Supporting Information for

A Visible Light-Promoted C-H Insertion Reaction of Diazoamides with 1,3-Diketones

Selvaraj Hariharan and Sengodagounder Muthusamy*

School of Chemistry, Bharathidasan University, Tiruchirappalli-620 024, India

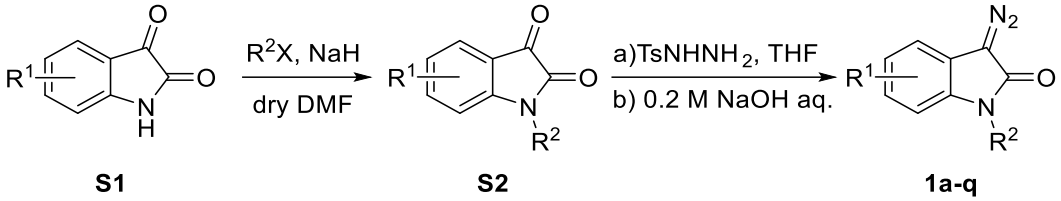
E-mail: muthu@bdu.ac.in

CONTENTS

General Information

Melting points were determined on a capillary melting point apparatus and uncorrected. IR spectra were recorded using the ATR technique on an FT-IR spectrophotometer. All compounds were fully characterized. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at 400 MHz using $CDCl_3$ in ppm (δ) related to tetramethylsilane (δ = 0.00) as an internal standard and are reported as follows: chemical shift (ppm), multiplicity (br = broad, s = singlet, d = doublet, t = triplet, dd = doublet of doublet, m = multiplet, td = triplet of doublet, Abq = AB Quartet) and coupling constant (Hz). Carbon-13 nuclear magnetic resonance $^{13}C\{^1H\}$ NMR spectra were recorded at 101 MHz in $CDCl_3$. Chemical shifts are reported in delta (δ) units, parts per million (ppm) relative to the center of the triplet at 77.7 ppm for $CDCl_3$. Fluorine-19 nuclear magnetic resonance ^{19}F NMR spectra were recorded at 162 MHz in CDCl3. The residual solvent signals were used as a reference and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.7 ppm). High-resolution mass analyses were recorded using ESI mode with Agilent QTOF G6545 spectrometer at 50,000 resolutions. The HPLC analysis of products was performed using ZORBAX column Eclipse XDB-C18, particle size of 5 μm, column inner diameter of 4.6 and length of 150 mm. All solvents were purified by distillation following a standard procedure. Thin layer chromatography (TLC) was performed on silica or alumina plates and components were visualized by observation under iodine/UV light at 254 nm. Flash chromatography was performed on silica gel (200-400 mesh) and Column chromatography was performed on silica gel (100-200 mesh). All the reactions were conducted in oven-dried glassware with magnetic stirring. The starting material was purchased from M/s Aldrich or M/s TCI and used as provided. Blue LEDs (9W), green LEDs (10W), and White CFL (10W) were purchased from a local market and used in this work. The distance between the LED source and reaction mixture is approximately 10 cm and reactions were carried out circularly using four LEDs at ambient temperature. An oil bath is used as a heat source for reflux conditions. An immersion cooler (Julabo FT903) is used as a cooling source for reaction conditions.

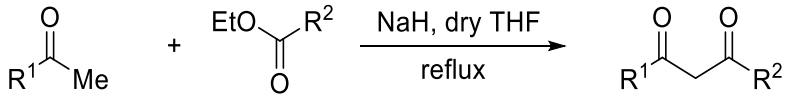
General procedure for the synthesis of diazoamides 1



S1 **S2** **1a-q**

The reaction of NaH (60% dispersion in mineral oil, 12 mmol) was added to a solution of isatin **S1** (10 mmol) in dry DMF (55 mL) at 0 °C under Argon atmosphere then a solution of halogenated reagents (alkyl, aryl halides 12 mmol) in DMF (15 mL) was added. The mixture was stirred for 20 min at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The reaction was quenched by the addition of water, and HCl (5:5 mL). The crude product was suspended in sat. NH_4Cl solution (50 mL) and extracted with EtOAc. Combined organic layers were dried over Na_2SO_4, concentrated, and purified by column chromatography on silica gel with hexanes/ethyl acetate (5:2) as eluent to provide the crude product as an orange solid. Continuously alkyl-protected isatin **S2** (10 mmol) and tosylhydrazine (12 mmol) were dissolved in THF (30 mL). Their action mixture was refluxed for 2 h and then allowed to reach room temperature. A solution of the obtained tosylhydrazone was treated with 0.2M NaOH solution (0.2M, 10mL) at room temperature. The reaction mixture was stirred for approximately 2 h, then neutralized by adding water, diluted with brine, and extracted with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by column chromatography on silica gel with hexanes/ethyl acetate (5:1) as eluent to provide diazoamide **1** as an orange solid.[1]

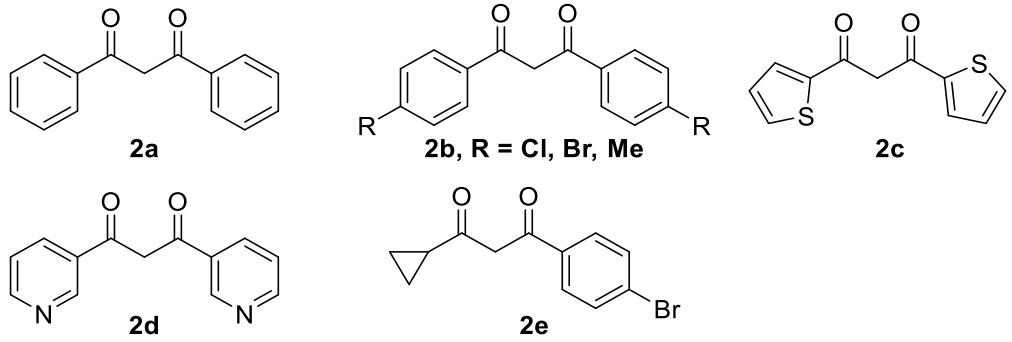
General procedure for the synthesis of 1,3-diketones 2



S3 **S4** **2a-f**

1,3-Diketones **2** were prepared by modified literature procedures.[2] Under an argon atmosphere, a 100 mL round-bottom flask was charged with the corresponding ketone **S3** (5 mmol, 1.0 equiv), methyl benzoate **S4** (7.5 mmol, 1.5 equiv), NaH (10 mmol, 2.0 equiv), and dry THF (0.5 M). The resulting mixture was heated to reflux and stirred for 10 h. Upon completion of the reaction, the mixture was cooled to room temperature and quenched with water (10 mL). The pH was adjusted

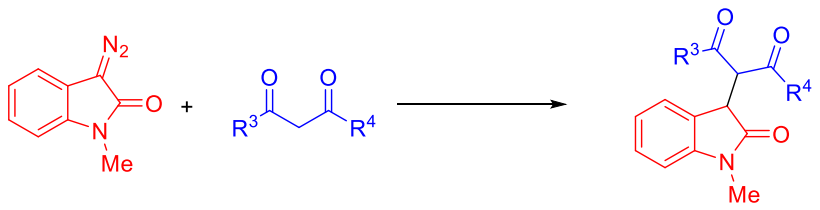
to 2–3 with aqueous HCl, and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with saturated aqueous NaCl (2 × 20 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (hexanes/ethyl acetate, 5:1) to afford the crude 1,3-diketone, which was further purified by recrystallization from MeOH/DCM to yield pure products **2**.



The following figure A shows reactants 1,3-diketones **2** and diazocarbonyl **1** are not involved in the optimized reaction conditions.

Optimization Table for 3a[b]

We investigated different ratios of diazoamide **1a** & 1,3-diketone **2b** substrates, using catalyst or neat conditions.



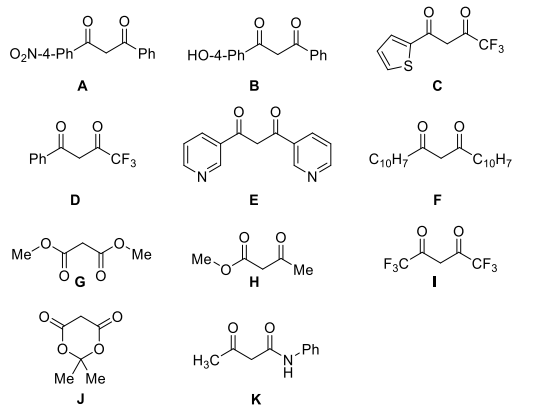
1a (**X** mmol) **2a** (**X** mmol) **3a**

Entry[a]	**1a**(equiv)	**2a**(equiv)	Catalyst	Time (h)	Yield 3%[b]
13[c]	1	1	-	24	65
14[c]	1	0.5	-	24	46
15[c]	1	0.8	-	24	40
16[c]	1	2	-	24	80
17[c]	1	3	-	24	84
18[c]	**1**	**1.5**	**-**	**24**	**85**
19[c]	1	1.5	-	12	60
20[e]	1	1.5	-	24	nr[d]
21	1	1.5	Eosin-Y	24	62
22	1	1.5	Rose Bengal	24	54
23	1	1.5	Rhodamine B	24	59
24	1	1.5	$Sc(OTf)_3$	24	nr[c]
25	1	1.5	AgOTf	24	nr[c]
26	1	1.5	BF_3OEt	24	nr[c]
27	1	1.5	(±)-CAS	24	nr[c]
28	1	1.5	TfOH	24	nr[c]
29	1	1.5	$Rh(OAc)_4$	24	nr[c]

[a]Reaction conditions: diazoamides **1a** (0.3 mmol, 1 equiv) and 1,3-diketones **2a** (0.4 mmol, 1.5 equiv) in DCM (5 mL), open-air atmosphere, room temperature, [b]isolated product, [c]blue LED, [d]no reaction, [e]reflux condition, .

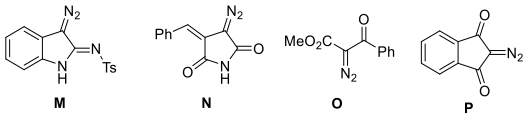
Unsuccessful reactants 1 & 2 under standard conditions.

1,3-diketone compounds



Active Methylene compounds

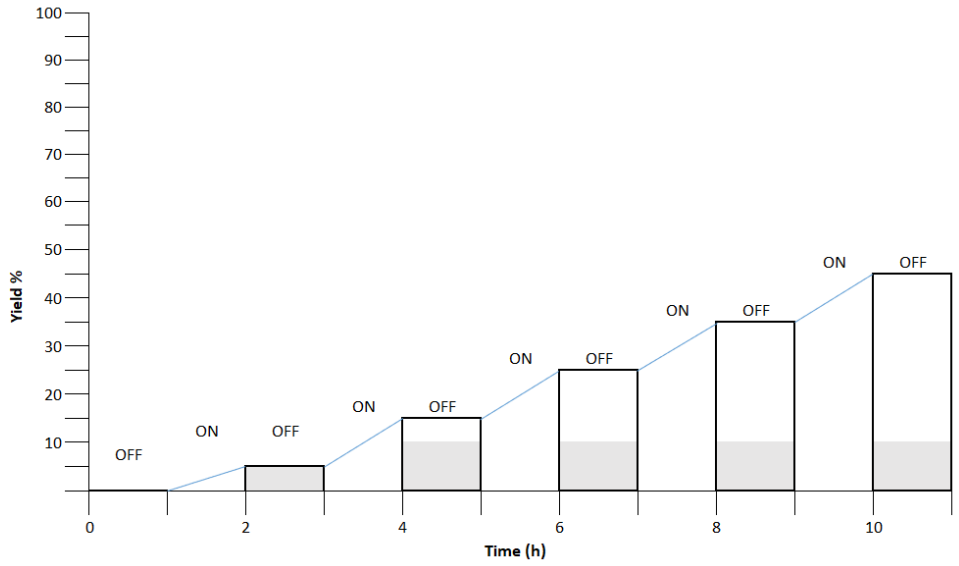
diazo compounds



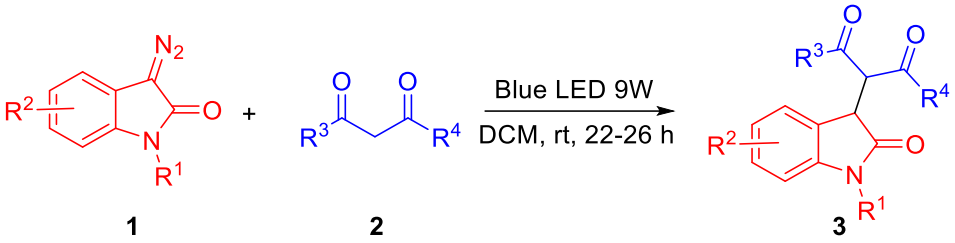
Reaction setup:

The procedures for light-on/off experiments.

To a mixture of **1a** (0.3 mmol), **2a** (0.4 mmol) in 2 mL DCM. The reaction mixture was stirred separately and irradiated with 9 W blue LEDs at room temperature for 2 h, 4 h, 6 h, 8 h, and 10 h. The desired product **3a** was isolated in 5%, 14%, 27%, 38% and 48%, respectively. Additionally, the reaction mixture was continuously stirred in the dark for 1h product not formed. Continuously, the reaction mixture was stirred and irradiated by 9 W Blue LEDs at room temperature for 2 h, then the reaction mixture was continuously stirred in the dark for 1 h, the corresponding product was also obtained in 5.4% yield. Additionally, when the reaction mixture was stirred and irradiated by 9 W blue LEDs at room temperature for 4 h, then the reaction mixture was continuously stirred in the dark for 1 h, the corresponding product was obtained in 14.1% yield. Additionally, when the reaction mixture was stirred and irradiated by 9 W blue LEDs at room temperature for 6h, then the reaction mixture was continuously stirred in the dark for 1 h, the corresponding product **3a** was still obtained in 27.2% yield. Additionally, when the reaction mixture was stirred and irradiated by 9 W blue LEDs at room temperature for 8 h, then the reaction mixture was continuously stirred in the dark for 1 h, the corresponding product **3a** was still obtained in 38.1% yield. Additionally, when the reaction mixture was stirred and irradiated by 9 W blue LEDs at room temperature for 10h, then the reaction mixture was continuously stirred in the dark for 1 h, the corresponding product **3a** was still obtained in 48% yield. The above results suggested that the continuous visible-light irradiation is necessary for promoting this transformation.

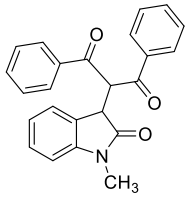


General Experiment Procedure A for the synthesis of 3-substituted-2-oxindoles 3



1 **2** **3**

A mixture of diazoamide **1** (0.3 mmol) and 1,3-diketone **2** (0.4 mmol) in dichloromethane (5 mL) was irradiated with blue LEDs (4 lamps) at room temperature (~30 °C) for 22–26 h. The reaction was monitored by TLC. Upon completion, the solvent was removed under reduced pressure, and the resulting residue was purified by flash chromatography on silica gel (230–400 mesh) using hexanes/ethyl acetate (1:4, v/v) as the eluent to afford the corresponding products **3**.



3a

2-(1-Methyl-2-oxo-2,3-dihydro-1*H*-indol-3-yl)-1,3-diphenylpropane-1,3-dione (3a)

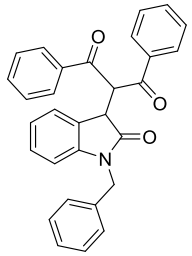
Diazoamide (**1a**, 52 mg, 0.300 mmol) and 1,3-diphenylpropane-1,3-dione (**2a**, 101 mg, 0.450 mmol) were stirred as described in general procedure **A** to furnish product **3a** (95 mg, 85%) as a colorless solid; **R_f** = 0.25 (EtOAc/hexanes = 1:4, v/v); **mp** 124-125°C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.07 (d, *J* = 7.4 Hz, 2H), 7.67-7.47 (m, 6H), 7.37-7.20 (m, 4H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.64 (d, *J* = 7.6 Hz, 1H), 6.13 (d, *J* = 3 Hz, 1H), 4.38 (d, *J* = 2.7 Hz, 1H), 2.99 (s, 3H) ppm;

^{13}C NMR ($CDCl_3$, 101 MHz) δ = 195.6, 195.5, 176.1, 144.1, 136.0, 135.8, 133.7, 133.4, 129.0, 128.6, 128.5, 128.4, 128.3, 126.0, 125.5, 122.7, 107.8, 57.4, 44.7, 26.2 ppm;

HRMS (ESI) m/z of 3a:$[M + Na]^+$ Calculated for $C_{24}H_{19}NO_3Na^+$ 392.1263, found 392.1269;

IR (neat): ν_{max} 3058, 2928, 1688, 1606, 1465, 1343, 1264, 1209, 964, 855, 741, 690 cm^{-1}.



3b

2-(1-Benzyl-2-oxo-2,3-dihydro-1*H*-indol-3-yl)-1,3-diphenylpropane-1,3-dione (3b)

Diazoamide (**1b**, 75 mg, 0.300 mmol) and 1,3-diphenylpropane-1,3-dione (**2a**, 101 mg, 0.451 mmol) were stirred as described in general procedure **A** to furnish product **3b** (113 mg, 84%) as a colorless solid; R_f = 0.25 (EtOAc/hexanes = 1:4, v/v); **mp** 152-154 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.93 (d, *J* = 7.6 Hz, 2H), 7.68 (d, *J* = 7.6 Hz, 2H), 7.43-7.30 (m, 4H), 7.25-7.21 (m, 2H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.08-7.06, (m, 3H), 6.95-6.93 (m, 3H) 6.85-6.81 (m, 1H), 6.42 (d, *J* = 7.6 Hz, 1H), 6.1 (d, *J* = 3.1 Hz, 1H), 4.63 (s, 2H), 4.39 (d, *J* = 2.8 Hz, 1H) ppm;

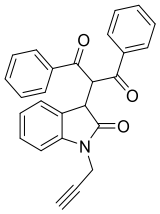
^{13}C NMR ($CDCl_3$, 101 MHz) δ = 195.4, 195.0, 176.1, 143.2, 135.8, 135.7, 135.5, 133.79, 133.75, 129.0, 128.8, 128.76, 128.70, 128.2, 127.5, 127.0, 126.2, 125.5, 122.7, 109.0, 56.9, 45.04, 44.02 ppm;

HRMS (ESI) m/z of 3b:$[M + H]^+$ Calculated for $C_{30}H_{24}NO_3^+$ 446.1756, found 446.1752;

IR (neat): ν_{max} 3057, 1700, 1607, 1457, 1361, 1265, 1214, 734, 698 cm^{-1}.

Experimental procedure for a gram-scale experiment for product 3b

A solution of *N*-benzyl diazoamide (**1**, 1 g, 4.011 mmol) and 1,3-diphenylpropane-1,3-dione (**2**, 1.349 g, 6.017 mmol) in DCM (15 mL) was stirred for 29 h as described in general procedure **A** to obtain product **3b** (1.41 g, 79%).



3c

2-[2-Oxo-1-(prop-2-yn-1-yl)-2,3-dihydro-1*H*-indol-3-yl]-1,3-diphenylpropane-1,3-dione (3c)

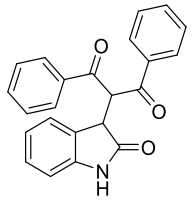
Diazoamide (**1c**, 61 mg, 0.309 mmol) and 1,3-diphenylpropane-1,3-dione (**2a**, 104 mg, 0.464 mmol) were stirred as described in general procedure **A** to afford product **3c** (102 mg, 84%) as a colorless solid; $\mathbf{R_f}$ = 0.26 (EtOAc/hexanes = 1:4, v/v); **mp** 140-142 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.06 (d, J = 7.6 Hz, 2H), 7.70 (d, J = 7.2 Hz, 2H), 7.63-7.60 (m, 1H), 7.53-7.49 (m, 3H), 7.39-7.35 (m, 2H), 7.31-7.25 (m, 2H), 7.0 (t, J = 7.6 Hz, 1H) 6.91 (d, J = 7.6 Hz, 1H), 6.13 (d, J = 3.2 Hz, 1H), 4.50- 4.45 (m, 2H), 4.19 (dd, J_1 = 17.6 Hz J_2 = 2.4Hz, 1H), 2.16 (t, J = 2.4 Hz, 1H) ppm;

^{13}C NMR ($CDCl_3$, 101 MHz) δ = 195.3, 195.2, 175.2, 142.2, 135.9, 135.7, 133.7, 133.6, 129.0, 128.68, 128.65, 128.4, 128.3, 126.1, 125.4, 123.1, 108.8, 72.2, 57.1, 44.7, 29.3 ppm;

HRMS (ESI) m/z of 3c:[M + Na]$^+$ Calculated for $C_{26}H_{19}NO_3Na^+$ 394.1437, found 394.1437;

IR (neat): ν_{max} 3284, 1702, 1607, 1471, 1356, 1215, 754, 684 cm^{-1}.



3d

2-(2-oxo-2,3-dihydro-1*H*-indol-3-yl)-1,3-diphenylpropane-1,3-dione (3d)

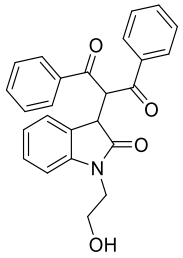
Diazoamide (**1d**, 49 mg, 0.307 mmol) and 1,3-diphenylpropane-1,3-dione (**2a**, 103 mg, 0.461 mmol) were stirred as described in general procedure **A** to afford product **3d** (44 mg, 40%) as a colorless solid; **Rf** = 0.19 (EtOAc/hexanes = 1:4, v/v); **mp** 148-150 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.09 (d, J = 7.6 Hz, 2H), 7.80-7.77 (m, 3H), 7.64-7.63 (m, 1H), 7.56-7.52 (m, 3H), 7.42-7.38 (m, 2H), 7.23-7.18 (m, 2H), 7.03-6.99 (m, 1H) 6.77 (d, J = 7.6 Hz, 1H), 6.14 (d, J = 3.6 Hz, 1H), 4.43 (d, J = 3.6 Hz, 1H) ppm;

^{13}C NMR ($CDCl_3$, 101 MHz) δ = 195.3, 194.9, 177.6, 141.0, 135.8, 135.6, 133.8, 133.6, 129.1, 128.7, 128.6, 128.5, 128.2, 126.2, 126.1, 122.7, 109.4, 56.8, 45.2 ppm;

HRMS (ESI) m/z of 3d:[M + Na]$^+$ Calculated for $C_{23}H_{17}NO_3Na^+$ 378.1106, found 378.1111;

IR (neat): ν_{max} 3284, 1702, 1607, 1471, 1356, 1215, 754, 684 cm^{-1}.



3f

2-[1-(2-hydroxyethyl)-2-oxo-2,3-dihydro-1*H*-indol-3-yl-1,3-diphenylpropane-1,3-dione (3f)

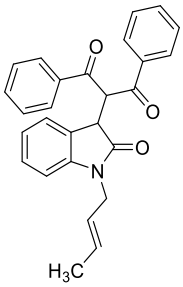
Diazoamide (**1e**, 62 mg, 0.305 mmol) and 1,3-diphenylpropane-1,3-dione (**2a**, 102 mg, 0.457 mmol) were stirred as described in general procedure **A** to afford product **3f** (120 mg, 82%) as a colorless solid; **Rf** = 0.16 (EtOAc/hexanes = 1:4, v/v); **mp** 130-132 °C.

^{1}H NMR (CDCl$_3$, 400 MHz) δ = 8.12 (d, *J* = 7.4 Hz, 2H), 7.76 (d, *J* = 7.4 Hz, 2H), 7.67-7.54 (m, 4H), 7.43-7.39 (m, 2H), 7.31-7.19 (m, 2H), 7.05-7.01 (m, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 6.2 (d, *J* = 3.4 Hz, 1H), 4.22 (d, *J* = 3.1 Hz, 1H), 3.95-3.68 (m, 4H), 1.82 (br, 1H, OH) ppm;

^{13}C NMR (CDCl$_3$, 101 MHz) δ = 195.6. 195.4, 176.8, 143.8, 135.9, 135.4, 134.0, 133.6, 129.2, 128.7, 128.5, 128.3, 128.2, 125.6, 125.5, 122.7, 108.5, 60.2, 57.1, 44.6, 43.2 ppm;

HRMS (ESI) m/z of 3f:$[M + H]^+$ Calculated for $C_{25}H_{22}NO_4^+$ 400.1548, found 400.1548;

IR (neat): ν_{max} 3280, 1700, 1603, 1468, 1352, 1211, 750, 680 cm^{-1}.



3g

3-{1-[(2*E*)-but-2-en-1-yl]-2-oxo-2,3-dihydro-1*H*-indol-3-yl}-1,3-diphenylpropane-1,3-dione (3g)

Diazoamide (**1f**, 65 mg, 0.304 mmol) and 1,3-diphenylpropane-1,3-dione (**2a**, 102 mg, 0.457 mmol) were stirred as described in general procedure **A** to afford product **3g** (100 mg, 81%) as a colorless solid; **Rf** = 0.24 (EtOAc/hexanes = 1:4, v/v); **mp** 150-152 °C.

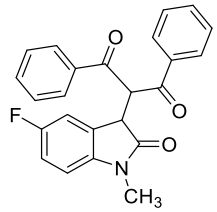
^{1}H NMR (CDCl$_3$, 400 MHz) δ = 7.94 (d, *J* = 7.2 Hz, 2H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.50-7.46 (m, 1H), 7.42-7.35 (m, 3H), 7.28-7.19 (m, 3H), 7.10-7.06 (m, 1H), 6.92-6.88 (m, 1H), 6.56 (d, *J* = 7.6

Hz, 1H), 6.06 (d, *J* = 2.8 Hz, 1H), 5.43-5.36 (m, 1H), 5.04-4.98 (m, 1H), 4.33 (d, *J* = 2.4 Hz, 1H), 4.00- 3.97 (m, 2H), 1.47 (d, *J* = 6.4 Hz, 3H) ppm;

^{13}C NMR ($CDCl_3$, 101 MHz) δ = 195.5, 195.3, 175.7, 143.3, 135.9, 135.7, 133.6, 133.5, 128.9, 128.6, 128.1, 126.3, 125.5, 123.9, 122.6, 108.7, 57.1, 44.8, 41.8, 17.6 ppm;

HRMS (ESI) m/z of 3g: $[M + H]^+$ Calculated for $C_{27}H_{24}NO_3^+$ 410.1756, found 410.1759;

IR (neat): ν_{max} 3285, 1702, 1608, 1472, 1357, 1216, 754, 684 cm^{-1}.



3h

2-(5-Fluoro-1-methyl-2-oxo-2,3-dihydro-1*H*-indol-3-yl)-1,3-diphenylpropane-1,3-dione (3h)

Diazoamide (**1g**, 59 mg, 0.308 mmol) and 1,3-diphenylpropane-1,3-dione (**2a**, 103 mg, 0.462 mmol) were stirred as described in general procedure **A** to afford product **3h** (102 mg, 83%) as a colorless solid; **Rf** = 0.24 (EtOAc/hexanes = 1:4, v/v); **mp** 147-149 °C.

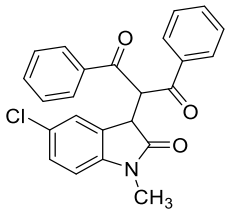
^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.02-8.05 (m, 2H), 7.64-7.67 (m, 2H), 7.57-7.61 (m, 1H), 7.50-7.52 (m, 3H), 7.32-7.40 (m, 2H), 7.03-7.10 (m, 1H), 6.60 (t, *J* = 7.6 Hz, 1H), 6.53-6.56 (m, 1H), 6.10 (d, *J* = 3.0 Hz, 1H), 4.31 (d, *J* = 1.9 Hz, 1H), 3.00 (s, 3H) ppm;

^{13}C NMR ($CDCl_3$, 101 MHz) δ = 195.4, 195.3, 175.7, 160.3, 157.9, 140.0, 135.8 (d, *J* = 3.0 Hz), 135.5, 133.9, 133.6, 129.0, 128.6, 128.5, 128.4, 127.2 (d, *J* = 9.0 Hz), 114.7, 114.5, 114.4 (d, *J* = 18.0 Hz), 108.2 (d, *J* = 8.0 Hz), 57.1, 45.0, 26.3 ppm;

^{19}F NMR ($CDCl_3$, 162 MHz) δ = -119.51 ppm;

HRMS (ESI) m/z of 3h:$[M + H]^+$ Calculated for $C_{24}H_{19}FNO_3^+$ 388.1349, found 388.1344;

IR (neat): ν_{max} 3064, 1700, 1603, 1492, 1456, 1353, 1272, 1216, 691 cm^{-1}.



3i

2-(5-Chloro-1-methyl-2-oxo-2,3-dihydro-1*H*-indol-3-yl)-1,3-diphenylpropane-1,3-dione (3i)

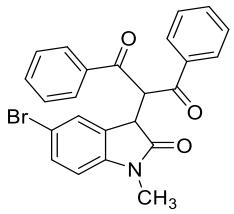
Diazoamide (**1h**, 64 mg, 0.308 mmol) and 1,3-diphenylpropane-1,3-dione (**2a**, 103 mg, 0.462 mmol) were stirred as described in general procedure **A** to obtain product **3i** (100 mg, 80%) as a colorless solid; **Rf** = 0.24 (EtOAc/hexanes = 1:4, v/v); **mp** 148-150 °C.

^{1}H NMR (CDCl$_3$, 400 MHz) δ = 8.03-8.01 (m, 2H), 7.66-7.45 (m, 6H), 7.35-7.14 (m, 4H), 6.54 (d, *J* = 8.3 Hz, 1H), 6.09 (d, *J* = 3.0 Hz, 1H), 4.28 (d, *J* = 3.0 Hz, 1H), 2.95(s, 3H) ppm;

^{13}C NMR (CDCl$_3$, 101 MHz) δ = 195.3, 195.2, 175.5, 142.7, 135.8, 135.5, 133.9, 133.6, 129.1, 128.68, 128.62, 128.4, 128.2, 128.0, 127.2, 126.4, 108.7, 57.1, 44.8, 26.3 ppm;

HRMS (ESI) m/z of 3i:[M + Na]$^+$ Calculated for $C_{24}H_{18}ClNO_3Na^+$ 426.0873, found 426.0872;

IR (neat): ν_{max} 3063, 1695, 1603, 1487, 1450, 1345, 1265, 1210, 808, 730, 690 cm^{-1}.



3j

2-(5-Bromo-1-methyl-2-oxo-2,3-dihydro-1*H*-indol-3-yl)-1,3-diphenylpropane-1,3-dione (3j)

Diazoamide (**1i**, 77 mg, 0.305 mmol) and 1,3-diphenylpropane-1,3-dione (**2a**, 102 mg, 0.458 mmol) were stirred as described in general procedure **A** to obtain product **3j** (116 mg, 84%) as a colorless solid; **Rf** = 0.24 (EtOAc/hexanes = 1:4, v/v); **mp** 138-140 °C.

^{1}H NMR (CDCl$_3$, 400 MHz) δ = 8.03 (d, *J* = 7.48 Hz, 2H), 7.65 (d, *J* = 7.4 Hz, 2H), 7.62-7.58 (m, 1H), 7.52-7.47 (m, 3H), 7.38-7.32 (m, 4H), 6.51 (d, *J* = 8 Hz, 1H), 6.08 (d, *J* = 2.9 Hz, 1H), 4.3 (d, *J* = 2.48 Hz, 1H), 2.96 (s, 3H), ppm;

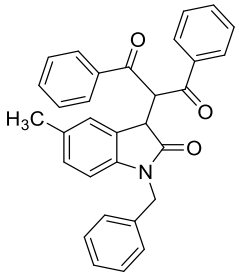
^{13}C NMR (CDCl$_3$, 101 MHz) δ = 195.3, 195.2, 175.5, 143.1, 135.8, 135.5, 133.9, 133.6, 131.2, 129.1, 129.0, 128.69, 128.61, 128.4, 127.6, 115.4, 109.1, 57.2, 44.7, 26.3 ppm;

HRMS (ESI) m/z of 3j:[M + Na]$^+$ Calculated for $C_{24}H_{18}BrNO_3Na^+$ 470.0368, found 470.0366;

IR (neat): ν_{max} 3063, 1695, 1603, 1487, 1450, 1345, 1265, 1210, 1139, 910, 730, 690 cm^{-1}.

Experimental procedure for a gram-scale experiment for product 3j

A solution of 5-Bromo-*N*-methyl diazoamide (**1i**, 1 g, 3.967 mmol) and 1,3-diphenylpropane-1,3-dione (**2**, 1.335 g, 5.950 mmol) in DCM (15 mL) was stirred for 29h as described in general procedure **A** to obtain product **3j** (1.37 g, 81%).



3k

2-(5-methyl-1-Benzyl-2-oxo-2,3-dihydro-1*H*-indol-3-yl)-1,3-diphenylpropane-1,3-dione (3k)

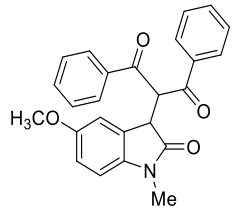
Diazoamide (**1j**, 79 mg, 0.349 mmol) and 1,3-diphenylpropane-1,3-dione (**2a**, 100 mg, 0.524 mmol) were stirred as described in general procedure **A** to furnish product **3k** (115 mg, 83%) as a yellow color liquid; **Rf** = 0.24 (EtOAc/hexanes = 1:4, v/v);

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.11-8.03 (m, 2H), 7.70 (d, *J* = 7.5 Hz, 2H), 7.61-7.26 (m, 10H), 7.20-6.86 (m, 3H), 6.54-6.40 (m, 1H), 6.21-6.19 (m, 1H), 4.75-4.72 (m, 2H), 4.51-4.48 (m, 1H), 2.25 (s, 3H) ppm;

^{13}C NMR ($CDCl_3$, 101 MHz) δ = 195.5, 195.0, 176.1, 143.2, 140.8, 135.9, 135.8, 135.7, 135.5, 135.4, 133.7, 133.6, 132.3, 130.2, 129.4, 129.0, 128.7, 128.5, 128.4, 128.1, 127.5, 127.4, 127.0, 126.2, 125.5, 122.8, 109.0, 108.7, 108.8, 45.08, 44.03, 21.1 ppm;

HRMS (ESI) m/z of 3k:$[M + H]^+$ Calculated for $C_{31}H_{26}NO_3^+$ 460.1913, found 460.1916;

IR (neat): ν_{max} 3062, 1702, 1606, 1494, 1451, 1357, 1278, 1227, 741, 693 cm^{-1}.



3l

2-(5-methoxy-1-methyl-2-oxo-2,3-dihydro-1*H*-indol-3-yl)-1,3-diphenylpropane-1,3-dione (3l)

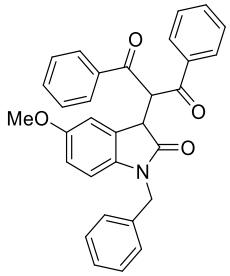
Diazoamide (**1k**, 57 mg, 0.304 mmol) and 1,3-diphenylpropane-1,3-dione (**2a**, 102 mg, 0.456 mmol) were stirred as described in general procedure **A** to furnish product **3l** (103 mg, 84%) as a colorless solid; **Rf** = 0.26 (EtOAc/hexanes = 1:4, v/v); **mp** 139-141 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.03 (d, *J* = 7.5 Hz, 2H), 7.64-7.45 (m, 6H), 7.34-7.31 (m, 2H), 6.89 (s, 1H), 6.73-6.71 (m, 1H), 6.50 (d, *J* = 8.48 Hz, 1H), 6.08 (d, *J* = 2.92 Hz, 1H), 4.33 (d, *J* = 1.88 Hz, 1H), 3.73 (s, 3H), 2.93 (s, 3H) ppm;

^{13}C NMR (CDCl$_3$, 101 MHz) δ =195.6, 195.5, 175.8, 155.9, 137.6, 136.0, 135.8, 133.7, 133.4, 129.0, 128.6, 128.4, 126.7, 113.3, 113.0, 108.1, 57.4, 55.8, 45.1, 26.3 ppm;

HRMS (ESI) m/z of 3l:[M + H]$^+$ Calculated for $C_{25}H_{22}NO_4^+$ 422.1398, found 422.1382;

IR (neat): ν_{max} 3062, 1699, 1606, 1494, 1451, 1355, 1278, 1225, 741, 693 cm^{-1}.



3m

2-[5-methoxy-2-oxo-1-benzyl-2,3-dihydro-1*H*-indol-3-yl]-1-phenylbutane-1,3-dione (3m)

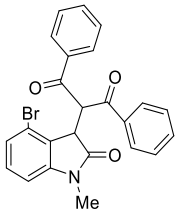
Diazoamide (**1l**, 84 mg, 0.308 mmol) and 1,3-diphenylpropane-1,3-dione (**2a**, 101 mg, 0.451 mmol) were stirred as described in general procedure **A** to afford product **3m** (117 mg, 81%) as a colorless solid; **Rf** = 0.26 (EtOAc/hexanes = 1:4, v/v); **mp** 140-142 °C.

^{1}H NMR (CDCl$_3$, 400 MHz) δ = 8.10 (d, J = 7.2 Hz, 2H), 7.86 (d, J = 7.2 Hz, 2H), 7.62-7.49 (m, 3H), 7.44-7.40 (m, 2H), 7.25-7.24 (m, 4H), 7.09-7.08 (m, 2H), 6.99-6.98 (m, 1H), 6.66 (dd, J_1 = 8.4 Hz J_2 = 2.4 Hz, 1H), 6.46 (d, J = 8.4 Hz, 1H), 6.25 (d, J = 3.2 Hz, 1H), 4.77 (s, 2H), 4.54 (d, J = 2.4 Hz, 1H), 3.75 (s, 3H) ppm;

^{13}C NMR (CDCl$_3$, 101 MHz) δ = 195.4, 194.9, 175.7, 155.9, 136.7, 135.8, 135.7, 135.5, 133.8, 133.7, 129.0, 128.8, 128.73, 128.70, 127.4, 127.0, 126.8, 113.2, 113.1, 109.3, 56.9, 55.7, 45.4, 44.0 ppm;

HRMS (ESI) m/z of 3q:[M + Na]$^+$ Calculated for $C_{31}H_{25}NO_4Na^+$ 498.1682, found 498.1699;

IR (neat): ν_{max} 3284, 1702, 1607, 1471, 1356, 1215, 754, 684 cm^{-1}.



3n

2-(4-Bromo-1-methyl-2-oxo-2,3-dihydro-1*H*-indol-3-yl)-1,3-diphenylpropane-1,3-dione (3n)

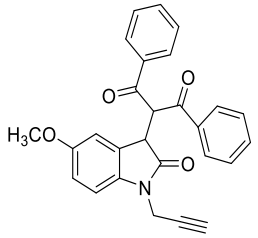
Diazoamide (**1m**, 78 mg, 0.309 mmol) and 1,3-diphenylpropane-1,3-dione (**2a**, 104 mg, 0.464 mmol) were stirred as described in general procedure **A** to obtain product **3n** (116 mg, 83%) as a colorless solid; **Rf** = 0.23 (EtOAc/hexanes = 1:4, v/v); **mp** 138-139 °C.

^{1}H NMR (CDCl$_3$, 400 MHz) δ = 8.22 (d, *J* = 7.5 Hz, 2H), 7.87 (d, *J* = 7.76 Hz, 2H), 7.67-7.54 (m, 4H), 7.44-7.40 (m, 2H), 7.18-7.11 (m, 2H), 6.88 (d, *J* = 3.6 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 4.34 (d, *J* = 3.64 Hz, 1H), 3.29 (s, 3H) ppm;

^{13}C NMR (CDCl$_3$, 101 MHz) δ =196.0, 194.9, 174.3, 147.1, 136.4, 136.0, 133.5, 133.4, 130.2, 129.1, 128.7, 128.5, 128.1, 125.6, 125.5, 118.2, 107.4, 54.8, 45.9, 26.6 ppm;

HRMS (ESI) m/z of 3m:[M + H]$^+$ Calculated for $C_{24}H_{19}BrNO_3^+$ 470.0368, found 470.0366;

IR (neat): ν_{max} 3061, 1701, 1630, 1592, 1482, 1449, 1336, 1275, 1240, 778, 691 cm^{-1}.



3o

2-[5-methoxy-2-oxo-1-(prop-2-yn-1-yl)-2,3-dihydro-1*H*-indol-3-yl]-1-phenylbutane-1,3-dione (3o)

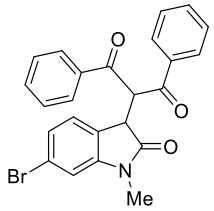
Diazoamide (**1n,** 70 mg, 0.302 mmol) and 1,3-diphenylpropane-1,3-dione (**2a**, 103 mg, 0.462 mmol) were stirred as described in general procedure **A** to afford product **3o** (110 mg, 84%) as a colorless solid; **Rf** = 0.26 (EtOAc/hexanes = 1:4, v/v); **mp** 140-142 °C;

^{1}H NMR (CDCl$_3$, 400 MHz) δ = 8.06 (d, *J* = 7.6 Hz, 2H), 7.72 (d, *J* = 8 Hz, 2H), 7.64-7.60 (m, 1H), 7.53-7.49 (m, 3H), 7.40-7.36 (m, 2H), 6.9 (s, 1H) 6.91 (s, 2H), 6.12 (d, *J* = 2.4 Hz, 1H), 4.47-4.43 (m, 2H), 4.15 (dd, J_1 = 17.6 Hz J_2 = 1.6Hz, 1H), 3.78 (s, 3H), 2.15 (s, 1H) ppm;

^{13}C NMR (CDCl$_3$, 101 MHz) δ = 195.3, 195.2, 174.9, 156.1, 135.9, 135.7, 133.7, 133.5, 129.0, 128.6, 128.5, 126.6, 113.3, 113.0, 109.2, 72.2, 57.2, 55.8, 45.1, 29.4 ppm;

HRMS (ESI) m/z of 3n:[M + H]$^+$ Calculated for $C_{27}H_{22}NO_4^+$ 424.1549, found 424.1556;

IR (neat): ν_{max} 3284, 1702, 1607, 1471, 1356, 1215, 754, 684 cm^{-1}.



3p

2-(6-Bromo-1-methyl-2-oxo-2,3-dihydro-1*H*-indol-3-yl)-1,3-diphenylpropane-1,3-dione (3p)

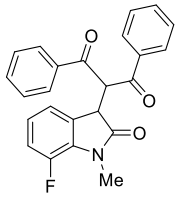
Diazoamide (**1o**, 77 mg, 0.305 mmol) and 1,3-diphenylpropane-1,3-dione (**2a**, 102 mg, 0.458 mmol) were stirred as described in general procedure **A** to obtain product **3p** (112 mg, 81%) as a colorless solid; **Rf** = 0.24 (EtOAc/hexanes = 1:4, v/v); **mp** 138-139 °C.

^{1}H NMR (CDCl$_3$, 400 MHz) δ = 7.87 (d, J = 7.76 Hz, 2H), 7.51 (d, J = 7.8 Hz, 2H), 7.40-7.36 (m, 1H), 7.32-7.26 (m, 3H),7.17-7.14 (m, 2H), 6.97-6.92 (m, 2H), 6.61 (s, 1H), 5.98 (d, J = 3 Hz, 1H), 4.09 (d, J = 2.7 Hz, 1H), 2.76 (s, 3H), ppm;

^{13}C NMR (CDCl$_3$, 101 MHz) δ = 195.36, 195.32, 176.0, 145.4, 135.8, 135.6, 133.8, 133.6, 129.0, 128.65, 128.63, 128.4, 127.4, 125.5, 124.5, 121.9, 111.3, 57.1, 44.5, 26.3 ppm;

HRMS (ESI) m/z of 3o:[M + H]$^+$ Calculated for $C_{24}H_{19}BrNO_3^+$ 448.0548, found 448.0547;

IR (neat): ν_{max} 3064, 1694, 1599, 1533, 1490, 1447, 1370, 1327, 908, 729, 690 cm^{-1}.



3q

2-(7-Fulro-1-methyl-2-oxo-2,3-dihydro-1*H*-indol-3-yl)-1,3-diphenylpropane-1,3-dione (3q)

Diazoamide (**1p**, 59 mg, 0.308 mmol) and 1,3-diphenylpropane-1,3-dione (**2a**, 103 mg, 0.462 mmol) were stirred as described in general procedure **A** to obtain product **3q** (101 mg, 84%) as a colorless solid; **Rf** = 0.24 (EtOAc/hexanes = 1:4, v/v); **mp** 138-139 °C.

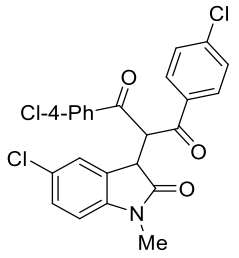
^{1}H NMR (CDCl$_3$, 400 MHz) δ = 8.07 (d, J = 7.6 Hz, 2H), 7.68-7.61 (m, 3H), 7.57-7.50 (m, 3H), 7.42-7.38 (m, 2H), 7.08-7.06 (m, 1H), 6.97-6.94 (m, 2H), 6.13 (d, J = 2.8 Hz, 1H), 4.38 (d, J = 2.4 Hz, 1H), 3.23 (d, J = 2.8 Hz, 3H) ppm;

^{13}C NMR (CDCl$_3$, 101 MHz) δ = 195.5, 195.4, 175.8, 148.5, 146.2, 135.9, 135.6, 133.8, 133.6, 130.8, 130.7, 129.0, 128.65, 128.61, 128.4, 128.3, 123.2, 123.1, 121.95, 121.92, 116.2 (d, J = 19 Hz), 57.5, 44.9(d, J = 2 Hz), 28.7(d, J = 5 Hz) ppm;

^{19}F NMR (CDCl$_3$, 162 MHz) δ = -133.49 (dd, J = 10.1, 5.8 Hz);

HRMS (ESI) m/z of 3p:[M + H]$^+$ Calculated for $C_{24}H_{19}FNO_3^+$ 388.1349, found 388.1344;

IR (neat): ν_{max} 3061, 1701, 1630, 1592, 1482, 1449, 1336, 1275, 1240, 778, 691 cm^{-1}.



3r

2-(5-Chloro-1-methyl-2-oxo-2,3-dihydro-1*H*-indol-3-yl)-1,3-bis(4-chlorophenyl)-propane -1,3-dione (3r)

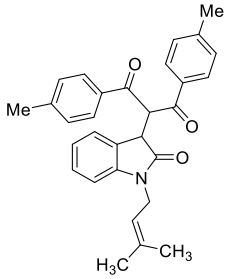
Diazoamide (**1h,** 64 mg, 0.308 mmol) and 4-chloro-1,3-diphenylpropane-1,3-dione (**2b**, 135 mg, 0.462 mmol) were stirred as described in general procedure **A** to furnish product **3r** (103 mg, 70%) as a white crystal; **Rf** = 0.48 (EtOAc/hexanes = 1:4, v/v); **mp** 140-142 °C.

^{1}H NMR (CDCl$_3$, 400 MHz) δ = 7.98 (d, J = 8.8 Hz, 2H), 7.6 (d, J = 8.4 Hz, 2H), 7.5 (d, J = 16.4 Hz, 2H), 7.40-7.37 (m, 2H), 7.25 (d, J = 10.8 Hz, 2H), 6.63 (d, J = 8 Hz, 1H), 5.98 (d, J = 2.8 Hz, 1H), 4.31 (s, 1H), 3.00 (s, 3H) ppm;

^{13}C NMR (CDCl$_3$, 101 MHz) δ = 193.8, 193.7, 175.4, 142.5, 140.6, 140.4, 133.9, 133.8, 130.0, 129.9, 129.59, 129.4, 129.1, 129.0 128.5, 128.3, 126.8, 126.5, 108.8, 57.2, 44.8, 26.4, ppm;

HRMS (ESI) m/z of 3s:[M + H]$^+$ Calculated for $C_{24}H_{17}Cl_3NO_3^+$ 472.0274, found 472.0269;

IR (neat): ν_{max} 3068, 1702, 1589, 1487, 1402, 1351, 1265, 1214, 1095, 815, 736 cm^{-1}.



3s

3-[1-(2-Methylpropyl)-2-oxo-2,3-dihydro-1*H*-indol-3-yl]-propane-1,3-dione (3s)

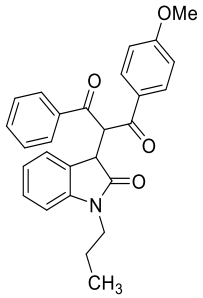
Diazoamide (**1q**, 69 mg, 0.303 mmol) and 1,3-di-p-tolylpropane-1,3-dione (**2c**, 114 mg, 0.455 mmol) were stirred as described in general procedure **A** to furnish product **3s** (113 mg, 82%) as a colorless solid; **Rf** = 0.25 (EtOAc/hexanes = 1:4, v/v); **mp** 138-140 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.95 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.30 (t, 3H), 7.19 (d, *J* = 8.0 Hz, 3H), 7.03-6.99 (m, 1H), 6.65 (d, *J* = 7.76Hz, 1H), 6.09 (d, *J* = 3.16Hz, 1H), 4.75-4.71 (m, 1H), 4.43 (d, *J* = 3 Hz, 1H), 4.21-4.18 (m, 2H), 2.41 (d, *J* = 14.1 Hz, 6H), 1.79 (s, 3H), 1.68 (s, 3H), ppm;

^{13}C NMR ($CDCl_3$, 101 MHz) δ = 195.0, 194.6, 175.7, 144.4 (*J* = 13 Hz), 143.3, 136.0, 133.5, 133.4, 129.6, 129.3, 128.8, 128.7, 127.9, 126.3, 125.8, 122.5, 118.3, 108.4, 57.0, 45.0, 38.2, 25.5, 21.69, 21.67, 18.1 ppm;

HRMS (ESI) m/z of 3t:$[M + Na]^+$ Calculated for $C_{30}H_{29}NO_3Na^+$ 474.2045, found 474.2046;

IR (neat): ν_{max} 3051, 2920, 1696, 1607, 1465, 1364, 1310, 1270, 1179, 826, 749 cm^{-1}.



3t

1-(4-methoxyphenyl)-2-(2-oxo-1-propylindolin-3-yl)-3-phenylpropane-1,3-dione (3t)

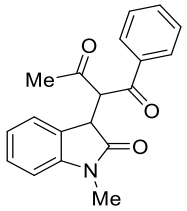
Diazoamide (**1r**, 62 mg, 0.308mmol) and 1-(4-methoxyphenyl)-3-phenylpropane-1,3-dione (**2d**, 101 mg, 0.462 mmol) were stirred as described in general procedure **A** to afford product **3t** (107 mg, 81%) as a colorless liquid; **Rf** = 0.24 (EtOAc/hexanes = 1:4, v/v);

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.94 (d, *J* = 7.6 Hz, 2H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.50-7.47 (m, 1H), 7.42-7.36 (m, 3H), 7.26 (t, *J* = 7.6 Hz, 2H), 6.84 (s, 1H), 6.68-6.62 (m, 1H), 6.47 (d, *J* = 8.4 Hz, 1H), 6.03 (d, *J* = 2.8 Hz, 1H), 4.28 (s, 1H), 3.66 (s, 3H), 3.36-3.34 (m, 2H), 1.38-1.33 (m, 2H), 0.74-0.70 (m, 3H) ppm;

^{13}C NMR ($CDCl_3$, 101 MHz) δ = 195.5, 195.2, 175.5, 155.7, 137.1, 136.0, 135.7, 133.6, 133.5, 129.0, 128.66, 128.63, 128.1, 126.8, 113.3, 113.1, 108.4, 57.1, 55.8, 45.2, 41.8, 20.5, 11.3 ppm;

HRMS (ESI) m/z of 3r:$[M + H]^+$ Calculated for $C_{27}H_{26}NO_4^+$ 428.1862, found 428.1852;

IR (neat): ν_{max} 3284, 1702, 1607, 1471, 1356, 1215, 754, 684 cm^{-1}.



3u

2-(1-methyl-2-oxo-2,3-dihydro-1*H*-indol-3-yl)-1-phenylbutane-1,3-dione (3u)

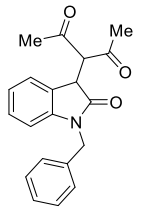
Diazoamide (**1a**, 53 mg, 0.306 mmol) and 1-Phenyl-1,3-butanedione (**2e**, 74 mg, 0.459 mmol) were stirred as described in the general procedure to furnish product **3u** (79 mg, 84%) as a liquid; **Rf** = 0.22 (EtOAc/hexanes = 1:4, v/v);

^{1}H NMR (CDCl$_3$, 400 MHz) δ = 7.93 (d, J = 7.6 Hz, 2H), 7.57-7.53 (m, 1H), 7.46-7.42 (m, 2H), 7.23-719 (m, 1H), 7.14 (d, J = 7.2 Hz, 1H), 6.94-6.90 (m, 1H), 6.78 (d, J = 8 Hz, 1H) 5.18 (d, J = 4 Hz, 1H), 4.06 (d, J = 3.6 Hz, 1H), 3.2 (s, 3H), 2.0 (s, 3H) ppm;

^{13}C NMR (CDCl$_3$, 101 MHz) δ = 202.2, 195.8, 175.9, 144.4, 136.1, 134.0, 129.1, 128.6, 128.5, 125.7, 124.9, 122.6, 108.2, 61.8, 45.0, 30.1, 26.5 ppm;

HRMS (ESI) m/z of 3u:[M + H]$^+$ Calculated for $C_{19}H_{18}NO_3^+$ 308.1278, found 308.1280;

IR (neat): ν_{max} 3057, 1702, 1629, 1594, 1481, 1339, 1261, 1124, 1092, 729, 696 cm^{-1}.



3v

3-(1-Benzyl-2-oxo-2,3-dihydro-1*H*-indol-3-yl)-pentane-2,4-dione (3v)[32]

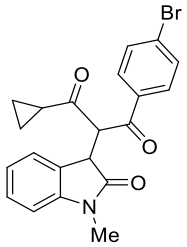
Diazoamide (**1b**, 75 mg, 0.300 mmol) and 2,4-Pentanedione (**2f**, 45 mg, 0.451 mmol) were stirred as described in general procedure **A** to furnish product **3v** (83 mg, 83%) as a white solid; **Rf** = 0.32 (EtOAc/hexanes = 1:4, v/v); **mp** 110-112 °C.

^{1}H NMR (CDCl$_3$, 400 MHz) δ = 7.42 (d, J = 7.3 Hz, 2H), 7.36-7.33 (m, 2H), 7.30-7.20 (m, 2H), 7.18-7.16 (m, 1H), 7.01 (d, J_1 = 7.8 Hz, J_2 = 0.84 Hz, 1H), 6.82 (d, J = 7.84 Hz, 1H) 5.08 (d, J = 15.6 Hz, 1H), 4.94 (d, J = 15.4 Hz, 1H), 3.66 (d, J = 18.5 Hz, 1H), 3.33 (d, J = 18.5 Hz, 1H), 2.10 (s, 3H), 1.90 (s, 3H), ppm;

^{13}C NMR (CDCl$_3$, 101 MHz) δ = 204.2, 199.6, 174.4, 144.1, 135.6, 129.3, 128.9, 127.8, 127.5, 127.4, 123.7, 123.1, 109.8, 63.5, 46.7, 44.6, 30.0, 25.8 ppm;

HRMS (ESI) m/z of 3v:[M + H]$^+$ Calculated for $C_{20}H_{20}NO_3^+$ 322.1443, found 322.1440;

IR (neat): ν_{max} 3058, 1706, 1630, 1594, 1482, 1339, 1261, 1120, 1092, 729, 696 cm^{-1}.



3x

(4-Bromophenyl)-3-cyclopropyl-2-(1-methyl-2-oxo-2,3-dihydro-1*H*-indol-3-yl)propane-1,3-dione (3x)

Diazoamide (**1a**, 53 mg, 0.306 mmol) and 1-(4-bromophenyl)-3-cyclopropylpropane-1,3-dione (**2g**, 122 mg, 0.459 mmol) was stirred as described in general procedure **A** to furnish product **3x** (101 mg, 80%) as a yellow color liquid; **Rf** = 0.29 (EtOAc/hexanes = 1:4, v/v); **mp** 138-140 °C.

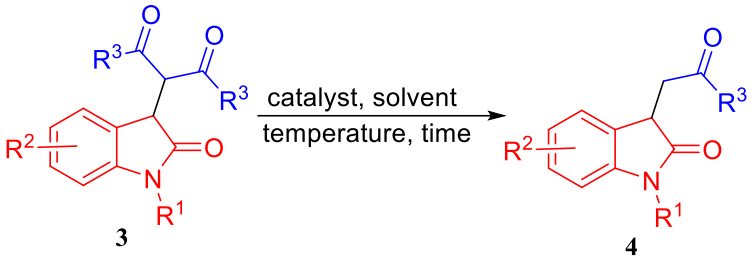
^{1}H NMR (CDCl$_3$, 400 MHz) δ = 7.80 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.41 (td, 1H), 7.24 (d, J = 7.2 Hz, 1H), 7.10-7.021 (m, 2H), 4.18 (d, J = 18.5 Hz, 1H), 3.88 (d, J = 18.5 Hz, 1H), 3.44 (s, 3H), 1.64-1.59 (m, 1H), 1.12-1.02 (m, 2H), 0.88-0.74 (m, 2H), ppm;

^{13}C NMR (CDCl$_3$, 101 MHz) δ = 202.1, 194.9, 174.5, 145.4, 135.0, 131.9, 129.6, 129.3, 128.6, 127.9, 123.8, 123.1, 108.7, 63.6, 42.3, 27.1, 17.1, 12.5, 11.9 ppm;

HRMS (ESI) m/z of 3x:[M + H]$^+$ Calculated for $C_{21}H_{19}BrNO_3^+$ 434.0368, found 434.0367;

IR (neat): ν_{max} 2924, 1718, 1692, 1609, 1585, 1474, 1379, 1349, 1077, 750 cm^{-1}.

General procedure for the synthesis of product 4[b]



3 4

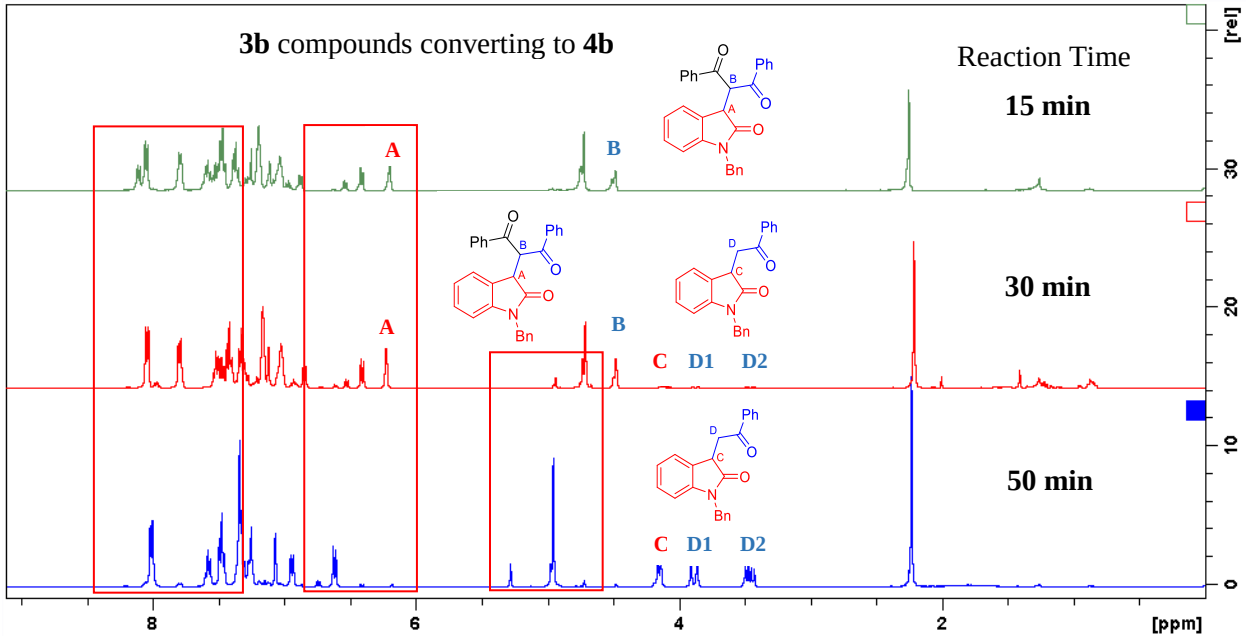
Optimization Table

Entry[a]	Solvent	Catalyst	Temp. (°C)	Time (h)	Yield (**4a**)[b] %
1[c]	**1,2-DCE**	**$Sc(OTf)_3$**	**70 °C**	**1**	**95**
2[c]	1,2-DCE	BF_3OEt	70 °C	1	87
3[c]	1,2-DCE	*P*-TSA	70 °C	1	40
4[c]	DMSO	TfOH	70 °C	2	08
5[c,d]	DMF	TfOH	70 °C	2	15
6[c]	THF	BF_3OEt	70 °C	2	16
7[e]	1,2-DCE	$Sc(OTf)_3$	35 °C	5	52

[a]Reaction conditions: **3** (0.2 mmol), LA (10 mol%), solvent (5 mL), at reflux, for 1 h under an open-air atmosphere. [b]Isolated yield. [c]The reaction was conducted at reflux. [d]The reaction is carried out under an argon atmosphere. [e]The reaction was conducted at room temperature.

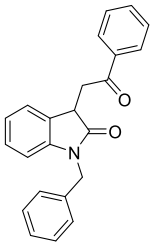
Decarbonylation reaction NMR titration

In a previous study the substituted 1,3-diketone **2** decarbonylated in $Sc(OTf)_3$ mediated reaction, so we herein investigated **3** with $Sc(OTf)_3$ in 1,2-DCE medium reaction in this case of compound **3b** converted **4b** see NMR studies for evidence. Lewis acid is promote retro aldol reaction of **3b** affords product **4b.**



General procedure B for the synthesis of products 4

A solution of compound **3** (0.2 mmol) in 1,2-dichloroethane (5 mL) was treated with $Sc(OTf)_3$ (10 mol%). The mixture was stirred at reflux for 1 h. Upon completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (100-200 mesh) using hexanes/ethyl acetate as the eluent to afford the corresponding product **4**.



4a

1-benzyl-3-(2-oxo-2-phenylethyl)-1,3-dihydro-2*H*-indol-2-one (4a)

Product **3b** (90 mg, 0.202 mmol) was stirred as described in general procedure **B** to furnish product **4a** (66 mg, 95%) as a colorless solid; **Rf** = 0.24 (EtOAc/hexanes = 1:4, v/v); **mp** 162-163 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.0-7.98 (m, 2H), 7.59-7.56 (m, 1H), 7.48-7.45 (m, 2H), 7.37-7.24 (m, 6H) 7.14 (t, J = 7.6 Hz, 1H), 6.95 (t, J = 7.6 Hz, 1H), 6.74 (d, J = 7.6 Hz, 1H), 4.97 (s, 2H), 4.18 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H), 3.89 (dd, J_1 = 18.4 Hz, J_2 = 3.2 Hz, 1H), 3.47 (dd, J_1 = 27.2 Hz, J_2 = 9.0 Hz, 1H) ppm;

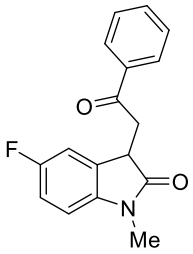
^{13}C NMR (CDCl$_3$, 101 MHz) δ = 196.8, 177.8, 143.4, 136.4, 135.9, 133.4, 129.1, 128.8, 128.7, 128.2, 128.0, 127.6, 127.4, 124.3, 122.5, 109.0, 44.0, 41.2, 40.0 ppm;

HRMS (ESI) m/z of 4a:[M + H]$^+$ Calculated for $C_{23}H_{20}NO_2^+$ 342.1494, found 342.1490;

IR (neat): ν_{max} 3057, 2914, 1702, 1605, 1356, 1216, 744 cm^{-1}.

Experimental procedure for a gram-scale experiment for product 4a

A compound of (**3b**, 1.4g, 3.142 mmol) in 1,2-DCE (15 mL) was stirred for 1h as described in general procedure B to obtain product **4a** (1.01 g, 94%).



4b

5-fluoro-1-methyl-3-(2-oxo-2-phenylethyl)-1,3-dihydro-2*H*-indol-2-one (4b)

Product **3h** (78 mg, 0.201mmol) was stirred as described in general procedure **B** to furnish product **4b** (54 mg, 93%) as a yellow color liquid; **Rf** = 0.24 (EtOAc/hexanes = 1:4, v/v); **mp** 162-163 °C.

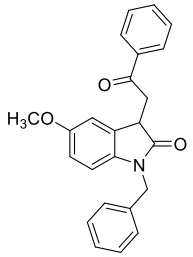
^{1}H NMR (CDCl$_3$, 400 MHz) δ = 7.98-7.96 (m, 2H), 7.60-7.56 (m, 1H), 7.49-7.45 (m, 2H), 7.04-6.9 (m, 2H), 6.78-6.75 (m, 1H), 4.04 (d, J = 8.4 Hz, 1H), 3.87-3.82 (m, 1H) 3.39 (dd, J_1 = 18.4 Hz, J_2 = 9.3 Hz, 1H), 3.25 (s, 3H) ppm;

^{13}C NMR (CDCl$_3$, 101 MHz) δ = 196.7, 177.3, 159.2 (d, J = 239 Hz), 140.3, 136.1, 130.6 (d, J = 8 Hz), 128.7, 128.1, 114.2 (d, J = 9.0 Hz), 112.8 (d, J = 25.0 Hz), 108.3 (d, J = 8.0 Hz), 41.5, 39.9, 26.5 ppm;

^{19}F NMR (CDCl$_3$, 162 MHz) δ = -120.37 ppm;

HRMS (ESI) m/z of 4b:[M + Na]$^+$ Calculated for $C_{17}H_{14}FNO_3Na^+$ 306.0906, found 306.0908;

IR (neat): ν_{max} 3067, 1703, 1607, 1499, 1456, 1353, 1272, 1219, 691 cm^{-1}.



4c

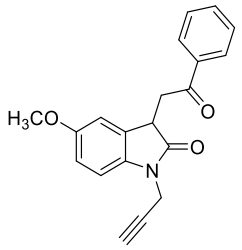
1-benzyl-5-methoxy-3-(2-oxo-2-phenylethyl)-1,3-dihydro-2*H*-indol-2-one (4c)[21c]

Product **3m** (70 mg, 0.147 mmol) was stirred as described in general procedure **B** to furnish product **4d** (54 mg, 96%) as a yellow color liquid; **Rf** = 0.24 (EtOAc/hexanes = 1:4, v/v); **mp** 162-163 °C; **^{1}H NMR ($CDCl_3$, 400 MHz)** δ = 7.98 (d, J = 8.8 Hz, 2H), 7.36-7.24 (m, 7H), 7.14 (t, 1H), 6.96-6.92 (m, 3H), 6.73 (d, J = 7.6 Hz, 1H), 4.97 (s, 2H), 4.16 (d, J = 7.6 Hz, 1H), 3.86 (s, 3H) 3.42 (dd, J_1 = 18 Hz, J_2 = 8.8 Hz, 1H) ppm;

^{13}C NMR ($CDCl_3$, 101 MHz) δ = 195.3, 178.0, 163.7, 143.4, 135.9, 130.5, 129.2, 128.8, 127.9, 127.6, 127.3, 124.5, 122.5, 113.8, 109.03, 55.5, 43.9, 41.3, 39.7 ppm;

HRMS (ESI) m/z of 4c:$[M + H]^+$ Calculated for $C_{24}H_{22}NO_3^+$ 372.1600, found 372.1595;

IR (neat): ν_{max} 3064, 1702, 1605, 1492, 1456, 1353, 1272, 1216, 691 cm^{-1}.



4d

5-methoxy-3-(2-oxo-2-phenylethyl)-1-(prop-2-yn-1-yl)-1,3-dihydro-2*H*-indol-2-one (4d)

Product **3o** (96 mg, 0.201 mmol) was stirred as described in general procedure **B** to furnish product **4d** (72 mg, 94%) as a colorless solid; **Rf** = 0.26 (EtOAc/hexanes = 1:4, v/v); **mp** 162-163 °C.

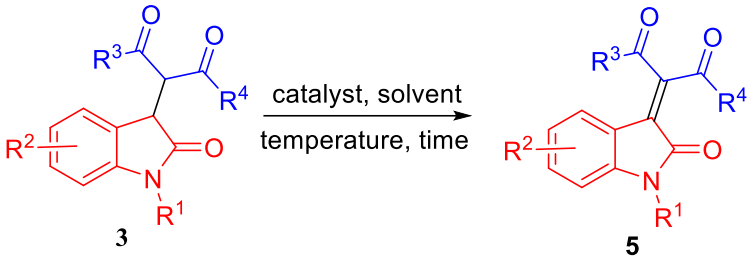
^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.01 (d, J = 7.4 Hz, 2H), 7.64-7.60 (m, 1H), 7.52-7.49 (m, 2H), 7.02 (d, J = 8.4 Hz, 1H), 6.95-6.94 (m, 1H), 6.87-6.84 (m, 1H), 4.65-4.52 (m, 2H), 4.15-4.13 (m, 1H), 3.89-3.84 (m, 1H), 3.78 (s, 3H), 3.42 (dd, J_1 = 18 Hz, J_2 = 8.8 Hz, 1H), 1.70 (s, 1H) ppm;

^{13}C NMR ($CDCl_3$, 101 MHz) δ = 196.8, 176.5, 156.2, 136.2, 135.8, 133.5, 130.2, 128.7, 128.1, 112.4, 112.1, 109.3, 72.2, 55.8, 41.5, 40.1, 29.5 ppm;

HRMS (ESI) m/z of 4d:$[M + Na]^+$ Calculated for $C_{20}H_{17}NO_3Na^+$ 342.1106, found 342.1110;

IR (neat): ν_{max} 3064, 1700, 1603, 1492, 1456, 1353, 1272, 1216, 691 cm^{-1}.

General procedure for the Synthesis of product 5[b]



3 5

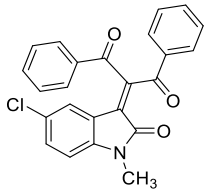
Optimization Table

entry[a]	solvent	Catalyst	Temp. (°C)	Time(h)	Yield 5a%[b]
1	**Acetone**	**DMAP**	**rt**	**5**	**94**
2	DCM	DMAP	rt	5	79
3	Toluene	DMAP	rt	5	60
4[c]	Acetone	DABCO	rt	5	nr[e]
5[c]	DMSO	-	reflux	24	90
6[d]	Toluene	-	reflux	24	nr[e]
7	Acetone	-	rt	8	nr[e]

[a]Reaction conditions: **3a** (0.2 mmol), base (1 equiv), solvent (5 mL), at room temperature, for 5 h under an open-air atmosphere. [b]Isolated yield. [c]The reaction was conducted at reflux. [d]The reaction carried out under argon atmosphere. [e]no reaction.

General procedure C for the Synthesis of products 5

To the compound **3** (0.2 mmol), DMAP (1 equiv) is charged with acetone (5 ml). The reaction is stirred at room temperature under air for 5 h. Then, the completion of the reaction was monitored using TLC. After the completion, the solvent was removed under reduced pressure. The resulting residue is purified by flash chromatography (silica gel, 200-400 mesh) hexanes/ethyl acetate to afford the corresponding products **5** (yellow solid).



5a

2-(5-Chloro-1-methyl-2-oxo-2,3-dihydro-1*H*-indol-3-yl)-1,3-diphenylpropane-1,3-dione (5a)

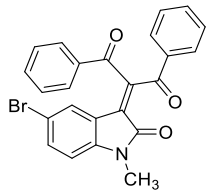
Product **3i** (82 mg, 0.203mmol) added DMAP (1 equiv) was stirred as described in general procedure **C** to obtain product **5a** (66 mg, 94%) as a yellow color solid; **Rf** = 0.19 (EtOAc/hexanes = 1:4, v/v); **mp** 148-150 °C.

^{1}H NMR (CDCl$_3$, 400 MHz) δ = 8.27-8.25(m, 2H), 8.18-8.16 (m, 2H), 7.69-7.65 (m, 1H), 7.61-7.41 (m, 5H), 7.24 (d, *J* = 9.2 Hz, 1H), 6.94 (d, *J* = 2 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 3.13 (s, 3H) ppm;

^{13}C NMR (CDCl$_3$, 101 MHz) δ = 191.6, 191.3, 165.1, 149.1, 143.3, 135.4, 134.1, 134.0, 131.0, 130.9, 129.7, 129.2, 128.8, 128.0, 127.4, 124.2, 120.2, 109.5, 29.7, 26.2 ppm;

HRMS (ESI) m/z of 5a:[M + H]$^+$ Calculated for $C_{24}H_{17}ClNO_3^+$ 402.0897, found 402.0895;

IR (neat): ν_{max} 3064, 1693, 1600, 1485, 1448, 1341, 1262, 1208, 808, 730, 690 cm^{-1}.



5b

2-(5-Bromo-1-methyl-2-oxo-2,3-dihydro-1*H*-indol-3-yl)-1,3-diphenylpropane-1,3-dione (5b)

Product **3j** (91 mg, 0.202 mmol) added DMAP (1 equiv) was stirred as described in general procedure **C** to obtain product **5b** (86 mg, 95%) as a yellow color solid; **Rf** = 0.19 (EtOAc/hexanes = 1:4, v/v); **mp** 148-150 °C.

^{1}H NMR (CDCl$_3$, 400 MHz) δ = 8.26 (d, *J* = 7.6 Hz, 2H), 8.17 (d, *J* = 7.6 Hz, 2H), 7.68-7.64 (m, 1H), 7.60-7.46 (m, 5H), 7.38-7.36 (m, 1H), 7.07 (s, 1H), 6.66 (d, *J* = 8.4 Hz, 1H), 3.11 (s, 3H) ppm;

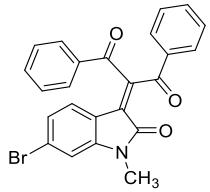
^{13}C NMR (CDCl$_3$, 101 MHz) δ = 191.6, 191.4, 165.0, 149.1, 143.8, 135.2, 134.2, 134.0, 133.9, 130.8, 129.7, 129.2, 128.8, 127,3, 127.0, 120.6, 115.2, 110.1, 26.2 ppm;

HRMS (ESI) m/z of 5b:[M + H]$^+$ Calculated for $C_{24}H_{17}BrNO_3^+$ 446.0392, found 446.0385;

IR (neat): ν_{max} 3063, 1695, 1603, 1487, 1450, 1345, 1265, 1210, 808, 730, 690 cm^{-1}.

Experimental procedure for a gram-scale experiment for product 5b

A compound of (**3j**, 1.2g, 2.676 mmol) in acetone (15 mL) was stirred for 6 h as described in general procedure **C** to obtain product **5b** (1.12 g, 94%).



5c

2-(6-Bromo-1-methyl-2-oxo-2,3-dihydro-1*H*-indol-3-yl)-1,3-diphenylpropane-1,3-dione (5c)

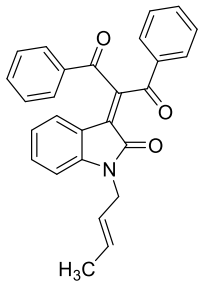
Product **3p** (91 mg, 0.202 mmol) was added DMAP (1 equiv), stirred as described in general procedure **C** to obtain product **5c** (79 mg, 96%) as a yellow color solid; **Rf** = 0.19 (EtOAc/hexanes = 1:4, v/v); **mp** 148-150 °C.

^{1}H NMR (CDCl$_3$, 400 MHz) δ = 8.17-8.09(m, 4H), 7.59-7.38 (m, 6H), 6.88-6.86 (m, 2H), 6.73 (d, *J* = 8.4 Hz, 1H), 3.18 (s, 3H) ppm;

^{13}C NMR (CDCl$_3$, 101 MHz) δ = 191.9, 191.5, 165.3, 148.1, 145.9, 135.4, 135.3, 134.2, 134.0, 130.8, 129.8, 129.2, 128.8, 127.4, 125.5, 125.3, 125.1, 117.8, 112.2, 26.2 ppm;

HRMS (ESI) m/z of 5c:[M + Na]$^+$ Calculated for $C_{24}H_{16}BrNO_3Na^+$ 468.0212, found 468.0206;

IR (neat): ν_{max} 3063, 1695, 1603, 1487, 1450, 1345, 1265, 1210, 808, 730, 690 cm^{-1}.



5d

3-{1-[(2*E*)-but-2-en-1-yl]-2-oxo-1,2-dihydro-3*H*-indol-3-ylidene}-1,3-diphenylpropane-1,3-dione (5d)

Product **3g** (85 mg, 0.207 mmol) was added DMAP (1 equiv), stirred as described in general procedure **C** to obtain product **5d** (79 mg, 93%) as a yellow color solid; **Rf** = 0.19 (EtOAc/hexanes = 1:4, v/v); **mp** 148-150 °C.

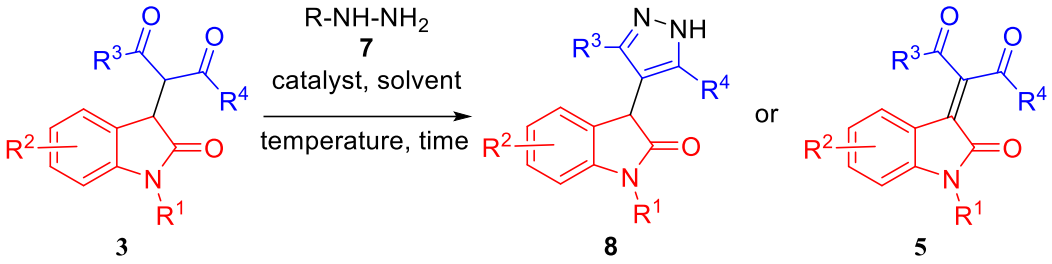
^{1}H NMR (CDCl$_3$, 400 MHz) δ = 8.34-8.24 (m, 4H), 7.69-7.51 (m, 6H), 7.30-7.26 (m, 1H), 7.03 (d, *J* = 7.3 Hz, 1H), 6.87-6.83 (m, 2H), 5.78-5.73 (m, 1H), 5.48-5.44 (m, 1H), 4.24 (d, *J* = 5.6 Hz, 2H), 1.71 (d, *J* = 6.5 Hz, 3H) ppm;

^{13}C NMR (CDCl$_3$, 101 MHz) δ = 192.2, 191.9, 165.0, 147.3, 144.4, 135.5, 135.1, 134.2, 134.0, 131.1, 130.9, 129.9, 129.8, 129.1, 128.7, 128.3, 124.2, 123.9, 122.4, 119.0, 41.8, 17.6 ppm;

HRMS (ESI) m/z of 5d:[M + H]$^+$ Calculated for $C_{27}H_{22}NO_3^+$ 408.1600, found 408.1595;

IR (neat): ν_{max} 3284, 1702, 1607, 1471, 1356, 1215, 754, 684 cm^{-1}.

General procedure for the Synthesis of product 8[b]



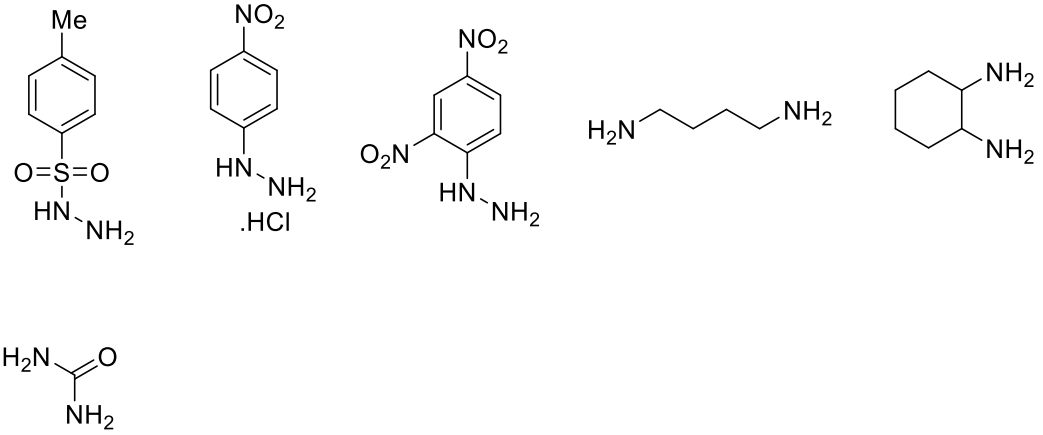
Optimization Table

entry[a]	solvent	Catalyst	Temp. (°C)	Time(h)	Yield	
					8a%[b]	**5**%[b]
1	**EtOH**	**AcOH**	**reflux**	**3**	**95**	**nr**[d]
2	MeOH	AcOH	reflux	8	69	10
3	EtOH	AcOH	rt	8	34	20
4[c]	DCM	AcOH	reflux	5	nr[d]	10
5[c]	EtOH	HCl	reflux	5	nr[d]	50
6	Acetone	AcOH	rt	8	nr[d]	38

[a]Reaction conditions: **3a** (0.2 mmol), **7** (0.6 mmol), acid (1 mol%), solvent (5 mL), under an open-air atmosphere. [b]Isolated yield. [c]The reaction was conducted at reflux. [d]no reaction.

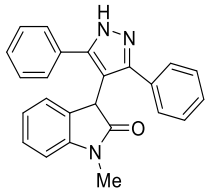
Unsuccessful reactants

More Basic nature hydrazine gives only an oxidized product **5**.



General procedure D for the preparation of pyrazole derivatives 8.

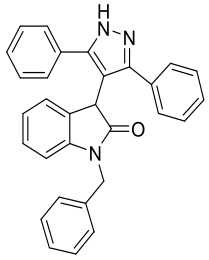
A compound of **3** (0.2 mmol), hydrazine monohydrate (0.6 mmol) in ethanol (5 mL) was stirred at reflux conditions for 3 h. The reaction was monitored by TLC until consumption of the starting material. After solvent removal under reduced pressure, the crude mixture was purified by column chromatography on silica gel (hexane/ethyl acetate 2:3) to afford the corresponding products **8**.



8a

3-(3,5-diphenyl-1H-pyrazol-4-yl)-1-methyl-1,3-dihydro-2H-indol-2-one (8a)

Compound **3a** (75 mg, 0.203 mmol) was stirred as described in general procedure **D** to furnish product **8a** (71 mg, 95%) as a white solid; **Rf** = 0.16 (EtOAc/hexanes = 3:2, v/v); **mp** 120-122 °C. **^{1}H NMR ($CDCl_3$, 400 MHz)** δ = 7.65 (br, 2H), 7.29 (br, 3H), 7.06-7.02 (m, 3H), 6.89-6.87 (m, 3H), 6.80-6.69 (m, 3H), 6.51 (d, J = 8 Hz, 1H), 4.68 (s, 1H), 2.88 (s, 3H) ppm; **^{13}C NMR ($CDCl_3$, 101 MHz)** δ = 176.5, 143.8, 129.7, 128.4, 127.9, 124.2, 122.4, 110.8, 107.8, 42.5, 26.2 ppm; **HRMS (ESI) m/z of 8a**:$[M + H]^+$ Calculated for $C_{24}H_{20}N_3O^+$ 366.1606, found 366.1609; **IR (neat)**: ν_{max} 3206, 3051, 2929, 1701, 1611, 1476, 1354, 1261, 745, 699 cm^{-1}.



8b

1-benzyl-3-(3,5-diphenyl-1*H*-pyrazol-4-yl)-1,3-dihydro-2*H*-indol-2-one (8b)

Compound **3b** (91 mg, 0.204 mmol) was stirred as described in general procedure **D** to furnish product **8b** (88 mg, 97%) as a white solid; **Rf** = 0.16 (EtOAc/hexanes = 3:2, v/v); **mp** 120-122 °C. **^{1}H NMR ($CDCl_3$, 400 MHz)** δ = 7.72 (br, 2H), 7.32 (br, 3H), 7.21-7.16 (m, 3H), 6.95-6.91 (m, 3H), 6.86-6.84 (m, 2H), 6.73-6.69 (m, 5H), 6.50 (d, J = 7.6 Hz, 2H), 4.81 (s, 1H), 4.72 (d, J = 15.6 Hz, 1H), 4.52 (d, J = 15.2 Hz, 1H) ppm;

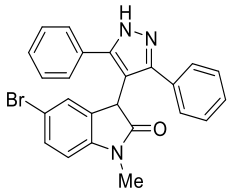
^{13}C NMR (CDCl$_3$, 101 MHz) δ = 176.5, 143.0, 135.8, 130.9, 129.2, 128.9, 128.8, 128.5, 128.2, 127.88, 127.84, 127.6, 124.3, 122.5, 110.3, 108.7, 44.2, 42.6 ppm;

HRMS (ESI) m/z of 8b:[M + H]$^+$ Calculated for $C_{30}H_{24}N_3^+$ 442.1919, found 442.1919;

IR (neat): ν_{max} 3172, 2926, 2856, 2173, 1705, 1611, 1488, 1353, 744, 698 cm^{-1}.

Experimental procedure for a gram-scale experiment for product 8b

A compound of (**3b**, 1.2g, 2.693 mmol) in ethanol (15 mL) was stirred for 4h as described in general procedure **D** to obtain product **8b** (1.11 g, 93%).



8c

5-bromo-3-(3,5-diphenyl-1*H*-pyrazol-4-yl)-1-methyl-1,3-dihydro-2*H*-indol-2-one (8c)

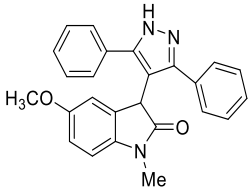
Compound **3j** (90 mg, 0.200 mmol) was stirred as described in general procedure **D** to furnish product **8c** (85 mg, 95%) as a white solid; **Rf** = 0.16 (EtOAc/hexanes = 3:2, v/v); **mp** 120-122 °C.

^{1}H NMR (CDCl$_3$, 400 MHz) δ = 7.62 (br, 2H), 7.30 (br, 3H), 7.13-7.11 (m, 1H), 7.01-6.93 (m, 5H), 6.70 (br, 2H), 6.33 (d, *J* = 8.4 Hz, 1H), 4.66 (s, 1H), 2.87 (s, 3H) ppm;

^{13}C NMR (CDCl$_3$, 101 MHz) δ = 176.0, 142.8, 131.4, 130.7, 129.0, 128.4, 127.7, 127.3, 115.0, 110.3, 109.1, 42.4, 26.3 ppm;

HRMS (ESI) m/z of 8c:[M + H]$^+$ Calculated for $C_{24}H_{19}BrN_3O^+$ 444.0712, found 444.0718;

IR (neat): ν_{max} 3202, 3053, 2960, 1702, 1607, 1484, 1451, 1344, 1263, 1136, 1095, 737, 699, 662 cm^{-1}.



8d

5-methoxy-3-(3,5-diphenyl-1H-pyrazol-4-yl)-1-methyl-1,3-dihydro-2H-indol-2-one (8d)

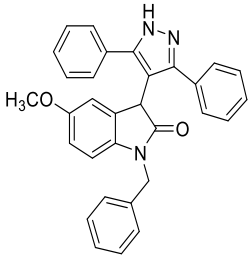
Compound **3l** (83 mg, 0.207 mmol) was stirred as described in general procedure **D** to furnish product **8d** (81 mg, 98%) as a white solid; **Rf** = 0.16 (EtOAc/hexanes = 3:2, v/v); **mp** 120-122 °C.

^{1}H NMR (CDCl$_3$, 400 MHz) δ = 7.87 (br, 1H), 7.67 (s, 2H), 7.29 (s, 3H), 7.0-6.92 (m, 3H), 6.73 (s, 2H), 6.58-6.55 (m, 1H), 6.47-6.40 (m, 2H), 4.67 (m, 1H), 3.55 (s, 3H), 2.88 (s, 3H) ppm;

^{13}C NMR (CDCl$_3$, 101 MHz) δ = 176.1, 155.9, 148.5, 147.6, 137.5, 131.4, 130.7, 128.9, 128.6, 128.4, 128.0, 127.6, 127.0, 112.8, 111.4, 110.8, 108.2, 55.9, 42.9, 26.3 ppm;

HRMS (ESI) m/z of 8d:[M + H]$^+$ Calculated for $C_{25}H_{22}N_3O_2^+$ 396.1712, found 1714;

IR (neat): ν_{max} 3062, 1699, 1606, 1494, 1451, 1355, 1278, 1225, 741, 693 cm^{-1}.



8d

3-(3,5-diphenyl-1Benzyl-pyrazol-4-yl)-5-methoxy-1,3-dihydro-2H-indol-2-one (8e)

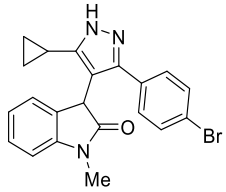
Compound **3m** (96 mg, 0.201 mmol) was stirred as described in general procedure **D** to furnish product **8e** (94 mg, 98%) as a white solid; **Rf** = 0.48 (EtOAc/hexanes = 3:2, v/v); **mp** 120-122 °C.

^{1}H NMR (CDCl$_3$, 400 MHz) δ = 7.70 (s, 2H), 7.27-7.17 (m, 8H), 6.91 (s, 1H), 6.70 (s, 4H), 6.43-6.36 (m, 3H), 4.78 (s, 1H), 4.54 (dd, J_1 = 53.6 Hz J_2 = 15.2 Hz, 2H), 3.44 (s, 3H) ppm;

^{13}C NMR (CDCl$_3$, 101 MHz) δ = 176.2, 155.9, 136.6, 136.0, 130.4, 128.9, 128.8, 128.6, 128.2, 127.9, 127.7, 127.6, 112.9, 111.3, 110.0, 109.2, 55.9, 44.3, 43.1 ppm;

HRMS (ESI) m/z of 8e:[M + H]$^+$ Calculated for $C_{31}H_{26}N_3O_2^+$ 472.2022, found 472.2025;

IR (neat): ν_{max} 3284, 1702, 1607, 1471, 1356, 1215, 754, 684 cm^{-1}.



8f

3-[3-(4-bromophenyl)-5-cyclopropyl-1H-pyrazol-4-yl]-1-methyl-1,3-dihydro-2H-indol-2-one (8f)

Compound **3x** (86 mg, 0.208 mmol) was stirred as described in general procedure **D** to furnish product **8f** (81 mg, 95%) as a white solid; **Rf** = 0.16 (EtOAc/hexanes = 3:2, v/v); **mp** 120-122 °C.

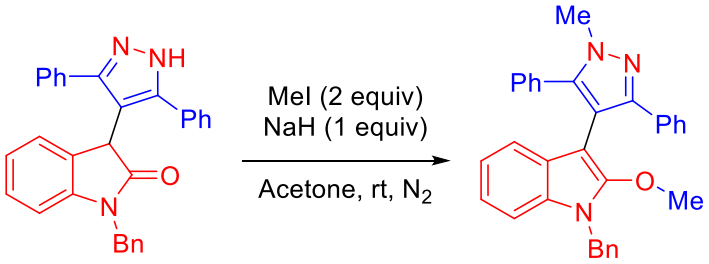
^{1}H NMR (CDCl$_3$, 400 MHz) δ = 7.52-7.35 (m, 4H), 7.21-7.18 (m, 2H), 6.98-6.90 (m, 2H), 6.78-6.76 (m, 1H), 4.66 (s, 1H), 3.17-3.12 (br, 3H), 2.98 (s, 1H), 0.80-0.31 (br, 4H) ppm;

^{13}C NMR (CDCl$_3$, 101 MHz) δ = 176.3, 143.9, 132.1, 131.5, 131.3, 130.0, 129.3, 128.1, 127.4, 124.3, 122.6, 111.4, 107.8, 42.2, 26.3, 6.1 ppm;

HRMS (ESI) m/z of 8f: $[M + H]^+$ Calculated for $C_{21}H_{19}BrN_3O^+$ 408.0712, found 408.0715;

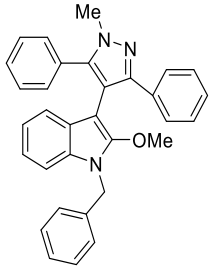
IR (neat): ν_{max} 3285, 1702, 1607, 1470, 1355, 1215, 754, 684 cm^{-1}.

General procedure E for the synthesis of compounds 9



8 **9**

In an oven-dried round-bottom flask, the compound **8** (0.2 mmol), NaH (1 equiv) in acetone (3 mL) under a nitrogen atmosphere. After that, a solution of alkyl halides (2 equiv) was added dropwise to the reaction mixture and stirred at room temperature for 3 h. The reaction was quenched by the addition of water and HCl (50:5 mL). The crude product was suspended in sat. NH_4Cl solution (50 mL) was extracted with EtOAc. Combined organic layers were dried over Na_2SO_4 concentrated, and purified through column chromatography over silica gel using (hexane/ethyl acetate 95:5) as eluents to afford the products **9**.



9a

1-benzyl-2-methoxy-3-(1-methyl-3,5-diphenyl-1H-pyrazol-4-yl)-1H-indole (9a)

Compound **8b** (60 mg, 0.135mmol) was stirred as described in general procedure **E** to furnish product **9a** (61 mg, 95%) as a white solid; **Rf** = 0.6 (EtOAc/hexanes = 1:4, v/v); **mp** 132-134 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.76-7.59 (m, 2H), 7.20 (s, 5H), 7.13-7.10 (m, 7H), 6.97-6.86 (m, 3H), 6.80-6.78 (m, 2H), 5.08 (d, J = 1.2 Hz, 2H), 3.90 (s, 3H), 3.53 (s, 3H) ppm;

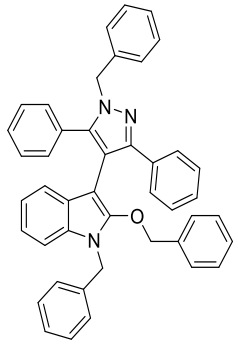
^{13}C NMR ($CDCl_3$, 101 MHz) δ = 149.8, 149.6, 144.7, 137.9, 133.8, 131.3, 130.4, 129.3, 129.2, 128.5, 128.4, 128.2, 127.2, 127.0, 126.8, 126.1, 120.1, 119.8, 118.5, 109.6, 108.6, 86.2, 59.9, 44.8, 37.9 ppm;

HRMS (ESI) m/z of 9a:$[M + H]^+$ Calculated for $C_{32}H_{28}N_3O^+$ 470.2232, found 470.2238;

IR (neat): ν_{max} 3031, 2929, 2311, 2172, 2113, 1711, 1611, 1456, 1358, 1086, 1026, 803, 755, 698 cm^{-1}.

Experimental procedure for a gram-scale experiment for product 9a

A compound of (**8b**, 1g, 2.264 mmol) in acetone (15 mL) was stirred for 5 h as described in general procedure **E** to obtain product **9a** (0.900 g, 84%).



9b

1-benzyl-3-(1-benzyl-3,5-diphenyl-1H-pyrazol-4-yl)-2-(benzyloxy)-1H-indole (9b)

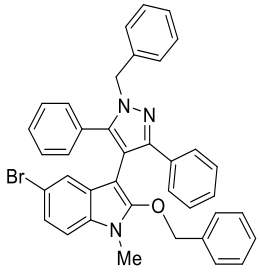
Compound **8b** (60 mg, 0.135mmol) was stirred as described in general procedure **E** to furnish product **9b** (80 mg, 94%) as a white solid; **Rf** = 0.6 (EtOAc/hexanes = 1:4, v/v); **mp** 138-140 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.81-7.80 (m, 2H), 7.35-7.16 (m, 20H), 7.09-7.02 (m, 3H), 6.96-6.90 (m, 4H), 5.58-5.46 (m, 2H), 5.21-5.11 (m, 2H), 4.94 -4.85(m, 2H) ppm;

^{13}C NMR ($CDCl_3$, 101 MHz) δ = 150.2, 148.9, 145.1, 137.99, 137.95, 136.3, 133.9, 131.3, 130.3, 129.4, 128.8, 128.6, 128.5, 128.4, 128.36, 128.32, 128.1, 127.8, 127.48, 127.40, 127.09, 127.07, 126.8, 126.3, 120.3, 119.9, 118.7, 110.04, 108.8, 87.7, 74.6, 53.7, 44.9 ppm;

HRMS (ESI) m/z of 9b: $[M + H]^+$ Calculated for $C_{44}H_{36}N_3O^+$ 622.2858, found 622.2852;

IR (neat): ν_{max} 3052, 2928, 2857, 1723, 1622, 1459, 1406, 1352, 1262, 1021, 920, 800, 731, 689 cm^{-1}.



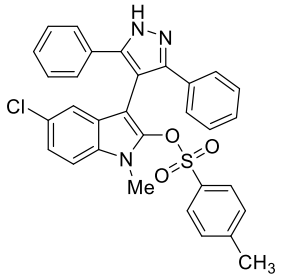
9c

3-(1-benzyl-3,5-diphenyl-1H-pyrazol-4-yl)-2-(benzyloxy)-5-bromo-1-methyl-1H-indole (9c)

Compound **8c** (60 mg, 0.135mmol) was stirred as described in general procedure **E** to furnish product **9c** (70 mg, 94%) as a white solid; **Rf** = 0.6 (EtOAc/hexanes = 1:4, v/v); **mp** 138-140 °C. **^{1}H NMR (CDCl$_3$, 400 MHz)** δ = 7.58-7.56 (m, 2H), 7.22-7.06 (m, 16H), 7.0-6.98 (m, 2H), 6.92-6.90 (m, 3H), 5.40-5.28 (m, 2H), 4.77 (ABq, $\Delta\delta_{AB}$ = 0.09, J = 5.2 Hz, 2H), 3.31 (s, 3H) ppm; **^{13}C NMR (CDCl$_3$, 101 MHz)** δ = 150.4, 149.6, 145.1, 137.8, 136.2, 133.7, 130.5, 130.4, 130.1, 129.4, 128.6, 128.5, 128.4, 128.36, 128.31, 127.8, 127.5, 127.4, 127.0, 126.8, 122.8, 120.8, 109.7, 109.3, 87.0, 74.5, 53.7, 28.0 ppm;

HRMS (ESI) m/z of 9c:[M + H]$^+$ Calculated for $C_{38}H_{31}BrN_3O^+$ 624.1651, found 624.1652;

IR (neat): ν_{max} 3060, 3032, 2934, 1954, 1811, 1714, 1623, 1580, 1530, 1493, 1449, 1401, 1098, 1021, 928, 734, 698 cm^{-1}.



10d

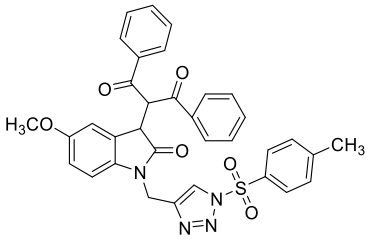
5-chloro-3-(3,5-diphenyl-1H-pyrazol-4-yl)-1-methyl-1H-indol-2-yl 4 -methylbenzenesulfonate (10d)

The Compound **8c** (90 mg, 0.225mmol), NaH (1 equiv) in acetone (3 mL) under nitrogen air. After that, a solution of alkyl halides (0.207 mmol, 1 equiv) was added dropwise to the reaction mixture, and it was stirred at room temperature for 4 hours. The reaction was quenched by the addition of water and HCl (5:5 mL). The crude product was suspended in sat. NH_4Cl solution (50 mL) was extracted with EtOAc. Combined organic layers were dried over Na_2SO_4, concentrated, and purified through column chromatography over silica gel using (hexane/ethyl acetate 95:5) as eluents to afford the product **10d.** (60 mg, 85%) as white solid; **Rf** = 0.4 (EtOAc/hexanes = 1:4, v/v); **mp** 118-120 °C; **^{1}H NMR (CDCl$_3$, 400 MHz)** δ = 8.41 (br, 1H), 7.28-7.26 (m, 2H), 7.20-7.10 (m, 13H), 6.85-6.83 (m, 2H), 3.66-365 (m, 3H), 2.09 (s, 3H) ppm; **^{13}C NMR (CDCl$_3$, 101 MHz)** δ = 146.5, 145.7, 138.9, 138.7, 132.2, 131.9, 131.6, 130.9, 129.4, 129.0, 128.5, 128.2, 127.7, 126.7, 126.3, 126.1, 125.8, 125.4, 123.03, 122.9, 119.9, 113.5, 111.1, 110.7, 105.75, 105.73, 95.3, 95.2, 29.4, 29.4, 21.5 ppm; **HRMS (ESI) m/z of 10d**:[M + H]$^+$ Calculated for $C_{31}H_{25}ClN_3O_3S^+$

554.1305, found 554.1303; **IR (neat)**: ν_{max} 3196, 3066, 2950, 2312, 2173, 2115, 1725, 1596, 1473, 1435, 1379, 1179, 1092, 804, 739 cm^{-1}.

General procedure F for the synthesis of compound 11 (click chemistry)

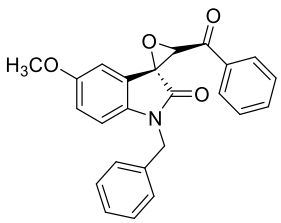
In an oven-dried round-bottom flask, the compound **3** (0.2 mmol), CuTC (2 mg, 6 mol%) in 1,2-DCE (3 mL) under open air. After that, solution of Tosylazide (0.207 mmol, 1.1 equiv) was added dropwise to the reaction mixture and stirred at room temperature for 4 h. Upon completion of the reaction removed the solvent was under reduced pressure and purified through column chromatography over silica gel using (hexane/ethyl acetate 95:5) as eluents to afford the product **11** (113 mg, 96%).



11

2-(5-methoxy-2-oxo-1-((1-tosyl-1H-1,2,3-triazol-4-yl)methyl)indolin-3-yl)-1,3 diphenylpropane-1,3-dione (11)

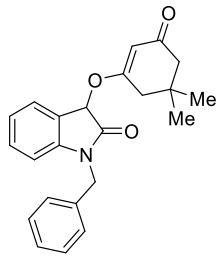
A compound **3o** (80 mg, 0.188 mmol, 1 equiv) was stirred as described in General procedure **F,** Red color liquid; **Rf** = 0.14 (EtOAc/hexanes = 3:2, v/v). **^{1}H NMR ($CDCl_3$, 400 MHz)** δ = 8.05 (s, 1H), 7.99 (d, *J* = 7.9 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 7.6 Hz, 2H), 7.55 (s, 1H), 7.45-7.42 (m, 3H), 7.29-7.21 (m, 4H), 6.71 (m, 1H), 6.59 (m, 2H), 6.05 (d, *J* = 3.6 Hz, 1H), 4.92- 4.67 (m, 2H), 4.15 (d, *J* = 3.6 Hz, 1H), 3.63 (s, 3H), 2.34 (s, 3H) ppm; **^{13}C NMR ($CDCl_3$, 101 MHz)** δ = 195.3, 195.0, 175.3, 156.0, 147.3, 135.8, 135.4, 134.0, 133.7, 132.9, 130.4, 129.2, 128.8, 128.7, 126.8, 122.6, 122.6, 112.9, 112.7, 109.2, 56.9, 55.7, 45.0, 35.5 21.85 ppm; **HRMS (ESI) m/z of 11**:$[M + Na]^+$ Calculated for $C_{34}H_{28}N_4O_6SNa^+$ 621.1808, found 621.1816; **IR (neat)**: ν_{max} 3284, 1702, 1607, 1471, 1356, 1215, 754, 684 cm^{-1}.



12

(2'*R*,3'*R*)-3'-benzoyl-1-benzyl-5-methoxyspiro[indole-3,2'-oxiran]-2(1H)-one (12)[24c]

To a solution of DMAP (1 equiv) and copper iodide (10 mol%) in acetone (4 mL) was added 1-benzyl-3-diazonio-5-methoxy-2-oxo-2,3-dihydro-1H-indol-3-ide (**5**) (50 mg, 0.13 mmol) the reaction mixture was stirred at room temperature to afford **12** (42 mg, 71%) as a colorless amorphous solid according to general procedure. **Rf** = 0.23 (EtOAc/hexanes = 1:4, v/v); **mp** 148-149 °C; **^{1}H NMR ($CDCl_3$, 400 MHz)** δ = 7.88 (d, *J* = 7.6 Hz, 2H), 7.56-7.52 (m, 1H), 7.42-7.40 (m, 2H), 7.27-7.18 (m, 5H), 6.67-6.57 (m, 3H), 4.96- 4.91 (m, 3H), 3.57 (s, 3H) ppm; **^{13}C NMR ($CDCl_3$, 101 MHz)** δ = 190.7, 170.1, 156.1, 137.7, 135.19, 135.15, 134.5, 129.0, 128.9, 128.3, 127.9, 127.3, 120.4, 116.3, 110.8, 110.6, 64.01, 61.2, 55.7, 44.5, ppm; **HRMS (ESI) m/z of 12**:[M + H]$^+$ Calculated for $C_{24}H_{20}NO_4^+$ 386.1392, found 386.1392; **IR (neat)**: ν_{max} 2923, 1701, 1599, 1445, 1363, 1187, 1147, 725 cm^{-1}.

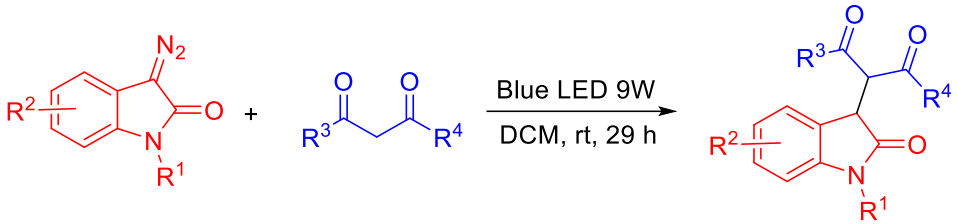


13

1-benzyl-3-[(5,5-dimethyl-3-oxocyclohex-1-en-1-yl)oxy]-1,3-dihydro-2H-indol-2-one (13)

Diazoamide (**1b,** 80 mg, 0.320 mmol) and 5,5-Dimethyl-1,3-cyclohexanedione (**2g**, 103 mg, 0.481 mmol) were stirred as described in general procedure A to furnish product **13** (79 mg, 68%) as colorless solid; **Rf** = 0.22 (EtOAc/hexanes = 3:2, v/v); mp 141-142 °C; **^{1}H NMR ($CDCl_3$, 400 MHz)** δ = 7.43 (d, *J* = 7.6 Hz, 1H), 7.37-7.28 (m, 6H), 7.09-7.06 (m, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 5.78 (s, 1H), 5.68 (s, 1H), 4.95- 4.92 (m, 2H), 2.55-2.44 (m, 2H), 2.31 (s, 2H), 1.15 (d, *J* = 5.2 Hz, 6H) ppm; **^{13}C NMR ($CDCl_3$, 101 MHz)** δ = 199.2, 175.1, 171.4, 143.4, 135.0, 130.7, 128.9, 127.9, 127.4, 125.7, 123.7, 123.3, 109.9, 103.3, 73.2, 50.8, 44.1, 42.7, 32.6, 28.4, 28.1 ppm; **HRMS (ESI) m/z of 14**:[M + H]$^+$ Calculated for $C_{23}H_{24}NO_3^+$ 384.1576, found 384.1577; **IR (neat)**: ν_{max} 2959, 1728, 1653, 1611, 1371, 1203, 1152, 689 cm^{-1}.

Gram Scale reaction



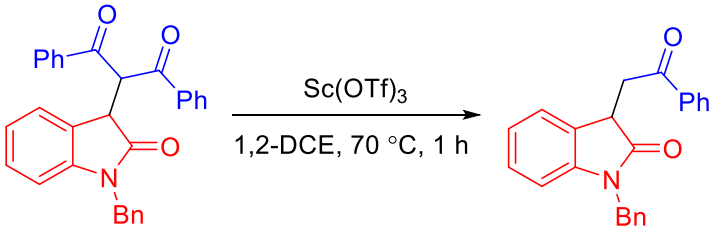
1b, 4.011 mmol
1i, 3.967 mmol

2a, 6.017 mmol
2a, 5.950 mmol

3b, 1.41 g, 79%
3j, 1.37 g, 81%

A solution of *N*-benzyl diazoamide (**1b**, 1 g, 4.011 mmol) and 1,3-diphenylpropane-1,3-dione (**2a**, 1.349 g, 6.017 mmol) in DCM (15 mL) was stirred for 29 h as described in general procedure **A** to obtain product **3b** (1.41 g, 79%).

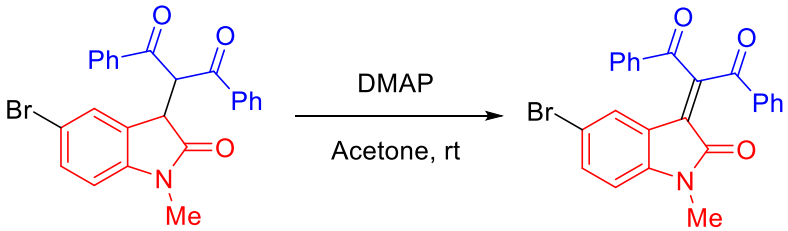
A solution of 5-Bromo-*N*-methyl diazoamide (**1i**, 1 g, 3.967 mmol) and 1,3-diphenylpropane-1,3-dione (**2a**, 1.335 g, 5.950 mmol) in DCM (15 mL) was stirred for 29 h as described in general procedure **A** to obtain product **3j** (1.37 g, 81%).



3b, 3.142 mmol

4a, 1.01 g, 94%

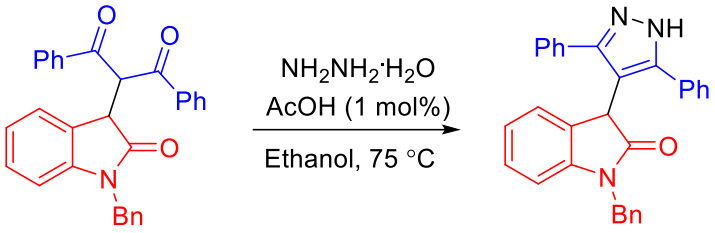
A compound of (**3b**, 1.4g, 3.142 mmol) in 1,2-DCE (15 mL) at 70 °C was stirred for 1 h as described in General Procedure **B** to obtain product **4a** (1.01 g, 94%).



3j, 2.676 mmol

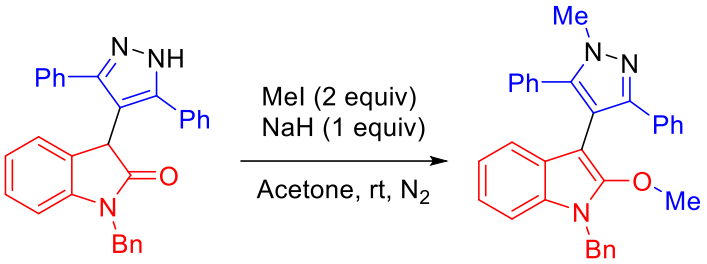
5b, 1.12 g, 94%, 6h

A compound of (**3j**, 1.2g, 2.676 mmol) in acetone (15 mL) was stirred for 6 h as described in general procedure **C** to obtain product **5b** (1.12 g, 94%).



3b, 2.693 mmol **8b**, 1.11 g, 93%, 4 h

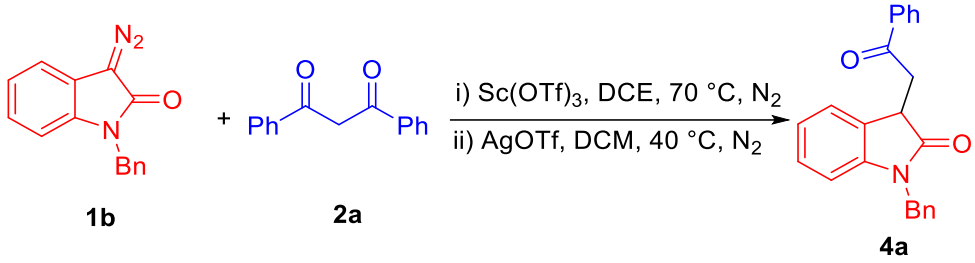
A compound of (**3b**, 1.2g, 2.693 mmol) in ethanol (15 mL) was stirred for 4 h as described in general procedure **D** to obtain product **8b** (1.11 g, 93%).



8b, 2.264 mmol **9a**, 0.900 g, 84%, 5 h

A compound of (**8b**, 1g, 2.264 mmol) in acetone (15 mL) was stirred for 5 h as described in general procedure **E** to obtain product **9a** (0.900 g, 84%).

Control experiments



1b **2a** **4a**

The reaction of diazoamide **1b** (0.3 mmol), 1,3-diketone **2a** (0.4 mmol), and $Sc(OTf)_3$ (10 mol %) is charged with 1,2-DCE (20 ml) stirred at 70 °C under N_2 atmosphere for 5-8 h or AgOTf (10 mol%) is charged with DCM (20 ml) stirred at 40 °C under N_2 atmosphere for 10-13 h. Then, the completion of the reaction was monitored using TLC. After the completion, the solvent was removed under reduced pressure. The resulting residue is purified by flash chromatography (silica gel, 230-400 mesh), hexanes/ethyl acetate 97:3 to afford the corresponding product **4a.**

^{1}H and $^{13}C\{^{1}H\}$ NMR spectra for compounds 3, 4, 5, 8, 9, 10, 11, 12 and 13.

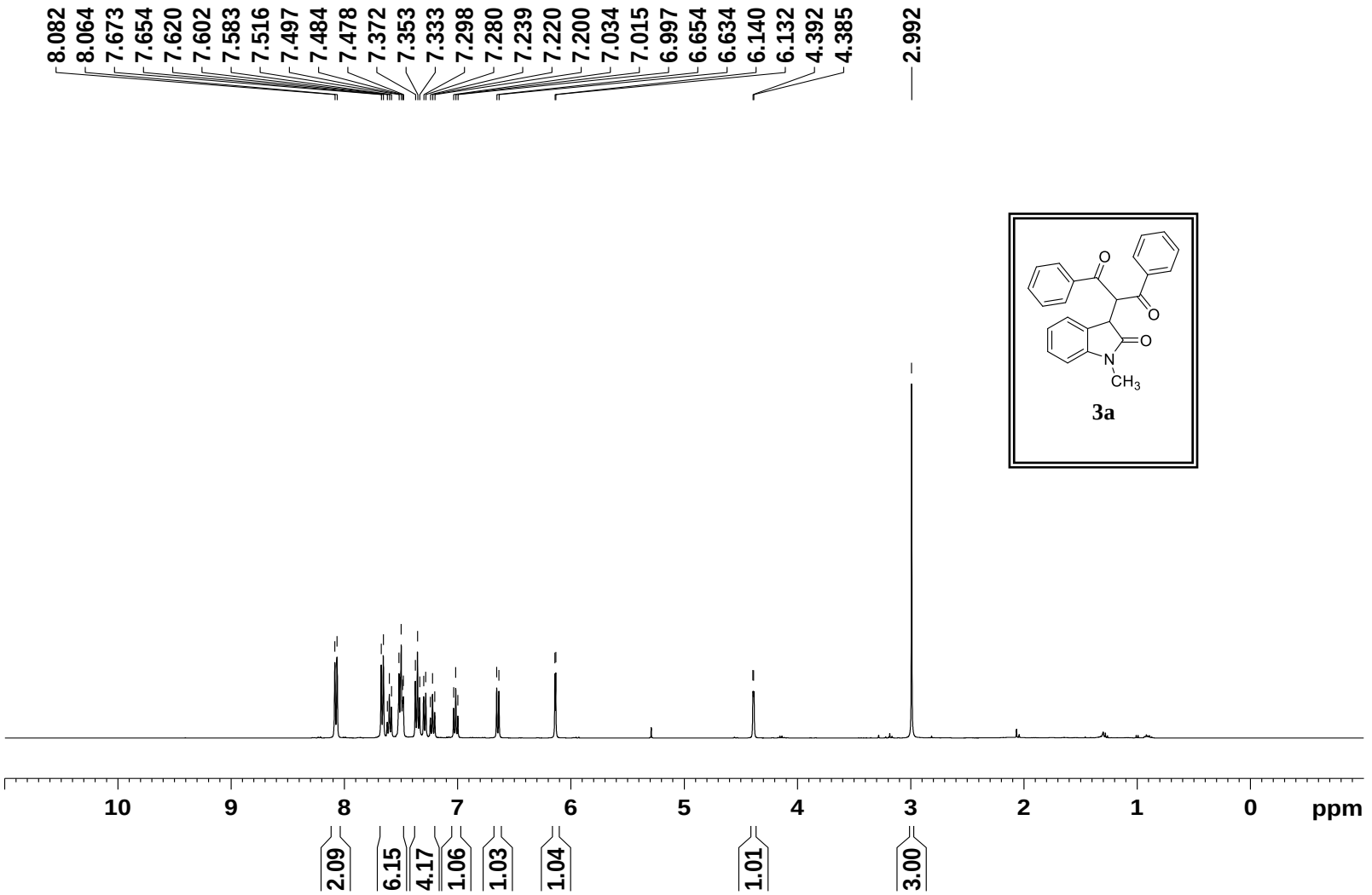


Figure 3: ^{1}H NMR spectrum of compound **3a** (400 MHz, $CDCl_3$)

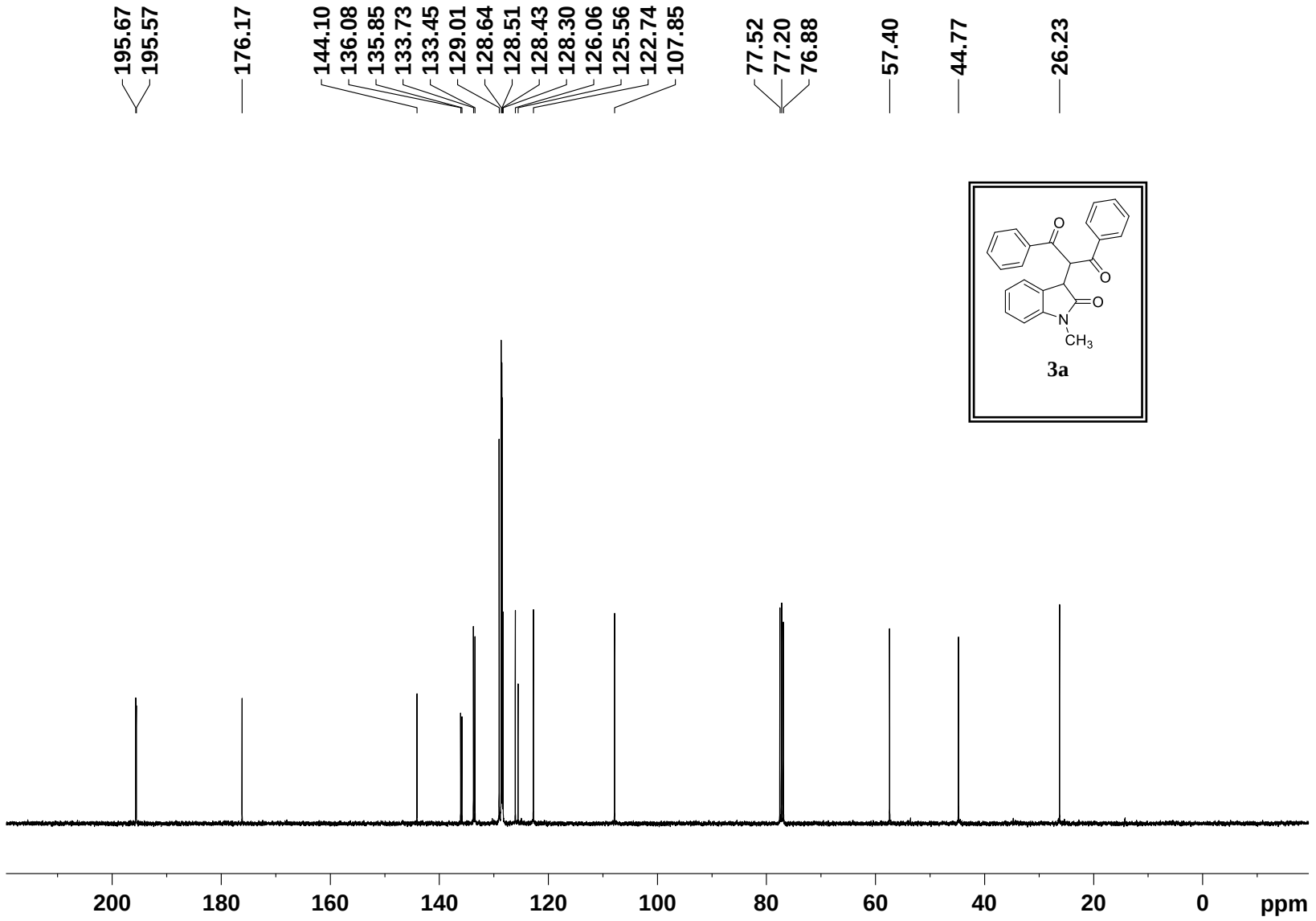


Figure 4: ^{13}C NMR spectrum of compound **3a** (101 MHz, $CDCl_3$)

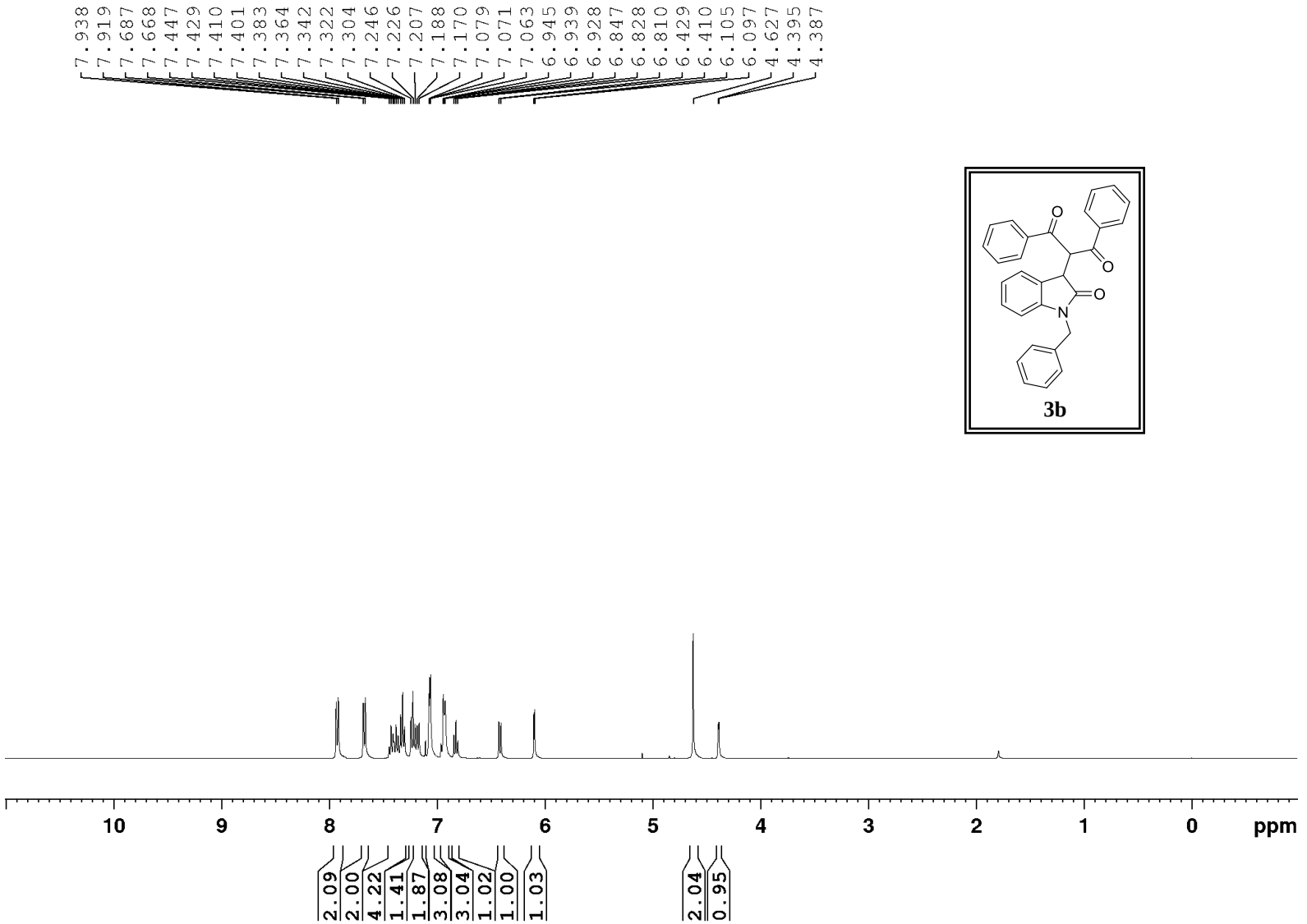


Figure 5: ^{1}H NMR spectrum of compound **3b** (400 MHz, $CDCl_3$)

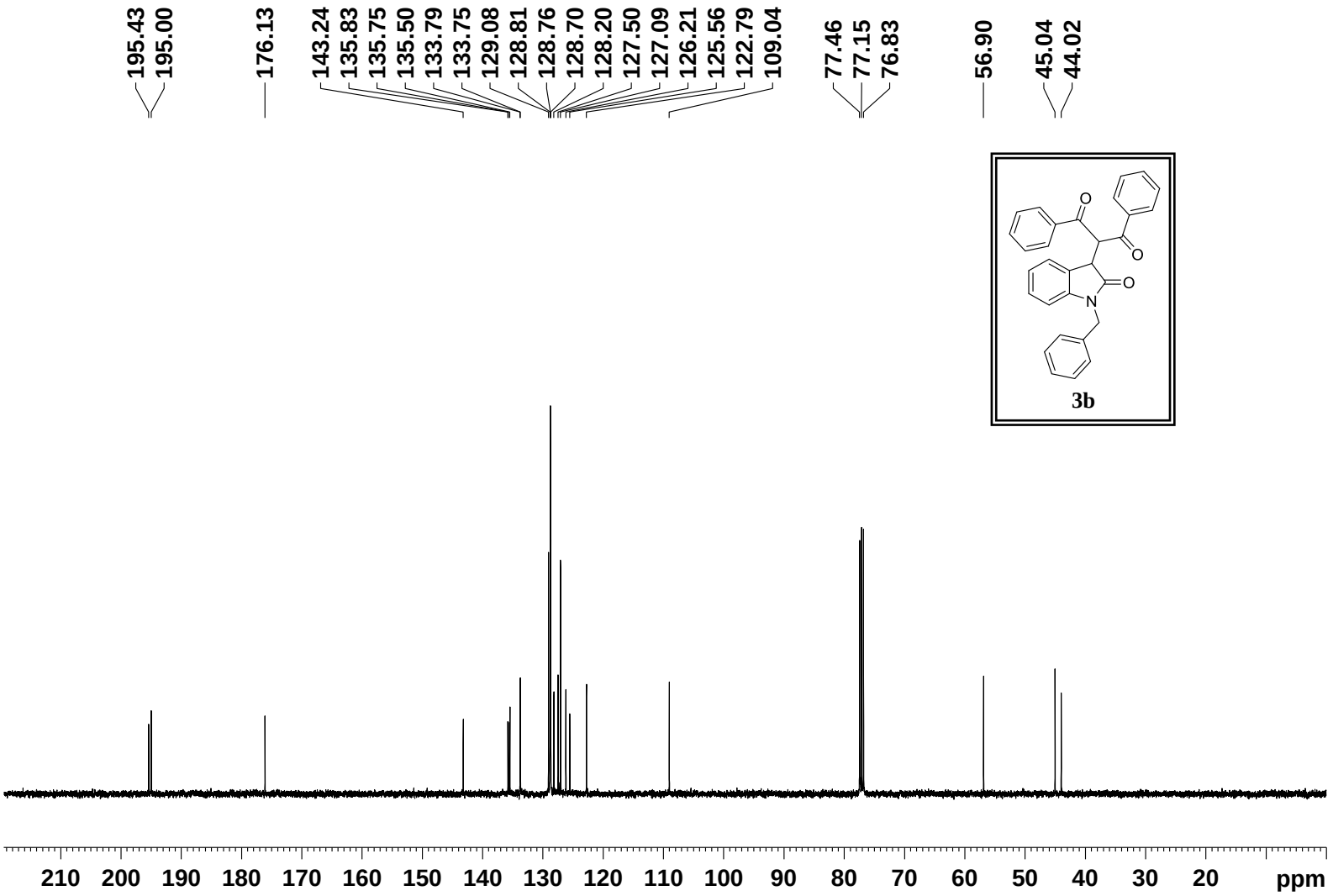


Figure 6: ^{13}C NMR spectrum of compound **3b** (101 MHz, $CDCl_3$)

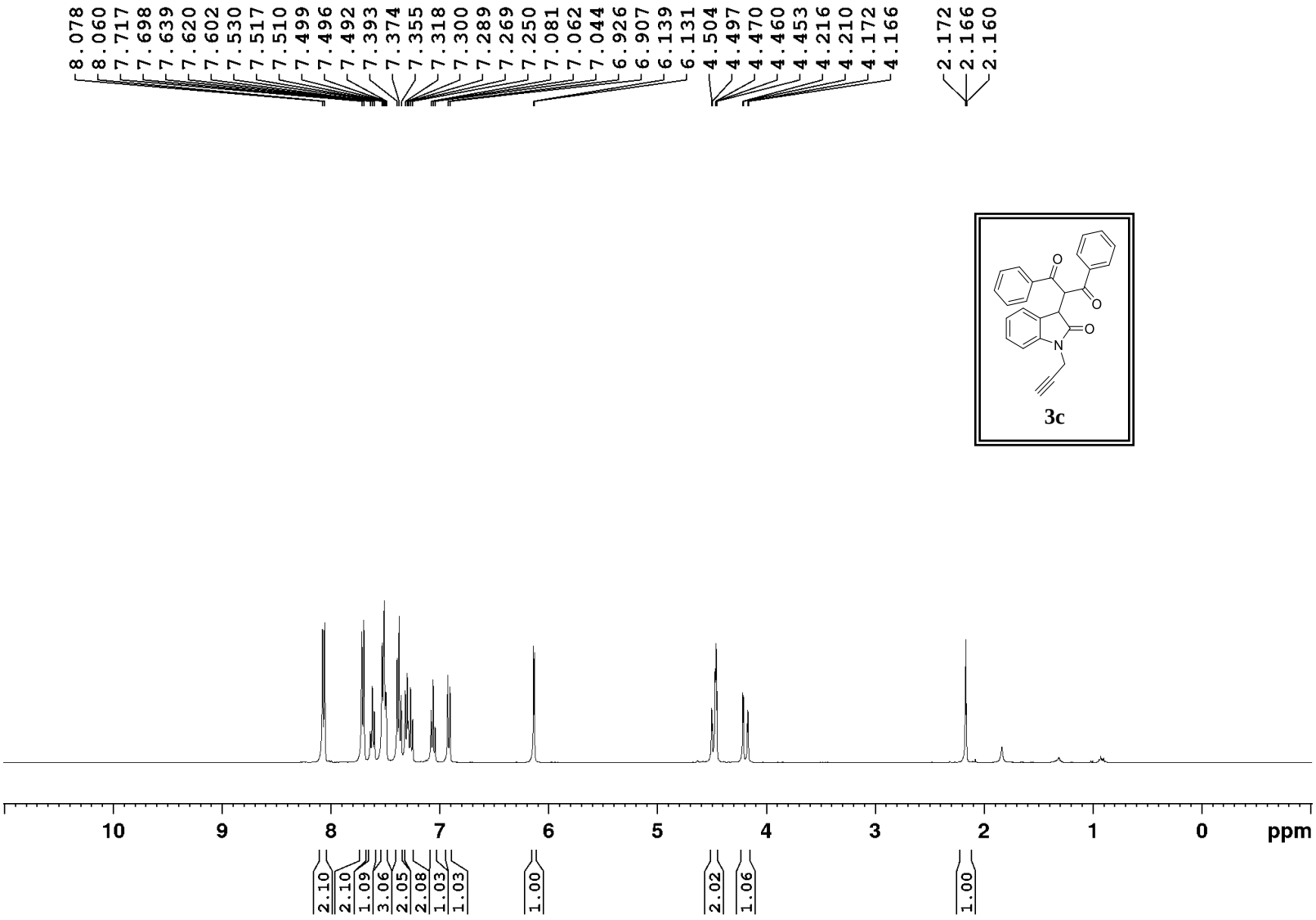


Figure 7: ^{1}H NMR spectrum of compound **3c** (400 MHz, $CDCl_3$)

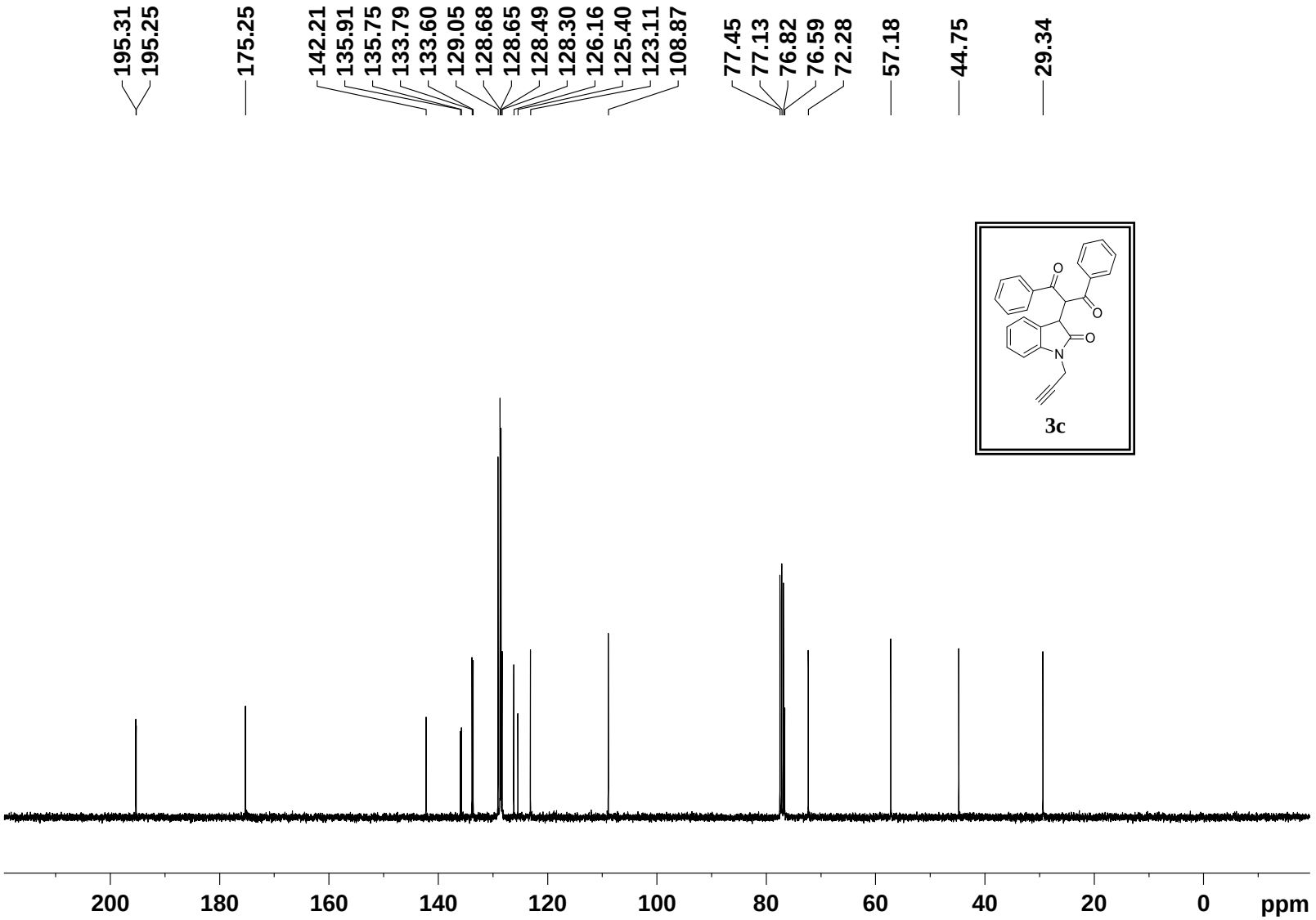


Figure 8: ^{13}C NMR spectrum of compound **3c** (101 MHz, $CDCl_3$)

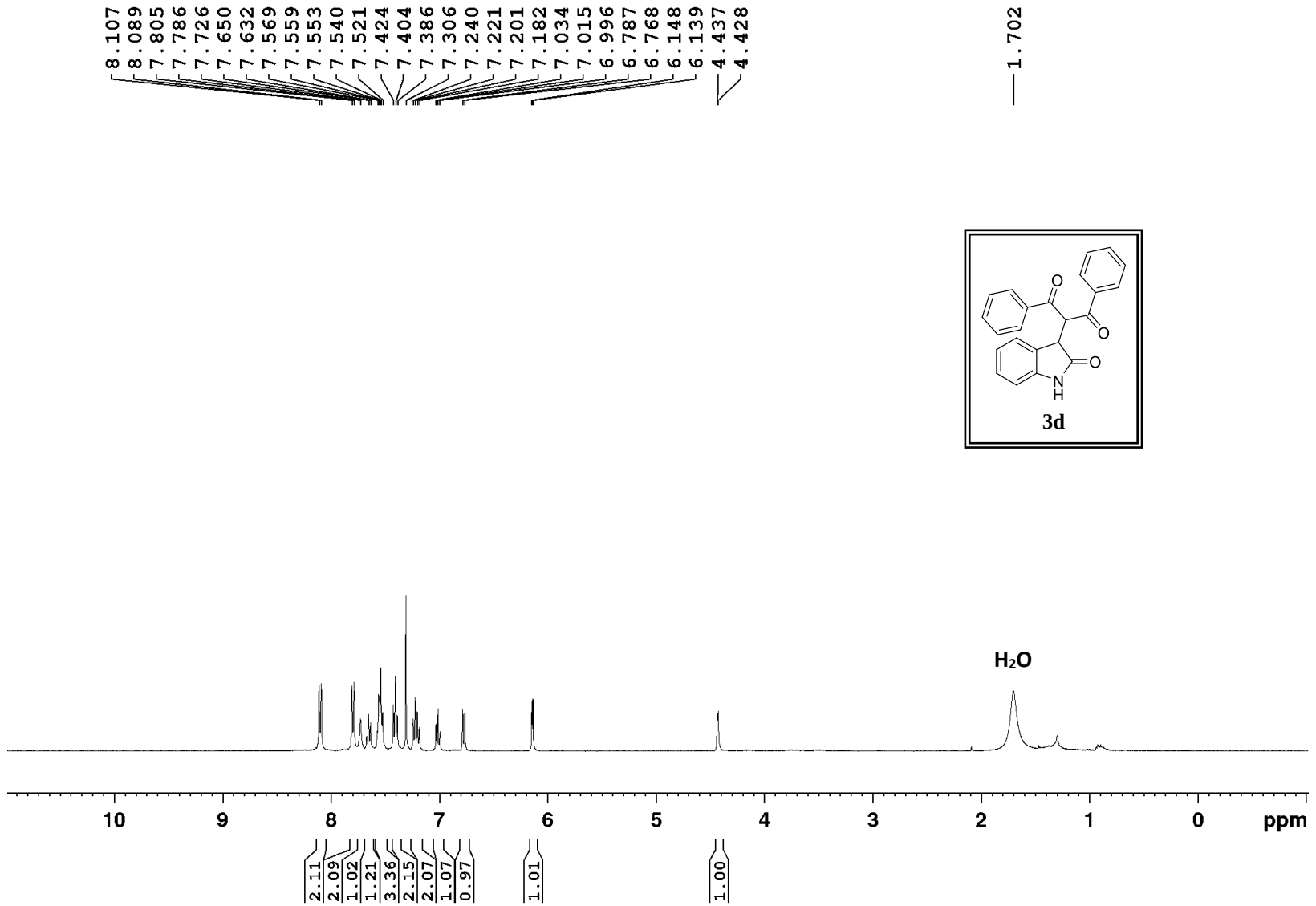


Figure 9: ^{1}H NMR spectrum of compound **3d** (400 MHz, $CDCl_3$)

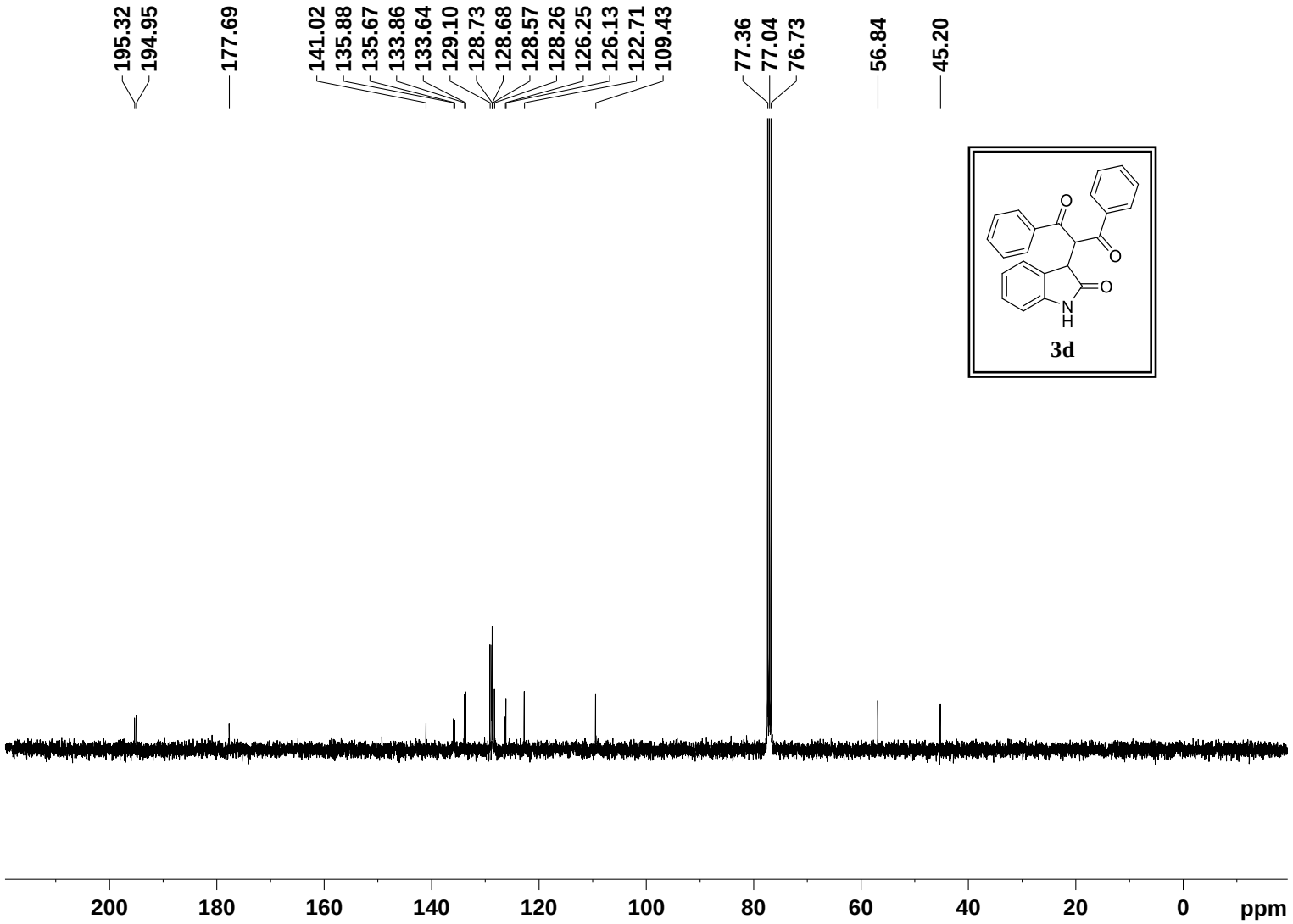


Figure 10: ^{13}C NMR spectrum of compound **3d** (101 MHz, $CDCl_3$)

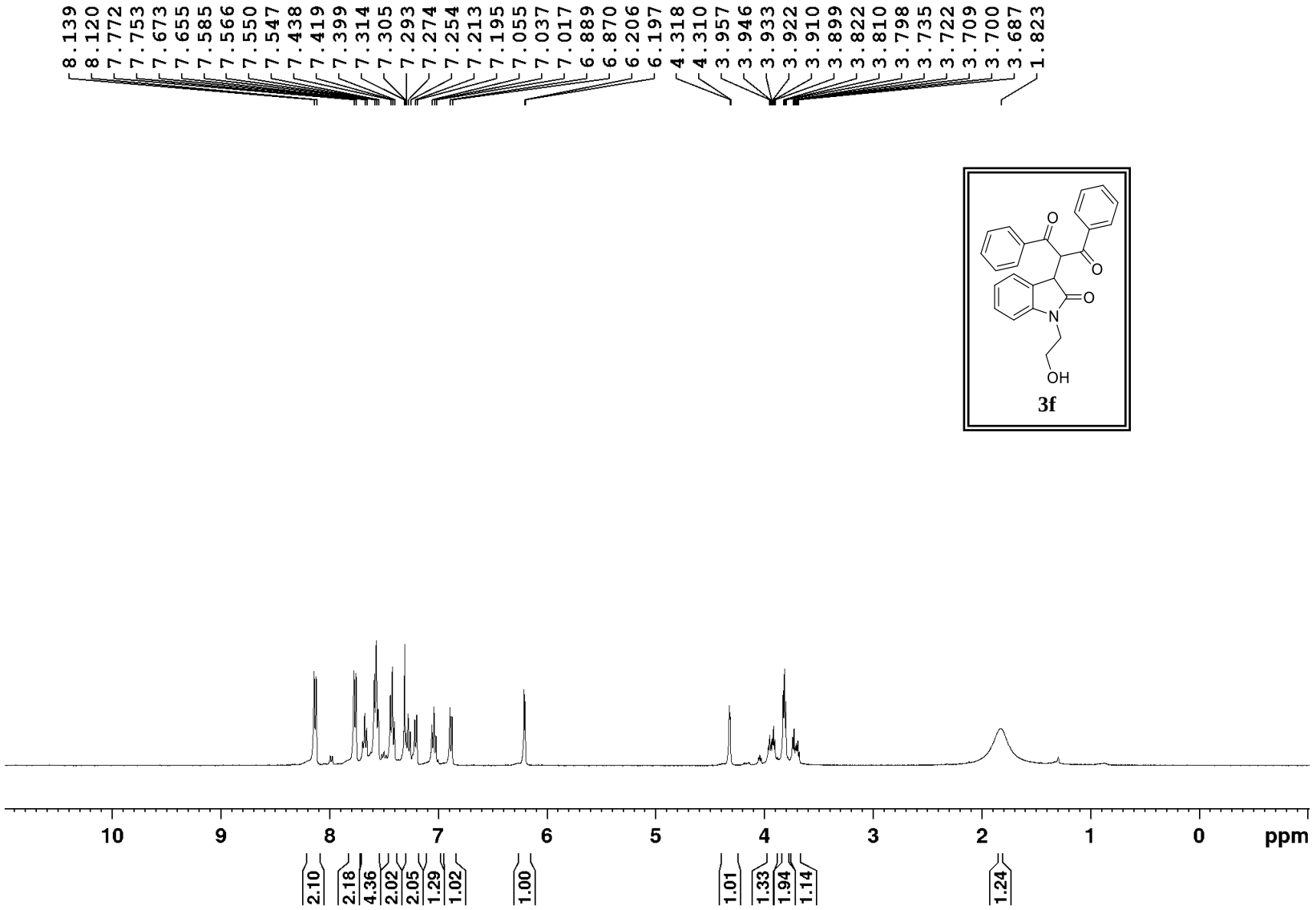


Figure 11: ^{1}H NMR spectrum of compound **3f** (400 MHz, $CDCl_3$)

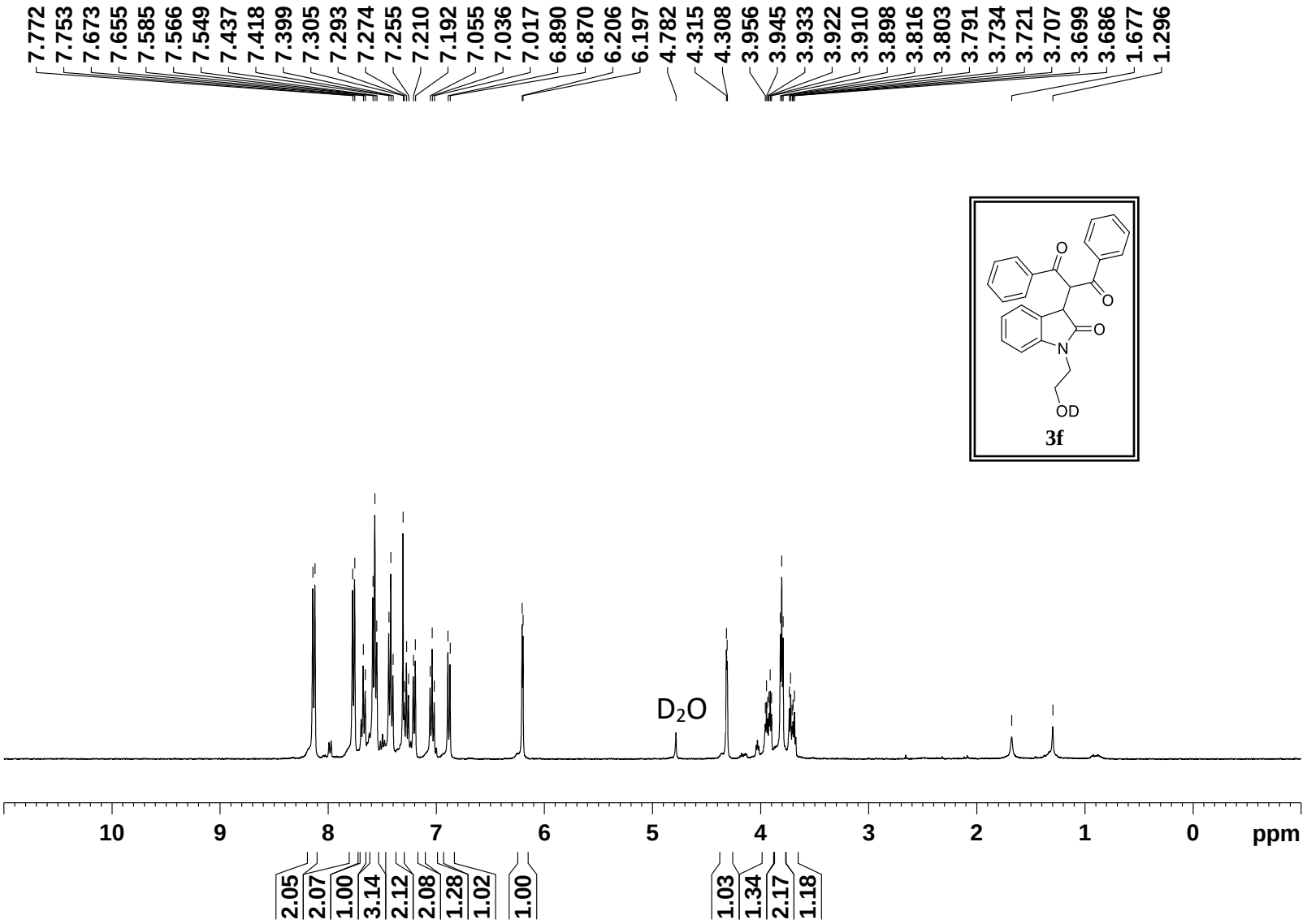


Figure 12: ^{1}H NMR spectrum of compound **3f** (400 MHz, $CDCl_3$, D_2O)

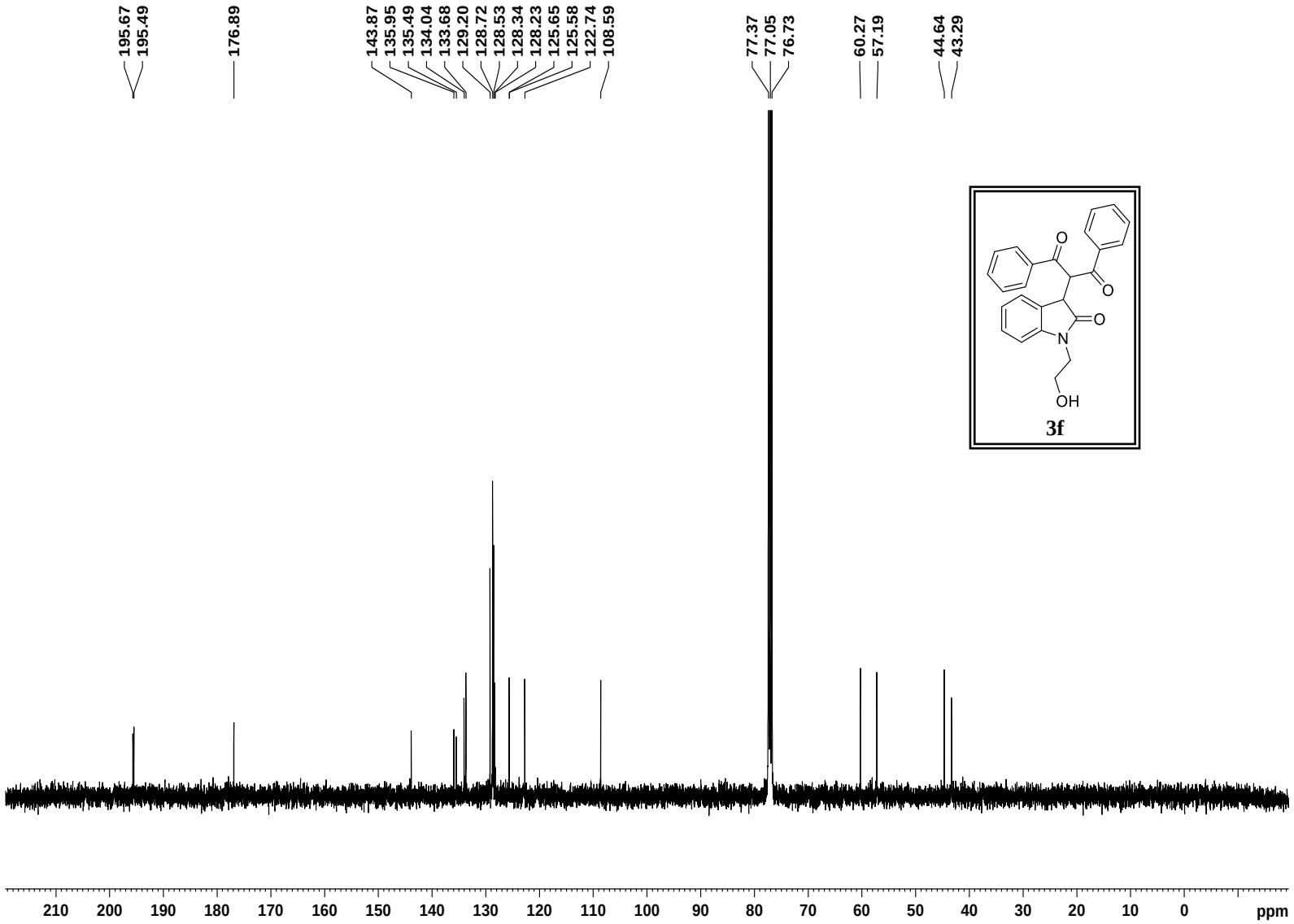


Figure 13: ^{13}C NMR spectrum of compound 3f (101 MHz, $CDCl_3$)

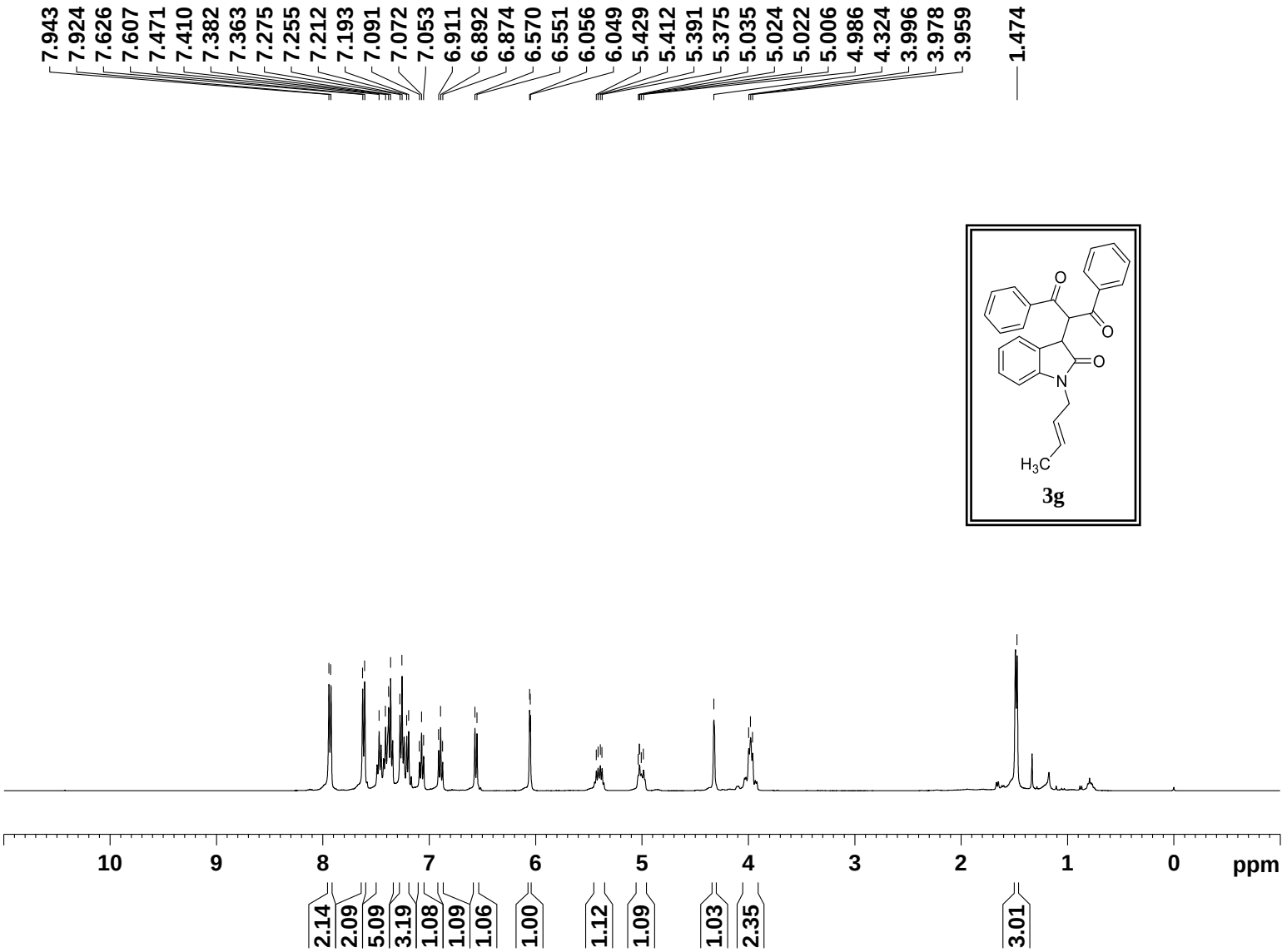


Figure 14: ^{1}H NMR spectrum of compound **3g** (400 MHz, $CDCl_3$)

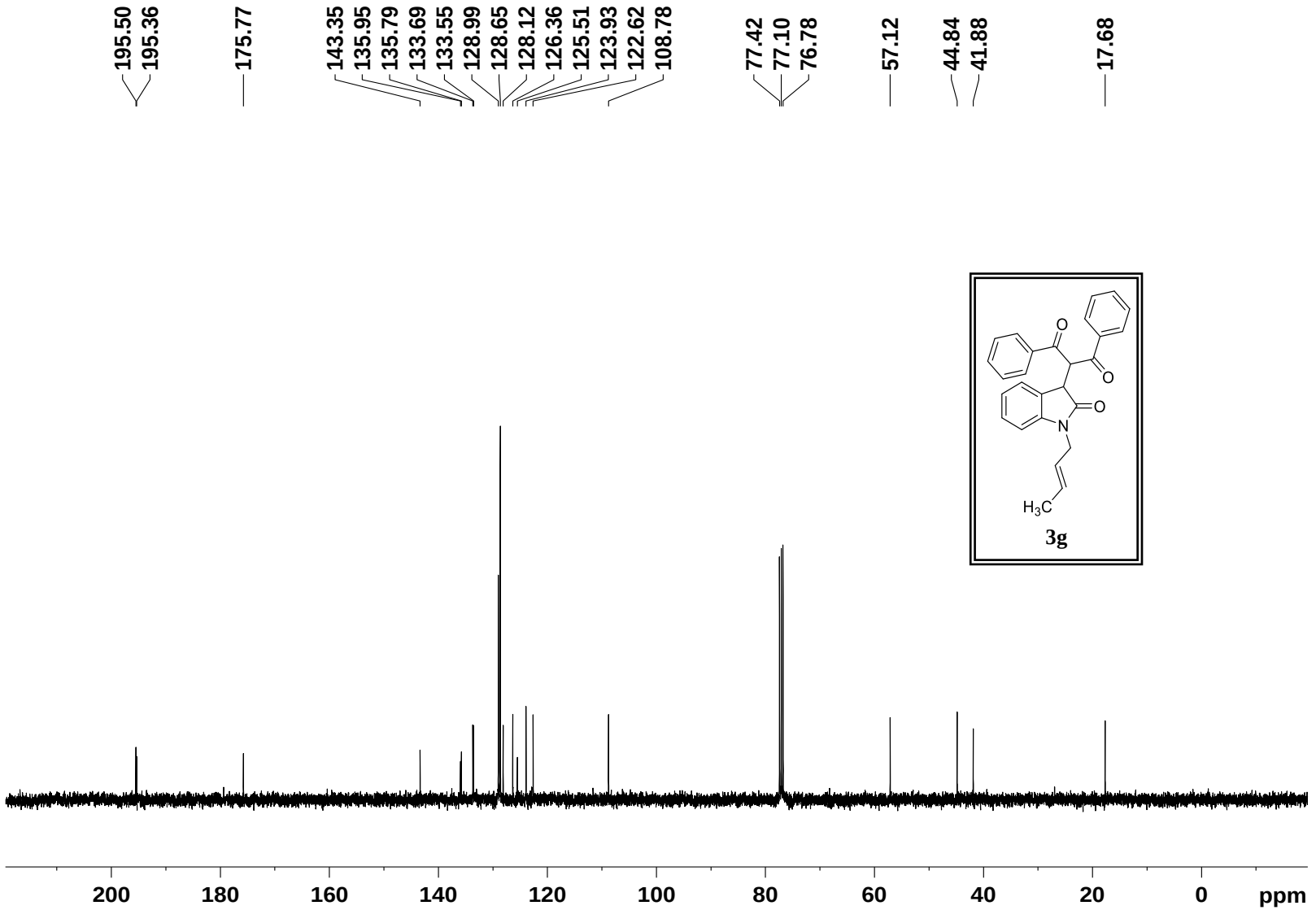


Figure 15: ^{13}C NMR spectrum of compound **3g** (101 MHz, $CDCl_3$)

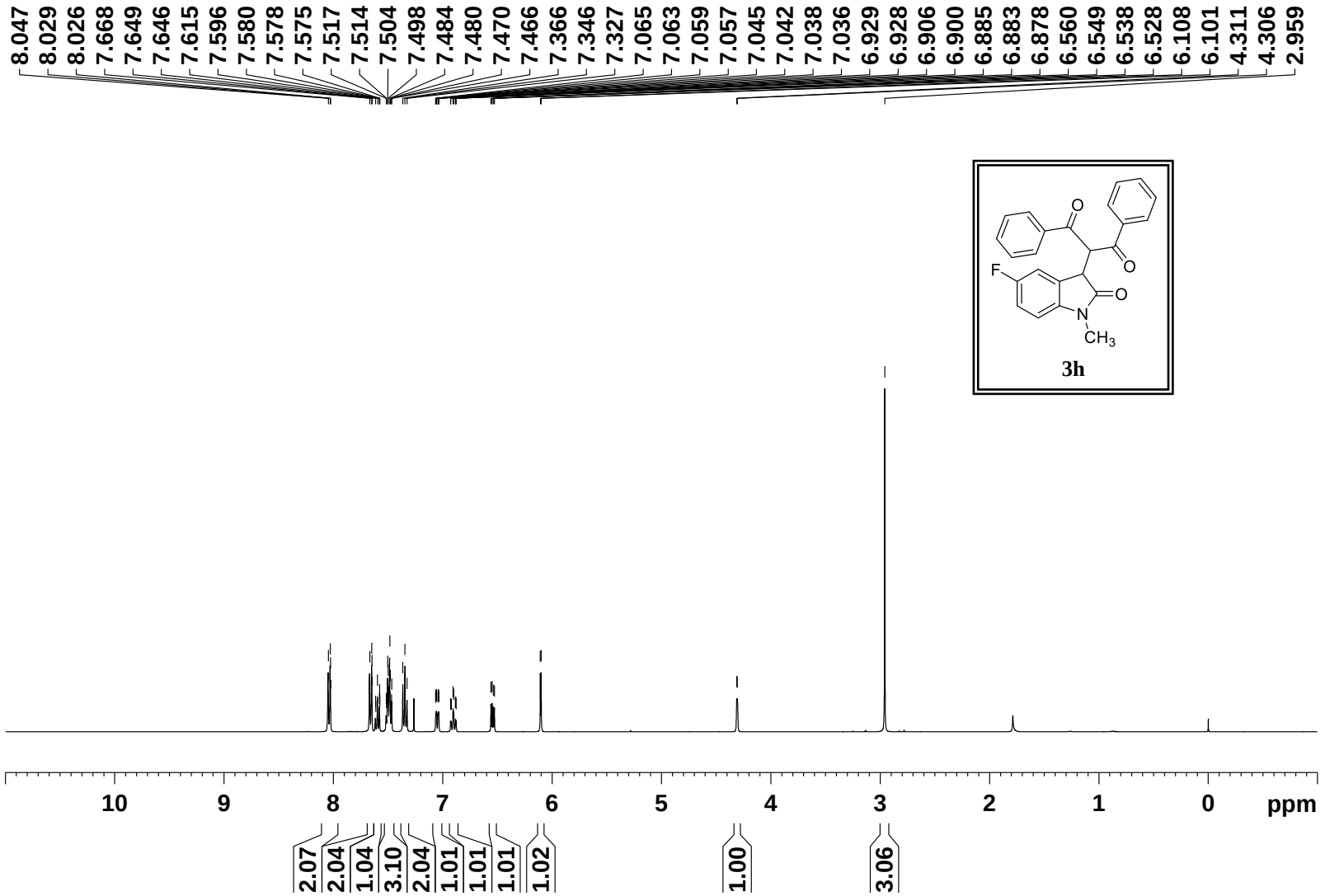


Figure 16: ^{1}H NMR spectrum of compound **3h** (400 MHz, $CDCl_3$)

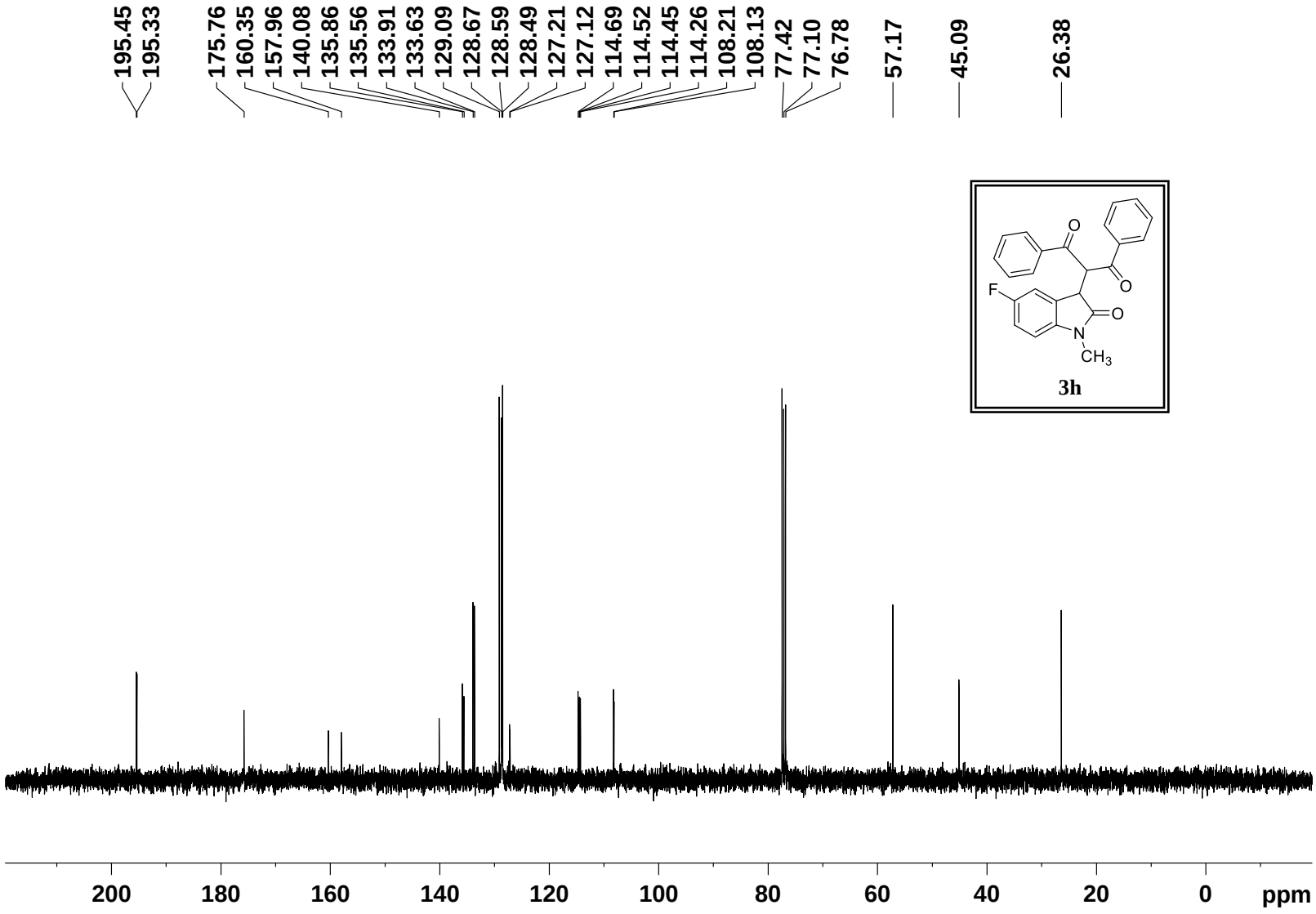


Figure 17: ^{13}C NMR spectrum of compound **3h** (101 MHz, $CDCl_3$)

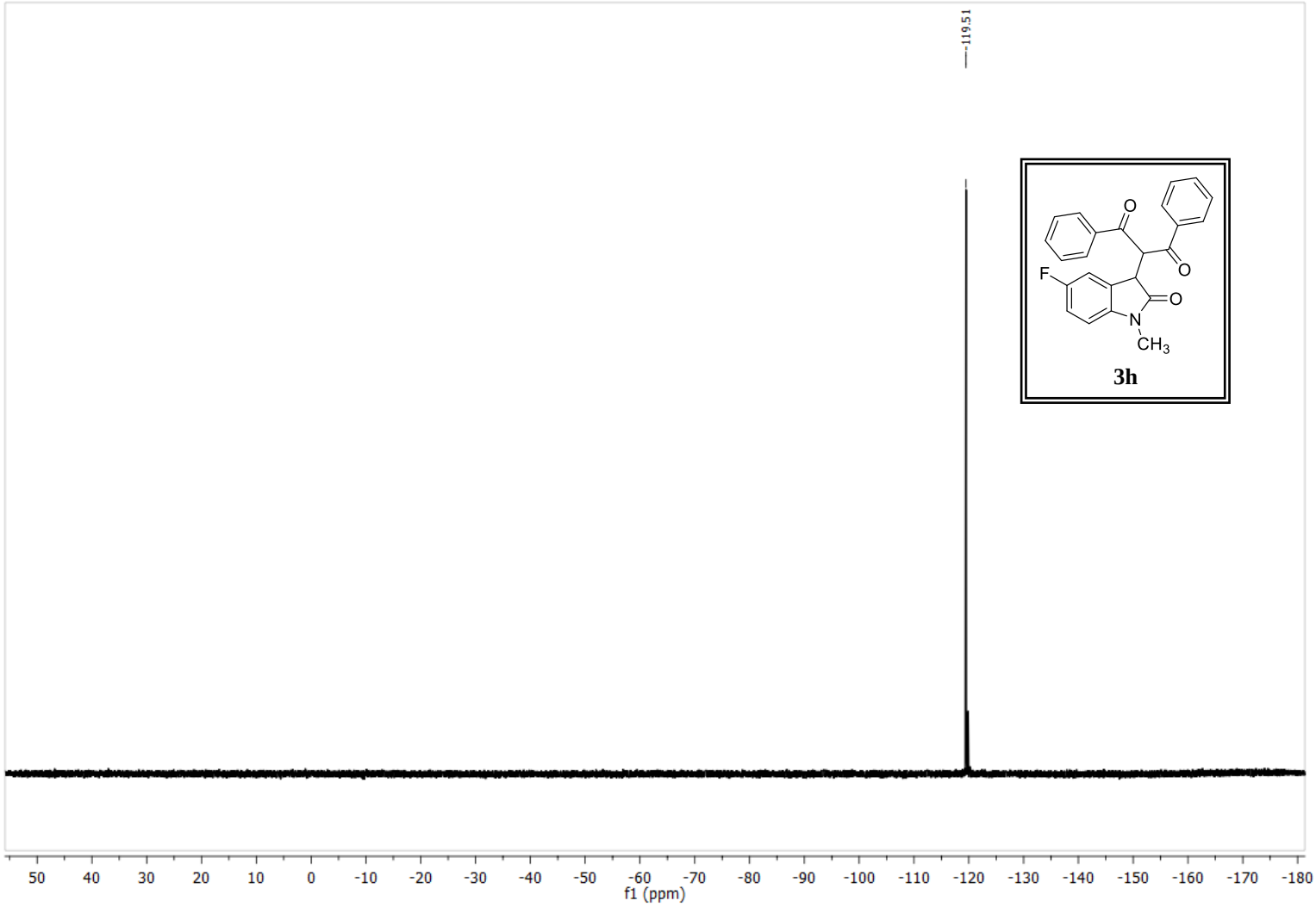


Figure 18: ^{19}F NMR spectrum of compound **3h** (162 MHz, $CDCl_3$)

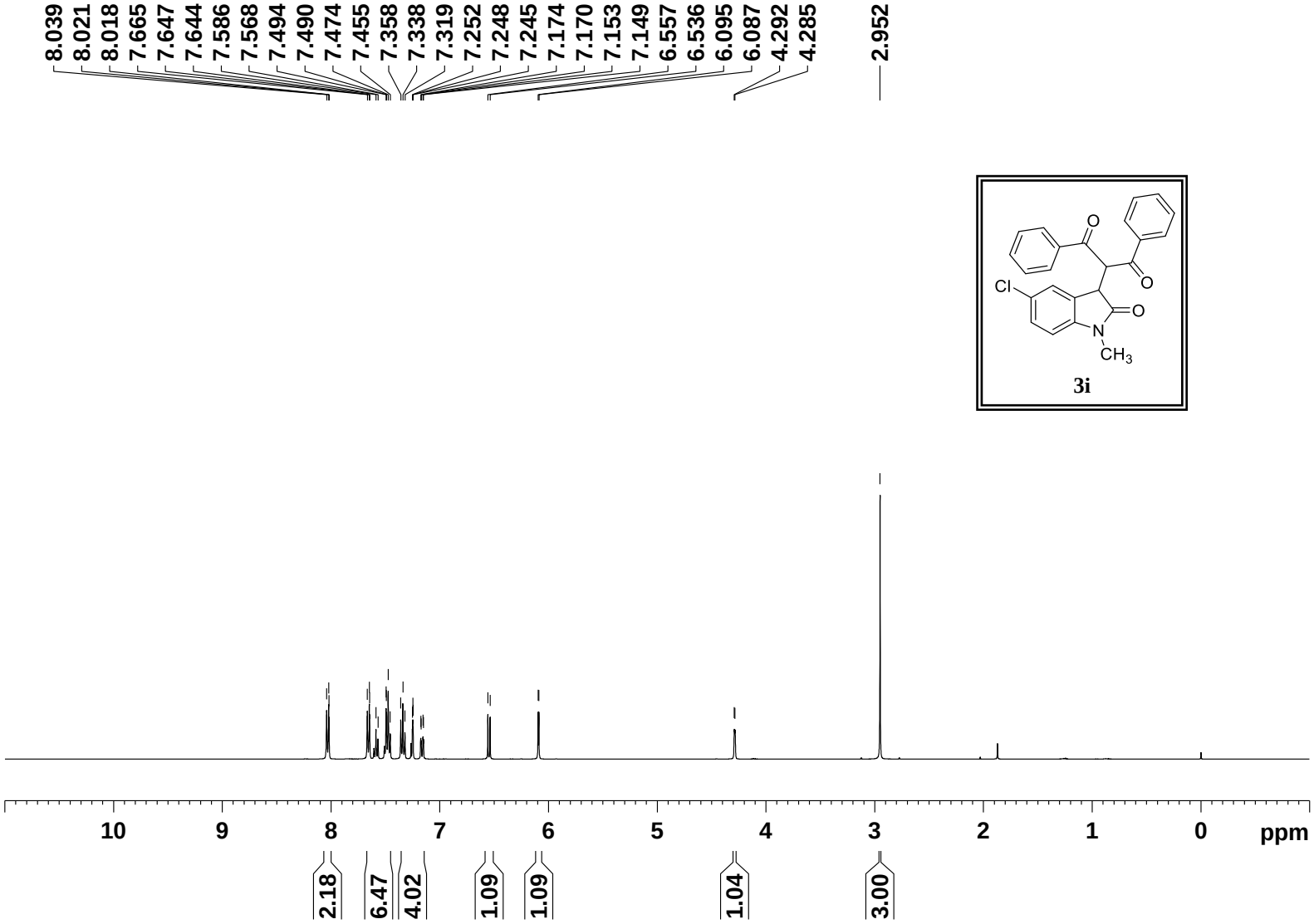


Figure 19: ^{1}H NMR spectrum of compound **3i** (400 MHz, $CDCl_3$)

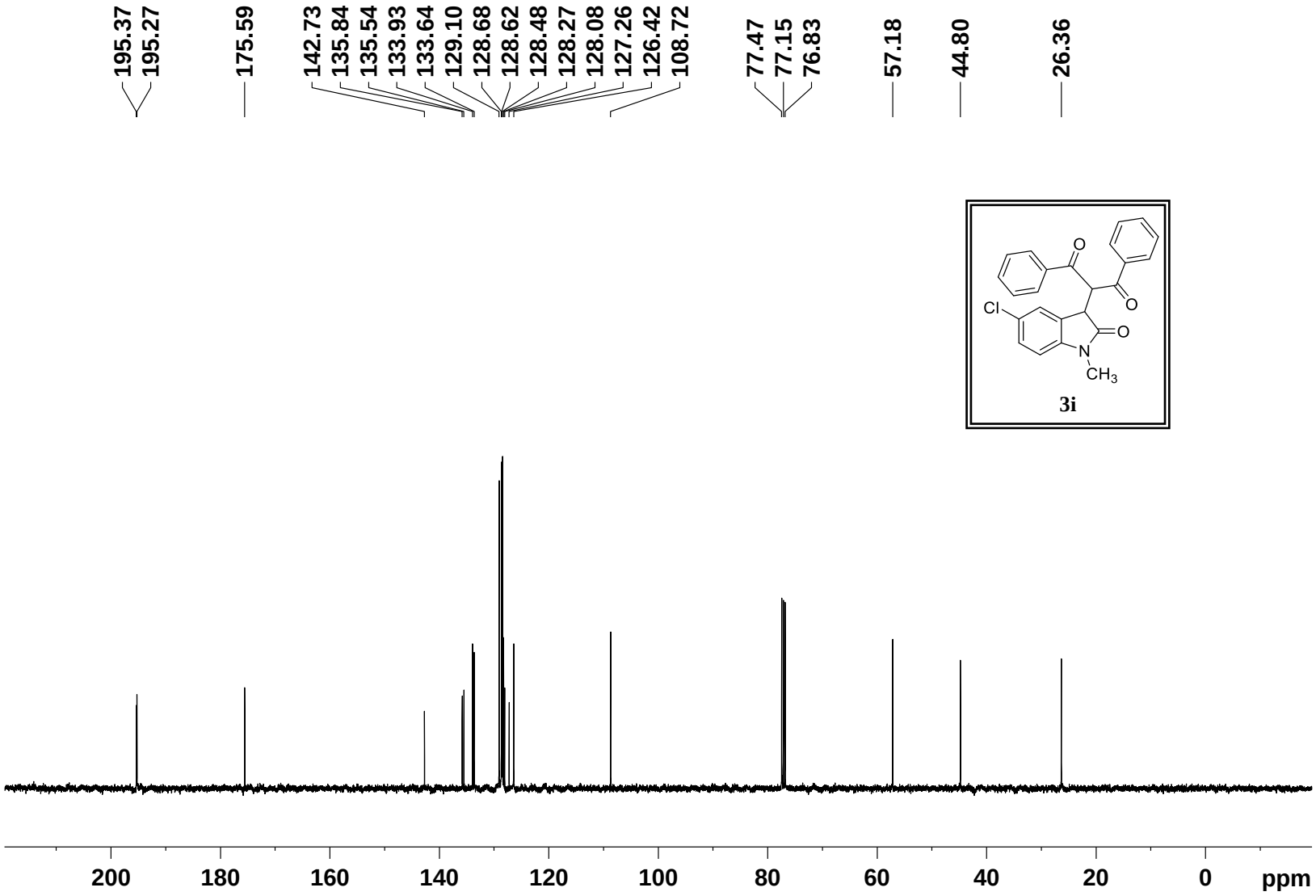


Figure 20: ^{13}C NMR spectrum of compound **3i** (101 MHz, $CDCl_3$)

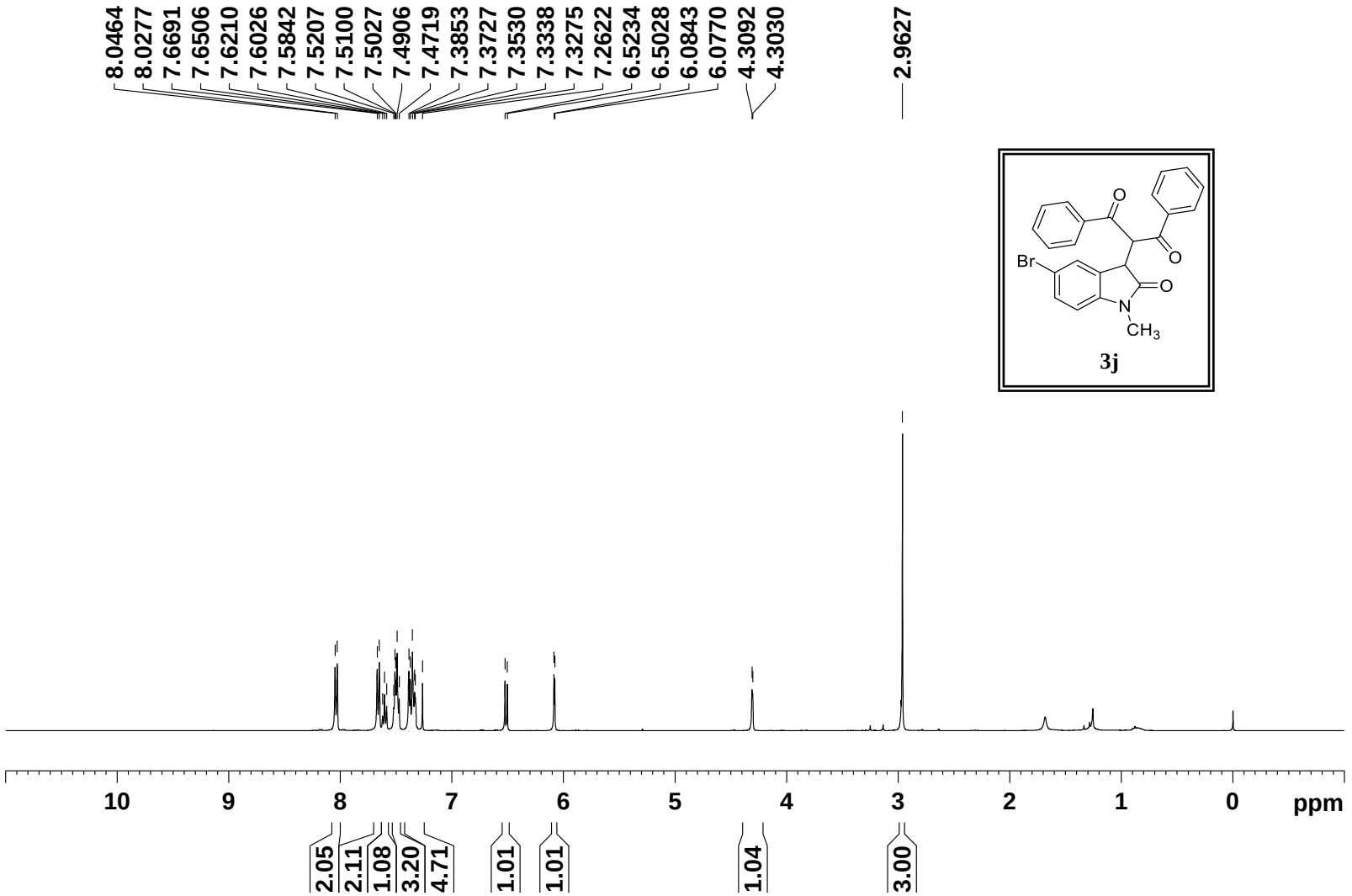


Figure 21: ^{1}H NMR spectrum of compound **3j** (400 MHz, $CDCl_3$)

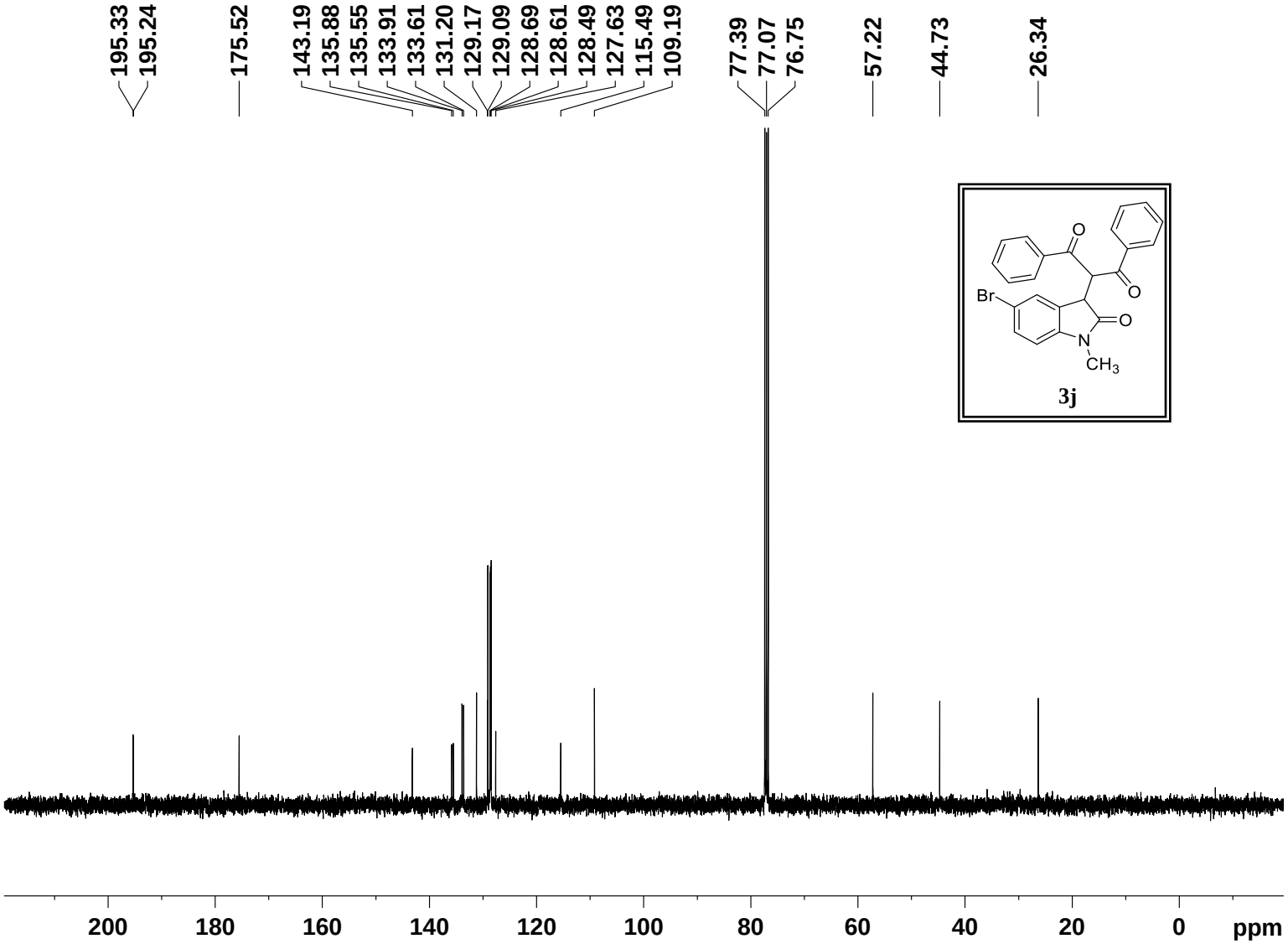


Figure 22: ^{13}C NMR spectrum of compound **3j** (101 MHz, $CDCl_3$)

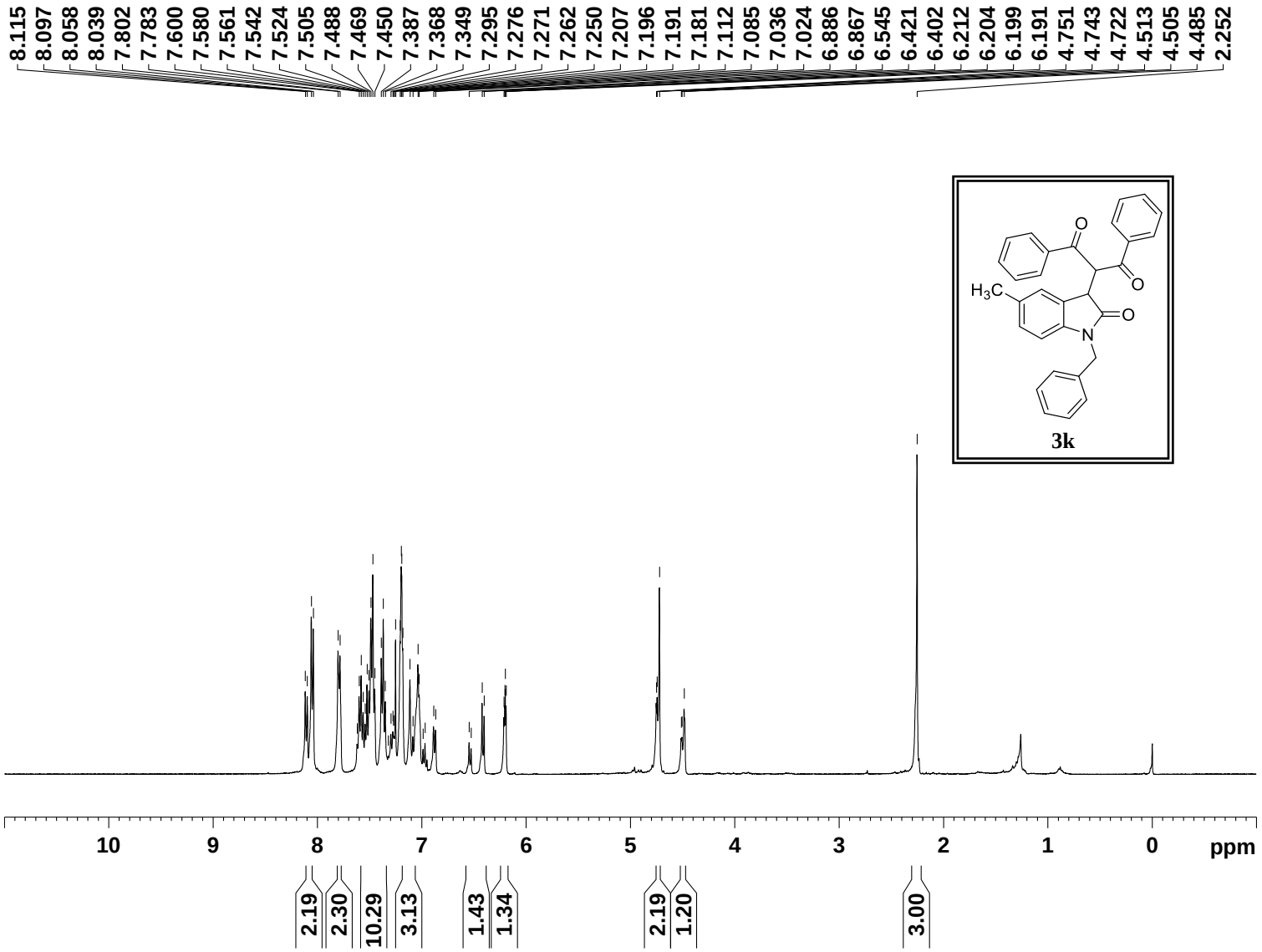


Figure 23: ^{1}H NMR spectrum of compound **3k** (400 MHz, $CDCl_3$)

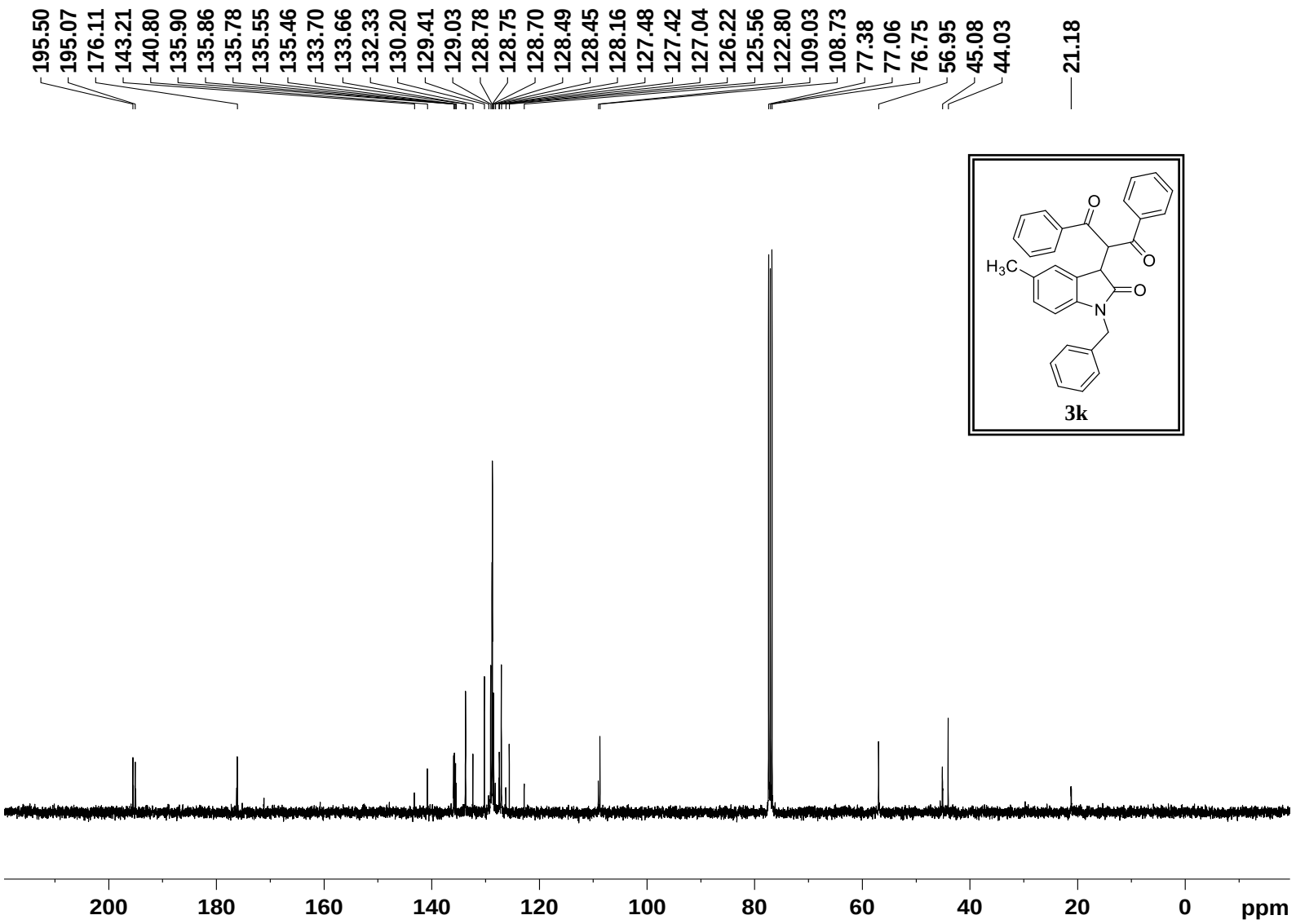


Figure 24: ^{13}C NMR spectrum of compound **3k** (101 MHz, $CDCl_3$)

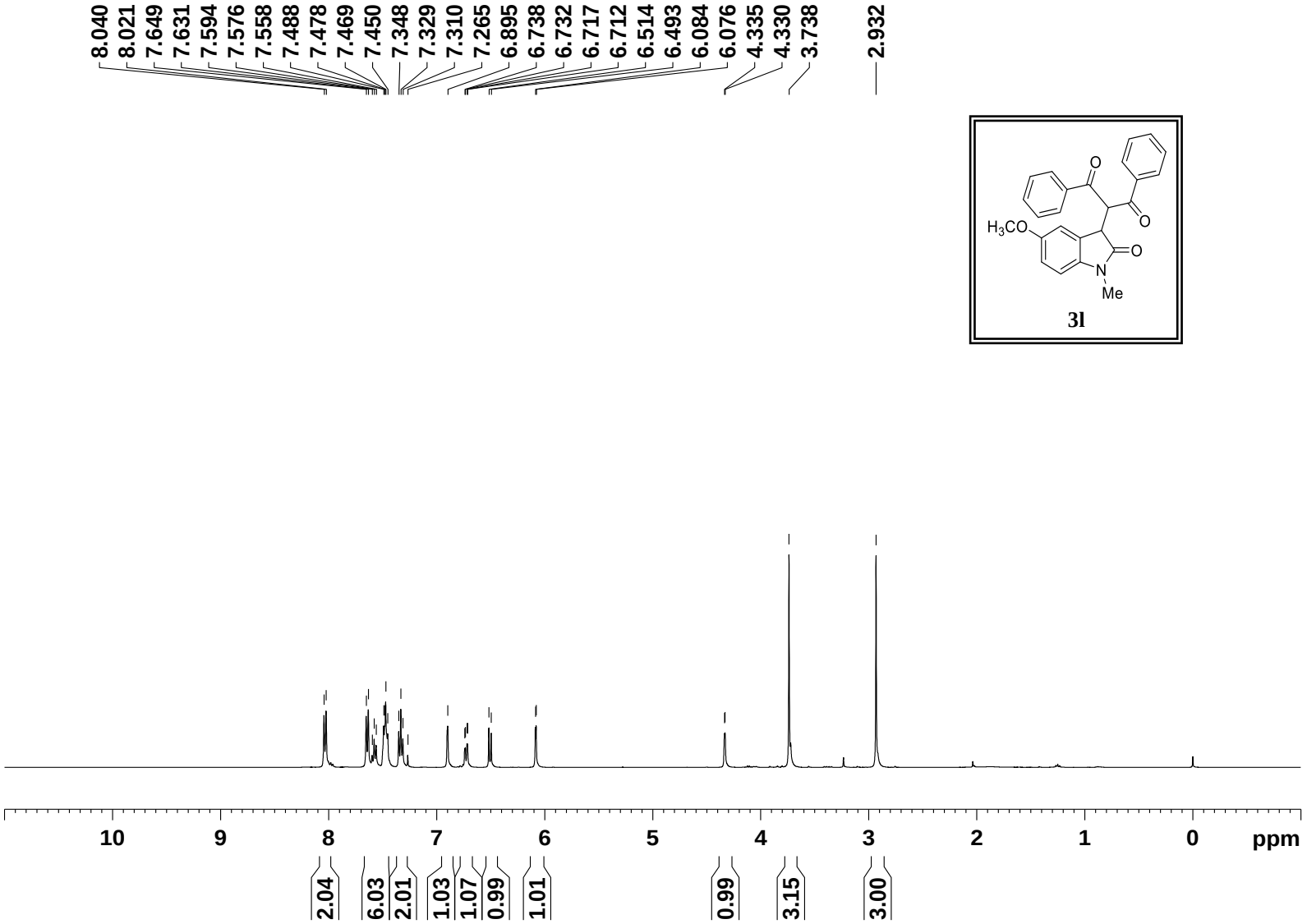


Figure 25: ^{1}H NMR spectrum of compound **3l** (400 MHz, $CDCl_3$)

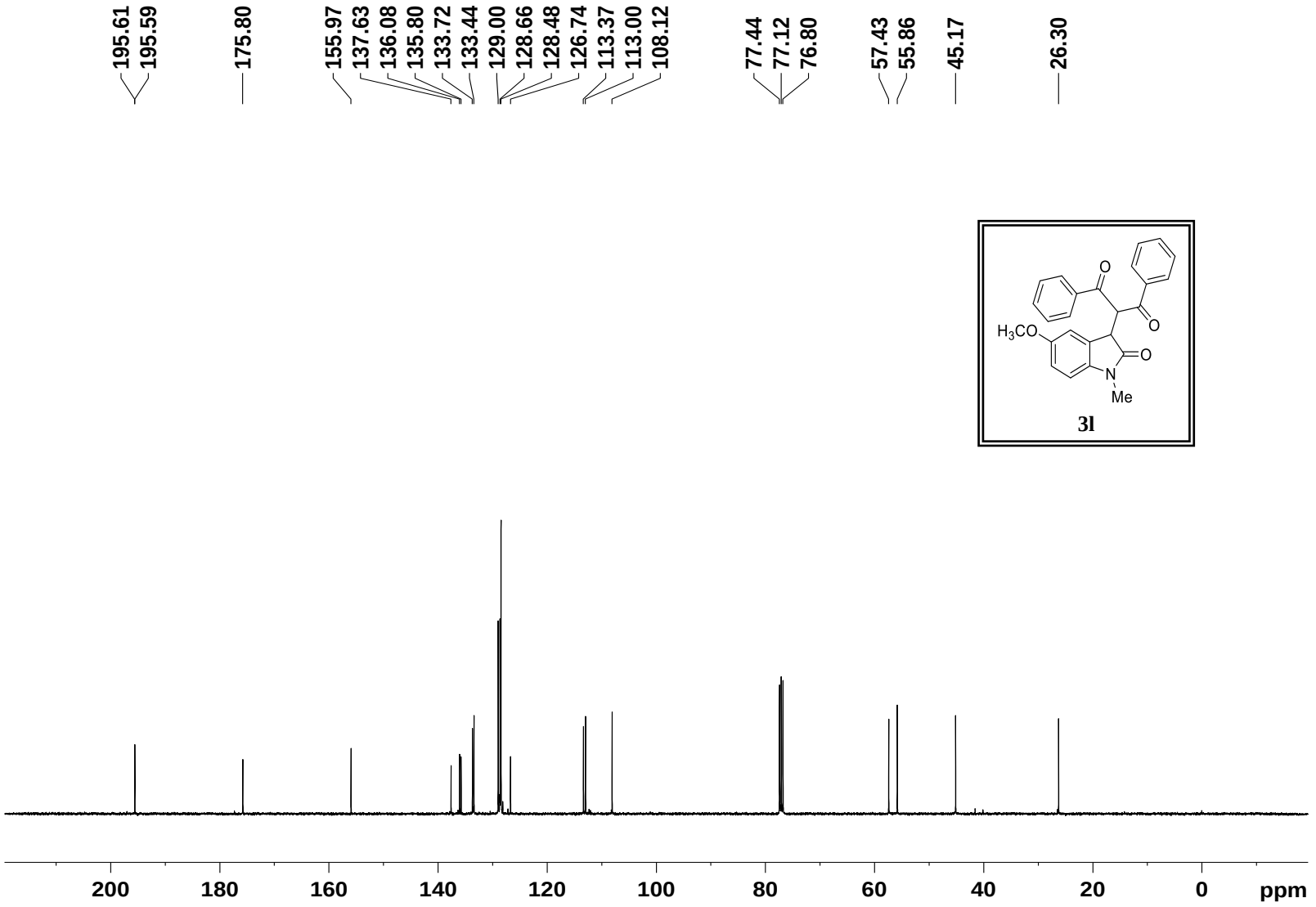


Figure 26: ^{13}C NMR spectrum of compound **3l** (101 MHz, $CDCl_3$)

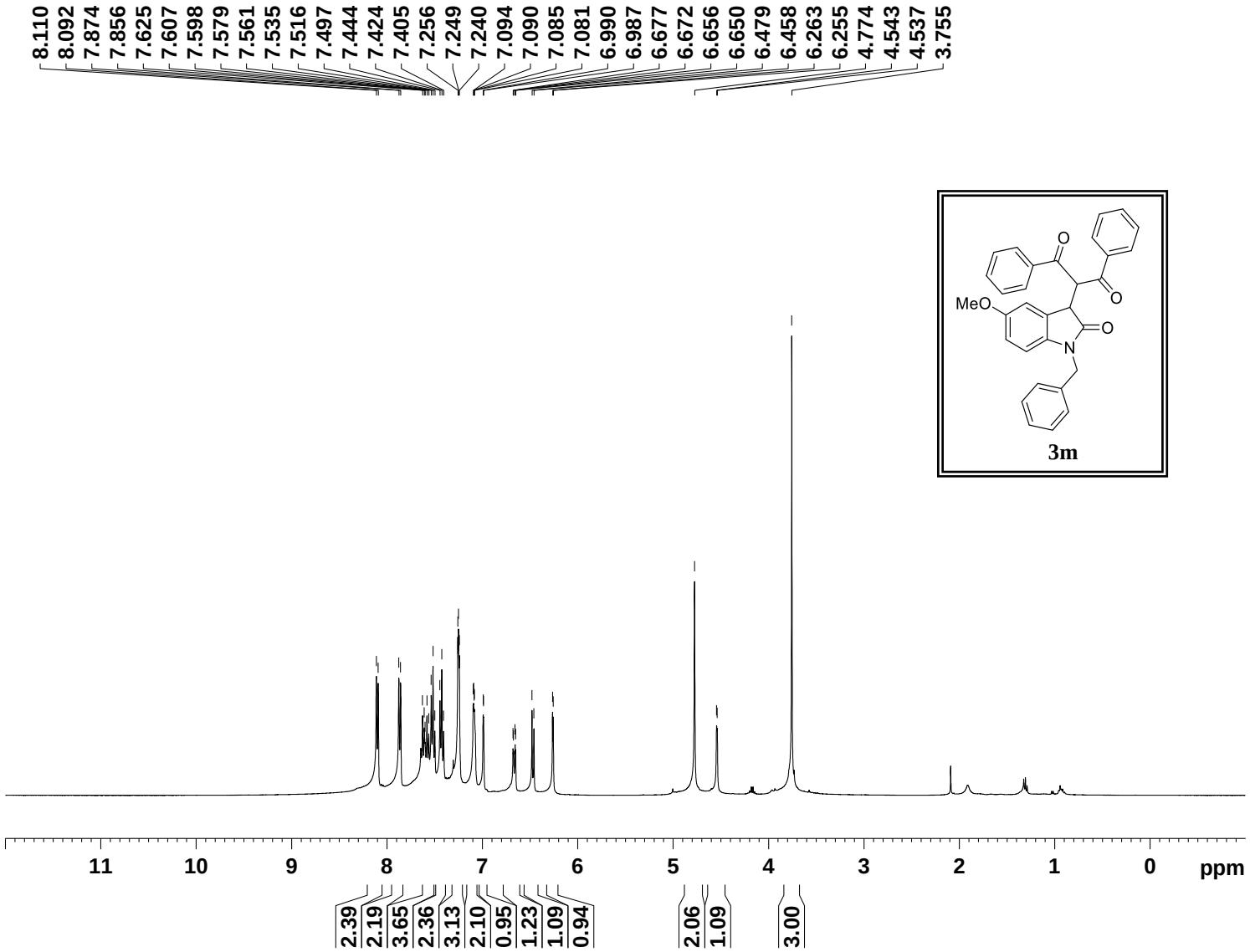


Figure 27: ^{1}H NMR spectrum of compound **3m** (400 MHz, $CDCl_3$)

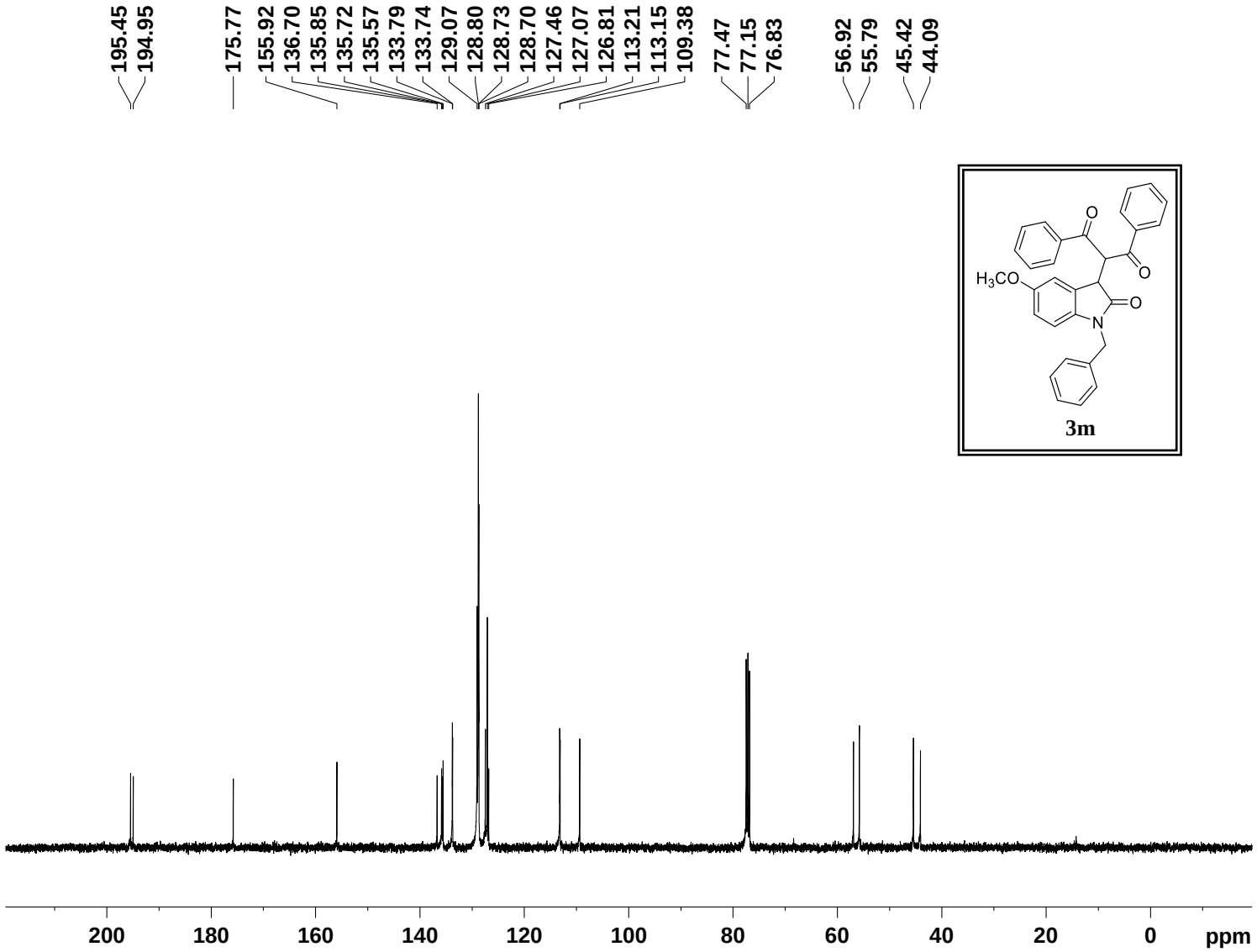


Figure 28: ^{13}C NMR spectrum of compound **3m** (101 MHz, $CDCl_3$)

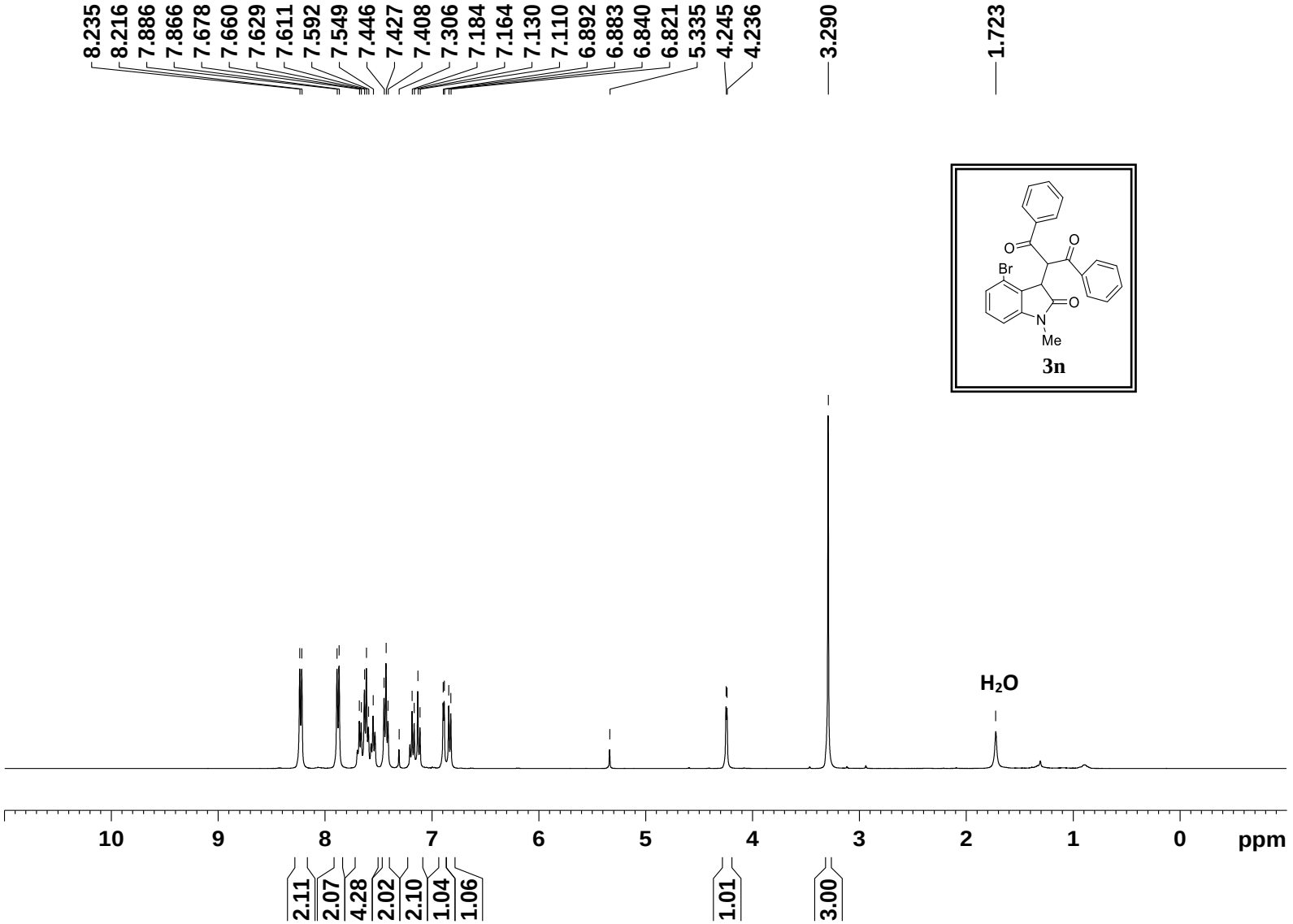


Figure 29: ^{1}H NMR spectrum of compound **3n** (400 MHz, $CDCl_3$)

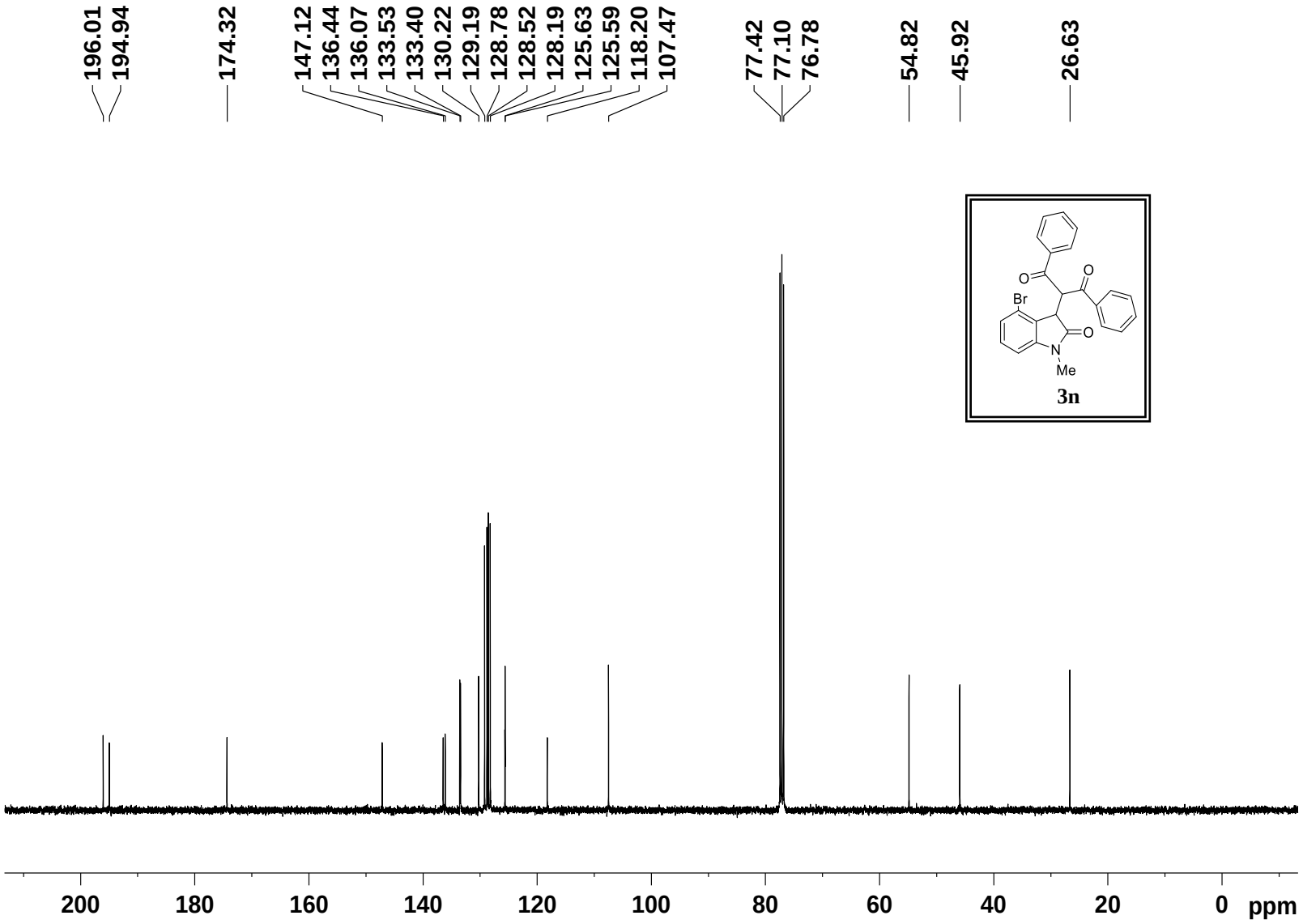


Figure 30: ^{13}C NMR spectrum of compound **3n** (101 MHz, $CDCl_3$)

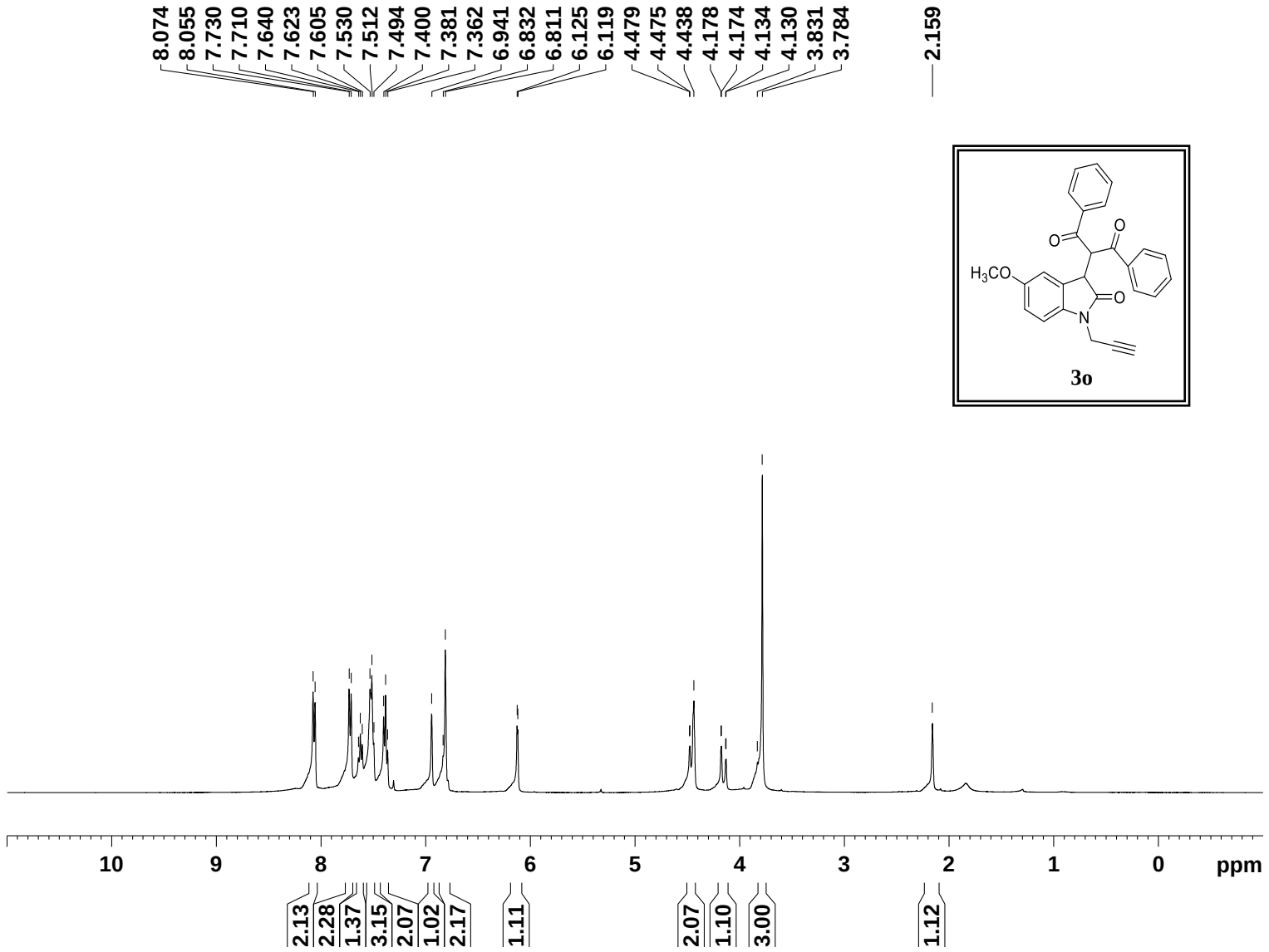


Figure 31: ^{1}H NMR spectrum of compound **3o** (400 MHz, $CDCl_3$)

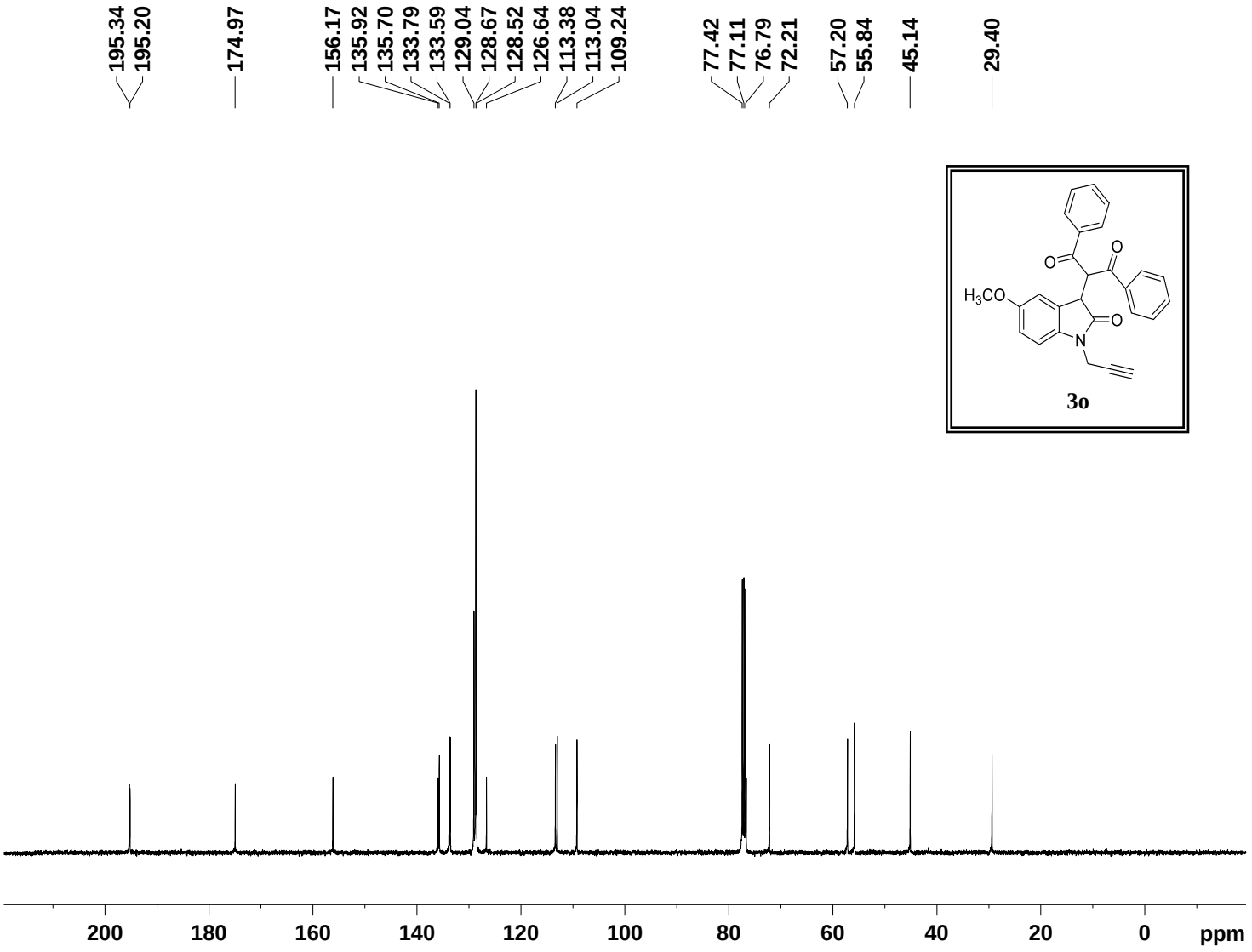


Figure 32: ^{13}C NMR spectrum of compound **3o** (101 MHz, $CDCl_3$)

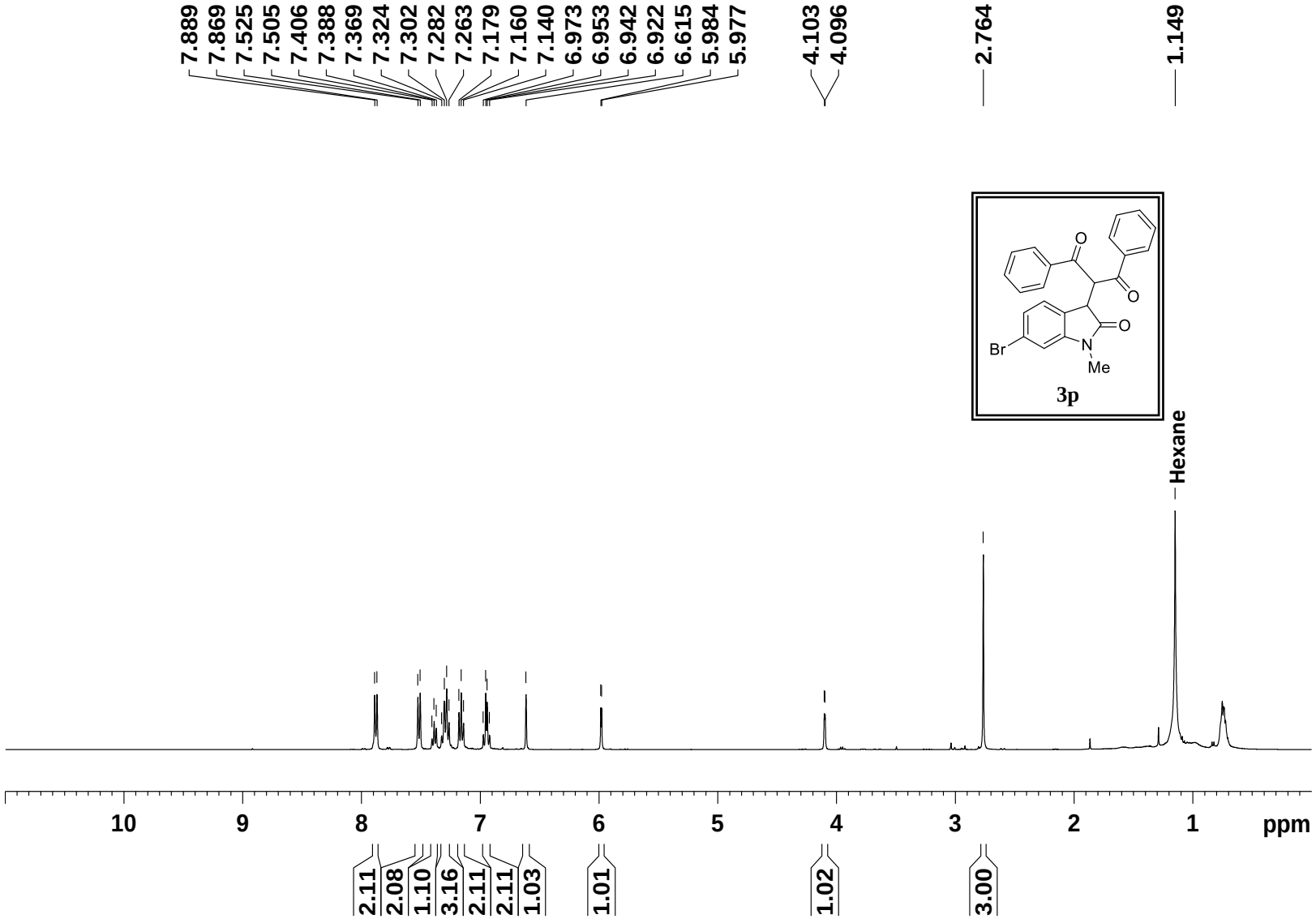


Figure 33: ^{1}H NMR spectrum of compound **3p** (400 MHz, $CDCl_3$)

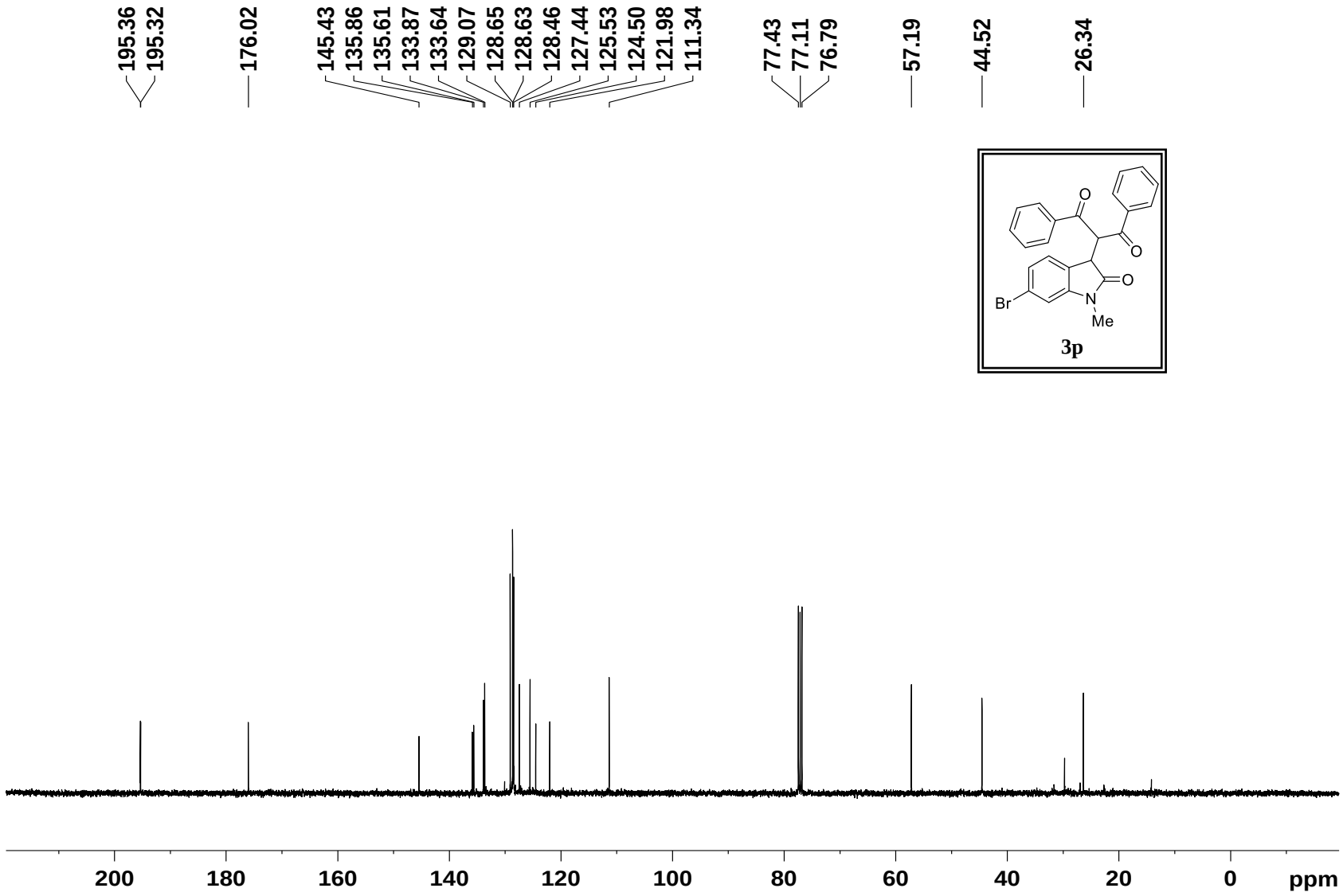


Figure 34: ^{13}C NMR spectrum of compound **3p** (101 MHz, $CDCl_3$)

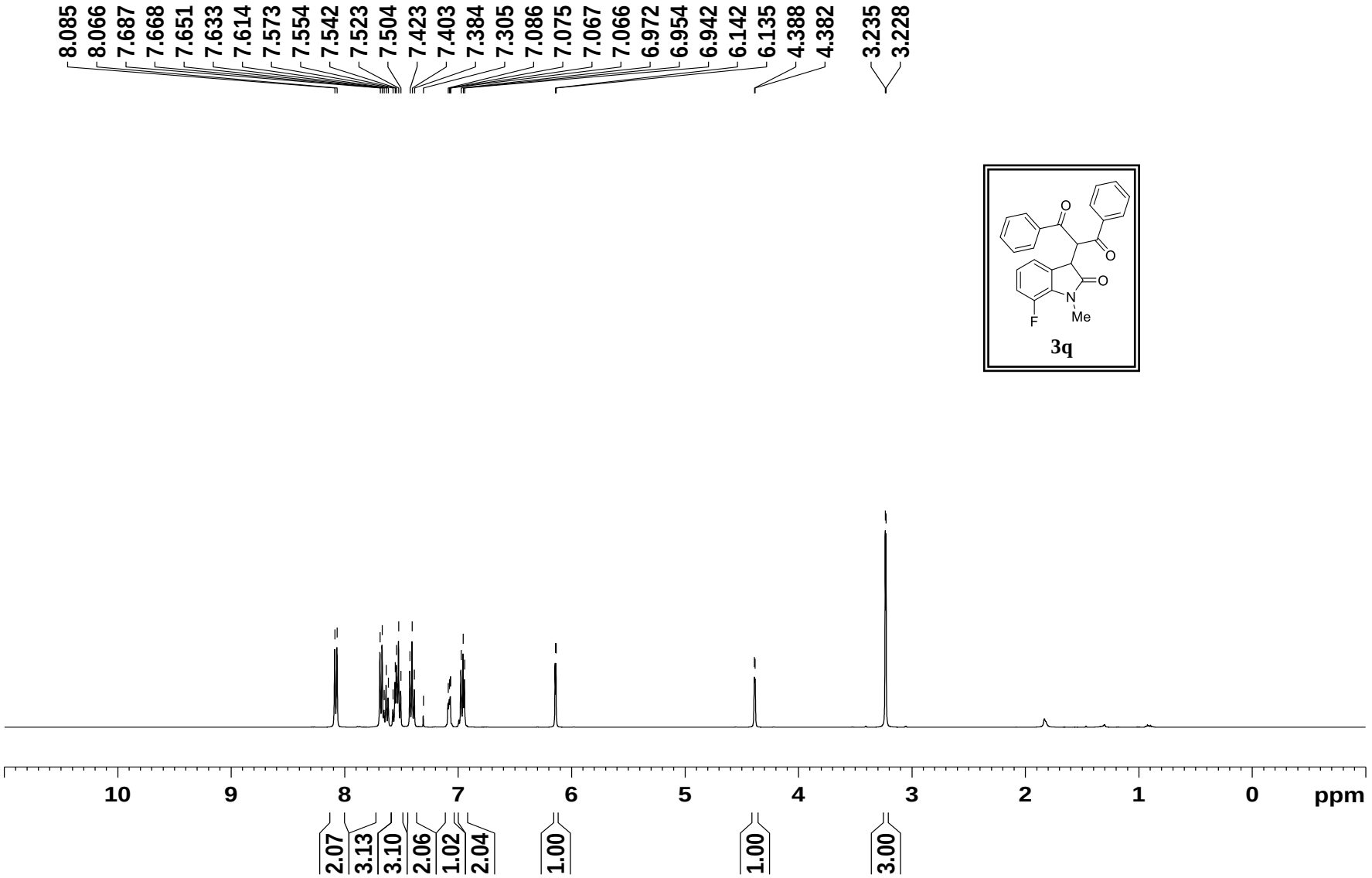


Figure 35: ^{1}H NMR spectrum of compound **3q** (400 MHz, $CDCl_3$)

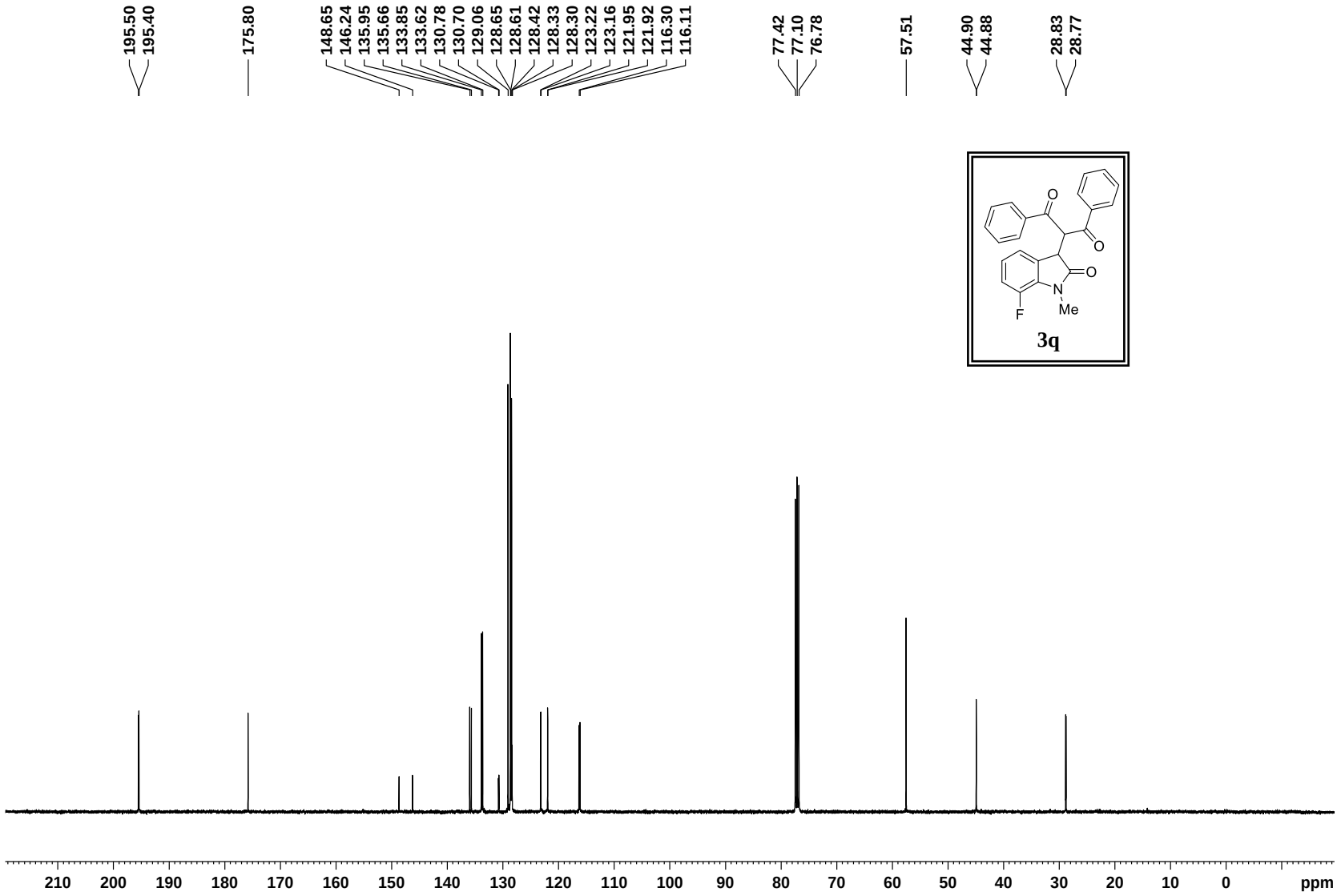


Figure 36: ^{13}C NMR spectrum of compound **3q** (101 MHz, $CDCl_3$)

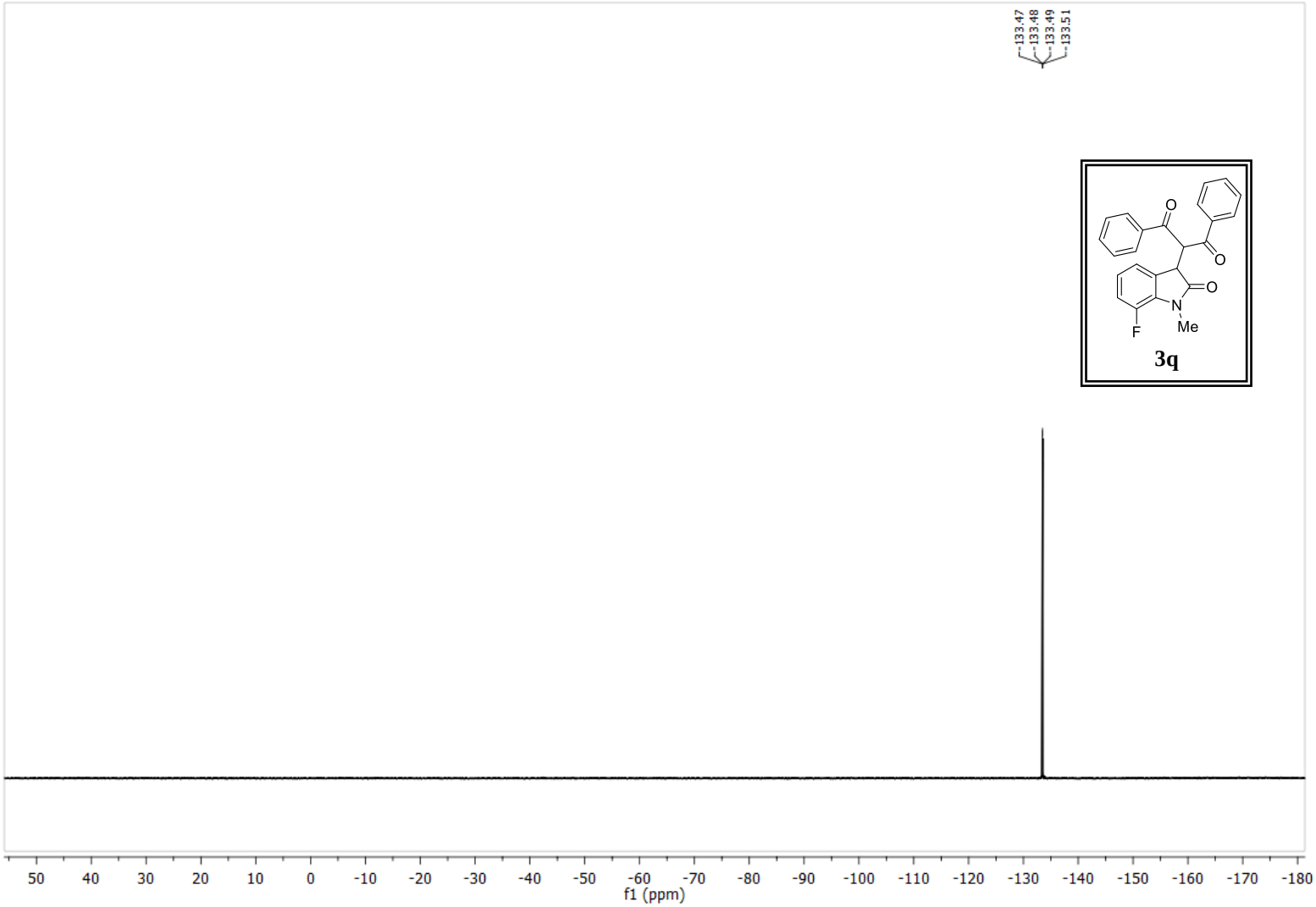


Figure 37: ^{19}F NMR spectrum of compound **3q** (162 MHz, $CDCl_3$)

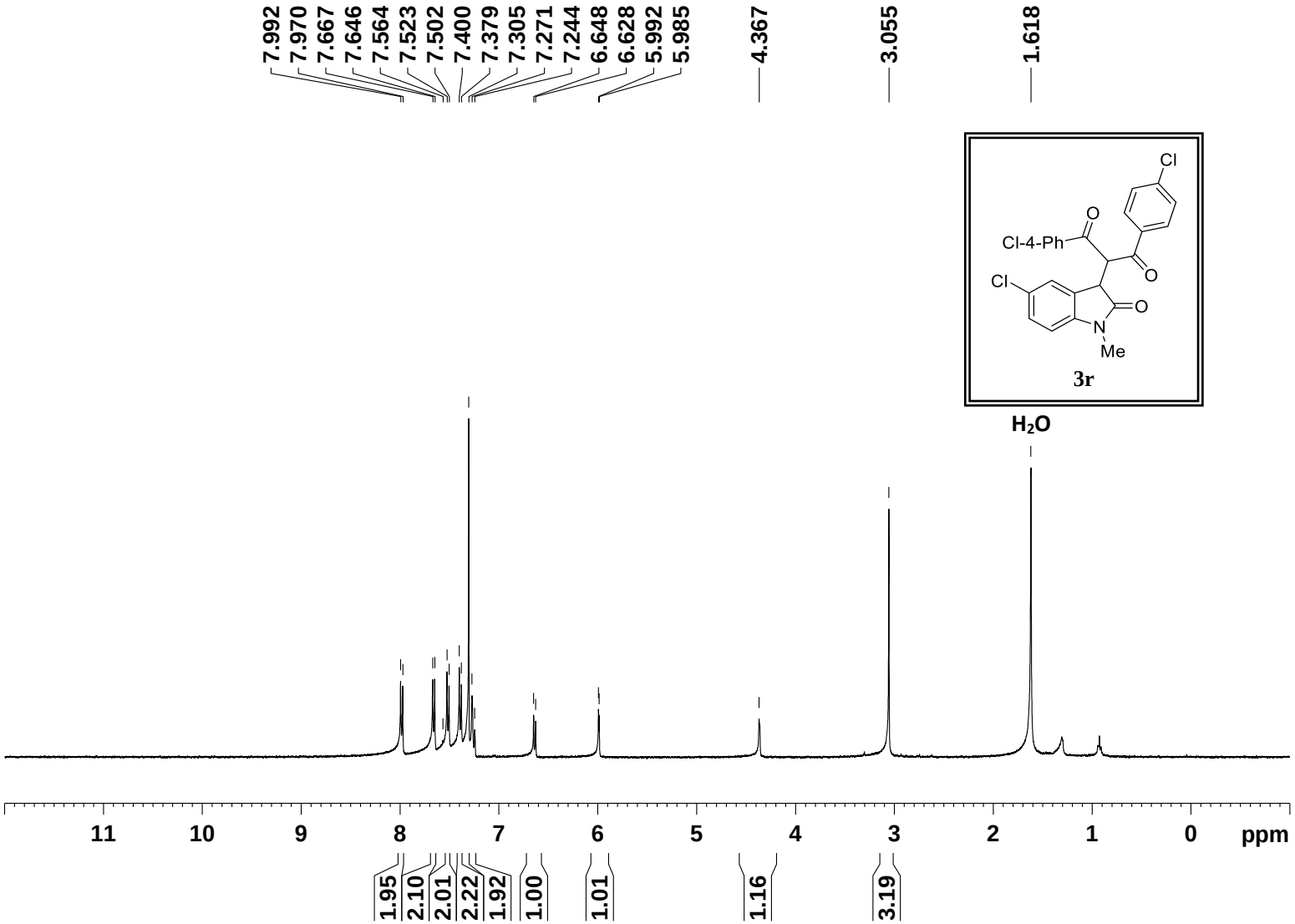


Figure 38: ^{1}H NMR spectrum of compound **3r** (400 MHz, $CDCl_3$)

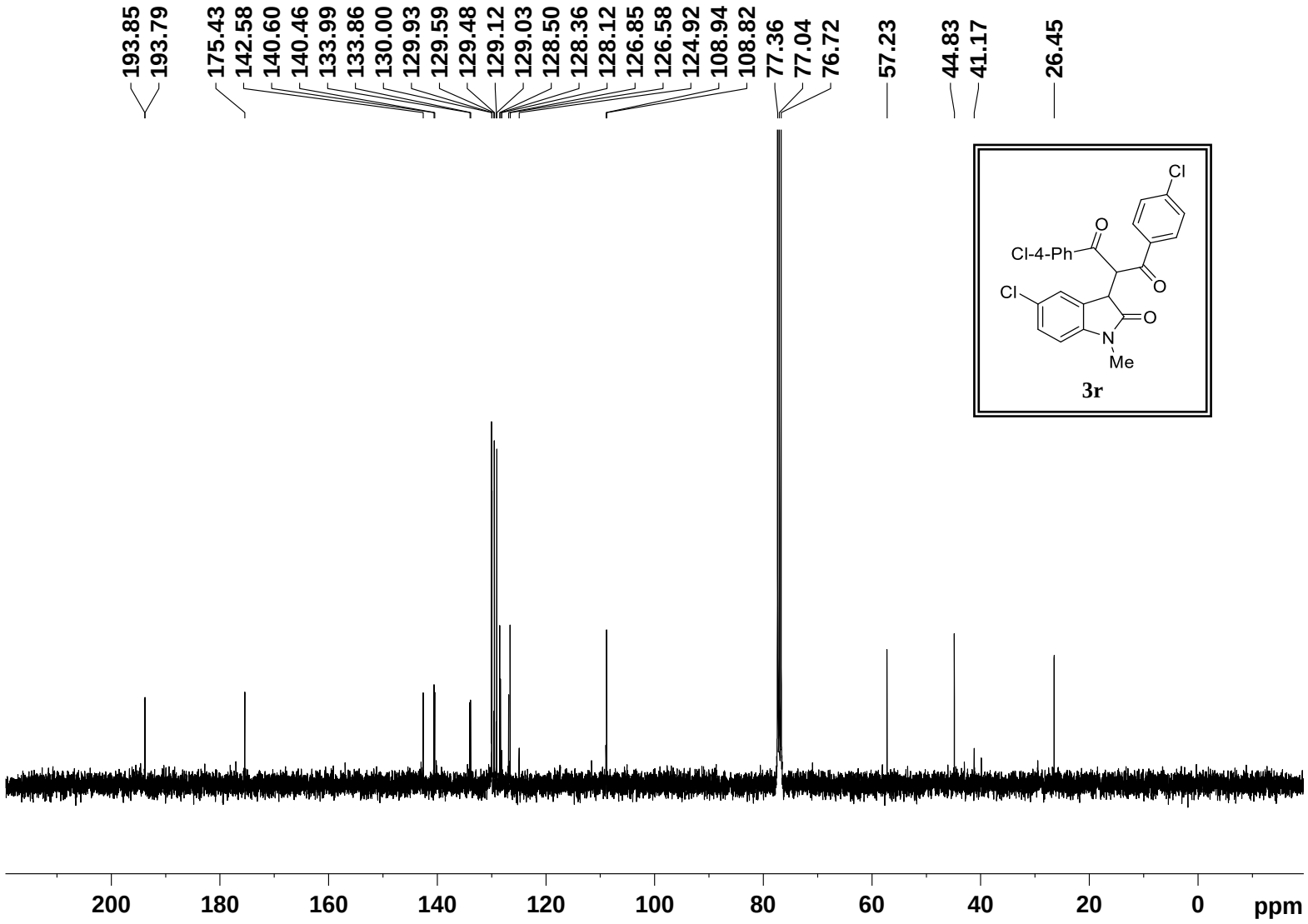


Figure 39: ^{13}C NMR spectrum of compound **3r** (101 MHz, $CDCl_3$)

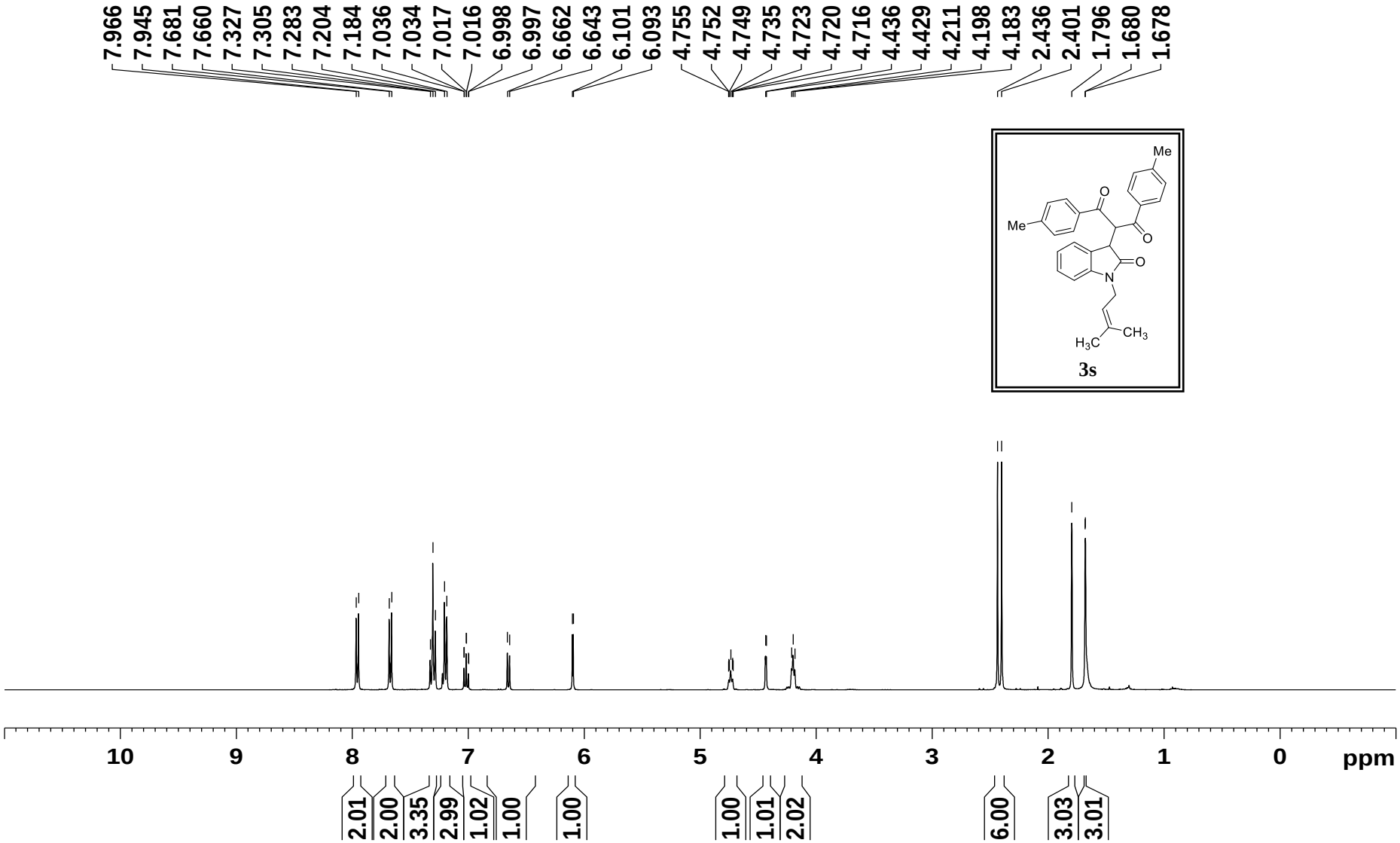


Figure 40: ^{1}H NMR spectrum of compound **3s** (400 MHz, $CDCl_3$)

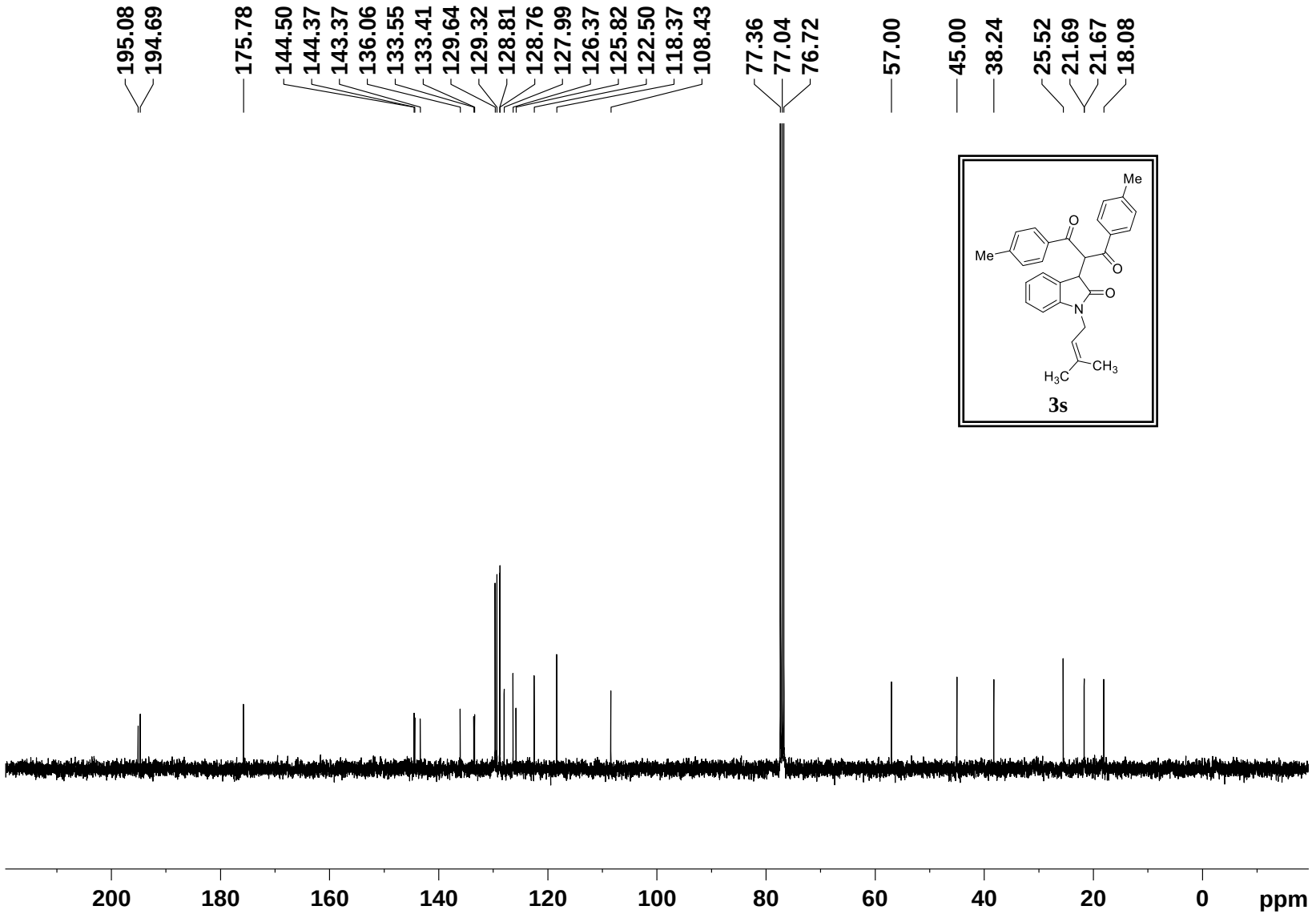


Figure 41: ^{13}C NMR spectrum of compound **3s** (101 MHz, $CDCl_3$)

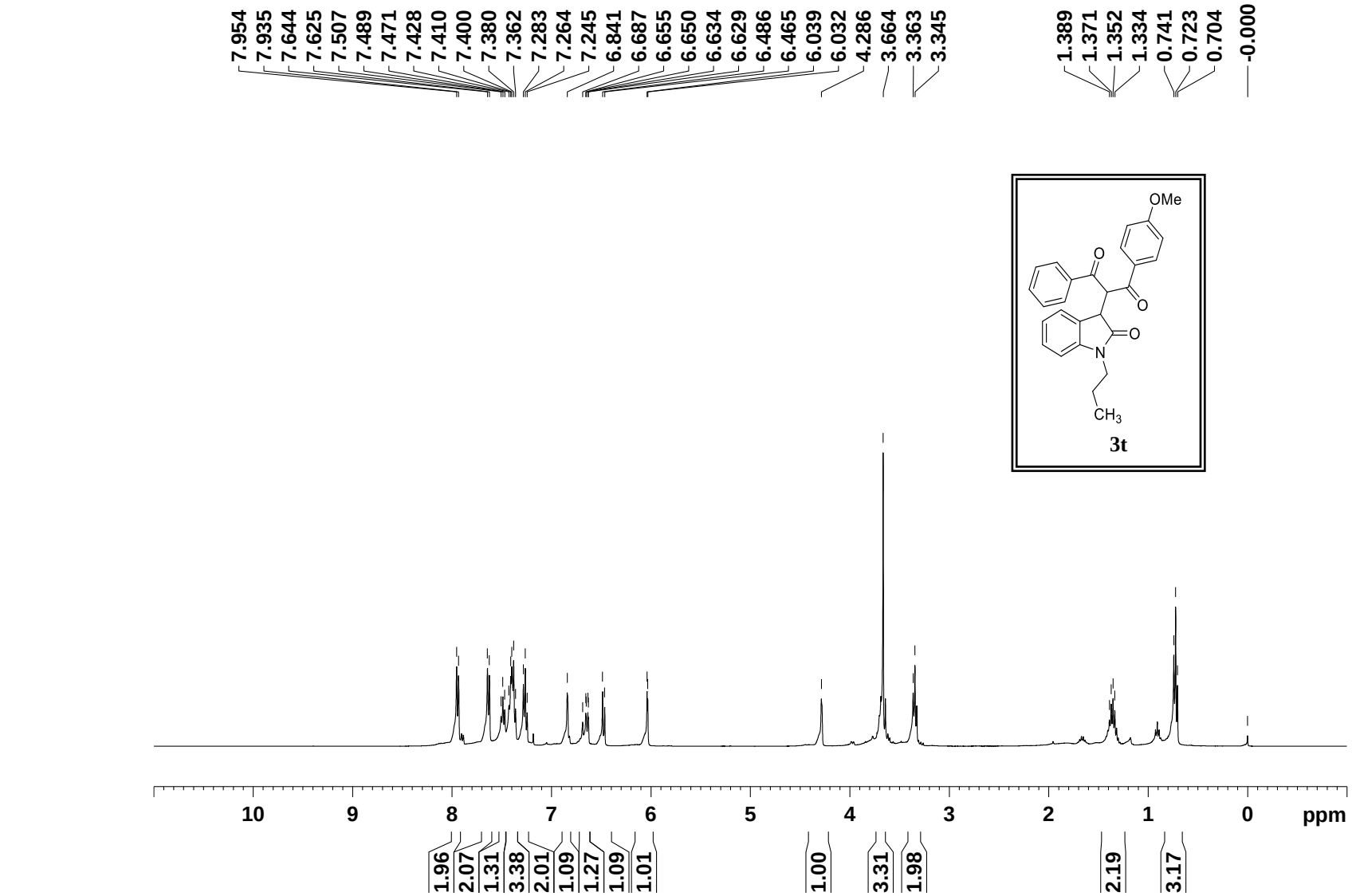


Figure 42: ^{1}H NMR spectrum of compound **3t** (400 MHz, $CDCl_3$)

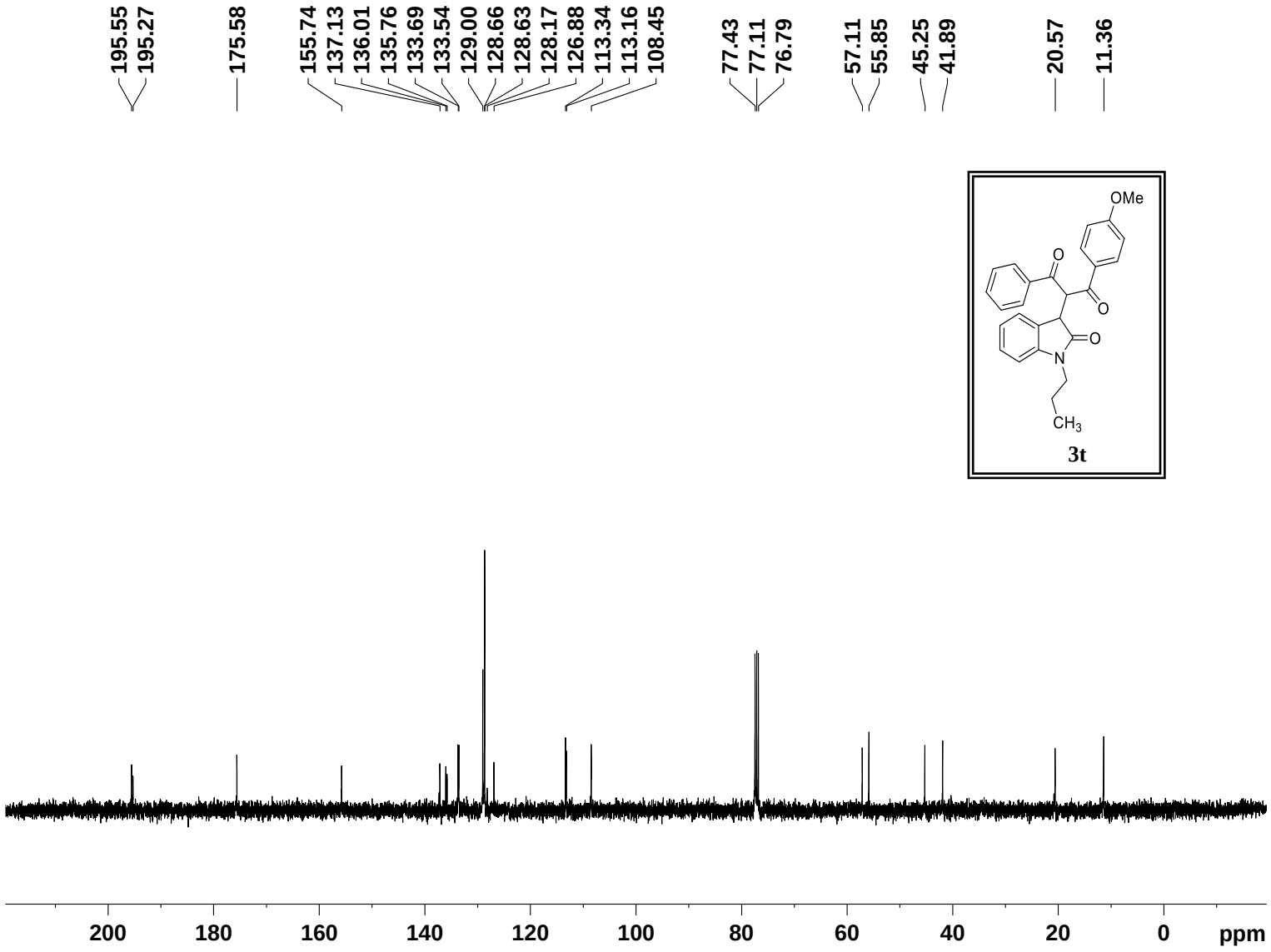


Figure 43: ^{13}C NMR spectrum of compound **3t** (101 MHz, $CDCl_3$)

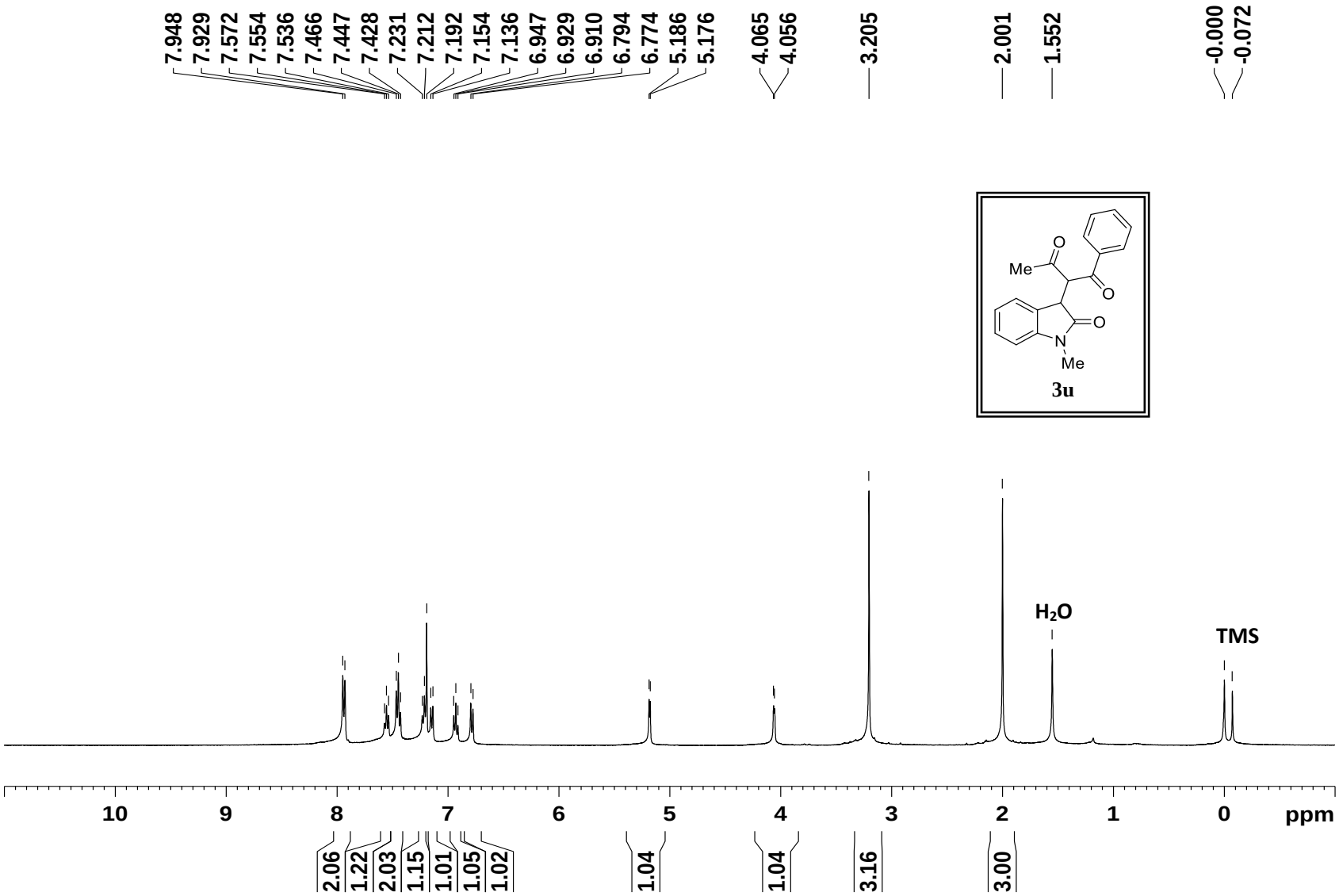


Figure 44: ^{1}H NMR spectrum of compound **3u** (400 MHz, $CDCl_3$)

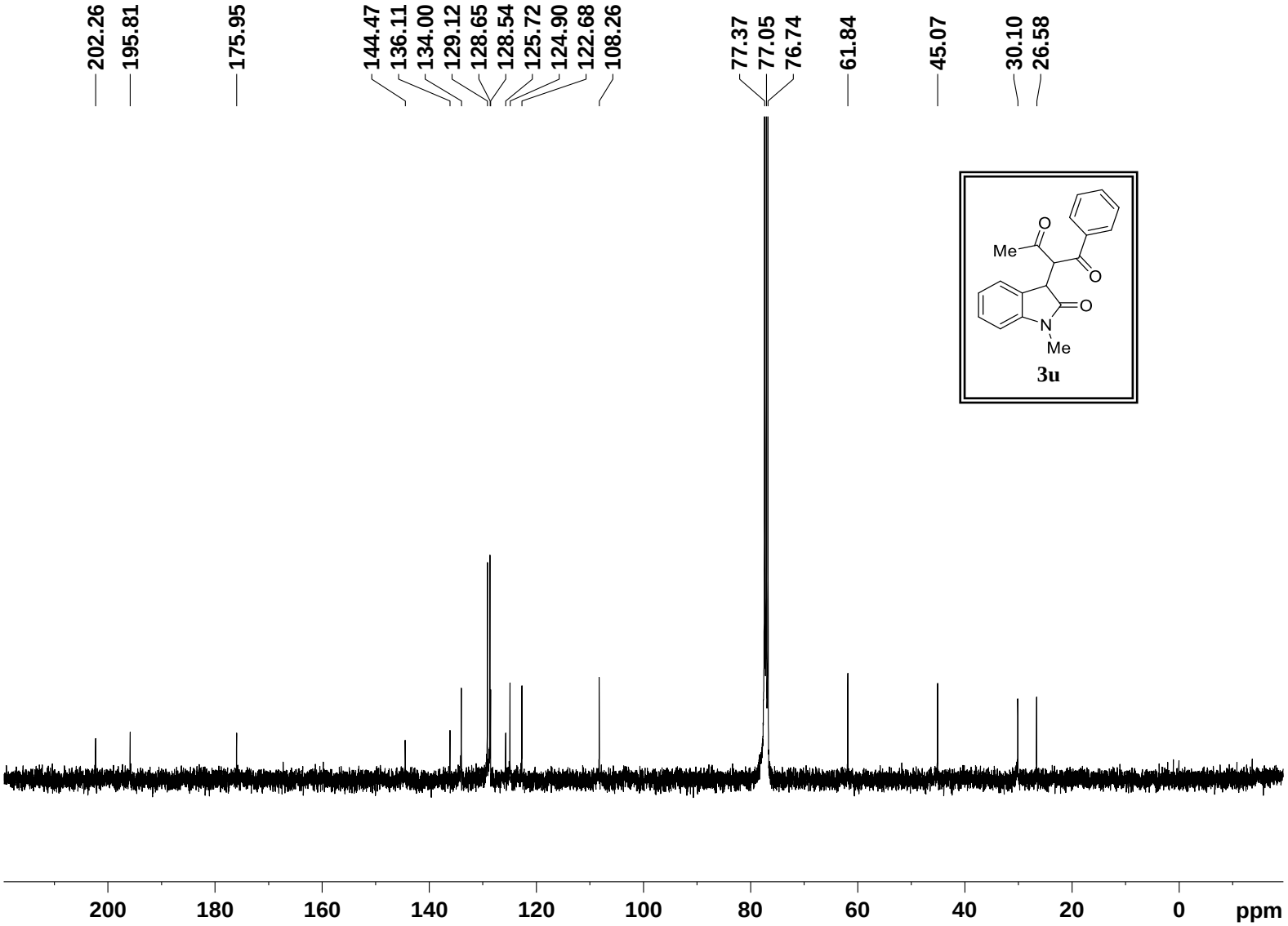


Figure 45: ^{13}C NMR spectrum of compound **3u** (101 MHz, $CDCl_3$)

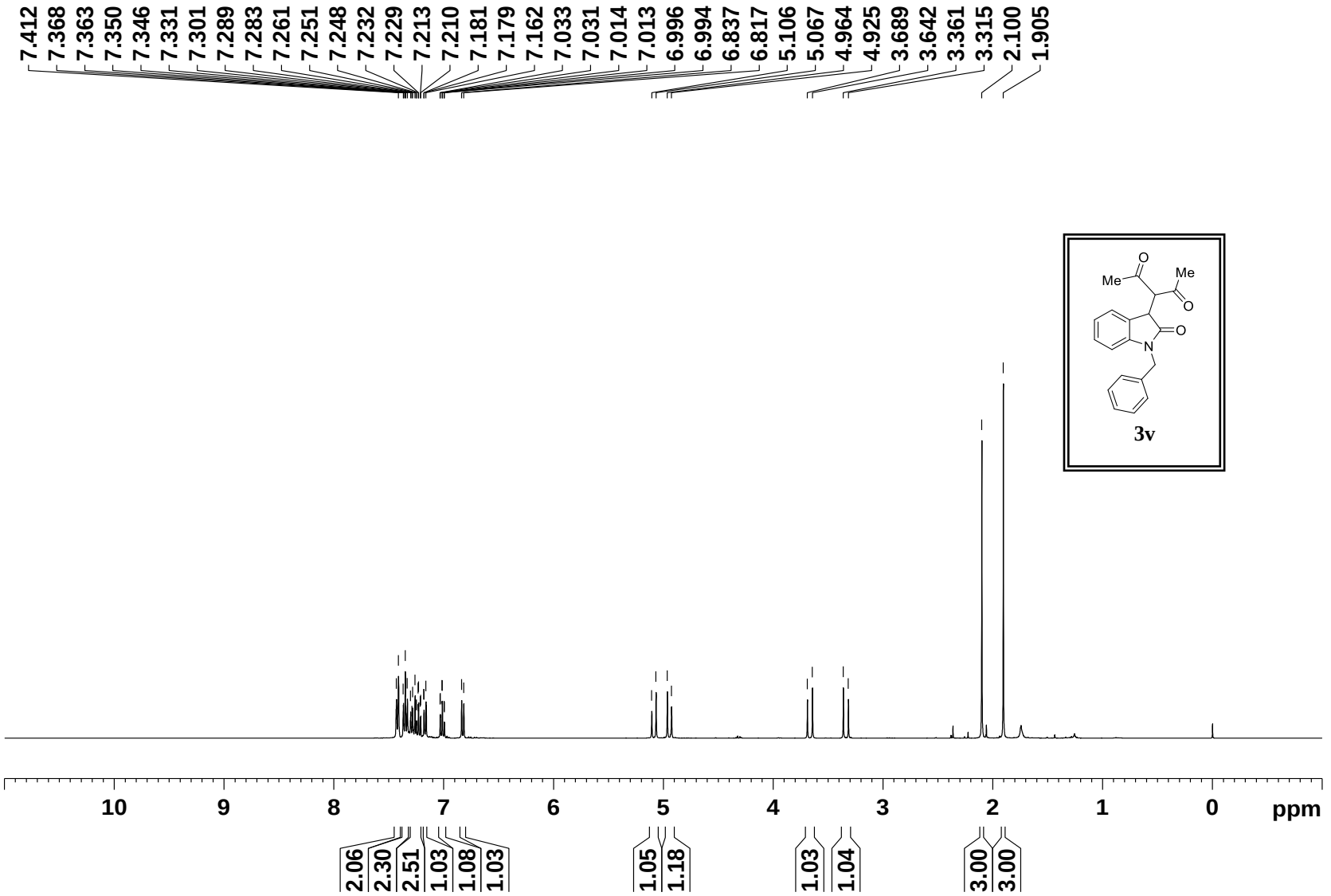


Figure 46: ^{1}H NMR spectrum of compound **3v** (400 MHz, $CDCl_3$)

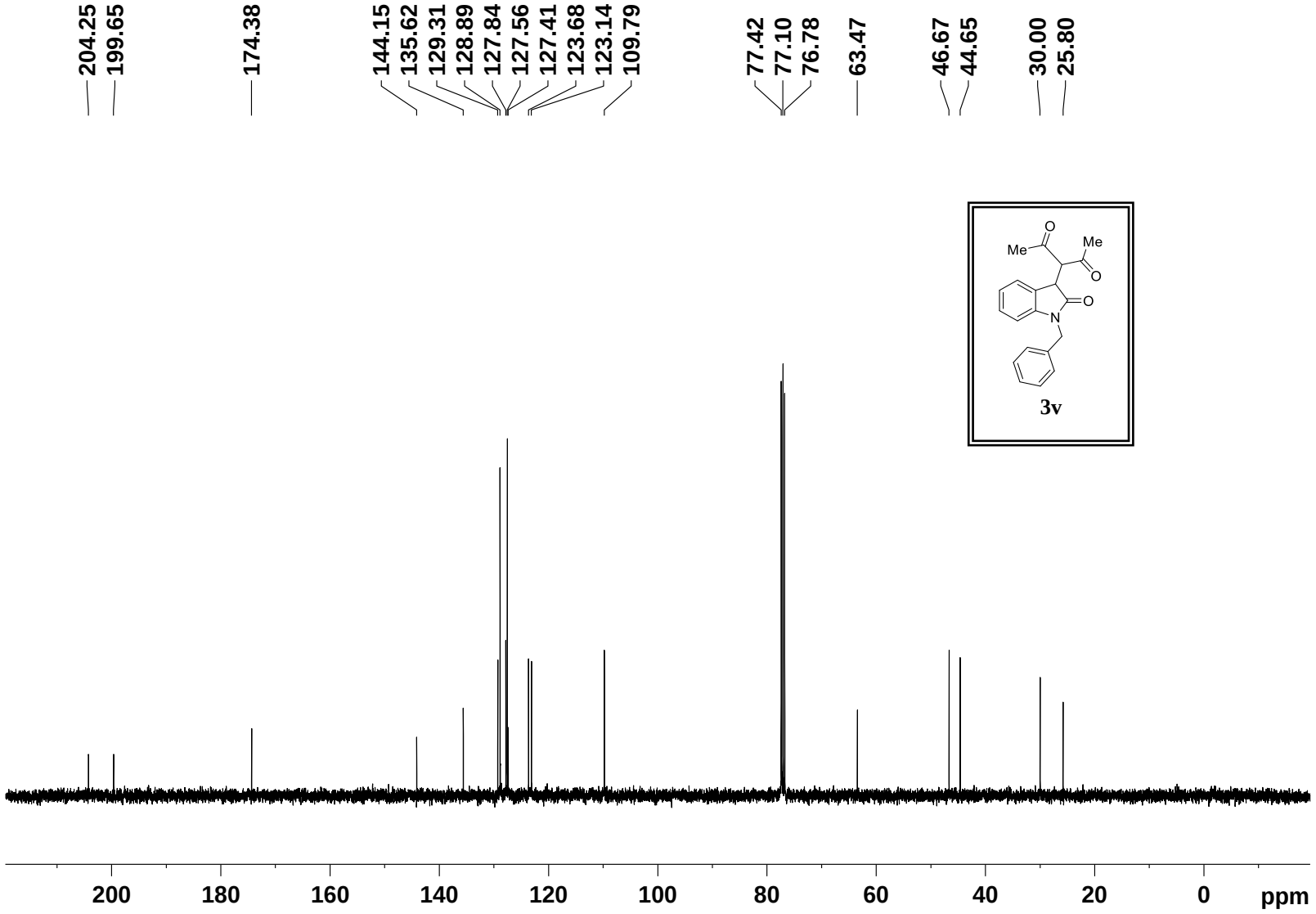


Figure 47: ^{13}C NMR spectrum of compound **3v** (101 MHz, $CDCl_3$)

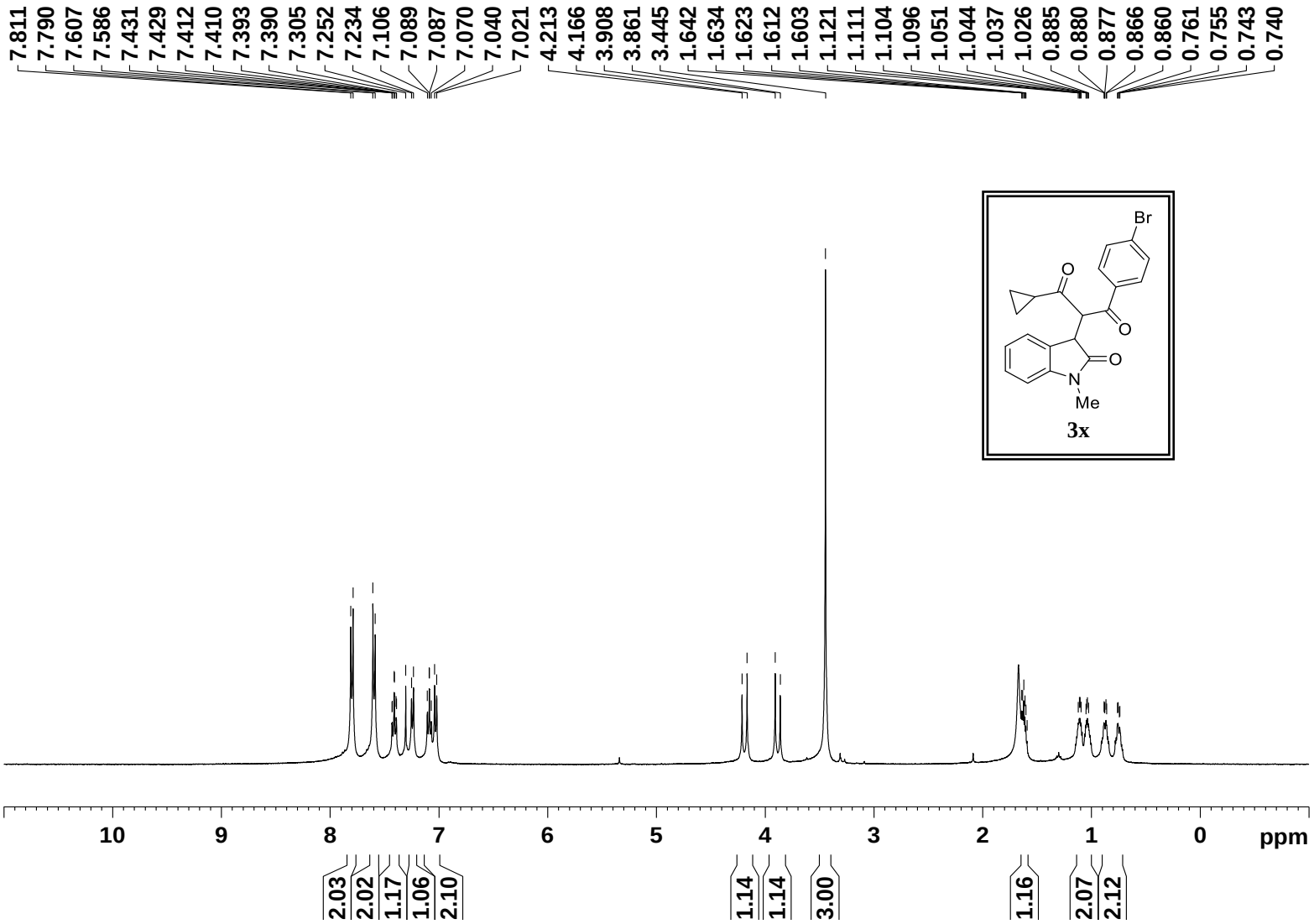


Figure 48: ^{1}H NMR spectrum of compound **3x** (400 MHz, $CDCl_3$)

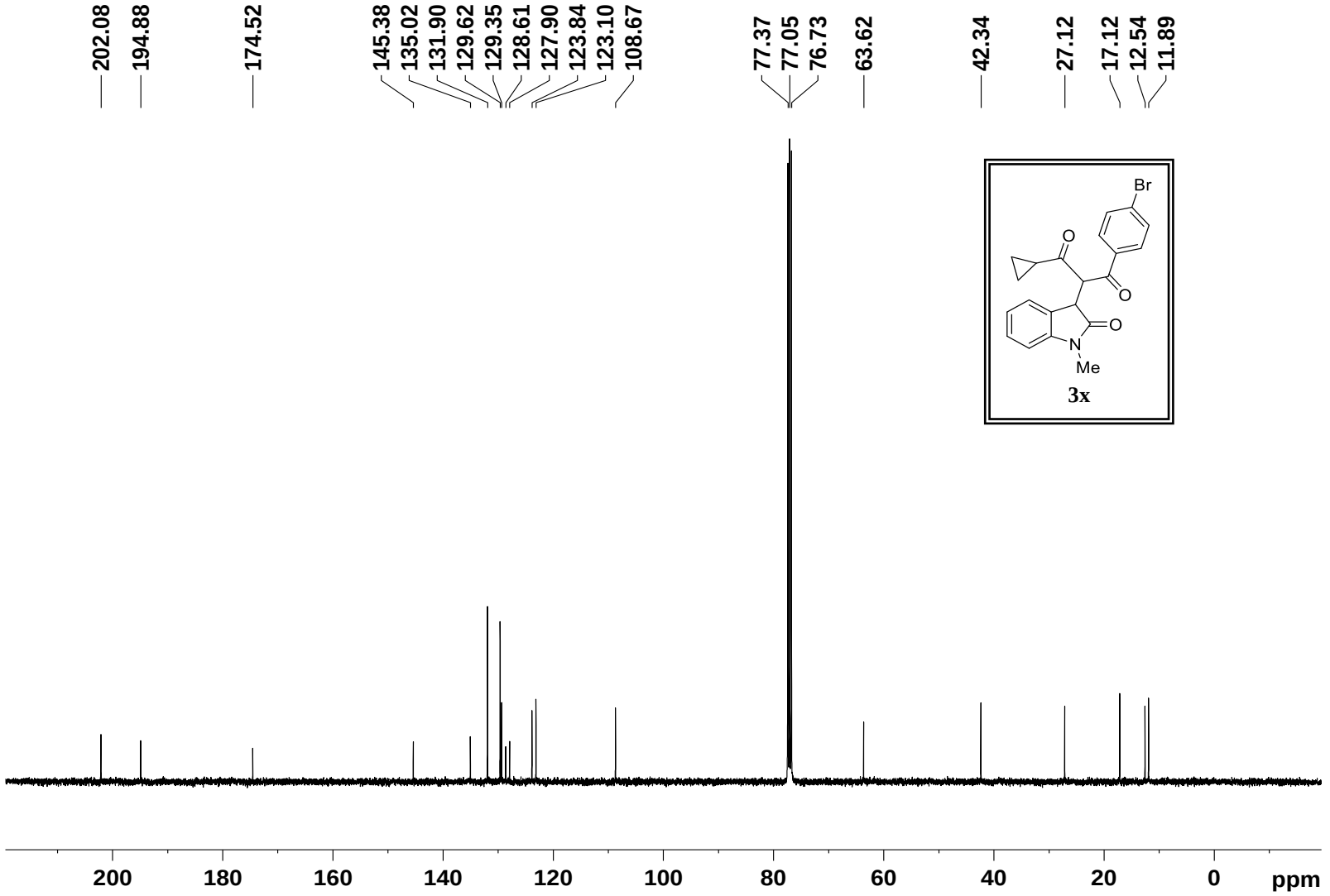


Figure 49: ^{13}C NMR spectrum of compound **3x** (101 MHz, $CDCl_3$)

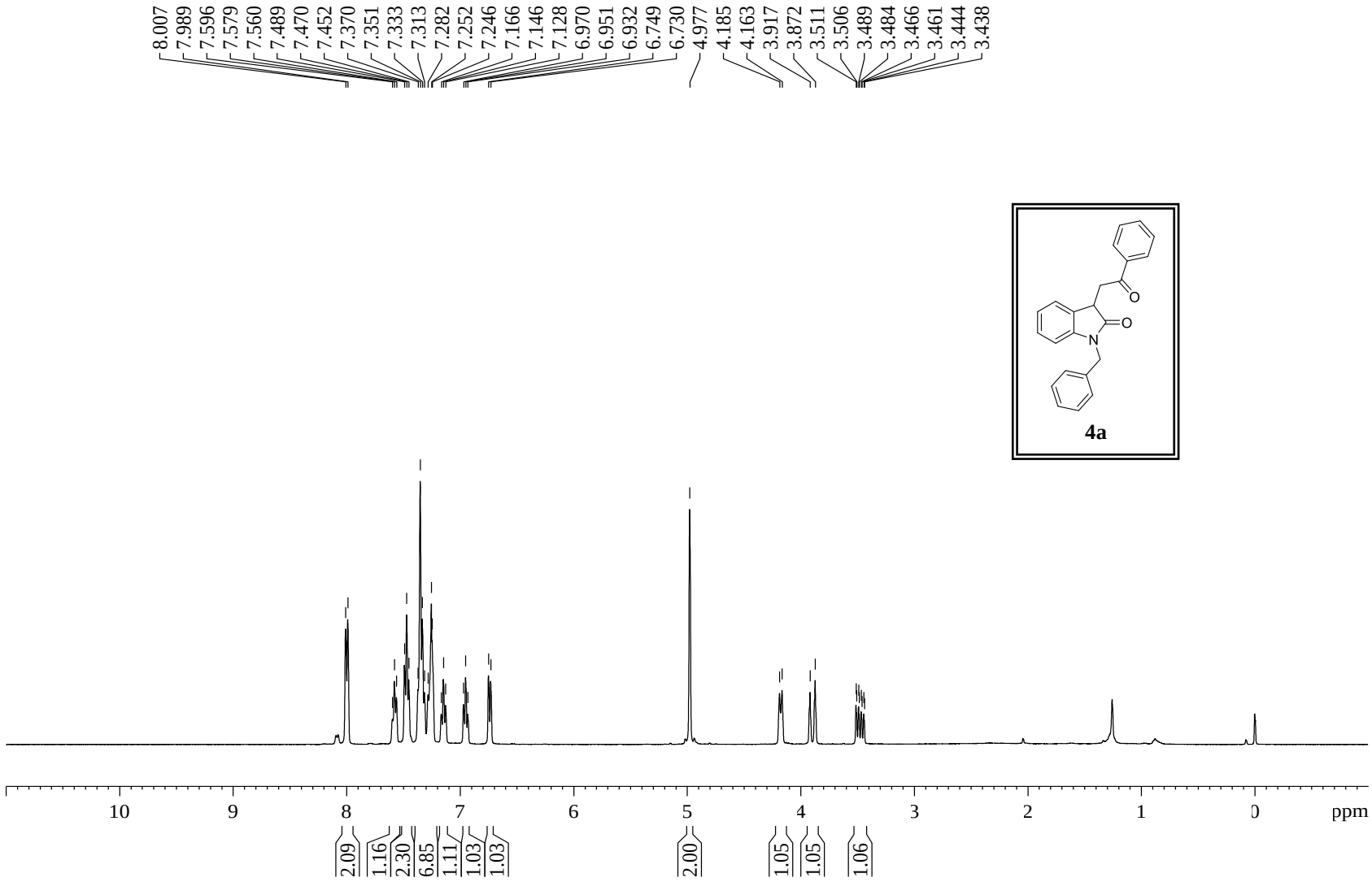


Figure 50: ^{1}H NMR spectrum of compound **4a** (400 MHz, $CDCl_3$)

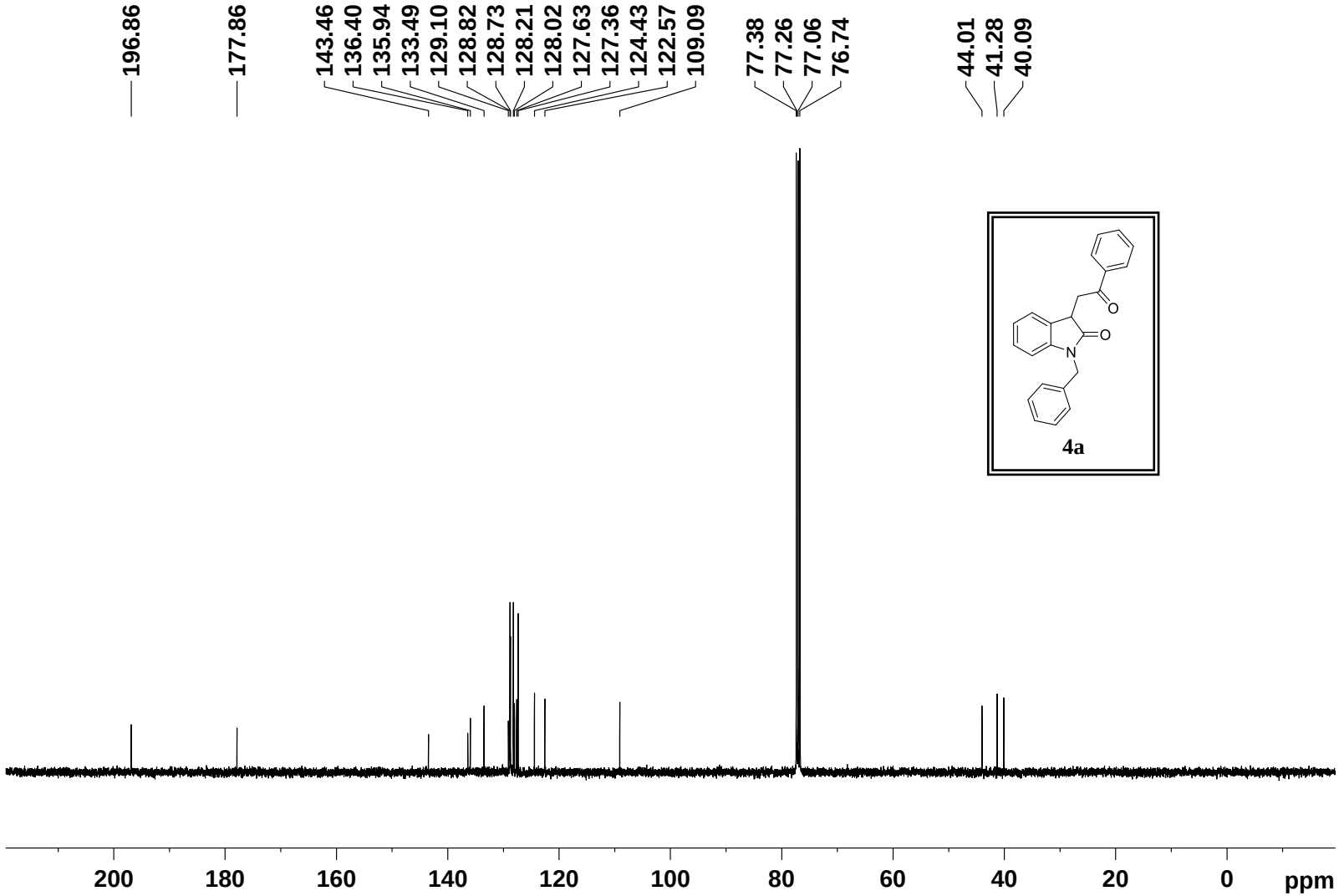


Figure 51: ^{13}C NMR spectrum of compound **4a** (101 MHz, $CDCl_3$)

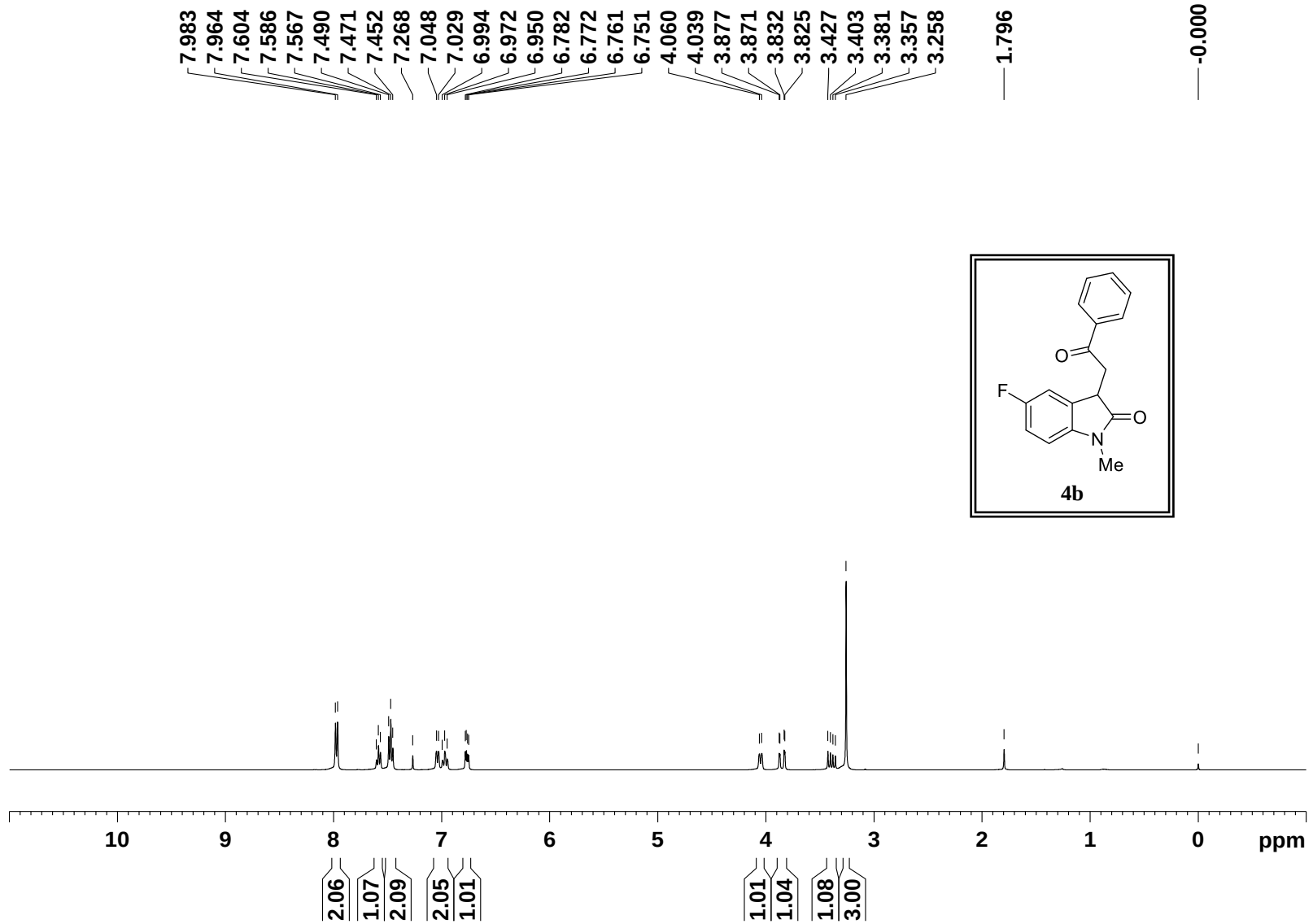


Figure 52: ^{1}H NMR spectrum of compound **4b** (400 MHz, $CDCl_3$)

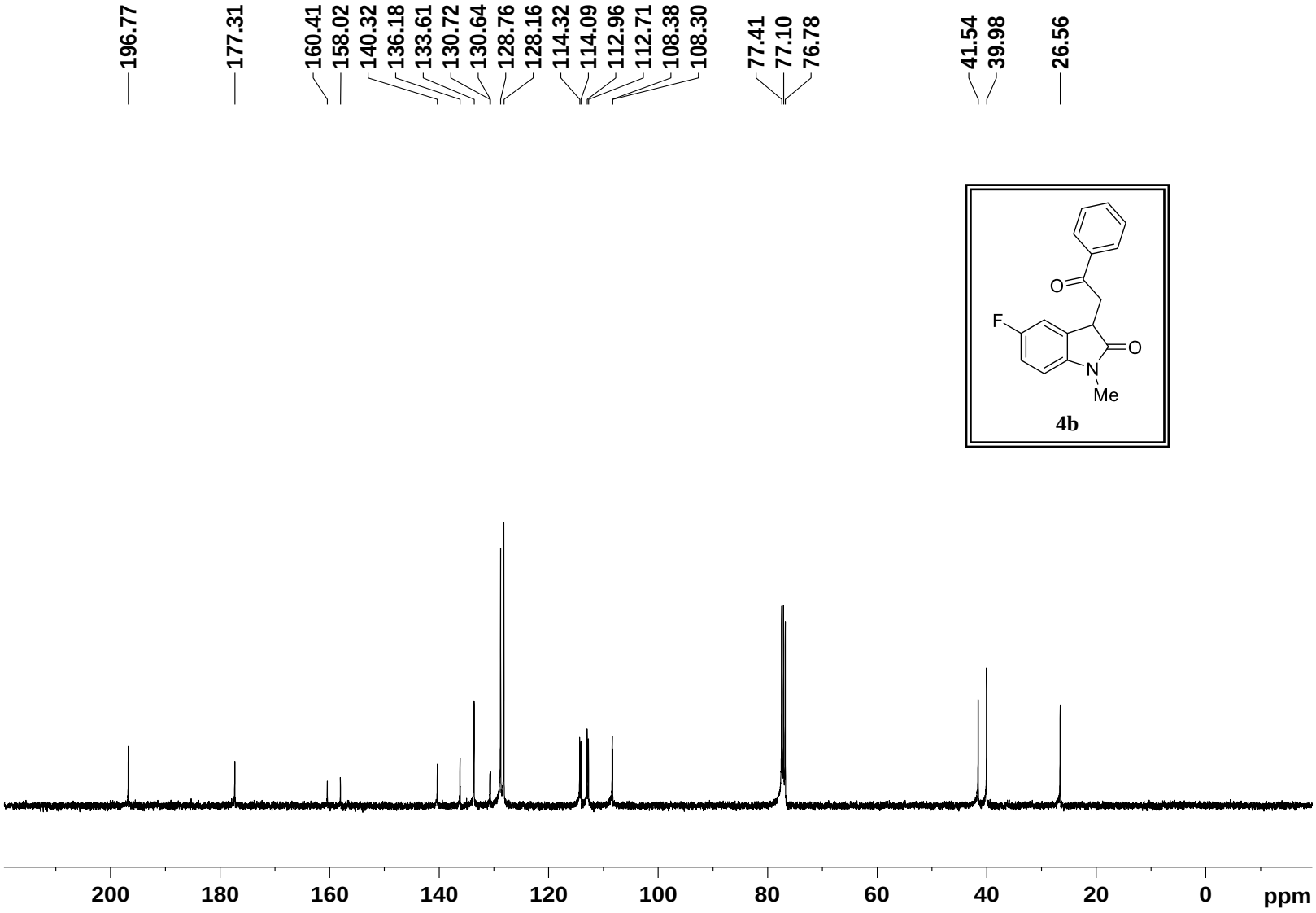


Figure 53: ^{13}C NMR spectrum of compound **4b** (101 MHz, $CDCl_3$)

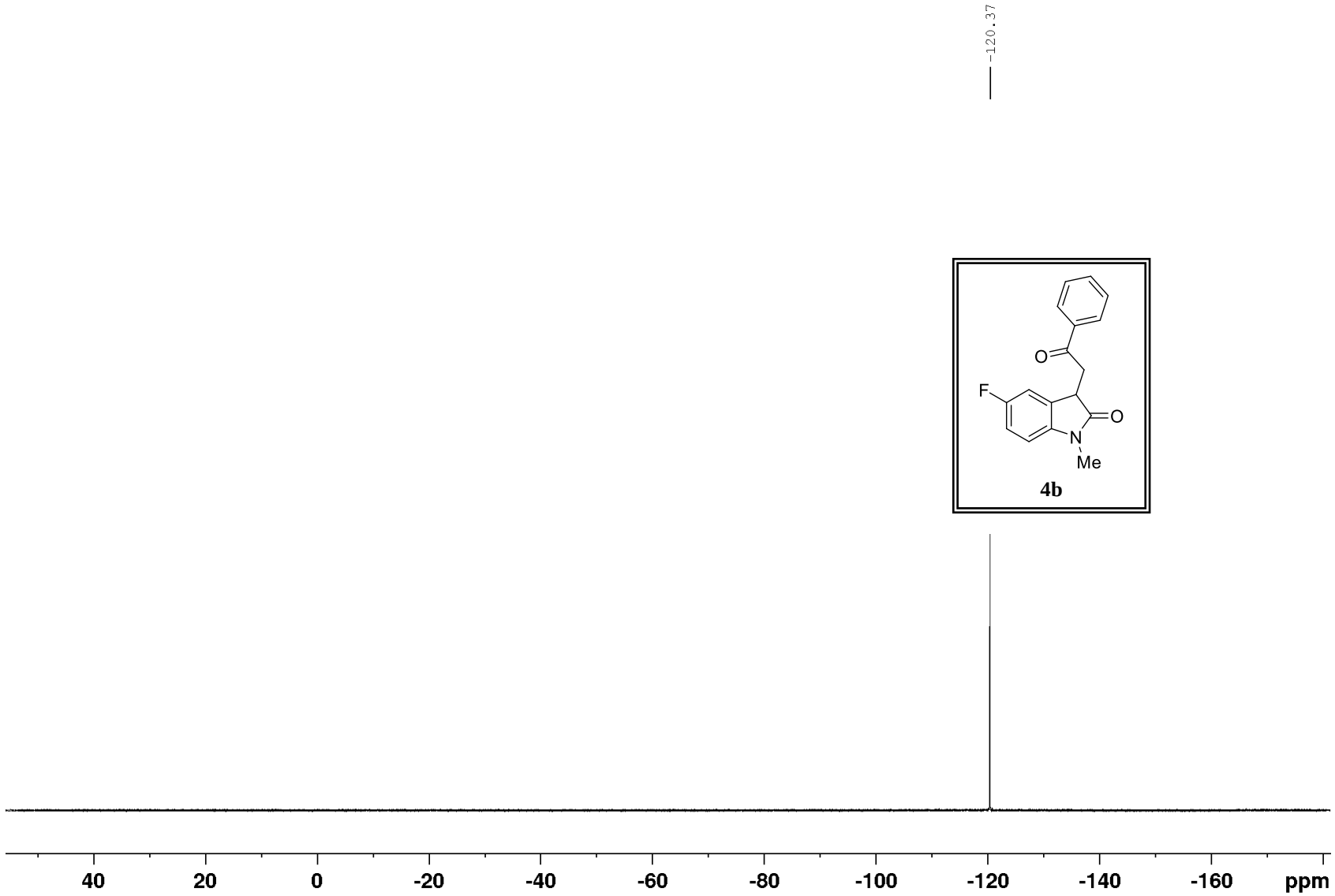


Figure 54: ^{19}F NMR spectrum of compound **3h** (162 MHz, $CDCl_3$)

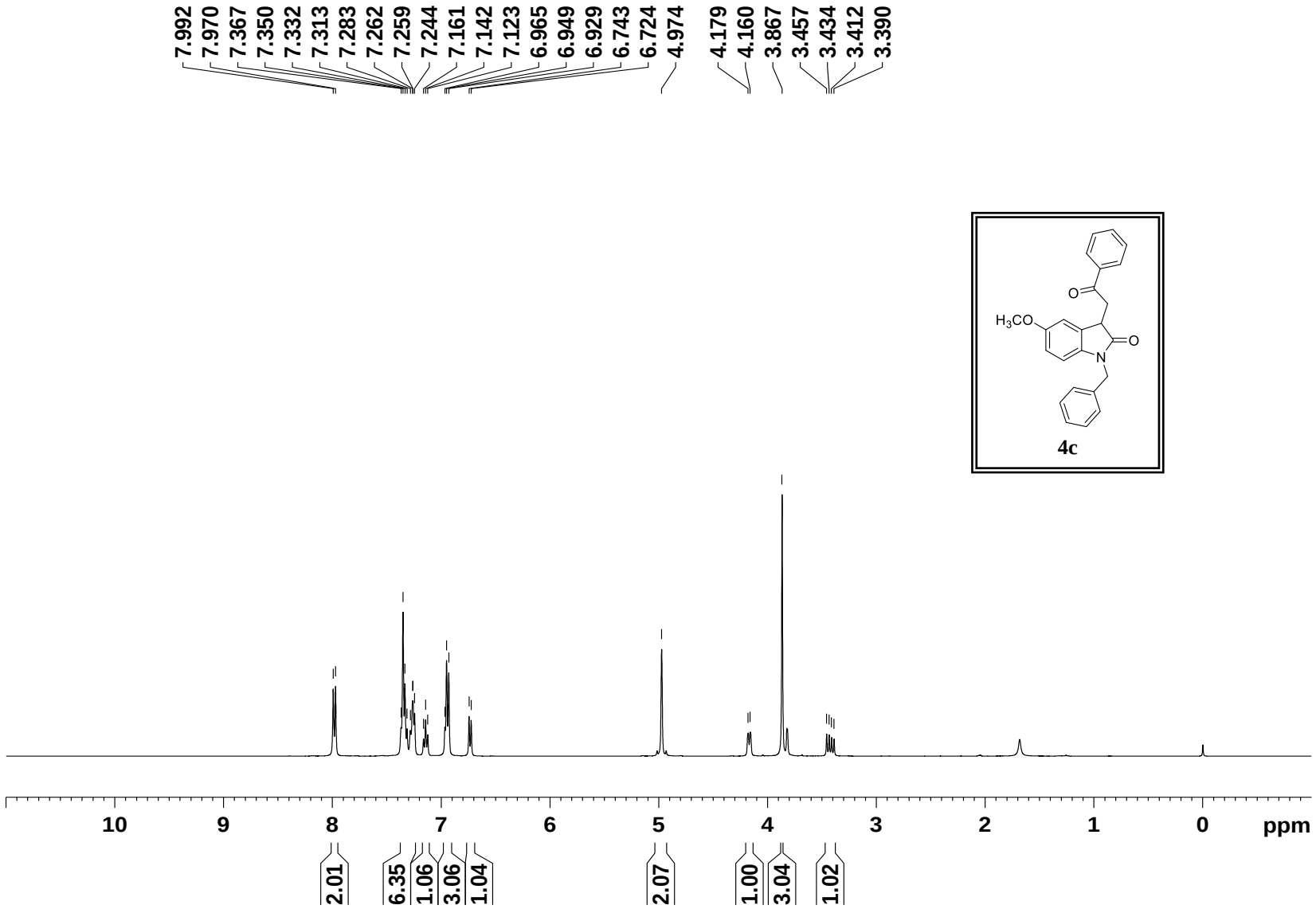


Figure 55: ^{1}H NMR spectrum of compound **4c** (400 MHz, $CDCl_3$)[3]

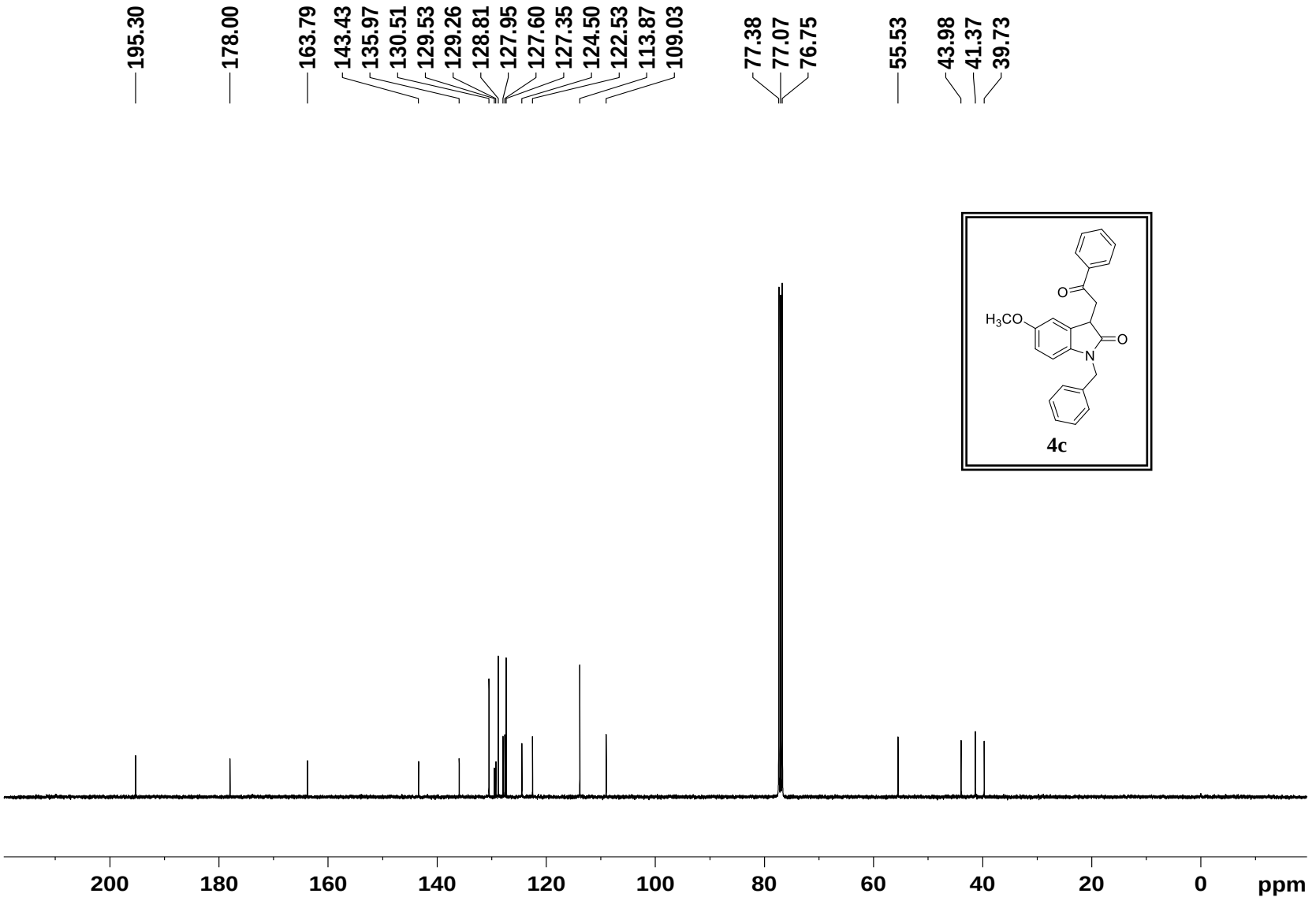


Figure 56: ^{13}C NMR spectrum of compound **4c** (101 MHz, $CDCl_3$)[3]

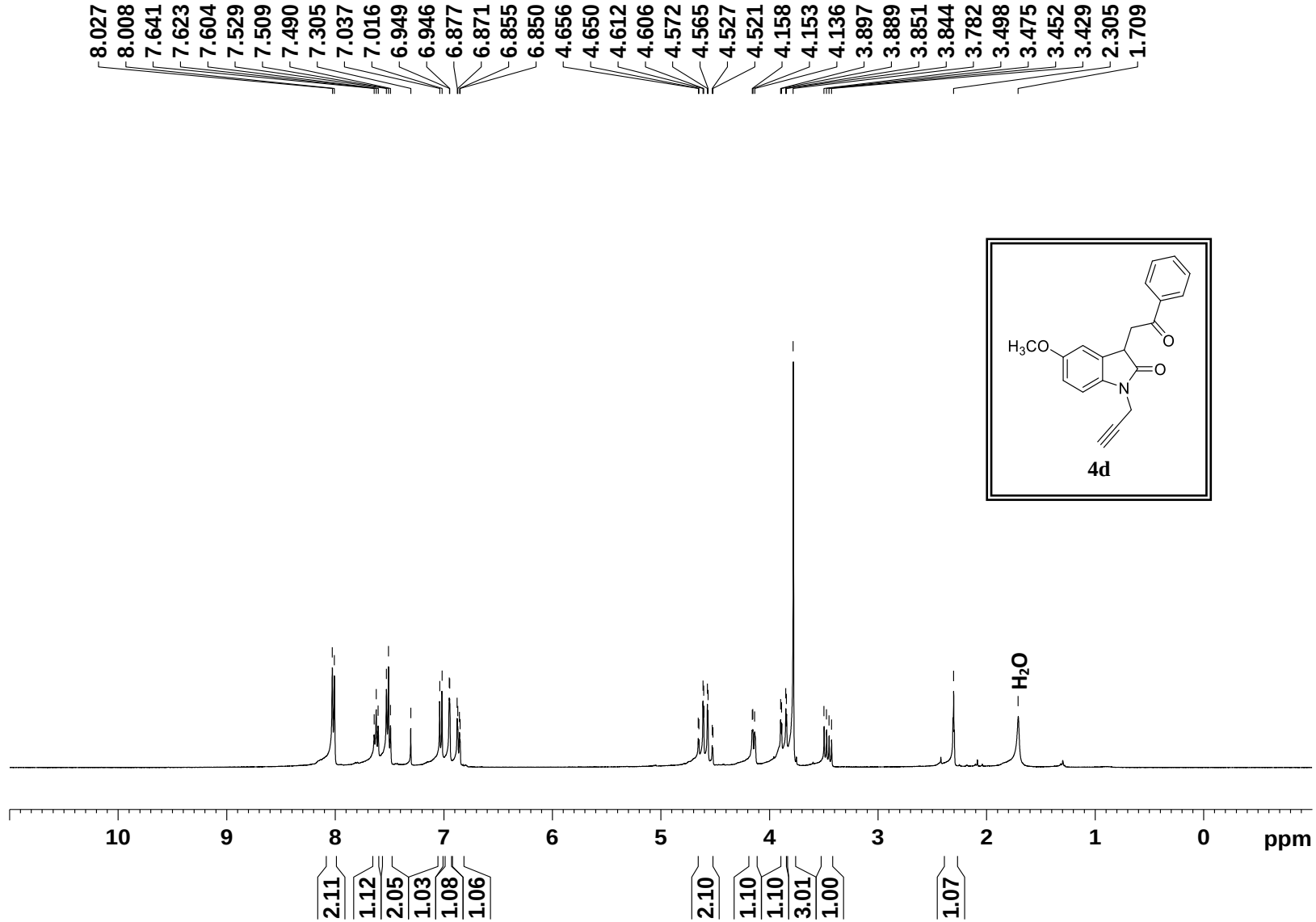


Figure 57: ^{1}H NMR spectrum of compound **4d** (400 MHz, $CDCl_3$)

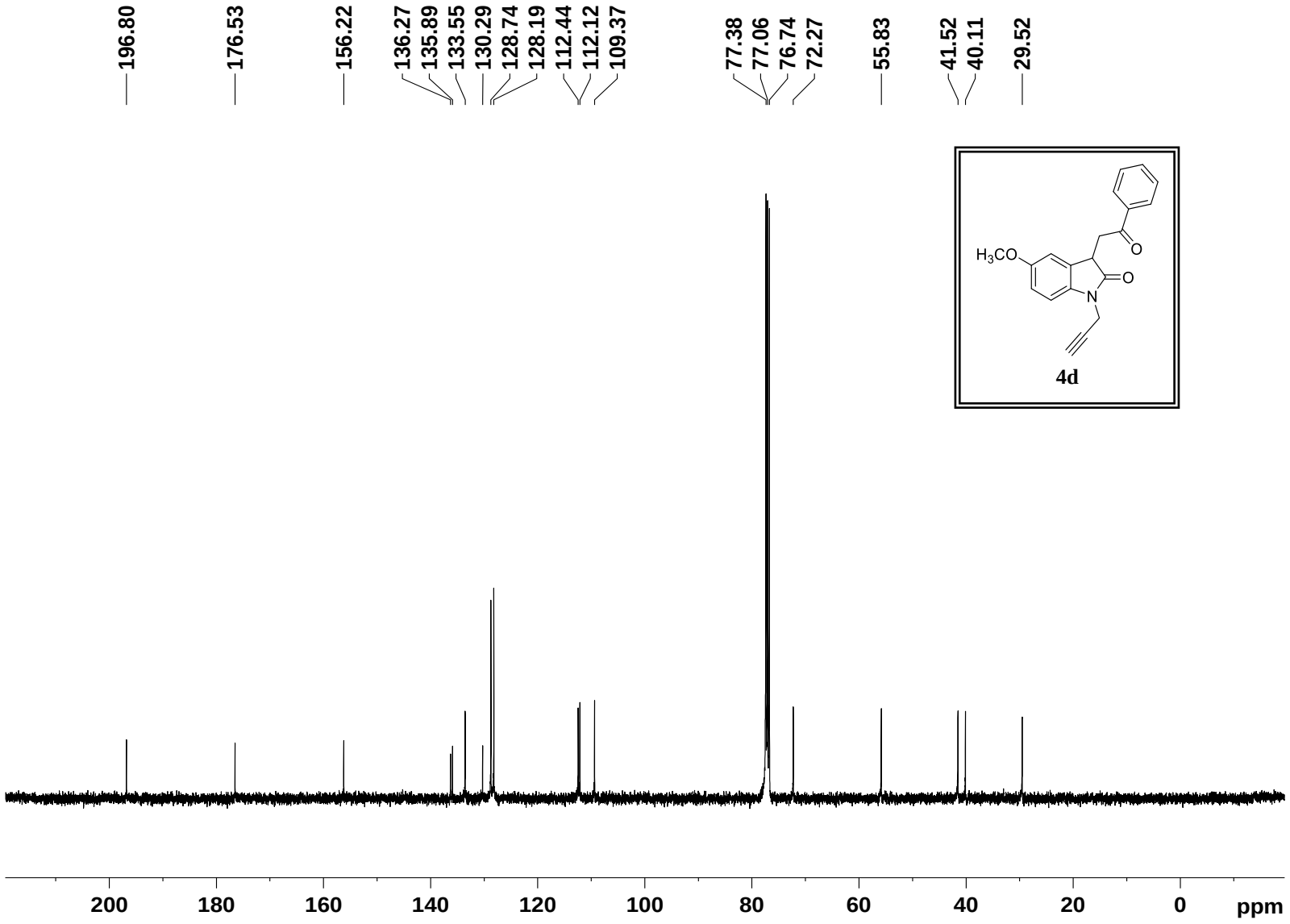


Figure 58: ^{13}C NMR spectrum of compound **4d** (101 MHz, $CDCl_3$)

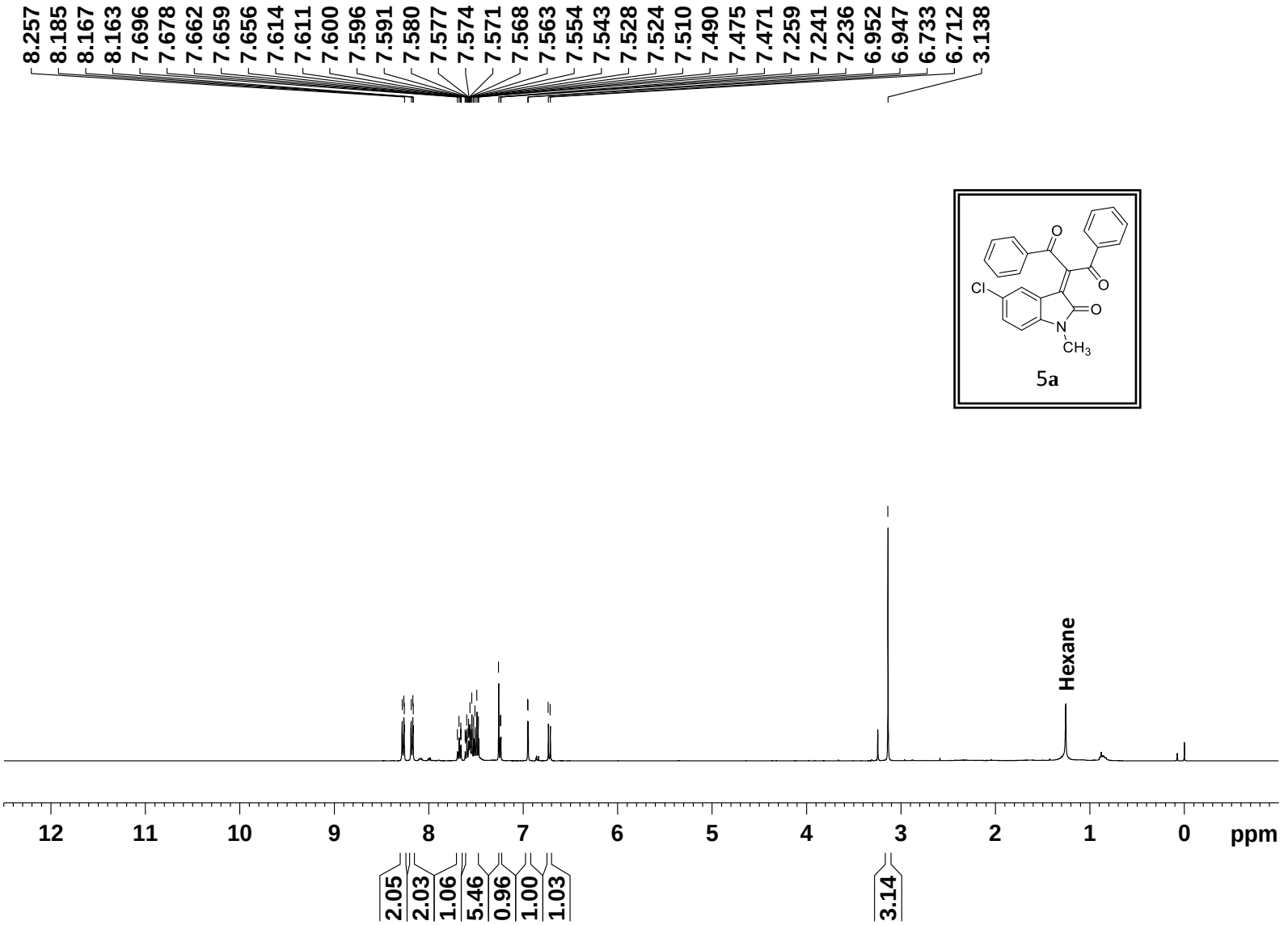


Figure 59: ^{1}H NMR spectrum of compound **5a** (400 MHz, $CDCl_3$)

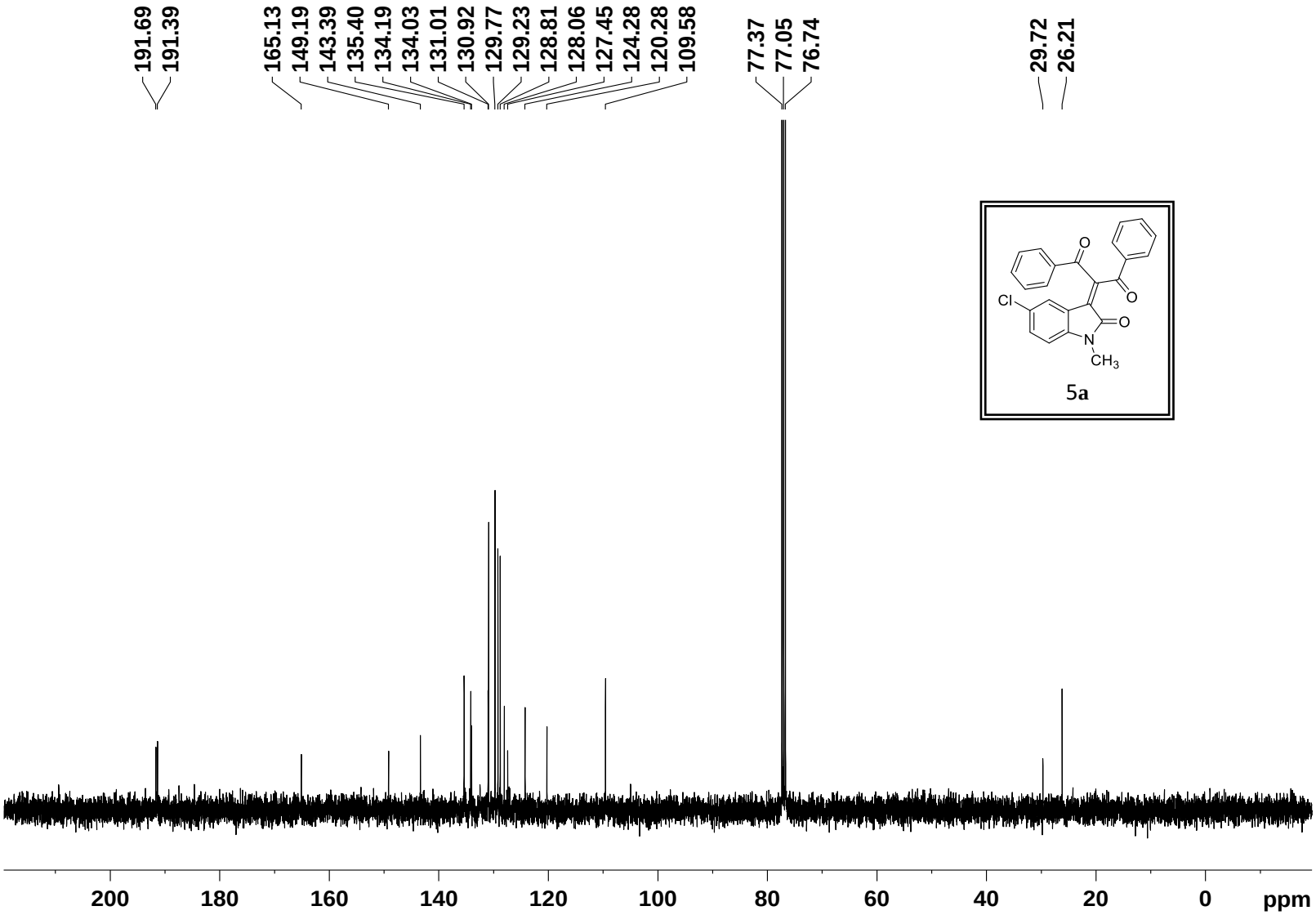


Figure 60: ^{13}C NMR spectrum of compound **5a** (101 MHz, $CDCl_3$)

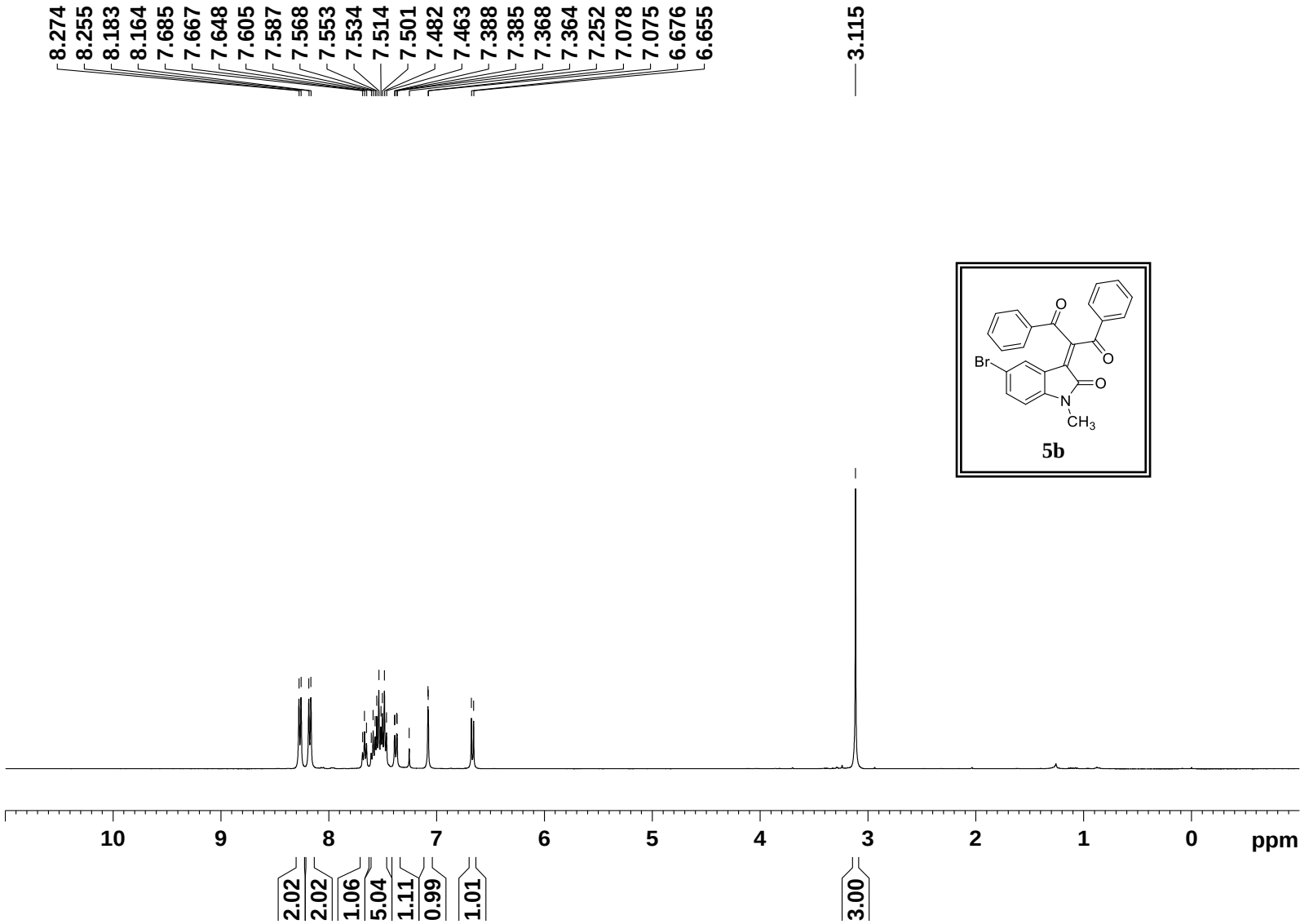


Figure 61: ^{1}H NMR spectrum of compound **5b** (400 MHz, $CDCl_3$

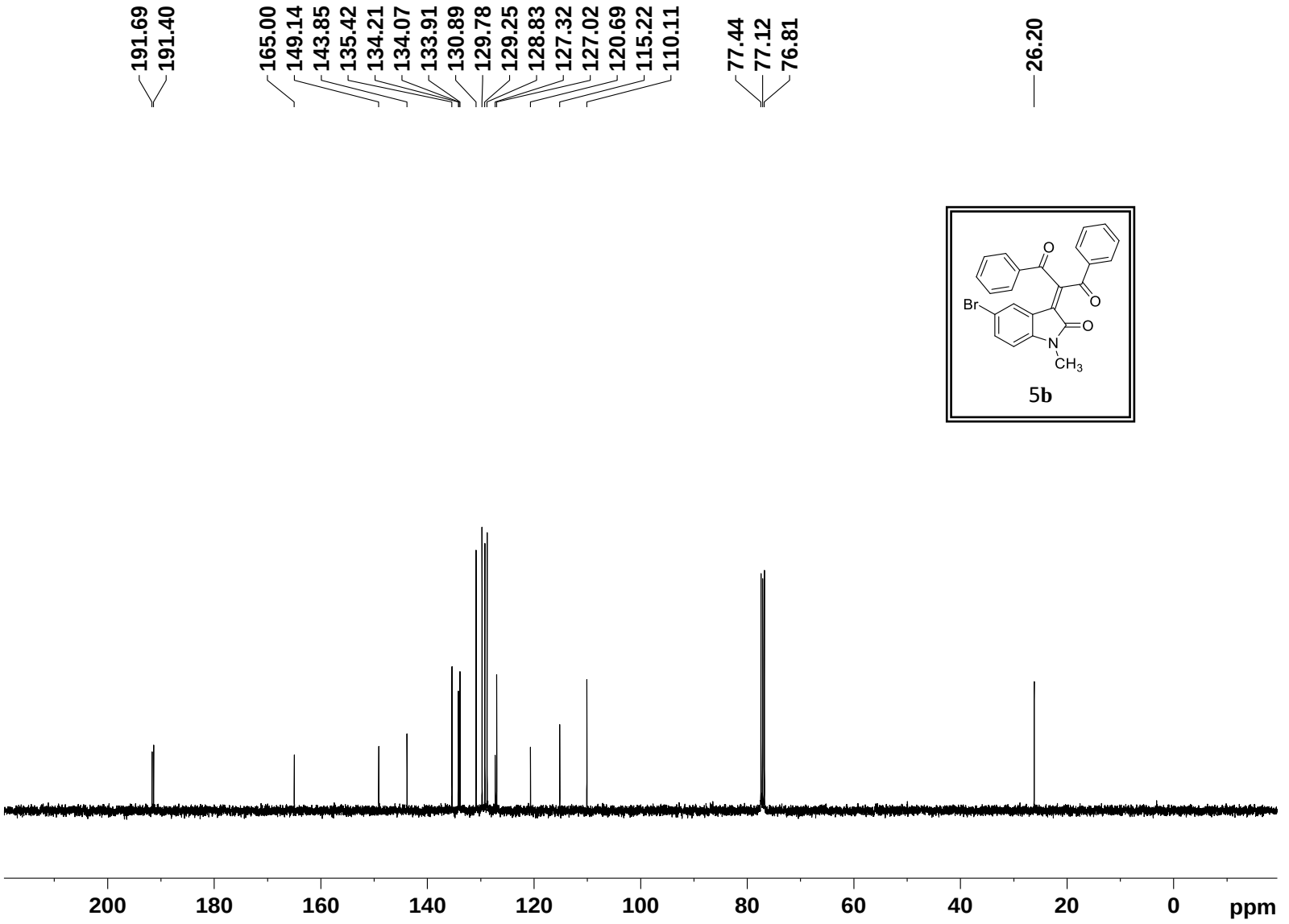


Figure 62: ^{13}C NMR spectrum of compound **5b** (101 MHz, $CDCl_3$)

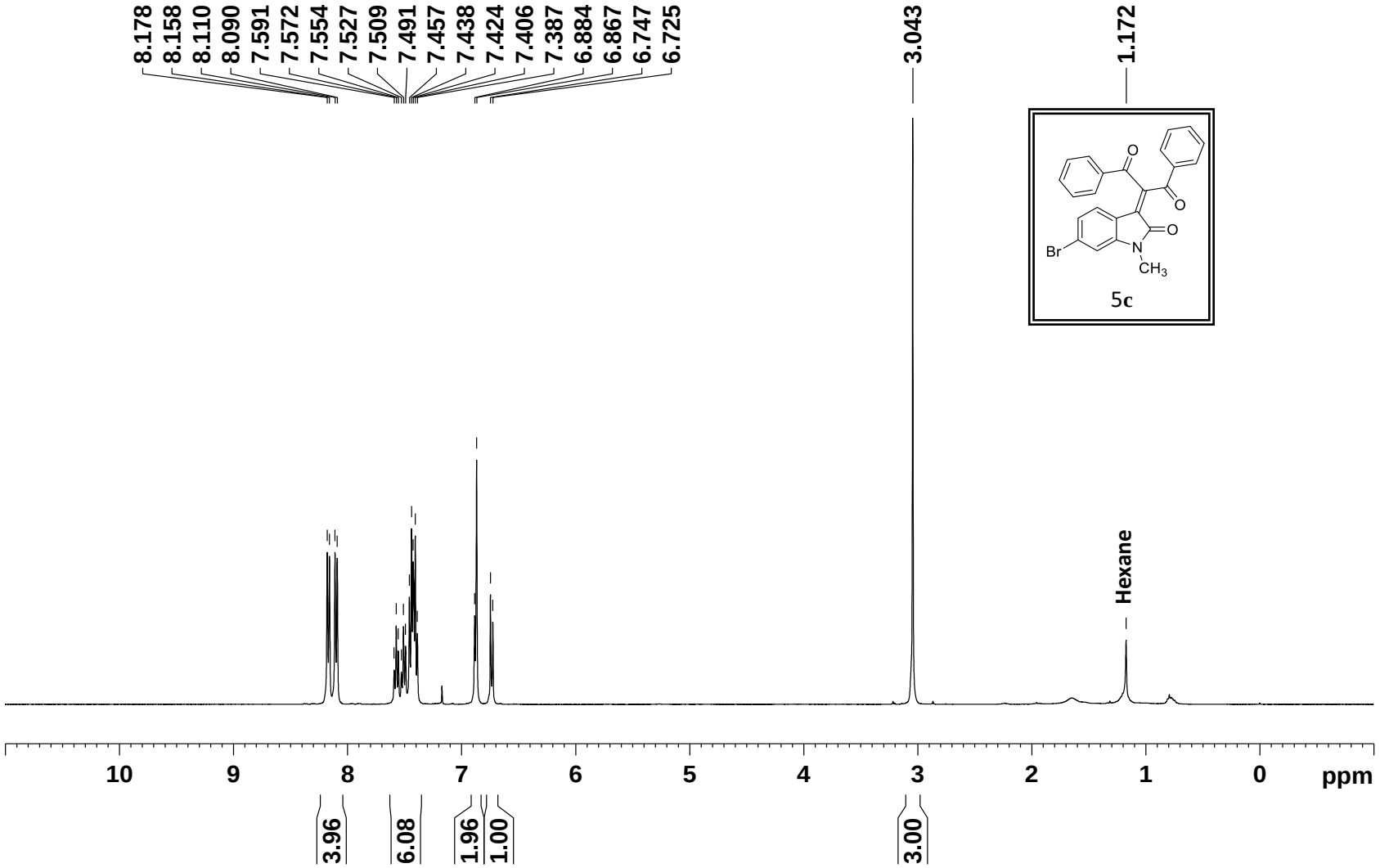


Figure 63: ^{1}H NMR spectrum of compound **5c** (400 MHz, $CDCl_3$

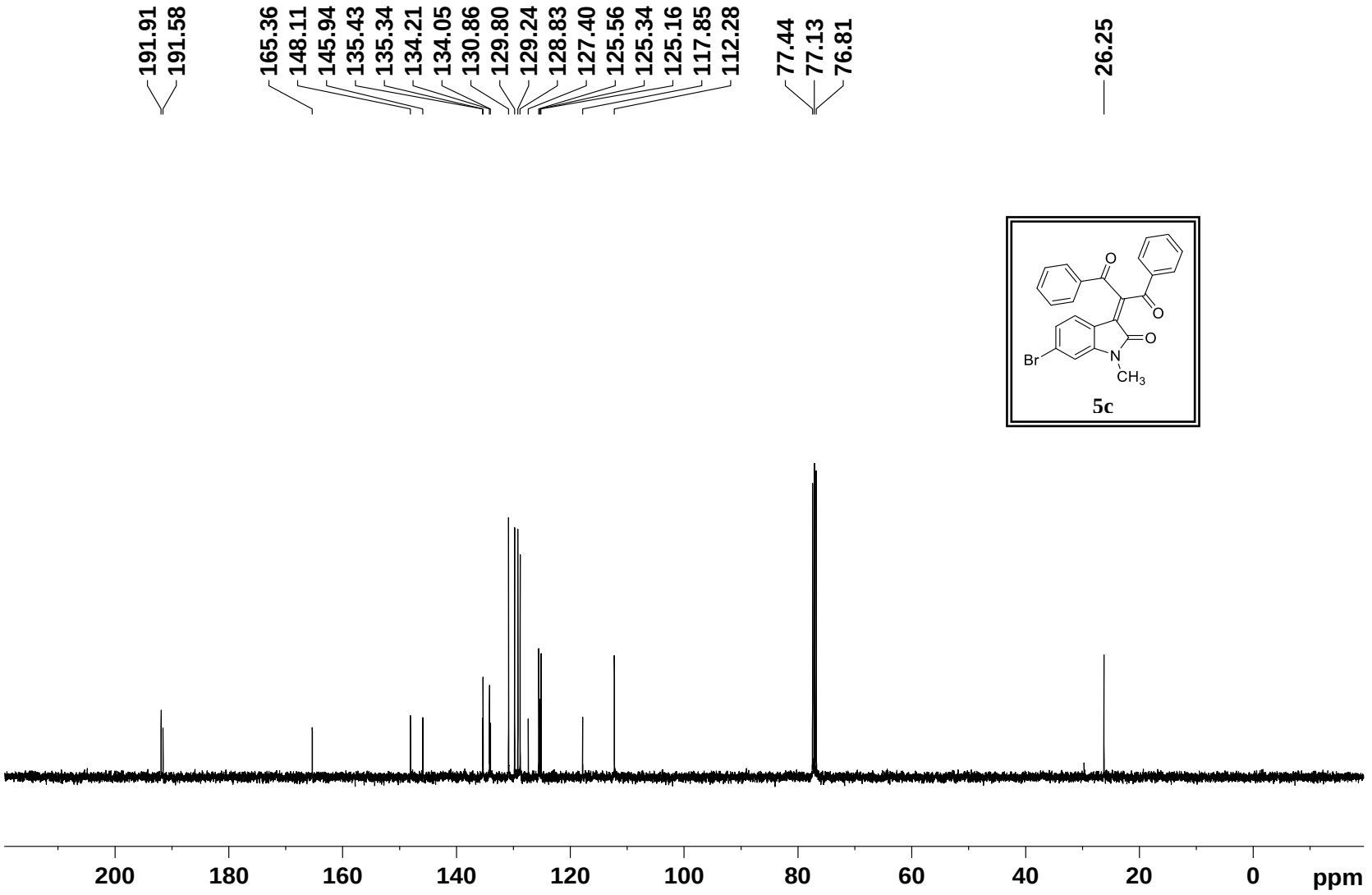


Figure 64: ^{13}C NMR spectrum of compound **5c** (101 MHz, $CDCl_3$)

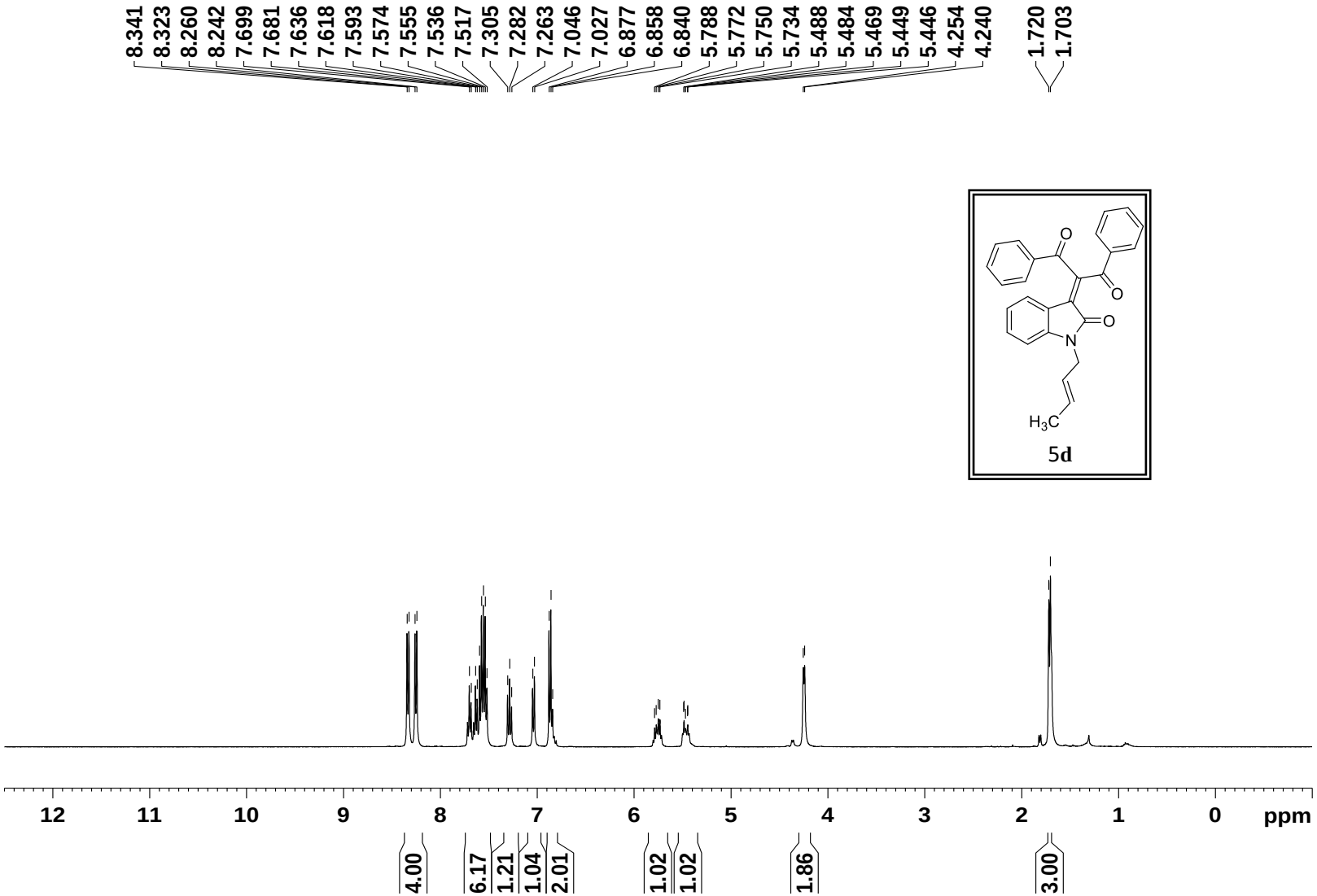


Figure 65: ^{1}H NMR spectrum of compound **5d** (400 MHz, $CDCl_3$)

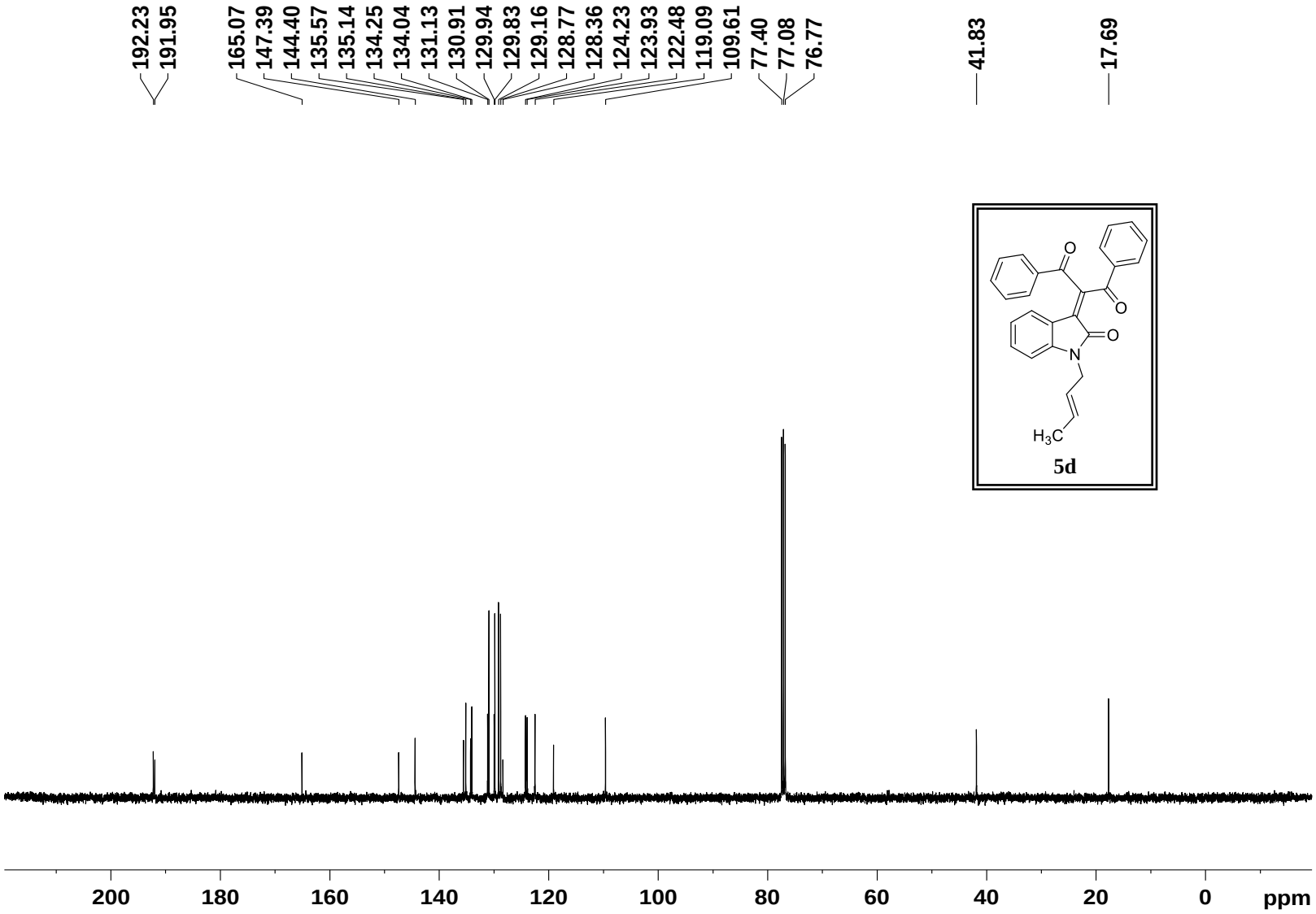


Figure 66: ^{13}C NMR spectrum of compound **5d** (101 MHz, $CDCl_3$)

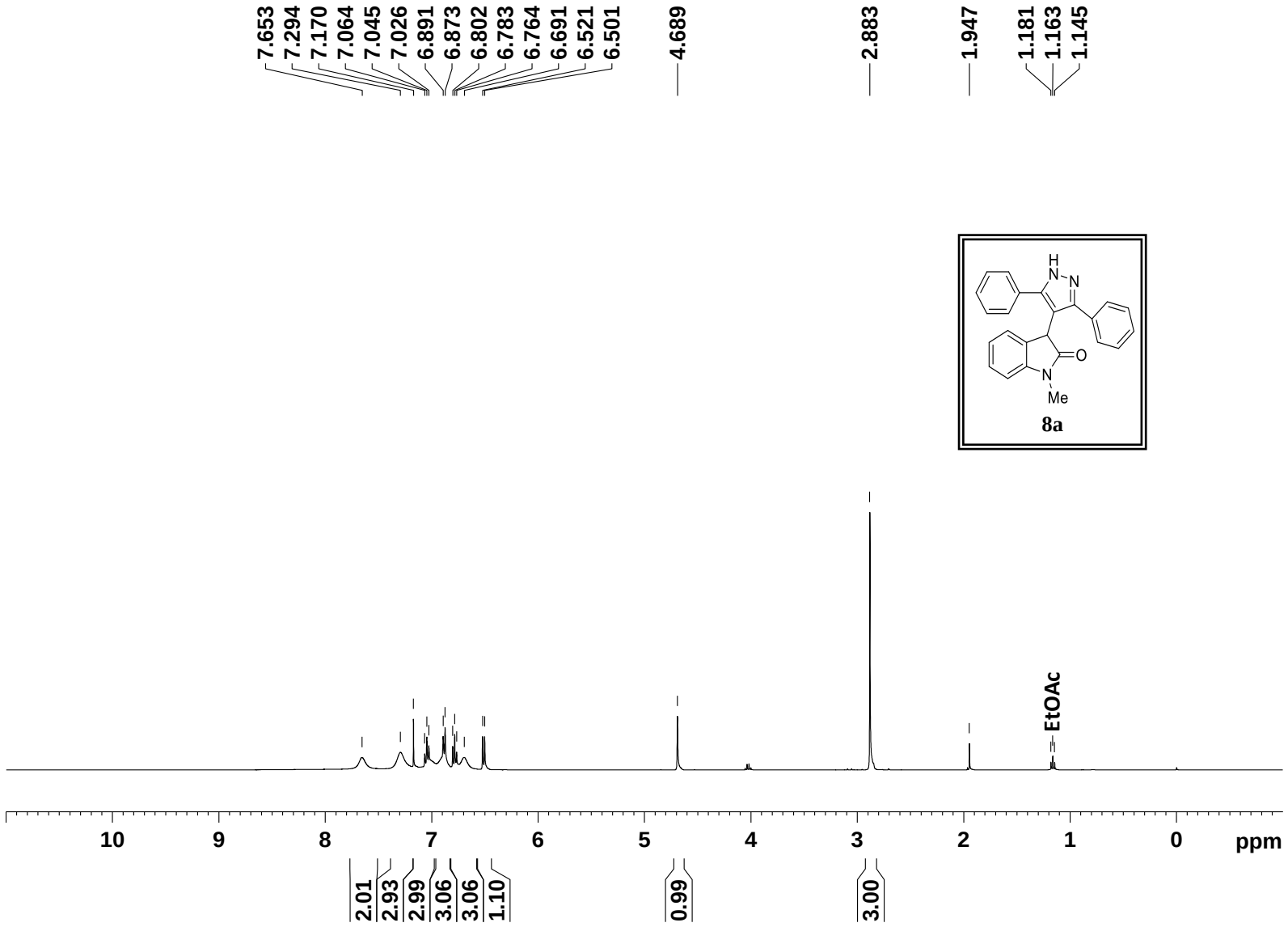


Figure 67: ^{1}H NMR spectrum of compound **8a** (400 MHz, $CDCl_3$)

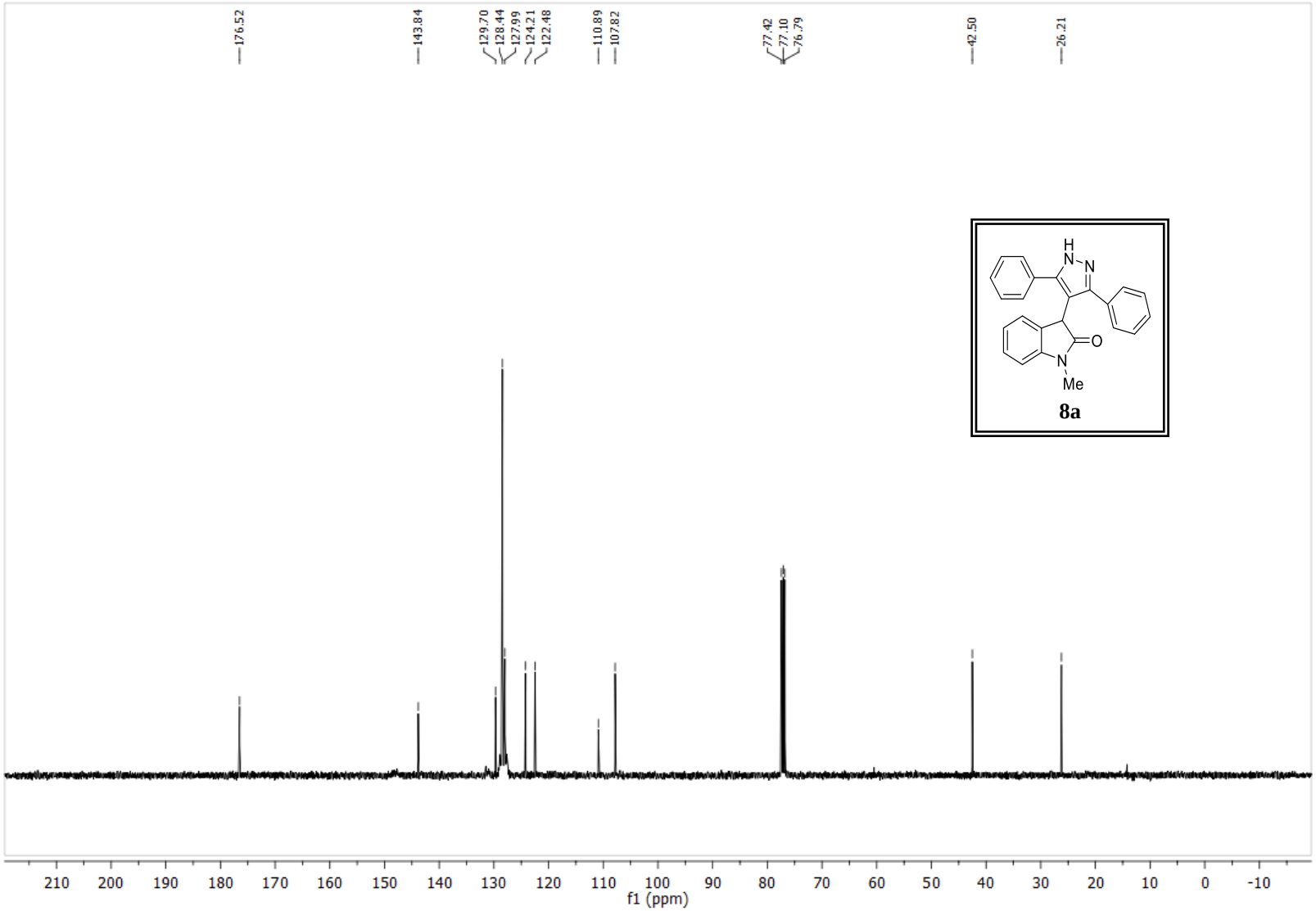


Figure 68: ^{13}C NMR spectrum of compound **8a** (101 MHz, $CDCl_3$)

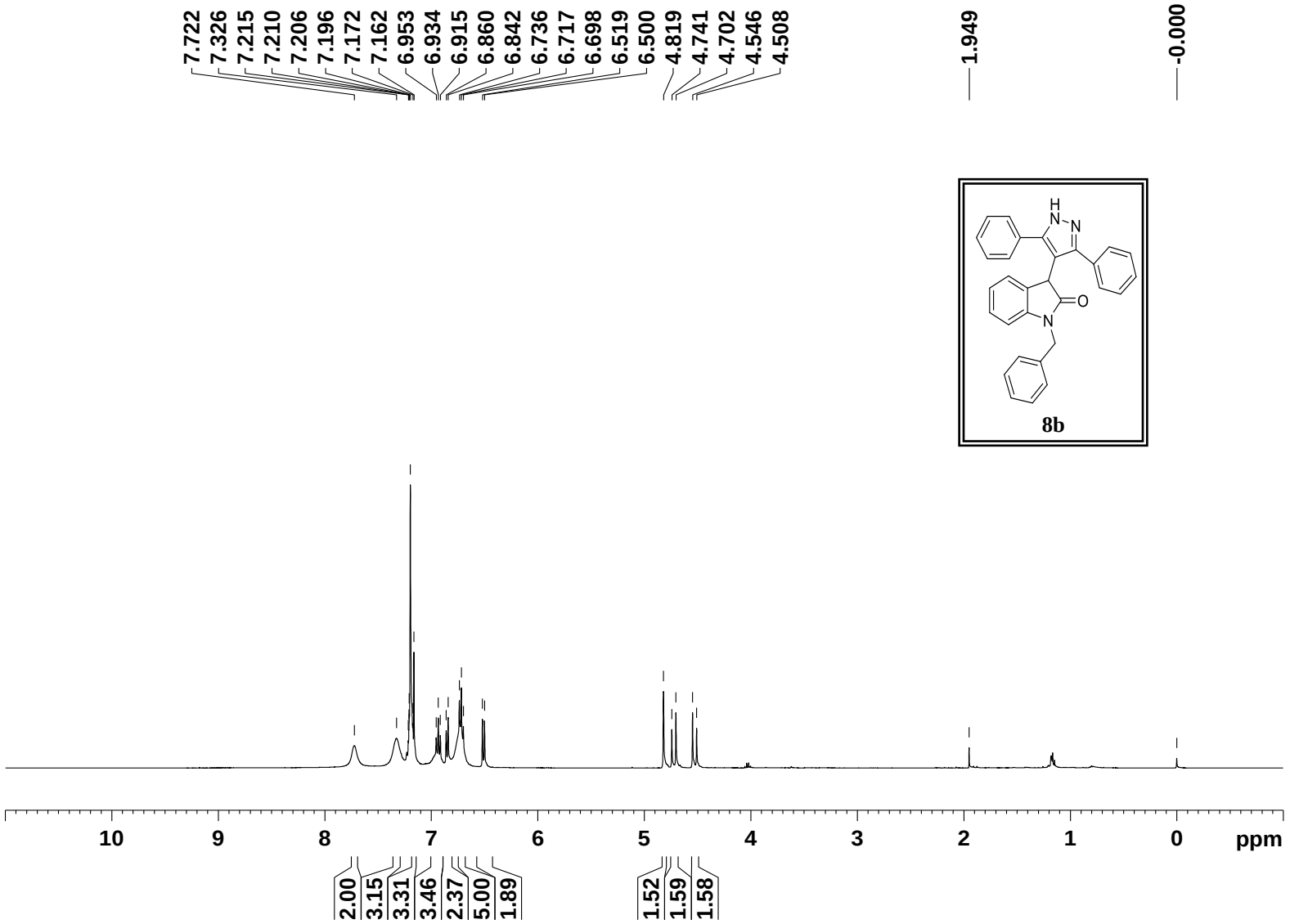


Figure 69: ^{1}H NMR spectrum of compound **8b** (400 MHz, $CDCl_3$)

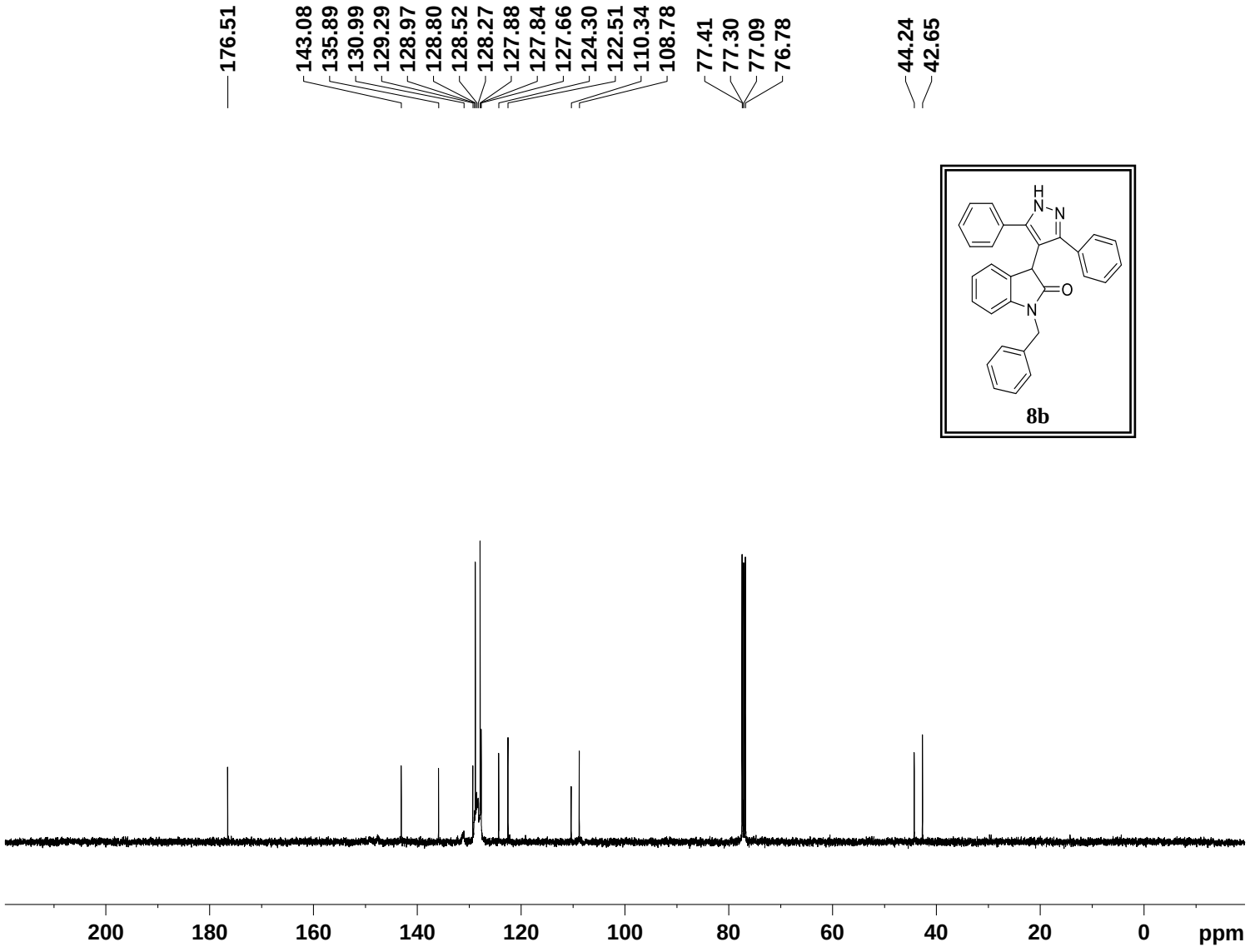


Figure 70: ^{13}C NMR spectrum of compound **8b** (101 MHz, $CDCl_3$)

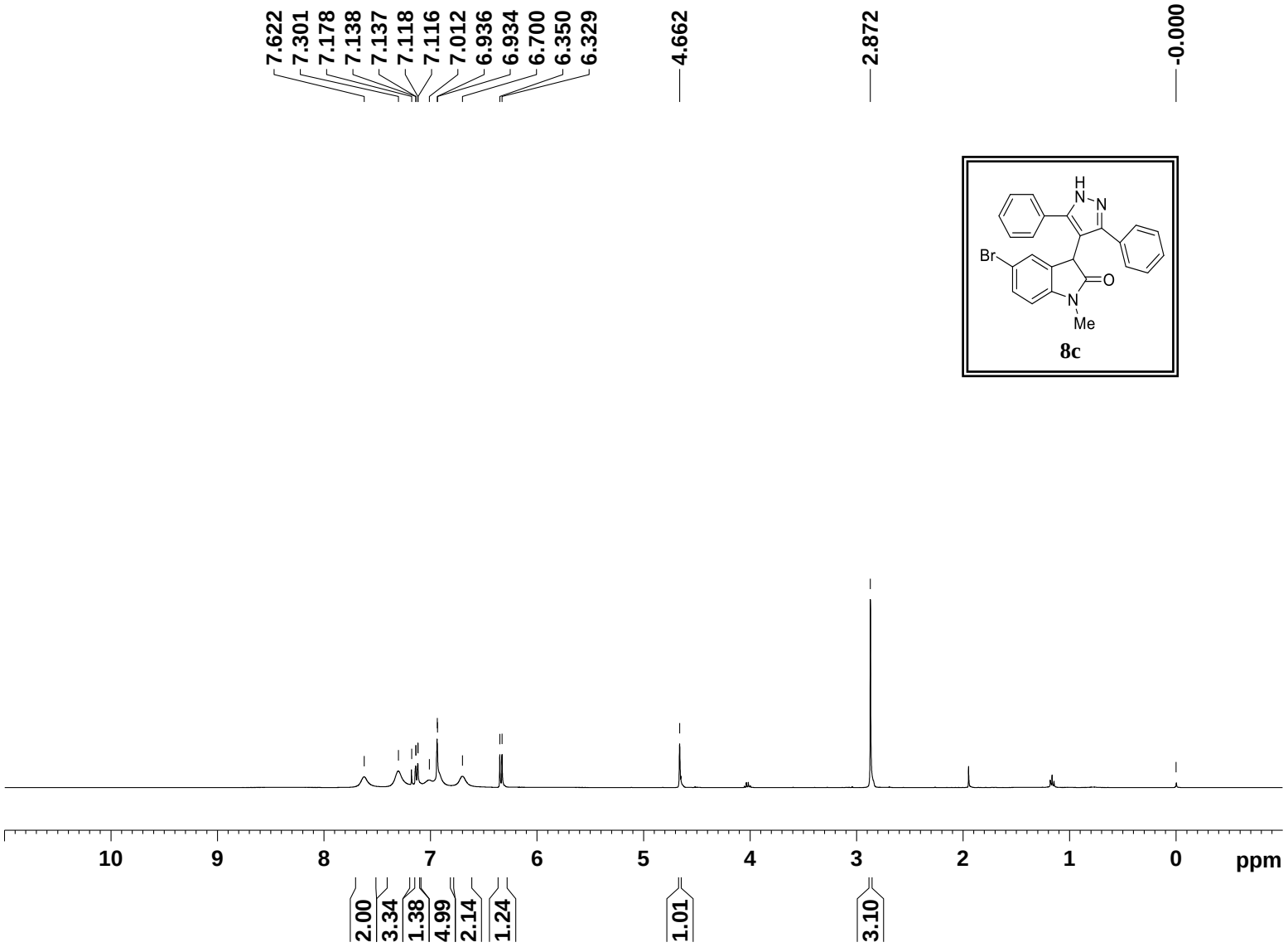


Figure 71: ^{1}H NMR spectrum of compound **8c** (400 MHz, $CDCl_3$)

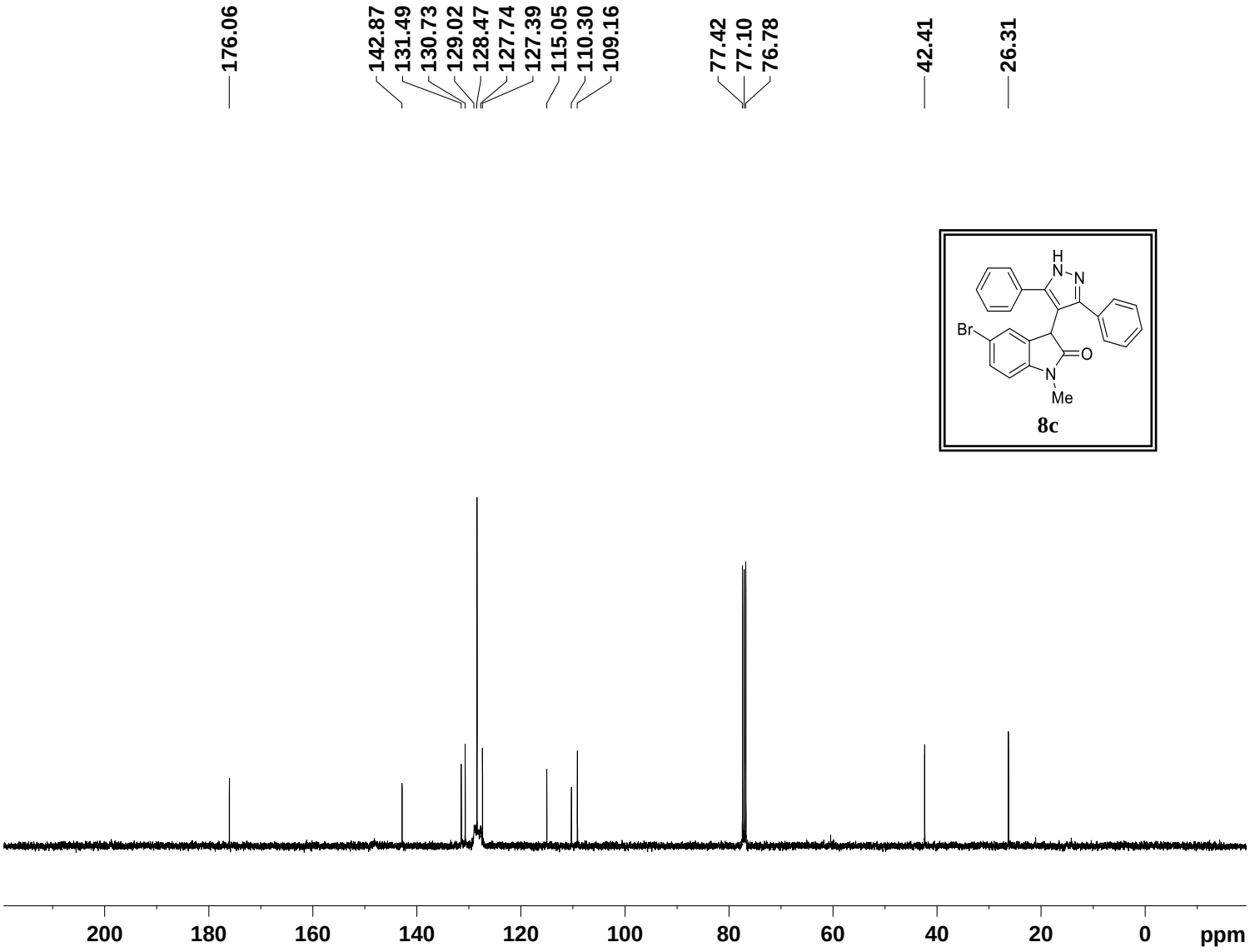


Figure 72: ^{13}C NMR spectrum of compound **8c** (101 MHz, $CDCl_3$)

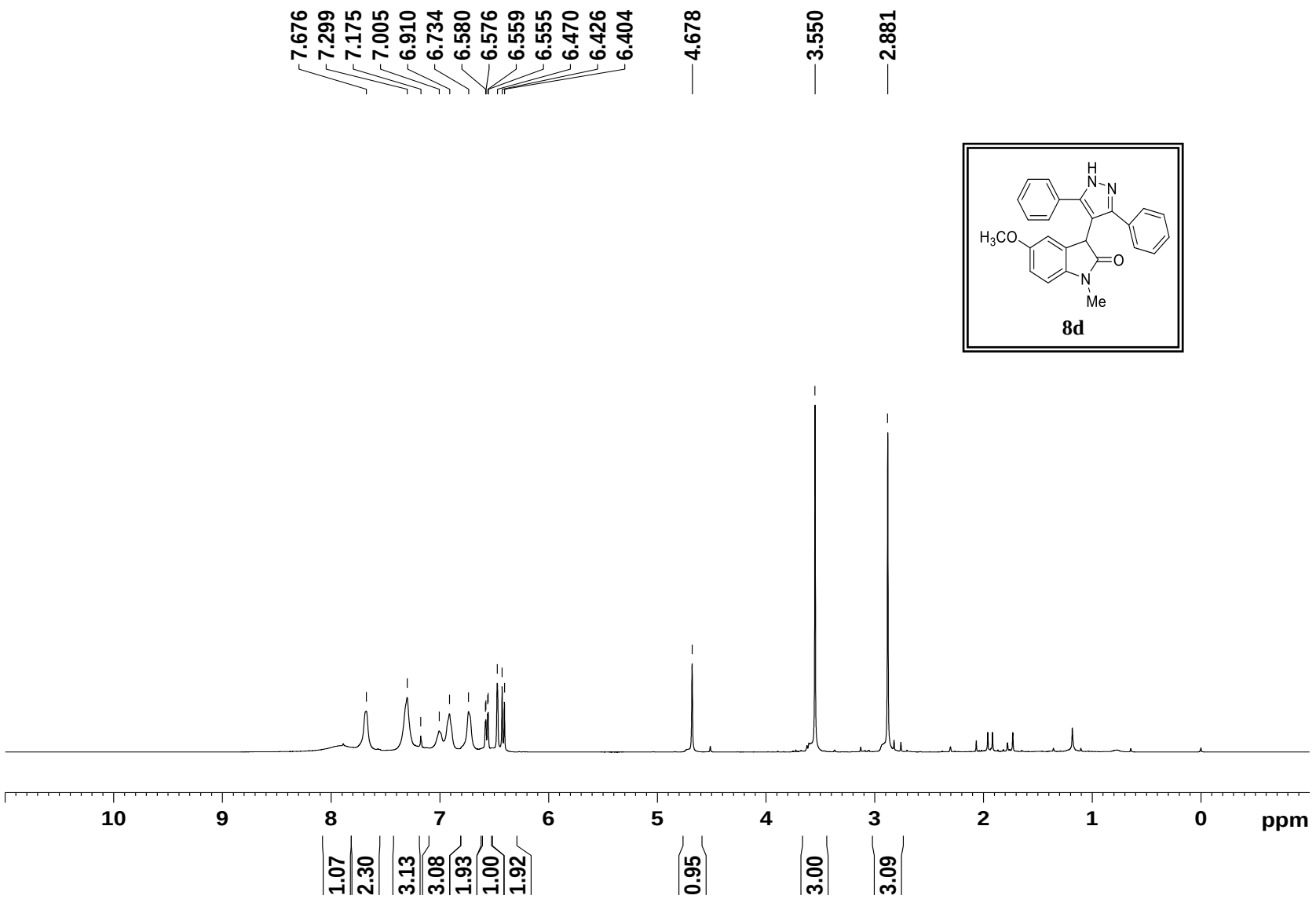


Figure 73: ^{1}H NMR spectrum of compound **8d** (400 MHz, $CDCl_3$)

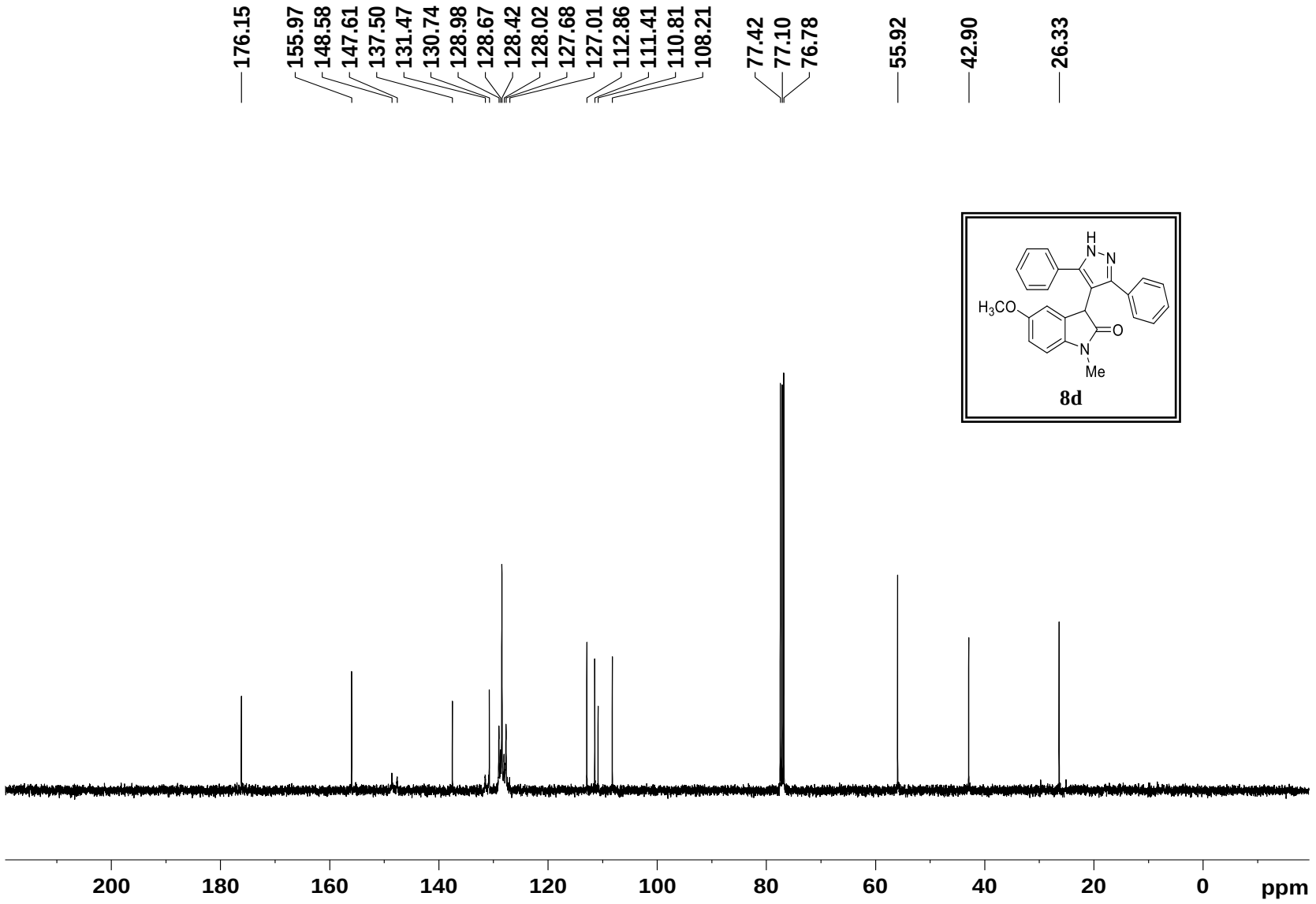


Figure 74: ^{13}C NMR spectrum of compound **8d** (101 MHz, $CDCl_3$)

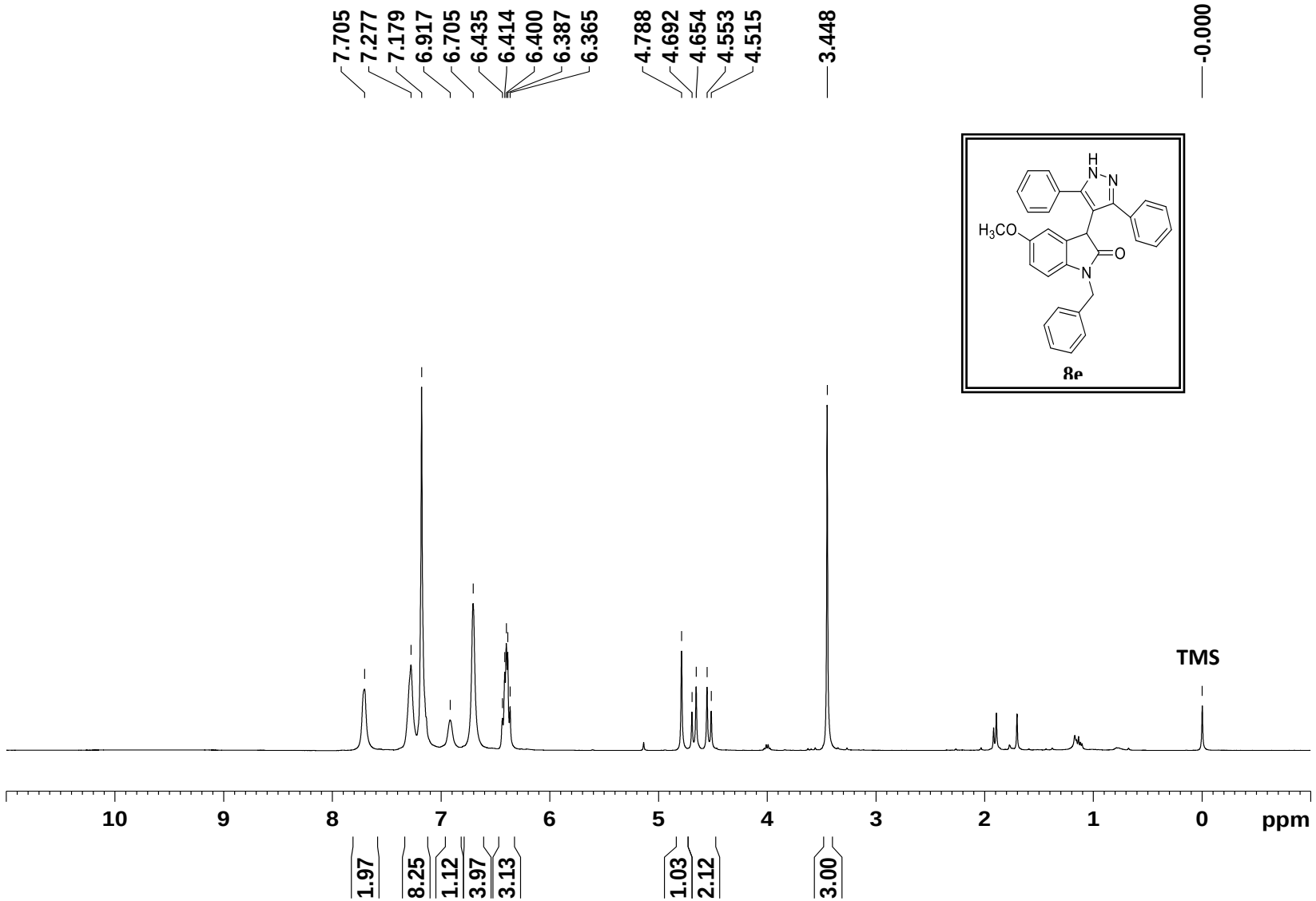


Figure 75: ^{1}H NMR spectrum of compound **8e** (400 MHz, $CDCl_3$)

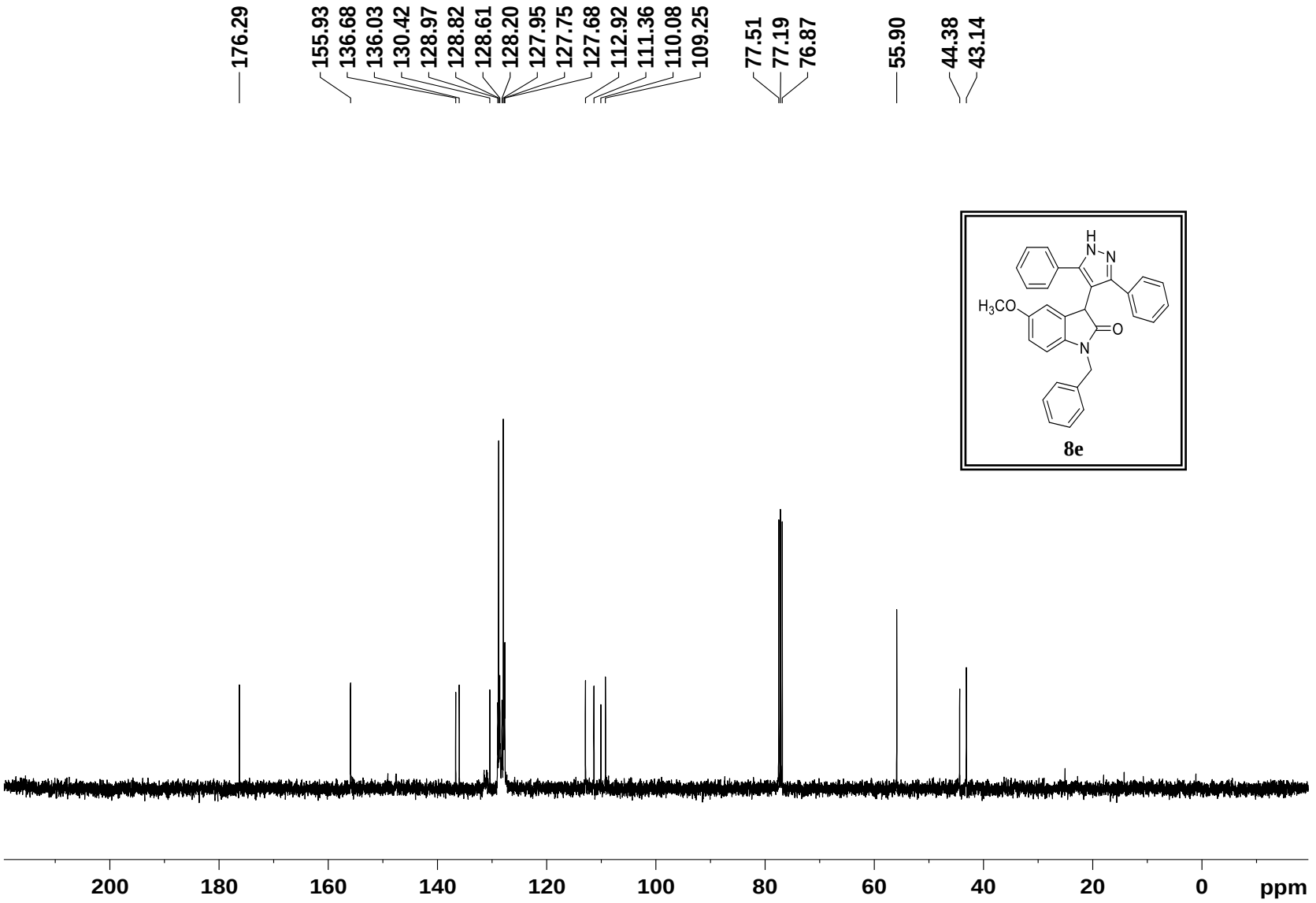


Figure 76: ^{13}C NMR spectrum of compound **8e** (101 MHz, $CDCl_3$)

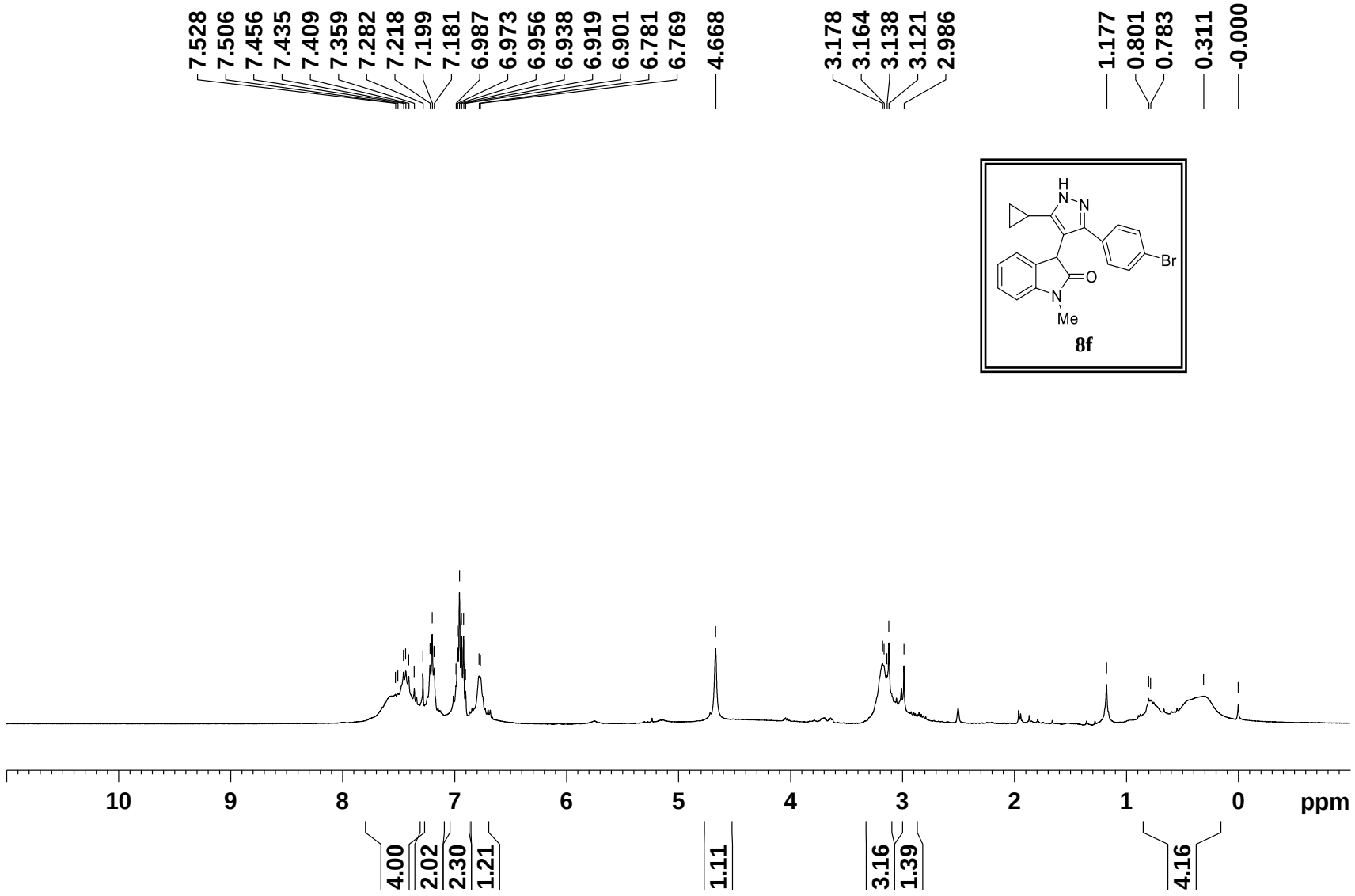


Figure 77: ^{1}H NMR spectrum of compound **8f** (400 MHz, $CDCl_3$+DMSO)

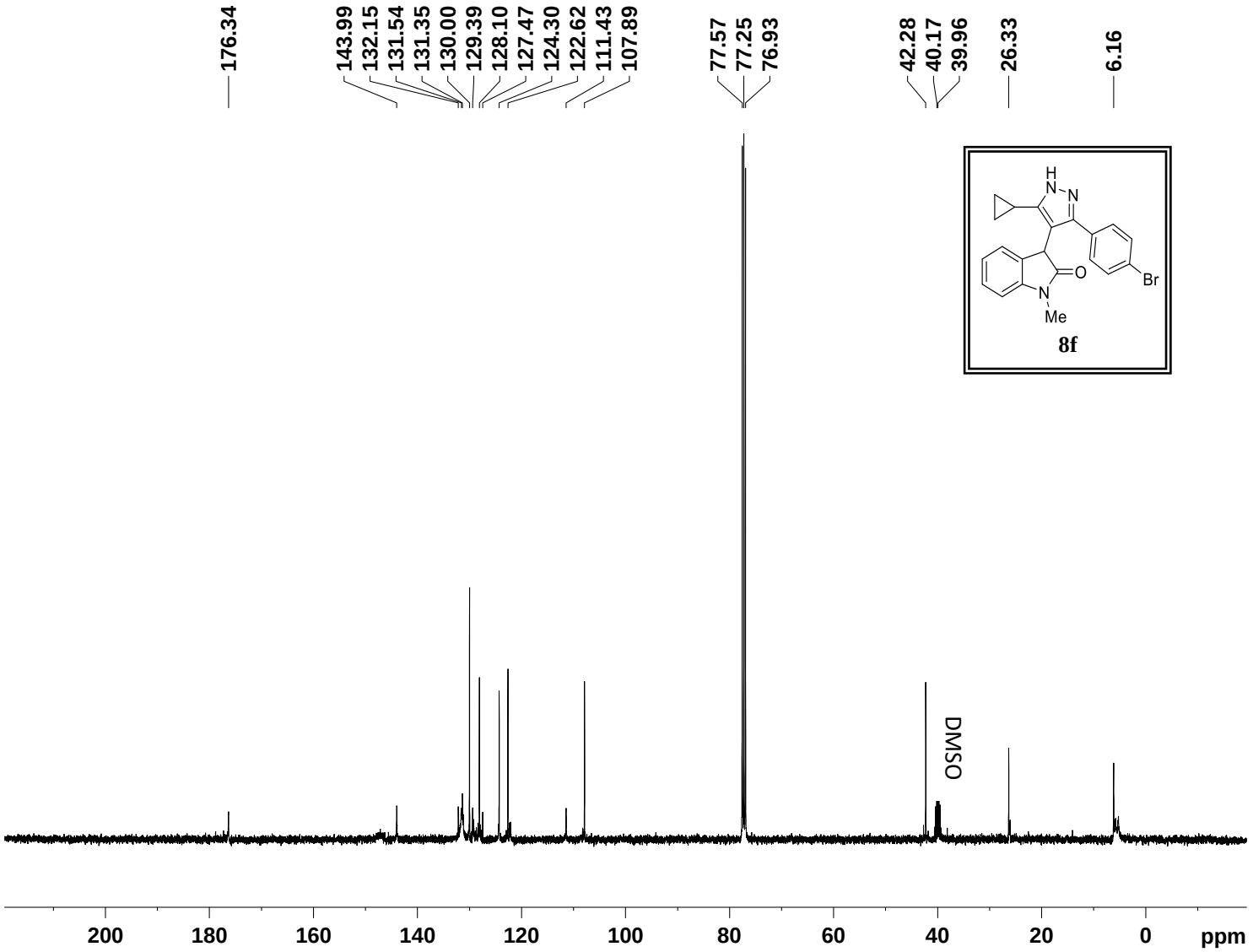


Figure 78: ^{13}C NMR spectrum of compound **8f** (101 MHz, $CDCl_3$+DMSO)

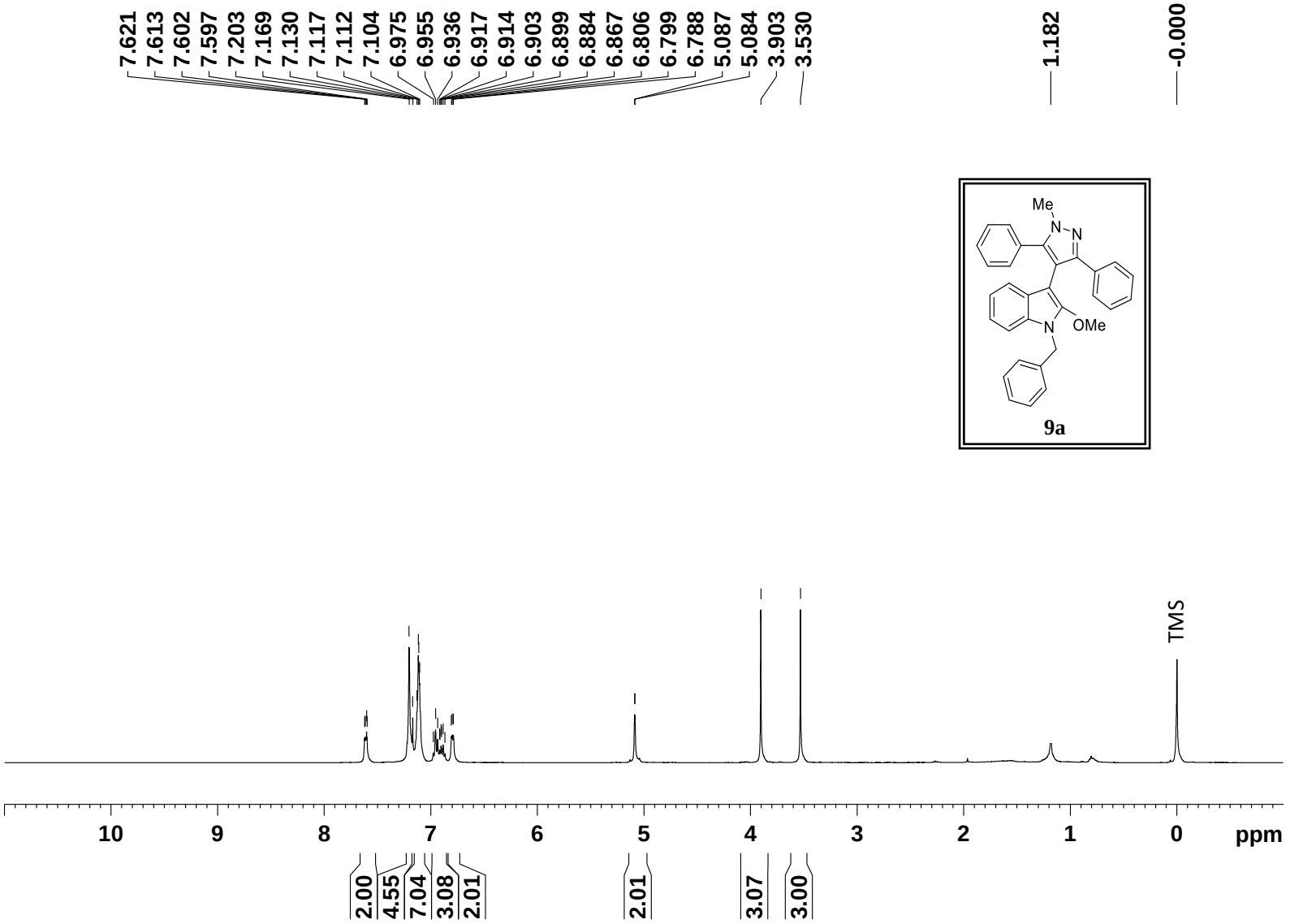


Figure 79: ^{1}H NMR spectrum of compound **9a** (400 MHz, $CDCl_3$)

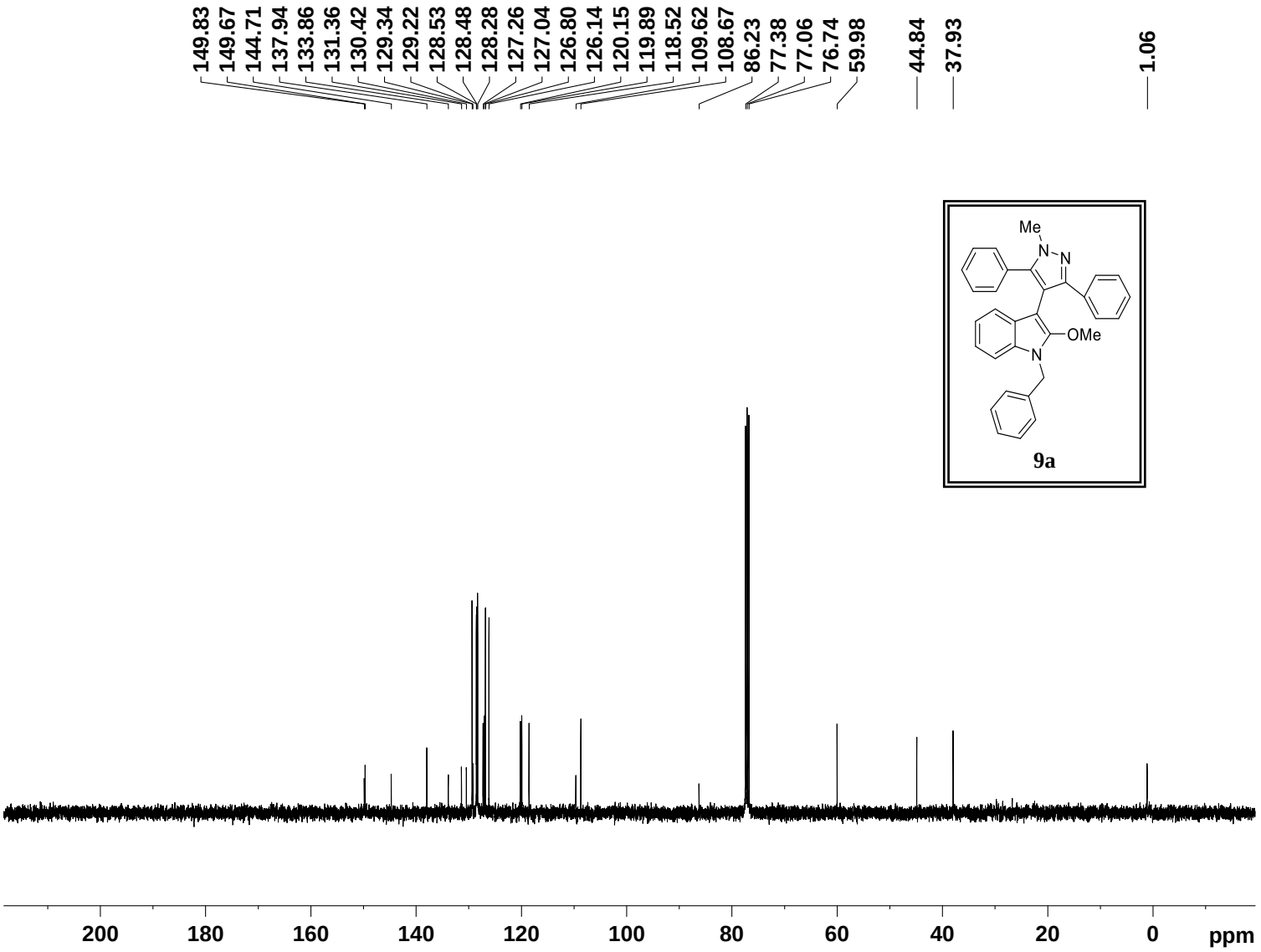


Figure 80: ^{13}C NMR spectrum of compound **9a** (101 MHz, $CDCl_3$)

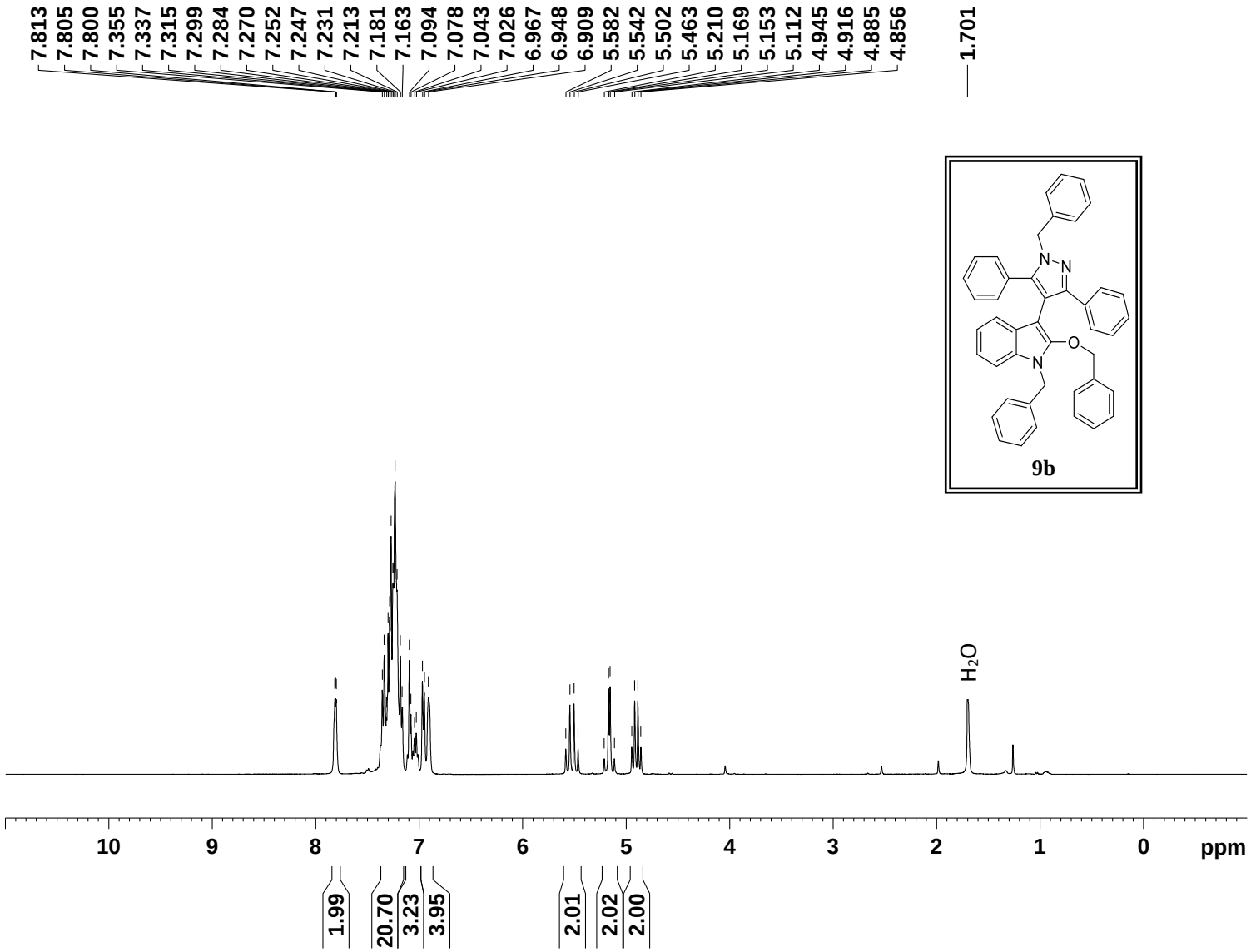


Figure 81: ^{1}H NMR spectrum of compound **9b** (400 MHz, $CDCl_3$)

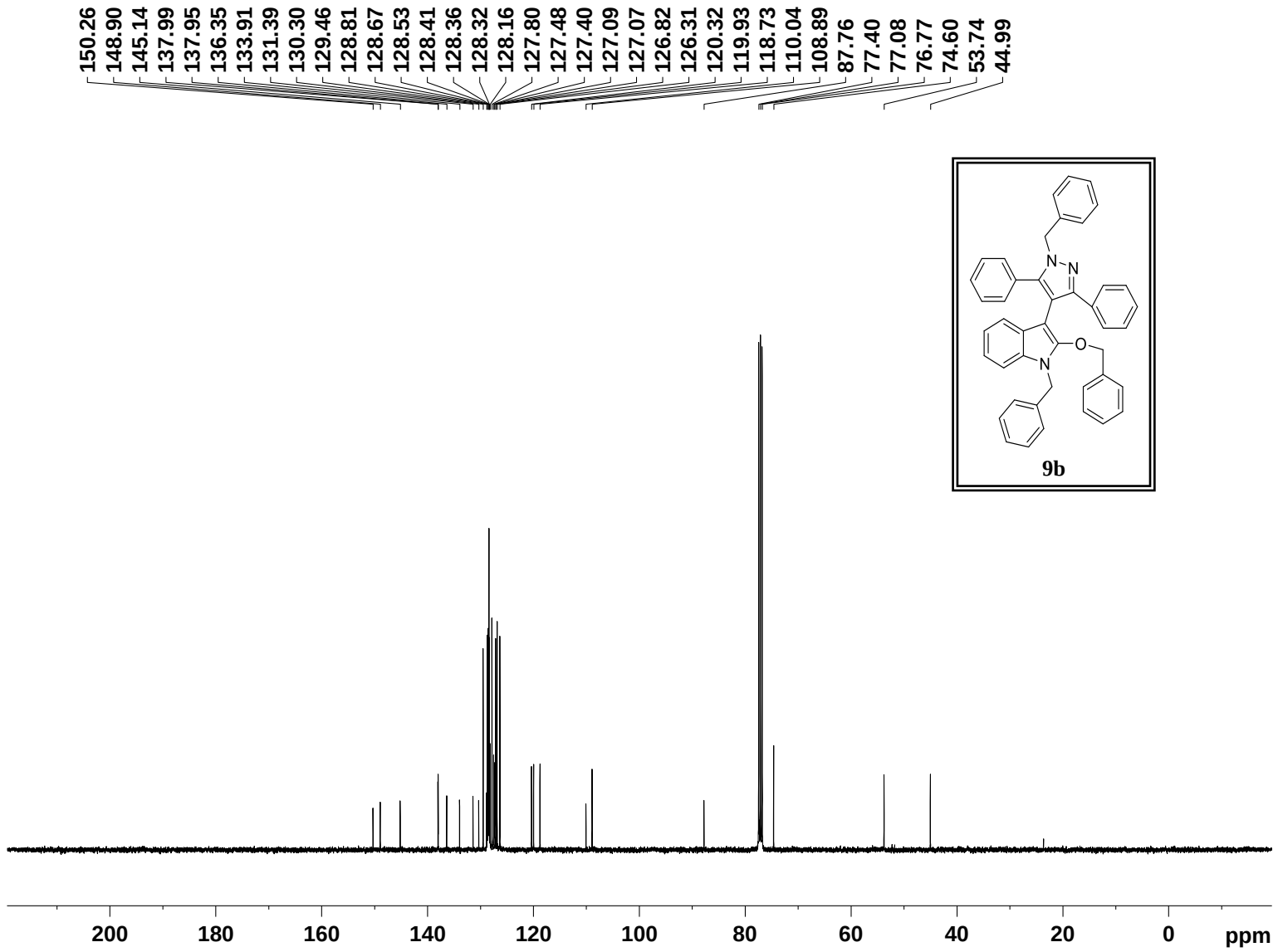


Figure 82: ^{13}C NMR spectrum of compound **9b** (101 MHz, $CDCl_3$)

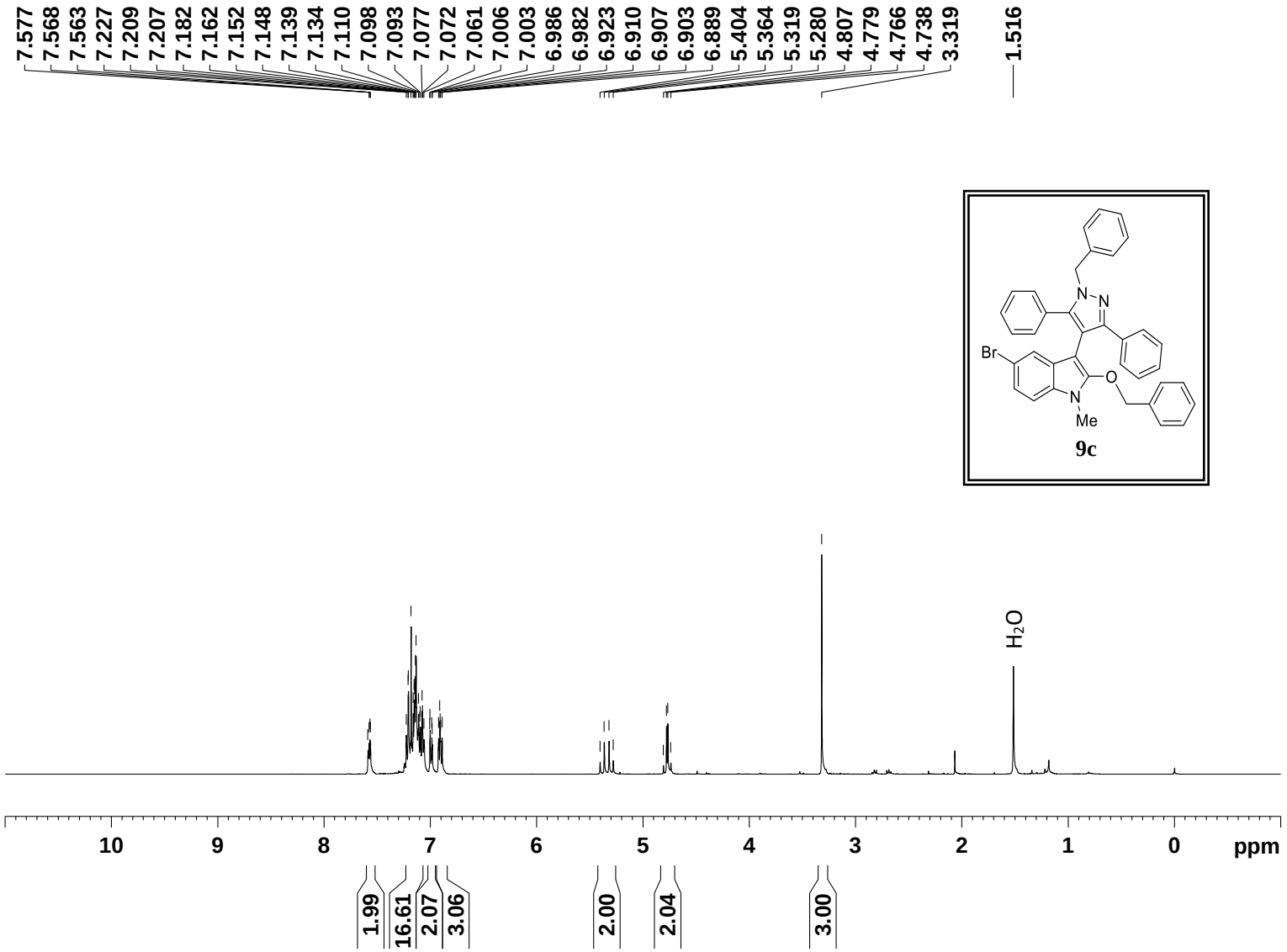


Figure 83: ^{1}H NMR spectrum of compound **9c** (400 MHz, $CDCl_3$)

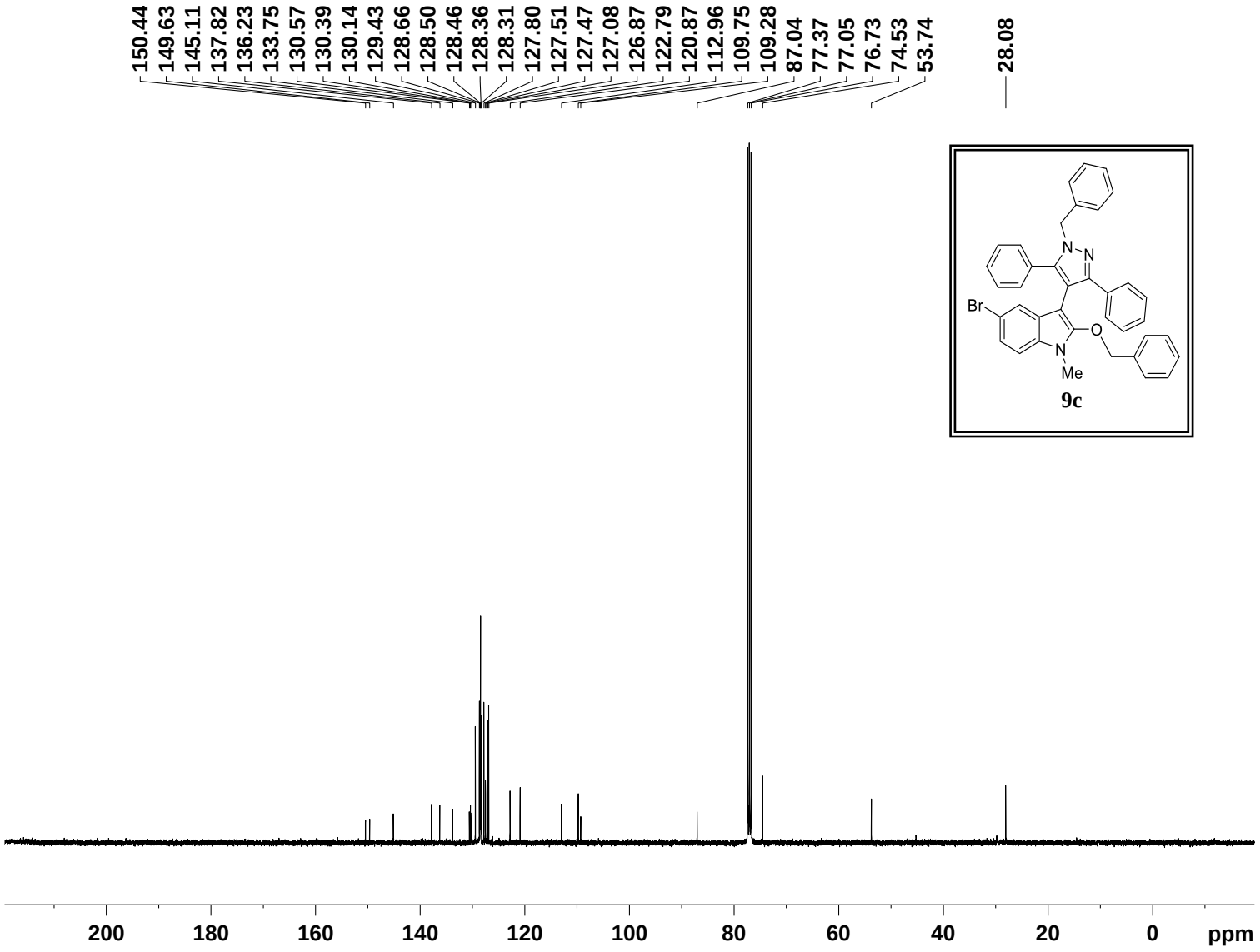


Figure 84: ^{13}C NMR spectrum of compound **9c** (101 MHz, $CDCl_3$)

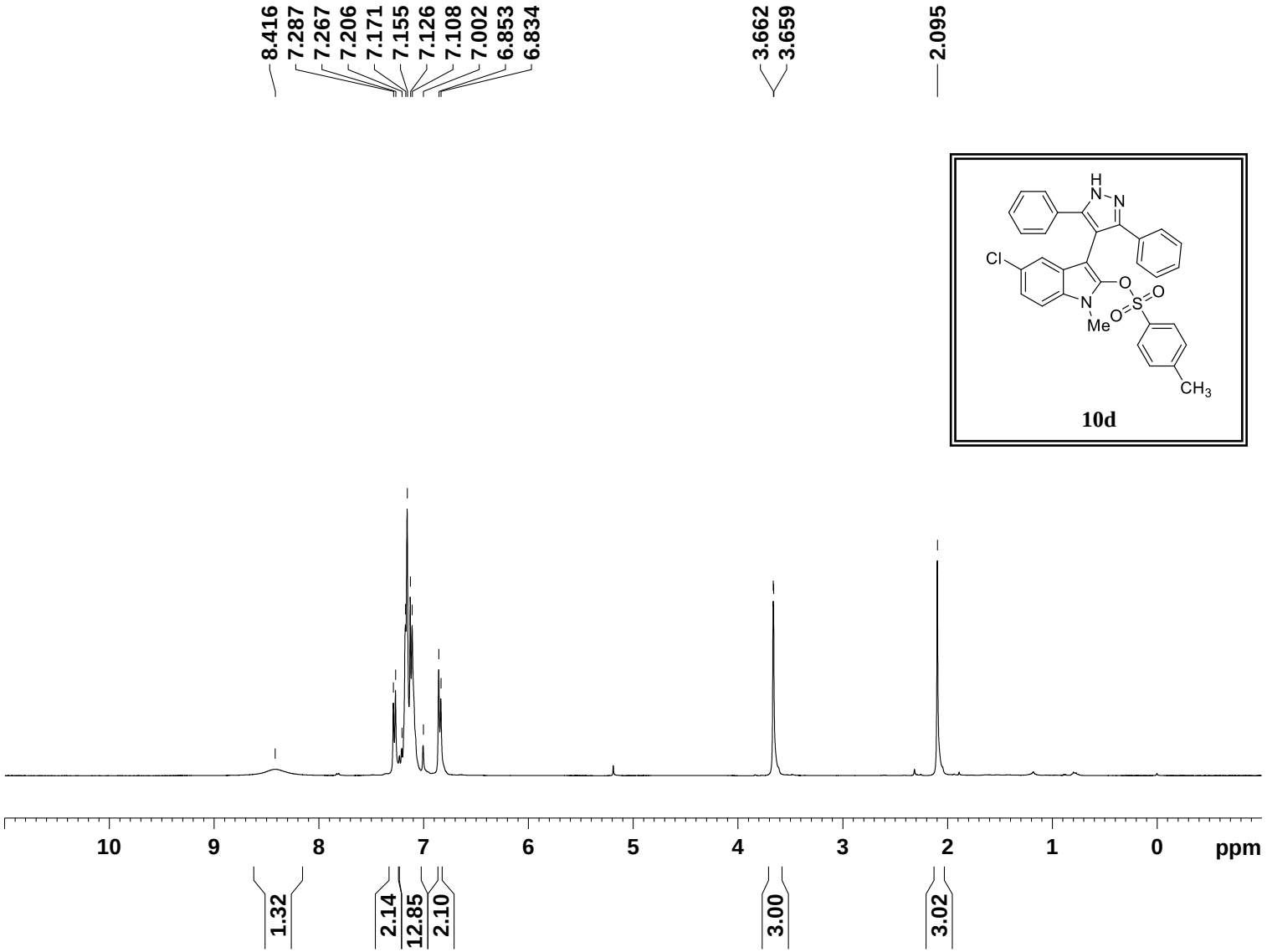


Figure 85: ^{1}H NMR spectrum of compound **10d** (400 MHz, $CDCl_3$)

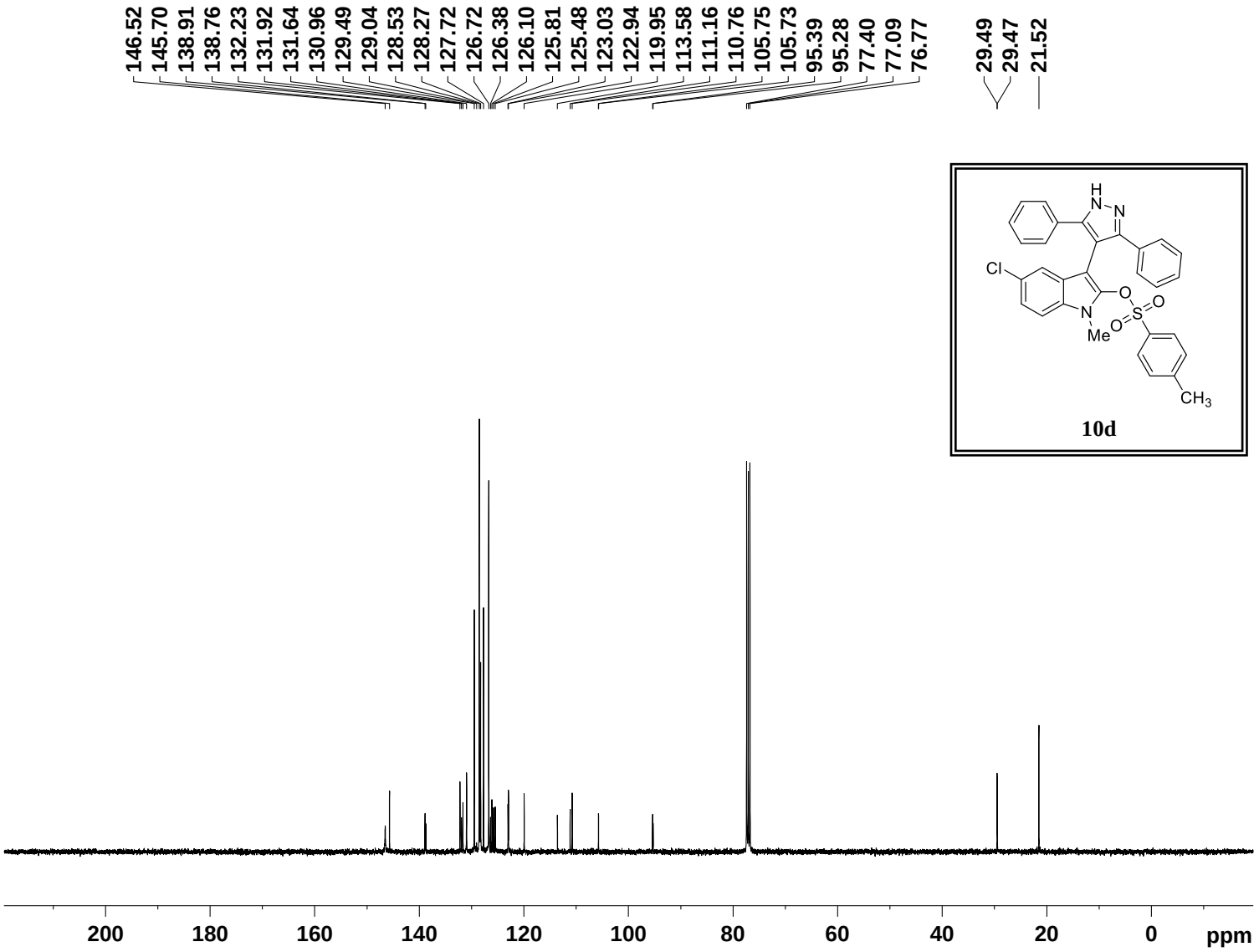


Figure 86: ^{13}C NMR spectrum of compound **10d** (101 MHz, $CDCl_3$)

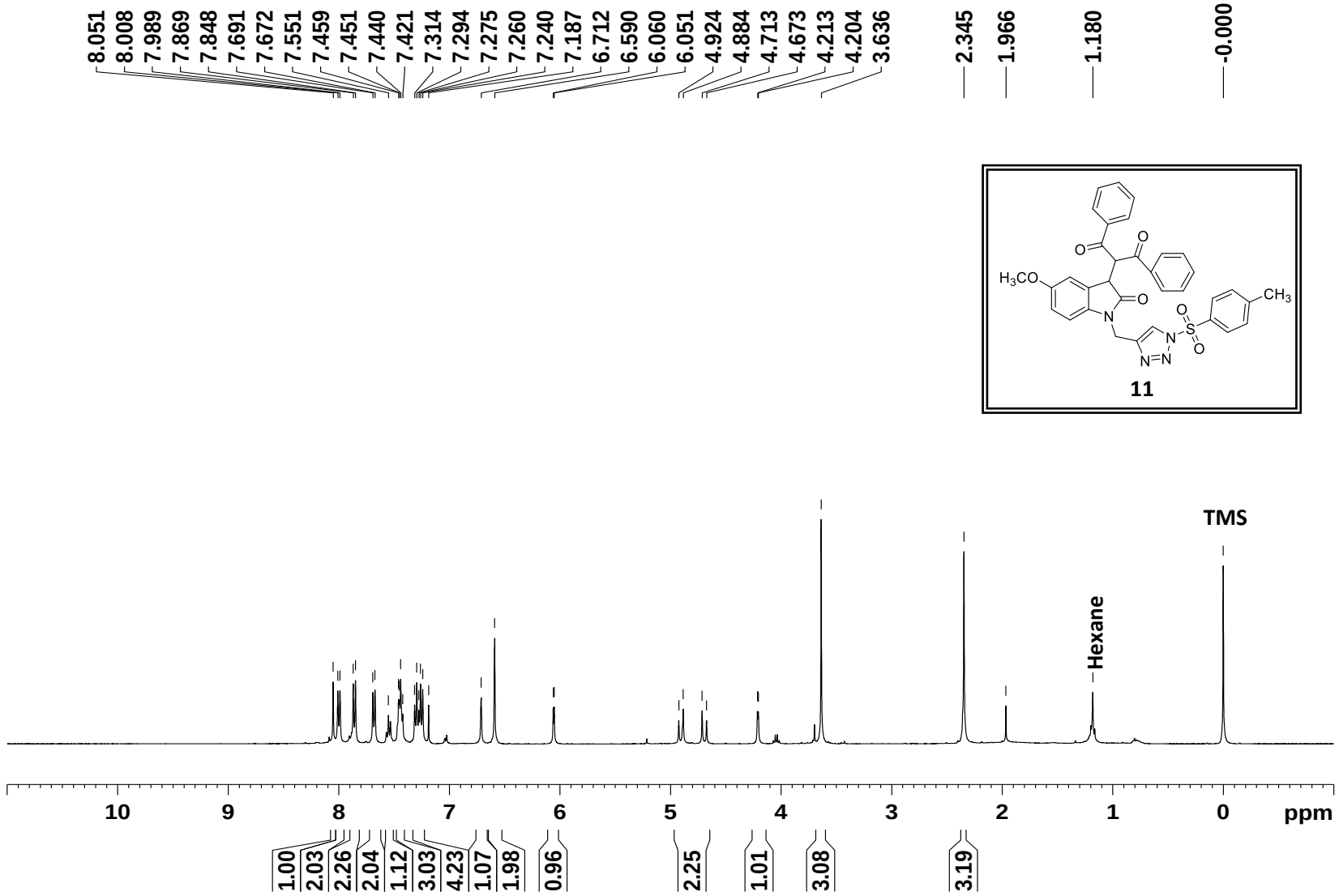


Figure 87: ^{1}H NMR spectrum of compound **11** (400 MHz, $CDCl_3$)

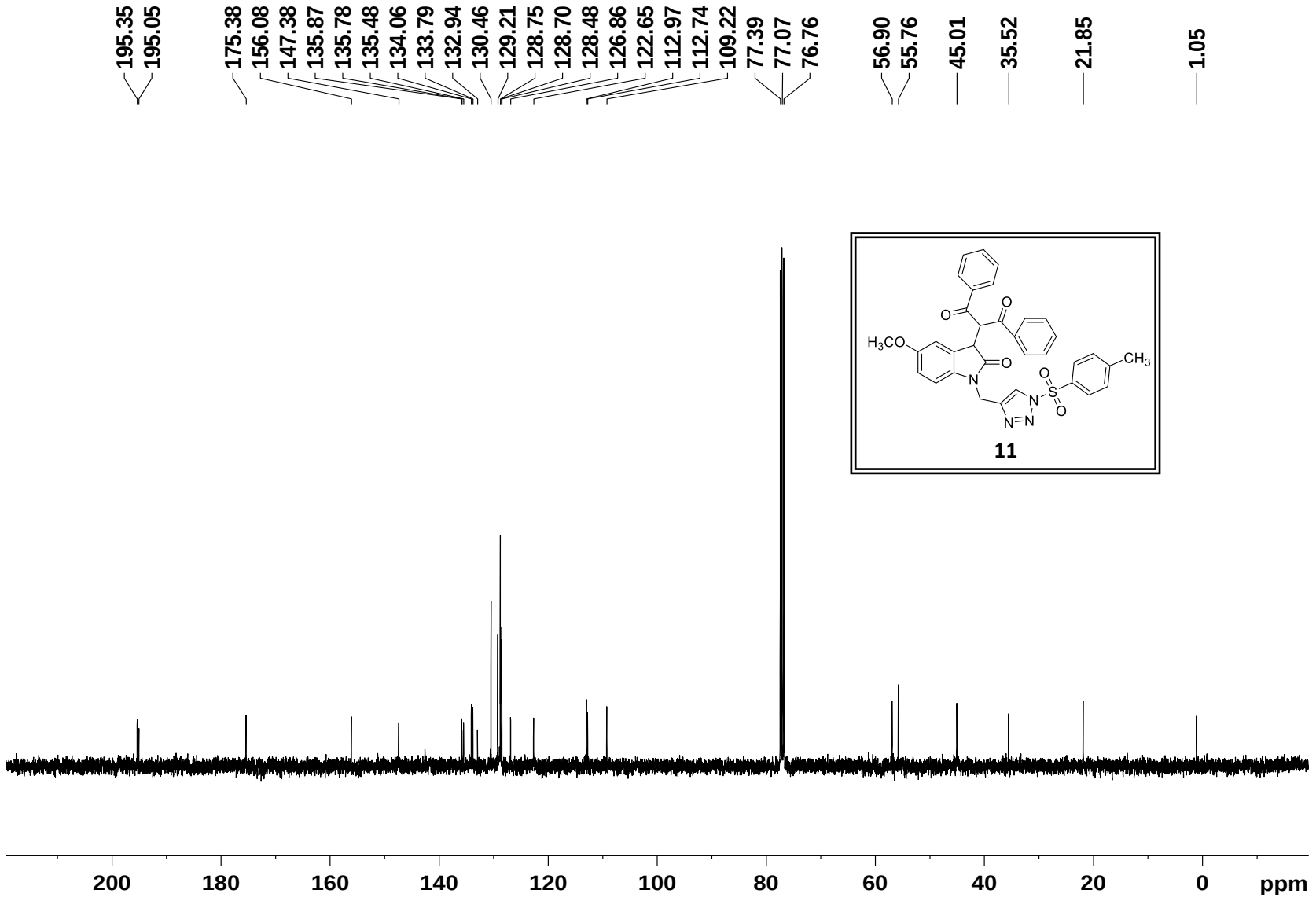


Figure 88: ^{13}C NMR spectrum of compound **11** (101 MHz, $CDCl_3$)

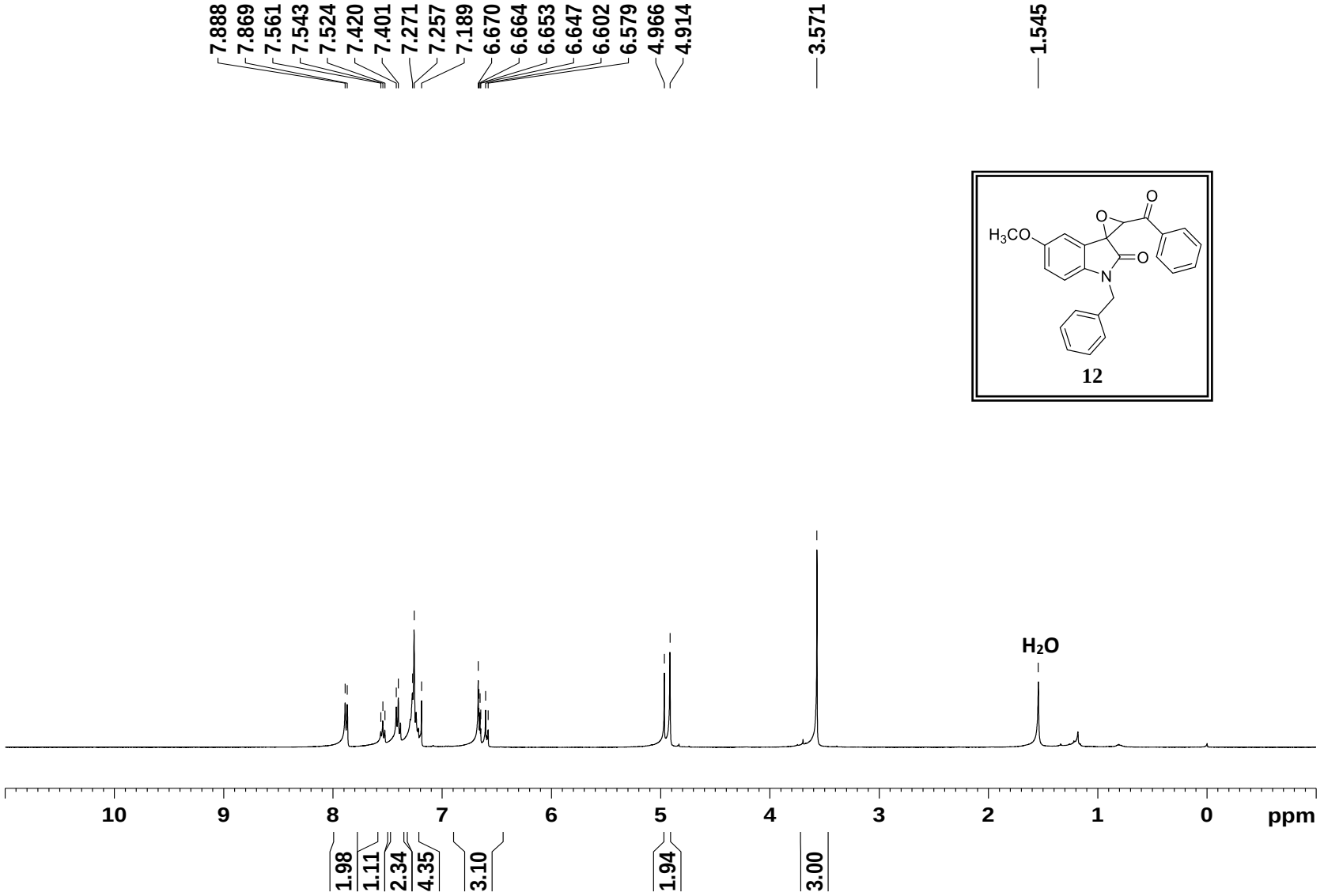


Figure 89: ^{1}H NMR spectrum of compound **12** (400 MHz, $CDCl_3$)[3]

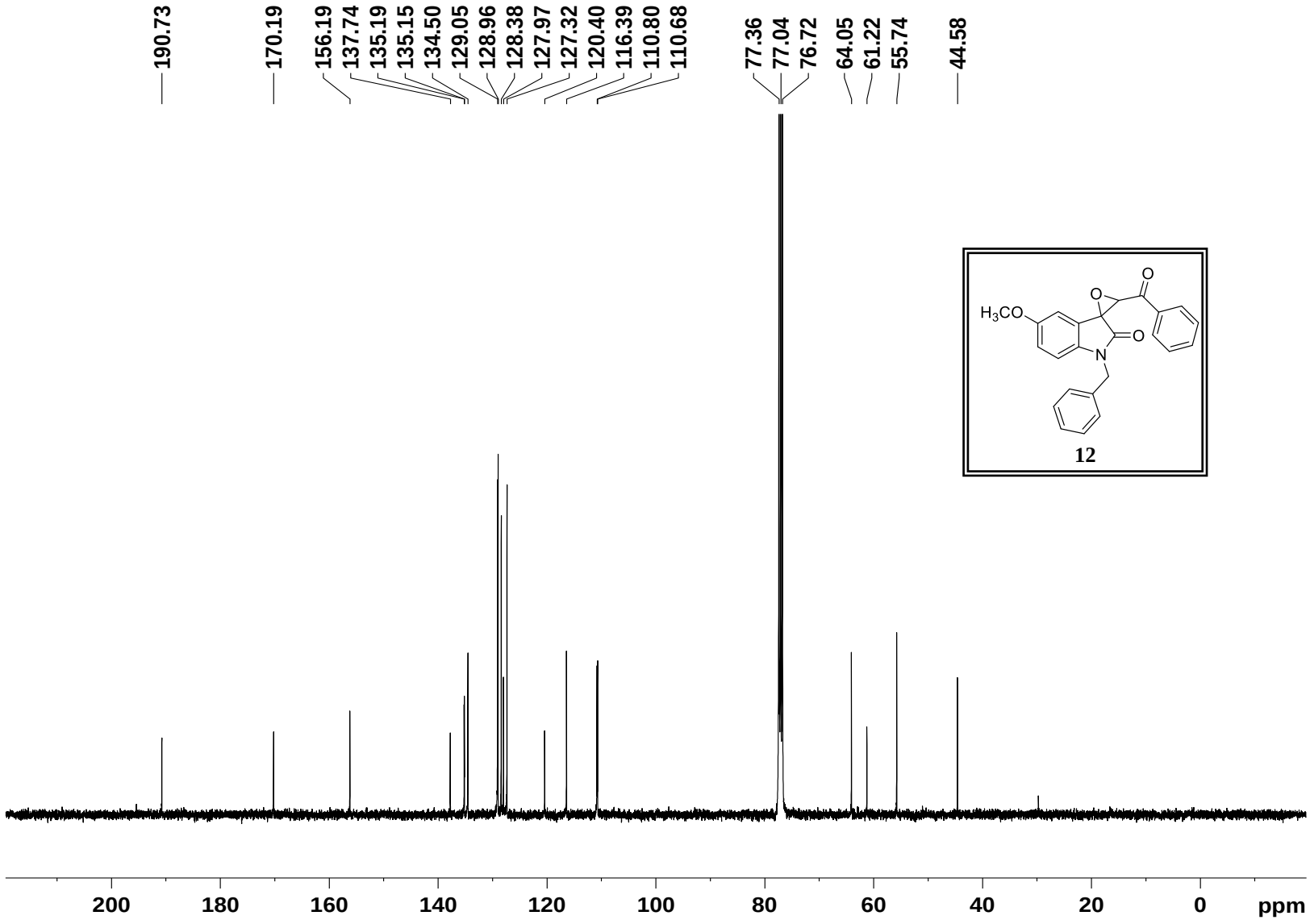


Figure 90: ^{13}C NMR spectrum of compound **12** (101 MHz, $CDCl_3$)[3]

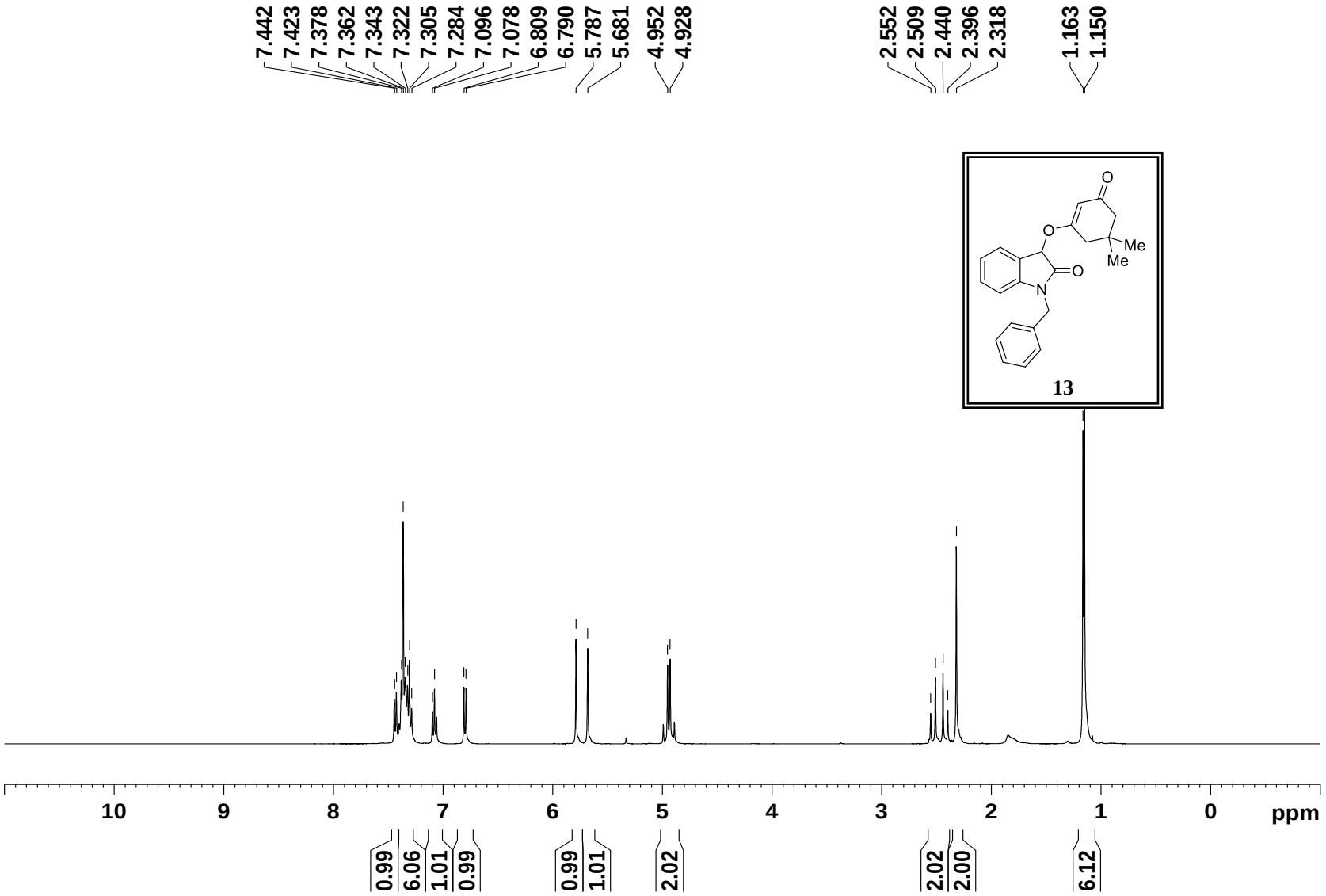


Figure 91: ^{1}H NMR spectrum of compound **13** (400 MHz, $CDCl_3$)

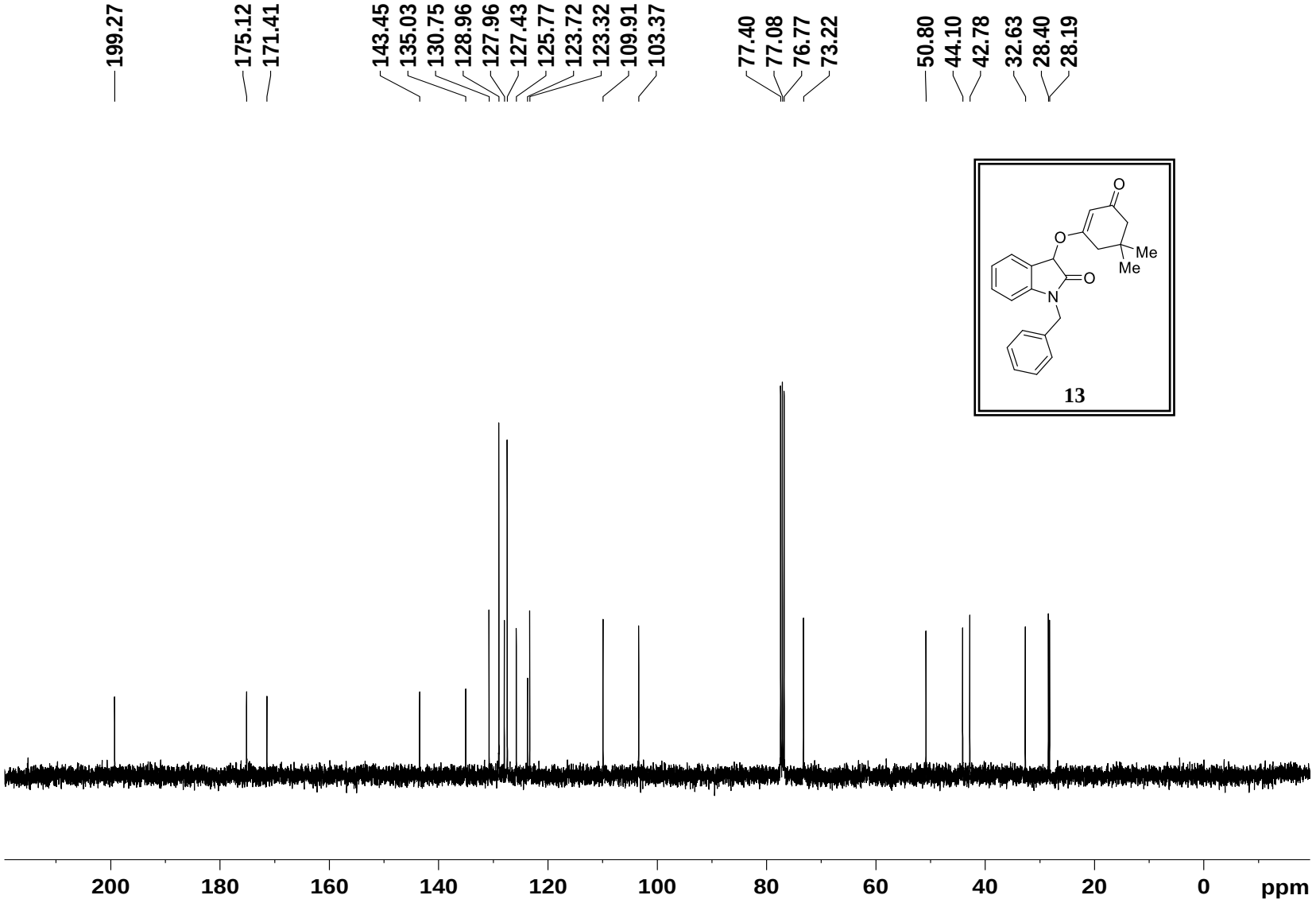
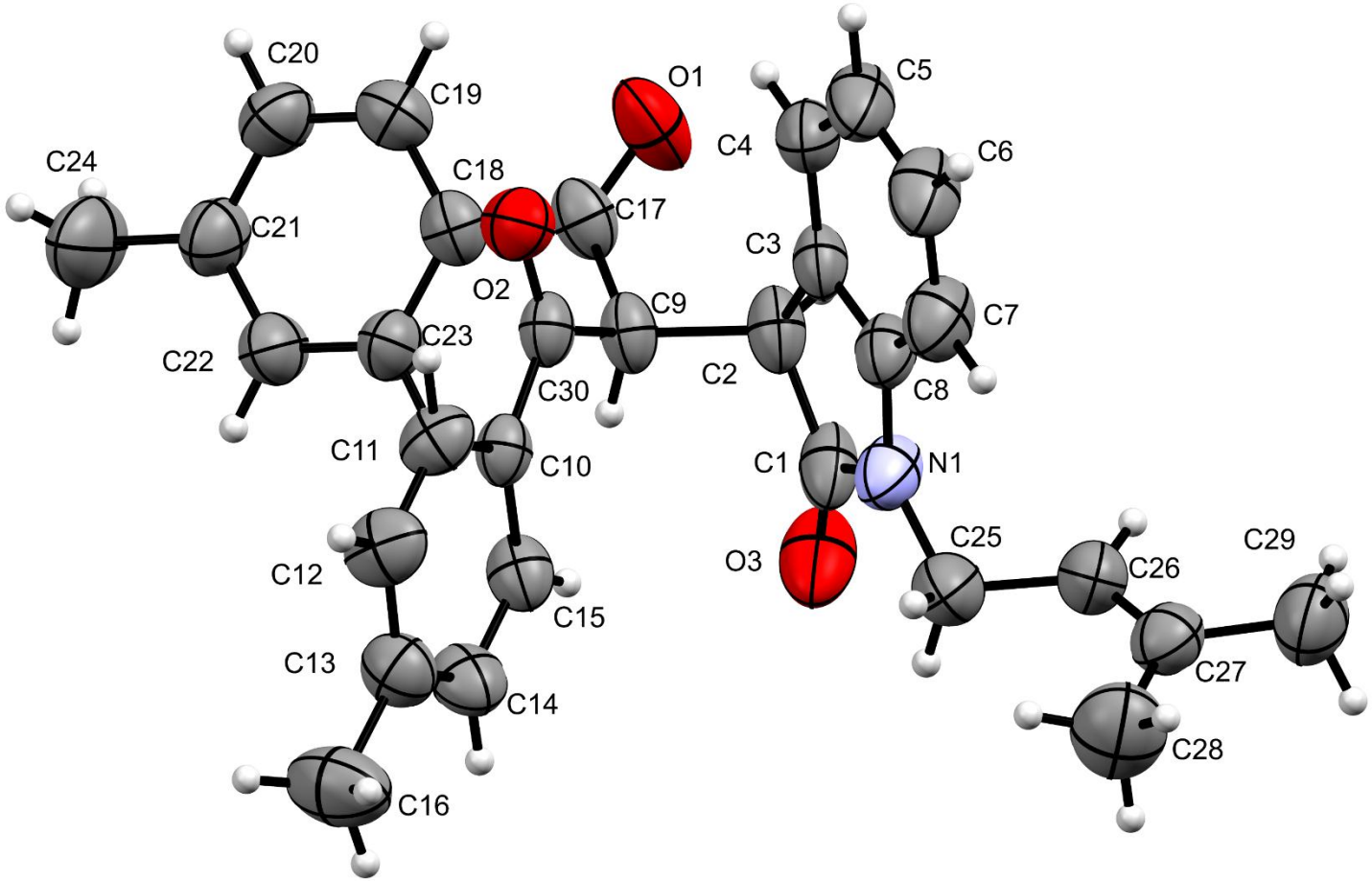


Figure 92: ^{13}C NMR spectrum of compound **13** (101 MHz, $CDCl_3$)



ORTEP drawing of the X-ray crystallographic structure of compound 3s.

The thermal ellipsoids are shown at the 50% probability level. Crystals suitable for X-Ray analysis was obtained via vapor diffusion (Chloroform) at room temperature. The crystal structure has been deposited at the Cambridge Crystallographic Date Center and allocated the deposition numbers CCDC 2348272.

Identification code	EXTER124_0m_a
Empirical formula	$C_{30}H_{29}NO_3$
Formula weight	451.54
Temperature/K	297.0
Crystal system	Triclinic
Identification code	EXTER124_0m_a
Empirical formula	$C_{30}H_{29}NO_3$
Space group	P-1
a/Å	9.8699(11)
b/Å	11.0458(11)
c/Å	12.3323(13)
α/°	75.493(4)
β/°	89.452(4)
γ/°	72.348(4)
Volume/Å^3	1237.1(2)
Z	2
ρ_{calc}g/cm^3	1.212
μ/mm^{-1}	0.078
F(000)	480.0
Crystal size/mm^3	0.201 × 0.183 × 0.139
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.42 to 50.7
Index ranges	$-11 \leq h \leq 11$, $-13 \leq k \leq 13$, $-14 \leq l \leq 14$
Reflections collected	40657
Independent reflections	4516 [R_{int} = 0.0486, R_{sigma} = 0.0230]
Data/restraints/parameters	4516/0/311
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0508, wR_2 = 0.1340
Final R indexes [all data]	R_1 = 0.0583, wR_2 = 0.1394
Largest diff. peak/hole / e Å^{-3}	0.26/-0.26

Crystal data for product 3s

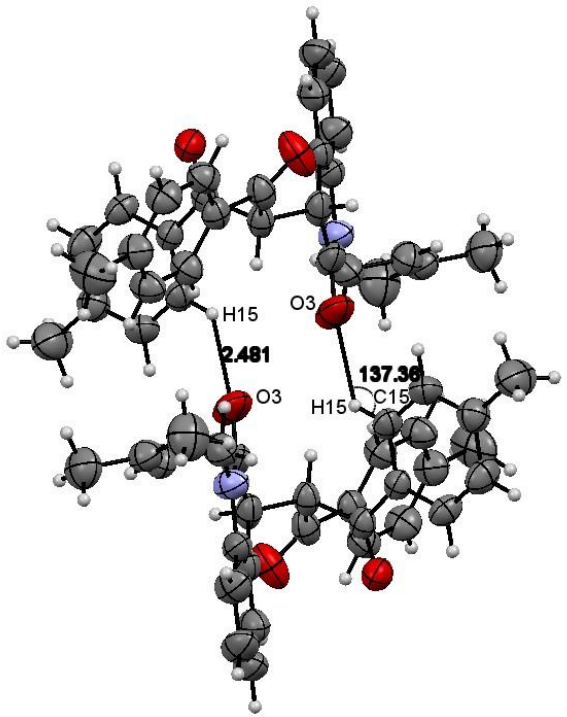
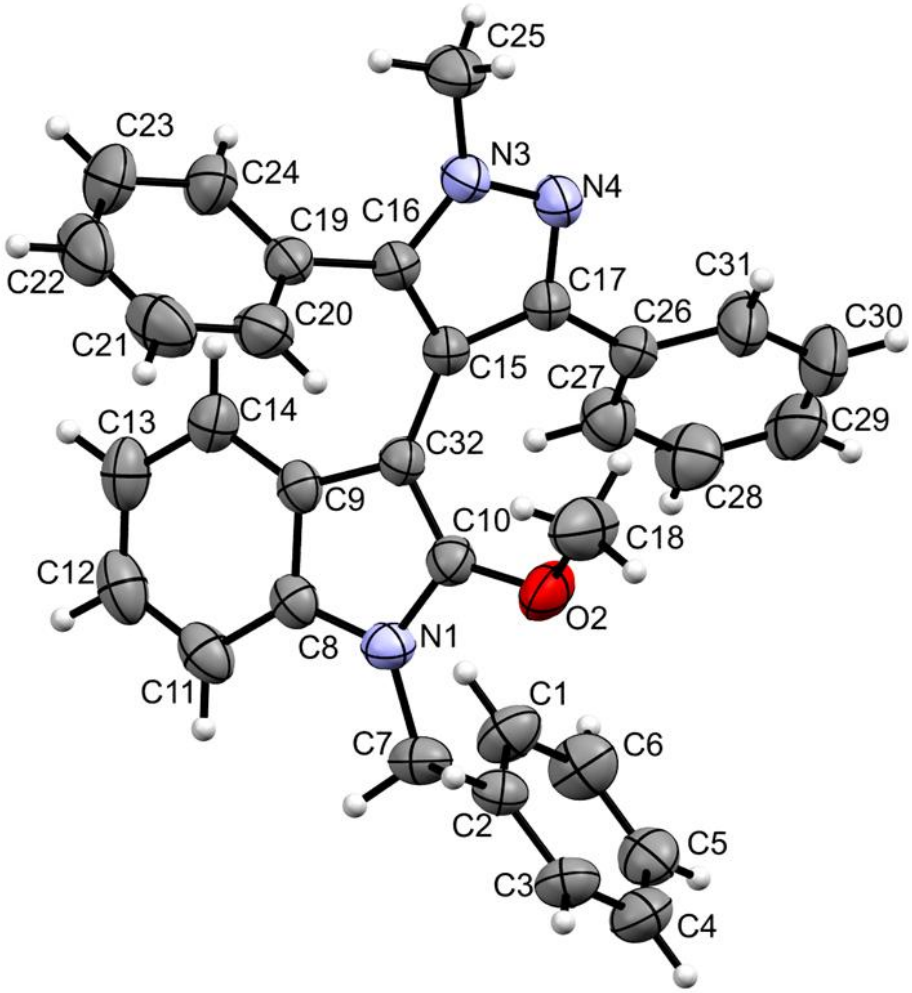


Figure 90. View of **3s** showing interactions and bond length in solid-state arrangement

(i) C-H---O

C15-H15---O3 Bond length H15-O3 = 2.481 Å

Bond angle C15-H15---O3 = 137.36 °

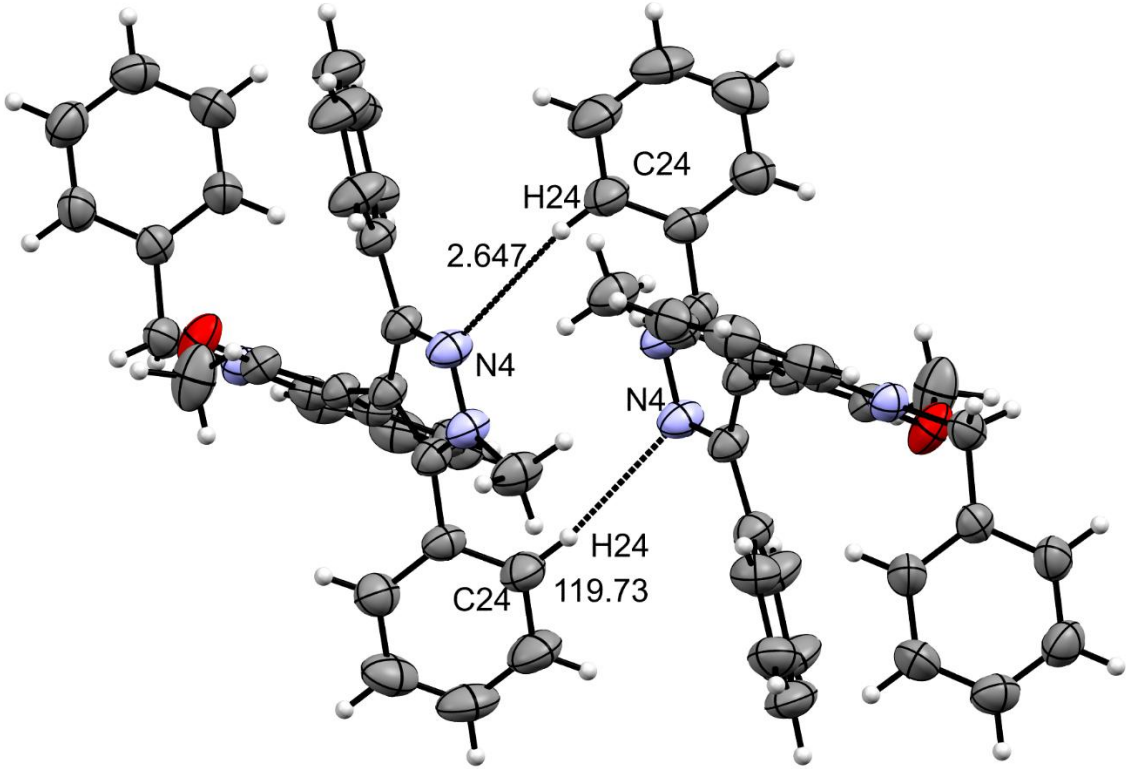


ORTEP drawing of the X-ray crystallographic structure of compound 9a.

The thermal ellipsoids are shown at the 50% probability level. Crystals suitable for X-Ray analysis was obtained *via* vapor diffusion (Chloroform) at room temperature. The crystal structure has been deposited at the Cambridge Crystallographic Date Center and allocated the deposition numbers CCDC 2484660.

Identification code	SHA_381_080125_0m_a
Empirical formula	C32H27N3O
Formula weight	451.54
Temperature/K	300k
Crystal system	Triclinic
Identification code	SHA_381_080125_0m_a
Empirical formula	$C_{30}H_{29}NO_3$
Space group	P-1
a/Å	8.9884(4)
b/Å	11.0210(4)
c/Å	14.0270(5)
α/°	110.534(1)
β/°	104.021(1)
γ/°	95.898(1)
Volume/$Å^3$	1235.23(8)
Z	2
$\rho_{calc}g/cm^3$	1.263
μ/mm^{-1}	0.077
F(000)	496.0
Crystal size/mm^3	0.201 × 0.183 × 0.139
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.42 to 50.7
Index ranges	$-11 \leq h \leq 11$, $-14 \leq k \leq 14$, $-18 \leq l \leq 18$
Reflections collected	40657
Independent reflections	4516 [R_{int} = 0.0486, R_{sigma} = 0.0230]
Data/restraints/parameters	4516/0/311
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0508, wR_2 = 0.1340
Final R indexes [all data]	R_1 = 0.0583, wR_2 = 0.1394
Largest diff. peak/hole / e $Å^{-3}$	0.26/-0.26

Crystal data for product 9a



F**igure 91**. View of **9a** showing interactions and bond length in solid-state arrangement

(i) C-H---N

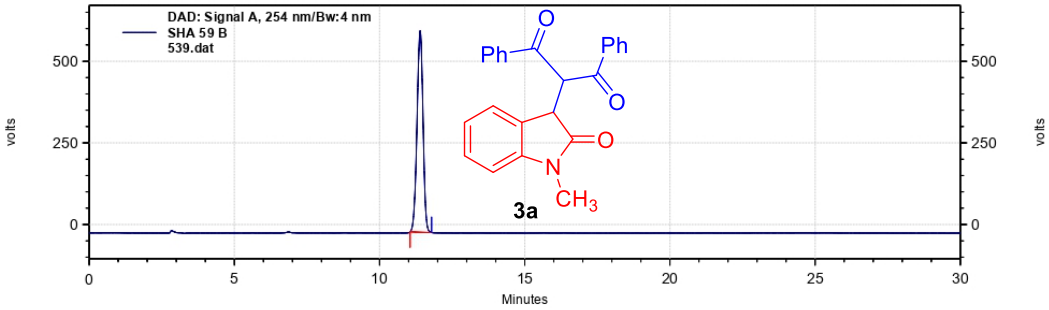
C24-H24---N4 Bond length H24-N4 = 2.647 Å

Bond angle C24-H24---N4 = 119.73 °

HPLC chromatogram for product 3a

Area % Report

Data File: D:\Ezchrom\hplc data\SHA 59 B2022_SMLab_70_ACN_30_H2O_0.6ML.met.rslt\539.dat
Method: D:\Ezchrom\Method\2022_SMLab_70_ACN_30_H2O_0.6ML.met
Acquired: 23-Nov-22 7:27:34 PM (GMT +05:30)
Printed: 23-Nov-22 10:42:13 PM (GMT +05:30)



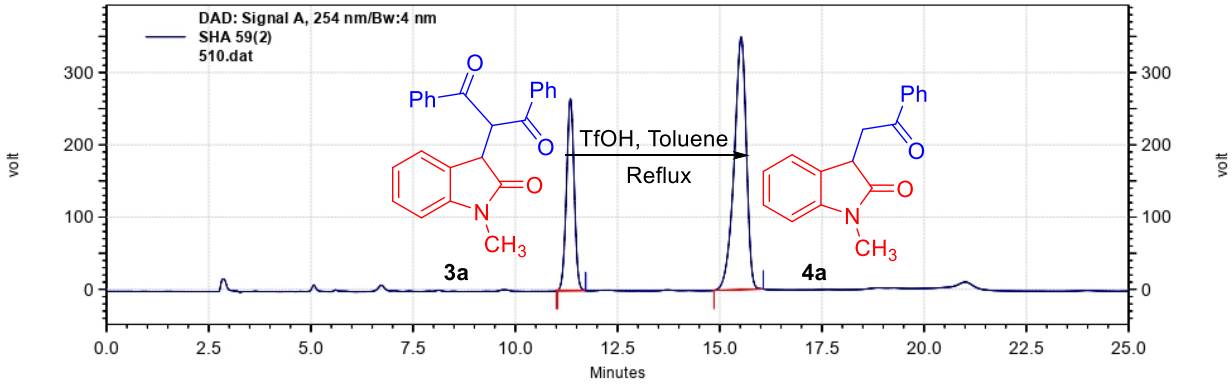
DAD: Signal A, 254 nm/Bw:4 nm
Results

Retention Time	Area	Area %	Height	Height %	**Name**
11.400	18641343	100.00	1294454	100.00	
Totals	18641343	100.00	1294454	100.00	

HPLC chromatogram for 3a converted into product 4a

Area % Report

Data File: D:\Ezchrom\hplc data\SHA 59(2) 2022_SMLab_70_ACN_30_H2O_0.6ML.met.rslt\510.dat
Method: D:\Ezchrom\Method\2022_SMLab_70_ACN_30_H2O_0.6ML.met
Acquired: 31-Oct-22 5:36:35 PM (GMT +05:30)
Printed: 08-Nov-22 1:20:59 PM (GMT +05:30)



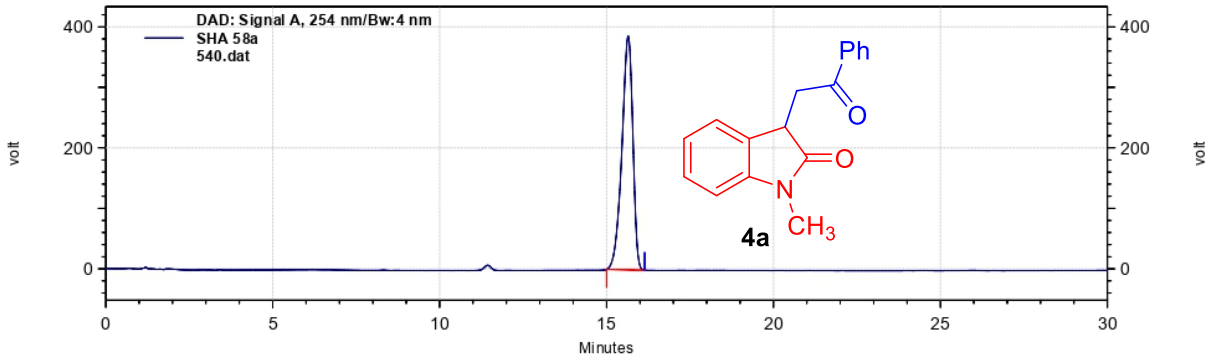
DAD: Signal A, 254 nm/Bw:4 nm
Results

Retention Time	Area	Area %	Height	Height %	Name
11.347	7341482	32.59	556671	43.17	
15.527	15181970	67.41	732959	56.83	
Totals	22523452	100.00	1289630	100.00	

HPLC chromatogram for product 4a

Area % Report

Data File: D:\Ezchrom\hplc data\SHA 58a2022_SMLab_70_ACN_30_H2O_0.6ML.met.rslt\540.dat
Method: D:\Ezchrom\Method\sha 58a.met
Acquired: 23-Nov-22 9:58:29 PM (GMT +05:30)
Printed: 23-Nov-22 10:35:21 PM (GMT +05:30)

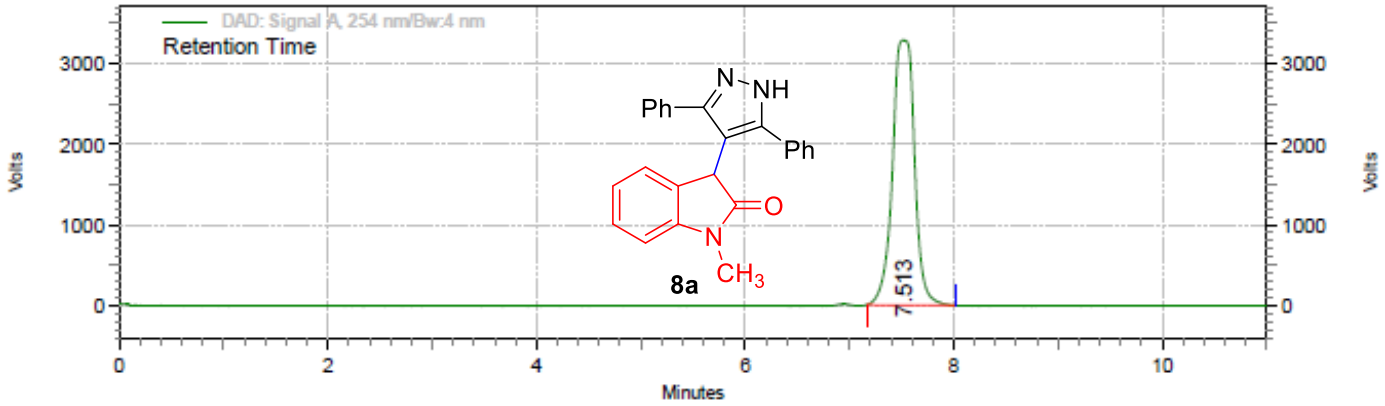


DAD: Signal A, 254 nm/Bw:4 nm
Results

Retention Time	Area	Area %	Height	Height %	**Name**
15.647	18480199	100.00	810915	100.00	
Totals	18480199	100.00	810915	100.00	

HPLC chromatogram for product 8a

Data File: D:\Ezchrom\hplc data\SHA 3782022_SMLab_70_ACN_30_H2O_0.6ML.met.rslt\757.dat
Method: D:\Ezchrom\Method\sha 378.met
Acquired: 19-Nov-24 3:28:42 PM (GMT +05:30)
Printed: 19-Nov-24 5:07:21 PM (GMT +05:30)

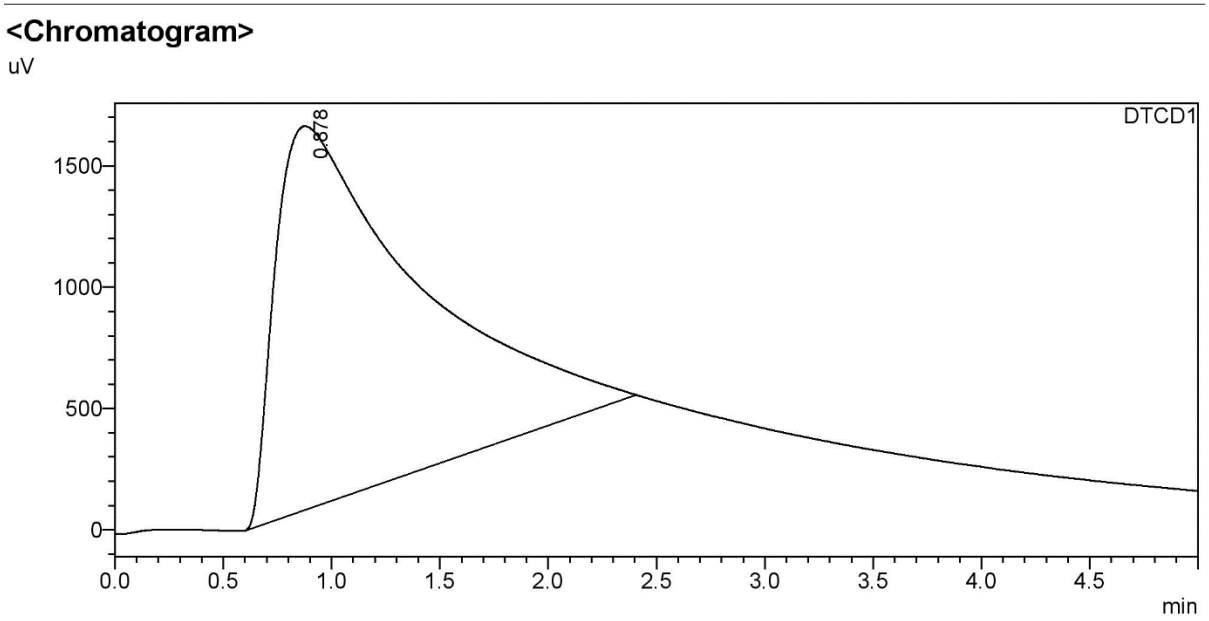


DAD: Signal A, 254 nm/Bw:4 nm
Results

Retention Time	Area	Area %	Height	Height %	Name
7.513	101352112	100.00	6889970	100.00	
Totals	101352112	100.00	6889970	100.00	

Experimental confirmation 6 for the H_2 liberation using GC-TCD detector

Compound **3j** (1 mmol), DMAP (10 mol%) was dissolved in 3 mL of acetone, and the mixture was placed in a reaction setup that was analyzed on a GC-TCD detector to witness the liberation of hydrogen gas.



<Peak Table>

DTCD1

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	0.878	71854	1582	0.000			
Total		71854	1582				

Figure 92. chromatogram for the evaluation of H_2

References

1. D. Qi, J. Bai, Z. Song, B. Li, C. Yang, L. Guo and W. Xia, *Org. Lett.* 2023, ***25***, 3, 506–511.
2. R. D. C. Gallo, M. Duarte, A. F. da Silva, C. Y. Okada, V. M. Deflon and I. D. Jurberg, *Org. Lett.*, 2021, **23**, 8916–8920.
3. S. Muthusamy and A. Prabu, *Org. & Biomol. Chem.*, 2022, **20**, 558–564.