Electronic Supplementary Material (ESI) for ChemComm.

N-Heterocyclic Carbene (NHC) Catalyzed Atom Economical Construction of 2,3-Disubstituted Indoles

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1. General information

Unless otherwise noted, all the reactions were performed in oven dried glassware with magnetic stirring and under an atmosphere of argon using Schlenk line technique. Reported temperatures are the oil bath surrounding temperature of the Schlenk tube or reaction vessel.

All the solvents which are used in the reactions were dried and freshly distilled solvents according to their standard procedures and transferred under argon. Dry DMF, DMSO, CH_3CN, *t*-BuOH, DME and 1,4-dioxane were purchased from Finar scientifics, India. Which were stored over activated 4 Å molecular sieves.

All the reagents, aldehydes, anilines, acrylates and catalysts (NHCs) were purchased from Sigma-Aldrich, Alfa Aesar, and TCI, used without further purification. DBU was used under argon atmosphere.

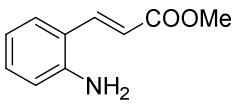
Analytical thin layer chromatography (TLC) was performed on Merck silica gel 60 F_{254} plates. Eluted plates were visualised by ultraviolet light (254 nm) lamp, iodine; 2,4-DNP, *p*-anisaldehyde were used as a developing agents followed by heating. Purification of products was carried out by column chromatography using 60-120 mesh silica and hexane, ethyl acetate were used as eluents, concentration under reduced pressure was performed by rotary evaporator at 40-45 ^{o}C, under reduced pressure. The yields were mentioned to the purified products.

^{1}HNMR spectra were recorded at room temperature on a Bruker A V 300, A V 400 and 500 MHz instruments. Chemical shifts (δ) are reported in ppm relative to TMS. The residual solvent signals were used as references like ($CDCl_3$ δ H 7.26 ppm, DMSO-d_6 δ H 2.54 ppm). Multiplicity of the compounds in the data reported as (s = singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet). Coupling constants ***(J)*** are represented in *Hz*.**^{13}CNMR** spectra were recorded on 75, 100, and 125 MHz spectrometers. Mass spectra was analysed by Electro spray Ionization (ESI) method was obtained on a Shimadzu LCMS-2020 mass spectrometer. High Resolution Mass Spectra data were obtained on a Thermo scientific Exactive^{TM} Orbitrap mass spectrometer or Q STAR XL Hybrid MS/MS. Infrared spectroscopy was performed neat on a BRUKER FT-IR spectrophotometer in chloroform, and IR [KBr] spectra were recorded on a THERMO NICOLER NEXUS 670 FT-IR instrument

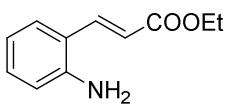
Melting points (MP) were determined using a Cintex – programmable melting point apparatus. MPs are uncorrected.

Synthesis of substituted *ortho*-amino cinnamates / cinnamides / cinnamonitiles (3a-h)

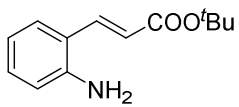
ortho-Amino cinnamates **3a-f** were synthesized by following literature reports.[1]



3a



3b



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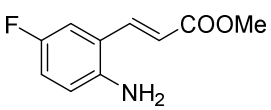
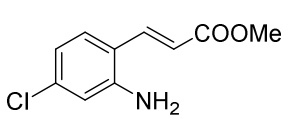
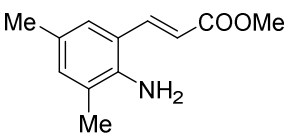


3d

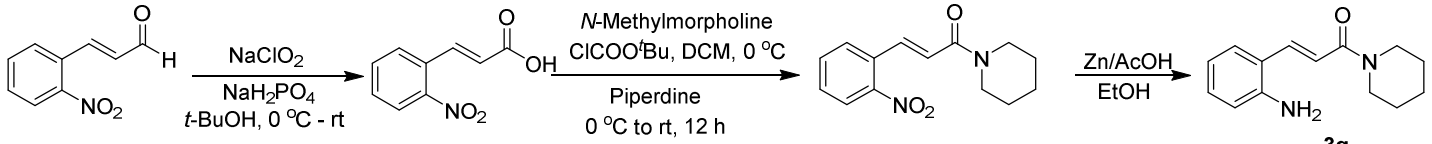


3e



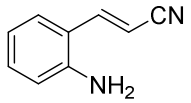
3f

ortho-Amino cinnamide **3g** was synthesized by following literature reports.[2]



3g

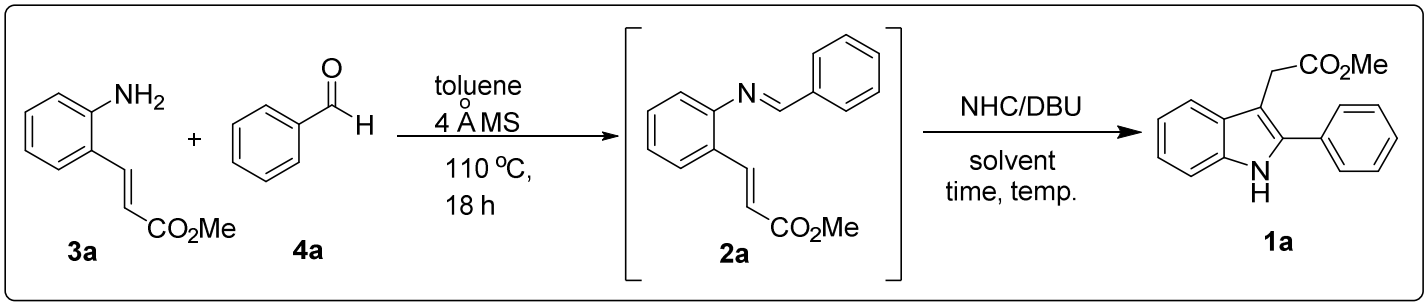
ortho-Aminocinnamonitrile **3g** was synthesized by following literature reports.[1]



3h

2. General experimental procedure for the optimization study

Experimental procedure for the synthesis of 1a via sequential aldimine formation—NHC catalysed reaction



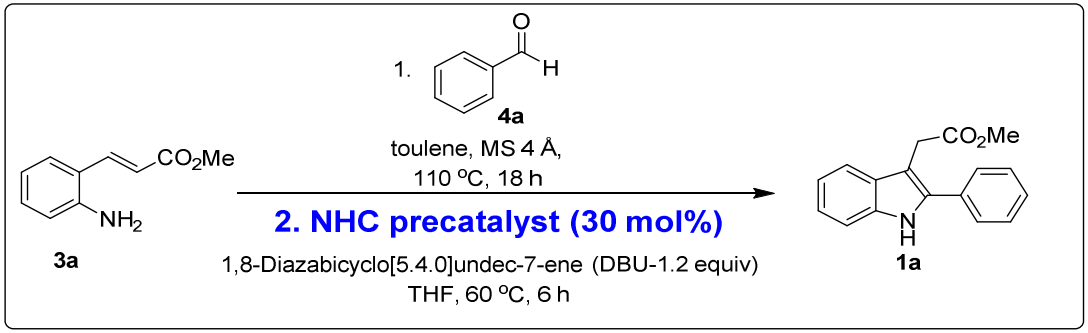
A clean and dry round bottom flask was charged with methyl (*E*)-3-(2-aminophenyl)acrylate **3a** (0.5 mmol, 88 mg), benzaldehyde **4a** (0.5 mmol, 53 mg) and added dry toluene (4 mL), 4 Å molecular sieves (1.5 g) (CAUTION: activated molecular sieves should be used, otherwise conversion to aldimine is not effective). The reaction mixture was stirred at reflux for 18 h. After completion of the reaction molecular sieves were filtered and solvent was removed and evacuated to obtain the crude aldimine **2a**, which was used in the NHC catalysed transformation.

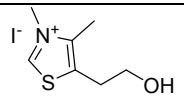
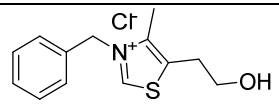
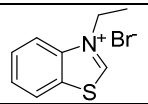
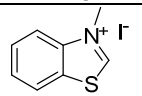
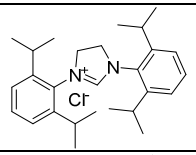
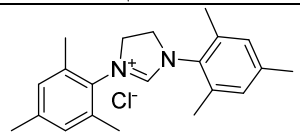
The crude aldimine **2a** and NHC were taken in a clean and dry Schlenk tube, it was evacuated and back filled with argon gas (3-5 cycles).Then added dry solvent (4 mL) followed by base (1.2 equiv) under positive pressure of argon. Then reaction mixture was stirred at the temperature and time as mentioned in optimisation tables S1-S4. Then the mixture was diluted with EtOAc (10 mL) and filtered of through a short pad of silica gel, by eluting with EtOAc (20 mL) and concentrated under reduced pressure. The resulting residue was purified by column chromatography to afford methyl 2-(2-phenyl-1*H*-indol-3-yl) acetate **1a** as a pure product.

Note: please see tables S1-S4, for various NHCs, bases, solvents and their ratios/quantities

3. Optimisation survey

Table S1: Screening of various NHC precatalysts



Entry	NHC precatalyst (30 mol %)	Structure of the NHC precatalyst	% Yield of 1a
1.	5-(2-Hydroxyethyl)-3,4-dimethylthiazolium iodide		—
2.	3-Benzyl-5-(2-hydroxyethyl)-4-methylthiazolium chloride		—
3.	3-Ethylbenzothiazolium bromide		—
4.	3-Methylbenzothiazolium iodide		—
5.	1,3-Bis-(2,6-diisopropylphenyl)imidazolinium chloride		—
6.	1,3-Bis(2,4,6-trimethylphenyl)imidazolinium chloride		—

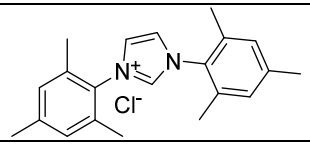
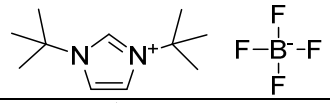
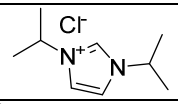
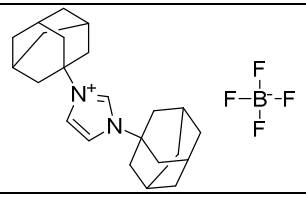
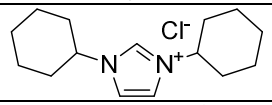
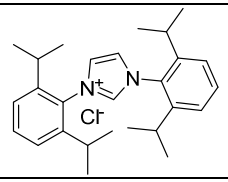
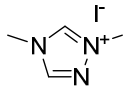
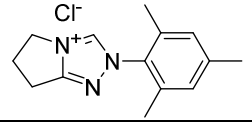
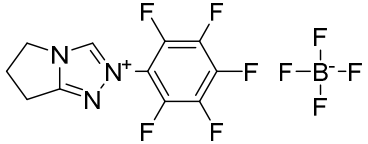
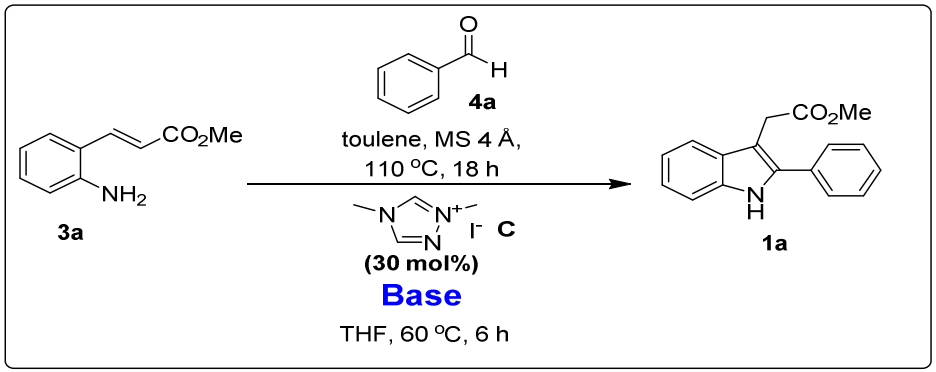
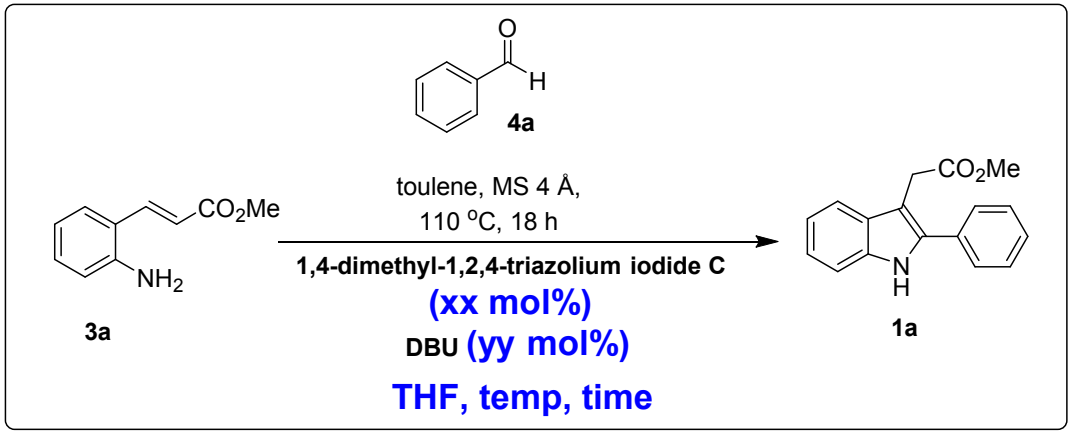
7.	1,3-Bis(2,4,6-trimethylphenyl)imidazolium chloride		—
8.	1,3-Di-tert-butylimidazolium tetrafluoroborate		—
9.	1,3-Diisopropylimidazolium chloride		—
10.	1,3-Bis(1-adamantyl)imidazolium tetrafluoroborate		—
11.	1,3-Dicyclohexylimidazolium chloride		—
12.	1,3-Bis(2,6-diisopropylphenyl)imidazolium chloride		—
13	**1,4-Dimethyl-1,2,4-triazolium iodide (C)**		**85**
14.	2-Mesityl-2,5,6,7-tetrahydropyrrolo[2,1-*c*][1,2,4]triazol-4-ium chloride		82
15.	6,7-Dihydro-2-pentafluorophenyl-5H-pyrrolo[2,1-c]-1,2,4-triazolium tetrafluoroborate		—

Table S2: Screening of various bases



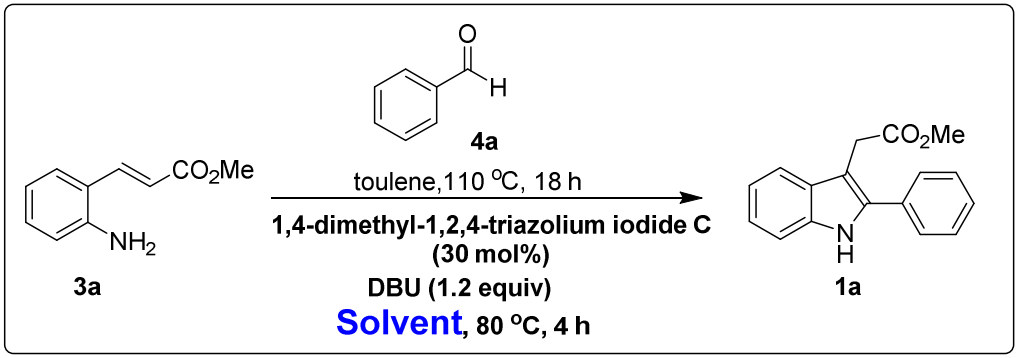
Entry	Base (1.2 equiv)	% Yield of 1a
1.	K_2CO_3	60
2.	K_3PO_4	62
3.	Et_3N	—
4.	1,4-Diazabicyclo[2.2.2]octane (DABCO)	—
5.	NaH	—
6.	1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD)	65
7.	PPh_3	—
8.	KOH	70
9.	K^{t}OBu	56
10.	Cs_2CO_3	68

Table S3: Screening of molar equivalents of NHC F, DBU and reaction conditions



Entry	NHC precatalyst C (1,4-dimethyl-1,2,4-triazolium iodide) (xx mol %)	DBU (yy mol %)	Temp. (°C)	Time (h)	% Yield of 1a
1.	30	120	60	6	85
2.	20	120	60	6	76
3.	10	120	60	6	64
4.	30	30	60	6	42
5.	30	60	60	6	62
6.	30	100	60	6	80
7.	30	120	rt	6	40
8.	30	120	rt	24	65
9.	30	120	40	6	68
10.	**30**	**120**	**80**	**4**	**90**

Table S4: Screening of various solvents



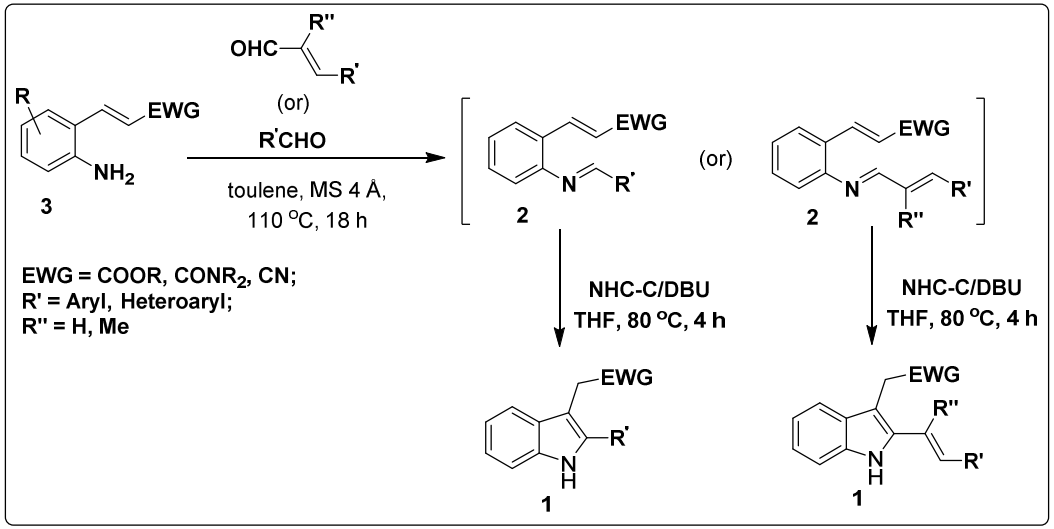
Entry	Solvent	% Yield of 1a
1.	CH_3CN	72
2.	1,4-Dioxane	78
3.	Dimethyl sulfoxide (DMSO)	82
4.	*N,N*-Dimethylformamide (DMF)	70
5.	1,2-Dimethoxyethane (DME)	64
6.	*t*-BuOH	68

Table S5: Reaction without using NHC precatalyst (or) base

(Optimized conditions mentioned entry 10, Table S3 were used)

Entry	NHC precatalyst	Base	Solvent	% Yield of 1a
1.	1,4-dimethyl-1,2,4-triazolium iodide	**No base**	THF	—
2.	**No catalyst**	DBU	THF	—

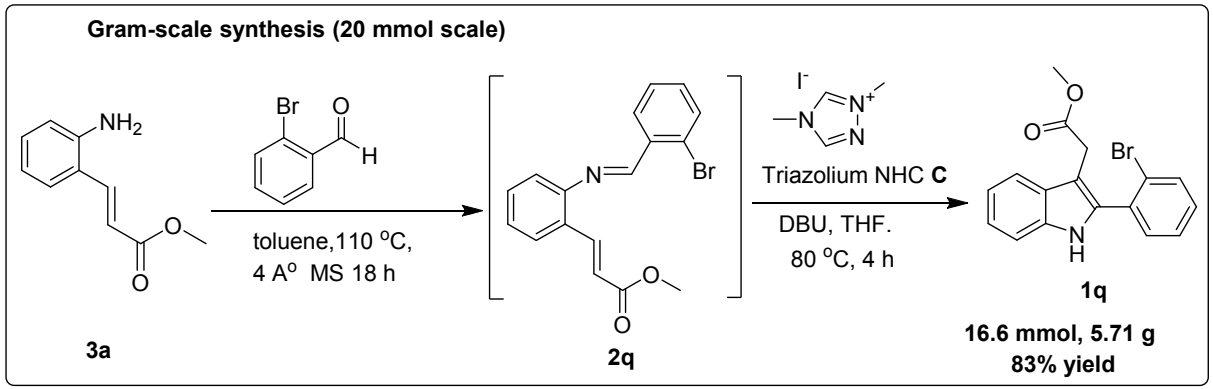
4. General procedure for NHC catalysed synthesis of 2-subsituted indole-3-acetic acid derivatives



A clean and dry round bottom flask was charged with *o*rtho-amino cinnamate / *o*rtho-amino cinnamide /*o*rtho-amino cinnamonitrile (1 equiv, 0.5 mmol) and aromatic/heteroaromatic/vinyl aldehyde (1 equiv, 0.5 mmol) (solid aldehydes were weighed in atmospheric conditions and liquid aldehydes were transferred via syringe under the positive pressure of argon) and added dry toluene (4 mL) and activated 4 Å molecular sieves (1.5 g). The reaction mixture was stirred at reflux temperature for 18-24 h to obtain for complete conversion of amine (reaction was monitored by TLC). After completion of the reaction molecular sieves were filtered off and solvent was removed and evacuated to obtain the crude aldimine, which was used in the NHC catalysed transformations.

The crude aldimine and NHC precatalyst **C** (30 mol%) were taken into a clean and dry Schlenk tube, and it was evacuated and back filled with argon gas (3-5 cycles). Then added dry freshly distilled THF (4 mL) via syringe followed by the addition of DBU (1.2 equiv) via syringe under positive pressure of argon. Then reaction mixture was stirred in a pre-heated oil bath at 80 ^{o}C for 4 h. The reaction mixture was brought to room temperature and diluted with EtOAc (10 mL) and filtered of through a short pad of silica gel by eluting with EtOAc (20 mL) and concentrated under reduced pressure. The resulting residue was purified by column chromatography to afford 2-subsituted indole-3-acetic acid derivatives.

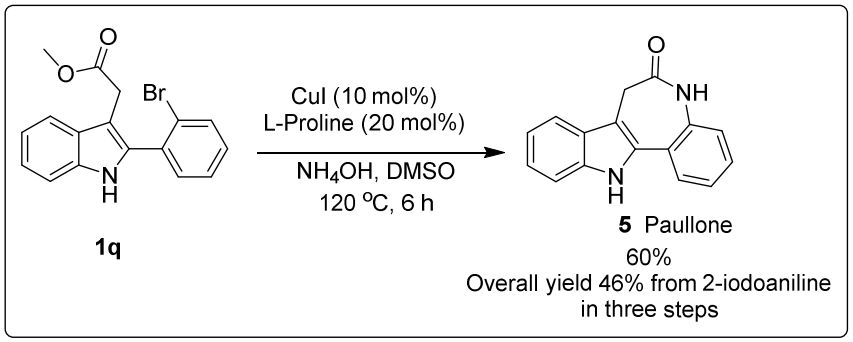
5. Experimental procedure for the NHC catalysed gram-scale synthesis of 1q



A clean and oven dried two necked round bottom flask was charged with methyl (*E*)-3-(2-aminophenyl) acrylate **3a**, (20 mmol, 3.54 g), 2-bromobenzaldehyde (20 mmol, 2.32 mL) and dry toluene (160 mL). To this added activated 4 Å molecular sieves (10 g). The reaction mixture was stirred at reflux temperature for 18 h. Then molecular sieves were filtered off, solvent was removed and evacuated to obtain the crude aldimine **2q**. Which was used in the NHC catalysed transformation.

The crude aldiimine **2q** and 1,4-dimethyl-1,2,4-triazolium iodide **C** (30 mol%, 4.48 g) were taken into a clean and dry round bottom flask and it was evacuated and back filled with argon gas (3-5 cycles). Then dry freshly distilled THF (160 mL) was added *via* cannula under the positive pressure of argon gas followed by the addition of DBU (1.2 equiv, 3 mL, from a freshly opened bottle) under positive pressure of argon. Then reaction mixture was stirred in a pre-heated oil bath at 80 ^{o}C for 4 h. After completion of the reaction, it was brought to room temperature and diluted with EtOAc (100 mL) and filtered of through a short pad of silica gel, by eluting with EtOAc (200 mL) and concentrated under reduced pressure. The resulting residue was purified by column chromatography to afford methyl 2-(2-(2-bromophenyl)-1*H*-indol-3-yl) acetate **1q** (5.71 g) as a yellow solid, with 83% yield.

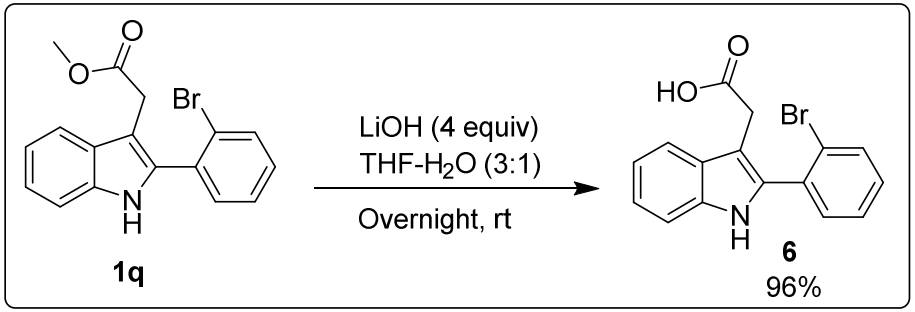
6. Experimental procedure for copper catalysed tandem-*N*-arylation followed by amide bond formation (Paullone synthesis)



Copper iodide (10 mol%, 0.2 mmol, 38 mg), L-proline (20 mol%, 0.4 mmol 46 mg), potassium carbonate (2 equiv, 4 mmol, 552 mg) and methyl 2-(2-(2-bromophenyl)-1*H*-indol-3-yl) acetate **1q,** (1 equiv, 2 mmol, 688 mg) were taken in a pressure tube under argon atmosphere. Then dry DMSO (8 mL), ammonium (2 mL, NH_3 in 25% aq.solution) were added under argon atmosphere. The tube was sealed and the reaction mixture was stirred at 120 ^oC for 6 h.

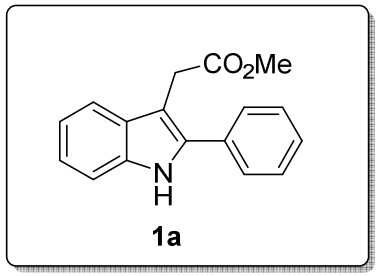
The reaction mixture was brought to room temperature and diluted with ethyl acetate (20 mL) and washed with ice cold water (3 x 20 mL). The organic phase was further diluted with ethyl acetate (50 mL) and washed with water (100 mL). Then it was dried over anhydrous sodium sulphate, filtered and concentrated. The crude was purified by column chromatography on silica gel to obtain paullone **5**.

7. Experimental procedure for base mediated ester hydrolysis



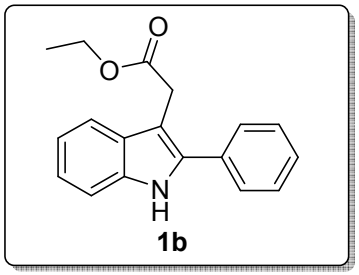
To a solution of methyl 2-(2-(2-bromophenyl)-1*H*-indol-3-yl) acetate **1q** (1 equiv, 1 mmol, 343 mg) in THF/H_2O (6 mL/2 mL) was added LiOH (4 equiv, 1 mmol, 96 mg) and the reaction mixture was stirred at room temperature overnight. The reaction mixture was concentrated under reduced pressure. The crude was diluted in ethyl acetate (30 mL) and neutralised using 1N HCl. The contents were extracted with ethyl acetate (2 x 50 mL). The organic phase was separated, dried over anhydrous sodium sulphate, filtered and concentrated. The crude was purified by column chromatography on silica gel to obtain the product 2-(2-(2-bromophenyl)-1*H*-indol-3-yl) acetic acid **6** in 96% yield.

8. Spectral data of products



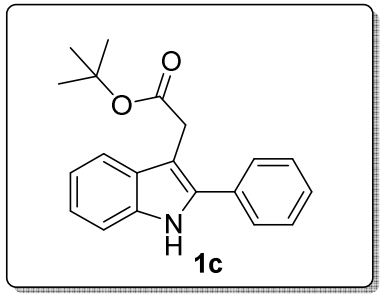
1a

methyl 2-(2-phenyl-1*H*-indol-3-yl)acetate (1a):- white solid, 120 mg (0.45 mmol), 90%, R_f = 0.5 (EtOAc/Hexane, 10:90); **MP** 118-120 °C; **IR** 742, 1009, 1171, 1435, 1723, 2922, 3369 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 3.71 (s, 3H), 3.86 (s, 2H), 7.21-7.25 (m, 2H), 7.36-7.44 (m, 2H), 7.46-7.54 (m, 2H), 7.63-7.70 (m, 3H), 8.16 (s, 1H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 31.0, 51.8, 105.6, 110.9, 119.3 120.1, 122.6, 128.1, 128.2, 129.0, 132.4, 135.7, 136.2, 172.7; **MS** (ESI) m/z 266 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{17}H_{16}NO_2$ $[M+H]^+$ 266.11756, found 266.11773. The spectroscopic data were in good agreement with the reported data.[1]



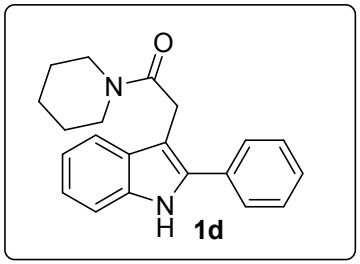
1b

ethyl 2-(2-phenyl-1*H*-indol-3-yl)acetate (1b):- pale yellow solid, 110 mg (0.395 mmol), 79%, R_f = 0.5 (EtOAc/Hexane, 10:90); **MP** 102-104 °C; **IR** 740, 1026, 1156, 1453, 1712, 3363 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 1.24 (t, *J* = 7.1 Hz, 3H), 3.82 (s, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 7.12-7.16 (m, 1H), 7.17-7.21 (m, 1H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.35-7.39 (m, 1H), 7.45 (t, *J* = 7.3 Hz, 2H), 7.62-7.65 (m, 2H), 7.67 (d, *J* = 7.7 Hz, 1H), 8.18 (br, 1H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 14.3, 31.3, 61.0, 105.6, 111.1, 119.3, 120.0, 122.5, 128.0, 128.3, 129.0, 129.1, 132.5, 136.0, 136.3, 172.6; **MS** (ESI) m/z 280 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{18}H_{18}NO_2$ $[M+H]^+$ 280.13321, found 280.13403. The spectroscopic data were in good agreement with the reported data.[2]



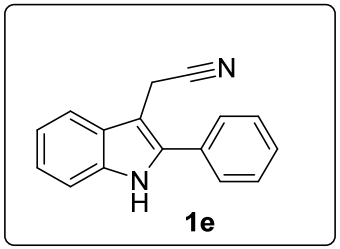
1c

tert-butyl 2-(2-phenyl-1*H*-indol-3-yl)acetate (1c):- cream solid, 113 mg (0.366 mmol), 73%, R_f = 0.46 (EtOAc/Hexane, 10:90); **MP** 107-109 ^oC; **IR** 726, 906, 1138, 1454, 1714, 2927, 3393 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 1.44 (s, 9H), 3.74 (s, 2H), 7.13-7.17 (m, 1H), 7.18-7.22 (m, 1H), 7.33-7.40 (m, 2H), 7.44-7.49 (m, 2H), 7.66-7.72 (m, 3H), 8.15 (s, 1H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 28.3, 32.6, 80.9, 106.2, 110.9, 119.5, 119.9, 122.4, 127.9, 128.3, 128.9, 129.2, 132.6, 135.8, 136.1, 171.7; **MS** (ESI) m/z 308 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{20}H_{22}NO_2$ $[M+H]^+$ 308.16451, found 308.16452.



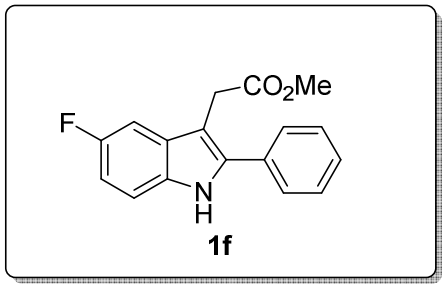
1d

2-(2-phenyl-1*H*-indol-3-yl)-1-(piperidin-1-yl)ethan-1-one (1d):- pale yellow solid, 105 mg (0.33 mmol), 66%, R_f = 0.5 (EtOAc/Hexane, 30:70); **MP** 190-192^{o}C; **IR** 697, 1224, 1455, 1627, 2933, 3251 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 1.14 (m,2H), 1.40 (m,2H), 1.43-1.51 (m,2H), 3.13-3.19 (m, 2H), 3.46-3.53 (m,2H), 3.92 (s, 2H),7.13 (t, *J* = 7.5 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.40 (d, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.54 (d, *J* = 7.2 Hz, 2H), 7.73 (d, *J* = 7.9 Hz, 1H), 8.16 (br, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ =24.4, 25.6, 26.0, 31.3, 43.1, 46.9, 106.9, 110.7, 119.8, 120.0, 122.4, 128.0, 128.3, 128.9, 132.7, 135.2, 135.9, 169.4 ; **MS** (ESI) m/z 319 $[M+H]^+$. The spectroscopic data were in good agreement with the reported data.[2]



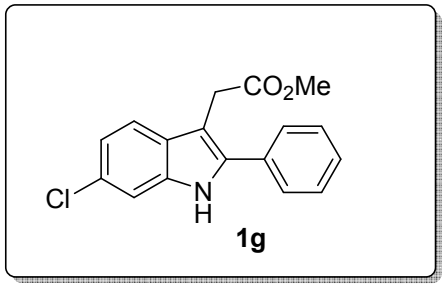
1e

2-(2-phenyl-1*H*-indol-3-yl)acetonitrile (1e):- pale yellow solid, 43 mg (0.13 mmol), 26%, (74%, 122 mg with isolated imine) R_f = 0.5 (EtOAc/Hexane, 10:90); **MP** 96-98 °C; 740, 1212, 1453, 2249, 2922, 3396 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 3.90 (s, 2H), 7.21-7.31 (m, 2H), 7.41-7.44 (m, 1H), 7.44-7.48 (m, 1H), 7.51-7.56 (m, 4H), 7.72 (d, *J* = 7.8 Hz, 1H), 8.27 (s, 1H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 13.8, 101.1, 111.2, 118.2, 118.4, 120.7, 123.1, 127.8, 128.2, 128.7, 129.3, 131.5, 135.6, 136.3; **MS** (ESI) m/z 231 $[M-H]^+$ **HRMS** (ESI, m/z): calcd for $C_{16}H_{13}N_2$ $[M+H]^+$ 233.10732, found 233.10684. The spectroscopic data were in good agreement with the literature report.[1]



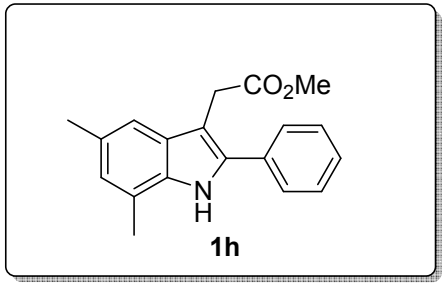
1f

methyl 2-(5-fluoro-2-phenyl-1*H*-indol-3-yl)acetate (1f):- Yellow solid, 115 mg (0.405 mmol), 81%, R_f = 0.5 (EtOAc/Hexane, 10:90); **MP** 112-114 °C; **IR** 771, 1174, 1454, 1724, 2923, 3358 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 3.74 (s, 3H), 3.81 (s, 2H), 6.95 (td, *J* = 9.1 Hz, 2.5 Hz, 1H), 7.24 (dd, *J* = 8.8 Hz, 4.3 Hz, 1H), 7.31 (dd, *J* = 9.6 Hz, 2.4 Hz, 1H), 7.39-7.44 (m, 1H), 7.46-7.52 (m, 2H), 7.58-7.65 (m, 2H), 8.27 (s, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ = 30.8, 52.1, 104.2, 105.6, 110.8, 111.6, 128.2, 129.0, 129.4, 132.1, 137.9, 157.1, 159.0, 172.6; **MS** (ESI) m/z 284 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{17}H_{15}FNO_2$ $[M+H]^+$ 284.10813, found 284.10833.



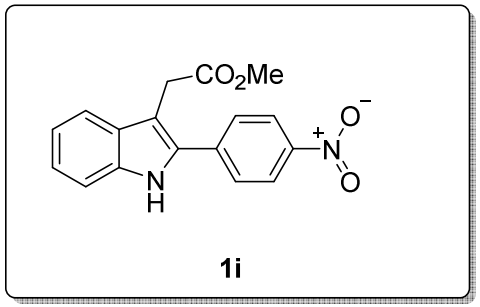
1g

methyl 2-(6-chloro-2-phenyl-1*H*-indol-3-yl)acetate (1g):- pale yellow solid, 90 mg (0.30 mmol), 60%, R_f = 0.5 (EtOAc/Hexane, 10:90); **MP** 104-106 °C; **IR** 769, 1456, 1722, 2922, 3352 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 3.72 (s, 3H), 3.82 (s, 2H), 7.10-7.15 (m, 1H), 7.33-7.37 (m, 1H), 7.38-7.45 (m, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 2H), 8.17 (s, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ = 30.8, 52.1, 105.7, 110.8, 120.1, 120.9, 127.6, 128.2, 128.4, 129.1, 131.9, 136.1, 136.9, 172.5; **MS** (ESI) m/z 298 $[M-H]^+$ **HRMS** (ESI, m/z): calcd for $C_{17}H_{13}ClNO_2$ $[M-H]^+$ 298.06293, found 298.06574.



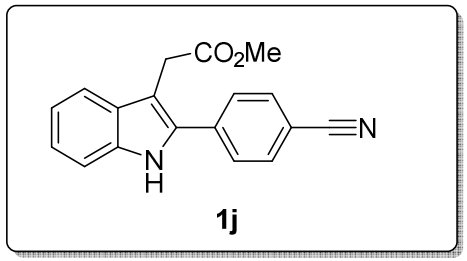
1h

methyl 2-(5,7-dimethyl-2-phenyl-1*H*-indol-3-yl)acetate (1h):- White solid, 87 mg (0.295 mmol), 59%, R_f = 0.5 (EtOAc/Hexane, 10:90); **MP** 140-142 °C; **IR** 768, 1167, 1451, 1722, 2921, 3368 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 2.46 (s, 3H), 2.48 (s, 3H), 3.73 (s, 3H), 3.83 (s, 2H), 6.88 (s, 1H), 7.27-7.30 (m, 1H), 7.37-7.42 (m, 1H), 7.50 (t, *J* = 7.3 Hz, 2H), 7.67 (d, *J* = 7.1 Hz, 2H), 7.95 (s, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ = 16.6, 21.5, 31.0, 52.1, 105.5, 116.5, 119.8, 125.0, 128.0, 128.3, 128.8, 128.9, 129.7, 132.7, 133.6, 136.1, 172.8; **MS** (ESI) m/z 294 $[M+H]^+$. The spectroscopic data were in good agreement with the reported data.[1]



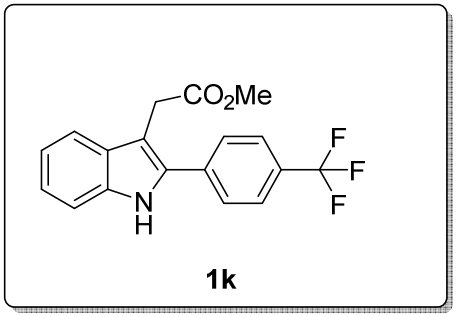
1i

methyl 2-(2-(4-nitrophenyl)-1*H*-indol-3-yl)acetate (1i):- Yellowish orange solid, 111 mg (0.355 mmol), 71%, R_f = 0.5 (EtOAc/Hexane, 30:70); **MP** 164-166 ^oC; **IR** 772, 1017, 1451, 1859, 2944, 3318 cm^{-1}; **^{1}H-NMR** (300 MHz, DMSO-d_6) δ = 3.63 (s, 3H), 3.95 (s, 2H), 7.08 (t, *J* = 7.3 Hz, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 2H), 8.38 (d, *J* = 8.8 Hz, 2H), 11.68 (s, 1H); **^{13}C-NMR** (101 MHz, DMSO-d_6) δ = 30.0, 52.1, 107.4, 111.6, 119.3, 119.6, 123.1, 124.1, 128.5, 128.6, 133.3, 136.5, 138.9, 146.3, 171.9; **MS** (ESI) m/z 311 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{17}H_{14}N_2O_4Na$ $[M+Na]^+$ 333.08458, found 333.08443.



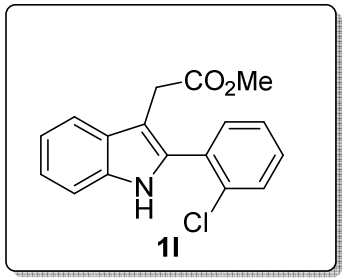
1j

methyl 2-(2-(4-cyanophenyl)-1*H*-indol-3-yl)acetate (1j):- cream colour solid, 128 mg (0.44 mmol), 88%, R_f = 0.5 (EtOAc/Hexane, 10:90); **MP** 130-132 ^oC; **IR** 746, 1174, 1725, 2226, 2923, 3355 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 3.74 (s, 3H), 3.86 (s, 2H), 7.17-7.22 (m, 1H), 7.25-7.30 (m, 1H), 7.36-7.42 (m, 1H), 7.67-7.82 (m, 5H), 8.29 (s, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ = 30.9, 52.3, 107.7, 111.2, 111.3, 118.7, 119.6, 120.6, 123.7, 128.5, 128.8, 132.7, 133.9, 136.2, 136.8, 172.3; **MS** (ESI) m/z 291 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{18}H_{14}N_2O_2Na$ $[M+Na]^+$ 313.09475, found 313.09457. The spectroscopic data were in good agreement with the reported data.[1]



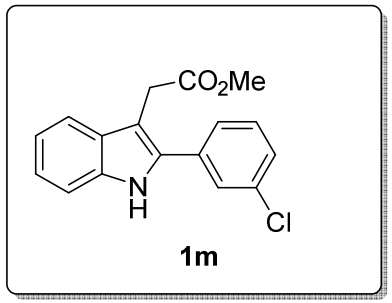
1k

methyl 2-(2-(4-(trifluoromethyl)phenyl)-1*H*-indol-3-yl)acetate (1k):- off-white solid, 129 mg (0.385 mmol), 77%, R_f = 0.5 (EtOAc/Hexane, 10:90); **MP** 122-124 ^oC; **IR** 743, 1120, 1323, 1724, 2923, 3361 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 3.75 (s, 3H), 3.86 (s, 2H), 7.17-7.22 (m, 1H), 7.23-7.28 (m, 1H), 7.34-7.41 (m, 1H), 7.67-7.78 (m, 5H), 8.25 (s, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ = 16.5, 21.5, 31.0, 52.0, 105.6, 116.5, 119.7, 125.0, 127.9, 128.2, 128.8, 128.9, 129.7, 132.7, 133.6, 136.0, 172.8**; MS** (ESI) m/z 334 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{18}H_{15}F_3NO_2$ $[M+H]^+$ 334.10494, found 334.10529.



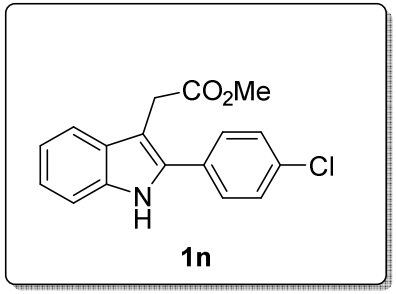
1l

methyl 2-(2-(2-chlorophenyl)-1*H*-indol-3-yl)acetate (1l):- pale Yellow solid, 103 mg (0.345 mmol), 69%, R_f = 0.5 (EtOAc/Hexane, 10:90); **MP** 102-104 ^oC; **IR** 723, 905, 1172, 1452, 1726, 2926, 3394 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 3.67 (s, 3H), 3.74 (s, 2H), 7.16-7.21 (m, 1H), 7.23-7.28 (m, 1H), 7.35-7.40 (m, 3H), 7.52-7.55 (m, 1H), 7.57-7.62 (m, 1H), 7.68 (d, *J* = 7.9. Hz, 1H), 8.32 (s, 1H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 30.4, 52.0, 107.6, 111.1, 119.4, 120.0, 122.8, 127.0, 127.9, 130.0, 130.1, 131.0, 132.8, 133.24, 133.8, 135.6, 172.5**; MS** (ESI) m/z 300 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{17}H_{15}ClNO_2$ $[M+H]^+$ 300.07858, found 300.07872.



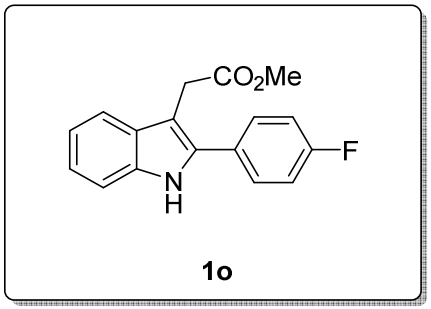
1m

methyl 2-(2-(3-chlorophenyl)-1*H*-indol-3-yl)acetate (1m):- cream colour solid, 112 mg (0.37 mmol), 74%, R_f = 0.5 (EtOAc/Hexane, 10:90); **MP** 130-132 °C; **IR** 772, 1218, 1443, 1608, 2926, 3395 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 3.73 (s, 3H), 3.84 (s, 2H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.34-7.38 (m, 2H), 7.39-7.44 (m, 1H), 7.56 (d, *J* = 7.3 Hz, 1H) 7.64-7.69 (m, 2H), 8.16 (s, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ = 30.8, 52.1, 106.4, 111.3, 119.4, 120.3, 123.0, 126.4, 128.1, 128.9, 130.2, 134.1, 134.6, 134.9, 135.8, 172.3; **MS** (ESI) m/z 300 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{17}H_{15}ClNO_2$ $[M+H]^+$ 300.07858, found 300.07867.



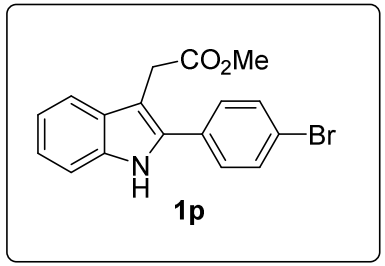
1n

methyl 2-(2-(4-chlorophenyl)-1*H*-indol-3-yl)acetate (1n):- off-white solid, 114 mg (0.38 mmol), 76%, R_f = 0.5 (EtOAc/Hexane, 10:90); **MP** 104-106 °C; **IR** 739, 1092, 1453, 1721, 2924, 3367 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 3.73 (s, 3H), 3.83 (s, 2H), 7.15-7.20 (m, 1H), 7.21-7.25 (m, 1H), 7.34 (d, *J* = 8.0. Hz 1H), 7.42-7.46 (m, 2H), 7.54-7.61 (m, 2H), 7.67 (d, *J* = 7.9 Hz 1H), 8.20 (s, 1H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 30.9, 52.1, 105.9, 111.0, 119.2, 120.2, 122.9, 128.9, 129.2, 129.4, 130.8, 134.1, 135.0, 135.8, 172.7; **MS** (ESI) m/z 300 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{17}H_{14}NO_2Cl$ Na $[M+Na]^+$ 322.06053, found 322.05997.



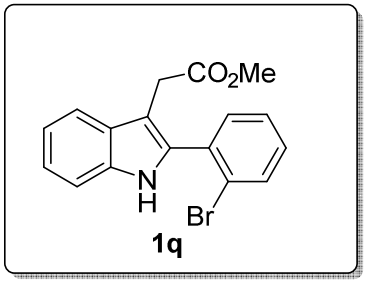
1o

methyl 2-(2-(4-fluorophenyl)-1*H*-indol-3-yl)acetate (1o):- Yellow solid, 114 mg (0.40 mmol), 80%, R_f = 0.5 (EtOAc/Hexane, 10:90); **MP** 109-111 ^oC; **IR** 742, 1221, 1457, 1721, 2925, 3366 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 3.73 (s, 3H), 3.82 (s, 2H), 7.15-7.21 (m, 3H), 7.21-7.26 (m, 1H), 7.34-7.40 (m, 1H), 7.60-7.71 (m, 3H), 8.16 (s, 1H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 30.8, 52.1, 105.5, 110.9, 116.0, 119.7, 122.7, 128.5, 128.8, 130.0, 135.5, 161.4, 163.8, 172.7; **MS** (ESI) m/z 284 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{17}H_{15}NO_2F$ $[M+H]^+$ 284.10813, found 284.10896.



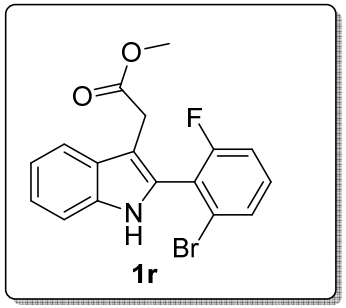
1p

methyl 2-(2-(4-bromophenyl)-1*H*-indol-3-yl)acetate (1p):- light peach solid, 145 mg (0.42 mmol), 84%, R_f = 0.5 (EtOAc/Hexane, 10:90); **MP** 120-122 ^oC; **IR** 744, 1172, 1436, 1726, 2923, 3387 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 3.73 (s, 3H), 3.83 (s, 2H), 7.15-7.21 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.50-7.56 (m, 2H), 7.58-7.64 (m, 2H), 7.66 (d, *J* = 7.9 Hz, 1H), 8.17 (s, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ = 30.7, 52.0, 106.1, 111.0, 119.3, 120.1, 122.3, 122.9, 128.9, 129.7, 131.2, 132.1, 135.0, 135.7, 172.6; **MS** (ESI) m/z 344 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{17}H_{14}NO_2BrNa$ $[M+Na]^+$ 366.01001, found 366.00944. The spectroscopic data were in good agreement with the reported data.[1]



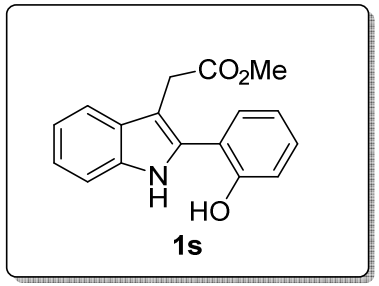
1q

methyl 2-(2-(2-bromophenyl)-1*H*-indol-3-yl)acetate (1q):- pale yellow solid, 146 mg (0.425 mmol), 85%, R_f = 0.5 (EtOAc/Hexane, 10:90); **MP** 110-112 °C; **IR** 740, 1271, 1433, 1722, 3393 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 3.63 (s, 3H), 3.68 (s, 2H), 7.13-7.19 (m, 1H), 7.19-7.25 (m, 1H), 7.25-7.30 (m, 1H), 7.33-7.41 (m, 2H), 7.53 (dt, *J* = 6.3 Hz, 3.2 Hz, 1H), 7.63-7.67 (m, 1H), 7.67-7.71 (m, 1H), 8.23 (s, 1H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 31.0, 51.8, 107.2, 111.1, 119.4, 120.0, 122.7, 124.0, 127.4, 127.8, 130.2, 133.0, 133.2, 133.3, 134.7, 135.5, 172.4; **MS** (ESI) m/z 346 $[M+2H]^+$ **HRMS** (ESI, m/z): calcd for $C_{17}H_{15}BrNO_2$ $[M+H]^+$ 344.02807, found 344.02845.



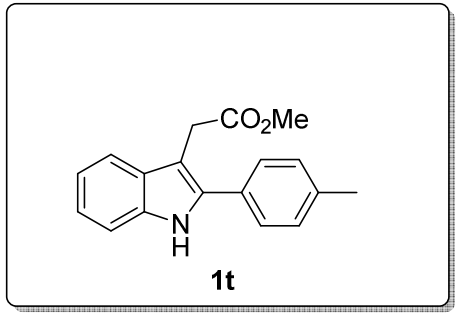
1r

methyl 2-(2-(2-bromo-6-fluorophenyl)-1*H*-indol-3-yl)acetate (1r):- cream colour solid, 131 mg (0.36 mmol), 72%, R_f = 0.5 (EtOAc/Hexane, 10:90); **MP** 130-132 °C; **IR** 743, 1246, 1438, 1723, 2924, 3393 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 3.56 (s, 3H), 3.64 (s, 2H), 7.12-7.18 (m, 2H), 7.21-7.25 (m, 1H), 7.27-7.31 (m, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 8.23 (s, 1H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 30.8, 51.8, 109.0, 111.2, 115.0, 119.7, 122.0, 122.8, 125.9, 127.7, 128.7, 131.5, 136.0, 160.0, 162.5, 171.8; **MS** (ESI) m/z 362 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{17}H_{14}BrFNO_2$ $[M+H]^+$ 362.01865, found 362.01936.



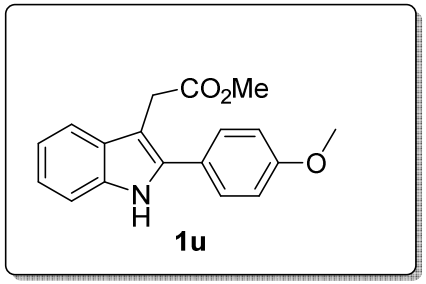
1s

methyl 2-(2-(2-hydroxyphenyl)-1*H*-indol-3-yl)acetate (1s):- reddish brown colour liquid, 79 mg (0.28 mmol), 56%, R_f = 0.4 (EtOAc/Hexane, 10:90); **IR** 753, 1213, 1457, 1725, 2924, 3381 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 3.72 (s, 5H), 6.92-7.02 (m, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.19-7.26 (m, 1H), 7.27-7.35 (m, 3H), 7.52 (d, *J* =7.7 Hz, 1H), 8.26 (s, 1H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 30.7, 52.5, 107.3, 111.1, 116.8, 118.5, 118.6, 120.1, 120.5, 122.8, 128.1, 130.5, 130.8, 131.8, 136.2, 154.4, 173.9 ; **MS** (ESI) m/z 282 $[M+H]^+$.



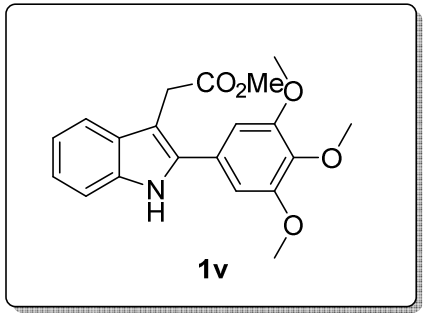
1t

methyl 2-(2-(p-tolyl)-1*H*-indol-3-yl)acetate (1t):- brownish yellow colour liquid, 98 mg (0.35 mmol), 70%, R_f = 0.5 (EtOAc/Hexane, 10:90) ; **IR** 772, 1171, 1436, 1728, 2923, 3394 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 2.41 (s, 3H), 3.72 (s, 3H), 3.84 (s, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 7.7 Hz, 2H), 7.64 (d, *J* = 7.7 Hz, 1H), 8.14 (s, 1H) ; **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 21.3, 31.1, 52.1, 105.0, 111.0, 119.1, 120.0, 122.4, 128.2, 129.1, 129.6, 129.5, 135.8, 136.4, 138.0, 173.1; **MS** (ESI) m/z 280 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{18}H_{18}NO_2$ $[M+H]^+$ 280.13321, found 280.13310.



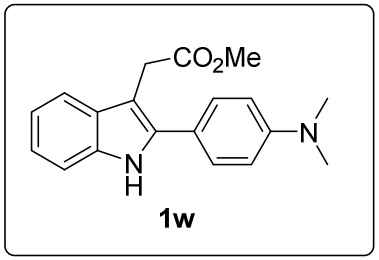
1u

methyl 2-(2-(4-methoxyphenyl)-1*H*-indol-3-yl)acetate (1u):- cream colour solid, 101 mg (0.34 mmol), 68%, R_f = 0.5 (EtOAc/Hexane, 10:90); **MP** 102-104 °C; **IR** 728, 1248, 1459 ,1726, 2839, 3393 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 3.72 (s, 3H), 3.83 (s, 2H), 3.87 (s, 3H), 6.98-7.05 (m, 2H), 7.19-7.21 (m, 2H), 7.33-7.37 (m, 1H), 7.54-7.61 (m, 2H), 7.65 (d, *J* = 7.8 Hz, 1H), 8.13 (s, 1H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ =31.0, 52.0, 55.3, 104.7, 110.8, 114.4, 119.0, 120.0, 122.2, 124.8, 129.0, 129.5, 135.6, 136.2, 159.5, 172.9; **MS** (ESI) m/z 296 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{18}H_{18}NO_3$ $[M+H]^+$ 296.12812, found 296.12805. The spectroscopic data were in good agreement with the reported data.[1]



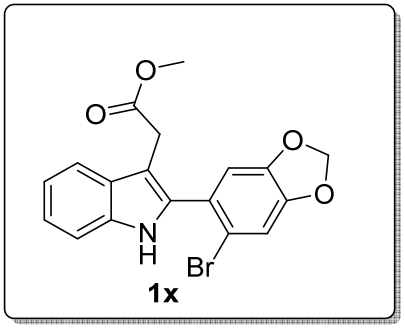
1v

methyl 2-(2-(3,4,5-trimethoxyphenyl)-1*H*-indol-3-yl)acetate (1v):- pale Yellow solid, 114 mg (0.32 mmol), 64%, R_f = 0.5 (EtOAc/Hexane, 20:80); **MP** 126-128 °C; **IR** 724, 1120, 1433, 1727, 2935, 3356 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 3.73 (s, 3H), 3.86 (s, 2H), 3.90 (s, 6H), 3.93 (s, 3H), 6.94 (s, 2H), 7.15-7.20 (m, 1H), 7.20-7.25 (m, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 8.35 (s, 1H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 31.1, 52.1, 56.2, 61.0, 105.3, 105.5, 110.9, 119.3, 120.1, 122.5, 127.9, 129.0, 135.7, 136.5, 137.9, 153.5, 172.8; **MS** (ESI) m/z 356 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{20}H_{22}NO_5$ $[M+H]^+$ 356.14925, found 356.14956.



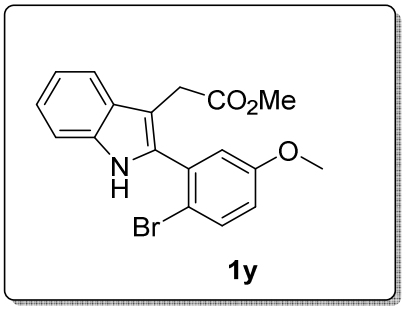
1w

methyl 2-(2-(4-(dimethylamino)phenyl)-1*H*-indol-3-yl)acetate (1w):- yellow colour liquid, 20 mg (0.065 mmol), 13%, (46 mg (0.15 mmol), 30%, with isolated imine), R_f = 0.5 (EtOAc/Hexane, 10:90); IR 746, 1167, 1515, 1610, 1730, 2923, 3374 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 3.00 (s, 6H), 3.72 (s, 3H), 3.82 (s, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 7.10-7.20 (m, 2H), 7.34 (m, 1H), 7.49-7.56 (m, 2H), 7.60-7.65 (m, 1H), 8.16 (s, 1H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 31.1, 40.5, 52.0, 104.0, 110.6, 112.7, 118.8, 119.8, 121.9, 129.1, 135.5, 136.9, 150.0, 173.0; **MS** (ESI) m/z 309 $[M+H]^+$ **HRMS** (ESI, m/z):calcd for $C_{19}H_{21}N_2O_2$ $[M+H]^+$ 309.15975, found 309.15860.



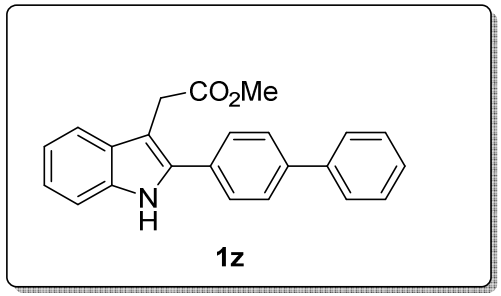
1x

methyl 2-(2-(6-bromobenzo[d][1,3]dioxol-5-yl)-1*H*-indol-3-yl)acetate (1x):- cream colour solid, 145 mg (0.375 mmol), 75%, R_f = 0.5 (EtOAc/Hexane, 10:90); **MP** 120-122 °C; **IR** 772, 1223, 1458, 1727, 2923, 3394 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 3.69 (s, 3H), 3.71 (s, 2H), 6.08 (s, 2H), 7.06 (s, 1H), 7.15-7.22 (m, 2H), 7.23-7.29 (m, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 8.18 (s, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 30.8, 51.9, 102.2, 107.2, 111.0, 112.3, 113.1, 115.1, 119.3, 120.0, 122.7, 126.1, 127.7, 134.7, 135.3, 147.3, 149.0, 172.3; **MS** (ESI) m/z 388 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{18}H_{15}NO_4Br$ $[M+H]^+$ 388.01790, found 388.01878.



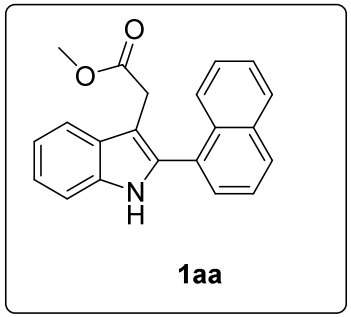
1y

methyl 2-(2-(2-bromo-5-methoxyphenyl)-1*H*-indol-3-yl)acetate (1y):- off-white solid, 129 mg (0.345 mmol), 69%, R_f = 0.5 (EtOAc/Hexane, 10:90); **MP** 128-130 ^oC; **IR** 745, 1014, 1223 ,1458 ,1728, 2924, 3387 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 3.68 (s, 3H), 3.73 (s, 2H), 3.83 (s, 3H), 6.87 (dd, J_1 = 8.8 Hz, J_2 = 3.1 Hz, 1H), 7.16-7.22 (m, 2H), 7.23-7.28 (m, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 8.8 Hz, 1H), 7.70 (d, J = 7.0 Hz, 1H), 8.28 (s, 1H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 30.9, 52.0, 55.6, 107.2, 111.0, 113.9, 116.7, 118.0, 119.4, 120.0, 122.8, 127.8, 133.7, 134.0, 134.7, 135.4, 158.8, 172.7; **MS** (ESI) m/z 374 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{18}H_{17}O_3NBr$ $[M+H]^+$ 374.03863, found 374.03920.



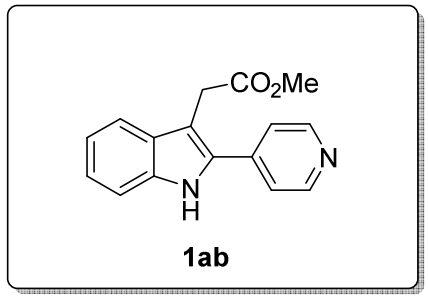
1z

methyl 2-(2-([1,1'-biphenyl]-4-yl)-1*H*-indol-3-yl)acetate (1z):- pale yellow solid, 137 mg (0.40 mmol), 80%, R_f = 0.5 (EtOAc/Hexane, 10:90); **MP** 156-158 ^oC; **IR** 789, 1172, 1435, 1727, 2923 ,3372 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 3.74 (s, 3H), 3.89 (s, 2H), 7.18 (t, J = 7.4 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 7.36-7.42 (m, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.65 (d, J = 7.4 Hz, 2H), 7.68 (d, J = 7.8 Hz, 1H), 7.70-7.76 (m, 4H), 8.19 (s, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ = 31.0, 52.1, 105.8, 110.9, 119.3, 120.2, 122.7, 127.0, 127.6, 127.7, 128.6, 128.9, 129.1, 131.3, 135.8, 140.4, 140.8, 172.7; **MS** (ESI) m/z 342 $[M+H]^+$ **HRMS** (ESI, m/z): calcd $C_{23}H_{20}NO_2$ $[M+H]^+$ 342.14886, found 342.14892.



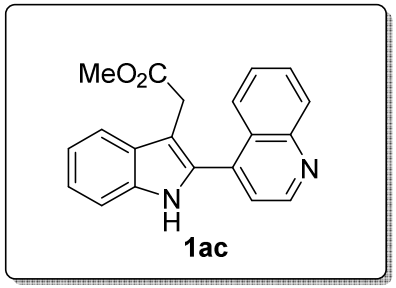
1aa

methyl 2-(2-(naphthalen-2-yl)-1*H*-indol-3-yl)acetate (1aa):- light yellowish liquid, 98 mg (0.31 mmol), 62%, R_f = 0.5 (EtOAc/Hexane, 10:90); IR 744, 1169, 1434 ,1722, 2922, 3392 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 3.75 (s, 3H), 3.93 (s, 2H), 7.17-7.22 (m, 1H), 7.23-7.29 (m, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.50-7.58 (m, 2H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.78 (dd, J_1 = 8.5 Hz, J_2 = 1.7 Hz, 1H), 7.86-7.99 (m, 3H), 8.14 (s, 1H), 8.29 (s, 1H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 31.0, 52.1, 106.0, 110.9, 119.3, 120.2, 122.7, 125.9, 126.5, 126.7, 127.4, 127.8, 128.2, 128.7, 129.1, 129.7, 132.8, 133.5, 135.9, 136.2, 172.7; **MS** (ESI) m/z 316 $[M+H]^+$ **HRMS** (ESI, m/z): calcd $C_{21}H_{18}NO_2$ $[M+H]^+$ 316.13321, found 316.13321.



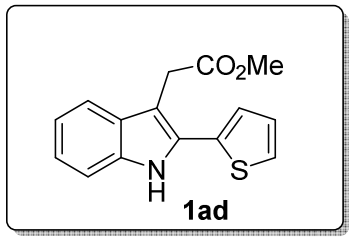
1ab

methyl 2-(2-(pyridin-4-yl)-1*H*-indol-3-yl)acetate (1ab):- yellow solid, 104 mg (0.39 mmol), 78%, R_f = 0.5 (EtOAc/Hexane, 40:60); **MP** 118-120 ^oC; **IR** 724, 906, 1217, 1414, 1603, 1728, 2928 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 3.73 (s, 3H), 3.90 (s, 2H), 7.15-7.20 (m, 1H), 7.22-7.30 (m, 1H), 7.35-7.38 (m, 1H), 7.57-7.59 (m, 2H), 7.61-7.71 (m, 1H), 8.62-8.66 (m, 2H), 9.23 (s, 1H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 31.3, 52.5, 108.0, 111.4, 119.6, 120.5, 122.3, 123.7, 128.9, 133.1, 136.5, 140.1, 150.4, 172.3; **MS** (ESI) m/z 267 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{16}H_{15}N_2O_2$ $[M+H]^+$ 267.11280, found 267.11210.



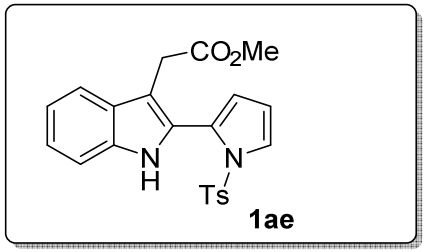
1ac

methyl 2-(2-(quinolin-4-yl)-1*H*-indol-3-yl)acetate (1ac):- cream colour solid, 130 mg (0.41 mmol), 82%, R_f = 0.5 (EtOAc/Hexane, 30:70); **MP** 138-140 ^oC; **IR** 745, 1167, 1435 ,1732, 2923, 3345 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 3.62 (s, 3H), 3.70 (s, 2H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.43-7.53 (m, 3H), 7.63-7.77 (m, 2H), 7.88 (d, *J* = 8.4 Hz, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 8.85-8.87 (m, 1H), 9.06 (s, 1H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 30.8, 52.0, 108.8, 111.3, 119.5, 120.4, 122.8, 123.3, 125.9, 127.1, 127.2, 128.2, 129.7, 132.0, 136.4, 138.6, 148.4, 149.8, 172.0; **MS** (ESI) m/z 317 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{20}H_{17}N_2O_2$ $[M+H]^+$ 317.12605, found 317.12802.

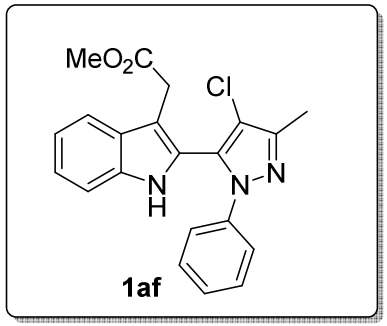


1ad

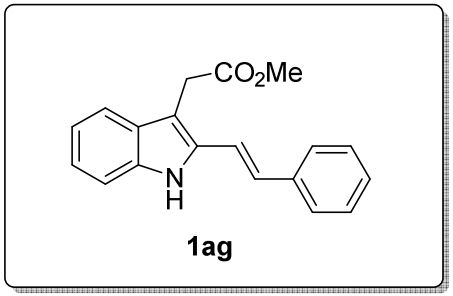
methyl 2-(2-(thiophen-2-yl)-1*H*-indol-3-yl)acetate (1ad):- pale yellow solid, 121 mg (0.45 mmol), 89%, R_f = 0.5 (EtOAc/Hexane, 10:90); **MP** 110-112^oC; **IR** 696, 1191, 1433, 1716, 2950, 3365 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 3.69 (s, 3H), 3.92 (s, 2H), 7.10-7.15 (m, 2H), 7.15-7.22 (m, 1H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.33-7.36 (m, 2H), 7.54-7.64 (m, 1H), 8.21 (s, 1H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 31.0, 52.1, 106.2, 110.9, 119.1, 120.3, 123.0, 125.8, 125.9, 128.0, 129.0, 130.0, 133.9, 135.7, 172.4; **MS** (ESI) m/z 272 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{15}H_{14}NSO_2$ $[M+H]^+$ 272.07398 found 272.07384.



methyl 2-(2-(1-tosyl-1*H*-pyrrol-2-yl)-1*H*-indol-3-yl)acetate (1ae):- light brown solid, 165 mg (0.405 mmol), 81%, R_f = 0.5 (EtOAc/Hexane, 10:90); **MP** 118-120 °C; **IR** 745, 1170, 1451, 1731, 3399 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 2.29 (s, 3H), 3.15 (s, 2H), 3.61 (s, 3H), 6.38 (t, *J* = 3.3 Hz, 1H), 6.52-6.56 (m, 1H), 6.96 (d, *J* = 8.2 Hz, 2H), 7.12-7.18 (m, 3H), 7.23-7.29 (m, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.52-7.58 (m, 2H), 8.65 (s, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ = 21.6, 30.6, 52.0, 109.9, 111.3, 112.0, 119.3, 119.6, 120.0, 123.2, 124.3, 124.7, 127.0, 129.5, 134.5, 135.7, 145.1, 172.2; **MS** (ESI) m/z 409 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{22}H_{21}N_2SO_4$ $[M+H]^+$ 409.12165, found 409.12151.

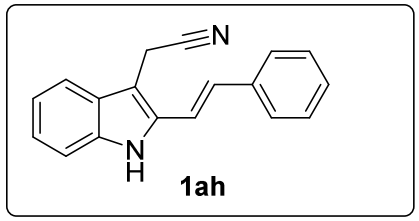


methyl 2-(2-(4-chloro-3-methyl-1-phenyl-1*H*-pyrazol-5-yl)-1*H*-indol-3-yl)acetate (1af):- cream colour solid, 165 mg (0.437 mmol), 87%, R_f = 0.5 (EtOAc/Hexane, 20:80); **MP** 166-168 °C; **IR** 745, 1157, 1452, 1732, 2923, 3358 cm^{-1}; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 2.28 (s, 3H), 3.66 (s, 3H), 3.74 (s, 2H), 7.15-7.23 (m, 1H), 7.24-7.28 (m, 1H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.40-7.56 (m, 3H), 7.59-7.70 (m, 3H), 8.22 (s, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ = 13.0, 31.0, 51.9, 108.5, 111.0, 119.3, 120.0, 122.7, 124.9, 128.1, 128.4, 129.1, 136.2, 138.1, 149.9, 172.1; **MS** (ESI) m/z 380 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{21}H_{19}N_3ClO_2$ $[M+H]^+$ 380.11603 found 380.11612.



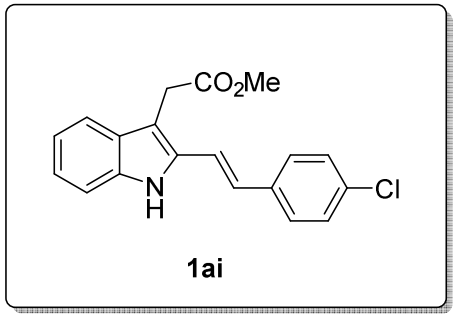
1ag

methyl (*E*)-2-(2-styryl-1*H*-indol-3-yl)acetate (1ag):- off-white solid, 124 mg (0.425 mmol), 85%, R_f = 0.5 (EtOAc/Hexane, 10:90); **MP** 104-106 ^oC ; **IR** 748, 771, 1158, 1436, 1720, 2921, 3382 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 3.68 (s, 3H), 3.86 (s, 2H), 6.86 (d, *J* = 16.3 Hz, 1H*),* 7.11 (t, *J* = 7.4 Hz, 1H*)*, 7.15-7.30 (m, 4H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.49 (d, *J* = 7.7 Hz, 2H), 7.58 (d, *J* = 7.9 Hz, 1H), 8.26 (s, 1H); **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 30.1, 52.2, 108.7, 110.6, 116.6, 119.0, 120.0, 123.4, 126.4 (2C), 127.5, 127.9, 128.8 (2C), 133.7, 136.4, 136.9, 171.7; **MS** (ESI) m/z 292 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{19}H_{18}NO_2$ $[M+H]^+$ 292.13080, found 292.13319. The spectroscopic data were in good agreement with the reported data.[3]



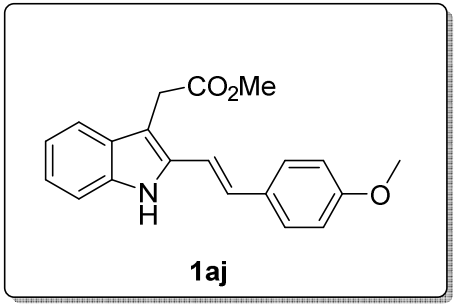
1ah

***(E)*-2-(2-styryl-1*H*-indol-3-yl)acetonitrile (1ah):-** yellowish green solid, 73 mg (0.28 mmol), 56% (with isolated imine), R_f = 0.5 (EtOAc/Hexane, 10:90); **MP** 130-132 ^oC; **IR** 749, 950, 1322, 1451, 2249, 2924, 3356 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 3.93 (s, 2H), 6.93 (d, *J* = 11.64 Hz, 1H), 7.19 (dd, *J* = 11.7, 4.6 Hz, 2H), 7.23--7.36 (m, 3H), 7.39 (dd, *J* = 12.7, 4.9 Hz, 2H), 7.53 (d, *J* = 7.3 Hz, 2H),7.63 (d, *J* = 7.9 Hz, 1H), 8.30 (s, 1H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ =13.1, 103.5, 110.9, 115.3, 117.8, 118.2, 120.6, 123.8, 126.5, 127.7, 128.3, 128.9, 129.0, 133.5, 136.1, 136.3; **MS** (ESI) m/z 257 $[M-H]^+$.



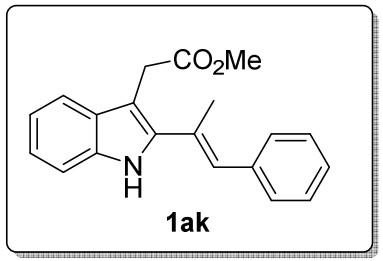
1ai

methyl (*E*)-2-(2-(4-chlorostyryl)-1*H*-indol-3-yl)acetate (1ai):- yellow solid, 108 mg (0.33 mmol), 66%, R_f = 0.5 (EtOAc/Hexane, 10:90); **MP** 130-132 ^oC; **IR** 743, 1163, 1489, 1725, 2924, 3380 cm^{-1}; **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 3.68 (s, 3H), 3.86 (s, 2H), 6.77 (d, *J* = 16.4 Hz, 1H), 7.06-7.24 (m, 3H), 7.27-7.35 (m, 3H), 7.36-7.42 (m, 2H), 7.58 (d, *J* = 7.8 Hz, 1H), 8.29 (s, 1H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 30.3, 52.2, 110.7, 117.1, 119.0, 120.1, 123.5, 126.0, 127.5, 128.9, 130.0, 133.3, 135.4, 136.4, 172.1; **MS** (ESI) m/z 326 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{19}H_{17}NClO_2$ $[M+H]^+$ 326.09423, found 326.09417.



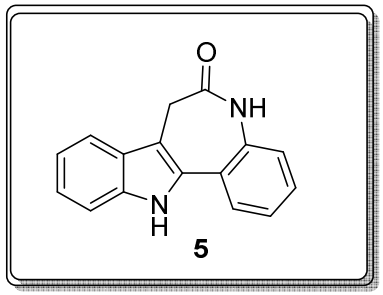
1aj

methyl (*E*)-2-(2-(4-methoxystyryl)-1*H*-indol-3-yl)acetate (1aj):- pale yellow solid, 102 mg (0.315 mmol), 63%, R_f = 0.5 (EtOAc/Hexane, 10:90); **MP** 100-102 ^oC; **IR** 745, 1246, 1430, 1652, 1713, 2952, 3365 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 3.68 (s, 3H), 3.84 (s, 3H), 3.86 (s, 2H), 6.84 (d, *J* = 16.4 Hz, 1H), 6.91 (d, *J* = 8.5 Hz, 2H), 7.05-7.14 (m, 2H), 7.19 (t, *J* = 7.6Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.57 (t, *J* = 7.8 Hz, 1H), 8.26 (s, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ = 30.3, 52.1, 55.4, 108.0, 110.5, 114.3, 114.6, 118.8, 120.0, 123.1, 127.2, 127.7, 127.8, 128.9, 129.6, 134.0, 136.2, 159.5, 172.1; **MS** (ESI) m/z 322 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{20}H_{20}NO_3$ $[M+H]^+$ 322.14377, found 322.14362.



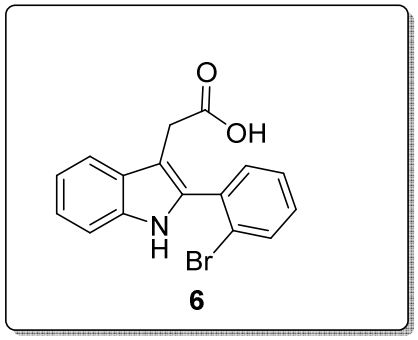
1ak

methyl (*E*)-2-(2-(1-phenylprop-1-en-2-yl)-1*H*-indol-3-yl)acetate (1ak):- Brown colour liquid, 86 mg (0.28 mmol), 56%, R_f = 0.4 (EtOAc/Hexane, 10:90); **IR** 772, 1171, 1435, 1725, 2923, 3390 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ = 2.33 (s, 3H), 3.72 (s, 3H), 3.93 (s, 2H), 6.93 (s, 1H), 7.13-7.18 (m, 1H), 7.19-7.23 (m, 1H), 7.27-7.31 (m, 1H), 7.32-7.35 (m, 1H), 7.38-7.43 (m, 4H), 7.63 (d, *J* = 7.8 Hz, 1H), 8.10 (s, 1H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 18.1, 31.3, 52.0, 105.4, 110.7, 119.0, 120.0, 122.5, 127.0, 128.3(2C), 129.2, 131.2, 135.2, 137.3, 139.2, 172.7; **MS** (ESI) m/z 306 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{20}H_{20}NO_2$ $[M+H]^+$ 306.14886, found 306.14783.



5

7,12-dihydrobenzo[2,3]azepino[4,5-b]indol-6(5*H*)-one (5) :- pale yellow solid, 300 mg (1.2 mmol), 60%, R_f = 0.3 (EtOAc/Hexane, 50:50); **MP** 280-282 ^oC; **IR** (KBr) 3221,1643 cm^{-1}; **^{1}H-NMR** (300 MHz, DMSO-d_6) δ = 3.50 (s, 2H), 7.07-7.43 (m, 6H), 7.64-7.73 (m, 2H), 10.10 (s, 1H), 11.6 (s,1H); **^{13}C-NMR** (75 MHz, DMSO-d_6) δ = 31.6, 107.5, 111.4, 117.9, 119.1, 122.1, 122.2, 122.8, 123.6, 126.8, 127.9, 128.7, 132.4, 135.4, 137.4, 171.5; **MS** (ESI) m/z 247 $[M-H]^+$ **HRMS** (ESI, m/z): calcd for $C_{16}H_{11}NO_2$ $[M-H]^+$ 247.08659, found 247.08905. The spectroscopic data were in good agreement with literature report.[1]



6

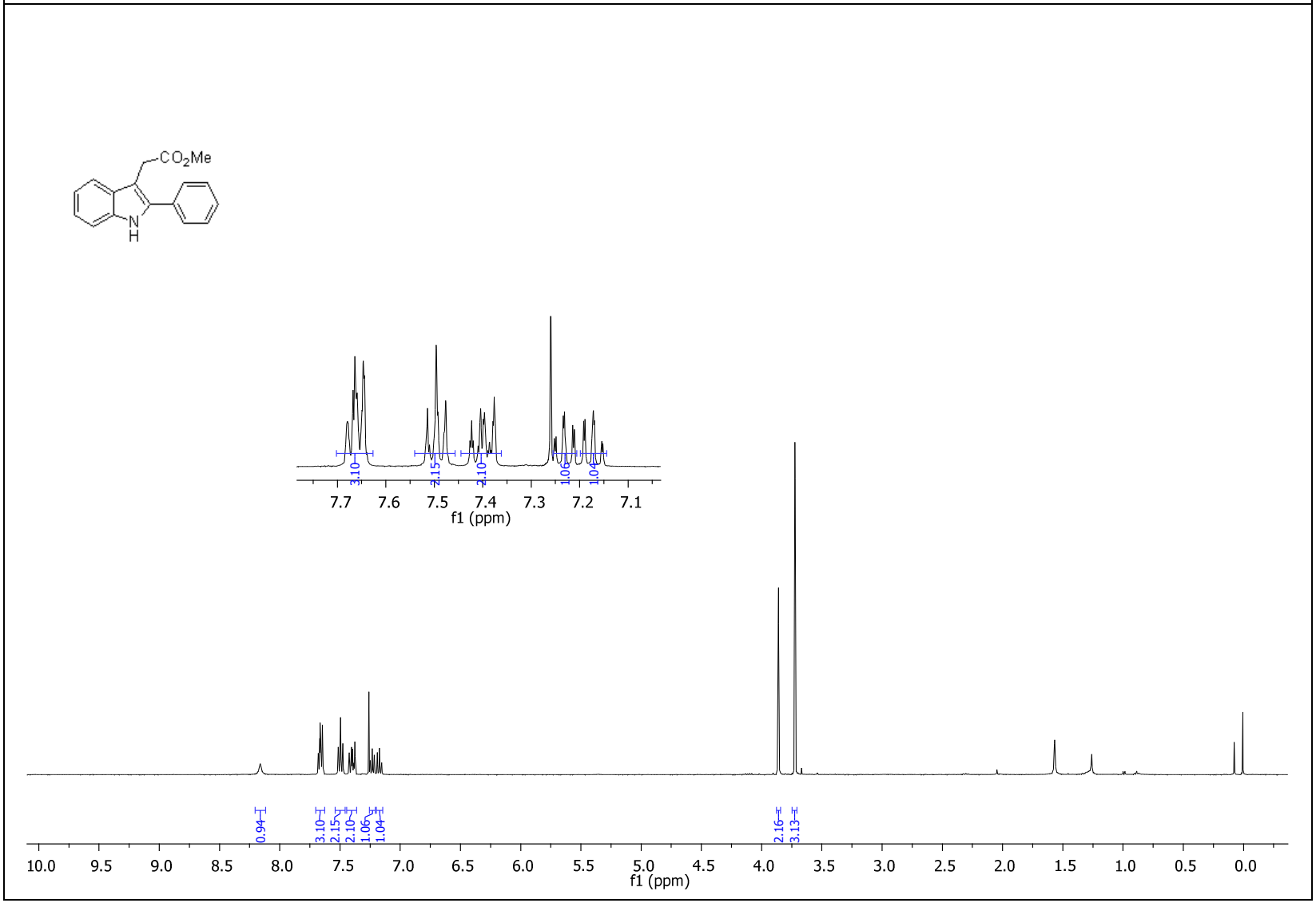
2-(2-(2-bromophenyl)-1*H*-indol-3-yl)acetic acid (6) :- white solid, 316 mg (0.96 mmol), 96%, R_f = 0.5 (EtOAc/Hexane, 70:30); **MP** 192-194 ^{o}C; **IR** 745, 1452, 1705, 2923, 3403 cm^{-1}; **^{1}H-NMR** (300 MHz, DMSO-d_6) δ = 3.48 (s, 2H), 7.03 (t, *J* = 7.1Hz, 1H), 7.13 (t, *J* = 7.1Hz, 1H), 7.33-7.46 (m, 2H), 7.47-7.57 (m, 3H), 7.79 (d, *J* = 7.9Hz, 1H), 11.25 (s, 1H), 12.16 (s, 1H); **^{13}C-NMR** (75 MHz, DMSO-d_6) δ = 30.5, 106.3, 111.1, 118.7, 119.0, 121.5, 123.6, 127.5, 130.4, 132.8, 132.8, 133.5, 134.6, 135.5, 172.7; **MS** (ESI) m/z 330 $[M+H]^+$ **HRMS** (ESI, m/z): calcd for $C_{16}H_{13}BrNO_2$ $[M+H]^+$ 330.01242, found 330.01260.

9. References

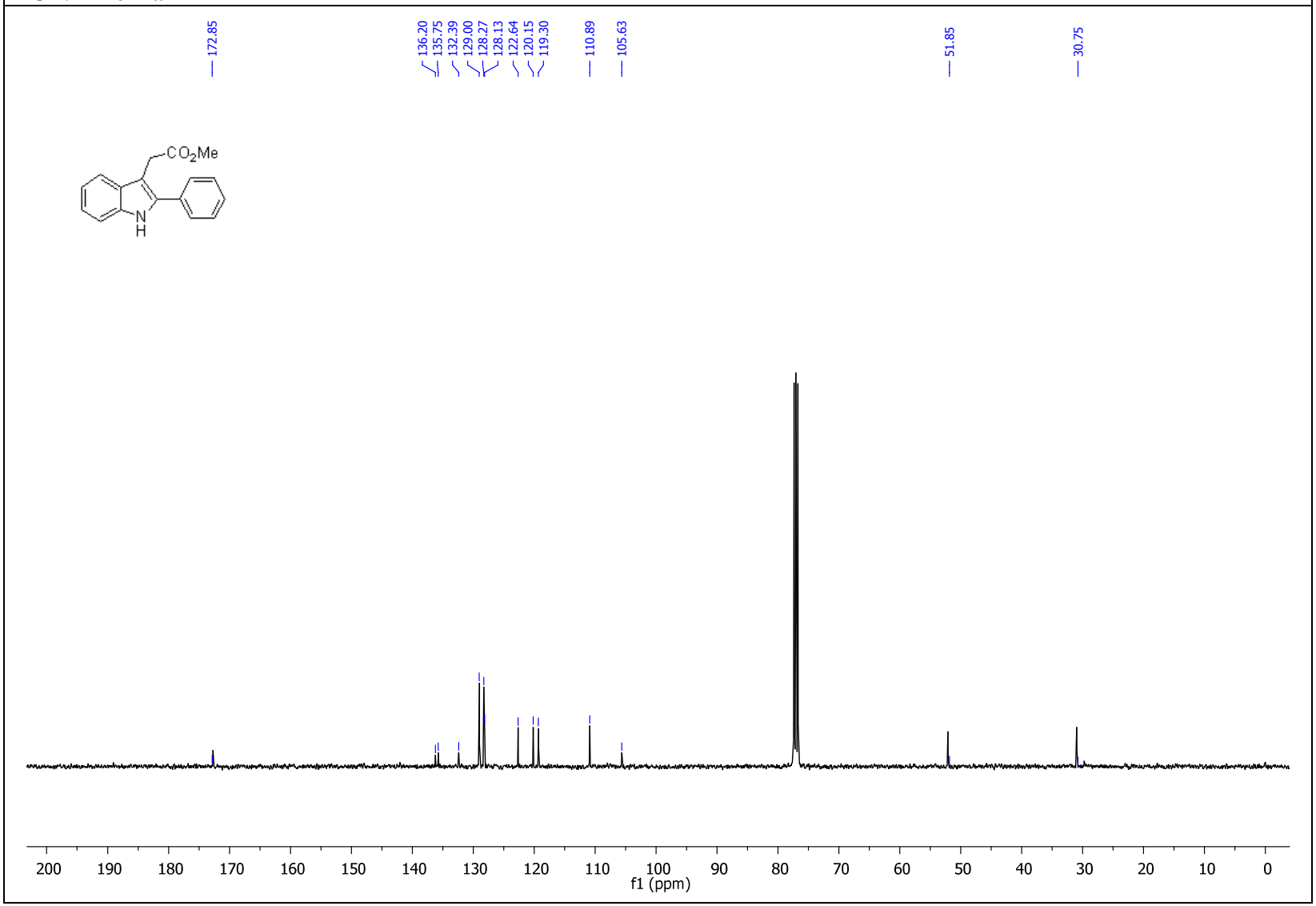
1. M. Tobisu, H. Fujihara, K. Koh and N. Chatani, *J. Org. Chem*., 2010, **75**, 4841.
2. S. J. Lee, H.-A. Seo and C.-H. Cheon, *Adv. Synth. Catal*., 2016, **358**, 1566.
3. H.-A. Seo and C.-H. Cheon, *J. Org. Chem.,* 2016*,* **81**, 7917.

10. Copies of ^{1}H and ^{13}C NMR spectra of the products

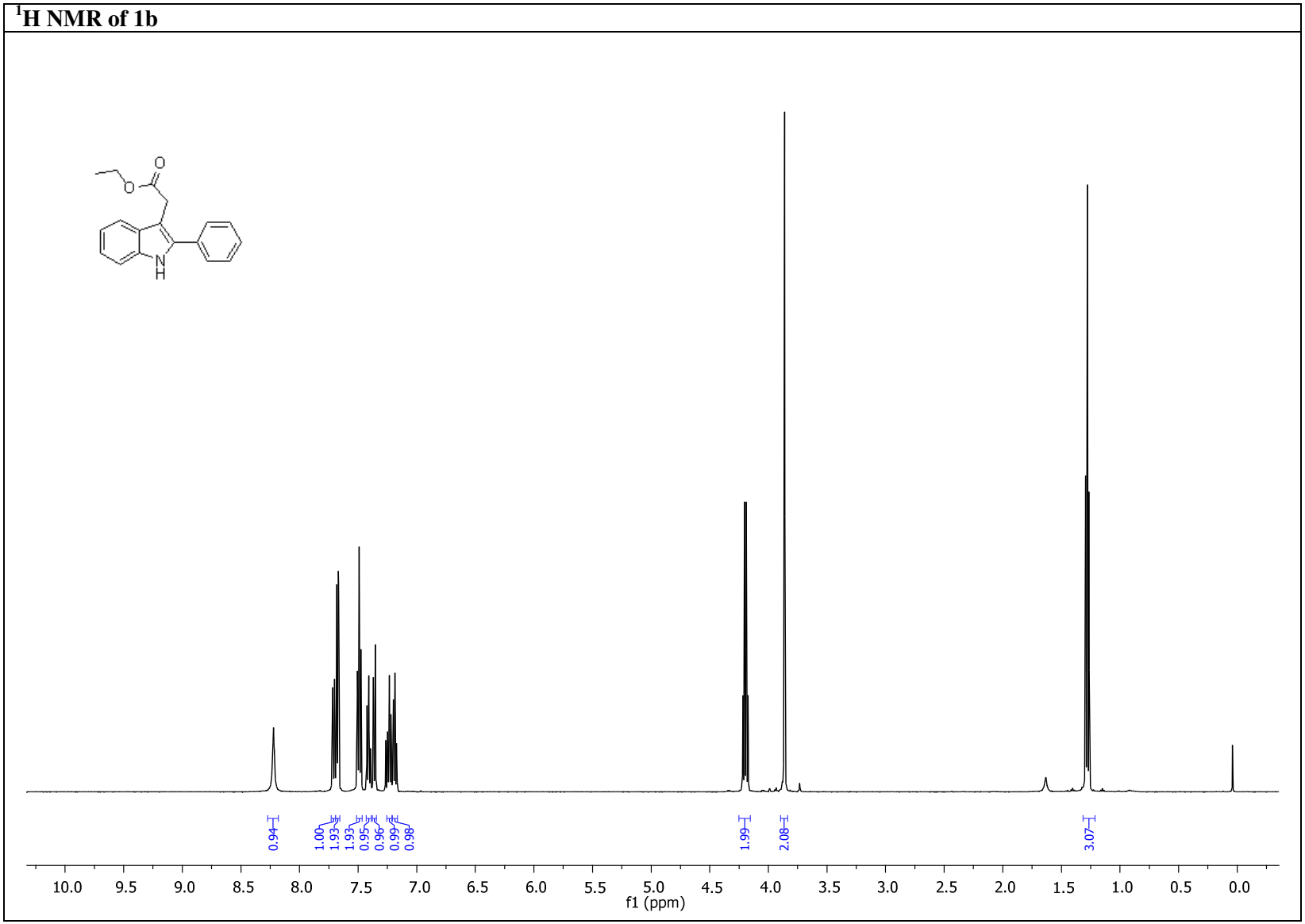
^{1}H NMR of 1a



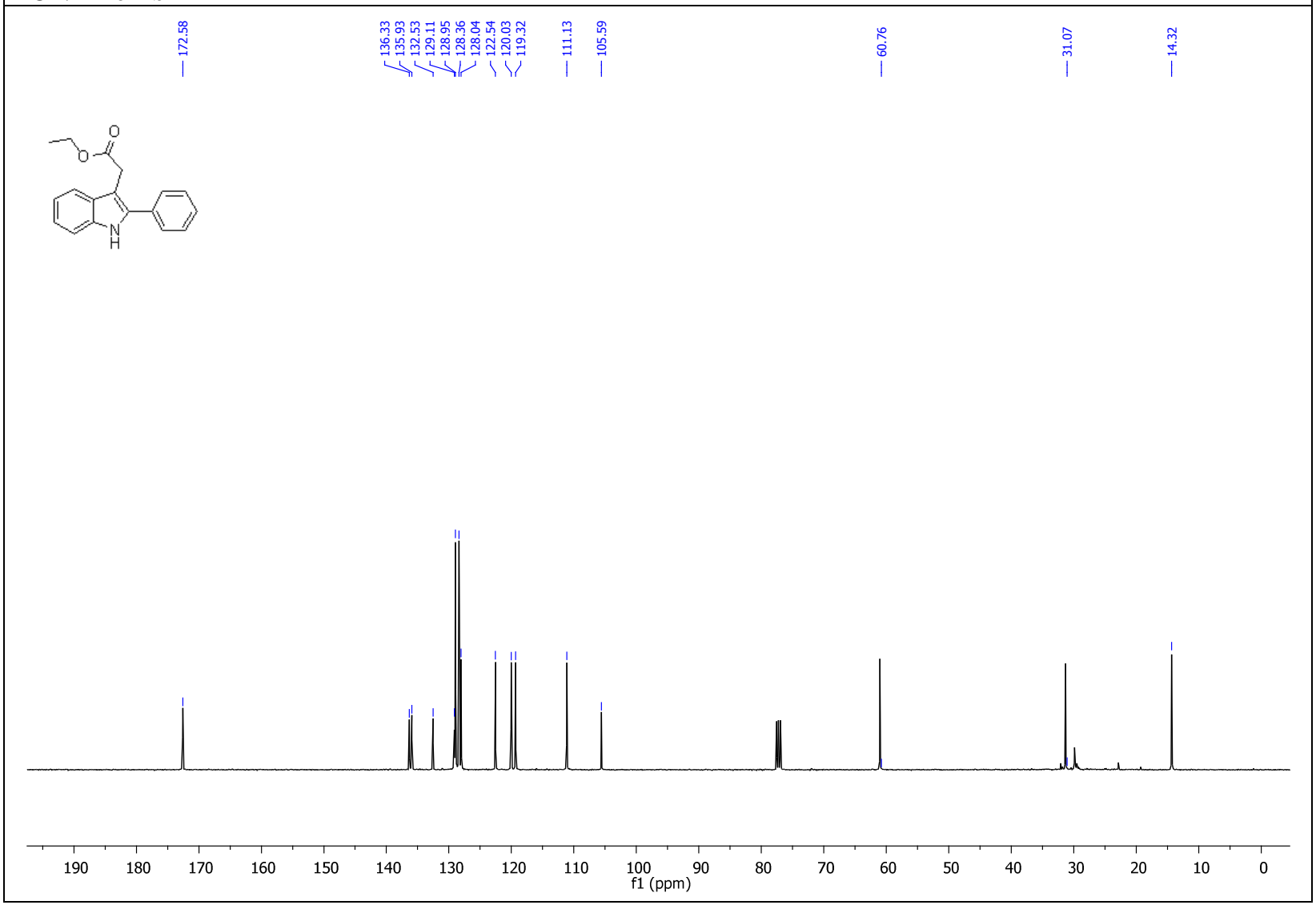
^{13}C NMR of 1a


172.85
136.20
135.75
132.39
129.00
128.27
128.13
122.64
120.15
119.30
110.89
105.63
51.85
30.75
CO2Me
N
H
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

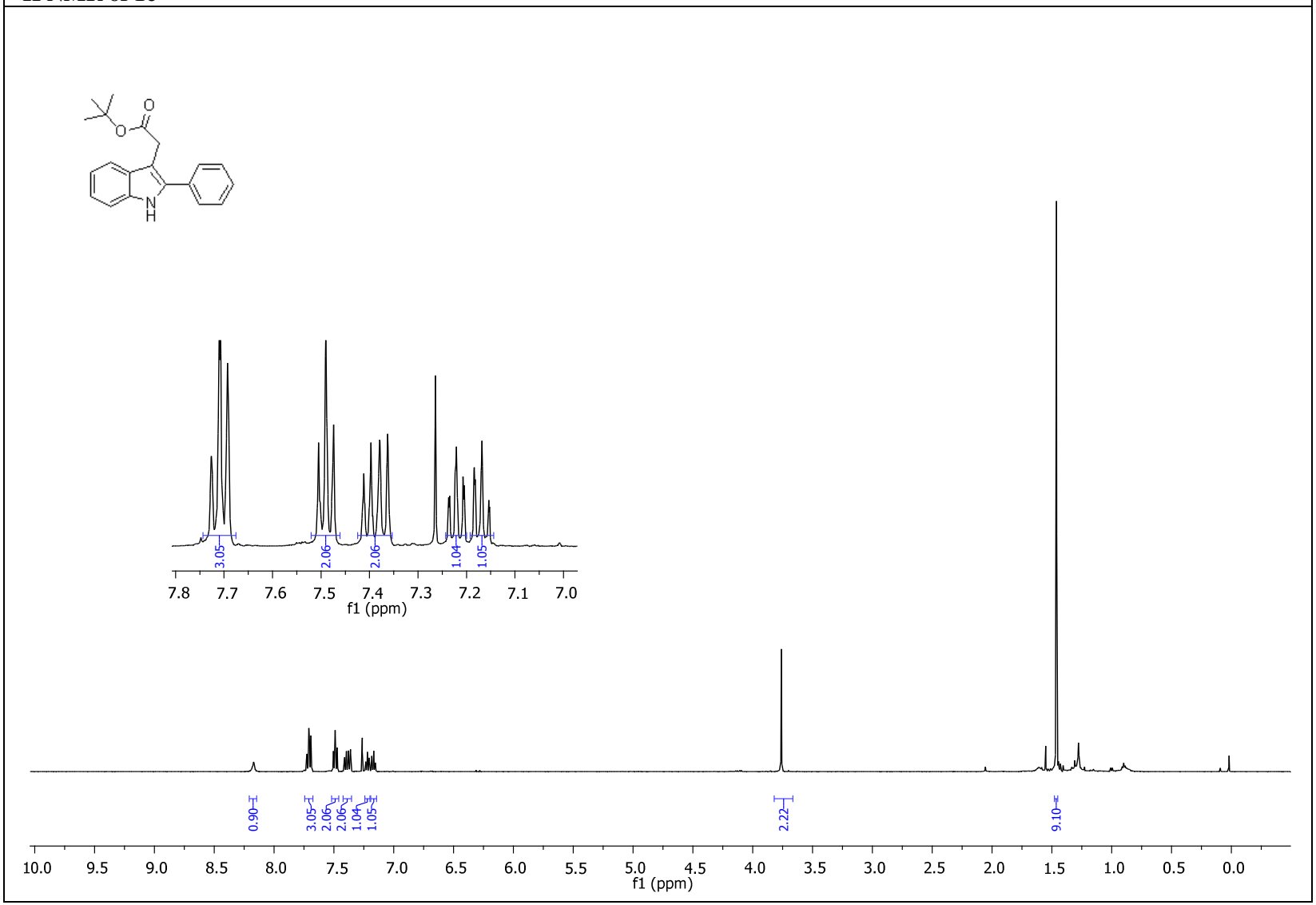
^{1}H NMR of 1b


O
O
N
H
0.94
1.00
1.93
1.93
0.95
0.96
0.99
0.98
1.99
2.08
3.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

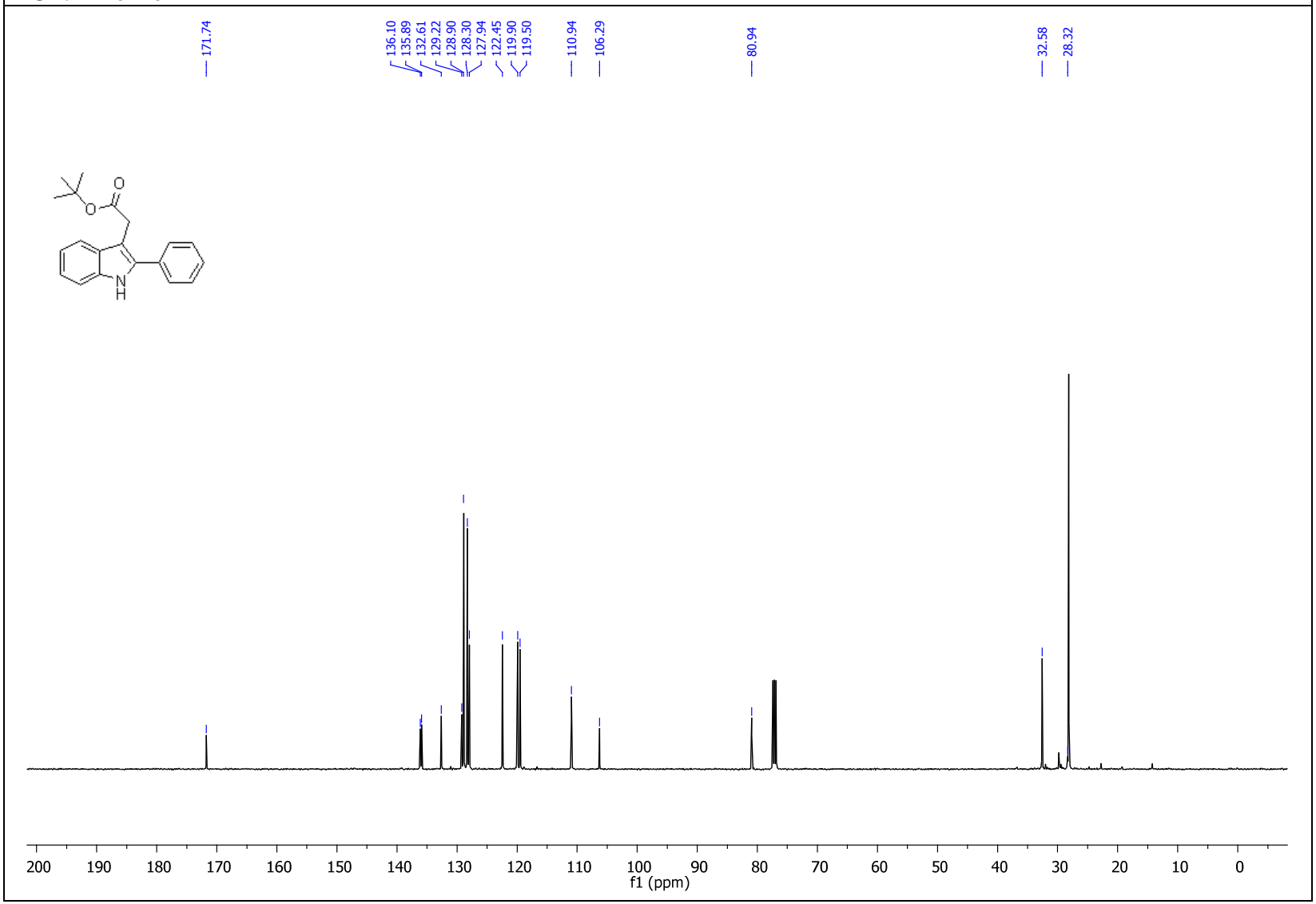
^{13}C NMR of 1b


172.58
136.33
135.93
132.53
129.11
128.95
128.36
128.04
122.54
120.03
119.32
111.13
105.59
60.76
31.07
14.32
O
O
N
H
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{1}H NMR of 1c


O
O
N
H
3.05
2.06
2.06
1.04
1.05
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
0.90
3.05
2.06
2.06
1.04
1.05
2.22
9.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

^{13}C NMR of 1c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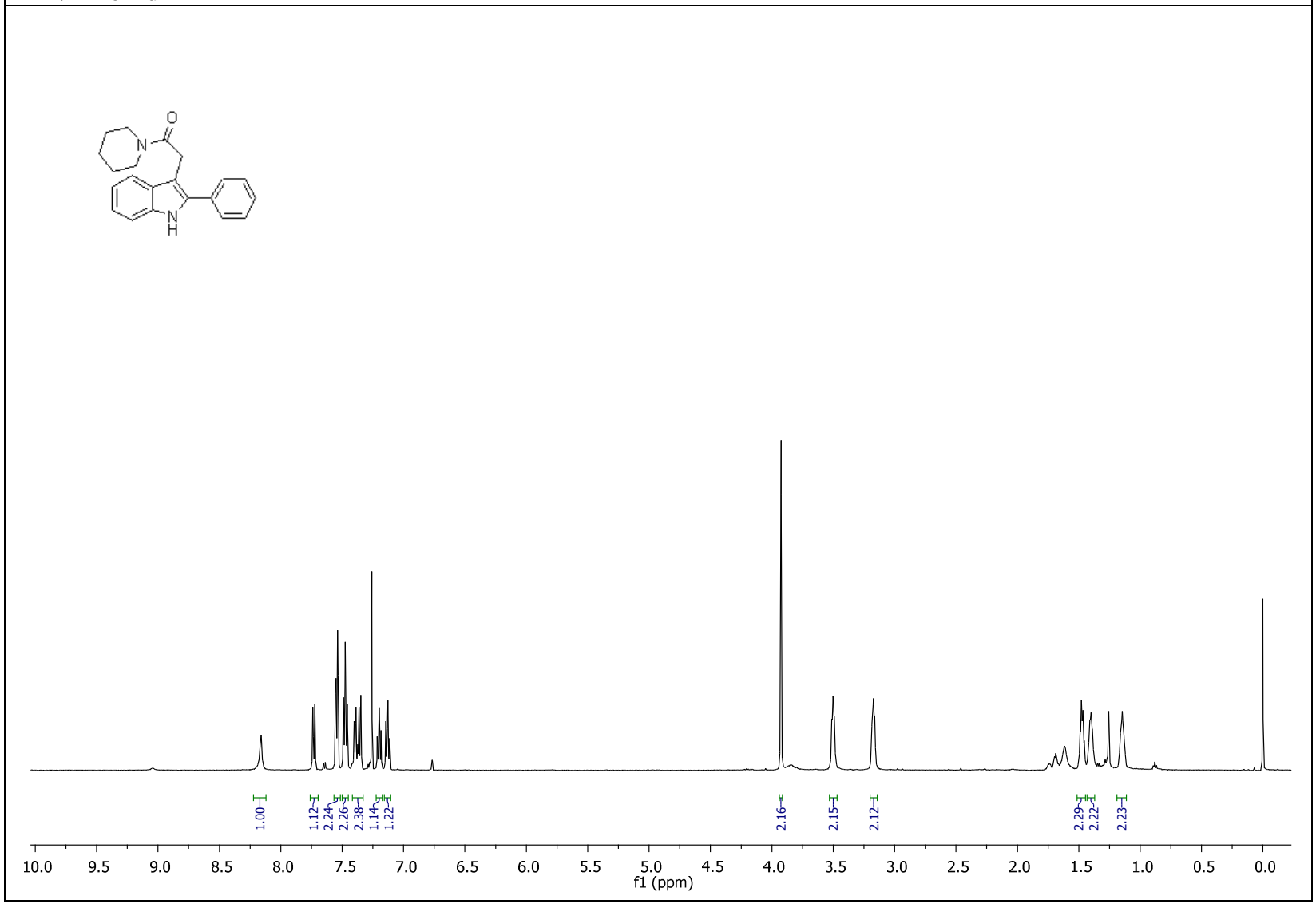
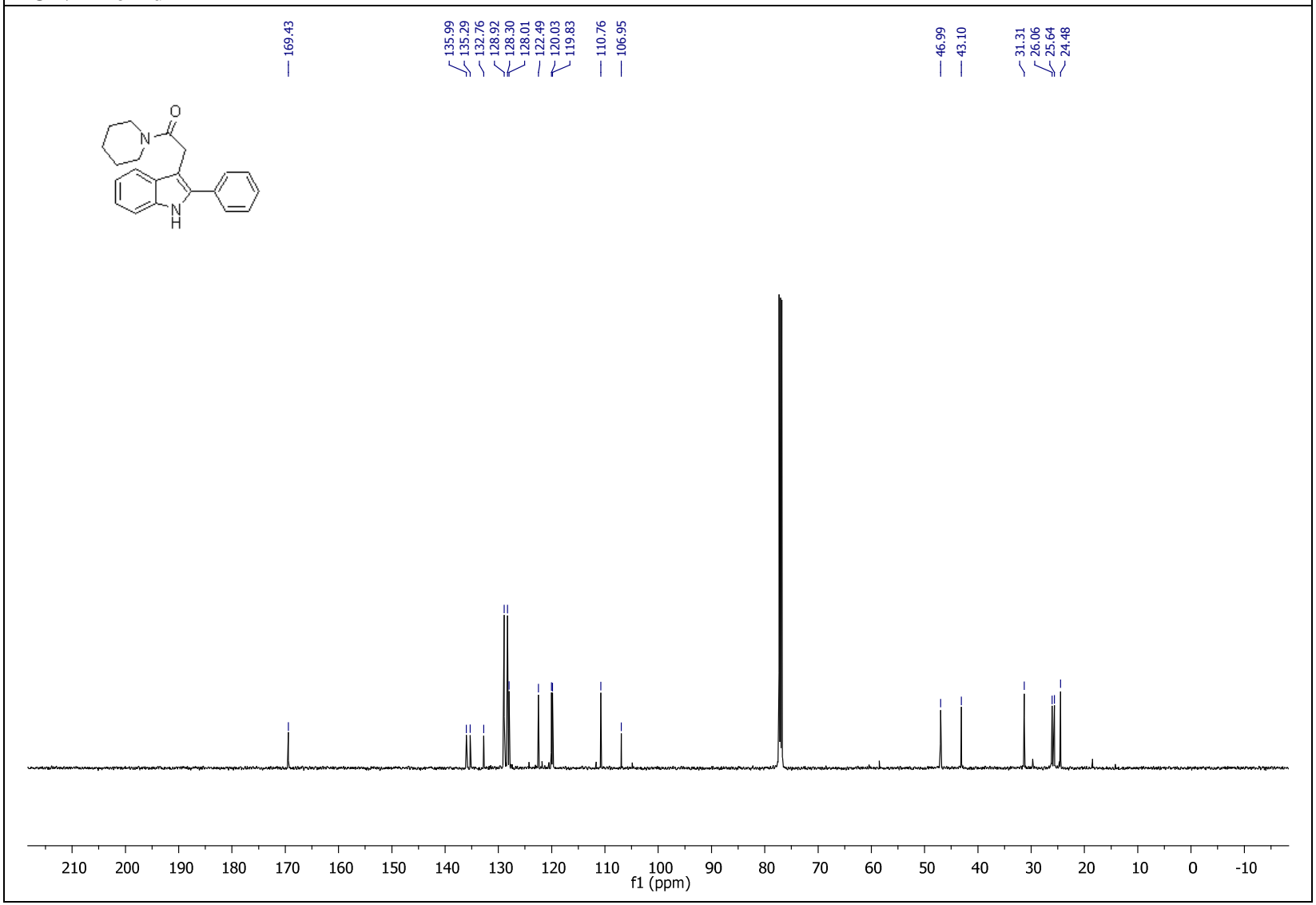
135.89
132.61
129.22
128.90
128.30
127.94
122.45
119.90
119.50
110.94
106.29
80.94
32.58
28.32
O
O
N
H
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

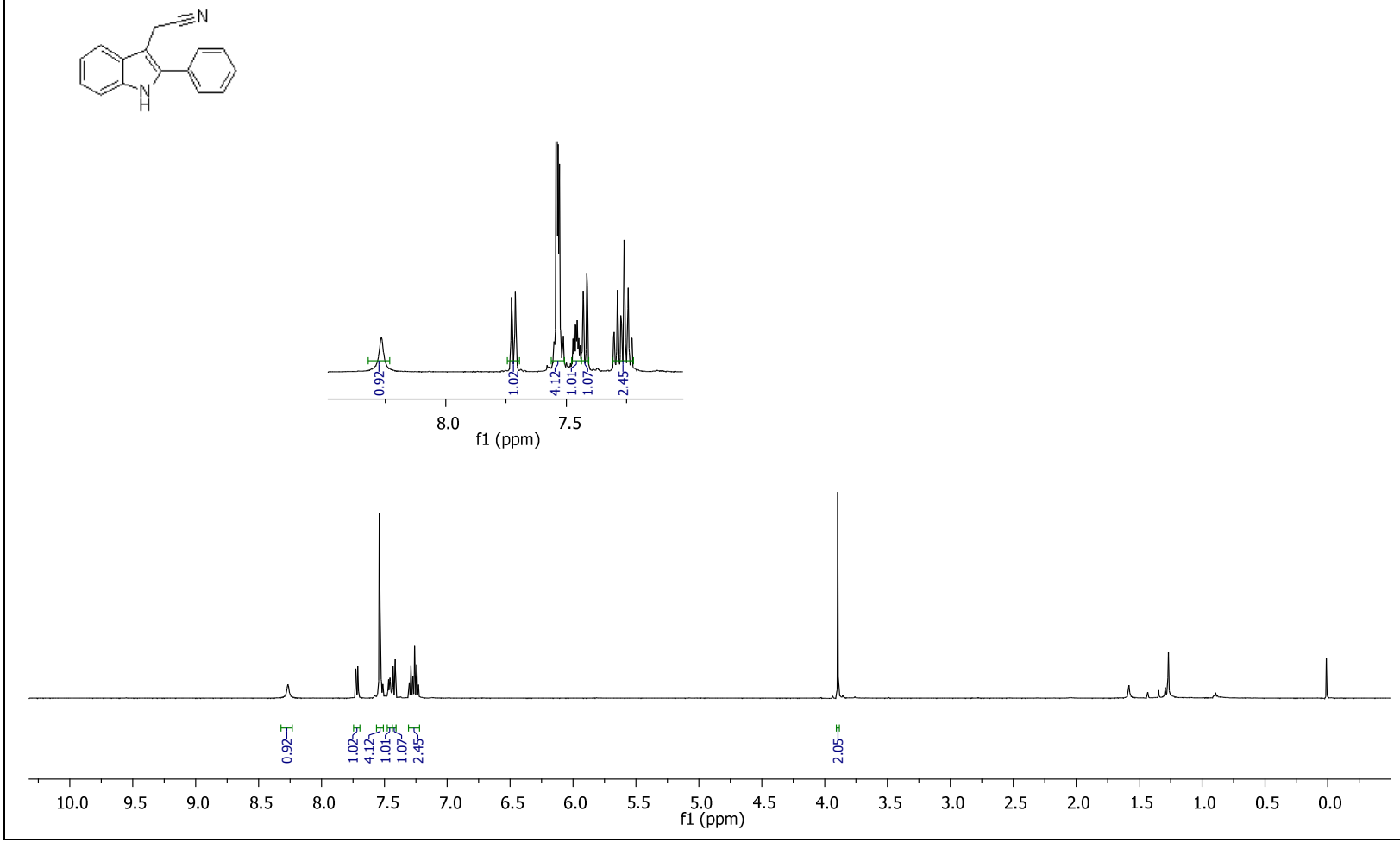
^{1}H NMR of 1d


O
N
N
H
1.00
1.12
2.24
2.26
2.38
1.14
1.22
2.16
2.15
2.12
2.29
2.22
2.23
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

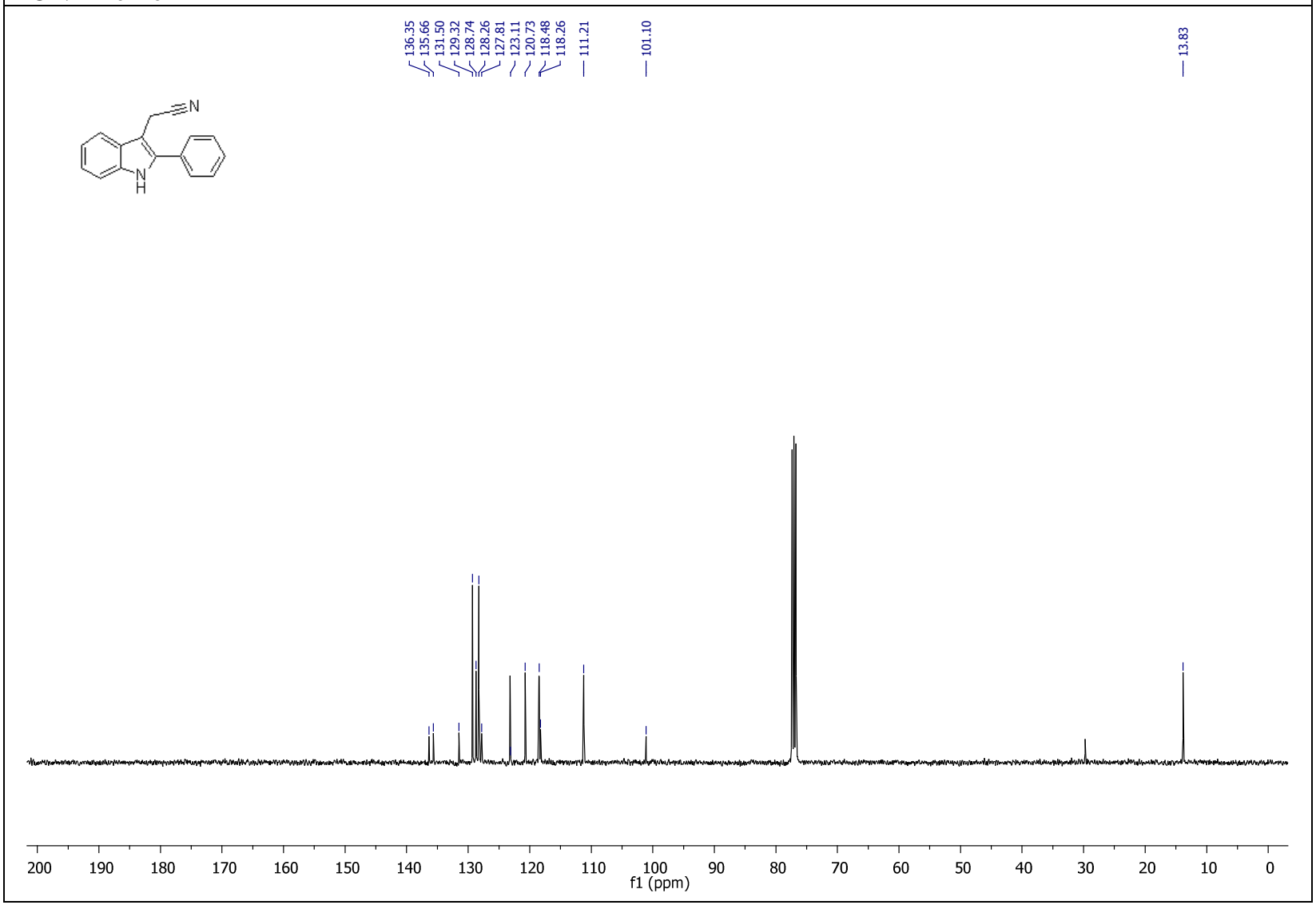
^{13}C NMR of 1d


169.43
135.99
135.29
132.76
128.92
128.30
128.01
122.49
120.03
119.83
110.76
106.95
46.99
43.10
31.31
26.06
25.64
24.48
O
N
N
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{1}H NMR of 1e


N
N
H
0.92
1.02
4.12
1.01
1.07
2.45
8.0
7.5
f1 (ppm)
0.92
1.02
4.12
1.01
1.07
2.45
2.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

^{13}C NMR of 1e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123.11
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118.26
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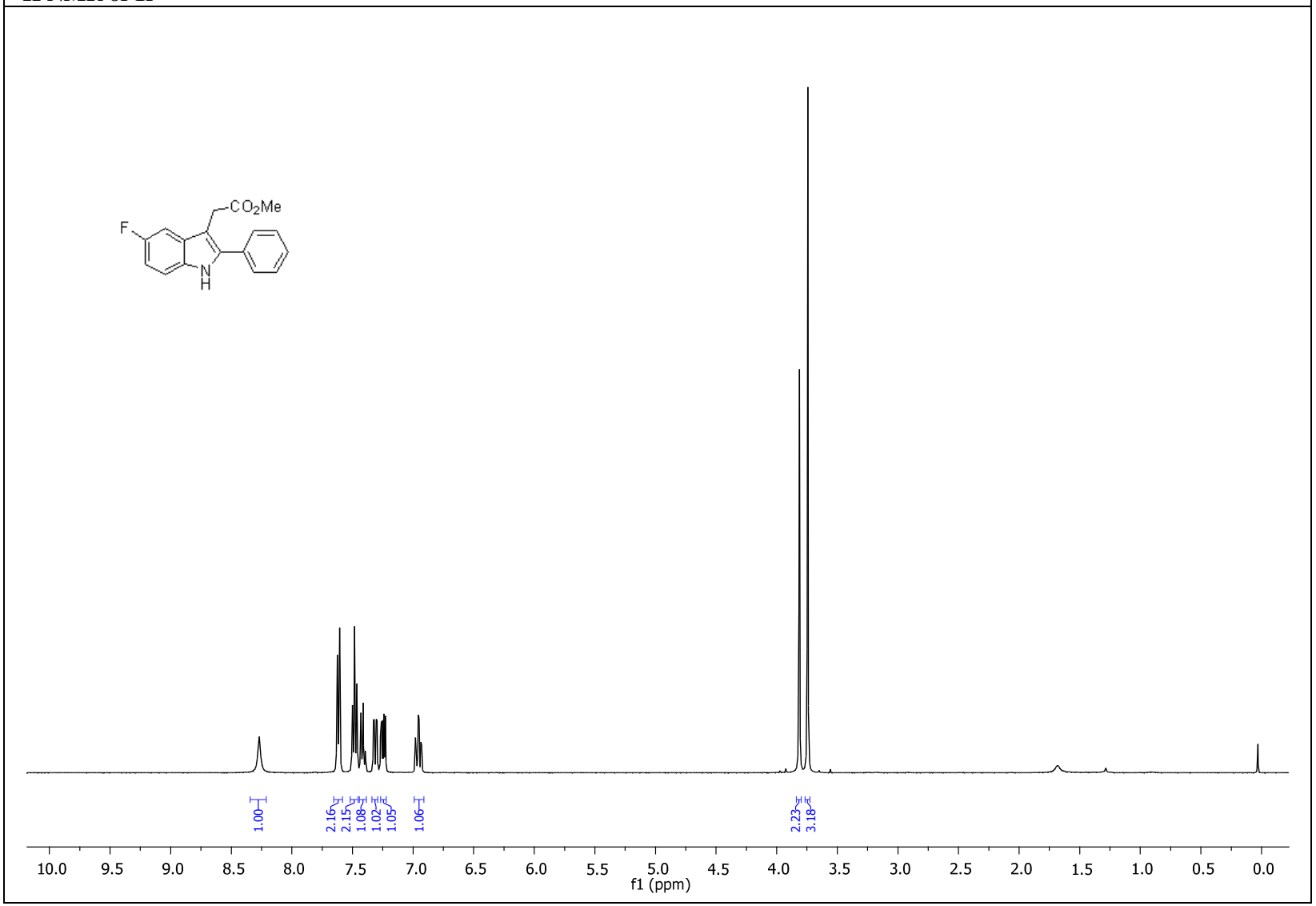
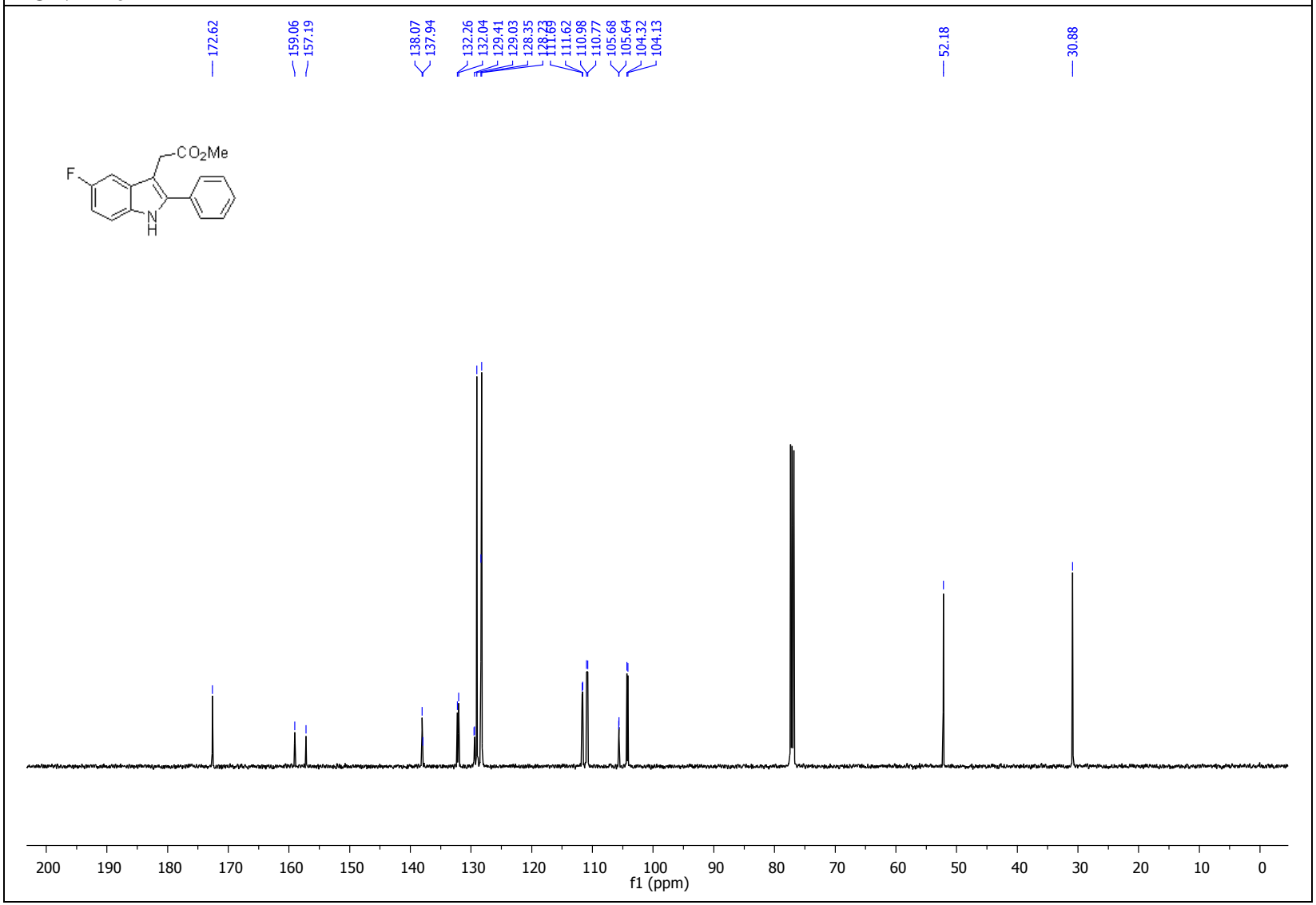
13.83
N
N
H
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

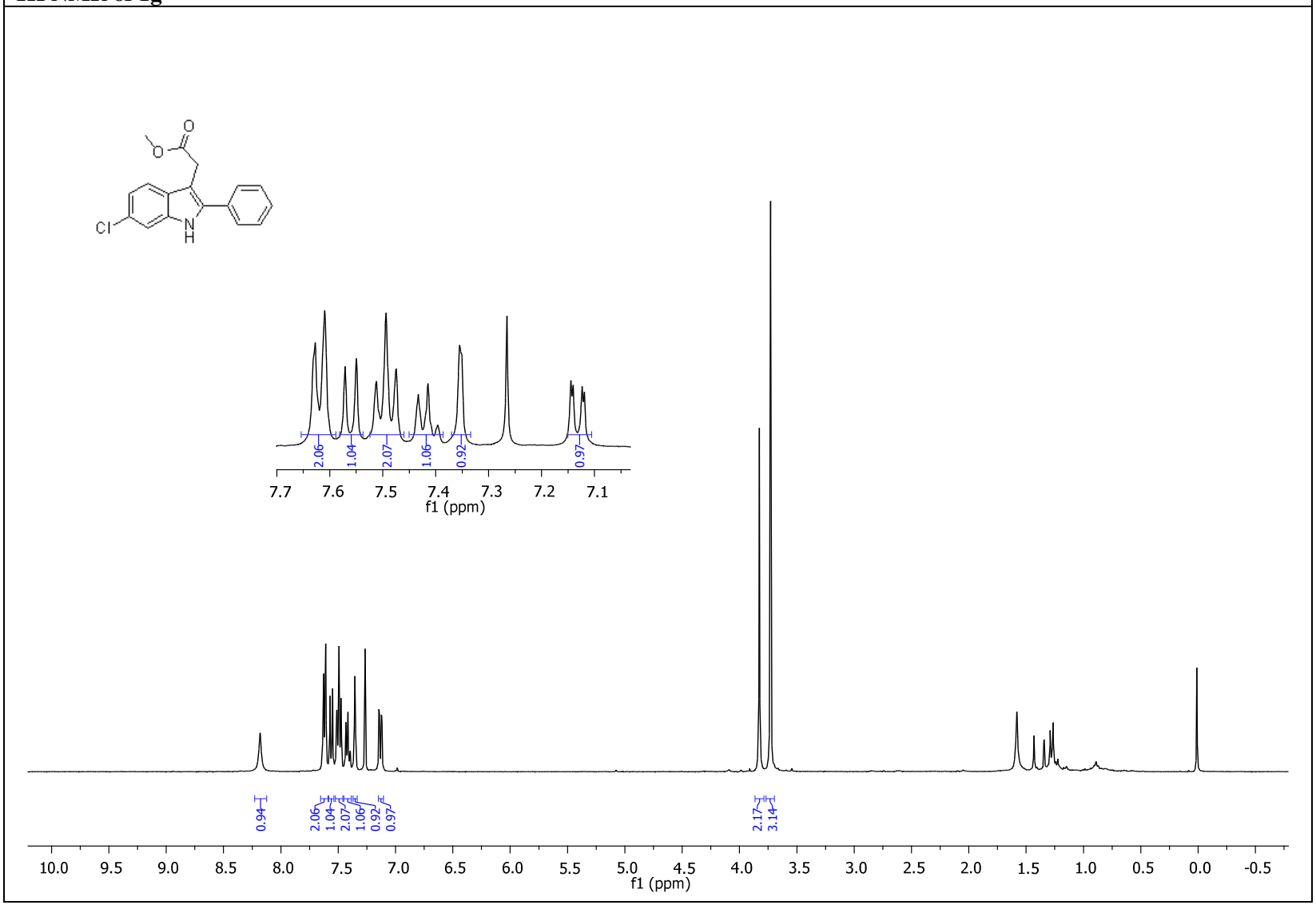
^{1}H NMR of 1f


F
CO2Me
N
H
1.00
2.16
2.15
1.08
1.02
1.05
1.06
2.23
3.18
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

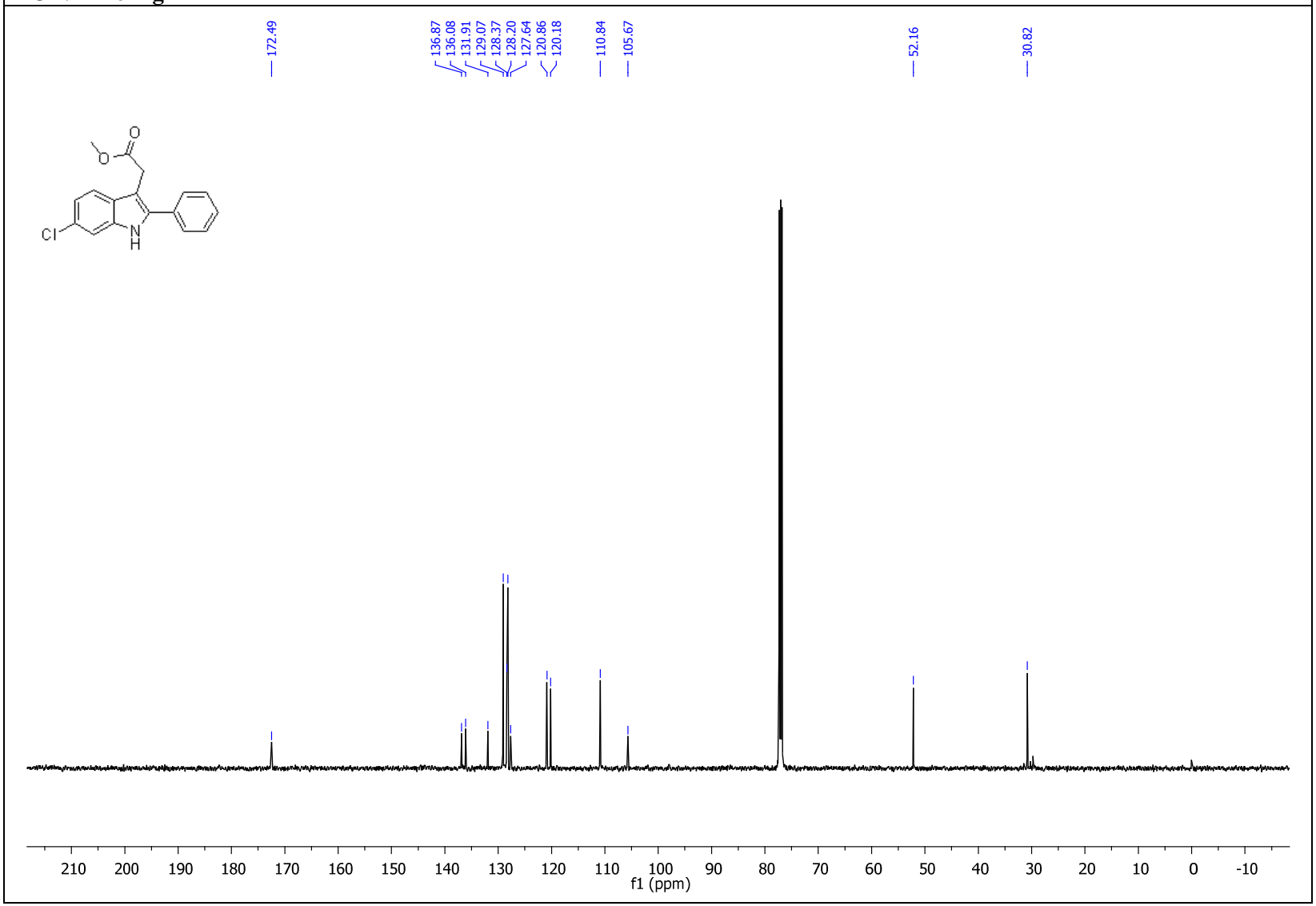
^{13}C NMR of 1f


172.62
159.06
157.19
138.07
137.94
132.26
132.04
129.41
129.03
128.35
111.62
110.98
110.77
105.68
105.64
104.32
104.13
52.18
30.88
CO2Me
F
N
H
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

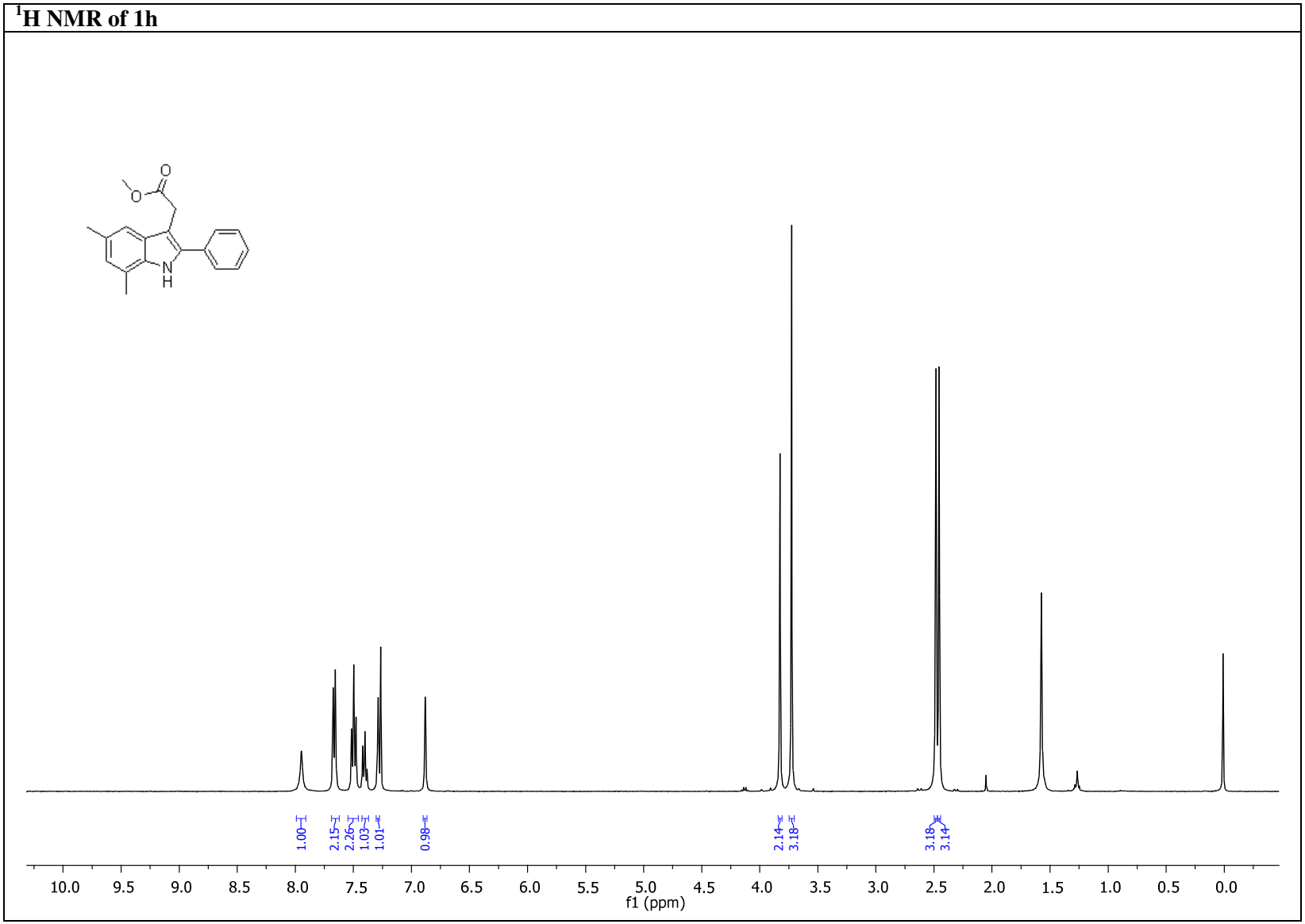
1H NMR of 1g


O
O
Cl
N
H
2.06
1.04
2.07
1.06
0.92
0.97
7.7
7.6
7.5
7.4
7.3
7.2
7.1
f1 (ppm)
0.94
2.06
1.04
2.07
1.06
0.92
0.97
2.17
3.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

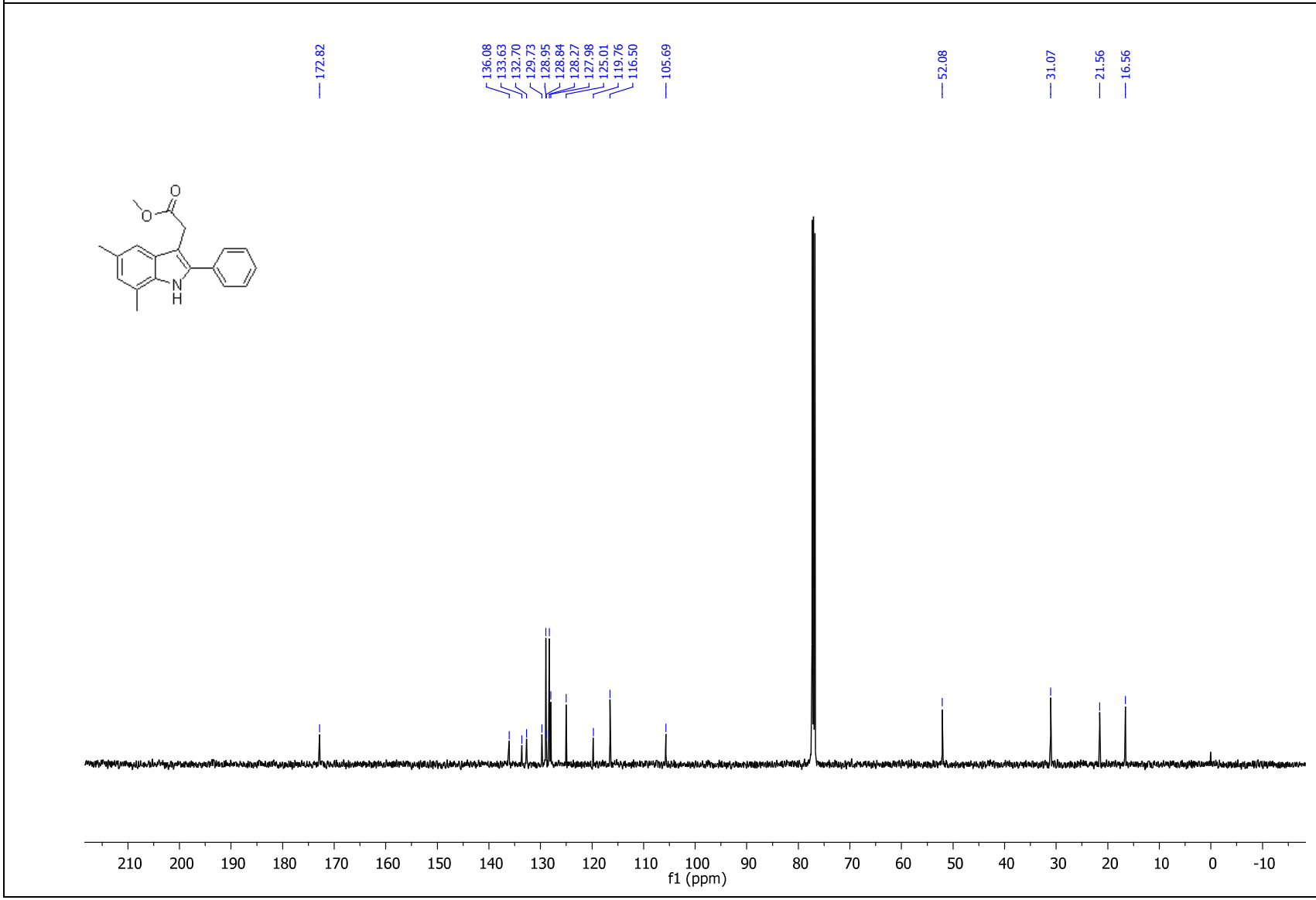
^{13}C NMR of 1g


172.49
136.87
136.08
131.91
129.07
128.37
128.20
127.64
120.86
120.18
110.84
105.67
52.16
30.82
O
O
Cl
N
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

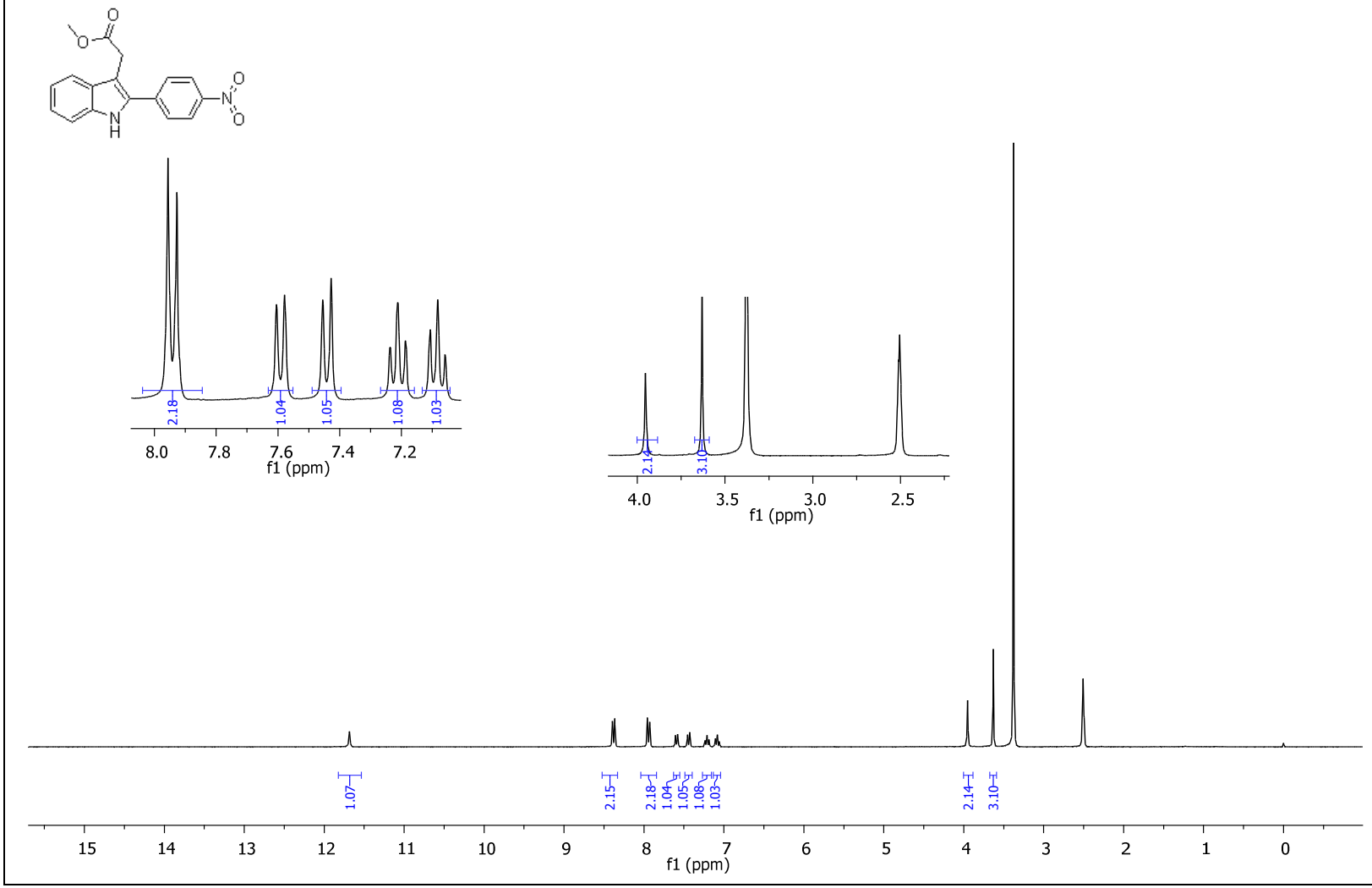
^{1}H NMR of 1h


O
O
N
H
1.00
2.15
2.26
1.03
1.01
0.98
2.14
3.18
3.18
3.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

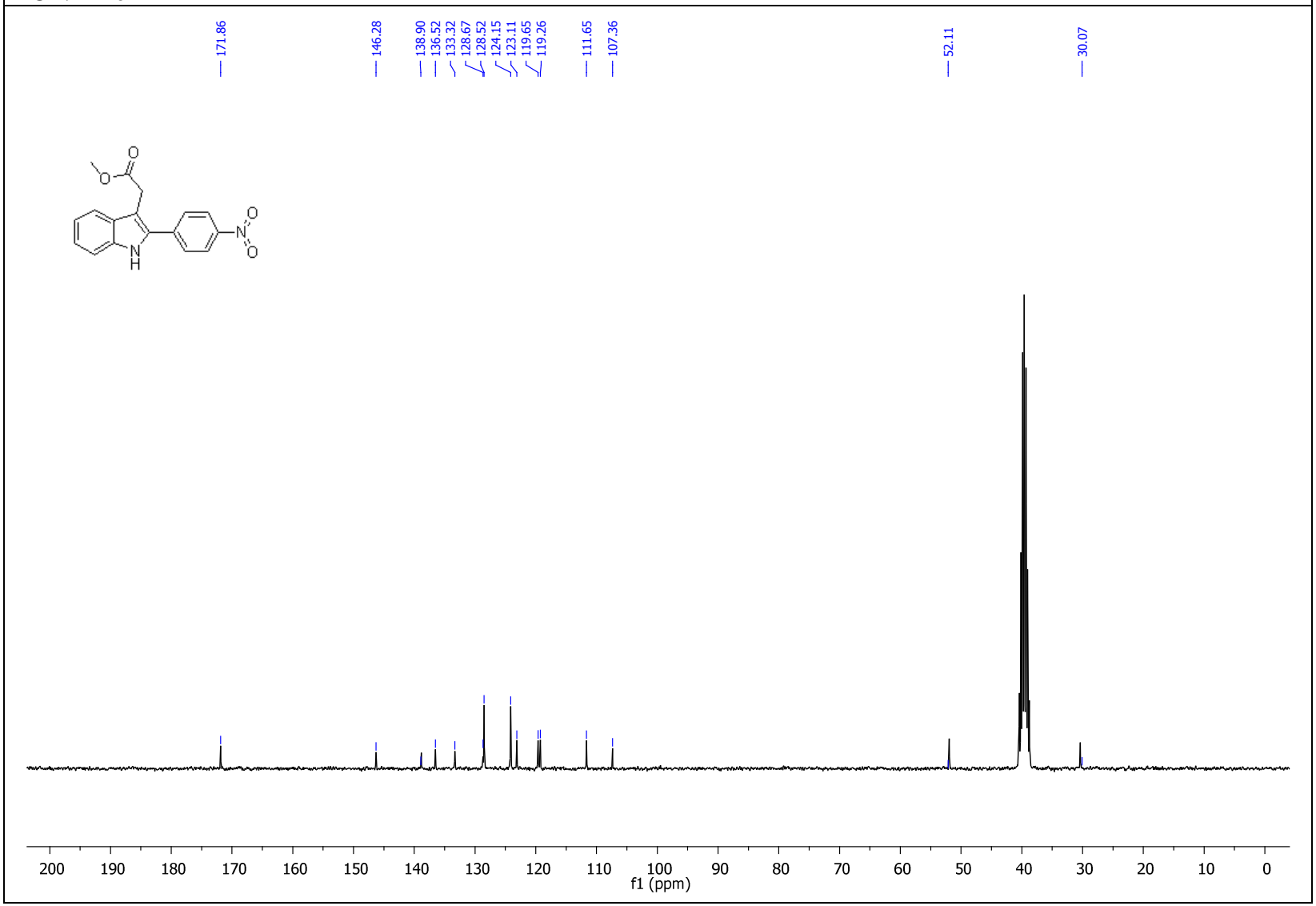
^{13}C NMR of 1h


172.82
136.08
133.63
132.70
129.73
128.95
128.84
128.27
127.98
125.01
119.76
116.50
105.69
52.08
31.07
21.56
16.56
O
O
N
H
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

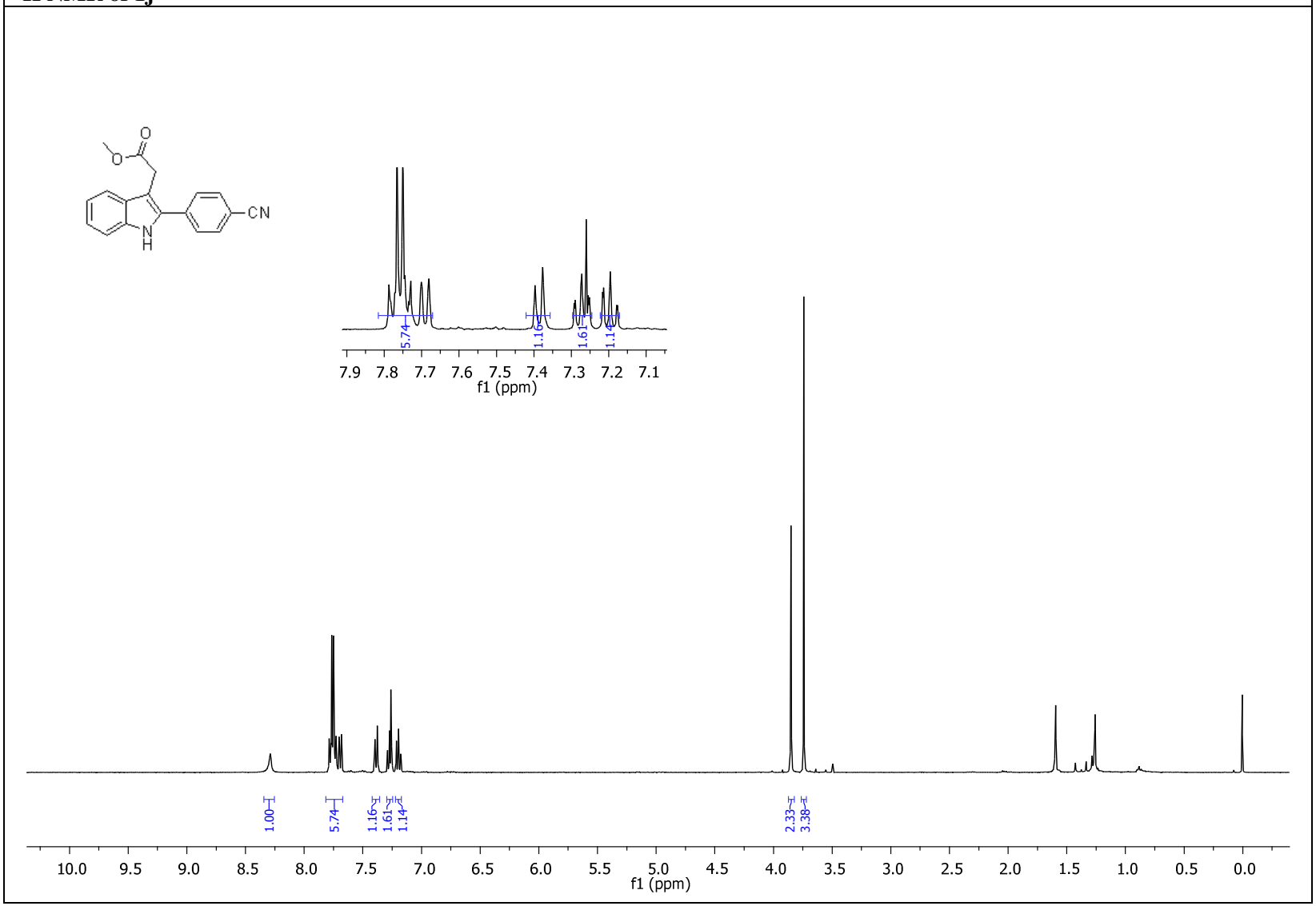
^{1}H NMR of 1i


O
O
N
O
O
N
H
2.18
1.04
1.05
1.08
1.03
8.0
7.8
7.6
7.4
7.2
f1 (ppm)
2.14
3.10
4.0
3.5
3.0
2.5
f1 (ppm)
1.07
2.15
2.18
1.04
1.05
1.08
1.03
2.14
3.10
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

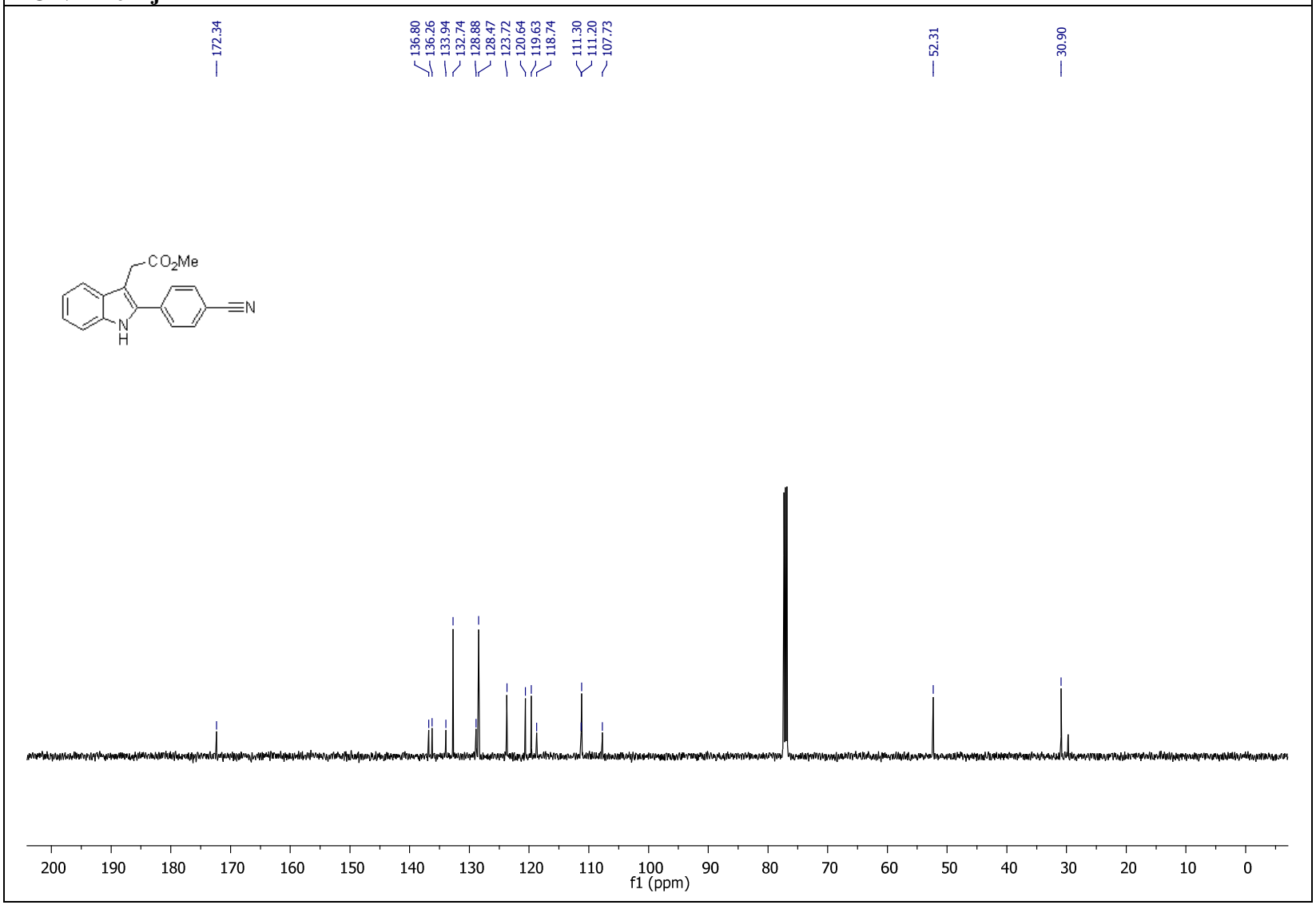
^{13}C NMR of 1i


171.86
146.28
138.90
136.52
133.32
128.67
128.52
124.15
123.11
119.65
119.26
111.65
107.36
52.11
30.07
O
O
N
H
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

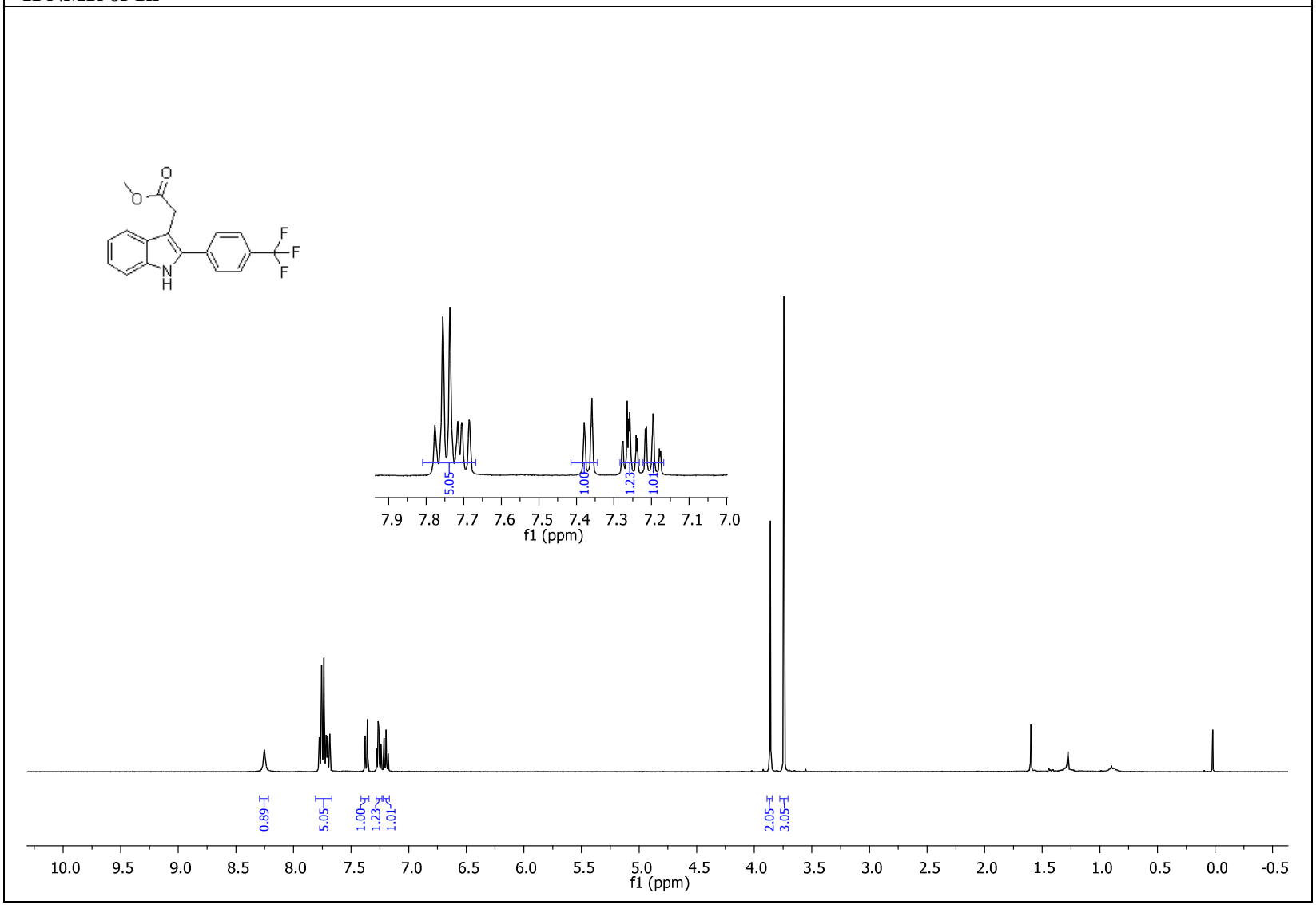
^{1}H NMR of 1j


O
O
CN
N
H
5.74
1.16
1.61
1.14
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)
1.00
5.74
1.16
1.61
1.14
2.33
3.38
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

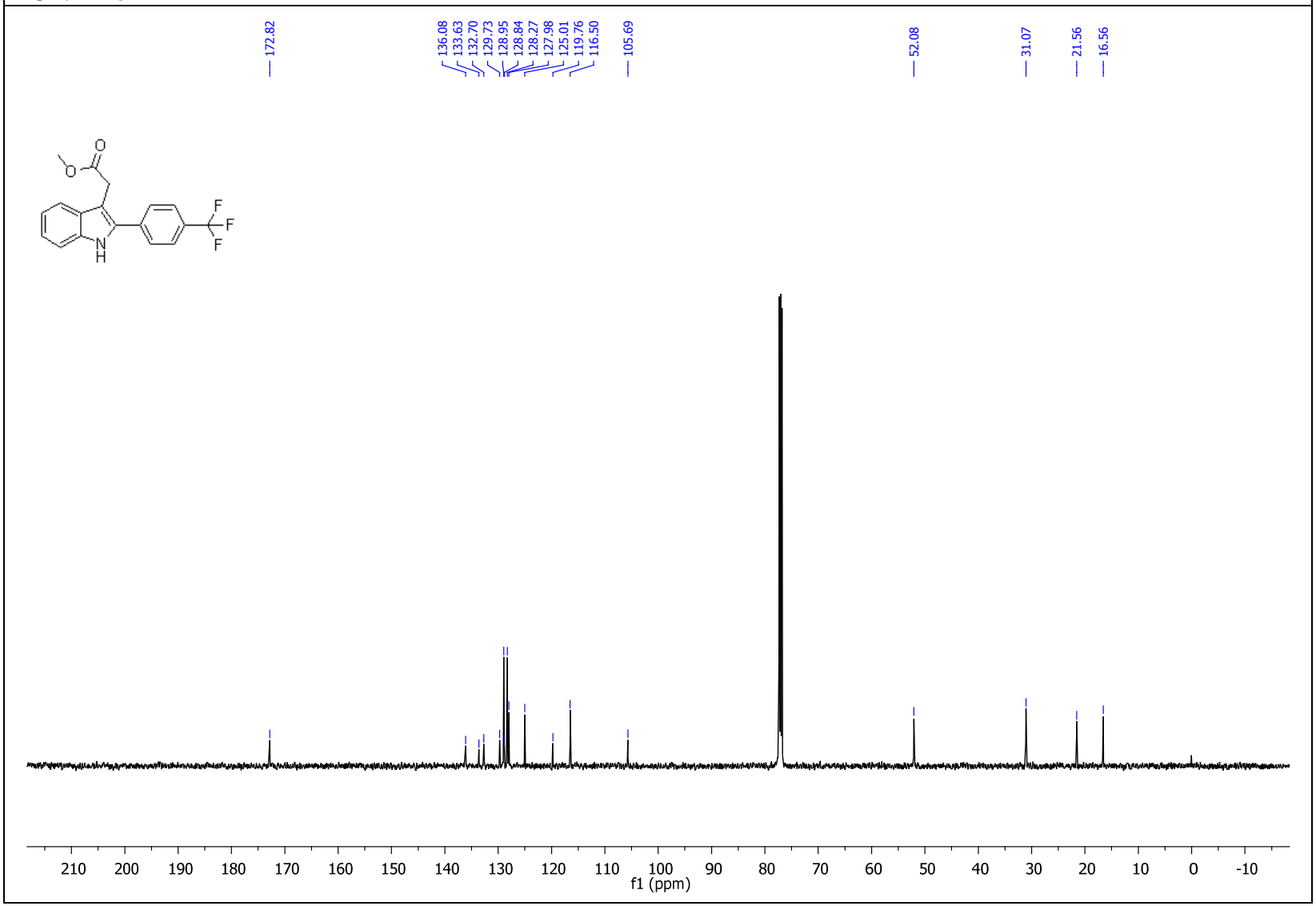
^{13}C NMR of 1j


172.34
136.80
136.26
133.94
132.74
128.88
128.47
123.72
120.64
119.63
118.74
111.30
111.20
107.73
52.31
30.90
CO2Me
N
H
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

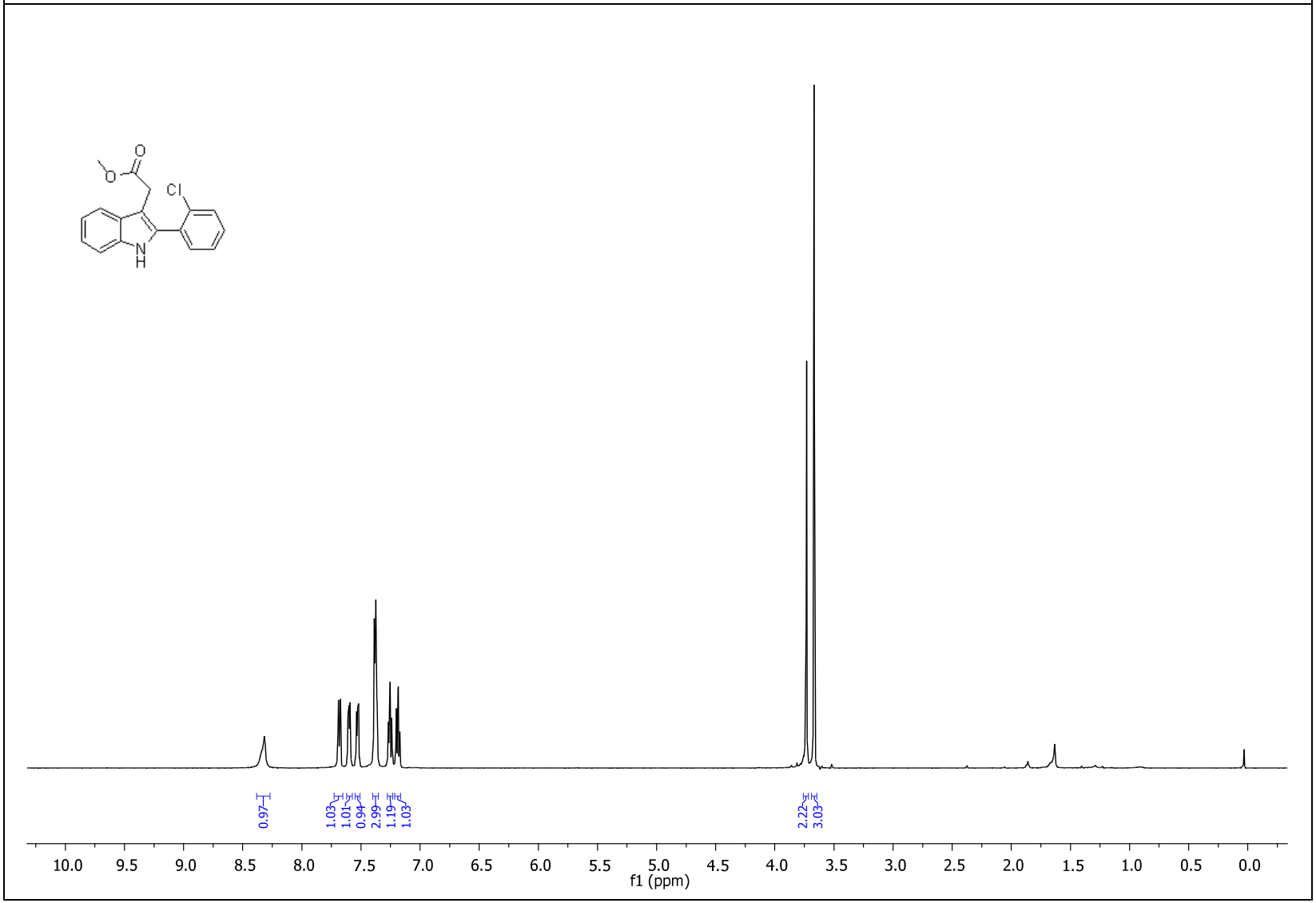
^{1}H NMR of 1k


O
O
N
H
F
F
F
5.05
1.00
1.23
1.01
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
0.89
5.05
1.00
1.23
1.01
2.05
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

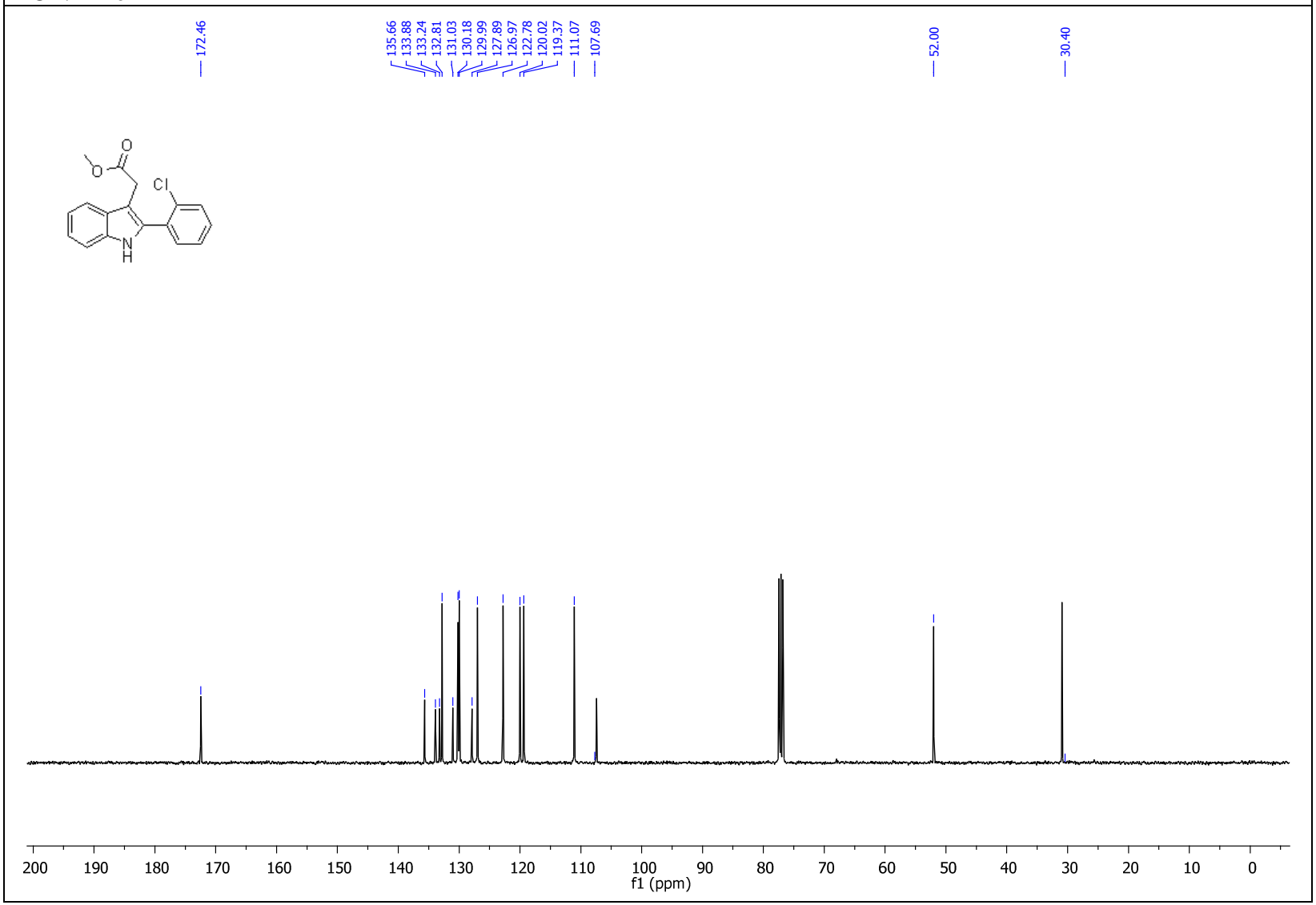
^{13}C NMR of 1k


172.82
136.08
133.63
132.70
129.73
128.95
128.84
128.27
127.98
125.01
119.76
116.50
105.69
52.08
31.07
21.56
16.56
O
O
N
H
F
F
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

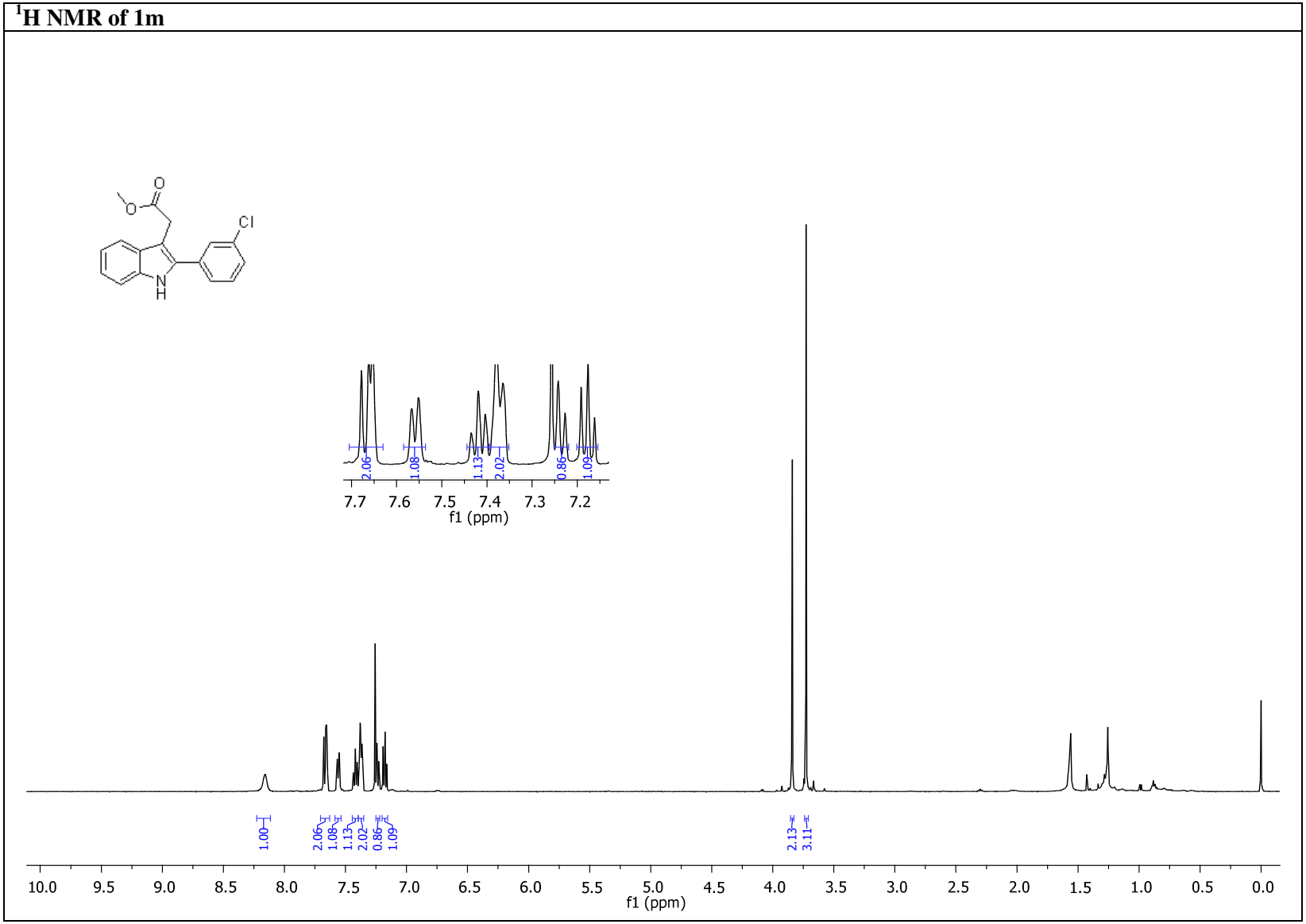
^{1}H NMR of 1l


O
O
Cl
N
H
0.97
1.03
1.01
0.94
2.99
1.19
1.03
2.22
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

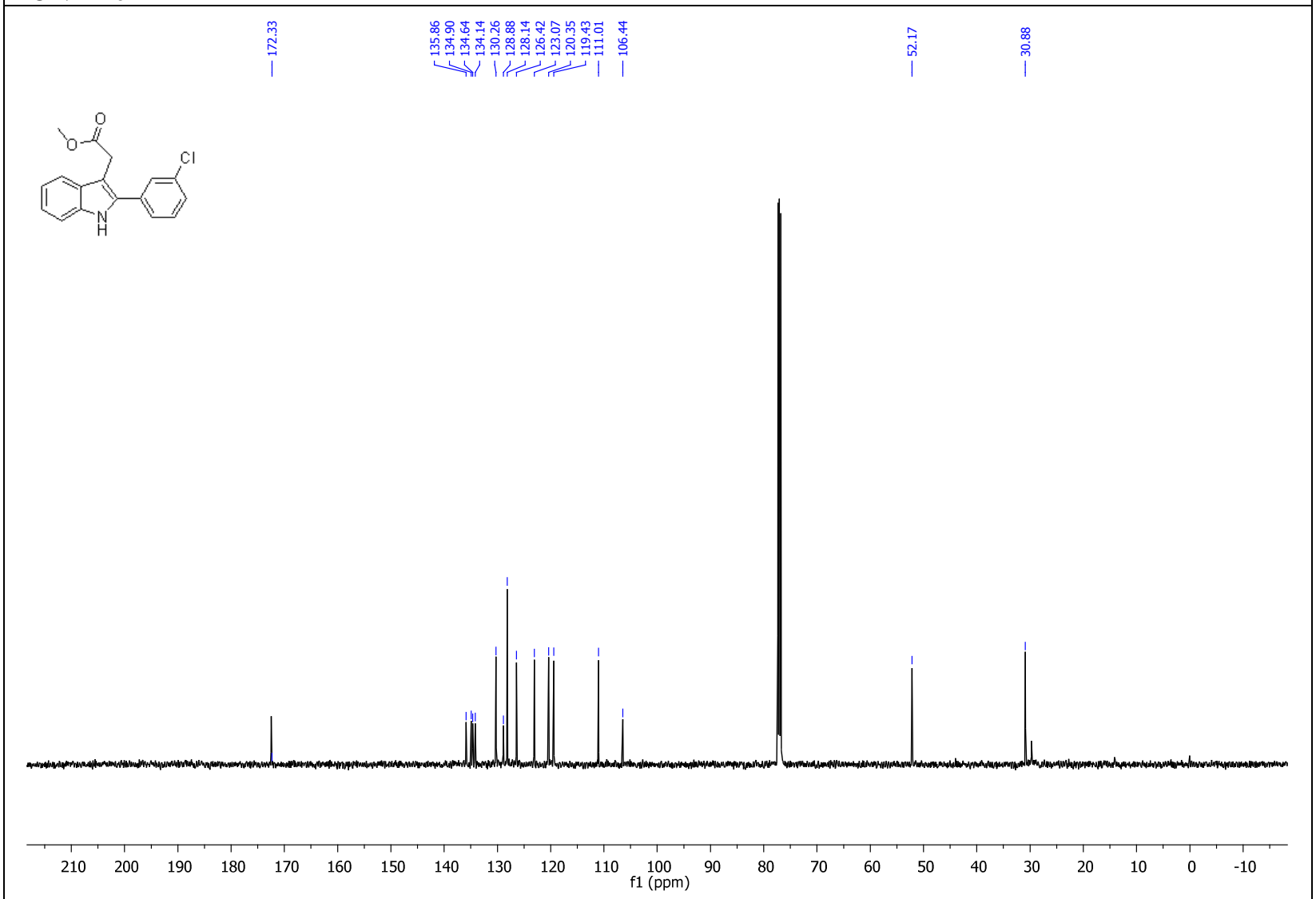
^{13}C NMR of 1l


172.46
135.66
133.88
133.24
132.81
131.03
130.18
129.99
127.89
126.97
122.78
120.02
119.37
111.07
107.69
52.00
30.40
O
O
Cl
N
H
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

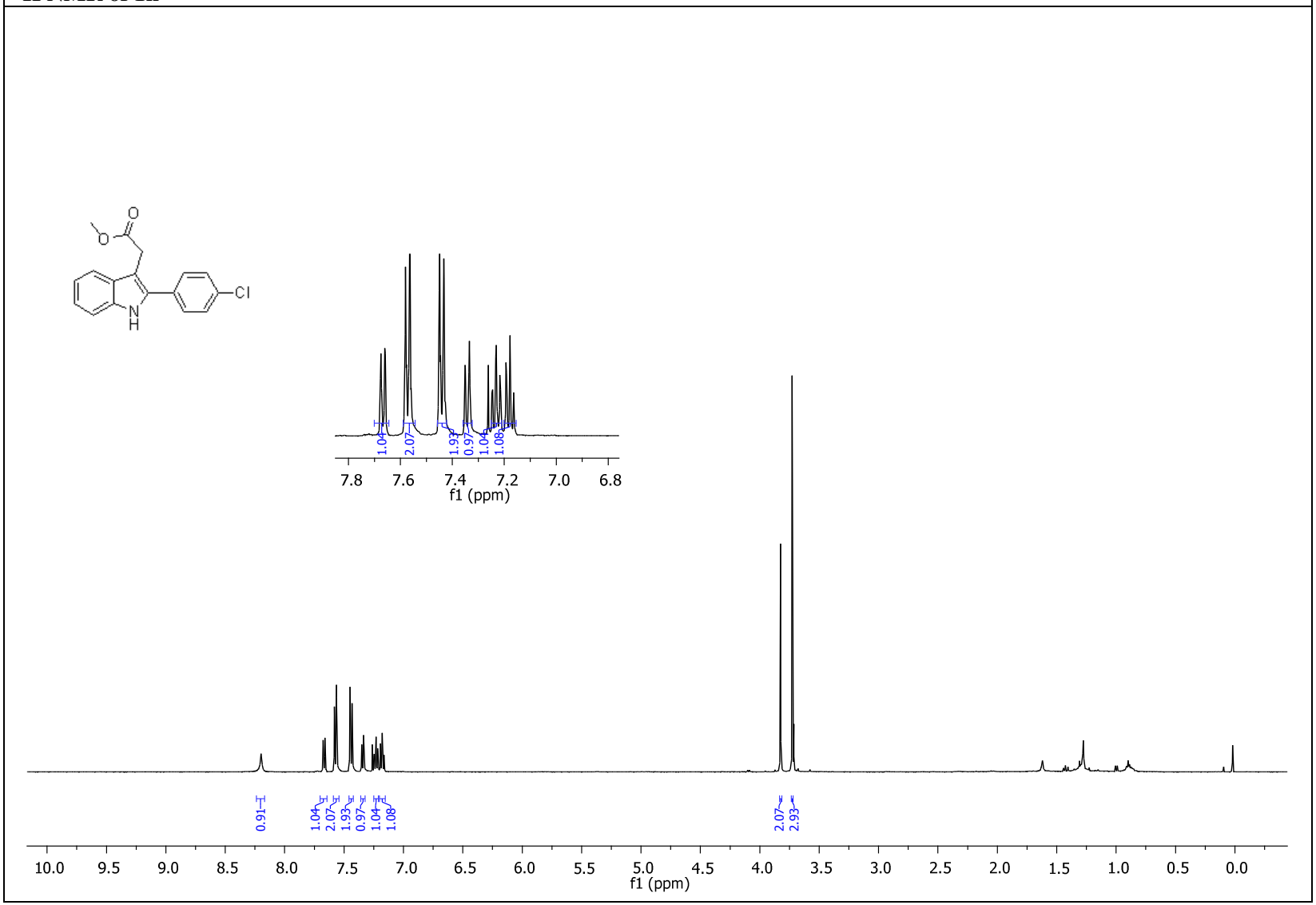
^{1}H NMR of 1m


O
O
Cl
N
H
2.06
1.08
1.13
2.02
0.86
1.09
7.7
7.6
7.5
7.4
7.3
7.2
f1 (ppm)
1.00
2.06
1.08
1.13
2.02
0.86
1.09
2.13
3.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

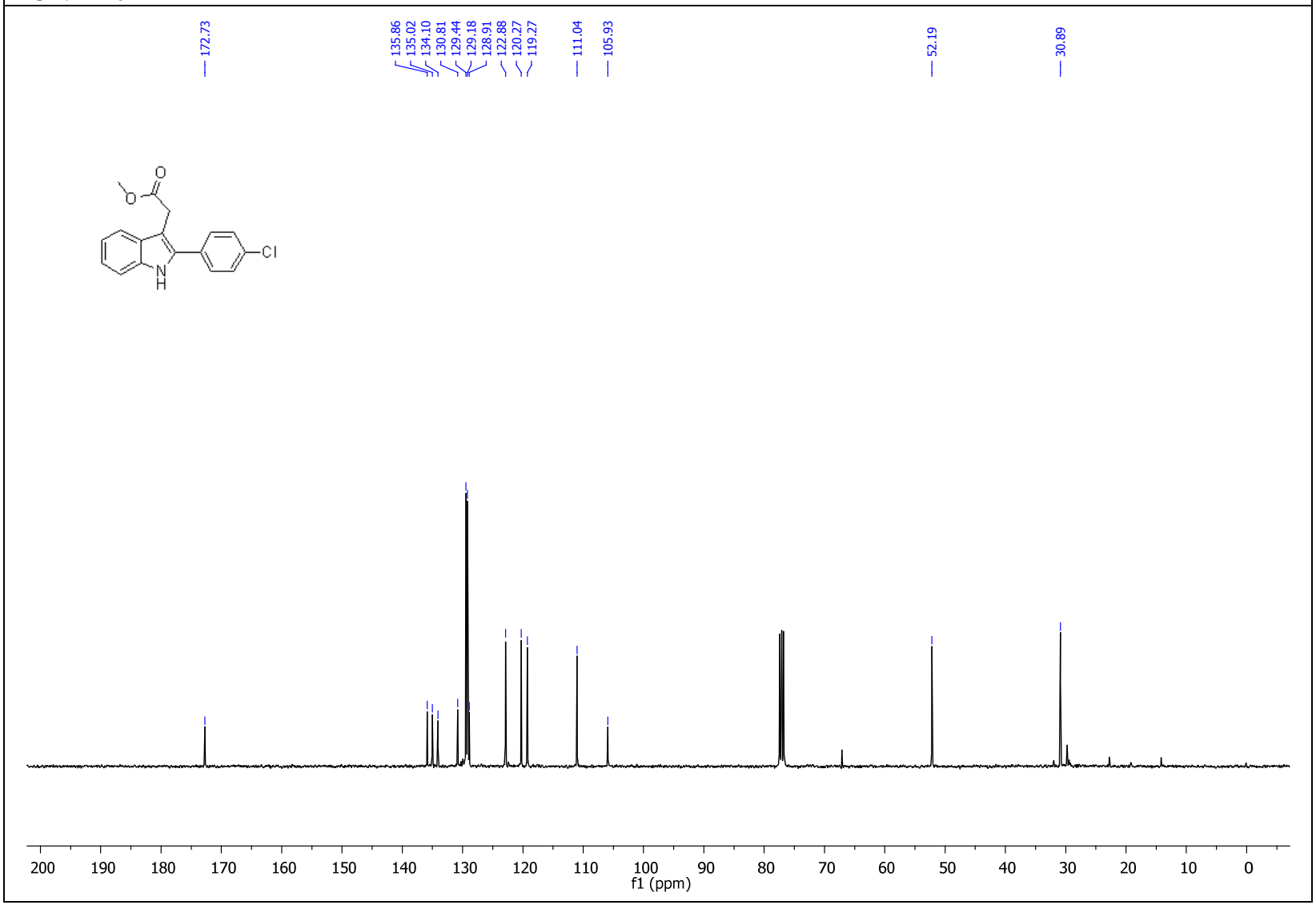
^{13}C NMR of 1m


172.33
135.86
134.90
134.64
134.14
130.26
128.88
128.14
126.42
123.07
120.35
119.43
111.01
106.44
52.17
30.88
O
O
Cl
N
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

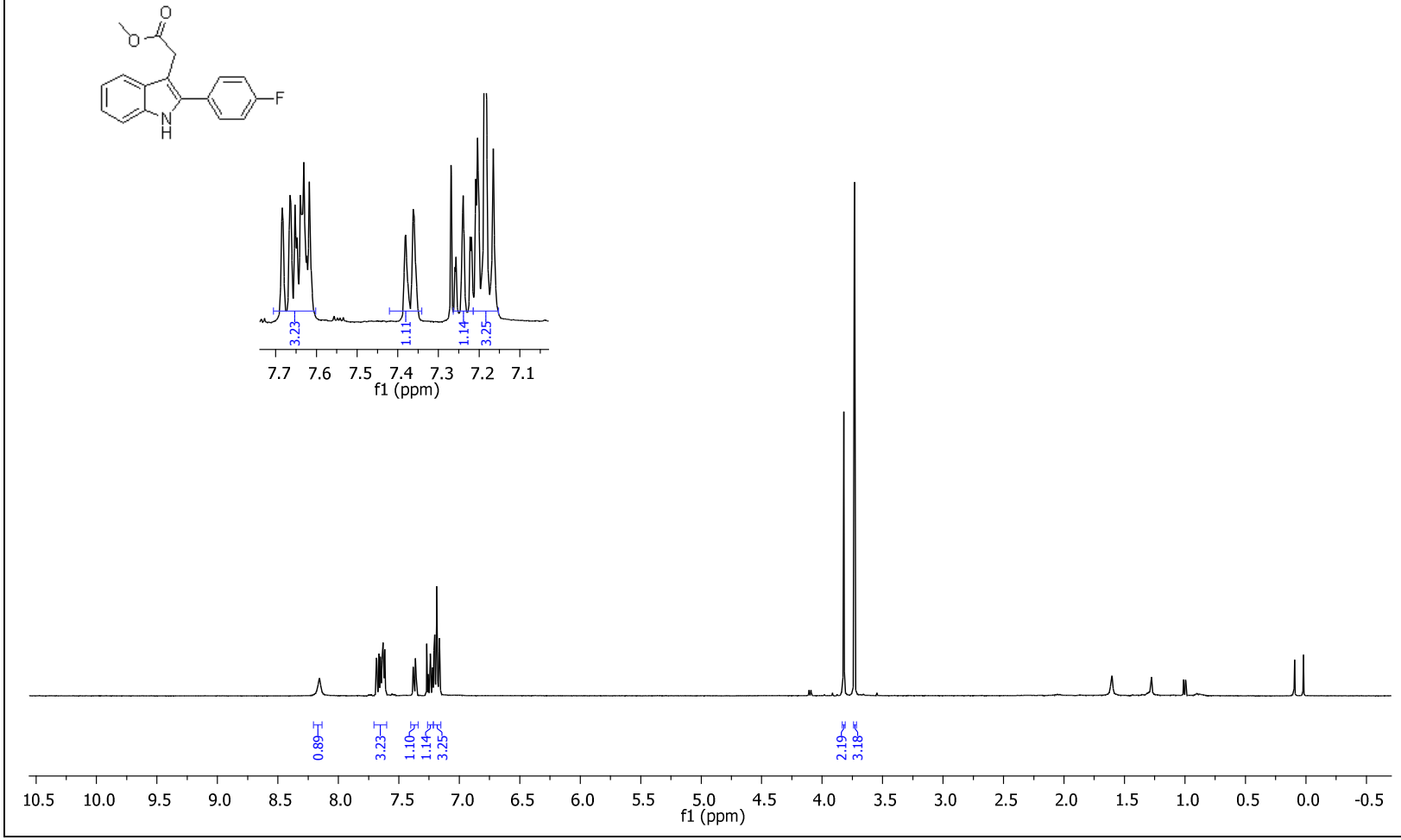
^{1}H NMR of 1n


O
O
N
H
Cl
7.8
7.6
7.4
7.2
7.0
6.8
f1 (ppm)
0.91
1.04
2.07
1.93
0.97
1.04
1.08
2.07
2.93
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

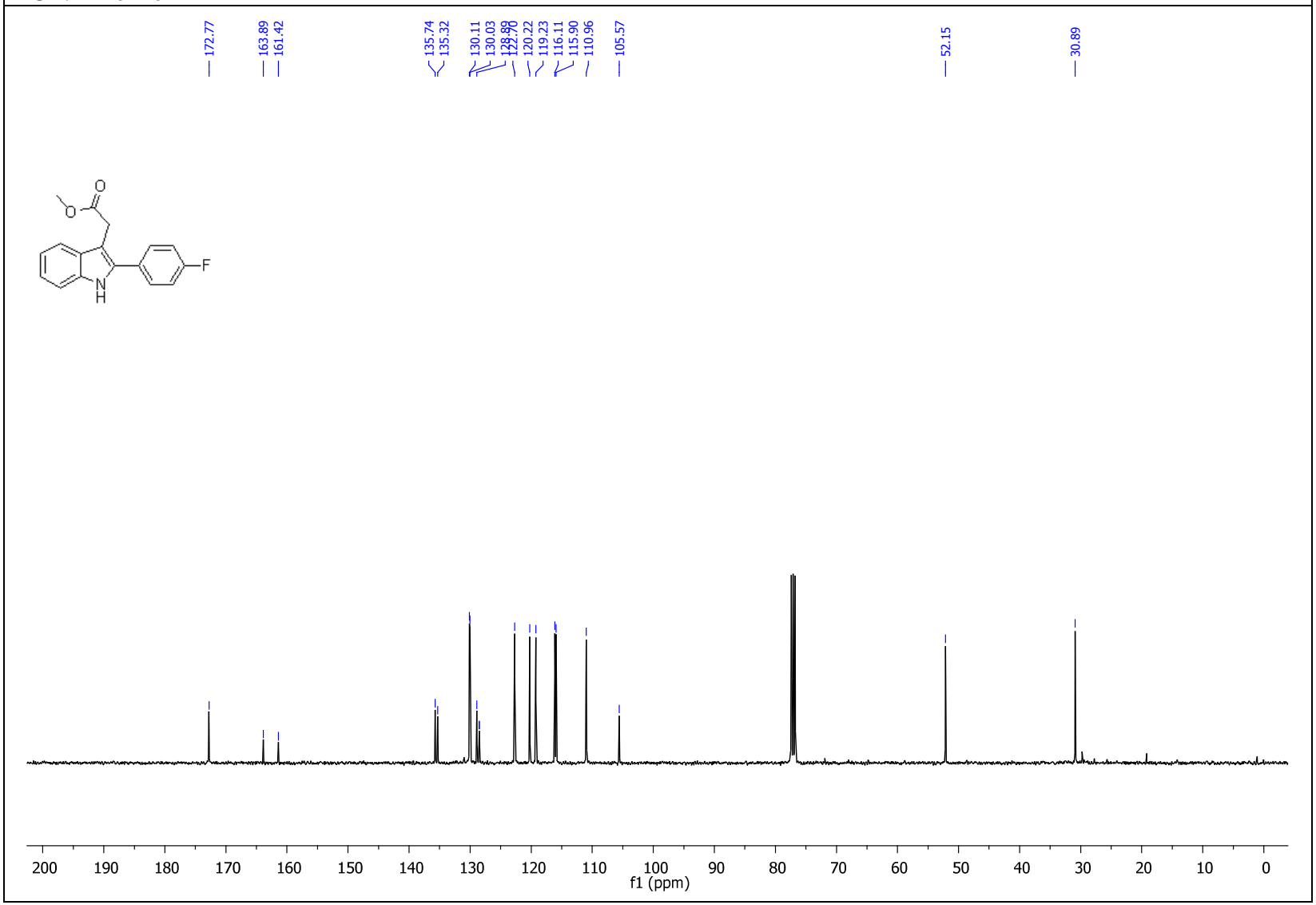
^{13}C NMR of 1n


172.73
135.86
135.02
134.10
130.81
129.44
129.18
128.91
122.88
120.27
119.27
111.04
105.93
52.19
30.89
O
O
N
H
Cl
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

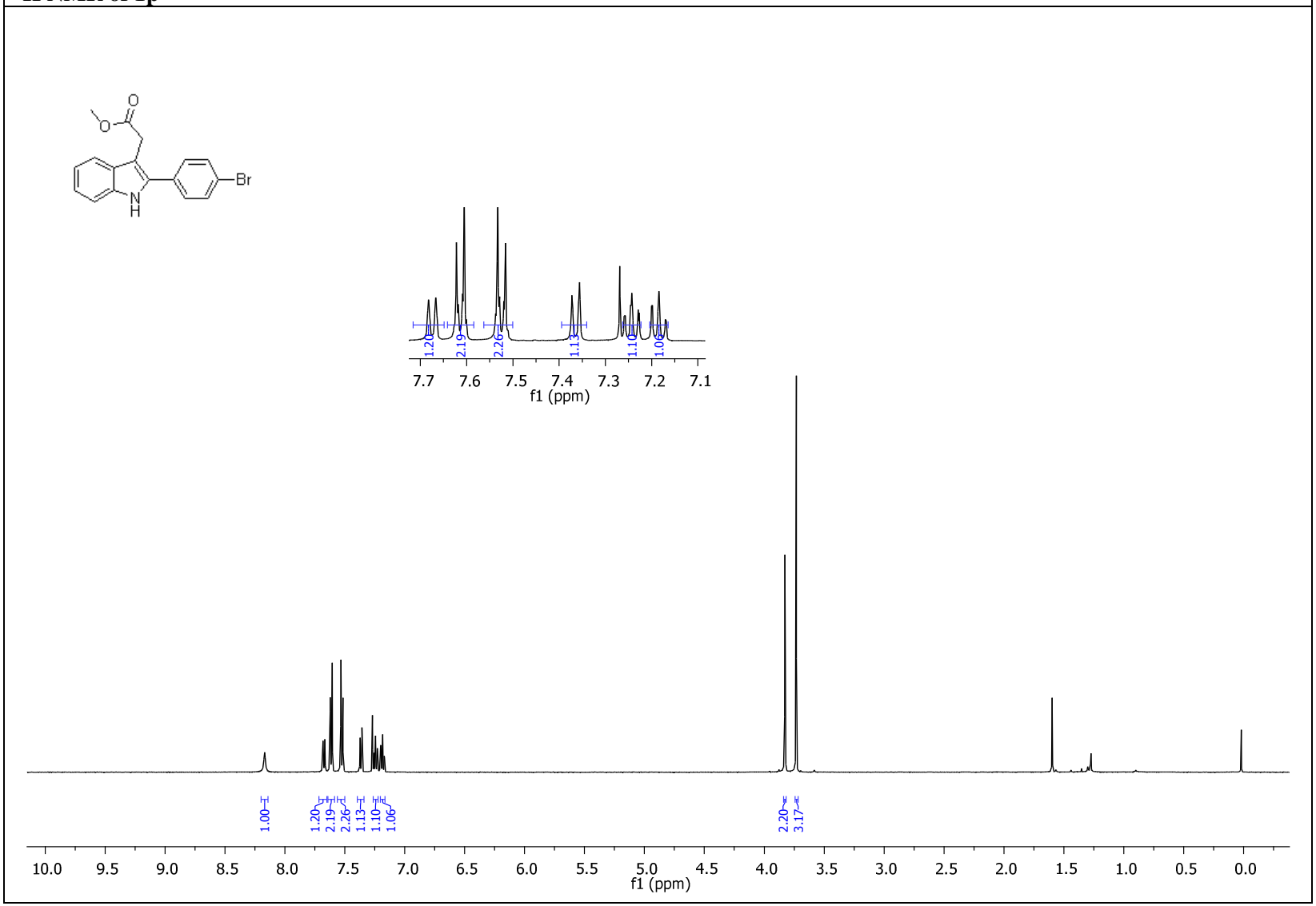
^{1}H NMR of 1o


O
O
N
H
F
3.23
1.11
1.14
3.25
7.7 7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)
0.89
3.23
1.10
1.14
3.25
2.19
3.18
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

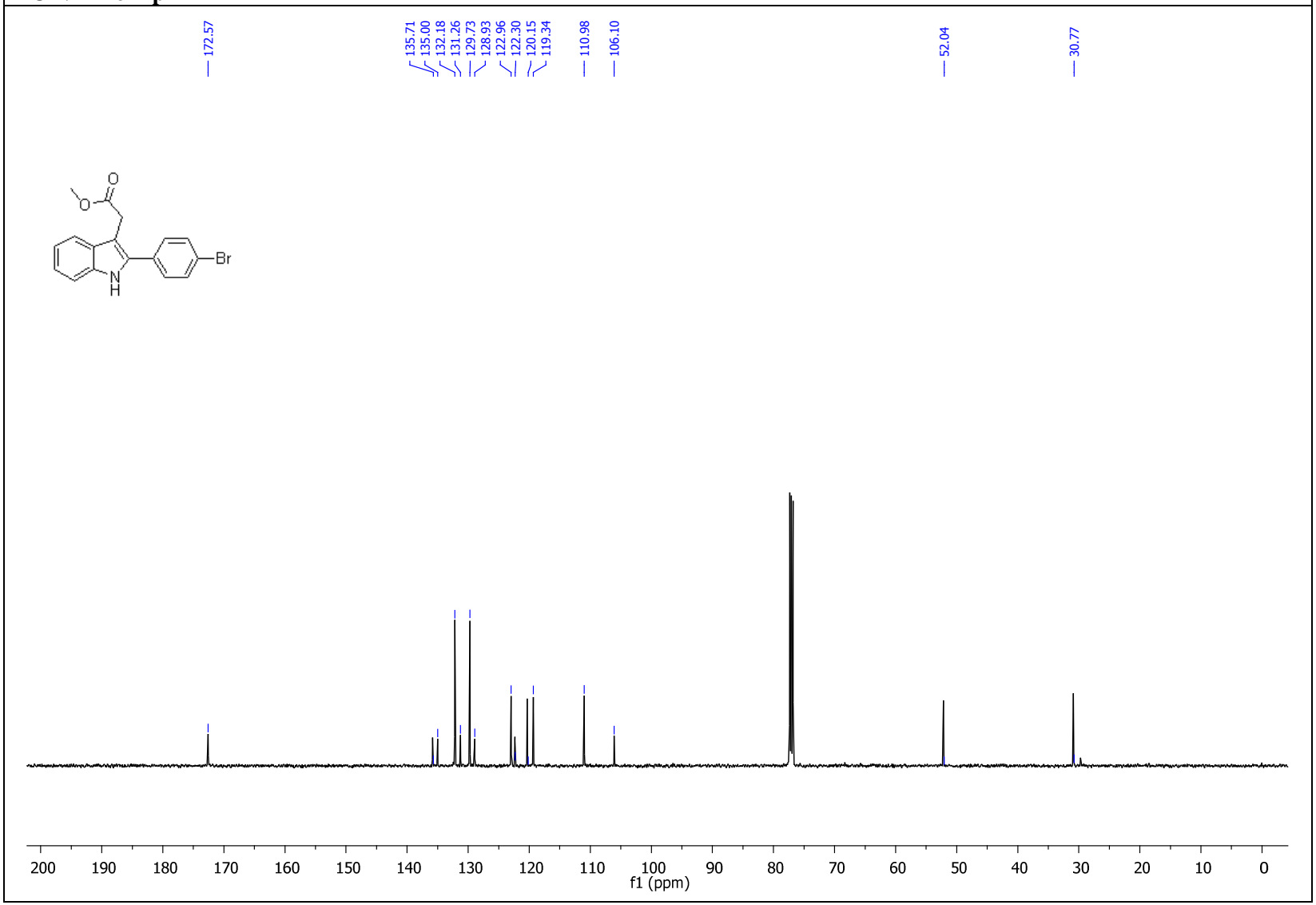
^{13}C NMR of 1o


172.77
163.89
161.42
135.74
135.32
130.11
130.03
128.89
122.90
120.22
119.23
116.11
115.90
110.96
105.57
52.15
30.89
O
O
F
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

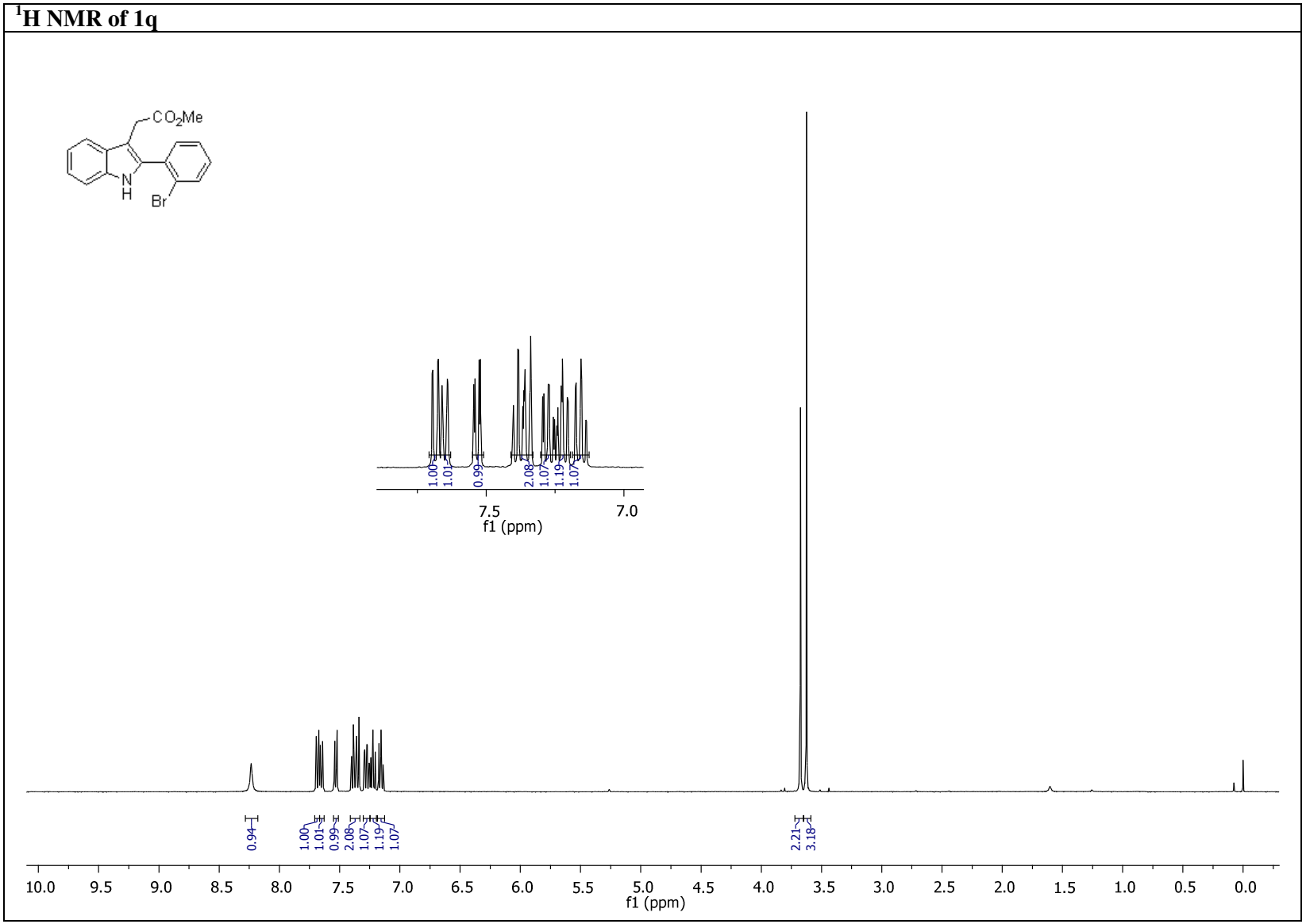
^{1}H NMR of 1p


O
O
N
H
Br
1.20
2.19
2.26
1.13
1.10
1.06
7.7
7.6
7.5
7.4
7.3
7.2
7.1
f1 (ppm)
1.00
1.20
2.19
2.26
1.13
1.10
1.06
2.20
3.17
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

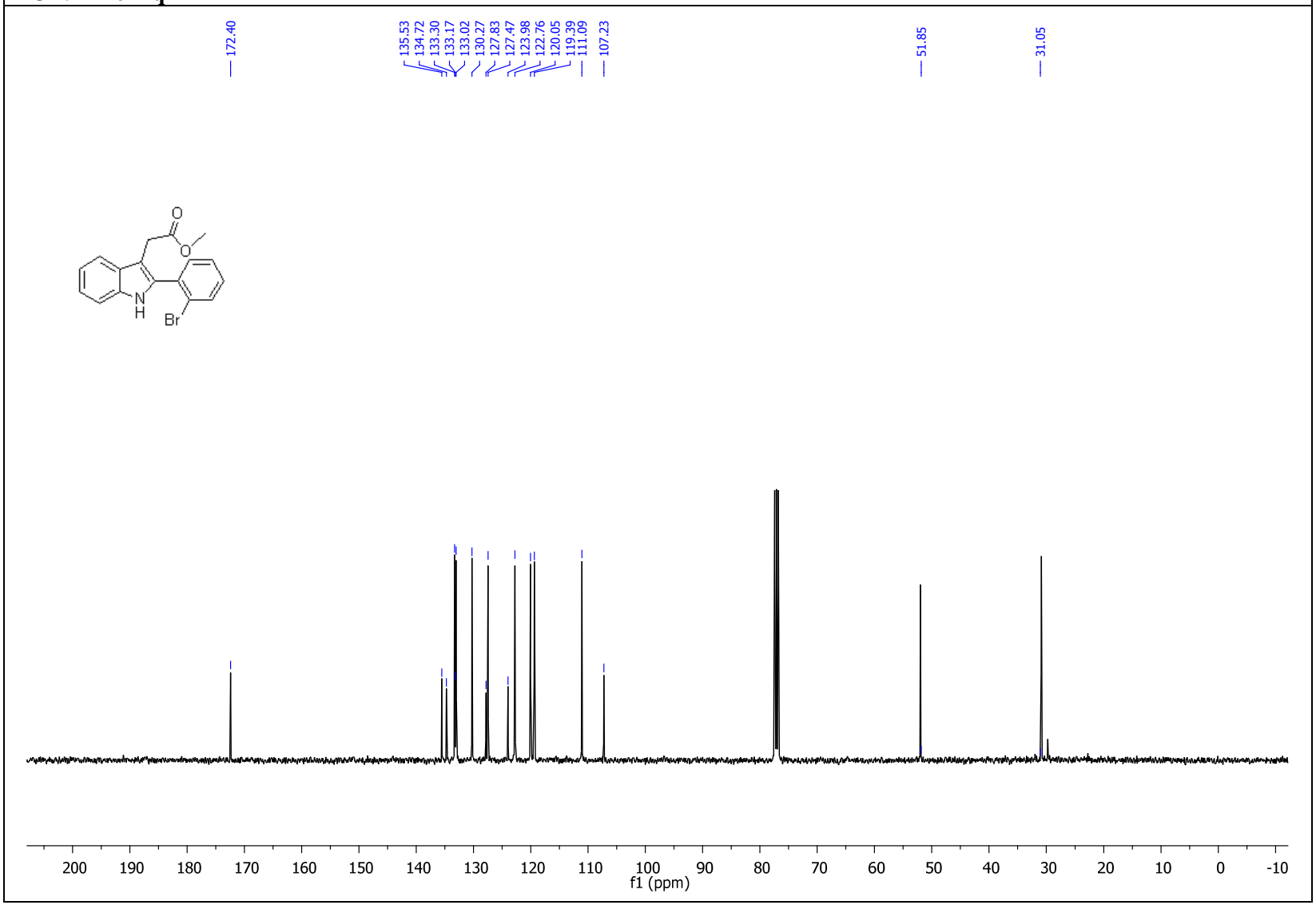
^{13}C NMR of 1p


172.57
135.71
135.00
132.18
131.26
129.73
128.93
122.96
122.30
120.15
119.34
110.98
106.10
52.04
30.77
O
O
N
H
Br
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

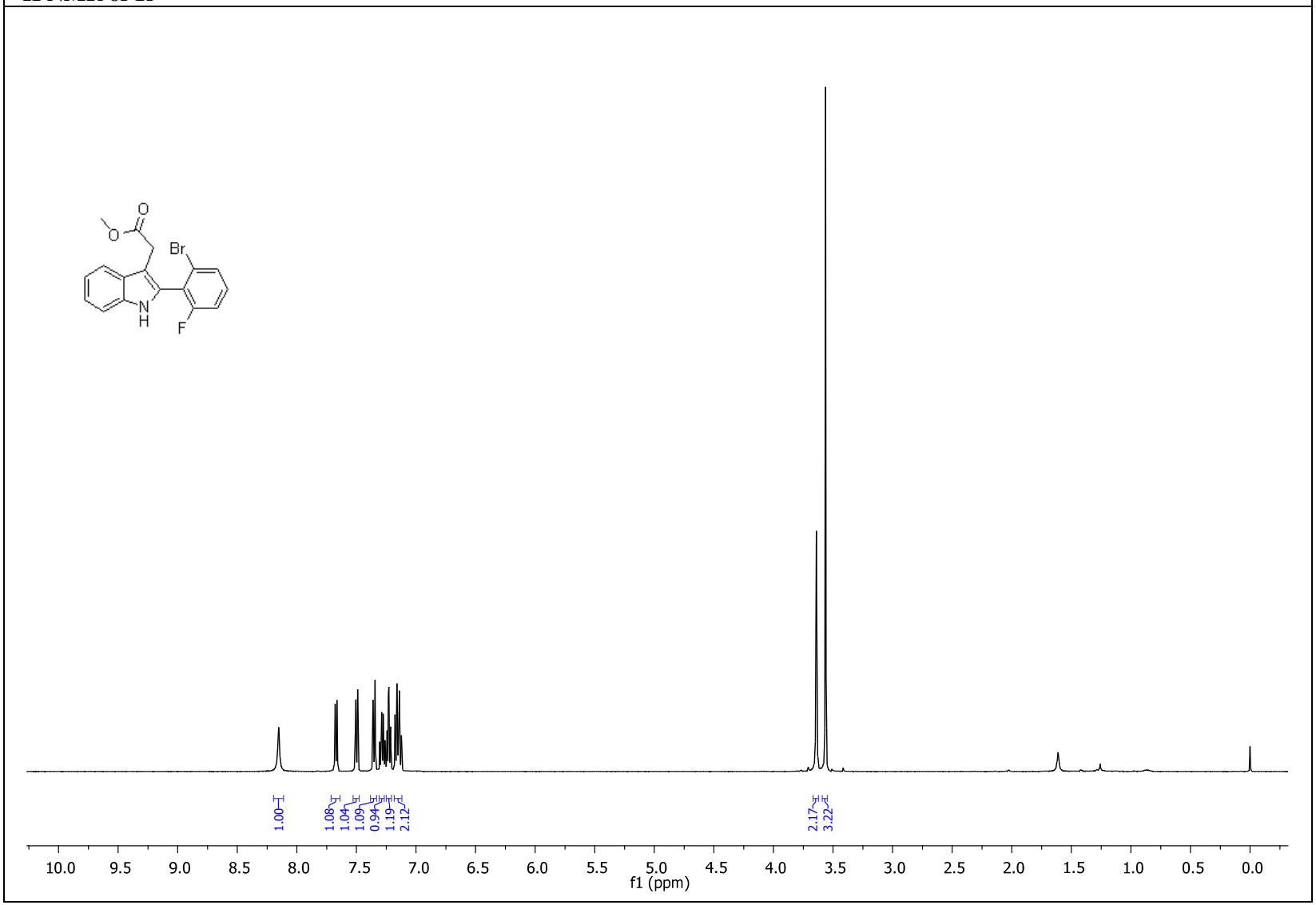
^{1}H NMR of 1q


CO2Me
N
H
Br
1.00
1.01
0.99
2.08
1.07
1.19
1.07
7.5
7.0
f1 (ppm)
0.94
1.00
1.01
0.99
2.08
1.07
1.19
1.07
2.21
3.18
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

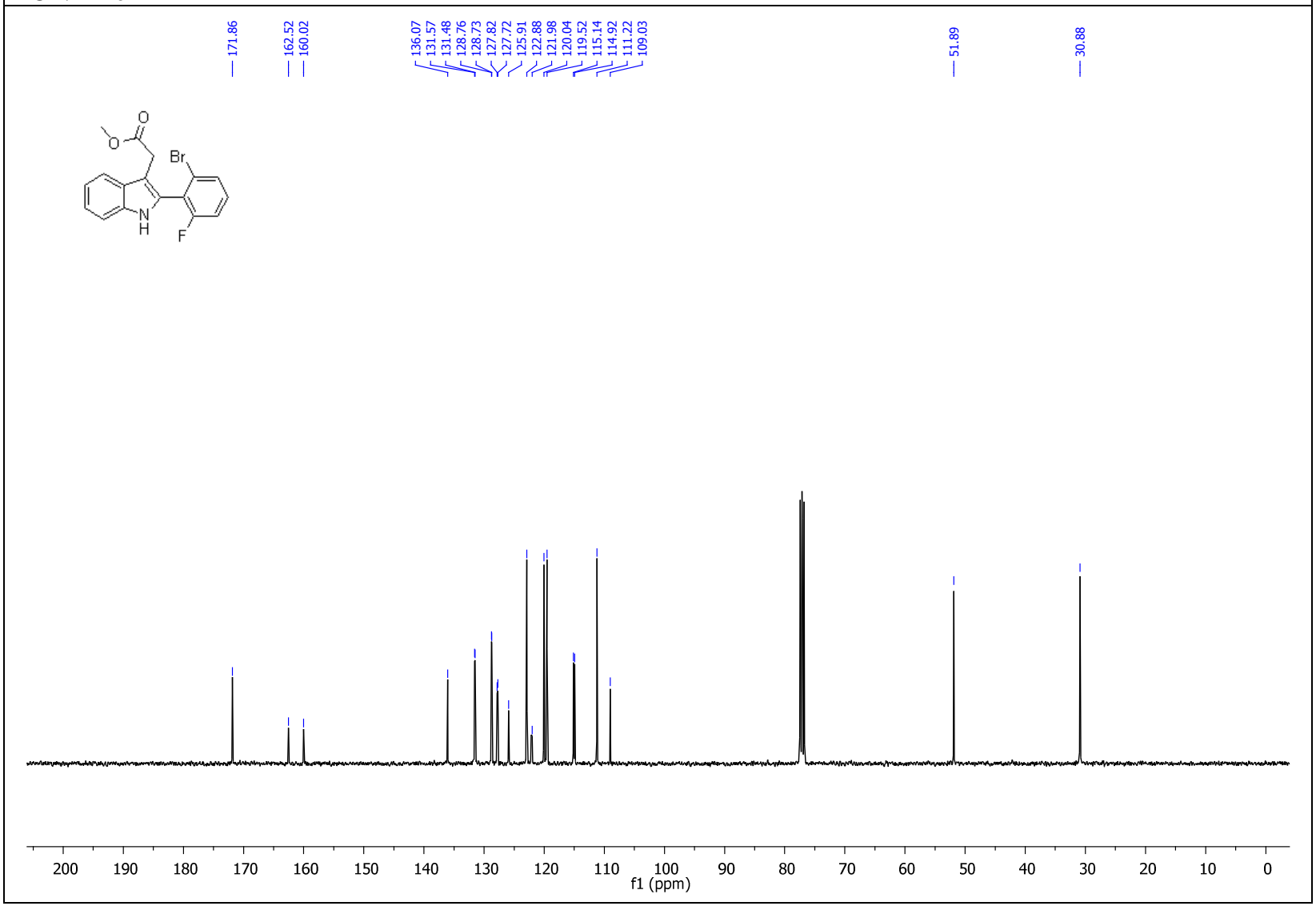
^{13}C NMR of 1q


172.40
135.53
134.72
133.30
133.17
133.02
130.27
127.83
127.47
123.98
122.76
120.05
119.39
111.09
107.23
51.85
31.05
O
O
N
H
Br
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

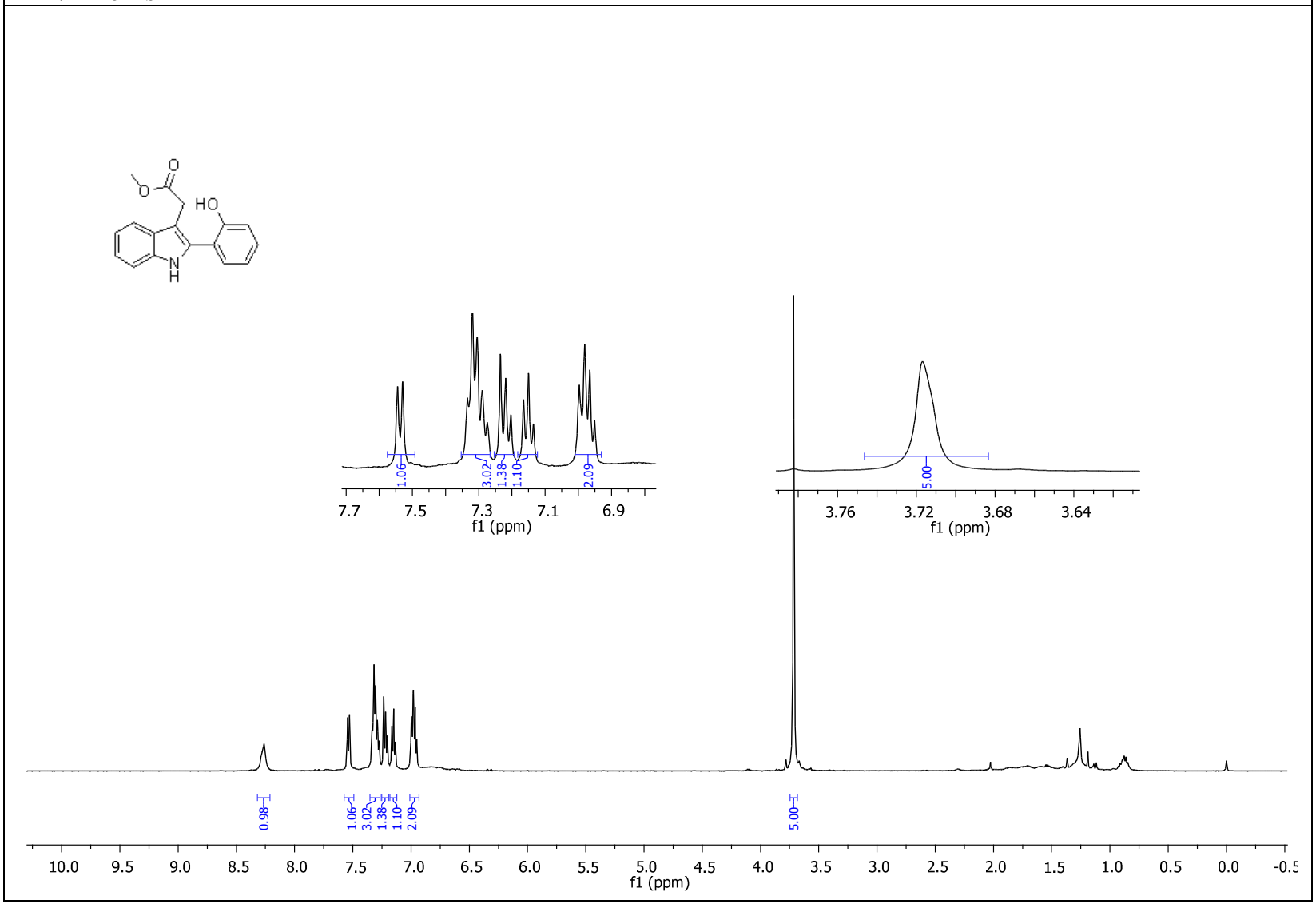
^{1}H NMR of 1r


O
O
Br
N
H
F
1.00
1.08
1.04
1.09
0.94
1.19
2.12
2.17
3.22
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

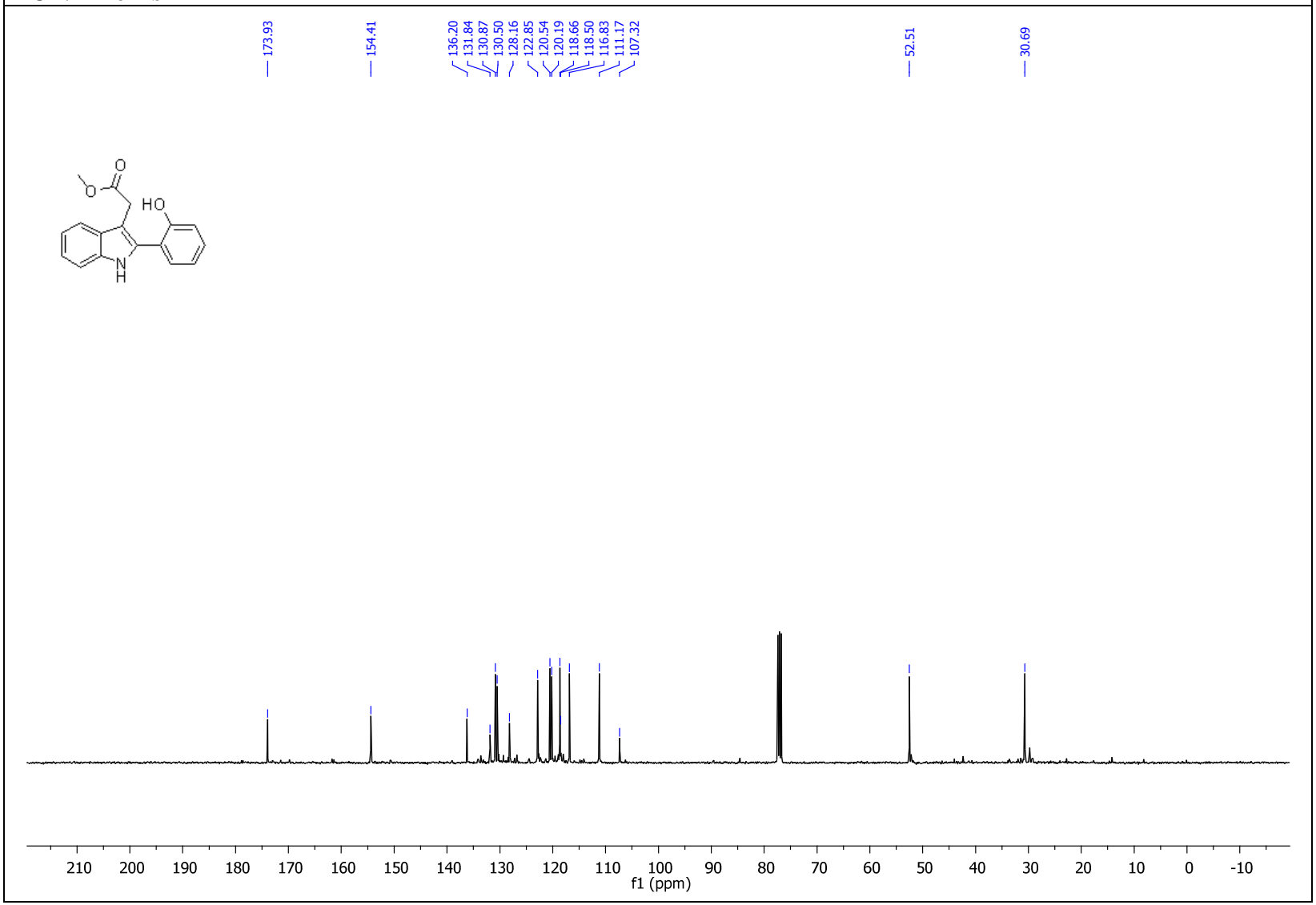
^{13}C NMR of 1r


171.86
162.52
160.02
136.07
131.57
131.48
128.76
128.73
127.82
127.72
125.91
122.88
121.98
120.04
119.52
115.14
114.92
111.22
109.03
51.89
30.88
O
O
Br
N
H
F
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

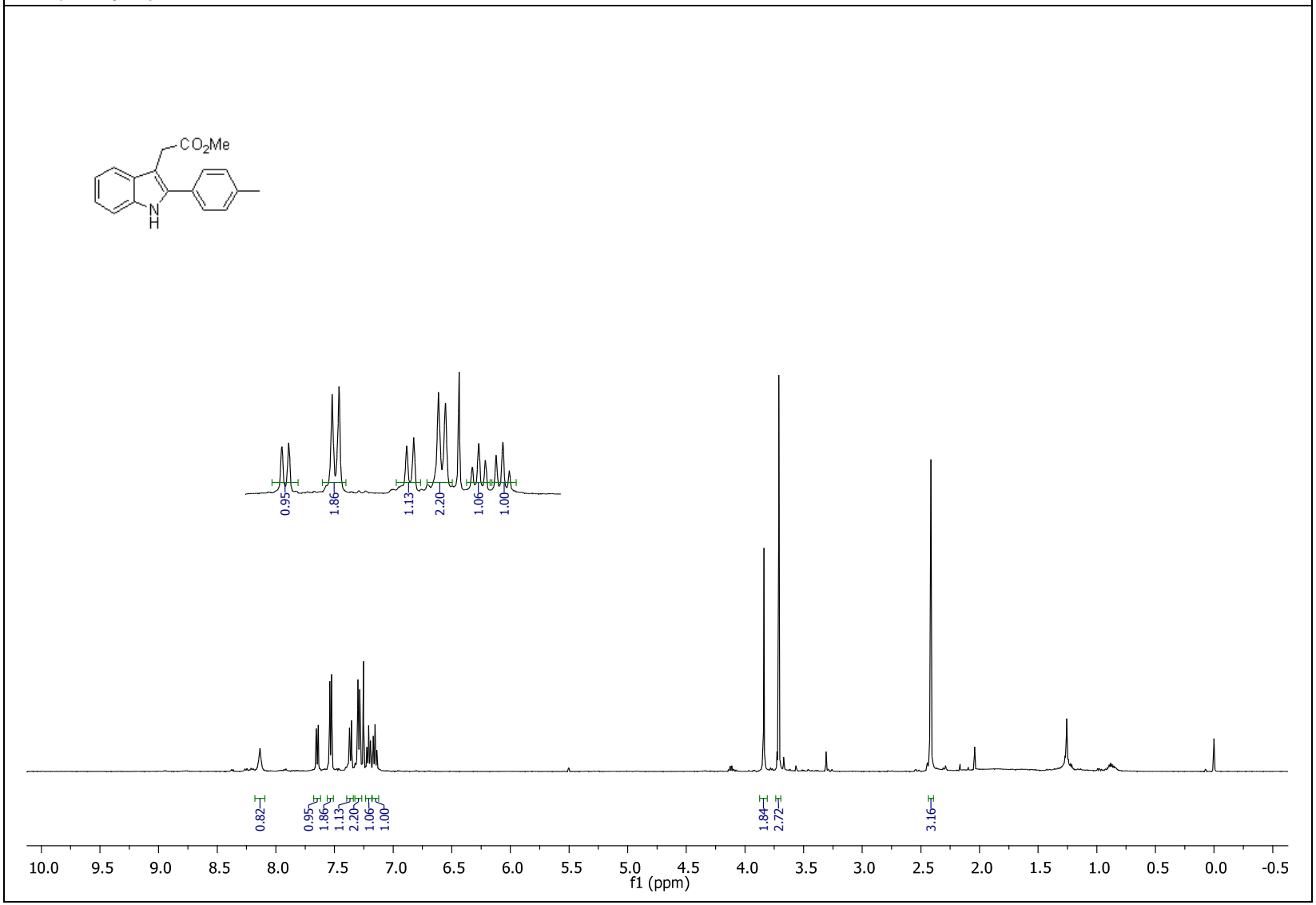
^{1}H NMR of 1s


O
O
HO
N
H
1.06
3.02
1.38
1.10
2.09
7.7
7.5
7.3
7.1
6.9
f1 (ppm)
5.00
3.76
3.72
3.68
3.64
f1 (ppm)
0.98
1.06
3.02
1.38
1.10
2.09
5.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

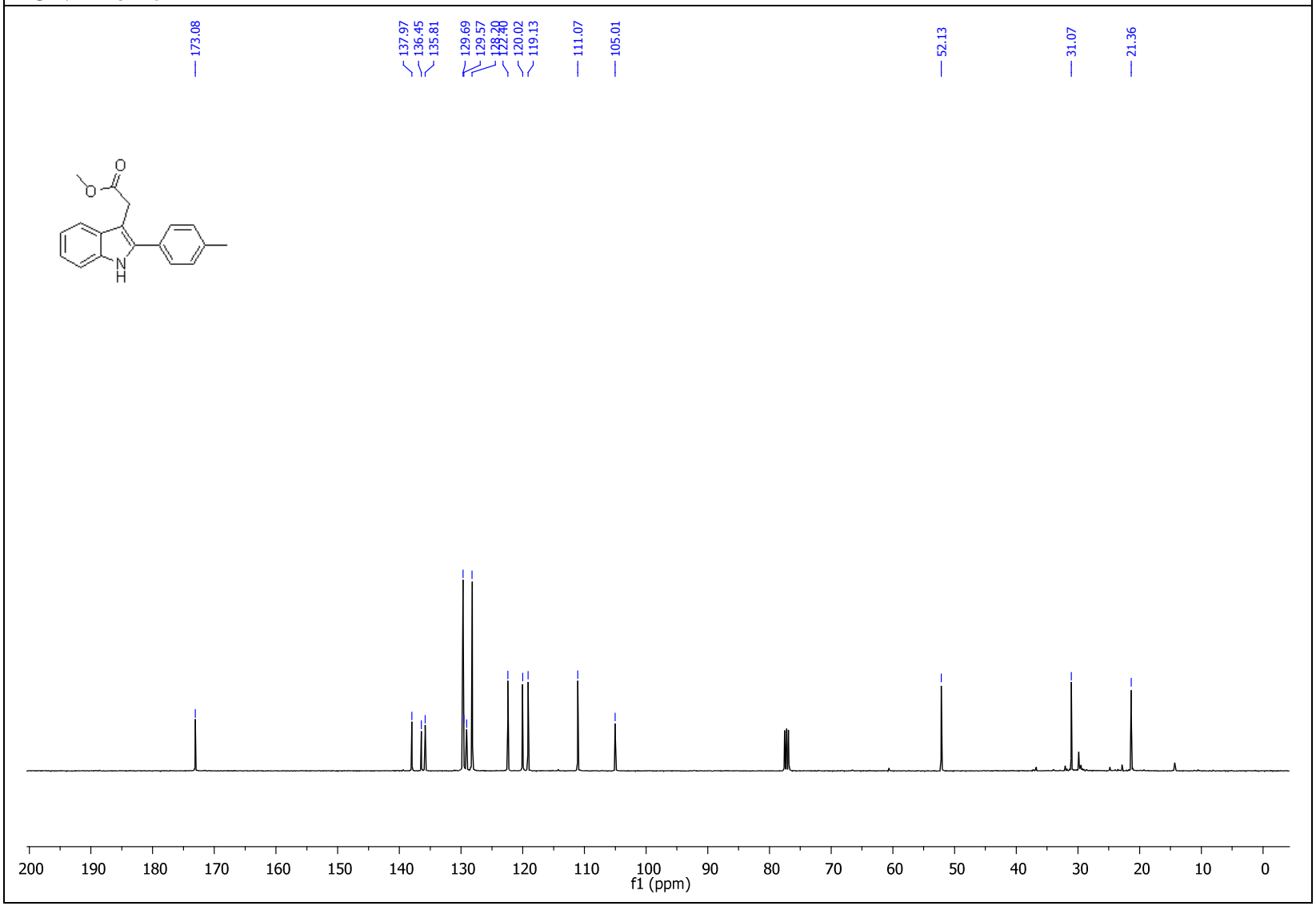
^{13}C NMR of 1s


173.93
154.41
136.20
131.84
130.87
130.50
128.16
122.85
120.54
120.19
118.66
118.50
116.83
111.17
107.32
52.51
30.69
O
O
HO
N
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

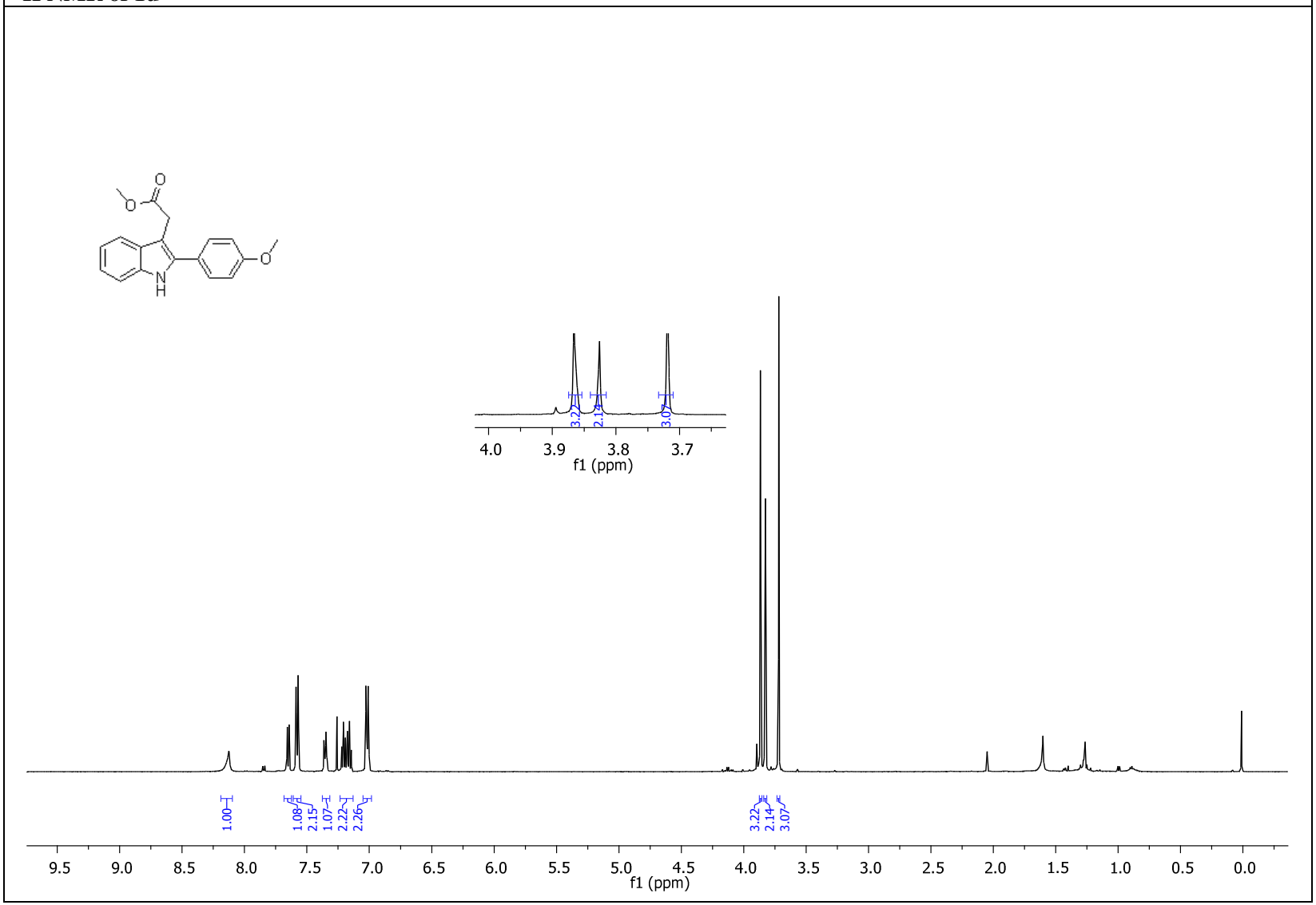
^{1}H NMR of 1t


CO2Me
N
H
0.95
1.86
1.13
2.20
1.06
1.00
0.82
1.84
2.72
3.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

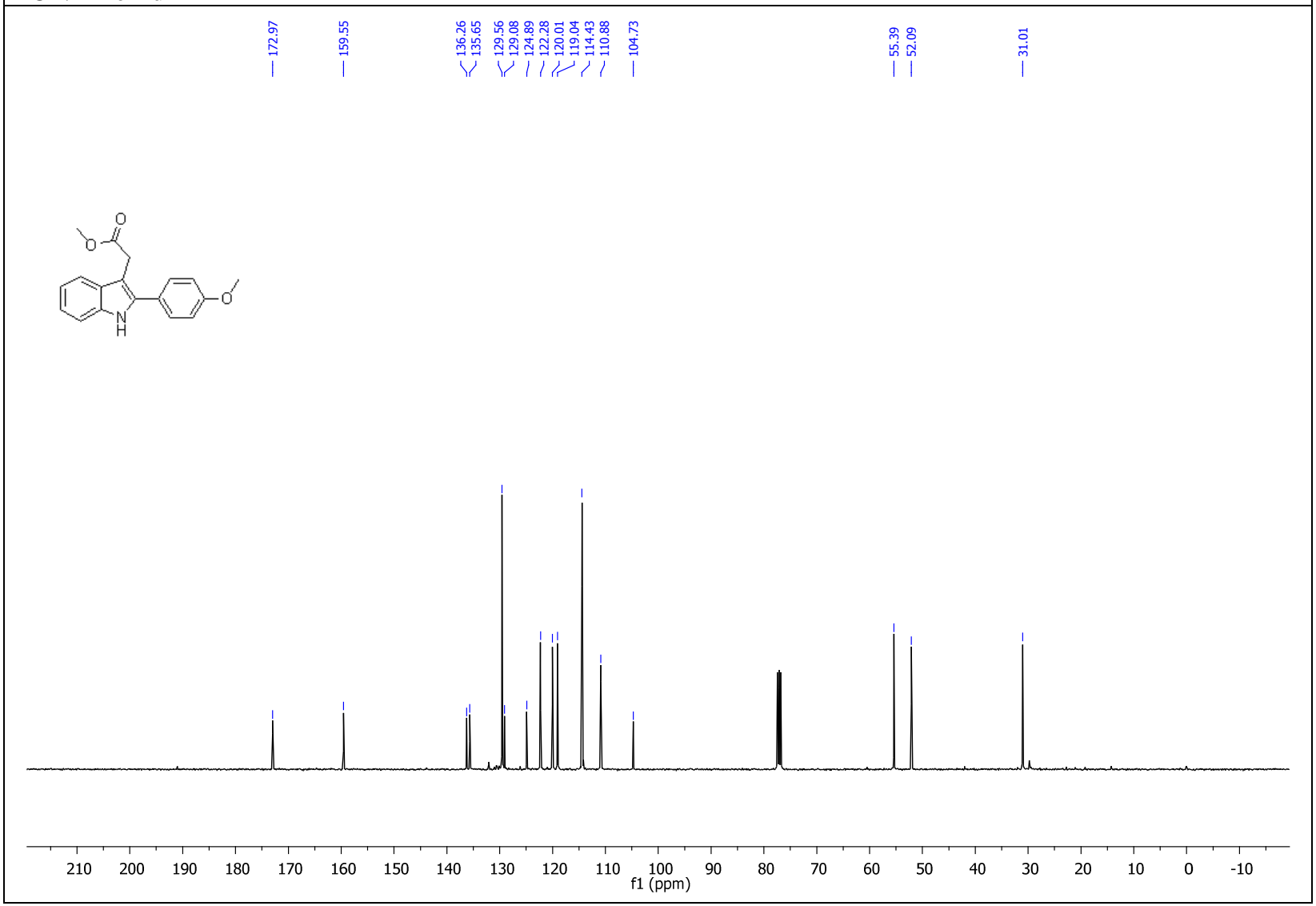
^{13}C NMR of 1t


173.08
137.97
136.45
135.81
129.69
129.57
128.20
122.40
120.02
119.13
111.07
105.01
52.13
31.07
21.36
O
O
N
H
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

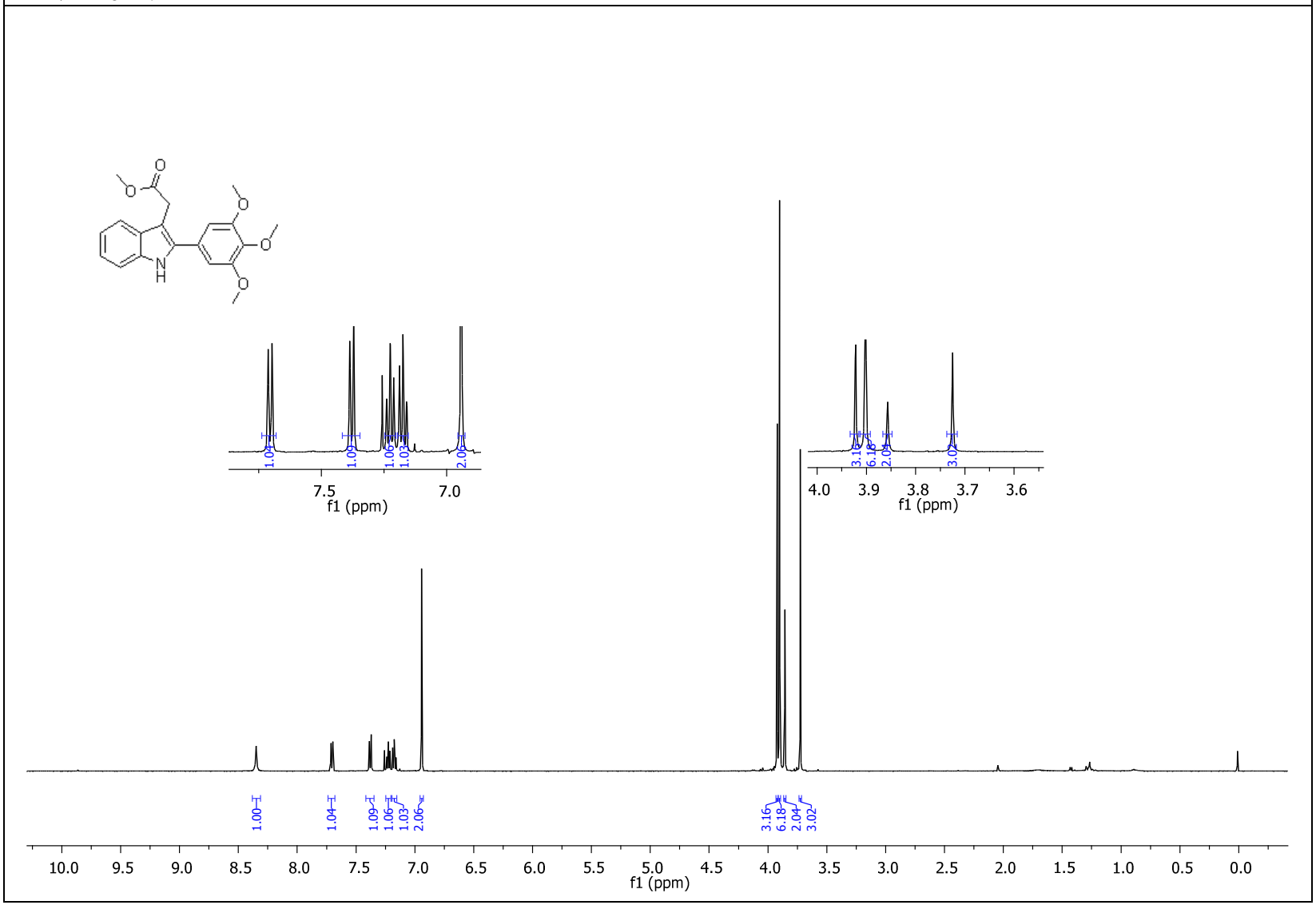
^{1}H NMR of 1u


O
O
O
N
H
4.0
3.9
3.8
3.7
f1 (ppm)
3.22
2.14
3.07
1.00
1.08
2.15
1.07
2.22
2.26
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

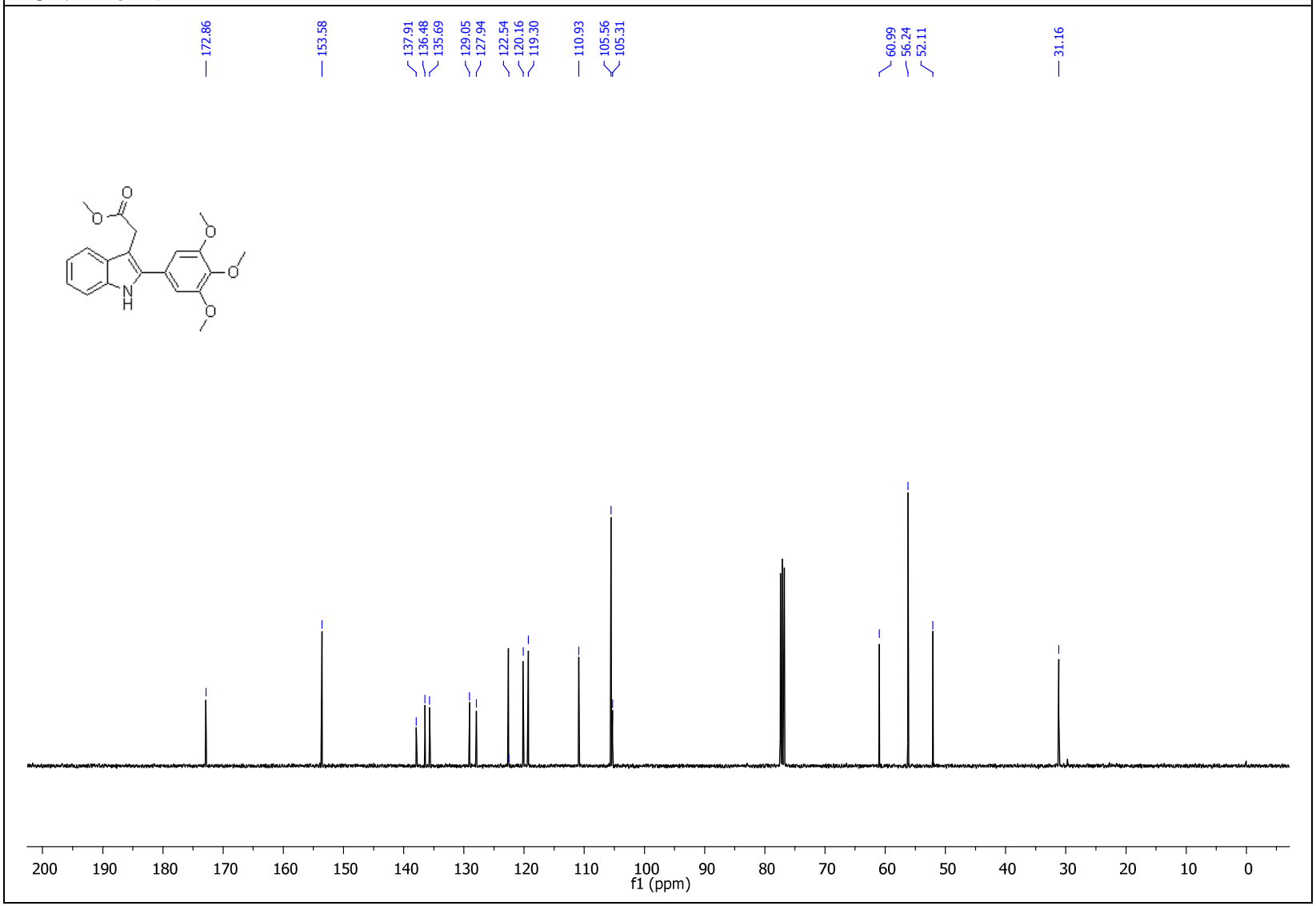
^{13}C NMR of 1u


172.97
159.55
136.26
135.65
129.56
129.08
124.89
122.28
120.01
119.04
114.43
110.88
104.73
55.39
52.09
31.01
O
O
N
H
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

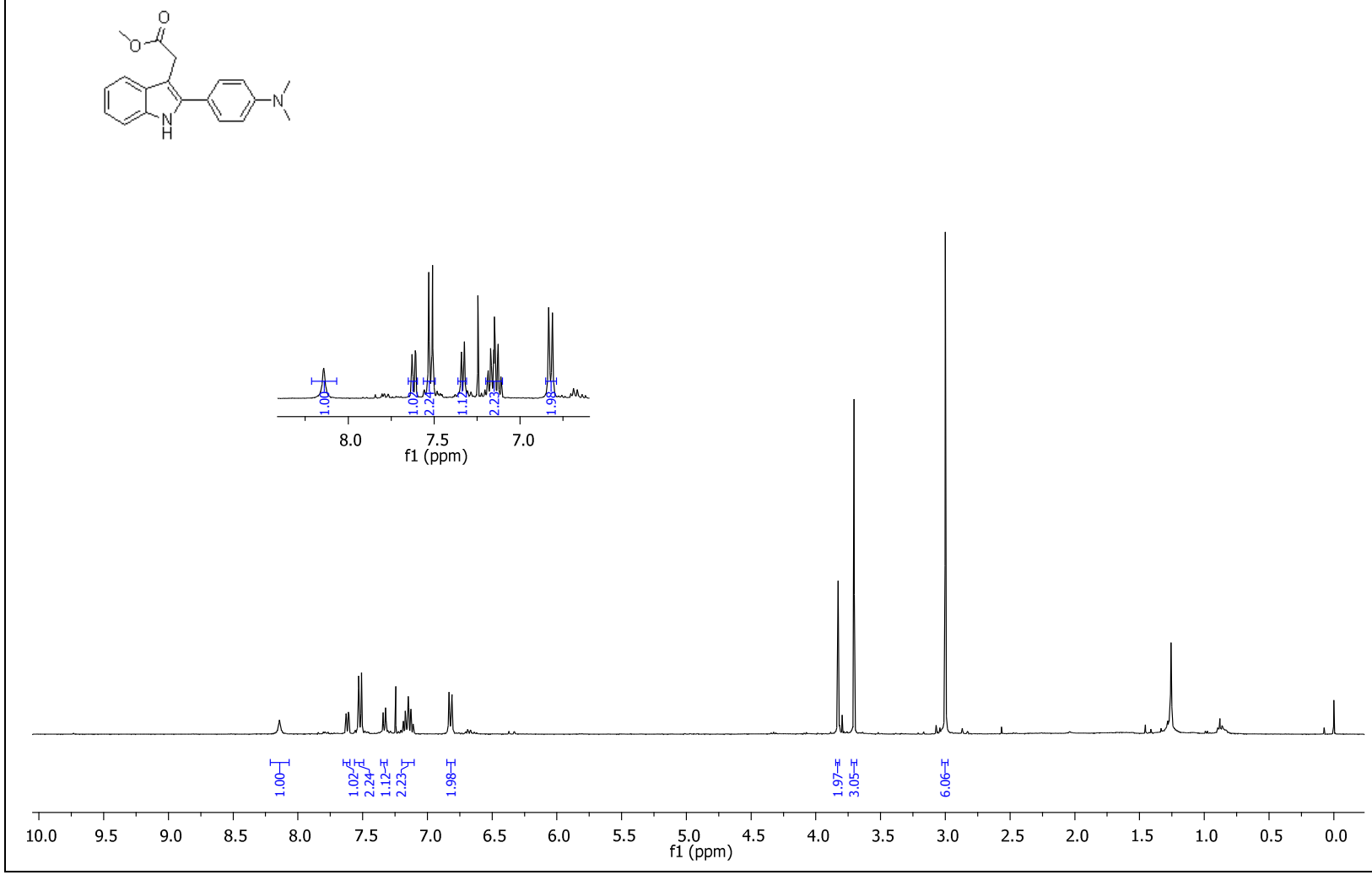
^{1}H NMR of 1v


1.00
1.04
1.09
1.06
1.03
2.06
3.16
6.18
2.04
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
7.5 7.0
f1 (ppm)
4.0 3.9 3.8 3.7 3.6
f1 (ppm)

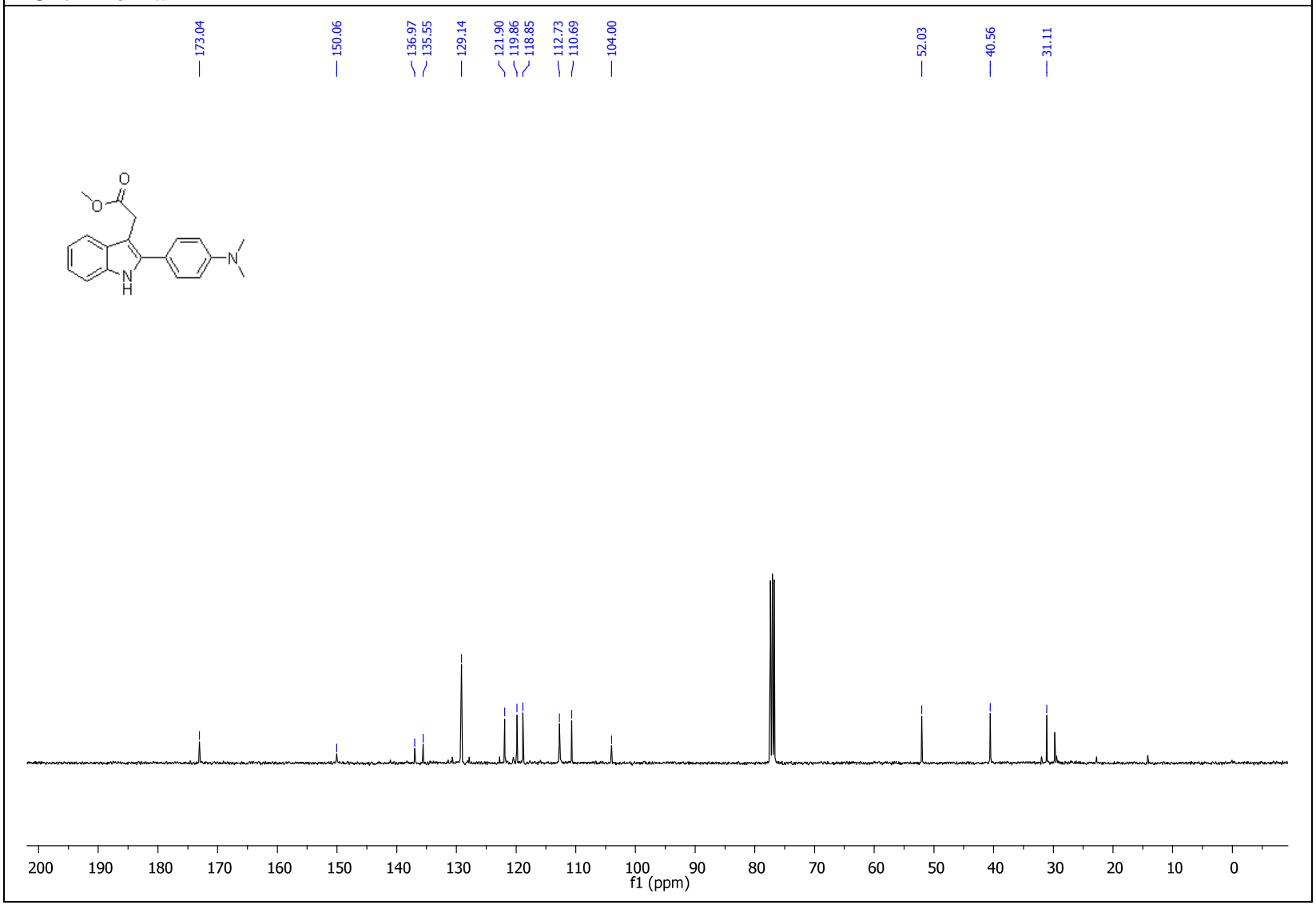
^{13}C NMR of 1v


172.86
153.58
137.91
136.48
135.69
129.05
127.94
122.54
120.16
119.30
110.93
105.56
105.31
60.99
56.24
52.11
31.16
O
O
O
O
O
N
H
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

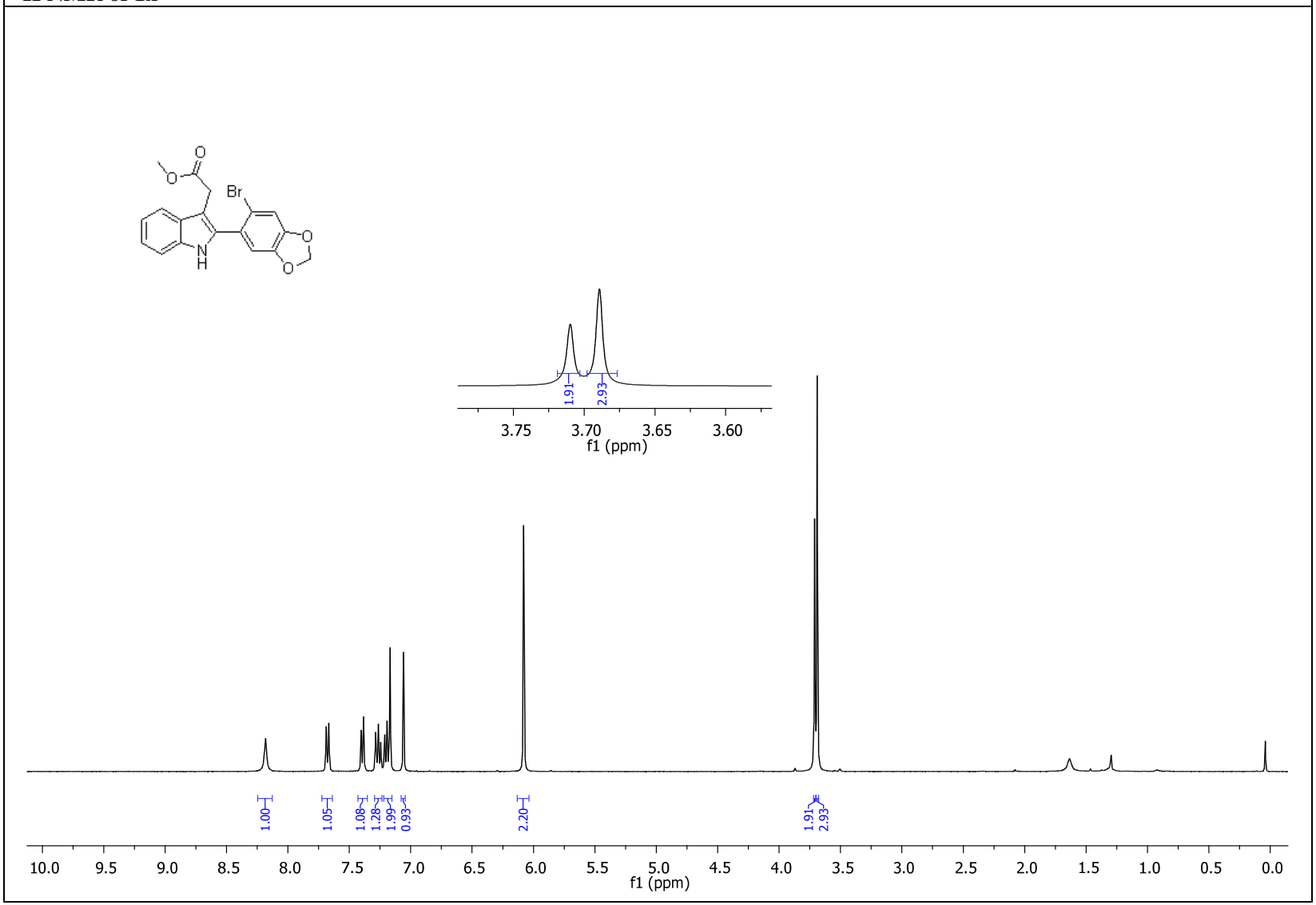
^{1}H NMR of 1w


O
O
N
H
N
1.00
1.02
2.24
1.12
2.23
1.98
1.97
3.05
6.06
8.0
7.5
7.0
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

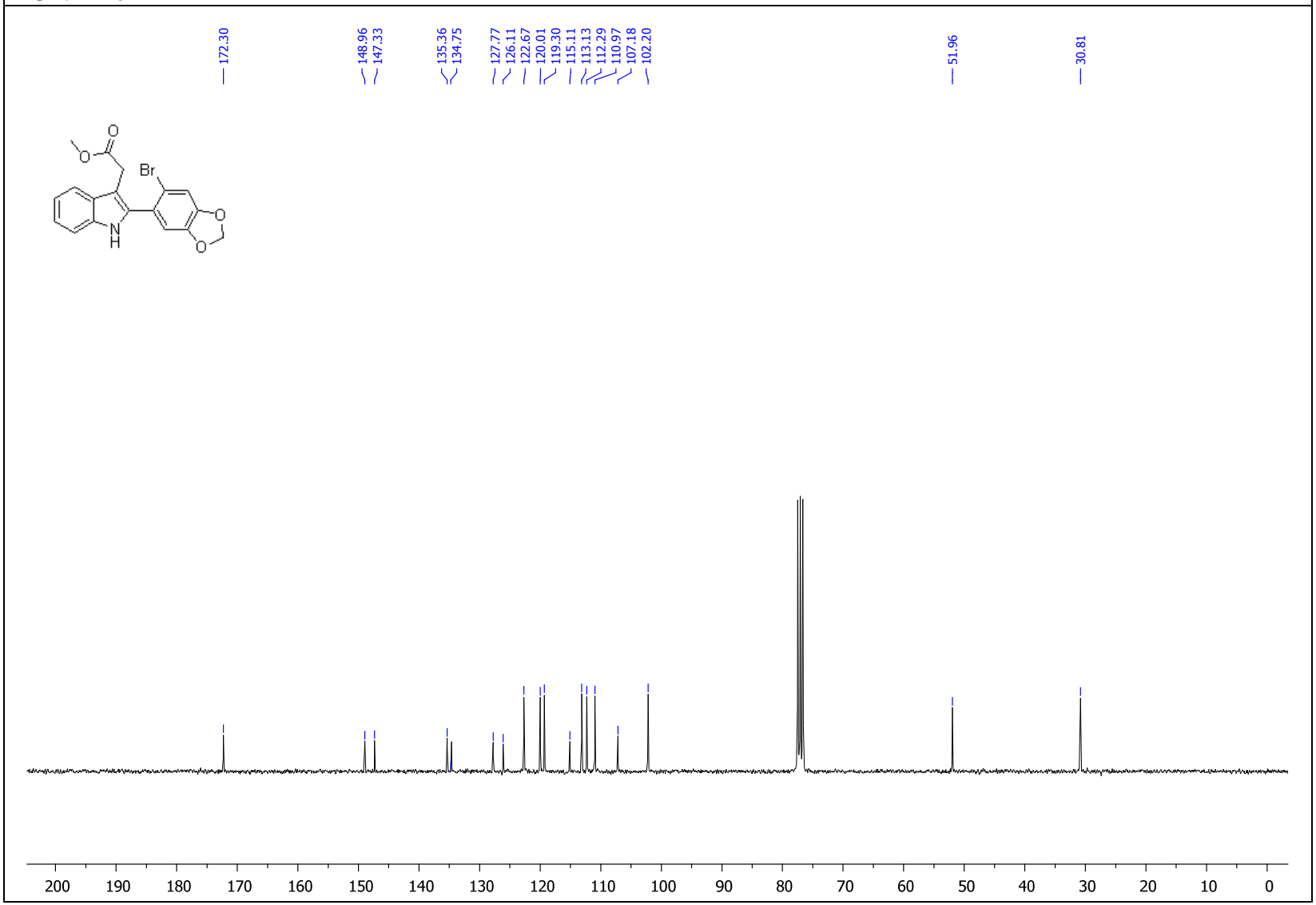
^{13}C NMR of 1w


173.04
150.06
136.97
135.55
129.14
121.90
119.86
118.85
112.73
110.69
104.00
52.03
40.56
31.11
O
O
N
H
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

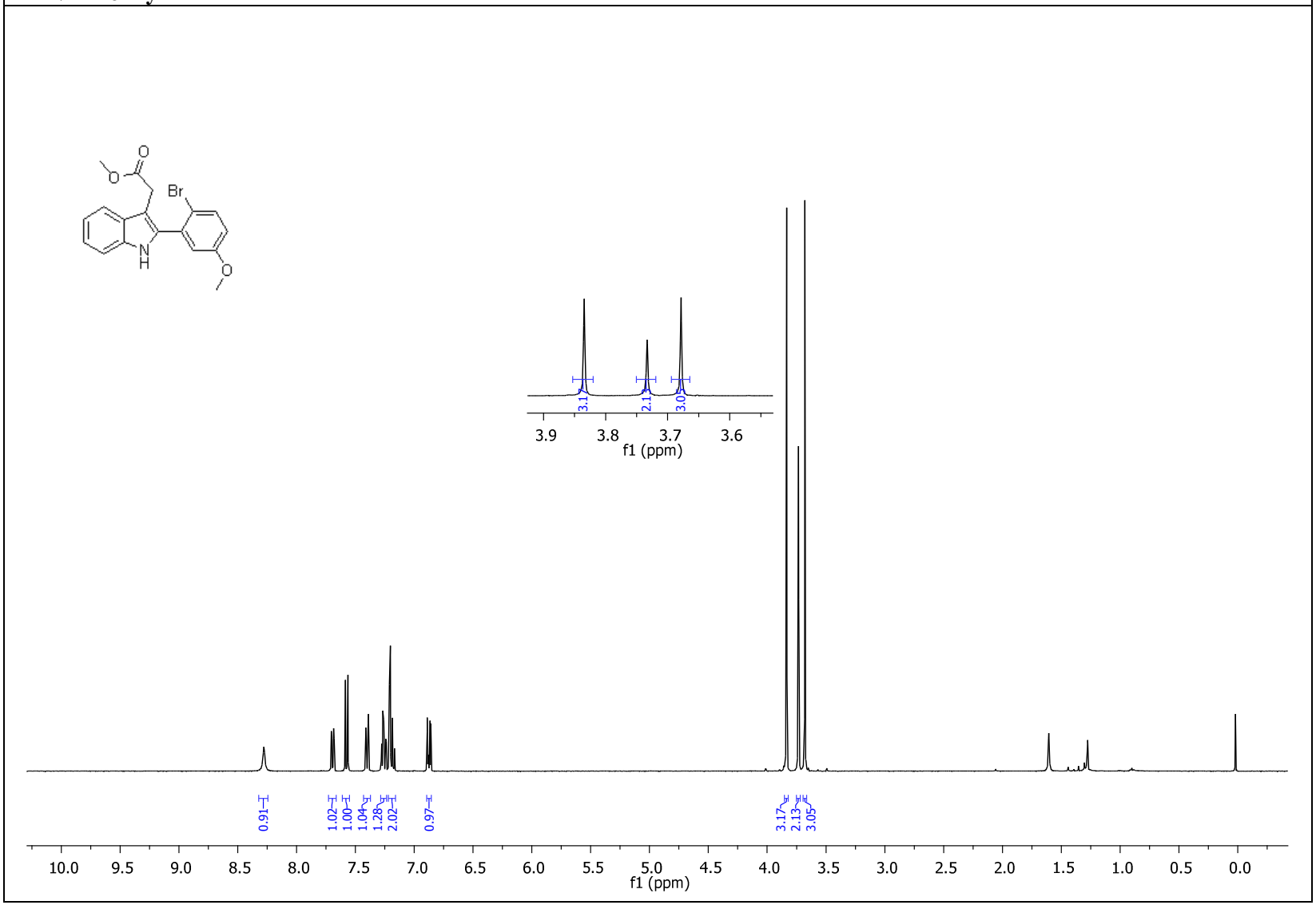
^{1}H NMR of 1x


O
O
Br
N
H
O
O
1.91
2.93
3.75
3.70
3.65
3.60
f1 (ppm)
1.00
1.05
1.08
1.28
1.99
0.93
2.20
1.91
2.93
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

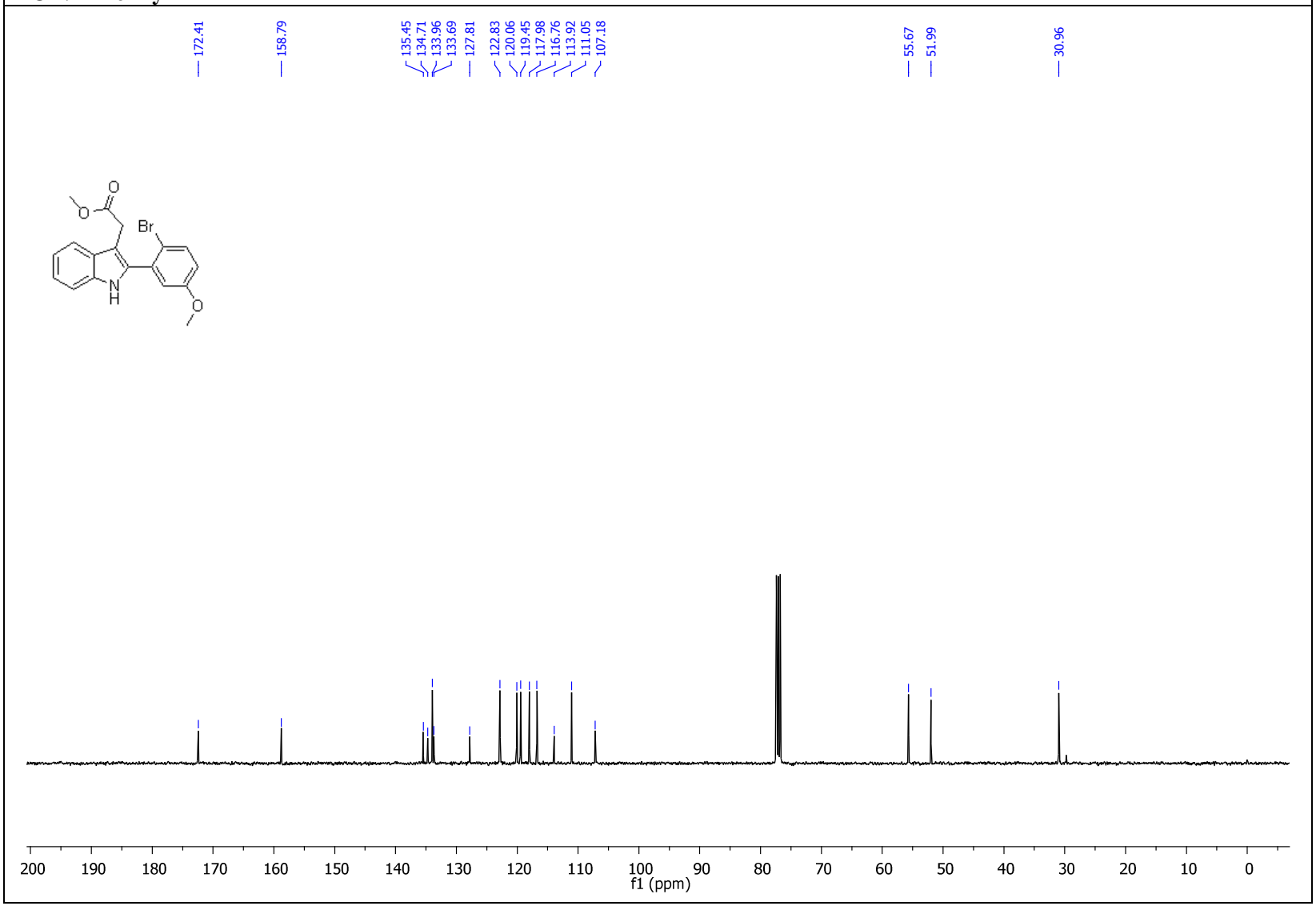
^{13}C NMR of 1x


172.30
148.96
147.33
135.36
134.75
127.77
126.11
122.67
120.01
119.30
115.11
113.13
112.29
110.97
107.18
102.20
51.96
30.81
O
O
Br
N
H
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

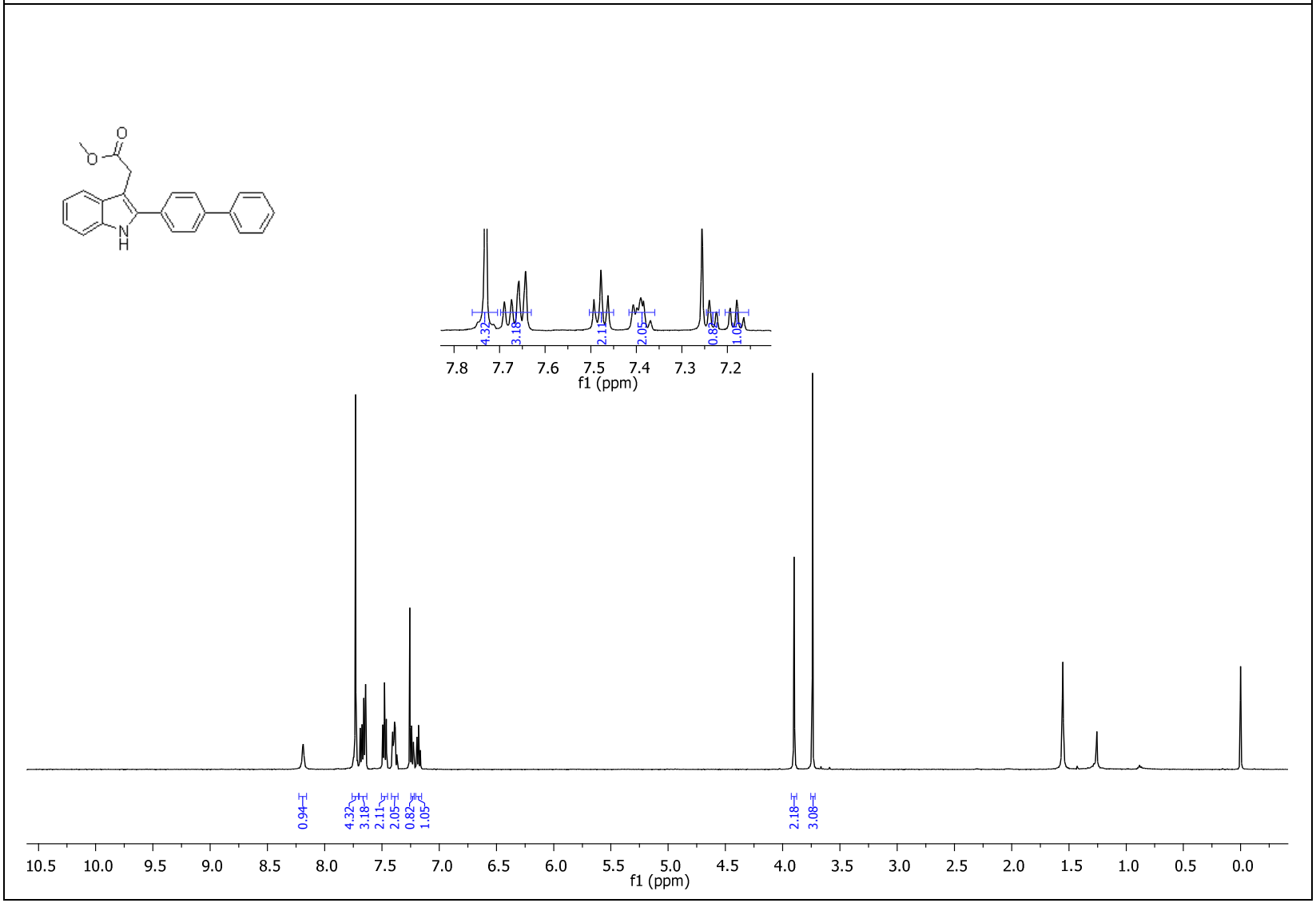
^{1}H NMR of 1y


O
O
Br
N
H
O
3.1
2.1
3.0
3.9
3.8
3.7
3.6
f1 (ppm)
0.91
1.02
1.00
1.04
1.28
2.02
0.97
3.17
2.13
3.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

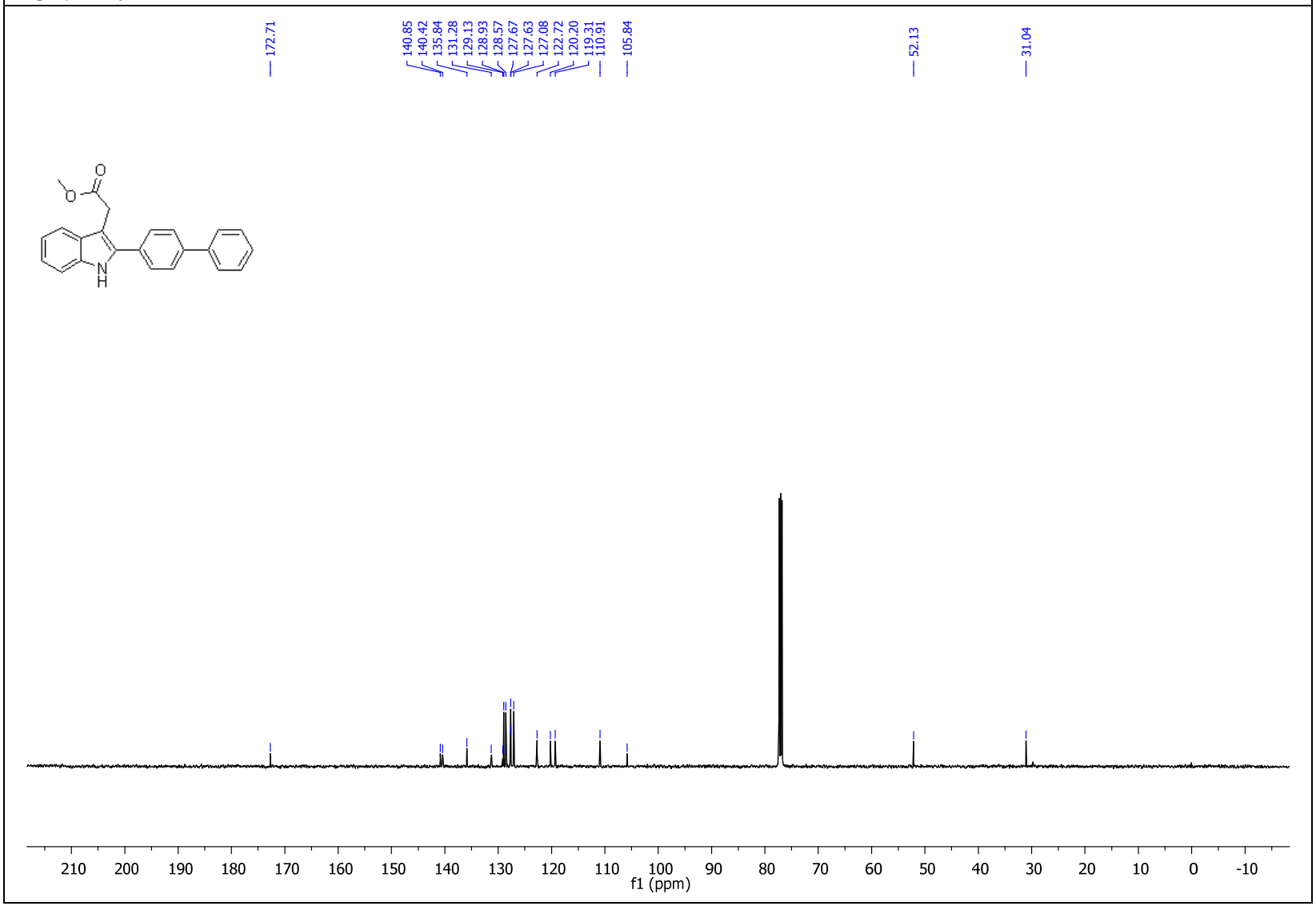
^{13}C NMR of 1y


172.41
158.79
135.45
134.71
133.96
133.69
127.81
122.83
120.06
119.45
117.98
116.76
113.92
111.05
107.18
55.67
51.99
30.96
O
O
Br
N
H
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

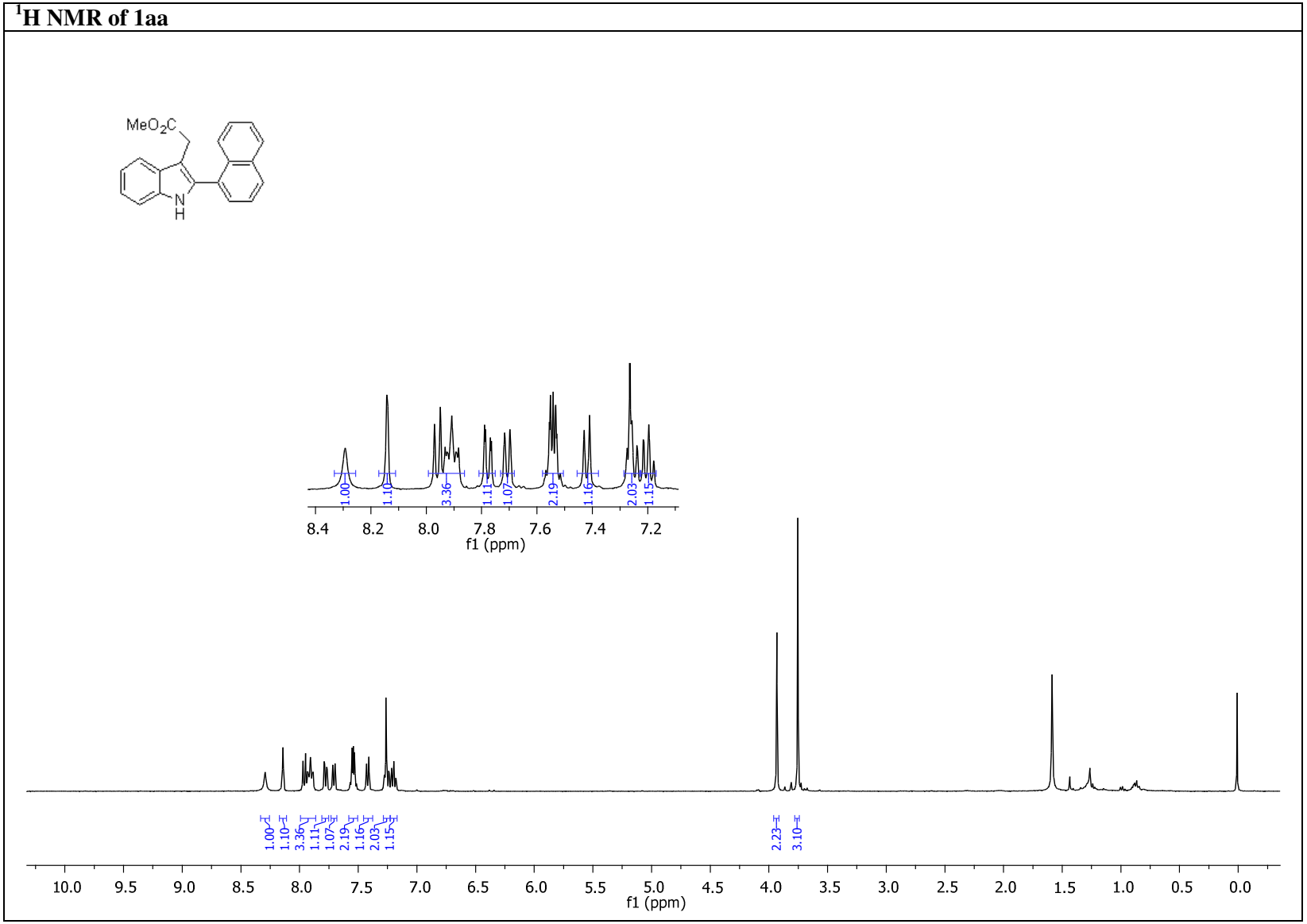
^{1}H NMR of 1z


O
O
N
H
4.32
3.18
2.11
2.05
0.82
1.05
7.8
7.7
7.6
7.5
7.4
7.3
7.2
f1 (ppm)
0.94
4.32
3.18
2.11
2.05
0.82
1.05
2.18
3.08
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

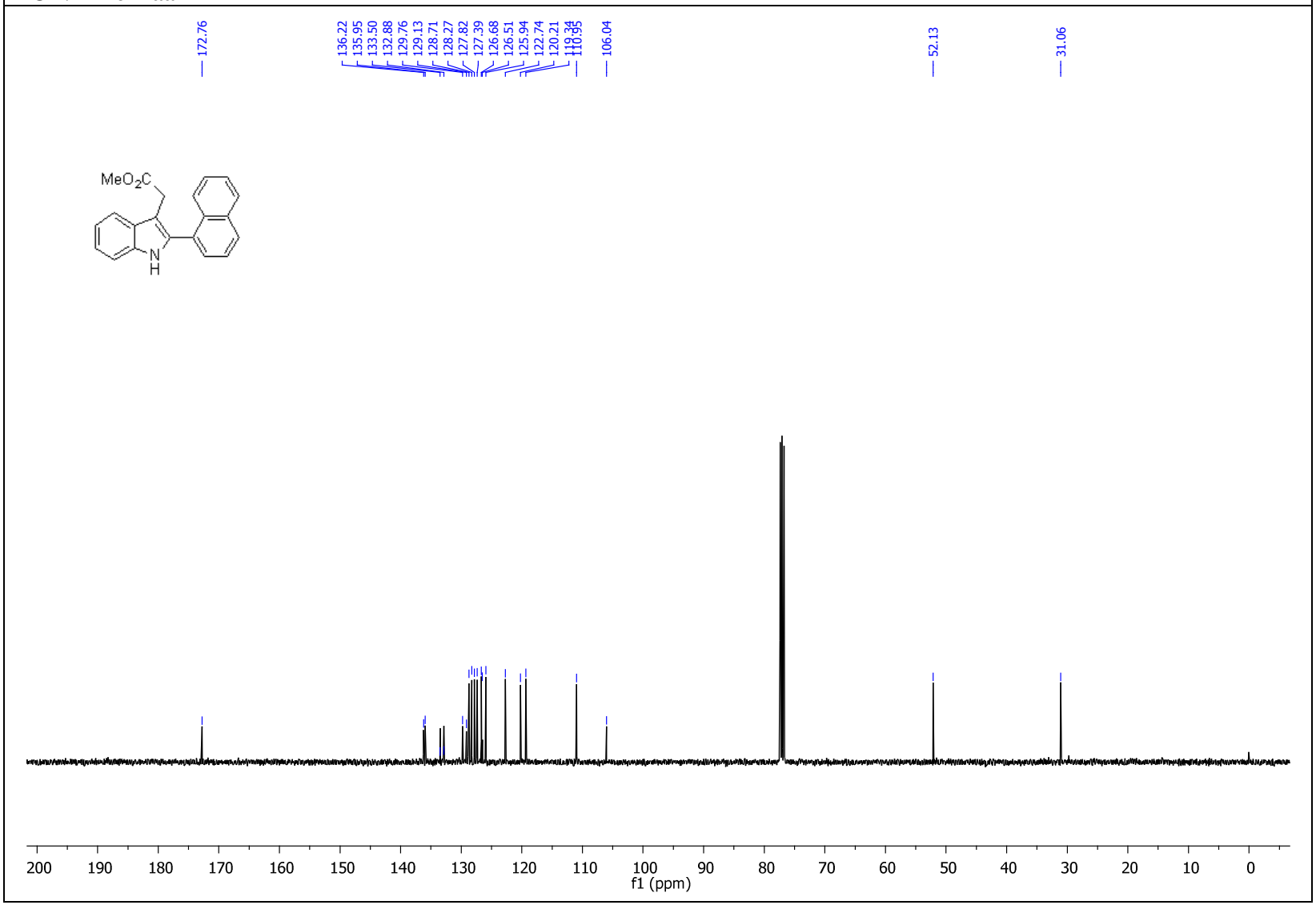
^{13}C NMR of 1z


172.71
140.85
140.42
135.84
131.28
129.13
128.93
128.57
127.67
127.63
127.08
122.72
120.20
119.31
110.91
105.84
52.13
31.04
O
O
N
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

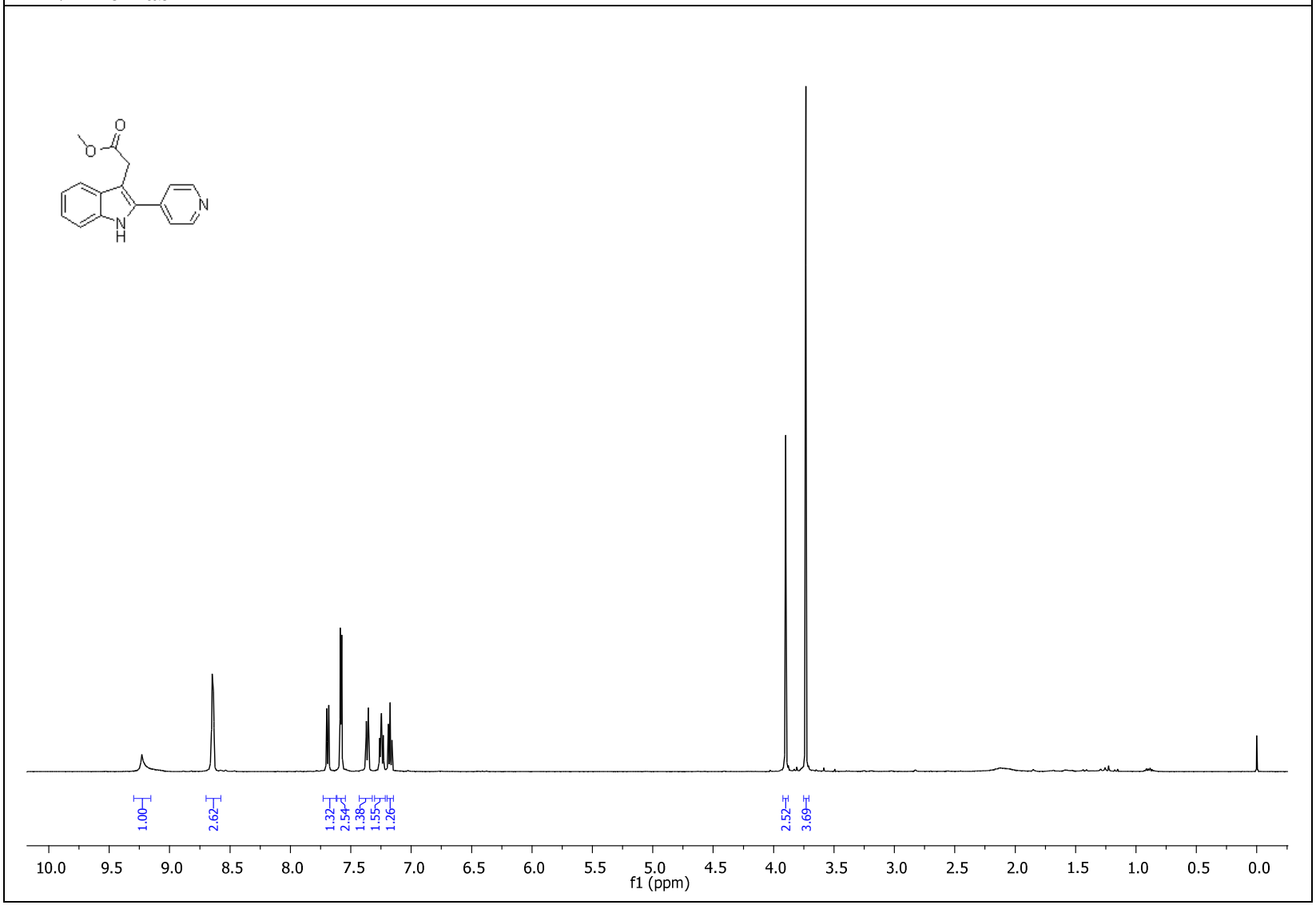
^{1}H NMR of 1aa


MeO2C
N
H
1.00
1.10
3.36
1.11
1.07
2.19
1.16
2.03
1.15
8.4
8.2
8.0
7.8
7.6
7.4
7.2
f1 (ppm)
2.23
3.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

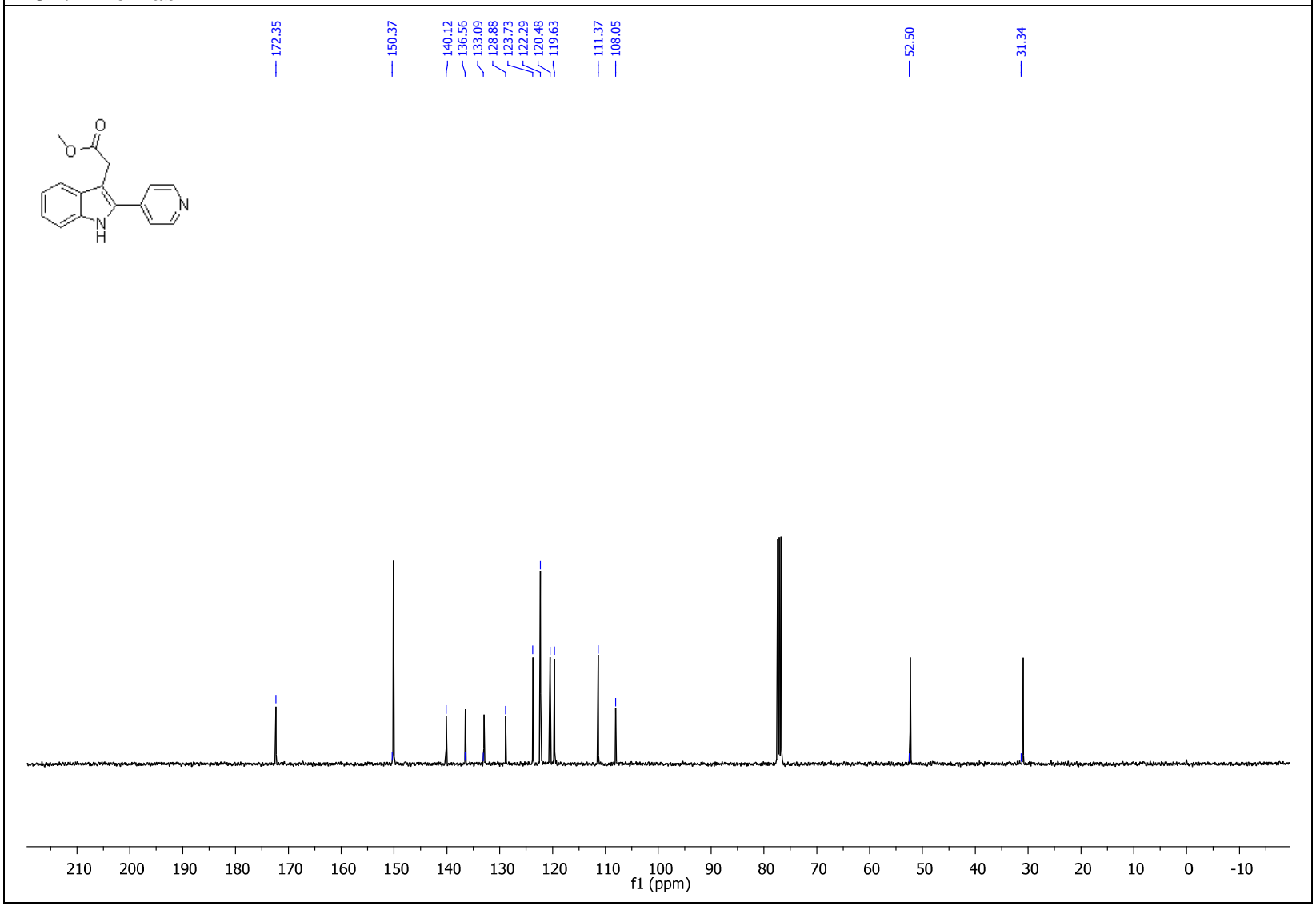
^{13}C NMR of 1aa



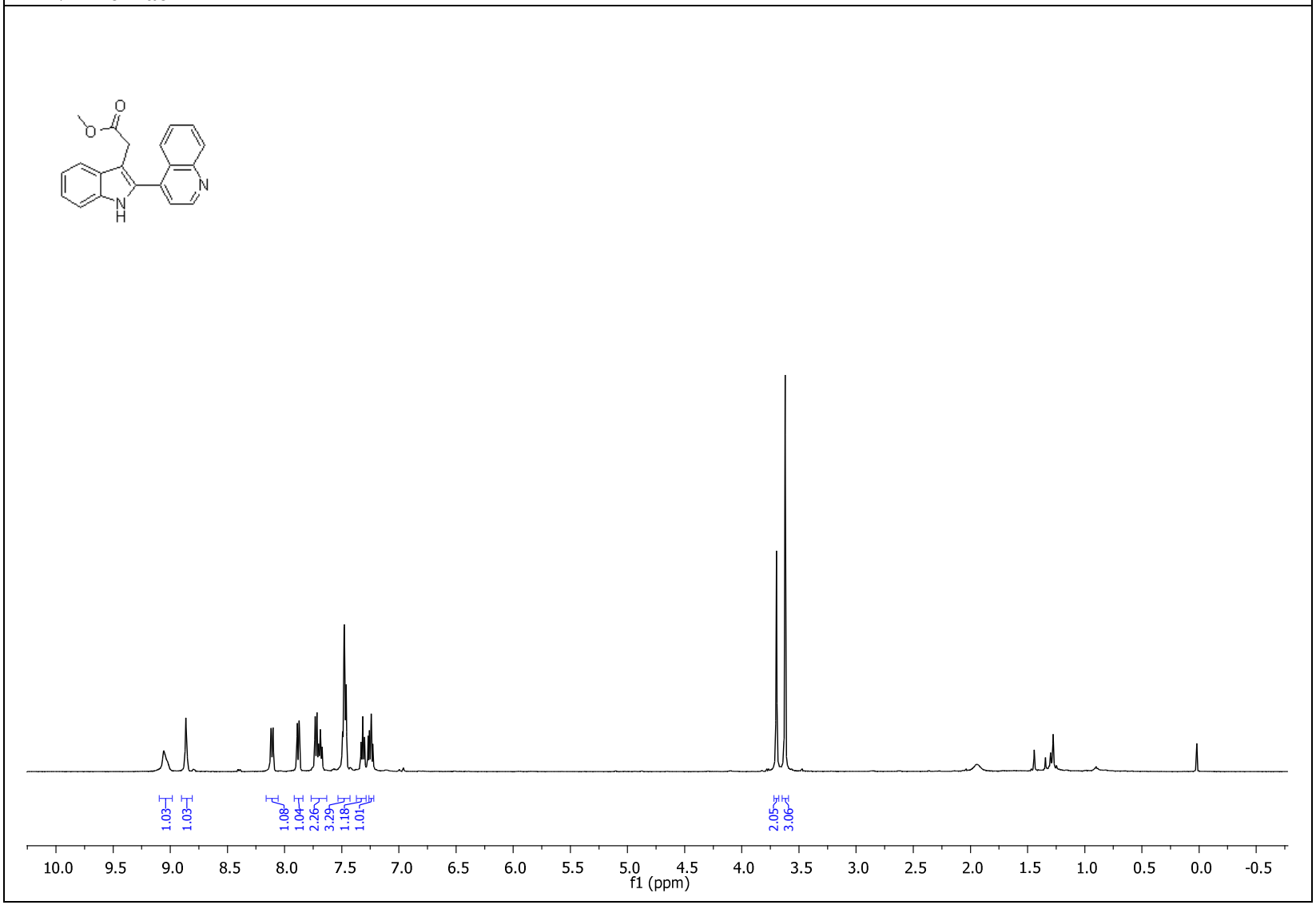
^{1}H NMR of 1ab


O
O
N
H
N
1.00
2.62
1.32
2.54
1.38
1.55
1.26
2.52
3.69
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

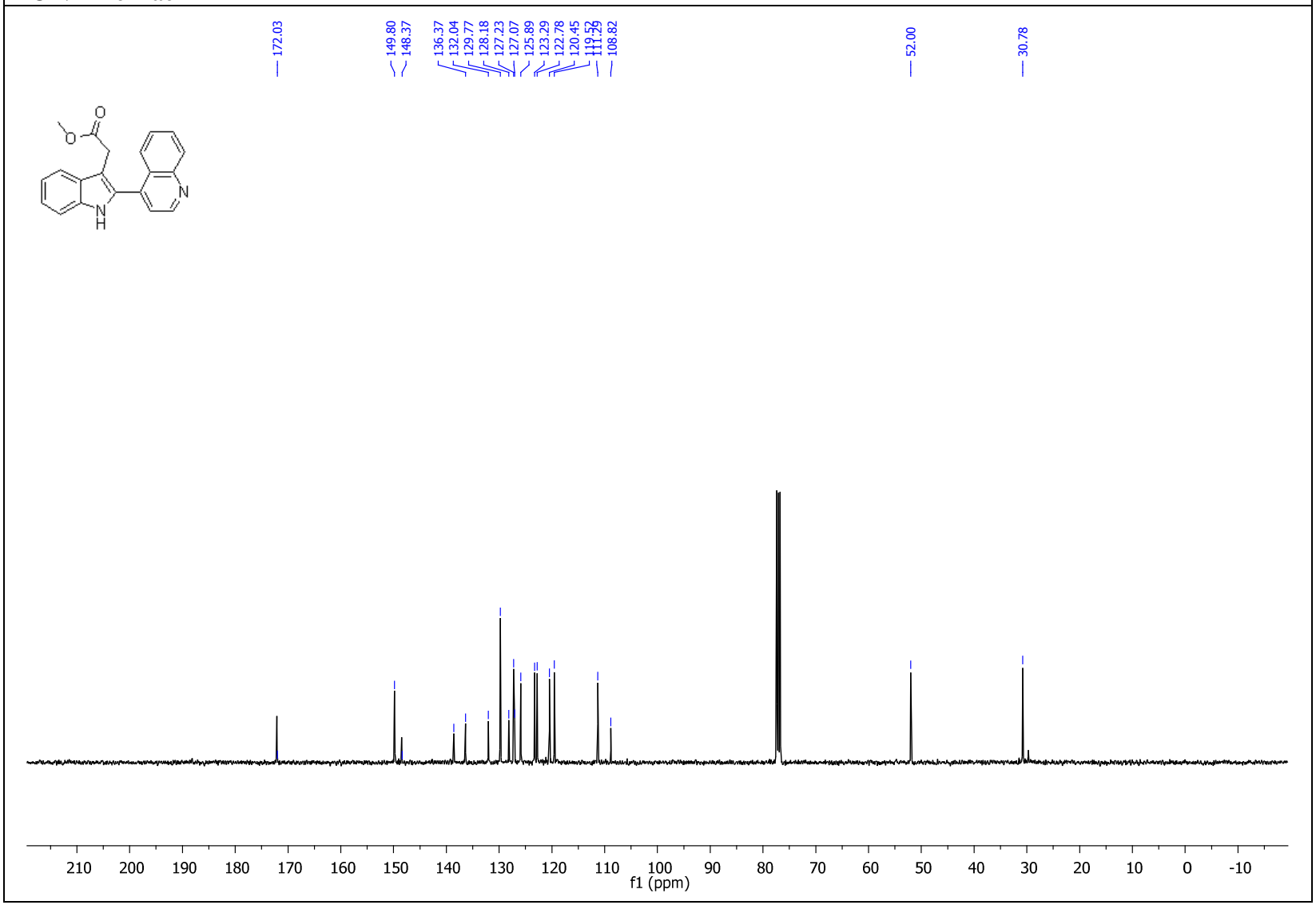
^{13}C NMR of 1ab



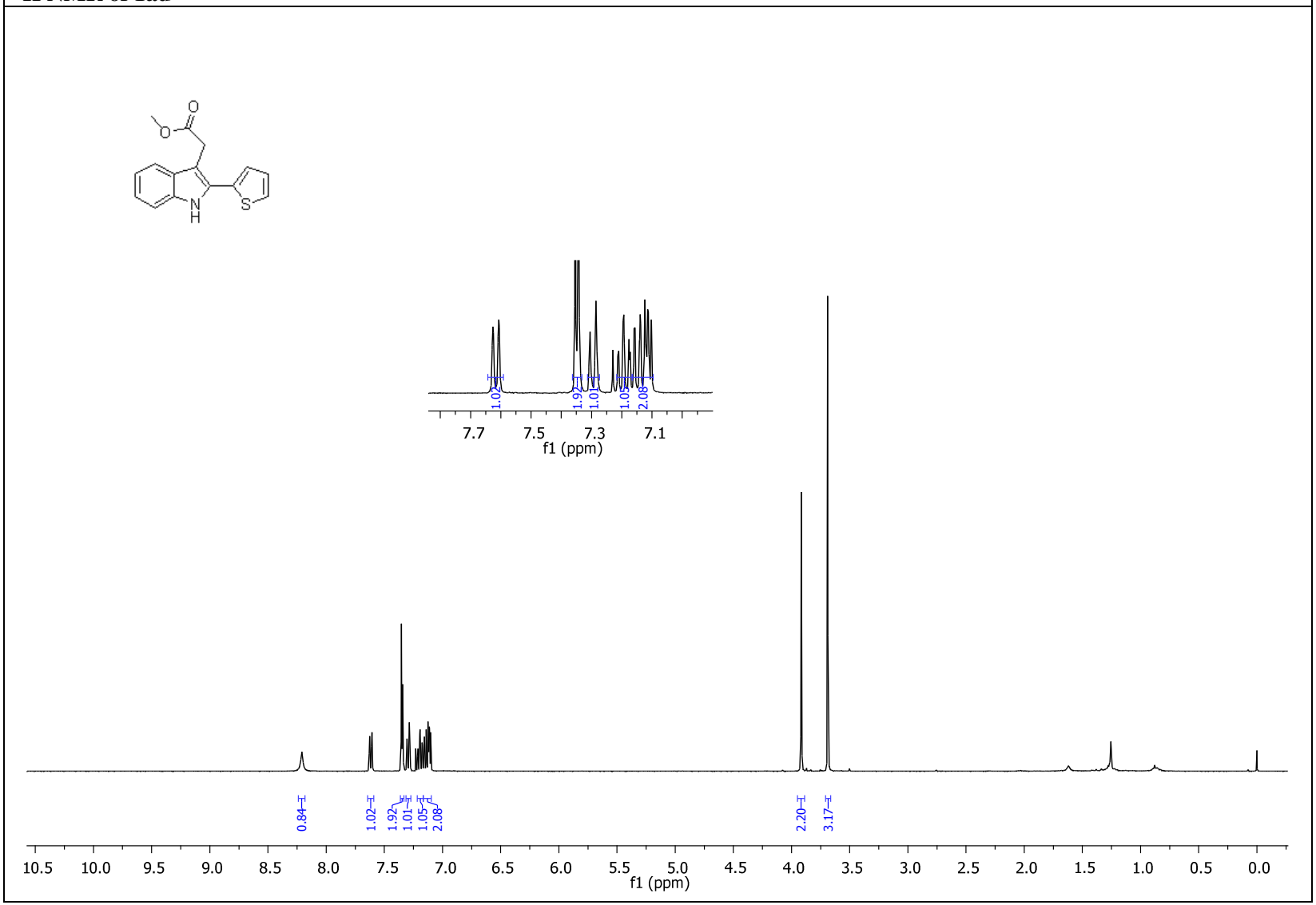
^{1}H NMR of 1ac


O
O
N
H
N
1.03
1.03
1.08
1.04
2.26
3.29
1.18
1.01
2.05
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

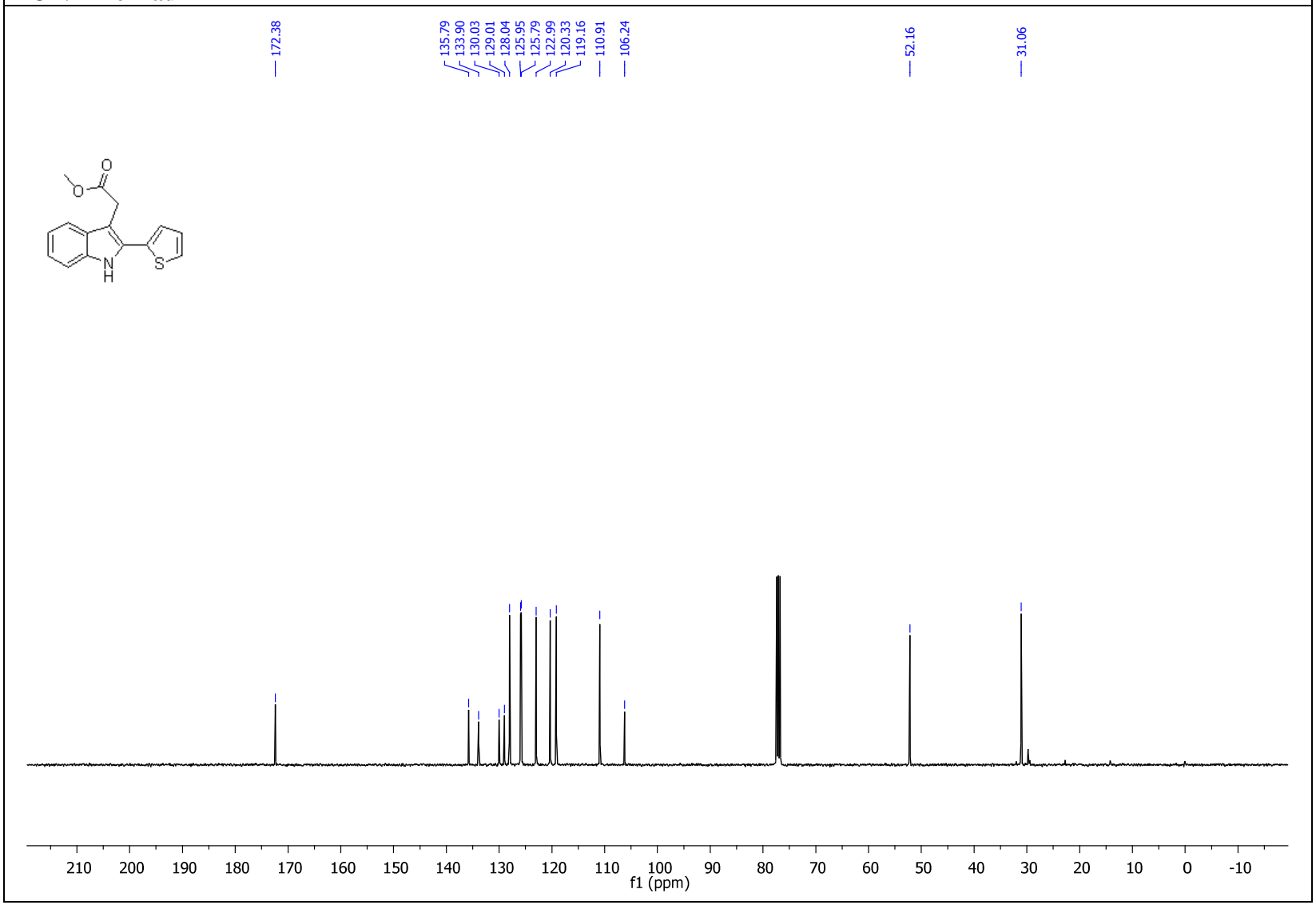
^{13}C NMR of 1ac



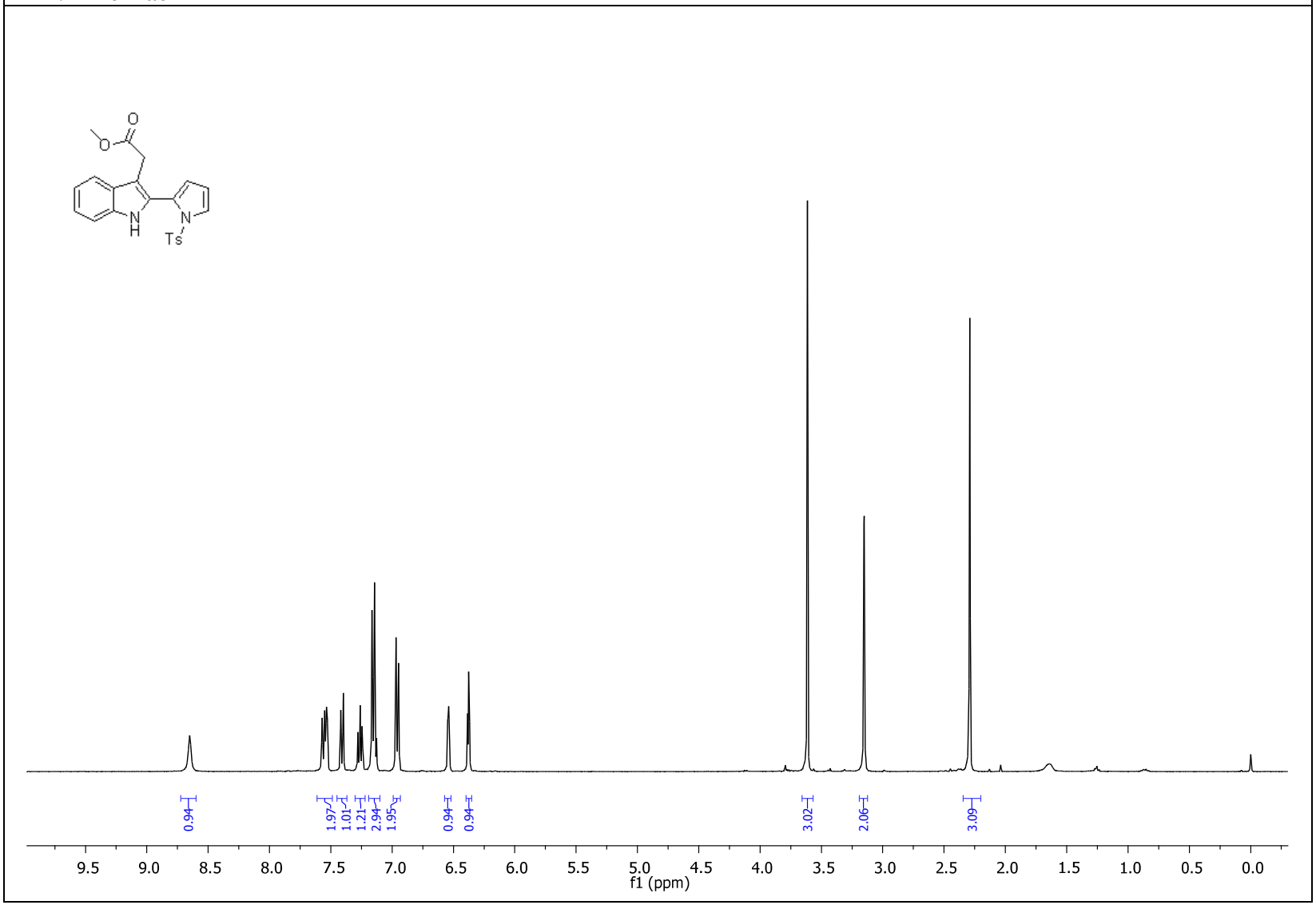
^{1}H NMR of 1ad


O
O
N
H
S
1.02
1.92
1.01
1.05
2.08
7.7
7.5
7.3
7.1
f1 (ppm)
0.84
1.02
1.92
1.01
1.05
2.08
2.20
3.17
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

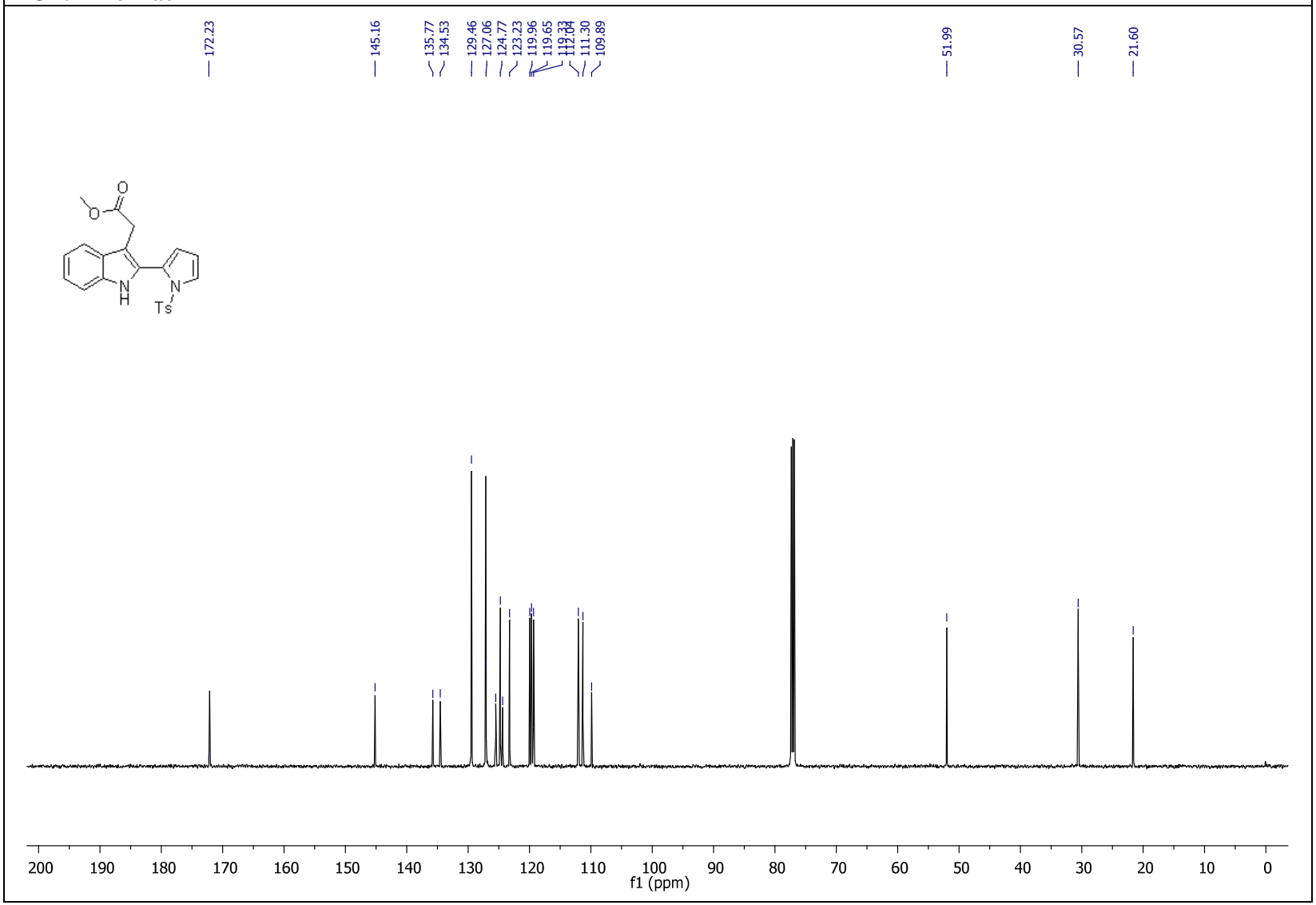
^{13}C NMR of 1ad



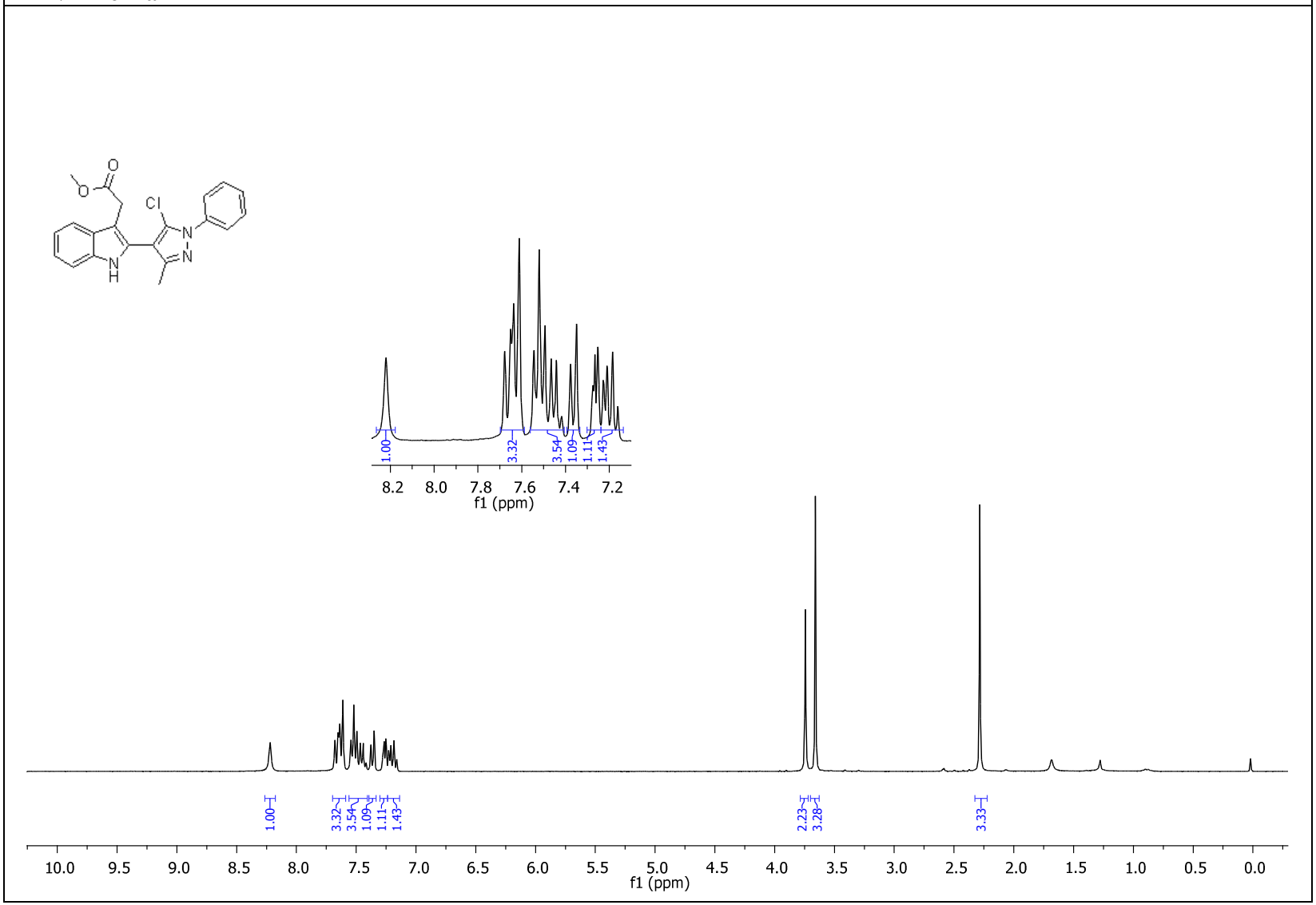
^{1}H NMR of 1ae


O
O
N
H
N
Ts
0.94
1.97
1.01
1.21
2.94
1.95
0.94
0.94
3.02
2.06
3.09
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

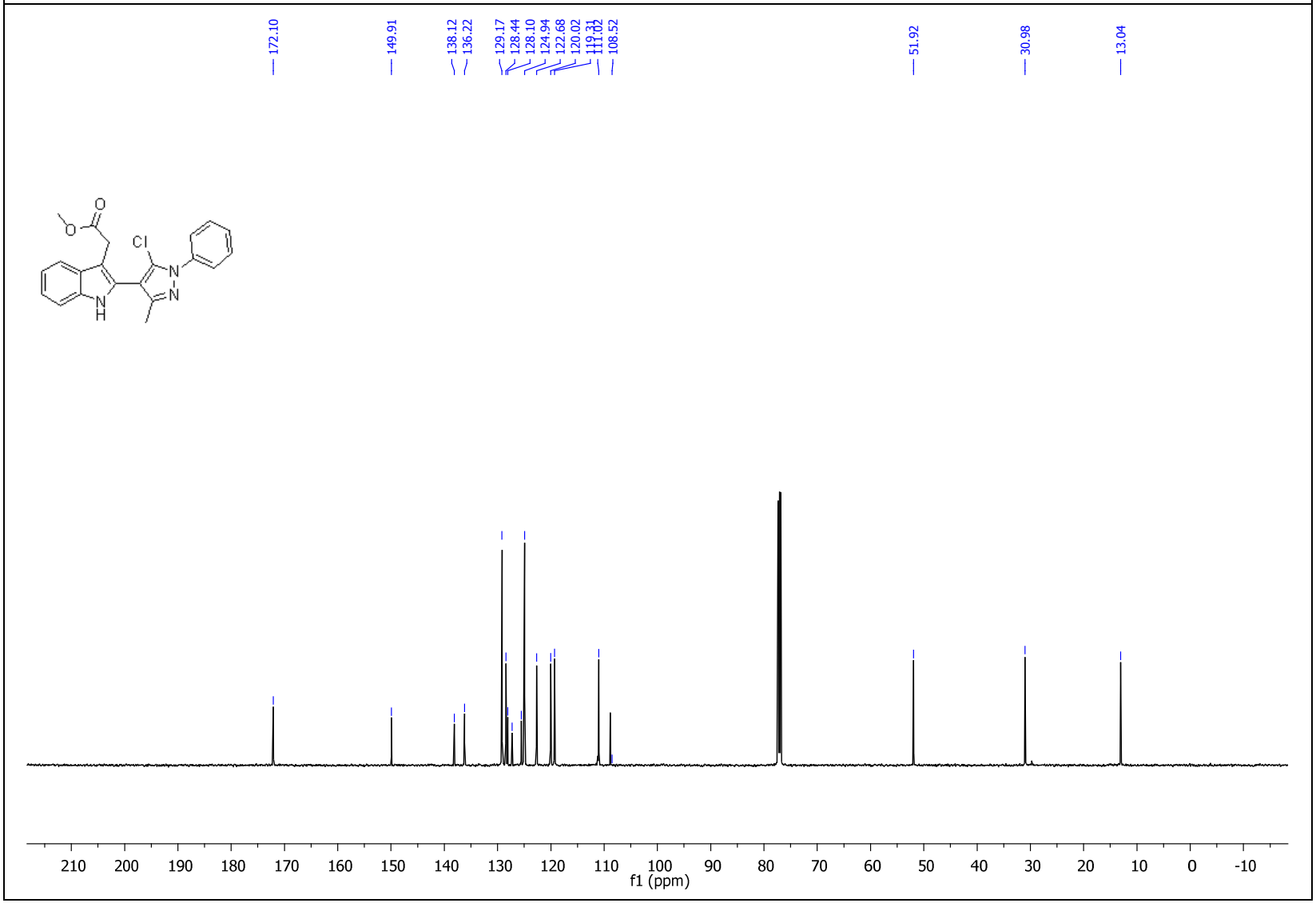
^{13}C NMR of 1ae



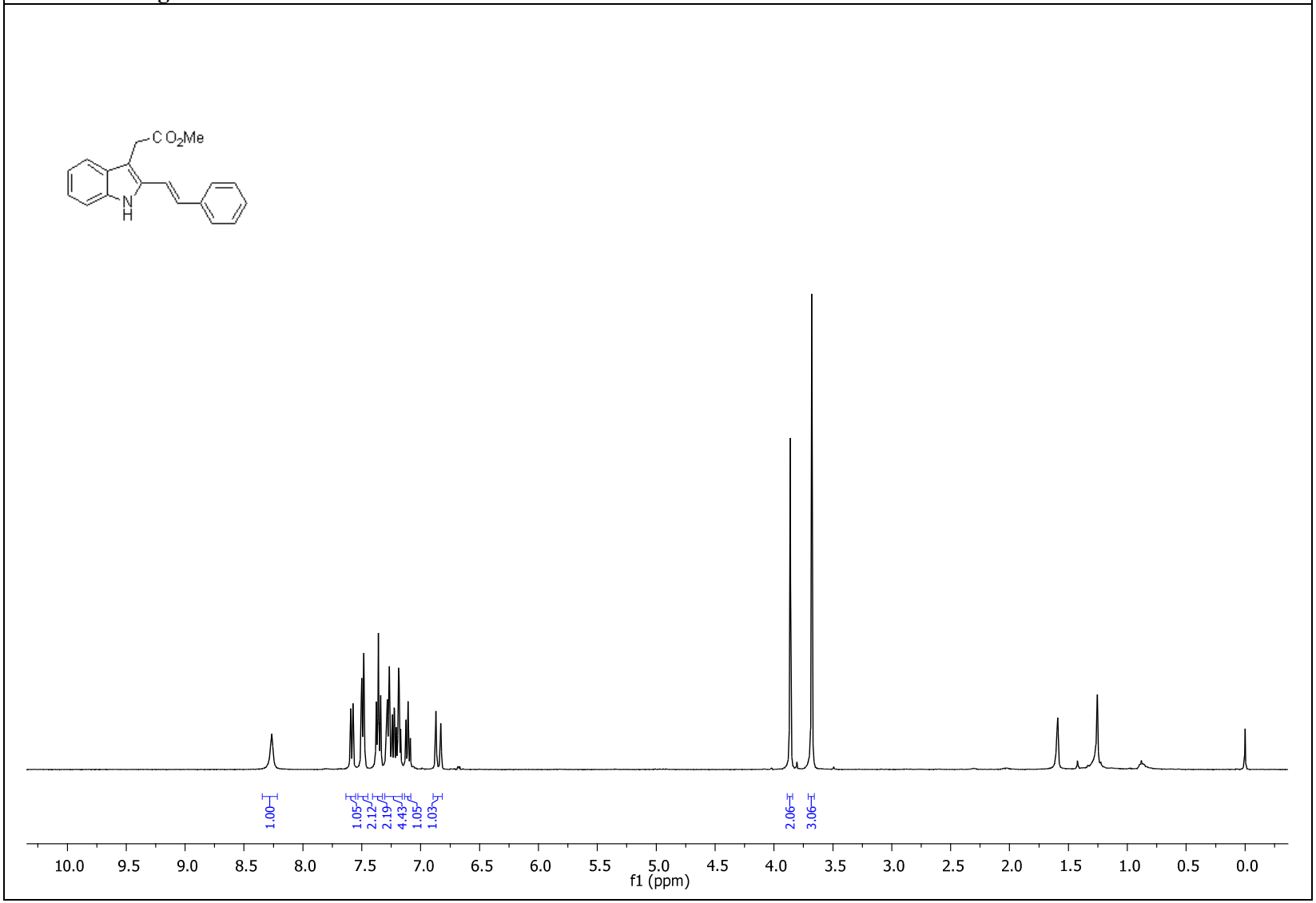
^{1}H NMR of 1af


O
O
Cl
N
N
H
1.00
3.32
3.54
1.09
1.11
1.43
8.2
8.0
7.8
7.6
7.4
7.2
f1 (ppm)
1.00
3.32
3.54
1.09
1.11
1.43
2.23
3.28
3.33
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

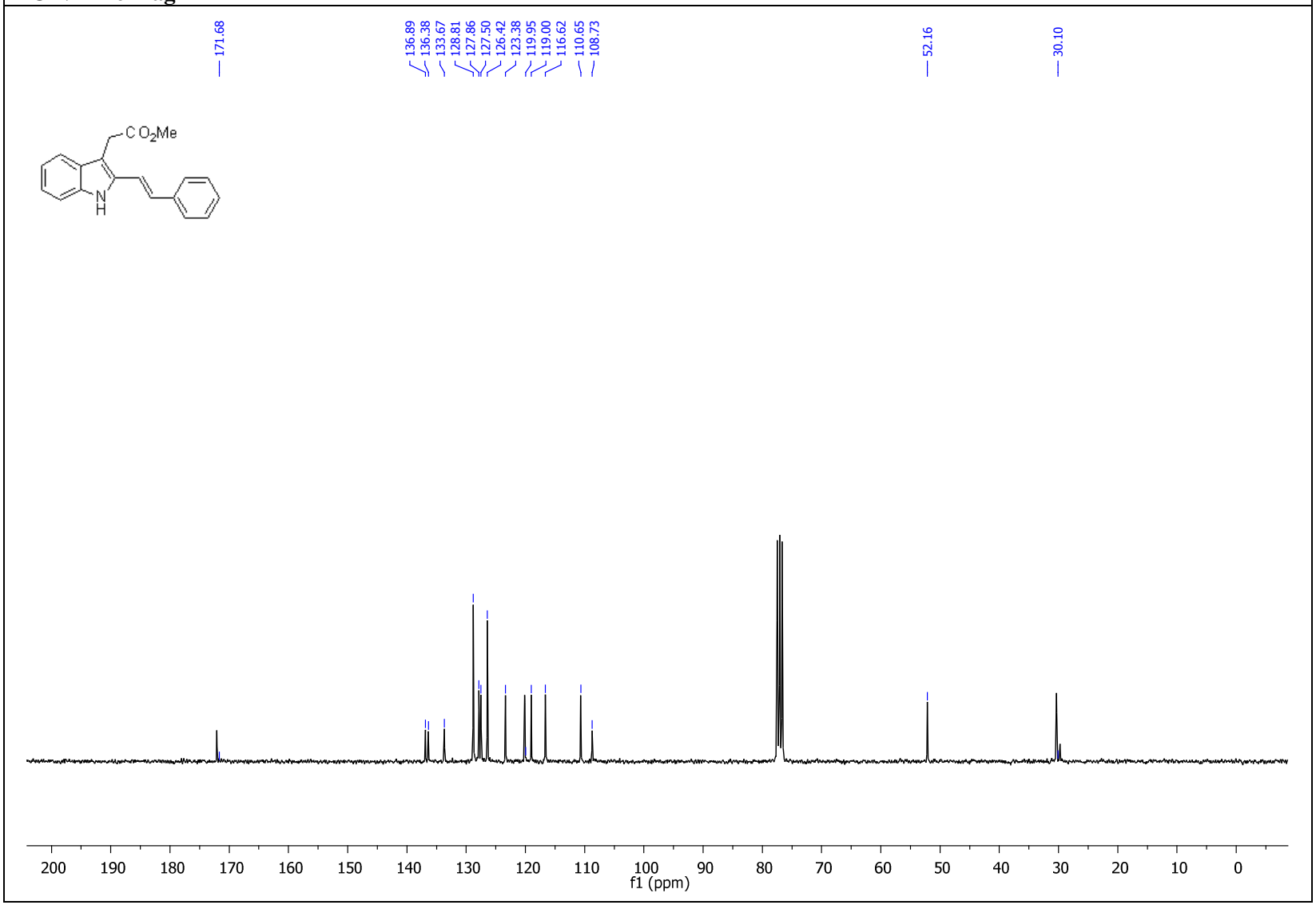
^{13}C NMR of 1af



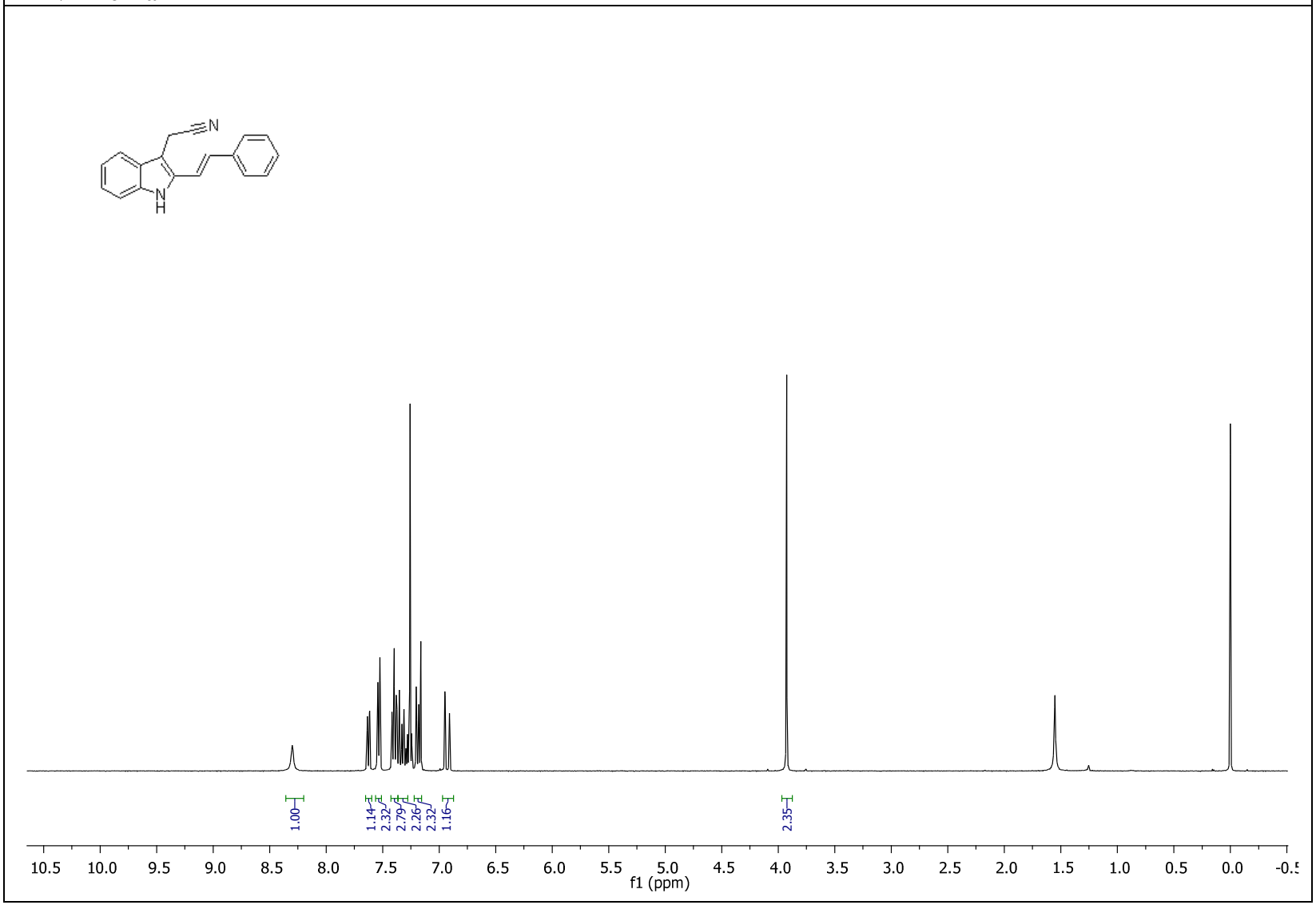
^{1}H NMR of 1ag


CO2Me
N
H
1.00
1.05
2.12
2.19
4.43
1.05
1.03
2.06
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

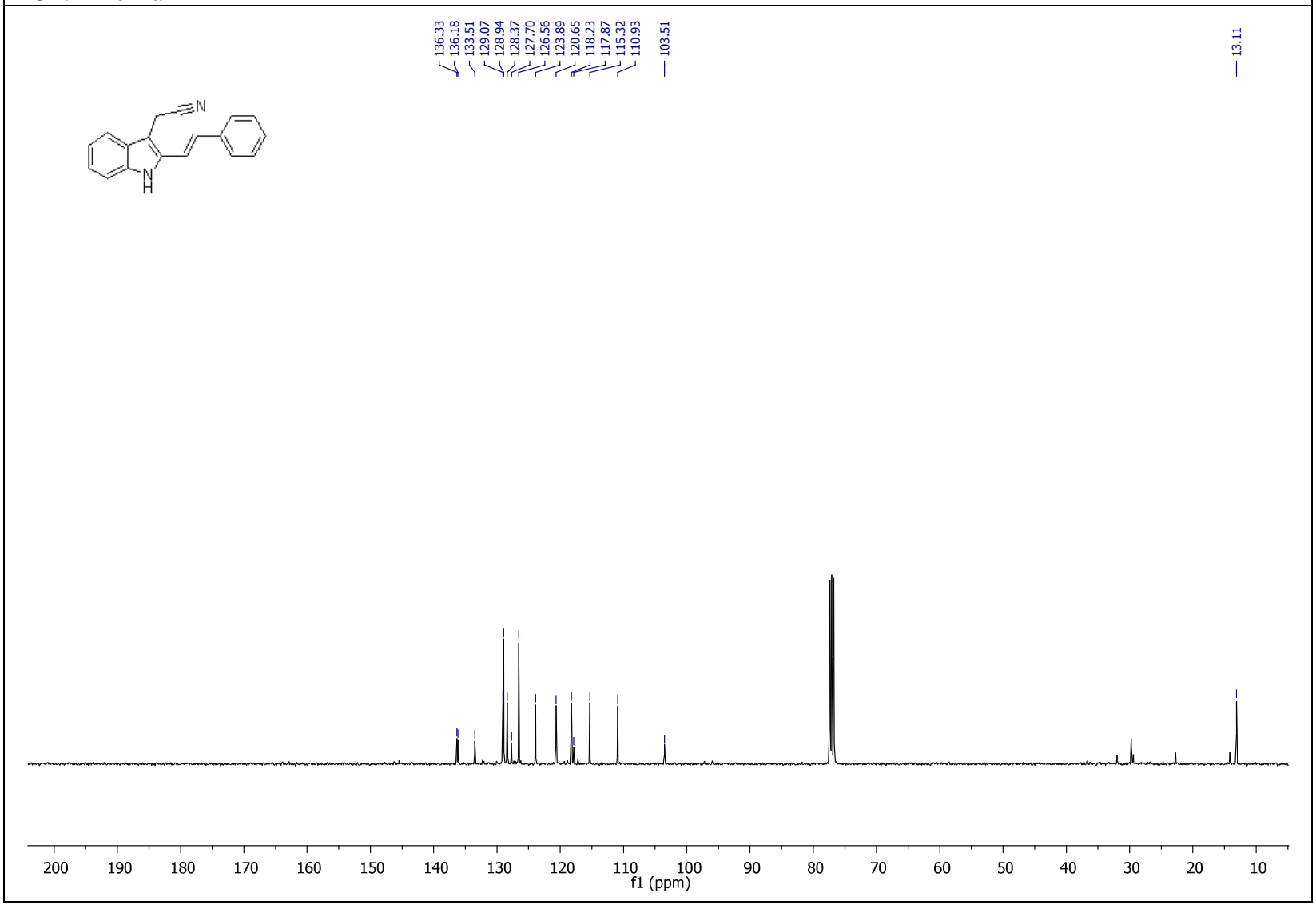
^{13}C NMR of 1ag



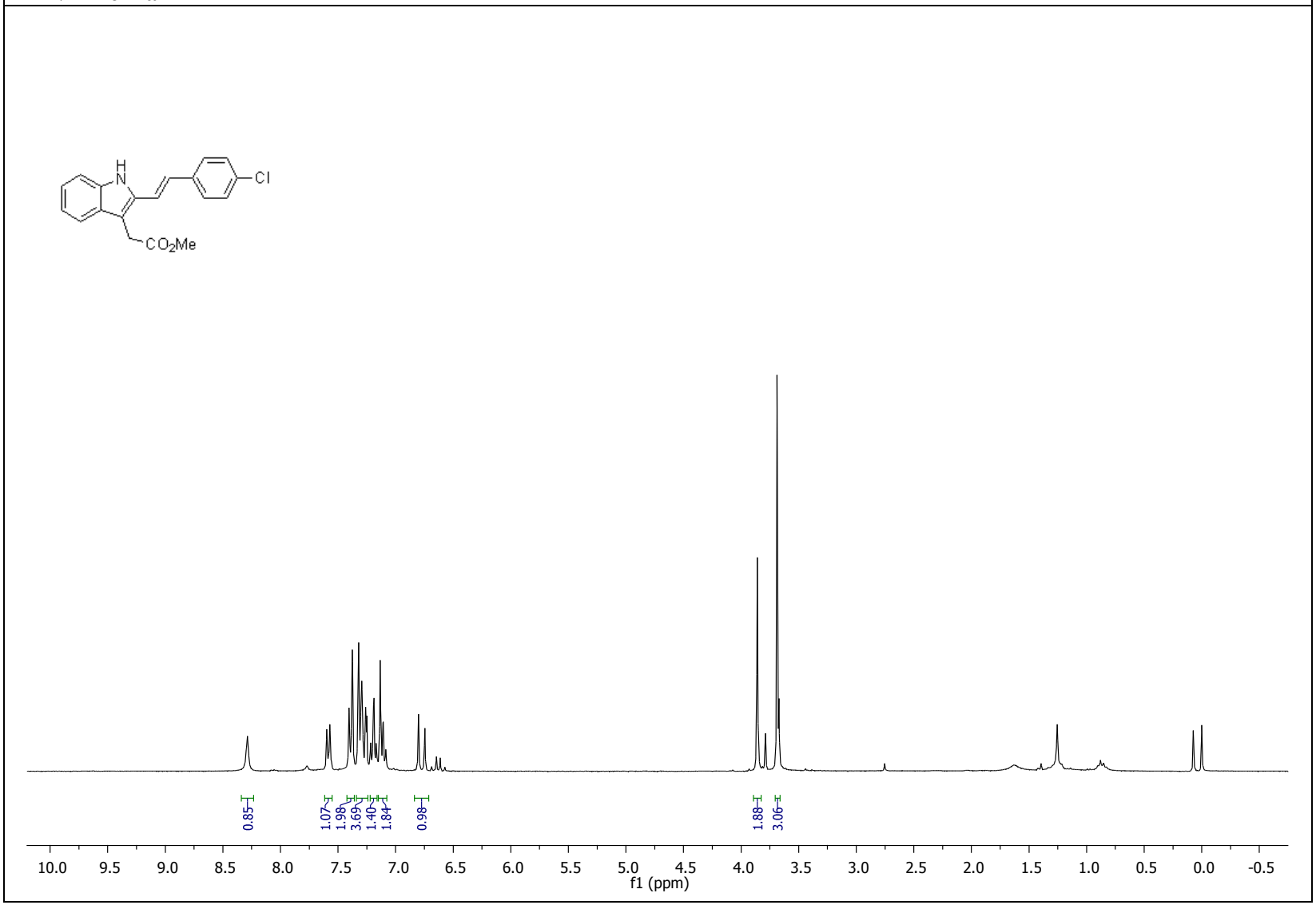
^{1}H NMR of 1ah


N
N
H
1.00
1.14
2.32
2.79
2.26
2.32
1.16
2.35
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

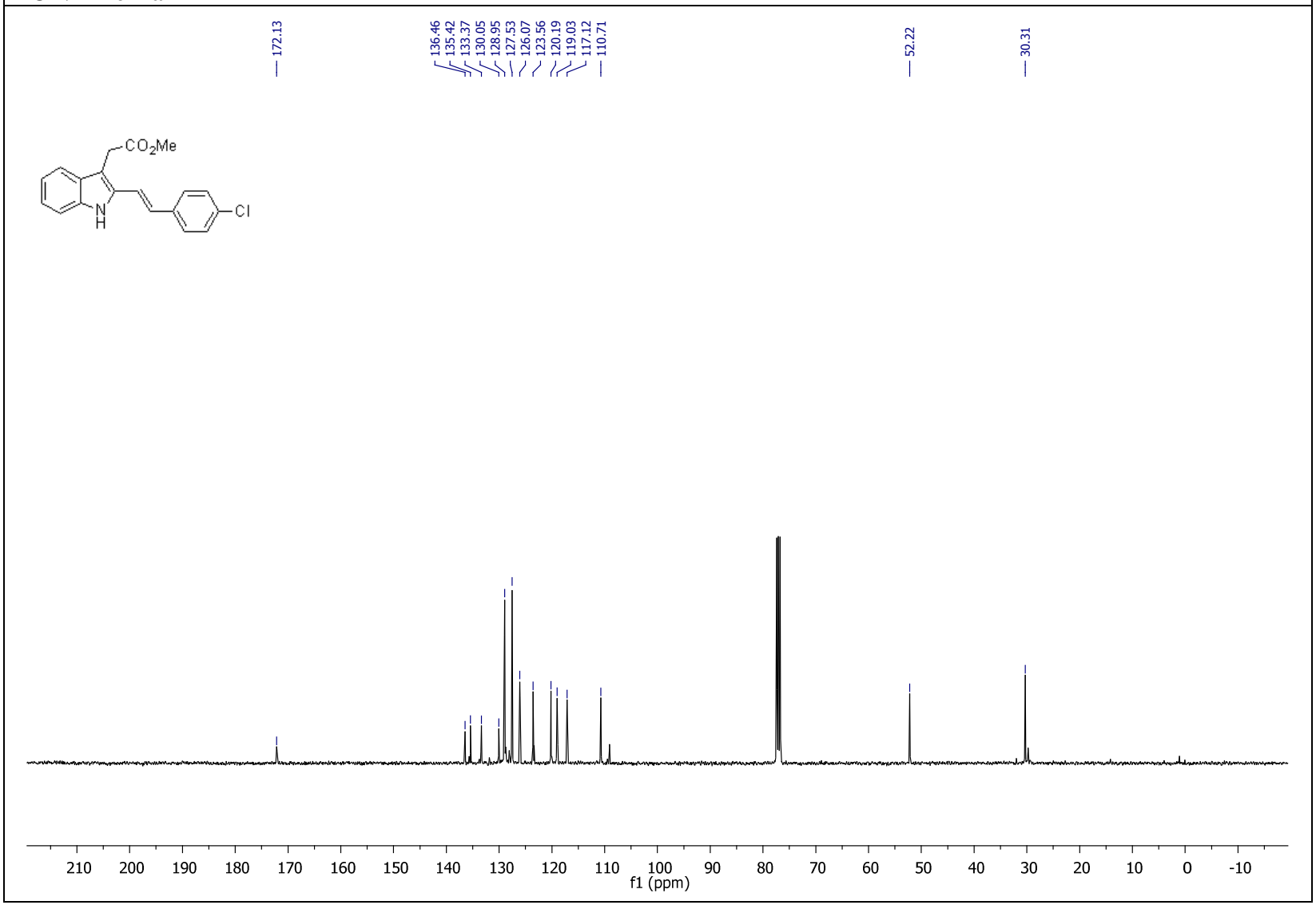
^{13}C NMR of 1ah



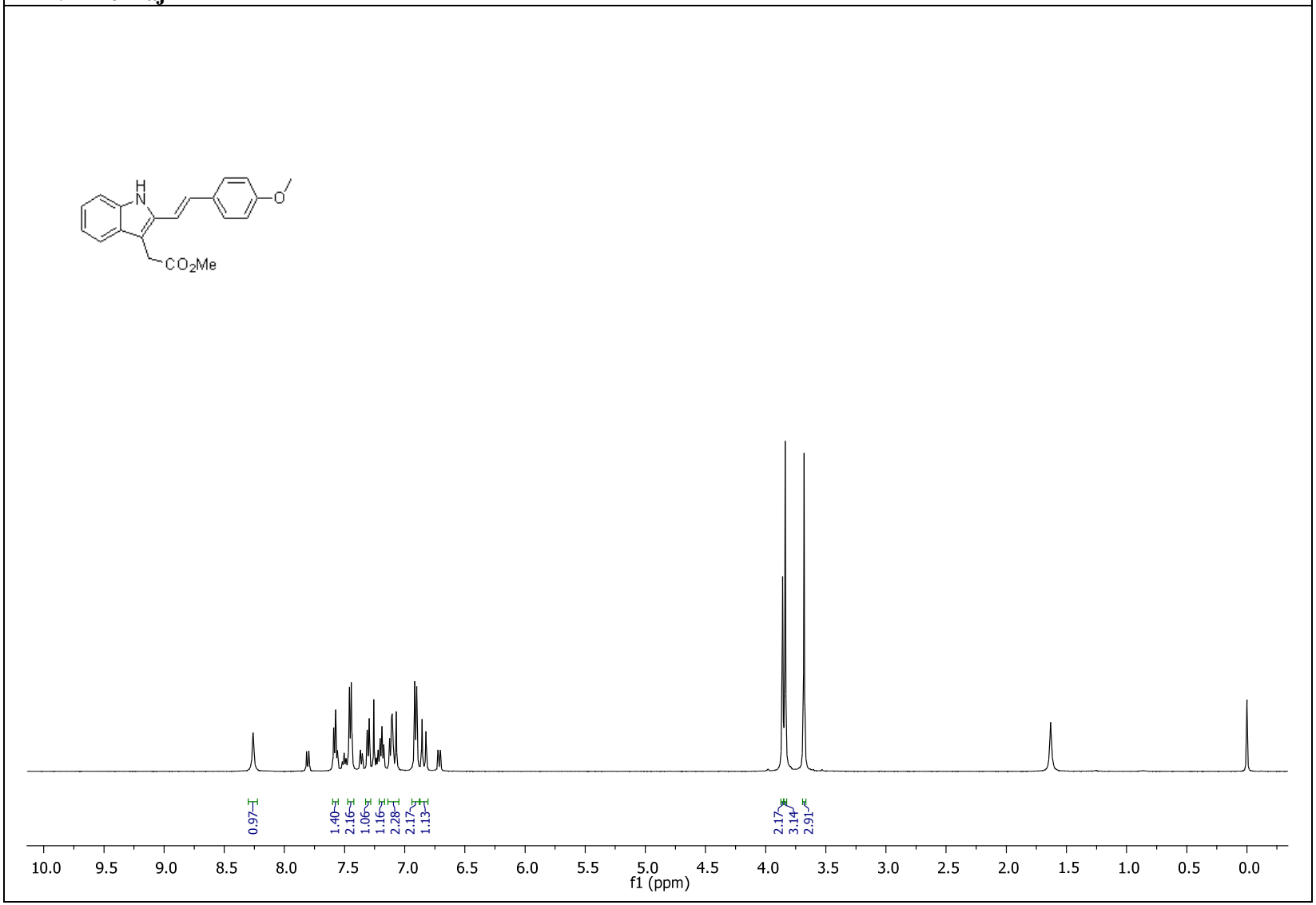
^{1}H NMR of 1ai


H
N
Cl
CO2Me
0.85
1.07
1.98
3.69
1.40
1.84
0.98
1.88
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

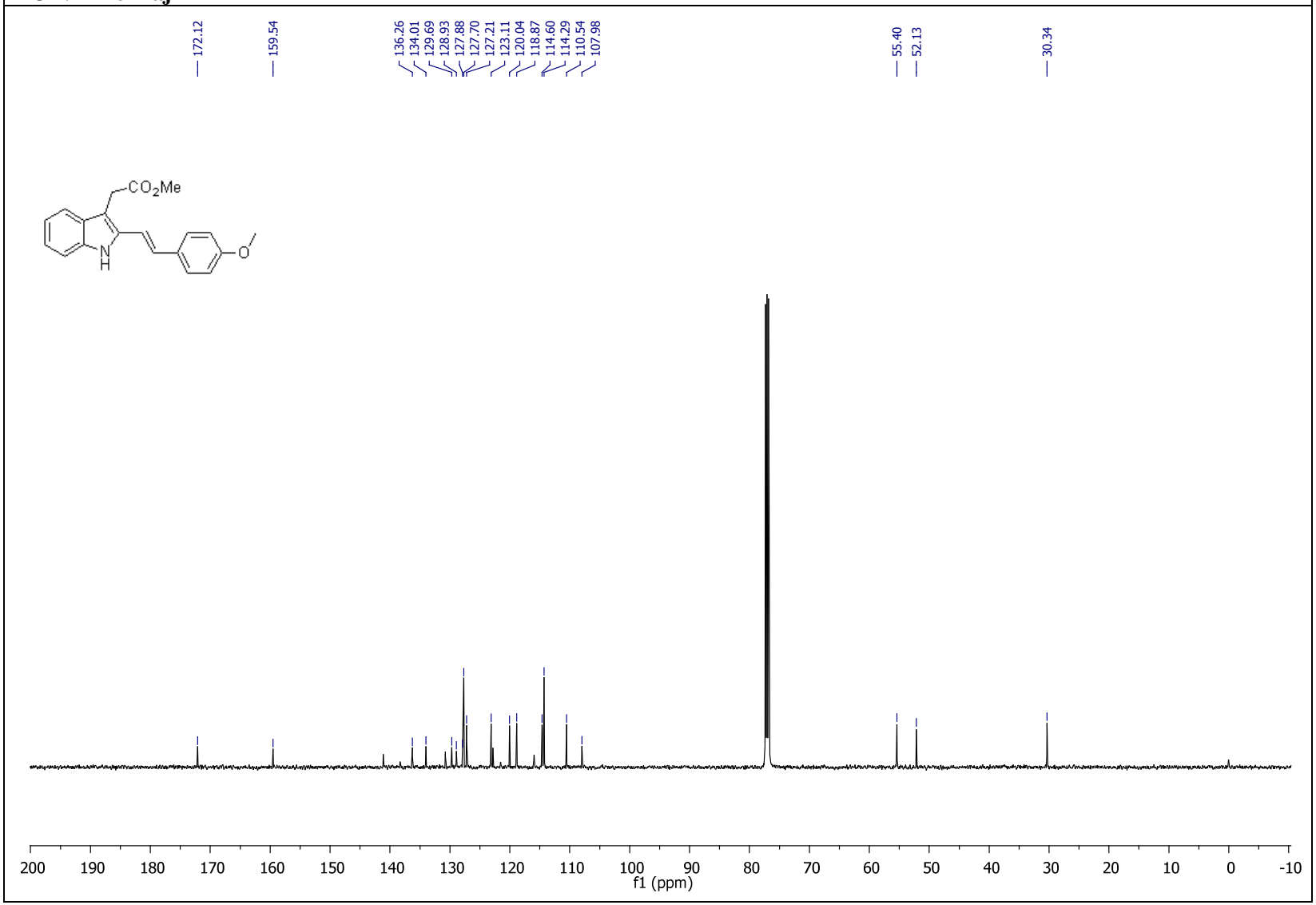
^{13}C NMR of 1ai



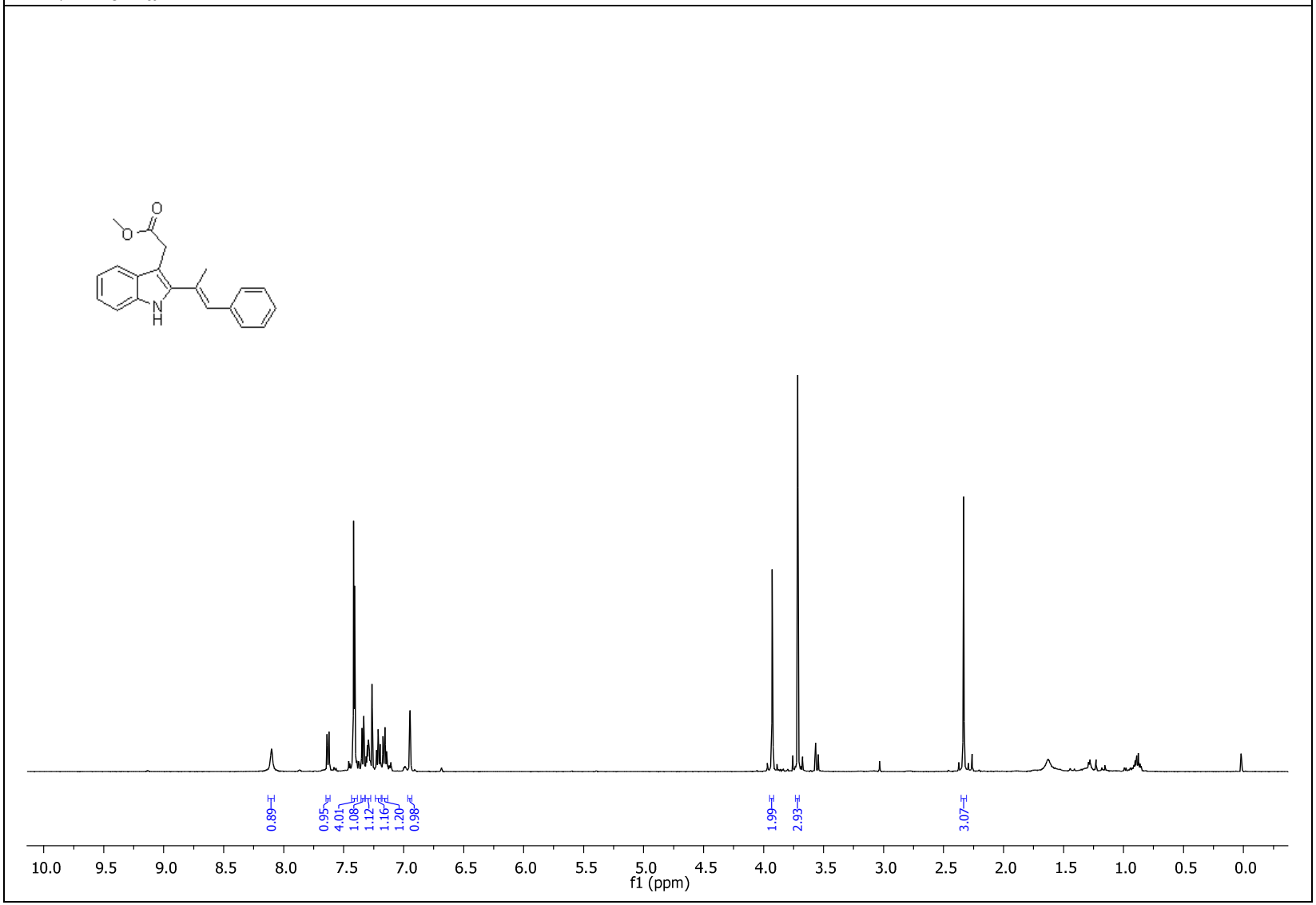
^{1}H NMR of 1aj


H
N
O
CO2Me
0.97
1.40
2.16
1.06
1.16
2.28
2.17
1.13
2.17
3.14
2.91
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

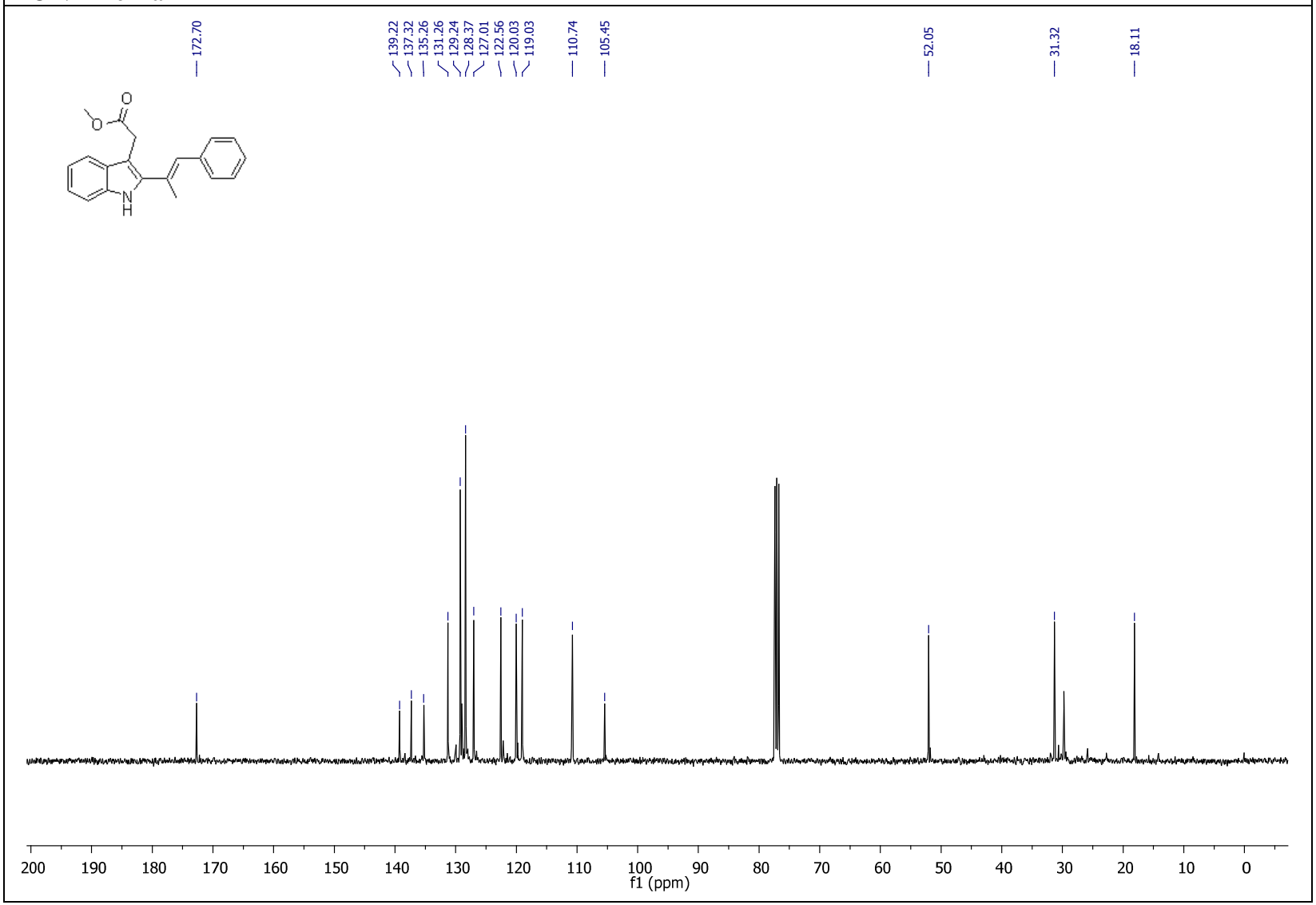
^{13}C NMR of 1aj



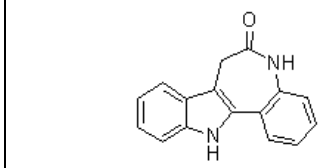
^{1}H NMR of 1ak

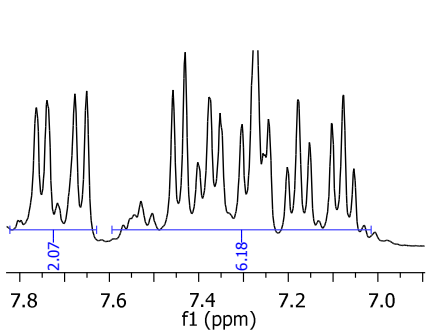

O
O
N
H
0.89
0.95
4.01
1.08
1.12
1.16
1.20
0.98
1.99
2.93
3.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

^{13}C NMR of 1ak



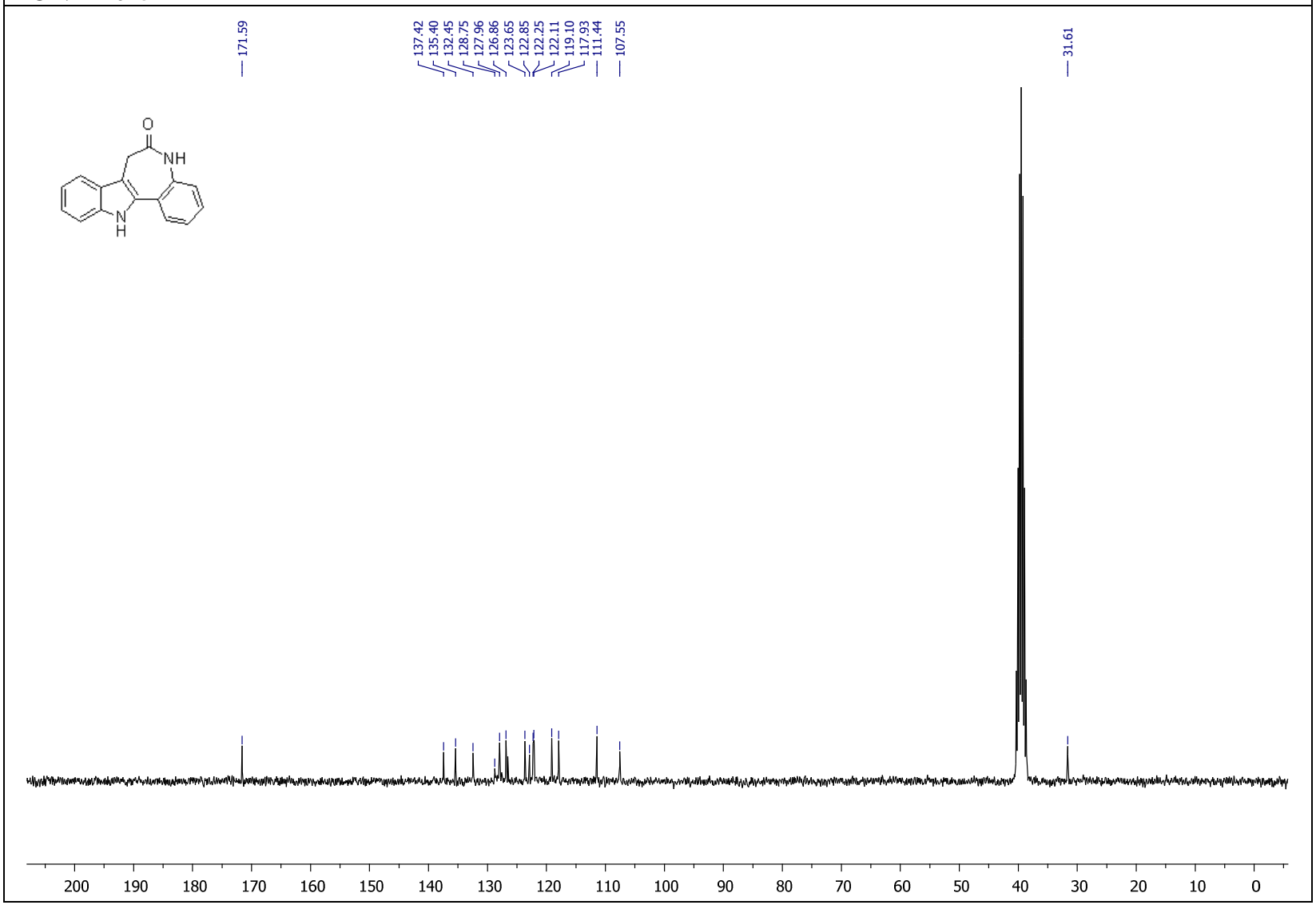
^{1}H NMR of 5


O
NH
N
H

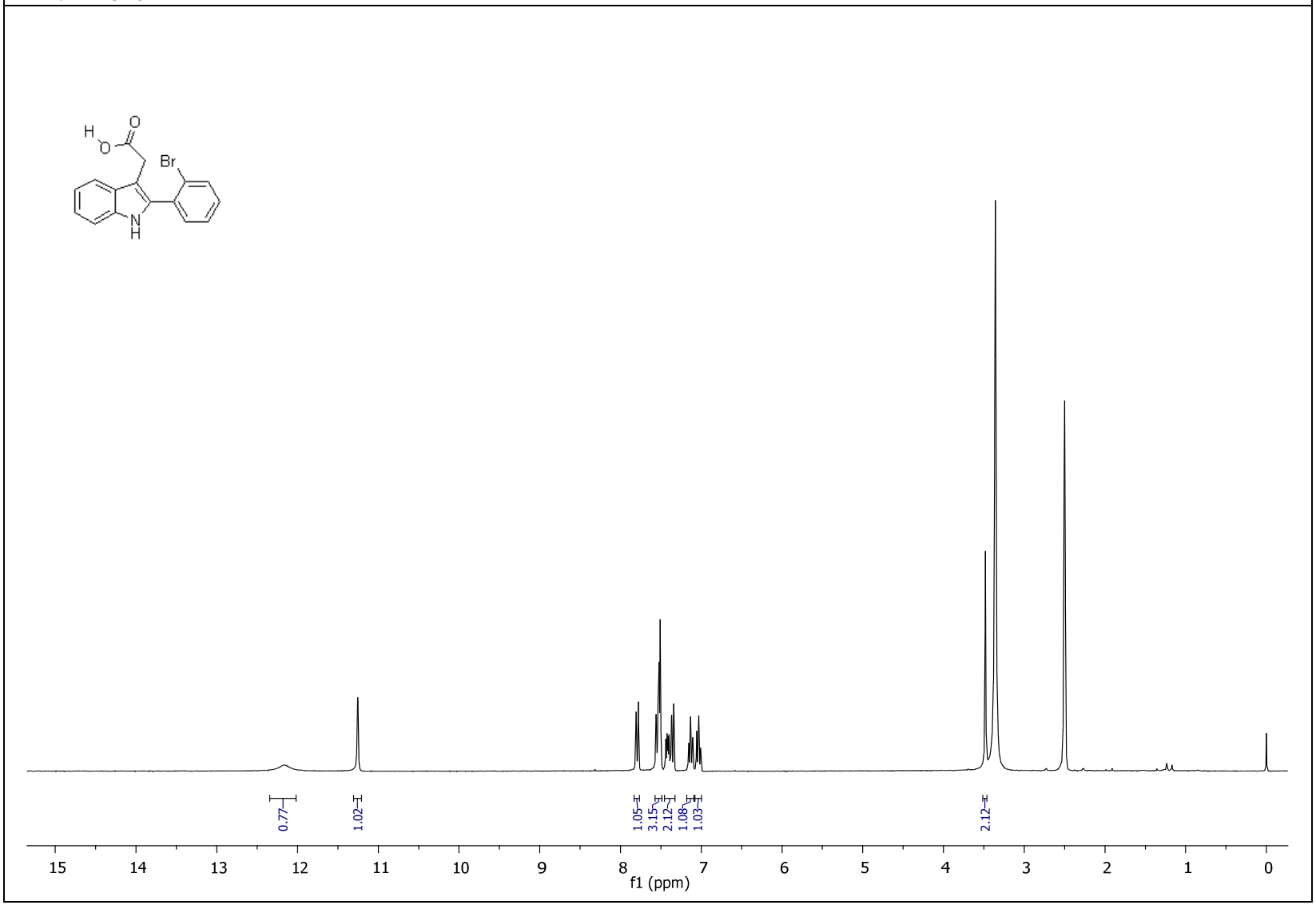

2.07
6.18
7.8
7.6
7.4
7.2
7.0
f1 (ppm)

0.82
0.82
2.07
6.18
1.63
14.0
13.5
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

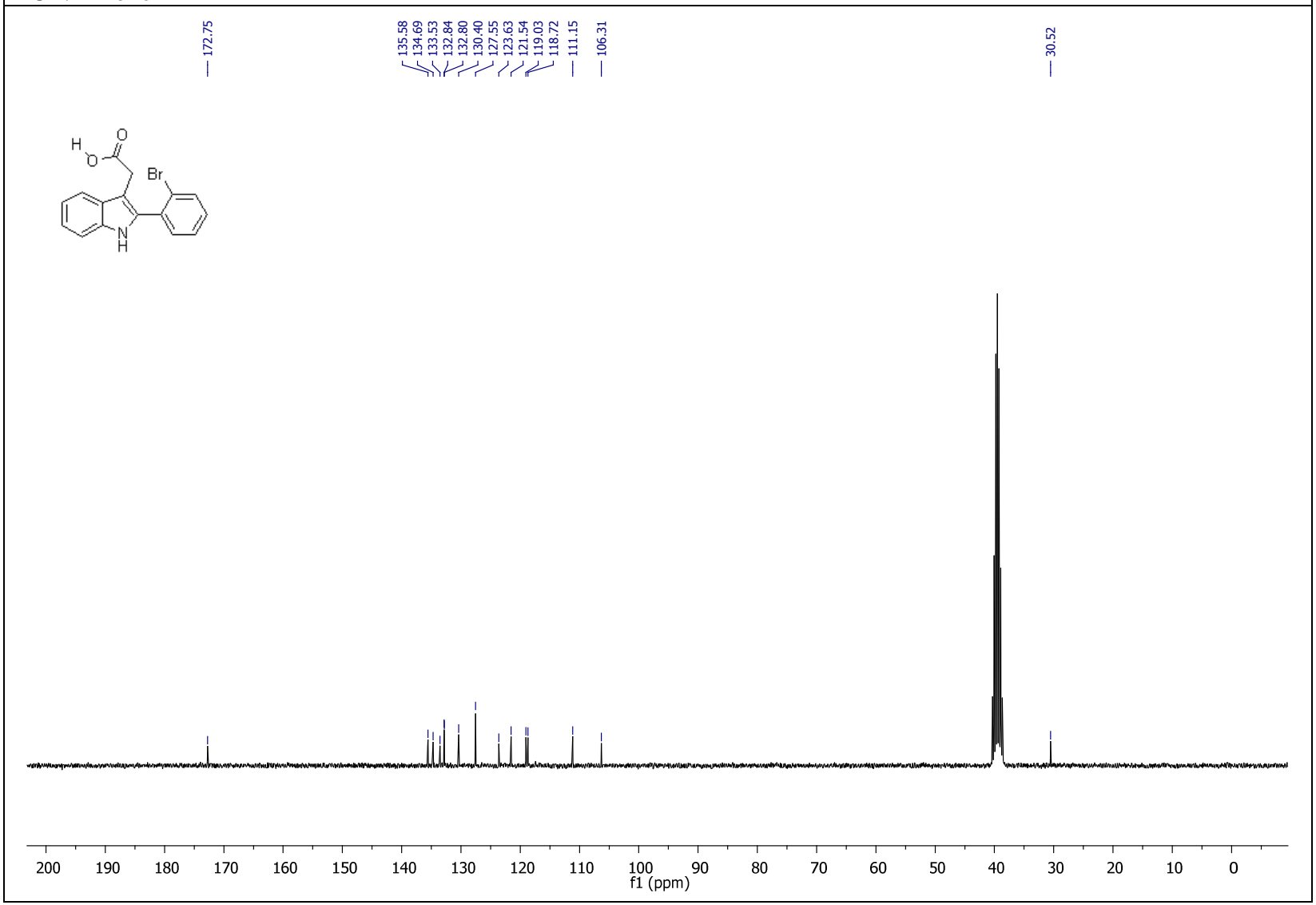
^{13}C NMR of 5


171.59
137.42
135.40
132.45
128.75
127.96
126.86
123.65
122.85
122.25
122.11
119.10
117.93
111.44
107.55
31.61
O
NH
N
H
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{1}H NMR of 6


H
O
O
Br
N
H
0.77
1.02
1.05
3.15
2.12
1.08
1.03
2.12
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

^{13}C NMR of 6


172.75
135.58
134.69
133.53
132.84
132.80
130.40
127.55
123.63
121.54
119.03
118.72
111.15
106.31
30.52
H
O
O
Br
N
H
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)