bruker D8 Advance diffractometer with Cu-Kα1 radiation (λ = 1.5406 Å). The UV–vis diffuse reflection spectroscopy (DRS) were performed on a Varian Cary 500 Scan UV–vis system. The fourier transform infrared (FT-IR) spectra were obtained on a Nicolet 670 FT-IR spectrometer with KBr as the diluents. The scanning emission microscope (SEM) measurements were carried out by using Hitachi S4800 Field Emission Scanning Electron Microscope. Transmission electron microscopy (TEM) was operated by Tecnai20 FEG microscope. The N_2 adsorption-desorption isotherms were measured on an ASAP 2020 apparatus (Micromeritic Instruments, USA) at liquid nitrogen temperature (77 K). The BET surface area was calculated using the Brunauer–Emmett–Teller (BET) method. X-Ray photoelectron spectroscopy (XPS) data were collected on a Thermo Scientific ESCALAB250 instrument with a monochromatized Al Kα line source (200 W). Photoluminescence (PL) lifetime spectra were recorded on an Edinburgh FI/FSTCSPC 920 spectrophotometer. Electron paramagnetic resonance (EPR) measurement was carried out with Bruker model A300 spectrometer. Electrochemical System in a conventional three electrode cell, using a Pt sheet as the counter electrode and a saturated calomel electrode as the reference electrode, and the active area is confined to ca. 0.25 cm^2 . The working electrode was prepared on fluorine-tin oxide (FTO) glass. Mott-schottky were measured without any irradiation, to obtain the intrinsic features of the flat-band potentials and carrier densities. The redox potentials were measured in deaerated MeCN containing tetrabutylammonium tetrafluoroborate (0.1 M) as supporting electrolyte, a glassy carbon as working electrode, a platinum wire as counter electrode, a silver wire as pseudo reference and ferrocene as internal standard. The scan rate was 100 $mV•s^{-1}$. Potentials are reported with respect to the saturated calomel electrode (SCE) as reference.

The photochemical reactions were carried out by using standard Schlenk techniques under nitrogen atmosphere with 420 nm LEDs (15 W) or commercial 455 nm LEDs (Eaglerise ELP8X3LS 3W). Thin-layer chromatography (TLC) was performed using silica gel plates 60 F254: Visualization was accomplished with short wavelength UV light (254 nm) and near UV light (366 nm) sources. Gas chromatography mass spectra (GC-MS) were taken at Thermo Trace 1300 gas chromatograph mass spectrometer and a TR-5MS column (0.25 mm × 30 m, Film: 0.25 μm). High performance liquid chromatography mass spectra (HPLC–MS) were obtained from the central analytic mass spectrometry facilities of Fuzhou University. Column chromatographic purification of products was accomplished using 200-300 mesh silica gel. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on Bruker Avance spectrometers (400 MHz, 101 MHz, or 600 MHz, 151 MHz)

in $CDCl_3$ or DMSO-d_6 solutions with internal solvent signals (for ^1H and ^{13}C) as reference (7.26, 77.2 for $CDCl_3$, 2.50 and 39.5 for DMSO-d_6). ^1H NMR data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, br. s. = broad singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, hept = heptet, dd = doublet of doublets, ddd = doublet of doublets of doublets, td = triplet of doublets, qd = quartet of doublets, m = multiplet), coupling constants (Hz), and numbers of protons. Data for ^{13}C NMR are reported in terms of chemical shift, multiplicity (wherever applicable, s = singlet, d = doublet, t = triplet, q = quartet), coupling constants (Hz), and no special nomenclature is used for equivalent carbons. ^{19}F data are reported as follows: chemical shift (ppm), multiplicity (wherever applicable, s = singlet, d = doublet, t = triplet, q = quartet), coupling constants (Hz), and numbers of fluorines (wherever applicable).

Photographs of the Photochemical Reaction Devices

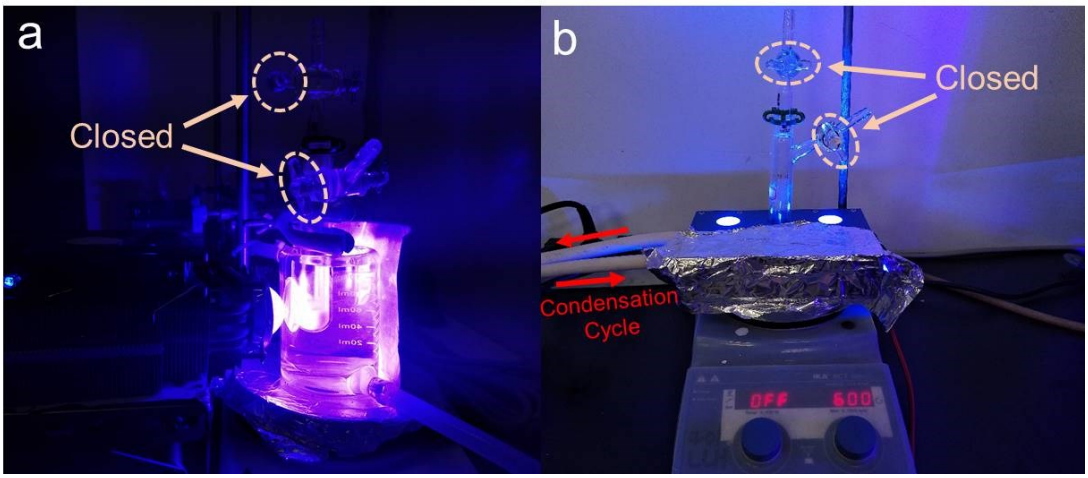
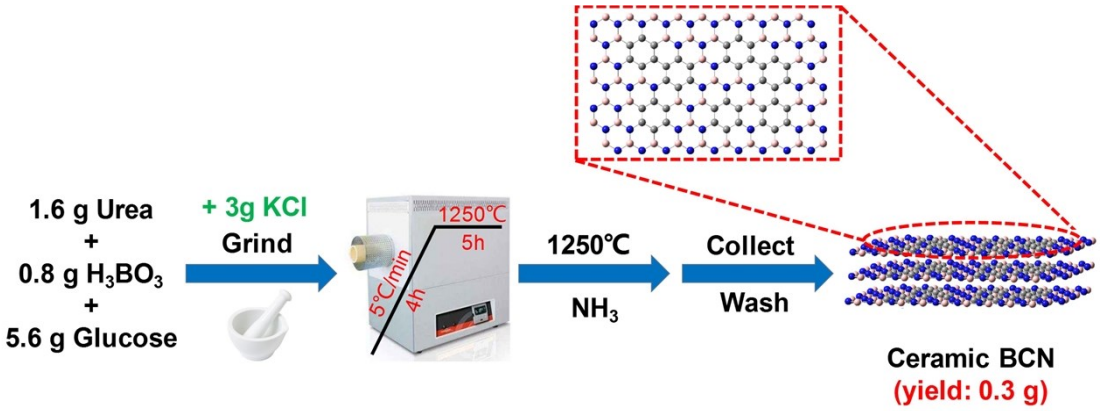


Figure S1. Photograph of the photochemical reaction devices. (a) Reactions were irradiated using a simple photoreactor consisting of 15 W 420 nm LEDs. The reactor was illuminated from the right side with a temperature control device. (b) Reactions were irradiated using a simple photoreactor consisting of Eaglerise ELP8X3LS 3W blue LEDs (λ = 455 nm), which was connected to HAAKE-FK cyclic water-cooling system, the reactor was illuminated from the bottom side.

Synthesis of BCN

Typically, urea (1.6 g), boric acid (0.8 g), and glucose (5.6 g) were fully grinded with an agate mortar for 20 min. Then, 3 g KCl was poured into the mortar and the mixture was grinded again for 10 min. Afterwards, the mixed precursor was put into a horizontal tube furnace. Ammonia was pumped into the tube for 20 min to expel air before heating up. Then the mixture was heated to 1250 °C for 5 h at a heating rate of 5 °C min^{-1} under a flow of ammonia (200 ml min^{-1}). The obtained product was washed with 200 ml water for 5 times and

dried overnight at 80 °C in vacuum oven. The resulting final sample was denoted as BCN.



Scheme. 1. Preparation procedure and structure diagram of BCN.

Synthesis of CNU, mpg-CN, and CCN

CNU was synthesized according to the reported literature.[1] Briefly, 10 g of urea was placed in a crucible with a cover. It was heated in muffle furnace with a heating rate of 5 °C /min to 550 °C and maintained for 2 hours in the air flow. Then the final products were collected after naturally cooled down to the room temperature.

mpg-CN was synthesized according to the reported literature.[2] A mixture of cyanamide (3 g) and colloidal silica aqueous solution (Ludox HS40, 40 wt. %, 7.50 g) was stirred in a glass vial at room temperature for about 30 minutes until cyanamide was dissolved completely. Water was slowly evaporated upon stirring the mixture overnight at 80 °C. The resulting transparent mixtures were then heated at a rate of 2.3 °C /min over 4 h to reach a temperature of 550 °C and then tempered at this temperature for another 4 h. The resulting brown-yellow powder was treated with a 4M NH_4HF_2 for 24 h to remove the silica template. The powders were then centrifuged and washed three times with distilled water and twice with ethanol. Finally, the powders were dried at 60 °C under vacuum for overnight.

CCN was synthesized according to the reported literature.[3] Melamine (8 g) was heated to 500 °C for 4 h at a rate of 12 °C min^{-1} in a muffle furnace in an air atmosphere. After that, 600 mg of the preheated sample was ground with KCl (3.3 g) and LiCl (2.7 g) in a glovebox. Then, the mixture was heated to 550 °C for 4 h under a N_2 atmosphere (2 L/min) in a muffle furnace. After it was cooled to room temperature, the product was washed with boiling deionized water several times and collected by filtration, followed by drying at 60 °C under vacuum.

Characterization of BCN Photocatalyst

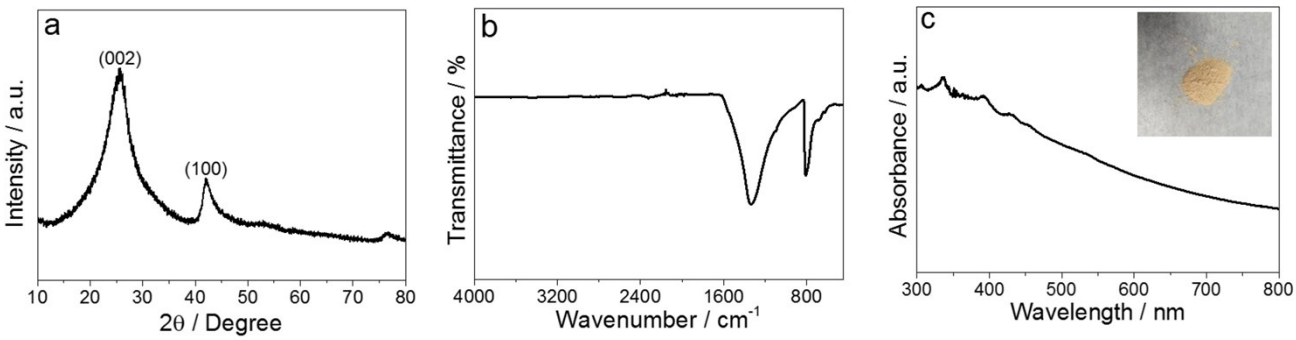


Figure S2. Structure and optical characterizations of BCN. (a) Powder X-ray diffraction (XRD) pattern, (b) FT-IR, (c) UV-Vis diffuse reflection spectroscopy (DRS), inset picture is the photograph of BCN.

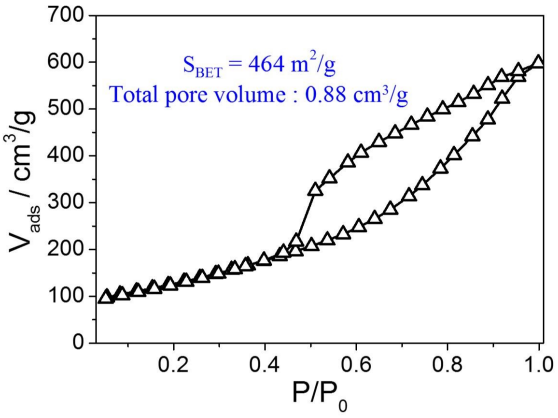


Figure S3. Nitrogen adsorption–desorption isotherms for BCN.

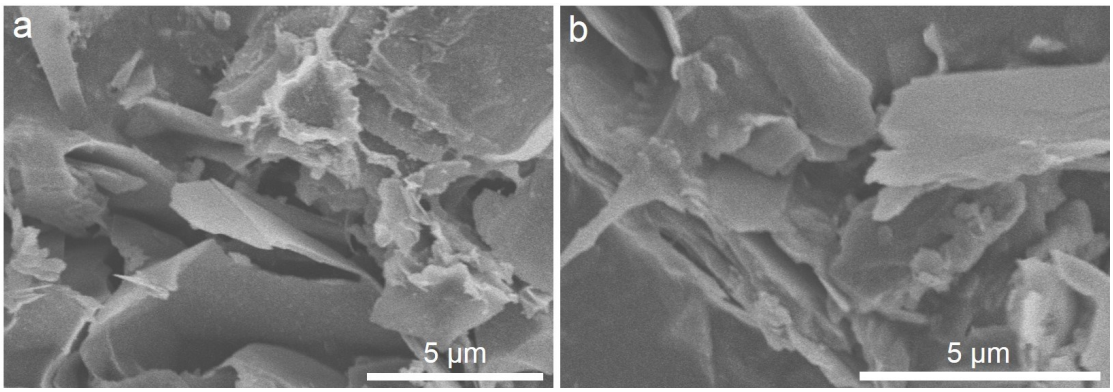


Figure S4. SEM images of BCN, the morphology of nanosheets can be clearly observed.

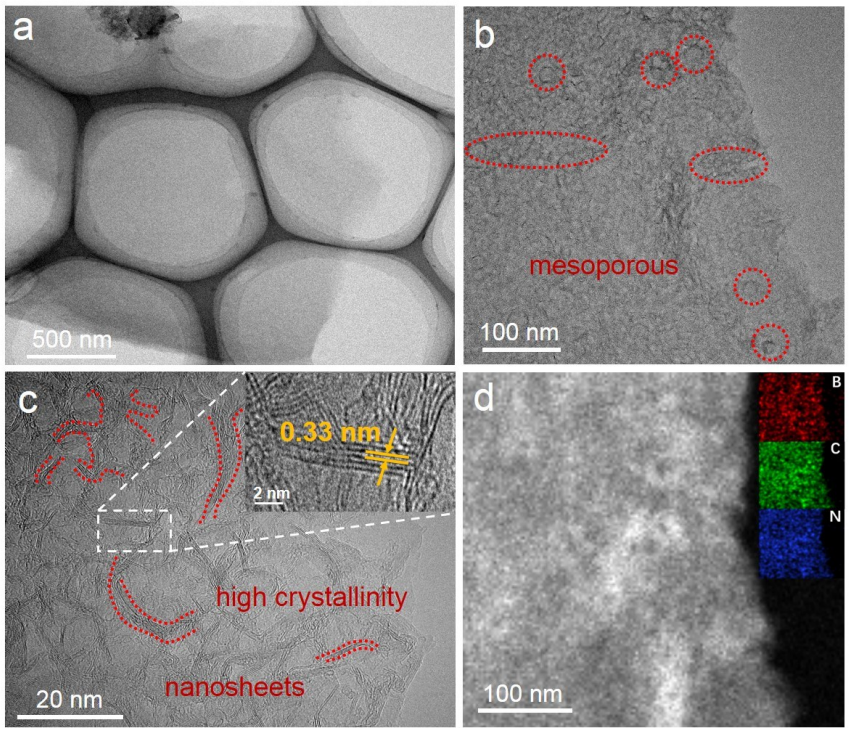


Figure S5. TEM image of (a) BCN (scale bar is 500 nm), (b) BCN (scale bar is 100 nm), and (c) BCN (scale bar is 20 nm); inset picture show the HRTEM image of BCN (scale bar is 2 nm), (d) High-Angle Annular Dark Field (HAADF) image of BCN and elemental mapping images of B, C, and N.

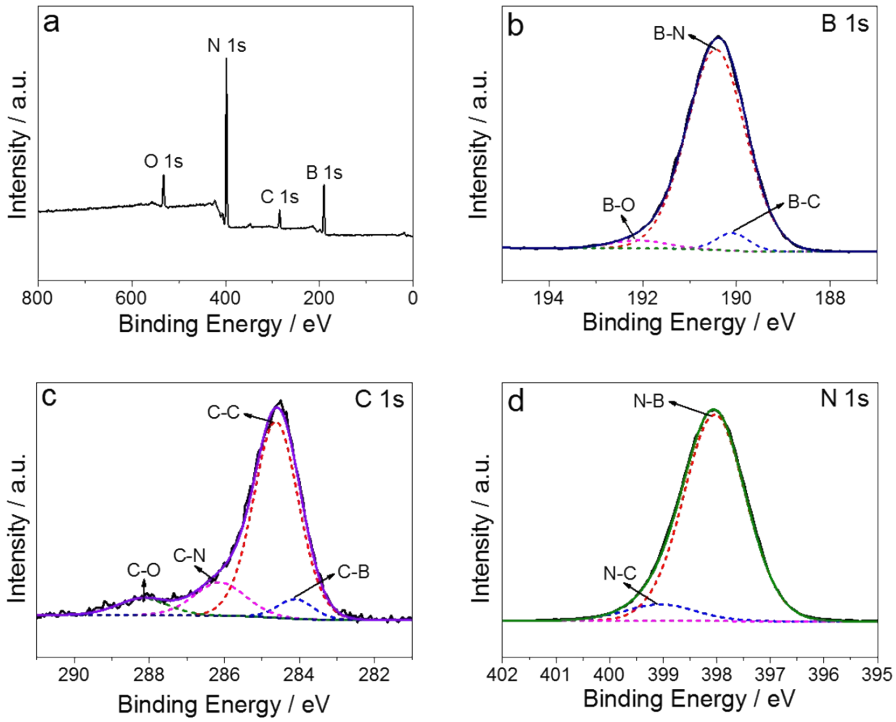


Figure S6. (a) XPS survey spectrum of BCN, (b–d) XPS high-resolution spectra of B 1s, C 1s, and N 1s of BCN, respectively.

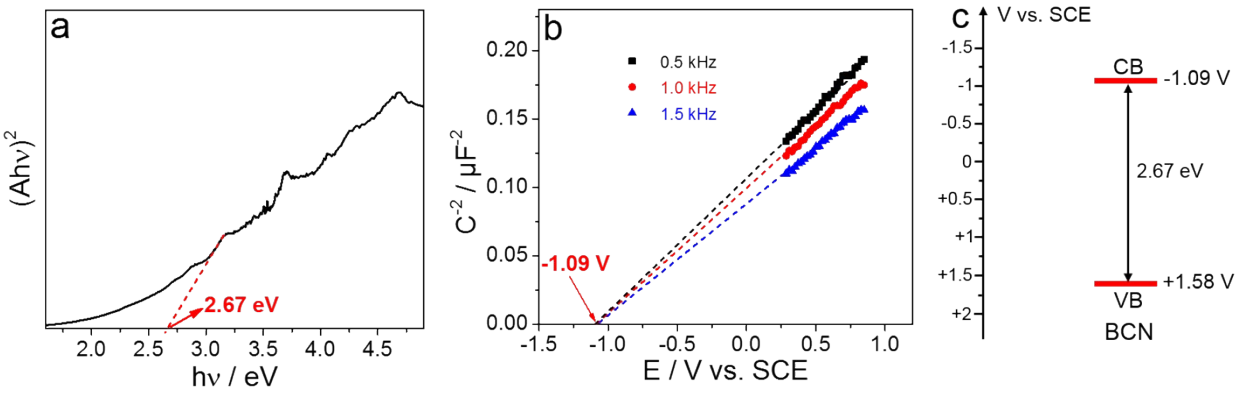


Figure S7. The band structure of the BCN ceramic. (a) The $(Ahv)^2$ versus E plots. (b) Determination of the conduction band minimum of BCN by Mott−Schottky method. (c) Determined band structure (relates to SCE) of BCN.

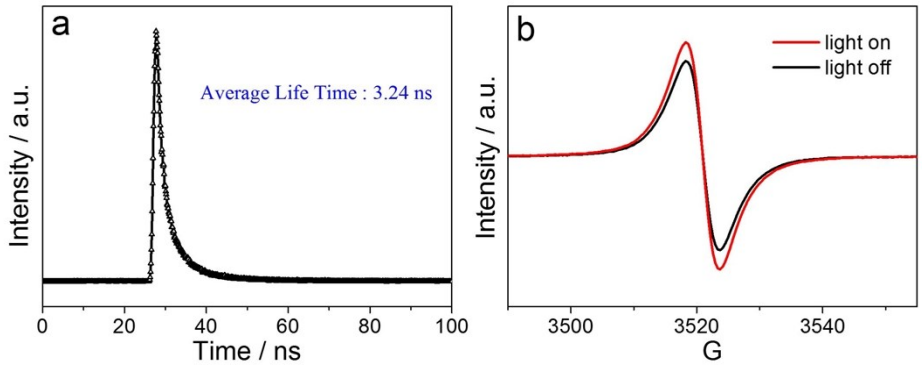
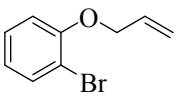


Figure S8. (a) Time-resolved PL lifetime spectra under 380 nm excitation. (b) EPR spectrum of BCN.

General Procedure for C–X Functionalizations

Preparation of substrates: The substrates for **general procedure 2** were synthesized according to the reported literature.[4]

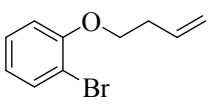
Preparation of 1-(alloxy)-2-bromobenzene **(1cc)**



2- Bromophenol (87 μL, 0.75 mmol, 1.0 equiv), K_2CO_3 (225 mg, 1.63 mmol, 2.2 equiv) and DMF (2.0 mL) were taken in an oven-dried *Schlenk* flask under nitrogen. Allyl chloride (200 μL, 2.5 mmol, 3.3 equiv) was added under stirring and the mixture was stirred at 80 °C for 20 h. H_2O (10 mL) was added and the resulting mixture was extracted with dichloromethane (3×10 mL, DCM). The combined organic layer was washed with brine (10 mL), dried over anhydrous $MgSO_4$ and concentrated under vacuum. The crude mixture was purified by flash column chromatography (pentane : DCM = 95:5) to afford *1-(alloxy)-*

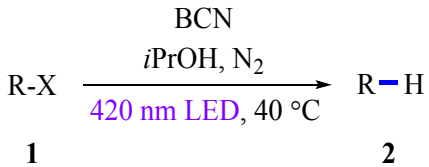
2-bromobenzene as pale yellow oil in 91% (145 mg, 0.68 mmol) isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.8 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 6.98 – 6.80 (m, 2H), 6.11 (ddd, *J* = 20.1, 9.4, 4.3 Hz, 1H), 5.53 (d, *J* = 17.2 Hz, 1H), 5.35 (d, *J* = 10.6 Hz, 1H), 4.64 (d, *J* = 2.5 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 155.02 (s), 133.47 (s), 132.71 (s), 128.45 (s), 122.07 (s), 117.76 (s), 113.70 (s), 112.38 (s), 69.69 (s). **MS** (m/z, EI): 213, 172, 133, 105, 63.

Preparation of 1-(3-buten-1-yloxy)-2-bromobenzene (**1dd)**

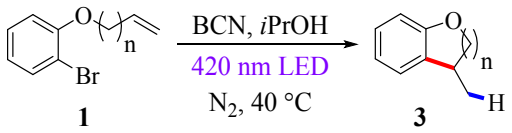


2-Bromophenol (87 µL, 0.75 mmol, 1.0 equiv), K_2CO_3 (225 mg, 1.63 mmol, 2.2 equiv) and DMF (2.0 mL) were taken in an oven-dried *Schlenk* flask under nitrogen. 4-Chloro-1-butene (253 µL, 2.5 mmol, 3.3 equiv) was added under stirring and the mixture was stirred at 85 °C for 48 h. H_2O (10 mL) was added and the resulting mixture was extracted with dichloromethane (3×10 mL, DCM). The combined organic layer was washed with brine (10 mL), dried over anhydrous $MgSO_4$ and concentrated under vacuum. The crude mixture was purified by flash column chromatography (pentane : DCM = 95:5) to afford *1-(3-buten-1-yloxy)-2-bromobenzene* as light brown oil in 87% (148 mg, 0.65 mmol) isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.8 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.01 – 6.80 (m, 2H), 6.00 (td, *J* = 16.6, 7.0 Hz, 1H), 5.21 (dd, *J* = 28.3, 13.7 Hz, 2H), 4.10 (t, *J* = 6.5 Hz, 2H), 2.64 (q, *J* = 6.6 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 155.38 (s), 134.28 (s), 133.46 (s), 128.50 (s), 121.96 (s), 117.38 (s), 113.48 (s), 112.45 (s), 68.59 (s), 33.67 (s). **MS** (m/z, EI): 227, 198, 174, 147, 65, 55.

General procedure 1: Hydrodehalogenation of (het)aryl and alkyl halides. To a Schlenk tube containing a stirring bar was added BCN (10 mg), *i*PrOH (6 mL) and halide (Br or Cl, 0.2 mmol), then the tube was degassed in vacuo and refilled with N_2 for 5 times. With the purple LED (420 nm, 15 W) switch on, the reaction mixture was stirred for a certain time (noted in the text) at 40 °C until the reactant was fully consumed which was determined by GC-MS. After reaction, the mixture was filtered and extracted by CH_2Cl_2, solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate and pentane/diethyl ether as eluent to afford the final hydrodehalogenation product.

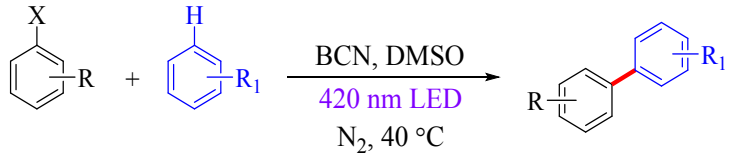


General procedure 2: Intramolecular cyclizations of inactive *o*-alkenyl bromobenzenes. Typically, to a Schlenk tube containing a stirring bar was added BCN (20 mg), K_2CO_3 (55 mg, 2 equiv), *i*PrOH (6 mL) and reactant *o*-alkenyl bromobenzene (0.2 mmol), then the tube was degassed in vacuo and refilled with N_2 for 5 times. With the purple LED (420 nm, 15 W) switch on, the reaction mixture was stirred for 72 h at 40 °C, and the reaction progress was monitored by TLC or GC-MS. After reaction, the mixture was filtered and extracted by CH_2Cl_2, solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel using pure petroleum ether as eluent to afford the final intramolecular cyclized product.



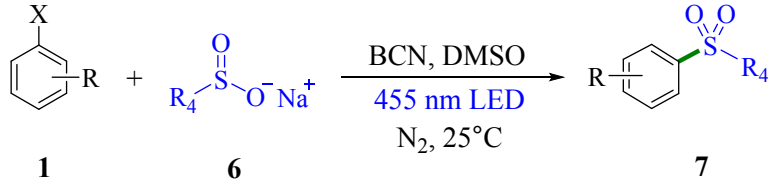
1 **3**

General procedure 3: C(sp^2)-H (het)arylations with C(sp^2)-Br. To a Schlenk tube containing a stirring bar was added BCN (20 mg), (het)aryl bromide (0.2 mmol), and (het)arenes (20 equiv.), then DMSO (2 mL) was added to the mixture. After that, the tube was degassed in vacuo and refilled with N_2 for 5 times. With the purple LED (420 nm, 15 W) switch on, the reaction mixture was stirred for 24 h at 40 °C, and the reaction progress was monitored by TLC or GC-MS. After reaction, the mixture was filtered and extracted by ethyl acetate for several times, the organic layers were combined and dried over anhydrous Na_2SO_4, solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to afford the final C-C cross-coupling product.



1 **4** **5**

General procedure 4: C(sp^2/sp^3)-Br sulfonylations using sulfinates. To a Schlenk tube containing a stirring bar was added BCN (10 mg), (het)aryl halide (Br or Cl, 0.2 mmol), and sulfinate (1 mmol, 5 equiv.), then DMSO (2 mL) was added to the mixture. After that, the tube was degassed in vacuo and refilled with N_2 for 5 times. With the blue LED (455 nm, 3 W) switch on, the reaction mixture was stirred for 72 h at 25 °C, reaction progress was monitored by TLC or GC-MS. After reactions, the mixture was filtered and extracted by ethyl acetate for several times, the organic layers were combined and dried over anhydrous Na_2SO_4, solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to afford the final C-S cross-coupling product.



1 **6** **7**

General procedure for gram-scale synthesis of 7c: To a round-bottom flask (50 mL) containing a stirring bar was added BCN (225 mg), 2-bromo-5-(trifluoromethyl)benzonitrile (1.125 g, 4.5 mmol), and sodium benzenesulfinate (3.694 g, 22.5 mmol, 5 equiv.), then DMSO (40 mL) was added to the mixture. After that, the reaction flask was degassed in vacuo and refilled with N_2 for 5 times. With the blue LED (470 nm, 15 W) switch on, the reaction mixture was stirred for 72 h at 25 °C, reaction progress was monitored by TLC or GC-MS. After reactions, mixture was filtered and extracted by ethyl acetate for several times, the organic layers were combined and dried over anhydrous Na_2SO_4, solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to afford the final product **7c**. Yield: 1.2788 g, 91%.

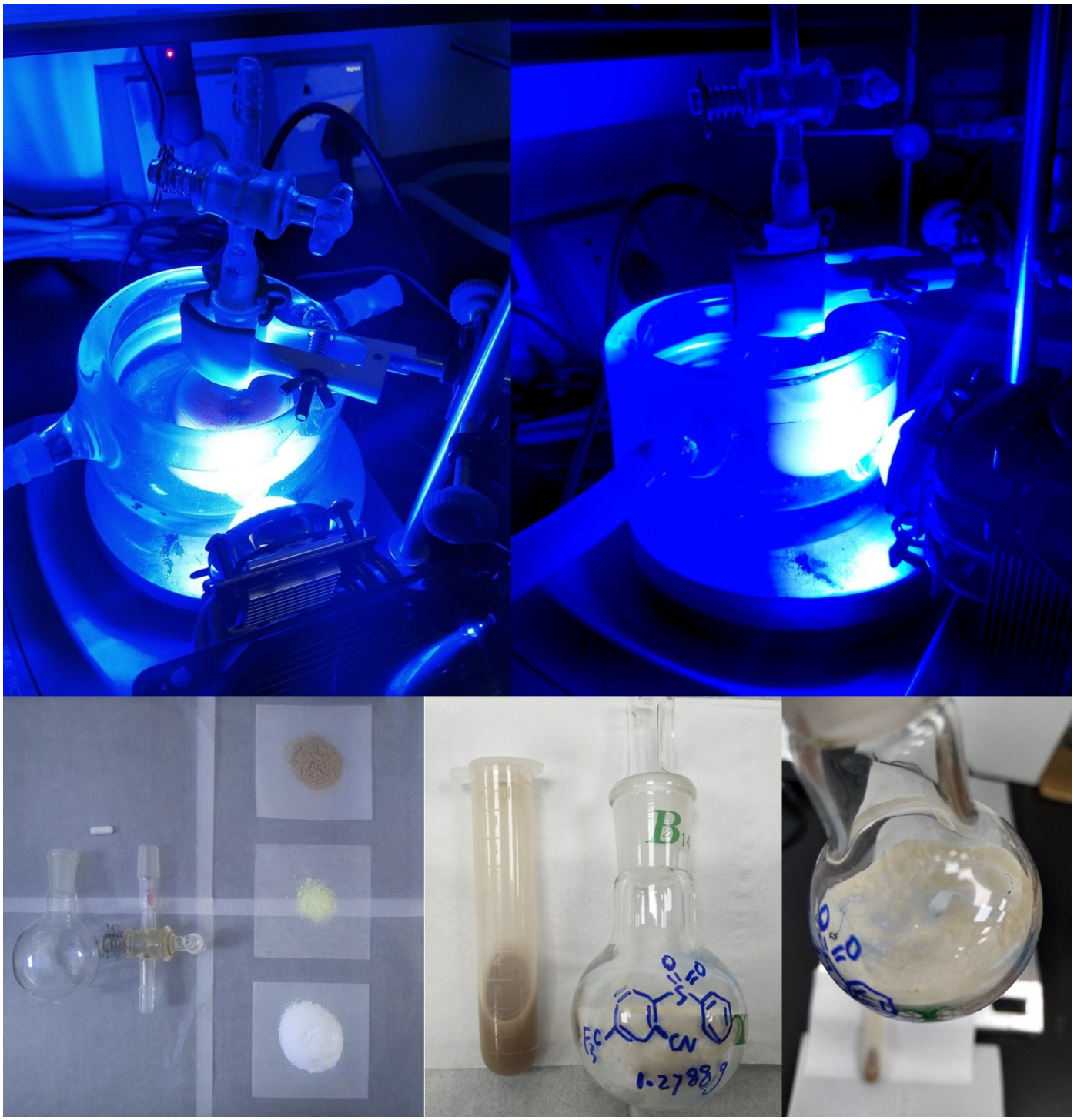


Figure S9. Enlarged pictures of the gram-scale reaction for synthesis of **7c**.

The stability tests of BCN were conducted under standard reaction conditions for five recycles. The recovered catalyst could be afforded by centrifugation or filtration. The following is the process of recovering the catalyst: (a). After the reaction, the reaction mixture was transferred to a centrifuge tube and the mixture was centrifuged (rpm 10000.) for 3 min. The solid in the centrifuge tube was washed six times (2×EA, 2×water, 2×EA). For C-Br sulfonylation reaction, the solid was washed five times (3×water, 2×EA). All the collected samples were transferred to vacuum oven to dry for 5 h at 60 °C.The recovered photocatalyst was used for the

following reaction. (b). After the reaction, the reaction mixture was extracted from the reactor and filtered using a filter paper with subsequent wash by EA for five times. The collected samples were transferred to vacuum oven to dry for 5 h at 60 °C.

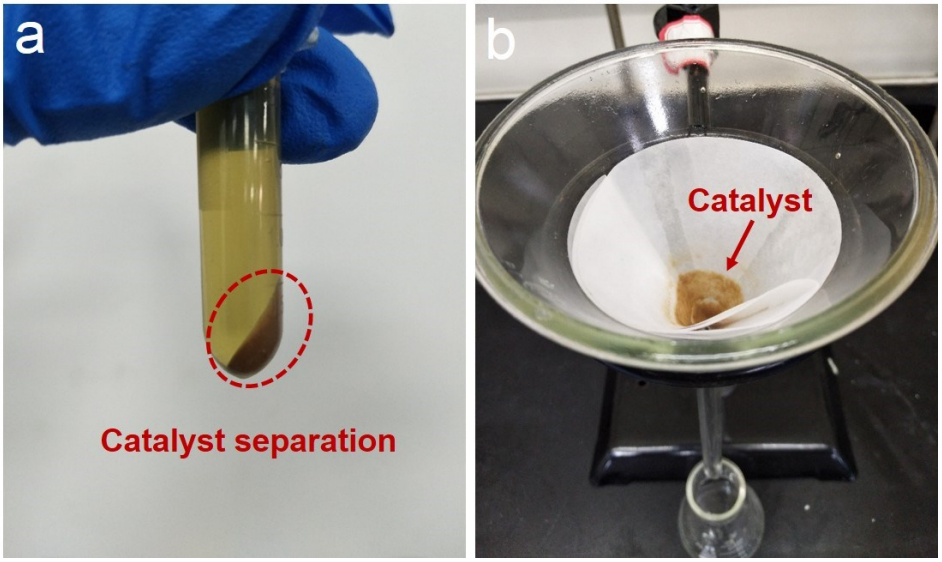
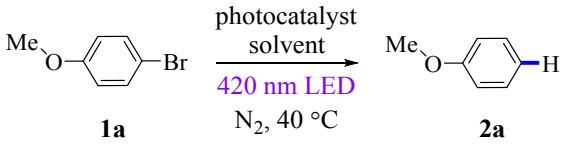


Figure S10. Photographs of affording recovered catalyst by (a) centrifugation and (b) filtration of crude reaction mixture.

Reaction condition optimizations

Table 1. Optimization experiments for photocatalytic hydrodehalogenation reaction of (het)aryl halides [a].



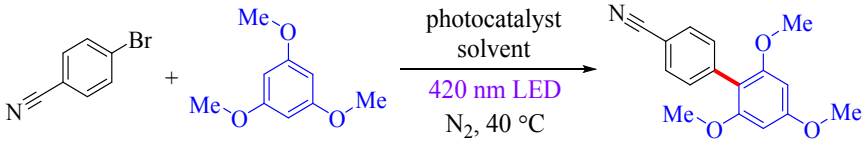
1a **2a**

entry	photocatalyst	light	solvent	yield[b][%]
1	BCN	+	MeCN	trace
2	BCN	+	1,4-dioxane	trace
3	BCN	+	THF	1
4	BCN	+	H_2O	trace
5[c]	BCN	+	MeCN/H_2O	trace
6	BCN	+	MeOH	76
7	BCN	+	EtOH	89
8	BCN	+	*i*PrOH	93
9	BCN	-	*i*PrOH	n.d.

10	-	+	*i*PrOH	n.d.
11	-	-	*i*PrOH	n.d.
12	CNU	+	*i*PrOH	n.d.
13	mpg-CN	+	*i*PrOH	n.d.
14[d]	BCN	+	*i*PrOH	63
15[e]	BCN	+	*i*PrOH	28
16[f]	BCN	+	*i*PrOH	75
17[g]	BCN	+	*i*PrOH	60

[a] Unless otherwise noted, the reactions were conducted with 10 mg photocatalyst, 0.2 mmol **1a** and 6 mL solvent at 40 °C for 10 h under N_2 atmosphere. [b] The yield was determined by GC-MS. [c] V(CH_3CN) : V(H_2O) = 5 : 1. [d] 0.5 mmol of **1a** was used. [e] 1.0 mmol of **1a** was used. [f] The reaction was conducted at 25 °C. [g] The reaction was conducted at 10 °C.

Table 2. Optimization experiments for direct C-H functionalizations of (het)arenes with (het)aryl bromides[a].



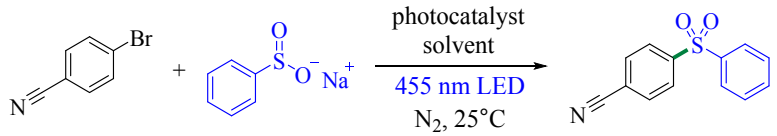
1b **4a** **5a**

entry	photocatalyst	equiv of **2**	light	solvent	yield[b][%]
1	BCN (5mg)	5	+	DMF	11
2	BCN (5mg)	5	+	CH_3CN	13
3	BCN (5mg)	5	+	DMSO	23
4	CNU (5mg)	5	+	DMSO	9
5	mpg-CN (5mg)	5	+	DMSO	4
6	BCN (5mg)	10	+	DMSO	34
7	BCN (10mg)	10	+	DMSO	42
8	BCN (20mg)	10	+	DMSO	52
9	BCN (20mg)	20	+	DMSO	73
10[c]	BCN (20mg)	20	+	DMSO	85(76) [f]
11[c]	-	20	+	DMSO	2

12[c]	BCN (20mg)	20	-	DMSO	n.d.
13[c]	-	20	-	DMSO	n.d.
14[d]	BCN (20mg)	20	+	DMSO	72
15[e]	BCN (20mg)	20	+	DMSO	62

[a] Unless otherwise noted, the reactions were carried out with a certain amount of photocatalyst, 0.2 mmol **1b**, a certain equivalent of **4a** and 2 ml solvent at 40 °C for 12 h under N_2 atmosphere. DMSO is short for "dimethyl sulfoxide". DMF is short for N,N-dimethylformamide. [b] The yield was determined by GC-MS. [c] The reaction time prolonged to 24 h. [d] The reaction was conducted at 25 °C. [e] The reaction was conducted at 10 °C. [f] The data in parenthesis was the isolated yield.

Table 3. Optimization experiments for C-X sulfonylations of (het)aryl halides with sulfinates[a].



1b **6a** **7a**

Entry	Photocatalyst	Light	Solvent	Yield[b][%]
1	CNU	+	DMSO	trace
2	mpg-CN	+	DMSO	n.d.
3	CCN	+	DMSO	n.d.
4	BCN	+	DMSO	51
5	BCN	+	CH_3CN	n.d.
6	BCN	+	THF	n.d.
7	BCN	+	DMF	27
8[c]	BCN	+	DMSO	78(69)[d]
9[c]	-	+	DMSO	n.d.
10[c]	BCN	-	DMSO	n.d.
11[c]	-	-	DMSO	n.d.

[a] Unless otherwise noted, the reactions were carried out with 10 mg photocatalyst, 0.2 mmol **1b**, 5 equivalent of **6a** (1 mmol) and 2 ml solvent at 25 °C for 24 h under N_2 atmosphere. [b] The yield was determined by GC-MS. [c] The reaction time was 72 h. [d] The data in parenthesis was the

isolated yield.

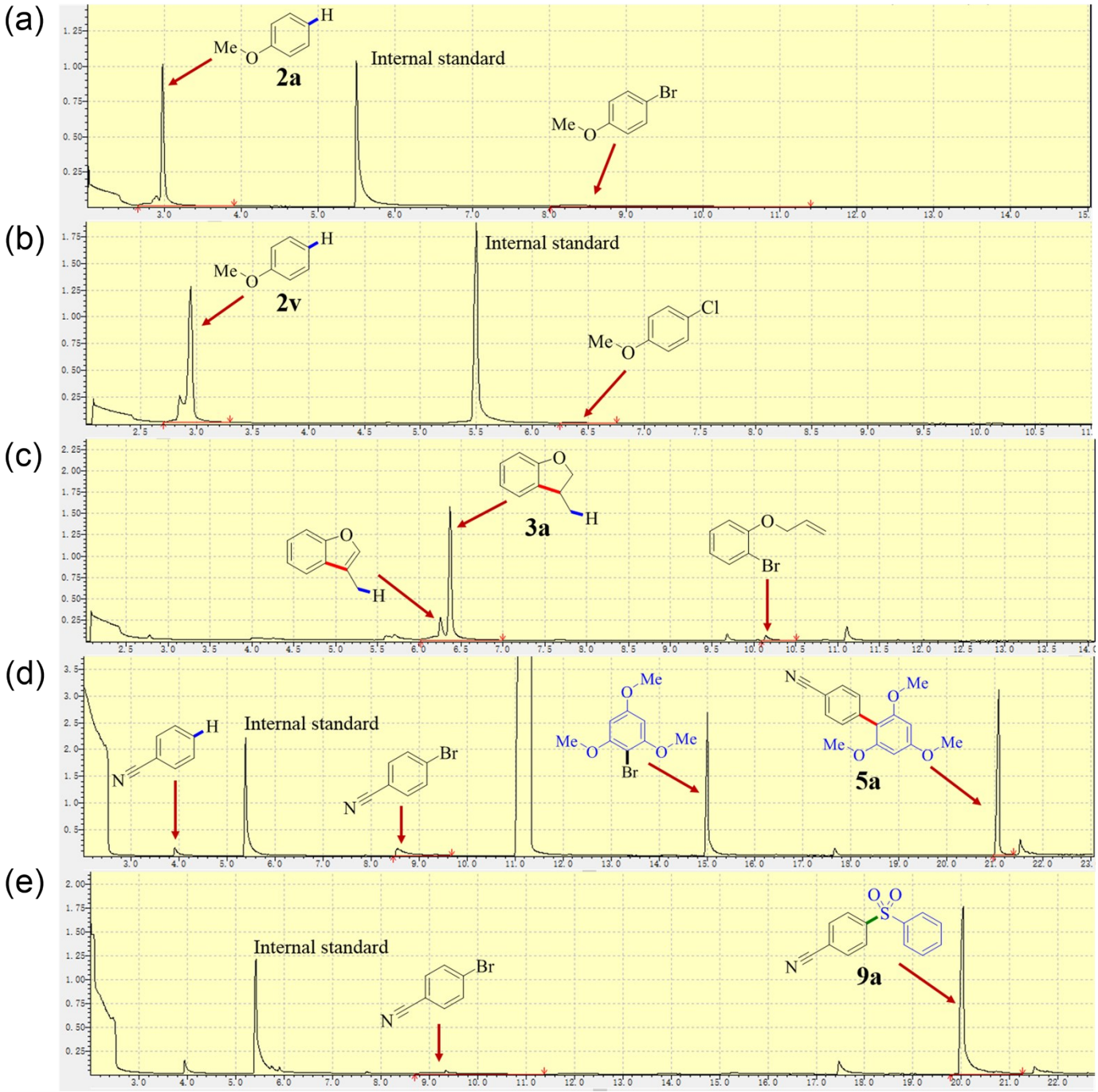


Figure S11. Gas chromatogram of five types of C-X transformations. (a) Hydrodebromination, (b) Hydrodechlorination, (c) Intramolecular cyclization, (d) C-H arylation, and (e) C-Br sulfonylation.

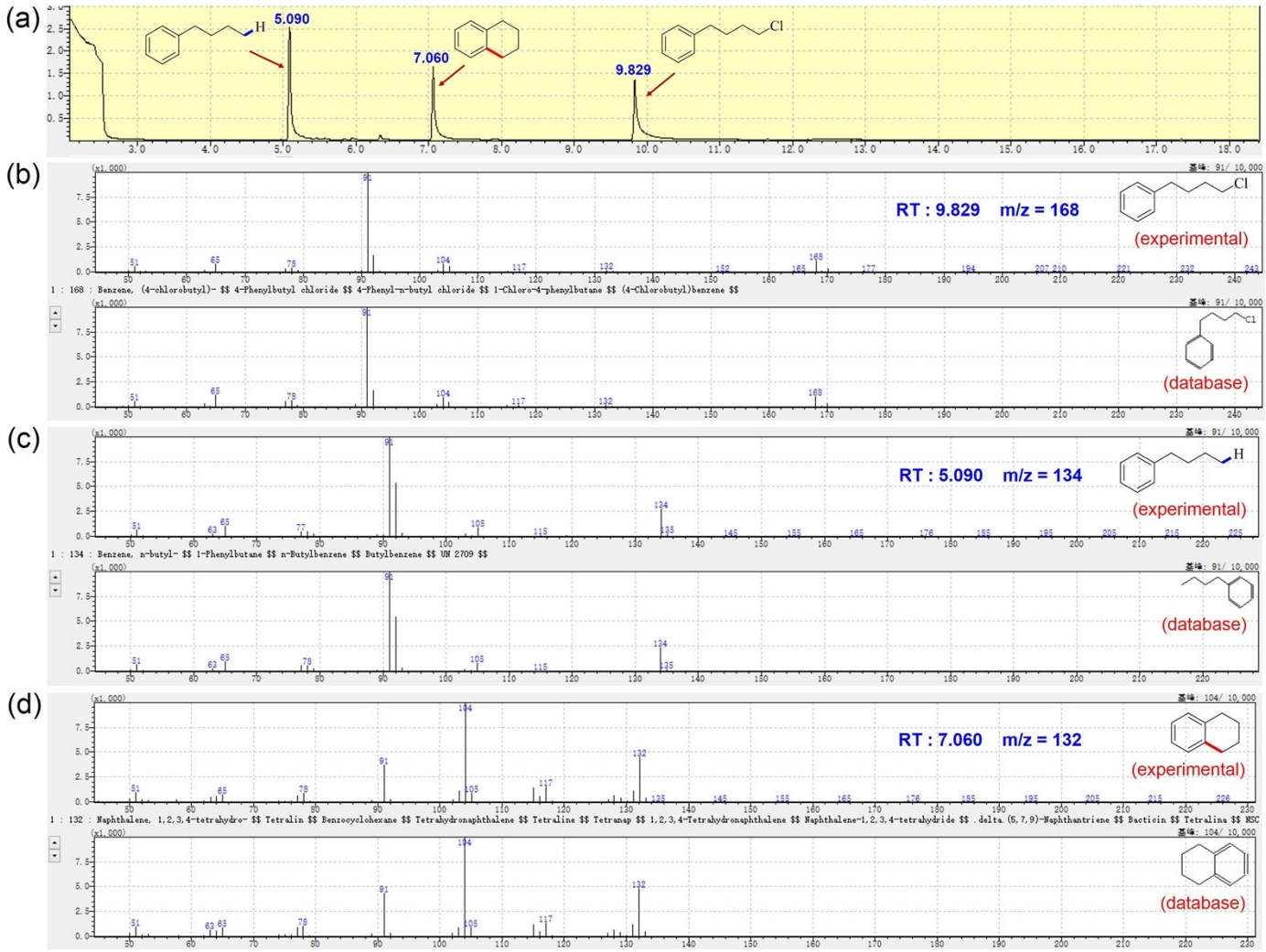


Figure S12. (a) Gas chromatogram of hydrodehalogenation and intramolecular cyclization of inert 1-chloro-4-phenylbutane, (b)-(d) MS spectras of reactant and products.

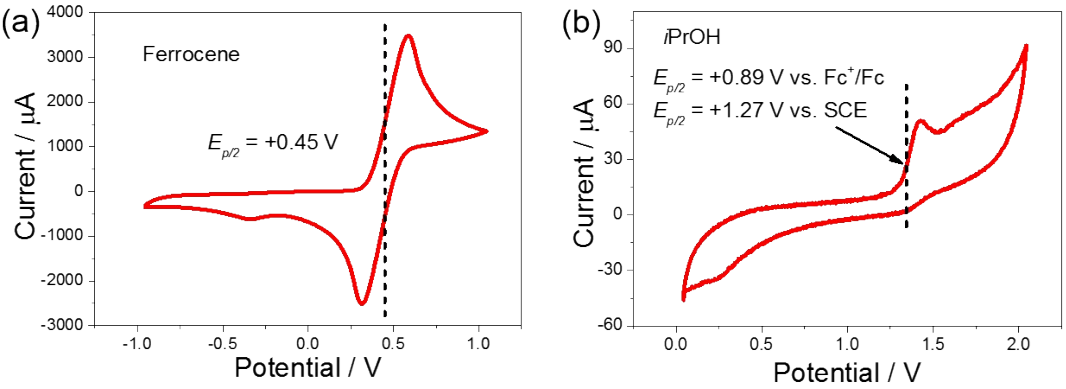
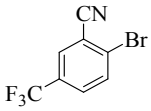
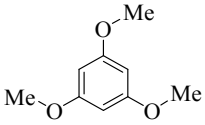
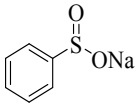
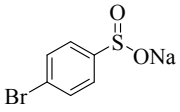
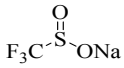


Figure S13. Cyclic voltammetry of (a) ferrocene as internal standard and (b) isopropanol in deaerated MeCN. The isopropanol concentration was 10 mM.

Table 4. Oxidation and reduction potentials of a few investigated compounds.

Entry	Compound	Ox./red. Potential / V *vs.* SCE *	Ref.
1		-1.02	*(5)*
2	*i*PrOH	+1.27	*(6)*
3		+1.34	*(7)*
4		+1.04	*(7)*
5		+0.37	*(8)*
6		+0.54	*(8)*
7		+1.16	*(8)*

* Note that the reduction/ oxidation potential values may vary slightly depending on the solvent and reaction conditions.

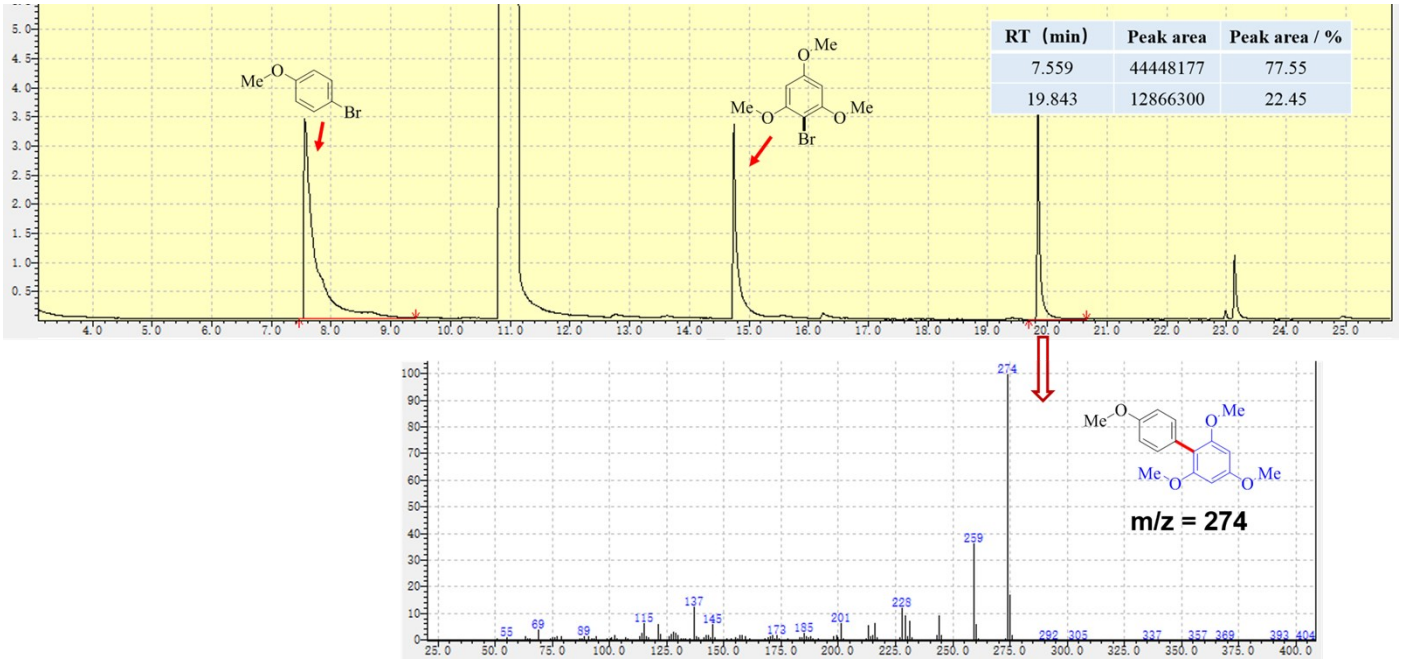


Figure S14. GC-MS spectra of the crude reaction mixture yielding **5x**. The peak at 19.84 min corresponds to

the product peak.

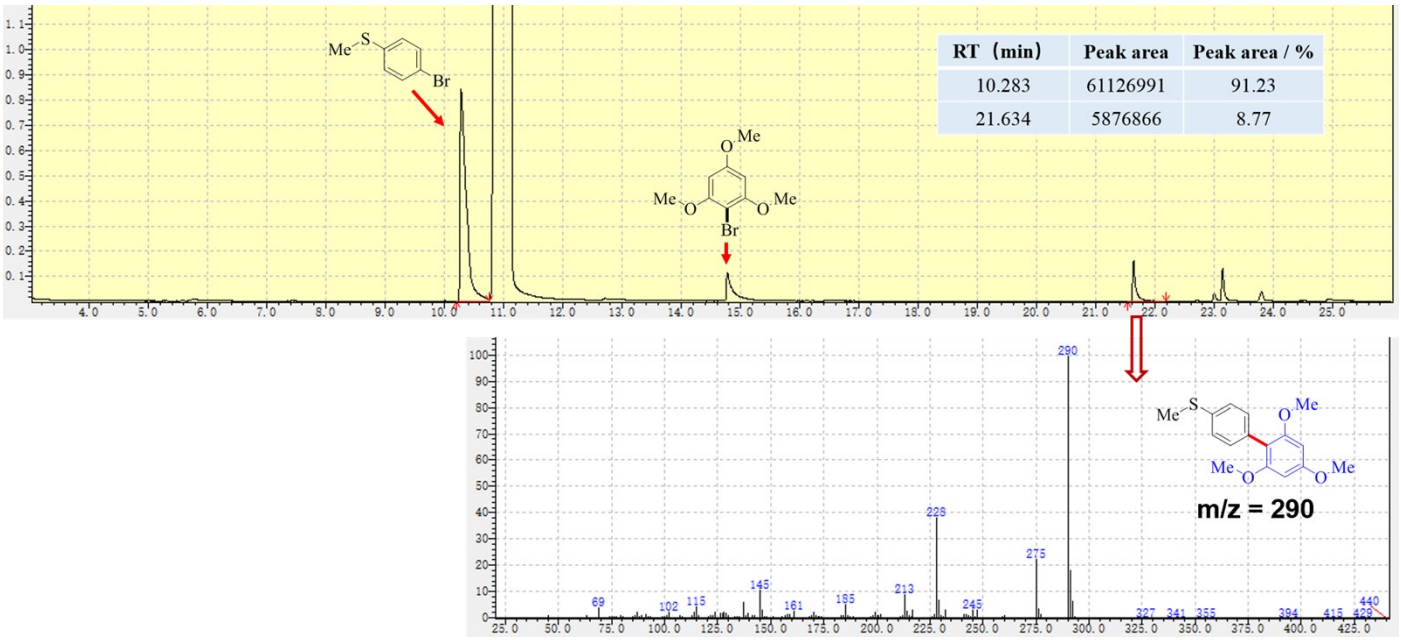


Figure S15. GC-MS spectra of the crude reaction mixture yielding **5y**. The peak at 21.63 min corresponds to the product peak.

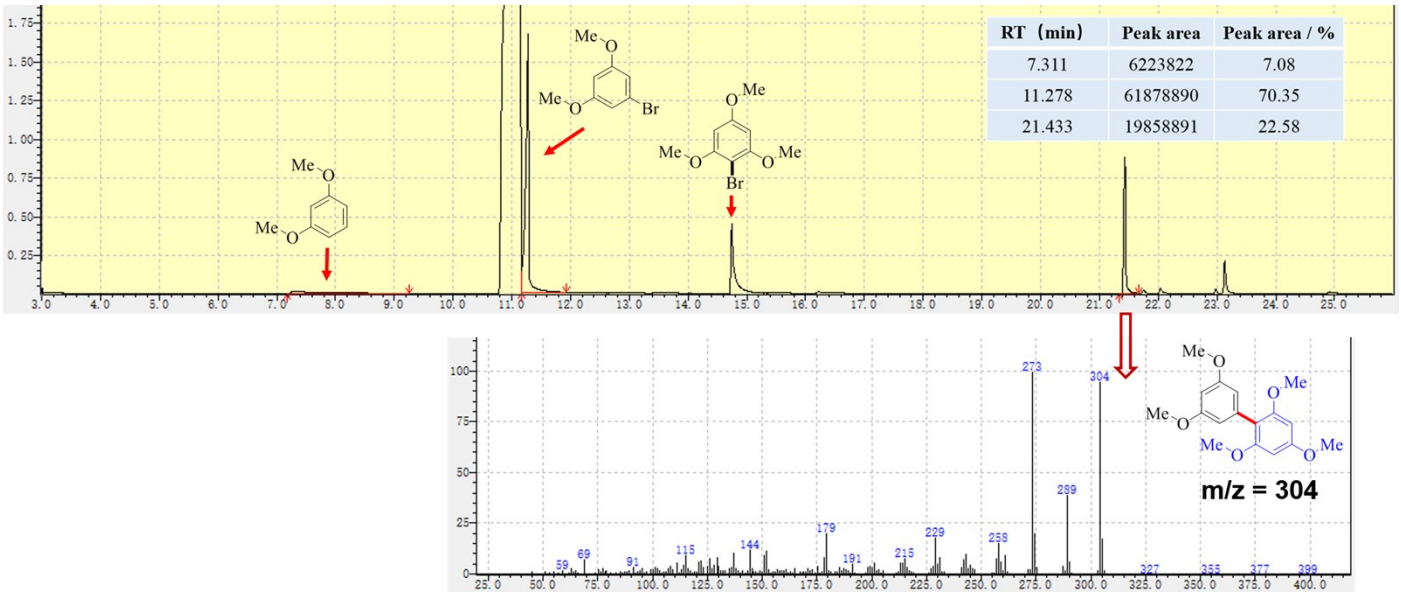


Figure S16. GC-MS spectra of the crude reaction mixture yielding **5z**. The peak at 21.43 min corresponds to the product peak.

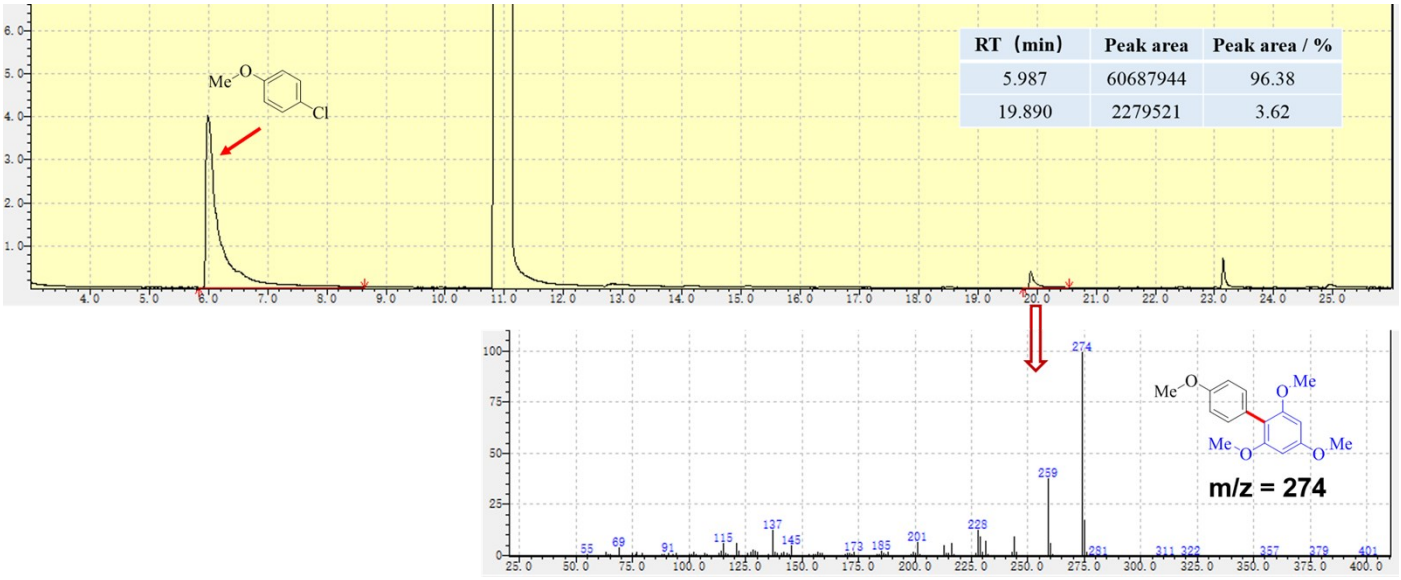


Figure S17. GC-MS spectra of the crude reaction mixture yielding **5x'**. The peak at 19.89 min corresponds to the product peak.

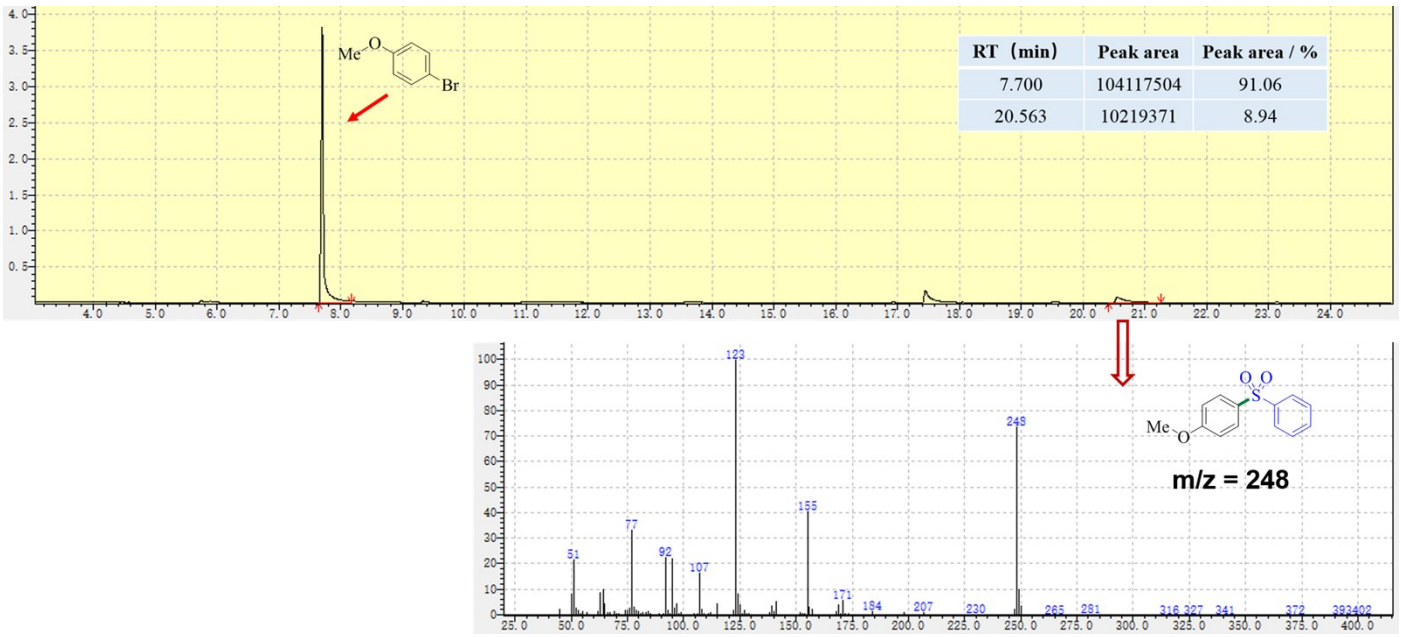


Figure S18. GC-MS spectra of the crude reaction mixture yielding **7s**. The peak at 20.56 min corresponds to the product peak.

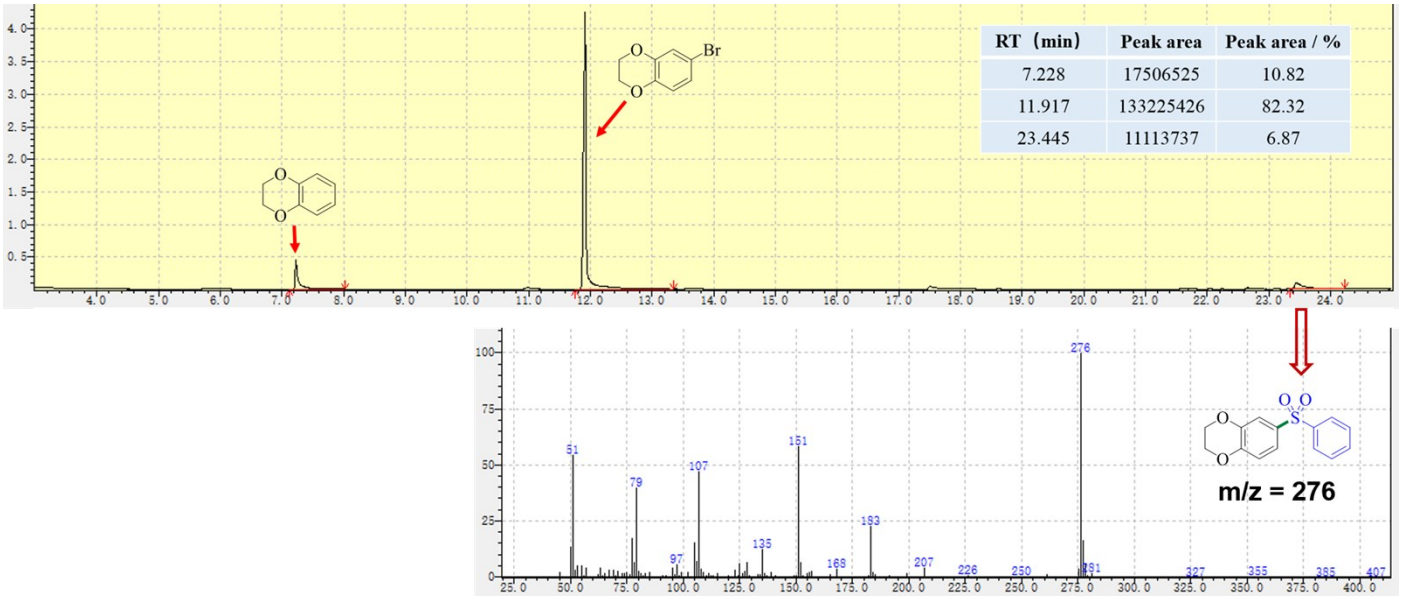


Figure S19. GC-MS spectra of the crude reaction mixture yielding **7t**. The peak at 23.44 min corresponds to the product peak.

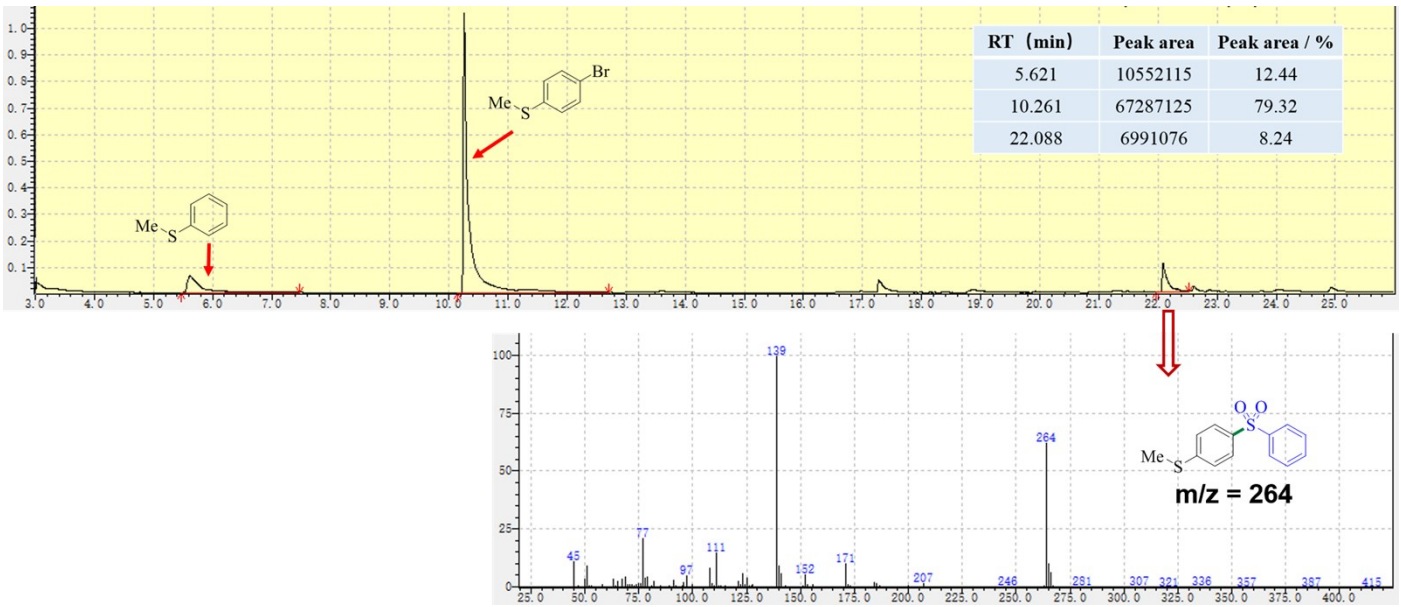


Figure S20. GC-MS spectra of the crude reaction mixture yielding **7u**. The peak at 22.09 min corresponds to the product peak.

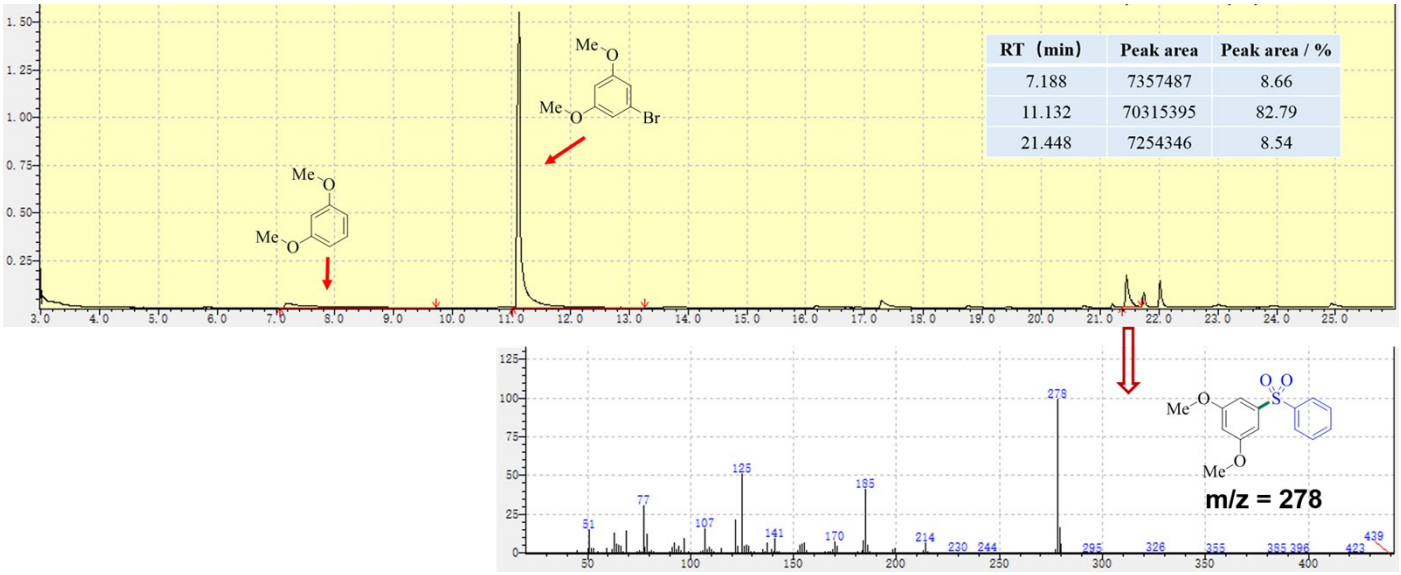
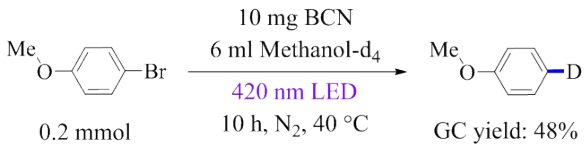


Figure S21. GC-MS spectra of the crude reaction mixture yielding **7v**. The peak at 21.45 min corresponds to the product peak.

Mechanism Study

Mechanism study for procedure 1

Deuteration experiment



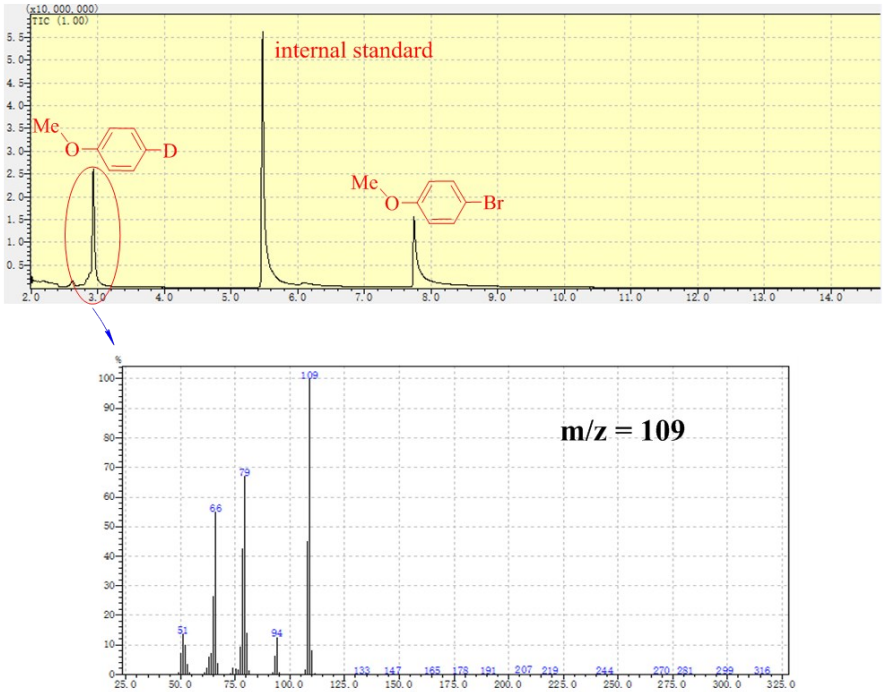


Figure S22. GC-MS analysis of deuterium hydrodehalogenation in perdeuterated methanol.

Radical capture test

A solution of **1a** and two equivalent TEMPO in 6 ml *i*PrOH with 10 mg BCN reacted at sdandard condition. The reaction mixture was analyzed by GC-MS, which showed the exact molecular weight of 263, indicating the formation of the proposed TEMPO adduct to the aryl radical intermediate.

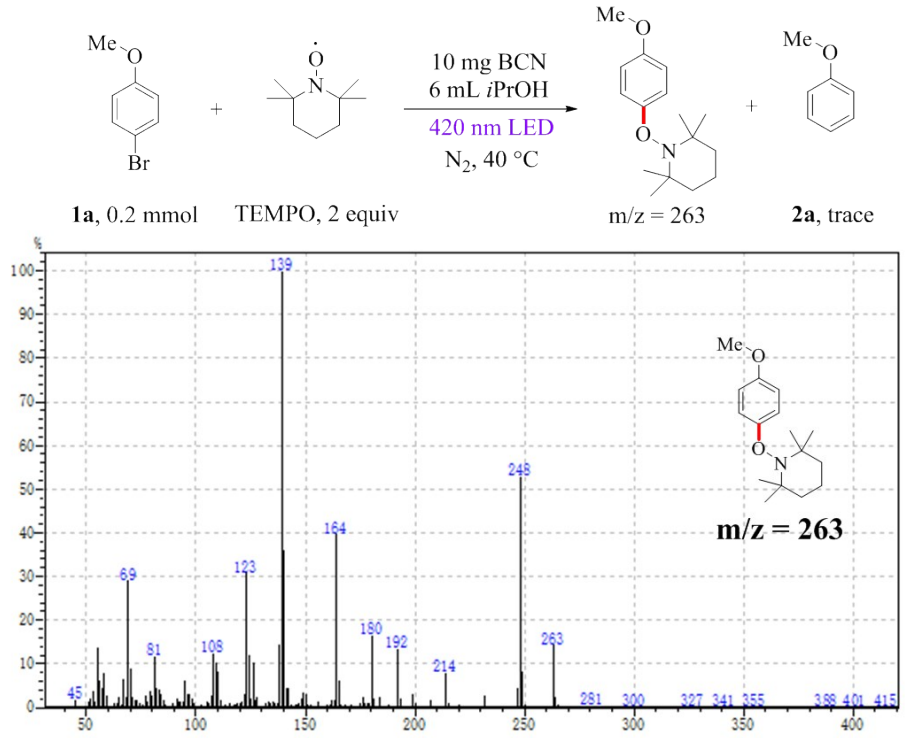


Figure S23. Mass Spectra of TEMPO-aryl radical adduct for hydrodehalogenation process.

Mechanism study for procedure 3

Table 5. Hammett correlation data for C-H arylation of arene with aryl bromide.

para-substituent of Ar-Br	σ_p [a]	Yield / %	$k_{R/H}$ [b]	log $k_{R/H}$
p-CN	0.66	76	3.43	0.54
p-COMe	0.50	69	2.82	0.45
p-COOMe	0.45	63	2.39	0.38
p-CHO	0.42	59	2.15	0.33
p-$CONH_2$	0.36	55	1.92	0.28
p-H	0	34	1.00	0.00

[a]. Hammett constants were found in the reference (5).[9] [b]. The $k_{R/H}$ was calculated according to the methods in references (6) and (7).[10,11]

Kinetic Isotope Effect (KIE) experiment

To a Schlenk tube containing a stirring bar was added BCN (20 mg), **1b** (0.2 mmol), naphthalene-d_8 (10 equiv), and naphthalene (10 equiv), then DMSO (2 mL) was added to the mixture. After that, the tube was degassed in vacuo and refilled with N_2 for 5 times. With the purple LED (420 nm, 15 W) switch on, the reaction mixture was stirred for 24 h at 40 °C, reaction progress was monitored by TLC and GC-MS. After reaction, mixture was filtered and extracted by ethyl acetate for several times, the organic layers were combined and dried over anhydrous Na_2SO_4, solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (200:1, v:v) as eluent to afford the final mixed products with a weight of 25.4 mg, the ratio of K_H : K_D was 1.25 determined by ^{1}H NMR spectrum.[12]

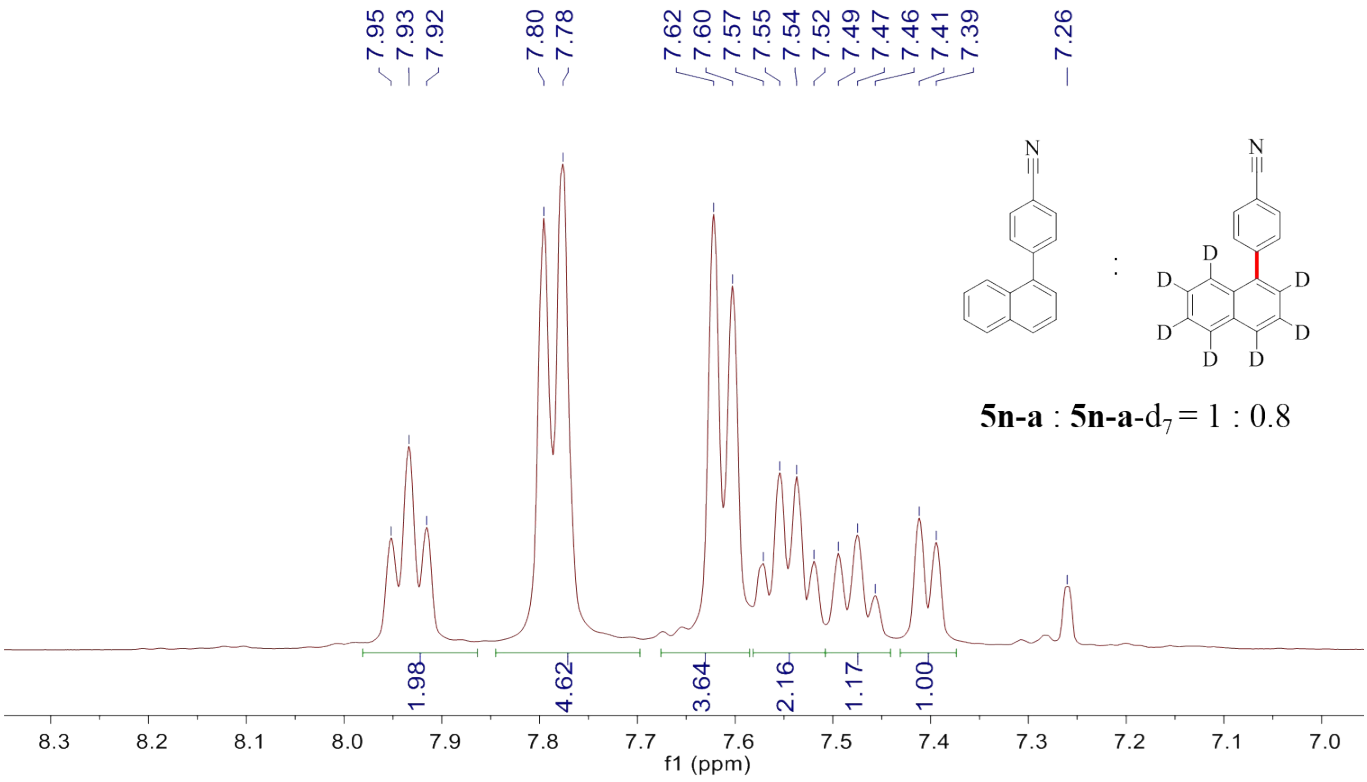


Figure S24. The ^{1}H NMR spectrum of mixture produced from KIE experiment.

Radical capture test

A solution including **1b**, **4a** and 2 equivalent TEMPO in DMSO with 20 mg BCN reacted under sdandard conditions for 12 h. The reaction mixture was analyzed by GC-MS, which shows the exact molecular weight of 323, indicating the formation of the proposed TEMPO adduct to the aryl radical intermediate ascribing to the oxidation of **4a** by BCN under light irradiation.

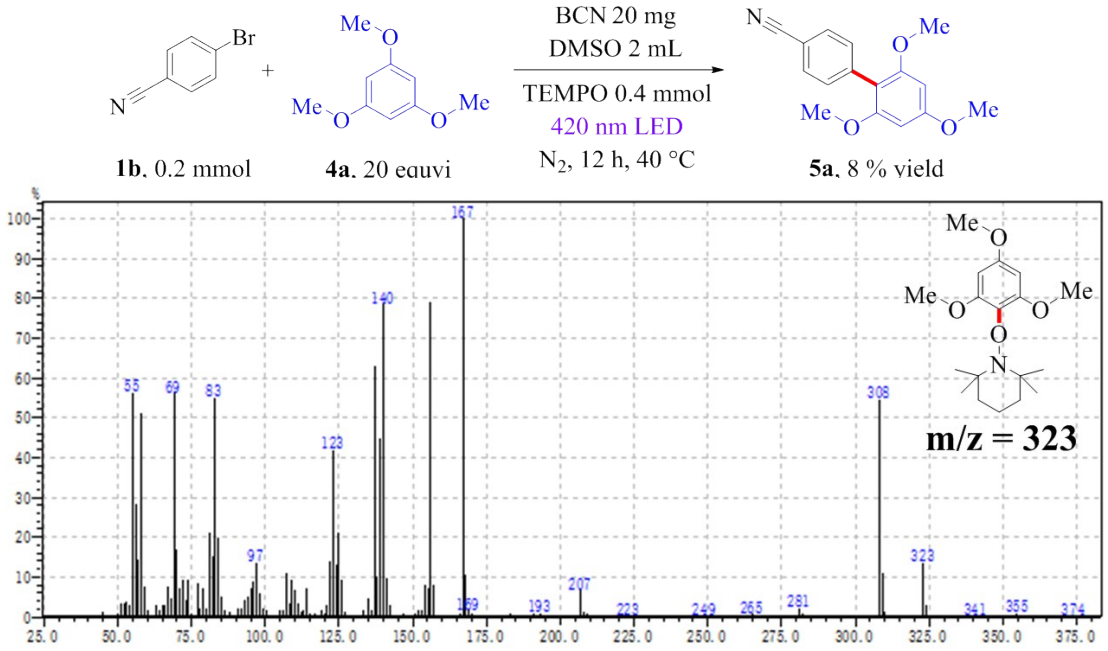


Figure S25. Mass spectra of TEMPO-aryl radical adduct for C-H arylation of arene with aryl bromide.

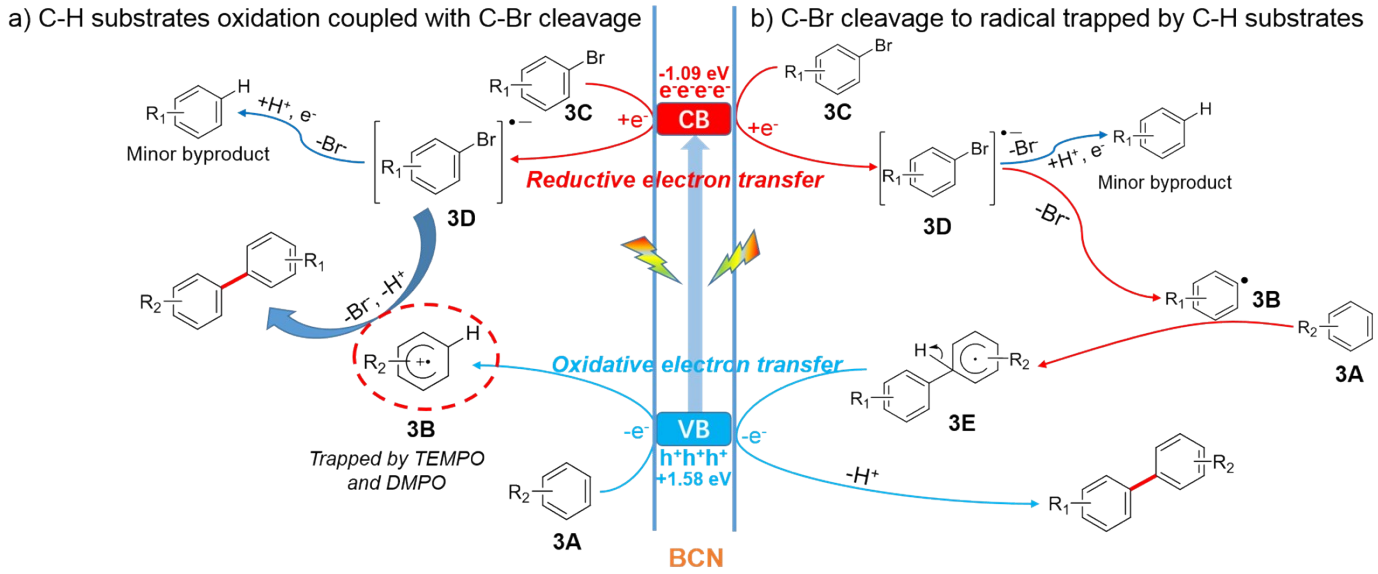


Figure S26. Alternative mechanisms for C-H (het)arylation to form C-C bonds by BCN photoredox catalysis.

Mechanism study for procedure 4

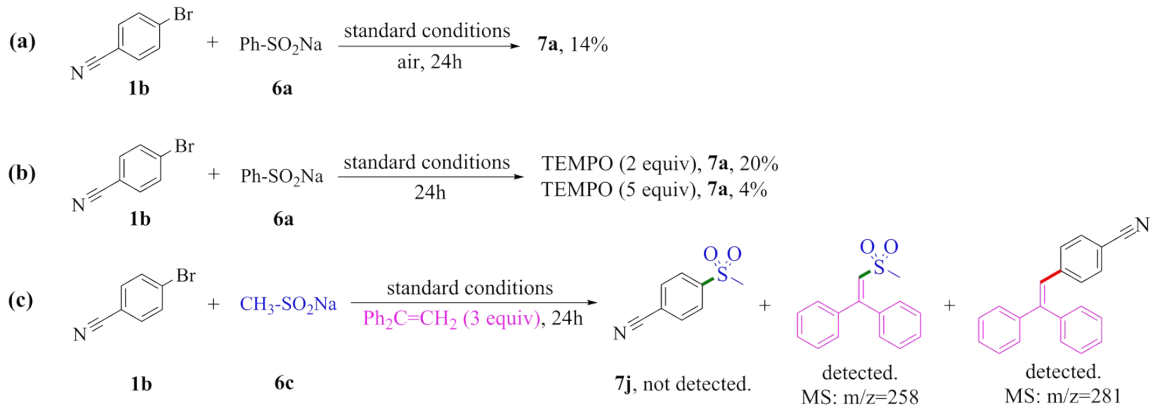


Figure S27. Mechanism study for C-Br sulfonylation by BCN photoredox catalysis.

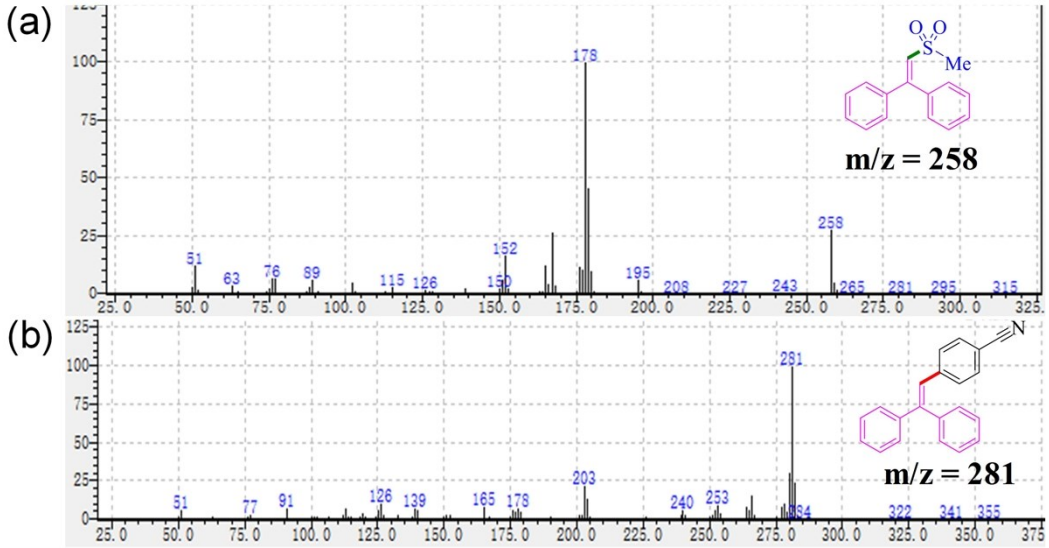


Figure S28. Mass spectra of (a) 1,1-diphenylethylene-sulfonyl radical adduct and (b) 1,1-diphenylethylene-aryl radical adduct for photoredox C-Br sulfonylation reaction.

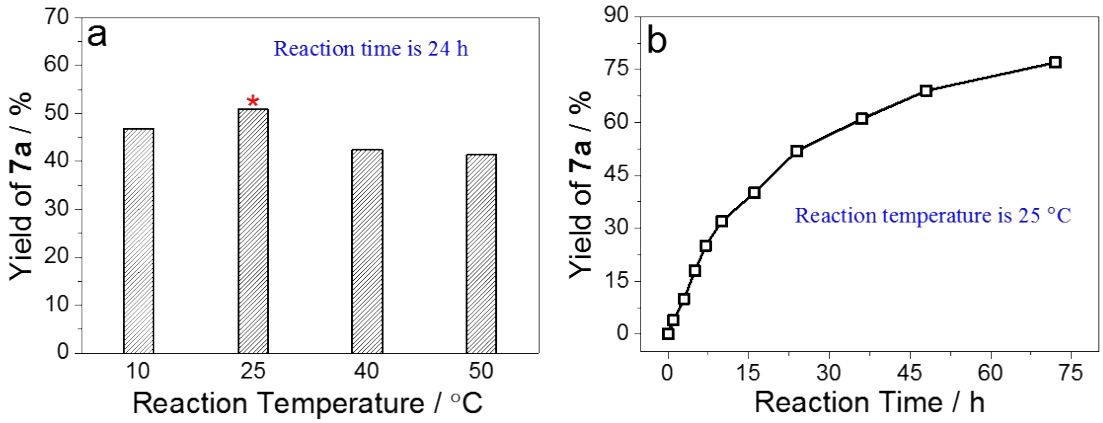


Figure S29. (a) Reaction temperature investigation for C-Br sulfonylation. (b) Kenetic profile of yielding **7a** at 25 °C.

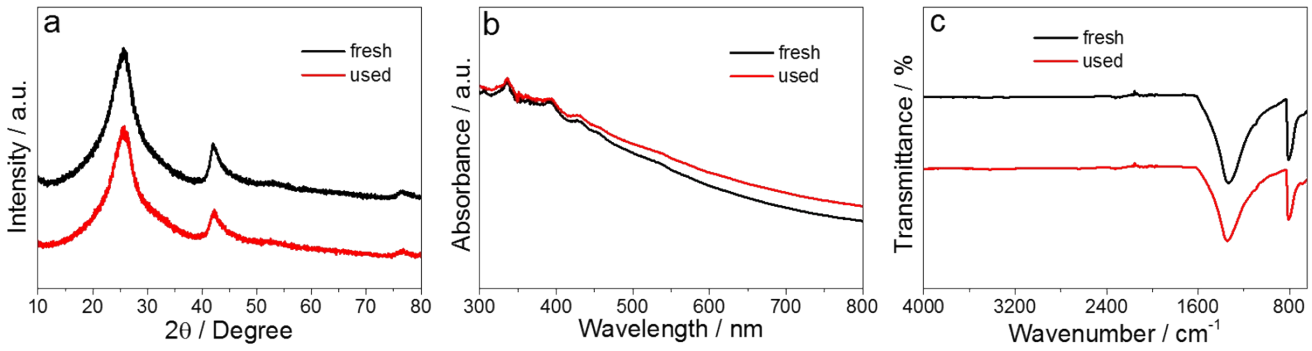


Figure S30. (a) XRD, (b) UV-Vis DRS, and (c) FT-IR spectra of fresh and recycled BCN after C(sp^2)-H (het)arylation reactions.

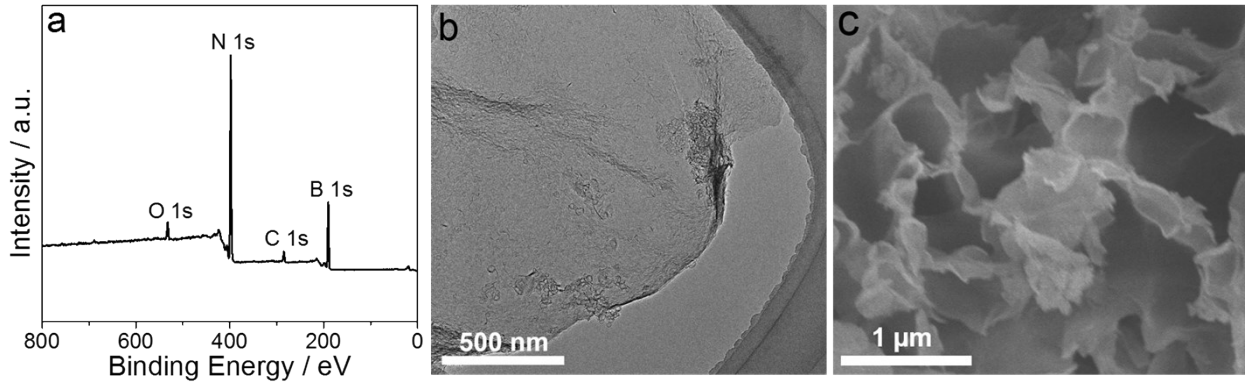
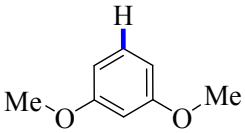


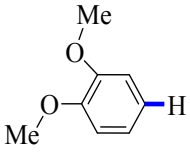
Figure S31. (a) XPS spectrum. (b) TEM. and (c) SEM image of recycled BCN after C(sp^2)-H (het)arylation reactions.

Characterization Data for Isolated Products



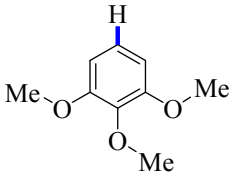
1,3-Dimethoxy-benzene (**2b**)

The compound was prepared according to **general procedure 1**. The product was colorless oil. Yield (25.4 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (t, J = 8.2 Hz, 1H), 6.52 (d, J = 8.3 Hz, 2H), 6.48 (s, 1H), 3.80 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.01 (s), 130.01 (s), 106.32 (s), 100.63 (s), 55.40 (s). MS (m/z, EI): 138, 109, 95, 78, 52.



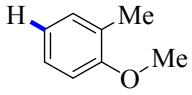
1,2-Dimethoxy-benzene (**2c**)

The compound was prepared according to **general procedure 1**. The product was colorless oil. Yield (15.2 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.96 – 6.86 (m, 4H), 3.88 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.14 (s), 120.95 (s), 111.45 (s), 55.93 (s). MS (m/z, EI): 138, 123, 95, 77, 65.



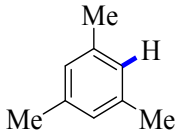
1,2,3-Trimethoxy-benzene (**2d**)

The compound was prepared according to **general procedure 1**. The product was colorless oil. Yield (24.9 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98 (t, J = 8.3 Hz, 1H), 6.57 (d, J = 8.3 Hz, 2H), 3.85 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.61 (s), 138.22 (s), 123.72 (s), 105.32 (s), 60.89 (s), 56.14 (s). MS (m/z, EI): 168, 153, 125, 110, 93, 65.



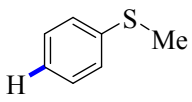
1-Methoxy-2-methyl-benzene (**2e**)

The compound was prepared according to **general procedure 1**. The product was colorless oil. Yield (14.4 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (dd, J = 16.3, 7.7 Hz, 2H), 6.87 (dd, J = 16.8, 7.9 Hz, 2H), 3.85 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.87 (s), 130.74 (s), 126.92 (s), 126.74 (s), 120.40 (s), 110.05 (s), 55.36 (s), 16.33 (s). MS (m/z, EI): 122, 107, 91, 77, 65, 51.



Mesitylene (**2f**)

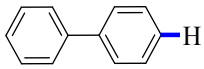
The compound was prepared according to **general procedure 1**. The product was colorless oil. Yield (16.6 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.83 (s, 3H), 2.31 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.87 (s), 127.05 (s), 21.34 (s). MS (m/z, EI): 120, 105, 91, 77.



Methylsulfanyl-benzene (**2g**)

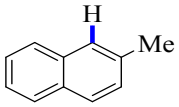
The compound was prepared according to **general procedure 1**. The product was colorless oil. Yield (14.4 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.27 (m, 4H), 7.18 (t, J = 6.4 Hz, 1H), 2.52 (s, 3H). ^{13}C

NMR (101 MHz, $CDCl_3$): δ 138.52 (s), 128.92 (s), 126.74 (s), 125.13 (s), 15.96 (s). MS (m/z, EI): 124, 109, 91, 78, 65, 51.



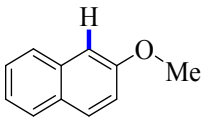
Biphenyl (**2h**)

The compound was prepared according to **general procedure 1**. The product was white solid. Yield (29.3 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, J = 7.6 Hz, 4H), 7.47 (t, J = 7.3 Hz, 4H), 7.37 (t, J = 7.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.38 (s), 128.88 (s), 127.38 (s), 127.30 (s). MS (m/z, EI): 154, 128, 89, 76, 51.



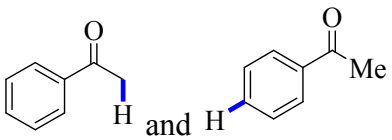
2-Methyl-naphthalene (**2i**)

The compound was prepared according to **general procedure 1**. The product was colorless oil. Yield (21.9 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 – 7.73 (m, 3H), 7.64 (s, 1H), 7.50 – 7.40 (m, 2H), 7.34 (d, J = 8.4 Hz, 1H), 2.54 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 135.56 (s), 133.82 (s), 131.85 (s), 128.24 (s), 127.82 (s), 127.73 (s), 127.36 (s), 126.97 (s), 125.99 (s), 125.08 (s), 21.84 (s). MS (m/z, EI): 142, 115, 89, 71, 51.



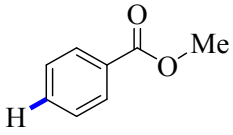
2-Methoxy-naphthalene (**2j**)

The compound was prepared according to **general procedure 1**. The product was white solid. Yield (26.5 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 – 7.71 (m, 3H), 7.47 (t, J = 7.5 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.18 (d, J = 10.3 Hz, 2H), 3.94 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.73 (s), 134.71 (s), 129.52 (s), 129.10 (s), 127.78 (s), 126.87 (s), 126.49 (s), 123.72 (s), 118.83 (s), 105.91 (s), 55.40 (s). MS (m/z, EI): 158, 143, 115, 89, 63.



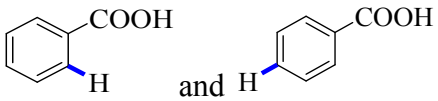
1-Phenyl-ethanone (**2k, 2l**)

The compound was prepared according to **general procedure 1**. The product was colorless oil. Yield (**2k**, 20.4 mg, 85%; **2l**, 15.6 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 7.8 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.46 (t, J = 7.3 Hz, 2H), 2.60 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.33 (s), 137.24 (s), 133.22 (s), 128.68 (s), 128.42 (s), 26.70 (s). MS (m/z, EI): 120, 105, 77, 51.



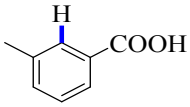
Benzoic acid methyl ester (**2m**)

The compound was prepared according to **general procedure 1**. The product was colorless oil. Yield (19.6 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 7.8 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 2H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.25 (s), 133.03 (s), 130.30 (s), 129.70 (s), 128.48 (s), 52.21 (s). MS (m/z, EI): 136, 105, 77, 51.



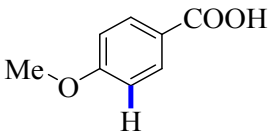
Benzoic acid (**2n, 2z**)

The compound was prepared according to **general procedure 1**. The product was white solid. Yield (**2n**, 20.5 mg, 84%; **2z**, 22.7 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.54 (s, 1H), 8.14 (d, *J* = 7.9 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.61 (s), 133.96 (s), 130.36 (s), 129.47 (s), 128.62 (s). MS (m/z, EI): 122, 105, 77, 51.



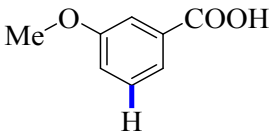
3-Methyl-benzoic acid (**2o, 2aa**)

The compound was prepared according to **general procedure 1**. The product was white solid. Yield (**2o**, 26.1 mg, 96%; **2aa**, 26.1 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.85 (s, 1H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.73 (s), 138.45 (s), 134.74 (s), 130.86 (s), 129.40 (s), 128.53 (s), 127.53 (s), 21.39 (s). MS (m/z, EI): 136, 119, 91, 65, 45.



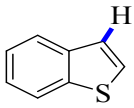
4-Methoxy-benzoic acid (**2p**)

The compound was prepared according to **general procedure 1**. The product was white solid. Yield (28.3 mg, 93%). ^{1}H NMR (400 MHz, DMSO): δ 12.65 (s, 1H), 7.89 (d, *J* = 8.6 Hz, 2H), 7.01 (d, *J* = 8.7 Hz, 2H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 167.04 (s), 162.87 (s), 131.37 (s), 123.00 (s), 113.82 (s), 55.44 (s). MS (m/z, EI): 152, 135, 107, 77, 63.



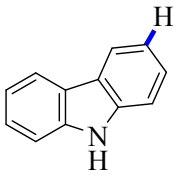
3-Methoxy-benzoic acid (**2q**)

The compound was prepared according to **general procedure 1**. The product was white solid. Yield (29.2 mg, 96%). ^{1}H NMR (400 MHz, DMSO): δ 8.65 (s, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.44 (s, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.17 (dd, *J* = 8.2, 2.6 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 167.18 (s), 159.27 (s), 132.23 (s), 129.74 (s), 121.59 (s), 118.91 (s), 113.94 (s), 55.27 (s). MS (m/z, EI): 152, 135, 107, 92, 77, 63.



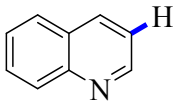
Benzo[b]thiophene (**2r**)

The compound was prepared according to **general procedure 1**. The product was white solid. Yield (17.2 mg, 64%).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 7.2 Hz, 1H), 7.85 (d, *J* = 7.0 Hz, 1H), 7.46 (d, *J* = 5.3 Hz, 1H), 7.43 – 7.32 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 139.85 (s), 139.72 (s), 126.42 (s), 124.33 (s), 124.27 (s), 123.97 (s), 123.74 (s), 122.62 (s). MS (m/z, EI): 134, 108, 89, 67, 45.



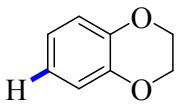
9H-Carbazole (**2s**)

The compound was prepared according to **general procedure 1**. The product was white solid. Yield (28.1 mg, 84%). ^{1}H NMR (400 MHz, DMSO): δ 11.37 (s, 1H), 8.10 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, DMSO): δ 139.73 (s), 125.44 (s), 122.36 (s), 120.10 (s), 118.41 (s), 110.93 (s). MS (m/z, EI): 167, 139, 113, 83.



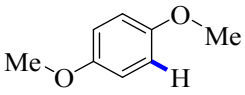
Quinoline (**2t**)

The compound was prepared according to **general procedure 1**. The product was colorless oil. Yield (15.5 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.92 (d, *J* = 3.5 Hz, 1H), 8.15 (d, *J* = 8.3 Hz, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.39 (dd, *J* = 8.1, 4.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.52 (s), 148.41 (s), 136.19 (s), 129.62 (s), 129.58 (s), 128.42 (s), 127.91 (s), 126.67 (s), 121.20 (s). MS (m/z, EI): 129, 102, 76, 51.



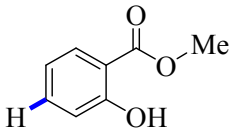
2,3-Dihydro-benzo[1,4]dioxine (**2u**)

The compound was prepared according to **general procedure 1**. The product was colorless oil. Yield (17.7 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.90 – 6.82 (m, 4H), 4.26 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.72 (s), 121.53 (s), 117.42 (s), 64.46 (s). MS (m/z, EI): 136, 121, 108, 80, 52.



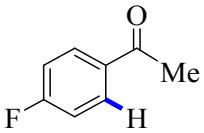
1,4-Dimethoxy-benzene (**2w**)

The compound was prepared according to **general procedure 1**. The product was white solid. Yield (22.6 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.85 (s, 4H), 3.77 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.89 (s), 114.78 (s), 55.86 (s). MS (m/z, EI): 138, 123, 95.



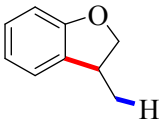
2-Hydroxy-benzoic acid methyl ester (**2x**)

The compound was prepared according to **general procedure 1**. The product was colorless oil. Yield (21.3 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.77 (s, 1H), 7.83 (dd, J = 8.0, 1.6 Hz, 1H), 7.48 – 7.42 (m, 1H), 6.98 (d, J = 8.3 Hz, 1H), 6.90 – 6.85 (m, 1H), 3.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.71 (s), 161.67 (s), 135.84 (s), 130.02 (s), 119.30 (s), 117.69 (s), 112.48 (s), 52.42 (s). MS (m/z, EI): 152, 120, 92, 65, 45.



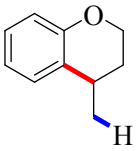
1-(4-Fluoro-phenyl)-ethanone (**2y**)

The compound was prepared according to **general procedure 1**. The product was colorless oil. Yield (24.0 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 – 7.93 (m, 2H), 7.12 (t, J = 8.1 Hz, 2H), 2.58 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.57 (s), 165.88 (d, J = 254.6 Hz), 133.73 (d, J = 3.0 Hz), 131.05 (d, J = 9.3 Hz), 115.76 (d, J = 21.9 Hz), 26.63 (s). MS (m/z, EI): 138, 123, 95, 75, 45.



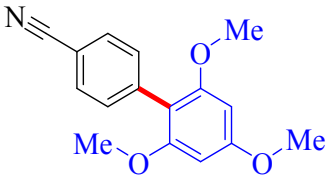
3-Methyl-2,3-dihydro-benzofuran (**3a**)

The compound was prepared according to **general procedure 2**. The product was colorless oil (18.8 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (dd, *J* = 18.6, 7.6 Hz, 2H), 6.88 (t, *J* = 7.3 Hz, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 4.69 (t, *J* = 8.7 Hz, 1H), 4.08 (t, *J* = 7.9 Hz, 1H), 3.56 (h, *J* = 7.2 Hz, 1H), 1.34 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.85 (s), 132.38 (s), 128.11 (s), 123.91 (s), 120.55 (s), 109.58 (s), 78.58 (s), 36.62 (s), 19.43 (s). MS (m/z, EI): 134, 119, 91, 65.



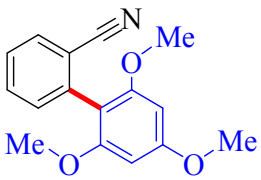
4-Methyl-chroman (**3b**)

The compound was prepared according to **general procedure 2**. The product was light yellow oil (18.1 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (d, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 7.7 Hz, 1H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 4.29 – 4.14 (m, 2H), 2.98 (h, *J* = 6.2 Hz, 1H), 2.11 (dd, *J* = 9.2, 3.6 Hz, 1H), 1.75 (dd, *J* = 8.5, 5.1 Hz, 1H), 1.36 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.47 (s), 128.76 (s), 127.73 (s), 127.33 (s), 120.32 (s), 116.84 (s), 63.96 (s), 30.45 (s), 28.62 (s), 22.32 (s). MS (m/z, EI): 148, 133, 105, 91, 77.



2',4',6'-trimethoxy-[1,1'-biphenyl]-4-carbonitrile (**5a**)

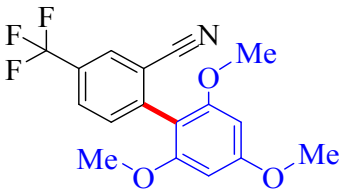
The compound was prepared according to **general procedure 3**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (20:1, v:v) as an eluent to provide white solid (40.9 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.6 Hz, 2H), 7.45 (d, *J* = 7.7 Hz, 2H), 6.23 (s, 2H), 3.88 (s, 3H), 3.73 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.53 (s), 158.21 (s), 139.69 (s), 132.27 (s), 131.36 (s), 119.56 (s), 110.57 (s), 109.88 (s), 91.00 (s), 55.90 (s), 55.53 (s). MS (m/z, EI): 269, 226, 196, 140, 116.



2',4',6'-trimethoxy-[1,1'-biphenyl]-2-carbonitrile (**5b**)

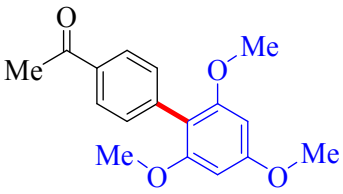
The compound was prepared according to **general procedure 3**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (20:1, v:v) as an eluent to provide white

solid (44.7 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.38 (dd, *J* = 16.7, 8.0 Hz, 2H), 6.24 (s, 2H), 3.87 (s, 3H), 3.75 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.01 (s), 158.44 (s), 138.93 (s), 132.67 (s), 132.53 (s), 131.94 (s), 126.96 (s), 119.00 (s), 114.87 (s), 108.73 (s), 91.02 (s), 55.87 (s), 55.47 (s). MS (m/z, EI): 269, 240, 196, 153, 125.



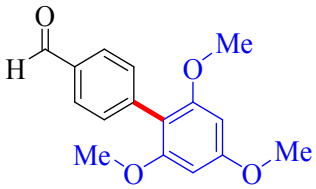
2',4',6'-trimethoxy-4-(trifluoromethyl)-[1,1'-biphenyl]-2-carbonitrile (**5c**)

The compound was prepared according to **general procedure 3**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (20:1, v:v) as an eluent to provide colorless oil (61.3 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 1H), 6.25 (s, 2H), 3.87 (s, 3H), 3.76 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.65 (s), 158.35 (s), 142.82 (s), 133.57 (s), 129.41 (q, *J* = 3.6 Hz), 128.48 (q, *J* = 3.3 Hz), 123.45 (q, *J* = 272.3 Hz), 117.77 (s), 115.76 (s), 107.33 (s), 91.00 (s), 55.82 (s), 55.52 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.82 (s). MS (m/z, EI): 337, 308, 294, 208, 125, 69.



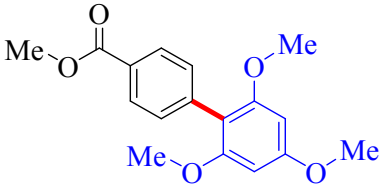
1-(2',4',6'-trimethoxy-[1,1'-biphenyl]-4-yl)ethan-1-one (**5d**)

The compound was prepared according to **general procedure 3**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (15:1, v:v) as an eluent to provide white solid (39.5 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.6 Hz, 2H), 7.46 (d, *J* = 7.6 Hz, 2H), 6.24 (s, 2H), 3.87 (s, 3H), 3.73 (s, 6H), 2.62 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.12 (s), 161.24 (s), 158.36 (s), 139.91 (s), 135.22 (s), 131.66 (s), 127.78 (s), 111.41 (s), 91.06 (s), 55.96 (s), 55.51 (s), 26.67 (s). MS (m/z, EI): 286, 271, 228, 135.



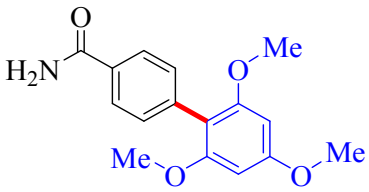
2',4',6'-trimethoxy-[1,1'-biphenyl]-4-carbaldehyde (**5e**)

The compound was prepared according to **general procedure 3**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (15:1, v:v) as an eluent to provide white solid (32.1 mg, 59% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.02 (s, 1H), 7.89 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 6.24 (s, 2H), 3.88 (s, 3H), 3.74 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.39 (s), 161.39 (s), 158.34 (s), 141.44 (s), 134.61 (s), 132.18 (s), 129.15 (s), 111.21 (s), 91.02 (s), 55.97 (s), 55.55 (s). MS (m/z, EI): 272, 229, 199, 119.



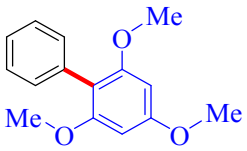
methyl 2',4',6'-trimethoxy-[1,1'-biphenyl]-4-carboxylate (**5f**)

The compound was prepared according to **general procedure 3**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (20:1, v:v) as an eluent to provide white solid (38.1 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.7 Hz, 2H), 7.42 (d, *J* = 7.7 Hz, 2H), 6.24 (s, 2H), 3.92 (s, 3H), 3.87 (s, 3H), 3.72 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.40 (s), 161.17 (s), 158.36 (s), 139.59 (s), 131.48 (s), 128.96 (s), 128.12 (s), 111.58 (s), 91.08 (s), 55.96 (s), 55.51 (s), 52.04 (s). MS (m/z, EI): 302, 271, 228, 149, 135.



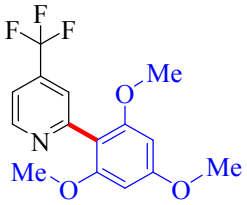
2',4',6'-trimethoxy-[1,1'-biphenyl]-4-carboxamide (**5g**)

The compound was prepared according to **general procedure 3**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (1:1, v:v) as an eluent to provide white solid (31.6 mg, 55% yield). ^{1}H NMR (400 MHz, DMSO) δ 7.92 (s, 1H), 7.81 (d, *J* = 7.5 Hz, 2H), 7.28 (s, 1H), 7.25 (d, *J* = 7.5 Hz, 2H), 6.32 (s, 2H), 3.82 (s, 3H), 3.66 (s, 6H). ^{13}C NMR (101 MHz, DMSO) δ 168.07 (s), 160.66 (s), 157.77 (s), 137.44 (s), 132.11 (s), 130.89 (s), 126.64 (s), 110.69 (s), 91.15 (s), 55.69 (s), 55.32 (s). MS (m/z, EI): 287, 271, 228, 135.



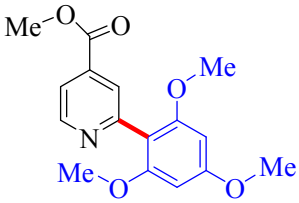
2,4,6-trimethoxy-1,1'-biphenyl (**5h**)

The compound was prepared according to **general procedure 3**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (30:1, v:v) as an eluent to provide white solid (16.6 mg, 34% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (t, J = 7.2 Hz, 2H), 7.37 – 7.27 (m, 3H), 6.25 (s, 2H), 3.88 (s, 3H), 3.73 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.63 (s), 158.47 (s), 134.24 (s), 131.32 (s), 127.74 (s), 126.61 (s), 112.66 (s), 91.05 (s), 56.00 (s), 55.49 (s). MS (m/z, EI): 244, 214, 128, 115, 91.



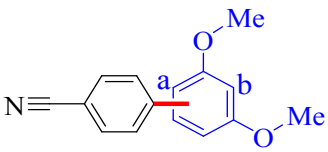
4-(trifluoromethyl)-2-(2,4,6-trimethoxyphenyl)pyridine (**5i**)

The compound was prepared according to **general procedure 3**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (2:1, v:v) as an eluent to provide colorless oil (40.1 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1H), 7.54 (s, 1H), 7.39 (s, 1H), 6.21 (s, 2H), 3.86 (s, 3H), 3.72 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.06 (s), 158.92 (s), 156.06 (s), 149.98 (s), 138.00 (q, J = 33.7 Hz), 122.66 (q, J = 3.5 Hz), 116.99 (q, J = 3.5 Hz), 110.97 (s), 90.96 (s), 56.01 (s), 55.54 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.64 (s). MS (m/z, EI): 313, 282, 244, 210, 148.



methyl 2-(2,4,6-trimethoxyphenyl)isonicotinate (**5j**)

The compound was prepared according to **general procedure 3**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (1:1, v:v) as an eluent to provide colorless oil (37.0 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, J = 4.7 Hz, 1H), 7.85 (s, 1H), 7.73 (d, J = 4.7 Hz, 1H), 6.20 (s, 2H), 3.93 (s, 3H), 3.85 (s, 3H), 3.70 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.13 (s), 161.79 (s), 158.90 (s), 155.77 (s), 149.90 (s), 137.26 (s), 126.23 (s), 120.61 (s), 111.46 (s), 90.90 (s), 56.00 (s), 55.52 (s), 52.63 (s). MS (m/z, EI): 303, 272, 244, 138, 101.

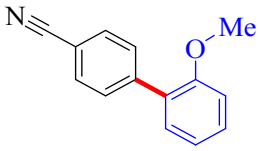


2',4'-dimethoxy-[1,1'-biphenyl]-4-carbonitrile (**5k-a**) and 2',6'-dimethoxy-[1,1'-biphenyl]-4-carbonitrile (**5k-b**)

The compound was prepared according to **general procedure 3**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (40:1, v:v) as an eluent to provide white solid mixture (34.9 mg, 73% yield, **5k-a** : **5k-b** = 20 : 13).

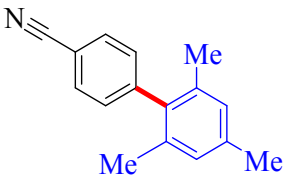
5k-a : ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 4.9 Hz, 1H), 6.62 (d, *J* = 10.8 Hz, 2H), 3.90 (s, 3H), 3.85 (s, 3H). MS (m/z, EI): 239, 209, 153, 127.

5k-b : ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.66 (m, 4H), 7.36 (t, *J* = 8.3 Hz, 1H), 6.70 (d, *J* = 8.4 Hz, 2H), 3.77 (s, 6H). MS (m/z, EI): 239, 196, 153, 127



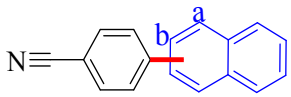
2'-methoxy-[1,1'-biphenyl]-4-carbonitrile (**5l**)

The compound was prepared according to **general procedure 3**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (100:1, v:v) as an eluent to provide white solid (21.3 mg, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (q, *J* = 8.3 Hz, 4H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.35 (s), 143.43 (s), 131.76 (s), 130.63 (s), 130.26 (s), 129.99 (s), 128.61 (s), 121.10 (s), 119.20 (s), 111.42 (s), 110.40 (s), 55.56 (s). MS (m/z, EI): 209, 194, 166, 140, 113.



2',4',6'-trimethyl-[1,1'-biphenyl]-4-carbonitrile (**5m**)

The compound was prepared according to **general procedure 3**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (100:1, v:v) as an eluent to provide colorless oil (20.8 mg, 47% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 6.98 (s, 2H), 2.36 (s, 3H), 1.99 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.50 (s), 137.64 (s), 137.22 (s), 135.37 (s), 132.39 (s), 130.42 (s), 128.44 (s), 119.09 (s), 110.72 (s), 21.12 (s), 20.69 (s). MS (m/z, EI): 221, 206, 190, 165, 119, 89.

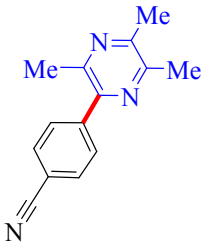


4-(naphthalen-1-yl)benzonitrile (**5n-a**) and 4-(naphthalen-2-yl)benzonitrile (**5n-b**)

The compound was prepared according to **general procedure 3**. Crude product was purified by flash column chromatography on silica gel using pure petroleum ether as an eluent to provide **5n-a** and **5n-b** (**5n-a**, colorless solid, 22.4 mg, 49% yield; **5n-b**, white solid, 7.0 mg, 15% yield).

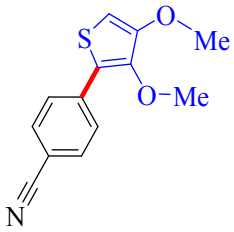
5n-a : ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (t, *J* = 7.3 Hz, 2H), 7.79 (d, *J* = 7.9 Hz, 3H), 7.61 (d, *J* = 7.0 Hz, 2H), 7.55 (dd, *J* = 13.6, 6.9 Hz, 2H), 7.51 – 7.44 (m, 1H), 7.41 (d, *J* = 6.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.75 (s), 138.29 (s), 133.90 (s), 132.22 (s), 131.05 (s), 130.90 (s), 128.88 (s), 128.65 (s), 127.13 (s), 126.75 (s), 126.27 (s), 125.44 (s), 125.28 (s), 119.01 (s), 111.27 (s). MS (m/z, EI): 229, 201, 101.

5n-b : ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 – 8.05 (m, 1H), 7.96 (d, *J* = 8.6 Hz, 1H), 7.94 – 7.87 (m, 2H), 7.84 – 7.80 (m, 2H), 7.79 – 7.75 (m, 2H), 7.71 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.57 – 7.52 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.75 (s), 136.56 (s), 133.62 (s), 133.28 (s), 132.80 (s), 129.09 (s), 128.52 (s), 128.10 (s), 127.86 (s), 126.92 (s), 126.89 (s), 126.69 (s), 125.00 (s), 119.11 (s), 111.05 (s). MS (m/z, EI): 229, 201, 101.



4-(3,5,6-trimethylpyrazin-2-yl)benzonitrile (**5o**)

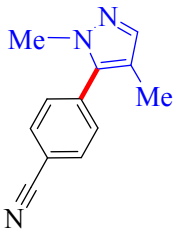
The compound was prepared according to **general procedure 3**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (20:1, v:v) as an eluent to provide yellow solid (17.4 mg, 39% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 27.7, 7.7 Hz, 4H), 2.66 – 2.43 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.12 (s), 149.50 (s), 148.14 (s), 147.42 (s), 143.70 (s), 132.29 (s), 129.98 (s), 118.81 (s), 112.18 (s), 22.40 (s), 21.83 (s), 21.69 (s). MS (m/z, EI): 223, 140, 114, 54.



4-(3,4-dimethoxythiophen-2-yl)benzonitrile (**5p**)

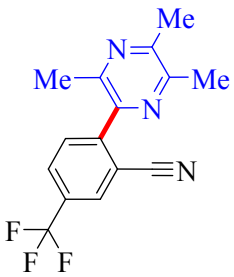
The compound was prepared according to **general procedure 3**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (10:1, v:v) as an eluent to provide yellow solid (16.2 mg, 33% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.7 Hz, 2H), 7.63 (d, *J* = 7.8 Hz, 2H), 6.27 (s, 1H), 3.87 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.70 (s), 145.26 (s), 137.89 (s), 133.10 (s), 132.53

(s), 131.29 (s), 126.90 (s), 123.30 (s), 119.11 (s), 110.25 (s), 96.56 (s), 60.43 (s), 57.45 (s). MS (m/z, EI): 245, 230, 146, 75.



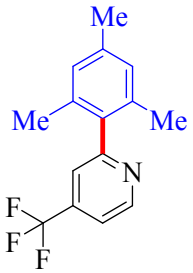
4-(1,4-dimethyl-1H-pyrazol-5-yl)benzonitrile (**5q**)

The compound was prepared according to **general procedure 3**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (1:1, v:v) as an eluent to provide white solid (24.4 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 7.8 Hz, 2H), 7.47 (d, J = 7.3 Hz, 2H), 7.42 (s, 1H), 3.81 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.52 (s), 135.25 (s), 132.56 (s), 130.36 (s), 127.53 (s), 118.52 (s), 115.70 (s), 112.19 (s), 37.68 (s), 9.22 (s). MS (m/z, EI): 197, 169, 91.



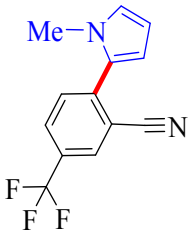
5-(trifluoromethyl)-2-(3,5,6-trimethylpyrazin-2-yl)benzonitrile (**5r**)

The compound was prepared according to **general procedure 3**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (3:1, v:v) as an eluent to provide white solid (21.0 mg, 36% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.93 (d, J = 7.9 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 2.60 (d, J = 14.8 Hz, 6H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.77 (s), 149.78 (s), 147.86 (s), 146.24 (s), 145.72 (s), 131.22 (s), 130.40 (q, J = 4.1 Hz), 129.48 (q, J = 2.9 Hz), 124.08 (q, J = 59.6 Hz), 116.51 (s), 113.96 (s), 22.02 (s), 21.59 (s), 21.55 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.06 (s). MS (m/z, EI): 291, 140, 54.



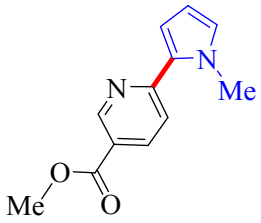
2-mesityl-4-(trifluoromethyl)pyridine (**5s**)

The compound was prepared according to **general procedure 3**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (20:1, v:v) as an eluent to provide colorless oil (22.3 mg, 42% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 7.47 (s, 2H), 6.95 (s, 2H), 2.33 (s, 3H), 2.01 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.66 (s), 150.67 (s), 138.35 (s), 137.55 (q, J = 230.3 Hz), 136.41 (s), 128.68 (s), 120.62 (q, J = 4.0 Hz), 117.36 (q, J = 4.0 Hz), 100.12 (s), 21.23 (s), 20.23 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.73 (s). MS (m/z, EI): 265, 249, 196, 181, 125.



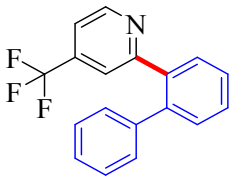
2-(1-methyl-1H-pyrrol-2-yl)-5-(trifluoromethyl)benzonitrile (**5t**)

The compound was prepared according to **general procedure 3**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (20:1, v:v) as an eluent to provide yellow oil (41.5 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.84 (d, J = 8.2 Hz, 1H), 7.57 (d, J = 8.2 Hz, 1H), 6.87 – 6.83 (m, 1H), 6.52 (d, J = 1.8 Hz, 1H), 6.28 (d, J = 2.9 Hz, 1H), 3.65 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.26 (s), 131.15 (s), 130.76 (q, J = 3.8 Hz), 129.56 (s), 129.10 (q, J = 3.4 Hz), 128.77, 126.40 (s), 123.19 (q, J = 272.3 Hz), 117.58 (s), 113.15 (s), 113.07 (s), 109.04 (s), 35.17 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.93 (s). MS (m/z, EI): 250, 222, 154, 78.



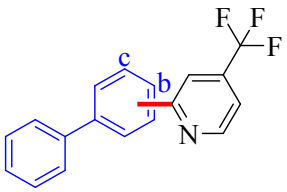
methyl 6-(1-methyl-1H-pyrrol-2-yl)nicotinate (**5u**)

The compound was prepared according to **general procedure 3**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (10:1, v:v) as an eluent to provide yellow oil (23.8 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, J = 4.8 Hz, 1H), 8.09 (s, 1H), 7.58 (d, J = 5.0 Hz, 1H), 6.78 – 6.73 (m, 1H), 6.74 – 6.68 (m, 1H), 6.20 (t, J = 3.1 Hz, 1H), 4.01 (s, 3H), 3.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.98 (s), 153.66 (s), 149.35 (s), 137.79 (s), 131.56 (s), 127.35 (s), 120.68 (s), 118.92 (s), 111.91 (s), 108.09 (s), 52.75 (s), 37.32 (s). MS (m/z, EI): 216, 157, 78.



2-([1,1'-biphenyl]-2-yl)-4-(trifluoromethyl)pyridine (**5v-a**)

The compound was prepared according to **general procedure 3**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (40:1, v:v) as an eluent to provide white solid (19.2 mg, 32% yield). ^{1}H NMR (600 MHz, DMSO) δ 8.84 (d, *J* = 5.1 Hz, 1H), 7.73 (d, *J* = 7.5 Hz, 1H), 7.61 – 7.51 (m, 3H), 7.51 – 7.45 (m, 1H), 7.31 – 7.24 (m, 3H), 7.13 (s, 1H), 7.08 (dd, *J* = 7.0, 2.4 Hz, 2H). ^{13}C NMR (151 MHz, DMSO) δ 159.82 (s), 150.91 (s), 140.53 (s), 140.38 (s), 137.77 (s), 136.04 (q, *J* = 33.4 Hz), 130.42 (s), 130.40 (s), 129.39 (s), 129.33 (s), 128.31 (s), 127.82 (s), 127.07 (s), 120.23 (q, *J* = 3.4 Hz), 117.11 (q, *J* = 3.0 Hz). ^{19}F NMR (565 MHz, DMSO) δ -63.77. MS (m/z, EI): 299, 230, 149.

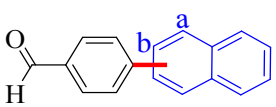


2-([1,1'-biphenyl]-4-yl)-4-(trifluoromethyl)pyridine (**5v-b**) and 2-([1,1'-biphenyl]-3-yl)-4-(trifluoromethyl)pyridine (**5v-c**)

The compound was prepared according to **general procedure 3**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (40:1, v:v) as an eluent to provide white solid mixture (19.1 mg, 32% yield, **5v-b** : **5v-c** = 5 : 4).

5v-b : ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (s, 2H), 8.13 (d, *J* = 7.4 Hz, 2H), 8.00 (d, *J* = 10.5 Hz, 3H), 7.75 (d, *J* = 7.4 Hz, 2H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.40 (t, *J* = 7.1 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.79 (s). MS (m/z, EI): 299, 230, 149.

5v-c : ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.72 – 7.63 (m, 5H), 7.49 (t, *J* = 6.7 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.75 (s). MS (m/z, EI): 299, 230, 149.

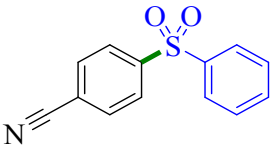


4-(naphthalen-1-yl)benzaldehyde (**5w-a**) and 4-(naphthalen-2-yl)benzaldehyde (**5w-b**)

The compound was prepared according to **general procedure 3**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (50:1, v:v) as an eluent to provide white solid (**5w-a**, 20.9 mg, 45% yield; **5w-b**, 6.5 mg, 14% yield).

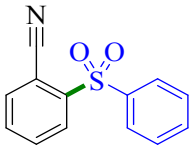
5w-a : ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.12 (s, 1H), 8.02 (d, *J* = 7.3 Hz, 2H), 7.93 (t, *J* = 8.1 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 7.3 Hz, 2H), 7.54 (dd, *J* = 16.6, 8.2 Hz, 2H), 7.46 (dd, *J* = 13.6, 7.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.10 (s), 147.35 (s), 138.91 (s), 135.43 (s), 133.91 (s), 131.21 (s), 130.88 (s), 129.84 (s), 128.66 (s), 128.58 (s), 127.11 (s), 126.60 (s), 126.18 (s), 125.56 (s), 125.45 (s). MS (m/z, EI): 232, 203, 176, 101, 88.

5w-b : ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.08 (s, 1H), 8.11 (s, 1H), 7.99 (d, *J* = 8.1 Hz, 2H), 7.95 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 6.4 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 3H), 7.77 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.57 – 7.52 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.09 (s), 147.24 (s), 137.10 (s), 135.33 (s), 133.65 (s), 133.23 (s), 130.47 (s), 128.93 (s), 128.53 (s), 128.05 (s), 127.84 (s), 126.78 (s), 126.74 (s), 125.25 (s). MS (m/z, EI): 232, 202, 116, 101, 72.



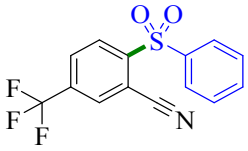
4-(phenylsulfonyl)benzonitrile (**7a**)

The compound was prepared according to **general procedure 4**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (5:1, v:v) as an eluent to provide white solid (33.5 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.1 Hz, 2H), 7.94 (d, *J* = 7.7 Hz, 2H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.93 (s), 140.20 (s), 134.14 (s), 133.19 (s), 129.75 (s), 128.37 (s), 128.07 (s), 117.25 (s), 117.01 (s). MS (m/z, EI): 243, 178, 150, 125, 77, 51.



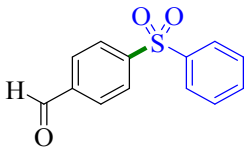
2-(phenylsulfonyl)benzonitrile (**7b**)

The compound was prepared according to **general procedure 4**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (5:1, v:v) as an eluent to provide colorless oil (27.2 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.1 Hz, 1H), 8.07 (d, *J* = 7.9 Hz, 2H), 7.86 – 7.74 (m, 2H), 7.66 (dt, *J* = 21.2, 7.2 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.76 (s), 139.62 (s), 135.77 (s), 134.32 (s), 133.50 (s), 133.41 (s), 129.91 (s), 129.53 (s), 128.77 (s), 115.71 (s), 111.50 (s). MS (m/z, EI): 243, 179, 150, 125, 77, 51.



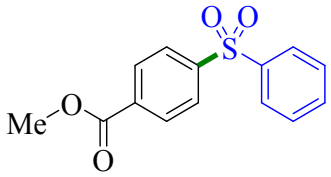
2-(phenylsulfonyl)-5-(trifluoromethyl)benzonitrile (**7c**)

The compound was prepared according to **general procedure 4**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (8:1, v:v) as an eluent to provide white solid (56.6 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 8.2 Hz, 1H), 8.14 – 8.00 (m, 4H), 7.68 (t, J = 7.4 Hz, 1H), 7.59 (t, J = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.12 (s), 138.66 (s), 135.58 (q, J = 34.5 Hz), 134.90 (s), 132.61 (q, J = 3.6 Hz), 130.75 (s), 130.34 (q, J = 3.5 Hz), 129.78 (s), 129.01 (s), 122.15 (q, J = 273.7 Hz), 114.53 (s), 112.63 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.41 (s). MS (m/z, EI): 311, 294, 247, 141, 125, 77, 51.



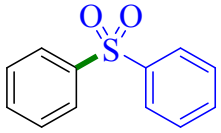
4-(phenylsulfonyl)benzaldehyde (**7d**)

The compound was prepared according to **general procedure 4**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (10:1, v:v) as an eluent to provide yellow solid (24.1 mg, 49% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.07 (s, 1H), 8.10 (d, J = 8.0 Hz, 2H), 7.98 (dd, J = 13.8, 8.0 Hz, 4H), 7.64 – 7.48 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.86 (s), 146.81 (s), 140.68 (s), 139.25 (s), 133.93 (s), 130.44 (s), 129.68 (s), 128.48 (s), 128.07 (s). MS (m/z, EI): 246, 153, 125, 77, 51.



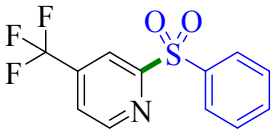
methyl 4-(phenylsulfonyl)benzoate (**7e**)

The compound was prepared according to **general procedure 4**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (10:1, v:v) as an eluent to provide white solid (35.9 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 7.9 Hz, 2H), 8.00 (d, J = 8.0 Hz, 2H), 7.95 (d, J = 7.9 Hz, 2H), 7.62 – 7.55 (m, 1H), 7.51 (t, J = 7.6 Hz, 2H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.59 (s), 145.59 (s), 140.91 (s), 134.39 (s), 133.74 (s), 130.56 (s), 129.57 (s), 127.96 (s), 127.80 (s), 52.79 (s). MS (m/z, EI): 276, 245, 183, 152, 125, 77, 51.



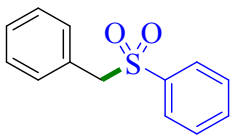
Sulfonyldibenzene (**7f**)

The compound was prepared according to **general procedure 4**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (20:1, v:v) as an eluent to provide white solid (17.0 mg, 39% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.8 Hz, 4H), 7.61 – 7.45 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.74 (s), 133.32 (s), 129.42 (s), 127.81 (s). MS (m/z, EI): 218, 152, 125, 97, 77, 51.



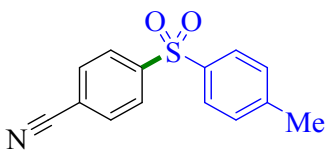
2-(phenylsulfonyl)-4-(trifluoromethyl)pyridine (**7g**)

The compound was prepared according to **general procedure 4**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (10:1, v:v) as an eluent to provide yellow oil (21.8 mg, 38% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, J = 4.8 Hz, 1H), 8.43 (s, 1H), 8.09 (d, J = 7.7 Hz, 2H), 7.67 (dd, J = 12.5, 5.8 Hz, 2H), 7.57 (t, J = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.61 (s), 151.74 (s), 140.78 (q, J = 35.4 Hz), 138.06 (s), 134.45 (s), 129.46 (s), 129.37 (s), 122.76 (q, J = 3.1 Hz), 118.27 (q, J = 3.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.66 (s). MS (m/z, EI): 287, 268, 223, 154, 126, 97, 77, 51.



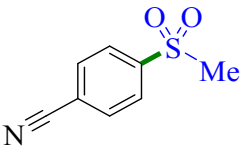
(benzylsulfonyl)benzene (**7h**)

The compound was prepared according to **general procedure 4**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (10:1, v:v) as an eluent to provide white solid (43.2 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, J = 16.5, 7.6 Hz, 3H), 7.46 (t, J = 7.6 Hz, 2H), 7.30 (dt, J = 24.6, 7.3 Hz, 3H), 7.10 (d, J = 7.4 Hz, 2H), 4.33 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.86 (s), 133.80 (s), 130.88 (s), 128.96 (s), 128.83 (s), 128.68 (s), 128.63 (s), 128.16 (s), 62.92 (s). MS (m/z, EI): 232, 167, 152, 91, 77, 51.



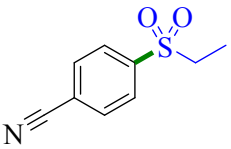
4-tosylbenzonitrile (**7i**)

The compound was prepared according to **general procedure 4**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (10:1, v:v) as an eluent to provide white solid (33.9 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.2 Hz, 2H), 7.80 (dd, J = 17.1, 8.1 Hz, 4H), 7.33 (d, J = 8.0 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.33 (s), 145.37 (s), 137.20 (s), 133.13 (s), 130.38 (s), 128.21 (s), 128.13 (s), 117.30 (s), 116.79 (s), 21.73 (s). MS (m/z, EI): 257, 139, 107, 91, 65, 51.



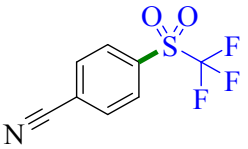
4-(methylsulfonyl)benzonitrile (**7j**)

The compound was prepared according to **general procedure 4**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (8:1, v:v) as an eluent to provide white solid (22.1 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.4 Hz, 2H), 7.89 (d, J = 7.9 Hz, 2H), 3.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.58 (s), 133.33 (s), 128.33 (s), 117.74 (s), 117.16 (s), 44.36 (s). MS (m/z, EI): 181, 166, 119, 75, 51.



4-(ethylsulfonyl)benzonitrile (**7k**)

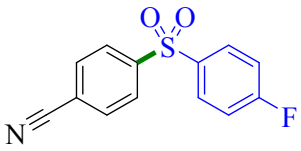
The compound was prepared according to **general procedure 4**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (8:1, v:v) as an eluent to provide white solid (25.7 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 7.9 Hz, 2H), 7.88 (d, J = 8.0 Hz, 2H), 3.15 (q, J = 7.4 Hz, 2H), 1.29 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.77 (s), 133.18 (s), 129.12 (s), 117.70 (s), 117.20 (s), 50.61 (s), 7.41 (s). MS (m/z, EI): 195, 167, 150, 119, 77, 51.



4-((trifluoromethyl)sulfonyl)benzonitrile (**7l**)

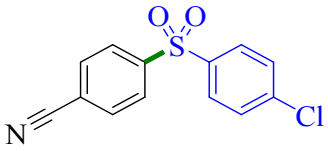
The compound was prepared according to **general procedure 4**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (30:1, v:v) as an eluent to provide pale yellow solid (37.6 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.1 Hz, 2H), 7.99 (d, J = 8.1

Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.42 (s), 135.70 (s), 133.63 (s), 131.53 (s), 120.46 (s), 116.56 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -77.64 (s). MS (m/z, EI): 235, 166, 150, 75, 51.



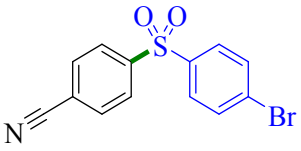
4-((4-fluorophenyl)sulfonyl)benzonitrile (**7m**)

The compound was prepared according to **general procedure 4**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (10:1, v:v) as an eluent to provide white solid (33.4 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.2 Hz, 2H), 7.97 (dd, J = 7.8, 5.5 Hz, 2H), 7.81 (d, J = 8.1 Hz, 2H), 7.22 (t, J = 8.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.05 (d, J = 257.8 Hz), 145.80 (s), 136.31 (d, J = 3.2 Hz), 133.29 (s), 131.02 (d, J = 9.7 Hz), 128.33 (s), 117.30 (s), 117.19 (d, J = 1.5 Hz), 117.07 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.34 (s). MS (m/z, EI): 261, 159, 111, 95, 75, 51.



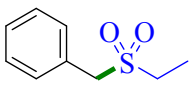
4-((4-chlorophenyl)sulfonyl)benzonitrile (**7n**)

The compound was prepared according to **general procedure 4**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (10:1, v:v) as an eluent to provide white solid (26.6 mg, 48% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 7.8 Hz, 2H), 7.88 (d, J = 7.9 Hz, 2H), 7.81 (d, J = 7.9 Hz, 2H), 7.51 (d, J = 7.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.57 (s), 141.07 (s), 138.75 (s), 133.32 (s), 130.15 (s), 129.56 (s), 128.40 (s), 117.32 (s), 117.16 (s). MS (m/z, EI): 277, 159, 127, 72, 59.



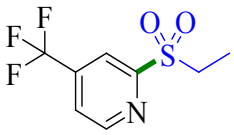
4-((4-bromophenyl)sulfonyl)benzonitrile (**7o**)

The compound was prepared according to **general procedure 4**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (10:1, v:v) as an eluent to provide white solid (25.8 mg, 40% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.1 Hz, 2H), 7.80 (d, J = 8.7 Hz, 4H), 7.68 (d, J = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.52 (s), 139.29 (s), 133.33 (s), 133.14 (s), 129.68 (s), 129.59 (s), 128.41 (s), 117.34 (s), 117.16 (s). MS (m/z, EI): 323, 242, 205, 171, 150, 102, 75.



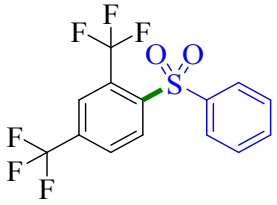
((ethylsulfonyl)methyl)benzene (**7p**)

The compound was prepared according to **general procedure 4**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (5:1, v:v) as an eluent to provide white solid (28.3 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 5H), 4.22 (s, 2H), 2.85 (q, J = 7.5 Hz, 2H), 1.34 (t, J = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 130.60 (s), 129.18 (s), 129.11 (s), 128.19 (s), 58.81 (s), 45.49 (s), 6.51 (s). MS (m/z, EI): 184, 91, 65.



2-(ethylsulfonyl)-4-(trifluoromethyl)pyridine (**7q**)

The compound was prepared according to **general procedure 4**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (5:1, v:v) as an eluent to provide pale yellow oil (27.2 mg, 57% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (d, J = 4.8 Hz, 1H), 8.32 (s, 1H), 7.79 (d, J = 4.7 Hz, 1H), 3.47 (q, J = 7.4 Hz, 2H), 1.34 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.60 (s), 151.55 (s), 140.89 (q, J = 35.6 Hz), 123.23 (q, J = 3.5 Hz), 120.68 (s), 118.53 (q, J = 3.5 Hz), 46.50 (s), 6.91 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.72 (s). MS (m/z, EI): 239, 220, 174, 147, 126, 75.



1-(phenylsulfonyl)-2,4-bis(trifluoromethyl)benzene (**7r**)

The compound was prepared according to **general procedure 4**. Crude product was purified by flash column chromatography on silica gel using petroleum ether: acetyl acetate (5:1, v:v) as an eluent to provide white solid (39.6 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 8.2 Hz, 1H), 8.13 – 8.00 (m, 2H), 7.89 (d, J = 7.8 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.79 (s), 140.37 (s), 135.48 (q, J = 34.3 Hz), 134.09 (s), 133.39 (s), 130.12 (q, J = 34.7 Hz), 129.68 (q, J = 6.5, 4.8 Hz), 129.41 (s), 128.24 (s), 125.86 (tq, J = 6.2, 3.6 Hz), 123.57 (q, J = 64.2 Hz), 120.84 (q, J = 65.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.91 (s), -63.44 (s). MS (m/z, EI): 354, 335, 261, 213, 194, 141, 93, 77.

References

1 Zhang, G., Lan, Z. A., Lin, L., Lin, S. & Wang, X. Overall water splitting by Pt/g-C_3N_4 photocatalysts without using sacrificial agents. *Chem. Sci.* **7**, 3062-3066, (2016).

2 Wang, X. *et al.* Polymer Semiconductors for Artificial Photosynthesis - Hydrogen Evolution by Mesoporous Graphitic Carbon Nitride with Visible Light. *J. Am. Chem. Soc.* **131**, 1680-1681 (2009).

3 Lin, L., Ou, H., Zhang, Y. & Wang, X. Tristriazine-Based Crystalline Graphitic Carbon Nitrides for Highly Efficient Hydrogen Evolution Photocatalysis. *ACS. Catal.* **6**, 3921-3931, (2016).

4 Trivedi, R. & Tunge, J. Regioselective Iron-Catalyzed Decarboxylative Allylic Etherification. *Org. Lett.* **11**, 5650-5652 (2009).

5 Neumeier, M. *et al.* Dichromatic Photocatalytic Substitutions of Aryl Halides with a Small Organic Dye. *Chemistry.* **24**, 105-108, (2018).

6 Li, R. *et al.* Photocatalytic Selective Bromination of Electron-Rich Aromatic Compounds Using Microporous Organic Polymers with Visible Light. *ACS. Catal.* **6**, 1113-1121, (2016).

7 Nicewicz, D., Roth, H. & Romero, N. Experimental and Calculated Electrochemical Potentials of Common Organic Molecules for Applications to Single-Electron Redox Chemistry. *Synlett.* **27**, 714-723, (2015).

8 Meyer, A. U., Strakova, K., Slanina, T. & Konig, B. Eosin Y (EY) Photoredox-Catalyzed Sulfonylation of Alkenes: Scope and Mechanism. *Chemistry.* **22**, 8694-8699, (2016).

9 Hansch, C., Leo, A. & Taft, R. W. A survey of Hammett substituent constants and resonance and field parameters. *Chem. Rev.* **91**, 165-195, (1991).

10 Yang, Y. *et al.* Nickel-catalyzed fluoroethylation of arylboronic acids via Suzuki-type coupling. *Org. Chem. Front.* **6**, 1463-1470, (2019).

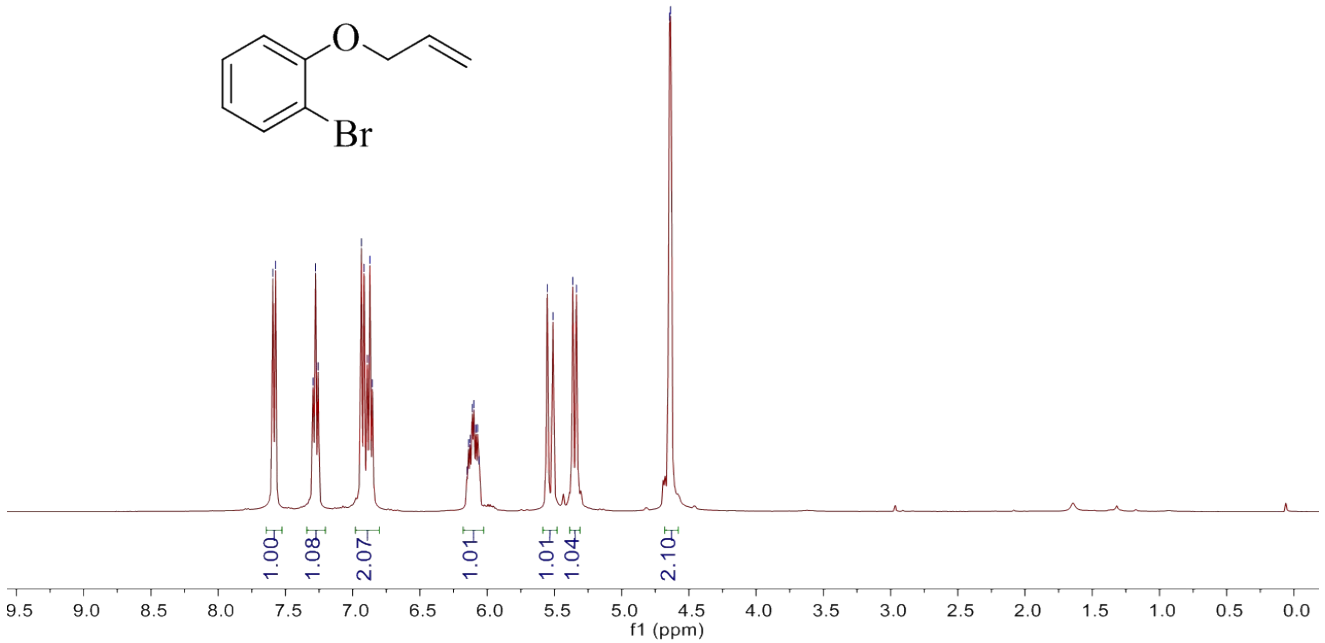
11 Dong, Z.-B., Manolikakes, G., Shi, L., Knochel, P. & Mayr, H. Structure–Reactivity Relationships in Negishi Cross-Coupling Reactions. *Chem. Eur. J.* **16**, 248-253, (2010).

12 Zheng, M., Ghosh, I., König, B. & Wang, X. Metal-free Semiconductor Photocatalysis for sp^2 C−H Functionalization with Molecular Oxygen. *ChemCatChem.* **11**, 703-706, (2019).

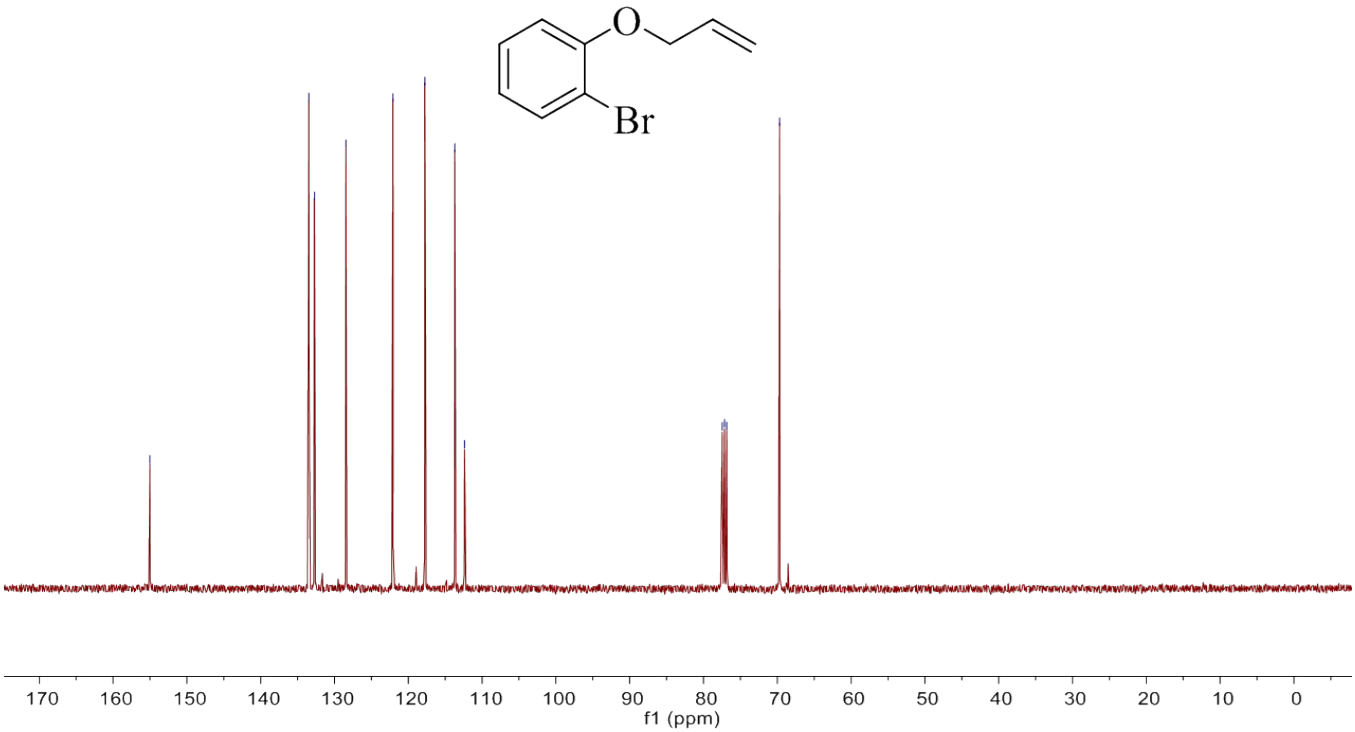
NMR Spectra

1cc

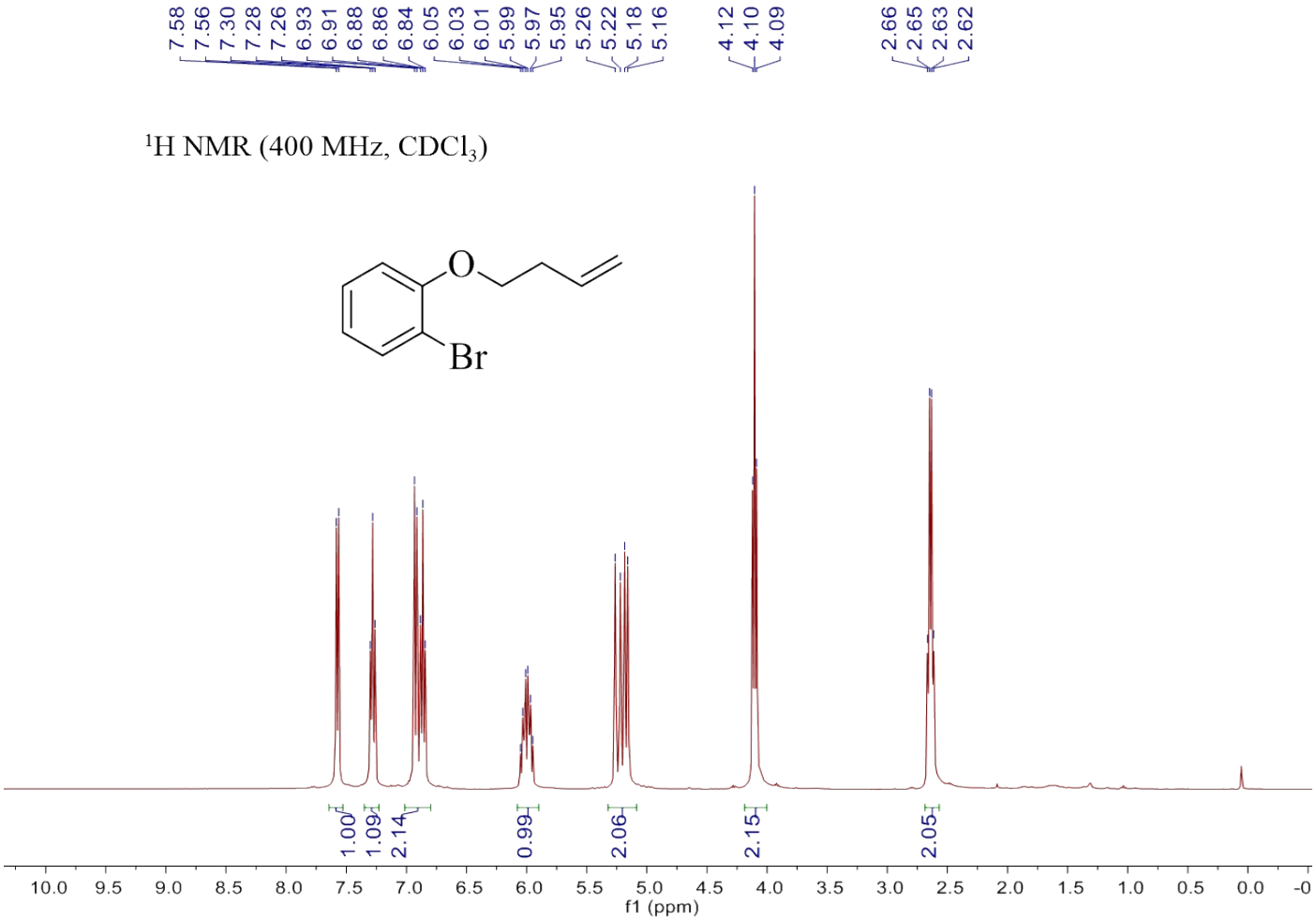
^{1}H NMR (400 MHz, $CDCl_3$)



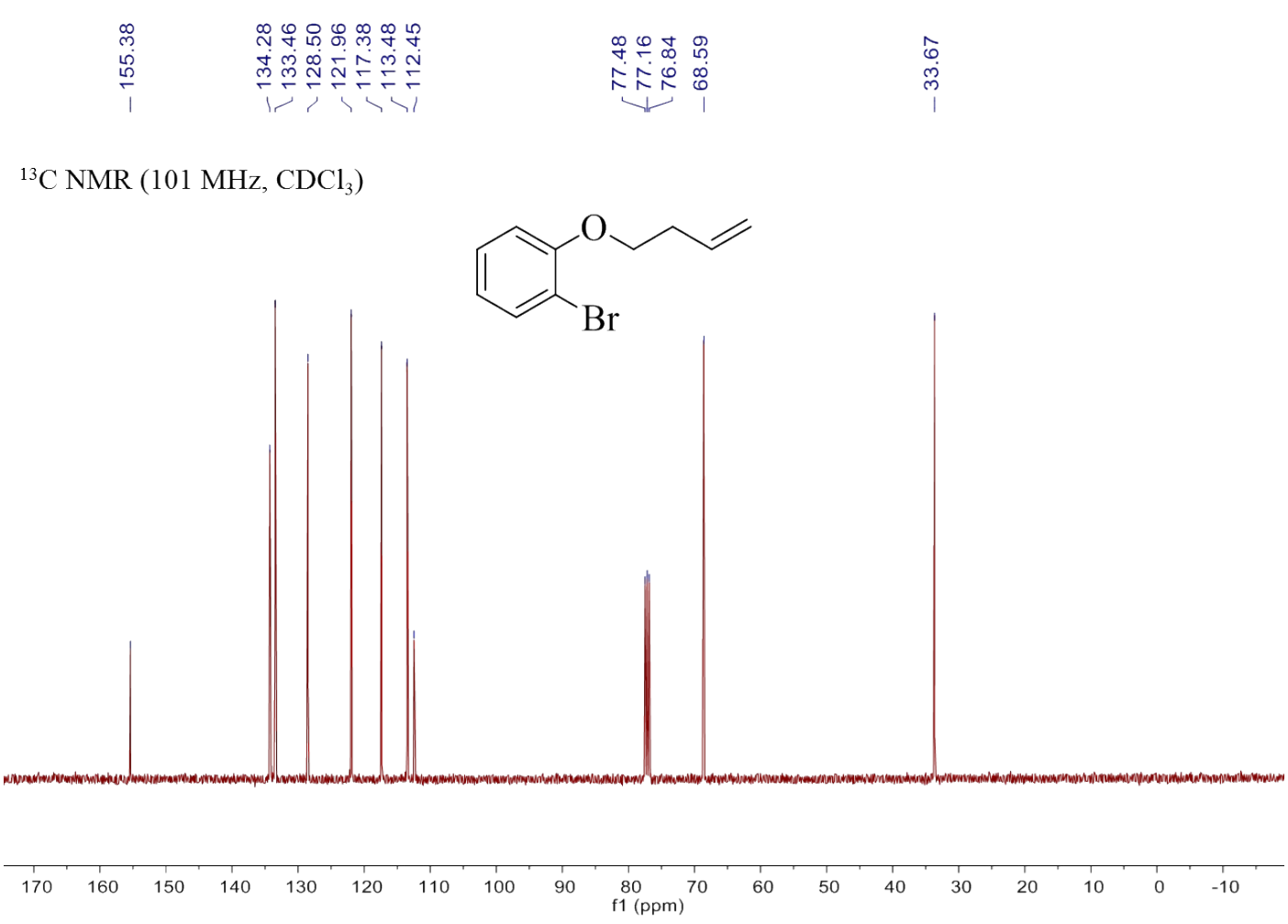
^{13}C NMR (101 MHz, $CDCl_3$)



1dd

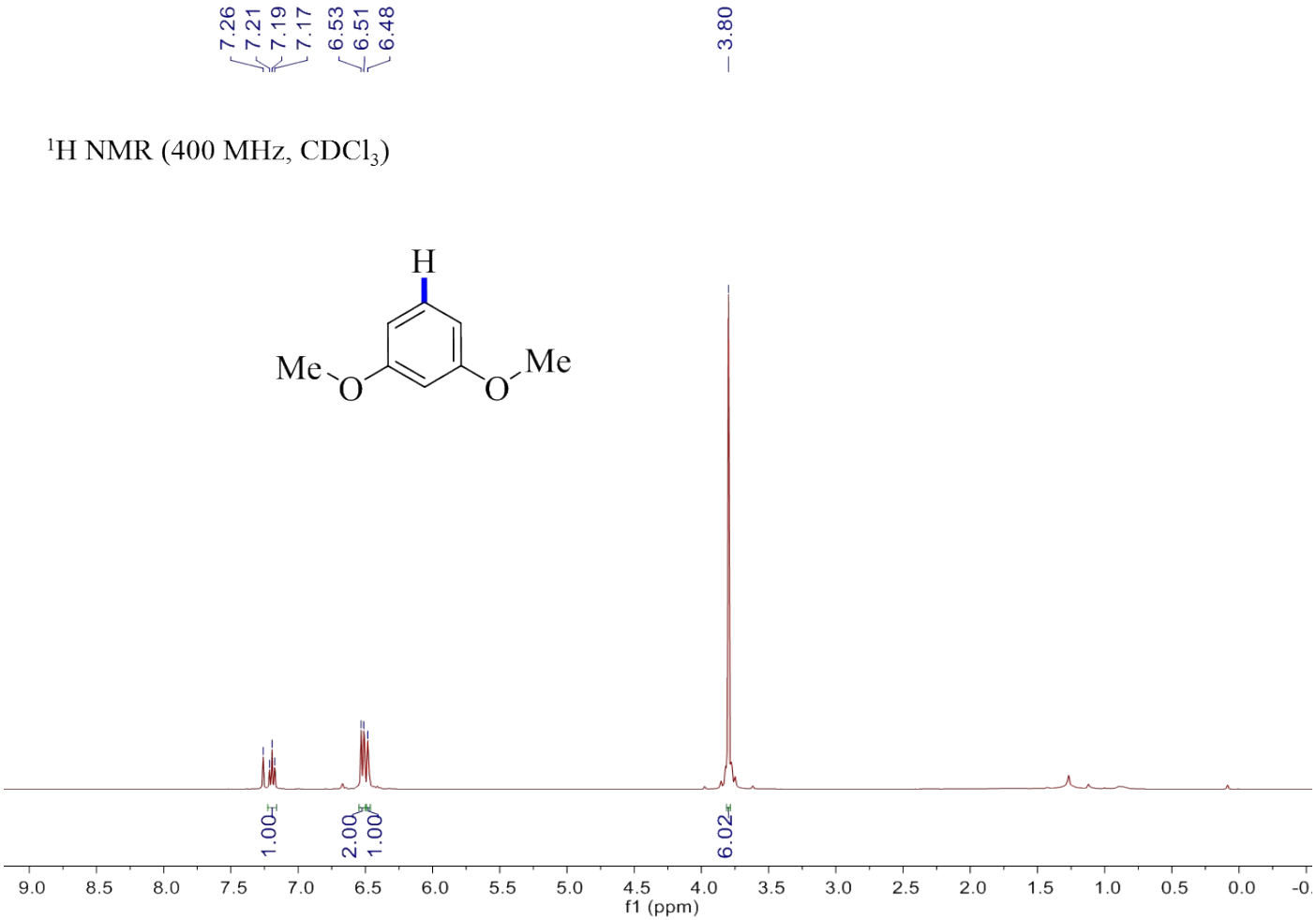


^{1}H NMR (400 MHz, $CDCl_3$)

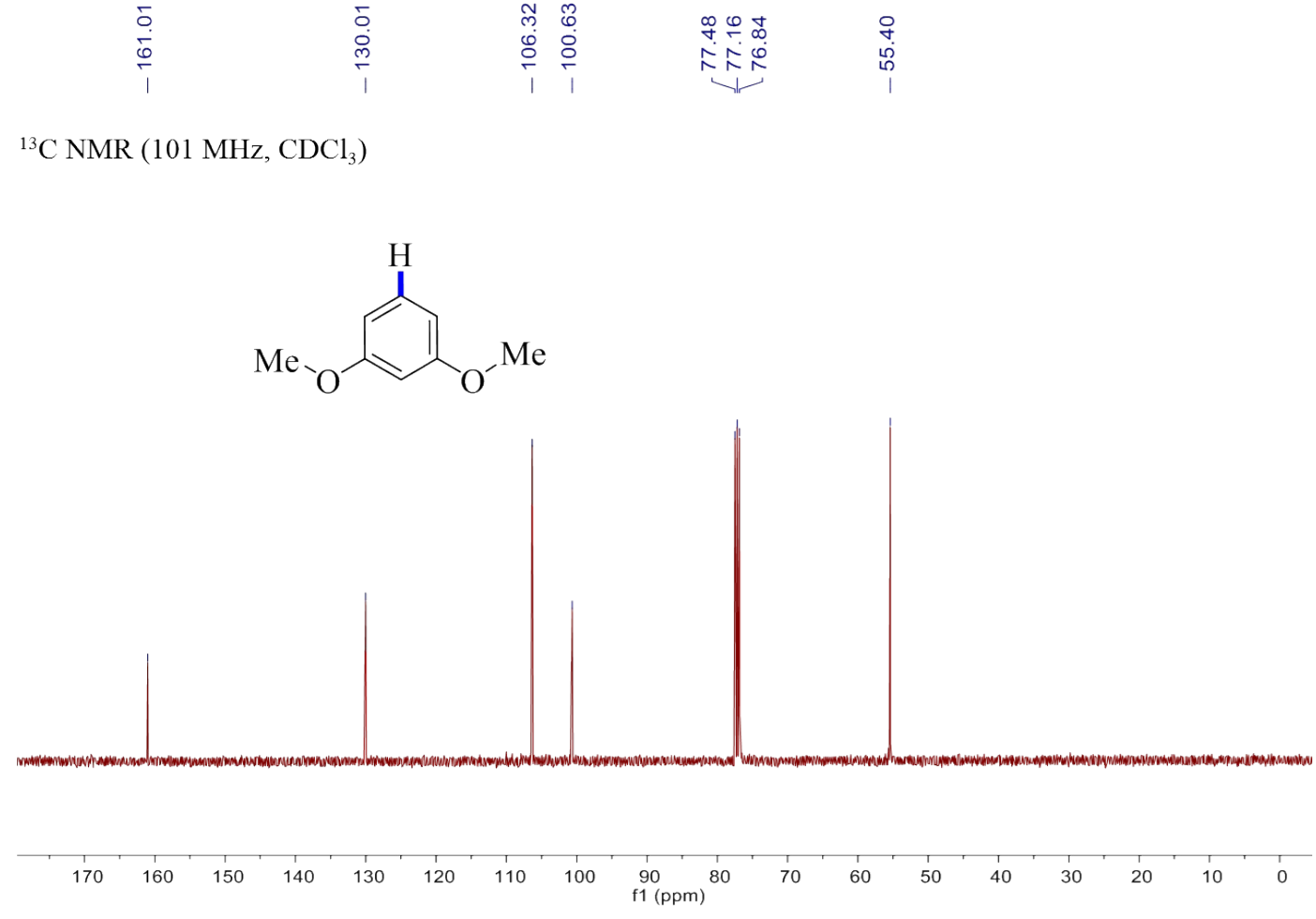


^{13}C NMR (101 MHz, $CDCl_3$)

2b

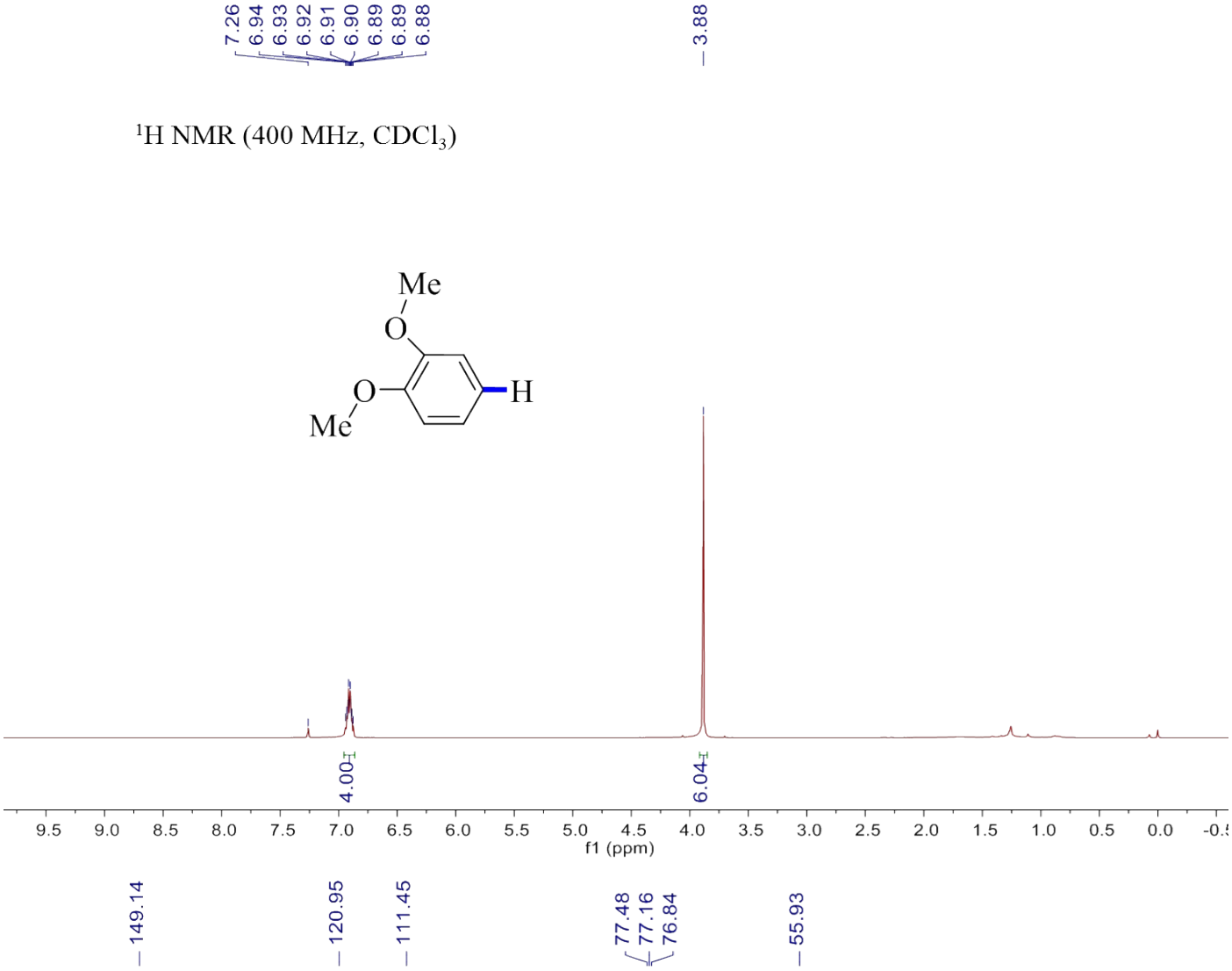


^{1}H NMR (400 MHz, $CDCl_3$)

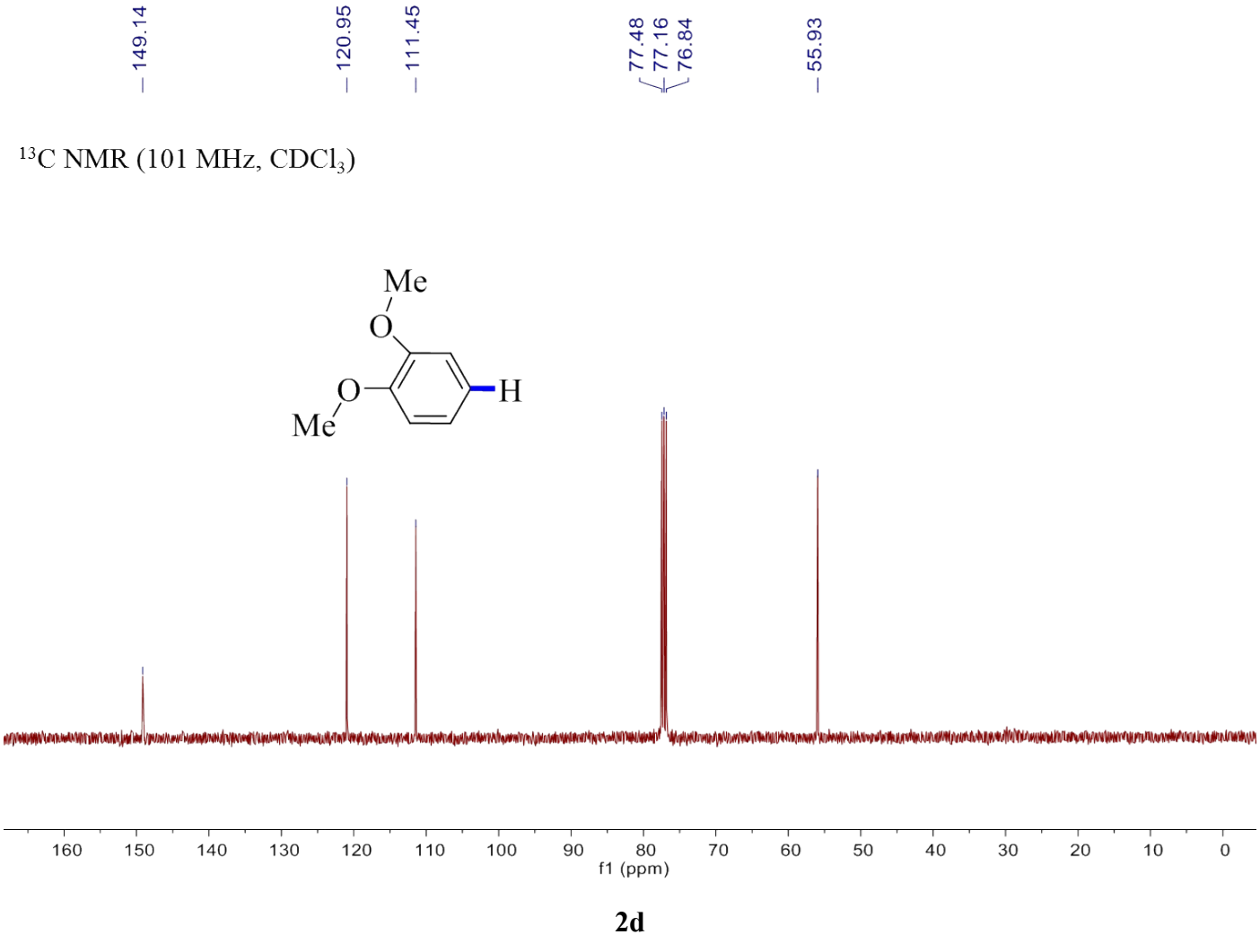


^{13}C NMR (101 MHz, $CDCl_3$)

2c

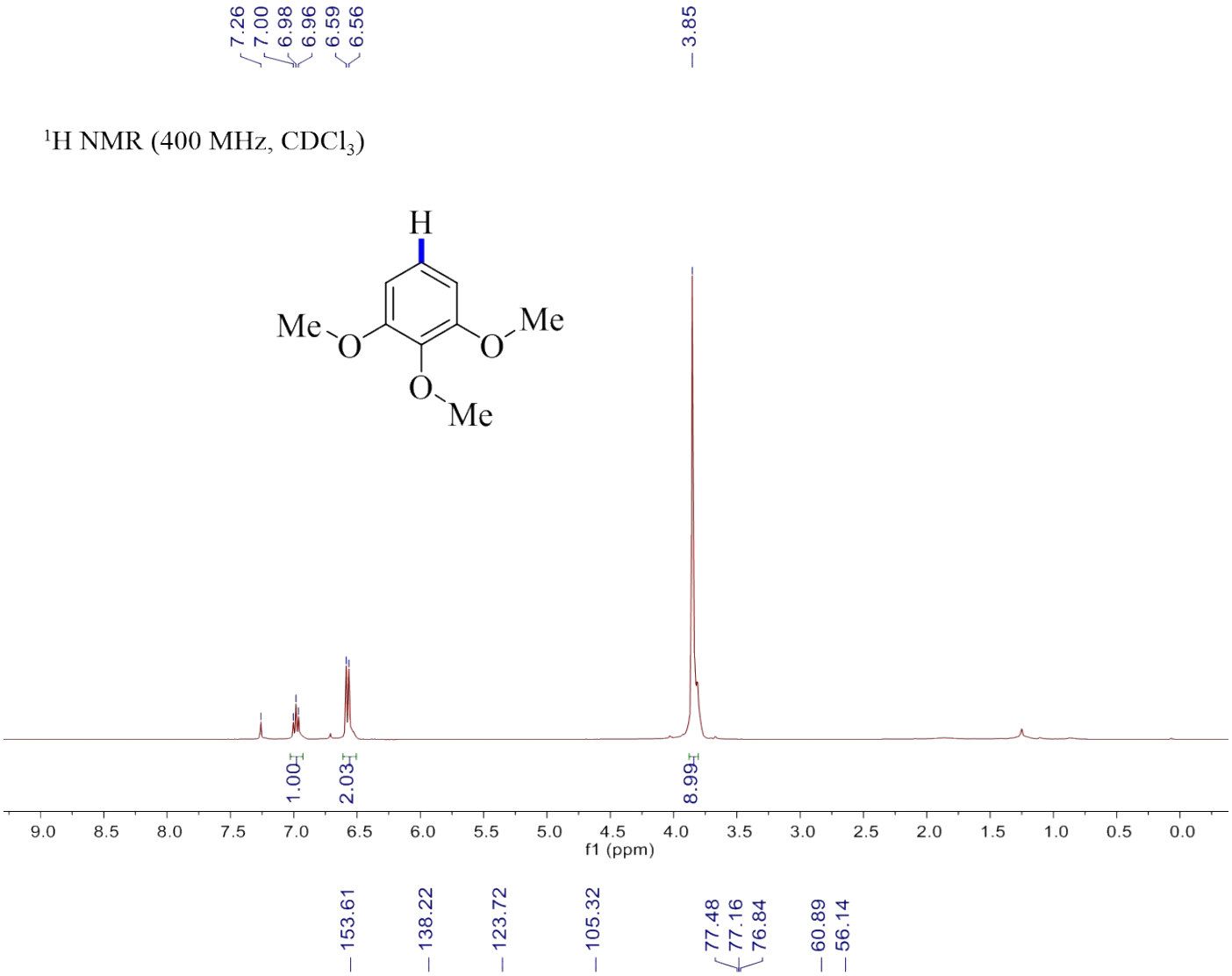


^{1}H NMR (400 MHz, $CDCl_3$)

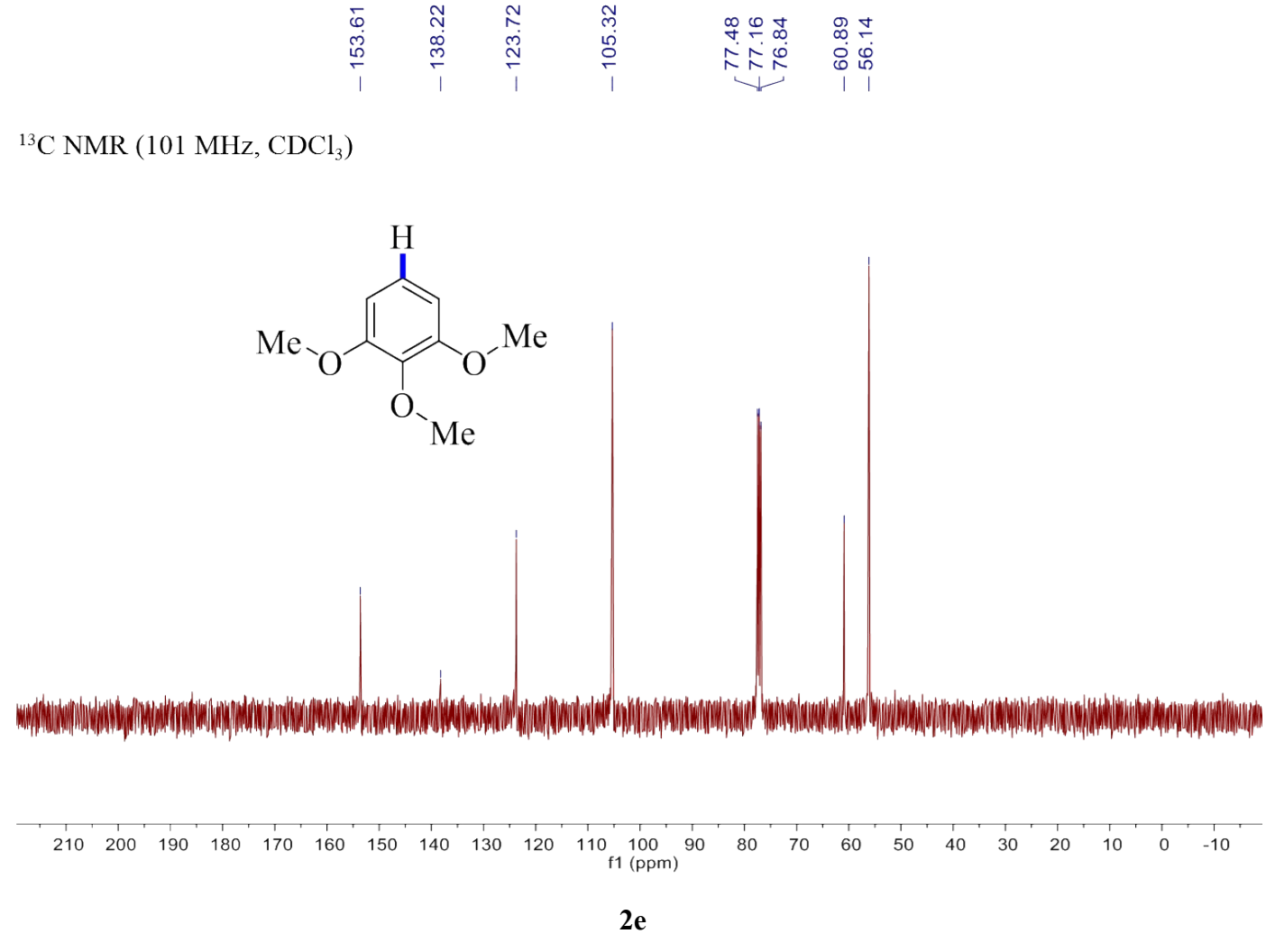


^{13}C NMR (101 MHz, $CDCl_3$)

2d

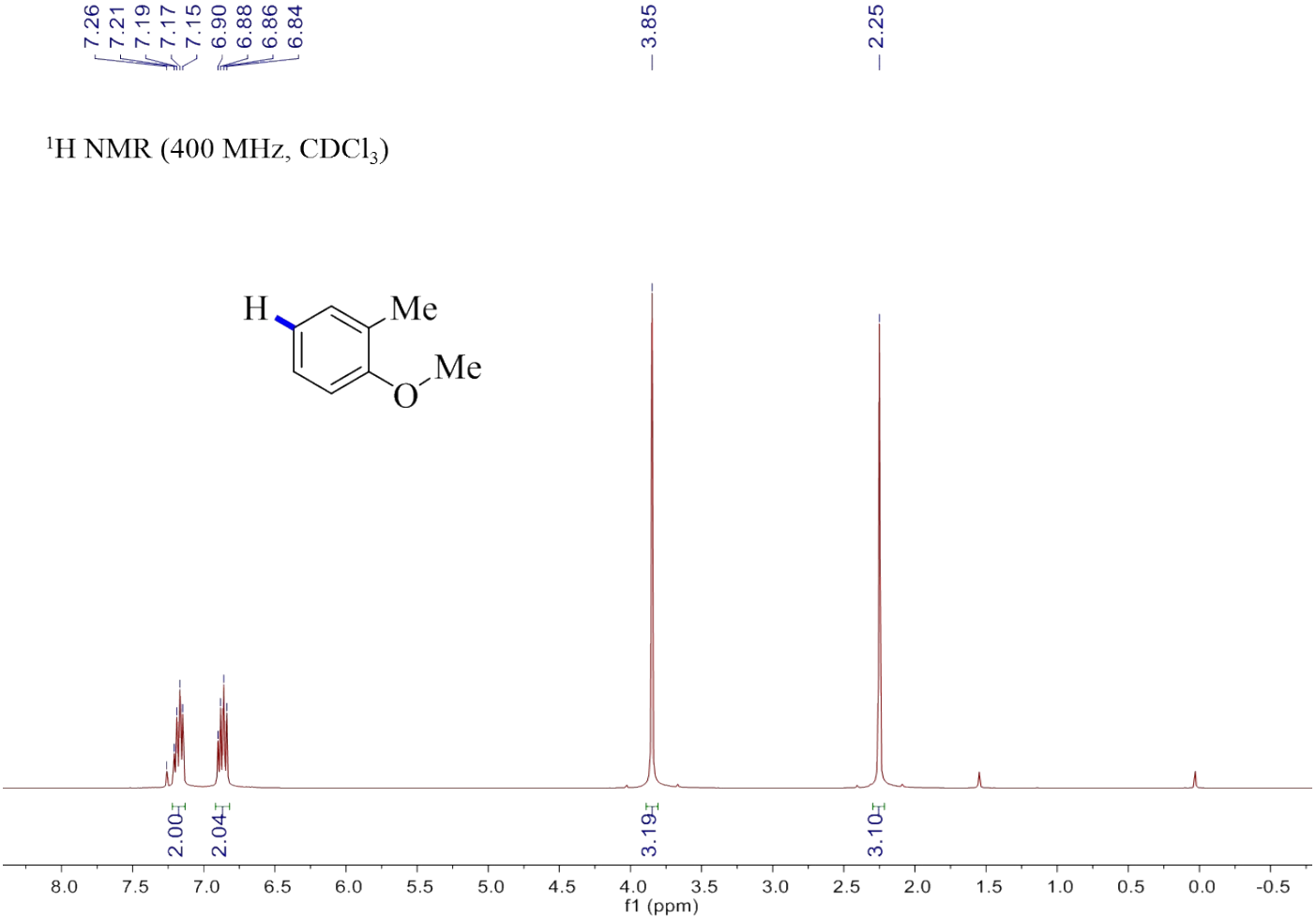


^{1}H NMR (400 MHz, $CDCl_3$)

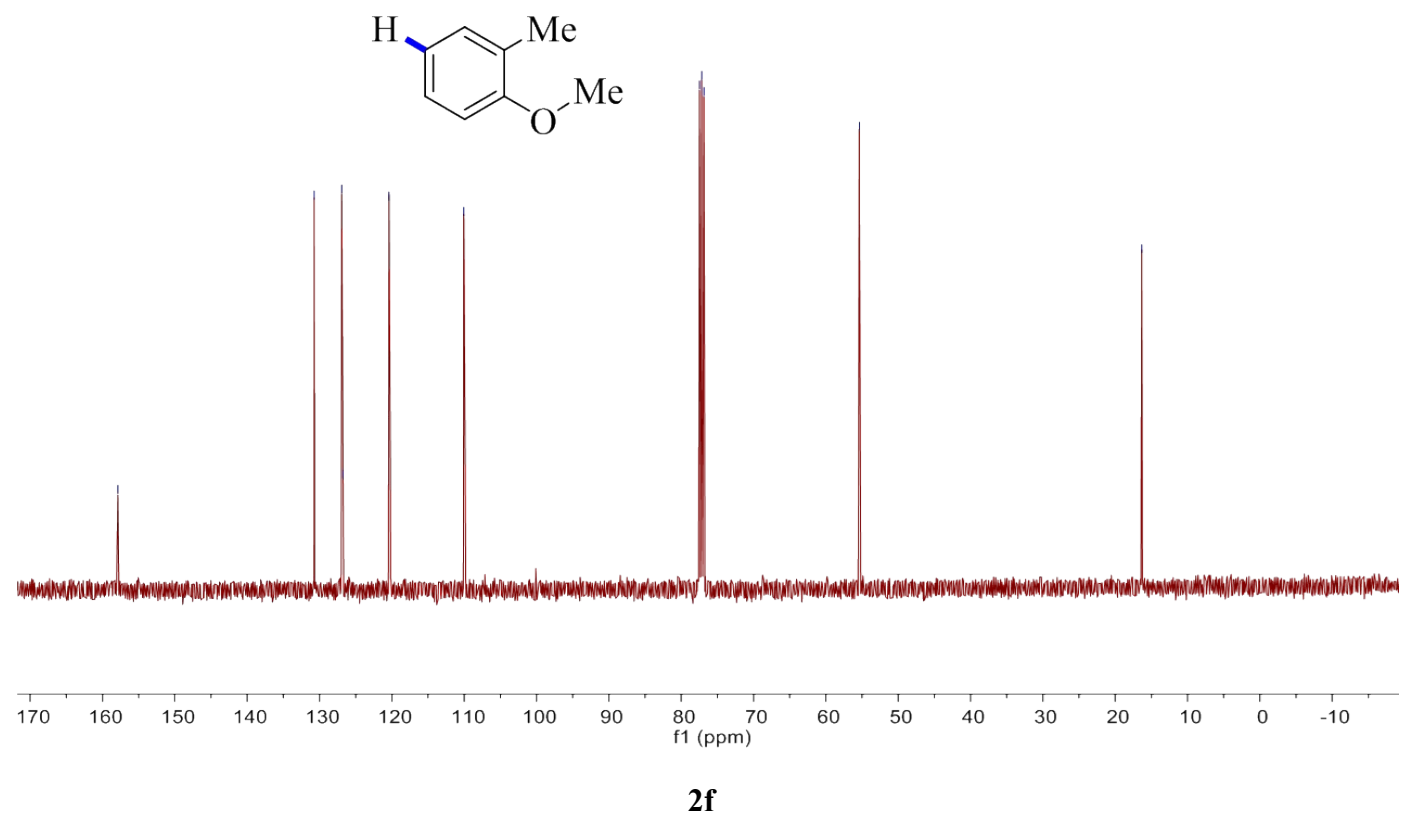


^{13}C NMR (101 MHz, $CDCl_3$)

2e

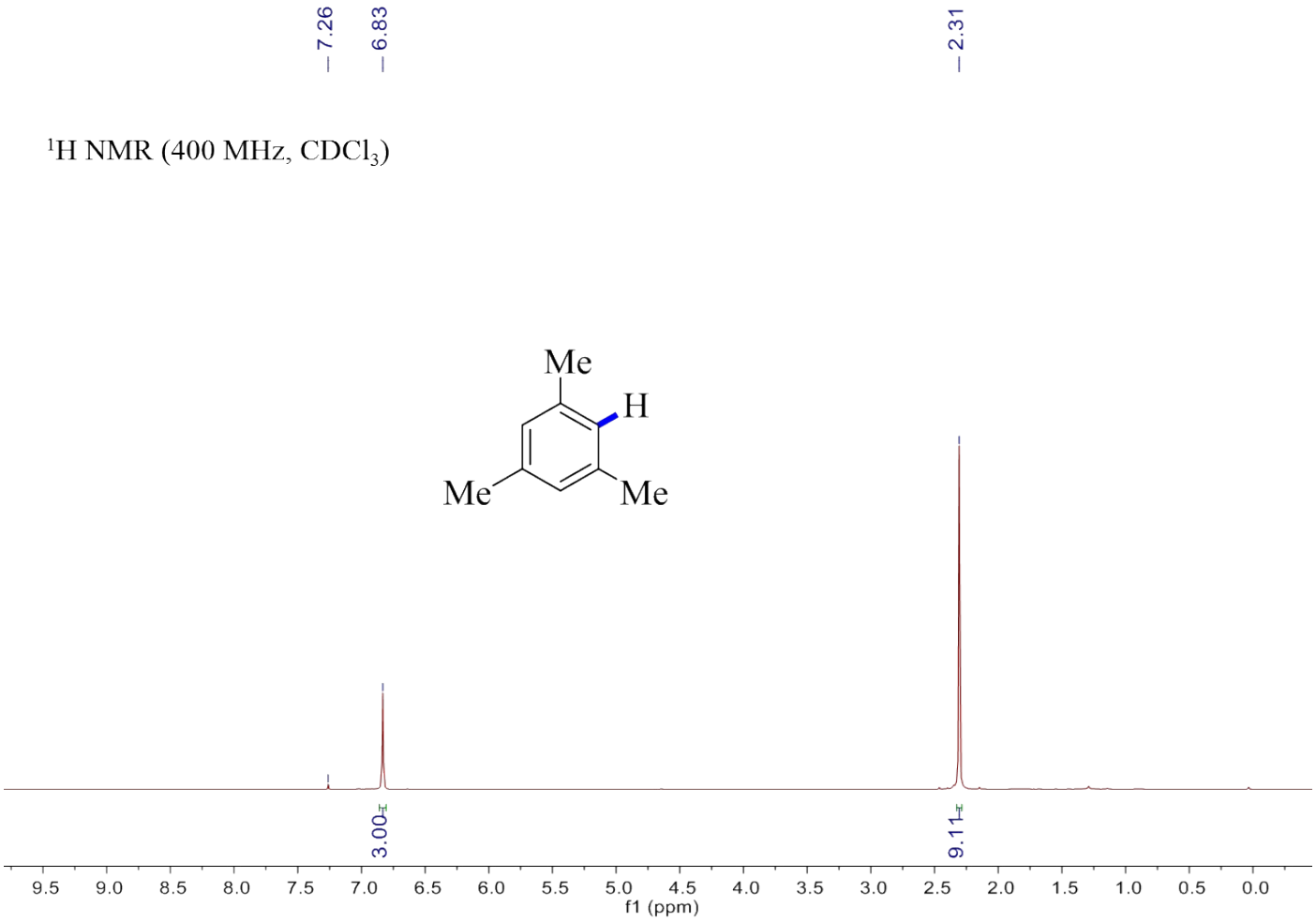


^{1}H NMR (400 MHz, $CDCl_3$)

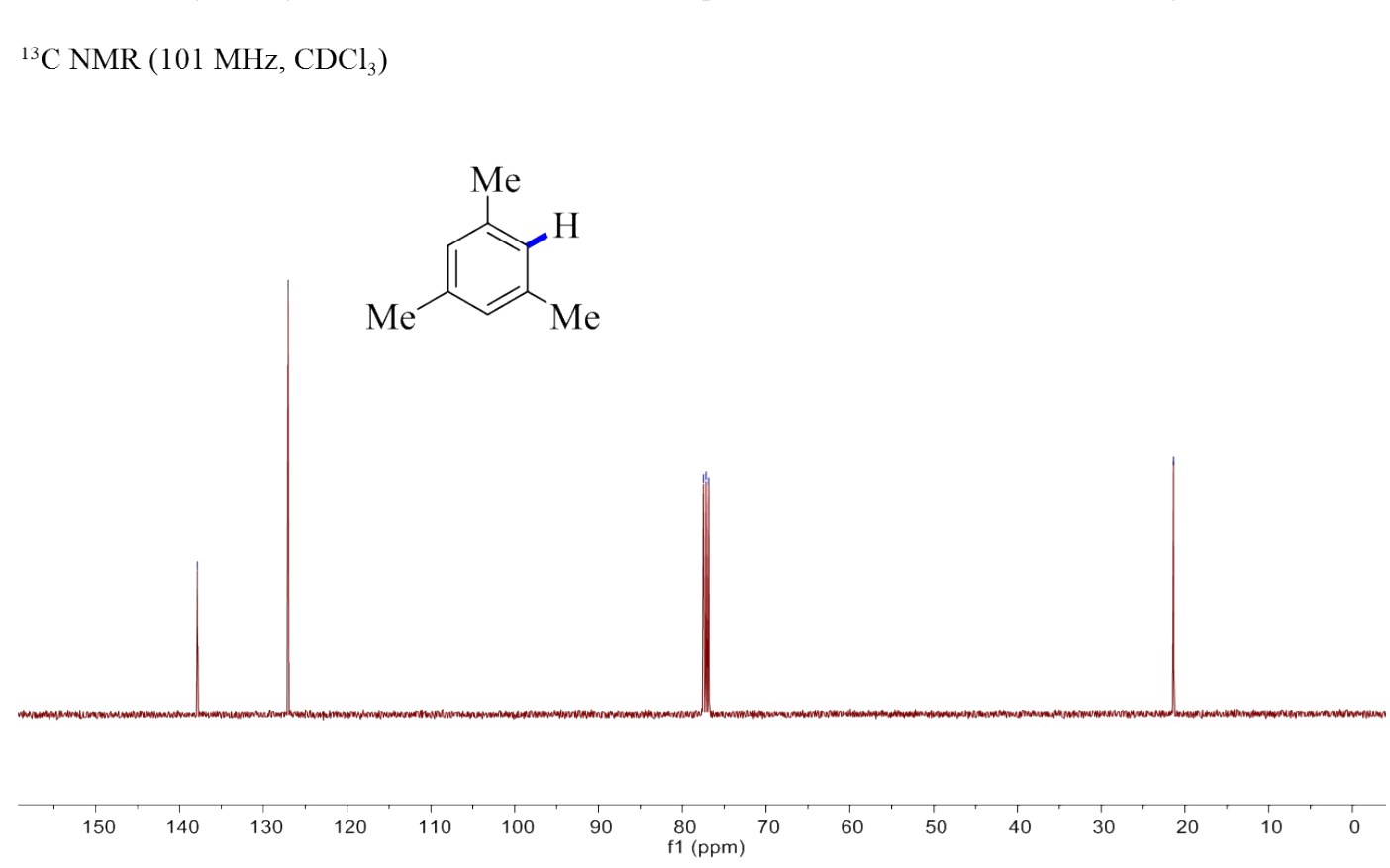


^{13}C NMR (101 MHz, $CDCl_3$)

2f



^{1}H NMR (400 MHz, $CDCl_3$)



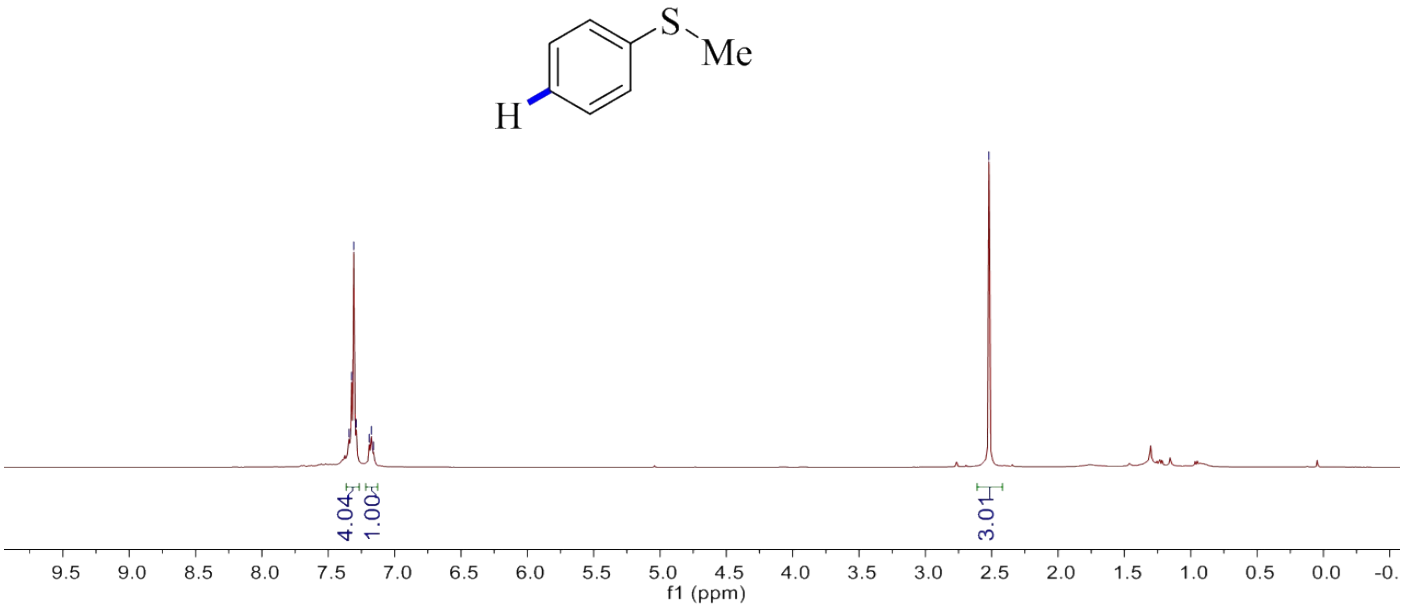
^{13}C NMR (101 MHz, $CDCl_3$)

2g

7.34
7.32
7.31
7.29
7.19
7.17
7.16

2.52

^{1}H NMR (400 MHz, $CDCl_3$)

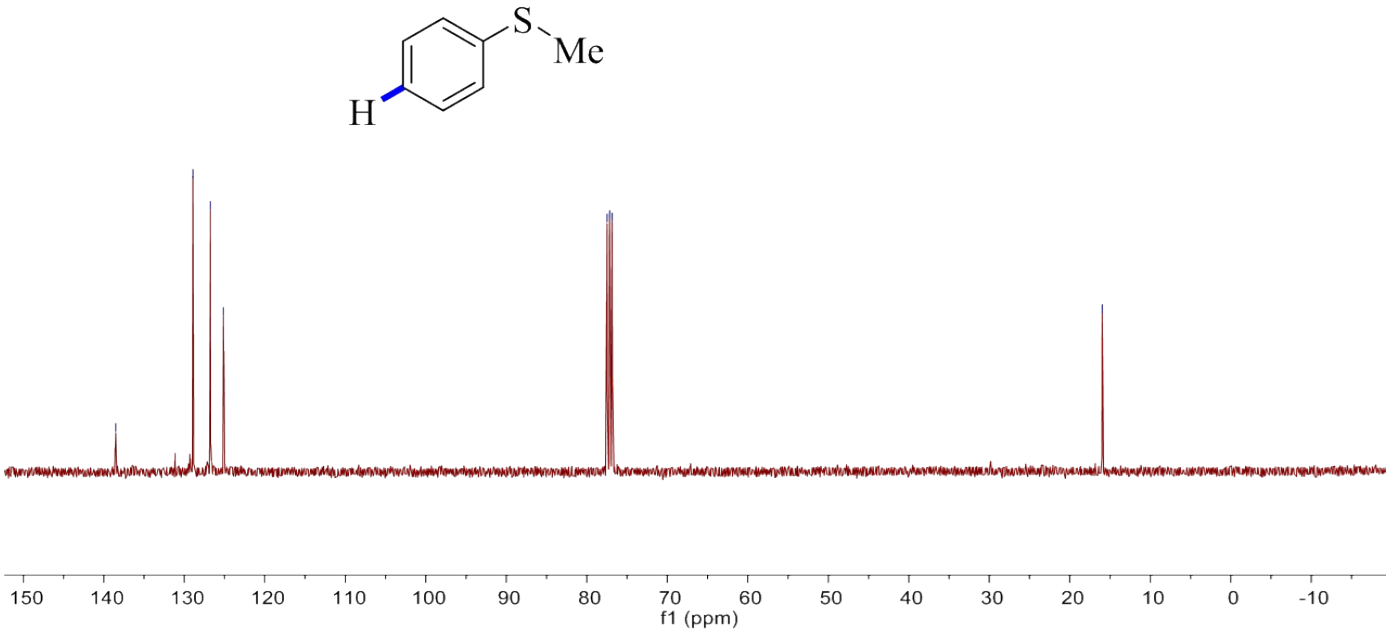


138.52
128.92
126.74
125.13

77.48
77.16
76.84

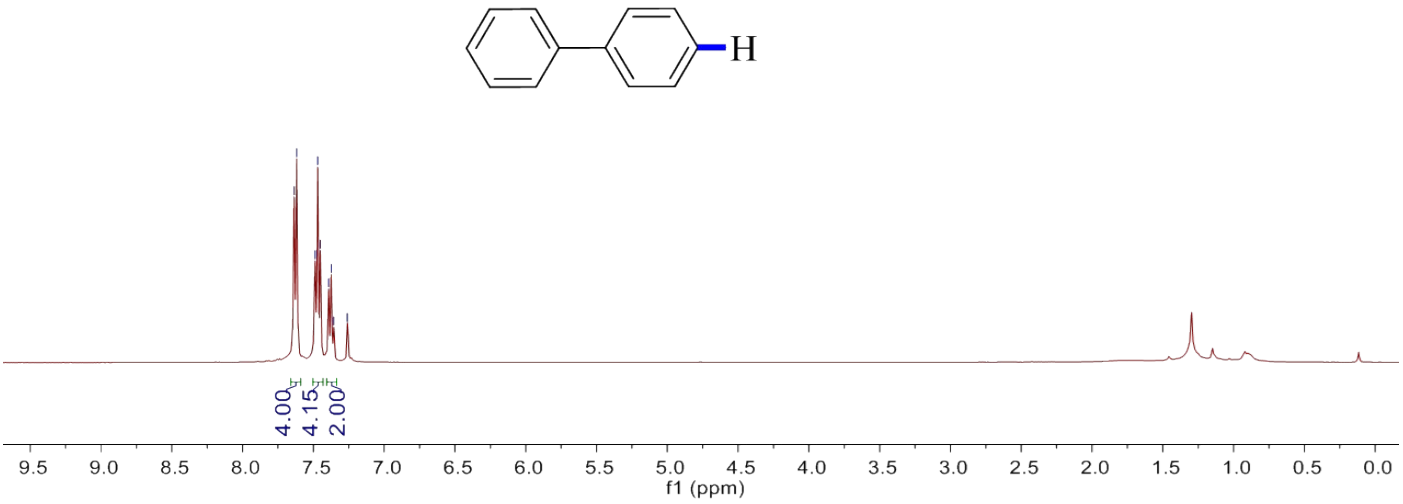
15.96

^{13}C NMR (101 MHz, $CDCl_3$)

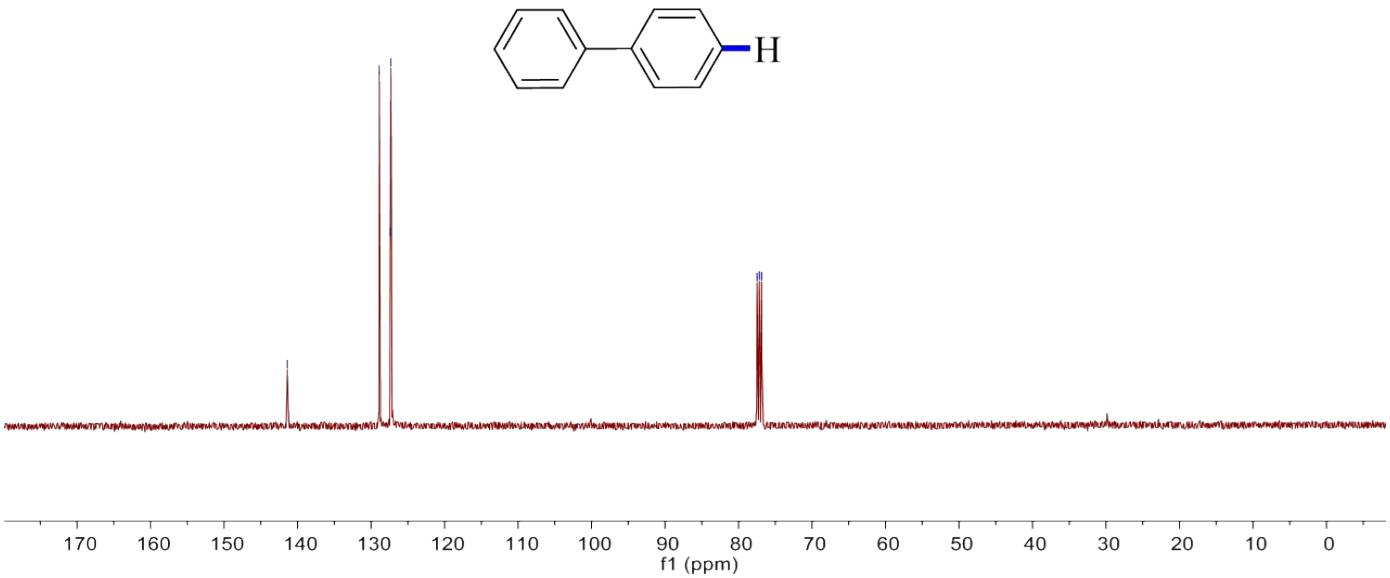


2h

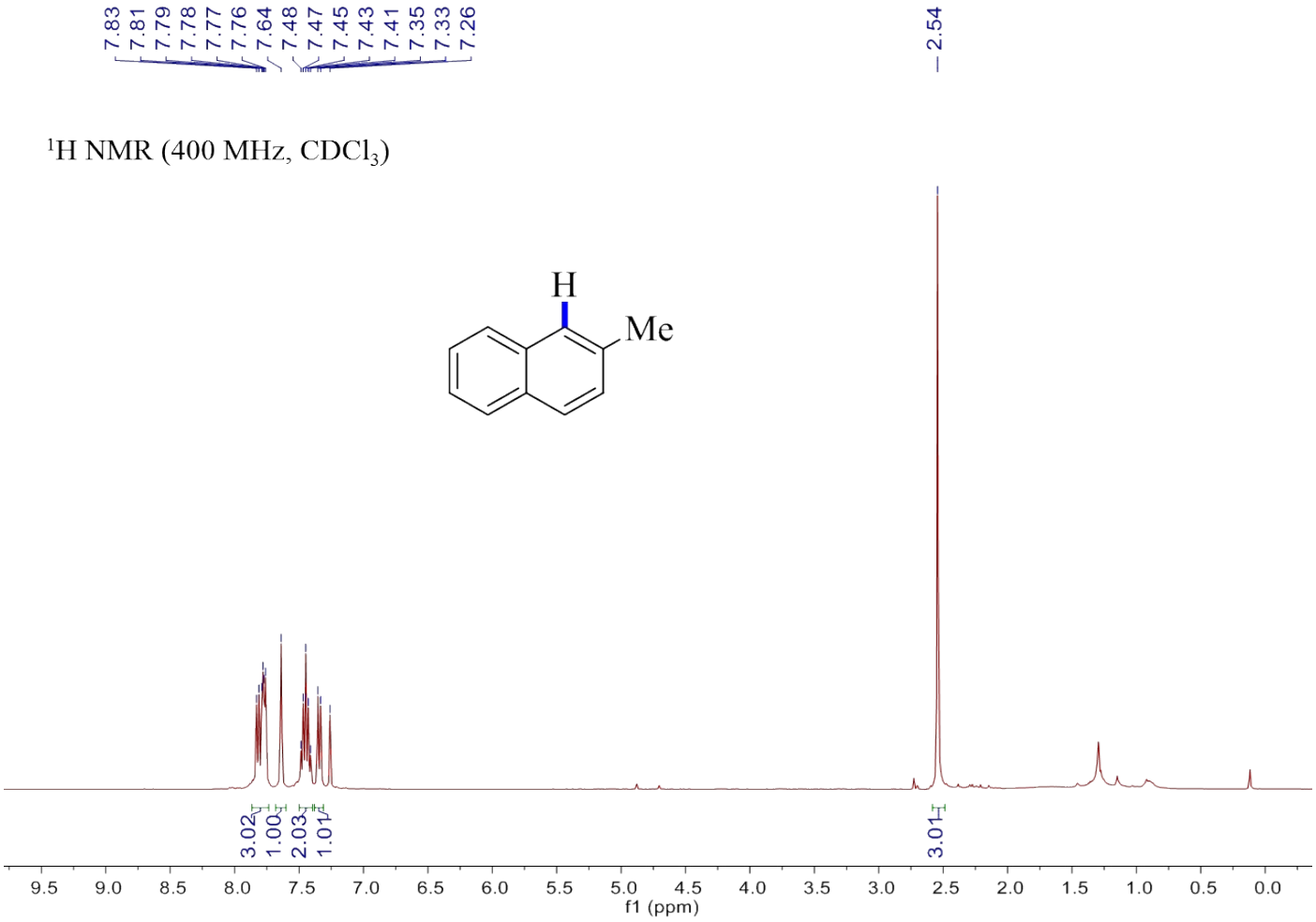
^{1}H NMR (400 MHz, $CDCl_3$)



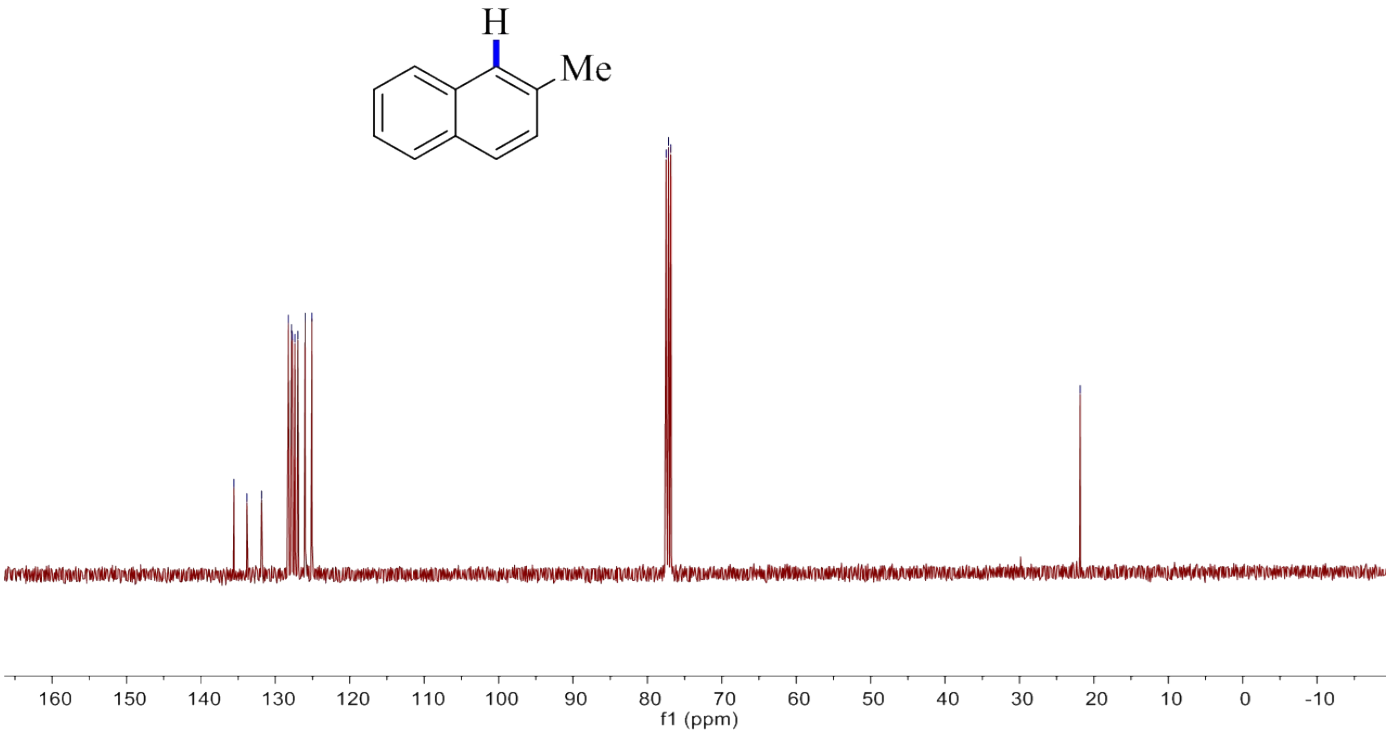
^{13}C NMR (101 MHz, $CDCl_3$)



2i



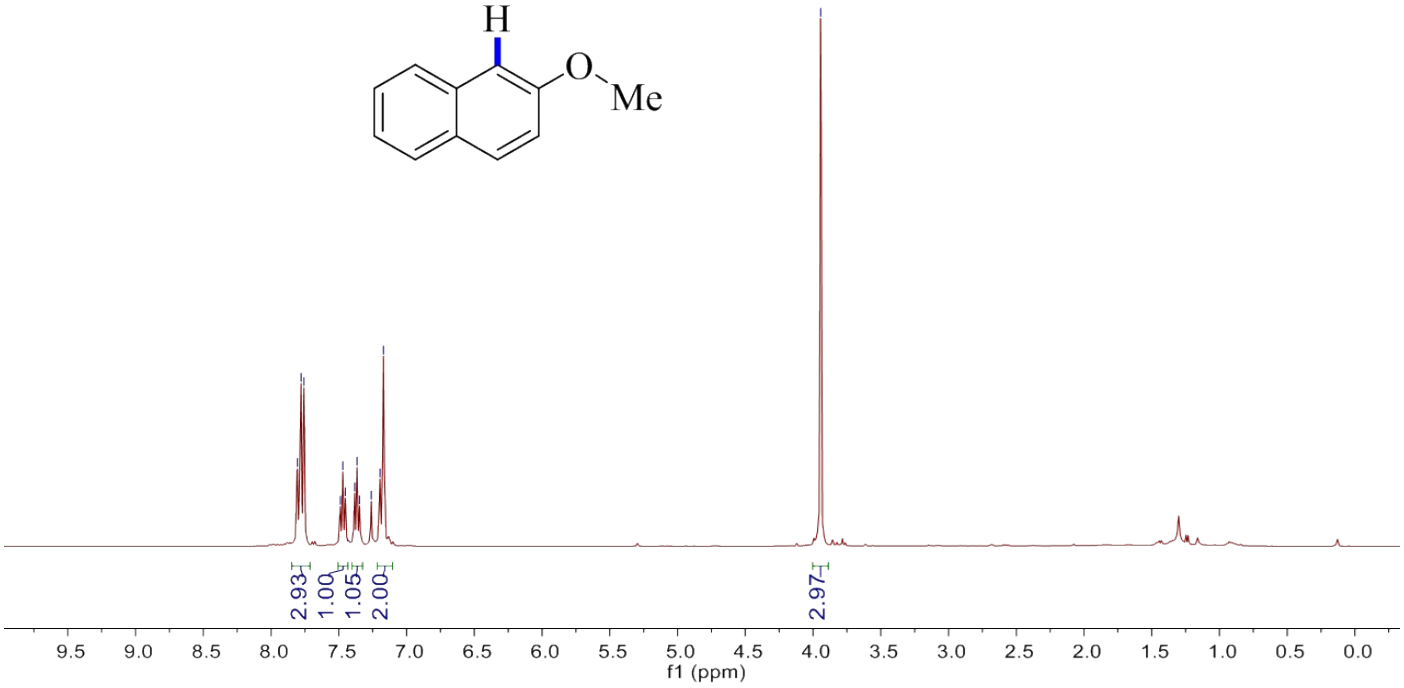
^{1}H NMR (400 MHz, $CDCl_3$)



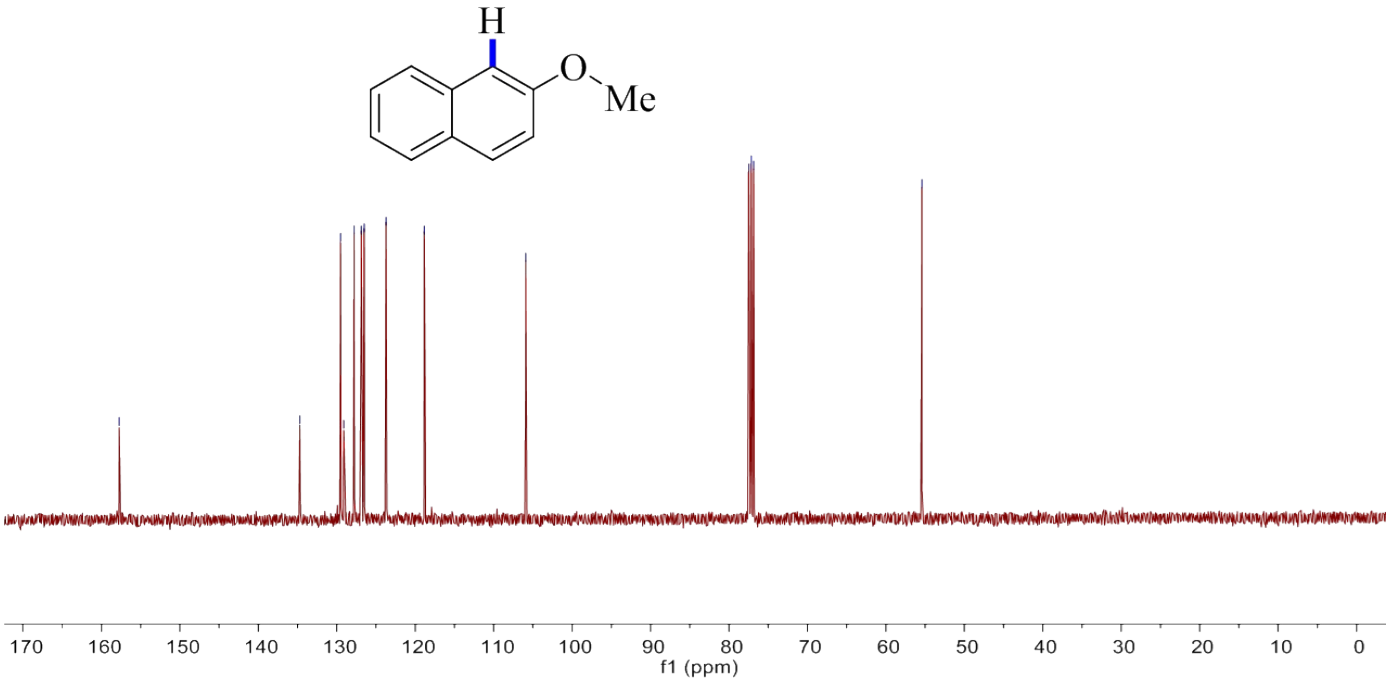
^{13}C NMR (101 MHz, $CDCl_3$)

2j

^{1}H NMR (400 MHz, $CDCl_3$)

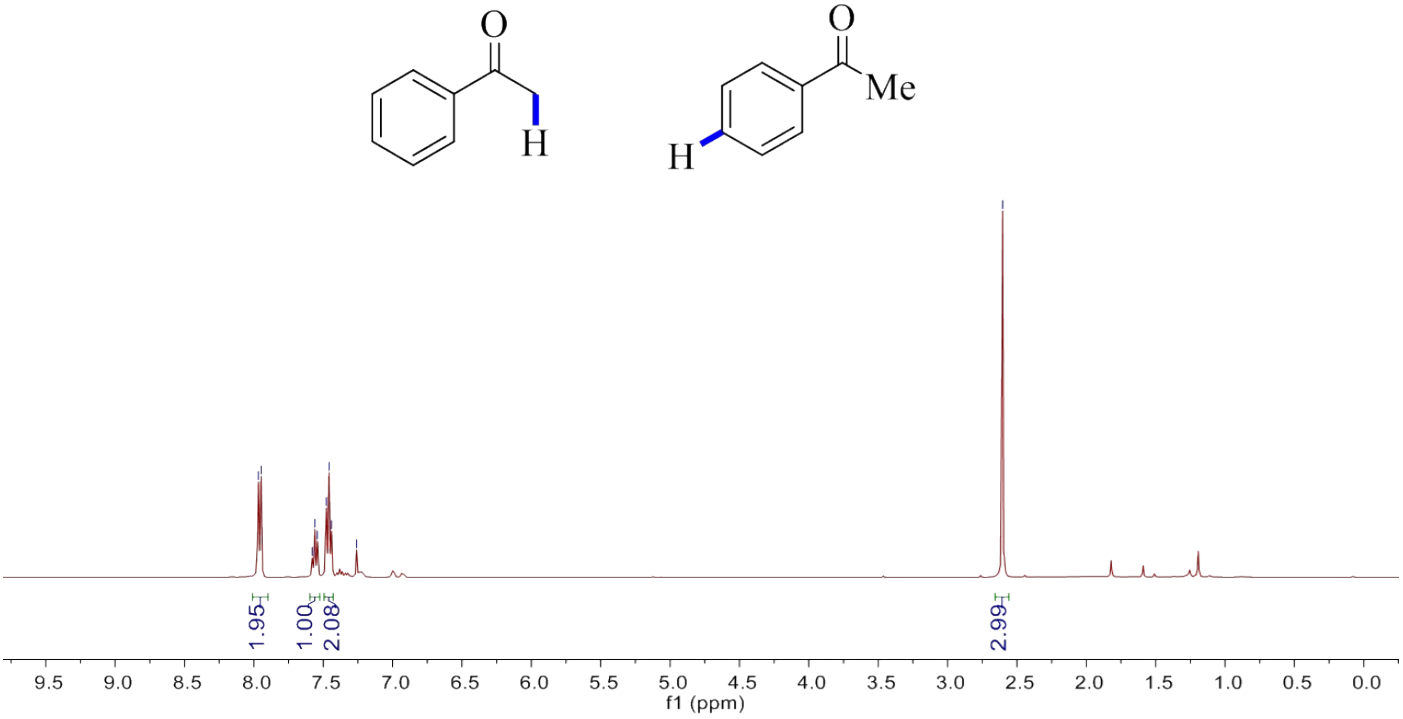


^{13}C NMR (101 MHz, $CDCl_3$)

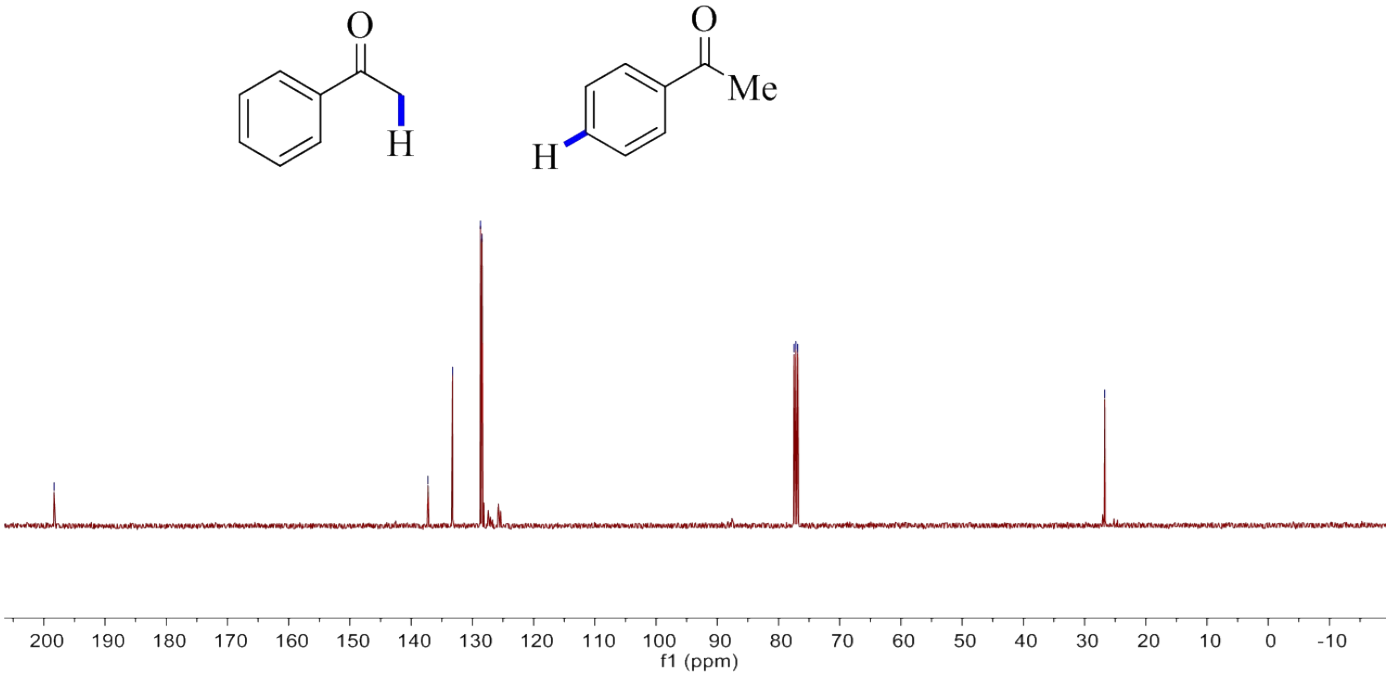


2k, 2l

^{1}H NMR (400 MHz, $CDCl_3$)

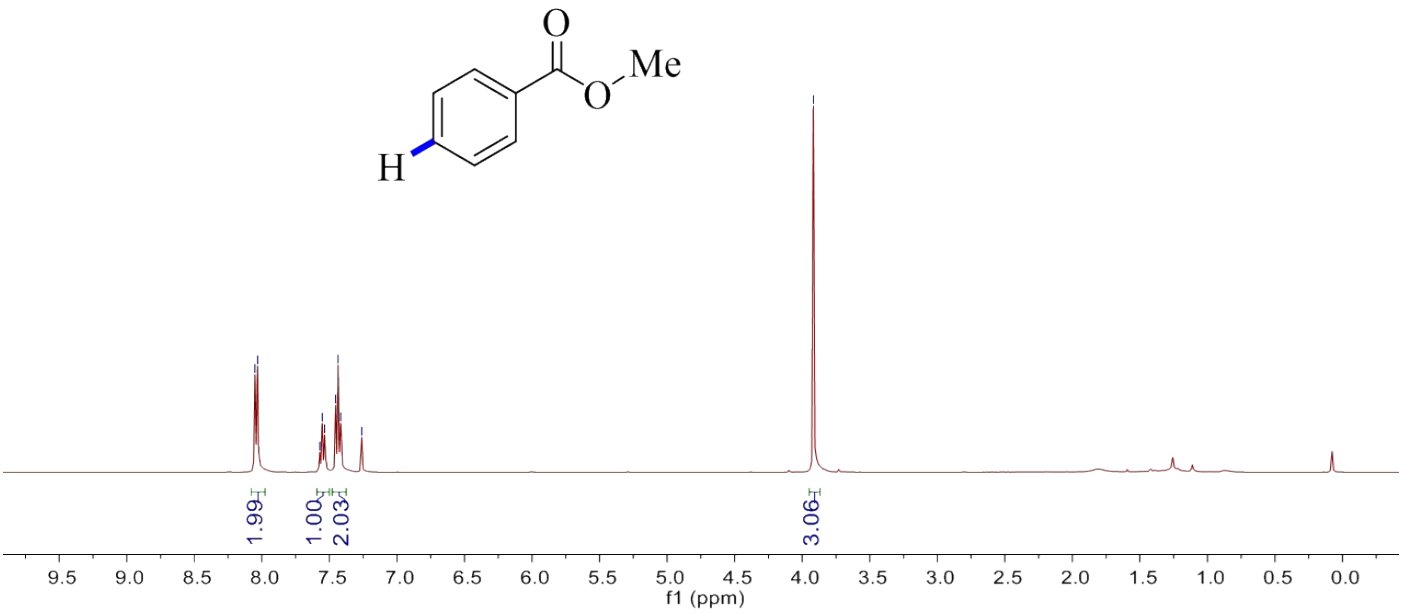


^{13}C NMR (101 MHz, $CDCl_3$)

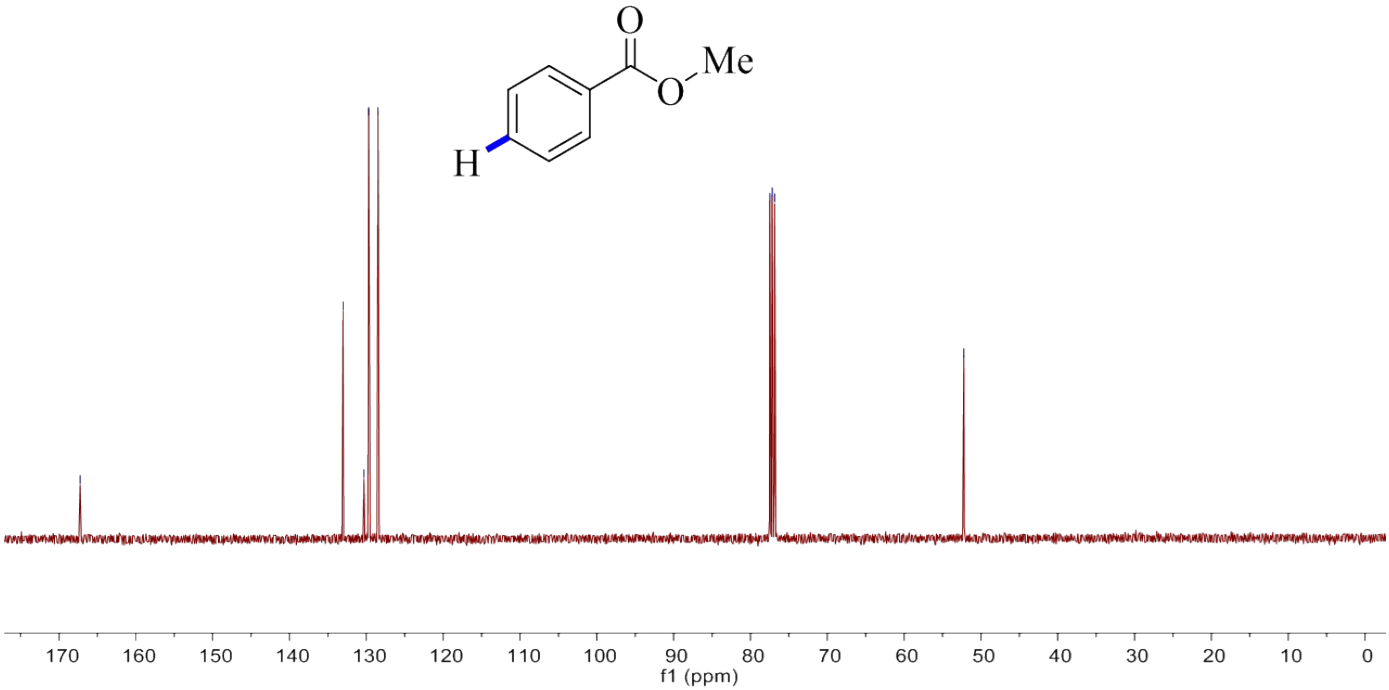


2m

^{1}H NMR (400 MHz, $CDCl_3$)

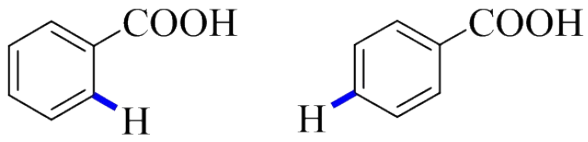


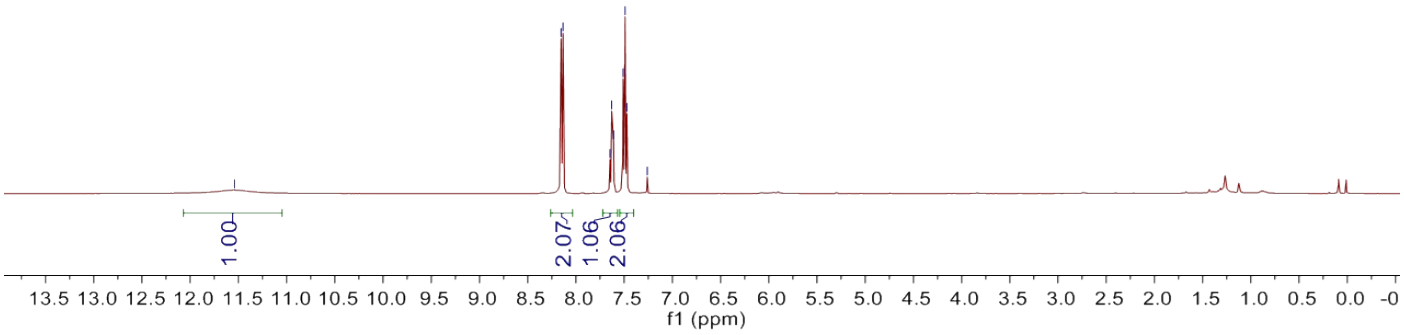
^{13}C NMR (101 MHz, $CDCl_3$)



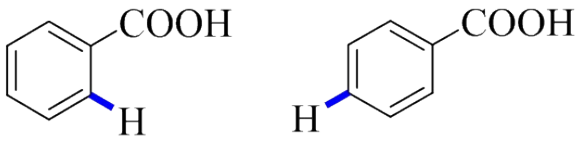
2n, 2z

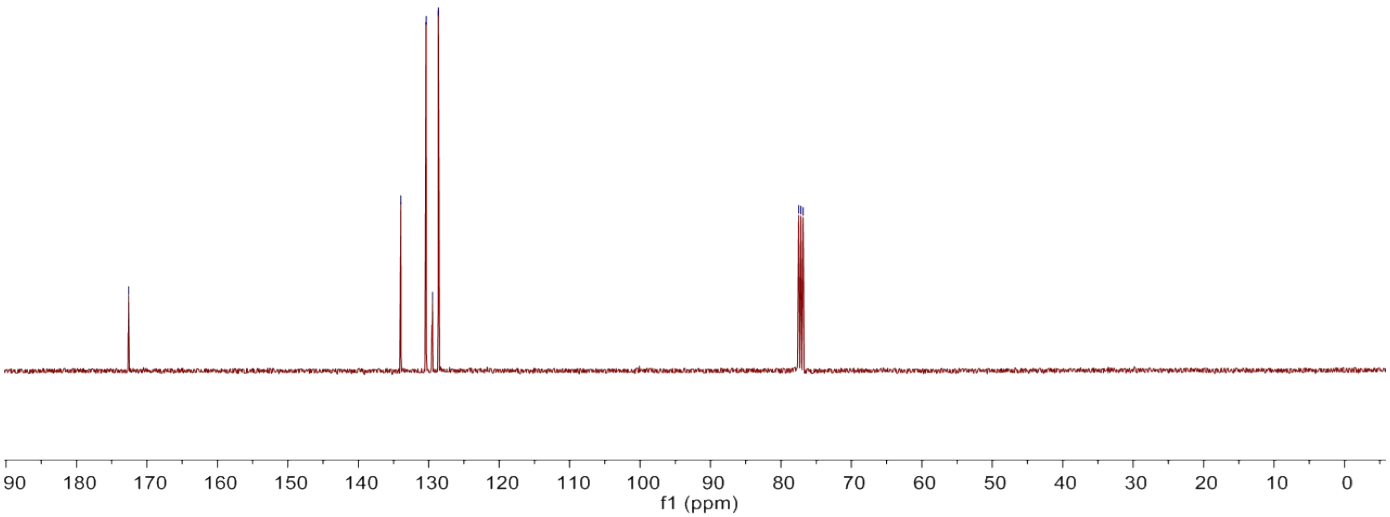
^{1}H NMR (400 MHz, $CDCl_3$)





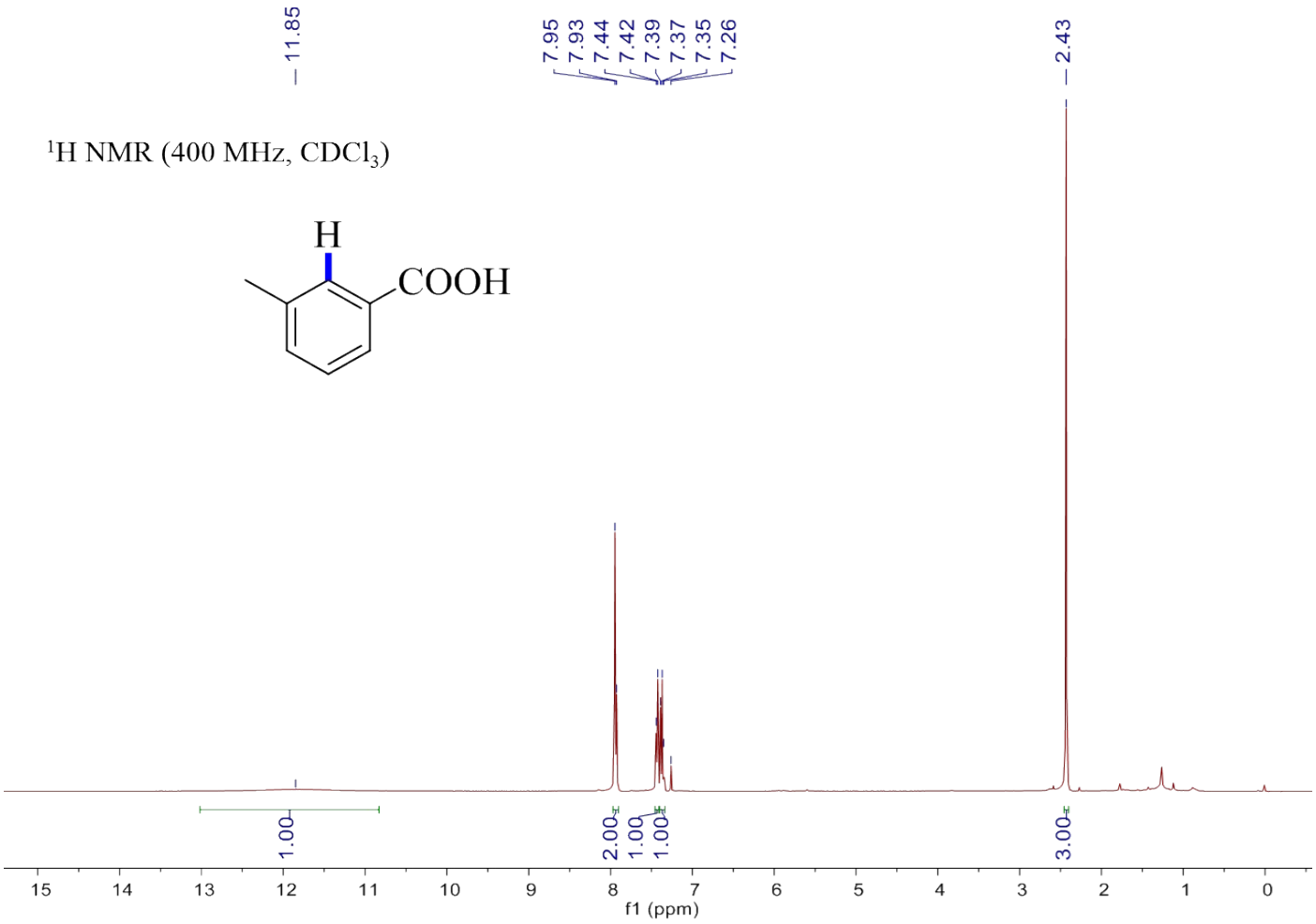
^{13}C NMR (101 MHz, $CDCl_3$)



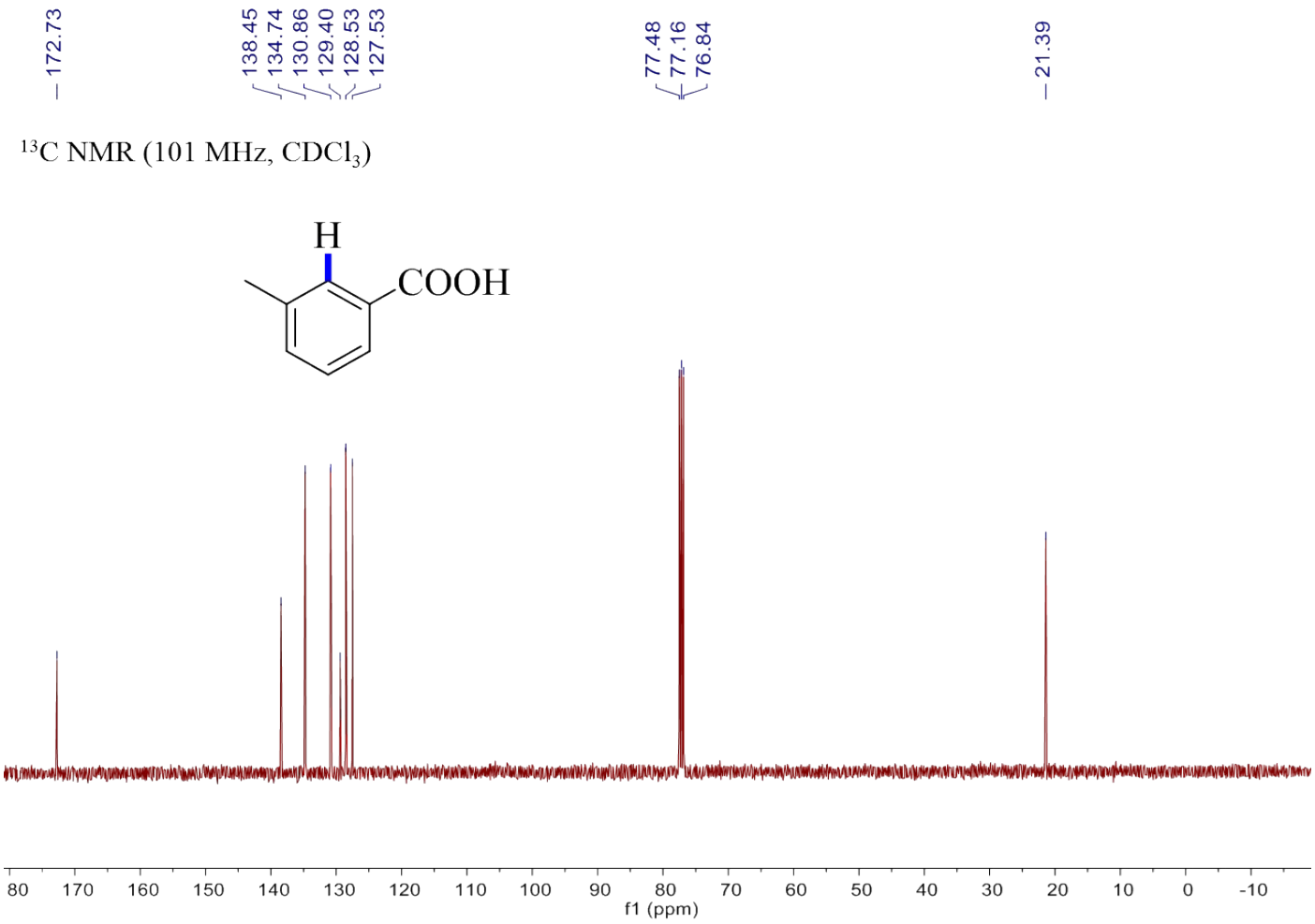


2o, 2aa

^{1}H NMR (400 MHz, $CDCl_3$)



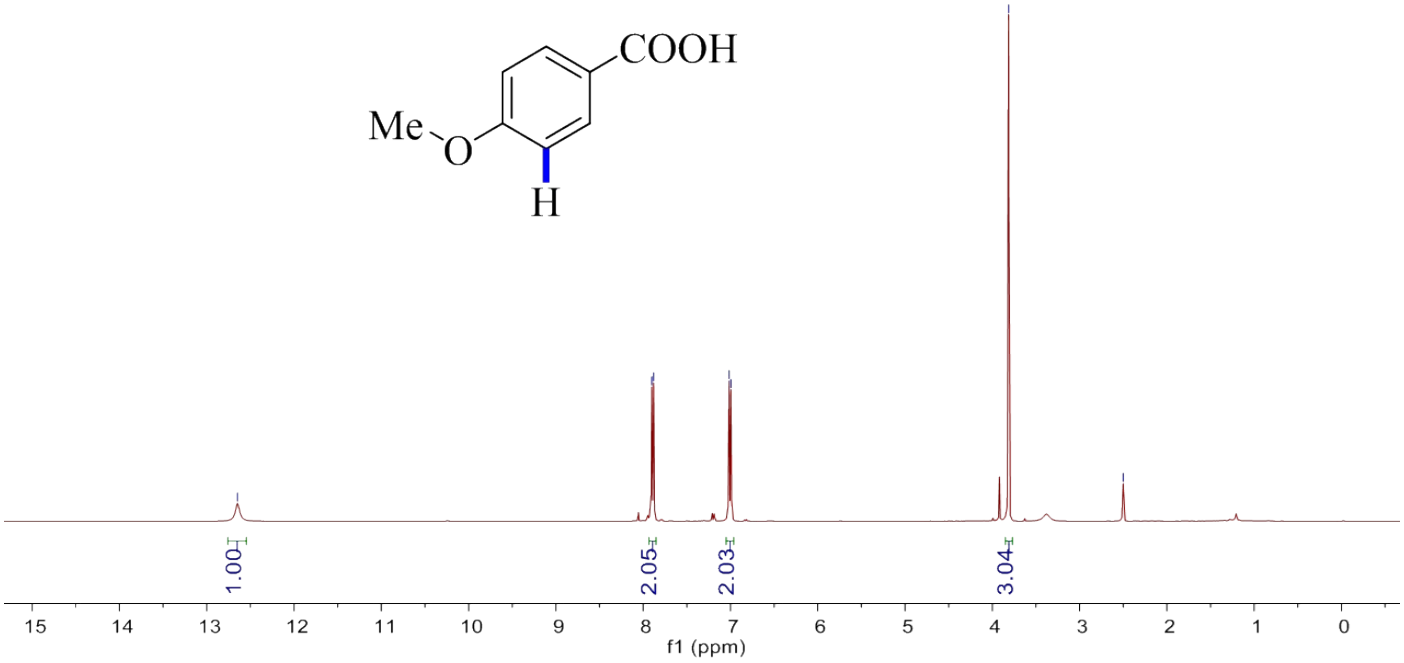
^{13}C NMR (101 MHz, $CDCl_3$)



2p

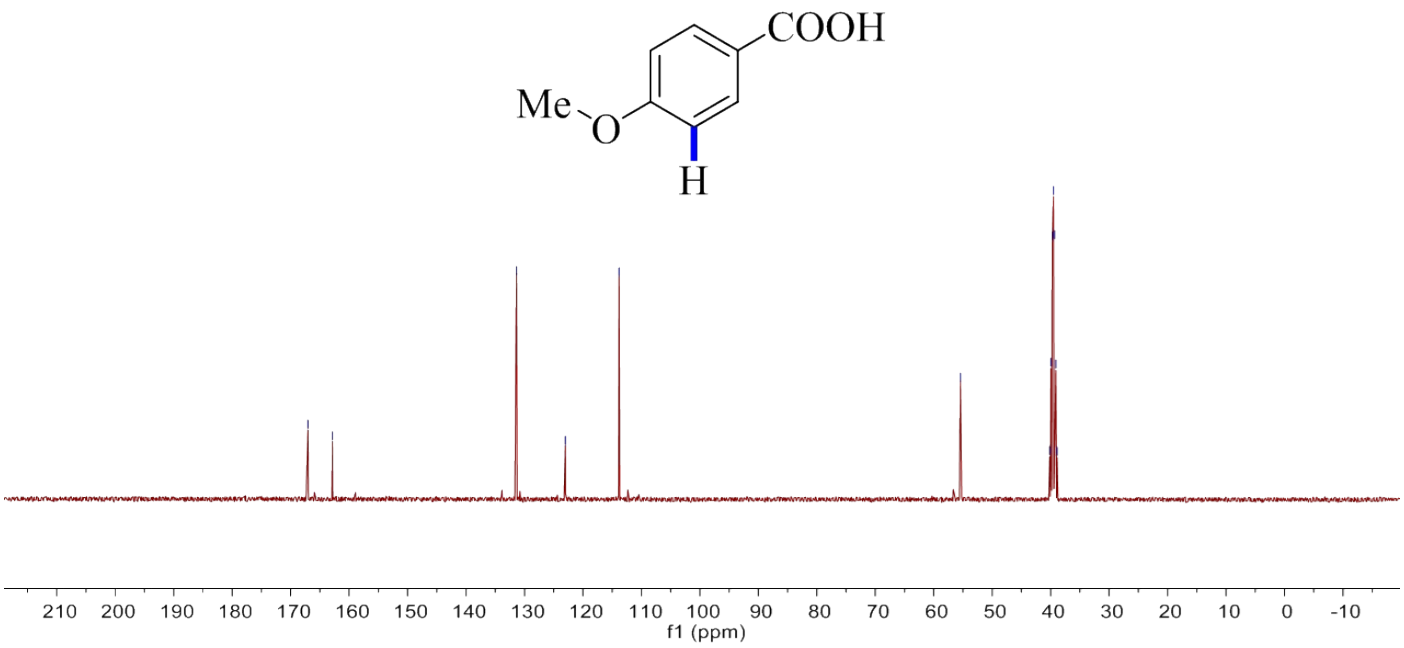
12.65
7.90
7.88
7.02
6.99
3.81
2.50

^{1}H NMR (400 MHz, DMSO-d6)



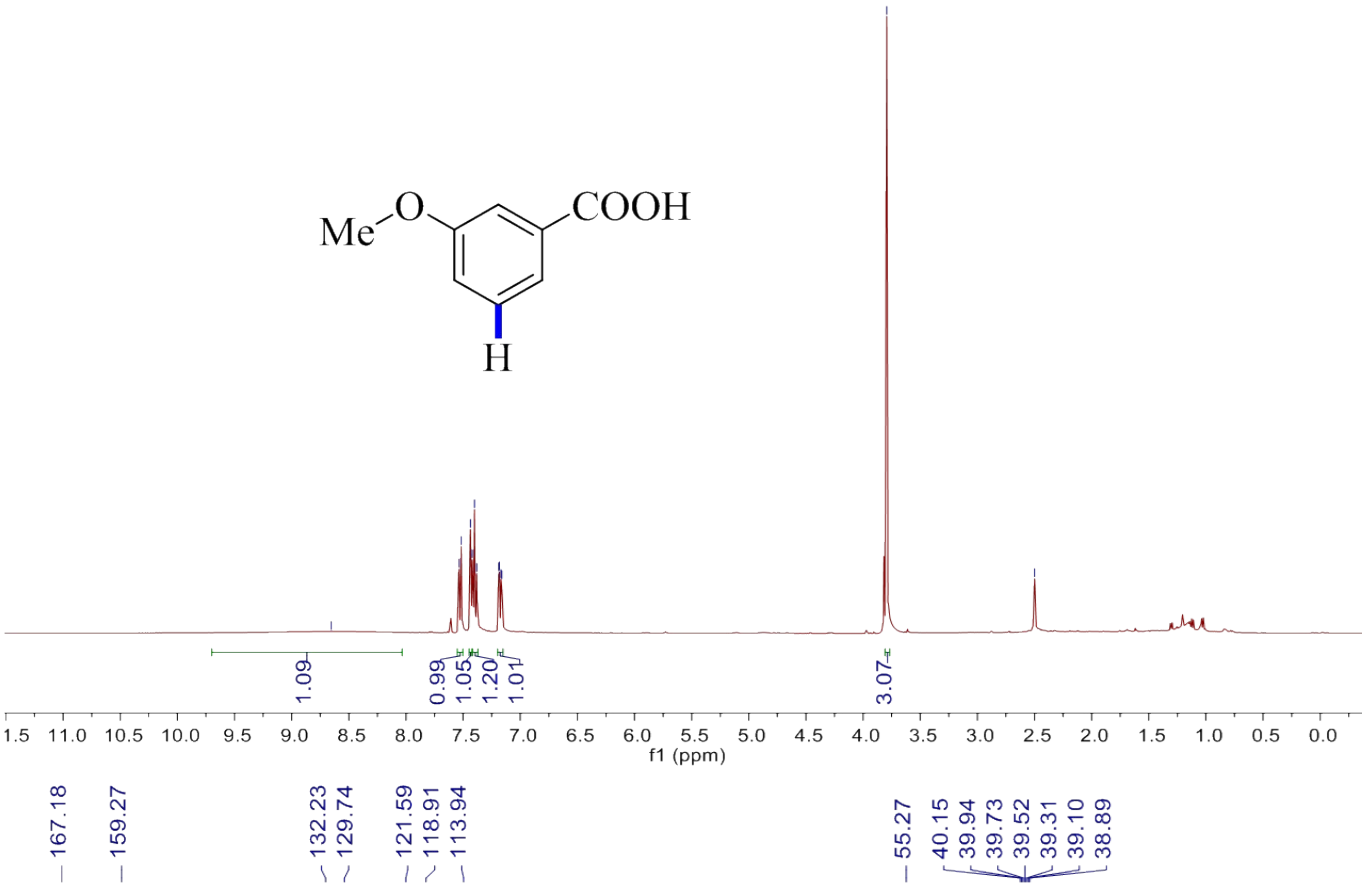
167.04
162.87
131.37
123.00
113.82
55.44
40.15
39.94
39.73
39.52
39.31
39.10
38.89

^{13}C NMR (101 MHz, DMSO-d6)

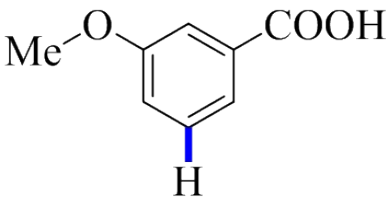


2q

^{1}H NMR (400 MHz, DMSO-d6)

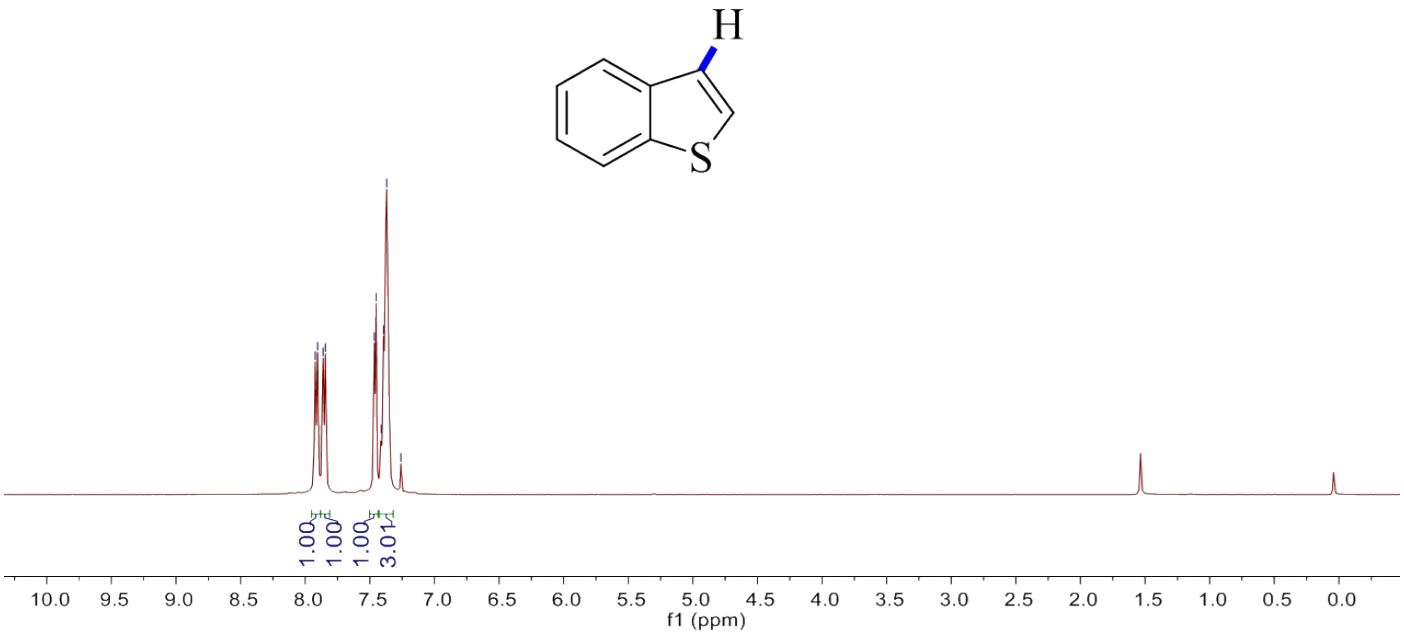


^{13}C NMR (101 MHz, DMSO-d6)

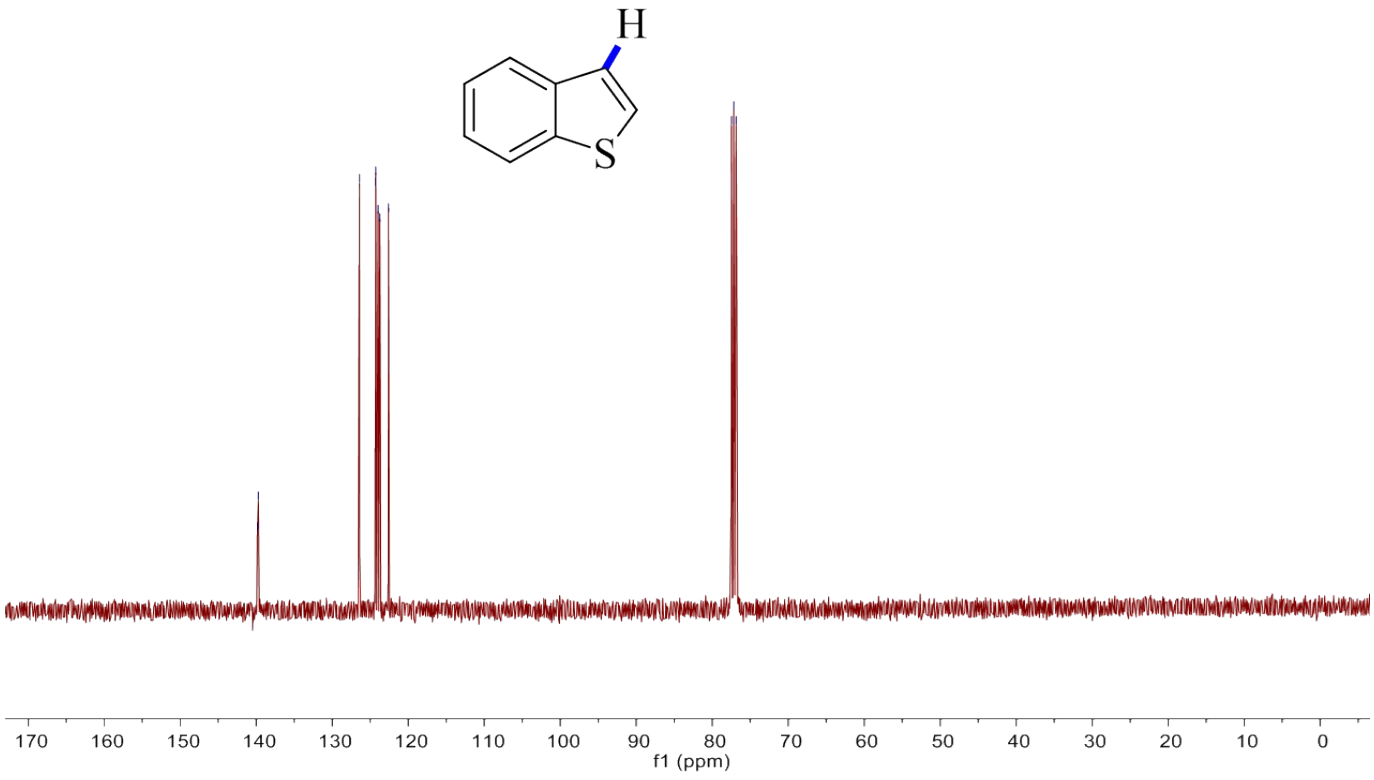


2r

^{1}H NMR (400 MHz, $CDCl_3$)

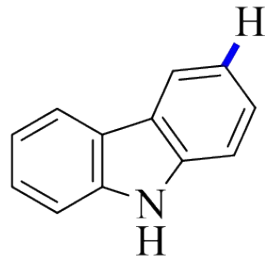


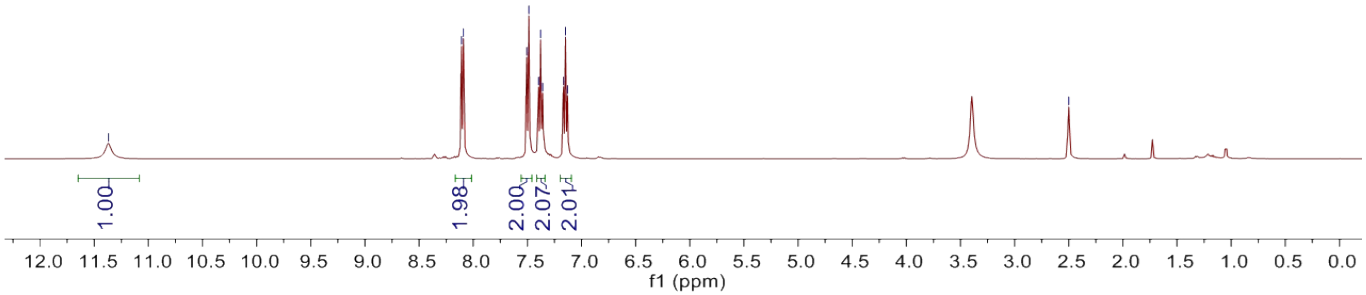
^{13}C NMR (101 MHz, $CDCl_3$)



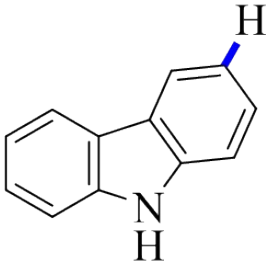
2s

^{1}H NMR (400 MHz, DMSO-d6)



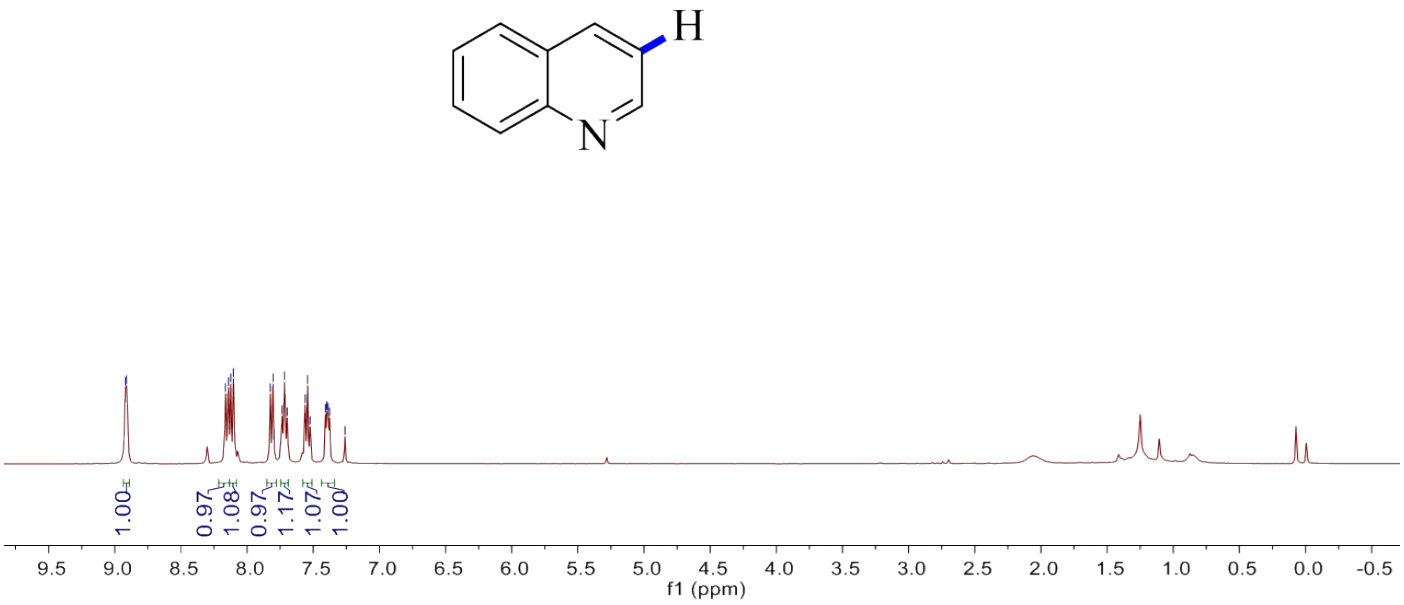


^{13}C NMR (101 MHz, DMSO-d6)

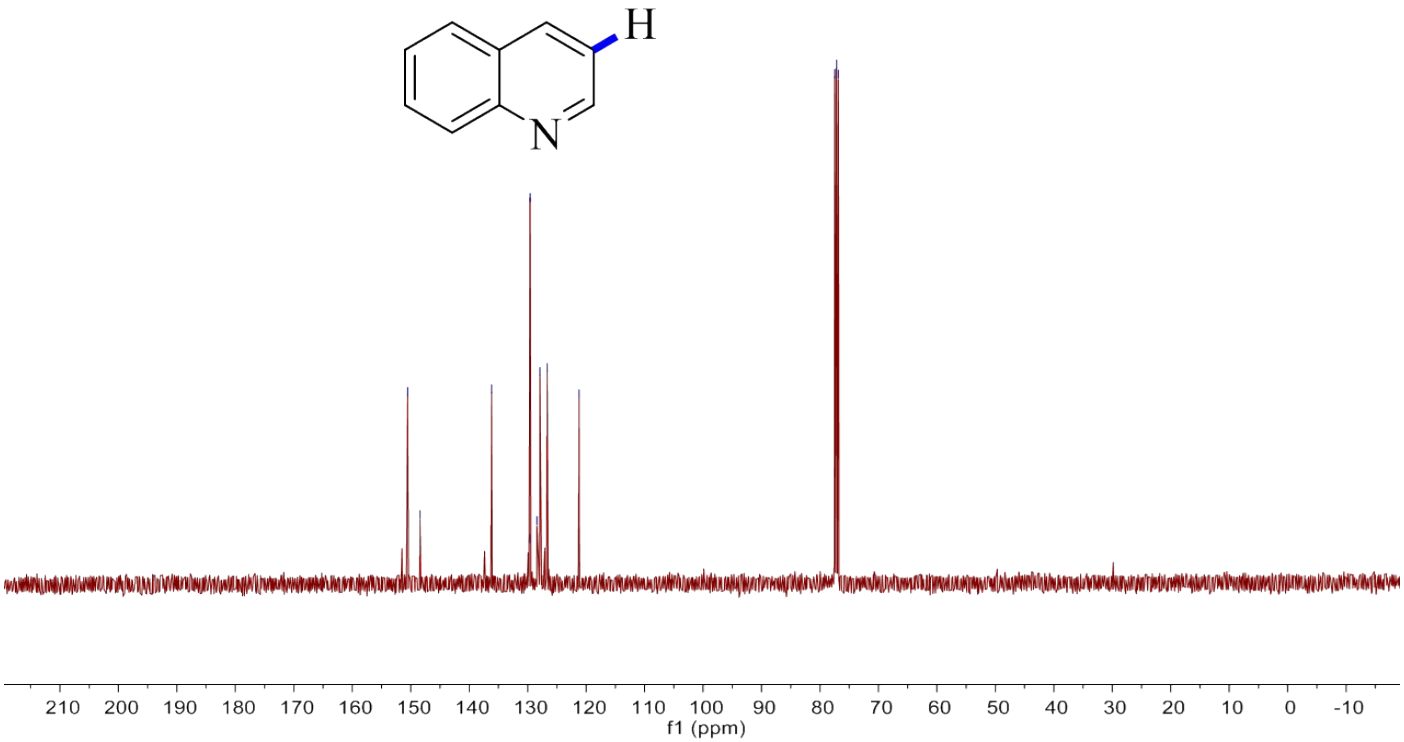


2t

^{1}H NMR (400 MHz, $CDCl_3$)

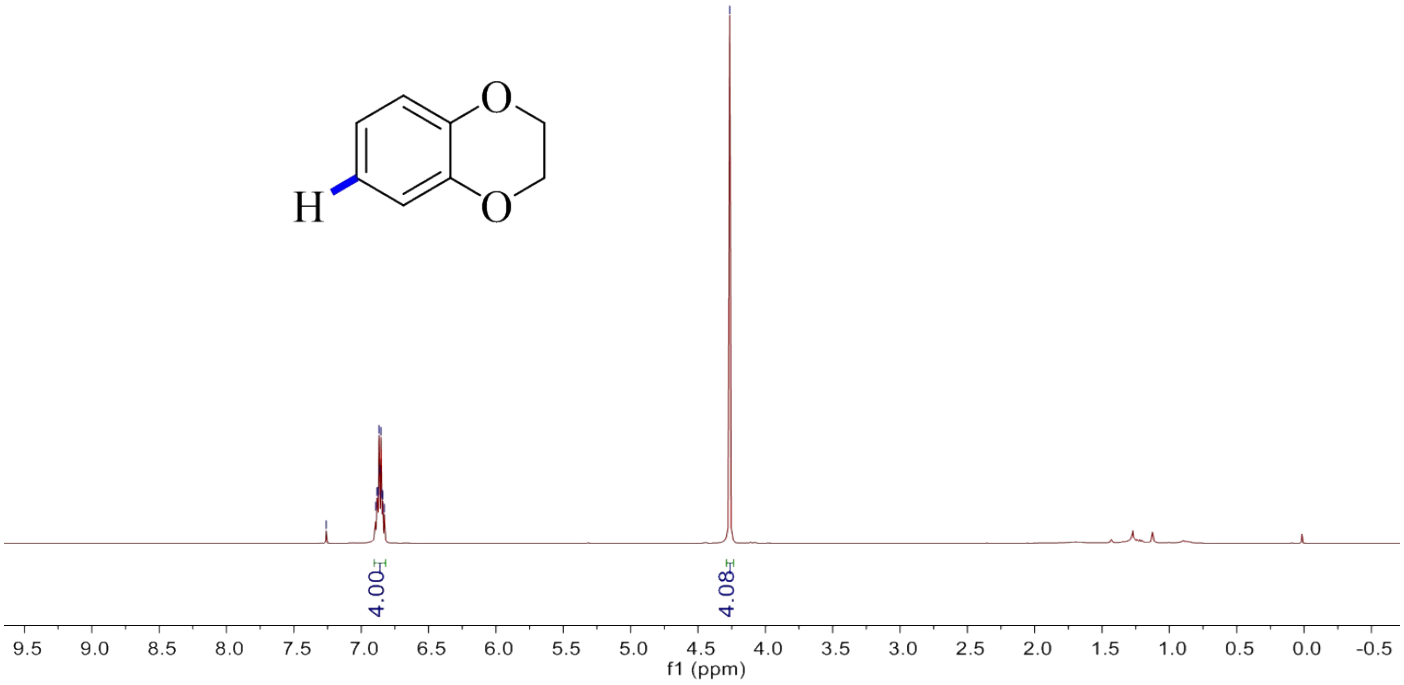


^{13}C NMR (101 MHz, $CDCl_3$)

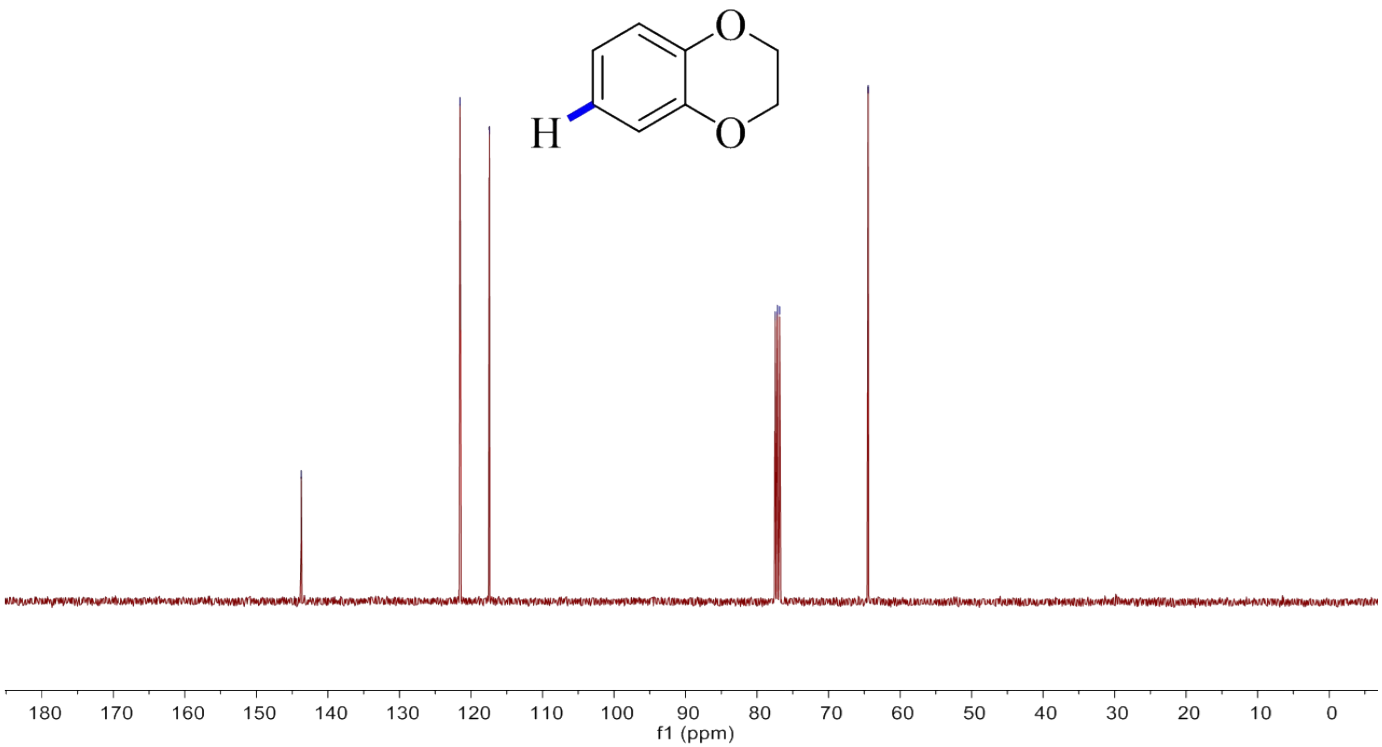


2u

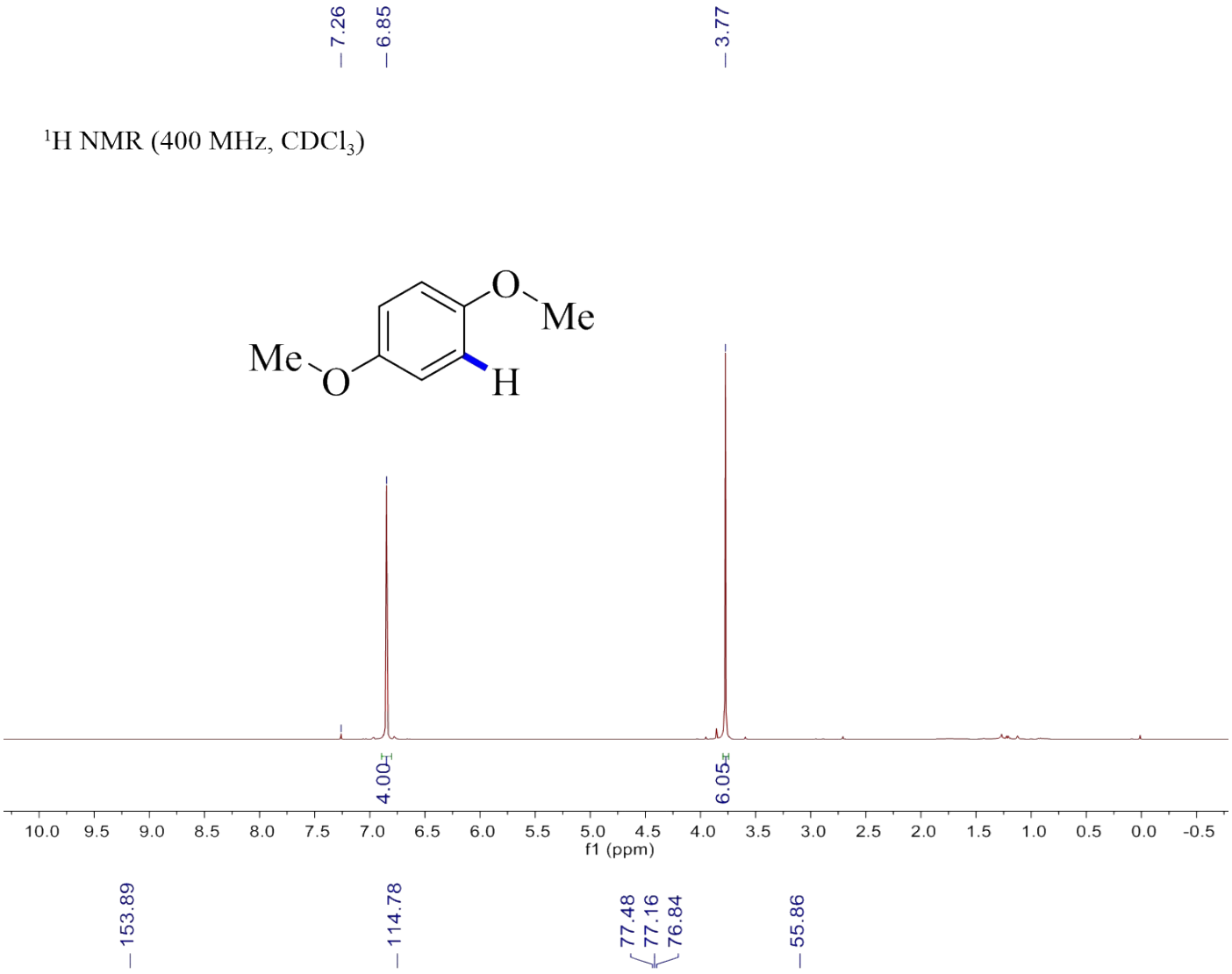
^{1}H NMR (400 MHz, $CDCl_3$)



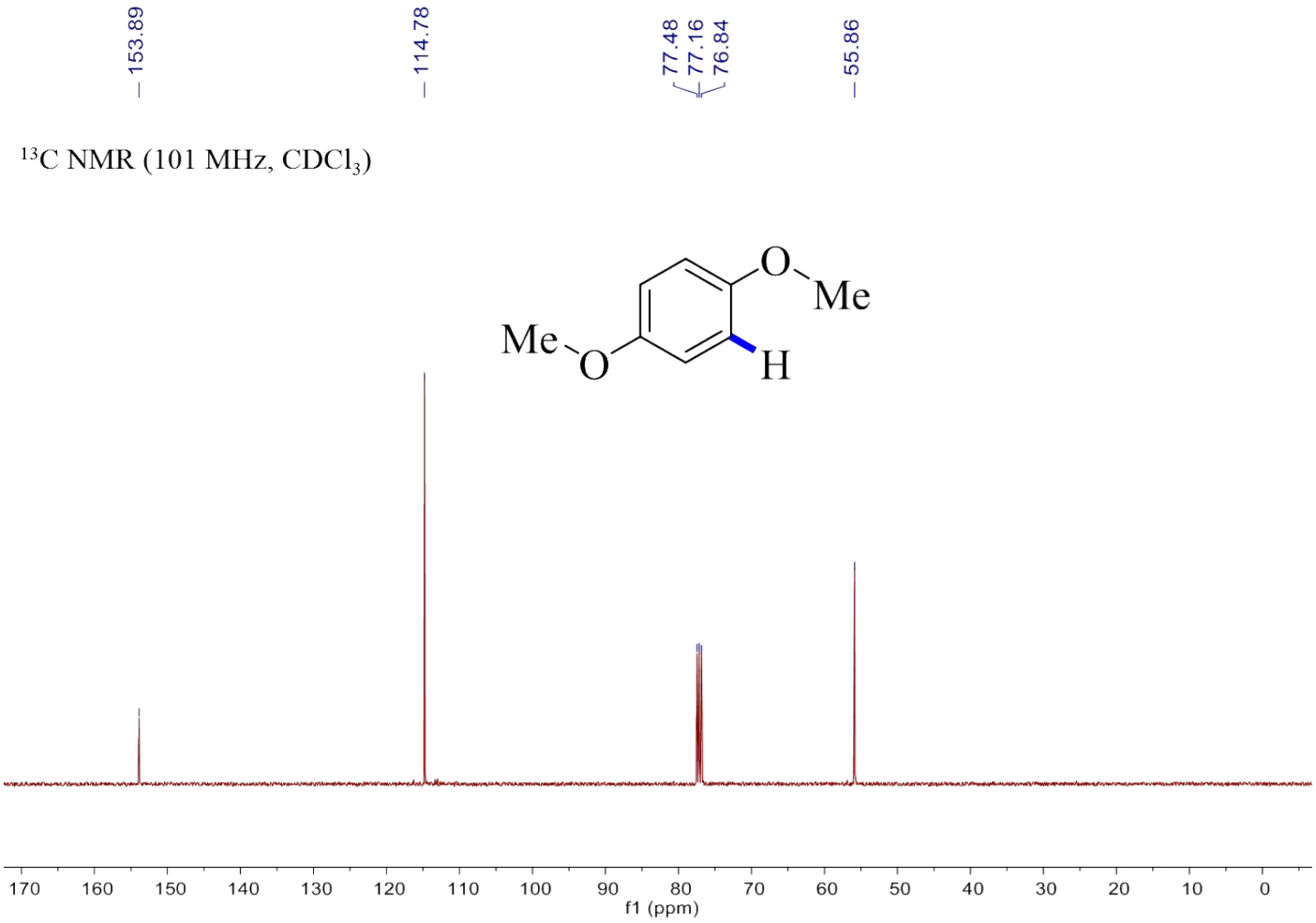
^{13}C NMR (101 MHz, $CDCl_3$)



2w

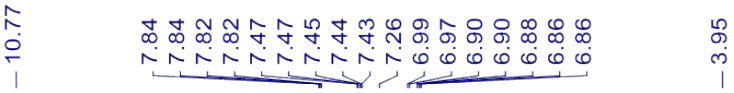


^{1}H NMR (400 MHz, $CDCl_3$)

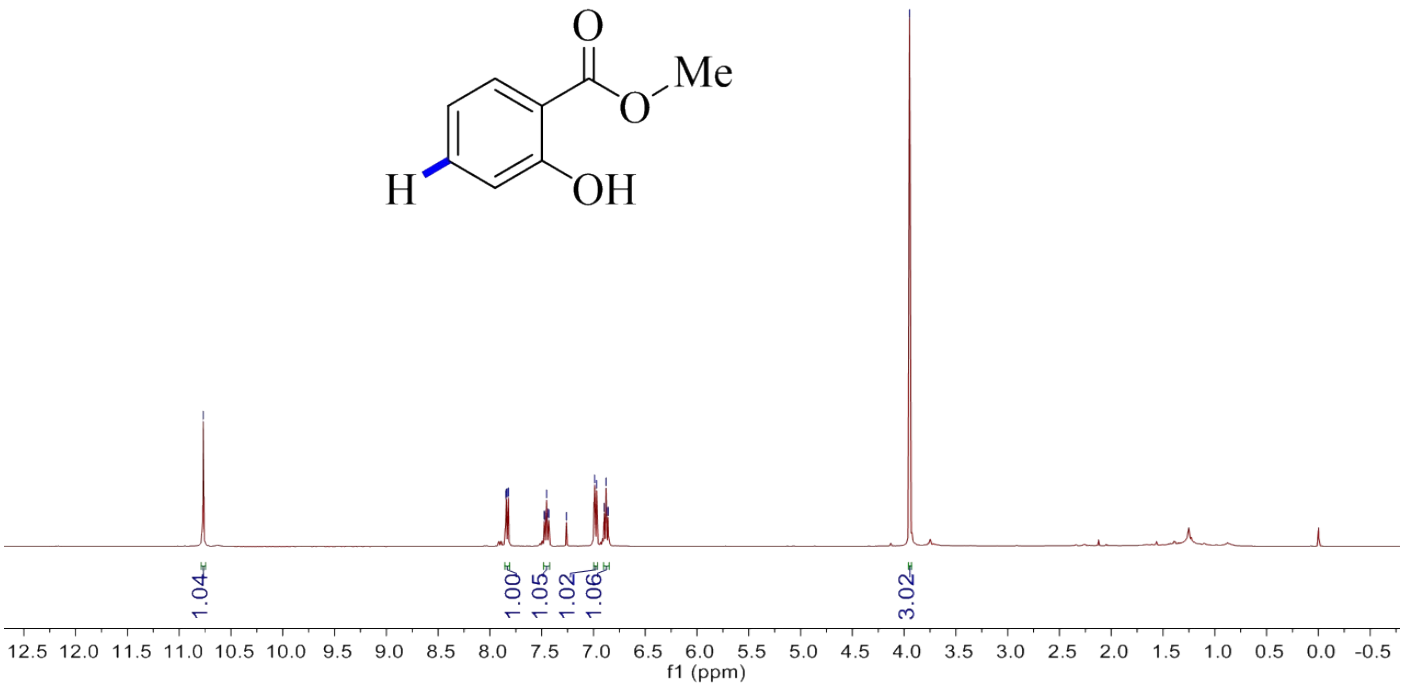


^{13}C NMR (101 MHz, $CDCl_3$)

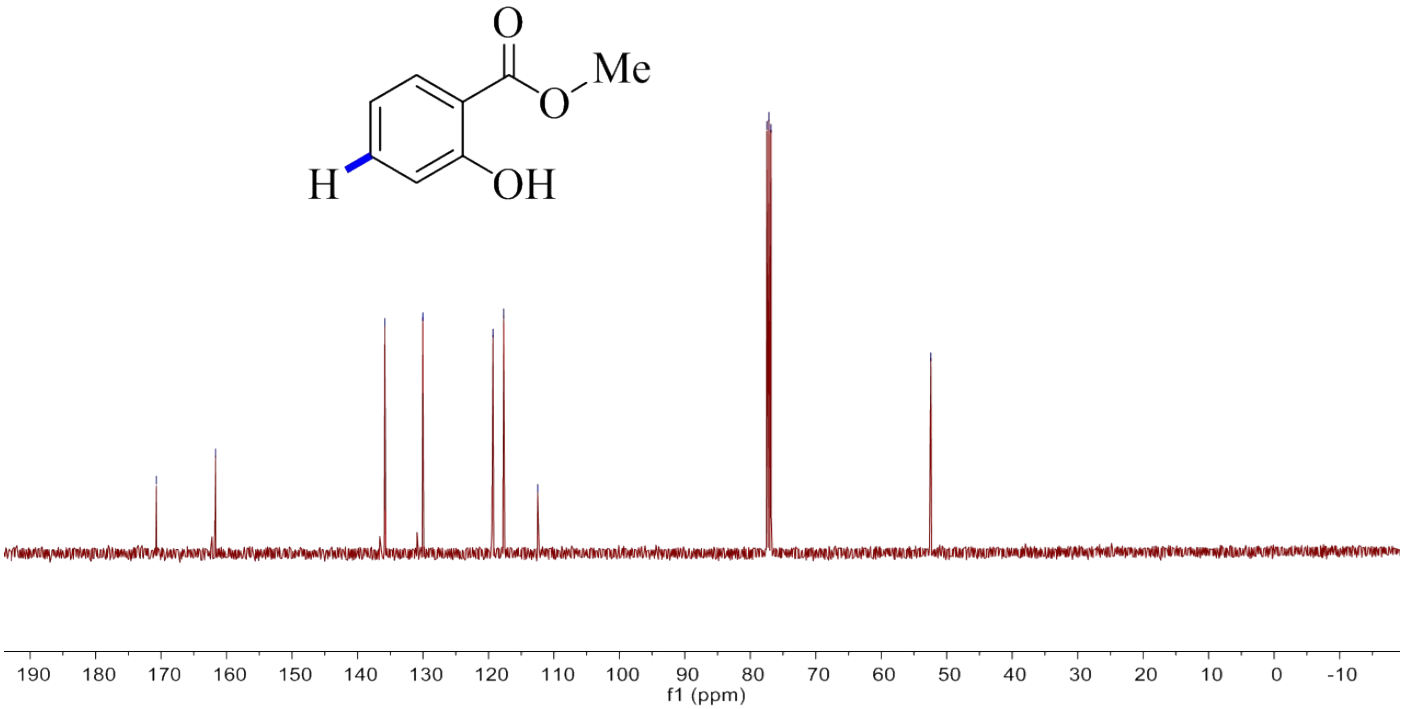
2x



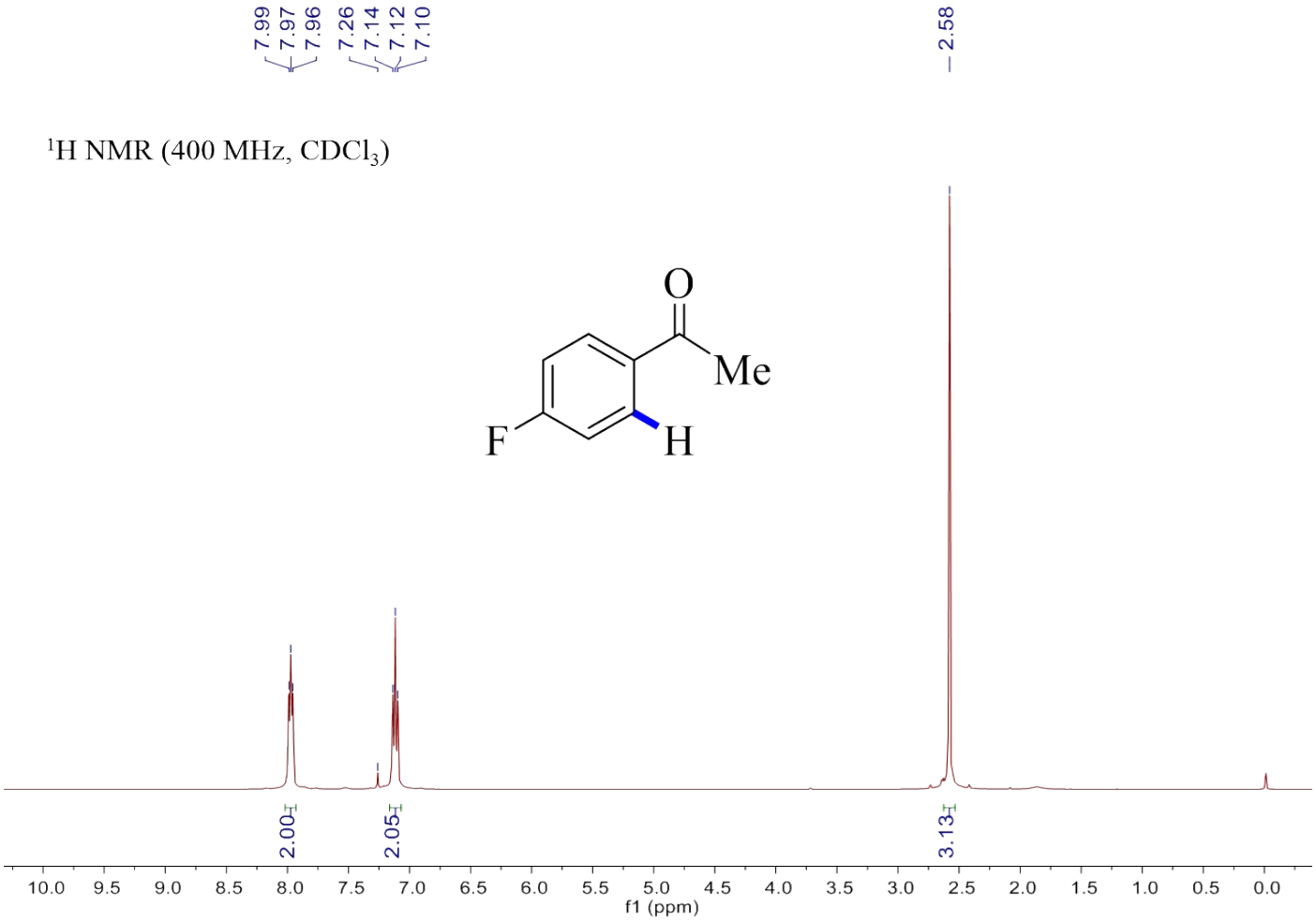
^{1}H NMR (400 MHz, $CDCl_3$)



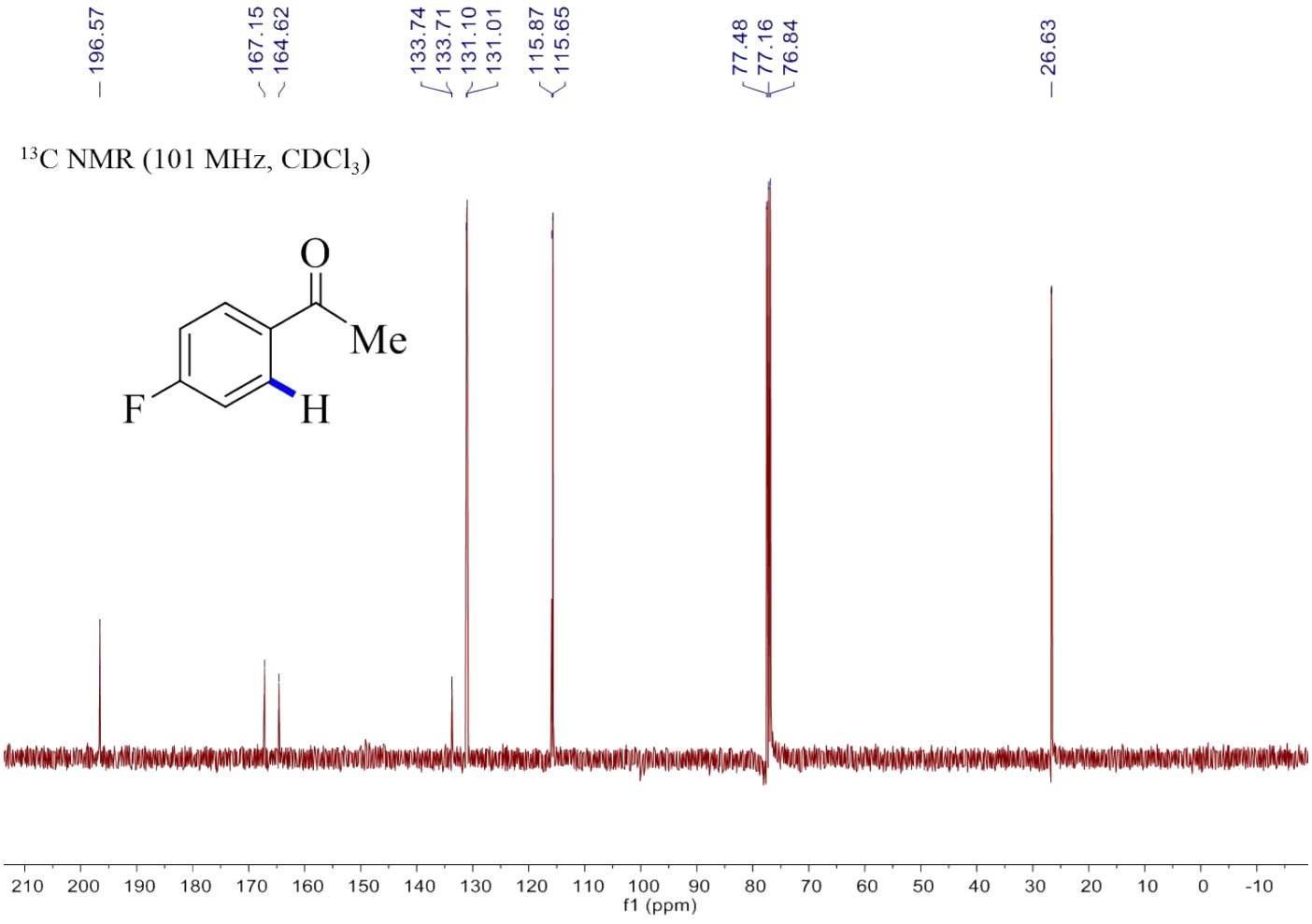
^{13}C NMR (101 MHz, $CDCl_3$)



2y

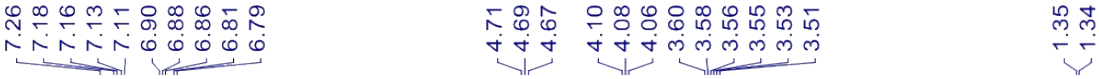


^{1}H NMR (400 MHz, $CDCl_3$)

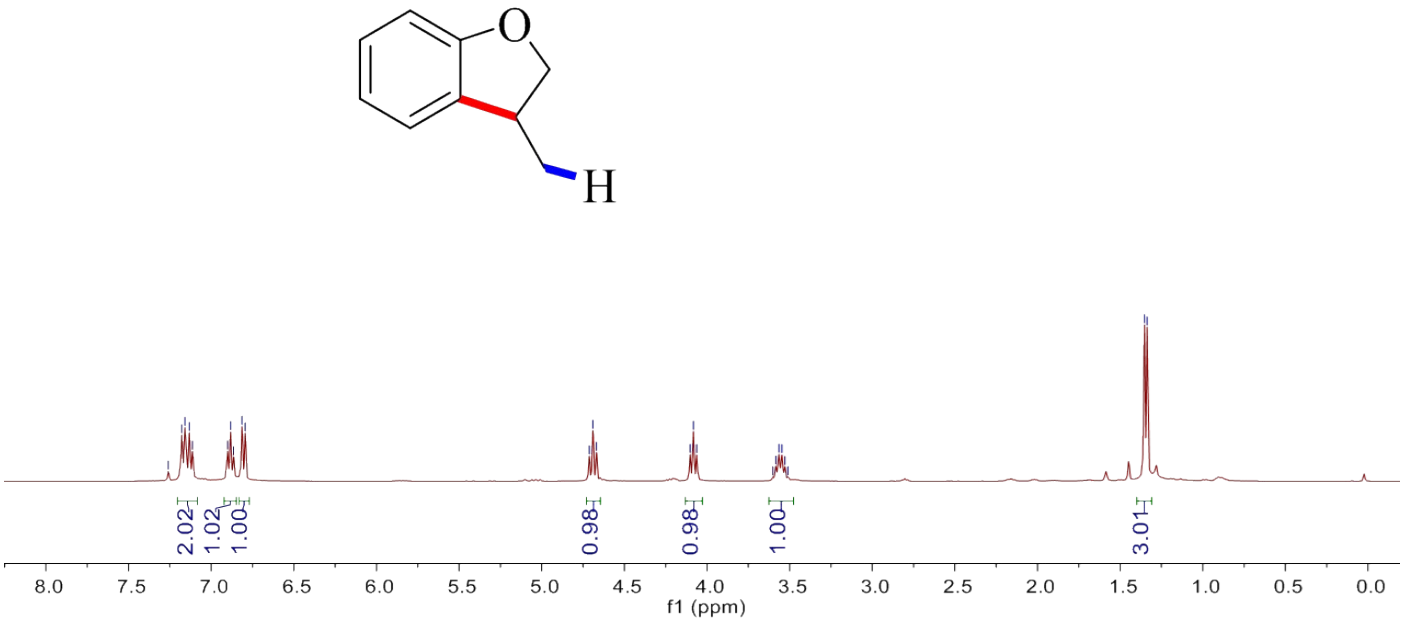


^{13}C NMR (101 MHz, $CDCl_3$)

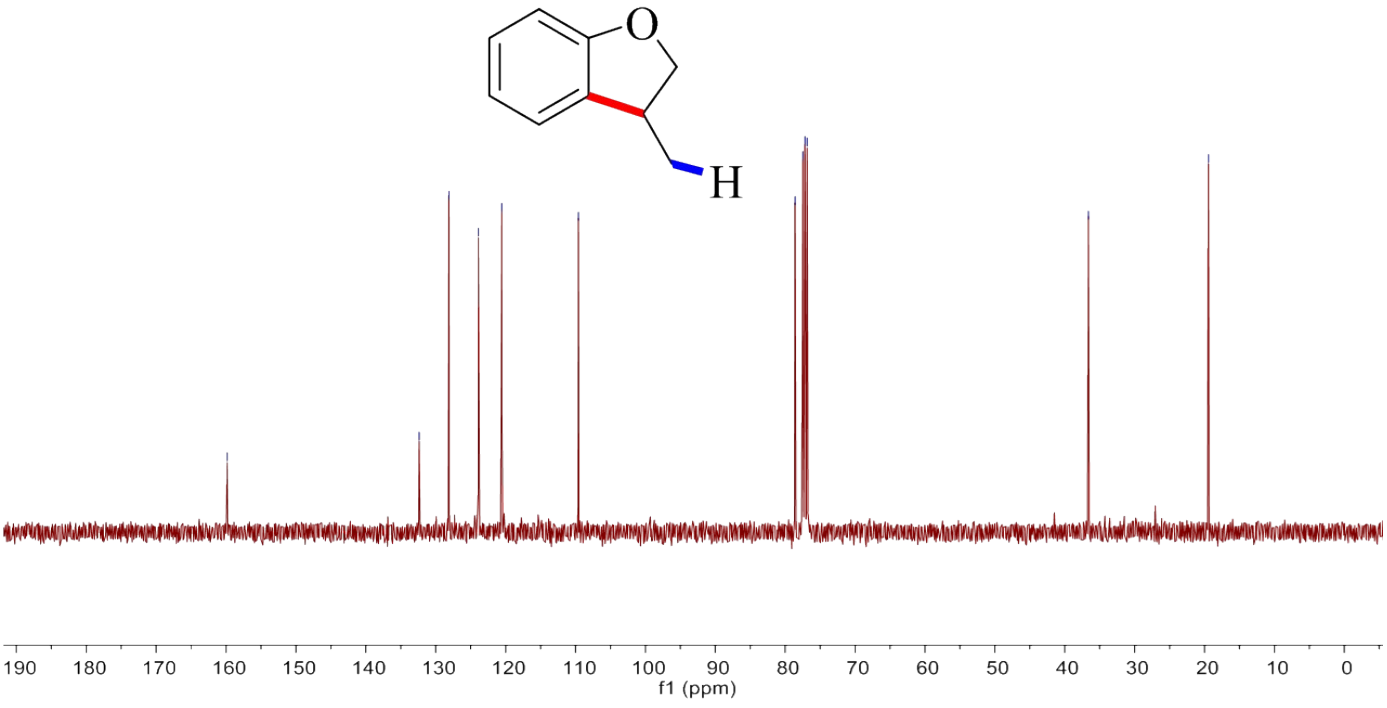
3a



^{1}H NMR (400 MHz, $CDCl_3$)

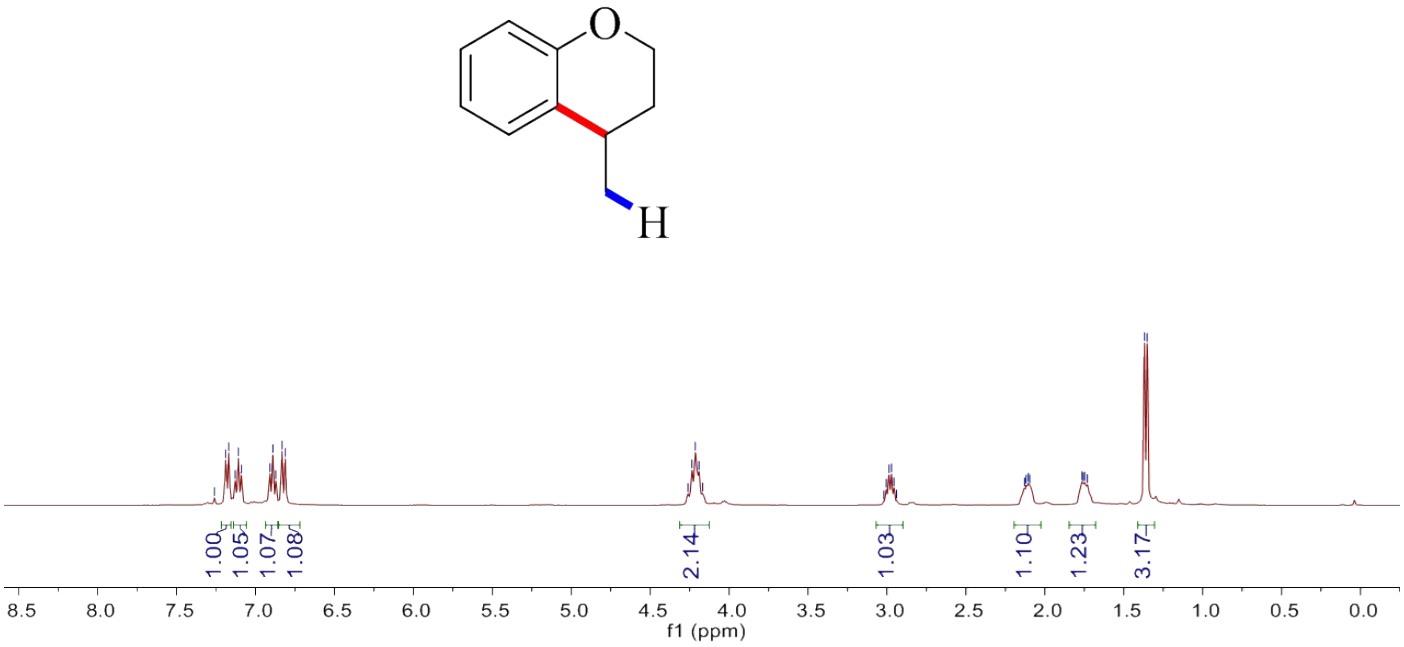


^{13}C NMR (101 MHz, $CDCl_3$)

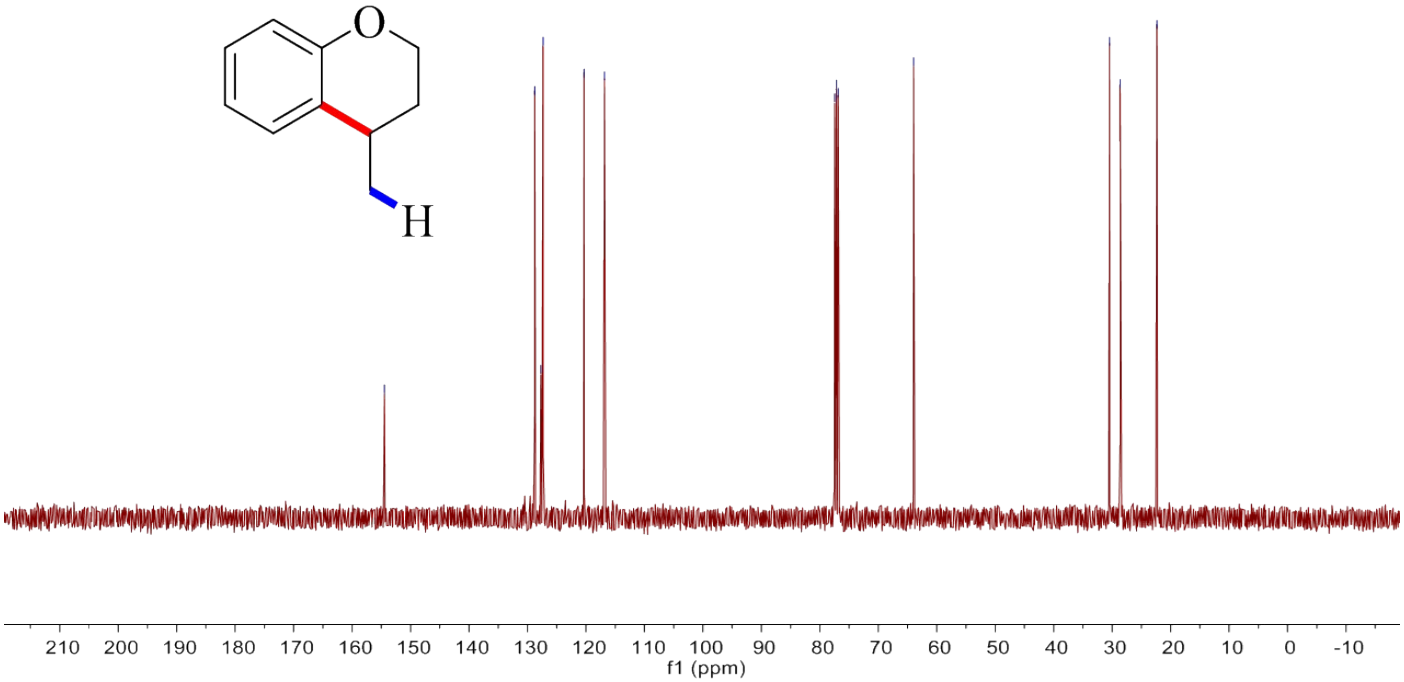


3b

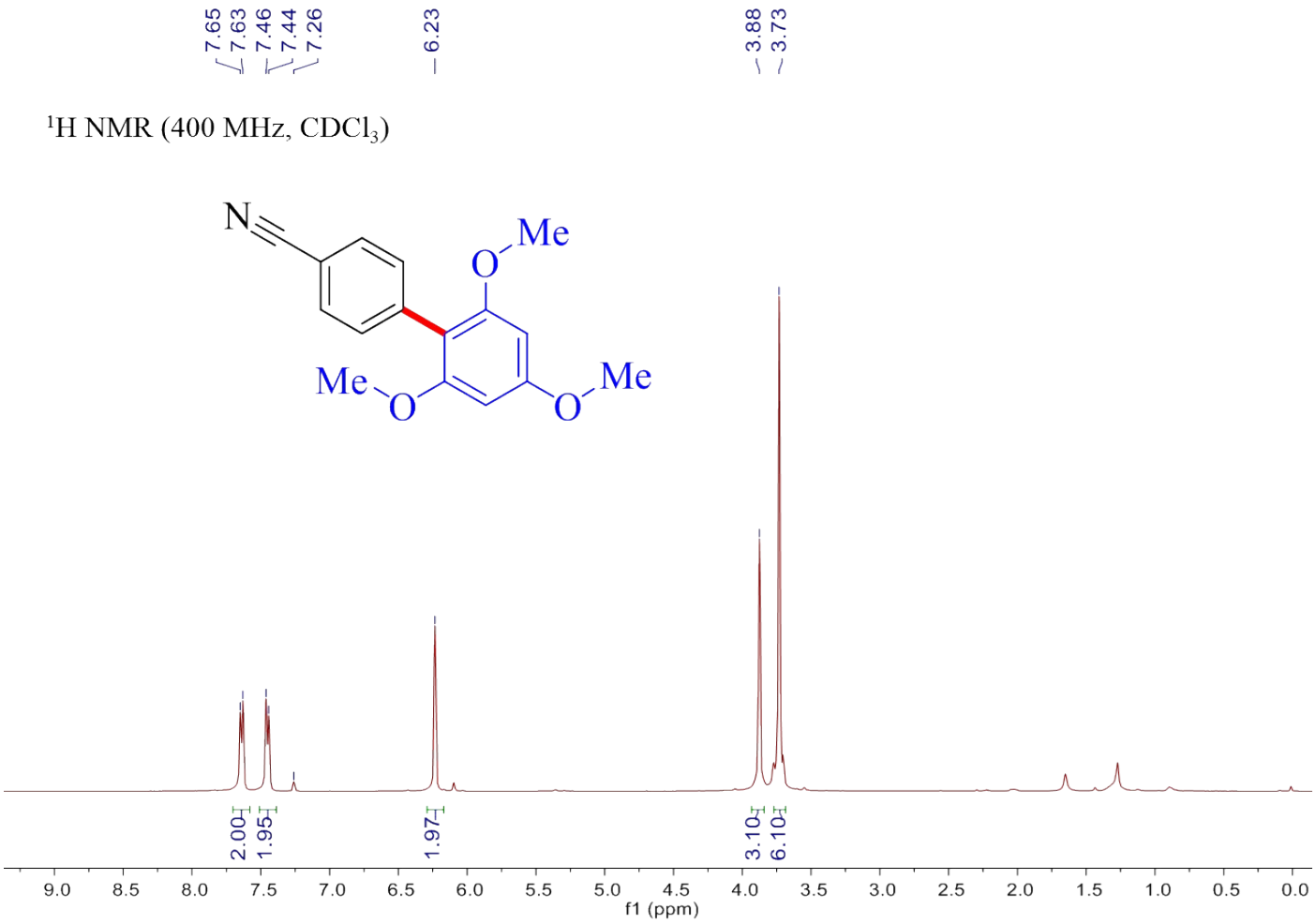
^{1}H NMR (400 MHz, $CDCl_3$)



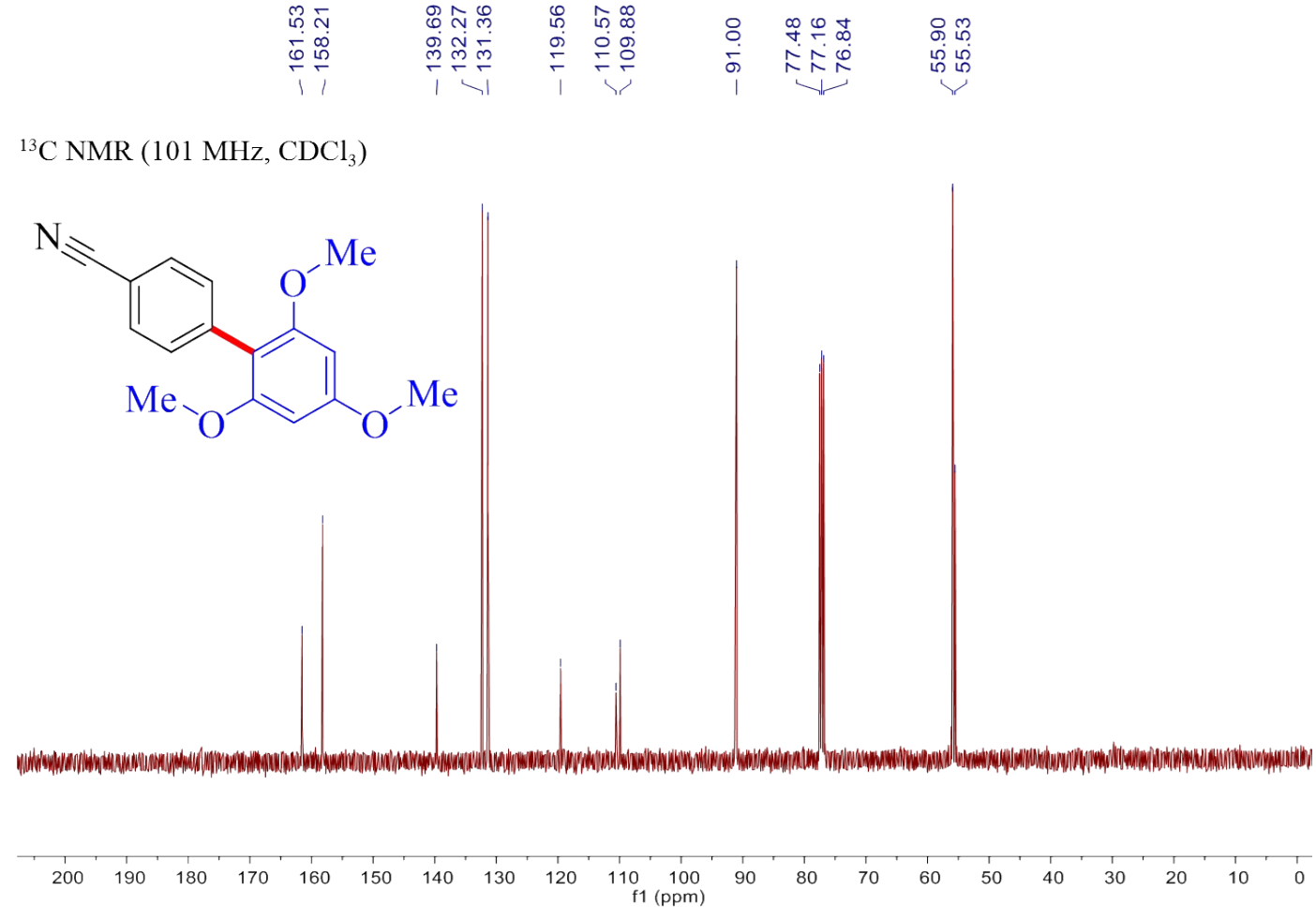
^{13}C NMR (101 MHz, $CDCl_3$)



5a

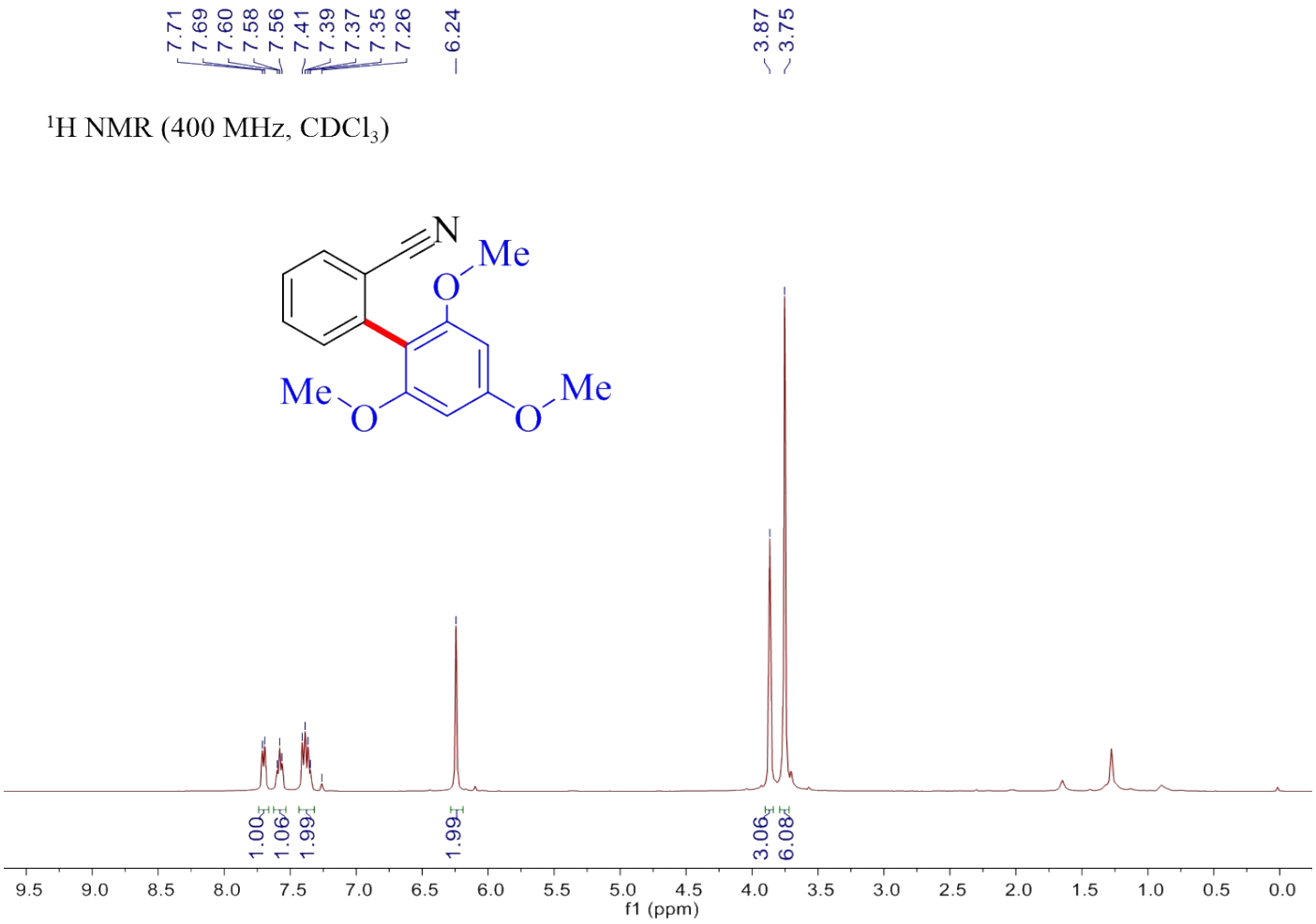


^{1}H NMR (400 MHz, $CDCl_3$)

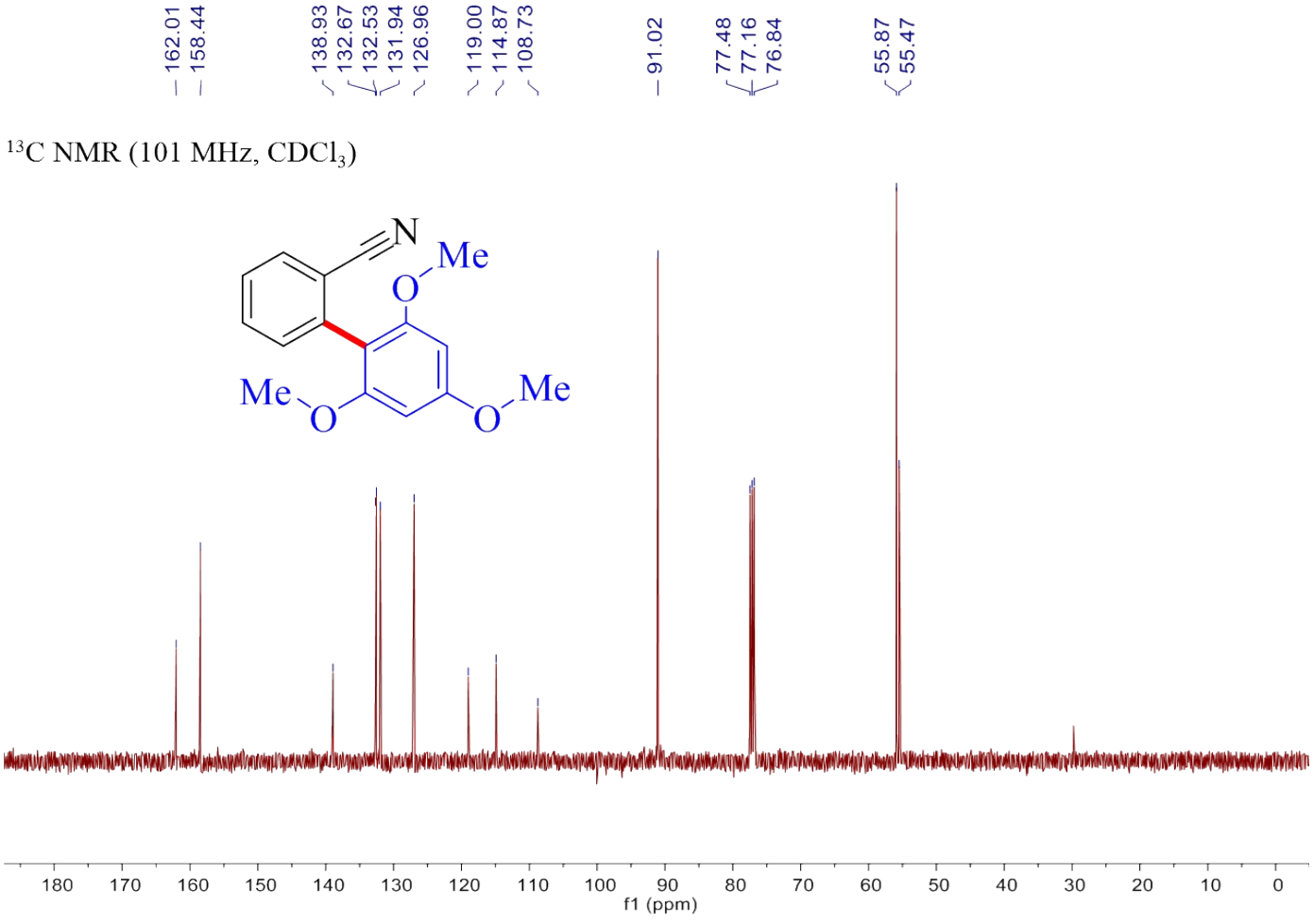


^{13}C NMR (101 MHz, $CDCl_3$)

5b



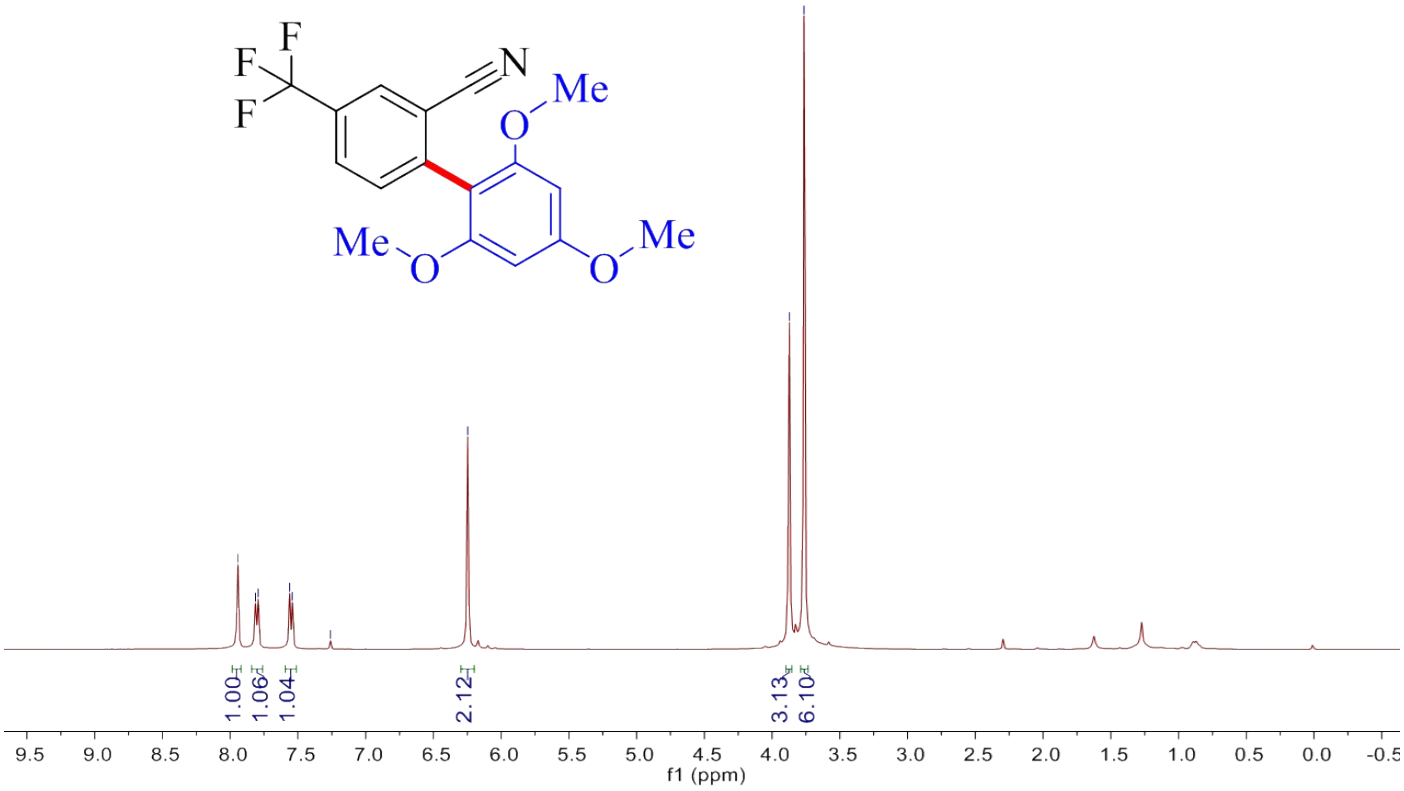
^{1}H NMR (400 MHz, $CDCl_3$)



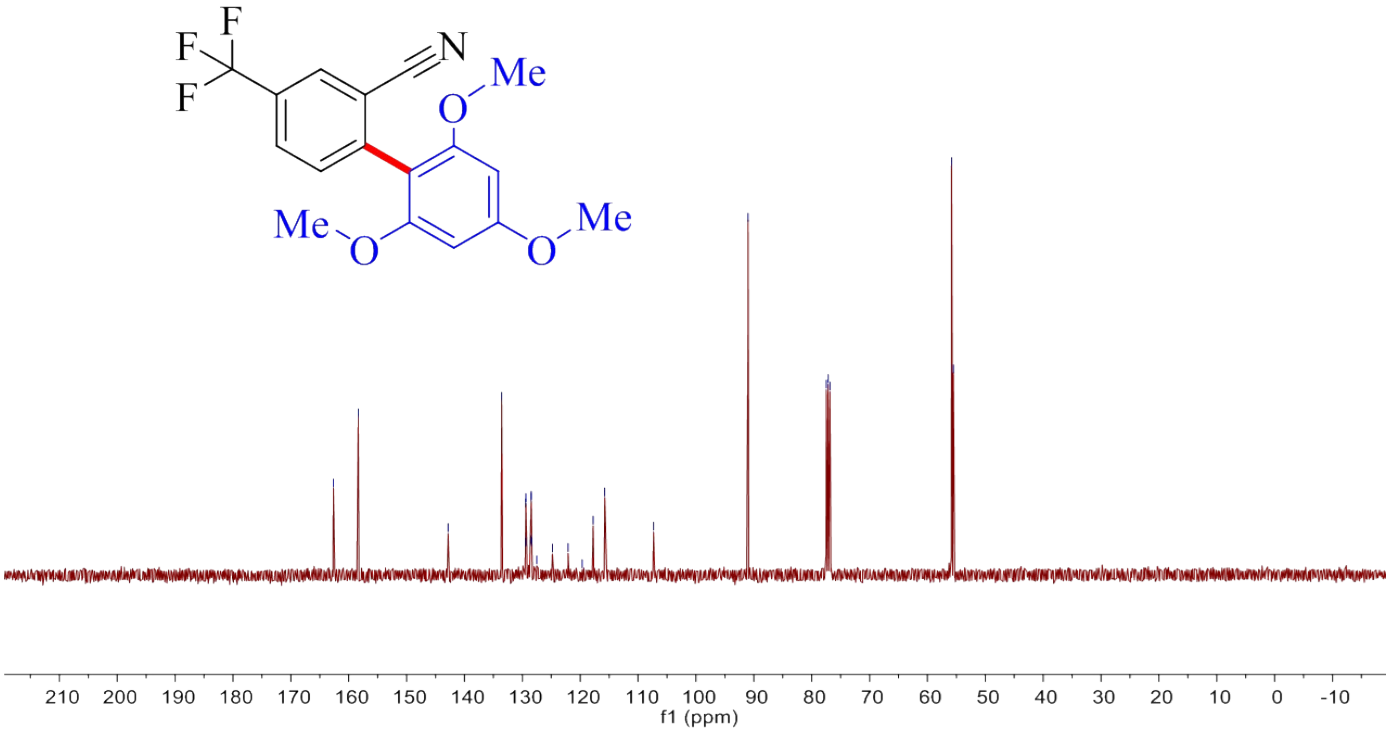
^{13}C NMR (101 MHz, $CDCl_3$)

5c

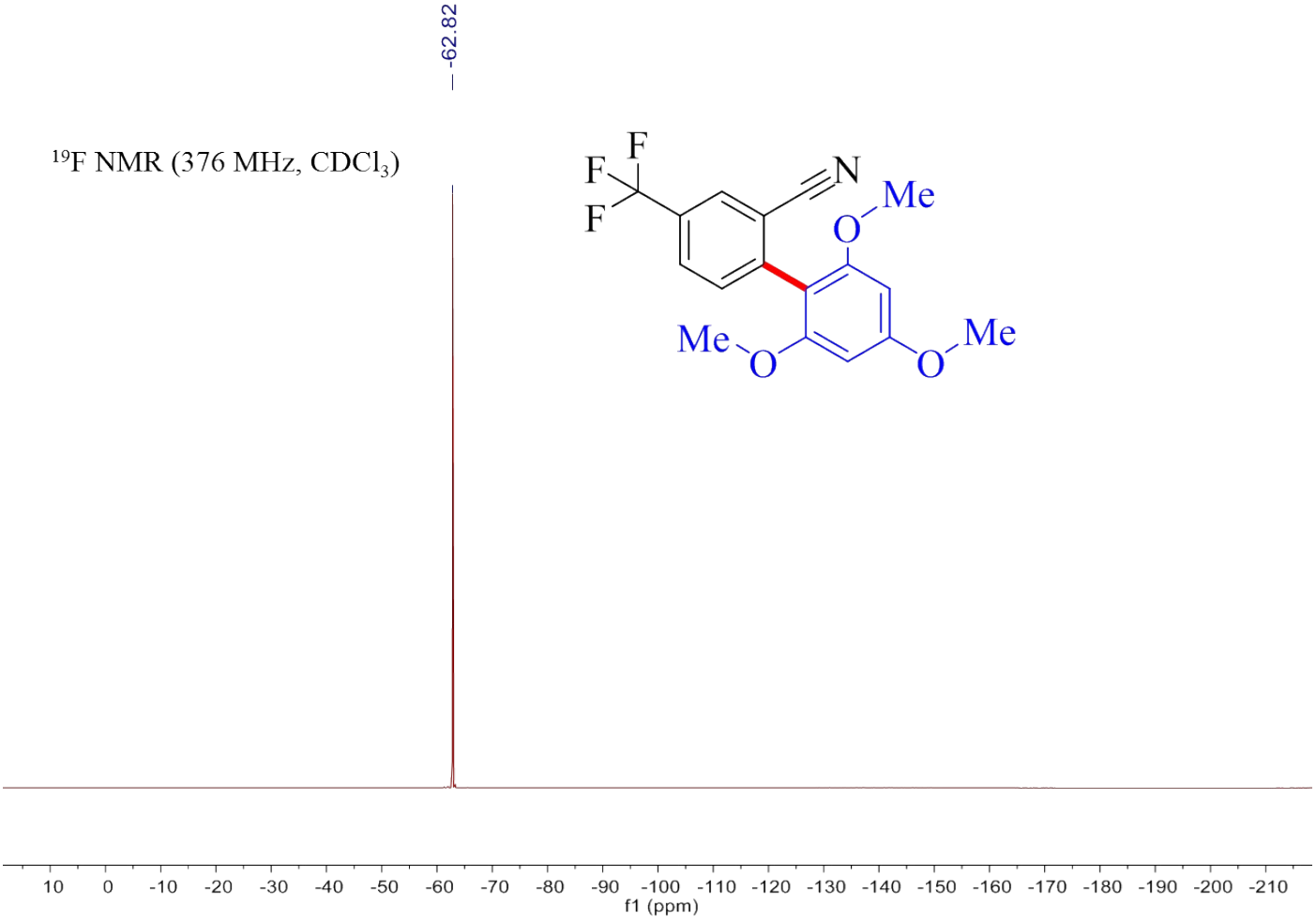
^{1}H NMR (400 MHz, $CDCl_3$)



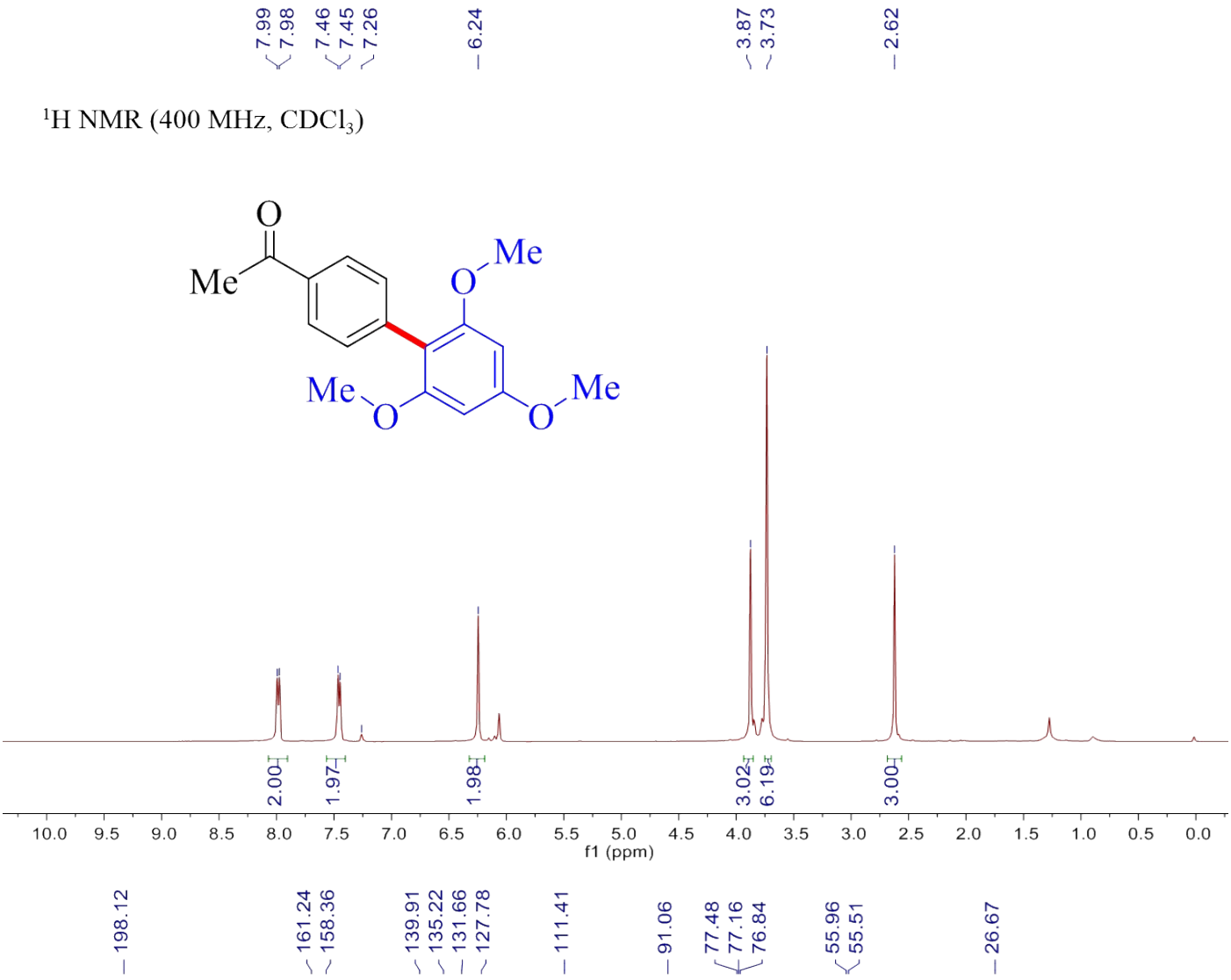
^{13}C NMR (101 MHz, $CDCl_3$)



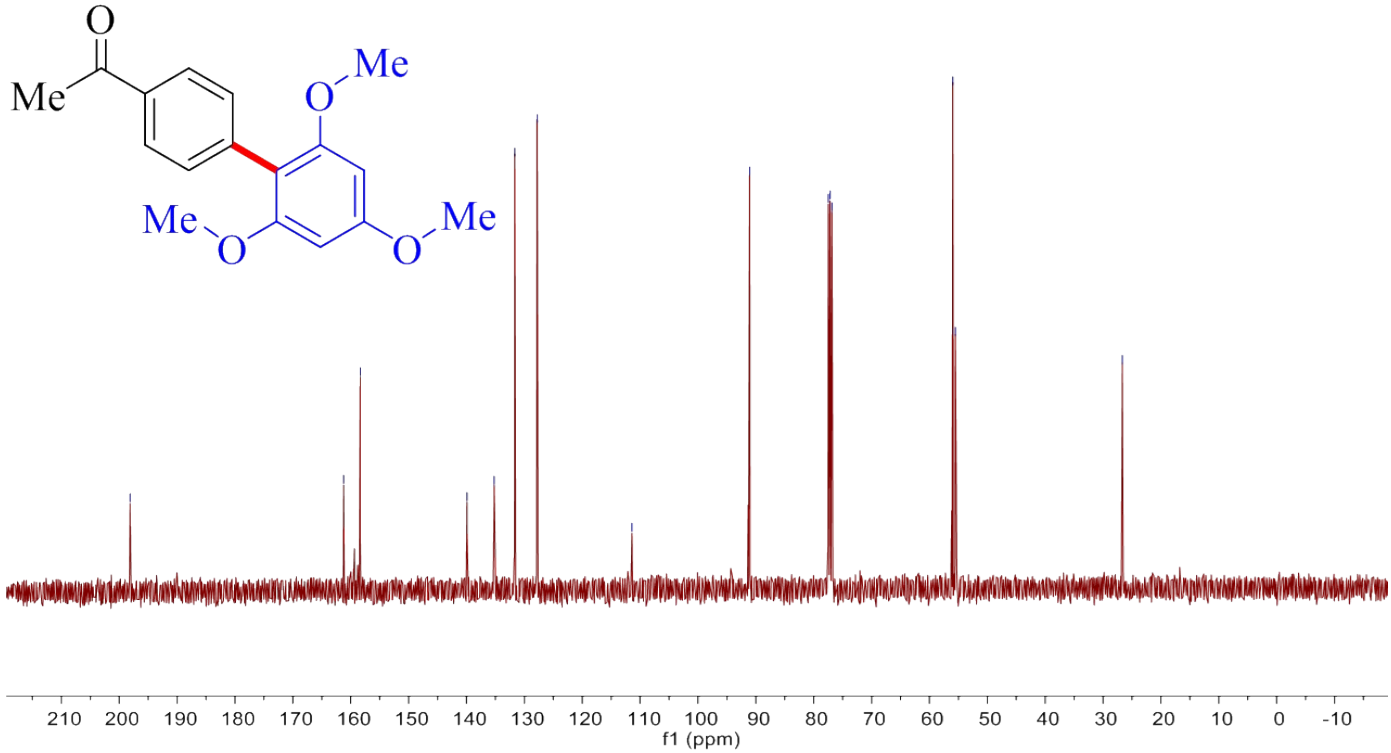
^{19}F NMR (376 MHz, $CDCl_3$)



5d



^{1}H NMR (400 MHz, $CDCl_3$)

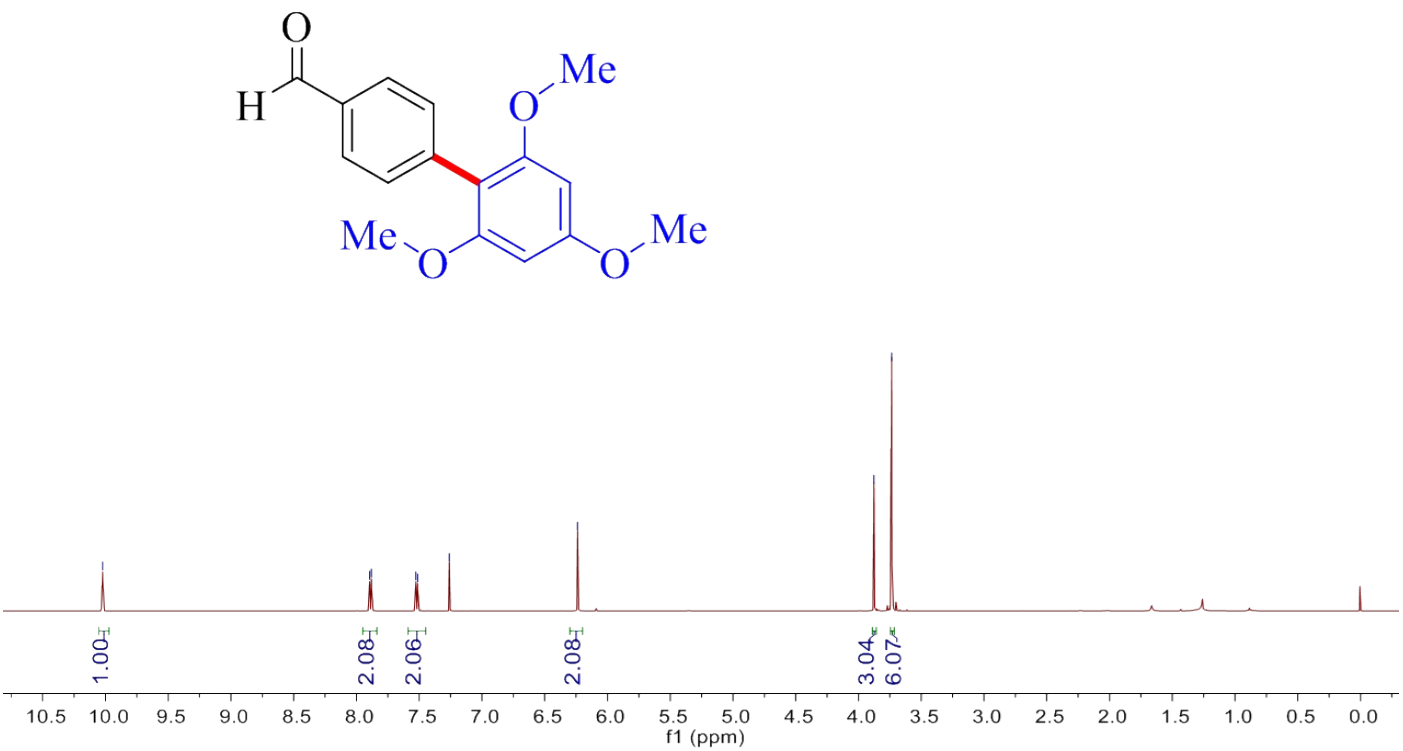


^{13}C NMR (101 MHz, $CDCl_3$)

5e

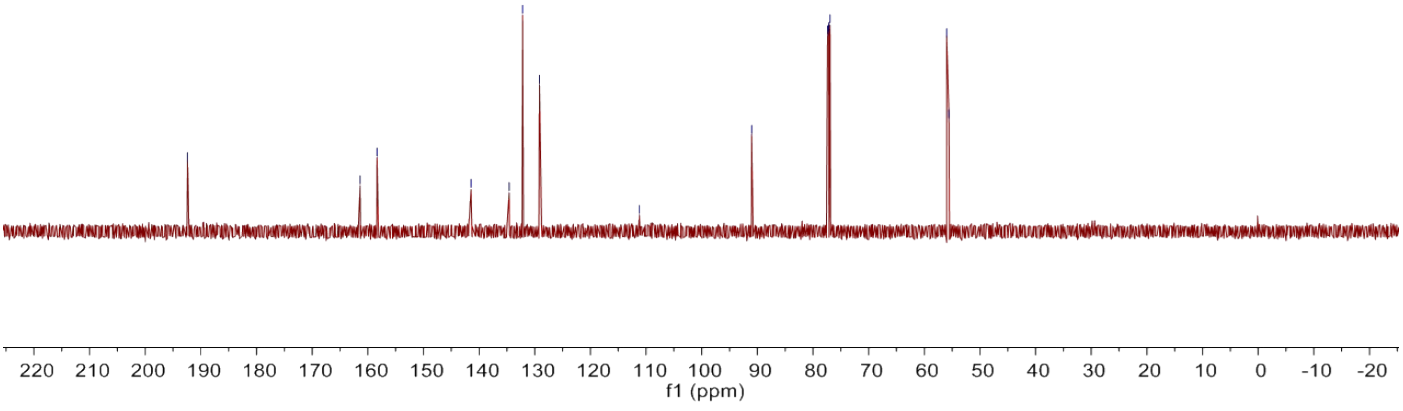
10.02, 7.89, 7.88, 7.53, 7.51, 7.26, 6.24, 3.88, 3.74

^{1}H NMR (600 MHz, $CDCl_3$)



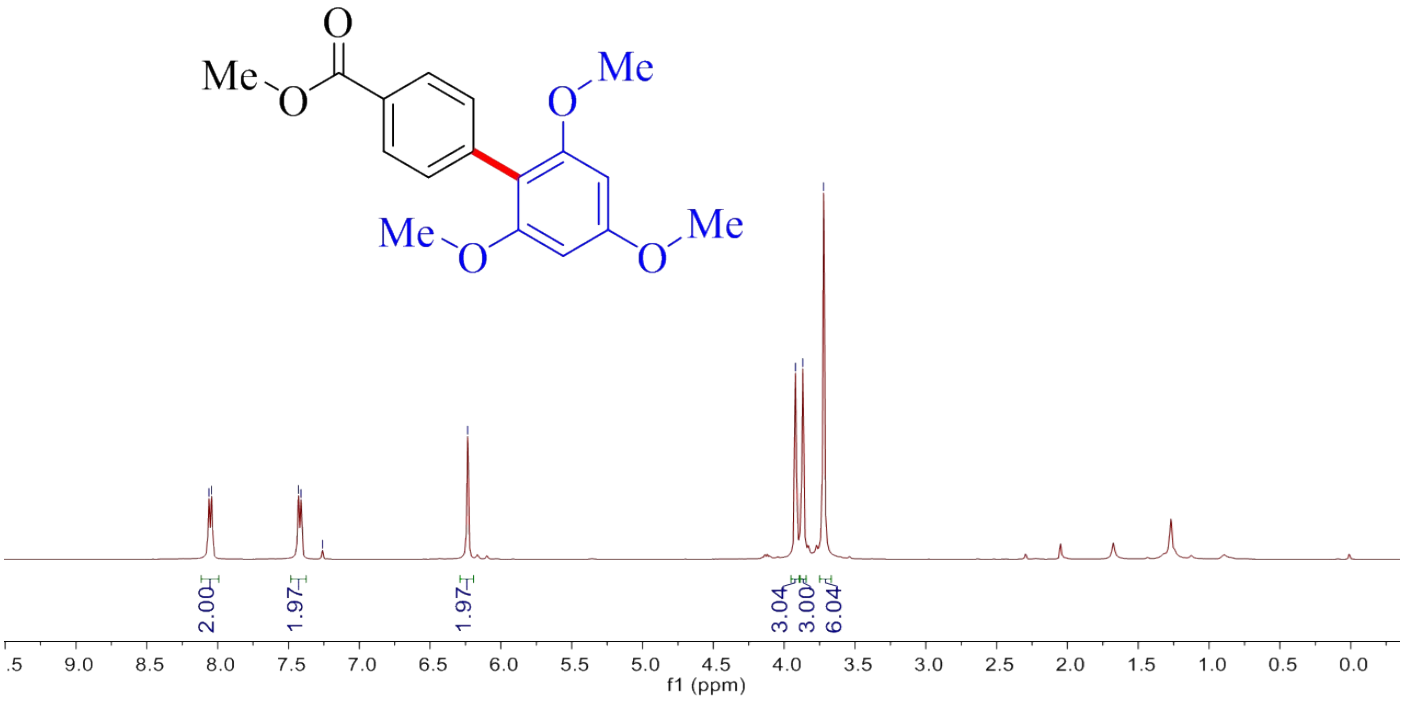
192.39, 161.39, 158.34, 141.44, 134.61, 132.18, 129.15, 111.21, 91.02, 77.37, 77.16, 76.95, 55.97, 55.55

^{13}C NMR (151 MHz, $CDCl_3$)

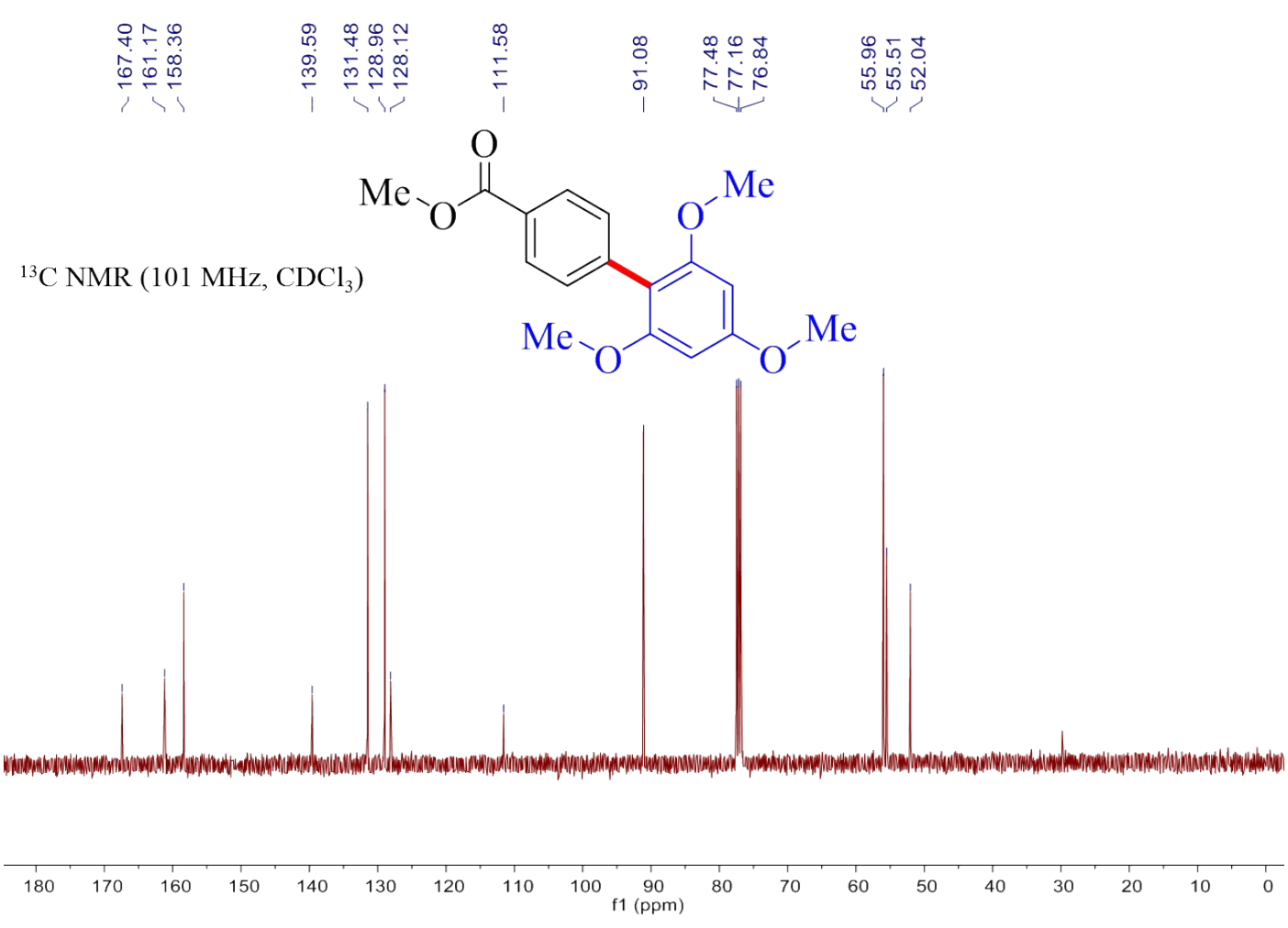


5f

^{1}H NMR (400 MHz, $CDCl_3$)

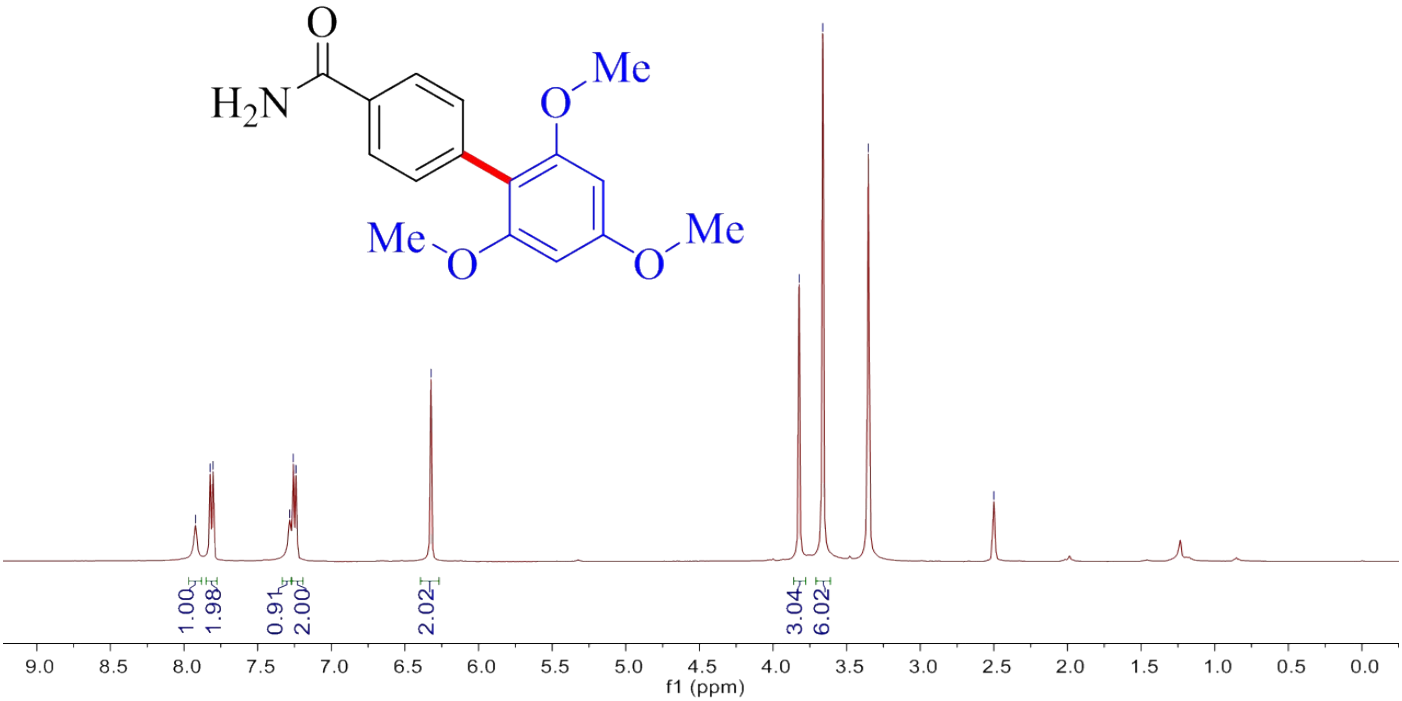


^{13}C NMR (101 MHz, $CDCl_3$)

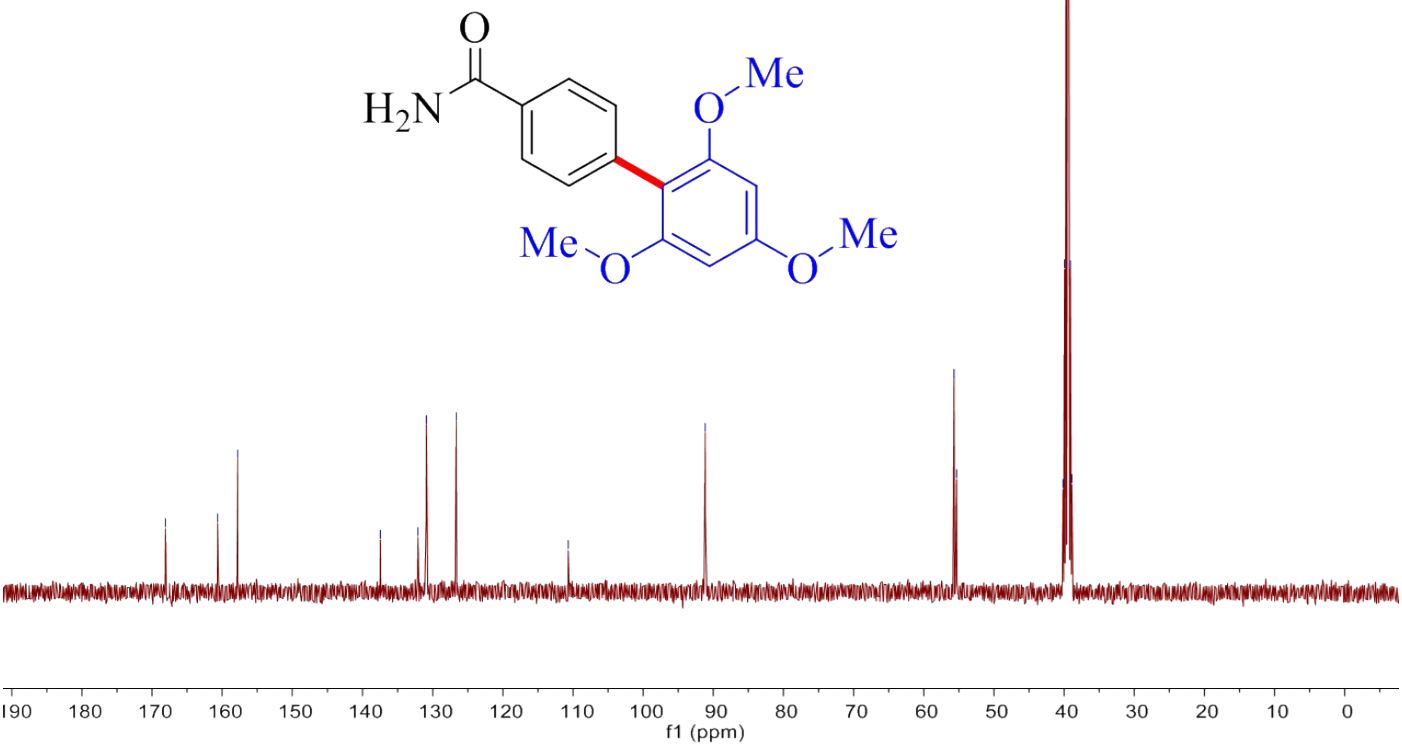


5g

^{1}H NMR (400 MHz, DMSO-d6)

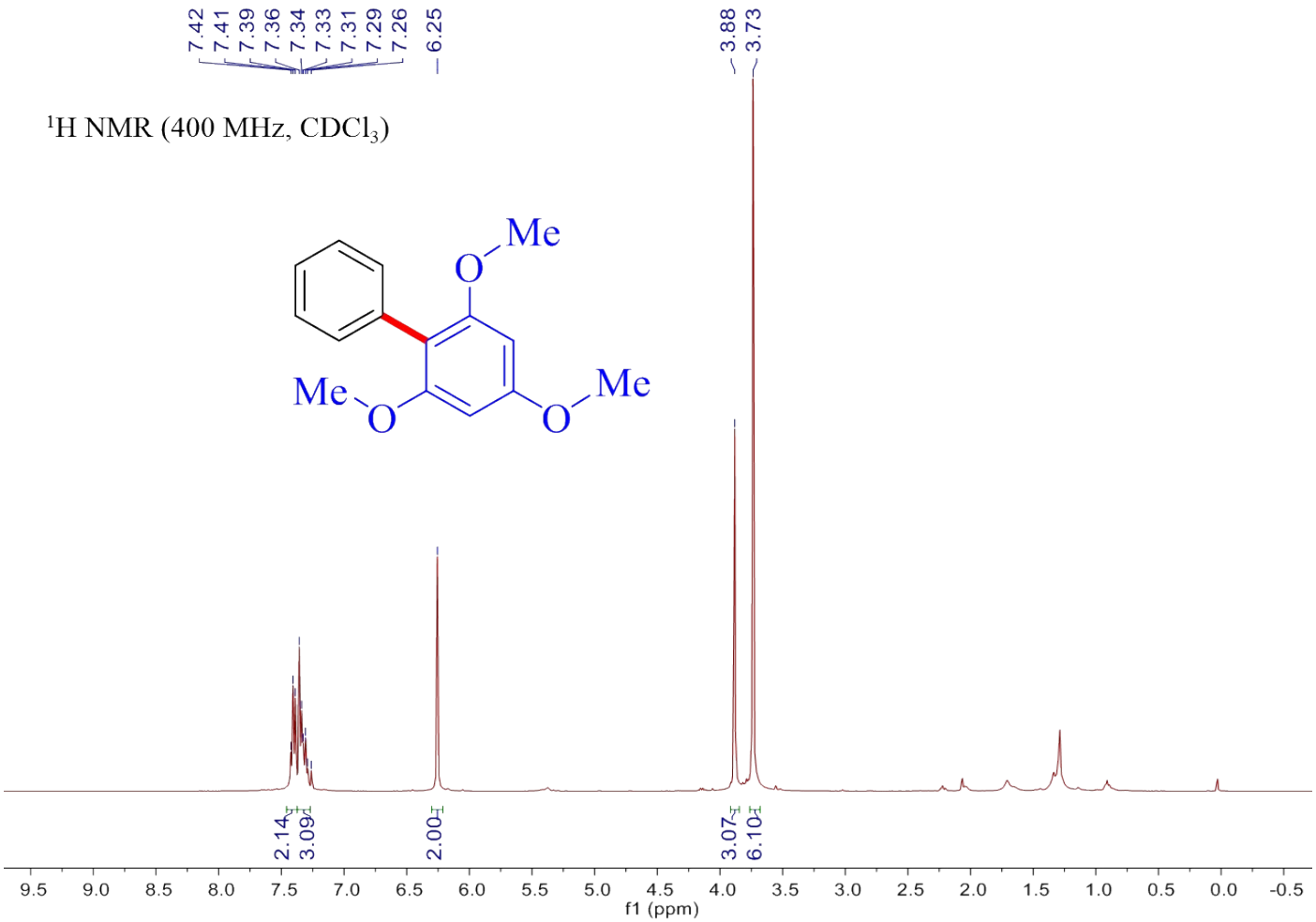


^{13}C NMR (101 MHz, DMSO-d6)

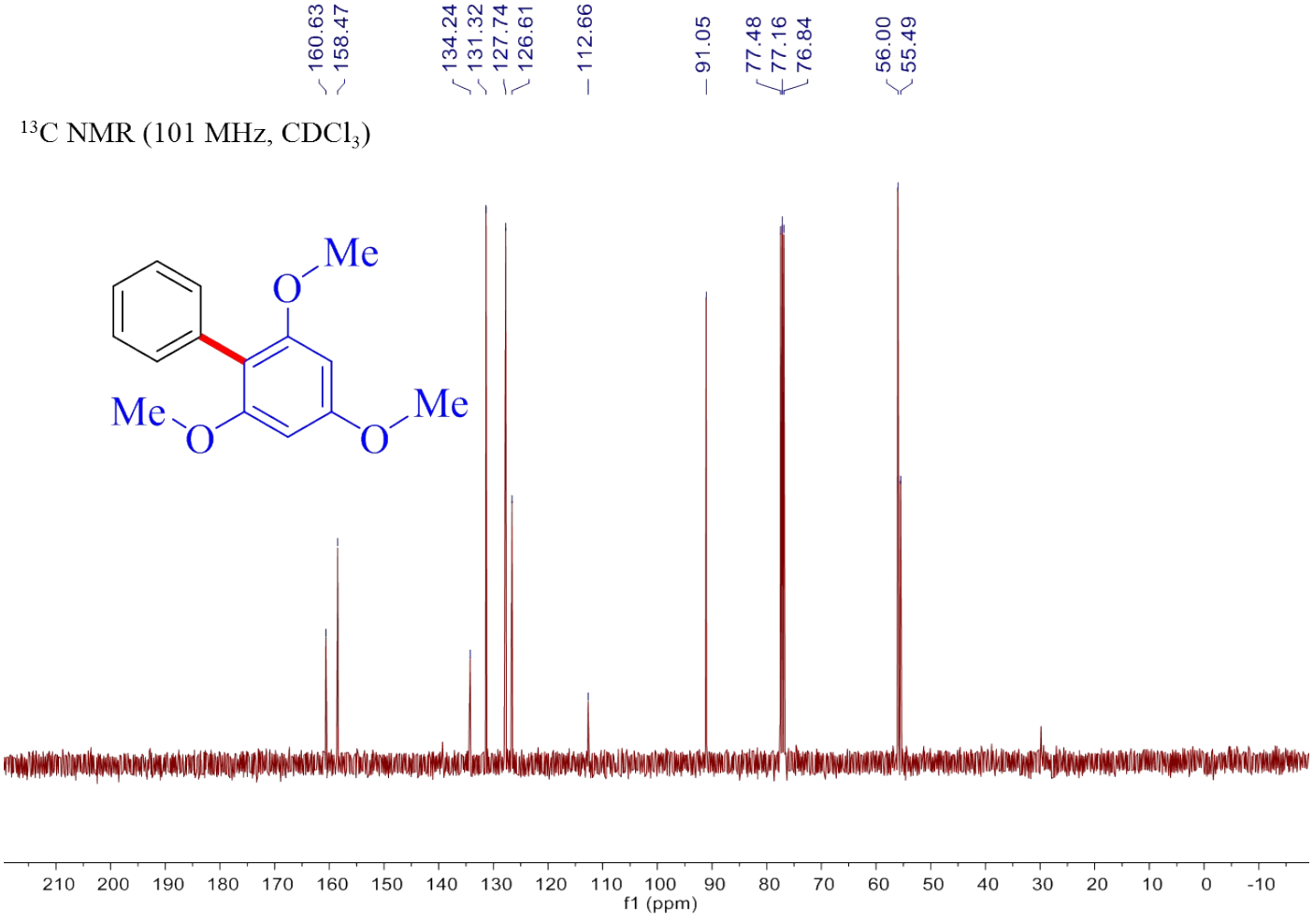


5h

^{1}H NMR (400 MHz, $CDCl_3$)

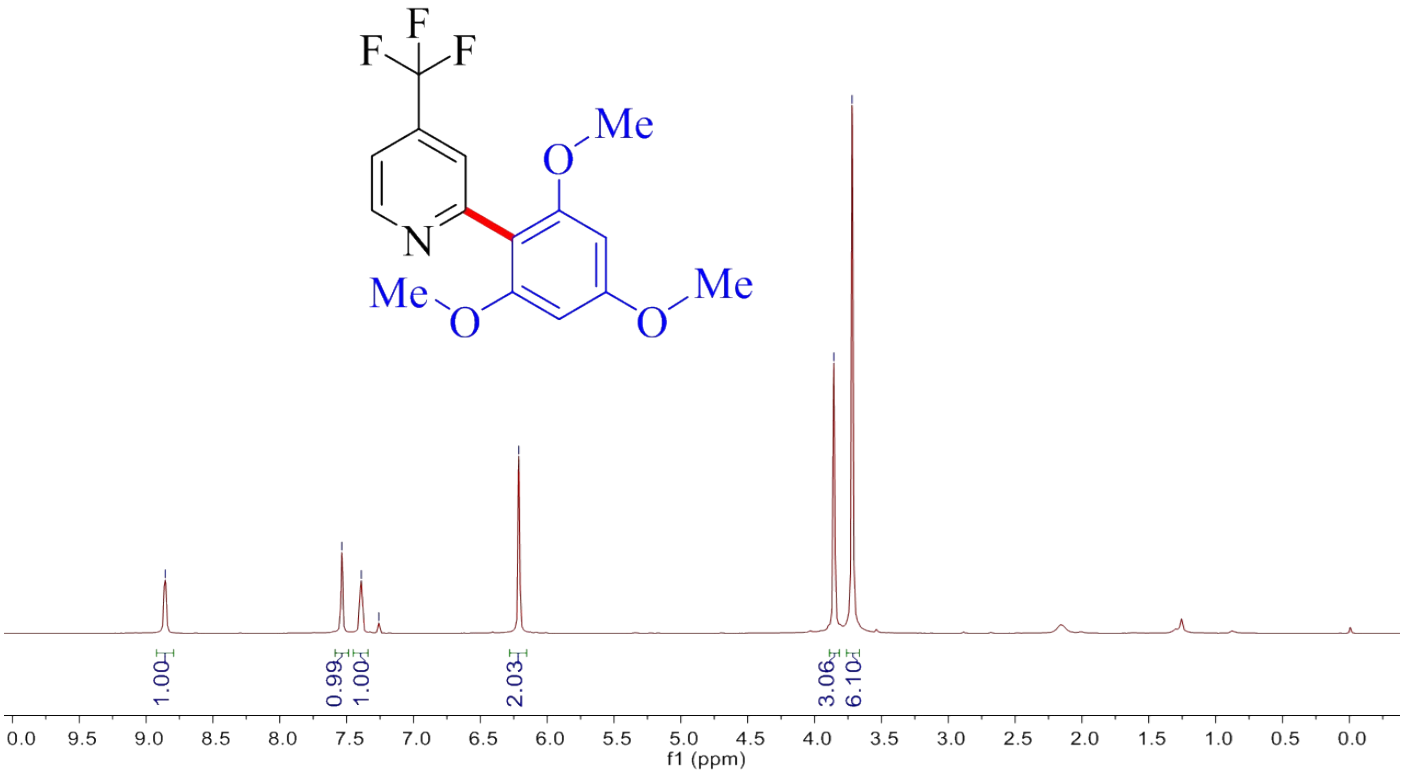


^{13}C NMR (101 MHz, $CDCl_3$)

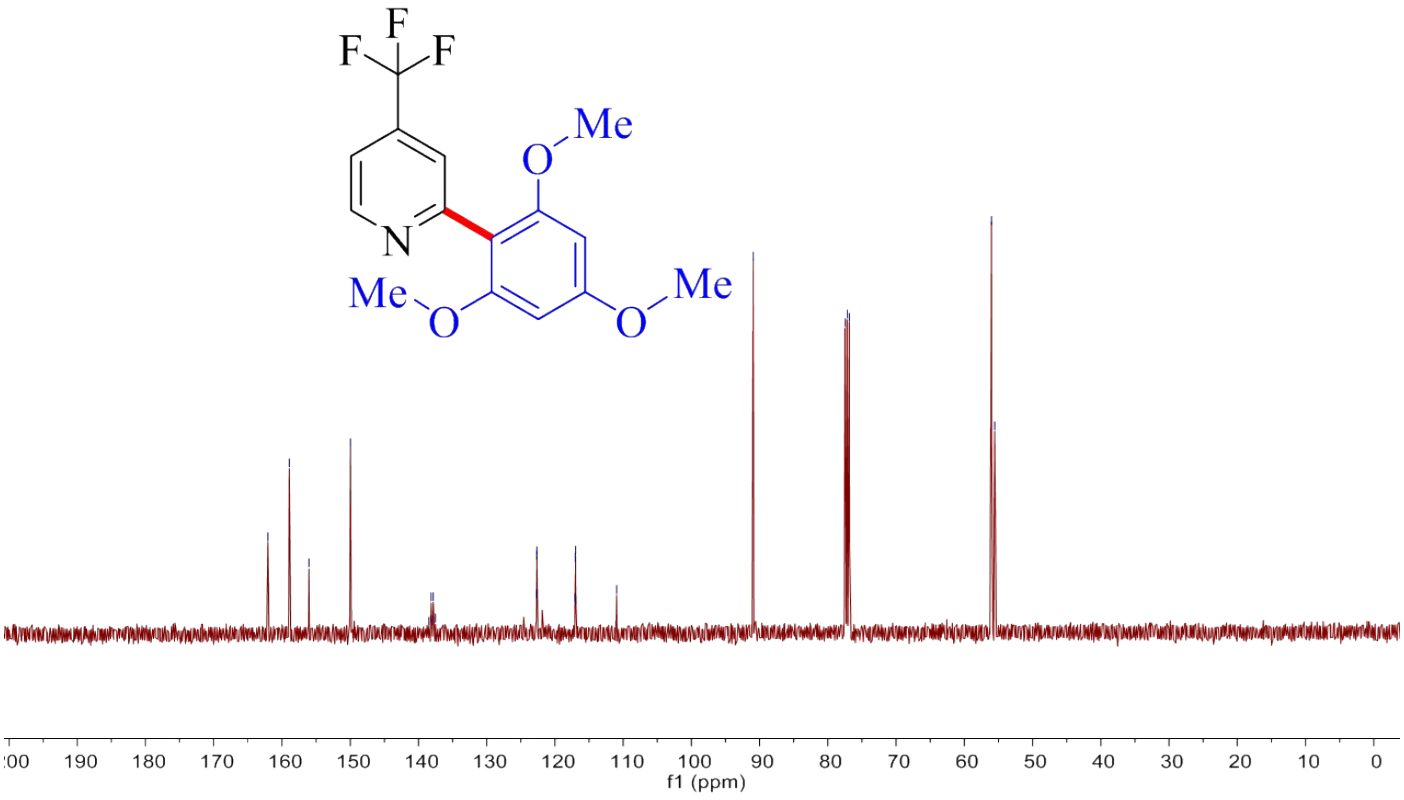


5i

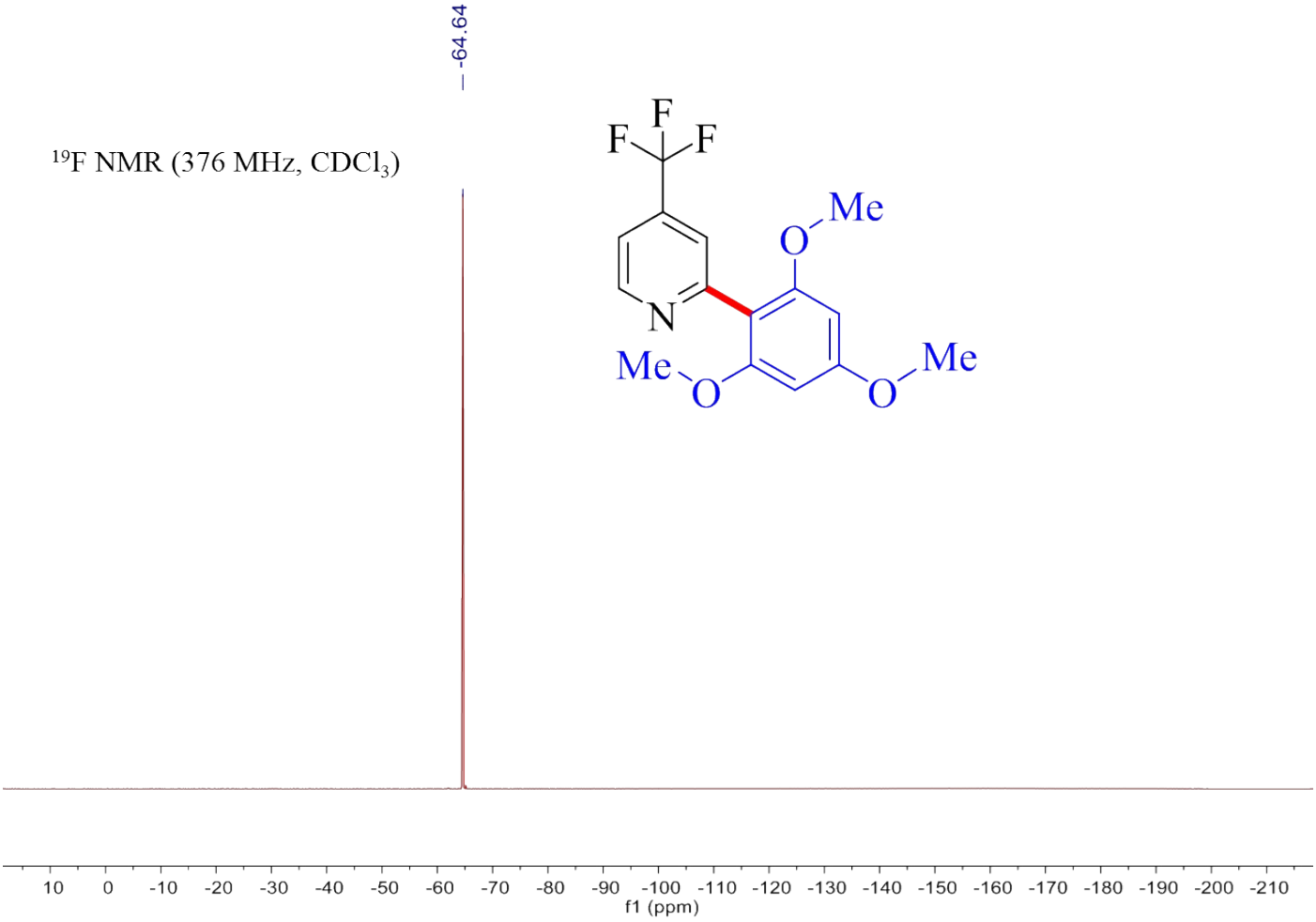
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

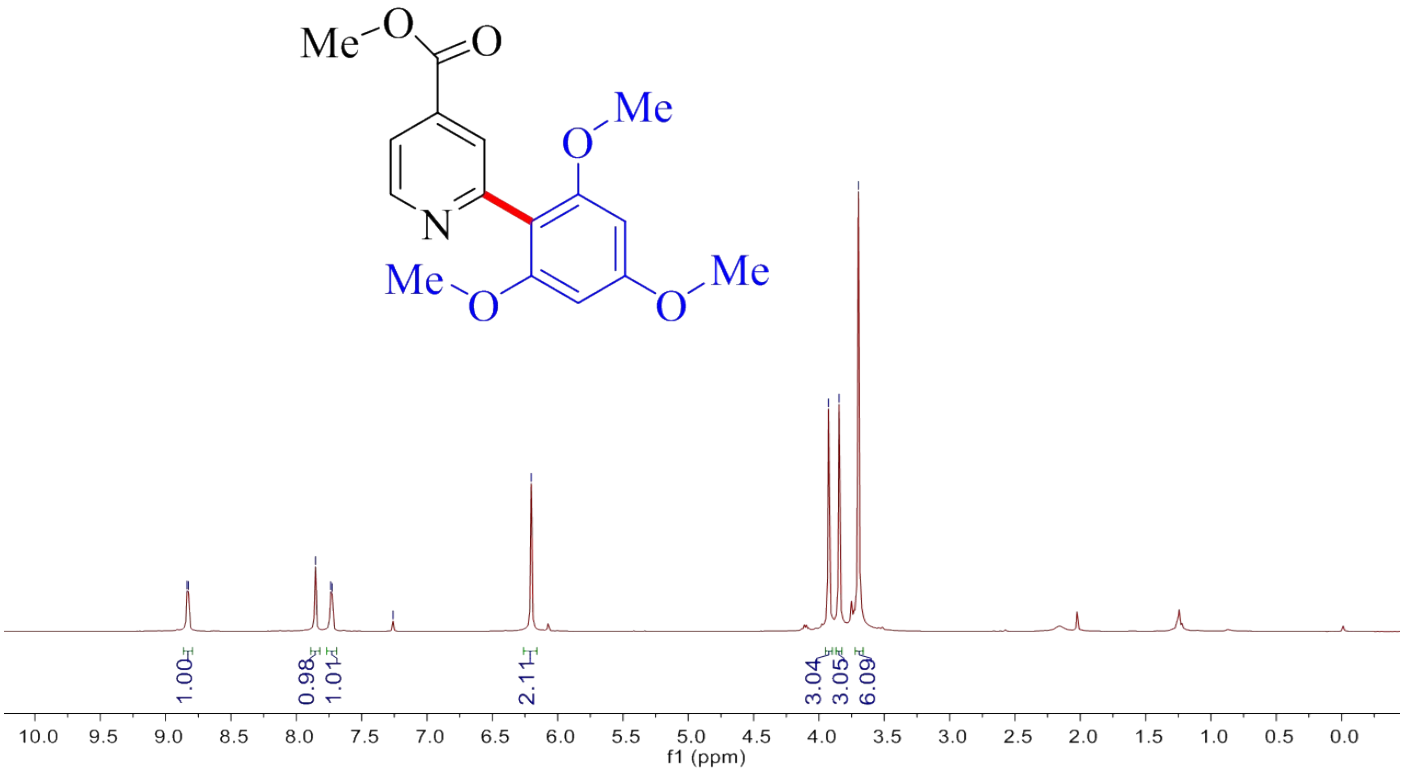


^{19}F NMR (376 MHz, $CDCl_3$)

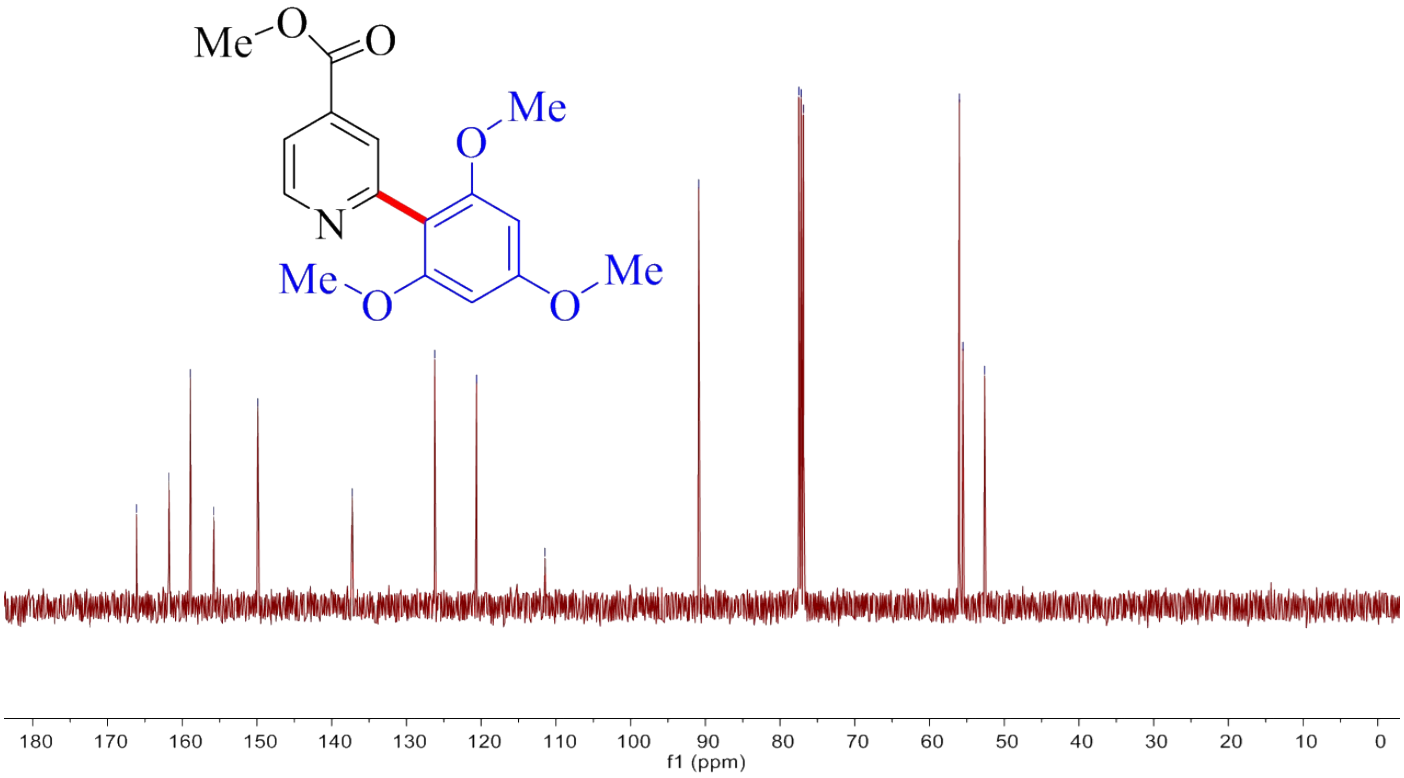


5j

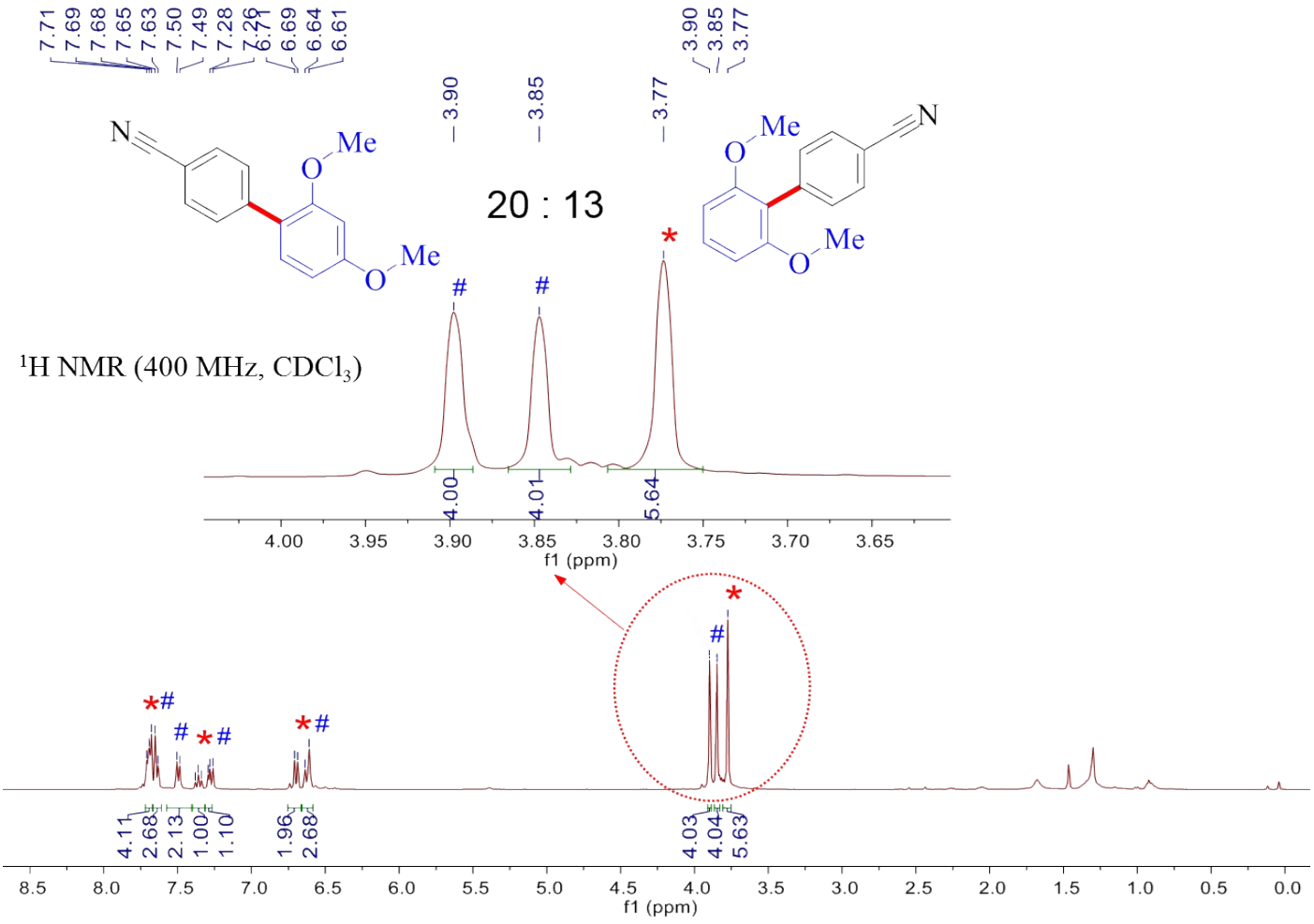
^{1}H NMR (400 MHz, $CDCl_3$)



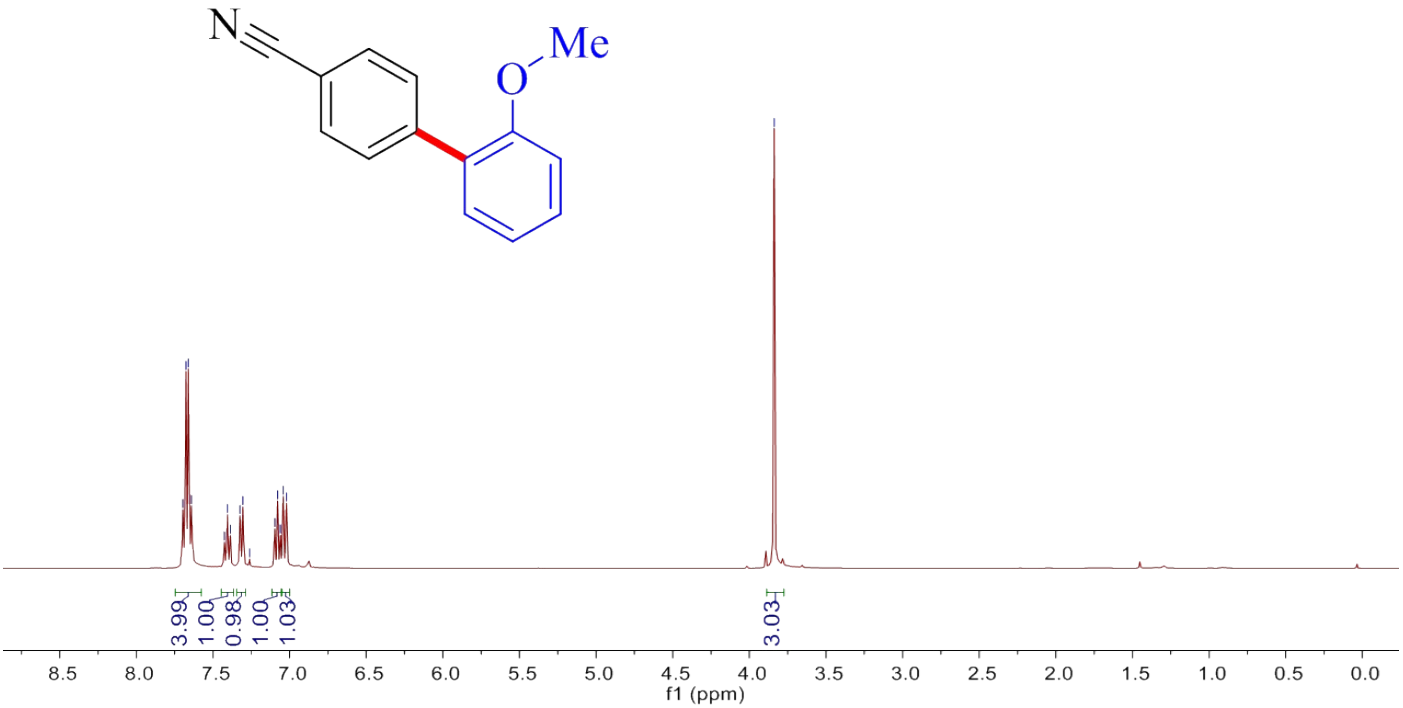
^{13}C NMR (101 MHz, $CDCl_3$)



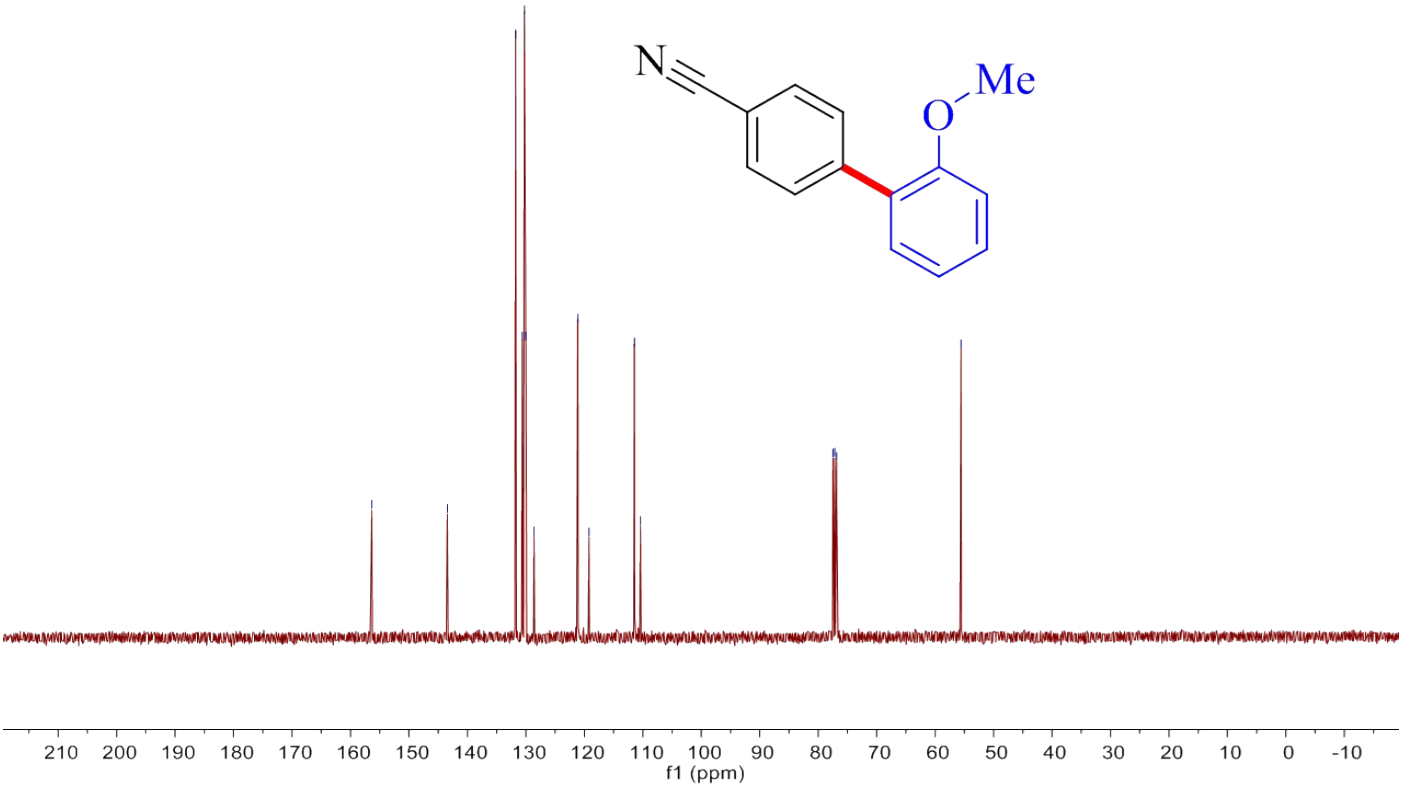
5k


7.71
7.69
7.68
7.65
7.63
7.50
7.49
7.28
7.26
6.71
6.69
6.64
6.61
3.90
3.85
3.77
N
Me
O
Me
O
20 : 13
N
Me
O
Me
O
*
#
#
^{1}H NMR (400 MHz, CDCl$_3$)
4.00
4.01
5.64
4.00 3.95 3.90 3.85 3.80 3.75 3.70 3.65
f1 (ppm)
*#
#
*#
*#
4.11
2.68
2.13
1.00
1.10
1.96
2.68
4.03
4.04
5.63
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

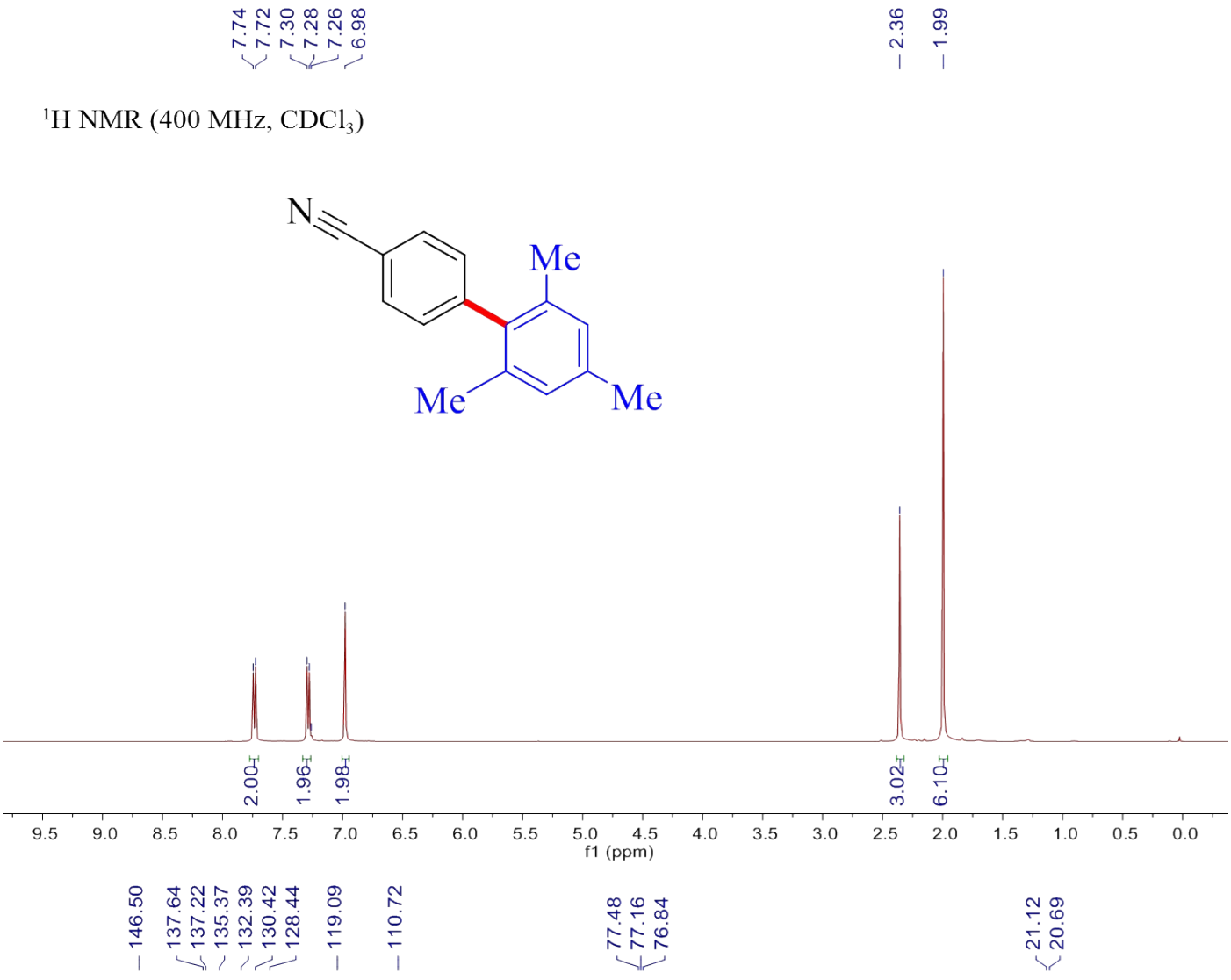
^{1}H NMR (400 MHz, $CDCl_3$)



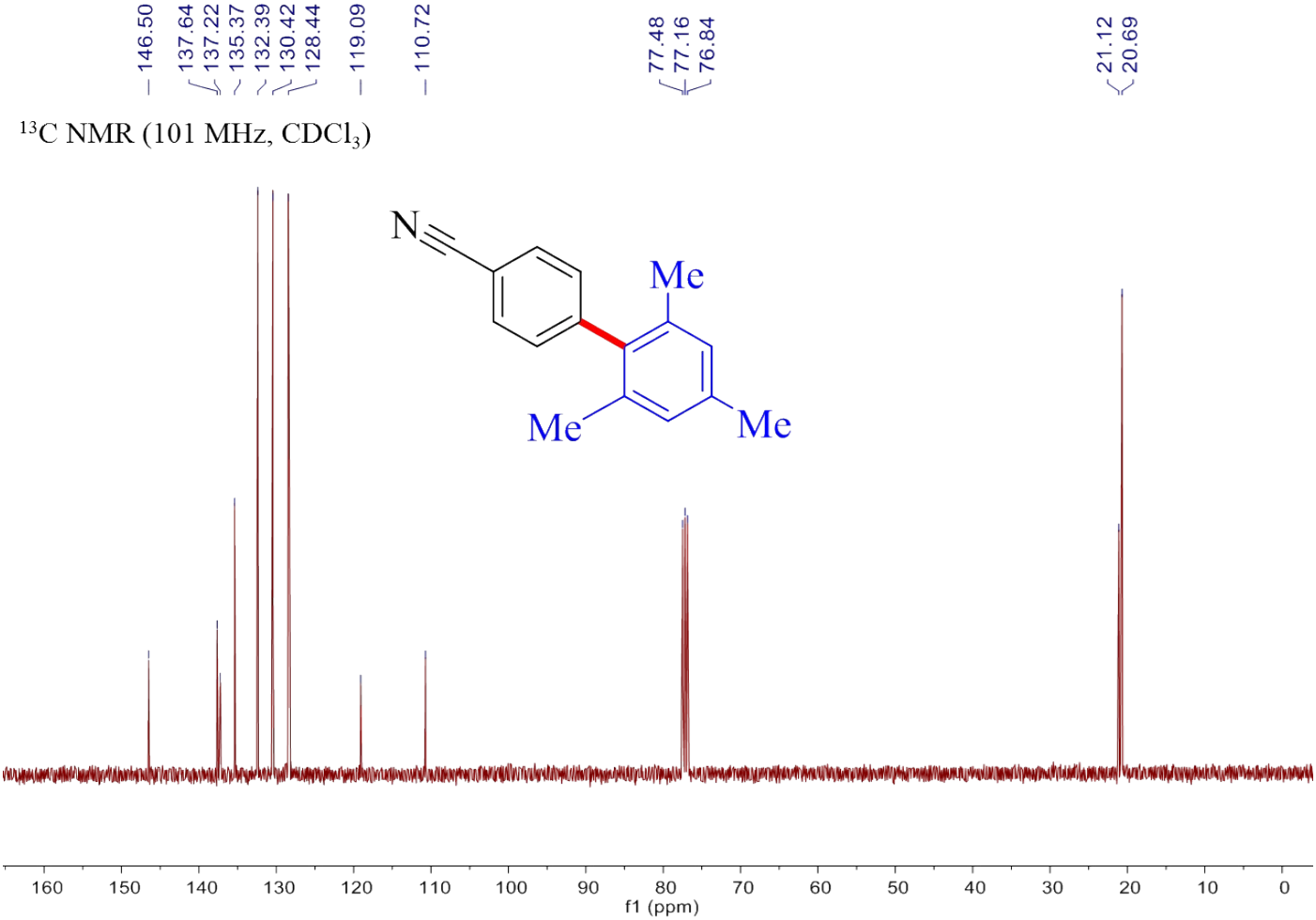
^{13}C NMR (101 MHz, $CDCl_3$)



5m



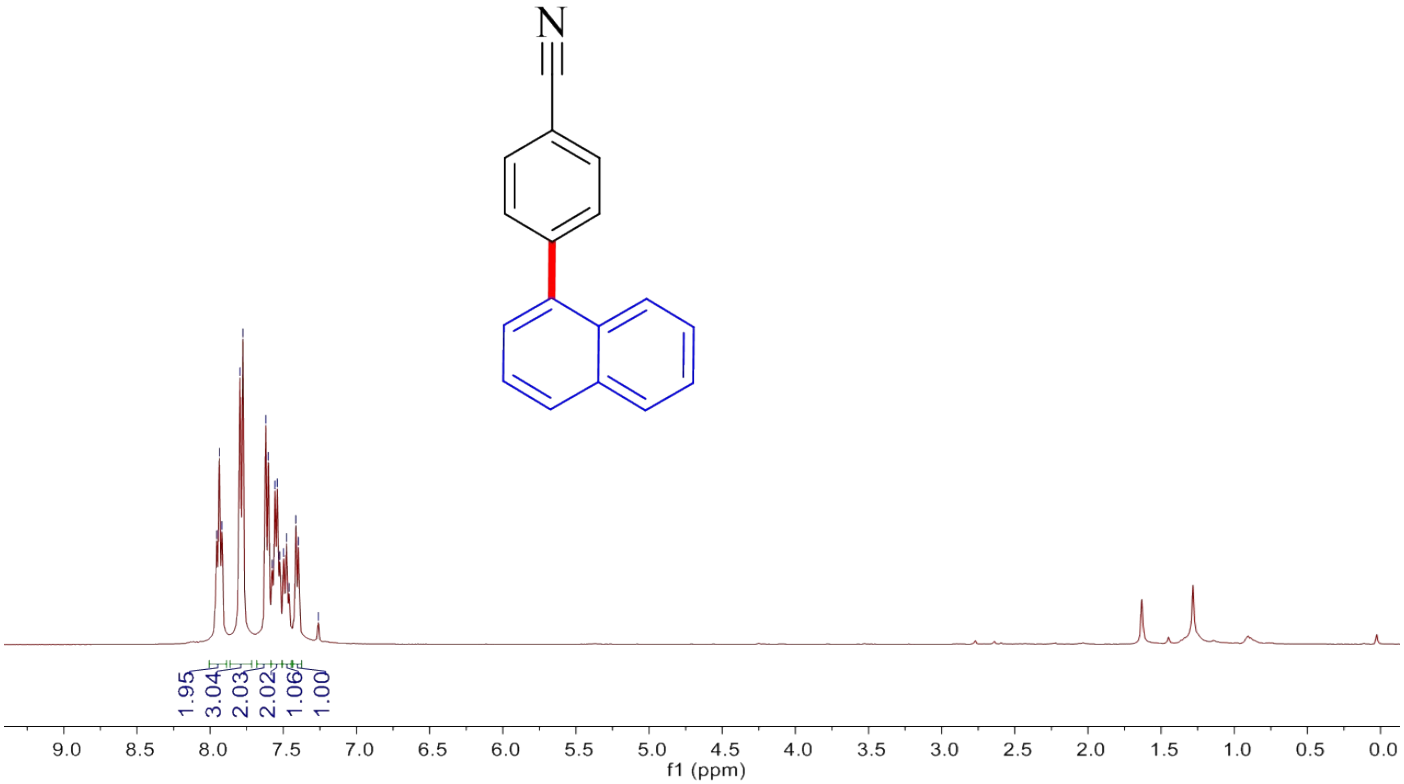
^{1}H NMR (400 MHz, $CDCl_3$)



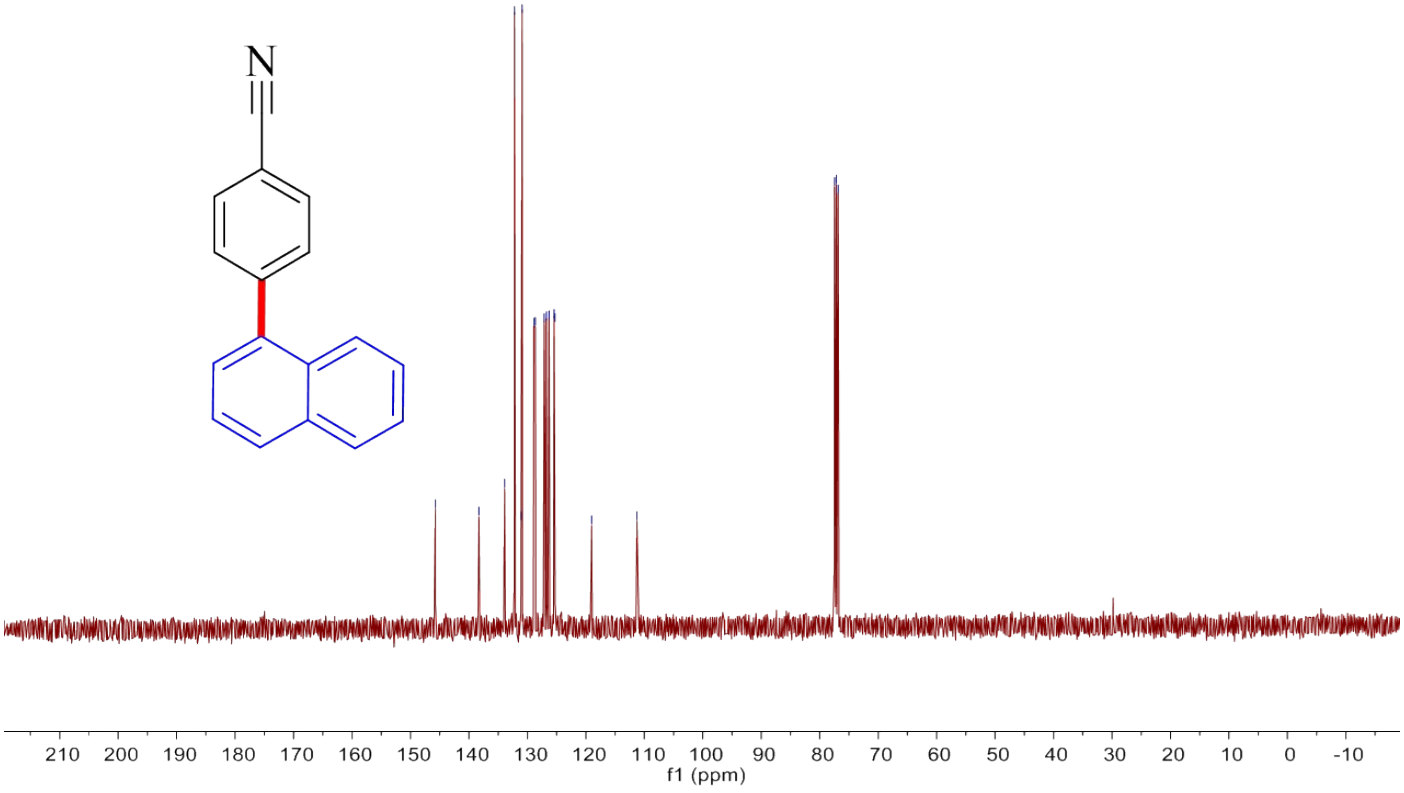
^{13}C NMR (101 MHz, $CDCl_3$)

5n-a

^{1}H NMR (400 MHz, $CDCl_3$)

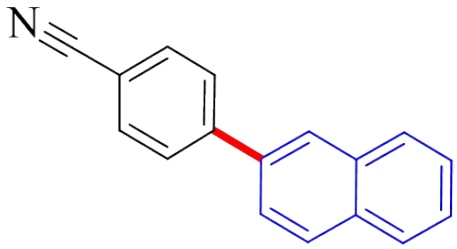


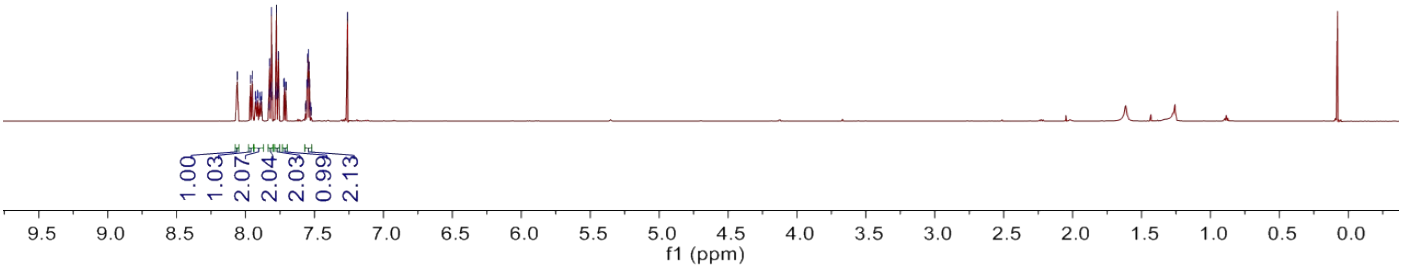
^{13}C NMR (101 MHz, $CDCl_3$)

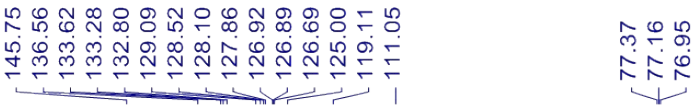


5n-b

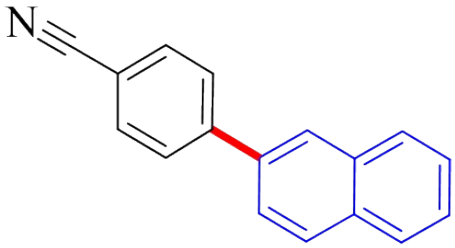
^{1}H NMR (600 MHz, $CDCl_3$)

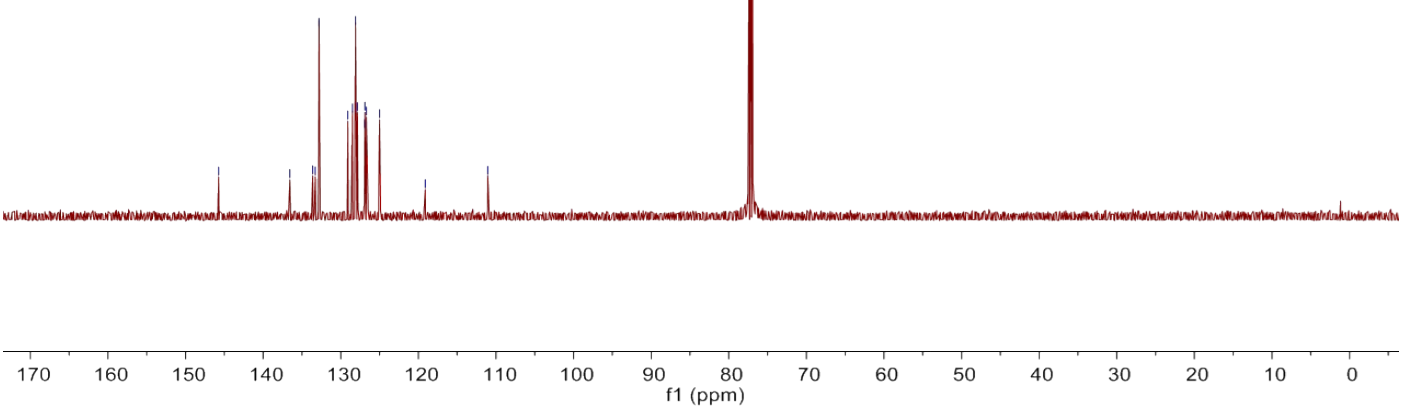






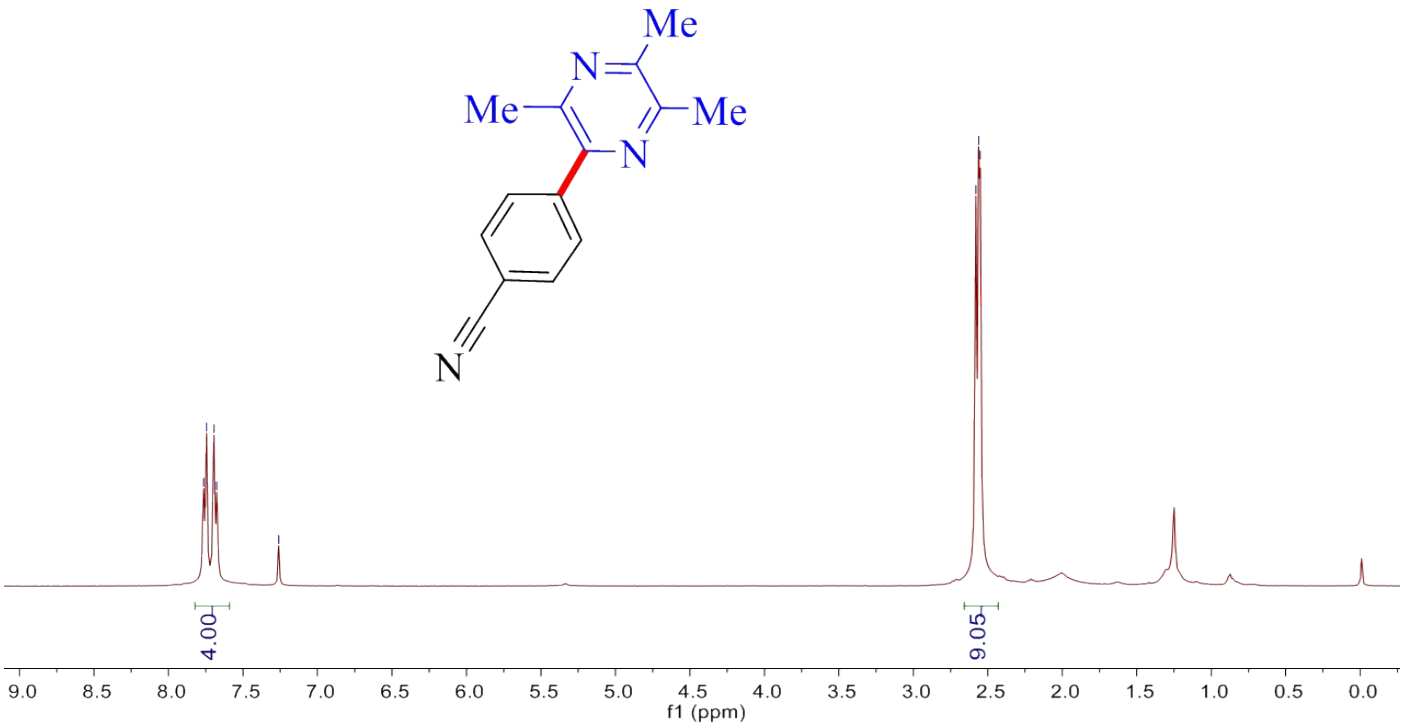
^{13}C NMR (151 MHz, $CDCl_3$)



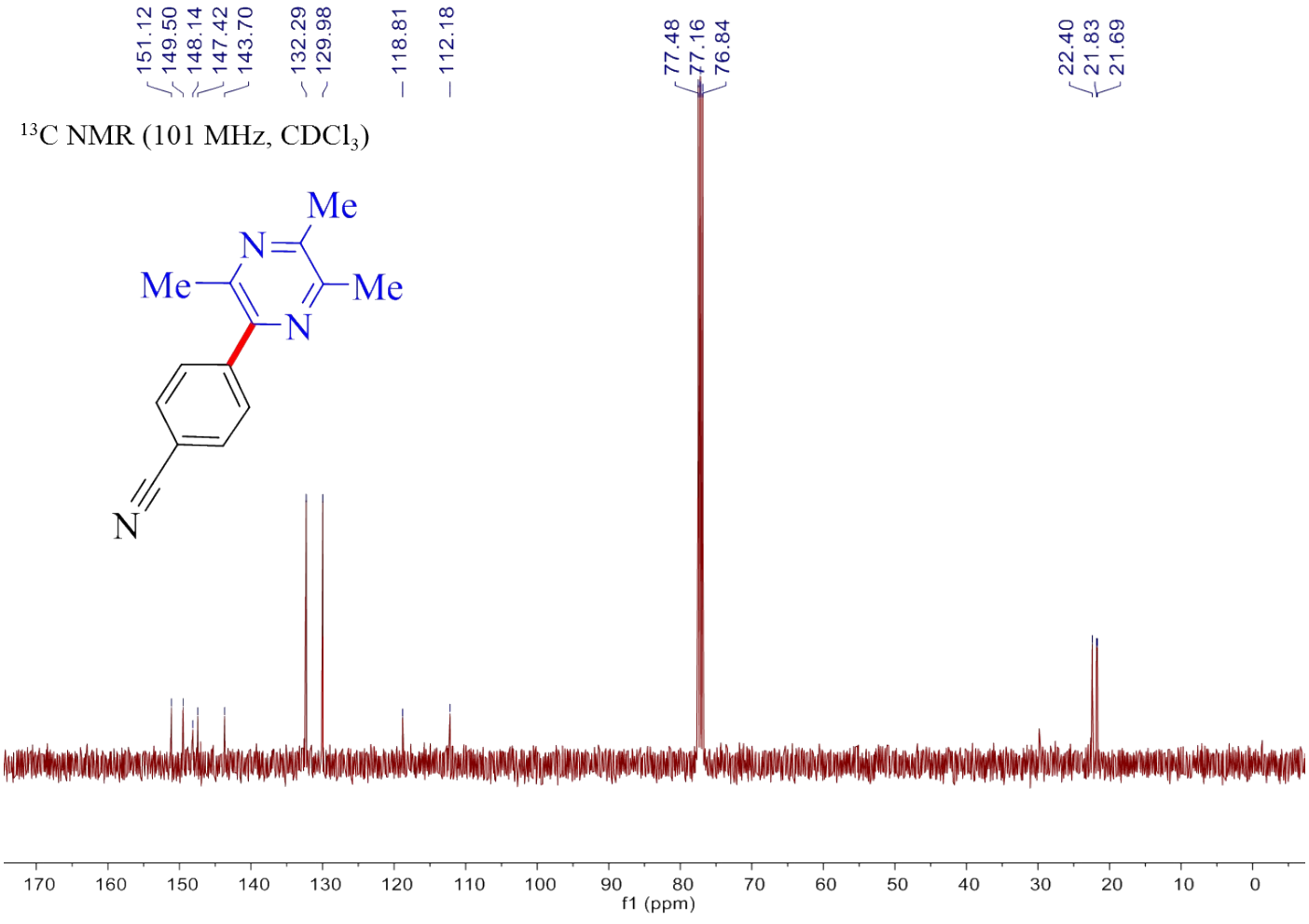


5o

^{1}H NMR (400 MHz, $CDCl_3$)

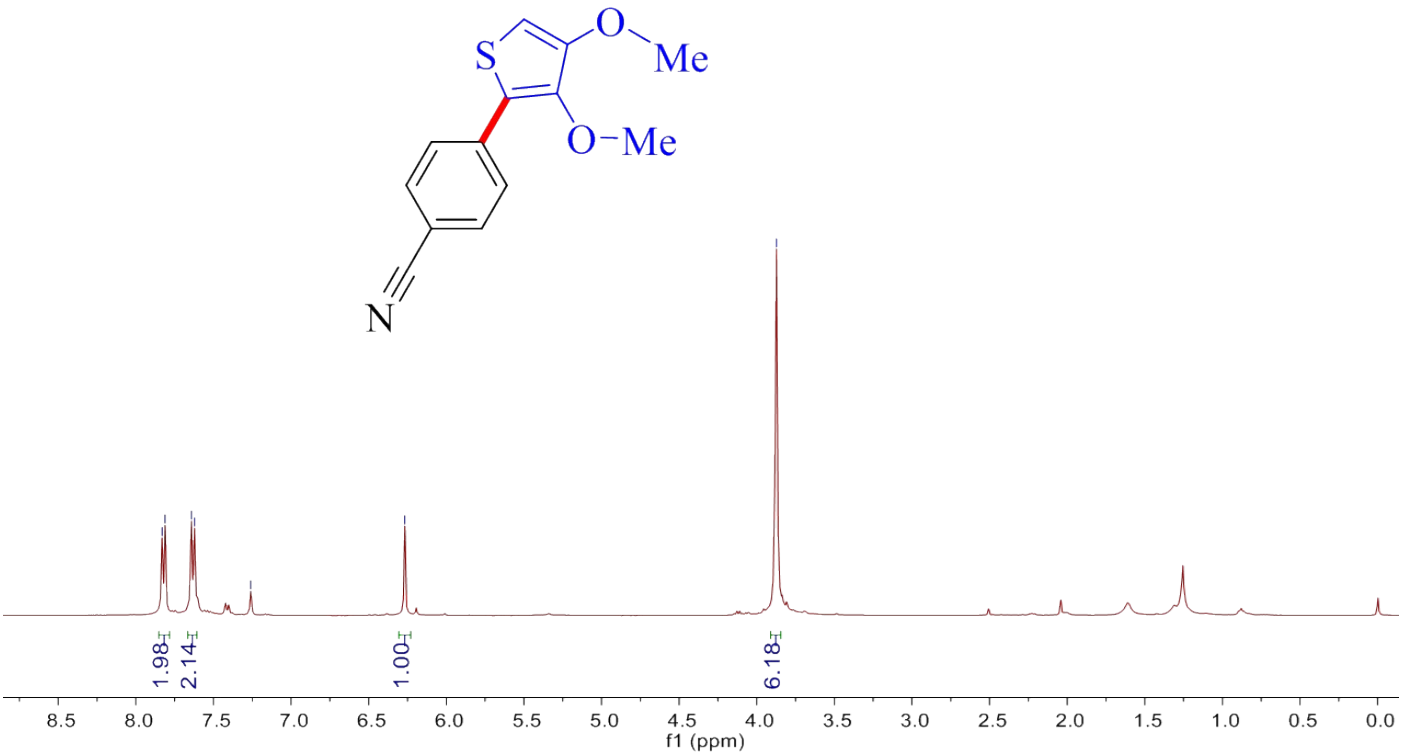


^{13}C NMR (101 MHz, $CDCl_3$)

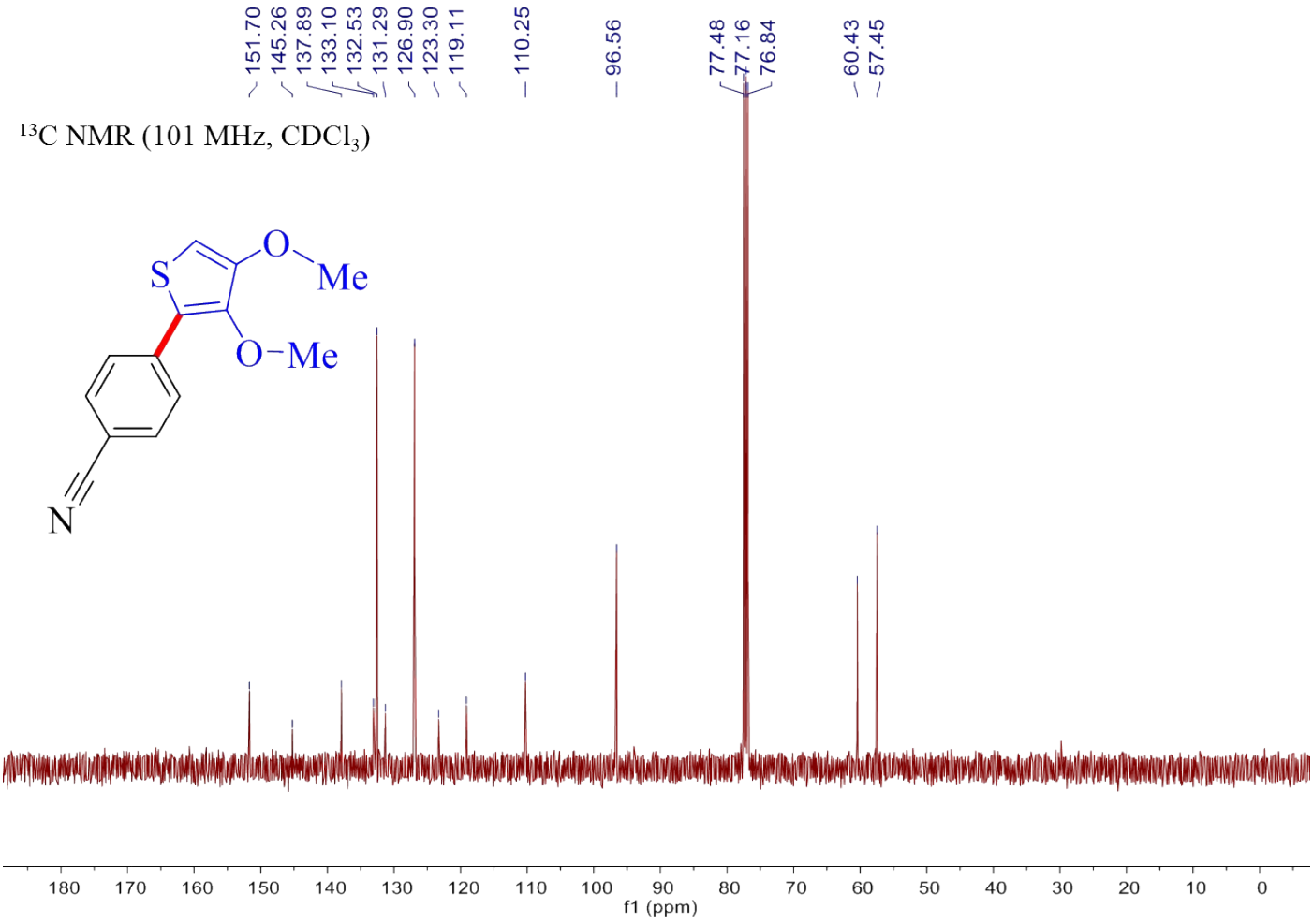


5p

^{1}H NMR (400 MHz, $CDCl_3$)

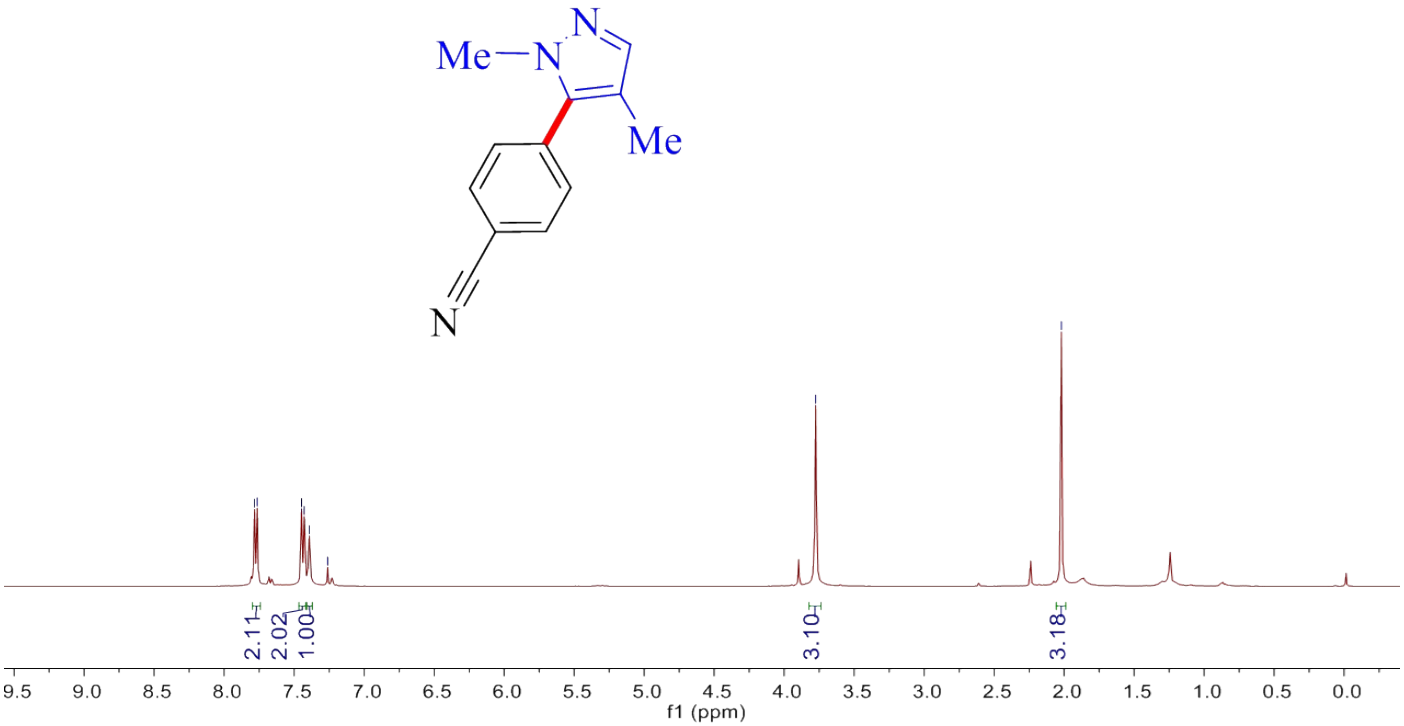


^{13}C NMR (101 MHz, $CDCl_3$)

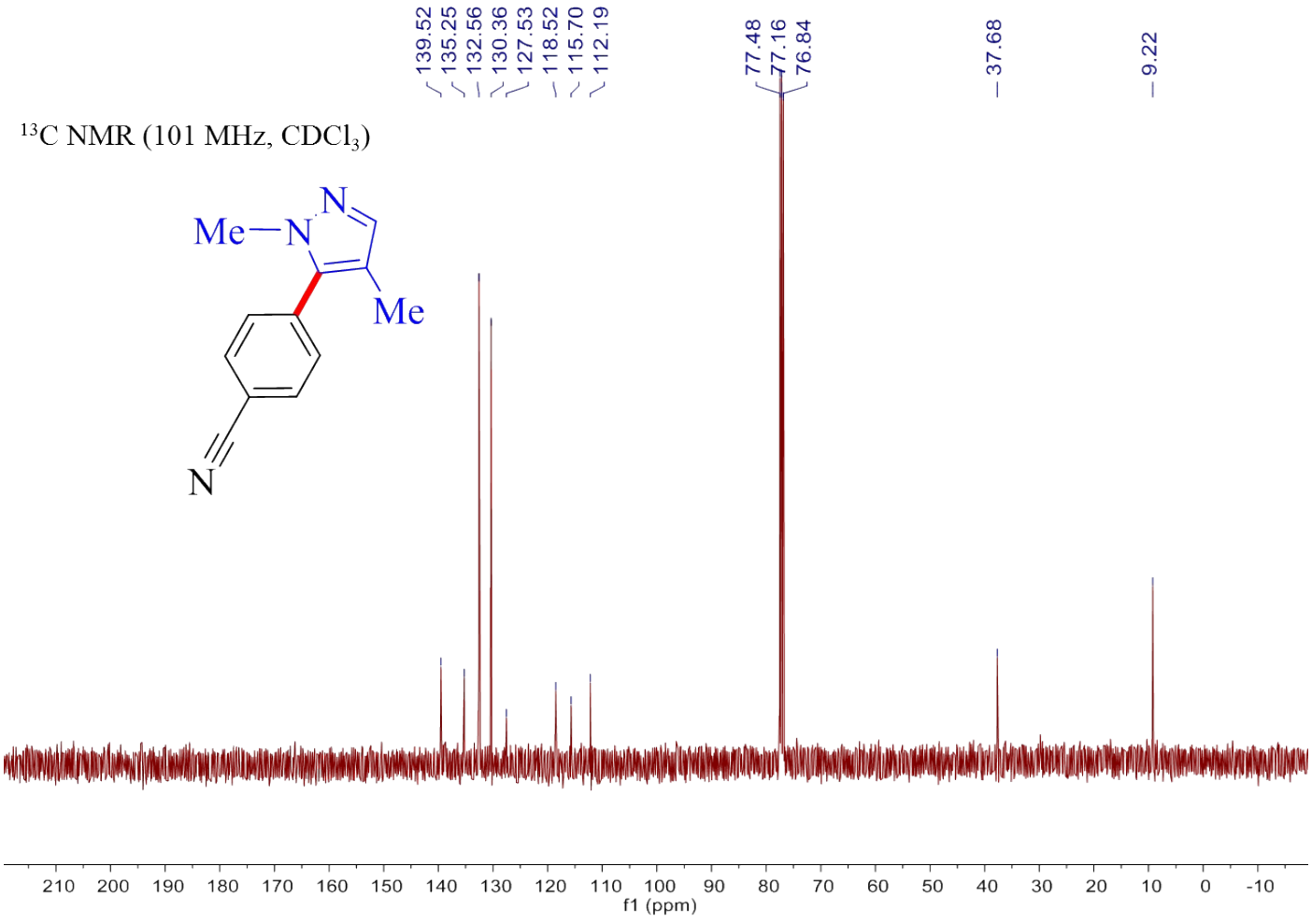


5q

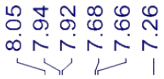
^{1}H NMR (400 MHz, $CDCl_3$)



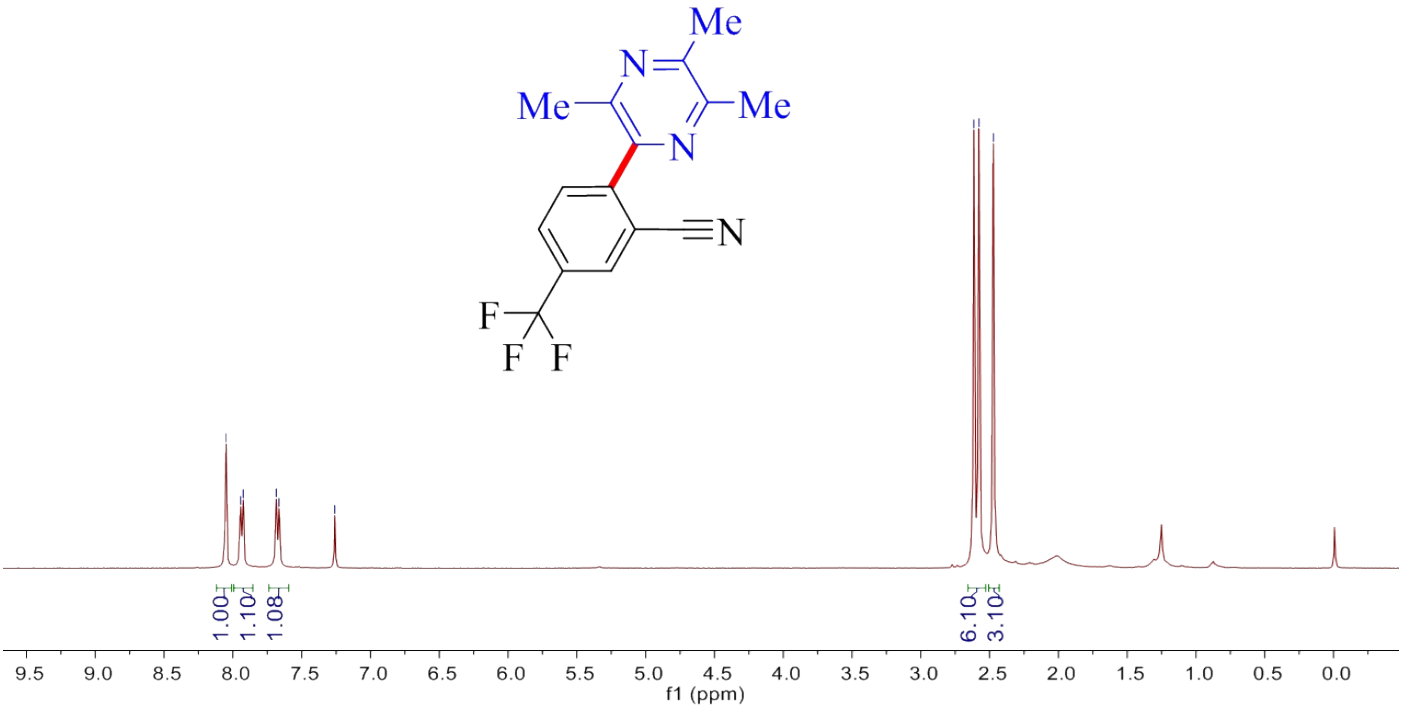
^{13}C NMR (101 MHz, $CDCl_3$)

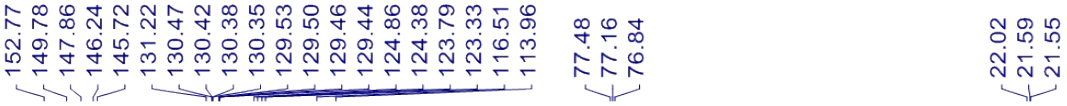


5r

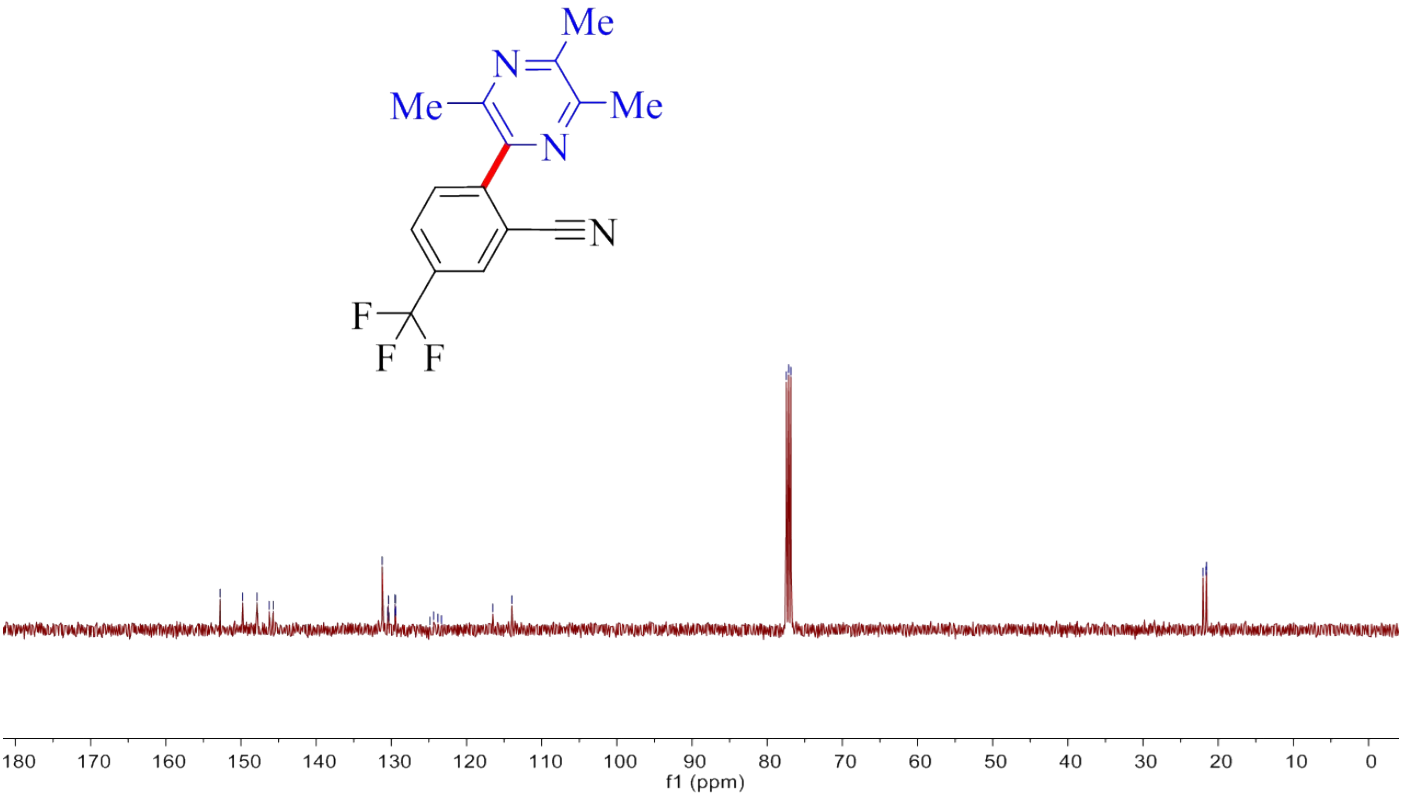


^{1}H NMR (400 MHz, $CDCl_3$)

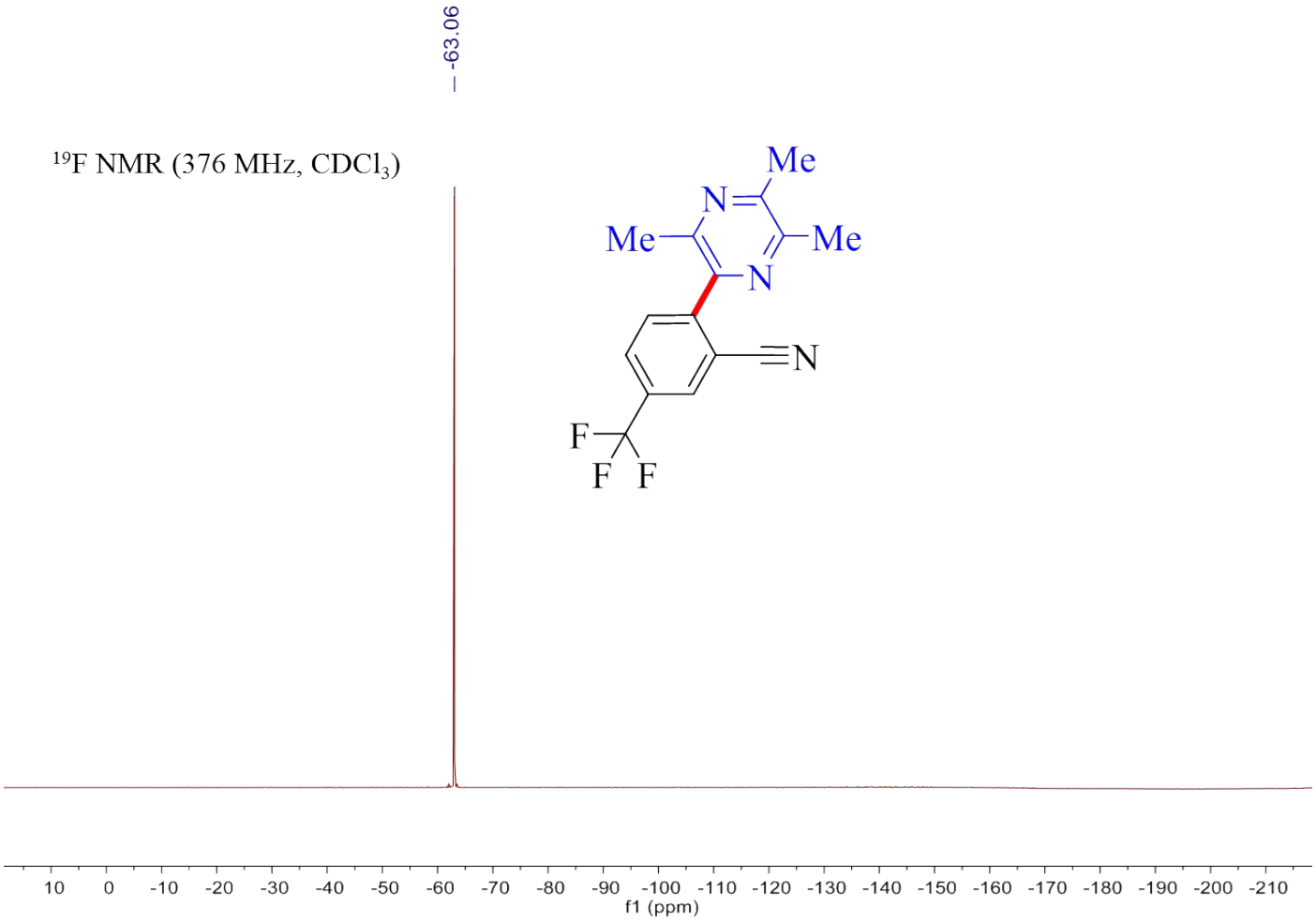




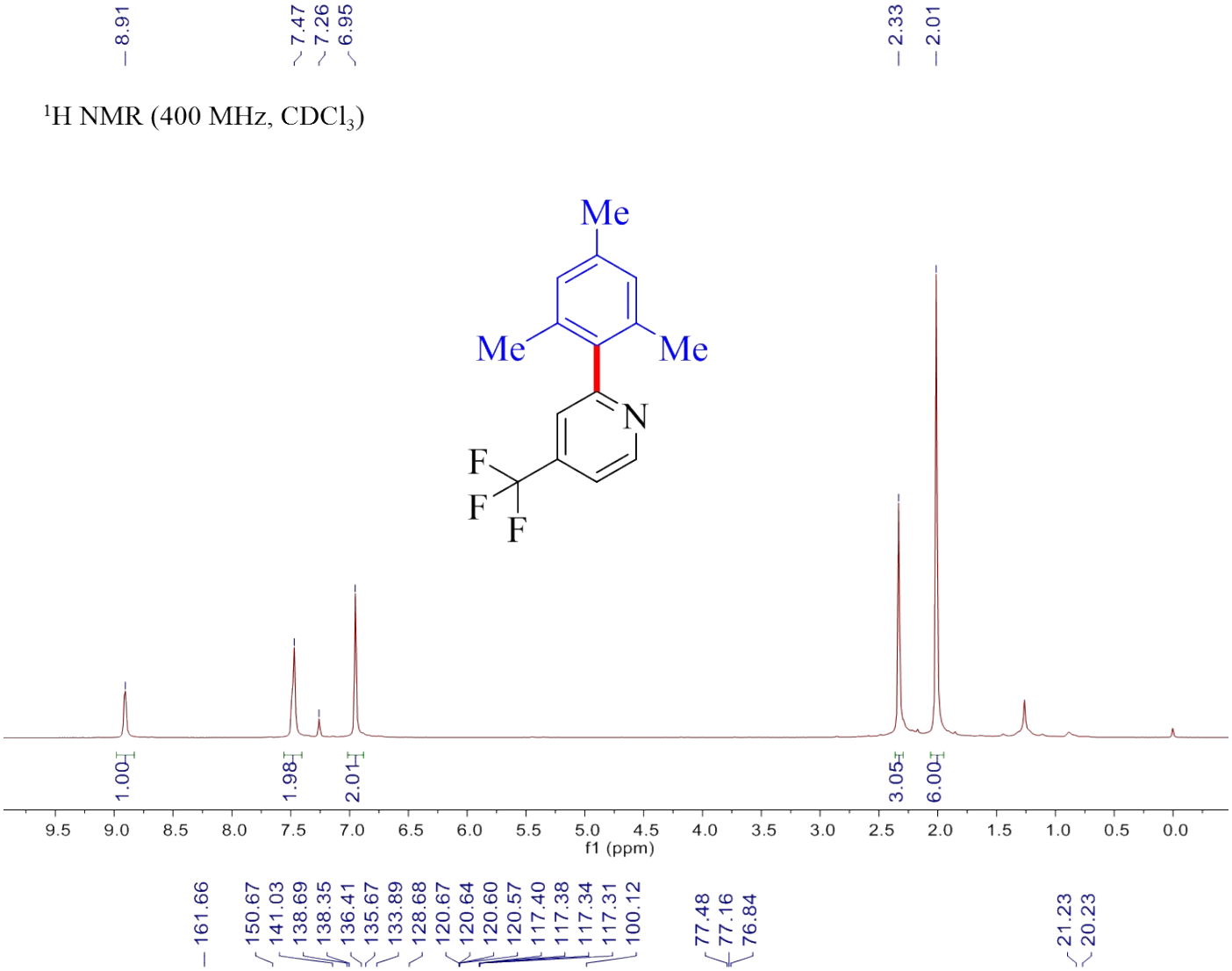
^{13}C NMR (101 MHz, $CDCl_3$)



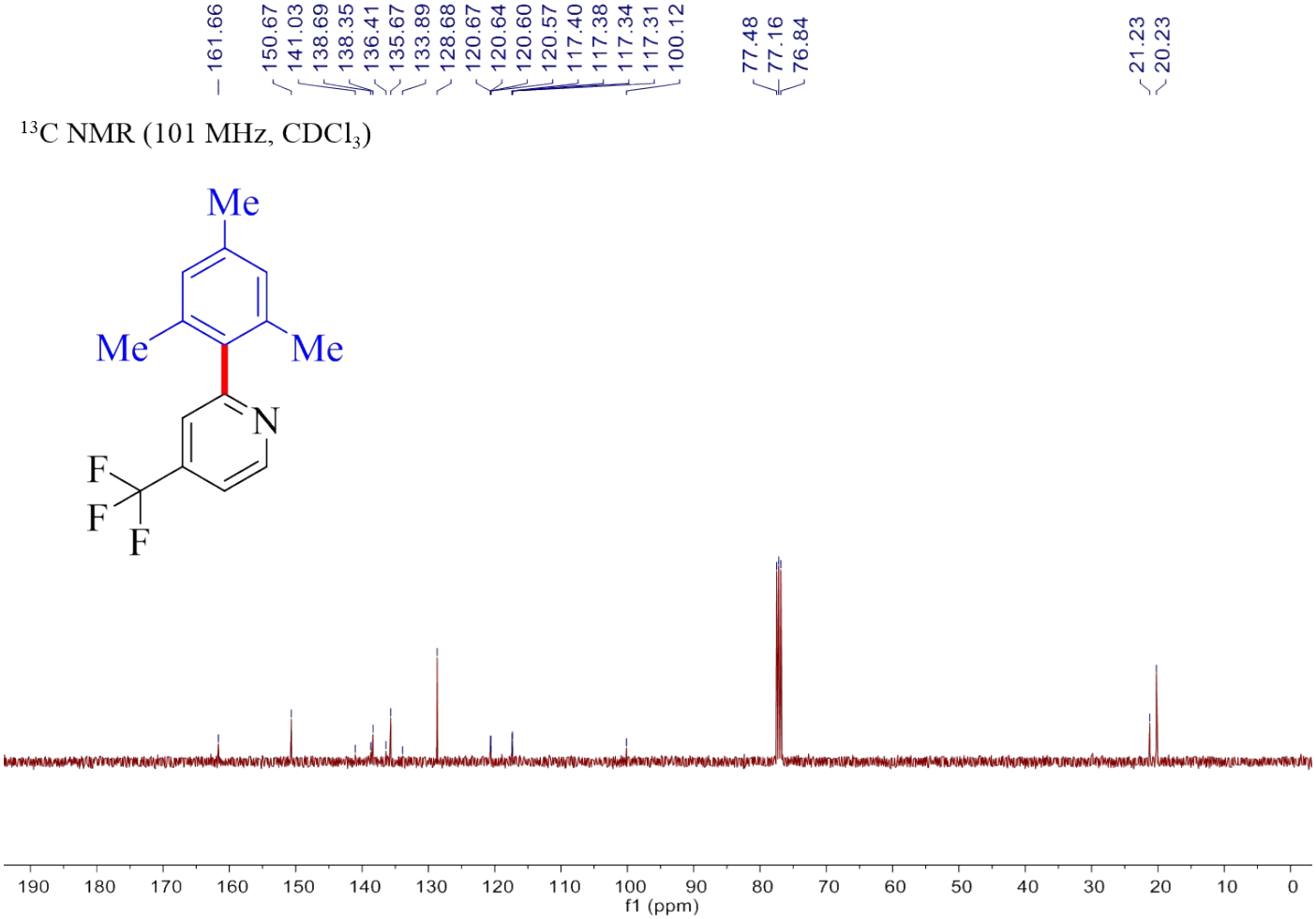
^{19}F NMR (376 MHz, $CDCl_3$)



5s

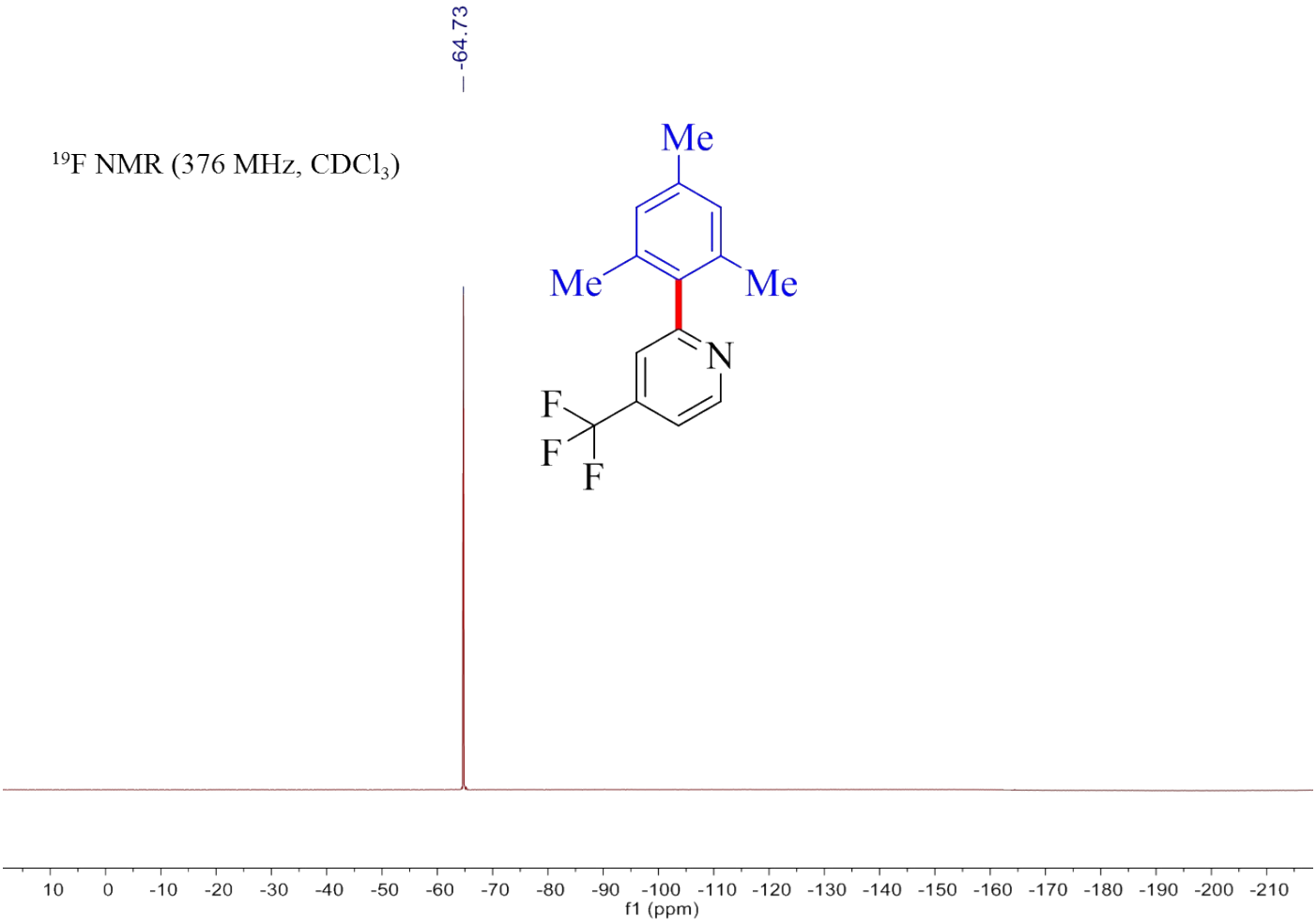


^{1}H NMR (400 MHz, $CDCl_3$)

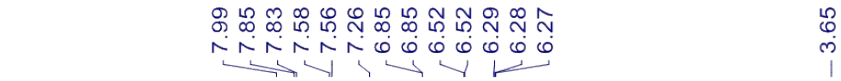


^{13}C NMR (101 MHz, $CDCl_3$)

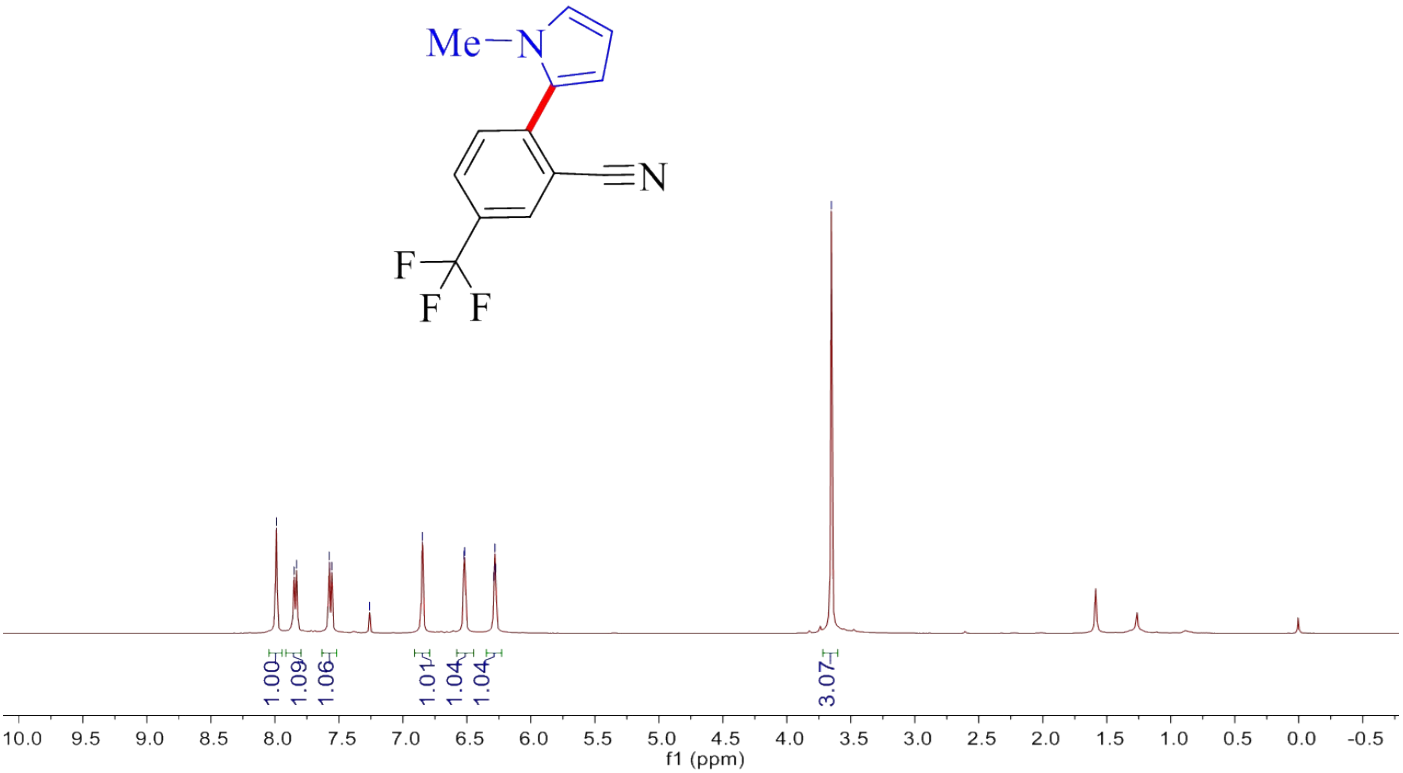
^{19}F NMR (376 MHz, $CDCl_3$)

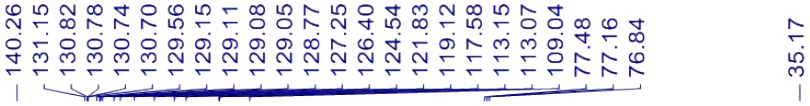


5t

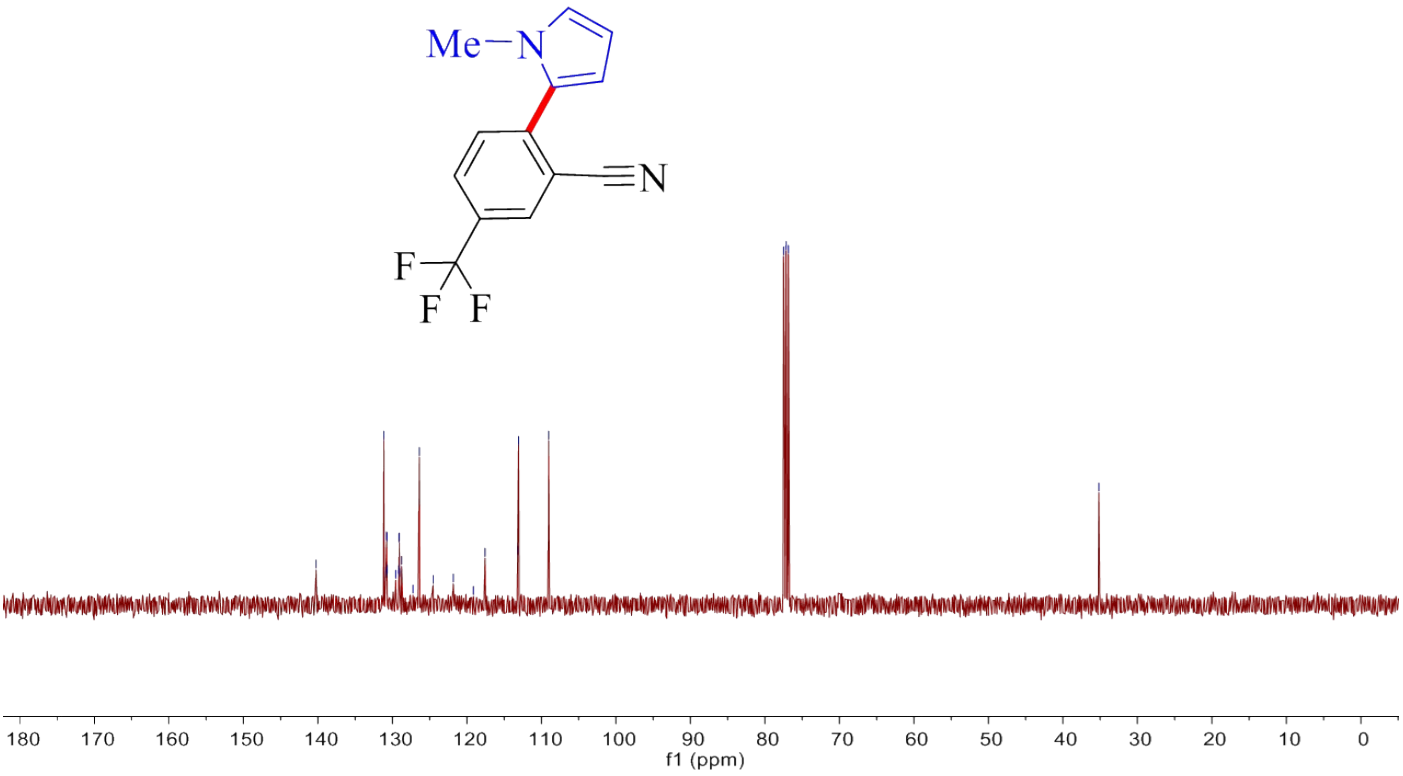


^{1}H NMR (400 MHz, $CDCl_3$)

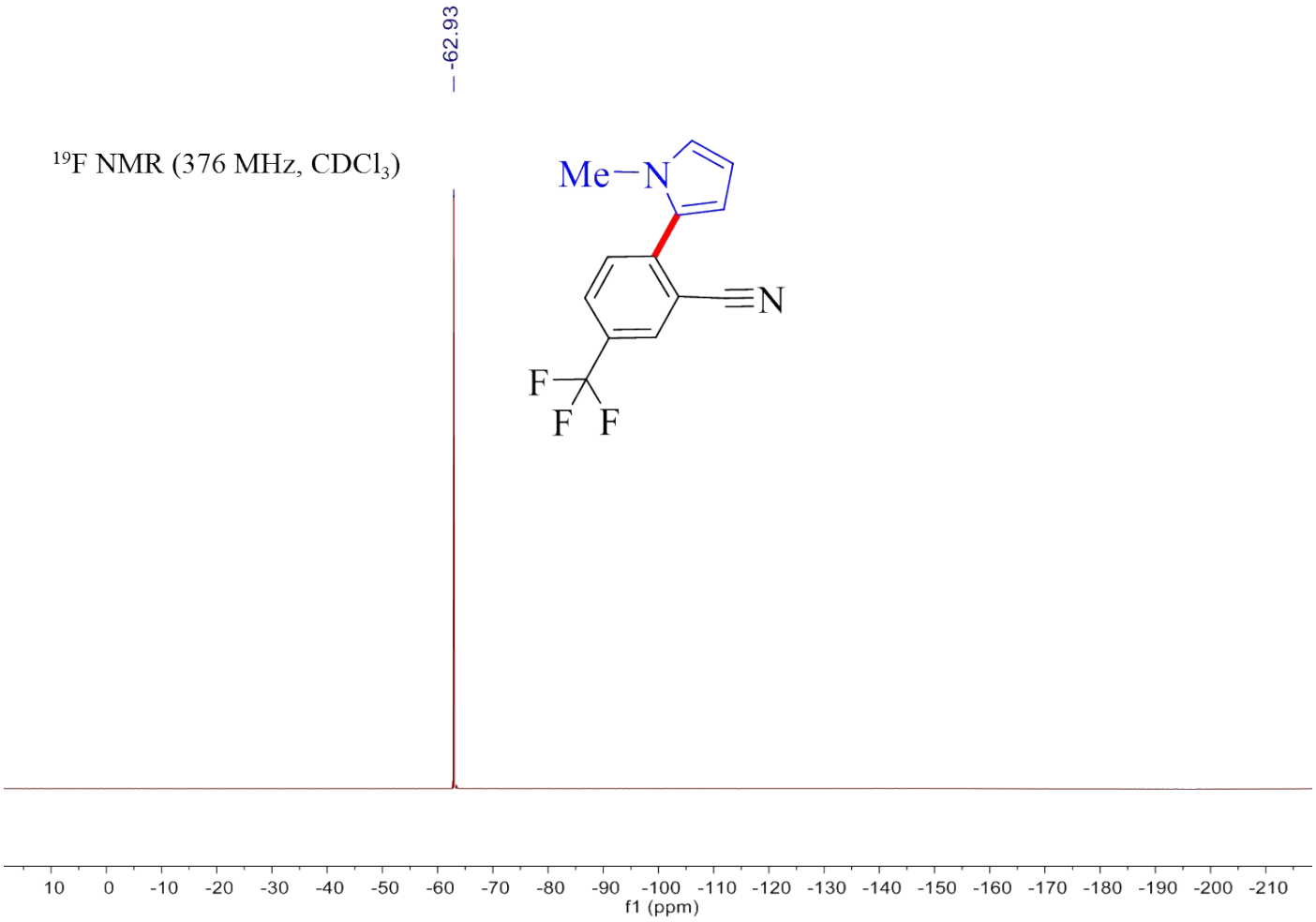




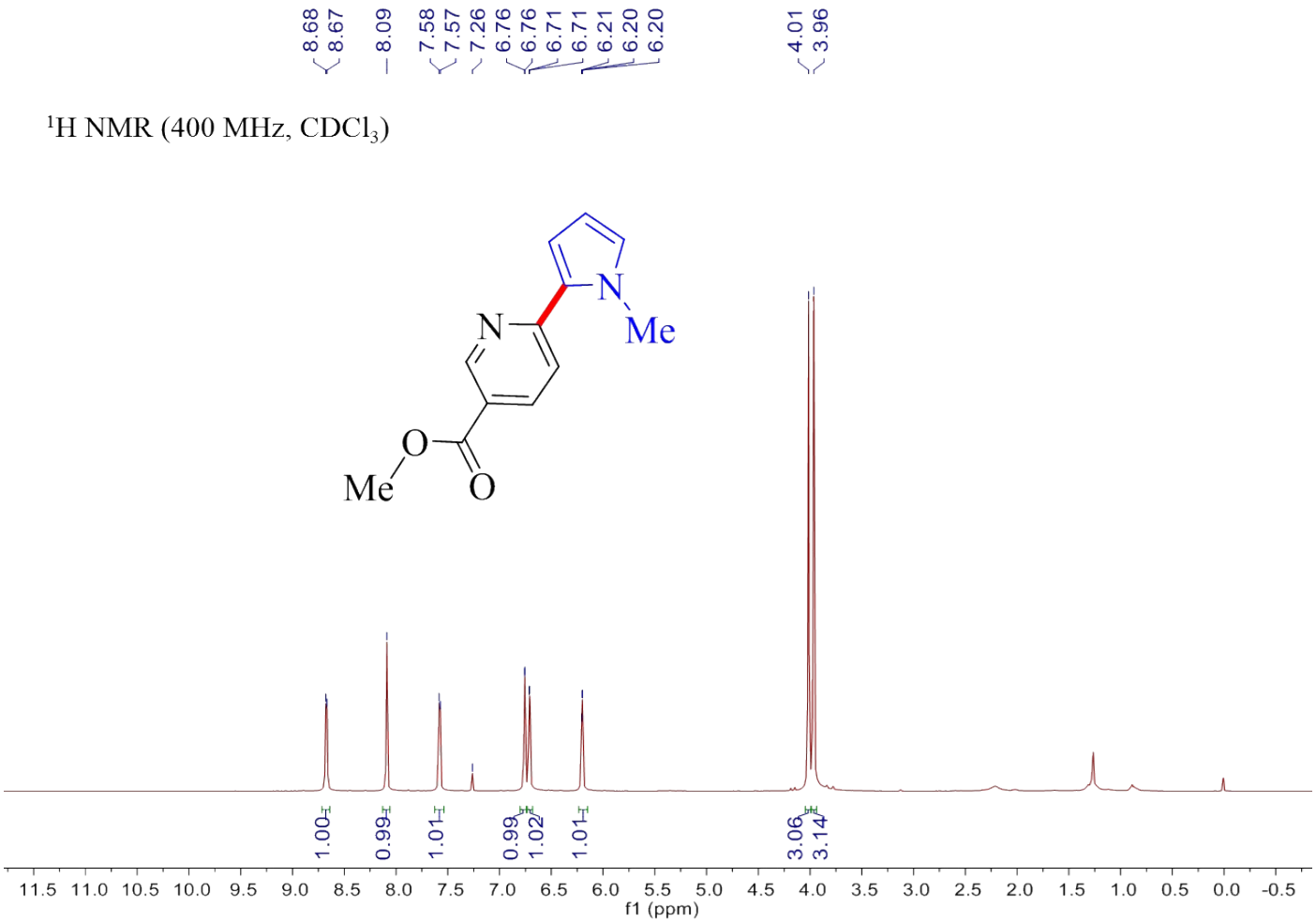
^{13}C NMR (101 MHz, $CDCl_3$)



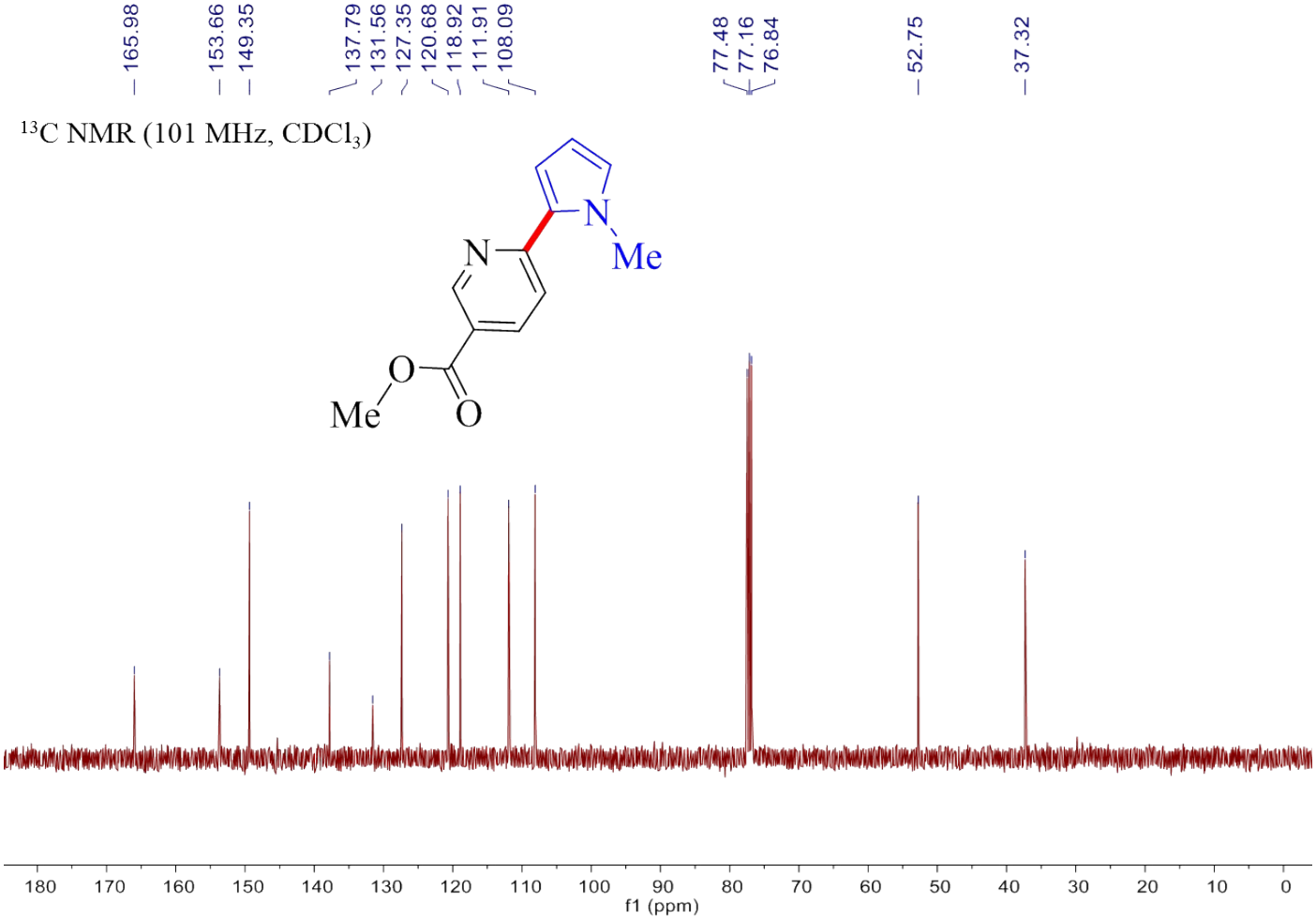
^{19}F NMR (376 MHz, $CDCl_3$)



5u

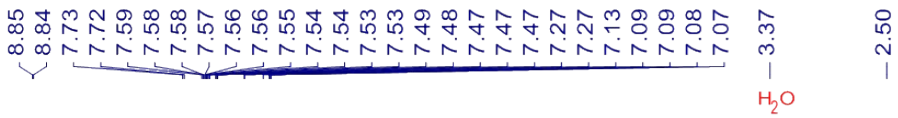


^{1}H NMR (400 MHz, $CDCl_3$)

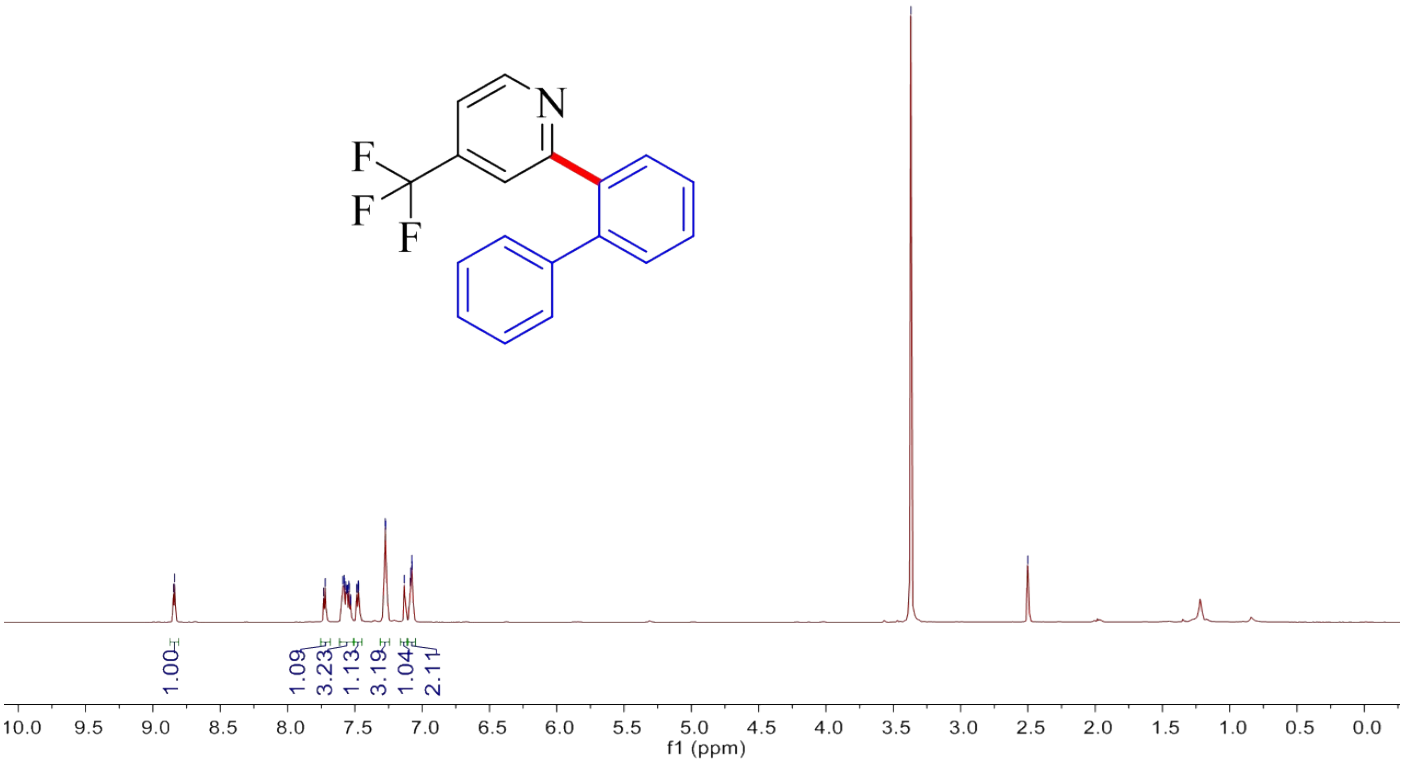


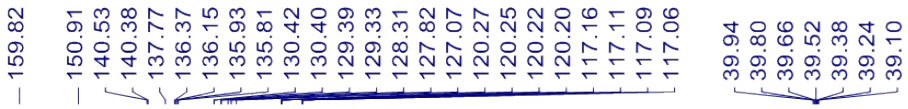
^{13}C NMR (101 MHz, $CDCl_3$)

5v-a

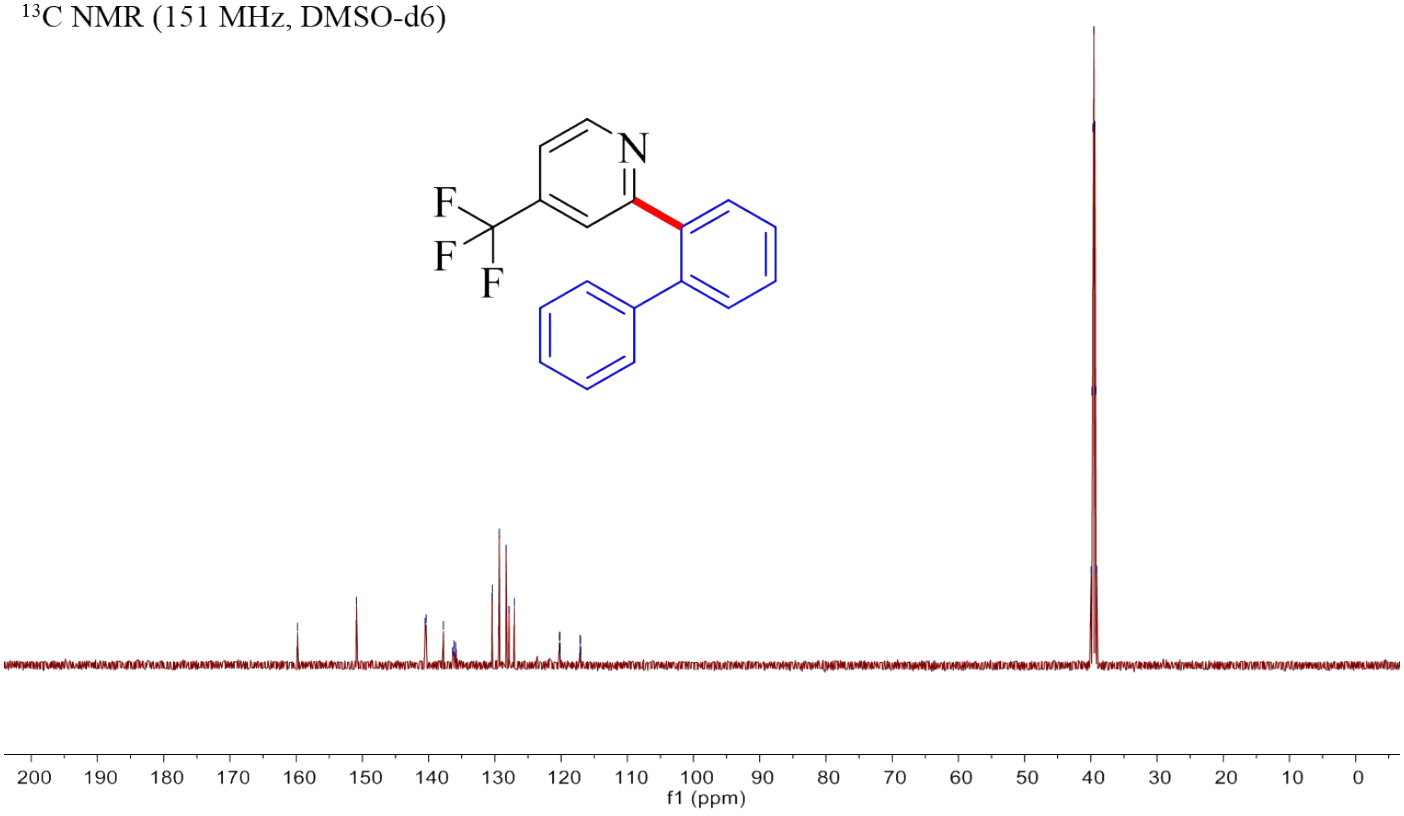


^{1}H NMR (600 MHz, DMSO-d6)

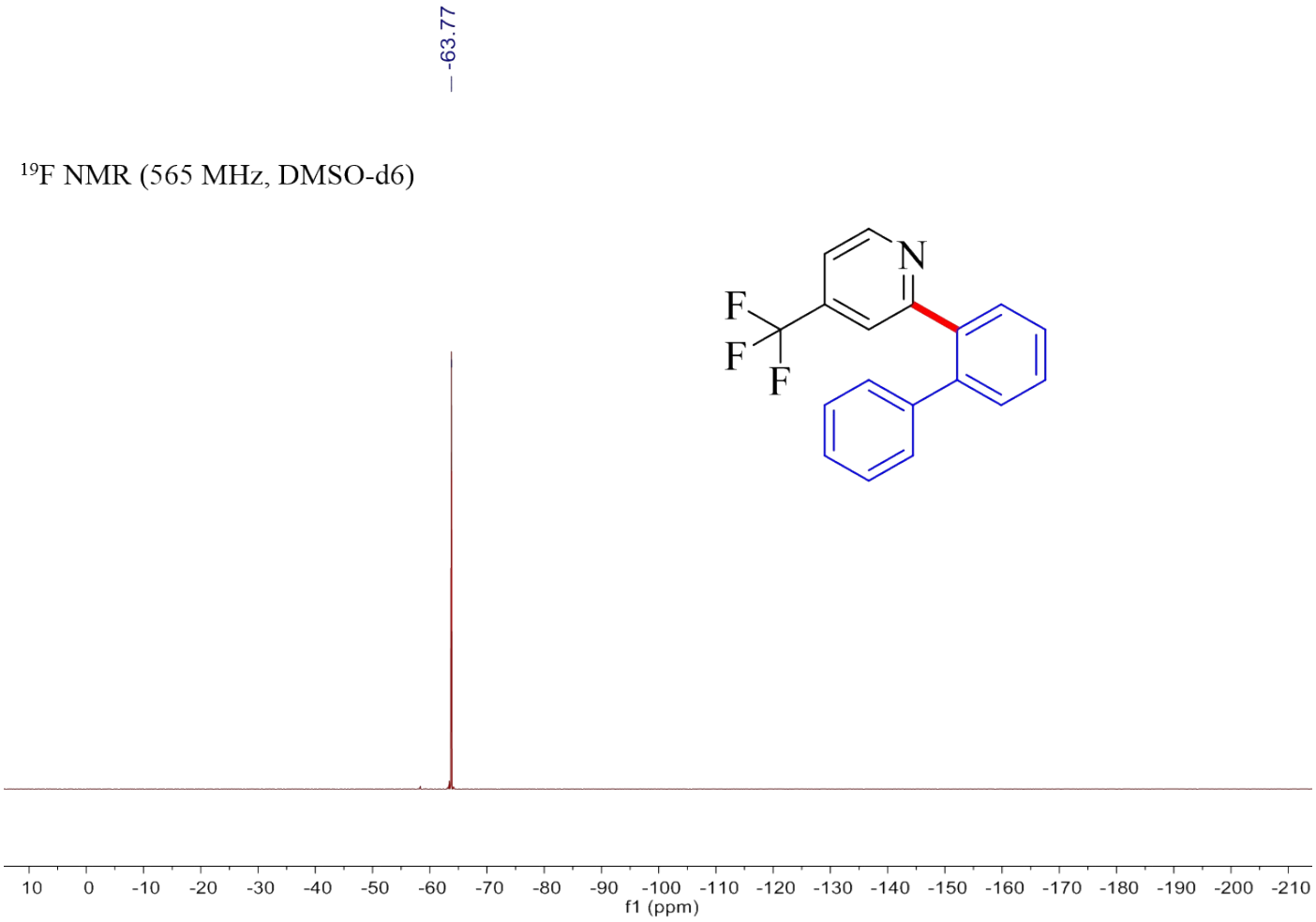




^{13}C NMR (151 MHz, DMSO-d6)

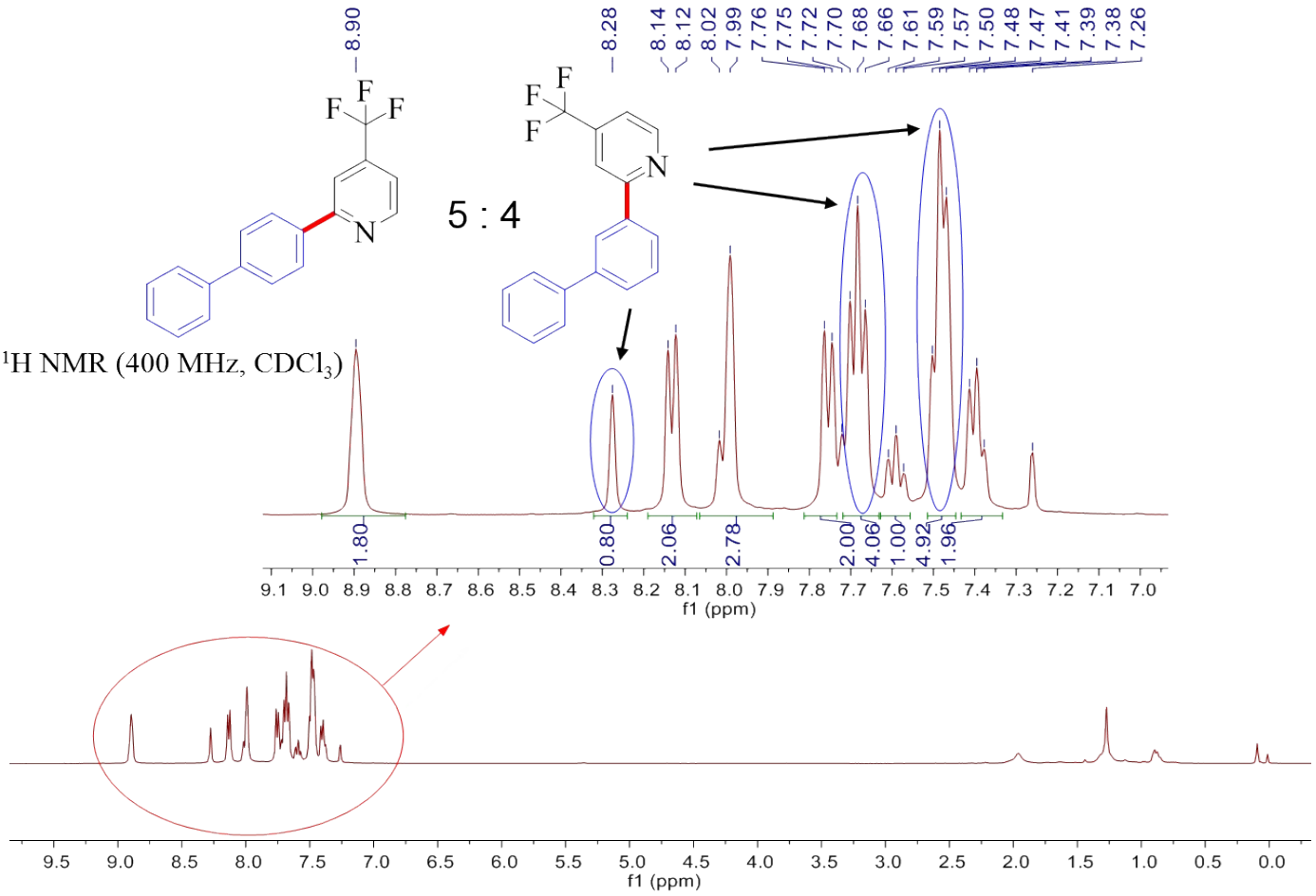


^{19}F NMR (565 MHz, DMSO-d6)

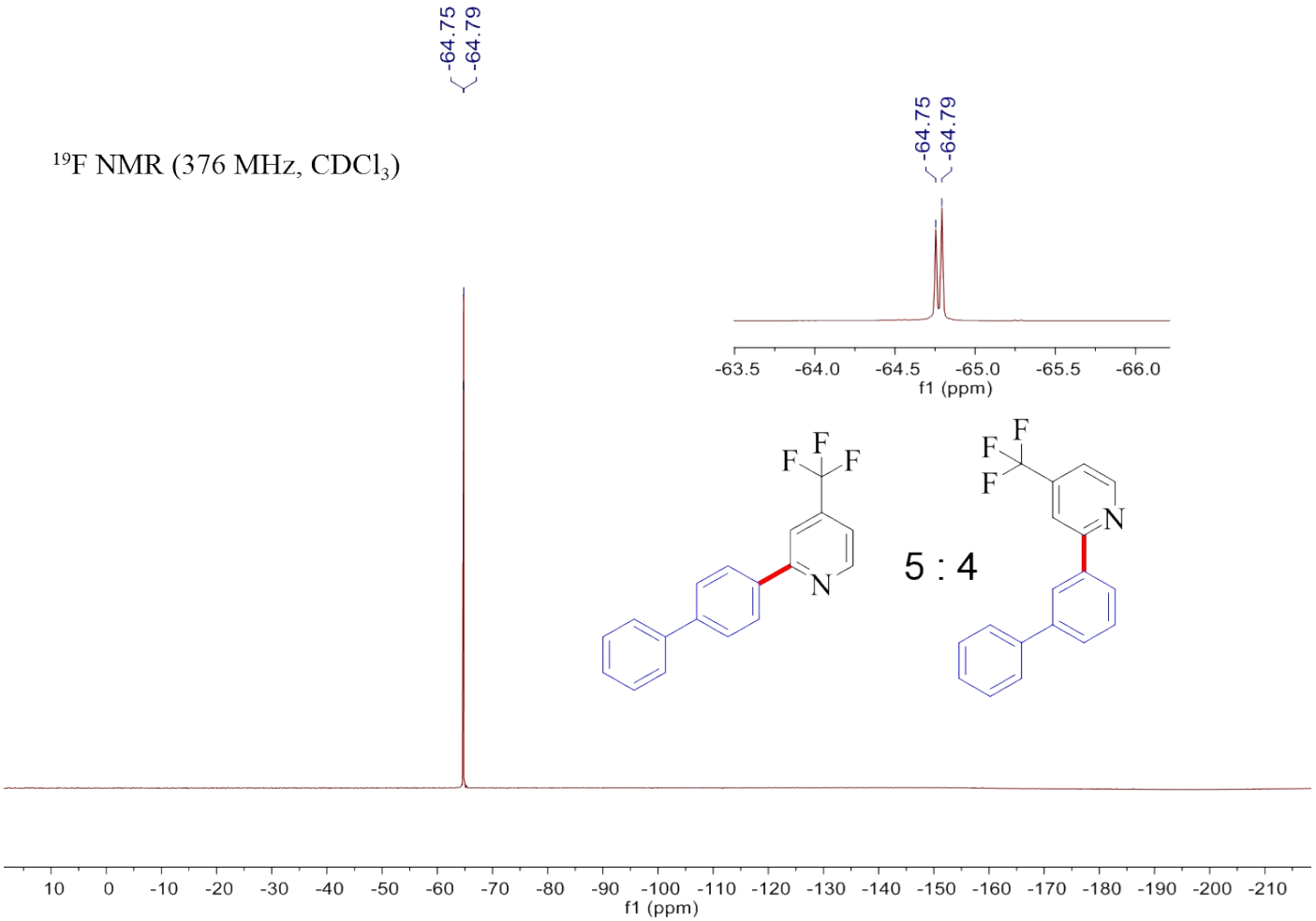


5v-b and **5v-c**

^{1}H NMR (400 MHz, $CDCl_3$)

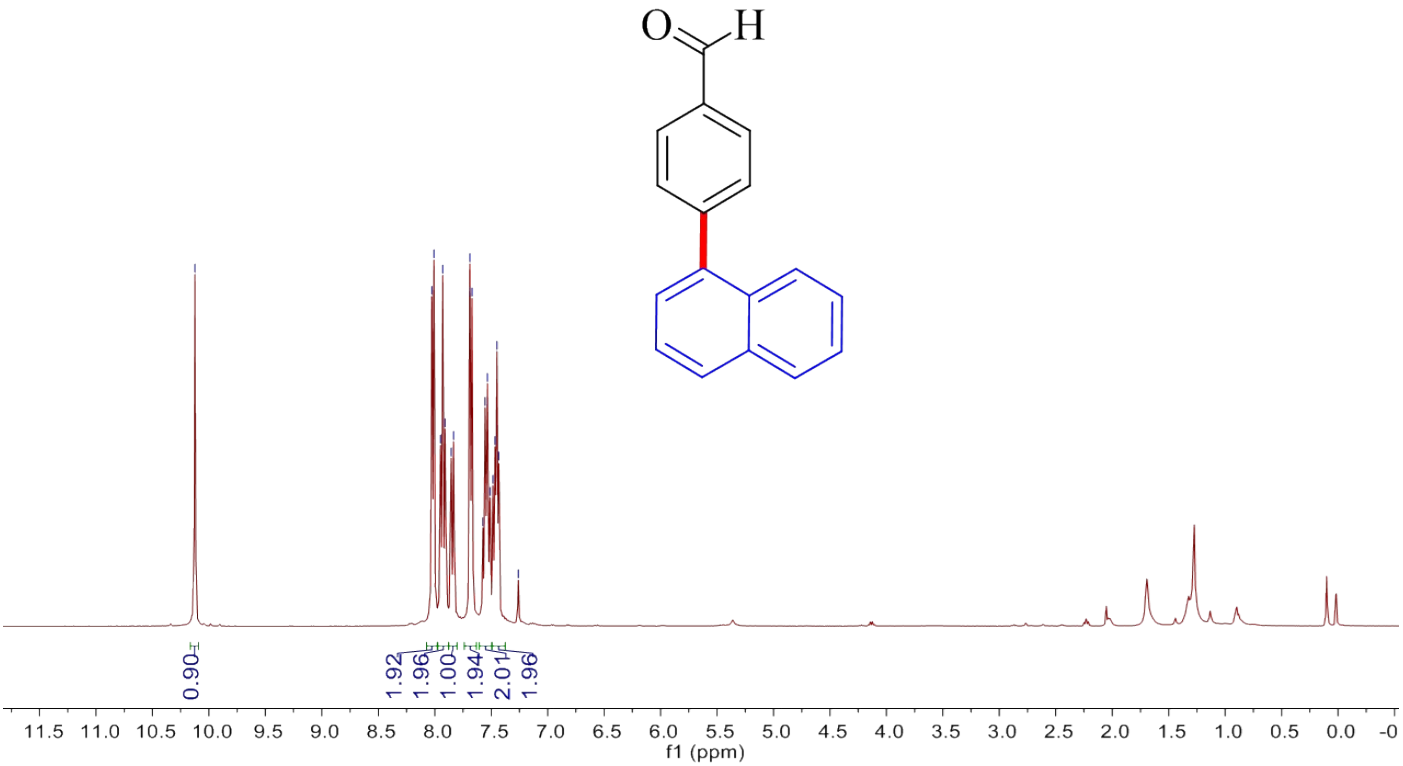


^{19}F NMR (376 MHz, $CDCl_3$)

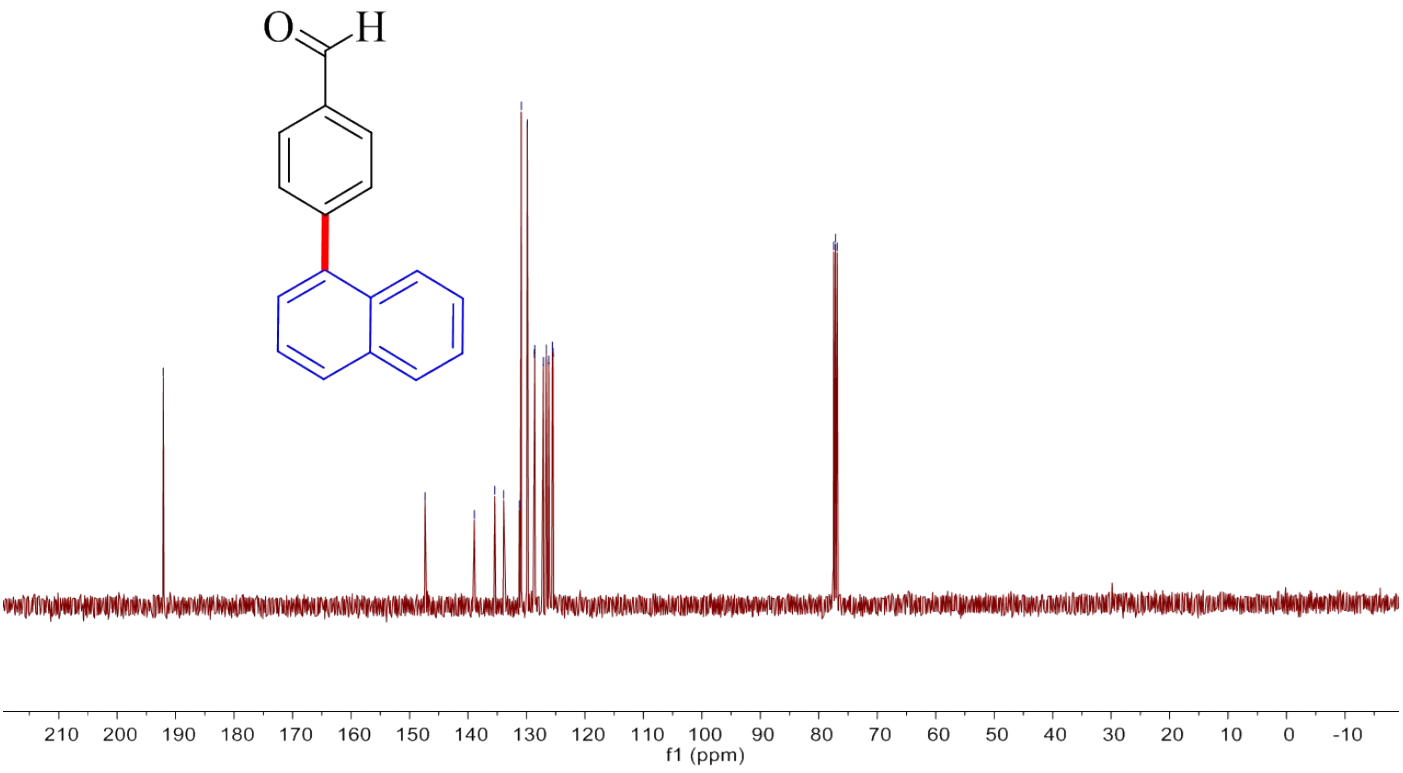


5w-a

^{1}H NMR (400 MHz, $CDCl_3$)

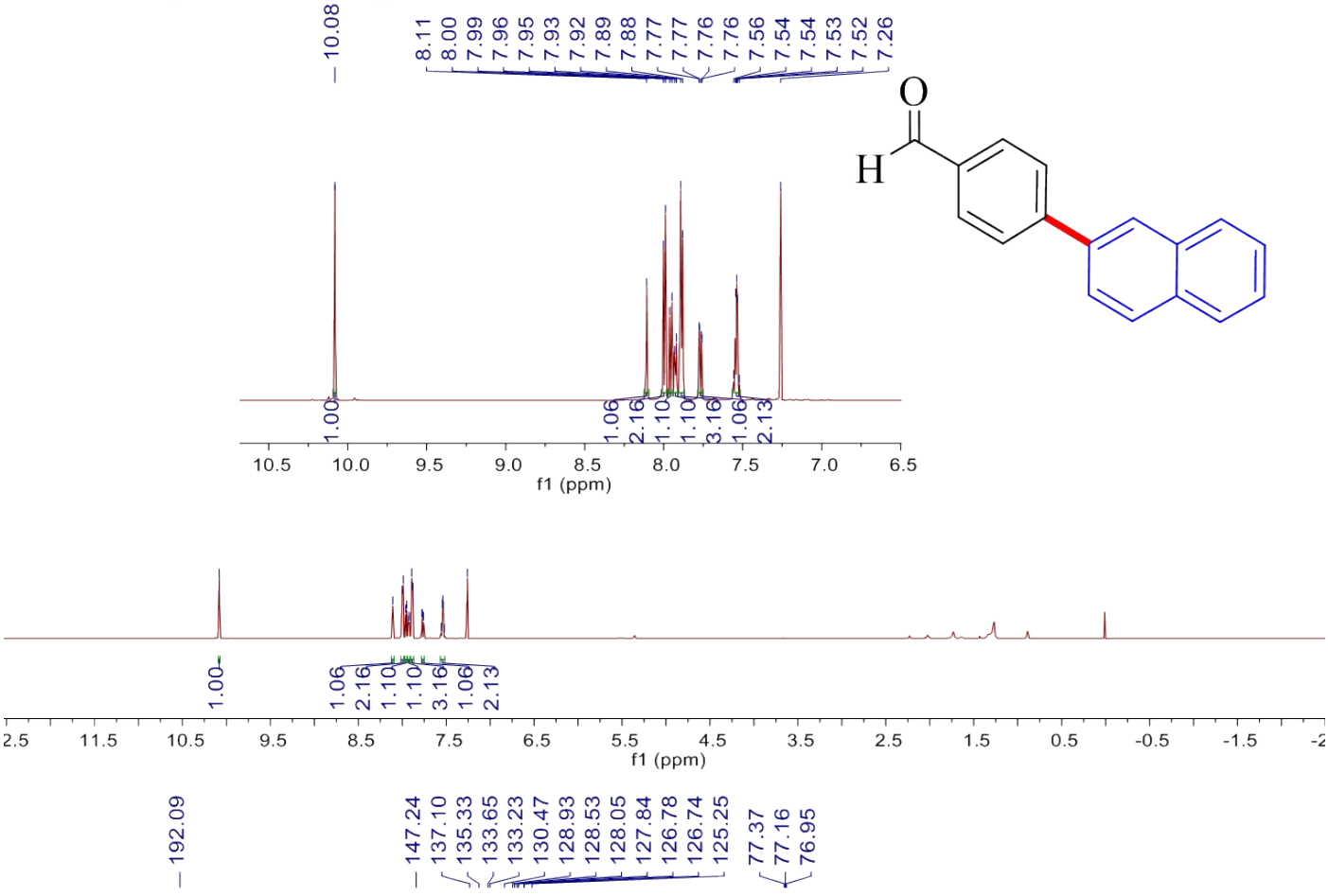


^{13}C NMR (101 MHz, $CDCl_3$)

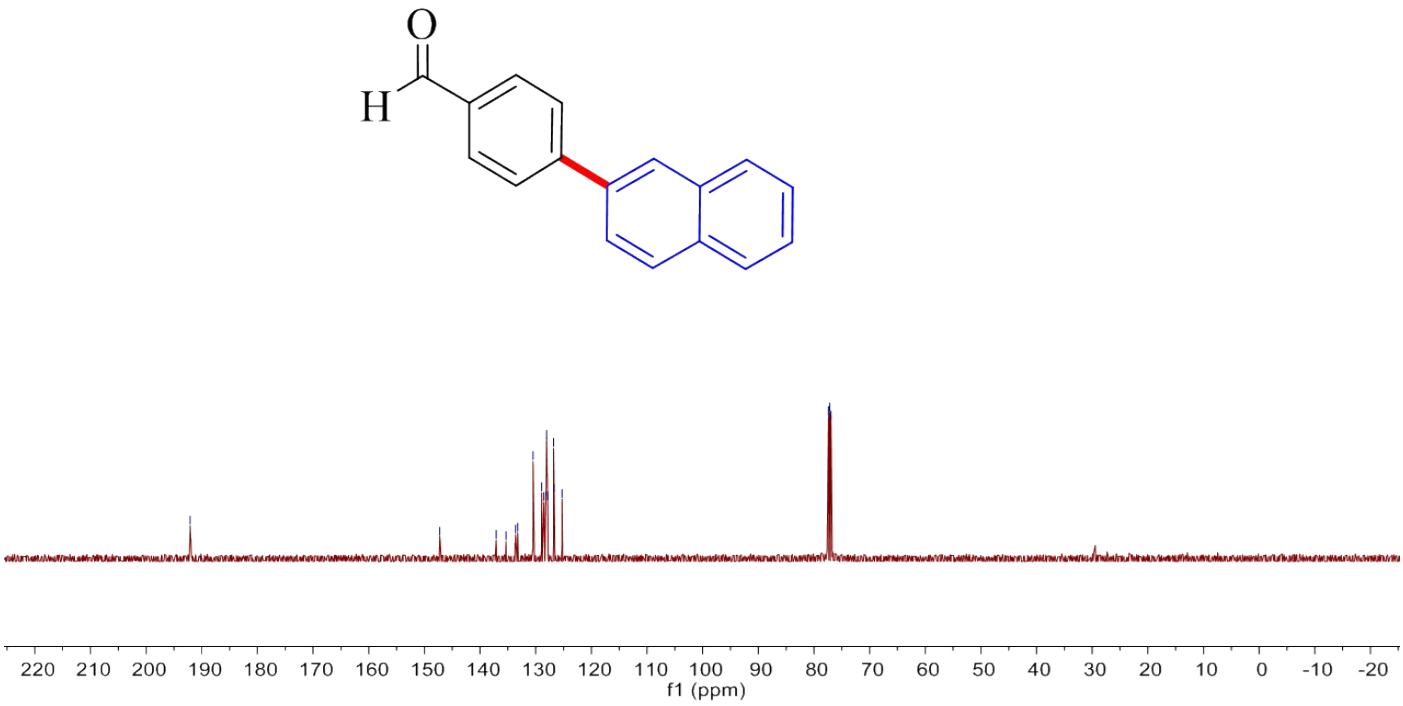


5w-b

^{1}H NMR (600 MHz, $CDCl_3$)

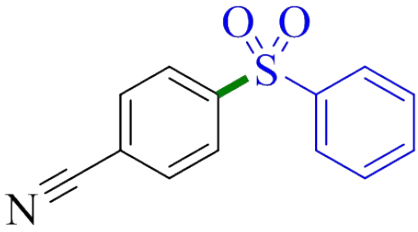


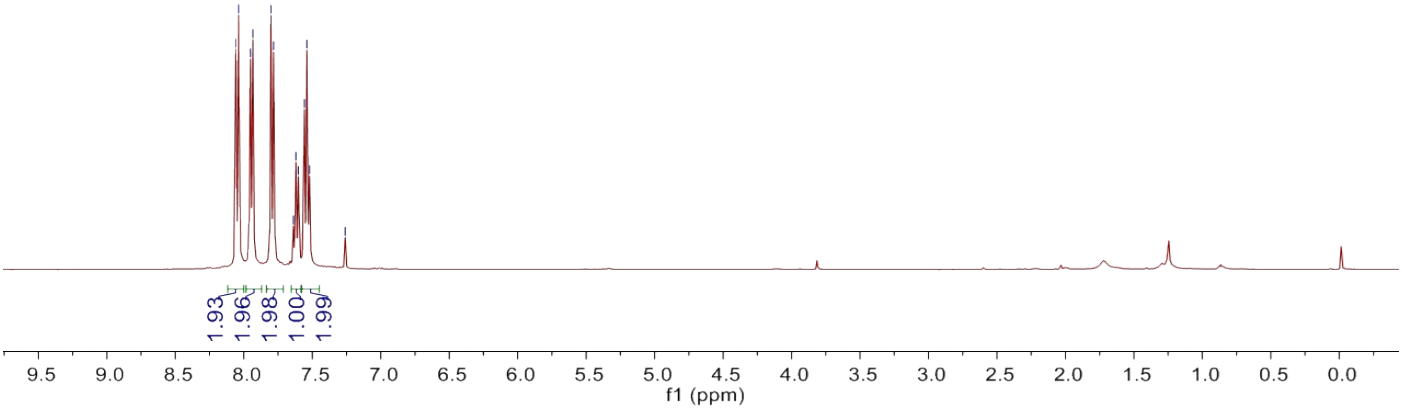
^{13}C NMR (151 MHz, $CDCl_3$)



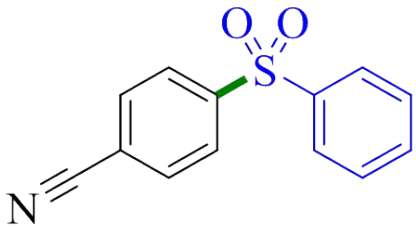
7a

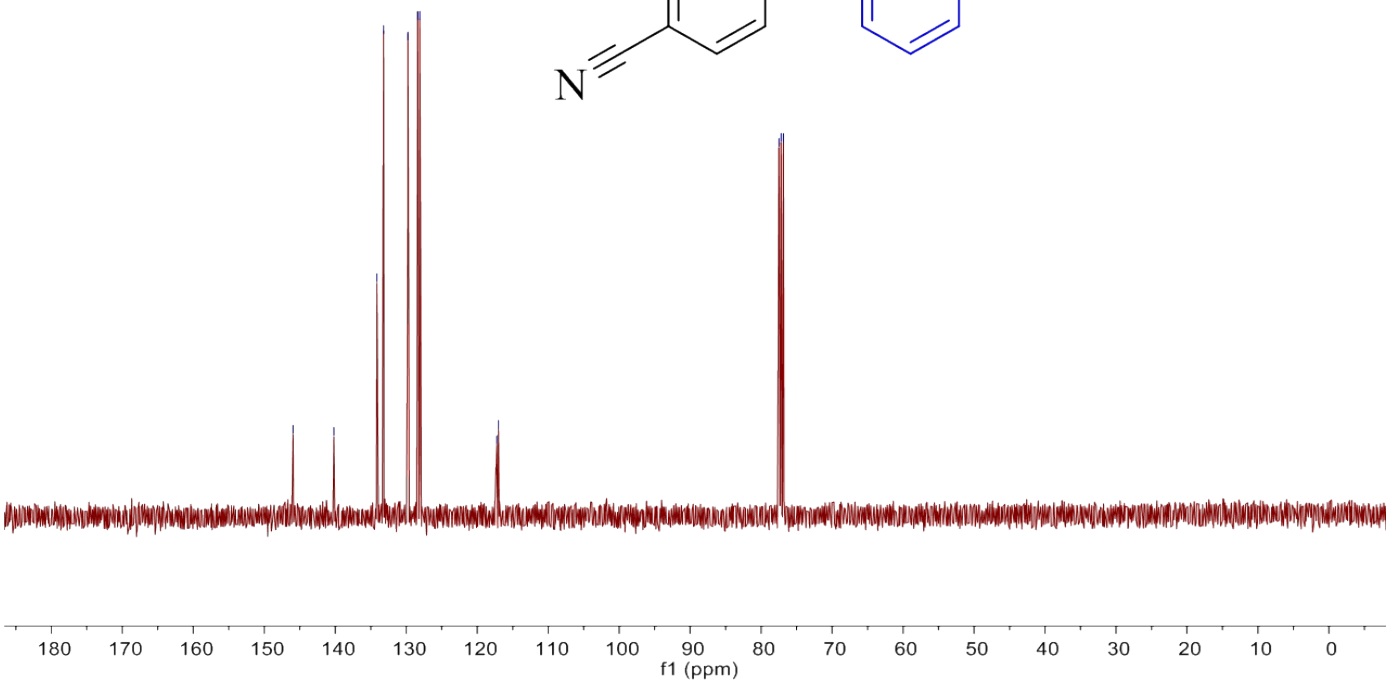
^{1}H NMR (400 MHz, $CDCl_3$)





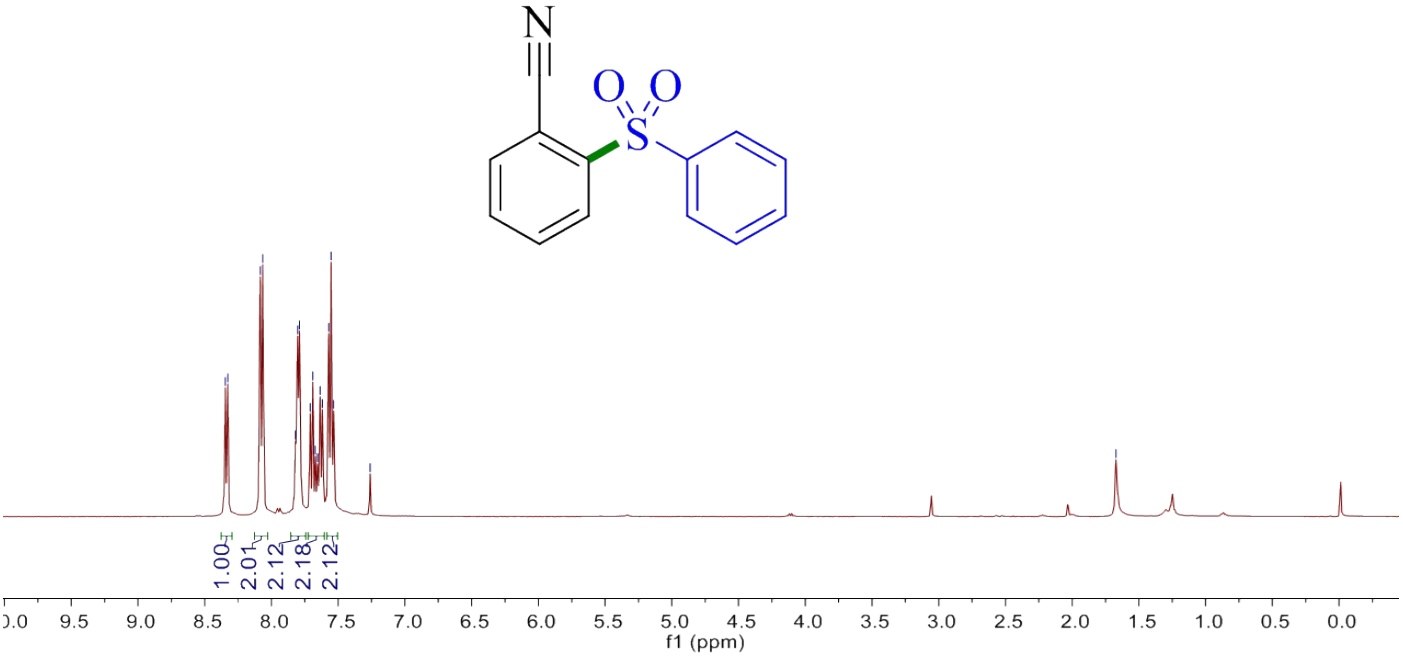
^{13}C NMR (101 MHz, $CDCl_3$)



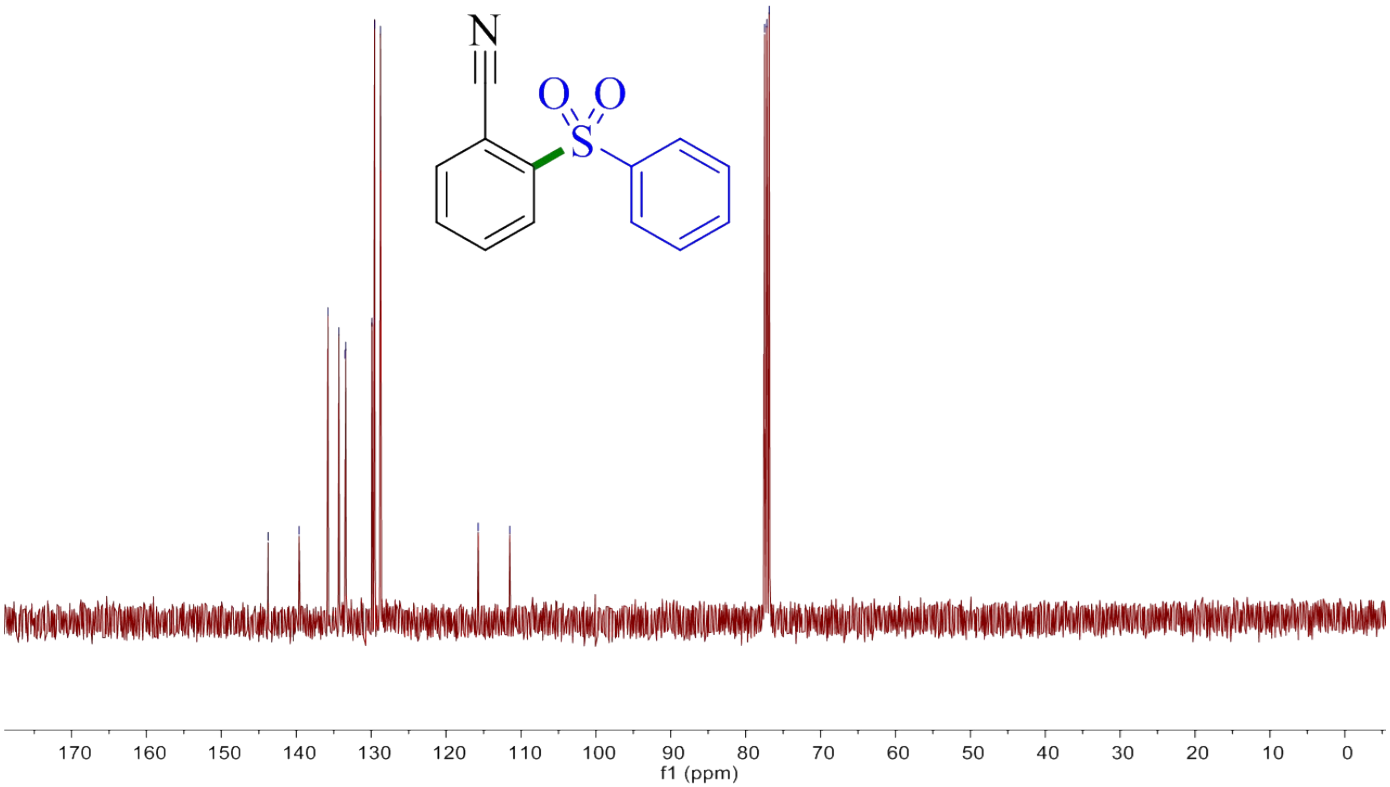


7b

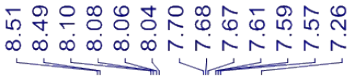
^{1}H NMR (400 MHz, $CDCl_3$)



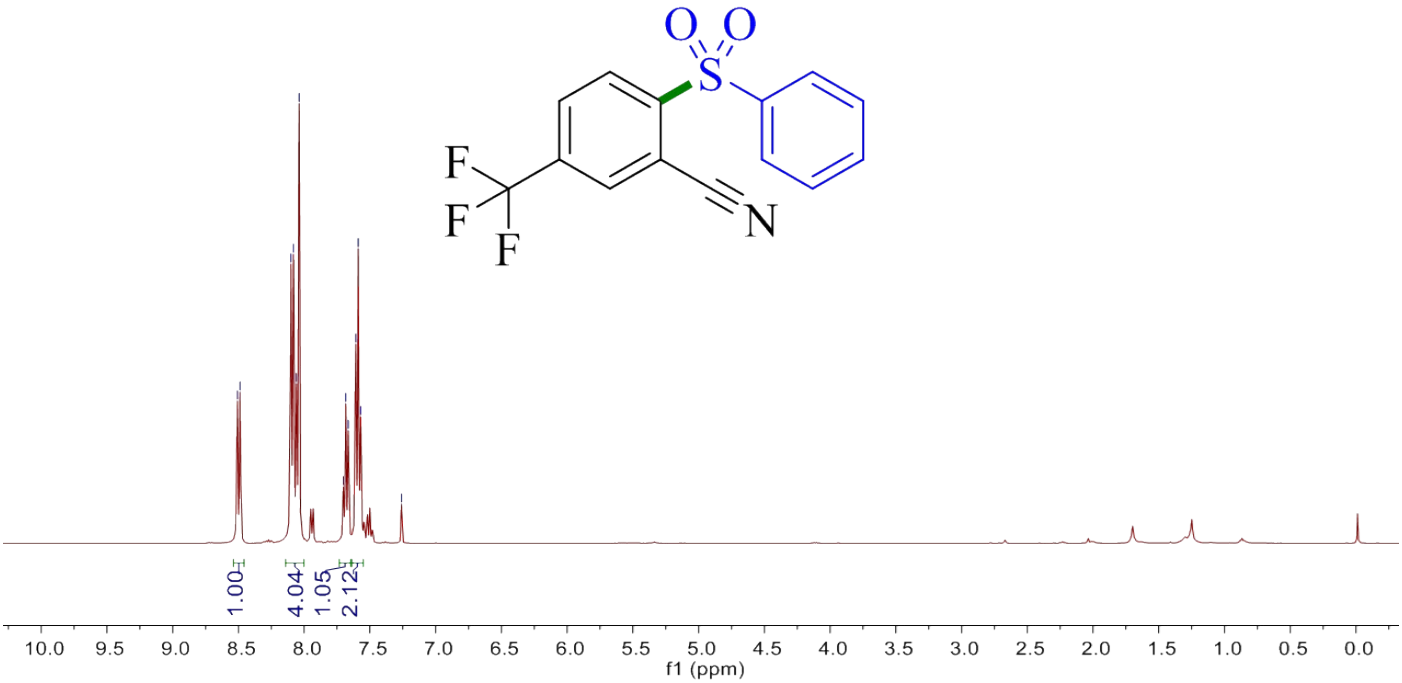
^{13}C NMR (101 MHz, $CDCl_3$)



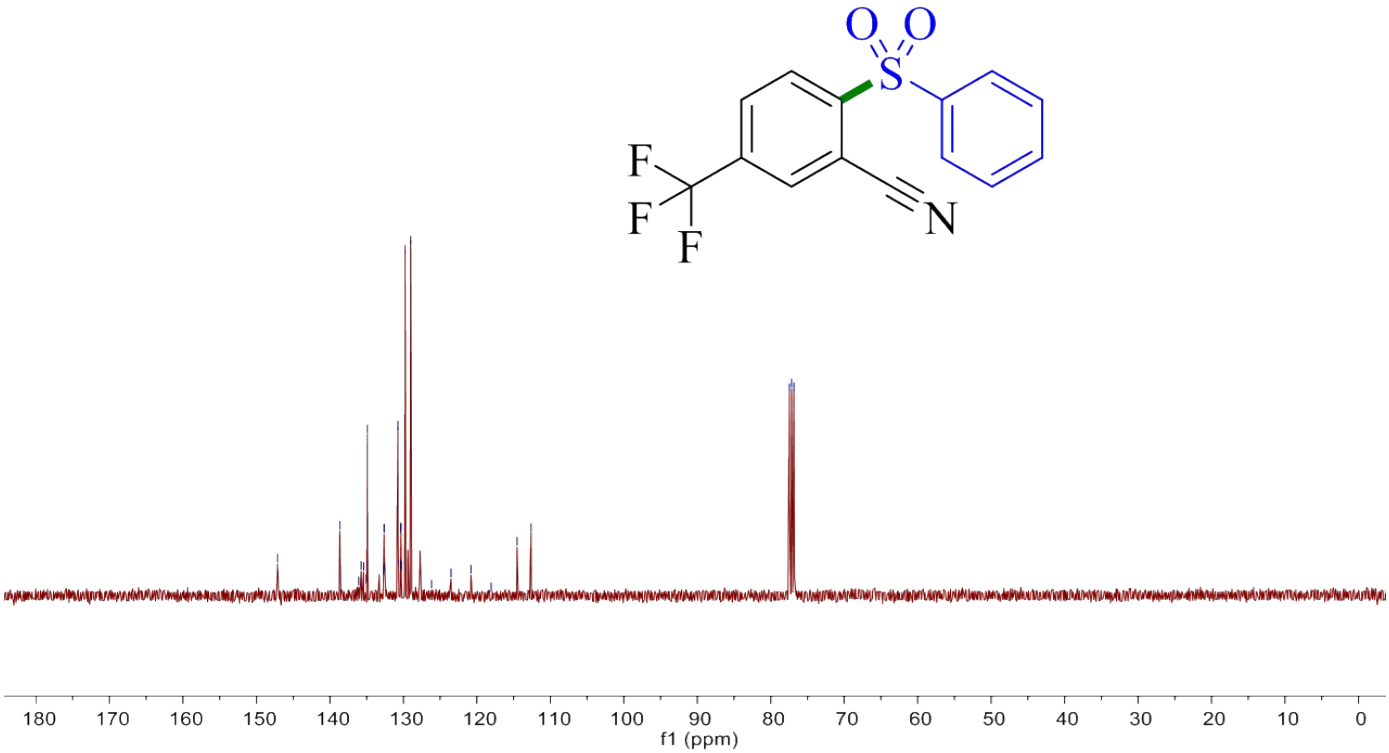
7c



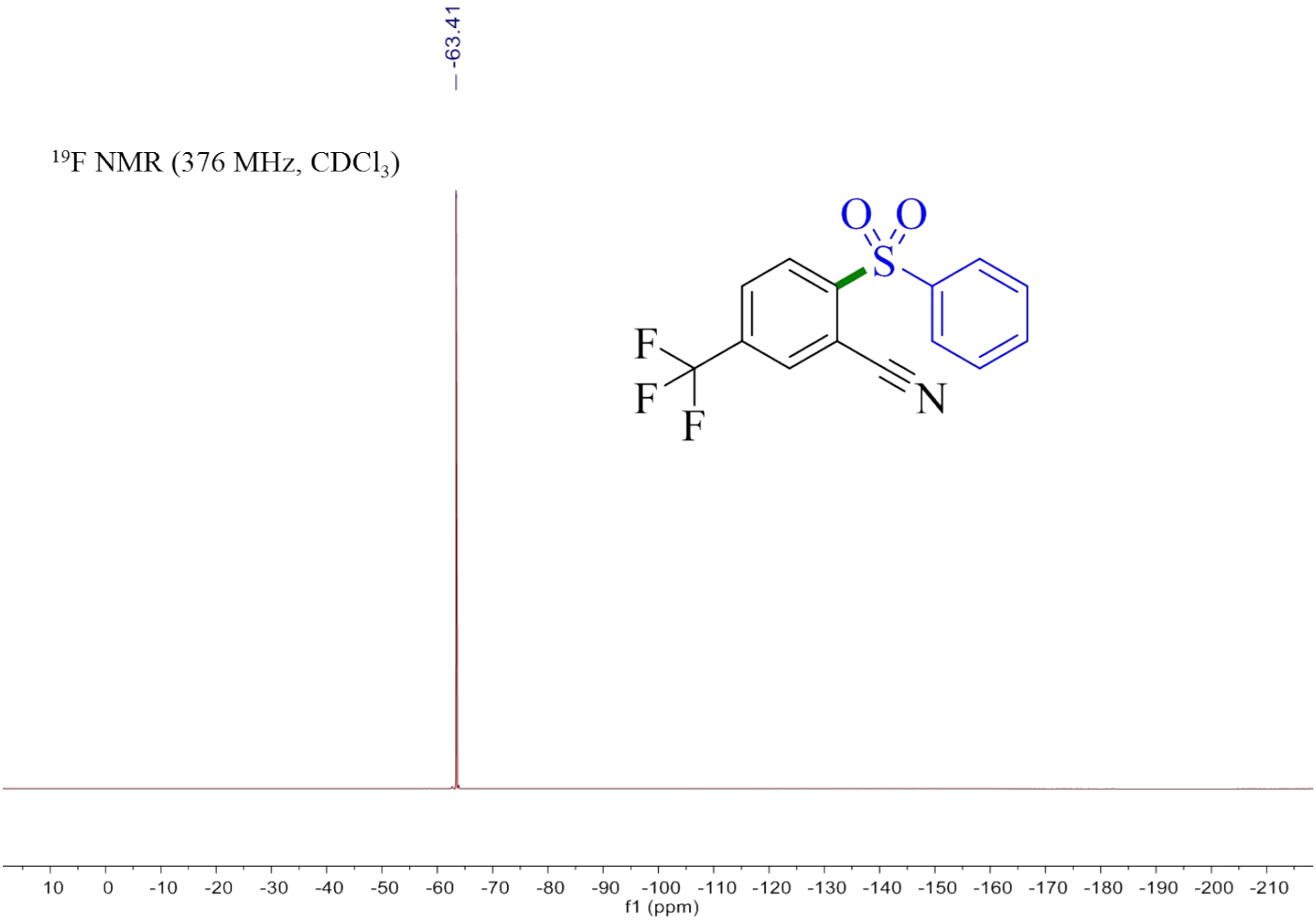
^{1}H NMR (400 MHz, $CDCl_3$)



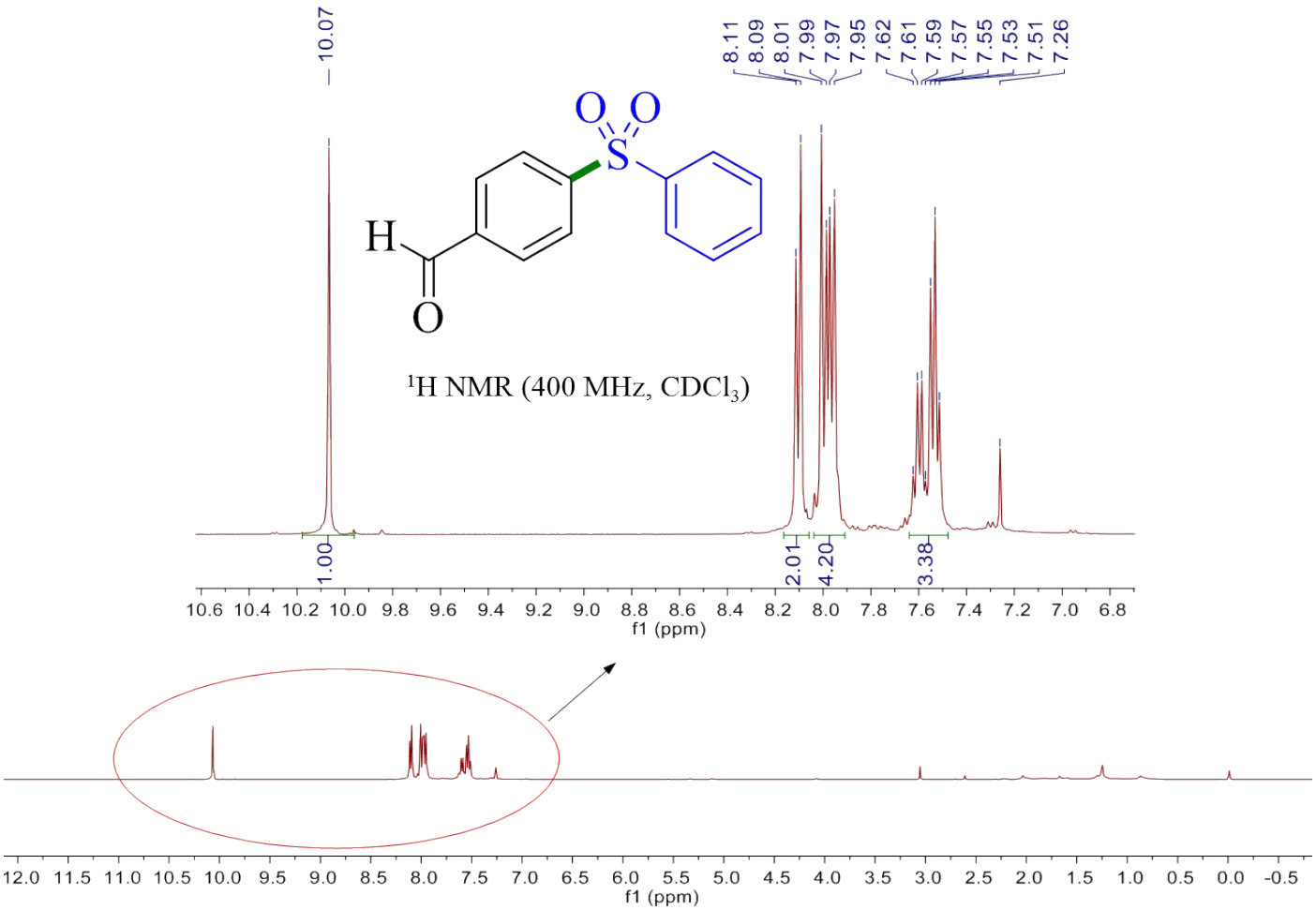
^{13}C NMR (101 MHz, $CDCl_3$)



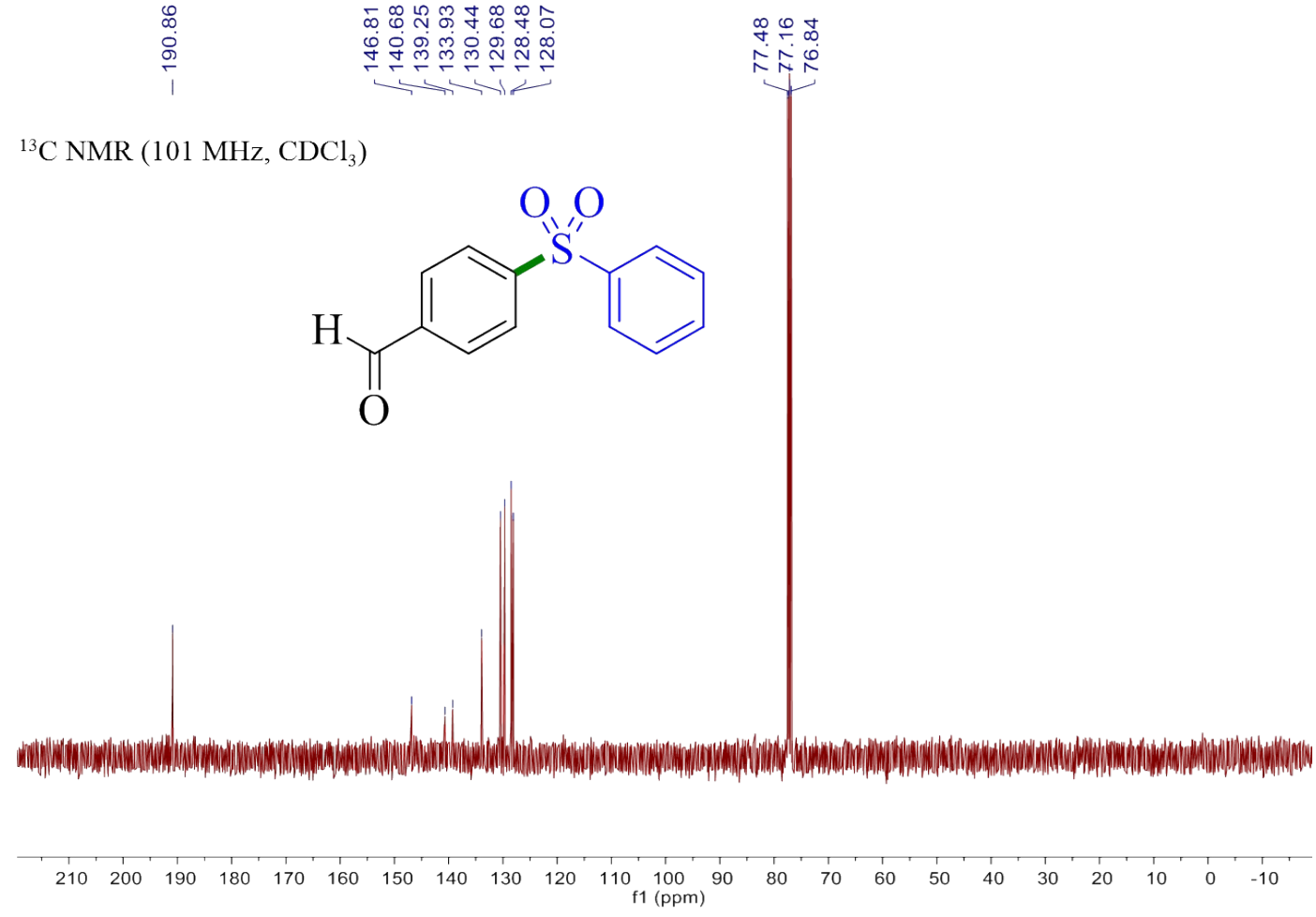
^{19}F NMR (376 MHz, $CDCl_3$)



7d

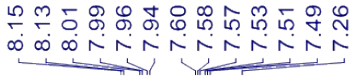


^{1}H NMR (400 MHz, $CDCl_3$)

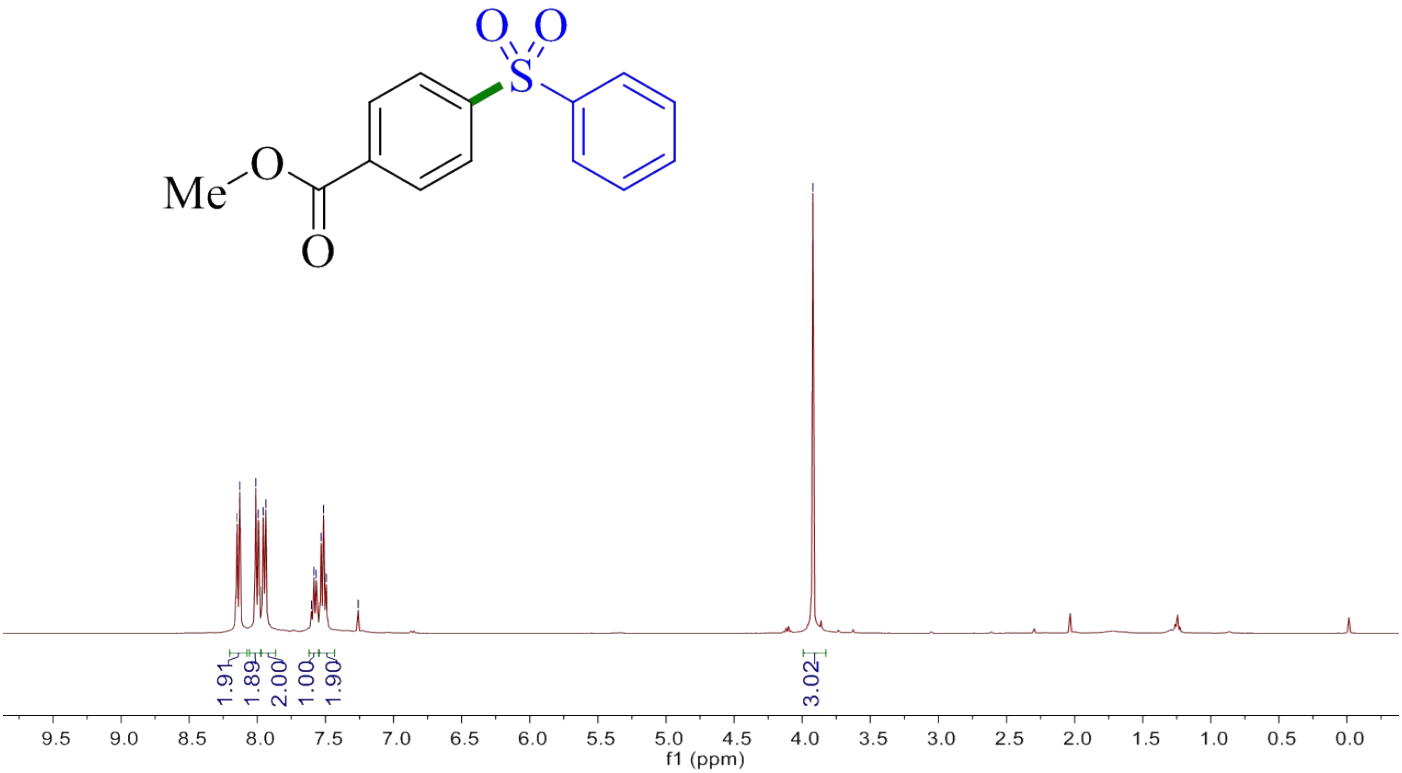


^{13}C NMR (101 MHz, $CDCl_3$)

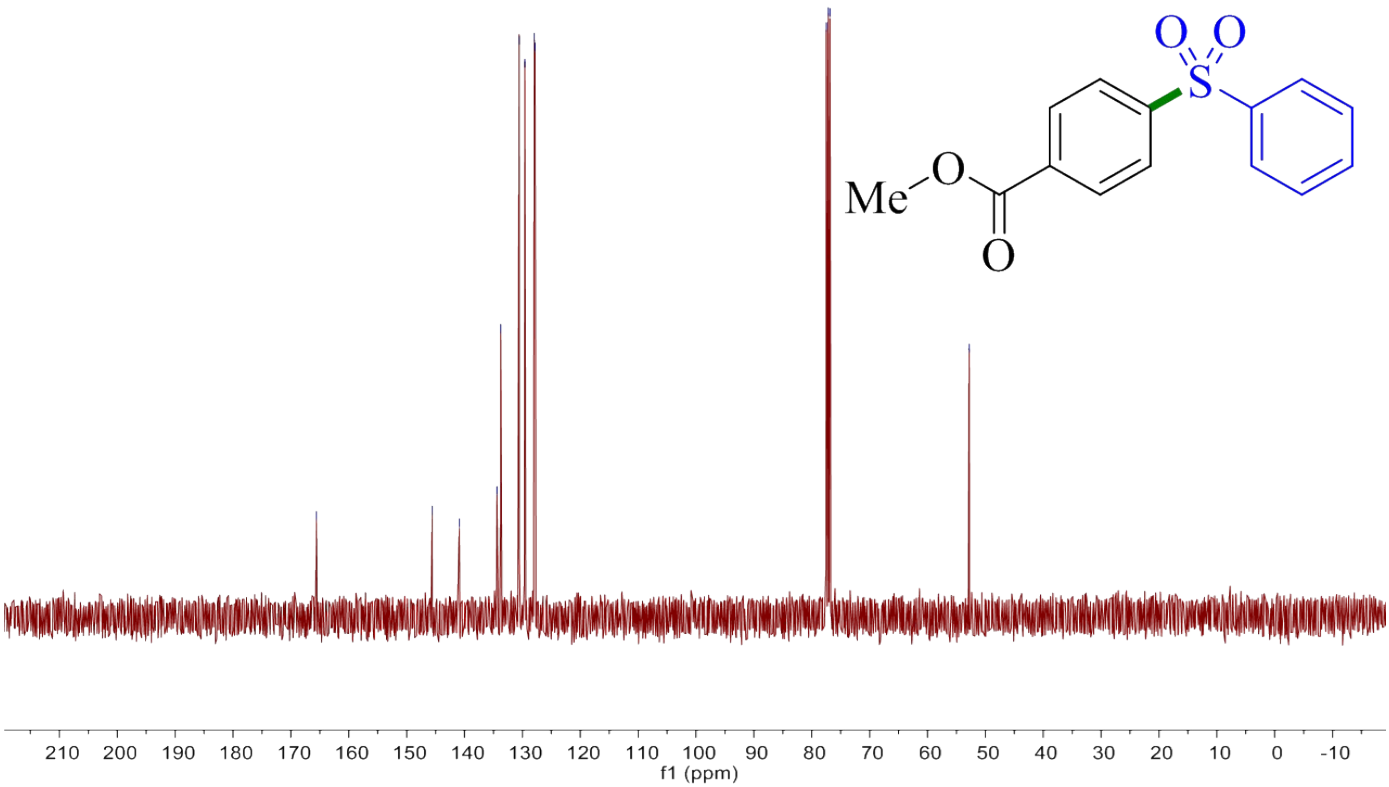
7e



^{1}H NMR (400 MHz, $CDCl_3$)

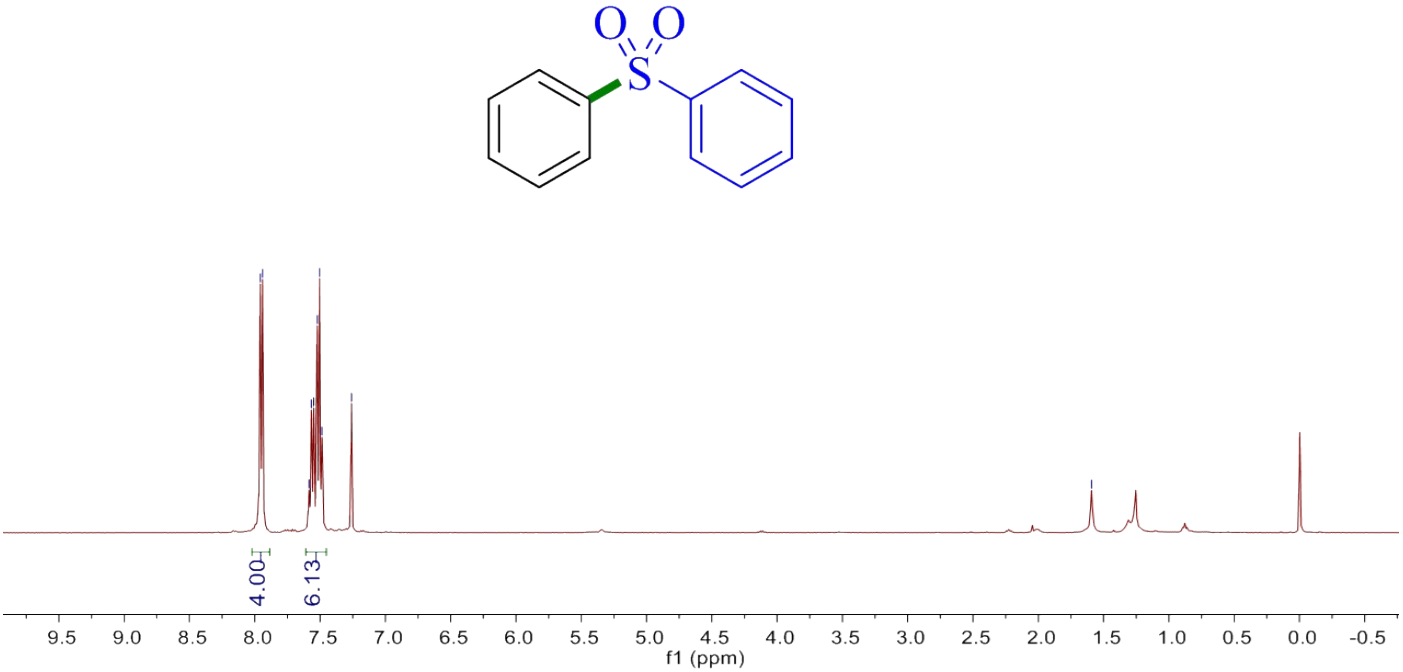


^{13}C NMR (101 MHz, $CDCl_3$)

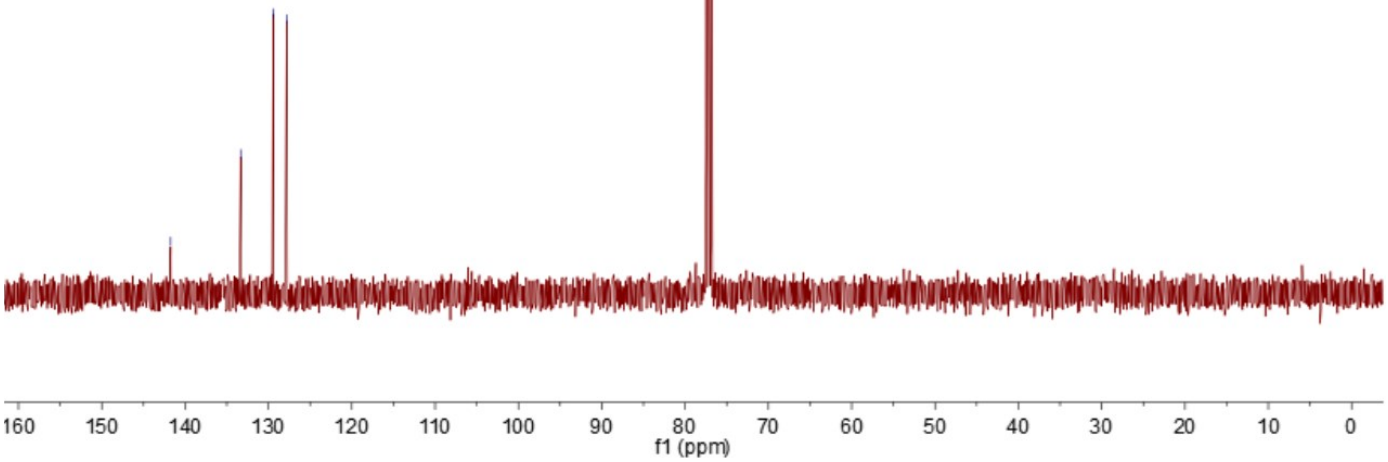


7f

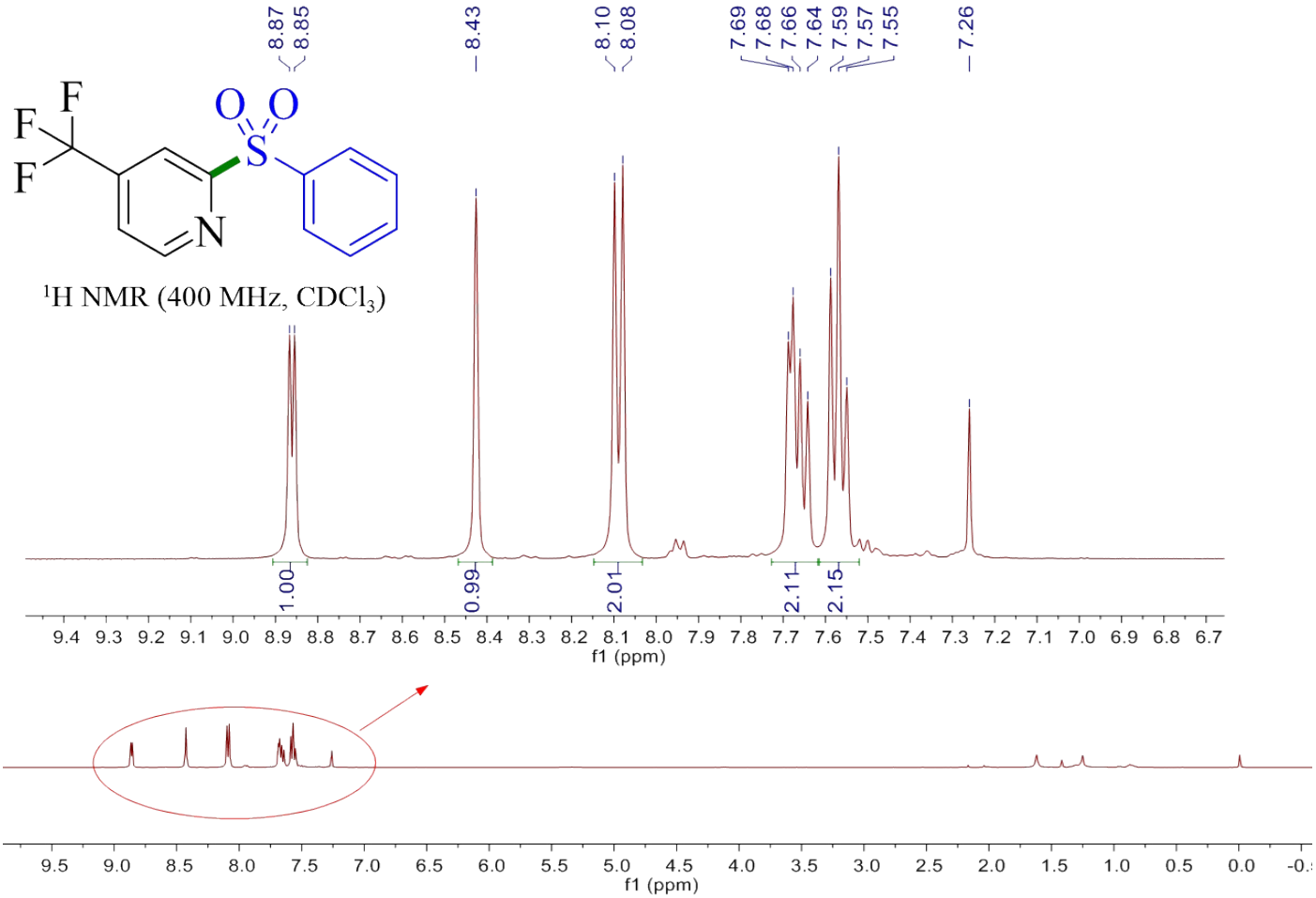
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

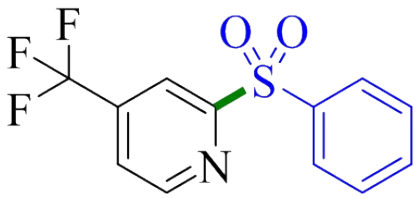


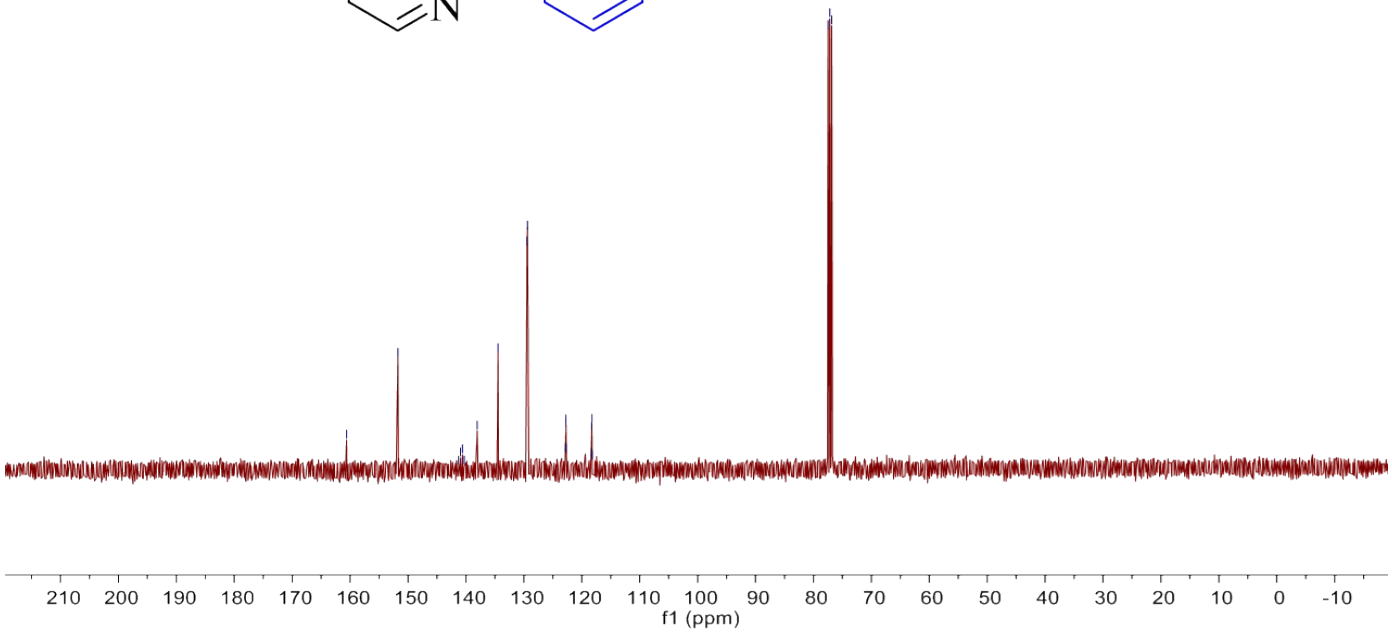
7g



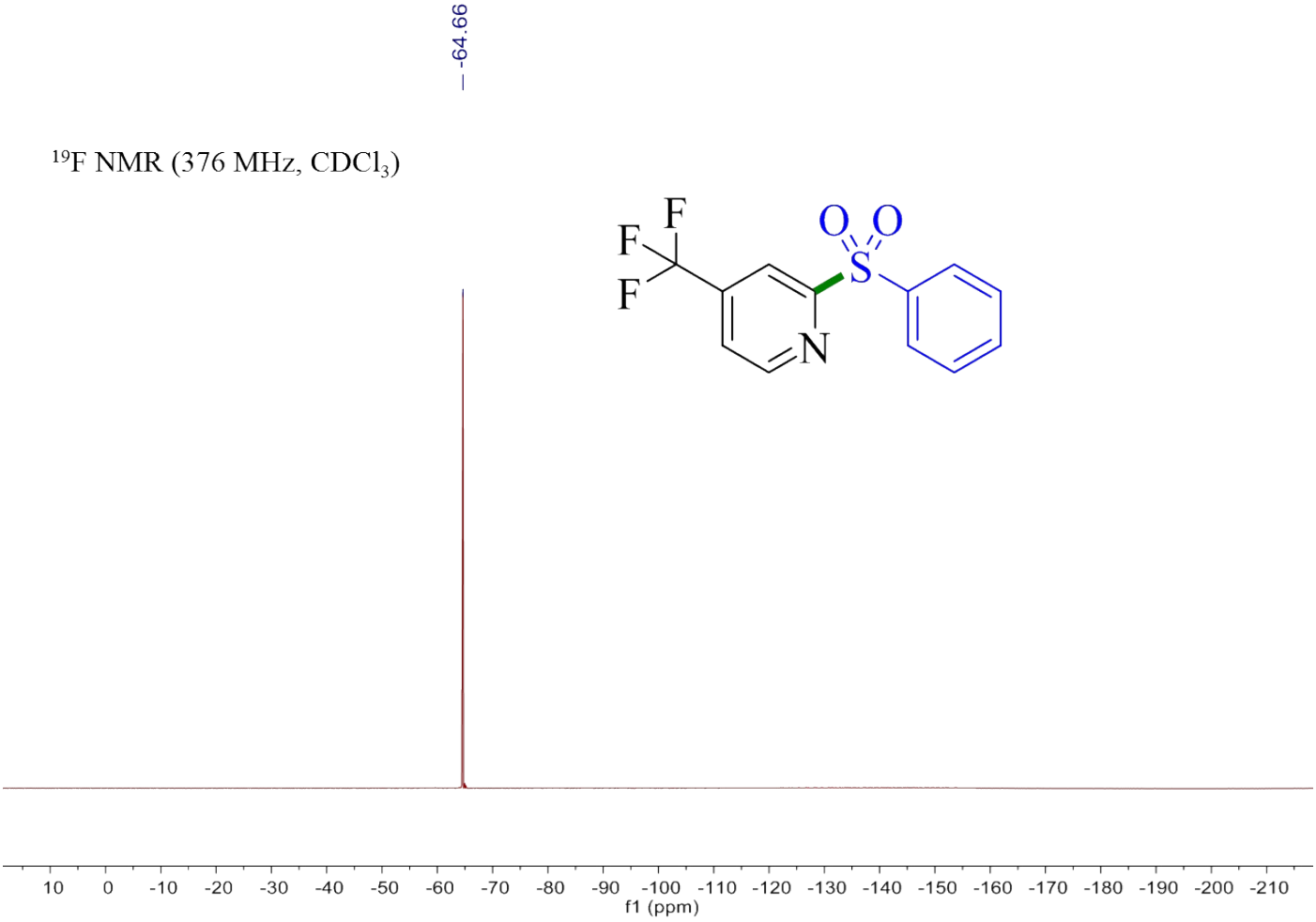
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (101 MHz, $CDCl_3$)



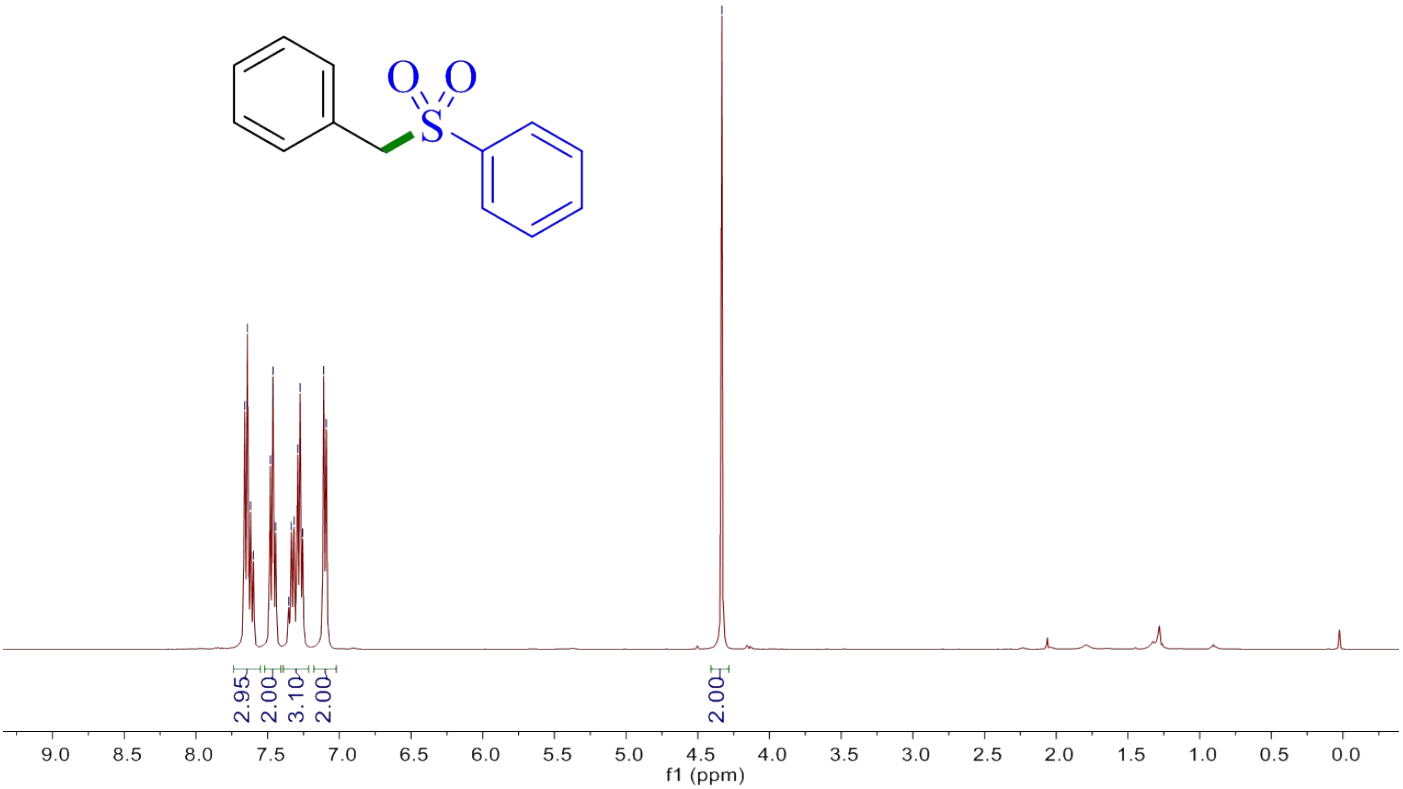


^{19}F NMR (376 MHz, $CDCl_3$)

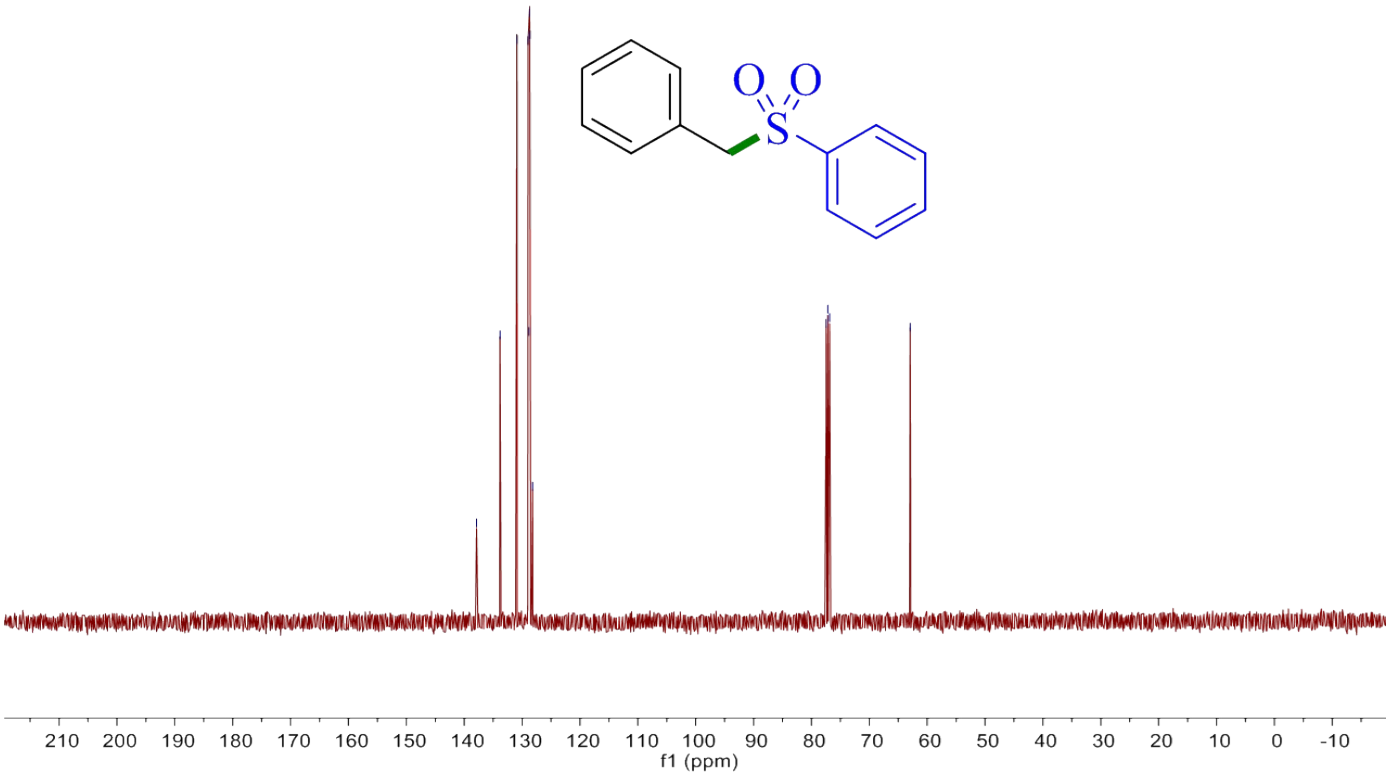


7h

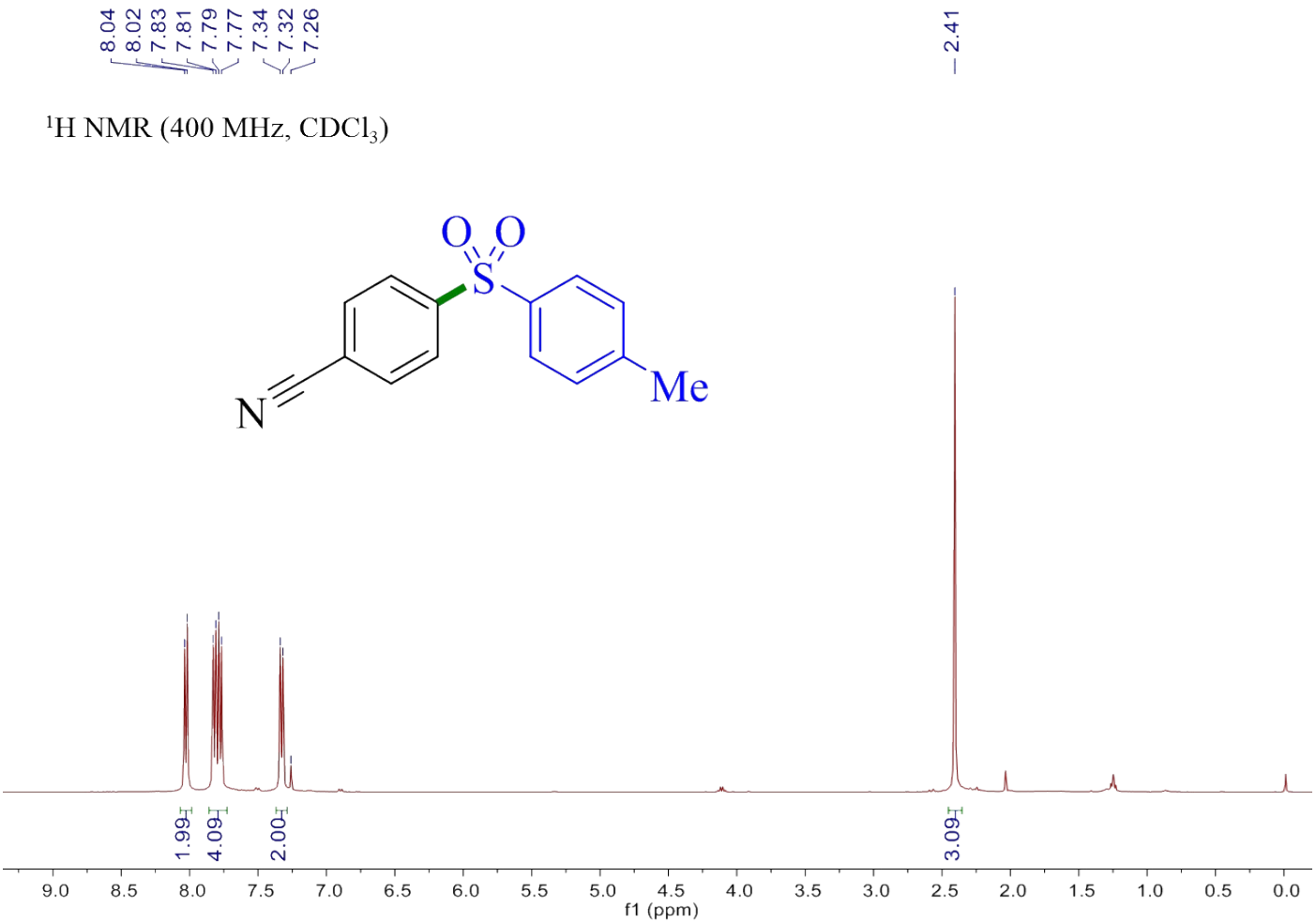
^{1}H NMR (400 MHz, $CDCl_3$)



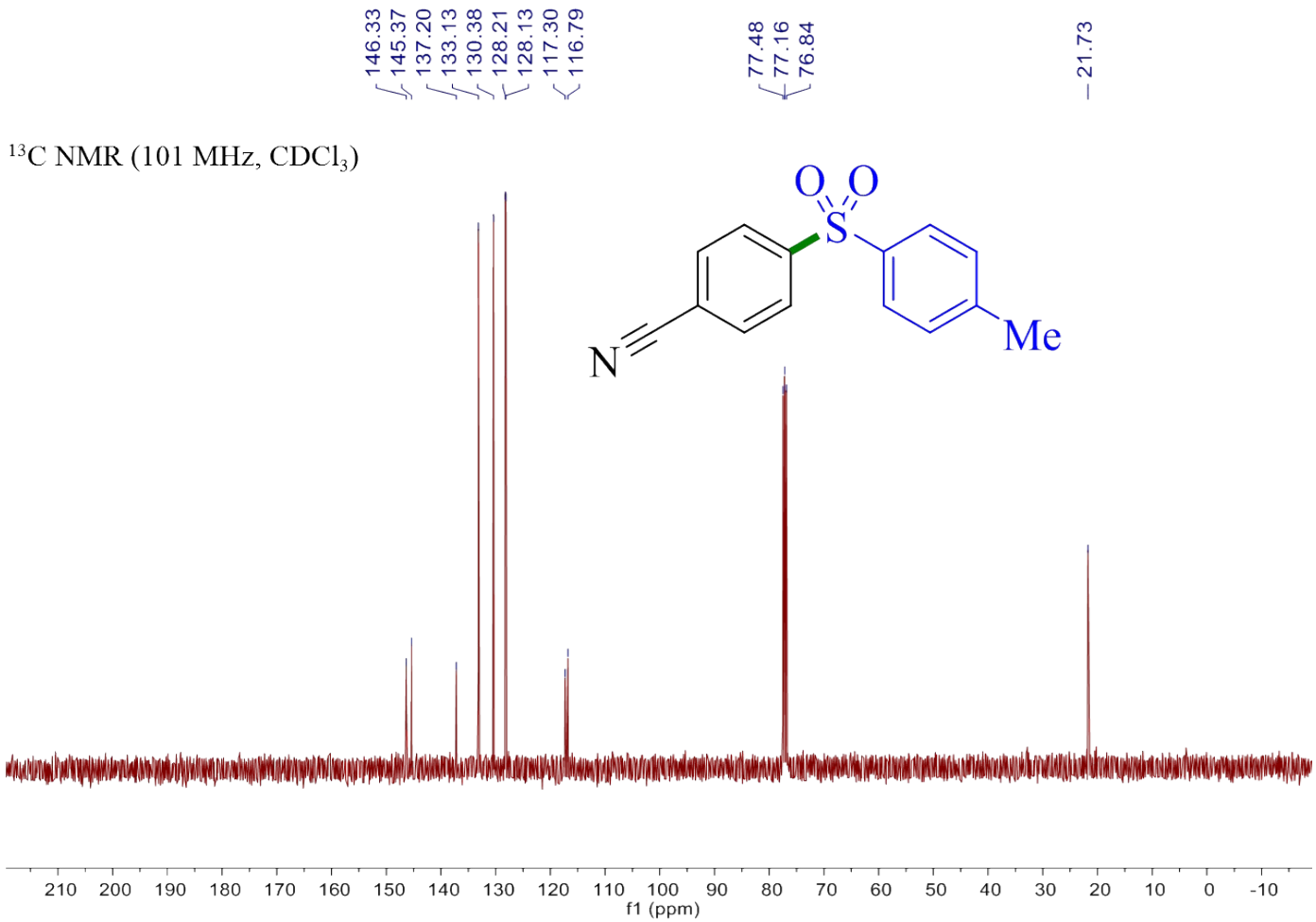
^{13}C NMR (101 MHz, $CDCl_3$)



7i



^{1}H NMR (400 MHz, $CDCl_3$)

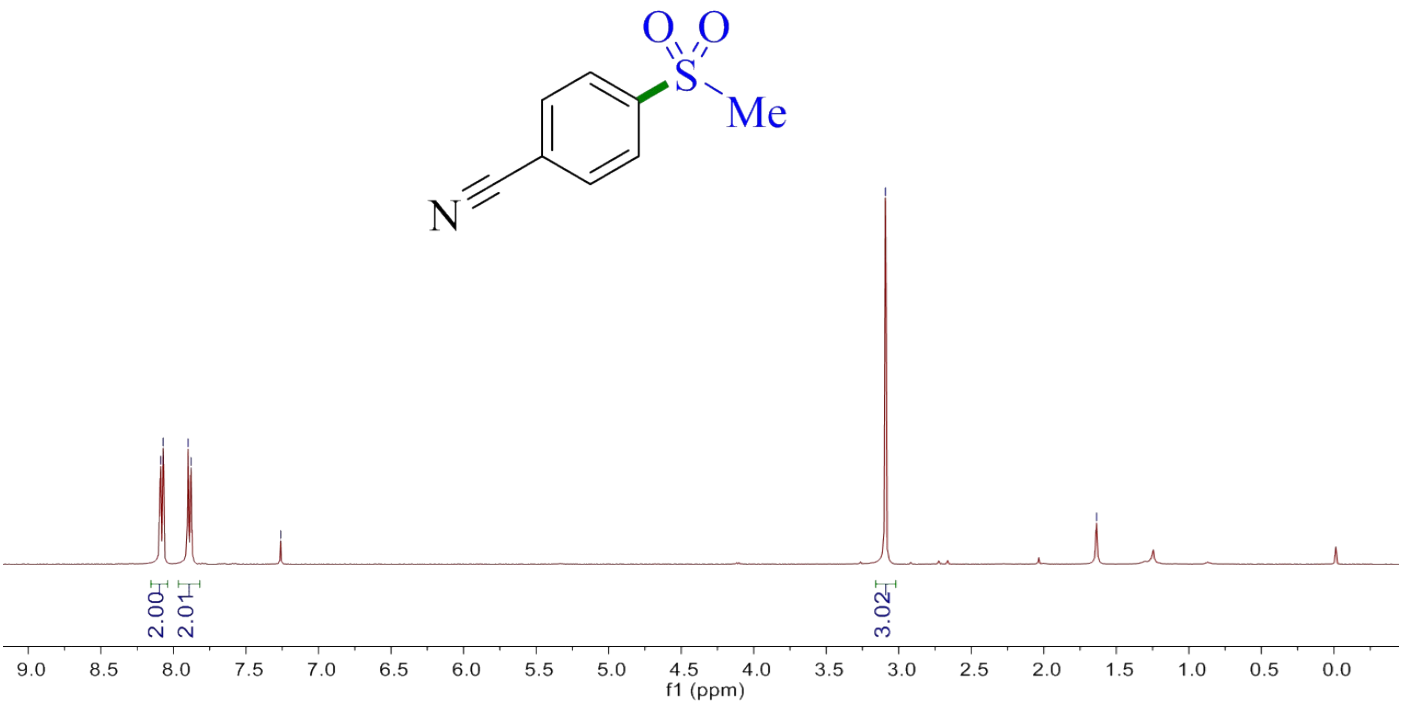


^{13}C NMR (101 MHz, $CDCl_3$)

7j

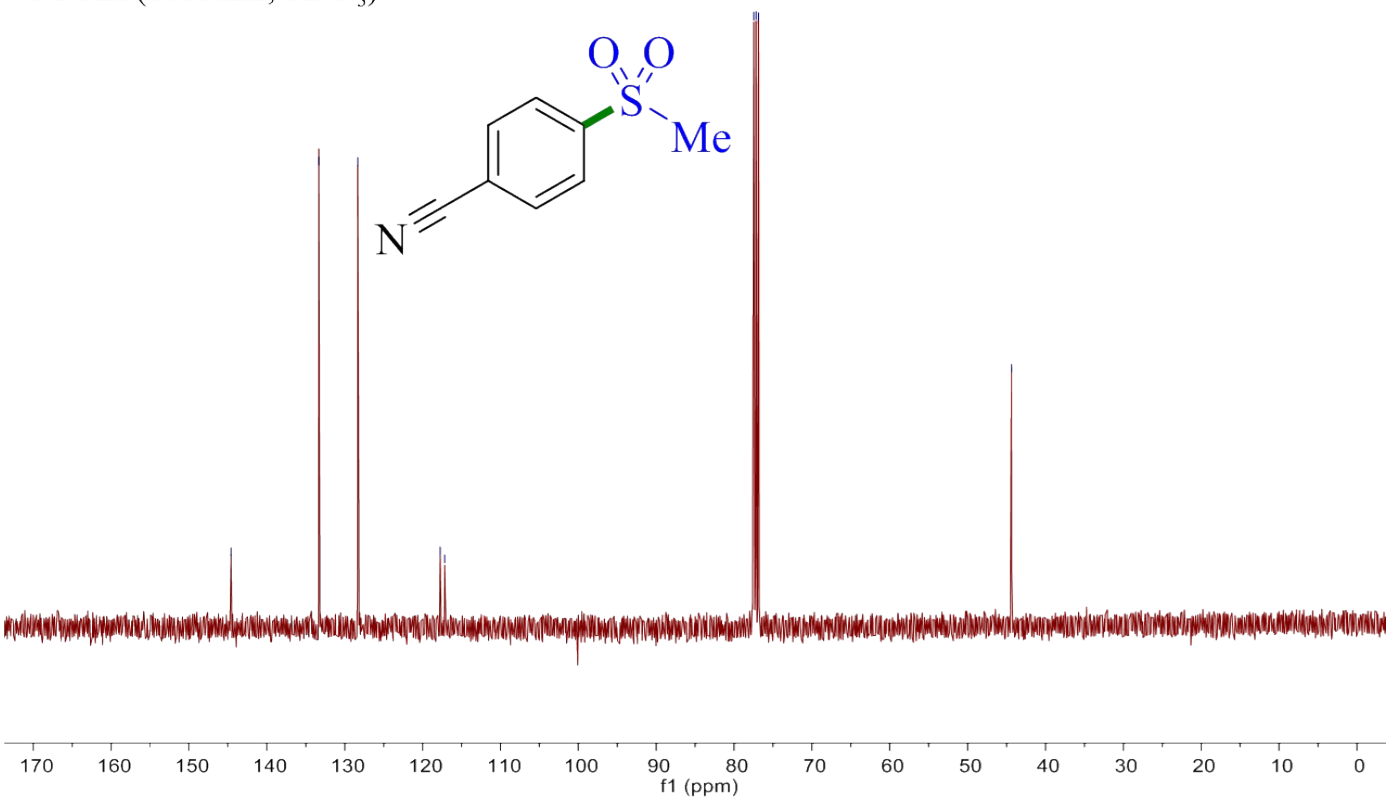
8.09
8.07
7.90
7.88
7.26
3.09
1.64
H_2O

^{1}H NMR (400 MHz, $CDCl_3$)



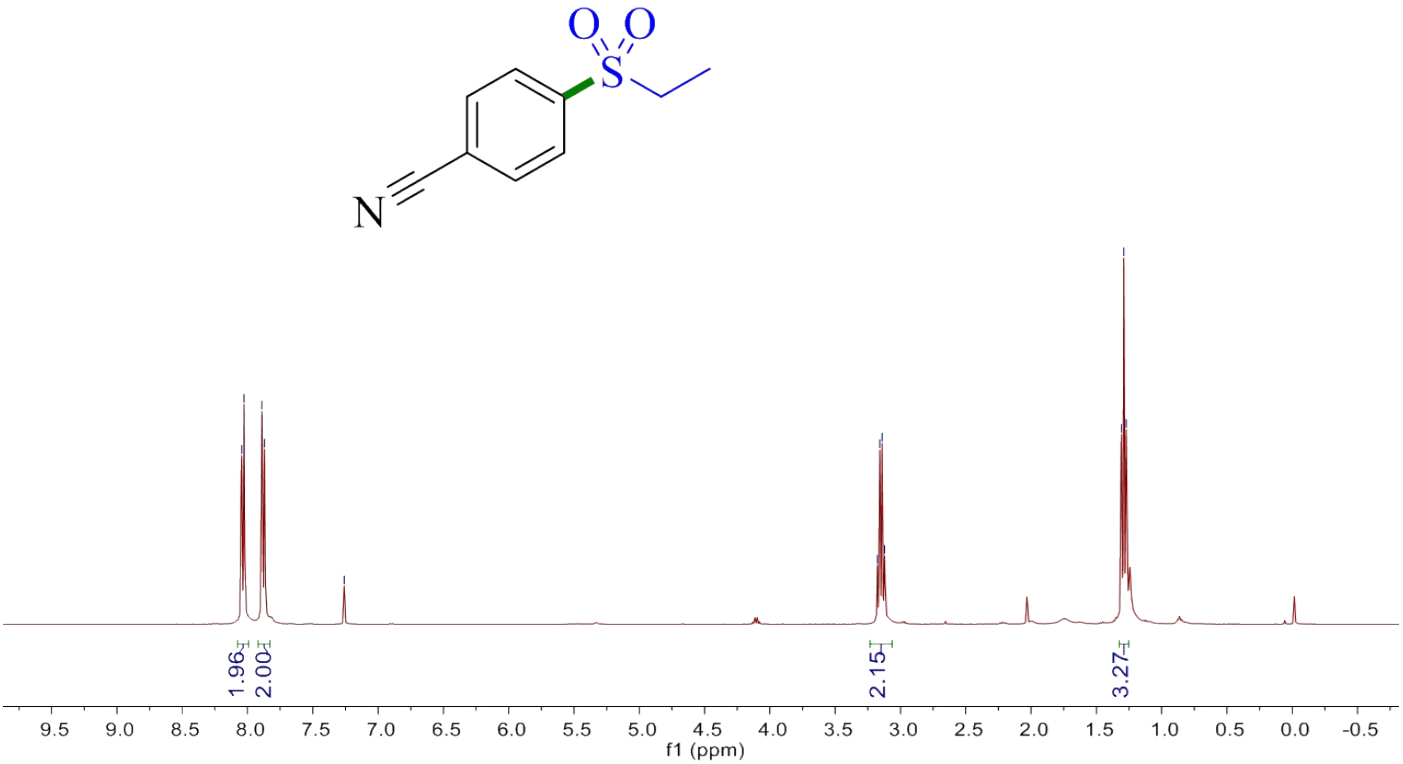
144.58
133.33
128.33
117.74
117.16
77.48
77.16
76.84
44.36

^{13}C NMR (101 MHz, $CDCl_3$)

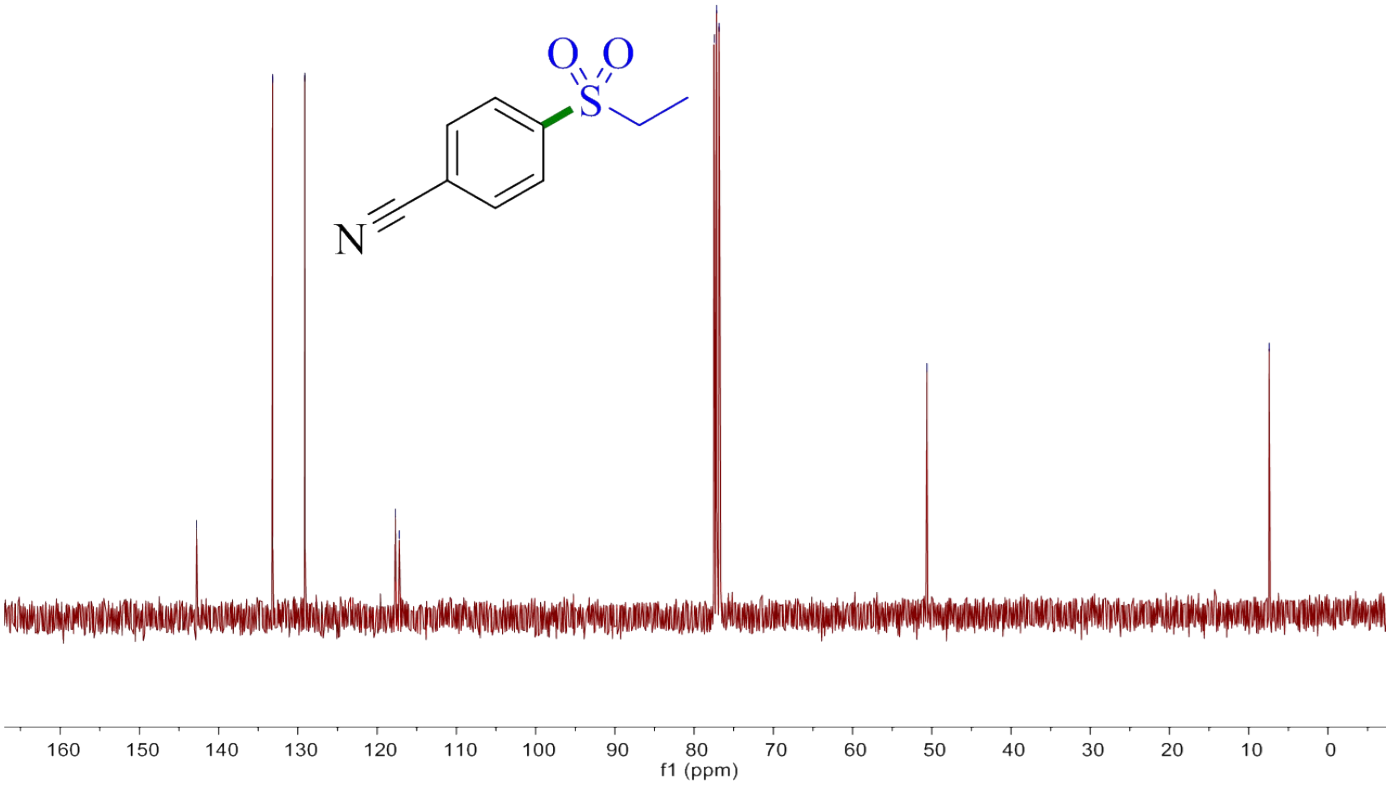


7k

^{1}H NMR (400 MHz, $CDCl_3$)

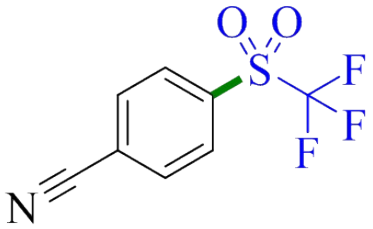


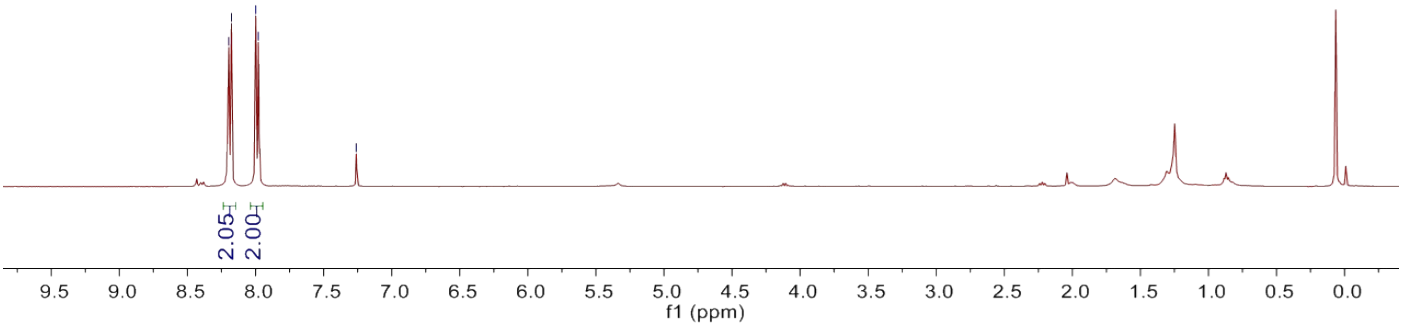
^{13}C NMR (101 MHz, $CDCl_3$)



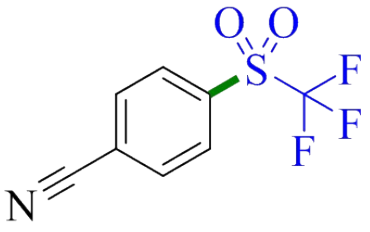
7l

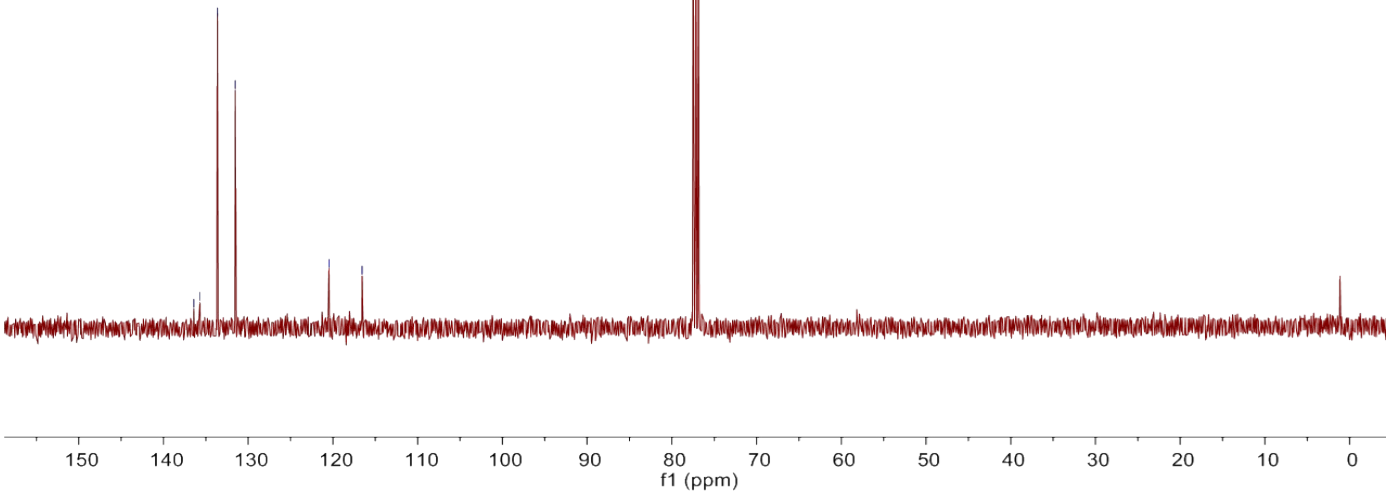
^{1}H NMR (400 MHz, $CDCl_3$)



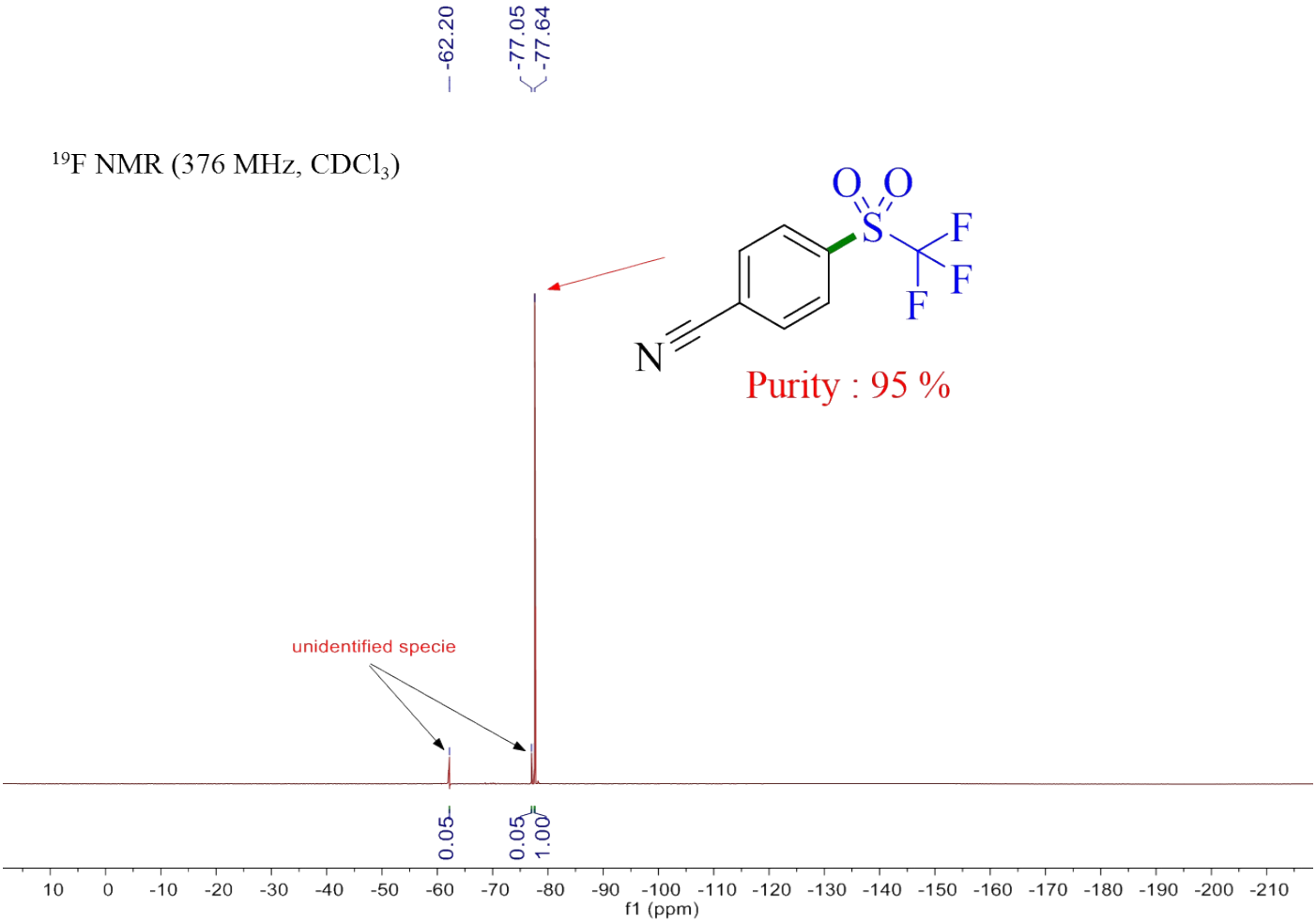


^{13}C NMR (101 MHz, $CDCl_3$)



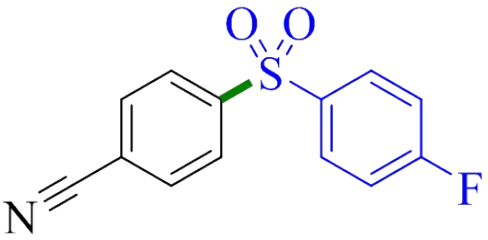


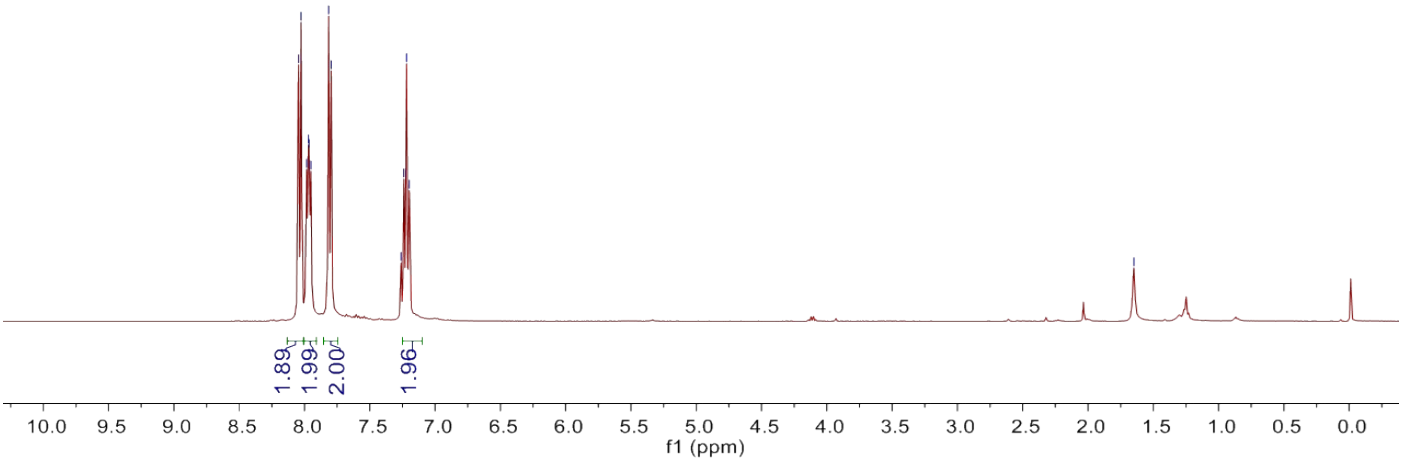
^{19}F NMR (376 MHz, $CDCl_3$)

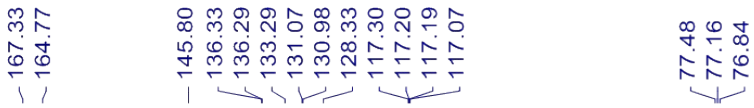


7m

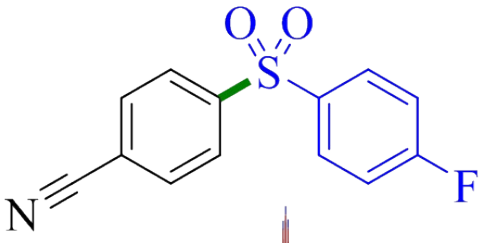
^{1}H NMR (400 MHz, $CDCl_3$)

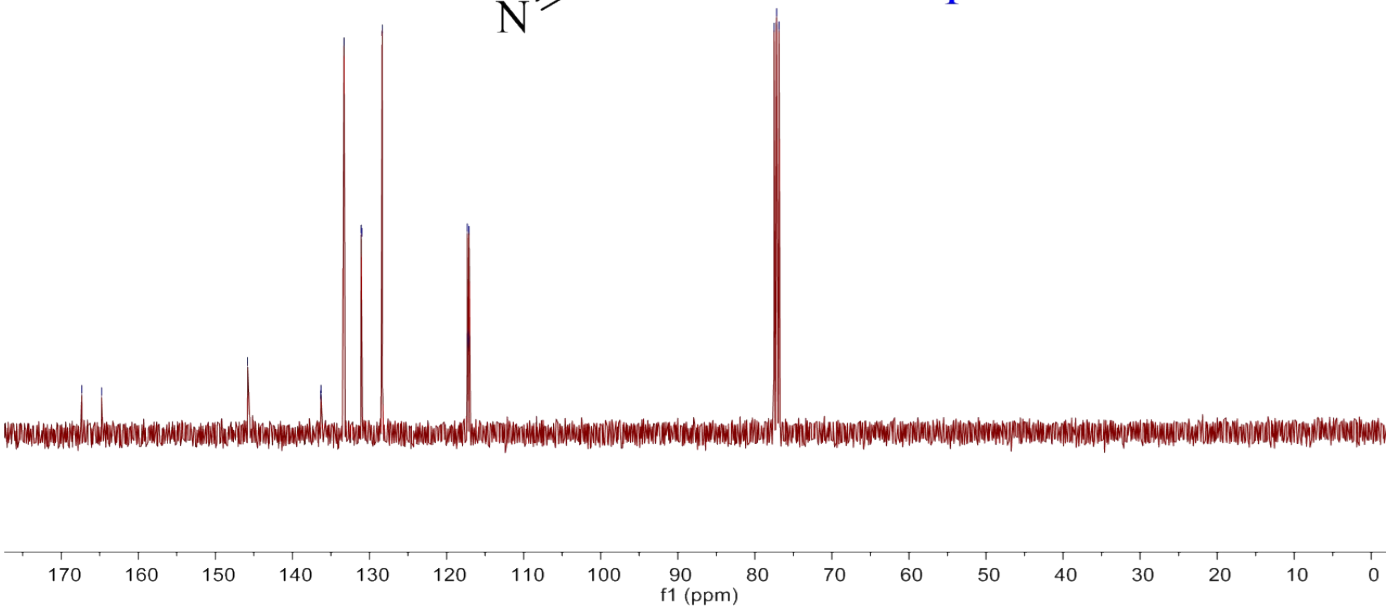




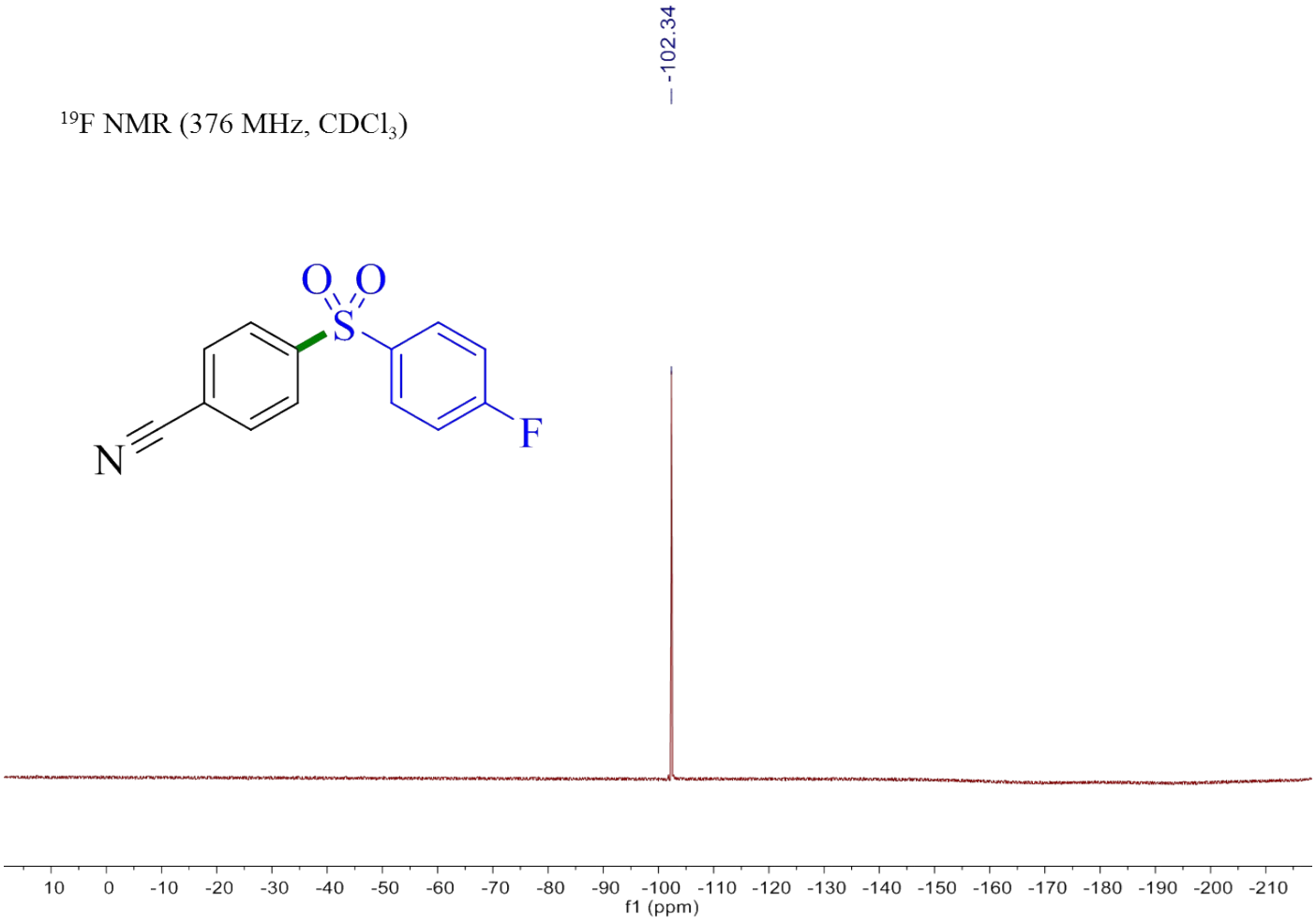


^{13}C NMR (101 MHz, $CDCl_3$)

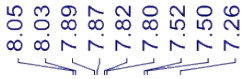




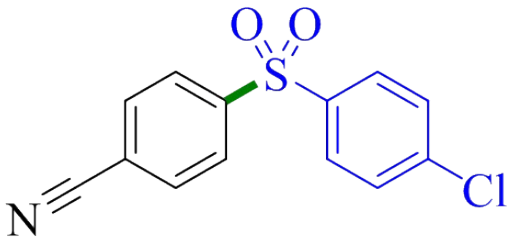
^{19}F NMR (376 MHz, $CDCl_3$)

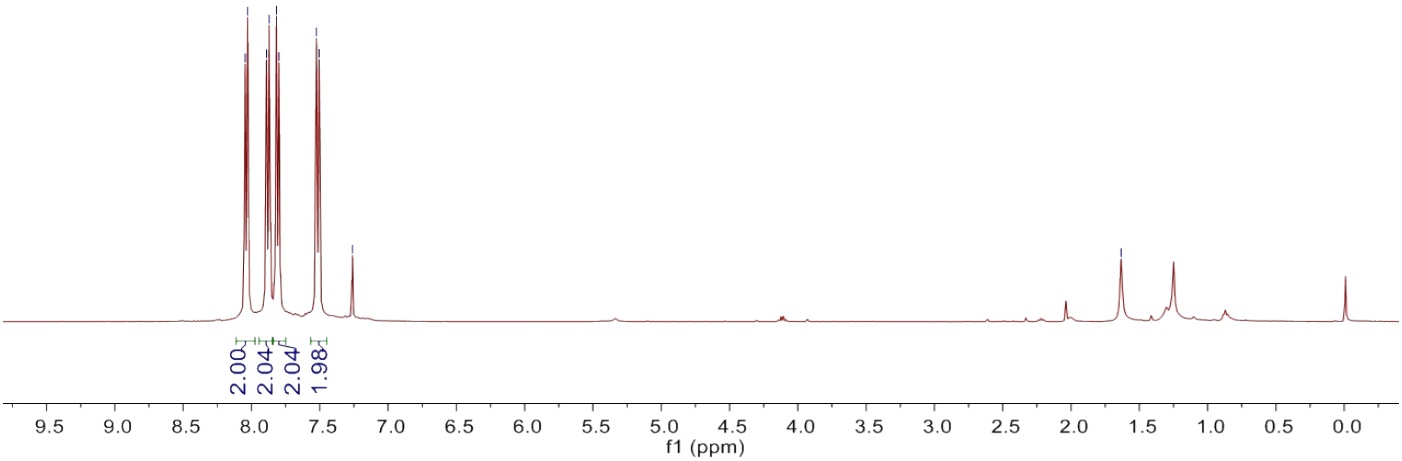


7n

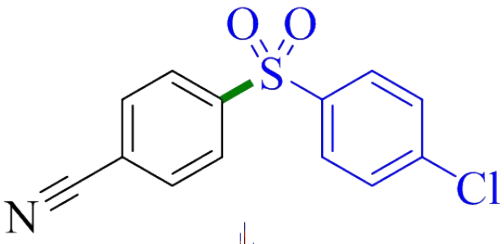


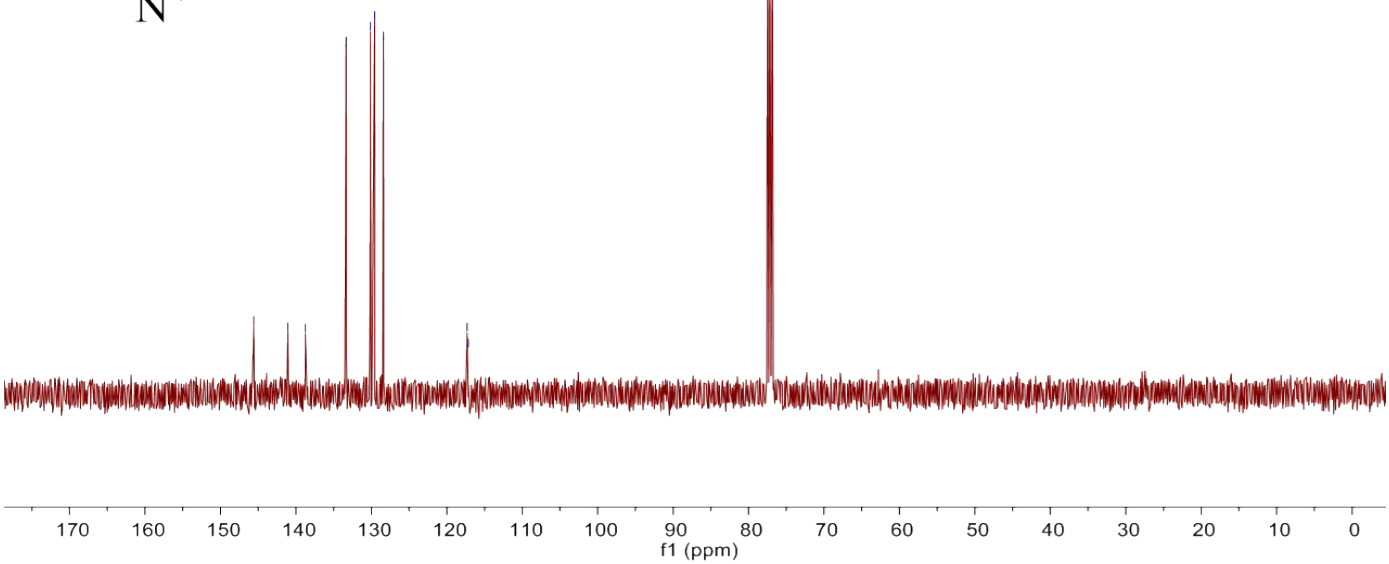
^{1}H NMR (400 MHz, $CDCl_3$)





^{13}C NMR (101 MHz, $CDCl_3$)



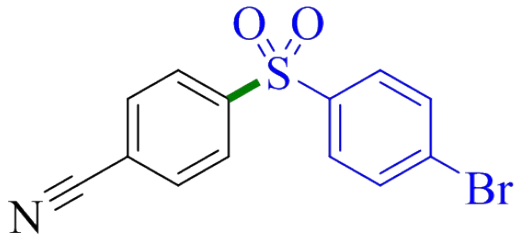


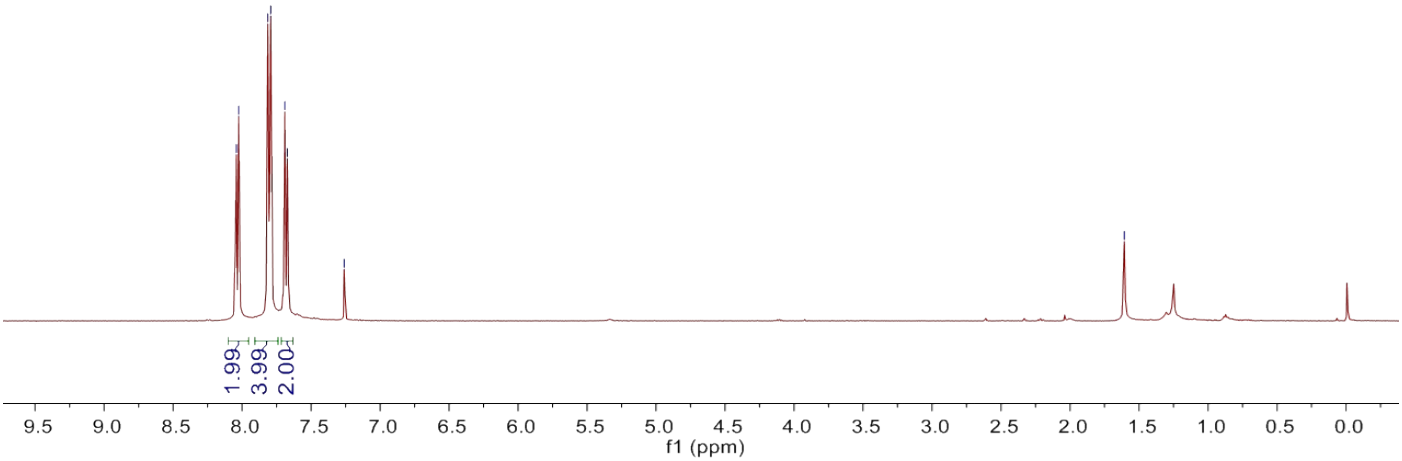
7o

8.04
8.02
7.81
7.79
7.69
7.67
7.26

1.61
H_2O

^{1}H NMR (400 MHz, $CDCl_3$)

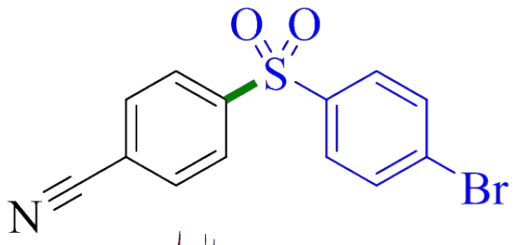




145.52
139.29
133.33
133.14
129.68
129.59
128.41
117.34
117.16

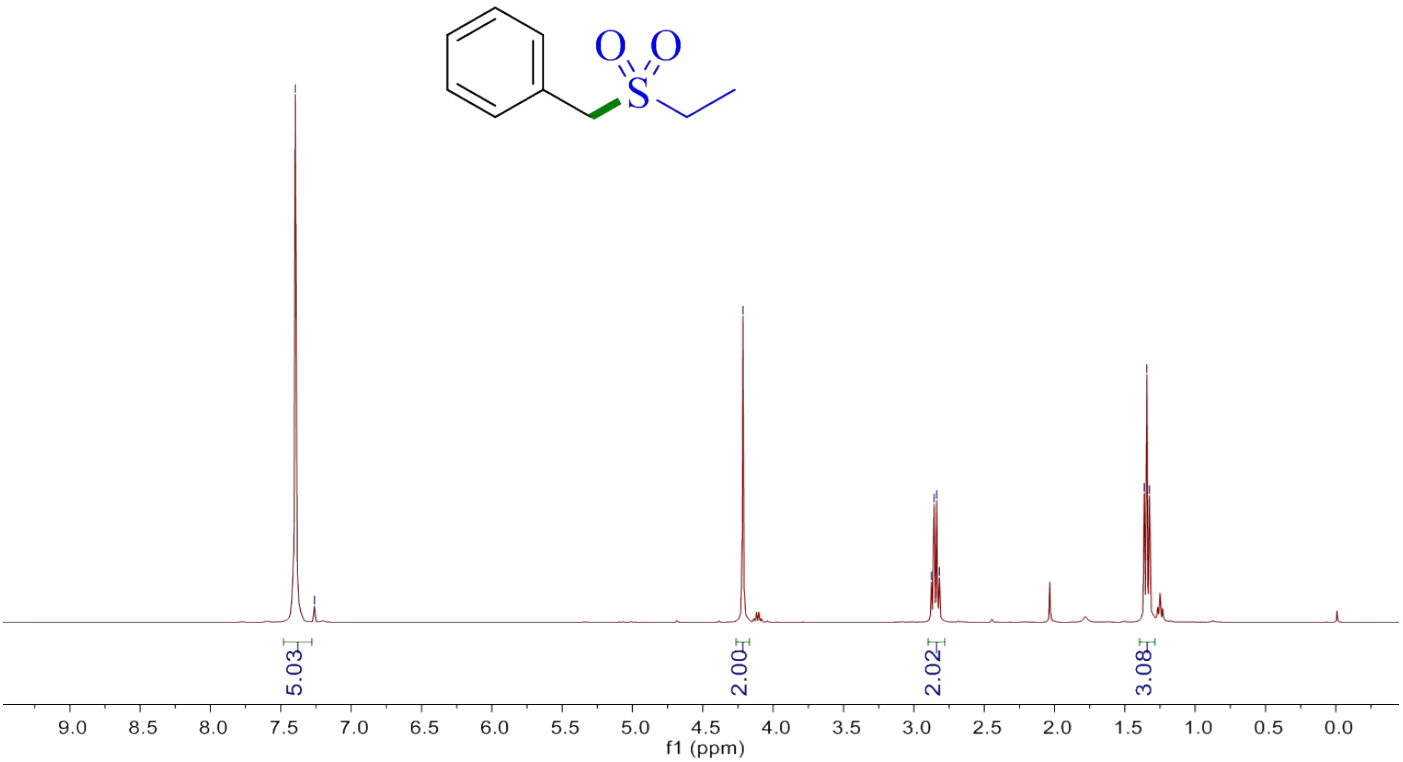
77.48
77.16
76.84

^{13}C NMR (101 MHz, $CDCl_3$)

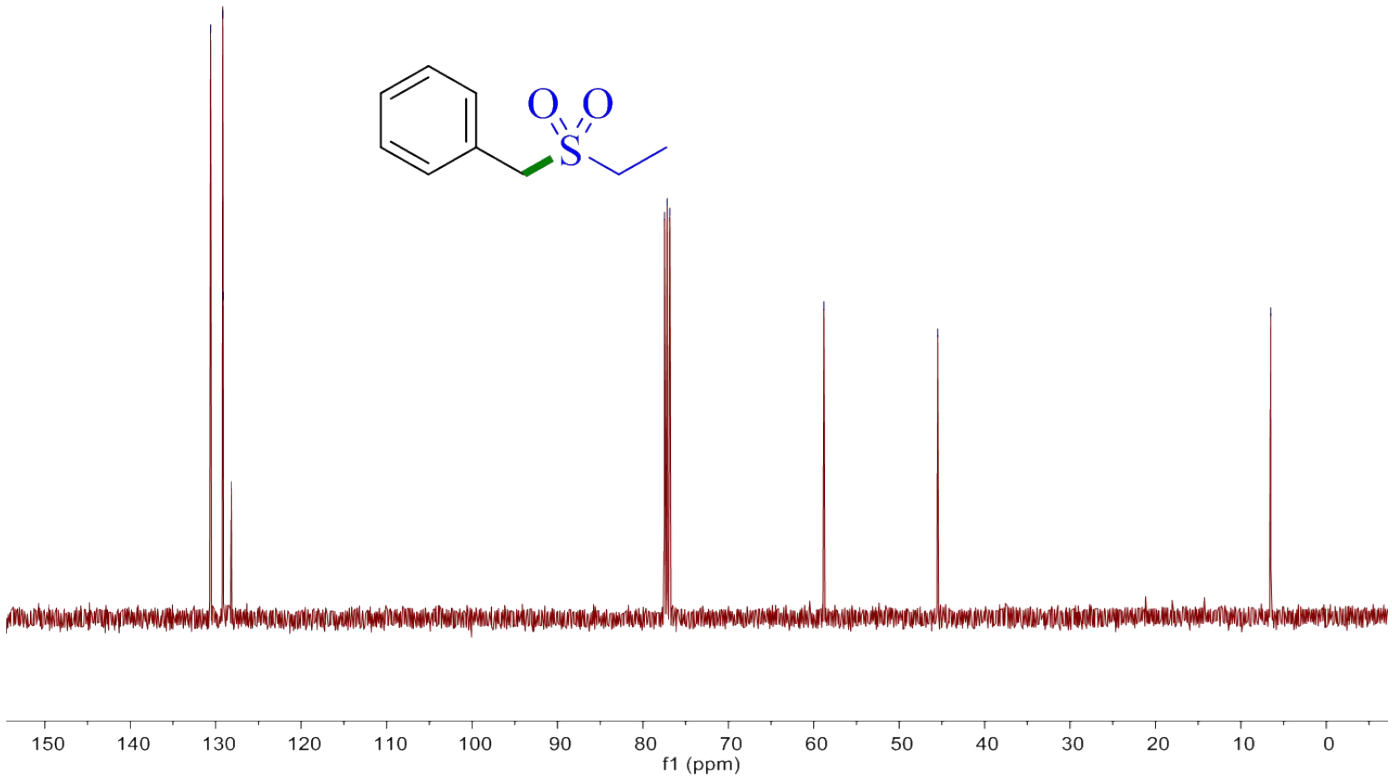


7p

^{1}H NMR (400 MHz, $CDCl_3$)

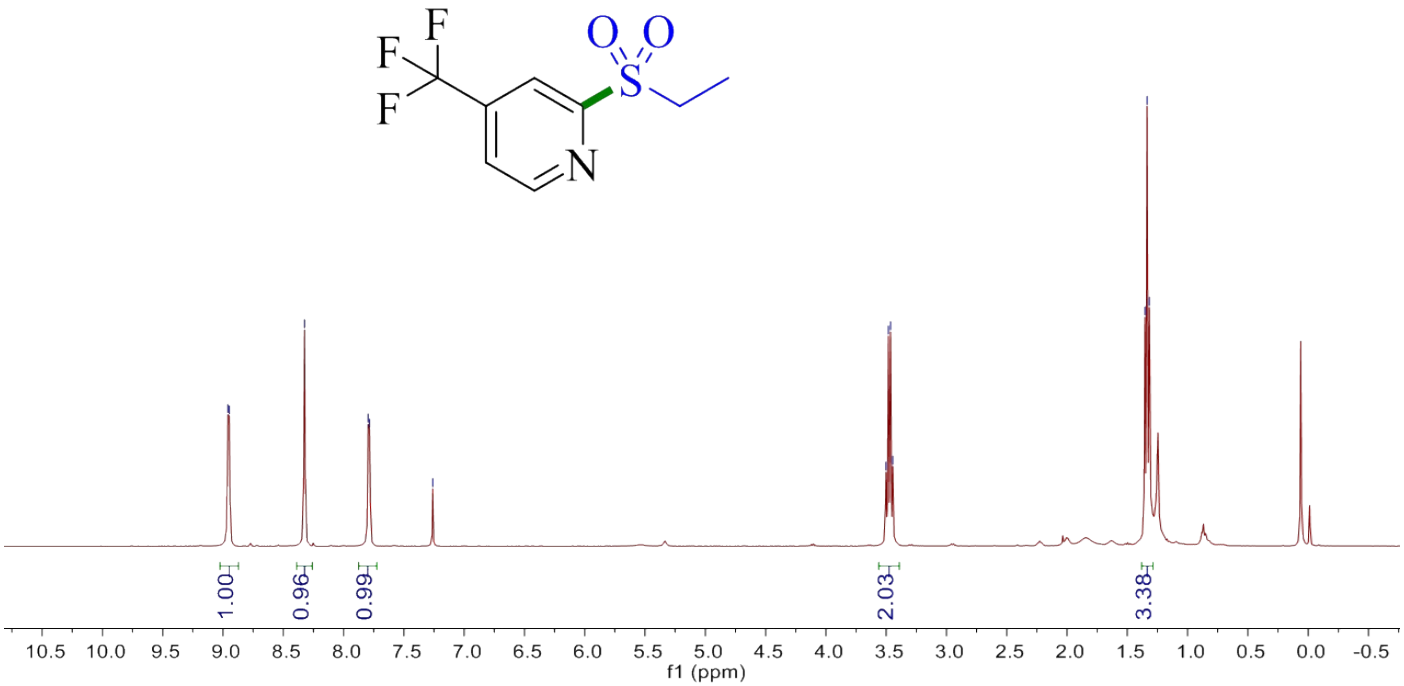


^{13}C NMR (101 MHz, $CDCl_3$)

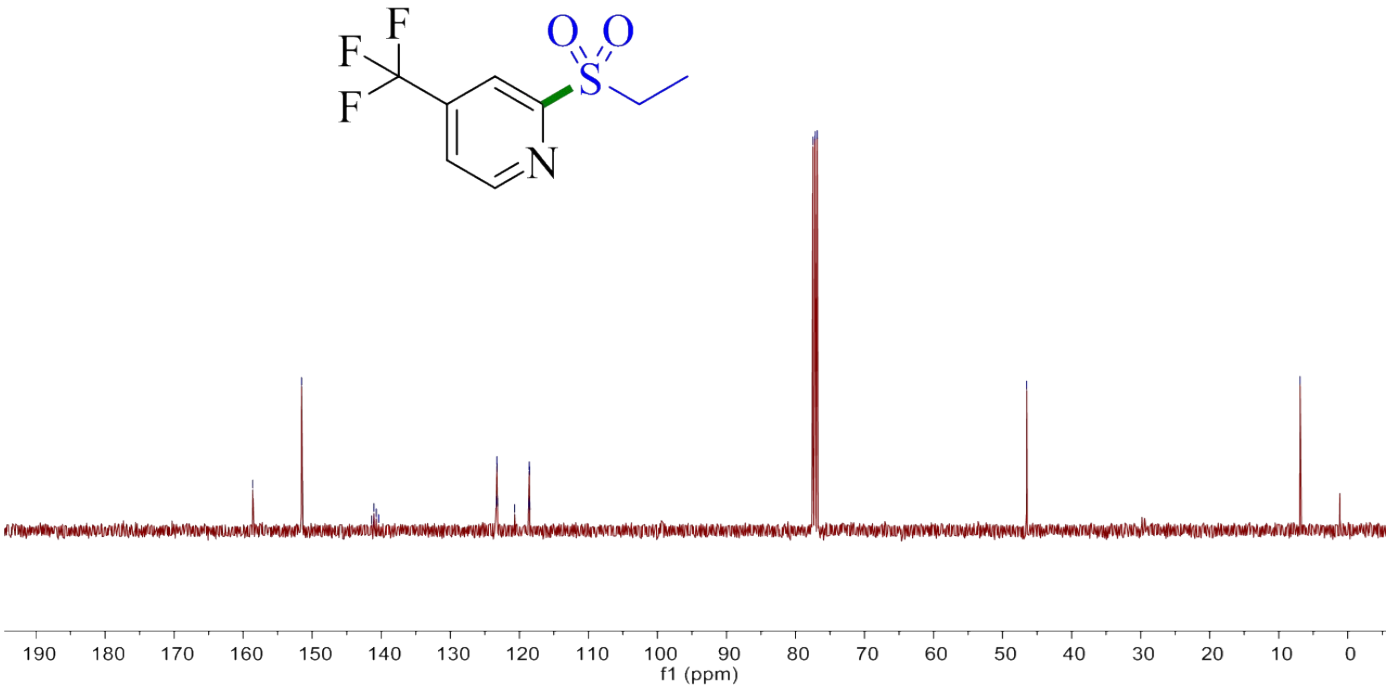


7q

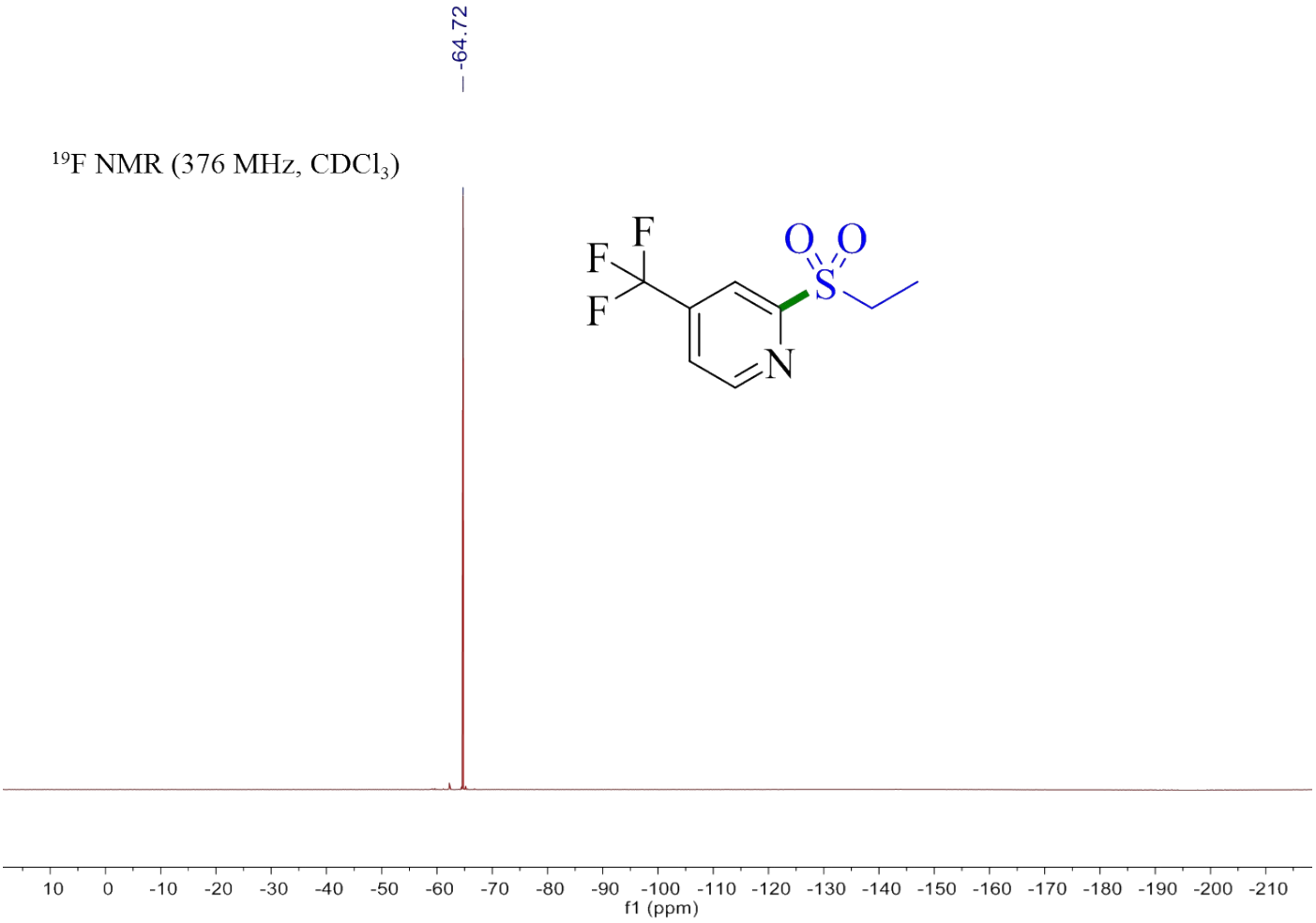
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

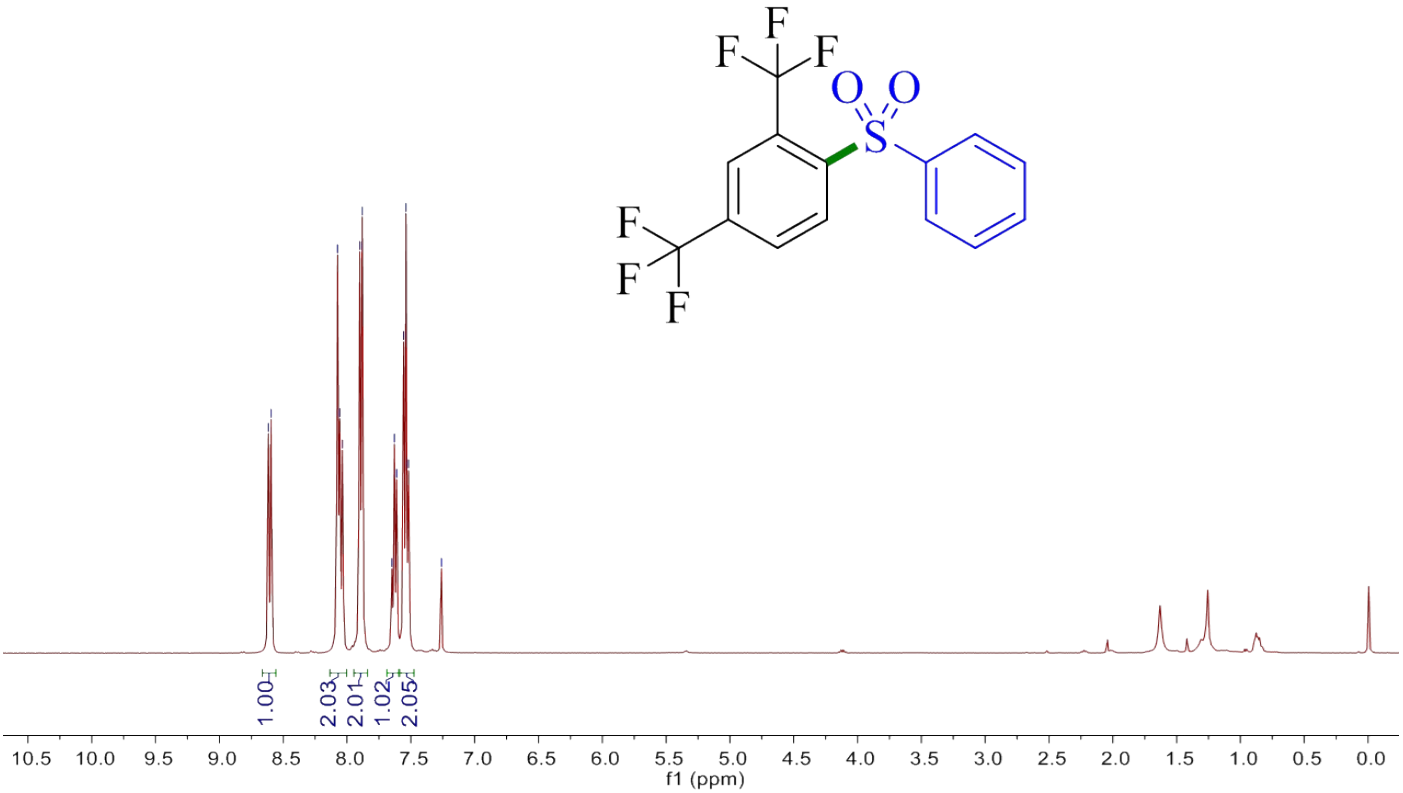


^{19}F NMR (376 MHz, $CDCl_3$)

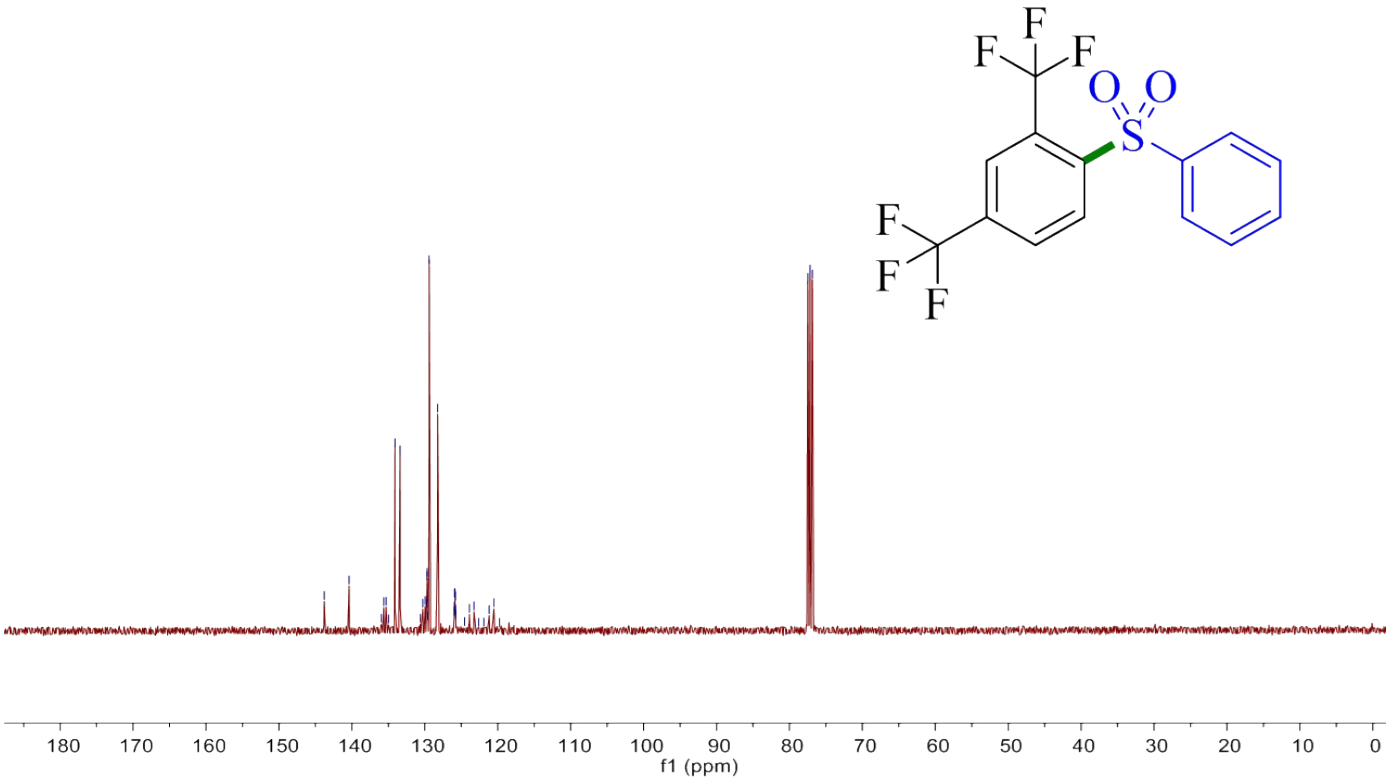


7r

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$)