

Supporting Information for

**Iron-Catalyzed Aerobic Difunctionalization of Alkenes:
Highly Efficient C-S and C-C Bond Formation****

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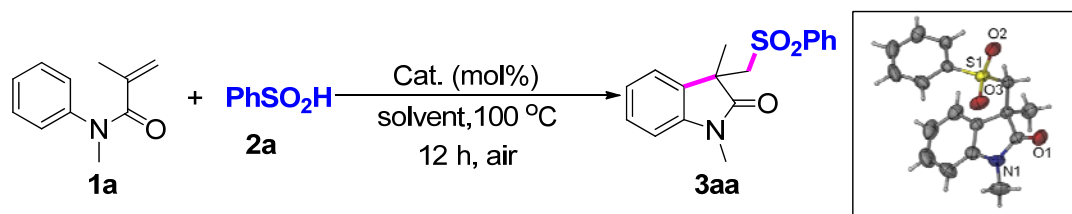
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General Remarks

All commercially available compounds were purchased from Sigma-Aldrich, Alfa-Aesar and Acros (with the exception of anhydrous FeCl_2 purchased from Strem) and used as received. TFA and other solvents were from Beijing Ouhe and Beijing Chemical Works and used as received without further purification. Reactions were performed without regard for exclusion of ambient air or moisture in a schlenk tube under standard conditions (specific reaction conditions are described below). Analysis of crude reaction mixture was done on an Agilent 7890 GC System with an Agilent 5975 Mass Selective Detector. Products were purified by flash chromatography or by preparative thin-layer chromatography on silica gel. ^1H -NMR spectra were recorded on a Bruker AVIII-400 spectrometers. Chemical shifts (in ppm) were calibrated with CDCl_3 (tetramethylsilane, $\delta = 0$ ppm) and DMSO($\delta = 2.54$ ppm). ^{13}C -NMR spectra were obtained by using the same NMR spectrometers and were calibrated with CDCl_3 ($\delta = 77.00$ ppm) and DMSO($\delta = 40.45$ ppm.) Mass spectra were recorded using a PE SCLEX QSTAR spectrometer. High resolution mass spectra were obtained with a Bruker APEX IV Fourier transform ion cyclotron resonance mass spectrometer using electrospray ionisation (ESI). Fourier-transform infrared (FTIR) spectra were obtained with a Nicolet Nexus 470 Fourier transform infrared spectrometer.

Table S1. Screening with Different Reaction Conditions for the direct oxysulfonylation of activated alkynes.^a

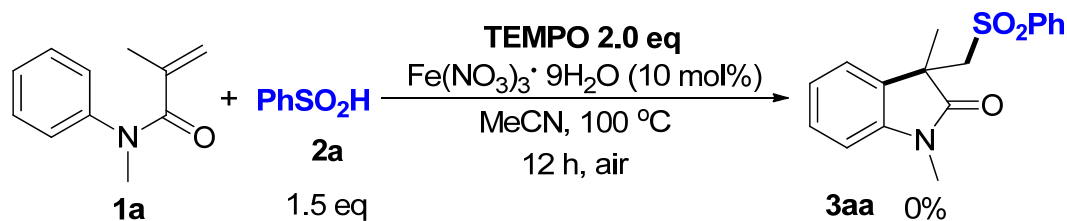


entry	Cat. (mol%)	solvent	yield of 3aa (%) ^b
1	Fe(NO ₃) ₃ · 9H ₂ O (5)	MeCN	48
2	Fe(NO ₃) ₃ · 9H ₂ O (10)	MeCN	77
3	Fe(NO ₃) ₃ · 9H ₂ O (20)	MeCN	63
4	Fe(NO ₃) ₃ · 9H ₂ O (10)	DCE	53
5	Fe(NO ₃) ₃ · 9H ₂ O (10)	CHCl ₃	49
6	Fe(NO ₃) ₃ · 9H ₂ O (10)	THF	70
7	Fe(NO ₃) ₃ · 9H ₂ O (10)	DMSO	trace
8	Fe(NO ₃) ₃ · 9H ₂ O (10)	DMF	trace
9	Fe(NO ₃) ₃ · 9H ₂ O (10)	HOAc	trace
10	Fe(NO ₃) ₃ · 9H ₂ O (10)	toluene	44
11	Fe(NO ₃) ₃ · 9H ₂ O (10)	TFA	ND
12^c	Fe(NO₃)₃ · 9H₂O (10)	MeCN	94
13 ^d	Fe(NO ₃) ₃ · 9H ₂ O (10)	MeCN	38
14	FeCl ₃ (10)	MeCN	trace
15	NiCl ₂ (10)	MeCN	trace
16	AuCl ₃ (10)	MeCN	ND
17	PtCl ₂ (10)	MeCN	trace
18	AgNO ₃ (10)	MeCN	49
19	Cu(NO ₃) ₂ (10)	MeCN	32
20	Pd(OAc) ₂ (10)	MeCN	trace
21	TEMPO (10)	MeCN	trace
22	NHPI (10)	MeCN	trace
23	none	MeCN	16

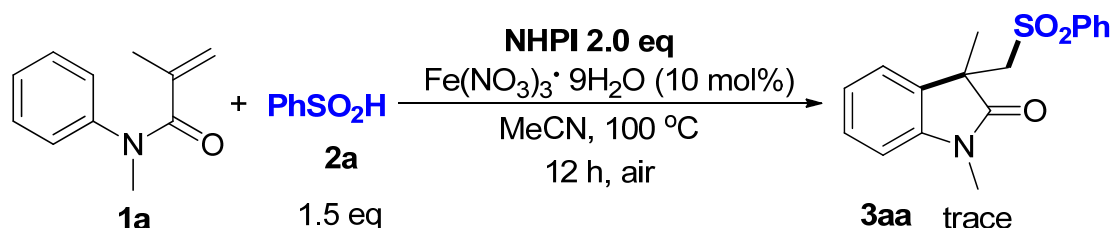
[a] Reaction conditions are as follows: **1a** (0.2 mmol), **2a** (0.4 mmol), solvent (2 mL), stirred at 100 °C under air for 12 h. [b] Isolated yields. [c] 0.3 mmol PhSO₂H (**2a**) was used. [d] The reaction was carried out under Ar.

Mechanistic Studies

Eq S1

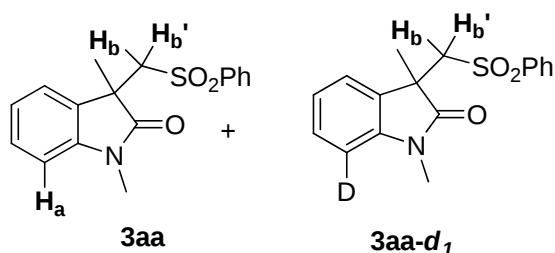
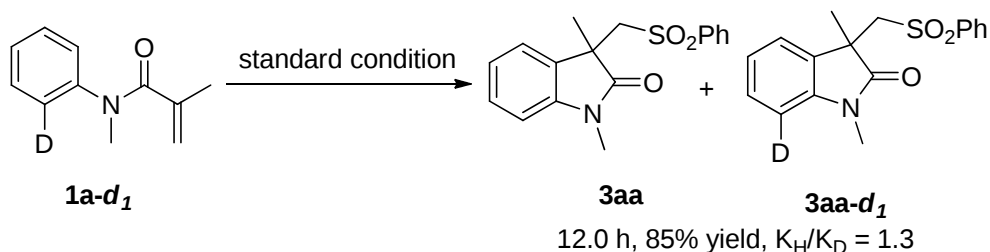


Eq S2



Eq. S3 **Competing kinetic isotope effect (KIE) experiment:**

- a) Intramolecular KIE experiment:** **1a-d₁** were synthesized deuterium substrates according to the literature procedure.^[S5] In a Schlenk tube, **1a-d₁** (35.5 mg, 0.20 mmol), PhSO_2H **2a** (43 mg, 0.3 mmol) were added, then MeCN (2 mL) were added. The mixture was allowed to stir at 100 °C for 12 hours (monitored by TLC). After substrate was consumed, the reaction was cooled to room temperature and the solvent was removed under vacuum, the residue was purified by column chromatography to give the product **3aa** and **3aa-d₁**. The products were under ^1H -NMR analysis (Figure S1).



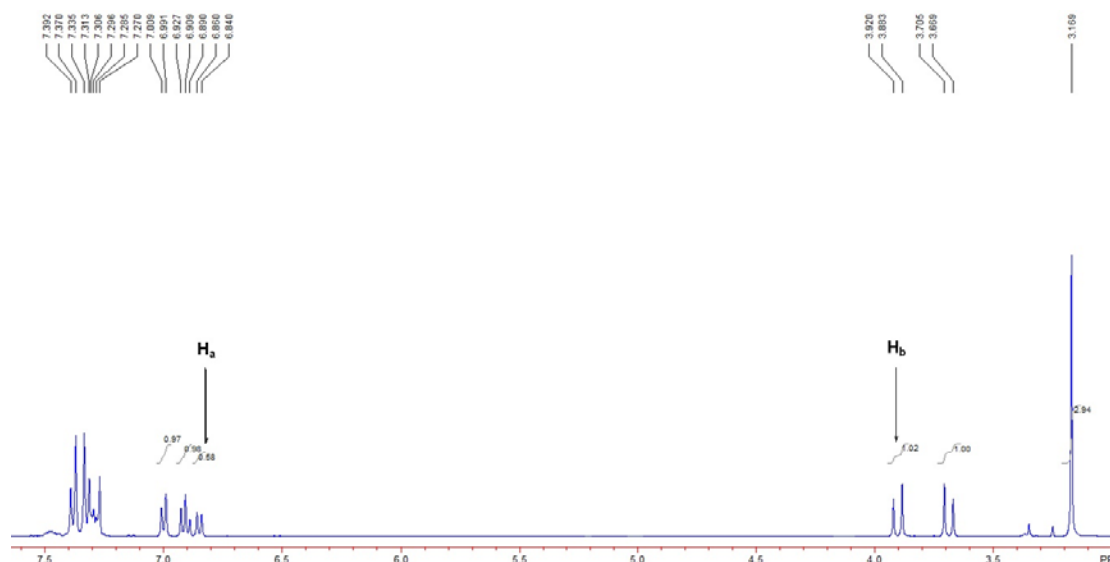
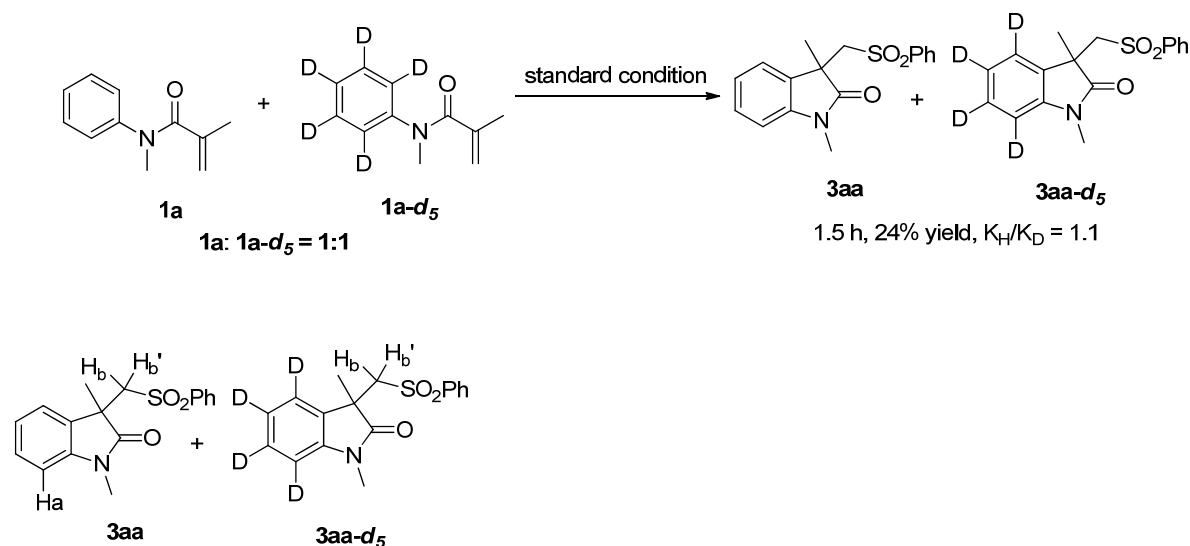


Figure S1 Intramolecular KIE experiment

b) Intermolecular KIE experiment: **1a-d₅** were synthesized deuterium substrates according the literature procedure.^[S5] In a Schlenk tube, **1a** (17.5 mg, 0.1 mmol), **1a-d₅** (18.0 mg, 0.1 mmol), PhSO₂H **2a** (43 mg, 0.3mmol) were added, then MeCN (2 mL) were added. The mixture was allowed to stir at 100°C for 12 hours (monitored by TLC). After substrate was consumed, the reaction was cooled to room temperature and the solvent was removed under vacuum, the residue was purified by column chromatography to give the product **3aa** and **3aa-d₅**. The products were under ¹H-NMR analysis (Figure S2).



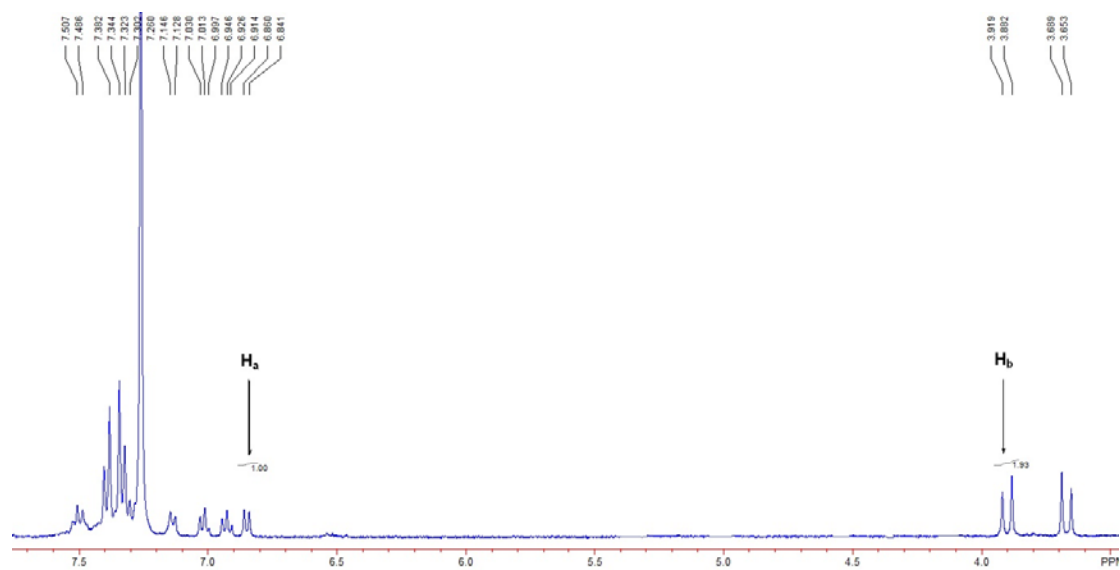
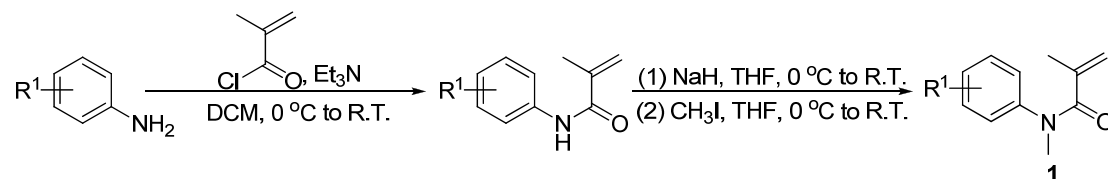


Figure S2 Intermolecular KIE experiment

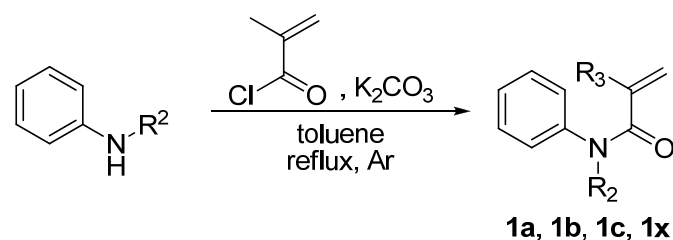
Experimental Section:

Typical Procedure for the Synthesis of Substrates

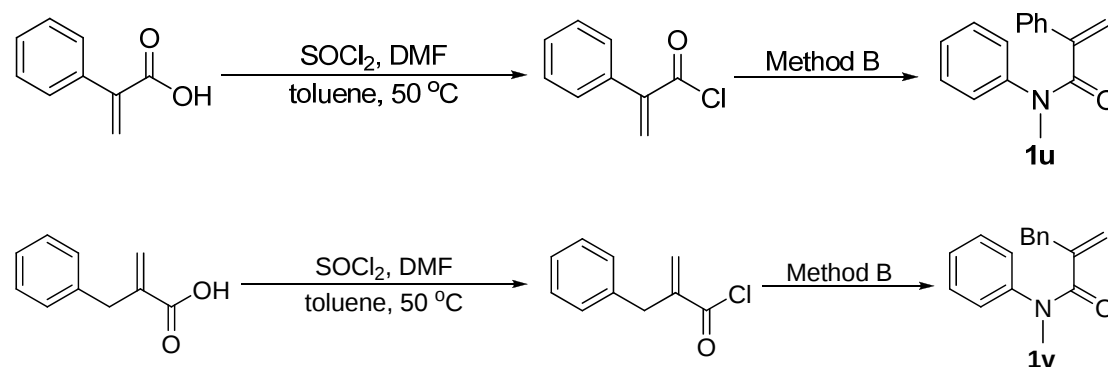
Method A: Substrate 1 was prepared according to literatures.^{s2}



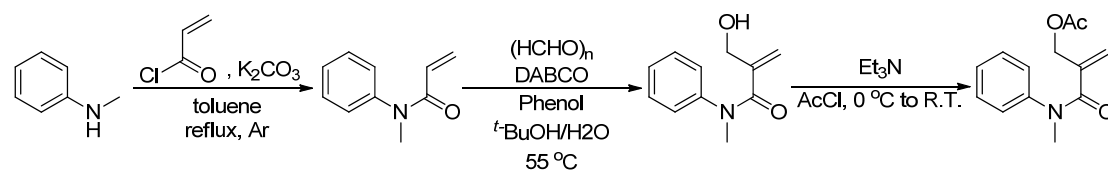
Method B: Substrate 1 was prepared according to literature.^{s3}



Substrates 1u and 1v were prepared according to literatures.^{s3, s4}



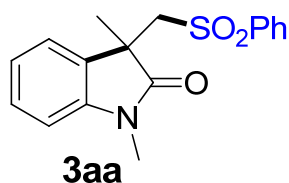
Substrate 1w was prepared according to literature.^{s2}



General Procedure for the Synthesis of Oxindoles

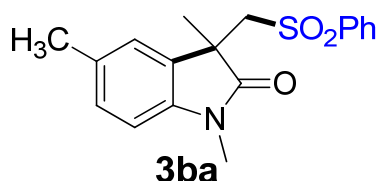
1 (0.2 mmol) and 2 (0.4 mmol or 0.3 mmol), and Fe(NO₃)₃ • 9H₂O (8 mg, 0.02 mmol) were added to a Schlenk tube with a magnetic bar. 2.0 mL MeCN was added and the mixture was heated to 100 °C for 12 hours (or 24 hours). The reaction mixture was diluted with EtOAc (5 mL) and filtered. The filtrate was concentrated *in vacuo* giving the resulting material, which was purified by column chromatography to give product 3.

Characterization of new compounds.



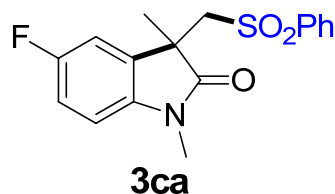
1) 1, 3-Dimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (3aa)

The reaction of **1a** (35.0 mg, 0.2 mmol), PhSO₂H **2a** (43 mg, 0.3 mmol), Fe(NO₃)₃ • 9H₂O (8 mg, 0.02 mmol) in MeCN (2 mL) afforded 59.2 mg (94%) of **3aa**; **3aa**: white solid; Mp: 159.3-161.9 °C. ¹H NMR (CDCl₃, 400 MHz): 7.55-7.48 (m, 3H); 7.38 (t, *J* = 8.0 Hz, 2H); 7.28 (d, *J* = 8.0 Hz, 1H); 7.03 (d, *J* = 7.6 Hz, 1H); 6.88-6.84 (m, 2H); 3.88 (d, *J* = 14.4 Hz, 1H, CH₂); 3.70 (d, *J* = 14.4 Hz, 1H, CH₂); 3.17 (s, 3H); 1.39 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): 177.5; 143.2; 139.8; 133.3; 129.4; 128.8; 128.5; 127.7; 123.9; 122.4; 108.3; 61.7; 45.5; 26.4; 25.4. IR (neat): ν = 2974; 1711; 1613; 1309; 753; cm⁻¹. FTMS: calc. for C₁₇H₁₇NO₃S (M+H)⁺, 316.1002; found, 316.0996.



2) 1, 3, 5-Trimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (3ba)

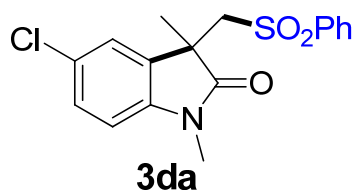
The reaction of **1b** (38.0 mg, 0.2 mmol), PhSO₂H **2a** (56 mg, 0.4 mmol), Fe(NO₃)₃ • 9H₂O (8 mg, 0.02 mmol) in MeCN (2 mL) afforded 56.2 mg (85%) of **3ba**; **3ba**: white solid; Mp: 148.8-151.0 °C. ¹H NMR (CDCl₃, 400 MHz): 7.53-7.49 (m, 1H); 7.42-7.40 (m, 2H); 7.35-7.31 (m, 2H); 7.03 (d, *J* = 8.0 Hz, 1H); 6.74 (d, *J* = 8.0 Hz, 1H); 6.63 (s, 1H); 3.90 (d, *J* = 14.4 Hz, 1H, CH₂); 3.69 (d, *J* = 14.4 Hz, 1H, CH₂); 3.18 (s, 3H); 2.11 (s, 3H); 1.35 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): 177.4; 141.0; 139.9; 133.0; 131.7; 129.2; 128.9; 128.6; 127.6; 124.6; 108.0; 61.8; 45.5; 26.5; 25.3; 20.8. IR (neat): ν = 2967; 1720; 1706; 1306; 1151; cm⁻¹. FTMS: calc. for C₁₈H₁₉NO₃S (M+H)⁺, 330.1158; found, 330.1149.



3) 5-Fluoro-1, 3-dimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (3ca)

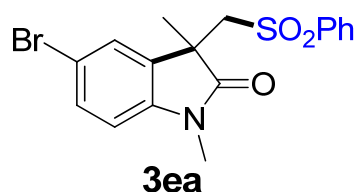
The reaction of **1c** (40.0 mg, 0.2 mmol), PhSO₂H **2a** (56 mg, 0.4 mmol), Fe(NO₃)₃ • 9H₂O (8 mg, 0.02 mmol) in MeCN (2 mL) afforded 60.1 mg (90%) of **3ca**; **3ca**: white solid; Mp: 168.6-169.4 °C. ¹H NMR (CDCl₃, 400 MHz): 7.59-7.50 (m, 3H); 7.41 (t, *J* = 8.0 Hz, 2H); 7.01-6.93 (m, 1H); 6.80-6.73 (m, 2H); 3.86 (d, *J* = 14.4 Hz, 1H, CH₂); 3.67 (d, *J* = 14.4 Hz, 1H, CH₂); 3.18 (s, 3H); 1.38 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): 177.2; 159.0 (d, *J* = 240 Hz); 139.8; 139.3 (d, *J* = 1.6 Hz); 133.5; 131.1 (d, *J* = 8.9 Hz); 128.9; 127.6; 114.9 (d, *J* = 24.0 Hz); 112.2 (d, *J* = 24.7 Hz); 108.8 (d, *J* = 7.7 Hz); 61.6; 46.0; 26.6; 25.2. IR (neat): ν = 2970; 1710;

1497; 1150; 862; cm^{-1} . FTMS: calc. for $\text{C}_{17}\text{H}_{16}\text{FNO}_3\text{S}$ ($\text{M}+\text{H}$)⁺, 334.0908; found, 334.0902.



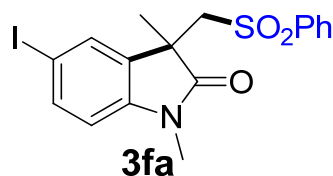
4) 5-Chloro-1, 3-dimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (3da)

The reaction of **1d** (42.0 mg, 0.2 mmol), PhSO_2H **2a** (56 mg, 0.4 mmol), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (8 mg, 0.02 mmol) in MeCN (2 mL) afforded 61.4 mg (88%) of **3da**; **3da**: white solid; Mp: 147.6-148.9 °C. ^1H NMR (CDCl_3 , 400 MHz): 7.59-7.55 (m, 1H); 7.47-7.43 (m, 2H); 7.40-7.37 (m, 2H); 7.22 (d, $J = 8.4$ Hz, 1H); 6.81-6.78 (m, 2H); 3.88 (d, $J = 14.4$ Hz, 1H, CH_2); 3.69 (d, $J = 14.4$ Hz, 1H, CH_2); 3.20 (s, 3H); 1.36 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): 177.1; 142.0; 139.6; 133.6; 131.0; 128.8; 128.6; 127.7; 127.5; 124.4; 109.3; 61.6; 45.6; 26.6; 25.1. IR (neat): $\nu = 2969$; 1726; 1612; 1491; 1154; cm^{-1} . FTMS: calc. for $\text{C}_{17}\text{H}_{16}\text{ClNO}_3\text{S}$ ($\text{M}+\text{H}$)⁺, 350.0612; found, 350.0605.



5) 5-Bromo-1, 3-dimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (3ea)

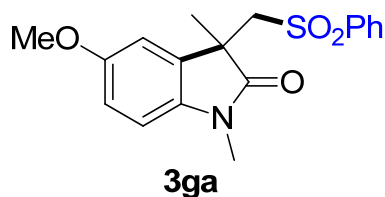
The reaction of **1e** (51.0 mg, 0.2 mmol), PhSO_2H **2a** (56 mg, 0.4 mmol), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (8 mg, 0.02 mmol) in MeCN (2 mL) afforded 71.5 mg (91%) of **3ea**; **3ea**: yellow solid; Mp: 161.8-163.1 °C. ^1H NMR (CDCl_3 , 400 MHz): 7.58 (d, $J = 7.2$ Hz, 1H); 7.46-7.44 (m, 2H); 7.41-7.34 (m, 3H); 6.90 (d, $J = 1.2$ Hz, 1H); 6.75 (d, $J = 8.0$ Hz, 1H); 3.89 (d, $J = 14.4$ Hz, 1H, CH_2); 3.69 (d, $J = 14.4$ Hz, 1H, CH_2); 3.21 (s, 3H); 1.36 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): 177.0; 142.5; 139.6; 133.6; 131.5; 131.3; 128.9; 127.4; 127.1; 115.0; 109.8; 61.6; 45.6; 26.6; 25.1. IR (neat): $\nu = 2982$; 2929; 1733; 1462; 541; cm^{-1} . FTMS: calc. for $\text{C}_{17}\text{H}_{16}\text{BrNO}_3\text{S}$ ($\text{M}+\text{H}$)⁺, 394.0107; found, 394.0107.



6) 5-Iodo-1, 3-dimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (3fa)

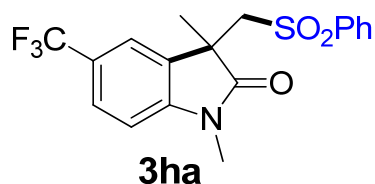
The reaction of **1f** (61.0 mg, 0.2 mmol), PhSO_2H **2a** (56 mg, 0.4 mmol), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (8 mg, 0.02 mmol) in MeCN (2 mL) afforded 84.5 mg (96%) of **3fa**; **3fa**: white solid; Mp: 173.0-174.6 °C. ^1H NMR (CDCl_3 , 400 MHz): 7.61 (d, $J = 7.2$ Hz, 1H); 7.54 (d, $J = 8.0$ Hz, 1H); 7.44-7.36 (m, 4H); 7.04 (d, $J = 1.2$ Hz, 1H); 6.65 (d, $J = 8.0$ Hz, 1H); 3.88 (d, $J = 14.4$ Hz, 1H, CH_2); 3.69 (d, $J = 14.4$ Hz, 1H, CH_2); 3.20 (s, 3H); 1.34 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): 176.8; 143.2; 139.5; 137.4; 133.8; 132.5; 131.6; 128.9; 127.4; 110.4; 85.1; 61.6; 45.4; 26.6; 25.1.

IR (neat): ν = 2969; 1711; 1604; 1487; 1344; 1154; cm^{-1} . FTMS: calc. for $\text{C}_{17}\text{H}_{16}\text{INO}_3\text{S}$ ($\text{M}+\text{H}$)⁺, 441.9968; found, 441.9960.



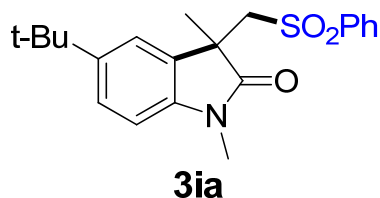
7) 5-Methoxy-1,3-dimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (3ga)

The reaction of **1g** (41.0 mg, 0.2 mmol), PhSO_2H **2a** (56 mg, 0.4 mmol), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (8 mg, 0.02 mmol) in MeCN (2 mL) afforded 40.1 mg (58%) of **3ga**; **3ga**: white solid; Mp: 129.1-131.4 °C. ^1H NMR (CDCl_3 , 400 MHz): 7.53-7.46 (m, 3H); 7.39-7.35 (m, 2H); 6.81-6.75 (m, 2H); 6.55 (d, J = 2.4 Hz, 1H); 3.88 (d, J = 14.4 Hz, 1H); 3.67 (d, J = 14.4 Hz, 1H); 3.65 (s, 3H); 3.16 (s, 3H); 1.38 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): 177.2; 155.8; 140.0; 136.7; 133.2; 130.6; 128.8; 127.8; 113.3; 111.0; 108.7; 61.8; 55.5; 46.0; 26.6; 25.3. IR (neat): ν = 2928; 1714; 1602; 1503; 1152; cm^{-1} . FTMS: calc. for $\text{C}_{18}\text{H}_{19}\text{NO}_4\text{S}$ ($\text{M}+\text{H}$)⁺, 346.1108; found, 346.1111.



8) 1,3-Dimethyl-3-((phenylsulfonyl)methyl)-5-(trifluoromethyl)indolin-2-one (3ha)

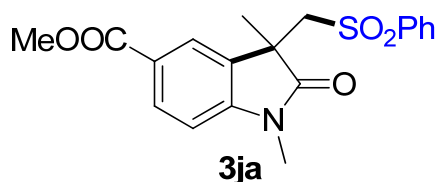
The reaction of **1h** (49.0 mg, 0.2 mmol), PhSO_2H **2a** (56 mg, 0.4 mmol), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (8 mg, 0.02 mmol) in MeCN (2 mL) afforded 54.0 mg (71%) of **3ha**; **3ha**: yellow solid; Mp: 145.4-147.2 °C. ^1H NMR (CDCl_3 , 400 MHz): 7.55-7.51 (m, 2H); 7.46-7.44 (m, 2H); 7.38-7.34 (m, 2H); 7.11 (s, 1H); 6.95 (d, J = 8.0 Hz, 1H); 3.93 (d, J = 14.8 Hz, 1H, CH_2); 3.76 (d, J = 14.4 Hz, 1H, CH_2); 3.27 (s, 3H); 1.40 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): 177.6; 146.4; 139.7; 133.6; 129.3; 129.0; 126.5 (q, J = 4.0 Hz); 126.2 (q, J = 253 Hz); 124.9 (q, J = 33.2 Hz); 122.9; 120.8 (q, J = 3.0 Hz); 108.2; 61.7; 45.4; 26.7; 25.1. IR (neat): ν = 2975; 2934; 1724; 1624; 1506; cm^{-1} . FTMS: calc. for $\text{C}_{18}\text{H}_{16}\text{NF}_3\text{O}_3\text{S}$ ($\text{M}+\text{H}$)⁺, 384.0876; found, 384.0867.



9) 5-(tert-Butyl)-1,3-dimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (3ia)

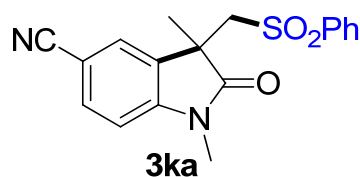
The reaction of **1i** (46.0 mg, 0.2 mmol), PhSO_2H **2a** (56 mg, 0.4 mmol), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (8 mg, 0.02 mmol) in MeCN (2 mL) afforded 45.0 mg (61%) of **3ia**; **3ia**: yellow solid; Mp: 55.4-57.3 °C. ^1H NMR (CDCl_3 , 400 MHz): 7.52-7.47 (m, 3H); 7.38-7.34 (m, 2H); 7.32-7.30 (m, 1H); 7.18 (s, 1H); 6.77 (d, J = 8.4 Hz, 1H); 3.87 (d, J = 14.4 Hz, 1H); 3.72 (d, J = 14.8 Hz, 1H, CH_2); 3.13 (s, 3H); 1.41 (s, 3H); 1.25 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): 177.8; 145.6; 140.8; 140.0; 133.4;

128.8; 128.2; 127.8; 125.3; 121.5; 107.8; 61.9; 45.8; 34.4; 31.5; 26.4; 25.4. IR (neat): ν = 2964; 2905; 1716; 1501; 1148; 571; cm^{-1} . FTMS: calc. for $\text{C}_{21}\text{H}_{25}\text{NO}_3\text{S}$ ($\text{M}+\text{H}$)⁺, 372.1628; found, 372.1621.



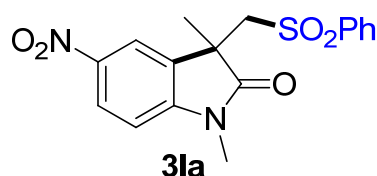
10) 1, 3-Dimethyl-2-oxo-3-((phenylsulfonyl)methyl)indoline-5-carboxylate (3ja)

The reaction of **1j** (47.0 mg, 0.2 mmol), PhSO_2H **2a** (56 mg, 0.4 mmol), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (8 mg, 0.02 mmol) in MeCN (2 mL) afforded 50.2 mg (70%) of **3ja**; **3ja**: white solid; Mp: 148.6-149.8 °C. ^1H NMR (CDCl_3 , 400 MHz): 8.00 (dd, J = 8.4 Hz, J = 1.6 Hz, 1H); 7.49-7.42 (m, 4H); 7.35-7.28 (m, 2H); 6.91 (d, J = 8.0 Hz, 1H); 3.94 (d, J = 14.4 Hz, 1H, CH_2); 3.85 (s, 3H); 3.78 (d, J = 14.8 Hz, 1H, CH_2); 3.27 (s, 3H); 1.39 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): 177.9; 166.2; 147.5; 139.8; 133.1; 131.2; 129.1; 128.9; 127.4; 125.0; 124.3; 108.0; 61.6; 51.9; 45.2; 26.8; 25.1. IR (neat): ν = 2971; 1728; 1703; 1617; 1273; cm^{-1} . FTMS: calc. for $\text{C}_{19}\text{H}_{19}\text{NO}_5\text{S}$ ($\text{M}+\text{H}$)⁺, 374.1057; found, 374.1058.



11) 1, 3-Dimethyl-2-oxo-3-((phenylsulfonyl)methyl)indoline-5-carbonitrile (3ka)

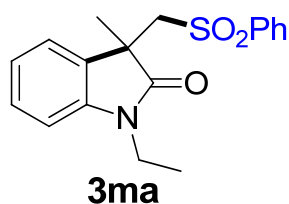
The reaction of **1k** (40.0 mg, 0.2 mmol), PhSO_2H **2a** (56 mg, 0.4 mmol), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (8 mg, 0.02 mmol) in MeCN (2 mL) afforded 50.3 mg (74%) of **3ka**; **3ka**: white solid; Mp: 173.1-175.4 °C. ^1H NMR (CDCl_3 , 400 MHz): 7.63-7.58 (m, 2H); 7.51-7.41 (m, 4H); 7.12 (s, 1H); 6.96 (d, J = 8.4 Hz, 1H); 3.91 (d, J = 14.8 Hz, 1H, CH_2); 3.76 (d, J = 14.8 Hz, 1H, CH_2); 3.28 (s, 3H); 1.40 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): 177.4; 147.2; 139.6; 133.83; 133.80; 130.4; 129.1; 127.4; 127.2; 118.7; 108.8; 105.6; 61.4; 45.2; 26.8; 25.0. IR (neat): ν = 2225; 1731; 1618; 1500; 1151; cm^{-1} . FTMS: calc. for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_3\text{S}$ ($\text{M}+\text{H}$)⁺, 341.0954; found, 341.0951.



12) 1, 3-Dimethyl-5-nitro-3-((phenylsulfonyl)methyl)indolin-2-one (3la)

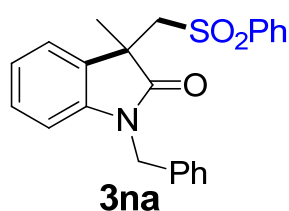
The reaction of **1l** (44.0 mg, 0.2 mmol), PhSO_2H **2a** (56 mg, 0.4 mmol), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (8 mg, 0.02 mmol) in MeCN (2 mL) afforded 62.6 mg (87%) of **3la**; **3la**: yellow solid; Mp: 198.6-200.3 °C. ^1H NMR (d_6 -DMSO, 400 MHz): 8.12 (dd, J = 8.4 Hz, J = 2.4 Hz, 1H); 7.90 (d, J = 2.4 Hz, 1H); 7.52-7.48 (m, 1H); 7.38-7.24 (m, 4H); 7.21 (d, J = 8.8 Hz, 1H); 4.64 (d, J = 15.2 Hz, 1H, CH_2); 3.82 (d, J = 14.8 Hz, 1H, CH_2); 3.24 (s, 3H); 1.33 (s, 3H). ^{13}C NMR (d_6 -DMSO,

100 MHz): 177.6; 149.2; 142.2; 139.4; 133.0; 130.0; 128.8; 126.9; 125.5; 120.0; 108.6; 59.8; 44.9; 26.7; 24.0. IR (neat): ν = 3058; 1728; 1615; 1513; 1136; cm^{-1} . FTMS: calc. for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_5\text{S}$ ($\text{M}+\text{H}$)⁺, 361.0853; found, 361.0852.



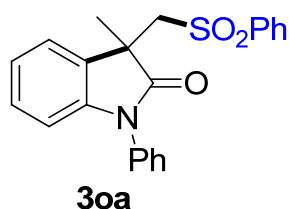
13) 1-Ethyl-3-methyl-3-((phenylsulfonyl)methyl)indolin-2-one (3ma)

The reaction of **1m** (38.0 mg, 0.2 mmol), PhSO_2H **2a** (42 mg, 0.3 mmol), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (8 mg, 0.02 mmol) in MeCN (2 mL) afforded 59.4 mg (90%) of **3ma**; **3ma**: white solid; Mp: 172.5-173.6 °C. ^1H NMR (CDCl_3 , 400 MHz): 7.53-7.48 (m, 3H); 7.35 (t, J = 8.0 Hz, 2H); 7.24 (t, J = 7.6 Hz, 1H); 6.95 (d, J = 7.6 Hz, 1H); 6.87 (d, J = 7.6 Hz, 1H); 6.81 (t, J = 7.6 Hz, 1H); 3.87 (d, J = 14.4 Hz, 1H, CH_2); 3.83-3.75 (m, 1H); 3.72-3.68 (m, 2H); 1.37 (s, 3H); 1.31 (t, J = 7.2 Hz, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): 177.1; 142.2; 140.0; 133.2; 129.6; 128.8; 128.4; 127.5; 123.9; 122.2; 108.4; 61.6; 45.4; 34.8; 25.4; 12.1. IR (neat): ν = 2976; 1711; 1613; 1472; 1127; 754; cm^{-1} . FTMS: calc. for $\text{C}_{18}\text{H}_{19}\text{NO}_3\text{S}$ ($\text{M}+\text{H}$)⁺, 330.1158; found, 330.1159.



14) 1-Benzyl-3-methyl-3-((phenylsulfonyl)methyl)indolin-2-one (3na)

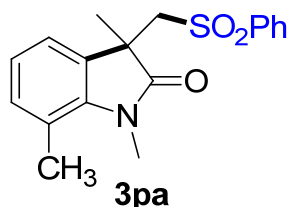
The reaction of **1n** (50.0 mg, 0.2 mmol), PhSO_2H **2a** (42 mg, 0.3 mmol), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (8 mg, 0.02 mmol) in MeCN (2 mL) afforded 66.4 mg (85%) of **3na**; **3na**: colorless oil; ^1H NMR (CDCl_3 , 400 MHz): 7.54-7.50 (m, 3H); 7.38-7.30 (m, 6H); 7.27-7.25 (m, 1H); 7.14-7.10 (m, 1H); 7.00-6.98 (m, 1H); 6.82-6.78 (m, 1H); 6.70 (d, J = 8.0 Hz, 1H); 4.99 (d, J = 15.6 Hz, 1H, CH_2); 3.79 (d, J = 16.0 Hz, 1H, CH_2); 3.93 (d, J = 14.8 Hz, 1H, CH_2); 3.75 (d, J = 14.4 Hz, 1H, CH_2); 1.44 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): 177.8; 142.3; 140.0; 135.7; 133.3; 129.4; 128.9; 128.6; 128.4; 127.7; 127.5; 127.3; 123.8; 122.5; 109.5; 61.5; 45.6; 44.2; 25.9. IR (neat): ν = 3031; 2974; 1719; 1612; 748; cm^{-1} . FTMS: calc. for $\text{C}_{23}\text{H}_{21}\text{NO}_3\text{S}$ ($\text{M}+\text{H}$)⁺, 392.1315; found, 392.1320.



15) 3-Methyl-1-phenyl-3-((phenylsulfonyl)methyl)indolin-2-one (3oa)

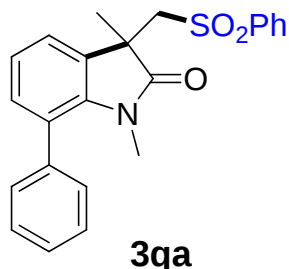
The reaction of **1o** (47.0 mg, 0.2 mmol), PhSO_2H **2a** (42 mg, 0.3 mmol), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (8 mg, 0.02 mmol) in MeCN (2 mL) afforded 65.1 mg (86%) of **3oa**; **3oa**: white solid; Mp:

210.1-212.9 °C. ¹H NMR (CDCl₃, 400 MHz): 7.55-7.51 (m, 7H); 7.49-7.33 (m, 3H); 7.17 (t, *J* = 8.0 Hz, 1H); 6.95 (d, *J* = 7.2 Hz, 1H); 6.82 (t, *J* = 8.0 Hz, 2H); 3.98 (d, *J* = 14.4 Hz, 1H, CH₂); 3.79 (d, *J* = 14.4 Hz, 1H, CH₂); 1.49 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): 177.3; 143.6; 140.3; 134.5; 133.2; 129.6; 129.2; 129.0; 128.4; 128.2; 127.5; 126.8; 123.8; 122.8; 109.6; 62.3; 45.6; 25.6. IR (neat): *ν* = 3038; 2946; 1728; 1637; 733; cm⁻¹. FTMS: calc. for C₂₂H₁₉NO₃S (M+H)⁺, 378.1158; found, 378.1162.



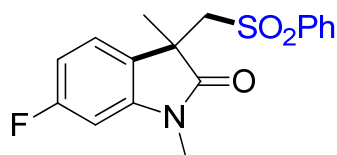
16) 1, 3, 7-Trimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (3pa)

The reaction of **1p** (38.0 mg, 0.2 mmol), PhSO₂H **2a** (56 mg, 0.4 mmol), Fe(NO₃)₃ • 9H₂O (8 mg, 0.02 mmol) in MeCN (2 mL) afforded 25.0 mg (38%) of **3pa**; **3pa**: yellow solid; Mp: 160.0-161.3 °C. ¹H NMR (CDCl₃, 400 MHz): 7.56-7.50 (m, 3H); 7.41-7.36 (m, 2H); 7.00 (d, *J* = 6.8 Hz, 1H); 6.88 (d, *J* = 6.8 Hz, 1H); 6.78 (t, *J* = 7.2 Hz, 1H); 3.89 (d, *J* = 14.8 Hz, 1H, CH₂); 3.65 (d, *J* = 14.4 Hz, 1H, CH₂); 3.44 (s, 3H); 2.58 (s, 3H); 1.35 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): 178.4; 141.1; 140.0; 133.3; 132.3; 128.8; 127.9; 127.8; 122.4; 121.9; 120.0; 62.2; 45.0; 29.9; 25.9; 19.0. IR (neat): *ν* = 2981; 1709; 1649; 1141; 1082; cm⁻¹. FTMS: calc. for C₁₈H₁₉NO₃S (M+H)⁺, 330.1158; found, 330.1154.



17) 1, 3-Dimethyl-7-phenyl-3-((phenylsulfonyl)methyl)indolin-2-one (3qa)

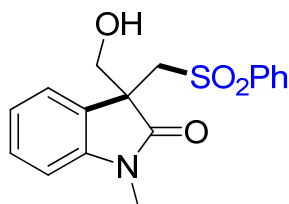
The reaction of **1q** (50.0 mg, 0.2 mmol), PhSO₂H **2a** (56 mg, 0.4 mmol), Fe(NO₃)₃ • 9H₂O (8 mg, 0.02 mmol) in MeCN (2 mL) afforded 43.0 mg (55%) of **3qa**; **3qa**: yellow solid; Mp: 207.6-210.0 °C. ¹H NMR (CDCl₃, 400 MHz): 7.57-7.49 (m, 5H); 7.47-7.37 (m, 5H); 7.91 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H); 7.01 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H); 6.87 (t, *J* = 7.6 Hz, 1H); 3.92 (d, *J* = 14.8 Hz, 1H, CH₂); 3.73 (d, *J* = 14.4 Hz, 1H, CH₂); 2.70 (s, 3H); 1.43 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): 178.7; 140.2; 138.7; 133.3; 131.5; 130.3; 129.4; 128.9; 128.2; 127.7; 127.6; 126.3; 125.8; 122.9; 121.8; 62.1; 45.0; 30.6; 25.7. IR (neat): *ν* = 2977; 1714; 1684; 1307; 1147; cm⁻¹. FTMS: calc. for C₂₃H₂₁NO₃S (M+H)⁺, 392.1319; found, 392.1310.



3ra

18) 6-Fluoro-1, 3-dimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (3ra)

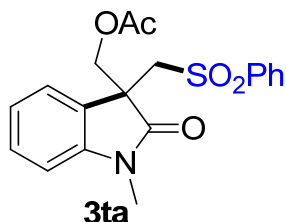
The reaction of **1r** (39.0 mg, 0.2 mmol), PhSO₂H **2a** (56 mg, 0.4 mmol), Fe(NO₃)₃ • 9H₂O (8 mg, 0.02 mmol) in MeCN (2 mL) afforded 60.1 mg (87%) of **3ra**; **3ra**: white solid; Mp: 177.2-179.6 °C. ¹H NMR (CDCl₃, 400 MHz): 7.59-7.54 (m, 3H); 7.43-7.39 (m, 2H); 7.16 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H); 7.69 (d, *J* = 1.2 Hz, 1H); 6.85 (d, *J* = 8.4 Hz, 1H); 3.87 (d, *J* = 14.8 Hz, 1H, CH₂); 3.69 (d, *J* = 14.8 Hz, 1H, CH₂); 3.20 (s, 3H); 1.41 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): 177.4; 144.5 (d, *J* = 1.6 Hz); 140.8 (d, *J* = 216.0 Hz); 133.6; 131.0; 129.1 (d, *J* = 20.7 Hz); 127.6 (d, *J* = 6.2 Hz); 121.6; 119.1; 118.1; 108.8; 61.6; 45.9; 26.7; 25.2; IR (neat): ν = 2975; 1726; 1621; 1496; 1085; 687; cm⁻¹. MS (70 eV): *m/z* (%). 333.1 (M⁺, 100).



3sa

19) 3-(Hydroxymethyl)-1-methyl-3-((phenylsulfonyl)methyl)indolin-2-one (3sa)

The reaction of **1s** (38.0 mg, 0.2 mmol), PhSO₂H **2a** (56 mg, 0.4 mmol), Fe(NO₃)₃ • 9H₂O (8 mg, 0.02 mmol) in MeCN (2 mL) afforded 36.4 mg (55%) of **3sa**; **3sa**: white solid; Mp: 172.4-174.6 °C. ¹H NMR (CDCl₃, 400 MHz): 7.57-7.54 (m, 3H); 7.40 (t, *J* = 7.6 Hz, 2H); 7.33 (t, *J* = 8.0 Hz, 1H); 7.10 (d, *J* = 7.6 Hz, 1H); 6.96-6.87 (m, 2H); 4.08 (d, *J* = 14.8 Hz, 1H, CH₂); 3.88 (d, *J* = 14.8 Hz, 1H, CH₂); 3.72 (d, *J* = 10.8 Hz, 1H, CH₂); 3.64 (d, *J* = 11.2 Hz, 1H, CH₂); 3.20 (s, 3H); 2.63 (brs, 1H). ¹³C NMR (CDCl₃, 100 MHz): 176.3; 143.9; 140.0; 133.4; 129.2; 128.9; 127.7; 125.5; 124.7; 122.7; 108.6; 67.5; 58.2; 50.8; 26.5; IR (neat): ν = 3434; 2924; 1706; 1616; 1307; 1147; cm⁻¹. FTMS: calc. for C₁₇H₁₇NO₄S (M+H)⁺, 332.0951; found, 332.0943.

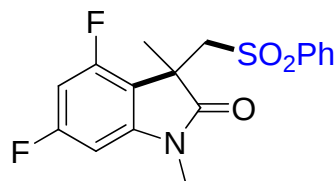


3ta

20) 1-Methyl-2-oxo-3-((phenylsulfonyl)methyl)indolin-3-ylmethyl acetate (3ta)

The reaction of **1t** (47.0 mg, 0.2 mmol), PhSO₂H **2a** (56 mg, 0.4 mmol), Fe(NO₃)₃ • 9H₂O (8 mg, 0.02 mmol) in MeCN (2 mL) afforded 47.8 mg (64%) of **3ta**; **3ta**: white solid; Mp: 178.3-180.9 °C. ¹H NMR (CDCl₃, 400 MHz): 7.58-7.50 (m, 3H); 7.40 (t, *J* = 7.6 Hz, 2H); 7.33 (t, *J* = 7.6 Hz, 1H); 7.09 (d, *J* = 7.6 Hz, 1H); 6.93-6.85 (m, 2H); 4.31 (d, *J* = 14.8 Hz, 1H, CH₂); 4.03 (d, *J* = 14.8 Hz, 1H, CH₂); 3.94 (d, *J* = 17.6 Hz, 1H, CH₂); 3.88 (d, *J* = 18.4 Hz, 1H, CH₂); 3.17

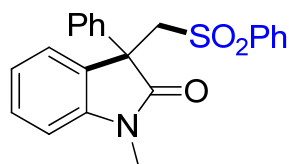
(s, 3H); 1.97 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): 174.3; 169.9; 143.9; 139.7; 133.5; 129.4; 128.9; 127.8; 125.2; 125.1; 122.5; 108.5; 67.1; 58.0; 49.2; 26.6; 20.5; IR (neat): ν = 2936; 1746; 1719; 1616; 1471; 751; cm^{-1} . FTMS: calc. for $\text{C}_{19}\text{H}_{19}\text{NO}_5\text{S}$ ($\text{M}+\text{H}$) $^+$, 374.1057; found, 374.1060.



3ua

21) 4, 6-Difluoro-1, 3-dimethyl-3-((phenylsulfonyl)methyl)indolin-2-one (3ua)

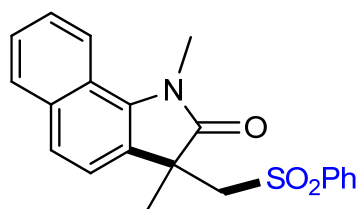
The reaction of **1u** (42.0 mg, 0.2 mmol), PhSO_2H **2a** (56 mg, 0.4 mmol), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (8 mg, 0.02 mmol) in MeCN (2 mL) afforded 57.2 mg (81%) of **3ua**; **3ua**: yellow solid; Mp: 155.1-156.4 $^\circ\text{C}$. ^1H NMR (CDCl_3 , 400 MHz): 7.58-7.54 (m, 3H); 7.43 (t, J = 7.6 Hz, 2H); 6.46 (d, J = 8.0 Hz, 1H); 6.24-6.20 (m, 1H); 3.88 (d, J = 14.4 Hz, 1H, CH_2); 3.83 (d, J = 14.4 Hz, 1H, CH_2); 3.20 (s, 3H); 1.42 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): 177.3; 162.8 (dd, J = 260.0 Hz, J = 13.0 Hz); 160.1 (dd, J = 261.1 Hz, J = 14.4 Hz); 145.9 (d, J = 12.1 Hz); 139.4; 129.3; 129.0 (d, J = 7.1 Hz); 128.1; 127.6; 97.7 (t, J = 26.2 Hz); 93.7 (dd, J = 27.0 Hz, J = 3.5 Hz); 60.7; 44.3; 27.1; 23.6. IR (neat): ν = 2974; 1718; 1654; 1318; 766; cm^{-1} . FTMS: calc. for $\text{C}_{17}\text{H}_{15}\text{F}_2\text{NO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$, 352.0814; found, 352.0813.



3va

22) 1-Methyl-3-phenyl-3-((phenylsulfonyl)methyl)indolin-2-one (3va)

The reaction of **1v** (38.0 mg, 0.2 mmol), PhSO_2H **2a** (56 mg, 0.4 mmol), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (8 mg, 0.02 mmol) in MeCN (2 mL) afforded 52.8 mg (70%) of **3va**; **3va**: yellow solid; Mp: 185.1-188.4 $^\circ\text{C}$. ^1H NMR (CDCl_3 , 400 MHz): 7.91 (d, J = 7.2 Hz, 2H); 7.79-7.70 (m, 4H); 7.54-7.50 (m, 3H); 7.45-7.41 (m, 2H); 7.00 (d, J = 8.4 Hz, 3H); 4.27 (s, 1H); 3.26 (s, 1H); 3.20 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): 168.9; 142.4; 133.8; 133.3; 129.8; 129.3; 129.1; 128.9; 128.7; 128.6; 128.0; 127.9; 127.8; 127.7; 127.2; 59.5; 43.0; 38.0. IR (neat): ν = 3058; 2988; 1713; 1613; 757; cm^{-1} . MS (70 eV): m/z (%). 377.1 (M^+ , 100).

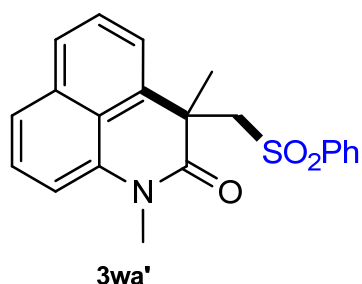


3wa

23) 1, 3-Dimethyl-3-((phenylsulfonyl)methyl)-1H-benzo[g]indol-2(3H)-one (3wa)

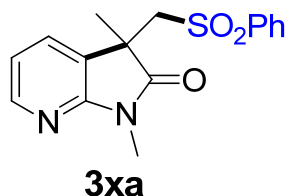
The reaction of **1w** (45.0 mg, 0.2 mmol), PhSO_2H **2a** (56 mg, 0.4 mmol), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (8 mg,

0.02 mmol) in MeCN (2 mL) afforded 40.1 mg (55%) of **3wa**; **3wa**: white solid; Mp: 199.3-200.8 °C. ¹H NMR (CDCl₃, 400 MHz): 8.64 (d, *J* = 8.4 Hz, 1H); 8.41 (d, *J* = 8.4 Hz, 1H); 7.56-7.49 (m, 3H); 7.44-7.40 (m, 3H); 7.39-7.32 (m, 2H); 7.05 (d, *J* = 8.4 Hz, 1H); 4.61 (d, *J* = 14.4 Hz, 1H, CH₂); 3.96 (d, *J* = 14.4 Hz, 1H, CH₂); 3.62 (s, 3H); 1.68 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): 171.1; 142.1; 141.1; 140.5; 134.6; 133.4; 129.6; 129.0; 127.4; 126.9; 126.0; 125.3; 122.9; 119.4; 107.2; 65.9; 45.6; 33.5; 30.6; IR (neat): ν = 3058; 2977; 1655; 1585; 1387; 1141; cm⁻¹. FTMS: calc. for C₂₁H₁₉NO₃S (M+H)⁺; 366.1158; found, 366.1155.



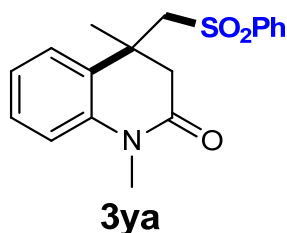
24) **1, 3-Dimethyl-3-((phenylsulfonyl)methyl)-1H-benzo[de]quinolin-2(3H)-one (3wa')**

The reaction of **1w** (45.0 mg, 0.2 mmol), PhSO₂H **2a** (56 mg, 0.4 mmol), Fe(NO₃)₃ • 9H₂O (8 mg, 0.02 mmol) in MeCN (2 mL) afforded 15.3 mg (21%) of **3wa'**; **3wa'**: yellow solid; Mp: 210.6-212.5 °C. ¹H NMR (CDCl₃, 400 MHz): 7.64 (d, *J* = 8.0 Hz, 1H); 7.50 (d, *J* = 8.0 Hz, 1H); 7.44 (t, *J* = 7.6 Hz, 2H); 7.40 (d, *J* = 7.6 Hz, 2H); 7.24-7.16 (m, 4H); 6.97 (d, *J* = 7.6 Hz, 1H); 4.62 (d, *J* = 14.8 Hz, 1H, CH₂); 3.92 (d, *J* = 14.4 Hz, 1H, CH₂); 3.50 (s, 3H); 1.63 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): 170.8; 140.4; 136.2; 133.3; 133.2; 132.9; 128.6; 127.5; 126.7; 126.5; 126.4; 123.6; 122.6; 119.1; 108.8; 65.7; 45.5; 33.6; 29.9. IR (neat): ν = 2928; 1710; 1676; 1528; 1149; cm⁻¹. FTMS: calc. for C₂₁H₁₉NO₃S (M+H)⁺, 366.1158; found, 366.1149.



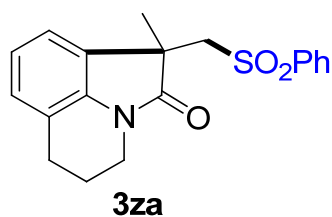
25) **1, 3-Dimethyl-3-((phenylsulfonyl)methyl)-1H-pyrrolo[2,3-b]pyridin-2(3H)-one (3xa)**

The reaction of **1x** (35.0 mg, 0.2 mmol), PhSO₂H **2a** (56 mg, 0.4 mmol), Fe(NO₃)₃ • 9H₂O (8 mg, 0.02 mmol) in MeCN (2 mL) afforded 45.5 mg (72%) of **3xa**; **3xa**: yellow solid; Mp: 166.4-169.1 °C. ¹H NMR (CDCl₃, 400 MHz): 8.22 (dd, *J* = 5.2 Hz, *J* = 1.6 Hz, 1H); 7.63-7.57 (m, 3H); 7.54-7.43 (m, 3H); 6.90 (dd, *J* = 7.2 Hz, *J* = 5.6 Hz, 1H); 3.85 (d, *J* = 14.8 Hz, 1H, CH₂); 3.68 (d, *J* = 14.4 Hz, 1H, CH₂); 3.22 (s, 3H); 1.45 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): 177.3; 147.5; 139.7; 133.7; 132.0; 129.2; 128.0; 127.8; 120.9; 118.2; 61.1; 45.3; 25.6; 24.8. IR (neat): ν = 2964; 1718; 1622; 1588; 841; cm⁻¹. FTMS: calc. for C₁₆H₁₆N₂O₃S (M+H)⁺, 317.0954; found, 317.0953.



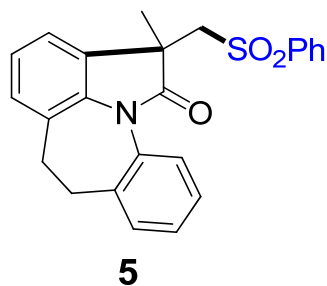
26) 1, 4-Dimethyl-4-((phenylsulfonyl)methyl)-3,4-dihydroquinolin-2(1H)-one (3ya)

The reaction of **1y** (38.0 mg, 0.2 mmol), PhSO₂H **2a** (56 mg, 0.4 mmol), Fe(NO₃)₃ • 9H₂O (8 mg, 0.02 mmol) in MeCN (2 mL) afforded 53.5 mg (81%) of **3ya**; **3ya**: brown solid; Mp: 132.3-134.8 °C. ¹H NMR (CDCl₃, 400 MHz): 7.63 (d, *J* = 7.2 Hz, 2H); 7.56-7.52 (m, 1H); 7.43-7.39 (m, 3H); 7.25-7.21 (m, 1H); 7.10-7.06 (m, 1H); 6.81 (d, *J* = 8.0 Hz, 1H); 3.40 (d, *J* = 14.8 Hz, 1H, CH₂); 3.28 (d, *J* = 14.4 Hz, 1H, CH₂); 3.22 (s, 3H); 2.96 (d, *J* = 16.0 Hz, 1H, CH₂); 2.58 (d, *J* = 16.0 Hz, 1H, CH₂); 1.78 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): 168.2; 140.7; 139.2; 133.2; 129.6; 129.0; 128.6; 127.3; 126.0; 123.4; 115.0; 61.9; 44.2; 36.1; 29.2; 24.8. IR (neat): ν = 2919; 1677; 1599; 1368; 1130; 750; cm⁻¹. FTMS: calc. for C₁₈H₁₉NO₃S (M+H)⁺, 330.1158; found, 330.1155.



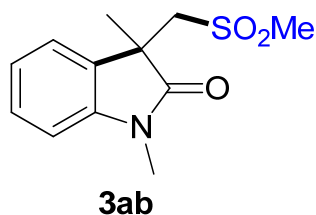
27) 1-Methyl-1-((phenylsulfonyl)methyl)-5,6-dihydro-1H-pyrrolo[3,2,1-ij]quinolin-2(4H)-one, (3za)

The reaction of **1z** (40.0 mg, 0.2 mmol), PhSO₂H **2a** (42 mg, 0.3 mmol), Fe(NO₃)₃ • 9H₂O (8 mg, 0.02 mmol) in MeCN (2 mL) afforded 50.8 mg (74%) of **3za**; **3za**: white solid; Mp: 141.6-143.1 °C. ¹H NMR (CDCl₃, 400 MHz): 7.56-7.52 (m, 3H); 7.40-7.37 (m, 2H); 7.02 (dd, *J* = 7.6 Hz, *J* = 0.8 Hz, 1H); 6.91 (d, *J* = 7.6 Hz, 1H); 6.79 (t, *J* = 8.0 Hz, 1H); 3.84 (d, *J* = 14.4 Hz, 1H); 3.72-3.60 (m, 3H); 2.80-2.76 (m, 2H), 2.04-1.97 (m, 2H); 1.41 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): 176.4; 140.0; 139.0; 133.3; 128.8; 128.1; 127.7; 127.2; 121.91; 121.89; 120.3; 61.7; 46.7; 39.0; 25.0; 24.5; 20.9. IR (neat): ν = 2974; 1711; 1613; 1309; 753; cm⁻¹. FTMS: calc. for C₁₉H₁₉NO₃S (M+H)⁺, 342.1158; found, 342.1152.



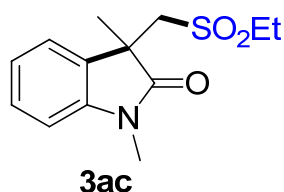
28) 7-Methyl-7-((phenylsulfonyl)methyl)-11,12-dihydrobenzo[6,7]azepino[3,2,1-hi]indol-6(7H)-one (5)

The reaction of **4** (53.0 mg, 0.2 mmol), PhSO₂H **2a** (56 mg, 0.4 mmol), Fe(NO₃)₃ • 9H₂O (8 mg, 0.02 mmol) in MeCN (2 mL) afforded 55.2 mg (68%) of **5**; **5**: brown solid; Mp: 240.3-242.1 °C. ¹H NMR (CDCl₃, 400 MHz): 7.91-7.87 (m, 1H); 7.59-7.54 (m, 4H); 7.36-7.29 (m, 3H); 7.22-7.19 (m, 2H); 6.99 (d, *J* = 8.4 Hz, 1H); 6.73 (d, *J* = 7.6 Hz, 1H); 4.03 (d, *J* = 14.4 Hz, 1H, CH₂); 3.78 (d, *J* = 14.8 Hz, 1H, CH₂); 3.08-3.02 (m, 4H); 1.45 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): 178.0; 140.2; 136.7; 134.3; 133.2; 130.4; 129.6; 129.3; 129.2; 128.9; 128.1; 127.6; 126.59; 126.55; 126.53; 122.2; 121.2; 67.6; 45.4; 33.72; 33.69; 26.4. IR (neat): ν = 2976; 2926; 1722; 1449; 1321; cm⁻¹. FTMS: calc. for C₂₄H₂₁NO₃S (M+H)⁺, 404.1315; found, 404.1315.



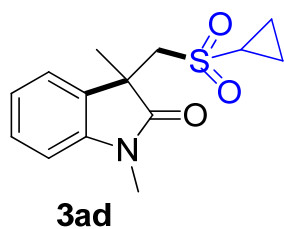
29) 1, 3-Dimethyl-3-((methylsulfonyl)methyl)indolin-2-one (3ab)

The reaction of **1a** (35.0 mg, 0.2 mmol), MeSO₂H **2b** (48 mg, 0.6 mmol), Fe(NO₃)₃ • 9H₂O (8 mg, 0.02 mmol) in MeCN (2 mL) afforded 32.4 mg (64%) of **3ab**; **3ab**: white solid; Mp: 116.0-117.5 °C. ¹H NMR (CDCl₃, 400 MHz): 7.37-7.33 (m, 2H); 7.12 (t, *J* = 7.6 Hz, 1H); 6.92 (d, *J* = 7.6 Hz, 1H); 3.72 (d, *J* = 14.8 Hz, 1H, CH₂); 3.60 (d, *J* = 14.8 Hz, 1H, CH₂); 3.26 (s, 3H); 2.61 (s, 3H); 1.46 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): 177.7; 143.4; 130.0; 129.1; 123.4; 122.6; 108.9; 60.7; 45.5; 43.2; 26.5; 24.9. IR (neat): ν = 2929; 1714; 1613; 1154; 1123; 756; cm⁻¹. FTMS: calc. for C₁₂H₁₅NO₃S (M+H)⁺, 254.0845; found, 254.0840.



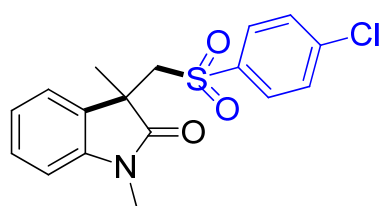
30) 3-((Ethylsulfonyl)methyl)-1,3-dimethylindolin-2-one (3ac)

The reaction of **1a** (35.0 mg, 0.2 mmol), EtSO₂H **2c** (40 mg, 0.4 mmol), Fe(NO₃)₃ • 9H₂O (8 mg, 0.02 mmol) in MeCN (2 mL) afforded 44.2 mg (83%) of **3ac**; **3ac**: colorless oil; ¹H NMR (CDCl₃, 400 MHz): 7.38-7.32 (m, 2H); 7.11 (t, *J* = 7.6 Hz, 1H); 6.91 (d, *J* = 8.0 Hz, 1H); 3.64 (d, *J* = 14.4 Hz, 1H, CH₂); 3.54 (d, *J* = 14.4 Hz, 1H, CH₂); 3.26 (s, 3H); 2.76-2.66 (m, 2H); 1.46 (s, 3H). 1.26 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): 177.9; 143.2; 130.2; 128.9; 123.4; 122.5; 108.7; 57.7; 49.4; 45.4; 26.5; 24.9; 6.27. IR (neat): ν = 2976; 2940; 1713; 1613; 1122; 758; cm⁻¹. FTMS: calc. for C₁₃H₁₇NO₃S (M+H)⁺, 268.1002; found, 268.0998.



31) 3-((Cyclopropylsulfonyl)methyl)-1,3-dimethylindolin-2-one (3ad)

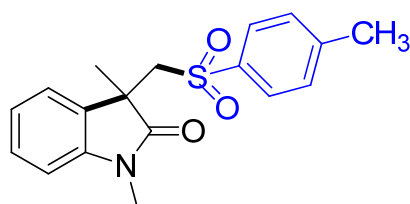
The reaction of **1a** (35.0 mg, 0.2 mmol), cyclopropanesulfinic acid **2d** (42.4 mg, 0.4 mmol), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (8 mg, 0.02 mmol) in MeCN (2 mL) afforded 48.5 mg (87%) of **3ad**; **3ad**: colorless oil; ^1H NMR (CDCl_3 , 400 MHz): 7.39-7.31 (m, 2H); 7.10 (dd, $J = 7.2$ Hz, $J = 1.2$ Hz, 1H); 6.91 (d, $J = 8.0$ Hz, 1H); 3.77 (d, $J = 14.4$ Hz, 1H, CH_2); 3.62 (d, $J = 14.4$ Hz, 1H, CH_2); 3.26 (s, 3H); 2.01-1.95 (m, 1H); 1.46 (s, 3H); 1.04-0.99 (m, 2H); 0.88-0.83 (m, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): 177.9; 143.3; 130.3; 128.9; 123.7; 122.4; 108.7; 59.8; 45.4; 31.4; 26.5; 25.0; 5.9; 5.12; 5.06. IR (neat): $\nu = 2973$; 1715; 1613; 1123; 758; cm^{-1} . FTMS: calc. for $\text{C}_{14}\text{H}_{17}\text{NO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$, 280.1002; found, 280.1004.



3ae

32) 3-(((4-Chlorophenyl)sulfonyl)methyl)-1,3-dimethylindolin-2-one (3ae)

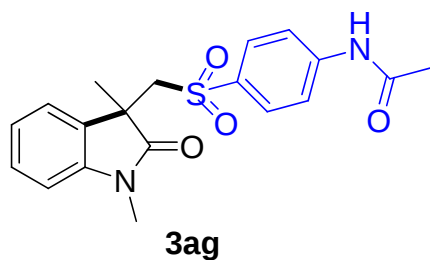
The reaction of **1a** (35.0 mg, 0.2 mmol), 4-chlorobenzenesulfinic acid **2e** (53.1 mg, 0.3 mmol), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (8 mg, 0.02 mmol) in MeCN (2 mL) afforded 54.0 mg (77%) of **3ae**; **3ae**: white solid; Mp: 168.5-170.9 °C. ^1H NMR (CDCl_3 , 400 MHz): 7.38-7.29 (m, 5H); 6.98 (d, $J = 7.2$ Hz, 1H); 6.91-6.84 (m, 2H); 3.91 (d, $J = 14.4$ Hz, 1H, CH_2); 3.70 (d, $J = 14.8$ Hz, 1H, CH_2); 3.17 (s, 3H); 1.38 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): 177.4; 143.2; 140.0; 138.2; 129.2; 129.1; 129.0; 128.7; 123.9; 122.4; 108.4; 61.8; 45.4; 26.4; 25.4. IR (neat): $\nu = 2973$; 2929; 1715; 1613; 1087; cm^{-1} . FTMS: calc. for $\text{C}_{17}\text{H}_{16}\text{ClNO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$, 350.0612; found, 350.0607.



3af

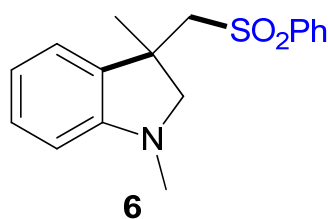
33) 1, 3-Dimethyl-3-(tosylmethyl)indolin-2-one (3af)

The reaction of **1a** (35.0 mg, 0.2 mmol), 4-methylbenzenesulfinic acid **2f** (46.8 mg, 0.3 mmol), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (8 mg, 0.02 mmol) in MeCN (2 mL) afforded 57.0 mg (87%) of **3af**; **3af**: white solid; Mp: 131.6-133.4 °C. ^1H NMR (CDCl_3 , 400 MHz): 7.36 (d, $J = 8.4$ Hz, 2H); 7.29-7.25 (m, 1H); 7.15 (d, $J = 8.0$ Hz, 2H); 7.06 (d, $J = 7.2$ Hz, 1H); 6.92-6.88 (m, 1H); 6.84 (d, $J = 7.6$ Hz, 1H); 3.85 (d, $J = 14.4$ Hz, 1H, CH_2); 3.67 (d, $J = 14.8$ Hz, 1H, CH_2); 3.15 (s, 3H); 2.38 (s, 3H); 1.38 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): 177.5; 144.2; 143.1; 136.9; 129.45; 129.36; 128.4; 127.7; 124.0; 122.3; 108.3; 61.8; 45.5; 26.4; 25.4; 21.4. IR (neat): $\nu = 2967$; 1727; 1696; 1613; 1153; 755; cm^{-1} . FTMS: calc. for $\text{C}_{18}\text{H}_{19}\text{NO}_3\text{S}$ ($\text{M}+\text{H}$) $^+$, 330.1158; found, 330.1153.



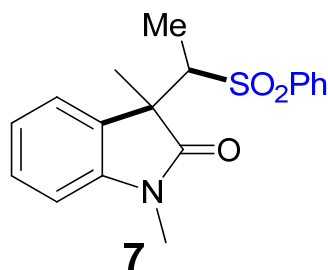
34) N-(4-(((1, 3-dimethyl-2-oxoindolin-3-yl)methyl)sulfonyl)phenyl)acetamide (3ag)

The reaction of **1a** (35.0 mg, 0.2 mmol), 4-Acetamidobenzenesulfinic acid **2g** (60 mg, 0.3 mmol), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (8 mg, 0.02 mmol) in MeCN (2 mL) afforded 46 mg (62%) of **3ag**; **3ag**: white solid; Mp: 212.1-214.2 °C. ^1H NMR (CDCl_3 , 400 MHz): 8.31 (s, 1H); 7.53 (d, $J = 8.4$ Hz, 2H); 7.34-7.25 (m, 3H); 7.04 (d, $J = 7.2$ Hz, 1H); 6.92-6.84 (m, 2H); 3.86 (d, $J = 14.4$ Hz, 1H, CH_2); 3.69 (d, $J = 14.4$ Hz, 1H, CH_2); 3.15 (s, 3H); 2.16 (s, 3H); 1.37 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): 177.8; 169.2; 143.1; 133.8; 129.3; 128.9; 128.7; 124.0; 123.1; 122.6; 119.1; 108.5; 61.9; 45.6; 26.6; 25.6; 24.6. IR (neat): $\nu = 3585$; 3326; 2969; 1725; 1590; 841; cm^{-1} . FTMS: calc. for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_4\text{S}$ ($\text{M}+\text{H}$) $^+$, 373.1216; found, 373.1212.



34) 1, 3-Dimethyl-3-((phenylsulfonyl)methyl)indoline (6)

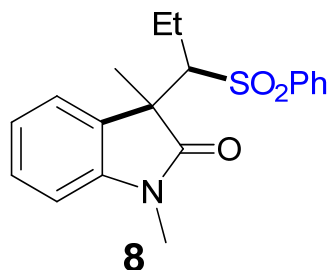
6: yellow oil ; ^1H NMR (CDCl_3 , 400 MHz): 7.91-7.88 (m, 2H); 7.63-7.59 (m, 1H); 7.54-7.50 (m, 2H); 7.09 (td, $J = 7.6$ Hz, $J = 1.2$ Hz, 1H); 6.94 (d, $J = 7.6$ Hz, 1H); 6.65 (td, $J = 7.6$ Hz, $J = 0.8$ Hz, 1H); 6.47 (d, $J = 7.6$ Hz, 1H); 3.88 (d, $J = 9.6$ Hz, 1H); 3.37 (d, $J = 14.0$ Hz, 1H); 3.30 (d, $J = 14.0$ Hz, 1H); 3.13 (d, $J = 9.6$ Hz, 1H); 2.76 (s, 3H); 1.68 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): 151.7; 141.4; 135.9; 133.5; 129.2; 128.6; 127.5; 121.9; 118.1; 107.7; 66.3; 63.2; 43.5; 35.5; 23.7. FTMS: calc. for $\text{C}_{17}\text{H}_{19}\text{NO}_2\text{S}$ ($\text{M}+\text{H}$) $^+$, 302.1209; found, 302.1205.



35) 1, 3-Dimethyl-3-(1-(phenylsulfonyl)ethyl)indolin-2-one (7)

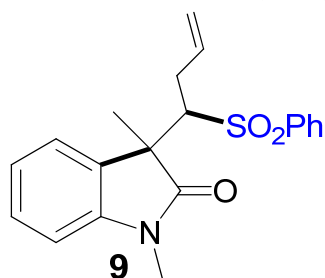
7: yellow oil ; ^1H NMR (CDCl_3 , 400 MHz): 7.96 (d, $J = 8.4$ Hz, 2H); 7.85 (d, $J = 8.8$ Hz, 2H); 7.81 (d, $J = 8.0$ Hz, 1H); 7.53 (t, $J = 7.6$ Hz, 2H); 7.11 (t, $J = 8.4$ Hz, 1H); 6.86 (d, $J = 7.6$ Hz, 1H); 3.75 (q, $J = 7.2$ Hz, 1H, CH); 3.22 (s, 3H); 3.06 (s, 3H); 1.73 (d, $J = 8.0$ Hz, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): 178.2; 133.7; 133.5; 129.4; 129.1; 128.5; 128.3; 127.3; 126.6; 123.0; 108.0;

63.9; 44.4; 26.4; 23.6; 12.3; IR (neat): ν = 2929; 1710; 1305; 1149; 745; cm^{-1} . FTMS: calc. for $\text{C}_{18}\text{H}_{19}\text{NO}_3\text{S}$ ($\text{M}+\text{H}$)⁺, 330.1158; found, 330.1157.



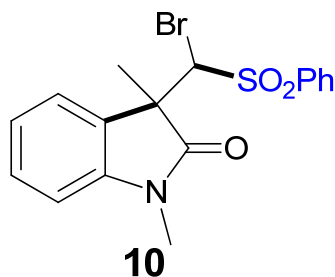
36) 1, 3-Dimethyl-3-(1-(phenylsulfonyl)propyl)indolin-2-one (8)

8: colorless oil ; ^1H NMR (CDCl_3 , 400 MHz): 7.67-7.65 (m, 2H); 7.64-7.54 (m, 1H); 7.44 (t, J = 7.2 Hz, 2H); 7.36-7.28 (m, 2H); 7.04-7.00 (m, 1H); 6.90 (d, J = 8.0 Hz, 1H); 3.80 (t, J = 5.6 Hz, 1H, CH); 3.24 (s, 3H); 2.31-2.23 (m, 2H); 1.41 (s, 3H). 0.98 (t, J = 7.6 Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): 179.5; 143.5; 140.1; 133.3; 130.2; 128.8; 128.6; 128.5; 124.1; 122.2; 108.7; 71.7; 48.8; 26.6; 25.0; 19.6; 14.6. IR (neat): ν = 2969; 1714; 1612; 1304; 1147; 753; cm^{-1} . FTMS: calc. for $\text{C}_{19}\text{H}_{21}\text{NO}_3\text{S}$ ($\text{M}+\text{H}$)⁺, 344.1315; found, 344.1307.



37) 1, 3-Dimethyl-3-(1-(phenylsulfonyl)but-3-en-1-yl)indolin-2-one (9)

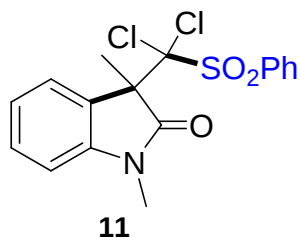
9: yellow oil ; ^1H NMR (CDCl_3 , 400 MHz): 7.67 (d, J = 7.2 Hz, 2H); 7.55 (d, J = 7.6 Hz, 1H); 7.44 (t, J = 7.6 Hz, 2H); 7.35 (t, J = 7.2 Hz, 2H); 7.06 (t, J = 7.6 Hz, 1H); 6.91 (d, J = 7.6 Hz, 1H); 5.70-5.60 (m, 1H, CH); 5.06 (dd, J = 17.2 Hz, J = 1.2 Hz, 1H); 4.97 (dd, J = 10.0 Hz, J = 1.2 Hz, 1H); 4.01 (t, J = 6.0 Hz, 1H); 3.25 (s, 3H); 2.99-2.96 (m, 2H); 1.41 (s, 3H).; ^{13}C NMR (CDCl_3 , 100 MHz): 179.5; 143.5; 139.6; 135.0; 133.4; 130.1; 128.8; 128.7; 128.5; 124.3; 122.3; 117.8; 108.8; 69.6; 48.8; 30.6; 26.7; 25.2; FTMS: calc. for $\text{C}_{20}\text{H}_{21}\text{NO}_3\text{S}$ ($\text{M}+\text{H}$)⁺, 356.1315; found, 356.1315.



38) 3-(Bromo(phenylsulfonyl)methyl)-1,3-dimethylindolin-2-one (10)

10: white solid; Mp: 176.3-178.6 °C. ^1H NMR (CDCl_3 , 400 MHz): 7.70 (d, J = 8.0 Hz, 2H); 7.63-7.59 (m, 1H); 7.44 (t, J = 7.6 Hz, 1H); 7.47-7.43 (m, 2H); 7.38 (t, J = 8.0 Hz, 1H); 7.03 (t, J = 7.6 Hz, 1H); 6.95 (d, J = 7.6 Hz, 1H); 5.42 (s, 1H, CH); 3.31 (s, 3H); 1.55 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): 176.7; 143.2; 136.7; 134.2; 129.8; 129.3; 128.8; 128.1; 124.8; 122.5; 108.8;

71.0; 49.0; 27.4; 26.8. IR (neat): ν = 2976; 1720; 1656; 1304; 653; cm^{-1} . FTMS: calc. for $\text{C}_{17}\text{H}_{16}\text{BrNO}_3\text{S}$ ($\text{M}+\text{H}$)⁺, 394.0107.; found, 394.0104.



39) 3-(Dichloro(phenylsulfonyl)methyl)-1,3-dimethylindolin-2-one (11)

11: white solid; Mp: 164.8-166.9 °C. ¹H NMR (CDCl_3 , 400 MHz): 7.91 (d, J = 7.2 Hz, 2H); 7.67-7.63 (m, 2H); 7.50-7.47 (m, 2H); 7.38 (t, J = 8.0 Hz, 1H); 7.04 (t, J = 8.0 Hz, 1H); 6.92 (d, J = 8.0 Hz, 1H); 3.30 (s, 3H). 1.84 (s, 3H); ¹³C NMR (CDCl_3 , 100 MHz): 173.0; 143.0; 134.8; 133.7; 132.2; 129.7; 128.4; 127.8; 126.0; 122.4; 108.5; 102.9; 53.8; 26.8; 23.3. IR (neat): ν = 2967; 1718; 1645; 1304; 688. MS (70 eV): m/z (%). 383.0 (M^+ , 100).

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177.524

143.195

139.844

133.268

129.364

128.821

128.539

127.665

123.947

122.451

108.321

77.317

77.000

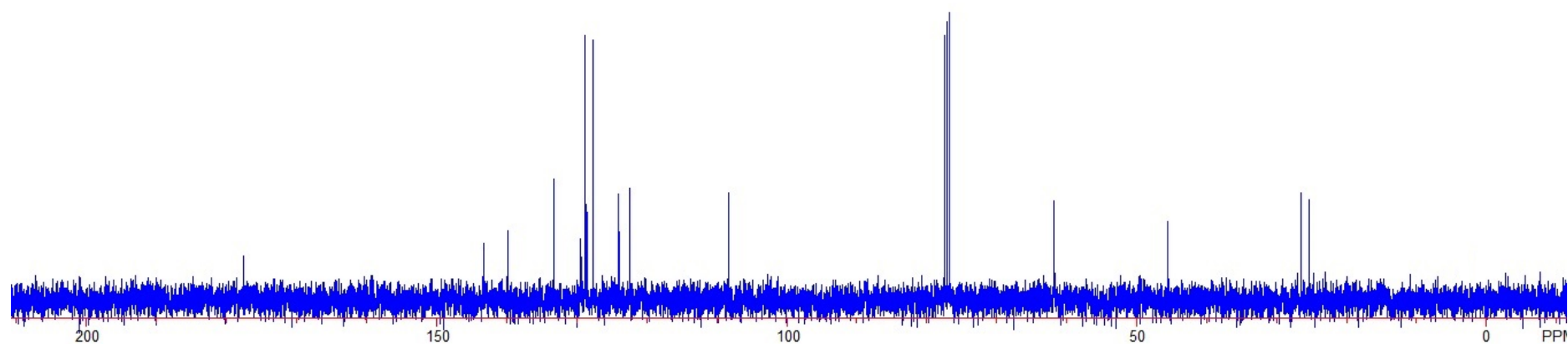
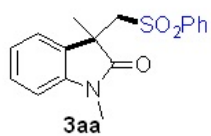
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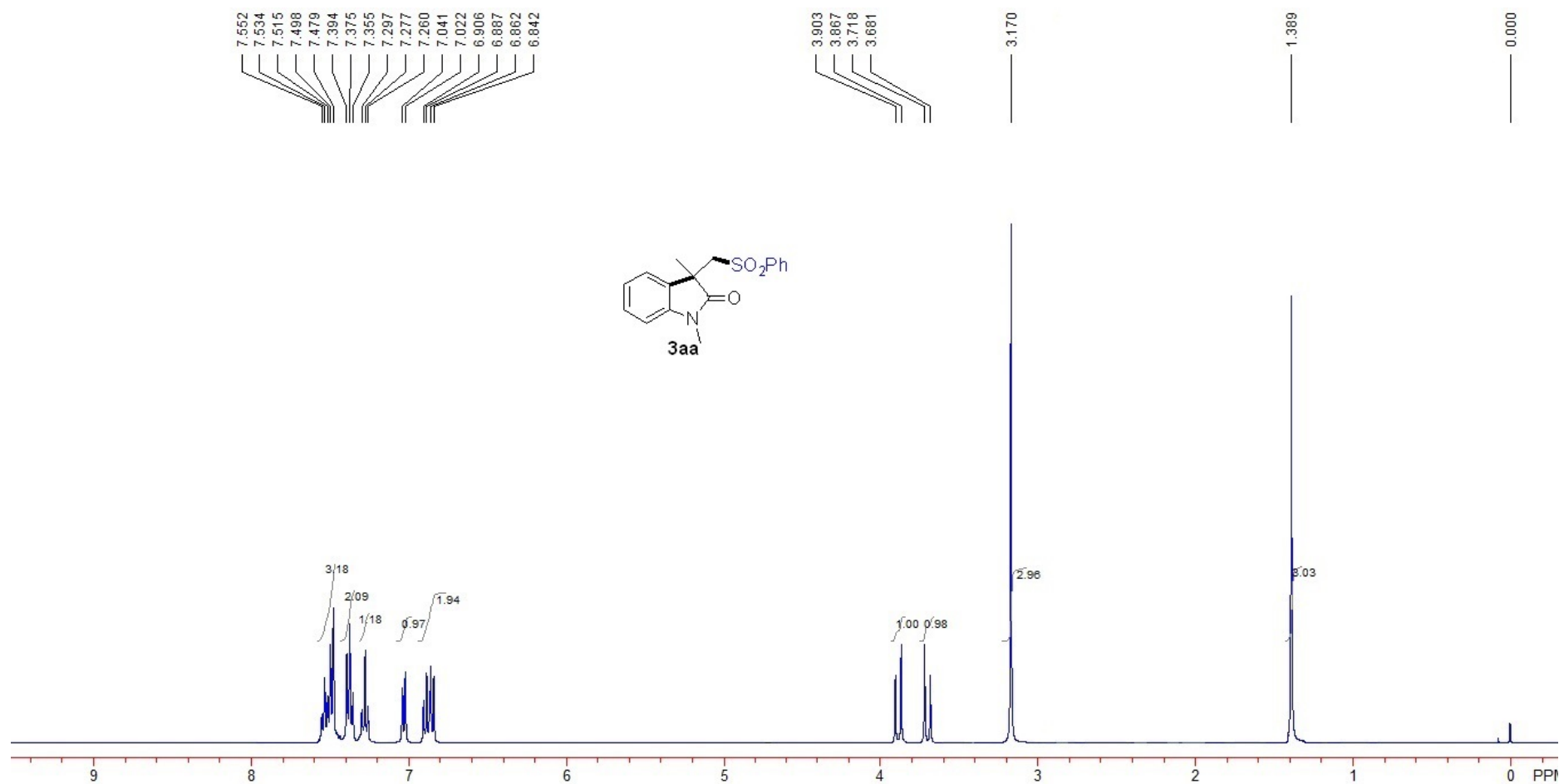
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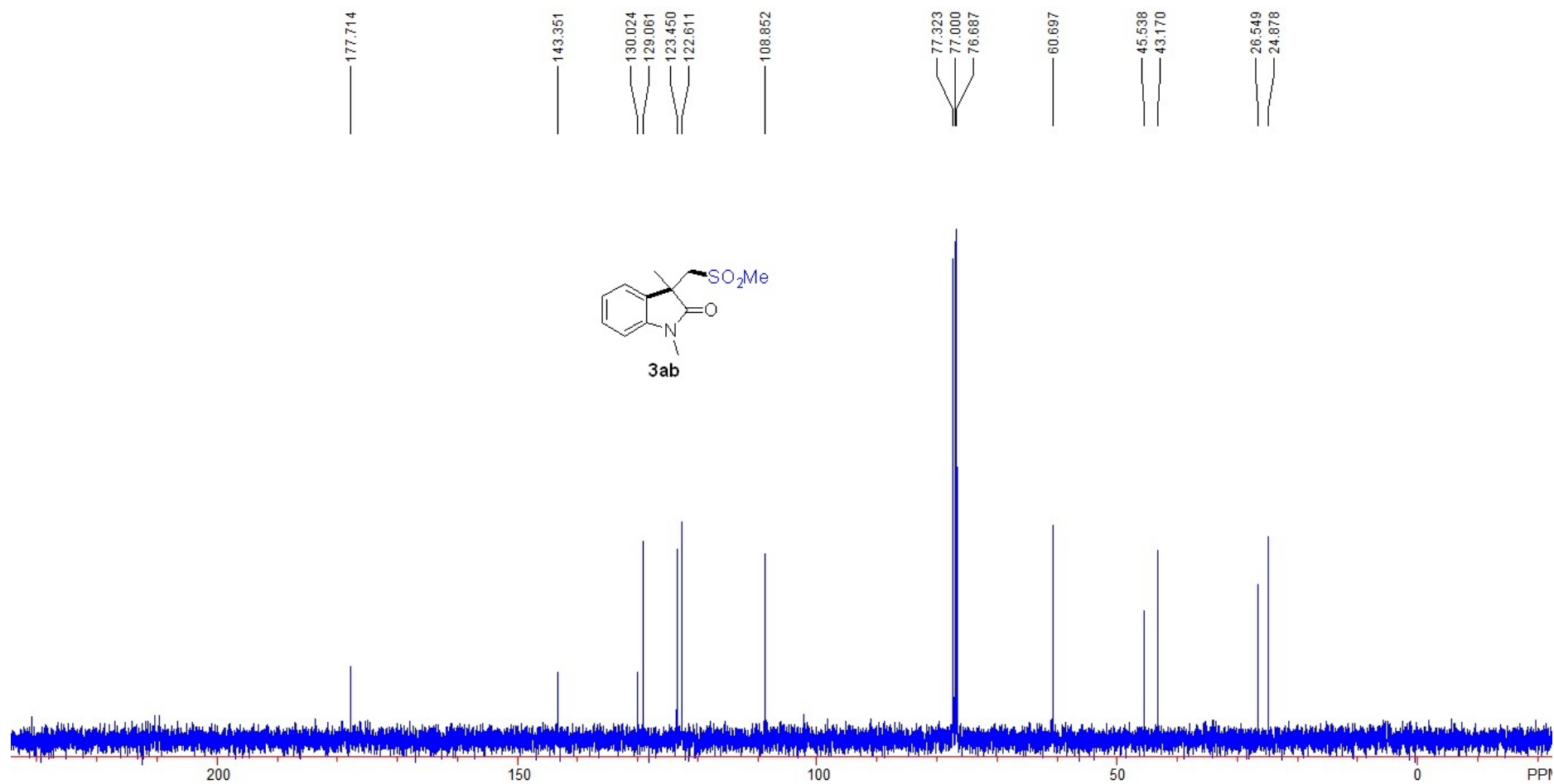
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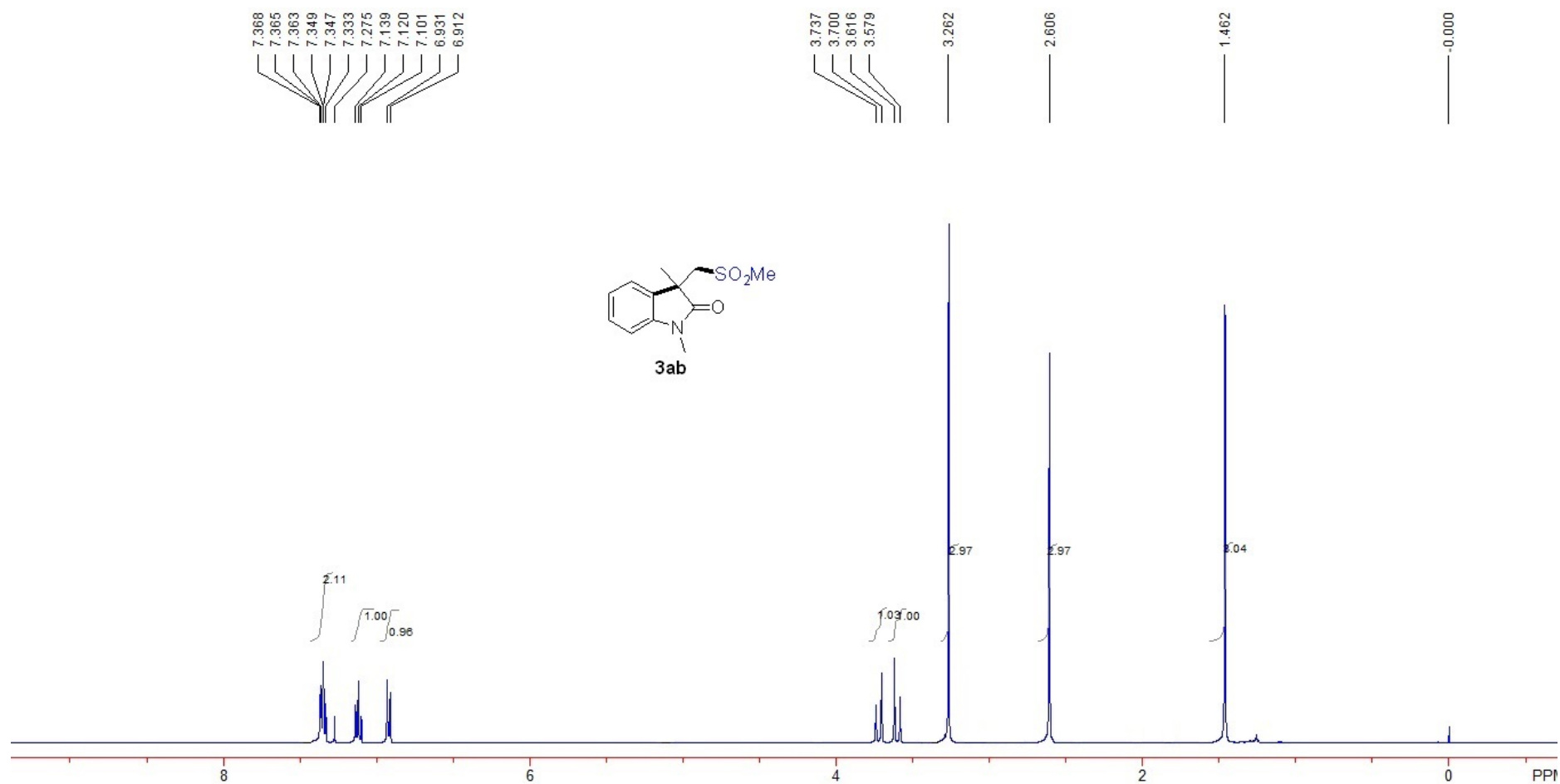
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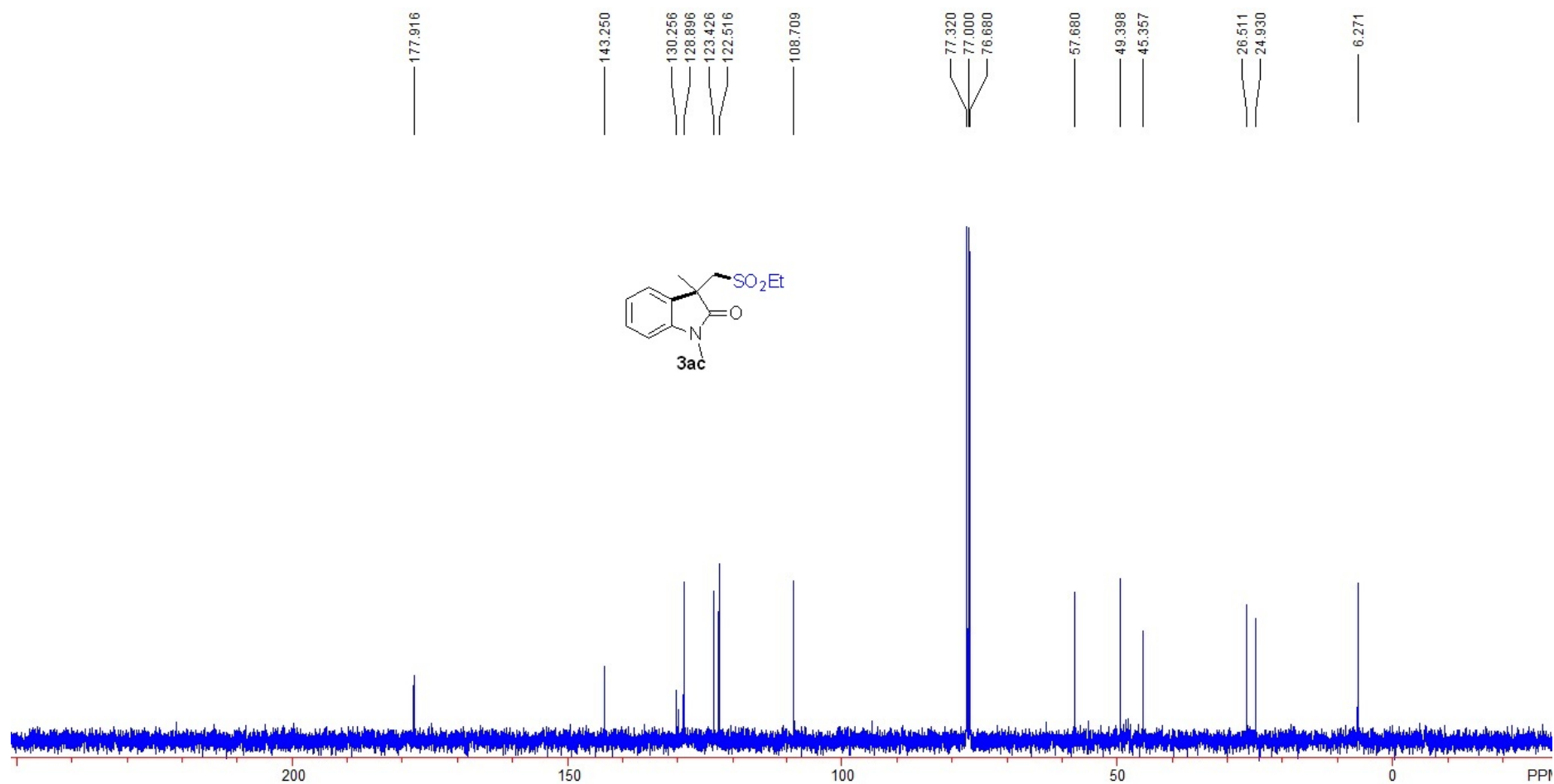
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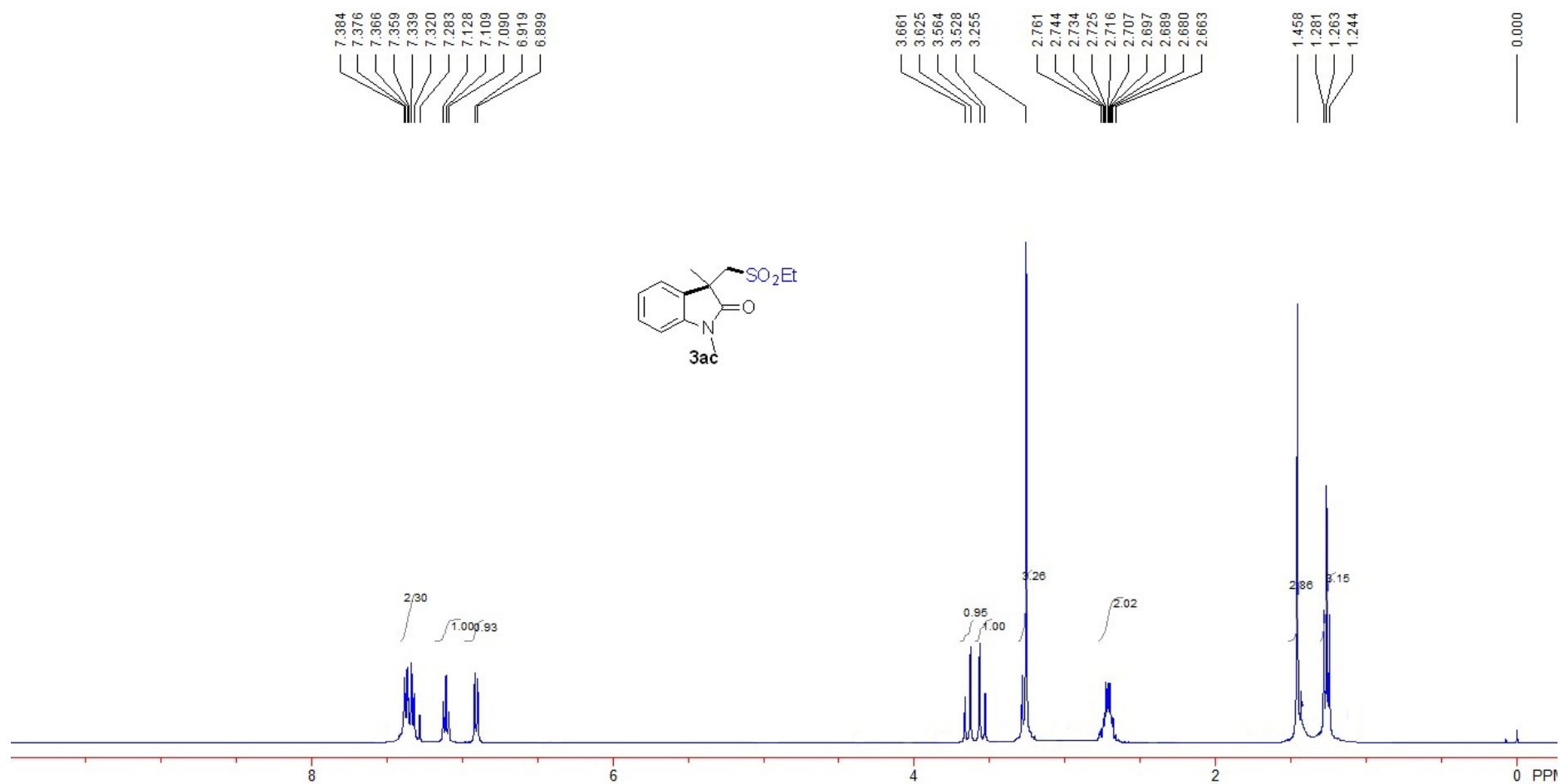


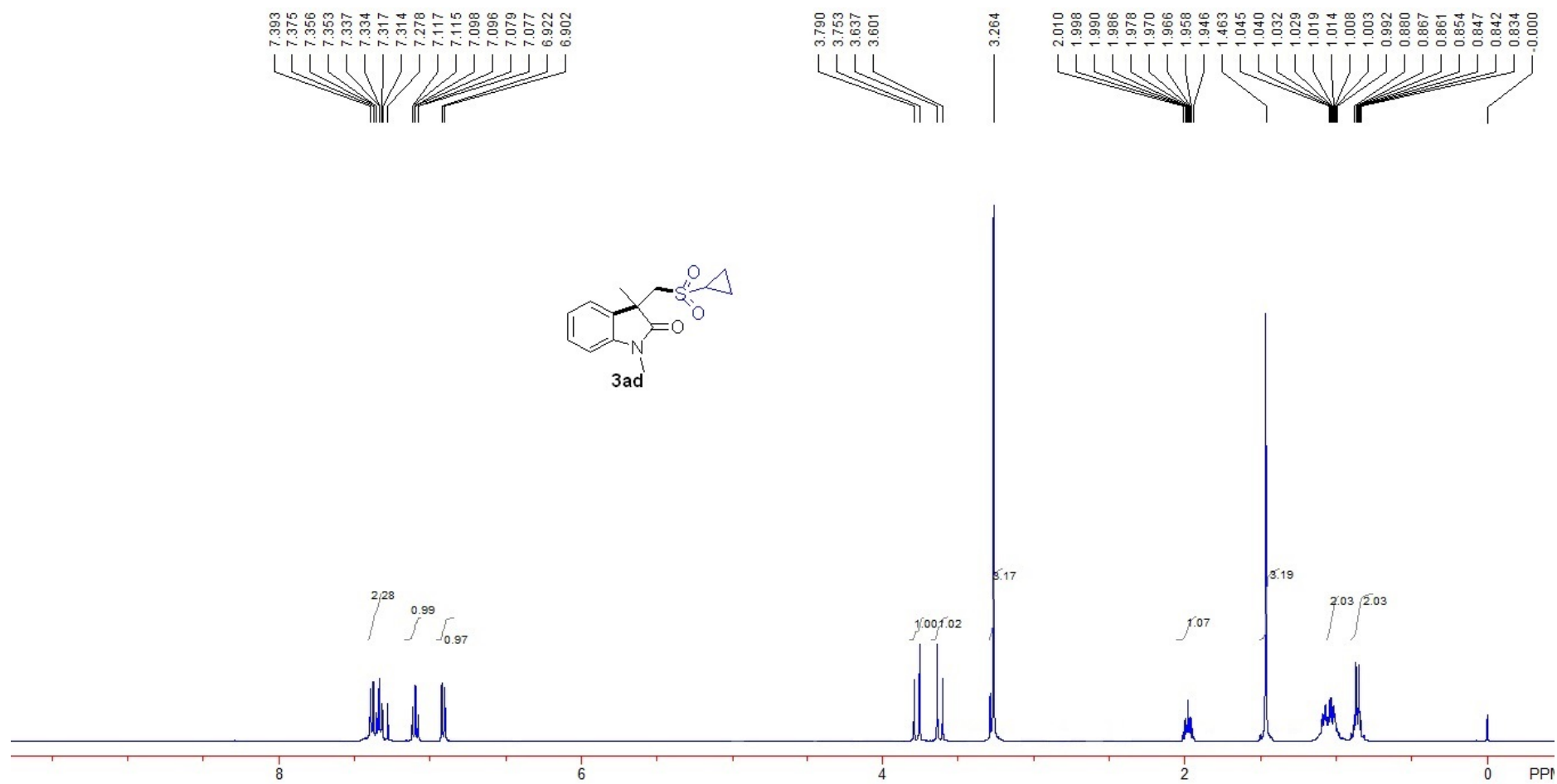


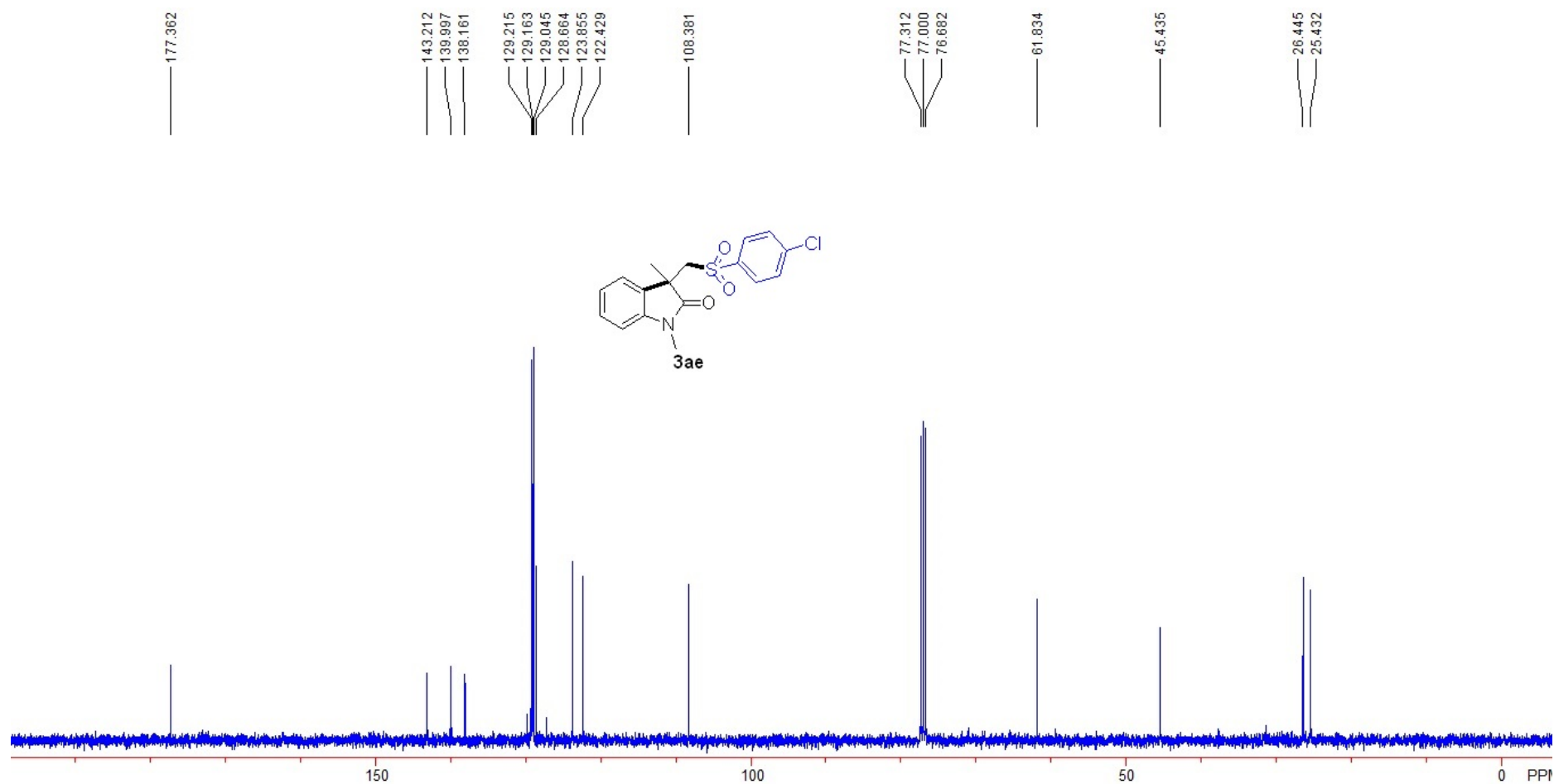


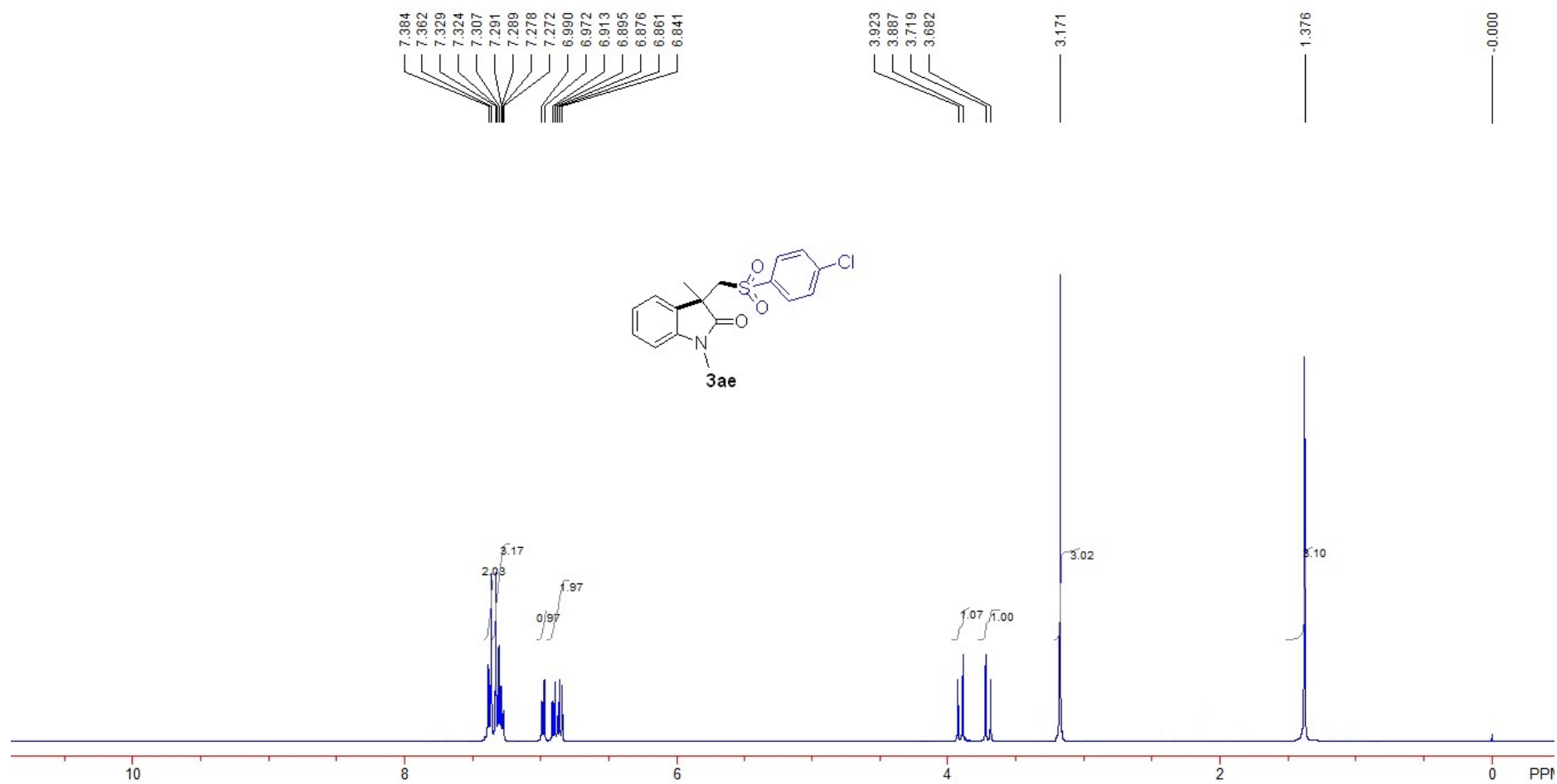


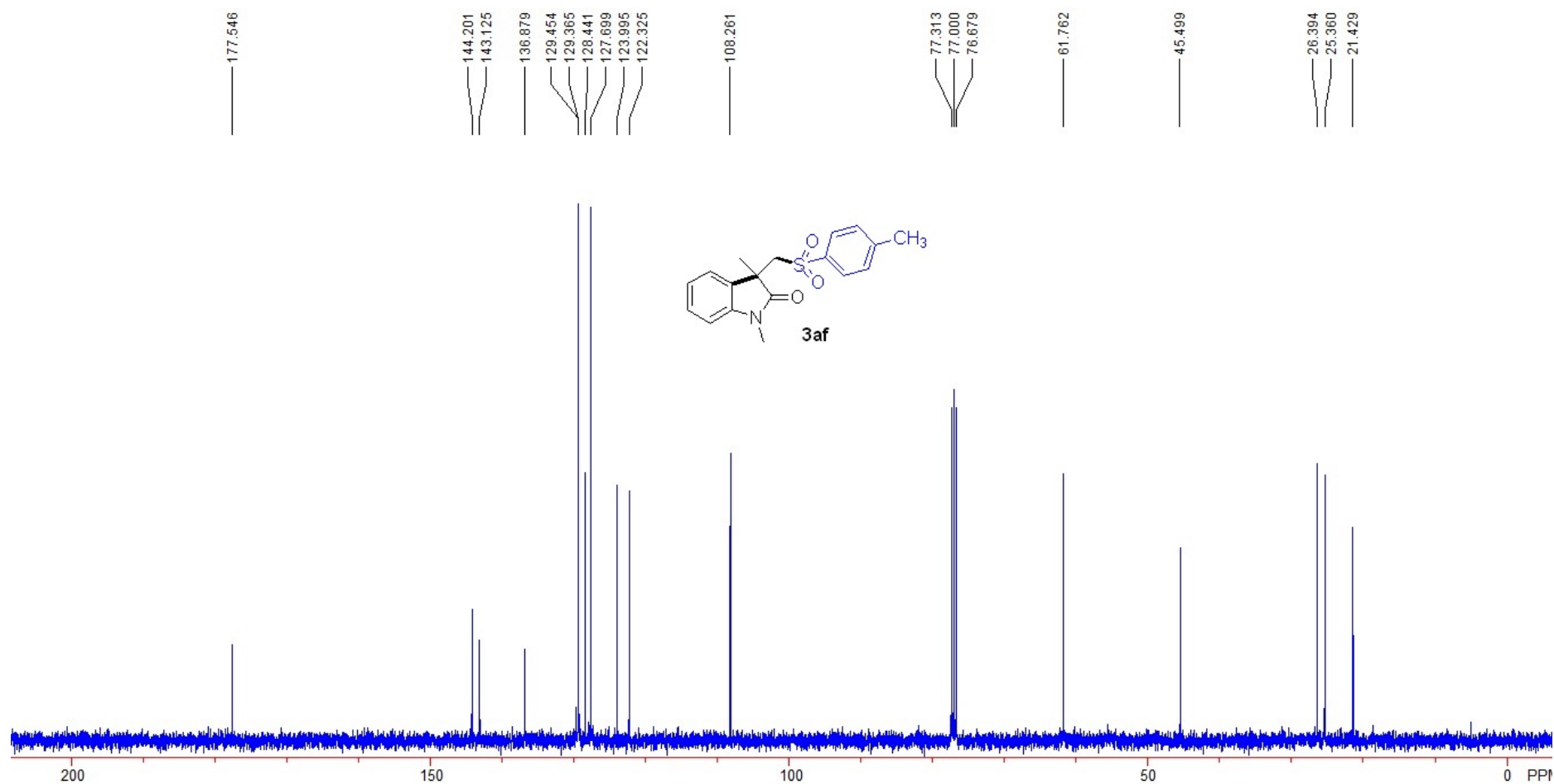


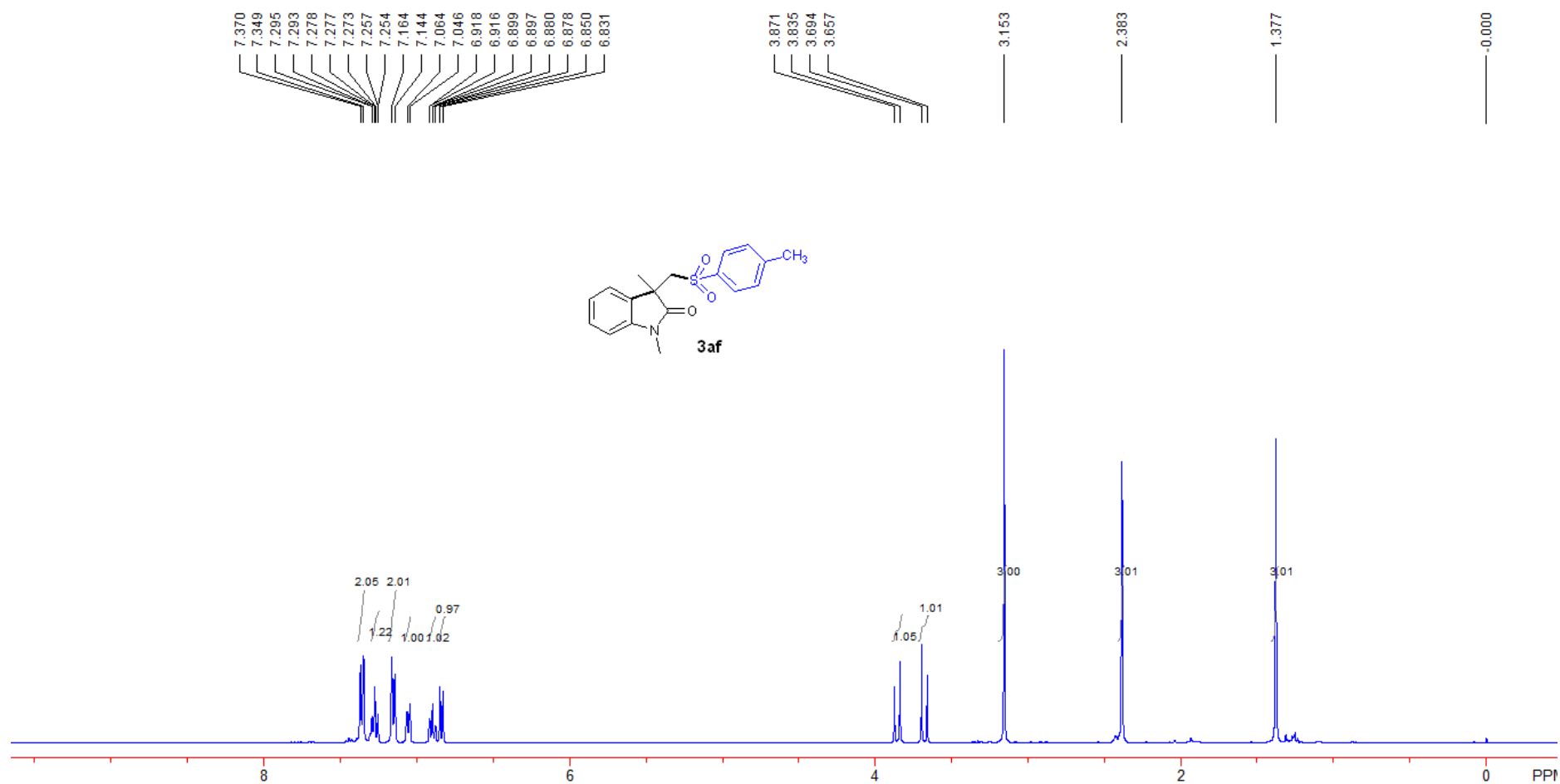


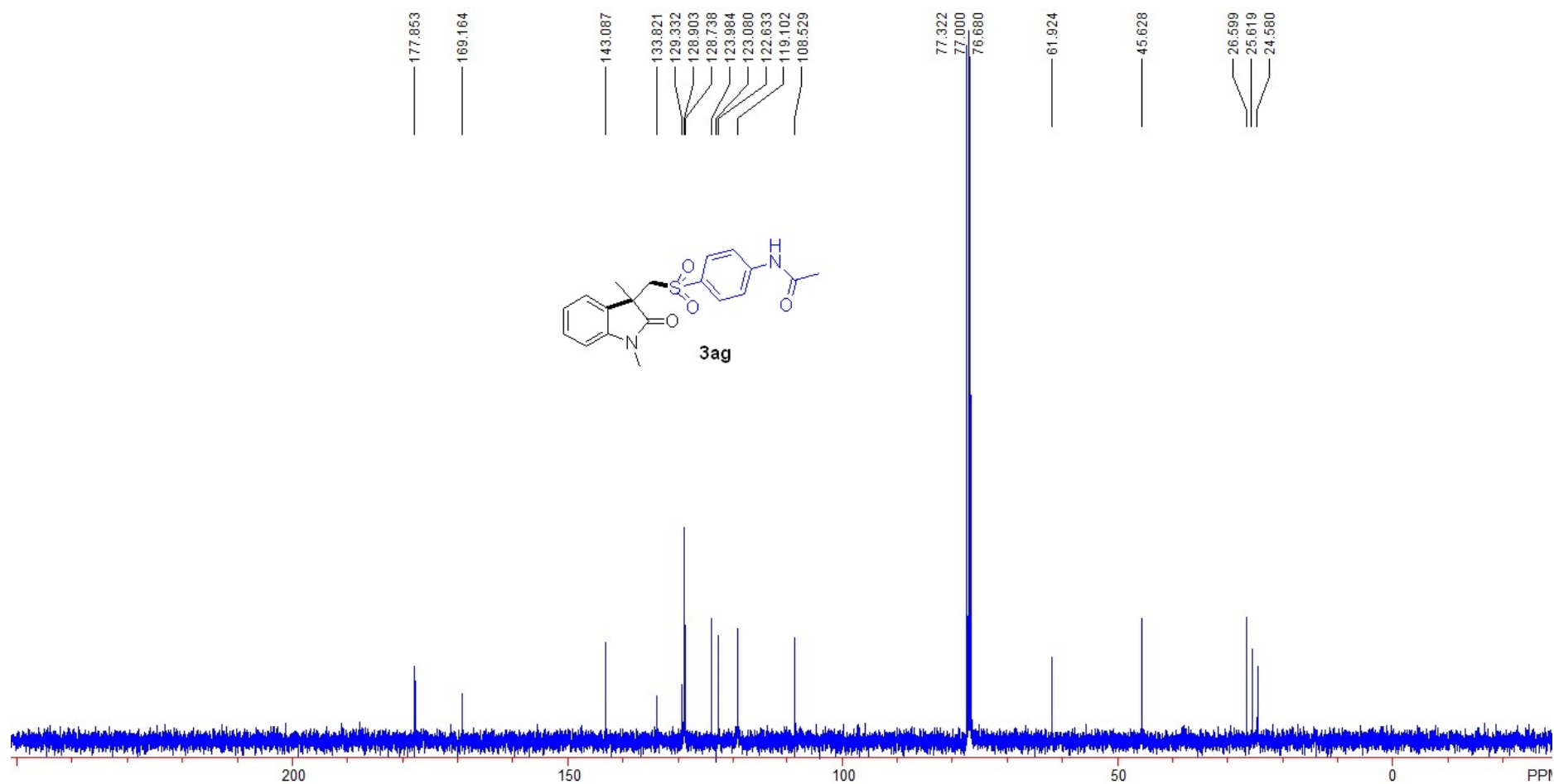


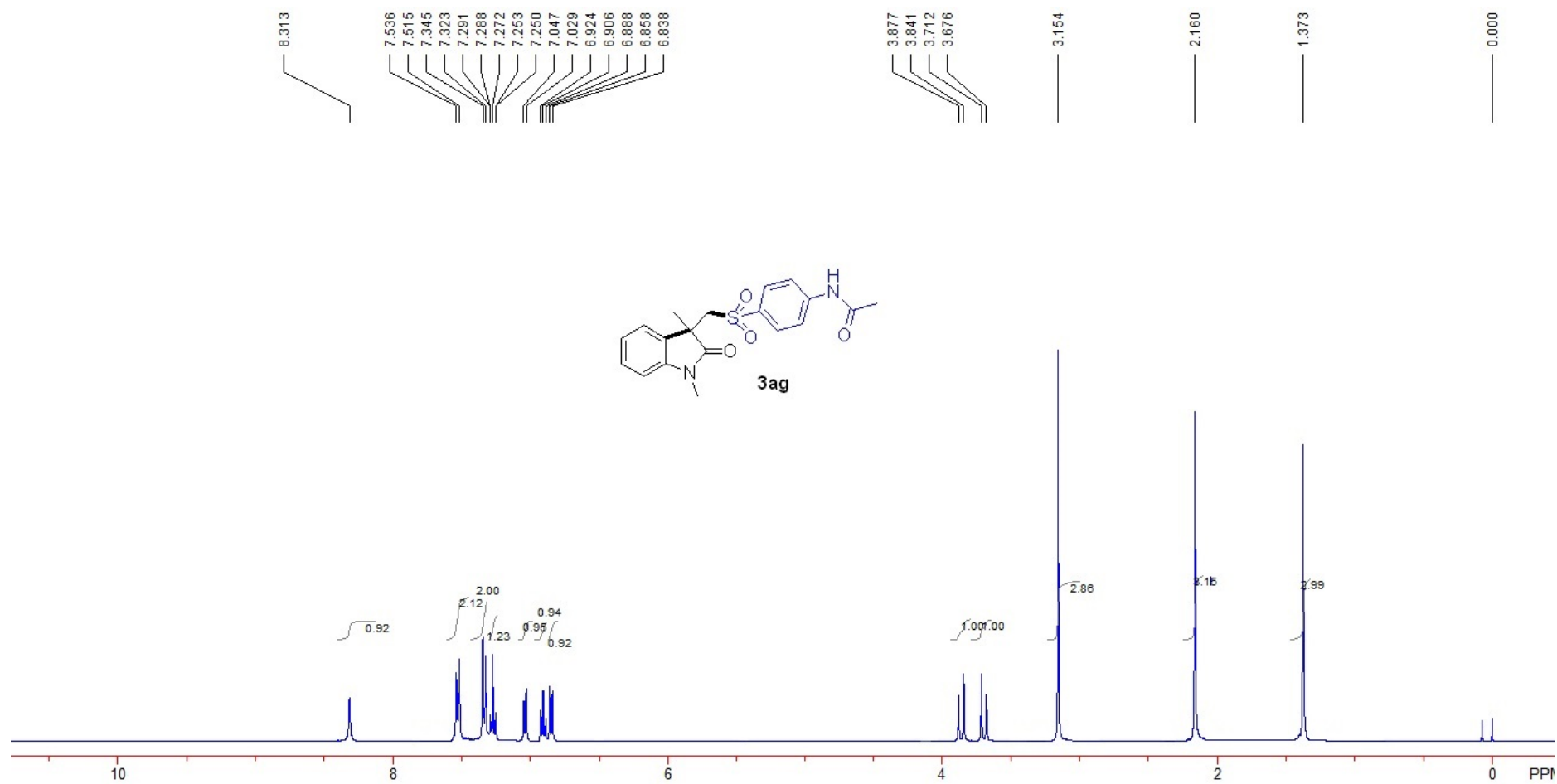


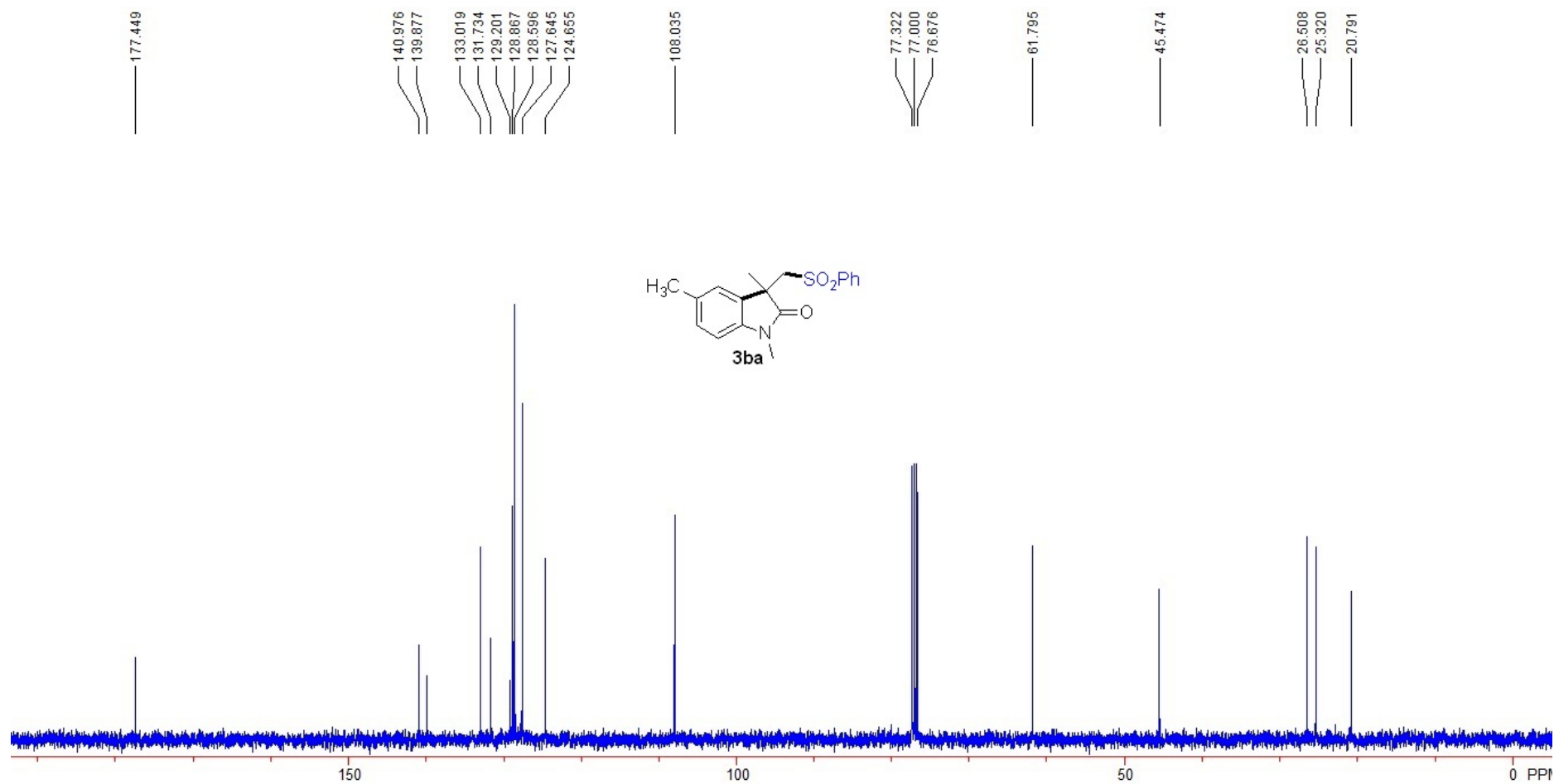


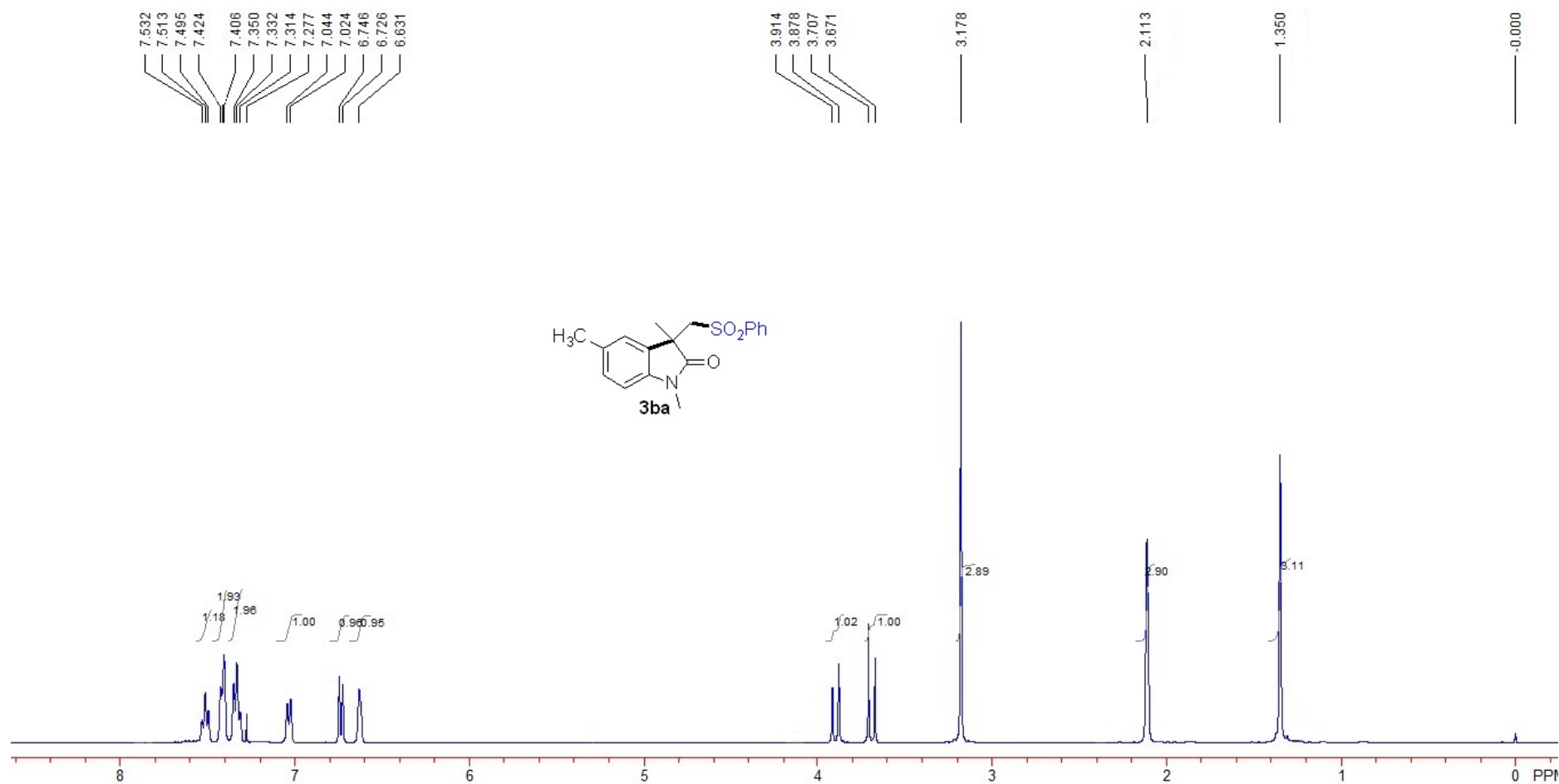


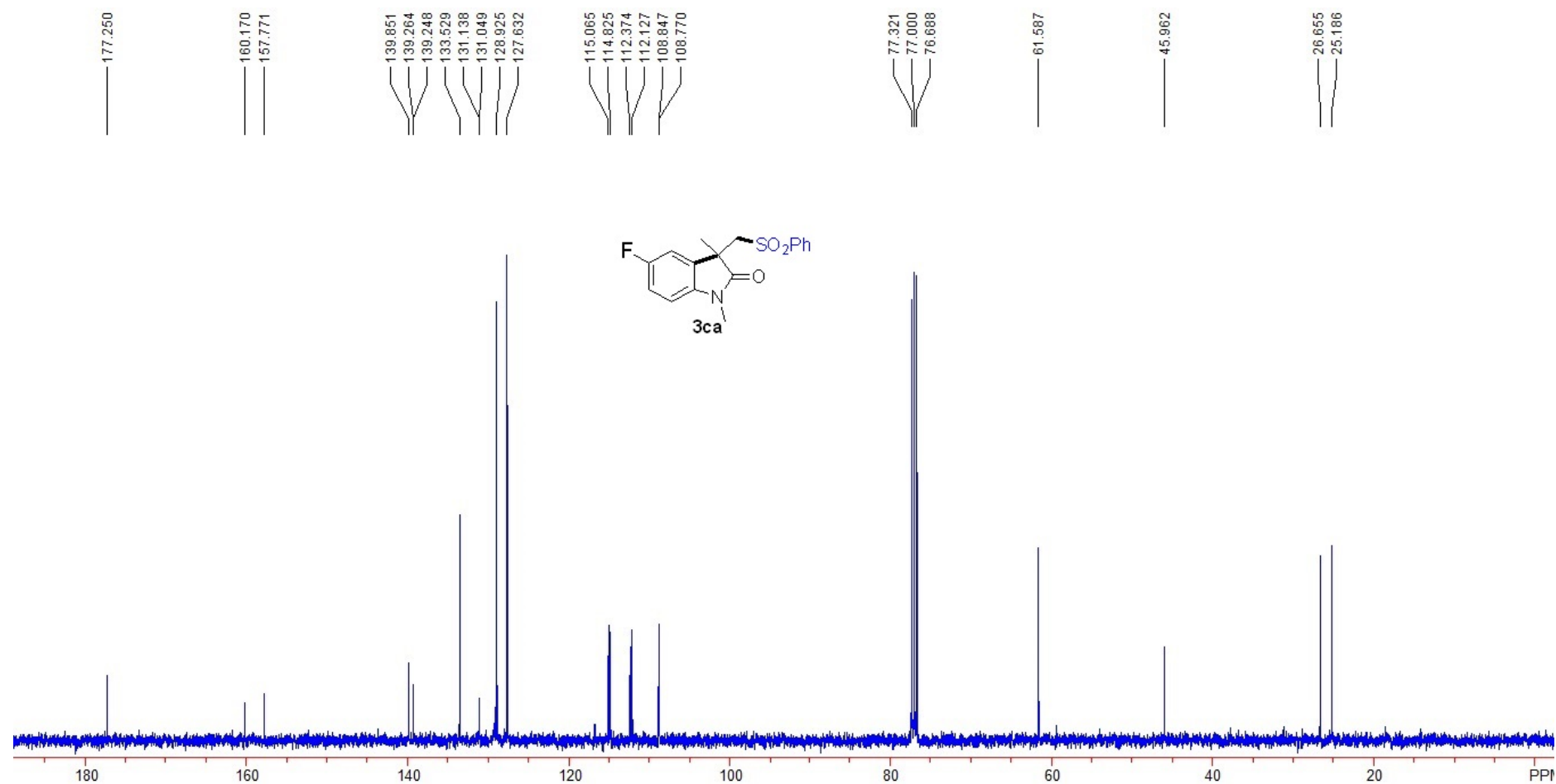


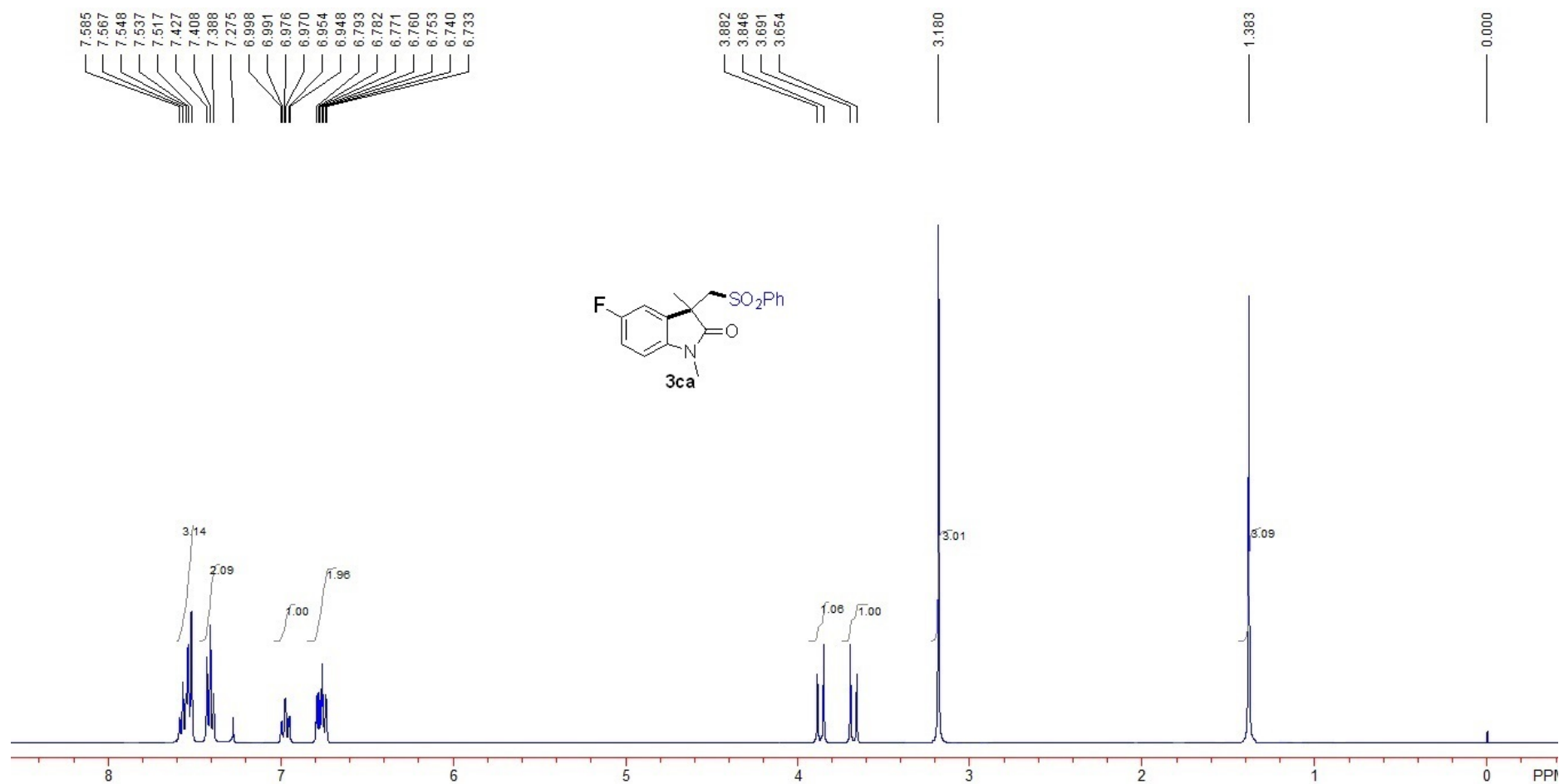


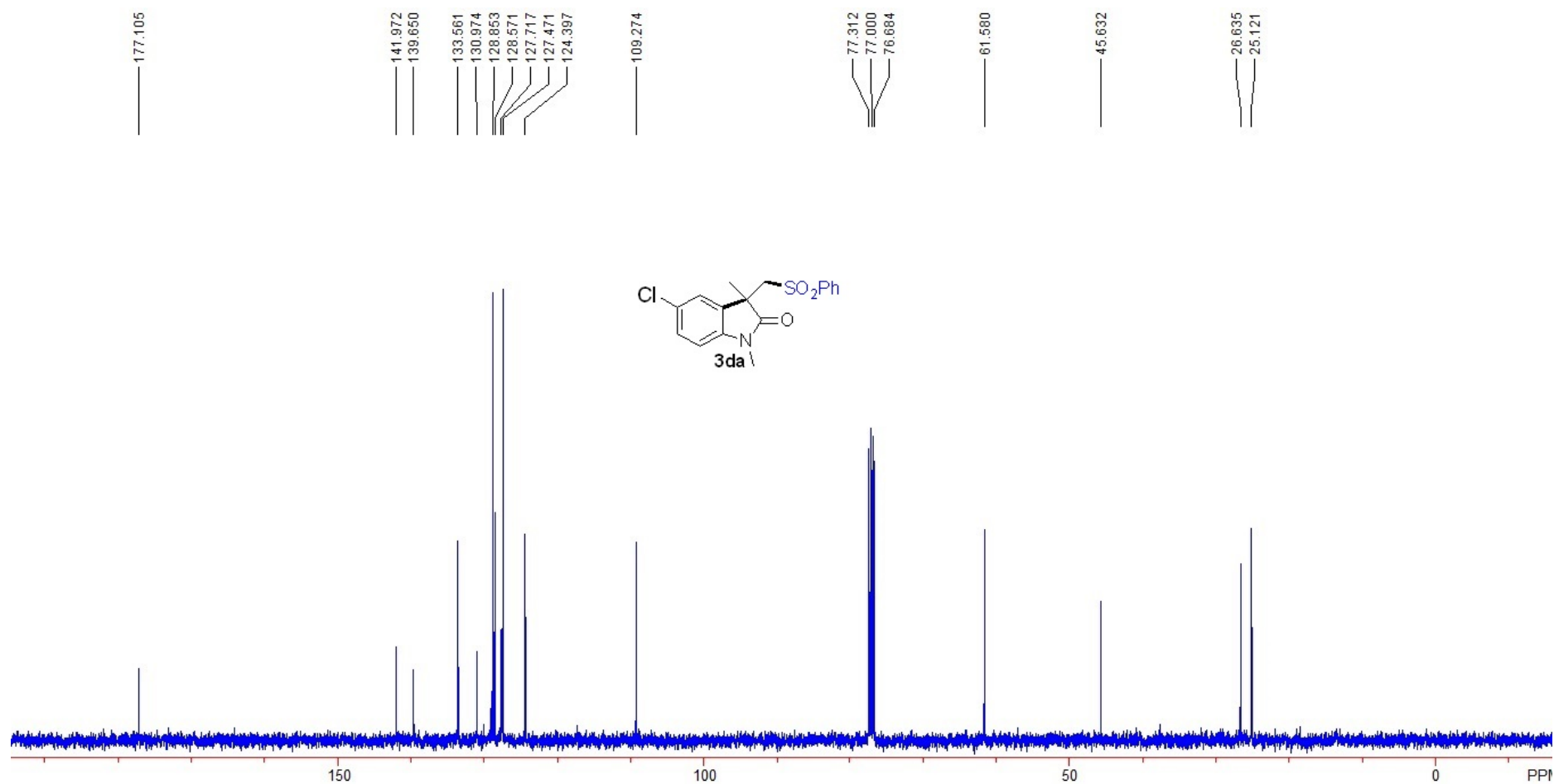


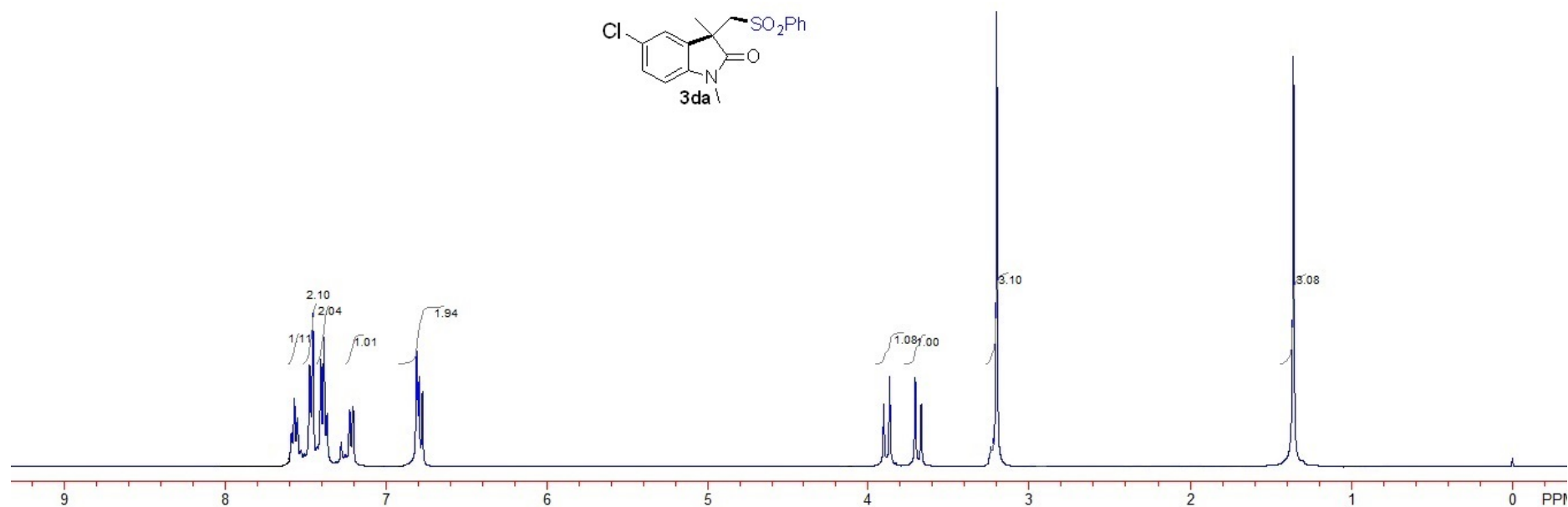
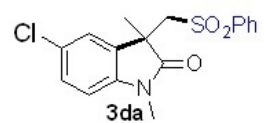
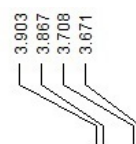
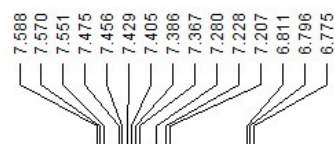


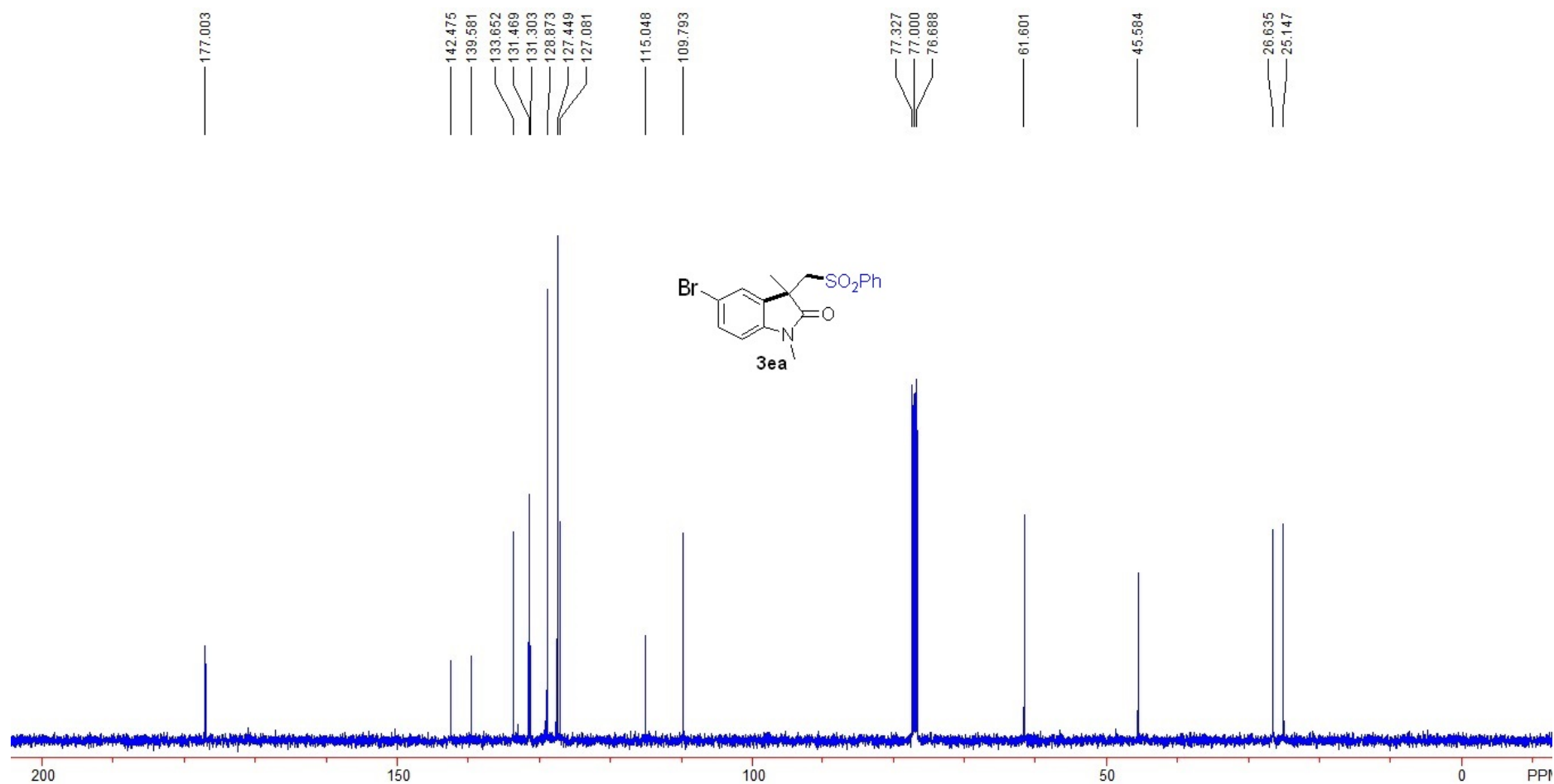


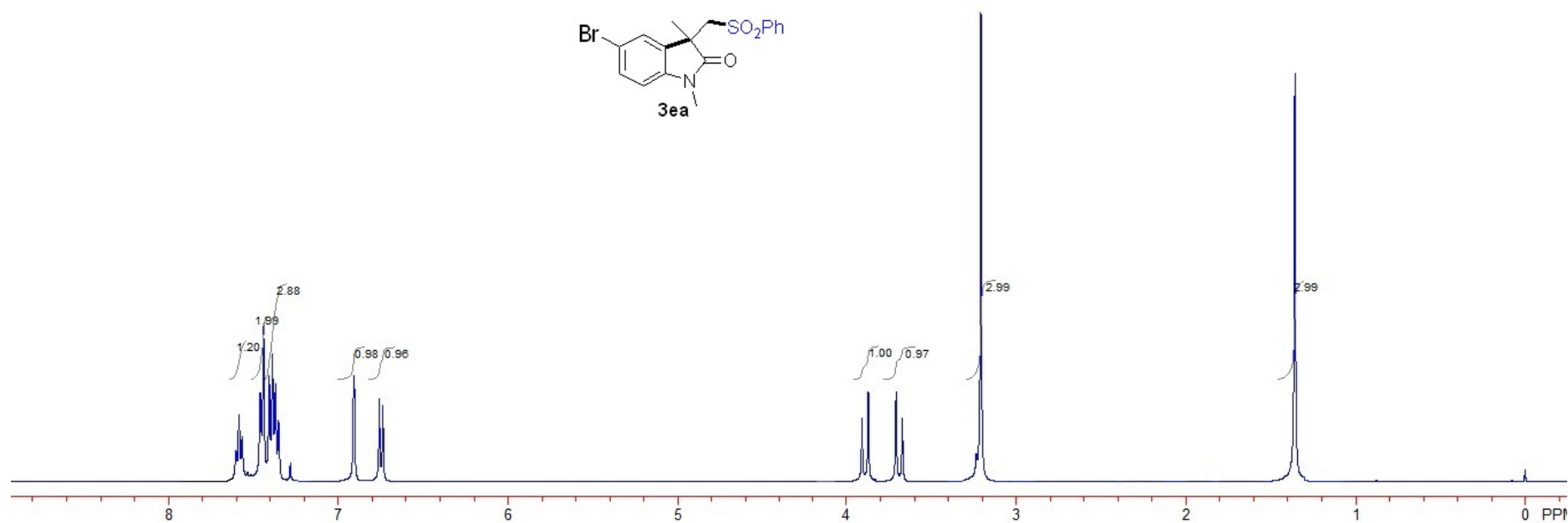
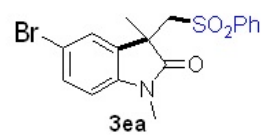
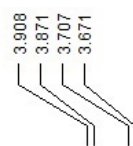
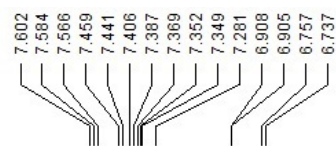


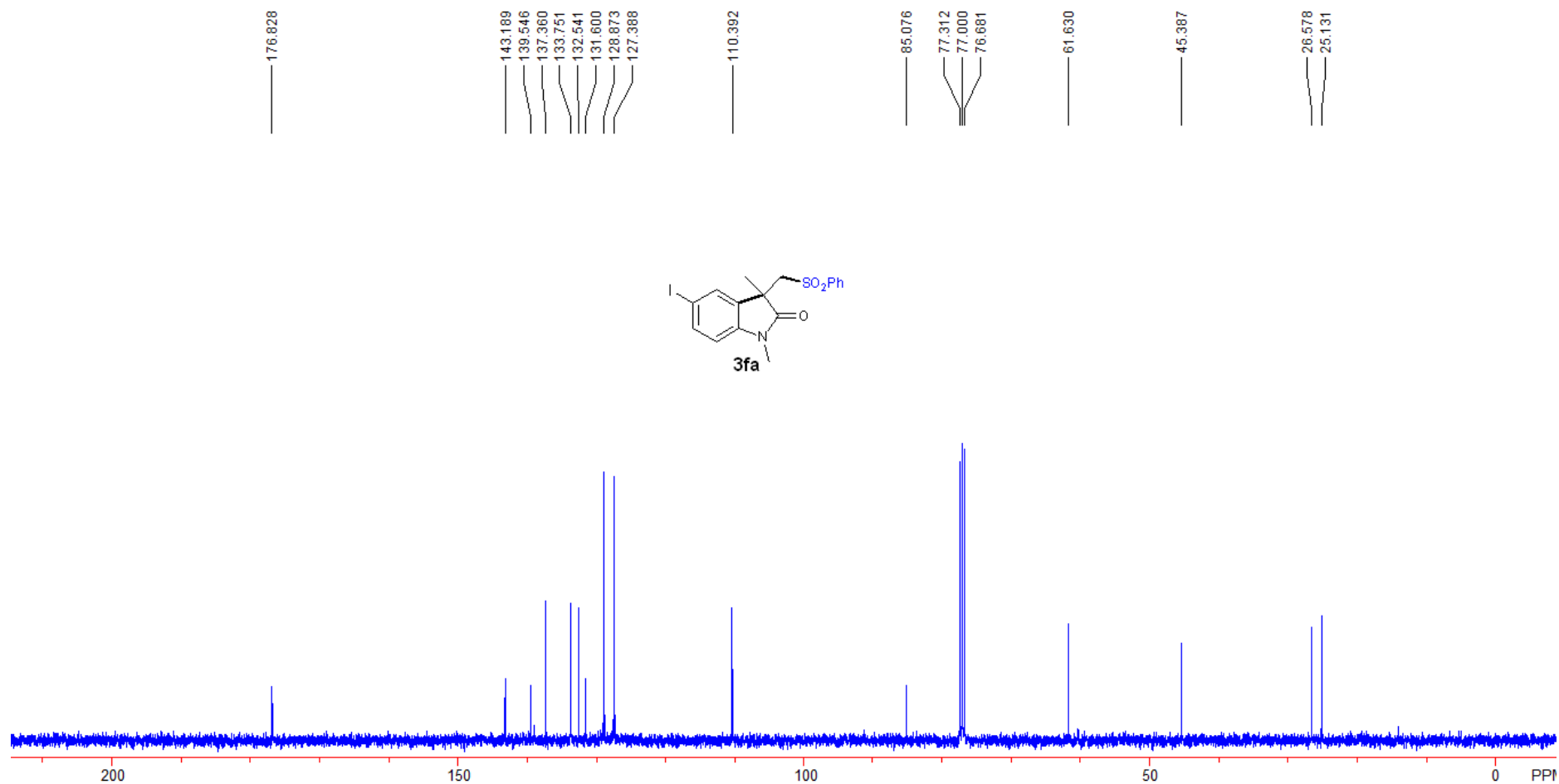


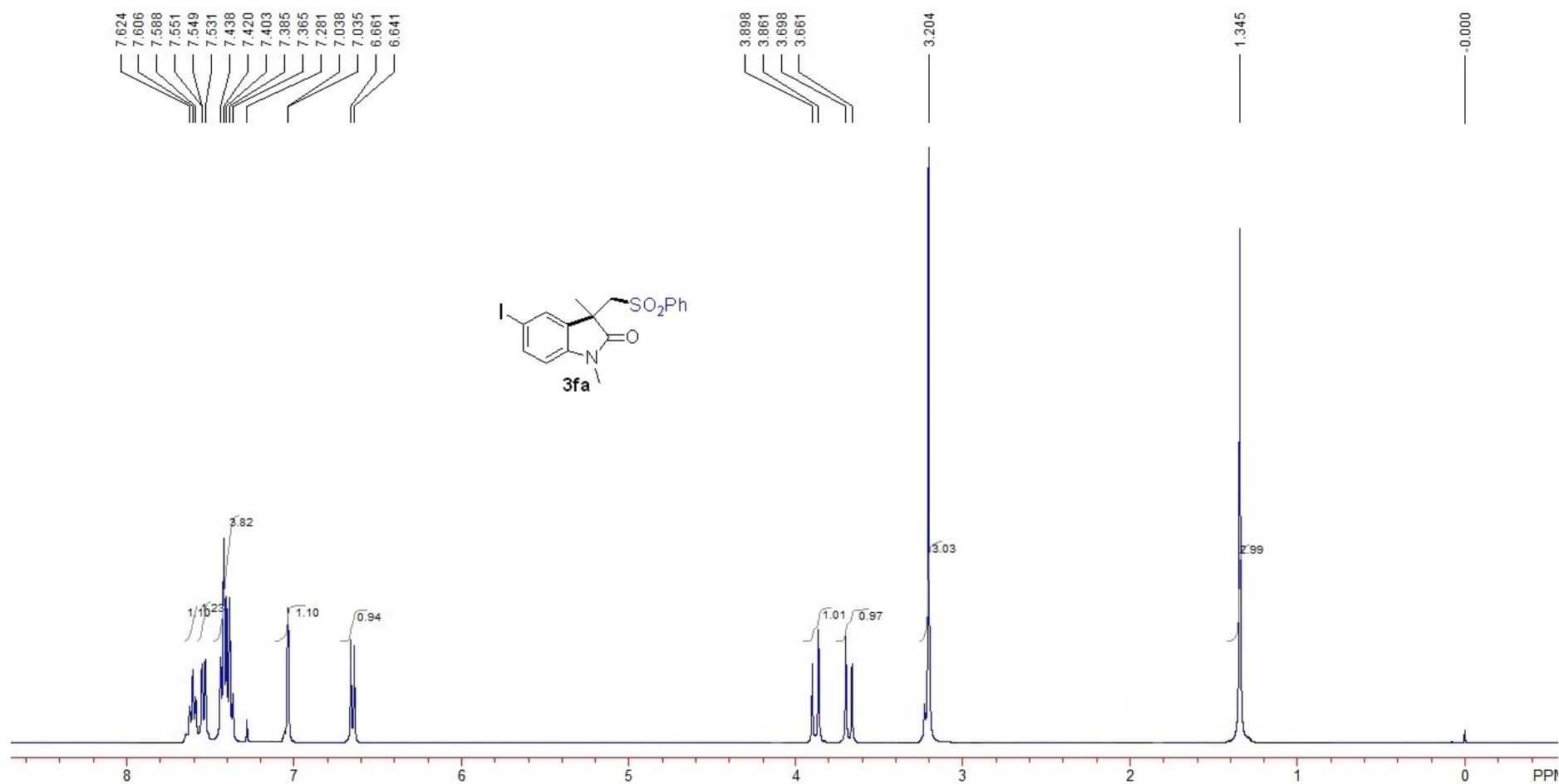


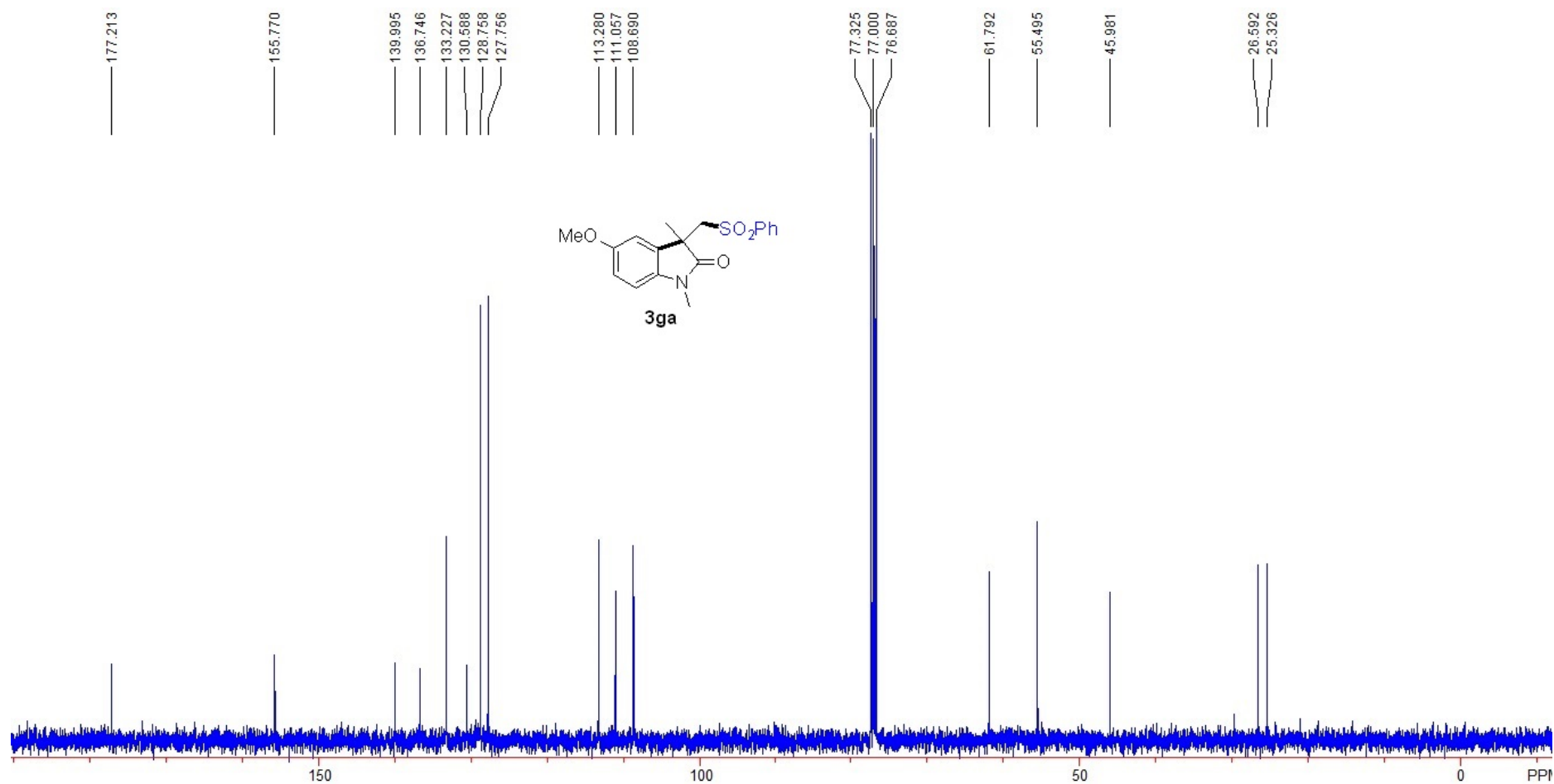


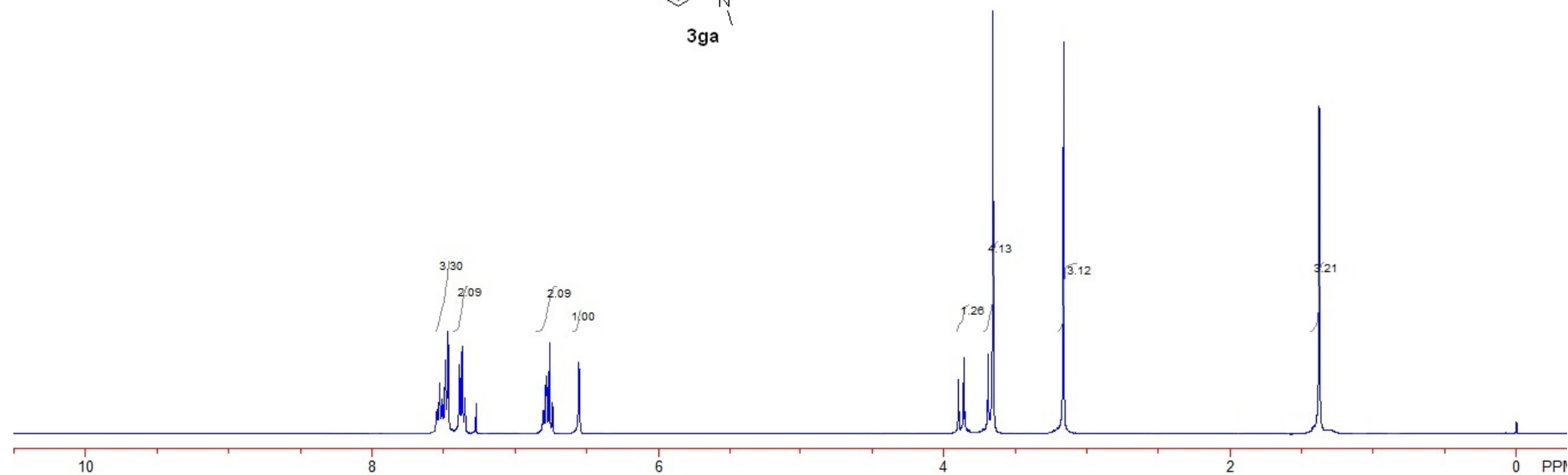
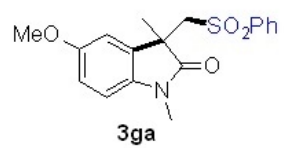
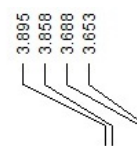
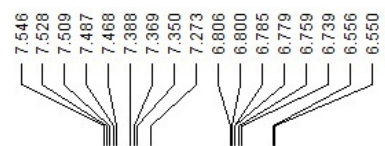


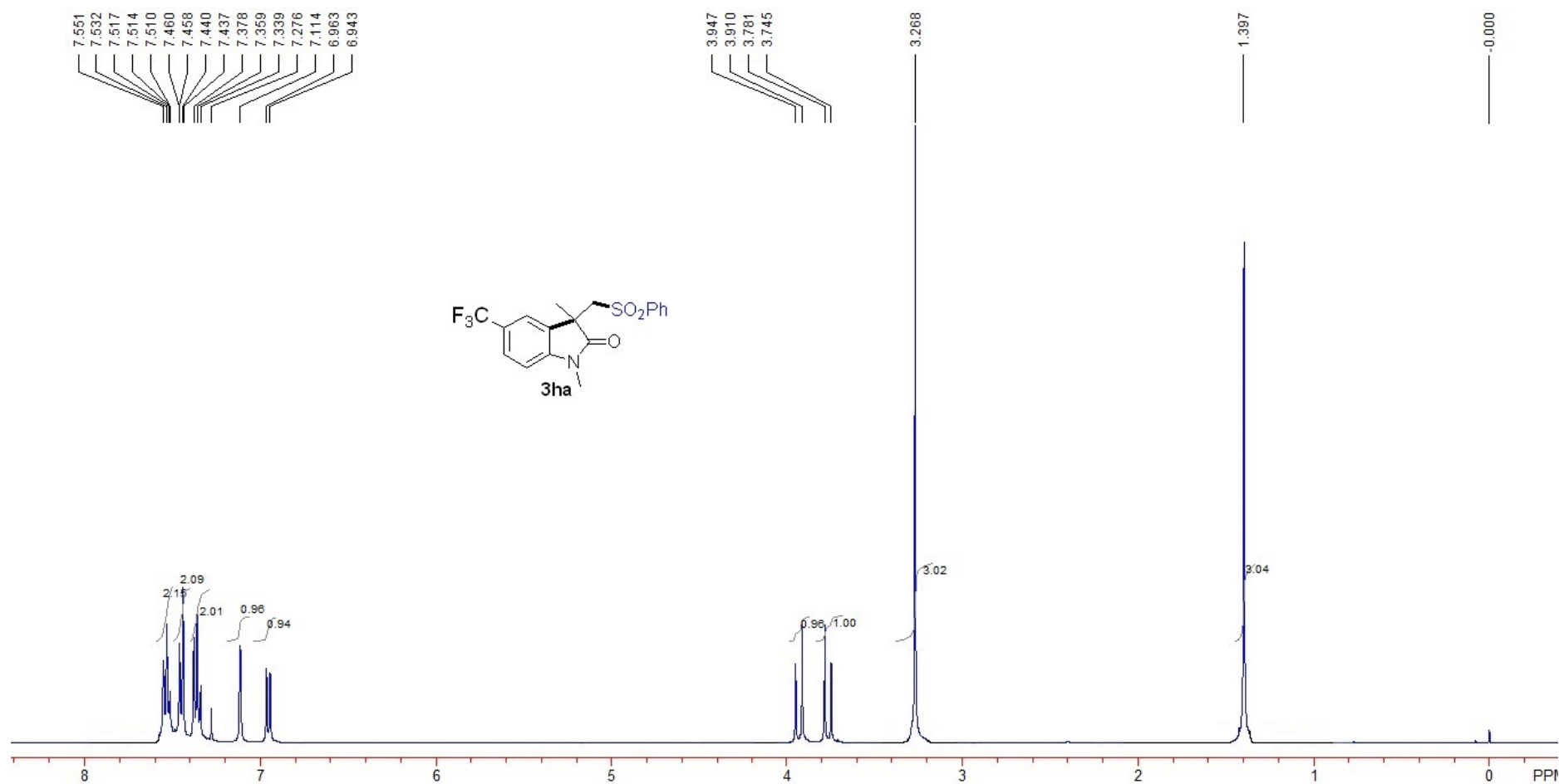


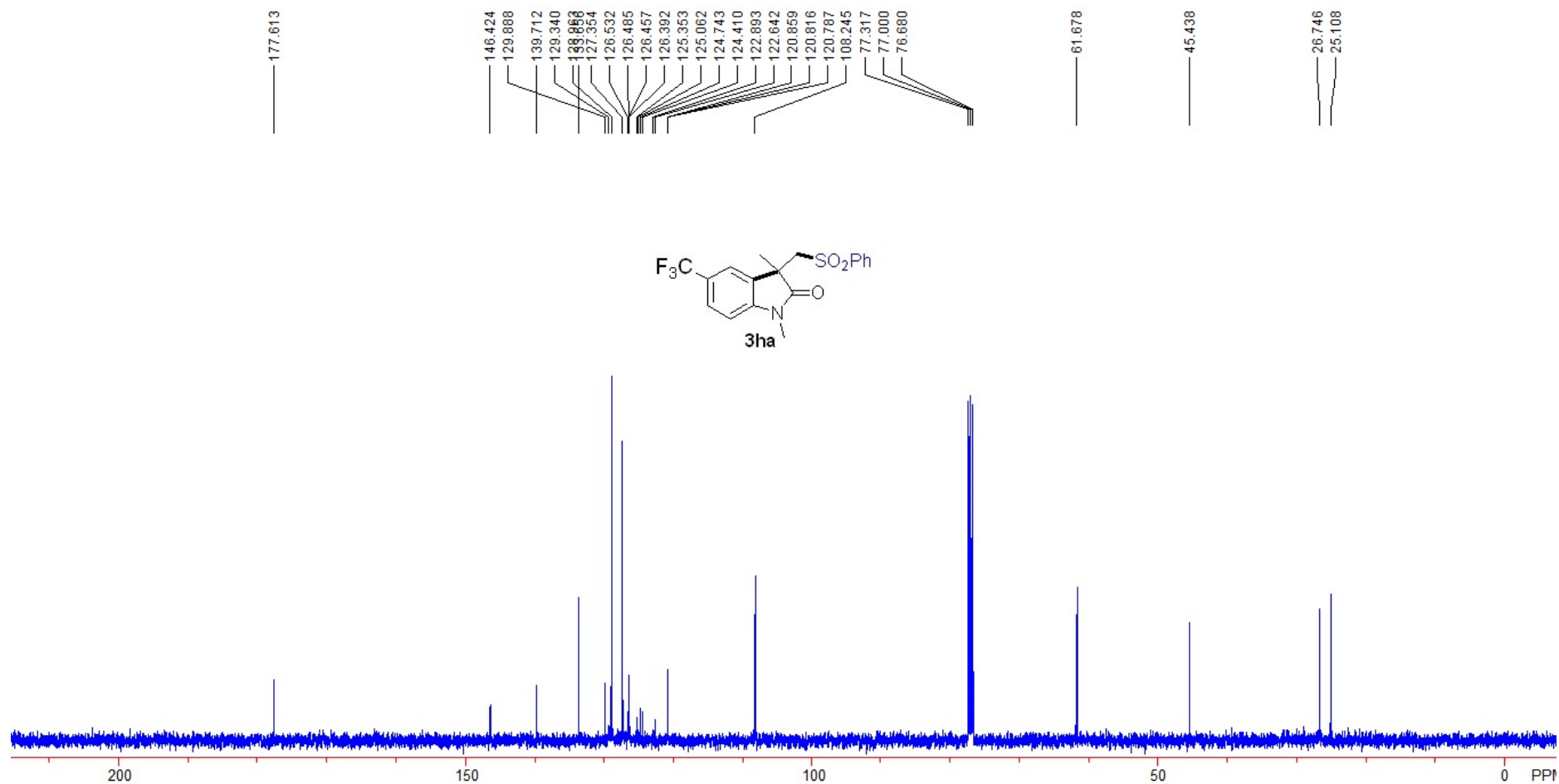


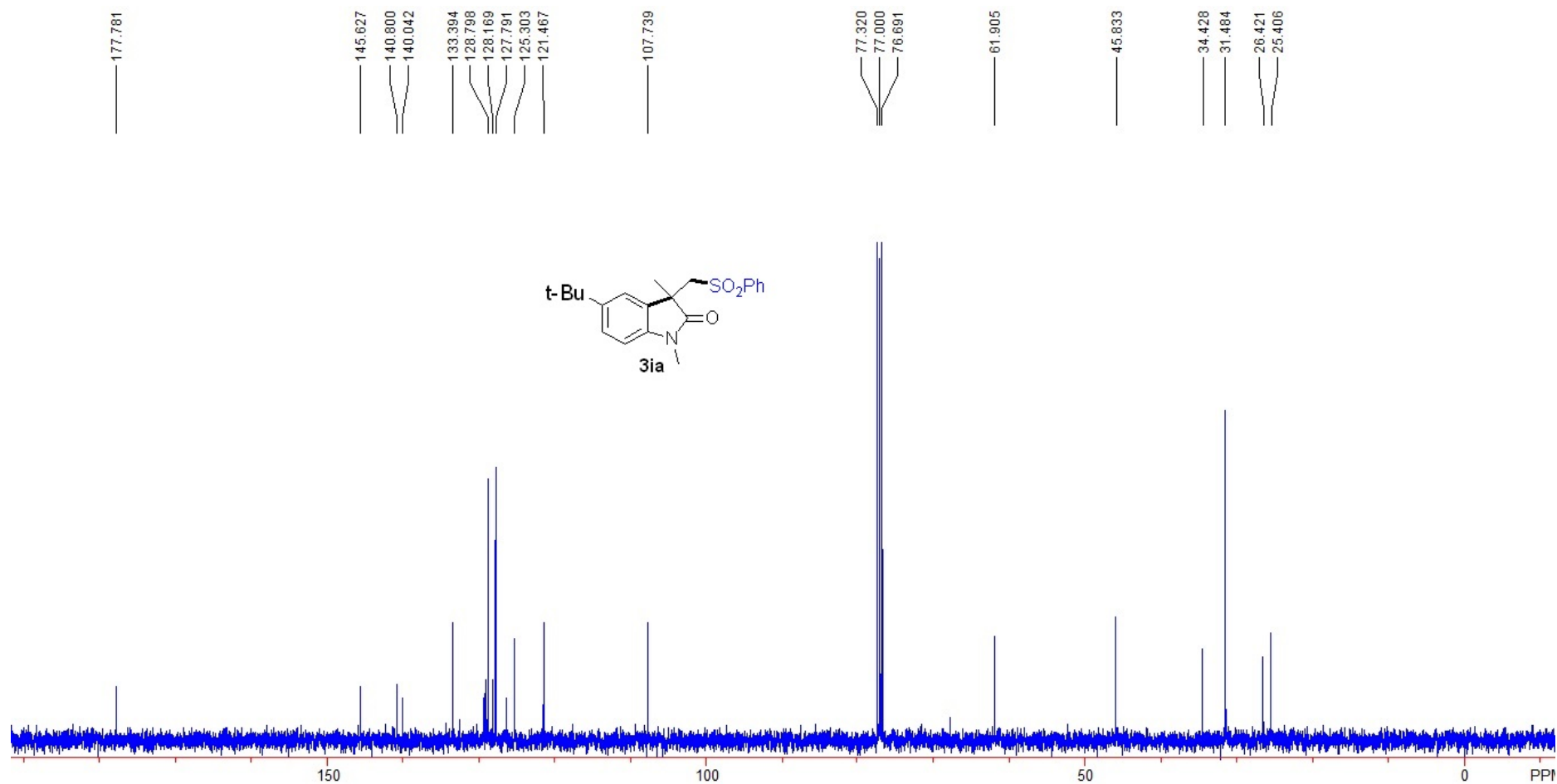


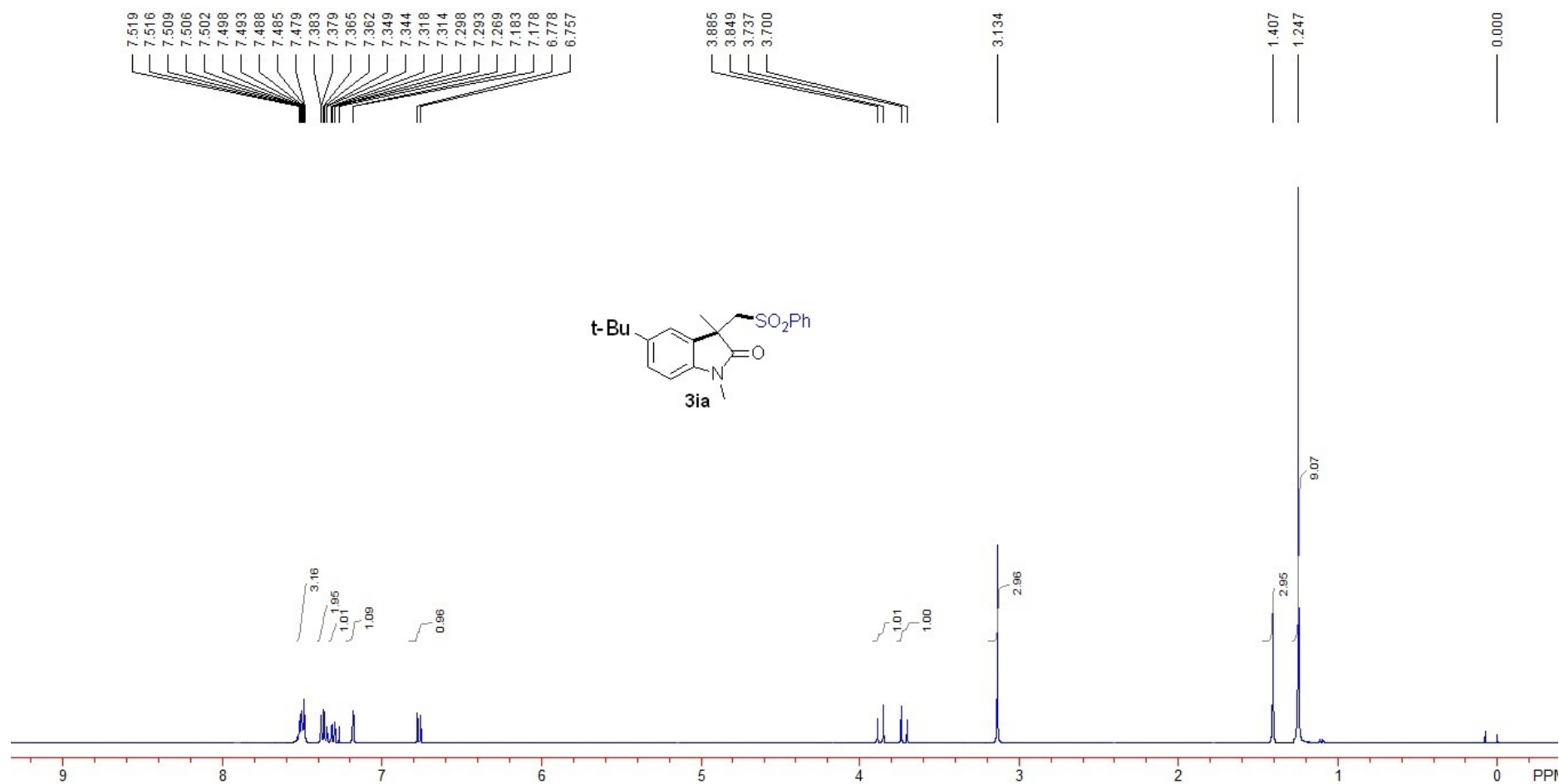


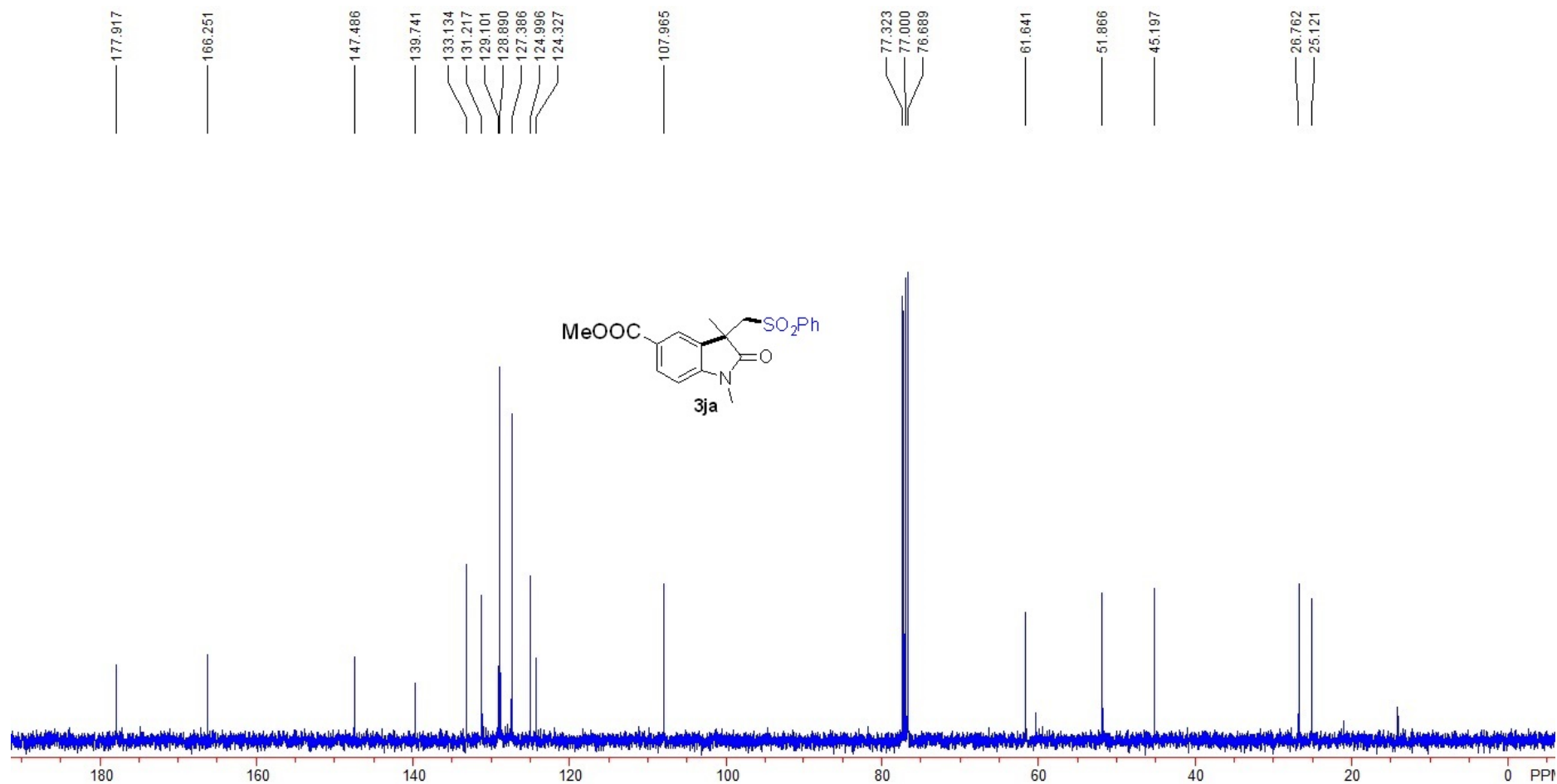


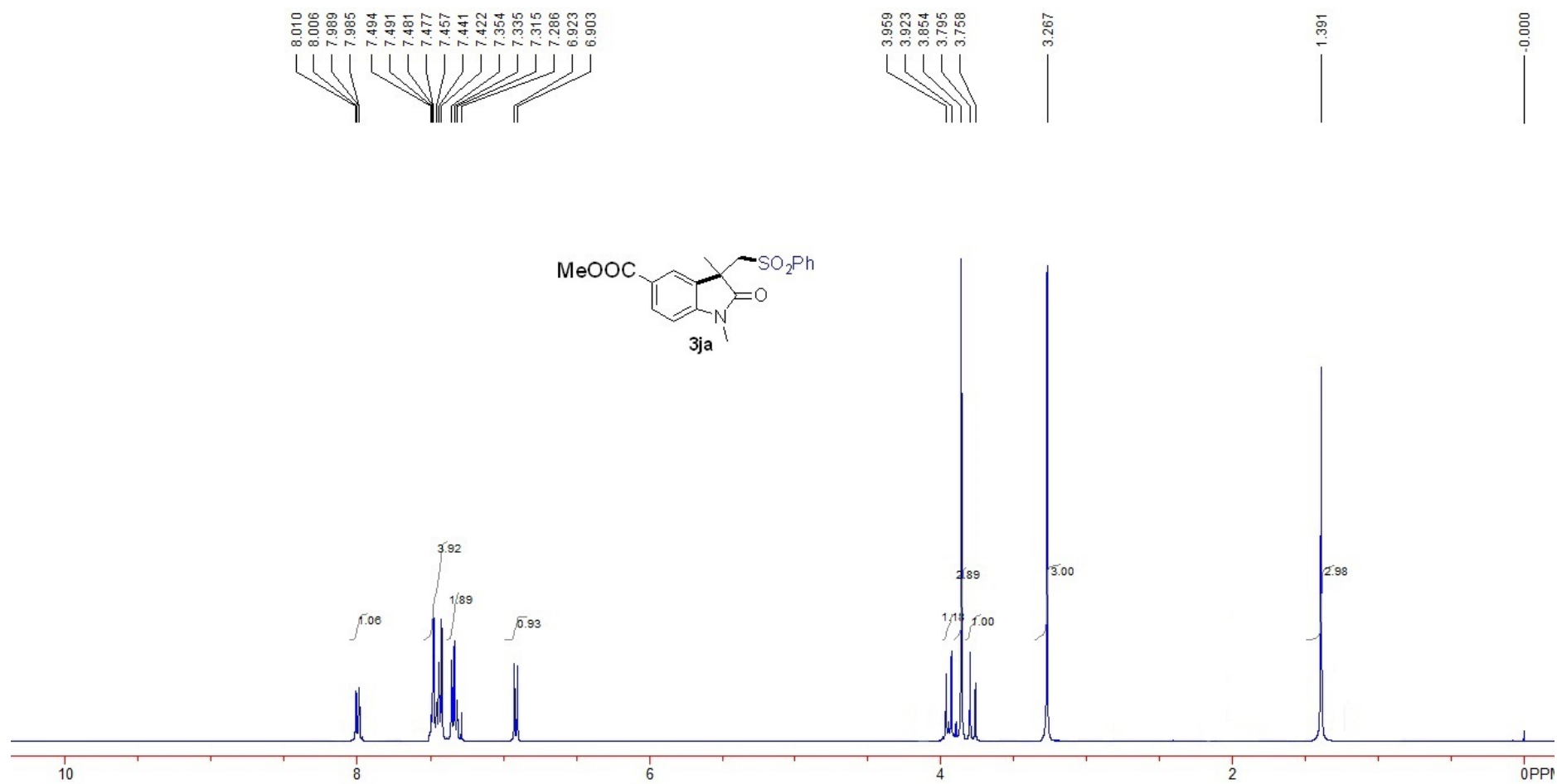


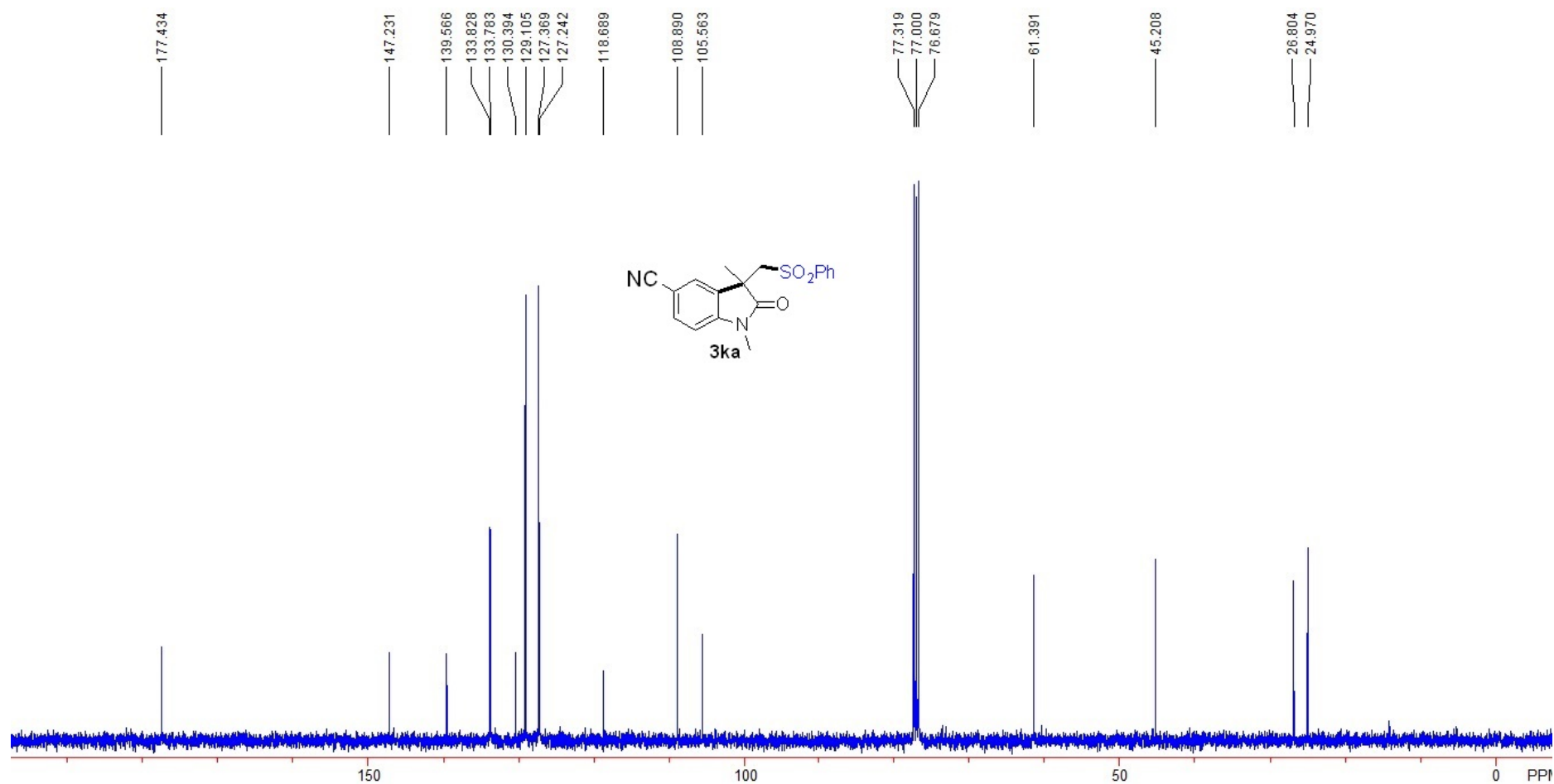


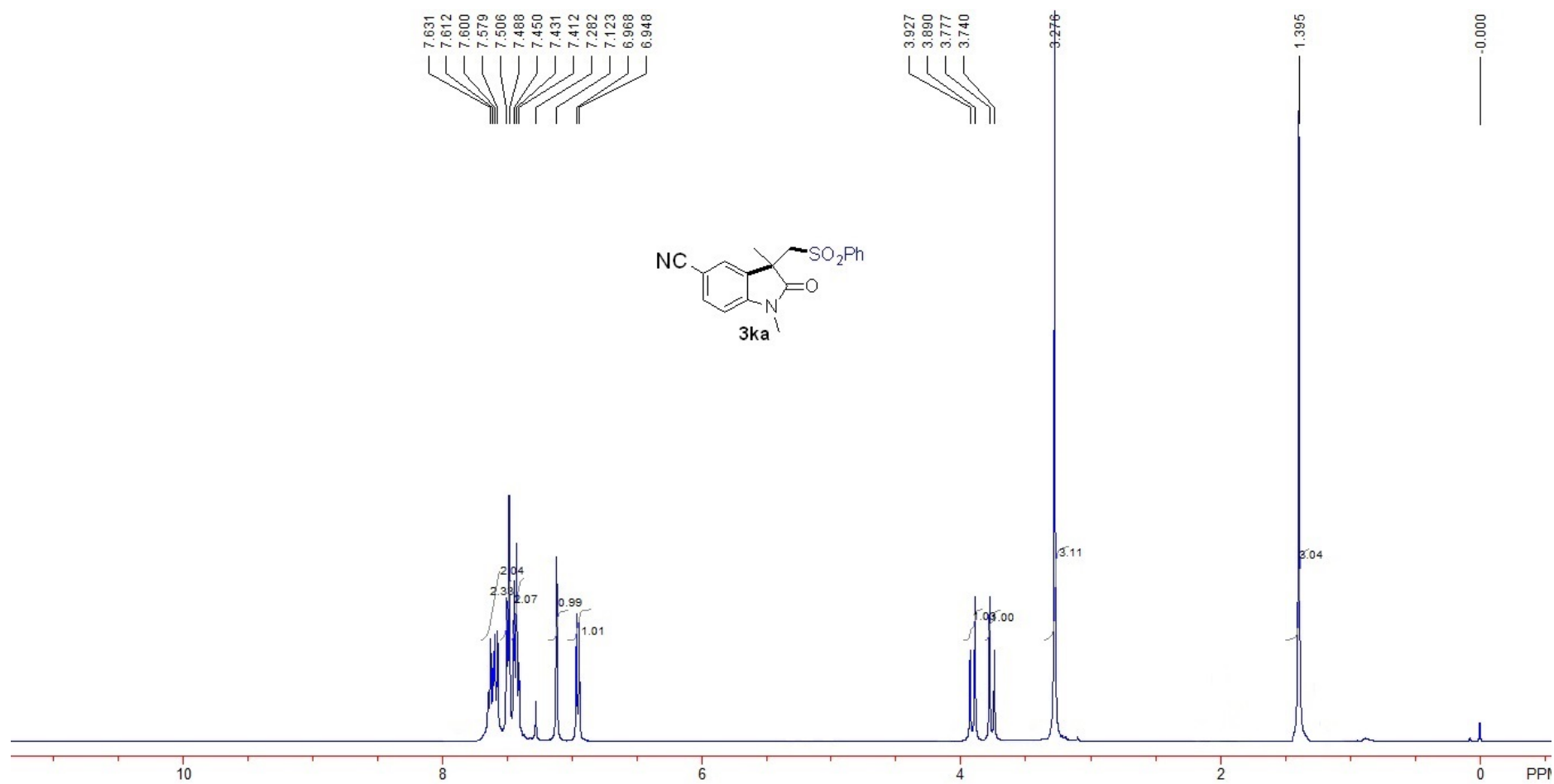


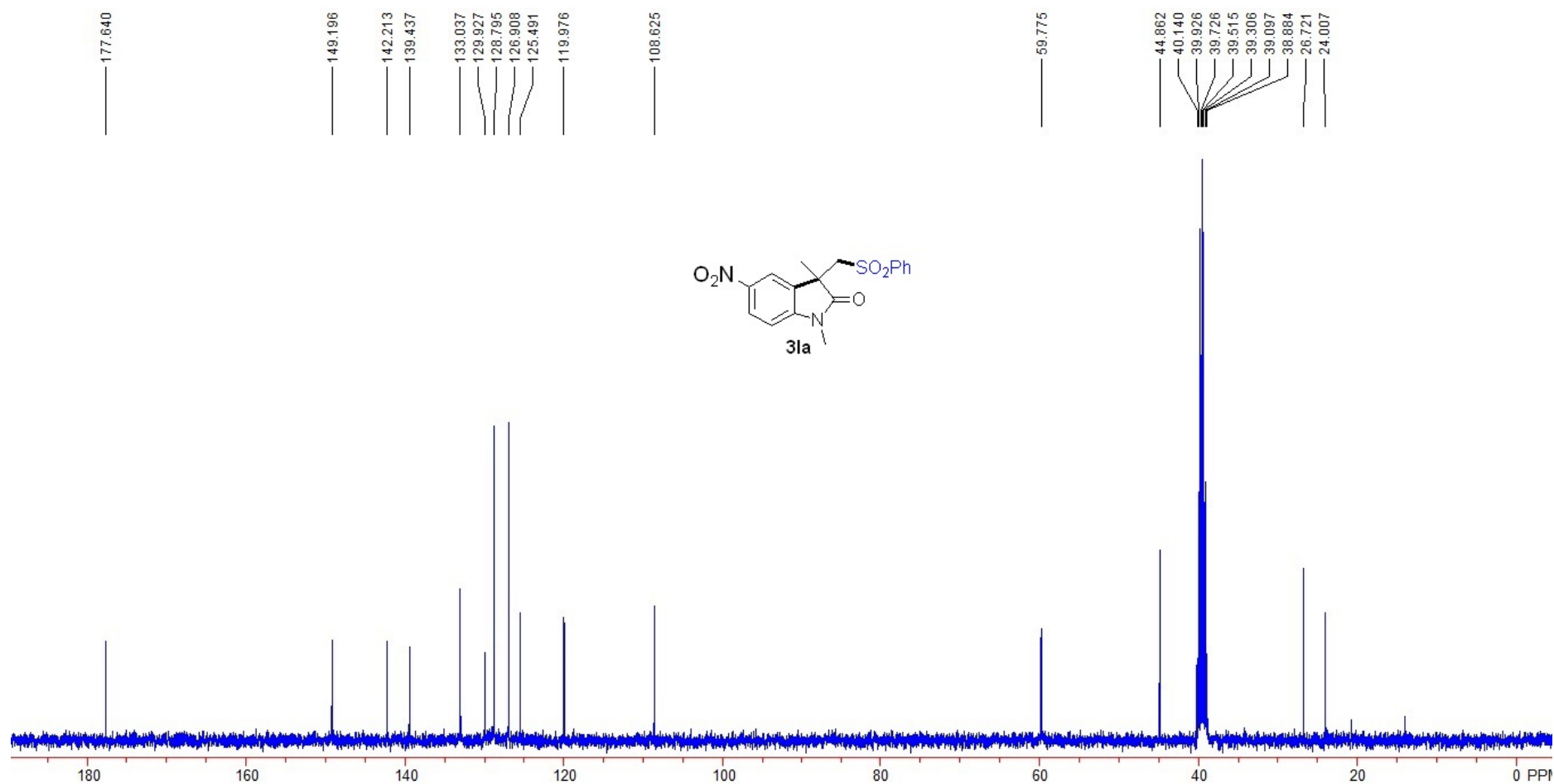


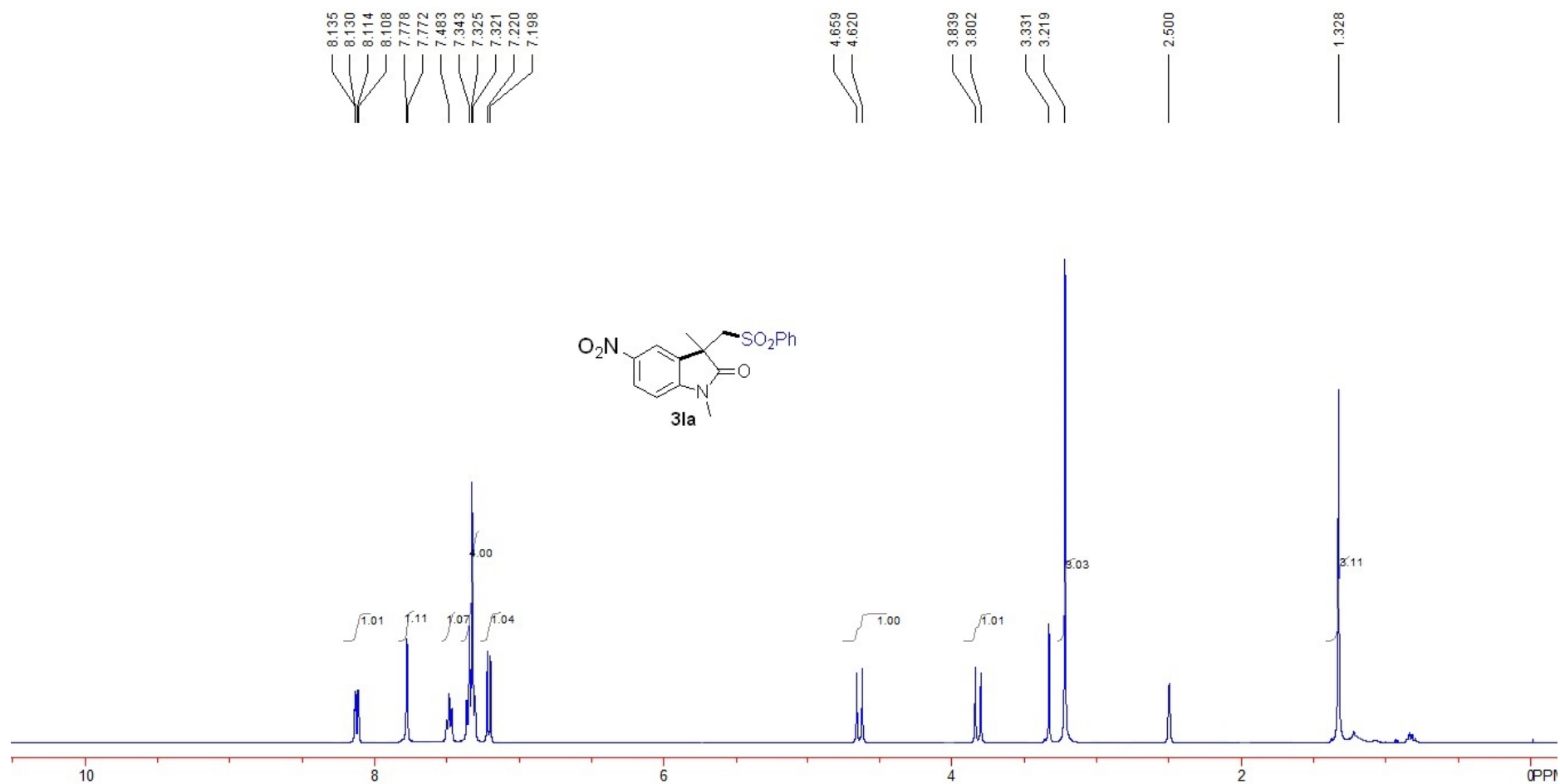


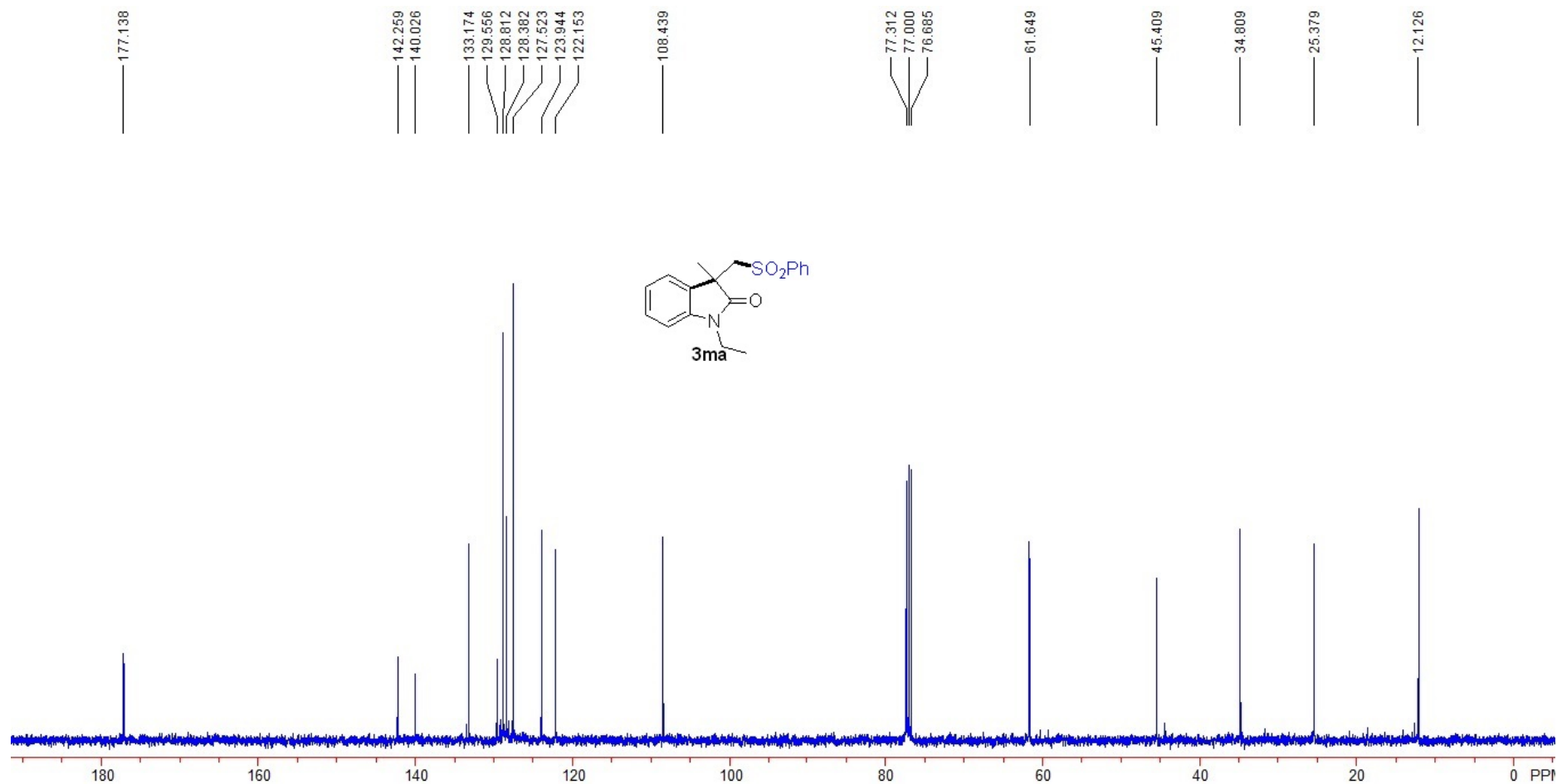


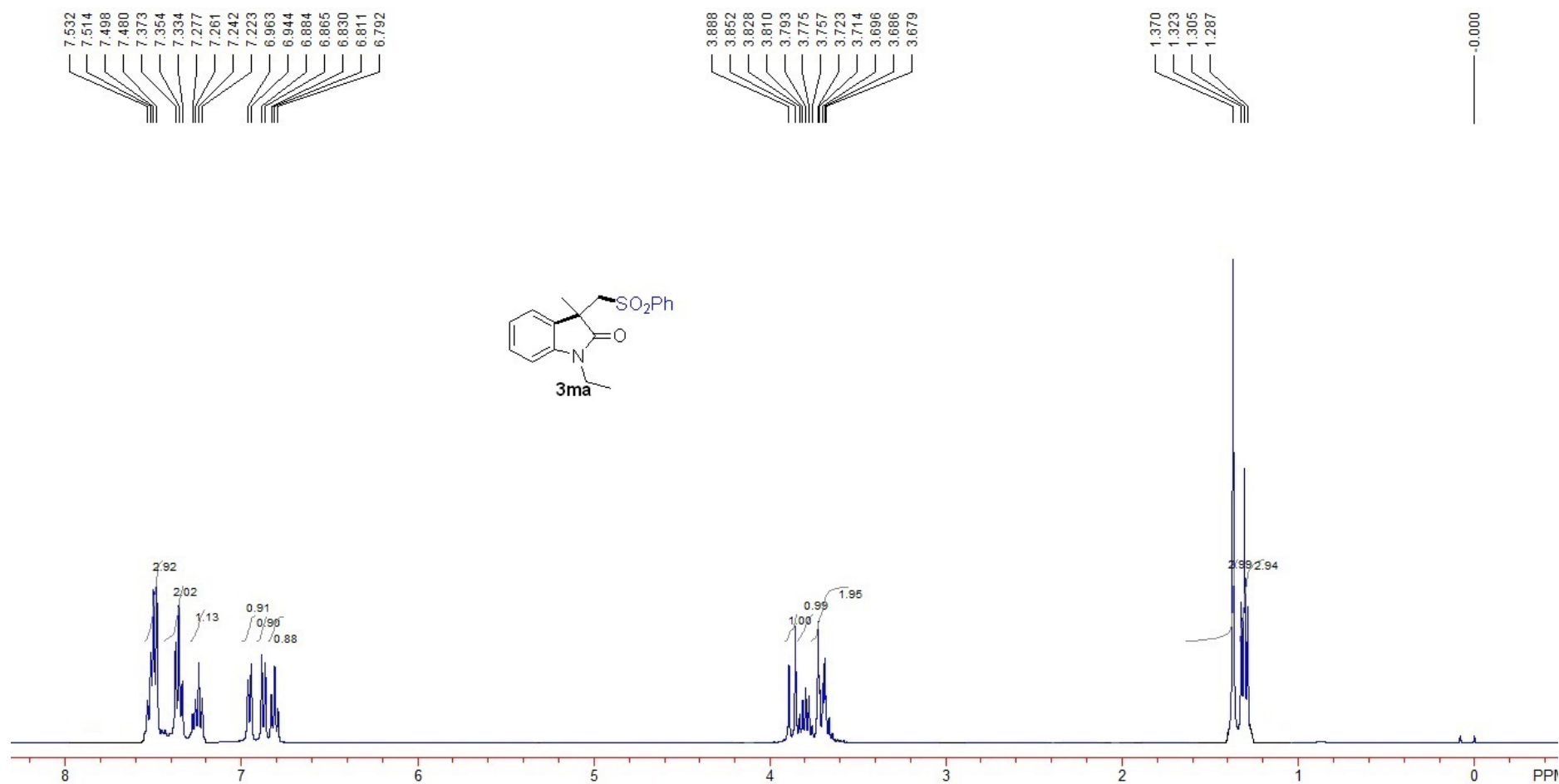


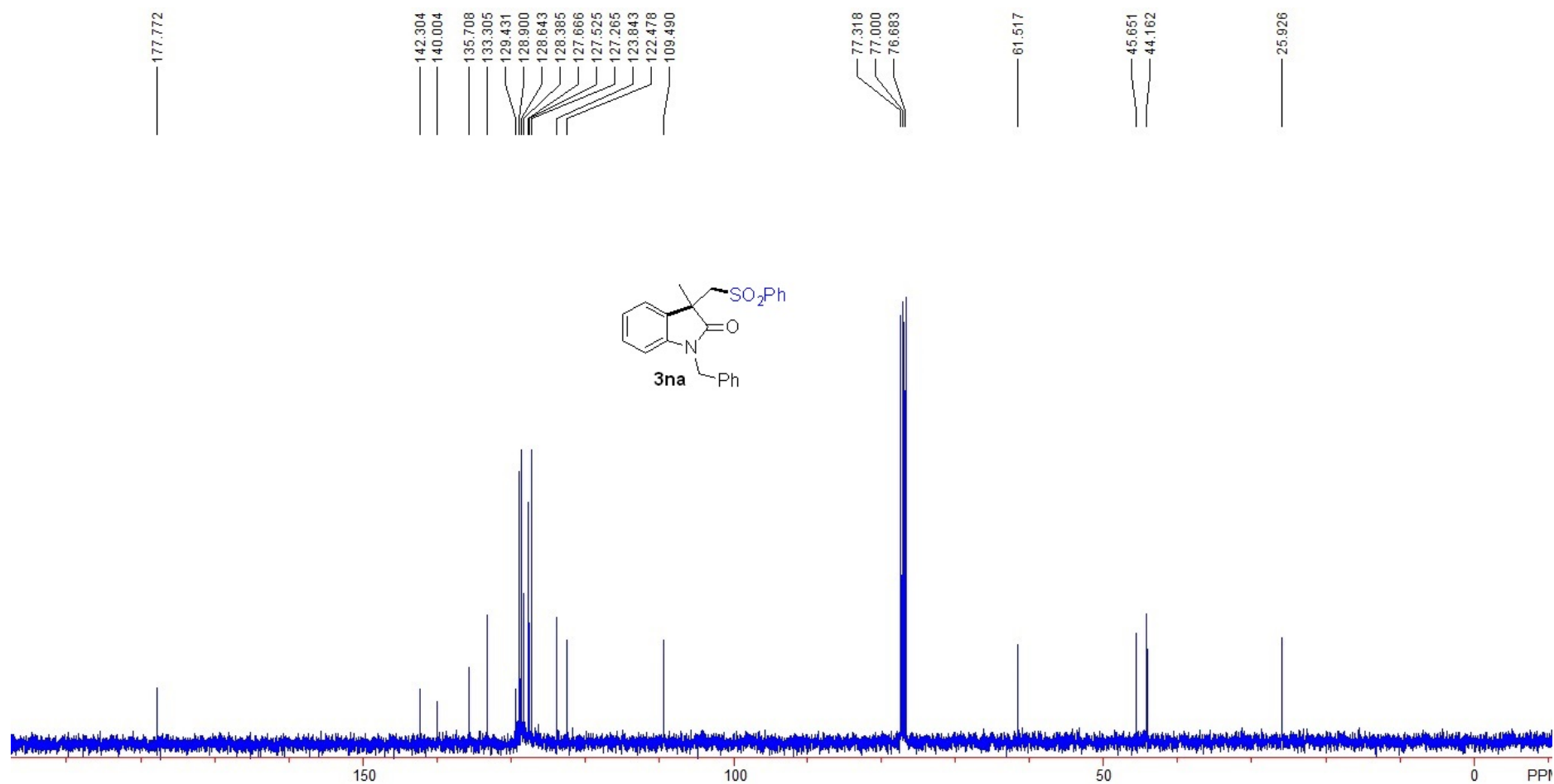


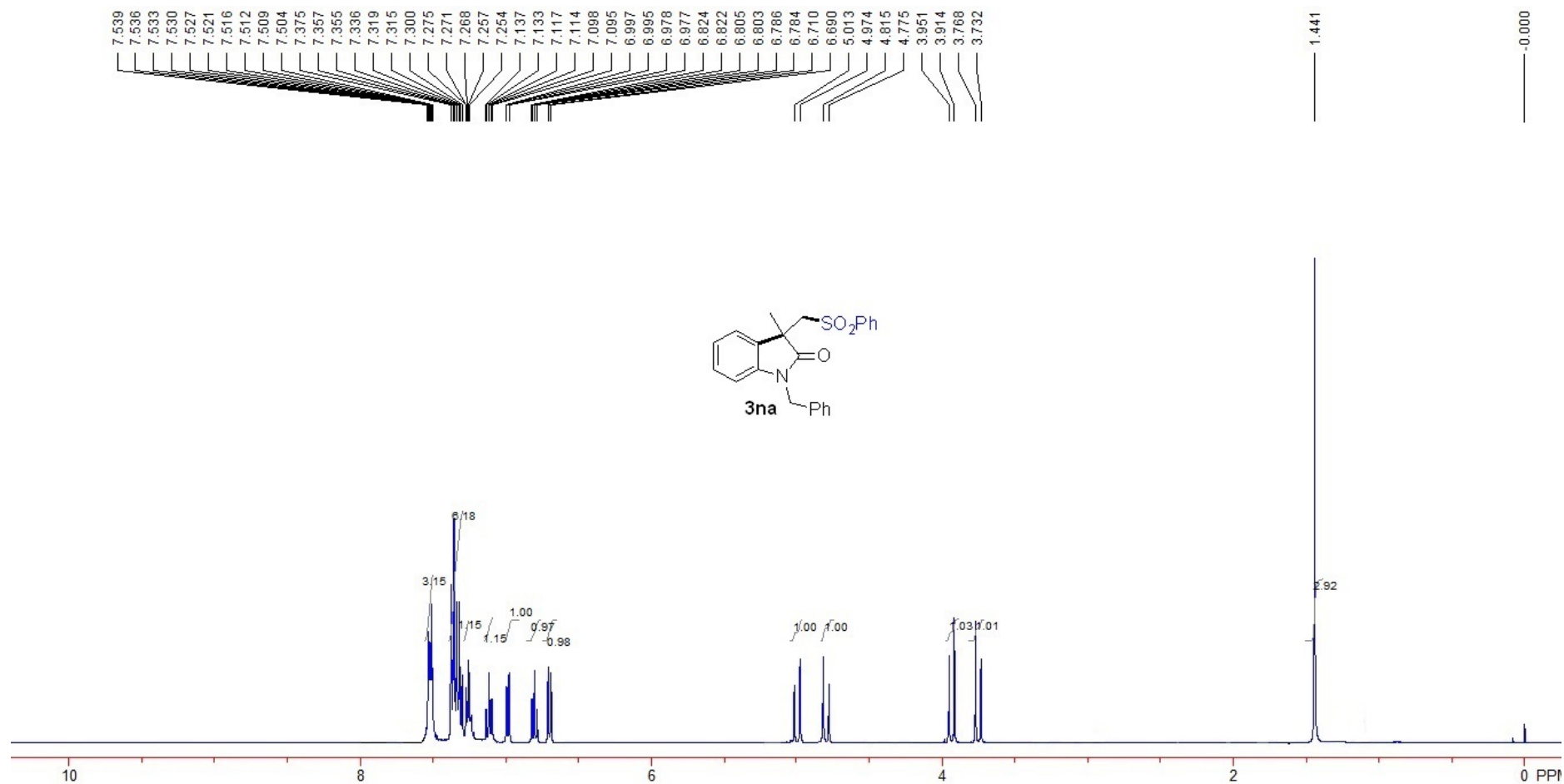


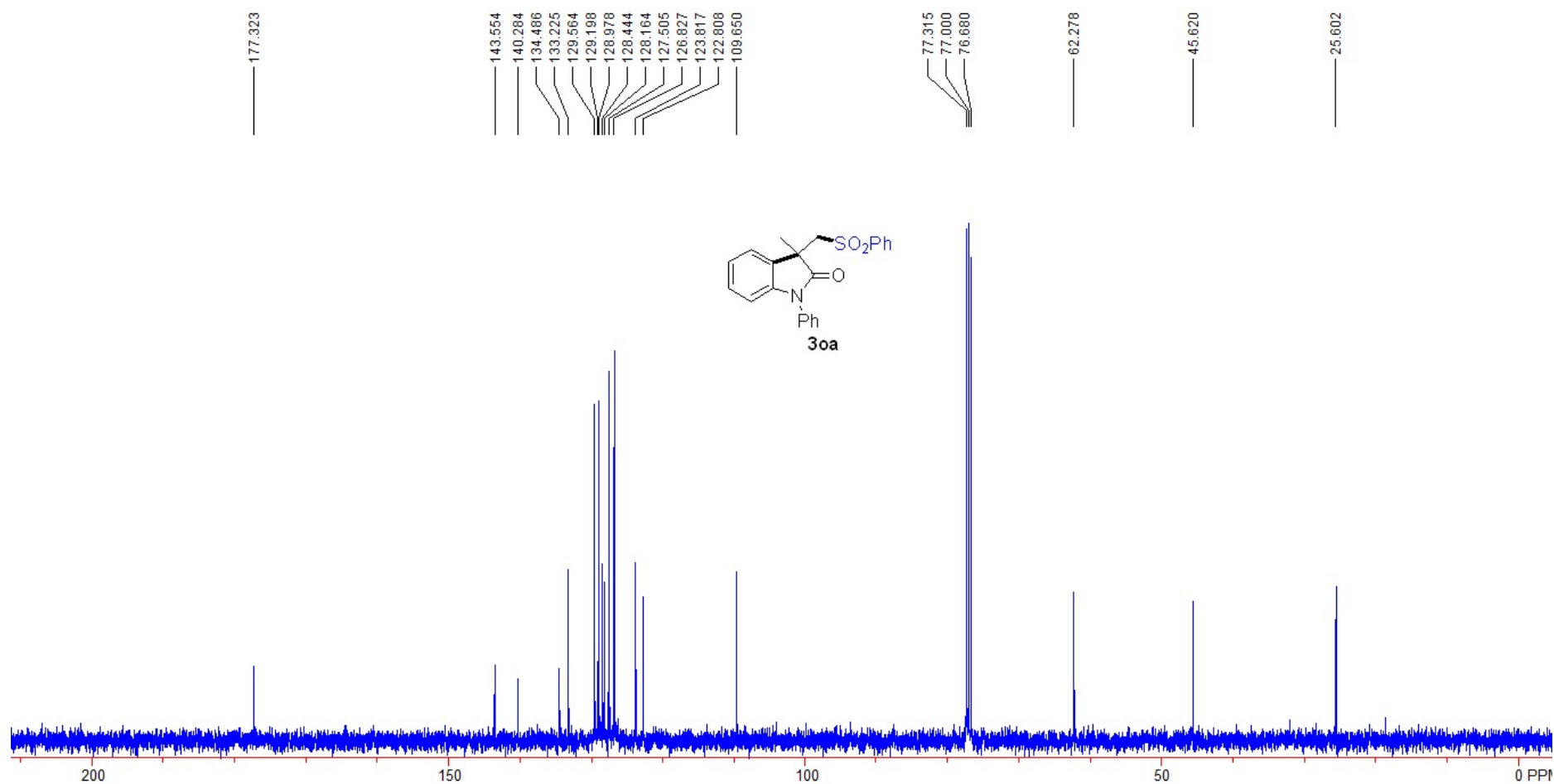










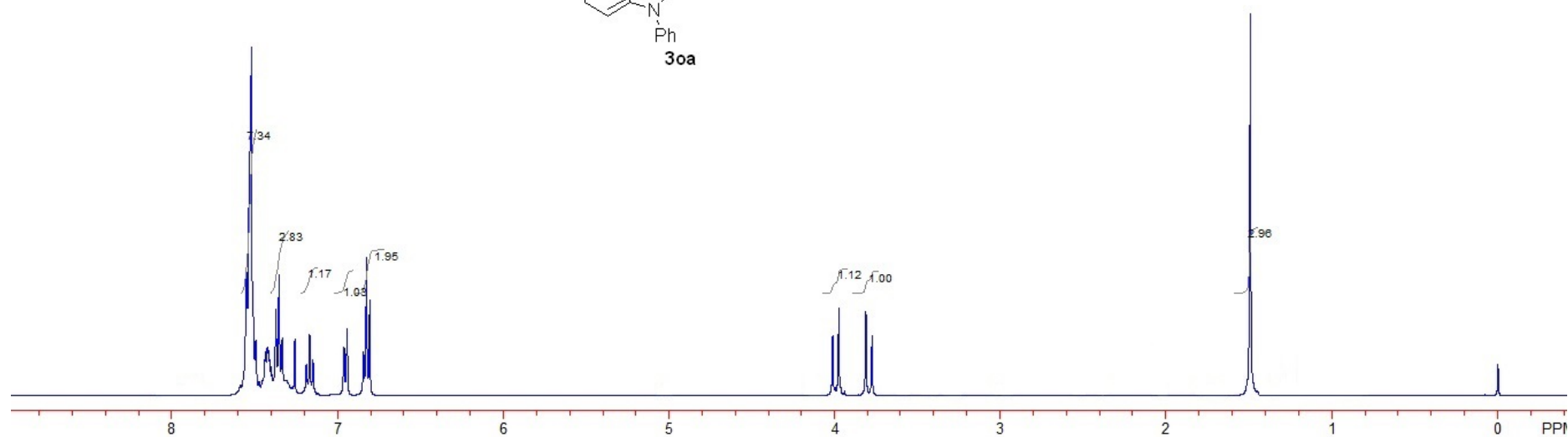
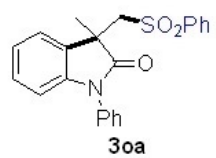


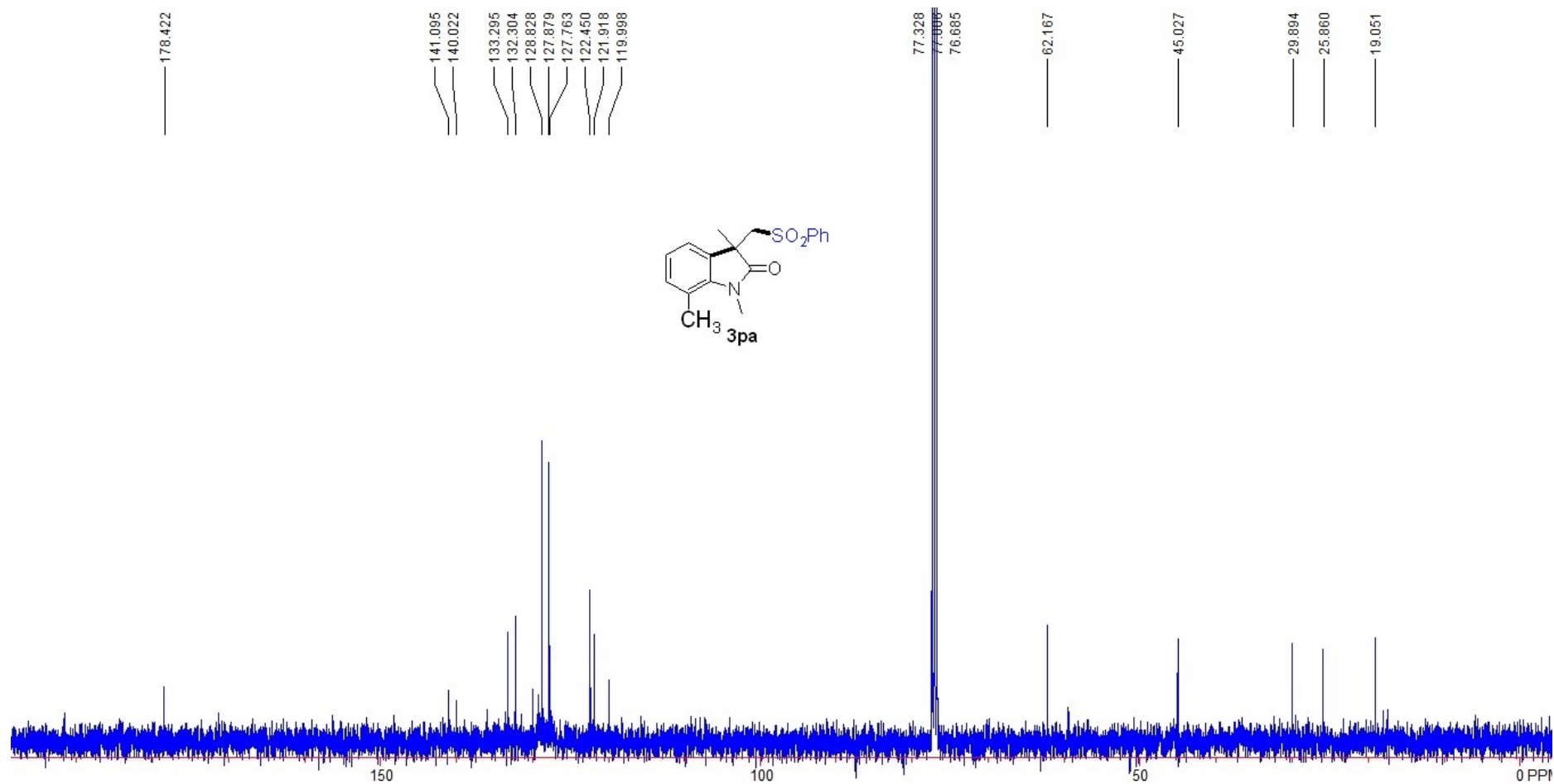
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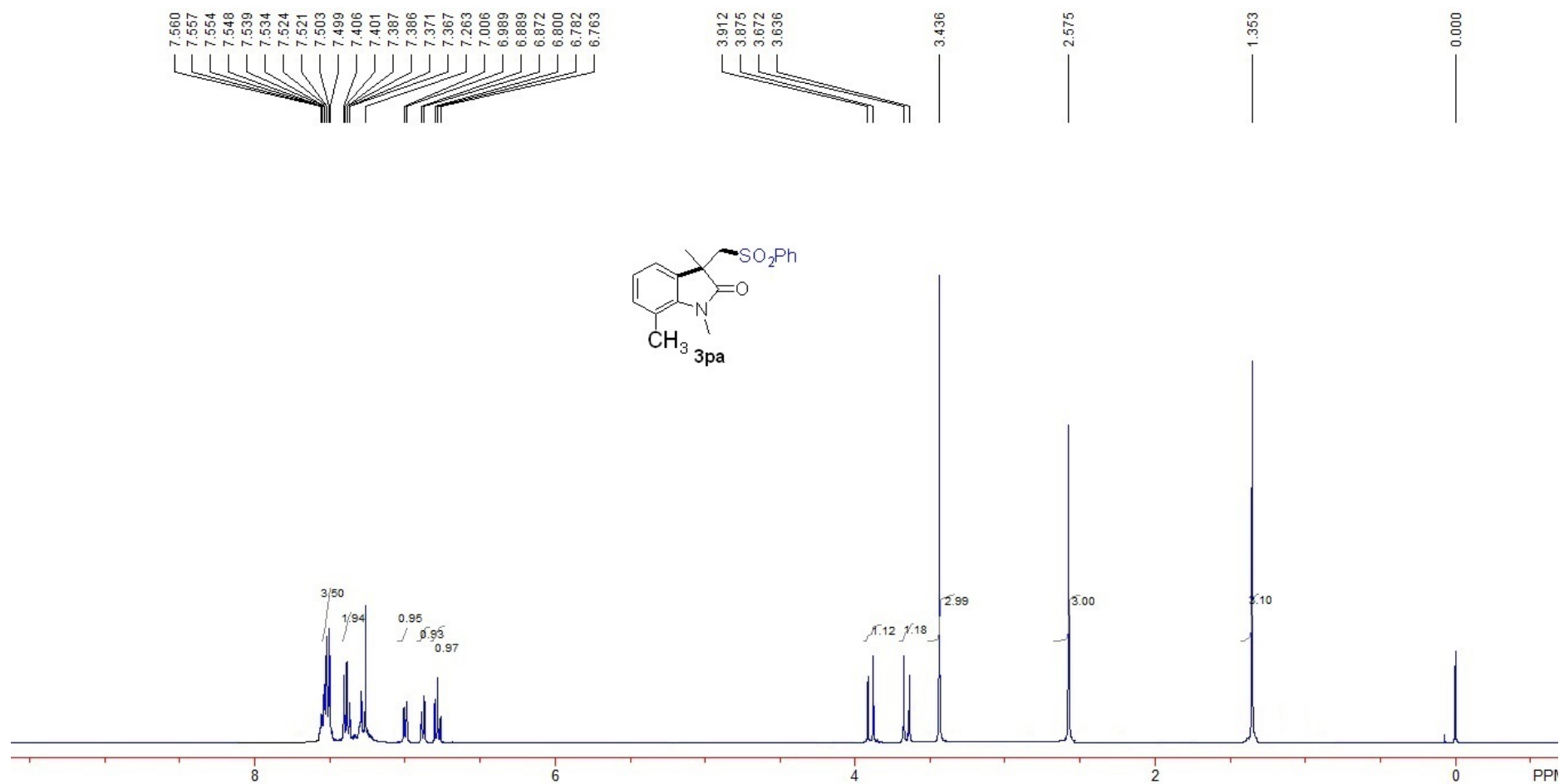
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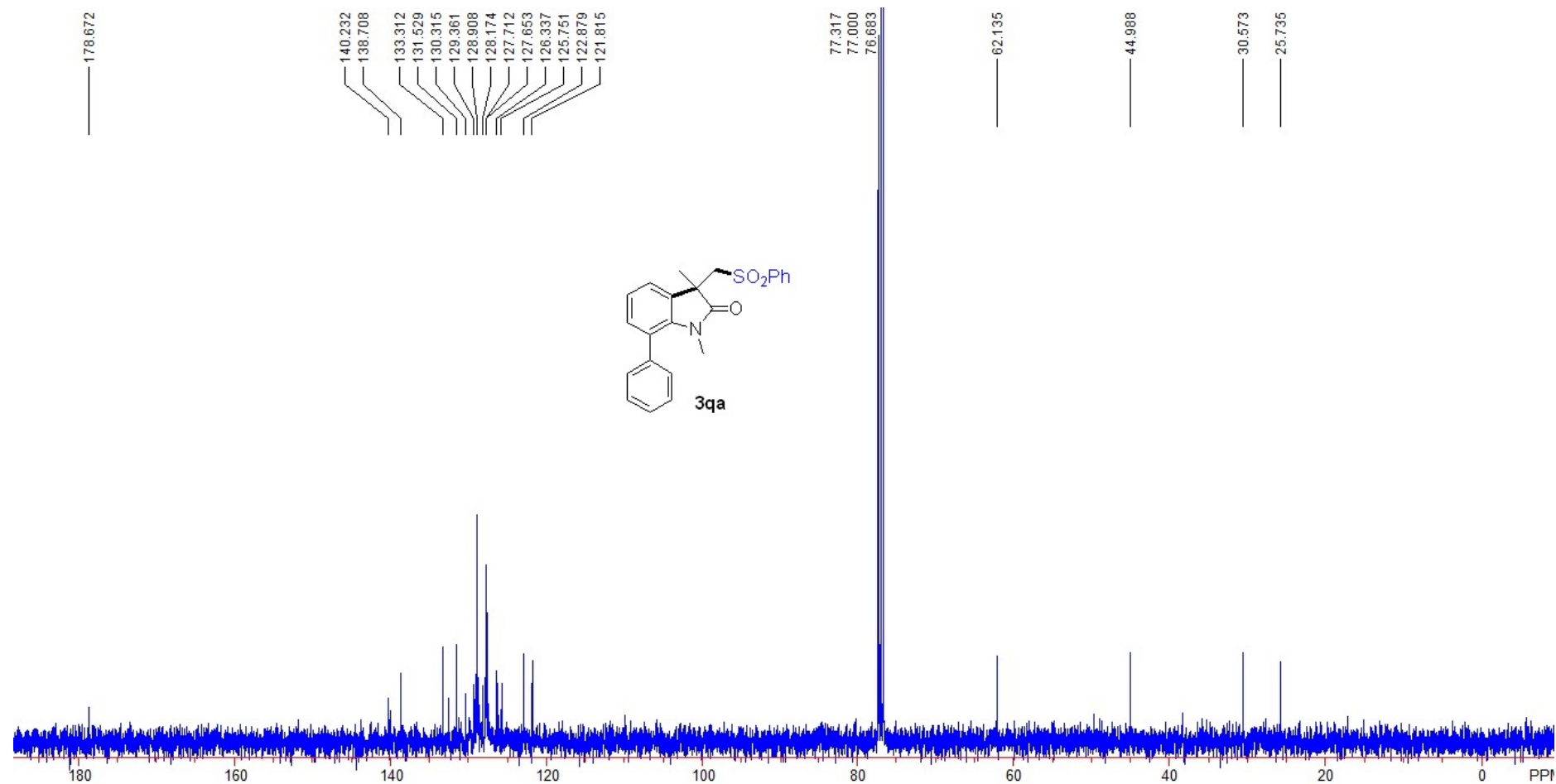
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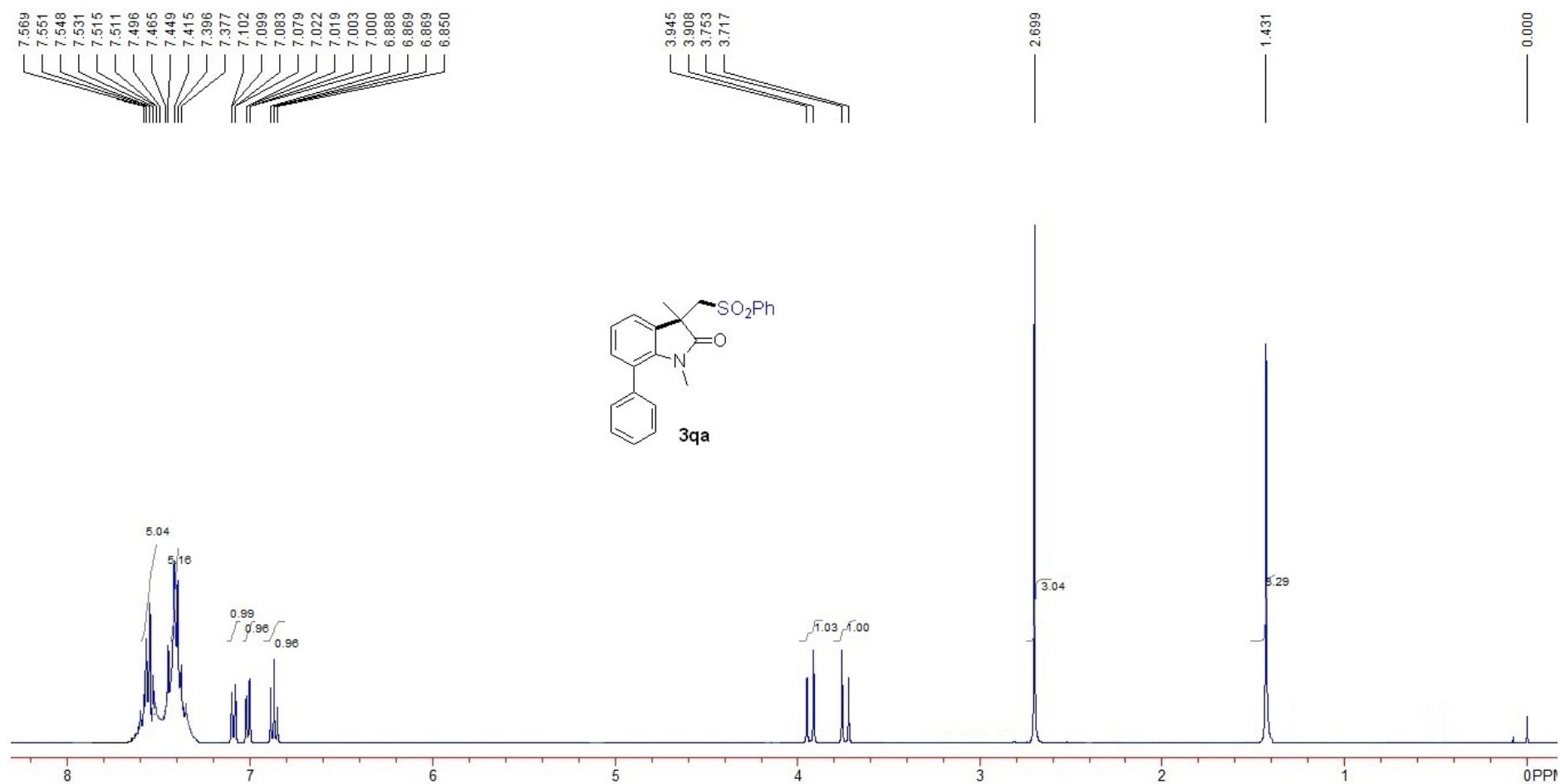
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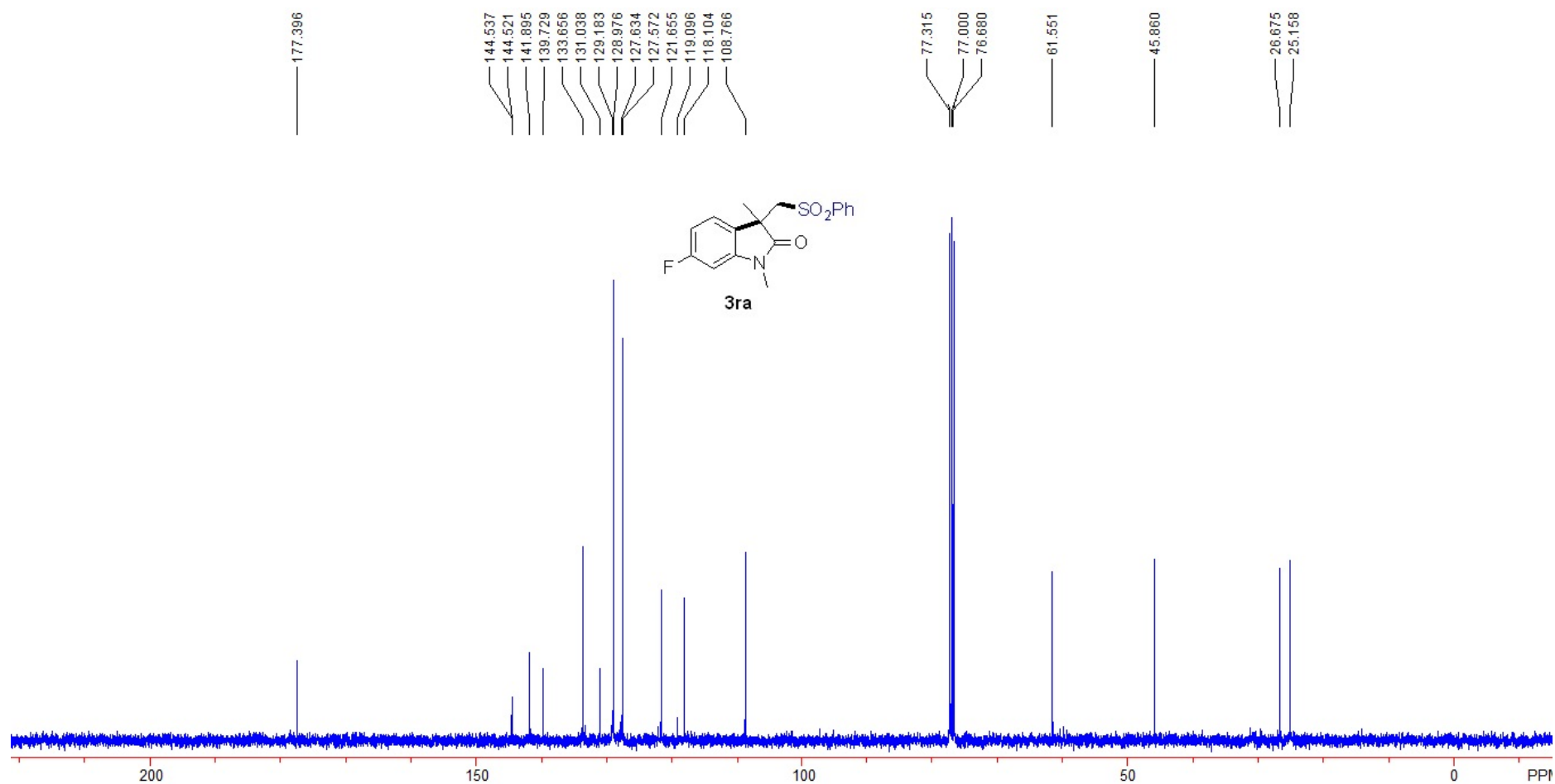


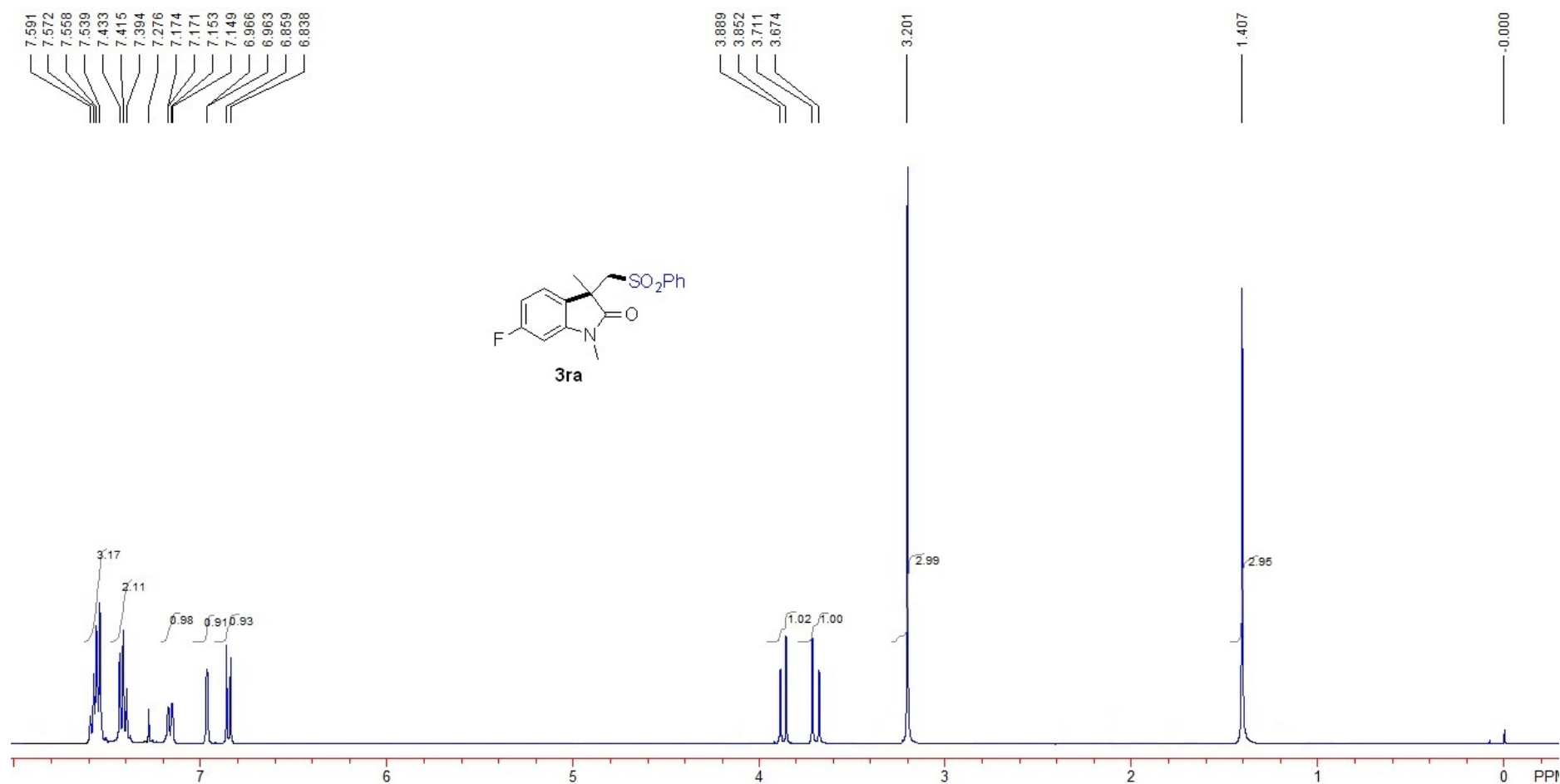


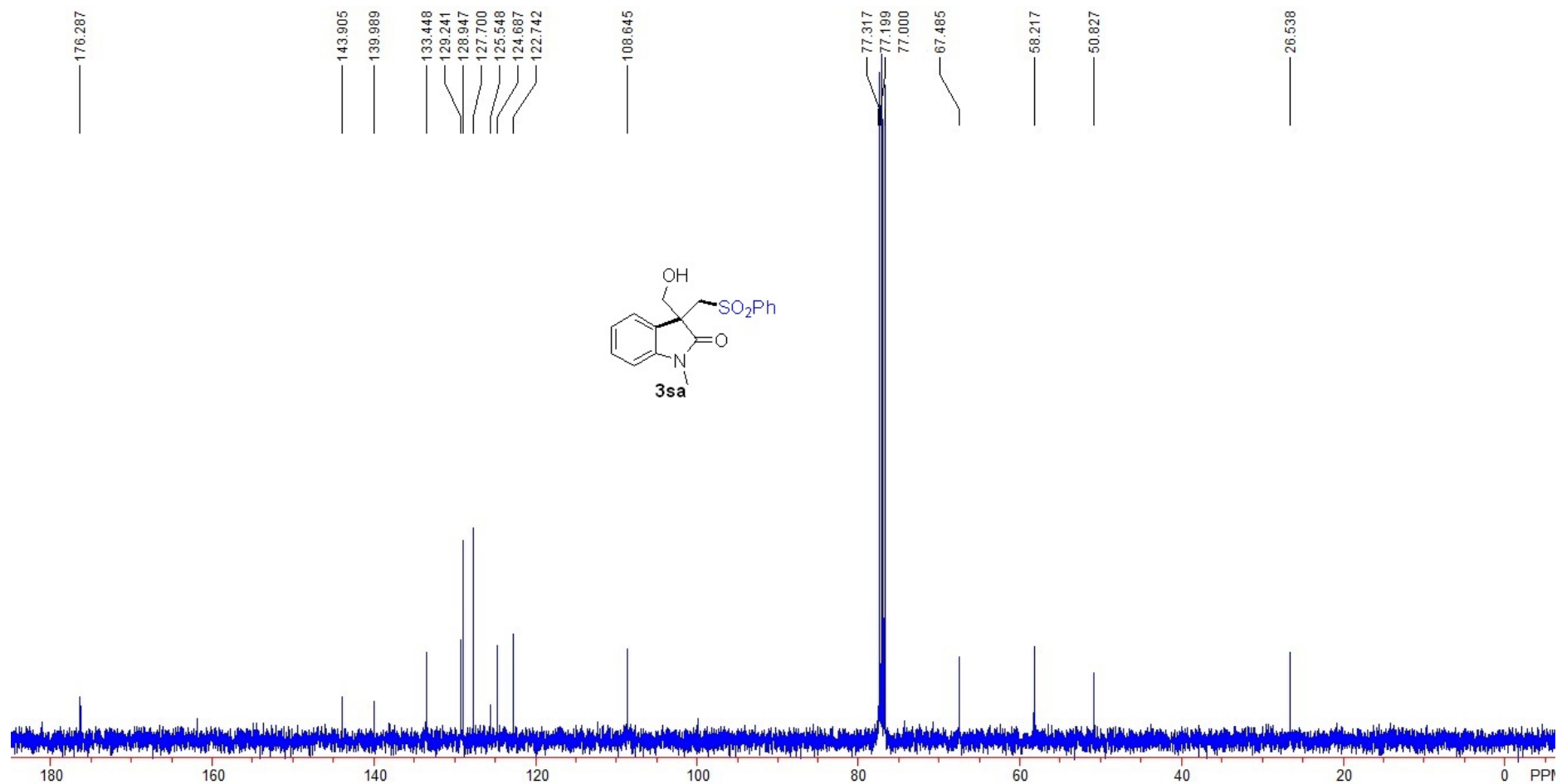


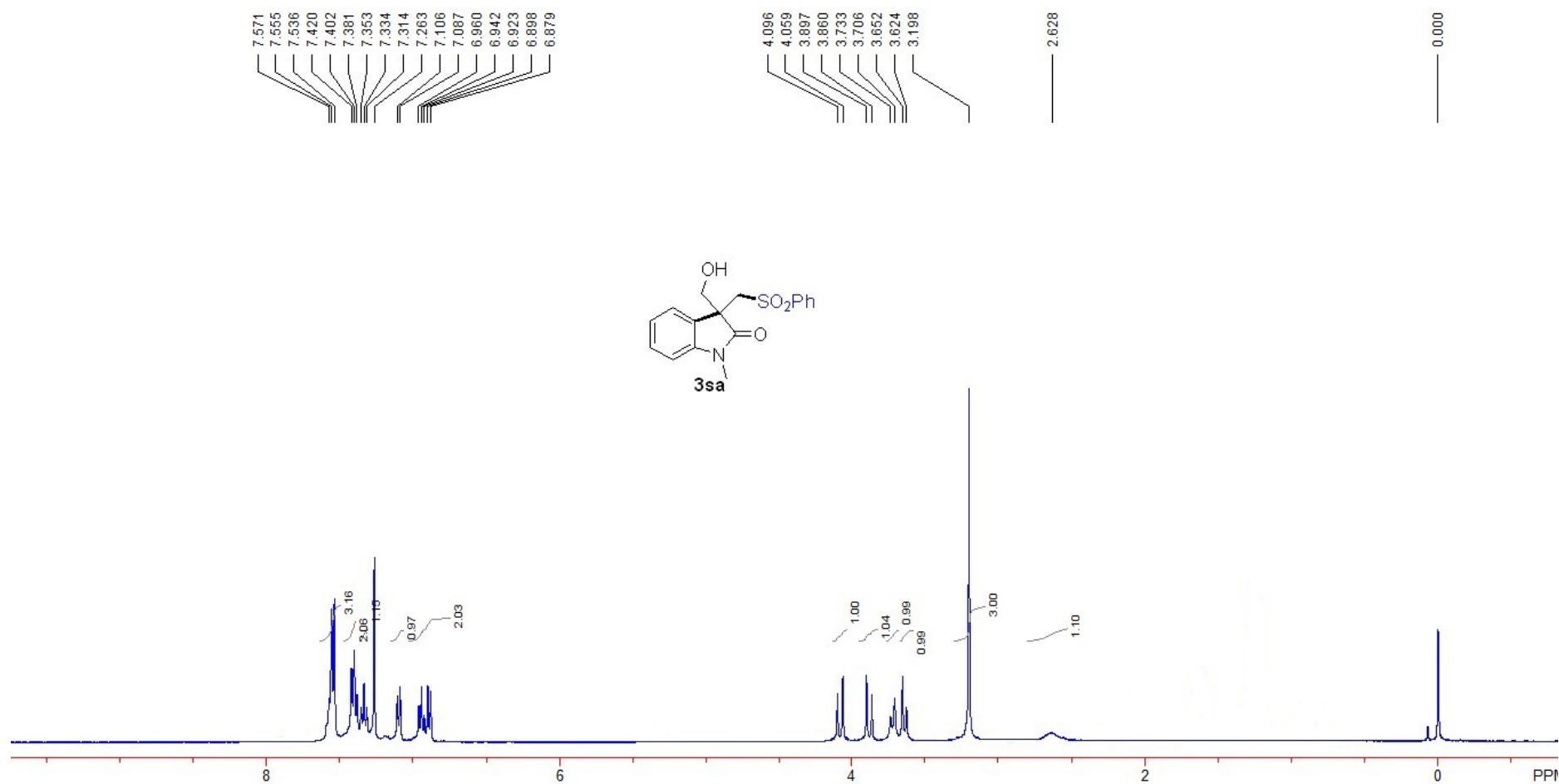


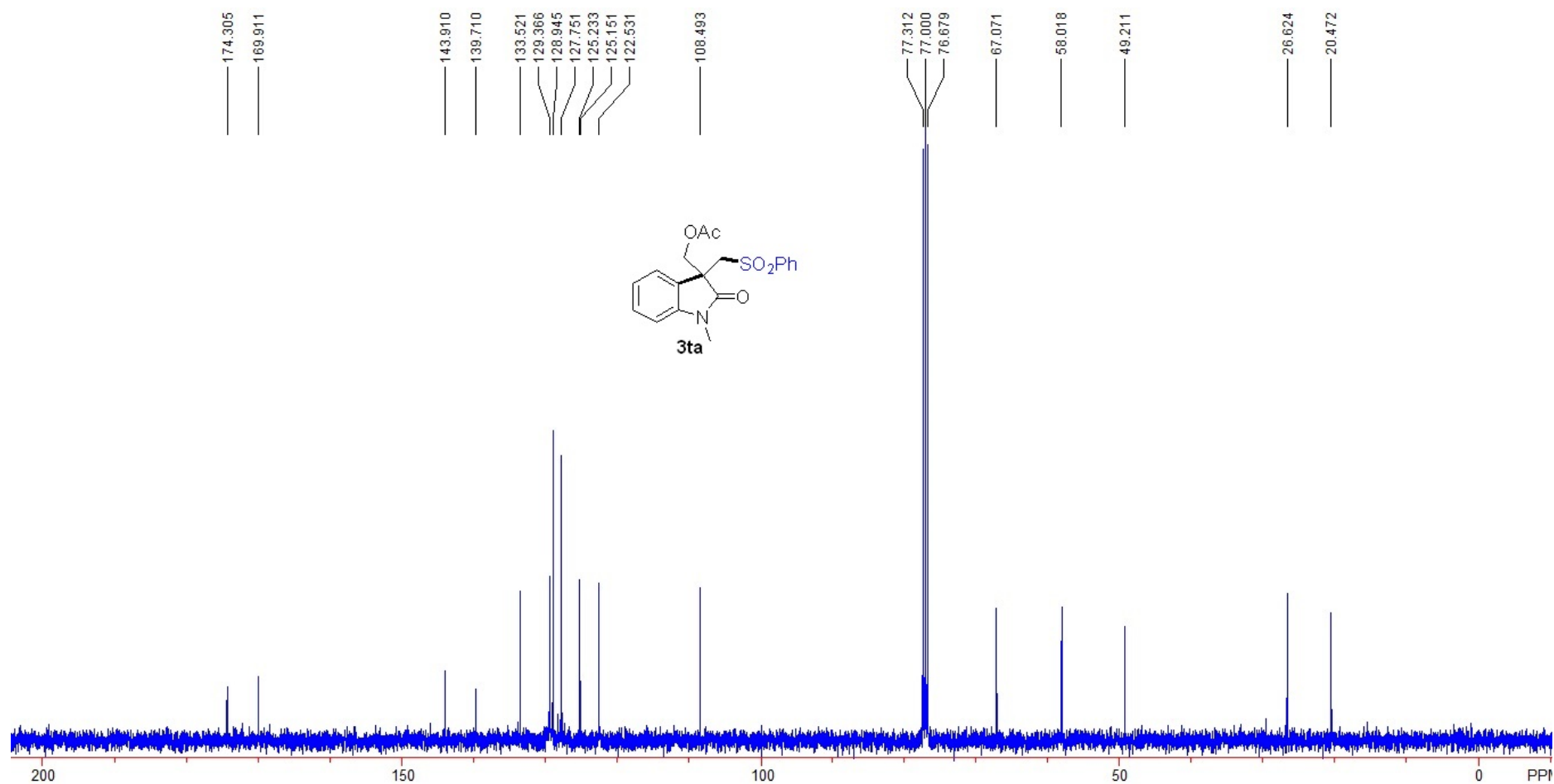


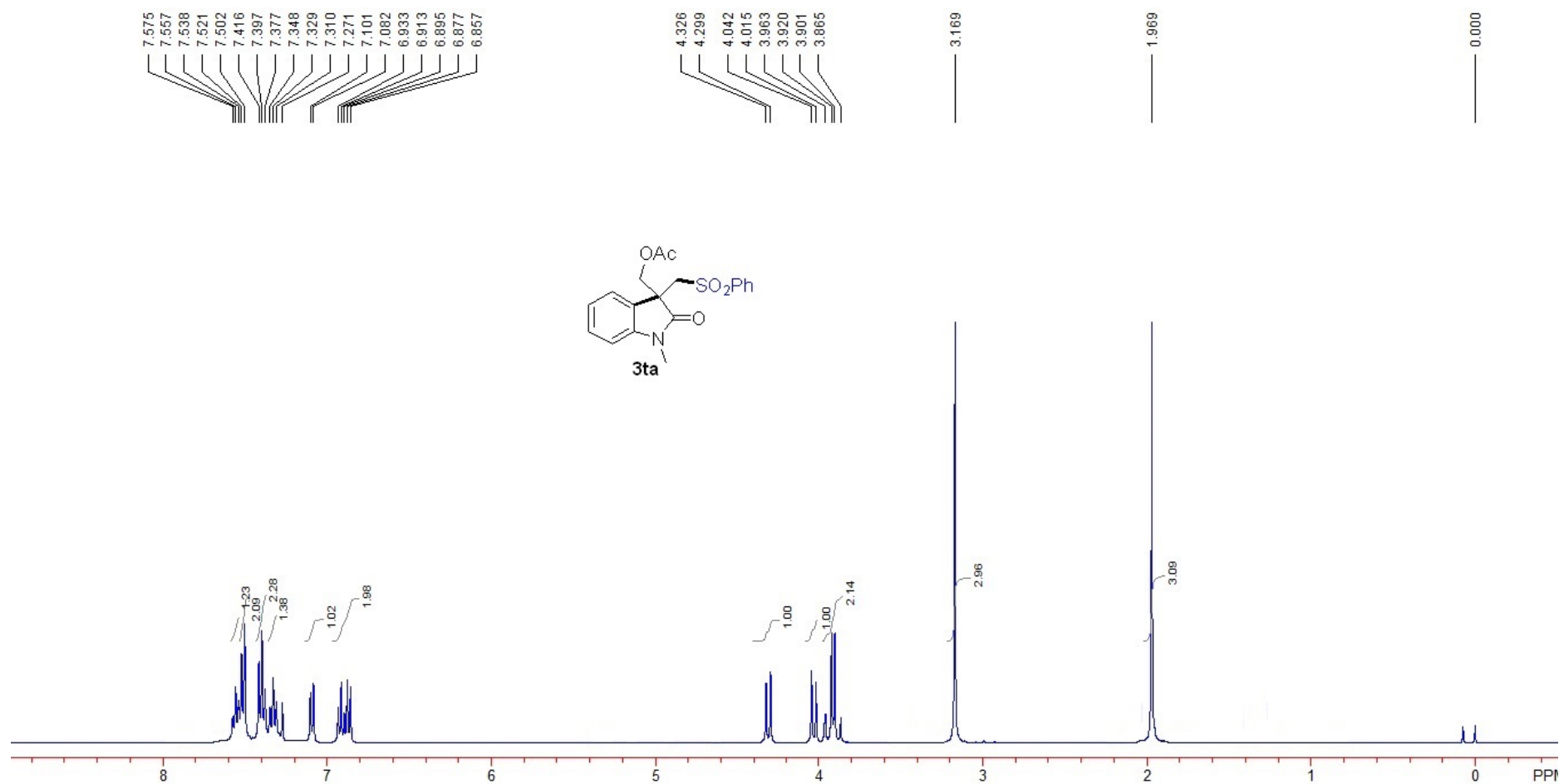


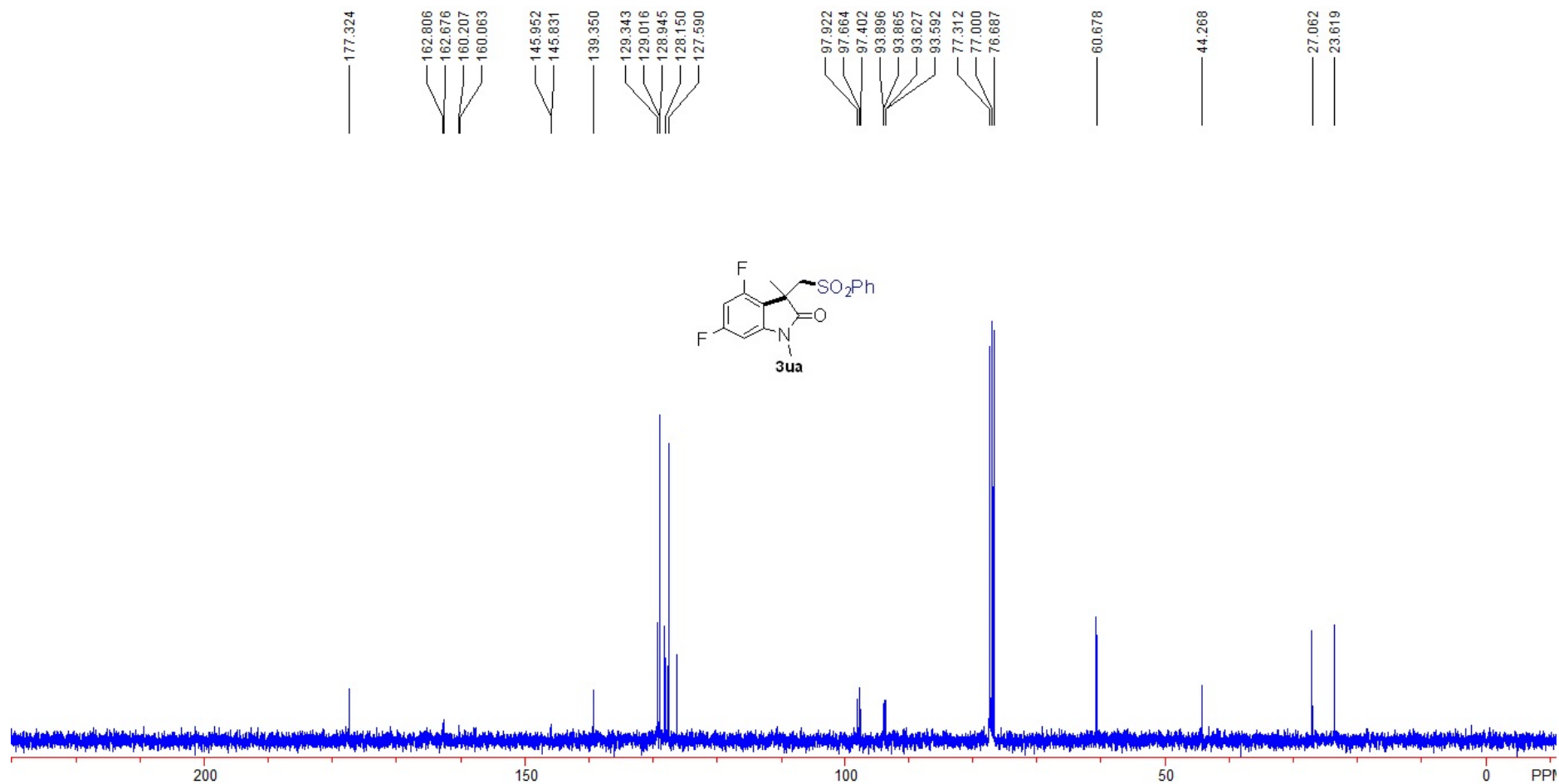


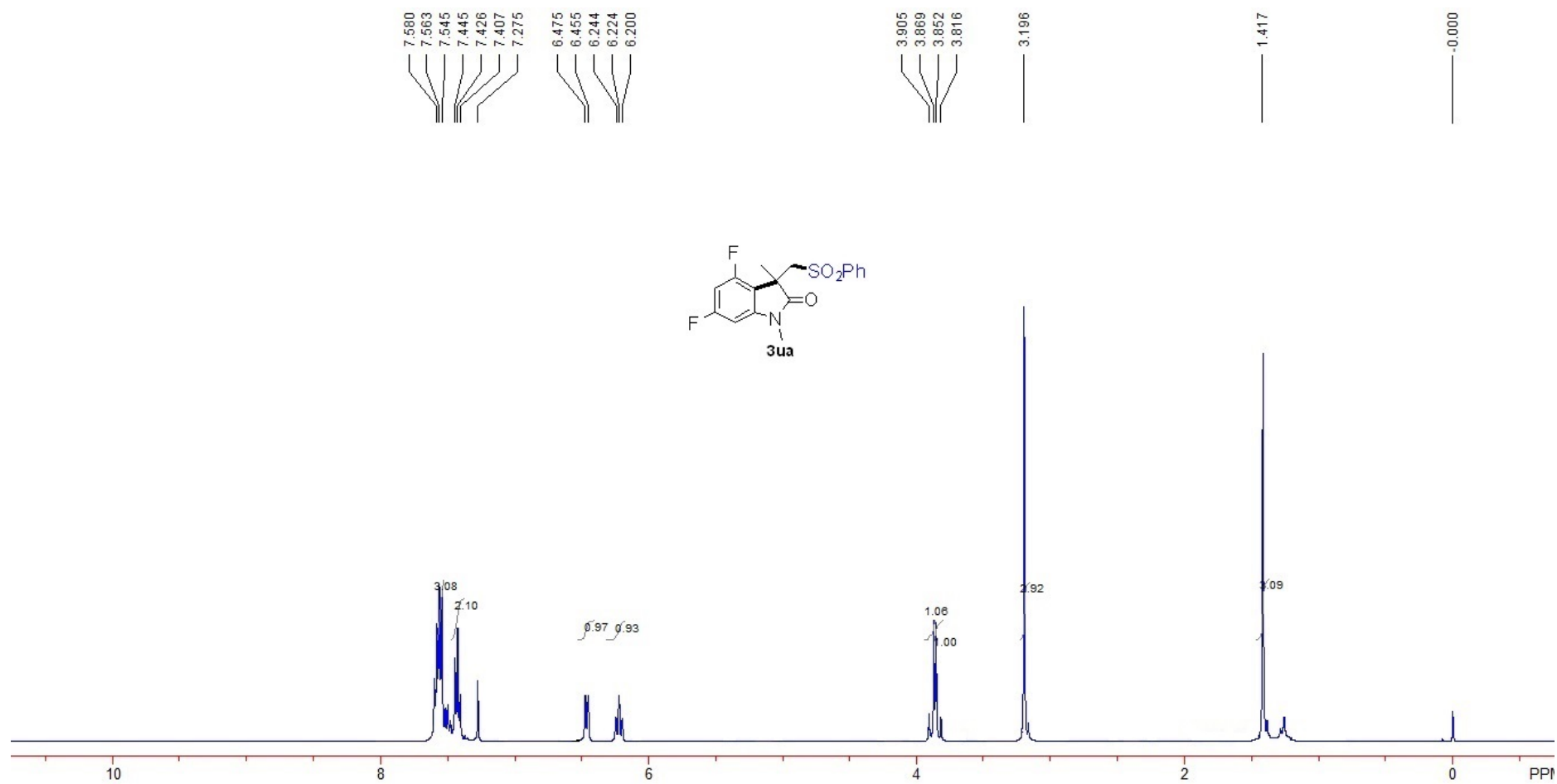


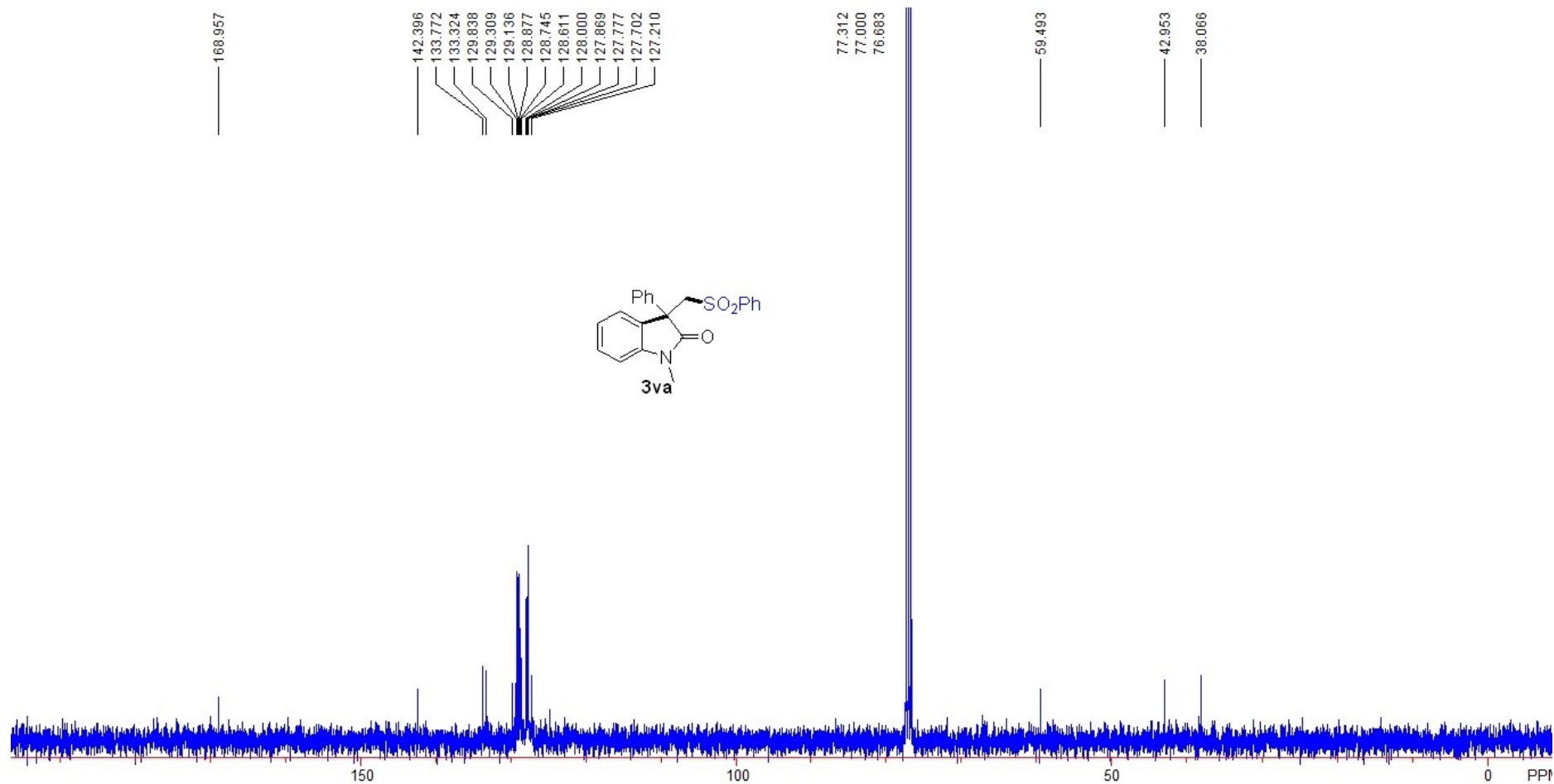


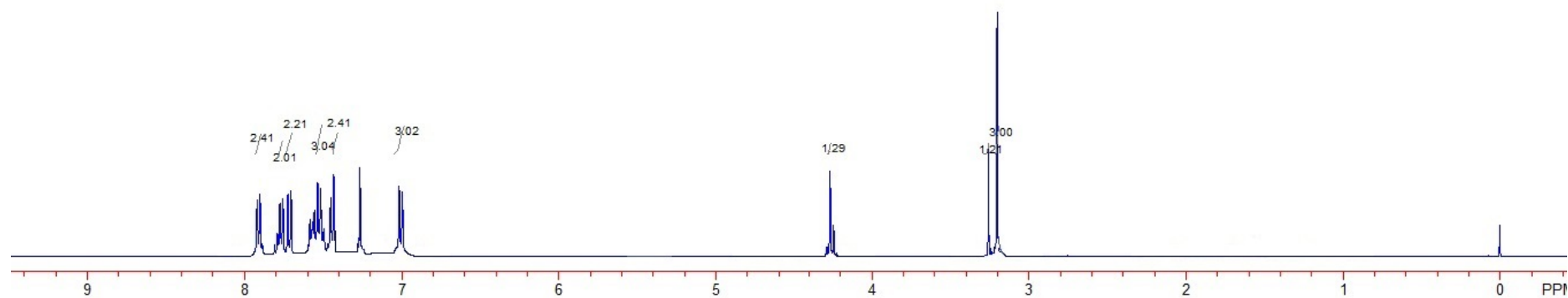
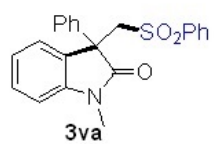
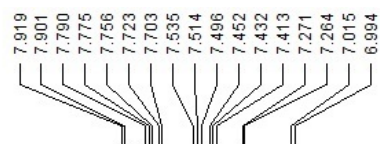


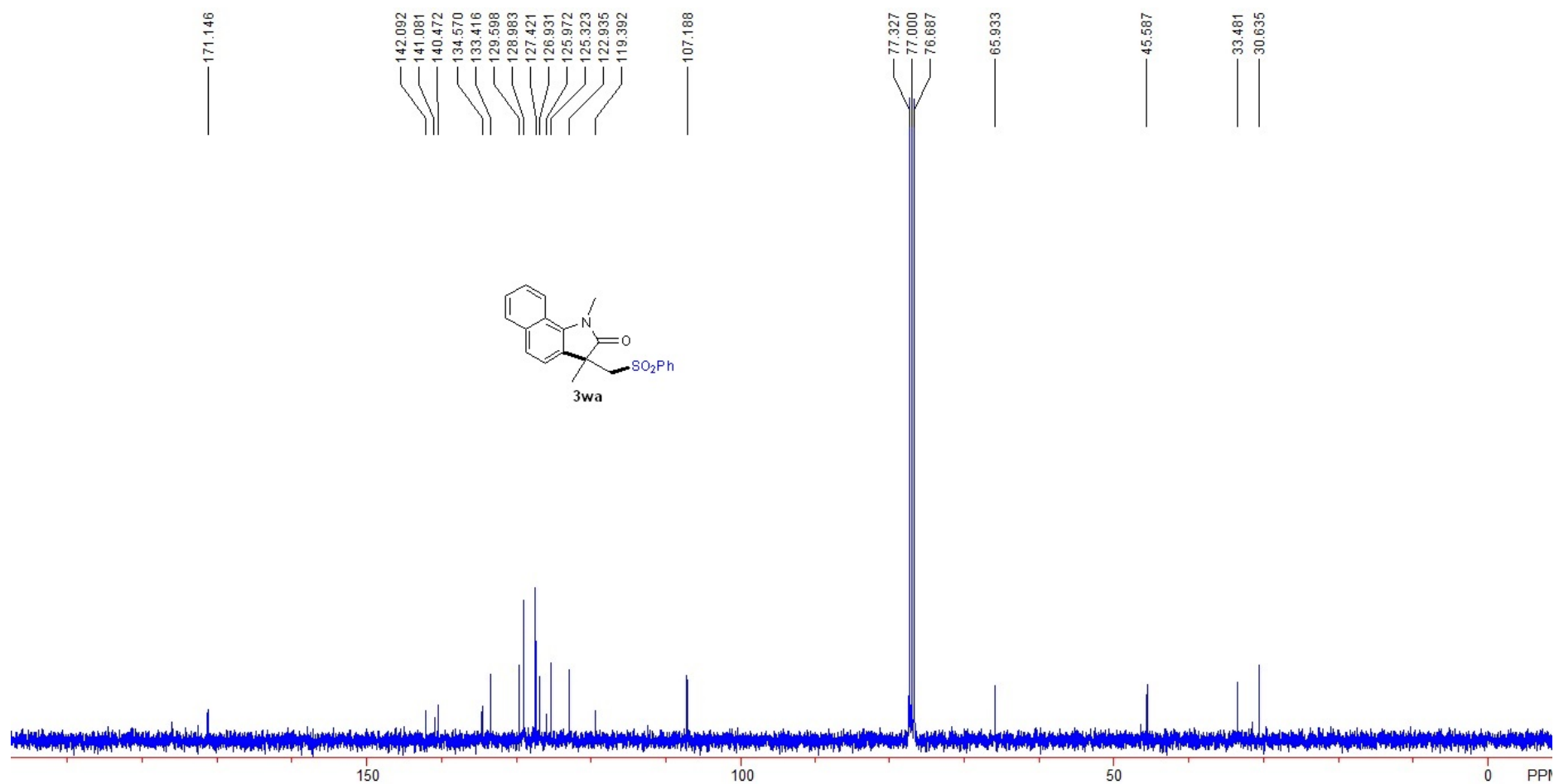


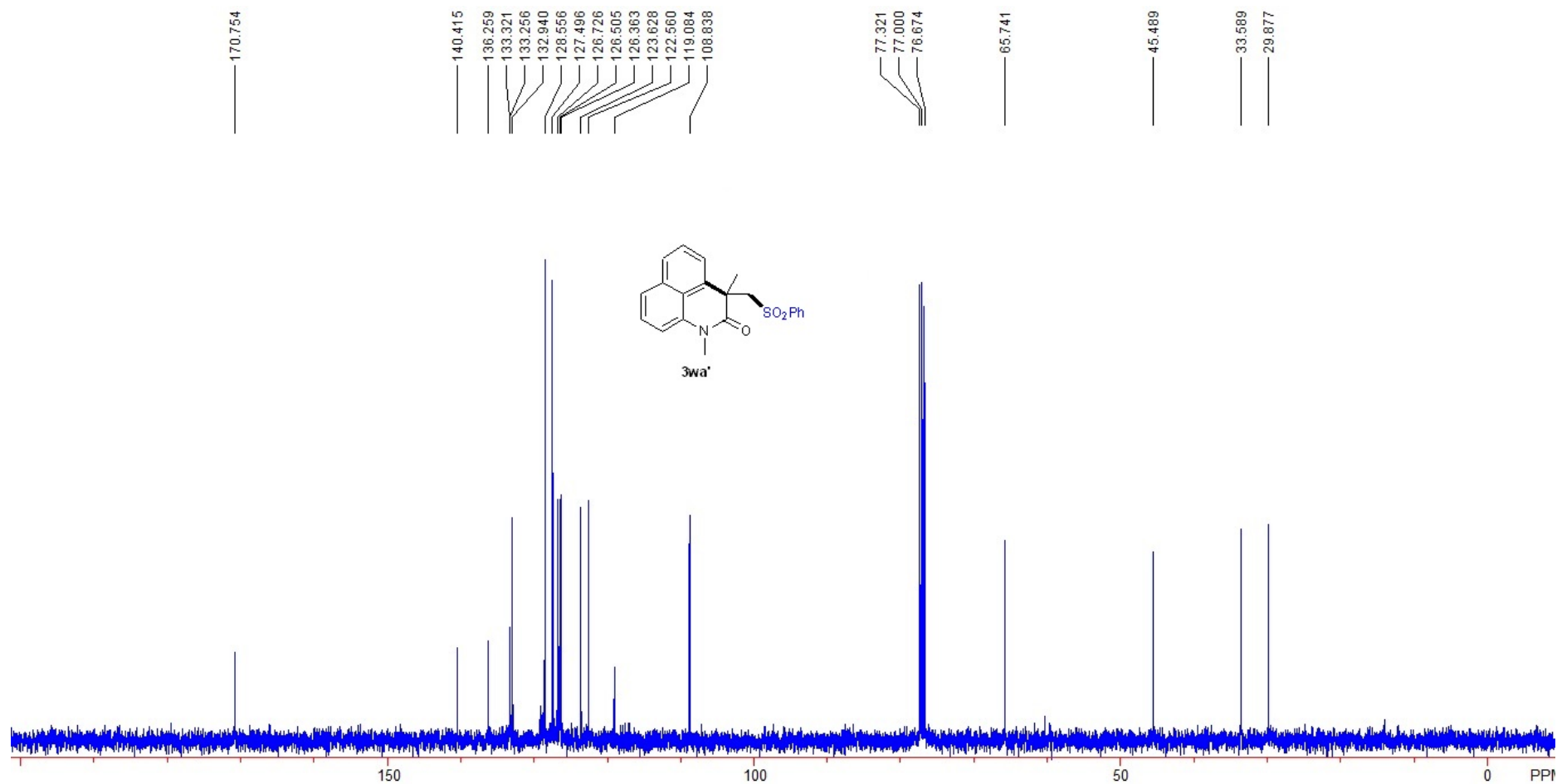


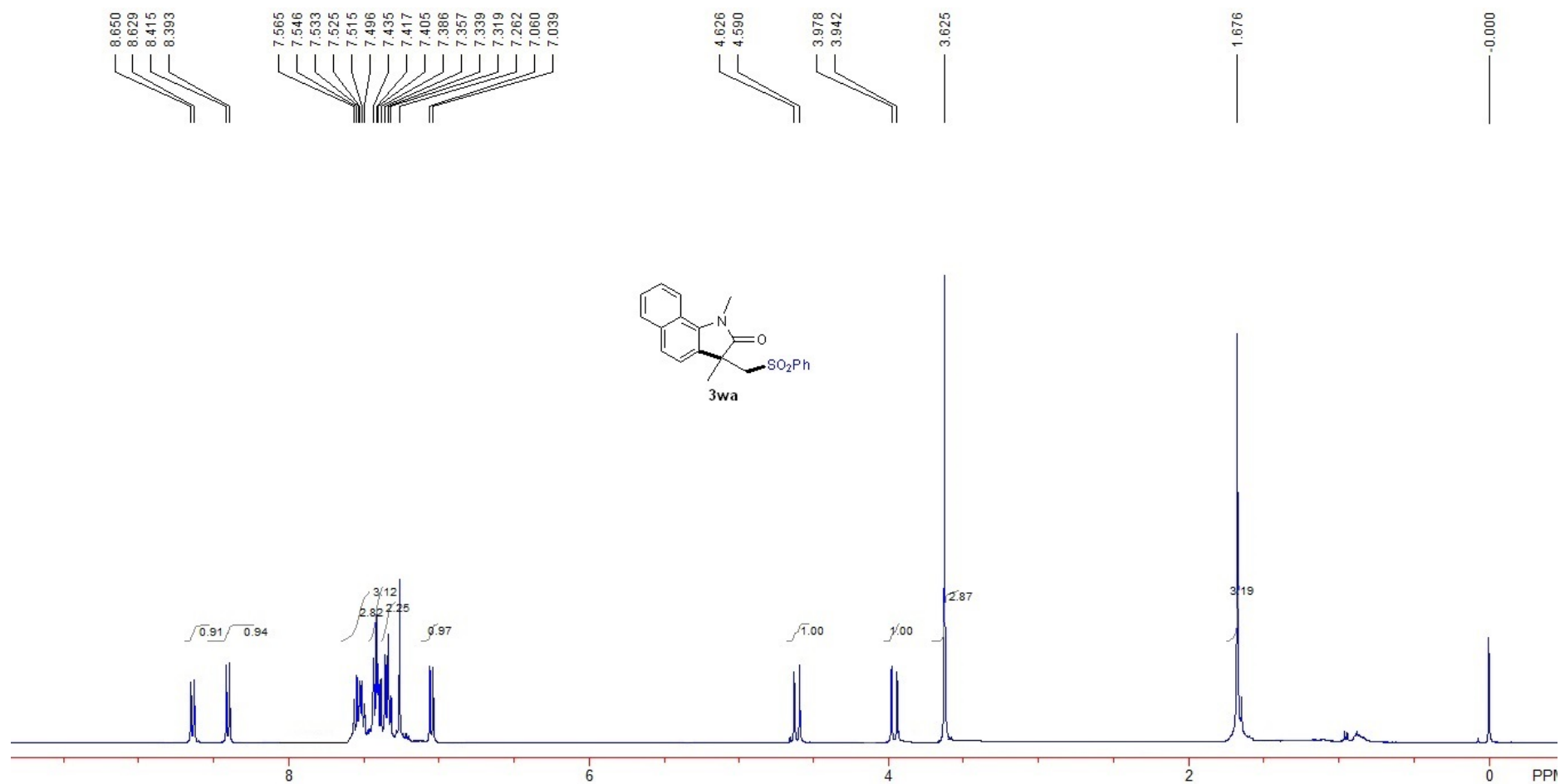


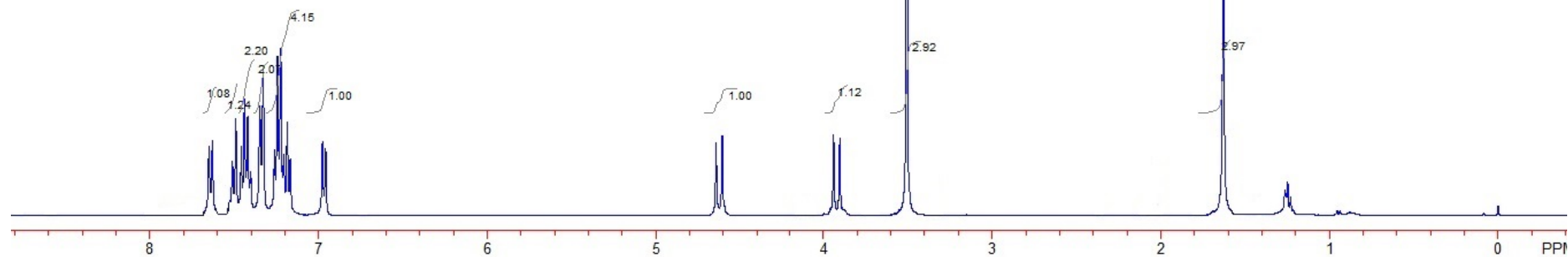
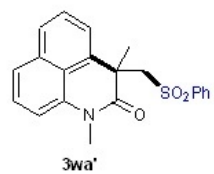
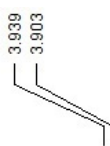
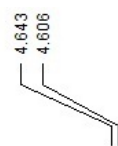
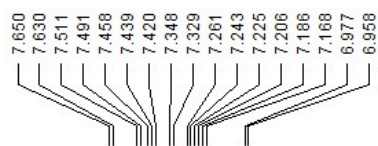


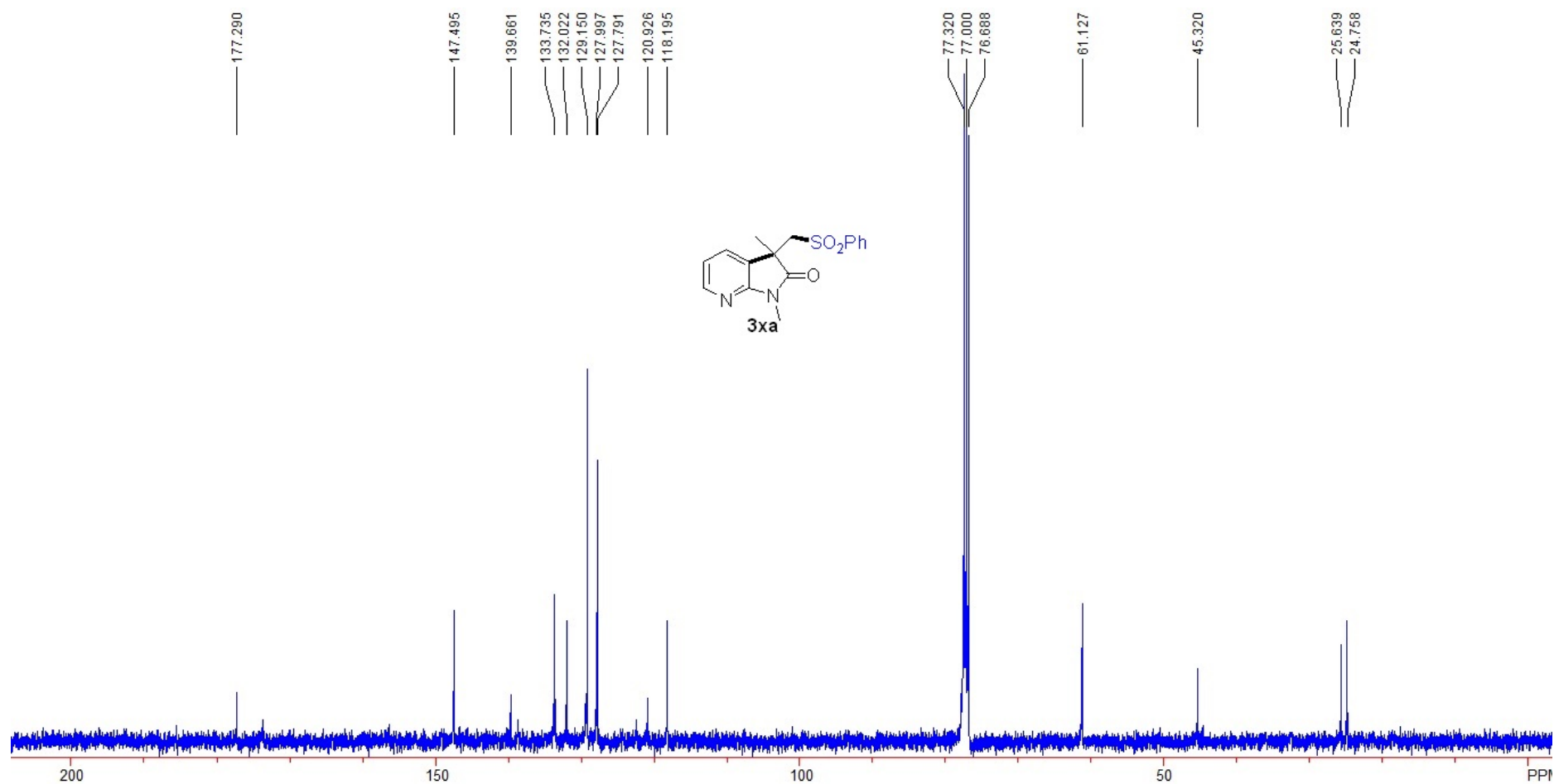


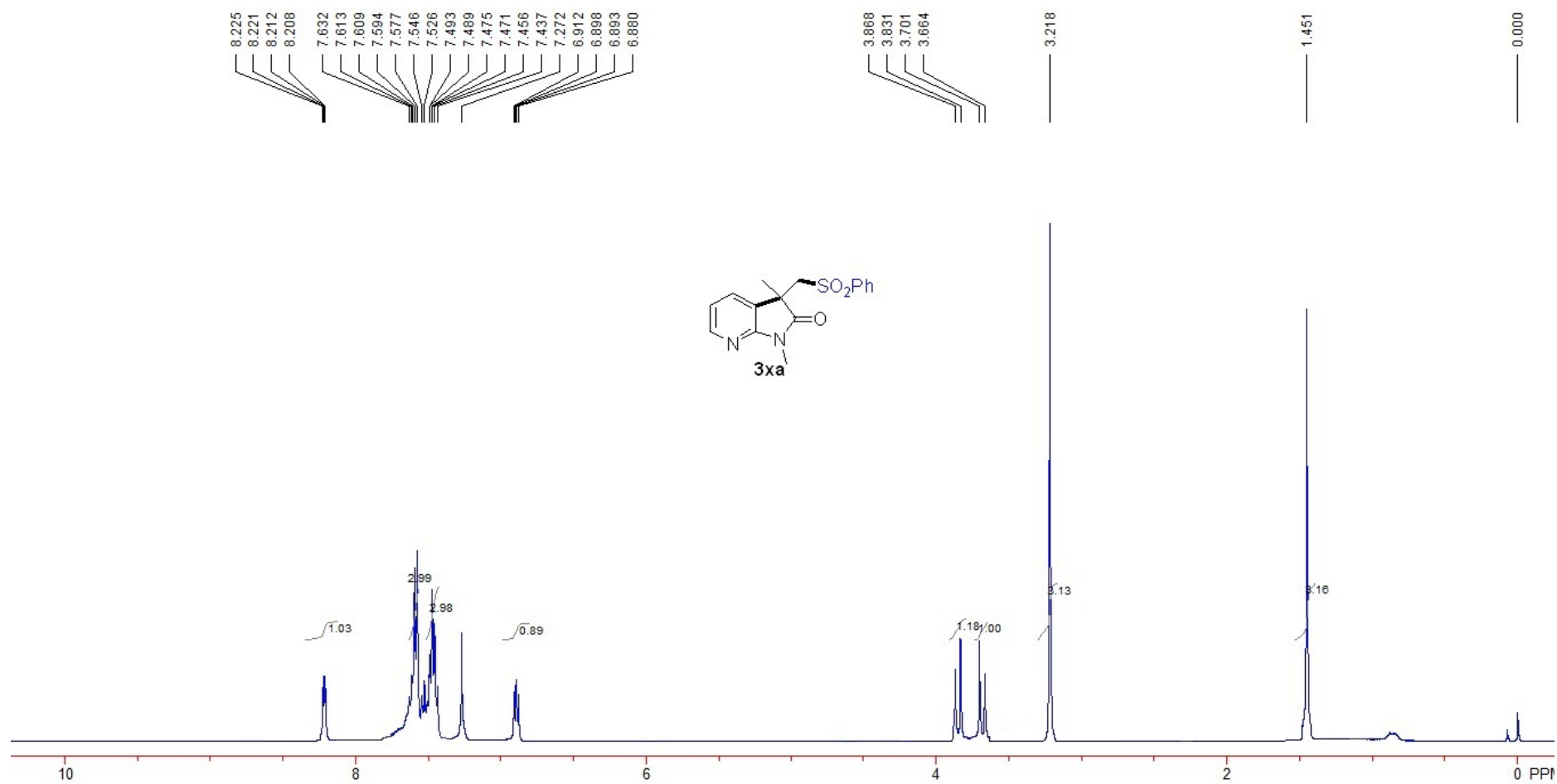


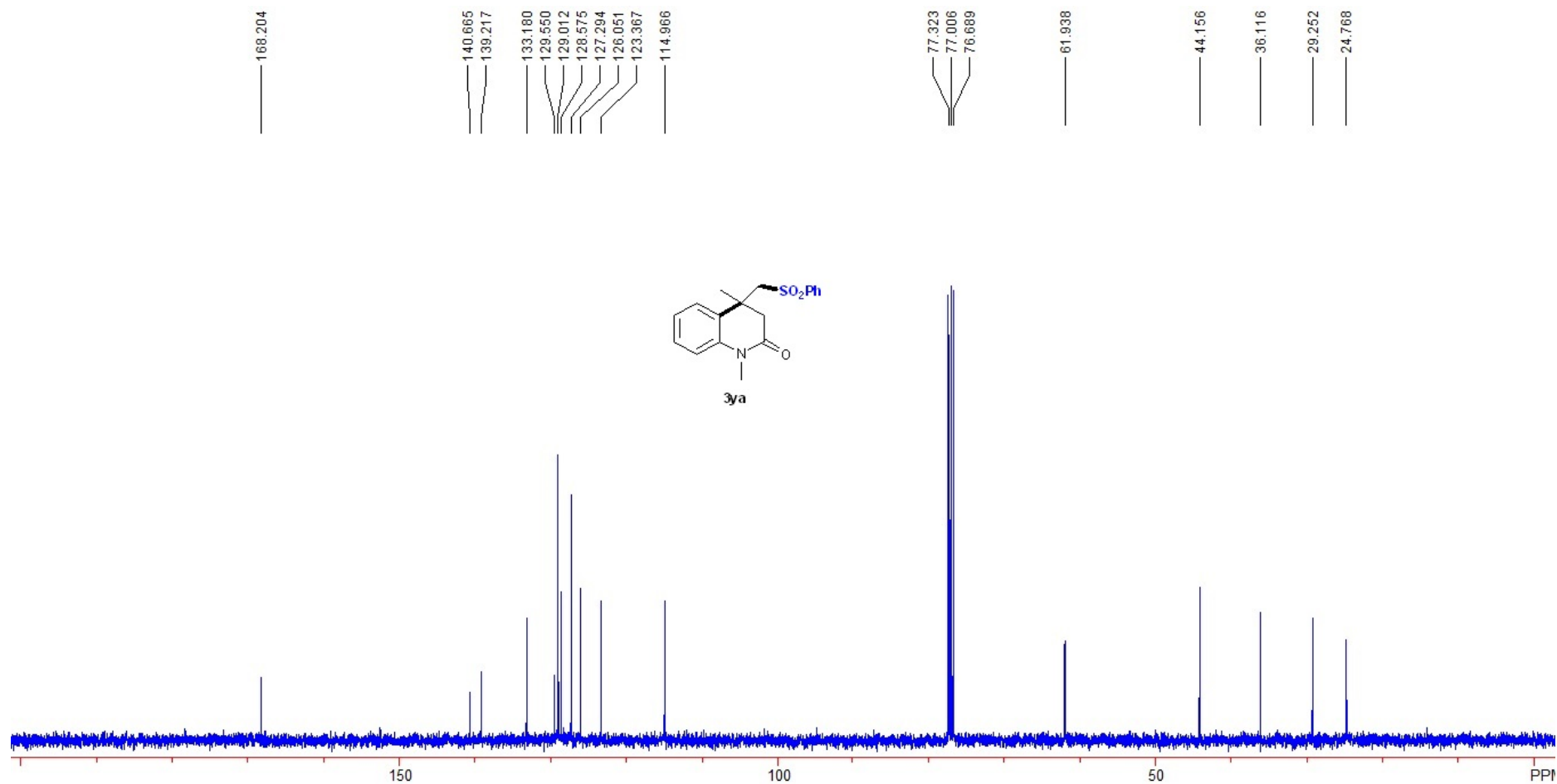


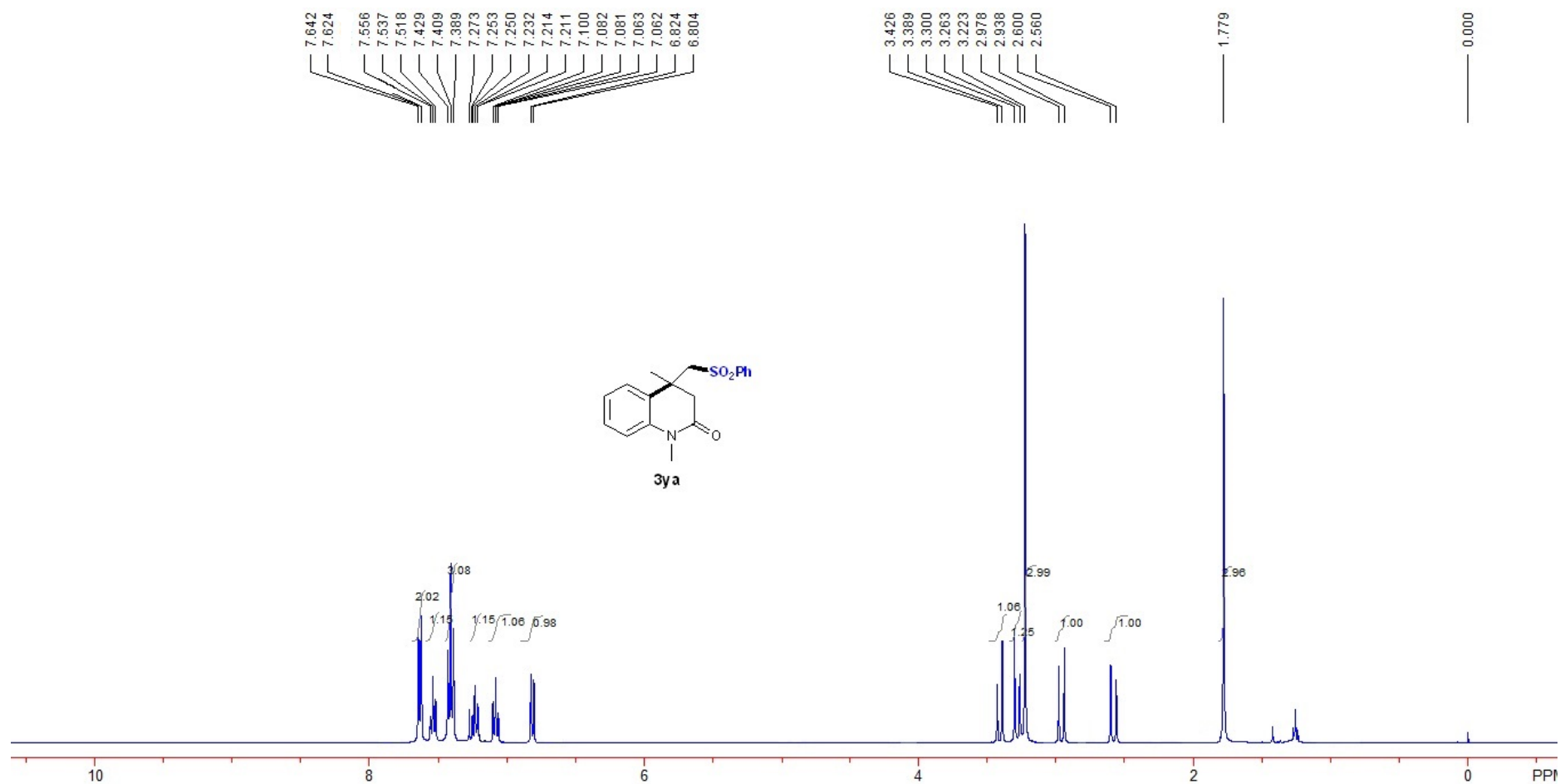


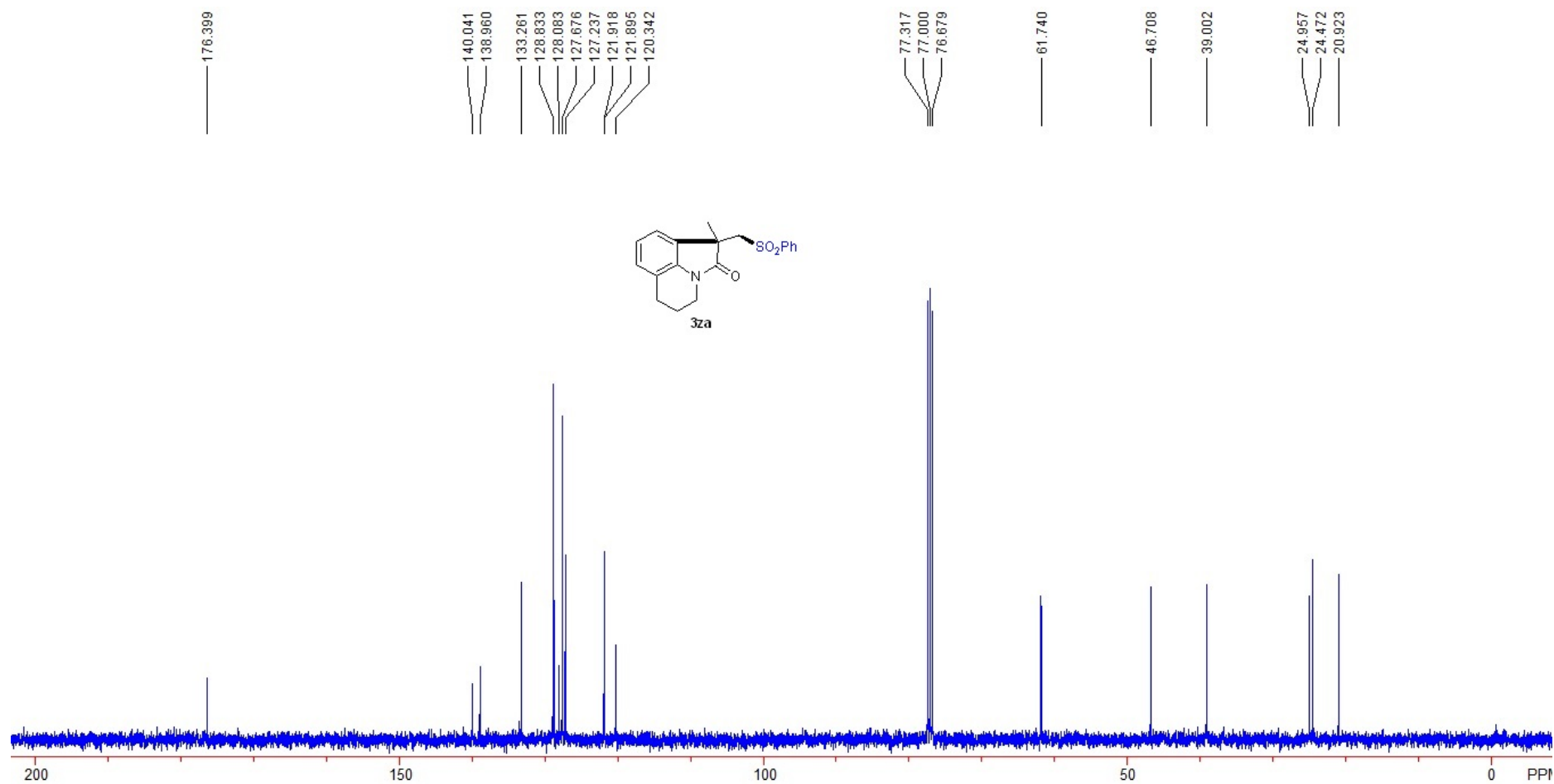


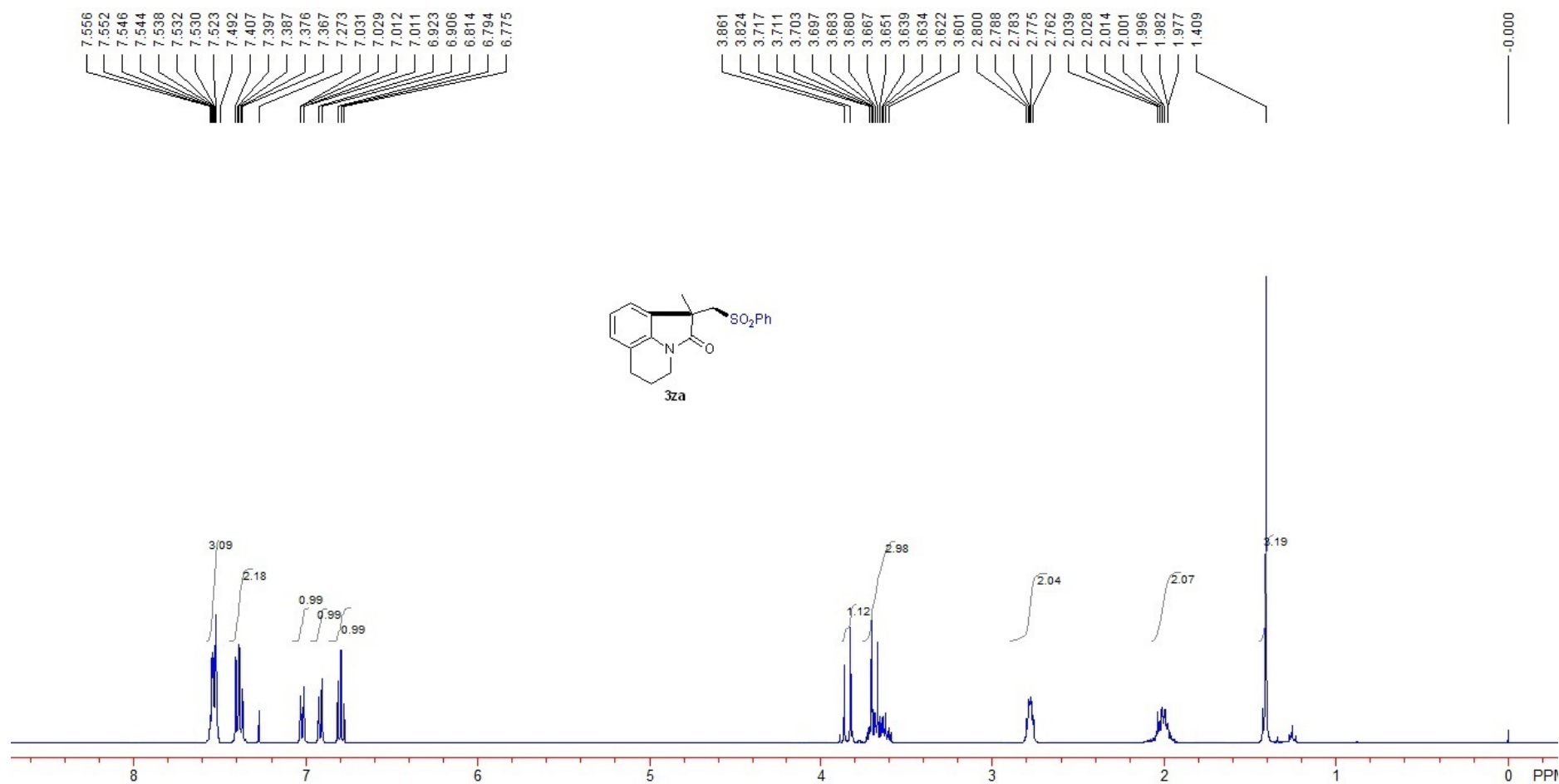


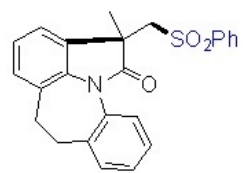
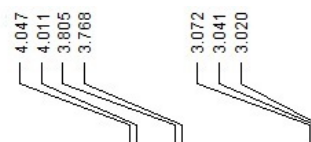
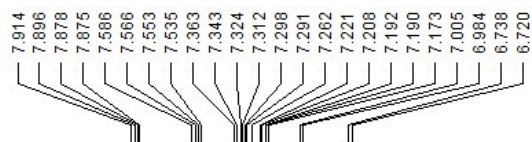




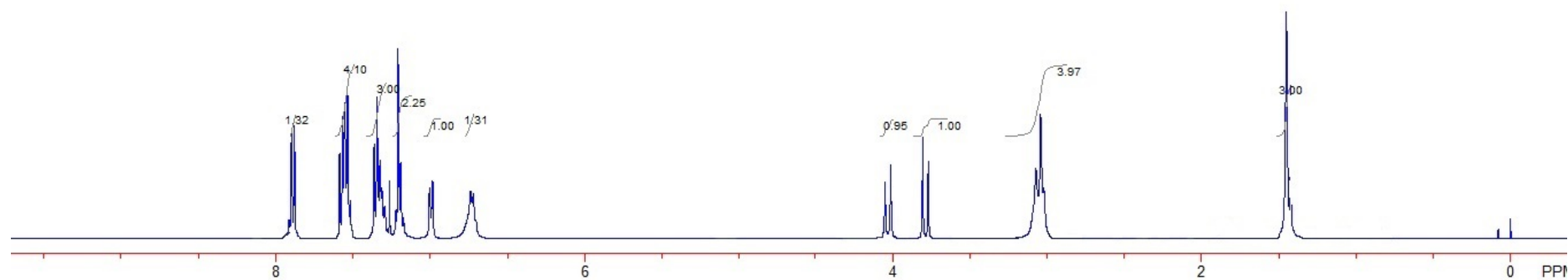


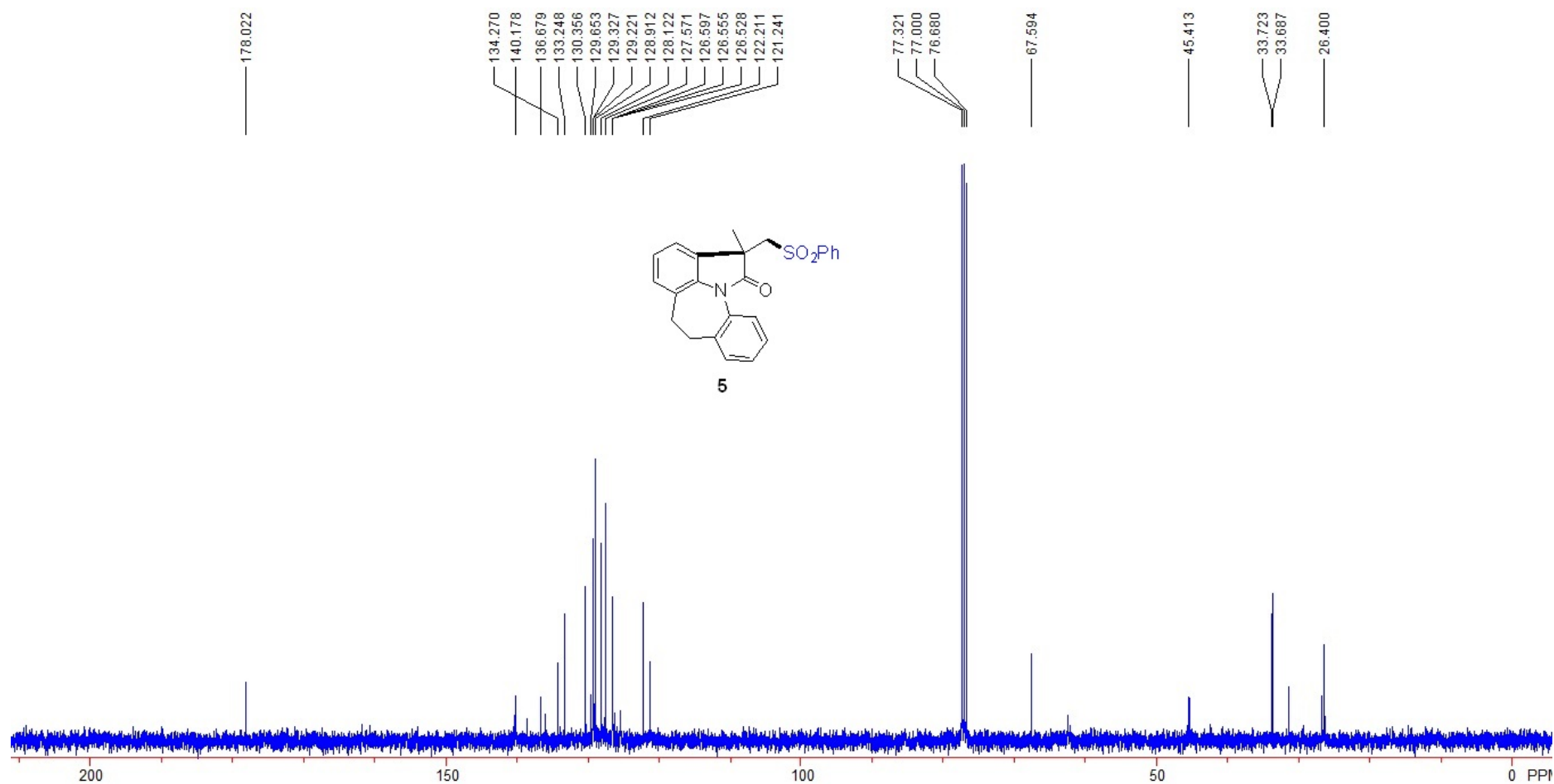


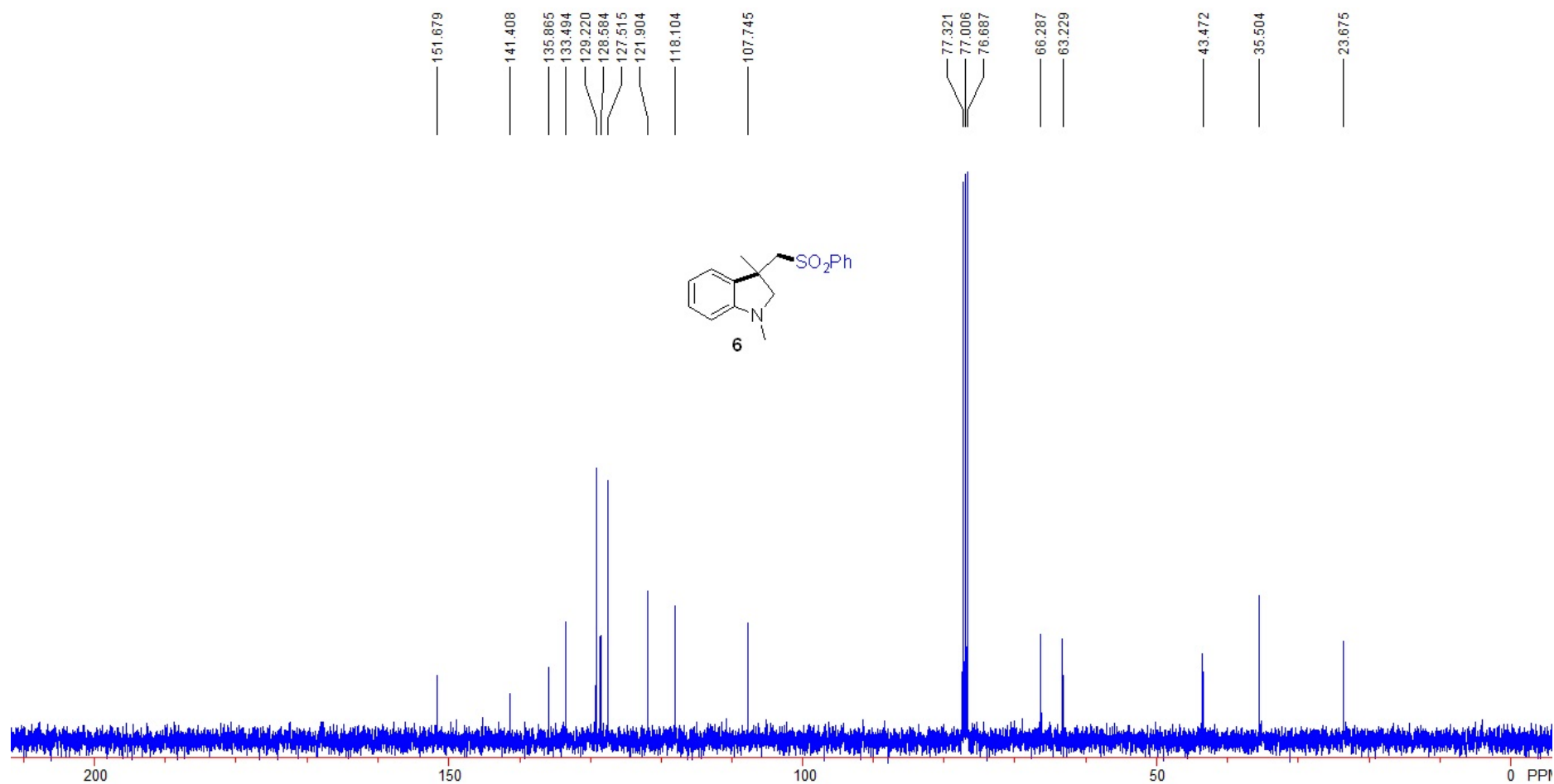


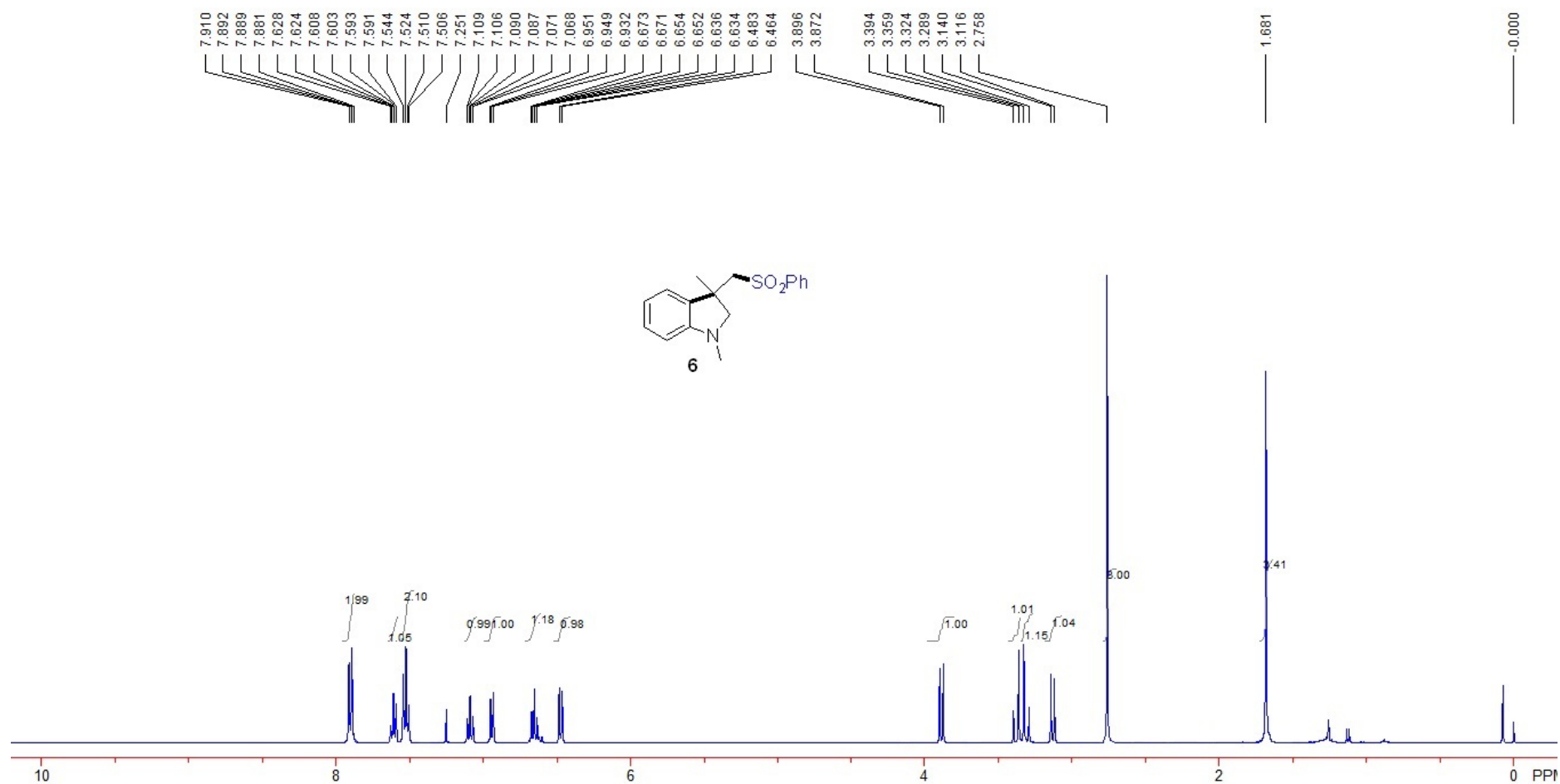


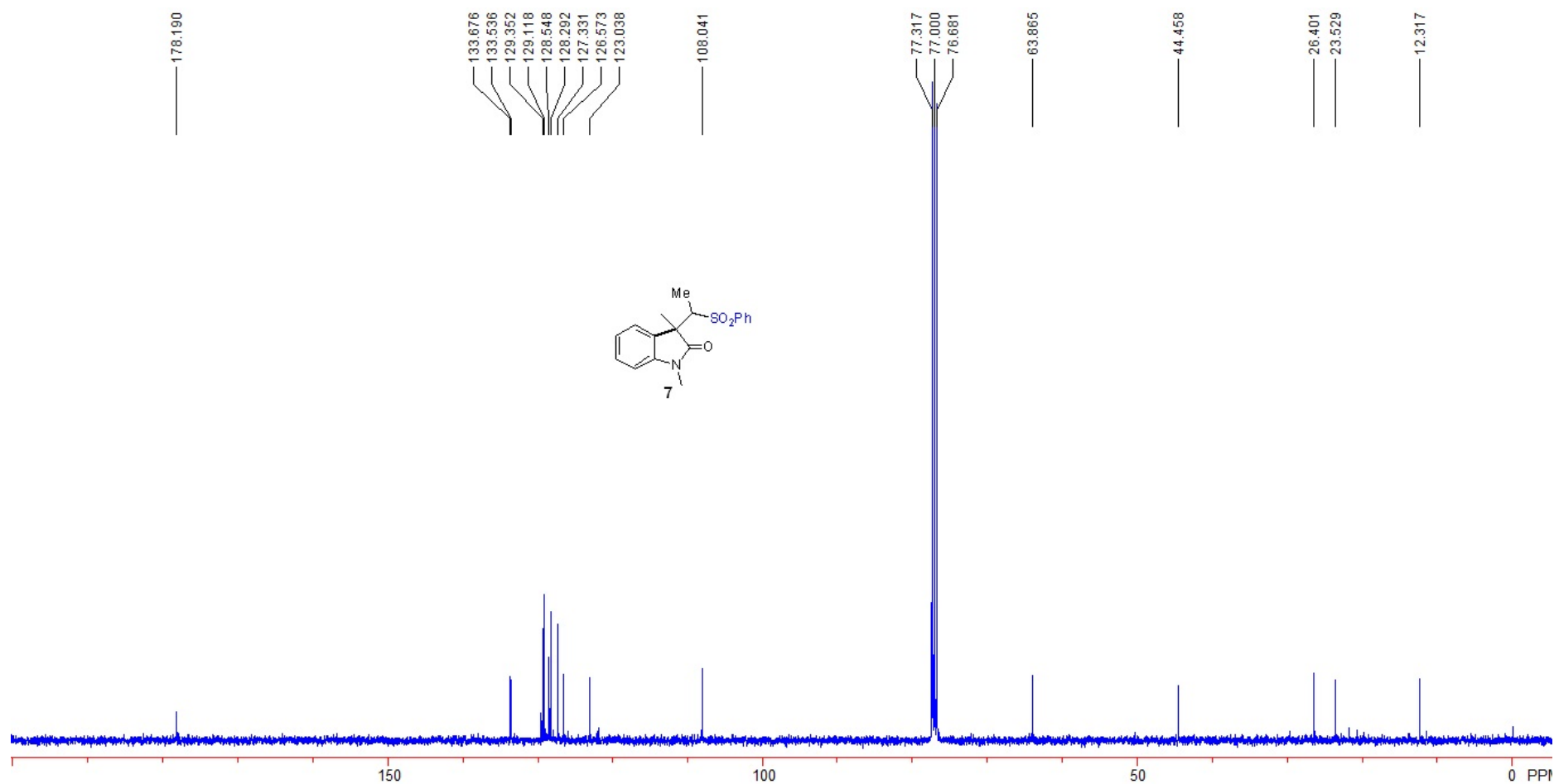
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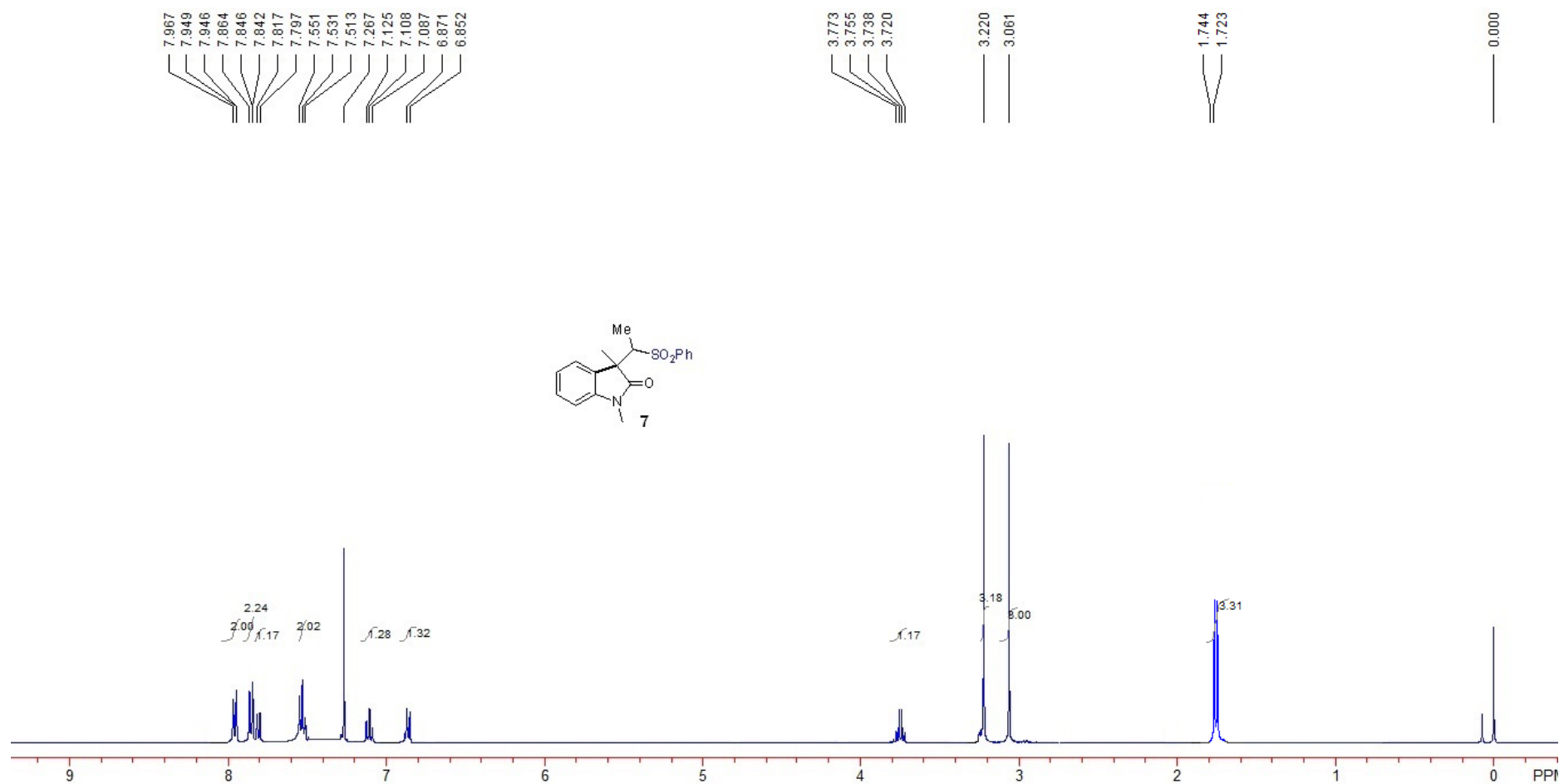


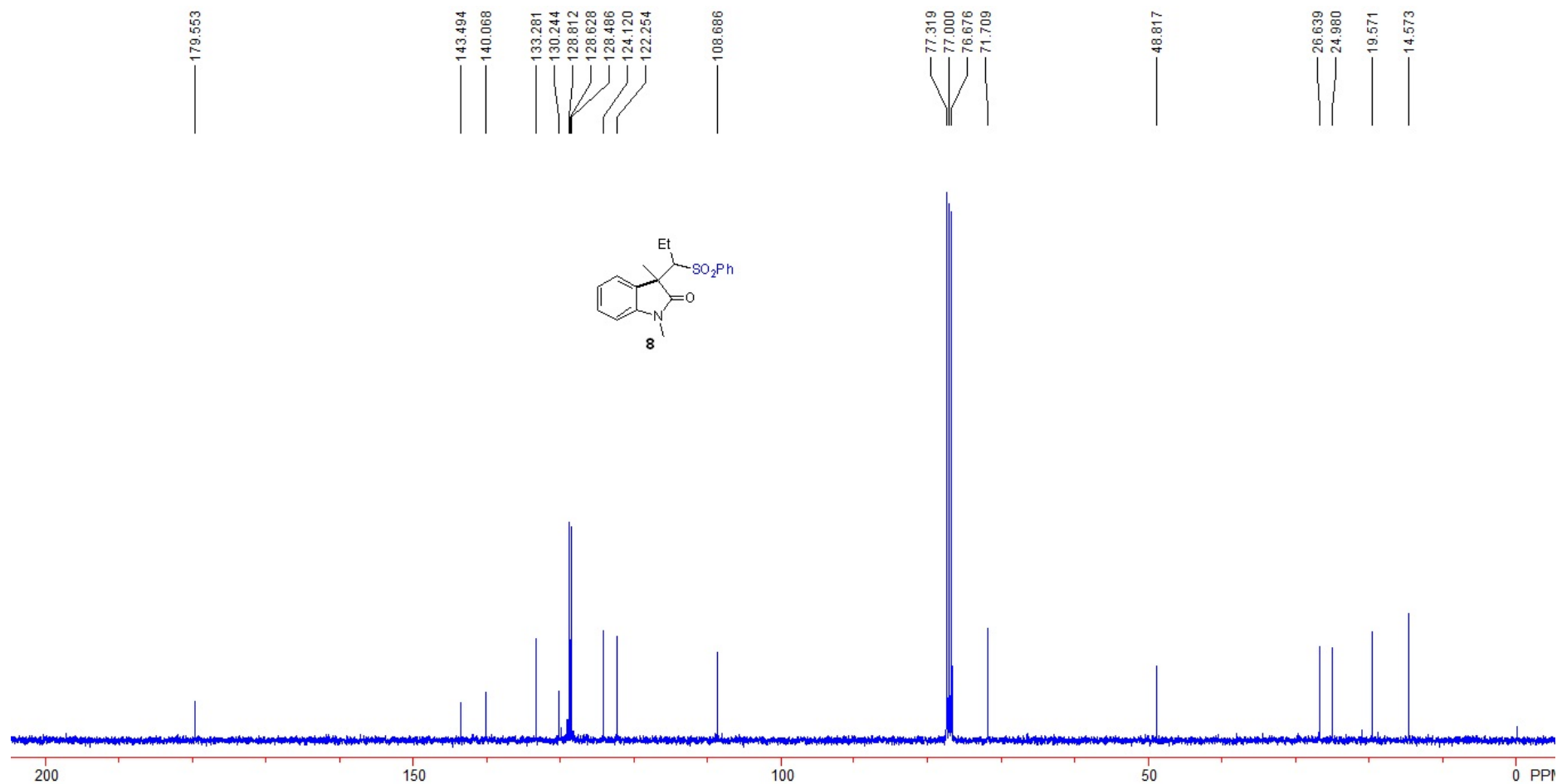


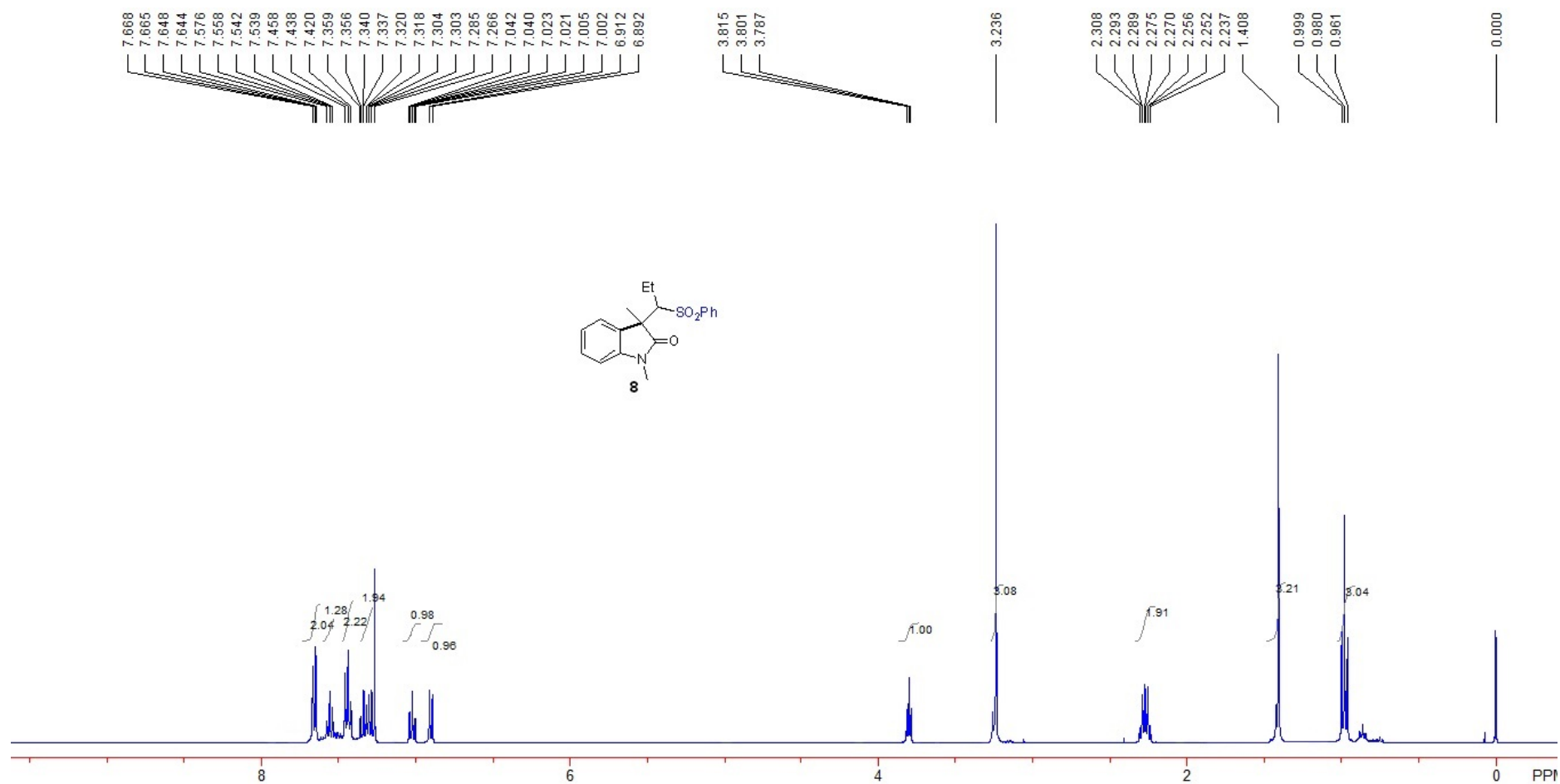


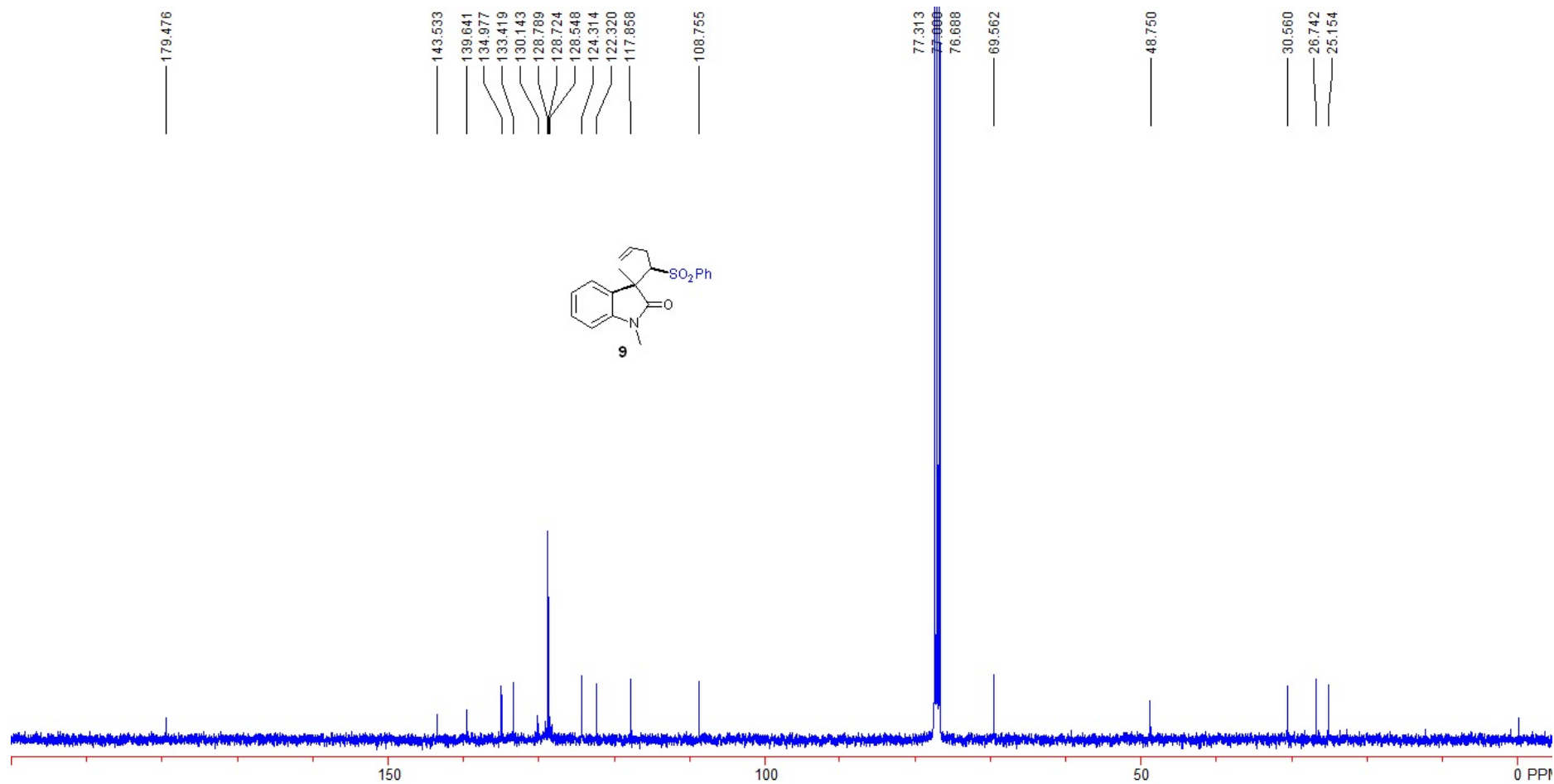


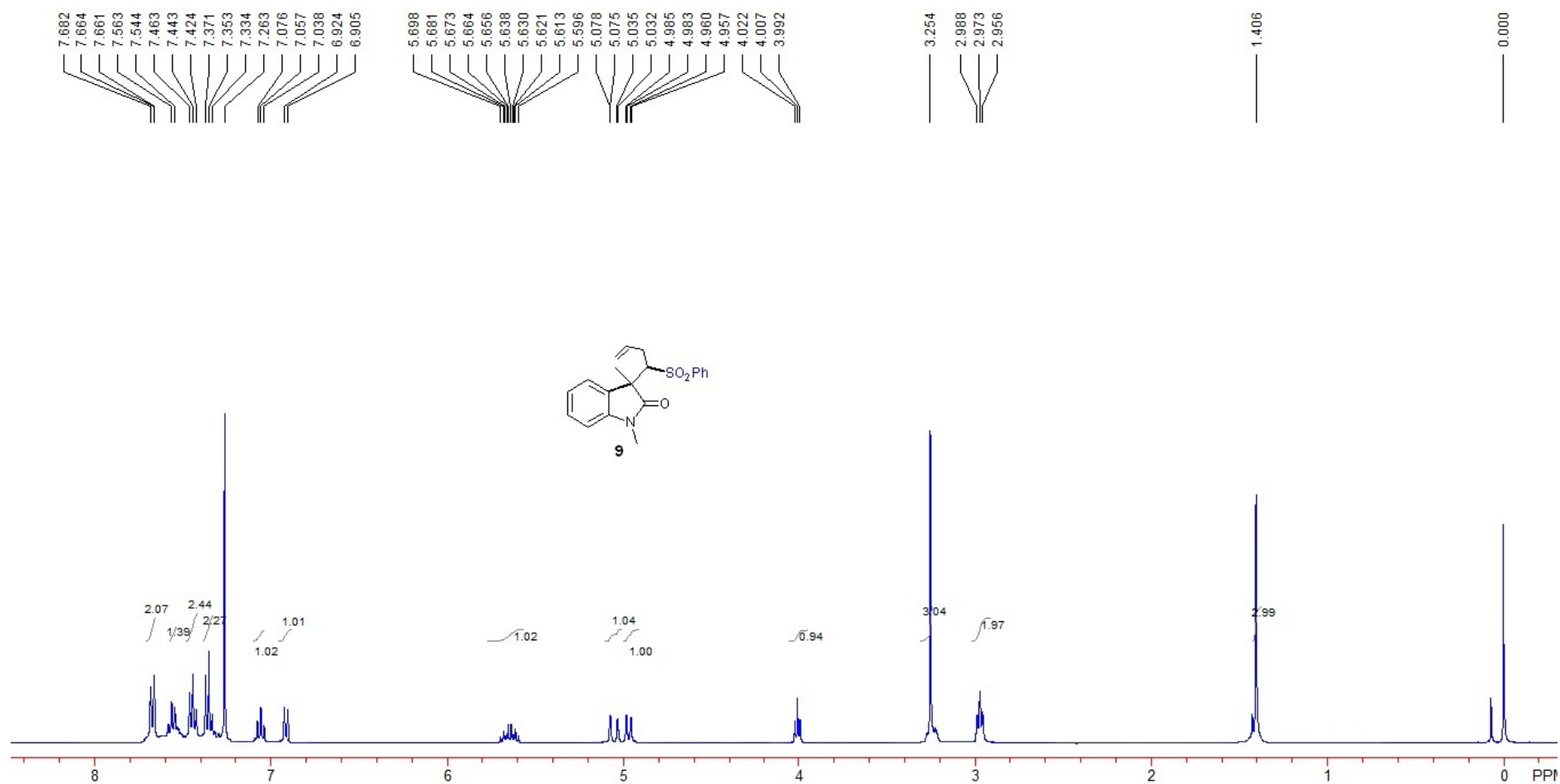


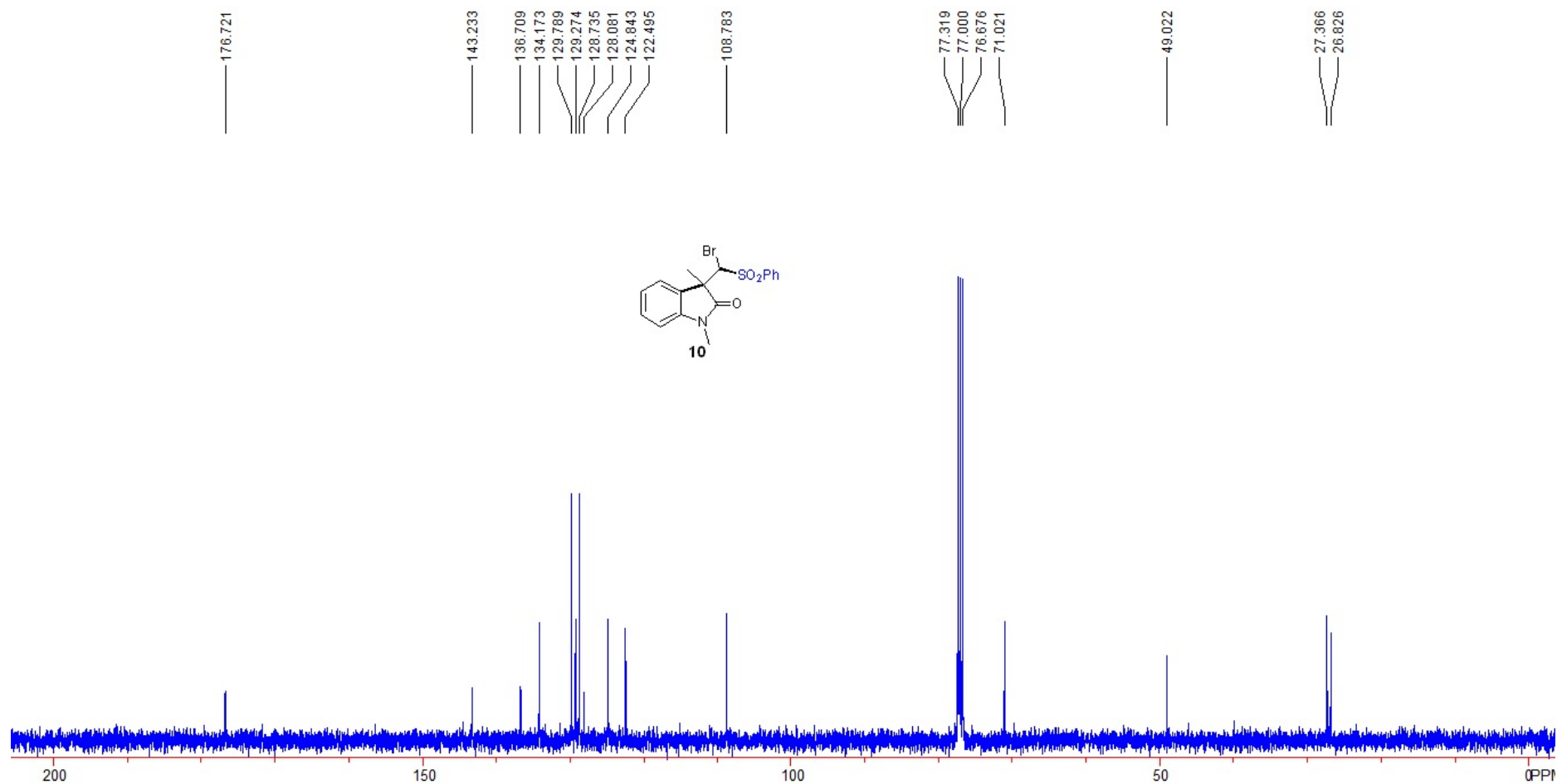


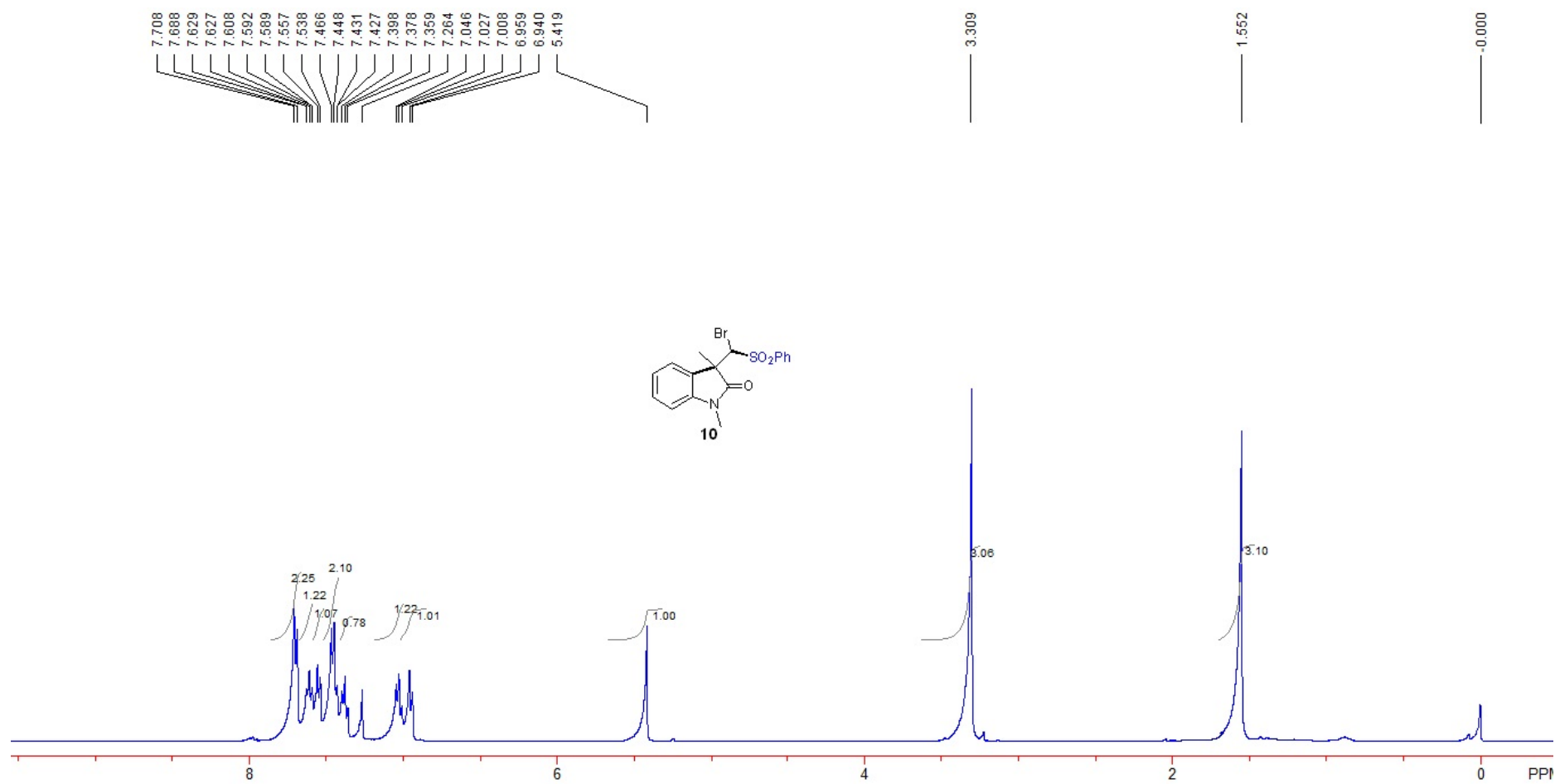


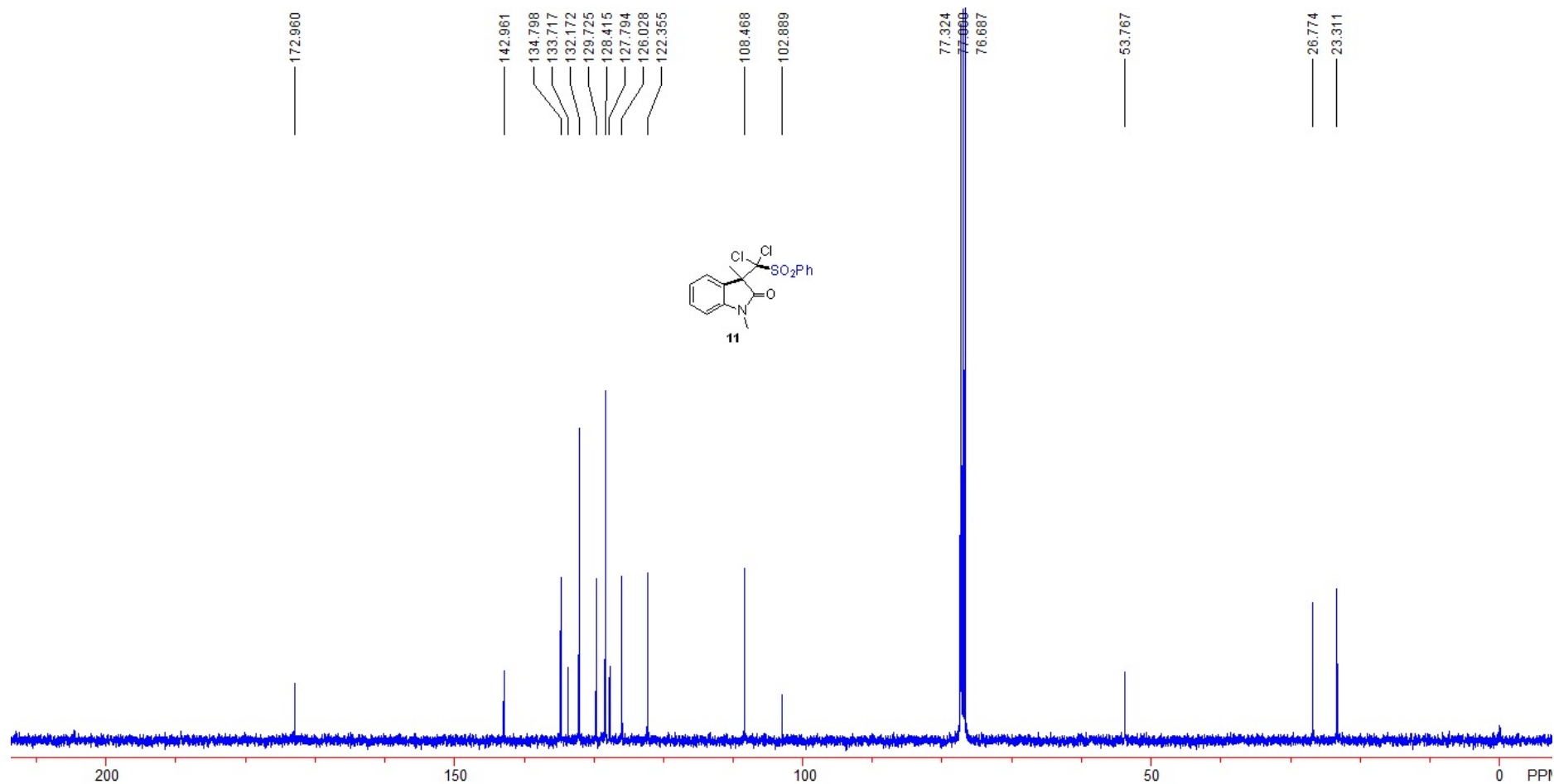


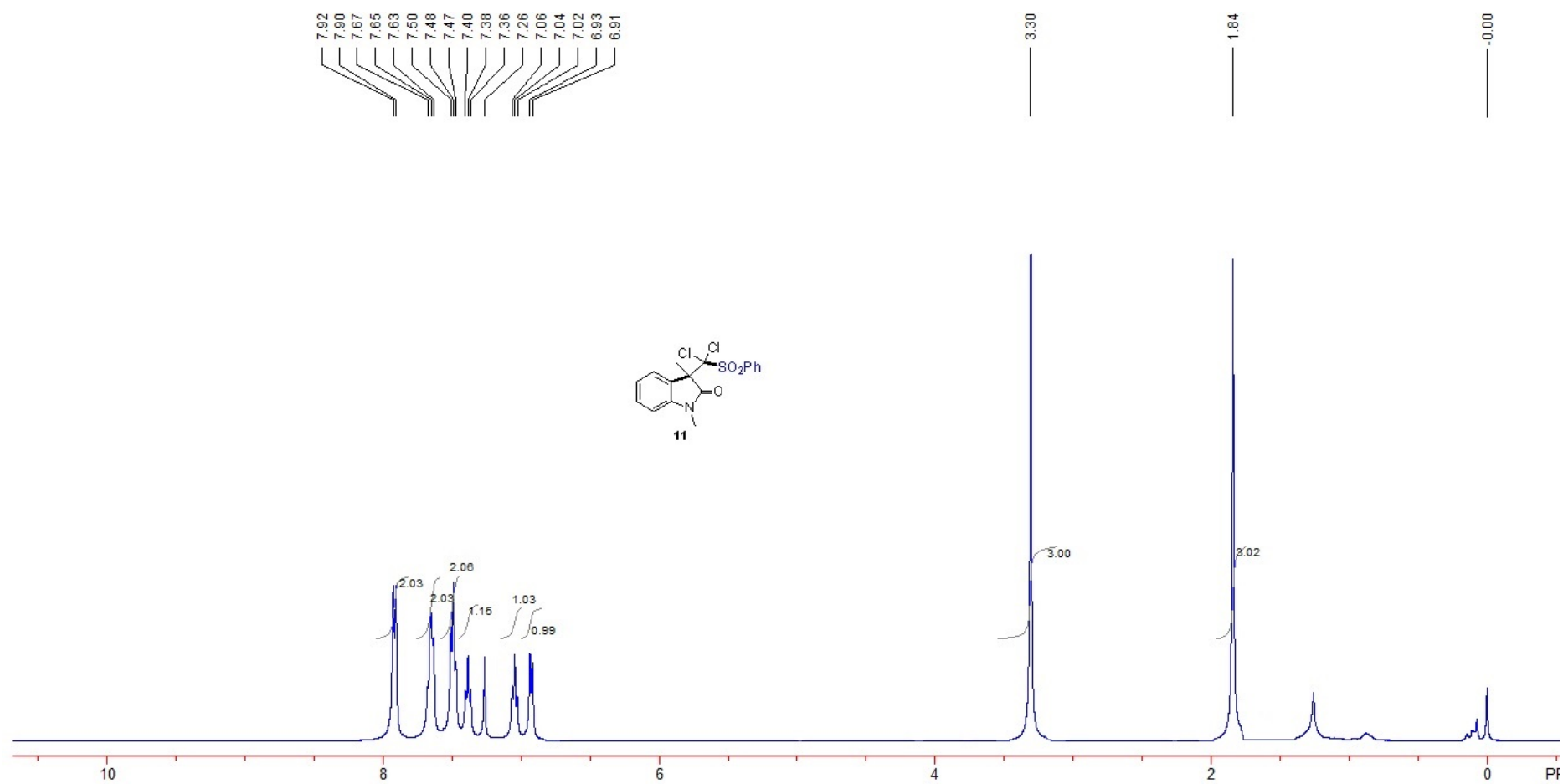












X-ray structures of **3aa**

