Electronic Supplementary Material (ESI) for ChemComm.

Assembly of indenamine derivatives through *in situ* formed *N*-sulfonyliminium ions initiated cyclization

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Supporting Information

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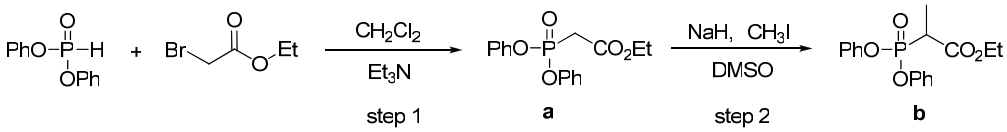
General information

Reactions were monitored by analytical thin-layer chromatography (TLC) using ultraviolet light, phosphomolybdic acid or $KMnO_4$ for visualization. Purification of products was accomplished by flash chromatography on silica gel (200-300 mesh) and the purified compounds show a single spot by analytical TLC. ^1H NMR and ^{13}C NMR spectra were recorded at 400 and 100 MHz respectively using $CDCl_3$ as the solvent with TMS as an internal standard. Chemical shifts δ and coupling constants J are given in ppm (parts per million) and Hz (Hertz) respectively. High-resolution mass spectra (HRMS) were performed on an ITCI-Orbitrap Elite spectrometer. Melting points were measured on a micro melting apparatus and uncorrected.

The following starting materials **1b-1g**, **1i-1p and 1r-1t** were prepared according to the literature procedures. The rest of chemicals were obtained from commercial sources and used without further purification. Solvents were dried before using it.

N-Tosylaldimine **4a** was readily accessible from the condensation of *p*-toluenesulfonamide (**2e**, 5 mmol) with commercially available methyl-*trans*-cinnamaldehyde (**1a**, 5 mmol). The reaction was carried out at room temp. in CH_2Cl_2 solution using $TiCl_4/NEt_3$ as catalyst, according to a known procedure.[1]

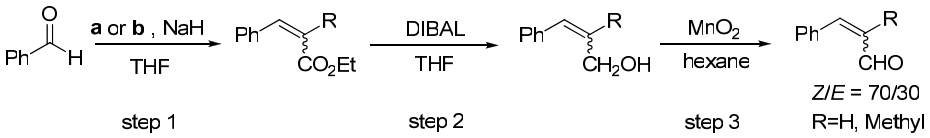
General procedures for the synthesis of (*Z*)-starting materials[2]



Step 1: To a solution of diphenyl phosphite (11.70g, 50 mmol) in anhydrous dichloromethane (50 mL) at 0 °C was added ethyl bromoacetate (8.25g, 50 mmol), followed by addition of triethylamine (7.07g, 70 mmol). The resulting mixture was stirred at 0 °C for 30 min, then warmed to room temperature and stirred for further 3 h. The resulting suspension was quenched with water (2×20 mL) and the aqueous phase was extracted with ethyl acetate (2×30 mL). The combined organic phase was washed with water and brine, dried over magnesium sulfate and concentrated *in vacuo*. Purification of the residue by flash column chromatography on silica gel (petroleum ether/EtOAc = 6/1) to afford the ethyl diphenylphosphonoacetate **a** (11.68g, 73% yield).

Step 2: To a solution of ethyl diphenylphosphonoacetate **a** (6.40g, 20 mmol) in DMSO (50 mL)

was added NaH (1.60g, 40 mmol, 60 % mineral dispersion) at about 15 °C in a water bath. The mixture was warmed to room temperature and stirred for 30 min, methyl iodide (4.14g, 30 mmol) was then added to the above solution. After being stirred for 3 h at room temperature, the reaction was quenched with saturated NH_4Cl, and the mixture was extracted with ethyl acetate (2×30 mL). The combined extracts were washed with water (2×30 mL) followed by brine, dried by $MgSO_4$, and concentrated to give a pale yellow residue. The crude product was subjected to flash column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to provide ethyl 2-diphenylphosphonopropionate **b** (4.40g, 66% yield).



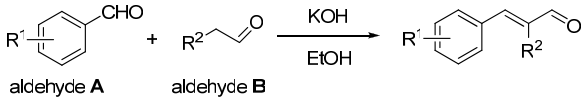
Step 1: To a suspension of NaH (0.52g, 13 mmol, 60 % mineral dispersion) in THF (40 mL) in a flame dried Schlenk flask at 0 °C was slowly added **a** or **b** (13 mmol). After completion of the gas formation, the reaction mixture was cooled to -78 °C, and a solution of benzaldehyde (1.06g, 10 mmol) in THF (20 mL) was added. After being stirred for 3 h at -78 °C, the reaction mixture was warmed to room temperature and quenched by addition of H_2O (20 mL), the organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were dried ($MgSO_4$) and concentrated under vacuum. The crude product was separated by flash column chromatography on silica gel to give the corresponding α,β-unsaturated ester (R=H, 1.53g, 87% yield; R=Methyl, 1.36g, 72% yield).

Step 2: To a solution of unsaturated ester (5 mmol) in THF (20 mL) at -78 °C was slowly dropwise added a 1 M solution of diisobutylaluminiumhydride in hexane (10 mL, 10 mmol) and the reaction mixture was stirred for 3 h. After addition of a saturated sodium-potassium tartrate solution (20 mL), the reaction mixture was stirred at room temperature for 1 h. After then, the organic layer was separated and washed with brine (2×20 mL). The aqueous layer was extracted with ethyl acetate (2×20 mL). The combined organic layers were dried ($MgSO_4$), the solvent was removed under vacuum and the resulting crude alcohol was used without further purification (R=H, 0.60g, 90% yield; R=Methyl, 0.62g, 85% yield).

Step 3: The allylic alcohol (3 mmol) was dissolved in hexane (15 mL) and activated MnO_2 (0.77g, 9 mmol) was added. The suspension was stirred for 20 h at room temperature, then filtered

through Celite and the residue was washed with ethyl acetate (20 mL). The combined filtrates were concentrated under vacuum to give a mixture of (*Z*) and (*E*)-isomers (*Z*/*E* = 70:30). After being separated by flash chromatography on silica gel, the (*Z*)-isomer of the corresponding cinnamylaldehyde was obtained (R=H, 0.24g, 62% yield; R=Methyl, 0.23g, 53% yield).

General procedures for the synthesis of (*E*)-starting materials: 1b-1e, 1g, 1i, 1l-1p, 1r-1t[3]

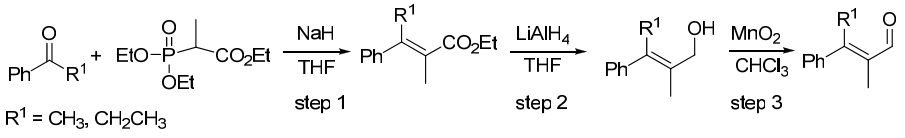


To a stirred solution of KOH (0.56g, 0.01 mol) in EtOH (25 mL, 95%) was added aldehyde **A** (0.01 mol), the mixture was cooled to 0 °C and aldehyde **B** (0.02 mol) was added slowly so that the reaction temperature did not exceed 10 °C. After being stirred for 6 h, the reaction was quenched by addition of HCl (50 mL, 3M, aq.) and extraction with Et_2O (3×15 mL). The organic layer was dried over $MgSO_4$ and concentrated to give the crude product as a color residue. The crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc = 9/1) to afford substituted cinnamyl aldehydes ((*E*)-isomers were obtained exclusively) **1b-1e, 1g, 1i, 1l-1p and 1r-1t**.

The synthesis of starting material: 1f[4]

To a stirred solution of benzophenone (3.60g, 0.02 mol) and $TiCl_4$ (2.2 ml of 1:1 solution of $TiCl_4/CH_2Cl_2$, 0.08 mol) in anhydrous DCM (30 mL) under argon at 0 °C was added Et_3N (8.10g, 0.08 mol) slowly and stirred for 0.5 h at 0 °C. After being further stirred for 8 h at 25 °C, the reaction was quenched by addition of saturated aqueous NH_4Cl solution (20 mL) and stirred for 0.5 h. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2×25 mL). The combined organic was washed with brine (10 mL) and dried over Na_2SO_4, and concentrated. The crude product was purified by column chromatography on silica gel (petroleum ether /EtOAc = 10/1) to afford the corresponding product **1f** ((*E*)-isomers were obtained exclusively).

The synthesis of starting materials: 1j, 1k[5]



Step 1: To a stirred suspension of NaH (1.96g, 0.049 mol, 60 % mineral dispersion) in anhydrous THF (30 mL) at 0 °C was added triethyl 2-phosphonopropionate (1.20g, 0.05 mol) dropwise. The reaction mixture was then heated to 40 °C and stirred for 1 h. After cooling to 0 °C, phenyl ketone (0.049 mol) was added dropwise and the resulting mixture was stirred at 40 °C for further 12 h. After then, the reaction was quenched with water. The organic layer was collected, and the aqueous layer was extracted with diethyl ether (2×25 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was subjected to flash chromatography (petroleum ether /EtOAc = 95/5) to afford the corresponding α,β-unsaturated ester .

Step 2: To a solution of unsaturated ester (0.02 mol) obtained above and anhydrous THF (30 mL) was carefully added $LiAlH_4$ (1.52g, 0.04 mol) in a few portions at 0 °C. The reaction mixture was gradually warmed to room temperature and stirred for 12 h. The reaction mixture was then cooled to 0 °C and quenched with 1 M aqueous HCl. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2×25 mL). The combined organics were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was subjected to flash chromatography (petroleum ether /EtOAc = 1/1) to afford the corresponding allylic alcohol.

Step 3: To a stirred solution of allylic alcohol (0.02 mol) obtained above and anhydrous $CHCl_3$ (30 mL) was added activated MnO_2 (5.22g, 0.06 mol). After being stirred at 60 °C for overnight, the reaction mixture was filtered through a pad of celite. The resulting filtrate was concentrated under reduced pressure. The crude product was subjected to flash chromatography (petroleum ether /EtOAc = 95/5) to afford the corresponding aldehydes **1j** and **1k** ((*E*)-isomers were obtained exclusively).

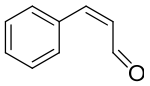
General procedure for the iron-catalyzed cyclization reaction

To a stirred solution of aldehydes **1a-1u** (0.20 mmol) in toluene (3 mL) was added sulfonylamines **2** (0.24 mmol) and $FeCl_3$ (20 mol %). The resulting mixture was stirred at 40-100 °C. After the aldehyde was completely consumed (monitored by TLC), the reaction was quenched by addition of H_2O (3 mL) and then extracted with ethyl acetate (2×5 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to afford the corresponding products.

General procedures for the removal of the *N*-tosyl group

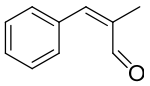
According to the procedures reported by the literatures, several conditions such as Mg/CH_3OH,[6] LAH/THF,[7] $NaOH/CH_3OH$,[8] and sodium naphthalenide solution[9] were tested to **3a** (0.5 mmol). However, these conditions result in the isolation of its C-C double bond regioisomer **3a'** exclusively.

Characterization data



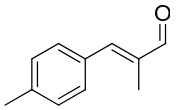
(*Z*)-cinnamaldehyde[10]

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.97 (d, J = 8.1 Hz, 1H), 7.63 (d, J = 11.6 Hz, 1H), 7.43 (m, 5H), 6.20 (dd, J = 11.6, 8.1 Hz, 1H).



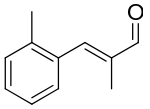
(*Z*)-2-methyl-3-phenylacrylaldehyde ((*Z*)-1a)[10]

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.90 (s, 1H), 7.60 (s, 1H), 7.39-7.30 (m, 5H), 1.98 (s, 3H).



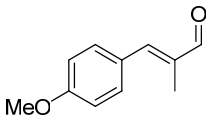
(*E*)-2-methyl-3-*p*-tolylacrylaldehyde (1b)

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.55 (s, 1H), 7.44 (d, J = 8.0 Hz, 2H), 7.26-7.21 (m, 3H), 2.39 (s, 3H), 2.07 (s, 3H).



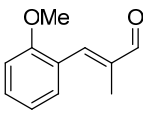
(*E*)-2-methyl-3-*o*-tolylacrylaldehyde (1c)

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.65 (s, 1H), 7.45 (s, 1H), 7.35-7.26 (m, 4H), 2.36 (s, 3H), 1.94 (s, 3H).



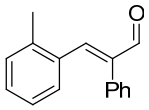
(*E*)-3-(4-methoxyphenyl)-2-methylacrylaldehyde (1d)

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.51 (s, 1H), 7.52 (d, J = 8.7 Hz, 2H), 7.16 (s, 1H), 6.96 (d, J = 8.7 Hz, 2H), 3.83 (s, 3H), 2.06 (s, 3H).



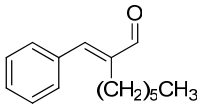
(*E*)-3-(2-methoxyphenyl)-2-methylacrylaldehyde (1e)

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.60 (s, 1H), 7.6 (s, 1H), 7.45-7.35 (m, 2H), 7.02-6.93 (m, 3H), 3.87 (s, 3H), 2.00 (s, 3H).



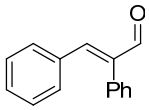
(*E*)-2-phenyl-3-*o*-tolylacrylaldehyde (1g)

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.65 (s, 1H), 7.46-7.31 (m, 4H), 7.27-7.22 (m, 4H), 7.17-7.15 (m, 2H), 6.87 (t, J = 7.6 Hz, 1H), 3.70 (d, J = 7.6 Hz, 3H).



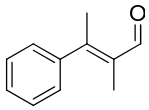
(*E*)-α-hexylcinnamaldehyde (1h)

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.55 (s, 1H), 7.51-7.39 (m, 5H), 7.21 (s, 1H), 2.54-2.50 (m, 2H), 1.53-1.29 (m, 10H), 0.88 (m, 3H).



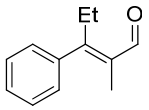
(*E*)-2,3-diphenylacrylaldehyde (1i)

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.77 (s, 1H), 7.43-7.39 (m, 4H), 7.29-7.19 (m, 7H).



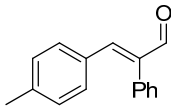
(*E*)-2-methyl-3-phenylbut-2-enal (1j)

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.45 (s, 1H), 7.38 (d, J = 5.6 Hz, 3H), 7.26-7.20 (m, 2H), 2.28 (s, 3H), 1.92 (s, 3H).



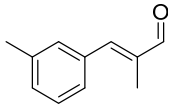
(*E*)-2-methyl-3-phenylpent-2-enal (1k)

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.31 (s, 1H), 7.42-7.26 (m, 3H), 7.16-7.14 (m, 2H), 2.92 (dd, J = 7.5 Hz, 2H), 1.62 (s, 3H), 1.06 (t, J = 7.5 Hz, 3H).



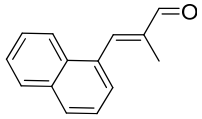
(*E*)-2-phenyl-3-*p*-tolylacrylaldehyde (1l)

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.74 (s, 1H), 7.41-7.35 (m, 4H), 7.20-7.02 (m, 6H), 2.30 (s, 3H).



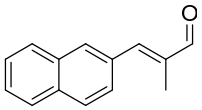
(*E*)-2-methyl-3-*m*-tolylacrylaldehyde (1m)

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.57 (s, 1H), 7.34-7.21(m, 5H), 2.40 (s, 3H), 2.08 (s, 3H).



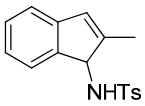
(*E*)-2-methyl-3-(naphthalen-1-yl)acrylaldehyde (1o)

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.77 (s, 1H), 7.94-7.87 (m, 4H), 7.55-7.47 (m, 4H), 1.96 (s, 3H).



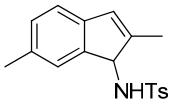
(*E*)-2-methyl-3-(naphthalen-2-yl)acrylaldehyde (1p)

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.63 (s, 1H), 7.99 (s, 1H), 7.87-7.84 (m, 3H), 7.63-7.53 (m, 3H), 7.40 (s, 1H), 2.17 (s, 3H).



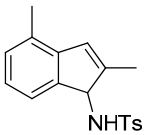
4-methyl-*N*-(2-methyl-1*H*-inden-1-yl)benzenesulfonamide (3a): 59 mg, 98%.

White solid; m.p. 130-132 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J = 8.2 Hz, 2H), 7.37- 6.75 (m, 7H), 6.32 (s, 1H), 4.70 (d, J = 9.5 Hz, 1H), 4.54 (d, J = 9.5 Hz, 1H), 2.47 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.9, 143.5, 143.3, 143.1, 138.4, 129.7, 128.3, 127.7, 127.1, 124.8, 123.2, 120.2, 62.3, 21.5, 13.7; HRMS (ESI, *m/z*) calcd for $C_{17}H_{21}N_2O_2S$ $[M+NH_4]^+$: 317.1318. Found: 317.1315.



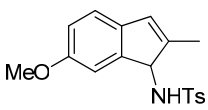
***N*-(2,6-dimethyl-1*H*-inden-1-yl)-4-methylbenzenesulfonamide (3b): 58 mg, 92%.**

White solid; m.p. 145-147 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J = 8.2 Hz, 2H), 7.38-7.25 (m, 3H), 6.95 (s, 2H), 6.39 (s, 1H), 6.27 (s, 1H), 4.66 (d, J = 9.5 Hz, 1H), 4.50 (d, J = 9.5 Hz, 1H), 2.49 (s, 3H), 2.16 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 143.6, 143.5, 140.4, 138.5, 134.5, 129.8, 128.7, 127.5, 127.3, 124.4, 119.8, 62.2, 21.5, 21.1, 13.7; HRMS (ESI, *m/z*) calcd for $C_{18}H_{19}NNaO_2S$ $[M+Na]^+$: 336.1029. Found: 336.1036.



***N*-(2,4-dimethyl-1*H*-inden-1-yl)-4-methylbenzenesulfonamide (3c): 61 mg, 98%.**

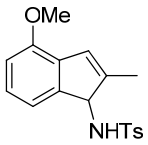
White solid; m.p. 147-148 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J = 8.2 Hz, 2H), 7.37-7.25 (m, 3H), 6.97 (d, J = 7.6 Hz, 1H), 6.85 (t, J = 7.5 Hz, 1H), 6.57 (d, J = 7.4 Hz, 1H), 6.43 (s, 1H), 4.70 (d, J = 9.6 Hz, 1H), 4.49 (d, J = 9.6 Hz, 1H), 2.47 (s, 3H), 2.28 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 143.5, 143.2, 143.7, 138.4, 129.8, 129.5, 129.4, 127.2, 125.9, 124.9, 120.6, 62.6, 21.5, 18.0, 13.9; HRMS (APCI, *m/z*) calcd for $C_{18}H_{20}NO_2S$ $[M+H]^+$: 314.1029. Found: 314.1216.



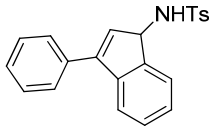
***N*-(6-methoxy-2-methyl-1*H*-inden-1-yl)-4-methylbenzenesulfonamide (3d): 43 mg, 65%.**

White solid; m.p. 140-141 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 8.3 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.26 (s, 1H), 6.97 (d, J = 8.2 Hz, 1H), 6.70 (d, J = 8.1 Hz, 1H), 6.29-6.26 (m, 2H),

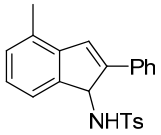
4.69 (d, J = 9.6 Hz, 1H), 4.50 (d, J = 9.6 Hz, 1H), 3.61 (s, 3H), 2.46 (s, 3H), 1.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.7, 145.1, 143.6, 143.5, 138.6, 135.8, 129.7, 127.1, 120.5, 113.8, 109.7, 62.3, 55.2, 21.4, 13.6; HRMS (ESI, *m/z*) calcd for $C_{18}H_{19}NNaO_3S$ $[M+Na]^+$: 352.0978. Found: 352.0982.



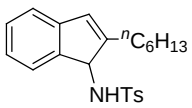
***N*-(4-methoxy-2-methyl-1*H*-inden-1-yl)-4-methylbenzenesulfonamide (3e): 53 mg, 81%.**
White solid; m.p. 145-146 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 8.1 Hz, 2H), 7.37-7.26 (m, 3H), 6.96-6.92 (m, 1H), 6.73 (d, J = 8.2 Hz, 1H), 6.47-6.42 (m, 2H), 4.71 (d, J = 9.6 Hz, 1H), 4.51 (d, J = 9.6 Hz, 1H), 3.80 (s, 3H), 2.47 (s, 3H), 1.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 145.2, 143.9, 143.4, 138.4, 131.1, 129.6, 127.1, 126.1, 123.7, 116.1, 110.8, 62.6, 55.3, 21.4, 13.7; HRMS (ESI, *m/z*) calcd for $C_{18}H_{19}NNaO_3S$ $[M+Na]^+$: 352.0978. Found: 352.0986.



4-methyl-*N*-(3-phenyl-1*H*-inden-1-yl)benzenesulfonamide (3f): 48 mg, 67%.
White solid; m.p. 115-117 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, J = 8.2 Hz, 2H), 7.46-7.33 (m, 8H), 7.32-7.29 (m, 2H), 7.26-7.22 (m, 2H), 6.08 (s, 1H), 5.05 (d, J = 9.7 Hz, 1H), 4.59 (d, J = 9.7 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.1, 144.2, 143.6, 141.8, 138.0, 134.4, 130.9, 129.8, 128.6, 128.4, 128.3, 127.4, 127.2, 126.4, 124.1, 120.8, 59.4, 21.5; HRMS (ESI, *m/z*) calcd for $C_{22}H_{19}NNaO_2S$ $[M+Na]^+$: 384.1029. Found: 384.1037.

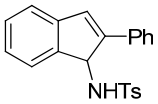


4-methyl-*N*-(4-methyl-2-phenyl-1*H*-inden-1-yl)benzenesulfonamide (3g): 61 mg, 81%.
White solid; m.p. 147-148 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 8.2 Hz, 2H), 7.34-7.32 (m, 4H), 7.25-7.19 (m, 4H), 7.10-7.07 (m, 1H), 7.05-6.97 (m, 3H), 5.45 (d, J = 9.0 Hz, 1H), 4.47 (d, J = 9.0 Hz, 1H), 2.49 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.8, 144.3, 143.8, 141.0, 138.7, 133.6, 130.8, 130.0, 128.7, 128.0, 127.7, 127.2, 127.1, 126.5, 122.3, 60.0, 21.8, 18.3; HRMS (ESI, *m/z*) calcd for $C_{23}H_{21}NNaO_2S$ $[M+Na]^+$: 398.1185. Found: 398.1184.



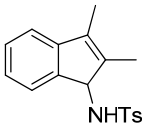
***N*-(2-hexyl-1*H*-inden-1-yl)-4-methylbenzenesulfonamide (3h): 68 mg, 92%.**
White solid; m.p. 90-92 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.17-7.13 (m, 1H), 7.08 (d, J = 7.3 Hz, 1H), 6.98-6.94 (m, 1H), 6.87 (m, 1H), 6.31 (s, 1H), 4.75 (d, J = 9.6 Hz, 1H), 4.55 (d, J = 9.6 Hz, 1H), 2.46 (s, 3H), 2.24-2.08 (m, 2H), 1.37-1.22 (m, 8H), 0.90 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 143.5, 143.4, 143.0, 138.5, 129.7,

128.3, 127.2, 126.6, 124.9, 123.5, 120.2, 61.2, 31.5, 29.0, 28.1, 27.9, 22.5, 21.4, 14.0; HRMS (ESI, *m/z*) calcd for $C_{22}H_{27}NNaO_2S$ $[M+Na]^+$: 392.1655. Found: 392.1659.



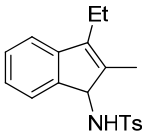
4-methyl-*N*-(2-phenyl-1*H*-inden-1-yl)benzenesulfonamide (3i): 62 mg, 86%.

White solid; m.p. 145-146 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 8.1 Hz, 2H), 7.35-7.21 (m, 10H), 7.09 (m, 1H), 7.00 (m, 1H), 5.44 (d, J = 9.1 Hz, 1H), 4.51 (d, J = 9.1 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.2, 144.1, 143.6, 142.1, 138.4, 133.2, 129.7, 128.7, 128.6, 128.5, 127.8, 127.4, 126.8, 126.2, 124.6, 121.2, 59.5, 21.5; HRMS (ESI, *m/z*) calcd for $C_{22}H_{19}NNaO_2S$ $[M+Na]^+$: 384.1029. Found: 384.1034.



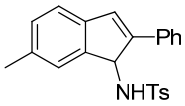
***N*-(2,3-dimethyl-1*H*-inden-1-yl)-4-methylbenzenesulfonamide (3j): 53 mg, 85%.**

White solid; m.p. 175-176 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.26-7.20 (m, 2H), 7.08 (d, J = 7.4 Hz, 1H), 7.00 (t, J = 7.4 Hz, 1H), 6.77 (d, J = 7.3 Hz, 1H), 4.69 (d, J = 9.2 Hz, 1H), 4.44 (d, J = 9.2 Hz, 1H), 2.48 (s, 3H), 1.94 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.1, 143.5, 142.7, 138.6, 137.8, 134.0, 129.8, 128.2, 127.2, 125.0, 122.9, 118.2, 62.3, 21.5, 11.0, 10.2; HRMS (ESI, *m/z*) calcd for $C_{18}H_{19}NNaO_2S$ $[M+Na]^+$: 336.1029. Found: 336.1035.



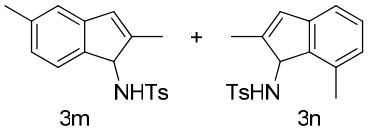
***N*-(3-ethyl-2-methyl-1*H*-inden-1-yl)-4-methylbenzenesulfonamide (3k): 49 mg, 75%.**

White solid; m.p. 159-160 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 8.1 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.25-7.10 (m, 3H), 6.98 (t, J = 7.2 Hz, 1H), 6.77 (d, J = 7.5 Hz, 1H), 4.69 (d, J = 9.3 Hz, 1H), 4.44 (d, J = 9.3 Hz, 1H), 2.47 (s, 3H), 2.42 (m, 2H), 1.81 (s, 3H), 1.10 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.1, 143.4, 143.0, 139.9, 138.6, 137.3, 129.7, 128.1, 127.2, 124.8, 123.1, 118.4, 62.3, 21.5, 18.3, 12.8, 10.8; HRMS (APCI, *m/z*) calcd for $C_{19}H_{22}NO_2S$ $[M+H]^+$: 328.1366. Found: 328.1372.



4-methyl-*N*-(6-methyl-2-phenyl-1*H*-inden-1-yl)benzenesulfonamide (3l): 62 mg, 83%.

White solid; m.p. 168-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, J = 8.2 Hz, 2H), 7.36-7.33 (m, 4H), 7.25-7.21 (m, 4H), 7.12 (d, J = 8.0 Hz, 1H), 7.03 (d, J = 8.0 Hz, 1H), 6.96 (s, 1H), 6.71 (s, 1H), 5.41 (d, J = 9.2 Hz, 1H), 4.49 (d, J = 9.2 Hz, 1H), 2.50 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.2, 144.3, 143.6, 139.4, 138.7, 136.1, 133.3, 129.8, 129.1, 128.5, 127.6, 127.6, 126.7, 125.5, 120.9, 59.4, 21.5, 21.3; HRMS (ESI, *m/z*) calcd for $C_{23}H_{21}NNaO_2S$ $[M+Na]^+$: 398.1185. Found: 398.1187.



3m 3n

***N*-(2,5-dimethyl-1*H*-inden-1-yl)-4-methylbenzenesulfonamide (3m)**

***N*-(2,7-dimethyl-1*H*-inden-1-yl)-4-methylbenzenesulfonamide (3n)**

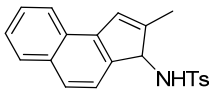
White solid as mixture of unseparated two cyclization products: **3m** : **3n** = 2.3 : 1 (determine by ^{1}H NMR), 56mg, 90%. HRMS (ESI, *m/z*) calcd for $C_{18}H_{19}NNaO_2S$ $[M+Na]^+$: 336.1029. Found: 336.1030.

3m:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.1 Hz, 2H), 7.26 (d, J = 8.1 Hz, 2H), 7.07-6.70 (m, 3H), 6.23 (s, 1H), 4.84 (d, J = 9.3 Hz, 1H), 4.45 (d, J = 9.3 Hz, 1H), 2.42 (s, 3H), 2.11 (s, 3H), 1.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.1, 143.2, 143.1, 139.9, 139.2, 134.3, 129.4, 128.4, 127.1, 126.8, 125.3, 117.8, 62.3, 21.4, 17.9, 14.3.

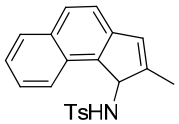
3n:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.07-6.70 (m, 3H), 6.72-6.56 (m, 1H), 4.62 (s, 2H), 2.46 (s, 3H), 2.25 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.2, 143.4, 143.3, 140.4, 138.5, 138.0, 129.6, 128.1, 127.6, 122.9, 121.0, 62.0, 21.5, 21.2, 13.8.



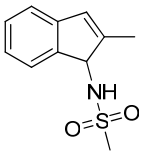
4-methyl-*N*-(2-methyl-3*H*-cyclopenta[a]naphthalen-3-yl)benzenesulfonamide (3o): 51mg, 73%.

White solid; m.p. 148-150 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89-7.76 (m, 4H), 7.49-7.34 (m, 5H), 6.98 (d, J = 8.3 Hz, 1H), 6.86 (s, 1H), 4.82 (d, J = 9.7 Hz, 1H), 4.64 (d, J = 9.7 Hz, 1H), 2.47 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5, 143.6, 140.1, 139.4, 138.4, 133.6, 129.8, 128.3, 127.2, 126.8, 125.8, 125.6, 125.0, 124.9, 123.7, 121.1, 63.2, 21.6, 14.0; HRMS (ESI, *m/z*) calcd for $C_{21}H_{19}NNaO_2S$ $[M+Na]^+$: 372.1029. Found: 372.1040.



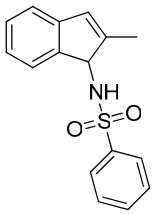
4-methyl-*N*-(2-methyl-1*H*-cyclopenta[a]naphthalen-1-yl)benzenesulfonamide (3p): 67mg, 90%.

White solid; m.p. 181-182 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72-7.58 (m, 5H), 7.20-7.11 (m, 6H), 6.32 (s, 1H), 5.07 (d, J = 9.1 Hz, 1H), 4.58 (d, J = 9.1 Hz, 1H), 2.37 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3, 143.4, 141.4, 138.9, 136.6, 131.8, 129.6, 129.5, 129.2, 128.7, 128.2, 127.1, 126.4, 124.3, 122.7, 119.6, 62.3, 21.5, 14.4; HRMS (ESI, *m/z*) calcd for $C_{21}H_{19}NNaO_2S$ $[M+Na]^+$: 372.1029. Found: 372.1033.



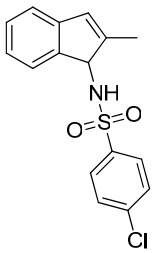
***N*-(2-methyl-1*H*-inden-1-yl)methanesulfonamide (3af): 41mg, 91%.**

White solid; m.p. 98-99 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 7.4 Hz, 1H), 7.20 (t, J = 7.4 Hz, 1H), 7.11-7.08 (m, 2H), 6.36 (s, 1H), 4.72 (d, J = 9.6 Hz, 1H), 4.58 (d, J = 9.6 Hz, 1H), 3.07 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.4, 143.4, 143.0, 128.4, 127.9, 124.9, 123.4, 120.3, 62.5, 42.3, 13.9; HRMS (ESI, *m/z*) calcd for $C_{11}H_{13}NNaO_2S$ $[M+Na]^+$: 246.0559. Found: 246.0560.



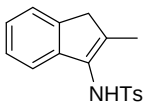
***N*-(2-methyl-1*H*-inden-1-yl)benzenesulfonamide (3ag): 47mg, 82%.**

White solid; m.p. 137-139 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 7.6 Hz, 2H), 7.65-7.53 (m, 3H), 7.18-7.01 (m, 2H), 6.91 (t, J = 7.4 Hz, 1H), 6.68 (d, J = 7.4 Hz, 1H), 6.30 (s, 1H), 4.67 (s, 2H), 1.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.7, 143.2, 143.0, 141.4, 132.7, 129.1, 128.3, 127.8, 127.0, 124.8, 123.2, 120.2, 62.3, 13.7; HRMS (ESI, *m/z*) calcd for $C_{16}H_{15}NNaO_2S$ $[M+Na]^+$: 308.0716. Found: 308.0715.



4-chloro-*N*-(2-methyl-1*H*-inden-1-yl)benzenesulfonamide (3ah): 56mg, 87%.

White solid; m.p. 125-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.3 Hz, 2H), 7.16-6.94 (m, 3H), 6.81 (d, J = 7.3 Hz, 1H), 6.30 (s, 1H), 4.81 (d, J = 9.1 Hz, 1H), 4.64 (d, J = 9.0 Hz, 1H), 1.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.4, 143.1, 143.0, 140.0, 139.1, 129.4, 128.5, 128.4, 128.0, 124.9, 123.2, 120.3, 62.4, 13.8; HRMS (ESI, *m/z*) calcd for $C_{16}H_{14}NNaO_2SCl$ $[M+Na]^+$: 342.0326. Found: 342.0327.



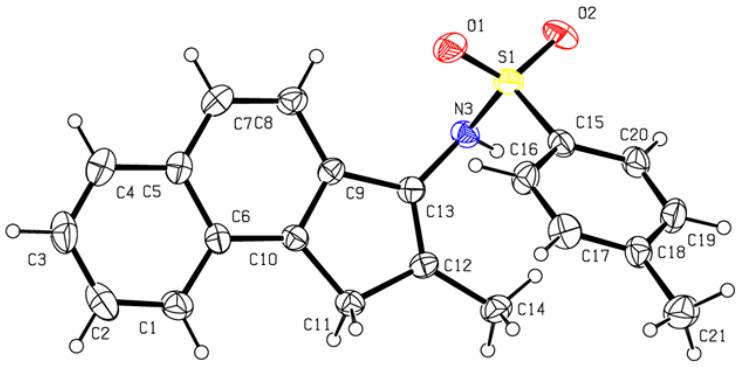
4-methyl-*N*-(2-methyl-1*H*-inden-3-yl)benzenesulfonamide (3a')

White solid; m.p. 122-123 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 6.9 Hz, 1H), 7.22-7.03 (m, 5H), 6.17 (s, 1H), 3.26 (s, 2H), 2.38 (s, 3H), 1.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.6, 142.3, 141.1, 140.3, 137.0, 130.7, 129.4, 127.2, 126.1, 124.5, 123.3, 118.4, 40.7, 21.4, 13.2.

Crystallographic data

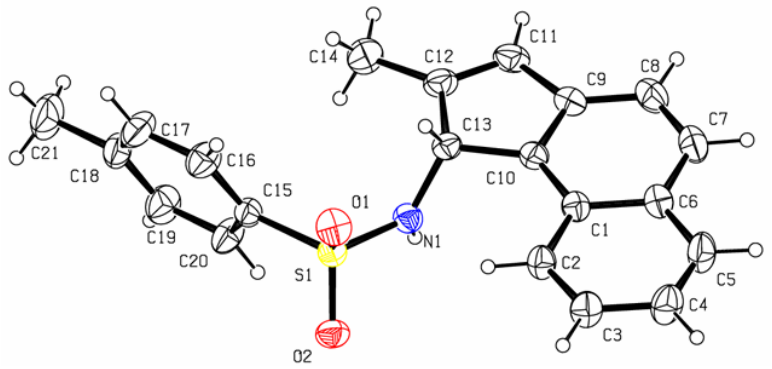
CCDC 965332 (**3o'**) and 965333 (**3p**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

X-ray Crystallographic data of 3o'



Empirical formula	$C_{21}H_{19}NO_2S$
Formula weight	349.43
Temperature/K	301.19(10)
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	10.2086(5)
b/Å	7.3342(6)
c/Å	23.4547(12)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/$Å^3$	1756.09(19)
Z	4
$\rho_{calc}mg/mm^3$	1.322
m/mm^{-1}	0.198
F(000)	736.0
Crystal size/mm^3	0.11 × 0.1 × 0.06
2Θ range for data collection	6.84 to 52.04°
Index ranges	$-12 \le h \le 12$, $-7 \le k \le 9$, $-28 \le l \le 14$
Reflections collected	4431
Independent reflections	2372[R(int) = 0.0480]
Data/restraints/parameters	2372/1/232
Goodness-of-fit on F^2	1.015
Final R indexes [I>=2σ (I)]	$R_1 = 0.0492$, $wR_2 = 0.0806$
Final R indexes [all data]	$R_1 = 0.0771$, $wR_2 = 0.0940$
Largest diff. peak/hole / e $Å^{-3}$	0.18/-0.26
Flack parameter	0.06(12)

X-ray Crystallographic data of 3p



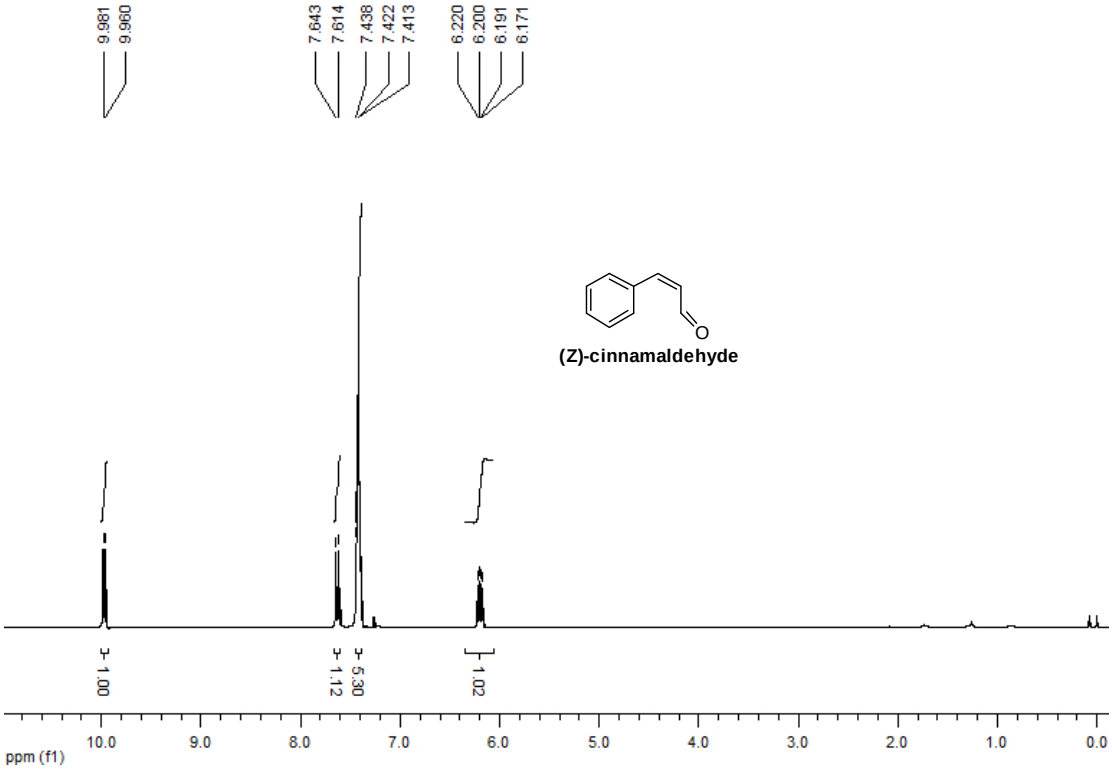
Empirical formula	$C_{21}H_{19}NO_2S$
Formula weight	349.43
Temperature/K	293.80(10)
Crystal system	triclinic
Space group	P-1
a/Å	8.5924(14)
b/Å	10.4758(18)
c/Å	10.797(2)
α/°	97.496(15)
β/°	111.360(17)
γ/°	90.383(14)
Volume/Å^3	895.8(3)
Z	2
ρ_{calc}mg/mm^3	1.295
m/mm^{-1}	0.194
F(000)	368.0
Crystal size/mm^3	0.36 × 0.34 × 0.28
2Θ range for data collection	6.38 to 52.02°
Index ranges	$-10 \le h \le 10$, $-12 \le k \le 12$, $-13 \le l \le 12$
Reflections collected	5643
Independent reflections	3519[R(int) = 0.0255]
Data/restraints/parameters	3519/42/232
Goodness-of-fit on F^2	1.104
Final R indexes [I>=2σ (I)]	R_1 = 0.0566, wR_2 = 0.1392
Final R indexes [all data]	R_1 = 0.0780, wR_2 = 0.1524
Largest diff. peak/hole / e Å^{-3}	0.35/-0.35

References

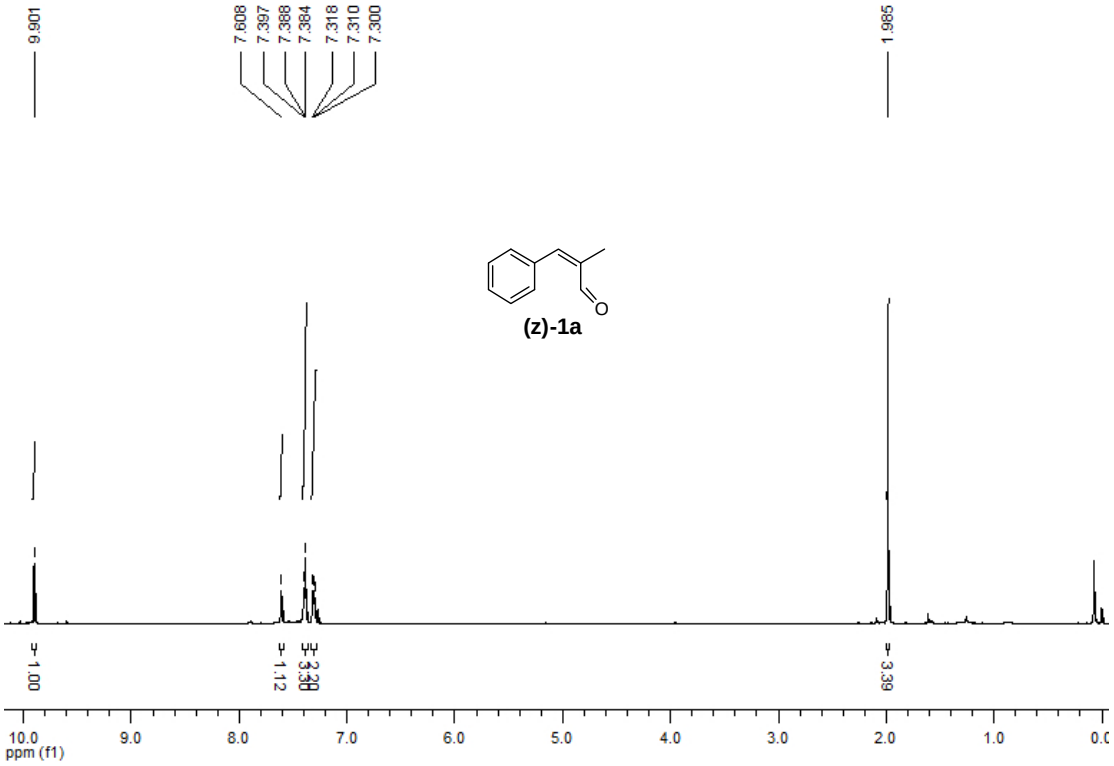
1. W. B. Jennings, C. J. Lovely, *Tetrahedron Lett.,* 1988, **29**, 3725.
2. (a) C. Gignoux, A. F. Newton, A. Barthelme, W. Lewis, M, -L. Alcaraz*b*, R. A. Stockman, *Org. Biomol. Chem*., 2012, **10**, 67; (b) S. Pachali, C. Hofmann, G. Rapp, R. Schobert, A. Baro, W. Frey, S. Laschat, *Eur. J. Org. Chem.,* 2009, **17**, 2828; (c) K. Ando, *J. Org. Chem.,* 1998, **63***,* 8411.
3. M. Larsson, H. –E. Högberg, *Tetrahedron* 2001, **57**, 7541.
4. P. Bharathi, M. Periasamy, *Org. Lett.,* 1999, **1**, 857.
5. J. Mo, X, K. Chen, Y, R. Chi, *J. Am. Chem. Soc.,* 2012, **134**, 8810.
6. M. T. Barry, M. S. Steven, *J. Am. Chem. Soc.,* 2012, **134**, 494.
7. E. S. Erica, S. Richmond, *J. Am. Chem. Soc.,* 2013, **135**, 4696.
8. J. Biao, C.-G. Yang, J. Wang, *J. Org. Chem.*, 2001, **66**, 4865.
9. M. Bongjin, H. Sangbae, Y. Yeojin, K. Hyejin, *Org. Lett.,* 2005, **7**,1031.
10. M. Bellassoued, A. Majidi, *J. Org. Chem.,* 1993, **58**, 2517.

^{1}H and ^{13}C NMR Spectra

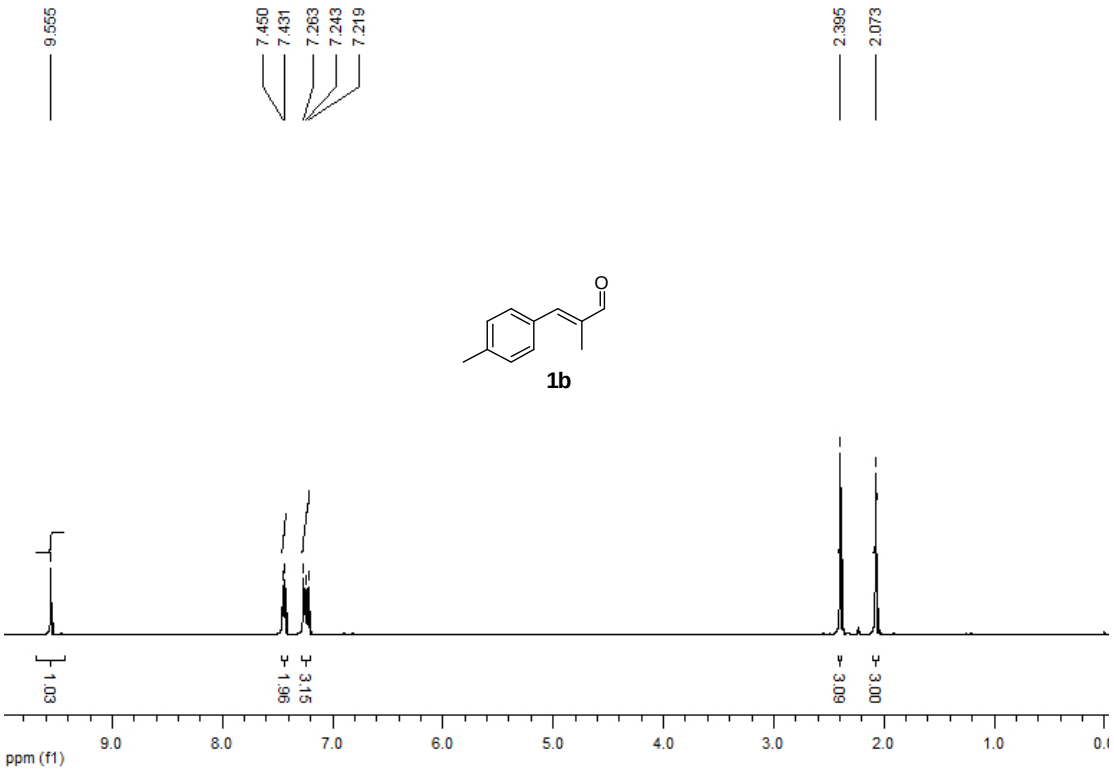
^{1}H NMR



^{1}H NMR



^{1}H NMR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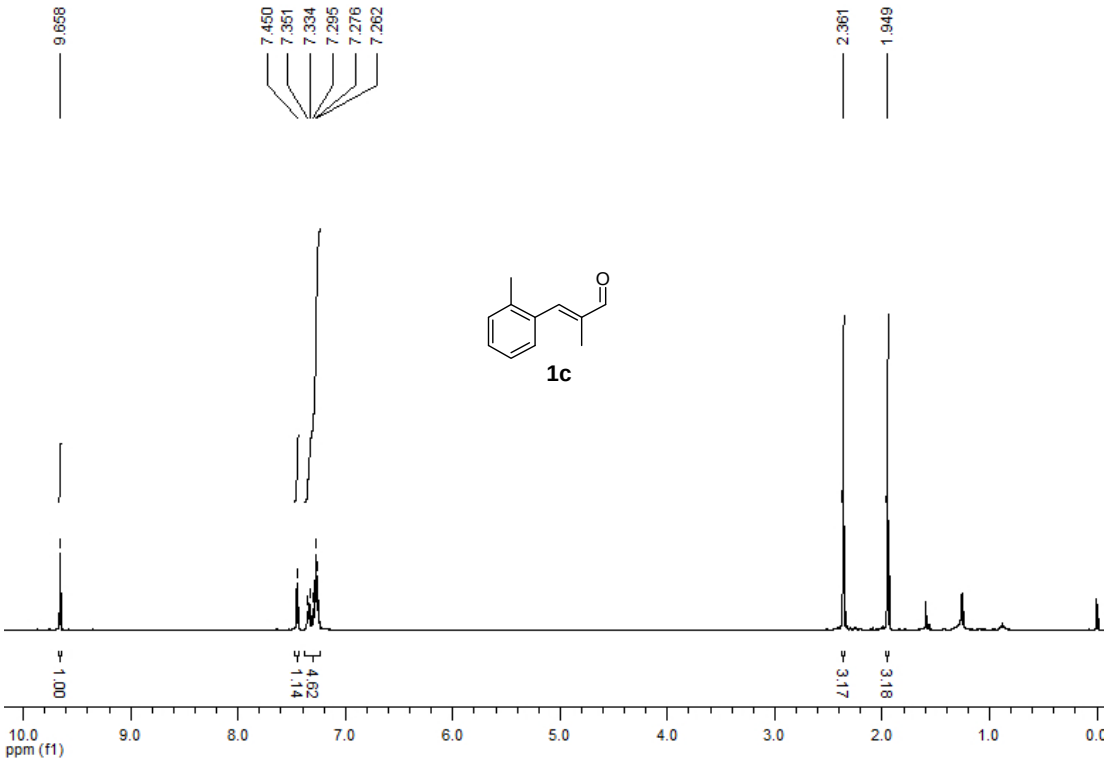
7.450
7.431
7.263
7.243
7.219
2.395
2.073
1b
1.03
1.96
3.15
3.09
3.00
ppm (f1)

^{1}H NMR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7.450
7.351
7.334
7.295
7.276
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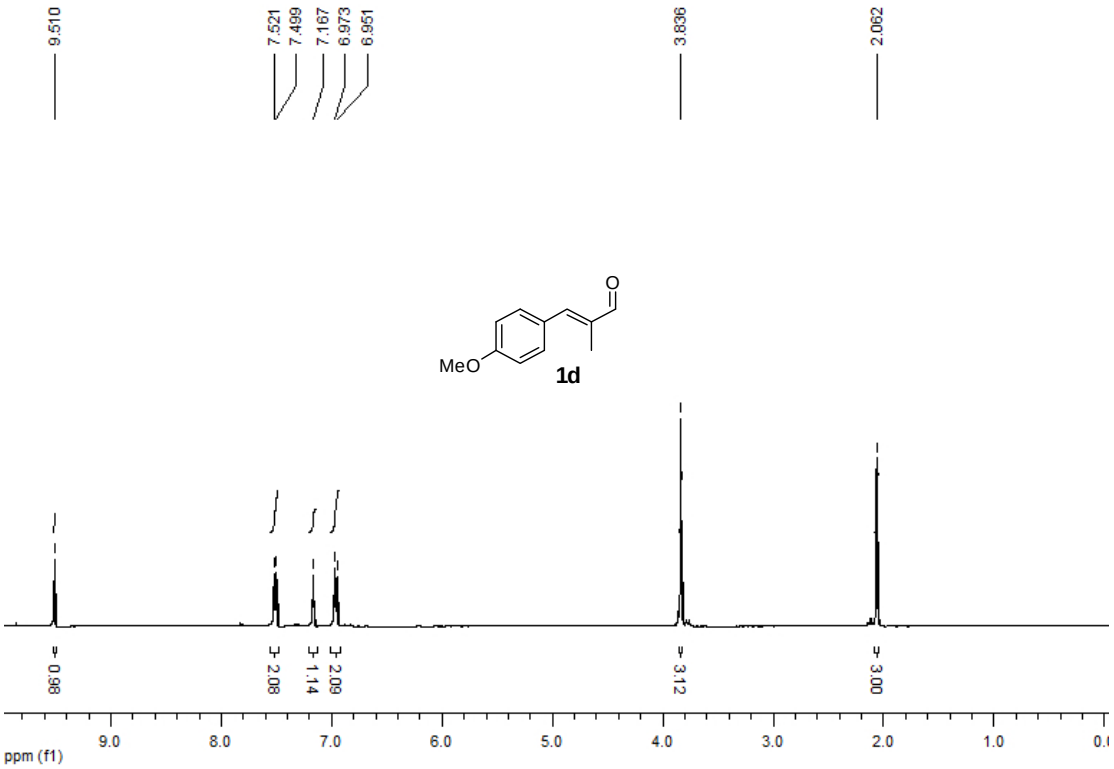
1c
1.00
4.92
1.14
3.17
3.18
ppm (f1)

^{1}H NMR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7.521
7.499
7.167
6.973
6.951
3.836
2.062
MeO
O
1d
0.98
2.08
1.14
2.09
3.12
3.00
9.0
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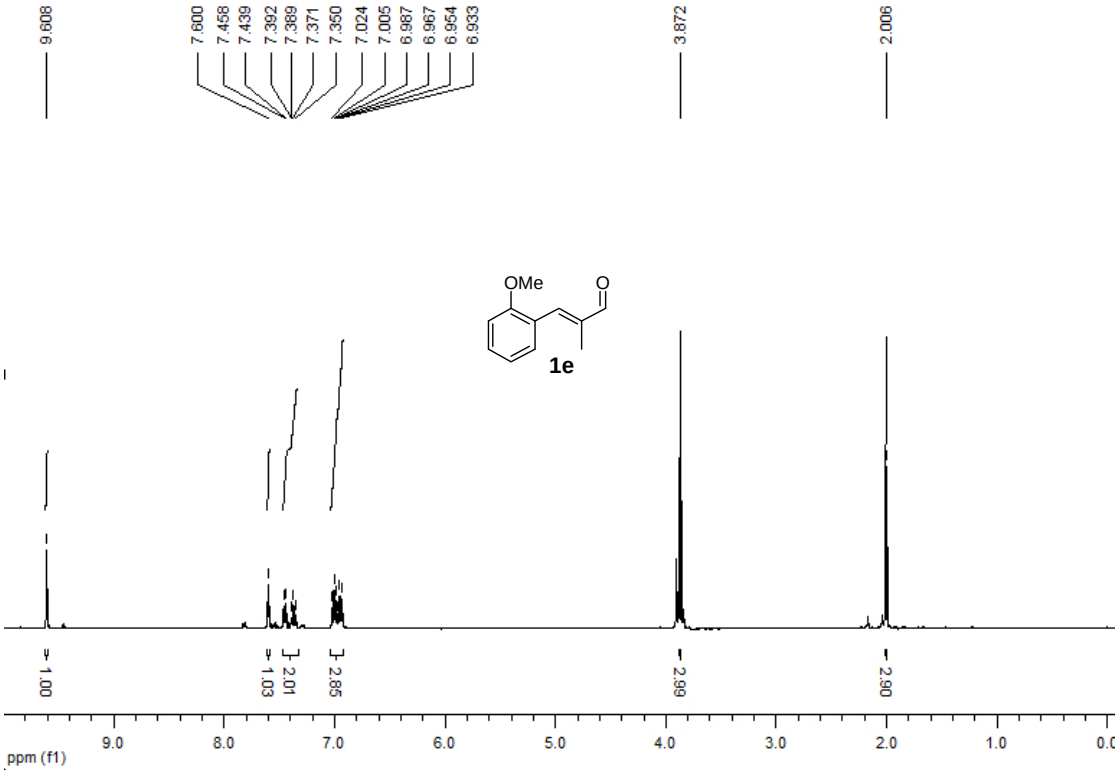
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

^{1}H NMR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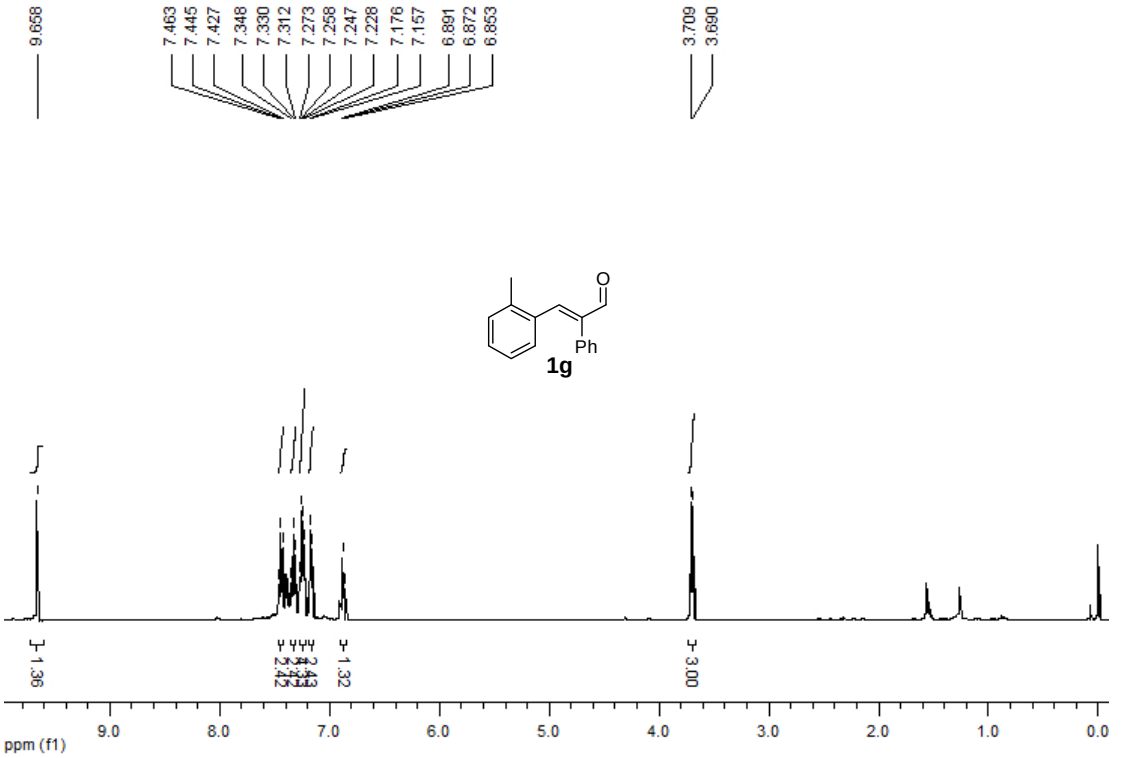
7.600
7.458
7.439
7.392
7.389
7.371
7.350
7.024
7.005
6.987
6.967
6.954
6.933
3.872
2.006
OMe
O
1e
1.00
1.03
2.01
2.85
2.99
2.90
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

^{1}H NMR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7.445
7.427
7.348
7.330
7.312
7.273
7.258
7.247
7.228
7.176
7.157
6.891
6.872
6.853
3.709
3.690
O
Ph
1g
1.36
2.42
1.32
3.00
9.0
8.0
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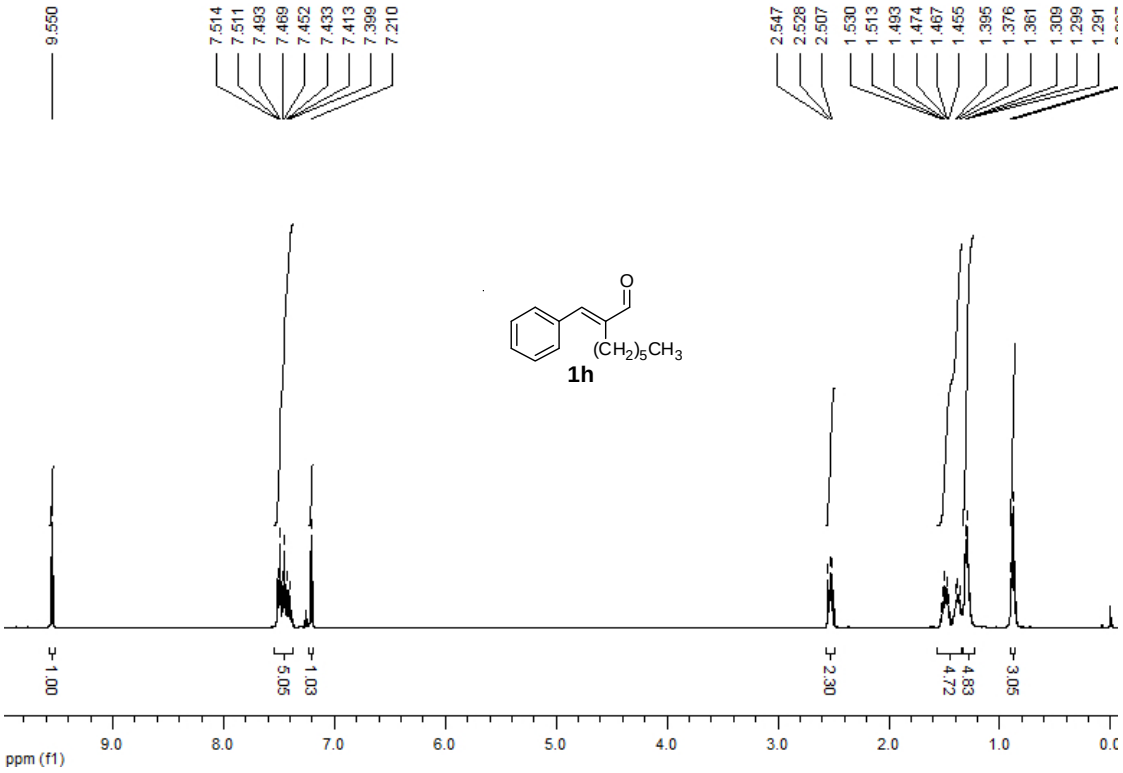
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

^{1}H NMR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7.511
7.493
7.469
7.452
7.433
7.413
7.399
7.210
2.547
2.528
2.507
1.530
1.513
1.493
1.474
1.467
1.455
1.395
1.376
1.361
1.309
1.299
1.291
O
(CH2)5CH3
1h
1.00
5.05
1.03
2.30
4.83
4.72
3.05
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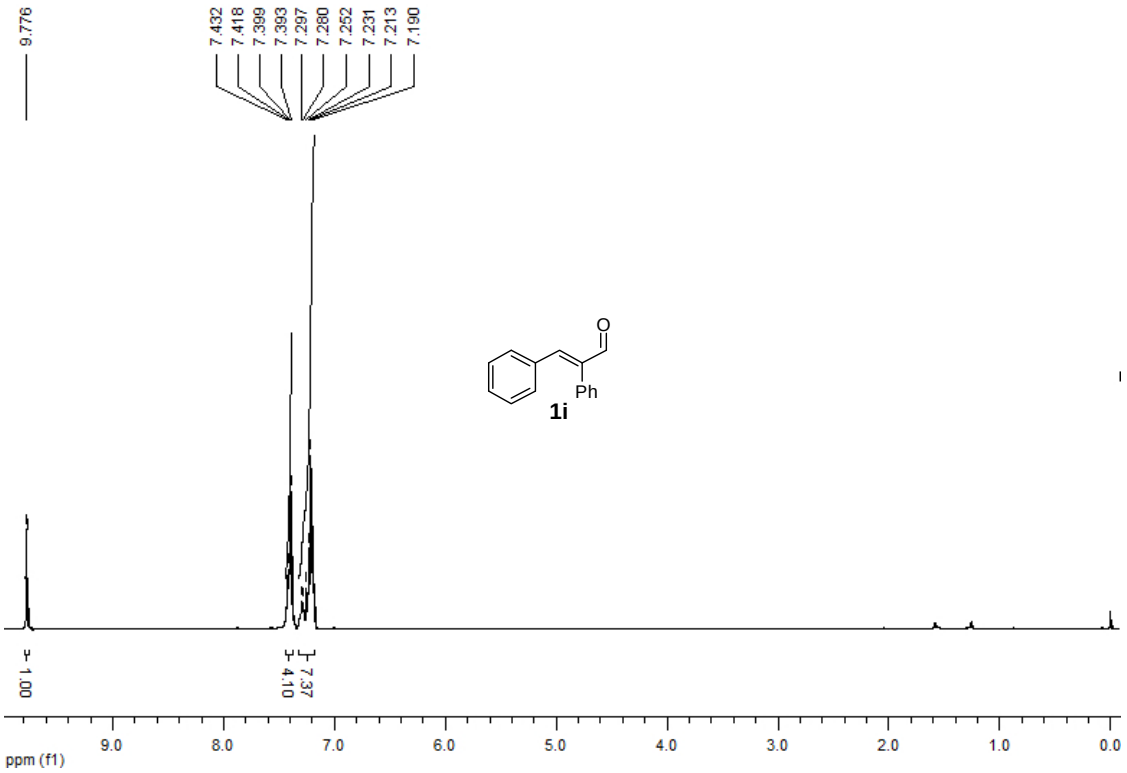
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

^{1}H NMR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7.432
7.418
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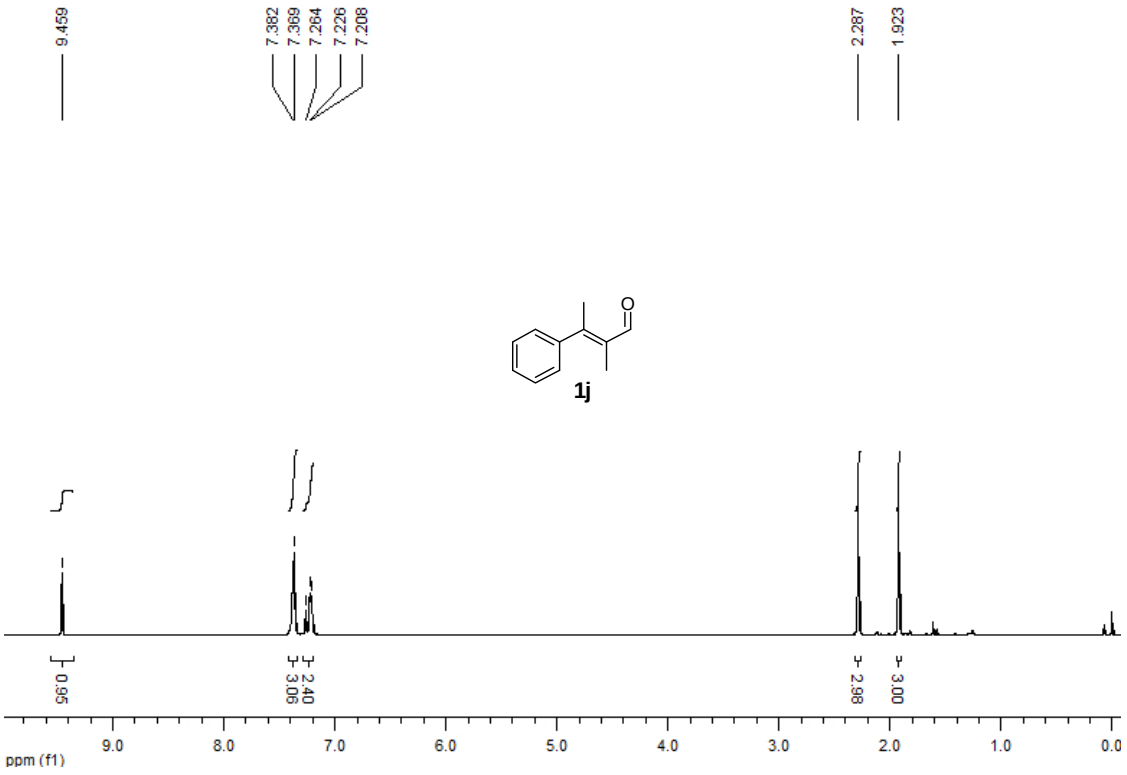
7.280
7.252
7.231
7.213
7.190
O
Ph
1i
1.00
7.37
4.10
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

^{1}H NMR


9.459
7.382
7.369
7.264
7.226
7.208
2.287
1.923
O
1j
0.95
3.06
2.40
2.98
3.00
9.0
8.0
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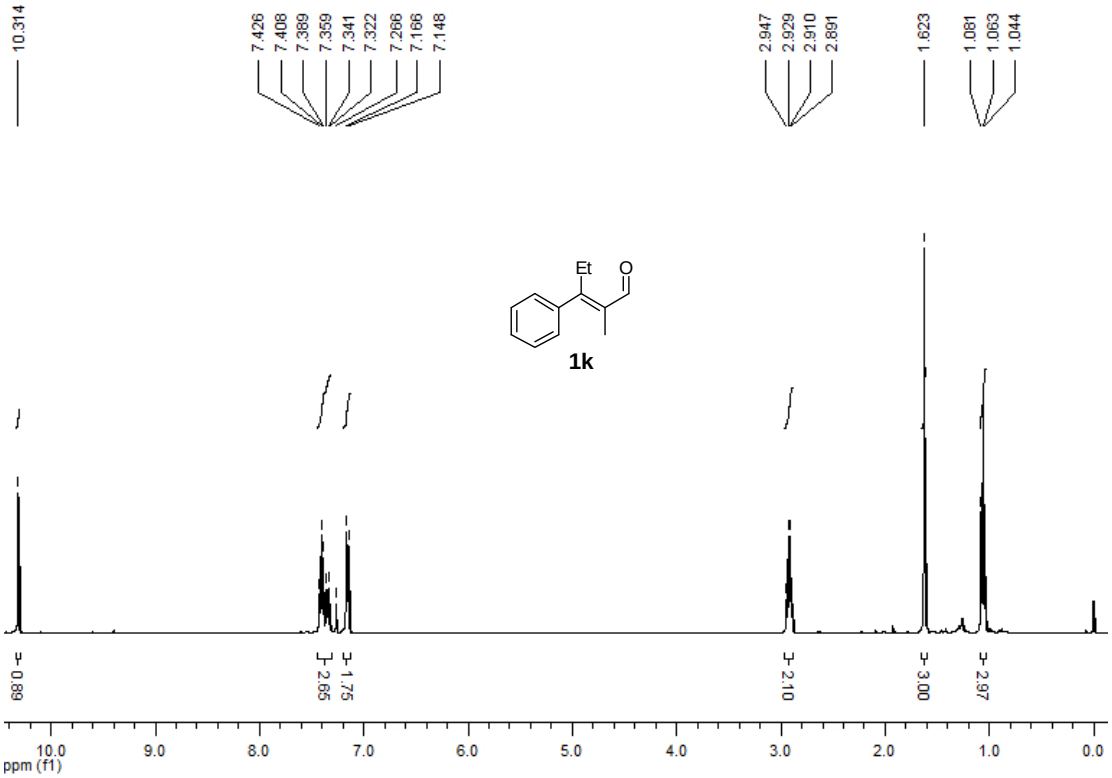
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

^{1}H NMR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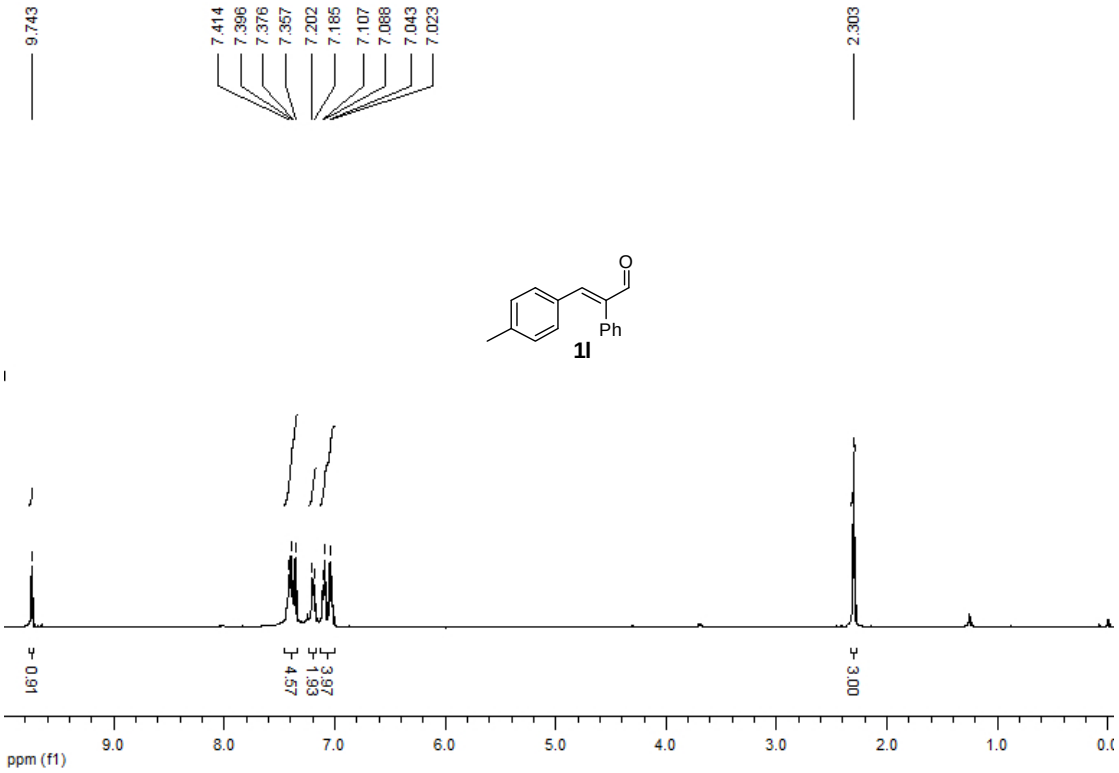
7.389
7.359
7.341
7.322
7.266
7.166
7.148
2.947
2.929
2.910
2.891
1.623
1.081
1.063
1.044
Et
O
1k
0.89
2.66
1.75
2.10
3.00
2.97
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

^{1}H NMR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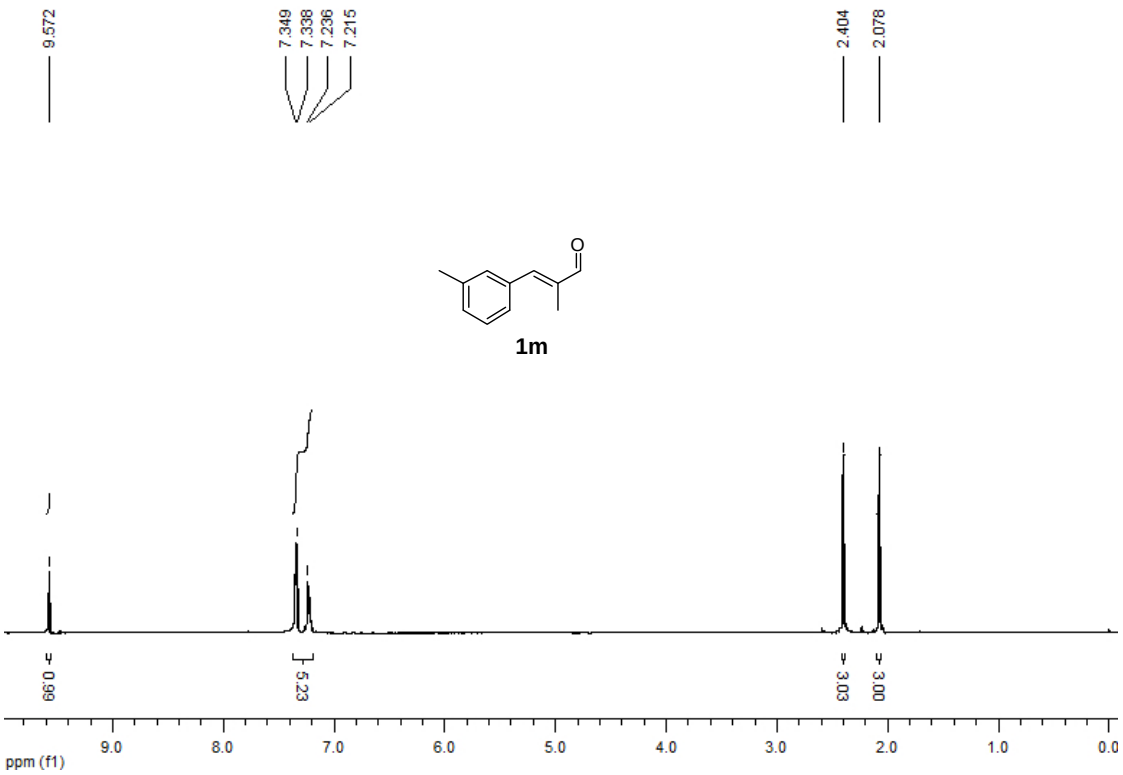
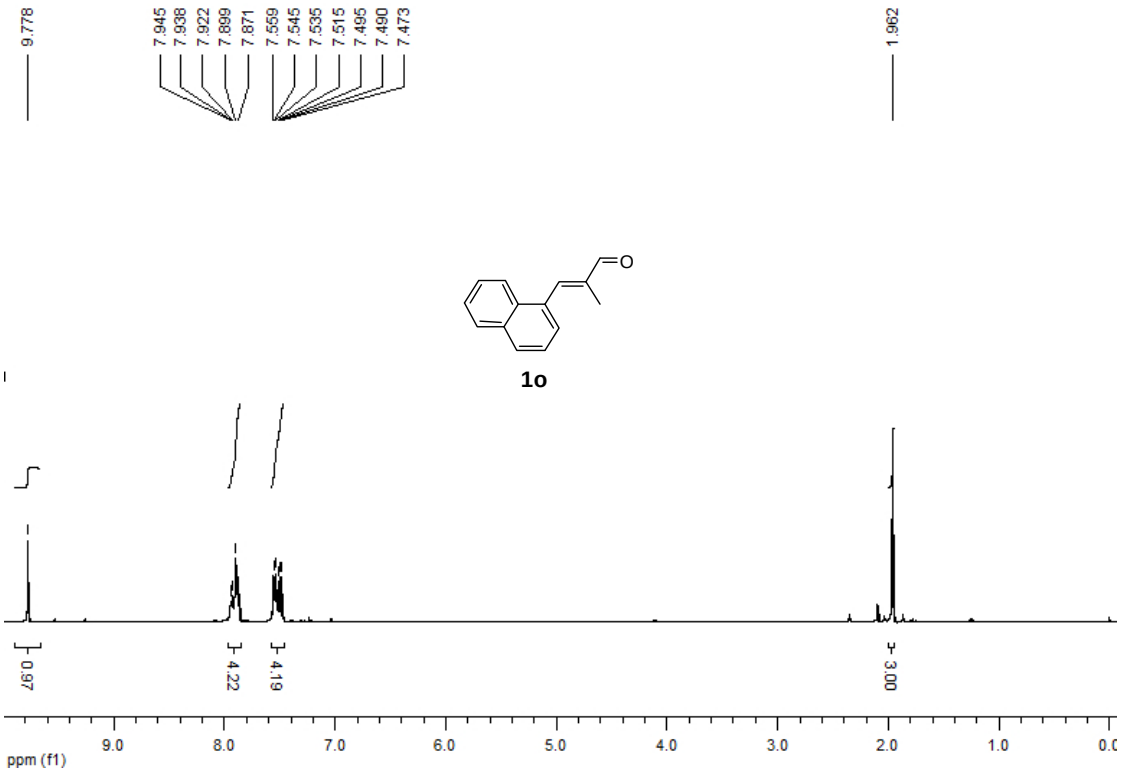
7.043
7.023
2.303
O
Ph
1l
0.91
4.57
1.93
1.97
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

^{1}H NMR



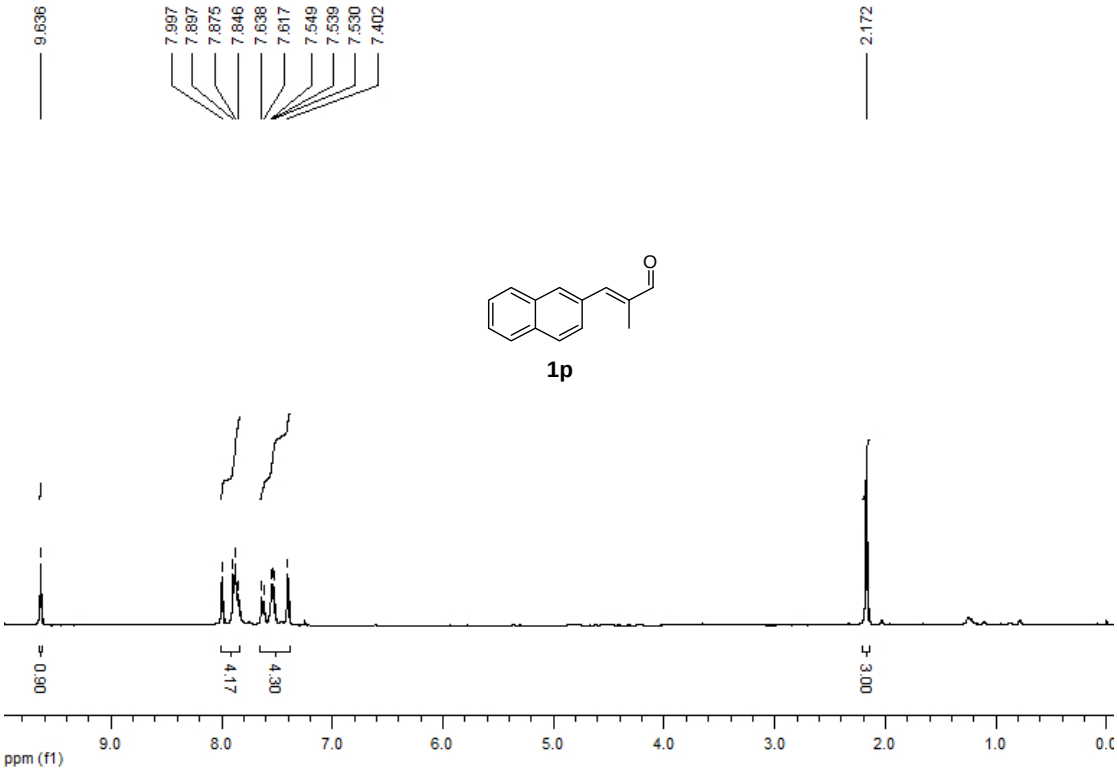
1m

^{1}H NMR



1o

^{1}H NMR


9.636
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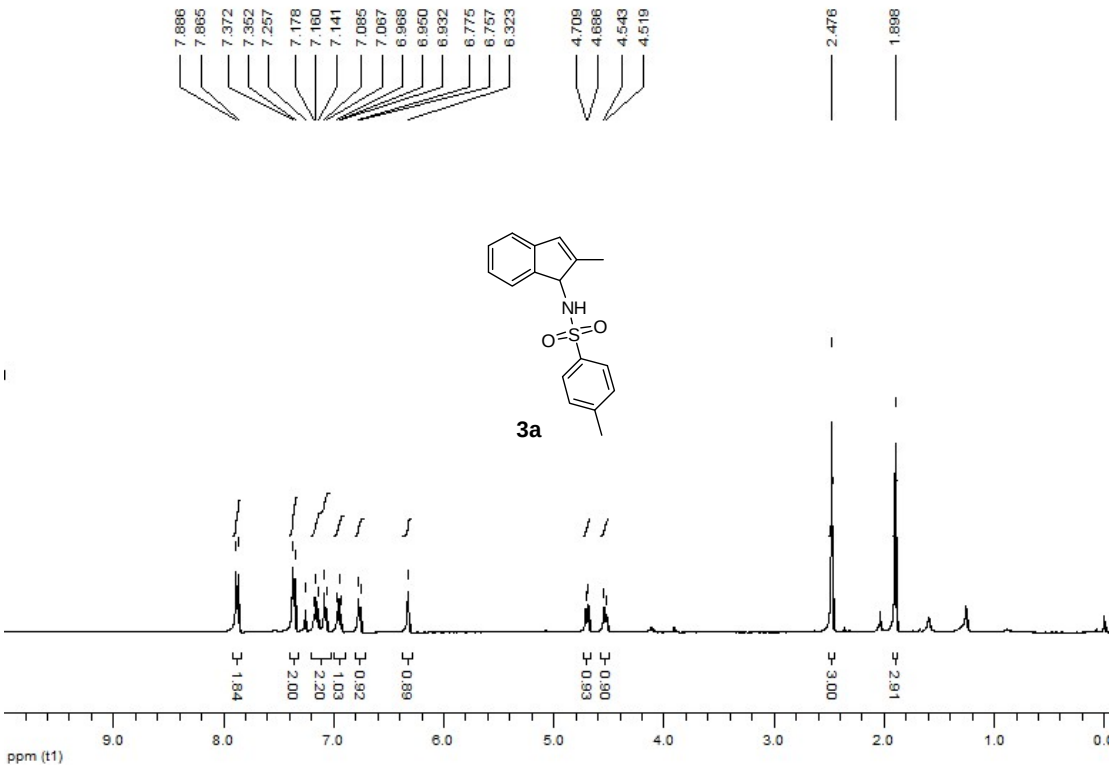
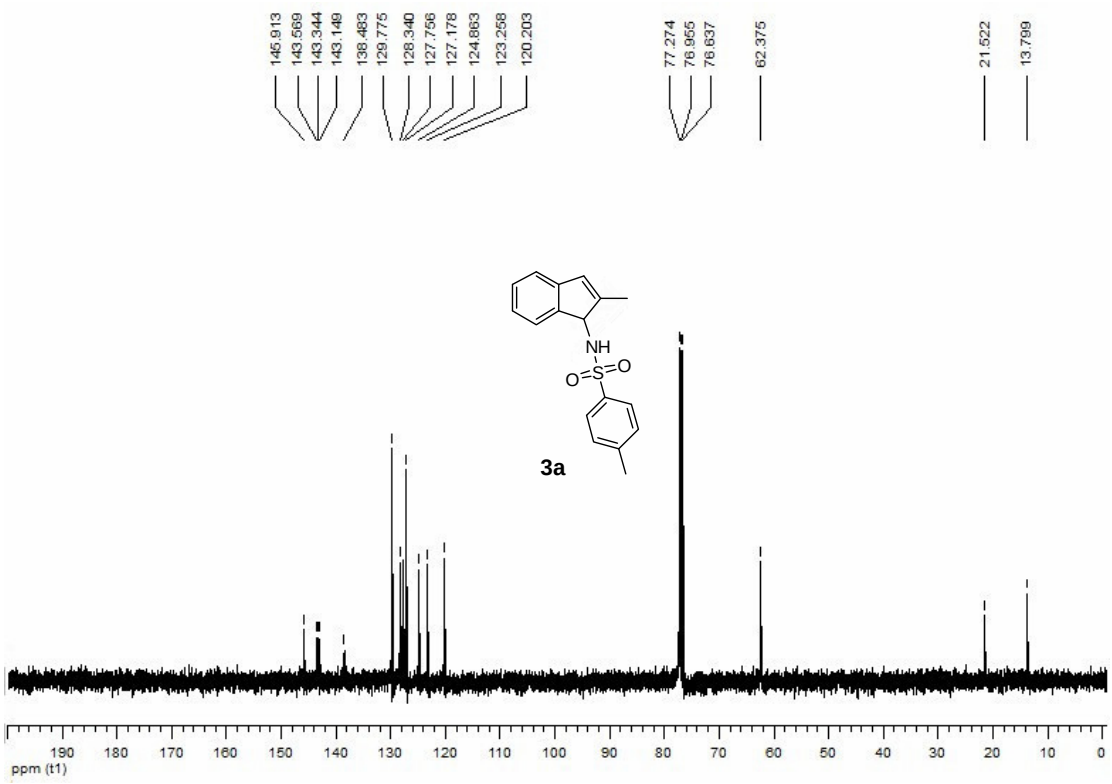
7.897
7.875
7.846
7.638
7.617
7.549
7.539
7.530
7.402
2.172
O
1p
0.90
4.17
4.30
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

^{1}H NMR



^{13}C NMR



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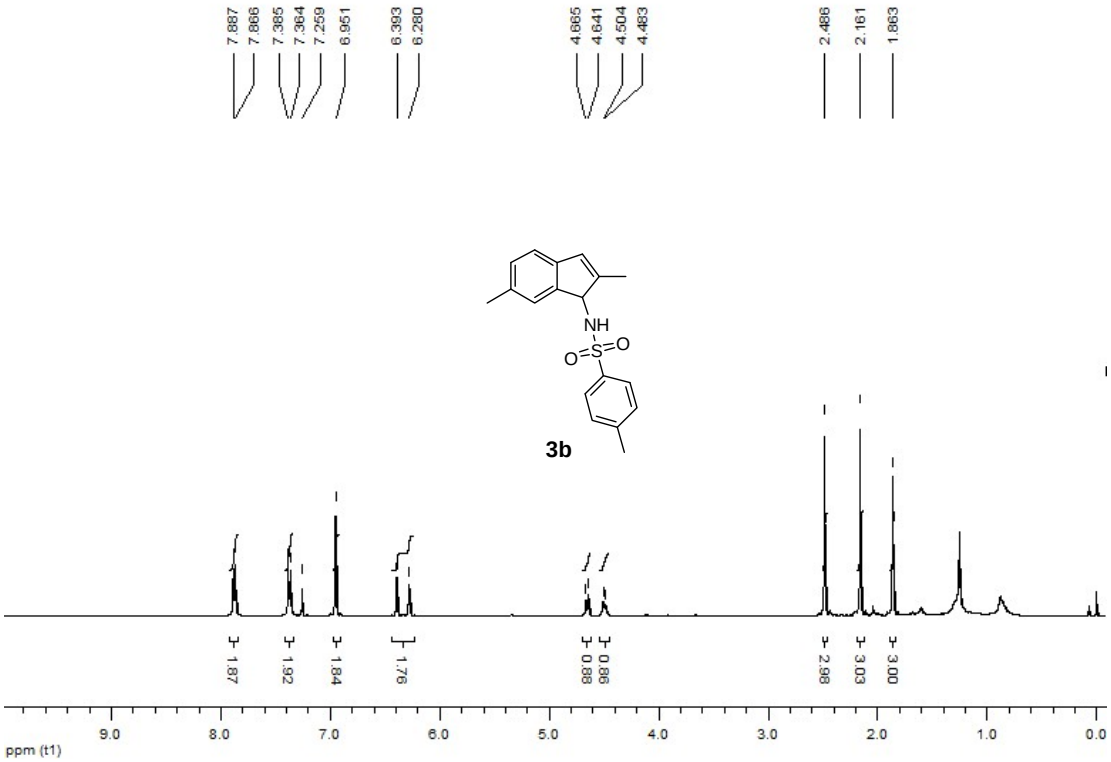

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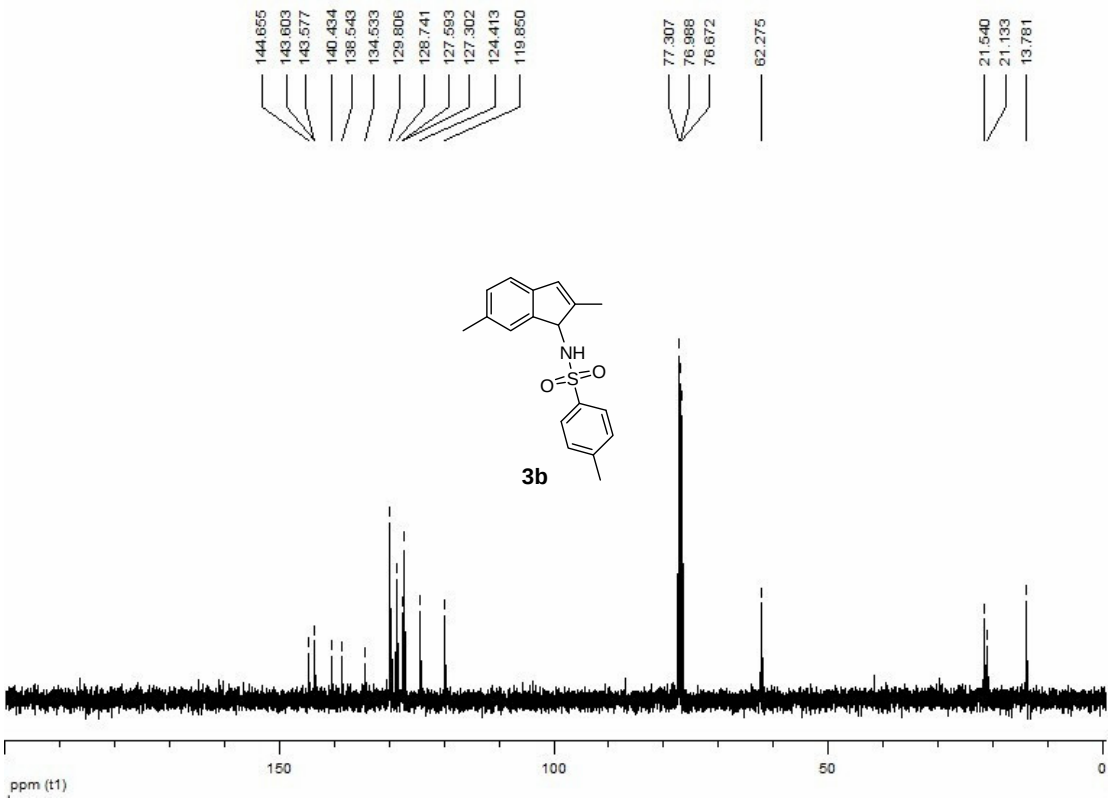

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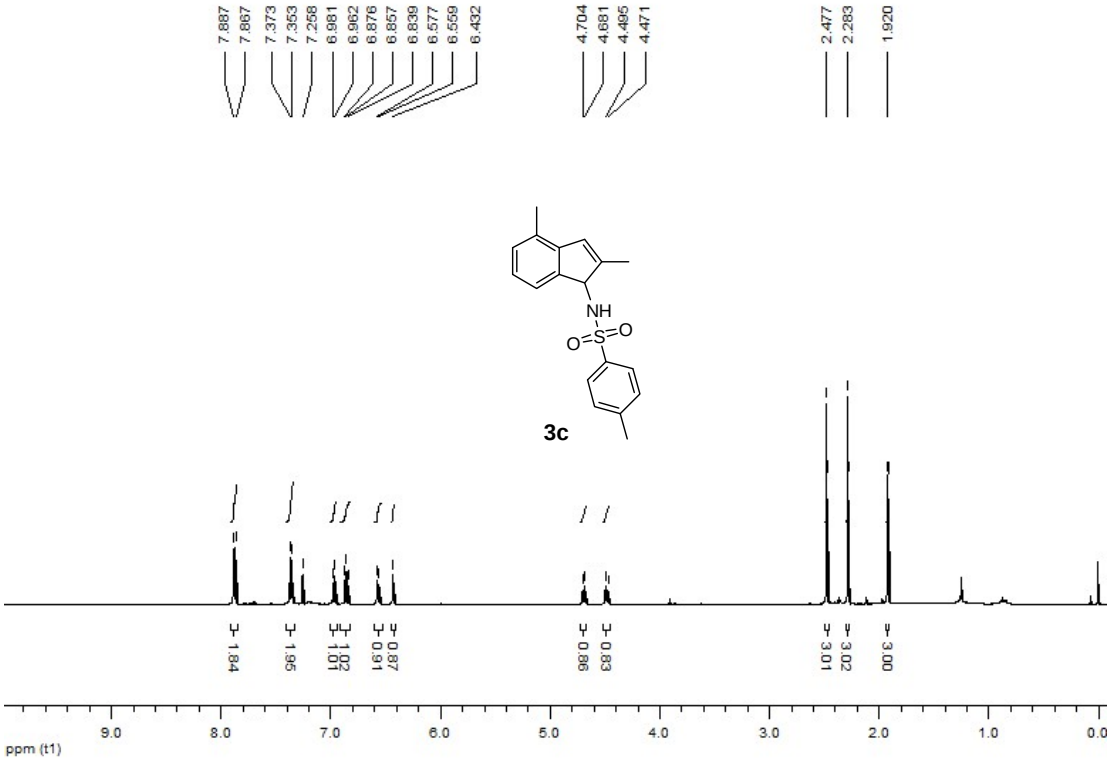

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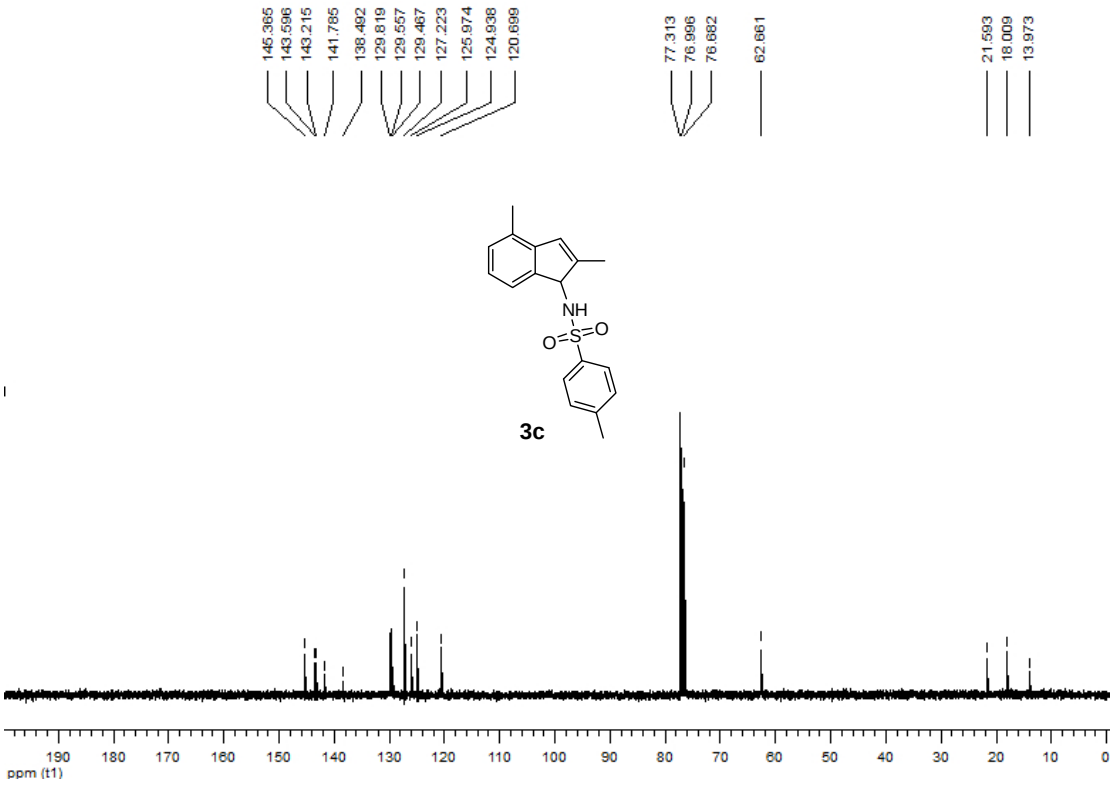

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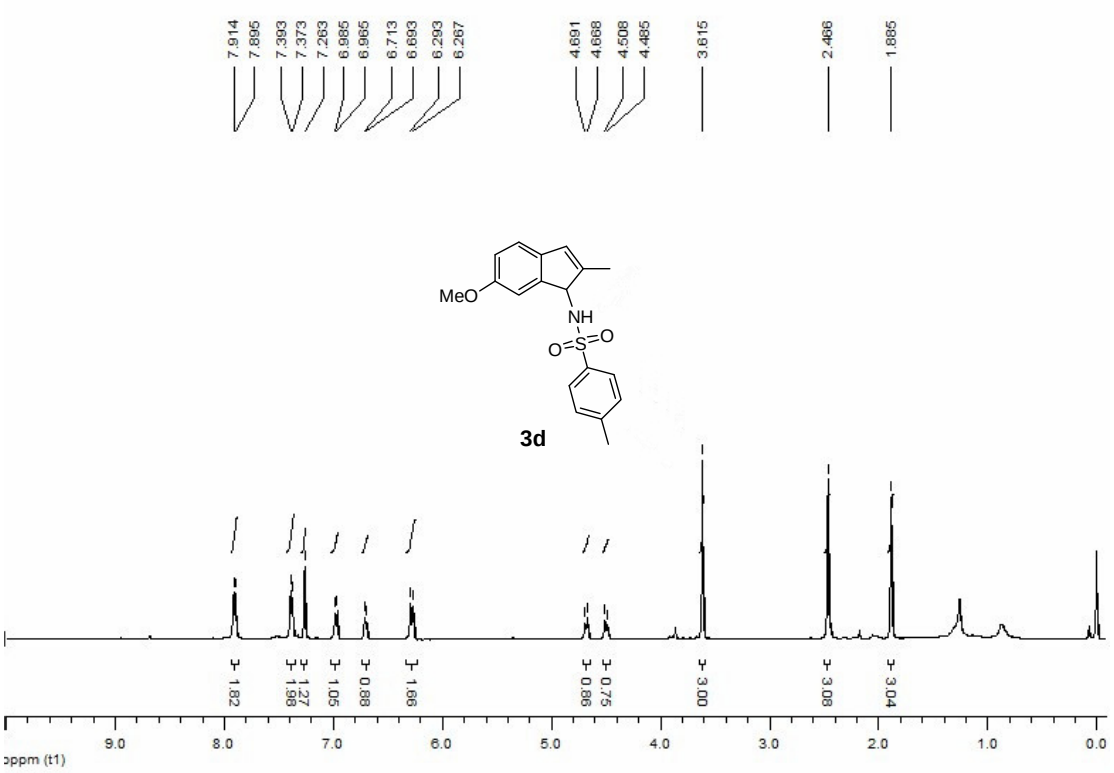

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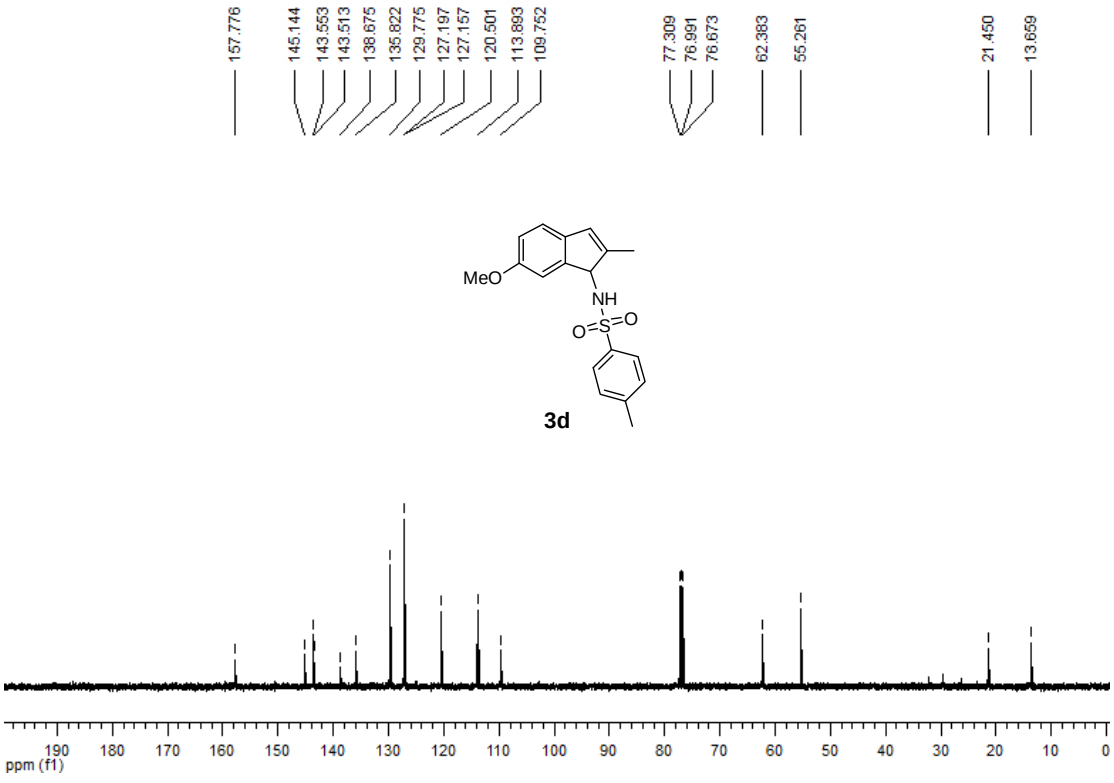

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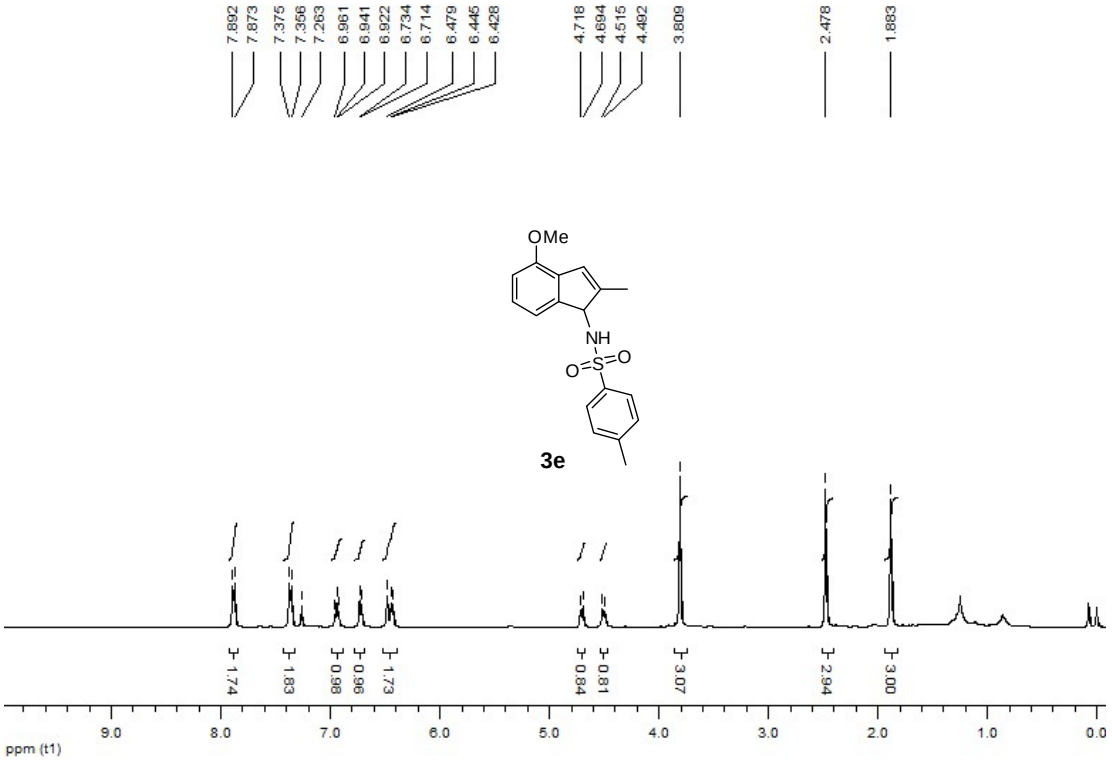

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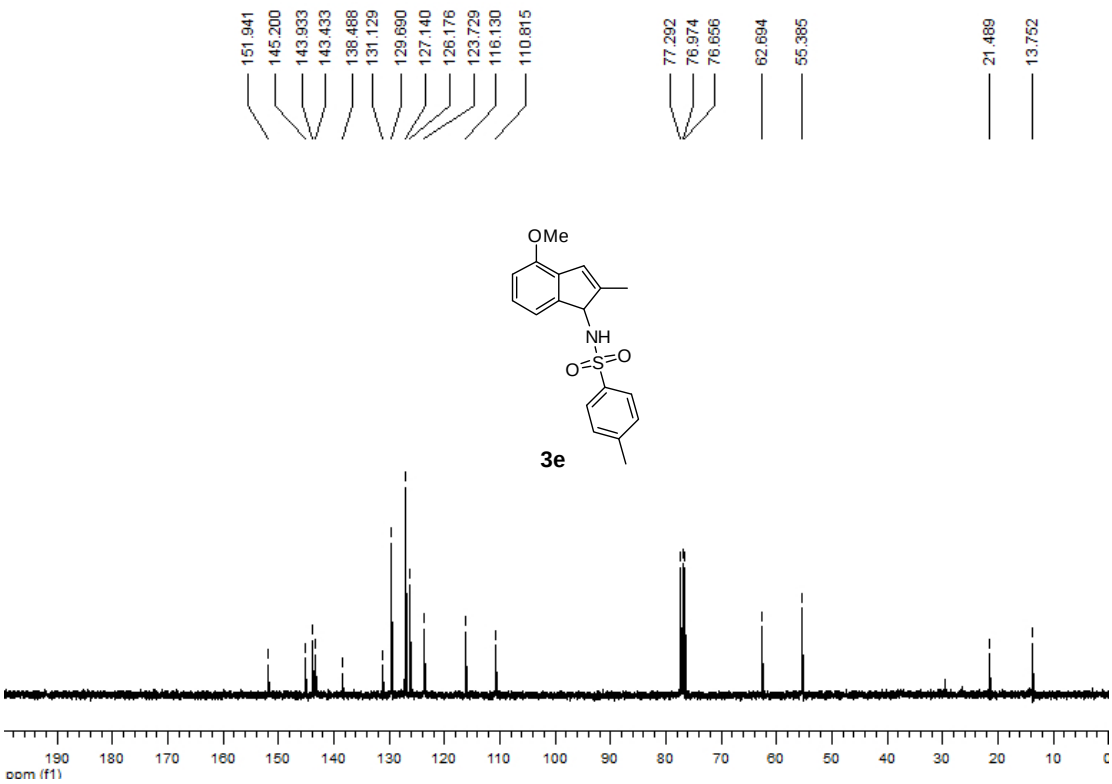

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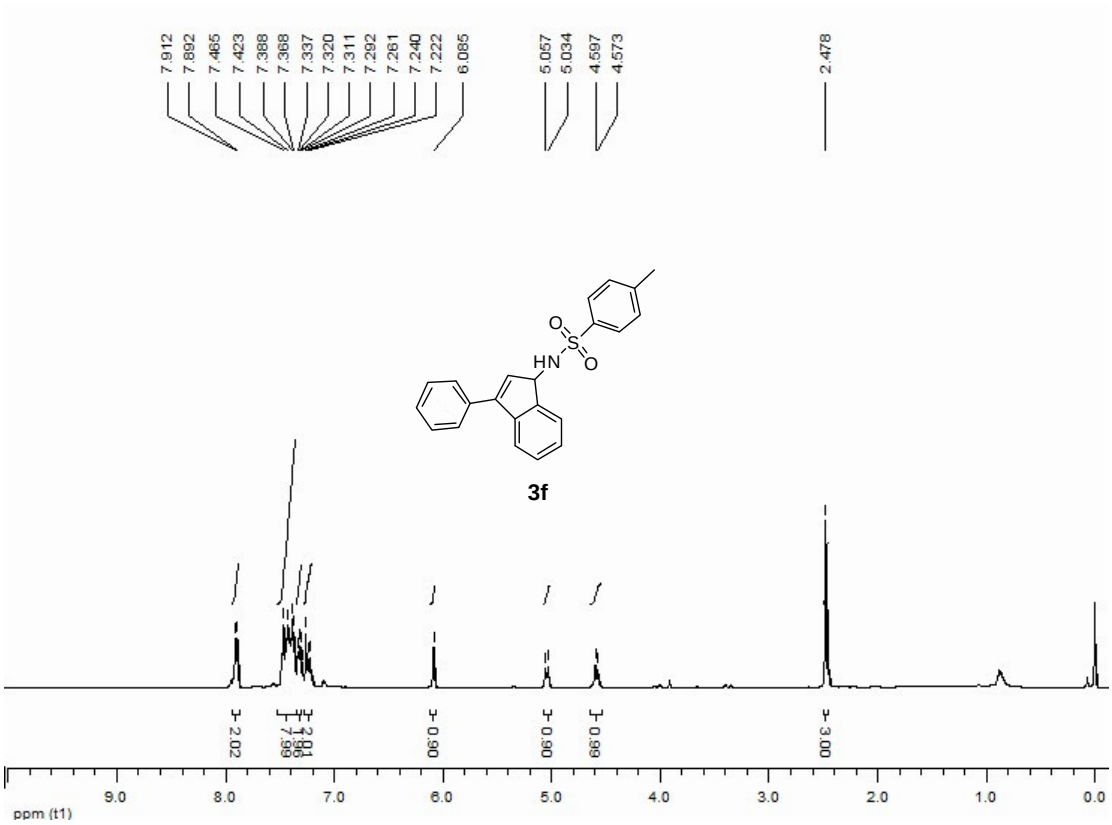

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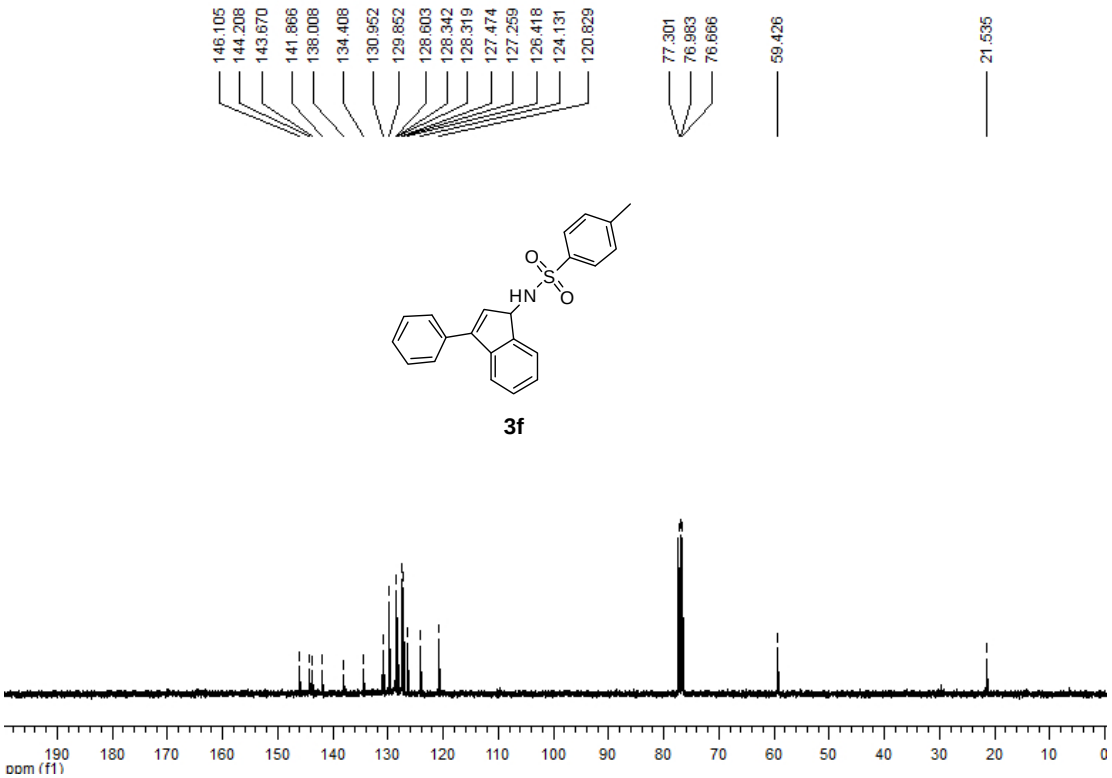

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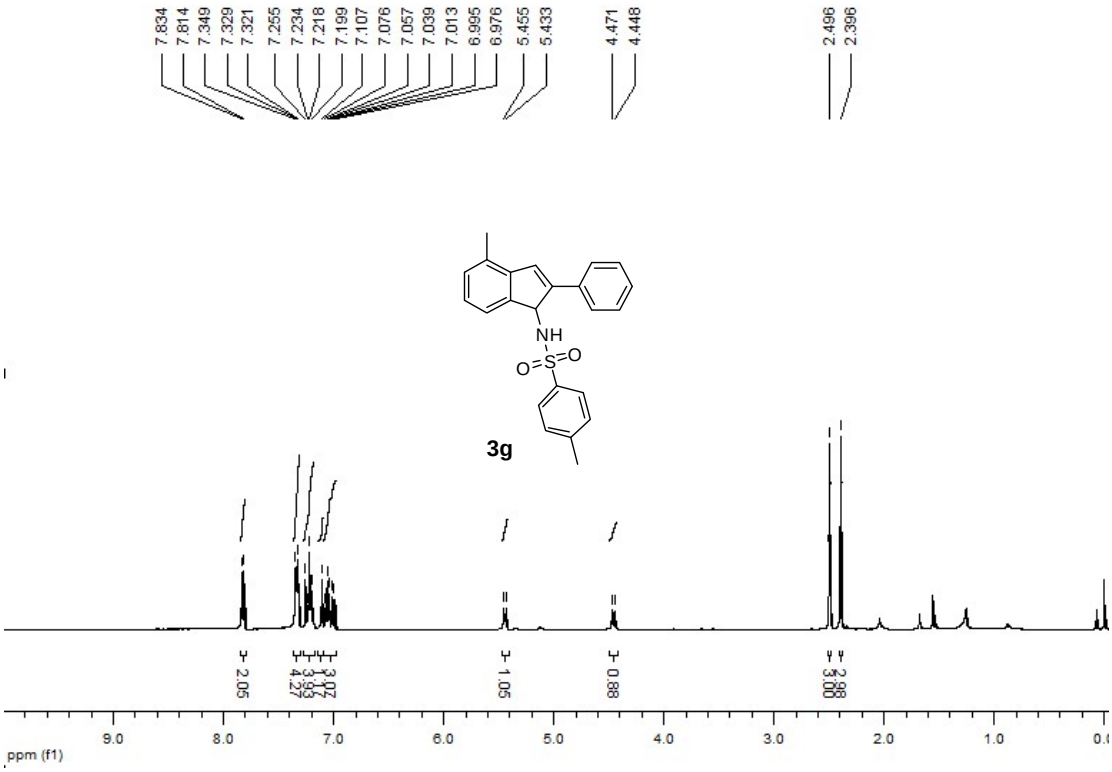

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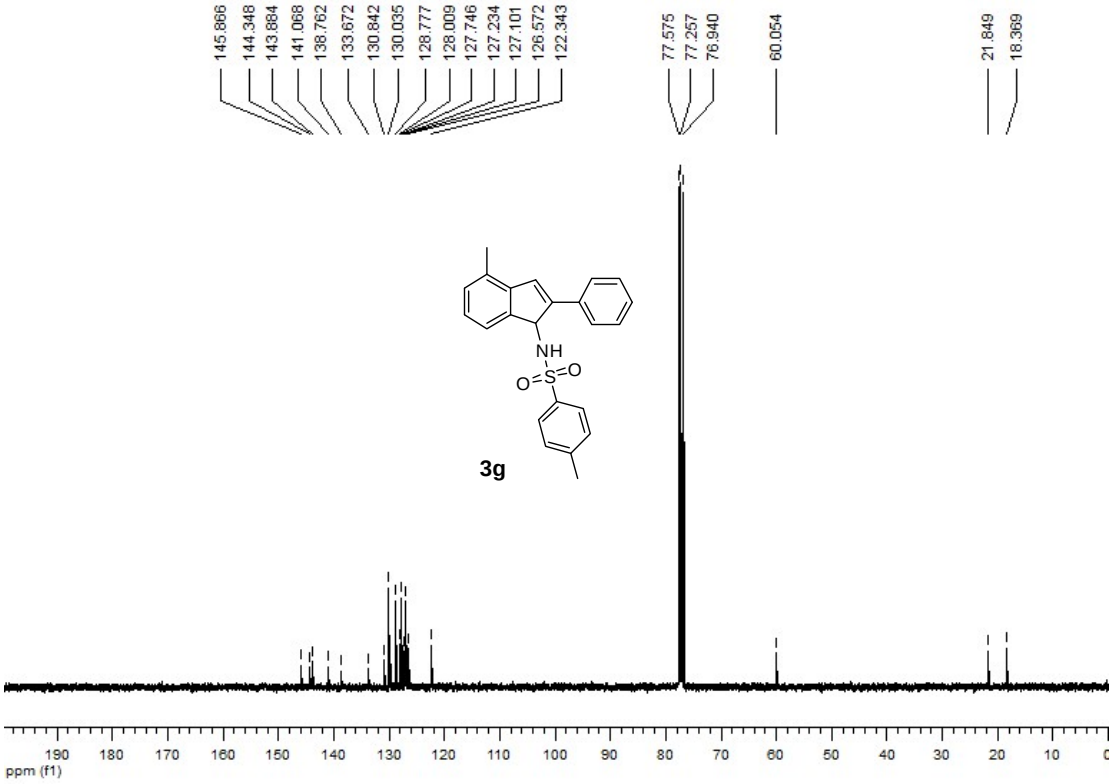

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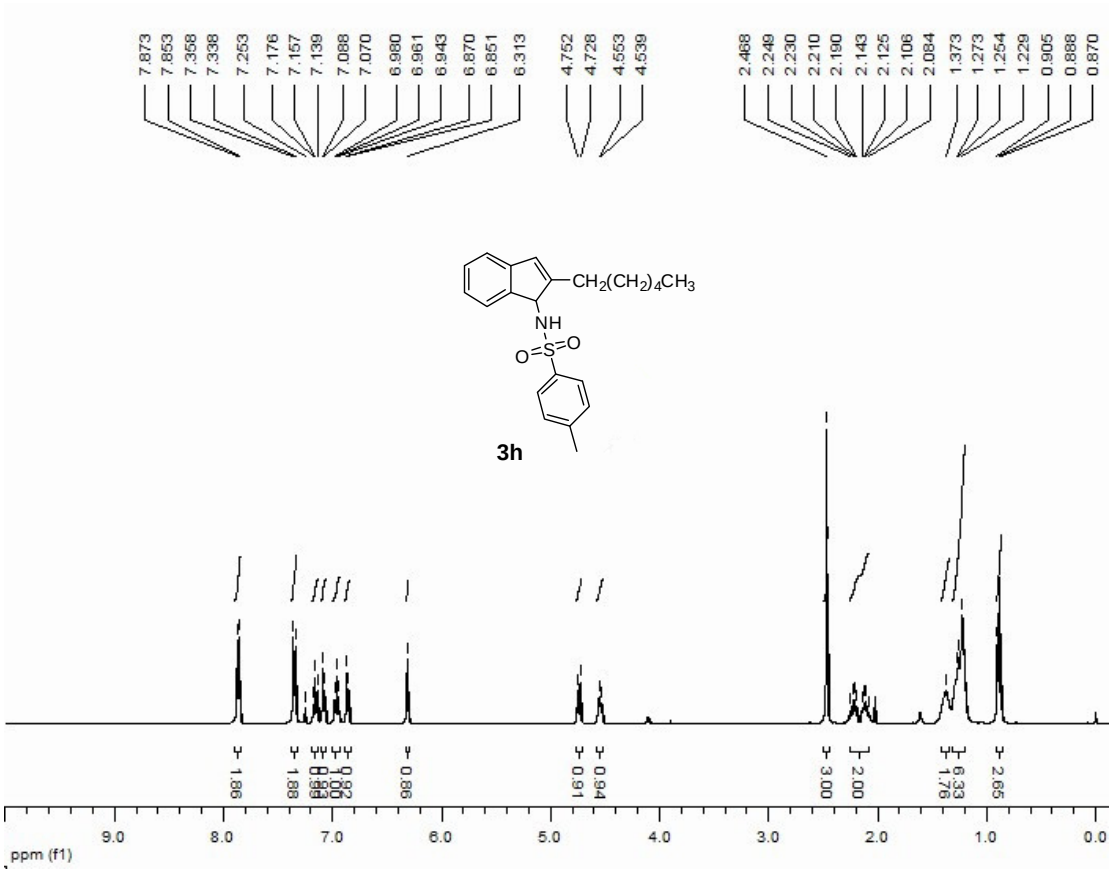

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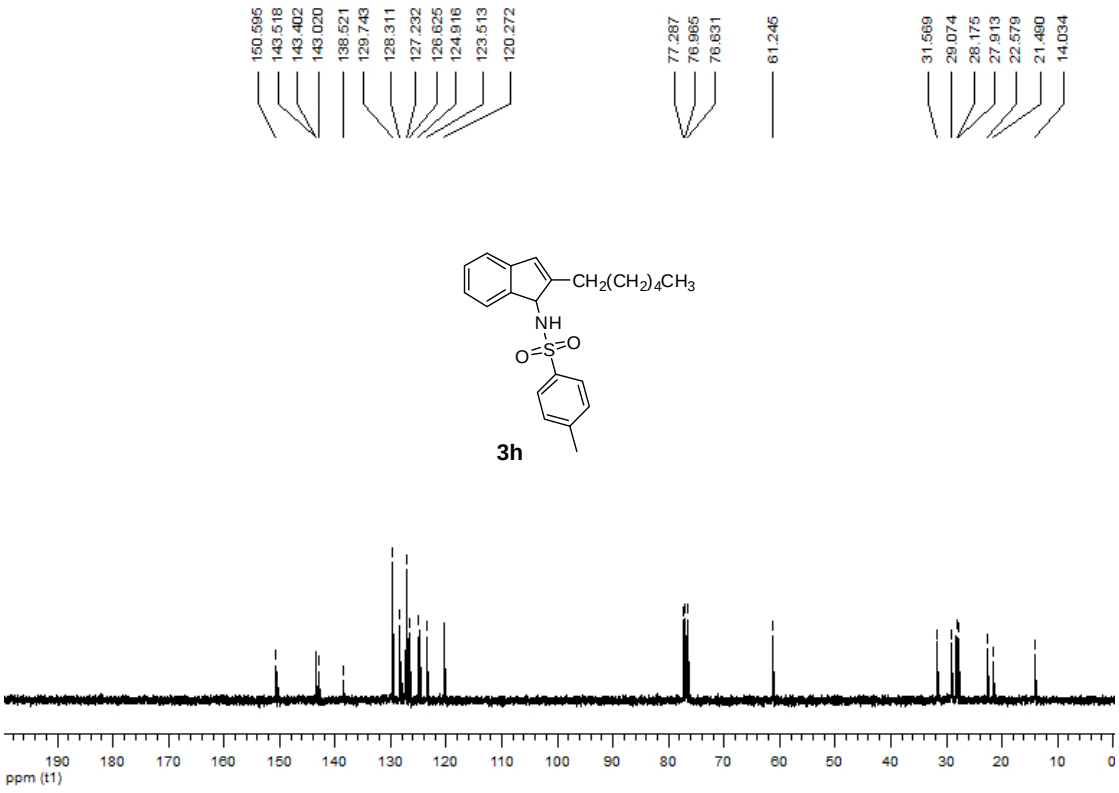

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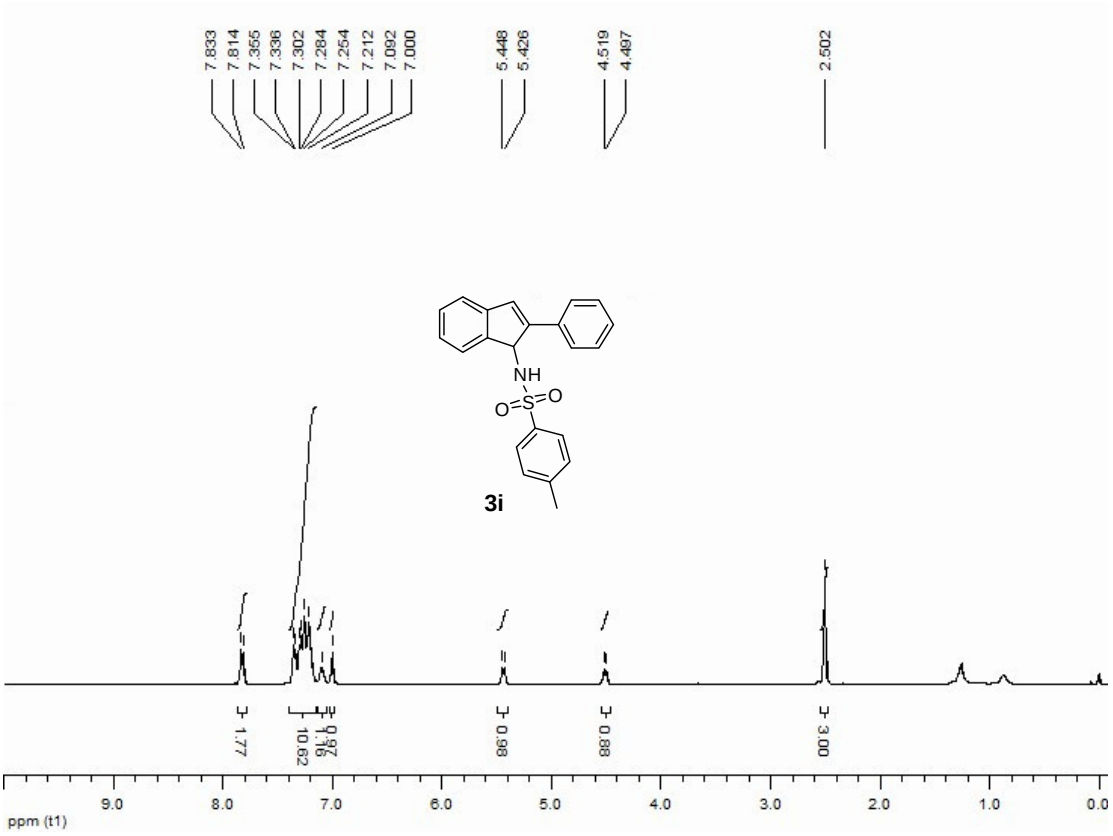
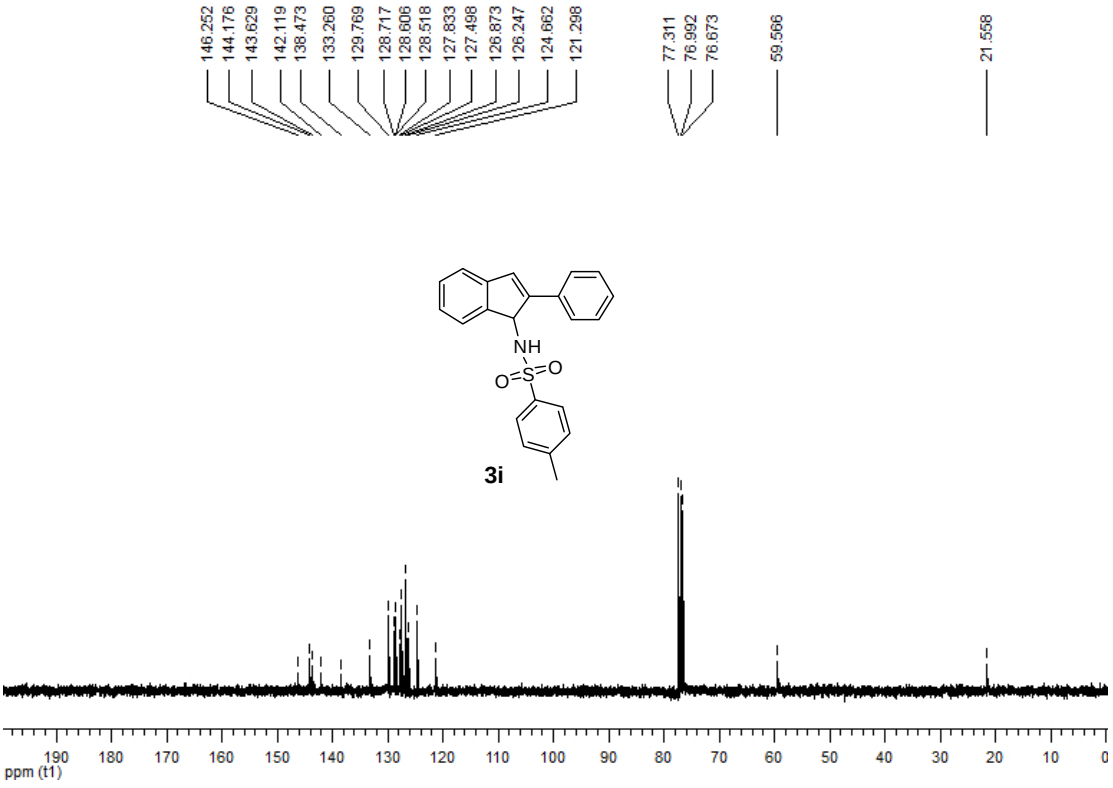


^{13}C NMR



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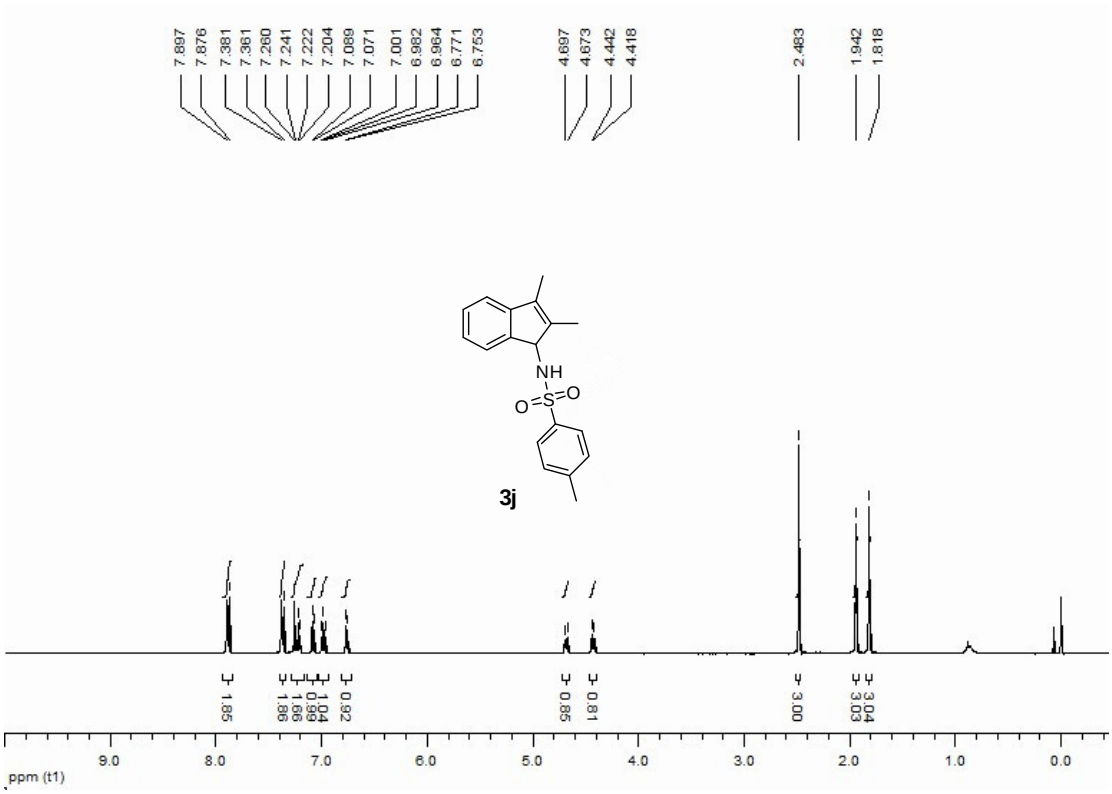
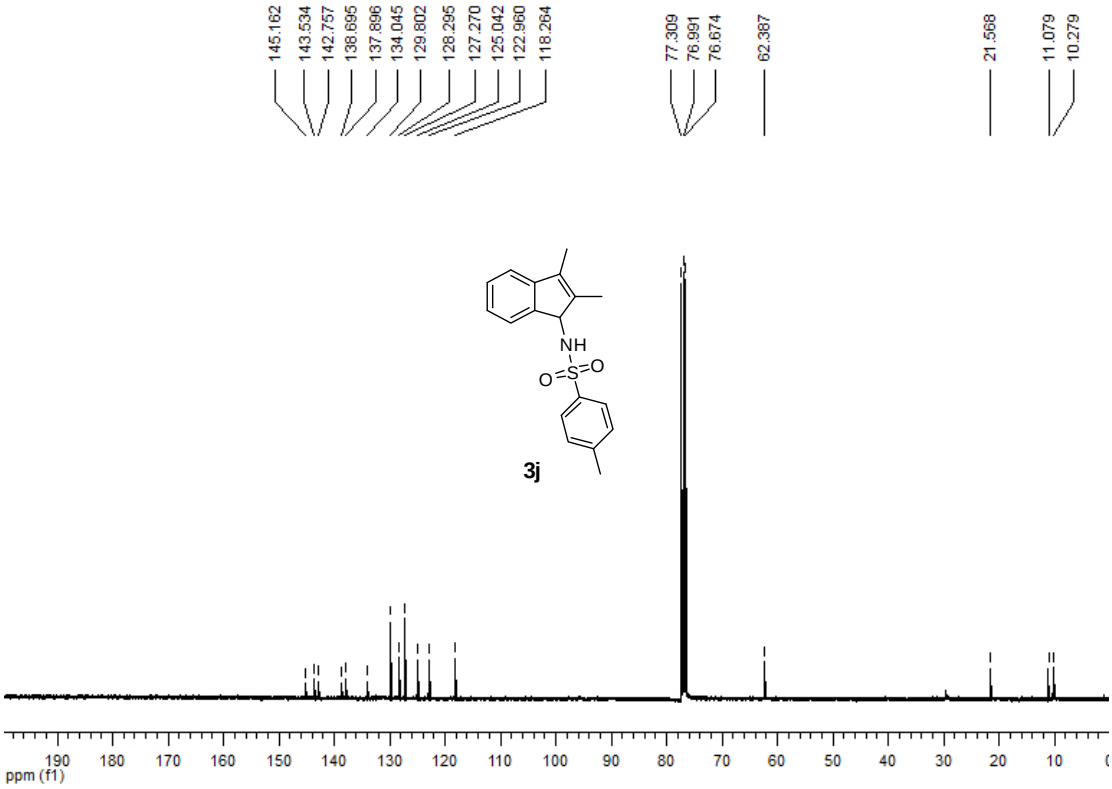
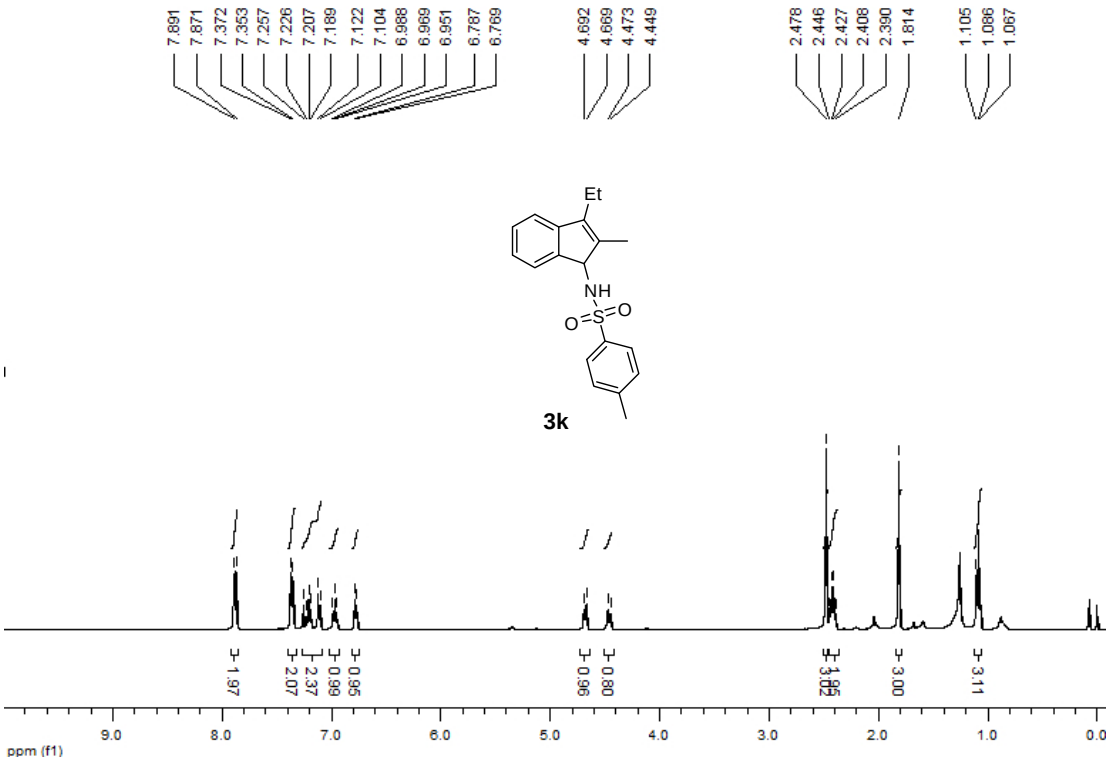


^{13}C NMR



^{1}H NMR



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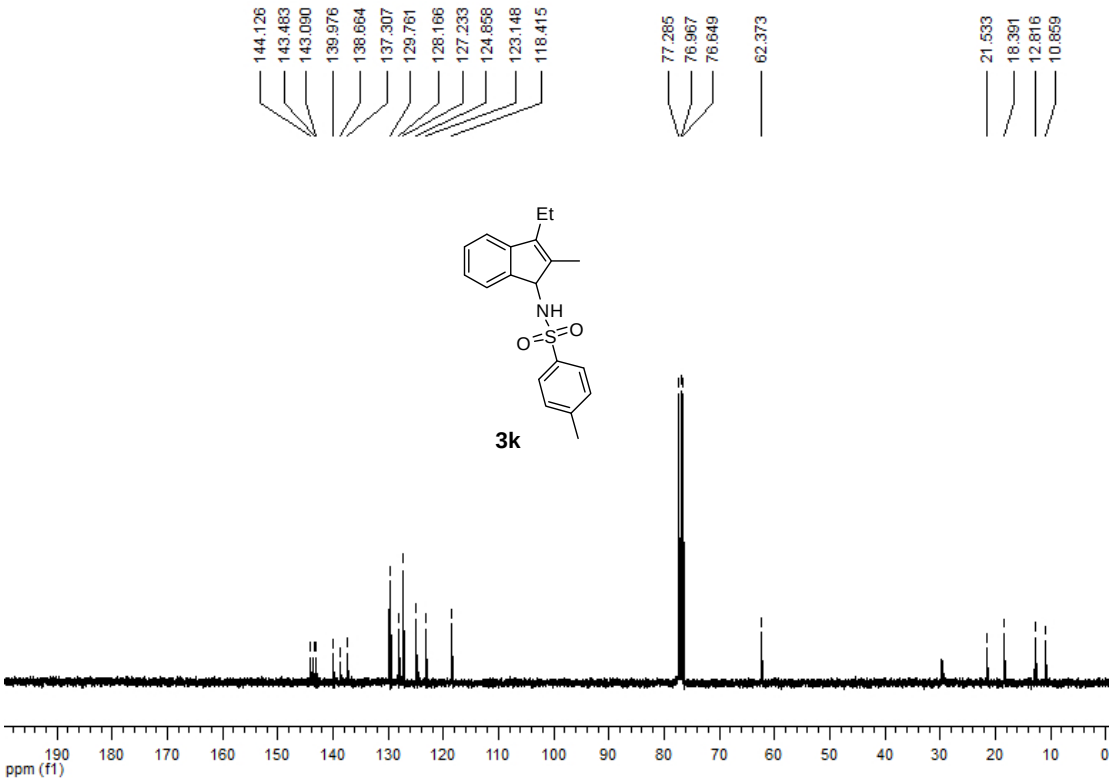
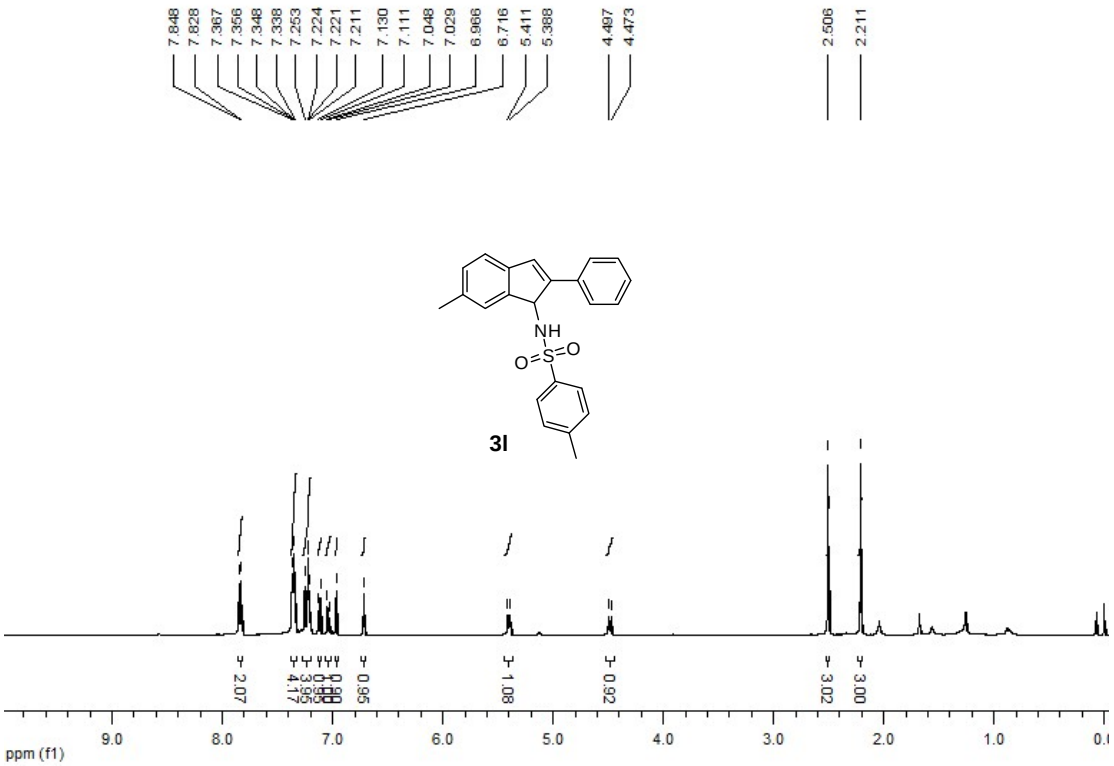
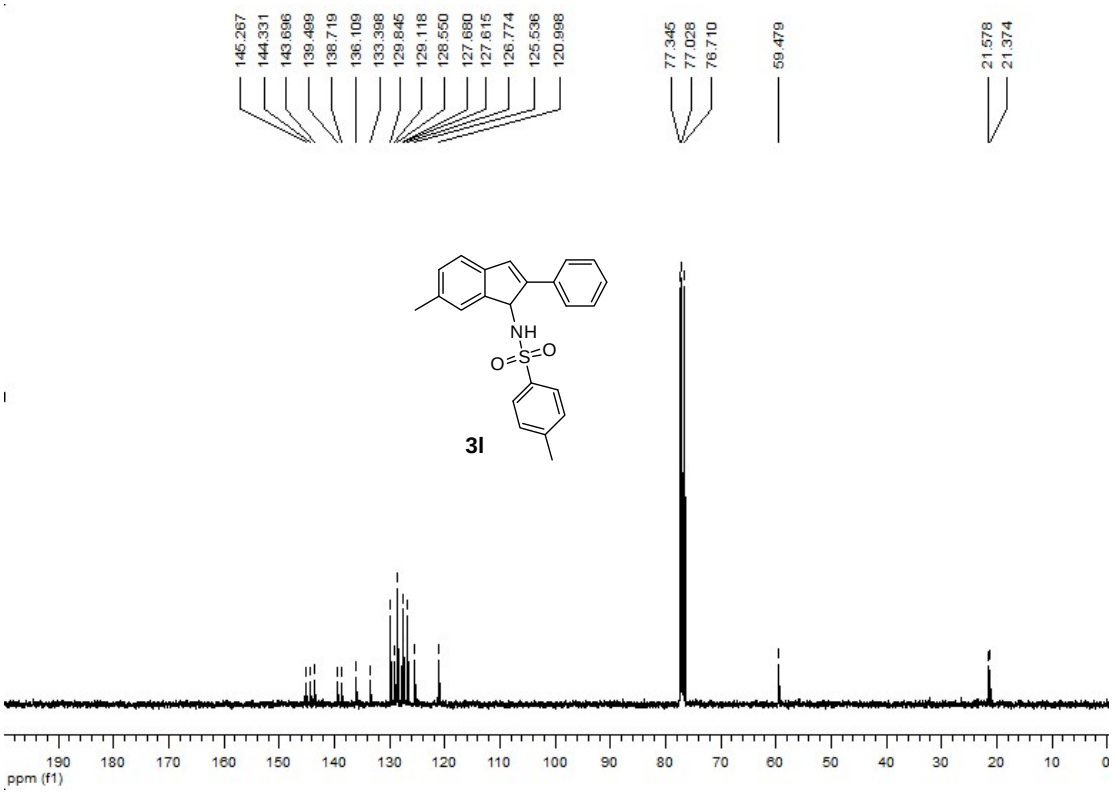


^{1}H NMR



^{13}C NMR



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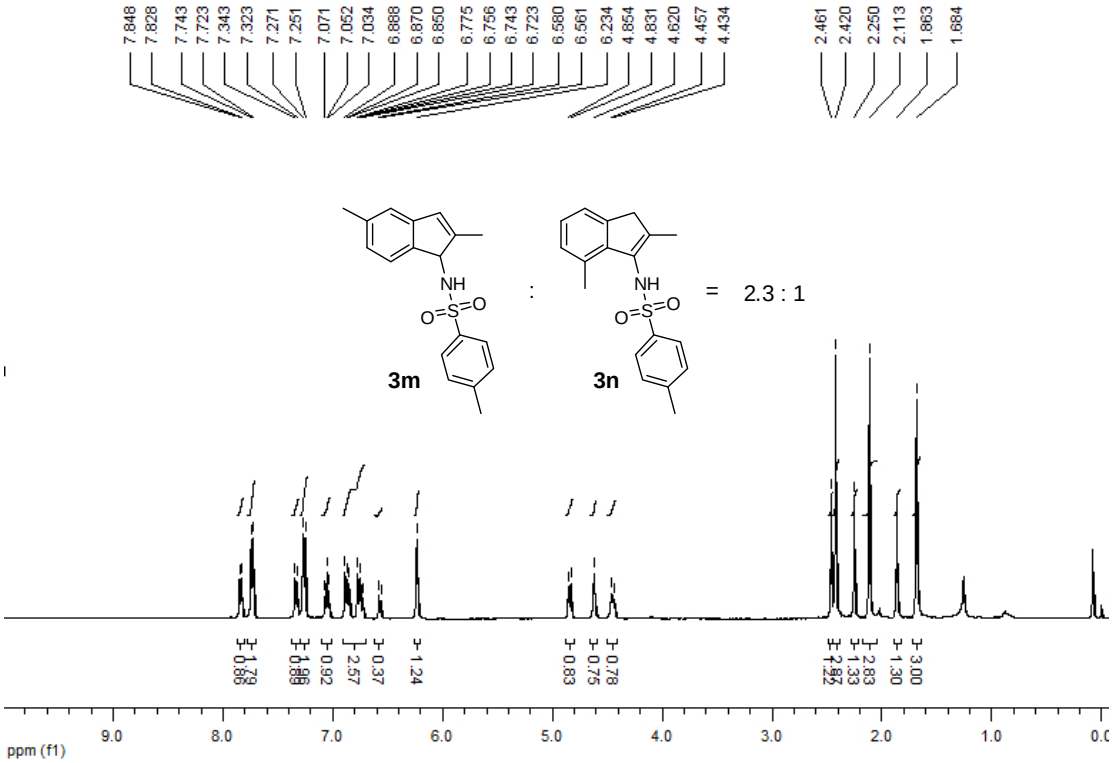

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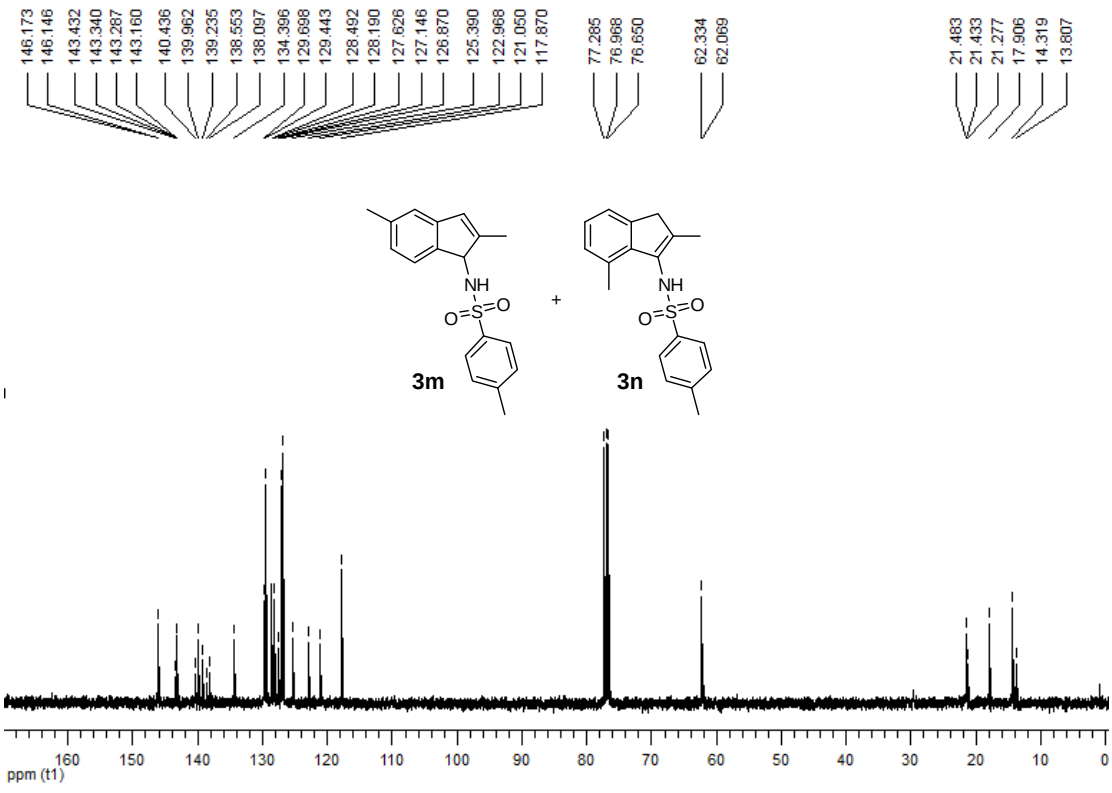

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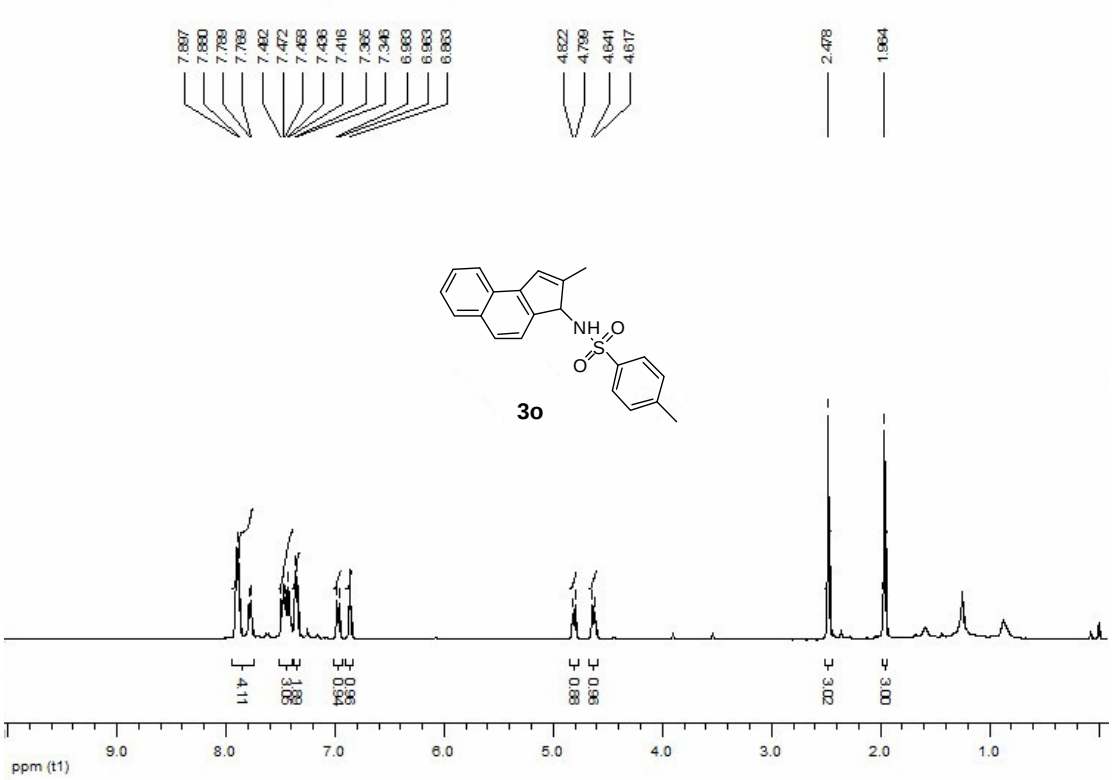

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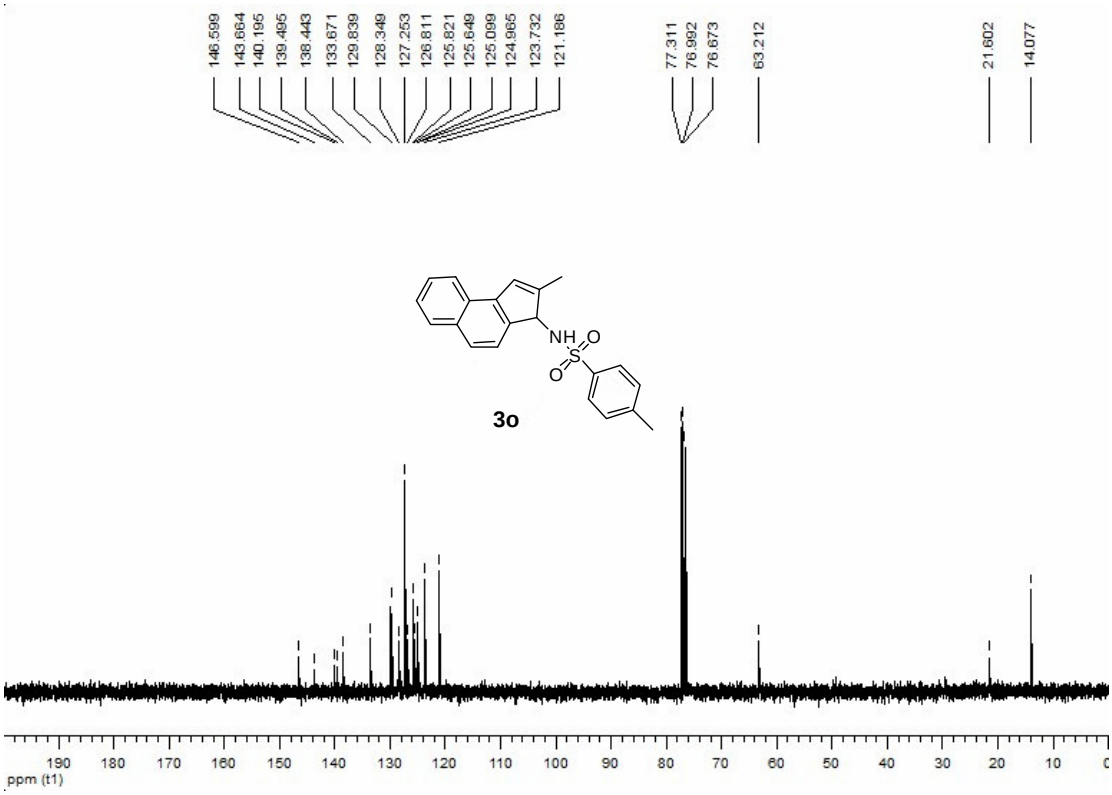

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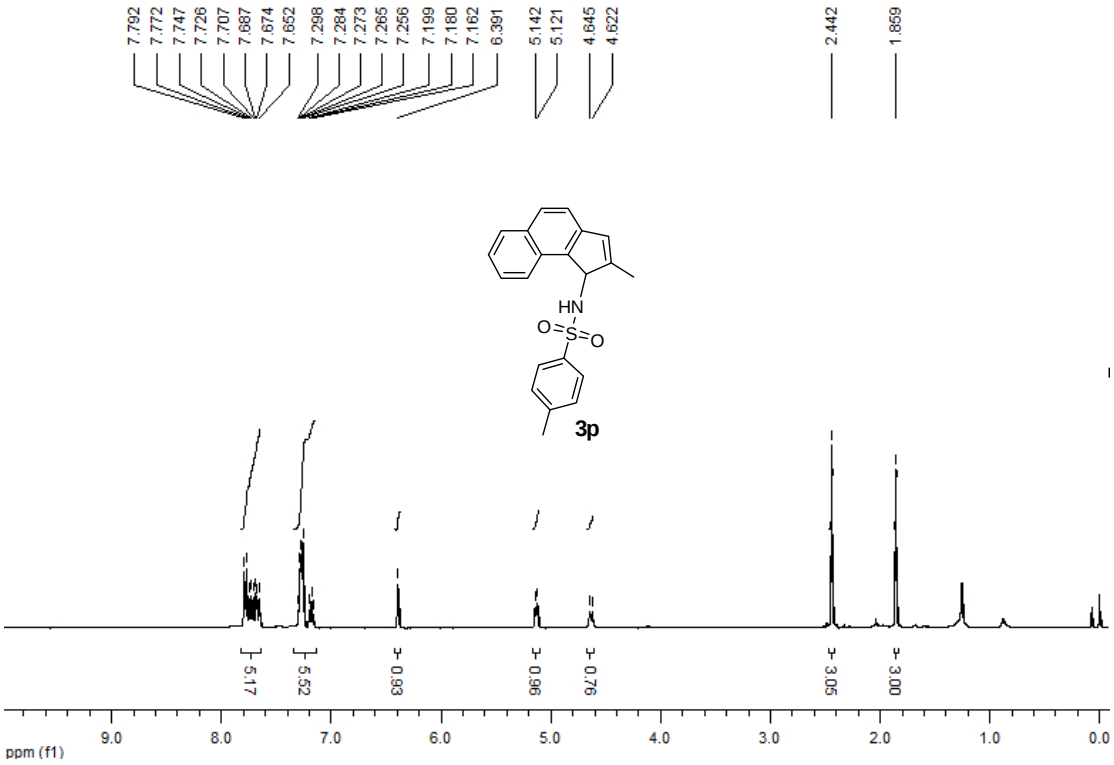

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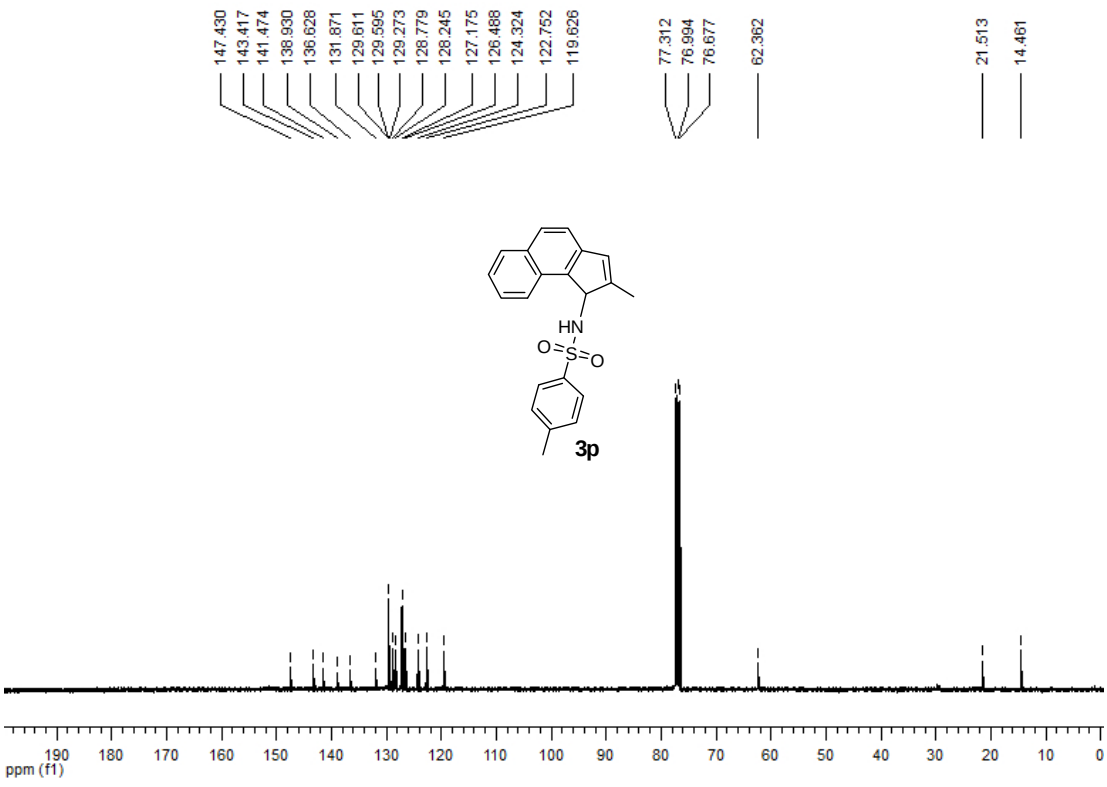

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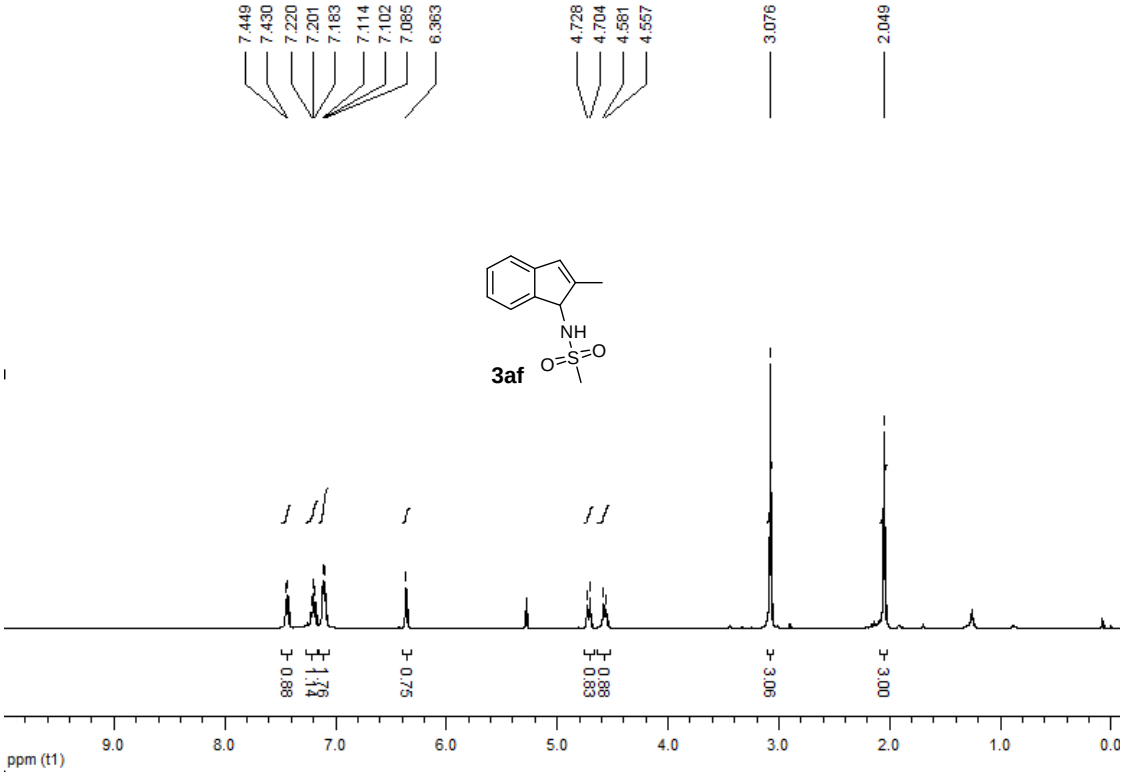

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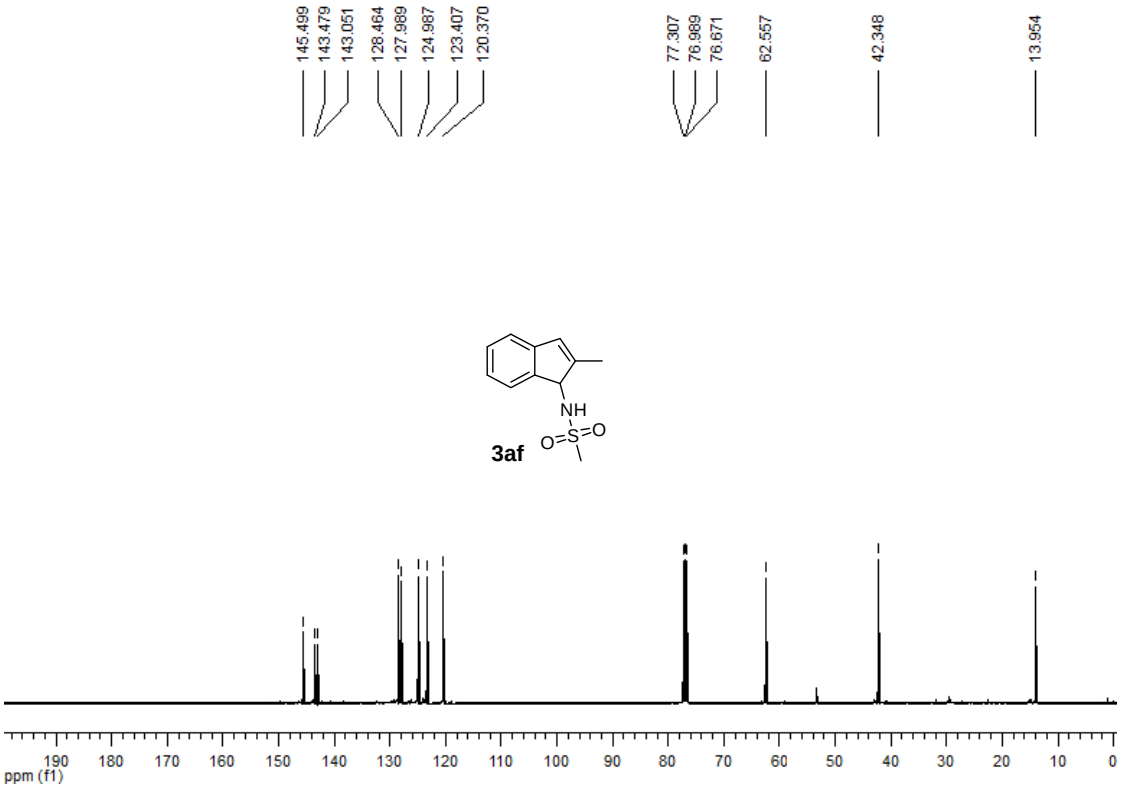

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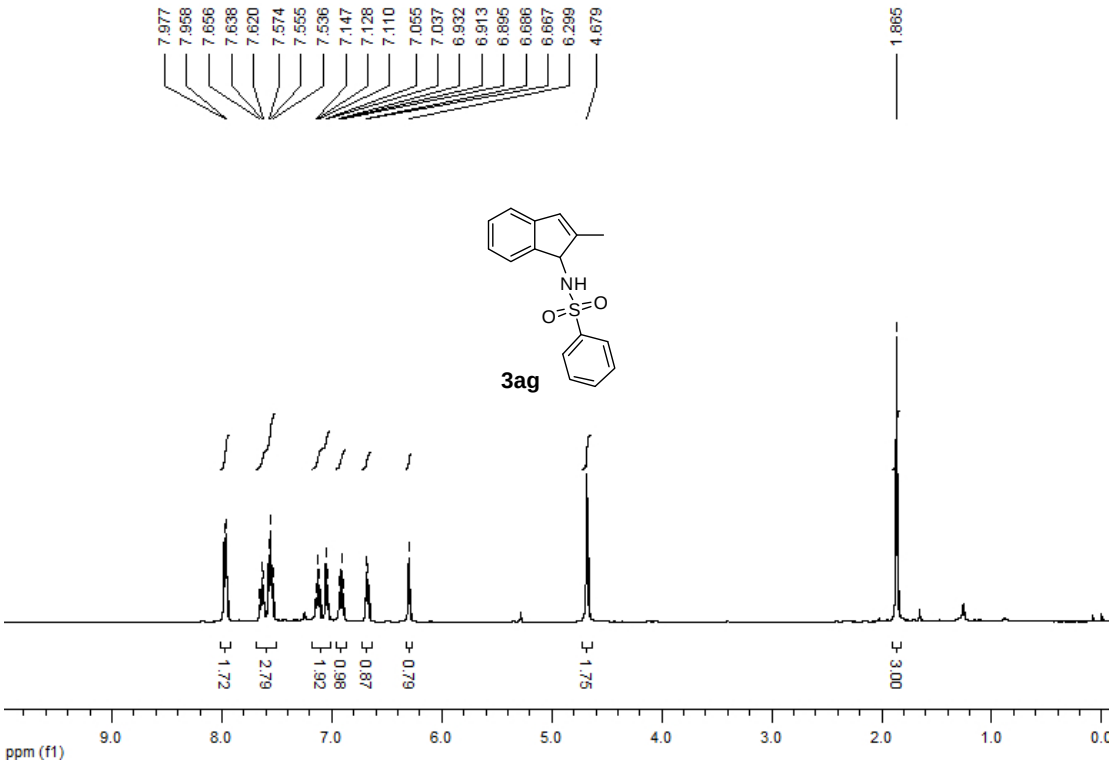

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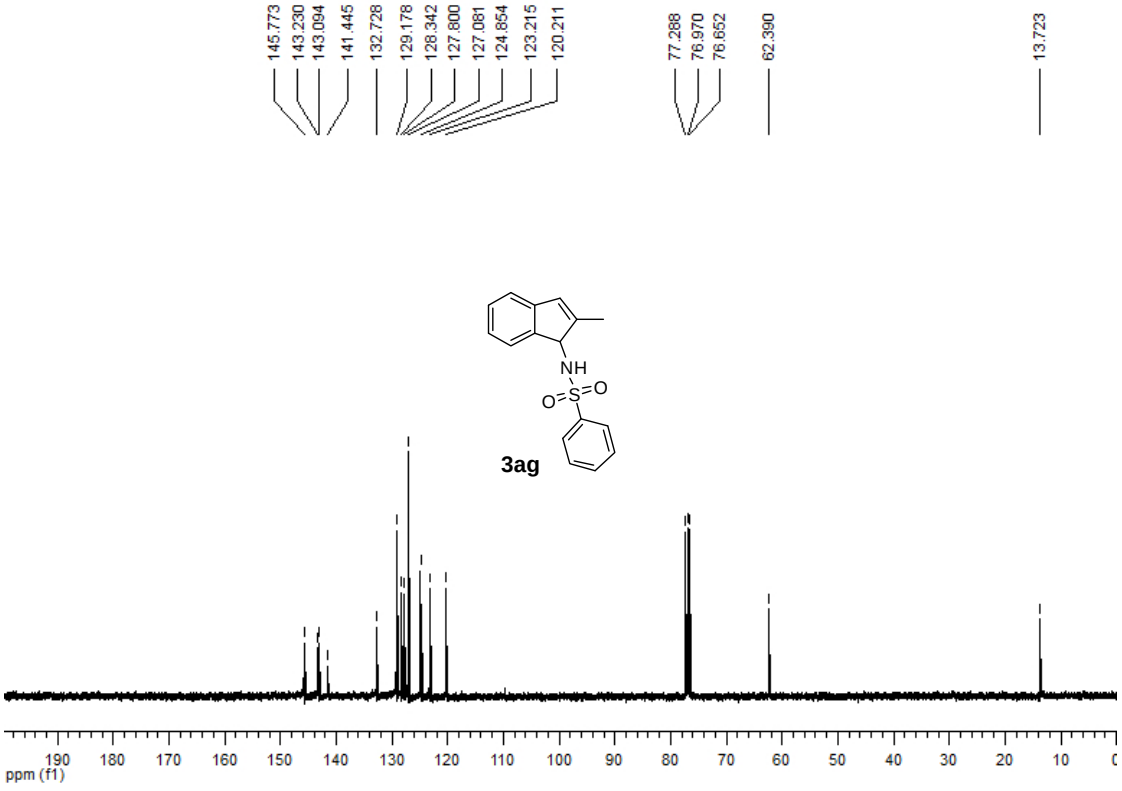

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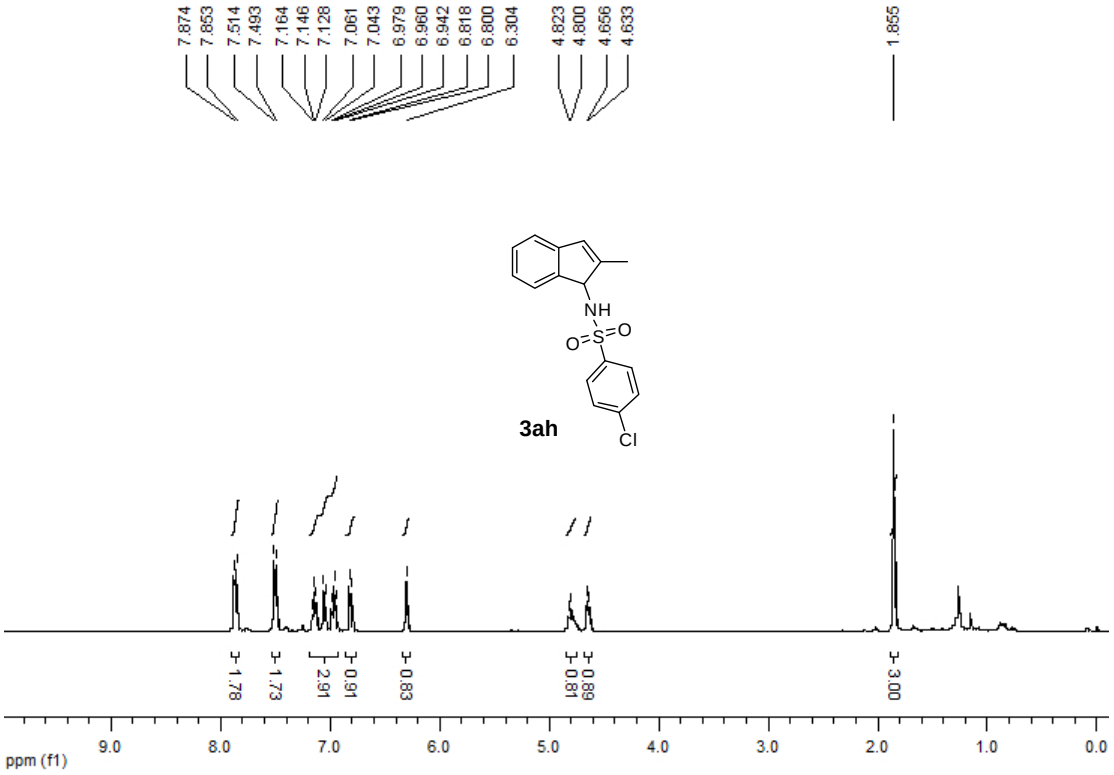

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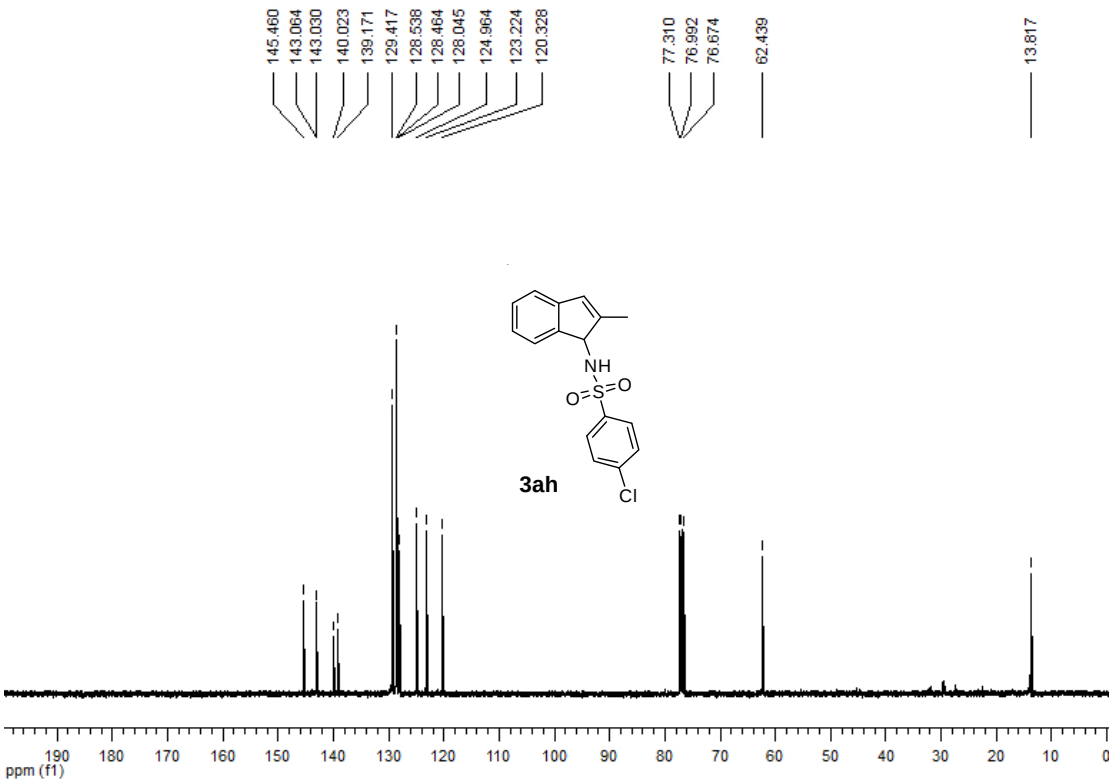
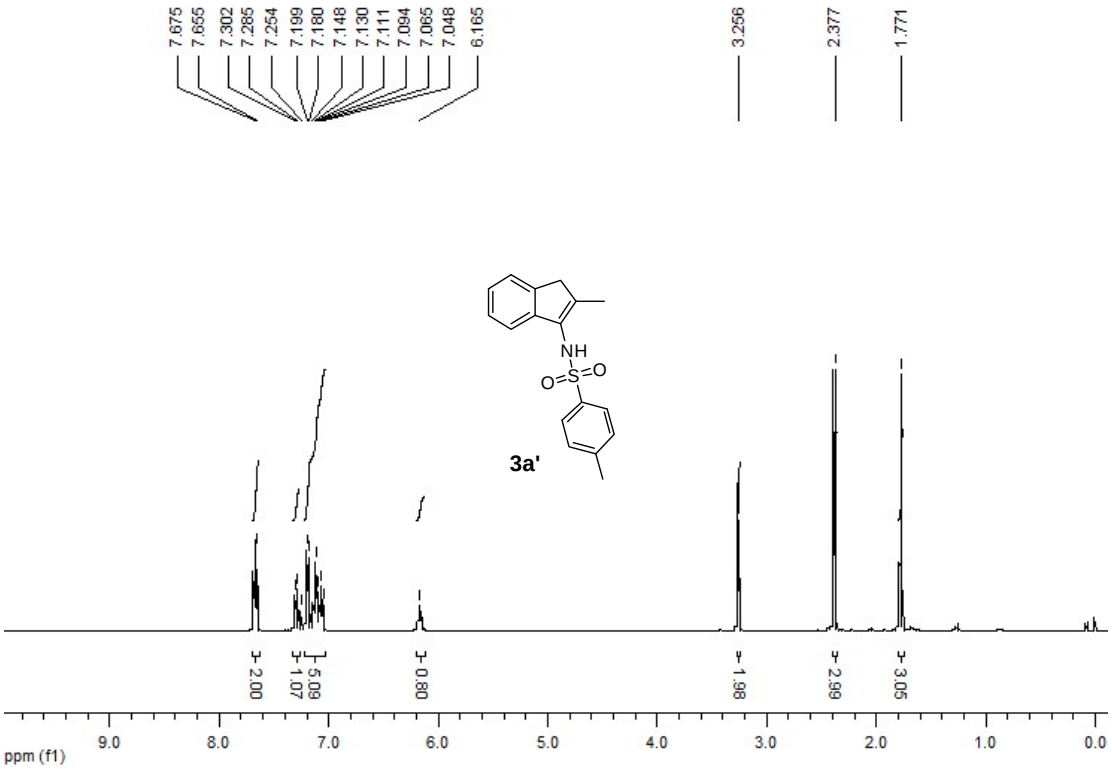


^{1}H NMR



^{13}C NMR