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1. General Information

1.1. Experimental Information

Unless otherwise noted, all reactions were carried out under nitrogen or argon atmosphere with standard Schlenk techniques. Reaction mixture was stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths (except for photochemical reactions which were subjected to a specific apparatus). All the commercially available reagents and solvents were purchased from commercial sources and used as received.

1.2. Chromatography and Instrumentation

Analytical thin layer chromatography (TLC) was performed on silica gel (GF 254) plates which was visualized under UV light (254 or 356 nm).
Flash column chromatography (FCC) was performed on silica gel (200-300 or 300-400 mesh) unless otherwise specified.
NMR spectra (^{1}H, ^{13}C, ^{19}F and ^{11}B spectra) were recorded using Bruker AVANCE III 400 MHz or 500 MHz spectrometers in ambient conditions unless otherwise stated. Chemical shifts (δ values) were reported in ppm with the residual solvent resonances of the deuterated solvents for reference. Coupling constants (*J*) were given in Hertz (Hz) and refer to apparent multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, hex = hextet, h = heptet, m= multiplet, br = broad signal, dd = doublet of doublets, etc.). The ^{1}H NMR spectra were recorded as follows: chemical shift (multiplicity, coupling constants, number of protons). ^{11}B chemical shifts were measured utilizing external $Et_2O{\cdot}BF_3$ (δ = 0 ppm) as reference.
The high-resolution mass spectra (HRMS) were recorded on Agilent Micromass 6540 Q-Tof LC/MS by Electrospray ionisation (ESI).
UV-Vis absorption spectra were recorded with a Shimadzu UV-3600 spectrophotometer.
Single crystal X-ray crystallography were carried on a Bruker SMART Apex III CCD diffractometer by means of graphitemonochromated (Mo-Kα radiation, λ = 0.7107 Å and Cu-Kα radiation, λ = 1.5406 Å). APEX III program was used to determine the unit cell parameters and for data collection. The data were integrated and corrected for Lorentz and polarization effects using SAINT. Absorption correction was applied with SADABS. The structure was solved by direct method and refined by full-matrix least-squares method on F^2 using the SHELXTL or Olex-2 crystallographic software package[1]. All non-hydrogen atom positions were determined to utilize the difference Fourier synthesis, while the hydrogen atoms were placed at geometrically calculated positions using a riding model. X-ray data can be obtained from the Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/.

1.3. Photochemical Reactions

1.3.1. Setup of the Photochemical Instruments

Most photochemical reactions were performed in 10 mL sealed tubes made from boronsilicate glass (SYNTHWARE), and preparative scale reactions were performed in 25 mL sealed tubes made from boronsilicate glass (SYNTHWARE). The tubes were placed into a commercially available photochemical reaction apparatus (Shanshi SSSTECH-LAL1CV1.0) equipped with a thermostatic system and a voltage regulator. The reaction setup is detailed in Figure S1.

Figure S1. Photochemical reaction setup.

1.3.2.Emission Spectra of the LEDs

The maximum emission wavelength of the most commonly used LED is about 400 nm (Figure S2A). In optimization experiments, other LEDs with different wavelengths were also used. Their emission spectra are as follows (Figure S2B–S2D).

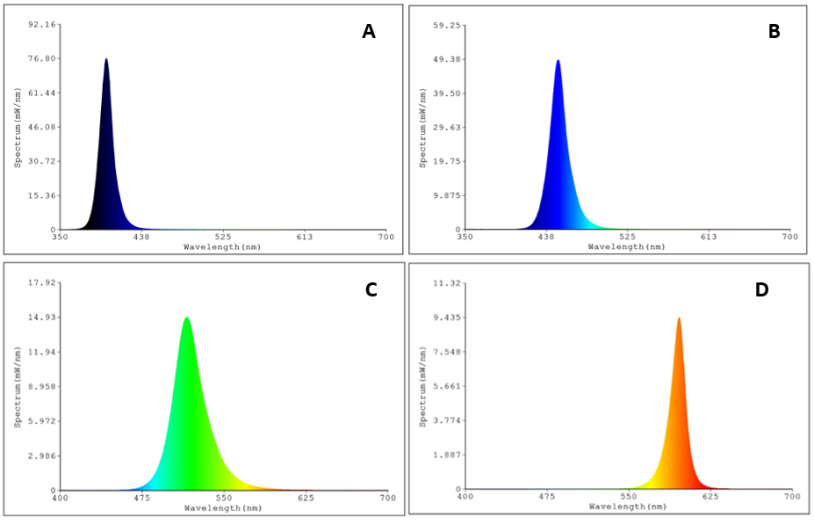


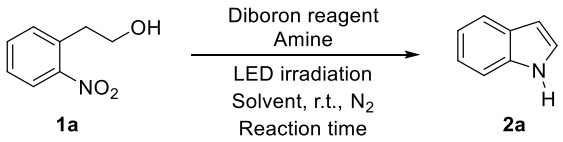
Figure S2. (A) Emission spectrum of a 395-400 nm LED (λ_{max} = 399.9 nm). (B) Emission spectrum of a 450-455 nm LED (λ_{max} = 450.5 nm). (C) Emission spectrum of a 520-525 nm LED (λ_{max} = 520.6 nm). (D) Emission spectrum of a 590-595 nm LED (λ_{max} = 592.3 nm).

2. Reaction Optimization

2.1. Reaction Optimization for the Synthesis of 1*H*-indole Derivatives

Experimental procedure: To a flame-dried Schlenk tube with a Teflon-coated magnetic stirring bar, 2-(2-nitrophenyl)ethan-1-ol (**1a**, 33 mg, 0.2 mmol) and a diboron reagent were added in degassed solvents, followed by the addition of amine under nitrogen atmosphere. The mixture was vigorously stirred under the irradiation of blue LEDs at room temperature. Upon completion, the crude mixture was purified on preparative TLC using DCM as the eluent to afford the desired product. Table S1 reports the experiments performed.

Table S1. Selected reaction optimization for 1*H*-indole derivatives.



Entry	Diboron reagent	Amine	Solvent	Light source	Time (h)	Yield (%)[a]
1	B_2nep_2 (0.5 equiv.)	DIPEA (20 mol%)	THF/MeOH (0.4 mL/50 µL)	400 nm LED (6 W)	12	35
2	B_2nep_2 (1.0 equiv.)	DIPEA (20 mol%)	THF/MeOH (0.4 mL/50 µL)	400 nm LED (6 W)	12	52
3	B_2nep_2 (2.2 equiv.)	DIPEA (20 mol%)	THF/MeOH (0.4 mL/50 µL)	400 nm LED (6 W)	12	82
4	B_2nep_2 (2.2 equiv.)	DIPEA (20 mol%)	THF (0.4 mL)	400 nm LED (6 W)	12	70
5	B_2nep_2 (2.2 equiv.)	DIPEA (20 mol%)	1,4-Dioxane (0.4 mL)	400 nm LED (6 W)	12	22
6	B_2nep_2 (2.2 equiv.)	DIPEA (20 mol%)	CH_3CN (0.4 mL)	400 nm LED (6 W)	12	38
7	B_2nep_2 (2.2 equiv.)	DIPEA (20 mol%)	DCE (0.4 mL)	400 nm LED (6 W)	12	27
8	B_2nep_2 (2.2 equiv.)	DIPEA (20 mol%)	Toluene (0.4 mL)	400 nm LED (6 W)	12	50
9[b]	$B_2(OH)_4$ (2.2 equiv.)	DIPEA (20 mol%)	THF/MeOH (0.4 mL/50 µL)	400 nm LED (6 W)	12	62
10	B_2cat_2 (2.2 equiv.)	DIPEA (20 mol%)	THF/MeOH (0.4 mL/50 µL)	400 nm LED (6 W)	12	Trace
11	B_2pin_2 (2.2 equiv.)	DIPEA (20 mol%)	THF/MeOH (0.4 mL/50 µL)	400 nm LED (6 W)	12	30
12	B_2nep_2 (2.2 equiv.)	Triethylamine (20 mol%)	THF/MeOH (0.4 mL/50 µL)	400 nm LED (6 W)	12	60

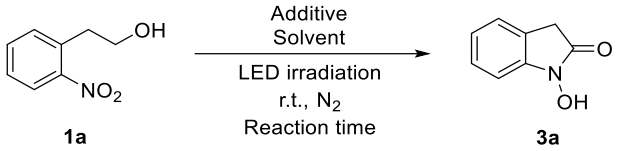
13	B_2nep_2 (2.2 equiv.)	K_2CO_3 (20 mol%)	THF/MeOH (0.4 mL/50 μL)	400 nm LED (6 W)	12	38
14	B_2nep_2 (2.2 equiv.)	KO^{t}Bu (20 mol%)	THF/MeOH (0.4 mL/50 μL)	400 nm LED (6 W)	12	23
15	B_2nep_2 (2.2 equiv.)	None	THF/MeOH (0.4 mL/50 μL)	400 nm LED (6 W)	12	40
16	None	DIPEA (20 mol%)	THF/MeOH (0.4 mL/50 μL)	400 nm LED (6 W)	12	Trace
17[c]	B_2nep_2 (2.2 equiv.)	DIPEA (20 mol%)	THF/MeOH (0.4 mL/50 μL)	400 nm LED (6 W)	12	48
18[d]	B_2nep_2 (2.2 equiv.)	DIPEA (20 mol%)	THF/MeOH (0.4 mL/50 μL)	In dark	12	Nd

[a] Isolated yields. [b] The reaction condition of entry 8 was more effective for the synthesis of 2-substitued indoles. [c] The tube was unsealed and exposed to air. [d] The tube was wrapped with tin foil to ensure the reaction was performed in dark with all other conditions being equal.

2.2. Reaction Optimization for the Synthesis of 1-Hydroxyindolin-2-one Derivatives

Experimental procedure: To a flame-dried Schlenk tube with a Teflon-coated magnetic stirring bar, 2-(2-nitrophenyl)ethan-1-ol (**1a**, 33 mg, 0.2 mmol), additives and degassed solvent (0.4 mL) were added under nitrogen atmosphere. The mixture was vigorously stirred under the irradiation of LEDs at room temperature. After reaction, 1,3,5-tribromobenzene (63 mg, 0.2 mmol, 1.0 equiv.) was added and the solvent was evaporated under reduced pressure. DMSO-d_6 (0.6 mL) was then added and the mixture was analyzed by ^{1}H NMR spectroscopy to determine the NMR yield. Table S2 reports the experiments performed.

Table S2. Selected reaction optimization for the derivatives of cyclic hydroxamic acids.



1a **3a**

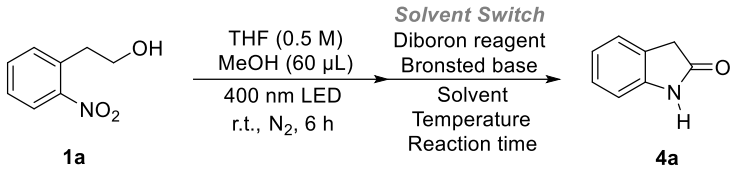
Entry	Additive	Solvent	Light source[a]	Time (h)	Yield (%)[a]
1	none	THF (0.5 M)	400 nm LED (6 W)	6	60
2	MeOH (30 μL)	THF (0.5 M)	400 nm LED (6 W)	6	81
3	MeOH (50 μL)	THF (0.5 M)	400 nm LED (6 W)	6	91 (88)[b]
4	MeOH (50 μL)	CH_3CN (0.5 M)	400 nm LED (6 W)	6	43
5	None	MeOH (0.5 M)	400 nm LED (6 W)	6	54
6	MeOH (50 μL)	DCM (0.5 M)	400 nm LED (6 W)	6	26
7[c]	MeOH (50 μL)	THF (0.5 M)	In dark	6	Nd
8	MeOH (50 μL)	THF (0.5 M)	White LED (10 W)	6	11
9	MeOH (50 μL)	THF (0.5 M)	520 nm LED (6 W)	6	Nd
10	MeOH (50 μL)	THF (0.5 M)	590 nm LED (6 W)	6	Nd
11[d]	Air	THF (0.5 M)	400 nm LED (6 W)	6	32

[a] NMR yields using 1,3,5-tribromobenzene (63 mg, 0.2 mmol) as an internal standard. [b] Isolated yield. [c] The tube was wrapped with tin foil to ensure the reaction was performed in dark with all other conditions being equal. [d] The tube was unsealed and exposed to air.

2.3. Reaction Optimization for the Synthesis of Indolin-2-one Derivatives

Experimental procedure: To a flame-dried Schlenk tube with a ground-glass bottle-neck (for rotary evaporation) and a Teflon-coated magnetic stirring bar, 2-(2-nitrophenyl)ethan-1-ol (**1a**, 33 mg, 0.2 mmol), additives and degassed solvent (0.4 mL) were added under nitrogen atmosphere. The mixture was vigorously stirred under the irradiation of blue LEDs for 6 hours at ambient temperature. After that, the sealing plug was removed and the mixture was exposed to air. The solvent was evaporated in *vacuo*, and the residue was redissolved in another solvent (***solvent switch***). Diboron reagent and Bronsted base were added to the reaction mixture, which was then stirred with different temperatures for another reaction time. Upon completion, 1,3,5-tribromobenzene (63 mg, 0.2 mmol, 1.0 equiv.) was added and the solvent was evaporated under reduced pressure. DMSO-d_6 (0.6 mL) was then added and the mixture was analyzed by ^{1}H NMR spectroscopy to determine the NMR yield. Table S3 reports the experiments performed.

Table S3. Selected reaction optimization for indolin-2-one derivatives.



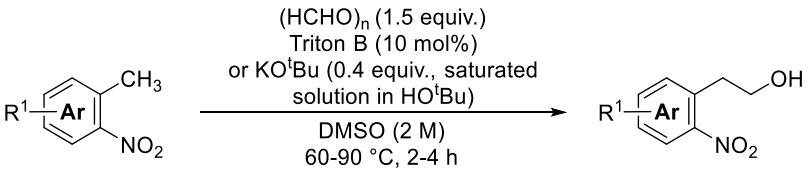
Entry	Diboron reagent	Bronsted base	Solvent	Temp. (˚C)	Time (h)	Yield (%)[a]
1	B_2pin_2 (1.5 equiv.)[b]	KOAc (2.0 equiv.)	MeOH (0.2 M)	50 ˚C	2 h	79
2	$B_2(OH)_4$ (1.5 equiv.)	KOAc (2.0 equiv.)	MeOH (0.2 M)	50 ˚C	2 h	89 (87)[c]
3	$B_2(OH)_4$ (1.0 equiv.)	KOAc (2.0 equiv.)	MeOH (0.2 M)	50 ˚C	2 h	55
4	$B_2(OH)_4$ (1.5 equiv.)	KOAc (2.0 equiv.)	MeOH (0.2 M)	50 ˚C	30 min	75
5	$B_2(OH)_4$ (1.5 equiv.)	K_2CO_3 (2.0 equiv.)	MeOH (0.2 M)	50 ˚C	2 h	43
6	$B_2(OH)_4$ (1.5 equiv.)	KOAc (2.0 equiv.)	MeOH (0.2 M)	r.t.	2 h	38
7[d]	$B_2(OH)_4$ (1.5 equiv.)	KOAc (2.0 equiv.)	THF (0.5 M) with MeOH (60 μL)	50 ˚C	2 h	75 (63)[c]

[a] NMR yields using 1,3,5-tribromobenzene (63 mg, 0.2 mmol) as an internal standard. [b] When using borate esters instead of $B_2(OH)_4$, products obtained from FCC were often mixed with trace amount of borate esters. [c] Isolated yield. [d] No solvent switch.

3. Synthesis of Substrates

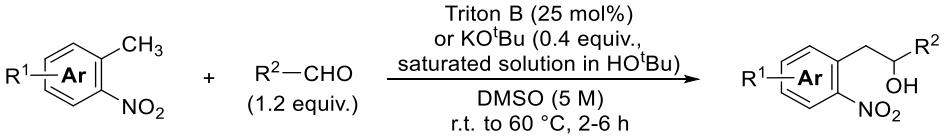
3.1. General Procedures for the Synthesis of Substrates

3.1.1. General Procedure S1



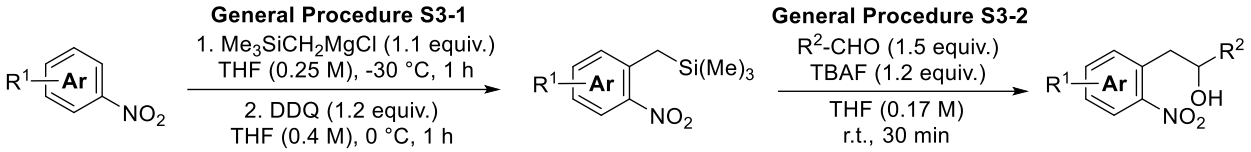
Prepared following a modified literature procedure[2]: A 25-mL round-bottomed flask equipped with a Teflon-coated stirring bar was charged with the derivative of 1-methyl-2-nitrobenzene (1.0 equiv.), paraformaldehyde (1.5 equiv.), DMSO (c = 2.0 M) and benzyltrimethylammonium hydroxide (i.e. Triton B, 40% w/w in methanol, 0.10 equiv.). In some cases, triton B was replaced by KO^{t}Bu (saturated solution in HO^{t}Bu, 0.4 equiv.). The flask was sealed with a rubber plug to prevent the leakage of acetaldehyde. The reaction mixture was stirred at 60-90 °C for 2–4 h (the reaction is exothermic). Subsequently, the mixture was cooled to room temperature, quenched with 1 M HCl aqueous solution and extracted with EtOAc (5–10 mL × 3). The combined organic layer was then washed with brine (15 mL), dried over Na_2SO_4, filtered and evaporated. Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel afforded the corresponding substrate.

3.1.2. General Procedure S2



Prepared following a modified literature procedure[3]: An oven-dried tube equipped with a Teflon-coated magnetic stirring bar was charged with the derivative of 1-methyl-2-nitrobenzene (1.0 equiv.), aldehyde (1.2 equiv.), benzyltrimethylammonium hydroxide (i.e. Triton B, 40% w/w in methanol, 0.25 equiv.) and anhydrous DMSO (c = 5.0 M). In some cases, triton B was replaced by KOtBu (saturated solution in HOtBu, 0.4 equiv.). The mixture was vigorously stirred for 20 min at room temperature, and then heated to 60 °C for 2–6 hours until the reaction was quenched by water (5–10 mL) and the mixture was extracted with EtOAc (5–10 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and evaporated. Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the corresponding substrate.

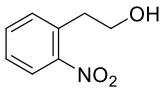
3.1.3. General Procedure S3



Prepared following a modified literature procedure[4]: (Trimethylsilyl)methylmagnesium chloride (i.e. Peterson reagent, 1.1 equiv.) was added dropwise to a stirred THF solution (0.25 M) of nitroarene (1.0 equiv.) under nitrogen atmosphere at -30 ˚C. The reaction mixture was stirred for 1 h, then a THF solution (0.4 M) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (i.e. DDQ, 1.2 equiv.) was added dropwise, and the temperature was allowed to rise to 0 ˚C under stirring. After 1 h, the mixture was poured in 10–30 mL of 5% acetic acid and extracted with CH_2Cl_2 (5–10 mL × 3). The organic layer was washed with saturated solution of $NaHCO_3$ (5–10 mL), dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to afford the [(trimethylsilyl)methyl]nitroarene.
An oven-dried round-bottom flask with a magnetic stirring bar was charged with tetrabutylammonium fluoride (i.e. TBAF, 1.2 equiv.), in which a THF solution (0.25 M) of the aldehyde (1.5 equiv.) was added dropwise at room temperature under nitrogen atmosphere. After then, a THF solution (0.5 M) of above [(trimethyl)methyl]nitroarene was added dropwise at room temperature. The mixture was stirred for 30 minutes until 37% hydrochloric acid was added to quench the reaction. The mixture was extracted with CH_2Cl_2, washed with water, dried over Na_2SO_4, evaporated and submitted to a flash chromatographic purification, giving the corresponding substrate.

3.2. Characterization of Substrates

2-(2-Nitrophenyl)ethan-1-ol (1a)



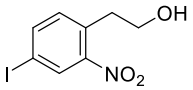
1a was prepared following **General Procedure S1** from 1-methyl-2-nitrobenzene (1.0 equiv., 685 mg, 5 mmol), paraformaldehyde (1.5 equiv., 225 mg, 7.5 mmol) and benzyltrimethylammonium hydroxide (i.e. Triton B, 40% w/w in methanol, 0.25 equiv.) in DMSO (2.5 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product as brown oil (669 mg, 80%). All recorded NMR data were in consistent with the reported data[2].

NMR Data of 1a:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.54 (ddd, *J* = 8.0, 7.6, 1.4 Hz, 1H), 7.43 – 7.34 (m, 2H), 3.92 (t, *J* = 6.5 Hz, 2H), 3.15 (t, *J* = 6.5 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 149.86, 133.80, 133.07, 132.87, 127.67, 124.89, 62.76, 36.15.

2-(4-Iodo-2-nitrophenyl)ethan-1-ol (1b)



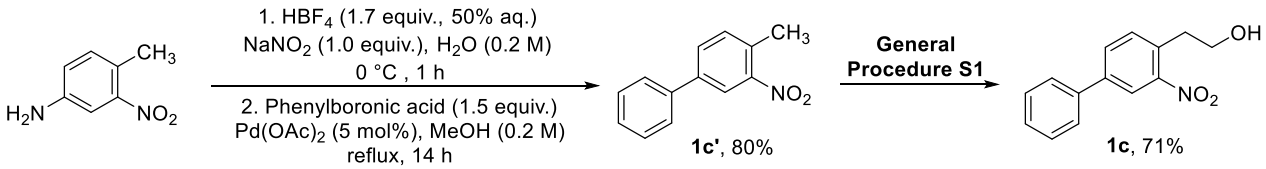
1b was prepared following **General Procedure S1** from 4-iodo-1-methyl-2-nitrobenzene (1.0 equiv., 789 mg, 3 mmol), paraformaldehyde (1.5 equiv., 135 mg, 4.5 mmol) and benzyltrimethylammonium hydroxide (i.e. Triton B, 40% w/w in methanol, 0.25 equiv.) in DMSO (1.5 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product as brown oil (571 mg, 65%). All recorded NMR data were in consistent with the reported data[5].

NMR Data of 1b:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 1.7 Hz, 1H), 7.82 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.14 (d, *J* = 8.1 Hz, 1H), 3.86 (t, *J* = 6.4 Hz, 2H), 3.06 (t, *J* = 6.4 Hz, 2H), 2.22 (br, s, 1H, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.12, 141.83, 134.34, 133.49, 133.29, 90.85, 62.26, 35.70.

2-(3-Nitro-[1,1'-biphenyl]-4-yl)ethan-1-ol (1c)



4-Methyl-3-nitro-1,1'-biphenyl (**1c'**) was prepared following a modified procedure from the reported literature[6]. A mixture of

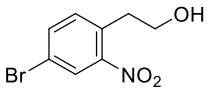
4-methyl-3-nitroaniline (1.0 equiv., 1.0 g, 6.57 mmol) and hydrobromic acid (1.7 equiv., 11.2 mmol, 1.34 mL, 48% aqueous solution) was cooled to 0 °C. A solution of sodium nitrite (1.0 equiv., 453 mg, 6.57 mmol) in H_2O (5 M) was then added rapidly with stirring. The temperature was kept around 0 °C by the addition of small pieces of ice. After 1 h, the mixture was filtered and the filter cake was dissolved in 1.5 mL acetone. A large amount of diethyl ether (about 50 mL) was then poured into the solution with precipitation appearing. The precipitated solid was separated by filtration, and transferred into a three-necked round-bottomed flask equipped with a stirring bar. Phenylboronic acid (1.5 equiv., 1.2 g, 9.86 mmol) and $Pd(OAc)_2$ (5 mol%, 74 mg, 0.33 mmol) were added into the flask until the flask was sealed, evacuated and refilled with N_2 (× 3). Anhydrous MeOH (33 mL) were added via a syringe under a continuous nitrogen flow. The reaction was proceeded at 80 °C for 14 h until it was cooled to room temperature. The mixture was extracted with EtOAc (20 mL × 3). The combined organic layer was washed with brine (20 mL), dried over Na_2SO_4, filtered and evaporated. Purification by flash column chromatography (eluting with PE) on silica gel afforded the product **1c'** as colorless oil (1.12 g, 80%). 2-(3-Nitro-[1,1'-biphenyl]-4-yl)ethan-1-ol (**1c**) was prepared following **General Procedure S1** from **1c'** (1.0 equiv., 426 mg, 2.0 mmol), paraformaldehyde (1.5 equiv., 90 mg, 3.0 mmol) and benzyltrimethylammonium hydroxide (i.e. Triton B, 40% w/w in methanol, 0.25 equiv.) in DMSO (1.0 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product faint yellow oil (345 mg, 71%).

NMR Data of 1c:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 2.0 Hz, 1H), 7.76 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.61 – 7.57 (m, 3H), 7.50 – 7.45 (m, 3H), 3.98 (t, *J* = 6.4 Hz, 2H), 3.20 (t, *J* = 6.4 Hz, 2H), 1.79 (br, s, 1H, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.24, 141.12, 138.50, 133.36, 132.52, 131.39, 129.24, 128.50, 127.09, 123.27, 62.83, 35.97.

2-(4-Bromo-2-nitrophenyl)ethan-1-ol (1d)



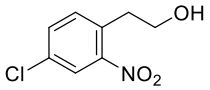
1d was prepared following **General Procedure S1** from 4-bromo-1-methyl-2-nitrobenzene (1.0 equiv., 1.30 g, 6 mmol), paraformaldehyde (1.5 equiv., 270 mg, 9 mmol) and benzyltrimethylammonium hydroxide (i.e. Triton B, 40% w/w in methanol, 0.20 equiv.) in DMSO (1.5 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product as dark brown oil (1.18 g, 88%). All recorded NMR data were in consistent with the reported data[5].

NMR Data of 1d:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 1.9 Hz, 1H), 7.64 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 3.87 (t, *J* = 6.4 Hz, 2H), 3.09 (t, *J* = 6.4 Hz, 2H), 2.14 (br, s, 1H, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.15, 136.00, 134.26, 132.91, 127.71, 120.53, 62.33, 35.65.

2-(4-Chloro-2-nitrophenyl)ethan-1-ol (1e)



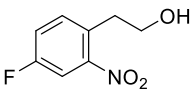
1e was prepared following **General Procedure S1** from 4-chloro-1-methyl-2-nitrobenzene (1.0 equiv., 1.37 g, 8 mmol), paraformaldehyde (1.5 equiv., 360 mg, 12 mmol) and benzyltrimethylammonium hydroxide (i.e. Triton B, 40% w/w in methanol, 0.20 equiv.) in DMSO (2.0 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product as brown oil (1.34 g, 84%). All recorded NMR data were in consistent with the reported data[5].

NMR Data of 1e:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 2.2 Hz, 1H), 7.52 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 3.93 (t, *J* = 6.3 Hz, 2H), 3.14 (t, *J* = 6.3 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.12, 134.09, 133.37, 133.14, 132.48, 125.02, 62.60, 35.69.

2-(4-Fluoro-2-nitrophenyl)ethan-1-ol (1f)



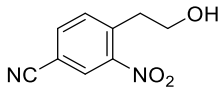
1f was prepared following **General Procedure S1** from 4-fluoro-1-methyl-2-nitrobenzene (1.0 equiv., 620 mg, 4 mmol), paraformaldehyde (1.5 equiv., 180 mg, 6 mmol) and benzyltrimethylammonium hydroxide (i.e. Triton B, 40% w/w in methanol, 0.20 equiv.) in DMSO (1.0 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product as brown oil (422 mg, 57%). All recorded NMR data were in consistent with the reported data[7].

NMR Data of 1f:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (dd, J_{F-H} = 8.4 Hz, J_{H-H} = 2.8 Hz, 1H), 7.42 (dd, J_{F-H} = 5.6 Hz, J_{H-H} = 8.6 Hz, 1H), 7.28 (ddd, J_{F-H} = 7.5 Hz, J_{H-H} = 8.6, 2.8 Hz, 1H), 3.89 (t, *J* = 6.4 Hz, 2H), 3.13 (t, *J* = 6.4 Hz, 2H), 2.25 (br, s, 1H, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.80 (d, *J* = 247.8 Hz), 149.91 (d, *J* = 7.9 Hz), 134.38 (d, *J* = 7.7 Hz), 129.90, 120.43 (d, *J* = 20.9 Hz), 112.32 (d, *J* = 26.1 Hz), 62.52, 35.54.

4-(2-Hydroxyethyl)-3-nitrobenzonitrile (1g)



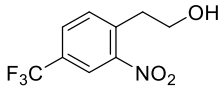
1g was prepared following **General Procedure S1** from 4-methyl-3-nitrobenzonitrile (1.0 equiv., 486 mg, 3 mmol), paraformaldehyde (1.5 equiv., 135 mg, 4.5 mmol) and benzyltrimethylammonium hydroxide (i.e. Triton B, 40% w/w in methanol, 0.20 equiv.) in DMSO (1.5 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product as brown oil (576 mg, 61%). All recorded NMR data were in consistent with the reported data[8].

NMR Data of 1g:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, *J* = 1.7 Hz, 1H), 7.81 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 3.94 (t, *J* = 6.2 Hz, 2H), 3.21 (t, *J* = 6.2 Hz, 2H), 2.00 (br, s, 1H, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 149.95, 139.57, 135.57, 134.21, 128.47, 116.67, 111.89, 61.99, 36.07.

2-(2-Nitro-4-(trifluoromethyl)phenyl)ethan-1-ol (1h)



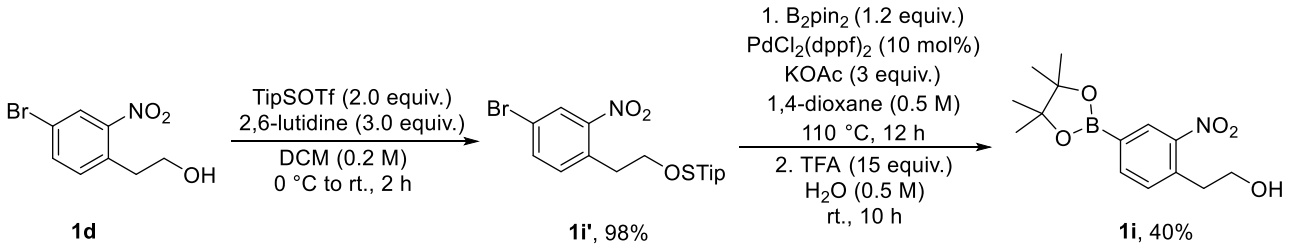
1h was prepared following **General Procedure S1** from 1-methyl-2-nitro-4-(trifluoromethyl)benzene (1.0 equiv., 1.03 g, 5 mmol), paraformaldehyde (1.5 equiv., 225 mg, 7.5 mmol) and benzyltrimethylammonium hydroxide (i.e. Triton B, 40% w/w in methanol, 0.25 equiv.) in DMSO (2.5 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product as colorless oil (705 mg, 60%).

NMR Data of 1h:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 1.1 Hz, 1H), 7.79 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.60 (d, *J* = 8.1 Hz, 1H), 3.96 (t, *J* = 6.2 Hz, 2H), 3.22 (t, *J* = 6.2 Hz, 2H), 1.88 (br, s, 1H, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 149.82, 138.08, 133.91, 130.43 (q, *J* = 33.6 Hz), 129.35 (q, *J* = 3.0 Hz), 122.98 (q, *J* = 273.6 Hz), 122.19 (q, *J* = 3.7 Hz), 62.32, 35.99.

2-(2-Nitro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol (1i)



(4-Bromo-2-nitrophenethoxy)triisopropylsilane (**1i'**) and 2-(2-Nitro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol (**1i**) were prepared following modified procedures from reported literatures[9]. A solution of 2-(4-bromo-2-nitrophenyl)ethan-1-ol (**1d**, 1.0 equiv., 1.7g, 7.9 mmol) in DCM (0.2 M) was cooled to 0 °C by using an ice bath. 2,6-lutidine (3.0 equiv., 2.5 g, 23.6 mmol) and triisopropylsilyl trifluoromethanesulfonate (i.e. TipSOTf, 2.0 equiv., 4.8 g, 15.7 mmol) were added dropwise via syringes sequentially. Upon completion, the mixture was warmed to room temprature and stirred for 2 h until 10 mL saturated $NaHCO_3$ was added to quench the reaction. The mixture was then extracted with Et_2O (20 mL × 3). The combined organic layer was washed with brine (20 mL), dried over Na_2SO_4, filtered and evaporated. Purification by flash column chromatography (eluting with 20 % v/v CH_2Cl_2/PE) on silica gel afforded the product **1i'** as faint yellow oil (3.12 g, 98%). A 25 mL pressure Schlenk tube was charged with **1i'** (1.0 equiv., 1.2 g, 3 mmol), $PdCl_2$(dppf) (10 mol %, 219 mg, 0.3 mmol), B_2pin_2 (1.2 equiv., 914 mg, 3.6 mol) and KOAc (3.0 equiv., 883 mg, 9 mmol). Then the tube was sealed, evacuated and refilled with N_2 (× 3). Ultra-dry 1,4-dioxane (6 mL) was added via syringe under a continuous nitrogen flow. The reaction was proceeded at 110 °C overnight until it was cooled to room temperature and quenched by water (6 mL). Trifluoroacetic acid (15 equiv., 5.1 g, 3.4 mL, 45 mmol) was then added with further stirring for 10 h. Upon completion, the mixture was extracted with EtOAc (10 mL × 3). The combined organic layer was washed with brine (10 mL), dried over Na_2SO_4, filtered and evaporated. Purification by flash column chromatography (eluting with 20 % v/v CH_2Cl_2/PE) on silica gel afforded the

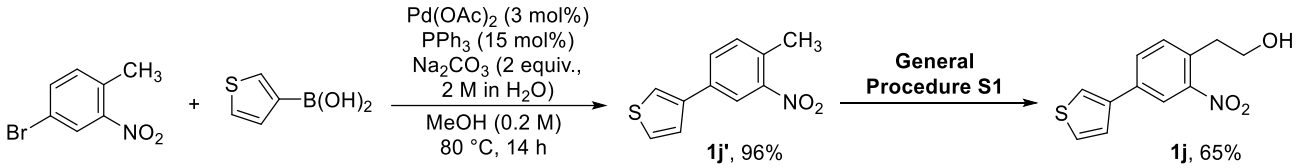
product **1i** as yellow oil (352 mg, 40%).

NMR Data of 1i:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, *J* = 1.0 Hz, 1H), 7.93 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 3.94 (t, *J* = 6.4 Hz, 2H), 3.17 (t, *J* = 6.4 Hz, 2H), 1.34 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 149.78, 138.94, 136.44, 132.26, 130.92, 130.15, 84.64, 62.85, 36.35, 24.98.

2-(2-Nitro-4-(thiophen-3-yl)phenyl)ethan-1-ol (1j)



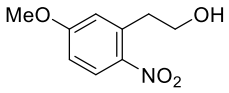
2-Methyl-1-nitro-3-(phenylethynyl)benzene (**1j'**) was prepared following a modified procedure from the reported literature[10]. A flame-dried 100-mL three-necked round-bottomed flask equipped with a Teflon-coated stirring bar was fitted with a reflux condenser and rubber septum. 4-Bromo-1-methyl-2-nitrobenzene (1.0 equiv., 400 mg, 1.85 mmol), thiophen-3-yl boronic acid (1.56 equiv., 368 mg, 2.88 mol), $Pd(OAc)_2$ (3 mol %, 12 mg, 0.056 mmol) and PPh_3 (15 mol %, 72 mg, 0.276 mol) were sequentially added into the flask. Then the system was evacuated and refilled with N_2 (× 3). Anhydrous MeOH (9.5 mL) were added via a syringe under a continuous nitrogen flow. The reaction was proceeded at 80 °C overnight until it was cooled to room temperature. The mixture was extracted with EtOAc (10 mL × 3). The combined organic layer was washed with brine (10 mL), dried over Na_2SO_4, filtered and evaporated. Purification by flash column chromatography (eluting with PE) on silica gel afforded the product **1j'** as gray oil (389 mg, 96%). 2-(2-Nitro-4-(thiophen-3-yl)phenyl)ethan-1-ol (**1j)** was prepared following **General Procedure S1** from **1j'** (1.0 equiv., 219 mg, 1.0 mmol), paraformaldehyde (1.5 equiv., 45 mg, 1.5 mmol) and benzyltrimethylammonium hydroxide (i.e. Triton B, 40% w/w in methanol, 0.25 equiv.) in DMSO (0.5 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product as brown oil (162 mg, 65%). All recorded NMR data were in consistent with the reported data[11].

NMR Data of 1j:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 1.9 Hz, 1H), 7.75 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.54 (dd, *J* = 2.9, 1.4 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.39 (dd, *J* = 5.0, 1.4 Hz, 1H), 3.96 (t, *J* = 6.4 Hz, 2H), 3.18 (t, *J* = 6.4 Hz, 2H), 1.64 (br, s, 1H, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.22, 139.70, 135.82, 133.39, 132.23, 130.68, 127.24, 125.99, 122.55, 121.93, 62.86, 36.01.

2-(5-Methoxy-2-nitrophenyl)ethan-1-ol (1k)



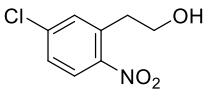
1k was prepared following **General Procedure S1** from 4-methoxy-2-methyl-1-nitrobenzene (1.0 equiv., 501 mg, 3 mmol), paraformaldehyde (1.5 equiv., 135 mg, 4.5 mmol) and benzyltrimethylammonium hydroxide (i.e. Triton B, 40% w/w in methanol, 0.20 equiv.) in DMSO (1.5 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product as brown oil (278 mg, 47%). All recorded NMR data were in consistent with the reported data[12].

NMR Data of 1k:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 9.0 Hz, 1H), 6.82 (d, *J* = 2.7 Hz, 1H), 6.79 (dd, *J* = 9.0, 2.7 Hz, 1H), 3.87 (t, *J* = 6.6 Hz, 2H), 3.84 (s, 3H), 3.15 (t, *J* = 6.5 Hz, 2H), 2.56 (br, s, 1H, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.07, 142.33, 137.24, 127.81, 117.68, 112.45, 62.46, 55.87, 37.10.

2-(5-Chloro-2-nitrophenyl)ethan-1-ol (1l)



1l was prepared following **General Procedure S1** from 4-chloro-2-methyl-1-nitrobenzene (1.0 equiv., 515 mg, 3 mmol), paraformaldehyde (1.5 equiv., 135 mg, 4.5 mmol) and benzyltrimethylammonium hydroxide (i.e. Triton B, 40% w/w in methanol, 0.20 equiv.) in DMSO (1.5 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product as brown oil (502 mg, 83%). All recorded NMR data were in consistent with the reported data[5].

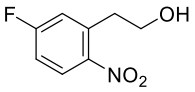
NMR Data of 1l:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.7 Hz, 1H), 7.43 (d, *J* = 2.3 Hz, 1H), 7.36 (dd, *J* = 8.7, 2.3 Hz, 1H), 3.95 (t,

J = 6.3 Hz, 2H), 3.16 (t, J = 6.2 Hz, 2H), 1.69 (br, s, 1H, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 148.10, 139.39, 136.16, 132.80, 127.87, 126.49, 62.46, 36.10.

2-(5-Fluoro-2-nitrophenyl)ethan-1-ol (1m)



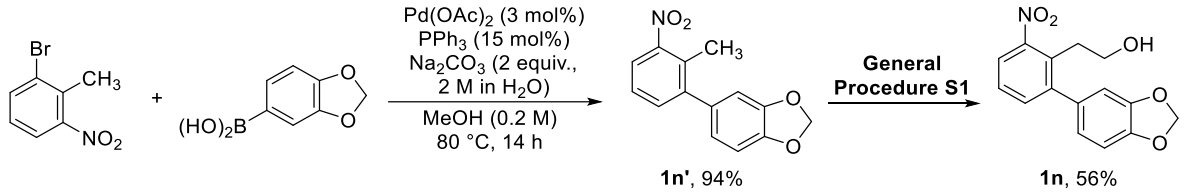
1m was prepared following **General Procedure S1** from 4-fluoro-2-methyl-1-nitrobenzene (1.0 equiv., 620 mg, 4 mmol), paraformaldehyde (1.5 equiv., 135 mg, 4.5 mmol) and benzyltrimethylammonium hydroxide (i.e. Triton B, 40% w/w in methanol, 0.20 equiv.) in DMSO (1.5 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product as yellow oil (407 mg, 55%). All recorded NMR data were in consistent with the reported data[13].

NMR Data of 1m:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (dd, $J_{H\text{-}H}$ = 9.1 Hz, $J_{F\text{-}H}$ = 5.2 Hz, 1H), 7.13 (dd, $J_{F\text{-}H}$ = 9.0 Hz, $J_{H\text{-}H}$ = 2.8 Hz, 1H), 7.06 (ddd, $J_{H\text{-}H}$ = 9.2, 2.8 Hz, $J_{F\text{-}H}$ = 7.3 Hz, 1H), 3.95 (t, J = 6.3 Hz, 2H), 3.18 (t, J = 6.3 Hz, 2H), 1.84 (br, s, 1H, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.59 (d, J = 257.6 Hz), 145.84, 137.85 (d, J = 9.4 Hz), 127.84 (d, J = 9.8 Hz), 119.55 (d, J = 23.4 Hz), 114.76 (d, J = 24.1 Hz), 62.38, 36.38.

2-(2-(Benzo[d][1,3]dioxol-5-yl)-6-nitrophenyl)ethan-1-ol (1n)



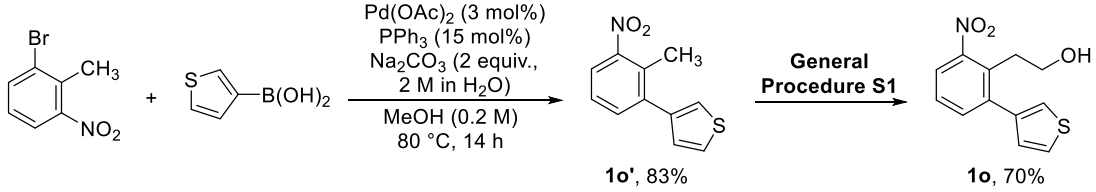
2-(2-(Benzo[d][1,3]dioxol-5-yl)-6-nitrophenyl)ethan-1-ol (**1n**) was prepared following a similar procedure of **1j** from 1-Bromo-2-methyl-3-nitrobenzene (1.0 equiv., 500 mg, 2.3 mmol) and benzo[d][1,3]dioxol-5-ylboronic acid (1.2 equiv., 458 mg, 2.76 mmol). 5-(2-Methyl-3-nitrophenyl)benzo[d][1,3]dioxole (**1n'**) was obtained as faint yellow oil (557 mg, 94%). 2-(2-(Benzo[d][1,3]dioxol-5-yl)-6-nitrophenyl)ethan-1-ol (**1n**) was prepared following **General Procedure S1** from **1n'** (1.0 equiv., 550 mg, 2.14 mmol), paraformaldehyde (1.5 equiv., 96 mg, 3.2 mmol) and benzyltrimethylammonium hydroxide (i.e. Triton B, 40% w/w in methanol, 0.25 equiv.) in DMSO (0.6 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product as yellow solid (344 mg, 56%).

NMR Data of 1n:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (dd, J = 7.9, 1.6 Hz, 1H), 7.41 (dd, J = 7.7, 1.6 Hz, 1H), 7.36 (dd, J = 7.8, 7.8 Hz, 1H), 6.87 (d, J = 7.9 Hz, 1H), 6.75 (d, J = 1.6 Hz, 1H), 6.71 (dd, J = 7.9, 1.7 Hz, 1H), 6.03 (s, 2H), 3.65 (t, J = 6.9 Hz, 2H), 3.11 (t, J = 6.9 Hz, 2H), 1.49 (br, s, 1H, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.63, 147.79, 147.48, 145.13, 134.67, 133.56, 130.79, 126.93, 123.70, 122.69, 109.79, 108.47, 101.48, 62.49, 32.07.

2-(2-Nitro-6-(thiophen-3-yl)phenyl)ethan-1-ol (1o)



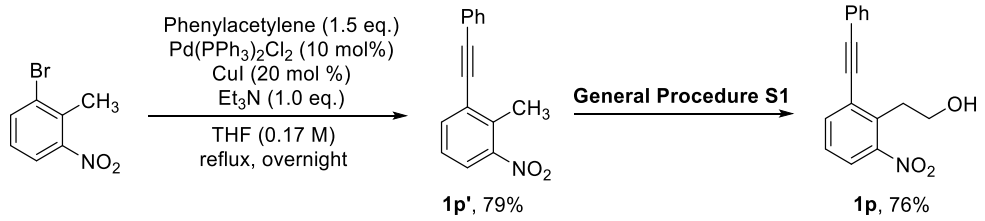
2-(2-Nitro-6-(thiophen-3-yl)phenyl)ethan-1-ol (**1o**) was prepared following a similar procedure of **1j** from 1-Bromo-2-methyl-3-nitrobenzene (1.0 equiv., 500 mg, 2.3 mmol) and thiophen-3-yl boronic acid (1.2 equiv., 385 mg, 3.01 mmol). 3-(2-methyl-3-nitrophenyl)thiophene (**1o'**) was obtained as white solid (419 mg, 83%). 2-(2-Nitro-6-(thiophen-3-yl)phenyl)ethan-1-ol (**1o**) was prepared following **General Procedure S1** from **1o'** (1.0 equiv., 419 mg, 1.9 mmol), paraformaldehyde (1.5 equiv., 90 mg, 3 mmol) and benzyltrimethylammonium hydroxide (i.e. Triton B, 40% w/w in methanol, 0.25 equiv.) in DMSO (0.5 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product as yellow oil (331 mg, 70%).

NMR Data of 1o:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (dd, J = 8.0, 1.5 Hz, 1H), 7.48 (dd, J = 7.9, 1.5 Hz, 1H), 7.42 (dd, J = 5.0, 3.0 Hz, 1H), 7.37 (dd, J = 7.9, 8.0 Hz, 1H), 7.27 (dd, J = 3.0, 1.3 Hz, 1H), 7.10 (dd, J = 5.0, 1.3 Hz, 1H), 3.67 (t, J = 6.9 Hz, 2H), 3.14 (t, J = 6.9 Hz, 2H), 1.63 (br, s, 1H, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.67, 140.44, 139.88, 134.70, 131.09, 128.80, 126.97, 126.24, 124.10, 123.81, 62.51, 32.15.

2-(2-Nitro-6-(phenylethynyl)phenyl)ethan-1-ol (1p)



1p', 79% **1p**, 76%

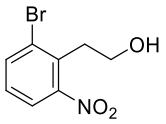
2-Methyl-1-nitro-3-(phenylethynyl)benzene (**1p'**) and 2-(2-Nitro-6-(phenylethynyl)phenyl)ethan-1-ol (**1p**) were prepared following modified procedures from the reported literature[14]. A flame-dried 100-mL three-necked round-bottomed flask equipped with a Teflon-coated stirring bar was fitted with a thermometer, a reflux condenser and a rubber septum. 1-Bromo-2-methyl-3-nitrobenzene (1.0 equiv., 2.15 g, 10 mmol), $Pd(Ph_3P)_2Cl$ (10 mol %, 700 mg, 1.0 mmol) and CuI (20 mol %, 380 mg, 2.0 mol) were sequentially added into the flask. Then the system was evacuated and refilled with N_2 (× 3). Dry THF (60 mL), Et_3N (1.0 equiv., 1.0 g, 10 mmol) and phenylacetylene (1.5 equiv., 1.6 g, 15 mmol) were added via syringes under a continuous nitrogen flow. The reaction was proceeded at 70 ˚C overnight until it was cooled to room temperature and quenched by water (20 mL). The mixture was extracted with EtOAc (20 mL × 3). The combined organic layer was washed with brine (20 mL), dried over Na_2SO_4, filtered and evaporated. Purification by flash column chromatography (eluting with 20 % v/v CH_2Cl_2/PE) on silica gel afforded the product **1p'** as yellow oil (1.87 g, 79%). 2-(2-Nitro-6-(phenylethynyl)phenyl)ethan-1-ol (**1p**) was prepared following **General Procedure S1** from **1p'** (1.0 equiv., 950 mg, 4 mmol), paraformaldehyde (1.5 equiv., 180 mg, 6.0 mmol) and benzyltrimethylammonium hydroxide (i.e. Triton B, 40% w/w in methanol, 0.25 equiv.) in DMSO (2.0 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product as colorless oil (813 mg, 76%).

NMR Data of 1p:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 – 7.74 (m, 2H), 7.58 – 7.50 (m, 2H), 7.43 – 7.31 (m, 4H), 4.05 (t, *J* = 6.8 Hz, 2H), 3.41 (t, *J* = 6.8 Hz, 2H), 1.85 (br, s, 1H, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.24, 136.49, 134.87, 131.79, 129.25, 128.69, 127.28, 126.74, 124.28, 122.32, 95.51, 86.12, 62.33, 34.22.

2-(2-Bromo-6-nitrophenyl)ethan-1-ol (1q)



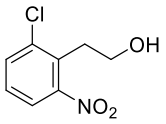
1q was prepared following **General Procedure S1** from 2-bromo-1-methyl-5-nitrobenzene (1.0 equiv., 648 mg, 3 mmol), paraformaldehyde (1.5 equiv., 135 mg, 4.5 mmol) and benzyltrimethylammonium hydroxide (i.e. Triton B, 40% w/w in methanol, 0.25 equiv.) in DMSO (1.5 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product as brown oil (554 mg, 75%). All recorded NMR data were in consistent with the reported data[15].

NMR Data of 1q:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.74 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.25 (dd, *J* = 8.1, 8.1 Hz, 1H), 3.96 (t, *J* = 6.9 Hz, 2H), 3.30 (t, *J* = 6.9 Hz, 2H), 1.65 (br, s, 1H, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.98, 137.29, 132.52, 128.50, 127.20, 123.72, 61.40, 35.41.

2-(2-Chloro-6-nitrophenyl)ethan-1-ol (1r)



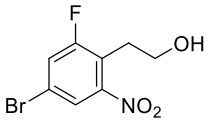
1r was prepared following **General Procedure S1** from 1-chloro-2-methyl-3-nitrobenzene (1.0 equiv., 772 mg, 4.5 mmol), paraformaldehyde (1.5 equiv., 203 mg, 6.75 mmol) and benzyltrimethylammonium hydroxide (i.e. Triton B, 40% w/w in methanol, 0.25 equiv.) in DMSO (2.5 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product as yellow oil (744 mg, 82%). All recorded NMR data were in consistent with the reported data[16].

NMR Data of 1r:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.63 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.32 (dd, *J* = 8.1, 8.1 Hz, 1H), 3.94 (t, *J* = 6.8 Hz, 2H), 3.27 (t, *J* = 6.9 Hz, 2H), 1.87 (br, s, 1H, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.16, 136.82, 133.93, 131.18, 128.09, 123.08, 61.29, 32.81.

2-(4-Bromo-2-fluoro-6-nitrophenyl)ethan-1-ol (1s)



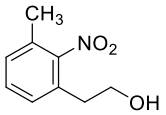
1s was prepared following **General Procedure S1** from 5-bromo-1-fluoro-2-methyl-3-nitrobenzene (1.0 equiv., 702 mg, 3 mmol), paraformaldehyde (1.5 equiv., 135 mg, 4.5 mmol) and benzyltrimethylammonium hydroxide (i.e. Triton B, 40% w/w in methanol, 0.25 equiv.) in DMSO (1.5 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product as brown oil (554 mg, 70%).

NMR Data of 1s:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (dd, $J_{F\text{-}H}$ = 1.8 Hz, $J_{H\text{-}H}$ = 1.8 Hz, 1H), 7.49 (dd, $J_{F\text{-}H}$ = 8.6 Hz, $J_{H\text{-}H}$ = 1.8 Hz, 1H), 3.87 (t, *J* = 6.5 Hz, 2H), 3.14 (td, $J_{H\text{-}H}$ = 6.5 Hz, $J_{F\text{-}H}$ = 2.1 Hz, 2H), 1.89 (br, s, 1H, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.41 (d, *J* = 254.4 Hz), 151.26 (d, *J* = 4.8 Hz), 123.74 (d, *J* = 4.1 Hz), 123.51 (d, *J* = 27.4 Hz), 121.55 (d, *J* = 20.3 Hz), 120.34 (d, *J* = 11.3 Hz), 61.61, 28.24.

2-(3-Methyl-2-nitrophenyl)ethan-1-ol (1t)



1t was prepared following **General Procedure S1** from 1,3-dimethyl-2-nitrobenzene (1.0 equiv., 756 mg, 5 mmol), paraformaldehyde (2.0 equiv., 305 mg, 10 mmol) and KO^{t}Bu (0.4 equiv., 224 mg, saturated solution in HO^{t}Bu) in DMSO (2.5 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product as yellowish-brown oil (770 mg, 85%). All recorded NMR data were in consistent with the reported data[17].

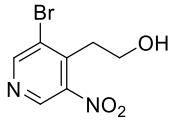
NMR Data of 1t:

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98 (d, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 7.5 Hz, 1H), 6.69 (dd, *J* = 7.5, 7.4 Hz, 1H), 3.91 (t, *J* = 6.2 Hz, 2H), 2.82 (t, *J* = 6.2 Hz, 2H), 2.19 (s, 3H), 1.62 (br, s, 2H, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.39, 129.15, 128.54, 123.44, 122.85, 118.56, 63.31, 35.10, 17.97.

2-(3-Nitropyridin-4-yl)ethan-1-ol (1u) is commercially available, and its preparation will not be described here.

2-(3-Bromo-5-nitropyridin-4-yl)ethan-1-ol (1v)



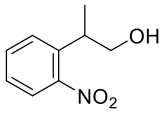
1v was prepared following **General Procedure S1** from 3-bromo-4-methyl-5-nitropyridine (1.0 equiv., 868 mg, 4 mmol), paraformaldehyde (1.5 equiv., 180 mg, 6 mmol) and benzyltrimethylammonium hydroxide (i.e. Triton B, 40% w/w in methanol, 0.25 equiv.) in DMSO (1.0 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product as yellowish-brown oil (445 mg, 45%).

NMR Data of 1v:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (s, 1H), 8.88 (s, 1H), 3.93 (t, *J* = 6.6 Hz, 2H), 3.38 (t, *J* = 6.6 Hz, 2H), 2.07 (br, s, 1H, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.25, 148.07, 144.02, 142.01, 124.83, 60.56, 34.66.

2-(2-Nitrophenyl)propan-1-ol (1w)



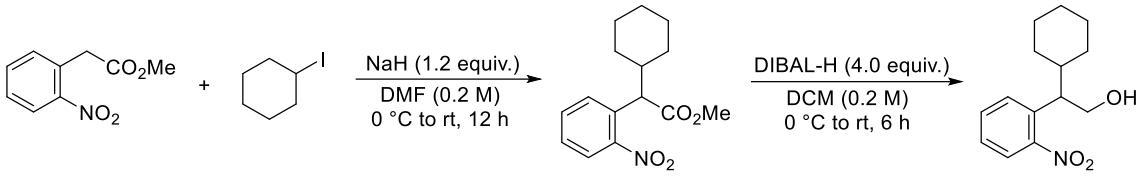
1w was prepared following **General Procedure S1** from 1-ethyl-2-nitrobenzene (1.0 equiv.,302 mg, 2 mmol), paraformaldehyde (1.5 equiv., 90 mg, 3 mmol) and KO^{t}Bu (0.4 equiv., 90 mg, saturated solution in HO^{t}Bu) in DMSO (0.5 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product as a yellowish-brown oil (116 mg, 32%). All recorded NMR data were in consistent with the reported data[18].

NMR Data of 1w:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 – 7.68 (m, 1H), 7.60 – 7.51 (m, 1H), 7.50 – 7.45 (m, 1H), 7.34 (ddd, *J* = 8.1, 7.3, 1.5 Hz, 1H), 3.74 (d, *J* = 6.7 Hz, 2H), 3.48 (m, 1H), 2.05 (br, s, 1H, OH), 1.30 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.75, 138.21, 132.72, 128.31, 127.24, 124.13, 67.81, 36.46, 17.63.

2-Cyclohexyl-2-(2-nitrophenyl)ethan-1-ol (1x)



1x', 80% **1x**, 57%

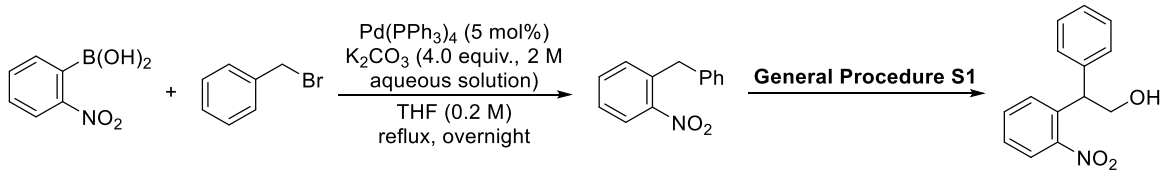
Methyl 2-cyclohexyl-2-(2-nitrophenyl)acetate (**1x'**) and 2-cyclohexyl-2-(2-nitrophenyl)ethan-1-ol (**1x**) were prepared following modified procedures from a reported literature[19]. To a cooled solution (0 °C) of methyl 2-(2-nitrophenyl)acetate (1.0 equiv., 1.0 g, 5.12 mmol) and alkyl iodide (1.1 equiv., 1.18 g, 5.63 mmol) in anhydrous DMF (25 mL, 0.2 M) was slowly added NaH (1.2 equiv., 147 mg, 6.14 mmol). Then the reaction was warmed to room temperature and stirred for 12 h. After reaction, the mixture was diluted with 10 mL of H_2O, and extracted with 3 × 20 mL of Et_2O. The combined organic layers were dried over Na_2SO_4, filtered, and the filtrate was concentrated in *vacuo*. Purification of the residue by flash column chromatography gave **1x'** as a yellow oil (1.13 g, 80%). To a solution of **1x'** (1.0 equiv., 554 mg, 2.0 mmol) in 10 mL of anhydrous DCM (0.2 M), DIBAL-H (4.0 equiv., 2.5 M solution in toluene, 3.2 mL) was added dropwise. After addition, the reaction mixture was diluted with 20 mL of Et_2O. The mixture was cooled to 0 °C and 0.4 mL of H_2O, 1 mL of a 25% aqueous solution of NaOH and 1 mL of H_2O were sequentially added. The ice bath was then removed and the reaction was warmed up to room temperature and stirred for 15 min. The mixture was filtered, and the filtrate was diluted with 30 mL of H_2O, which was extracted with 3 x 10 mL of Et_2O afterwards. The combined organic layers were dried over Na_2SO_4, evaporated in *vacuo*, and purified by flash column chromatography to afford **1x** as dark brown oil (284 mg, 57%).

NMR Data of 1x:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.56 (ddd, *J* = 8.0, 7.9, 1.2 Hz, 1H), 7.51 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.38 – 7.32 (m, 1H), 4.03 (dd, *J* = 10.9, 4.2 Hz, 1H), 3.87 (dd, *J* = 10.9, 8.1 Hz, 1H), 3.08 (ddd, *J* = 9.5, 8.1, 4.2 Hz, 1H), 2.13 – 0.73 (m, 11H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.34, 136.89, 132.32, 128.97, 127.14, 123.77, 64.46, 47.87, 39.71, 31.51, 31.23, 26.35.

2-(2-Nitrophenyl)-2-phenylethan-1-ol (1y)



1y', 96% **1y**, 60%

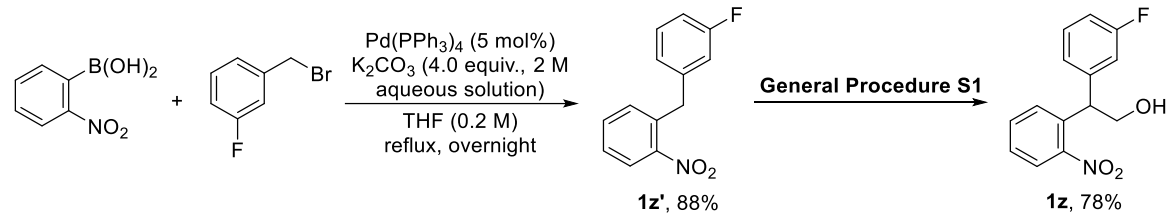
1-Benzyl-2-nitrobenzene (**1y'**) and 2-(2-nitrophenyl)-2-phenylethan-1-ol (**1y**) were prepared following modified procedures from a reported literature[19]. A stirred solution of (2-nitrophenyl)boronic acid (1.0 equiv., 417 mg, 2.5 mmol) in redistilled THF (12.5 mL) was added benzyl bromide (1.0 equiv., 428 mg, 2.5 mmol), 2 M aqueous solution of K_2CO_3 (4.0 equiv., 1.38 g, 10 mmol) and $Pd(PPh_3)_4$ (5 mol %, 144 mg, 0.125 mmol) under nitrogen atmosphere. The reaction proceeded at a reflux for 12 h, affording a reddish solution. The mixture was then extracted with EtOAc (15 mL × 3). The combined organic layers were washed with H_2O and brine, dried over anhydrous Na_2SO_4 and evaporated in *vacuo*. The residue was purified by column chromatography on silica gel (eluting with PE) to provide **1y'** (512 mg, 96%) as a faint yellow oil. **1y** was then prepared following **General Procedure S1** from **1y'** (1.0 equiv., 426 mg, 2.0 mmol), paraformaldehyde (1.5 equiv., 90 mg, 3.0 mmol) and benzyltrimethylammonium hydroxide (i.e. Triton B, 40% w/w in methanol, 0.25 equiv.) in DMSO (1.0 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product **1y** as yellowish-brown oil (385 mg, 79%).

NMR Data of 1y:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.60 – 7.51 (m, 3H), 7.39 (ddd, *J* = 8.5, 7.0, 1.9 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.28 – 7.23 (m, 2H), 4.88 (dd, *J* = 6.8, 7.0 Hz, 1H), 4.23 (dd, *J* = 11.1, 6.8 Hz, 1H), 4.18 (dd, *J* = 11.1, 7.0 Hz, 1H), 1.79 (br, s, 1H, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.54, 139.79, 135.99, 132.74, 129.94, 128.89, 128.57, 127.65, 127.30, 124.66, 65.62, 47.43.

2-(3-Fluorophenyl)-2-(2-nitrophenyl)ethan-1-ol (1z)



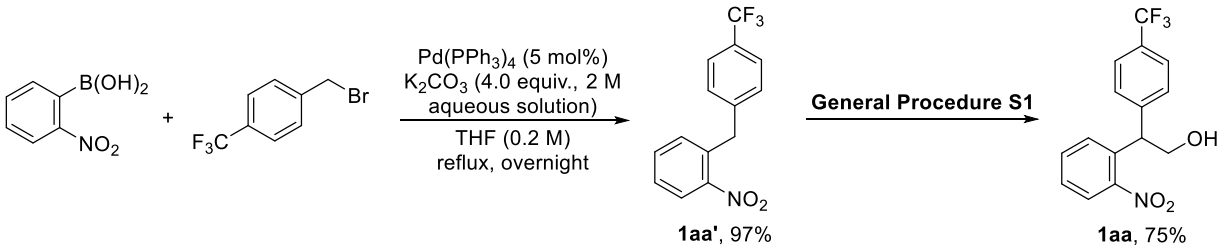
1-(3-Fluorobenzyl)-2-nitrobenzene (**1z'**) and 2-(3-fluorophenyl)-2-(2-nitrophenyl)ethan-1-ol (**1z**) were prepared following a similar procedure of **1y** from (2-nitrophenyl)boronic acid (1.0 equiv., 668 mg, 4.0 mmol) and 1-(bromomethyl)-3-fluorobenzene (1.0 equiv., 756 mg, 4.0 mmol). 1-(3-Fluorobenzyl)-2-nitrobenzene (**1z'**) was obtained as faint yellow oil (814 mg, 88%). 2-(3-Fluorophenyl)-2-(2-nitrophenyl)ethan-1-ol (**1z**) was prepared following **General Procedure S1** from **1z'** (1.0 equiv., 578 mg, 2.5 mmol), paraformaldehyde (1.5 equiv., 113 mg, 3.75 mmol) and benzyltrimethylammonium hydroxide (i.e. Triton B, 40% w/w in methanol, 0.25 equiv.) in DMSO (1.25 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product **1z** as yellow oil (509 mg, 78%).

NMR Data of 1z:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.57 (ddd, *J* = 7.6, 7.6, 1.4 Hz, 1H), 7.49 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.40 (ddd, *J* = 8.6, 7.3, 1.5 Hz, 1H), 7.31 – 7.24 (m, 1H), 7.03 (d, *J* = 7.7 Hz, 1H), 6.99 – 6.89 (m, 2H), 4.86 (dd, *J* = 6.6, 6.6 Hz, 1H), 4.19 (dd, *J* = 11.1, 6.6 Hz, 1H), 4.14 (dd, *J* = 11.1, 6.6 Hz, 1H), 1.91 (br, s, 1H, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.04 (d, *J* = 246.3 Hz), 150.39, 142.48 (d, *J* = 6.8 Hz), 135.35, 132.92, 130.30 (d, *J* = 8.3 Hz), 129.92, 127.93, 124.80, 124.33 (d, *J* = 2.9 Hz), 115.55 (d, *J* = 21.7 Hz), 114.22 (d, *J* = 21.3 Hz), 65.38, 47.13.

2-(2-Nitrophenyl)-2-(4-(trifluoromethyl)phenyl)ethan-1-ol (1aa)



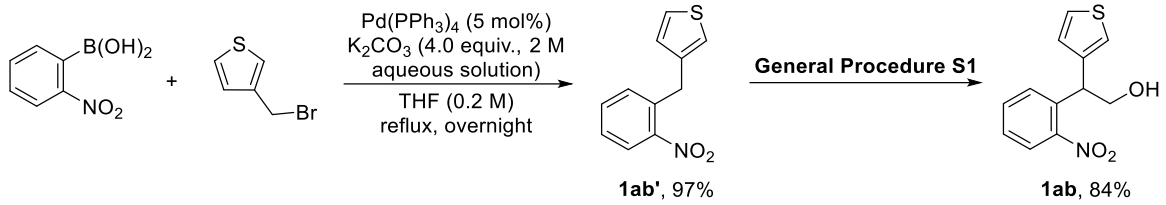
1-Nitro-2-(4-(trifluoromethyl)benzyl)benzene (**1aa'**) and 2-(2-nitrophenyl)-2-(4-(trifluoromethyl)phenyl)ethan-1-ol (**1aa**) were prepared following a similar procedure of **1y** from (2-nitrophenyl)boronic acid (1.0 equiv., 1.67 g, 10.0 mmol) and 1-(bromomethyl)-4-(trifluoromethyl)benzene (1.0 equiv., 2.39 g, 10.0 mmol). 1-Nitro-2-(4-(trifluoromethyl)benzyl)benzene (**1aa'**) was obtained as yellow oil (2.74 g, 97%). 2-(2-Nitrophenyl)-2-(4-(trifluoromethyl)phenyl)ethan-1-ol (**1aa**) was prepared following **General Procedure S1** from **1aa'** (1.0 equiv., 844 mg, 3.0 mmol), paraformaldehyde (1.5 equiv., 135 mg, 4.5 mmol) and benzyltrimethylammonium hydroxide (i.e. Triton B, 40% w/w in methanol, 0.25 equiv.) in DMSO (1.5 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product **1aa** as yellow oil (700 mg, 75%).

NMR Data of 1aa:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.62 – 7.55 (m, 4H), 7.49 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.45 – 7.36 (m, 2H), 4.93 (t, *J* = 6.7 Hz, 1H), 4.23 (dd, *J* = 11.3, 6.7 Hz, 1H), 4.21 (dd, *J* = 11.3, 6.7 Hz, 1H), 1.81 (br, s, 1H, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.38, 144.10, 135.12, 133.03, 130.09, 129.53 (q, *J* = 31.9 Hz), 129.00, 128.11, 125.73 (q, *J* = 3.9 Hz), 124.95, 124.15 (q, *J* = 274.2 Hz), 65.34, 47.35.

2-(2-Nitrophenyl)-2-(thiophen-3-yl)ethan-1-ol (1ab)



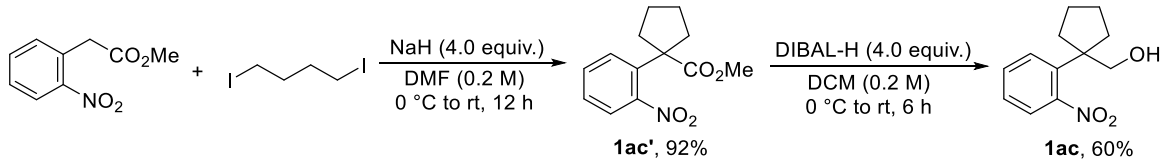
3-(2-Nitrobenzyl)thiophene (**1ab'**) and 2-(2-nitrophenyl)-2-(thiophen-3-yl)ethan-1-ol (**1ab**) were prepared following a similar procedure of **1y** from (2-nitrophenyl)boronic acid (1.0 equiv., 556 g, 3.3 mmol) and 3-(bromomethyl)thiophene (1.0 equiv., 590 g, 3.3 mmol). 3-(2-Nitrobenzyl)thiophene (**1ab'**) was obtained as carnation oil (710 mg, 97%). 2-(2-Nitrophenyl)-2-(thiophen-3-yl)ethan-1-ol (**1ab**) was prepared following **General Procedure S1** from **1ab'** (1.0 equiv., 702 mg, 3.2 mmol), paraformaldehyde (1.5 equiv., 144 mg, 4.8 mmol) and benzyltrimethylammonium hydroxide (i.e. Triton B, 40% w/w in methanol, 0.25 equiv.) in DMSO (1.6 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product **1ab** as dull green oil (670 mg, 84%).

NMR Data of 1ab:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.53 (ddd, *J* = 8.0, 7.6, 1.4 Hz, 1H), 7.43 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.37 (ddd, *J* = 8.6, 7.5, 1.5 Hz, 1H), 7.28 (dd, *J* = 3.0, 5.0 Hz, 1H), 7.14 (dd, *J* = 2.9, 1.2 Hz, 1H), 6.94 (dd, *J* = 5.0, 1.4 Hz, 1H), 4.91 (dd, *J* = 6.7, 6.7 Hz, 1H), 4.18 (dd, *J* = 13.3, 6.8 Hz, 1H), 4.13 (dd, *J* = 13.0, 7.0 Hz, 1H), 1.98 (br, s, 1H, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.35, 140.47, 135.90, 132.83, 130.03, 127.90, 127.72, 126.20, 124.51, 122.17, 65.84, 43.37.

(1-(2-Nitrophenyl)cyclopentyl)methanol (1ac)



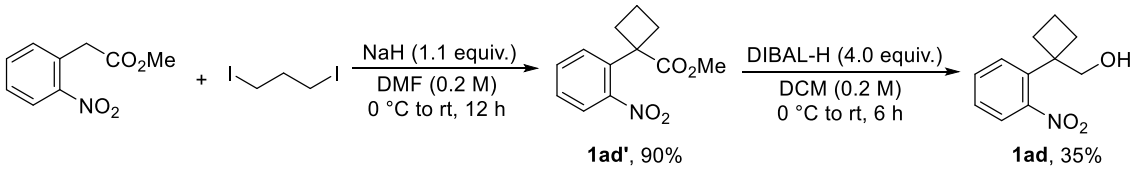
Methyl 1-(2-nitrophenyl)cyclopentane-1-carboxylate (**1ac'**) and (1-(2-nitrophenyl)cyclopentyl)methanol (**1ac**) were prepared following modified procedures from a reported literature[19]. To a cooled solution (0 °C) of methyl 2-(2-nitrophenyl)acetate (1.0 equiv., 500 mg, 2.56 mmol) and alkyl iodide (1.1 equiv., 871 mg, 2.81 mmol) in anhydrous DMF (0.2 M) was slowly added NaH (4.0 equiv., 246 mg, 10.2 mmol). Then the reaction was warmed to room temperature and stirred for 12 h. After reaction, the mixture was diluted with 10 mL of H_2O, and extracted with 3 × 15 mL of Et_2O. The combined organic layers were dried over Na_2SO_4, filtered, and the filtrate was concentrated in *vacuo*. Purification of the residue by flash column chromatography gave **1ac'** as a brown oil (542 mg, 90%). To a solution of **1ac'** (1.0 equiv., 912 mg, 3.66 mmol) in 11 mL of anhydrous DCM (0.2 M), DIBAL-H (4.0 equiv., 2.5 M solution in toluene, 3.5 mL) was added dropwise. After addition, the reaction mixture was diluted with 20 mL of Et_2O. The mixture was cooled to 0 °C and 0.4 mL of H_2O, 1 mL of a 25% aqueous solution of NaOH and 1 mL of H_2O were sequentially added. The ice bath was then removed and the reaction was warmed up to room temperature and stirred for 15 min. The mixture was filtered, and the filtrate was diluted with 30 mL of H_2O, which was extracted with 3 x 10 mL of Et_2O afterwards. The combined organic layers were dried over Na_2SO_4, evaporated in *vacuo*, and purified by flash column chromatography to afford **1ac** as dark brown oil (486mg, 60%).

NMR Data of 1ac:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 – 7.47 (m, 2H), 7.46 – 7.42 (m, 1H), 7.36 – 7.30 (m, 1H), 3.77 (s, 2H), 1.79 – 1.57 (m, 8H), 1.55 (br, s, 1H, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.58, 139.53, 132.26, 130.97, 127.33, 123.97, 67.71, 53.41, 34.10, 23.57.

(1-(2-Nitrophenyl)cyclobutyl)methanol (1ad)



Methyl 1-(2-nitrophenyl)cyclobutane-1-carboxylate (**1ad'**) and (1-(2-nitrophenyl)cyclobutyl)methanol (**1ad**) were prepared following modified procedures from a reported literature[19]. To a cooled solution (0 °C) of methyl 2-(2-nitrophenyl)acetate (1.0 equiv., 500 mg, 2.56 mmol) and alkyl iodide (1.1 equiv., 651 mg, 2.81 mmol) in anhydrous DMF (0.2 M) was slowly added

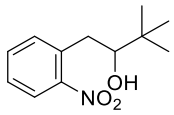
NaH (4.0 equiv., 192 mg, 8 mmol). Then the reaction was warmed to room temperature and stirred for 12 h. After reaction, the mixture was diluted with 10 mL of H_2O, and extracted with 3 × 15 mL of Et_2O. The combined organic layers were dried over Na_2SO_4, filtered, and the filtrate was concentrated in *vacuo*. Purification of the residue by flash column chromatography gave **1ad'** as a brown oil (423 mg, 90%). To a solution of **1ad'** (1.0 equiv., 860 mg, 3.66 mmol) in 11 mL of anhydrous DCM (0.2 M), DIBAL-H (4.0 equiv., 2.5 M solution in toluene, 3.5 mL) was added dropwise. After addition, the reaction mixture was diluted with 20 mL of Et_2O. The mixture was cooled to 0 °C and 0.4 mL of H_2O, 1 mL of a 25% aqueous solution of NaOH and 1 mL of H_2O were sequentially added. The ice bath was then removed and the reaction was warmed up to room temperature and stirred for 15 min. The mixture was filtered, and the filtrate was diluted with 30 mL of H_2O, which was extracted with 3 x 10 mL of Et_2O afterwards. The combined organic layers were dried over Na_2SO_4, evaporated in *vacuo*, and purified by flash column chromatography to afford **1ad** as brown oil (265 mg, 35%).

NMR Data of 1ad:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.51 (td, *J* = 7.6, 1.3 Hz, 1H), 7.31 (td, *J* = 8.1, 1.3 Hz, 1H), 7.27 – 7.21 (m, 1H), 4.09 (s, 2H), 2.35 – 2.16 (m, 3H), 2.09 – 2.07 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.19, 141.91, 132.07, 130.70, 127.09, 124.22, 68.92, 47.38, 30.32, 15.89.

3,3-Dimethyl-1-(2-nitrophenyl)butan-2-ol (1ae)



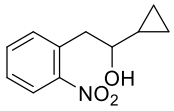
1ae was prepared following **General Procedure S2** from 1-methyl-2-nitrobenzene (1.0 equiv., 549 mg, 4.0 mmol), pivalaldehyde (1.2 equiv., 413 mg, 4.8 mmol), benzyltrimethylammonium hydroxide (i.e. Triton B, 40% w/w in methanol, 0.25 equiv.) in DMSO (0.8 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product as colorless oil (688 mg, 77%). All recorded NMR data were in consistent with the reported data[20].

NMR Data of 1ae:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (dd, *J* = 8.5, 1.3 Hz, 1H), 7.52 (ddd, *J* = 7.5, 7.5, 1.4 Hz, 1H), 7.41 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.35 (ddd, *J* = 8.7, 7.5, 1.5 Hz, 1H), 3.46 (dd, *J* = 10.8, 2.1 Hz, 1H), 3.21 (dd, *J* = 13.4, 2.2 Hz, 1H), 2.79 (dd, *J* = 13.4, 10.8 Hz, 1H), 1.80 (br, s, 1H, OH), 0.99 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.14, 135.32, 133.40, 132.76, 127.34, 124.75, 80.01, 35.46, 34.98, 25.73.

1-Cyclopropyl-2-(2-nitrophenyl)ethan-1-ol (1af)



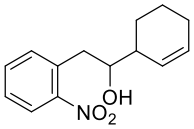
1af was prepared following **General Procedure S2** from 1-methyl-2-nitrobenzene (1.0 equiv., 549 mg, 4.0 mmol), cyclopropanecarbaldehyde (1.2 equiv., 336 mg, 4.8 mmol), benzyltrimethylammonium hydroxide (i.e. Triton B, 40% w/w in methanol, 0.25 equiv.) in DMSO (0.8 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product as colorless oil (489 mg, 59%). All recorded NMR data were in consistent with the reported data[20].

NMR Data of 1af:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 – 7.80 (m, 1H), 7.55 – 7.46 (m, 1H), 7.46 – 7.39 (m, 1H), 7.38 – 7.29 (m, 1H), 3.38 – 3.25 (m, 1H), 3.20 – 3.01 (m, 2H), 2.09 (br, s, 1H, OH), 1.02 – 0.82 (m, 1H), 0.57 – 0.13 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 149.97, 133.86, 133.54, 132.73, 127.49, 124.70, 76.64, 40.33, 17.89, 3.16, 2.78.

1-(Cyclohex-3-en-1-yl)-2-(2-nitrophenyl)ethan-1-ol (1ag)



1ag was prepared following **General Procedure S2** from 1-methyl-2-nitrobenzene (1.0 equiv., 549 mg, 4.0 mmol), cyclohex-2-ene-1-carbaldehyde (1.2 equiv., 529 mg, 4.8 mmol), KO^{t}Bu (0.4 equiv., 179 mg, saturated solution in HO^{t}Bu) in DMSO (0.8 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product as faint yellow oil (623 mg, 63%).

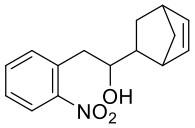
NMR Data of 1ag:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (ddd, *J* = 8.2, 1.3, 1.3 Hz, 1H), 7.54 (ddd, *J* = 7.5, 7.8, 1.4 Hz, 1H), 7.42 (ddd, *J* = 7.8, 1.4, 1.3 Hz, 1H), 7.38 (ddd, *J* = 7.6, 7.6, 1.4 Hz, 1H), 5.70 (s, 2H), 3.76 (ddd, *J* = 10.0, 5.1, 2.7 Hz, 1H), 3.67 (ddd,

J = 10.0, 6.3, 2.8 Hz, 1H), 3.28 (m, 1H), 3.24 (m, 1H), 2.88 (m, 1H), 2.26 – 1.63 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.04, 134.72, 133.32, 132.88, 127.52, 127.35, 126.21, 124.88, 75.83, 40.25, 37.85, 28.08, 25.44, 24.17.

1-(Bicyclo[2.2.1]hept-5-en-2-yl)-2-(2-nitrophenyl)ethan-1-ol (1ah)



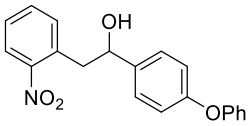
1ah was prepared following **General Procedure S2** from 1-methyl-2-nitrobenzene (1.0 equiv., 549 mg, 4.0 mmol), bicyclo[2.2.1]hept-5-ene-2-carbaldehyde (1.2 equiv., 586 mg, 4.8 mmol), KO^{t}Bu (0.4 equiv., 179 mg, saturated solution in HO^{t}Bu) in DMSO (0.8 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product as faint yellow oil (404 mg, 39%).

NMR Data of 1ah:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.54 (ddd, *J* = 7.6, 7.6, 1.4 Hz, 1H), 7.44 – 7.36 (m, 2H), 6.13 (dd, *J* = 5.5, 3.0 Hz, 1H), 6.10 (dd, *J* = 5.5, 2.9 Hz, 1H), 3.65 (ddd, *J* = 9.6, 9.6, 2.5 Hz, 1H), 3.40 (dd, *J* = 13.7, 2.5 Hz, 1H), 2.97 (s, 1H), 2.89 (s, 1H), 2.77 (dd, *J* = 13.7, 9.4 Hz, 1H), 1.75 (br, s, 1H, OH), 1.49 – 1.26 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.08, 137.03, 136.85, 134.24, 133.52, 132.87, 127.62, 124.93, 76.31, 46.94, 45.22, 43.29, 42.20, 39.90, 30.12.

2-(2-Nitrophenyl)-1-(4-phenoxyphenyl)ethan-1-ol (1ai)



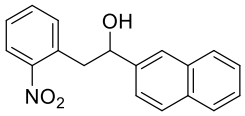
1ai was prepared following **General Procedure S2** from 1-methyl-2-nitrobenzene (1.0 equiv., 549 mg, 4.0 mmol), 4-phenoxybenzaldehyde (1.2 equiv., 951 mg, 4.8 mmol), KO^{t}Bu (0.4 equiv., 179 mg, saturated solution in HO^{t}Bu) in DMSO (0.8 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product as yellow oil (1.1 g, 81%).

NMR Data of 1ai:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.52 (ddd, *J* = 7.5, 7.5, 1.4 Hz, 1H), 7.40 (ddd, *J* = 7.8, 7.5, 1.5 Hz, 1H), 7.37 – 7.32 (m, 5H), 7.14 – 7.08 (m, 1H), 7.03 – 6.98 (m, 4H), 5.02 (dd, *J* = 8.6, 4.1 Hz, 1H), 3.38 (dd, *J* = 13.5, 4.1 Hz, 1H), 3.25 (dd, *J* = 13.6, 8.7 Hz, 1H), 2.16 (br, s, 1H, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.32, 156.94, 150.00, 138.73, 133.67, 133.42, 132.88, 129.89, 127.84, 127.27, 124.92, 123.43, 119.05, 118.96, 74.00, 42.95.

1-(Naphthalen-2-yl)-2-(2-nitrophenyl)ethan-1-ol (1aj)



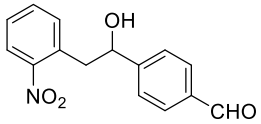
1aj was prepared following **General Procedure S2** from 1-methyl-2-nitrobenzene (1.0 equiv., 549 mg, 4.0 mmol), 2-naphthaldehyde (1.2 equiv., 750 mg, 4.8 mmol), benzyltrimethylammonium hydroxide (i.e. Triton B, 40% w/w in methanol, 0.25 equiv.) in DMSO (0.8 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product as a deep yellow solid (809 mg, 69%).

NMR Data of 1aj:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.0 Hz, 1H), 7.88 – 7.76 (m, 4H), 7.53 – 7.48 (m, 3H), 7.45 (ddd, *J* = 7.7, 7.7, 1.4 Hz, 1H), 7.35 (ddd, *J* = 7.8, 7.8, 1.5 Hz, 1H), 7.29 (dd, *J* = 7.6, 1.4 Hz, 1H), 5.13 (m, 1H), 3.42 (dd, *J* = 13.6, 4.0 Hz, 1H), 3.26 (dd, *J* = 13.6, 8.8 Hz, 1H), 2.56 (d, *J* = 2.9 Hz, 1H, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 149.78, 141.23, 133.62, 133.40, 133.26, 133.04, 132.80, 128.37, 128.04, 127.74, 127.67, 126.24, 125.97, 124.78, 124.39, 123.85, 74.29, 42.74.

4-(1-Hydroxy-2-(2-nitrophenyl)ethyl)benzaldehyde (1ak)



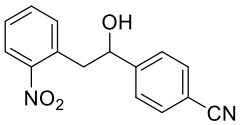
1ak was prepared following **General Procedure S2** from 1-methyl-2-nitrobenzene (1.0 equiv., 549 mg, 4.0 mmol), terephthalaldehyde (1.2 equiv., 644 mg, 4.8 mmol), benzyltrimethylammonium hydroxide (i.e. Triton B, 40% w/w in methanol, 0.25 equiv.) in DMSO (0.8 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product as faint yellow solid (423 mg, 39%).

NMR Data of 1ak:

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.97 (s, 1H, CHO), 7.95 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.86 – 7.82 (m, 2H), 7.58 – 7.54 (m, 2H), 7.51 (ddd, *J* = 7.5, 7.6, 1.4 Hz, 1H), 7.41 (ddd, *J* = 7.9, 7.7, 1.5 Hz, 1H), 7.30 (dd, *J* = 7.7, 1.5 Hz, 1H), 5.12 (d, *J* = 8.8, 3.1 Hz, 1H), 3.40 (dd, *J* = 13.5, 3.1 Hz, 1H), 3.16 (dd, *J* = 13.5, 8.8 Hz, 1H), 2.57 (br, s, 1H, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 192.13, 150.74, 149.81, 135.92, 133.76, 133.05, 132.89, 130.12, 128.09, 126.39, 125.05, 73.80, 42.97.

4-(1-Hydroxy-2-(2-nitrophenyl)ethyl)benzonitrile (1al)



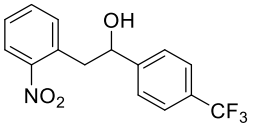
1al was prepared following **General Procedure S2** from 1-methyl-2-nitrobenzene (1.0 equiv., 274 mg, 2.0 mmol), 4-formylbenzonitrile (1.2 equiv., 315 mg, 2.4 mmol), benzyltrimethylammonium hydroxide (i.e. Triton B, 40% w/w in methanol, 0.25 equiv.) in DMSO (0.8 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product as dark brown solid (295 mg, 55%).

NMR Data of 1al:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.65 – 7.61 (m, 2H), 7.54 – 7.50 (m, 2H), 7.43 (dd, *J* = 7.8, 7.8, 1.6 Hz, 1H), 7.32 – 7.28 (m, 2H), 5.12 (dd, *J* = 8.6, 3.9 Hz, 1H), 3.39 (dd, *J* = 13.6, 3.9 Hz, 1H), 3.12 (dd, *J* = 13.6, 8.6 Hz, 1H), 2.47 (br, s, 1H, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 149.77, 149.19, 133.77, 133.13, 132.70, 132.46, 128.23, 126.52, 125.13, 118.88, 111.52, 73.52, 43.06.

2-(2-Nitrophenyl)-1-(4-(trifluoromethyl)phenyl)ethan-1-ol (1am)



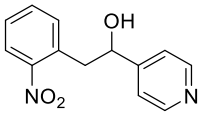
1am was prepared following **General Procedure S2** from 1-methyl-2-nitrobenzene (1.0 equiv., 274 mg, 2.0 mmol), 4-(trifluoromethyl)benzaldehyde (1.2 equiv., 418 mg, 2.4 mmol), benzyltrimethylammonium hydroxide (i.e. Triton B, 40% w/w in methanol, 0.25 equiv.) in DMSO (0.8 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product as yellow oil (423 mg, 68%).

NMR Data of 1am:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.57 – 7.51 (m, 3H), 7.43 (ddd, *J* = 7.8, 7.8, 1.4 Hz, 1H), 7.32 (dd, *J* = 7.7, 1.4 Hz, 1H), 5.12 (dd, *J* = 9.0, 3.7 Hz, 1H), 3.40 (dd, *J* = 13.6, 3.7 Hz, 1H), 3.16 (dd, *J* = 13.6, 9.0 Hz, 1H), 2.28 (br, s, 1H, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 149.88, 147.81 (q, *J* = 1.4 Hz), 133.76, 133.09, 132.99, 130.11 (q, *J* = 32.9 Hz), 128.14, 126.12, 125.62 (q, *J* = 3.8 Hz), 125.11, 124.24 (q, *J* = 272.1 Hz), 73.76, 43.12.

2-(2-Nitrophenyl)-1-(pyridin-4-yl)ethan-1-ol (1an)



1an was prepared following **General Procedure S2** from 1-methyl-2-nitrobenzene (1.0 equiv., 549 mg, 4.0 mmol), isonicotinaldehyde (1.2 equiv., 514 mg, 4.8 mmol) and benzyltrimethylammonium hydroxide (i.e. Triton B, 40% w/w in

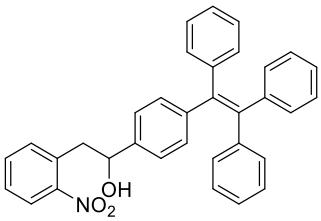
methanol, 0.25 equiv.) in DMSO (0.8 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product as colorless oil (713 mg, 73%).

NMR Data of 1an:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 – 8.45 (m, 2H), 7.98 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.53 (ddd, *J* = 7.5, 7.5, 1.4 Hz, 1H), 7.42 (ddd, *J* = 7.8, 7.8, 1.5 Hz, 1H), 7.36 – 7.29 (m, 3H), 5.05 (dd, *J* = 9.0, 3.7 Hz, 1H), 3.41 (dd, *J* = 13.6, 3.7 Hz, 1H), 3.32 (br, s, 1H, OH), 3.10 (dd, *J* = 13.6, 9.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.73, 149.97, 149.42, 133.36, 132.66, 132.63, 127.77, 124.15, 120.83, 71.28, 40.94.

2-(2-Nitrophenyl)-1-(4-(1,2,2-triphenylvinyl)phenyl)ethan-1-ol (1ao)



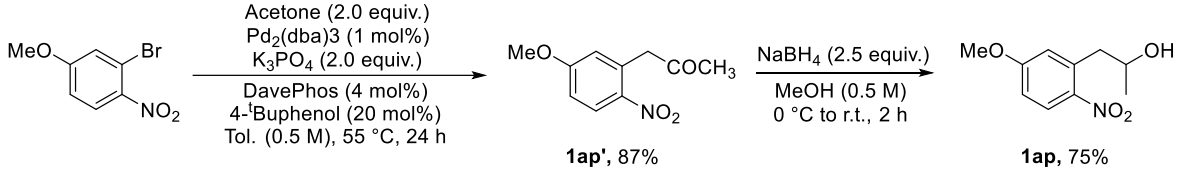
1ao was prepared following **General Procedure S2** from 1-methyl-2-nitrobenzene (1.0 equiv., 275 mg, 2.0 mmol), 4-(1,2,2-triphenylvinyl)benzaldehyde (1.2 equiv., 865 mg, 2.4 mmol), KO^{t}Bu (0.4 equiv., 90 mg, saturated solution in HO^{t}Bu) in DMSO (0.4 mL). Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel gave the product as beige solid (547 mg, 55%).

NMR Data of 1ao:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.48 (ddd, *J* = 7.5, 7.5, 1.4 Hz, 1H), 7.38 (ddd, *J* = 8.0, 7.7, 1.5 Hz, 1H), 7.21 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.14 – 6.99 (m, 19H), 4.95 (dd, *J* = 8.3, 4.7 Hz, 1H), 3.31 (dd, *J* = 13.5, 4.7 Hz, 1H), 3.21 (dd, *J* = 13.5, 8.3 Hz, 1H), 2.07 (br, s, 1H, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.07, 143.82, 143.80, 143.77, 143.48, 141.74, 141.23, 140.66, 133.66, 133.28, 132.70, 131.60, 131.45, 127.82, 127.78, 127.74, 126.60, 126.57, 125.16, 124.83, 74.20, 42.67.

1-(5-Methoxy-2-nitrophenyl)propan-2-ol (1ap)



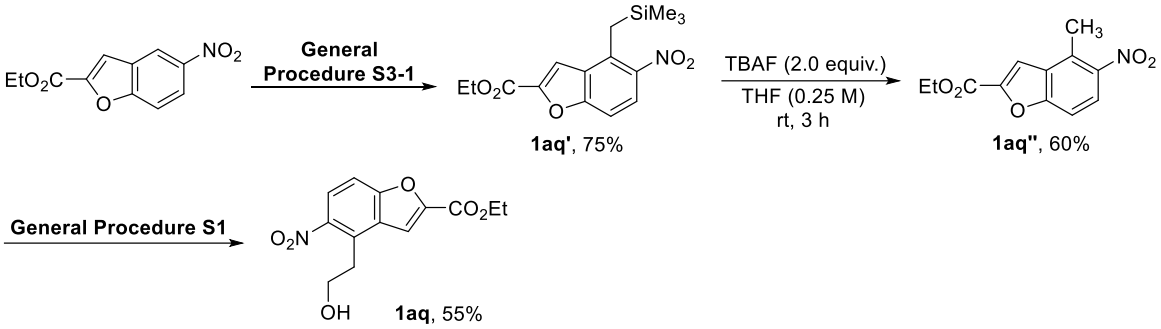
1-(5-Methoxy-2-nitrophenyl)propan-2-one (**1ap'**) and 1-(5-Methoxy-2-nitrophenyl)propan-2-ol (**1ap**) were prepared following modified procedures from a reported literature[21]. A flame-dried Schleck flask equipped with a Teflon-coated stirring bar was charged with 2-bromo-4-methoxy-1-nitrobenzene (1.0 equiv., 928 mg, 20 mmol), K_3PO_4 (2.0 equiv., 8.5 g, 40 mmol), DavePhos [i.e. 2'-(dicyclohexylphosphaneyl)-N,N-dimethyl-[1,1'-biphenyl]-2-amine, 4 mol%, 315 mg, 0.8 mmol] and 4-^{t}Buphenol (20 mol%, 600 mg, 4 mmol). Then the tube was transferred into a glove box (argon atmosphere) and $Pd_2(dba)_3$ (1 mol%, 115 mg, 0.2 mmol) was added. Acetone (2.0 equiv., 3.0 mL, 40 mmol) and toluene (0.5 M, 40 mL) was added *via* syringes before the flask was sealed and taken out of the glove box. The reaction was proceeded at 55 °C for 24 h until it was cooled to room temperature and quenched by water (20 mL). The mixture was extracted with EtOAc (20 mL × 3). The combined organic layer was washed with brine (20 mL), dried over Na_2SO_4, filtered and evaporated. Purification by flash column chromatography (eluting with 50 % v/v CH_2Cl_2/PE) on silica gel afforded the product **1ap'** as a dark brown oil (3.64 g, 87%). 1-(5-Methoxy-2-nitrophenyl)propan-2-ol (**1ap**) was prepared following a modified procedure from the reported literature. To a stirred solution of 1-(5-methoxy-2-nitrophenyl)propan-2-one (**1ap'**, 1.0 equiv., 960 mg, 4.6 mmol) in MeOH (0.6 M, 7.7 mL) at 0 °C, $NaBH_4$ (2.0 equiv., 347 mg, 9.2 mmol) was added portionwise. The reaction mixture was stirred at room temperature for 2 h before being acified with aqueous 10% HCl. The mixture was extracted with EtOAc (15 mL × 3), dried over Na_2SO_4, filtered and evaporated. Purification by flash column chromatography (eluting with CH_2Cl_2) on silica gel afforded the product **1ap** as a brown gel (732 mg, 75%).

NMR Data of 1ap:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 6.5, 3.6 Hz, 1H), 6.86 – 6.78 (m, 2H), 4.14 – 4.04 (m, 1H), 3.87 (s, 3H), 3.20 (dd, *J* = 13.3, 4.0 Hz, 1H), 2.93 (dd, *J* = 13.3, 8.2 Hz, 1H), 1.91 (br, s, 1H, OH), 1.29 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.00, 142.57, 137.40, 127.91, 118.11, 112.52, 68.24, 55.93, 43.31, 23.73.

2-(5-Nitrobenzofuran-6-yl)ethan-1-ol (1aq)



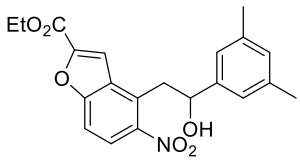
Following **General Procedure S3-1**, ethyl 5-nitro-6-((trimethylsilyl)methyl)benzofuran-2-carboxylate (**1aq'**) was obtained as beige solid in 75% yield (1.2 g) from 5-nitrobenzofuran-2-carboxylate (1.0 equiv., 1.17 g, 5.0 mmol) using 4:1 PE/DCM as eluent. Ethyl 6-methyl-5-nitrobenzofuran-2-carboxylate (**1aq"**) was prepared following a modified procedure from the reported literature. An oven-dried round-bottom flask with a magnetic stirring bar was charged with tetrabutylammonium fluoride (i.e. TBAF, 2.0 equiv., 816 mg, 3.12 mmol), in which a THF solution (0.25 M) of **1aq'** (1.0 equiv., 500 mg, 1.56 mmol) was added dropwise at room temperature under nitrogen atmosphere. After then, the mixture was stirred for 3 h until 37% hydrochloric acid was added to quench the reaction. The mixture was extracted with CH_2Cl_2 (20 mL × 3), washed with water, dried over Na_2SO_4, evaporated and submitted to a flash chromatographic purification, giving **1aq"** as reddish brown solid in 60% yield (233 mg). **1aq** was prepared following **General Procedure S1** from **1aq"** (1.0 equiv., 200 mg, 0.8 mmol), paraformaldehyde (1.5 equiv., 36 mg, 1.2 mmol) and benzyltrimethylammonium hydroxide (i.e. Triton B, 40% w/w in methanol, 0.25 equiv.) in DMSO (0.5 mL). Purification by flash column chromatography (eluting with 100:1 DCM/MeOH) on silica gel gave **1aq** as brown solid (123 mg, 55%).

NMR Data of 1aq:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 – 8.02 (m, 2H), 7.79 (d, *J* = 9.0 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.92 (br, s, 1H, OH), 3.70 (t, *J* = 5.6 Hz, 2H), 3.29 (t, *J* = 5.6 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.16, 155.51, 146.94, 145.61, 131.42, 128.84, 124.44, 114.51, 111.26, 60.96, 52.56, 32.94, 14.08.

Ethyl 6-(2-(3,5-dimethylphenyl)-2-hydroxyethyl)-5-nitrobenzofuran-2-carboxylate (1ar)



Following **General Procedure S3-2**, ethyl 6-(2-(3,5-dimethylphenyl)-2-hydroxyethyl)-5-nitrobenzofuran-2-carboxylate (**1ar**) was obtained as pale brown solid in 45% yield (160 mg) from ethyl 5-nitro-6-((trimethylsilyl)methyl)benzofuran-2-carboxylate (**1aq'**, 1.0 equiv., 300 mg, 0.93 mmol) and 3,5-dimethylbenzaldehyde (1.2 equiv., 150 mg, 1.1 mmol) using 100:1 DCM/MeOH as eluent.

NMR Data of 1ar:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 9.1 Hz, 1H), 7.66 (d, *J* = 1.0 Hz, 1H), 7.55 (dd, *J* = 9.1, 1.0 Hz, 1H), 7.06 (d, *J* = 1.6 Hz, 2H), 6.95 – 6.92 (m, 1H), 5.09 (dd, *J* = 8.9, 3.7 Hz, 1H), 4.46 (q, *J* = 7.1 Hz, 2H), 3.56 (dd, *J* = 13.4, 3.7 Hz, 1H), 3.47 (dd, *J* = 13.4, 8.9 Hz, 1H), 2.34 – 2.31 (s, 6H), 2.17 (br, s, 1H, OH), 1.45 (t, *J* = 7.1 Hz, 3H).

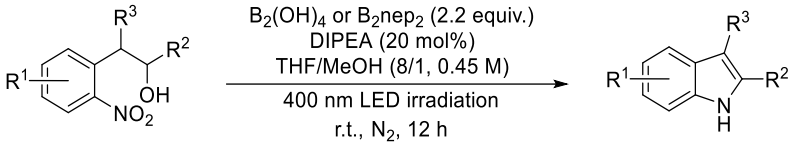
^{13}C NMR (100 MHz, $CDCl_3$): δ 158.96, 156.37, 147.72, 145.79, 143.91, 138.45, 131.16, 130.05, 129.70, 124.76, 123.37, 114.42, 111.53, 74.54, 62.13, 40.27, 21.44, 14.44.

The characterization data of **1as** was present at section **4.3.2**.

4. Substrate Scope

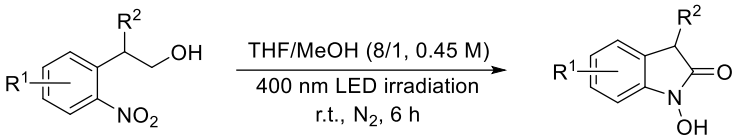
4.1. General Procedures for the Synthesis of Final Products

4.1.1. General Procedure A: Synthesis of 1*H*-indole derivatives



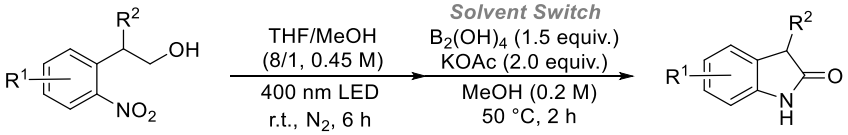
A flame-dried Schlenk tube with a Teflon-coated magnetic stirring bar was charged with $B_2(OH)_4$ (2.2 equiv., 40 mg, 0.44 mmol) or B_2nep_2 (2.2 equiv. 99 mg, 0.44 mmol). The tube was sealed, evacuated and refilled with N_2 (x 3). The substrate (1.0 equiv., 0.2 mmol), N, N-diisopropylethylamine (i.e. DIPEA, 0.2 equiv., 5 mg, 0.04 mmol), MeOH (50 μL, 10 M) and ultra dry THF (0.4 mL, 0.5 M) were sequentially added *via* syringes. The mixture was vigorously stirred under the irradiation of a 6 W 400 nm LED at room temperature for 12 h (the experiment setup is shown in Figure S1). After that, the crude mixture was purified on preparative TLC or flash column chromatography using PE/DCM (v/v = 20/1 – 1/1) as the eluent to afford the desired product. For preparative scale and gram-scale reaction, the equivalent of each additive remains constant.

4.1.2. General Procedure B: Synthesis of 1-hydroxyindolin-2-one derivatives



To a flame-dried Schlenk tube with a Teflon-coated magnetic stirring bar, the substrate (1.0 equiv., 0.2 mmol) and MeOH (50 μL, 10 M) were added in ultra dry THF (0.4 mL, 0.5 M) *via* syringes under nitrogen atmosphere. The mixture was vigorously stirred under the irradiation of a 6 W 400 nm LED at room temperature for 6 h (the experiment setup is shown in Figure S1). After that, the crude mixture was purified on preparative TLC or flash column chromatography using DCM/MeOH (v/v = 100/1 – 20/1) as the eluent to afford the desired product. For preparative scale and gram-scale reaction, the equivalent of each additive remains constant.

4.1.3. General Procedure C: Synthesis of indolin-2-one derivatives

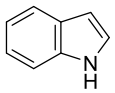


To a flame-dried Schlenk tube with a ground-glass bottle-neck (for rotary evaporation), the substrate (1.0 equiv., 0.2 mmol) and MeOH (50 μL, 10 M) were added in ultra dry THF (0.4 mL, 0.5 M) *via* syringes under nitrogen atmosphere. The mixture was vigorously stirred under the irradiation of a 6 W 400 nm LED at room temperature for 6 h (the experiment setup is shown in Figure S1). After that, the sealing plug was removed and the mixture was exposed to air. The solvent was evaporated in *vacuo*, and the residue was redissolved in 1 mL MeOH (*solvent switch*). $B_2(OH)_4$ (1.5 equiv., 27 mg, 0.3 mmol) and KOAc (2.0 equiv., 39 mg, 0.4 mmol) were added to the reaction mixture, which was then stirred at 50 ˚C for 2 h. Upon completion, the crude mixture was purified on preparative TLC or flash column chromatography using DCM or DCM/MeOH (v/v = 200/1 – 50/1) as the eluent to afford the desired product. For preparative scale and gram-scale reaction, the equivalent of each additive remains constant.

4.2. Characterization Data of the Products

4.2.1. Characterization Data for the Derivatives of 1*H*-indole

1*H*-indole (2a)



Following **General Procedure A**, **2a** was obtained as brown solid in 82% yield (20 mg) from 2-(2-nitrophenyl)ethan-1-ol (**1a**, 33 mg, 0.2 mmol) using 5:1 PE/DCM as eluent. 5,5,5',5'-Tetramethyl-2,2'-bi(1,3,2-dioxaborinane) (i.e. B_2nep_2, 99 mg, 0.44 mmol) was used. The NMR data were in consistent with the reported data[22].

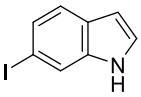
NMR Data of 2a:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (br, s, 1H, NH), 7.64 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.21 – 7.16 (m, 1H), 7.12 (d, *J* = 7.7 Hz, 1H), 7.10 – 7.07 (m, 1H), 6.53 (t, *J* = 2.5 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 135.84, 127.91, 124.28, 122.06, 120.82, 119.91, 111.16, 102.62.

HRMS (ESI$^+$) of 2a: *m/z* calcd for C_8H_7N $[M+H]^+$: 108.06513, Found:108.06511.

6-Iodo-1*H*-indole (2b)



Following **General Procedure A**, **2b** was obtained as faint yellow solid in 73% yield (35 mg) from 2-(4-iodo-2-nitrophenyl)ethan-1-ol (**1b**, 59 mg, 0.2 mmol) using 3:1 PE/DCM as eluent. 5,5,5',5'-Tetramethyl-2,2'-bi(1,3,2-dioxaborinane) (i.e. B_2nep_2, 99 mg, 0.44 mmol) was used. The NMR data were in consistent with the reported data[23].

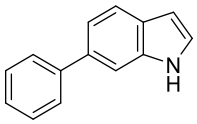
NMR Data of 2b:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (br, s, 1H, NH), 7.76 (d, *J* = 1.0 Hz, 1H), 7.40 (s, 2H), 7.14 (dd, *J* = 3.2, 2.1 Hz, 1H), 6.53 (ddd, *J* = 3.2, 2.1, 1.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.26, 128.79, 127.37, 124.69, 122.50, 120.14, 103.04, 85.90.

HRMS (ESI$^+$) of 2b: *m/z* calcd for C_8H_6NI $[M+H]^+$: 243.9614, Found: 243.9618.

6-Phenyl-1*H*-indole (2c)



Following **General Procedure A**, **2c** was obtained as faint yellow solid in 79% yield (30 mg) from 2-(3-nitro-[1,1'-biphenyl]-4-yl)ethan-1-ol (**1c**, 49 mg, 0.2 mmol) using 2:1 PE/DCM as eluent. 5,5,5',5'-Tetramethyl-2,2'-bi(1,3,2-dioxaborinane) (i.e. B_2nep_2, 99 mg, 0.44 mmol) was used. The NMR data were in consistent with the reported data[24].

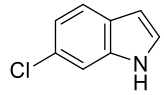
NMR Data of 2c:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (br, s, 1H, NH), 7.74 – 7.70 (m, 1H), 7.69 – 7.65 (m, 2H), 7.61 – 7.60 (m, 1H), 7.49 – 7.44 (m, 2H), 7.42 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.37 – 7.32 (m, 1H), 7.24 (dd, *J* = 3.2, 2.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.44, 136.50, 135.73, 128.83, 127.53, 127.34, 126.74, 124.94, 121.04, 119.95, 109.67, 102.69.

HRMS (ESI$^+$) of 2c: *m/z* calcd for $C_{14}H_{11}N$ $[M+H]^+$: 194.09643, Found: 194.09621.

6-Chloro-1*H*-indole (2d)



Following **General Procedure A**, **2d** was obtained as yellow solid in 78% yield (24 mg) from 2-(4-chloro-2-nitrophenyl)ethan-1-ol (**1e**, 40 mg, 0.2 mmol) using 5:1 PE/DCM as eluent. 5,5,5',5'-Tetramethyl-2,2'-bi(1,3,2-dioxaborinane) (i.e. B_2nep_2, 99 mg, 0.44 mmol) was used. The NMR data were in consistent with the reported data[25].

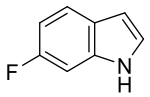
NMR Data of 2d:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (br, s, 1H, NH), 7.56 (d, *J* = 8.4 Hz, 1H), 7.38 (s, 1H), 7.19 (t, *J* = 2.4 Hz, 1H), 7.11 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.54 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 136.25, 127.98, 126.56, 124.96, 121.67, 120.71, 111.08, 102.91.

HRMS (ESI$^+$) of 2d: *m/z* calcd for C_8H_6NCl $[M+H]^+$: 152.0260, Found: 152.0262.

6-Fluoro-1*H*-indole (2e)



Following **General Procedure A**, **2e** was obtained as faint yellow solid in 72% yield (20 mg) from 2-(4-fluoro-2-nitrophenyl)ethan-1-ol (**1f**, 37 mg, 0.2 mmol) using 3:1 PE/DCM as eluent. 5,5,5',5'-Tetramethyl-2,2'-bi(1,3,2-dioxaborinane) (i.e. B_2nep_2, 99 mg, 0.44 mmol) was used. The NMR data were in consistent with the reported data[26].

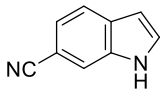
NMR Data of 2e:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (br, s, 1H, NH), 7.57 (dd, $J_{F\text{-}H}$ = 5.3 Hz, $J_{H\text{-}H}$ = 8.7, Hz, 1H), 7.18 (dd, *J* = 3.3, 2.3 Hz, 1H), 7.08 (dd, $J_{F\text{-}H}$ = 9.6 Hz, $J_{H\text{-}H}$ = 2.1 Hz, 1H), 6.92 (ddd, $J_{F\text{-}H}$ = 9.7 Hz, $J_{H\text{-}H}$ = 8.7, 2.3 Hz, 1H), 6.55 (ddd, *J* = 3.1, 2.0, 1.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.03 (d, *J* = 237.7 Hz), 135.80 (d, *J* = 12.0 Hz), 124.63 (d, *J* = 2.9 Hz), 124.48, 121.50 (d, *J* = 10.3 Hz), 108.75 (d, *J* = 25.7 Hz), 102.81, 97.42 (d, *J* = 27.3 Hz).

HRMS (ESI$^+$) of 2e: *m/z* calcd for C_8H_6NF $[M+H]^+$: 136.0558, Found: 136.0557.

1*H*-indole-6-carbonitrile (2f)



Following **General Procedure A**, **2f** was obtained as brown solid in 85% yield (24 mg) from 4-(2-hydroxyethyl)-3-nitrobenzonitrile (**1g**, 38 mg, 0.2 mmol) using 5:1 PE/DCM as eluent. 5,5,5',5'-Tetramethyl-2,2'-bi(1,3,2-dioxaborinane) (i.e. B_2nep_2, 99 mg, 0.44 mmol) was used. The NMR data were in consistent with the reported data[27].

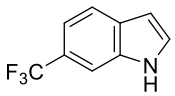
NMR Data of 2f:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (br, s, 1H, NH), 7.77 (d, *J* = 1.4 Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.35 (dd, *J* = 8.2, 1.4 Hz, 1H), 6.63 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 134.72, 131.31, 128.30, 122.76, 121.64, 120.92, 116.18, 104.21, 103.48.

HRMS (ESI$^+$) of 2f: *m/z* calcd for $C_9H_6N_2$ $[M+H]^+$: 143.06092, Found: 143.06040.

6-(Trifluoromethyl)-1*H*-indole (2g)



Following **General Procedure A**, **2g** was obtained as yellow solid in 62% yield (23 mg) from 2-(2-nitro-4-(trifluoromethyl)phenyl)ethan-1-ol (**1h**, 24 mg, 0.2 mmol) using 5:1 PE/DCM as eluent. 5,5,5',5'-Tetramethyl-2,2'-bi(1,3,2-dioxaborinane) (i.e. B_2nep_2, 99 mg, 0.44 mmol) was used. The NMR data were in consistent with the reported data[28].

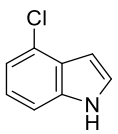
NMR Data of 2g:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (br, s, 1H, NH), 7.73 (d, *J* = 8.3 Hz, 1H), 7.69 (s, 1H), 7.41 – 7.33 (m, 2H), 6.63 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 134.76, 130.35, 126.93, 125.35 (q, *J* = 271.7 Hz), 124.28 (q, *J* = 32.0 Hz), 121.24, 116.67 (q, *J* = 3.3 Hz), 108.73 (q, *J* = 4.7 Hz), 103.13.

HRMS (ESI$^+$) of 2g: *m/z* calcd for $C_9H_6NF_3$ $[M+H]^+$: 186.0524, Found: 186.0525.

4-Chloro-1H-indole (2h)



Following **General Procedure A**, **2h** was obtained as brown solid in 77% yield (23 mg) from 2-(2-chloro-6-nitrophenyl)ethan-1-ol (**1r**, 40 mg, 0.2 mmol) using 2:1 PE/DCM as eluent. 5,5,5',5'-Tetramethyl-2,2'-bi(1,3,2-dioxaborinane) (i.e. B_2nep_2, 99 mg, 0.44 mmol) was used. The NMR data were in consistent with the reported data[29].

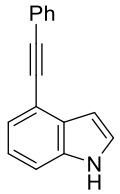
NMR Data of 2h:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (br, s, 1H, NH), 7.30 (m, 1H), 7.24 (dd, *J* = 3.3, 2.4 Hz, 1H), 7.16 – 7.09 (m, 2H), 6.68 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 136.59, 126.90, 126.20, 124.82, 122.70, 119.69, 109.80, 101.44.

HRMS (ESI$^+$) of 2h: *m/z* calcd for C_8H_6NCl $[M+H]^+$: 152.0260, Found: 152.0262.

4-(Phenylethynyl)-1*H*-indole (2i)



Following **General Procedure A**, **2i** was obtained as brown solid in 78% yield (34 mg) from 2-(2-nitro-6-(phenylethynyl)phenyl)ethan-1-ol (**1p**, 53 mg, 0.2 mmol) using 3:1 PE/DCM as eluent. 5,5,5',5'-Tetramethyl-2,2'-bi(1,3,2-dioxaborinane) (i.e. B_2nep_2, 99 mg, 0.44 mmol) was used.

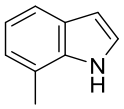
NMR Data of 2i:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (br, s, 1H, NH), 7.62 (m, 2H), 7.44 – 7.32 (m, 5H), 7.28 (dd, *J* = 2.8, 2.6 Hz, 1H), 7.19 (dd, *J* = 7.8, 7.7 Hz, 1H), 6.83 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 135.54, 131.78, 129.52, 128.47, 128.17, 124.89, 123.91, 122.01, 115.01, 111.78, 102.61, 91.92, 88.51, 88.51.

HRMS (ESI$^+$) of 2i: *m/z* calcd for $C_{16}H_{11}N$ $[M+H]^+$: 218.09595, Found: 218.09643.

7-Methyl-1H-indole (2j)



Following **General Procedure A**, **2j** was obtained as yellow solid in 85% yield (22 mg) from 2-(3-methyl-2-nitrophenyl)ethan-1-ol (**1t**, 36 mg, 0.2 mmol) using 3:1 PE/DCM as eluent. 5,5,5',5'-Tetramethyl-2,2'-bi(1,3,2-dioxaborinane) (i.e. B_2nep_2, 99 mg, 0.44 mmol) was used. The NMR data were in consistent with the reported data[30].

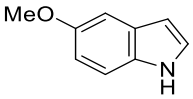
NMR Data of 2j:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (br, s, 1H, NH), 7.57 (d, *J* = 7.8 Hz, 1H), 7.20 (dd, *J* = 2.8, 2.6 Hz, 1H), 7.12 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.06 (d, *J* = 7.5 Hz, 1H), 6.62 (dd, *J* = 3.2, 2.0 Hz, 1H), 2.53 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 135.51, 127.47, 123.96, 122.58, 120.31, 120.12, 118.56, 103.18, 16.79.

HRMS (ESI$^+$) of 2j: *m/z* calcd for C_9H_9N $[M+H]^+$: 132.0809, Found: 132.0807.

6-Methoxy-1*H*-indole (2k)



Following **General Procedure A**, **2k** was obtained as yellow solid in 92% yield (27 mg) from 2-(5-methoxy-2-nitrophenyl)ethan-1-ol (**1k**, 40 mg, 0.2 mmol) using 5:1 PE/DCM as eluent. 5,5,5',5'-Tetramethyl-2,2'-bi(1,3,2-dioxaborinane) (i.e. B_2nep_2, 99 mg, 0.44 mmol) was used. The NMR data were in consistent with the reported data[28].

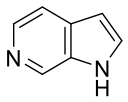
NMR Data of 2k:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (br, s, 1H, NH), 7.28 (d, *J* = 8.5 Hz, 1H), 7.18 (dd, *J* = 3.1, 2.5 Hz, 1H), 7.13 (d, *J* = 2.5 Hz, 1H), 6.88 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.50 (ddd, *J* = 3.1, 2.1, 1.0 Hz, 1H), 3.87 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.29, 131.08, 128.40, 125.00, 112.46, 111.83, 102.48, 102.45, 55.99.

HRMS (ESI$^+$) of 2k: *m/z* calcd for C_9H_9NO $[M+H]^+$: 148.0757, Found: 148.0757.

1*H*-pyrrolo[2,3-c]pyridine (2l)



Following **General Procedure A**, **2l** was obtained as dark brown solid in 60% yield (14 mg) from 2-(3-nitropyridin-4-yl)ethan-1-ol (**1u**, 34 mg, 0.2 mmol) using DCM as eluent. 5,5,5',5'-Tetramethyl-2,2'-bi(1,3,2-dioxaborinane) (i.e. B_2nep_2, 99 mg, 0.44 mmol) was used. The NMR data were in consistent with the reported data[31].

NMR Data of 2l:

^{1}H NMR (400 MHz, DMSO-d_6): δ 11.66 (br, s, 1H, NH), 8.80 (dd, *J* = 1.2, 1.0 Hz, 1H), 8.11 (d, *J* = 5.4 Hz, 1H), 7.60 (d, *J* = 3.0 Hz, 1H), 7.53 (dd, *J* = 5.4, 1.1 Hz, 1H), 6.50 (d, *J* = 3.0 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 137.67, 134.46, 133.23, 131.88, 129.31, 114.70, 100.46.

HRMS (ESI$^+$) of 2l: *m/z* calcd for $C_7H_6N_2$ $[M+H]^+$: 119.06037, Found: 119.06003.

4-Bromo-1*H*-pyrrolo[2,3-c]pyridine (2m)

Following **General Procedure A**, **2m** was obtained as dark brown solid in 48% yield (19 mg) from 2-(3-bromo-5-nitropyridin-4-yl)ethan-1-ol (**1v**, 49 mg, 0.2 mmol) using 1:1 PE/DCM as eluent. 5,5,5',5'-Tetramethyl-2,2'-bi(1,3,2-dioxaborinane) (i.e. B_2nep_2, 99 mg, 0.44 mmol) was used. The NMR data were in consistent with the reported data[32].

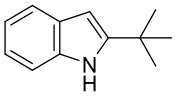
NMR Data of 2m:

^{1}H NMR (400 MHz, DMSO-d_6): δ 11.03 (br, s, 1H, NH), 8.60 (s, 1H), 8.17 (s, 1H), 7.45 (d, *J* = 3.1 Hz, 1H), 6.55 (d, *J* = 3.0 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 137.94, 134.05, 133.24, 132.40, 130.06, 112.56, 101.89.

HRMS (ESI$^+$) of 2m: *m/z* calcd for $C_7H_5N_2Br$ $[M+H]^+$: 196.9709, Found: 196.9709.

2-(Tert-butyl)-1*H*-indole (2n)



Following **General Procedure A**, **2n** was obtained as yellow solid in 97% yield (34 mg) from 3,3-dimethyl-1-(2-nitrophenyl)butan-2-ol (**1ae**, 45 mg, 0.2 mmol) using 5:1 PE/DCM as eluent. (Dihydroxyboranyl)boronic acid [i.e. $B_2(OH)_4$, 40 mg, 0.44 mol] was used. The NMR data were in consistent with the reported data[33].

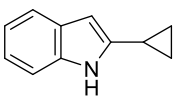
NMR Data of 2n:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (br, s, 1H, NH), 7.60 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.36 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.18 (ddd, *J* = 8.0, 7.0, 1.4 Hz, 1H), 7.13 (ddd, *J* = 8.0, 7.1, 1.2 Hz, 1H), 6.32 (s, 1H), 1.44 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 148.89, 135.88, 128.63, 121.18, 120.09, 119.71, 110.49, 97.07, 31.93, 30.42.

HRMS (ESI$^+$) of 2n: *m/z* calcd for $C_{12}H_{15}N$ $[M+H]^+$: 174.1278, Found: 174.1277.

2-Cyclopropyl-1*H*-indole (2o)



Following **General Procedure A**, **2o** was obtained as yellow solid in 95% yield (30 mg) from 1-cyclopropyl-2-(2-nitrophenyl)ethan-1-ol (**1af**, 41 mg, 0.2 mmol) using 10:1 PE/DCM as eluent. (Dihydroxyboranyl)boronic acid [i.e. $B_2(OH)_4$, 40 mg, 0.44 mol] was used. The NMR data were in consistent with the reported data[33].

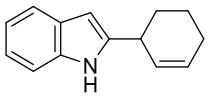
NMR Data of 2o:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (br, s, 1H, NH), 7.52 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.28 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.13 (ddd, *J* = 7.8, 7.8, 1.4 Hz, 1H), 7.08 (ddd, *J* = 7.4, 7.8, 1.3 Hz, 1H), 6.17 (s, 1H), 1.97 (m, 1H), 1.01 – 0.95 (m, 2H), 0.83 – 0.74 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 141.82, 135.87, 128.84, 121.13, 119.86, 119.81, 110.32, 97.87, 9.00, 7.44.

HRMS (ESI$^+$) of 2o: *m/z* calcd for $C_{11}H_{11}N$ $[M+H]^+$: 158.0964, Found: 158.0952.

2-(Cyclohex-2-en-1-yl)-1*H*-indole (2p)



Following **General Procedure A**, **2p** was obtained as colorless oil in 94% yield (37 mg) from 1-(cyclohex-2-en-1-yl)-2-(2-nitrophenyl)ethan-1-ol (**1ag**, 49 mg, 0.2 mmol) using 10:1 PE/DCM as eluent. (Dihydroxyboranyl)boronic acid [i.e. $B_2(OH)_4$, 40 mg, 0.44 mol] was used.

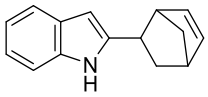
NMR Data of 2p:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (br, s, 1H, NH), 7.58 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.33 (dd, *J* = 7.4, 1.1 Hz, 1H), 7.16 (ddd, *J* = 7.5, 7.4, 1.3 Hz, 1H), 7.11 (ddd, *J* = 7.5, 7.4, 1.1 Hz, 1H), 6.30 (s, 1H), 5.83 (m, 2H), 3.11 – 3.01 (m, 1H), 2.55 – 1.73 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.42, 135.76, 128.68, 127.39, 126.07, 121.18, 120.04, 119.74, 110.52, 98.12, 33.30, 31.44, 28.86, 25.09.

HRMS (ESI$^+$) of 2p: *m/z* calcd for $C_{14}H_{15}N$ $[M+H]^+$: 198.1275, Found: 198.1277.

2-(Bicyclo[2.2.1]hept-5-en-2-yl)-1*H*-indole (2q)



Following **General Procedure A**, **2q** was obtained as colorless solid in 93% yield (39 mg) from 2-(2-nitrophenyl)-1-(pyridin-4-yl)ethan-1-ol (**1ah**, 52 mg, 0.2 mmol) using 10:1 PE/DCM as eluent. (Dihydroxyboranyl)boronic acid [i.e. $B_2(OH)_4$, 40 mg, 0.44 mol] was used. The NMR data were in consistent with the reported data[34].

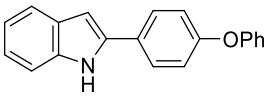
NMR Data of 2q:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (br, s, 1H, NH), 7.54 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.30 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.12 (ddd, *J* = 7.7, 7.7, 1.4 Hz, 1H), 7.07 (ddd, *J* = 7.5, 7.6, 1.2 Hz, 1H), 6.30 (s, 1H), 6.23 (dd, *J* = 5.6, 3.1 Hz, 1H), 6.19 (dd, *J* = 5.6, 3.1 Hz, 1H), 3.03 – 2.99 (m, 2H), 2.78 – 2.73 (m, 1H), 1.88 (ddd, *J* = 11.7, 4.4, 3.4 Hz, 1H), 1.65 (ddd, *J* = 11.6, 8.8, 2.5 Hz, 1H), 1.59 – 1.54 (m, 1H), 1.47 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.06, 137.63, 136.30, 128.77, 121.23, 120.00, 119.75, 110.34, 98.89, 48.22, 46.62, 42.02, 37.91, 32.78.

HRMS (ESI$^+$) of 2q: *m/z* calcd for $C_{15}H_{15}N$ $[M+H]^+$: 210.09134, Found: 210.09079.

2-(4-Phenoxyphenyl)-1*H*-indole (2r)



Following **General Procedure A**, **2r** was obtained as yellow solid in 96% yield (55 mg) from 2-(2-nitrophenyl)-1-(4-phenoxyphenyl)ethan-1-ol (**1ai**, 67 mg, 0.2 mmol) using 10:1 PE/DCM as eluent. (Dihydroxyboranyl)boronic acid [i.e. $B_2(OH)_4$, 40 mg, 0.44 mol] was used. The NMR data were in consistent with the reported data[35].

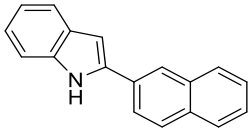
NMR Data of 2r:

^{1}H NMR (400 MHz, DMSO-d_6): δ 11.49 (br, s, 1H, NH), 7.90 – 7.85 (m, 2H), 7.51 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.45 – 7.37 (m, 3H), 7.17 (ddd, *J* = 7.5, 7.3, 1.1 Hz, 1H), 7.12 – 7.05 (m, 5H), 6.99 (ddd, *J* = 7.6, 7.1, 1.1 Hz, 1H), 6.83 (s, 1H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 156.48, 156.07, 137.19, 137.06, 130.10, 128.70, 127.65, 126.71, 123.62, 121.36, 119.88, 119.32, 118.95, 118.76, 111.19, 98.20.

HRMS (ESI$^+$) of 2r: *m/z* calcd for $C_{20}H_{15}NO$ $[M+H]^+$: 286.1215, Found: 286.1226.

2-(Naphthalen-2-yl)-1*H*-indole (2s)



Following **General Procedure A**, **2s** was obtained as colorless solid in 97% yield (47 mg) from 1-(naphthalen-2-yl)-2-(2-nitrophenyl)ethan-1-ol (**1aj**, 59 mg, 0.2 mmol) using 10:1 PE/DCM as eluent. (Dihydroxyboranyl)boronic acid [i.e. $B_2(OH)_4$, 40 mg, 0.44 mol] was used. The NMR data were in consistent with the reported data[33].

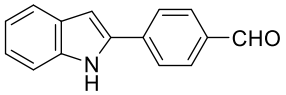
NMR Data of 2s:

^{1}H NMR (400 MHz, DMSO-d_6): δ 11.70 (br, s, 1H, NH), 8.39 (s, 1H), 8.04 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.98 (d, *J* = 8.6 Hz, 1H), 7.93 (ddd, *J* = 7.4, 7.0, 1.3 Hz, 2H), 7.57 (d, *J* = 6.9 Hz, 1H), 7.56 – 7.46 (m, 2H), 7.45 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.13 (ddd, *J* = 8.1, 7.0, 1.0 Hz, 1H), 7.08 – 6.98 (m, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 137.53, 137.36, 133.24, 132.26, 129.67, 128.67, 128.39, 127.84, 127.67, 126.68, 125.99, 123.80, 122.79, 121.79, 120.12, 119.43, 111.31, 99.54.

HRMS (ESI$^+$) of 2s: *m/z* calcd for $C_{18}H_{13}N$ $[M+H]^+$: 243.11188, Found: 243.11208.

4-(1*H*-indol-2-yl)benzaldehyde (2t)



Following **General Procedure A**, **2t** was obtained as yellow solid in 98% yield (43 mg) from 4-(1-hydroxy-2-(2-nitrophenyl)ethyl)benzaldehyde (**1ak**, 54 mg, 0.2 mmol) using 20:1 PE/DCM as eluent. (Dihydroxyboranyl)boronic acid [i.e. $B_2(OH)_4$, 40 mg, 0.44 mol] was used. The NMR data were in consistent with the reported data[36].

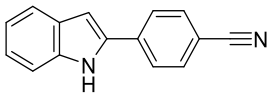
NMR Data of 2t:

^{1}H NMR (400 MHz, DMSO-d_6): δ 11.75 (br, s, 1H, NH), 10.01 (br, s, 1H, CHO), 8.09 (d, *J* = 8.1 Hz, 2H), 7.98 (d, *J* = 8.1 Hz, 2H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.15 (dd, *J* = 7.9, 7.9 Hz, 2H), 7.14 (s, 1H), 7.03 (dd, *J* = 7.4, 7.4 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 192.28, 137.74, 137.71, 136.10, 134.67, 130.25, 128.42, 125.19, 122.66, 120.60, 119.77, 111.59, 101.46.

HRMS (ESI$^+$) of 2t: *m/z* calcd for $C_{15}H_{11}NO$ $[M+H]^+$: 222.09134, Found: 222.09037.

4-(1*H*-indol-2-yl)benzonitrile (2u)



Following **General Procedure A**, **2u** was obtained as brown solid in 95% yield (41 mg) from 4-(1-hydroxy-2-(2-nitrophenyl)ethyl)benzonitrile (**1al**, 54 mg, 0.2 mmol) using 5:1 PE/DCM as eluent. (Dihydroxyboranyl)boronic acid [i.e. $B_2(OH)_4$, 40 mg, 0.44 mol] was used. The NMR data were in consistent with the reported data[33].

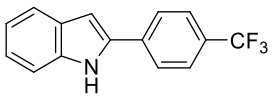
NMR Data of 2u:

^{1}H NMR (400 MHz, DMSO-d_6): δ 11.75 (br, s, 1H), 8.04 (d, *J* = 8.4 Hz, 2H), 7.91 (d, *J* = 8.5 Hz, 2H), 7.58 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.43 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.16 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.14 (s, 1H), 7.03 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 137.66, 136.52, 135.56, 132.86, 128.35, 125.34, 122.75, 120.65, 119.81, 118.99, 111.60, 109.15, 101.55.

HRMS (ESI$^+$) of 2u: *m/z* calcd for $C_{15}H_{11}N_2$ $[M+H]^+$: 219.09167, Found: 219.09108.

2-(4-(Trifluoromethyl) phenyl)-1*H*-indole (2v)



Following **General Procedure A**, **2v** was obtained as brown solid in 96% yield (50 mg) from 2-(2-nitrophenyl)-1-(4-(trifluoromethyl)phenyl)ethan-1-ol (**1am**, 62 mg, 0.2 mmol) using 10:1 PE/DCM as eluent. (Dihydroxyboranyl)boronic acid [i.e. $B_2(OH)_4$, 40 mg, 0.44 mol] was used. The NMR data were in consistent with the reported data[33].

NMR Data of 2v:

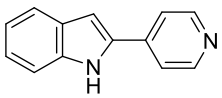
^{1}H NMR (400 MHz, DMSO-d_6): δ 11.73 (br, s, 1H, NH), 8.07 (d, *J* = 8.2 Hz, 2H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.15 (m, 1H), 7.09 – 6.99 (m, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 137.50, 136.09, 135.82, 128.39, 127.23 (q, *J* = 31.6 Hz), 125.82 (q, *J* = 3.2 Hz), 124.34 (q, *J* = 272.2 Hz), 125.33, 122.41, 120.50, 119.68, 111.54, 100.72.

^{19}F NMR (376 MHz, DMSO-d_6): δ -60.87.

HRMS (ESI$^+$) of 2v: *m/z* calcd for $C_{15}H_{10}F_3N$ [M+H]$^+$: 262.0832, Found: 262.0838.

2-(Pyridin-4-yl)-1*H*-indole (2w)



Following **General Procedure A**, **2w** was obtained as brown solid in 78% yield (30 mg) from 2-(2-nitrophenyl)-1-(pyridin-4-yl)ethan-1-ol (**1an**, 49 mg, 0.2 mmol) using 1:1 PE/DCM as eluent. (Dihydroxyboranyl)boronic acid [i.e. $B_2(OH)_4$, 40 mg, 0.44 mol] was used. The NMR data were in consistent with the reported data[33].

NMR Data of 2w:

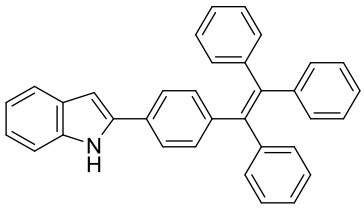
^{1}H NMR (400 MHz, $CDCl_3$): δ 11.78 (br, s, 1H, NH), 8.61 (dd, *J* = 4.6, 1.5 Hz, 2H), 7.82 (dd, *J* = 4.6, 1.6 Hz, 2H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 1H), 7.22 – 7.13 (m, 2H), 7.04 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.18, 139.01, 137.55, 134.61, 128.16, 122.86, 120.72, 119.80, 118.99, 111.64, 101.65.

HRMS (ESI$^+$) of 2w: *m/z* calcd for $C_{13}H_{10}N_2$ [M+H]$^+$: 195.0719, Found: 195.0717.

The characterization data of **2x** was present at section **4.3.3**.

2-(4-(1,2,2-Triphenylvinyl)phenyl)-1*H*-indole (2y)



Following **General Procedure A**, **2y** was obtained as faint yellow solid in 62% yield (56 mg) from (2-(2-nitrophenyl)-1-(4-(1,2,2-triphenylvinyl)phenyl)ethan-1-ol (**1ao**, 99 mg, 0.2 mmol) using 5:1 PE/DCM as eluent. (Dihydroxyboranyl)boronic acid [i.e. $B_2(OH)_4$, 40 mg, 0.44 mol] was used.

NMR Data of 2y:

^{1}H NMR (400 MHz, DMSO-d_6): δ 11.43 (br, s, 1H, NH), 7.62 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.22 – 6.93 (m, 19H), 6.83 (d, *J* = 2.0 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 143.23, 143.17, 143.04, 142.18, 140.73, 140.14, 137.21, 137.13, 131.21, 130.76, 130.68, 130.65, 130.24, 128.58, 127.93, 127.87, 127.80, 126.66, 126.63, 126.54, 124.31, 121.57, 119.97, 119.34, 111.20, 98.79.

HRMS (ESI$^+$) of 2y: *m/z* calcd for $C_{34}H_{25}N$ [M+H]$^+$: 448.2084, Found: 448.2060.

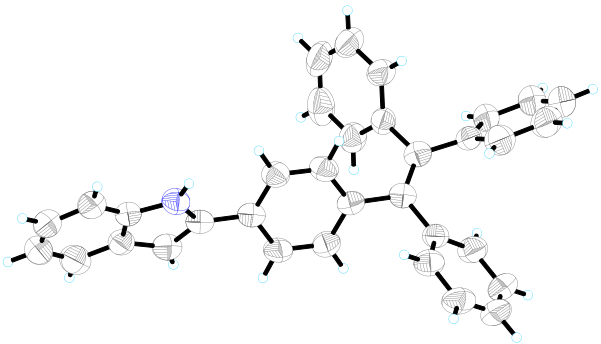
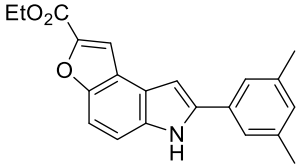


Figure S3. Crystal structure of **2y** (ellipsoids at 50% probability).

Ethyl 7-(3,5-dimethylphenyl)-6H-furo[3,2-e]indole-2-carboxylate (2z)



Following **General Procedure A**, **2z** was obtained as reddish brown solid in 92% yield (62 mg) from ethyl 6-(2-(3,5-dimethylphenyl)-2-hydroxyethyl)-5-nitrobenzofuran-2-carboxylate (**1ar**, 77 mg, 0.2 mmol) using DCM as eluent. (Dihydroxyboranyl)boronic acid [i.e. $B_2(OH)_4$, 40 mg, 0.44 mol] was used.

NMR Data of 2z:

^{1}H NMR (400 MHz, DMSO-d_6): δ 11.87 (br, s, 1H, NH), 7.97 (s, 1H), 7.56 (d, *J* = 8.9 Hz, 1H), 7.51 (d, *J* = 2.1 Hz, 2H), 7.42 (d, *J* = 8.9 Hz, 1H), 7.20 (d, *J* = 2.1 Hz, 1H), 6.97 (s, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 2.35 (s, 6H), 1.36 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 158.83, 151.44, 143.68, 138.53, 137.95, 133.10, 131.83, 129.06, 122.79, 121.47, 118.35, 113.53, 112.76, 105.70, 97.99, 60.82, 21.02, 14.22.

HRMS (ESI$^+$) of 2z: *m/z* calcd for $C_{21}H_{19}NO_3$ $[M+H]^+$: 334.14377, Found: 334.13531.

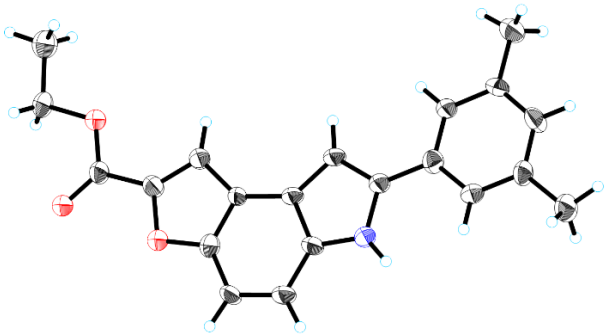
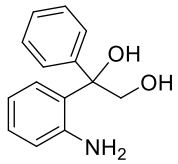


Figure S4. Crystal structure of **2z** (ellipsoids at 50% probability).

The characterization data of **2aa** was present at section **4.3.2**.

1-(2-Aminophenyl)-1-phenylethane-1,2-diol (2ab)



Following a modified **General Procedure A** (without the addition of DIPEA), **2ab** was obtained as brown solid in 82% yield (38 mg) from 2-(2-nitrophenyl)-2-phenylethan-1-ol (**1y**, 49 mg, 0.2 mmol) using DCM as eluent. (Dihydroxyboranyl)boronic acid [i.e. $B_2(OH)_4$, 40 mg, 0.44 mol] was used.

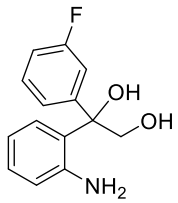
NMR Data of 2ab:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.23 (m, 6H), 7.13 (ddd, *J* = 7.6, 7.6, 1.5 Hz, 1H), 6.85 (ddd, *J* = 7.6, 7.5, 1.3 Hz, 1H), 6.65 (dd, *J* = 7.9, 1.2 Hz, 1H), 4.24 (d, *J* = 11.6 Hz, 1H), 3.84 (d, *J* = 11.6 Hz, 1H), 3.62 (br, s, 1H, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 145.21, 143.25, 129.04, 128.53, 128.23, 127.76, 127.36, 126.22, 119.08, 119.04, 79.31, 69.32.

HRMS (ESI$^+$) of 2ab: *m/z* calcd for $C_{14}H_{15}NO_2$ $[M-H]^-$: 228.10191, Found: 228.10249.

1-(2-Aminophenyl)-1-(3-fluorophenyl)ethane-1,2-diol (2ac)



Following a modified **General Procedure A** (without the addition of DIPEA), **2ac** was obtained as yellow solid in 85% yield (42 mg) from 2-(3-fluorophenyl)-2-(2-nitrophenyl)ethan-1-ol (**1z**, 52 mg, 0.2 mmol) using DCM as eluent. (Dihydroxyboranyl)boronic acid [i.e. $B_2(OH)_4$, 40 mg, 0.44 mol] was used.

NMR Data of 2ac:

^{1}H NMR (400 MHz, $CDCl_3$): δ δ 7.33 – 7.27 (m, 2H), 7.20 – 7.13 (m, 2H), 7.10 (ddd, *J* = 7.8, 1.3, 1.3 Hz, 1H), 6.98 (m, 1H), 6.87 (ddd, *J* = 7.6, 7.7, 1.3 Hz, 1H), 6.66 (dd, *J* = 7.9, 1.2 Hz, 1H), 4.21 (d, *J* = 11.6 Hz, 1H), 3.89 (br, s, 1H, OH),

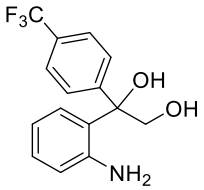
3.75 (d, *J* = 11.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.96 (d, *J* = 242.3 Hz), 146.17 (d, *J* = 6.5 Hz), 145.27, 129.95 (d, *J* = 8.0 Hz), 129.24, 127.54, 127.24, 121.86 (d, *J* = 1.7 Hz), 119.10, 119.01, 114.61 (d, *J* = 21.4 Hz), 113.52 (d, *J* = 22.8 Hz), 79.03, 69.14.

^{19}F NMR (376 MHz, $CDCl_3$): δ -112.45.

HRMS (ESI$^+$) of 2ac: *m/z* calcd for $C_{14}H_{14}NFO_2$ $[M-H]^-$: 246.09248, Found: 246.09315.

1-(2-Aminophenyl)-1-(4-(trifluoromethyl)phenyl)ethane-1,2-diol (2ad)



Following a modified **General Procedure A** (without the addition of DIPEA), **2ad** was obtained as yellow solid in 82% yield (49 mg) from 2-(2-nitrophenyl)-2-(4-(trifluoromethyl)phenyl)ethan-1-ol (**1aa**, 62 mg, 0.2 mmol) using DCM as eluent. (Dihydroxyboranyl)boronic acid [i.e. $B_2(OH)_4$, 40 mg, 0.44 mol] was used.

NMR Data of 2ad:

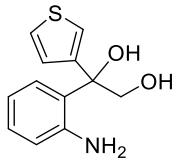
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.33 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.17 (ddd, *J* = 7.8, 7.7, 1.3 Hz, 1H), 6.88 (ddd, *J* = 7.8, 7.7, 1.3 Hz, 1H), 6.68 (dd, *J* = 7.8, 1.3 Hz, 1H), 4.29 (d, *J* = 11.5 Hz, 1H), 3.82 (d, *J* = 11.5 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 147.36 (q, *J* = 1.3 Hz), 145.34, 129.94 (q, *J* = 32.0 Hz), 129.44, 127.25, 127.16, 126.65, 125.40 (q, *J* = 3.8 Hz), 124.21 (q, *J* = 272.0 Hz), 119.23, 119.08, 79.20, 69.20.

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.52.

HRMS (ESI$^+$) of 2ad: *m/z* calcd for $C_{15}H_{14}NF_3O_2$ $[M+H]^+$: 296.08929, Found: 296.09033.

1-(2-Aminophenyl)-1-(thiophen-3-yl)ethane-1,2-diol (2ae)



Following a modified **General Procedure A** (without the addition of DIPEA), **2ae** was obtained as black solid in 88% yield (49 mg) from 2-(2-nitrophenyl)-2-(4-(trifluoromethyl)phenyl)ethan-1-ol (**1ab**, 41 mg, 0.2 mmol) using DCM as eluent. (Dihydroxyboranyl)boronic acid [i.e. $B_2(OH)_4$, 40 mg, 0.44 mol] was used.

NMR Data of 2ae:

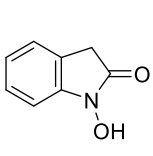
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (dd, *J* = 5.0, 3.1 Hz, 1H), 7.22 (dd, *J* = 3.1, 1.3 Hz, 1H), 7.19 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.12 (ddd, *J* = 7.8, 7.8, 1.3 Hz, 1H), 6.96 (dd, *J* = 5.0, 1.3 Hz, 1H), 6.80 (ddd, *J* = 7.8, 7.7, 1.2 Hz, 1H), 6.67 (dd, *J* = 7.8, 1.2 Hz, 1H), 4.26 (d, *J* = 11.5 Hz, 1H), 3.95 (d, *J* = 11.5 Hz, 1H), 3.70 (br, s, 1H, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 145.45, 145.28, 129.07, 127.57, 127.09, 126.77, 126.41, 122.23, 118.97, 118.85, 78.25, 68.48.

HRMS (ESI$^+$) of 2ae: *m/z* calcd for $C_{12}H_{13}SNO_2$ $[M+H]+$: 234.05833, Found: 234.05579.

4.2.2.Characterization Data for the Derivatives of 1-Hydroxyindolin-2-one

1-Hydroxyindolin-2-one (3a)



Following **General Procedure B**, **3a** was obtained as brown solid in 88% yield (26 mg) from 2-(2-nitrophenyl)ethan-1-ol (**1a**, 33 mg, 0.2 mmol; 10.0 mmol scale: 75% yield, 1.12 g) using 20:1 DCM/MeOH as eluent. The NMR data were in consistent with the reported data[37].

NMR Data of 3a:

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.63 (br, s, 1H, N–OH), 7.27 (ddd, *J* = 7.7, 7.7, 1.1 Hz, 1H), 7.23 (d, *J* = 7.3 Hz, 1H), 7.00 (ddd, *J* = 7.5, 7.5, 1.1 Hz, 1H), 6.91 (d, *J* = 7.7 Hz, 1H), 3.55 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 169.29, 143.62, 127.62, 124.35, 121.88, 121.12, 106.76, 33.39.

HRMS (ESI$^+$) of 3a: *m/z* calcd for $C_8H_7NO_2$ [M-H]$^-$: 148.03930, Found: 148.03894.

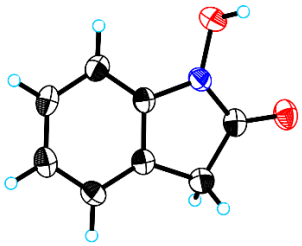
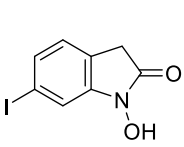


Figure S5. Crystal structure of **3a** (ellipsoids at 50% probability).

1-Hydroxy-6-iodoindolin-2-one (3b)



Following **General Procedure B**, **3b** was obtained as faint brown solid (0.2 mmol scale: 95% yield, 45 mg; 5.0 mmol scale: 77% yield, 1.06 g) from 2-(4-iodo-2-nitrophenyl)ethan-1-ol (**1b**, 59 mg, 0.2 mmol) using 20:1 DCM/MeOH as eluent. The NMR data were in consistent with the reported data[38].

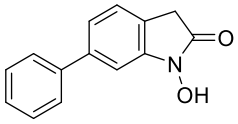
NMR Data of 3b:

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.77 (br, s, 1H, N–OH), 7.36 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.18 (d, *J* = 1.4 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 3.52 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 169.15, 144.96, 130.46, 126.48, 121.08, 114.98, 92.46, 33.21.

HRMS (ESI$^+$) of 3b: *m/z* calcd for $C_8H_6NO_2I$ [M-H]$^-$: 273.93595, Found: 273.93710.

1-Hydroxy-6-phenylindolin-2-one (3c)



Following **General Procedure B**, **3c** was obtained as White solid in 95% yield (43 mg) from 2-(3-nitro-[1,1'-biphenyl]-4-yl)ethan-1-ol (**1c**, 49 mg, 0.2 mmol) using 20:1 DCM/MeOH as eluent.

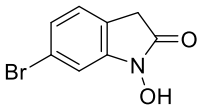
NMR Data of 3c:

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.75 (br, s, 1H, N–OH), 7.66 (d, *J* = 7.4 Hz, 2H), 7.47 (dd, *J* = 7.6, 7.5 Hz, 2H), 7.42 – 7.26 (m, 3H), 7.13 (s, 1H), 3.60 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 169.53, 144.35, 140.07, 140.03, 128.97, 127.56, 126.64, 124.86, 120.43, 104.83, 33.25.

HRMS (ESI$^+$) of 3c: *m/z* calcd for $C_{14}H_{11}NO_2$ [M-H]$^-$: 224.07061, Found: 224.07123.

6-Bromo-1-hydroxyindolin-2-one (3d)



Following **General Procedure B**, **3d** was obtained as faint yellow solid in 92% yield (42 mg) from 2-(4-bromo-2-nitrophenyl)ethan-1-ol (**1d**, 49 mg, 0.2 mmol) using 30:1 DCM/MeOH as eluent.

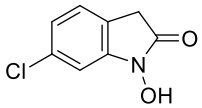
NMR Data of 3d:

^{1}H NMR (400 MHz, CD_3OD & CD_2Cl_2): δ 7.21 – 7.14 (m, 2H), 7.09 (dd, *J* = 7.8, 2.6 Hz, 1H), 3.43 (s, 2H).

^{13}C NMR (100 MHz, CD_3OD & CD_2Cl_2): δ 171.03, 145.12, 126.12, 125.76, 121.72, 120.33, 111.17, 34.00.

HRMS (ESI$^+$) of 3d: *m/z* calcd for $C_8H_6NO_2Br$ [M-H]$^-$: 225.94982, Found: 222.95055.

6-Chloro-1-hydroxyindolin-2-one (3e)



Following **General Procedure B**, **3e** was obtained as yellow solid in 91% yield (33 mg) from 2-(4-chloro-2-nitrophenyl)ethan-1-ol (**1e**, 40 mg, 0.2 mmol) using 20:1 DCM/MeOH as eluent.

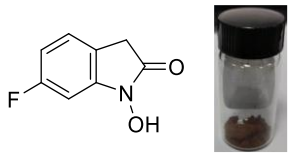
NMR Data of 3e:

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.83 (br, s, 1H, N–OH), 7.24 (d, *J* = 7.8 Hz, 1H), 7.04 (dd, *J* = 7.8, 2.0 Hz, 1H), 6.91 (d, *J* = 2.0 Hz, 1H), 3.56 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 169.57, 145.02, 132.18, 125.88, 121.48, 120.12, 106.83, 33.12.

HRMS (ESI$^+$) of 3e: *m/z* calcd for $C_8H_6NO_2Cl$ [M-H]$^-$: 182.00037, Found: 182.00027.

6-Fluoro-1-hydroxyindolin-2-one (3f)



Following **General Procedure B**, **3f** was obtained as dark brown solid (0.2 mmol scale: 95% yield, 31 mg; 5.4 mmol scale: 85% yield, 770 mg) from 2-(4-fluoro-2-nitrophenyl)ethan-1-ol (**1f**, 37 mg, 0.2 mmol) using 20:1 DCM/MeOH as eluent.

NMR Data of 3f:

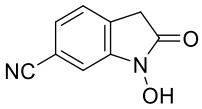
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.97 (br, s, 1H, N–OH), 7.15 (dd, $J_{F\text{-}H}$ = 5.5 Hz, $J_{H\text{-}H}$ = 8.4 Hz, 1H), 6.70 (ddd, $J_{F\text{-}H}$ = 10.0 Hz, $J_{H\text{-}H}$ = 8.4, 2.3 Hz, 1H), 6.64 (dd, $J_{F\text{-}H}$ = 8.7 Hz, $J_{H\text{-}H}$ = 2.3 Hz, 1H), 3.50 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 178.43, 162.86 (d, *J* = 242.6 Hz), 143.78 (d, *J* = 12.3 Hz), 125.61 (d, *J* = 10.6 Hz), 120.59 (d, *J* = 2.6 Hz), 108.82 (d, *J* = 24.5 Hz), 98.59 (d, *J* = 27.8 Hz), 35.79.

^{19}F NMR (376 MHz, $CDCl_3$): δ -112.84.

HRMS (ESI$^+$) of 3f: *m/z* calcd for $C_8H_6NO_2F$ [M-H]$^-$: 166.02988, Found: 166.02972.

1-Hydroxy-2-oxoindoline-6-carbonitrile (3g)



Following **General Procedure B**, **3g** was obtained as gray solid in 89% yield (31 mg) from 4-(2-hydroxyethyl)-3-nitrobenzonitrile (**1g**, 38 mg, 0.2 mmol) using 20:1 DCM/MeOH as eluent.

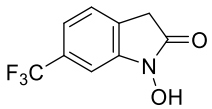
NMR Data of 3g:

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.94 (br, s, 1H, N–OH), 7.49 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.29 – 7.26 (m, 1H), 3.69 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 169.10, 144.42, 127.39, 126.68, 125.41, 118.86, 110.23, 108.89, 33.70.

HRMS (ESI$^+$) of 3g: *m/z* calcd for $C_9H_6N_2O_2$ [M-H]$^-$: 173.03455, Found: 173.03452.

1-Hydroxy-6-(trifluoromethyl)indolin-2-one (3h)



Following **General Procedure B**, **3h** was obtained as yellow solid in 84% yield (36 mg) from 2-(2-nitro-4-(trifluoromethyl)phenyl)ethan-1-ol (**1h**, 47 mg, 0.2 mmol) using 20:1 DCM/MeOH as eluent.

NMR Data of 3h:

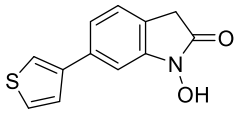
^{1}H NMR (400 MHz, DMSO-d_6): δ 11.38 (br, s, 1H, N–OH), 7.40 (d, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.04 (s, 1H), 3.59 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 169.18, 144.92, 128.46 (q, *J* = 31.7 Hz), 126.25 (q, *J* = 1.4 Hz), 124.90, 124.23 (q, *J* = 273.1 Hz), 118.52 (q, *J* = 4.1 Hz), 102.59 (q, *J* = 4.0 Hz), 33.51.

^{19}F NMR (376 MHz, DMSO-d_6) δ -60.96.

HRMS (ESI$^+$) of 3h: *m/z* calcd for $C_9H_6F_3NO_2$ [M-H]$^-$: 216.02669, Found: 216.02695.

1-Hydroxy-6-(thiophen-3-yl)indolin-2-one (3i)



Following **General Procedure B**, **3i** was obtained as gray solid in 85% yield (39 mg) from 2-(2-nitro-4-(thiophen-3-yl)phenyl)ethan-1-ol (**1j**, 33 mg, 0.2 mmol) using 20:1 DCM/MeOH as eluent.

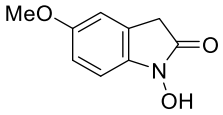
NMR Data of 3i:

^{1}H NMR (400 MHz, DMSO-d_6): 10.75 (br, s, 1H, N–OH), 7.90 (dd, *J* = 2.6, 1.0 Hz, 1H), 7.63 (dd, *J* = 5.0, 2.6 Hz, 1H), 7.56 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.36 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.26 (d, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 1.4 Hz, 1H), 3.57 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 169.52, 144.30, 141.27, 134.83, 127.08, 126.16, 124.79, 121.10, 120.03, 119.79, 104.28, 33.27.

HRMS (ESI$^+$) of 3i: *m/z* calcd for $C_{12}H_9NO_2S$ [M-H]$^-$: 230.02703, Found: 230.02731.

1-Hydroxy-5-methoxyindolin-2-one (3j)



Following **General Procedure B**, **3j** was obtained as faint yellow solid (0.2 mmol scale: 82% yield, 29 mg; 5.1 mmol scale: 70% yield, 640 mg) from (2-(5-methoxy-2-nitrophenyl)ethan-1-ol (**1k**, 39 mg, 0.2 mmol) using 50:1 DCM/MeOH as eluent. The NMR data were in consistent with the reported data[39].

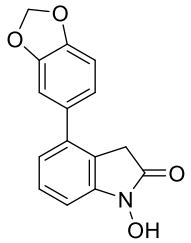
NMR Data of 3j:

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.56 (br, s, 1H, N–OH), 6.90 (d, *J* = 1.1 Hz, 1H), 6.86 – 6.79 (m, 2H), 3.71 (s, 3H), 3.51 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 168.92, 155.22, 137.20, 122.58, 112.06, 111.81, 107.25, 55.49, 33.69.

HRMS (ESI$^+$) of 3j: *m/z* calcd for $C_9H_9NO_3$ [M-H]$^-$: 178.04987, Found: 178.04994.

4-(Benzo[d][1,3]dioxol-5-yl)-1-hydroxyindolin-2-one (3k)



Following **General Procedure B**, **3k** was obtained as faint yellow solid in 79% yield (42 mg) from 2-(2-(benzo[d][1,3]dioxol-5-yl)-6-nitrophenyl)ethan-1-ol (**1n**, 57 mg, 0.2 mmol) using 20:1 DCM/MeOH as eluent.

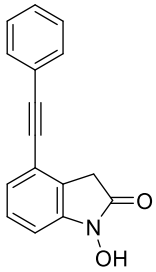
NMR Data of 3k:

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.74 (br, s, 1H, N–OH), 7.34 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.18 (d, *J* = 1.7 Hz, 1H), 7.04 (d, *J* = 7.9, 2.0 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 7.9 Hz, 1H), 6.07 (s, 2H), 3.67 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 169.18, 147.61, 146.83, 144.12, 137.00, 132.73, 128.23, 122.18, 121.78, 118.26, 108.48, 105.69, 101.14, 79.17, 33.55.

HRMS (ESI$^+$) of 3k: *m/z* calcd for $C_{15}H_{11}NO_4$ [M-H]$^-$: 268.06043, Found: 268.06128.

1-Hydroxy-4-(phenylethynyl)indolin-2-one (3l)



Following **General Procedure B**, **3l** was obtained as colorless solid in 72% yield (36 mg) from 2-(2-nitro-6-(phenylethynyl)phenyl)ethan-1-ol (**1p**, 53 mg, 0.2 mmol) using 50:1 DCM/MeOH as eluent.

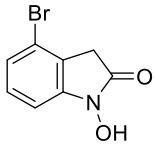
NMR Data of 3l:

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.51 (br, s, 1H, N–OH), 7.55 – 7.49 (m, 3H), 7.39 – 7.32 (m, 3H), 7.27 – 7.22 (m, 1H), 7.15 (d, *J* = 7.7 Hz, 1H), 3.63 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.37, 142.75, 131.84, 128.95, 128.60, 126.40, 123.11, 122.72, 119.90, 108.62, 94.10, 85.58, 34.08.

HRMS (ESI$^+$) of 3l: *m/z* calcd for $C_{16}H_{11}NO_2$ [M-H]$^-$: 248.07061, Found: 248.07138.

4-Bromo-1-hydroxyindolin-2-one (3m)



Following **General Procedure B**, **3m** was obtained as faint brown solid in 92% yield (42 mg) from 2-(2-bromo-6-nitrophenyl)ethan-1-ol (**1q**, 49 mg, 0.2 mmol) using 30:1 DCM/MeOH as eluent.

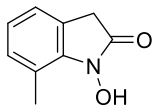
NMR Data of 3m:

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.87 (br, s, 1H, N–OH), 7.25 (dd, *J* = 7.9, 8.2 Hz, 1H), 7.19 (dd, *J* = 8.2, 1.0 Hz, 1H), 6.93 (dd, *J* = 7.9, 1.0 Hz, 1H), 3.52 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 168.43, 144.98, 129.88, 124.49, 121.76, 118.07, 106.07, 34.55.

HRMS (ESI$^+$) of 3m: *m/z* calcd for $C_8H_6BrNO_2$ [M-H]$^-$: 225.94982, Found: 255.95032.

1-Hydroxy-7-methylindolin-2-one (3n)



Following **General Procedure B**, **3n** was obtained as faint yellow solid in 88% yield (28 mg) from 2-(3-methyl-2-nitrophenyl)ethan-1-ol (**1t**, 36 mg, 0.2 mmol) using 30:1 DCM/MeOH as eluent. The NMR data were in consistent with the reported data[40].

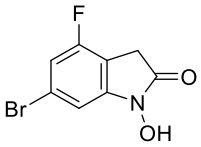
NMR Data of 3n:

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.54 (br, s, 1H, N–OH), 7.04 (d, *J* = 7.2 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.89 (dd, *J* = 7.2, 7.5 Hz, 1H), 3.49 (s, 2H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 170.28, 140.70, 130.57, 122.15, 121.91, 121.48, 118.43, 32.98, 16.90.

HRMS (ESI$^+$) of 3n: *m/z* calcd for $C_9H_9NO_2$ [M-H]$^-$: 162.05496, Found: 162.05486.

6-Bromo-4-fluoro-1-hydroxyindolin-2-one (3o)



Following **General Procedure B**, **3o** was obtained as faint gray solid in 90% yield (44 mg) from 2-(4-bromo-2-fluoro-6-nitrophenyl)ethan-1-ol (**1s**, 53 mg, 0.2 mmol) using 20:1 DCM/MeOH as eluent.

NMR Data of 3o:

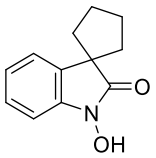
^{1}H NMR (400 MHz, DMSO-d_6): δ 10.99 (br, s, 1H, N–OH), 7.17 (dd, J_{F-H} = 8.5 Hz, J_{H-H} = 1.6 Hz, 1H), 6.93 (d, J_{H-H} = 1.6 Hz, 1H), 3.62 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 168.72, 157.14 (d, *J* = 258.5 Hz), 146.74 (d, *J* = 10.5 Hz), 120.95 (d, *J* = 10.1 Hz), 112.37 (d, *J* = 24.4 Hz), 106.49 (d, *J* = 2.0 Hz), 103.41 (d, *J* = 2.4 Hz), 30.11.

^{19}F NMR (376 MHz, DMSO-d_6) δ -116.64.

HRMS (ESI$^+$) of 3o: *m/z* calcd for $C_8H_5NO_2BrF$ [M-H]$^-$: 243.94040, Found: 243.94069.

1'-Hydroxyspiro[cyclopentane-1,3'-indolin]-2'-one (3p)



Following **General Procedure B**, **3p** was obtained as yellow solid in 86% yield (35 mg) from (1-(2-nitrophenyl)cyclopentyl)methanol (**1ac**, 44 mg, 0.2 mmol) using 50:1 DCM/MeOH as eluent. The NMR data were in consistent with the reported data[41].

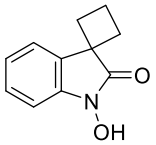
NMR Data of 3p:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 2H), 7.08 (ddd, *J* = 7.5, 7.5, 1.0 Hz, 1H), 2.12 – 1.75 (m, 8H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.98, 140.70, 133.53, 127.83, 123.61, 122.07, 108.45, 37.78, 26.76, 24.96.

HRMS (ESI$^+$) of 3p: *m/z* calcd for $C_{12}H_{13}NO_2$ [M-H]$^-$: 202.08658, Found: 202.08626.

1'-Hydroxyspiro[cyclobutane-1,3'-indolin]-2'-one (3q)



Following **General Procedure B**, **3q** was obtained as yellow solid in 82% yield (31 mg) from (1-(2-nitrophenyl)cyclobutyl)methanol (**1ad**, 41 mg, 0.2 mmol) using 50:1 DCM/MeOH as eluent.

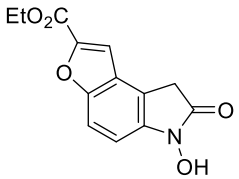
NMR Data of 3q:

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.65 (br, s, 1H, N–OH), 7.48 (d, *J* = 7.3 Hz, 1H), 7.32 (ddd, *J* = 7.7, 7.7, 1.1 Hz, 1H), 7.19 – 7.11 (m, 2H), 2.57 (m, 2H), 2.39 – 2.16 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.16, 140.78, 130.99, 128.28, 123.68, 122.09, 108.43, 47.24, 30.72, 16.93.

HRMS (ESI$^+$) of 3q: *m/z* calcd for $C_{11}H_{11}NO_2$ [M-H]$^-$: 188.07065, Found: 188.07061.

Ethyl 6-hydroxy-7-oxo-7,8-dihydro-6H-furo[3,2-e]indole-2-carboxylate (3r)



Following **General Procedure B**, **3r** was obtained as taupe solid in 90% yield (47 mg) from ethyl 4-(2-hydroxyethyl)-5-nitrobenzofuran-2-carboxylate (**1aq**, 56 mg, 0.2 mmol) using 20:1 DCM/MeOH as eluent.

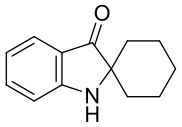
NMR Data of 3r:

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.75 (br, s, 1H, N–OH), 7.72 – 7.63 (m, 2H), 7.13 (dd, *J* = 8.5, 2.0 Hz, 1H), 4.36 (q, *J* = 7.0 Hz, 2H), 3.76 (s, 2H), 1.33 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 169.42, 158.56, 152.02, 146.48, 140.14, 123.66, 114.01, 111.88, 110.89, 107.85, 61.37, 33.09, 14.12.

HRMS (ESI$^+$) of 3r: *m/z* calcd for $C_{13}H_{11}NO_5$ [M-H]$^-$: 260.05535, Found: 260.05594.

Spiro[cyclohexane-1,2'-indolin]-3'-one (3s)



Following **General Procedure B**, **3s** was obtained as yellow oil in 92% yield (37 mg) from 2-cyclohexyl-2-(2-nitrophenyl)ethan-1-ol (**1x**, 50 mg, 0.2 mmol) using 3:1 PE/DCM as eluent. The NMR data were in consistent with the reported data[41].

NMR Data of 3s:

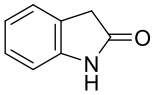
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.43 (ddd, *J* = 8.0, 7.1, 1.2 Hz, 1H), 6.87 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.80 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 5.04 (br, s, 1H, NH), 1.94 – 1.68 (m, 5H), 1.53 – 1.36 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 204.94, 160.03, 137.09, 125.12, 120.62, 118.91, 112.72, 67.08, 32.98, 24.93, 22.72.

HRMS (ESI$^+$) of 3s: *m/z* calcd for $C_{13}H_{15}NO$ $[M+H]^+$: 202.12264, Found: 202.12175.

4.2.3.Characterization Data for the Derivatives of indolin-2-one

Indolin-2-one (4a)



Following **General Procedure C**, **4a** was obtained as faint yellow solid in 87% yield (23 mg) from 2-(2-nitrophenyl)ethan-1-ol (**1a**, 33 mg, 0.2 mmol) using DCM as eluent. The NMR data were in consistent with the reported data[42].

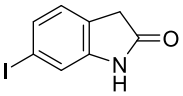
NMR Data of 4a:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (br, s, 1H, NH), 7.22 (dd, *J* = 7.7, 7.7 Hz, 2H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 7.7 Hz, 1H), 3.54 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.25, 142.41, 128.06, 125.40, 124.84, 122.51, 109.69, 36.24.

HRMS (ESI$^+$) of 4a: *m/z* calcd for C_8H_7NO $[M+H]^+$: 134.06059, Found: 134.06052.

6-Iodoindolin-2-one (4b)



Following **General Procedure C**, **4b** was obtained as faint yellow solid in 80% yield (41 mg) from 2-(4-iodo-2-nitrophenyl)ethan-1-ol (**1b**, 59 mg, 0.2 mmol) using 100:1 DCM/MeOH as eluent. The NMR data were in consistent with the reported data[38].

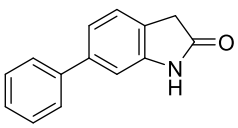
NMR Data of 4b:

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.43 (br, s, 1H, NH), 7.28 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.10 (d, *J* = 1.4 Hz, 1H), 7.01 (d, *J* = 7.7 Hz, 1H), 3.42 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 175.97, 145.34, 129.64, 126.42, 125.67, 117.38, 92.24, 35.44.

HRMS (ESI$^+$) of 4b: *m/z* calcd for C_8H_6IO $[M+H]^+$: 259.95621, Found: 259.95668.

6-Phenylindolin-2-one (4c)



Following **General Procedure C**, **4c** was obtained as colorless solid in 95% yield (39 mg) from 2-(4-iodo-2-nitrophenyl)ethan-1-ol (**1c**, 49 mg, 0.2 mmol) using DCM as eluent. The NMR data were in consistent with the reported data[43].

NMR Data of 4c:

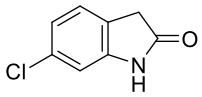
^{1}H NMR (400 MHz, DMSO-d_6): δ 10.46 (br, s, 1H, NH), 7.61 – 7.58 (m, 2H), 7.50 – 7.40 (m, 2H), 7.38 – 7.33 (m, 1H), 7.28 (d, *J* = 7.7 Hz, 1H), 7.20 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.03 (d, *J* = 1.7 Hz, 1H), 3.51 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 176.50, 144.44, 140.40, 139.84, 128.93, 127.39, 126.61, 125.12, 124.78, 119.80,

107.31, 35.58.

HRMS (ESI$^+$) of 4c: *m/z* calcd for $C_{14}H_{11}NO$ $[M+H]^+$: 210.09134, Found: 210.09079.

6-Chloroindolin-2-one (4d)



Following **General Procedure C**, **4d** was obtained as brown solid in 90% yield (30 mg) from2-(4-chloro-2-nitrophenyl)ethan-1-ol (**1e**, 20 mg, 0.2 mmol) using DCM as eluent. The NMR data were in consistent with the reported data[44].

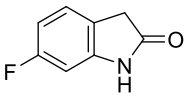
NMR Data of 4d:

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.49 (br, s, 1H, NH), 7.20 (d, J = 7.4 Hz, 1H), 6.96 (d, J = 7.7 Hz, 1H), 6.81 (s, 1H), 3.47 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 176.32, 145.14, 131.67, 125.73, 124.76, 120.71, 109.08, 35.30.

HRMS (ESI$^+$) of 4d: *m/z* calcd for C_8H_6NOCl $[M+H]^+$: 168.02107, Found: 168.02107.

6-Fluoroindolin-2-one (4e)



Following **General Procedure C**, **4e** was obtained as colorless solid in 92% yield (28 mg) from 2-(4-fluoro-2-nitrophenyl)ethan-1-ol (**1f**, 37 mg, 0.2 mmol) using DCM as eluent. The NMR data were in consistent with the reported data[45].

NMR Data of 4e:

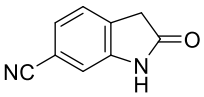
^{1}H NMR (400 MHz, DMSO-d_6): δ 10.49 (br, s, 1H, NH), 7.19 (dd, J_{H-H} = 8.0 Hz, J_{F-H} = 6.1 Hz, 1H), 6.71 (ddd, J_{F-H} = 10.4 Hz, J_{H-H} 8.0, 2.5 Hz, 1H), 6.62 (dd, J_{F-H} = 9.3 Hz, J_{H-H} = 2.5 Hz, 1H), 3.44 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 176.78, 161.84 (d, J = 240.4 Hz), 145.11 (d, J = 12.6 Hz), 125.49 (d, J = 9.9 Hz), 121.52 (d, J = 2.3 Hz), 107.07 (d, J = 21.7 Hz), 97.27 (d, J = 27.1 Hz), 35.15.

^{19}F NMR (376 MHz, DMSO-d_6) δ -114.16.

HRMS (ESI$^+$) of 4e: *m/z* calcd for C_8H_6NOF $[M-H]^-$: 150.03407, Found: 150.03473.

2-Oxoindoline-6-carbonitrile (4f)



Following **General Procedure C**, **4f** was obtained as yellow solid in 86% yield (27 mg) from 4-(2-hydroxyethyl)-3-nitrobenzonitrile (**1g**, 38 mg, 0.2 mmol) using DCM as eluent. The NMR data were in consistent with the reported data[46].

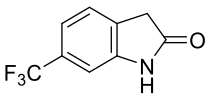
NMR Data of 4f:

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.66 (br, s, 1H, NH), 7.41 – 7.36 (m, 2H), 7.12 (d, J = 1.0 Hz, 1H), 3.59 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 175.79, 144.52, 132.05, 125.76, 125.34, 119.00, 111.25, 109.88, 35.88.

HRMS (ESI$^+$) of 4f: *m/z* calcd for $C_9H_6N_2O$ $[M-H]^-$: 157.03964, Found: 157.03934.

6-(Trifluoromethyl)indolin-2-one (4g)



Following **General Procedure C**, **4g** was obtained as yellow solid in 82% yield (33 mg) from 2-(2-nitro-4-(trifluoromethyl)phenyl)ethan-1-ol (**1h**, 47 mg, 0.2 mmol) using DCM as eluent. The NMR data were in consistent with the reported data[47].

NMR Data of 4g:

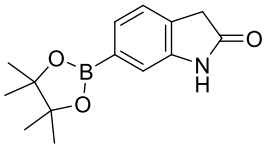
^{1}H NMR (400 MHz, DMSO-d_6): δ 10.61 (br, s, 1H, NH), 7.41 (d, J = 7.7 Hz, 1H), 7.28 (dd, J = 7.8, 1.6 Hz, 1H), 7.02 (d, J = 1.7 Hz, 1H), 3.58 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 176.05, 144.50, 130.79, 128.16 (q, *J* = 32.7 Hz), 125.03, 124.25 (q, *J* = 272.0 Hz), 117.96 (q, *J* = 4.0 Hz), 104.99 (q, *J* = 3.9 Hz), 35.73.

^{19}F NMR (376 MHz, DMSO-d_6) δ -60.89.

HRMS (ESI$^+$) of 4g: *m/z* calcd for $C_9H_6NOF_3$ $[M+H]^+$: 202.04743, Found: 202.04698.

6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)indolin-2-one (4h)



Following **General Procedure C**, **4h** was obtained as yellow solid in 82% yield (42 mg) from (2-(2-nitro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol (**1i**, 59 mg, 0.2 mmol) using DCM as eluent. The NMR data were in consistent with the reported data[48].

NMR Data of 4h:

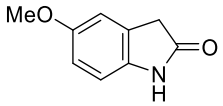
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.47 (br, s, 1H, NH), 7.59 (s, 1H), 7.55 (d, *J* = 7.3 Hz, 1H), 7.21 (d, *J* = 7.3 Hz, 1H), 3.51 (s, 2H), 1.36 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.20, 142.47, 130.29, 124.21, 123.82, 114.15, 108.71, 84.20, 34.40, 25.01.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.2.

HRMS (ESI$^+$) of 4h: *m/z* calcd for $C_{14}H_{18}NBO_3$ $[M+H]^+$: 260.14441, Found: 260.14525.

5-Methoxyindolin-2-one (4i)



Following **General Procedure C**, **4i** was obtained as brown solid in 80% yield (26 mg) from (2-(5-methoxy-2-nitrophenyl)ethan-1-ol (**1k**, 39 mg, 0.2 mmol) using DCM as eluent. The NMR data were in consistent with the reported data[49].

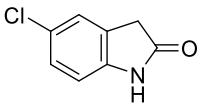
NMR Data of 4i:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (br, s, 1H, NH), 6.85 (d, *J* = 2.3 Hz, 1H), 6.79 (d, *J* = 8.5 Hz, 1H), 6.75 (dd, *J* = 8.5, 2.4 Hz, 1H), 3.78 (s, 3H), 3.52 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.69, 155.83, 136.09, 126.78, 112.64, 111.96, 110.10, 55.94, 36.83.

HRMS (ESI$^+$) of 4i: *m/z* calcd for $C_9H_9NO_2$ $[M+H]^+$: 164.07061, Found: 164.07028.

5-Chloroindolin-2-one (4j)



Following **General Procedure C**, **4j** was obtained as yellow solid in 95% yield (32 mg) from 2-(3-chloro-2-nitrophenyl)ethan-1-ol (**1l**, 40 mg, 0.2 mmol) using DCM as eluent. The NMR data were in consistent with the reported data[50].

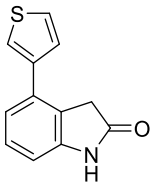
NMR Data of 4j:

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.46 (br, s, 1H, NH), 7.25 (d, *J* = 2.1 Hz, 1H), 7.20 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.80 (d, *J* = 8.3 Hz, 1H), 3.49 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 175.99, 142.59, 128.06, 127.20, 125.09, 124.50, 110.30, 35.83.

HRMS (ESI$^+$) of 4j: *m/z* calcd for C_8H_6NOCl $[M+H]^+$: 168.02087, Found: 168.02107.

4-(Thiophen-3-yl)indolin-2-one (4k)



Following **General Procedure C**, **4k** was obtained as yellow solid in 85% yield (36 mg) from 2-(2-nitro-6-(thiophen-3-yl)phenyl)ethan-1-ol (**1o**, 50 mg, 0.2 mmol) using DCM as eluent.

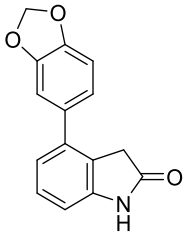
NMR Data of 4k:

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.46 (br, s, 1H, NH), 7.80 (dd, *J* = 2.9, 1.4 Hz, 1H), 7.64 (dd, *J* = 5.0, 2.9 Hz, 1H), 7.50 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.23 (dd, *J* = 7.8, 7.7 Hz, 1H), 7.19 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.78 (dd, *J* = 7.6, 1.2 Hz, 1H), 3.68 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 176.06, 144.31, 139.87, 131.86, 127.98, 127.32, 126.43, 122.96, 122.51, 120.63, 108.03, 36.46.

HRMS (ESI$^+$) of 4k: *m/z* calcd for $C_{12}H_9NOS$ $[M+H]^+$: 216.04776, Found: 216.04195.

4-(Benzo[d][1,3]dioxol-5-yl)indolin-2-one (4l)



Following **General Procedure C**, **4l** was obtained as yellow solid in 77% yield (39 mg) from 2-(2-(benzo[d][1,3]dioxol-5-yl)-6-nitrophenyl)ethan-1-ol (**1n**, 57 mg, 0.2 mmol) using DCM as eluent.

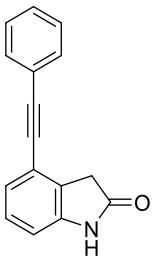
NMR Data of 4l:

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.44 (br, s, 1H, NH), 7.23 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.15 (d, *J* = 1.8 Hz, 1H), 7.02 (dd, *J* = 8.0, 1.8 Hz, 1H), 6.99 – 6.94 (m, 2H), 6.79 (d, *J* = 7.7 Hz, 1H), 6.06 (s, 2H), 3.58 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 176.11, 147.55, 146.69, 144.15, 137.19, 133.44, 127.98, 123.04, 121.60, 121.29, 108.40, 108.35, 107.98, 101.10, 35.88.

HRMS (ESI$^+$) of 4l: *m/z* calcd for $C_{15}H_{11}NO_3$ $[M+H]^+$: 254.08117, Found: 254.07477.

4-(Phenylethynyl)indolin-2-one (4m)



Following **General Procedure C**, **4m** was obtained as colorless solid in 70% yield (32 mg) from 2-(2-nitro-6-(phenylethynyl)phenyl)ethan-1-ol (**1p**, 53 mg, 0.2 mmol) using DCM as eluent.

NMR Data of 4m:

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.51 (br, s, 1H, NH), 7.60 – 7.55 (m, 2H), 7.45 – 7.42 (m, 3H), 7.22 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.09 (d, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 3.59 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 175.67, 143.80, 131.48, 128.96, 128.75, 128.25, 127.95, 123.62, 122.11, 118.43, 109.55, 92.57, 86.80, 35.62.

HRMS (ESI$^+$) of 4m: *m/z* calcd for $C_{16}H_{11}NO$ $[M+H]^+$: 234.09077, Found: 234.09134.

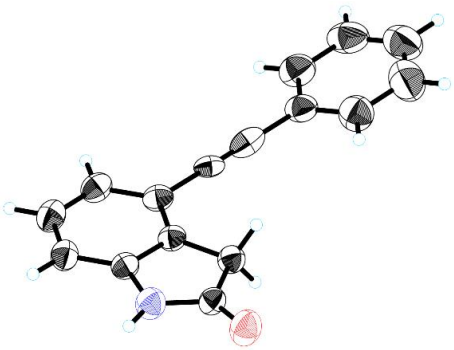
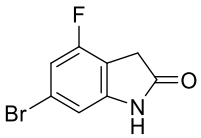


Figure S6. Crystal structure of **4m** (ellipsoids at 50% probability).

6-Bromo-4-fluoroindolin-2-one (4n)



Following **General Procedure C**, **4n** was obtained as faint gray solid in 88% yield (40 mg) from 2-(4-bromo-2-fluoro-6-nitrophenyl)ethan-1-ol (**1s**, 53 mg, 0.2 mmol) using DCM as eluent.

NMR Data of 4n:

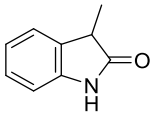
^{1}H NMR (400 MHz, DMSO-d_6): δ 10.71 (br, s, 1H, NH), 7.07 (d, J_{F-H} = 8.5 Hz, 1H), 6.82 (d, J_{F-H} = 1.2 Hz, 1H), 3.51 (s, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 175.38, 157.49 (d, J = 248.1 Hz), 147.14 (d, J = 12.8 Hz), 120.44 (d, J = 10.7 Hz), 111.46 (d, J = 24.6 Hz), 111.08, 108.76 (d, J = 2.6 Hz), 38.89.

^{19}F NMR (376 MHz, DMSO-d_6) δ -115.26.

HRMS (ESI$^+$) of 4n: *m/z* calcd for $C_8H_5NO_2BrF$ $[M-H]^-$: 227.94548, Found: 227.94591.

3-Methylindolin-2-one (4o)



Following **General Procedure C**, **4o** was obtained as yellow solid in 84% yield (25 mg) from 2-(2-nitrophenyl)propan-1-ol (**1w**, 36 mg, 0.2 mmol) using 100:1 DCM/MeOH as eluent. The NMR data were in consistent with the reported data[51].

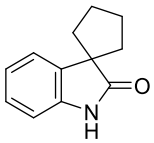
NMR Data of 4o:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (br, s, 1H, NH), 7.21 (m, 2H), 7.06 – 7.01 (m, 1H), 6.90 (m, 1H), 3.47 (q, J = 7.6 Hz, 1H), 1.50 (d, J = 7.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 181.27, 141.24, 131.38, 128.01, 123.98, 122.52, 109.77, 41.14, 15.38.

HRMS (ESI$^+$) of 4o: *m/z* calcd for C_9H_9NO $[M+H]^+$: 148.07556, Found: 148.07569.

Spiro[cyclopentane-1,3'-indolin]-2'-one (4p)



Following **General Procedure C**, **4p** was obtained as yellow solid in 85% yield (32 mg) from (1-(2-nitrophenyl)cyclopentyl)methanol (**1ac**, 44 mg, 0.2 mmol) using DCM as eluent. The NMR data were in consistent with the reported data[52].

NMR Data of 4p:

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.24 (br, s, 1H, NH), 7.28 – 7.05 (m, 2H), 6.99 – 6.85 (m, 1H), 6.85 – 6.72 (m, 1H), 2.03 – 1.62 (m, 8H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 182.68, 141.13, 136.70, 127.23, 122.47, 121.60, 108.99, 53.39, 37.74, 25.99.

HRMS (ESI$^+$) of 4p: *m/z* calcd for $C_{12}H_{13}NO$ [M-H]$^-$: 187.09971, Found: 187.09810.

The characterization data of **4q** was present at section **4.3.4**.

4.2.4.Crystallographic Data

Detailed crystallographic data are listed in the table below.

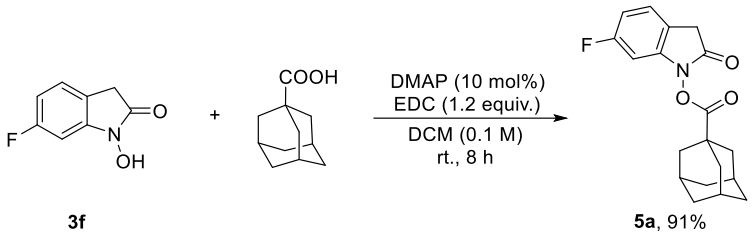
Table S4. Crystallographic data and structure refinement parameters.

	2y	**2z**	**3a**	**4m**[a]
Empirical formula	$C_{34}H_{25}N$	$C_{21}H_{19}NO_3$	$C_8H_7NO_2$	$C_{16}H_{11}NO$
CCDC Number	2163568	2163570	2163566	2163569
Molecular weight	447.55	333.37	149.15	233.26
Crystal size (mm^3)	0.2 × 0.15 × 0.1	0.2 × 0.1 × 0.05	0.22 × 0.2 × 0.1	0.2 × 0.1 × 0.05
Temperature (K)	296.15	296.15	193.00	193.00
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	GaKα (λ = 1.34139)	GaKα (λ = 1.34139)
Crystal system	monoclinic	monoclinic	orthorhombic	trigonal
Space group	$P2_1/n$	Cc	Fdd2	R-3
a (Å)	9.9280(19)	14.0103(13)	11.8514(10)	35.383(2)
b (Å)	9.4716(18)	35.603(3)	30.185(3)	35.383(2)
c (Å)	52.455(10)	11.3760(13)	7.5330(10)	5.2350(4)
α (°)	90	90	90	90
β (°)	90.791(6)	117.174(3)	90	90
γ (°)	90	90	90	120
V (Å^3)	4932.1(17)	5048.1(9)	2694.8(5)	5675.8(8)
Z	8	12	16	18
ρ_c (g cm^{-3})	1.205	1.316	1.470	1.228
μ (mm^{-1})	0.069	0.088	0.569	0.388
***F* (000)**	1888.0	2112.0	1248.0	2196.0
2θ range for data collection (°)	4.166 to 55.996	4.022 to 55.062	10.198 to 107.9	4.346 to 108.062
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -68 ≤ l ≤ 68	-18 ≤ h ≤ 18, -46 ≤ k ≤ 46, -12 ≤ l ≤ 14	-14 ≤ h ≤ 8, -34 ≤ k ≤ 36, -9 ≤ l ≤ 8	-42 ≤ h ≤ 41, -42 ≤ k ≤ 42, -6 ≤ l ≤ 6
Reflections collected	46913	23828	2527	21591
Indep. reflns	11557 [R_{int} = 0.0914, R_{sigma} = 0.1079]	8815 [R_{int} = 0.0653, R_{sigma} = 0.0856]	1151 [R_{int} = 0.0530, R_{sigma} = 0.0595]	2310 [R_{int} = 0.0742, R_{sigma} = 0.0394]
Data/restr./paras	11557/27/632	8815/2/686	1151/1/101	2310/0/152
Goodness-of-fit on F^2	0.983	1.044	0.929	1.097
R_1, wR_2 (all data)	0.1877, 0.2298	0.1015, 0.2247	0.0477, 0.1027	0.0730, 0.1862
R_1, wR_2 [$I >= 2\sigma(I)$]	0.0702, 0.1797	0.0729, 0.2031	0.0384, 0.0902	0.0644, 0.1805
Largest diff. peak/hole (e. Å^{-3})	0.50/-0.34	0.60/-0.48	0.14/-0.14	0.42/-0.22

[a] For this case, the disordered molecules of solvent H_2O across the symmetrical elements were squeezed using PLATON.

4.3. Synthetic Applications

4.3.1.Post-functionalization Reactions



6-Fluoro-2-oxoindolin-1-yl (*3r,5r,7r*)-adamantane-1-carboxylate (5a): 5a was synthesized following a modified procedure from a reported literature[53]. To a stirred solution of 6-fluoro-1-hydroxyindolin-2-one (**3f**, 1.0 equiv., 167 mg, 1.0 mmol), 1-adamantanecarboxylic acid (1.2 equiv., 216 mg, 1.2 mmol) and 4-dimethylaminopyridine (i.e. DMAP, 0.1 equiv., 12 mg, 0.1 mmol) in DCM (0.2 M), a DCM solution (0.5 M) of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (i.e. EDC, 1.2 equiv., 230 mg, 1.2 mmol) was added dropwise. The mixture was stirred at room temperature for 8 h. After the reaction was completed, the mixture was filtered through a thin pad of celite and rinsed with additional DCM (20 mL × 3). The filtrate was concentrated in *vacuo*, and the residue was purified by column chromatography to afford **5a** as pink solid in 91% yield (283 mg).

NMR Data of 5a:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (dd, $J_{H\text{-}H}$ = 8.3 Hz, $J_{F\text{-}H}$ = 5.0 Hz, 1H), 6.75 (ddd, $J_{F\text{-}H}$ = 10.1 Hz, $J_{H\text{-}H}$ = 8.3, 2.4 Hz, 1H), 6.44 (dd, $J_{F\text{-}H}$ = 8.1 Hz, $J_{H\text{-}H}$ = 2.4 Hz, 1H), 3.57 (s, 2H), 2.17 – 2.06 (m, 9H), 1.79 (d, *J* = 3.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.18, 169.66, 162.97 (d, *J* = 245.7 Hz), 143.18 (d, *J* = 12.5 Hz), 126.16 (d, *J* = 9.4 Hz), 115.86 (d, *J* = 3.0 Hz), 109.59 (d, *J* = 22.3 Hz), 96.19 (d, *J* = 30.1 Hz), 38.69, 36.32, 33.47, 27.78.

HRMS (ESI$^+$) of 5a: *m/z* calcd for $C_{19}H_{21}NO_3$ $[M+H]^+$: 312.15942, Found: 312.15875.

4.3.2. Modification of Drug Flutamide

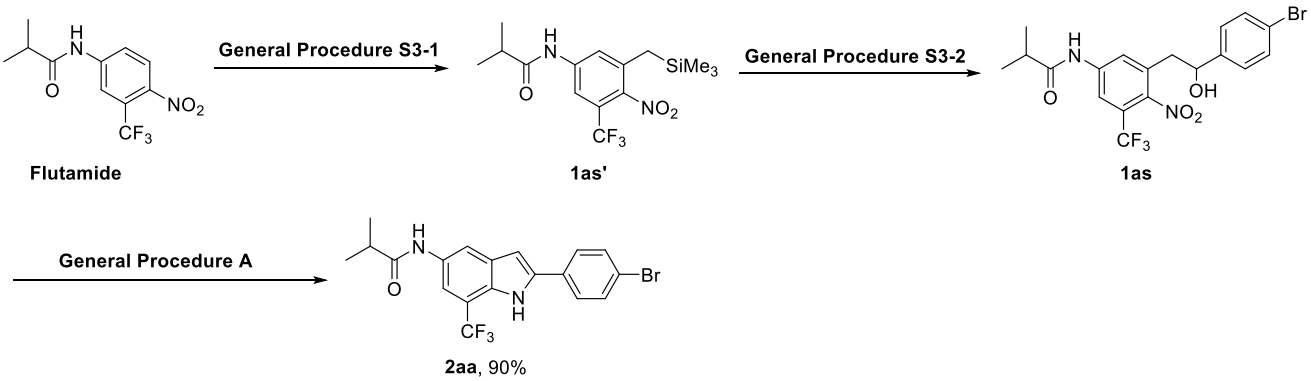


Figure S7. Modification route of Flutamide (a nonsteroidal anti-androgen drug for the treatment of prostate cancer).

***N*-(4-nitro-3-(trifluoromethyl)-5-((trimethylsilyl)methyl)phenyl)isobutyramide (1as'):** Following **General Procedure S3-1**, **1as'** was obtained as yellow solid in 90% yield (326 mg) from flutamide (1.0 equiv., 276 mg, 1.0 mmol) using DCM as eluent.

NMR Data of 1as':

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 2.2 Hz, 1H), 7.60 (br, s, 1H, NH), 7.58 (d, *J* = 2.1 Hz, 1H), 2.54 (hept, *J* = 6.8 Hz, 1H), 2.10 (s, 2H), 1.26 (d, *J* = 6.8 Hz, 6H), 0.05 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.05, 142.49, 139.43, 137.14, 123.81 (q, *J* = 33.9 Hz), 123.47, 122.12 (q, *J* = 274.3 Hz), 114.11 (q, *J* = 5.2 Hz), 36.91, 22.94, 19.54, -1.32.

***N*-(3-(2-(4-bromophenyl)-2-hydroxyethyl)-4-nitro-5-(trifluoromethyl)phenyl)isobutyramide (1as):** Following **General Procedure S3-2**, **1as** was obtained as yellow solid in 70% yield (199 mg) from **1as'** (1.0 equiv., 217 mg, 0.60 mmol) and 4-bromobenzaldehyde (1.2 equiv., 131 mg, 0.71 mmol) using 50:1 DCM/MeOH as eluent.

NMR Data of 1as:

^{1}H NMR (400 MHz, $CDCl_3$ & DMSO-d_6): δ 8.06 (d, *J* = 2.0 Hz, 1H), 7.69 (d, *J* = 2.0 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.22 – 7.17 (m, 2H), 4.82 (t, *J* = 6.5 Hz, 1H), 2.83 (d, *J* = 6.5 Hz, 2H), 2.54 (hept, *J* = 6.9 Hz, 1H), 2.48 (br, s, 2H, NH & OH), 1.20 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$ & DMSO-d_6): δ 177.01, 143.51, 142.79, 140.41, 133.00, 131.72, 127.36, 125.51, 123.47 (q, *J* = 33.6 Hz), 122.08 (q, *J* = 274.5 Hz), 121.64, 116.42 (q, *J* = 4.9 Hz), 72.90, 41.48, 36.34, 19.37.

***N*-(2-(4-bromophenyl)-7-(trifluoromethyl)-1*H*-indol-5-yl)isobutyramide (2aa):** Following a modified **General Procedure A**, **2aa** was obtained as faint yellow solid in 90% yield (78 mg) from **1as** (1.0 equiv., 95 mg, 0.2 mmol) using 2:1 PE/DCM as eluent. 5,5,5',5'-Tetramethyl-2,2'-bi(1,3,2-dioxaborinane) (i.e. B_2nep_2, 99 mg, 0.44 mmol) was used in this procedure and no MeOH was added.

NMR Data of 2aa:

^{1}H NMR (400 MHz, DMSO-d_6): δ 11.37 (br, s, 1H, NH), 9.91 (br, s, 1H, NH), 8.12 (d, *J* = 2.0 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 2H), 7.75 (d, *J* = 2.0 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.07 (d, *J* = 2.0 Hz, 1H), 2.60 (hept, *J* = 6.8 Hz, 1H), 1.13 (d, *J* = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 175.05, 139.61, 131.68, 131.52, 130.60, 128.61, 128.27, 126.37, 124.18 (q, *J* = 272.4 Hz), 121.16, 114.41, 112.40 (q, *J* = 5.5 Hz), 112.03 (q, *J* = 32.0 Hz), 100.84, 34.95, 19.53.

^{19}F NMR (376 MHz, DMSO-d_6): δ -59.79.

HRMS (ESI$^+$) of 2aa: *m/z* calcd for $C_{19}H_{16}F_3BrN_2O$ $[M+H]^+$: 425.04709, Found: 425.04620.

4.3.3.Synthesis of the Precursor of Indomethacin

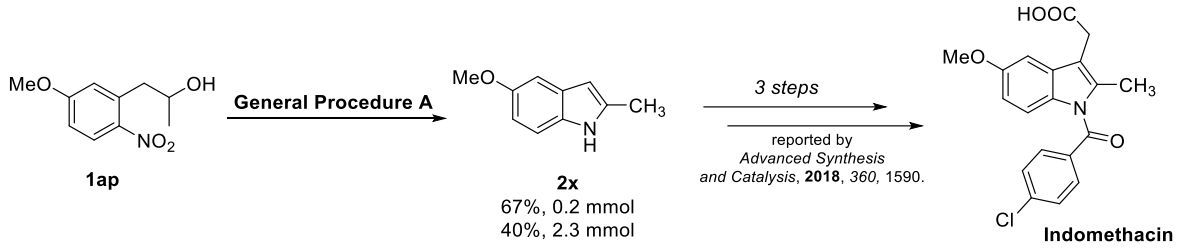


Figure S8. The synthetic route of Indomethacin (a nonsteroidal drug with anti-inflammatory, analgesic, and antipyretic properties)[29].

5-Methoxy-2-methyl-1*H*-indole (2x): Following **General Procedure A**, 5-methoxy-2-methyl-1H-indole (**2x**) was obtained as faint yellow oil (0.2 mmol scale: 67% yield, 22 mg; 2.3 mmol scale: 40% yield, 148 mg) from 1-(5-methoxy-2-nitrophenyl)propan-2-ol (**1ap**) using 3:1 PE/DCM as eluent. The NMR data were in consistent with the reported data[29].

NMR Data of 2x:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (br, s, 1H, NH), 7.14 (d, *J* = 8.7 Hz, 1H), 7.07 (d, *J* = 2.4 Hz, 1H), 6.84 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.20 (s, 1H), 3.89 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.08, 136.11, 131.26, 129.56, 111.00, 110.67, 102.00, 100.26, 55.96, 13.73.

HRMS (ESI$^+$) of 2x: *m/z* calcd for $C_{10}H_{11}NO$ $[M+H]^+$: 162.09134, Found: 162.09068.

4.3.4.Synthesis of the Precursor of Sunitnib

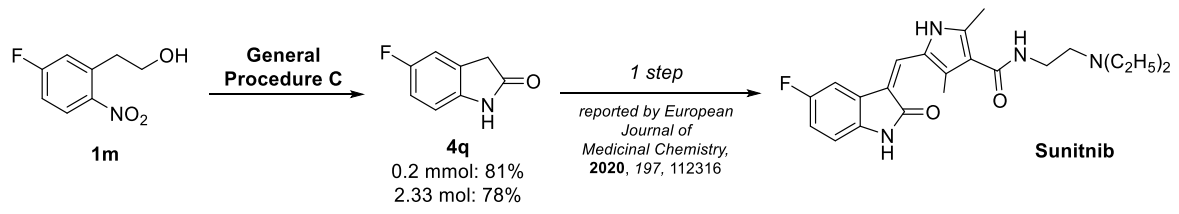


Figure S9. The synthetic route of Sunitnib (a novel multitargeted oral drug for the treatment of cancer)[54].

5-Fluoroindolin-2-one (4q): Following **General Procedure C**, 5-fluoroindolin-2-one (**4q**) was obtained as reddish brown oil (0.2 mmol scale: 81% yield, 24 mg; 2.33 mmol scale: 78% yield, 278 mg) using 100:1 DCM/MeOH as eluent. The NMR data were in consistent with the reported data[54].

NMR Data of 4q:

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.13 (br, s, 1H, NH), 6.97 (dd, *J* = 8.1, 2.6 Hz, 1H), 6.92 (ddd, *J* = 9.3 Hz, 8.9 Hz, 2.6 Hz, 1H), 6.79 (dd, *J* = 8.9, 4.3 Hz, 1H), 3.54 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.92, 159.09 (d, *J* = 236.3 Hz), 138.63 (d, *J* = 2.13 Hz), 126.92 (d, *J* = 8.7 Hz), 114.43 (d, *J* = 23.3 Hz), 112.68 (d, *J* = 25.9 Hz), 110.37 (d, *J* = 8.4 Hz), 36.81.

^{19}F NMR (376 MHz, $CDCl_3$): δ -120.99.

HRMS (ESI$^+$) of 4q: *m/z* calcd for $C_{10}H_{11}NO$ $[M+H]^+$: 150.03407, Found: 150.03477.

4.3.5. Cellular Staining Experiments with the Product 2y

In order to demonstrate the practicability of the product **2y** as an AIE-active molecule, relevant colocalization studies were conducted in Hela cells. As shown in Figure S10, **2y** can be employed as a specific lipid droplets (LD) probe which colocalized perfectly with the commercial LD dye Nile Red, and the Pearson's correlation coefficient (PCC) is 90.49%.

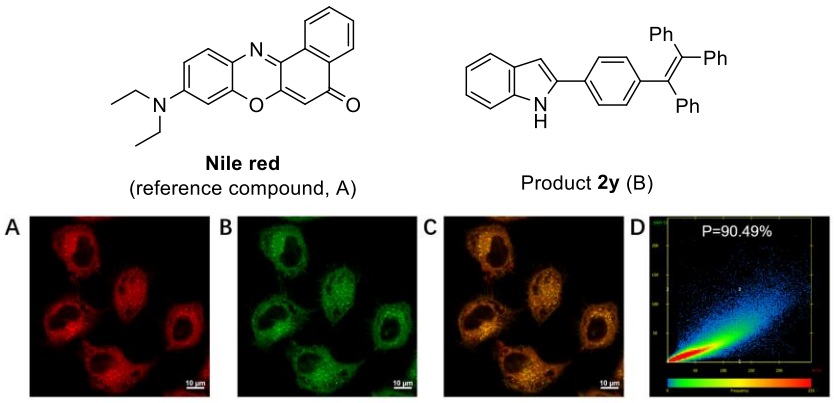
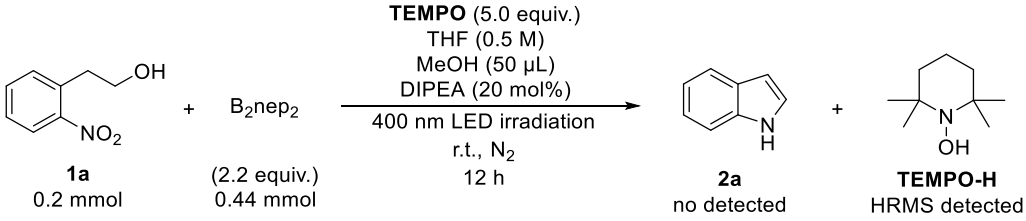


Figure S10. Colocalization study of **2y** in Hela cells. Confocal images of Hela cells stained with Nile red (A) and the product **2y** (B). (C) Merged images of A and B (Nile red: λ_{ex} = 561 nm, λ_{em} = 590-700 nm; **2y**: λ_{ex} = 488 nm, λ_{em} = 490-580 nm). (D) The Pearson correlation coefficient of A and B was 90.49%. Scale bar: 10 μm.

5. Mechanistic Studies

5.1. Radical Quenching Experiments



To a flame-dried Schlenk tube with a Teflon-coated magnetic stirring bar, the substrate **1a** (1.0 equiv., 0.2 mmol, 33.4 mg), (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (i.e. **TEMPO**, 5.0 equiv., 156 mg, 1.0 mmol), $B_2(nep)_2$ (2.2 equiv., 99 mg, 0.44 mmol), *N*, *N*-diisopropylethylamine (i.e. DIPEA, 0.2 equiv., 5 mg, 0.04 mmol) and MeOH (50 μL) were added in ultra dry THF (0.4 mL, 0.5 M) under nitrogen atmosphere. The mixture was vigorously stirred under the irradiation of a 6 W 400 nm LED at room temperature for 12 h. After that, a small portion (about 10 μL) of the reaction solution was sampled and evaporated in *vacuo*, which was then diluted with MeOH and analyzed by HRMS. Product **2a** was not detected, instead **TEMPO-H** was observed (as shown in Figure S11).

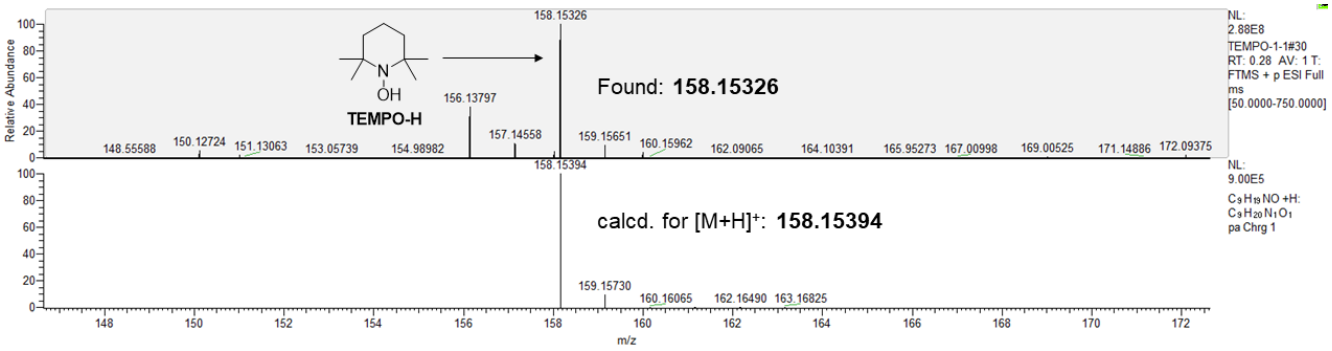
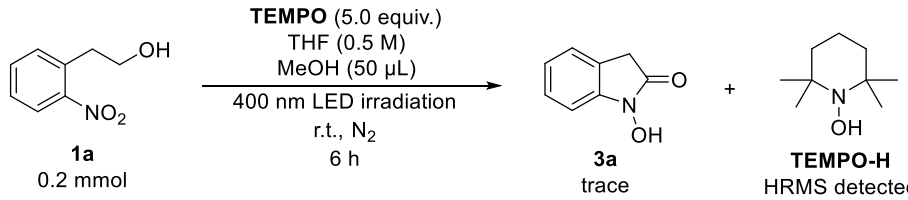


Figure S11. HRMS spectra of **TEMPO-H** and comparison with theoretical calculating values of *m/z*.



To a flame-dried Schlenk tube with a Teflon-coated magnetic stirring bar, the substrate **1a** (1.0 equiv., 0.2 mmol, 33.4 mg),

(2,2,6,6-tetramethylpiperidin-1-yl)oxyl (i.e. **TEMPO**, 5.0 equiv., 156 mg, 1.0 mmol) and MeOH (50 μL) were added in ultra dry THF (0.4 mL, 0.5 M) under nitrogen atmosphere. The mixture was vigorously stirred under the irradiation of a 6 W 400 nm LED at room temperature for 6 h. After that, a small portion (about 10 μL) of the reaction solution was sampled and evaporated in *vacuo*, which was then diluted with MeOH and analyzed by HRMS. The rest of the mixture was evaporated and subjected to ^{1}H NMR analysis using 1,3,5-tribromobenzene (63 mg, 0.2 mmol, 1.0 equiv.) as internal standard. Like the previous reaction, the production of **3a** was inhibited and **TEMPO-H** was detected by HRMS.

5.2. Exclusion of EDA complex

UV-Vis absorption spectrum is an effective means to directly represent the electronic properties of compounds, and is often used to prove the existence of electron-donor-acceptor (EDA) complex in photochemical reactions[55]. In this part, UV-Vis spectra of **1a**, B_2nep_2 and their 1:2.2 mixture (the molar ratio was in consistence with the reaction mixture) were recorded with a Shimadzu UV-3600 spectrophotometer. As shown in Figure S12, no bathochromic shift and hypochromatic shift were observed in the 1:2.2 mixture of **1a** and B_2nep_2 and the absorption was basically the same as **1a**.
NMR experiments were carried out by using a mixture of **1a** (33 mg, 0.2 mmol, 1.0 equiv.) and B_2nep_2 (0-54 mg, 0-0.6 mmol, 0-3 equiv.). ^{1}H NMR and ^{11}B NMR analysis of the mixtures were recorded at 298 K on a Bruker AVANCE III 400 MHz NMR spectrometer. As shown in Figure S13, the resonance signals of both **1a** and B_2nep_2 were not changed in the mixture, indicating that there is no Lewis base-boron adduct in the mixture of **1a** and the diboron reagent.
Collectively, the diboron reagent has no effect upon the nature of the substrate to be photoexcited under the irradiation of blue light in most cases, and the existence of EDA complex was excluded.

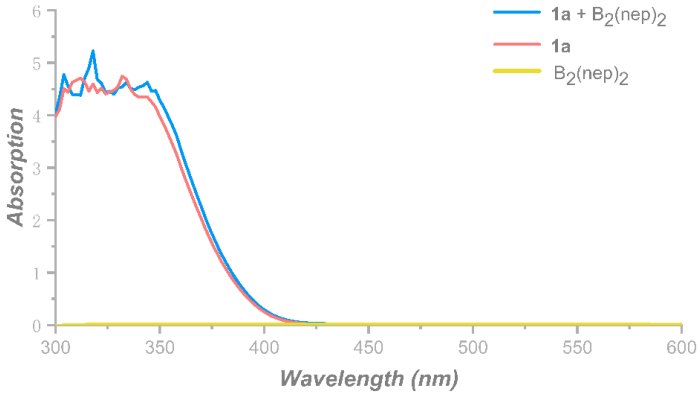


Figure S12. UV-Vis spectra of **1a** (c_{1a} = 1 × 10^{-5} M), B_2nep_2 (c_B = 1 × 10^{-5} M) and their 1:2.2 mixture (c_{1a} = 1 × 10^{-5} M, c_B = 2.2 × 10^{-5} M).

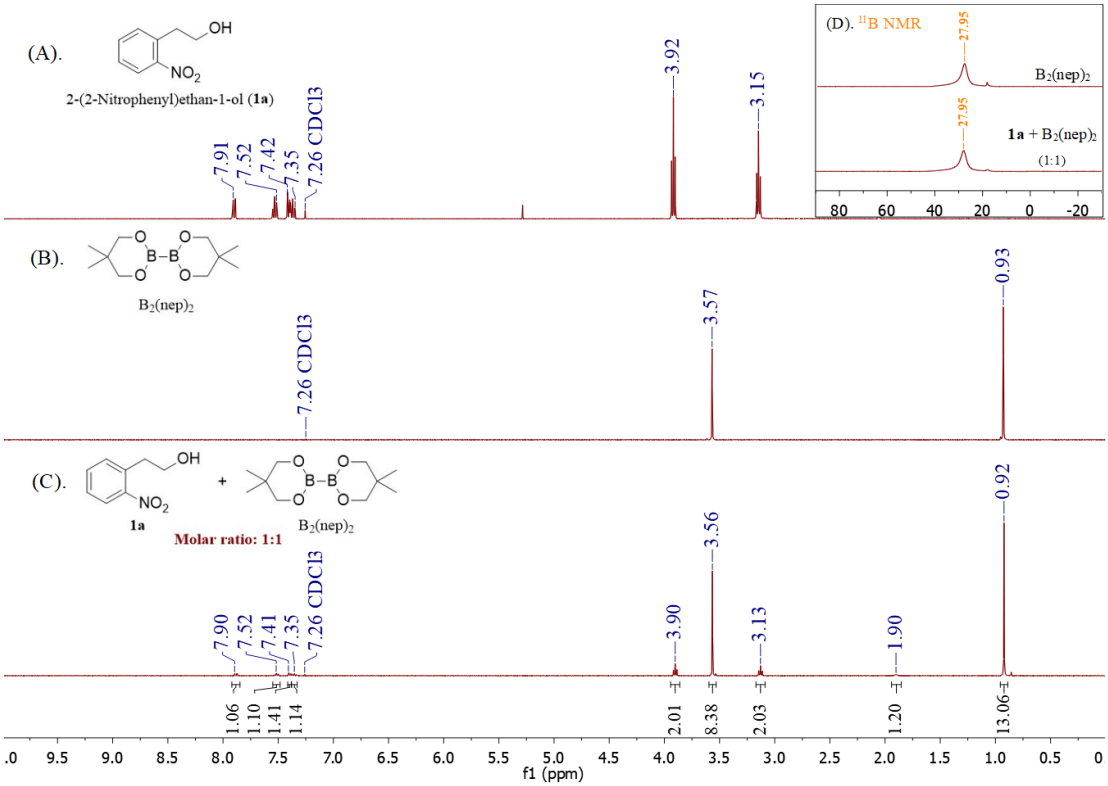
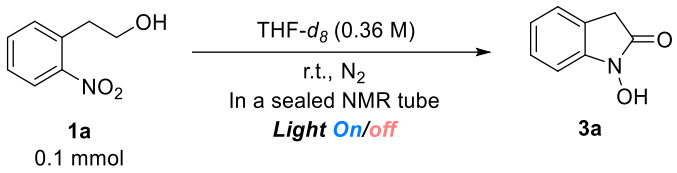


Figure S13. (A) ^{1}H NMR spectra of the substrate **1a** (for comparison). (B). ^{1}H NMR spectra of B_2nep_2. (C) ^{1}H NMR spectra of 1:1 mixture of **1a** and $B_2(nep)_2$. (D) ^{11}B NMR of 1:1 mixture of **1a** and $B_2(nep)_2$. Only main peaks of each clusters were shown for clarity.

5.3. Light On/Off Experiments



1a (16.7mg, 0.1 mmol) and THF-d_8 (0.55 mL, 0.36 M) were added into a brand-new NMR tube in a N_2-filled glovebox. Then the NMR tube was sealed with a rubber plug and thin parafilm until it was transferred out of the glove box. The mixture was measured using a Bruker AVANCE III 400 MHz NMR spectrometer to get ^{1}H NMR spectra of **1a** in THF-d_8. After that, the tube was placed into the photoreaction apparatus (the photoreaction apparatus with a 400 nm LED was placed adjacent to the NMR spectrometer beforehand) and stirred with interval irradiation (15 min irradiation followed by 15 min darkness). The yield of **3a** at each time point was determined by ^{1}H NMR analysis, as shown in Figure S14. It is worthy noting that the reaction performed in the NMR tube was more productive than in the commonly used Schlenk tube due to better photopermeability of the NMR tube. Based on the results shown in Figure S15, constant irradiation is required for the photoinduced cyclization as no conversion was observed in the dark periods.

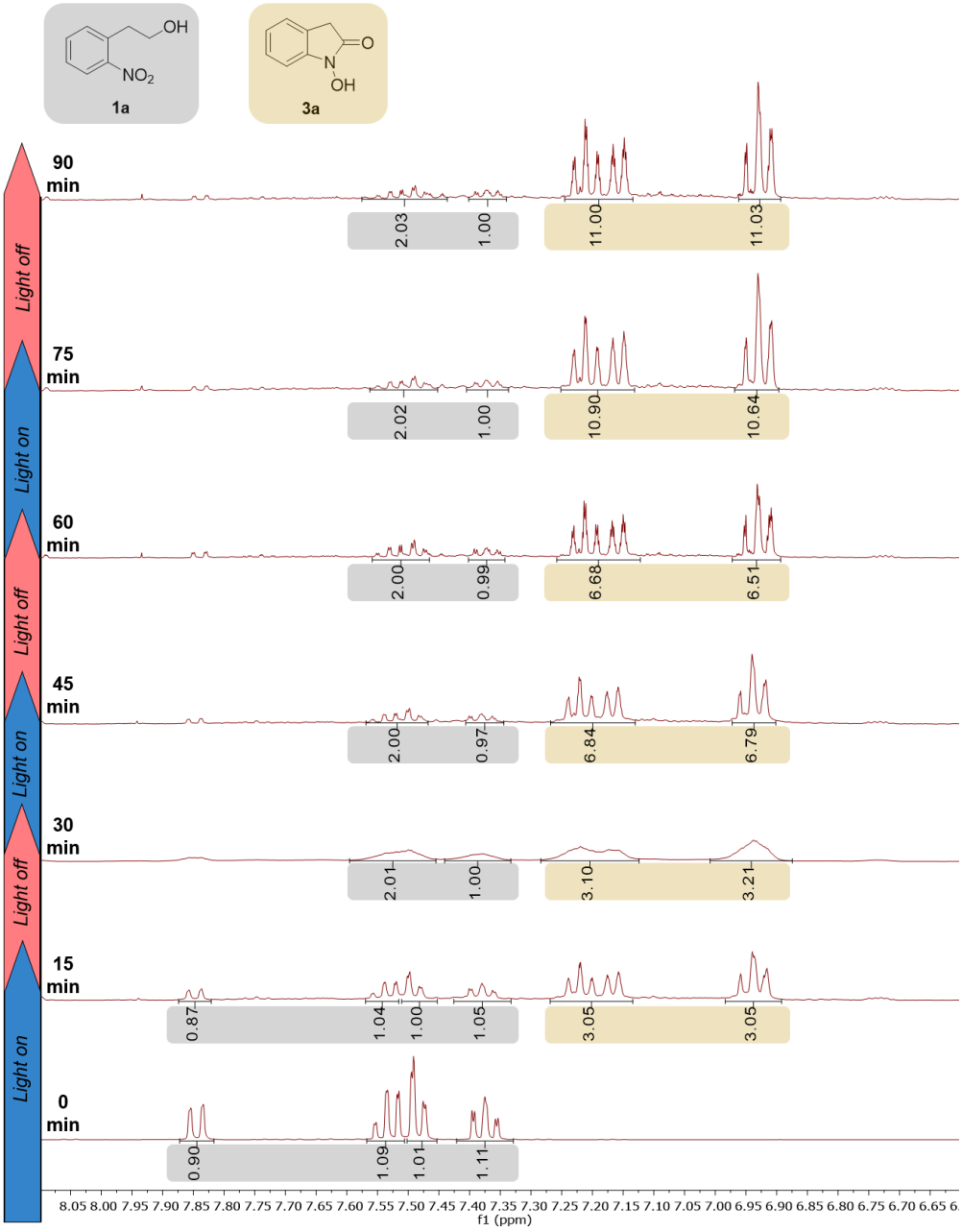


Figure S14. ^{1}H NMR analysis of light on/off experiments (chemical shifts were reported with the solvent resonances of THF-d_8 for reference). The integrals of **1a** were underlined with grey while the integrals of **3a** were underlined with beige. As no side product was found in ^{1}H NMR spectra, the crude NMR yields were determined using the normalization method.

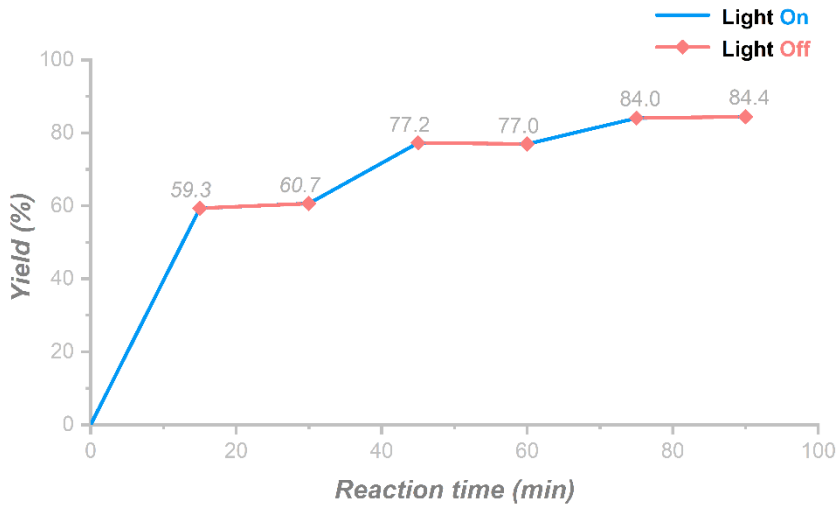


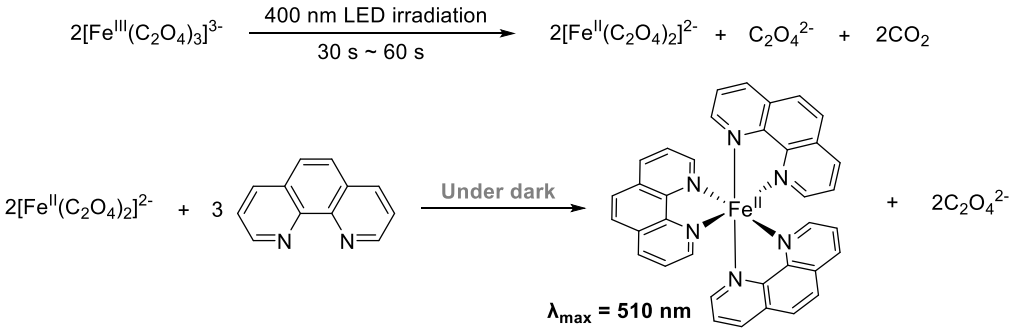
Figure S15. Light on/off experiment.

5.4. Quantum Yield Measurements

Quantum yield measurements were determined using standard ferrioxalate chemical actinometry as described by Yoon[56], Ritter[57], Aleman[58], and Glorious[59]. In this part, we use the photoreaction apparatus with 400 nm LEDs (please see section **1.3** for detailed information) as the light source to determine the quantum yield.

5.4.1. Determination of the Photon Flux at 400 nm

The photon flux of the LED (400 nm) was determined by monitoring the photoreduction of Fe(III) in potassium ferrioxalate to Fe(II), upon complextion with 1,10-phenanthroline:



The following solutions were prepared: (a). Actinometer solution: 147 mg (0.3 mmol) of potassium ferrioxalate trihydrate and 70 µL of H_2SO_4 (96%) were added to a 25 mL volumetric flask and filled to the mark with Nanopure water. (b). Phenanthroline-buffer solution: 50 mg (0.278 mmol) of 1,10-phenanthroline, 1.23 g (15 mmol) of sodium acetate and 0.25 mL of H_2SO_4 (96%) were added to a 25 mL volumetric flask and filled to the mark with Nanopure water. 1 mL of the actinometer solution was added to a vial (15 x 50 mm) and was irradiated by 400 nm LED for 30 seconds. After the irradiation, the mixture was quantitatively transferred to a 5 mL volumetric flask containing 1.0 mL of the phenanthroline-buffer solution. Then, the flask was filled to the mark with Nanopure water, wrapped up with aluminum foil, and was left in the dark for 2 h to ensure the quantitative formation of $Fe^{II}(phen)_3^{2+}$ complex. This procedure was repeated one more time by changing the irradiation time to 60 seconds. Additionally, the experiment of a control sample was carried out indark, following the same sample treatment.

The absorbance of each solution at 510 nm was measured using a Shimadzu UV-3600 spectrophotometer, establishing the blank with Nanopure water. For each sample, the absorbance was acquired three times and averaged. According to Lambert-Beer law, the moles of Fe(II) in each sample are related to the absorbance:

$$n[Fe^{2+}] = \frac{V \cdot \Delta_A}{l \cdot \varepsilon}$$

Where:

- Δ_A is the absorbance difference between irradiated sample and non-irradiated sample (control sample).
- V is the volume (in L) of the measurement sample (5 mL).
- ε is the extinction coefficient of the complex $Fe^{II}(phen)_3^{2+}$ at 510 nm (11000 $L \cdot mol^{-1} \cdot cm^{-1}$).
- l is the optical path of the sample in the spectrophotometer (1 cm).

The photon flux can be calculated using the following equation:

$$photon\ flux = \frac{n[Fe^{2+}]}{\Phi \cdot t \cdot f}$$

Where:

- Φ is the quantum yield for the photoreduction of ferrioxalate at 400 nm. We use the documentaed data of 405 nm as an approximation, which is 1.14.
- t is the reaction time of the photoreduction of ferrioxalate (30 s or 60 s).
- f is the fraction of light absorbed, and is calculated as $f = 1 - 10^{-A_{400nm}}$. Where A_{400nm} is the absorbance of the actinometer solution at 400 nm (which is 2.599 according to the UV-Vis spectra of actinometer solution, as shown in Figure S16).

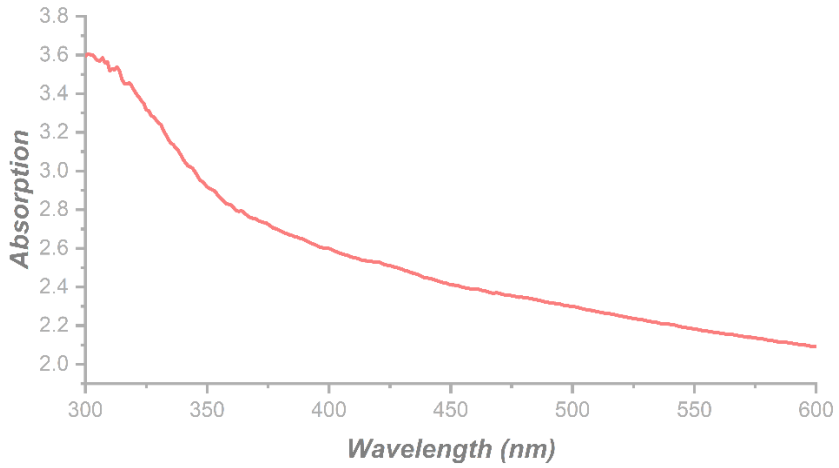


Figure S16. UV-Vis spectra of the actinometer solution.

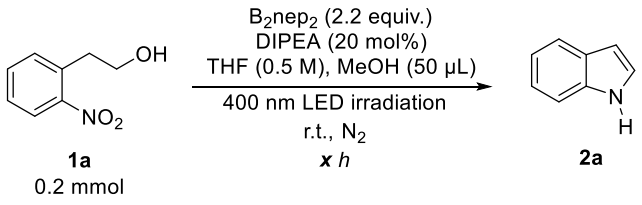
The photon flux of the 400 nm LED was thus determined to be $1.311*10^{-8}$ einsten·s^{-1}, as shown in Table S5.

Table S5. UV-Vis absorption data and calculated results of the photo flux.

Scan time	UV-Vis absorption at 510 nm		
	A_{30s}	A_{60s}	A_{dark}
1	1.099	1.807	0.022
2	1.010	1.786	0.016
3	1.193	1.779	0.017
Average	1.101	1.791	0.018
Δ_A	1.082	1.772	-
n[Fe^{2+}] (mol)	4.920×10^{-7}	8.056×10^{-7}	
Photon flux (einstein/s)	1.442×10^{-8}	1.181×10^{-8}	
	Average = 1.311×10^{-8}		

5.4.2.Determination of the Quantum Yield at 400 nm

Once we have determined the photon flux of the LED (400 nm), the same equation must be employed for the determination of the quantum yield. For that, the moles of the product for a given time must be determined. In view of the nature of nitroarenes to be photoexcited either with or without diboron reagents, we performed **General Procedure A** on **1a** to determine the rough quantum yield of the photoinduced cyclization reaction.



Following **General Procedure A**, the reaction was carried out in a Schlenk tube under the irradiation of the 400 nm LED, and ^{t}BuPh (20 μL) was added to the tube as an internal standard. After 0.5 h, a small portion (about 10 μL) of the reaction solution

was sampled and evaporated in *vacuo*, which was then diluted with MeOH and analyzed by GC-MS. The amount of product **2a** was determined to be 0.010 mmol. After 3 h, anothor sampling and analysis was also carried out, and the amount of **2a** was determined to be 0.051 mmol.

$$\Phi' = \frac{n[prod.]}{photon\ flux \cdot t' \cdot f'}$$

Where:

- *n [prod.]* is the amount of the product **2a** (in mol) that has been formed during the irradiation time.
- *t'* is the irradiation time (in seconds).
- *f'* is the fraction of light absorbed, and is calculated as $f' = 1 - 10^{-A'_{400nm}}$. Where A'_{400nm} was determined to be 4.762 according to the UV-Vis spectra of **1a** in THF (the concentration was in consistence with initial solution of the reaction), as shown in Figure S17.

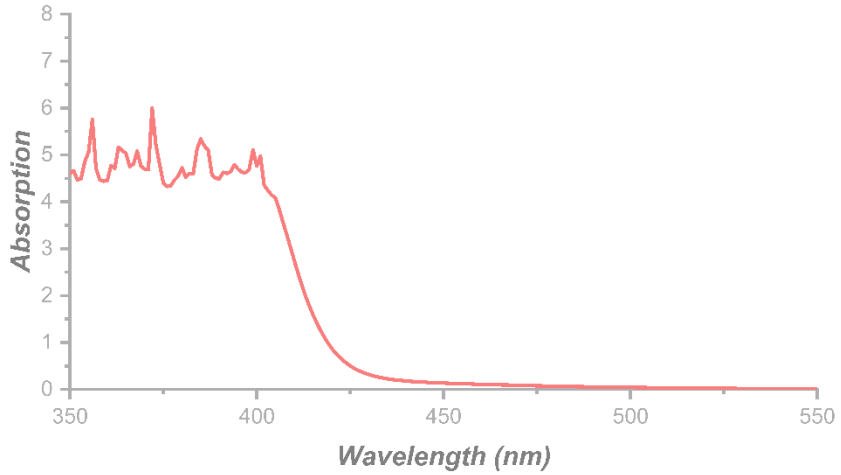
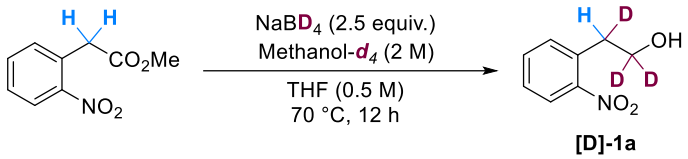


Figure S17. UV-Vis spectra of **1a** in THF (the concentration was in consistence with initial solution of the reaction).

The quantum yield was thus determined to be 0.39 (average of two runs). In fact, as the reaction progresses, the photosensitizer (i.e. the substrate nitroarene) is consumed and the real absorbance of the reaction mixture is changed. So the quantum yield measured following the standard ferrioxalate chemical actinometry is not completely accurate to some extent. That is to say, the actual value of f' is smaller than the measured one. But in spite of this, we can still get some necessary information about the nature of the radical reaction from this result. Although we still could not fully exclude the possibility of the radical chain process of this reaction, this result indicates that radical chain propagation, if present, is not the major pathway for the current reaction.

5.5. KIE Experiments

5.5.1.Preparation of the Deuterated Substrate



[D]-1a

To a flame-dried pressure-proof tube, methyl 2-(2-nitrophenyl)acetate (1.0 equiv., 500 mg, 2.56 mmol) and $NaBD_4$ (2.5 equiv., 268 mg, 6.4 mmol) were added inside a glove box (filled with Ar) until the tube was sealed. After transferring the tube out of the glove box, anhydrous THF (0.5 M, 5.2 mL) and methanol-d_4 (2 M, 1.3 mL) were added via syringes. The tube was stirred and heated at 70 °C for 12 hours. When the reaction was completed, the crude reaction mixture was allowed to room temperature and filtered through a short pad of neutral Al_2O_3 with EtOAc (10 mL × 3) as eluent. The filtrate was concentrated in *vacuo* and purified by flash column chromatography on neutral Al_2O_3 (eluting with CH_2Cl_2) afforded the product **[D]-1a** as yellow oil (237 mg, 55%). The ^1H NMR and HRMS spectra of **[D]-1a** were shown in Figure S18.

NMR Data of [D]-1a:

> **^1H NMR** (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.1 Hz, 1H), 7.55 (ddd, *J* = 8.0, 7.8, 1.3 Hz, 1H), 7.45 – 7.34 (m, 2H), 3.14 (s, 1H, benzylic C-H), 1.72 (br, s, 1H, OH).

HRMS (ESI^+) of [D]-1a: *m/z* calcd for $C_8H_6NO_3D_3$ $[M-H]^-$: 169.06870, Found: 169.06859.

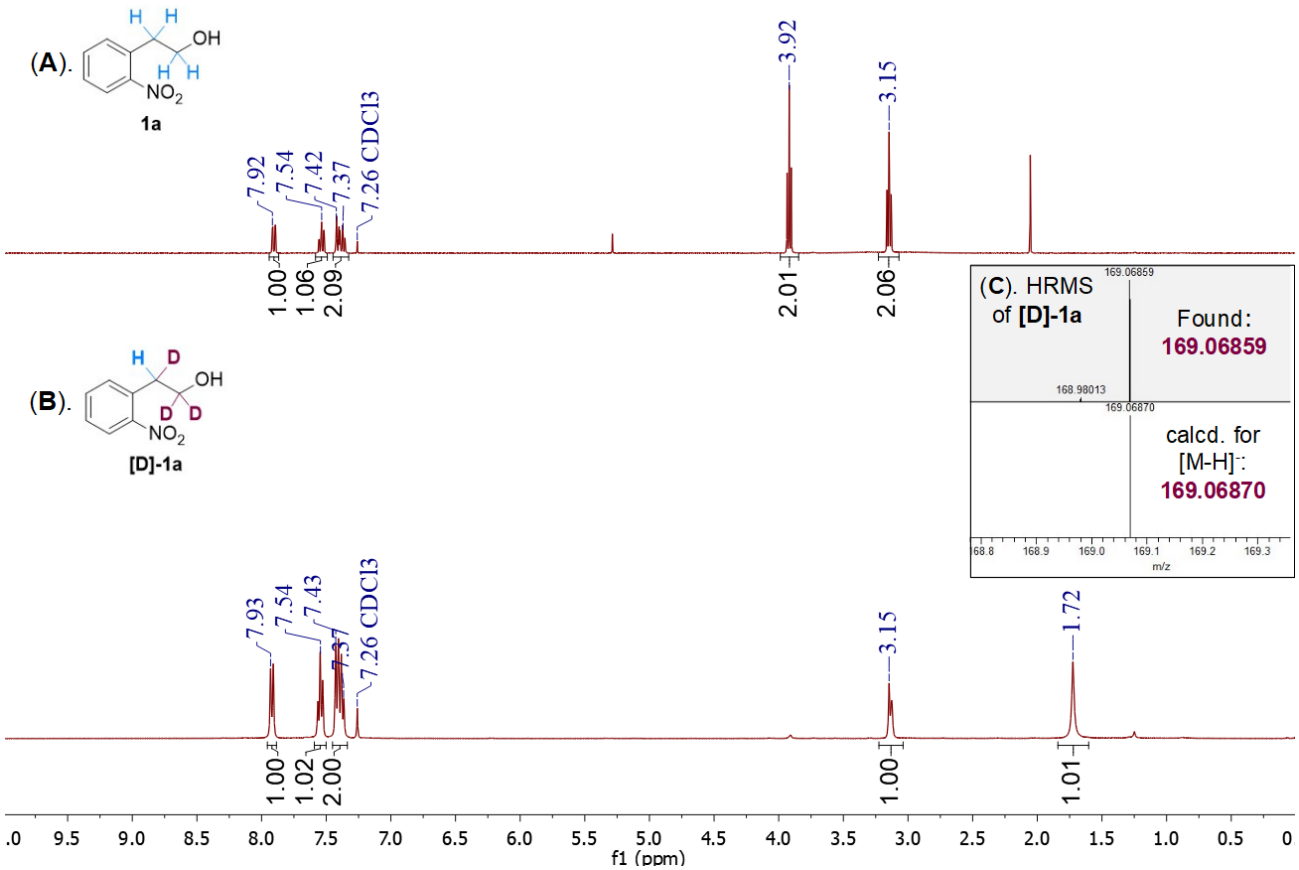
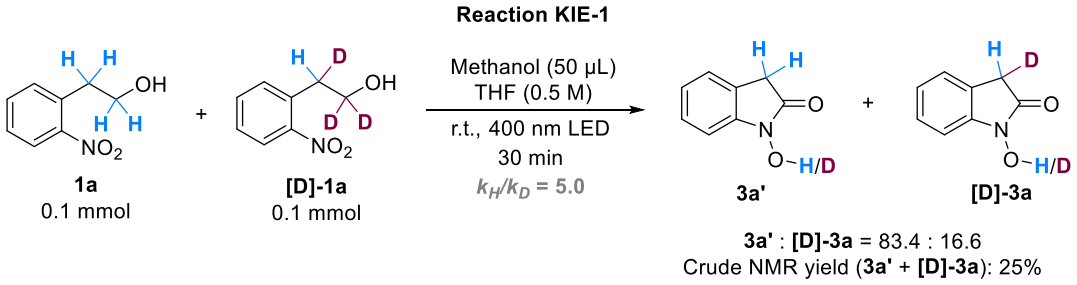


Figure S18. (A) ^{1}H NMR spectra of **1a** (for comparison), only main peaks of each cluster were shown for clarity. (B) ^{1}H NMR spectra of the deuterated substrate **[D]-1a**, only main peaks of each cluster were shown for clarity. (C) HRMS spectra of **[D]-1a**.

5.5.2.Kinetic Isotope effects



To a flame-dried Schlenk tube with a Teflon-coated magnetic stirring bar, the substrate **1a** (1.0 equiv., 0.1 mmol, 16.7 mg), deuterated substrate **[D]-1a** (1.0 equiv., 0.1 mmol, 17.0 mg) and MeOH (2.5 equiv., 20 μL, 0.5 mmol) were added in ultra-dry THF (0.4 mL, 0.5 M) *via* microsyringes under nitrogen atmosphere. The microsyringes were washed by 20 uL MeOH after each addition of substrates, and the washings were injected into the tube as well. The mixture was vigorously stirred under the irradiation of a 6 W 400 nm LED at room temperature for 30 min. After that, the solution was evaporated in *vacuo* to leave a crude mixture, which was analyzed by ^{1}H NMR for k_H/k_D. Due to H/D exchange during the reaction, the H/D ratio of N–OH(D) is unreliable for data analysis. In this part, we used the integral of benzylic C–H(D) as a key to determine the ratio of **3a'** and **[D]-3a**. The ^{1}H NMR spectra of the crude mixture was shown in Figure S19. k_H/k_D of **reaction KIE-1** was thus determined to be 5.0, which means that the reaction conforms to primary kinetic isotope effect (PKIE).

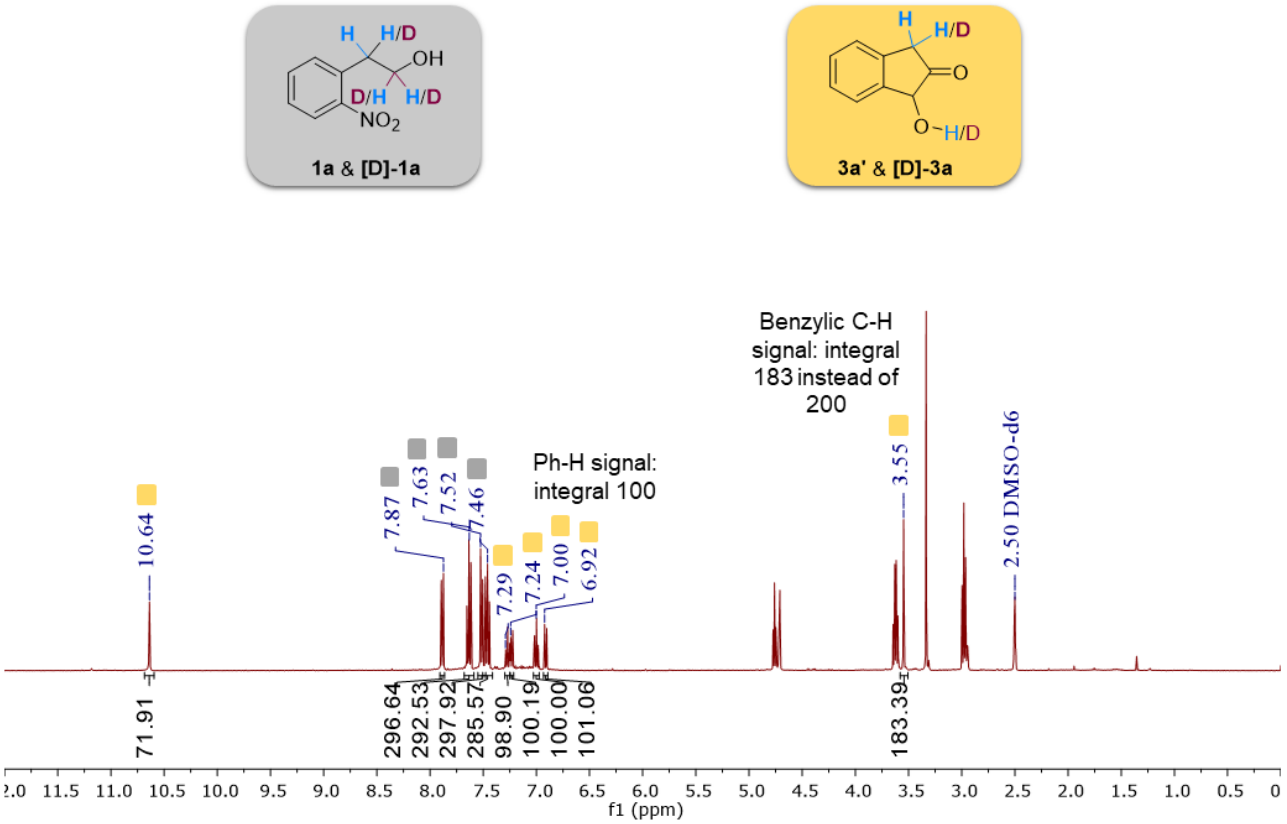
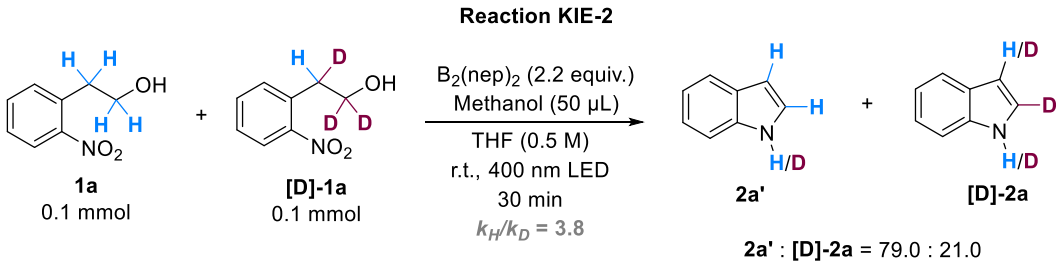


Figure S19. ^{1}H NMR spectra of the crude mixture of **reaction KIE-1**, only main peaks of each cluster were shown for clarity. The key signals of **1a** and **[D]-1a** were marked with grey tags while the key signals of products **3a'** and **[D]-3a** were marked with yellow tags.



To a flame-dried Schlenk tube with a Teflon-coated magnetic stirring bar, the substrate **1a** (1.0 equiv., 0.1 mmol, 16.7 mg), deuterated substrate **[D]-1a** (1.0 equiv., 0.1 mmol, 17.0 mg), $B_2(nep)_2$ (2.2 equiv., 99 mg, 0.44 mmol) and MeOH (50 μL) were added in ultra-dry THF (0.4 mL, 0.5 M) under nitrogen atmosphere. The mixture was vigorously stirred under the irradiation of a 6 W 400 nm LED at room temperature for 30 min. After that, the solution was evaporated in *vacuo* to leave a crude mixture, which was analyzed by ^{1}H NMR for k_H/k_D. The ^{1}H NMR spectra of the crude mixture was shown in Figure S20. k_H/k_D of **reaction KIE-2** was thus determined to be 3.8, which means that the reaction conforms to primary kinetic isotope effect (PKIE).

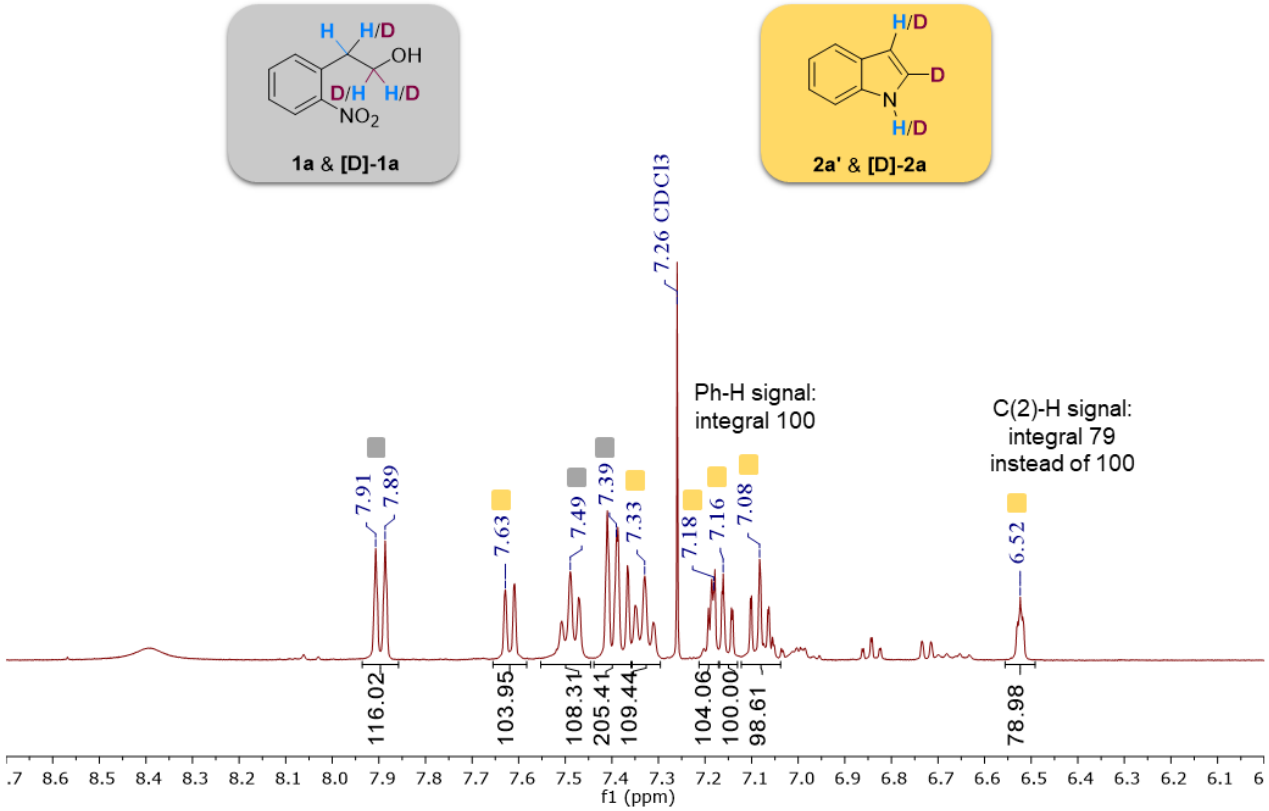
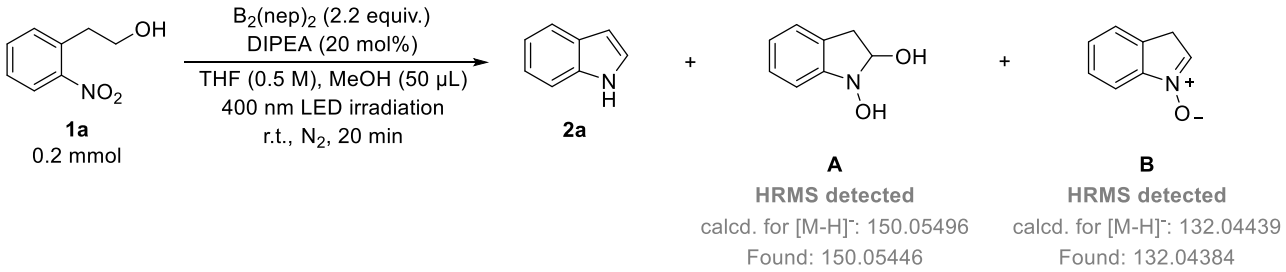


Figure S20. ^{1}H NMR spectra of the crude mixture of **reaction KIE-2**, only main peaks of each cluster were shown for clarity. The key signals of **1a** and **[D]-2a** were marked with grey tags while the key signals of products **2a'** and **[D]-2a** were marked with yellow tags.

5.6. HRMS Analysis for Proposed Intermediates



To a flame-dried 15 × 50 mm vial with a Teflon-coated magnetic stirring bar were charged with $B_2(nep)_2$ (3.0 equiv., 99 mg, 0.44 mmol). The vial was then brought into a N_2-filled glovebox where **1a** (1.0 equiv., 0.2 mmol, 33.4 mg), N, N-diisopropylethylamine (i.e. DIPEA, 0.2 equiv., 5 mg, 0.04 mmol), MeOH (50 μL) and ultra-dry THF (0.4 mL, 0.5 M) were added. The vial was sealed with a cap, removed from the glovebox, and placed into the photoreaction apparatus. The photoreaction apparatus was placed adjacent to a high-resolution mass spectrometer (Agilent Micromass 6540 Q-Tof LC/MS with electrospray ionisation) beforehand. The reaction was stirred with irradiation for 20 min, meanwhile, the sample bottle for HRMS analysis was filled with chromatographic MeOH (1.0 mL) and corresponding analysis program was all set. After reaction, 10 μL of the mixture was transferred into the sample bottle using a microsyringe and HRMS analysis was performed immediately. Proposed intermediates **A** and **B** were detected by HRMS with the negative ion mode, as shown in Figure S21. Although **B** is an isomeride of indolin-2-one, we prefer to identify the molecular ion peak of 132.04384 as belonging to **B** rather than indolin-2-one for the following reasons: (a). HRMS of pure indolin-2-one with the same negative ion mode did not show the molecular peak around 132, while the positive ion mode did (normally we use the positive ion mode to detect the derivatives of indolin-2-one); (b). No obvious signal of indolin-2-one was found in the ^{1}H NMR spectra collecting from the reaction mixture of the above reaction, which is incompatible with ionic intensity of the peak 132.04384 (about 1.23×10^8, as shown in Figure S21).

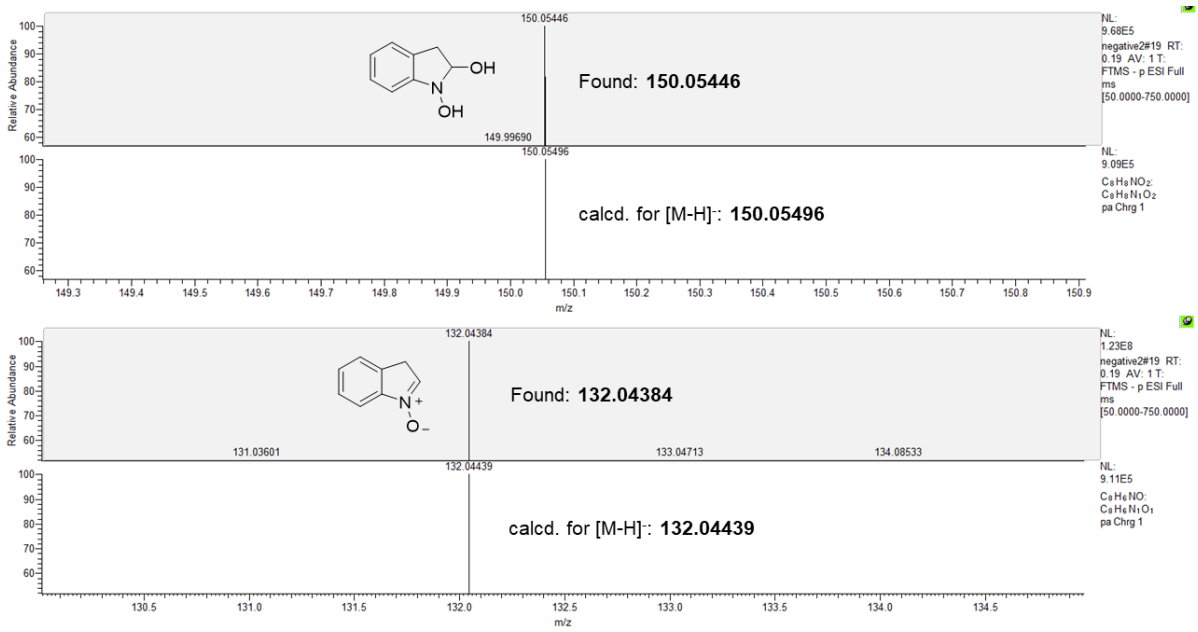
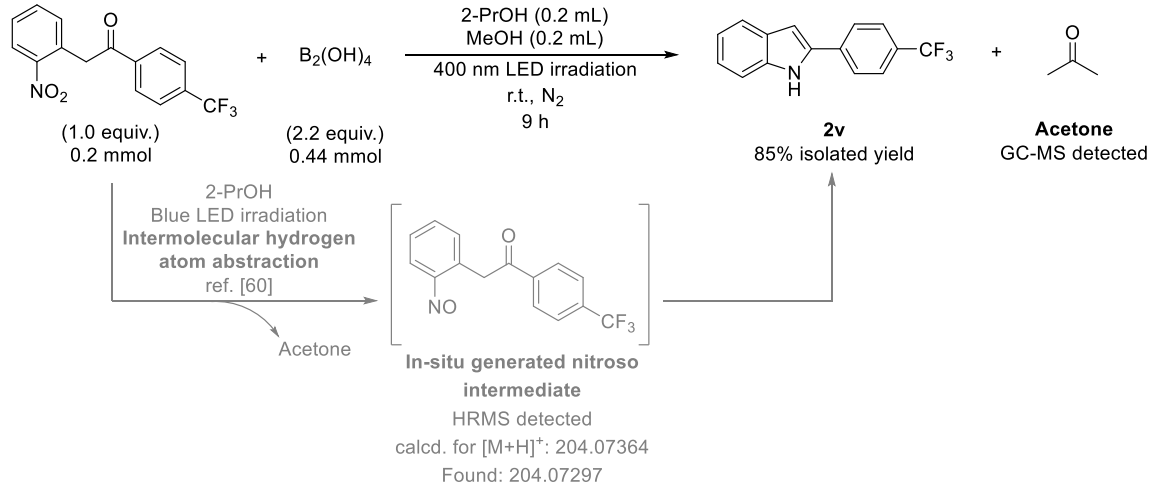


Figure S21. HRMS spectra of the proposed intermediates and comparison with theoretical calculating values of *m/z*

5.7. Cyclization of *o*-Nitrobenzylic Ketone with 2-PrOH as Hydrogen Donor



To a flame-dried Schlenk tube with a Teflon-coated magnetic stirring bar, 2-(2-nitrophenyl)-1-(4-(trifluoromethyl)phenyl)ethan-1-one (1.0 equiv., 0.2 mmol, 62 mg), $B_2(OH)_4$ (2.2 equiv., 54 mg, 0.44 mmol), isopropanol (0.2 mL) and MeOH (0.2 mL) were added under nitrogen atmosphere. Then the tube was placed into the photoreaction apparatus. The photoreaction apparatus was placed adjacent to a high-resolution mass spectrometer (Agilent Micromass 6540 Q-Tof LC/MS with electrospray ionisation) beforehand. The reaction was stirred with irradiation for 20 min, meanwhile, the sample bottle for HRMS analysis was filled with chromatographic MeOH (1.0 mL) and corresponding analysis program was all set. After 20 min, 10 μL of the mixture was transferred into the sample bottle using a microsyringe and HRMS analysis was performed immediately. **The nitroso intermediate** was thus detected by HRMS with the positive ion mode, as shown in Figure S22. The rest of the mixture was vigorously stirred under the irradiation of a 6 W 400 nm LED at room temperature for 9 h. After the reaction, a small portion (about 10 μL) of the reaction mixture was sampled and evaporated in *vacuo*, which was then diluted with MeOH and analyzed by GC-MS. The rest of the mixture was purified by flash column chromatography to afford **2v** in 85% yield (44 mg). **Acetone** was detected by GC-MS analysis, as shown in Figure S23. **Acetone** was the product of intermeolecular hydrogen atom abstraction of *o*-nitrobenzylic ketone and isopropanol[60].

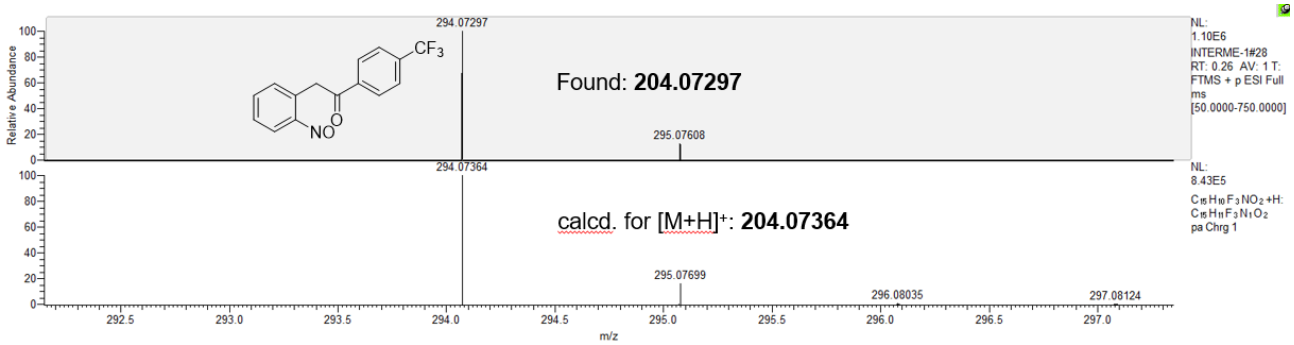


Figure S22. HRMS spectra of the proposed nitroso intermediate.

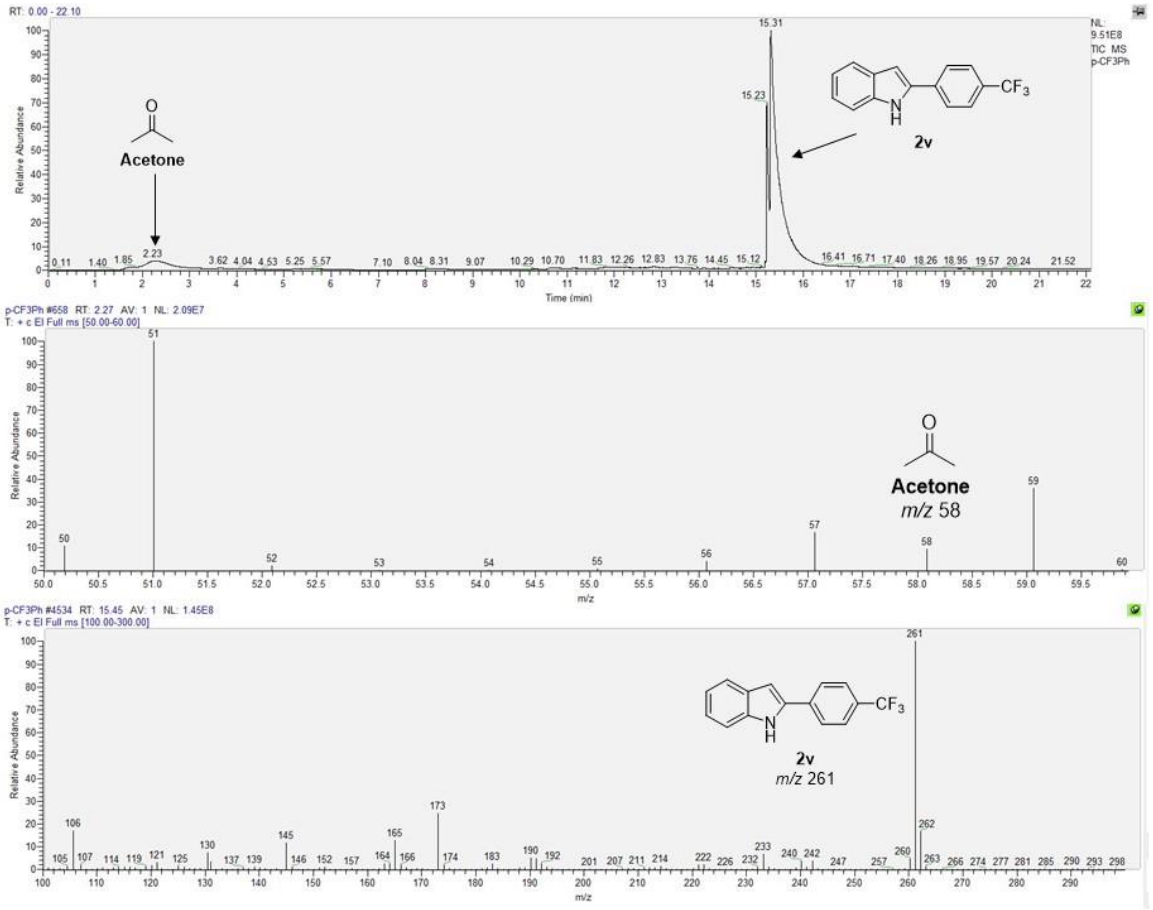
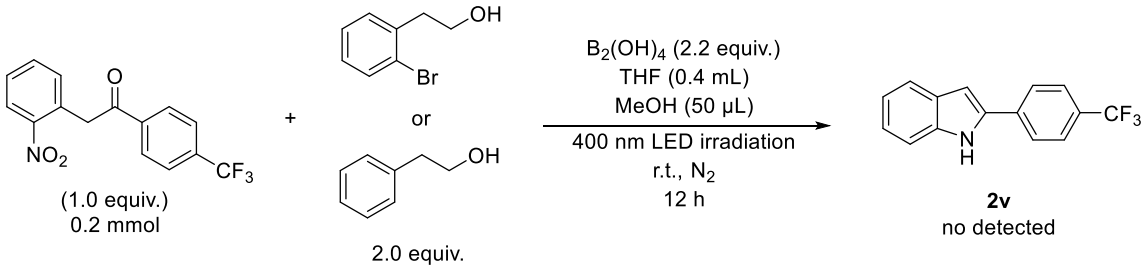


Figure S23. GC-MS analysis of cyclization reaction of *o*-nitrobenzylic ketone with 2-PrOH as hydrogen donor.



Based on the result of the above reaction (intermolecular HAT occurred between *o*-nitrobenzylic ketone and 2-PrOH), we wonder whether intermolecular HAT process is dominant under standard conditions. That is to say, we need to verify whether a nitro group is more likely to react with the hydroxyl group within a molecule, or with the hydroxyl group of another substrate molecule.

To a flame-dried Schlenk tube with a Teflon-coated magnetic stirring bar, 2-(2-nitrophenyl)-1-(4-(trifluoromethyl)phenyl)ethan-1-one (1.0 equiv., 62 mg, 0.2 mmol), $B_2(OH)_4$ (2.2 equiv., 54 mg, 0.44 mmol), 2-(2-bromophenyl)ethan-1-ol (2.0 equiv., 80 mg, 0.4 mmol), MeOH (50 μL) and ultra-dry THF (0.4 mL, 0.5 M) were added under nitrogen atmosphere. The mixture was vigorously stirred under the irradiation of a 6 W 400 nm LED at room temperature for 12 h. After reaction, a small portion (about 10 μL) of the reaction mixture was sampled and evaporated in *vacuo*, which was then diluted with MeOH and analyzed by GC-MS. Product **2v** was not detected. The same procedure was repeated one more

time by changing 2-(2-bromophenyl)ethan-1-ol to 2-phenylethan-1-ol (2.0 equiv., 49 mg, 0.4 mmol) and no product **2v** was detected. The result proved that the intramolecular hydrogen atom abstraction process is prefered under standard conditions, rather than intermolecular between two same substrate molecules.

5.8. Proposed Mechanisms of 1,3-*d*-HAA Initiated Intramolecular Rearrangement

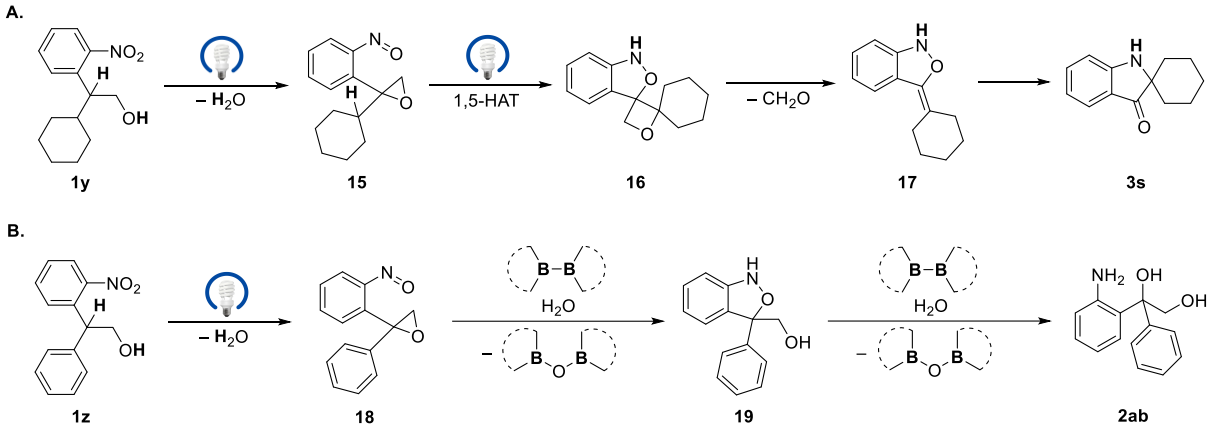


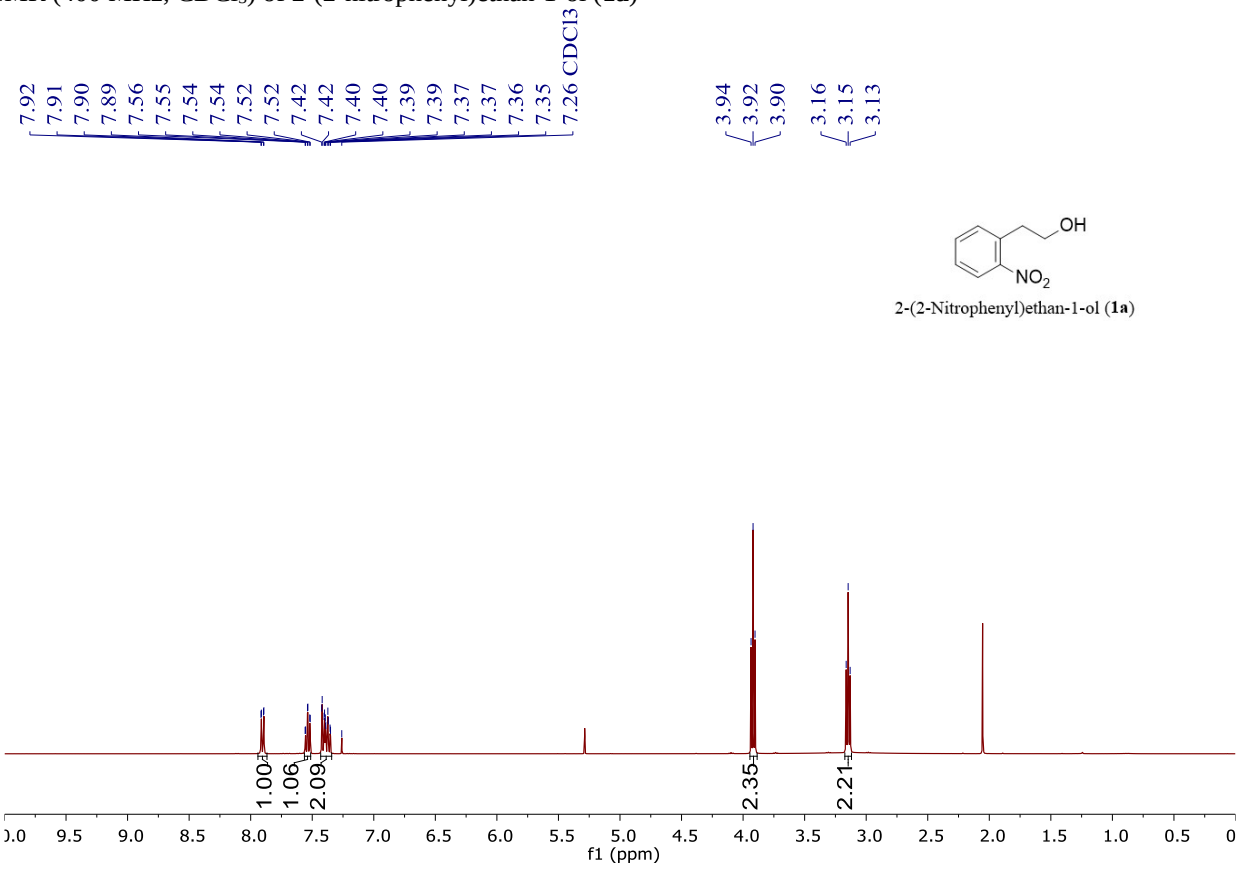
Figure S24. Proposed mechanisms of 1,3-double-HAA-initiated rearrangement reactions to afford **3s** and **2ab**-**2ae**.

Additionally, the reaction mechanisms of *β*-cyclohexyl and *β*-aryl-substituted substrates to 1,3-double hydrogen atom abstraction (*d*-HAA) initiated rearrangement were rationally explained (Figure 24). An enhanced steric hindrance around the benzylic site blocks the interaction of photoexcited nitro group with *α*-C–H of hydroxyl, but facilitates a thermodynamically favorable 1,5-HAT process[61] of the *β*-C–H of hydroxyalkyl to nitro group. The *ortho*-glycidyl nitrosobenzene intermediate **15** is delivered *via* hydrogen transfer of O–H to N=O and a quick dehydration. Then 1,5-HAT of *α*-C–H of glycidyl to the photoexcited nitroso group results in the formation of intermediate **16** which could be converted to **17** after deformylation which is similar to the fragmentation process of photo-induced carboranyl-olefin metathesis.[62] The spiro-product **3t** is thus generated *via* intramolecular rearrangement of **17**. However, in the case of *β*-aryl-substituted substrates, due to the lack of a suitable C–H bond for reduction of nitroso group, the diboron reagent/H_2O serve as external reductants for the reduction **of 18**, which leads to the formation of species **19**. The further reduction of **19** by diboron reagent/H_2O system gives rise to the product **2ab**.

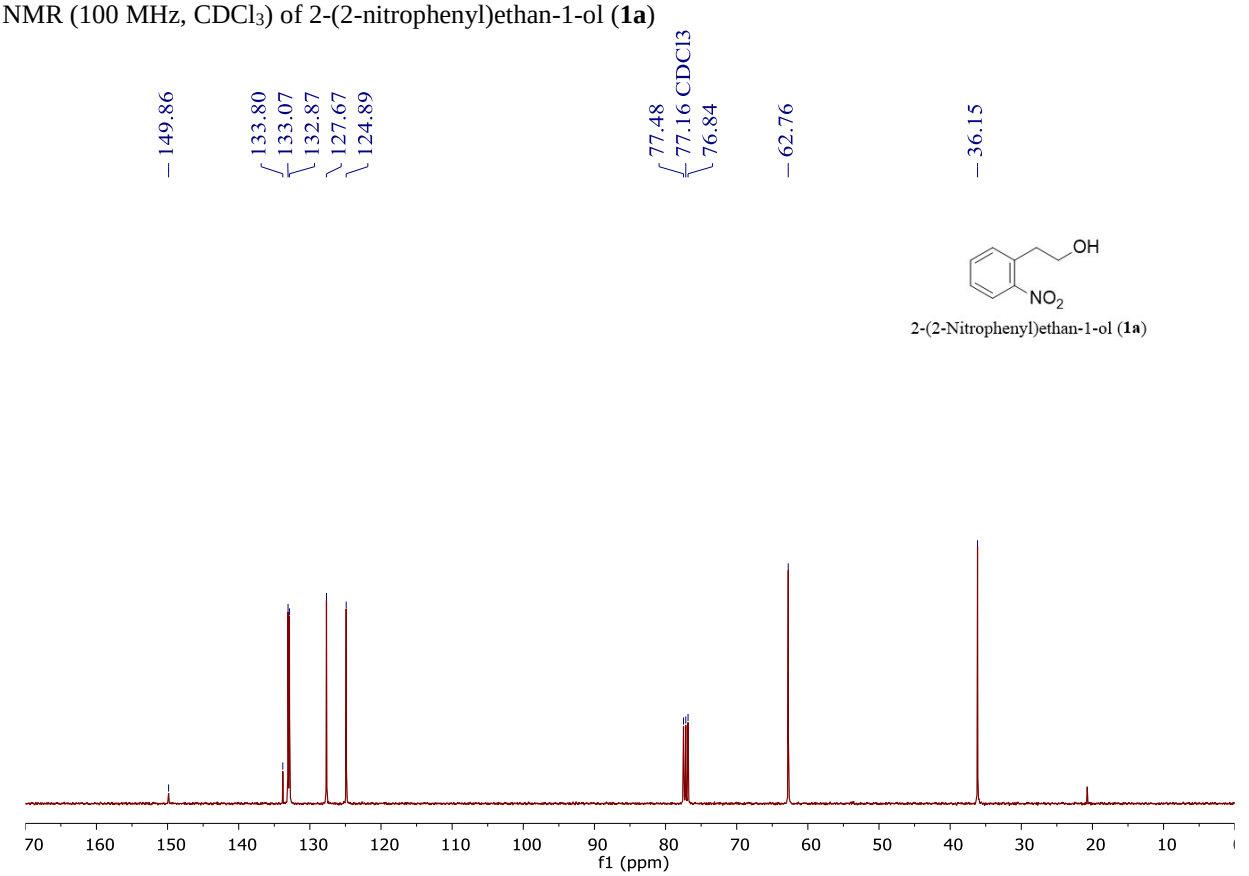
6. NMR Spectra

6.1. NMR Spectra of Substrates

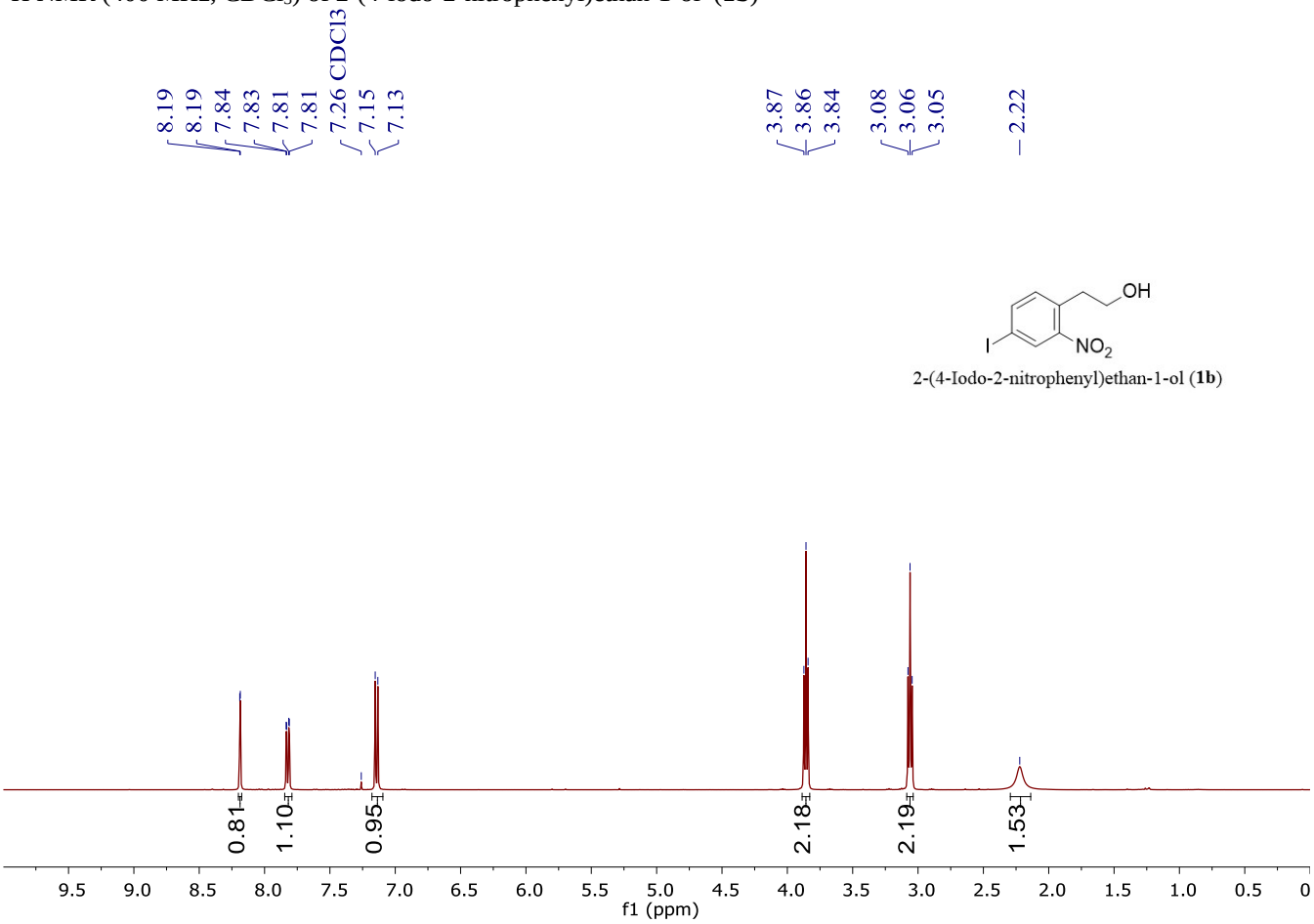
^{1}H NMR (400 MHz, $CDCl_3$) of 2-(2-nitrophenyl)ethan-1-ol (**1a**)



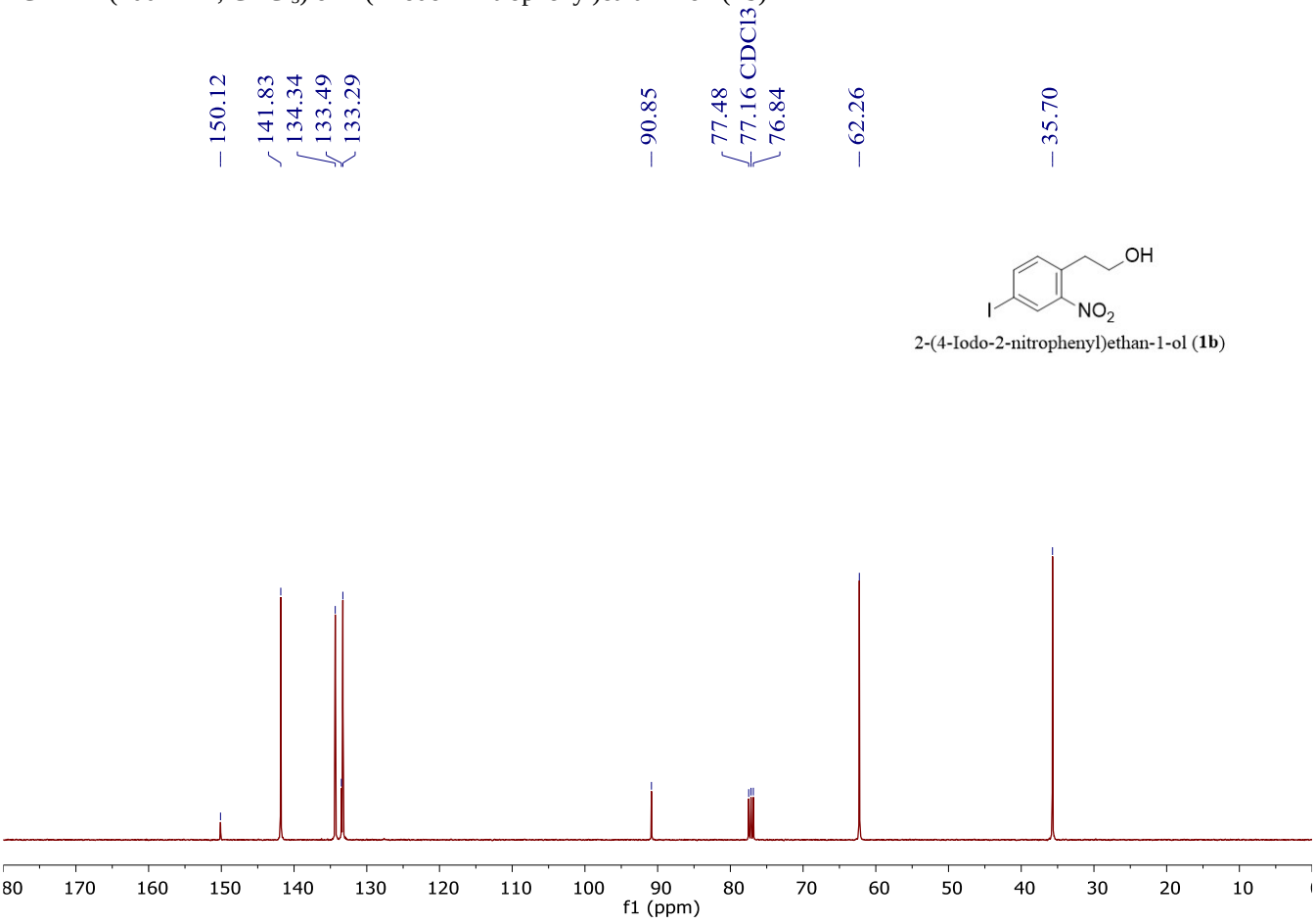
^{13}C NMR (100 MHz, $CDCl_3$) of 2-(2-nitrophenyl)ethan-1-ol (**1a**)



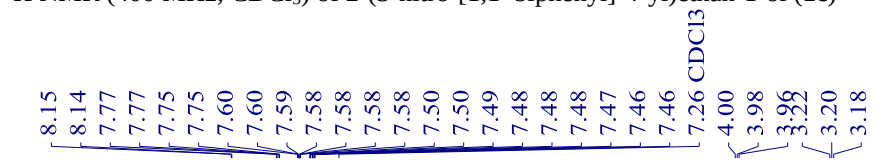
^{1}H NMR (400 MHz, $CDCl_3$) of 2-(4-iodo-2-nitrophenyl)ethan-1-ol (**1b**)

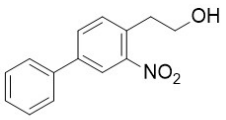


^{13}C NMR (100 MHz, $CDCl_3$) of 2-(4-iodo-2-nitrophenyl)ethan-1-ol (**1b**)

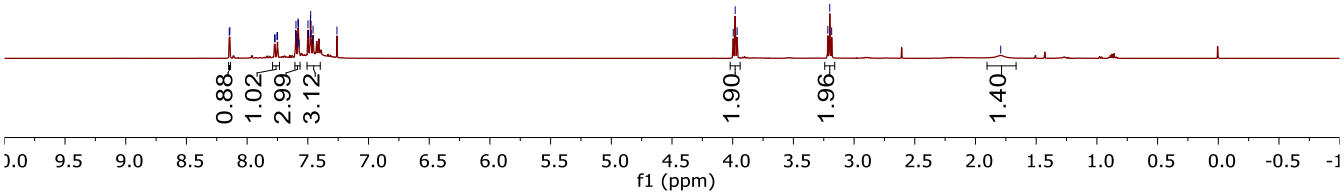


^{1}H NMR (400 MHz, $CDCl_3$) of 2-(3-nitro-[1,1'-biphenyl]-4-yl)ethan-1-ol (**1c**)

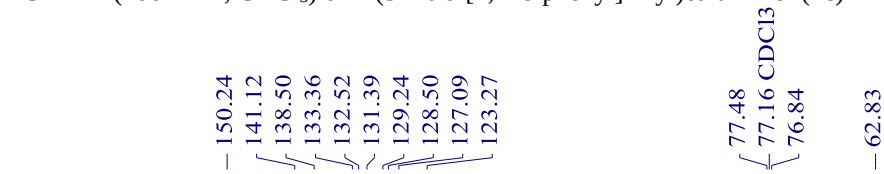


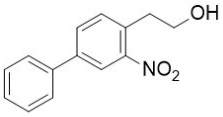


2-(3-Nitro-[1,1'-biphenyl]-4-yl)ethan-1-ol (**1c**)

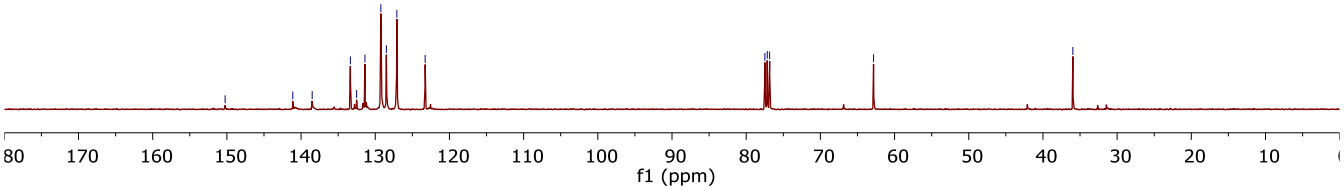


^{13}C NMR (100 MHz, $CDCl_3$) of 2-(3-nitro-[1,1'-biphenyl]-4-yl)ethan-1-ol (**1c**)

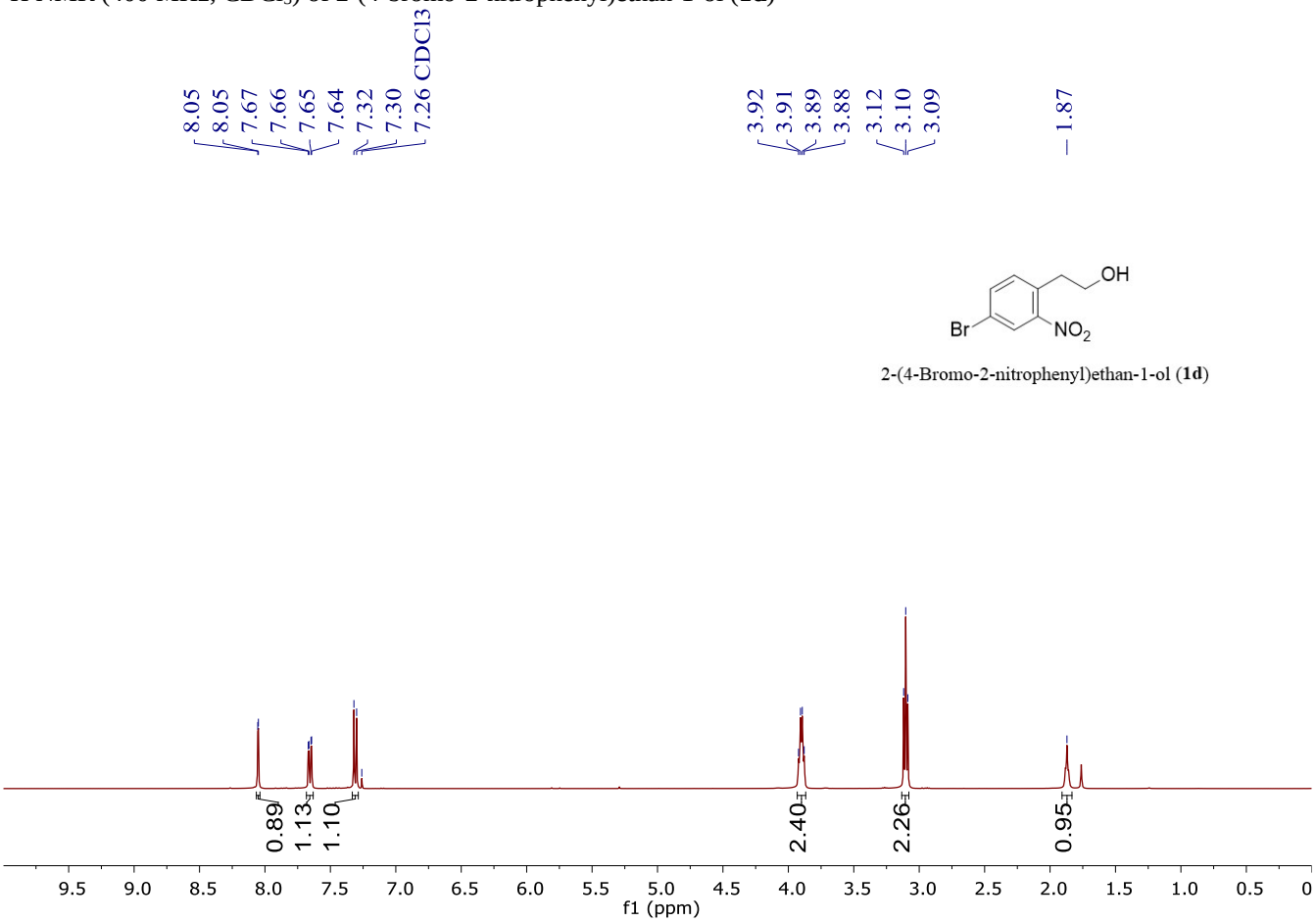




2-(3-Nitro-[1,1'-biphenyl]-4-yl)ethan-1-ol (**1c**)

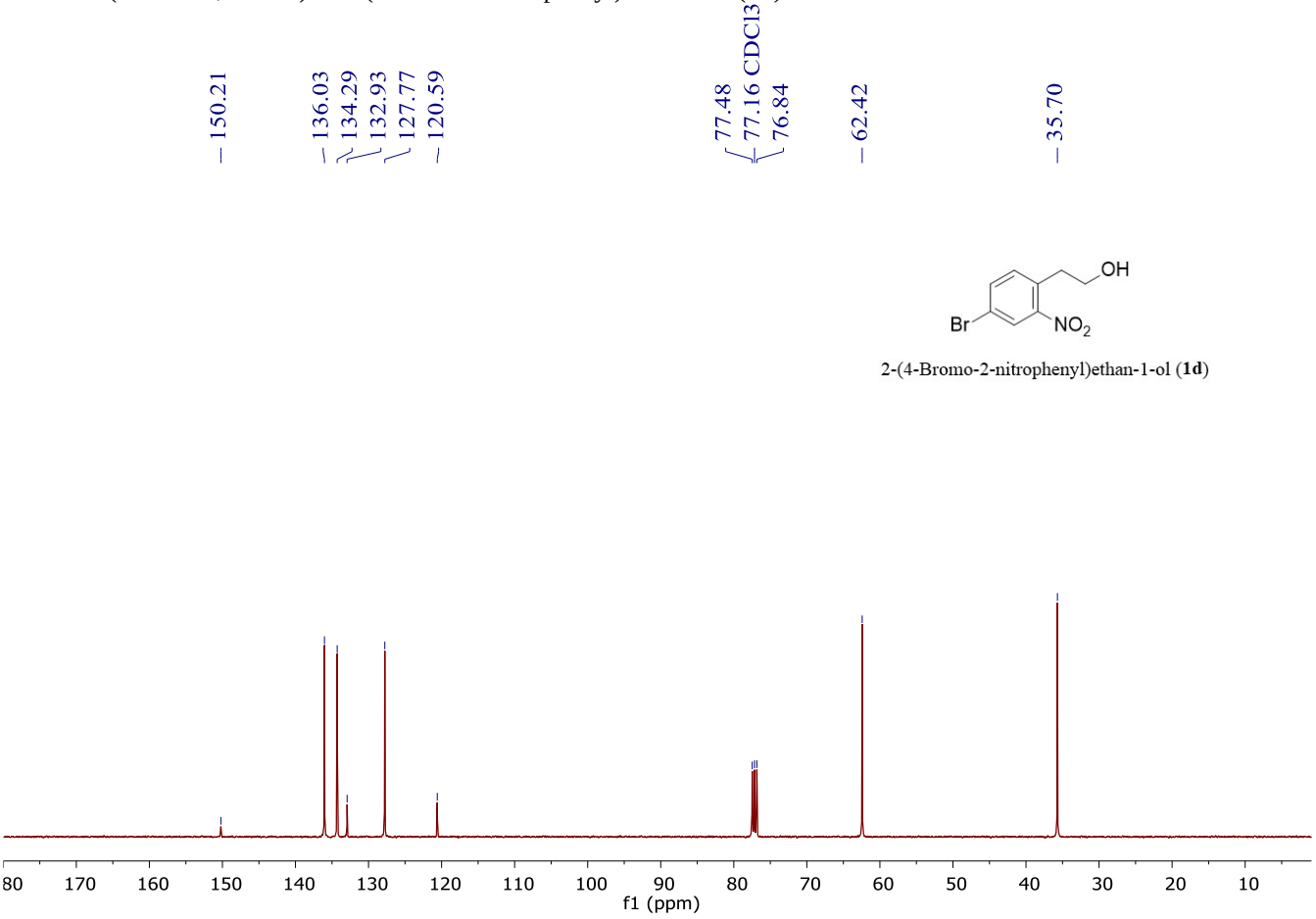


^{1}H NMR (400 MHz, $CDCl_3$) of 2-(4-bromo-2-nitrophenyl)ethan-1-ol (**1d**)



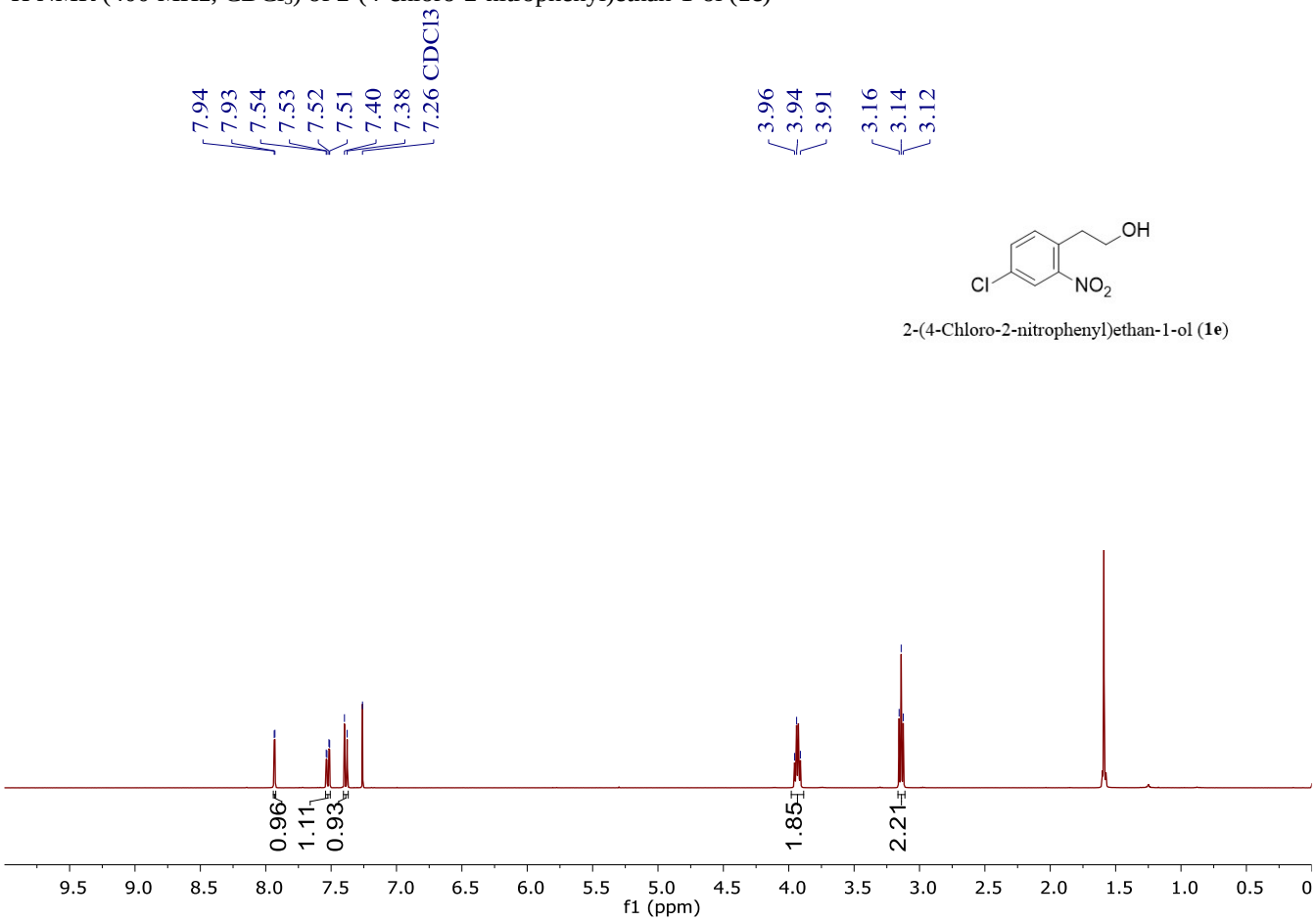
2-(4-Bromo-2-nitrophenyl)ethan-1-ol (**1d**)

^{13}C NMR (100 MHz, $CDCl_3$) of 2-(4-bromo-2-nitrophenyl)ethan-1-ol (**1d**)



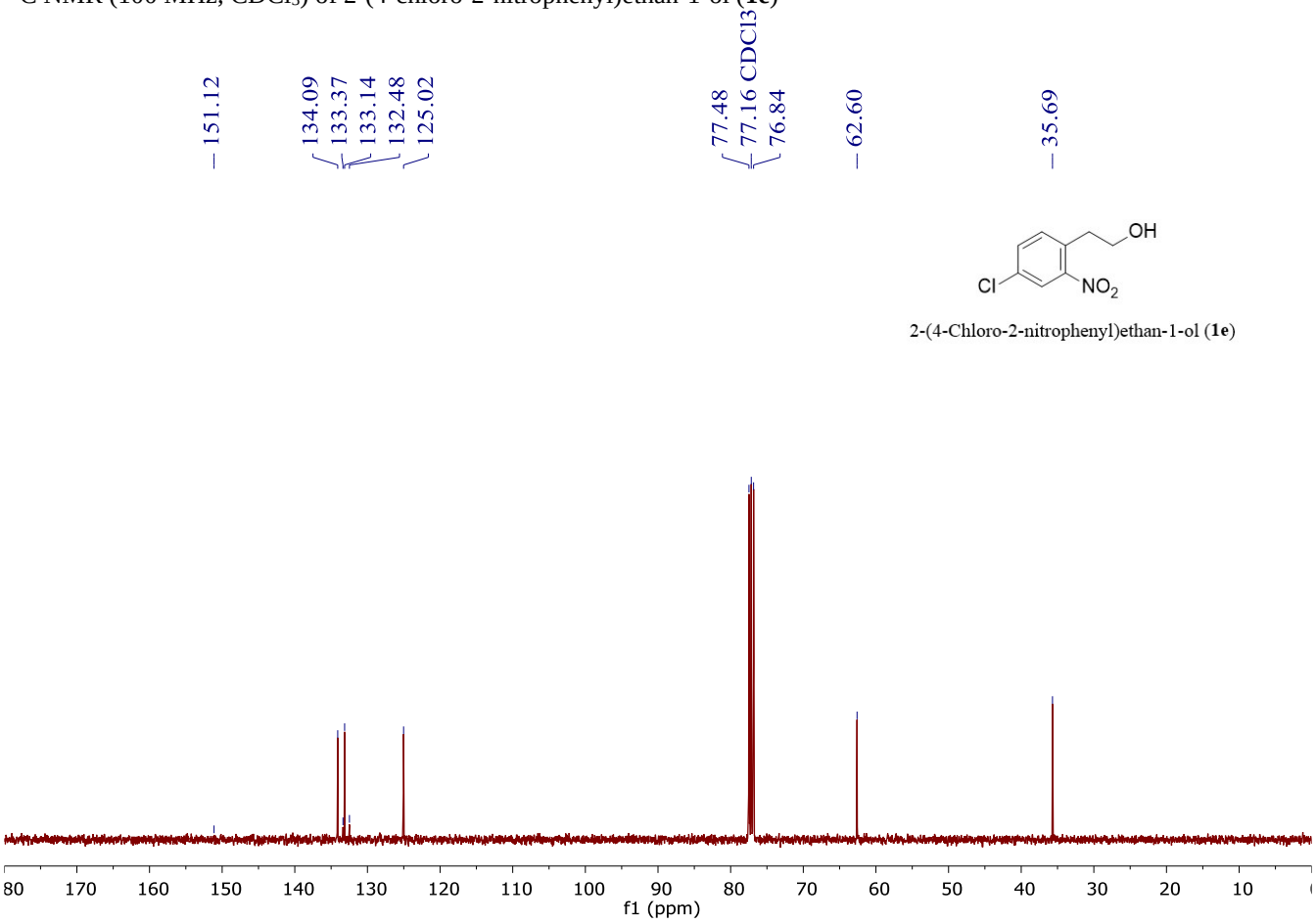
2-(4-Bromo-2-nitrophenyl)ethan-1-ol (**1d**)

^{1}H NMR (400 MHz, $CDCl_3$) of 2-(4-chloro-2-nitrophenyl)ethan-1-ol (**1e**)



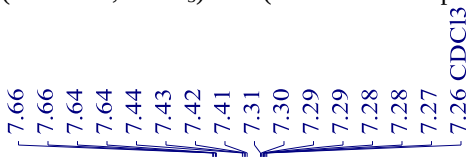
2-(4-Chloro-2-nitrophenyl)ethan-1-ol (**1e**)

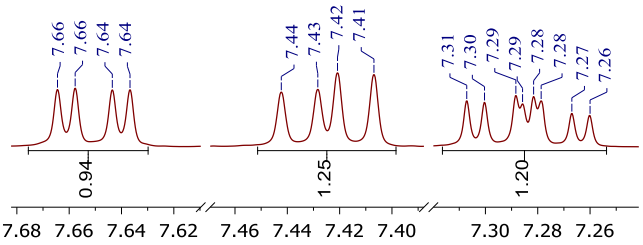
^{13}C NMR (100 MHz, $CDCl_3$) of 2-(4-chloro-2-nitrophenyl)ethan-1-ol (**1e**)

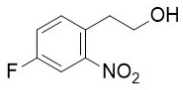


2-(4-Chloro-2-nitrophenyl)ethan-1-ol (**1e**)

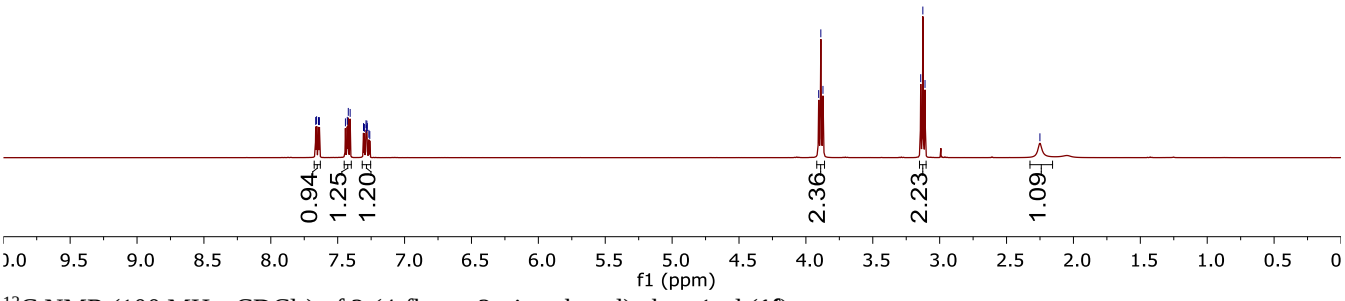
^{1}H NMR (400 MHz, $CDCl_3$) of 2-(4-fluoro-2-nitrophenyl)ethan-1-ol (**1f**)



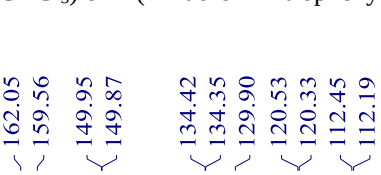


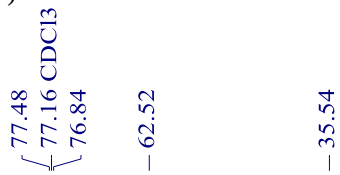


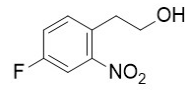
2-(4-Fluoro-2-nitrophenyl)ethan-1-ol (**1f**)



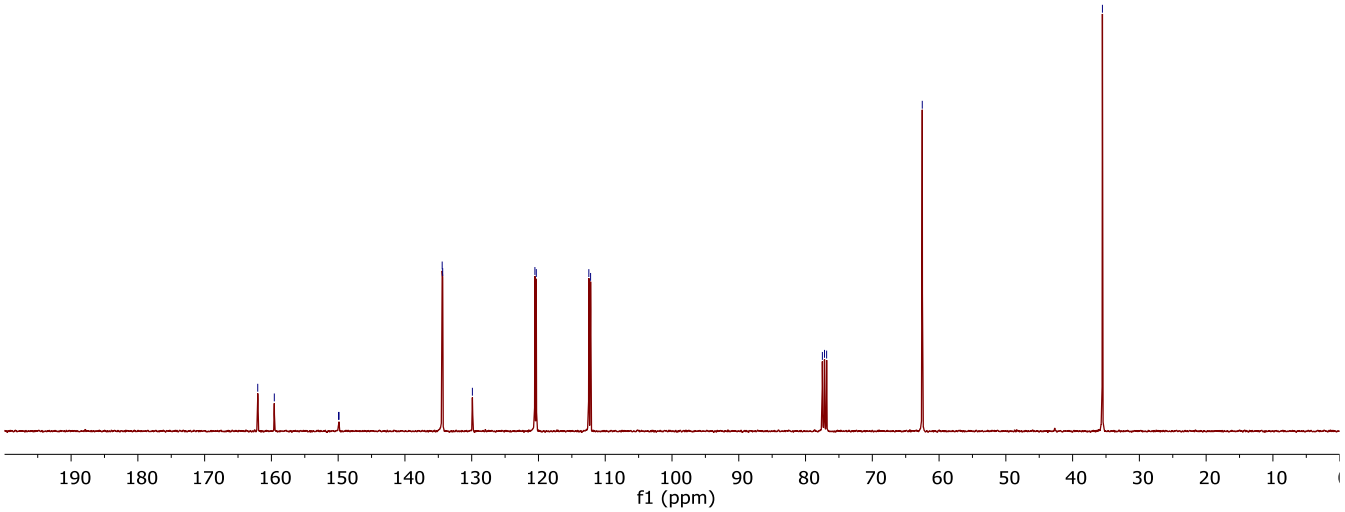
^{13}C NMR (100 MHz, $CDCl_3$) of 2-(4-fluoro-2-nitrophenyl)ethan-1-ol (**1f**)



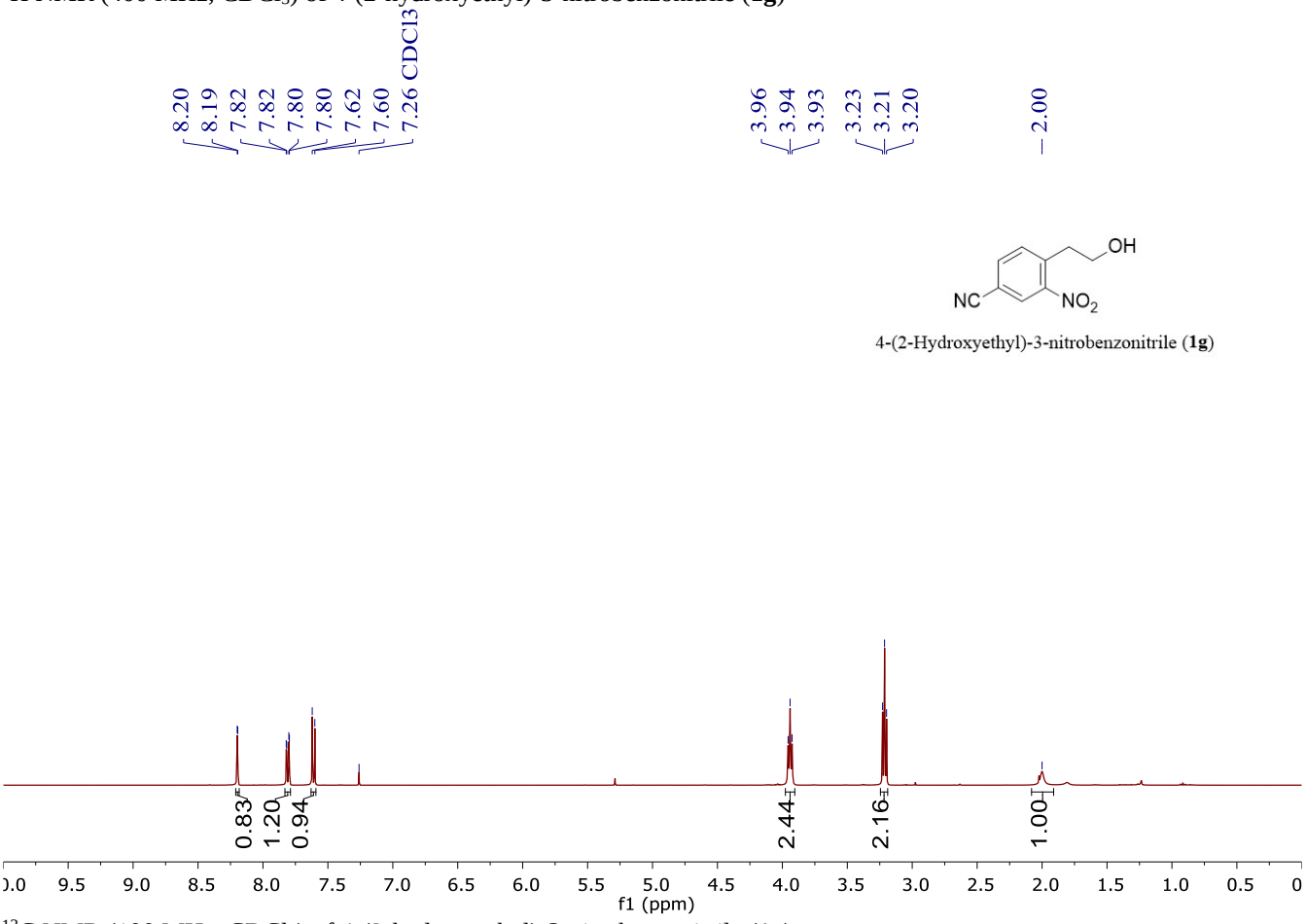




2-(4-Fluoro-2-nitrophenyl)ethan-1-ol (**1f**)

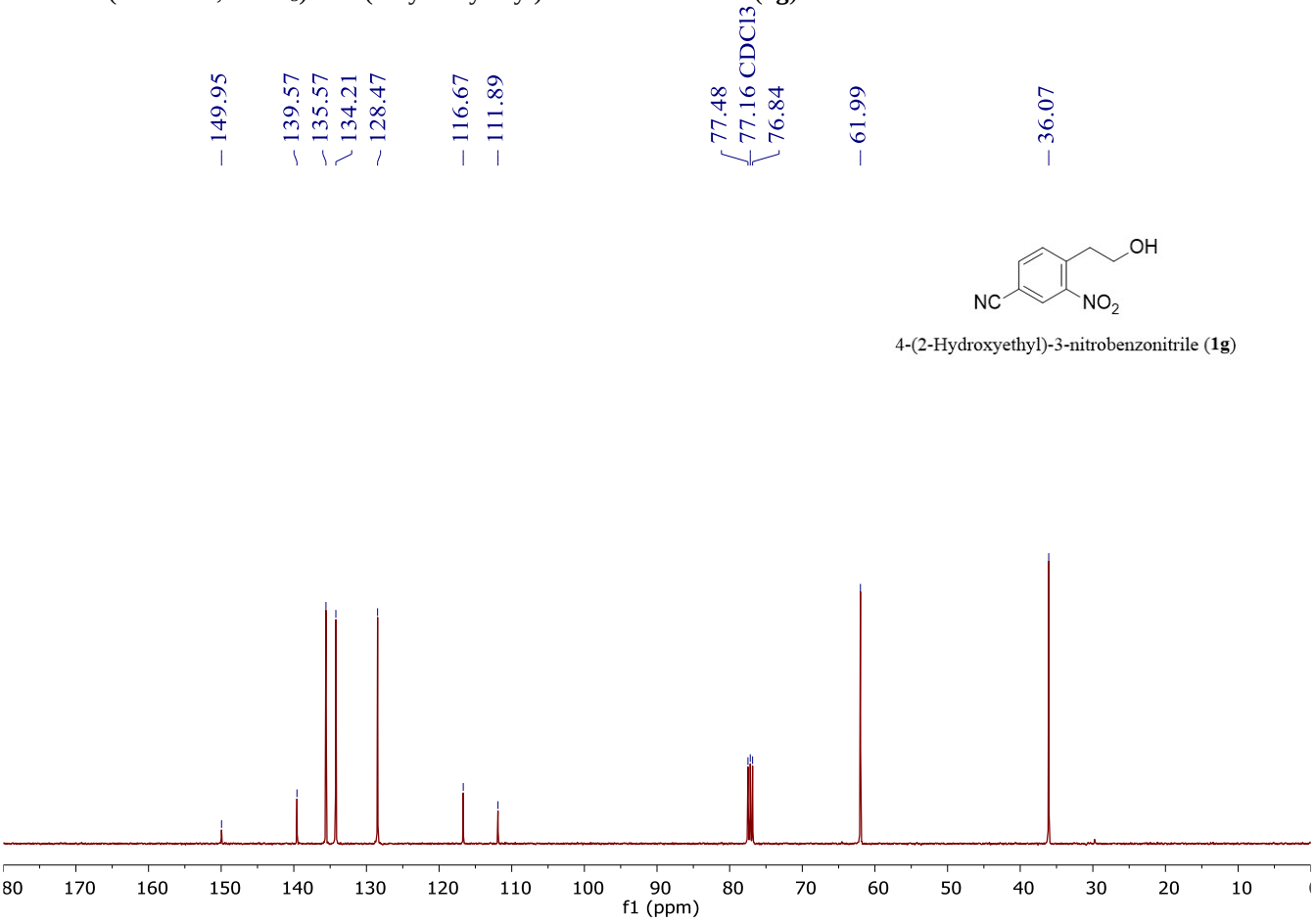


^{1}H NMR (400 MHz, $CDCl_3$) of 4-(2-hydroxyethyl)-3-nitrobenzonitrile (**1g**)



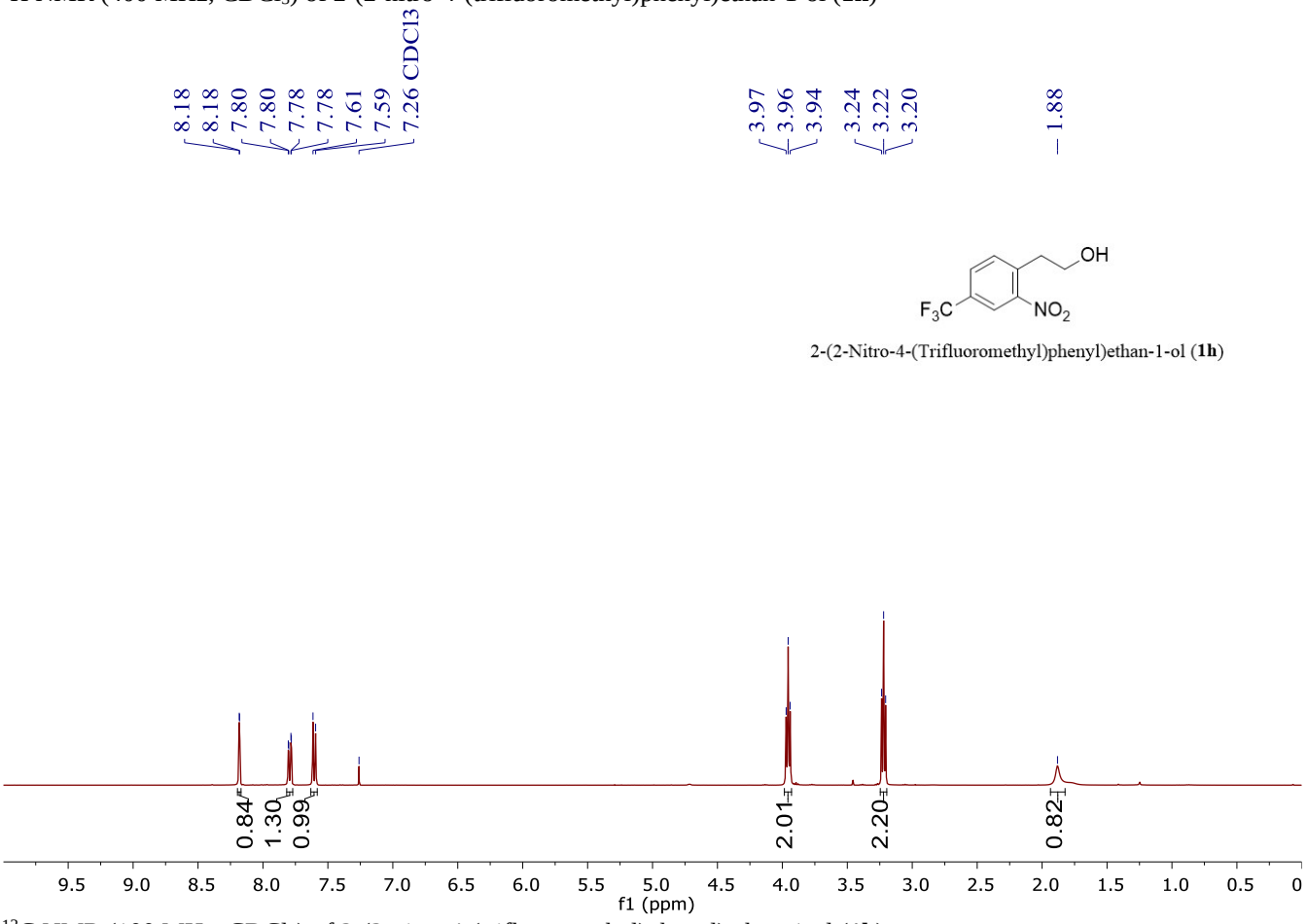
4-(2-Hydroxyethyl)-3-nitrobenzonitrile (**1g**)

^{13}C NMR (100 MHz, $CDCl_3$) of 4-(2-hydroxyethyl)-3-nitrobenzonitrile (**1g**)



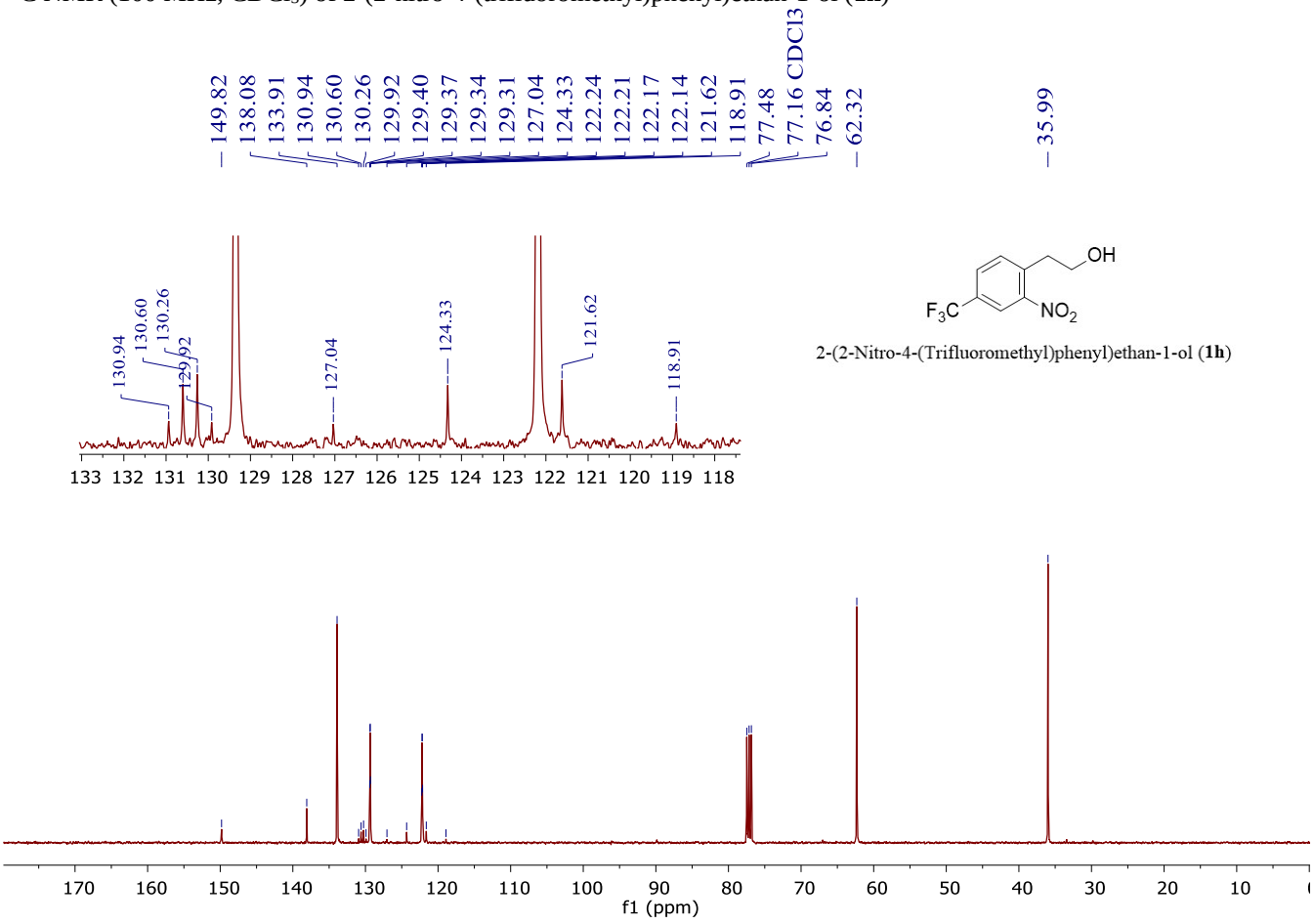
4-(2-Hydroxyethyl)-3-nitrobenzonitrile (**1g**)

^{1}H NMR (400 MHz, $CDCl_3$) of 2-(2-nitro-4-(trifluoromethyl)phenyl)ethan-1-ol (**1h**)



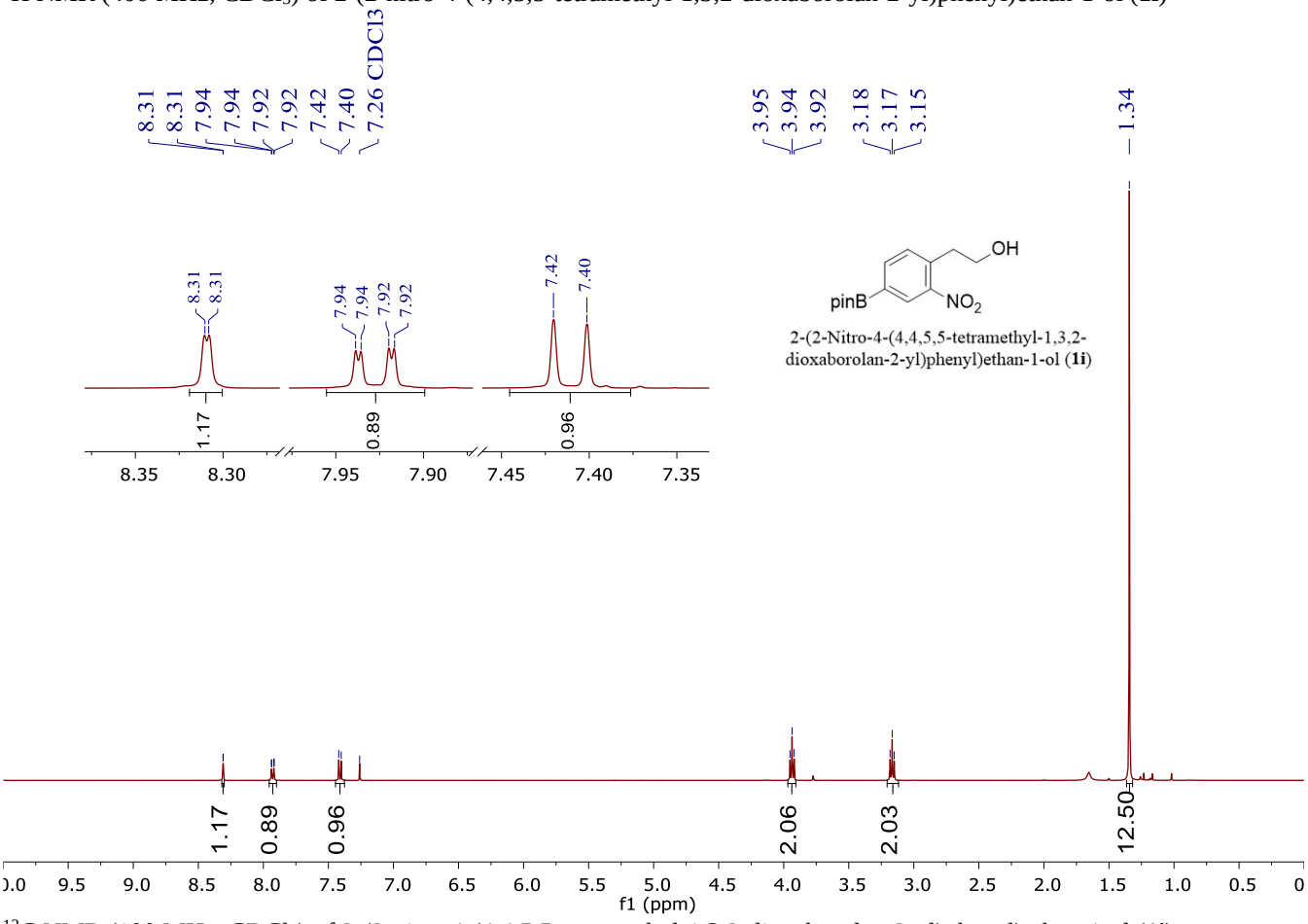
2-(2-Nitro-4-(Trifluoromethyl)phenyl)ethan-1-ol (**1h**)

^{13}C NMR (100 MHz, $CDCl_3$) of 2-(2-nitro-4-(trifluoromethyl)phenyl)ethan-1-ol (**1h**)

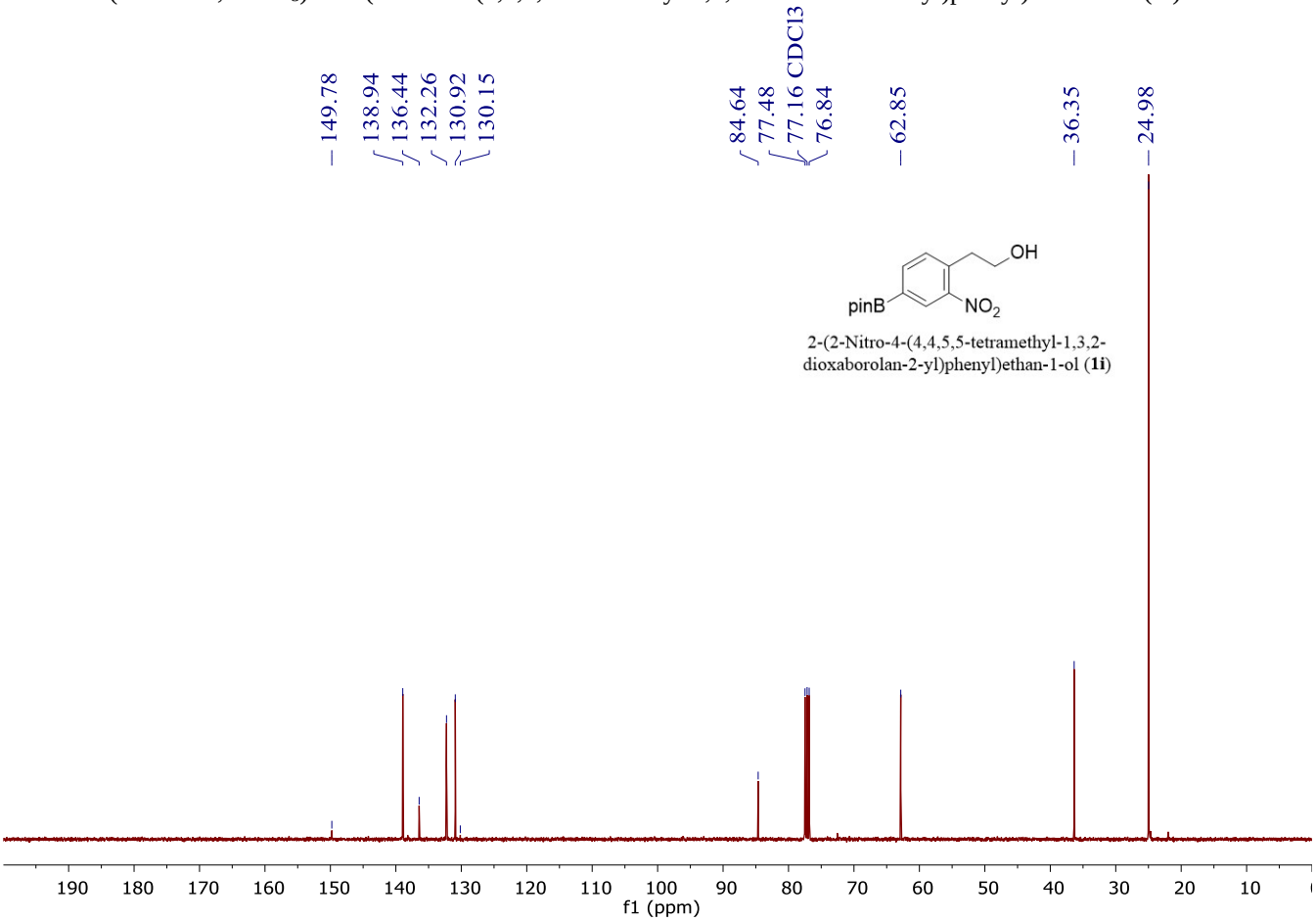


2-(2-Nitro-4-(Trifluoromethyl)phenyl)ethan-1-ol (**1h**)

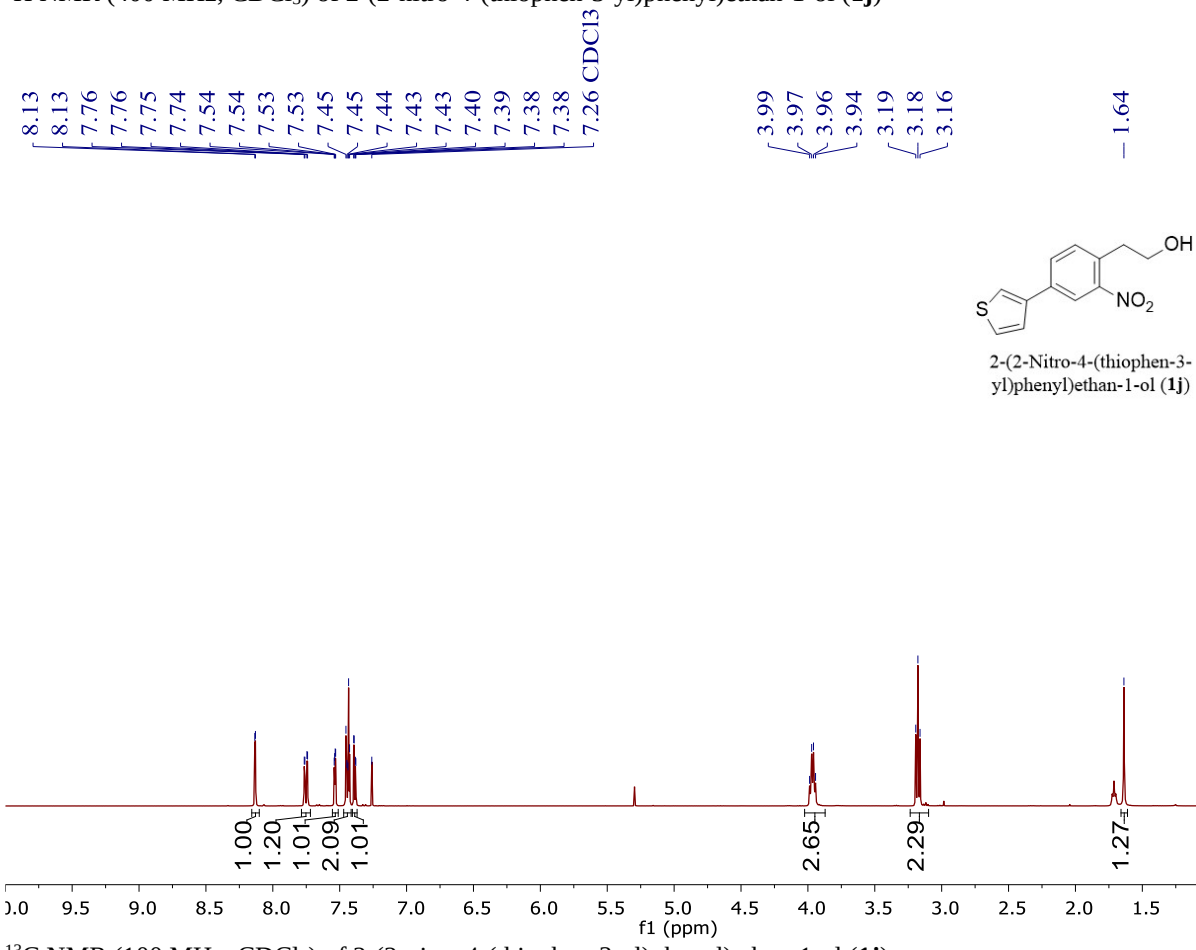
^{1}H NMR (400 MHz, $CDCl_3$) of 2-(2-nitro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol (**1i**)



^{13}C NMR (100 MHz, $CDCl_3$) of 2-(2-nitro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-ol (**1i**)

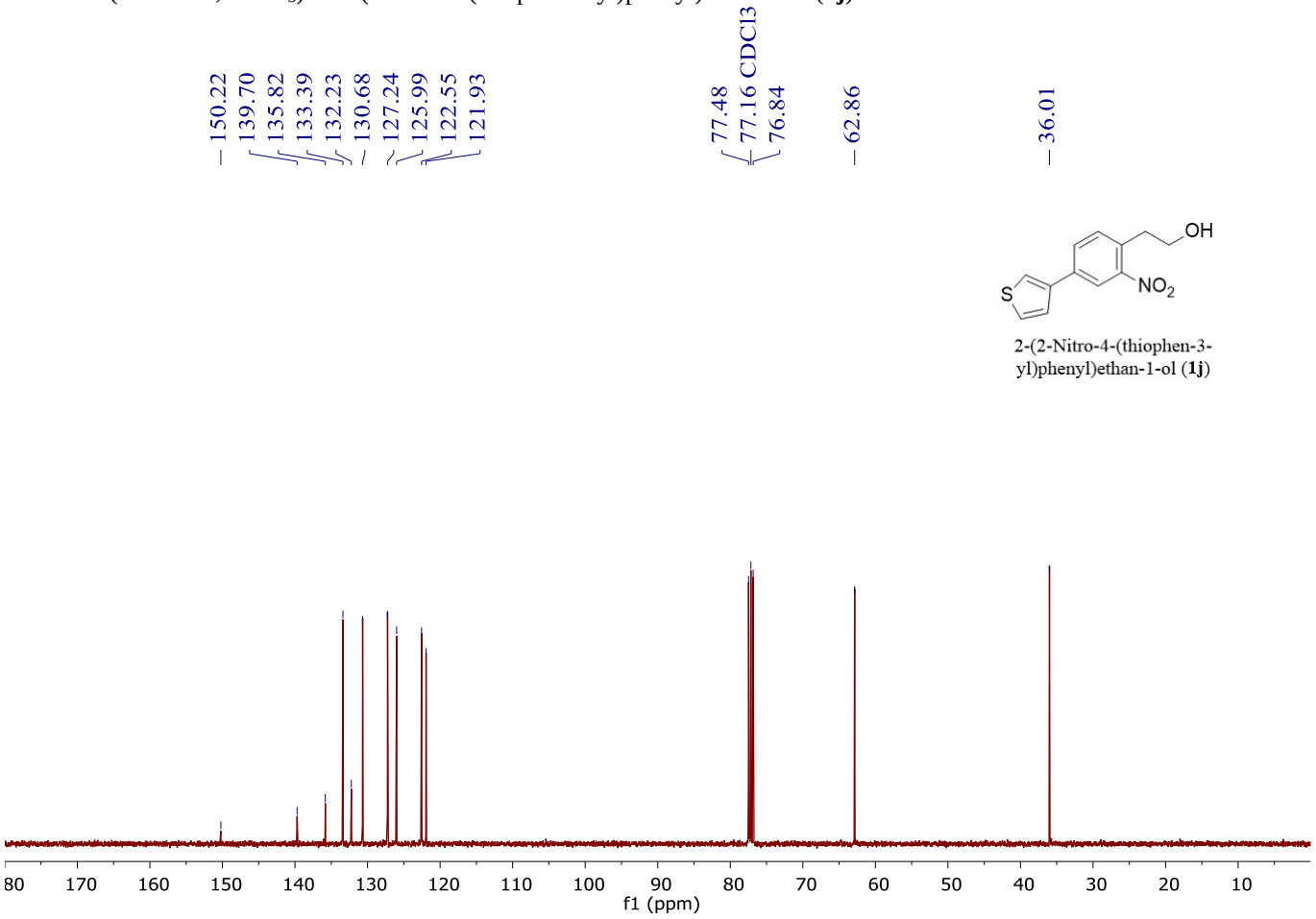


^{1}H NMR (400 MHz, $CDCl_3$) of 2-(2-nitro-4-(thiophen-3-yl)phenyl)ethan-1-ol (**1j**)



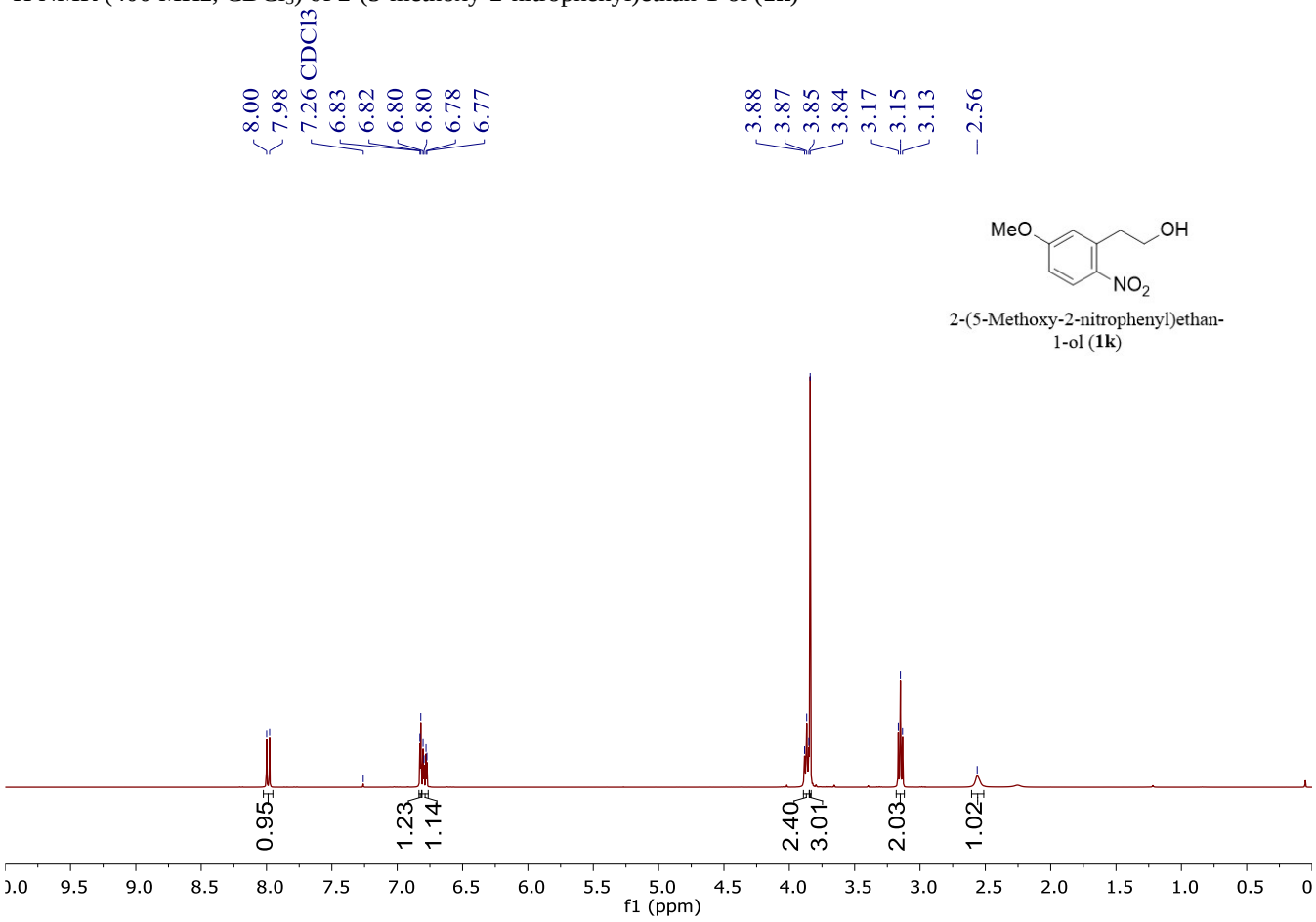
2-(2-Nitro-4-(thiophen-3-yl)phenyl)ethan-1-ol (**1j**)

^{13}C NMR (100 MHz, $CDCl_3$) of 2-(2-nitro-4-(thiophen-3-yl)phenyl)ethan-1-ol (**1j**)



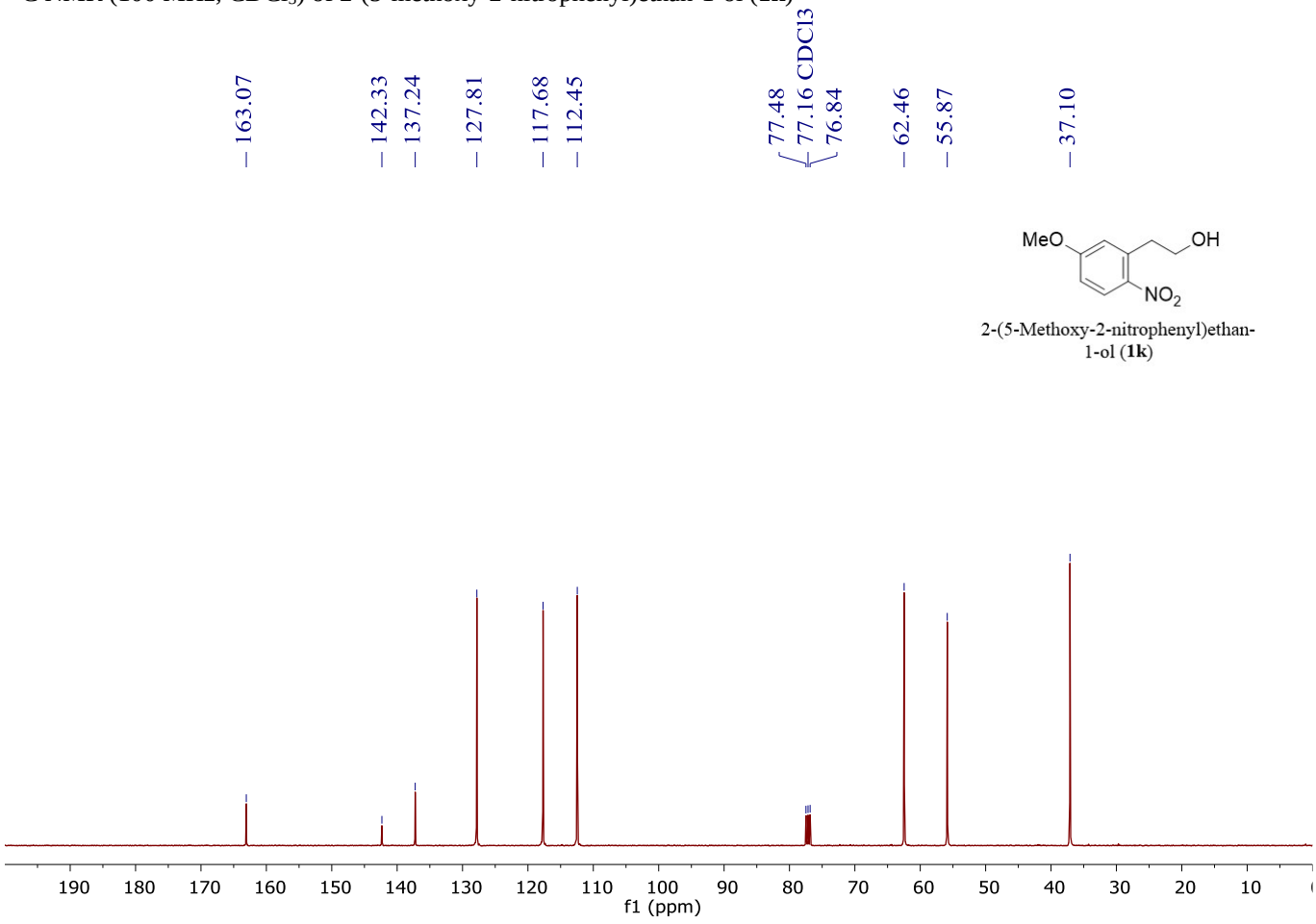
2-(2-Nitro-4-(thiophen-3-yl)phenyl)ethan-1-ol (**1j**)

^{1}H NMR (400 MHz, $CDCl_3$) of 2-(5-methoxy-2-nitrophenyl)ethan-1-ol (**1k**)



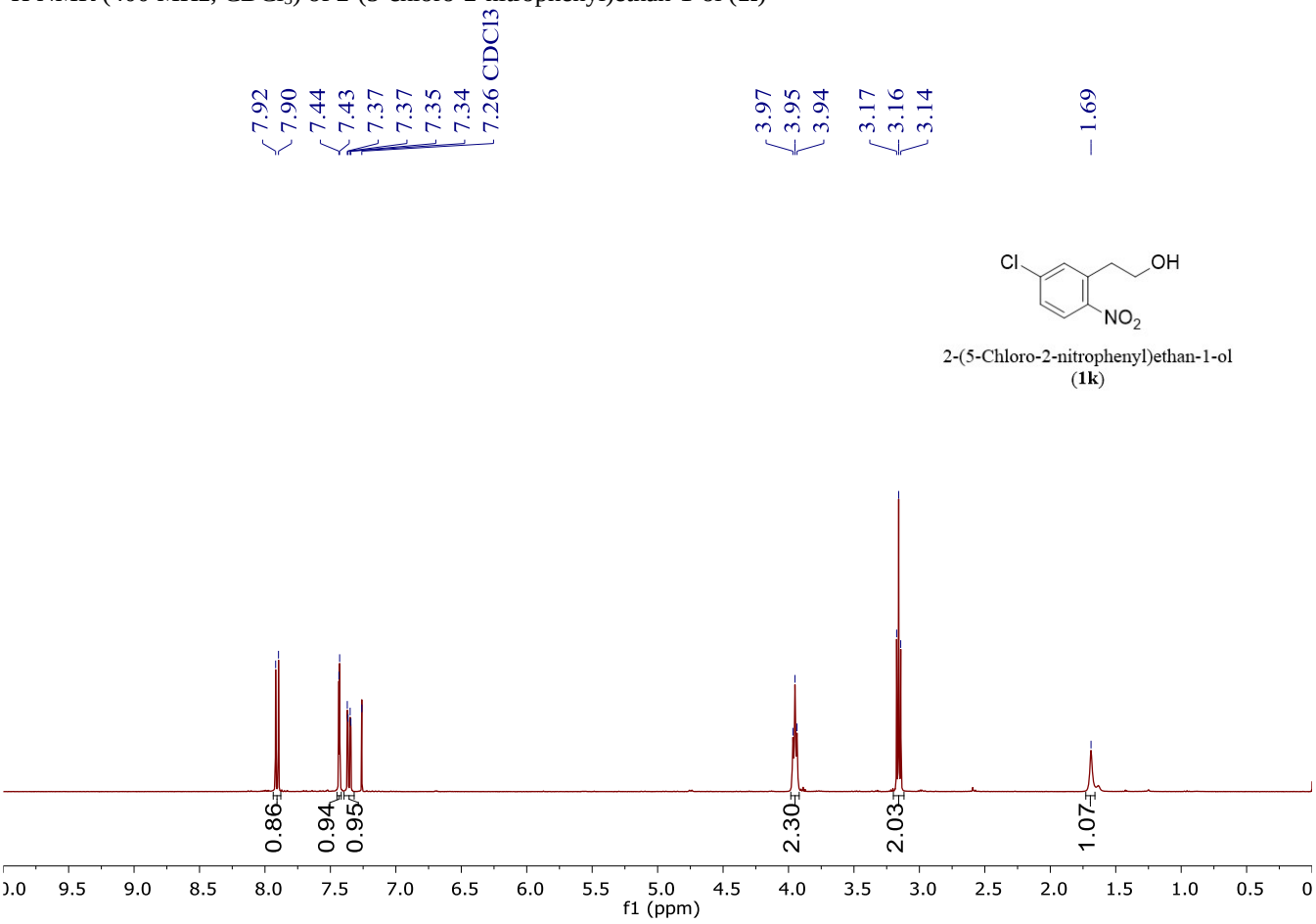
2-(5-Methoxy-2-nitrophenyl)ethan-1-ol (**1k**)

^{13}C NMR (100 MHz, $CDCl_3$) of 2-(5-methoxy-2-nitrophenyl)ethan-1-ol (**1k**)



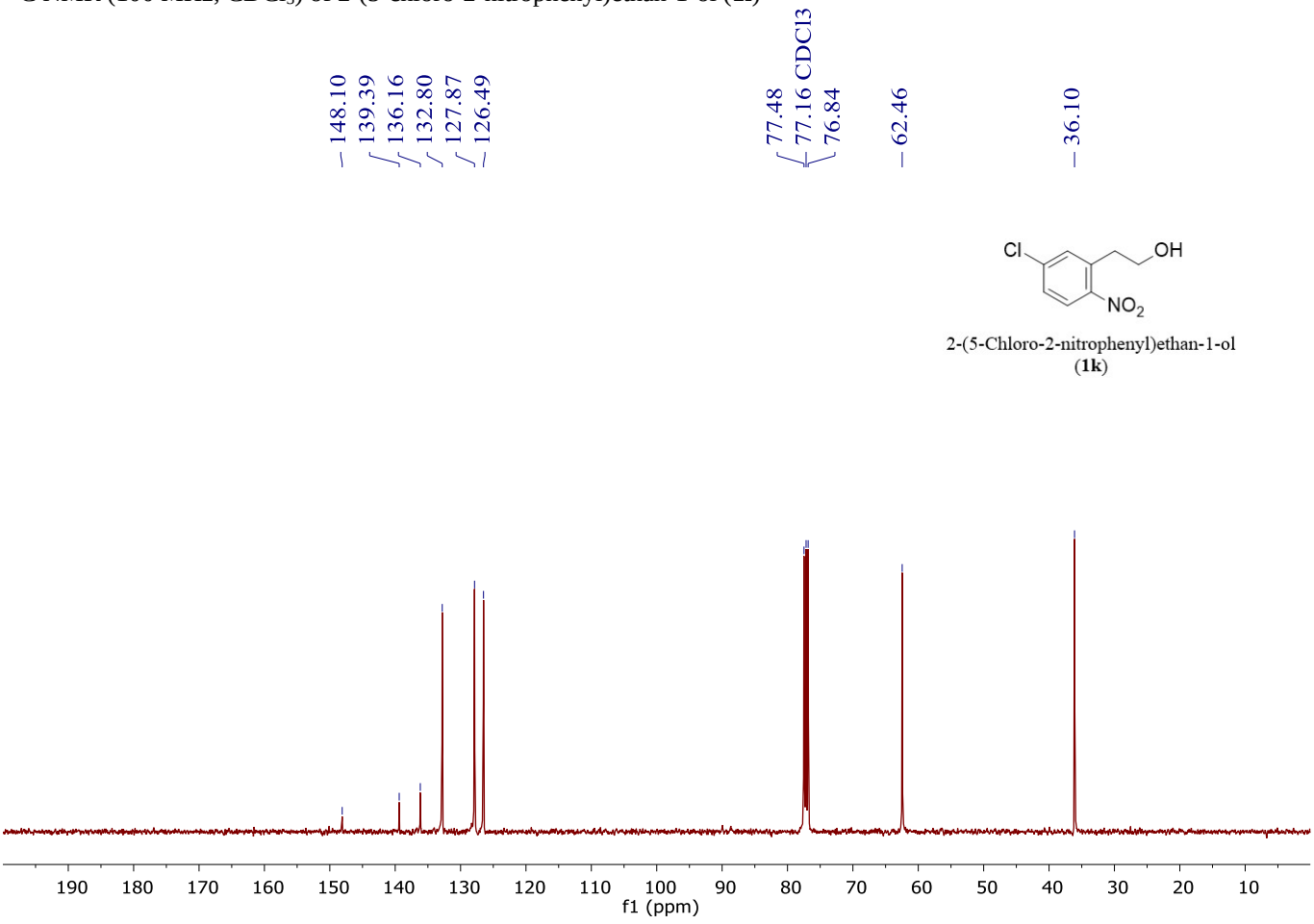
2-(5-Methoxy-2-nitrophenyl)ethan-1-ol (**1k**)

^{1}H NMR (400 MHz, $CDCl_3$) of 2-(5-chloro-2-nitrophenyl)ethan-1-ol (**1l**)



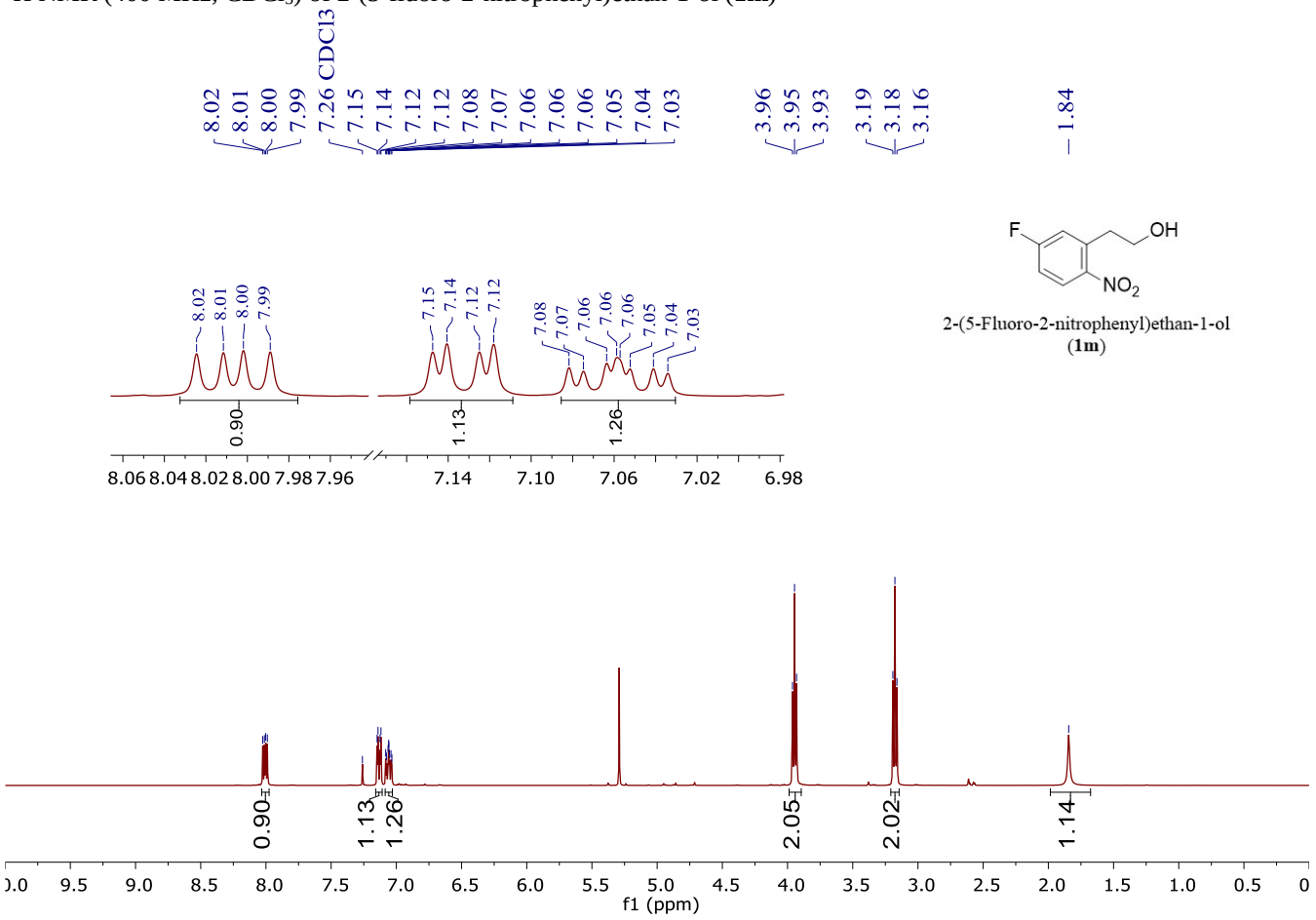
2-(5-Chloro-2-nitrophenyl)ethan-1-ol
(**1k**)

^{13}C NMR (100 MHz, $CDCl_3$) of 2-(5-chloro-2-nitrophenyl)ethan-1-ol (**1l**)



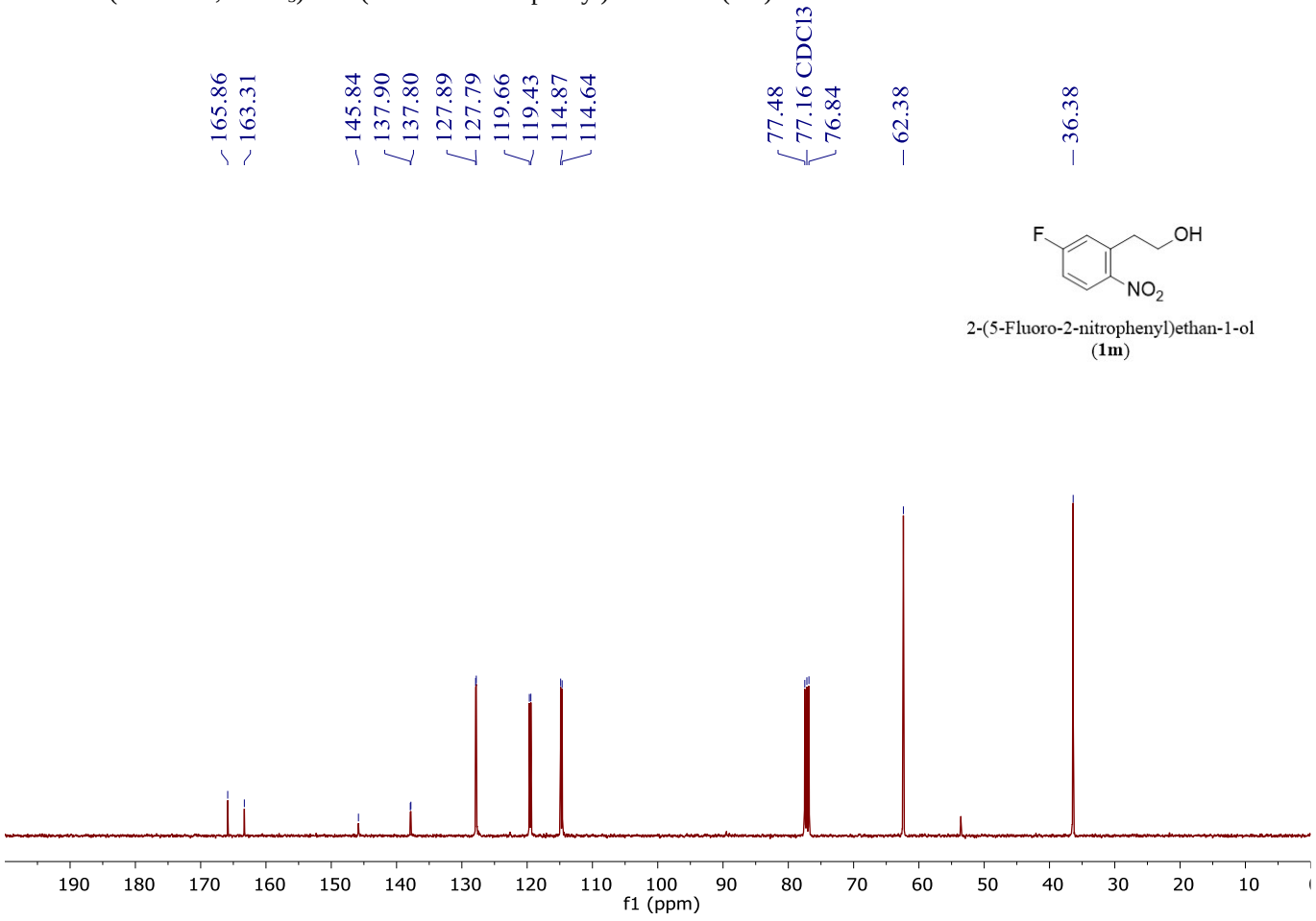
2-(5-Chloro-2-nitrophenyl)ethan-1-ol
(**1k**)

^{1}H NMR (400 MHz, $CDCl_3$) of 2-(5-fluoro-2-nitrophenyl)ethan-1-ol (**1m**)



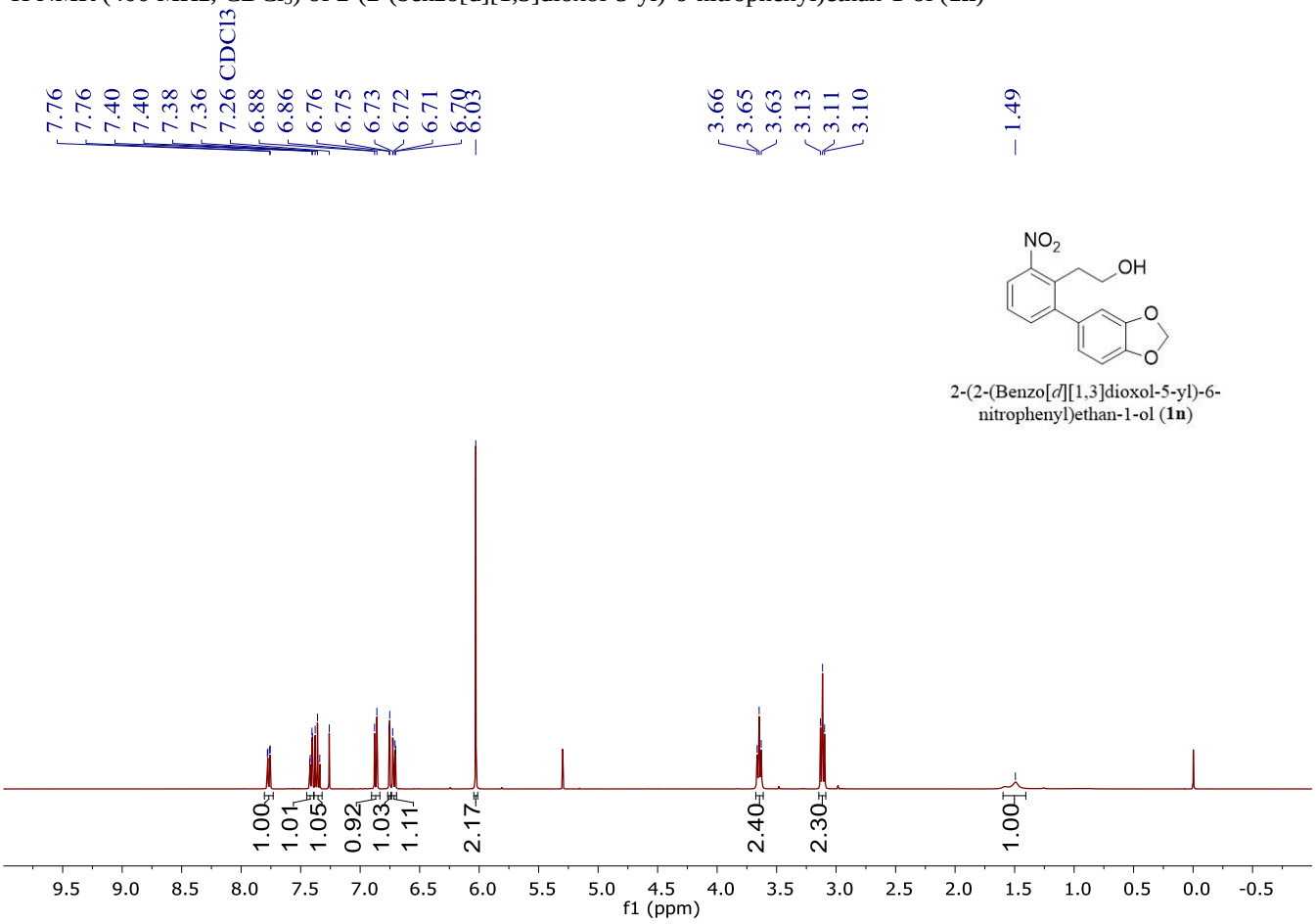
2-(5-Fluoro-2-nitrophenyl)ethan-1-ol
(**1m**)

^{13}C NMR (100 MHz, $CDCl_3$) of 2-(5-fluoro-2-nitrophenyl)ethan-1-ol (**1m**)



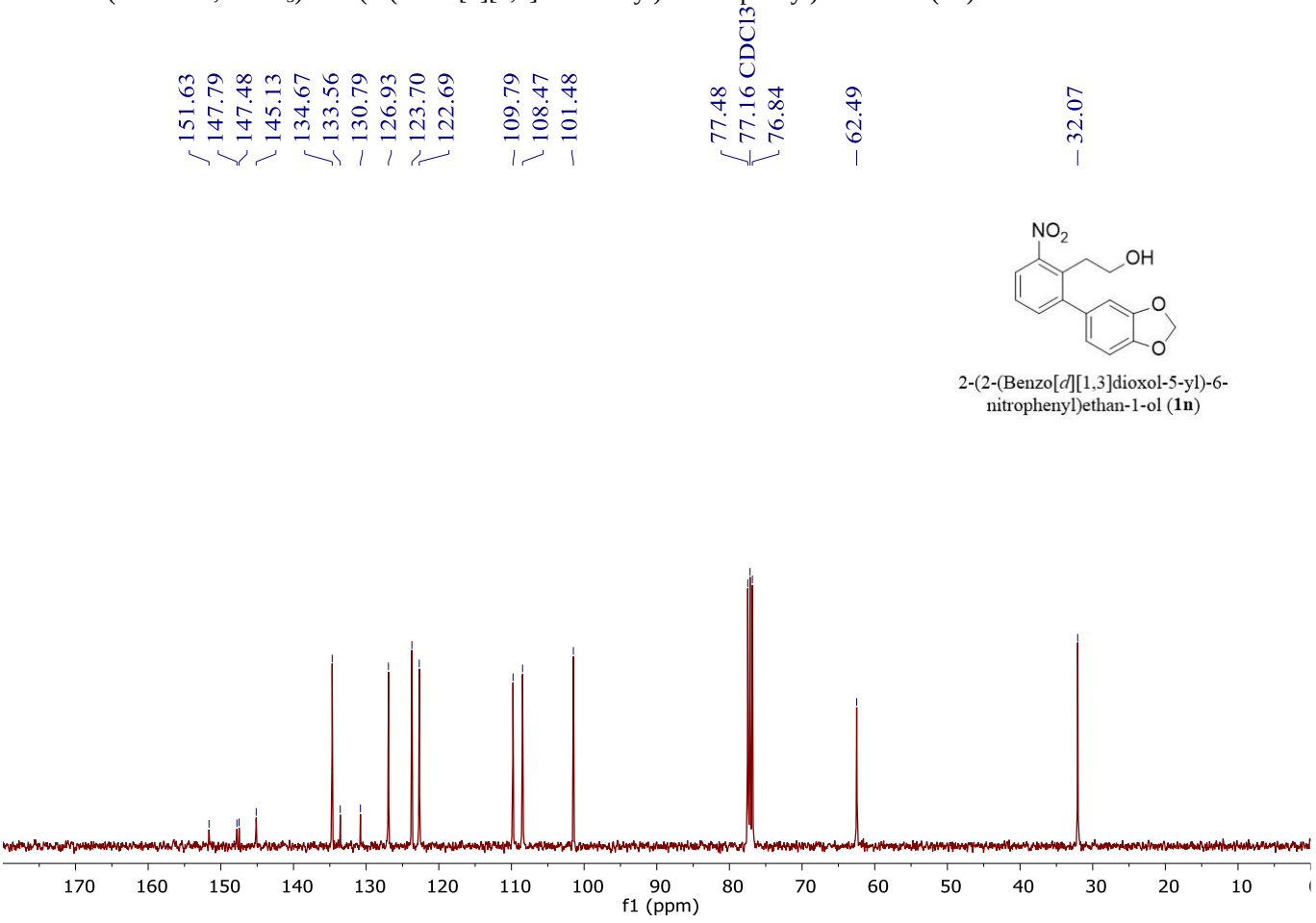
2-(5-Fluoro-2-nitrophenyl)ethan-1-ol
(**1m**)

^{1}H NMR (400 MHz, $CDCl_3$) of 2-(2-(benzo[d][1,3]dioxol-5-yl)-6-nitrophenyl)ethan-1-ol (**1n**)



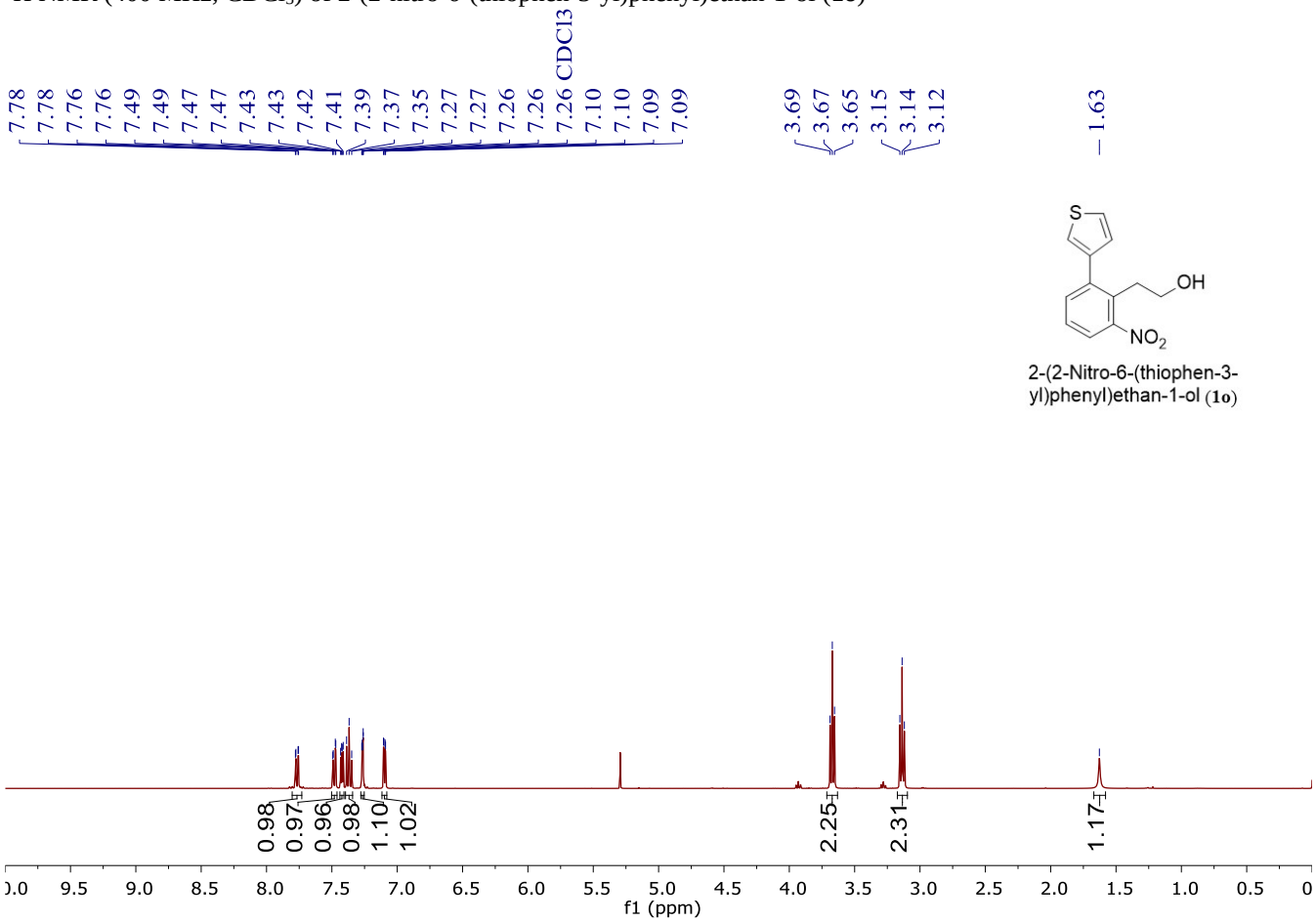
2-(2-(Benzo[*d*][1,3]dioxol-5-yl)-6-nitrophenyl)ethan-1-ol (**1n**)

^{13}C NMR (100 MHz, $CDCl_3$) of 2-(2-(benzo[d][1,3]dioxol-5-yl)-6-nitrophenyl)ethan-1-ol (**1n**)

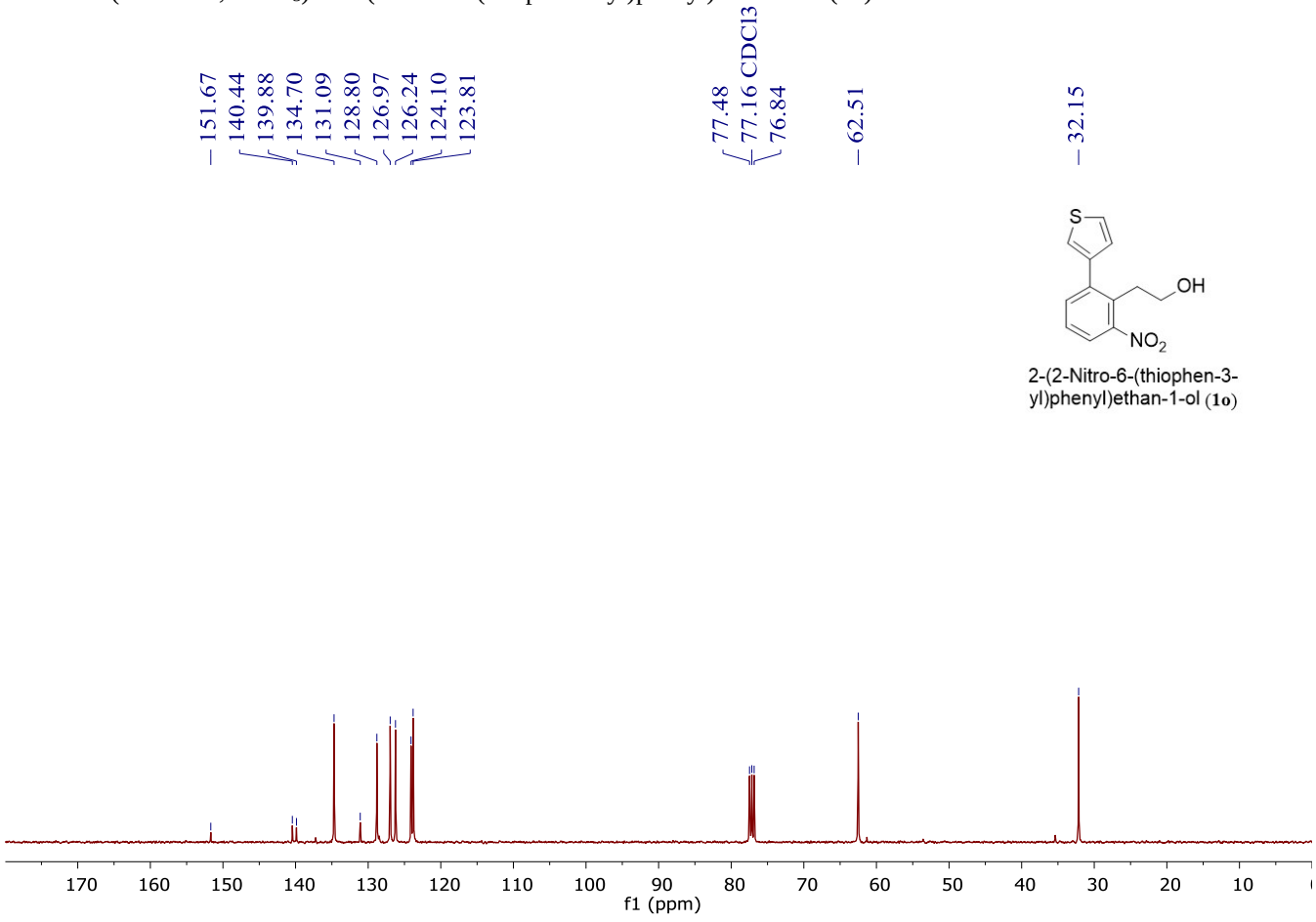


2-(2-(Benzo[*d*][1,3]dioxol-5-yl)-6-nitrophenyl)ethan-1-ol (**1n**)

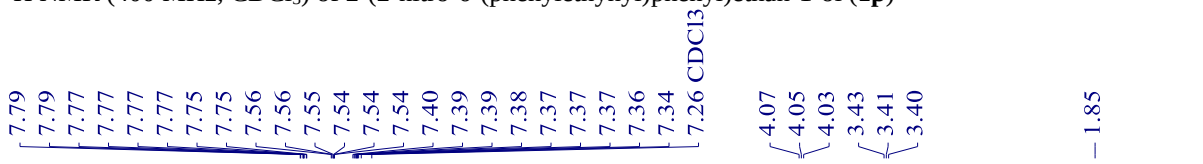
^{1}H NMR (400 MHz, $CDCl_3$) of 2-(2-nitro-6-(thiophen-3-yl)phenyl)ethan-1-ol (**1o**)

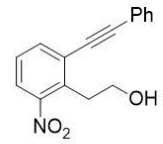


^{13}C NMR (100 MHz, $CDCl_3$) of 2-(2-nitro-6-(thiophen-3-yl)phenyl)ethan-1-ol (**1o**)

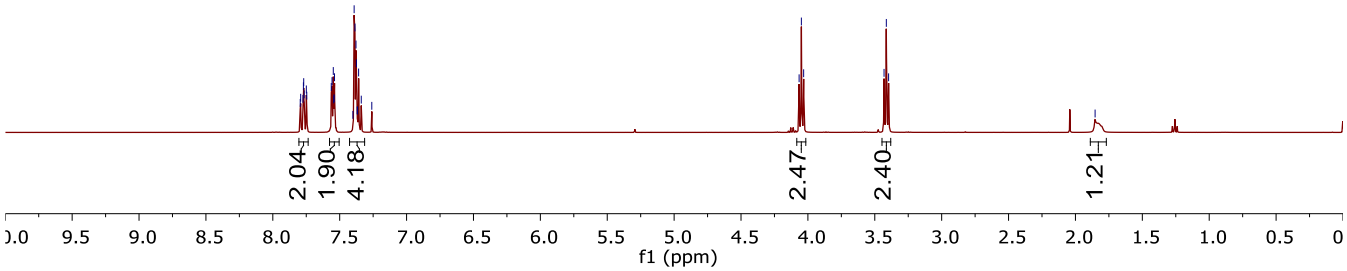


^{1}H NMR (400 MHz, $CDCl_3$) of 2-(2-nitro-6-(phenylethynyl)phenyl)ethan-1-ol (**1p**)

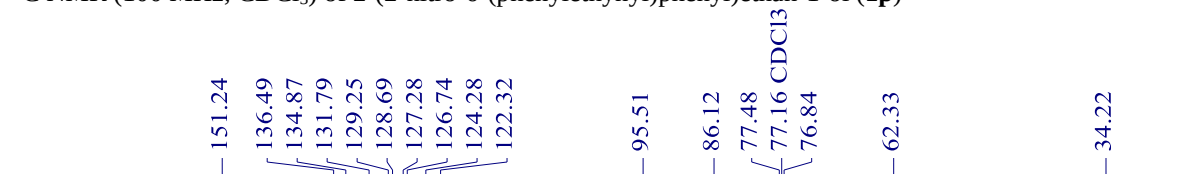


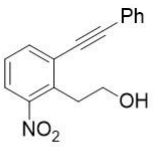


2-(2-Nitro-6-(phenylethynyl)phenyl)ethan-1-ol (**1p**)

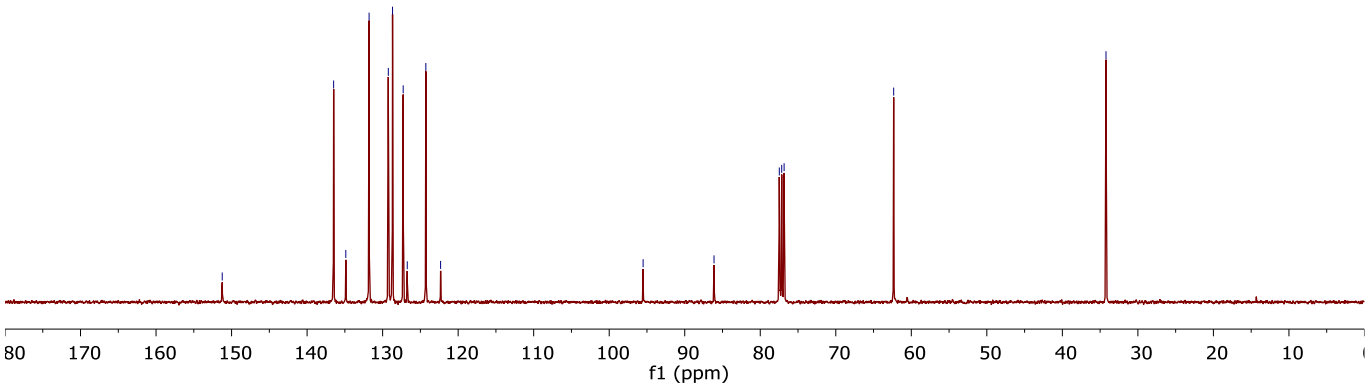


^{13}C NMR (100 MHz, $CDCl_3$) of 2-(2-nitro-6-(phenylethynyl)phenyl)ethan-1-ol (**1p**)

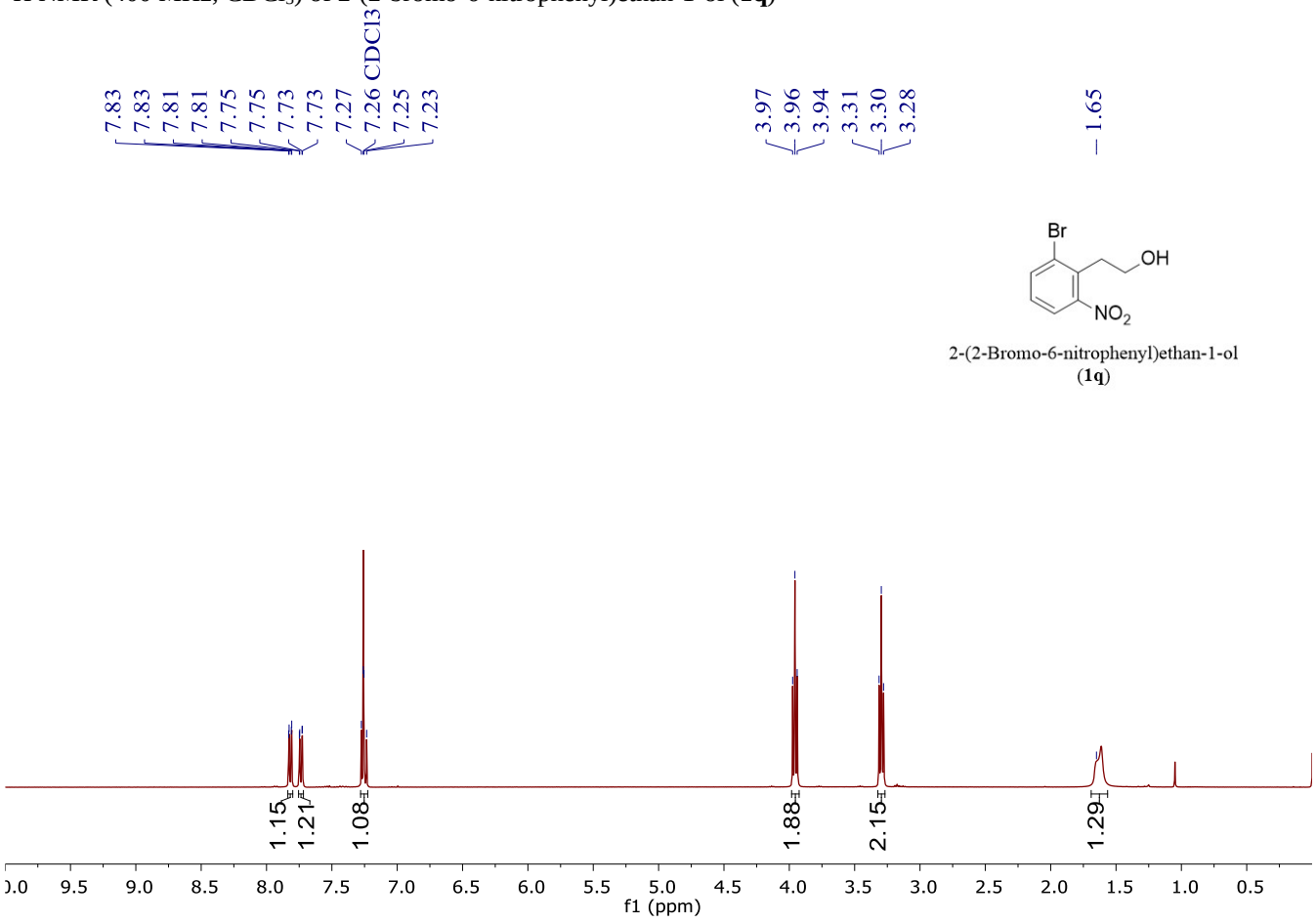




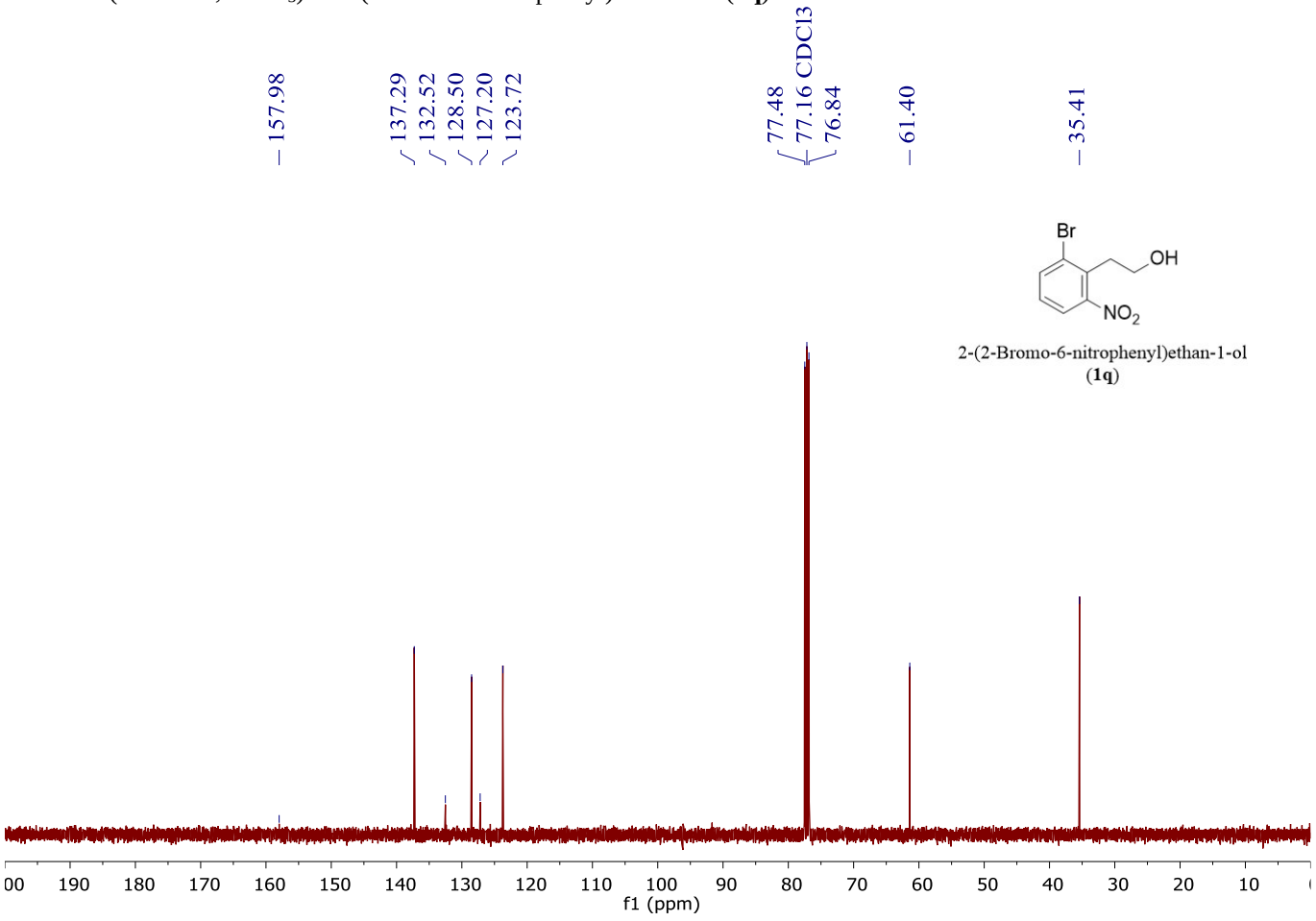
2-(2-Nitro-6-(phenylethynyl)phenyl)ethan-1-ol (**1p**)



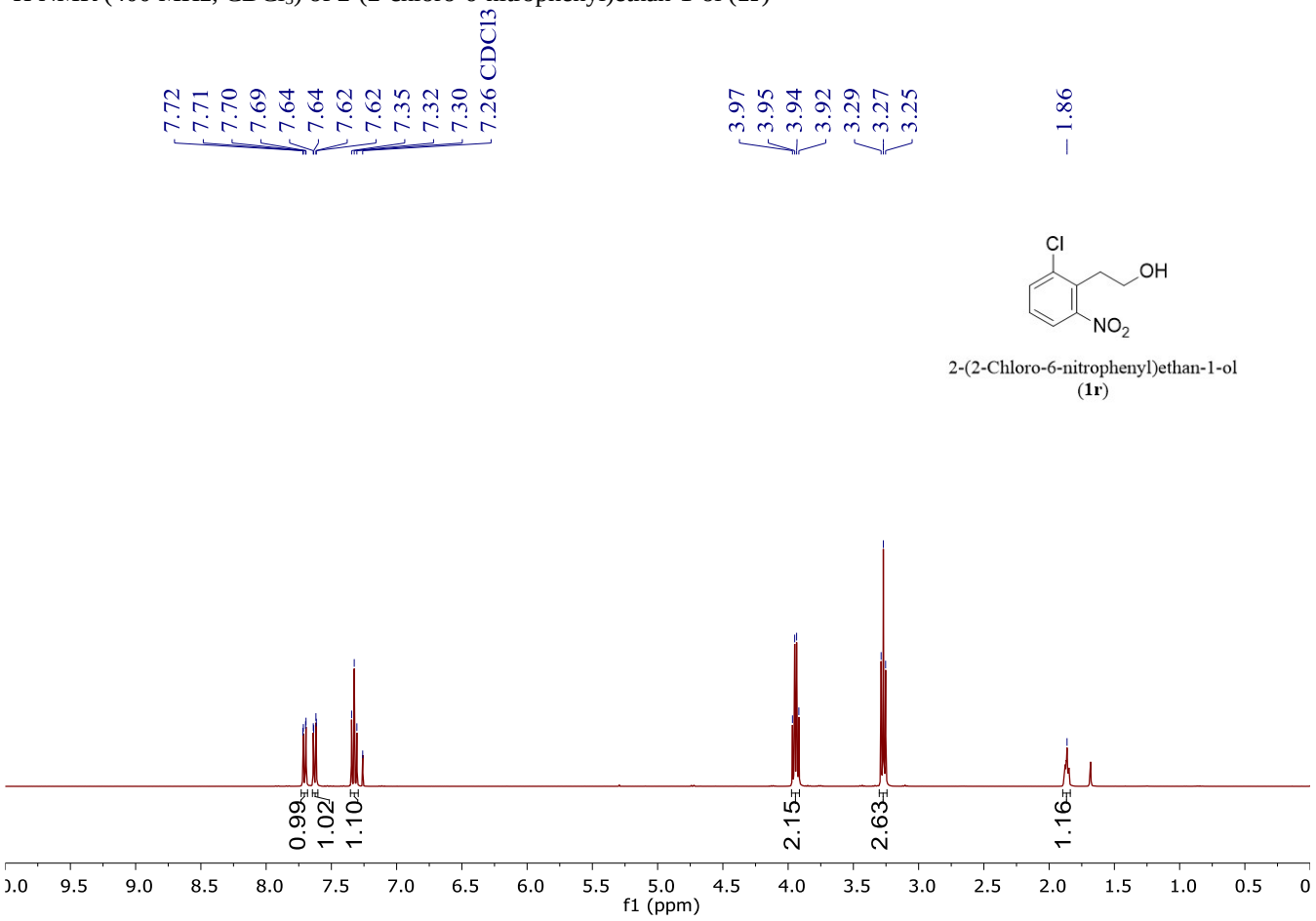
^{1}H NMR (400 MHz, $CDCl_3$) of 2-(2-bromo-6-nitrophenyl)ethan-1-ol (**1q**)



^{13}C NMR (100 MHz, $CDCl_3$) of 2-(2-bromo-6-nitrophenyl)ethan-1-ol (**1q**)

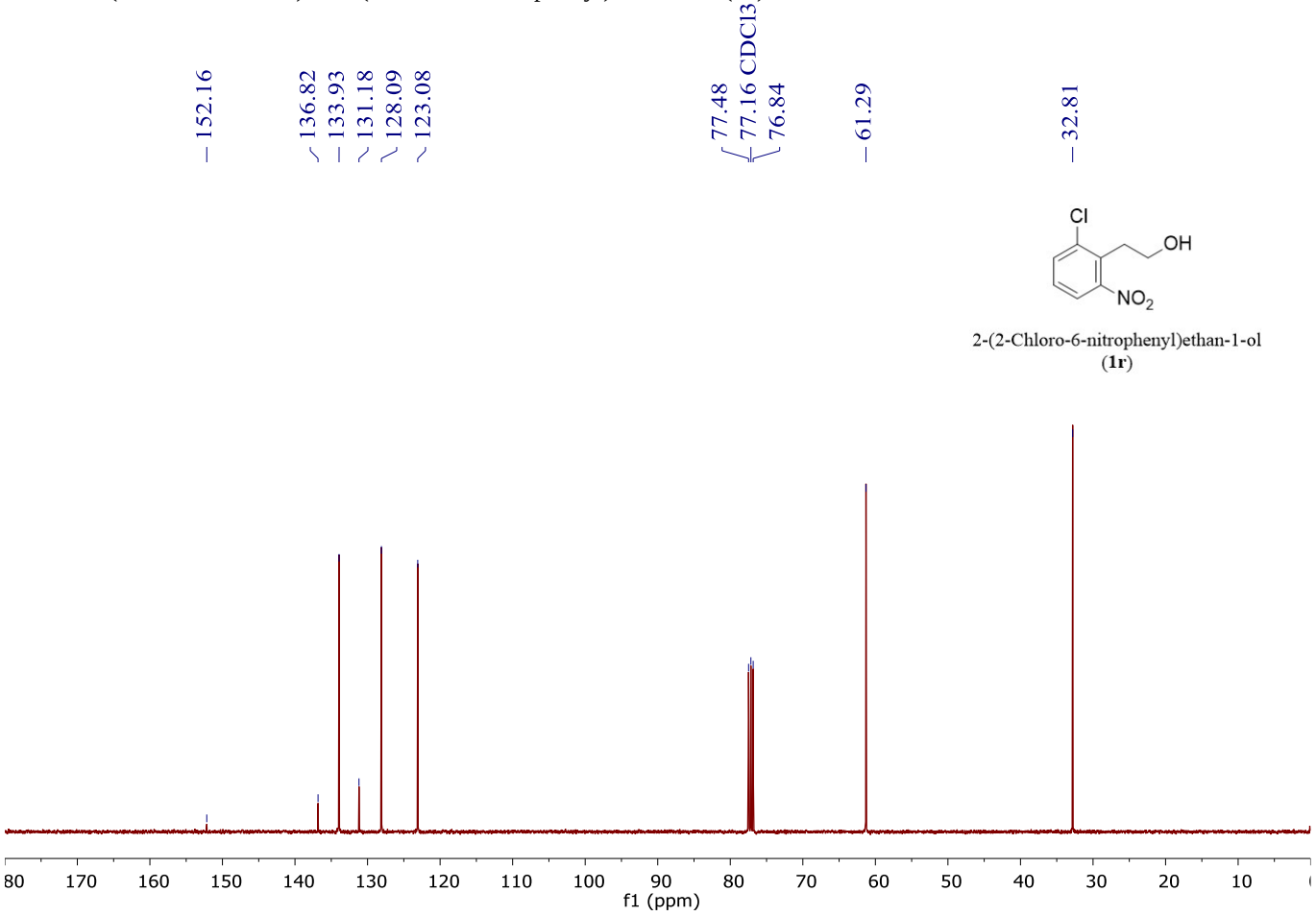


^{1}H NMR (400 MHz, $CDCl_3$) of 2-(2-chloro-6-nitrophenyl)ethan-1-ol (**1r**)



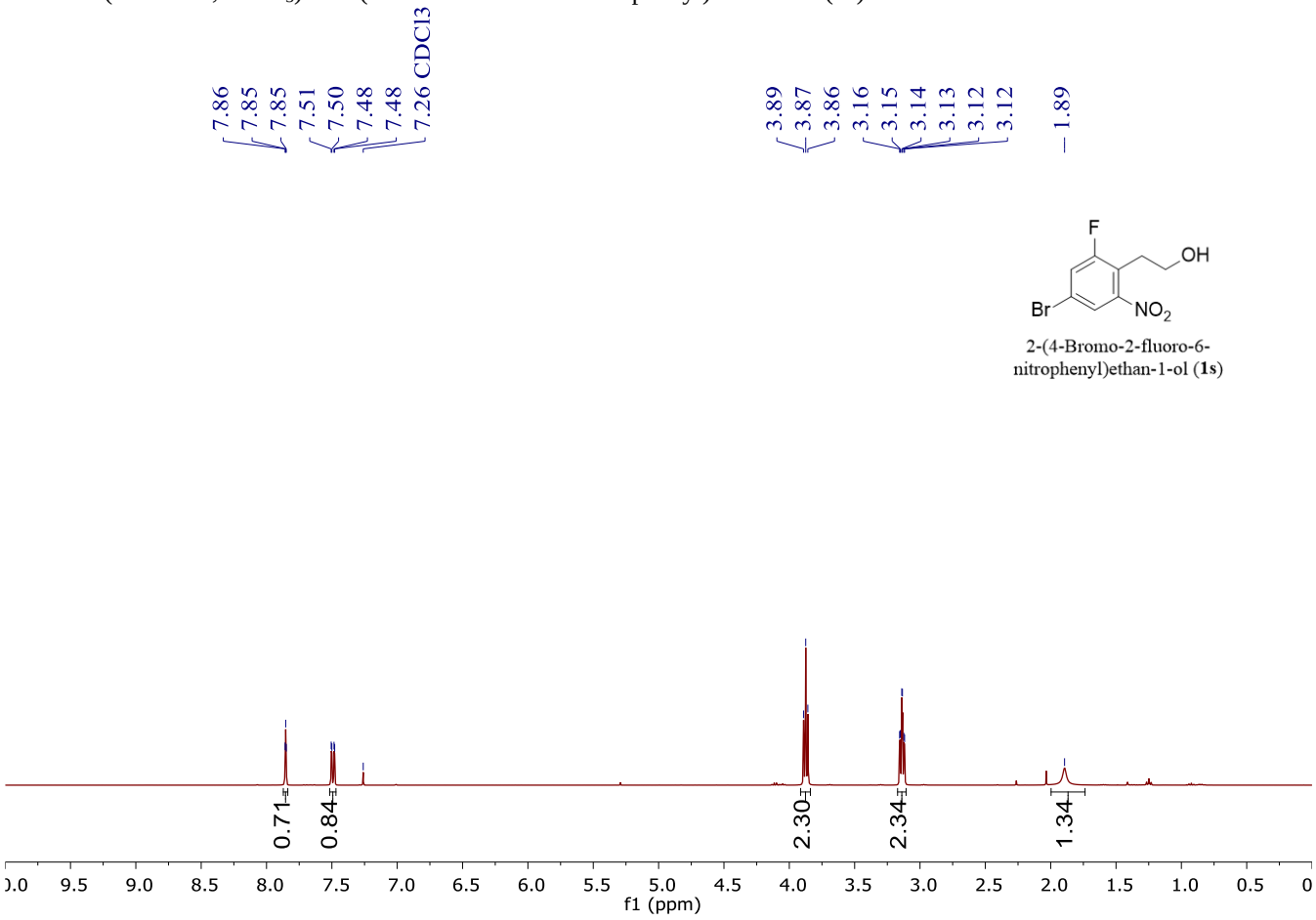
2-(2-Chloro-6-nitrophenyl)ethan-1-ol
(**1r**)

^{13}C NMR (100 MHz, $CDCl_3$) of 2-(2-chloro-6-nitrophenyl)ethan-1-ol (**1r**)

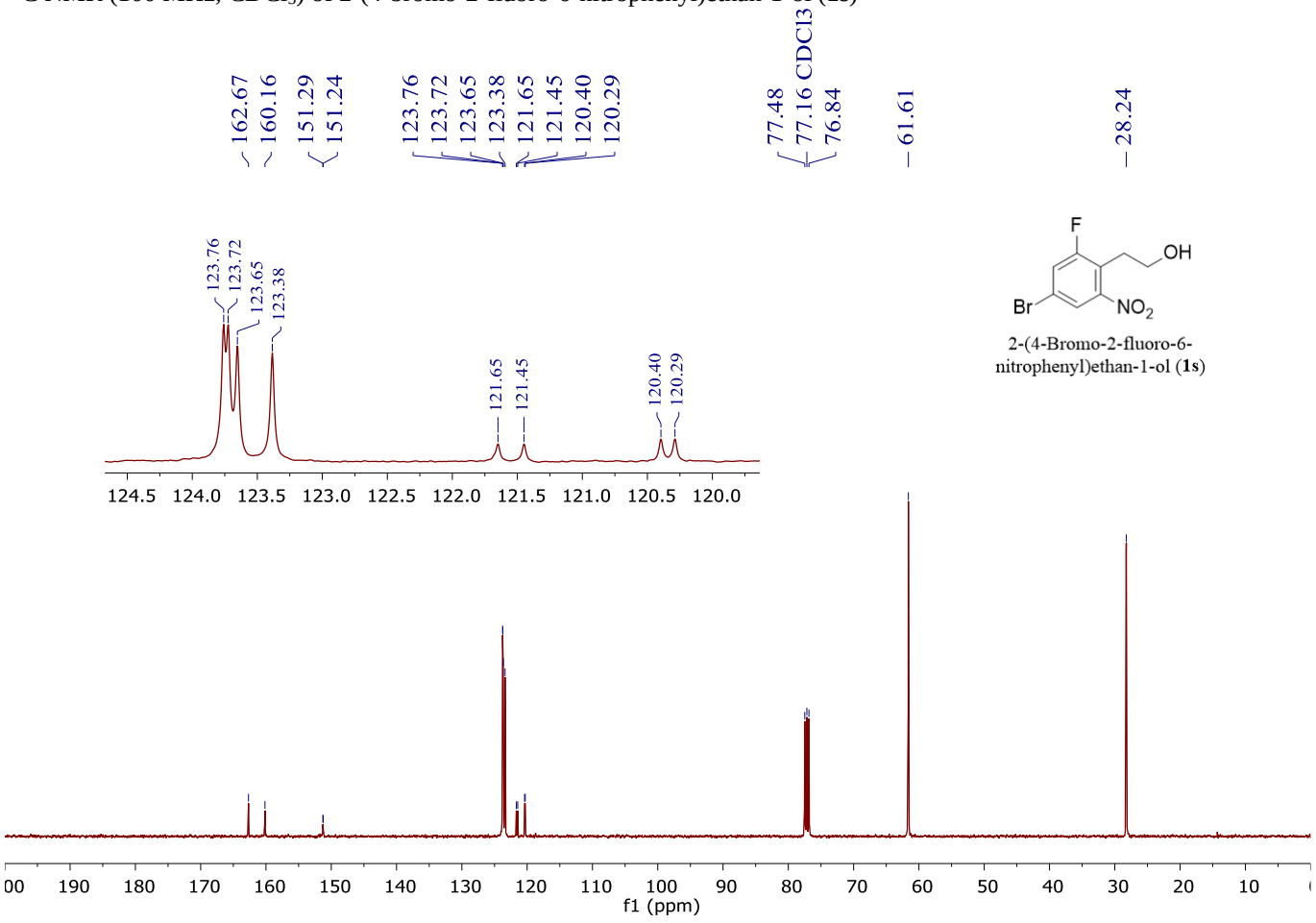


2-(2-Chloro-6-nitrophenyl)ethan-1-ol
(**1r**)

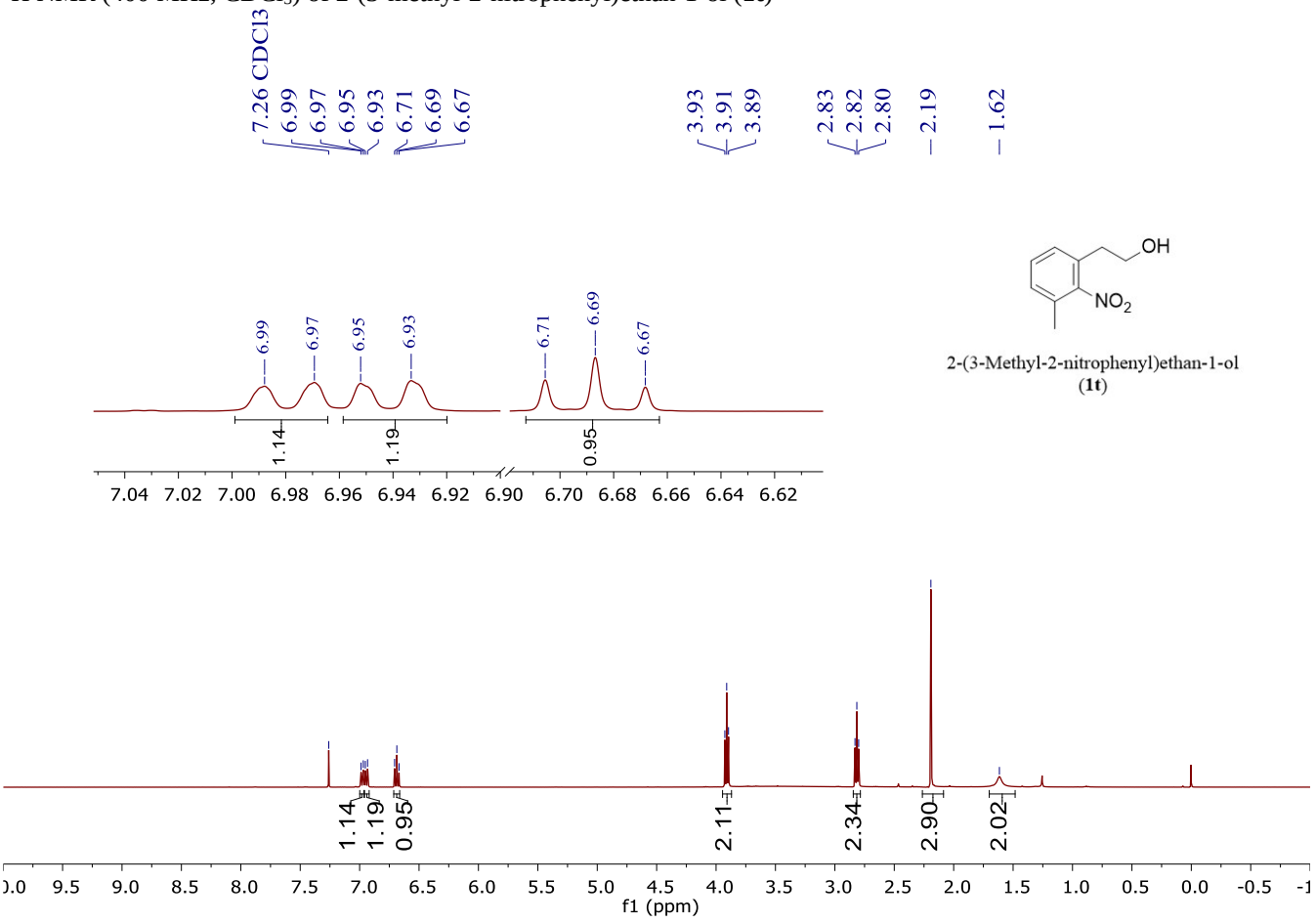
^{1}H NMR (400 MHz, $CDCl_3$) of 2-(4-bromo-2-fluoro-6-nitrophenyl)ethan-1-ol (**1s**)



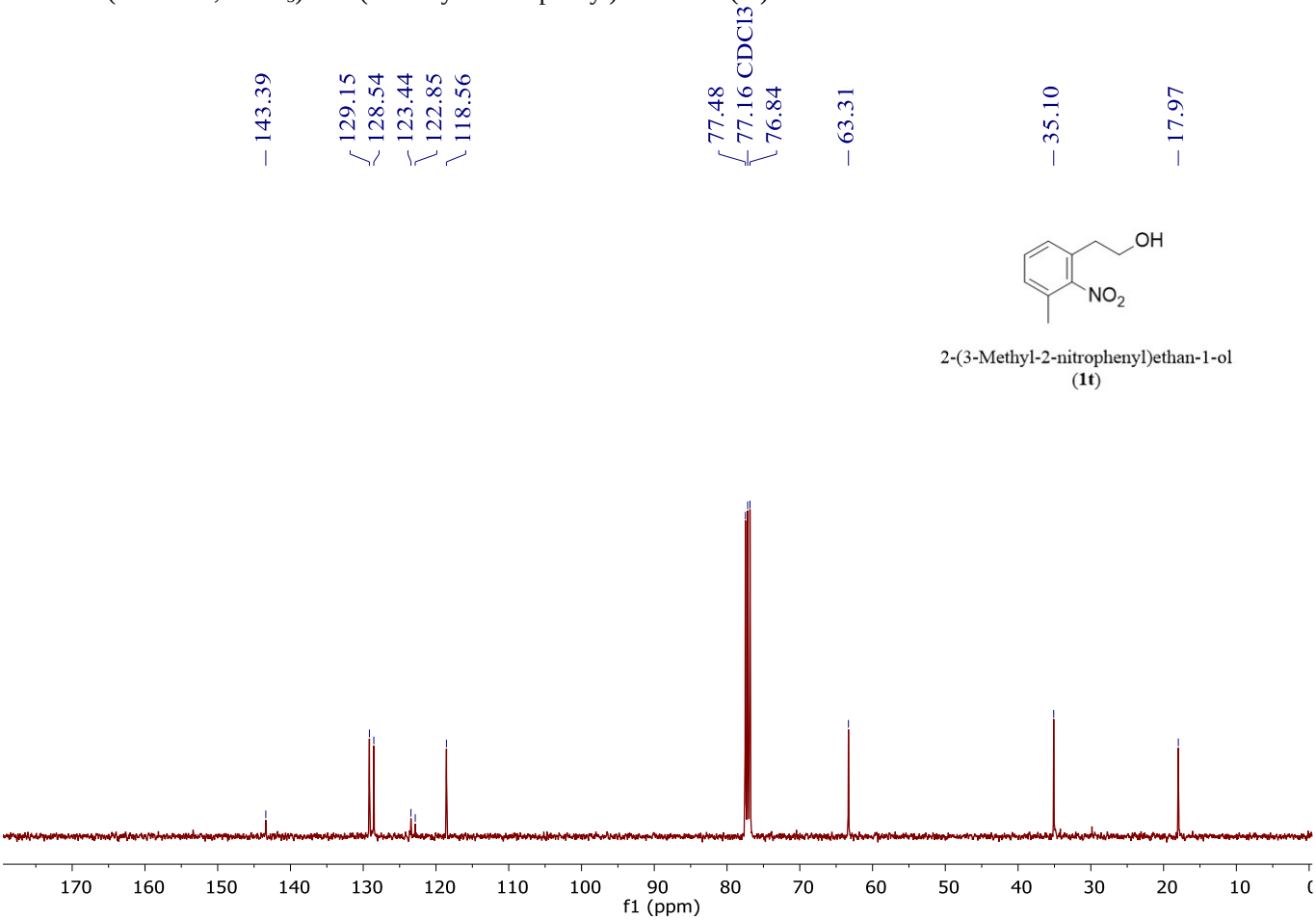
^{13}C NMR (100 MHz, $CDCl_3$) of 2-(4-bromo-2-fluoro-6-nitrophenyl)ethan-1-ol (**1s**)



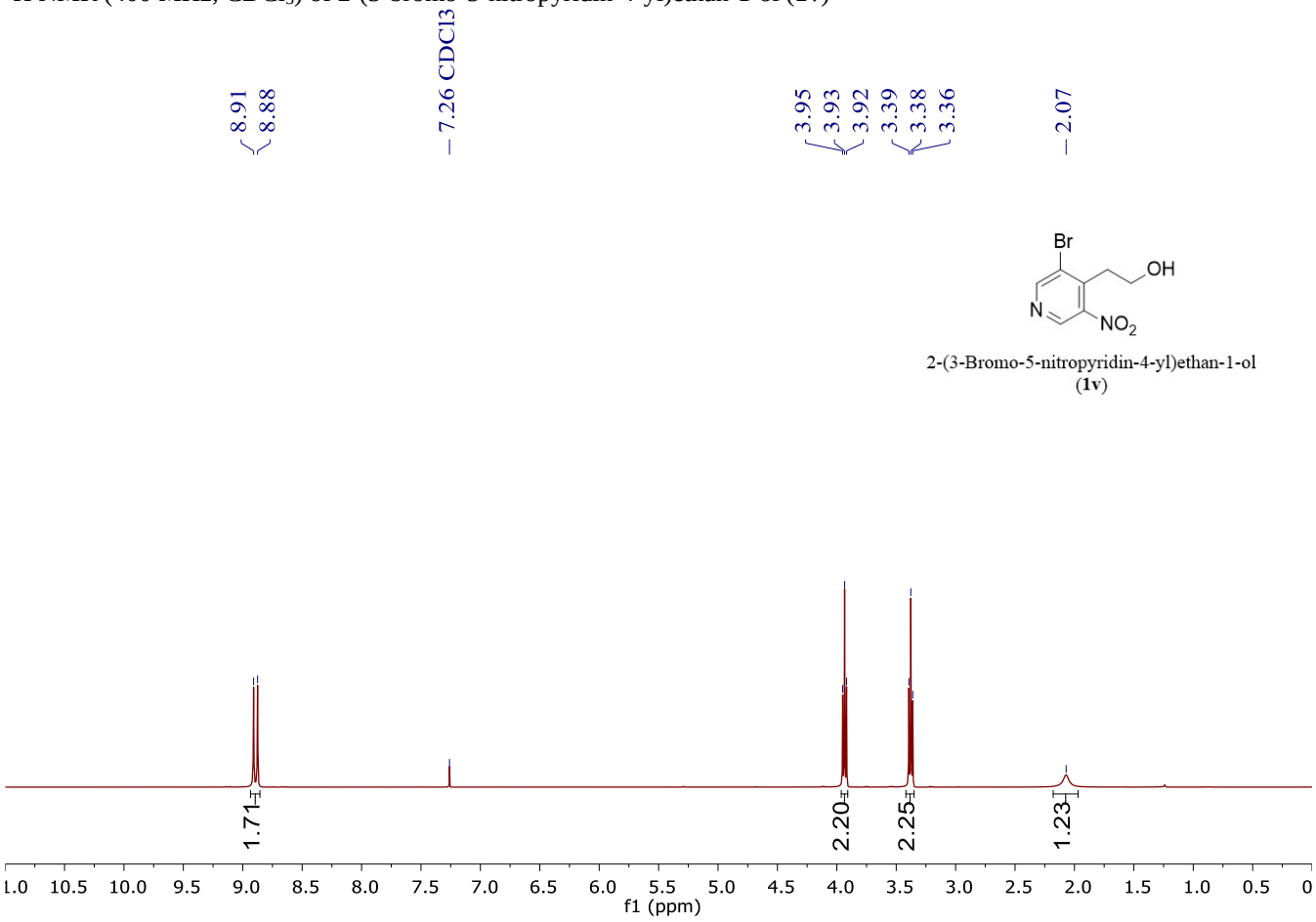
^{1}H NMR (400 MHz, $CDCl_3$) of 2-(3-methyl-2-nitrophenyl)ethan-1-ol (**1t**)



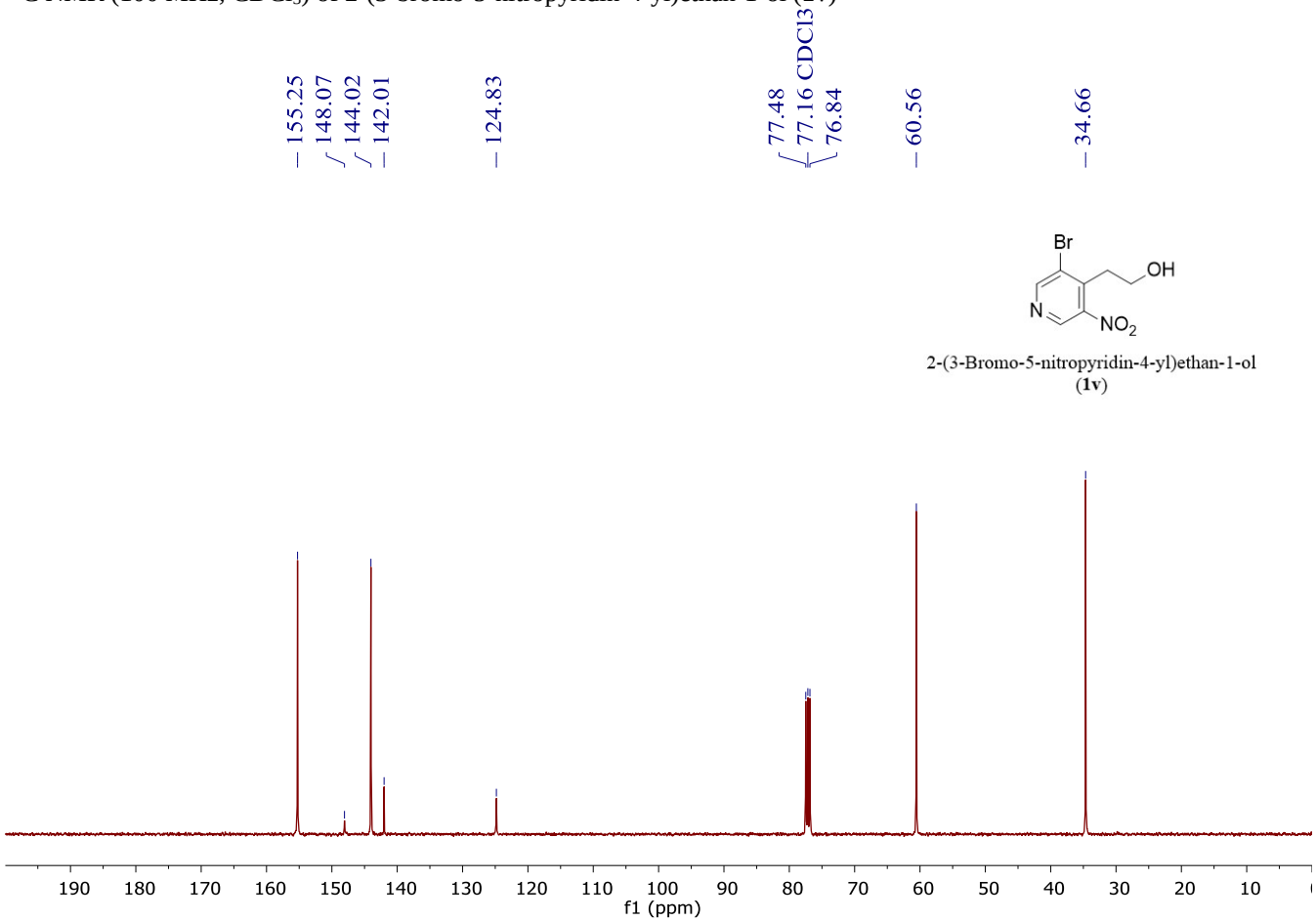
^{13}C NMR (100 MHz, $CDCl_3$) of 2-(3-methyl-2-nitrophenyl)ethan-1-ol (**1t**)



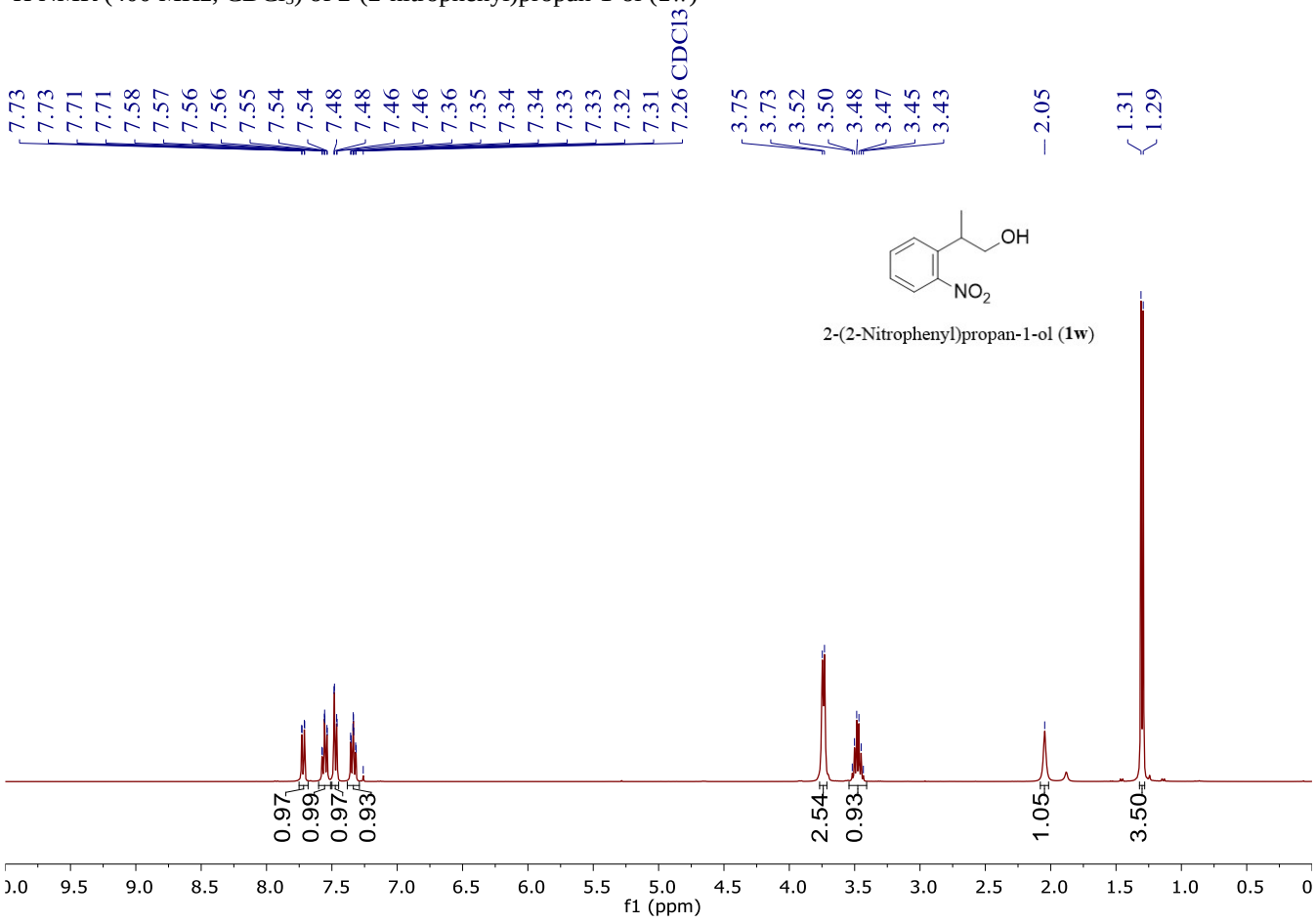
^{1}H NMR (400 MHz, $CDCl_3$) of 2-(3-bromo-5-nitropyridin-4-yl)ethan-1-ol (**1v**)



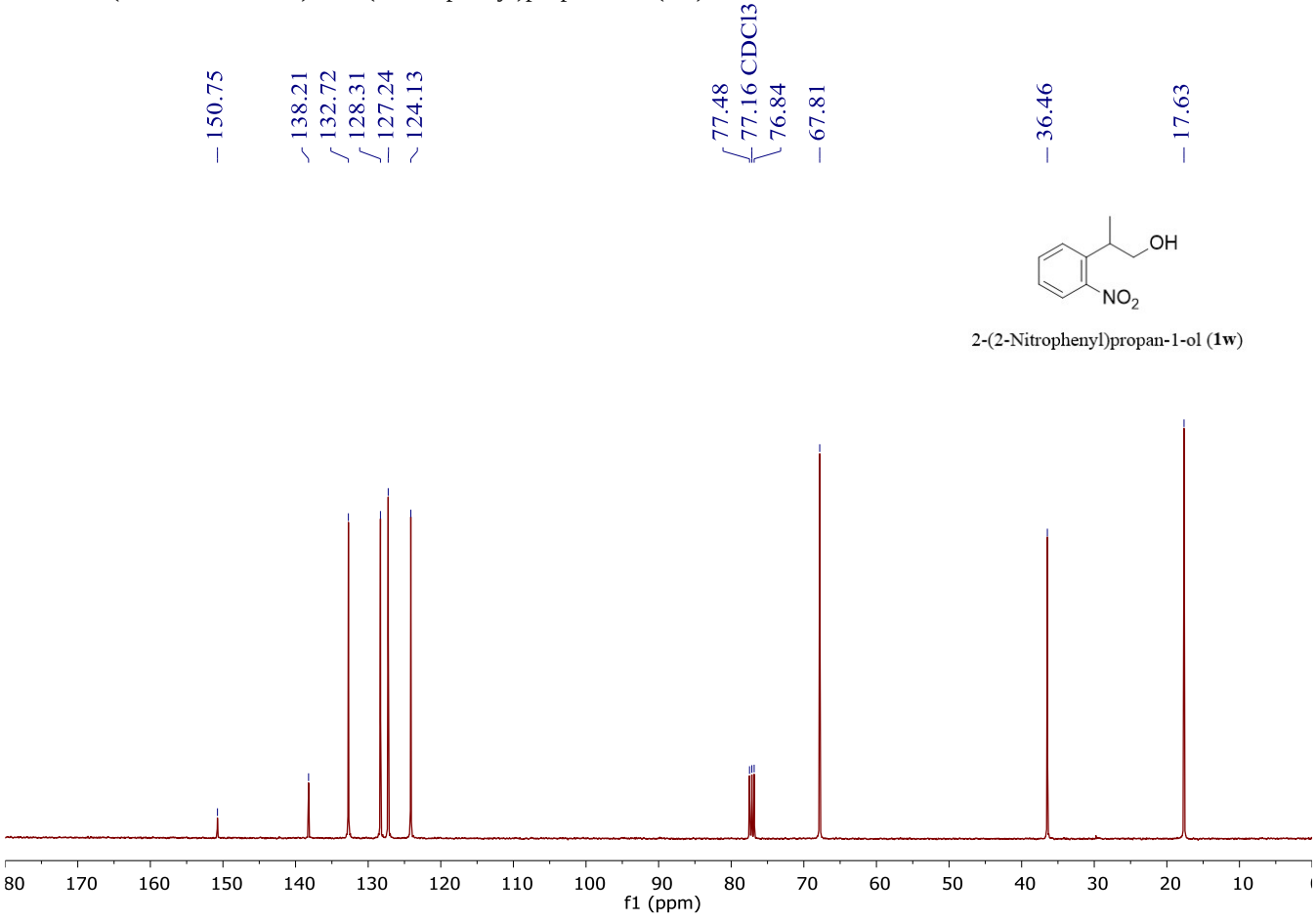
^{13}C NMR (100 MHz, $CDCl_3$) of 2-(3-bromo-5-nitropyridin-4-yl)ethan-1-ol (**1v**)



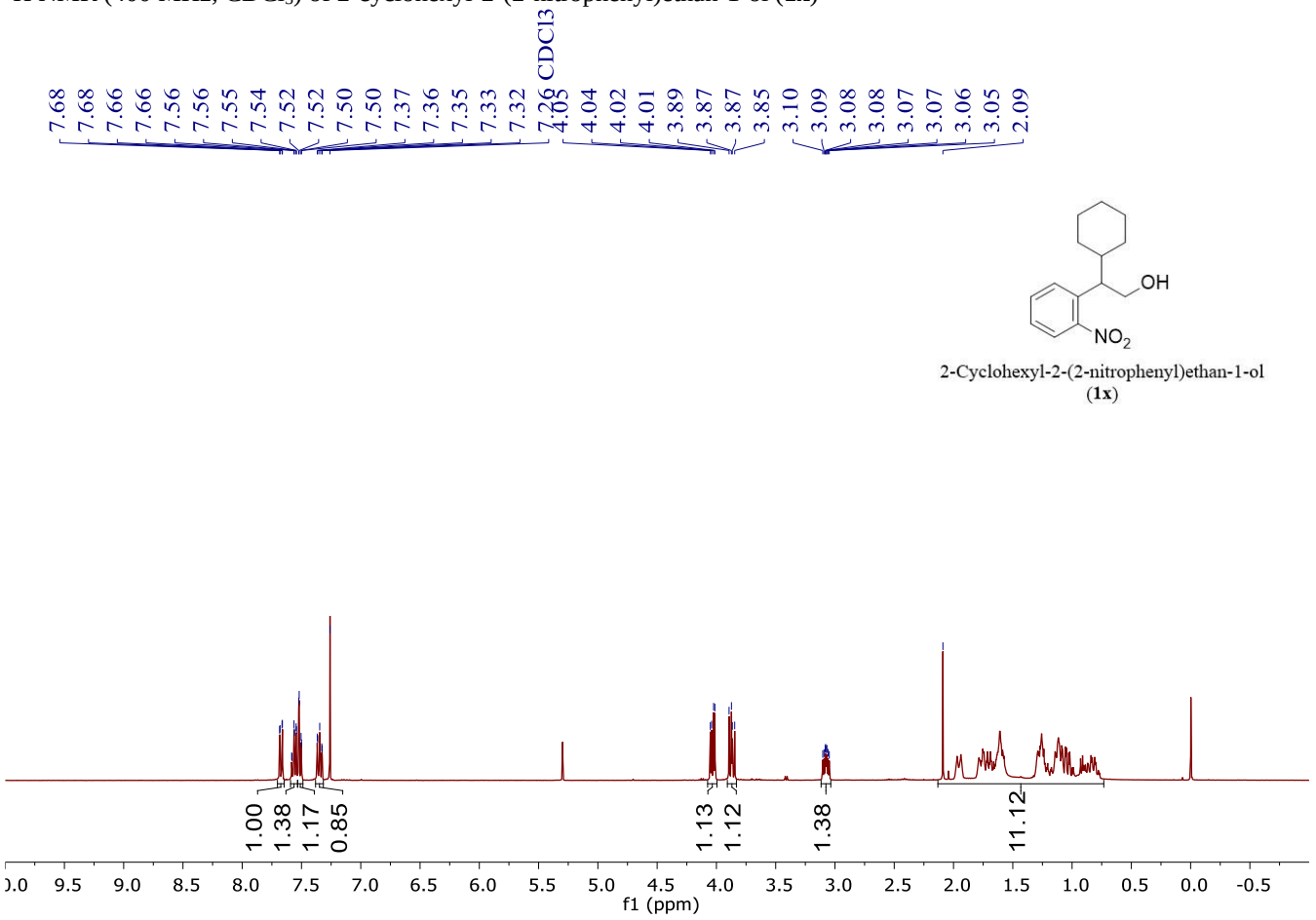
^{1}H NMR (400 MHz, $CDCl_3$) of 2-(2-nitrophenyl)propan-1-ol (**1w**)



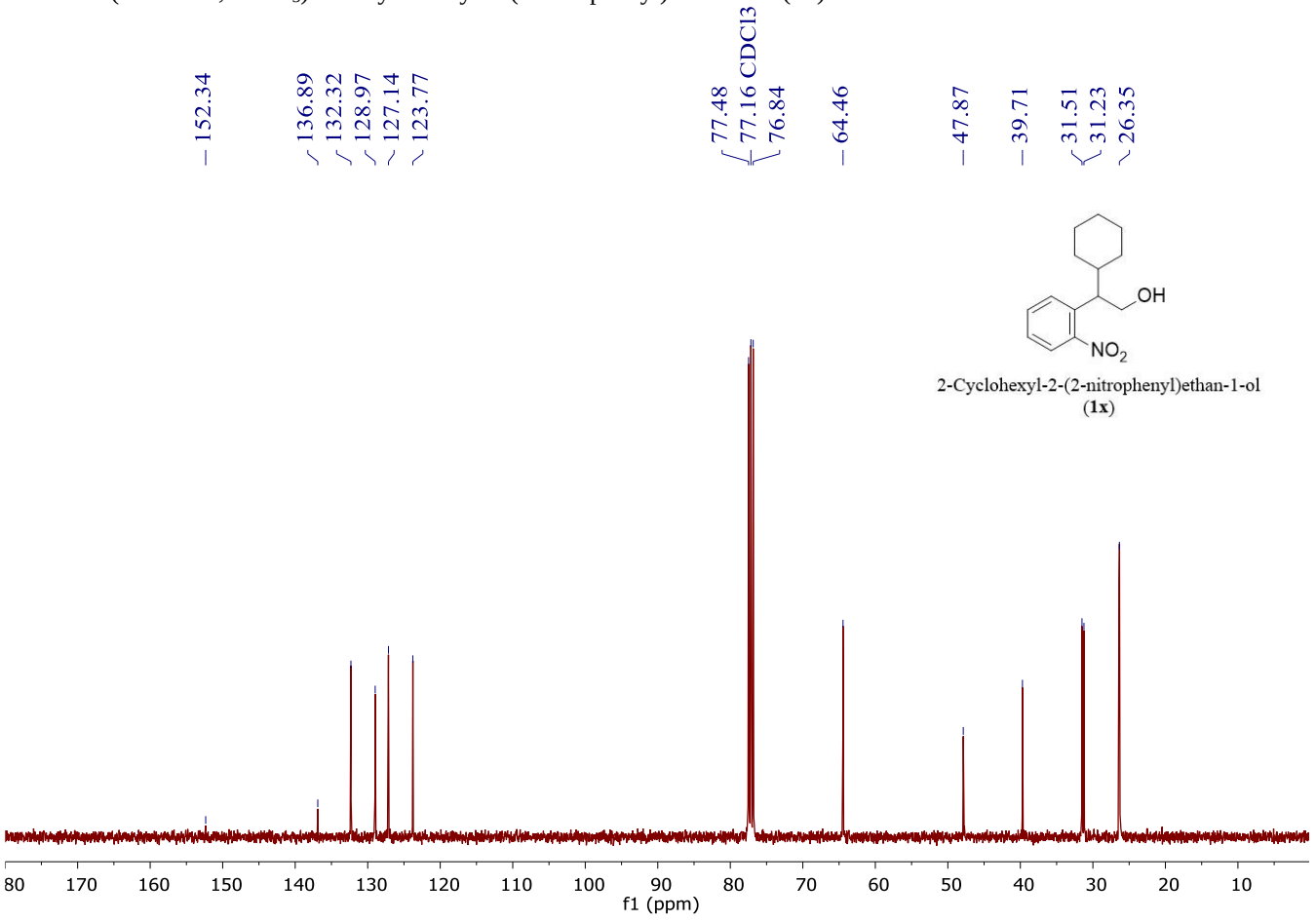
^{13}C NMR (100 MHz, $CDCl_3$) of 2-(2-nitrophenyl)propan-1-ol (**1w**)



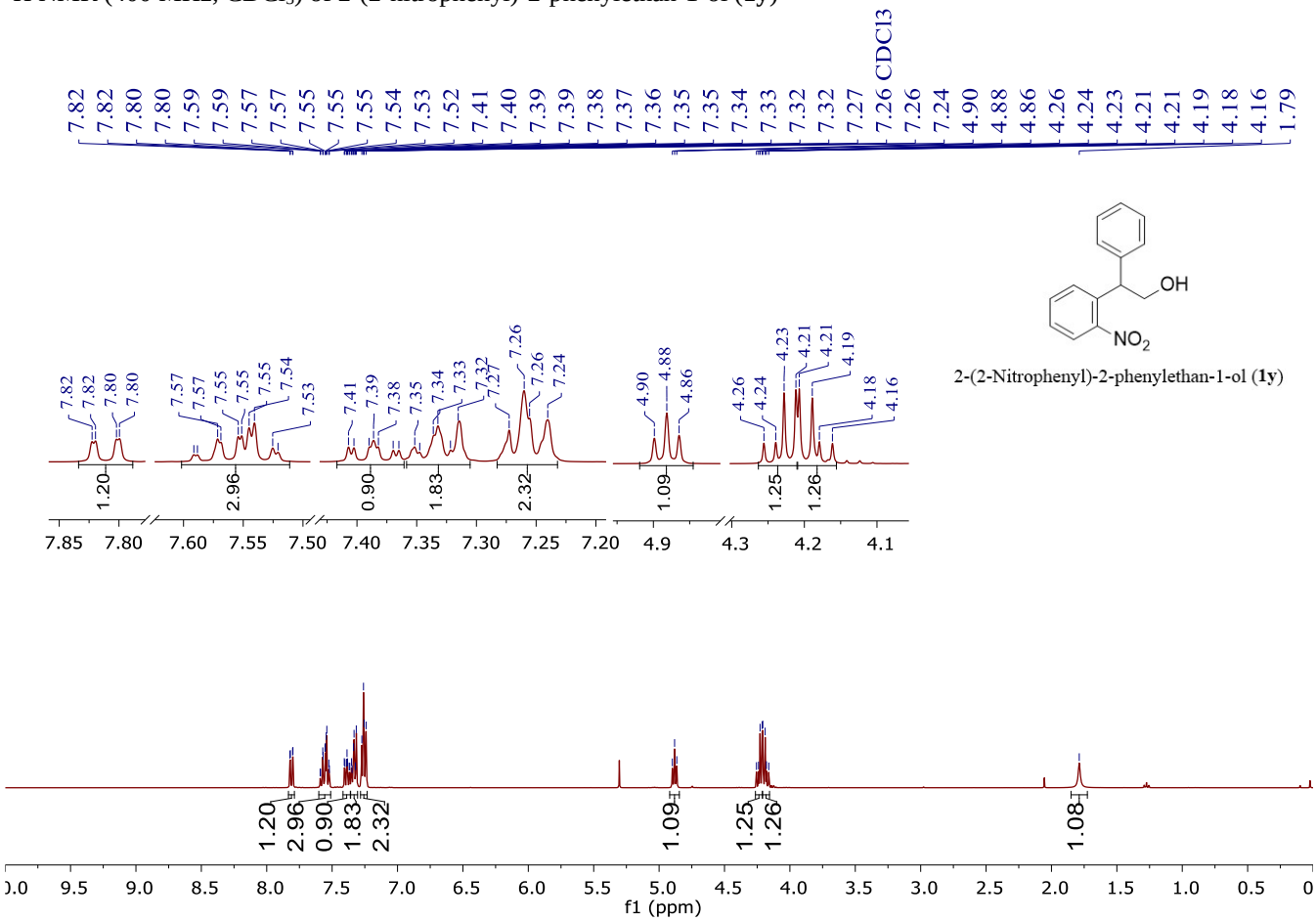
^{1}H NMR (400 MHz, $CDCl_3$) of 2-cyclohexyl-2-(2-nitrophenyl)ethan-1-ol (**1x**)



^{13}C NMR (100 MHz, $CDCl_3$) of 2-cyclohexyl-2-(2-nitrophenyl)ethan-1-ol (**1x**)

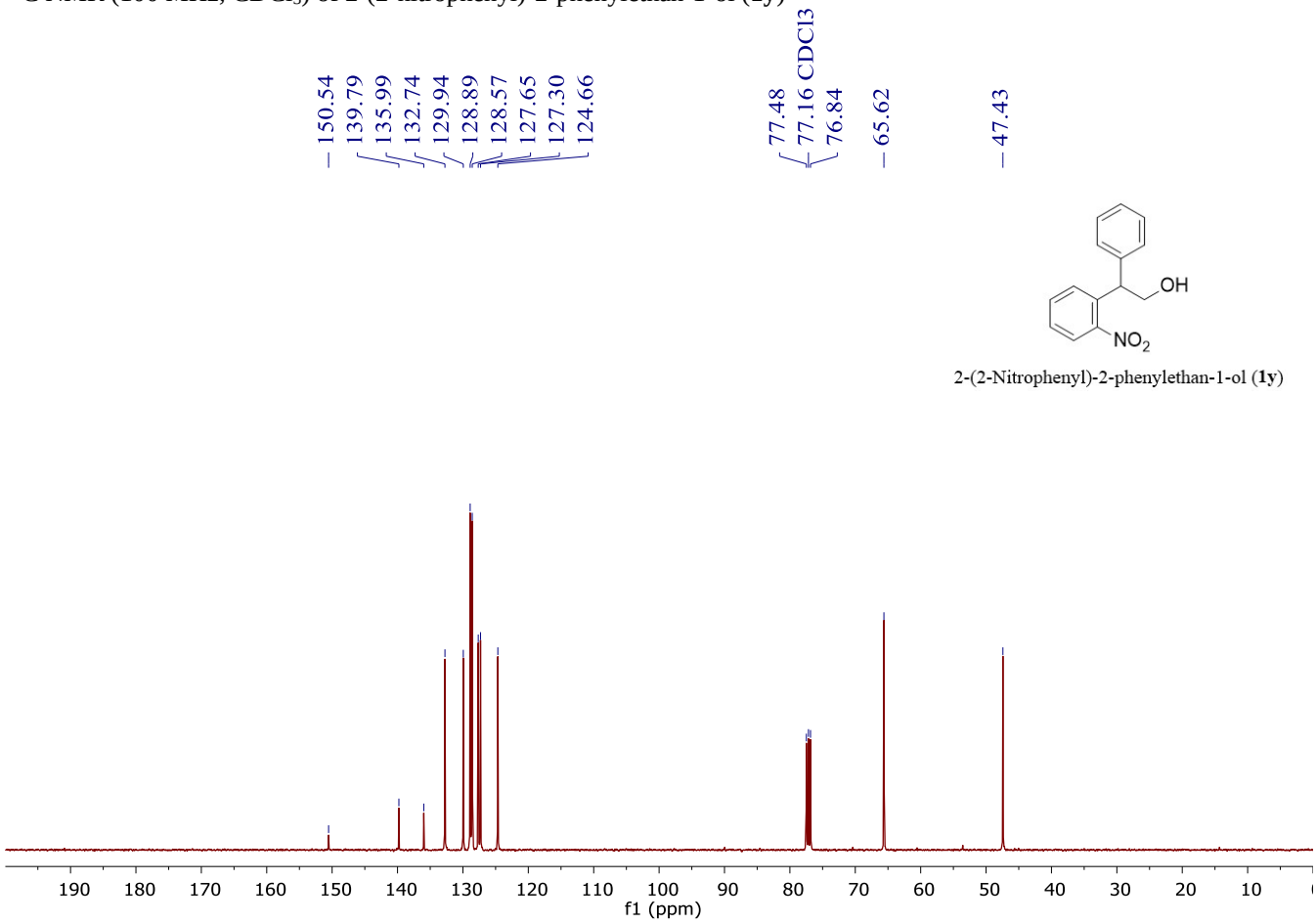


^{1}H NMR (400 MHz, $CDCl_3$) of 2-(2-nitrophenyl)-2-phenylethan-1-ol (**1y**)



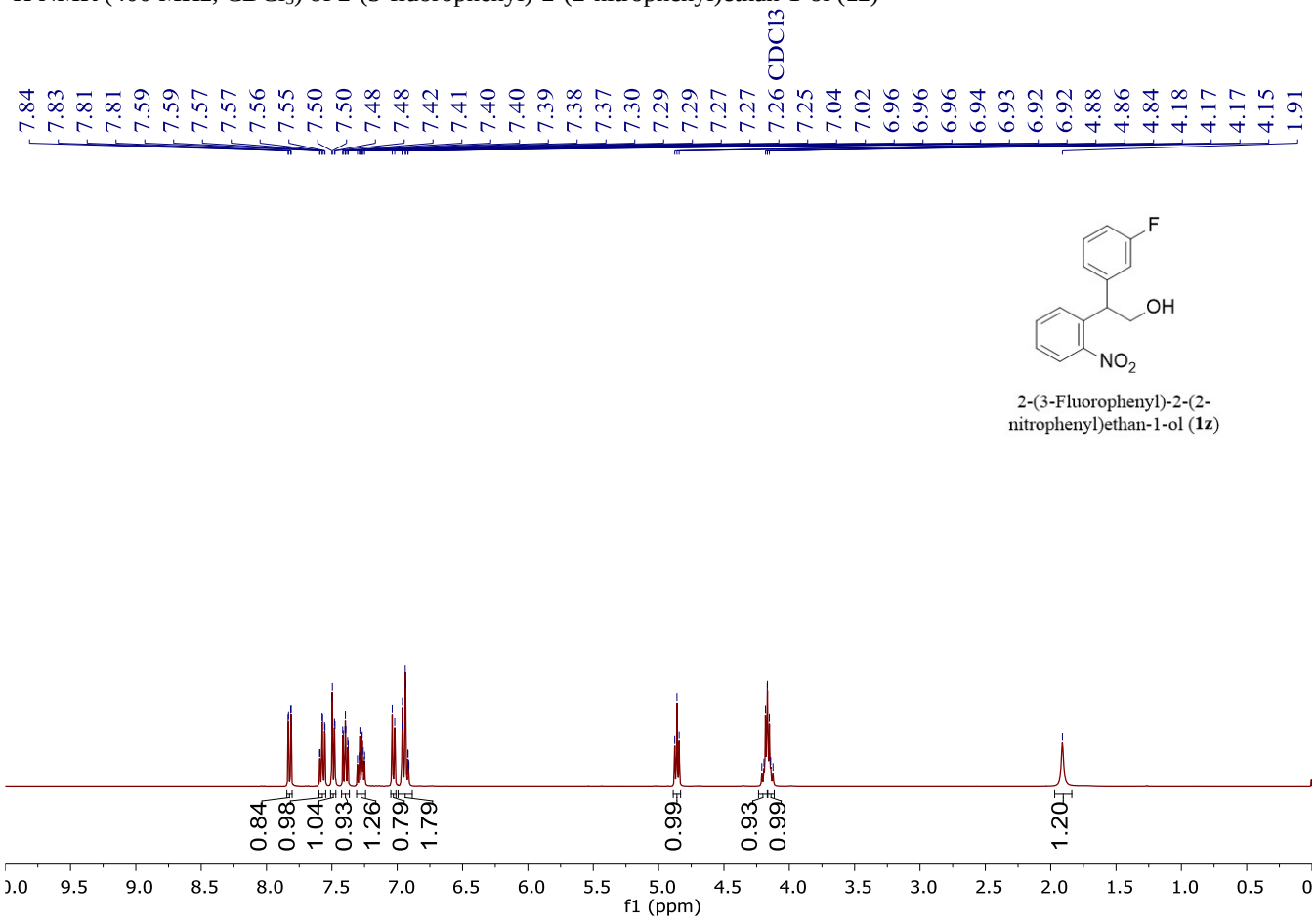
2-(2-Nitrophenyl)-2-phenylethan-1-ol (**1y**)

^{13}C NMR (100 MHz, $CDCl_3$) of 2-(2-nitrophenyl)-2-phenylethan-1-ol (**1y**)



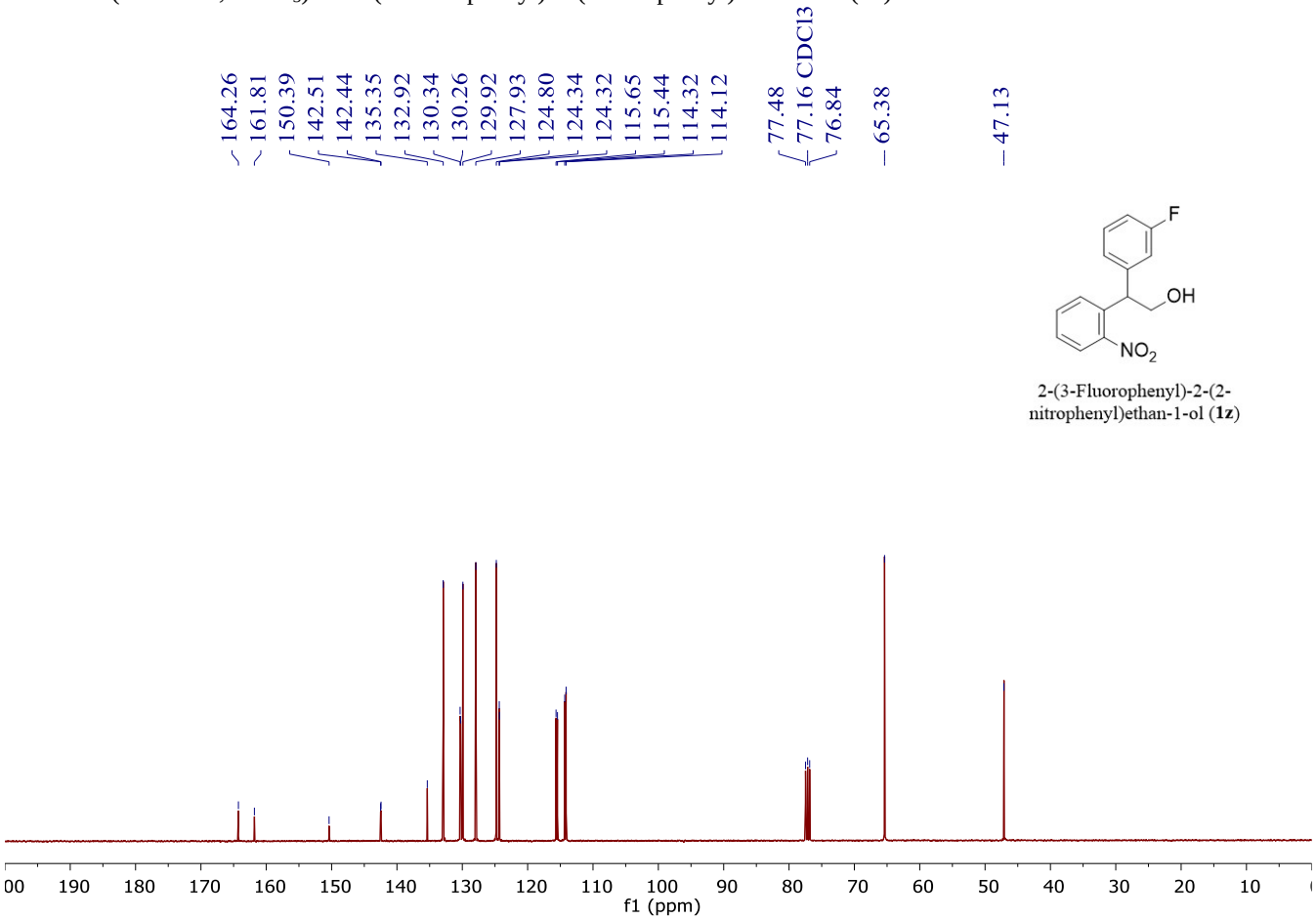
2-(2-Nitrophenyl)-2-phenylethan-1-ol (**1y**)

^{1}H NMR (400 MHz, $CDCl_3$) of 2-(3-fluorophenyl)-2-(2-nitrophenyl)ethan-1-ol (**1z**)



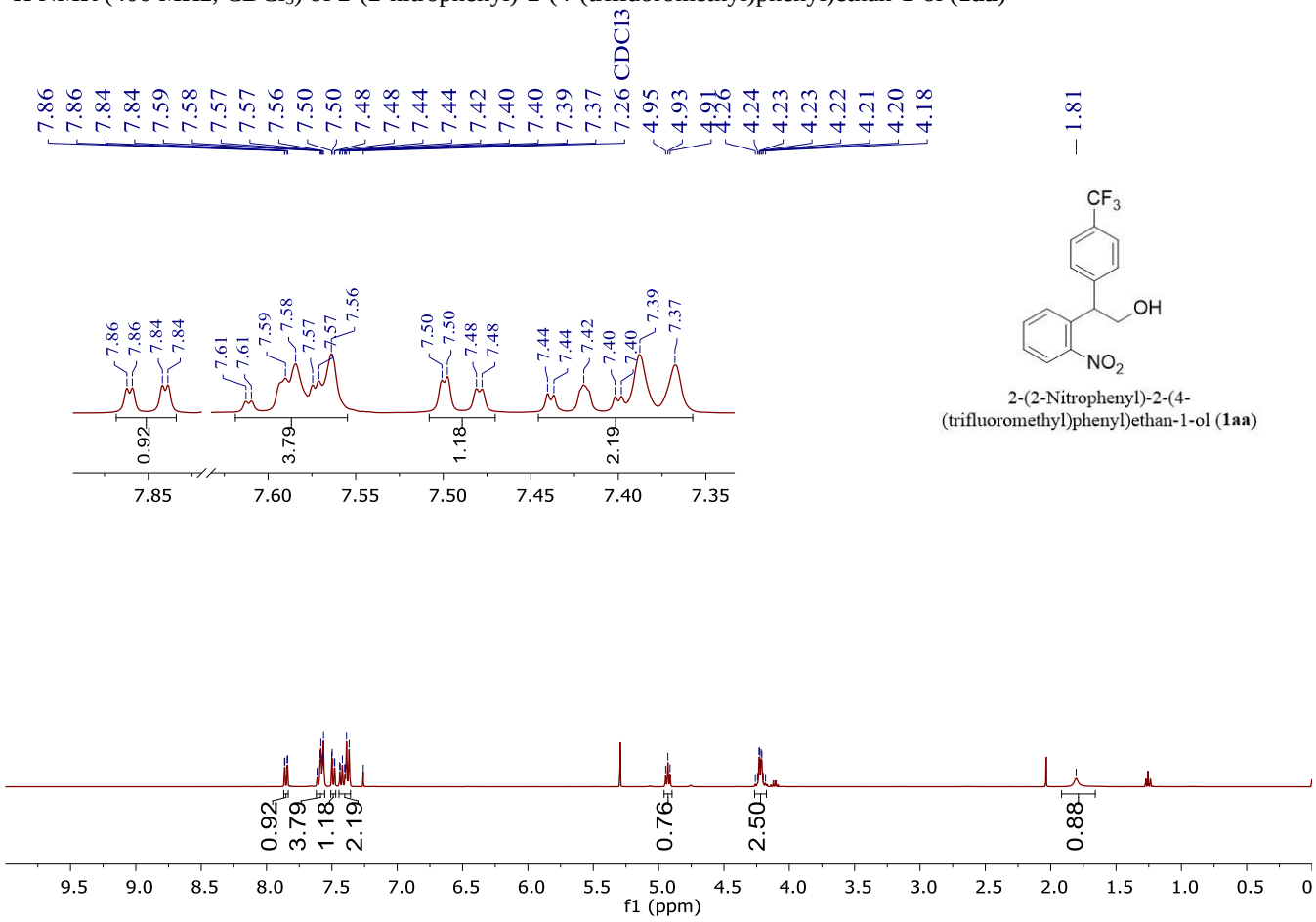
2-(3-Fluorophenyl)-2-(2-nitrophenyl)ethan-1-ol (**1z**)

^{13}C NMR (100 MHz, $CDCl_3$) of 2-(3-fluorophenyl)-2-(2-nitrophenyl)ethan-1-ol (**1z**)



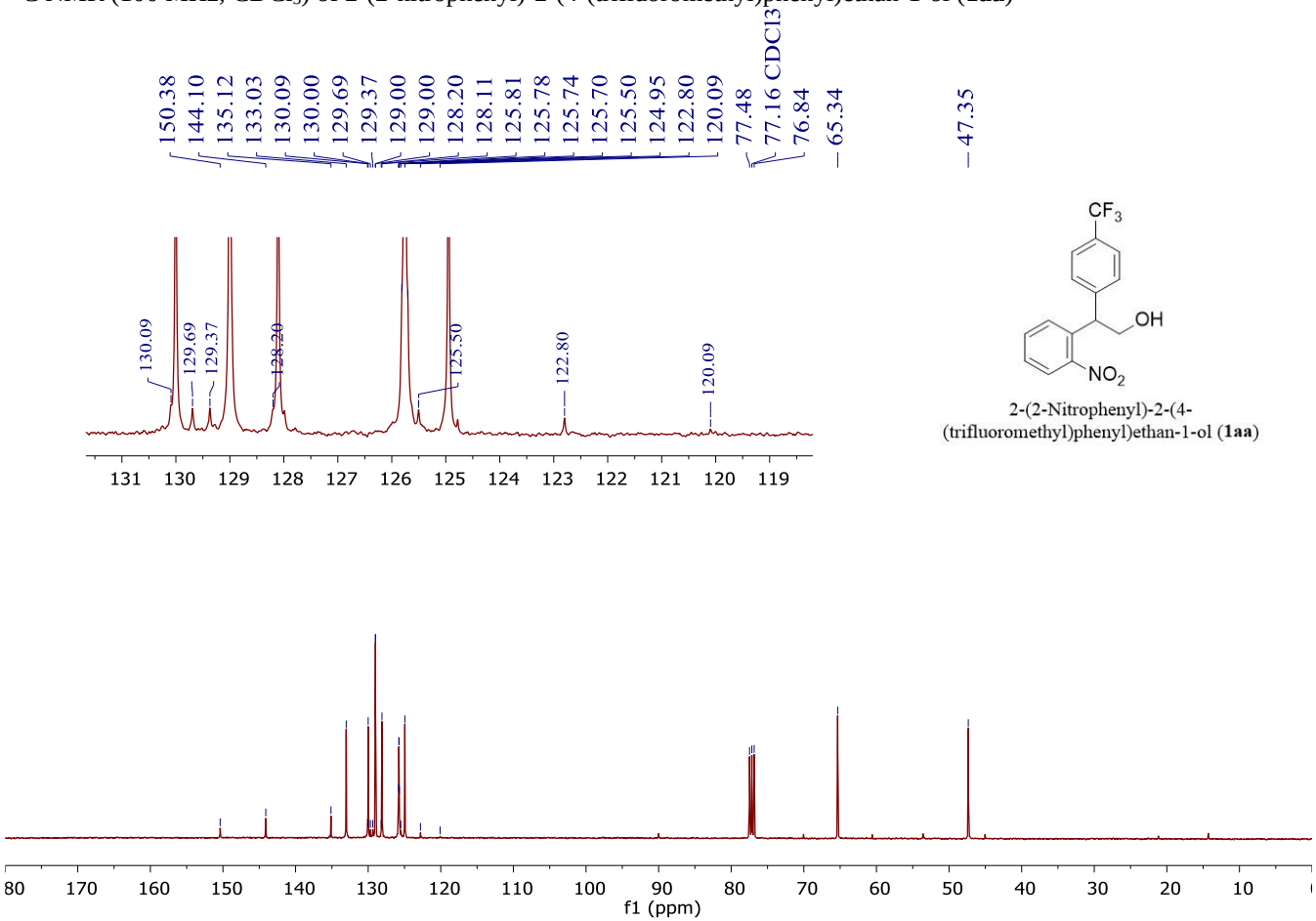
2-(3-Fluorophenyl)-2-(2-nitrophenyl)ethan-1-ol (**1z**)

^{1}H NMR (400 MHz, $CDCl_3$) of 2-(2-nitrophenyl)-2-(4-(trifluoromethyl)phenyl)ethan-1-ol (**1aa**)



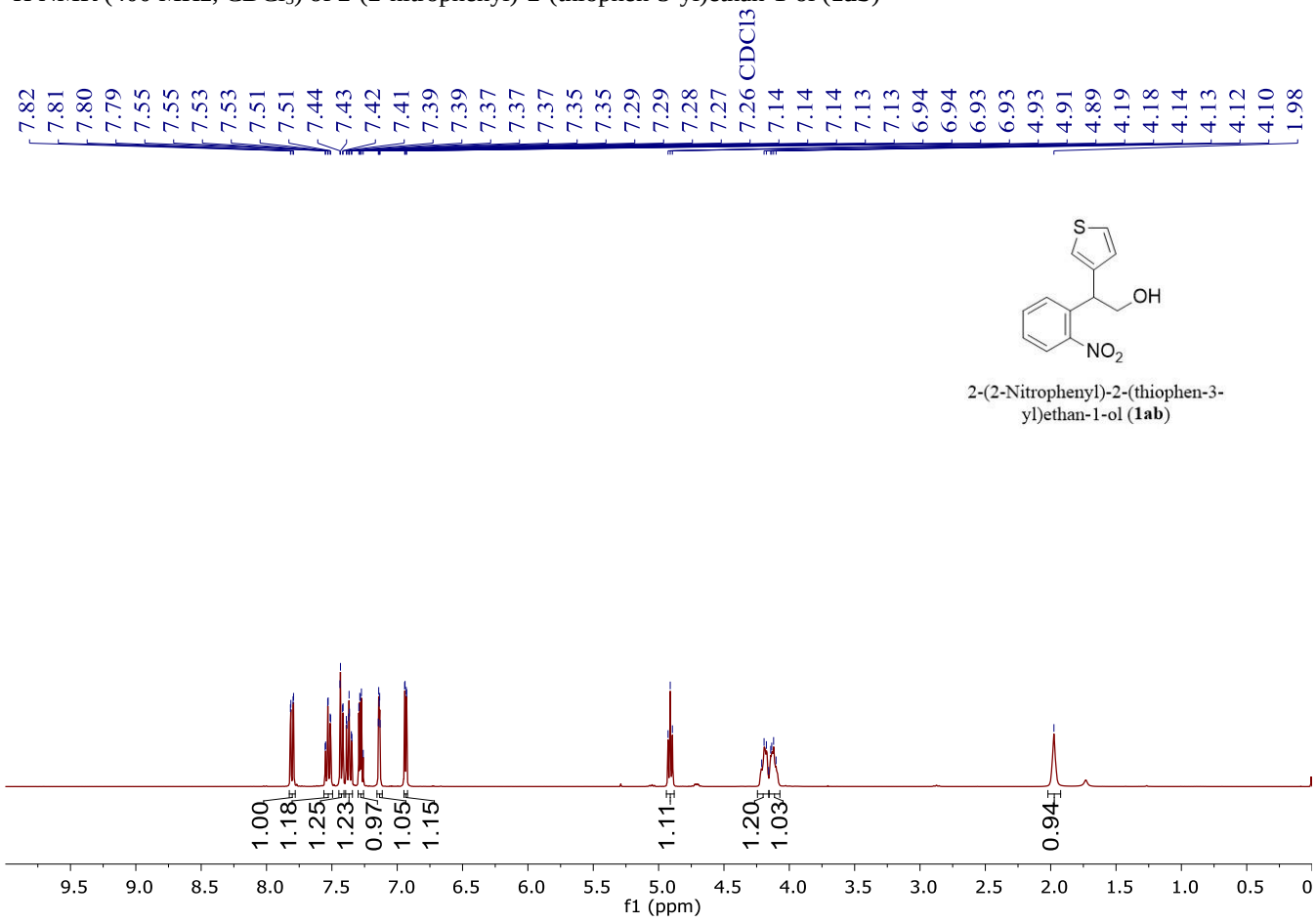
2-(2-Nitrophenyl)-2-(4-(trifluoromethyl)phenyl)ethan-1-ol (**1aa**)

^{13}C NMR (100 MHz, $CDCl_3$) of 2-(2-nitrophenyl)-2-(4-(trifluoromethyl)phenyl)ethan-1-ol (**1aa**)



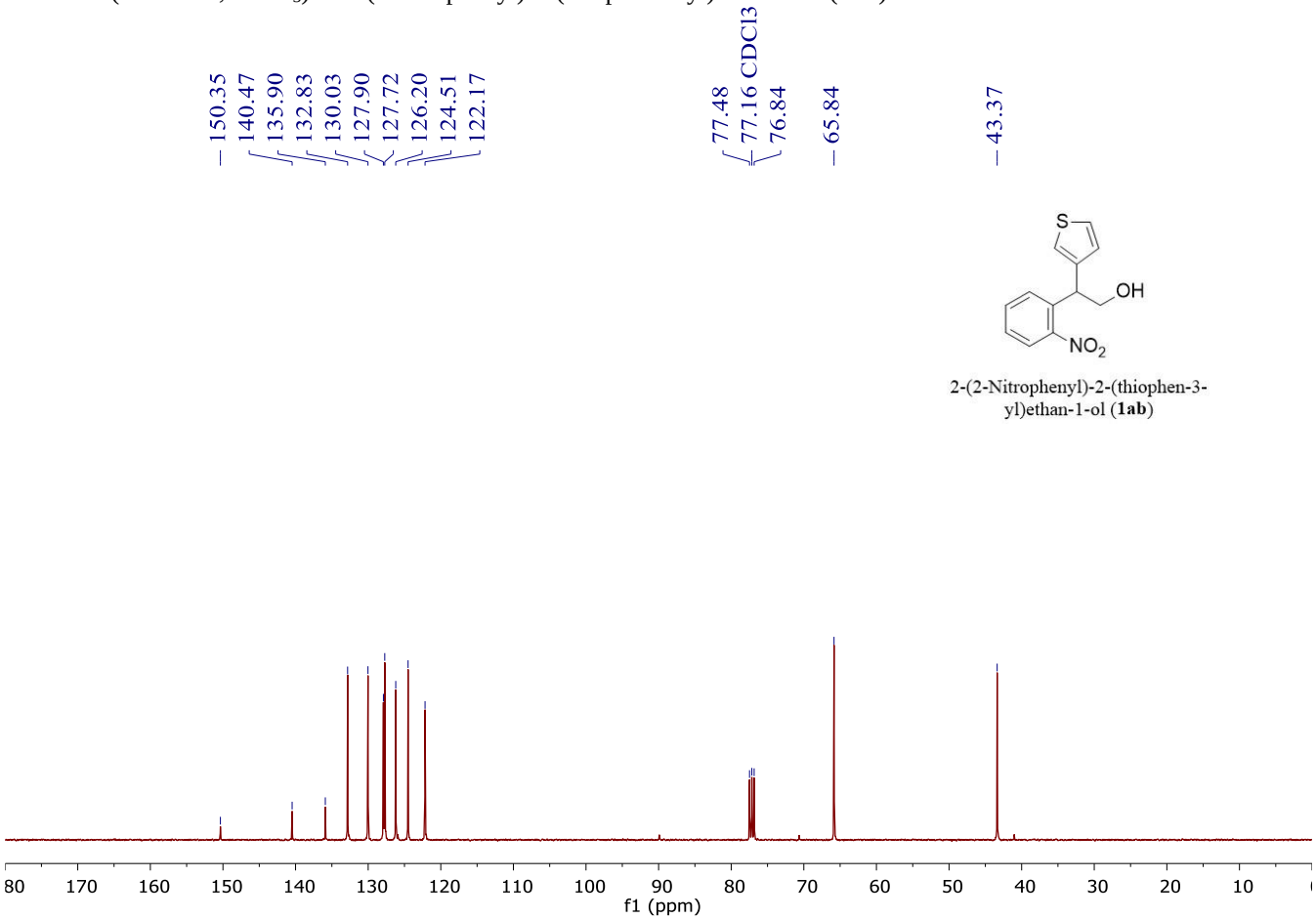
2-(2-Nitrophenyl)-2-(4-(trifluoromethyl)phenyl)ethan-1-ol (**1aa**)

^{1}H NMR (400 MHz, $CDCl_3$) of 2-(2-nitrophenyl)-2-(thiophen-3-yl)ethan-1-ol (**1ab**)



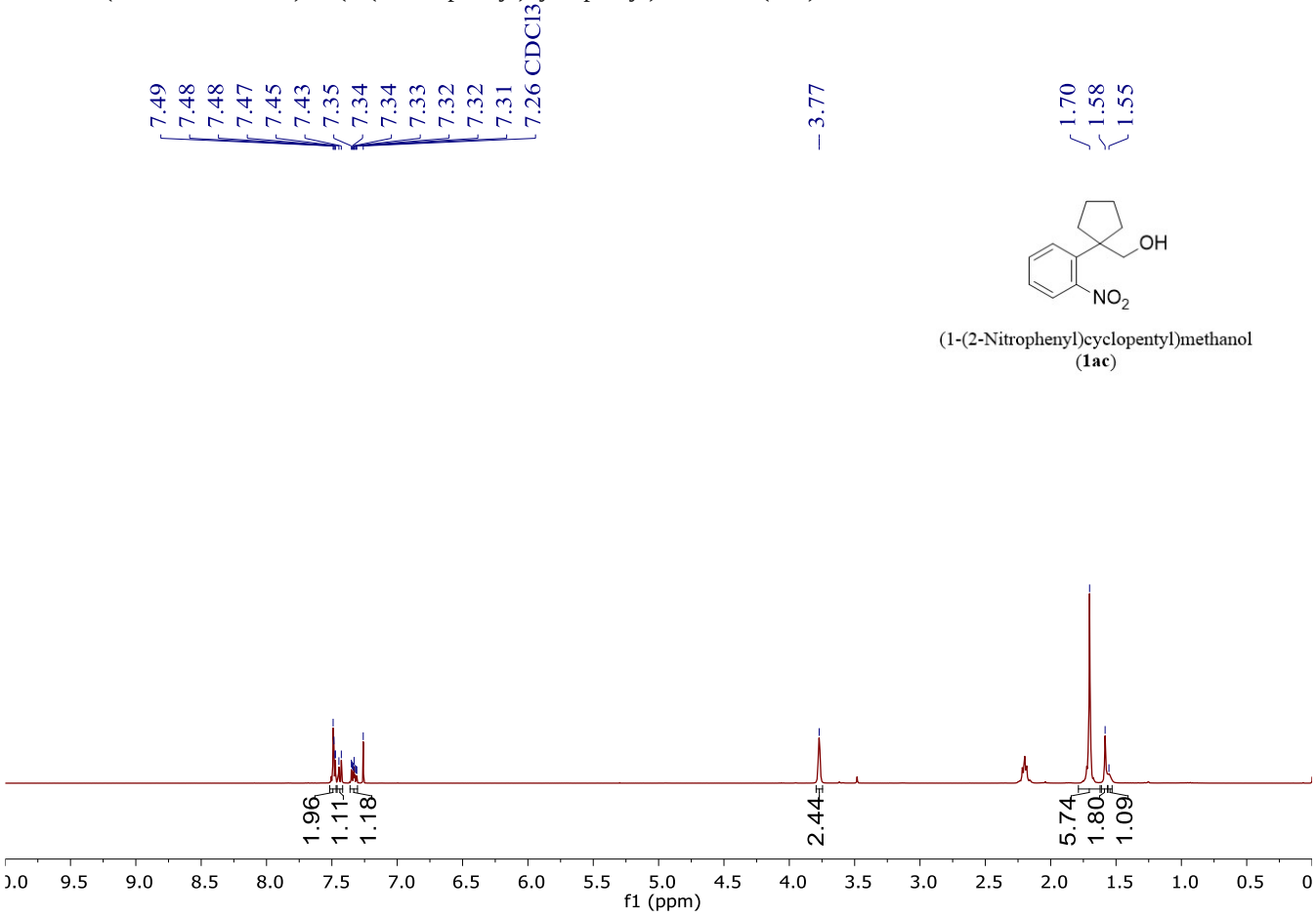
2-(2-Nitrophenyl)-2-(thiophen-3-yl)ethan-1-ol (**1ab**)

^{13}C NMR (100 MHz, $CDCl_3$) of 2-(2-nitrophenyl)-2-(thiophen-3-yl)ethan-1-ol (**1ab**)

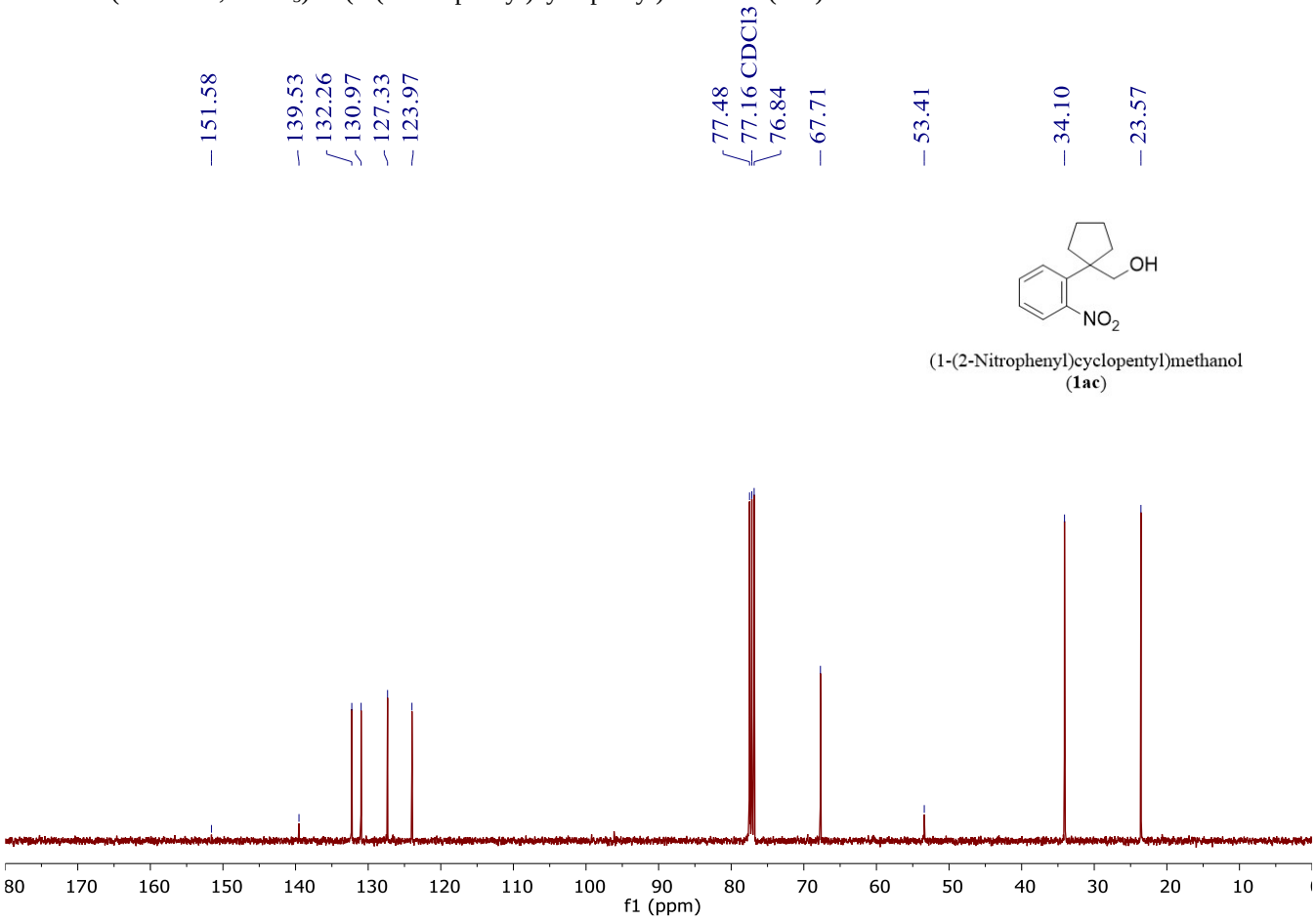


2-(2-Nitrophenyl)-2-(thiophen-3-yl)ethan-1-ol (**1ab**)

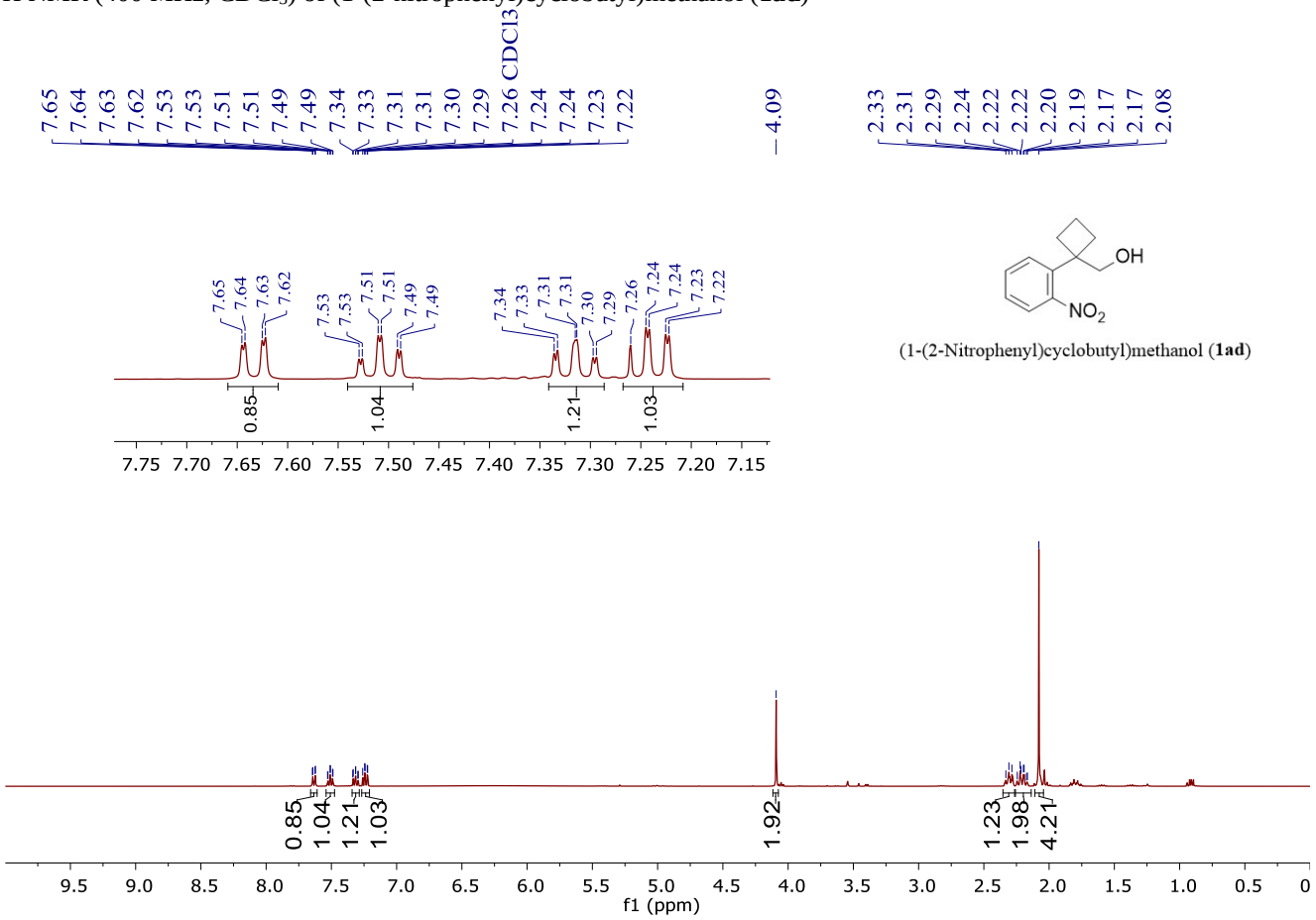
^{1}H NMR (400 MHz, $CDCl_3$) of (1-(2-nitrophenyl)cyclopentyl)methanol (**1ac**)



^{13}C NMR (100 MHz, $CDCl_3$) of (1-(2-nitrophenyl)cyclopentyl)methanol (**1ac**)

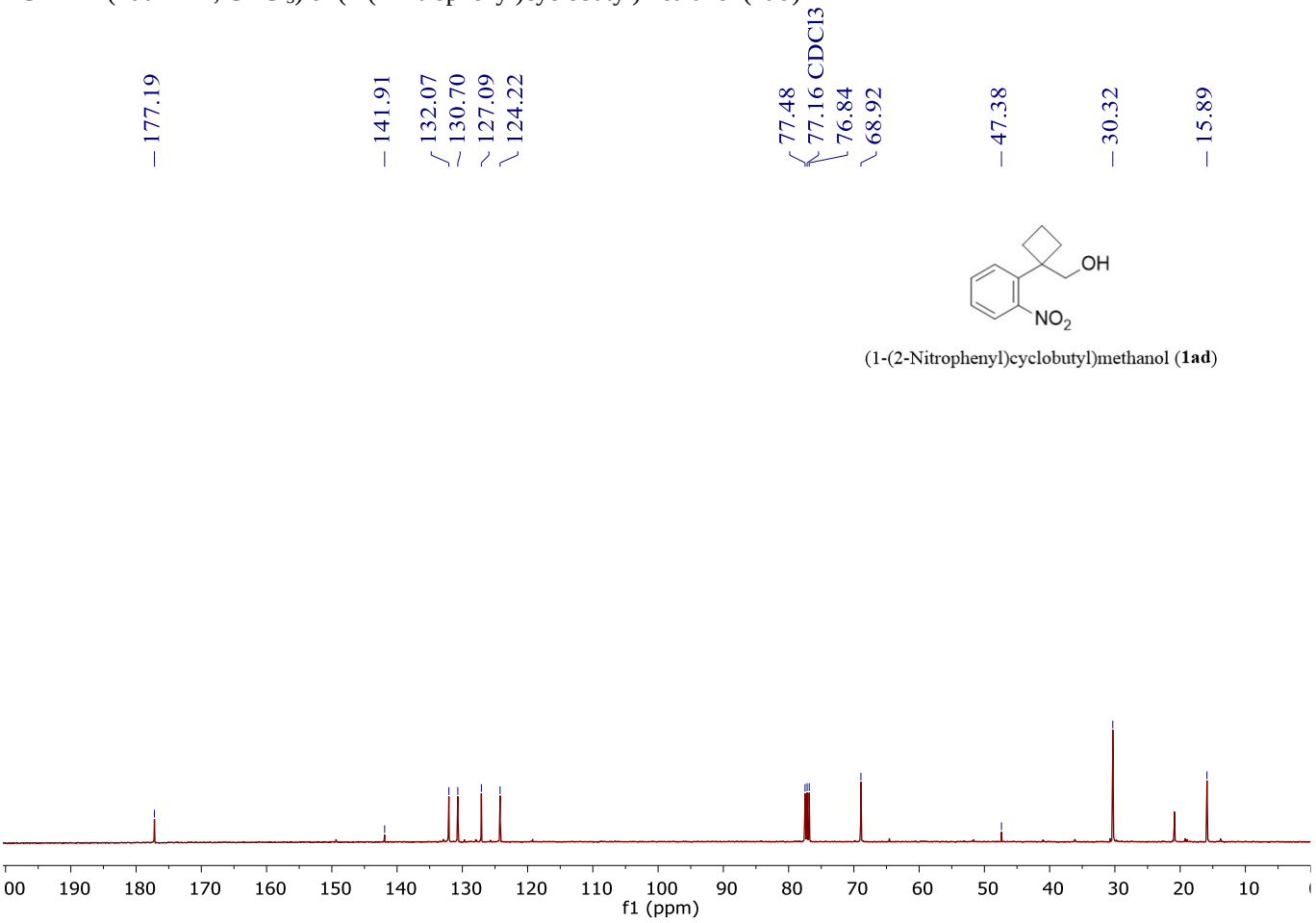


^{1}H NMR (400 MHz, $CDCl_3$) of (1-(2-nitrophenyl)cyclobutyl)methanol (**1ad**)



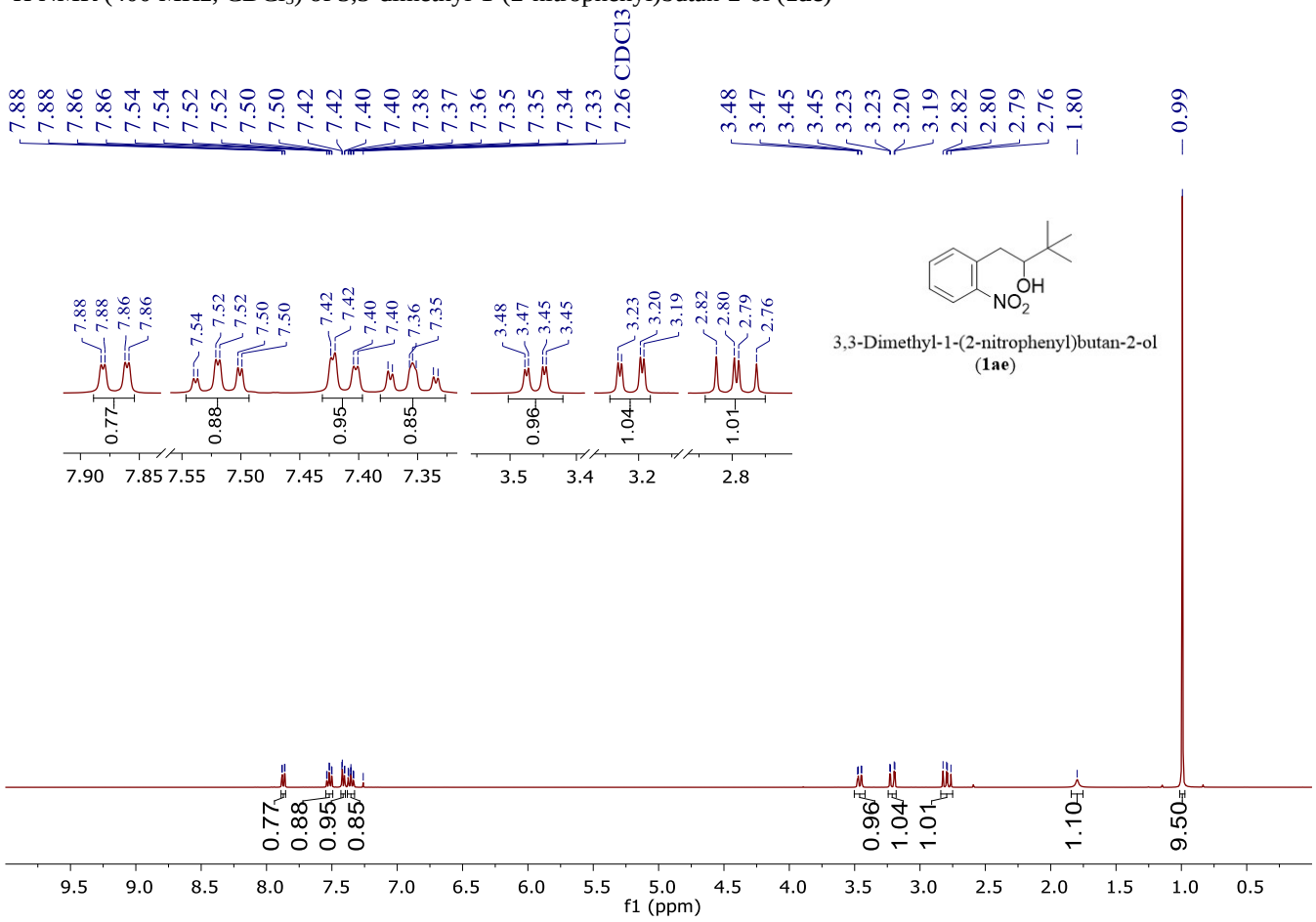
(1-(2-Nitrophenyl)cyclobutyl)methanol (**1ad**)

^{13}C NMR (100 MHz, $CDCl_3$) of (1-(2-nitrophenyl)cyclobutyl)methanol (**1ad**)

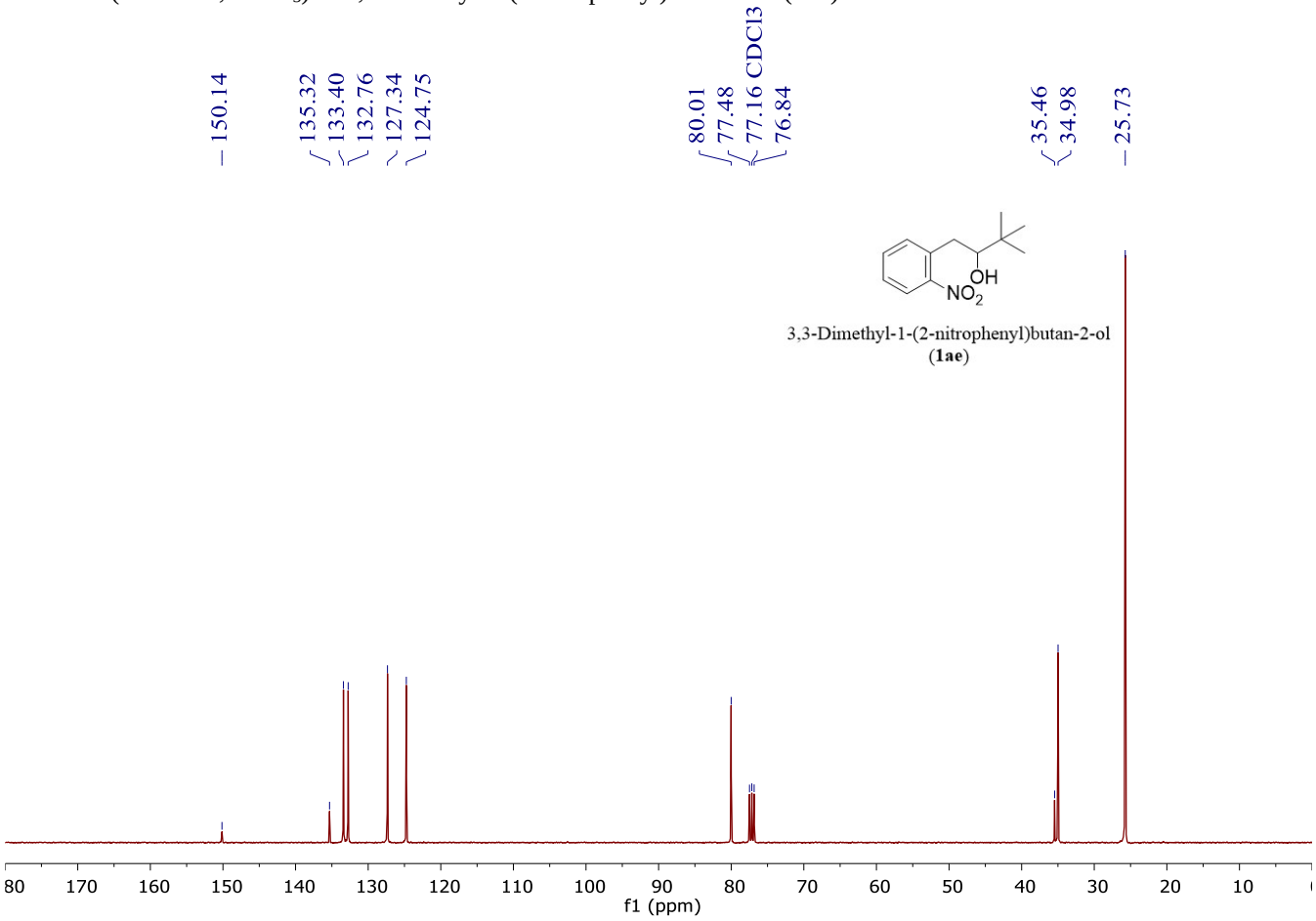


(1-(2-Nitrophenyl)cyclobutyl)methanol (**1ad**)

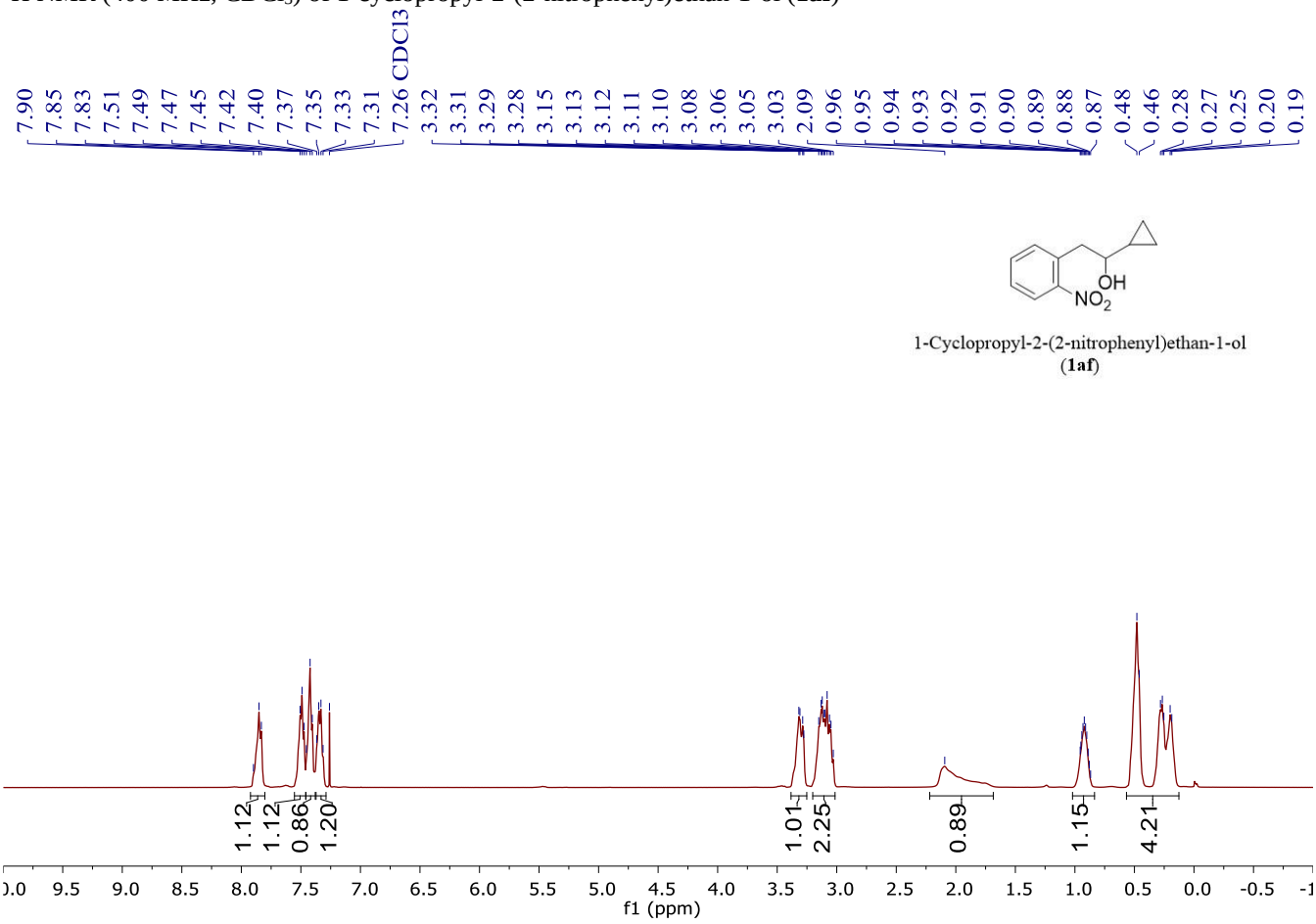
^{1}H NMR (400 MHz, $CDCl_3$) of 3,3-dimethyl-1-(2-nitrophenyl)butan-2-ol (**1ae**)



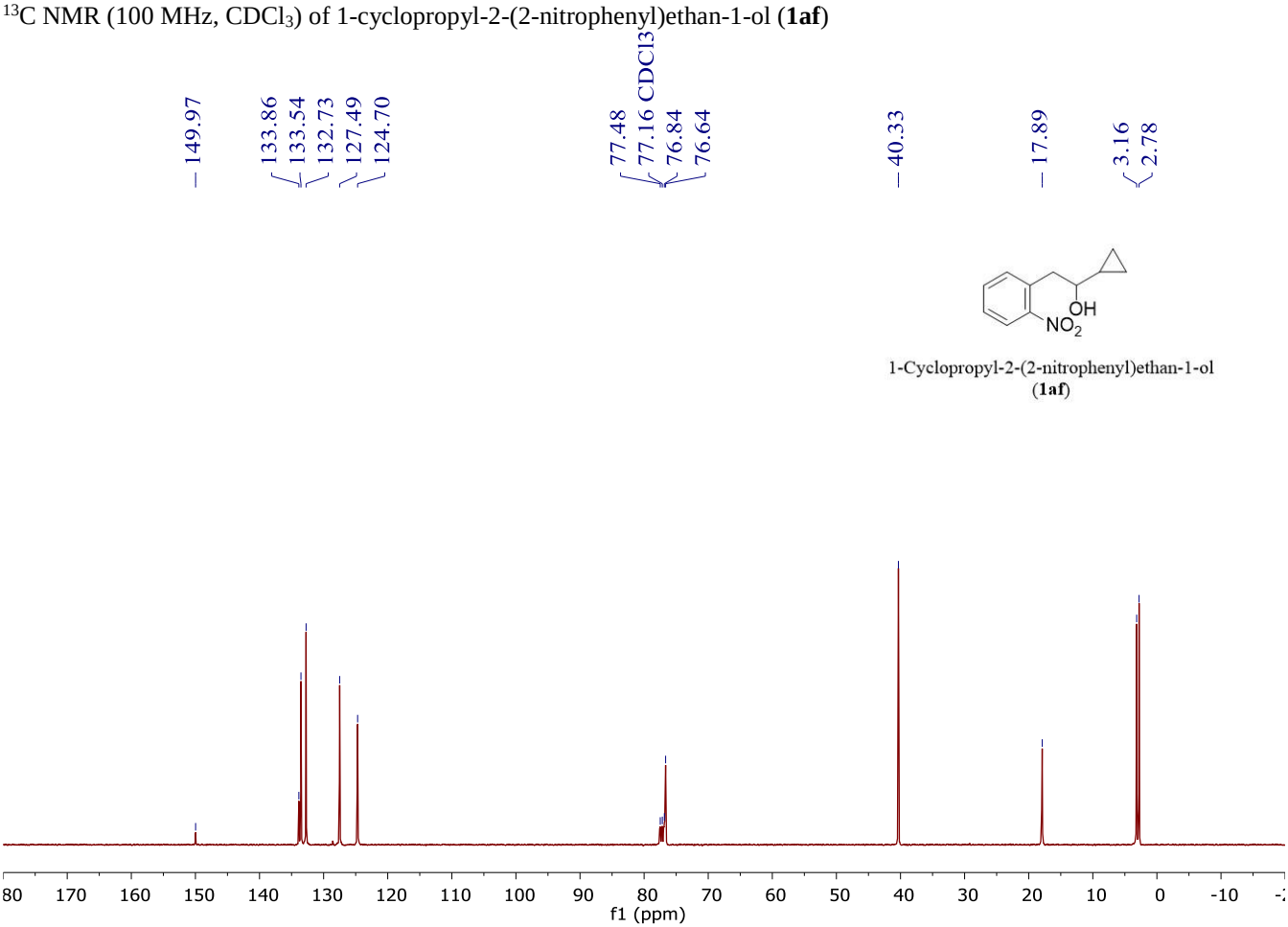
^{13}C NMR (100 MHz, $CDCl_3$) of 3,3-dimethyl-1-(2-nitrophenyl)butan-2-ol (**1ae**)



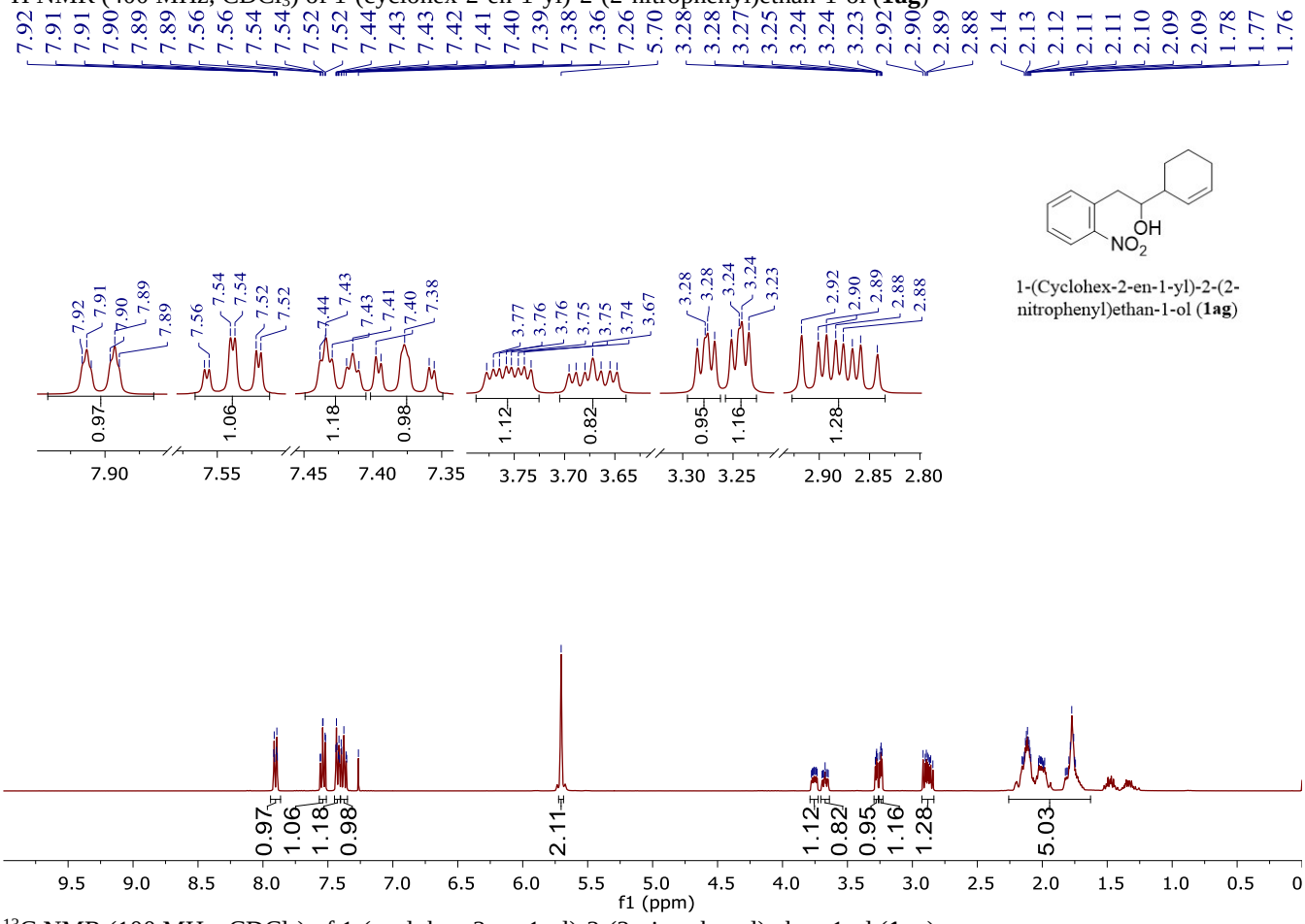
^{1}H NMR (400 MHz, $CDCl_3$) of 1-cyclopropyl-2-(2-nitrophenyl)ethan-1-ol (**1af**)



^{13}C NMR (100 MHz, $CDCl_3$) of 1-cyclopropyl-2-(2-nitrophenyl)ethan-1-ol (**1af**)

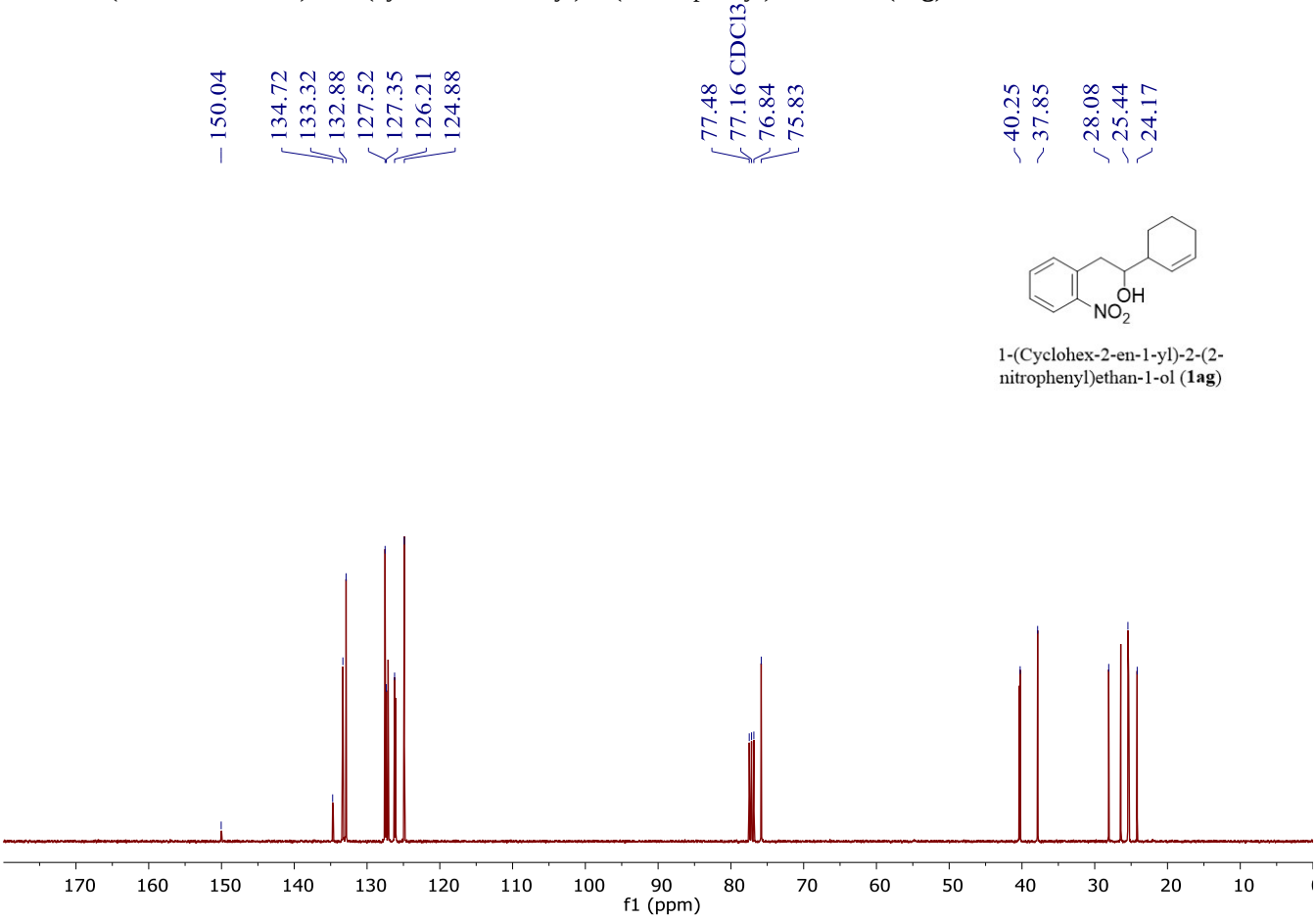


^{1}H NMR (400 MHz, $CDCl_3$) of 1-(cyclohex-2-en-1-yl)-2-(2-nitrophenyl)ethan-1-ol (**1ag**)



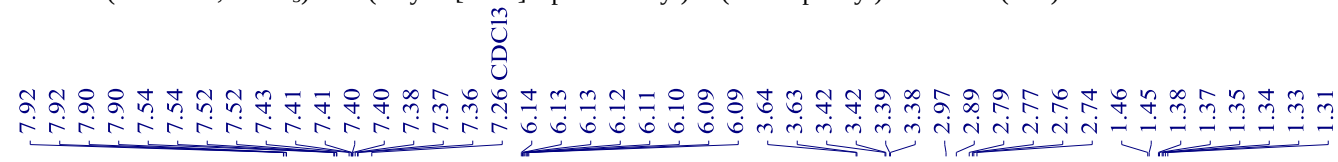
1-(Cyclohex-2-en-1-yl)-2-(2-nitrophenyl)ethan-1-ol (**1ag**)

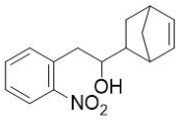
^{13}C NMR (100 MHz, $CDCl_3$) of 1-(cyclohex-2-en-1-yl)-2-(2-nitrophenyl)ethan-1-ol (**1ag**)



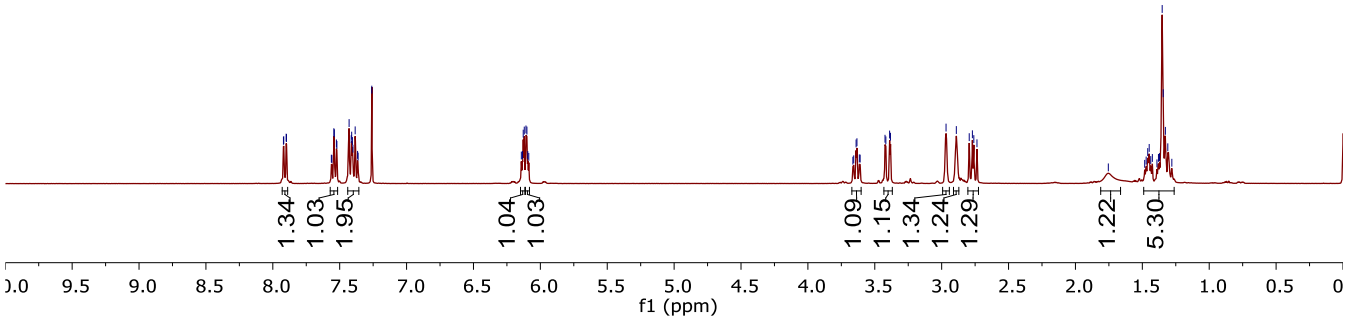
1-(Cyclohex-2-en-1-yl)-2-(2-nitrophenyl)ethan-1-ol (**1ag**)

^{1}H NMR (400 MHz, $CDCl_3$) of 1-(bicyclo[2.2.1]hept-5-en-2-yl)-2-(2-nitrophenyl)ethan-1-ol (**1ah**)

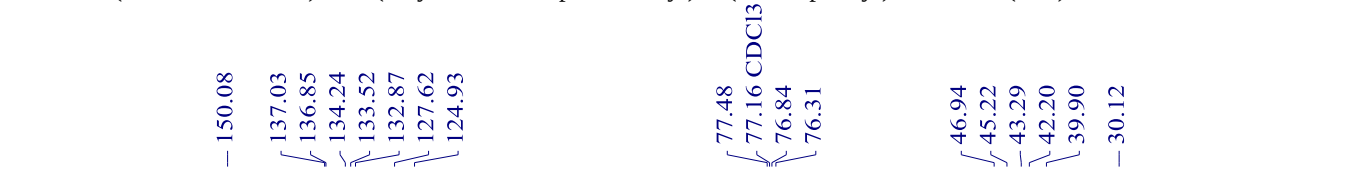


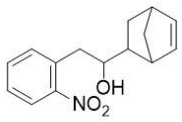


1-(Bicyclo[2.2.1]hept-5-en-2-yl)-2-(2-nitrophenyl)ethan-1-ol (**1ah**)

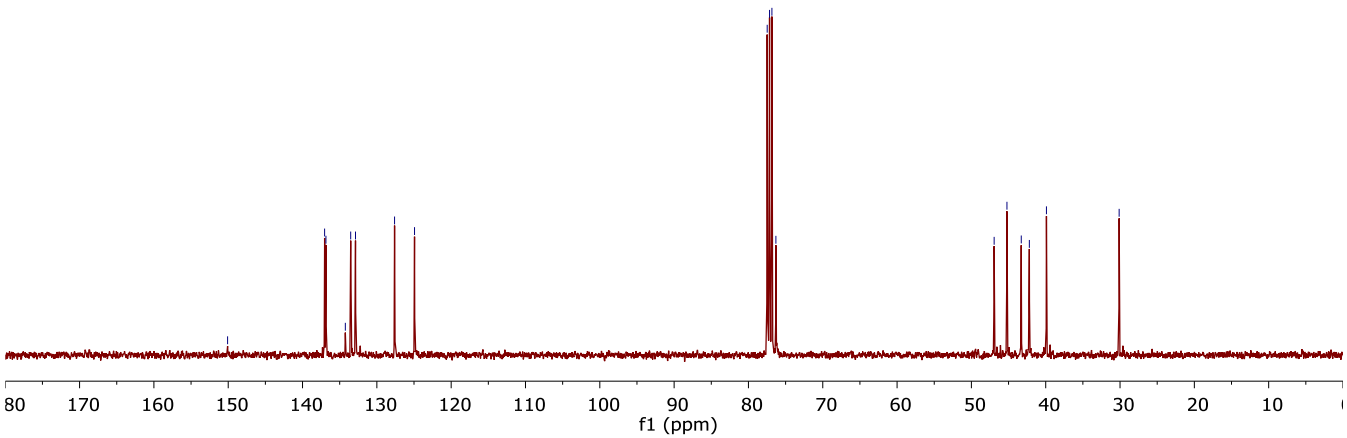


^{13}C NMR (100 MHz, $CDCl_3$) of 1-(bicyclo[2.2.1]hept-5-en-2-yl)-2-(2-nitrophenyl)ethan-1-ol (**1ah**)

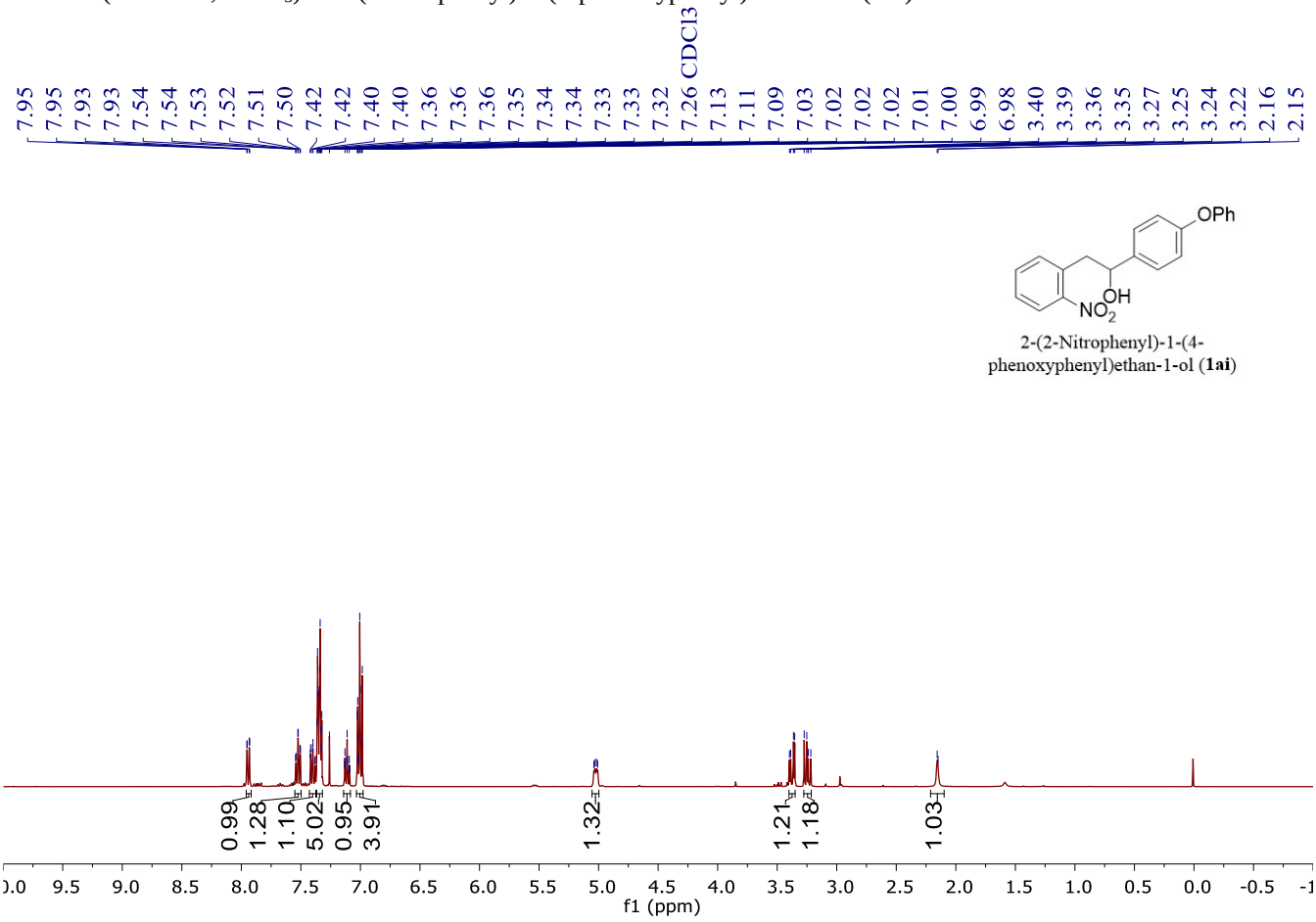




1-(Bicyclo[2.2.1]hept-5-en-2-yl)-2-(2-nitrophenyl)ethan-1-ol (**1ah**)

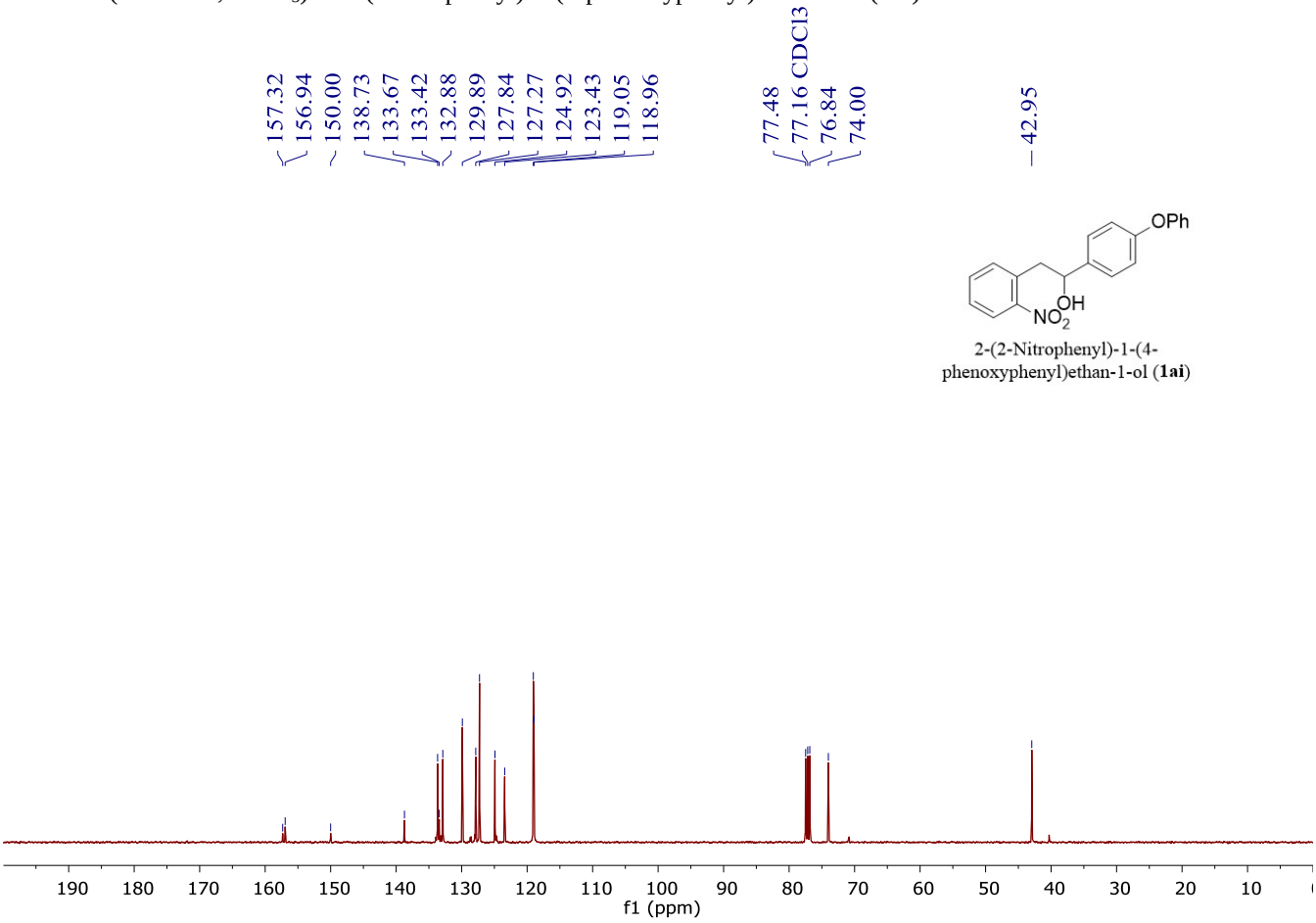


^{1}H NMR (400 MHz, $CDCl_3$) of 2-(2-nitrophenyl)-1-(4-phenoxyphenyl)ethan-1-ol (**1ai**)



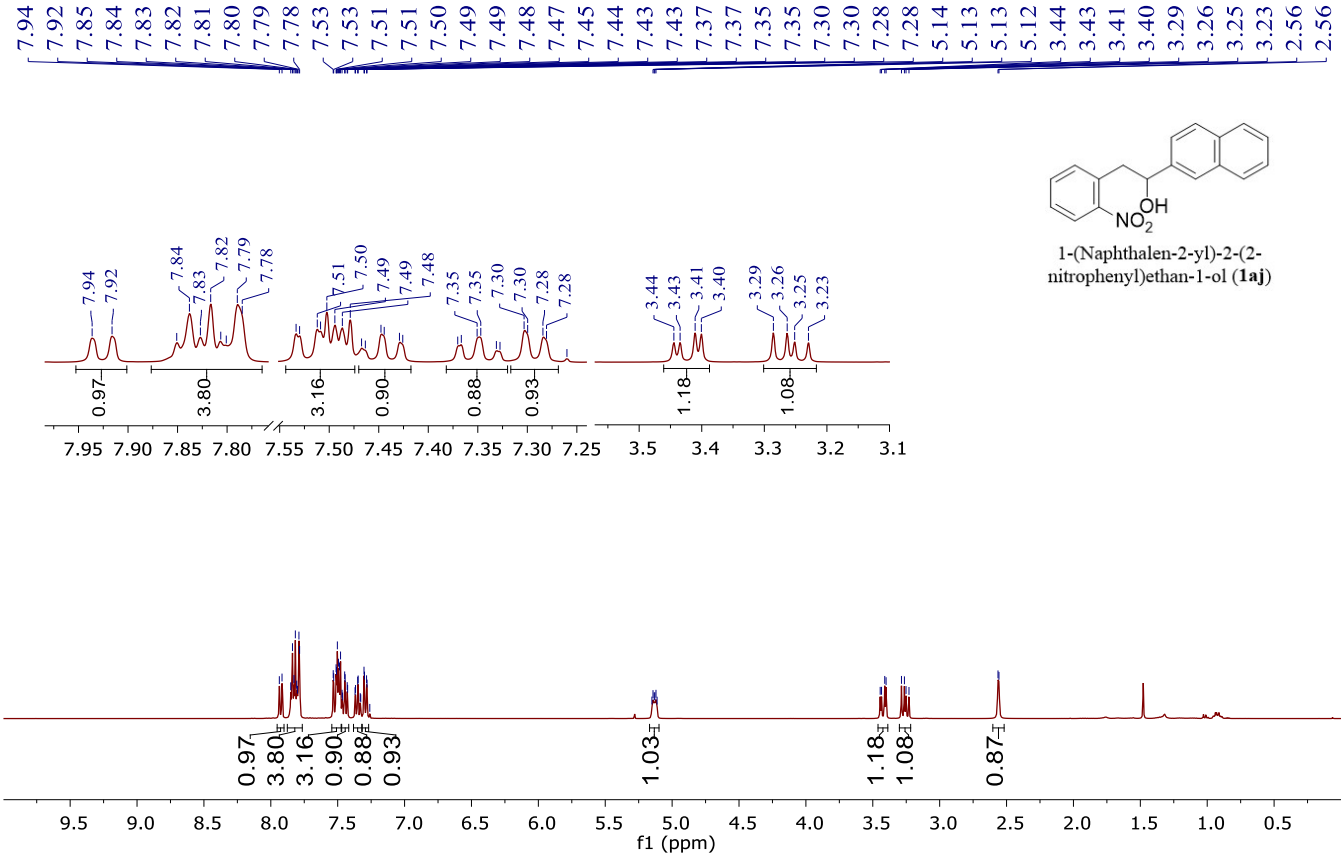
2-(2-Nitrophenyl)-1-(4-phenoxyphenyl)ethan-1-ol (**1ai**)

^{13}C NMR (100 MHz, $CDCl_3$) of 2-(2-nitrophenyl)-1-(4-phenoxyphenyl)ethan-1-ol (**1ai**)



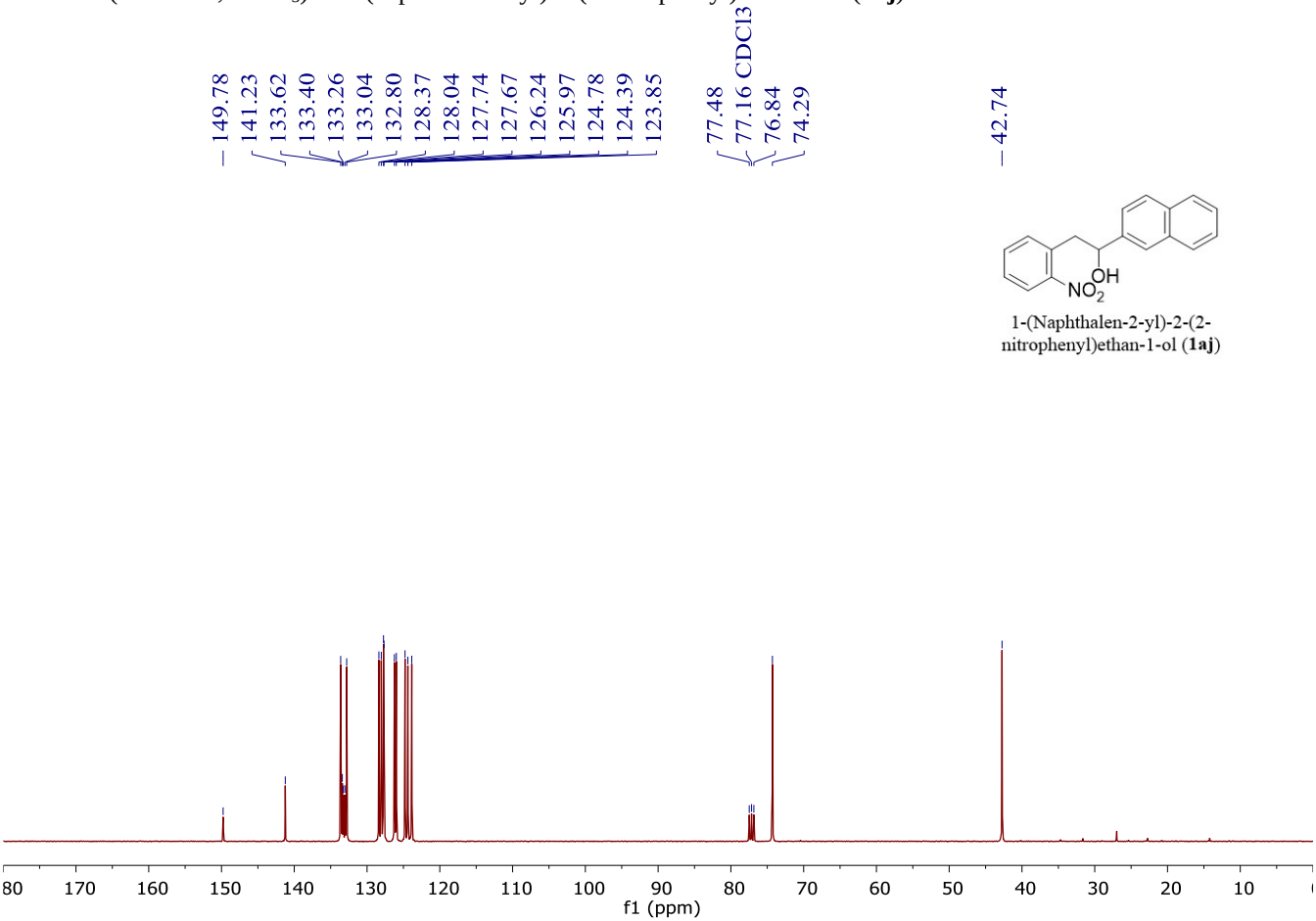
2-(2-Nitrophenyl)-1-(4-phenoxyphenyl)ethan-1-ol (**1ai**)

^{1}H NMR (400 MHz, $CDCl_3$) of 1-(naphthalen-2-yl)-2-(2-nitrophenyl)ethan-1-ol (**1aj**)



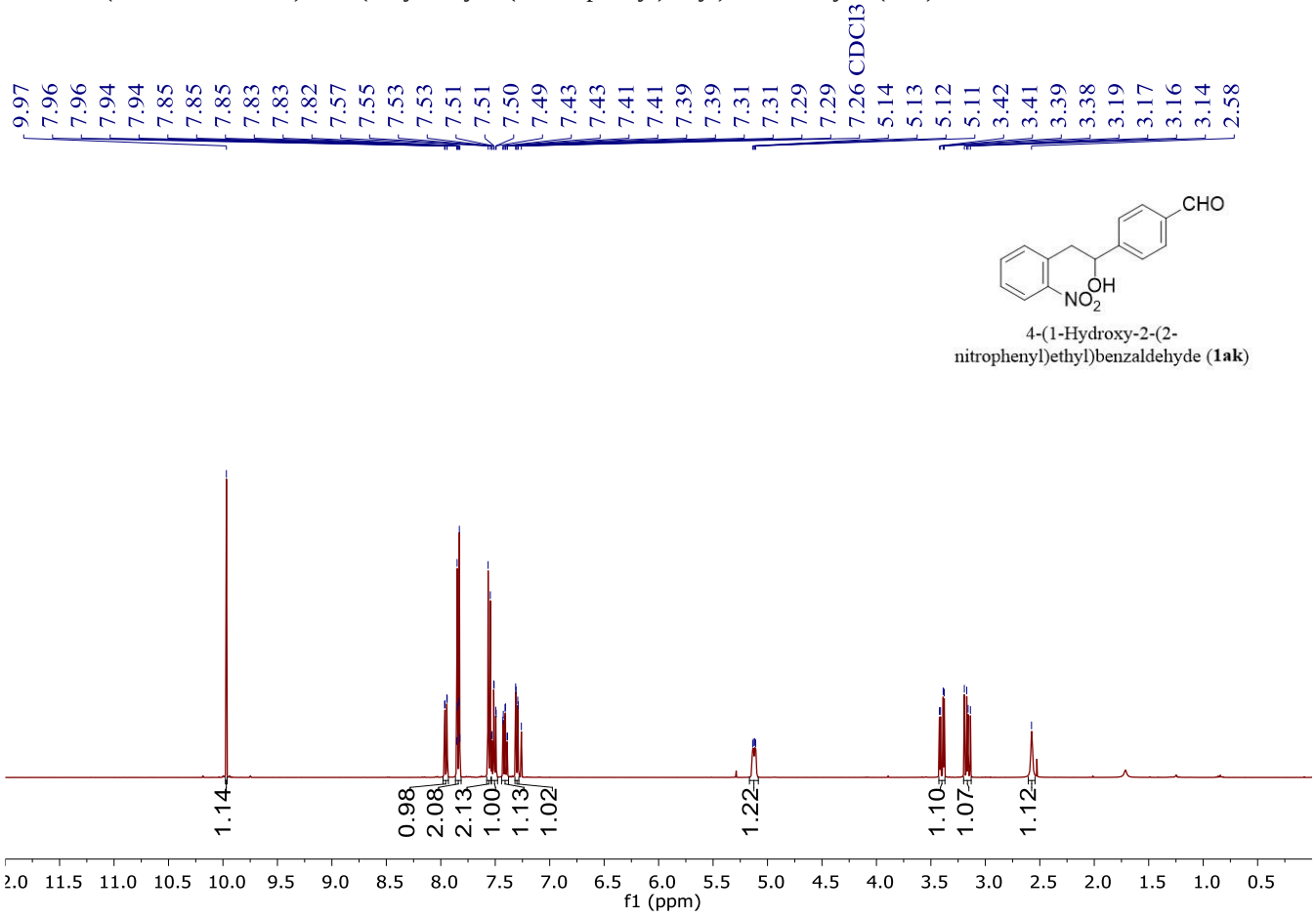
1-(Naphthalen-2-yl)-2-(2-nitrophenyl)ethan-1-ol (**1aj**)

^{13}C NMR (100 MHz, $CDCl_3$) of 1-(naphthalen-2-yl)-2-(2-nitrophenyl)ethan-1-ol (**1aj**)

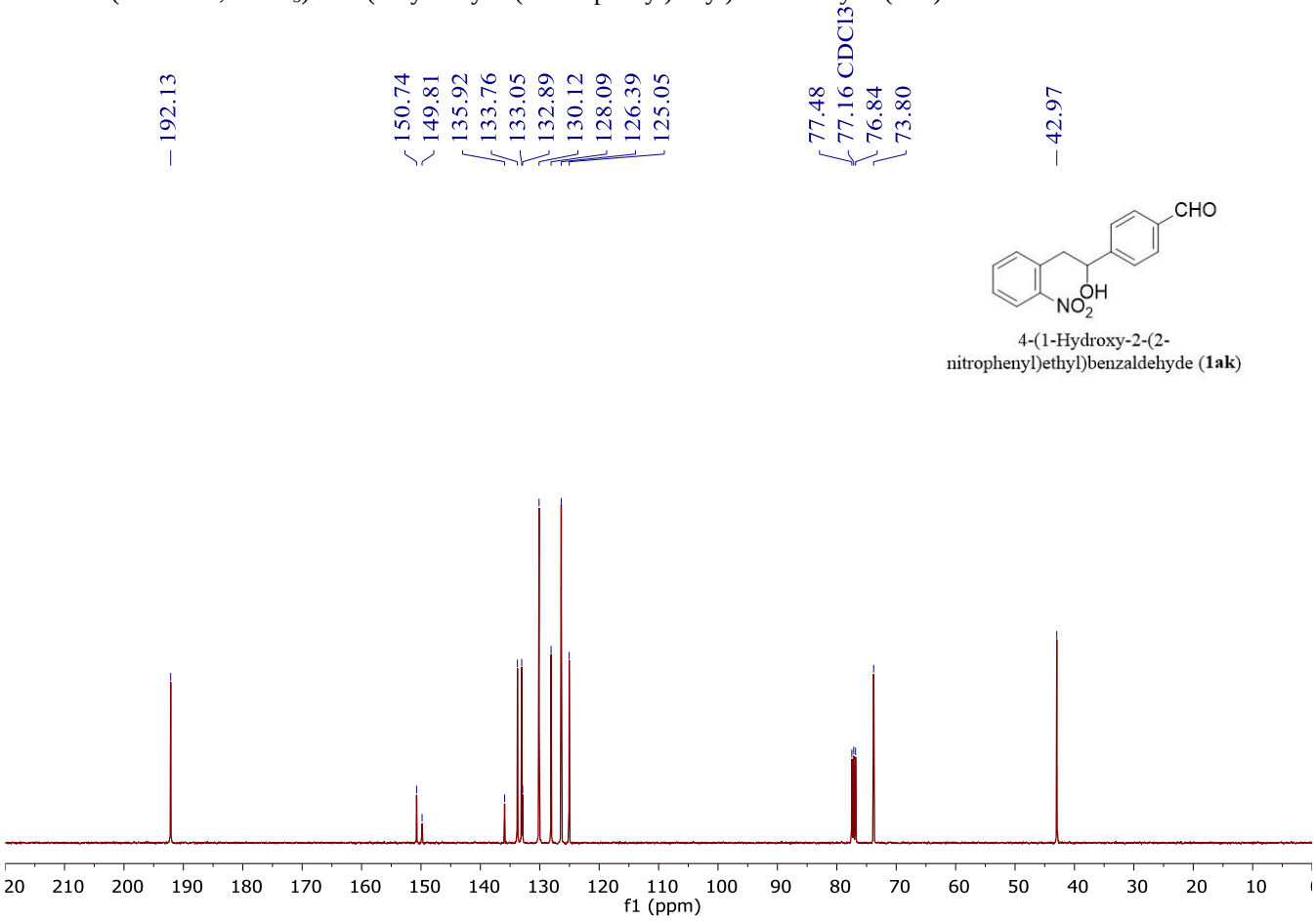


1-(Naphthalen-2-yl)-2-(2-nitrophenyl)ethan-1-ol (**1aj**)

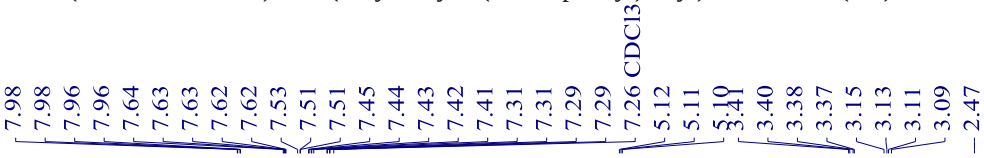
^{1}H NMR (400 MHz, $CDCl_3$) of 4-(1-hydroxy-2-(2-nitrophenyl)ethyl)benzaldehyde (**1ak**)

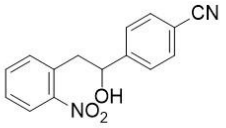


^{13}C NMR (100 MHz, $CDCl_3$) of 4-(1-hydroxy-2-(2-nitrophenyl)ethyl)benzaldehyde (**1ak**)

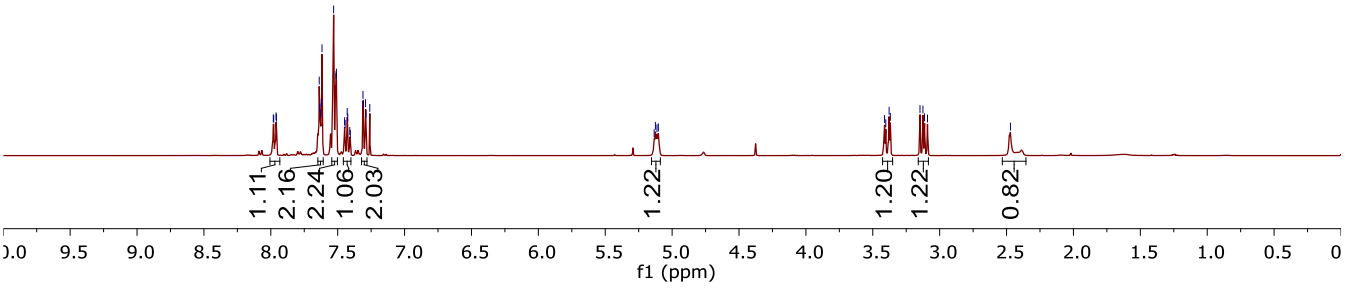


^{1}H NMR (400 MHz, $CDCl_3$) of 4-(1-hydroxy-2-(2-nitrophenyl)ethyl)benzonitrile (**1al**)

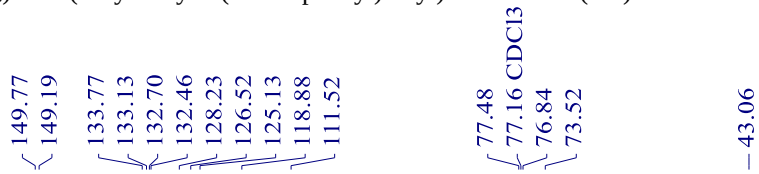


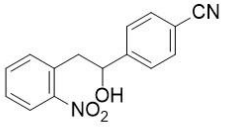


4-(1-Hydroxy-2-(2-nitrophenyl)ethyl)benzonitrile (**1al**)

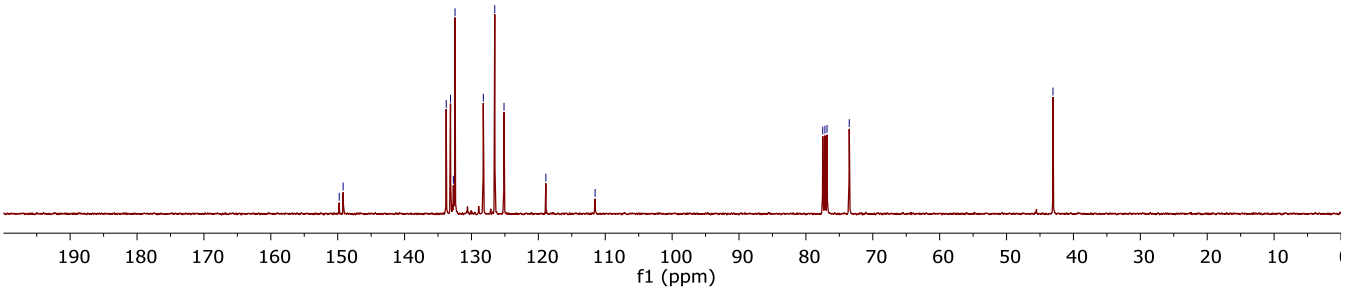


^{13}C NMR (100 MHz, $CDCl_3$) of 4-(1-hydroxy-2-(2-nitrophenyl)ethyl)benzonitrile (**1al**)

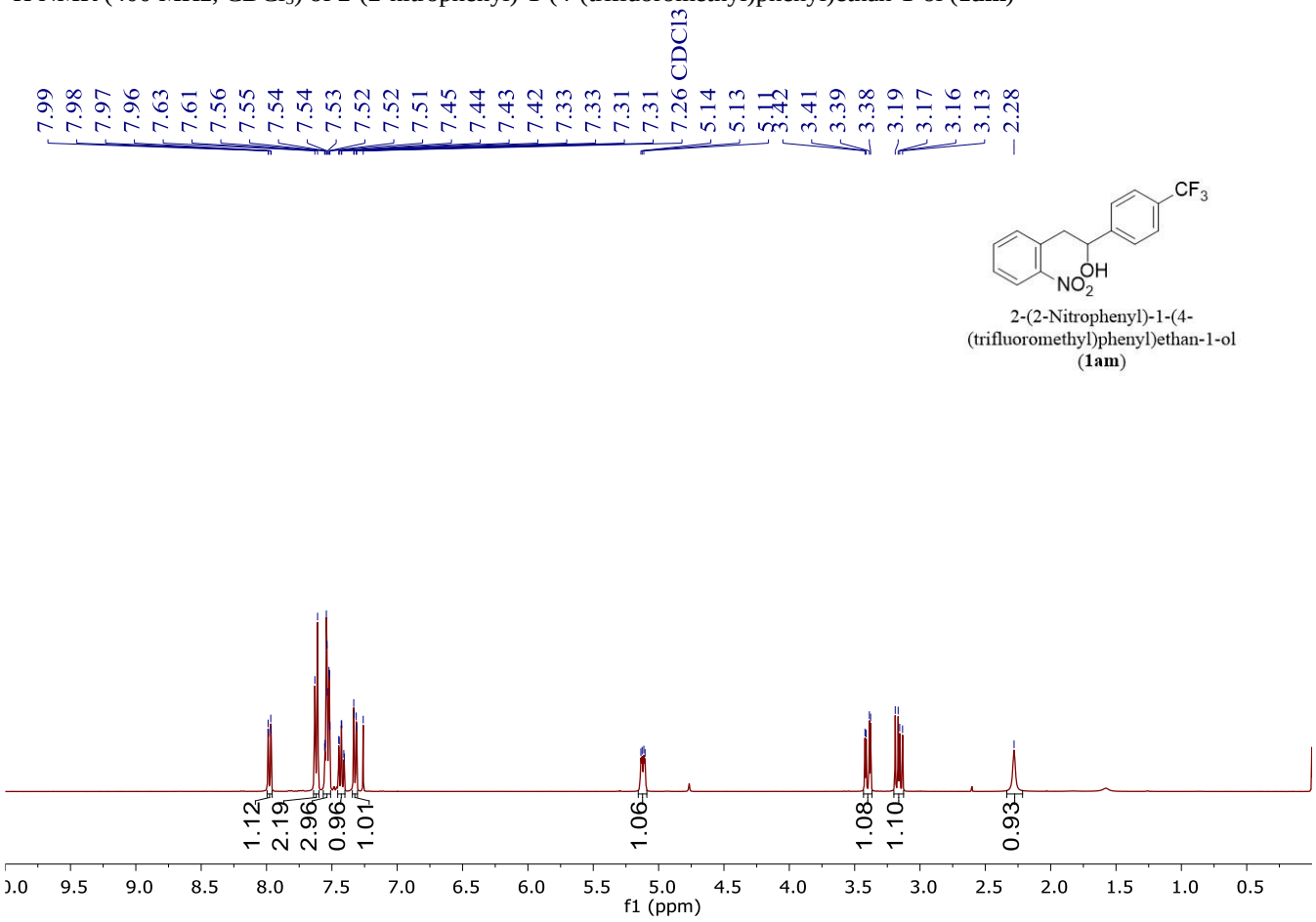




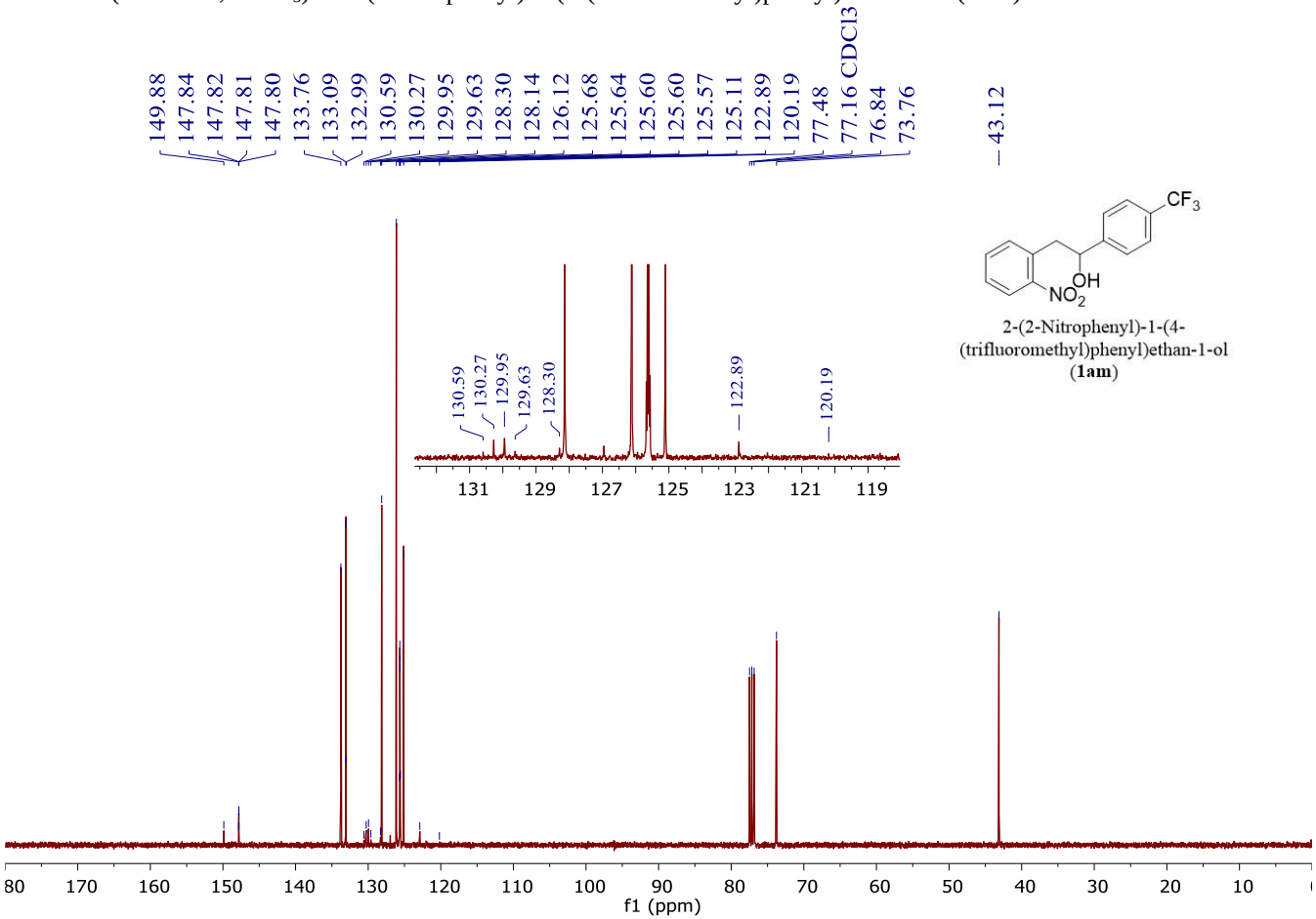
4-(1-Hydroxy-2-(2-nitrophenyl)ethyl)benzonitrile (**1al**)



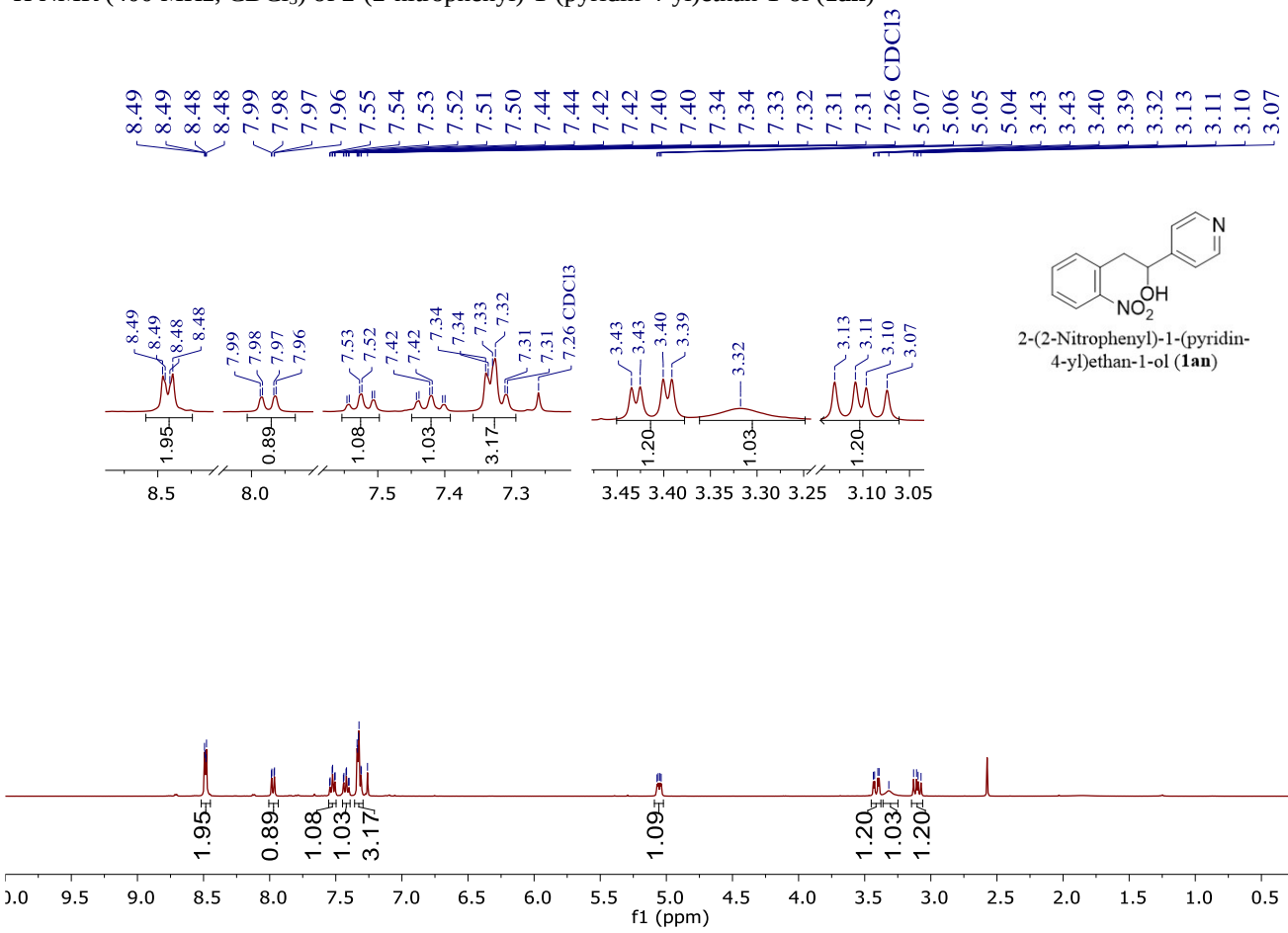
^{1}H NMR (400 MHz, $CDCl_3$) of 2-(2-nitrophenyl)-1-(4-(trifluoromethyl)phenyl)ethan-1-ol (**1am**)



^{13}C NMR (100 MHz, $CDCl_3$) of 2-(2-nitrophenyl)-1-(4-(trifluoromethyl)phenyl)ethan-1-ol (**1am**)

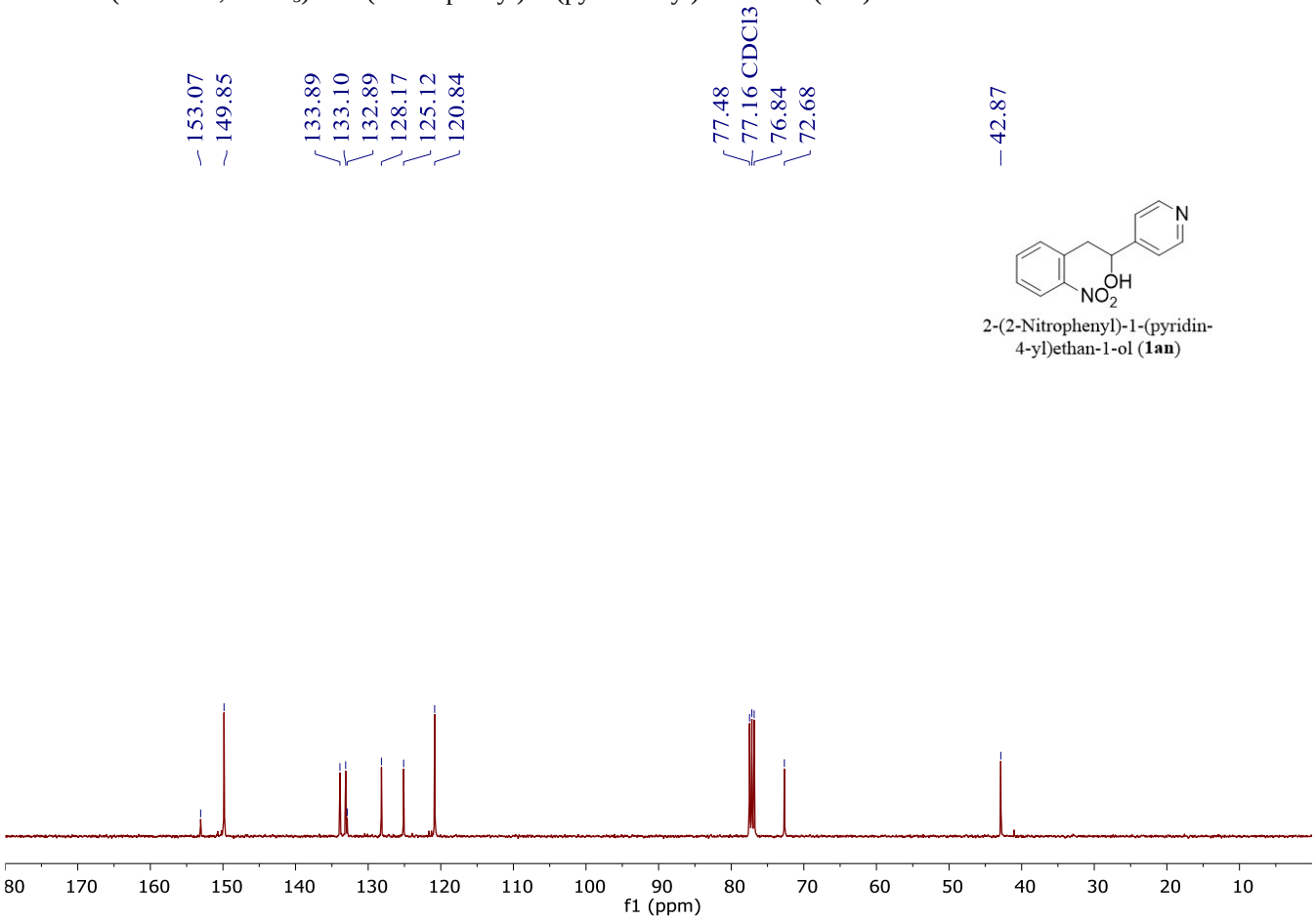


^{1}H NMR (400 MHz, $CDCl_3$) of 2-(2-nitrophenyl)-1-(pyridin-4-yl)ethan-1-ol (**1an**)



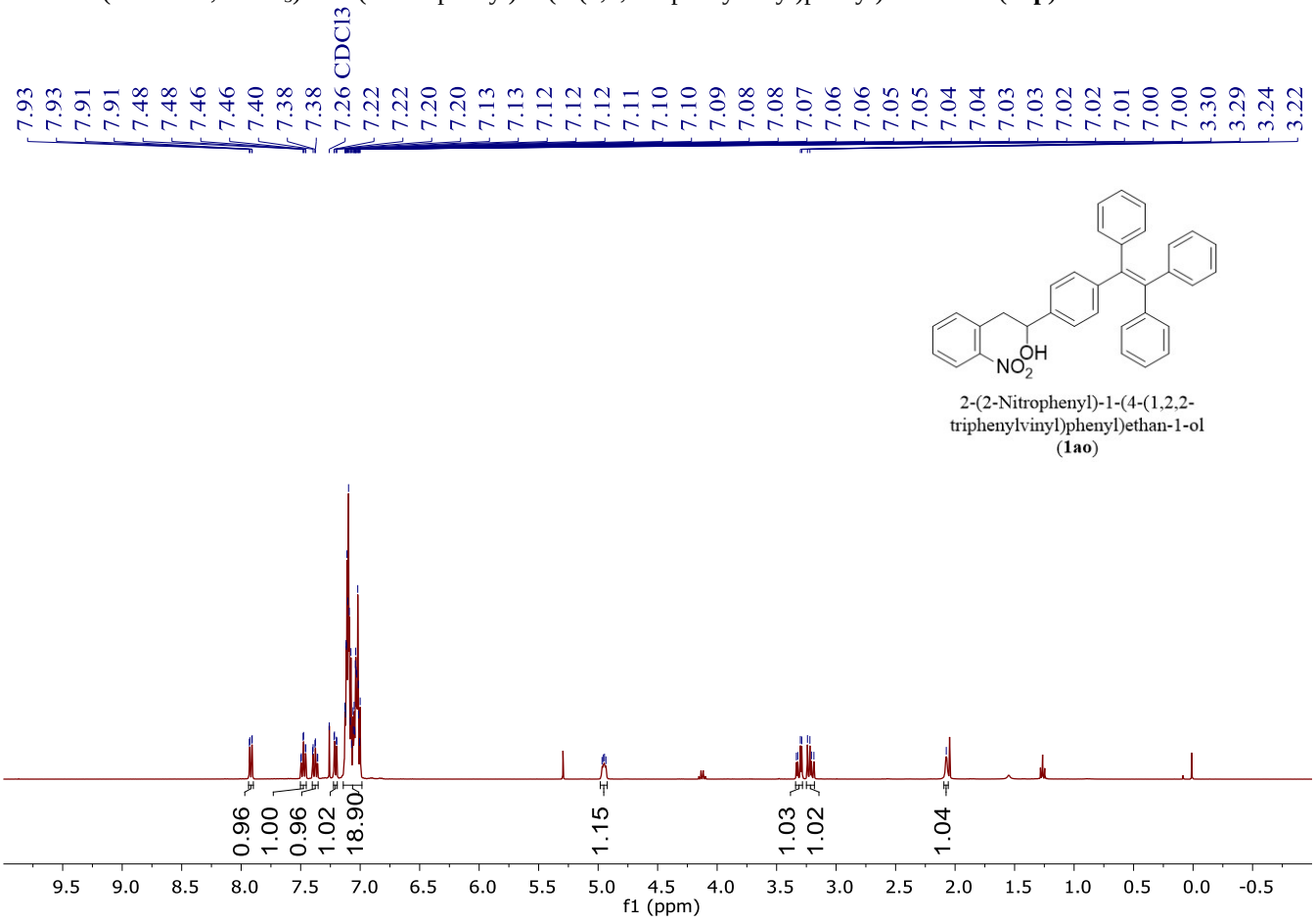
2-(2-Nitrophenyl)-1-(pyridin-4-yl)ethan-1-ol (**1an**)

^{13}C NMR (100 MHz, $CDCl_3$) of 2-(2-nitrophenyl)-1-(pyridin-4-yl)ethan-1-ol (**1an**)



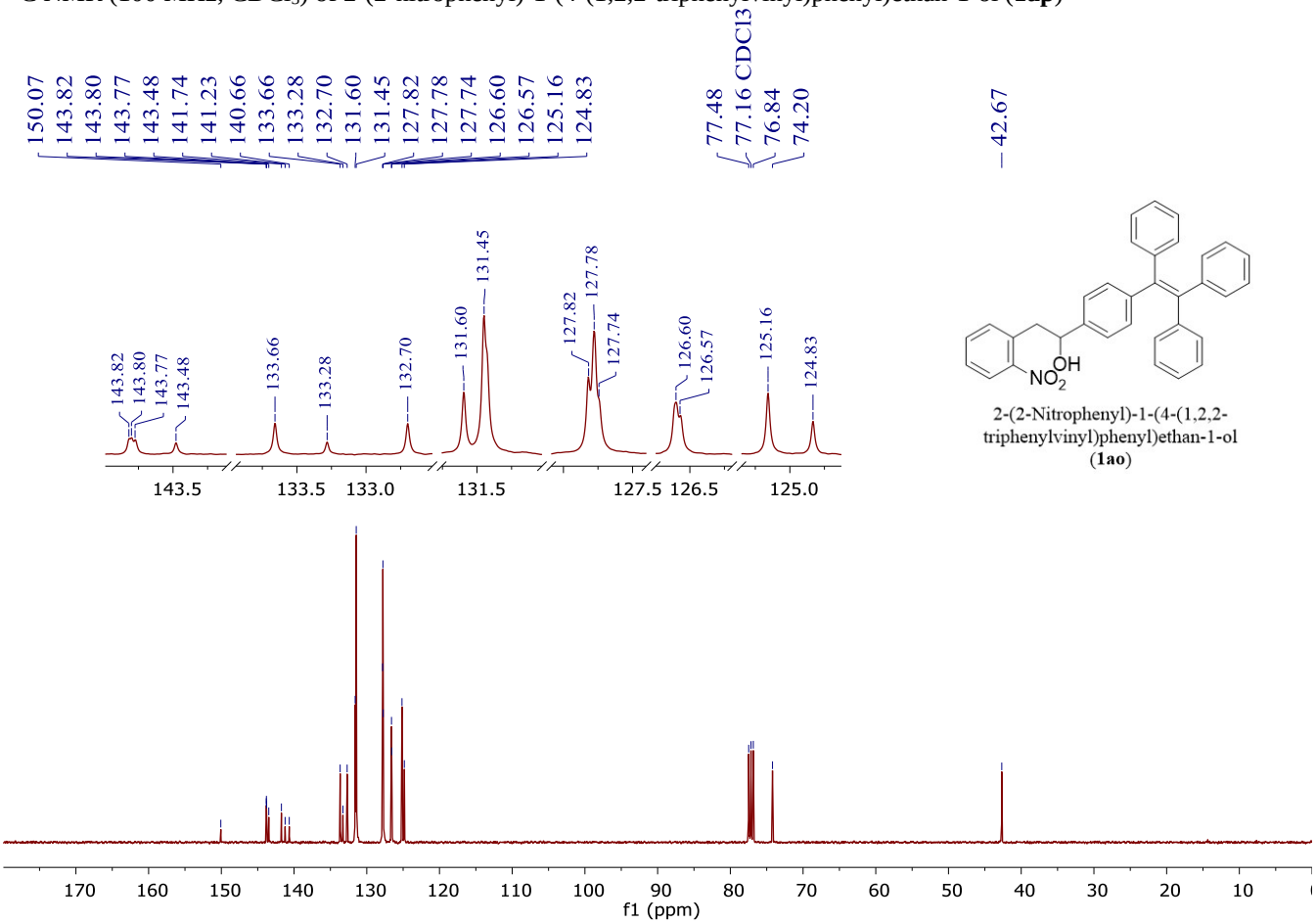
2-(2-Nitrophenyl)-1-(pyridin-4-yl)ethan-1-ol (**1an**)

^{1}H NMR (400 MHz, $CDCl_3$) of 2-(2-nitrophenyl)-1-(4-(1,2,2-triphenylvinyl)phenyl)ethan-1-ol (**1ap**)



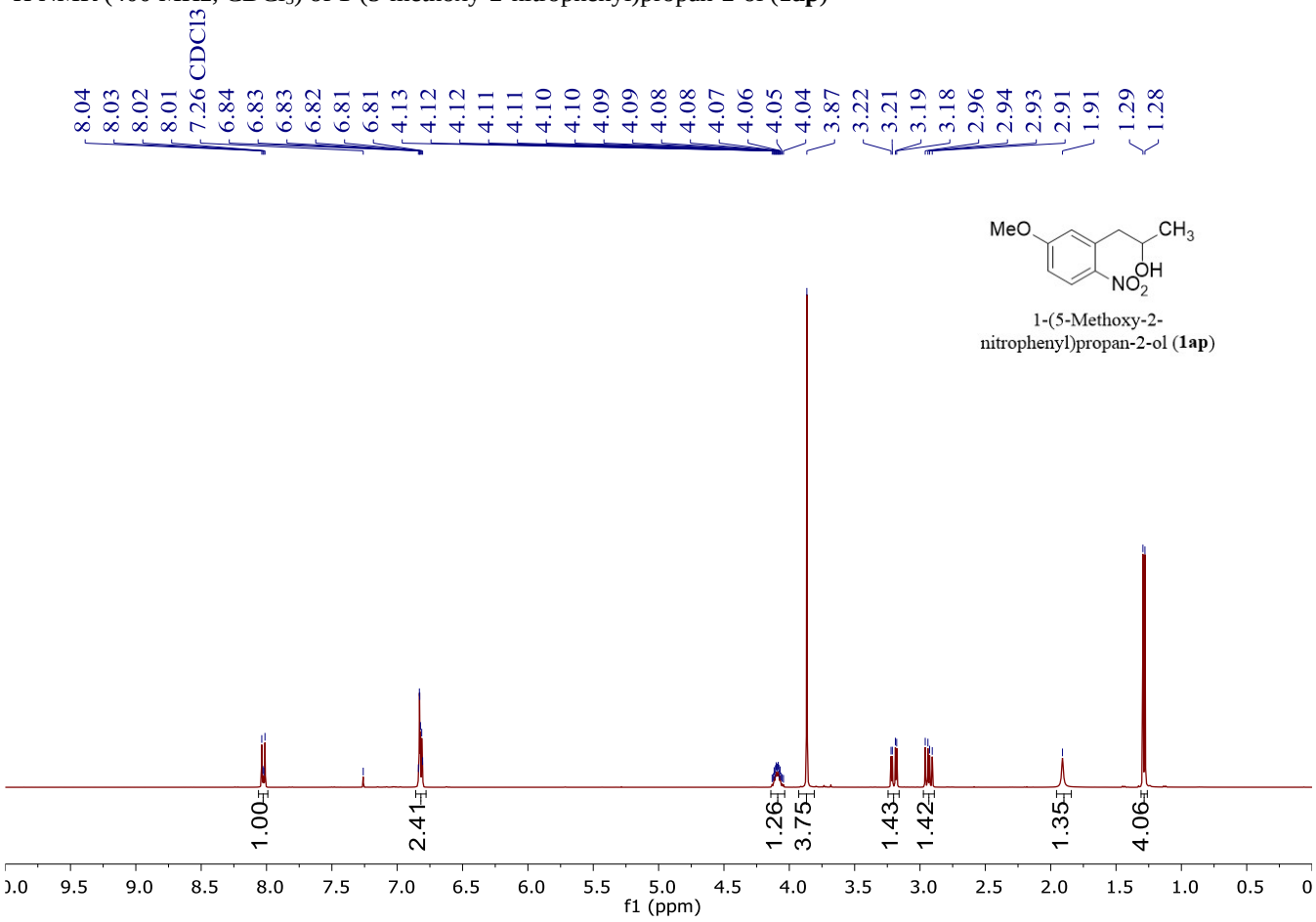
2-(2-Nitrophenyl)-1-(4-(1,2,2-triphenylvinyl)phenyl)ethan-1-ol (**1ao**)

^{13}C NMR (100 MHz, $CDCl_3$) of 2-(2-nitrophenyl)-1-(4-(1,2,2-triphenylvinyl)phenyl)ethan-1-ol (**1ap**)

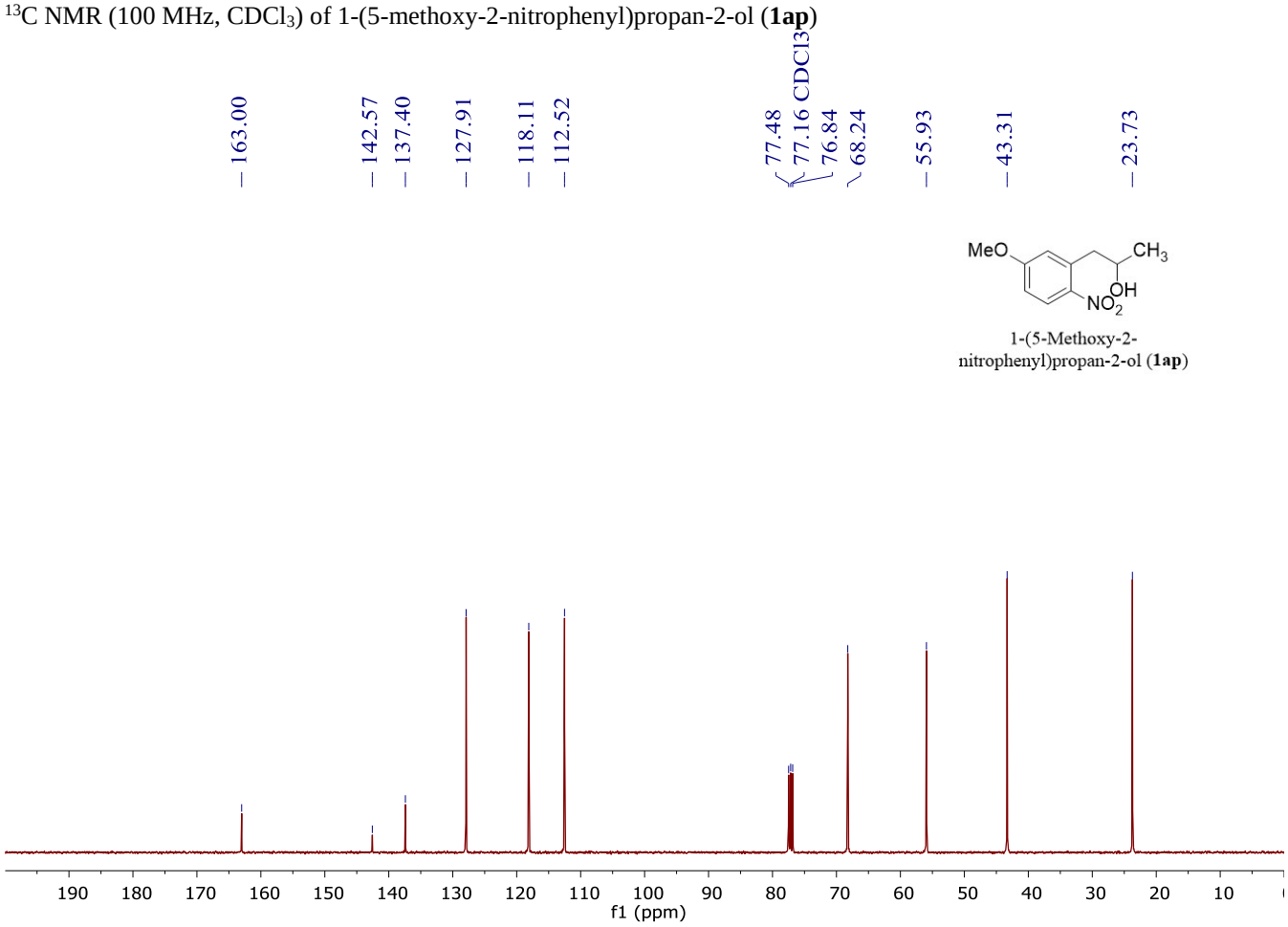


2-(2-Nitrophenyl)-1-(4-(1,2,2-triphenylvinyl)phenyl)ethan-1-ol (**1ao**)

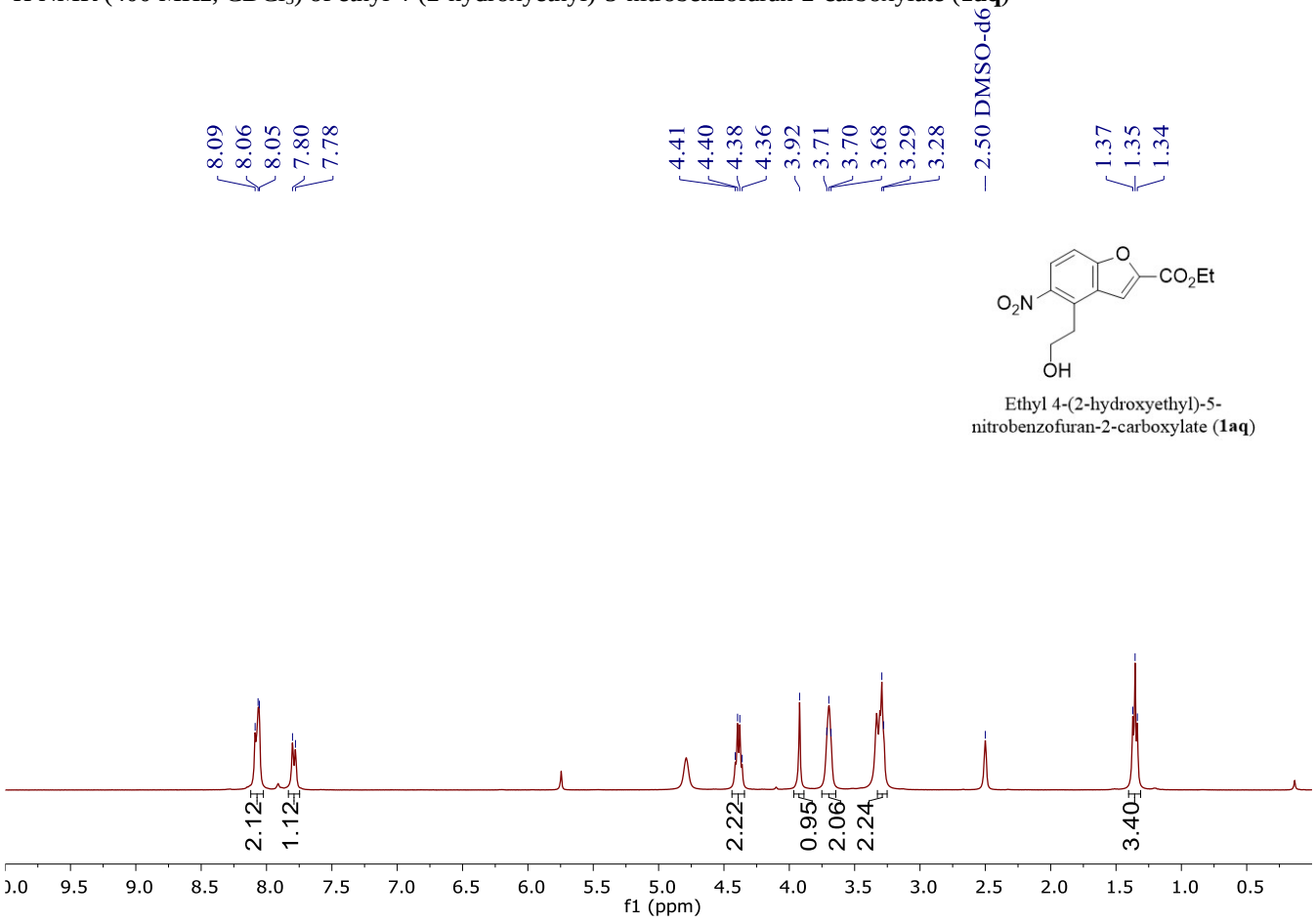
^{1}H NMR (400 MHz, $CDCl_3$) of 1-(5-methoxy-2-nitrophenyl)propan-2-ol (**1ap**)



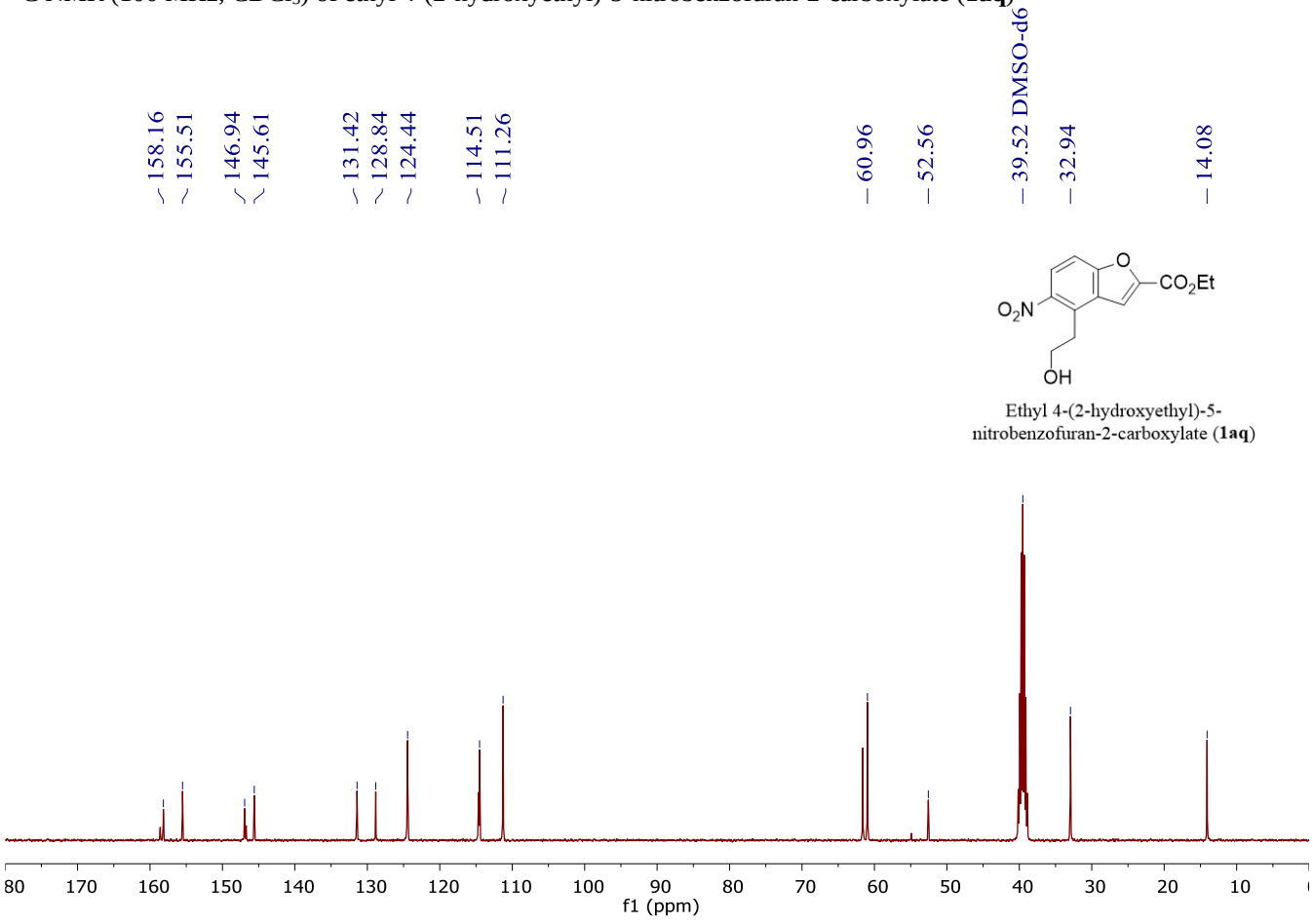
^{13}C NMR (100 MHz, $CDCl_3$) of 1-(5-methoxy-2-nitrophenyl)propan-2-ol (**1ap**)



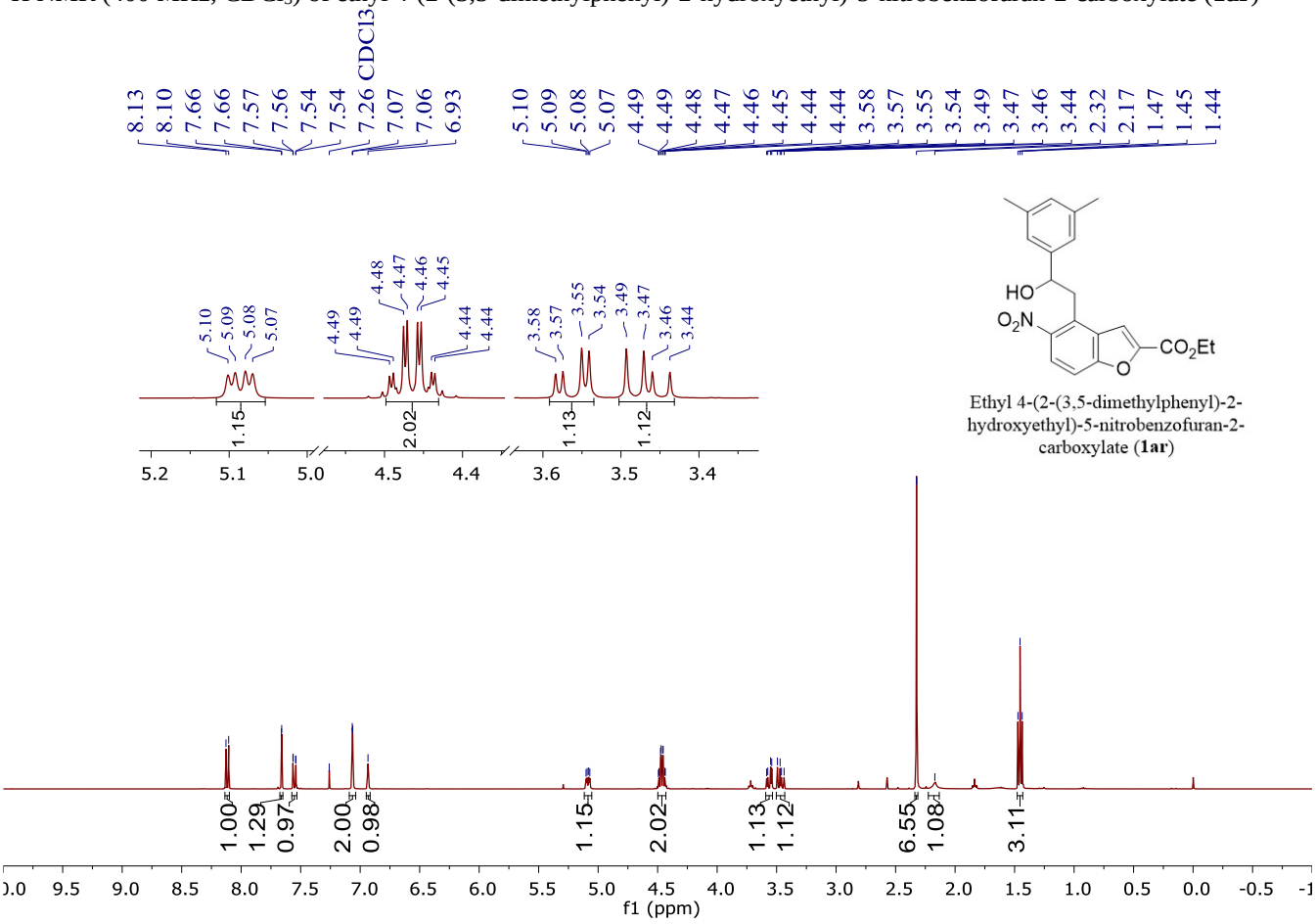
^{1}H NMR (400 MHz, $CDCl_3$) of ethyl 4-(2-hydroxyethyl)-5-nitrobenzofuran-2-carboxylate (**1aq**)



^{13}C NMR (100 MHz, $CDCl_3$) of ethyl 4-(2-hydroxyethyl)-5-nitrobenzofuran-2-carboxylate (**1aq**)

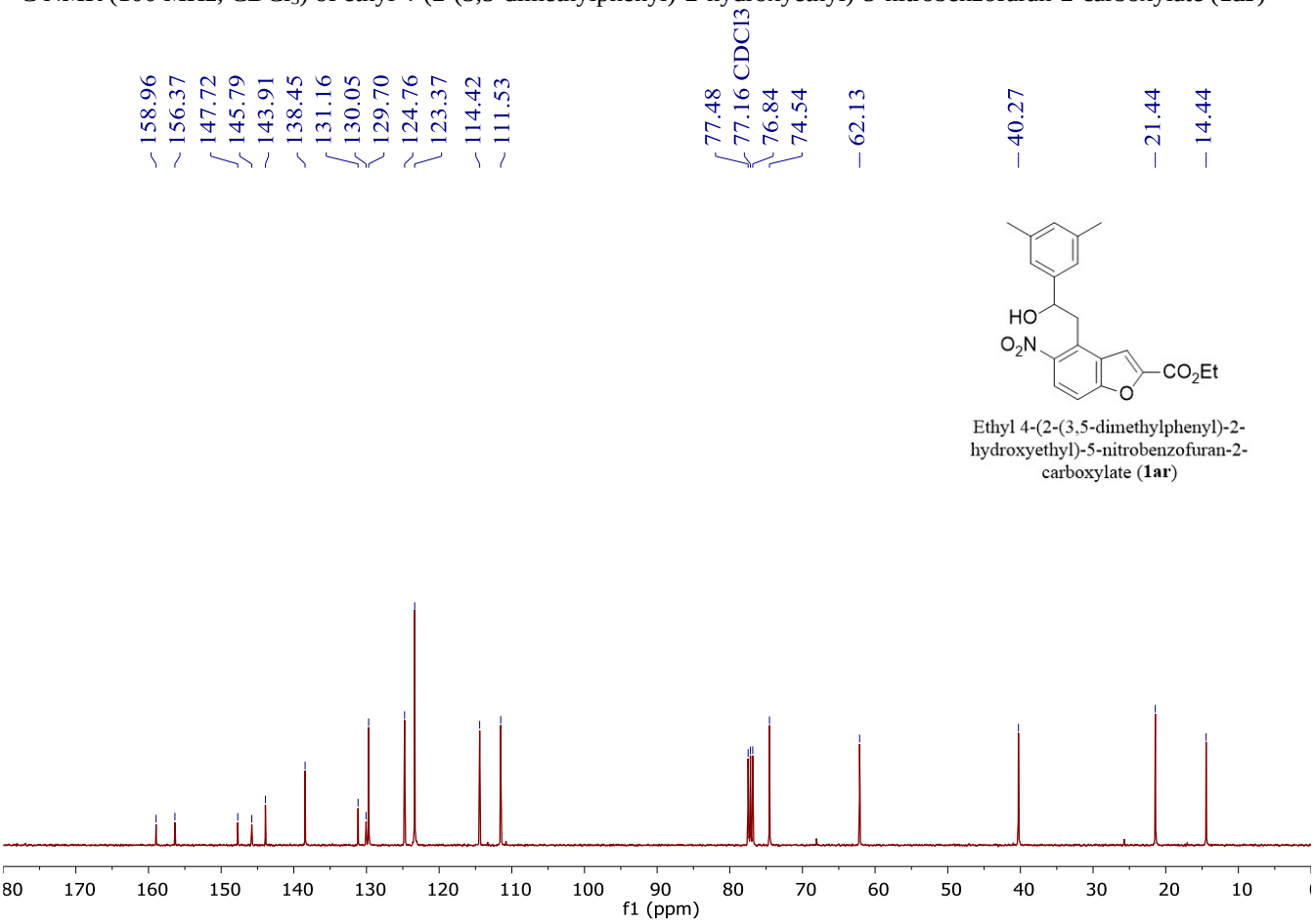


^{1}H NMR (400 MHz, $CDCl_3$) of ethyl 4-(2-(3,5-dimethylphenyl)-2-hydroxyethyl)-5-nitrobenzofuran-2-carboxylate (**1ar**)



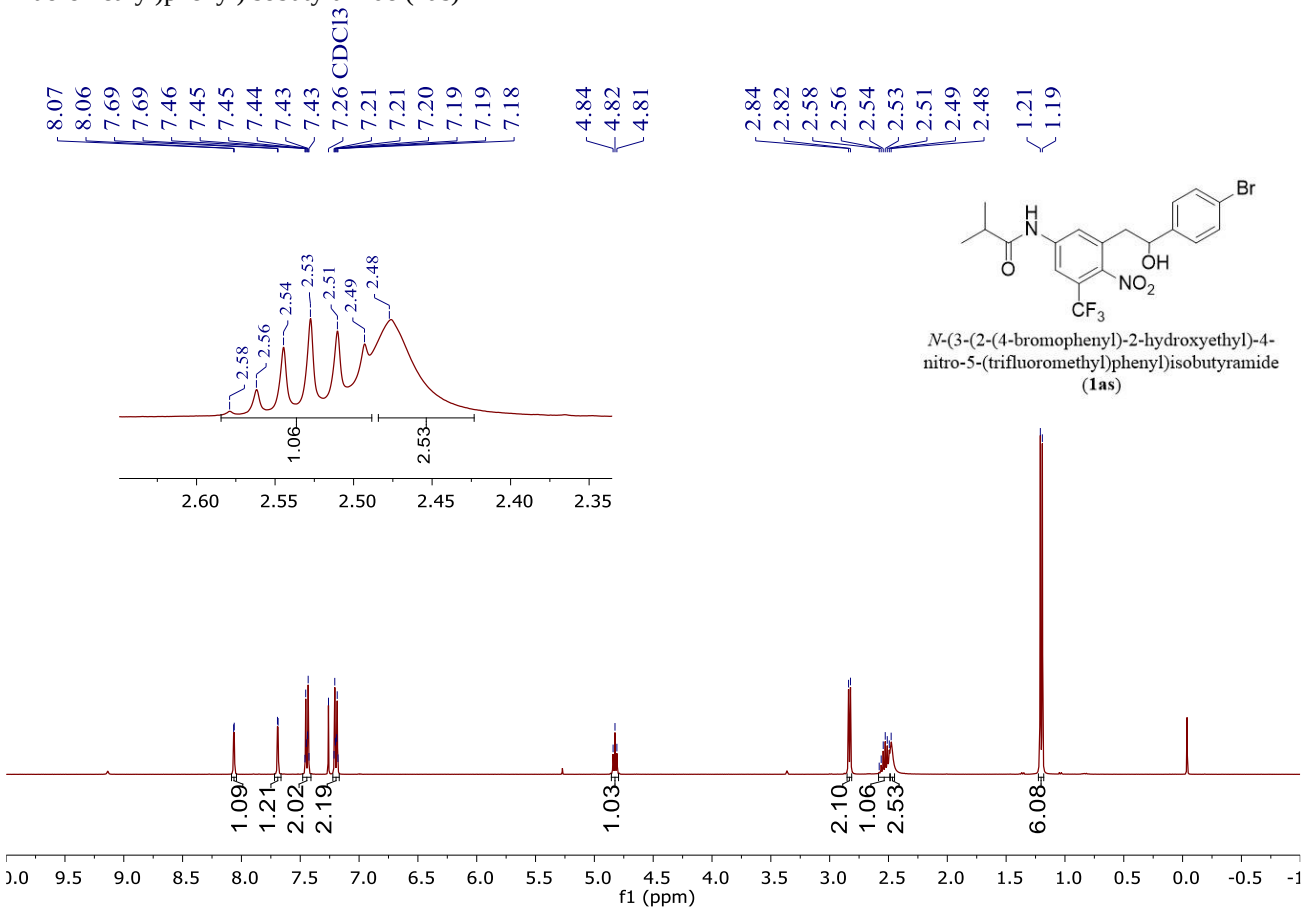
Ethyl 4-(2-(3,5-dimethylphenyl)-2-hydroxyethyl)-5-nitrobenzofuran-2-carboxylate (**1ar**)

^{13}C NMR (100 MHz, $CDCl_3$) of ethyl 4-(2-(3,5-dimethylphenyl)-2-hydroxyethyl)-5-nitrobenzofuran-2-carboxylate (**1ar**)

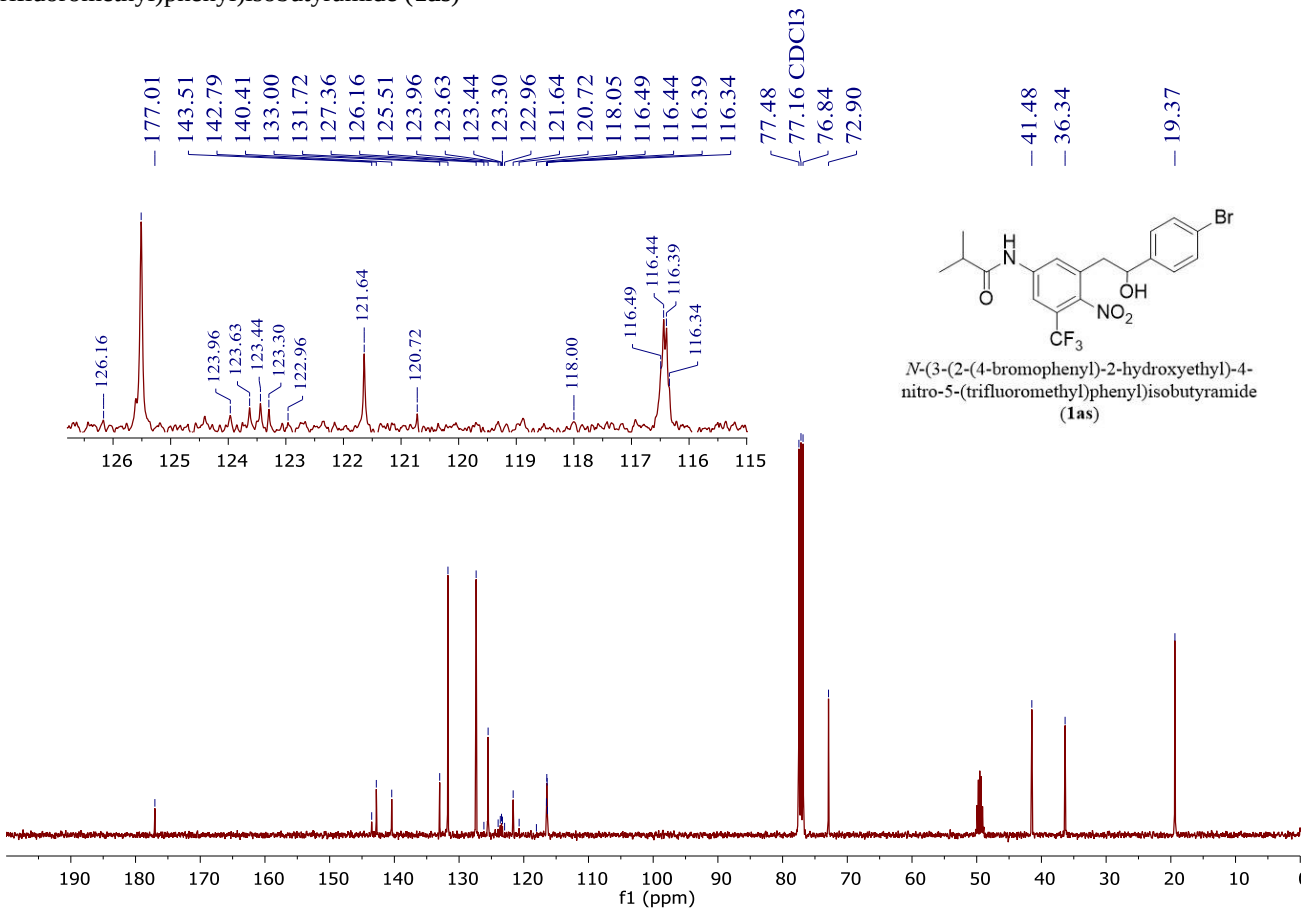


Ethyl 4-(2-(3,5-dimethylphenyl)-2-hydroxyethyl)-5-nitrobenzofuran-2-carboxylate (**1ar**)

^{1}H NMR (400 MHz, $CDCl_3$ & DMSO-d_6) of *N*-(3-(2-(4-bromophenyl)-2-hydroxyethyl)-4-nitro-5-(trifluoromethyl)phenyl)isobutyramide (**1as**)

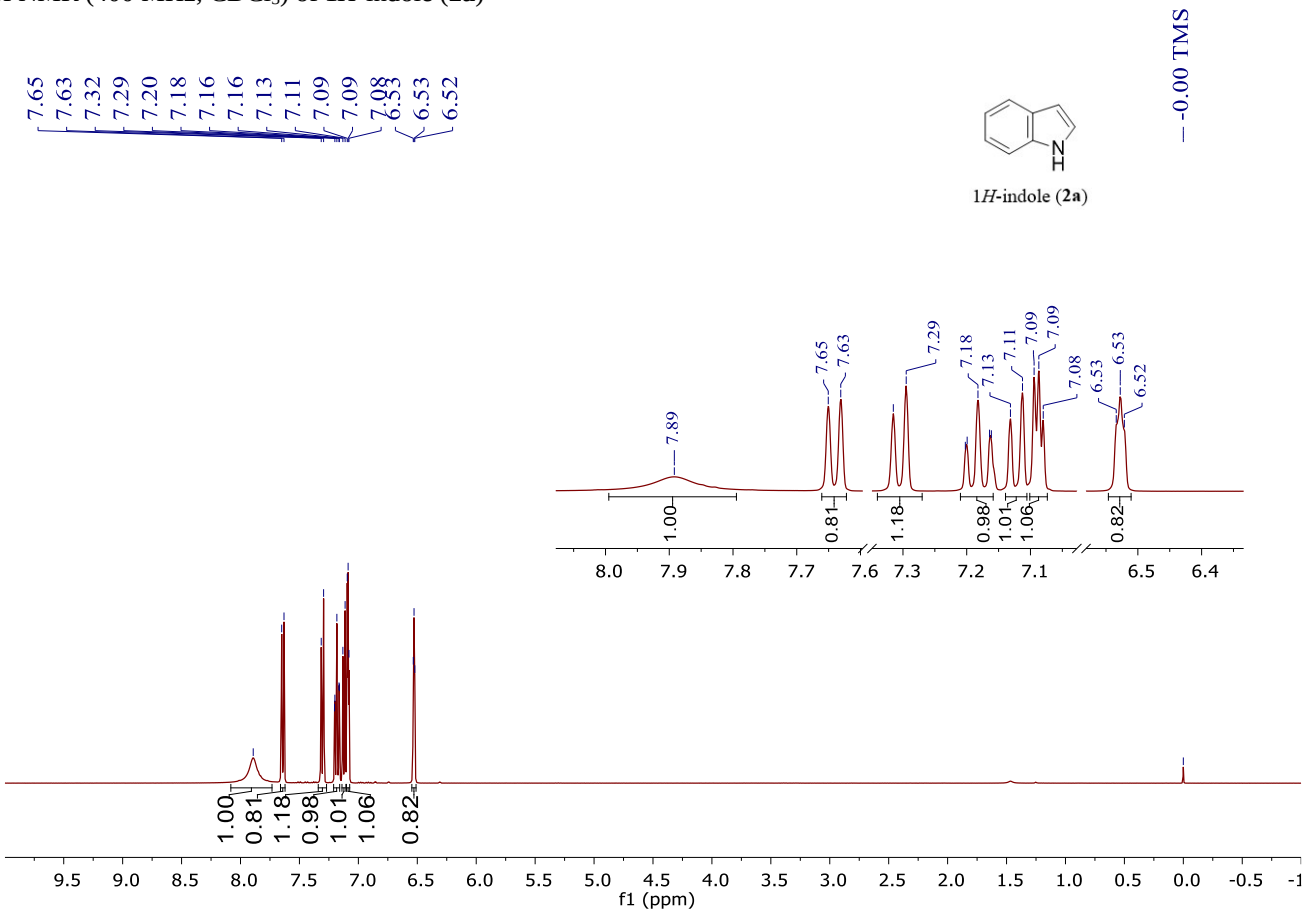


^{13}C NMR (100 MHz, $CDCl_3$ & DMSO-d_6) of *N*-(3-(2-(4-bromophenyl)-2-hydroxyethyl)-4-nitro-5-(trifluoromethyl)phenyl)isobutyramide (**1as**)

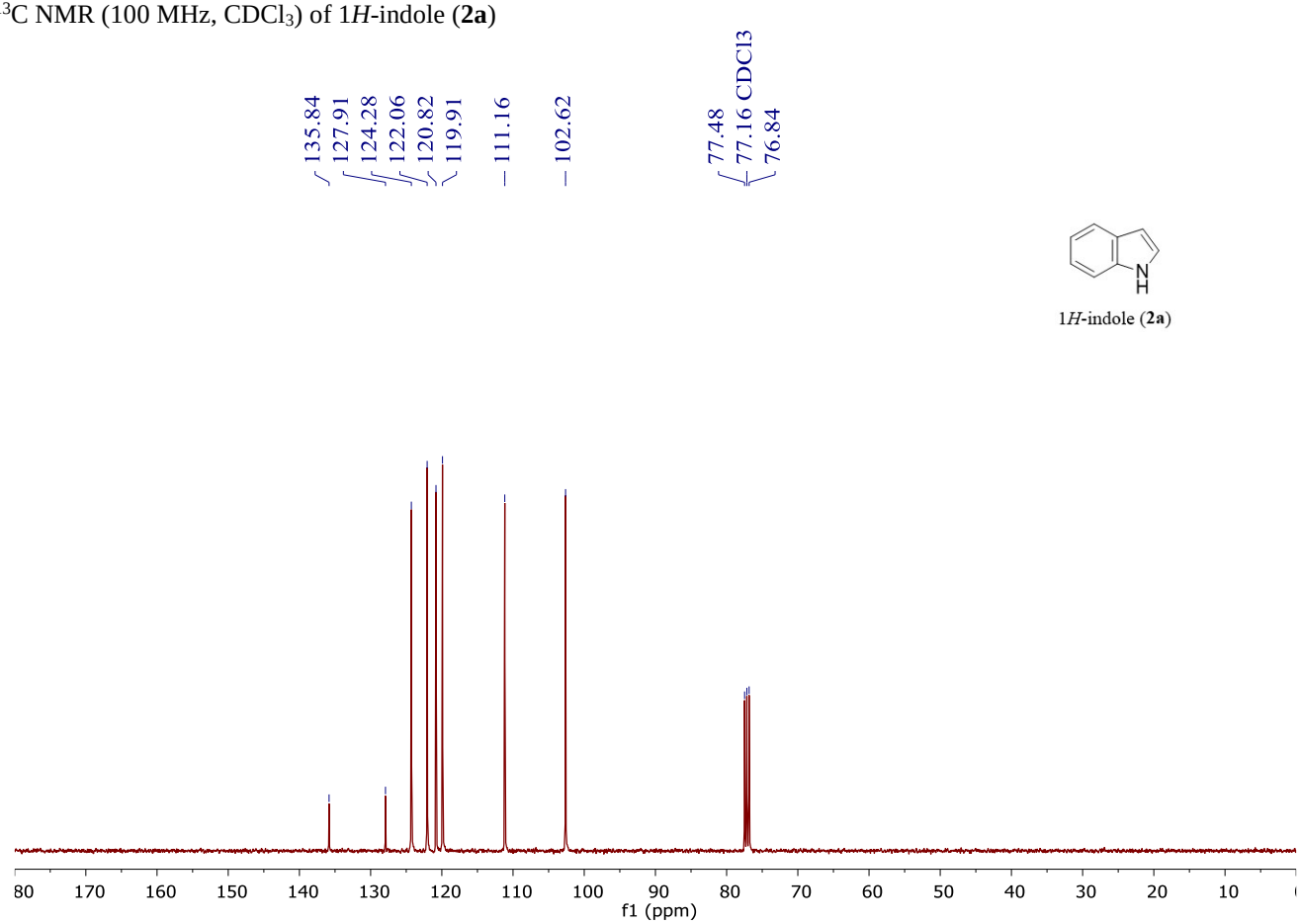


6.2. NMR Spectra of Products

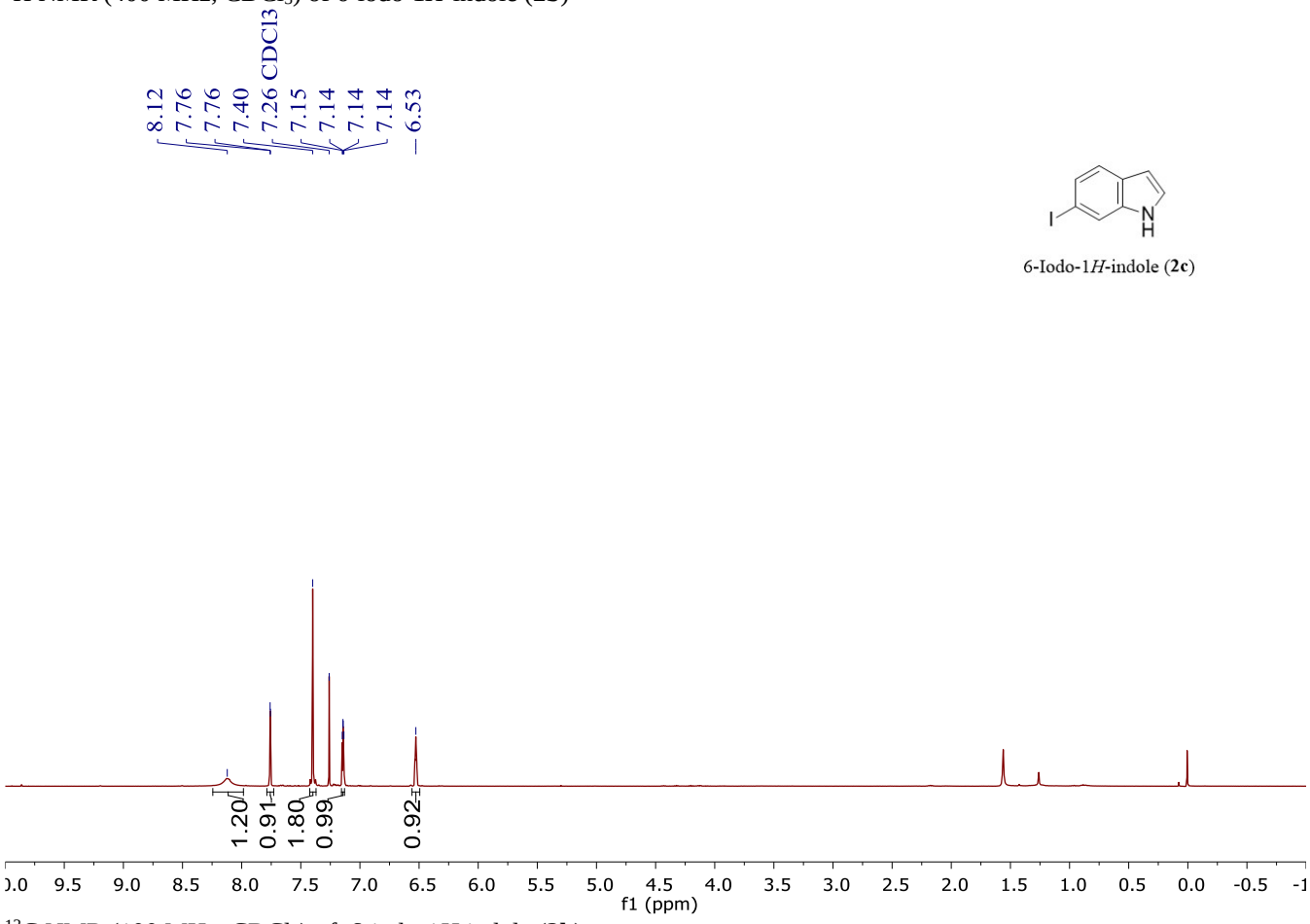
^{1}H NMR (400 MHz, $CDCl_3$) of 1*H*-indole (**2a**)



^{13}C NMR (100 MHz, $CDCl_3$) of 1*H*-indole (**2a**)

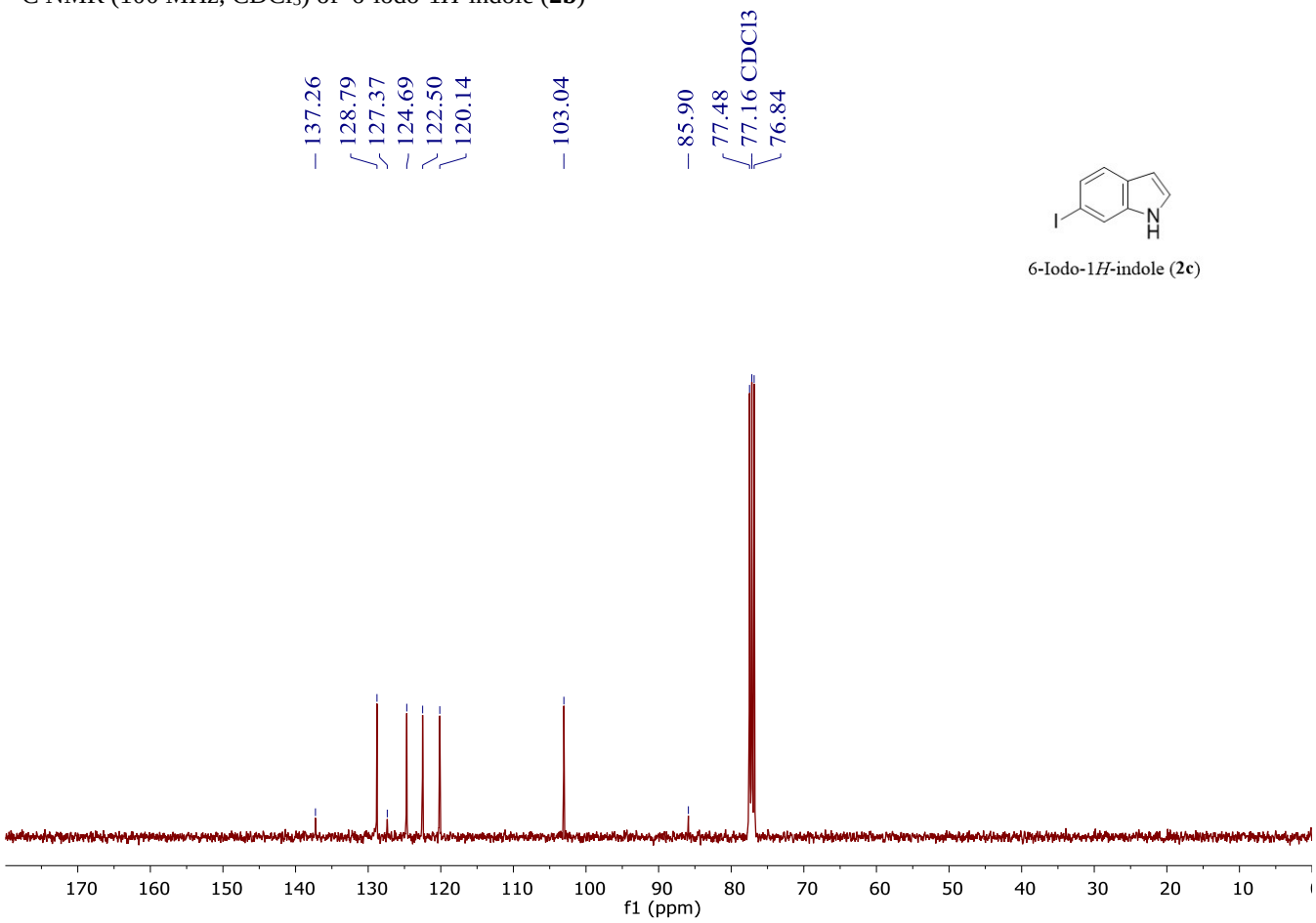


^{1}H NMR (400 MHz, $CDCl_3$) of 6-iodo-1*H*-indole (**2b**)



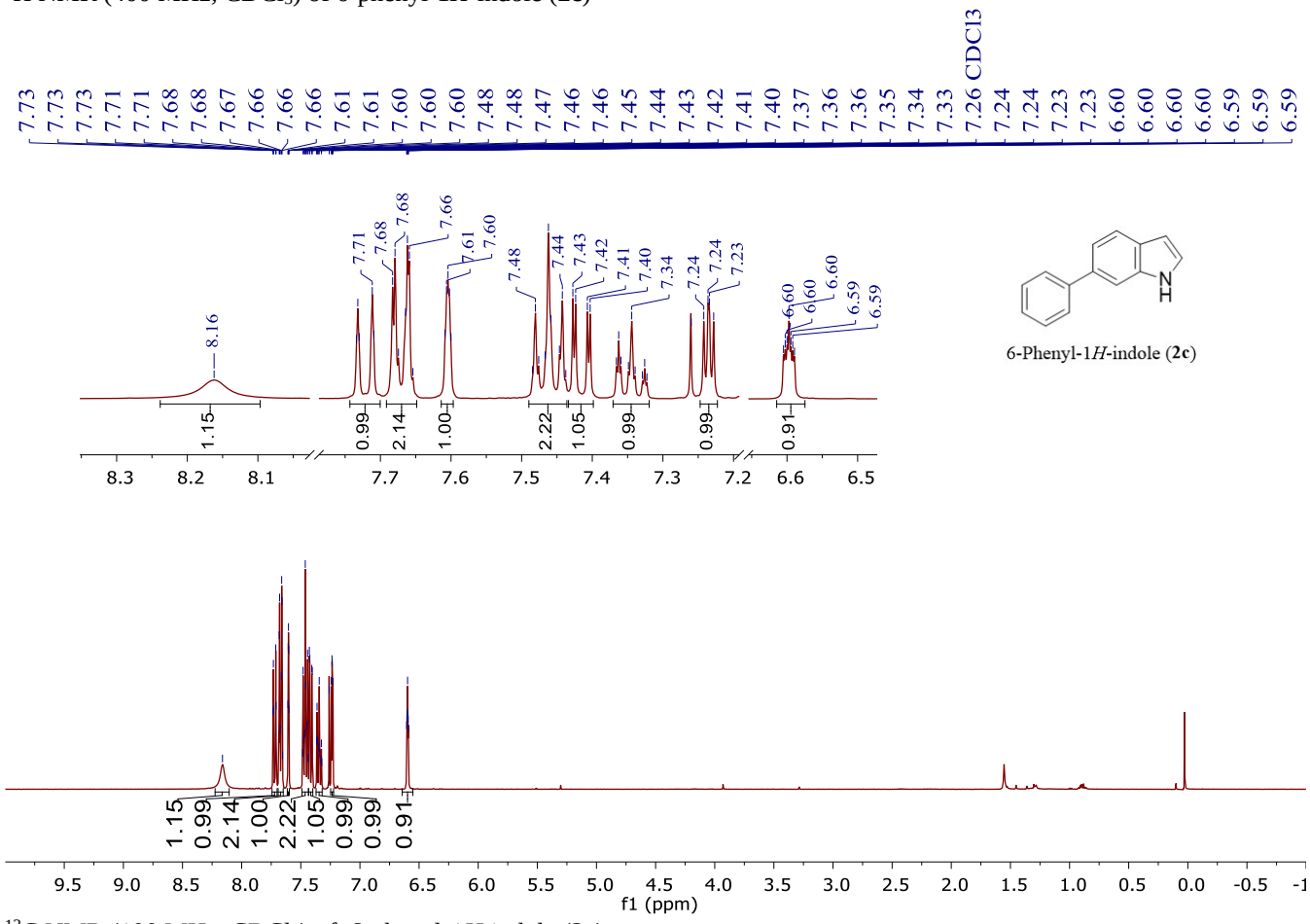
6-Iodo-1*H*-indole (**2c**)

^{13}C NMR (100 MHz, $CDCl_3$) of 6-iodo-1*H*-indole (**2b**)



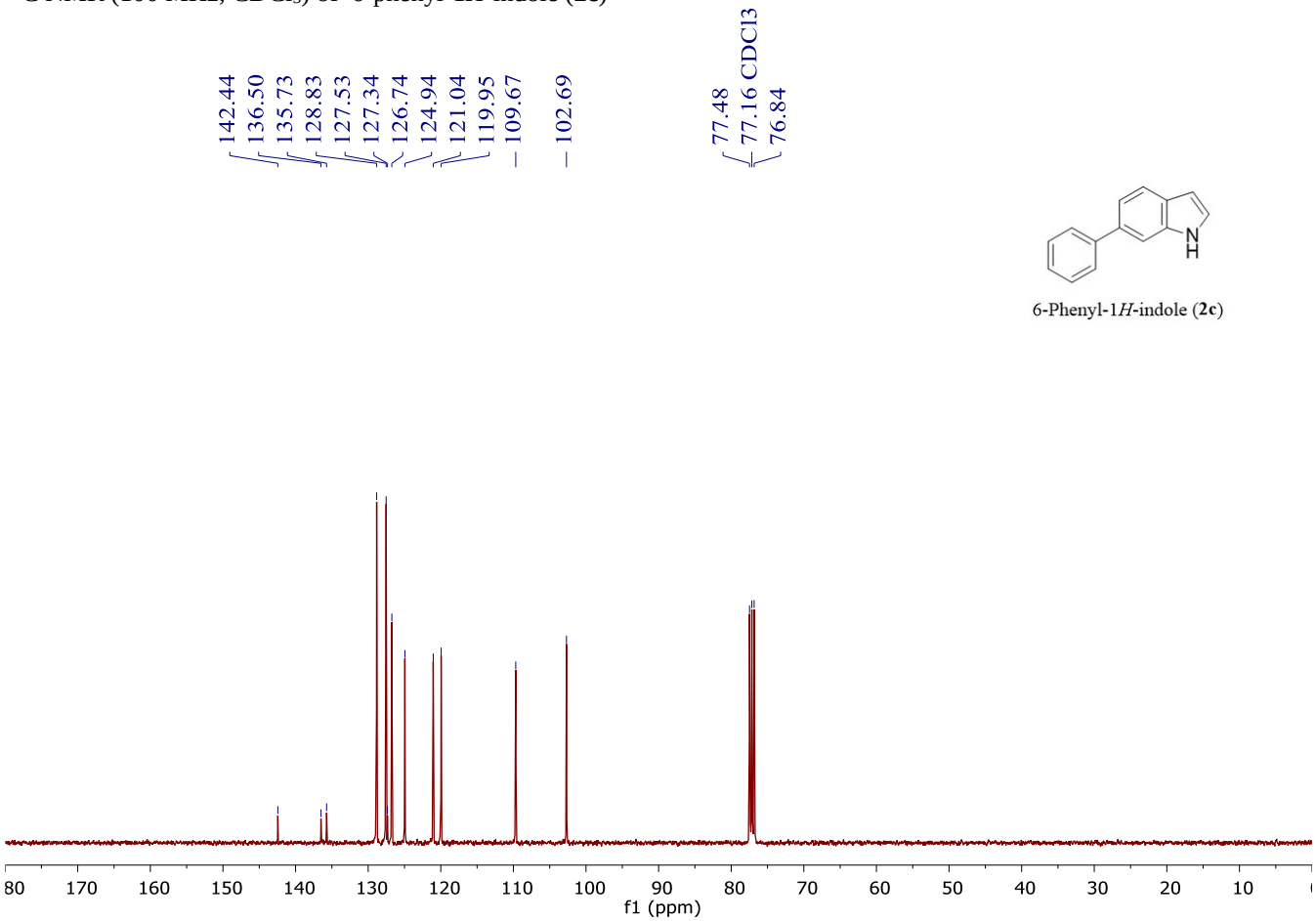
6-Iodo-1*H*-indole (**2c**)

^{1}H NMR (400 MHz, $CDCl_3$) of 6-phenyl-1*H*-indole (**2c**)



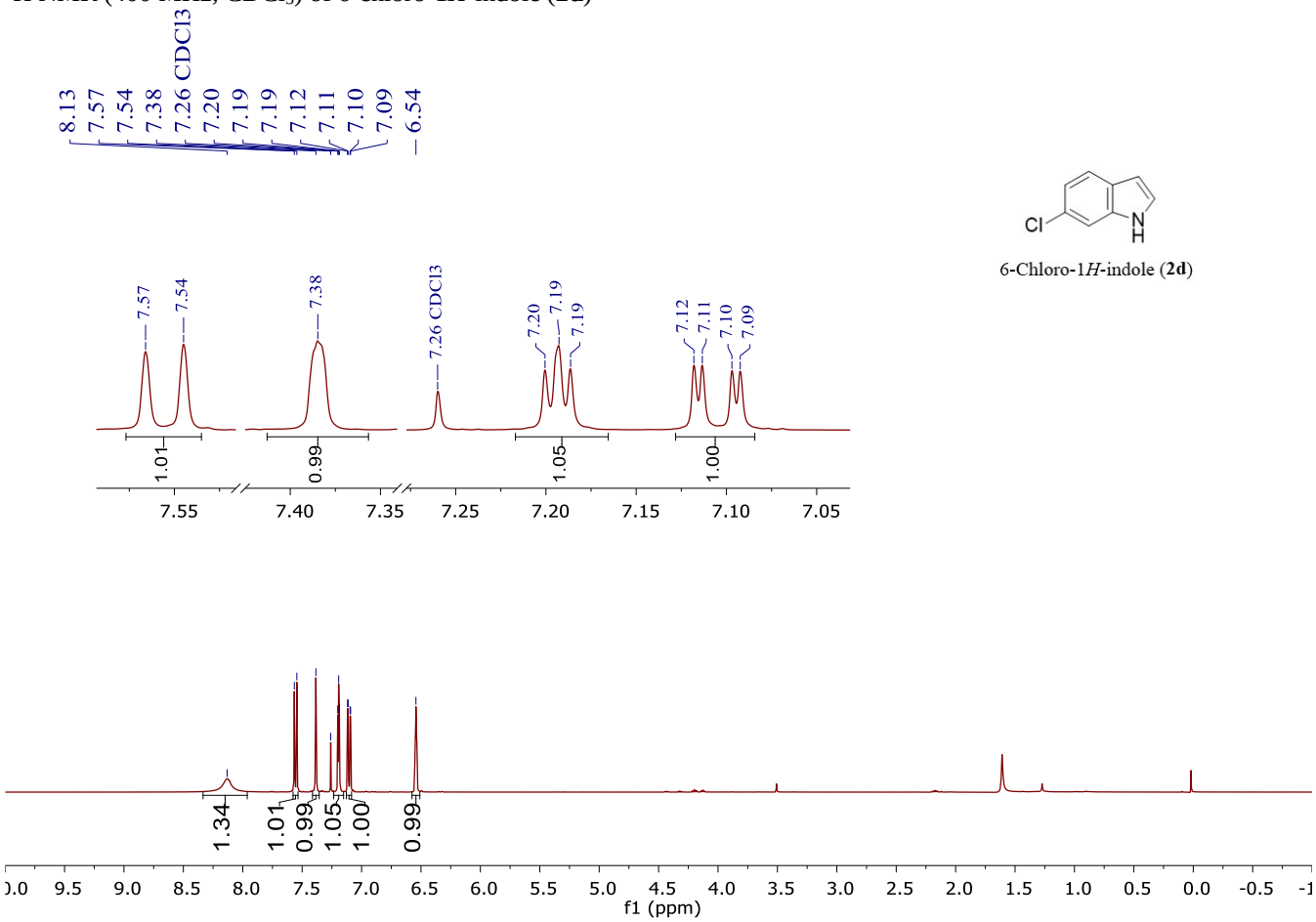
6-Phenyl-1*H*-indole (**2c**)

^{13}C NMR (100 MHz, $CDCl_3$) of 6-phenyl-1*H*-indole (**2c**)



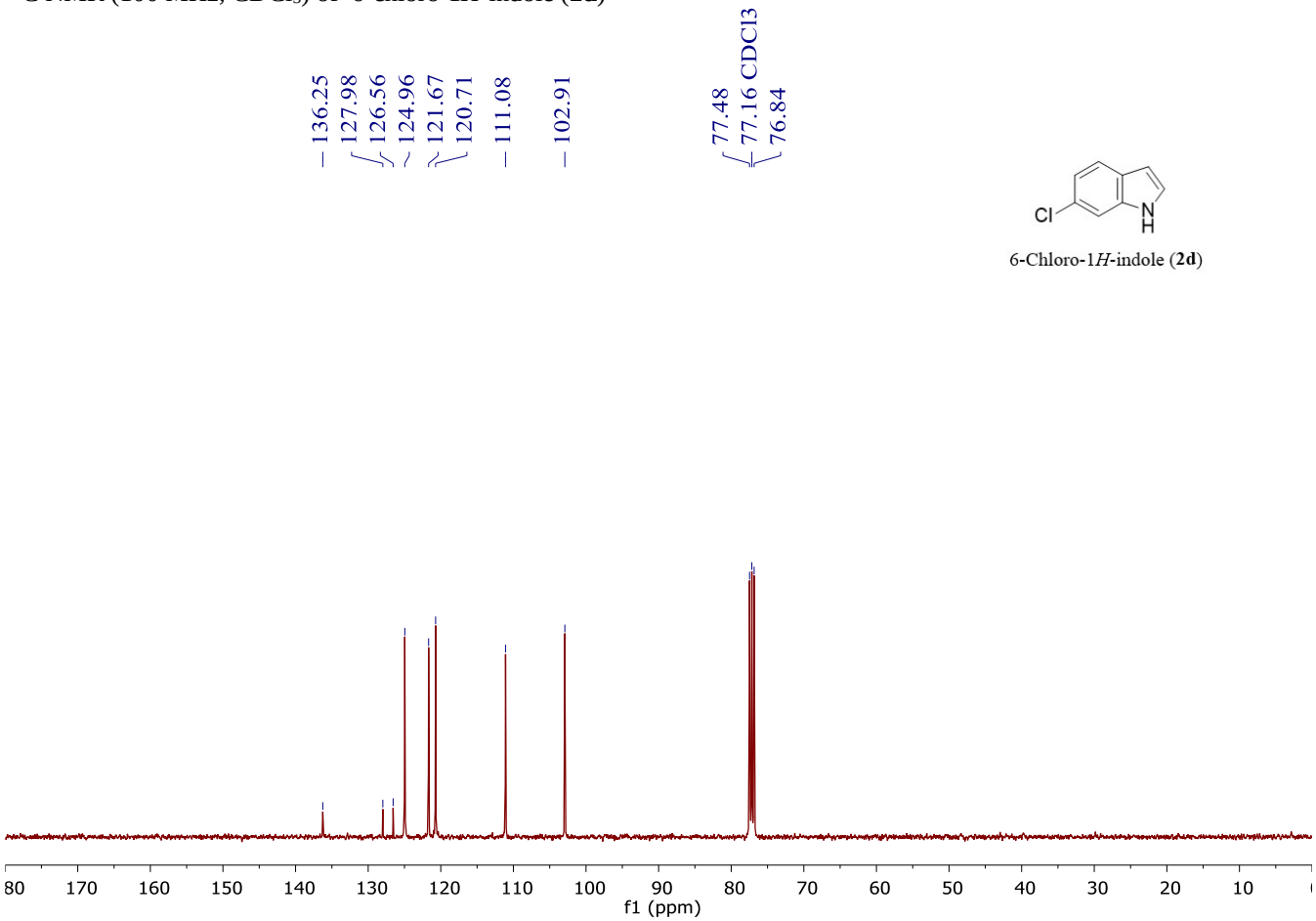
6-Phenyl-1*H*-indole (**2c**)

^{1}H NMR (400 MHz, $CDCl_3$) of 6-chloro-1*H*-indole (**2d**)



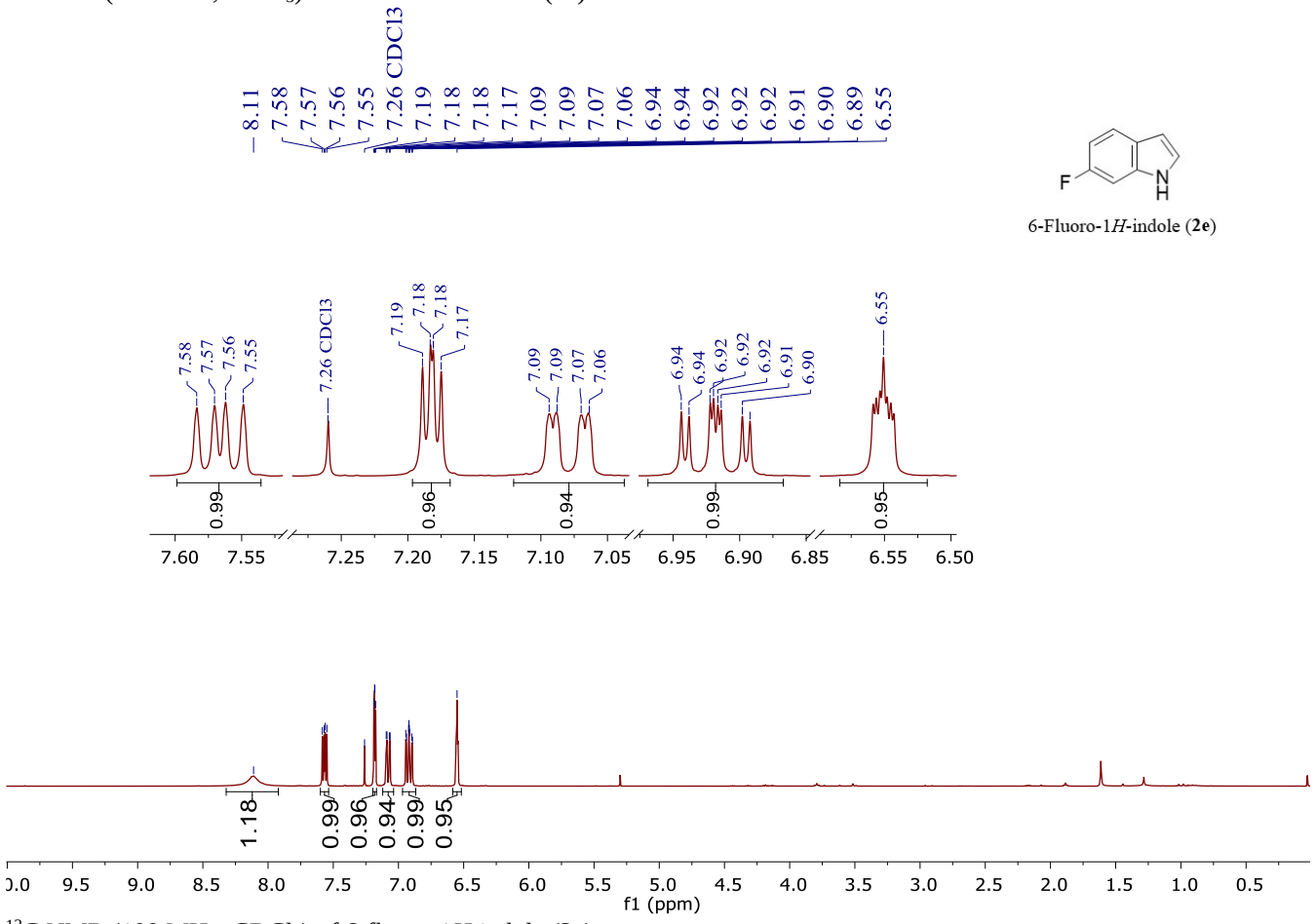
6-Chloro-1*H*-indole (**2d**)

^{13}C NMR (100 MHz, $CDCl_3$) of 6-chloro-1*H*-indole (**2d**)

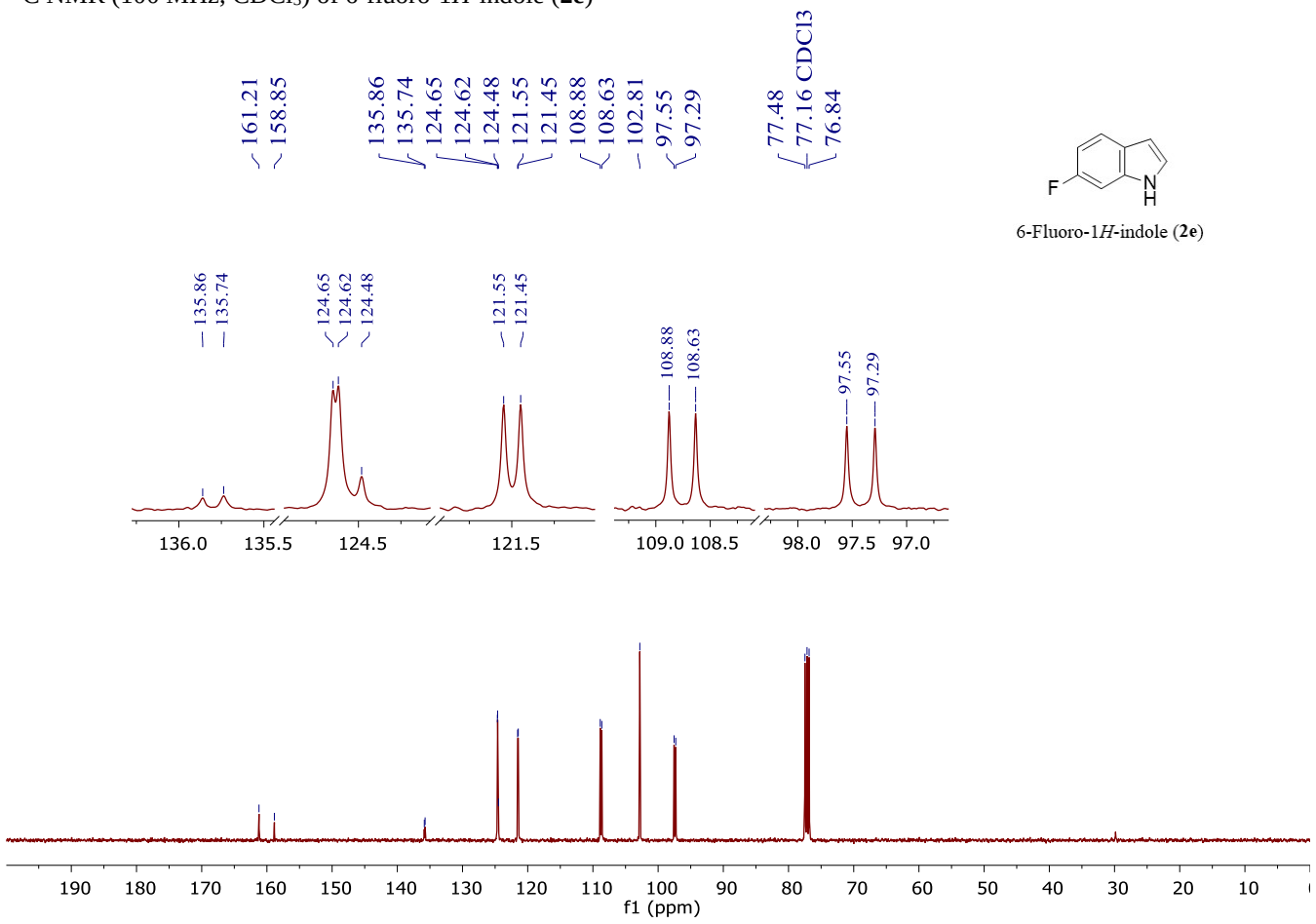


6-Chloro-1*H*-indole (**2d**)

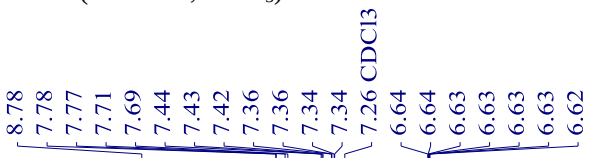
^{1}H NMR (400 MHz, $CDCl_3$) of 6-fluoro-1*H*-indole (**2e**)

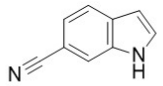


^{13}C NMR (100 MHz, $CDCl_3$) of 6-fluoro-1*H*-indole (**2e**)

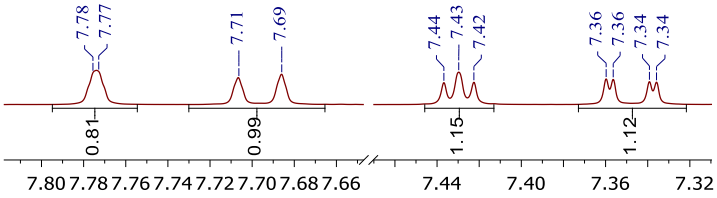


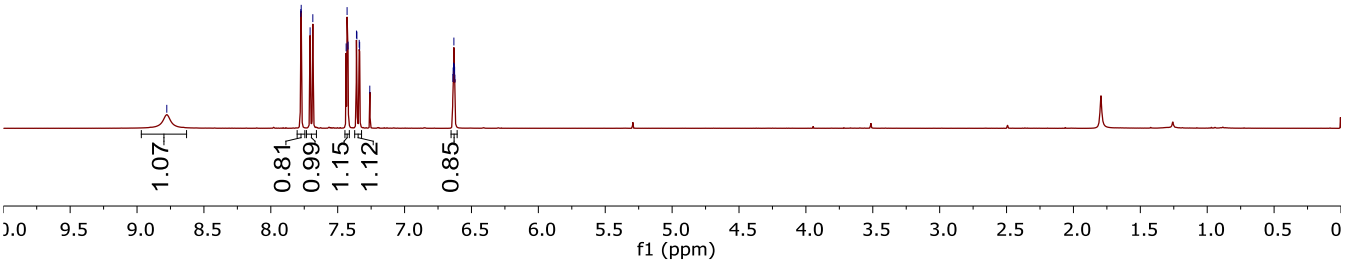
^{1}H NMR (400 MHz, $CDCl_3$) of 1*H*-indole-6-carbonitrile (**2f**)



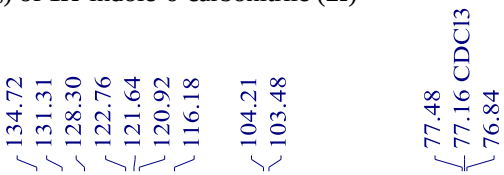


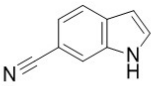
1*H*-indole-6-carbonitrile (**2f**)



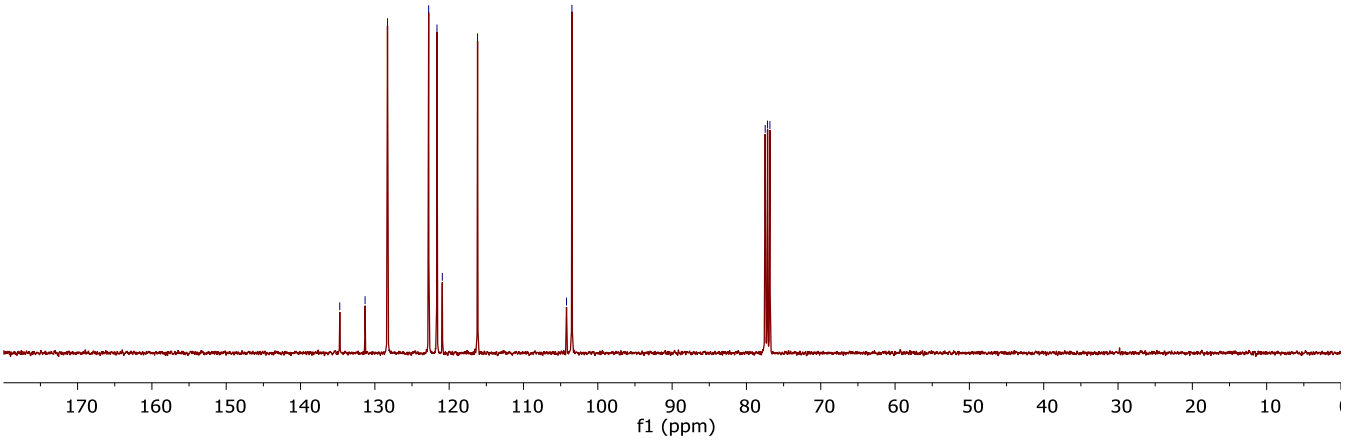


^{13}C NMR (100 MHz, $CDCl_3$) of 1*H*-indole-6-carbonitrile (**2f**)

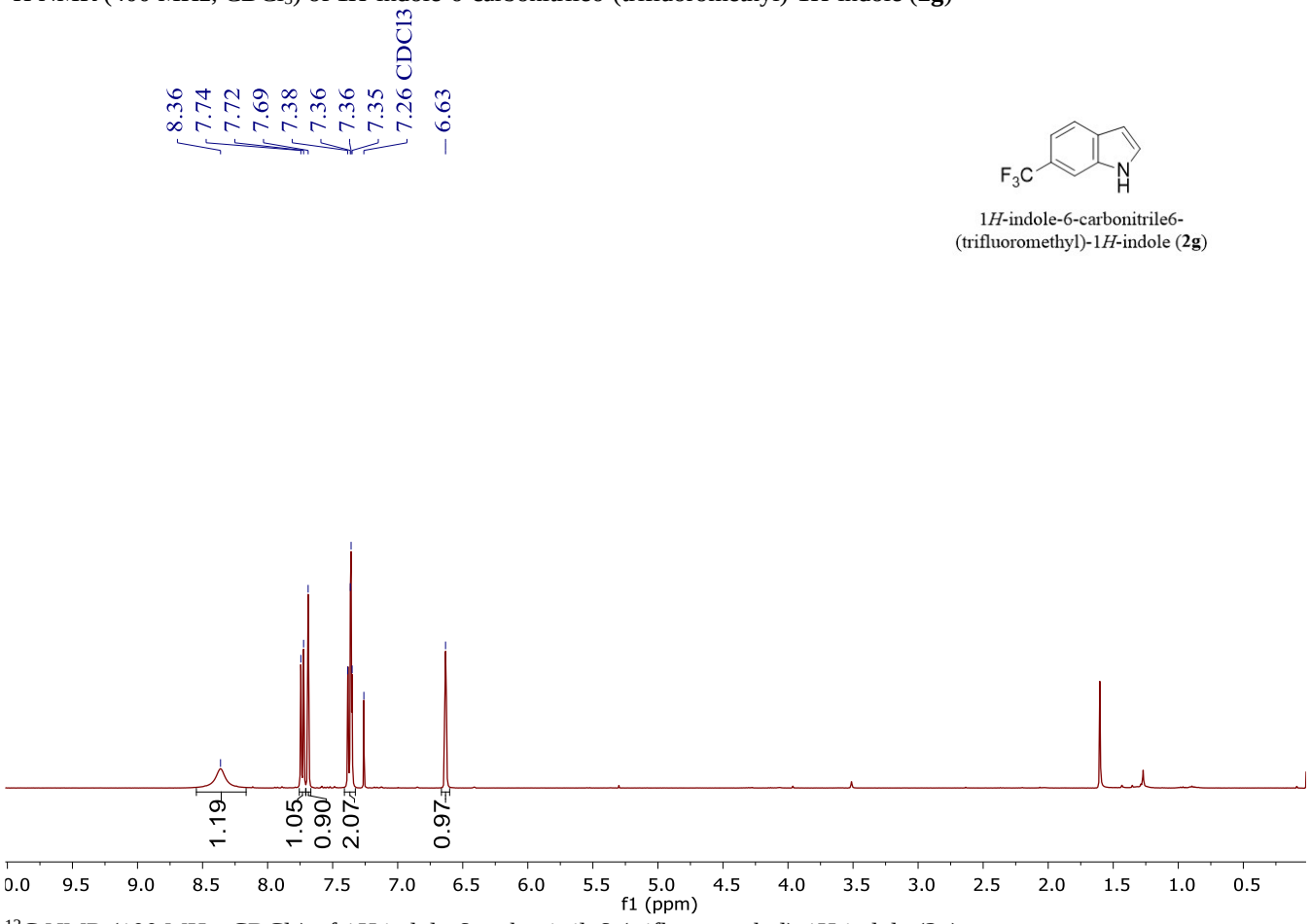




1*H*-indole-6-carbonitrile (**2f**)

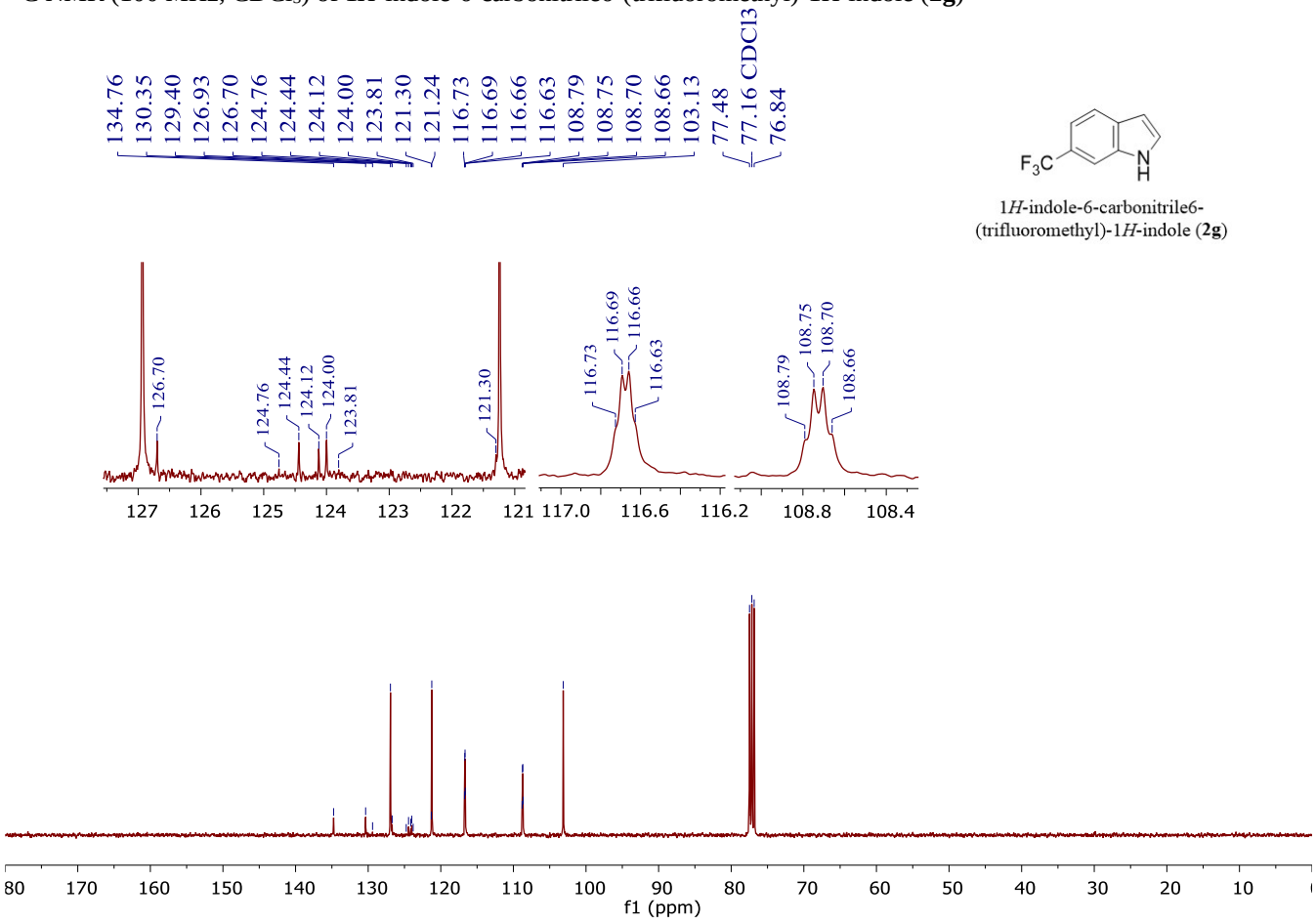


^{1}H NMR (400 MHz, $CDCl_3$) of 1*H*-indole-6-carbonitrile6-(trifluoromethyl)-1H-indole (**2g**)



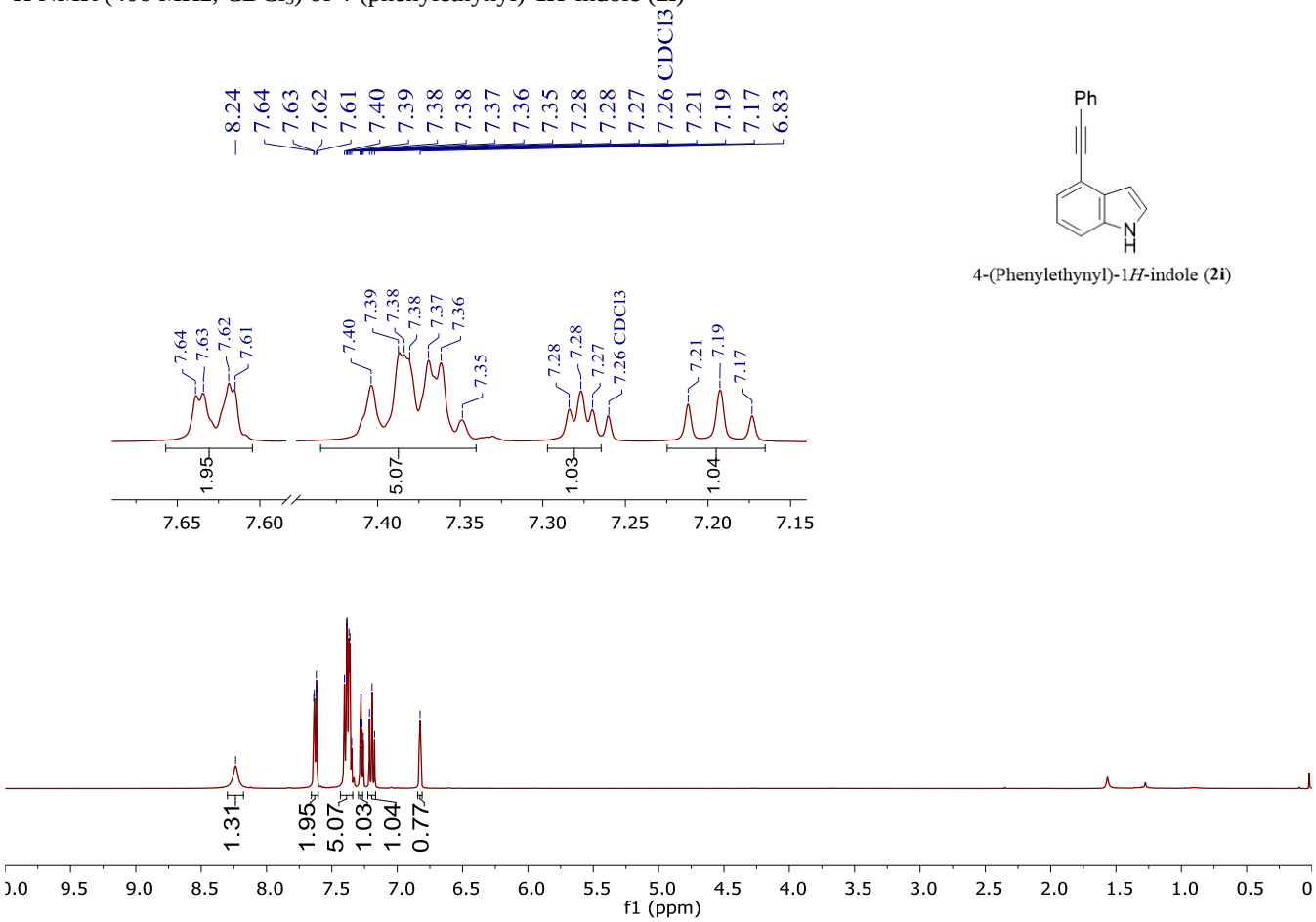
1*H*-indole-6-carbonitrile6-(trifluoromethyl)-1*H*-indole (**2g**)

^{13}C NMR (100 MHz, $CDCl_3$) of 1*H*-indole-6-carbonitrile6-(trifluoromethyl)-1H-indole (**2g**)



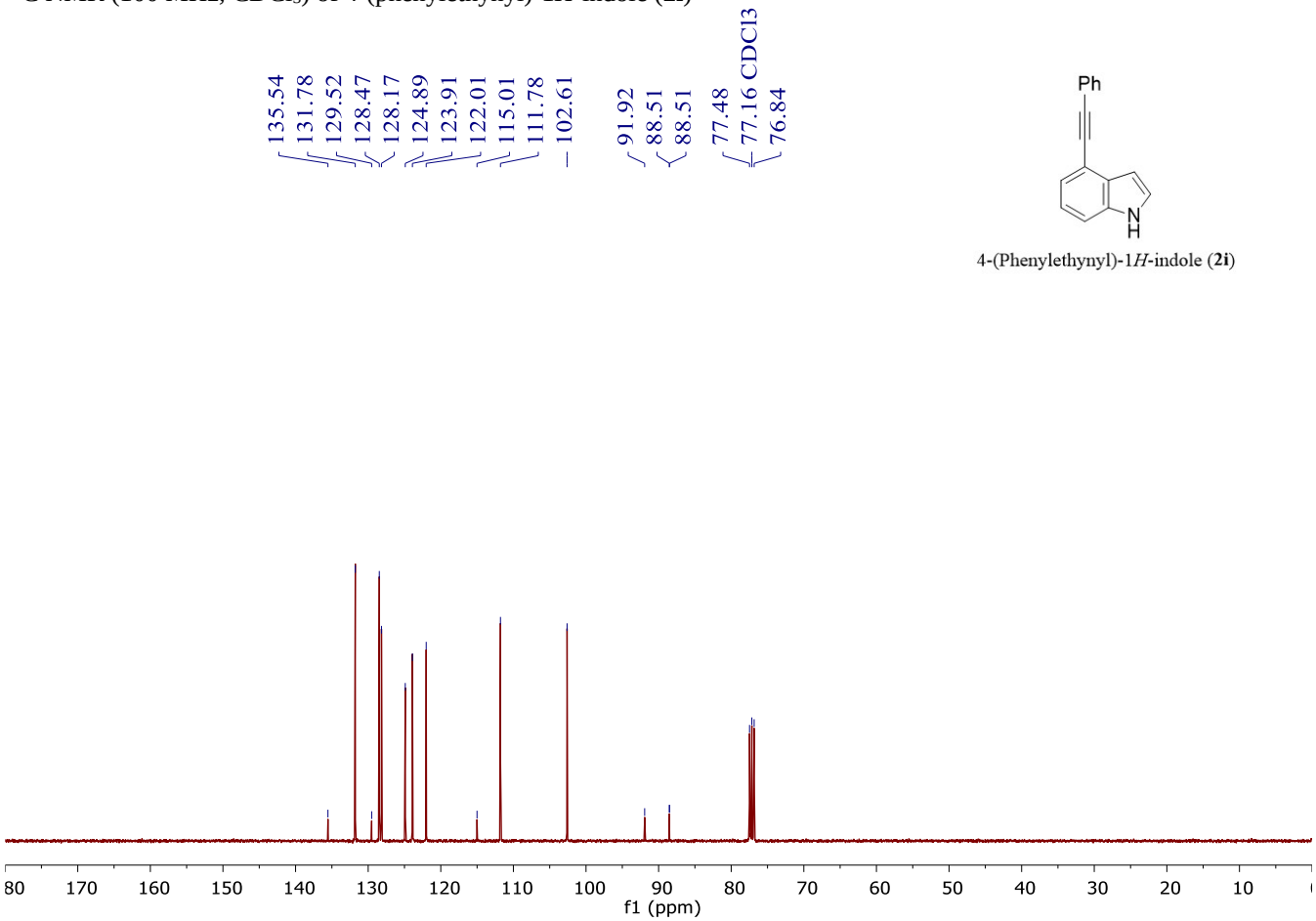
1*H*-indole-6-carbonitrile6-(trifluoromethyl)-1*H*-indole (**2g**)

^{1}H NMR (400 MHz, $CDCl_3$) of 4-(phenylethynyl)-1*H*-indole (**2i**)



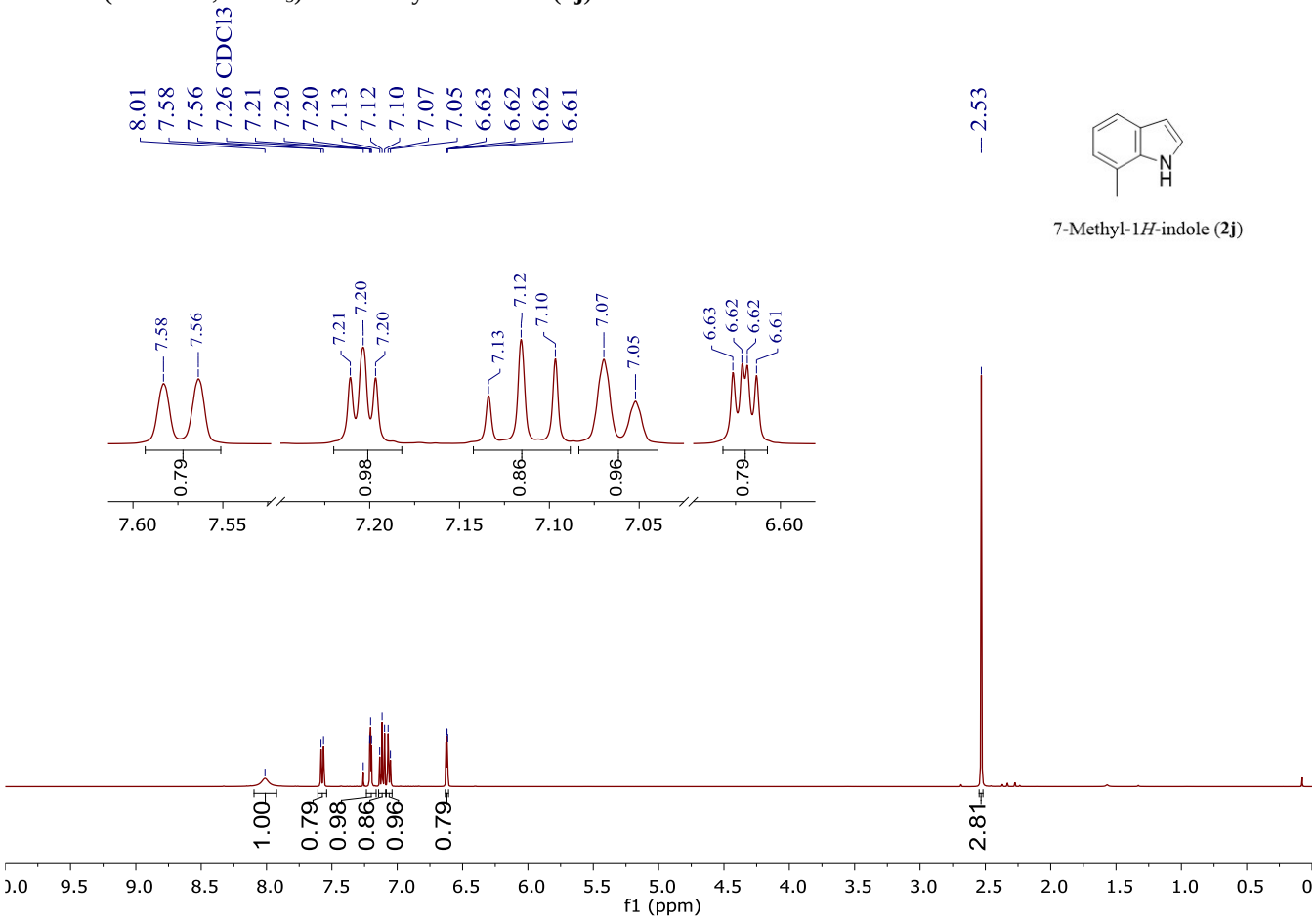
4-(Phenylethynyl)-1*H*-indole (**2i**)

^{13}C NMR (100 MHz, $CDCl_3$) of 4-(phenylethynyl)-1*H*-indole (**2i**)

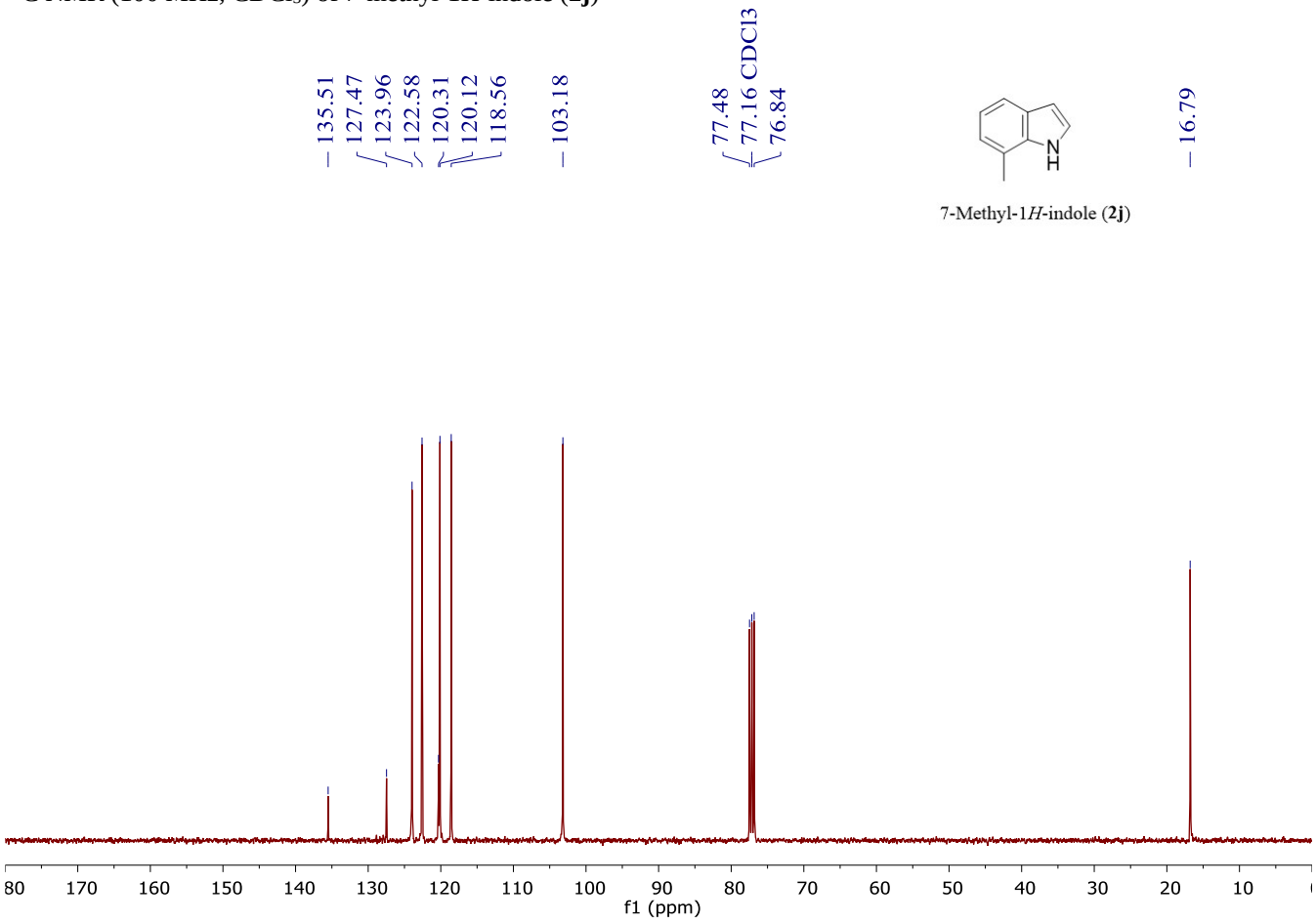


4-(Phenylethynyl)-1*H*-indole (**2i**)

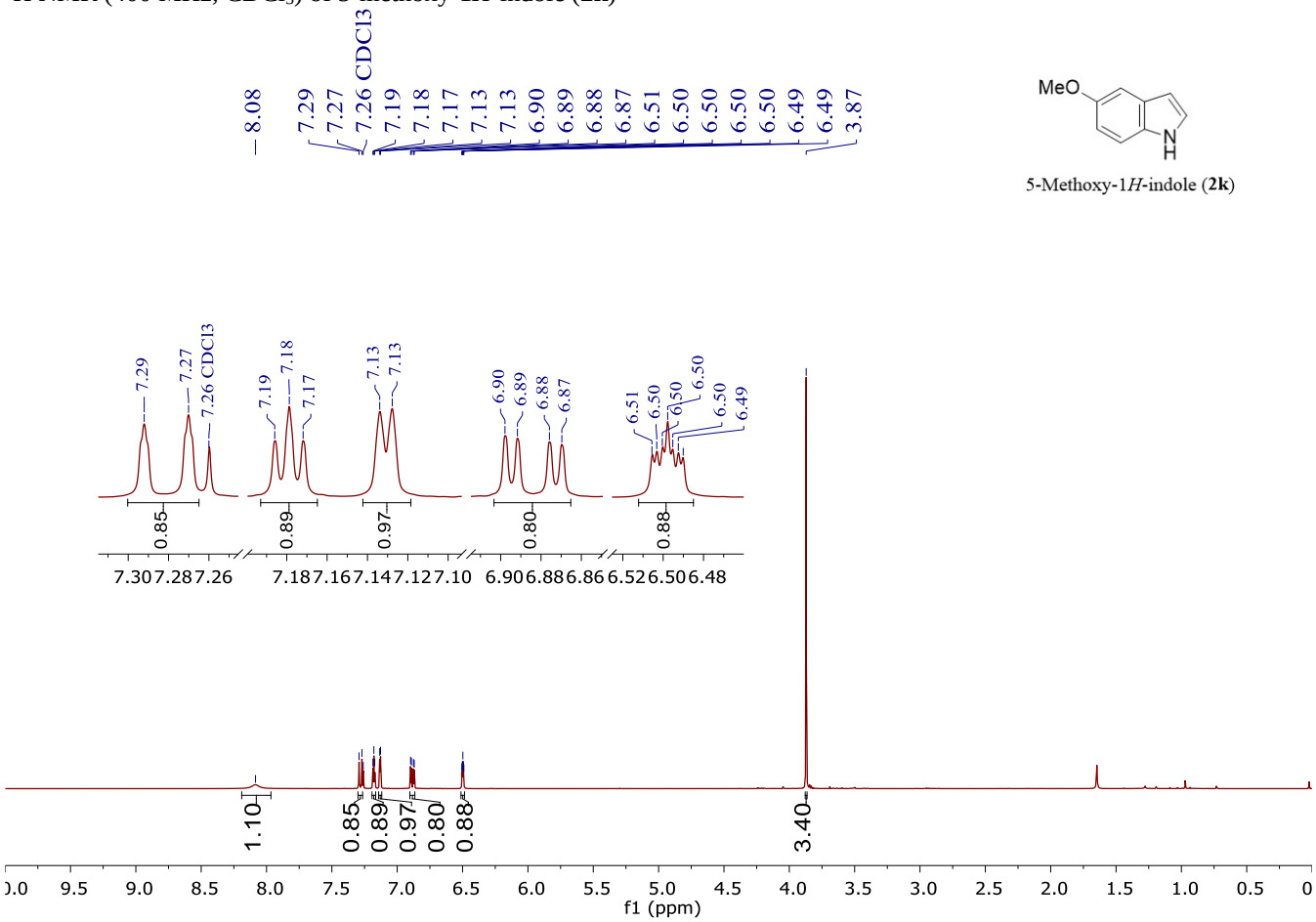
^{1}H NMR (400 MHz, $CDCl_3$) of 7-methyl-1H-indole (**2j**)



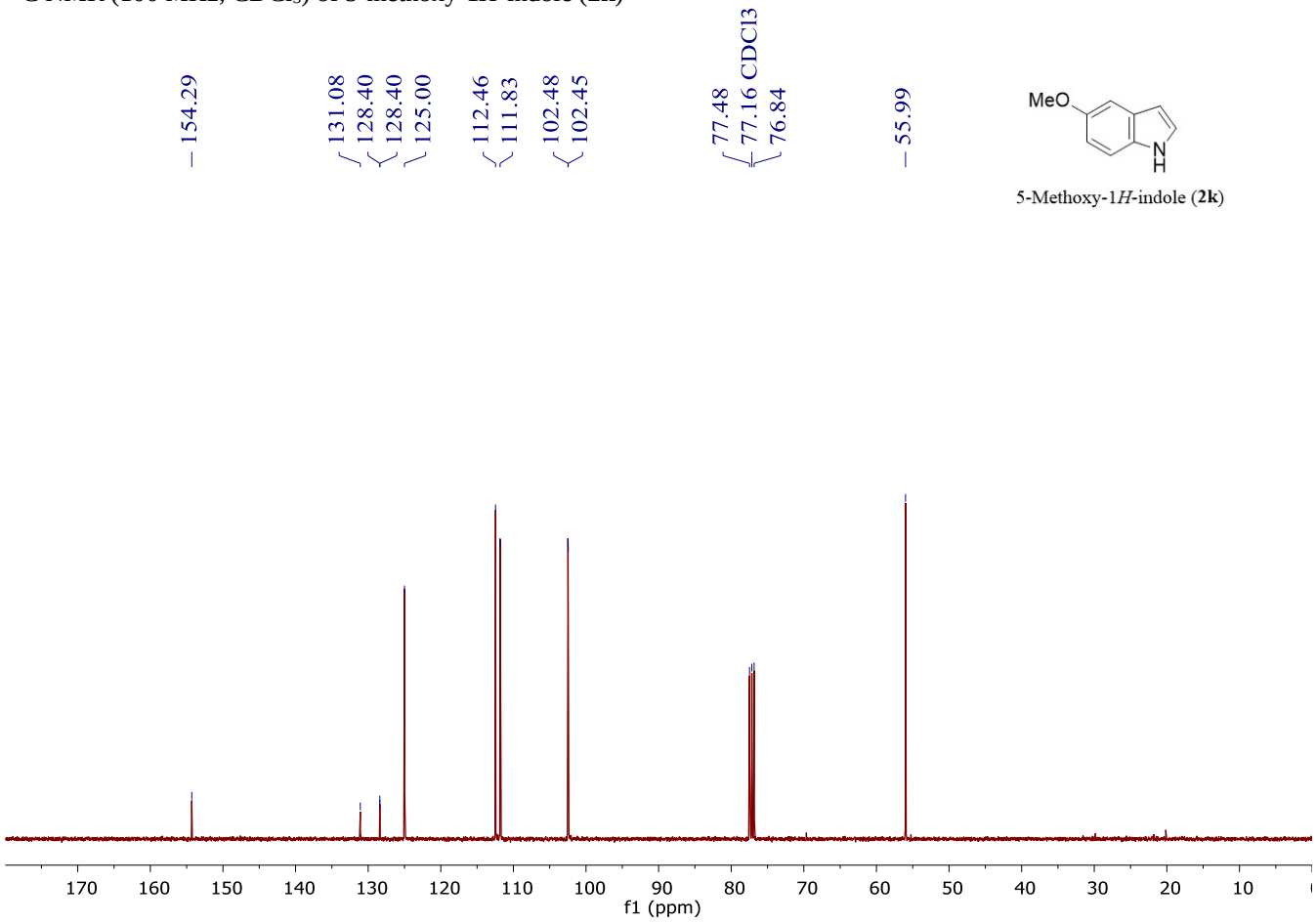
^{13}C NMR (100 MHz, $CDCl_3$) of 7-methyl-1H-indole (**2j**)



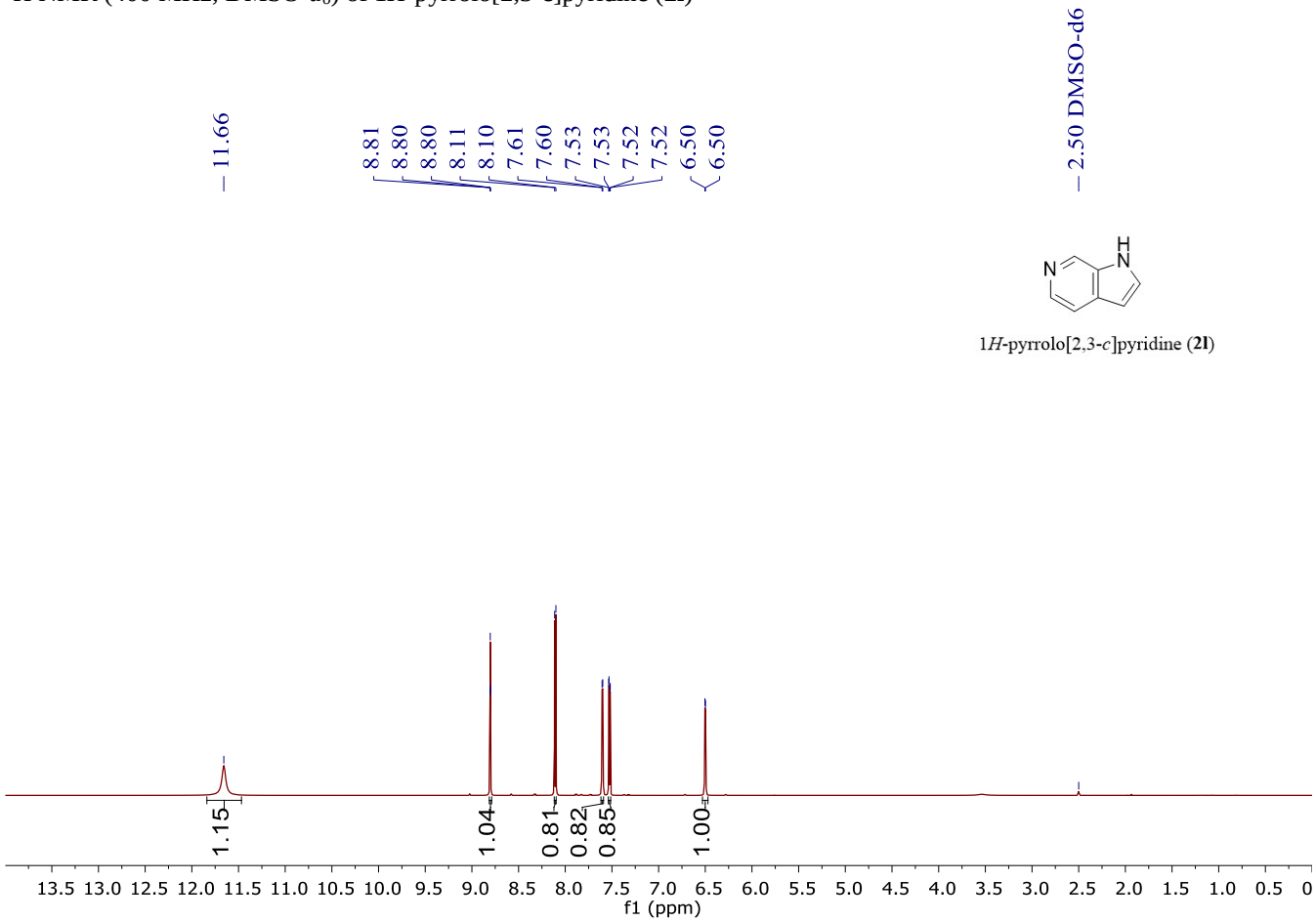
^{1}H NMR (400 MHz, $CDCl_3$) of 5-methoxy-1*H*-indole (**2k**)



^{13}C NMR (100 MHz, $CDCl_3$) of 5-methoxy-1*H*-indole (**2k**)

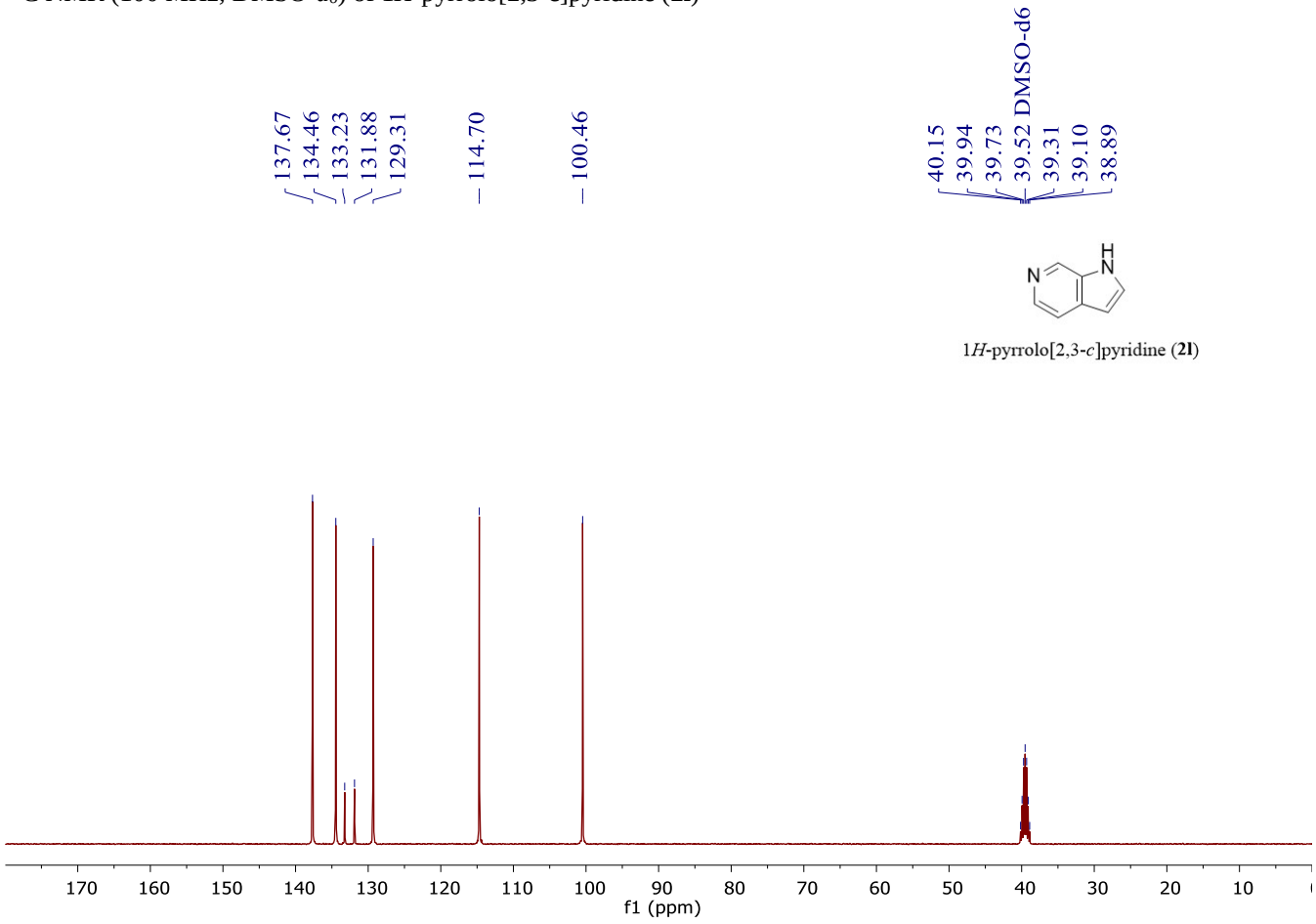


^{1}H NMR (400 MHz, DMSO-d_6) of 1*H*-pyrrolo[2,3-c]pyridine (**2l**)



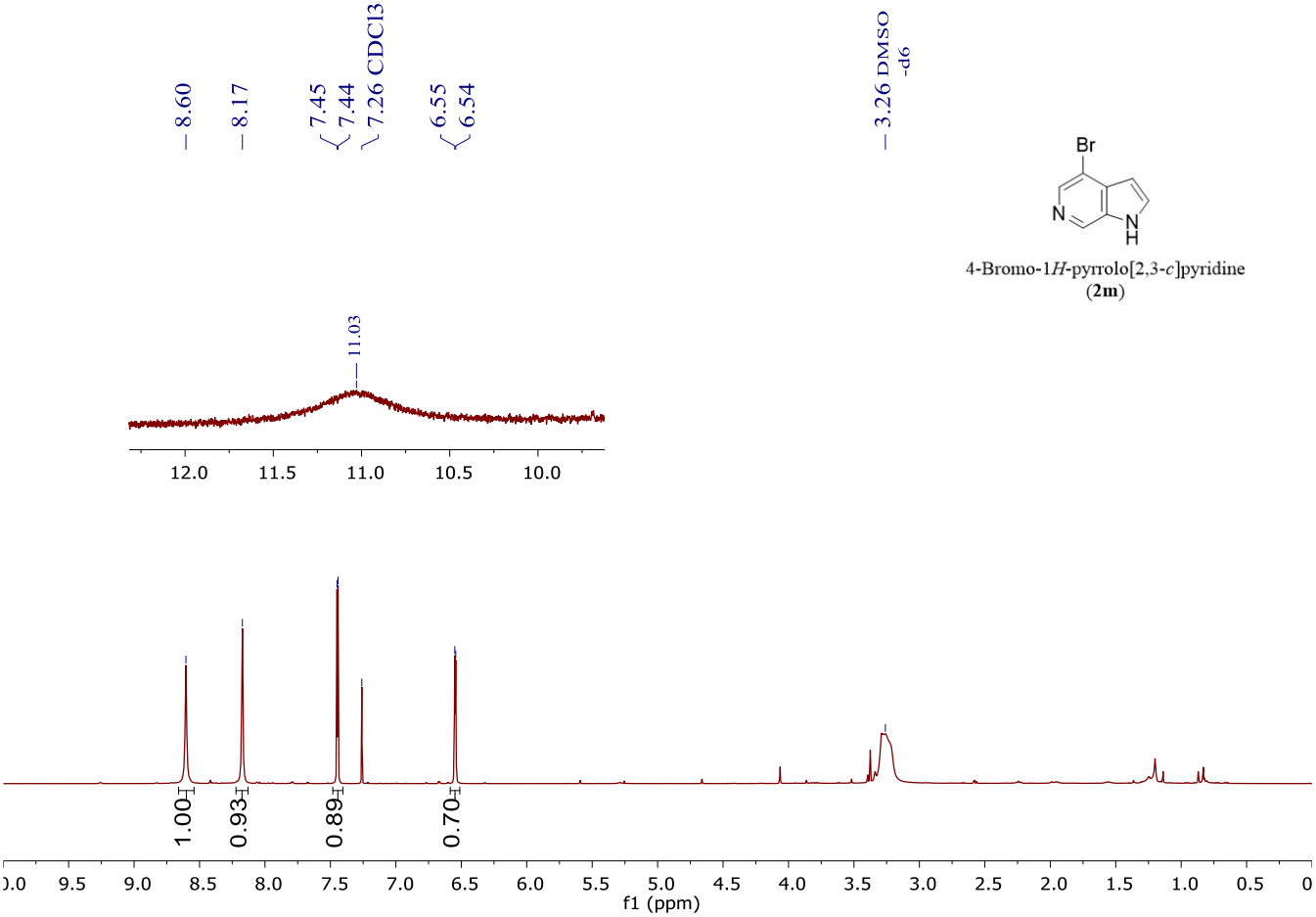
1*H*-pyrrolo[2,3-*c*]pyridine (**2l**)

^{13}C NMR (100 MHz, DMSO-d_6) of 1*H*-pyrrolo[2,3-c]pyridine (**2l**)



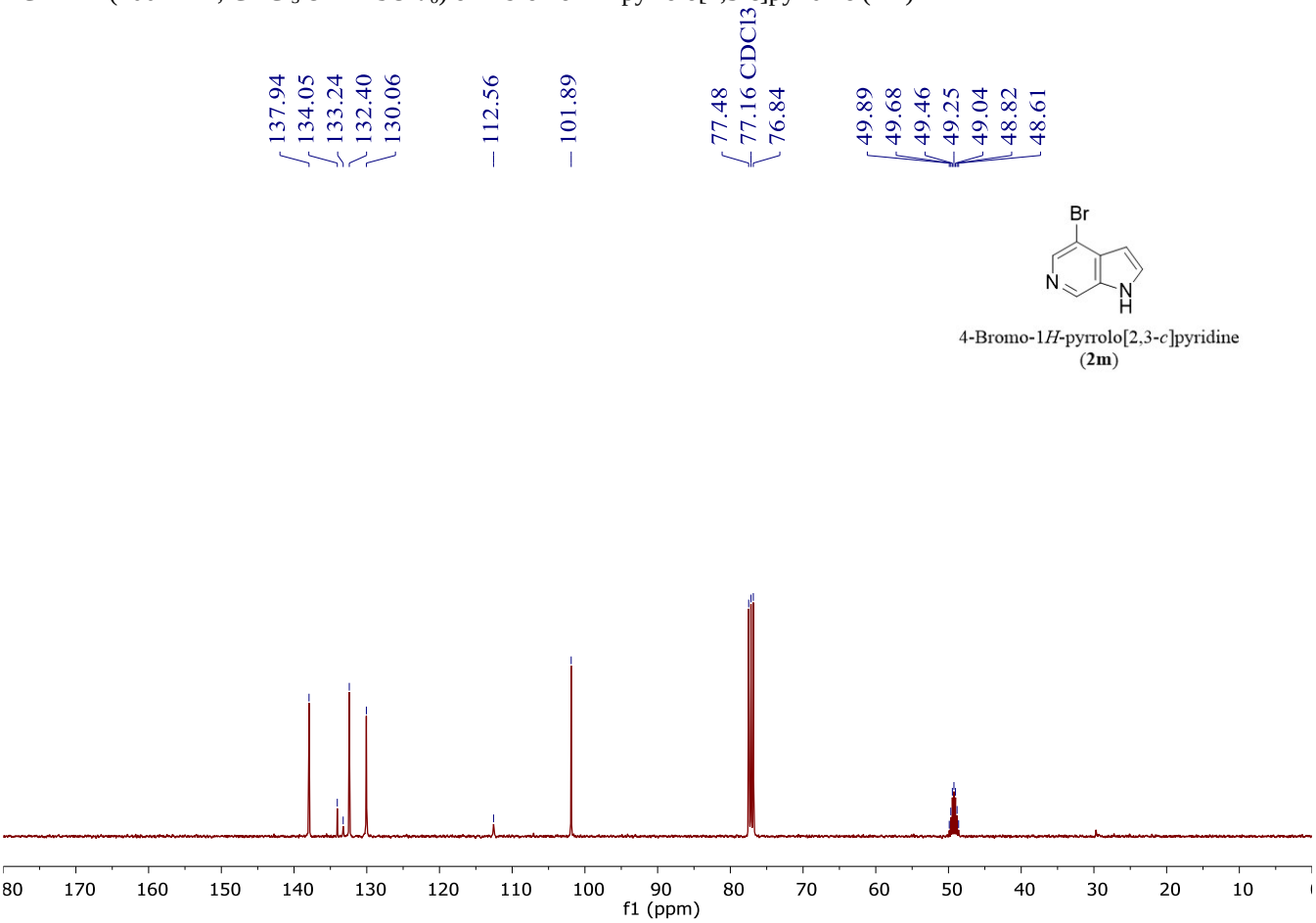
1*H*-pyrrolo[2,3-*c*]pyridine (**2l**)

^{1}H NMR (400 MHz, $CDCl_3$ & DMSO-d_6) of 4-bromo-1*H*-pyrrolo[2,3-c]pyridine (**2m**)



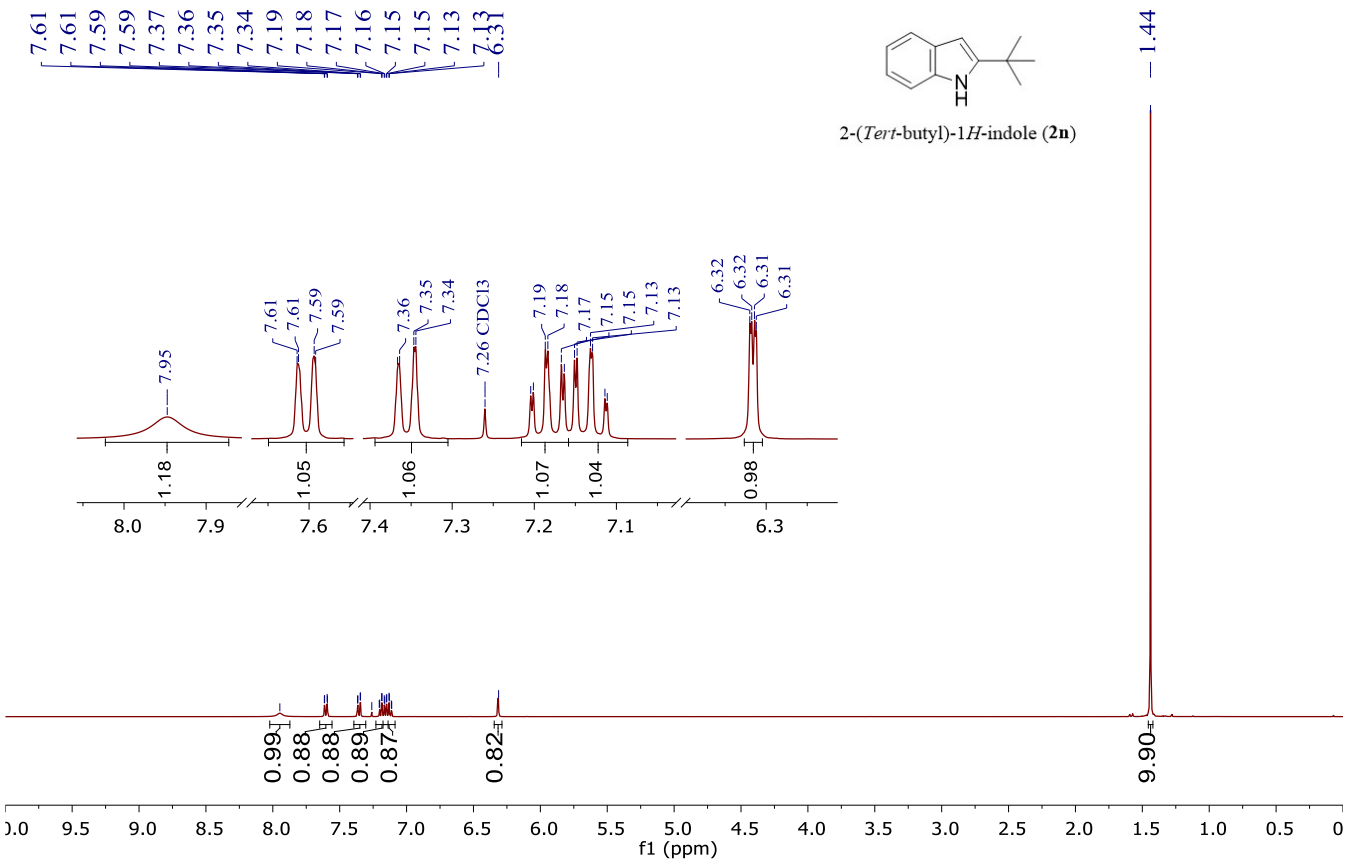
4-Bromo-1*H*-pyrrolo[2,3-*c*]pyridine
(**2m**)

^{13}C NMR (100 MHz, $CDCl_3$ & DMSO-d_6) of 4-bromo-1*H*-pyrrolo[2,3-c]pyridine (**2m**)

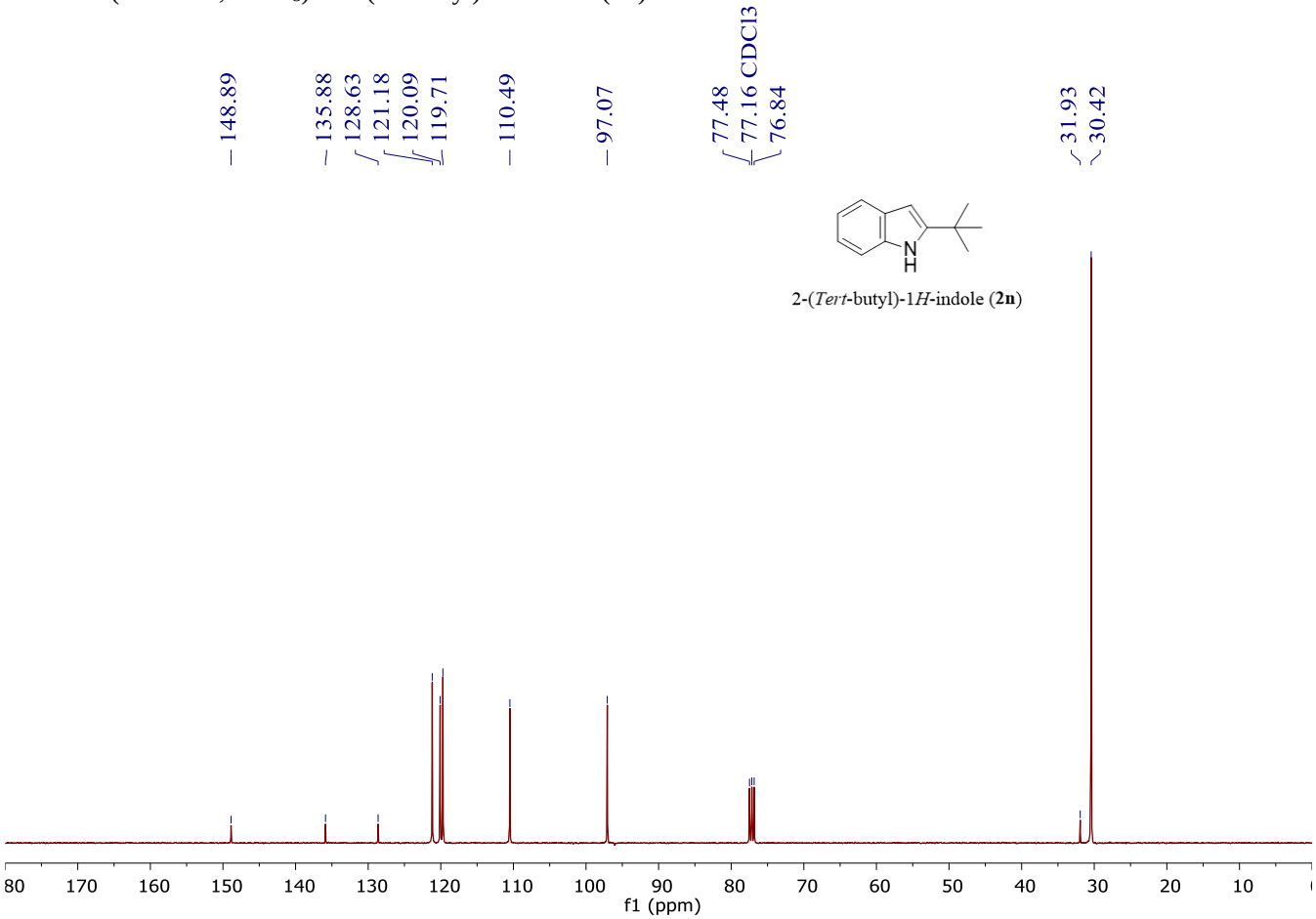


4-Bromo-1*H*-pyrrolo[2,3-*c*]pyridine
(**2m**)

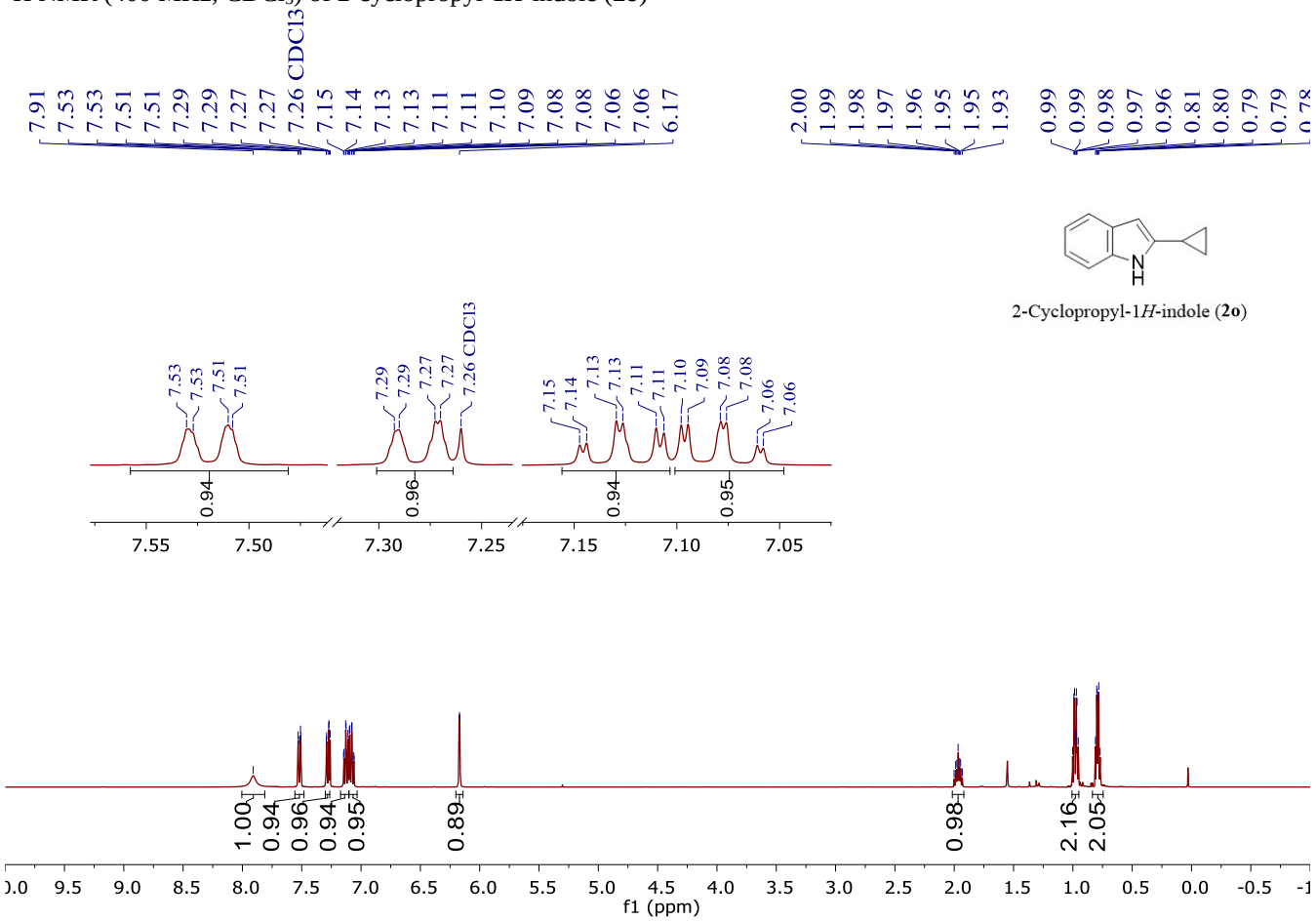
^{1}H NMR (400 MHz, $CDCl_3$) of 2-(tert-butyl)-1*H*-indole (**2n**)



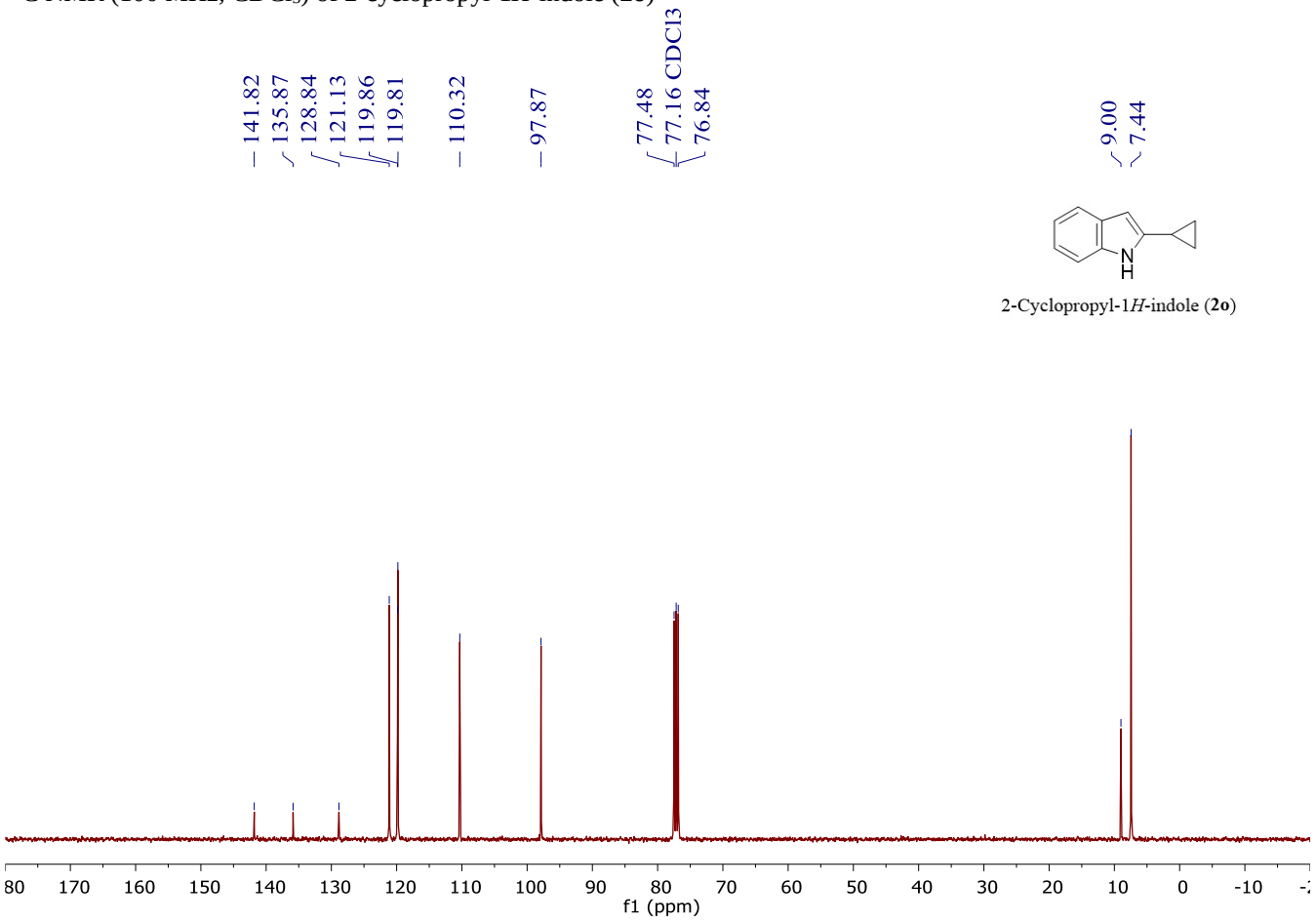
^{13}C NMR (100 MHz, $CDCl_3$) of 2-(tert-butyl)-1*H*-indole (**2n**)



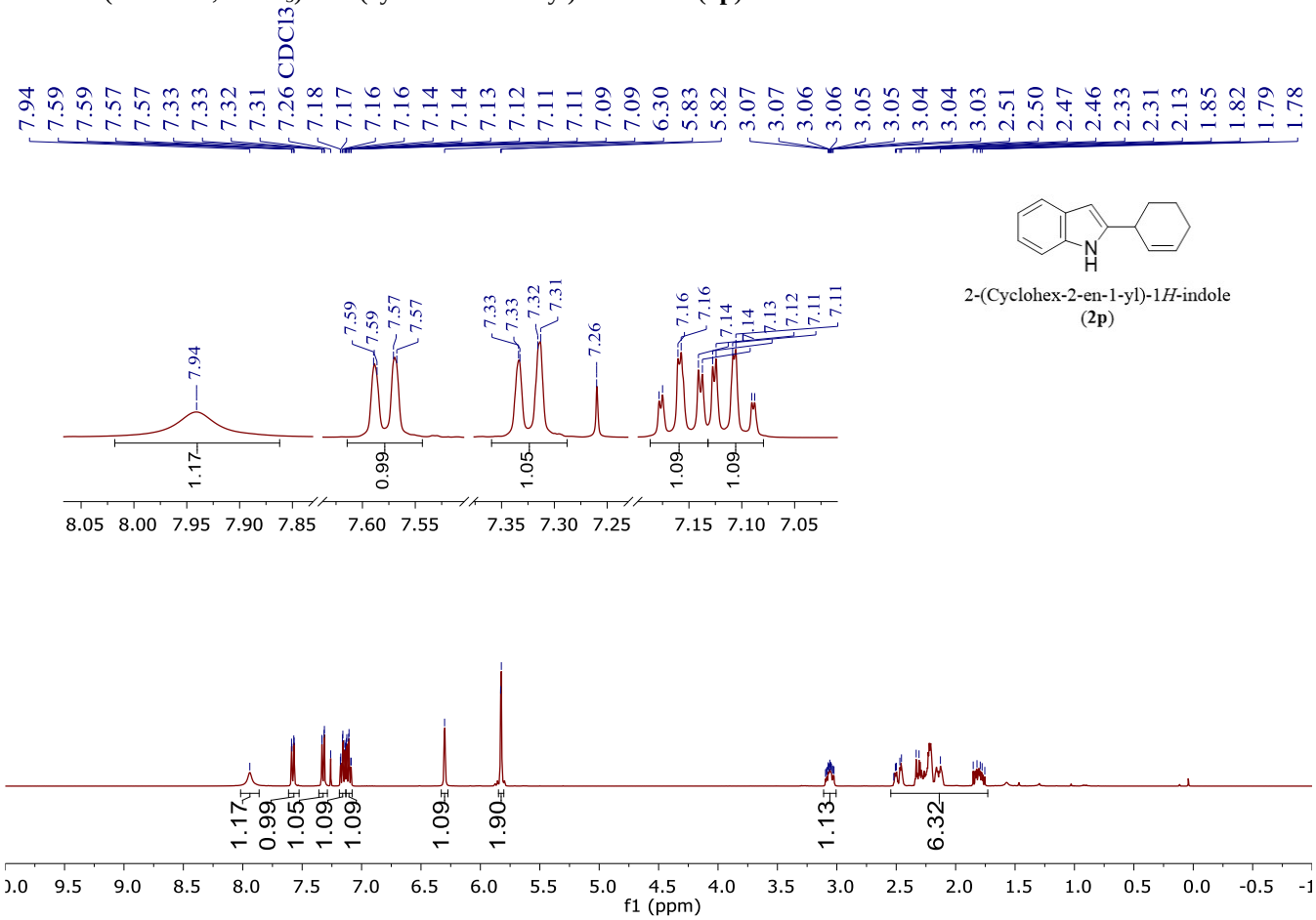
^{1}H NMR (400 MHz, $CDCl_3$) of 2-cyclopropyl-1*H*-indole (**2o**)



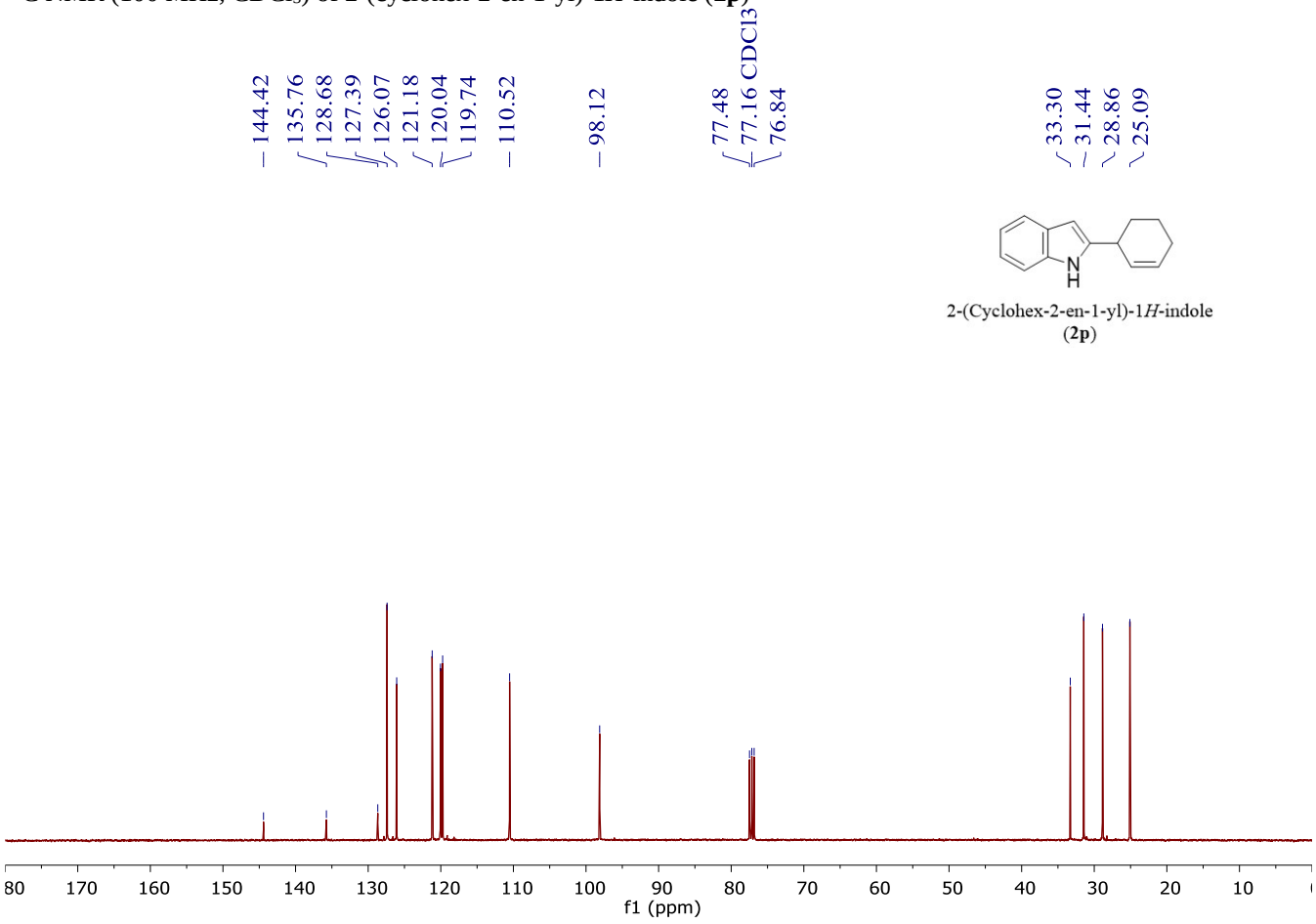
^{13}C NMR (100 MHz, $CDCl_3$) of 2-cyclopropyl-1*H*-indole (**2o**)



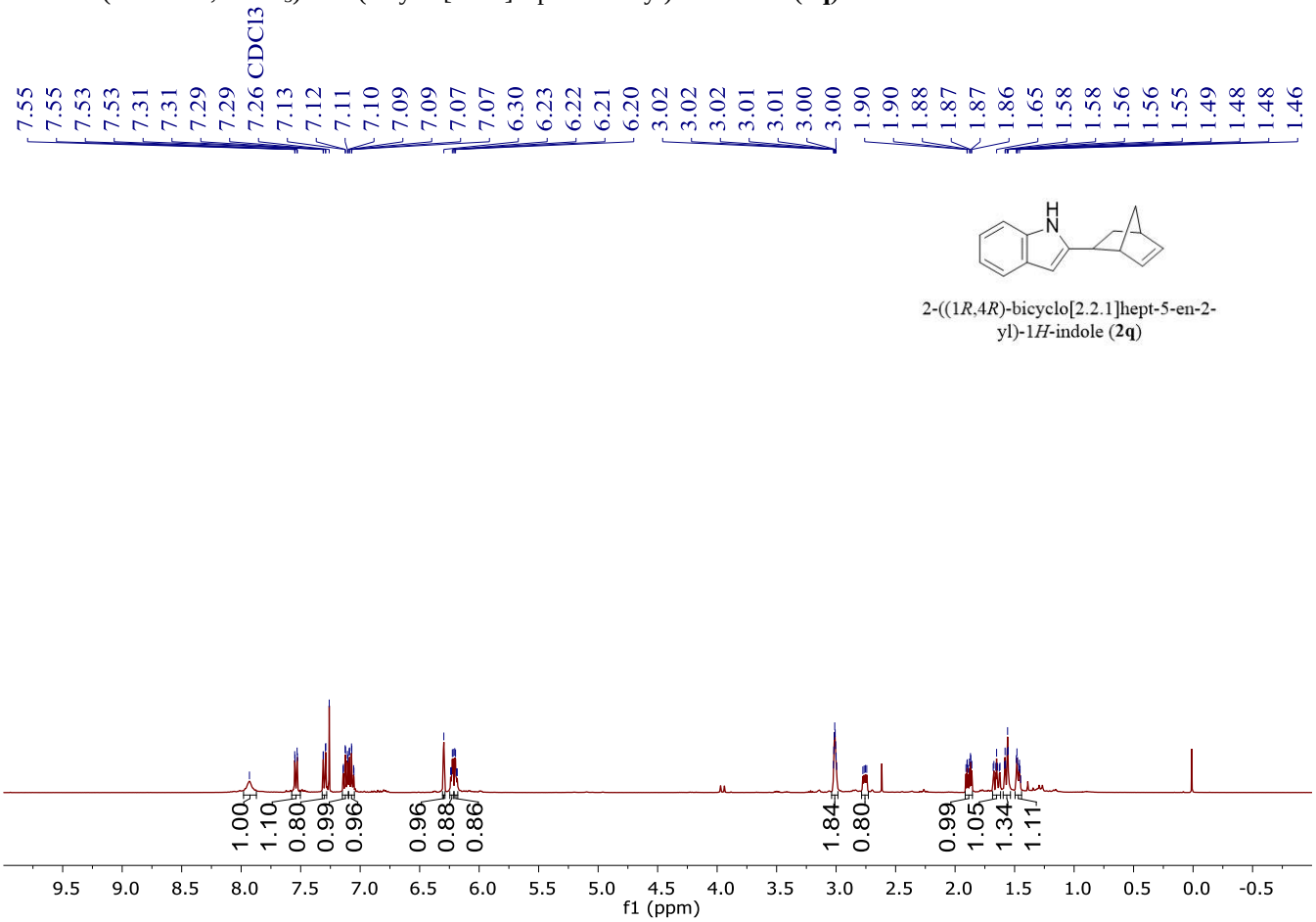
^{1}H NMR (400 MHz, $CDCl_3$) of 2-(cyclohex-2-en-1-yl)-1*H*-indole (**2p**)



^{13}C NMR (100 MHz, $CDCl_3$) of 2-(cyclohex-2-en-1-yl)-1*H*-indole (**2p**)

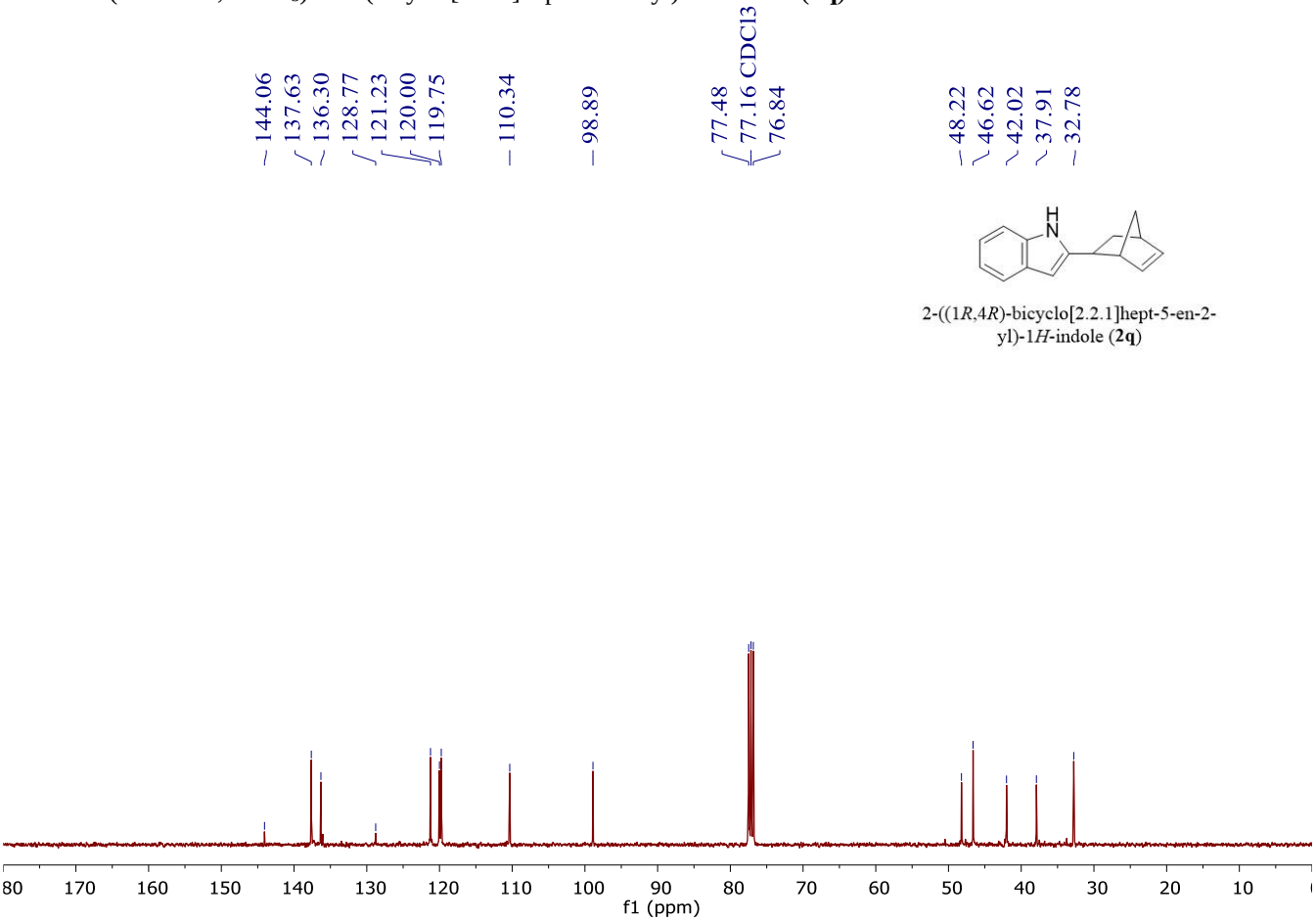


^{1}H NMR (400 MHz, $CDCl_3$) of 2-(bicyclo[2.2.1]hept-5-en-2-yl)-1*H*-indole (**2q**)



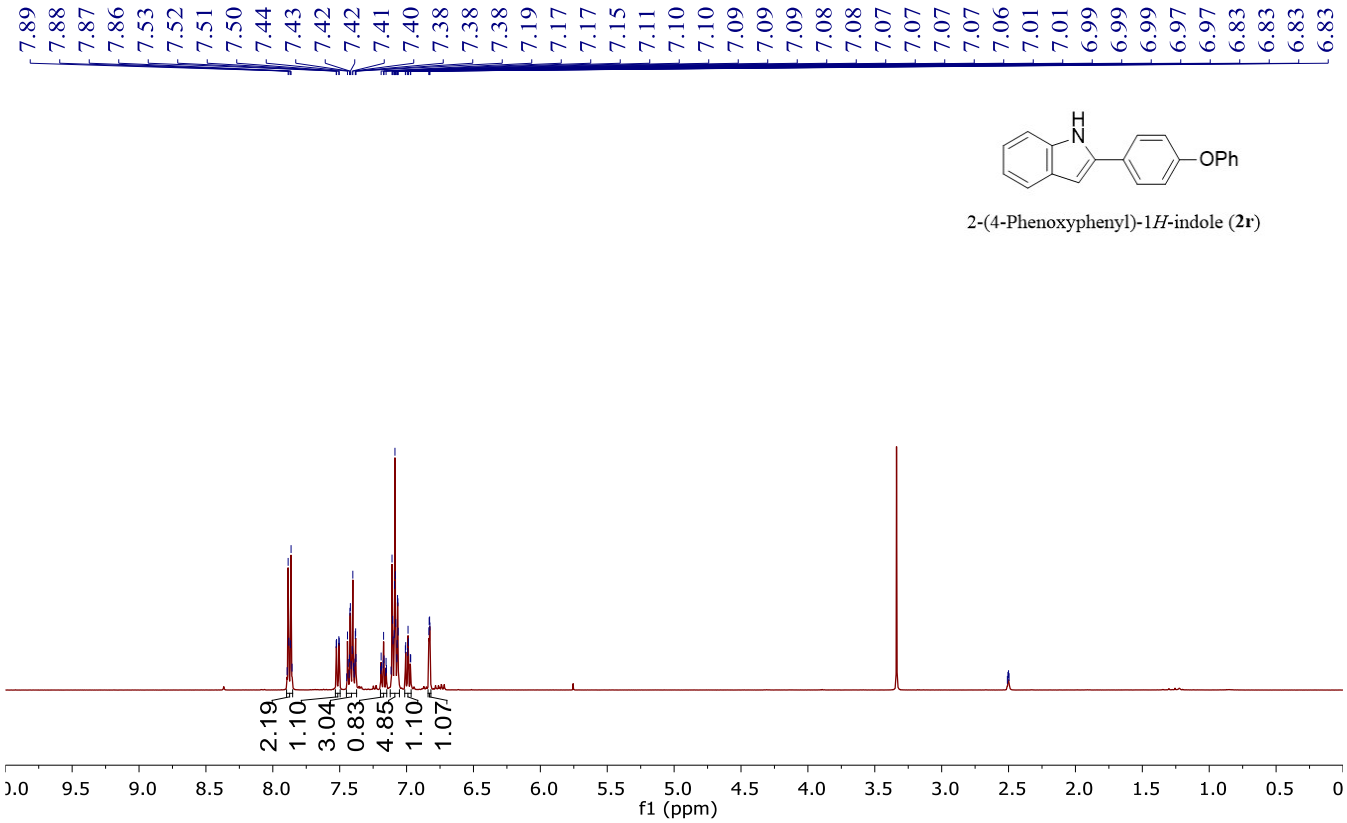
2-((1*R*,4*R*)-bicyclo[2.2.1]hept-5-en-2-yl)-1*H*-indole (**2q**)

^{13}C NMR (100 MHz, $CDCl_3$) of 2-(bicyclo[2.2.1]hept-5-en-2-yl)-1*H*-indole (**2q**)

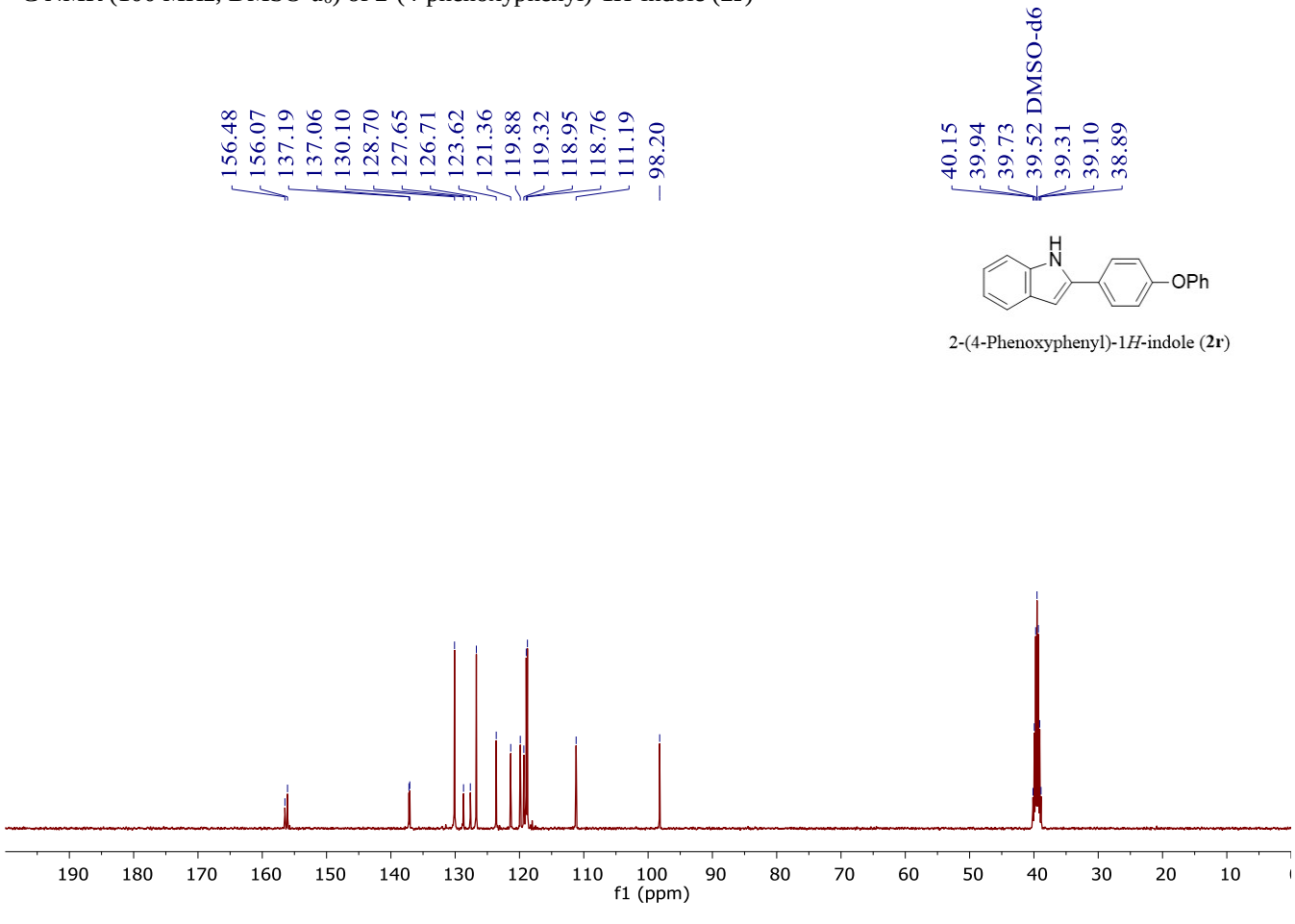


2-((1*R*,4*R*)-bicyclo[2.2.1]hept-5-en-2-yl)-1*H*-indole (**2q**)

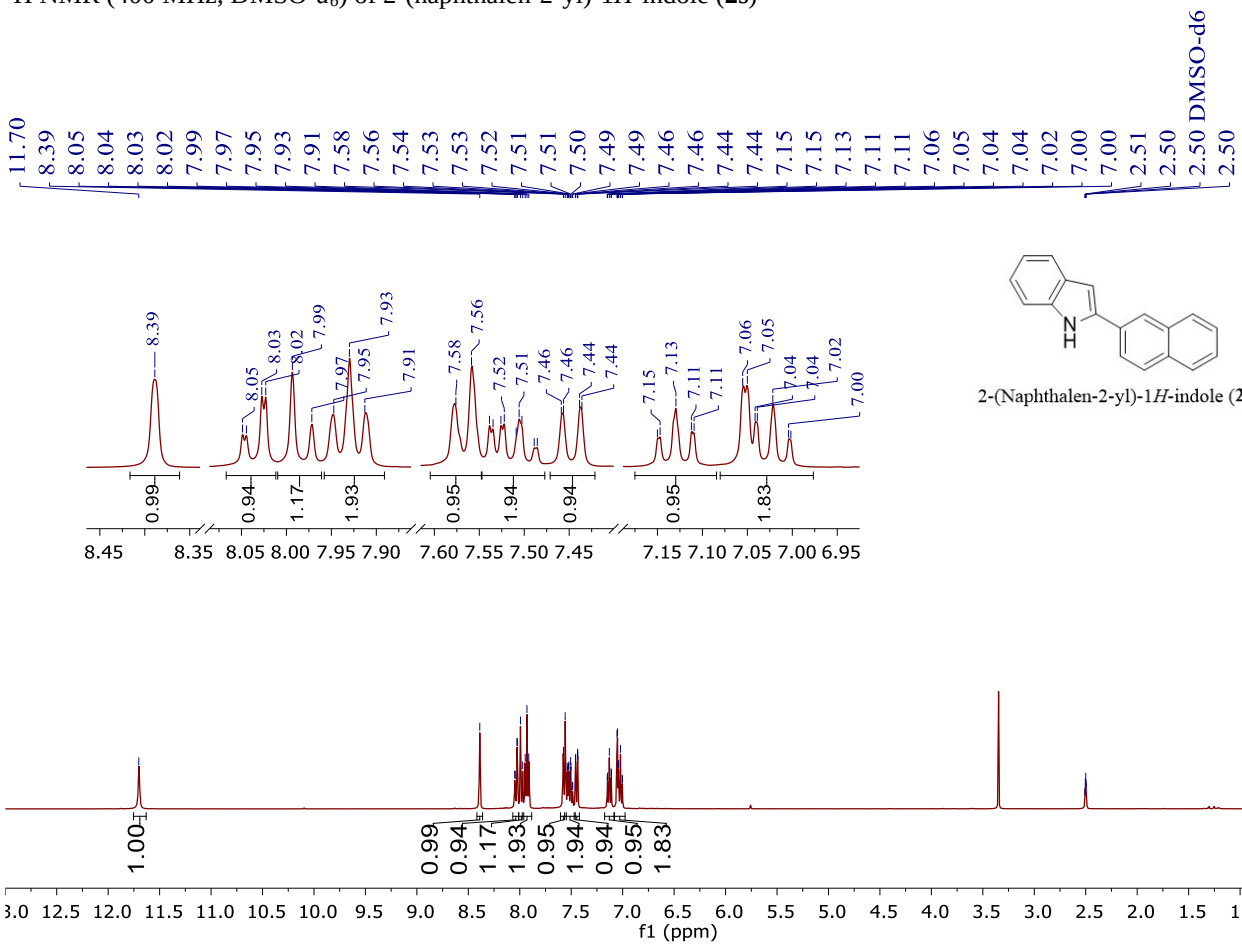
^{1}H NMR (400 MHz, DMSO-d_6) of 2-(4-phenoxyphenyl)-1*H*-indole (**2r**)



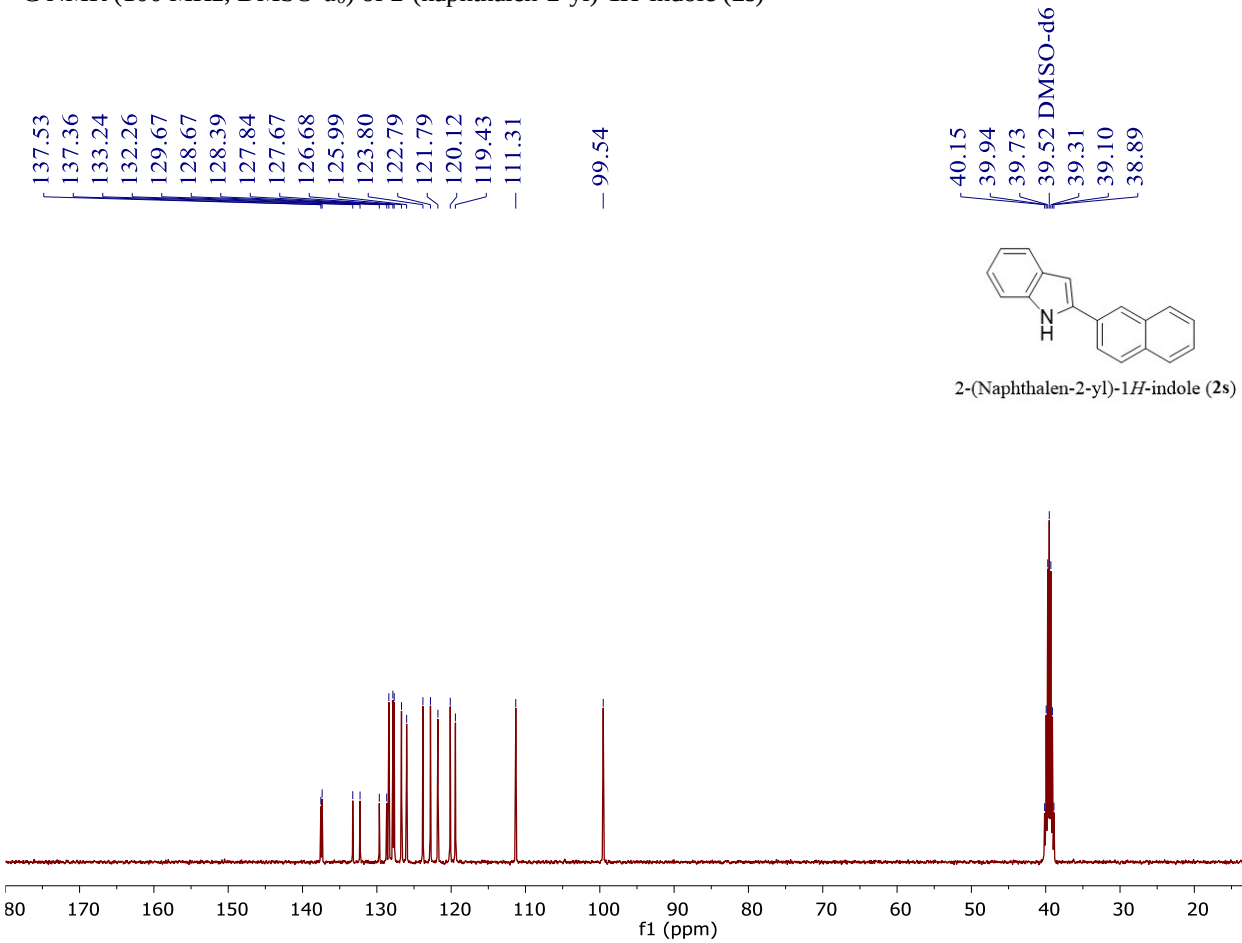
^{13}C NMR (100 MHz, DMSO-d_6) of 2-(4-phenoxyphenyl)-1*H*-indole (**2r**)



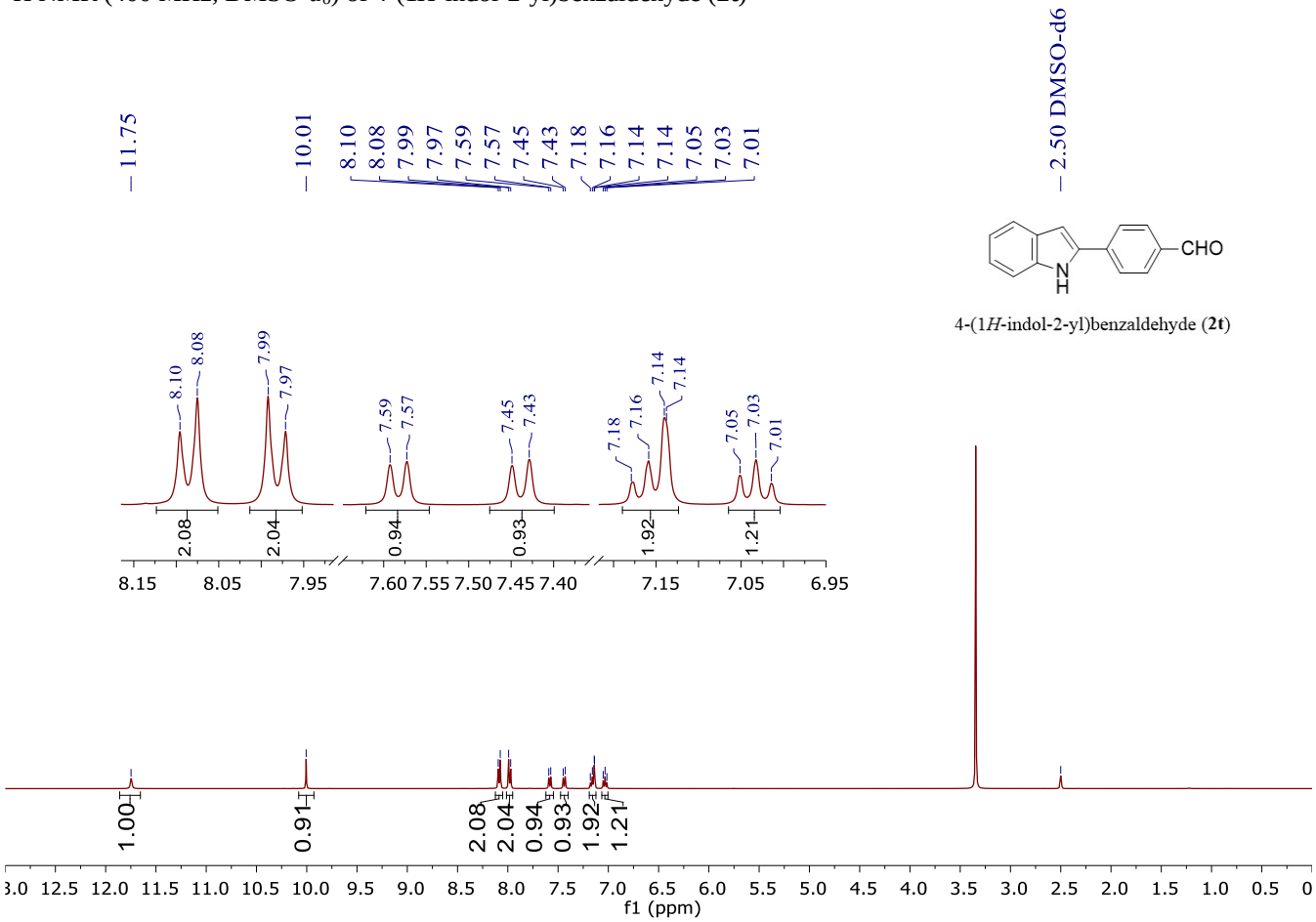
^{1}H NMR (400 MHz, DMSO-d_6) of 2-(naphthalen-2-yl)-1*H*-indole (**2s**)



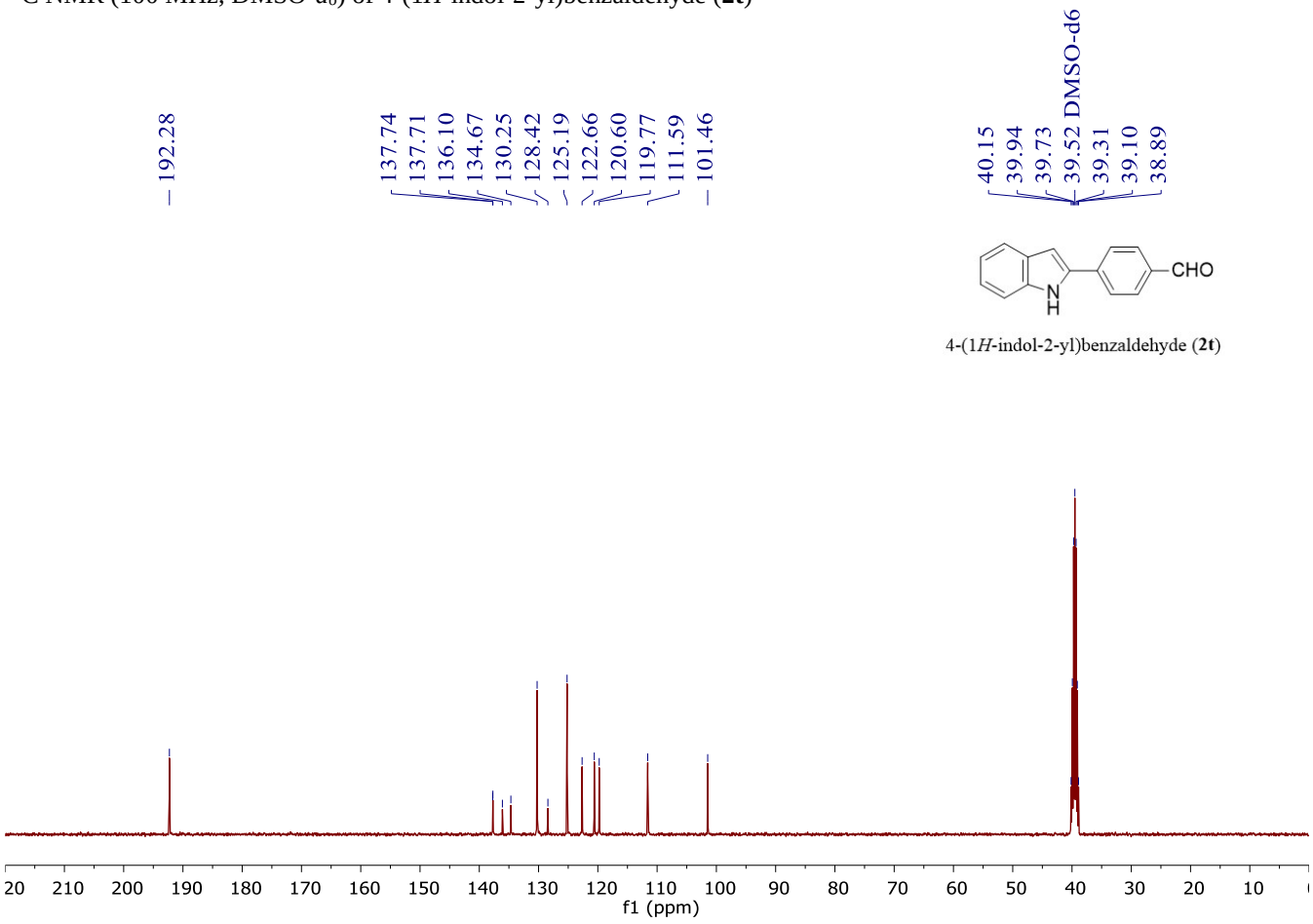
^{13}C NMR (100 MHz, DMSO-d_6) of 2-(naphthalen-2-yl)-1*H*-indole (**2s**)



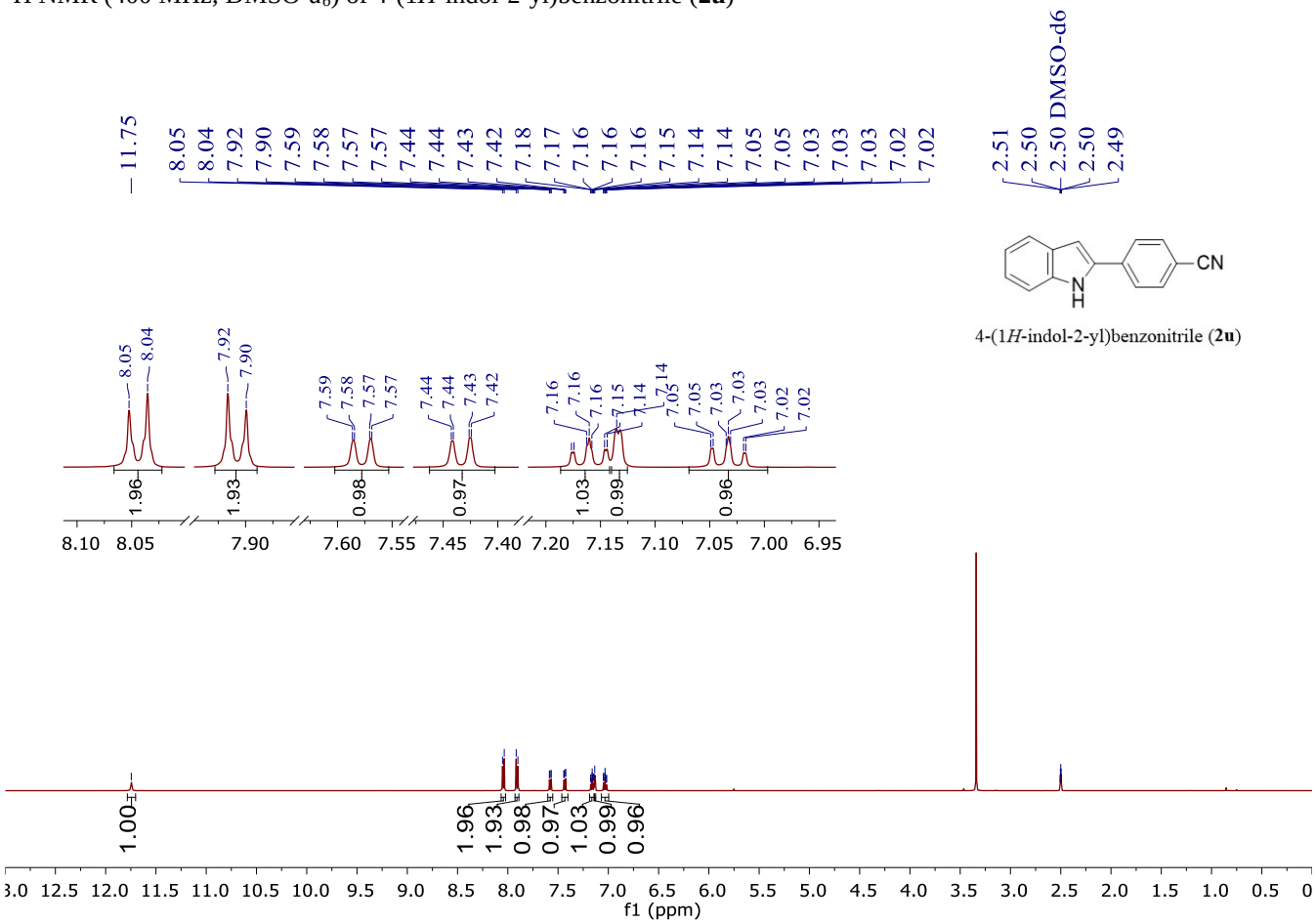
^{1}H NMR (400 MHz, DMSO-d_6) of 4-(1*H*-indol-2-yl)benzaldehyde (**2t**)



^{13}C NMR (100 MHz, DMSO-d_6) of 4-(1*H*-indol-2-yl)benzaldehyde (**2t**)

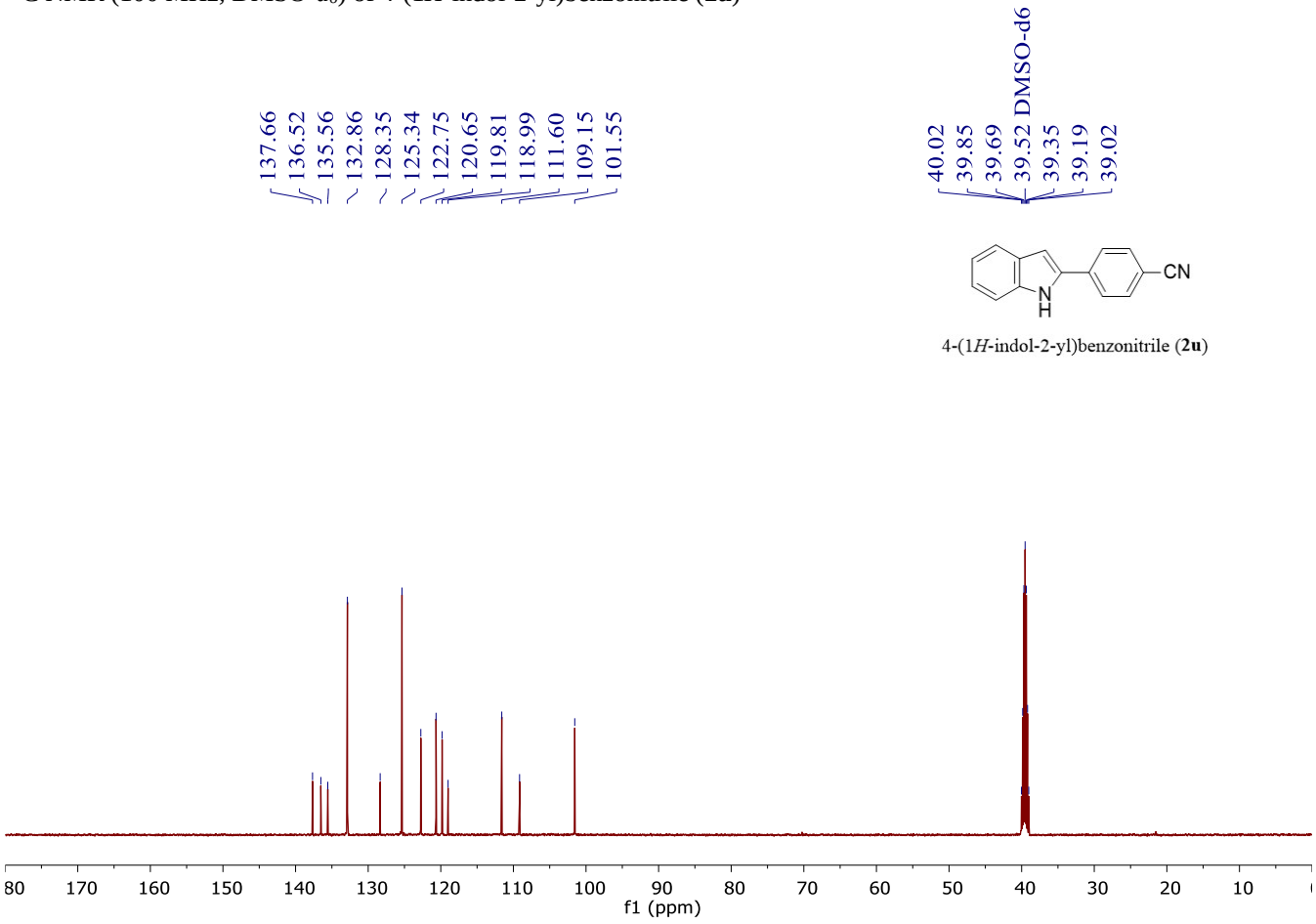


^{1}H NMR (400 MHz, DMSO-d_6) of 4-(1*H*-indol-2-yl)benzonitrile (**2u**)



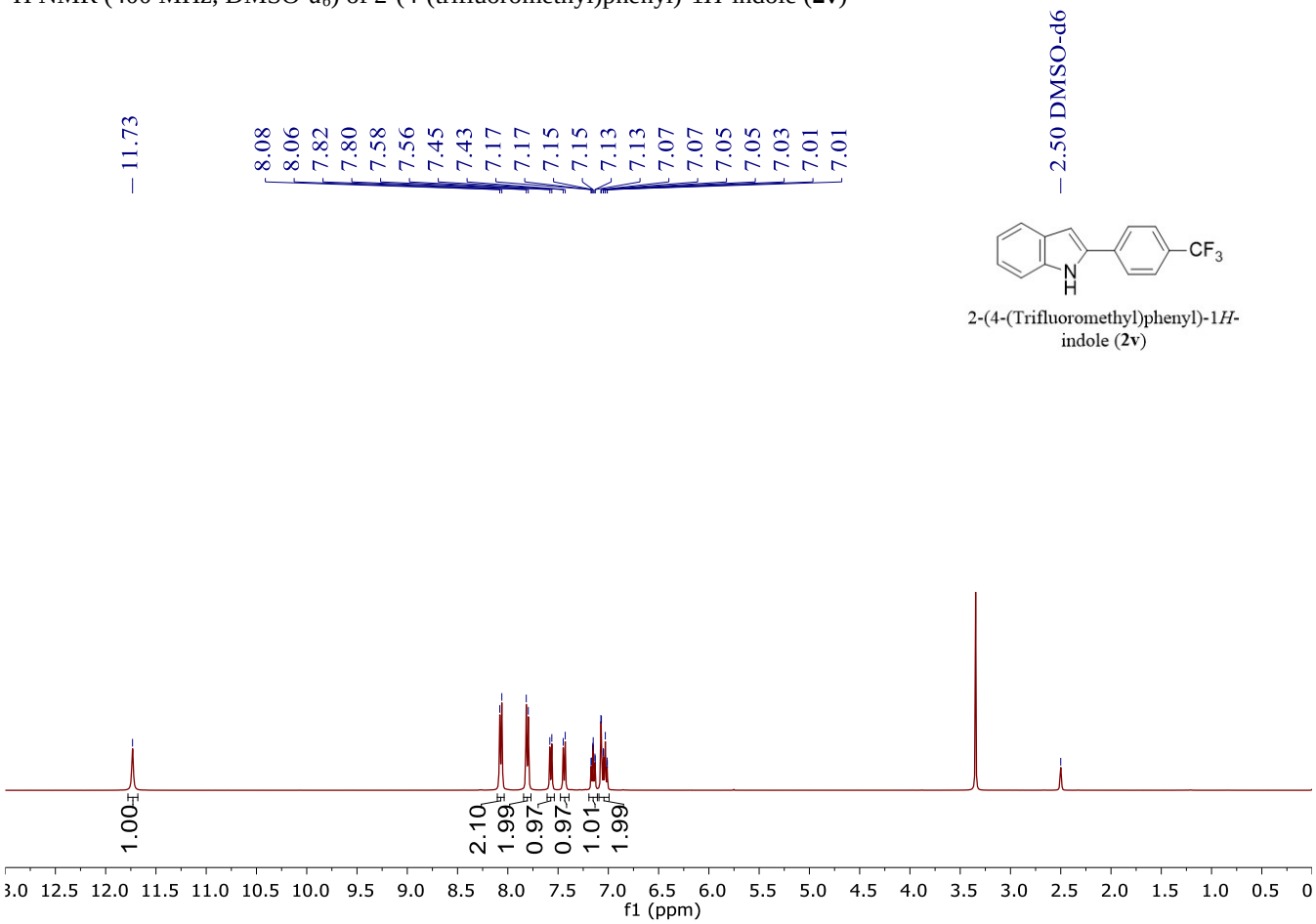
4-(1*H*-indol-2-yl)benzonitrile (**2u**)

^{13}C NMR (100 MHz, DMSO-d_6) of 4-(1*H*-indol-2-yl)benzonitrile (**2u**)

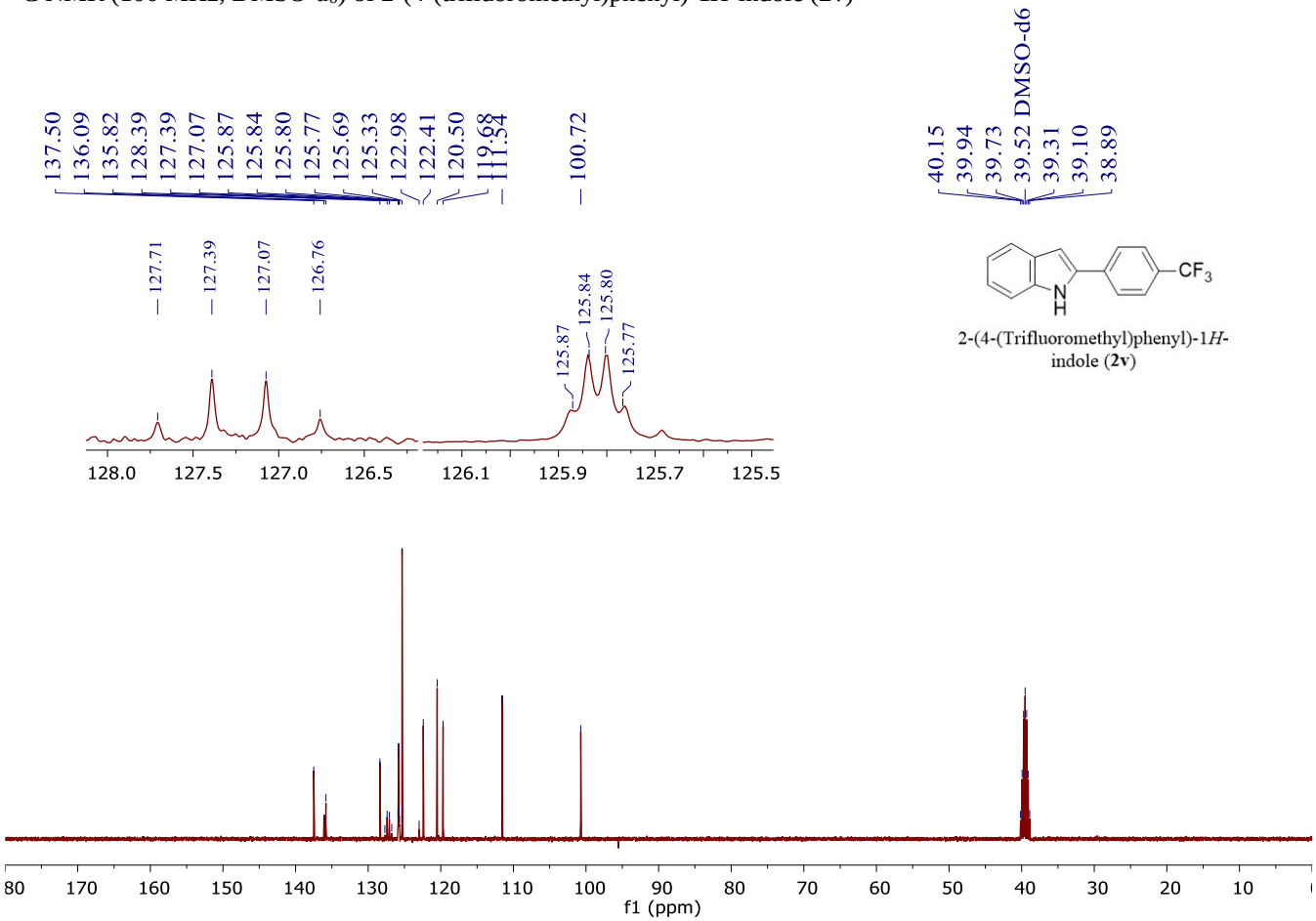


4-(1*H*-indol-2-yl)benzonitrile (**2u**)

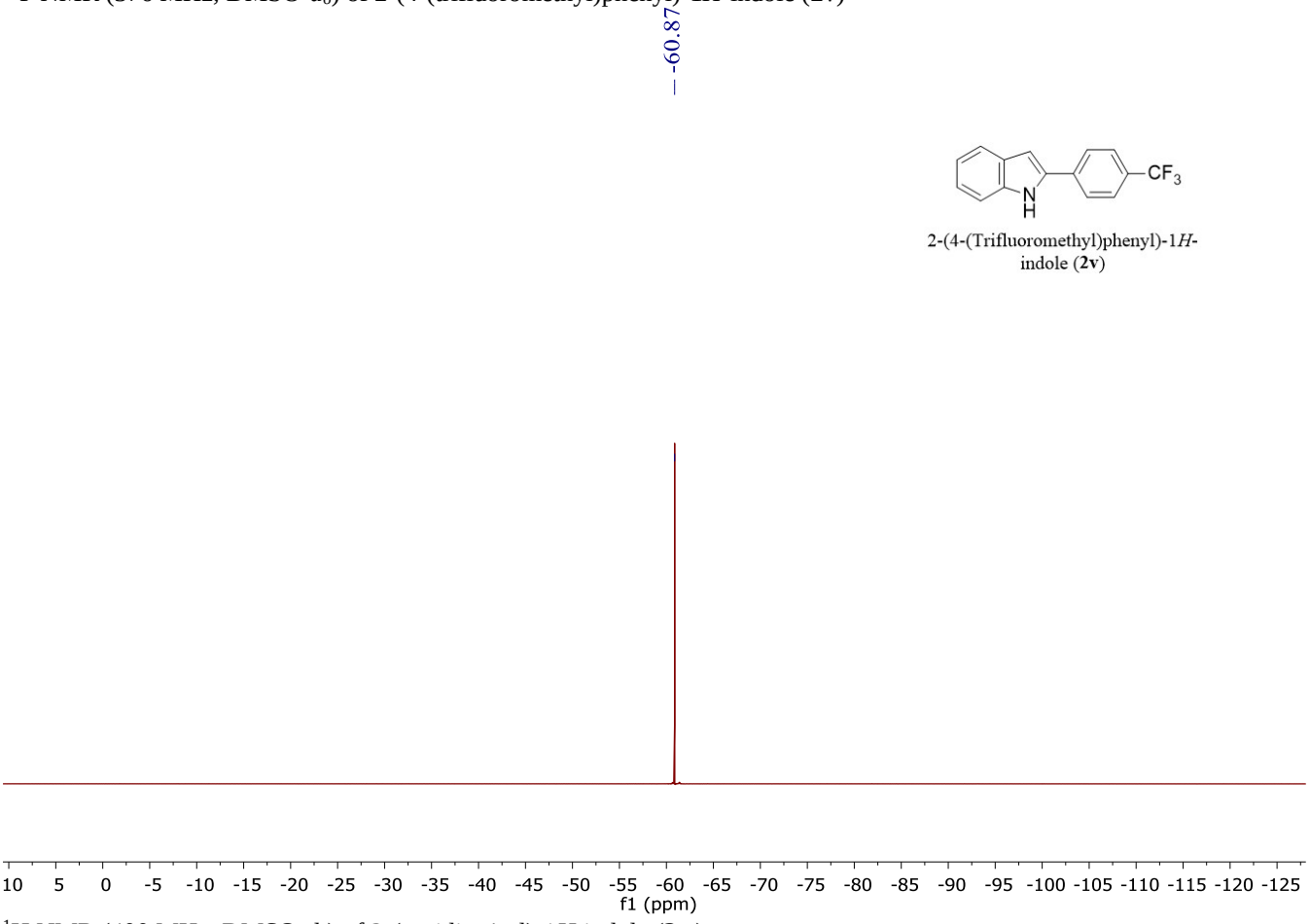
^{1}H NMR (400 MHz, DMSO-d_6) of 2-(4-(trifluoromethyl)phenyl)-1*H*-indole (**2v**)



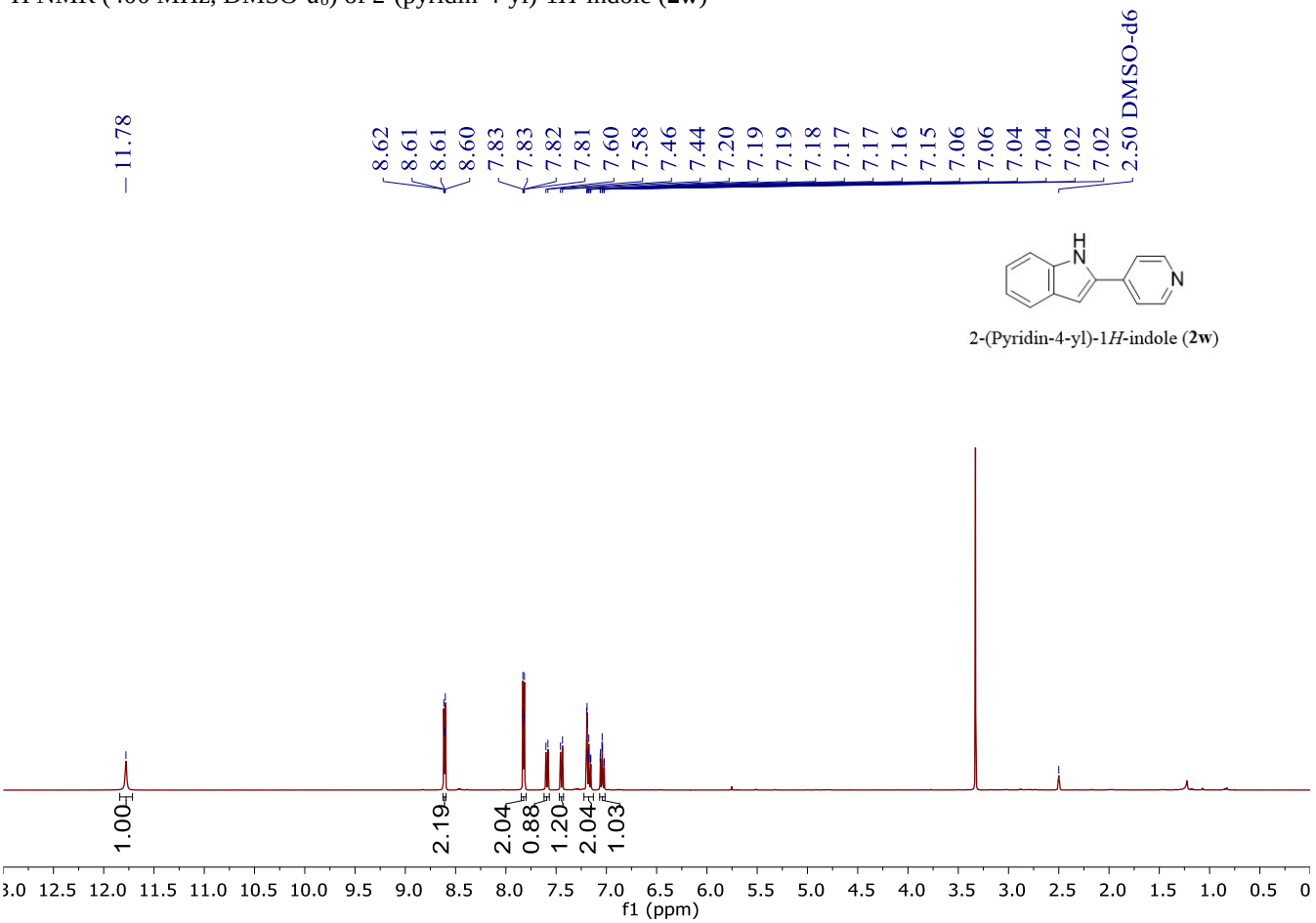
^{13}C NMR (100 MHz, DMSO-d_6) of 2-(4-(trifluoromethyl)phenyl)-1*H*-indole (**2v**)



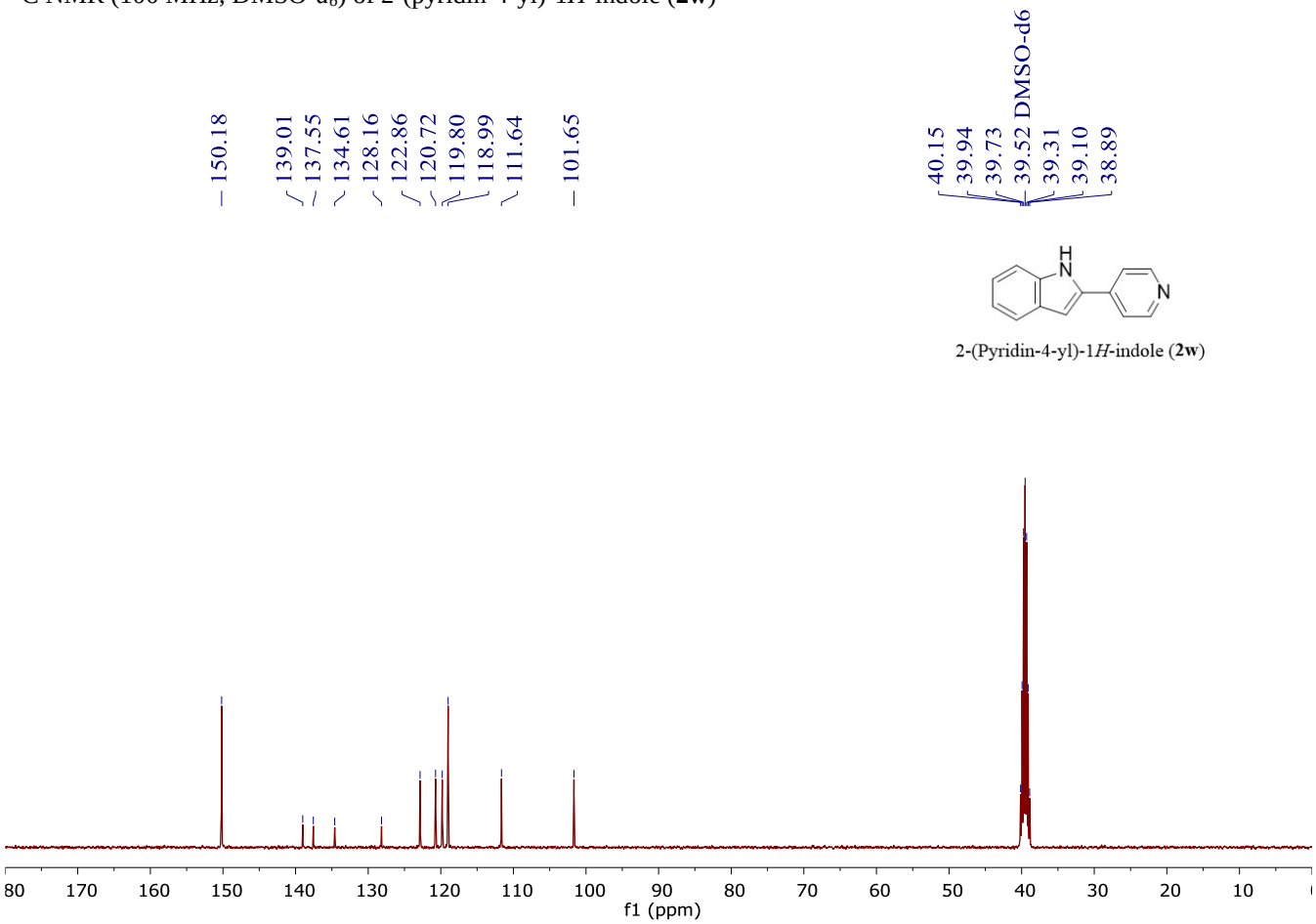
^{19}F NMR (376 MHz, DMSO-d_6) of 2-(4-(trifluoromethyl)phenyl)-1*H*-indole (**2v**)



^{1}H NMR (400 MHz, DMSO-d_6) of 2-(pyridin-4-yl)-1*H*-indole (**2w**)

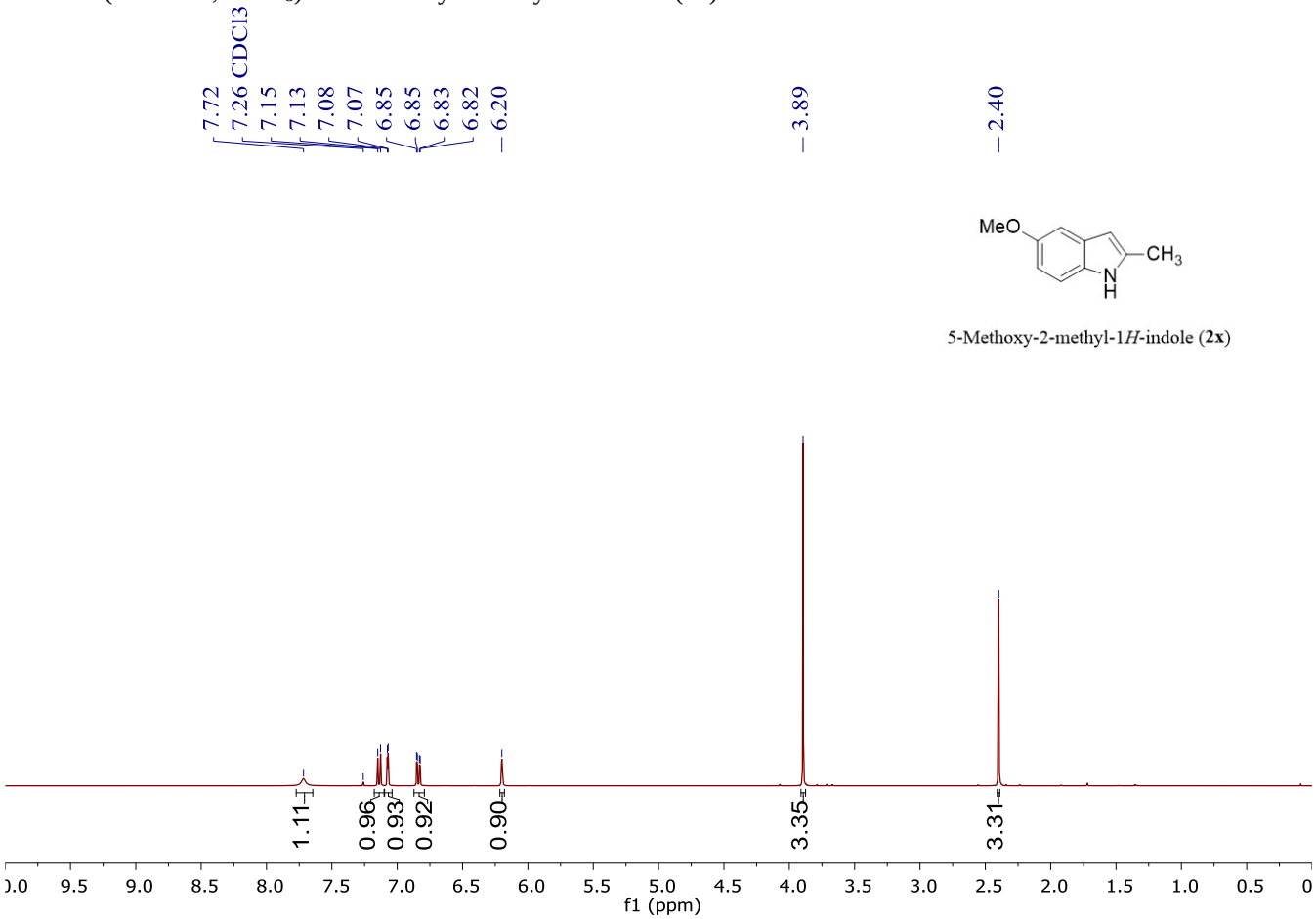


^{13}C NMR (100 MHz, DMSO-d_6) of 2-(pyridin-4-yl)-1*H*-indole (**2w**)



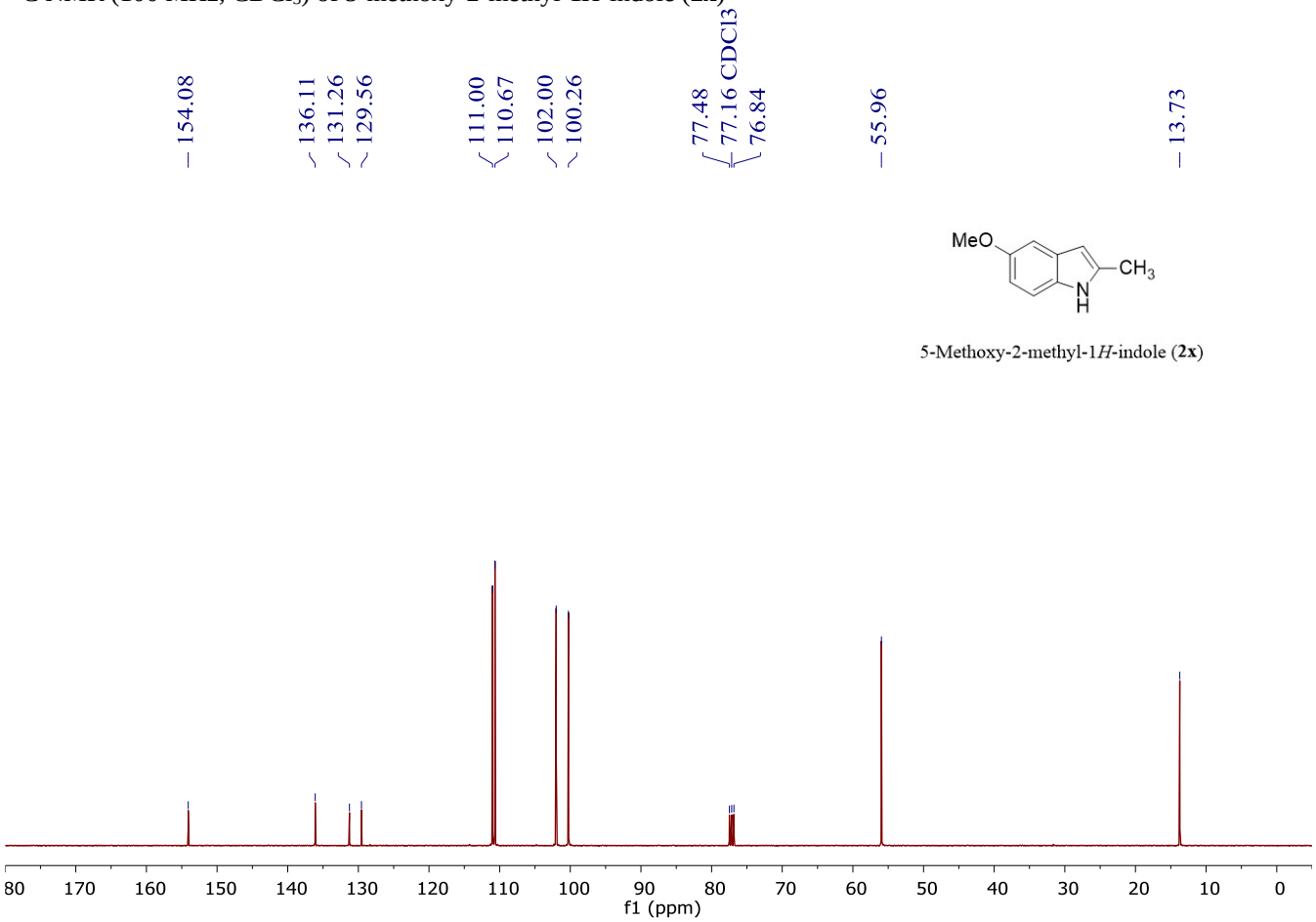
2-(Pyridin-4-yl)-1*H*-indole (**2w**)

^{1}H NMR (400 MHz, $CDCl_3$) of 5-methoxy-2-methyl-1*H*-indole (**2x**)



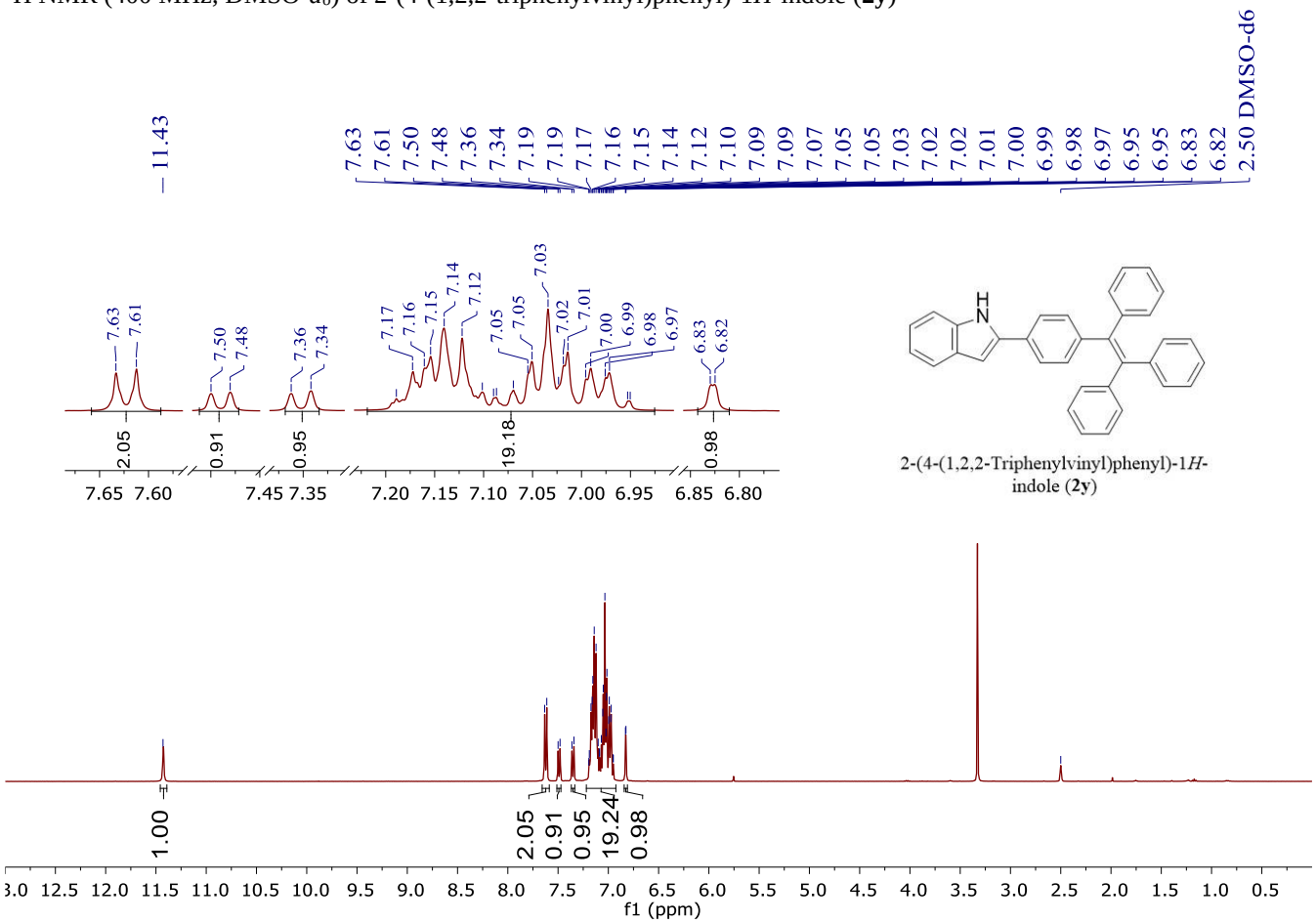
5-Methoxy-2-methyl-1*H*-indole (**2x**)

^{13}C NMR (100 MHz, $CDCl_3$) of 5-methoxy-2-methyl-1*H*-indole (**2x**)



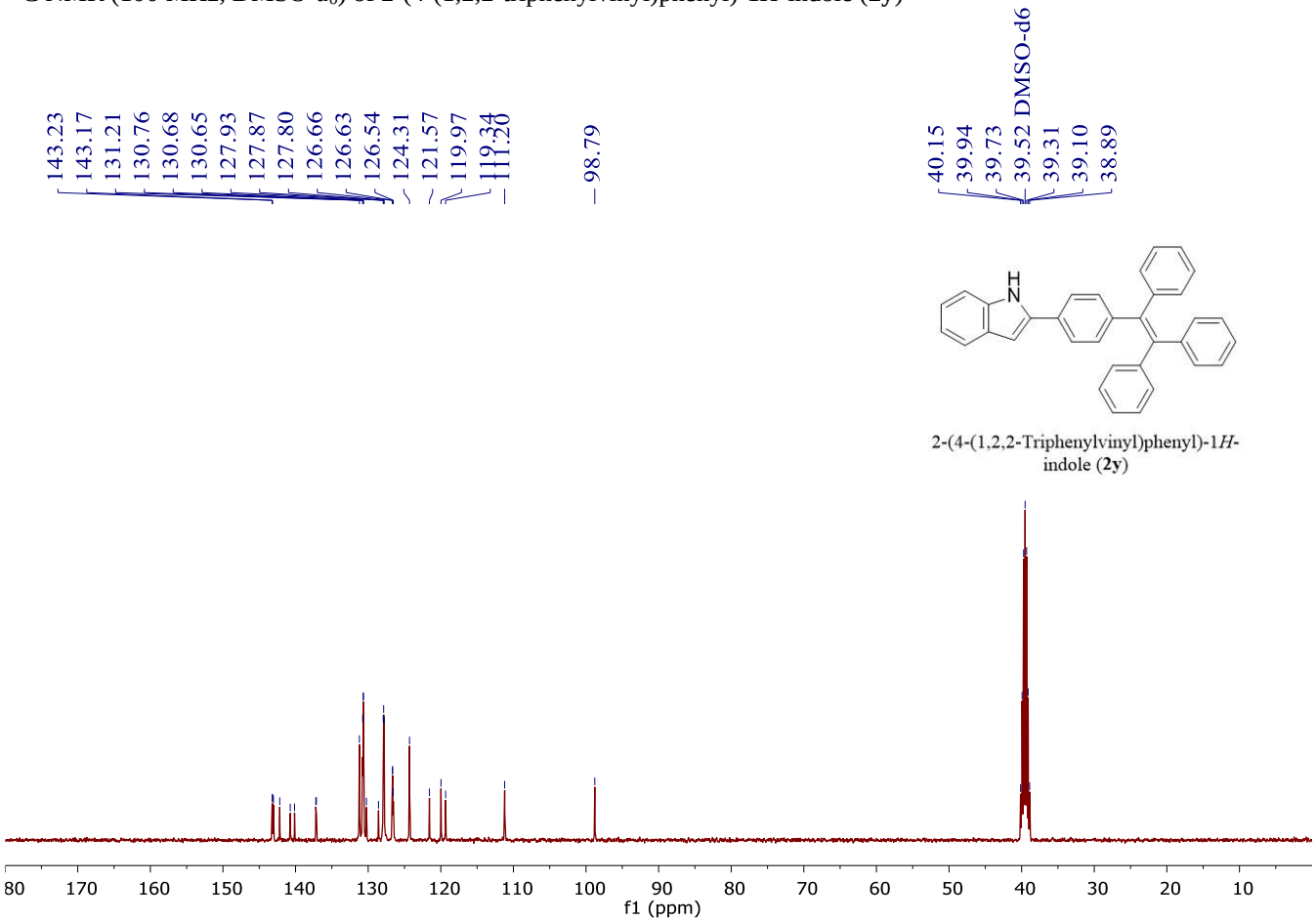
5-Methoxy-2-methyl-1*H*-indole (**2x**)

^{1}H NMR (400 MHz, DMSO-d_6) of 2-(4-(1,2,2-triphenylvinyl)phenyl)-1*H*-indole (**2y**)

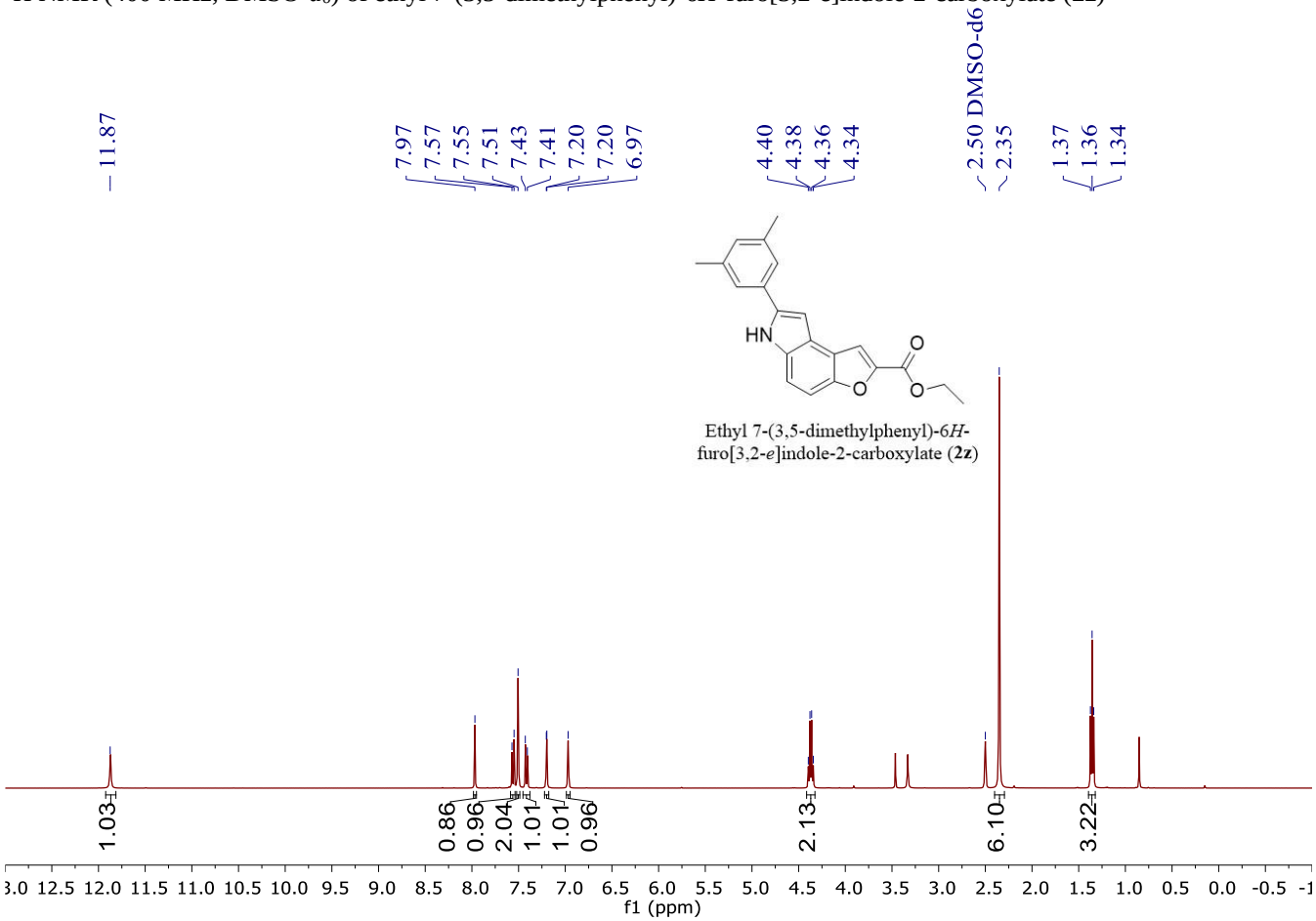


2-(4-(1,2,2-Triphenylvinyl)phenyl)-1*H*-indole (**2y**)

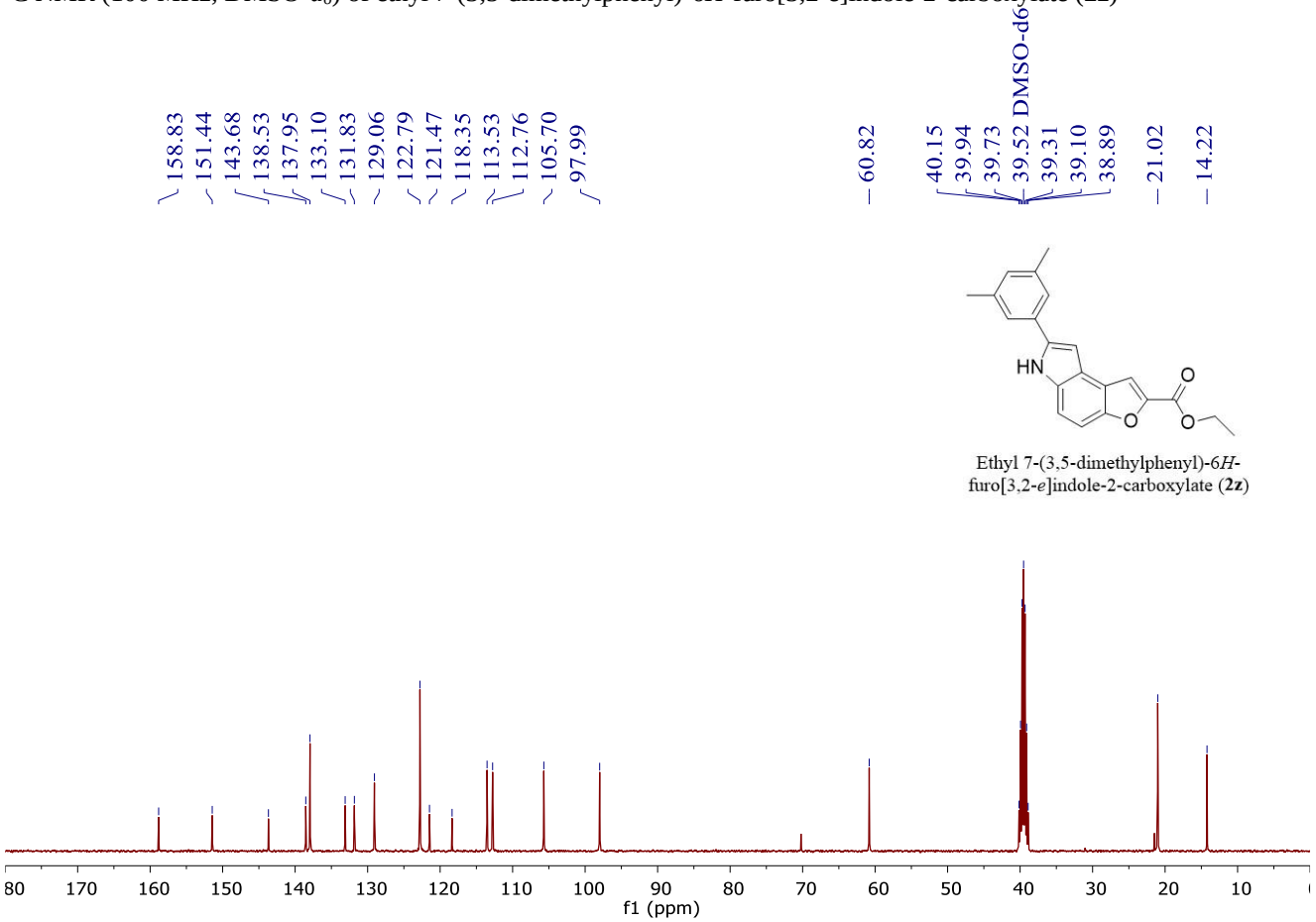
^{13}C NMR (100 MHz, DMSO-d_6) of 2-(4-(1,2,2-triphenylvinyl)phenyl)-1*H*-indole (**2y**)



^{1}H NMR (400 MHz, DMSO-d_6) of ethyl 7-(3,5-dimethylphenyl)-6*H*-furo[3,2-e]indole-2-carboxylate (**2z**)

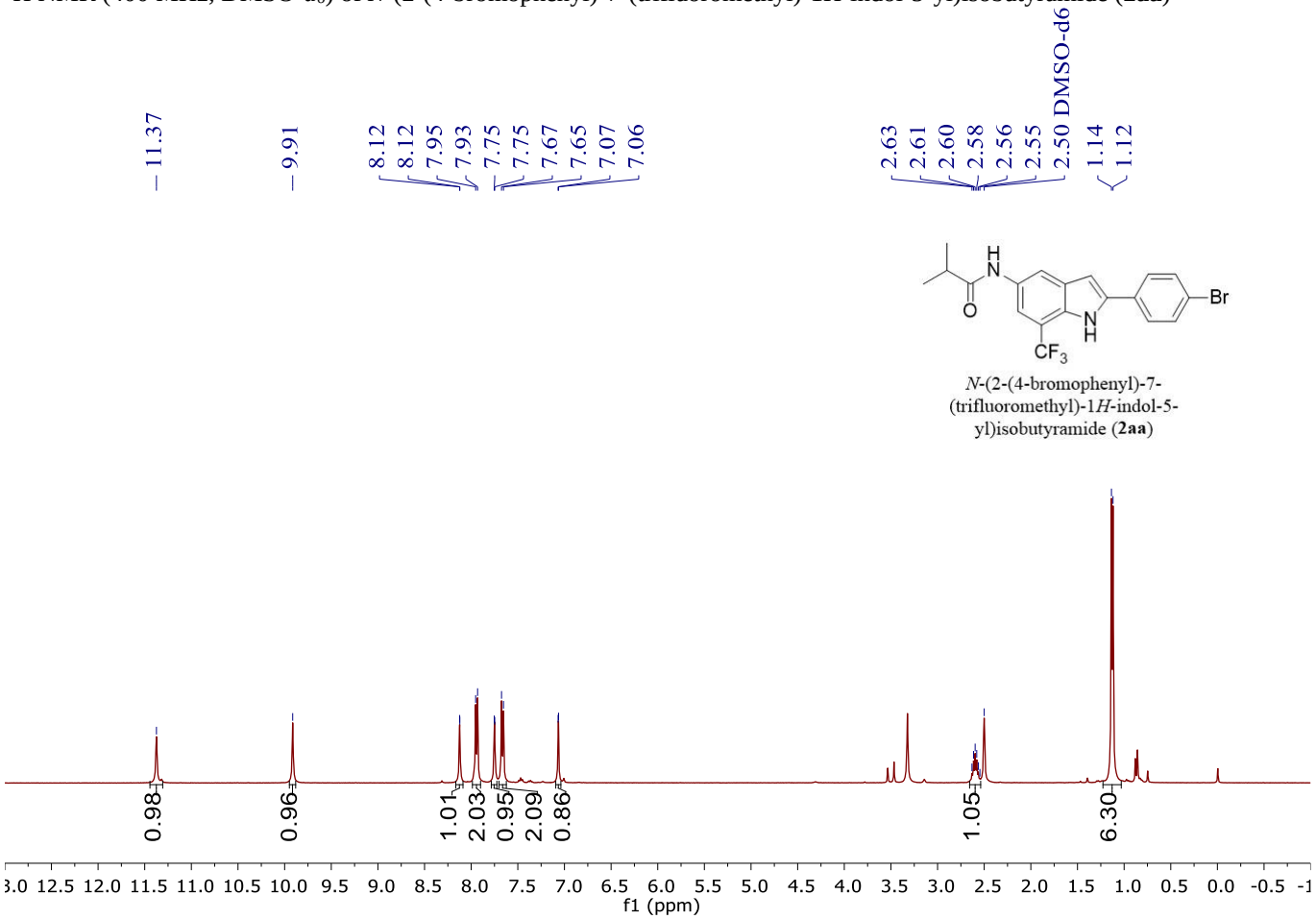


^{13}C NMR (100 MHz, DMSO-d_6) of ethyl 7-(3,5-dimethylphenyl)-6*H*-furo[3,2-e]indole-2-carboxylate (**2z**)



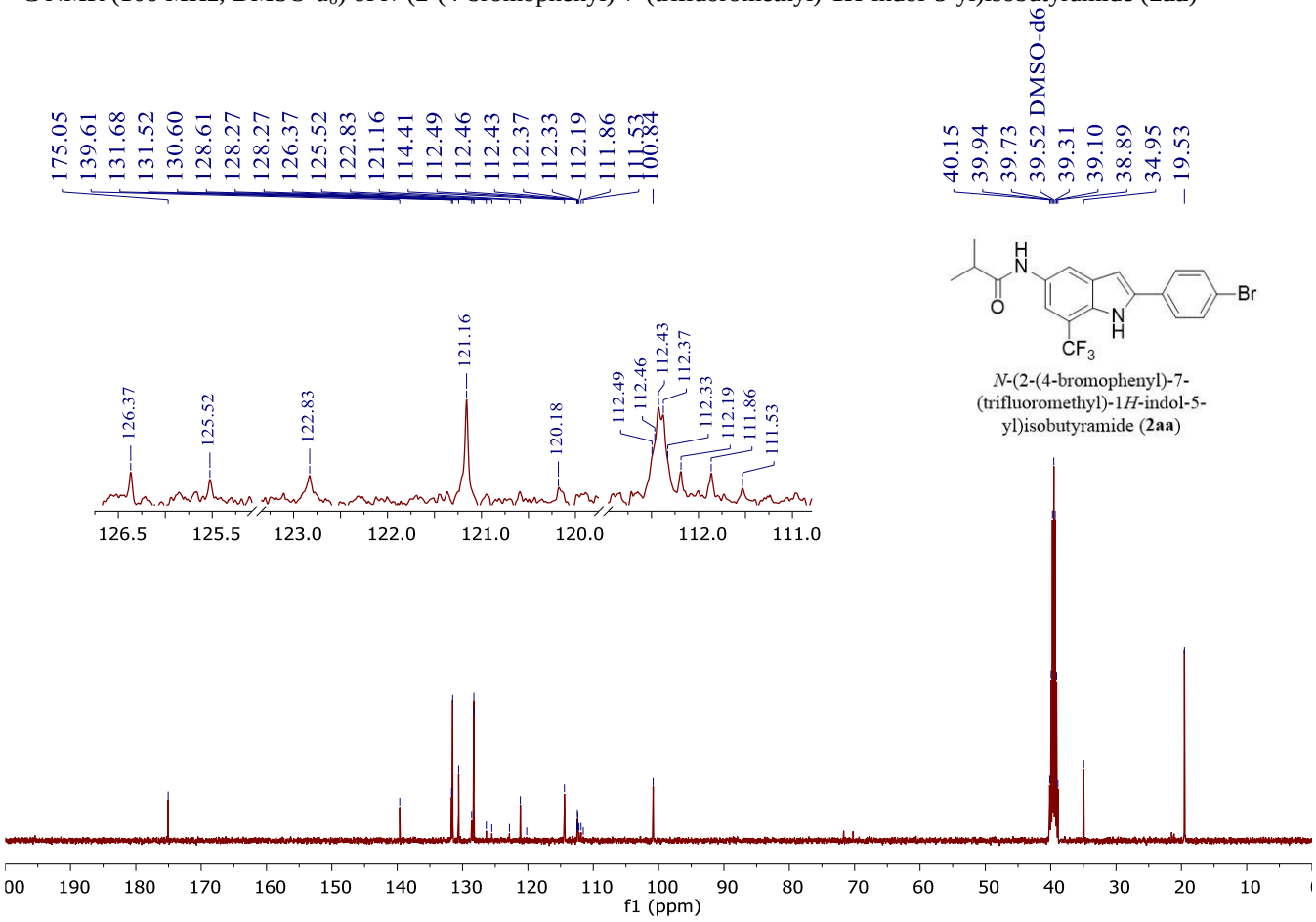
Ethyl 7-(3,5-dimethylphenyl)-6*H*-furo[3,2-*e*]indole-2-carboxylate (**2z**)

^{1}H NMR (400 MHz, DMSO-d_6) of *N*-(2-(4-bromophenyl)-7-(trifluoromethyl)-1H-indol-5-yl)isobutyramide (**2aa**)



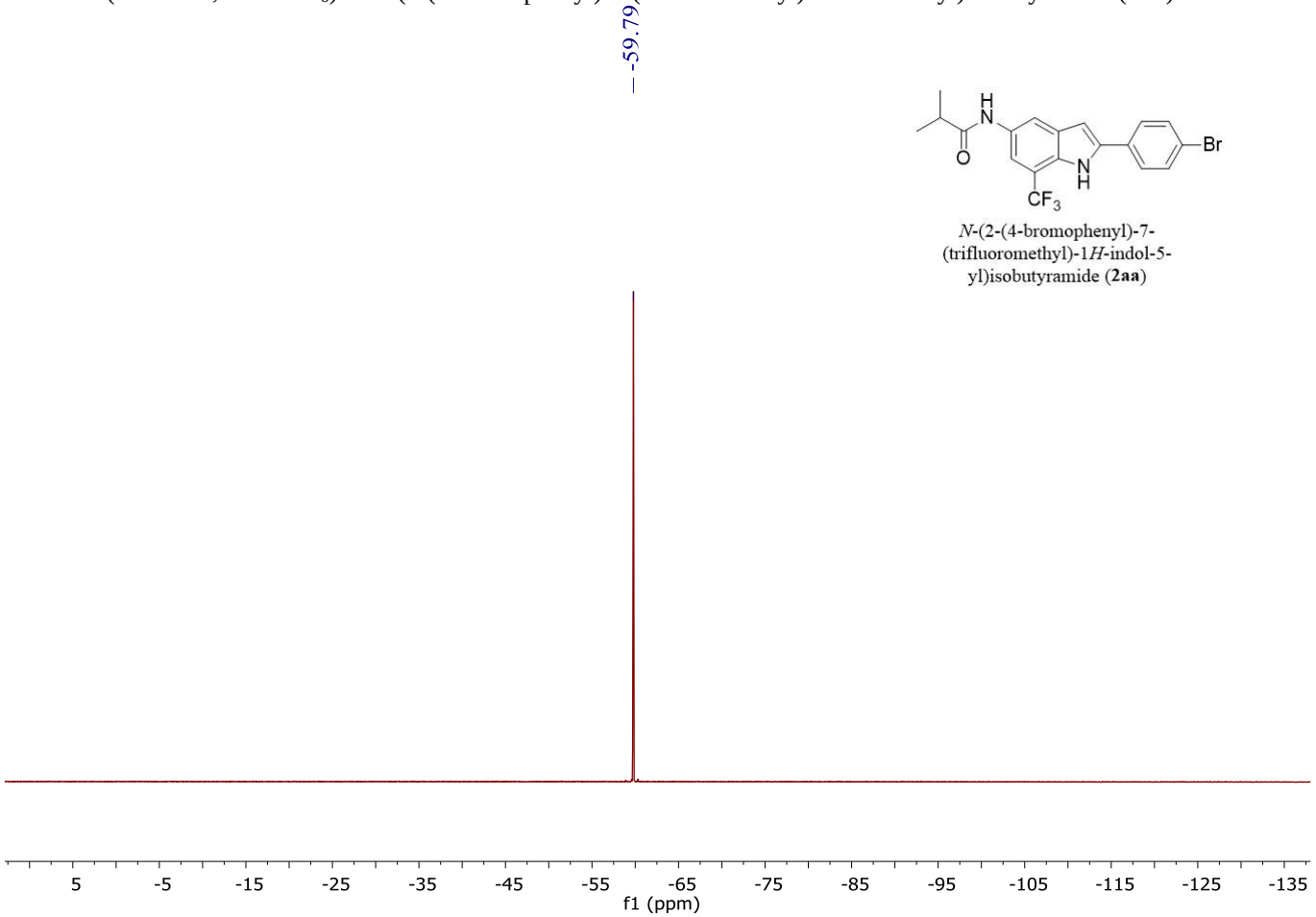
N-(2-(4-bromophenyl)-7-(trifluoromethyl)-1*H*-indol-5-yl)isobutyramide (**2aa**)

^{13}C NMR (100 MHz, DMSO-d_6) of *N*-(2-(4-bromophenyl)-7-(trifluoromethyl)-1H-indol-5-yl)isobutyramide (**2aa**)



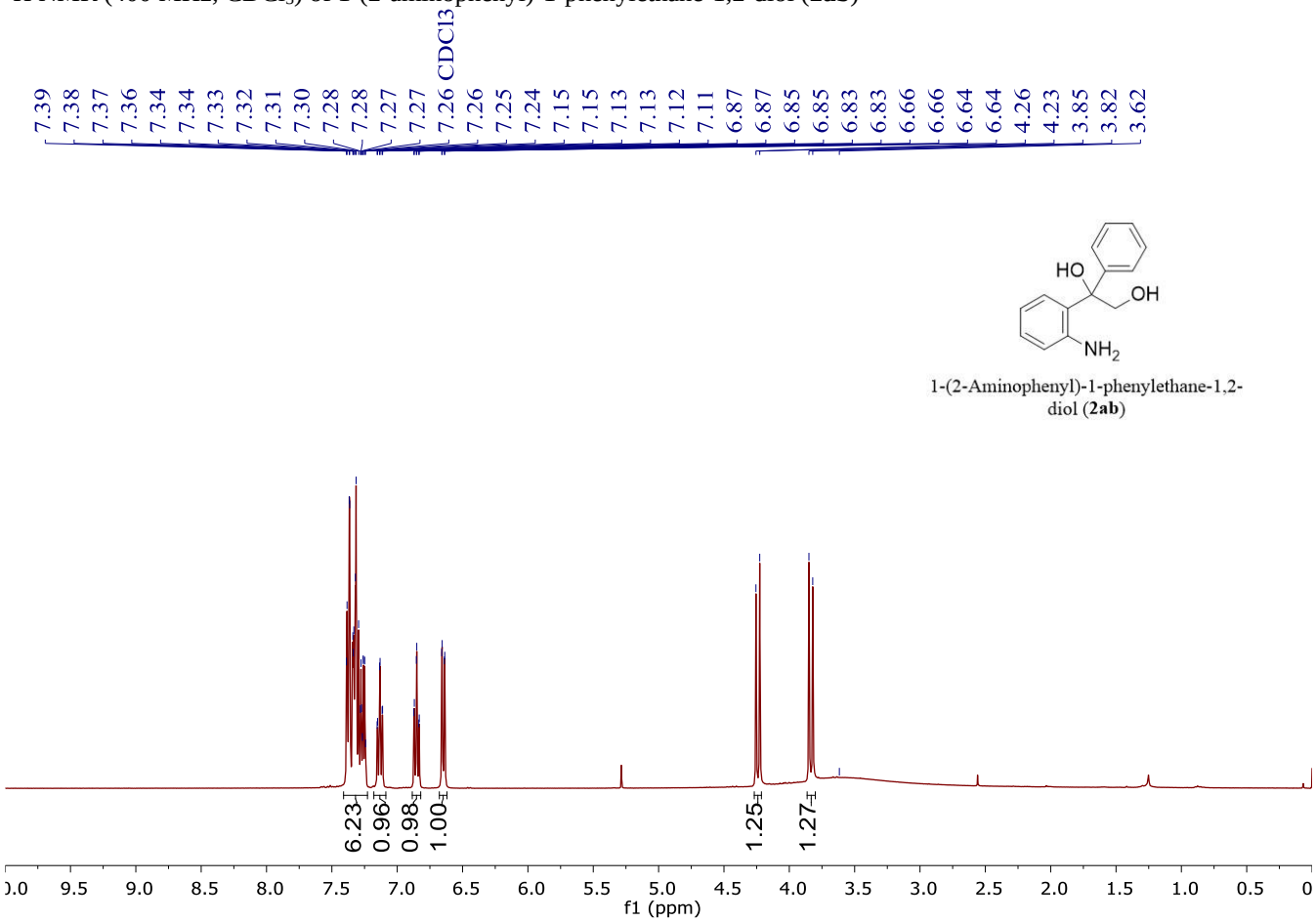
N-(2-(4-bromophenyl)-7-(trifluoromethyl)-1*H*-indol-5-yl)isobutyramide (**2aa**)

^{19}F NMR (376 MHz, DMSO-d_6) of *N*-(2-(4-bromophenyl)-7-(trifluoromethyl)-1H-indol-5-yl)isobutyramide (**2aa**)



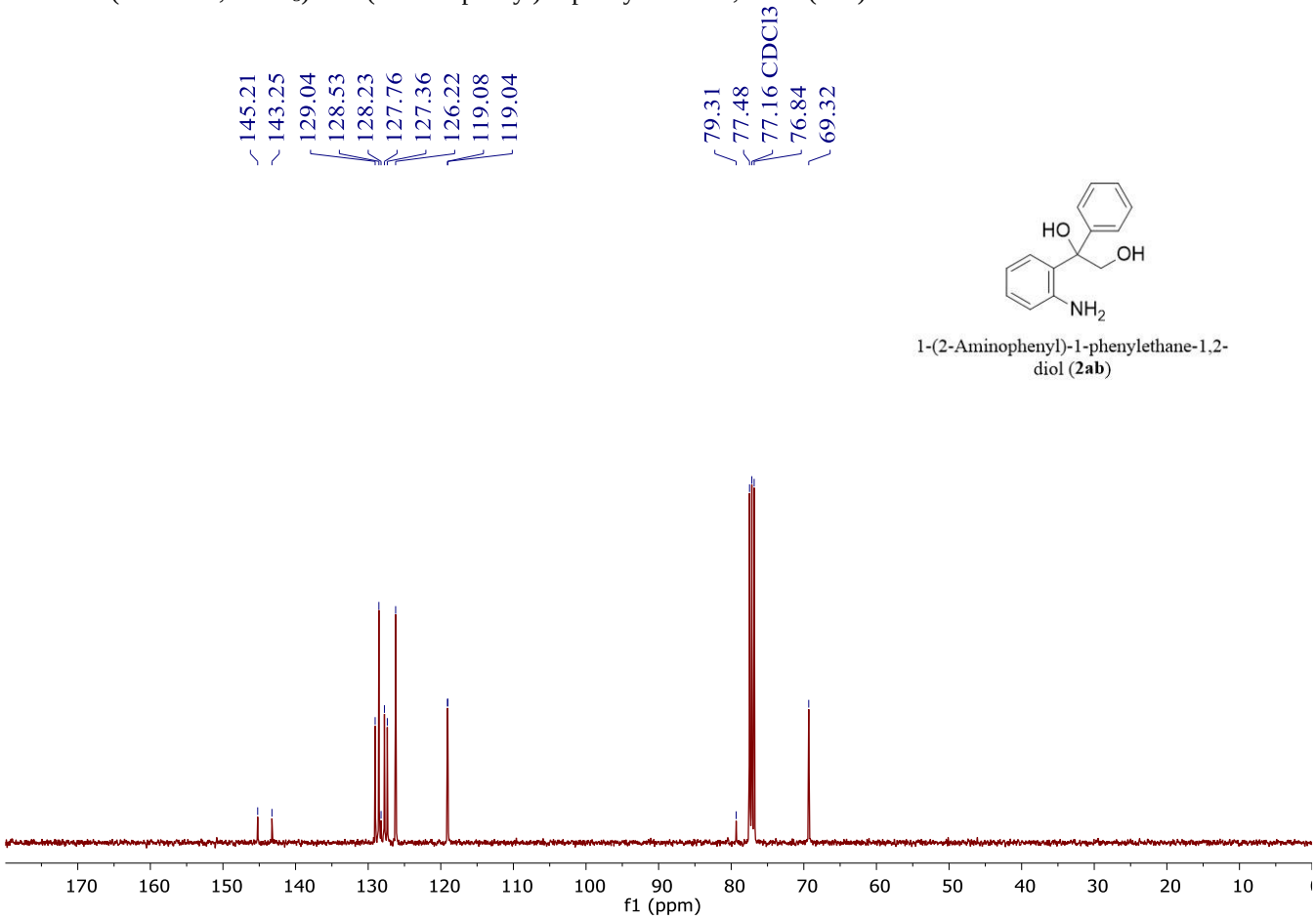
N-(2-(4-bromophenyl)-7-(trifluoromethyl)-1*H*-indol-5-yl)isobutyramide (**2aa**)

^{1}H NMR (400 MHz, $CDCl_3$) of 1-(2-aminophenyl)-1-phenylethane-1,2-diol (**2ab**)



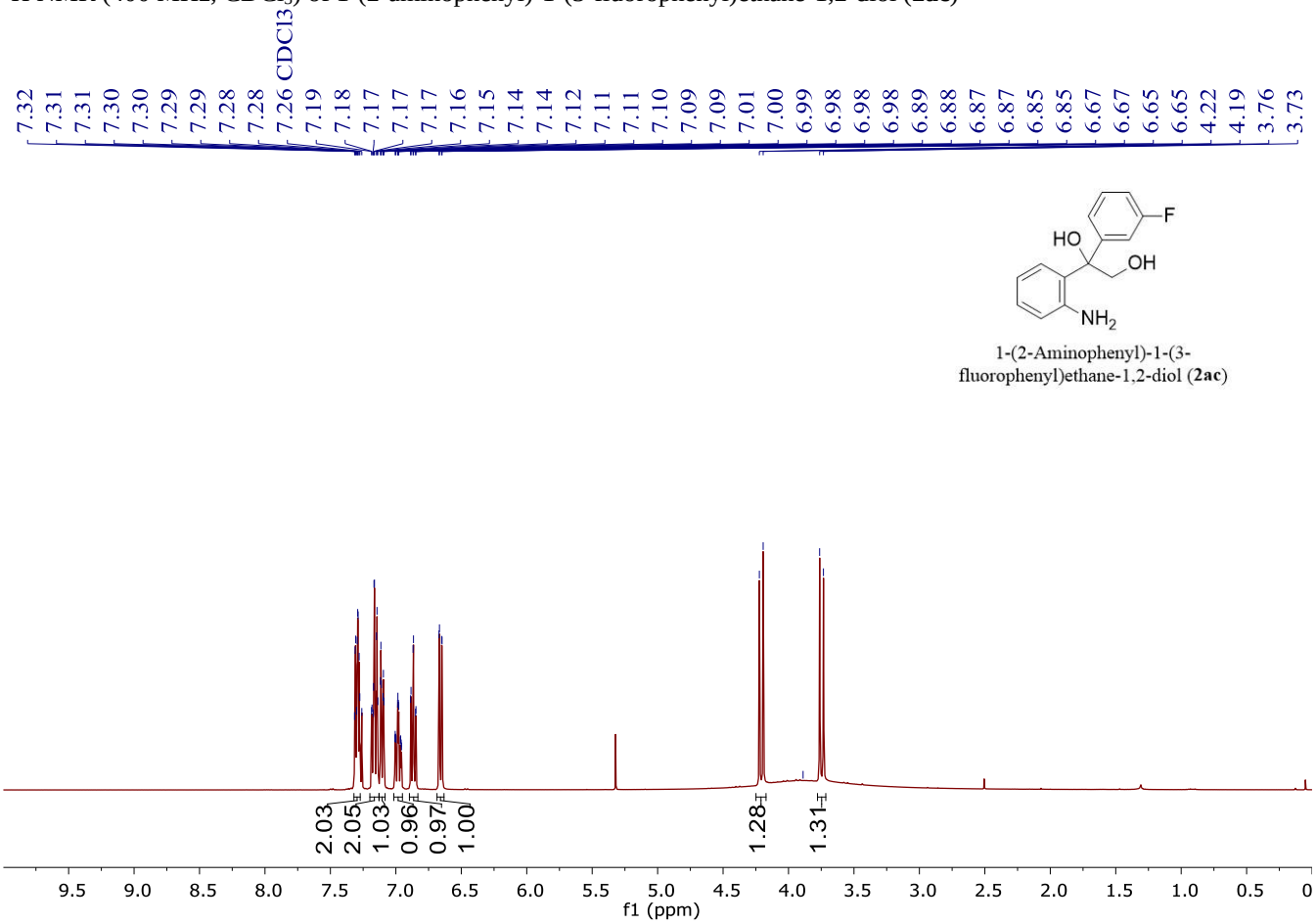
1-(2-Aminophenyl)-1-phenylethane-1,2-diol (**2ab**)

^{13}C NMR (100 MHz, $CDCl_3$) of 1-(2-aminophenyl)-1-phenylethane-1,2-diol (**2ab**)



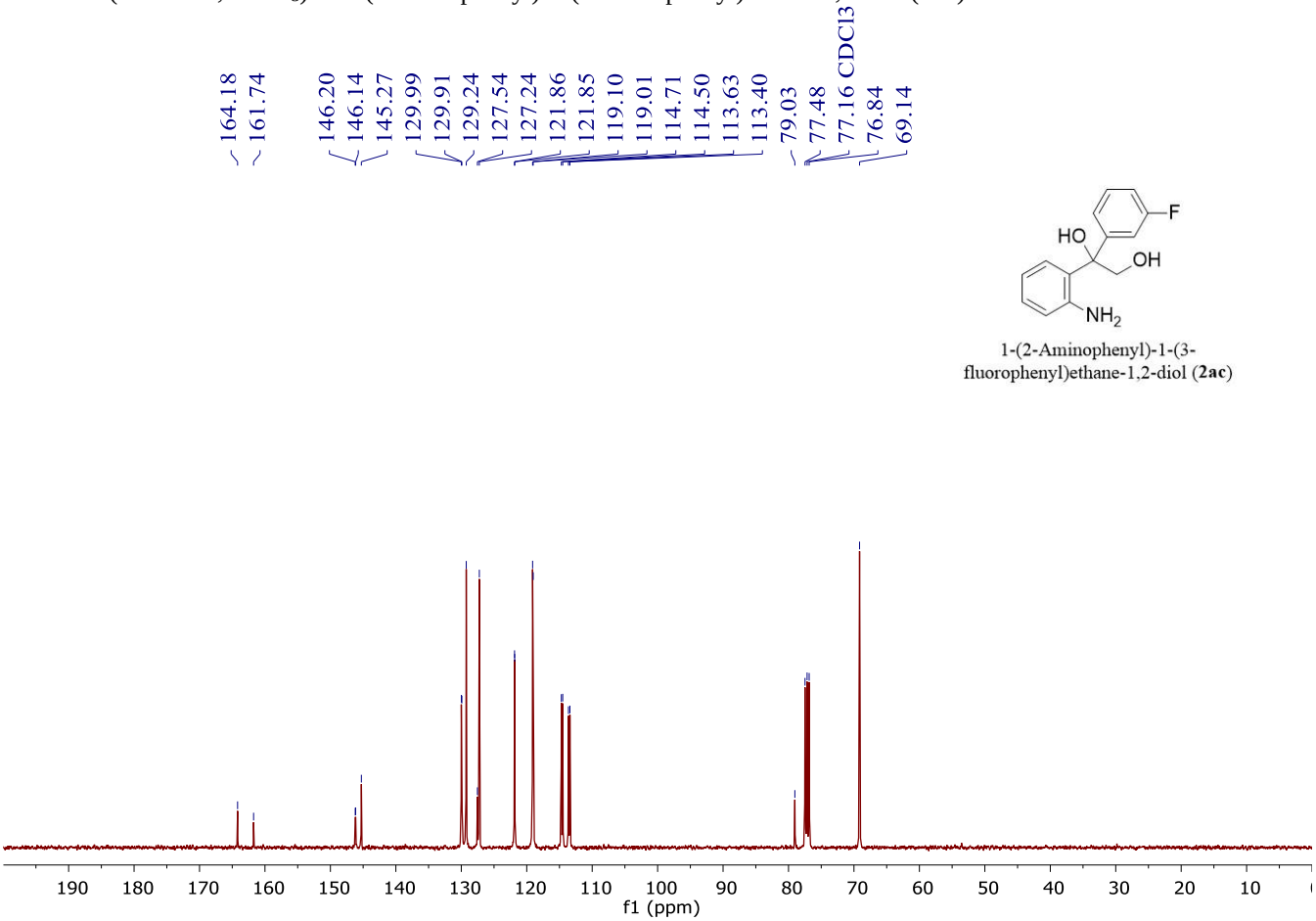
1-(2-Aminophenyl)-1-phenylethane-1,2-diol (**2ab**)

^{1}H NMR (400 MHz, $CDCl_3$) of 1-(2-aminophenyl)-1-(3-fluorophenyl)ethane-1,2-diol (**2ac**)



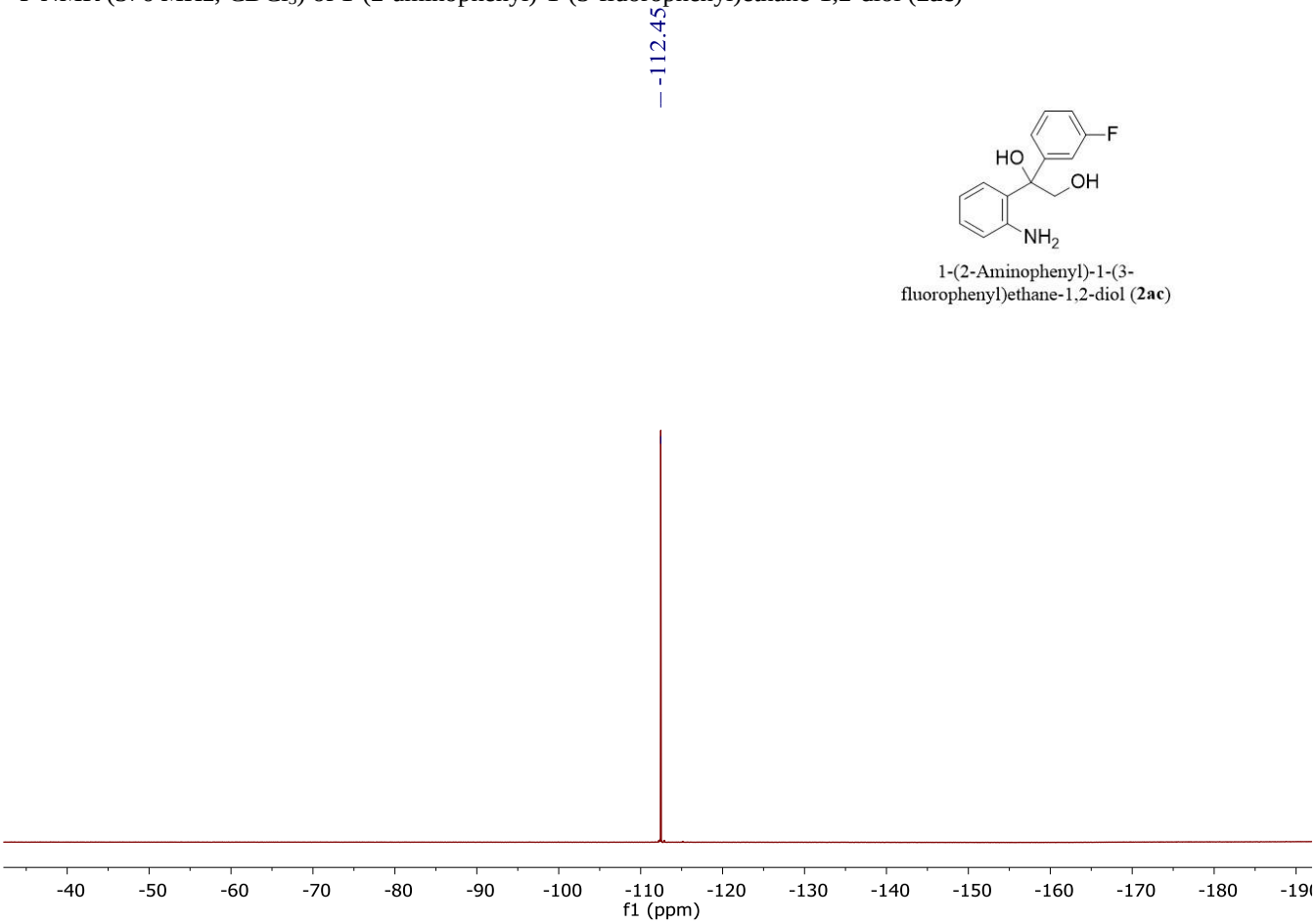
1-(2-Aminophenyl)-1-(3-fluorophenyl)ethane-1,2-diol (**2ac**)

^{13}C NMR (100 MHz, $CDCl_3$) of 1-(2-aminophenyl)-1-(3-fluorophenyl)ethane-1,2-diol (**2ac**)

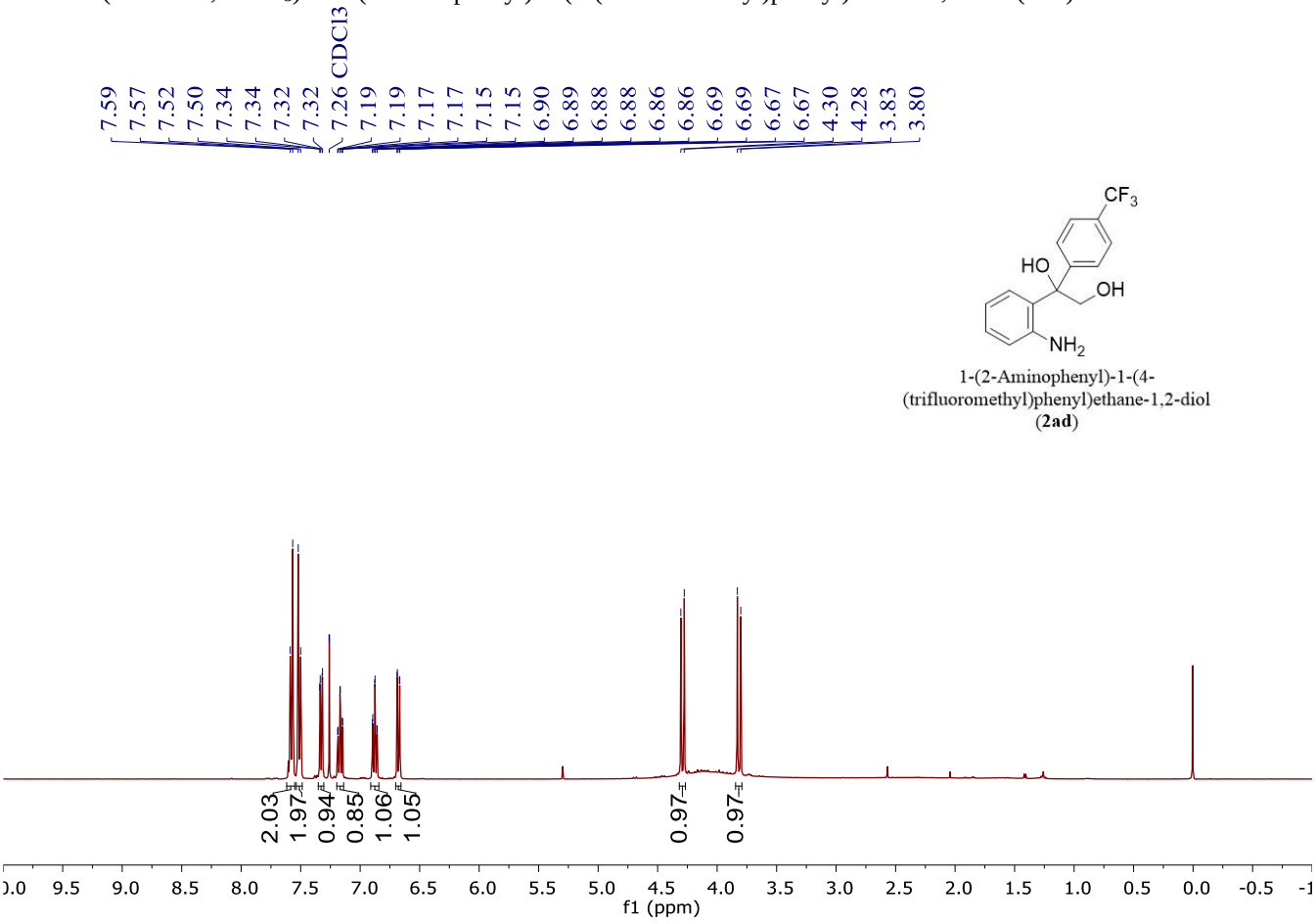


1-(2-Aminophenyl)-1-(3-fluorophenyl)ethane-1,2-diol (**2ac**)

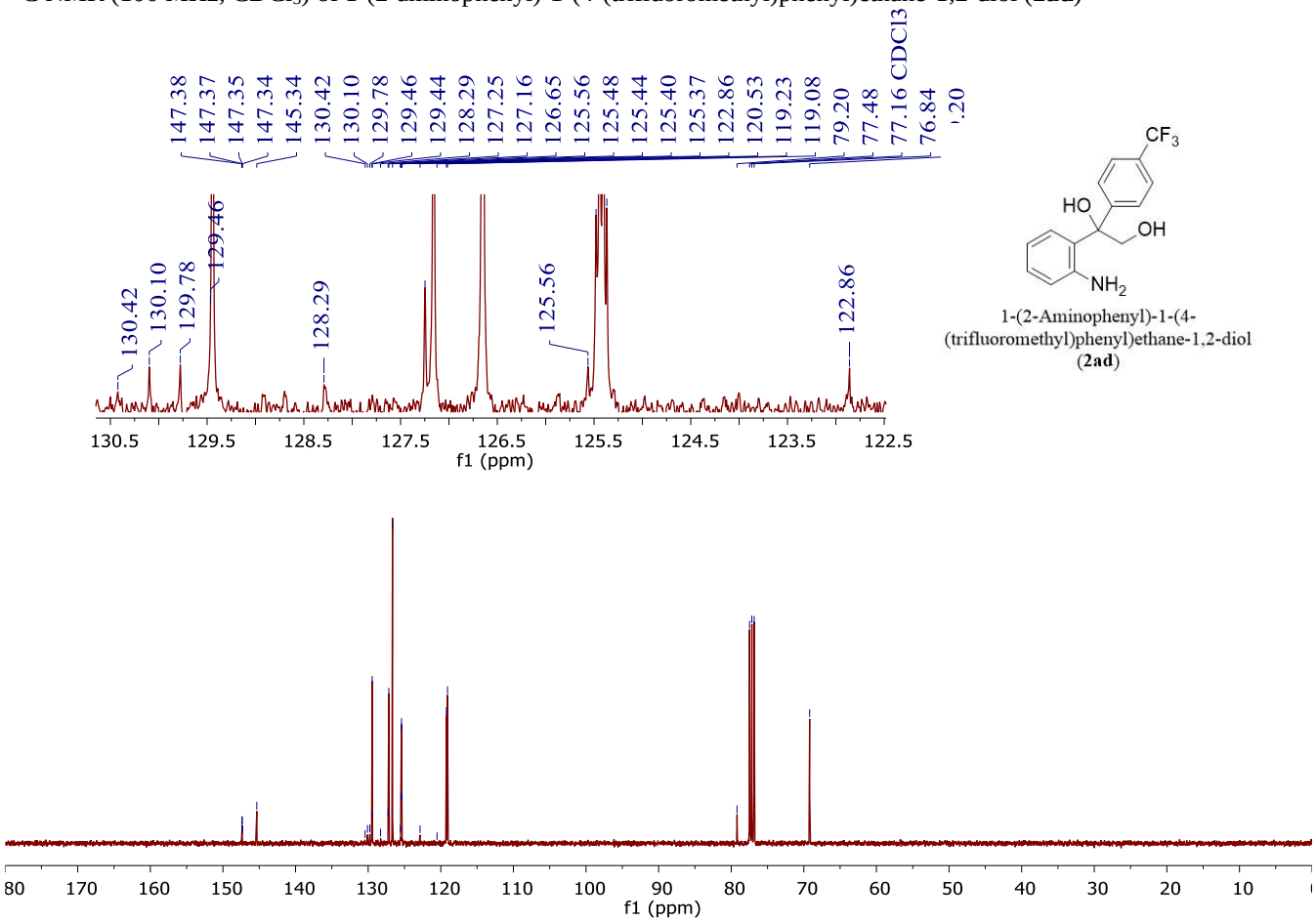
^{19}F NMR (376 MHz, $CDCl_3$) of 1-(2-aminophenyl)-1-(3-fluorophenyl)ethane-1,2-diol (**2ac**)



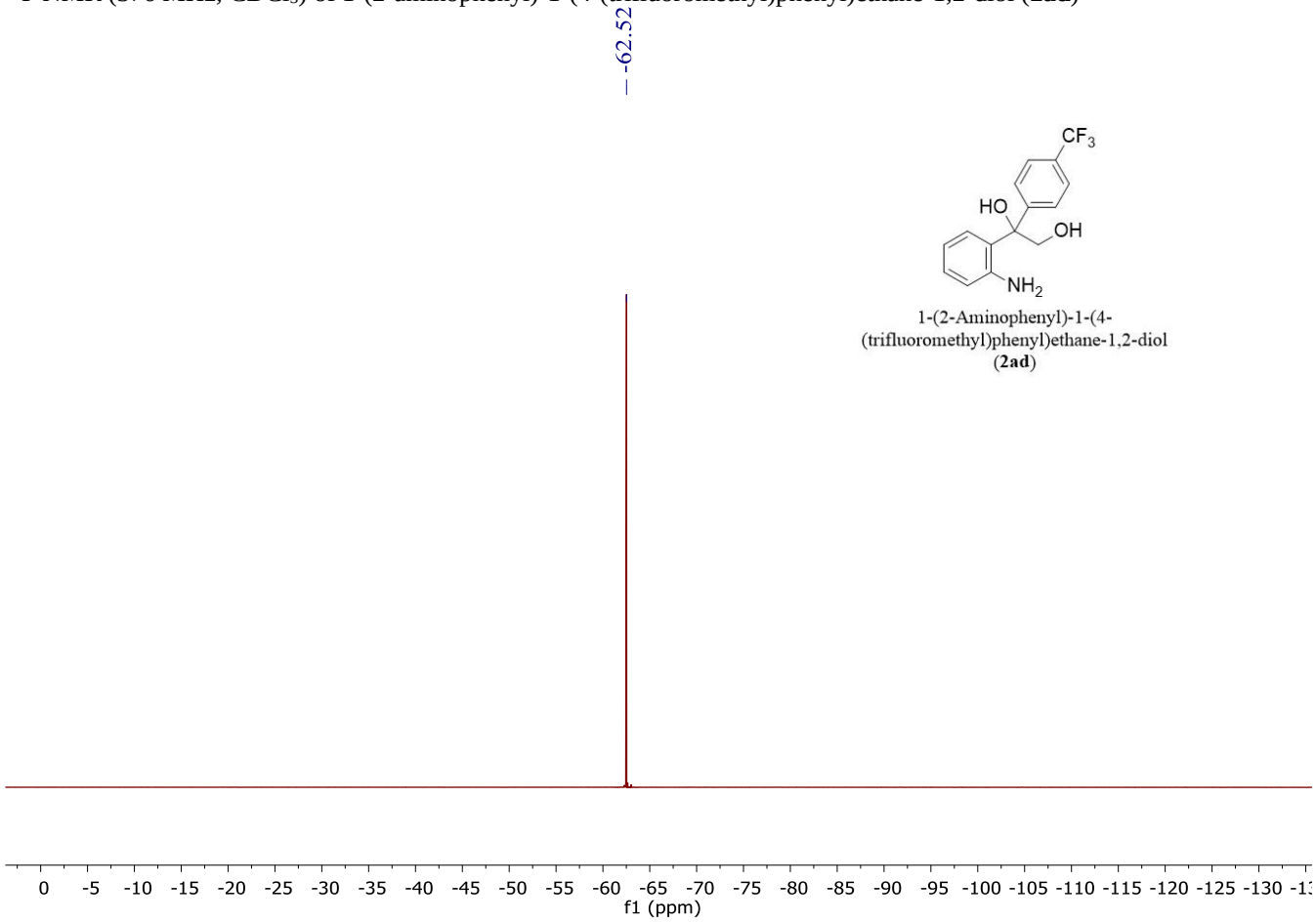
^{1}H NMR (400 MHz, $CDCl_3$) of 1-(2-aminophenyl)-1-(4-(trifluoromethyl)phenyl)ethane-1,2-diol (**2ad**)



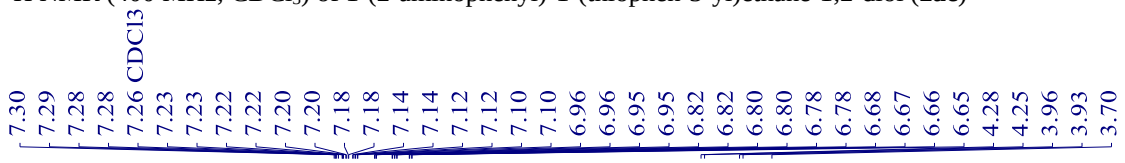
^{13}C NMR (100 MHz, $CDCl_3$) of 1-(2-aminophenyl)-1-(4-(trifluoromethyl)phenyl)ethane-1,2-diol (**2ad**)

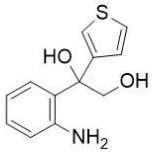


^{19}F NMR (376 MHz, $CDCl_3$) of 1-(2-aminophenyl)-1-(4-(trifluoromethyl)phenyl)ethane-1,2-diol (**2ad**)

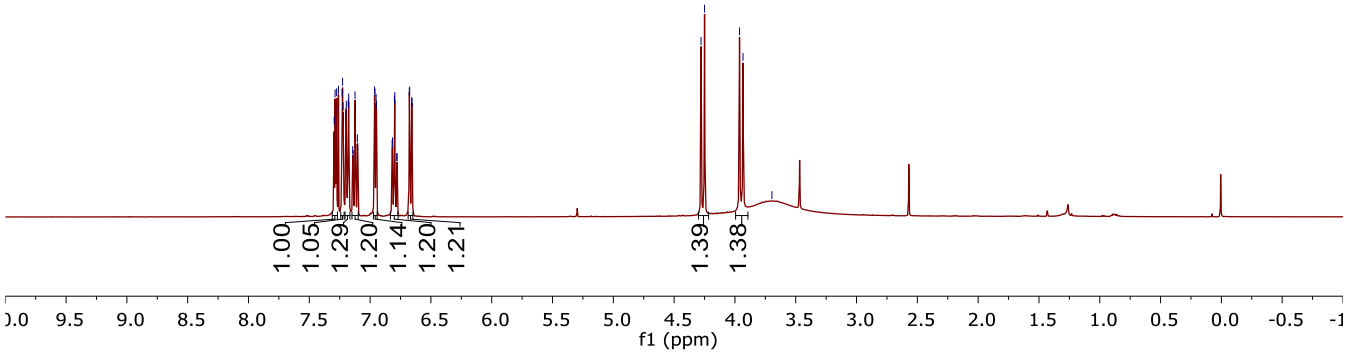


^{1}H NMR (400 MHz, $CDCl_3$) of 1-(2-aminophenyl)-1-(thiophen-3-yl)ethane-1,2-diol (**2ae**)

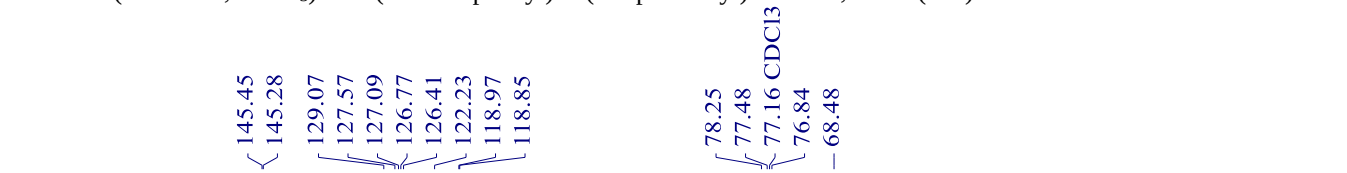


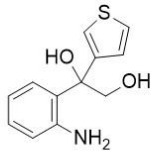


1-(2-Aminophenyl)-1-(thiophen-3-yl)ethane-1,2-diol (**2ae**)

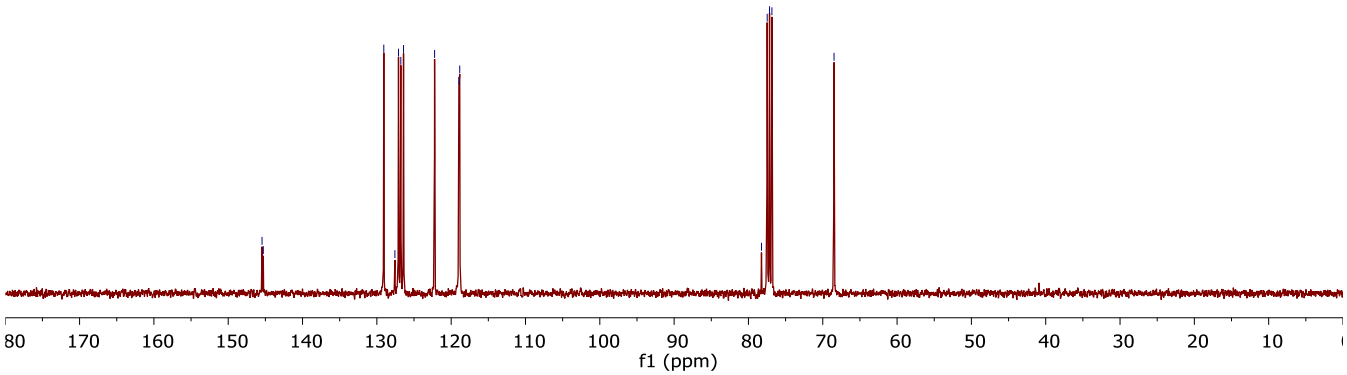


^{13}C NMR (100 MHz, $CDCl_3$) of 1-(2-aminophenyl)-1-(thiophen-3-yl)ethane-1,2-diol (**2ae**)

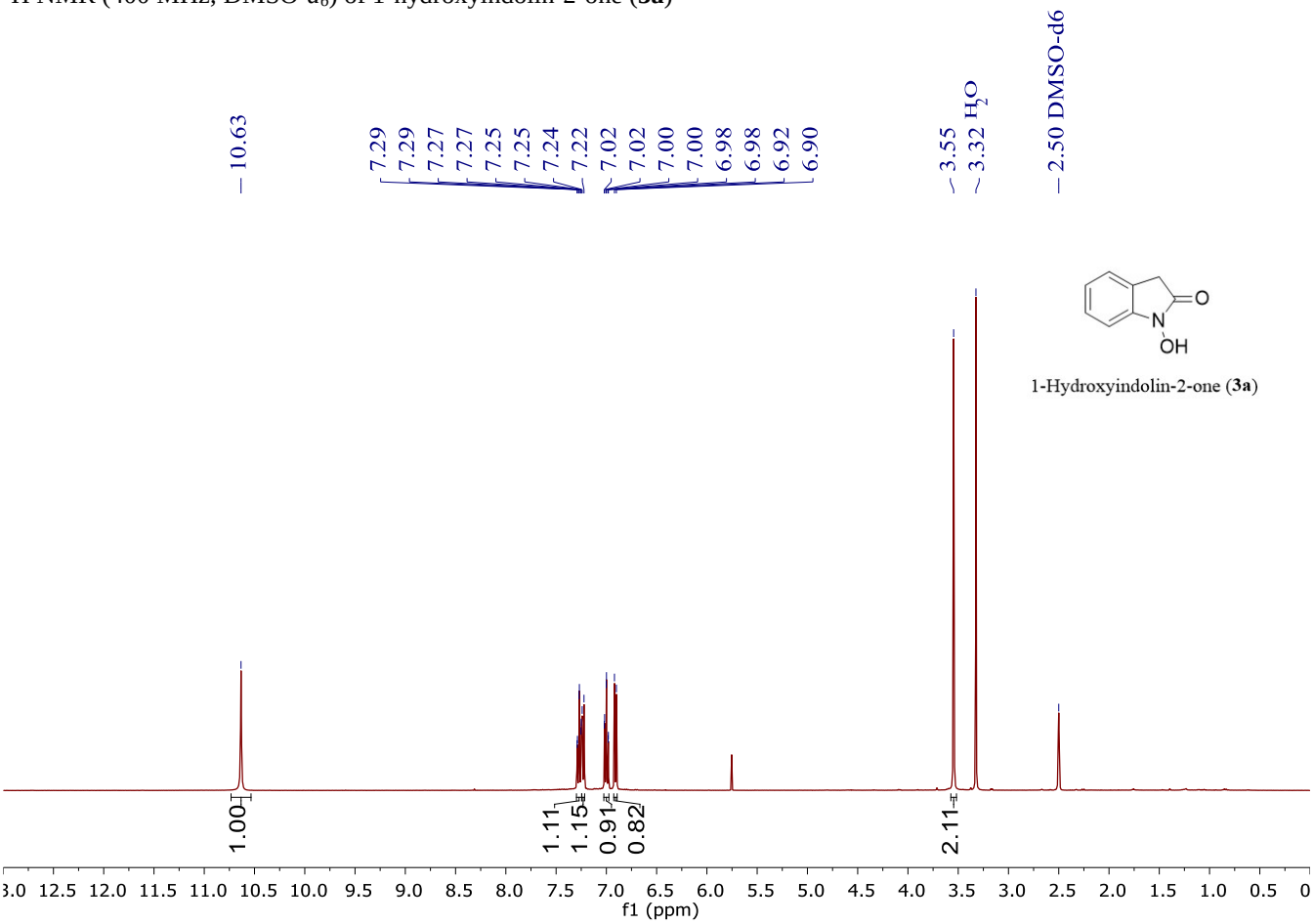




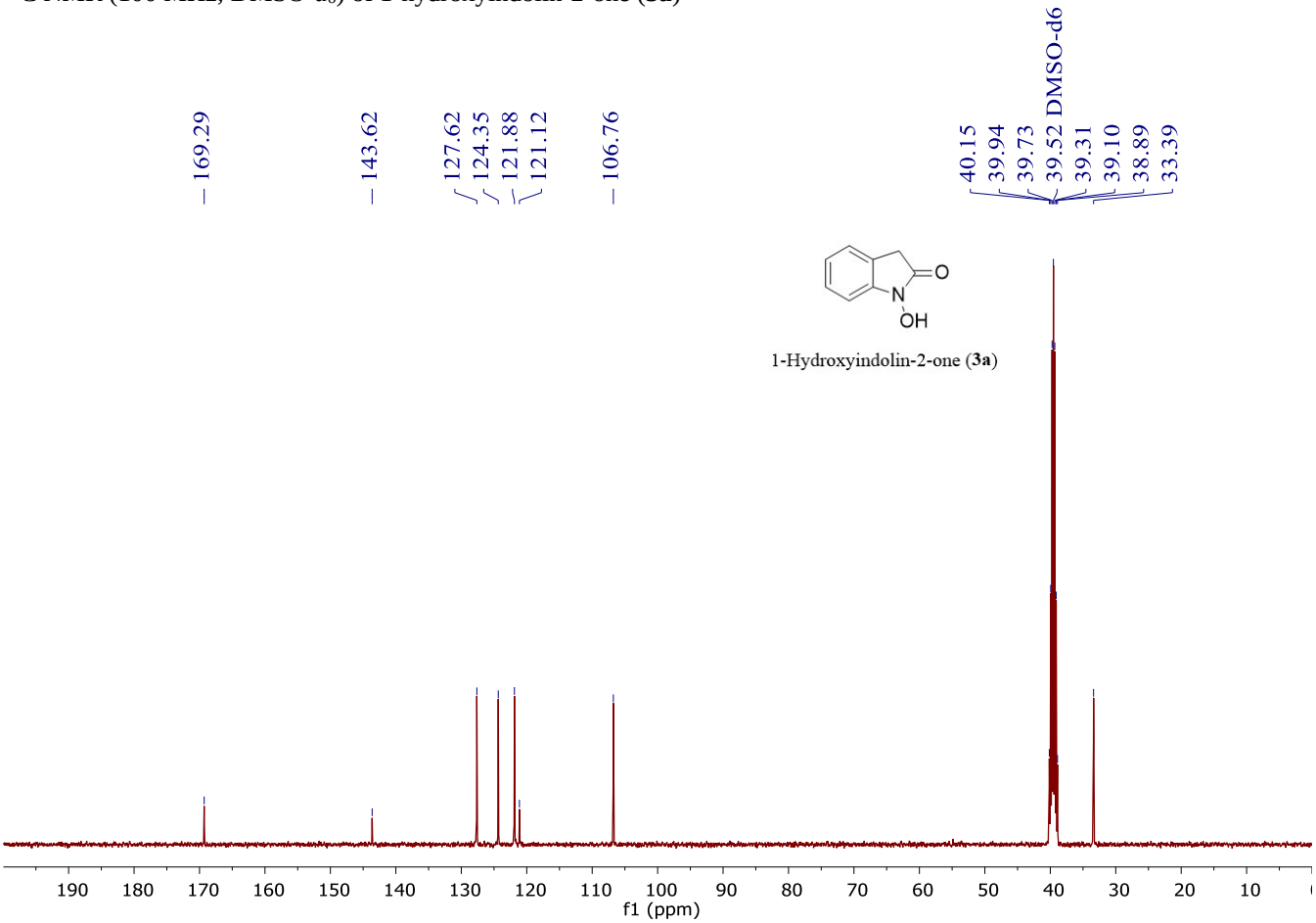
1-(2-Aminophenyl)-1-(thiophen-3-yl)ethane-1,2-diol (**2ae**)



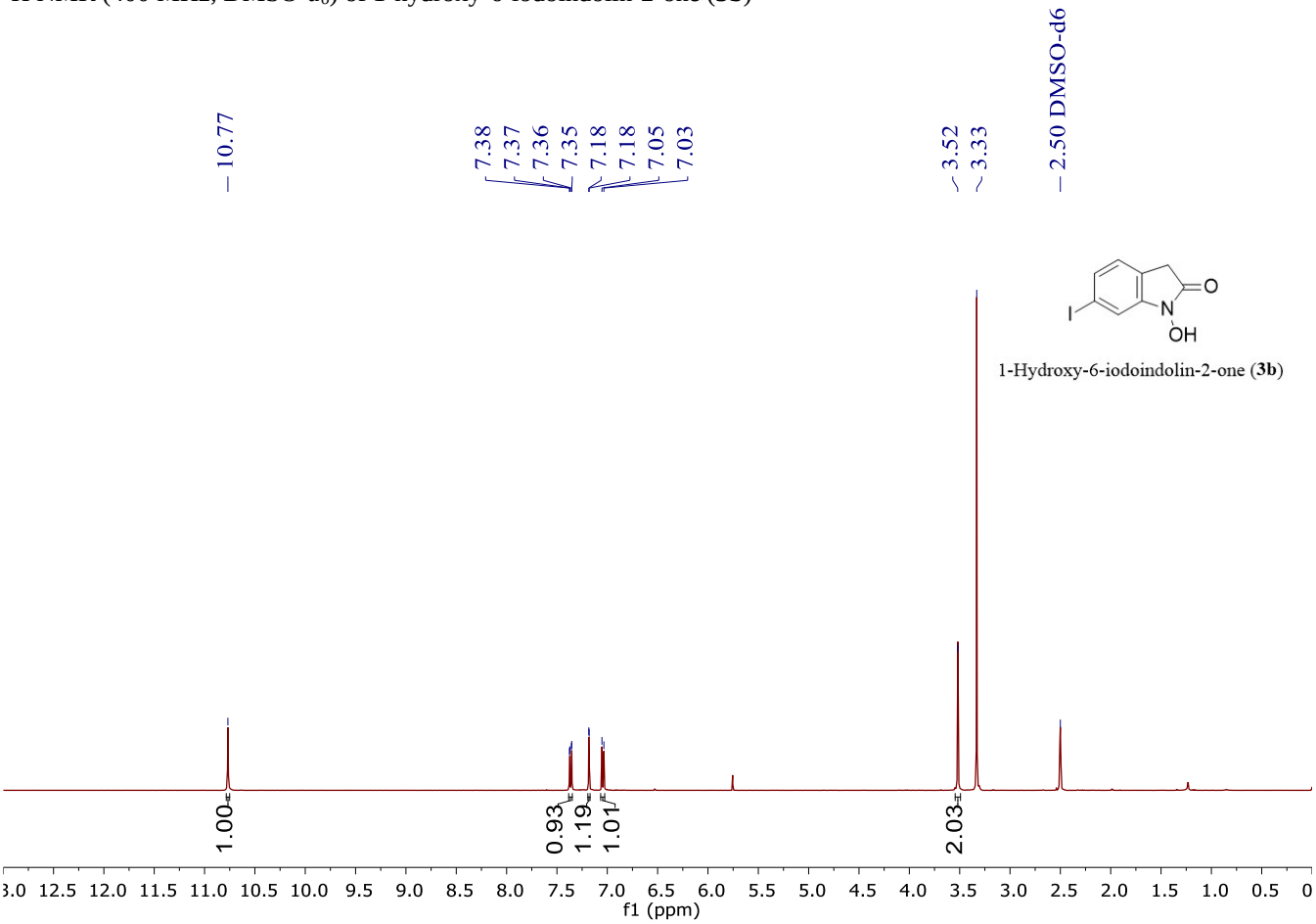
^{1}H NMR (400 MHz, DMSO-d_6) of 1-hydroxyindolin-2-one (**3a**)



^{13}C NMR (100 MHz, DMSO-d_6) of 1-hydroxyindolin-2-one (**3a**)

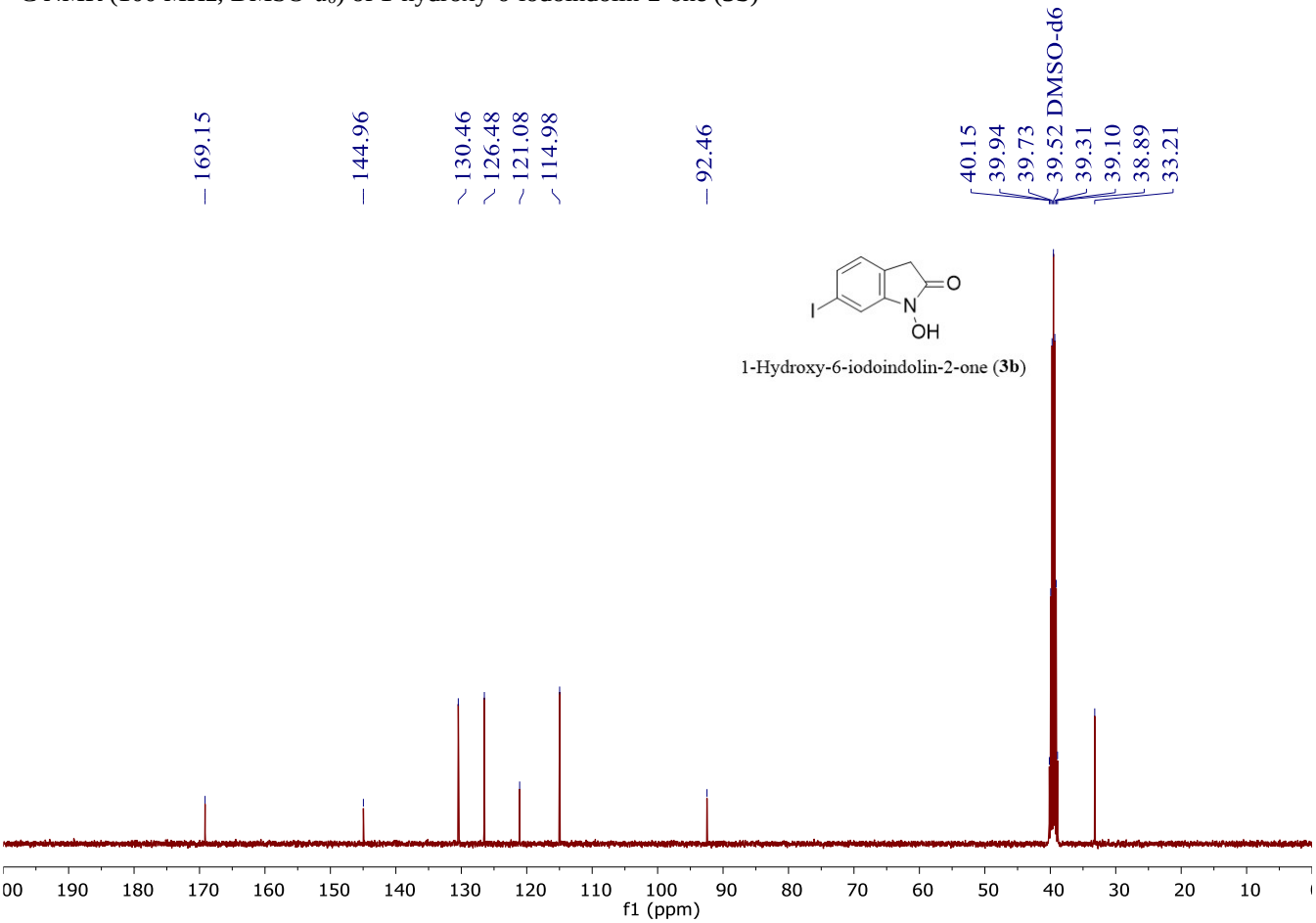


^{1}H NMR (400 MHz, DMSO-d_6) of 1-hydroxy-6-iodoindolin-2-one (**3b**)



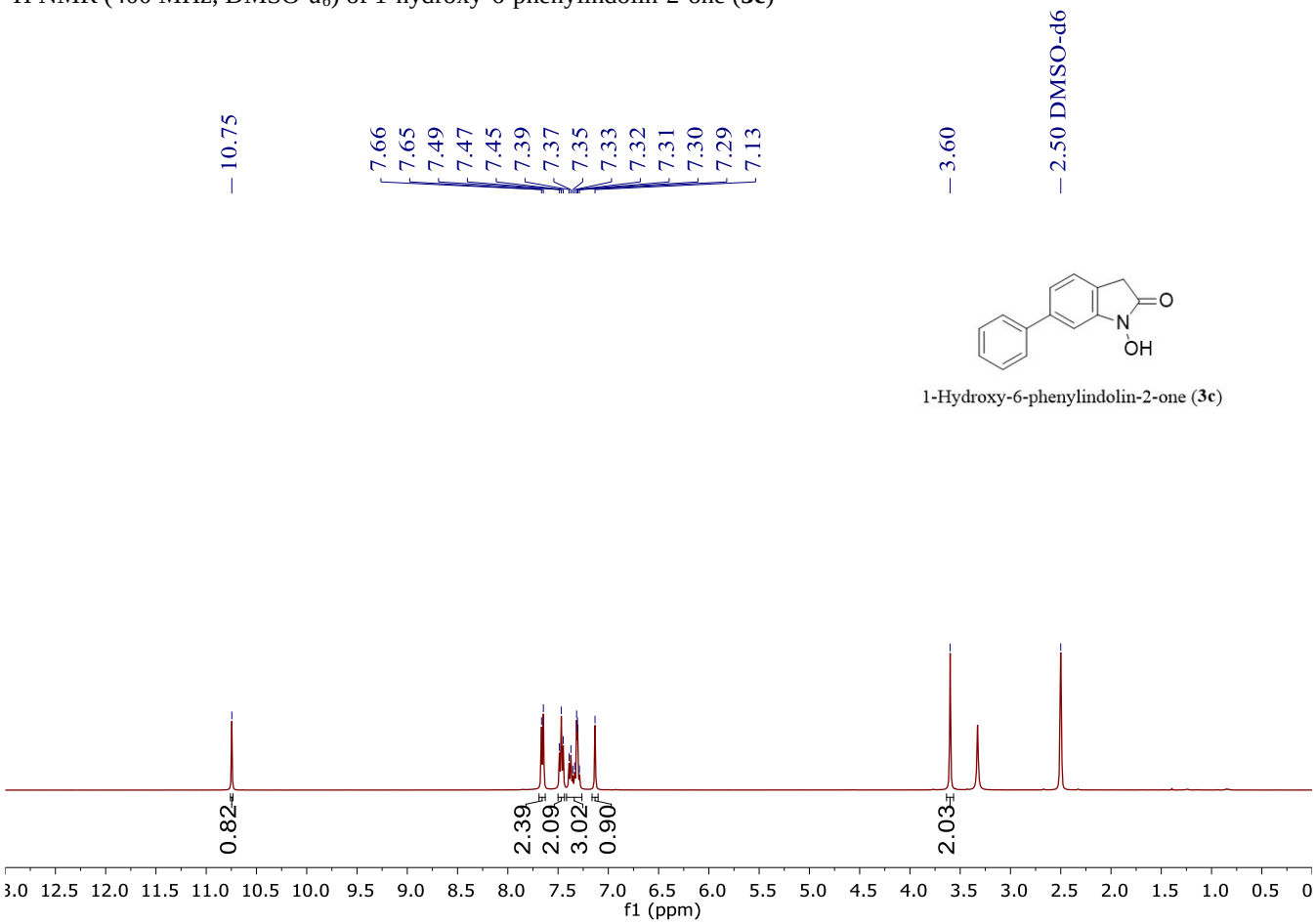
1-Hydroxy-6-iodoindolin-2-one (**3b**)

^{13}C NMR (100 MHz, DMSO-d_6) of 1-hydroxy-6-iodoindolin-2-one (**3b**)

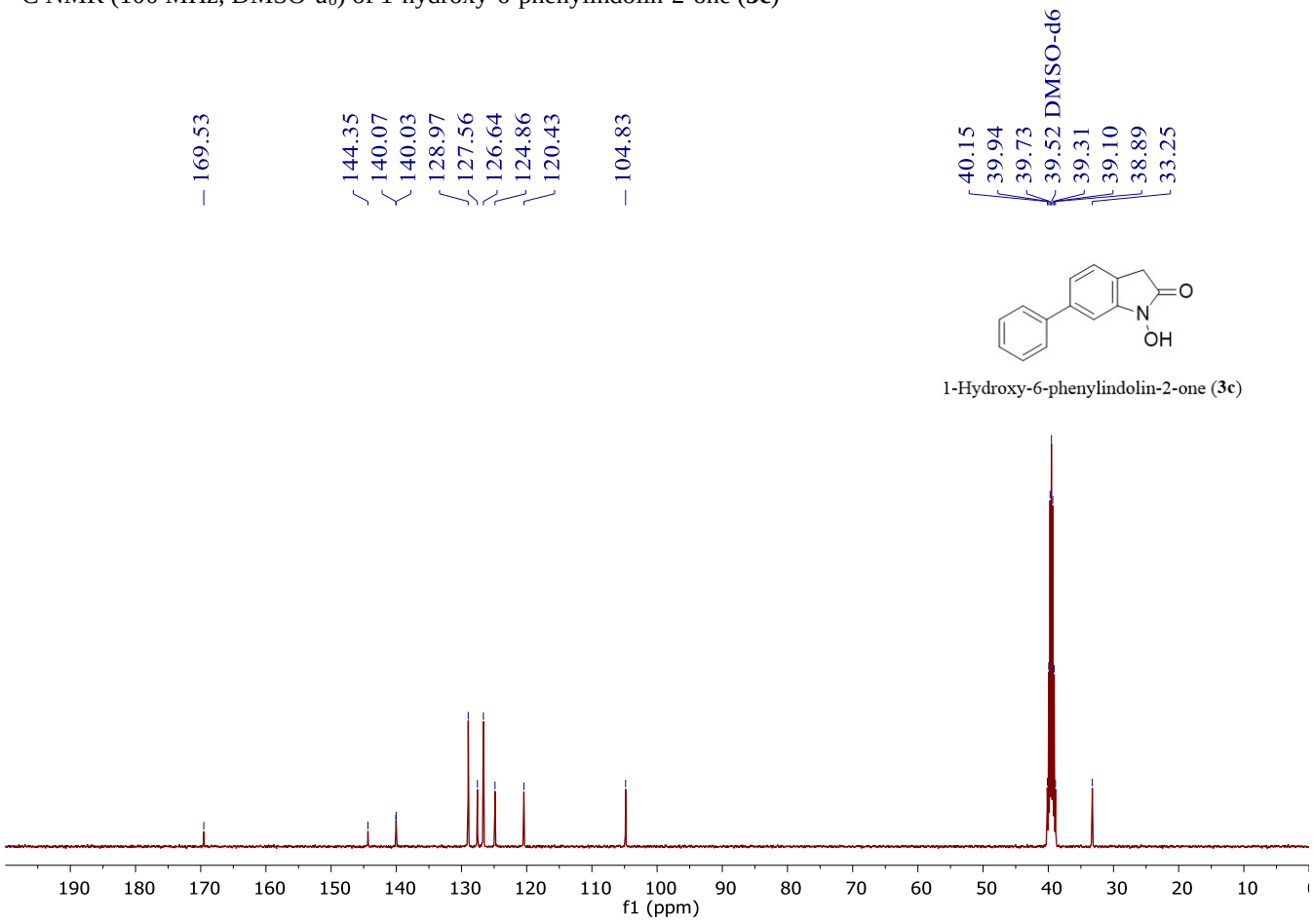


1-Hydroxy-6-iodoindolin-2-one (**3b**)

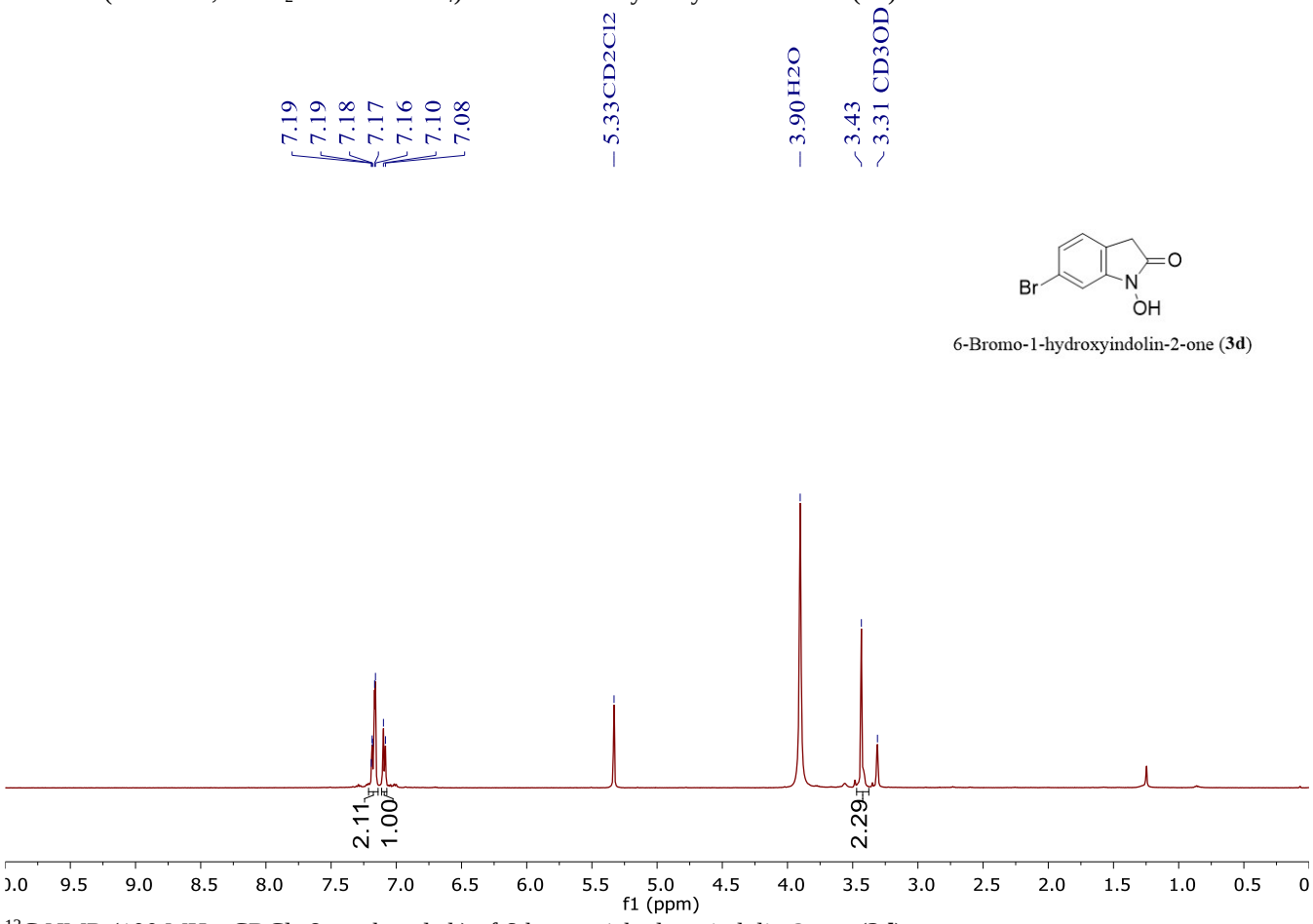
^{1}H NMR (400 MHz, DMSO-d_6) of 1-hydroxy-6-phenylindolin-2-one (**3c**)



^{13}C NMR (100 MHz, DMSO-d_6) of 1-hydroxy-6-phenylindolin-2-one (**3c**)

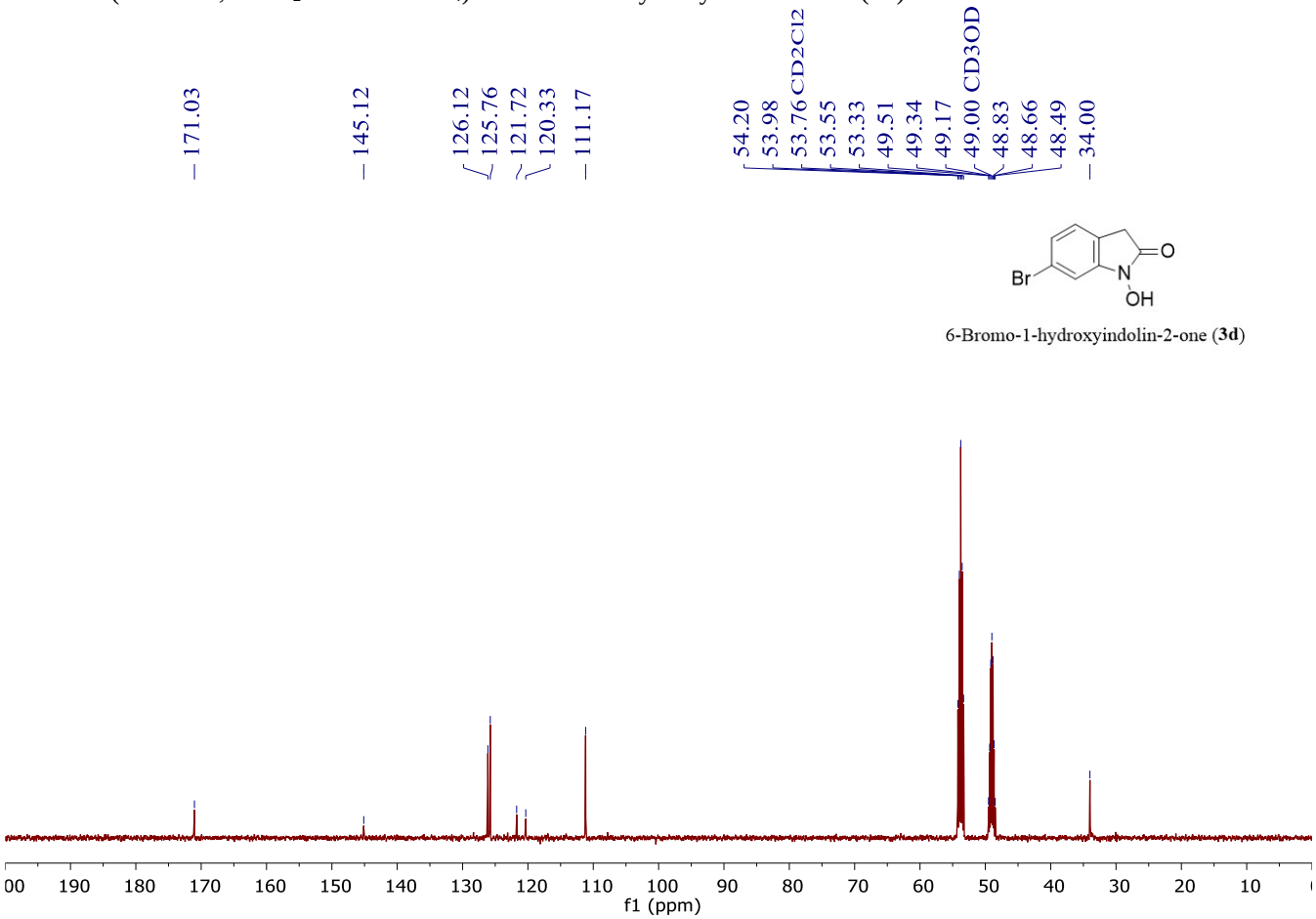


^{1}H NMR (400 MHz, $CDCl_2$ & methanol-d_4) of 6-bromo-1-hydroxyindolin-2-one (**3d**)



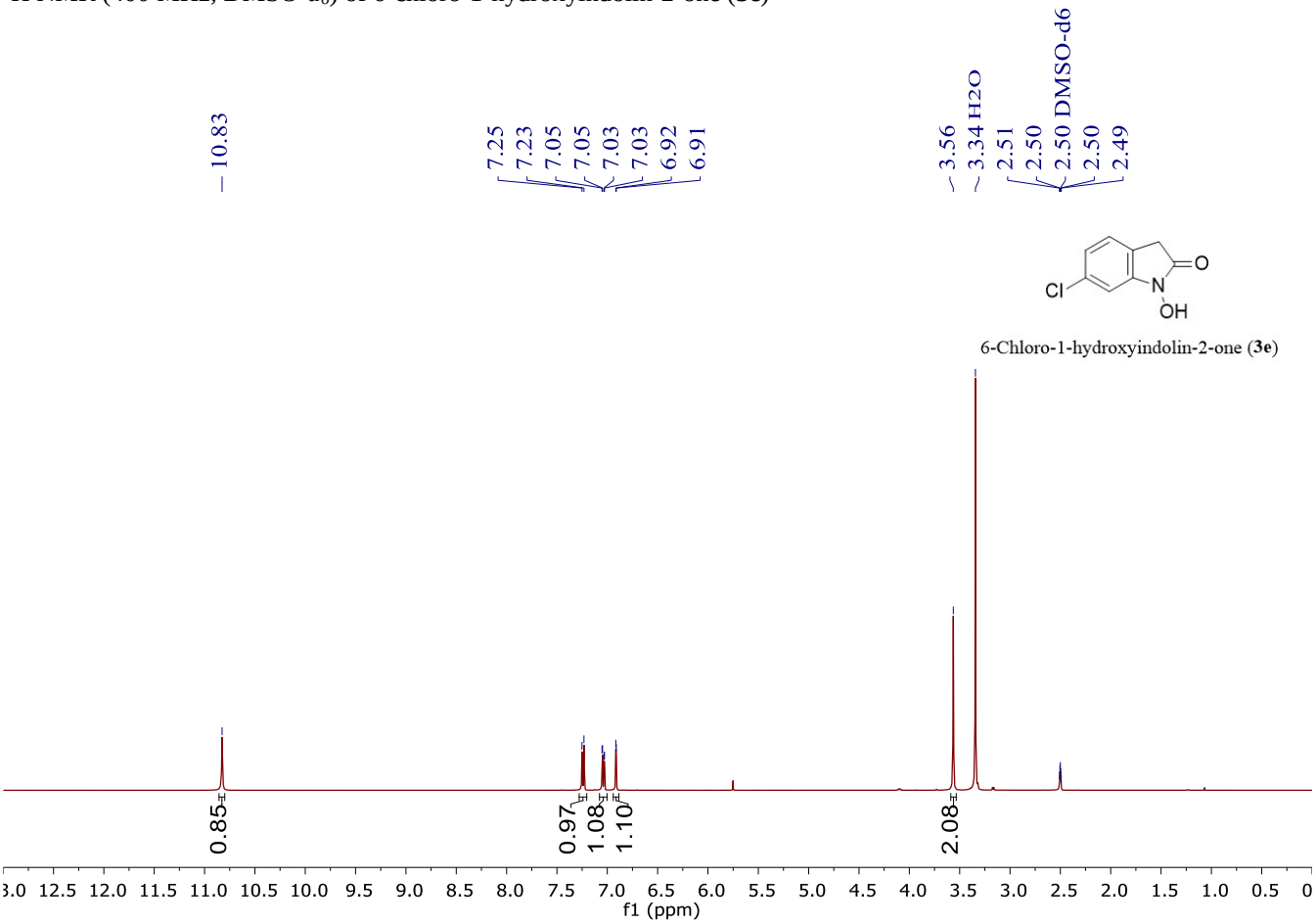
6-Bromo-1-hydroxyindolin-2-one (**3d**)

^{13}C NMR (100 MHz, $CDCl_2$ & methanol-d_4) of 6-bromo-1-hydroxyindolin-2-one (**3d**)



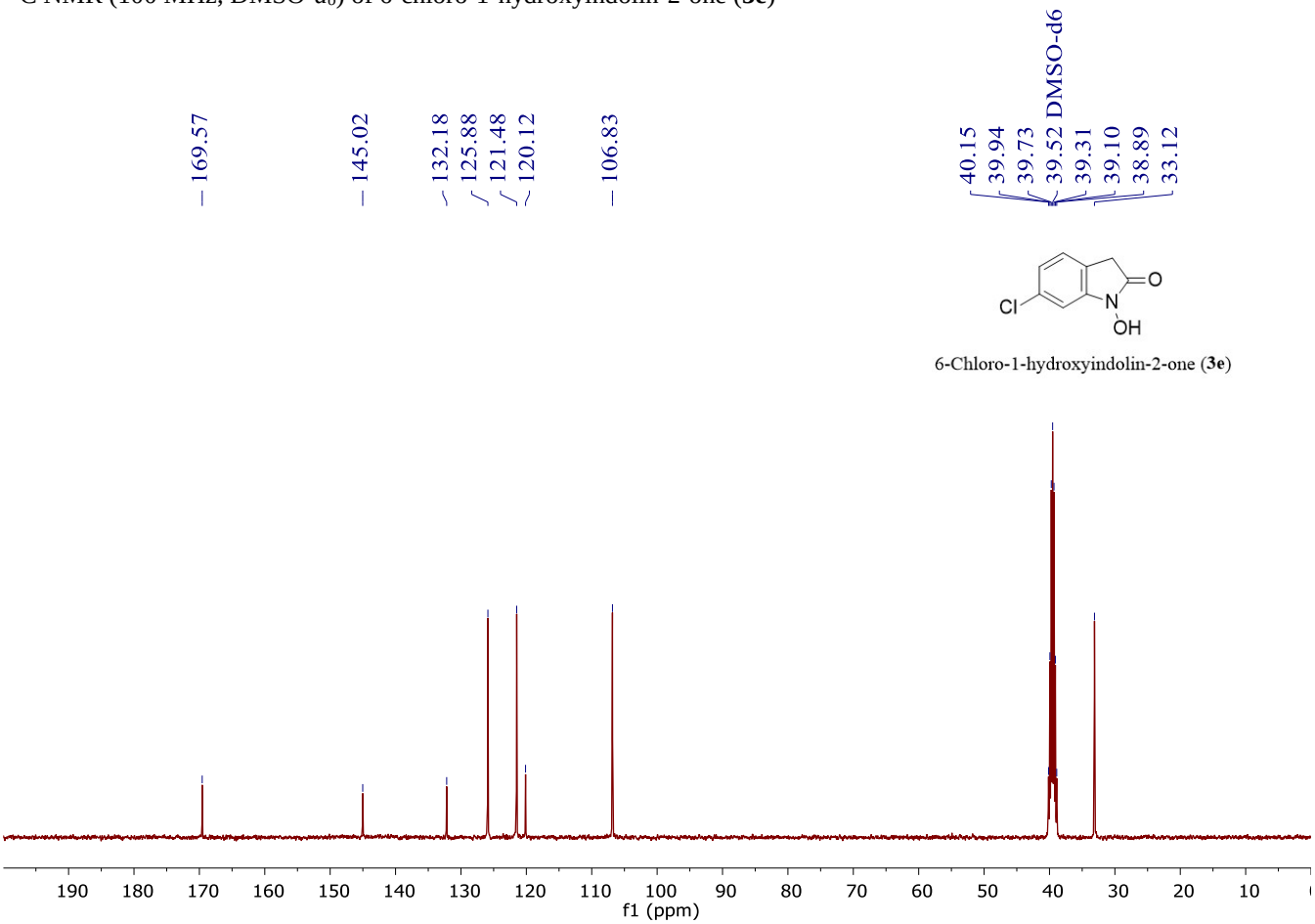
6-Bromo-1-hydroxyindolin-2-one (**3d**)

^{1}H NMR (400 MHz, DMSO-d_6) of 6-chloro-1-hydroxyindolin-2-one (**3e**)



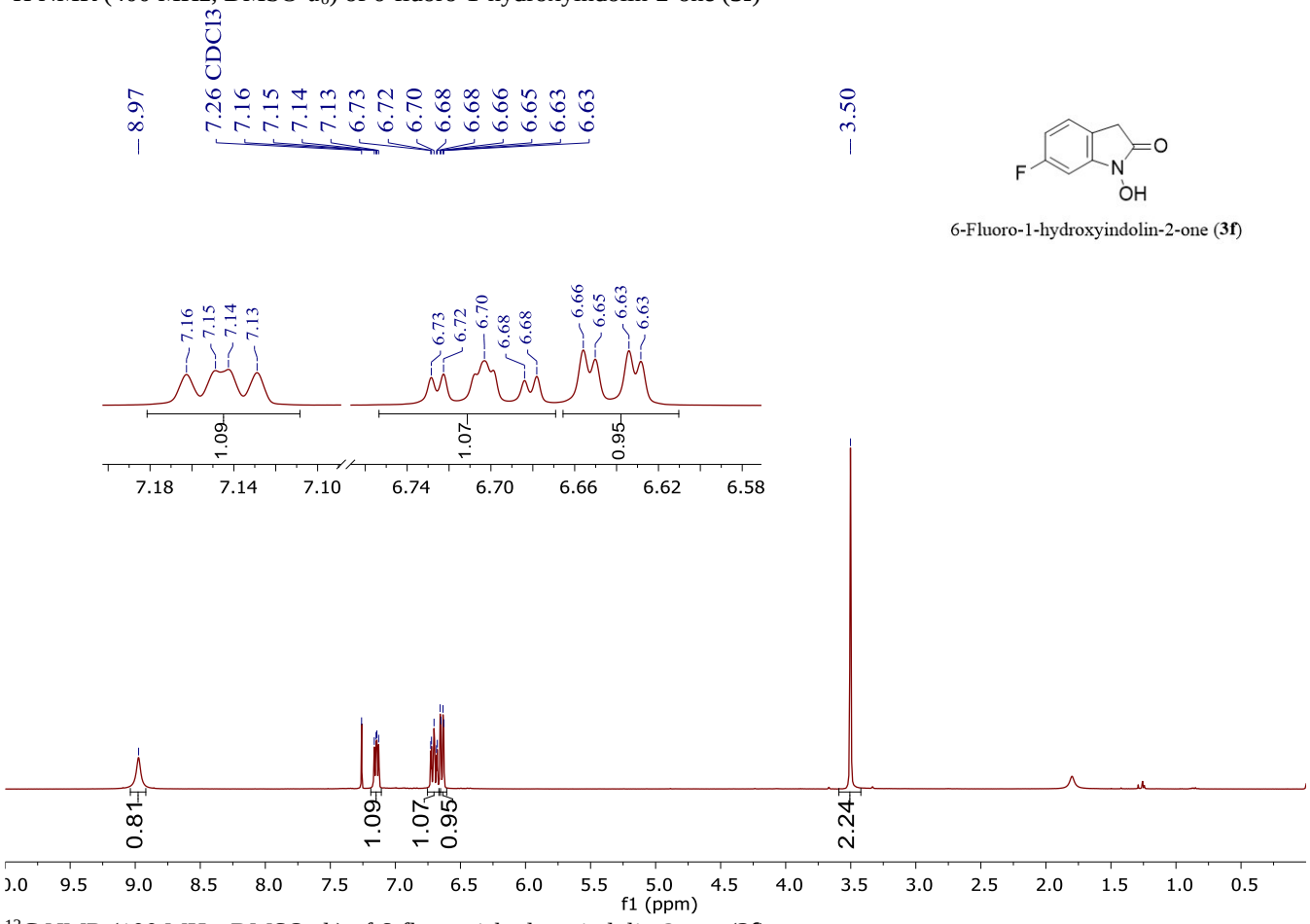
6-Chloro-1-hydroxyindolin-2-one (**3e**)

^{13}C NMR (100 MHz, DMSO-d_6) of 6-chloro-1-hydroxyindolin-2-one (**3e**)



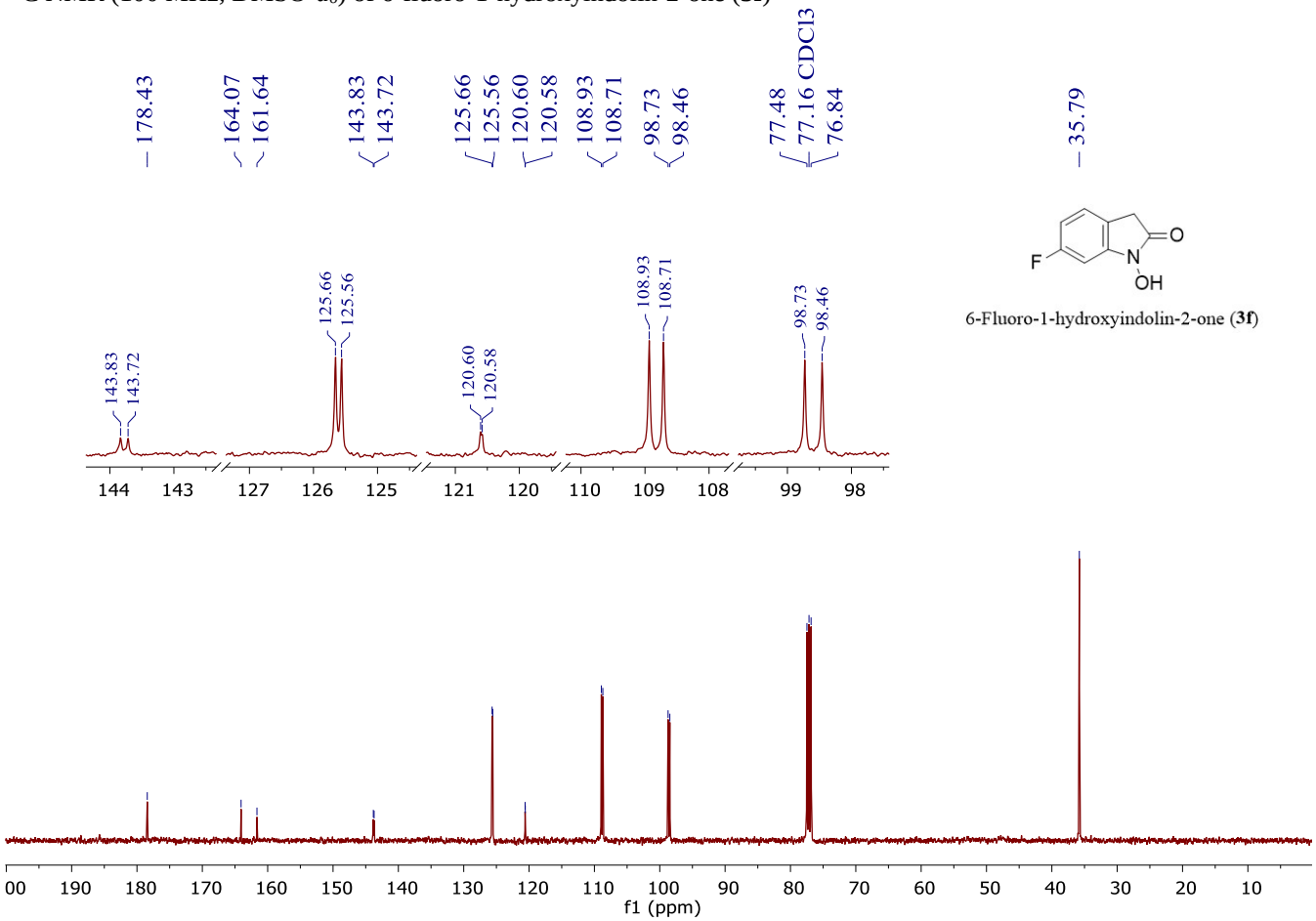
6-Chloro-1-hydroxyindolin-2-one (**3e**)

^{1}H NMR (400 MHz, DMSO-d_6) of 6-fluoro-1-hydroxyindolin-2-one (**3f**)



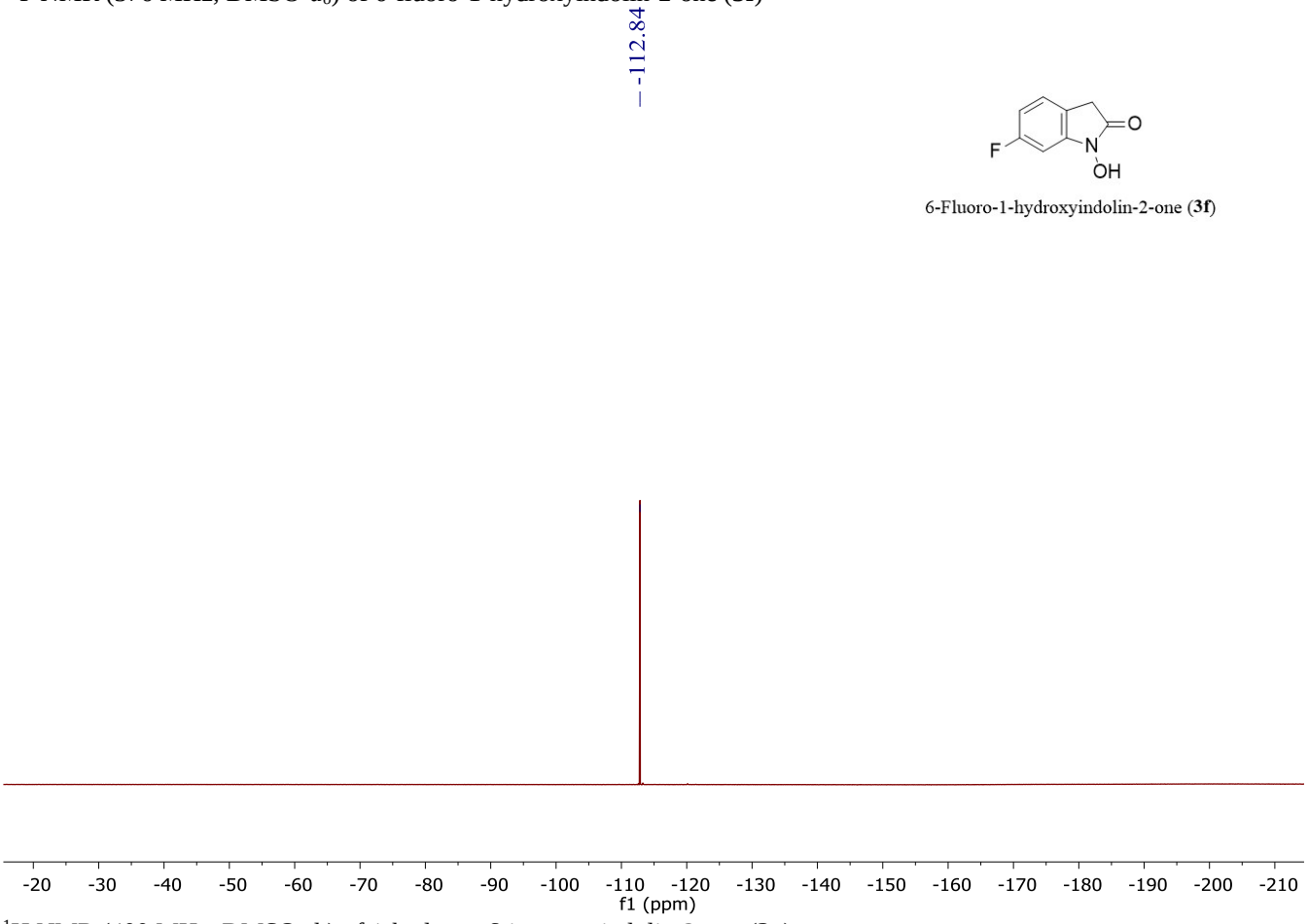
6-Fluoro-1-hydroxyindolin-2-one (**3f**)

^{13}C NMR (100 MHz, DMSO-d_6) of 6-fluoro-1-hydroxyindolin-2-one (**3f**)

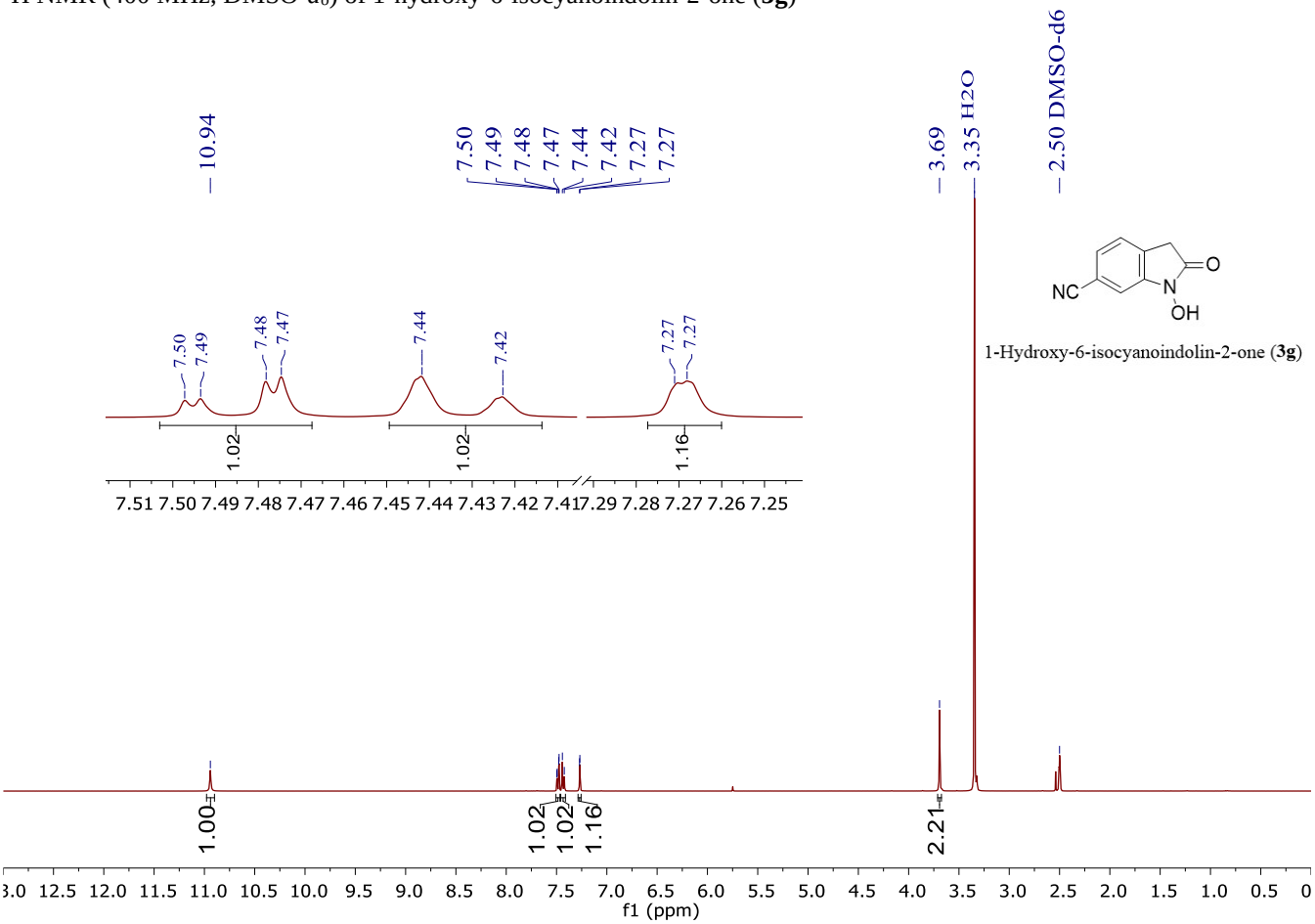


6-Fluoro-1-hydroxyindolin-2-one (**3f**)

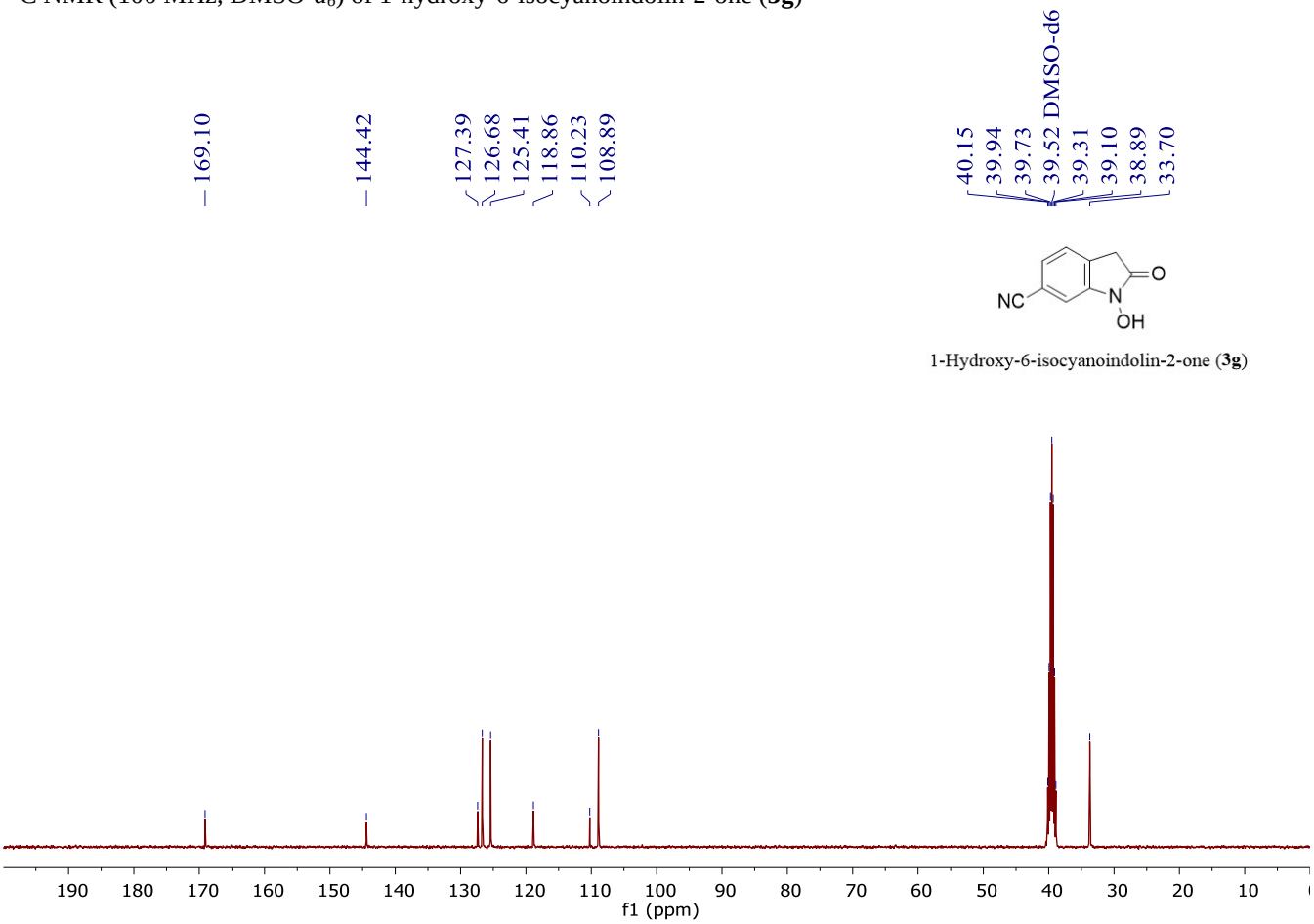
^{19}F NMR (376 MHz, DMSO-d_6) of 6-fluoro-1-hydroxyindolin-2-one (**3f**)



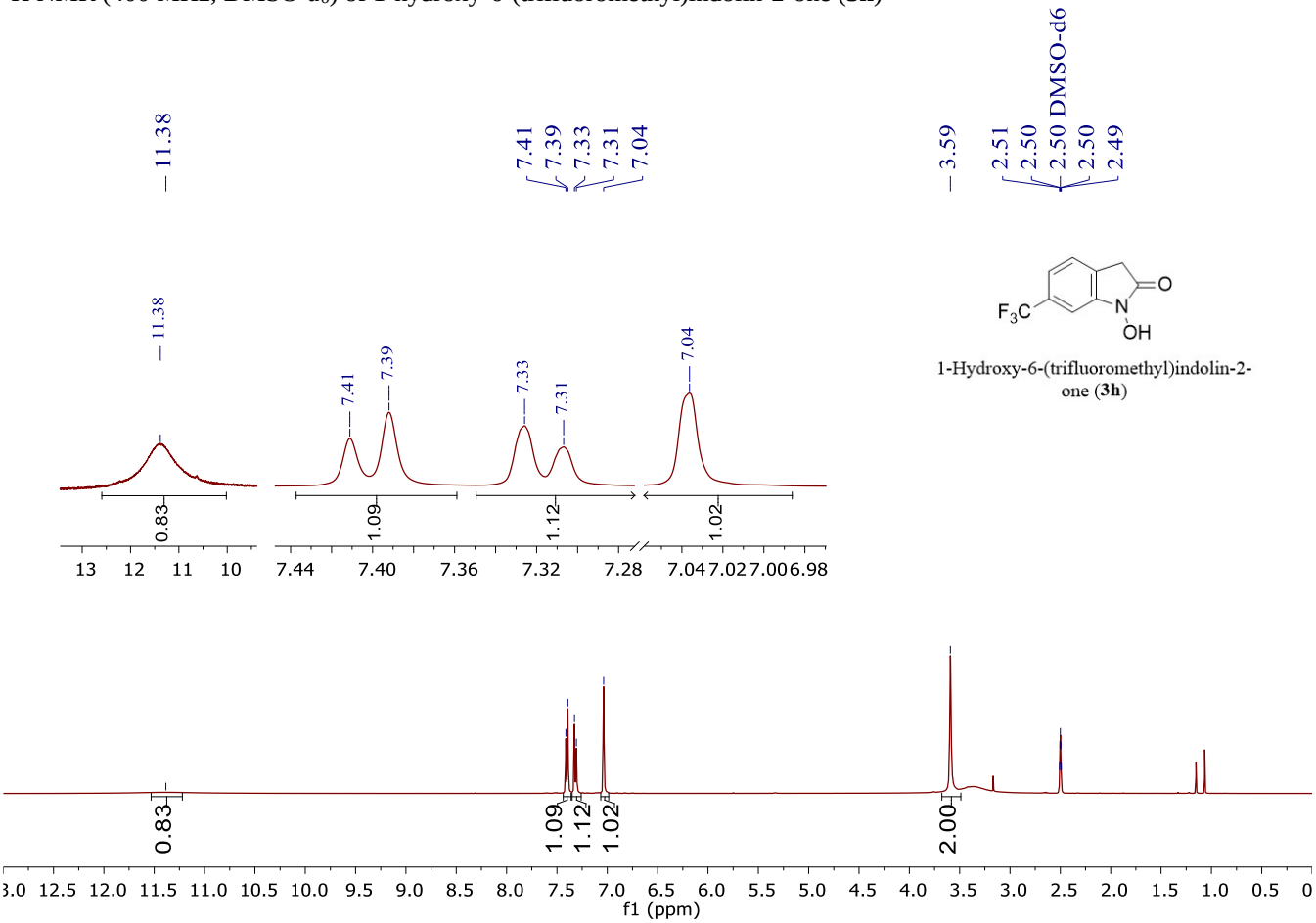
^{1}H NMR (400 MHz, DMSO-d_6) of 1-hydroxy-6-isocyanoindolin-2-one (**3g**)



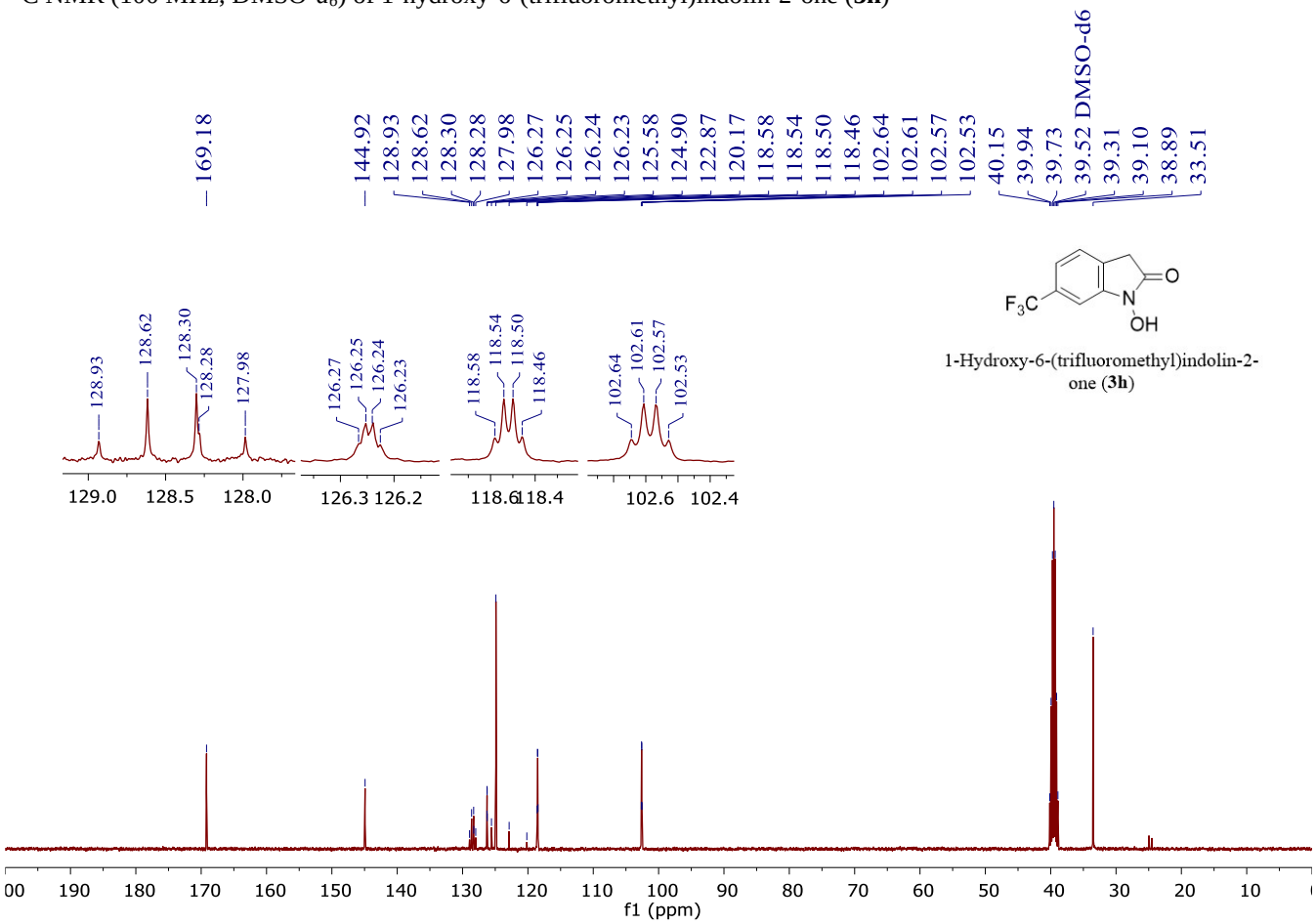
^{13}C NMR (100 MHz, DMSO-d_6) of 1-hydroxy-6-isocyanoindolin-2-one (**3g**)



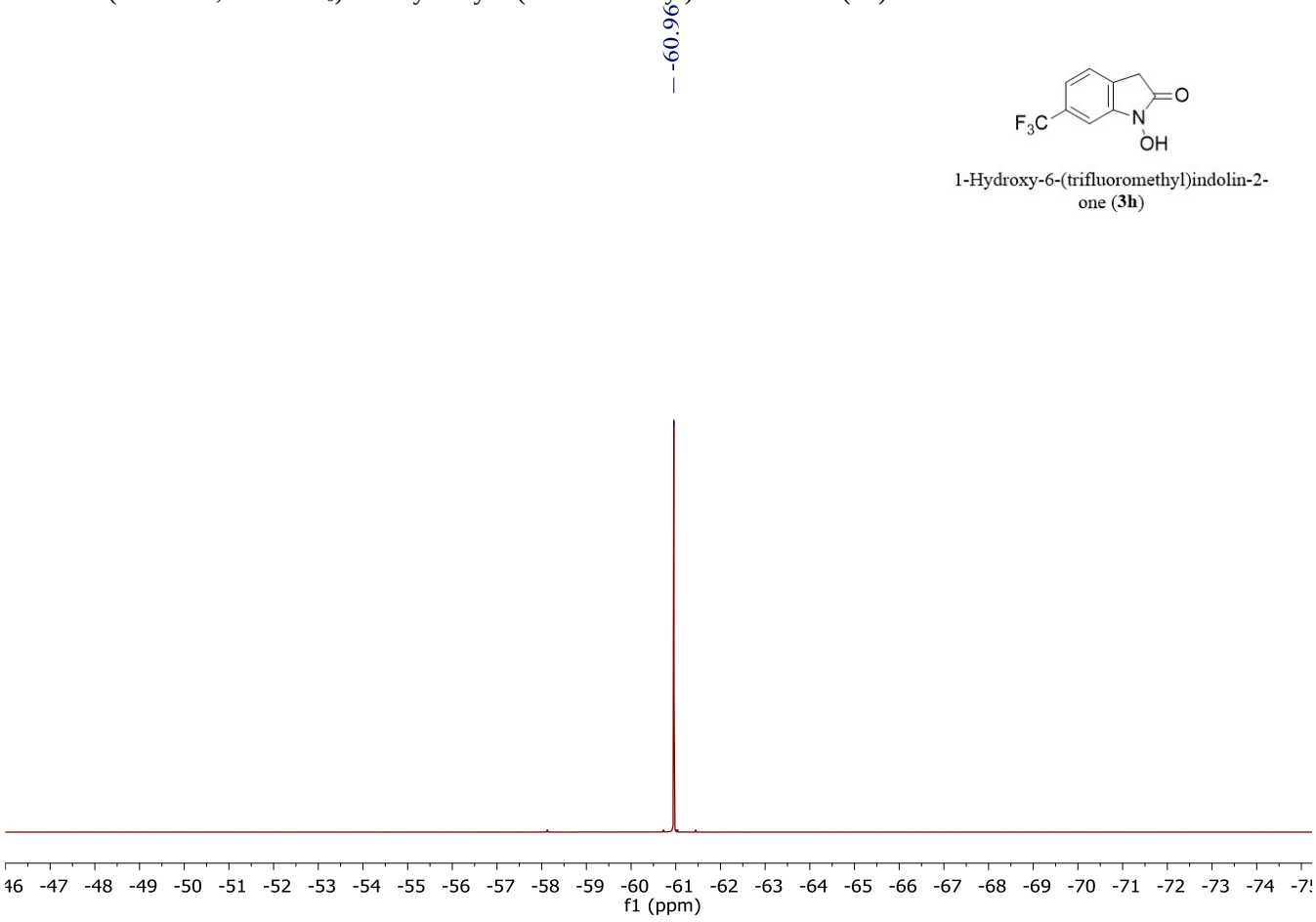
^{1}H NMR (400 MHz, DMSO-d_6) of 1-hydroxy-6-(trifluoromethyl)indolin-2-one (**3h**)



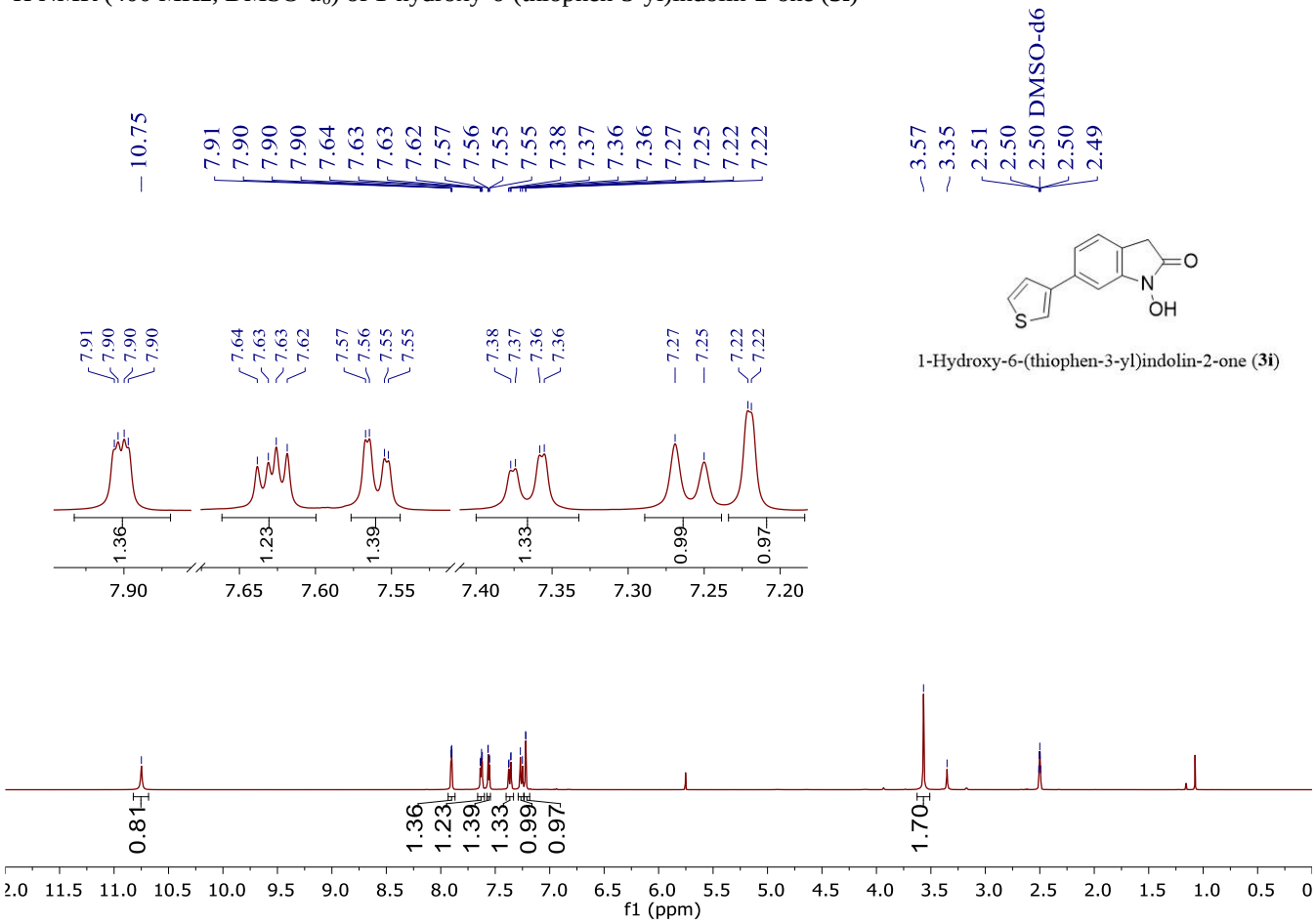
^{13}C NMR (100 MHz, DMSO-d_6) of 1-hydroxy-6-(trifluoromethyl)indolin-2-one (**3h**)



^{19}F NMR (376 MHz, DMSO-d_6) of 1-hydroxy-6-(trifluoromethyl)indolin-2-one (**3h**)

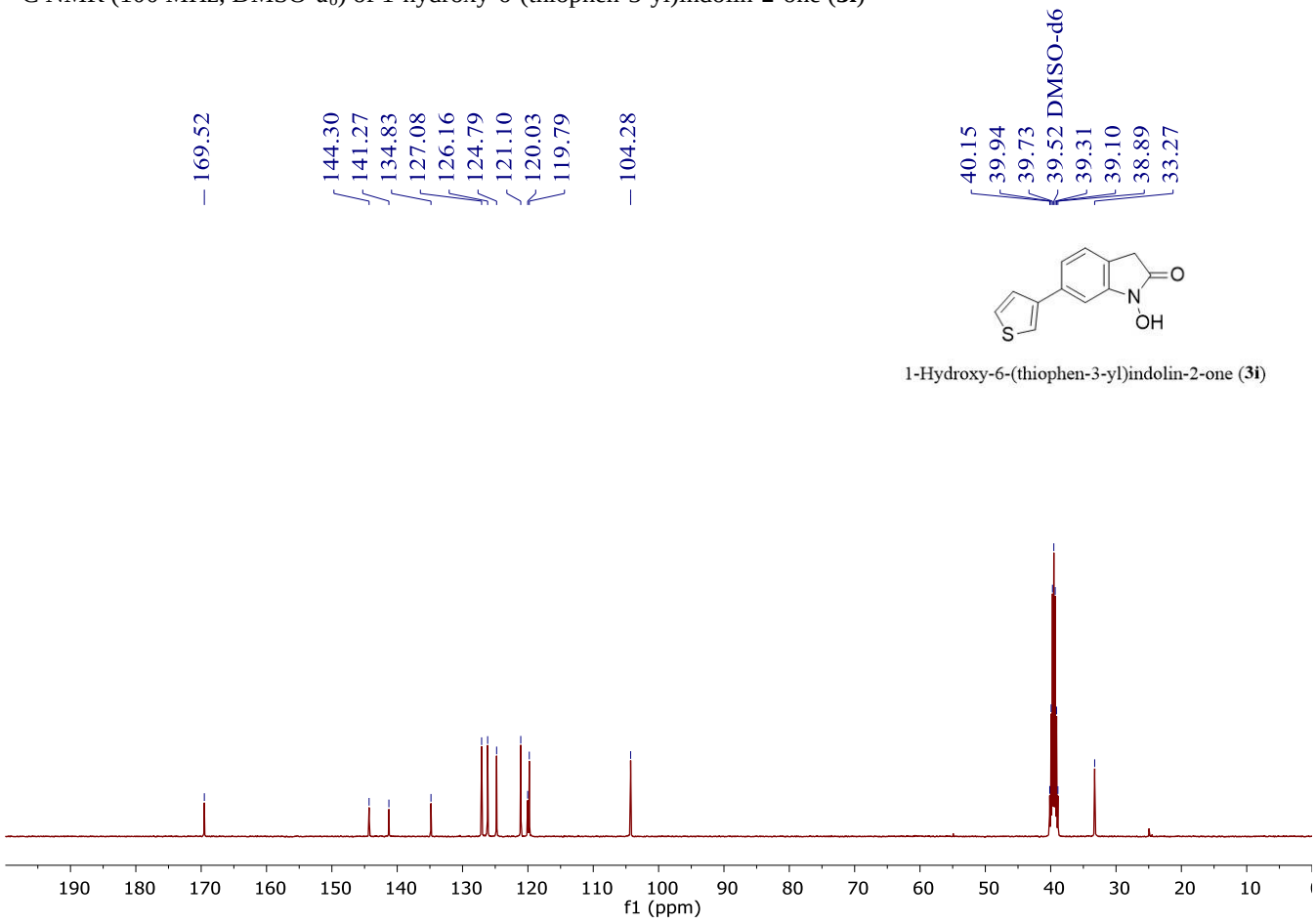


^{1}H NMR (400 MHz, DMSO-d_6) of 1-hydroxy-6-(thiophen-3-yl)indolin-2-one (**3i**)



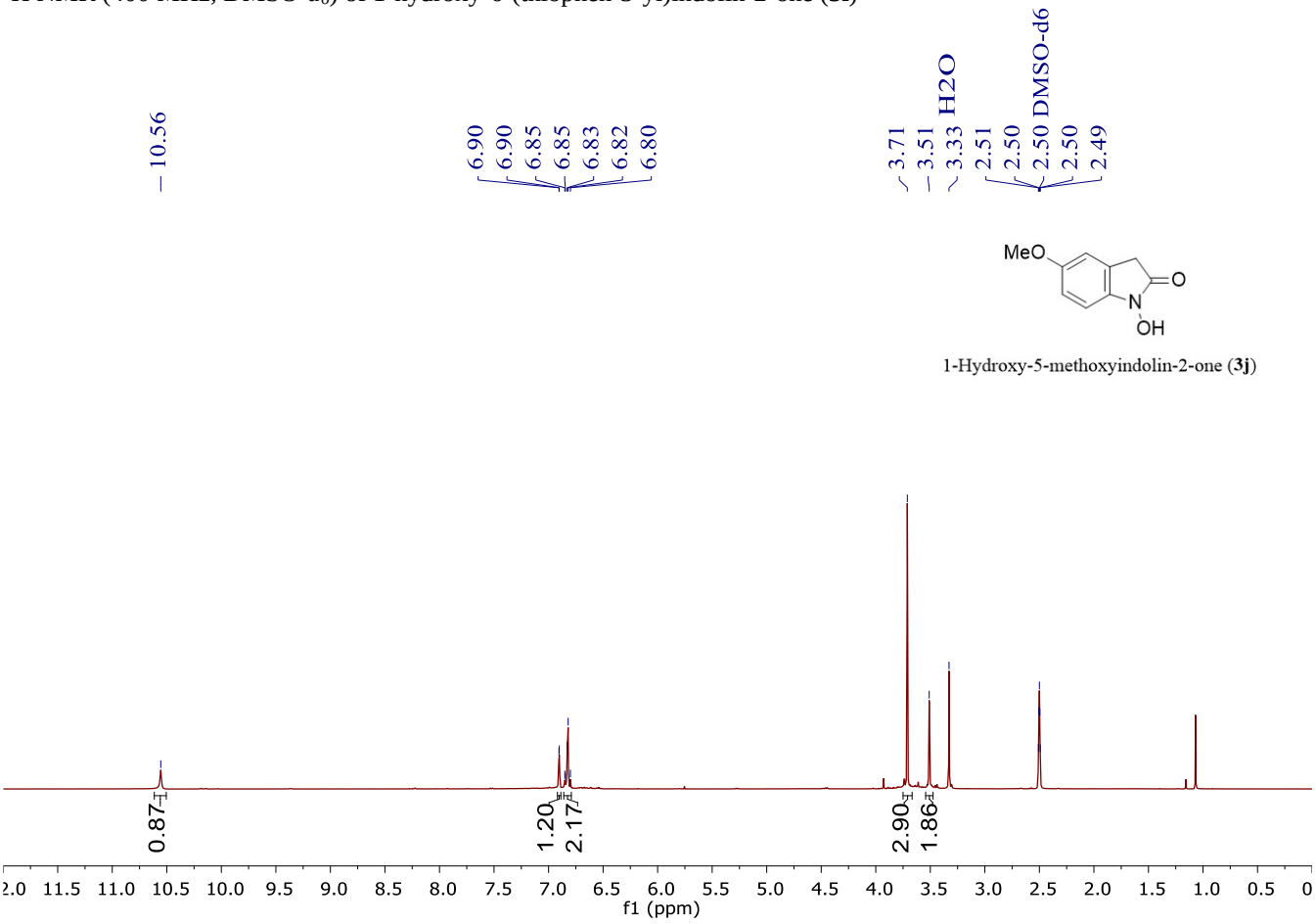
1-Hydroxy-6-(thiophen-3-yl)indolin-2-one (**3i**)

^{13}C NMR (100 MHz, DMSO-d_6) of 1-hydroxy-6-(thiophen-3-yl)indolin-2-one (**3i**)

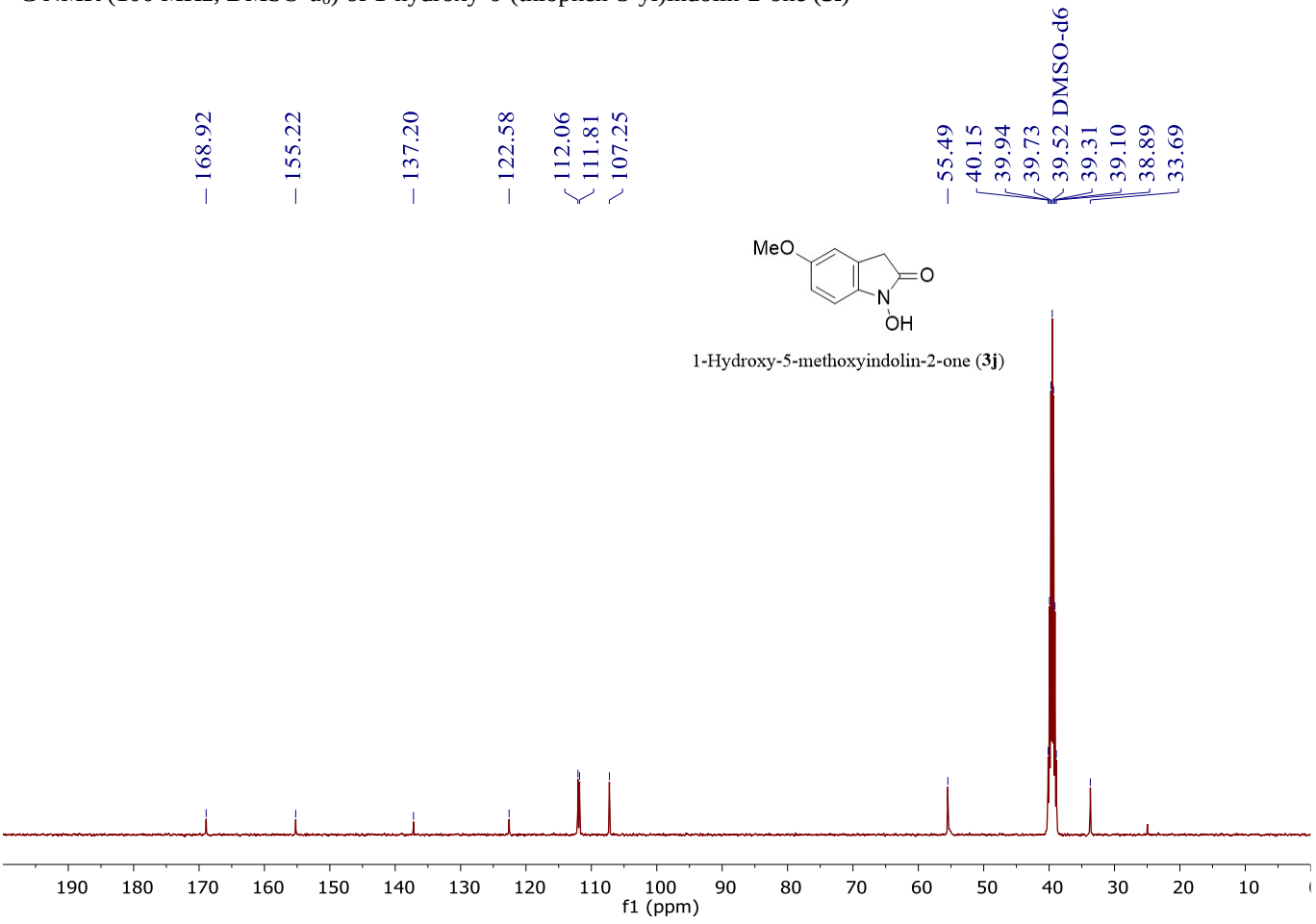


1-Hydroxy-6-(thiophen-3-yl)indolin-2-one (**3i**)

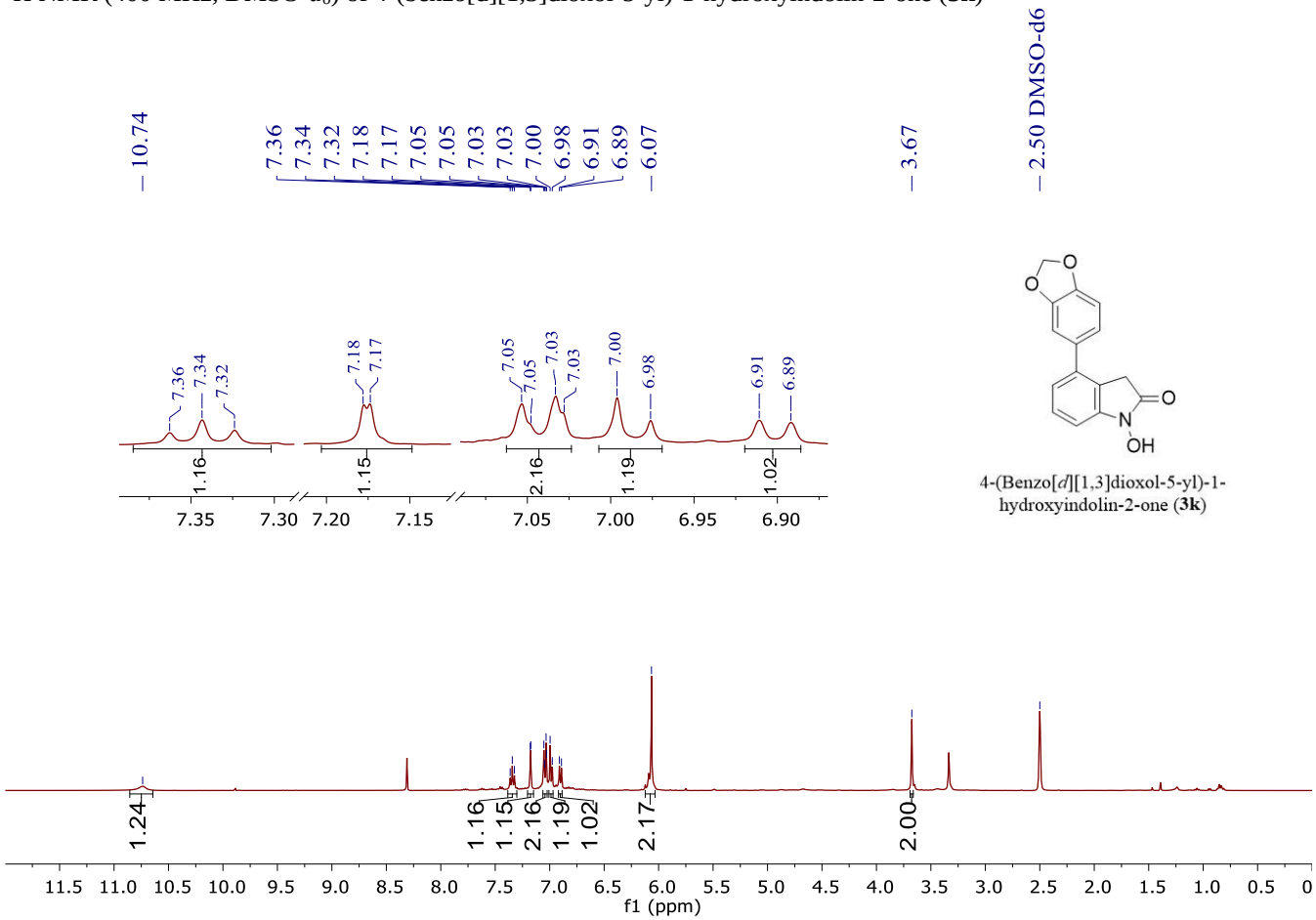
^{1}H NMR (400 MHz, DMSO-d_6) of 1-hydroxy-6-(thiophen-3-yl)indolin-2-one (**3i**)



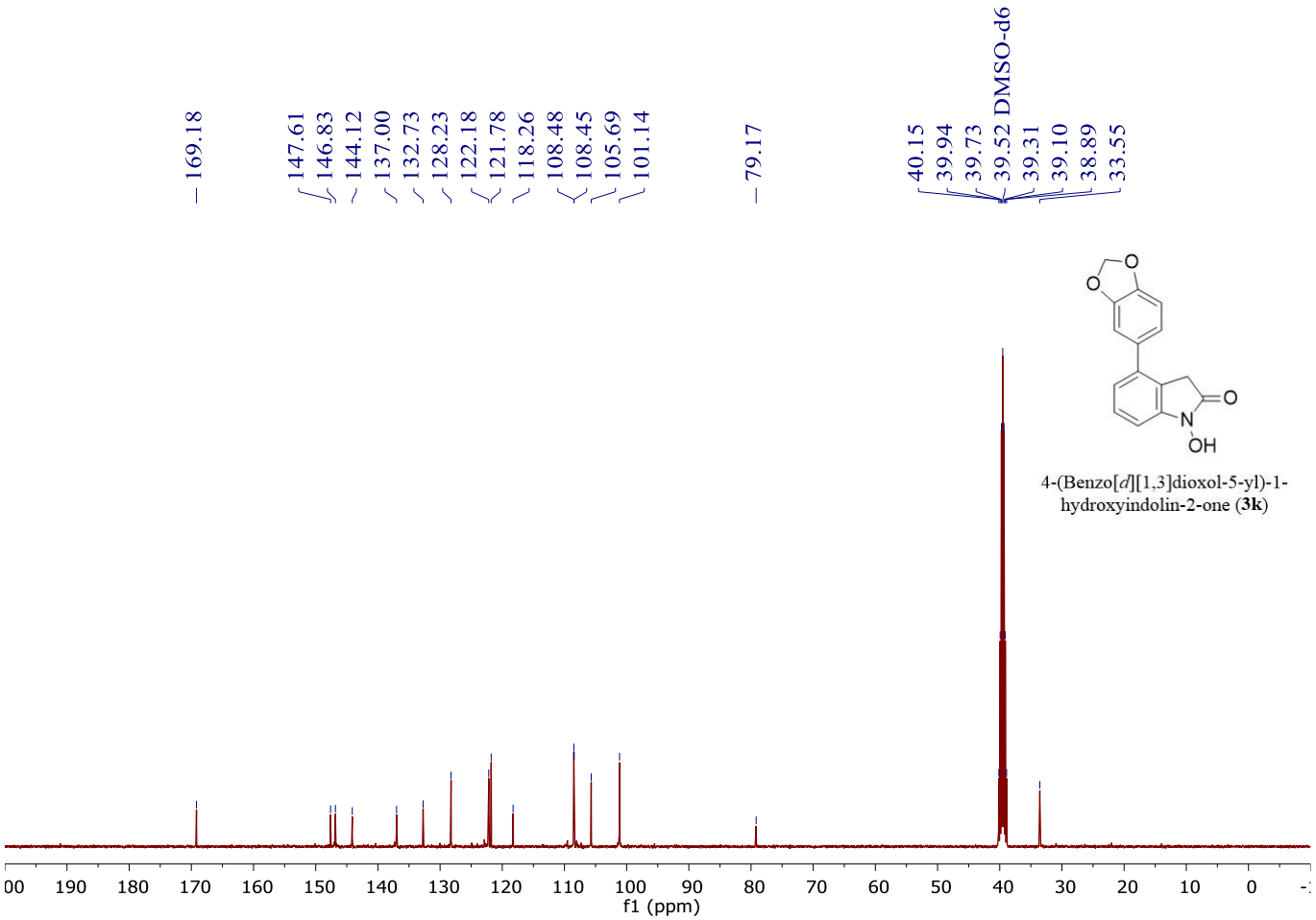
^{13}C NMR (100 MHz, DMSO-d_6) of 1-hydroxy-6-(thiophen-3-yl)indolin-2-one (**3i**)



^{1}H NMR (400 MHz, DMSO-d_6) of 4-(benzo[d][1,3]dioxol-5-yl)-1-hydroxyindolin-2-one (**3k**)

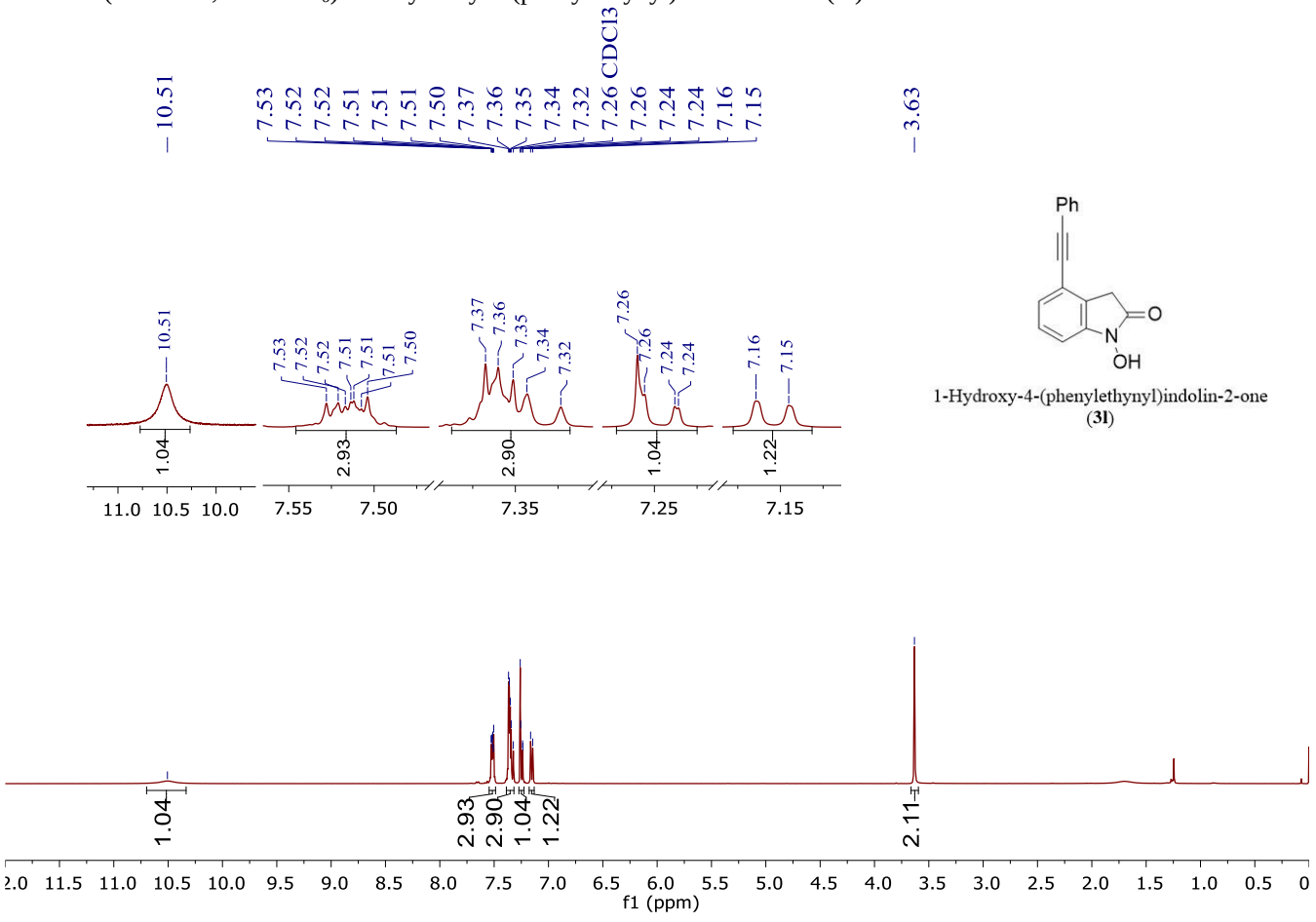


^{13}C NMR (100 MHz, DMSO-d_6) of 4-(benzo[d][1,3]dioxol-5-yl)-1-hydroxyindolin-2-one (**3k**)



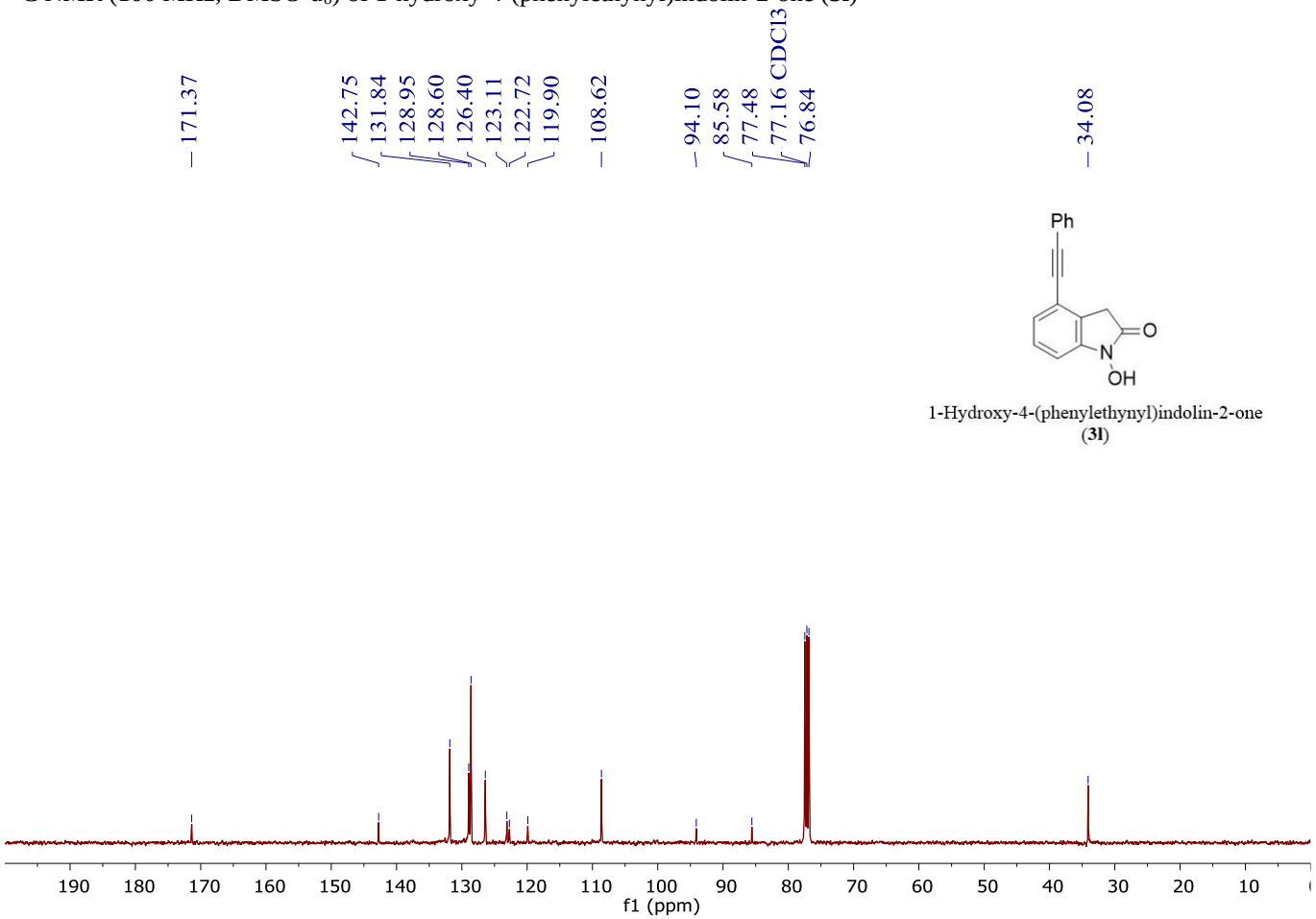
4-(Benzo[*d*][1,3]dioxol-5-yl)-1-hydroxyindolin-2-one (**3k**)

^{1}H NMR (400 MHz, DMSO-d_6) of 1-hydroxy-4-(phenylethynyl)indolin-2-one (**3l**)

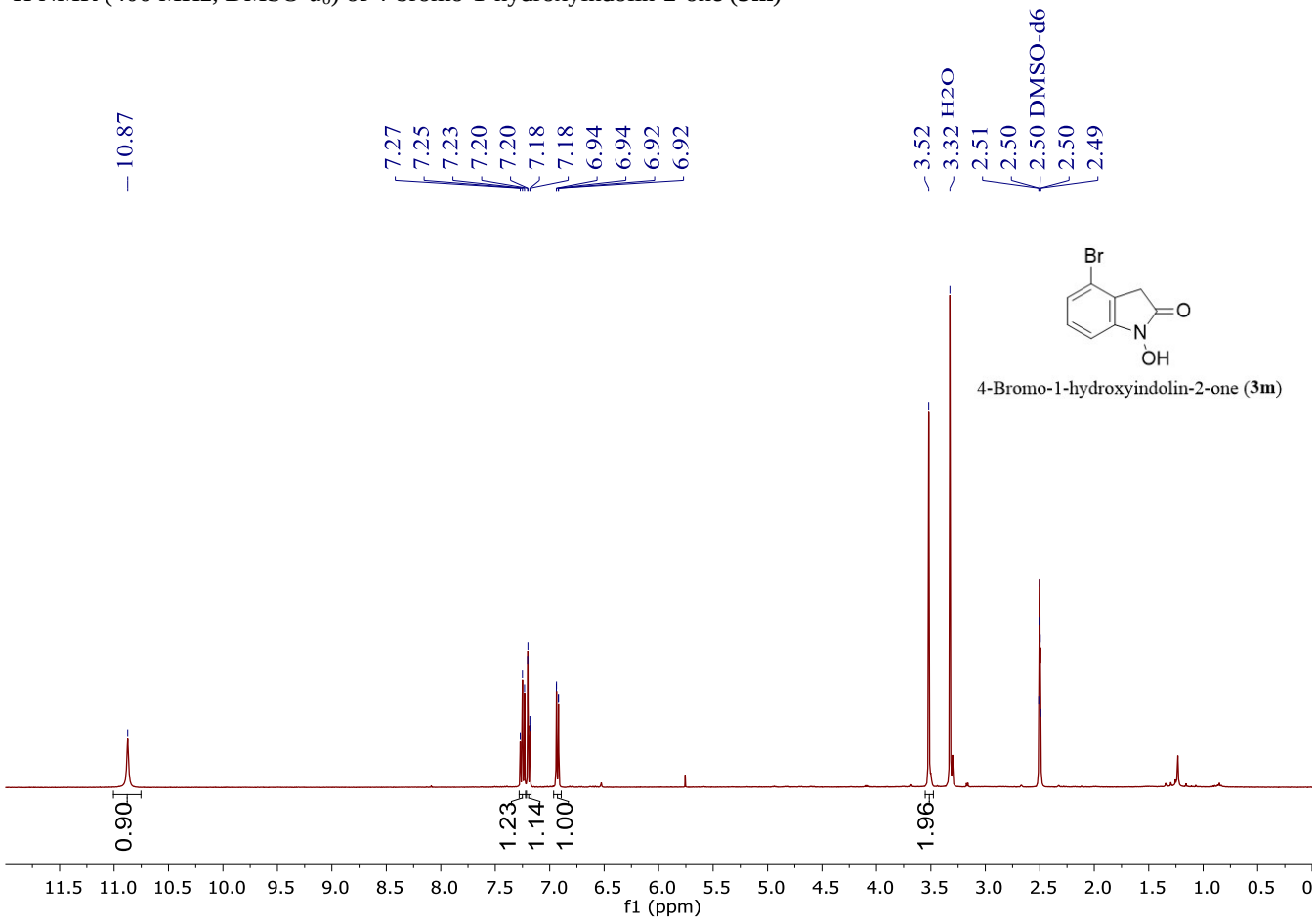


1-Hydroxy-4-(phenylethynyl)indolin-2-one (**3l**)

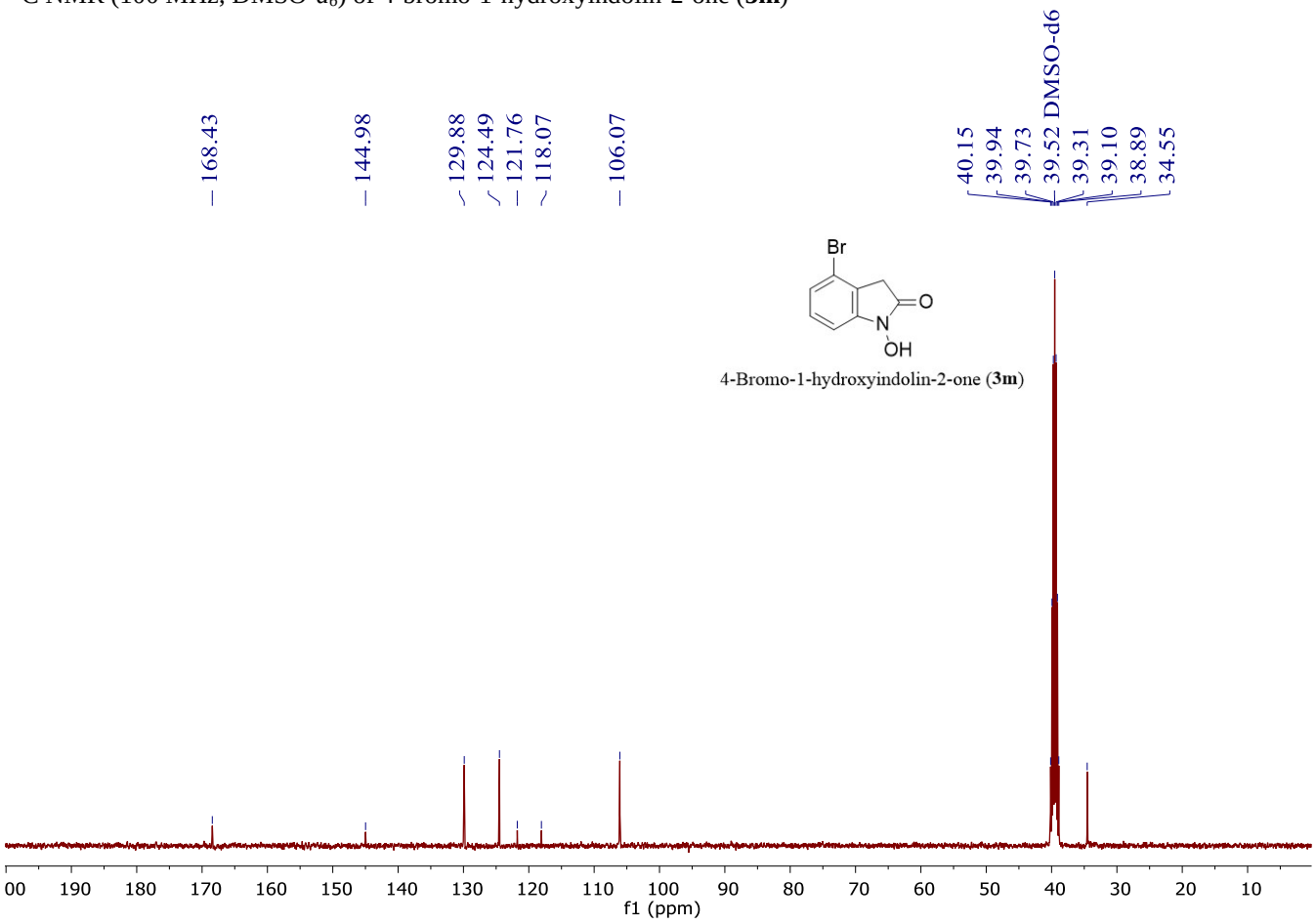
^{13}C NMR (100 MHz, DMSO-d_6) of 1-hydroxy-4-(phenylethynyl)indolin-2-one (**3l**)



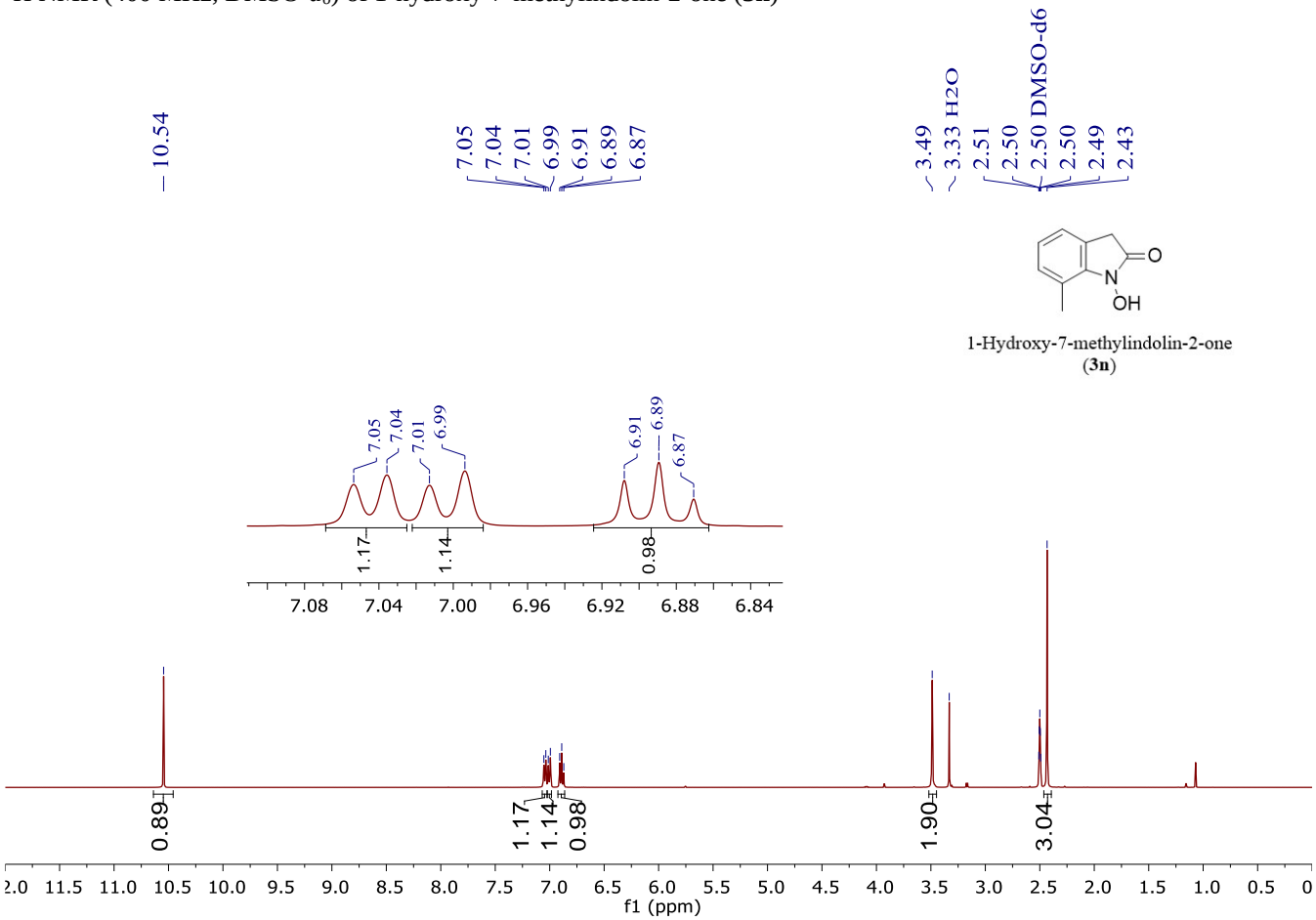
^{1}H NMR (400 MHz, DMSO-d_6) of 4-bromo-1-hydroxyindolin-2-one (**3m**)



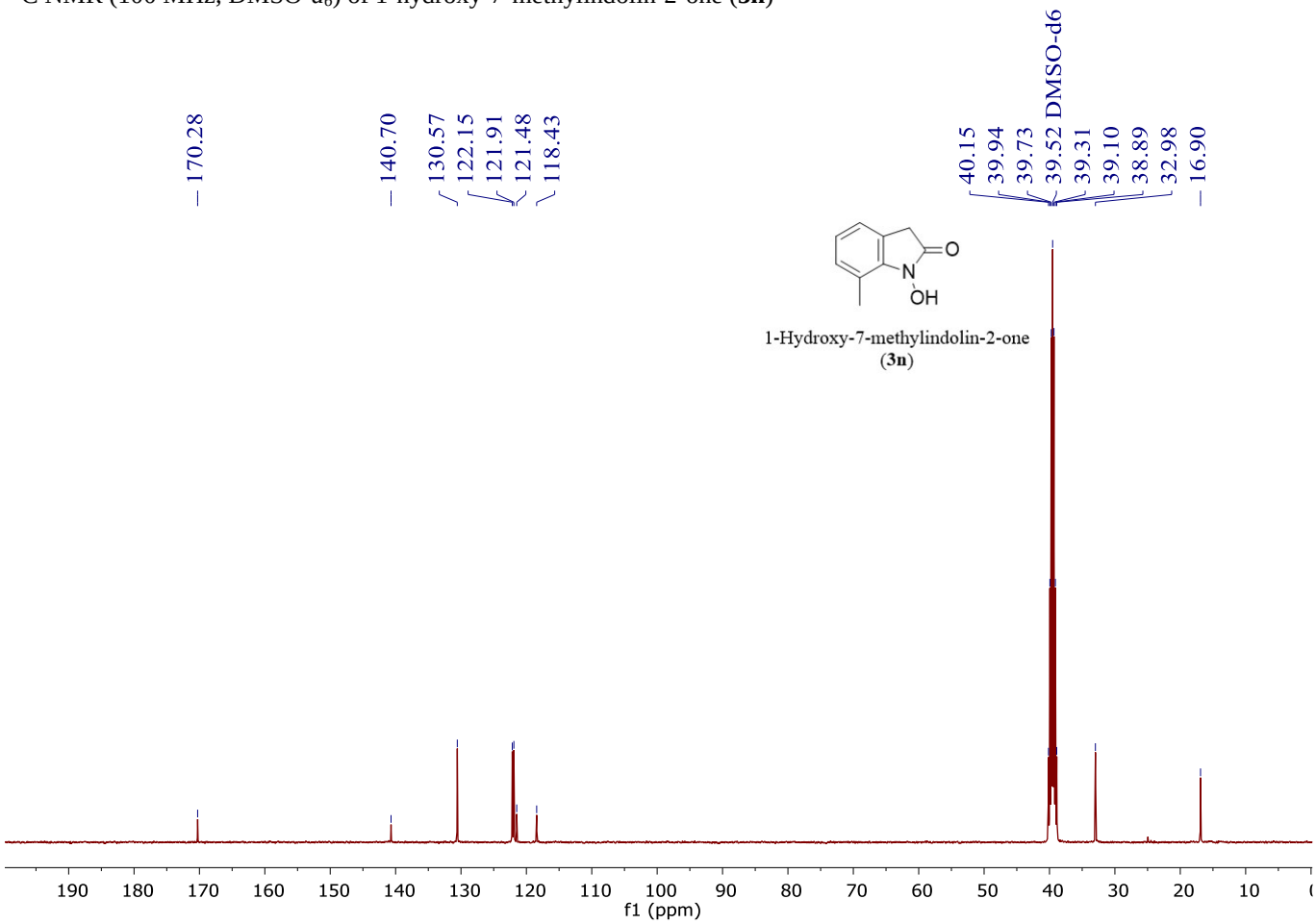
^{13}C NMR (100 MHz, DMSO-d_6) of 4-bromo-1-hydroxyindolin-2-one (**3m**)



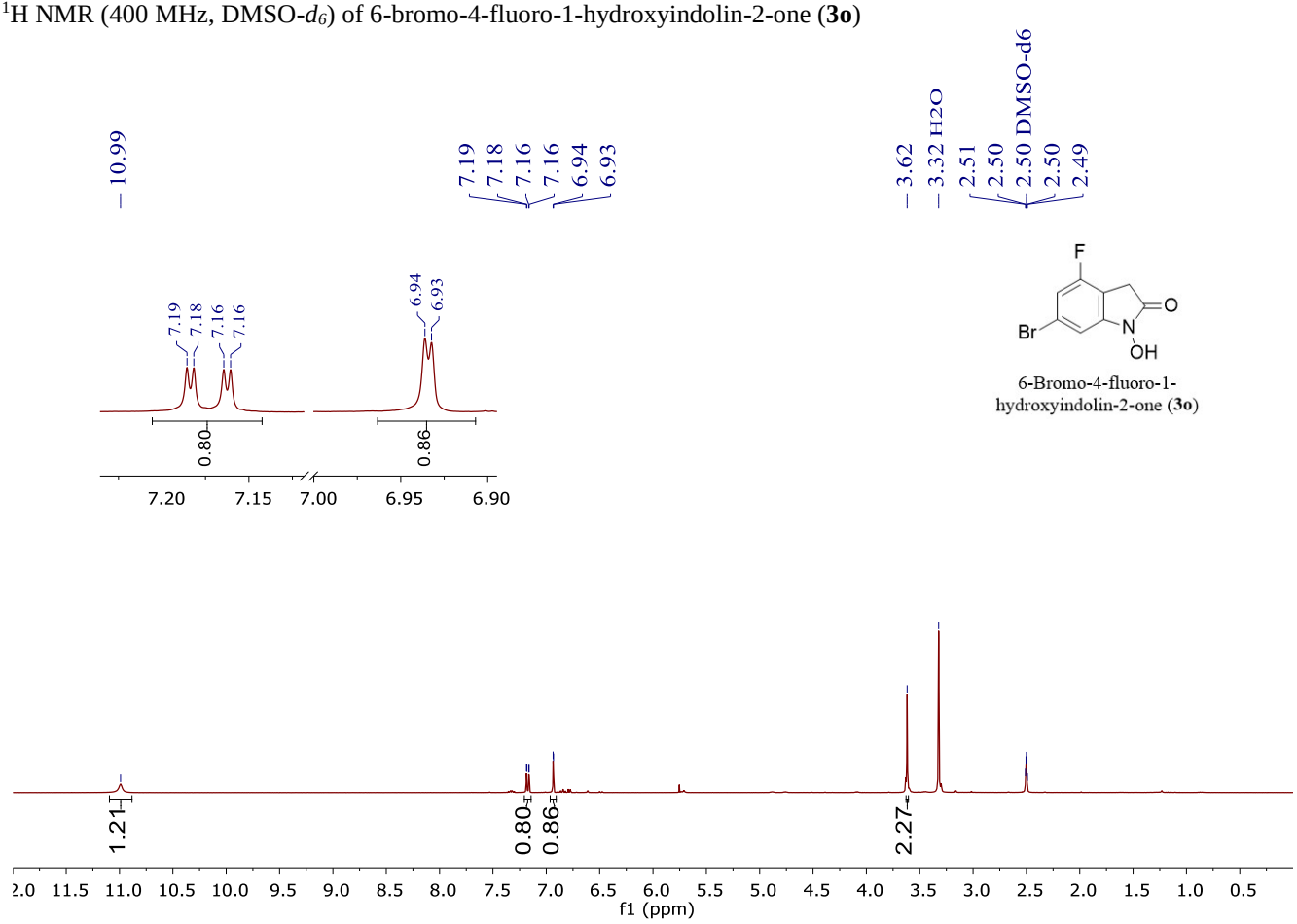
^{1}H NMR (400 MHz, DMSO-d_6) of 1-hydroxy-7-methylindolin-2-one (**3n**)



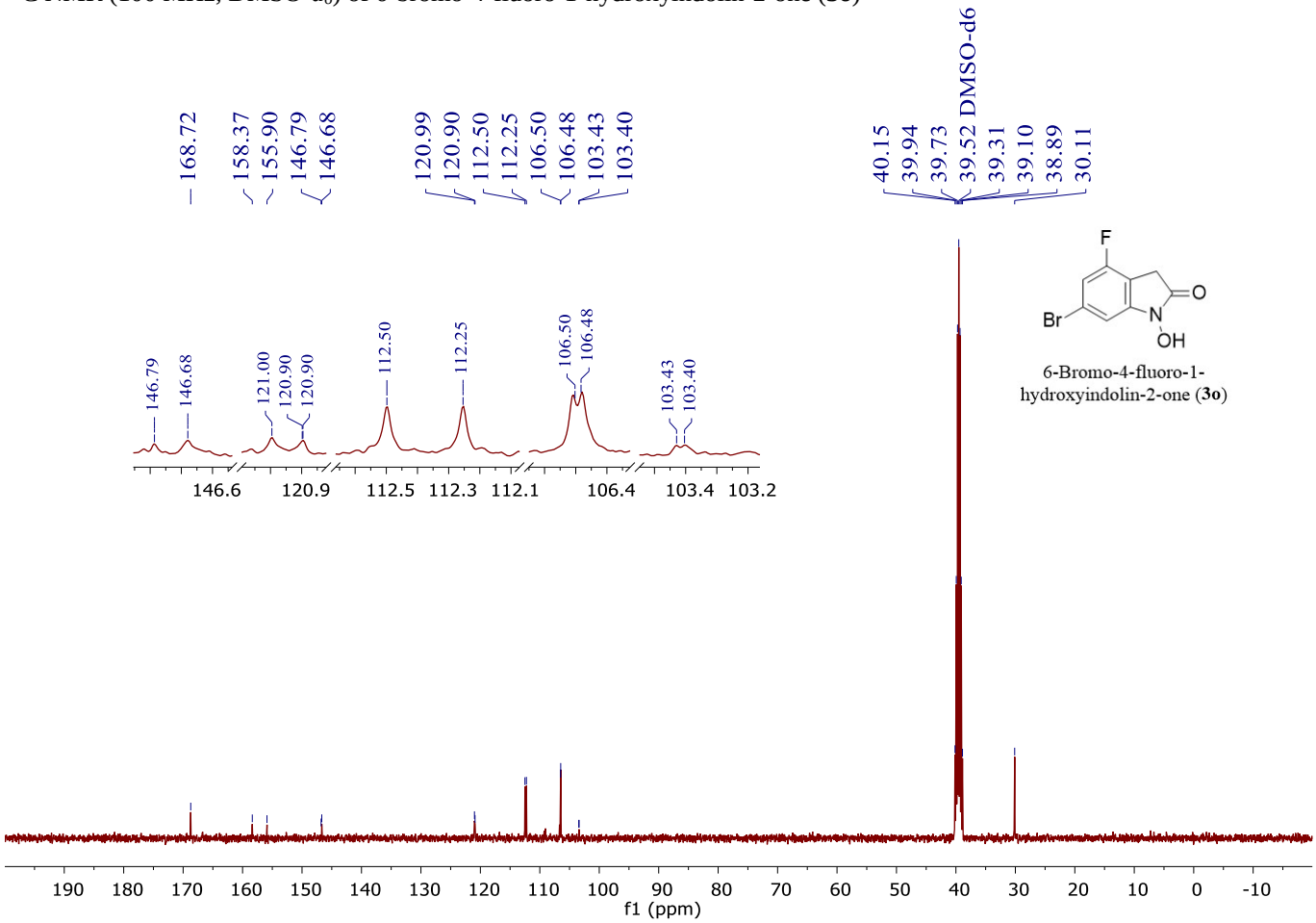
^{13}C NMR (100 MHz, DMSO-d_6) of 1-hydroxy-7-methylindolin-2-one (**3n**)



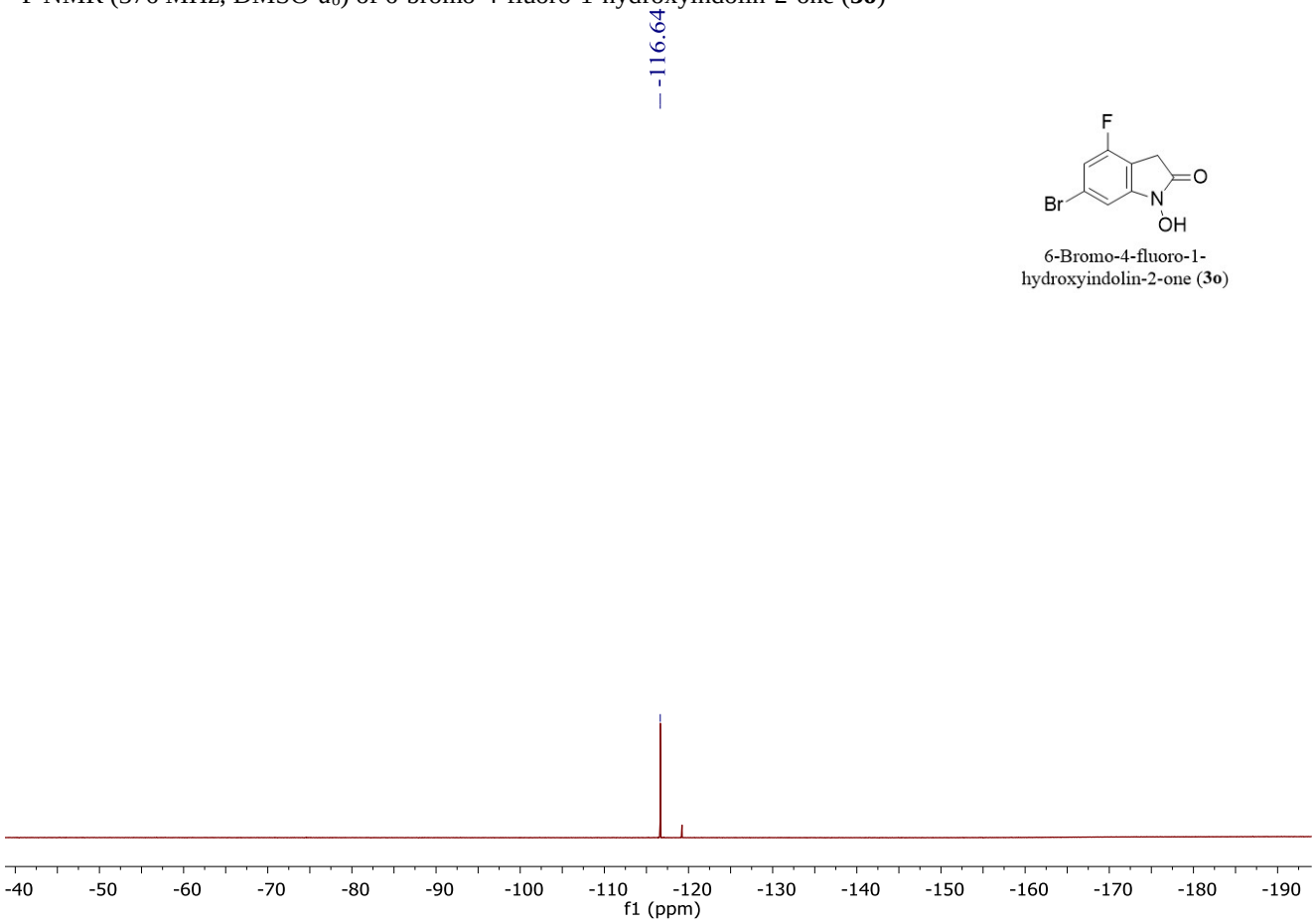
^{1}H NMR (400 MHz, DMSO-d_6) of 6-bromo-4-fluoro-1-hydroxyindolin-2-one (**3o**)



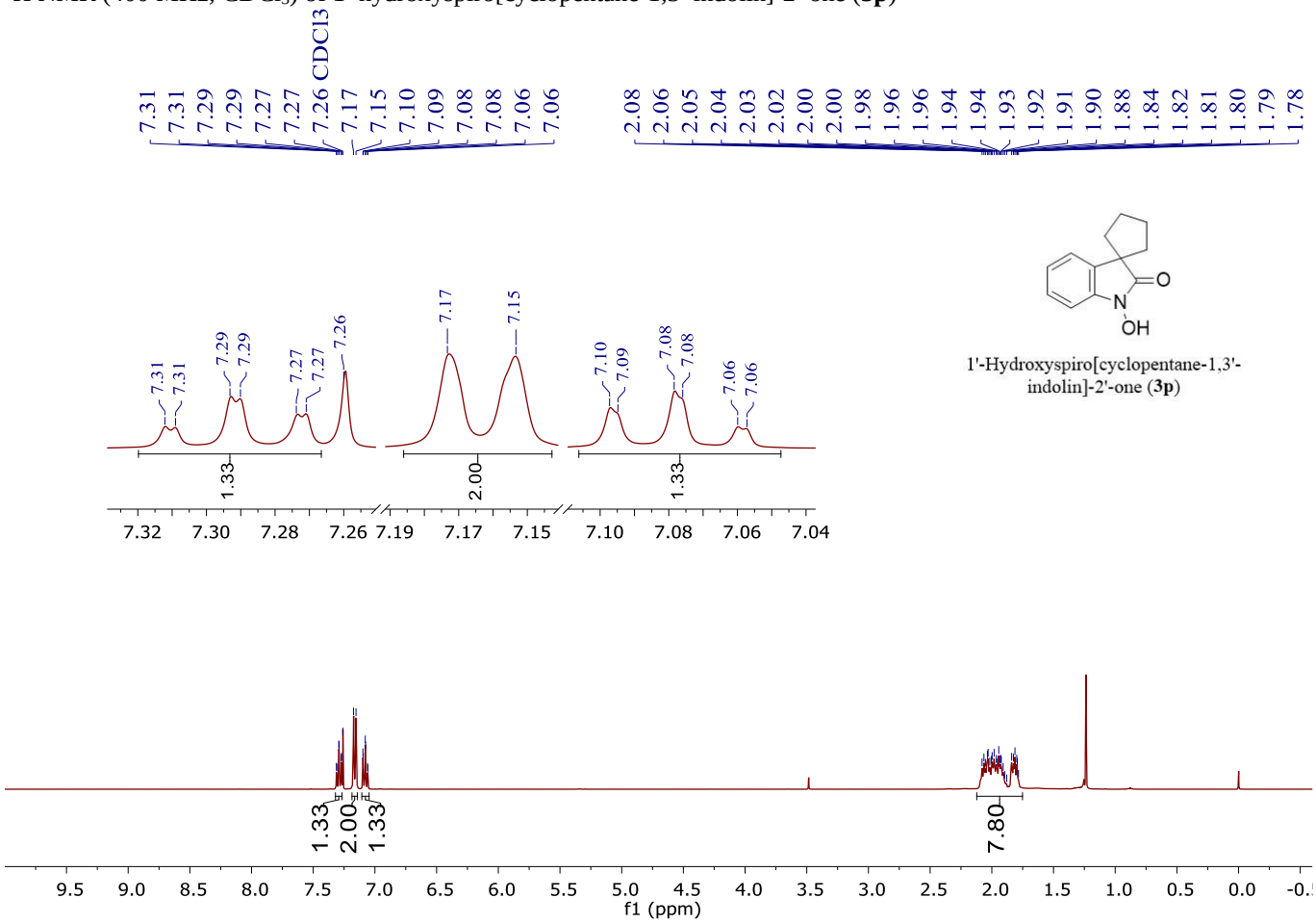
^{13}C NMR (100 MHz, DMSO-d_6) of 6-bromo-4-fluoro-1-hydroxyindolin-2-one (**3o**)



^{19}F NMR (376 MHz, DMSO-d_6) of 6-bromo-4-fluoro-1-hydroxyindolin-2-one (**3o**)

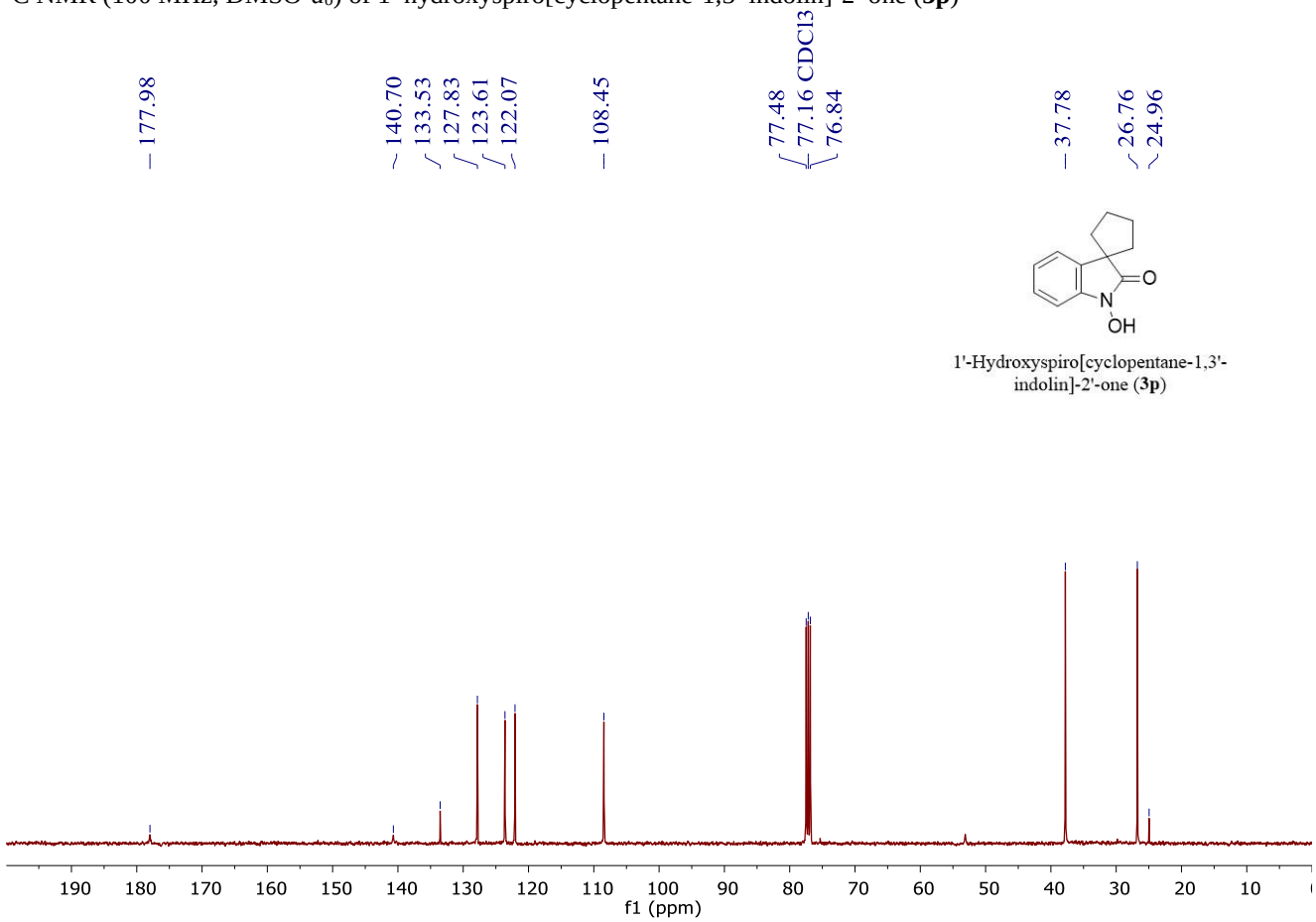


^{1}H NMR (400 MHz, $CDCl_3$) of 1'-hydroxyspiro[cyclopentane-1,3'-indolin]-2'-one (**3p**)



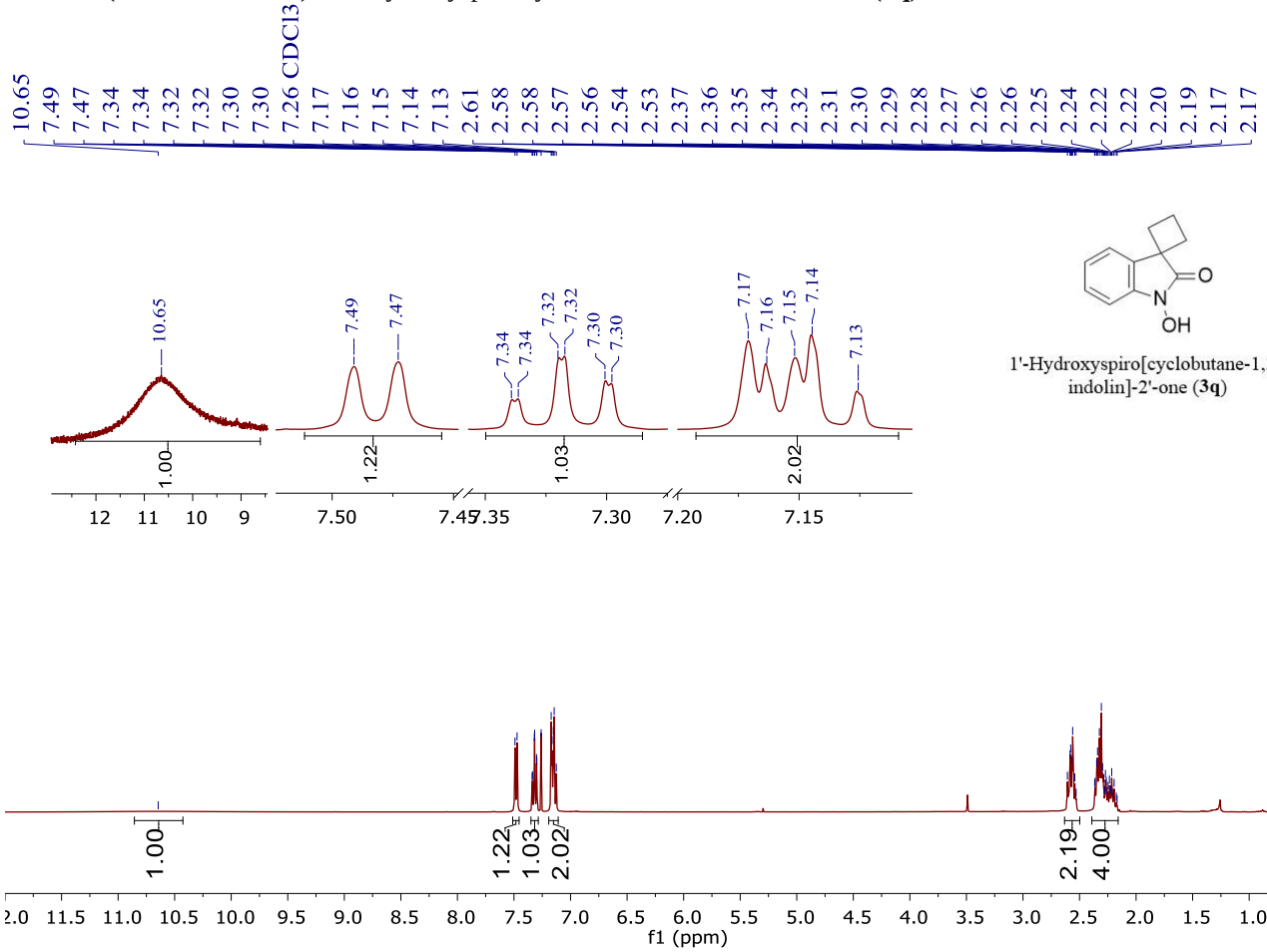
1'-Hydroxyspiro[cyclopentane-1,3'-indolin]-2'-one (**3p**)

^{13}C NMR (100 MHz, DMSO-d_6) of 1'-hydroxyspiro[cyclopentane-1,3'-indolin]-2'-one (**3p**)



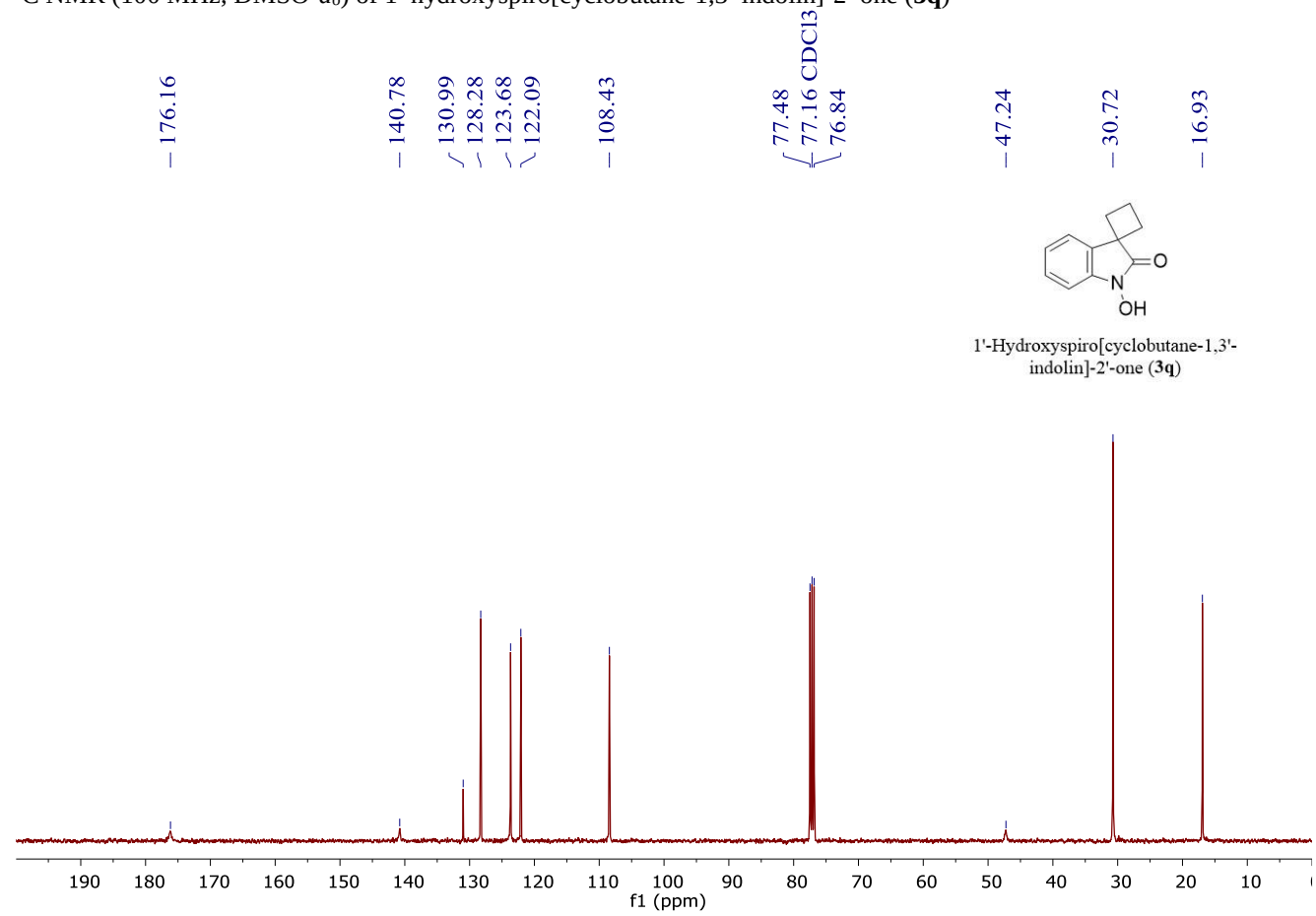
1'-Hydroxyspiro[cyclopentane-1,3'-indolin]-2'-one (**3p**)

^{1}H NMR (400 MHz, $CDCl_3$) of 1'-hydroxyspiro[cyclobutane-1,3'-indolin]-2'-one (**3q**)



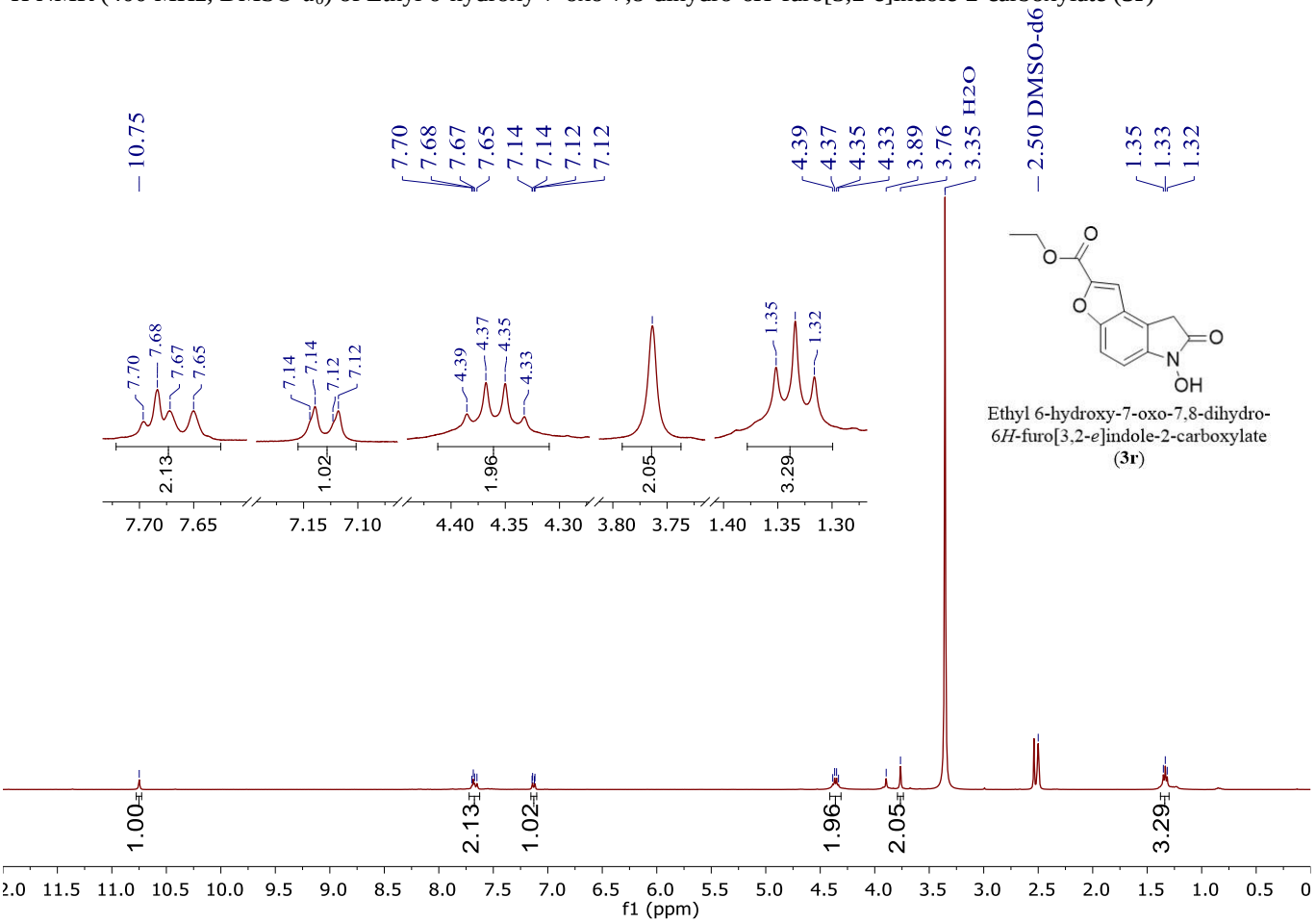
1'-Hydroxyspiro[cyclobutane-1,3'-indolin]-2'-one (**3q**)

^{13}C NMR (100 MHz, DMSO-d_6) of 1'-hydroxyspiro[cyclobutane-1,3'-indolin]-2'-one (**3q**)

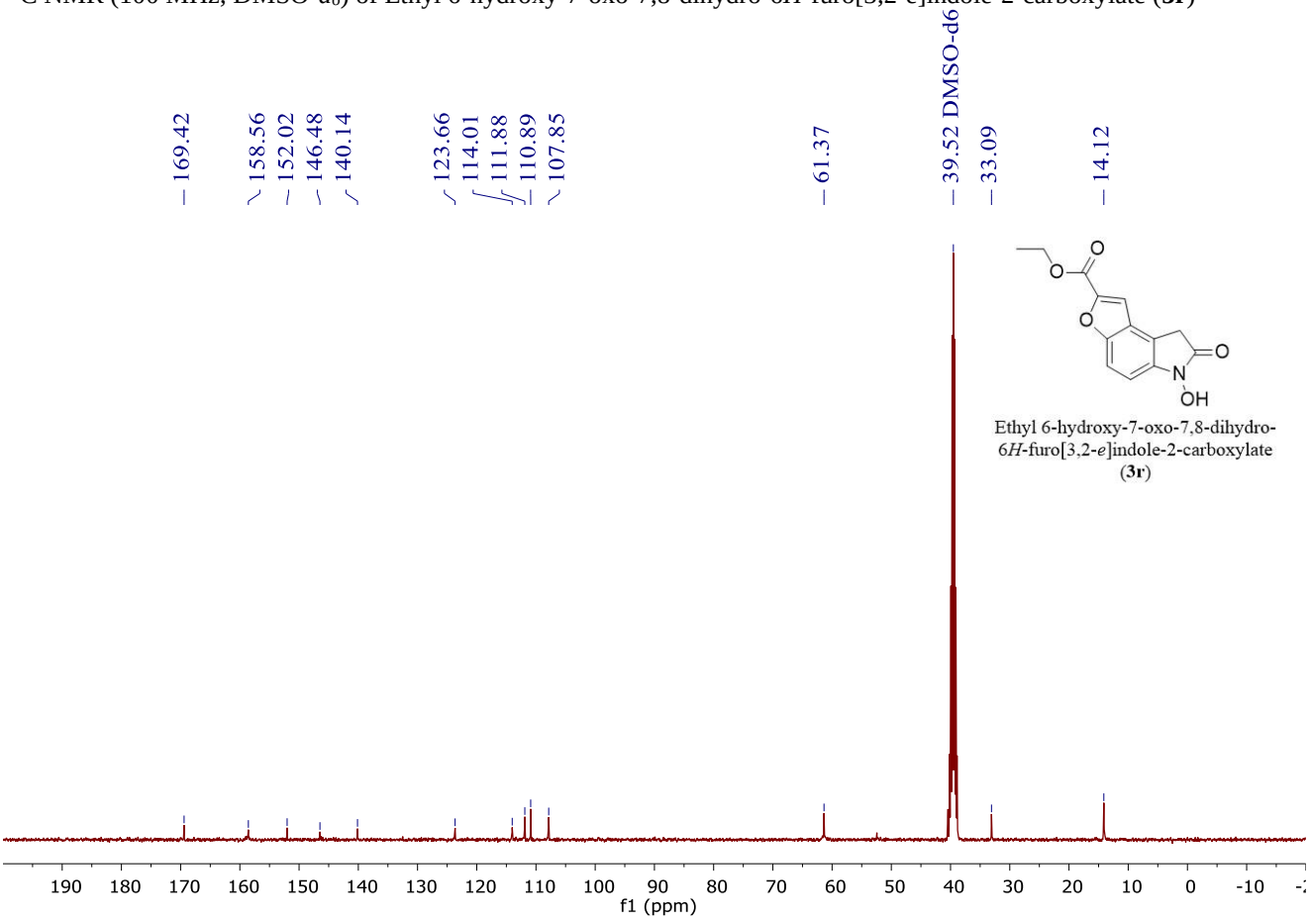


1'-Hydroxyspiro[cyclobutane-1,3'-indolin]-2'-one (**3q**)

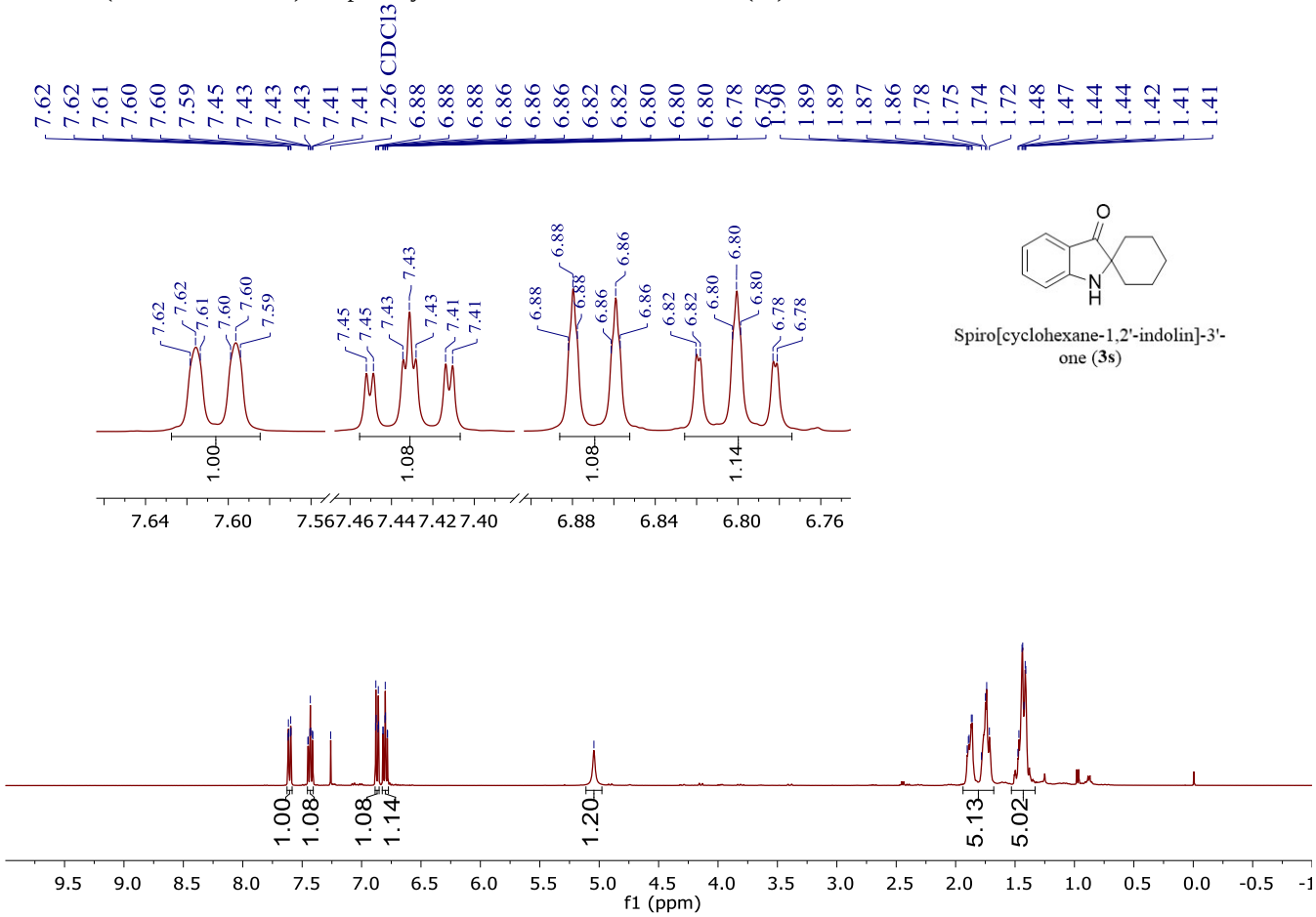
^{1}H NMR (400 MHz, DMSO-d_6) of Ethyl 6-hydroxy-7-oxo-7,8-dihydro-6*H*-furo[3,2-e]indole-2-carboxylate (**3r**)



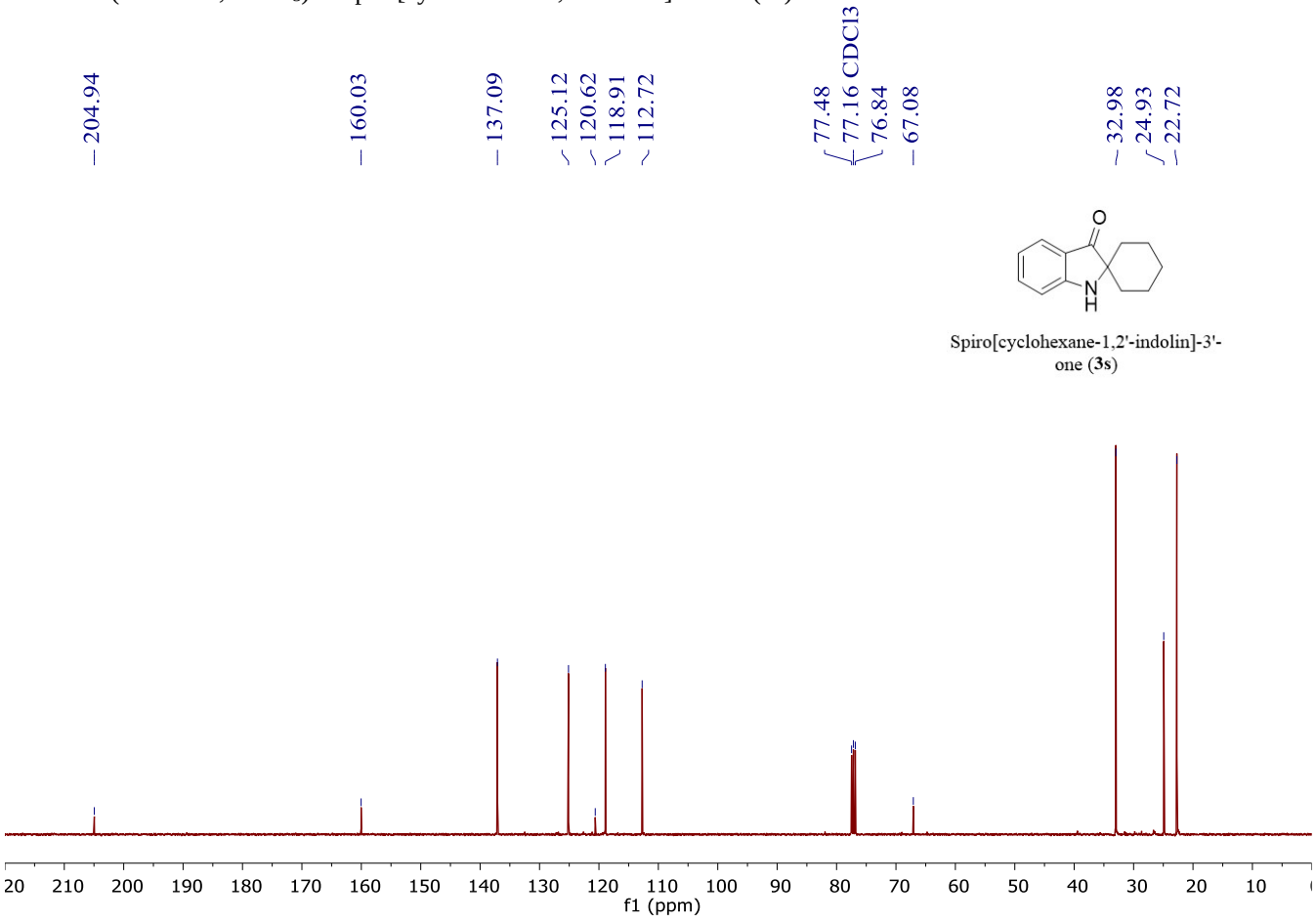
^{13}C NMR (100 MHz, DMSO-d_6) of Ethyl 6-hydroxy-7-oxo-7,8-dihydro-6*H*-furo[3,2-e]indole-2-carboxylate (**3r**)



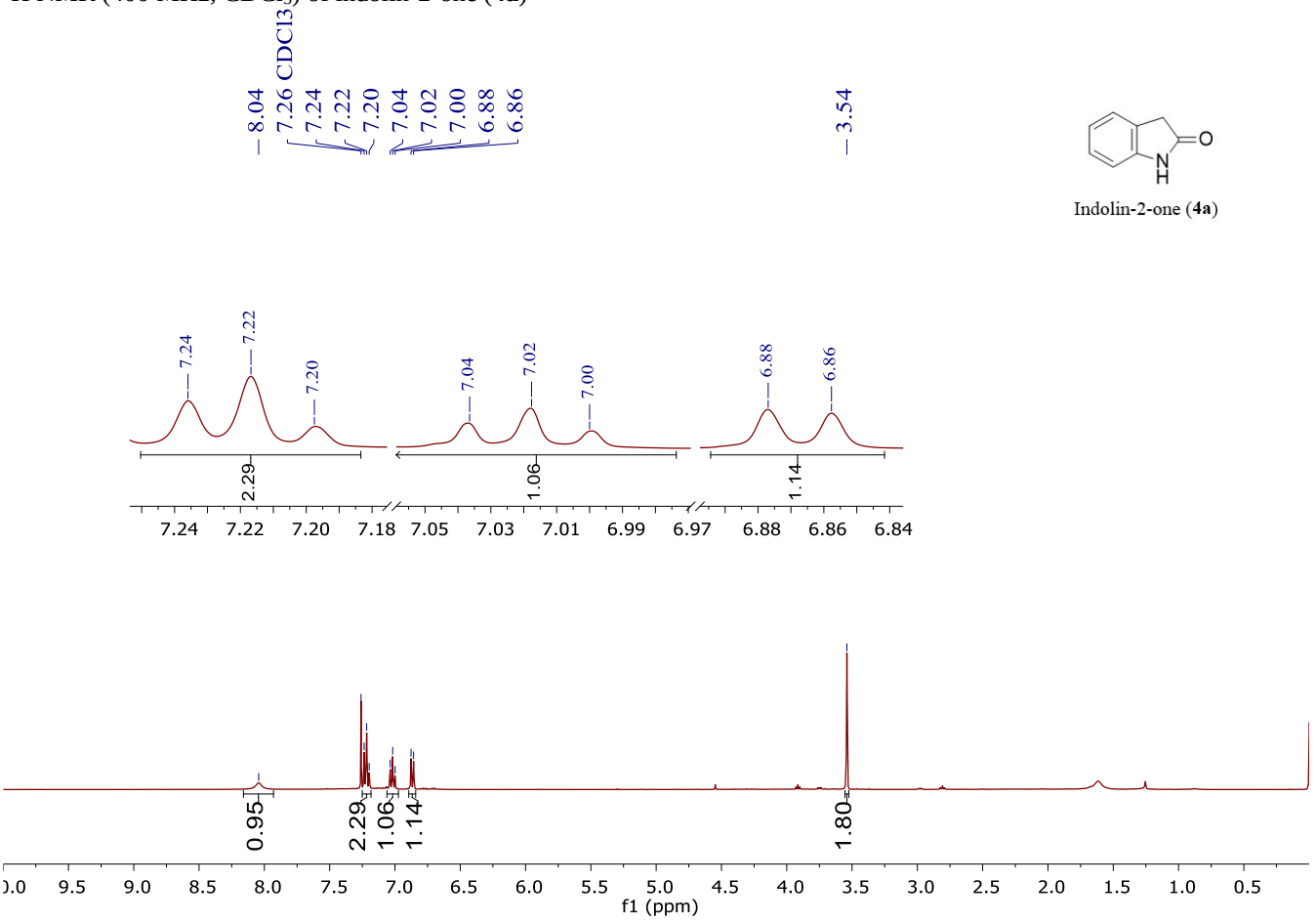
^{1}H NMR (400 MHz, $CDCl_3$) of spiro[cyclohexane-1,2'-indolin]-3'-one (**3s**)



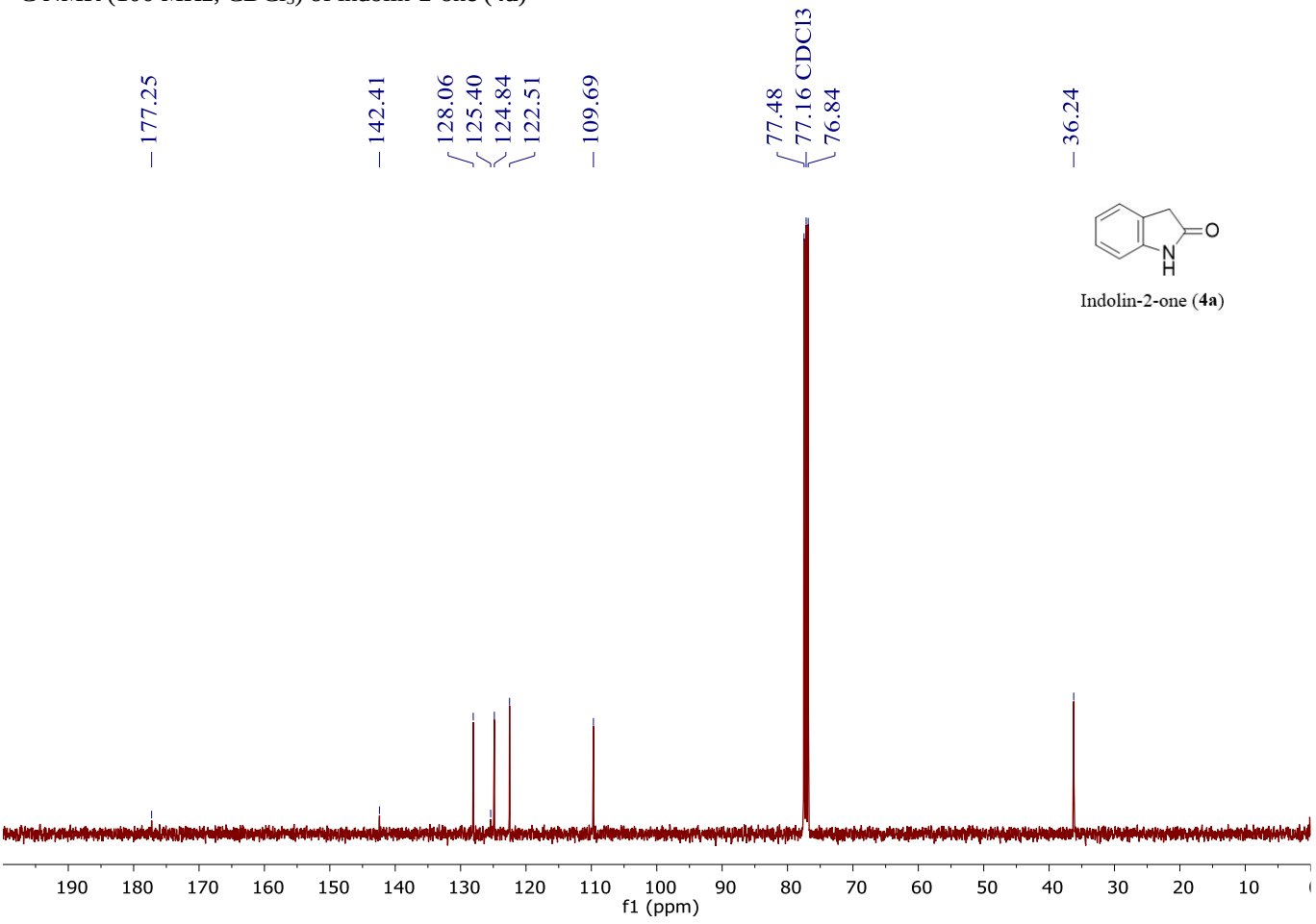
^{13}C NMR (100 MHz, $CDCl_3$) of spiro[cyclohexane-1,2'-indolin]-3'-one (**3s**)



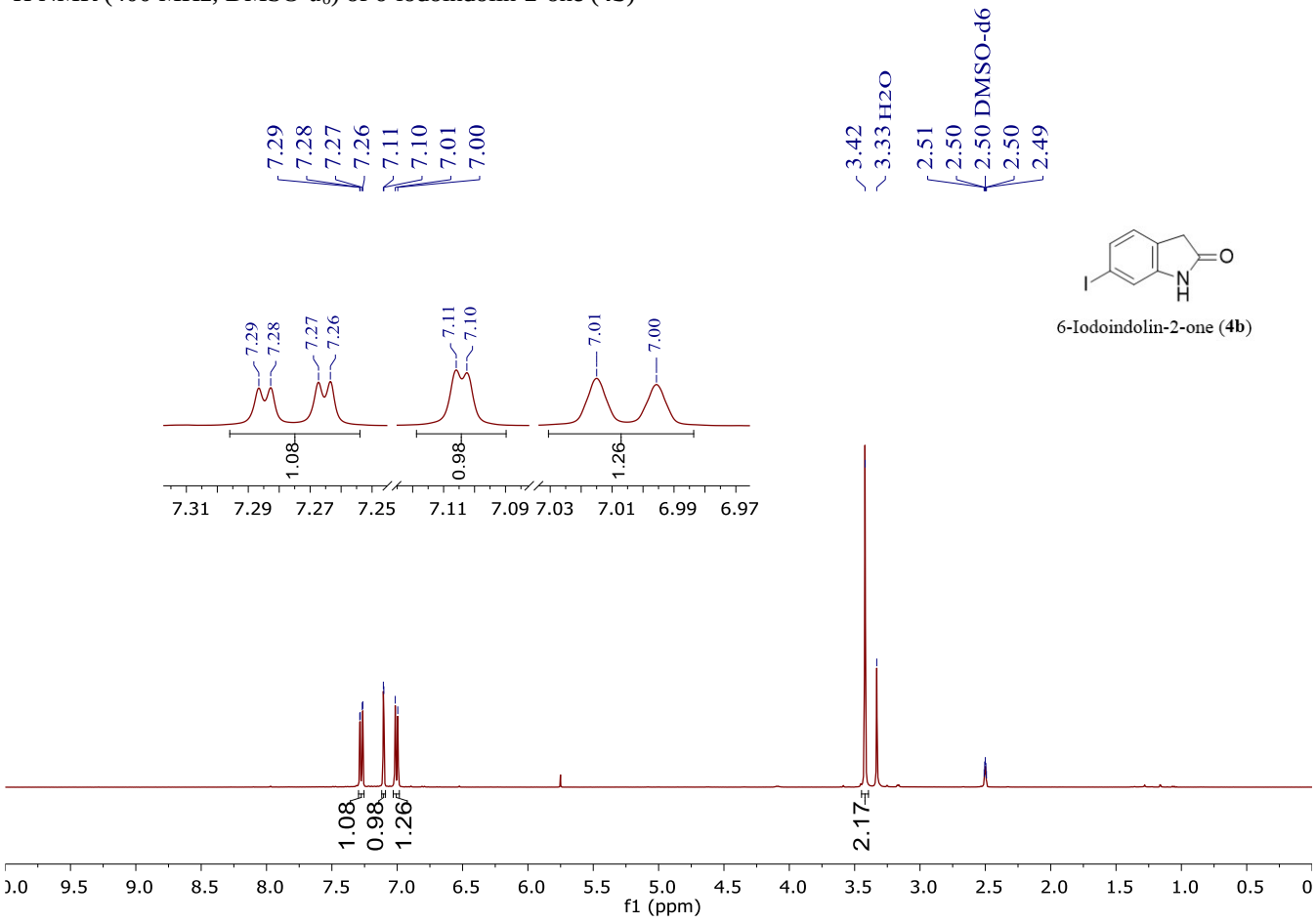
^{1}H NMR (400 MHz, $CDCl_3$) of indolin-2-one (**4a**)



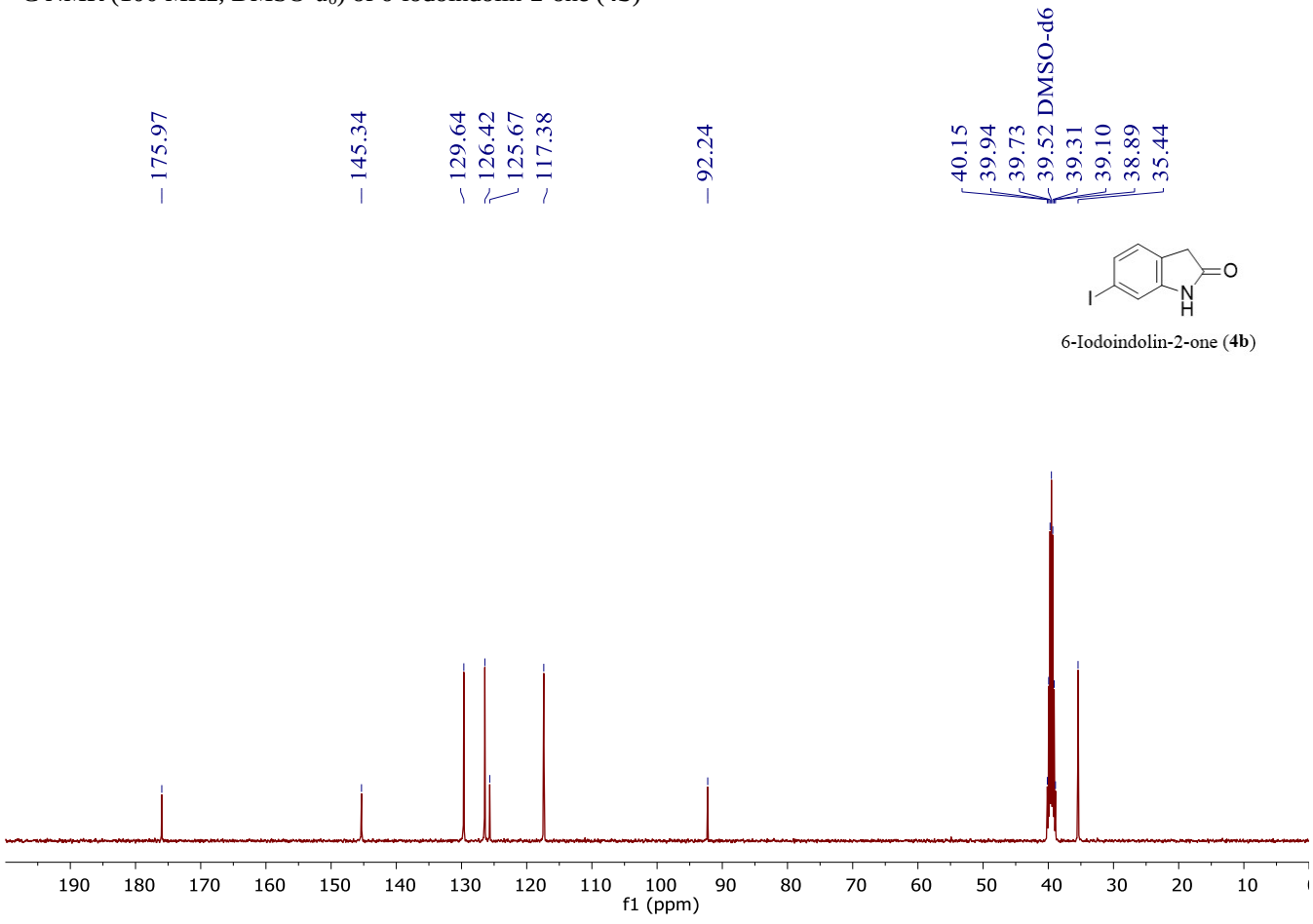
^{13}C NMR (100 MHz, $CDCl_3$) of indolin-2-one (**4a**)



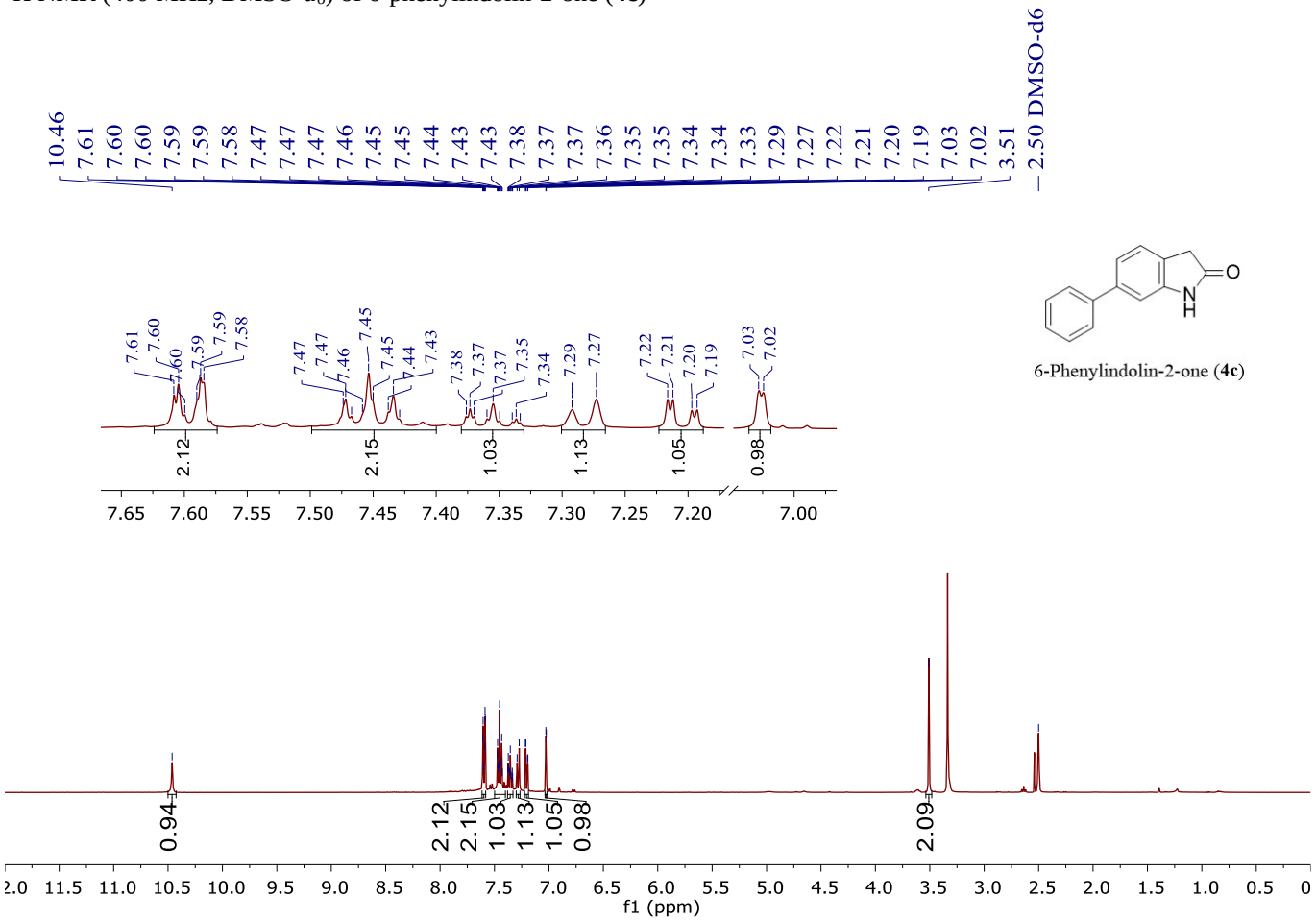
^{1}H NMR (400 MHz, DMSO-d_6) of 6-iodoindolin-2-one (**4b**)



^{13}C NMR (100 MHz, DMSO-d_6) of 6-iodoindolin-2-one (**4b**)

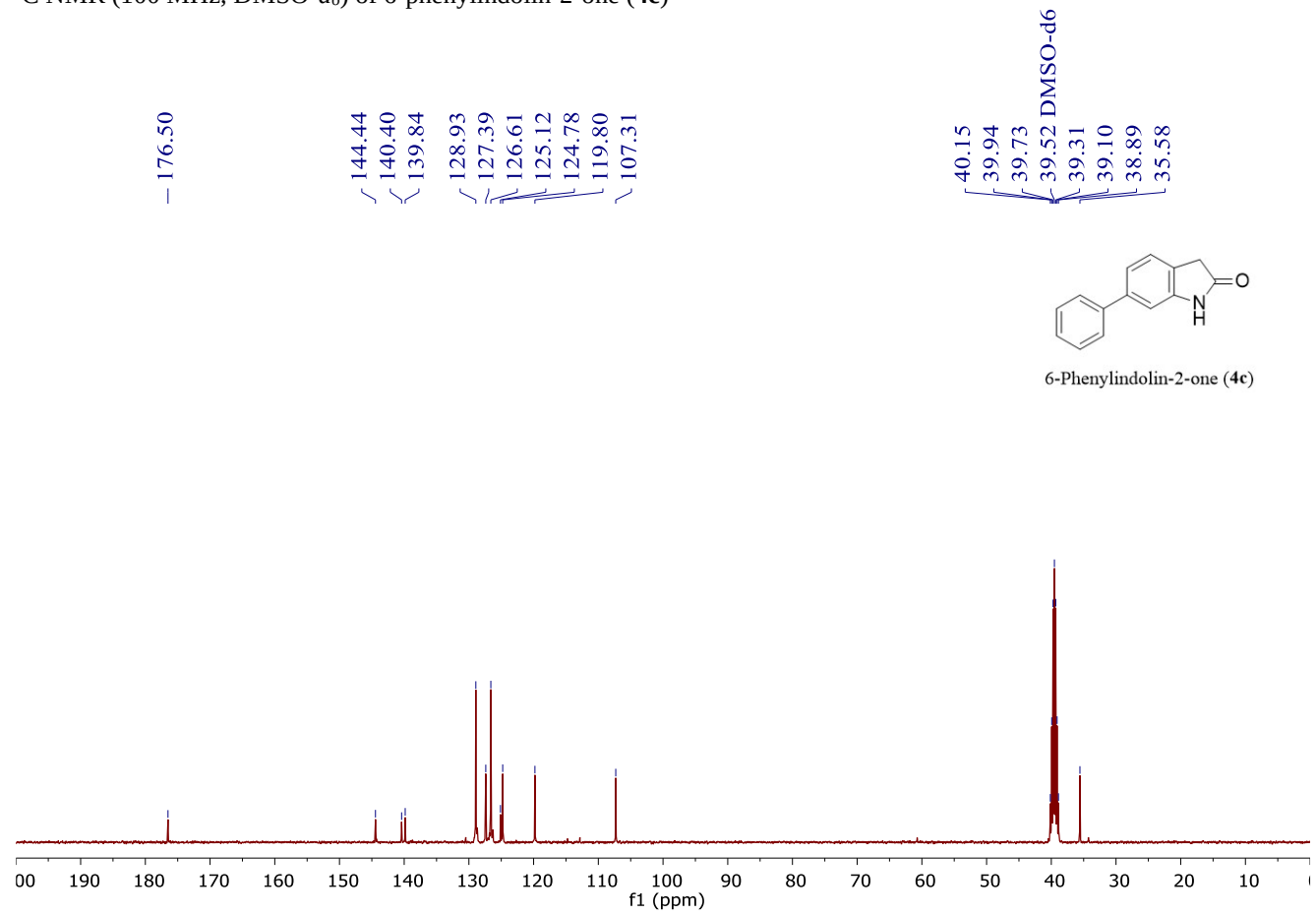


^{1}H NMR (400 MHz, DMSO-d_6) of 6-phenylindolin-2-one (**4c**)



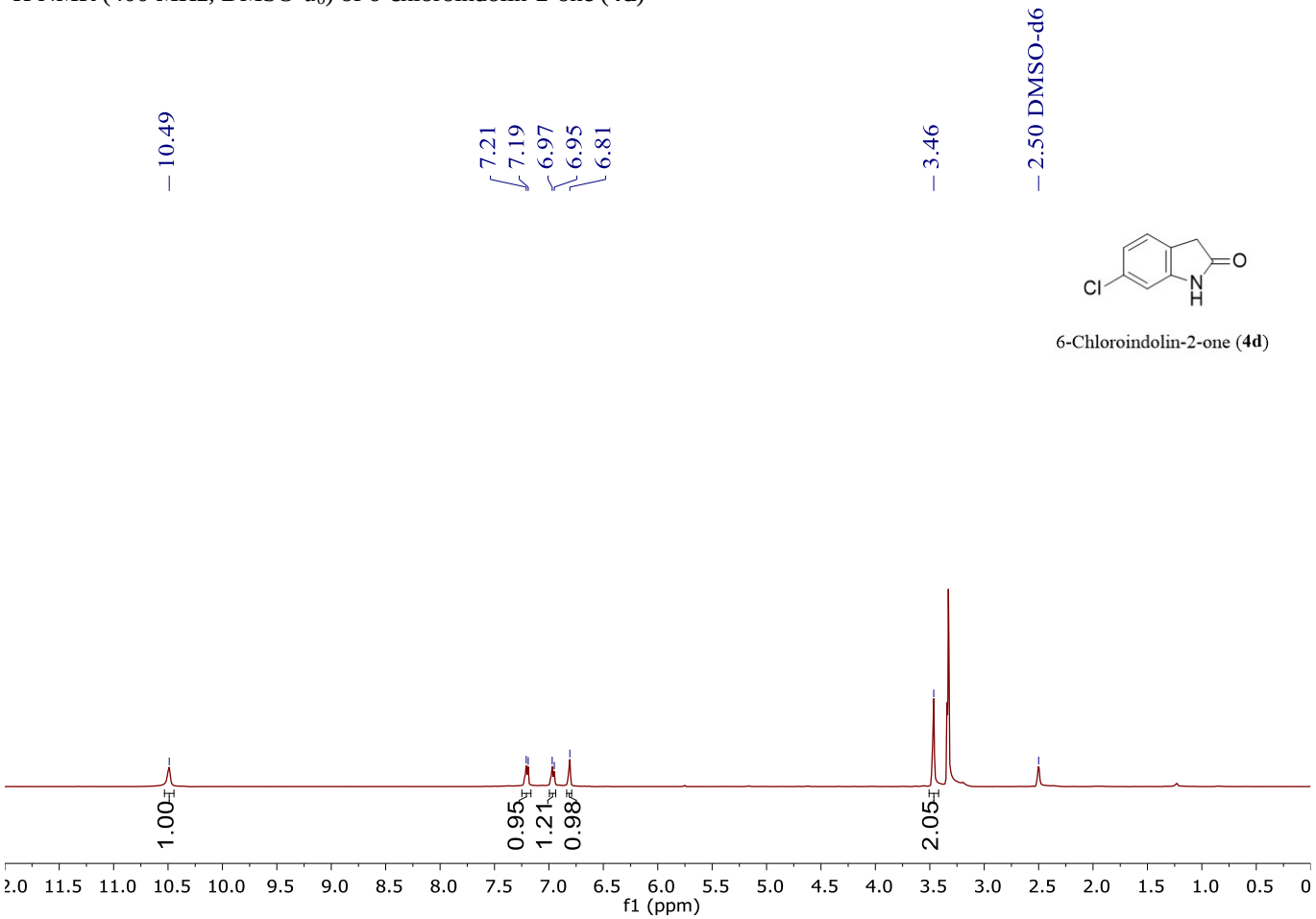
6-Phenylindolin-2-one (**4c**)

^{13}C NMR (100 MHz, DMSO-d_6) of 6-phenylindolin-2-one (**4c**)

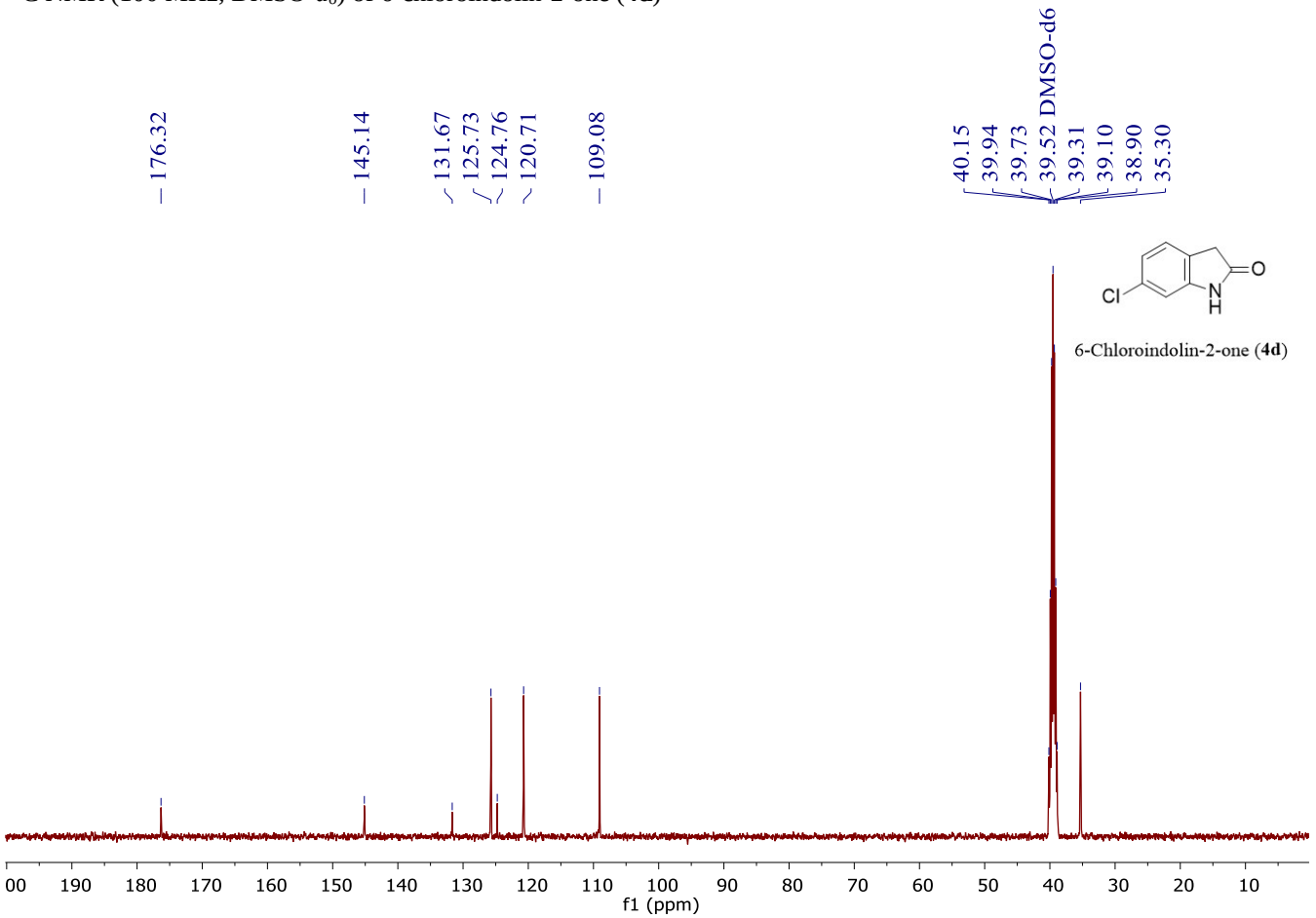


6-Phenylindolin-2-one (**4c**)

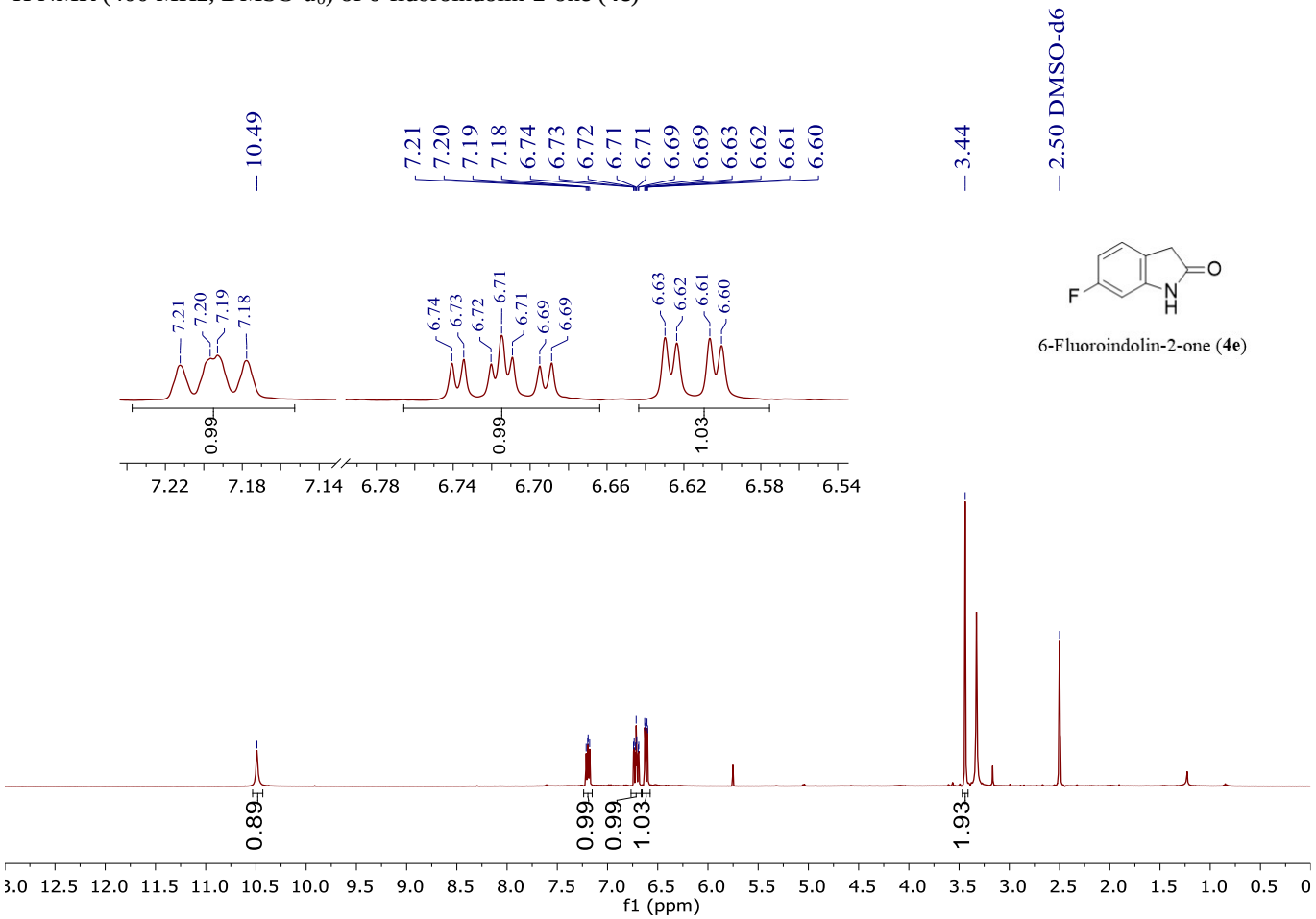
^{1}H NMR (400 MHz, DMSO-d_6) of 6-chloroindolin-2-one (**4d**)



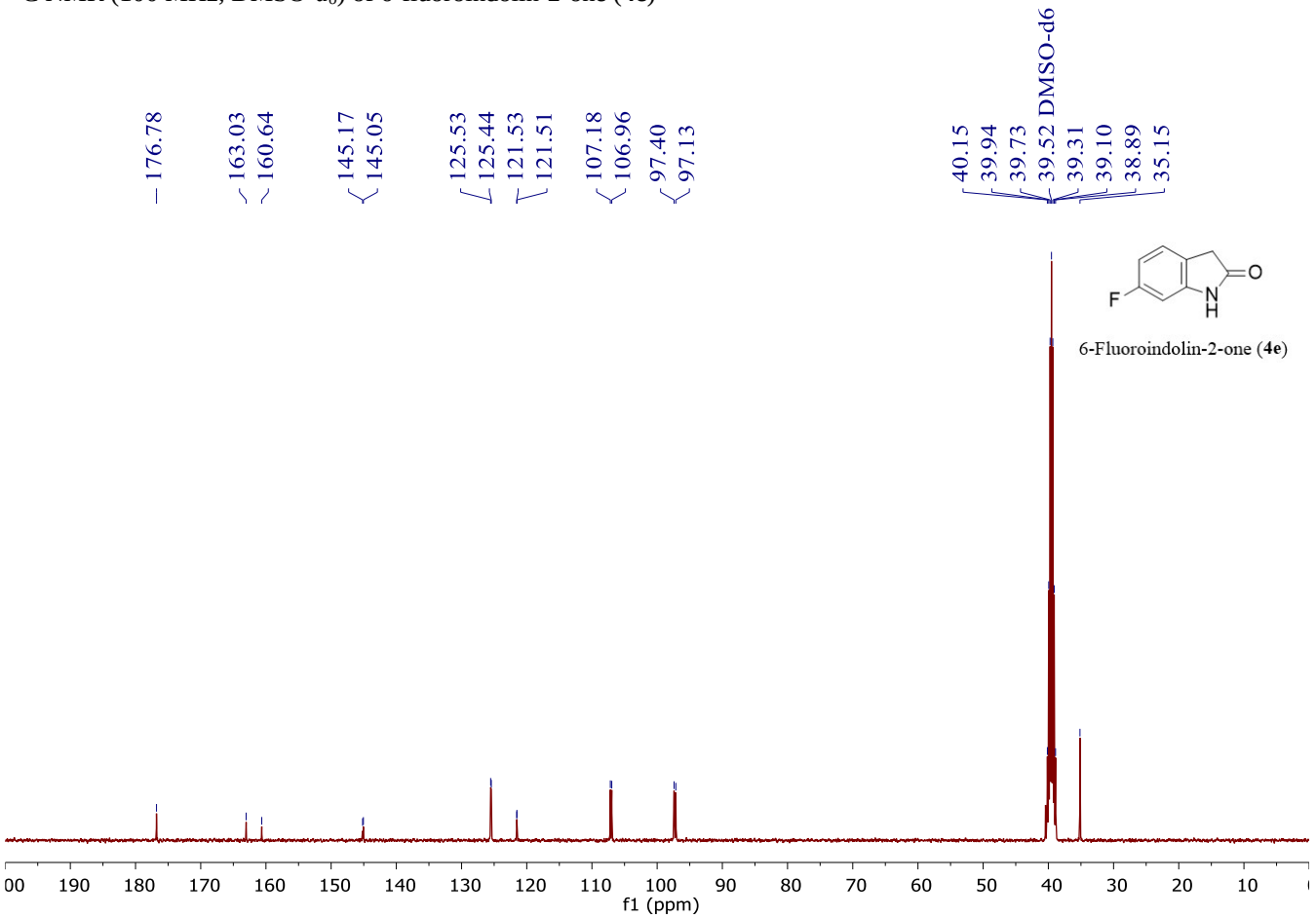
^{13}C NMR (100 MHz, DMSO-d_6) of 6-chloroindolin-2-one (**4d**)



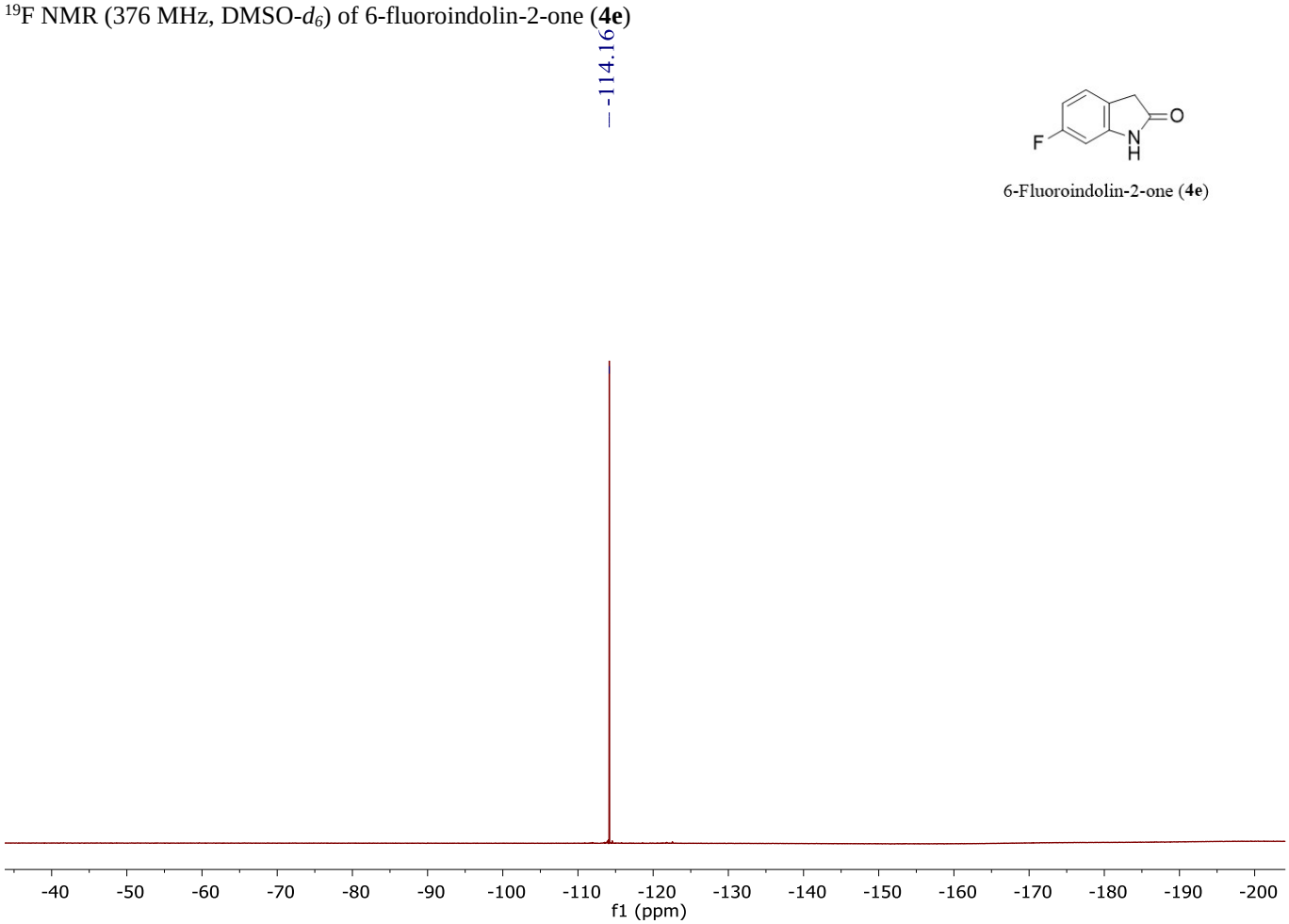
^{1}H NMR (400 MHz, DMSO-d_6) of 6-fluoroindolin-2-one (**4e**)



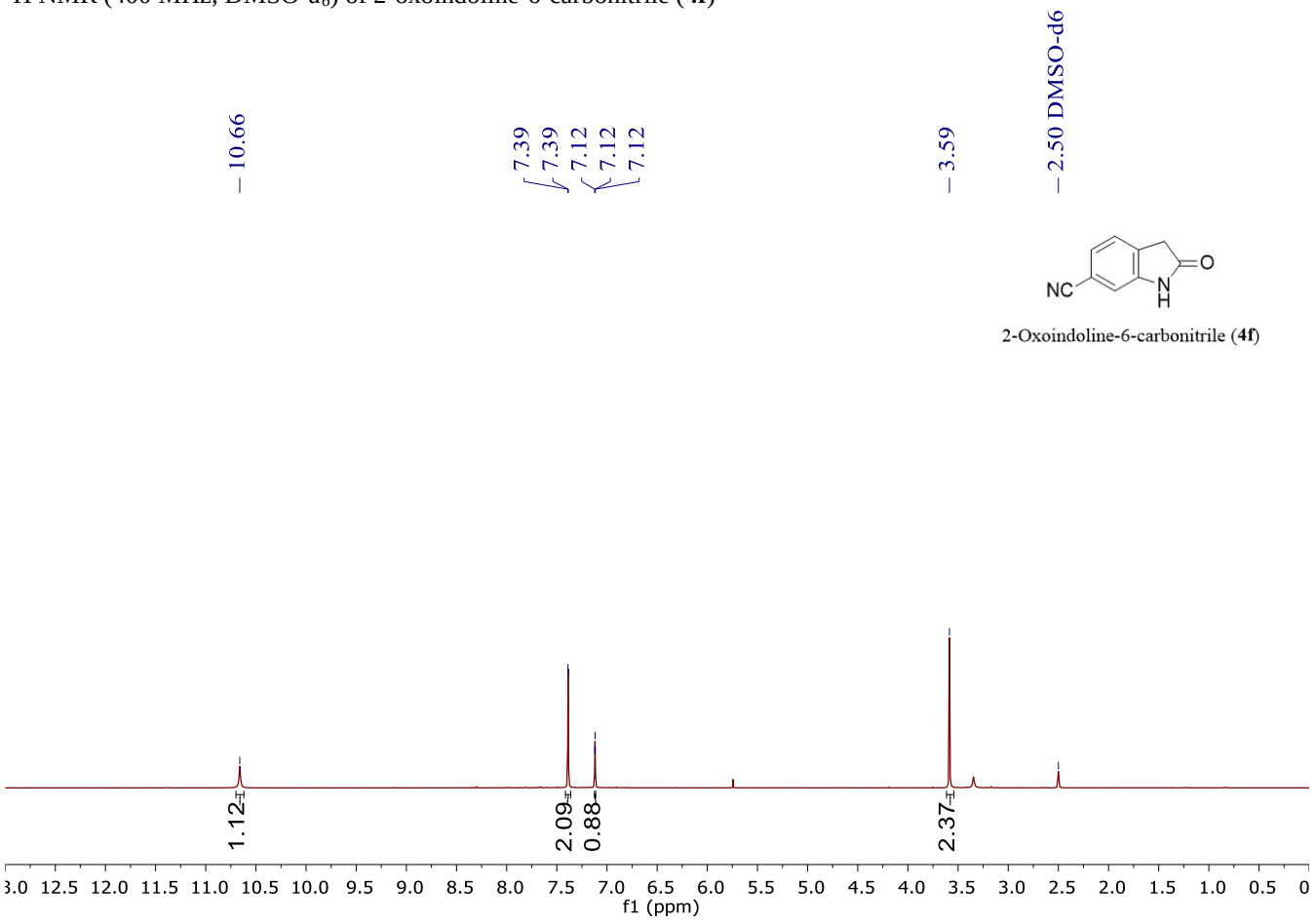
^{13}C NMR (100 MHz, DMSO-d_6) of 6-fluoroindolin-2-one (**4e**)



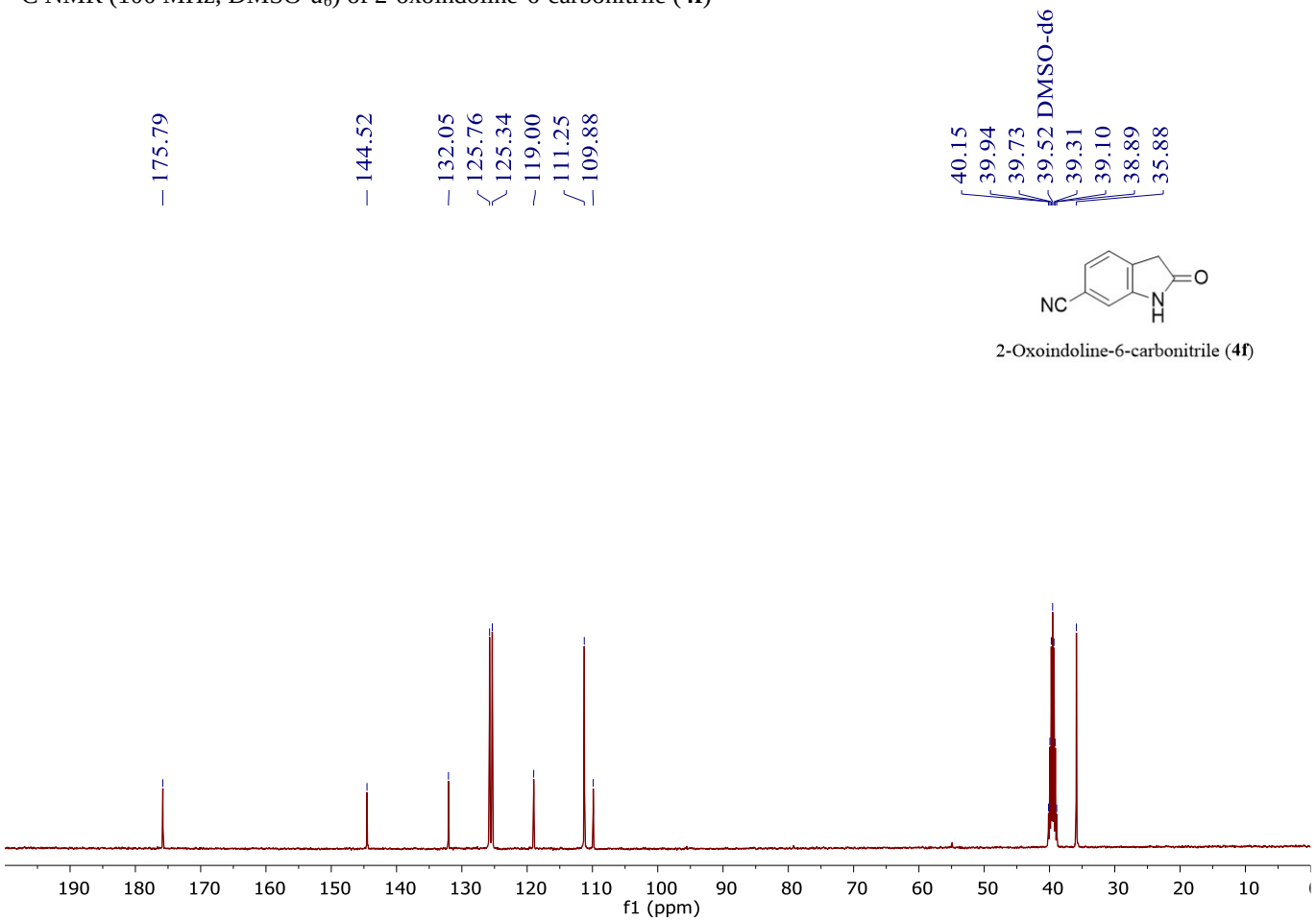
^{19}F NMR (376 MHz, DMSO-d_6) of 6-fluoroindolin-2-one (**4e**)



^{1}H NMR (400 MHz, DMSO-d_6) of 2-oxoindoline-6-carbonitrile (**4f**)

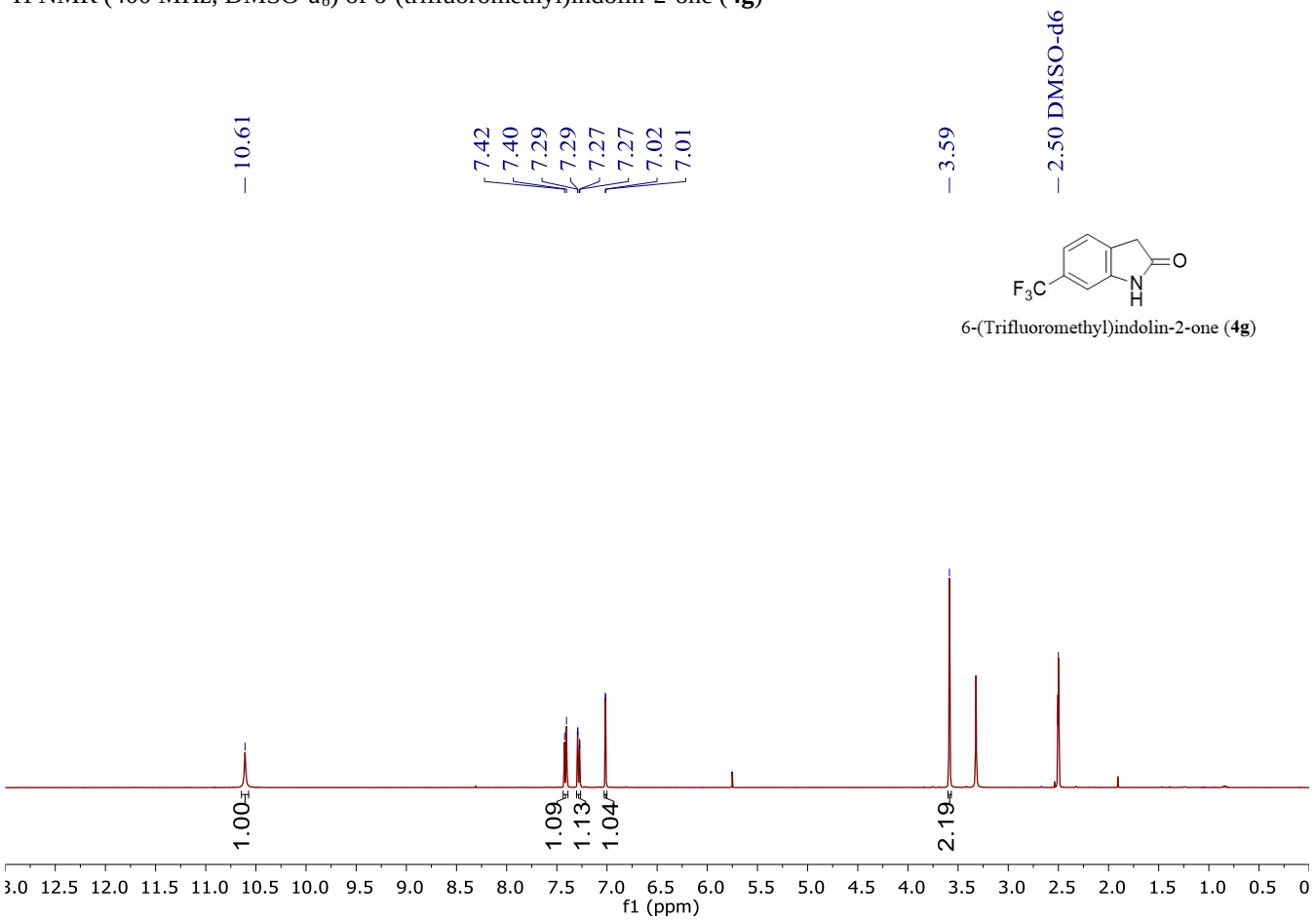


^{13}C NMR (100 MHz, DMSO-d_6) of 2-oxoindoline-6-carbonitrile (**4f**)



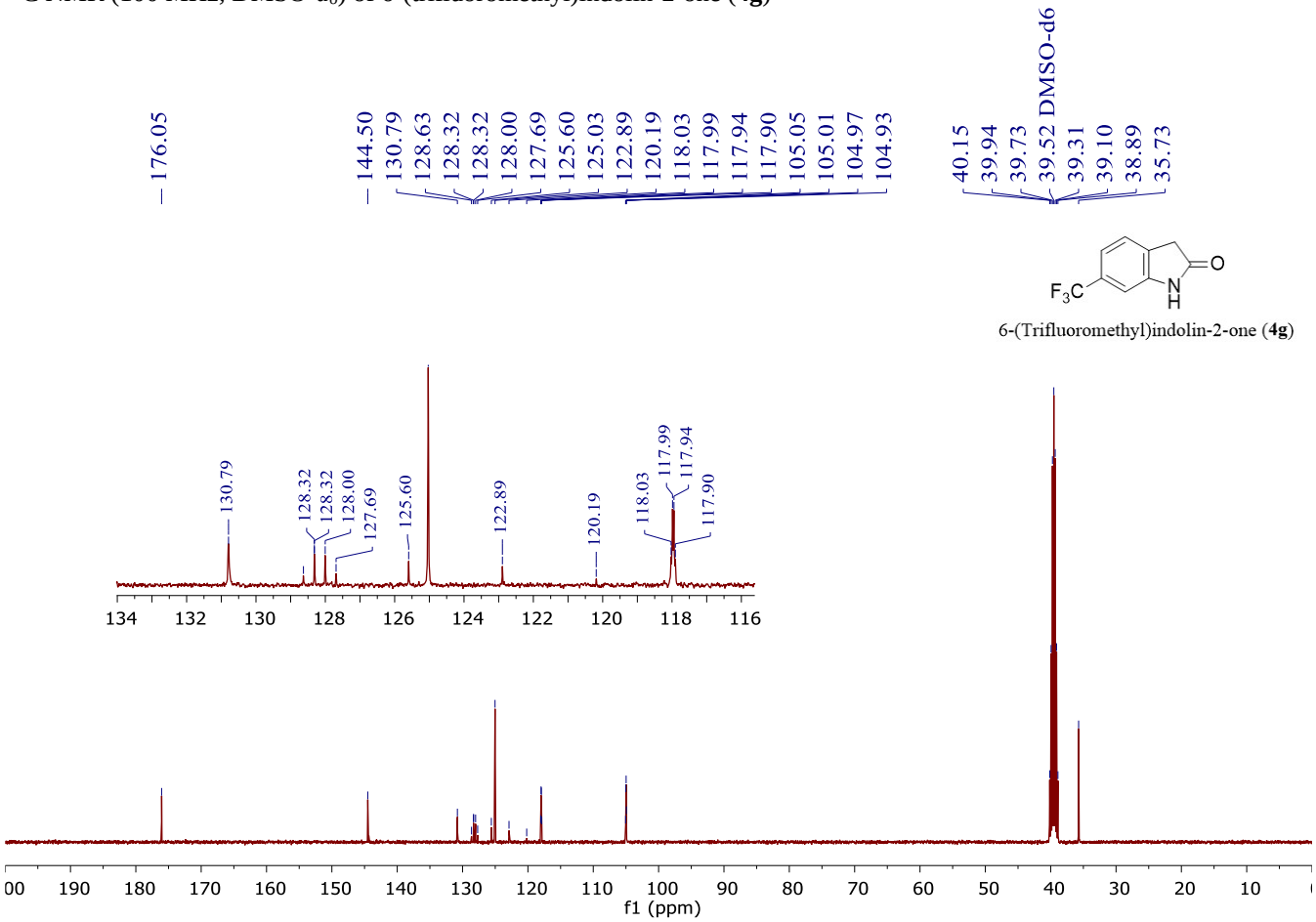
2-Oxoindoline-6-carbonitrile (**4f**)

^{1}H NMR (400 MHz, DMSO-d_6) of 6-(trifluoromethyl)indolin-2-one (**4g**)

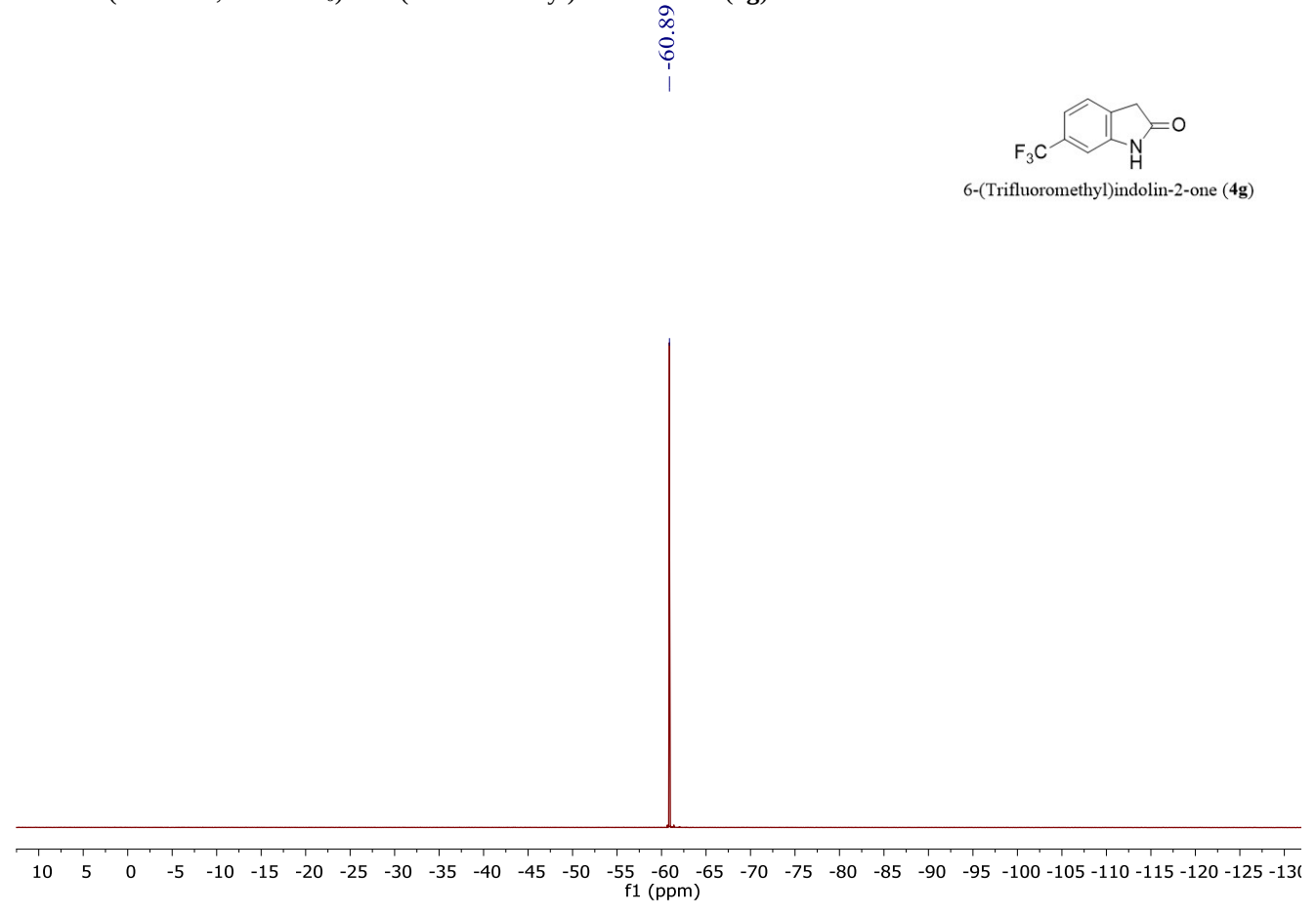


6-(Trifluoromethyl)indolin-2-one (**4g**)

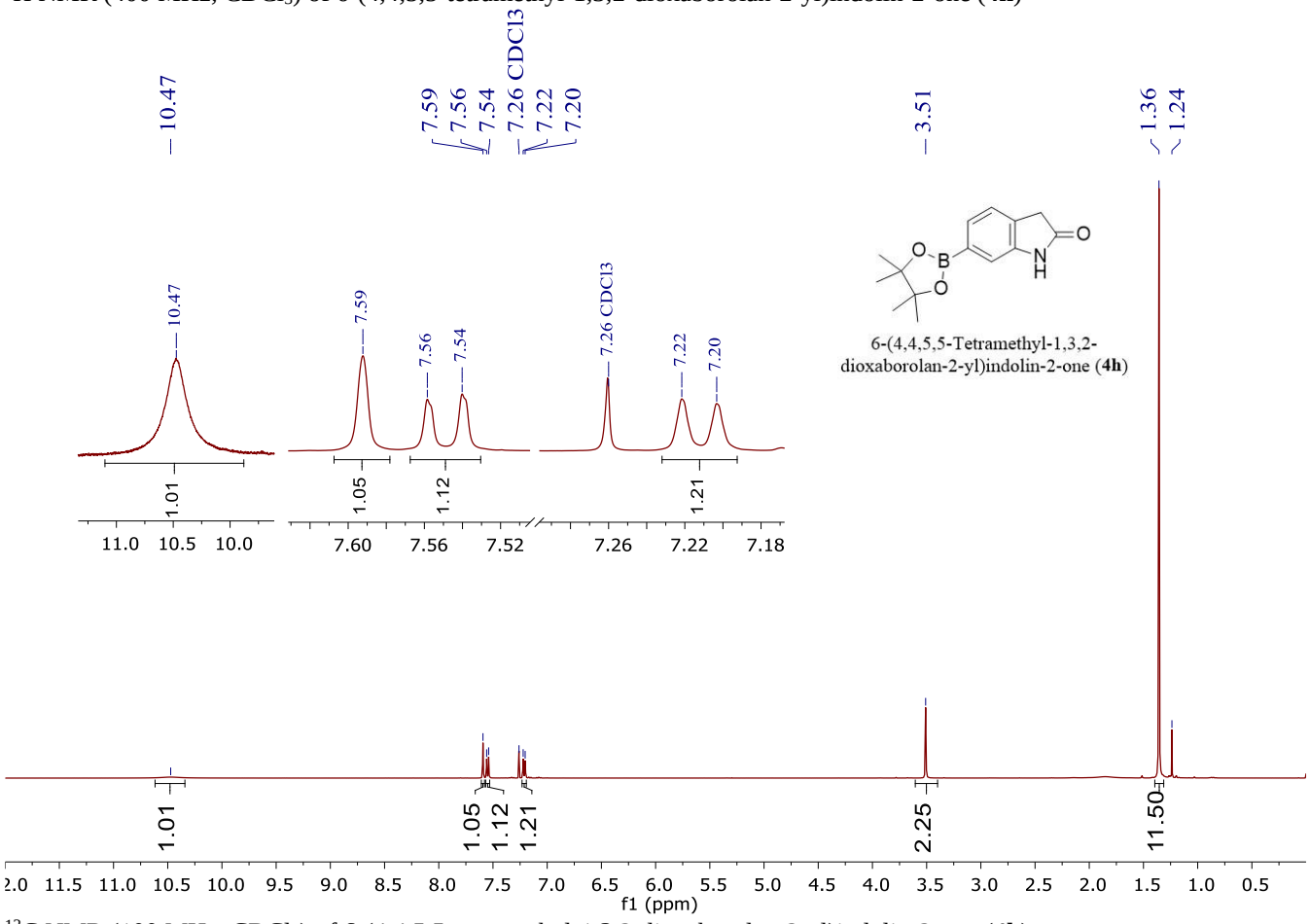
^{13}C NMR (100 MHz, DMSO-d_6) of 6-(trifluoromethyl)indolin-2-one (**4g**)



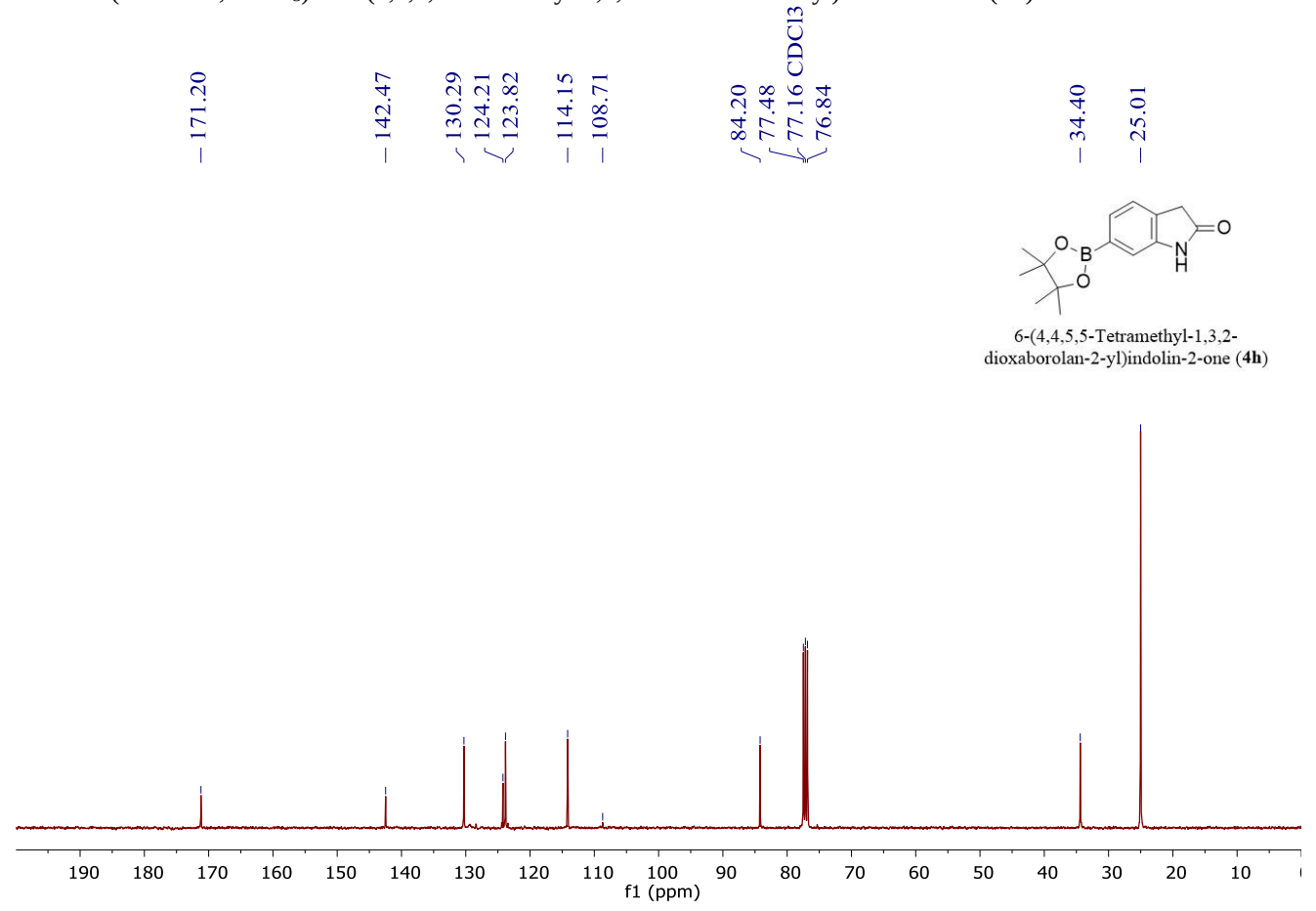
^{19}F NMR (376 MHz, DMSO-d_6) of 6-(trifluoromethyl)indolin-2-one (**4g**)



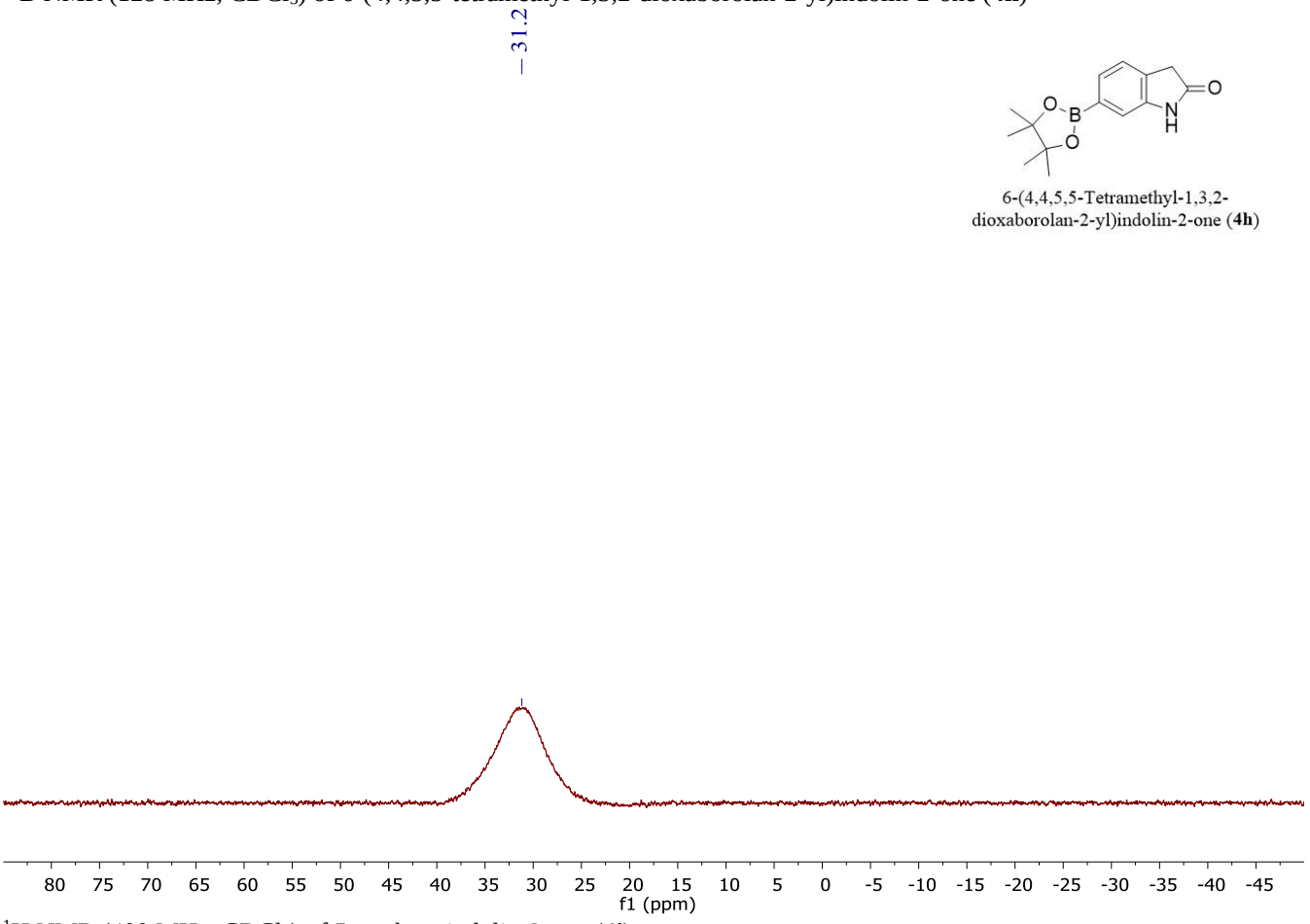
^{1}H NMR (400 MHz, $CDCl_3$) of 6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)indolin-2-one (**4h**)



^{13}C NMR (100 MHz, $CDCl_3$) of 6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)indolin-2-one (**4h**)

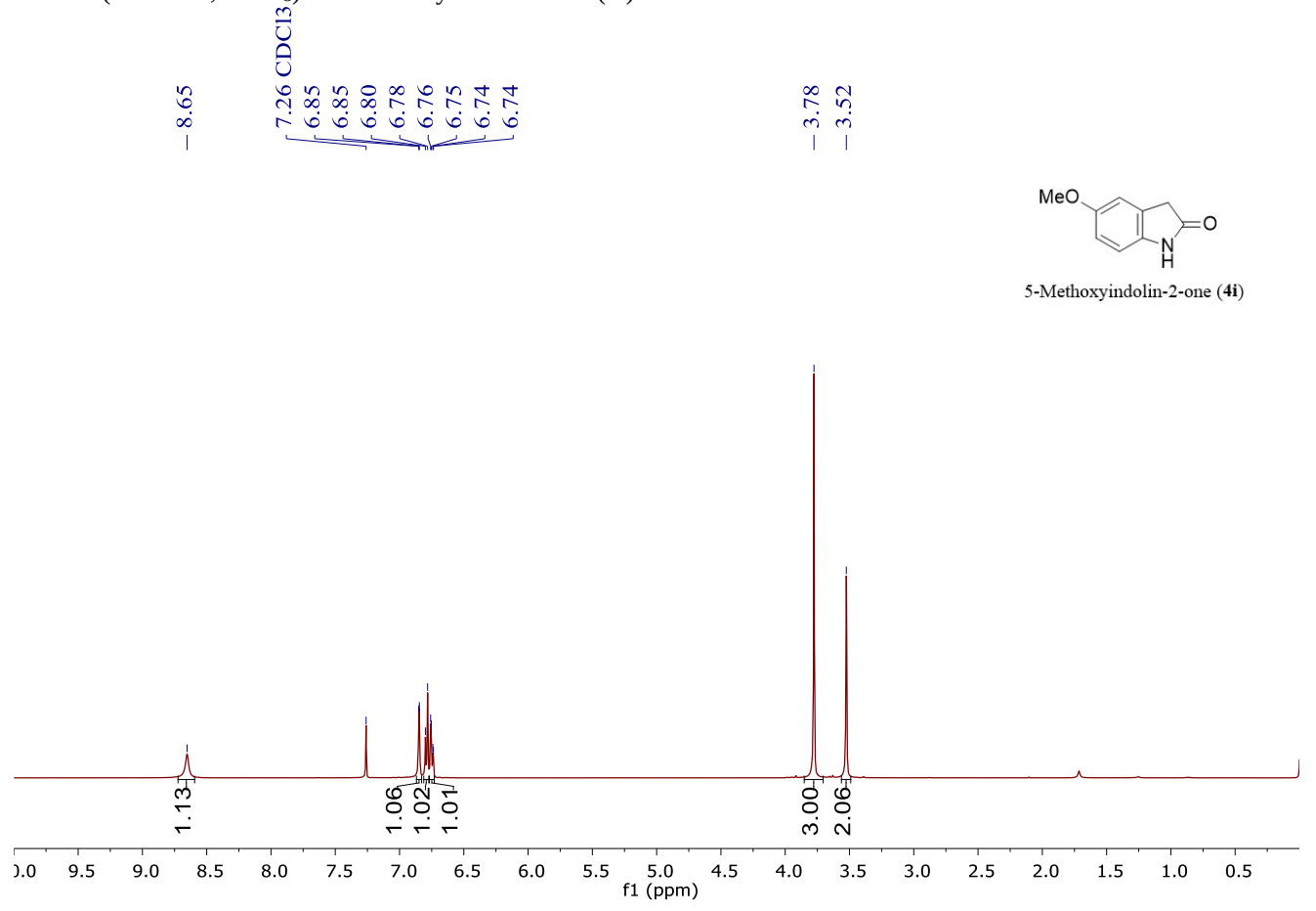


^{11}B NMR (128 MHz, $CDCl_3$) of 6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)indolin-2-one (**4h**)



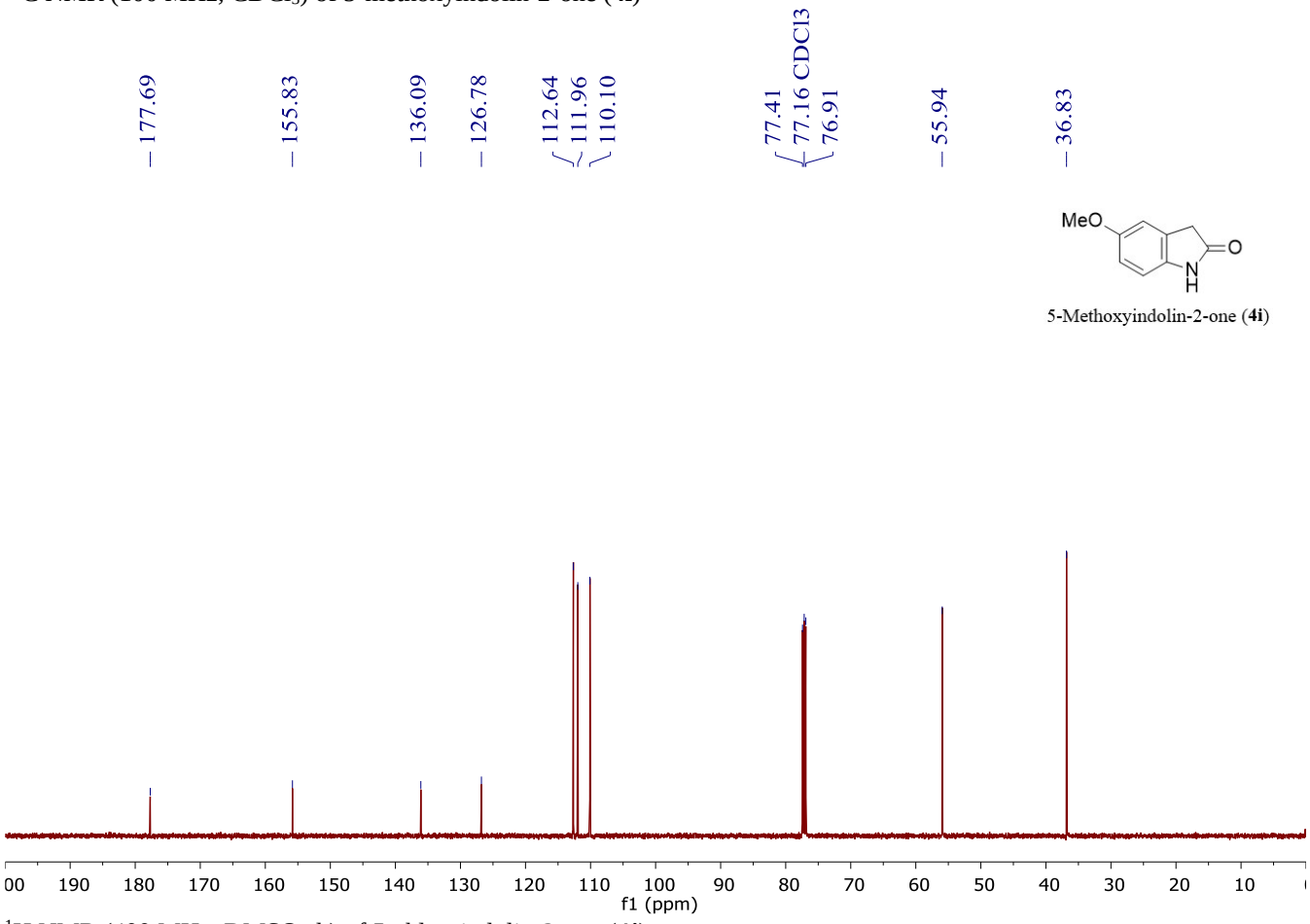
6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)indolin-2-one (**4h**)

^{1}H NMR (400 MHz, $CDCl_3$) of 5-methoxyindolin-2-one (**4i**)



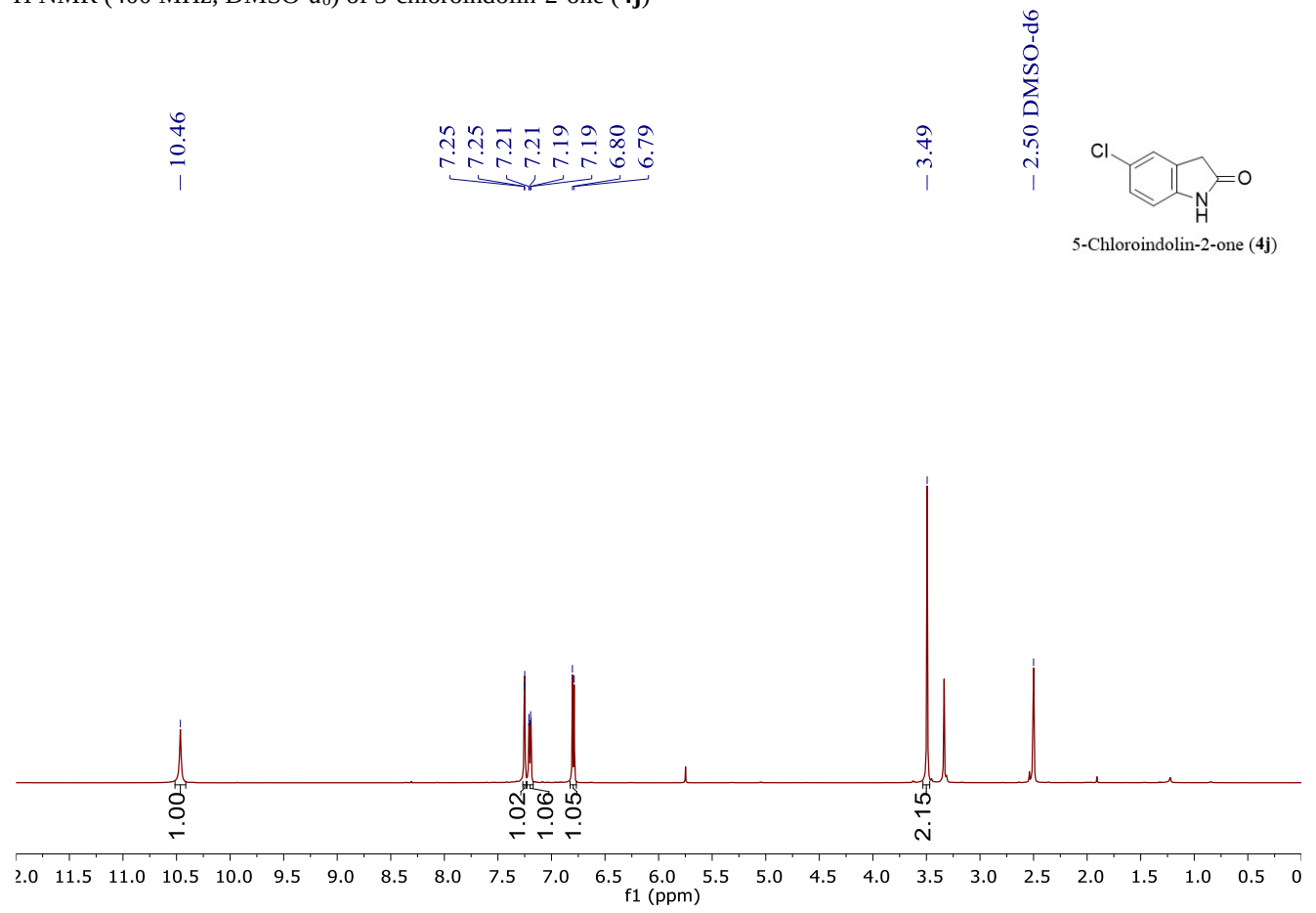
5-Methoxyindolin-2-one (**4i**)

^{13}C NMR (100 MHz, $CDCl_3$) of 5-methoxyindolin-2-one (**4i**)



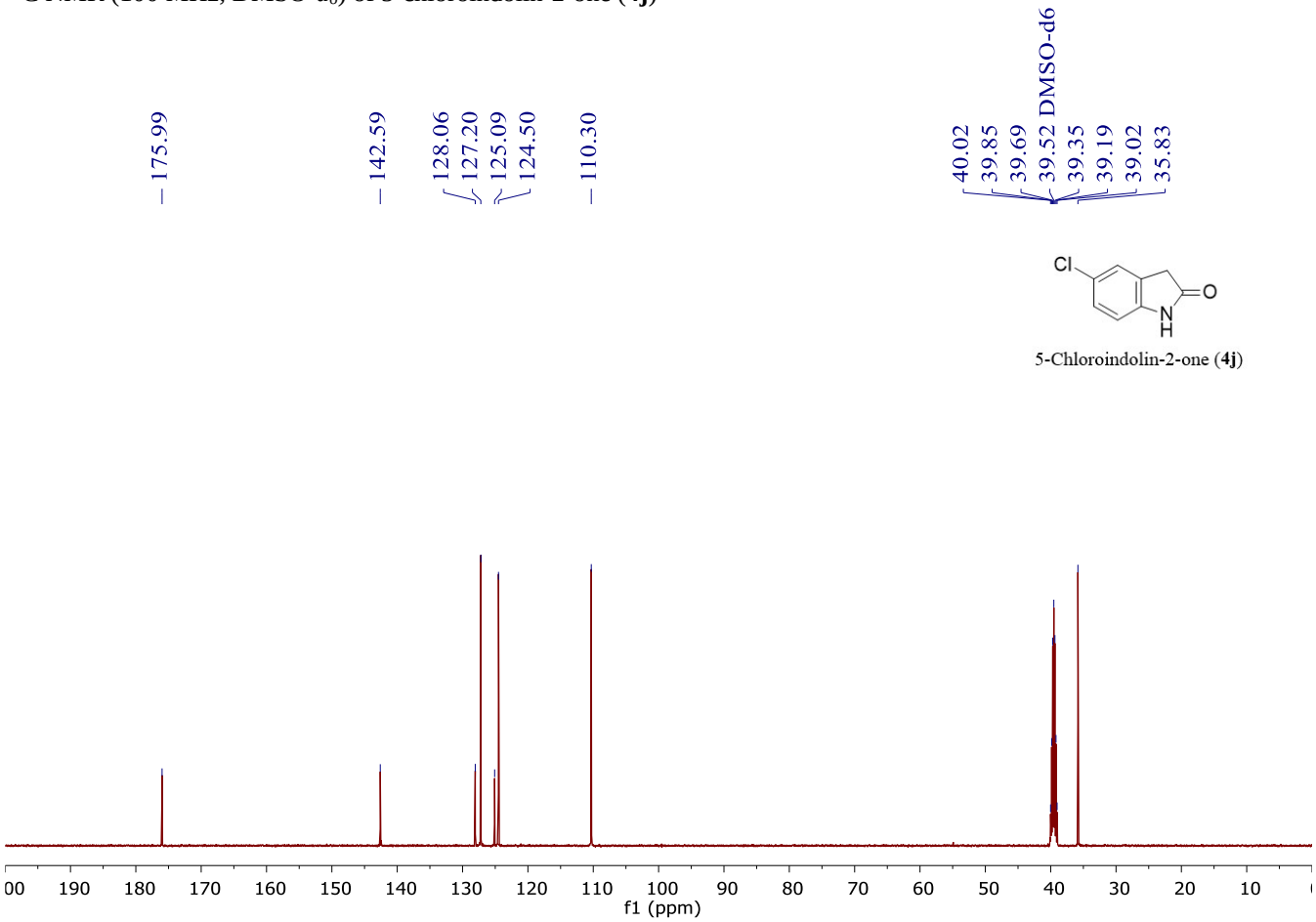
5-Methoxyindolin-2-one (**4i**)

^{1}H NMR (400 MHz, DMSO-d_6) of 5-chloroindolin-2-one (**4j**)

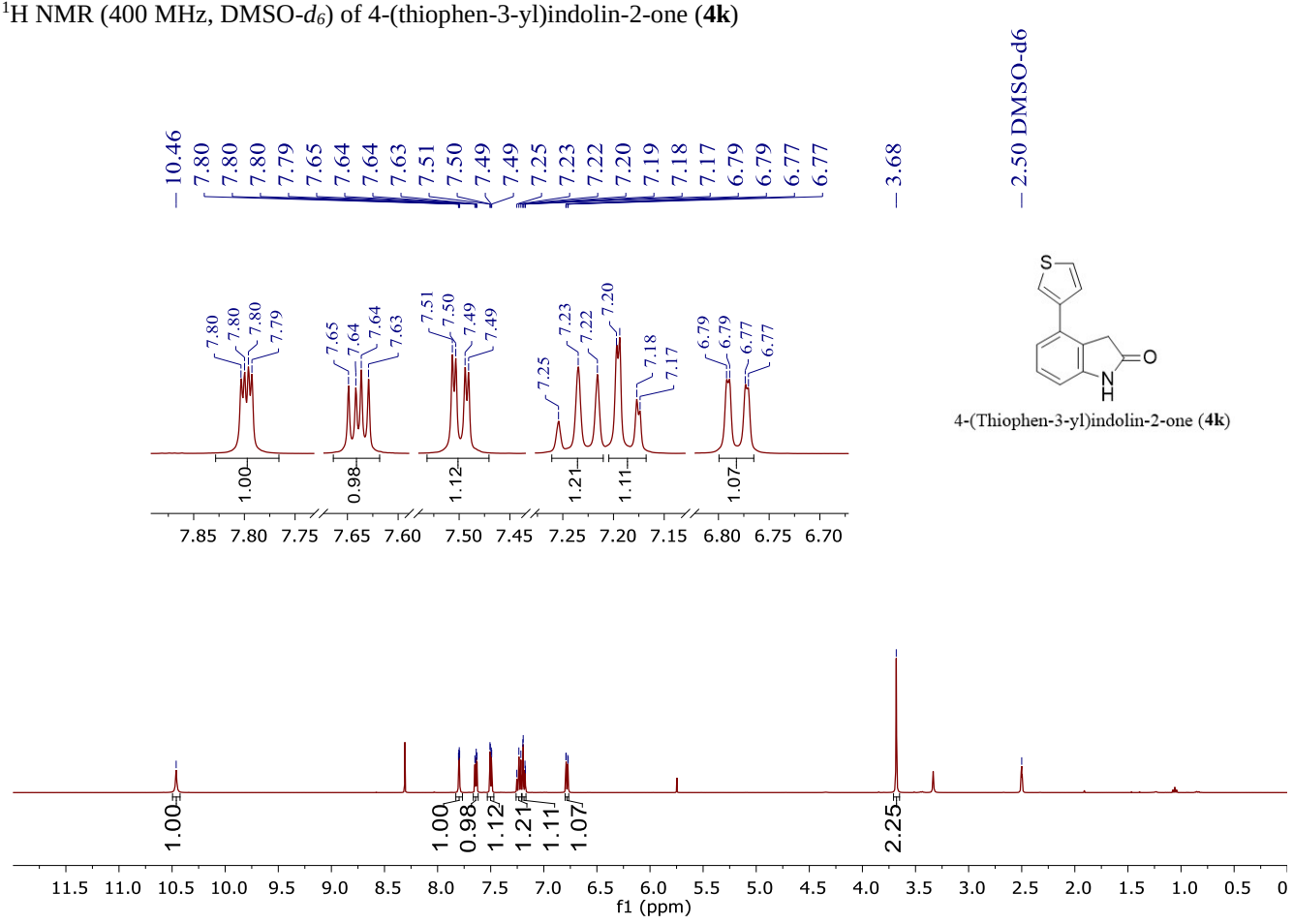


5-Chloroindolin-2-one (**4j**)

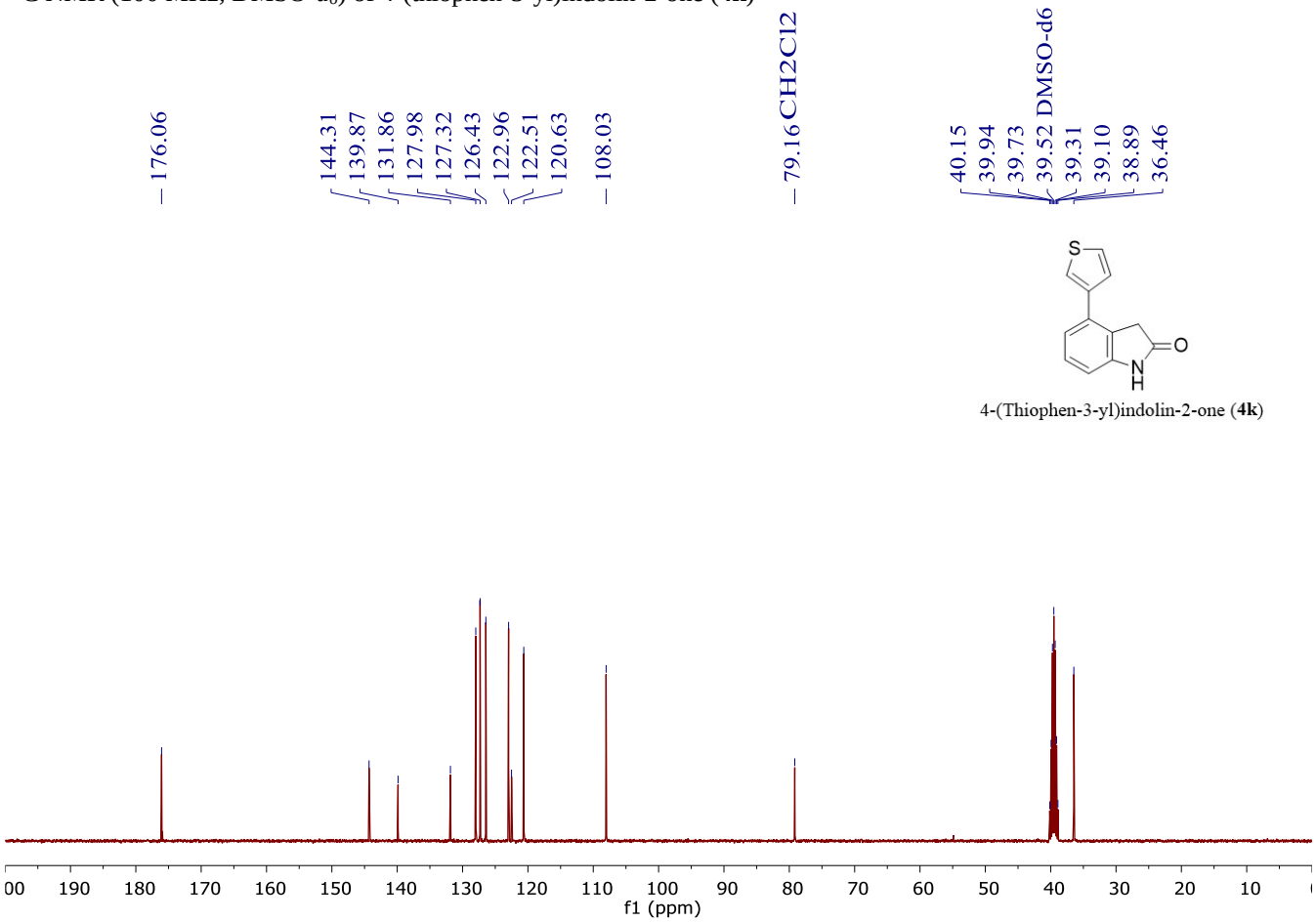
^{13}C NMR (100 MHz, DMSO-d_6) of 5-chloroindolin-2-one (**4j**)



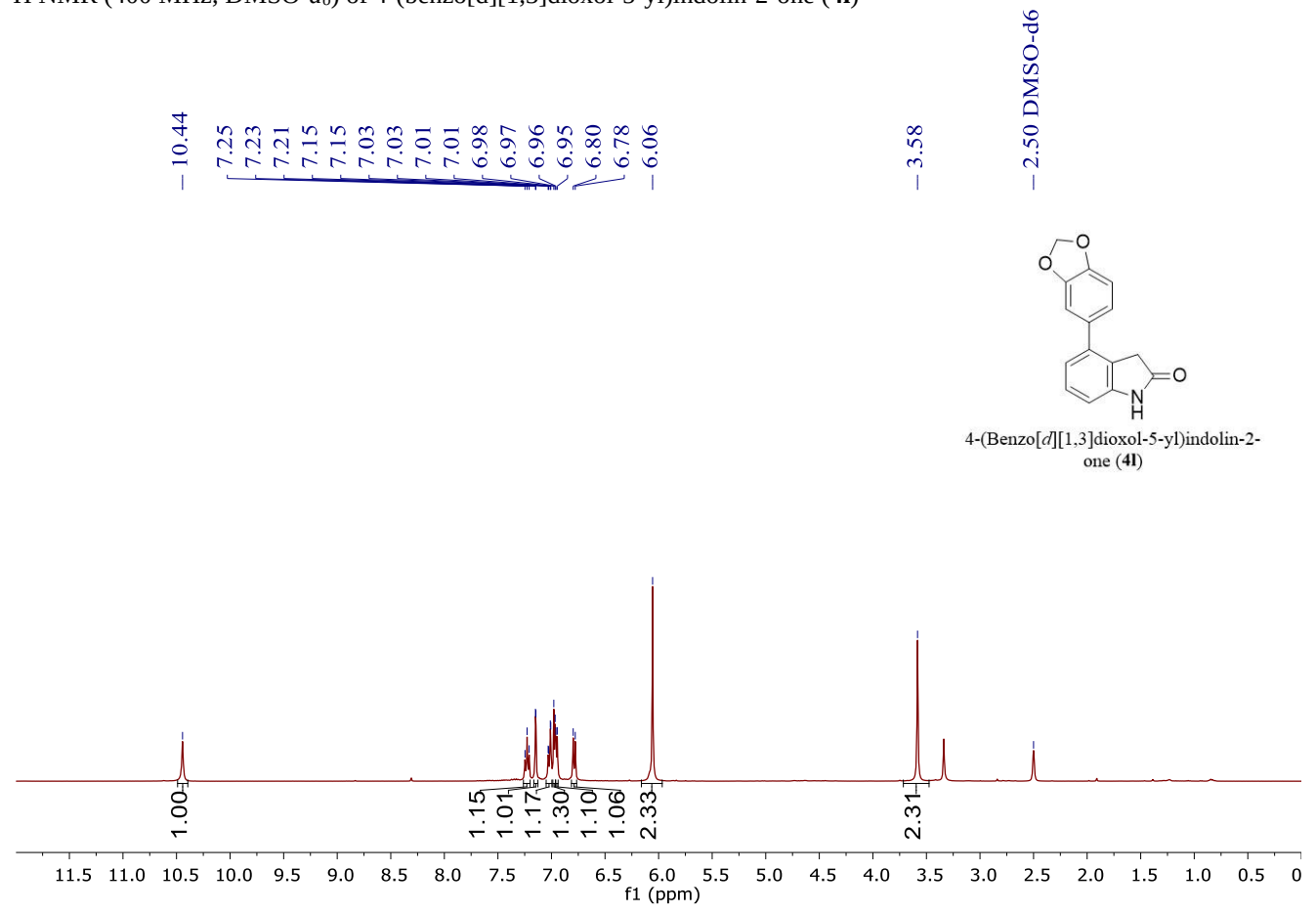
^{1}H NMR (400 MHz, DMSO-d_6) of 4-(thiophen-3-yl)indolin-2-one (**4k**)



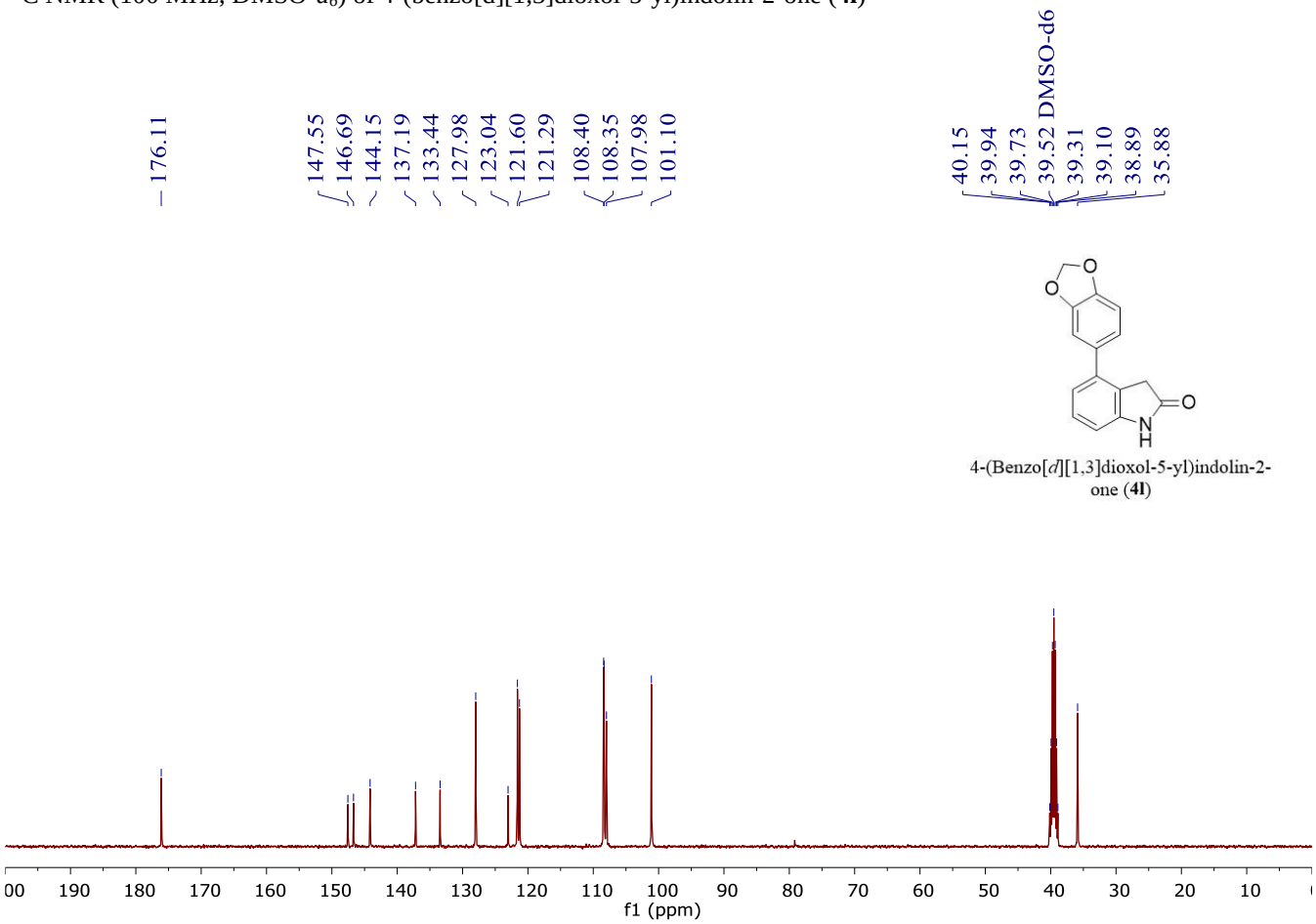
^{13}C NMR (100 MHz, DMSO-d_6) of 4-(thiophen-3-yl)indolin-2-one (**4k**)



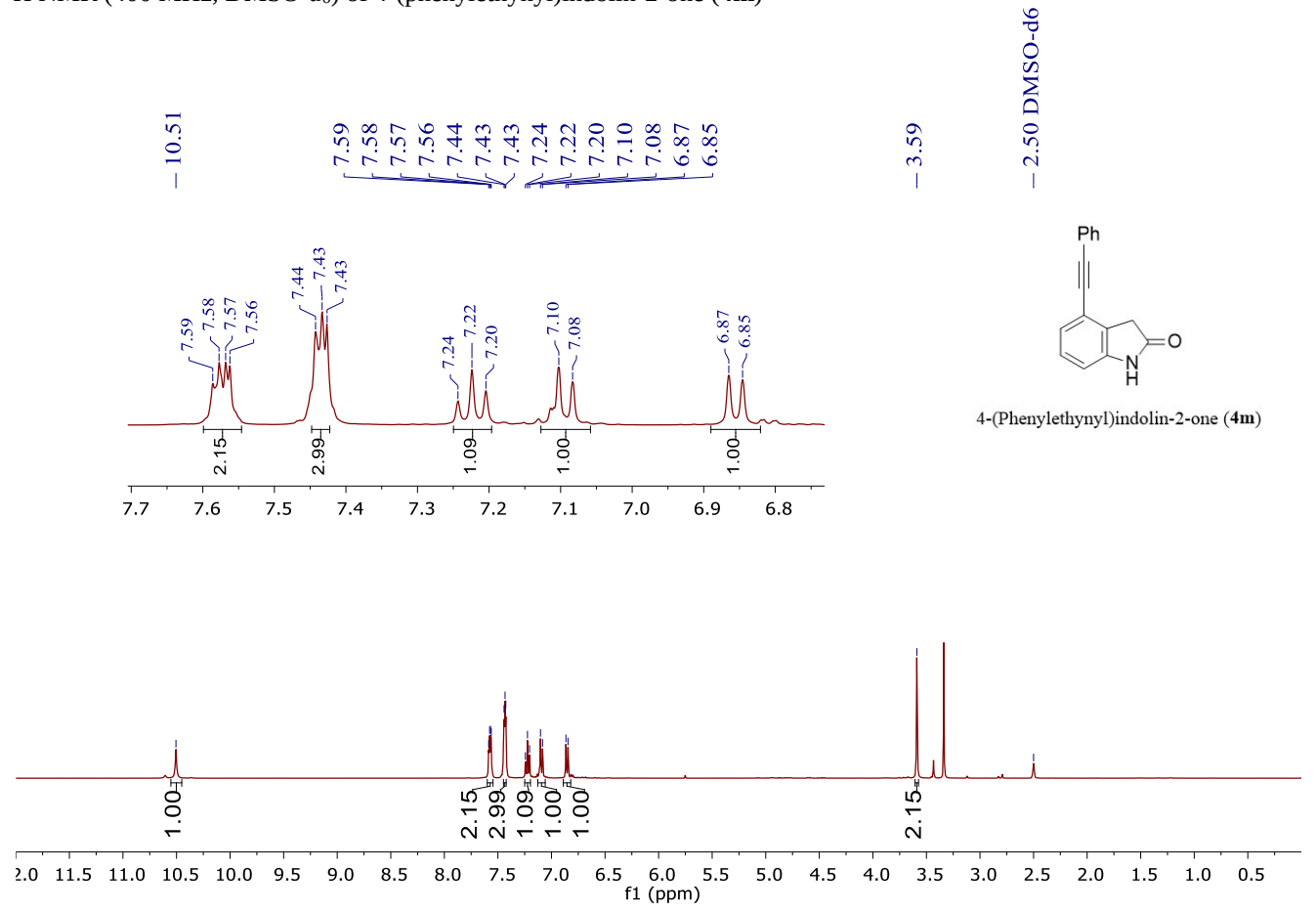
^{1}H NMR (400 MHz, DMSO-d_6) of 4-(benzo[d][1,3]dioxol-5-yl)indolin-2-one (**4l**)



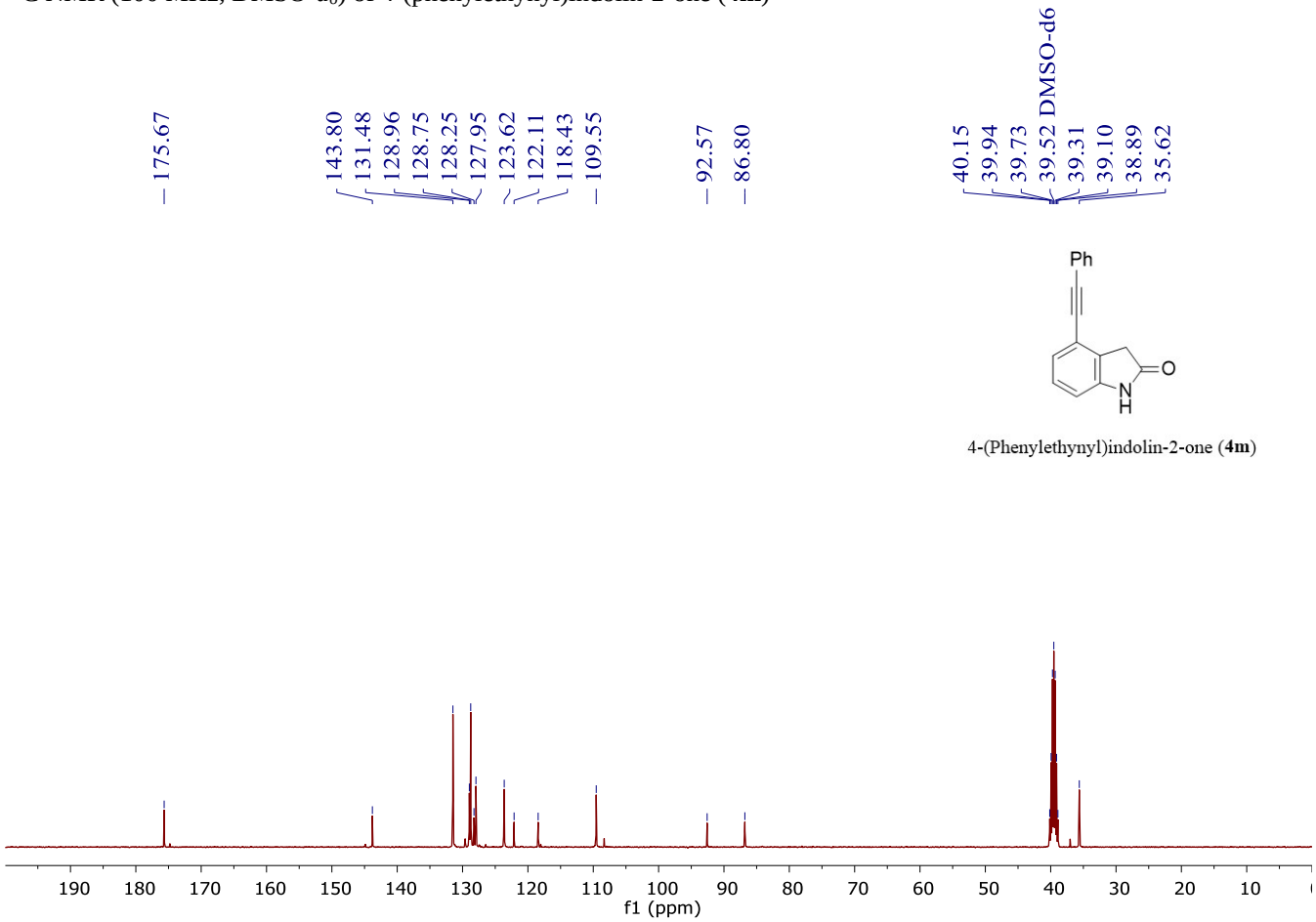
^{13}C NMR (100 MHz, DMSO-d_6) of 4-(benzo[d][1,3]dioxol-5-yl)indolin-2-one (**4l**)



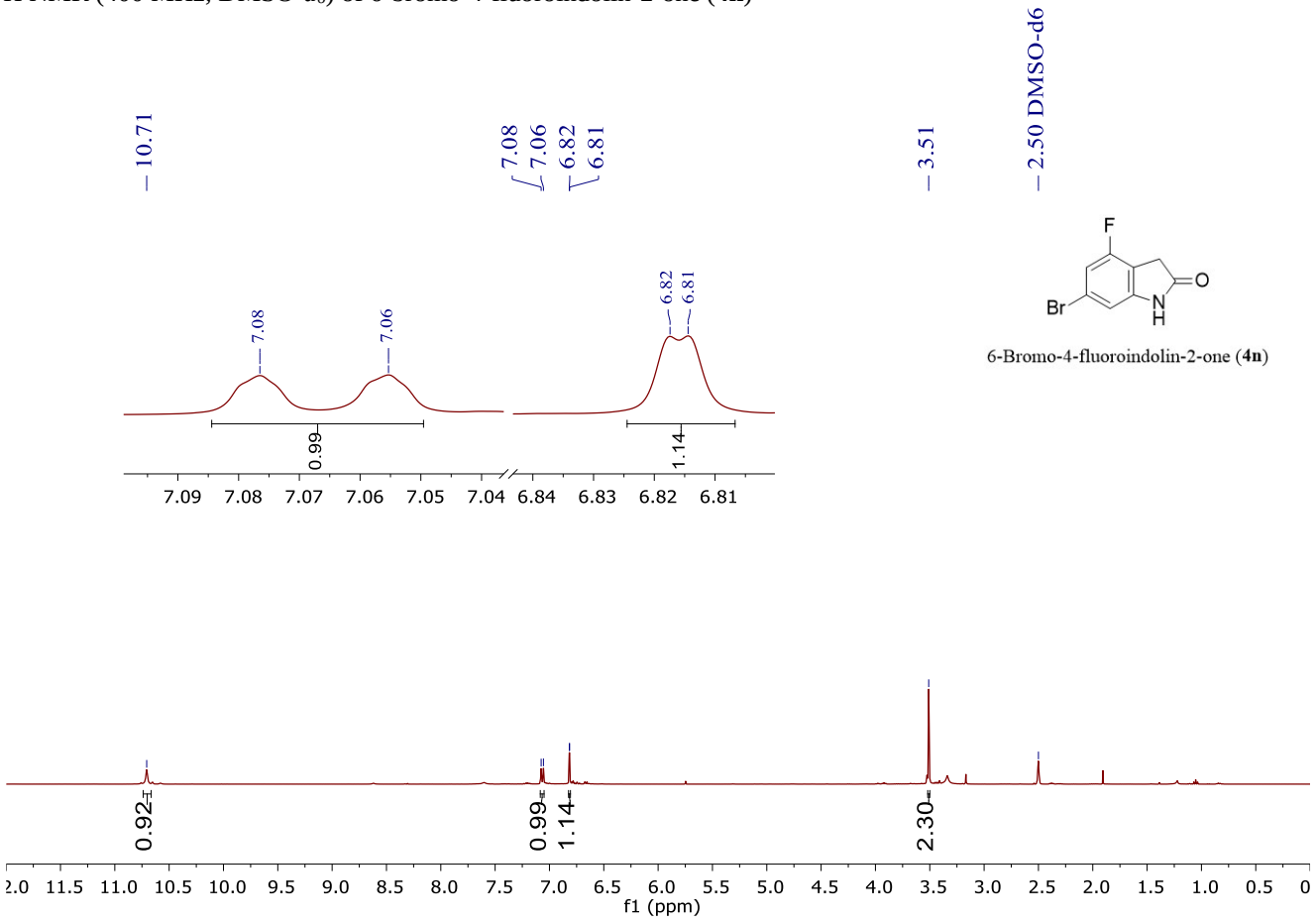
^{1}H NMR (400 MHz, DMSO-d_6) of 4-(phenylethynyl)indolin-2-one (**4m**)



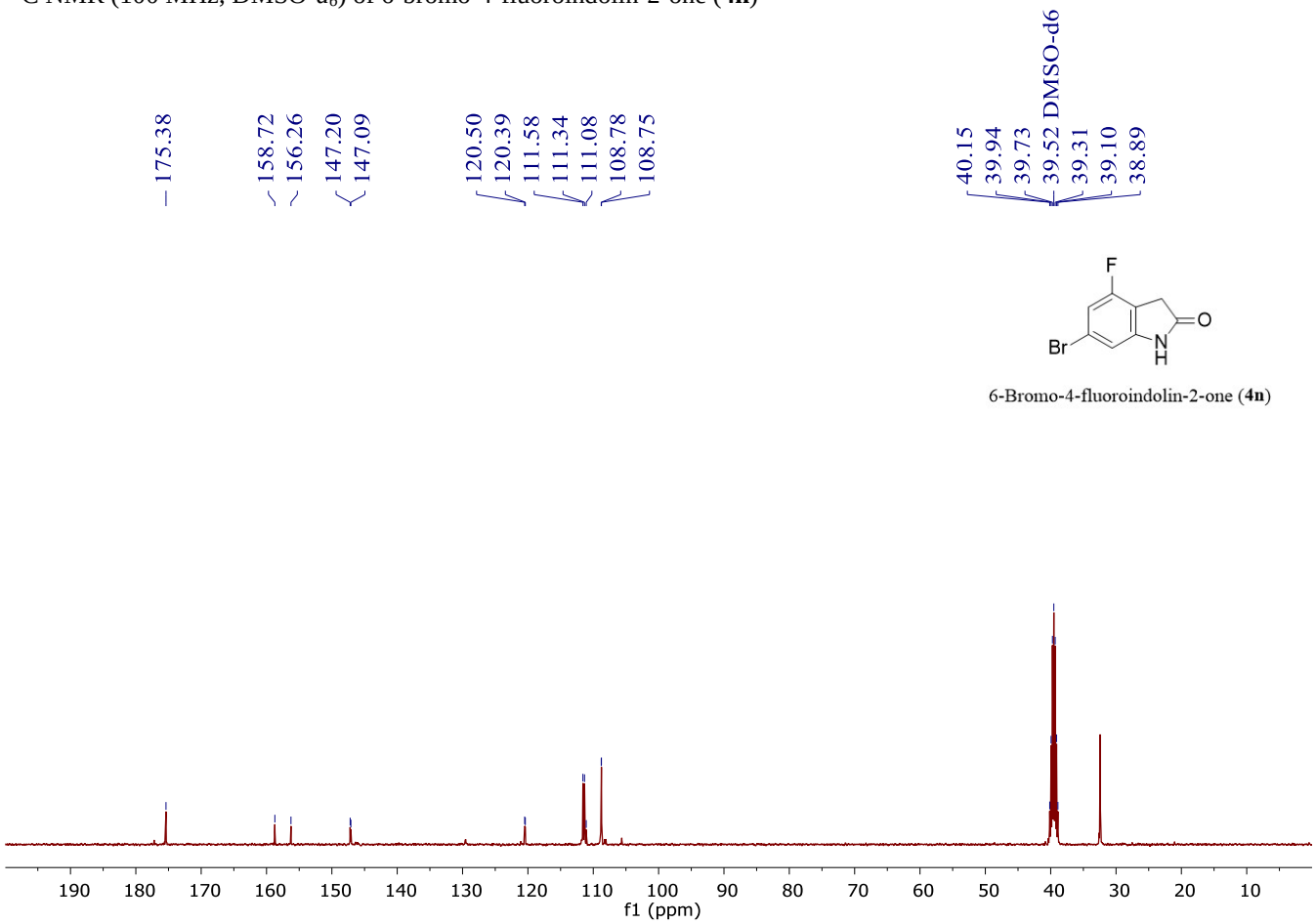
^{13}C NMR (100 MHz, DMSO-d_6) of 4-(phenylethynyl)indolin-2-one (**4m**)



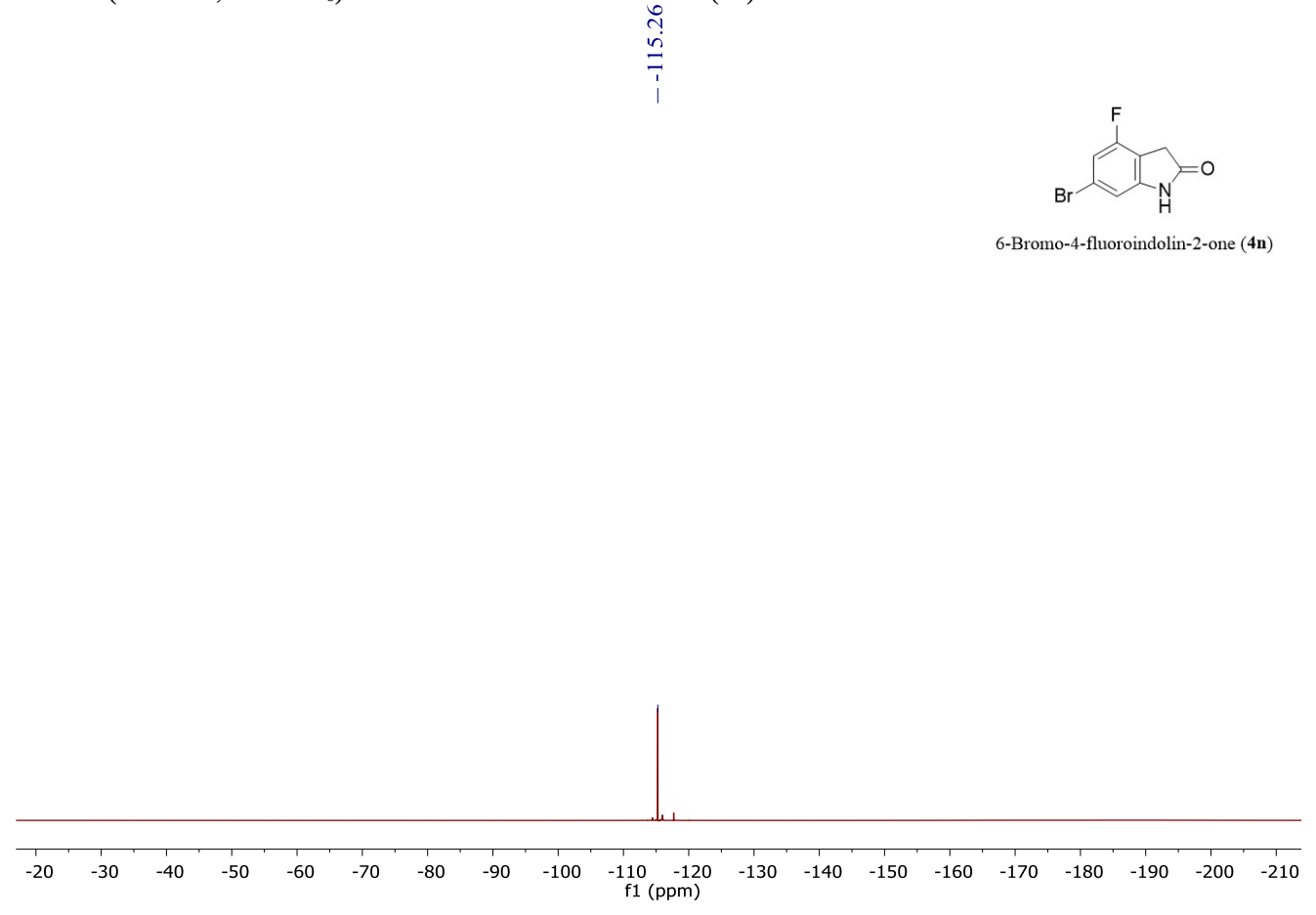
^{1}H NMR (400 MHz, DMSO-d_6) of 6-bromo-4-fluoroindolin-2-one (**4n**)



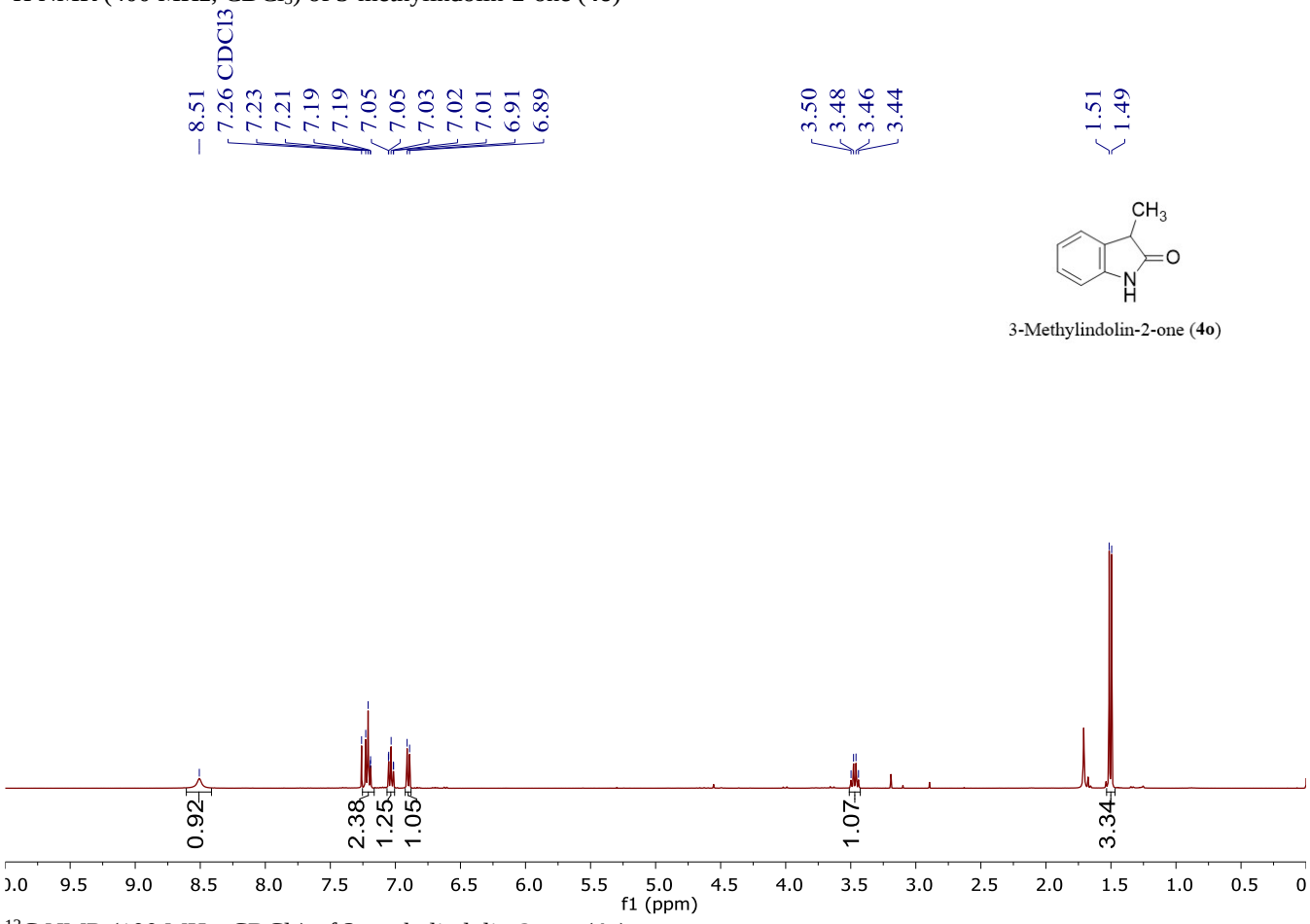
^{13}C NMR (100 MHz, DMSO-d_6) of 6-bromo-4-fluoroindolin-2-one (**4n**)



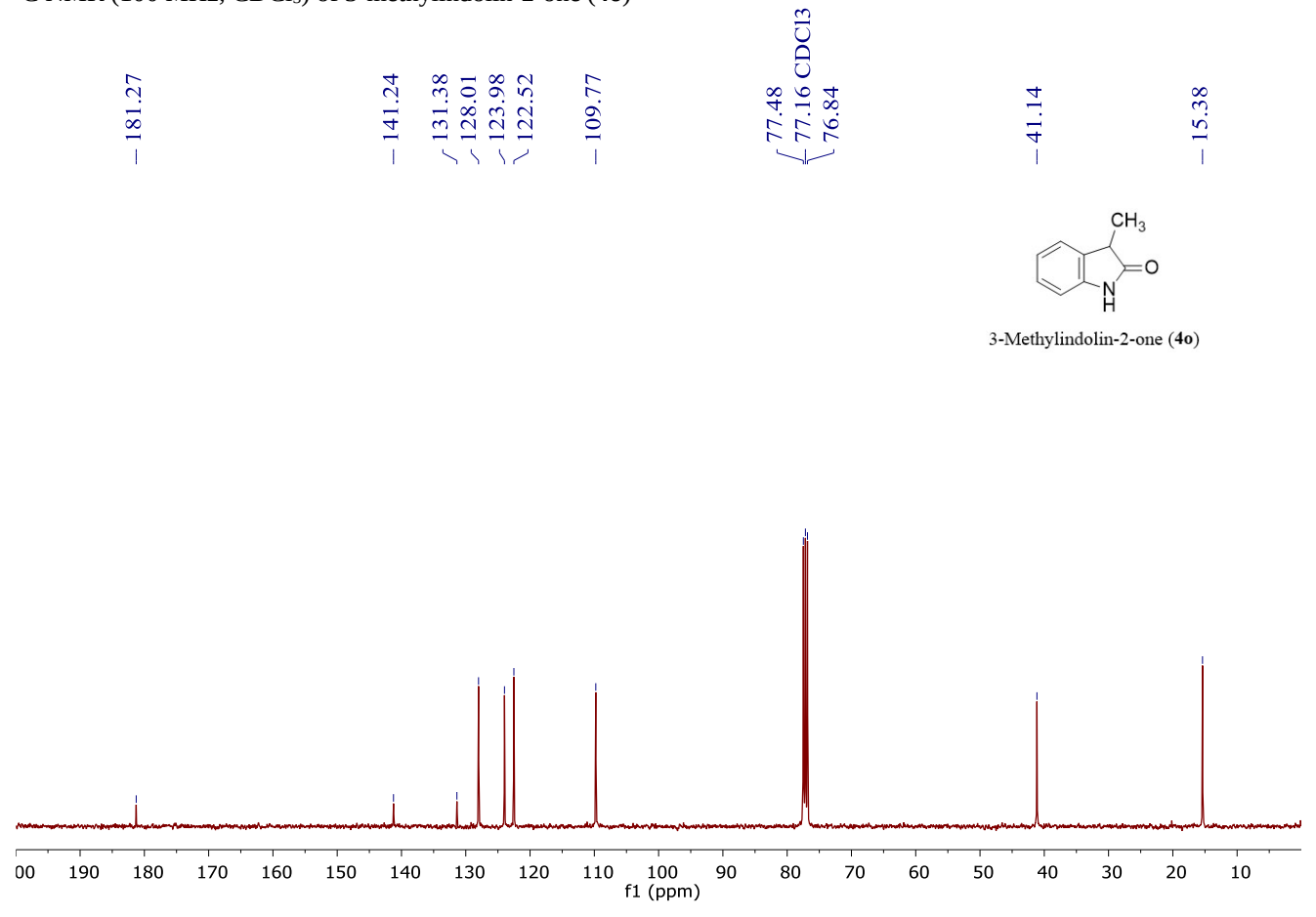
^{19}F NMR (376 MHz, DMSO-d_6) of 6-bromo-4-fluoroindolin-2-one (**4n**)



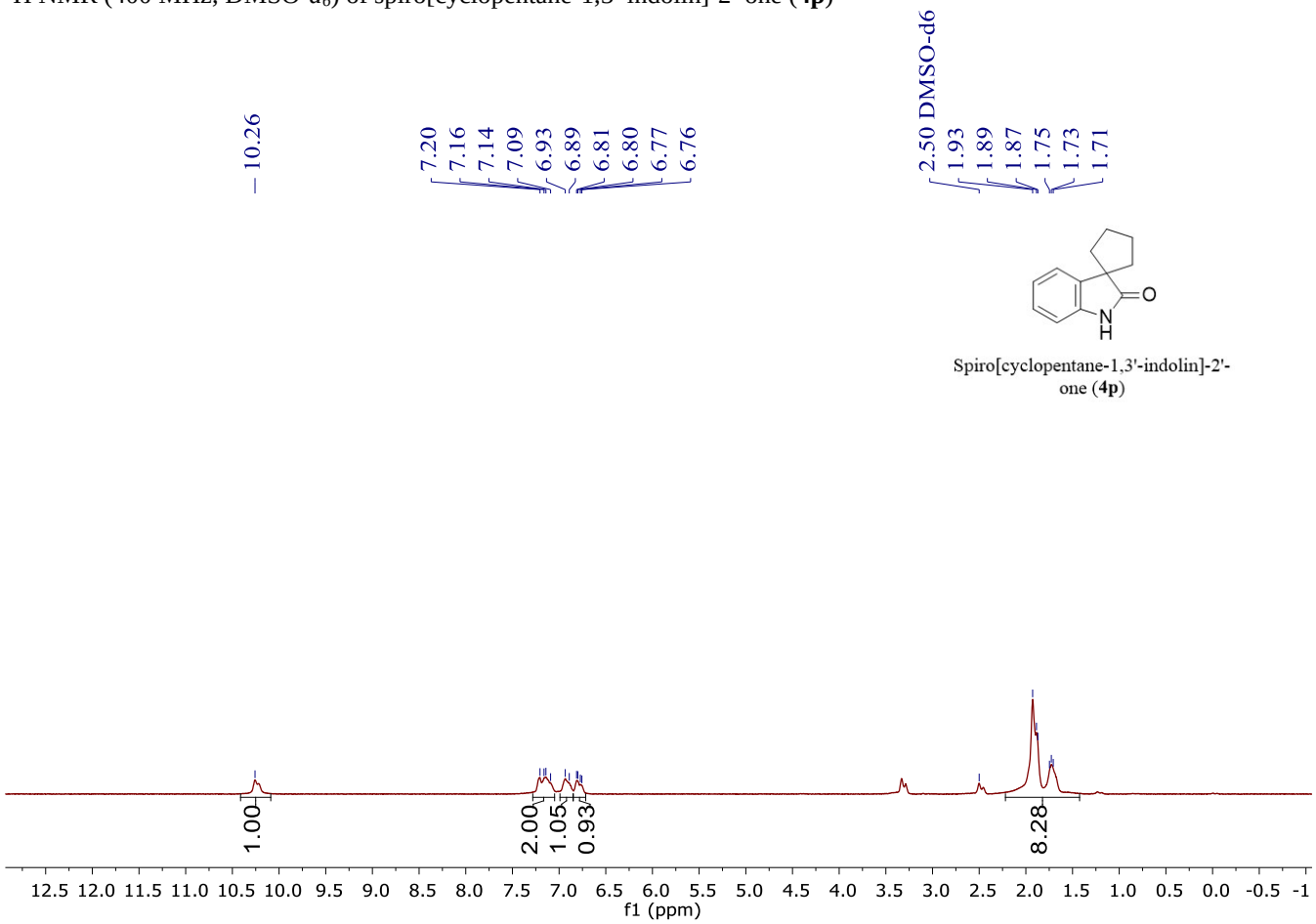
^{1}H NMR (400 MHz, $CDCl_3$) of 3-methylindolin-2-one (**4o**)



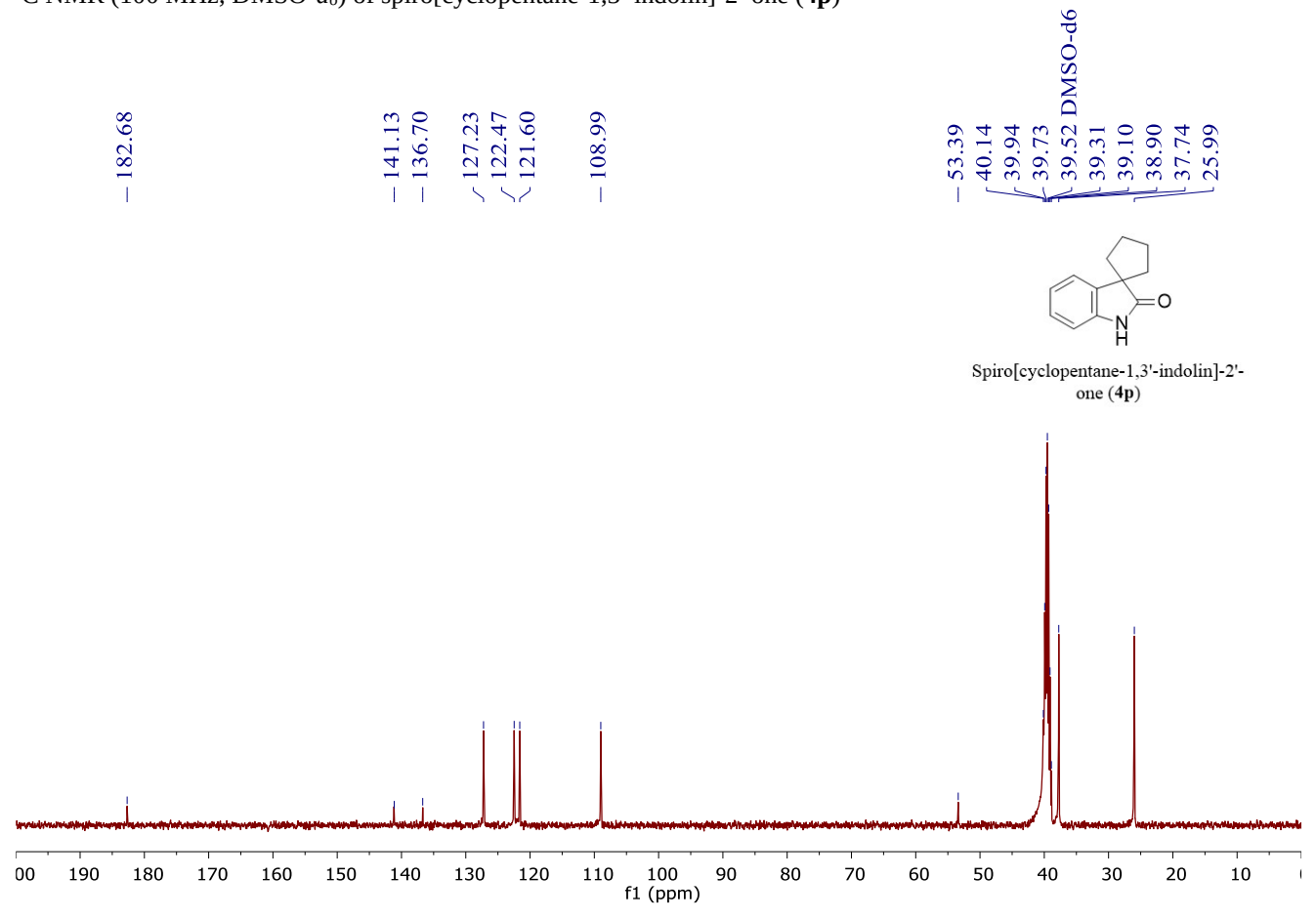
^{13}C NMR (100 MHz, $CDCl_3$) of 3-methylindolin-2-one (**4o**)



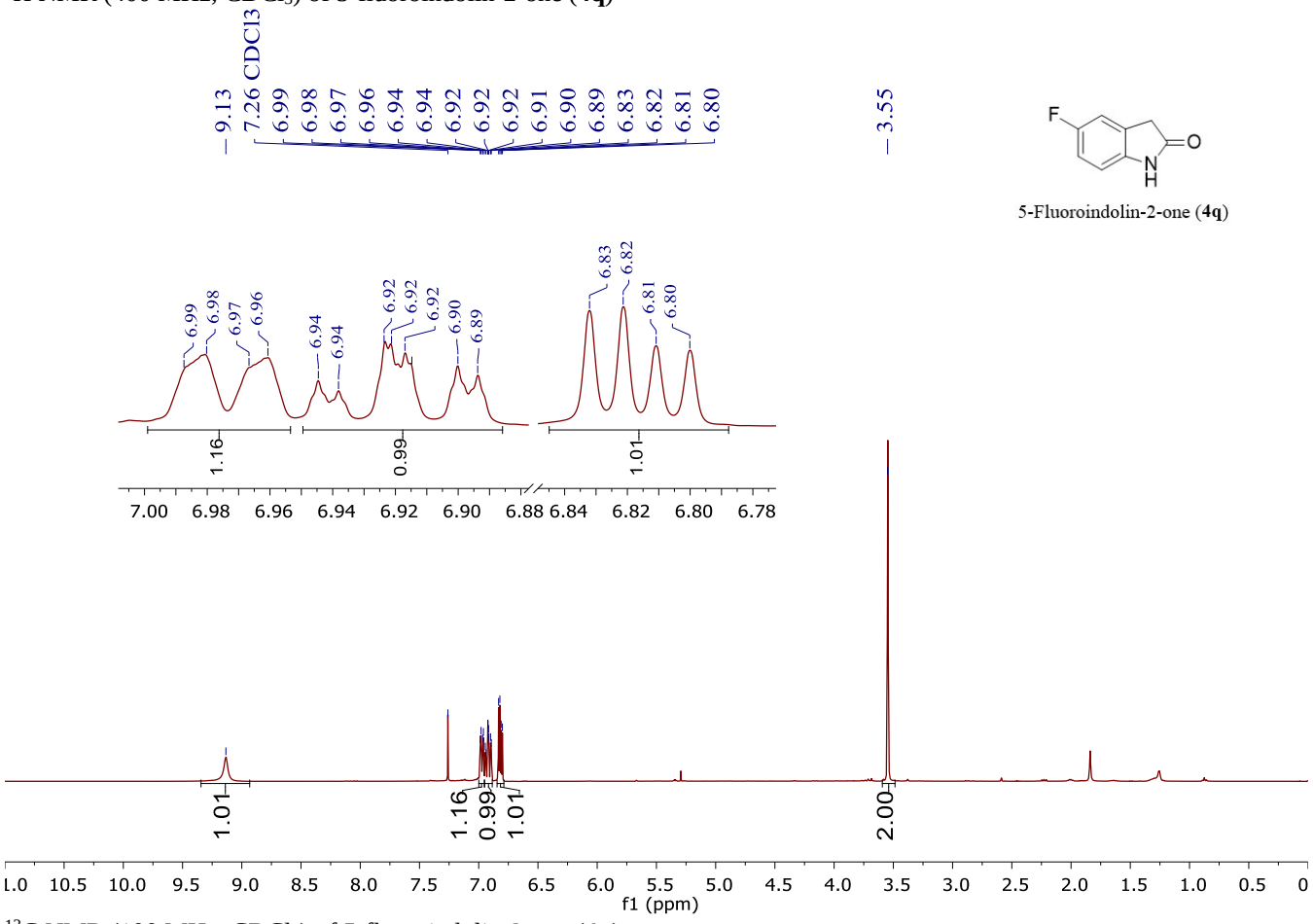
^{1}H NMR (400 MHz, DMSO-d_6) of spiro[cyclopentane-1,3'-indolin]-2'-one (**4p**)



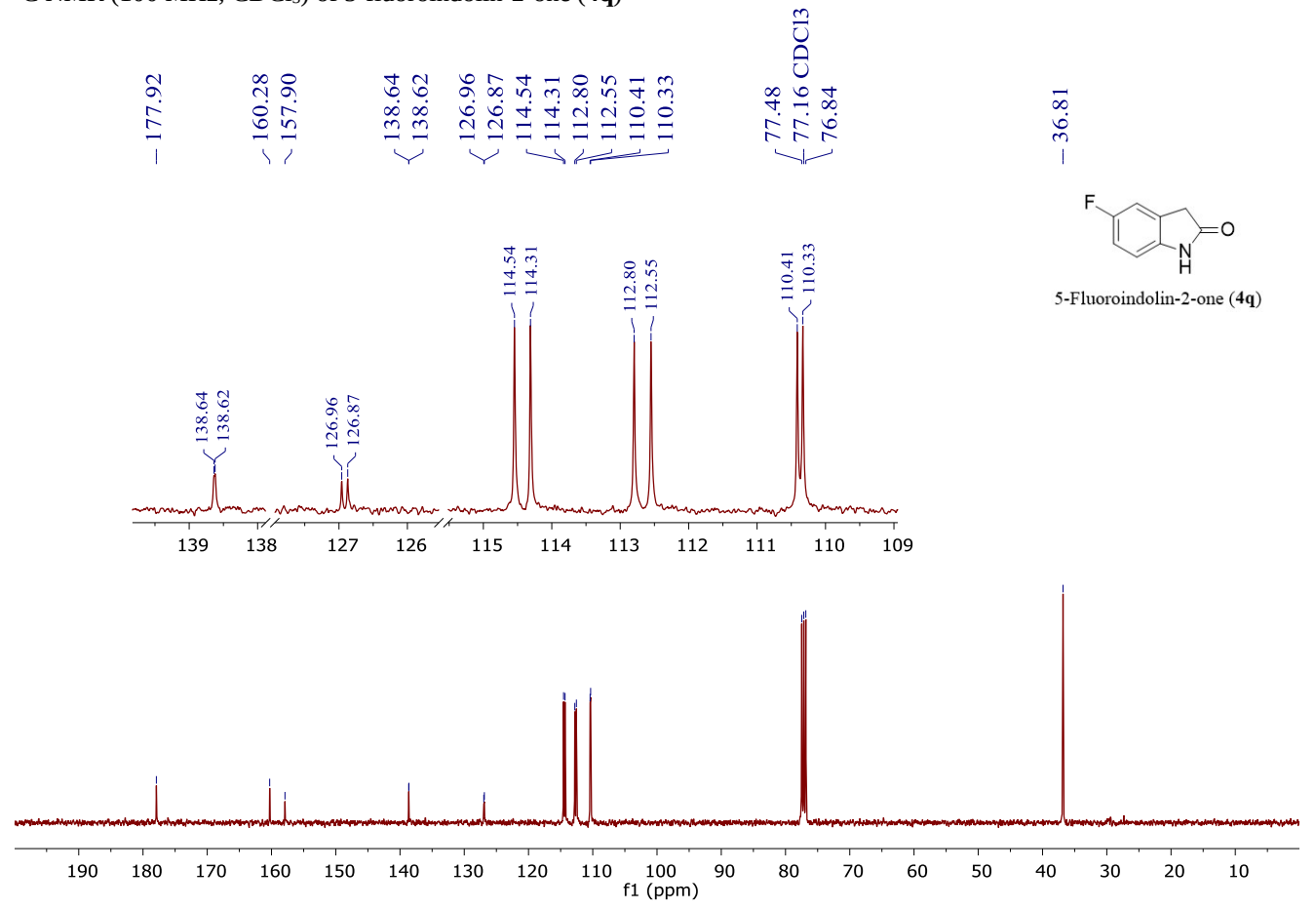
^{13}C NMR (100 MHz, DMSO-d_6) of spiro[cyclopentane-1,3'-indolin]-2'-one (**4p**)



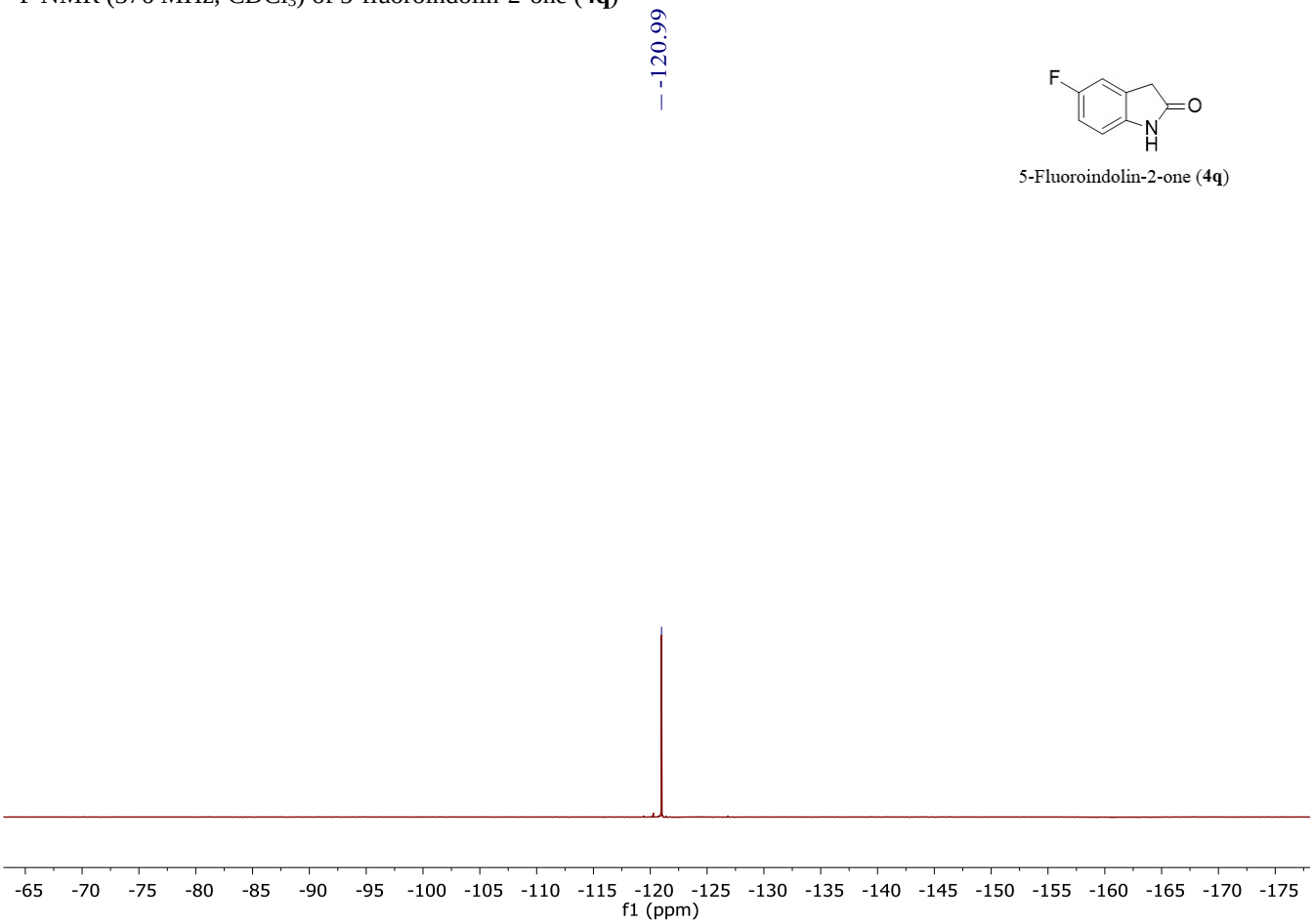
^{1}H NMR (400 MHz, $CDCl_3$) of 5-fluoroindolin-2-one (**4q**)



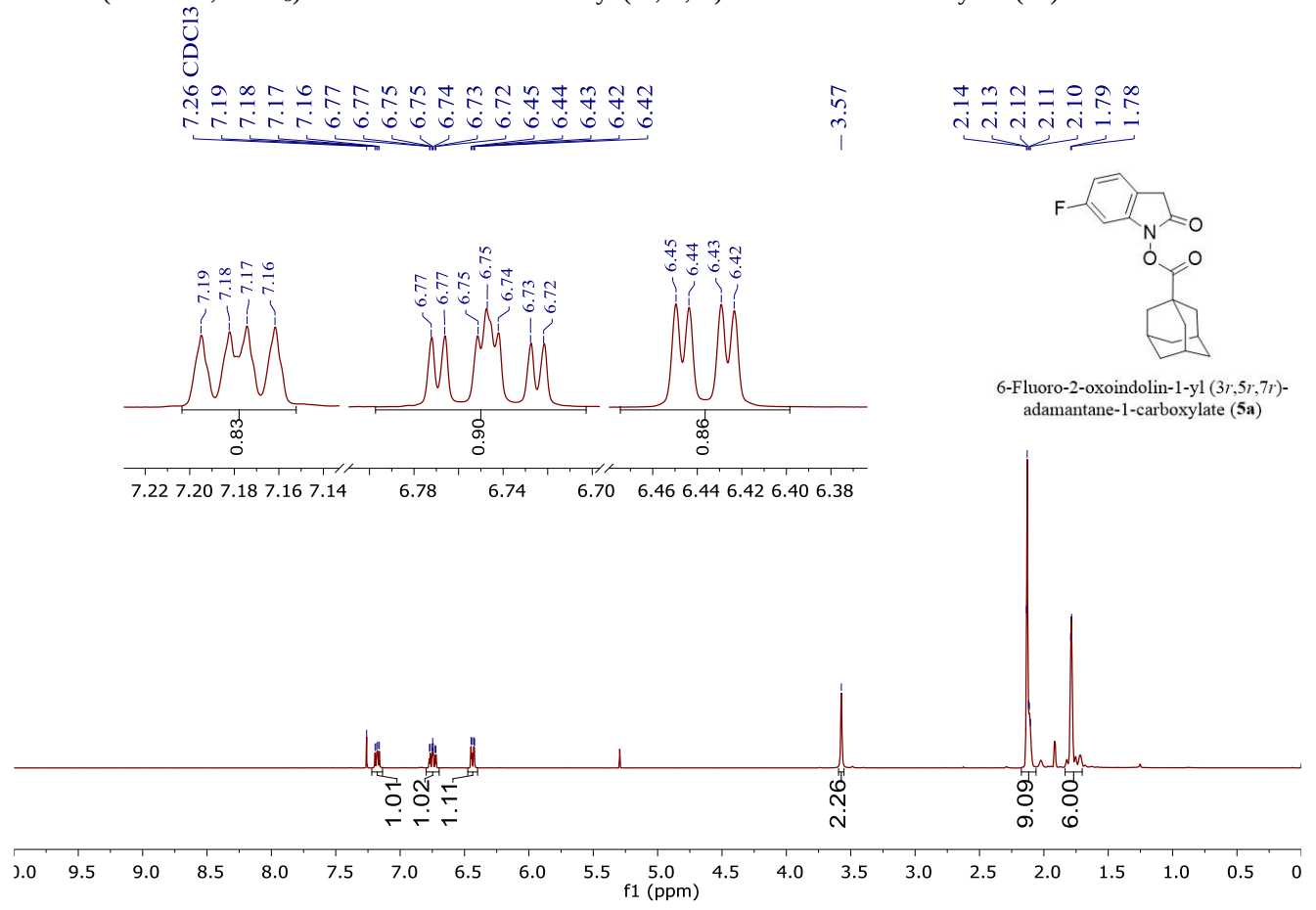
^{13}C NMR (100 MHz, $CDCl_3$) of 5-fluoroindolin-2-one (**4q**)



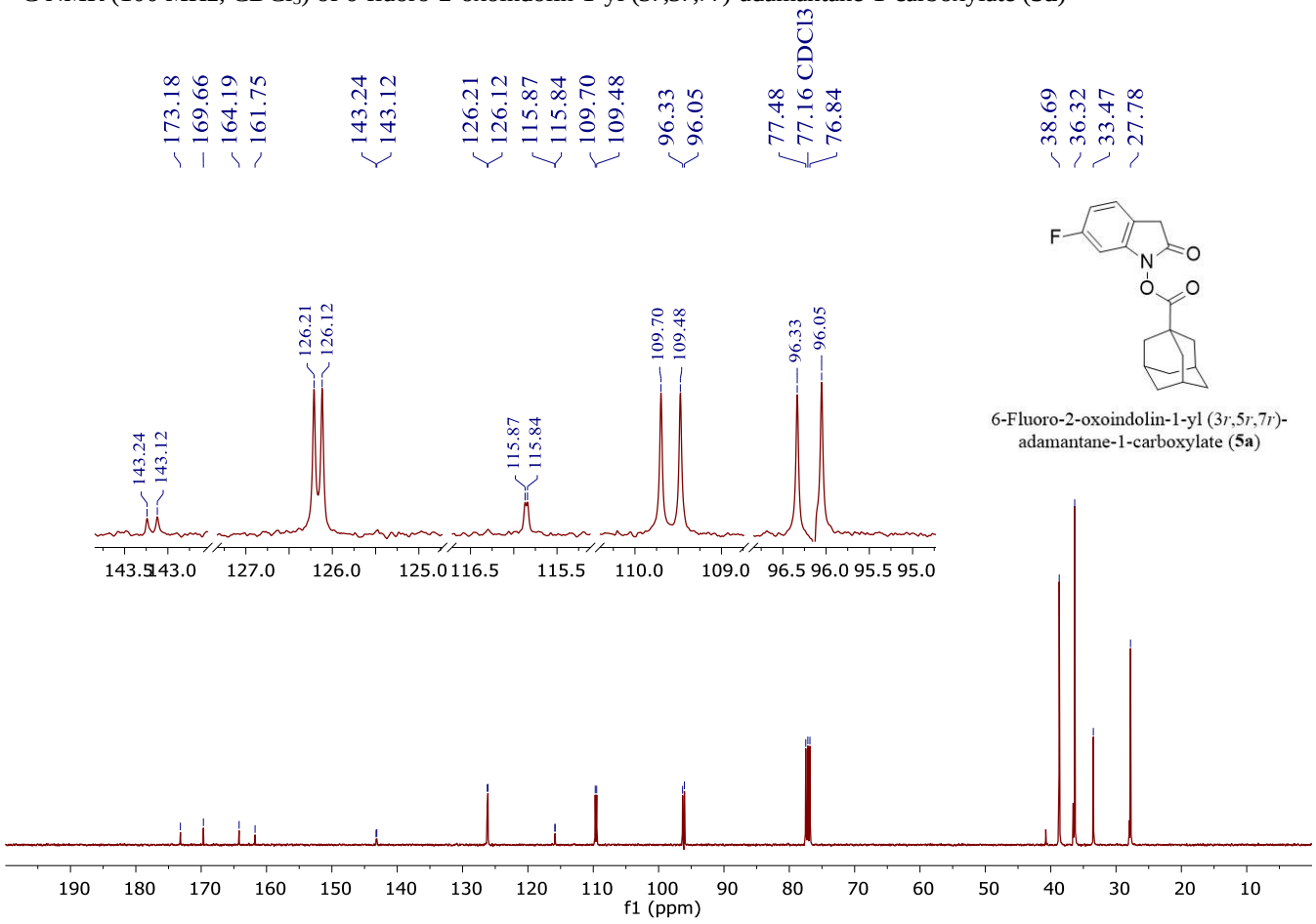
^{19}F NMR (376 MHz, $CDCl_3$) of 5-fluoroindolin-2-one (**4q**)



^{1}H NMR (400 MHz, $CDCl_3$) of 6-fluoro-2-oxoindolin-1-yl (*3r,5r,7r*)-adamantane-1-carboxylate (**5a**)



^{13}C NMR (100 MHz, $CDCl_3$) of 6-fluoro-2-oxoindolin-1-yl (*3r*,*5r*,*7r*)-adamantane-1-carboxylate (**5a**)



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