Regioselective Synthesis of 4-, and 7-Oxyindoles from 2,3-Dihalophenols. Application to the Preparation of Indole Inhibitors of Phospholipase A_2

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General Experimental Methods. All reactions involving air-sensitive compounds were carried out under an N_2 atmosphere in oven-dried glassware with magnetic stirring. Temperatures are reported as bath temperatures. THF were continuously refluxed and freshly distilled from sodium under nitrogen. Solvents used in extraction and purification were distilled prior to use. TLC was performed on alumina-backed plates coated with silica gel 60 with F_{254} indicator; the chromatograms were visualized by UV light (254 nm) and/or by staining with a Ce/Mo reagent, anisaldehyde or phosphomolybdic acid solution and subsequent heating. R_f values refer to silica gel. Flash column chromatography was carried out on silica gel 60, 230-400 mesh. Melting points were obtained with open capillary tubes and are uncorrected. ^{1}H NMR spectra were recorded at 400 or 300 MHz. Chemical shifts are reported in ppm from tetramethylsilane with the residual solvent resonance as the internal standard ($CHCl_3$: δ 7.26; DMSO-d_6: δ 2.54). Data are reported as follows: chemical shift, multiplicity (s: singlet, br s: broad singlet, d: doublet, dd: doublet of doublets, dt: doublet of triplets, t: triplet, td: triplet of doublets, q: quartet, m: multiplet), coupling constants (*J* in Hz) and integration. ^{13}C NMR spectra were recorded at 100.6 or 75.4 MHz using broadband proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as internal standard ($CDCl_3$: δ 77.16; DMSO-d_6: δ 40.15). Low-resolution electron impact mass spectra (EI-LRMS) were obtained at 70 eV on a mass spectrometer and only the molecular ions and/or base peaks as well as significant peaks in MS are given. High-resolution mass spectrometry (HRMS) was carried out on a mass spectrometer. Infrared spectra were recorded with a FT-IR spectrophotometer. Elemental analyses were performed on a microanalyzer. All commercially available reagents were used without purification unless otherwise indicated and were purchased from standard chemical suppliers. Although it is commercially available, 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (HIPrCl) was easily prepared from 2,6-diisopropylaniline and glyoxal.[1]

General Procedure for the Synthesis of *O*-2,3-Dihalophenyl *N,N´*-Diethylcarbamates 2. *n*-BuLi (8.25 mL of a 1.6 M solution in hexane, 13.2 mmol) was added to a solution of *i*-Pr_2NH (1.85 mL, 13.2

mmol) in THF (40 mL) at 0 ºC. After 30 min at 0 ºC, the LDA solution was cooled to −78 ºC, and the corresponding 3-halophenyl *N,N´*-diethylcarbamate **1**[2] (12 mmol) was added. The resulting solution was stirred for 30 min at −78 ºC, and then the corresponding electrophile, hexachloroethane or iodine (14.4 mmol), was added. After 30 min at low temperature, the reaction mixture was allowed to warm to room temperature and quenched with H_2O (sat. aq $Na_2S_2O_3$ in the case of using iodine as electrophile), and THF was removed under reduced pressure. The aqueous phase was extracted with Et_2O (3 x 30 mL), and the combined organic layers were washed with HCl 1M, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude was purified by column chromatography (hexane/EtOAc, 5/1) on silica gel to afford the title compounds **2**, whose spectroscopic and characterization data we have previously reported.[2]

General Procedure for the Synthesis of 2,3-Dihalophenylethers 3a-c,e-g. To a solution of the corresponding 2,3-dihalophenyl *N,N*-diethylcarbamate **2** (10 mmol) in EtOH (100 mL) was added a large excess of NaOH (4 g, 0.1 mol) and the mixture was refluxed for 5-8 h (completion of the hydrolysis was monitored by GC-MS). After the mixture was cooled to room temperature, most of the EtOH was removed under reduced pressure and the residue was diluted with Et_2O and water. The organic phase was rejected and then, the aqueous solution was carefully neutralized with a 1 M HCl solution. The aqueous solution was extracted with Et_2O (3 x 30 mL), and the combined organic layers were washed with brine, dried (Na_2SO_4), and evaporated under reduced pressure. Without further purification the crude product was dissolved in CH_3CN (30 mL) and then, K_2CO_3 (1.52 g, 11 mmol) and the corresponding alkyl halide (11-12 mmol) were added. The mixture was refluxed overnight and then cooled to room temperature. Most of the CH_3CN was evaporated under reduced pressure and the residue was diluted with H_2O. The aqueous solution was extracted with Et_2O (3 x 25 ml), and the combined organic layers were dried (Na_2SO_4), and evaporated under reduced pressure. The crude was purified by column chromatography (hexane/EtOAc) on silica gel to afford the title compounds:

1-Benzyloxy-3-chloro-2-iodobenzene (3b): Treatment of 3-chloro-2-iodophenyl *N,N*-diethylcarbamate **2a** (3.54 g, 10 mmol) with NaOH (4 g, 0.1 mol) and then, with benzyl chloride (1.39 g, 11 mmol) and K_2CO_3 (1.52 g, 11 mmol) according to the typical procedure, and purification by flash column chromatography (hexane/EtOAc, 20/1) on silica gel, gave **3b** (2.93 g, 85%) as a white solid: mp 34-36 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57-7.49 (m, 2H), 7.47-7.32 (m, 3H), 7.21 (t, J = 7.7 Hz, 1H), 7.11 (dd, J = 7.7, 1.4 Hz, 1H), 6.72 (dd, J = 7.7, 1.4 Hz, 1H), 5.16 (s, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 159.0 (C), 139.9 (C), 136.1 (C), 129.8 (CH), 128.7 (CH), 128.1 (CH), 127.0 (CH), 122.1 (CH), 110.2 (CH), 92.1 (C), 77.3 (CH_2); EI-LRMS *m/z* 346 (M^++2, 2), 344 (M^+, 7), 91 (100); HRMS calcd for $C_{13}H_{10}ClIO$, 343.9465; found, 343.9451.

***t*-Butyl (3-chloro-2-iodophenoxy)acetate (3c):** Treatment of 3-chloro-2-iodophenyl *N,N*-diethylcarbamate **2a** (3.54 g, 10 mmol) with NaOH (4 g, 0.1 mol) and then, with *t*-butyl bromoacetate (2.15 g, 11 mmol) and K_2CO_3 (1.52 g, 11 mmol) according to the typical procedure, and purification by flash column chromatography (hexane/EtOAc, 20/1) on silica gel, gave **3c** (2.62 g, 71%) as a colorless oil: R_f 0.17 (hexane/EtOAc, 20/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, J = 8.1 Hz, 1H), 7.08 (dd, J = 8.1, 1.3 Hz, 1H), 6.52 (dd, J = 8.1, 1.3 Hz, 1H), 4.56 (s, 2H); 1.45 (s, 9H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 167.0 (C), 158.5 (C), 129.7 (CH), 122.6 (CH), 109.6 (CH), 91.8 (C), 82.8 (C), 66.9 (CH_2), 28.1 (CH_3); EI-LRMS *m/z* 370 (M^++2, 3), 368 (M^+, 9), 312 (20), 267 (31), 237 (24), 185 (29), 75 (29), 57 (100); HRMS calcd for $C_{12}H_{14}ClIO_3$, 367.9676; found, 367.9662.

2-Chloro-1-iodo-3-methoxybenzene (3f): Treatment of 2-chloro-3-iodophenyl *N,N*-diethylcarbamate **2c** (3.54 g, 10 mmol) with NaOH (4 g, 0.1 mol) and then, with iodomethane (1.70 g, 12 mmol) and K_2CO_3 (1.52 g, 11 mmol) according to the typical procedure, and purification by flash column chromatography (hexane/EtOAc, 20/1) on silica gel, gave **3f** (2.39 g, 89%) as a white solid: mp 43-45 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ7.44 (dd, J = 7.9, 1.6 Hz, 1H), 6.93 (t, J = 7.9 Hz, 1H), 6.87 (dd, J = 7.9, 1.6 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 155.5 (C), 131.8 (CH), 128.7 (CH),

127.0 (C), 111.6 (CH), 99.9 (C), 56.5 (CH_3); EI-LRMS *m/z* 270 (M^++2, 31), 268 (M^+, 100), 253 (22), 225 (15), 126 (23); HRMS calcd for C_7H_6ClIO, 267.9152; found, 267.9163.

1-Benzyloxy-2-chloro-3-iodobenzene (3g): Treatment of 2-chloro-3-iodophenyl *N,N*-diethylcarbamate **2c** (3.54 g, 10 mmol) with NaOH (4 g, 0.1 mol) and then, with benzyl chloride (1.39 g, 11 mmol) and K_2CO_3 (1.52 g, 11 mmol) according to the typical procedure, and purification by flash column chromatography (hexane/EtOAc, 20/1) on silica gel, gave **3g** (2.55 g, 74%) as a colorless oil: R_f 0.20 (hexane/EtOAc, 25/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53-7.32 (m, 6H), 6.98-6.87 (m, 2H), 5.14 (s, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 154.6 (C), 136.1 (C), 132.1 (CH), 128.7 (CH), 128.6 (CH), 128.1 (CH), 127.7 (C), 127.1 (CH), 113.4 (CH), 100.0 (C), 71.0 (CH_2); EI-LRMS *m/z* 346 (M^++2, 3), 344 (M^+, 7), 91 (100); HRMS calcd for $C_{13}H_{10}ClIO$, 343.9465; found, 343.9456.

1-Bromo-2-iodo-3-methoxybenzene (3e):[3] Treatment of 3-bromo-2-iodophenyl *N,N*-diethylcarbamate **2b** (3.98 g, 10 mmol) with NaOH (4 g, 0.1 mol) and then, with iodomethane (1.70 g, 12 mmol) and K_2CO_3 (1.52 g, 11 mmol) according to the typical procedure, and purification by flash column chromatography (hexane/EtOAc, 20/1) on silica gel, gave **3e** (2.50 g, 80%) whose characterization data have already been reported in the main text.

General Procedure for the Synthesis of Triisopropylsilyl Ethers 3d, and 3h. To a solution of the corresponding 2,3-dihalophenyl *N,N*-diethylcarbamate **2** (3 mmol) in EtOH (15 mL) was added a large excess of NaOH (1.2 g, 0.03 mol) and the mixture was refluxed for 5-8 h (completion of the hydrolysis was monitored by GC-MS). After the mixture was cooled to room temperature, most of the EtOH was removed under reduced pressure and the residue was diluted with Et_2O and water. The organic phase was rejected and then, the aqueous solution was carefully neutralized with a 1 M HCl solution. The aqueous solution was extracted with Et_2O (3 x 30 mL), and the combined organic layers were washed with brine, dried (Na_2SO_4), and evaporated under reduced pressure. Without further purification the crude product was dissolved in CH_2Cl_2 (10 mL). Imidazole (0.31 g, 4.5 mmol) and triisopropylsilyl

chloride (0.87 g, 4.5 mmol) were successively added to the solution at room temperature, and the mixture was stirred for 2 h. After addition of H_2O (10 mL), the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The CH_2Cl_2 extract was washed with a saturated aq NaCl solution (10 mL), dried over Na_2SO_4, and evaporated under reduced pressure. The crude was purified by flash column chromatography (hexane) on silica gel to afford the title compounds.

3-Chloro-2-iodo-1-triisopropylsilyloxybenzene (3d): Reaction of 3-chloro-2-iodophenyl *N,N*-diethylcarbamate **2a** (1.06 g, 3 mmol) according to the typical procedure, and purification by flash column chromatography (hexane) on silica gel, gave **3d** (1.00 g, 81%) as a colorless oil: R_f 0.50 (hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11 (t, J = 7.9 Hz, 1H), 7.04 (dd, J = 8.1, 1.4 Hz, 1H), 6.70 (dd, J = 8.1, 1.4 Hz, 1H), 1.41-1.27 (m, 3H), 1.14 (t, J = 7.2 Hz, 18H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 157.4 (C), 139.8 (C), 129.5 (CH), 121.8 (CH), 115.6 (CH), 95.8 (C), 18.2 (CH_3), 13.2 (CH); EI-LRMS *m/z* 410 (M^+, 1), 367 (100), 339 (17), 311 (20), 155 (22); HRMS calcd for $C_{12}H_{17}ClIOSi$ (M^+–C_3H_7), 366.9782; found, 366.9768.

2-Chloro-1-iodo-3triisopropylsilyloxybenzene (3h): Reaction of 2-chloro-3-iodophenyl *N,N*-diethylcarbamate **2c** (1.06 g, 3 mmol) according to the typical procedure, and purification by flash column chromatography (hexane) on silica gel, gave **3h** (0.99 g, 80%) as a colorless oil: R_f 0.52 (hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ7.43 (dd, J = 8.0, 1.7 Hz, 1H), 6.88 (dd, J = 8.0, 1.7 Hz, 1H), 6.81 (t, J = 8.0 Hz, 1H), 1.37-1.23 (m, 3H), 1.11 (d, J = 6.9 Hz, 18H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 152.3 (C), 151.5 (C), 132.2 (CH), 128.5 (CH), 119.6 (CH), 99.5 (C), 18.0 (CH_3), 13.0 (CH); EI-LRMS *m/z* 410 (M^+, 1), 367 (100), 339 (32), 297 (22), 170 (37), 93 (23); HRMS calcd for $C_{12}H_{17}ClIOSi$ (M^+–C_3H_7), 366.9782; found, 366.9766.

General Procedure for the Synthesis of 2-Alkynyl-3-chlorophenyl Ethers 4, 2-Alkynyl-3-bromophenyl Ether 5a, and 3-Alkynyl-2-chlorophenyl Ethers 6.[4] A mixture of the corresponding aryl halide (1 equiv), alkyne (2 equiv for **4** and **6**, 1.2 equiv for **5a**), $PdCl_2(PPh_3)_2$ (6 mol%), and

TBAF·$3H_2O$ (3 equiv) was stirred under N_2 at 60 ºC for the desired time until complete consumption of starting material as monitored by GC/MS (2-3 h). After the mixture was washed with water, extracted with Et_2O (3 x 15 mL), and evaporated, the residue was purified by flash column chromatography (hexane/EtOAc) to afford the corresponding coupled products **4, 5a,** and **6**.

1-Chloro-2-(1-hexynyl)-3-methoxybenzene (4b): The reaction of **3a** (1.34 g, 5 mmol), 1-hexyne (0.82 g, 10 mmol), $PdCl_2(PPh_3)_2$ (0.21 g, 0.30 mmol) and TBAF·$3H_2O$ (4.73 g, 15 mmol) for 3 h according to the typical procedure, and purification by flash column chromatography (hexane/EtOAc, 50/1) on silica gel, afforded **4b** (0.76 g, 68%) as a brown oil: R_f 0.26 (hexane/EtOAc, 20/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11 (t, J = 8.3 Hz, 1H), 6.98 (dd, J = 8.3, 1.1 Hz, 1H), 6.73 (dd, J = 8.3, 1.1 Hz, 1H), 3.85 (s, 3H), 2.53 (t, J = 6.9 Hz, 2H), 1.69-1.46 (m, 4H), 0.95 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 161.1 (C), 137.2 (C), 128.5 (CH), 121.4 (CH), 113.5 (C), 108.6 (CH), 100.7 (C), 73.7 (C), 56.2 (CH_3), 30.8 (CH_2), 22.0 (CH_2), 19.7 (CH_2), 13.7 (CH_3); EI-LRMS *m/z* 224 (M^++2, 27), 222 (M^+, 85), 165 (100), 115 (90); HRMS calcd for $C_{13}H_{15}ClO$, 222.0811; found, 222.0776.

1-Chloro-3-methoxy-2-(1-pentynyl)benzene (4c): The reaction of **3a** (1.34 g, 5 mmol), 1-pentyne (0.68 g, 10 mmol), $PdCl_2(PPh_3)_2$ (0.21 g, 0.30 mmol) and TBAF·$3H_2O$ (4.73 g, 15 mmol) for 3 h according to the typical procedure, and purification by flash column chromatography (hexane/EtOAc, 20/1) on silica gel, afforded **4c** (0.73 g, 70%) as a brown oil: R_f 0.21 (hexane/EtOAc, 20/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (t, J = 8.3 Hz, 1H), 6.98 (dd, J = 8.3, 1.1 Hz, 1H), 6.72 (dd, J = 8.3, 1.1 Hz, 1H), 3.85 (s, 3H), 2.51 (t, J = 6.8 Hz, 2H), 1.73-1.62 (m, 2H), 1.09 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 161.1 (C), 137.2 (C), 128.5 (CH), 121.4 (CH), 113.5 (C), 108.6 (CH), 100.5 (C), 73.9 (C), 56.2 (CH_3), 22.2 (CH_2), 22.0 (CH_2), 13.5 (CH_3); EI-LRMS *m/z* 210 (M^++2, 23), 208 (M^+, 68), 165 (41), 115 (100); HRMS calcd for $C_{12}H_{13}ClO$, 208.0655; found, 208.0649.

1-Benzyloxy-3-chloro-2-phenylethynylbenzene (4d): The reaction of **3b** (0.86 g, 2.5 mmol), phenylacetylene (0.56 g, 5 mmol), $PdCl_2(PPh_3)_2$ (0.105 g, 0.15 mmol) and TBAF·$3H_2O$ (2.37 g, 7.5 mmol) for 3 h according to the typical procedure, and purification by flash column chromatography

(hexane/EtOAc, 15/1) on silica gel, afforded **4d** (0.39 g, 49%) as a brown oil: R_f 0.25 (hexane/EtOAc, 20/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63-7.51 (m, 4H), 7.46-7.31 (m, 6H), 7.18 (td, J = 8.0, 0.8 Hz, 1H), 7.08 (dt, J = 8.0, 0.8 Hz, 1H), 6.86 (dt, J = 8.0, 0.8 Hz, 1H), 5.20 (s, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 160.4 (C), 137.1 (C), 136.7 (C), 131.8 (CH), 129.4 (CH), 128.6 (CH), 128.5 (CH), 126.4 (CH), 128.0 (CH), 127.0 (CH), 123.5 (C), 121.9 (CH), 113.9 (C), 110.8 (CH), 99.2 (C), 82.9 (C), 70.8 (CH_2); EI-LRMS *m/z* 320 (M^++2, 8), 318 (M^+, 27), 241 (52), 163 (21), 91 (100); HRMS calcd for $C_{21}H_{15}ClO$, 318.0811; found, 318.0827.

1-Benzyloxy-3-chloro-2-(1-hexynyl)benzene (4e): The reaction of **3b** (1.72 g, 5 mmol), 1-hexyne (0.82 g, 10 mmol), $PdCl_2(PPh_3)_2$ (0.21 g, 0.30 mmol) and TBAF·$3H_2O$ (4.73 g, 15 mmol) for 2 h according to the typical procedure, and purification by flash column chromatography (hexane/EtOAc, 50/1) on silica gel, afforded **4e** (0.94 g, 63%) as a brown oil: R_f 0.25 (hexane/EtOAc, 20/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52-7.45 (m, 2H), 7.43-7.29 (m, 3H), 7.10 (t, J = 8.0 Hz, 1H), 7.02 (dd, J = 8.0, 1.1 Hz, 1H), 6.79 (dd, J = 8.0, 1.1 Hz, 1H), 5.15 (s, 2H), 2.56 (t, J = 6.8 Hz, 2H), 1.71-1.46 (m, 4H), 0.94 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 160.4 (C), 137.1 (C), 136.7 (C), 128.6 (CH), 128.4 (CH), 127.9 (CH), 127.0 (CH), 121.8 (CH), 114.4 (C), 110.7 (CH), 100.9 (C), 73.8 (C), 70.8 (CH_2), 30.9 (CH_2), 22.0 (CH_2), 19.7 (CH_2), 13.8 (CH_3); EI-LRMS *m/z* 300 (M^++2, 1), 298 (M^+, 2), 255 (21), 220 (11), 165 (10), 91 (100); HRMS calcd for $C_{19}H_{19}ClO$, 298.1124; found, 298.1125.

***t*-Butyl 3-chloro-2-(1-hexynyl)phenoxyacetate (4f):** The reaction of **3c** (1.11 g, 3 mmol), 1-hexyne (0.49 g, 6 mmol), $PdCl_2(PPh_3)_2$ (0.13 g, 0.18 mmol) and TBAF·$3H_2O$ (2.84 g, 9 mmol) for 3 h according to the typical procedure, and purification by flash column chromatography (hexane/EtOAc, 20/1) on silica gel, afforded **4f** (0.57 g, 59%) as a brown oil: R_f 0.19 (hexane/EtOAc, 20/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (t, J = 8.1 Hz, 1H), 7.00 (d, J = 8.1 Hz, 1H), 6.63 (d, J = 8.1 Hz, 1H), 4.56 (s, 2H), 2.51 (t, J = 6.9 Hz, 2H), 1.67-1.58 (m, 2H), 1.55-1.48 (m, 2H), 1.45 (s, 9H), 0.93 (t, J = 5.7 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 167.4 (C), 159.5 (C), 137.3 (C), 128.1 (CH), 122.3 (CH), 114.4 (C), 110.5 (CH), 101.0 (C), 82.4 (C), 73.4 (C), 66.6 (CH_2), 30.7 (CH_2), 28.0 (CH_3), 21.9 (CH_2), 19.7 (CH_2), 13.7

(CH_3); EI-LRMS *m/z* 324 (M^++2, 11), 322 (M^+, 28), 165 (41), 115 (33), 57 (100); HRMS calcd for $C_{18}H_{23}ClO_3$, 322.1336; found, 322.1341.

***O*-3-Chloro-2-(1-hexynyl)phenyl *N,N*-diethylcarbamate (4g):** The reaction of **2a** (1.77 g, 5 mmol), 1-hexyne (0.82 g, 10 mmol), $PdCl_2(PPh_3)_2$ (0.21 g, 0.30 mmol) and TBAF·$3H_2O$ (4.73 g, 15 mmol) for 3.5 h according to the typical procedure, and purification by flash column chromatography (hexane/EtOAc, 7/1) on silica gel, afforded **4g** (1.23 g, 80%) as a brown oil: R_f 0.25 (hexane/EtOAc, 5/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.16 (t, *J* = 8.0 Hz, 1H), 7.06 (dd, *J* = 8.0, 1.5 Hz, 1H), 3.47 (q, *J* = 7.2 Hz, 2H), 3.38 (q, *J* = 7.2 Hz, 2H), 2.45 (t, *J* = 6.9 Hz, 2H), 1.65-1.41 (m, 4H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 153.4 (C), 153.3 (C), 136.6 (C), 128.1 (CH), 126.0 (CH), 121.0 (CH), 118.8 (C), 100.7 (C), 73.2 (C), 42.4 (CH_2), 42.1 (CH_2), 30.7 (CH_2), 22.0 (CH_2), 19.6 (CH_2), 14.2 (CH_3), 13.7 (CH_3), 13.5 (CH_3); EI-LRMS *m/z* 309 (M^++2, 3), 307 (M^+, 8), 265 (5), 165 (5), 100 (100); IR (film) 2960, 2934, 2873, 1725, 1461, 1446, 1417, 1235, 1220, 1153, 936 cm^{-1}; HRMS calcd for $C_{17}H_{22}ClNO_2$, 307.1339; found, 307.1313.

1-Bromo-3-methoxy-2-phenylethynylbenzene (5a): The reaction of **3e** (0.94 g, 3 mmol), phenylacetylene (0.37 g, 3.6 mmol), $PdCl_2(PPh_3)_2$ (0.13 g, 0.18 mmol) and TBAF·$3H_2O$ (2.84 g, 9 mmol) for 3 h according to the typical procedure, and purification by flash column chromatography (hexane/EtOAc, 15/1) on silica gel, afforded **5a** (0.58 g, 67%) as a brown oil: R_f 0.19 (hexane/EtOAc, 20/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66-7.60 (m, 2H), 7.40-7.33 (m, 3H), 7.24 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.14 (t, *J* = 8.2 Hz, 1H), 6.84 (dd, *J* = 8.2, 1.1 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 161.1 (C), 131.8 (CH), 129.8 (CH), 128.6 (CH), 128.4 (CH), 127.1 (C), 124.7 (CH), 123.3 (C), 115.0 (C), 109.4 (CH), 98.3 (C), 84.7 (C), 56.3 (CH_3); EI-LRMS *m/z* 288 (M^++2, 99), 286 (M^+, 100), 211 (41), 182 (82), 163 (93); HRMS calcd for $C_{15}H_{11}BrO$, 285.9993; found, 285.9991.

2-Chloro-1-methoxy-3-phenylethynylbenzene (6a): The reaction of **3f** (1.34 g, 5 mmol), phenylacetylene (1.02 g, 10 mmol), $PdCl_2(PPh_3)_2$ (0.21 g, 0.30 mmol) and TBAF·$3H_2O$ (4.73 g, 15

mmol) for 2 h according to the typical procedure, and purification by flash column chromatography (hexane/EtOAc, 20/1) on silica gel, afforded **6a** (0.99 g, 82%) as a brown oil: R_f 0.23 (hexane/EtOAc, 20/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64-7.56 (m, 2H), 7.40-7.33 (m, 3H), 7.20 (d, J = 4.6 Hz, 2H), 6.91 (t, J = 4.6 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 155.4 (C), 131.8 (CH), 128.7 (CH), 128.5 (CH), 127.1 (CH), 126.8 (C), 125.1 (CH), 124.6 (C), 123.0 (C), 111.9 (CH), 94.7 (C), 86.3 (C), 56.4 (CH_3); EI-LRMS *m/z* 244 (M^++2, 32), 242 (M^+, 100), 199 (36), 163 (32); HRMS calcd for $C_{15}H_{11}ClO$, 242.0498; found, 242.0502.

2-Chloro-1-(1-hexynyl)-3-methoxybenzene (6b): The reaction of **3f** (0.67 g, 2.5 mmol), 1-hexyne (0.41 g, 5 mmol), $PdCl_2(PPh_3)_2$ (0.105 g, 0.15 mmol) and TBAF·$3H_2O$ (2.37 g, 7.5 mmol) for 2 h according to the typical procedure, and purification by flash column chromatography (hexane/EtOAc, 30/1) on silica gel, afforded **6b** (0.30 g, 53%) as a brown oil: R_f 0.19 (hexane/EtOAc, 30/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (t, J = 8.0 Hz, 1H), 7.04 (dd, J = 8.0, 1.7 Hz, 1H), 6.83 (dd, J = 8.0, 1.7 Hz, 1H), 3.87 (s, 3H), 2.47 (t, J = 6.9 Hz, 2H), 1.66-1.44 (m, 4H), 0.95 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 155.3 (C), 126.9 (CH), 125.3 (C), 125.2 (CH), 124.2 (C), 111.2 (CH), 96.4 (C), 77.6 (C), 56.3 (CH_3), 30.8 (CH_2), 22.1 (CH_2), 19.4 (CH_2), 13.8 (CH_3); EI-LRMS *m/z* 224 (M^++2, 37), 222 (M^+, 100), 172 (75), 115 (45); HRMS calcd for $C_{13}H_{15}ClO$, 222.0811; found, 222.0821.

1-Benzyloxy-2-chloro-3-phenylethynylbenzene (6c): The reaction of **3g** (0.86 g, 2.5 mmol), phenylacetylene (0.56 g, 5 mmol), $PdCl_2(PPh_3)_2$ (0.105 g, 0.15 mmol) and TBAF·$3H_2O$ (2.37 g, 7.5 mmol) for 2 h according to the typical procedure, and purification by flash column chromatography (hexane/EtOAc, 20/1) on silica gel, afforded **6c** (0.75 g, 94%) as a brown oil: R_f 0.18 (hexane/EtOAc, 20/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70-7.60 (m, 2H), 7.56-7.48 (m, 2H), 7.48-7.34 (m, 6H), 7.25 (dd, J = 7.7, 1.4 Hz, 1H), 7.17 (t, J = 7.7 Hz, 1H), 6.96 (dd, J = 7.7, 1.4 Hz, 1H), 5.19 (s, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 154.5 (C), 136.4 (C), 131.8 (CH), 128.73 (CH), 128.68 (CH), 128.5 (CH), 128.1 (CH), 127.1 (CH), 127.0 (CH), 125.5 (CH), 125.2 (C), 124.7 (C), 123.0 (C), 113.9 (CH), 94.7 (C), 86.4

(C), 70.9 (CH_2); EI-LRMS *m/z* 320 (M^++2, 5), 318 (M^+, 15), 283 (11), 163 (11), 91 (100); HRMS calcd for $C_{21}H_{15}ClO$, 318.0811; found, 318.0807.

1-Benzyloxy-2-chloro-3-(1-hexynyl)benzene (6d): The reaction of **3g** (0.86 g, 2.5 mmol), 1-hexyne (0.41 g, 5 mmol), $PdCl_2(PPh_3)_2$ (0.105 g, 0.15 mmol) and TBAF·$3H_2O$ (2.37 g, 7.5 mmol) for 2 h according to the typical procedure, and purification by flash column chromatography (hexane/EtOAc, 20/1) on silica gel, afforded **6d** (0.78 g, 84%) as a brown oil: R_f 0.22 (hexane/EtOAc, 20/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49-7.43 (m, 2H), 7.43-7.28 (m, 3H), 7.09-7.06 (m, 2H), 6.91-6.84 (m, 1H), 5.15 (s, 2H), 2.49 (t, J = 6.9 Hz, 2H), 1.70-1.44 (m, 4H), 0.97 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 154.5 (C), 136.5 (C), 128.7 (CH), 128.1 (CH), 127.1 (CH), 126.8 (CH), 125.6 (CH), 125.5 (C), 125.2 (C), 113.3 (CH), 96.4 (C), 77.7 (C), 71.0 (CH_2), 30.8 (CH_2), 22.1 (CH_2), 19.4 (CH_2), 13.8 (CH_3); EI-LRMS *m/z* 300 (M^++2, 2), 298 (M^+, 6), 91 (100); HRMS calcd for $C_{19}H_{19}ClO$, 298.1124; found, 298.1139.

2-Chloro-3-(1-hexynyl)phenol (6e): The reaction of 2-chloro-3-iodophenol (0.25 g, 1 mmol), 1-hexyne (0.16 g, 2 mmol), $PdCl_2(PPh_3)_2$ (0.042 g, 0.06 mmol) and TBAF·$3H_2O$ (0.95 g, 3 mmol) for 2 h according to the typical procedure, and purification by flash column chromatography (hexane/EtOAc, 8/1) on silica gel, afforded **6e** (0.071 g, 34%) as a brown oil: R_f 0.14 (hexane/EtOAc, 10/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.09 (t, J = 7.7 Hz, 1H), 7.02 (dd, J = 7.7, 1.7 Hz, 1H), 6.94 (dd, J = 7.7, 1.7 Hz, 1H), 5.55 (br s, 1H), 2.47 (t, J = 6.9 Hz, 2H), 1.68-1.43 (m, 4H), 0.96 (t, J = 7.4 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 151.7 (C), 127.6 (CH), 125.3 (CH), 124.4 (C), 121.7 (C), 115.5 (CH), 96.4 (C), 77.3 (C), 37.8 (CH_2), 22.1 (CH_2), 19.4 (CH_2), 13.8 (CH_3); EI-LRMS *m/z* 210 (M^++2, 32), 208 (M^+, 95), 165 (100); HRMS calcd for $C_{12}H_{13}ClO$, 208.0655; found, 208.0647.

General Procedure for the Synthesis of 4-Alkoxyindoles 7 and 7-Alkoxyindoles 8.[5] To a solution of $Pd(OAc)_2$ (22.4 mg, 0.10 mmol), 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (HIPrCl) (42.5 mg, 0.1 mmol), and KO*t*-Bu (0.67 g, 6 mmol) in toluene (6 mL) were added the corresponding *o*-

chloroarene derivative **4** or **6** (2 mmol) and benzylamine (0.26 g, 2.4 mmol) at room temperature. The resulting mixture was stirred at reflux for 2-20 h, after which GC/MS analysis indicated complete conversion of the starting material. CH_2Cl_2 (25 mL) and aq HCl (25 mL of a 2 M solution) were added to the cooled reaction mixture. The separated aqueous phase was extracted with CH_2Cl_2 (2 x 20mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The remaining residue was purified by column chromatography on silica gel (hexane/EtOAc) to afford the title compounds **7** and **8**:

1-Benzyl-2-butyl-4-methoxy-1*H*-indole (7b): From **4b** (0.45 g, 2 mmol) according to the typical procedure (3 h), and purification by flash column chromatography (hexane/EtOAc, 50/1) on silica gel, afforded **7b** (0.46 g, 79%) as a white solid: mp 52-54 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.22 (m, 3H), 7.09 (t, *J* = 8.0 Hz, 1H), 7.00 (dd, *J* = 7.7, 1.7 Hz, 2H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.59 (d, *J* = 7.6 Hz, 1H), 6.53 (s, 1H), 5.34 (s, 2H), 4.02 (s, 3H), 2.71 (t, *J* = 7.6 Hz, 2H), 1.80-1.67 (m, 2H), 1.53-1.39 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 152.7 (C), 140.0 (C), 138.6 (C), 138.1 (C), 128.8 (CH), 127.2 (CH), 126.0 (CH), 121.6 (CH), 118.4 (C), 103.1 (CH), 99.7 (CH), 96.5 (CH), 55.4 (CH_3), 46.7 (CH_2), 30.6 (CH_2), 26.4 (CH_2), 22.5 (CH_2), 14.0 (CH_3); EI-LRMS *m/z* 293 (M^+, 100), 250 (83), 91 (50); IR (KBr) 3023, 1544, 1496, 1448, 1358, 1250, 1084, 759, 720 cm^{-1}; HRMS calcd for $C_{20}H_{23}NO$, 293.1780; found, 293.1766. Anal. Calcd for $C_{20}H_{23}NO$: C, 81.87; H, 7.90; N, 4.77. Found: C, 82.09; H, 7.78; N, 4.70.

1-Benzyl-2-propyl-4-methoxy-1*H*-indole (7c): From **4c** (0.42 g, 2 mmol) according to the typical procedure (4 h), and purification by flash column chromatography (hexane/EtOAc, 50/1) on silica gel, afforded **7c** (0.41 g, 57%) which was contaminated by the starting material **4c**. Data for **7c**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28-7.21 (m, 2H), 7.11 (t, *J* = 8.0 Hz, 1H), 7.03 (t, *J* = 8.0 Hz, 2H), 6.98-6.90 (m, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.53 (d, *J* = 7.7 Hz, 1H), 6.46 (s, 1H), 5.31 (s, 2H), 3.98 (s, 3H), 2.63 (t, *J* = 7.5 Hz, 2H), 1.80-1.66 (m, 2H), 1.00 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 152.8 (C), 141.4 (C), 138.8 (C), 138.0 (C), 128.8 (CH), 127.2 (CH), 126.0 (CH), 121.6 (CH), 118.4 (C), 103.0

(CH), 99.7 (CH), 95.7 (CH), 55.4 (CH_3), 46.6 (CH_2), 28.8 (CH_2), 20.0 (CH_2), 12.5 (CH_3); EI-LRMS *m/z* 279 (M^+, 100), 250 (63), 91 (100).

1-Benzyl-4-benzyloxy-2-phenyl-1*H*-indole (7d): From **4d** (0.64 g, 2 mmol) according to the typical procedure (2.5 h), and purification by flash column chromatography (hexane/EtOAc, 20/1) on silica gel, gave **7d** (0.69 g, 89%) as a white solid: mp 112-114 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, J = 6.8 Hz, 2H), 7.51-7.27 (m, 11H), 7.13-7.01 (m, 3H), 6.90-6.82 (m, 2H), 6.67 (d, J = 7.8 Hz, 1H), 5.39 (s, 2H), 5.29 (s, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 152.5 (C), 140.6 (C), 139.6 (C), 138.3 (C), 137.7 (C), 132.8 (C), 129.3 (CH), 128.8 (CH), 128.64 (CH), 128.61 (CH), 128.0 (CH), 127.9 (CH), 127.5 (CH), 127.2 (CH), 126.1 (CH), 122.8 (CH), 119.3 (C), 104.4 (CH), 101.6 (CH), 99.9 (CH), 70.0 (CH_2), 48.1 (CH_2); EI-LRMS *m/z* 389 (M^+, 100), 298 (66), 91 (33); IR (KBr) 3030, 1504, 1450, 1259, 759, 670 cm^{-1}; HRMS calcd for $C_{28}H_{23}NO$, 389.1780; found, 389.1796.

1-Benzyl-4-benzyloxy-2-butyl-1*H*-indole (7e): From **4e** (0.60 g, 2 mmol) according to the typical procedure (3 h), and purification by flash column chromatography (hexane/EtOAc, 30/1) on silica gel, afforded **7e** (0.55 g, 75%) as a white solid: mp 80-82 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, J = 7.2 Hz, 2H), 7.57 (t, J = 7.2 Hz, 2H), 7.53-7.31 (m, 4H), 7.20 (t, J = 7.6 Hz, 1H), 7.16-7.07 (m, 2H), 7.02 (d, J = 8.2 Hz, 1H), 6.81-6.73 (m, 2H), 5.41 (s, 2H), 5.40 (s, 2H), 2.82 (t, J = 7.7 Hz, 2H), 1.94-1.80 (m, 2H), 1.66-1.50 (m, 2H), 1.10 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 151.9 (C), 139.9 (C), 138.7 (C), 138.1 (C), 137.8 (C), 128.7 (CH), 128.5 (CH), 127.7 (CH), 127.5 (CH), 127.2 (CH), 125.9 (CH), 121.5 (CH), 118.8 (C), 103.2 (CH), 101.1 (CH), 96.8 (CH), 69.9 (CH_2), 46.6 (CH_2), 30.5 (CH_2), 26.4 (CH_2), 22.5 (CH_2), 14.0 (CH_3); EI-LRMS *m/z* 369 (M^+, 76), 278 (95), 91 (100); IR (KBr) 3023, 1546, 1499, 1445, 1254, 1076, 746, 695 cm^{-1}; HRMS calcd for $C_{26}H_{27}NO$, 369.2093; found, 369.2104. Anal. Calcd for $C_{26}H_{27}NO$: C, 84.51; H, 7.37; N, 3.79. Found: C, 84.25; H, 7.45; N, 3.83.

1-Benzyl-7-methoxy-2-phenyl-1*H*-indole (8a): From **6a** (0.49 g, 2 mmol) according to the typical procedure (5 h), and purification by flash column chromatography (hexane/EtOAc, 50/1) on silica gel, gave **8a** (0.39 g, 63%) as a white solid: mp 100-102 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57-7.43 (m,

5H), 7.40 (dd, J = 8.0, 0.8 Hz, 1H), 7.34-7.23 (m, 3H), 7.18 (t, J = 7.5 Hz, 1H), 6.98 (dd, J = 8.3, 1.9 Hz, 2H), 6.74 (dd, J = 8.0, 0.8 Hz, 1H), 6.72 (s, 1H), 5.76 (s, 2H), 3.82 (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 147.7 (C), 142.5 (C), 140.6 (C), 132.9 (C), 130.5 (C), 129.7 (CH), 128.5 (CH), 128.3 (CH), 128.0 (CH), 127.6 (C), 126.6 (CH), 125.9 (CH), 120.6 (CH), 113.5 (CH), 103.44 (CH), 103.38 (CH), 55.5 (CH_3), 49.8 (CH_2); EI-LRMS *m/z* 313 (M^+, 80), 91 (100); IR (KBr) 3019, 1505, 1446, 1322, 1263, 1100, 796, 726, 702 cm^{-1}; HRMS calcd for $C_{22}H_{19}NO$, 313.1467; found, 313.1460.

1-Benzyl-2-butyl-7-methoxy-1*H*-indole (8b): From **6b** (0.45 g, 2 mmol) according to the typical procedure (2 h), and purification by flash column chromatography (hexane/EtOAc, 50/1) on silica gel, afforded **8b** (0.43 g, 74%) as a white solid: mp 72-74 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30-7.15 (m, 4H), 7.00 (t, J = 7.7 Hz, 1H), 6.97-6.89 (m, 2H), 6.60 (d, J = 7.7 Hz, 1H), 6.33 (s, 1H), 5.69 (s, 2H), 3.77 (s, 3H), 2.61 (t, J = 7.3 Hz, 2H), 1.73-1.60 (m, 2H), 1.48-1.33 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 147.3 (C), 142.0 (C), 140.3 (C), 130.3 (C), 128.5 (CH), 126.7 (CH), 126.6 (C), 125.9 (CH), 119.8 (CH), 113.0 (CH), 102.5 (CH), 100.2 (CH), 55.6 (CH_3), 48.8 (CH_2), 30.7 (CH_2), 26.4 (CH_2), 22.6 (CH_2), 14.1 (CH_3); EI-LRMS *m/z* 293 (M^+, 100), 251 (67), 91 (50); HRMS calcd for $C_{20}H_{23}NO$, 293.1780; found, 293.1780. Anal. Calcd for $C_{20}H_{23}NO$: C, 81.87; H, 7.90; N, 4.77. Found: C, 81.59; H, 7.83; N, 4.83.

1-Benzyl-7-benzyloxy-2-phenyl-1*H*-indole (8c): From **6c** (0.64 g, 2 mmol) according to the typical procedure (2 h), and purification by flash column chromatography (hexane/EtOAc, 25/1) on silica gel, afforded **8c** (0.55 g, 70%) as a white solid: mp 77-79 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52-7.02 (m, 15H), 6.84-6.75 (m, 2H), 6.73 (d, J = 7.7 Hz, 1H), 6.67 (s, 1H), 5.86 (s, 2H), 5.04 (s, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 146.8 (C), 142.6 (C), 140.7 (C), 137.0 (C), 132.9 (C), 130.7 (C), 129.7 (CH), 128.49 (CH), 128.47 (CH), 128.39 (CH), 128.1 (CH), 127.8 (CH), 127.7 (CH), 127.5 (C), 126.5 (CH), 125.6 (CH), 120.6 (CH), 113.7 (CH), 104.2 (CH), 103.3 (CH), 70.3 (CH_2), 49.7 (CH_2); EI-LRMS *m/z* 284 (50), 91 (100); IR (KBr) 3058, 1575, 1489, 1318, 1263, 738, 703 cm^{-1}; HRMS calcd for $C_{28}H_{23}NO$,

389.1780; found, 389.1779. Anal. Calcd for $C_{28}H_{23}NO$: C, 86.34; H, 5.95; N, 3.60. Found: C, 86.57; H, 5.87; N, 3.55.

1-Benzyl-7-benzyloxy-2-butyl-1*H*-indole (8d): From **6d** (0.60 g, 2 mmol) according to the typical procedure (2 h), and purification by flash column chromatography (hexane/EtOAc, 30/1) on silica gel, afforded **8d** (0.47 g, 64%) as a white solid: mp 51-53 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.24 (m, 7H), 7.22-7.14 (m, 2H), 7.07 (t, J = 7.8 Hz, 1H), 6.90-6.84 (m, 2H), 6.71 (d, J = 7.8 Hz, 1H), 6.44 (s, 1H), 5.74 (s, 2H), 5.08 (s, 2H), 2.70 (t, J = 7.1 Hz, 2H), 1.82-1.70 (m, 2H), 1.56-1.42 (m, 2H), 1.00 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 146.3 (C), 142.0 (C), 140.2 (C), 137.1 (C), 130.5 (C), 128.5 (CH), 128.4 (CH), 127.8 (CH), 127.7 (CH), 126.61 (CH), 126.55 (C), 125.5 (CH), 119.8 (CH), 113.2 (CH), 103.3 (CH), 100.1 (CH), 70.3 (CH_2), 48.6 (CH_2), 30.6 (CH_2), 26.3 (CH_2), 22.6 (CH_2), 14.0 (CH_3); EI-LRMS *m/z* 369 (M^+, 100), 327 (39), 91 (98); IR (KBr) 3027, 1497, 1458, 1244, 1096, 781, 726, 703 cm^{-1}; HRMS calcd for $C_{26}H_{27}NO$, 369.2093; found, 369.2085. Anal. Calcd for $C_{26}H_{27}NO$: C, 84.51; H, 7.37; N, 3.79. Found: C, 84.31; H, 7.34; N, 3.81.

General Procedure for *N*-Debenzylation of 4-Alkoxy-1-benzyl-1*H*-indoles 7. Synthesis of *N*-H Indoles 9.[6] The corresponding 1-benzyl-1*H*-indol **7** (1 mmol) was dissolved in DMSO (0.71 mL, 10 mmol) and added to a flame-dried flask. While stirring the solution at room temperature, KO*t*-Bu (7 mL of a 1 M solution in THF, 7 mmol) was added. Oxygen was then bubbled into the solution for 1 h. Upon completion (determined by GC/MS analysis), the reaction was quenched with saturated aqueous NH_4Cl. The aqueous phase was extracted with EtOAc (3 x 10 mL), and the combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The remaining residue was purified by flash column chromatography on silica gel (hexane/EtOAc) to afford the title compounds:

4-Benzyloxy-2-phenyl-1*H*-indole (9b): From **7d** (0.39 g, 1.0 mmol) according to the typical procedure, and purification by flash column chromatography (hexane/EtOAc, 10/1) on silica gel, gave **9b** (0.19 g, 64%) as a white solid: mp 140-142 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (br s, 1H), 7.70-

7.62 (m, 2H), 7.62-7.55 (m, 2H), 7.52-7.29 (m, 6H), 7.15 (t, J = 7.9 Hz, 1H), 7.09-7.03 (m, 2H), 6.66 (d, J = 7.5 Hz, 1H), 5.29 (s, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 152.6 (C), 138.3 (C), 137.6 (C), 136.6 (C), 132.4 (C), 129.1 (CH), 128.6 (CH), 127.9 (CH), 127.5 (CH), 125.0 (CH), 123.2 (CH), 120.4 (C), 104.7 (CH), 101.5 (CH), 97.6 (CH), 70.0 (CH_2); EI-LRMS *m/z* 299 (M^+, 56), 208 (100), 180 (26), 91 (38); IR (KBr) 3408, 3031, 1591, 1260, 1241, 762, 696 cm^{-1}; HRMS calcd for $C_{21}H_{17}NO$, 299.1310; found, 299.1310. Anal. Calcd for $C_{21}H_{17}NO$: C, 84.25; H, 5.72; N, 4.68. Found: C, 84.11; H, 5.78; N, 4.71.

4-Benzyloxy-2-butyl-1*H*-indole (9c): From **7e** (0.37 g, 1.0 mmol) according to the typical procedure, and purification by flash column chromatography (hexane/ EtOAc, 7/1) on silica gel, gave **9c** (0.20 g, 73%) as a white solid: mp 65-67 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (br s, 1H), 7.64-7.51 (m, 2H), 7.50-7.35 (m, 3H), 7.09 (t, J = 7.9 Hz, 1H), 6.97 (d, J = 7.9 Hz, 1H), 6.64 (d, J = 7.9 Hz, 1H), 6.48 (s, 1H), 5.28 (s, 2H), 2.74 (t, J = 7.6 Hz, 2H), 1.79-1.67 (m, 2H), 1.53-1.38 (m, 2H), 1.01 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 151.8 (C), 138.6 (C), 137.8 (C), 137.3 (C), 128.5 (CH), 127.8 (CH), 127.4 (CH), 121.6 (CH), 119.6 (C), 104.3 (CH), 101.2 (CH), 96.8 (CH), 69.9 (CH_2), 31.3 (CH_2), 27.9 (CH_2), 22.5 (CH_2), 14.0 (CH_3); EI-LRMS *m/z* 279 (M^+, 41), 188 (100), 91 (81); IR (KBr) 3405, 1614, 1513, 1439, 1248, 1101, 766 cm^{-1}; HRMS calcd for $C_{19}H_{21}NO$, 279.1623; found, 279.1599. Anal. Calcd for $C_{19}H_{21}NO$: C, 81.68; H, 7.58; N, 5.01. Found: C, 81.41; H, 7.64; N, 4.95.

General Procedure for the *O*-Demethylation of 4-, and 7-Methoxy-1*H*-indoles 7a-c, 8a, and 9a. Synthesis of 4-, and 7-Hydroxy-1*H*-indoles 10, 11, and 12a.[7] BBr_3 (6 mL of a 1 M solution in CH_2Cl_2, 6 mmol) was added dropwise to a solution of the corresponding 4- or 7-methoxy-1*H*-indole **7a-c**, **8a**, or **9a** (1 mmol) in CH_2Cl_2 (40 mL) at −78 ºC. The mixture was warmed to room temperature overnight, and then $KHCO_3$ (0.60 g, 6 mmol) were added. The resulting mixture was cooled to 0 ºC, and MeOH (20 mL) was added dropwise. After 30 min at 0 ºC, the mixture was warmed to room temperature and stirred for 1 h. The reaction was quenched with water. The separated aqueous phase was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers were dried over Na_2SO_4 and

concentrated under reduced pressure. The remaining residue was purified by column chromatography on silica gel (hexane/EtOAc) to afford the title compounds:

1-Benzyl-2-butyl-1*H*-indol-4-ol (10b): From **7b** (0.29 g, 1.0 mmol) according to the typical procedure, and purification by flash column chromatography (hexane/EtOAc, 7/1) on silica gel, gave **10b** (0.22 g, 80%) as a white solid: mp 80-82 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.22 (m, 3H), 7.04-6.95 (m, 3H), 6.85 (d, *J* = 8.1 Hz, 1H), 6.56 (d, *J* = 7.2 Hz, 1H), 6.47 (s, 1H), 5.51 (s, 1H), 5.32 (s, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 1.76-1.66 (m, 2H), 1.51-1.34 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 148.3 (C), 140.3 (C), 139.2 (C), 138.0 (C), 128.8 (CH), 127.3 (CH), 126.0 (CH), 121.7 (CH), 117.4 (C), 104.3 (CH), 102.8 (CH), 96.5 (CH), 46.7 (CH_2), 30.5 (CH_2), 26.4 (CH_2), 22.5 (CH_2), 14.0 (CH_3); EI-LRMS *m/z* 279 (M^+, 97), 236 (100), 91 (78); IR (KBr) 3465, 3375, 1584, 1547, 1451, 1356, 1253, 757, 721 cm^{-1}; HRMS calcd for $C_{19}H_{21}NO$, 279.1623; found, 279.1627.

1-Benzyl-2-propyl-1*H*-indol-4-ol (10c): From **7c** (0.28 g, 1.0 mmol) according to the typical procedure, and purification by flash column chromatography (hexane/EtOAc, 7/1) on silica gel, gave **10c** (0.25 g, 93%) as a white solid: mp 115-117 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33-7.18 (m, 3H), 7.01-6.92 (m, 3H), 6.82 (d, *J* = 8.5 Hz, 1H), 6.52 (d, *J* = 7.4 Hz, 1H), 6.41 (s, 1H), 5.31 (s, 2H), 5.12 (s, 1H), 2.65 (t, *J* = 7.7 Hz, 2H), 1.81-1.66 (m, 2H), 1.01 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 148.3 (C), 140.3 (C), 139.2 (C), 137.9 (C), 128.8 (CH), 127.3 (CH), 126.0 (CH), 121.8 (CH), 117.4 (C), 104.3 (CH), 102.9 (CH), 96.5 (CH), 46.8 (CH_2), 28.9 (CH_2), 21.7 (CH_2), 14.1 (CH_3); EI-LRMS *m/z* 265 (M^+, 100), 236 (86), 91 (96); IR (KBr) 3222, 1466, 1451, 1365, 1252, 1221, 758, 723 cm^{-1}; HRMS calcd for $C_{18}H_{19}NO$, 265.1467; found, 265.1438. Anal. Calcd for $C_{19}H_{21}NO$: C, 81.68; H, 7.58; N, 5.01. Found: C, 81.50; H, 7.53; N, 4.96.

1-Benzyl-2-phenyl-1*H*-indol-7-ol (11): From **8a** (0.31 g, 1.0 mmol) according to the typical procedure, and purification by flash column chromatography (hexane/EtOAc, 7/1) on silica gel, afforded **11** (0.28 g, 92%) as a brown solid: mp 45-47 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54-7.36 (m, 5H), 7.35-7.15 (m, 4H), 7.05-6.90 (m, 3H), 6.66 (s, 1H), 6.49 (d, *J* = 7.4 Hz, 1H), 5.70 (s, 2H), 5.02 (s,

1H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 142.83 (C), 142.77 (C), 140.5 (C), 132.8 (C), 131.3 (C), 129.7 (CH), 128.5 (2 x CH), 128.1 (CH), 127.0 (C), 126.8 (CH), 125.9 (CH), 120.6 (CH), 113.6 (CH), 108.1 (CH), 103.4 (CH), 49.5 (CH_2); EI-LRMS *m/z* 299 (M^+, 66), 207 (73), 91 (100); IR (KBr) 3436, 3023, 1583, 1494, 1264, 735, 700 cm^{-1}; HRMS calcd for $C_{21}H_{17}NO$, 299.1310; found, 299.1302. Anal. Calcd for $C_{21}H_{17}NO$: C, 84.25; H, 5.72; N, 4.68. Found: C, 83.96; H, 5.74; N, 4.65.

2-Phenyl-1*H*-indol-4-ol (12a): From **9a** (0.111 g, 0.5 mmol) according to the typical procedure, and purification by flash column chromatography (hexane/EtOAc, 4/1) on silica gel, afforded **12a** (0.094 g, 90%) as a colorless oil: R_f 0.32 (hexane/EtOAc, 3/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (br s, 1H), 7.63 (d, J = 7.8 Hz, 2H), 7.42 (t, J = 7.8 Hz, 2H), 7.31 (d, J = 7.4 Hz, 1H), 7.09-6.96 (m, 2H), 6.90 (s, 1H), 6.54 (d, J = 7.4 Hz, 1H), 5.47 (br s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 149.1 (C), 138.8 (C), 136.9 (C), 132.3 (C), 129.1 (CH), 127.7 (CH), 125.2 (CH), 123.4 (CH), 119.1 (C), 104.7 (CH), 104.2 (CH), 96.3 (CH); EI-LRMS *m/z* 209 (M^+, 100); IR (KBr) 3428, 1595, 1459, 1357, 1334, 1268, 754, 696 cm^{-1}; HRMS calcd for $C_{14}H_{11}NO$, 209.0841; found, 209.0847.

Synthesis of 2-Butyl-1*H*-indol-4-ol (12b): Palladium on carbon (10 wt. %) (5.5 mg, 0.05 mmol) was added to a hydrogenation vessel with a solution of 4-benzyloxy-2-butyl-1*H*-indole **9c** (0.140 g, 0.5 mmol) in MeOH (5 mL). The reactor was purged with hydrogen several times, charged with hydrogen (40 psi) and stirred for 5 h. The catalyst was filtered off and the solvent was removed under reduced pressure. The remaining residue was purified by column chromatography (hexane/EtOAc, 5/1) on silica gel to afford compound **12b** (0.058 g, 61%) as a colorless oil: R_f 0.19 (hexane/EtOAc, 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (br s, 1H), 6.97 (td, J = 7.8, 0.9 Hz, 1H), 6.91 (dd, J = 7.8, 0.9 Hz, 1H), 6.49 (d, J = 7.8 Hz, 1H), 6.26 (s, 1H), 4.97 (br s, 1H), 2.73 (t, J = 7.7 Hz, 2H), 1.74-1.64 (m, 2H), 1.46-1.36 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 148.3 (C), 139.0 (C), 137.8 (C), 121.9 (CH), 118.2 (C), 104.3 (CH), 103.8 (CH), 95.5 (CH), 31.4 (CH_2), 28.0 (CH_2), 22.5 (CH_2), 14.0

(CH_3); EI-LRMS *m/z* 189 (M^+, 35), 146 (100); IR (KBr) 3404, 2961, 1260, 1097, 1027, 801 cm^{-1}; HRMS calcd for $C_{12}H_{15}NO$, 189.1154; found, 189.1139.

Synthesis of Indole Inhibitor of Phospholipase A_2 LY315920 (15)

2-But-1-ynyl-1-chloro-3-methoxybenzene (4h): The reaction of **3a** (1.34 g, 5 mmol), 1-butyne (excess), $PdCl_2(PPh_3)_2$ (0.21 g, 0.30 mmol) and TBAF·$3H_2O$ (4.73 g, 15 mmol) according to the typical procedure above reported, and purification by flash column chromatography (hexane/EtOAc, 30/1) on silica gel, gave **4h** (0.68 g, 70%) as a brown oil: R_f 0.29 (hexane/EtOAc, 20/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11 (t, J = 8.2 Hz, 1H), 6.97 (d, J = 8.2 Hz, 1H), 6.72 (d, J = 8.2 Hz, 1H), 3.84 (s, 3H), 2.53 (q, J = 7.5 Hz, 2H), 1.26 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 161.0 (C), 137.3 (C), 128.6 (CH), 121.5 (CH), 113.4 (C), 108.7 (CH), 101.9 (C), 73.0 (C), 56.3 (CH_3), 14.0 (CH_2), 13.8 (CH_3); EI-LRMS *m/z* 196 (M^++2, 31), 194 (M^+, 100), 180 (75), 115 (90); HRMS calcd for $C_{11}H_{11}ClO$, 194.0498; found, 194.0495.

1-Benzyl-2-ethyl-4-methoxy-1H-indole (7f):[8] The reaction of **4f** (0.58 g, 3 mmol), benzylamine (0.39 g, 3.6 mmol), $Pd(OAc)_2$ (33.7 mg, 0.15 mmol), HIPrCl (63.8 mg, 0.15 mmol), and KO*t*-Bu (1.01 g, 9 mmol) in toluene (9 mL) according to the typical procedure above described, and purification by flash column chromatography (hexane/EtOAc, 50/1) on silica gel, gave **7f** (0.53 g, 67%) as a white solid: mp 62-64 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.23 (m, 3H), 7.11 (t, J = 8.0 Hz, 1H), 7.03-6.98 (m, 2H), 6.91 (d, J = 8.3 Hz, 1H), 6.60 (d, J = 8.0 Hz, 1H), 6.55 (s, 1H), 5.33 (s, 2H), 4.03 (s, 3H), 2.72 (q, J = 7.5 Hz, 2H), 1.38 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 152.8 (C), 141.4 (C), 138.8 (C), 138.0 (C), 128.8 (CH), 127.2 (CH), 126.0 (CH), 121.6 (CH), 118.4 (C), 103.0 (CH), 99.7 (CH), 95.7 (CH), 55.4 (CH_3), 46.6 (CH_2), 20.0 (CH_2), 12.5 (CH_3); EI-LRMS *m/z* 265 (M^+, 77), 91 (100); HRMS calcd for $C_{18}H_{19}NO$, 265.1467; found, 265.1485. Anal. Calcd for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.66; H, 7.14; N, 5.23.

1-Benzyl-2-ethyl-1*H*-indol-4-ol (10d):[9] The reaction of **7f** (0.53 g, 2 mmol) with BBr_3 (12 ml of a 1 M solution in CH_2Cl_2, 12 mmol), according to the typical procedure above described, and purification by flash column chromatography (hexane/ EtOAc, 6/1) on silica gel, gave **10d** (0.41 g, 81%) as a white solid: mp 92-94 ºC (lit.[9] mp 86-90 ºC); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.18 (m, 3H), 7.02-6.92 (m, 3H), 6.83 (dd, *J* = 8.2, 0.8 Hz, 1H), 6.52 (d, *J* = 7.7 Hz, 1H), 6.41 (s, 1H), 5.30 (s, 2H), 5.08 (s, 1H), 2.68 (q, *J* = 7.4 Hz, 2H), 1.33 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 148.4 (C), 141.9 (C), 139.3 (C), 137.9 (C), 128.9 (CH), 127.4 (CH), 126.0 (CH), 121.9 (CH), 117.3 (C), 104.3 (CH), 102.8 (CH), 94.6 (CH), 46.8 (CH_2), 20.0 (CH_2), 12.6 (CH_3); EI-LRMS *m/z* 251 (M^+, 100), 91 (78); IR (KBr) 3268, 1587, 1474, 1451, 1248, 1225, 766, 723 cm^{-1}; HRMS calcd for $C_{17}H_{17}NO$, 251.1310; found, 251.1299. Anal. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.06; H, 6.88; N, 5.48.

Synthesis of *tert*-Butyl (1-benzyl-2-ethyl-1*H*-indol-4-yloxy)acetate (13):[10] To 1-benzyl-2-ethyl-1*H*-indol-4-ol **10d** (0.38 g, 1.5 mmol) in anhydrous DMF (5 mL), NaH (0.043 g ,1.8 mmol) was added at 0 ºC. After stirring the mixture for 30 min at room temperature, *t*-butyl bromoacetate (0.32 g, 1.65 mmol) in DMF (1 mL) was added, and the resulting mixture was stirred overnight. Then, the reaction mixture was diluted with H_2O (50 mL) and extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and the resulting solution was concentrated under reduced pressure. The crude was purified by flash column chromatography (hexane/EtOAc, 10/1) on silica gel to afford compound **13** (0.43 g, 78%) as a white solid: mp 88-90 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.19 (m, 3H), 7.06-6.93 (m, 3H), 6.89 (d, *J* = 8.3 Hz, 1H), 6.59 (s, 1H), 6.45 (d, *J* = 7.7 Hz, 1H), 5.29 (s, 2H), 4.72 (s, 2H), 2.69 (q, *J* = 7.4 Hz, 2H), 1.55 (s, 9H), 1.35 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 168.5 (C), 151.1 (C), 141.6 (C), 138.9 (C), 137.9 (C), 128.7 (CH), 127.2 (CH), 126.0 (CH), 121.3 (CH), 118.7 (C), 103.7 (CH), 100.8 (CH), 97.0 (CH), 82.1 (C), 66.0 (CH_2), 46.6 (CH_2), 28.2 (CH_3), 20.0 (CH_2), 12.5 (CH_3); IR (KBr) 1754, 1587, 1505, 1451, 1369, 1252, 1155, 1104, 754, 711 cm^{-1}; HRMS calcd for $C_{23}H_{27}NO_3$, 365.1991; found, 365.1989. Anal. Calcd for $C_{23}H_{27}NO_3$: C, 75.59; H, 7.45; N, 3.83. Found: C, 75.41; H, 7.54; N, 3.75.

Synthesis of *t*-Butyl 2-[3-(2-amino-2-oxoacetyl)-1-benzyl-2-ethyl-1*H*-indol-4-yloxy]acetate (14):[10] To oxalyl chloride (0.29 g, 2.25 mmol) in anhydrous CH_2Cl_2 (30 mL) was dropwise added **13** (0.27 g, 0.75 mmol) over 1 h in CH_2Cl_2 (30 mL) at room temperature. The reaction was left to stir under N_2 for 1 h. Then, 1,1,1,3,3,3-hexamethyldisilazane (0.73 g, 4.5 mmol) was dropwise added at 0 ºC and the mixture was stirred at room temperature overnight. Cooled to 0 ºC, MeOH (0.5 mL) was added to the mixture and it was stirred for 3 h at room temperature. Usual workup and purification by flash column chromatography (hexane/EtOAc, 1/1) on silica gel to afford compound **14** (0.25 g, 75%), as a yellow solid: mp 176-178 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.21 (m, 3H), 7.10-6.98 (m, 3H), 6.85 (d, J = 8.4 Hz, 1H), 6.63 (br s, 1H), 6.51 (d, J = 8.0 Hz, 1H), 6.40 (br s, 1H), 5.33 (s, 2H), 4.63 (s, 2H), 2.94 (q, J = 7.7 Hz, 2H), 1.45 (s, 9H), 1.18 (t, J = 7.7 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 188.1 (C), 168.3 (C), 167.9 (C), 151.9 (C), 150.1 (C), 138.1 (C), 136.2 (C), 129.0 (CH), 127.7 (CH), 126.0 (CH), 123.6 (CH), 116.8 (C), 110.0 (C), 104.5 (CH), 104.4 (CH), 82.1 (C), 66.1 (CH_2), 46.9 (CH_2), 28.1 (CH_3), 19.1 (CH_2), 14.4 (CH_3); IR (KBr) 3455, 3288, 3144, 1762, 1692, 1637, 1147, 731 cm^{-1}; HRMS calcd for $C_{25}H_{28}N_2O_5$, 436.1998; found, 436.1977. Anal. Calcd for $C_{25}H_{28}N_2O_5$: C, 68.79; H, 6.47; N, 6.42. Found: C, 68.91; H, 6.44; N, 6.35.

Synthesis of 2-[3-(2-Amino-2-oxoacetyl)-1-benzyl-2-ethyl-1*H*-indol-4-yloxy]acetic acid (15) (LY315920):[9,10] To indole **14** (0.24 g, 0.55 mmol) in CH_2Cl_2 (3.3 mL), CF_3CO_2H (0.91 mL) was added and the reaction mixture left to stir and monitored by thin layer chromatography for completion. After 1 h, the solvent was removed by under reduced pressure and high vacuum to afford compound **15** (0.21 g, 98%) as a white solid: mp 228-230 ºC (dec.) (lit.[9] mp 230-234 ºC); ^{1}H NMR (300 MHz, DMSO-d_6) δ 13.01 (br s, 1H), 7.85 (s, 1H), 7.50 (s, 1H), 7.40-7.24 (m, 3H), 7.16-7.03 (m, 4H), 6.58 (dd, J = 6.3, 2.2 Hz, 1H), 5.57 (s, 2H), 4.72 (s, 2H), 2.95 (q, J = 7.5 Hz, 2H), 1.12 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75.4 MHz, DMSO-d_6) δ 189.1 (C), 170.5 (C), 168.2 (C), 151.6 (C), 149.4 (C), 137.5 (C), 137.3 (C), 128.7 (CH), 127.3 (CH), 126.0 (CH), 123.1 (CH), 116.0 (C), 109.7 (C), 104.4 (CH), 103.9 (CH), 64.6 (CH_2),

46.0 (CH_2), 18.5 (CH_2), 14.2 (CH_3); IR (KBr) 3427, 1732, 1651, 1633, 1614, 1506, 1097, 801 cm^{-1}; HRMS calcd for $C_{21}H_{20}N_2O_5$, 380.1372; found, 380.1378.

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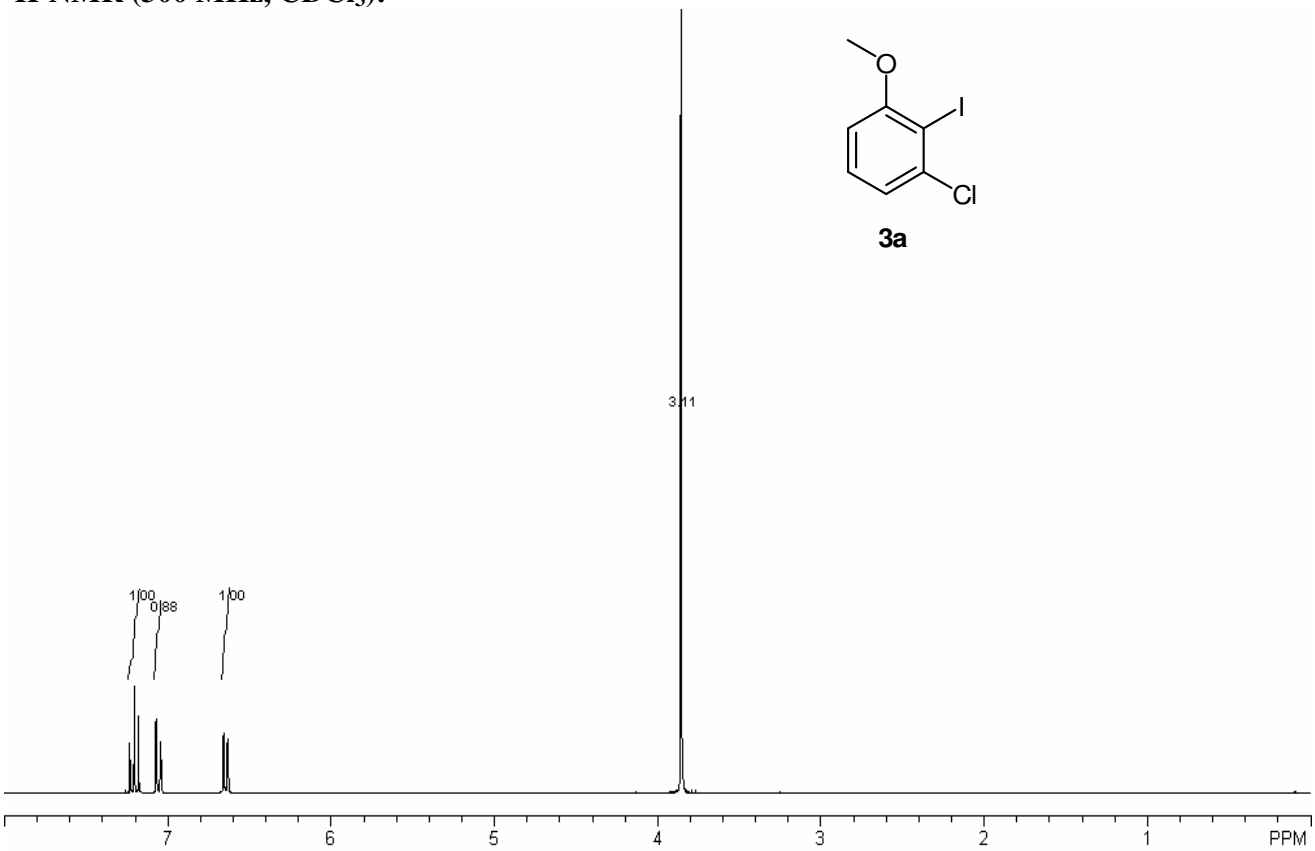
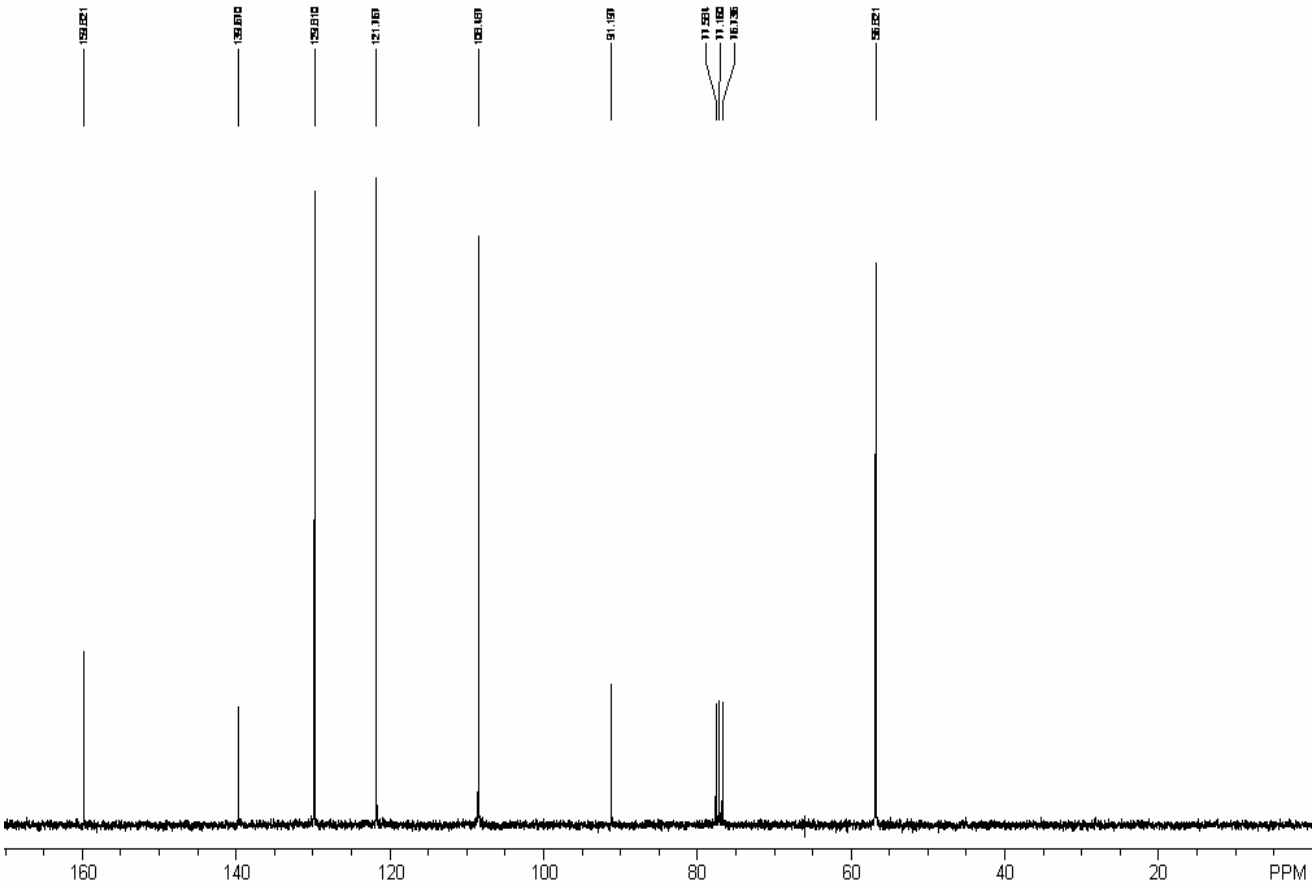
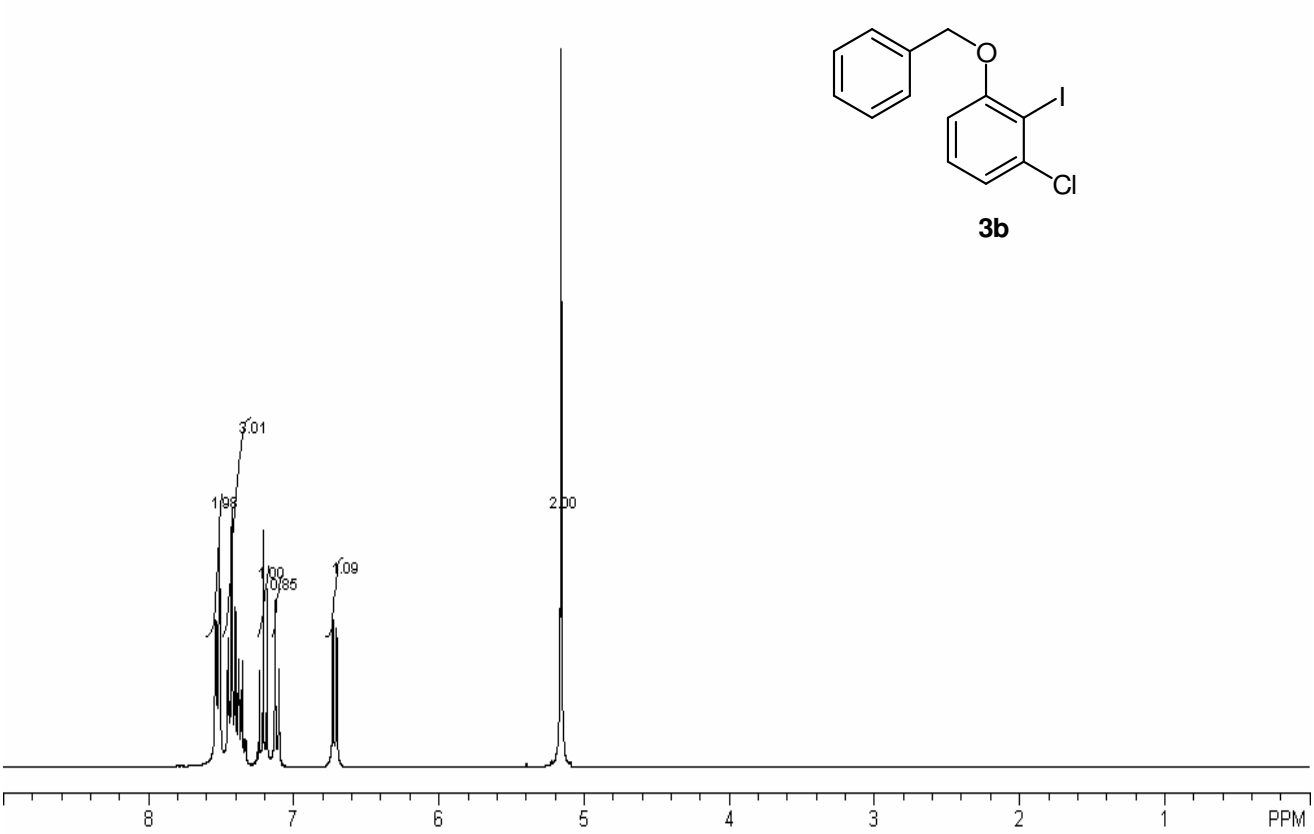
^{1}H-NMR (300 MHz, $CDCl_3$):



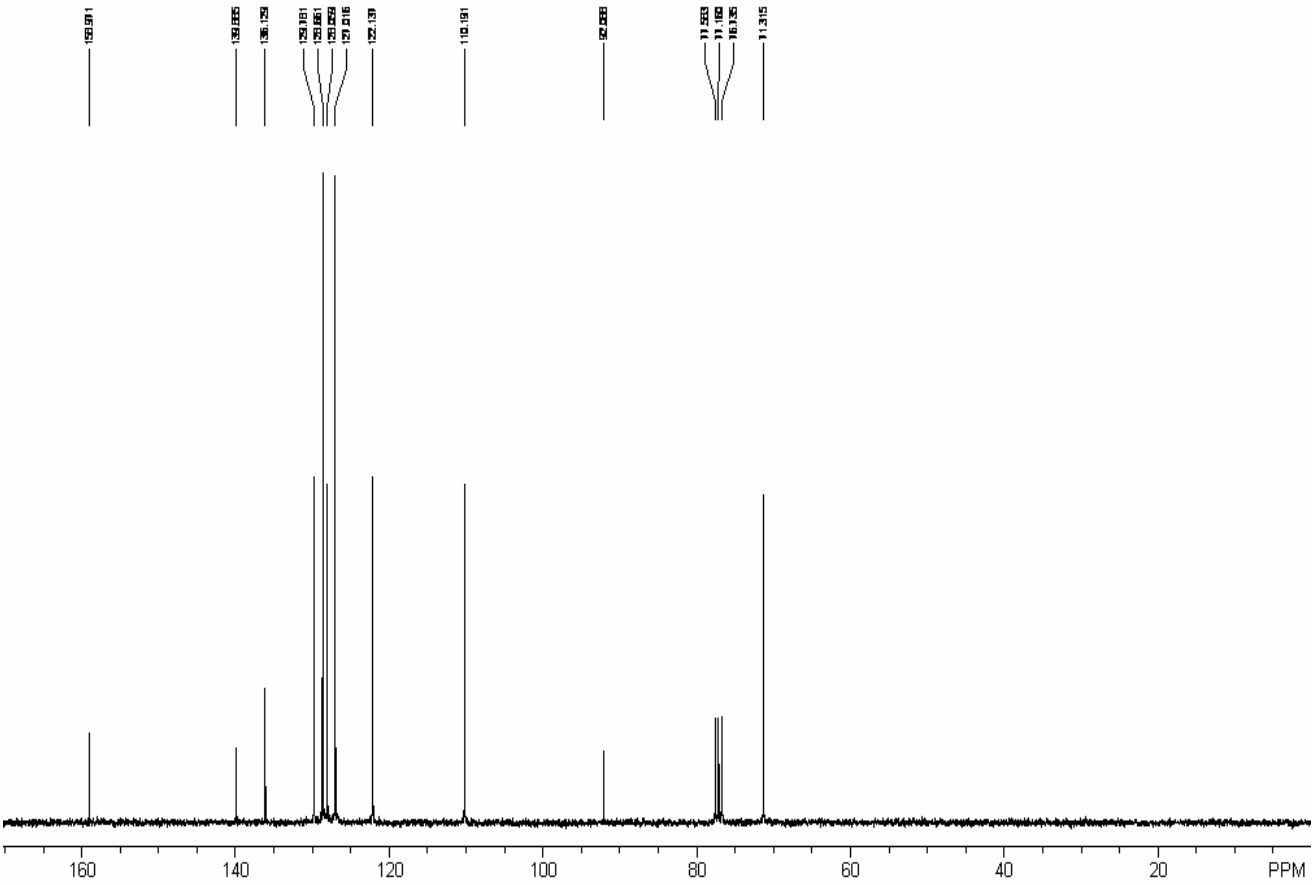
^{13}C-NMR (75.4 MHz, $CDCl_3$):



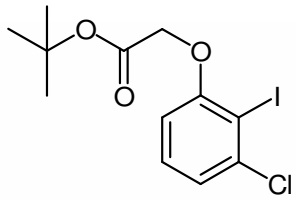
^{1}H-NMR (300 MHz, $CDCl_3$):



^{13}C-NMR (75.4 MHz, $CDCl_3$):



^{1}H-NMR (400 MHz, $CDCl_3$):



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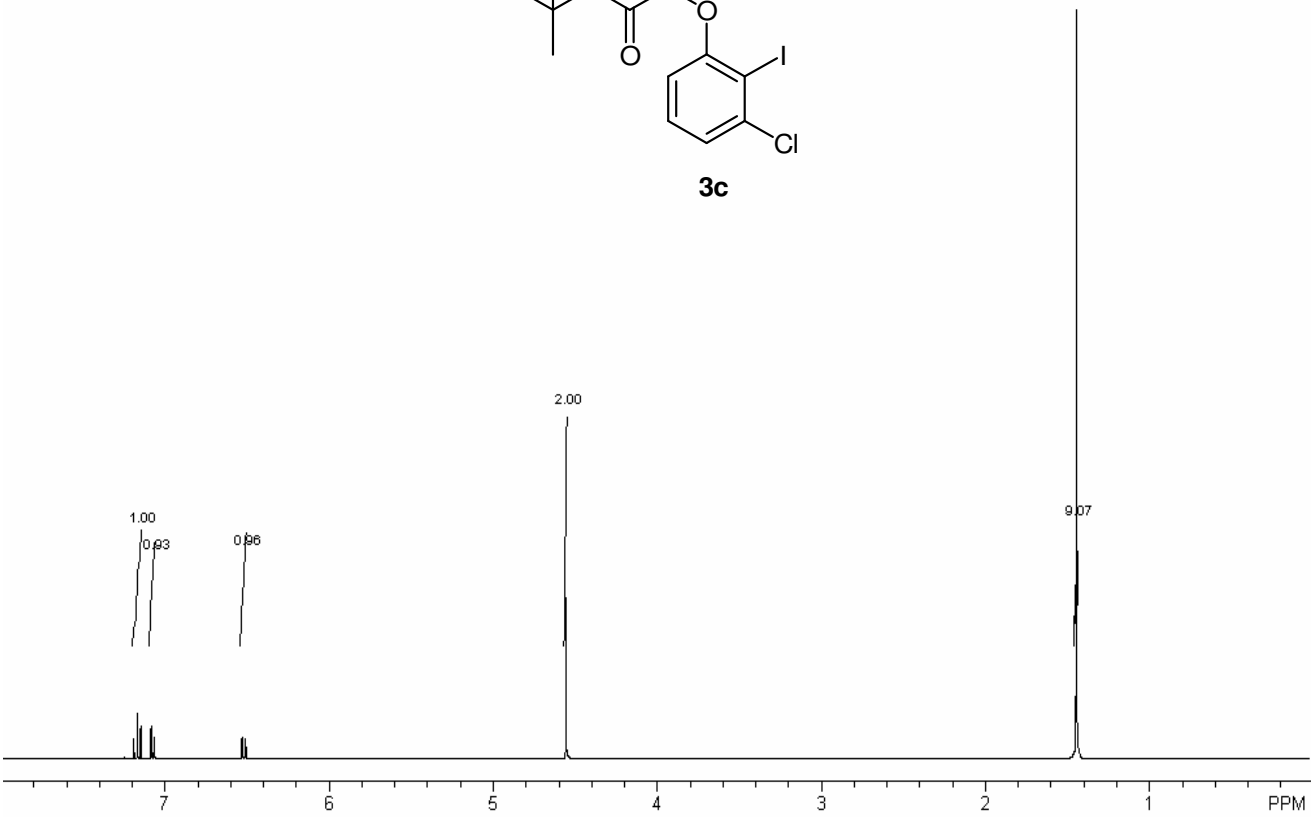
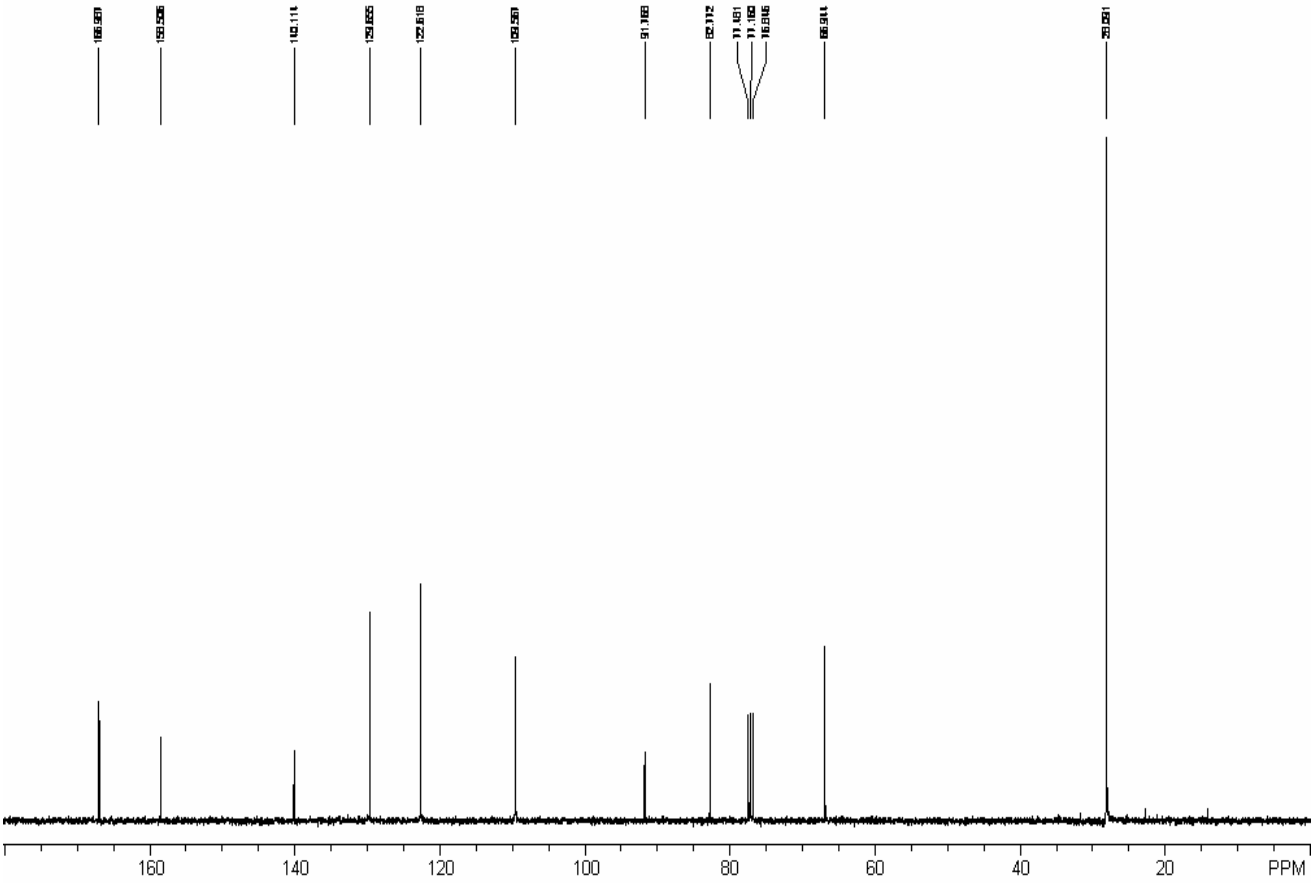
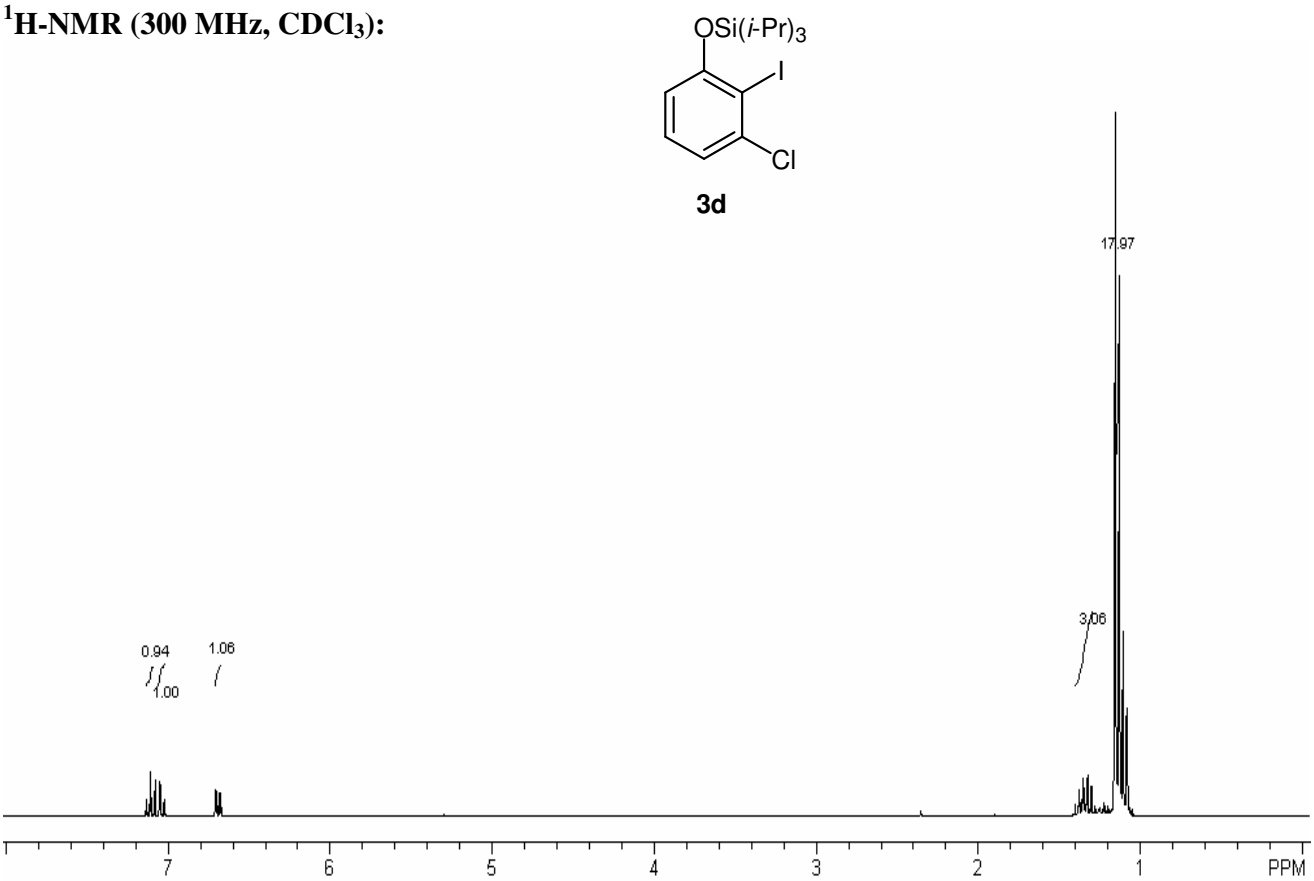


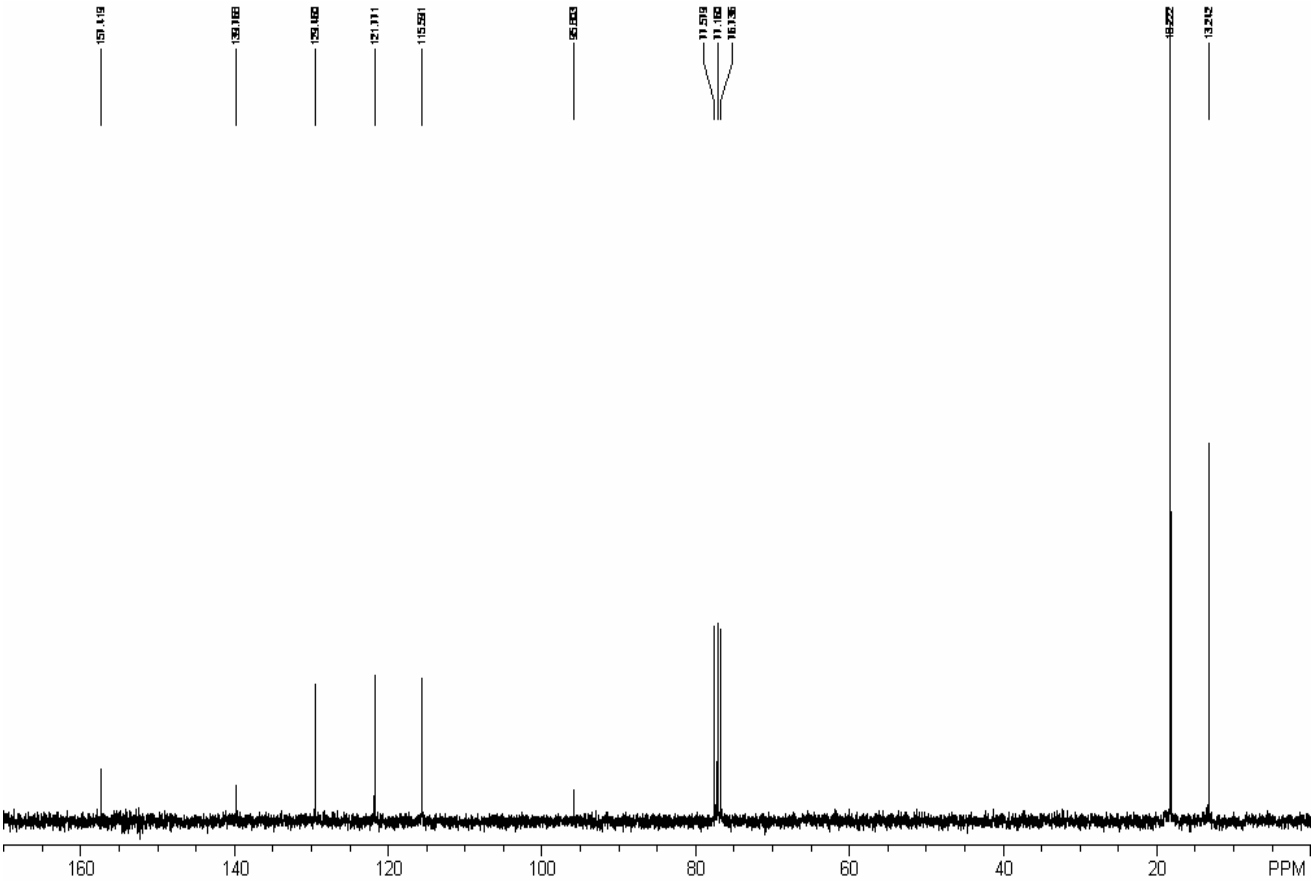
^{13}C-RMN (100.6 MHz, $CDCl_3$):



^{1}H-NMR (300 MHz, $CDCl_3$):



^{13}C-NMR (75.4 MHz, $CDCl_3$):



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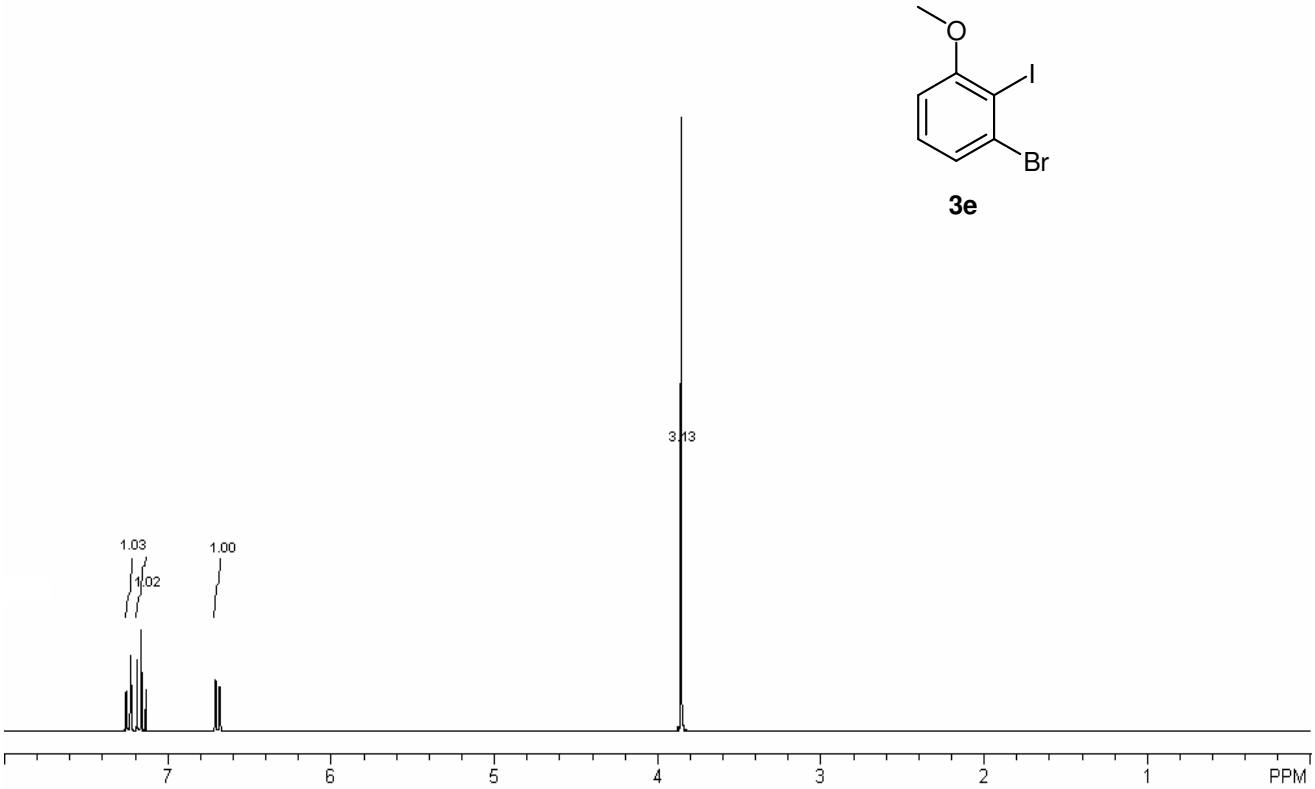
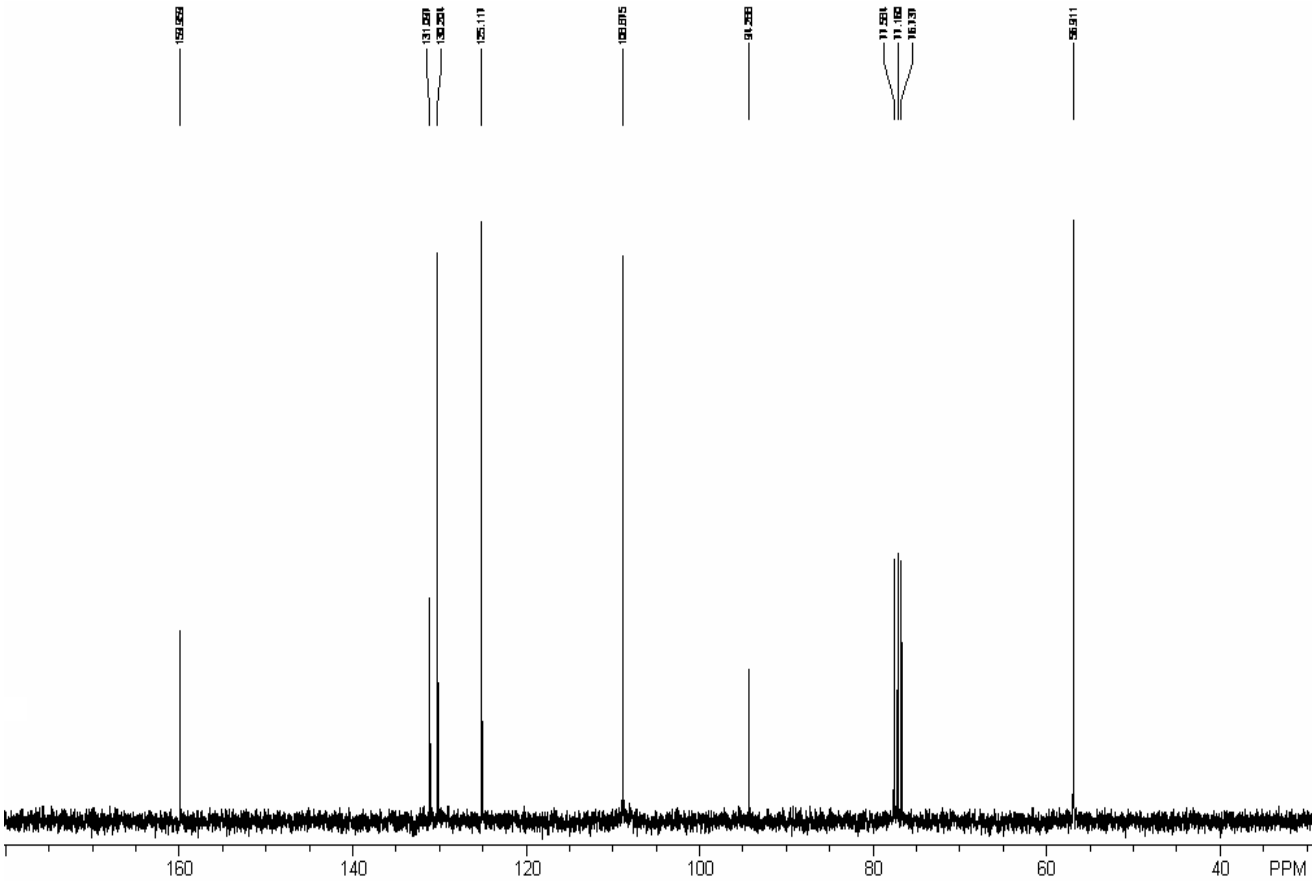


^{13}C-RMN (75.4 MHz, $CDCl_3$):



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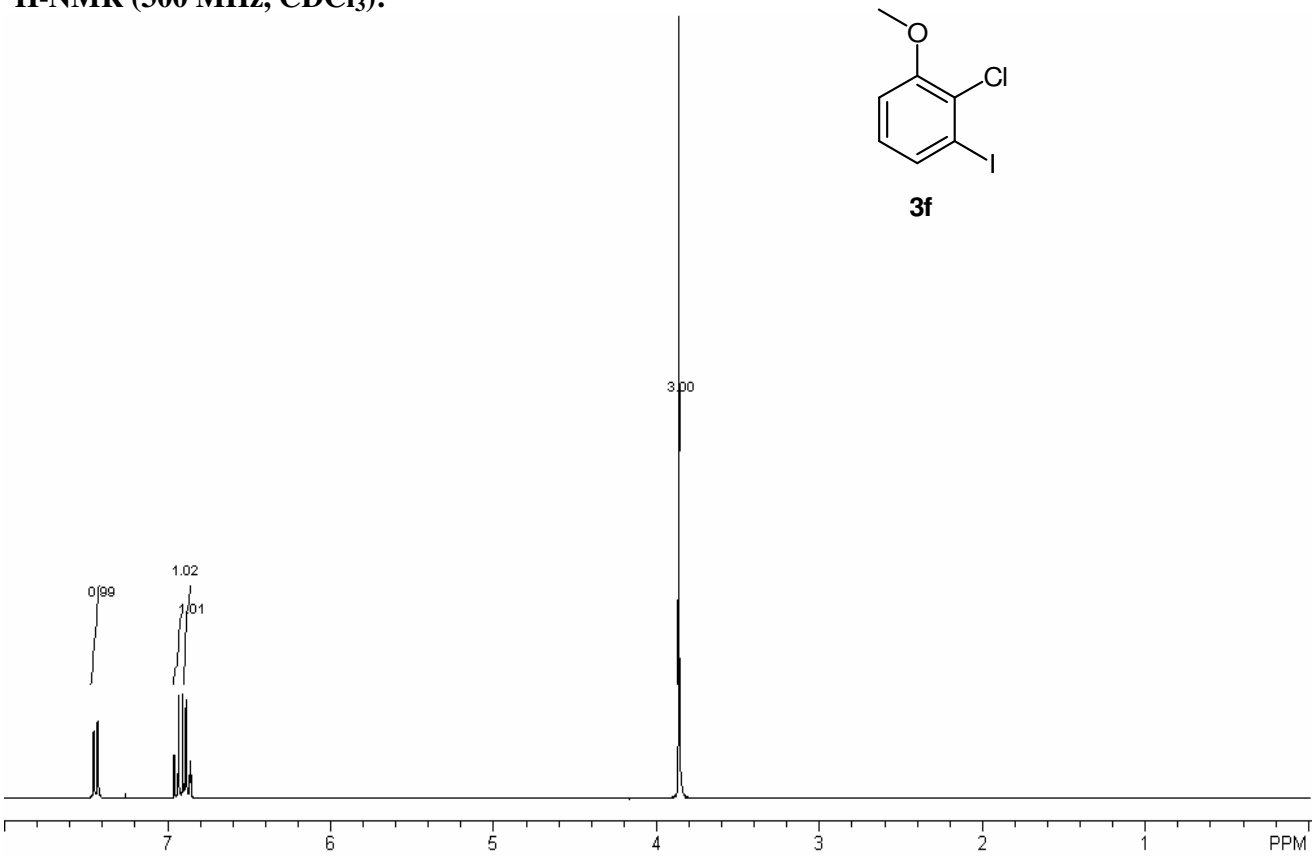

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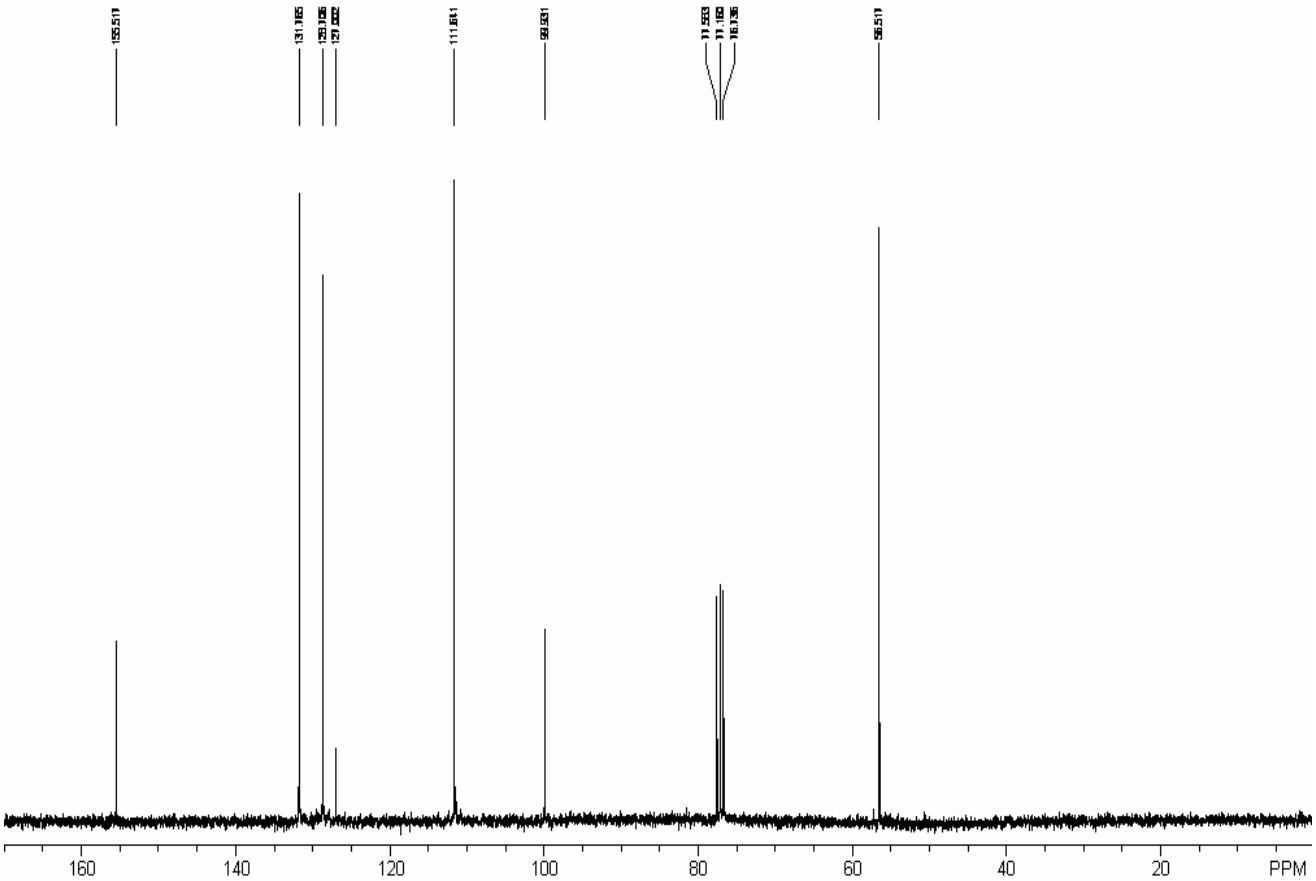

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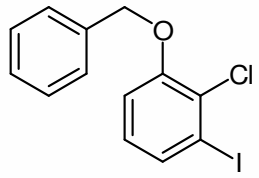

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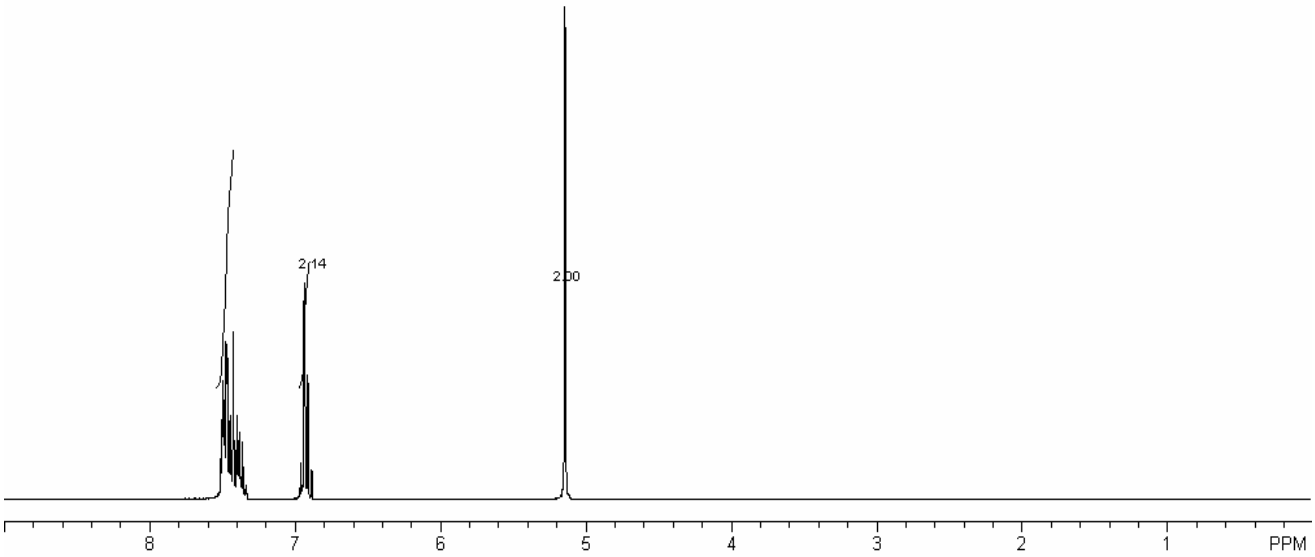
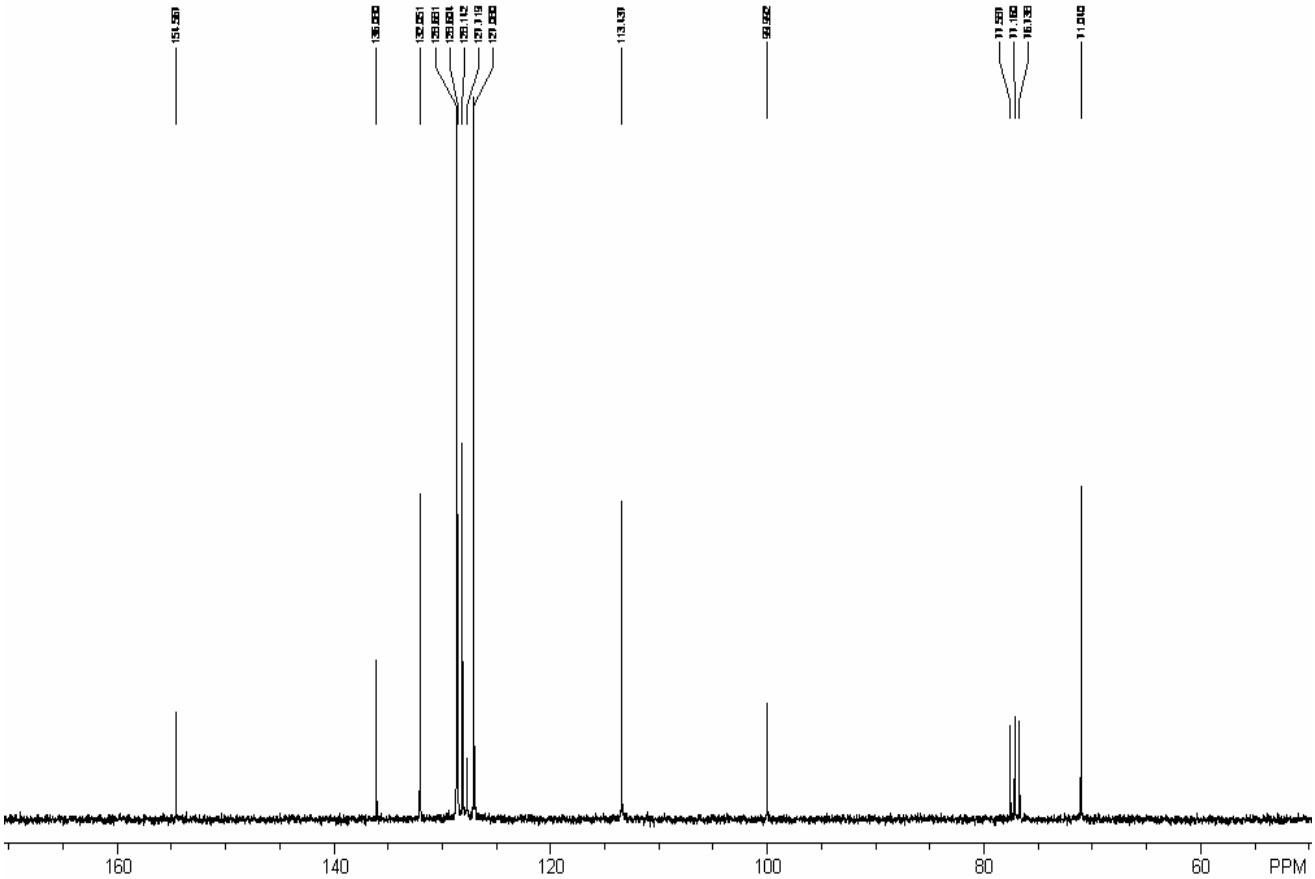


^{13}C-NMR (75.4 MHz, $CDCl_3$):



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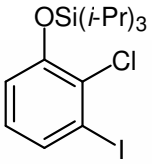

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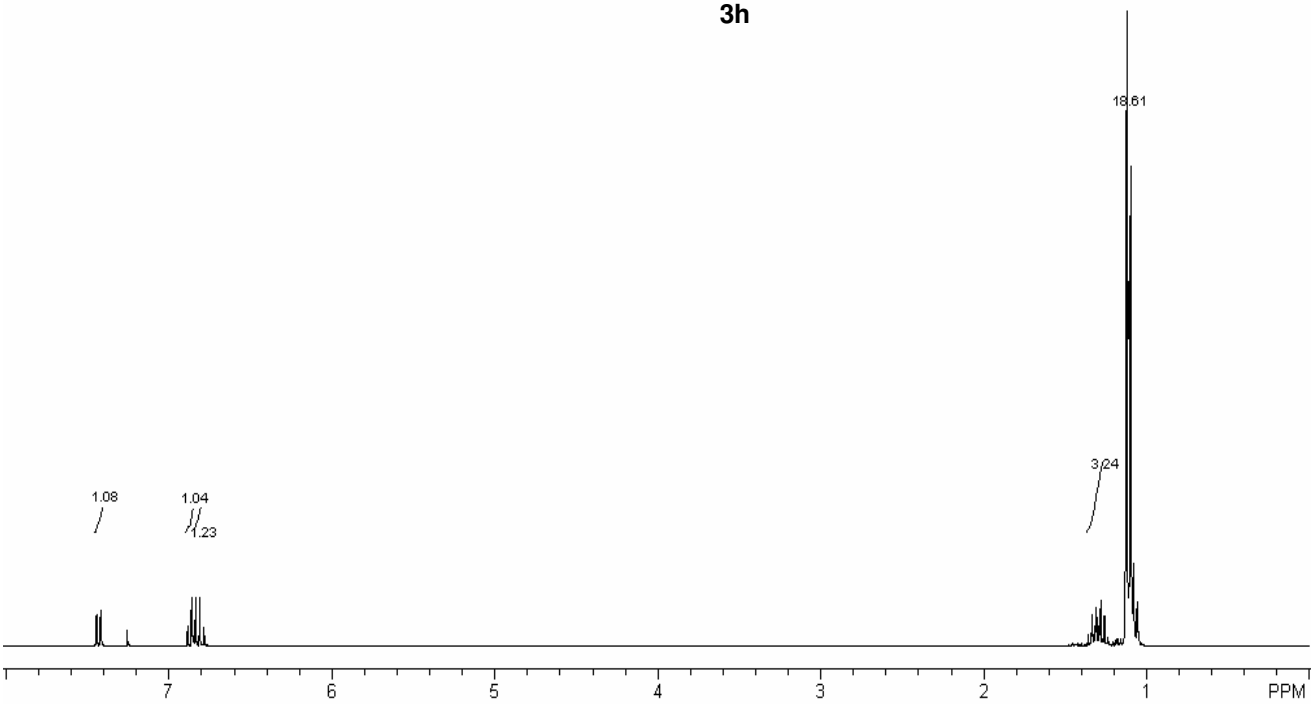
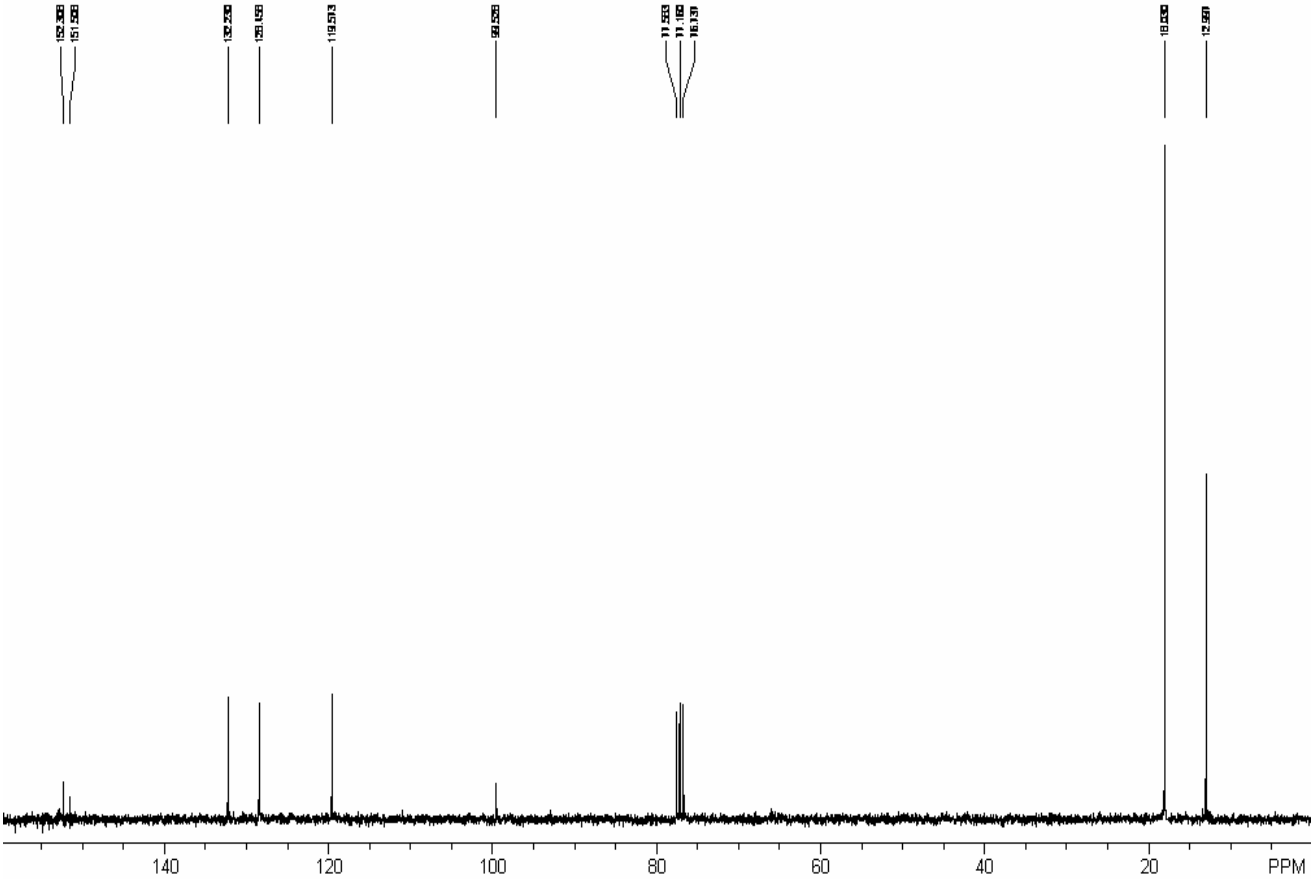


^{13}C-NMR (75.4 MHz, $CDCl_3$):



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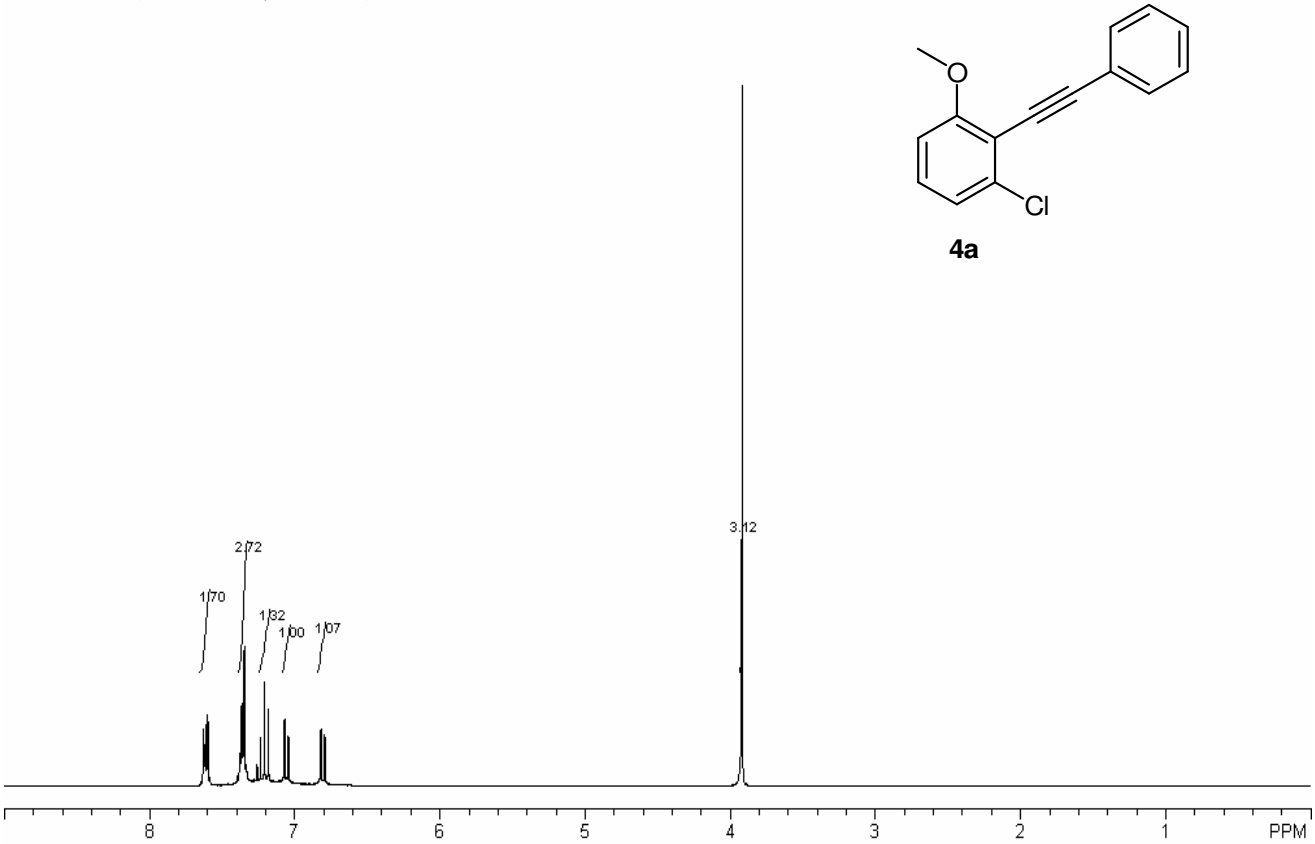

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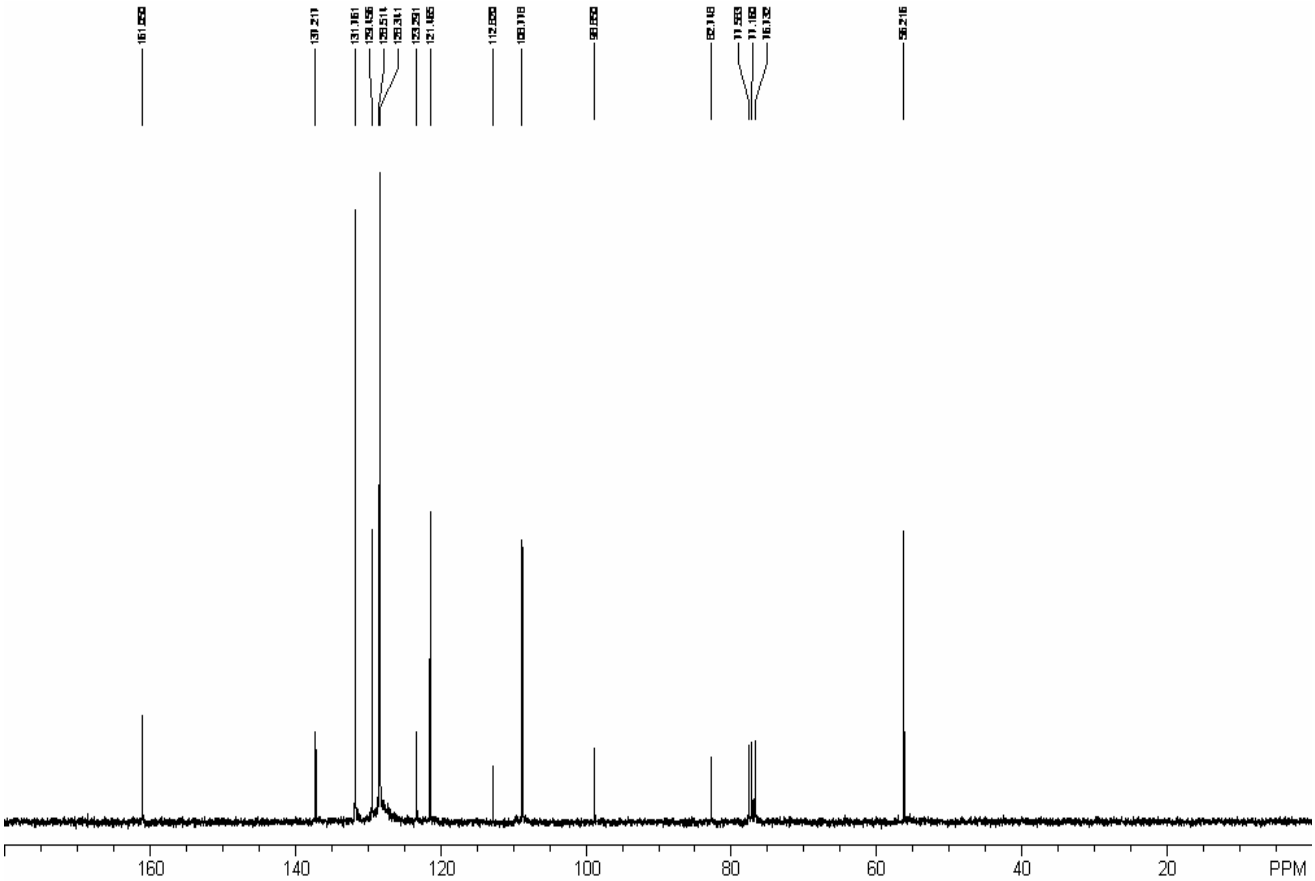

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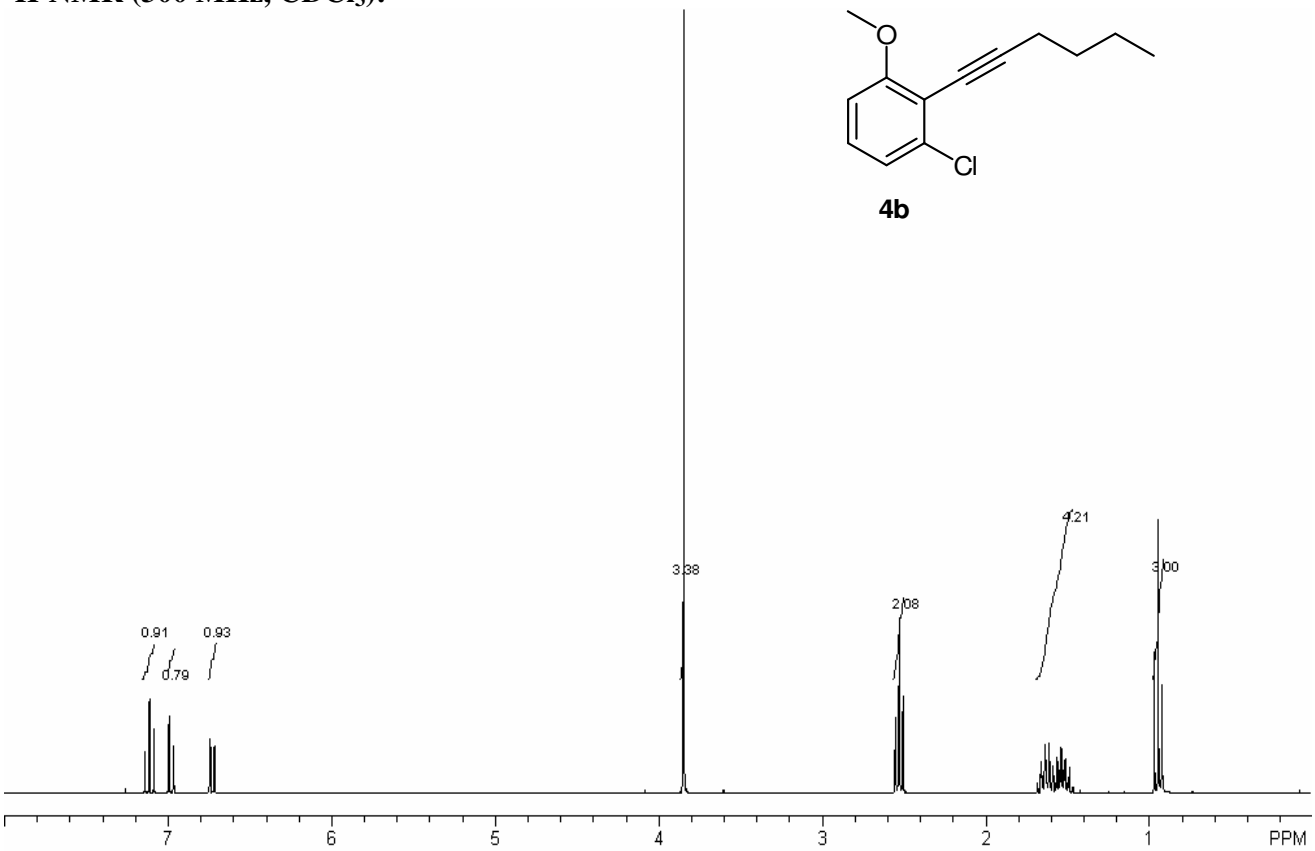

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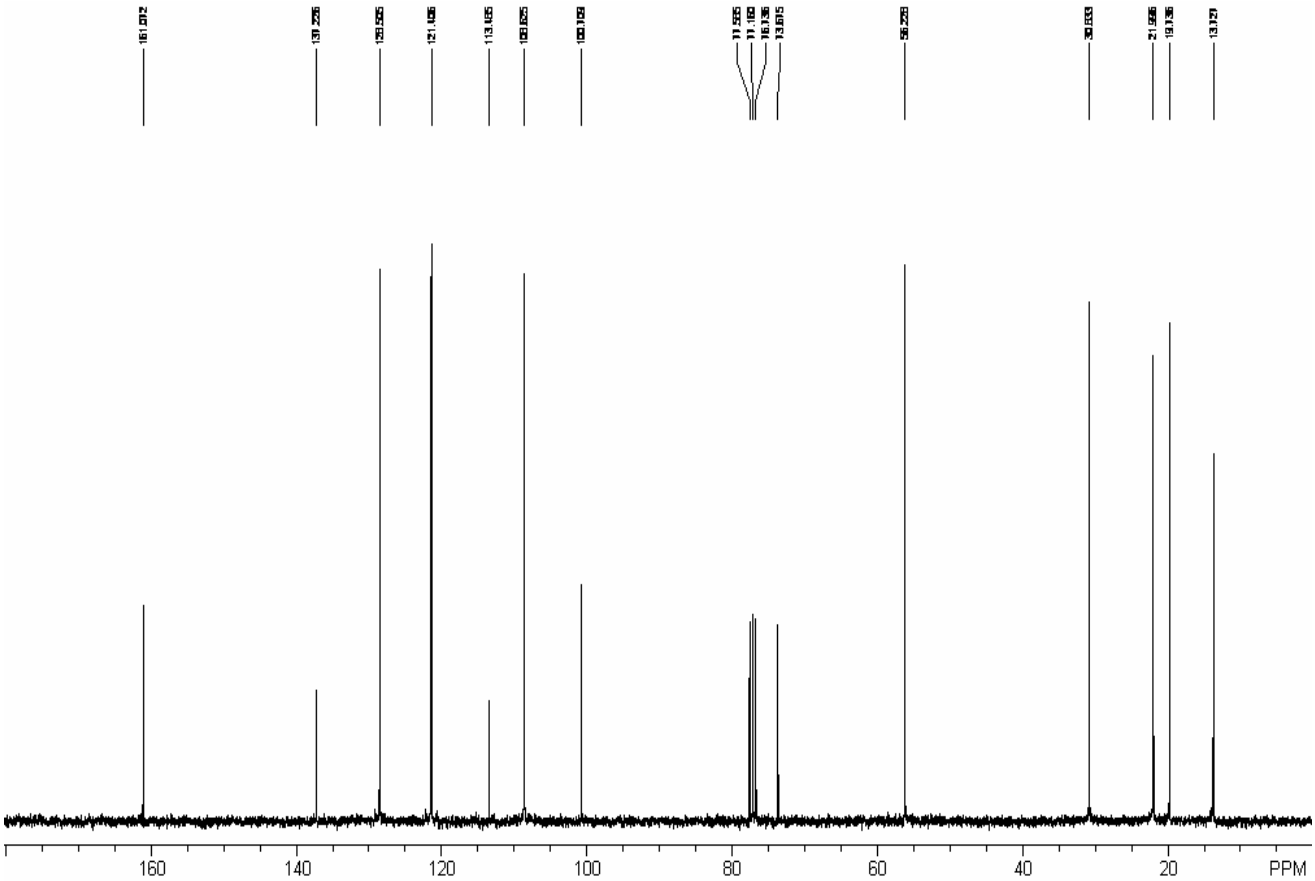
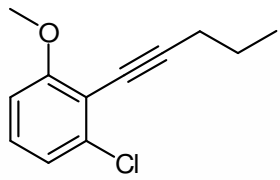


^{1}H-NMR (400 MHz, $CDCl_3$):



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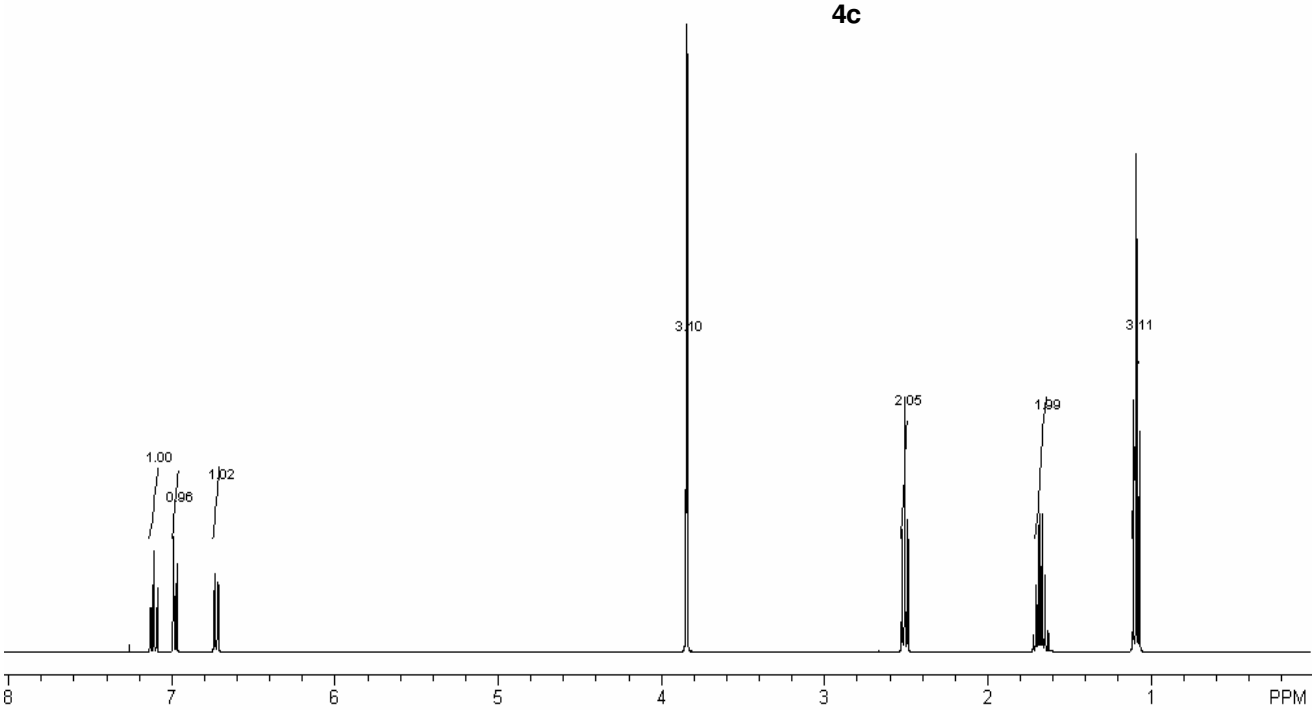
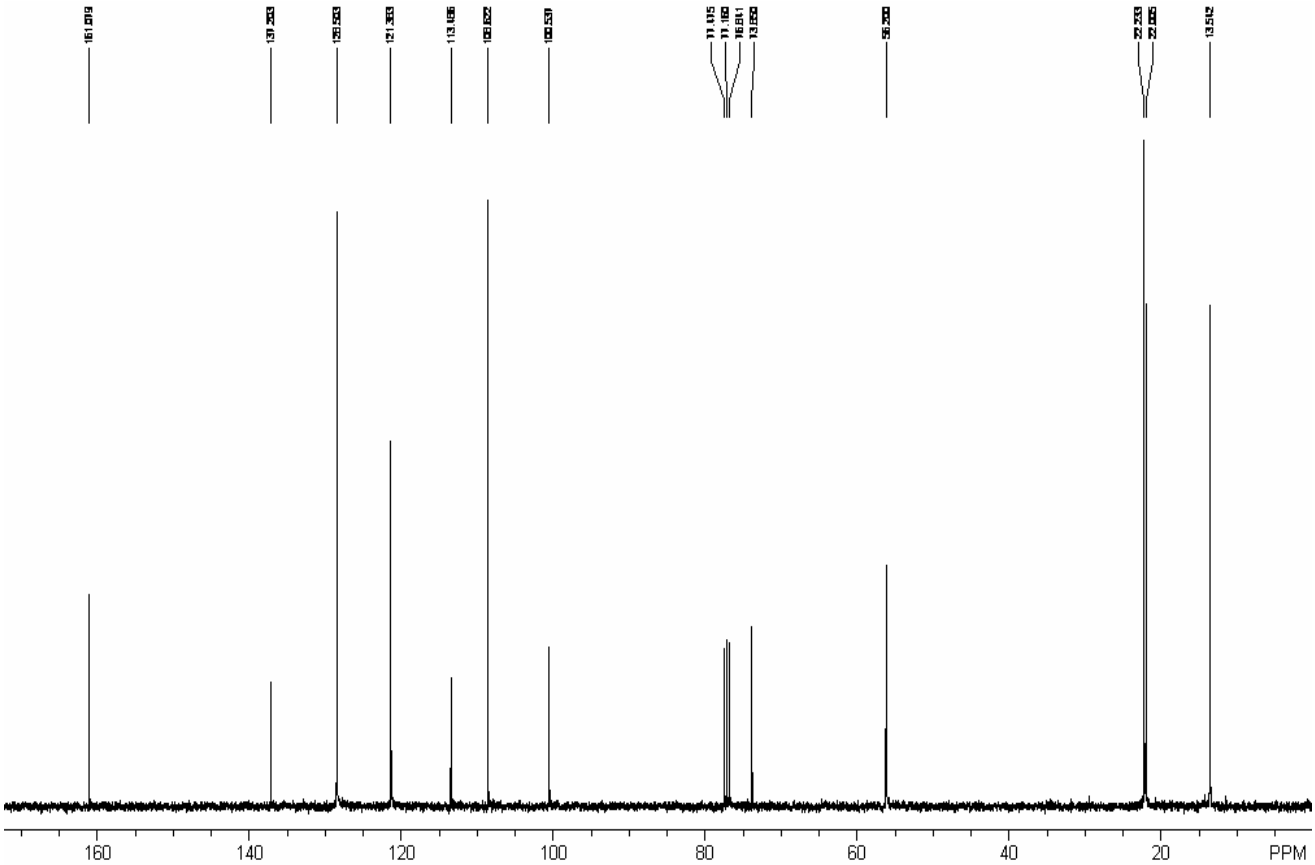


^{13}C-NMR (100.6 MHz, $CDCl_3$):



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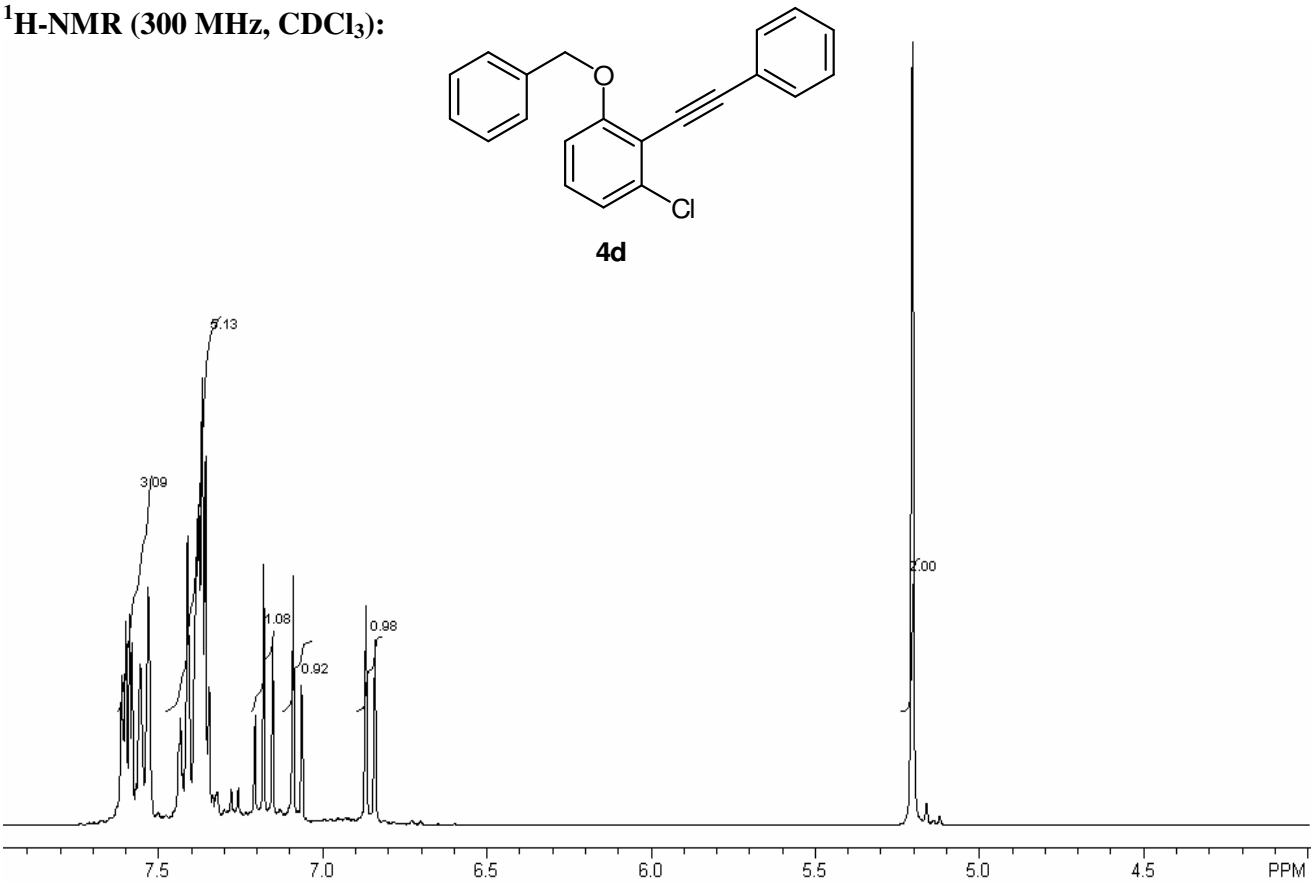

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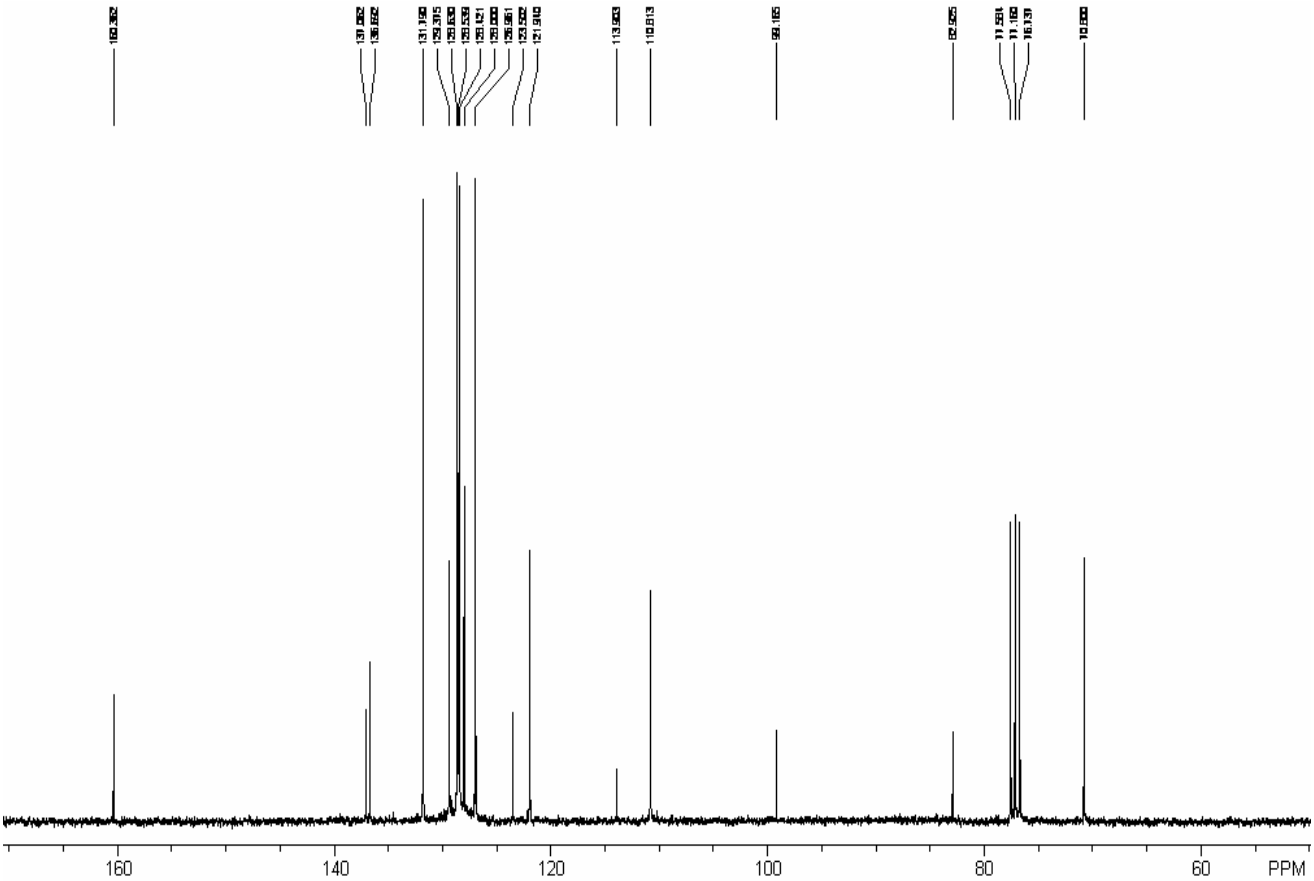

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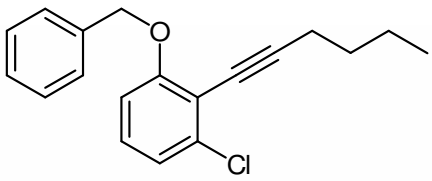

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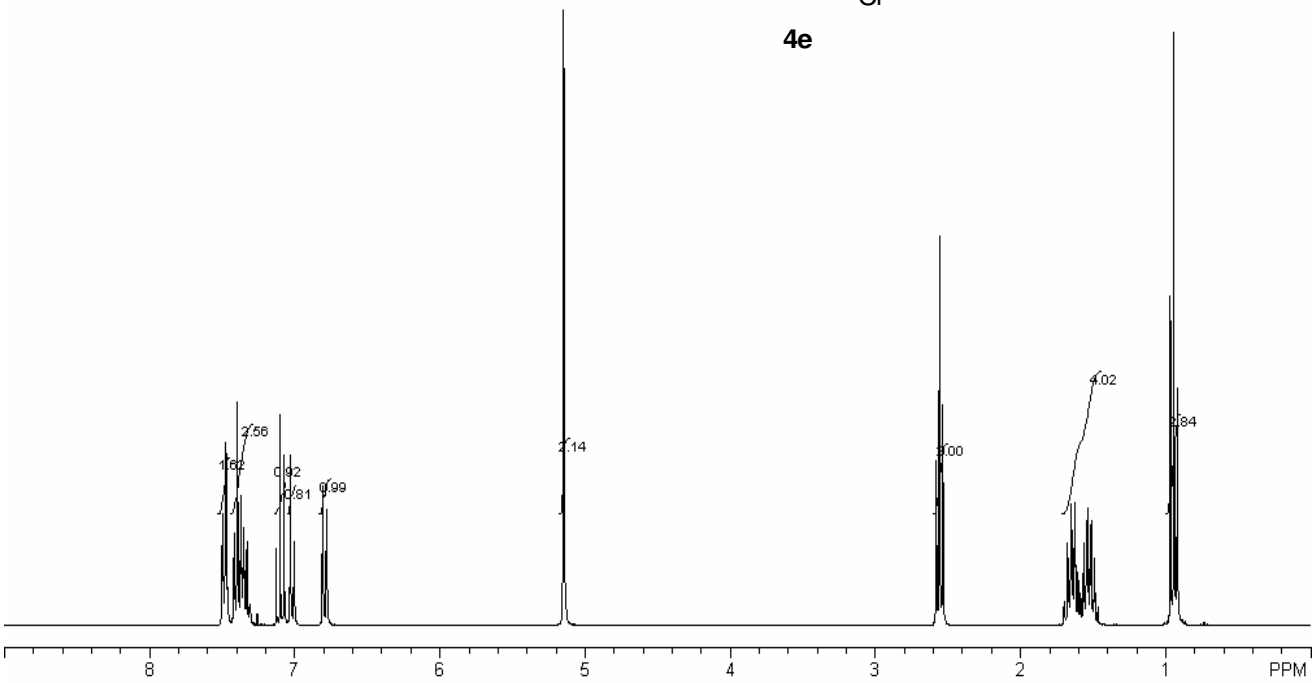

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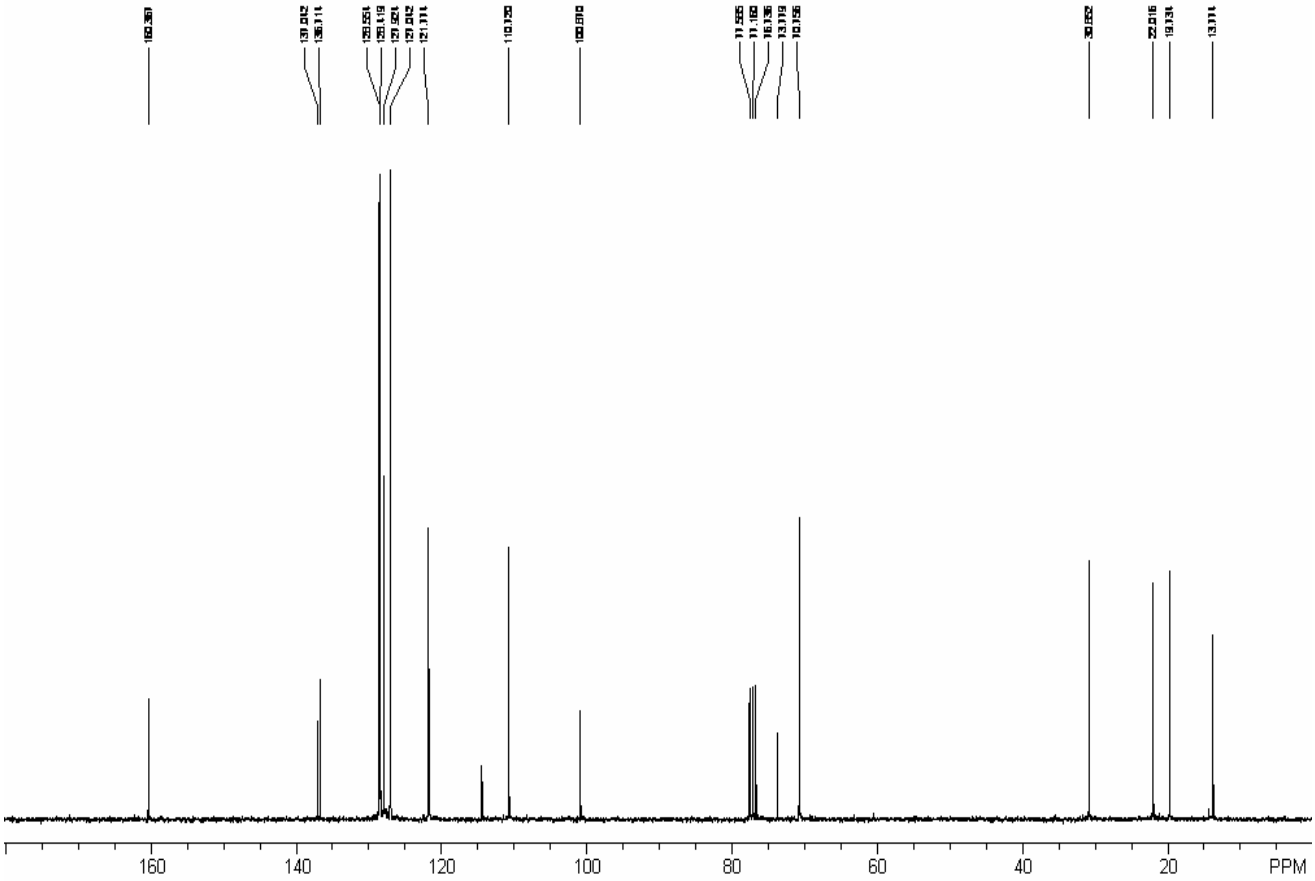
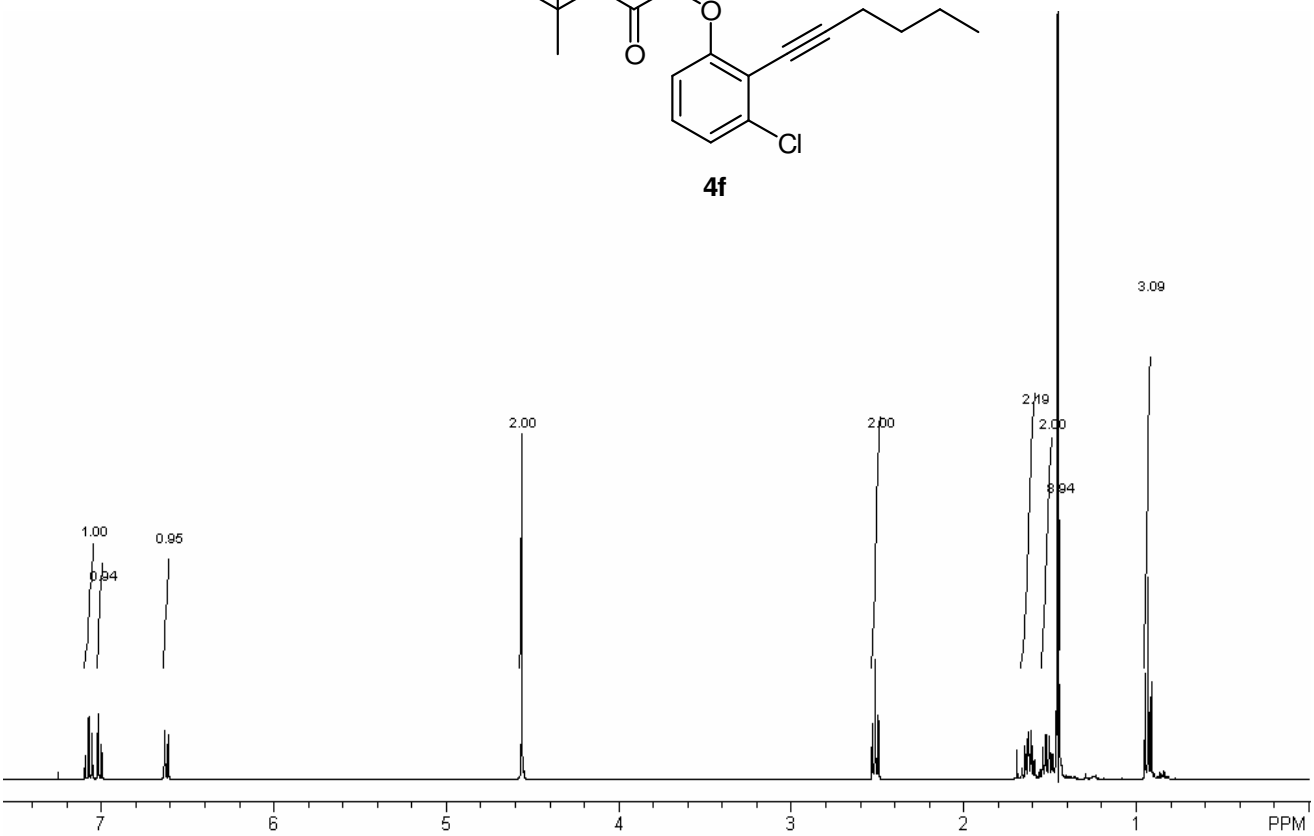


^{1}H-NMR (400 MHz, $CDCl_3$):



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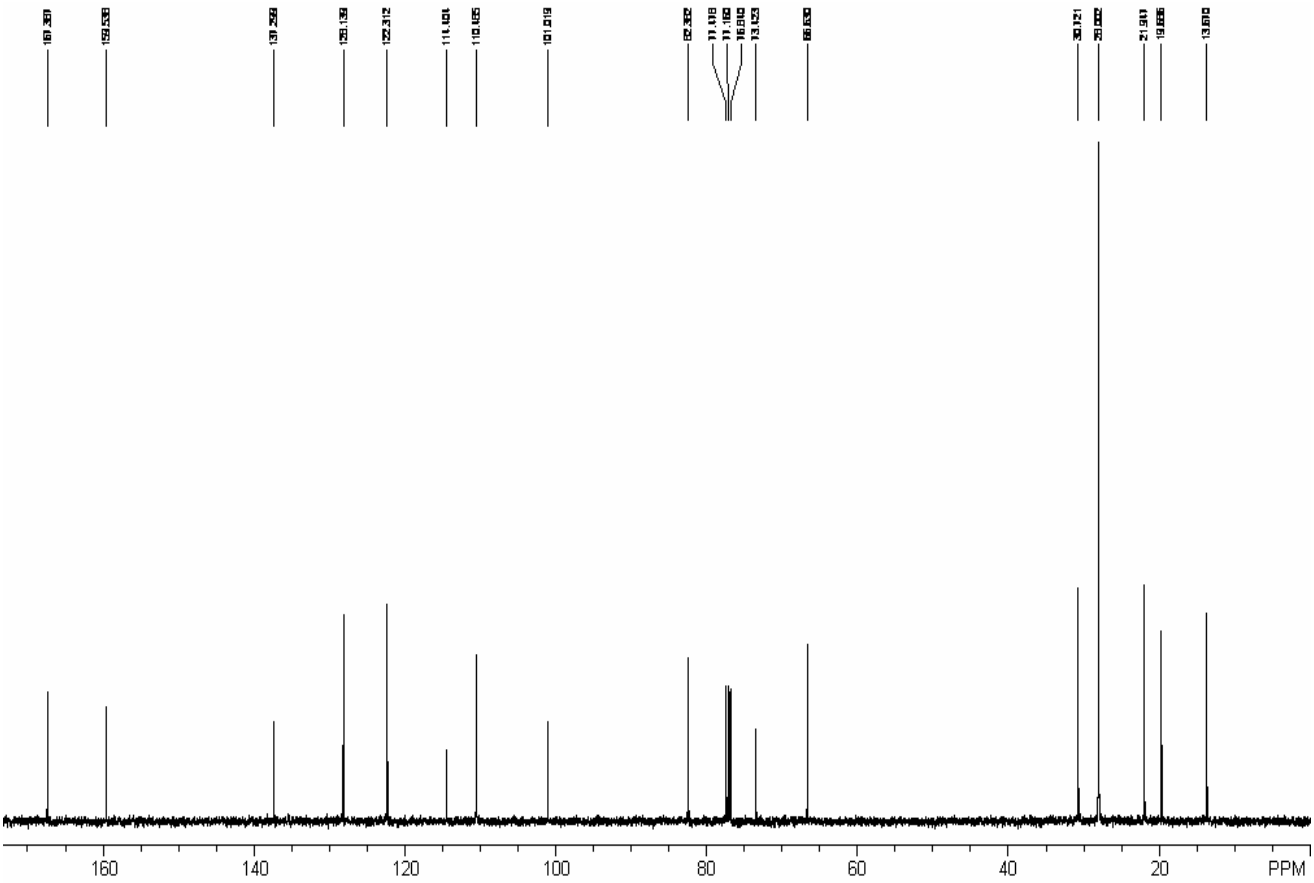

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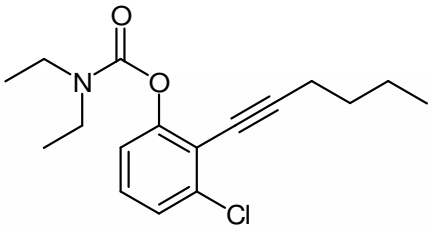

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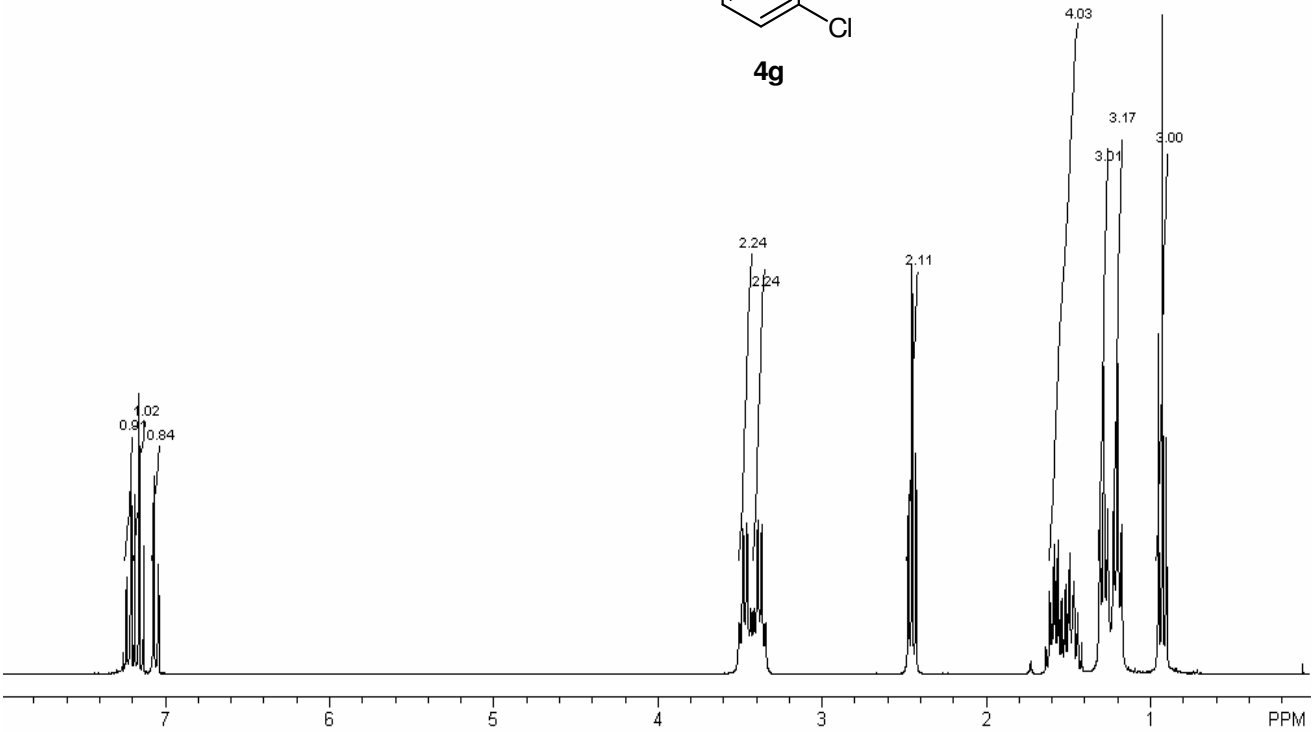
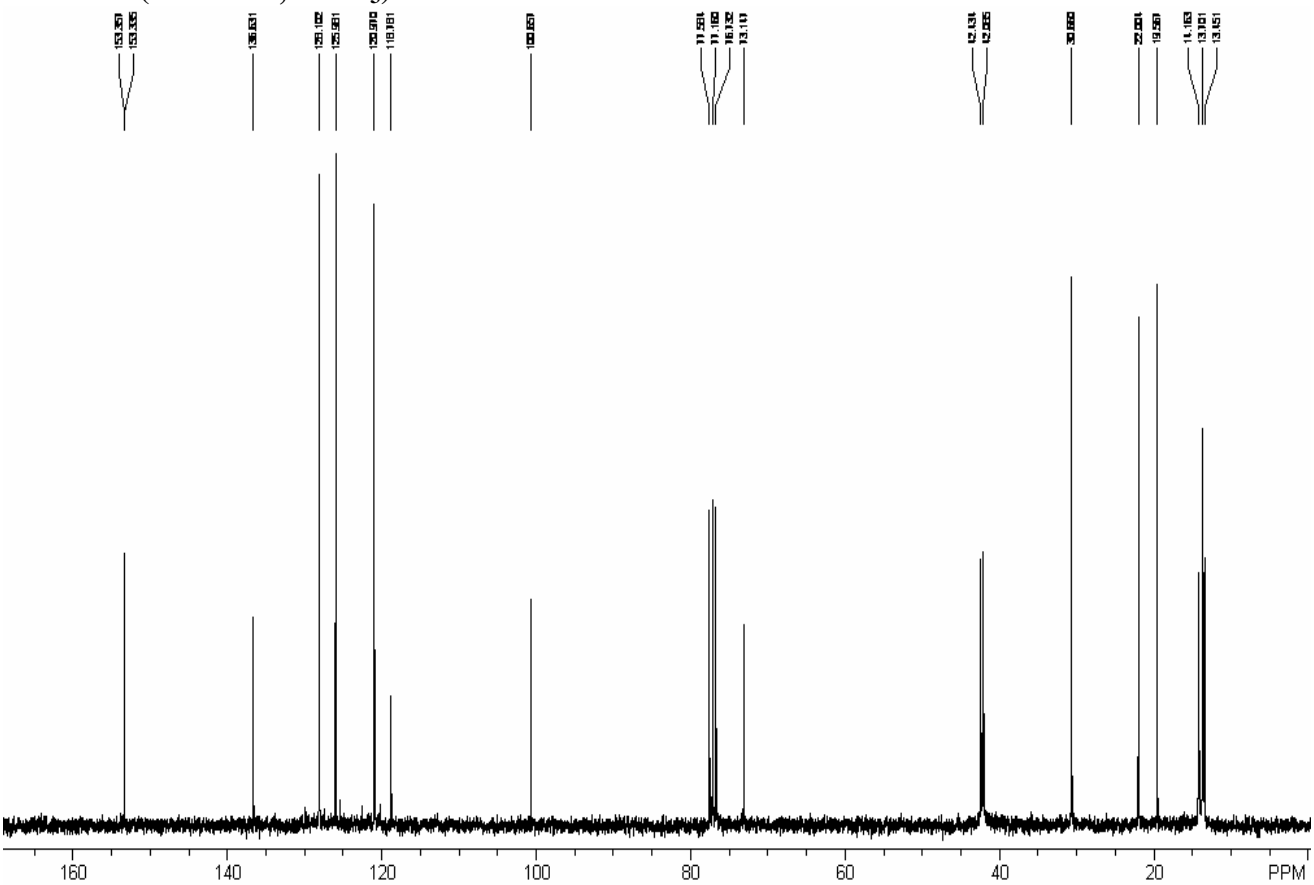
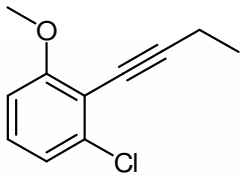


^{13}C-NMR (75.4 MHz, $CDCl_3$):



^{1}H-NMR (300 MHz, $CDCl_3$):



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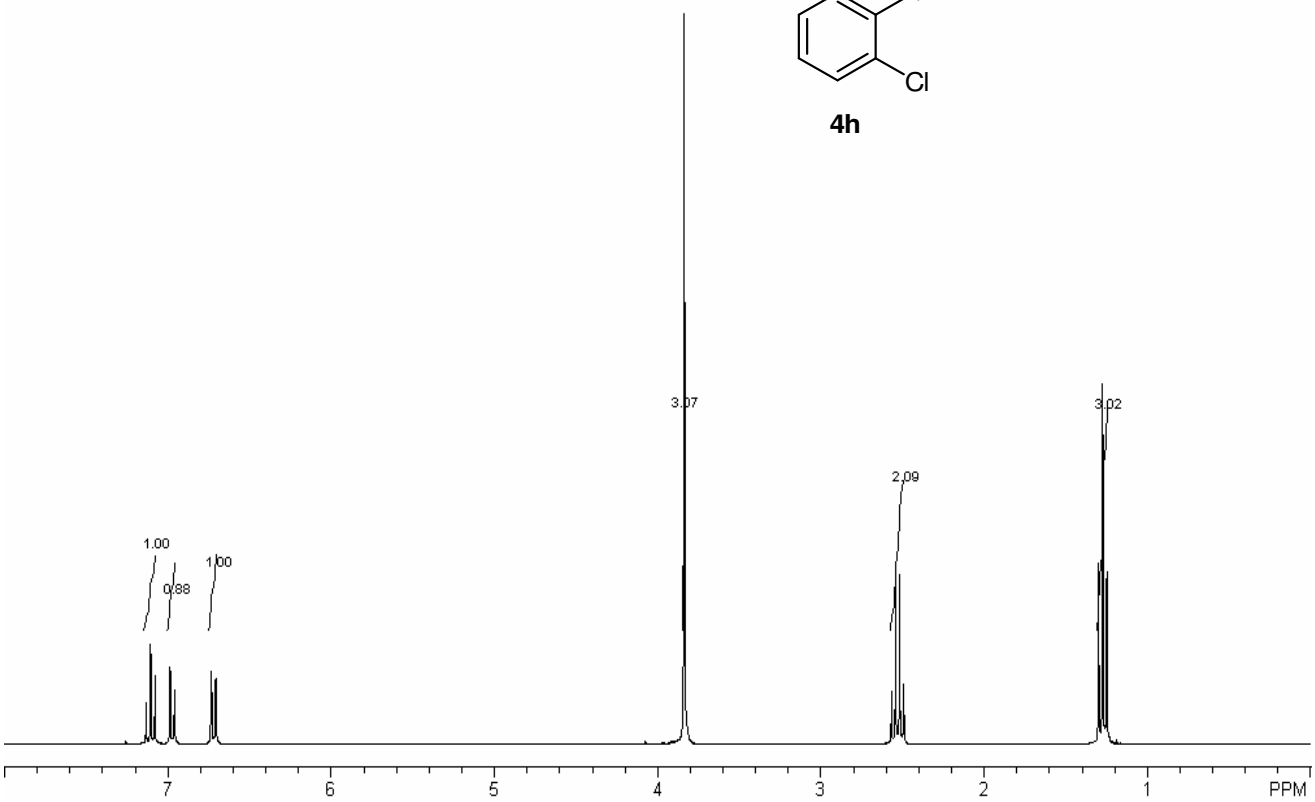
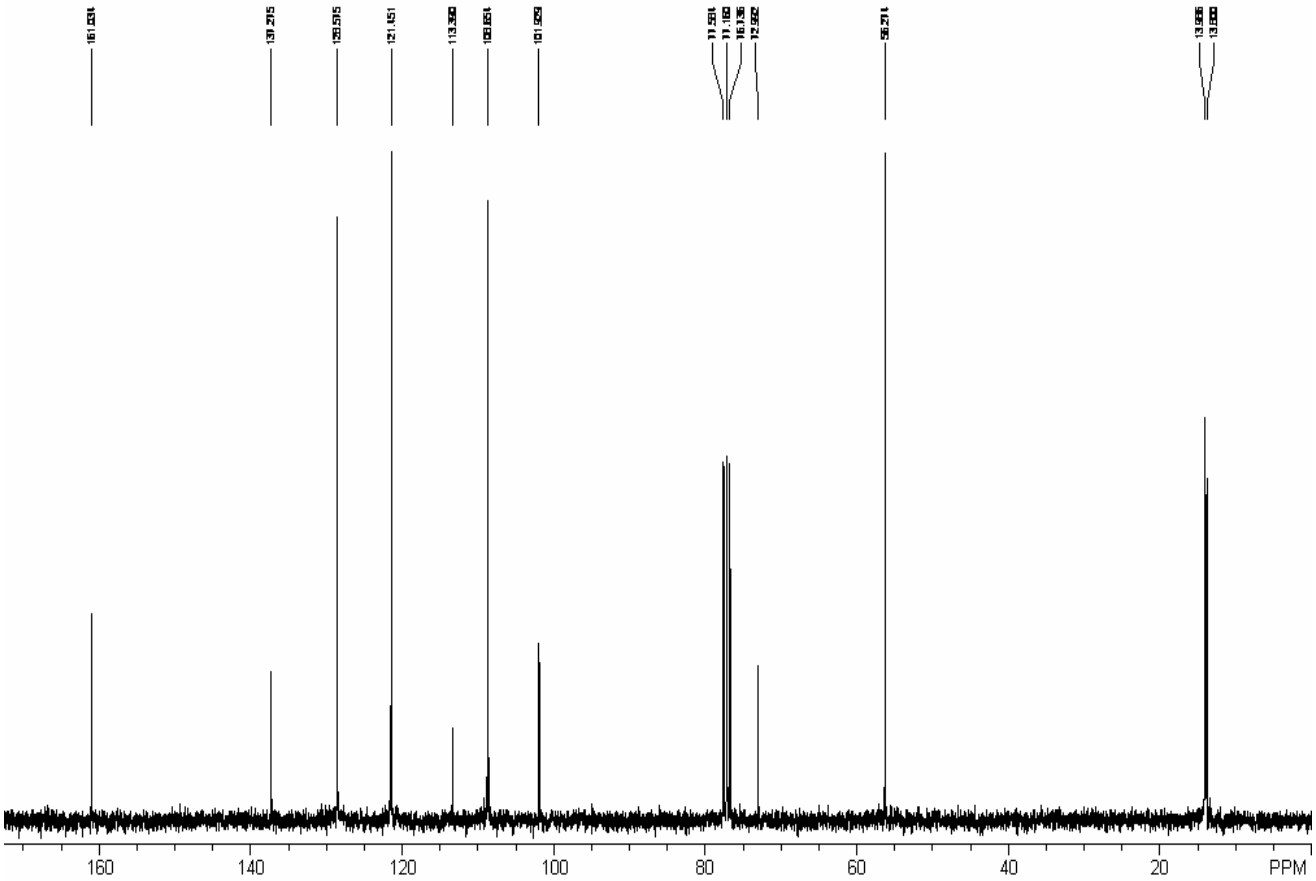


^{13}C-NMR (75.4 MHz, $CDCl_3$):



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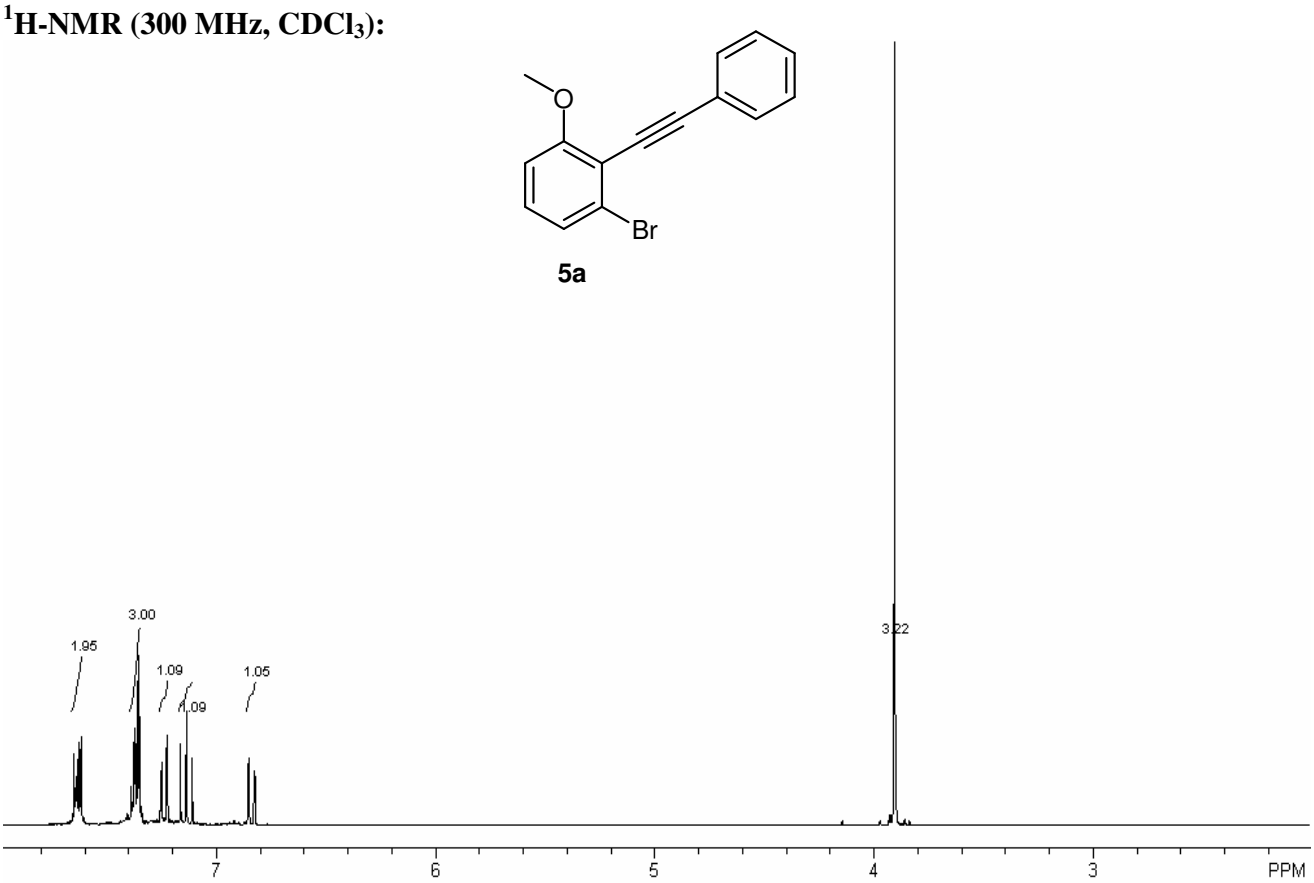

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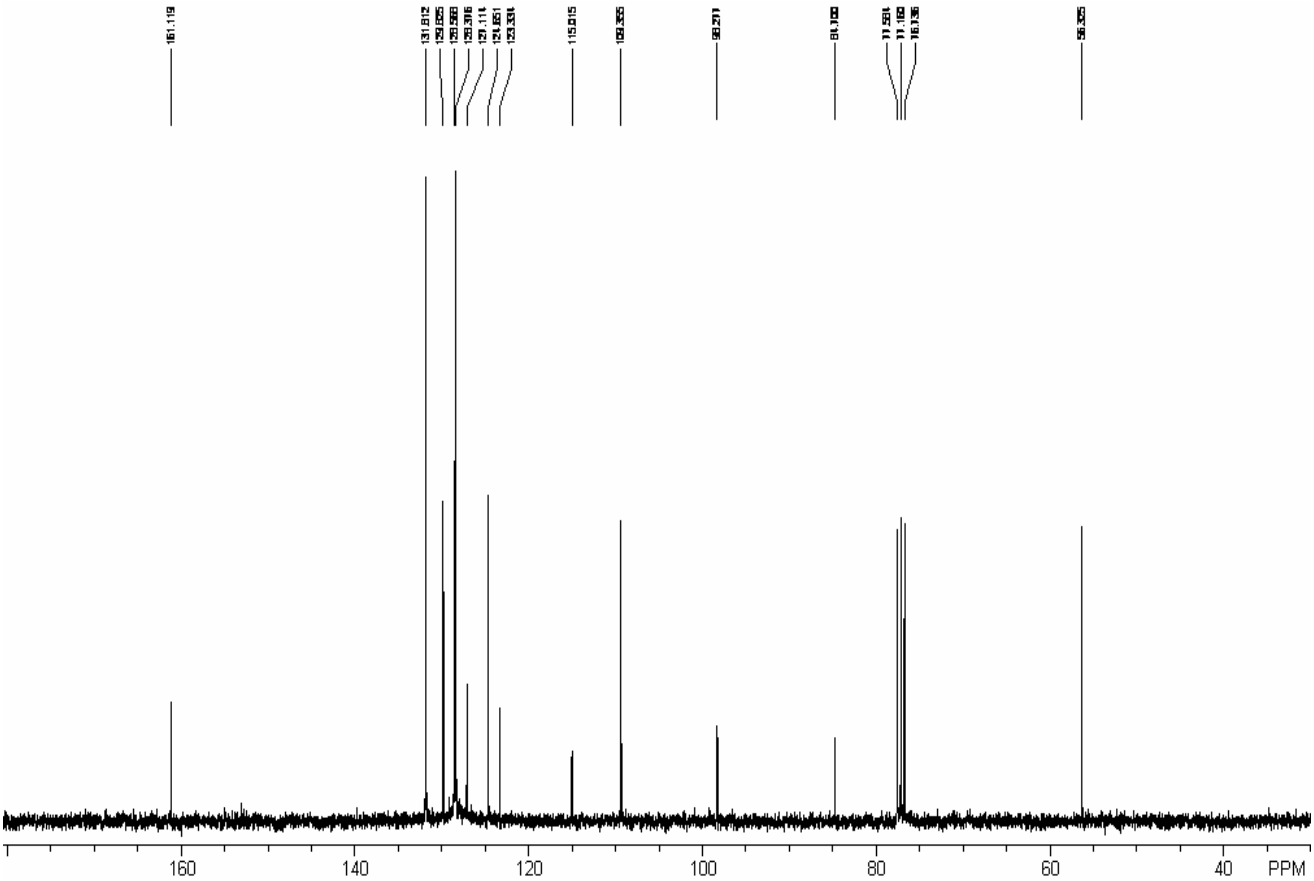

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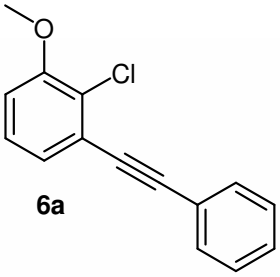
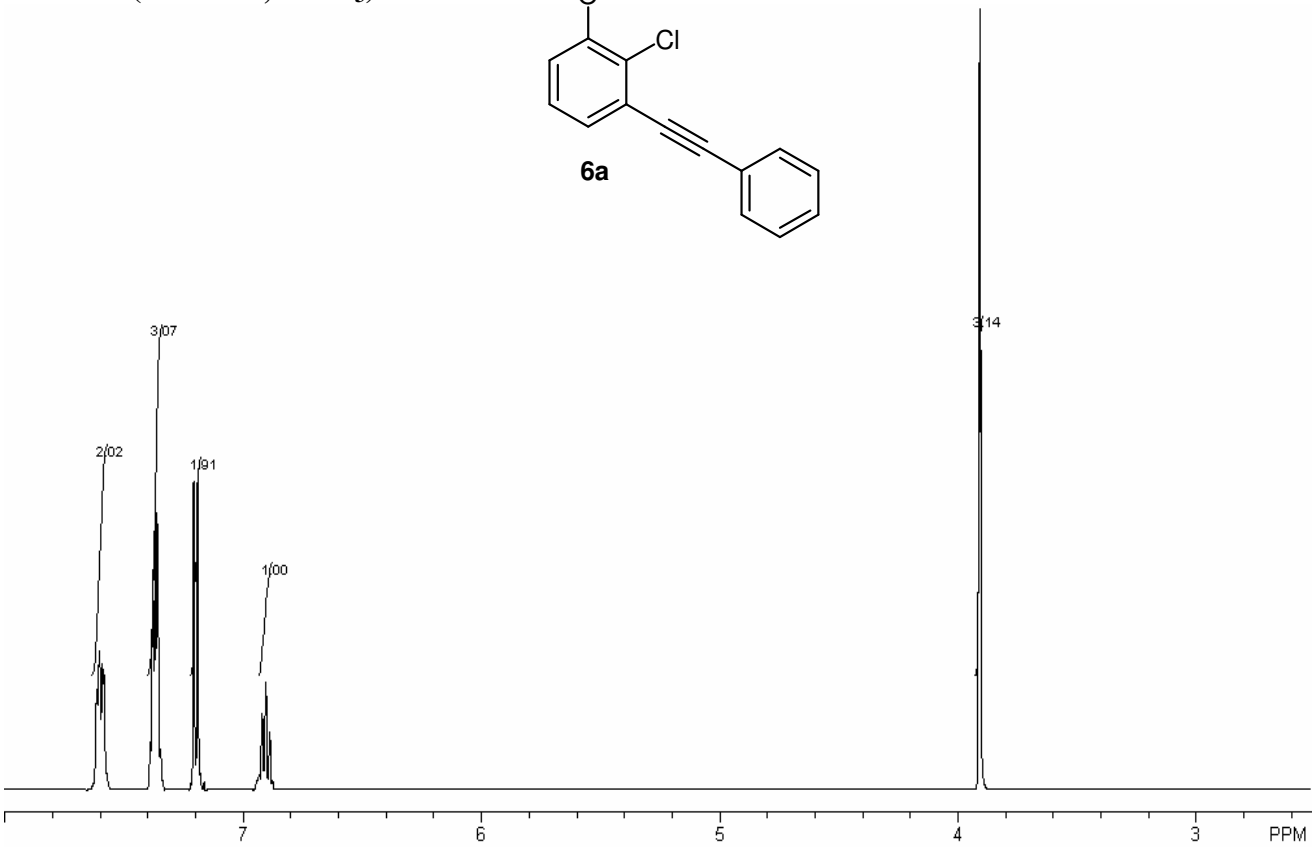
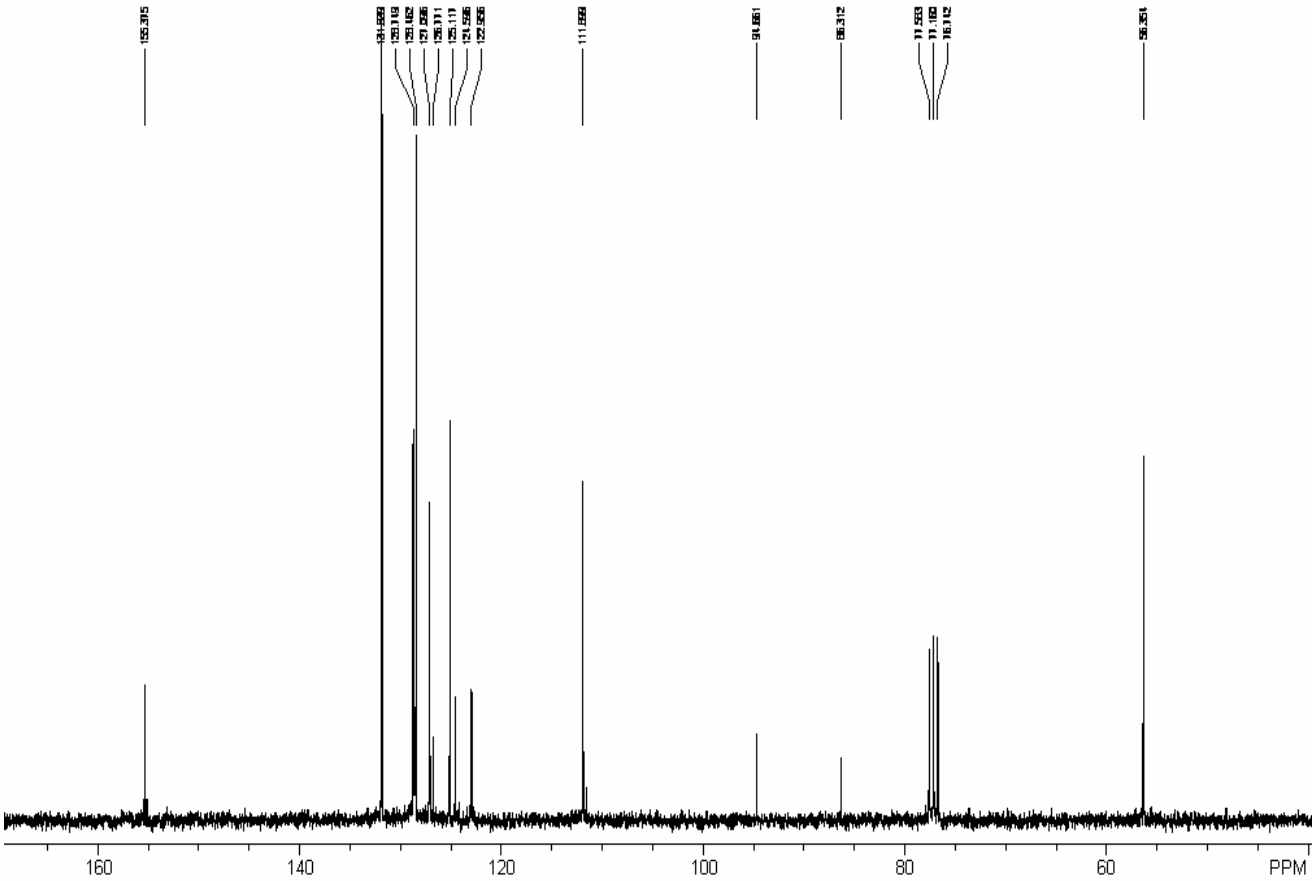
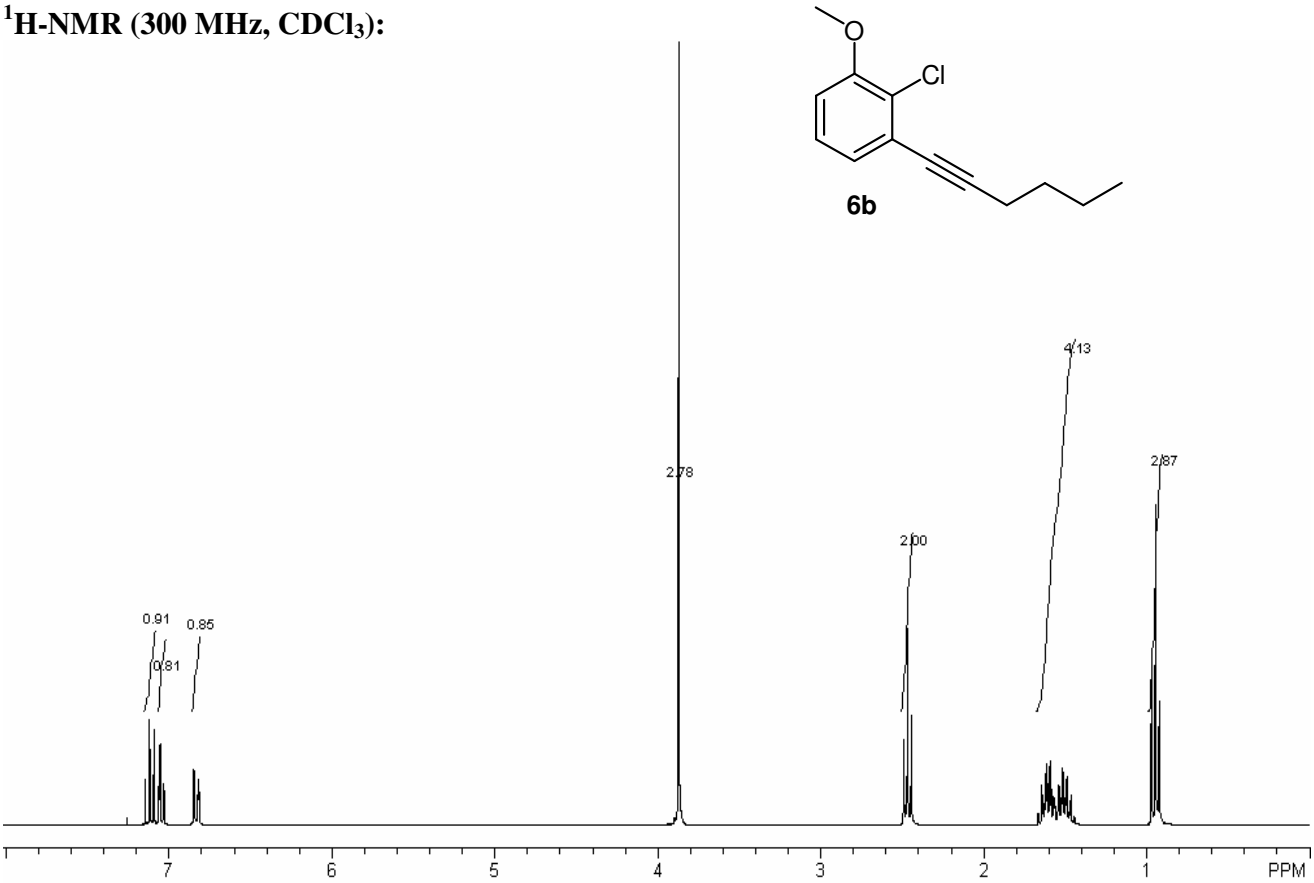




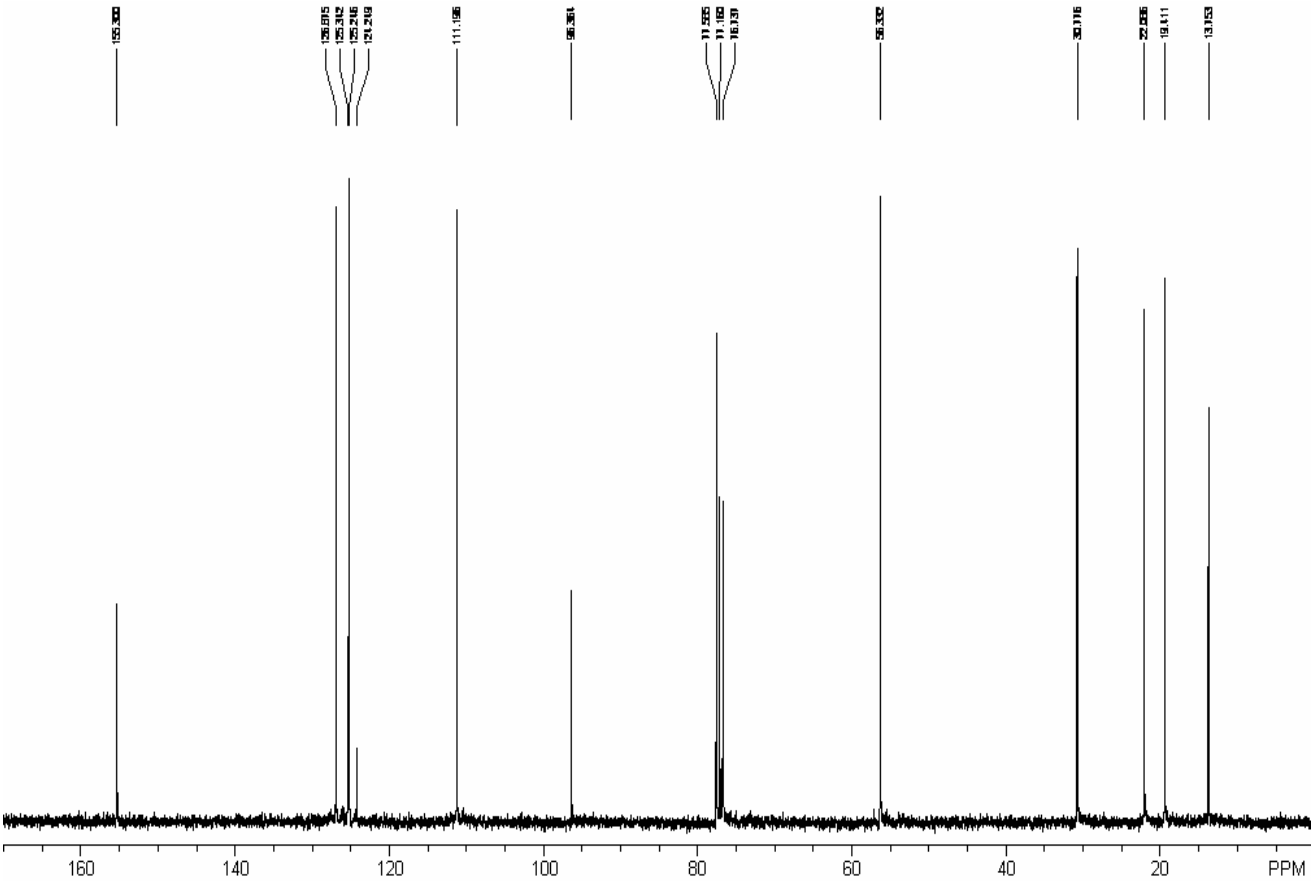
^{13}C-NMR (75.4 MHz, $CDCl_3$):



^{1}H-NMR (300 MHz, $CDCl_3$):



^{13}C-NMR (75.4 MHz, $CDCl_3$):



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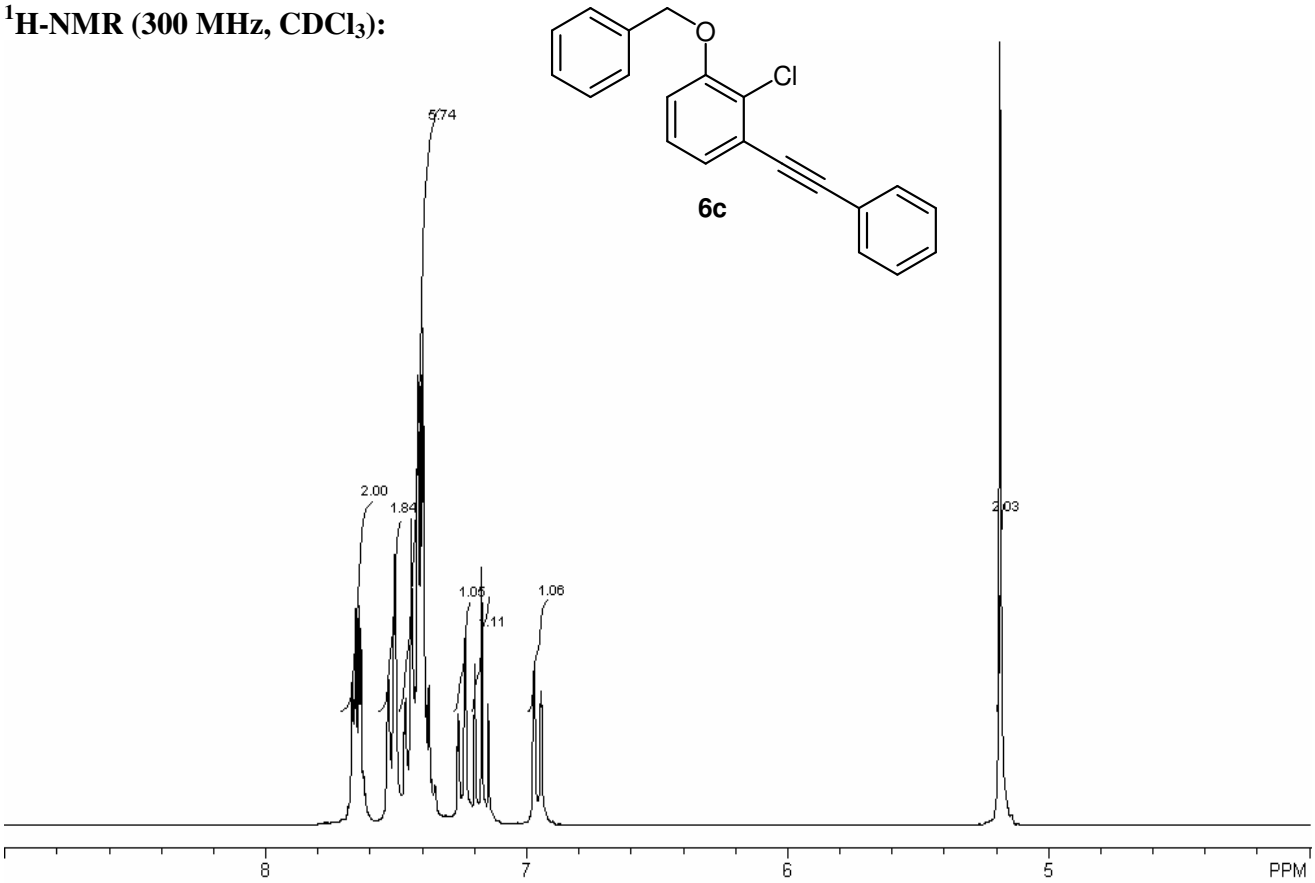

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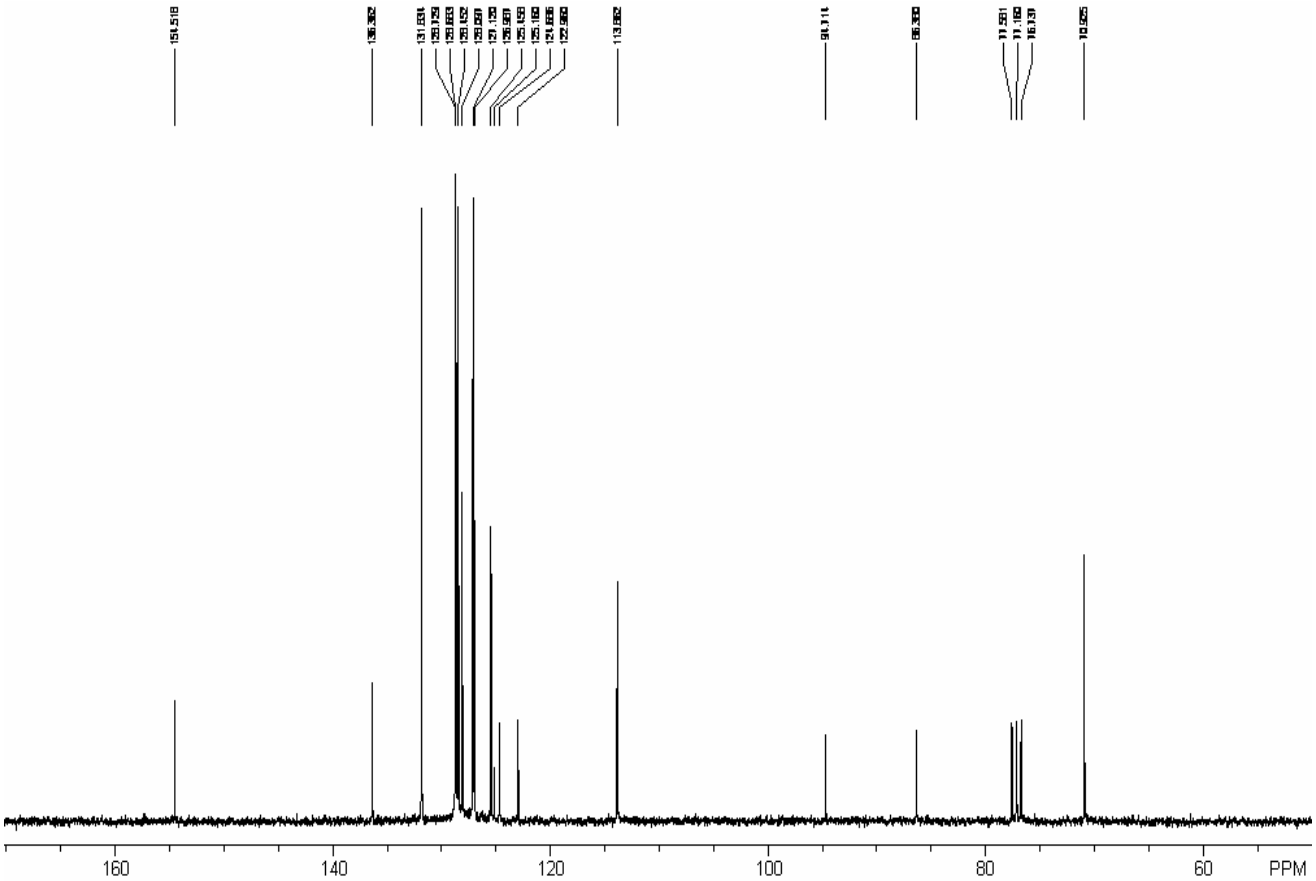
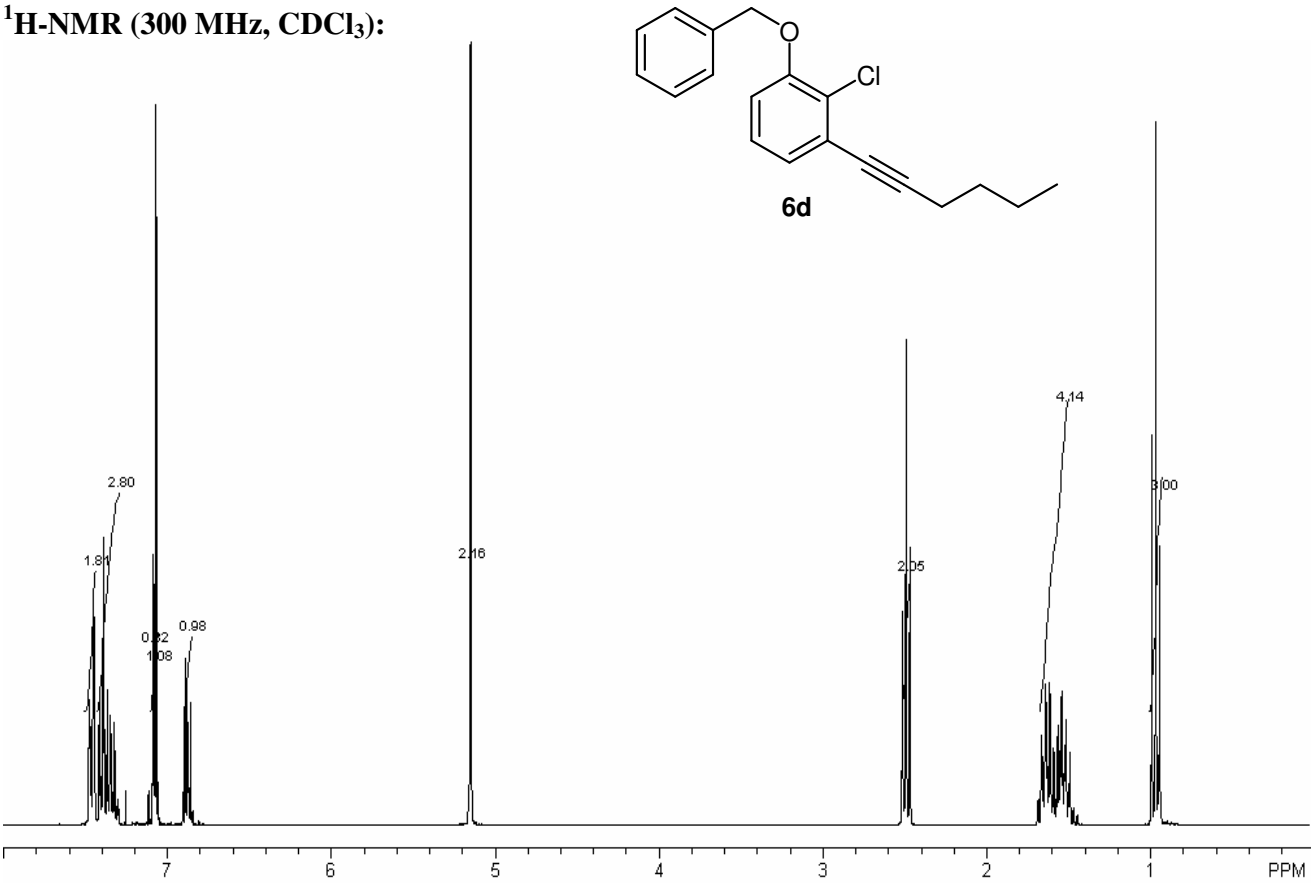
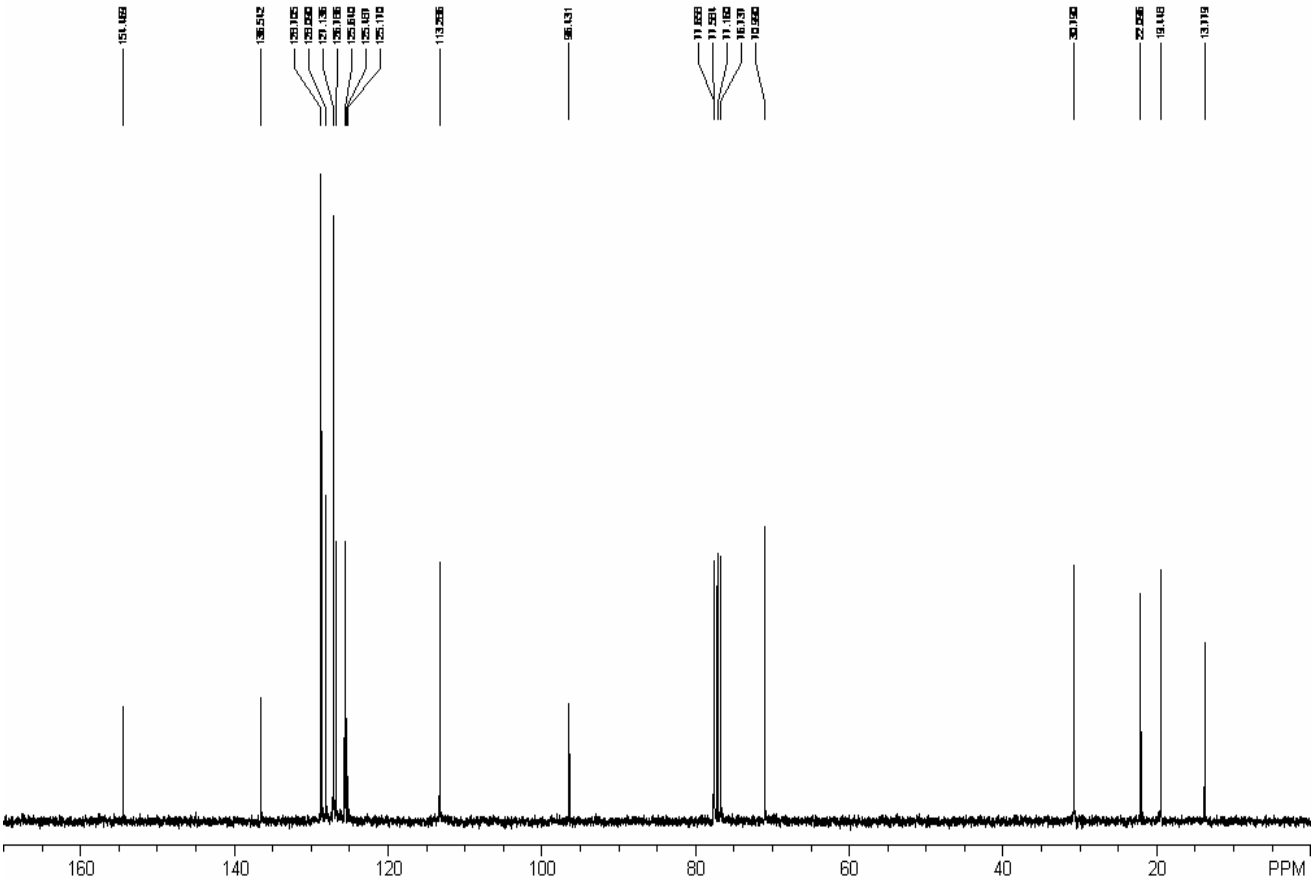


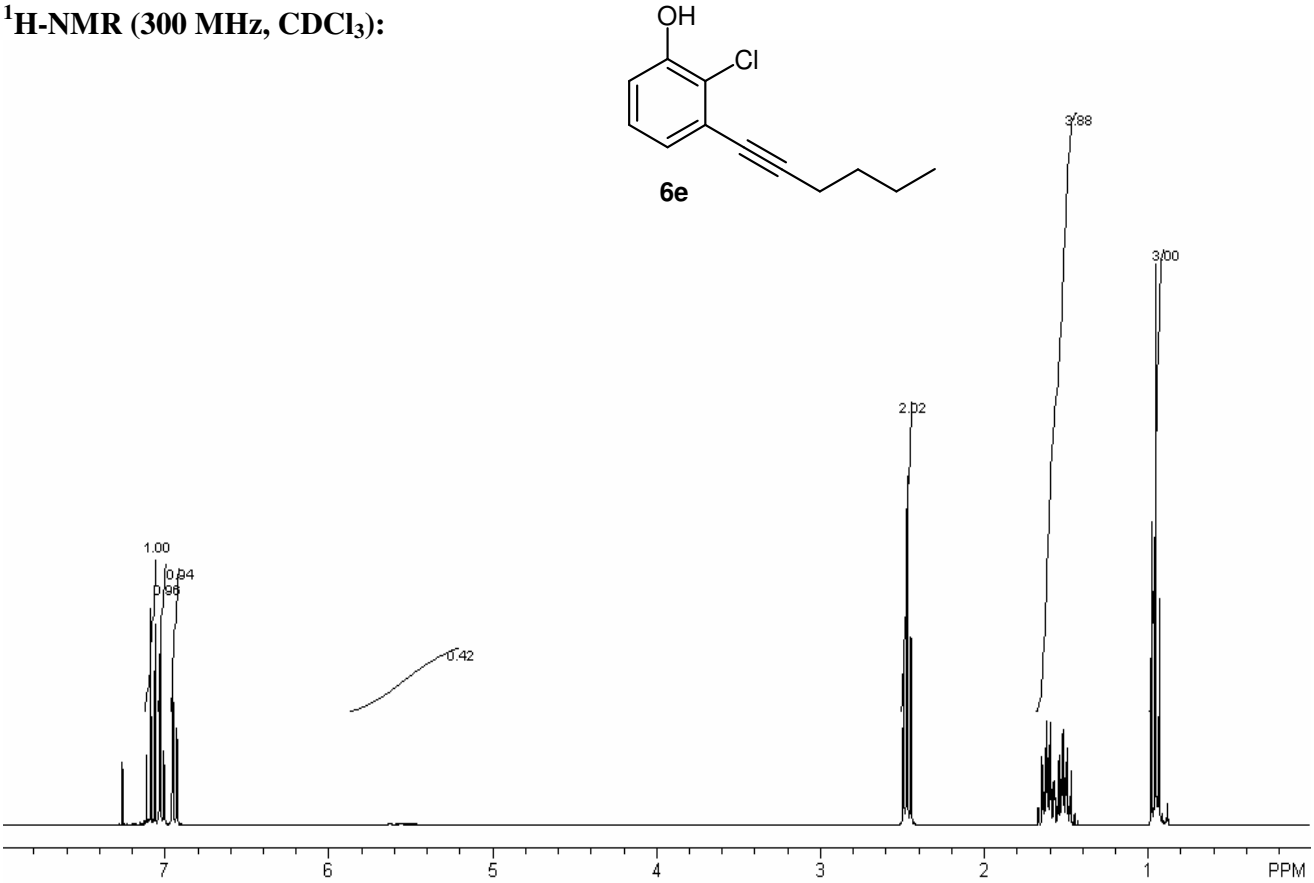
^{1}H-NMR (300 MHz, $CDCl_3$):



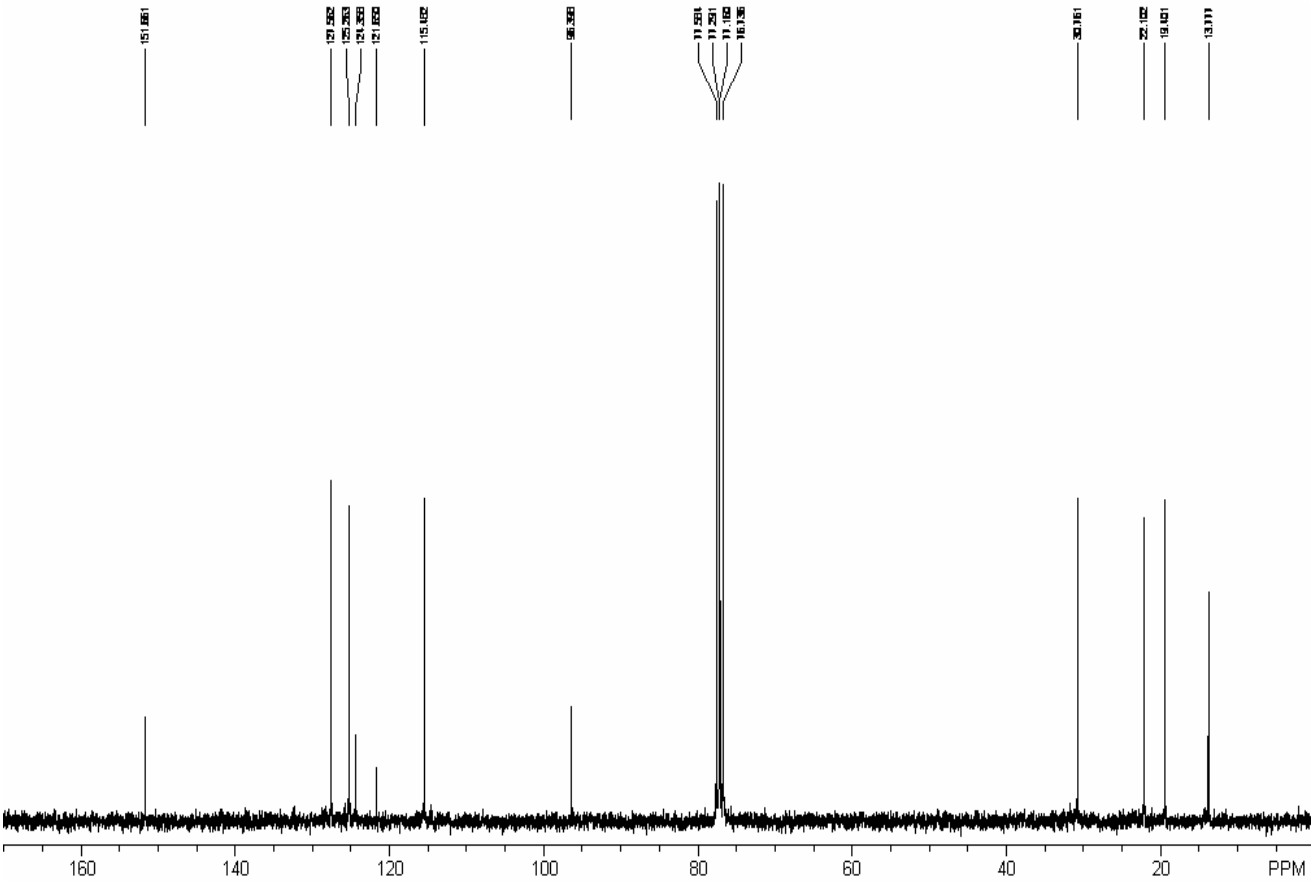
^{13}C-NMR (75.4 MHz, $CDCl_3$):



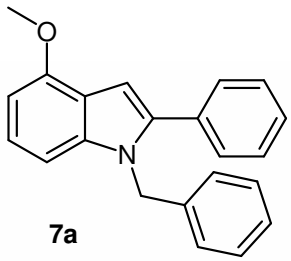
^{1}H-NMR (300 MHz, $CDCl_3$):



^{13}C-NMR (75.4 MHz, $CDCl_3$):



^{1}H-NMR (300 MHz, $CDCl_3$):



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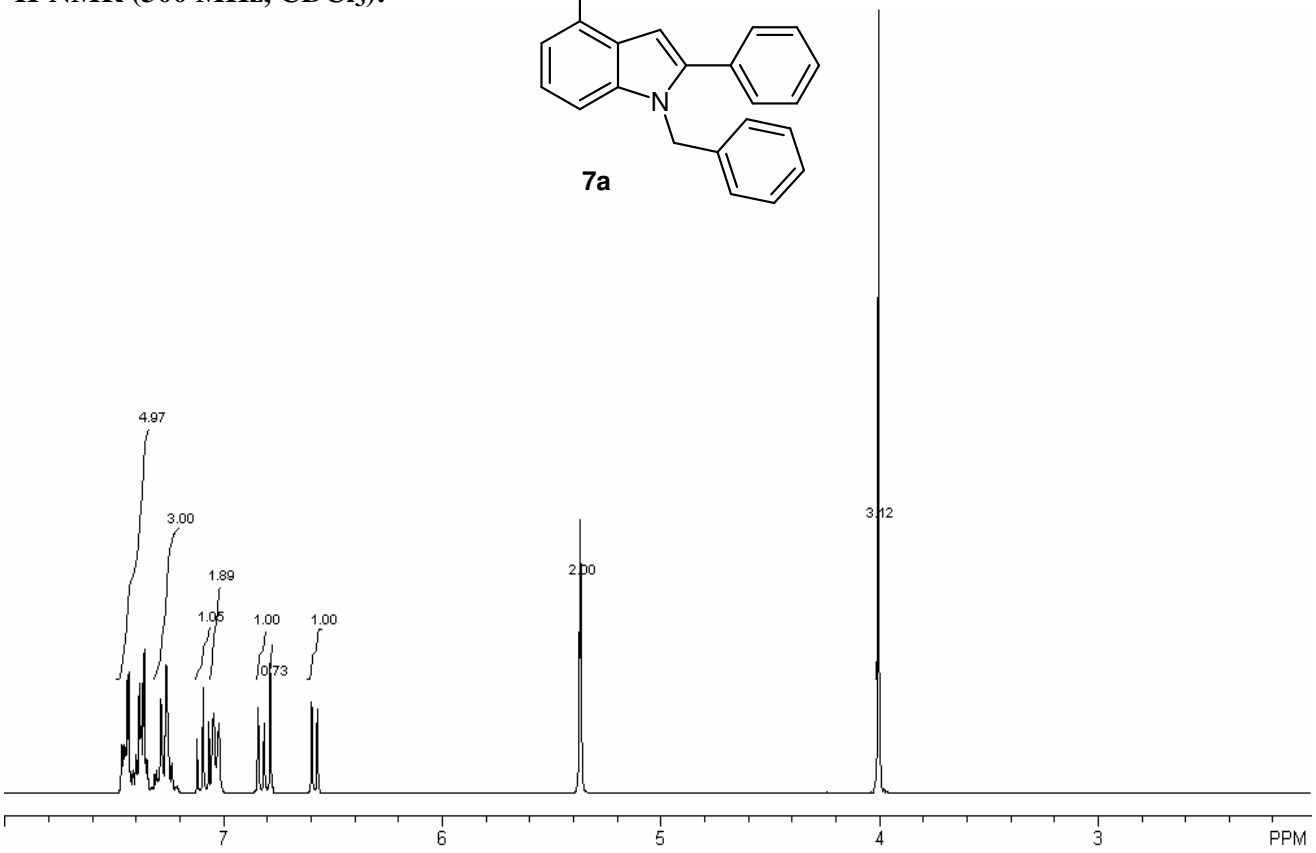
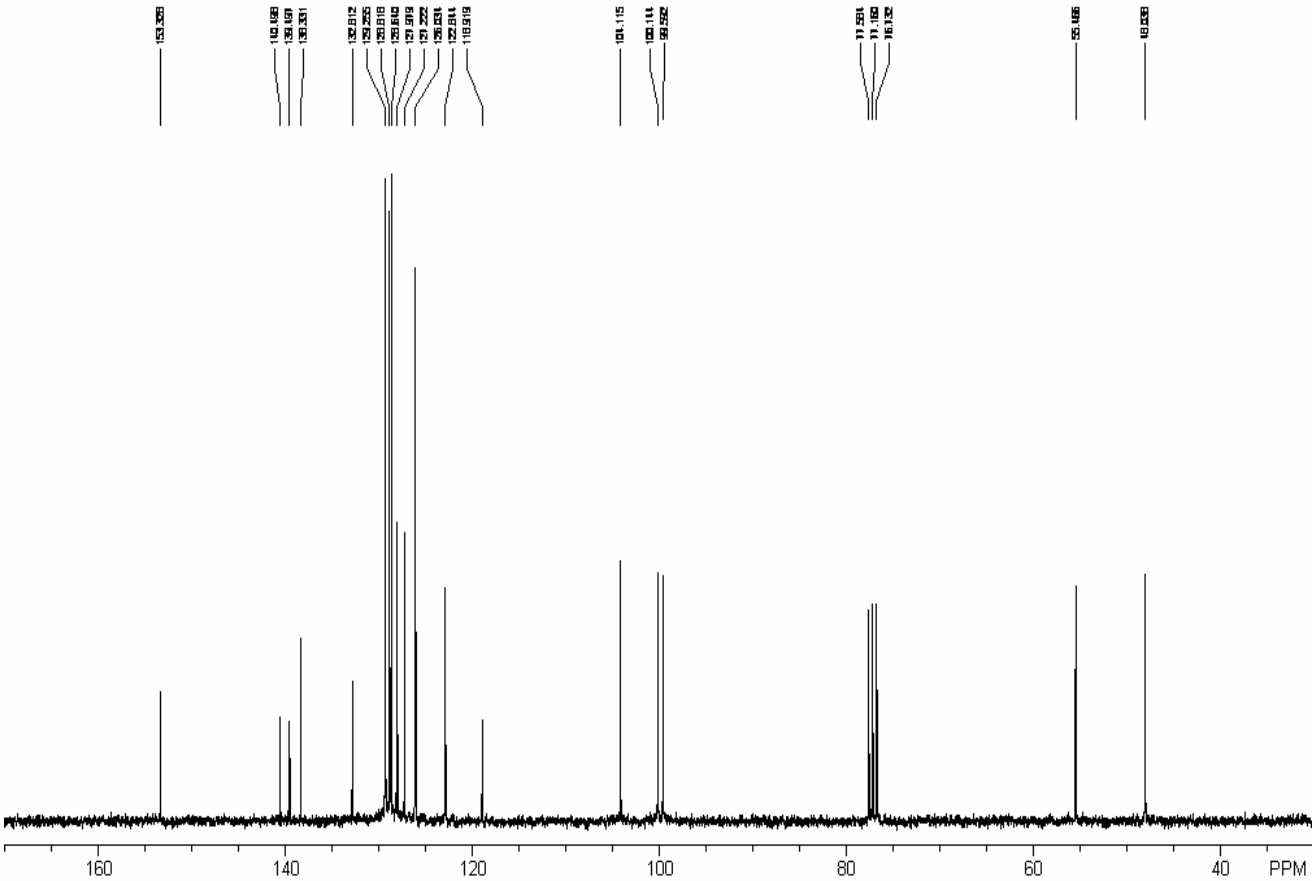


^{13}C-NMR (75.4 MHz, $CDCl_3$):



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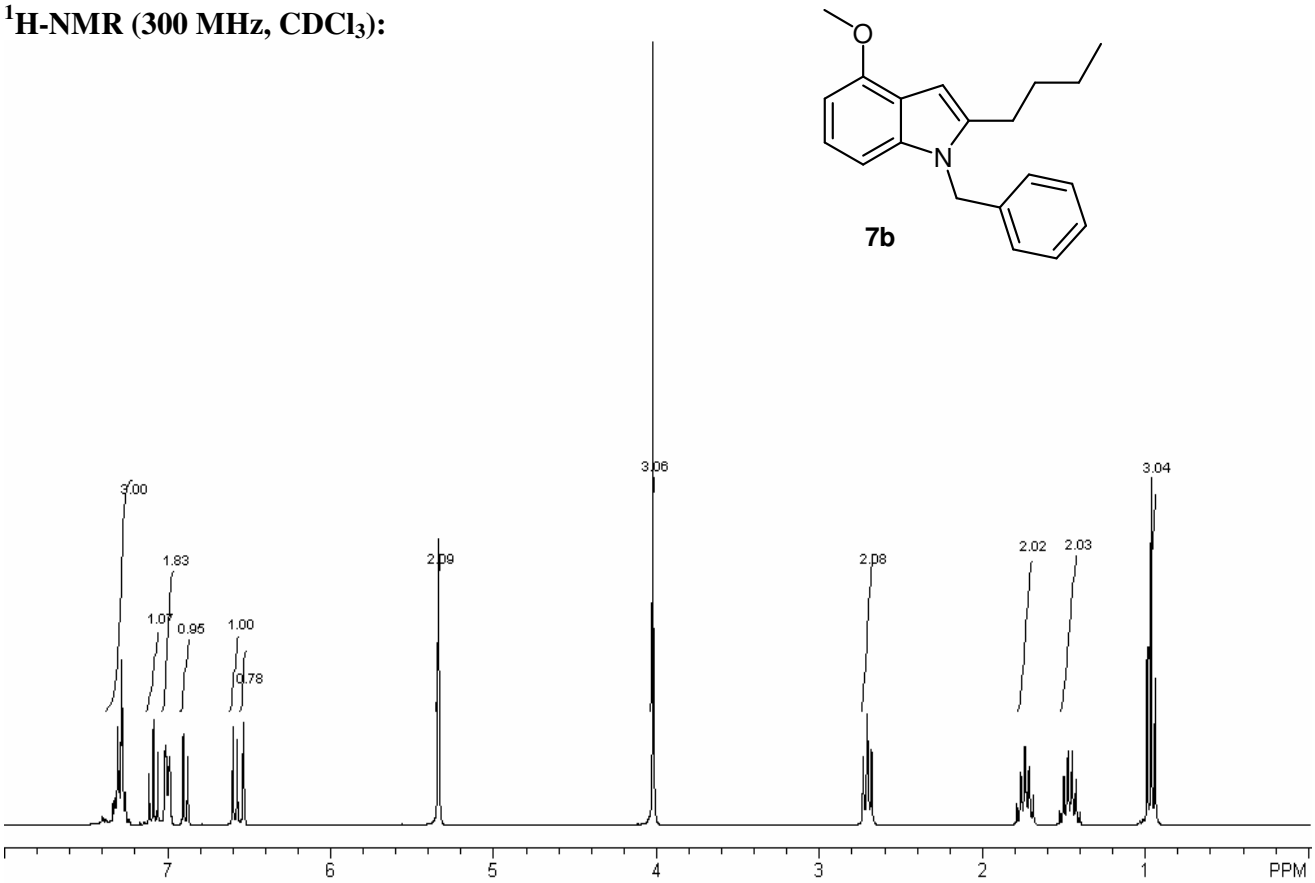
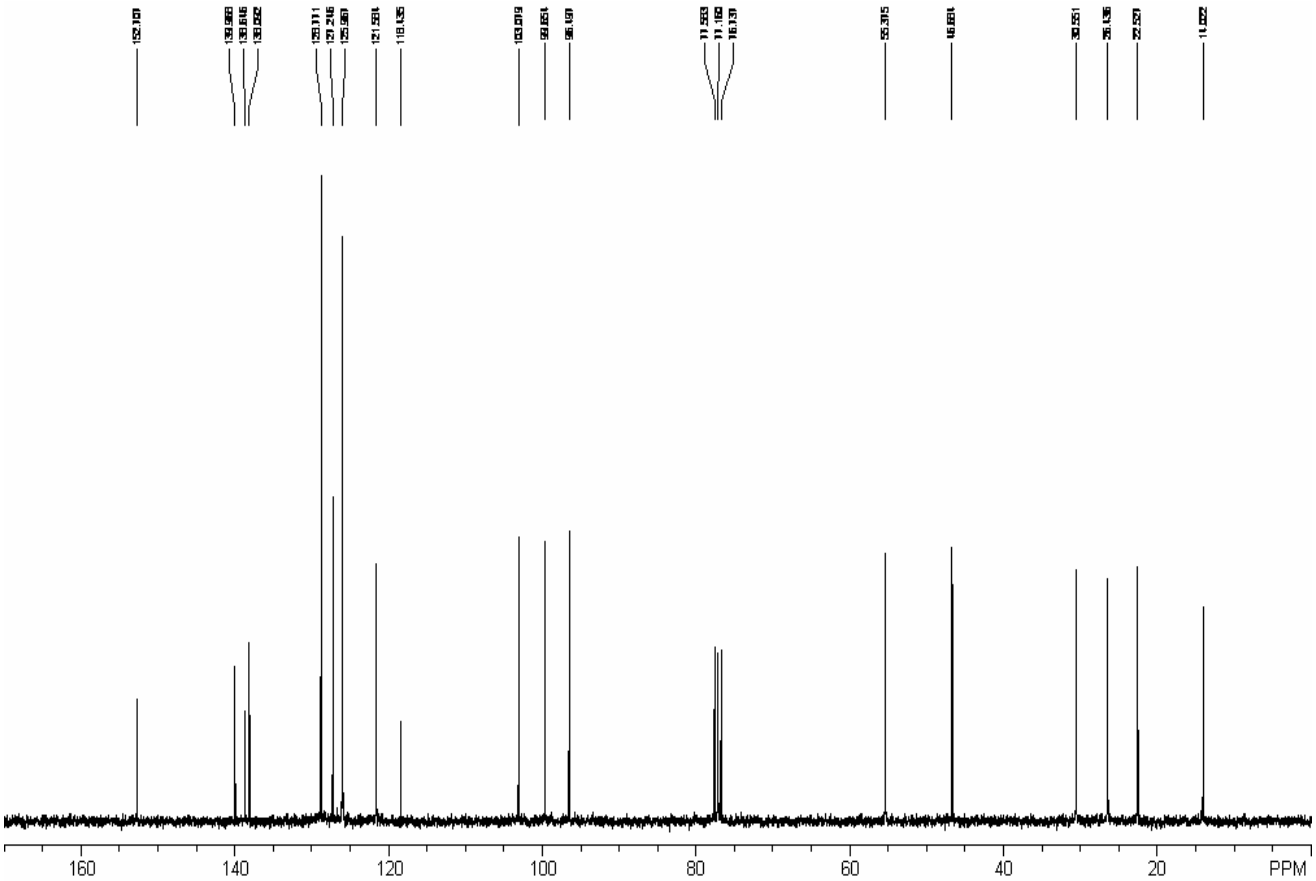


^{13}C-NMR (75.4 MHz, $CDCl_3$):



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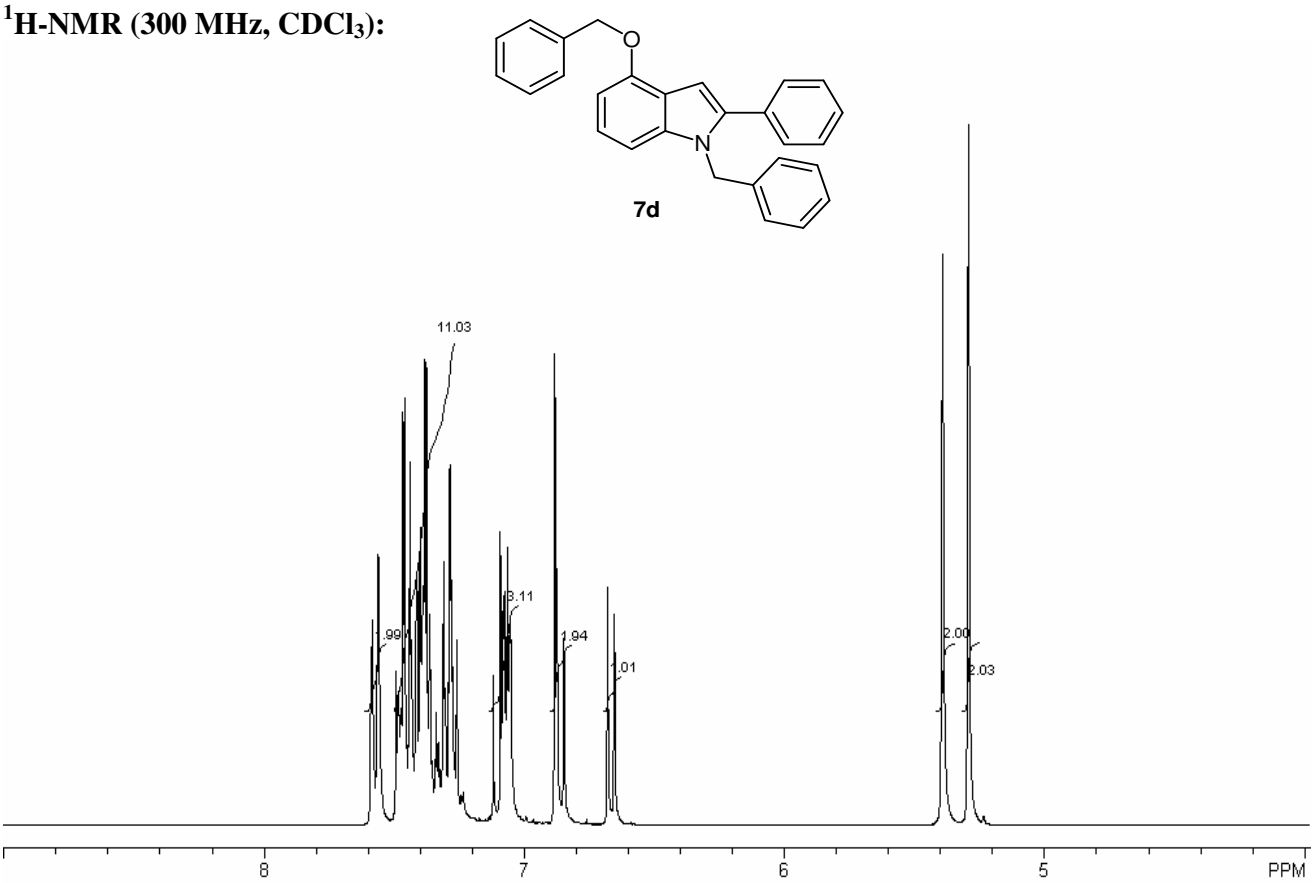

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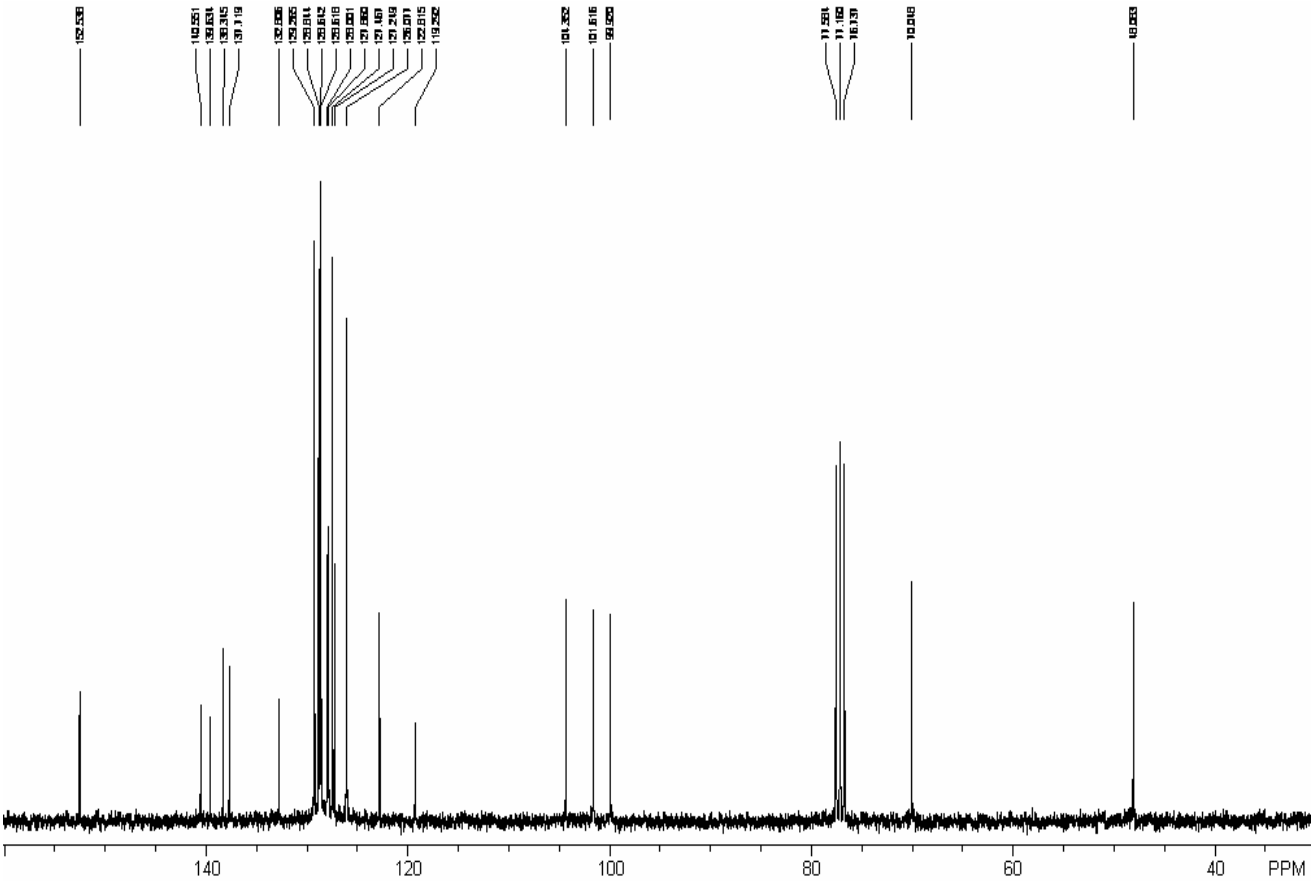

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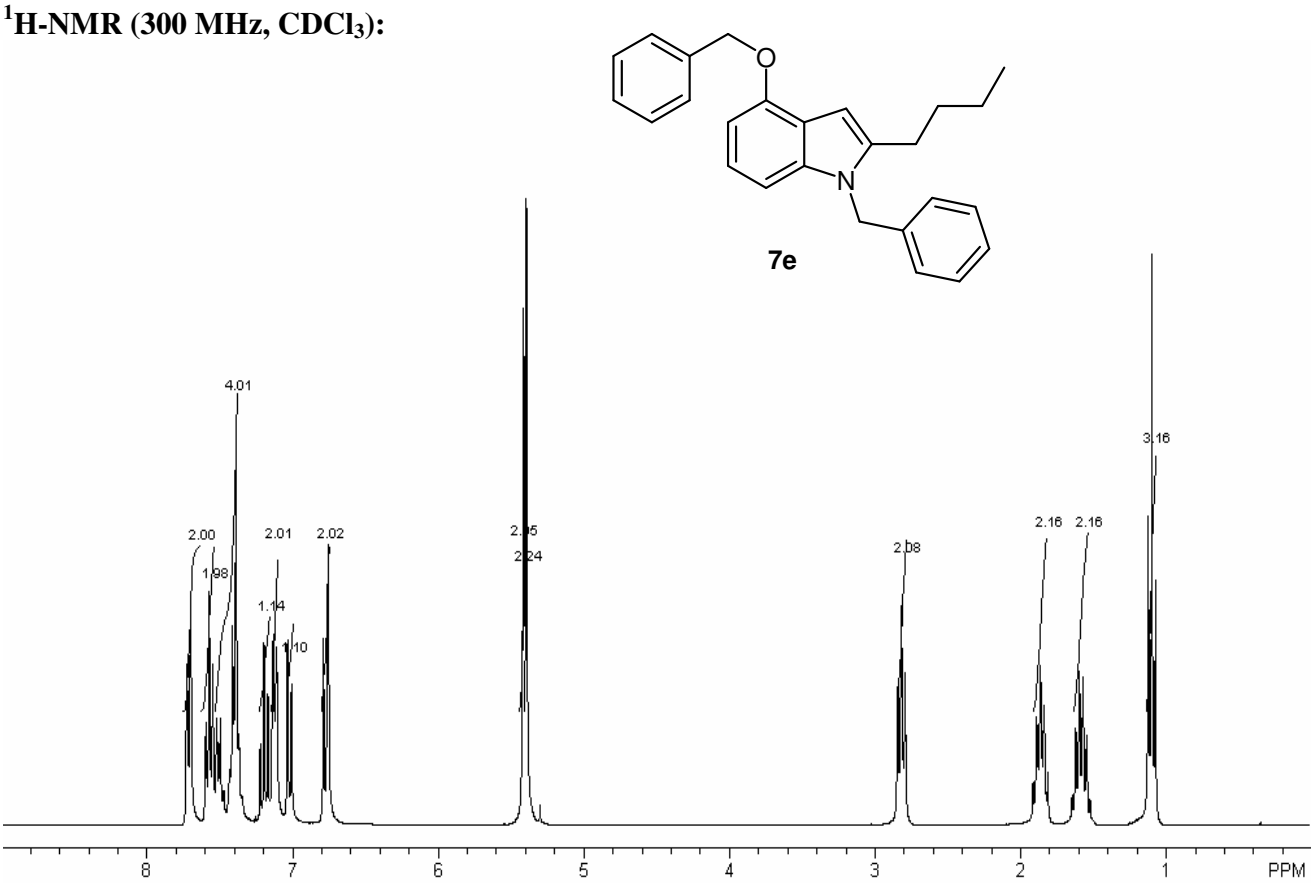

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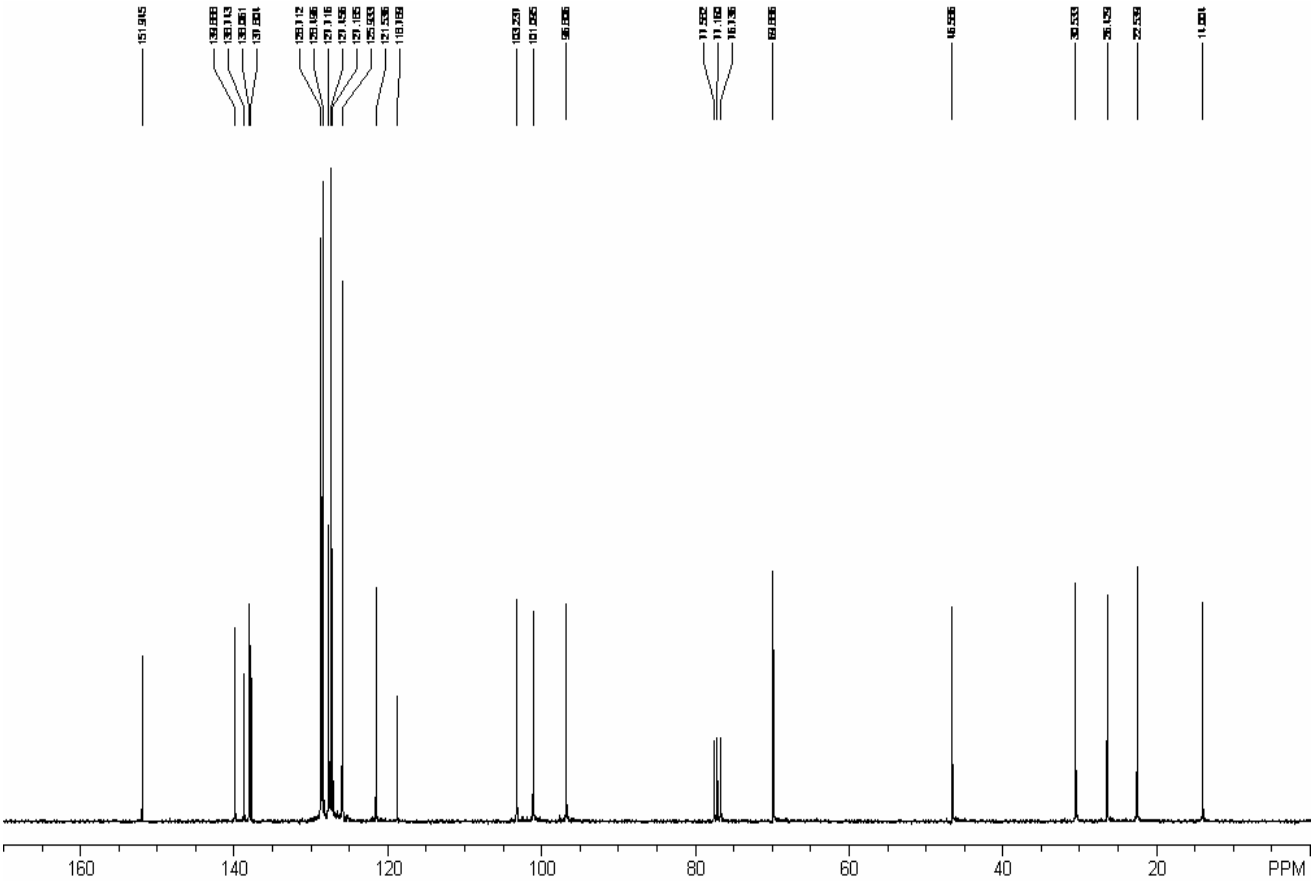

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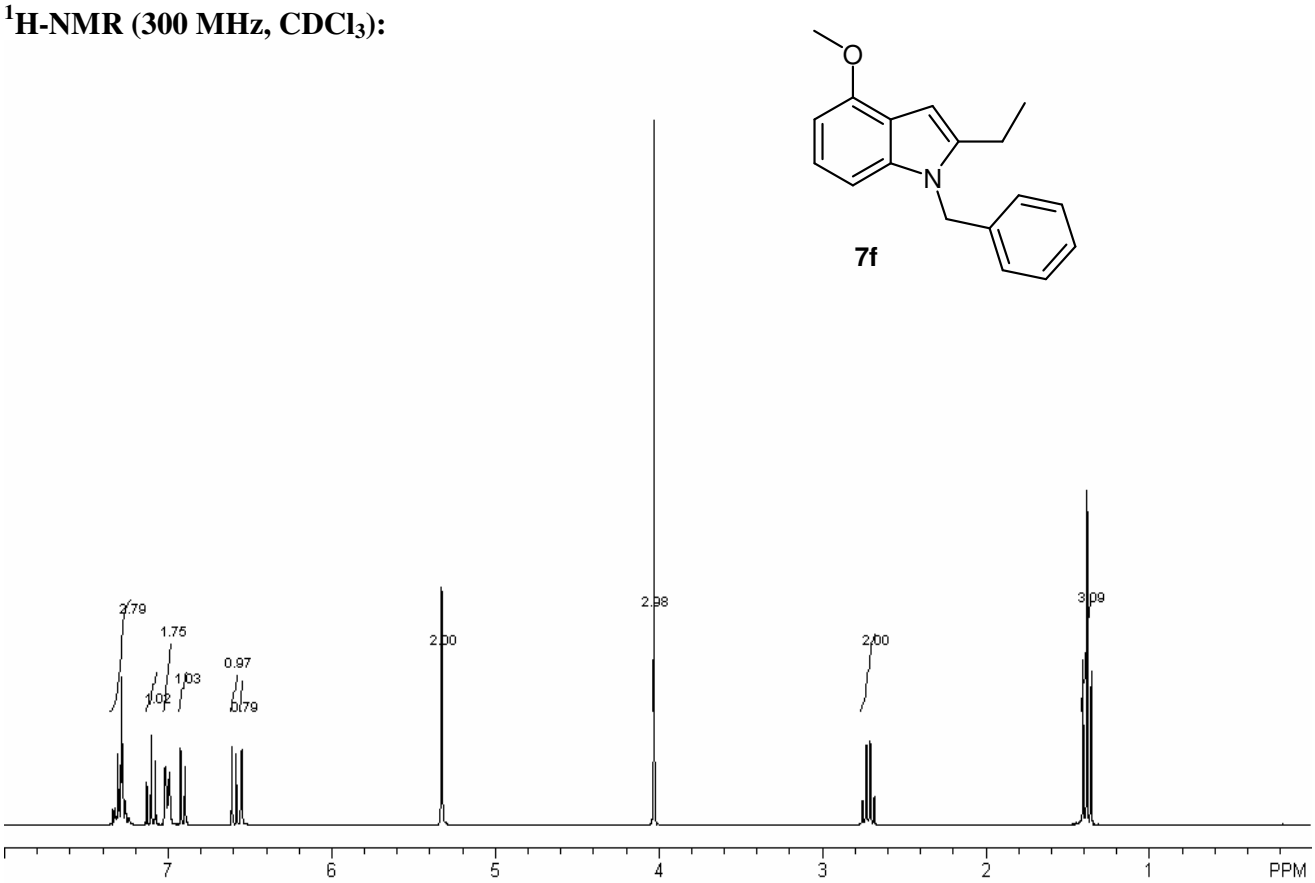

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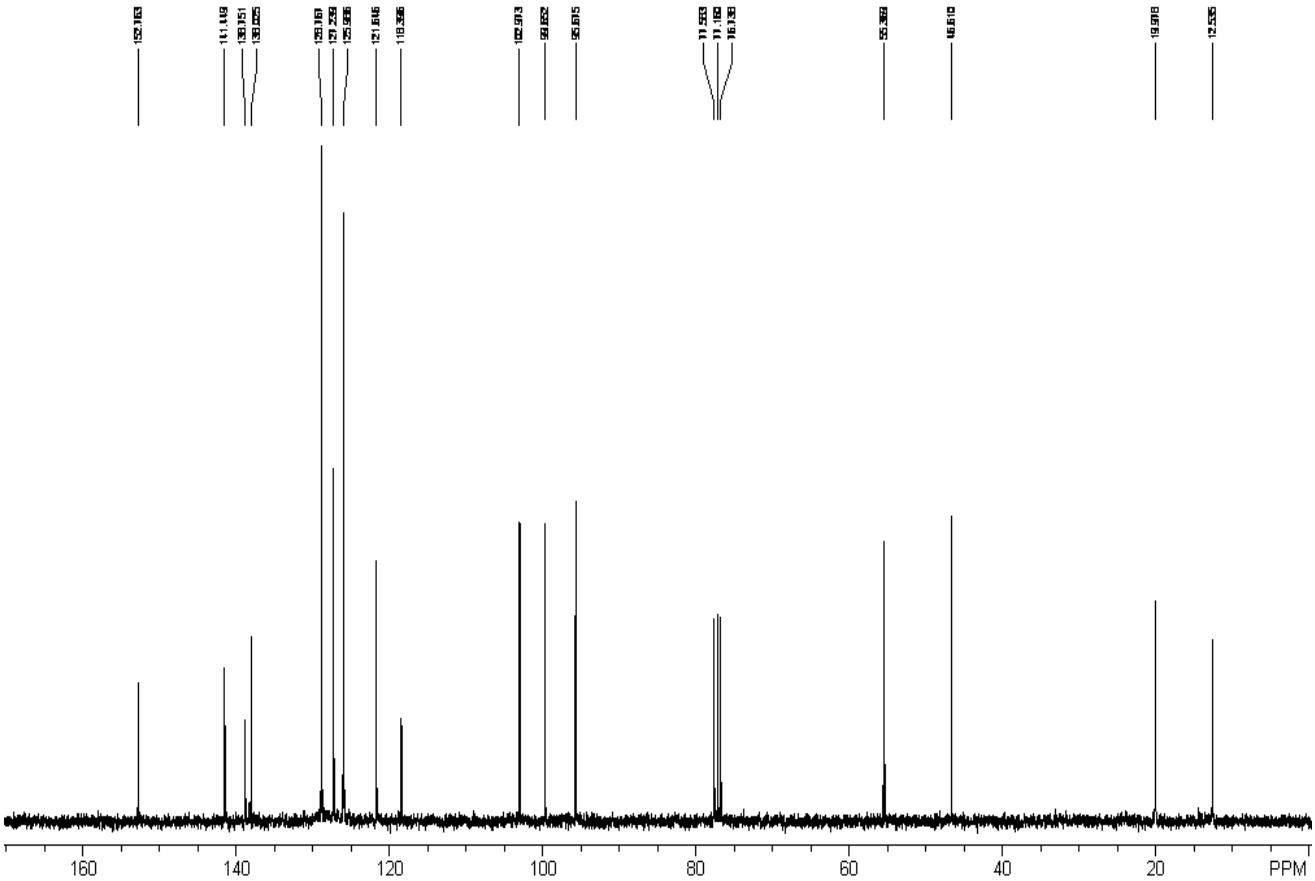

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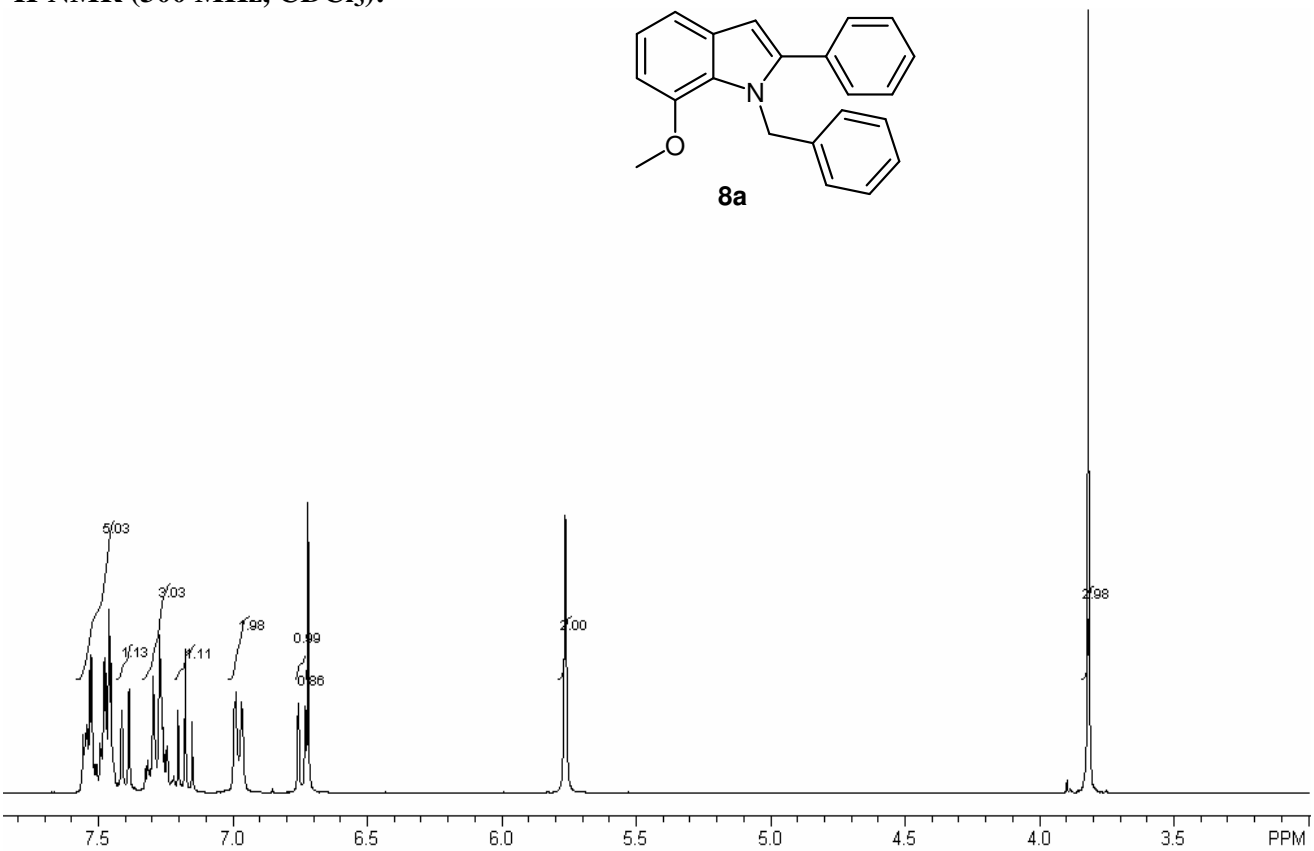
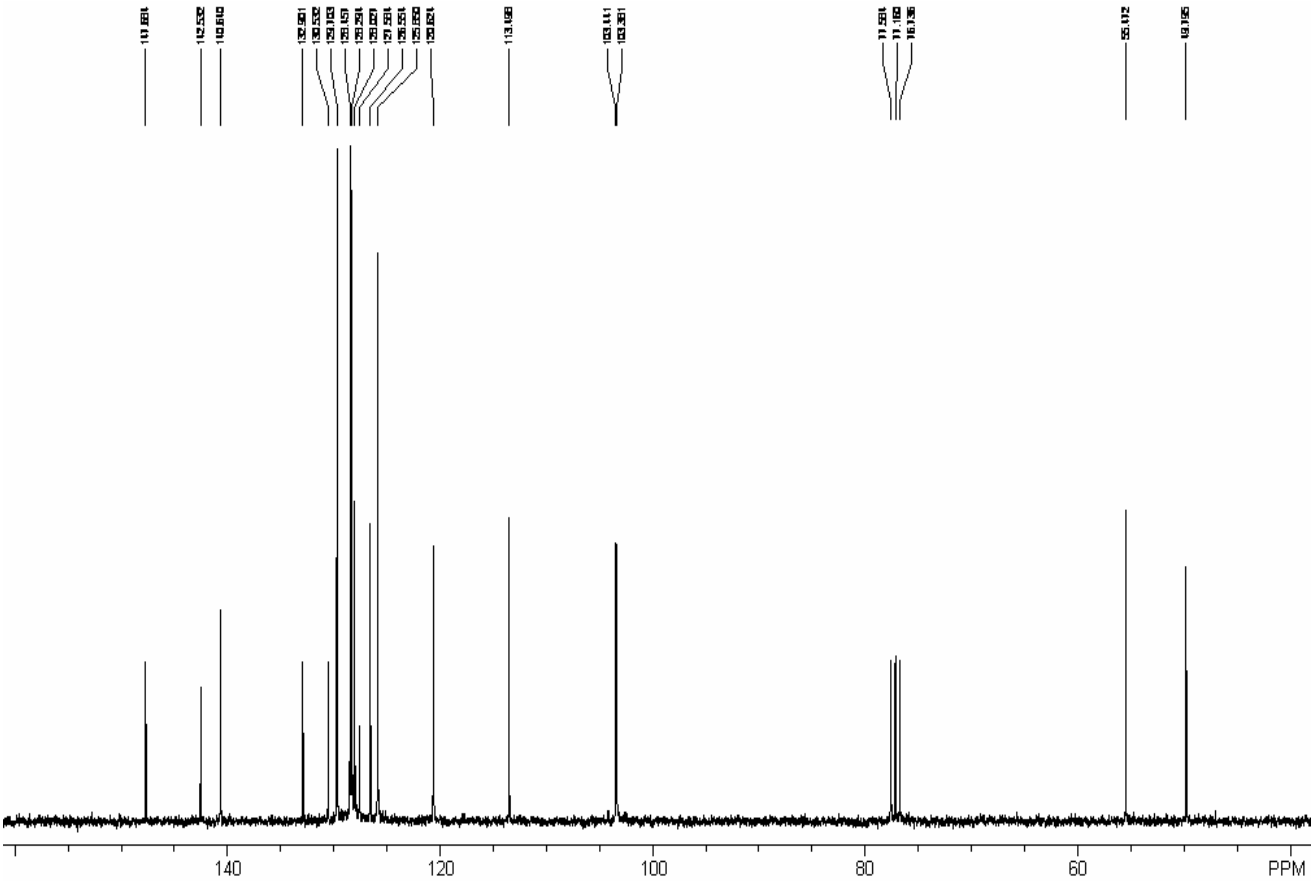


^{13}C-NMR (75.4 MHz, $CDCl_3$):



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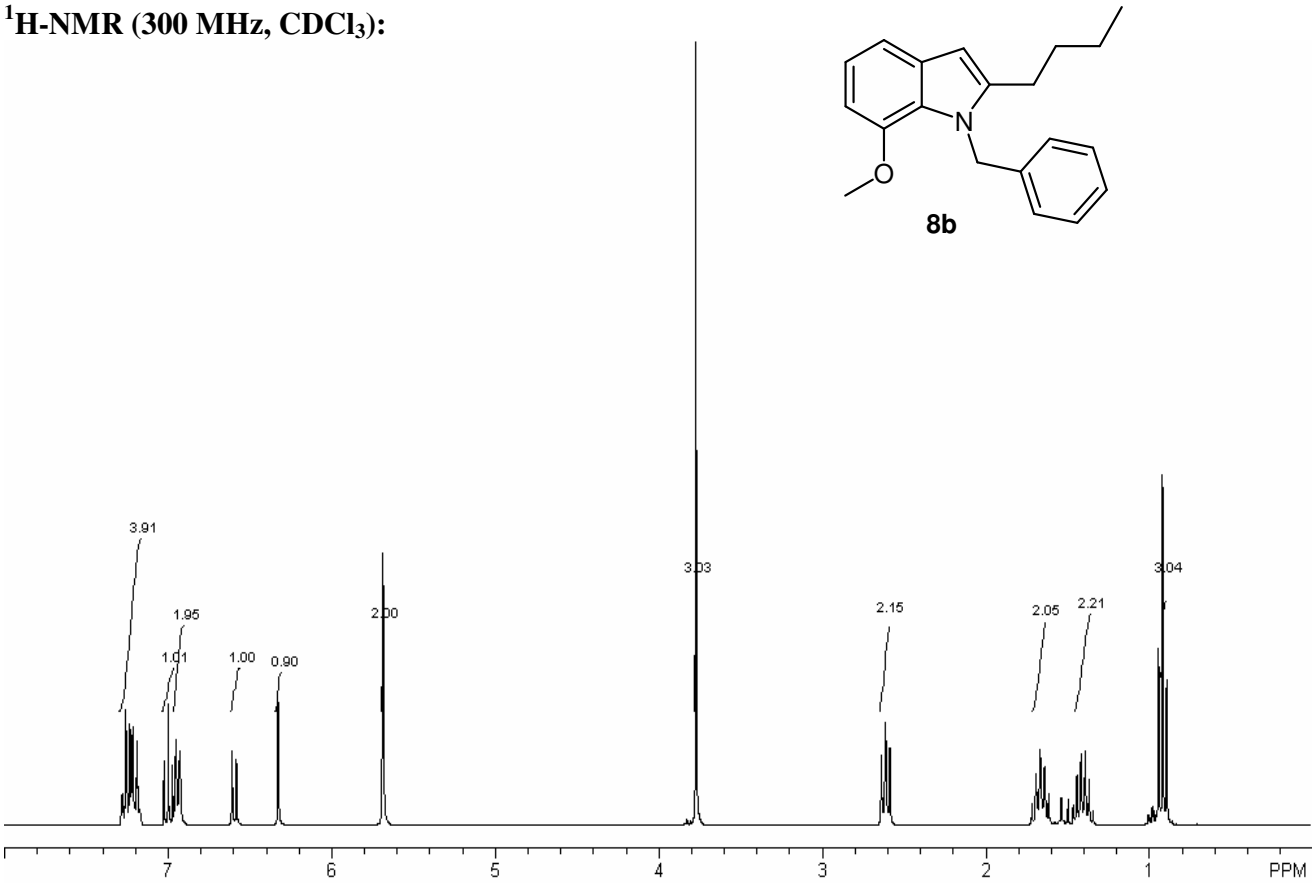

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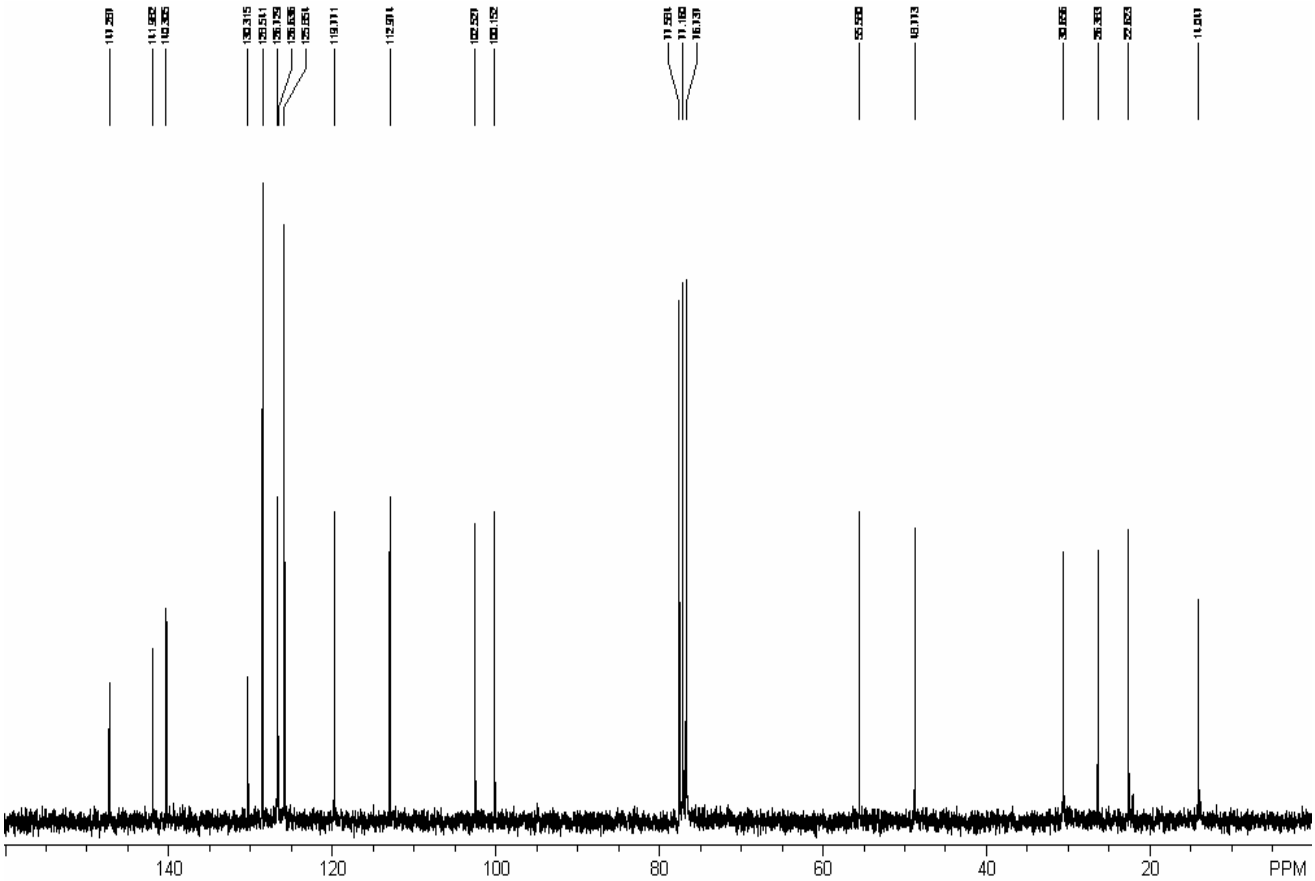

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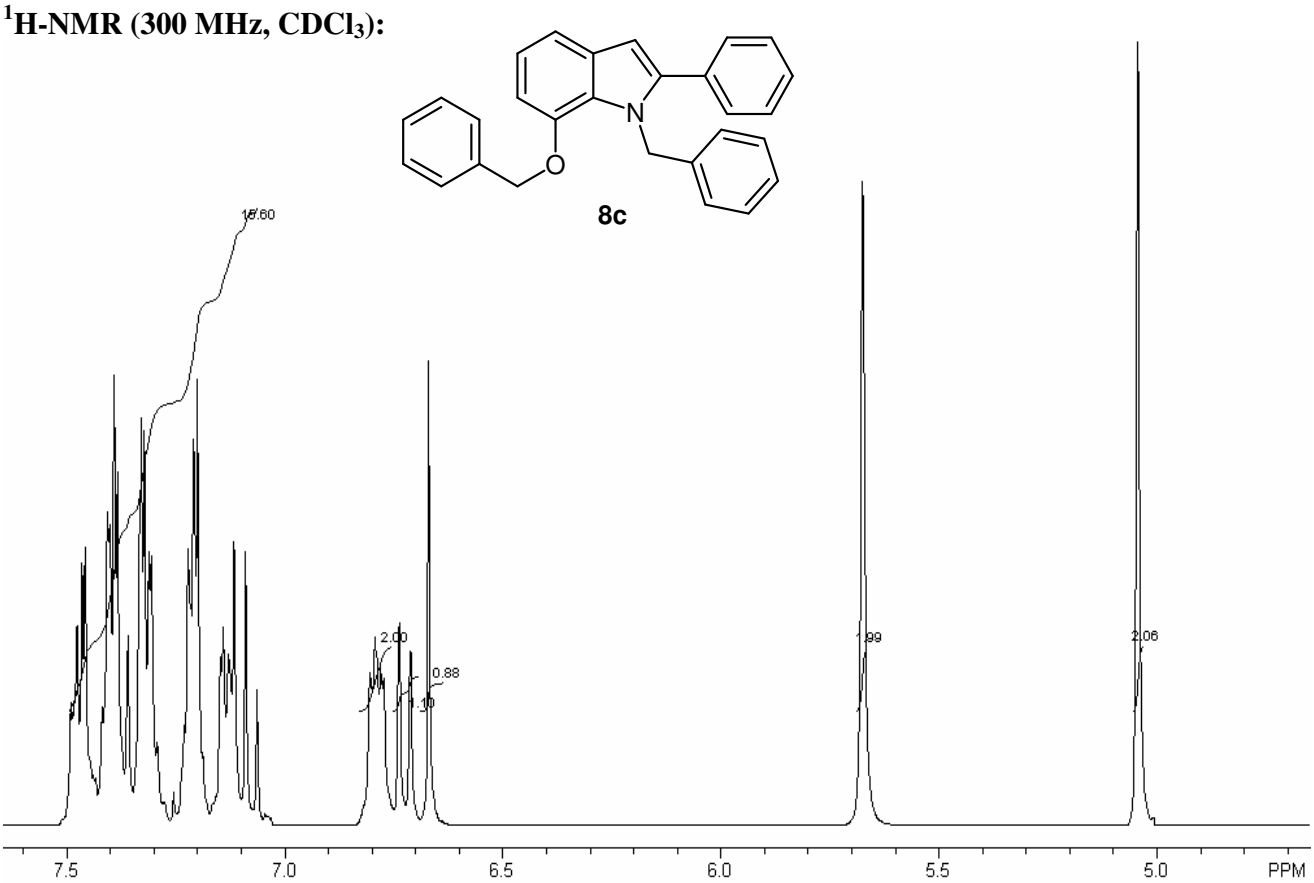

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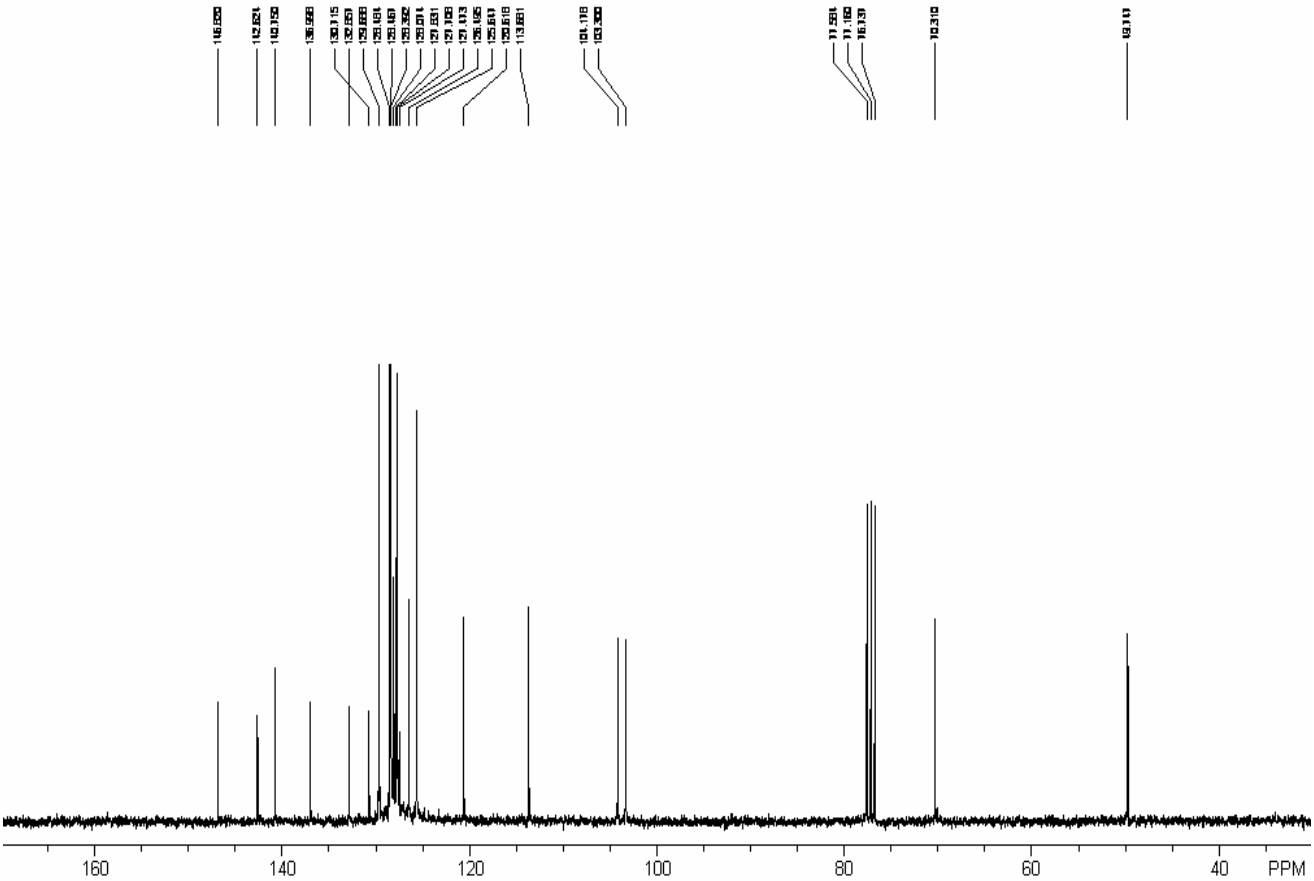

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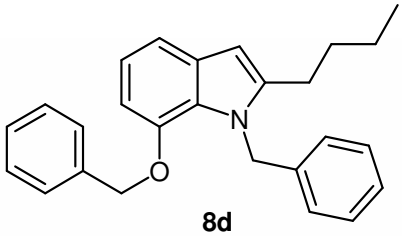

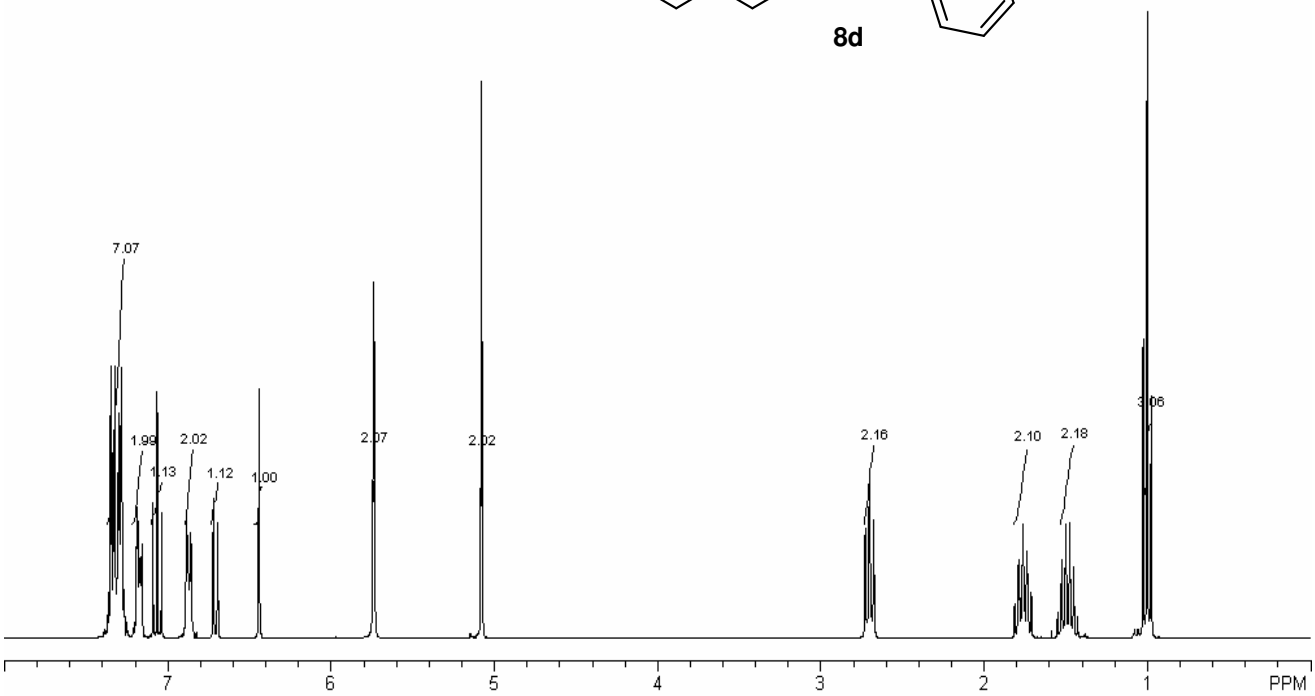

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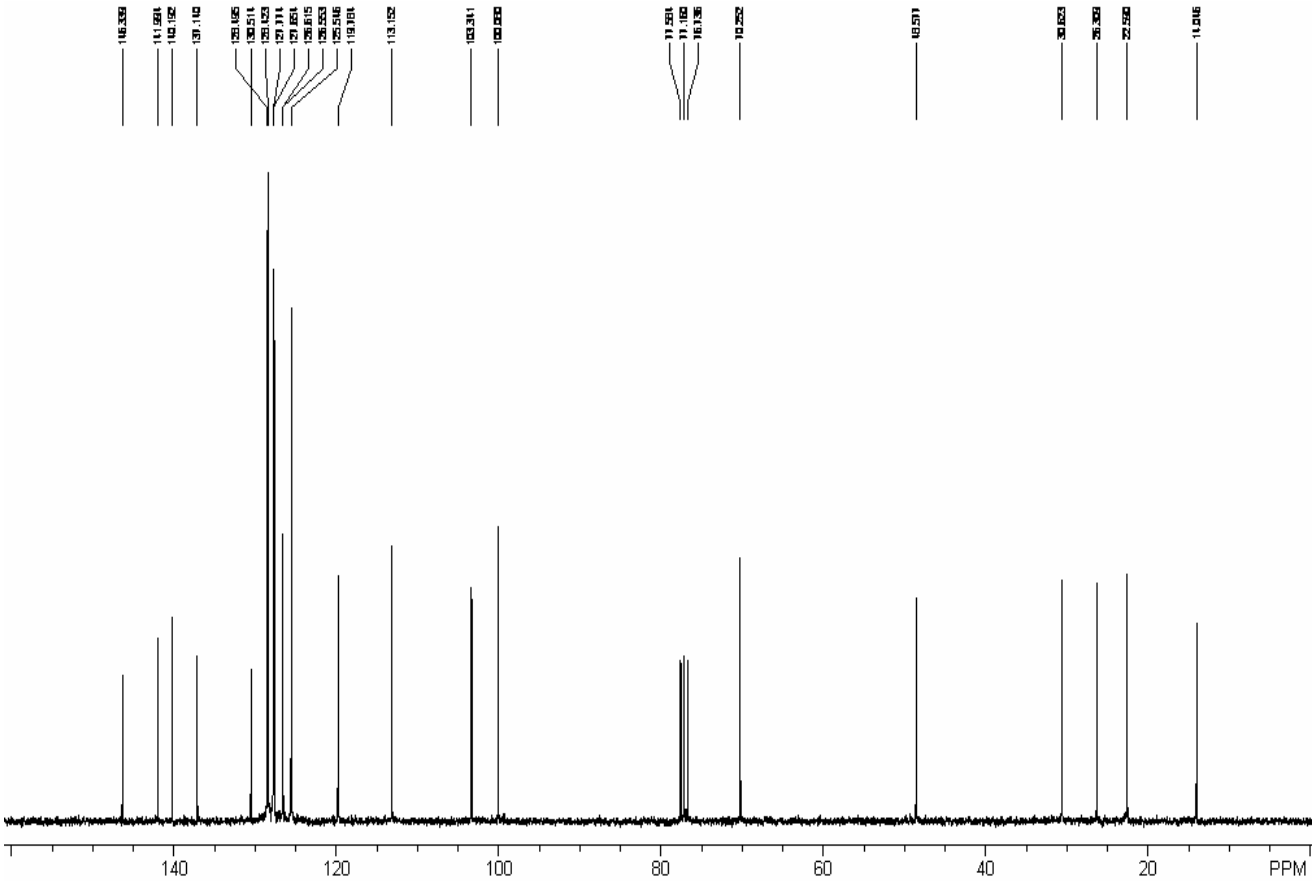

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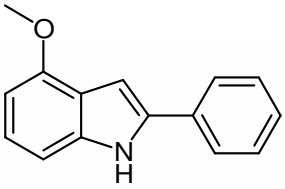

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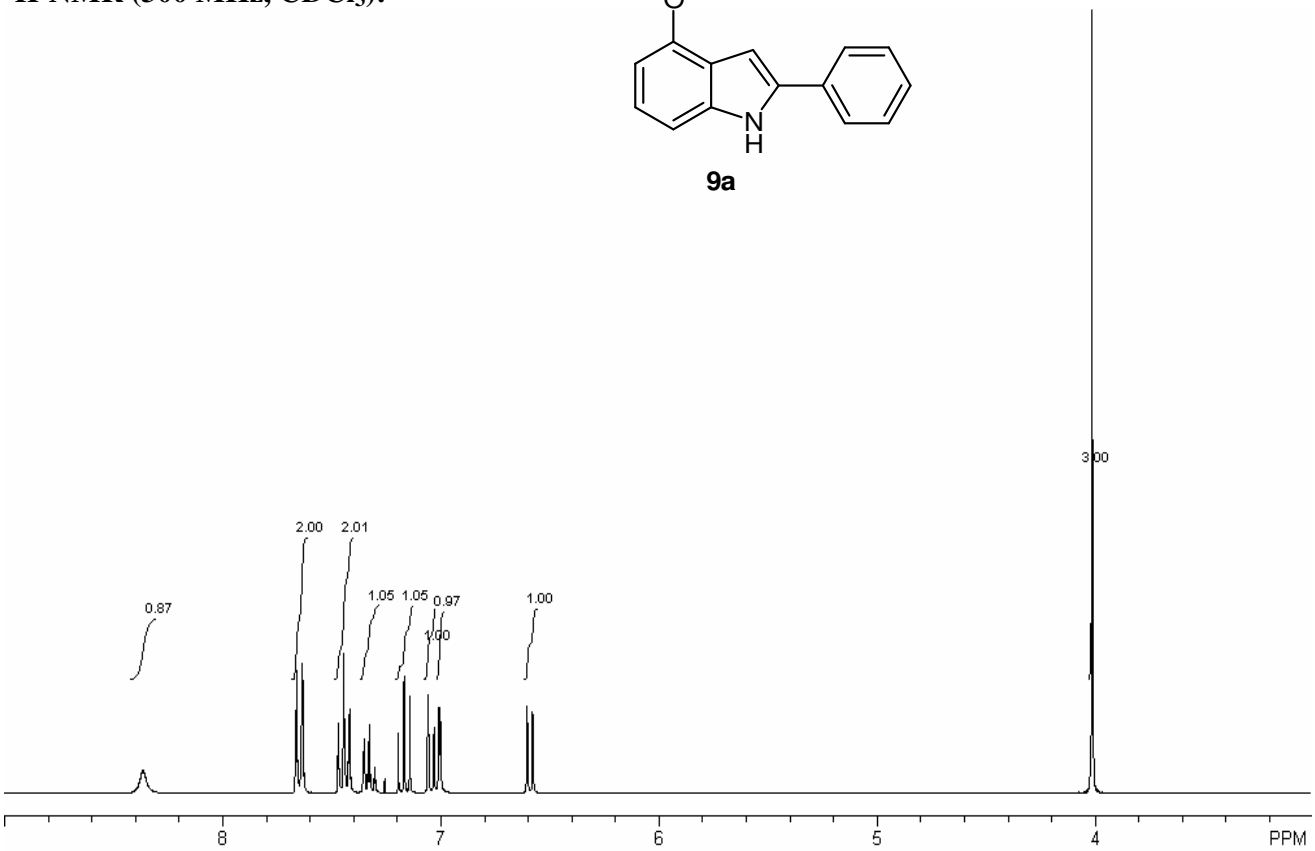
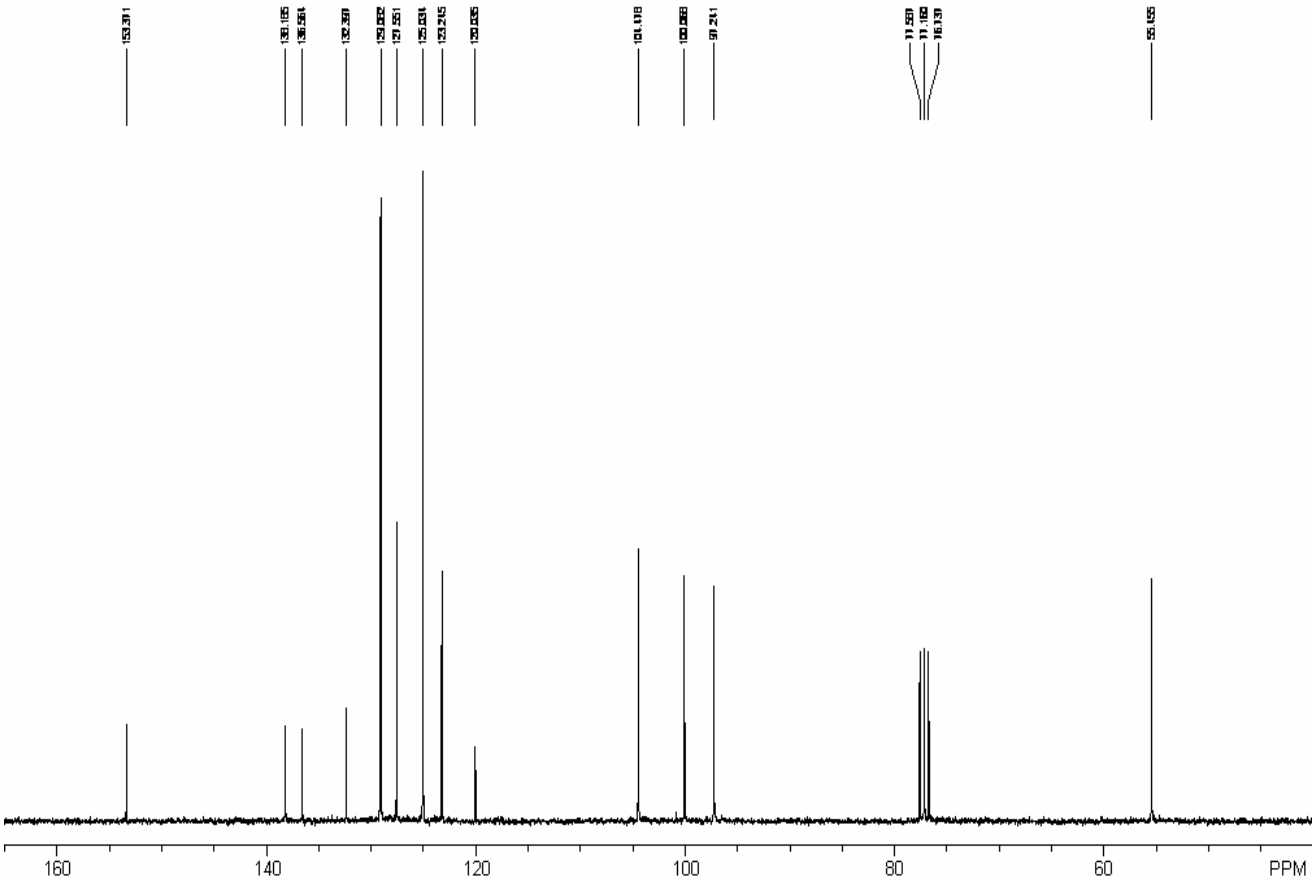


^{13}C-NMR (75.4 MHz, $CDCl_3$):



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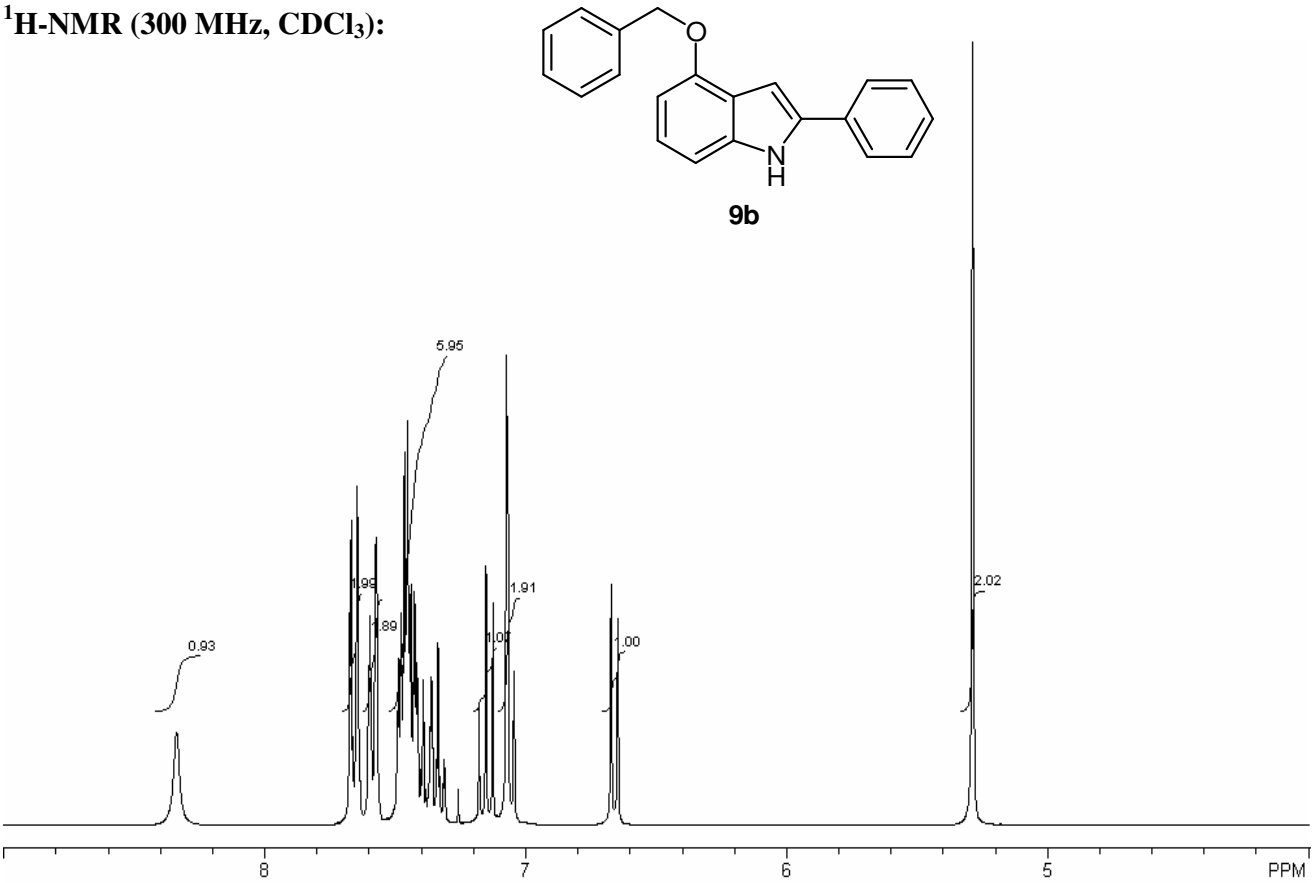

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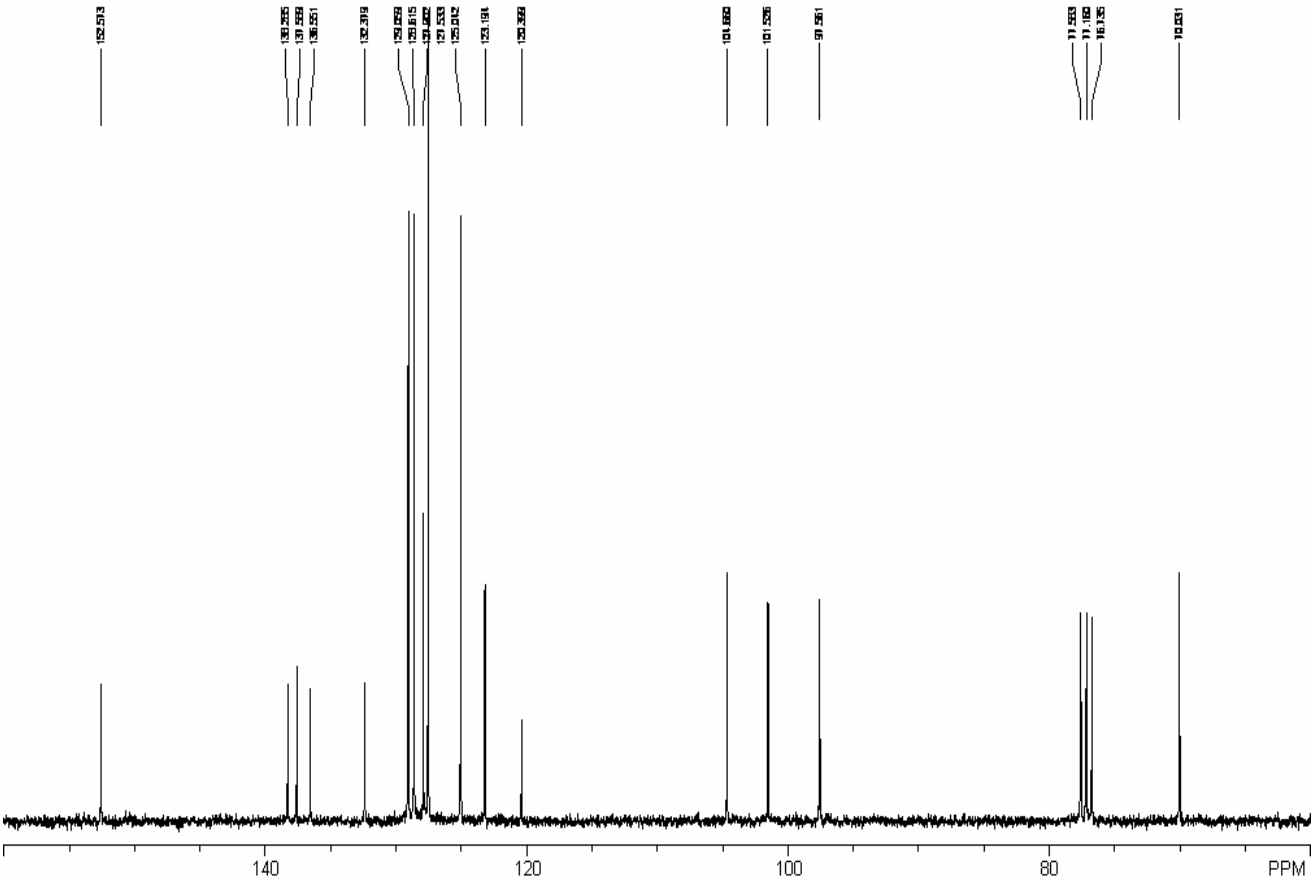

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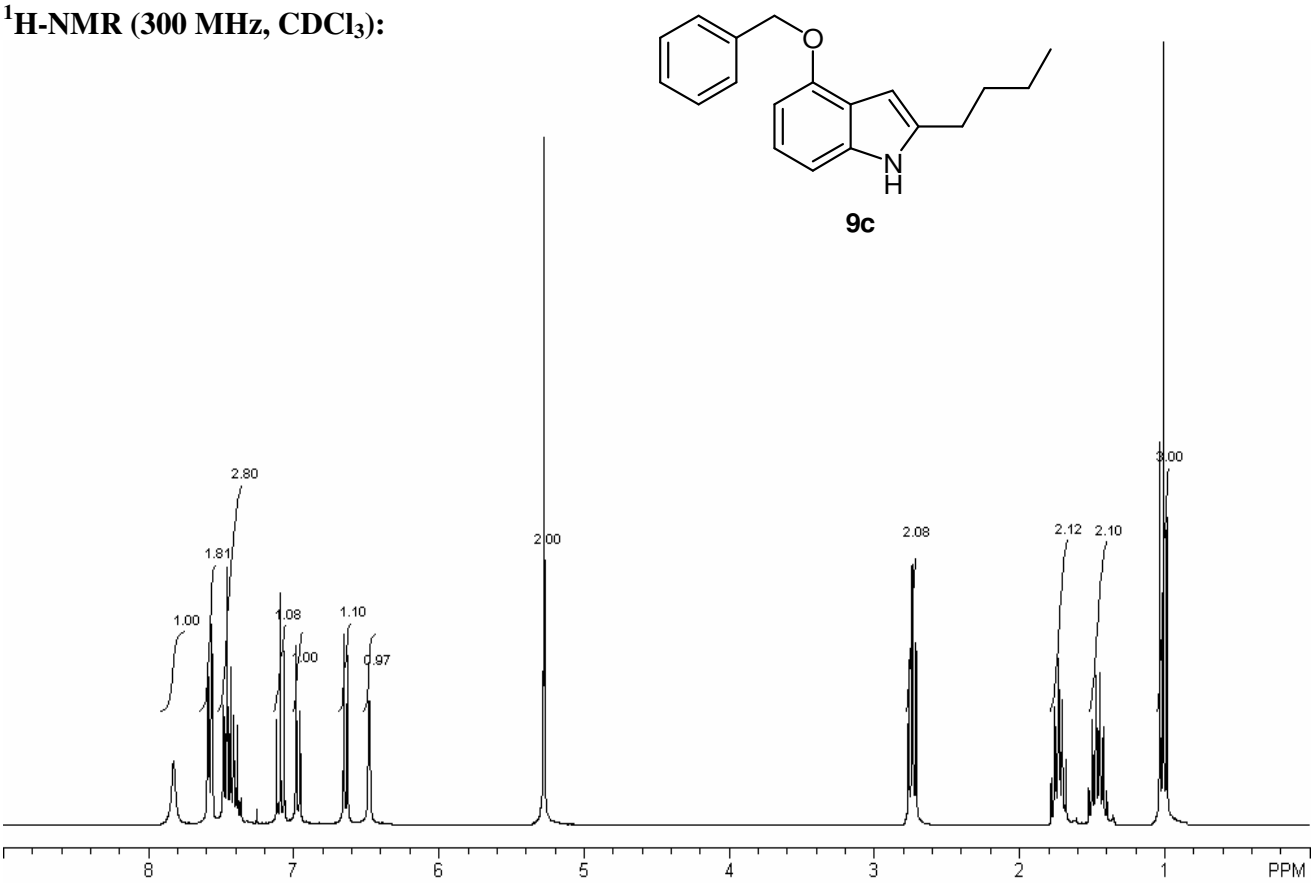

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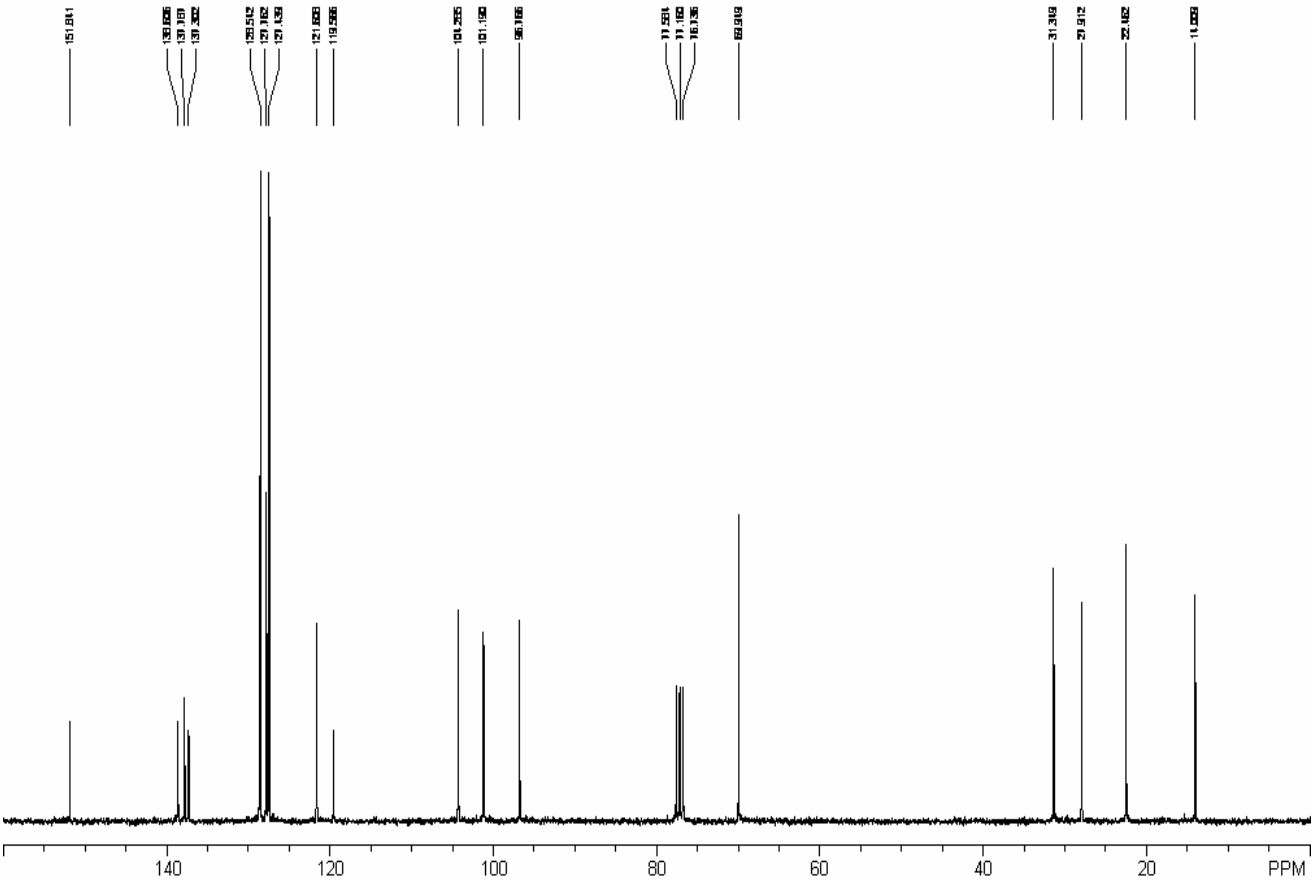

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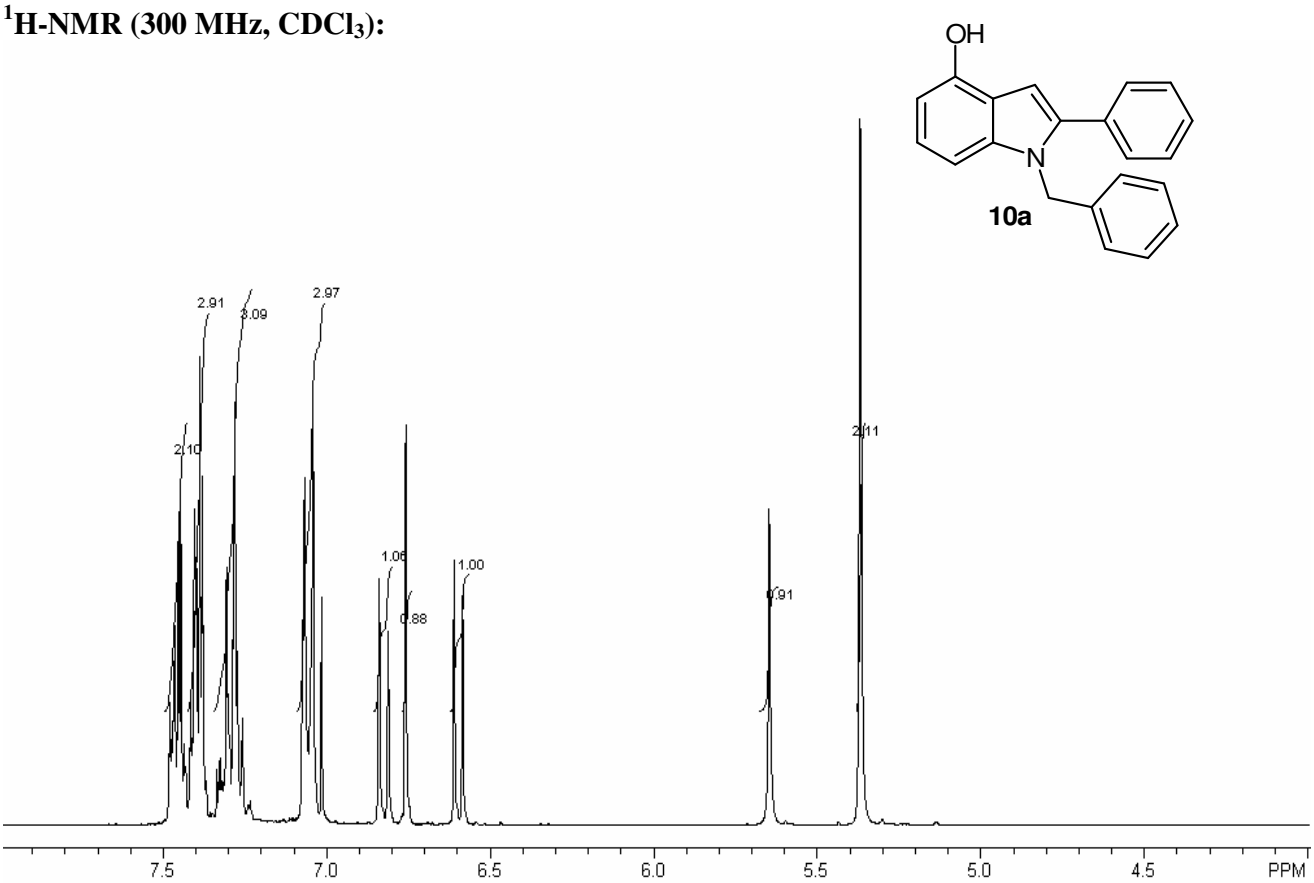
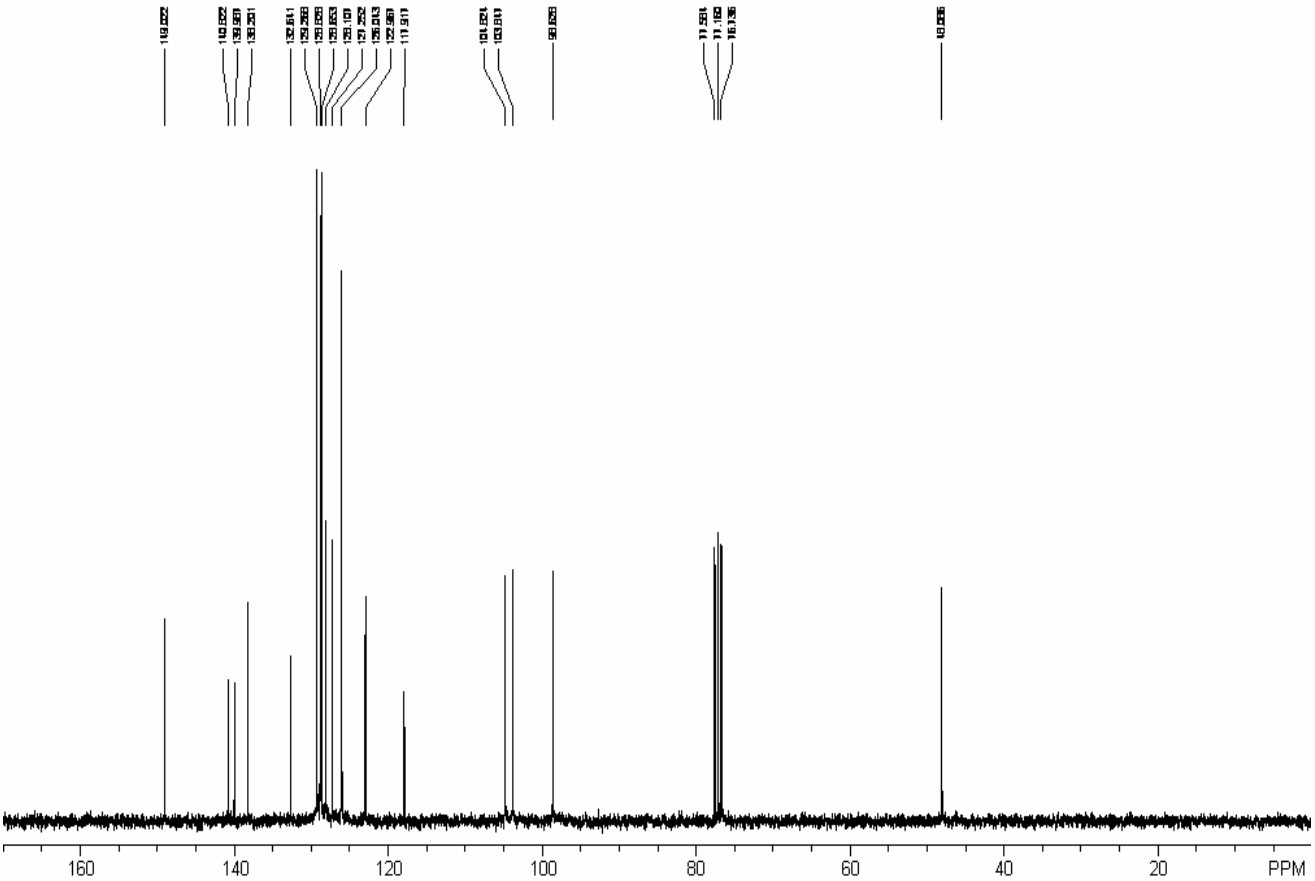
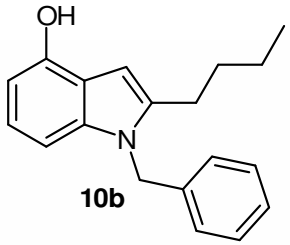
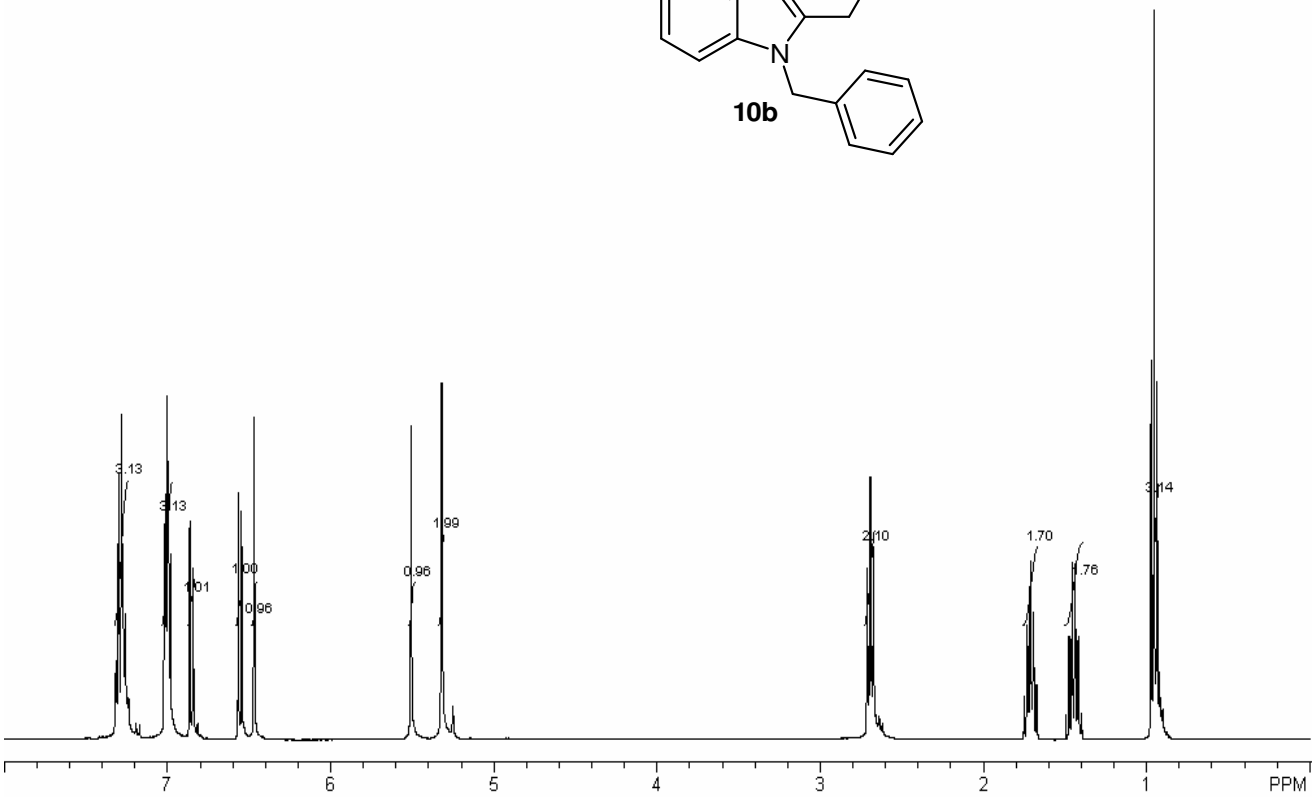


^{13}C-NMR (75.4 MHz, $CDCl_3$):

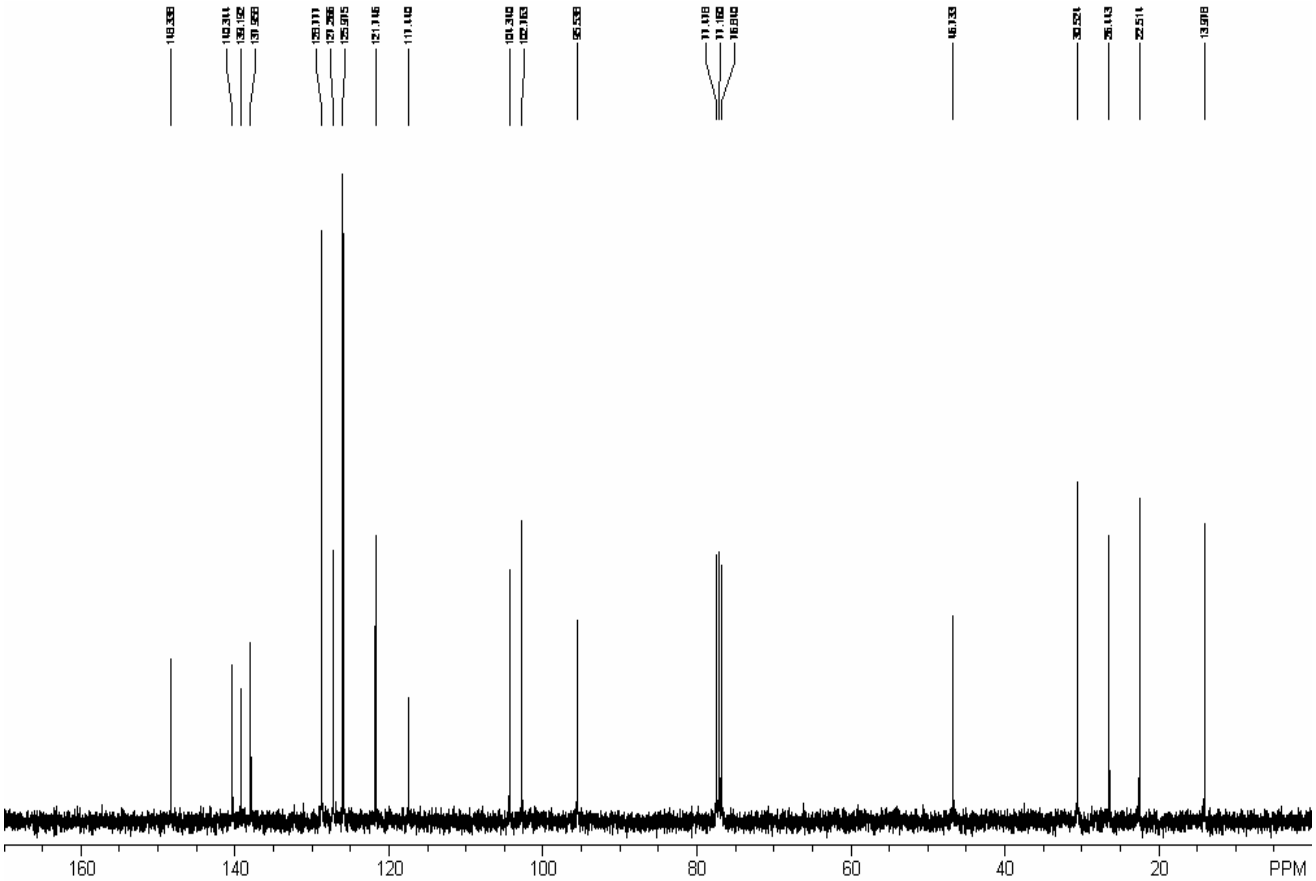


^{1}H-NMR (400 MHz, $CDCl_3$):

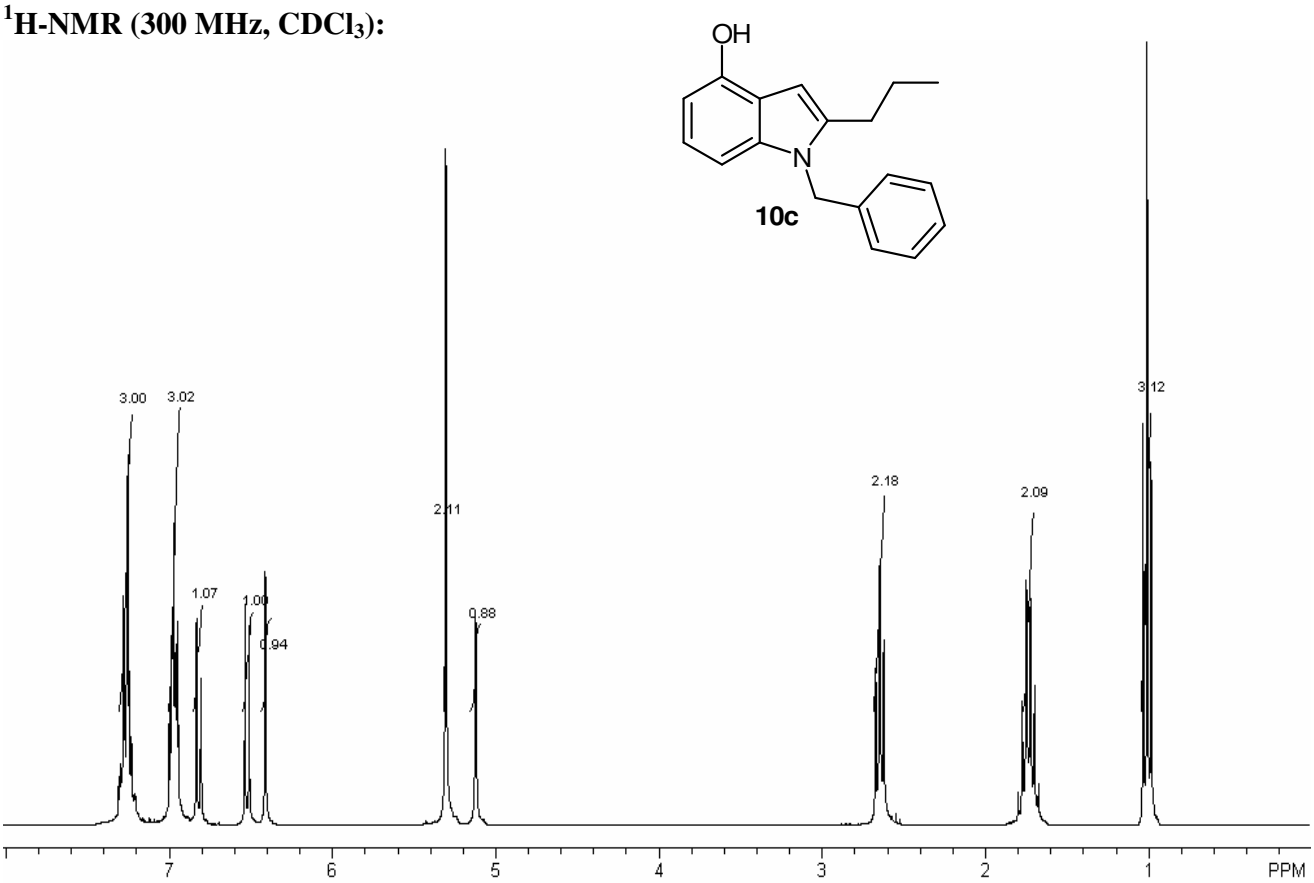




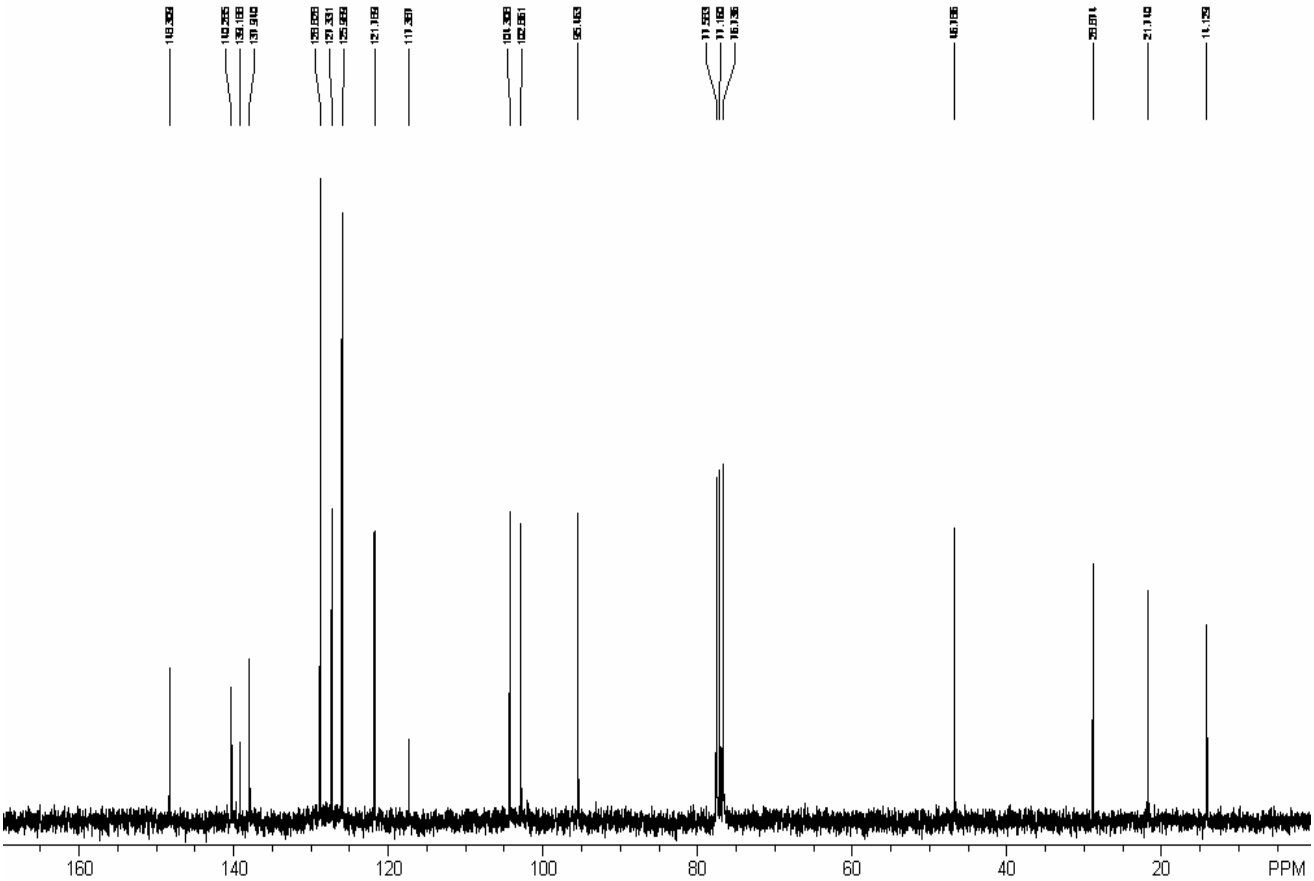
^{13}C-NMR (100.6 MHz, $CDCl_3$):



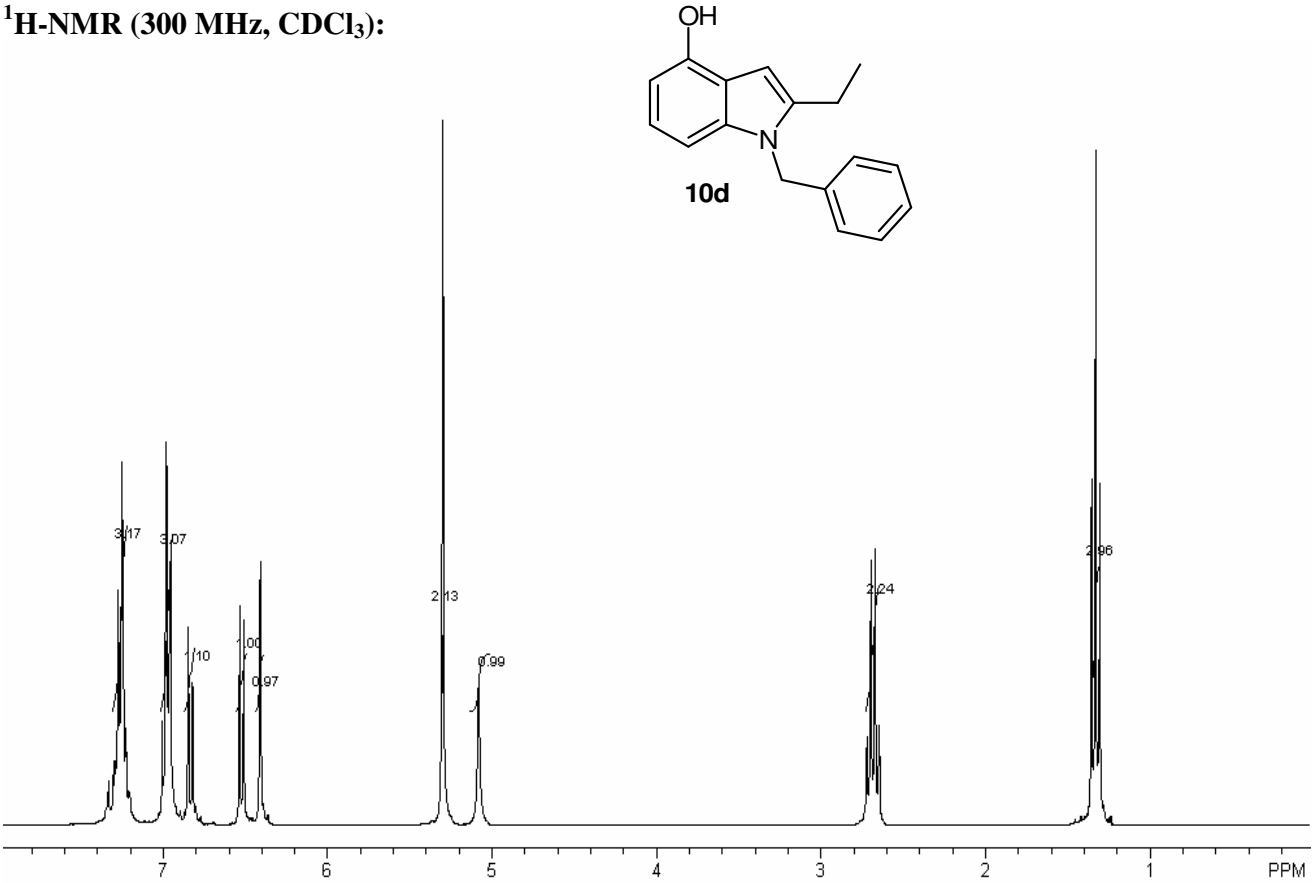
^{1}H-NMR (300 MHz, $CDCl_3$):



^{13}C-NMR (75.4 MHz, $CDCl_3$):



^{1}H-NMR (300 MHz, $CDCl_3$):



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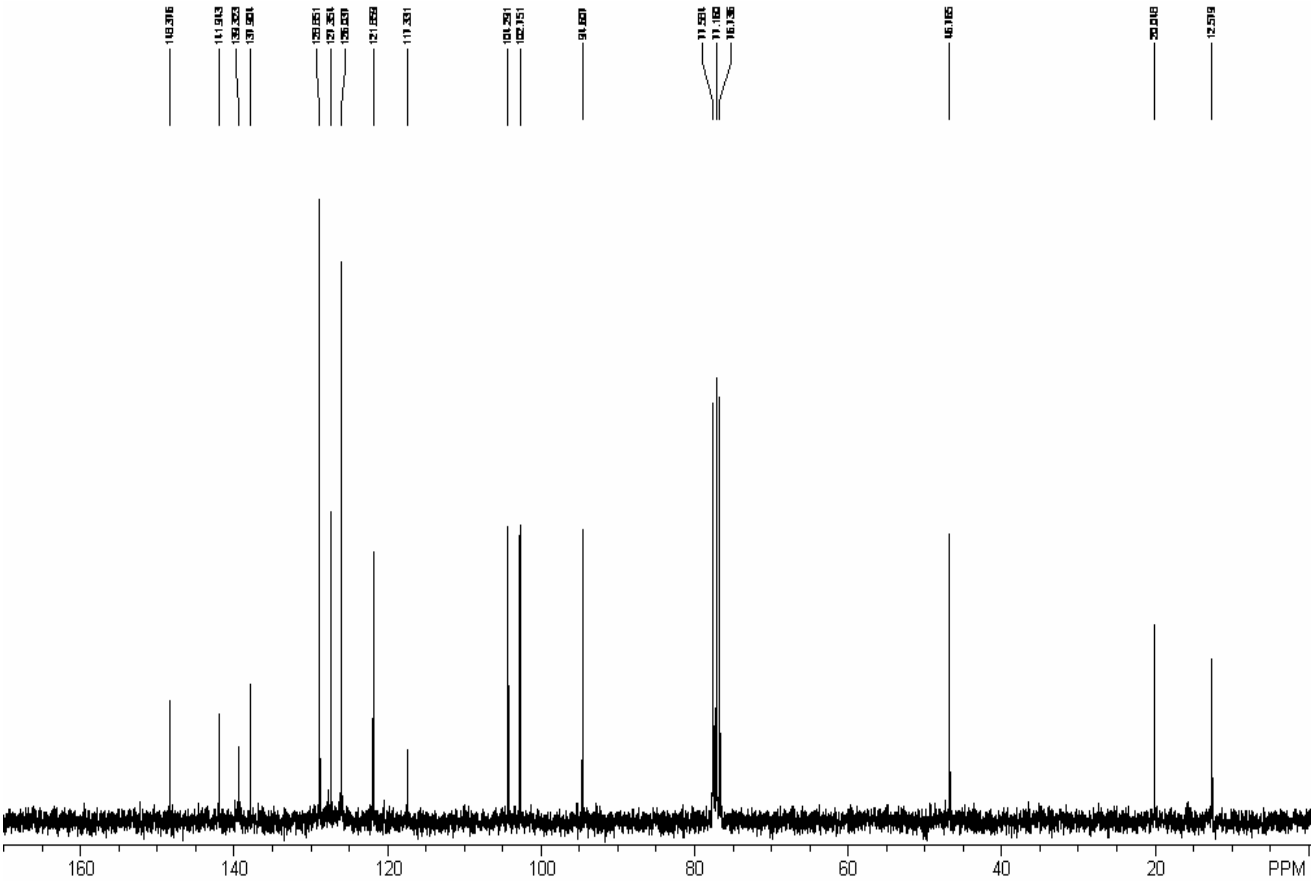

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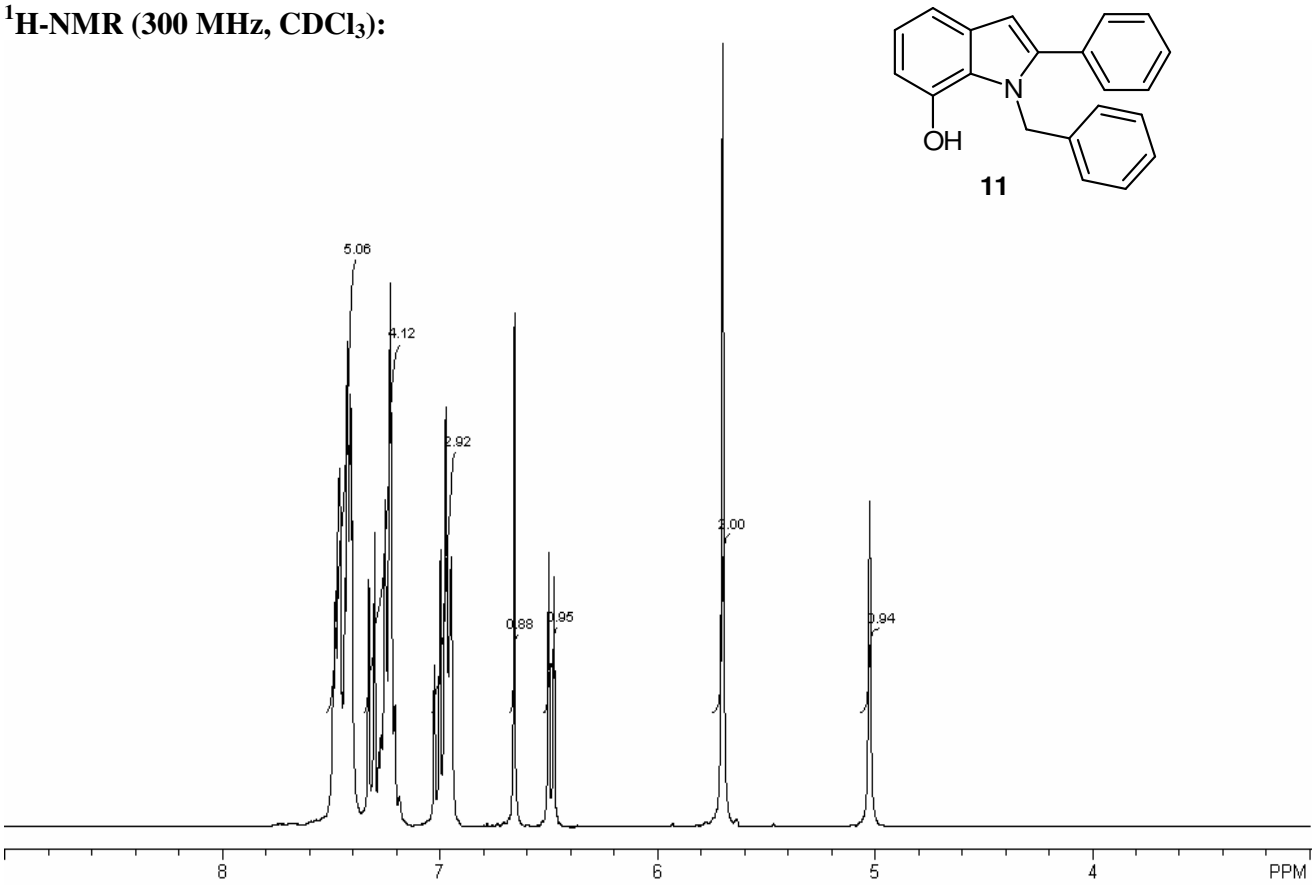
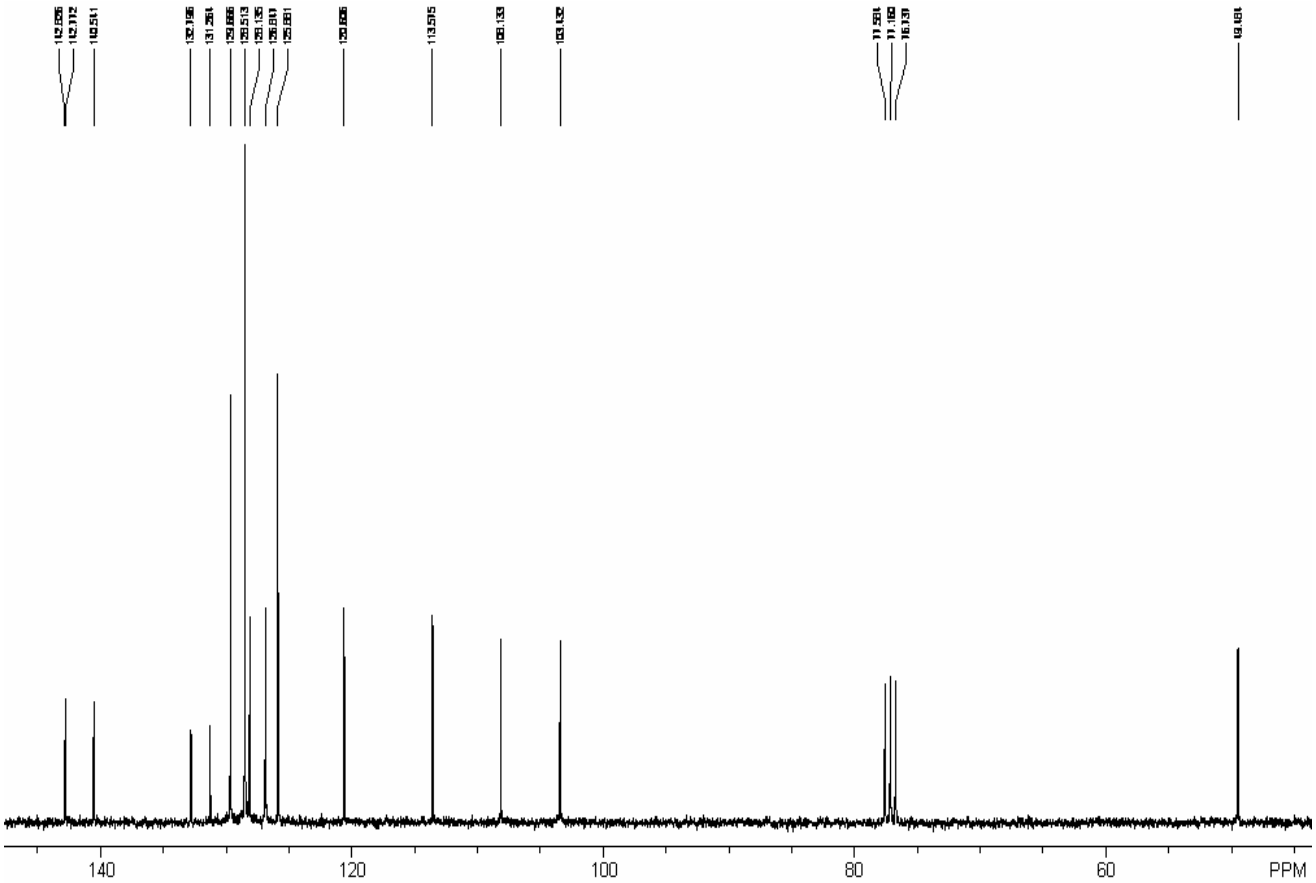
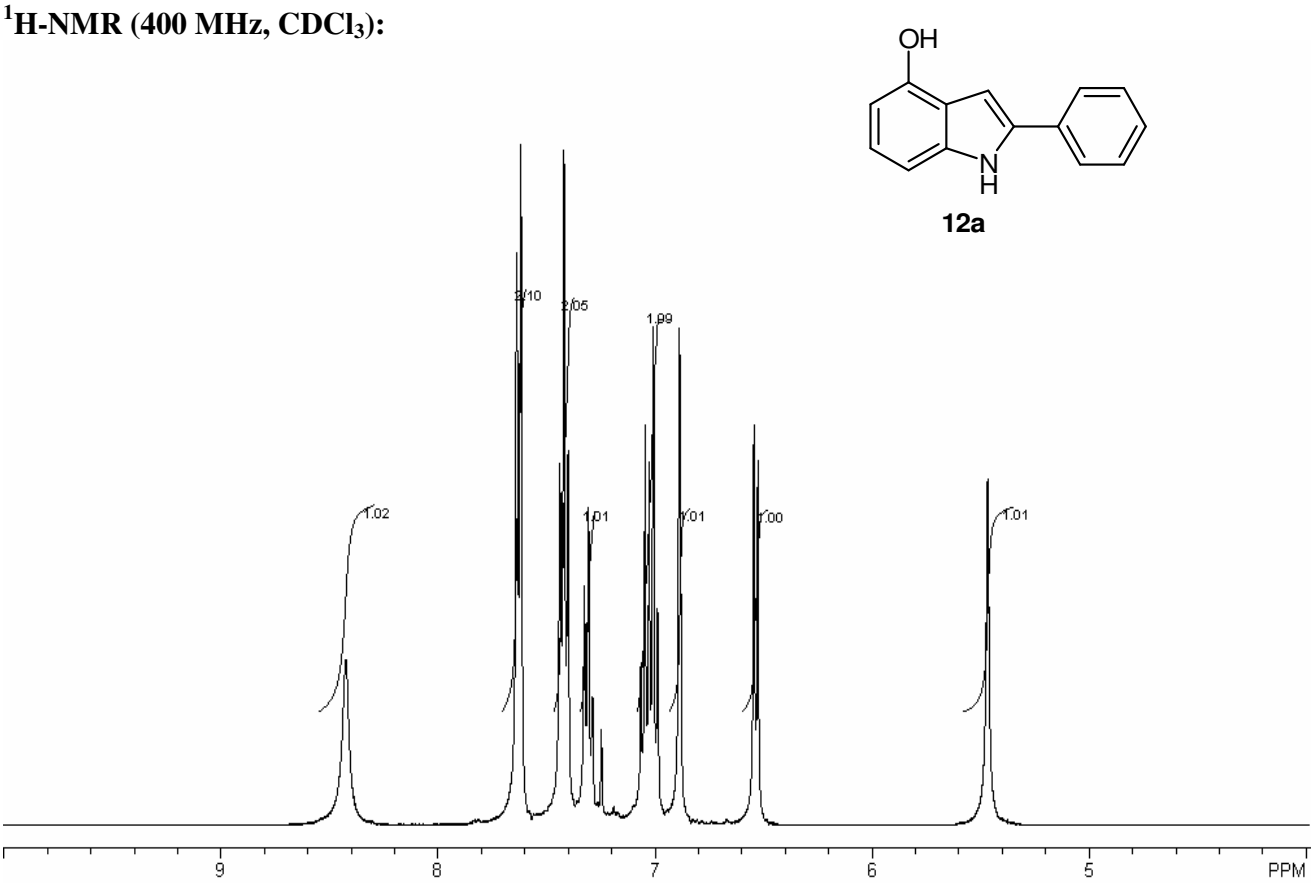


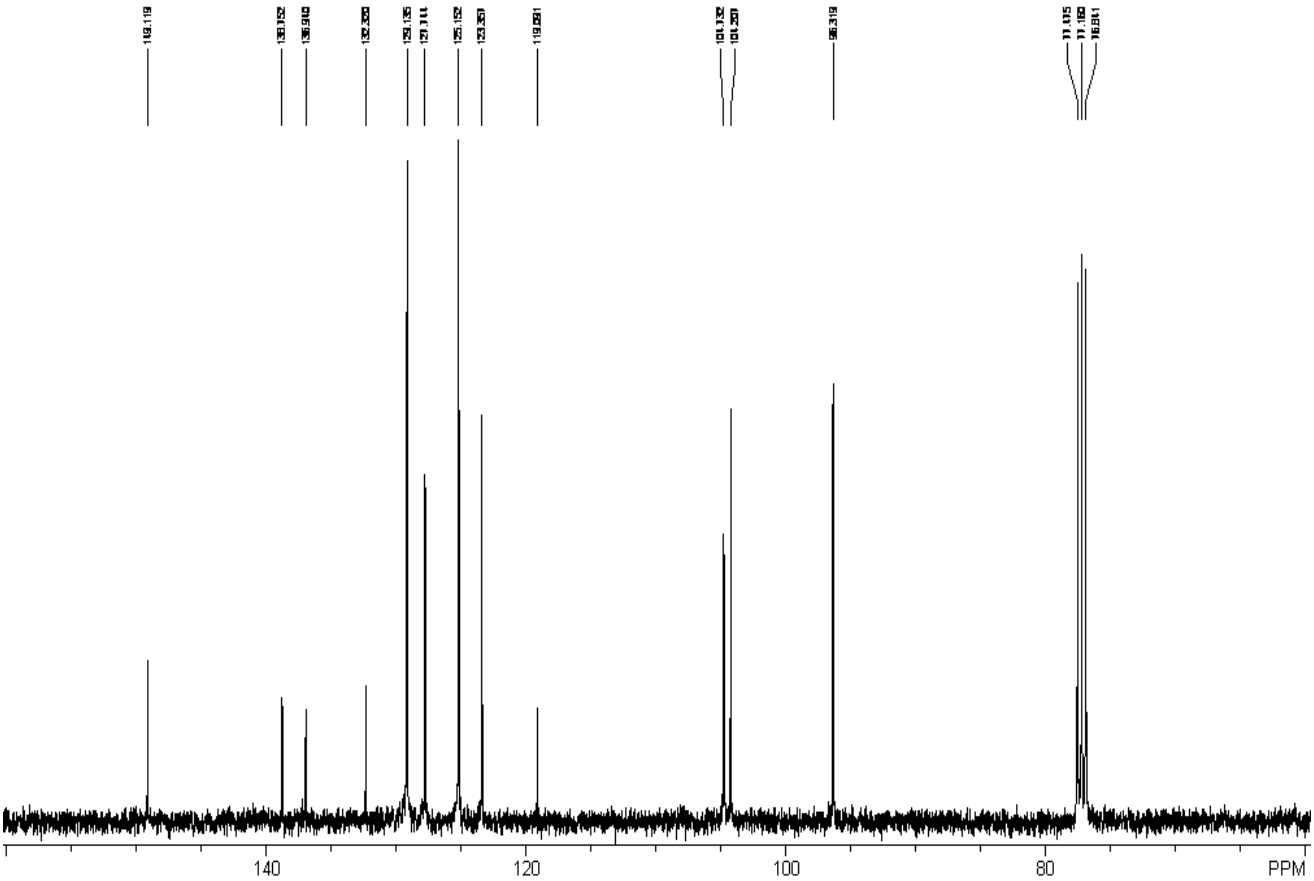
^{13}C-NMR (75.4 MHz, $CDCl_3$):



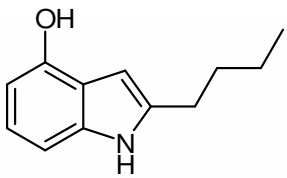
^{1}H-NMR (400 MHz, $CDCl_3$):



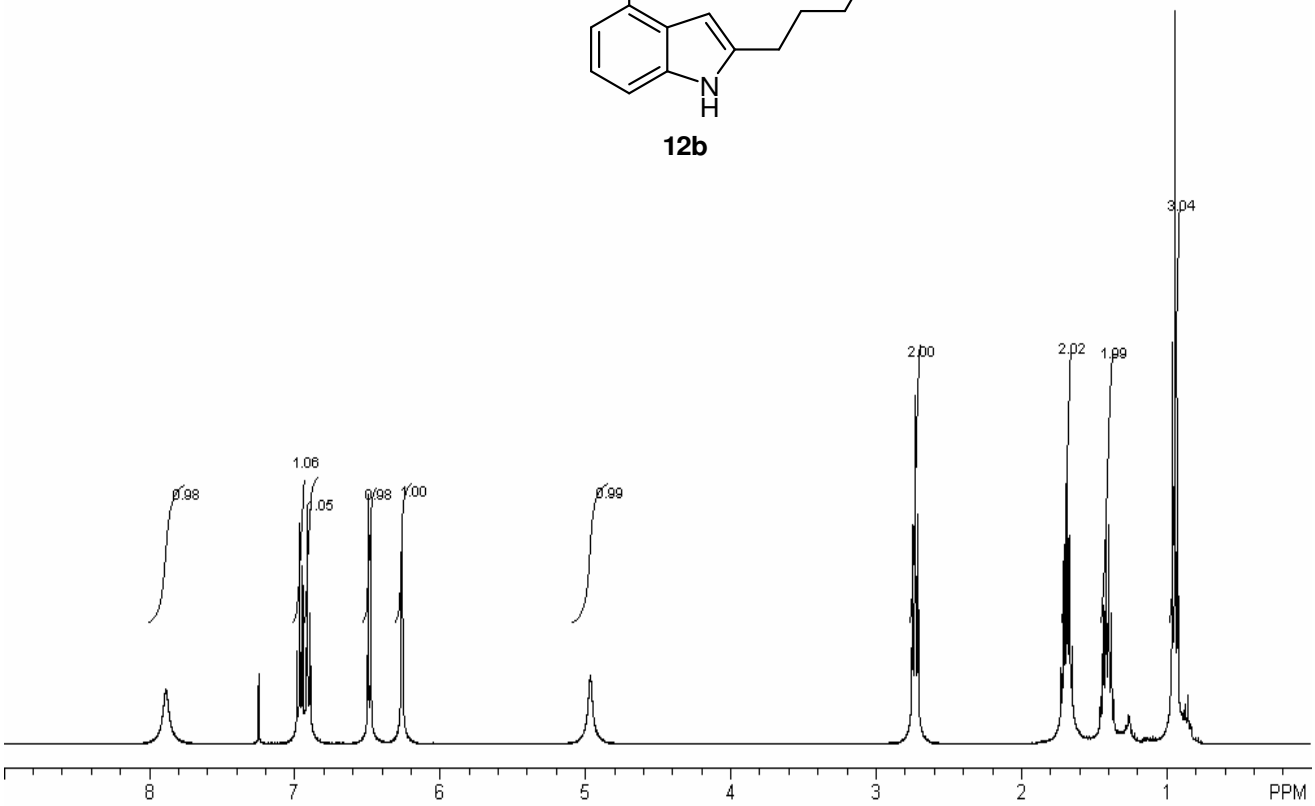
^{13}C-NMR (100.6 MHz, $CDCl_3$):



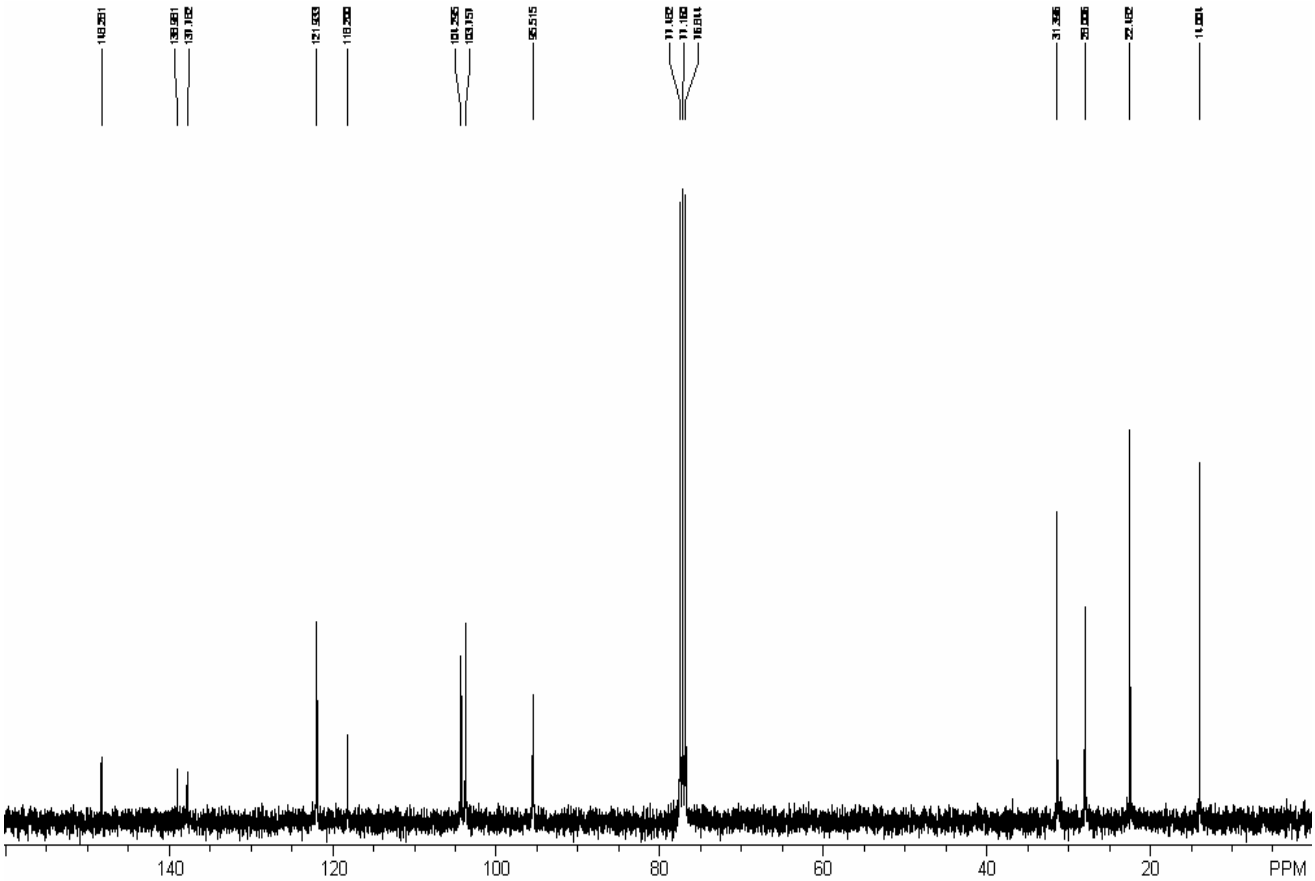
^{1}H-NMR (400 MHz, $CDCl_3$):



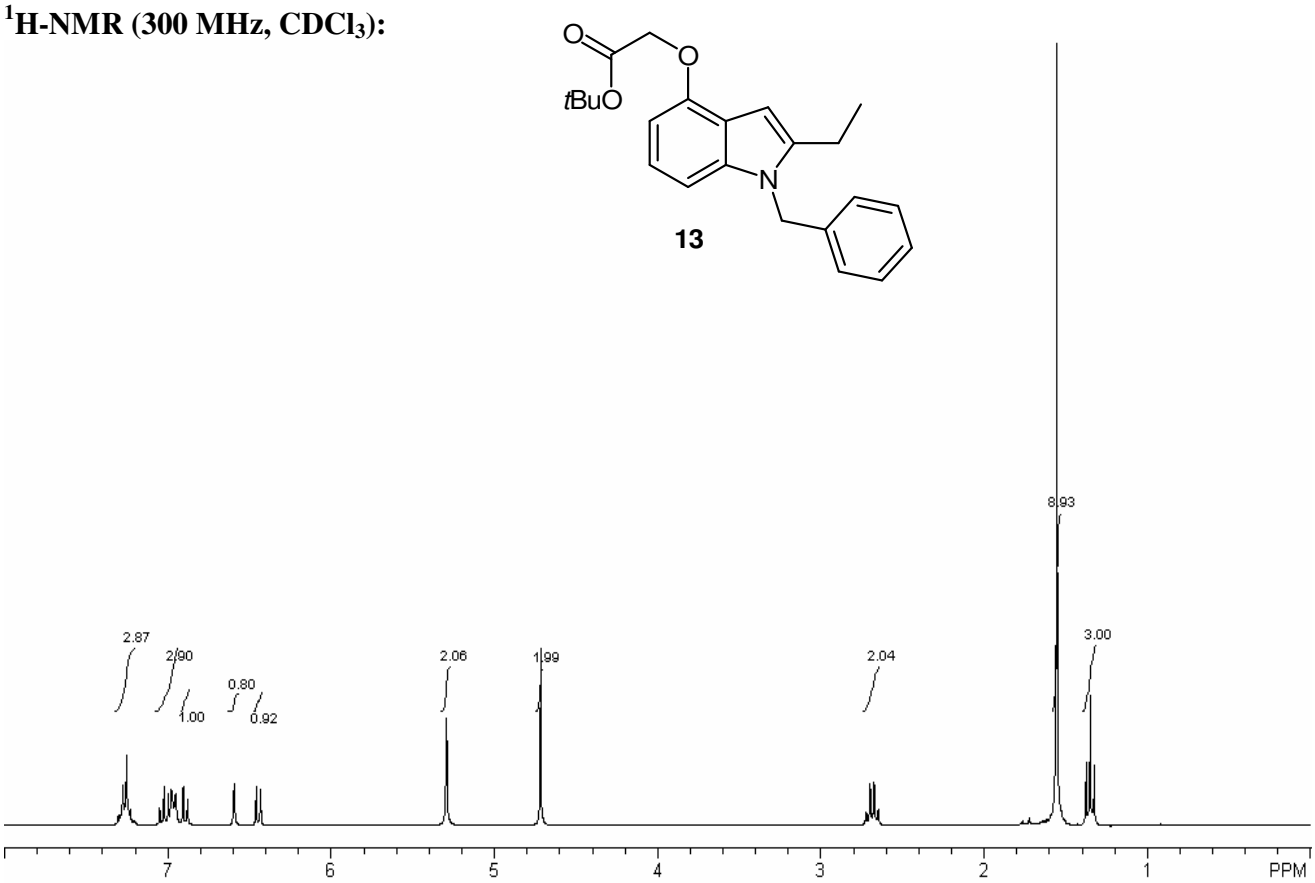
12b



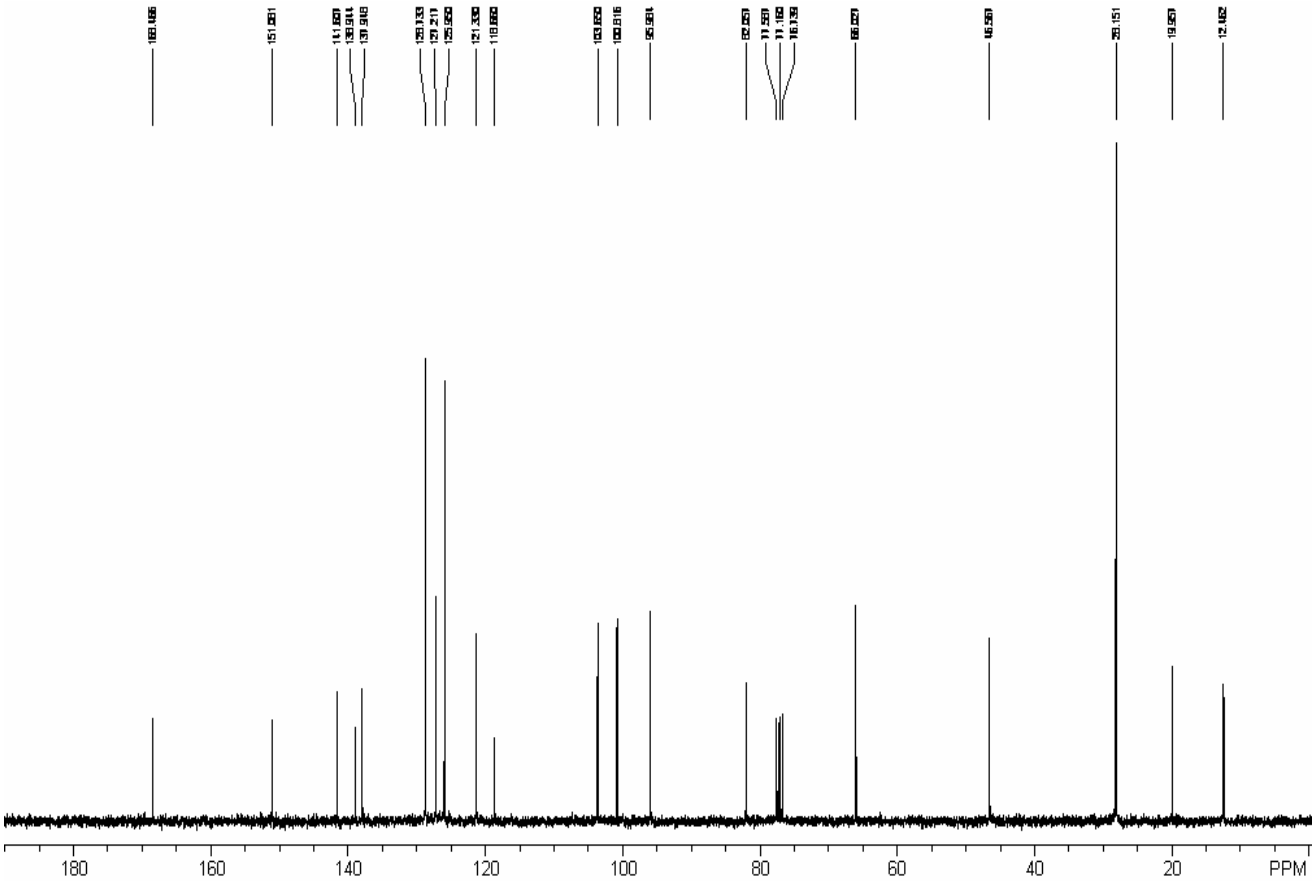
^{13}C-NMR (100.6 MHz, $CDCl_3$):



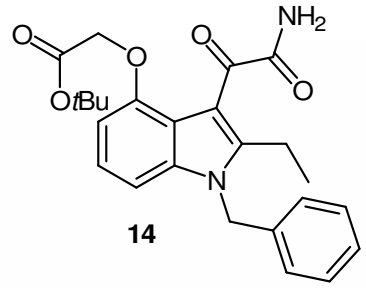
^{1}H-NMR (300 MHz, $CDCl_3$):

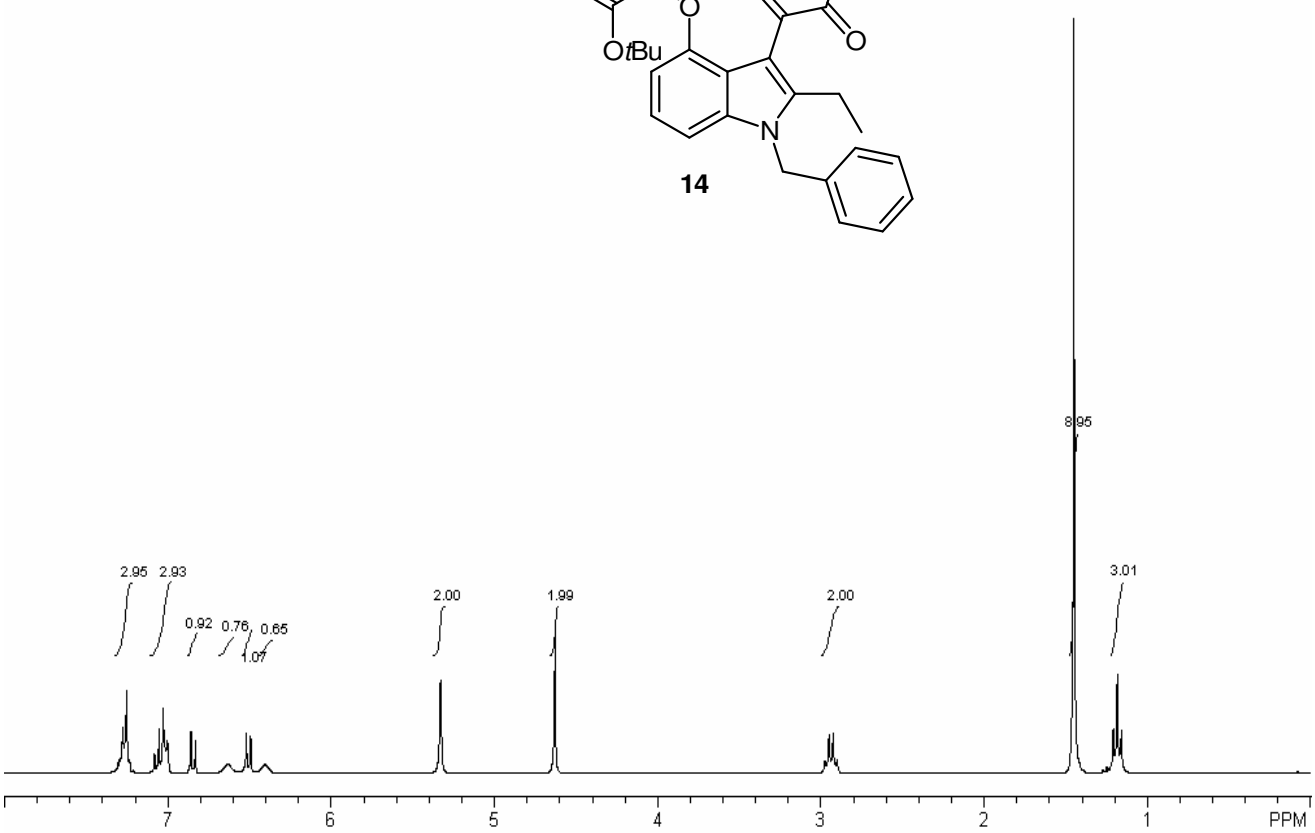


^{13}C-NMR (75.4 MHz, $CDCl_3$):

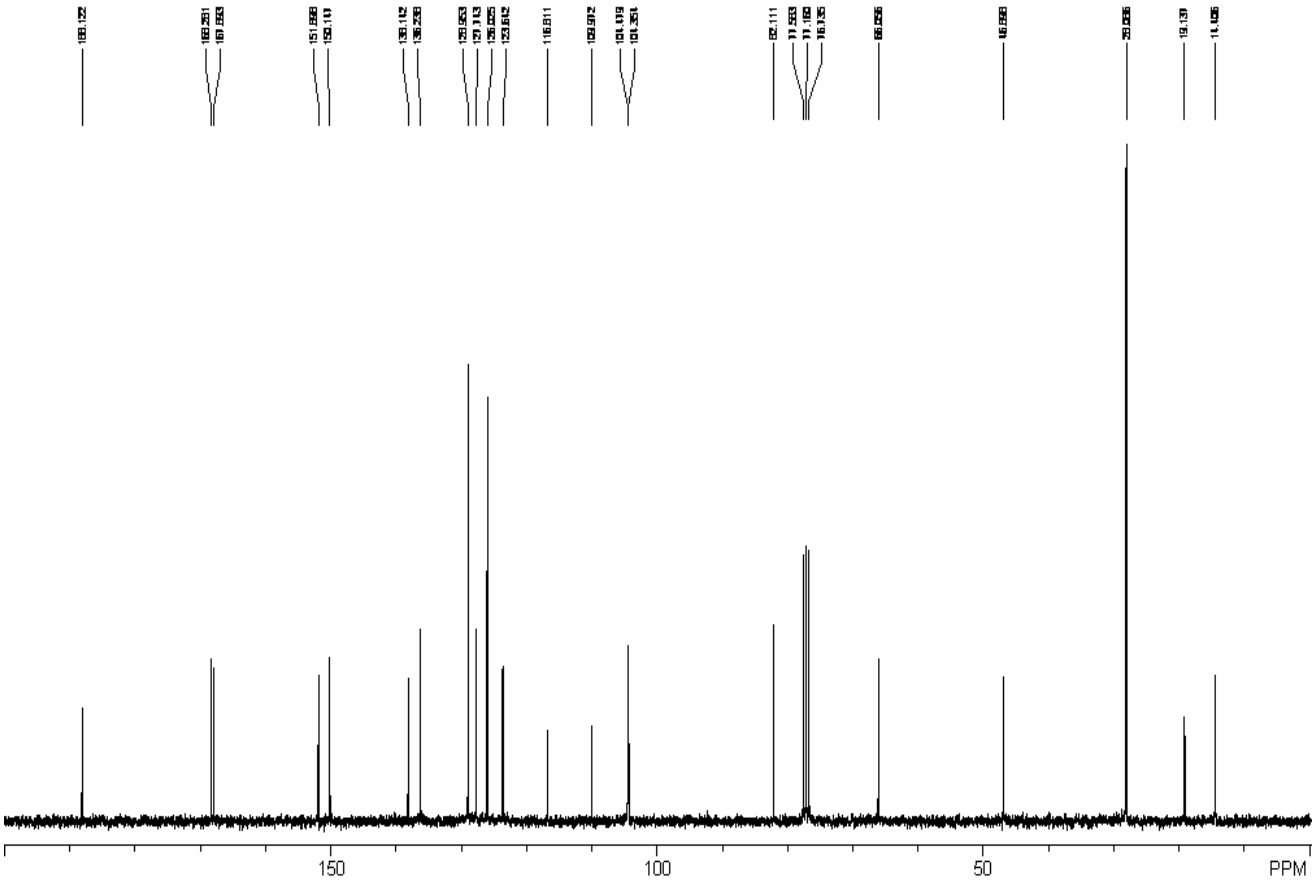


^{1}H-NMR (300 MHz, $CDCl_3$):

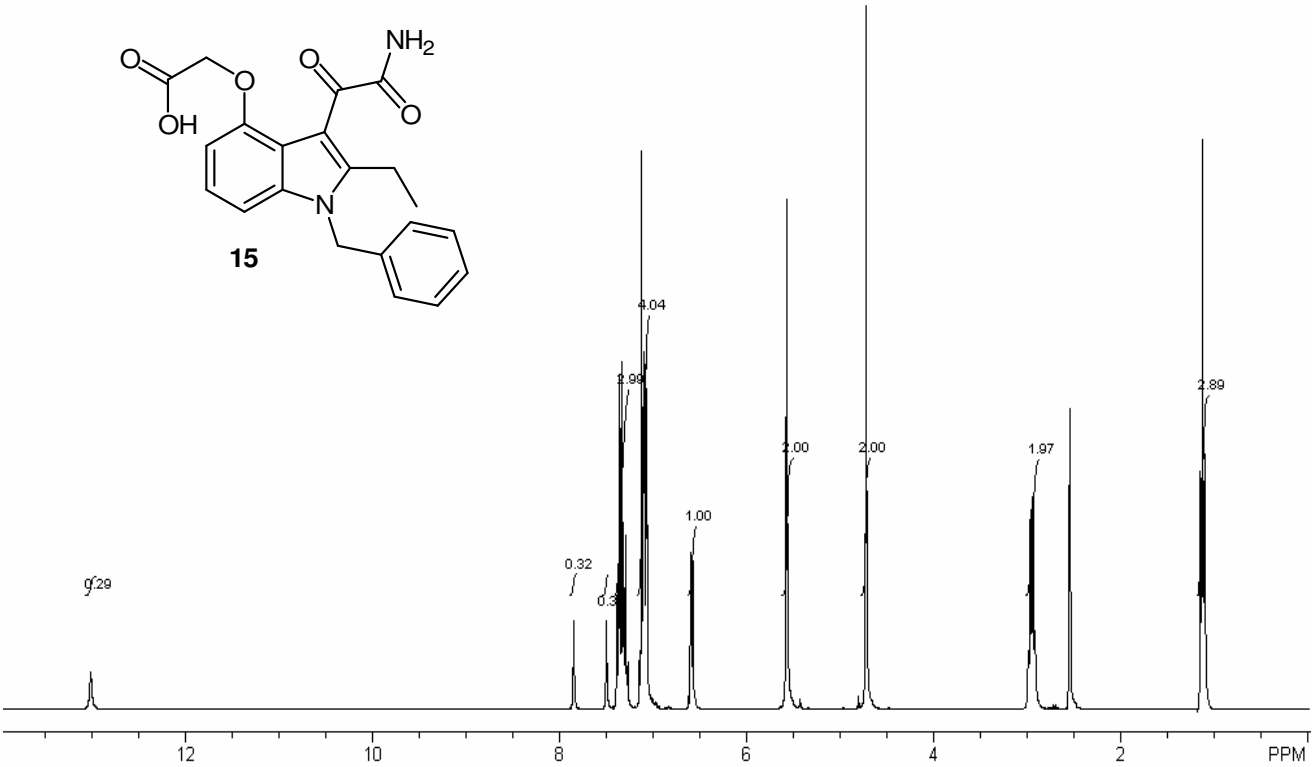
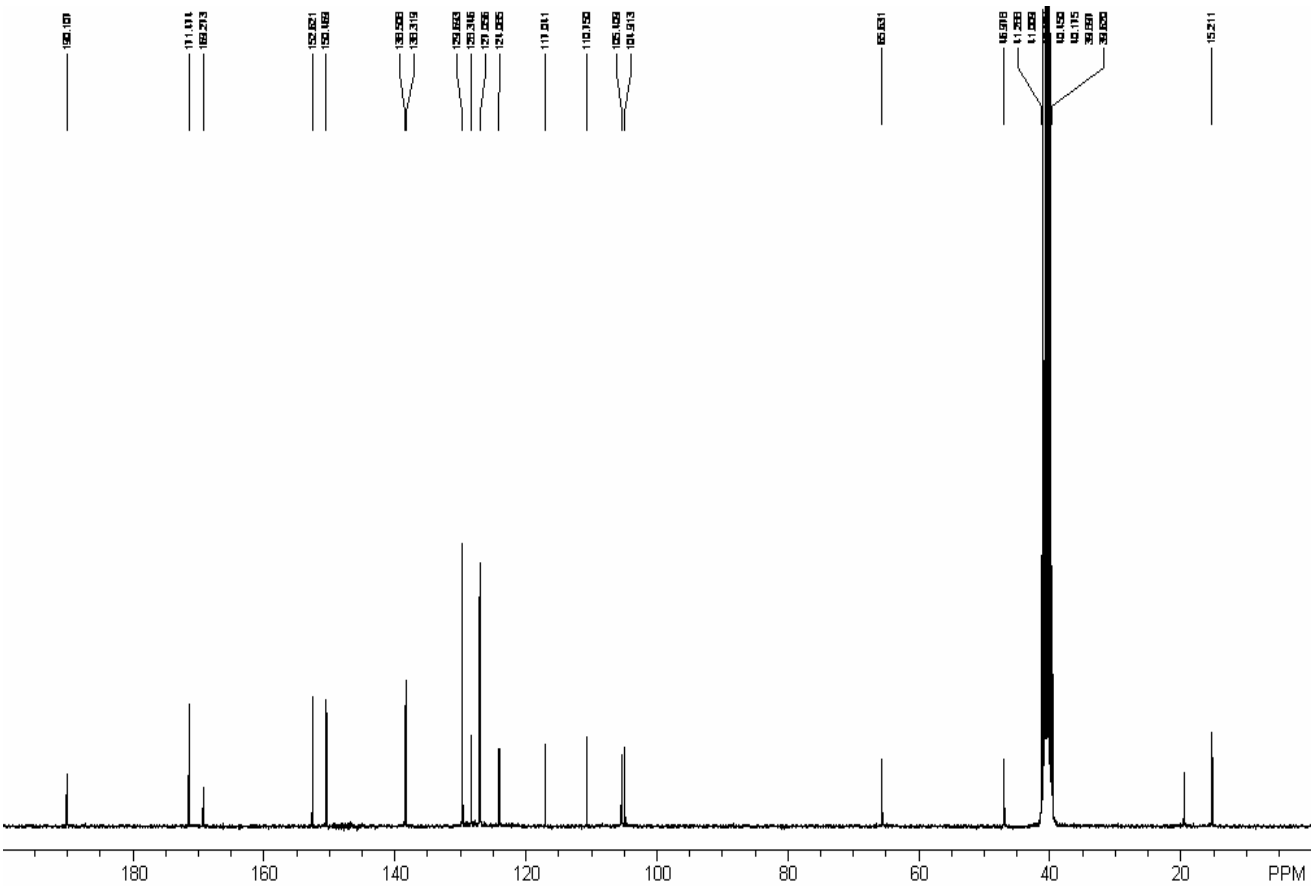




^{13}C-NMR (75.4 MHz, $CDCl_3$):



^{1}H-NMR (300 MHz, DMSO-d$_6$):



^{13}C-NMR (75.4 MHz, DMSO-d$_6$):