

A Route to Regioselectively Functionalized Carbazoles, Dibenzofurans, and Dibenzothiophenes through Anionic Cyclization of Benzyne-tethered Aryllithiums

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General Considerations. All reactions involving air-sensitive compounds were carried out under an N₂ 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 F₂₅₄ 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. ¹H NMR spectra were recorded at 400, 300, or 200 MHz. Chemical shifts are reported in ppm from tetramethylsilane with the residual solvent resonance as the internal standard (CHCl₃: δ 7.16; DMSO-d₆: 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. ¹³C NMR spectra were recorded at 100.6, 75.4, or 50.3 MHz using broadband proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as internal standard (CDCl₃: δ 76.95; DMSO-d₆: 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 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.

Synthesis of *N*-(2-Fluorophenyl)-*N*-methyl-2-nitroaniline (1a):¹ Under nitrogen atmosphere an oven-dried Schlenk flask was charged with Cs₂CO₃ (6.84 g, 21 mmol), Pd₂(dba)₃ (0.413 g, 0.45 mmol) and BINAP (0.420 g, 0.67 mmol). *N*-methyl-2-fluoroaniline (2.25 g, 18 mmol), 1-bromo-2-nitrobenzene (3.03 g, 15 mmol) and toluene (30 mL) were added, and the mixture was heated to 100 °C with stirring until the starting material had been consumed as judged by GC-MS analysis (ca. 16 h). The mixture was

cooled to room temperature, diluted with Et₂O (40 mL), filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/EtOAc, 50/1) to afford the titled compound (2.92 g, 79%) as an orange oil: *R_f* 0.21 (hexane/EtOAc, 50/1); ¹H NMR (400 MHz, CDCl₃) δ 7.87 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.30 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.11 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.05-6.81 (m, 5H), 3.21 (s, 3H); ¹³C NMR (100.6 MHz, CDCl₃) δ 156.2 (d, *J* = 249.7 Hz, C), 143.0 (C), 142.3 (C), 135.6 (d, *J* = 9.9 Hz, C), 133.3 (CH), 125.9 (CH), 125.2 (d, *J* = 7.8 Hz, CH), 124.6 (d, *J* = 2.0 Hz, CH), 123.4 (d, *J* = 2.9 Hz, CH), 122.5 (CH), 121.6 (CH), 116.8 (d, *J* = 20.1 Hz, CH), 41.1 (d, *J* = 2.5 Hz, CH₃); EI-LRMS *m/z* 246 (M⁺, 53), 198 (100); HRMS calcd for C₁₃H₁₁FN₂O₂, 246.0805; found, 246.0812.

Synthesis of *N*-(3-Dimethylaminopropyl)-*N*-(2-fluorophenyl)-2-nitroaniline (1b): A solution of *N*-(3-dimethylaminopropyl)-2-fluoroaniline (3.53 g, 18 mmol) in THF (60 mL) was treated with *n*-BuLi (7.2 mL of a 2.5M solution in hexane, 18 mmol) at –50 °C. The reaction mixture was stirred for 15 min at this temperature and then was allowed to reach room temperature and stirring was continued for 45 min. The reaction mixture was cooled to –78 °C and a solution of 1-chloro-2-nitrobenzene (4.26 g, 27 mmol) in THF (20 mL) was added dropwise. After 10 min at this temperature the reaction was refluxed overnight. The mixture was quenched with water, extracted with AcOEt (3 x 30 mL) and the combined organic layers were washed with a saturated Na₂CO₃ aqueous solution and dried over anhydrous Na₂SO₄. The solvents were removed under reduced pressure and the residue was purified by silica gel column chromatography (hexane/AcOEt, 15/1) to give the titled compound (3.31 g, 58%) as a red oil: *R_f* 0.45 (hexane/EtOAc, 10/1); ¹H NMR (400 MHz, CDCl₃) δ 7.62 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.46 (ddd, *J* = 8.0, 7.2, 1.6 Hz, 1H), 7.35 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.03-6.93 (m, 5H), 3.79-3.74 (m, 2H), 2.30 (t, *J* = 6.8 Hz, 2H), 2.18 (s, 6H), 1.85-1.74 (m, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 156.5 (d, *J* = 249.6 Hz, C), 143.1 (C), 141.9 (C), 134.4 (d, *J* = 10.0 Hz, C), 133.0 (CH), 125.8 (CH), 124.9 (d, *J* = 7.6 Hz, CH), 124.6 (d, *J* = 1.5 Hz, CH), 124.4 (d, *J* = 3.1 Hz, CH), 123.2 (CH), 121.5 (CH), 116.7 (d, *J* = 19.9 Hz,

CH), 56.5 (CH₂), 51.1 (d, $J = 2.2$ Hz, CH₂), 45.3 (CH₂), 25.5 (CH₃); EI-LRMS m/z 317 (M⁺, 2), 102 (100); HRMS calcd for C₁₇H₂₀FN₃O₂, 317.1540; found, 317.1551.

Typical Procedure for the Synthesis of *N*-Alkyl-*N*-(2-fluorophenyl)benzene-1,2-diamines **2a-b:**²

To a solution of the corresponding aromatic nitro compound **1a,b** (10 mmol) in MeOH (100 mL) was added anhydrous CuCl (2.97 g, 30 mmol). KBH₄ (3.78 g, 70 mmol) was added to this mixture in portions with stirring at room temperature. After the addition, the reaction mixture was stirred for 30 min. Then, MeOH was removed under reduced pressure, water (100 mL) was added, and the mixture was extracted with EtOAc (3 x 20 mL). The combined organic layers were dried over anhydrous Na₂SO₄. The solvents were removed under reduced pressure and the residue was purified by silica gel column chromatography (hexane/EtOAc) to provide the corresponding tertiary amine:

***N*-(2-Fluorophenyl)-*N*-methylbenzene-1,2-diamine (**2a**):** KBH₄ (3.78 g, 70 mmol) was added to a solution of **1a** (2.46 g, 10 mmol) and CuCl (2.97 g, 30 mmol) in MeOH (100 mL). Workup as above gave the title compound (2.03 g, 94%) as a yellow oil: R_f 0.14 (hexane/EtOAc, 25/1); ¹H NMR (400 MHz, CDCl₃) δ 7.09-6.88 (m, 6H), 6.80 (dd, $J = 8.0, 1.2$ Hz, 1H), 6.77 (dt, $J = 7.6, 1.2$ Hz, 1H), 3.95 (br s, 2H), 3.18 (s, 3H); ¹³C NMR (100.6 MHz, CDCl₃) δ 154.8 (d, $J = 245.8$ Hz, C), 142.1 (C), 138.4 (d, $J = 9.2$ Hz, C), 136.5 (C), 126.1 (CH), 124.6 (CH), 124.2 (d, $J = 3.0$ Hz, CH), 121.6 (d, $J = 7.6$ Hz, CH), 119.6 (d, $J = 3.0$ Hz, CH), 118.7 (CH), 116.2 (d, $J = 21.4$ Hz, CH), 115.7 (CH), 39.9 (d, $J = 2.9$ Hz, CH₃); EI-LRMS m/z 216 (M⁺, 100); HRMS calcd for C₁₃H₁₃FN₂, 216.1063; found, 216.1057.

***N*-(3-Dimethylaminopropyl)-*N*-(2-fluorophenyl)benzene-1,2-diamine (**2b**):** KBH₄ (3.78 g, 70 mmol) was added to a solution of **1b** (3.17 g, 10 mmol) and CuCl (2.97 g, 30 mmol) in MeOH (100 mL). Workup as above gave the title compound (2.64 g, 92%) as a white solid: mp 106-108 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.10-6.86 (m, 5H), 6.80-6.72 (m, 3H), 3.82 (br s, 2H), 3.58 (t, $J = 6.8$ Hz, 2H), 2.92-2.84 (m, 2H), 2.48 (s, 6H), 2.05-1.95 (m, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ 155.3 (d, $J = 245.8$ Hz, C), 142.9 (C), 137.0 (d, $J = 7.6$ Hz, C), 132.3 (C), 126.5 (CH), 125.9 (CH), 124.4 (d, $J = 3.1$ Hz, CH), 122.4 (d, $J = 7.6$ Hz, CH), 121.6 (d, $J = 3.0$ Hz, CH), 118.6 (CH), 116.5 (d, $J = 19.8$ Hz, CH),

116.1 (CH), 62.0 (CH₂), 51.1 (CH₂), 50.5 (d, $J = 3.1$ Hz, CH₂), 22.8 (CH₃); EI-LRMS m/z 287 (M^+ , 6), 58 (100); HRMS calcd for C₁₇H₂₂FN₃, 287.1798; found, 287.1794.

Typical Procedure for the Synthesis of 2-Fluorophenyl 2-Nitrophenyl Ether 7a and Thioether 7b: 2-Fluorophenol or 2-fluorothiophenol (20 mmol) was added dropwise under nitrogen to a solution of 1-chloro-2-nitrobenzene (4.73 g, 30 mmol) and solid copper oxide (I) (4.29 g, 30 mmol) in pyridine (50 mL) at room temperature. The resulting mixture was heated at reflux for 12 h, cooled to room temperature, and treated with HCl (1 M). The mixture was extracted with Et₂O (3 x 50 mL), and the combined organic layers were washed with saturated Na₂CO₃ aqueous solution and dried over anhydrous Na₂SO₄. The solvents were removed under reduced pressure and the residue was purified by silica gel column chromatography (hexane/EtOAc) to provide the corresponding ether or thioether:

2-Fluorophenyl 2-nitrophenyl ether (7a):³ Prepared from 2-fluorophenol (2.24 g, 20 mmol), Cu₂O (4.29 g, 30 mmol) and 1-chloro-2-nitrobenzene (4.73 g, 30 mmol) in pyridine (50 mL) according to the above procedure to give the title compound (3.45 g, 74%) as a yellow oil: R_f 0.13 (hexane/EtOAc, 25/1); ¹H NMR (200 MHz, CDCl₃) δ 7.95-7.87 (m, 1H), 7.51-7.40 (m, 1H), 7.22-7.03 (m, 5H), 6.92-6.84 (m, 1H); ¹³C NMR (50.3 MHz, CDCl₃) δ 153.7 (d, $J = 250.5$ Hz, C), 150.4 (C), 141.9 (d, $J = 12.0$ Hz, C), 140.0 (C), 134.2 (CH), 126.1 (d, $J = 6.9$ Hz, CH), 125.6 (CH), 124.9 (d, $J = 3.8$ Hz, CH), 123.0 (CH), 121.9 (CH), 118.2 (CH), 117.1 (d, $J = 17.7$ Hz, CH); EI-LRMS m/z 233 (M^+ , 21), 122 (100); HRMS calcd for C₁₂H₈FNO₃, 233.0488; found, 233.0480.

2-Fluorophenyl 2-nitrophenyl thioether (7b): Prepared from 2-fluorothiophenol (2.56 g, 20 mmol), Cu₂O (4.29 g, 30 mmol) and 1-chloro-2-nitrobenzene (4.73 g, 30 mmol) in pyridine (50 mL) according to the above procedure to give the title compound (3.89 g, 78%) as a yellow solid: mp 80-82 °C (lit.⁴ mp 75 °C); ¹H NMR (200 MHz, CDCl₃) δ 8.23 (d, $J = 8.2$ Hz, 1H), 7.66-7.14 (m, 6H), 6.82 (dd, $J = 7.8, 1.3$ Hz, 1H); ¹³C NMR (50.3 MHz, CDCl₃) δ 163.0 (d, $J = 251.3$ Hz, C), 144.9 (C), 137.7 (CH), 137.3 (C), 133.6 (CH), 132.8 (d, $J = 8.7$ Hz, CH), 127.5 (CH), 125.8 (CH), 125.5 (d, $J = 3.8$ Hz, CH), 125.2 (CH),

117.9 (d, $J = 19.4$ Hz, C), 116.7 (d, $J = 22.9$ Hz, CH); EI-LRMS m/z 249 (M^+ , 33), 185 (100); HRMS calcd for $C_{12}H_8FNO_2S$, 249.0260; found, 249.0269.

Typical Procedure for the Synthesis of 2-Aminophenyl 2-Fluorophenyl Ether 8a and Thioether

8b: To a solution of the corresponding aromatic nitro compound **7a,b** (10 mmol) in EtOH (25 mL) and HCl conc. (4 mL) iron powder (1.68 g, 30 mmol) was added. The mixture was refluxed for 6 h and then, it was filtered through Celite. The filter pad was washed with hot EtOAc (3 x 30 mL), the filtrate was concentrated and the residue was partitioned between EtOAc and brine. The organic layer was dried over anhydrous Na_2SO_4 , the solvents were removed under reduced pressure and the residue was purified by silica gel column chromatography (hexane/EtOAc) to provide the corresponding compound:

2-(2-Fluorophenoxy)aniline (8a):⁵ Fe powder (1.68 g, 30 mmol) was added to a solution of **7a** (2.33 g, 10 mmol) in EtOH (25 mL) and HCl (4 mL). Workup as above gave the title compound (1.87 g, 92%) as a yellow oil: R_f 0.20 (hexane/EtOAc, 20/1); 1H NMR (200 MHz, $CDCl_3$) δ 7.32-6.61 (m, 8H), 3.95 (br s, 2H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 153.2 (d, $J = 248.3$ Hz, C), 144.2 (d, $J = 11.5$ Hz, C), 143.0 (C), 137.9 (C), 124.5 (CH), 124.3 (d, $J = 3.8$ Hz, CH), 123.5 (d, $J = 6.9$ Hz), 119.4 (d, $J = 0.8$ Hz, CH), 118.1 (CH), 116.5 (d, $J = 18.2$ Hz, CH), 116.1 (CH); EI-LRMS m/z 203 (M^+ , 100); HRMS calcd for $C_{12}H_{10}FNO$, 203.0746; found, 203.0751.

2-(2-Fluorophenylthio)aniline (8b): Fe powder (1.68 g, 30 mmol) was added to a solution of **7b** (2.49 g, 10 mmol) in EtOH (25 mL) and HCl (4 mL). Workup as above gave the title compound (1.97 g, 90%) as a yellow solid: mp 38-40 °C (lit.⁴ mp 42-44 °C); 1H NMR (200 MHz, $CDCl_3$) δ 7.51 (d, $J = 7.4$ Hz, 1H), 7.34-7.24 (m, 1H), 7.21-6.75 (m, 6H), 4.35 (br s, 2H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 159.3 (d, $J = 243.3$ Hz, C), 149.0 (C), 137.5 (CH), 131.3 (CH), 128.1 (d, $J = 2.3$ Hz, CH), 126.8 (d, $J = 7.6$ Hz, CH), 124.5 (d, $J = 3.0$ Hz, CH), 123.8 (d, $J = 17.1$ Hz, C), 118.7 (CH), 115.4 (CH), 115.2 (d, $J = 21.3$ Hz, CH), 112.1 (C); EI-LRMS m/z 219 (M^+ , 100); HRMS calcd for $C_{12}H_{10}FNS$, 219.0518; found, 219.0528.

Typical Procedure for the Preparation of 2-Fluorophenyl 2-Iodophenyl Amines 3a-b, Ether 9a, and Thioether 9b:⁶ A cooled solution of NaNO₂ (0.61 g, 8.8 mmol) in H₂O (2 mL) was slowly added to a stirred solution of the corresponding aromatic amino compound **2** or **8** (8 mmol) in H₂O (8 mL) and H₂SO₄ (conc., 1.2 mL) cooled in an ice bath. After the addition, the mixture was stirred at this temperature for 30 min and then it was slowly poured into an ice-cold solution of KI (1.74 g, 10.5 mmol) in H₂O (4 mL). After a few minutes, copper powder (0.008 g, 0.12 mmol) was added, and the reaction mixture was refluxed for 30 min. The mixture was allowed to cool to room temperature, extracted with CH₂Cl₂ (4 x 30 mL). The combined organic layers were washed with Na₂S₂O₃ (20% aq., 10 mL), dried over anhydrous Na₂SO₄, and filtered. The solvents were removed under reduced pressure and the residue was purified by silica gel column chromatography (hexane/EtOAc) to provide the corresponding products:

***N*-(2-Fluorophenyl)-*N*-(2-iodophenyl)methylamine (3a):** A solution of **2a** (1.73 g, 8 mmol) in H₂O (8 mL) and H₂SO₄ (conc., 1.2 mL) was treated with NaNO₂ (0.61 g, 8.8 mmol) and KI (1.74 g, 10.5 mmol). Workup as described above yielded **3a** (1.57 g, 60%) as a colorless oil: *R_f* 0.30 (hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.93 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.35 (dt, *J* = 8.0, 1.6 Hz, 1H), 7.16 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.11-6.89 (m, 5H), 3.26 (s, 3H); ¹³C NMR (100.6 MHz, CDCl₃) δ 155.0 (d, *J* = 248.3 Hz, C), 151.6 (C), 140.1 (CH), 137.8 (d, *J* = 9.1 Hz, C), 129.2 (CH), 126.5 (CH), 125.4 (d, *J* = 1.5 Hz, CH), 124.2 (d, *J* = 3.5 Hz, CH), 121.8 (d, *J* = 7.8 Hz, CH), 120.0 (d, *J* = 2.3 Hz, CH), 116.3 (d, *J* = 19.8 Hz, CH), 98.0 (C), 41.1 (d, *J* = 2.3 Hz, CH₃); EI-LRMS *m/z* 327 (M⁺, 50), 185 (100); HRMS calcd for C₁₃H₁₁FIN, 326.9920; found, 326.9931. Anal. Calcd for C₁₃H₁₁FIN (327.1): C, 47.73; H, 3.39; N, 4.28. Found: C, 47.86; H, 3.38; N, 4.29.

***N*-(3-Dimethylaminopropyl)-*N*-(2-fluorophenyl)-2-iodoaniline (3b):** A solution of **2b** (2.30 g, 8 mmol) in H₂O (8 mL) and H₂SO₄ (conc., 1.2 mL) was treated with NaNO₂ (0.61 g, 8.8 mmol) and KI (1.74 g, 10.5 mmol). Workup as described above yielded **3b** (1.62 g, 51%) as a colorless oil: *R_f* 0.40 (AcOEt/Et₂NH, 20/1); ¹H NMR (400 MHz, CDCl₃) δ 7.85 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.31 (dt, *J* = 7.6,

1.6 Hz, 1H), 7.18 (dd, $J = 7.6, 1.2$ Hz, 1H), 7.04-6.92 (m, 2H), 6.90-6.83 (m, 2H), 6.73-6.68 (m, 1H), 3.65-3.60 (m, 2H), 2.34 (t, $J = 7.2$ Hz, 2H), 2.19 (s, 6H), 1.84-1.79 (m, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 155.5 (d, $J = 245.7$ Hz, C), 149.6 (C), 140.4 (CH), 137.0 (d, $J = 7.7$ Hz, C), 128.9 (CH), 126.7 (CH), 126.5 (CH), 124.1 (d, $J = 4.6$ Hz, CH), 121.9 (d, $J = 6.1$ Hz, CH), 121.8 (d, $J = 3.1$ Hz, CH), 116.5 (d, $J = 19.8$ Hz, CH), 99.2 (C), 57.1 (CH_2), 51.6 (d, $J = 3.0$ Hz, CH_2), 45.5 (CH_2), 26.2 (CH_3); EI-LRMS m/z 398 (M^+ , 0.1), 58 (100). Anal. Calcd for $\text{C}_{17}\text{H}_{20}\text{FIN}_2$ (398.3): C, 51.27; H, 5.06; N, 7.03. Found: C, 51.35; H, 5.08; N, 7.05.

2-Fluorophenyl 2-iodophenyl ether (9a): A solution of **8a** (1.63 g, 8 mmol) in H_2O (8 mL) and H_2SO_4 (conc., 1.2 mL) was treated with NaNO_2 (0.61 g, 8.8 mmol) and KI (1.74 g, 10.5 mmol). Workup as described above yielded **9a** (1.88 g, 75%) as a colorless oil: R_f 0.27 (hexane/EtOAc, 30/1); ^1H NMR (400 MHz, CDCl_3) δ 7.86 (dd, $J = 7.6, 1.2$ Hz, 1H), 7.30-7.07 (m, 4H), 6.99 (dt, $J = 8.0, 2.0$ Hz, 1H), 6.86 (dt, $J = 7.6, 1.6$ Hz, 1H), 6.78 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR (50.3 MHz, CDCl_3) δ 156.3 (C), 153.7 (d, $J = 249.6$ Hz, C), 143.3 (d, $J = 11.4$ Hz, C), 139.7 (CH), 129.4 (CH), 125.0 (CH), 124.9 (d, $J = 6.6$ Hz, CH), 124.6 (d, $J = 3.8$ Hz, CH), 121.1 (CH), 117.05 (CH), 117.01 (d, $J = 18.1$ Hz, CH), 87.1 (C); EI-LRMS m/z 314 (M^+ , 100); HRMS calcd for $\text{C}_{12}\text{H}_8\text{FIO}$, 313.9604; found, 313.9597. Anal. Calcd for $\text{C}_{12}\text{H}_8\text{FIO}$ (314.1): C, 45.89; H, 2.57. Found: C, 46.02; H, 2.58.

2-Fluorophenyl 2-iodophenyl thioether (9b): A solution of **8b** (1.75 g, 8 mmol) in H_2O (8 mL) and H_2SO_4 (conc., 1.2 mL) was treated with NaNO_2 (0.61 g, 8.8 mmol) and KI (1.74 g, 10.5 mmol). Workup as described above yielded **9b** (1.90 g, 72%) as a white solid: mp 48-50 $^\circ\text{C}$; ^1H NMR (200 MHz, CDCl_3) δ 7.84 (d, $J = 7.6$ Hz, 1H), 7.44-7.34 (m, 2H), 7.26-7.12 (m, 3H), 6.99-6.85 (m, 2H); ^{13}C NMR (50.3 MHz, CDCl_3) δ 161.6 (d, $J = 248.7$ Hz, C), 140.1 (C), 139.4 (CH), 134.9 (CH), 130.7 (d, $J = 7.8$ Hz, CH), 128.8 (CH), 128.7 (CH), 127.5 (CH), 125.0 (d, $J = 3.9$ Hz, CH), 120.7 (d, $J = 17.4$ Hz, C), 116.1 (d, $J = 21.9$ Hz, CH), 98.9 (C); EI-LRMS m/z 330 (M^+ , 14), 329 (100); HRMS calcd for $\text{C}_{12}\text{H}_8\text{FIS}$, 329.9375; found, 329.9370. Anal. Calcd for $\text{C}_{12}\text{H}_8\text{FIS}$ (330.2): C, 43.65; H, 2.44. Found: C, 43.74; H, 2.43.

Synthesis of *N*-(2-Bromophenyl)-*N*-(2-fluorophenyl)methylamine (3c): Under nitrogen atmosphere an oven-dried Schlenk flask was charged with Cs₂CO₃ (3.42 g, 10.5 mmol), Pd₂(dba)₃ (0.207 g, 0.225 mmol) and BINAP (0.210 g, 0.34 mmol). 2-Bromoaniline (1.55 g, 9 mmol), 1-bromo-2-fluorobenzene (1.32 g, 7.5 mmol) and toluene (30 mL) were added, and the mixture was heated to 100 °C with stirring for 48 h. The mixture was cooled to room temperature, diluted with Et₂O, filtered and concentrated under reduced pressure. The crude product was then purified by column chromatography (hexane) giving rise to ***N*-(2-bromophenyl)-2-fluoroaniline** (0.76 g, 38%) as a colorless oil: *R_f* 0.43 (hexane/EtOAc, 50/1); ¹H NMR (300 MHz, CDCl₃) δ 7.60 (d, *J* = 7.7 Hz, 1H), 7.37 (td, *J* = 8.3, 1.9 Hz, 1H), 7.31-7.07 (m, 4H), 7.06-6.96 (m, 1H), 6.88-6.79 (m, 1H), 6.18 (br s, 1H); ¹³C NMR (75.4 MHz, CDCl₃) δ 154.3 (d, *J* = 240.8 Hz, C), 140.5 (C), 133.1 (CH), 130.1 (d, *J* = 11.3 Hz, C), 128.2 (CH), 124.4 (d, *J* = 4.1 Hz, CH), 122.7 (d, *J* = 7.3 Hz, CH), 121.8 (CH), 120.1 (d, *J* = 1.7 Hz, CH), 116.5 (CH), 116.1 (d, *J* = 19.3 Hz, CH), 113.1 (C); EI-LRMS *m/z* 267 (M⁺+2, 62), 265 (M⁺, 64), 185 (100); HRMS calcd for C₁₂H₉BrFN, 264.9902; found, 264.9895. A solution of *N*-(2-bromophenyl)-2-fluoroaniline (0.67 g, 2.5 mmol) in DMF (4 mL) was treated with NaH (0.09 g, 3.75 mmol) at 0 °C for 30 min. Then, methyl iodide (0.462 g, 3.25 mmol) in DMF (2 mL) was added at 0 °C and the mixture was stirred at room temperature for 1 h. The mixture was diluted with H₂O, extracted with CH₂Cl₂ (3 x 20 mL), dried over Na₂SO₄ anhydrous, filtered and concentrated under reduced pressure. The crude product was then purified by column chromatography (hexane) yielding **3c** (0.66 g, 94%) as a colorless oil: *R_f* 0.28 (hexane); ¹H NMR (300 MHz, CDCl₃) δ 7.61 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.29 (td, *J* = 7.7, 1.4 Hz, 1H), 7.17 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.09-6.87 (m, 5H), 3.27 (s, 3H); ¹³C NMR (75.4 MHz, CDCl₃) δ 155.0 (d, *J* = 247.1 Hz, C), 148.4 (C), 137.7 (d, *J* = 9.1 Hz, C), 133.9 (CH), 128.2 (CH), 125.8 (CH), 125.6 (d, *J* = 1.9 Hz, CH), 124.2 (d, *J* = 3.8 Hz, CH), 122.1 (d, *J* = 7.6 Hz, CH), 120.7 (C), 120.5 (d, *J* = 2.9 Hz, CH), 116.3 (d, *J* = 20.0 Hz, CH), 40.8 (d, *J* = 2.0 Hz, CH₃); EI-LRMS *m/z* 281 (M⁺+2, 61), 279 (M⁺, 62), 185 (100); HRMS calcd for C₁₃H₁₁BrFN, 279.0059; found, 279.0065. Anal. Calcd for C₁₁H₁₁BrFN (280.1): C, 55.74; H, 3.96; N, 5.00. Found: C, 55.84; H, 3.95; N, 4.98.

General Procedure for the Synthesis of 4-Functionalized Carbazoles **4, 1-Functionalized Dibenzofurans **10** and 1-Functionalized Dibenzothiophenes **11**:** *t*-BuLi (2.2 mL of a 1.5 M solution in pentane, 3.3 mmol) was added to a solution of the corresponding 2-fluorophenyl 2-halophenyl derivative **3a-c** or **9a,b** (1 mmol) in THF (8 mL) at -78°C . The resulting solution was stirred for 20 min at this temperature and then, the reaction mixture was allowed to warm to 0°C and stirred for 30 min. After cooling to -78°C , the corresponding electrophile (1.2 mmol) was added dropwise and stirring continued at low temperature for further 30 min. The reaction mixture was then allowed to warm to room temperature, quenched with water and extracted with EtOAc (3 x 20 mL). The combined organic layers were dried (Na_2SO_4), and evaporated under reduced pressure. The crude product was purified by column chromatography (eluent: hexane/EtOAc) on silica gel to afford the corresponding compounds **4**, **10**, and **11**.

9-Methyl-9H-carbazole (4a**):**³ Treatment of **3a** (0.327 g, 1 mmol) with *t*-BuLi (2.2 mL, 3.3 mmol) according to the general procedure, using MeOH (excess) as electrophile and workup as described above yielded **4a** (0.143 g, 79%) as a white solid: mp $87-89^{\circ}\text{C}$ (lit.⁷ mp $87-88^{\circ}\text{C}$); ^1H NMR (400 MHz, CDCl_3) δ 8.17 (d, $J = 7.6$ Hz, 2H), 7.54 (dd, $J = 8.0, 7.6$ Hz, 2H), 7.43 (d, $J = 8.0$ Hz, 2H), 7.31 (t, $J = 7.6$ Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 140.8 (C), 125.6 (CH), 122.6 (C), 120.2 (CH), 118.7 (CH), 108.3 (CH), 28.9 (CH_3); EI-LRMS m/z 181 (M^+ , 100); IR (KBr) 2928, 1588, 1464 cm^{-1} . Anal. Calcd for $\text{C}_{13}\text{H}_{11}\text{N}$ (181.2): C, 86.15; H, 6.12; N, 7.73. Found: C, 86.10; H, 6.11; N, 7.70.

9-Methyl-4-phenylthio-9H-carbazole (4b**):** Treatment of **3a** (0.327 g, 1 mmol) with *t*-BuLi (2.2 mL, 3.3 mmol) according to the general procedure, using diphenyl disulfide (0.262 g, 1.2 mmol) as electrophile and workup as described above yielded **4b** (0.185 g, 64%) as a white solid: mp $108-110^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.62 (d, $J = 8.0$ Hz, 1H), 7.50-7.18 (m, 11H), 3.85 (s, 3H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 141.4 (C), 141.0 (C), 135.7 (C), 129.8 (CH), 129.1 (CH), 128.8 (C), 126.4 (CH), 125.8 (CH), 125.6 (CH), 123.8 (C), 122.7 (C), 122.3 (CH), 119.1 (CH), 108.1 (CH), 107.9 (CH), 29.1

(CH₃); EI-LRMS m/z 289 (M⁺, 100); IR (KBr) 2788, 1580, 1417 cm⁻¹. Anal. Calcd for C₁₉H₁₅NS (289.4): C, 78.86; H, 5.22; N, 4.84. Found: C, 78.94; H, 5.24; N, 4.85.

4-Bromo-9-methyl-9H-carbazole (4c): Treatment of **3a** (0.327 g, 1 mmol) with *t*-BuLi (2.2 mL, 3.3 mmol) according to the general procedure, using 1,2-dibromoethane (0.225 g, 1.2 mmol) as electrophile and workup as described above yielded **4c** (0.182 g, 70%) as a white solid: mp 97-99 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.79 (d, J = 8.0 Hz, 1H), 7.56-7.52 (m, 1H), 7.41-7.29 (m, 5H), 3.80 (s, 3H); ¹³C NMR (100.6 MHz, CDCl₃) δ 141.9 (C), 140.9 (C), 126.2 (CH), 126.0 (CH), 122.9 (CH), 122.5 (CH), 122.2 (C), 121.3 (C), 118.9 (CH), 116.6 (C), 108.2 (CH), 107.2 (CH), 29.0 (CH₃); EI-LRMS m/z 261 (M⁺+2, 100), 259 (M⁺, 100); IR (KBr) 2924, 1600, 1464 cm⁻¹; HRMS calcd for C₁₃H₁₀BrN, 258.9997; found, 258.9989. Anal. Calcd for C₁₃H₁₀BrN (260.1): C, 60.02; H, 3.87; N, 5.38. Found: C, 60.13; H, 3.88; N, 5.36.

N-Phenyl-(9-methyl-9H-carbazole)-1-carboxamide (4d): Treatment of **3c** (0.280 g, 1 mmol) with *t*-BuLi (2.2 mL, 3.3 mmol) according to the general procedure, using phenyl isocyanate (0.143 g, 1.2 mmol) as electrophile and workup as described above yielded **4d** (0.213 g, 71%) as a white solid: mp 153-155 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.33 (d, J = 8.0 Hz, 1H), 8.03 (br s, 1H), 7.73 (d, J = 8.0 Hz, 2H), 7.54-7.34 (m, 7H), 7.19 (t, J = 7.6 Hz, 2H), 3.82 (s, 3H); ¹³C NMR (75.4 MHz, CDCl₃) δ 167.7 (C), 141.2 (C), 138.0 (C), 130.6 (C), 129.1 (CH), 128.5 (C), 126.3 (CH), 125.1 (CH), 124.4 (CH), 123.4 (CH), 120.8 (C), 119.9 (CH), 119.4 (CH), 119.0 (C), 118.2 (CH), 110.8 (CH), 108.4 (CH), 29.0 (CH₃); EI-LRMS m/z 300 (M⁺, 53), 208 (100); IR (KBr) 3430, 2930, 1598, 1538, 1439 cm⁻¹; HRMS calcd for C₂₀H₁₆N₂O, 300.1263; found, 300.1269. Anal. Calcd for C₂₀H₁₆N₂O (300.4): C, 79.98; H, 5.37; N, 9.33. Found: C, 80.12; H, 5.38; N, 9.30.

4-(1-Ethyl-1-hydroxyethyl)-9-methyl-9H-carbazole (4e): Treatment of **3c** (0.280 g, 1 mmol) with *t*-BuLi (2.2 mL, 3.3 mmol) according to the general procedure, using 3-pentanone (0.103 g, 1.2 mmol) as electrophile and workup as described above yielded **4e** (0.198 g, 74%) as a white solid: mp 101-103 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.98 (br s, 1H), 7.53 (t, J = 8.1 Hz, 1H), 7.49-7.42 (m, 2H), 7.37 (dd,

$J = 8.1, 0.9$ Hz, 1H), 7.31 (t, $J = 8.1$ Hz, 1H), 7.26-7.18 (br s, 1H), 3.84 (s, 3H), 2.41-2.07 (m, 5H), 0.94 (t, $J = 7.5$ Hz, 6H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 142.3 (C), 140.9 (C), 127.0 (CH), 125.1 (CH), 124.6 (CH), 121.7 (C), 118.4 (CH), 117.6 (CH), 107.9 (CH), 107.7 (CH), 78.1 (C), 30.7 (CH_2), 28.8 (CH_3), 8.3 (CH_3); EI-LRMS m/z 267 (M^+ , 80), 182 (100); IR (KBr) 3534, 2981, 2960, 2935, 1475, 1325, 720 cm^{-1} ; HRMS calcd for $\text{C}_{18}\text{H}_{21}\text{NO}$, 267.1623; found, 267.1618. Anal. Calcd for $\text{C}_{18}\text{H}_{21}\text{NO}$ (267.4): C, 80.86; H, 7.92; N, 5.24. Found: C, 80.75; H, 7.95; N, 5.22.

9-(3-Dimethylaminopropyl)-9H-carbazole (4f): Treatment of **3b** (0.398 g, 1 mmol) with *t*-BuLi (2.2 mL, 3.3 mmol) according to the general procedure, using MeOH (excess) as electrophile and workup as described above yielded **4f** (0.177 g, 70%) as a white solid: mp 175-177 °C (lit.⁸ bp 165-168 °C / 0.58 torr); ^1H NMR (400 MHz, CDCl_3) δ 8.11 (d, $J = 8.0$ Hz, 2H), 7.49-7.46 (m, 4H), 7.26-7.22 (m, 2H), 4.39 (t, $J = 7.0$ Hz, 2H), 2.29 (t, $J = 6.8$ Hz, 2H), 2.23 (s, 6H), 2.06-2.01 (m, 2H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 140.4 (C), 125.5 (CH), 122.7 (C), 120.2 (CH), 118.6 (CH), 108.6 (CH), 56.5 (CH_2), 45.4 (CH_2), 40.6 (CH_2), 26.9 (CH_3); EI-LRMS m/z 252 (M^+ , 7), 58 (100); IR (KBr) 2947, 1596, 1460 cm^{-1} . Anal. Calcd for $\text{C}_{17}\text{H}_{20}\text{N}_2$ (252.4): C, 80.91; H, 7.99; N, 11.10. Found: C, 80.75; H, 8.02; N, 11.06.

9-(3-Dimethylaminopropyl)-4-tributylstannyl-9H-carbazole (4g): Treatment of **3b** (0.398 g, 1 mmol) with *t*-BuLi (2.2 mL, 3.3 mmol) according to the general procedure, using tri-*n*-butyltin chloride (0.391 g, 1.2 mmol) as electrophile and workup as described above yielded **4g** (0.330 g, 61%) as a brown oil: R_f 0.33 (EtOAc/Et₂NH, 20/1); ^1H NMR (400 MHz, CDCl_3) δ 8.11 (d, $J = 8.0$ Hz, 1H), 7.54-7.43 (m, 4H), 7.37 (dd, $J = 6.4, 2.0$ Hz, 1H), 7.28-7.23 (m, 1H), 4.41 (t, $J = 7.0$ Hz, 2H), 2.33 (t, $J = 6.8$ Hz, 2H), 2.26 (s, 6H), 2.09-2.01 (m, 2H), 1.68-1.59 (m, 6H), 1.43-1.25 (m, 12H), 0.90 (t, $J = 7.4$ Hz, 9H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 140.4 (C), 139.7 (C), 134.3 (C), 128.7 (C), 127.3 (CH), 125.0 (CH), 124.7 (CH), 124.4 (C), 120.5 (CH), 118.2 (CH), 108.8 (CH), 108.6 (CH), 56.6 (CH_2), 45.4 (CH_2), 40.4 (CH_2), 29.1 (CH_2), 27.3 (CH_2), 26.8 (CH_3), 13.6 (CH_3), 10.0 (CH_2); EI-LRMS m/z 484 ($\text{M}^+ - \text{C}_4\text{H}_9$, 0.1), 58 (100); IR (KBr) 2928, 1580, 1460 cm^{-1} . Anal. Calcd for $\text{C}_{29}\text{H}_{46}\text{N}_2\text{Sn}$ (541.4): C, 64.34; H, 8.56; N, 5.17. Found: C, 64.48; H, 8.59; N, 5.15.

9-(3-Dimethylaminopropyl)-4-[1-hydroxy-1-(4-methylphenyl)methyl]-9H-carbazole (4h):

Treatment of **3b** (0.398 g, 1 mmol) with *t*-BuLi (2.2 mL, 3.3 mmol) according to the general procedure, using 4-methylbenzaldehyde (0.144 g, 1.2 mmol) as electrophile and workup as described above yielded **4h** (0.216 g, 58%) as a white solid: mp 183-185 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.11 (d, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.42-7.37 (m, 1H), 7.27-7.22 (m, 3H), 7.11-7.06 (m, 3H), 6.49 (d, *J* = 4.6 Hz, 1H), 6.01 (d, *J* = 4.6 Hz, 1H), 4.42 (t, *J* = 6.8 Hz, 2H), 2.23 (s, 3H), 2.20 (t, *J* = 6.8 Hz, 2H), 2.13 (s, 6H), 1.90-1.80 (m, 2H); ¹³C NMR (100.6 MHz, DMSO-*d*₆) δ 141.0 (C), 140.3 (C), 140.1 (C), 139.8 (C), 135.7 (C), 128.6 (CH), 127.0 (CH), 125.2 (CH), 125.1 (CH), 123.8 (CH), 121.4 (C), 119.2 (C), 118.5 (CH), 117.6 (CH), 108.8 (CH), 108.0 (CH), 72.0 (CH), 56.0 (CH₂), 45.1 (CH₂), 39.9 (CH₂), 26.4 (CH₃), 20.7 (CH₃); EI-LRMS *m/z* 372 (M⁺, 0.1), 58 (100); IR (KBr) 3421, 2939, 1592, 1464 cm⁻¹; HRMS calcd for C₂₅H₂₈N₂O, 372.2202; found, 372.2189. Anal. Calcd for C₂₅H₂₈N₂O (372.5): C, 80.61; H, 7.58; N, 7.52. Found: C, 80.47; H, 7.61; N, 7.50.

Ethyl dibenzofuran-1-carboxylate (10a):⁹ Treatment of **9a** (0.314 g, 1 mmol) with *t*-BuLi (2.2 mL, 3.3 mmol) according to the general procedure, using ethyl chloroformate (0.130 g, 1.2 mmol) as electrophile and workup as described above yielded **10a** (0.161 g, 67%) as a white solid: mp 37-39 °C; ¹H NMR (200 MHz, CDCl₃) δ 8.87 (d, *J* = 8.0 Hz, 1H), 8.02 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.74 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.57-7.30 (m, 4H), 4.53 (q, *J* = 7.0 Hz, 2H), 1.50 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (50.3 MHz, CDCl₃) δ 166.5 (C), 156.7 (C), 156.5 (CH), 128.1 (CH), 126.2 (CH), 126.0 (CH), 125.6 (C), 125.4 (CH), 124.0 (C), 122.8 (C), 122.7 (CH), 115.7 (CH), 111.1 (CH), 61.1 (CH₂), 14.3 (CH₃); EI-LRMS *m/z* 240 (M⁺, 85), 195 (100); IR (KBr) 2978, 1720, 1576, 1444, 1281 cm⁻¹; HRMS calcd for C₁₅H₁₂O₃, 240.0786; found, 240.0790. Anal. Calcd for C₁₅H₁₂O₃ (240.3): C, 74.99; H, 5.03. Found: C, 75.14; H, 5.01.

1-Phenylthiodibenzofuran (10b): Treatment of **9a** (0.314 g, 1 mmol) with *t*-BuLi (2.2 mL, 3.3 mmol) according to the general procedure, using diphenyl disulfide (0.262 g, 1.2 mmol) as electrophile and workup as described above yielded **10b** (0.169 g, 61%) as a colorless oil: *R*_f 0.30 (hexane/EtOAc,

30/1); ^1H NMR (400 MHz, CDCl_3) δ 8.39 (d, $J = 7.6$ Hz, 1H), 7.60 (dd, $J = 8.4, 0.8$ Hz, 1H), 7.53 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.49 (ddd, $J = 8.4, 7.2, 1.2$ Hz, 1H), 7.43-7.23 (m, 8H); ^{13}C NMR (50.3 MHz, CDCl_3) δ 156.2 (C), 156.0 (C), 134.5 (C), 130.3 (CH), 129.8 (C), 129.3 (CH), 127.2 (CH), 127.1 (CH), 127.0 (CH), 126.3 (CH), 124.4 (C), 123.7 (C), 123.5 (CH), 122.7 (CH), 111.2 (CH), 110.5 (CH); EI-LRMS m/z 276 (M^+ , 100); IR (KBr) 3056, 1568, 1444, 1200 cm^{-1} ; HRMS calcd for $\text{C}_{18}\text{H}_{12}\text{OS}$, 276.0609; found, 276.0614. Anal. Calcd for $\text{C}_{18}\text{H}_{12}\text{OS}$ (276.4): C, 78.23; H, 4.38. Found: C, 78.45; H, 4.36.

1-(4-Methylbenzoyl)dibenzofuran (10c): Treatment of **9a** (0.314 g, 1 mmol) with *t*-BuLi (2.2 mL, 3.3 mmol) according to the general procedure, using *p*-tolunitrile (0.141 g, 1.2 mmol) as electrophile and workup as described above yielded **10c** (0.178 g, 62%) as a yellow solid: mp 98-100 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.76-7.67 (m, 2H), 7.64 (dd, $J = 8.4, 1.2$ Hz, 1H), 7.59-7.53 (m, 2H), 7.48 (t, $J = 8.4$ Hz, 1H), 7.39 (ddd, $J = 8.4, 7.6, 1.2$ Hz, 1H), 7.27-7.10 (m, 4H), 2.38 (s, 3H); ^{13}C NMR (50.3 MHz, CDCl_3) δ 176.3 (C), 156.2 (C), 156.0 (C), 141.5 (C), 135.3 (C), 134.9 (C), 129.2 (CH), 128.3 (CH), 127.3 (CH), 126.8 (CH), 122.7 (CH), 122.3 (C), 112.3 (CH), 111.4 (CH), 21.4 (CH_3); EI-LRMS m/z 286 (M^+ , 28), 270 (100); IR (KBr) 3064, 1658, 1594, 1452 cm^{-1} ; HRMS calcd for $\text{C}_{20}\text{H}_{14}\text{O}_2$, 286.0994; found, 286.1011. Anal. Calcd for $\text{C}_{20}\text{H}_{14}\text{O}_2$ (286.3): C, 83.90; H 4.93. Found: C, 83.78; H, 4.92.

N-Phenyldibenzofuran-1-carboxamide (10d): Treatment of **9a** (0.314 g, 1 mmol) with *t*-BuLi (2.2 mL, 3.3 mmol) according to the general procedure, using phenyl isocyanate (0.143 g, 1.2 mmol) as electrophile and workup as described above yielded **10d** (0.181 g, 63%) as a white solid: mp 212-214 $^{\circ}\text{C}$; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 8.17 (d, $J = 7.6$ Hz, 1H), 7.89 (d, $J = 8.0$ Hz, 1H), 7.83 (d, $J = 8.8$ Hz, 2H), 7.73 (d, $J = 8.0$ Hz, 1H), 7.69 (d, $J = 7.2$ Hz, 1H), 7.64 (t, $J = 7.6$ Hz, 1H), 7.54 (t, $J = 8.0$ Hz, 1H), 7.48-7.32 (m, 3H), 7.25 (t, $J = 8.0$ Hz, 1H), 7.13 (t, $J = 7.2$ Hz, 1H); ^{13}C NMR (50.3 MHz, $\text{DMSO}-d_6$) δ 166.0 (C), 155.9 (C), 155.7 (C), 139.1 (C), 131.4 (C), 128.9 (C), 128.3 (CH), 127.3 (CH), 123.9 (CH), 123.2 (CH), 122.6 (CH), 122.3 (C), 120.1 (CH), 118.2 (CH), 114.0 (CH), 111.7 (CH); EI-LRMS m/z 287 (M^+ , 27), 195 (100); IR (KBr) 3291, 1658, 1588, 1530, 1436 cm^{-1} ; HRMS calcd for $\text{C}_{19}\text{H}_{13}\text{NO}_2$,

287.0946; found, 287.0942. Anal. Calcd for $C_{19}H_{13}NO_2$ (287.3): C, 79.43; H, 4.56; N, 4.88. Found: C, 79.58; H, 4.55; N, 4.89.

1-(1-Ethyl-1-hydroxyethyl)dibenzofuran (10e): Treatment of **9a** (0.314 g, 1 mmol) with *t*-BuLi (2.2 mL, 3.3 mmol) according to the general procedure, using 3-pentanone (0.103 g, 1.2 mmol) as electrophile and workup as described above yielded **10e** (0.140 g, 55%) as a colorless oil: R_f 0.30 (hexane/EtOAc, 25/1); 1H NMR (200 MHz, $CDCl_3$) δ 8.74 (d, J = 8.0 Hz, 1H), 7.62-7.20 (m, 6H), 2.26-2.08 (m, 5H), 0.89 (t, J = 7.4 Hz, 6H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 157.2 (C), 156.1 (C), 141.5 (C), 129.7 (C), 126.9 (CH), 126.6 (CH), 126.1 (CH), 123.5 (C), 122.1 (CH), 120.7 (CH), 111.1 (CH), 110.7 (CH), 78.0 (C), 31.1 (CH_2), 8.1 (CH_3); EI-LRMS m/z 254 (M^+ , 8), 57 (100); HRMS calcd for $C_{17}H_{18}O_2$, 254.1307; found, 254.1301. Anal. Calcd for $C_{17}H_{18}O_2$ (254.3): C, 80.28; H, 7.13. Found: C, 80.39; H, 7.16.

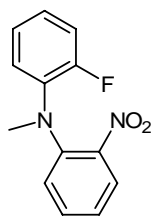
Dibenzothiophene (11a):³ Treatment of **9b** (0.330 g, 1 mmol) with *t*-BuLi (2.2 mL, 3.3 mmol) according to the general procedure, using MeOH (excess) as electrophile and workup as described above yielded **11a** (0.146 g, 79%) as a white solid: mp 100-102 °C (lit.³ mp 97-100 °C); 1H NMR (400 MHz, $CDCl_3$) δ 8.20-8.14 (m, 2H), 7.92-7.84 (m, 2H), 7.52-7.44 (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 139.3 (C), 135.4 (C), 126.6 (CH), 124.2 (CH), 122.7 (CH), 121.5 (CH); EI-LRMS m/z 184 (M^+ , 100); IR (KBr) 3040, 1588, 1425, 1227, 1064, 733 cm^{-1} . Anal. Calcd for $C_{12}H_8S$ (184.3): C, 78.22; H 4.38. Found: C, 78.29; H, 4.36.

1-Phenylthiodibenzothiophene (11b):¹⁰ Treatment of **9b** (0.330 g, 1 mmol) with *t*-BuLi (2.2 mL, 3.3 mmol) according to the general procedure, using diphenyl disulfide (0.262 g, 1.2 mmol) as electrophile and workup as described above yielded **11b** (0.228 g, 78%) as a white solid: mp 115-117 °C; 1H NMR (200 MHz, $CDCl_3$) δ 9.30-9.17 (m, 1H), 8.00-7.81 (m, 2H), 7.61-7.22 (m, 9H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 140.7 (C), 139.6 (C), 135.3 (C), 135.2 (C), 134.5 (C), 131.0 (C), 130.3 (CH), 129.9 (CH), 129.2 (CH), 126.7 (CH), 126.5 (CH), 126.4 (CH), 126.1 (CH), 124.2 (CH), 122.2 (CH); EI-

LRMS m/z 292 (M^+ , 100); IR (KBr) 3052, 1584, 1471 cm^{-1} ; HRMS calcd for $\text{C}_{18}\text{H}_{12}\text{S}_2$, 292.0380; found, 292.0386. Anal. Calcd for $\text{C}_{18}\text{H}_{12}\text{S}_2$ (292.4): C, 73.93; H, 4.14. Found: C, 74.05; H, 4.12.

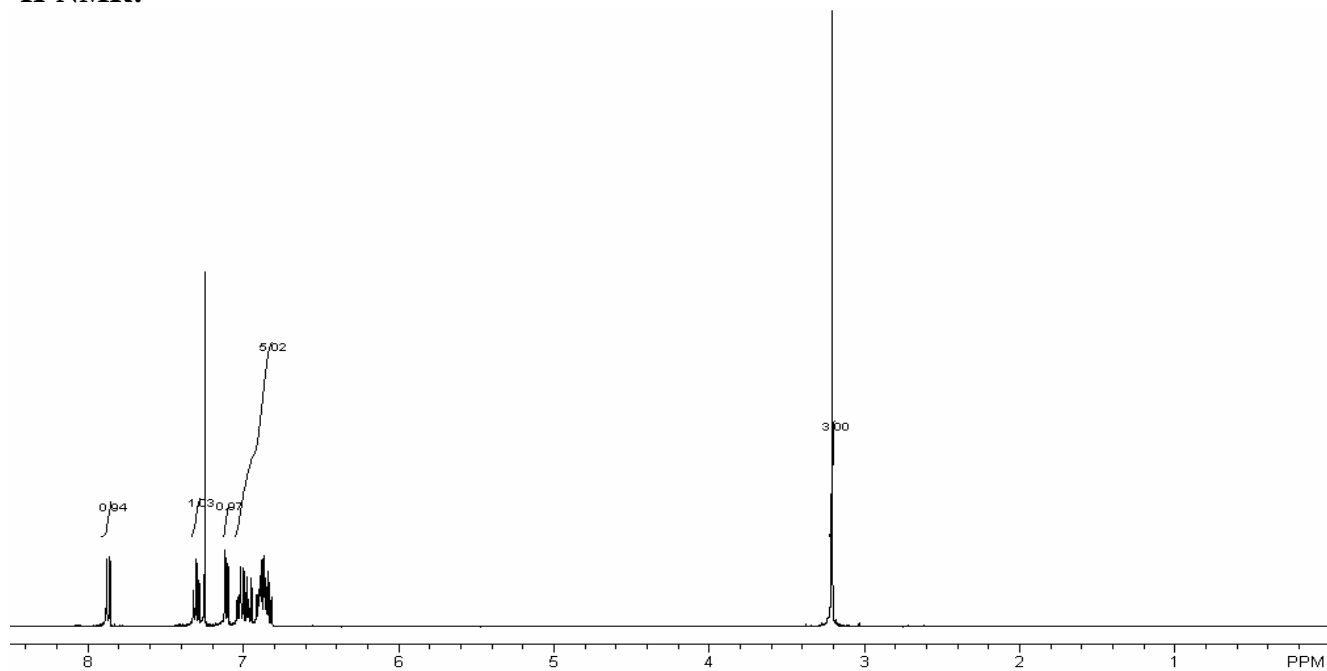
1-Bromodibenzothiophene (11c): Treatment of **9b** (0.330 g, 1 mmol) with *t*-BuLi (2.2 mL, 3.3 mmol) according to the general procedure, using 1,2-dibromoethane (0.225 g, 1.2 mmol) as electrophile and workup as described above yielded **11c** (0.200 g, 76%) as a white solid: mp 85-87 °C (lit.¹¹ mp 79-80 °C); ^1H NMR (400 MHz, CDCl_3) δ 9.22-9.19 (m, 1H), 7.86-7.84 (m, 1H), 7.77 (dd, J = 8.0, 0.8 Hz, 1H), 7.65 (dd, J = 7.6, 0.8 Hz, 1H), 7.54-7.50 (m, 2H), 7.22 (dd, J = 8.0, 7.6 Hz, 1H); ^{13}C NMR (50.3 MHz, CDCl_3) δ 141.5 (C), 139.7 (C), 134.9 (C), 132.5 (C), 129.8 (CH), 126.9 (CH), 126.6 (CH), 125.4 (CH), 123.8 (CH), 122.3 (CH), 121.7 (CH), 118.1 (C); EI-LRMS m/z 264 ($M^+ + 2$, 100), 262 (M^+ , 100); IR (KBr) 1580, 1541, 1429, 1394, 1021, 722 cm^{-1} ; HRMS calcd for $\text{C}_{12}\text{H}_7\text{BrS}$, 261.9452; found, 261.9457. Anal. Calcd for $\text{C}_{12}\text{H}_7\text{BrS}$ (263.2): C, 54.77; H, 2.68. Found: C, 54.90; H, 2.67.

1-[1-Hydroxy-1-(4-methylphenyl)methyl]dibenzothiophene (11d): Treatment of **9b** (0.330 g, 1 mmol) with *t*-BuLi (2.2 mL, 3.3 mmol) according to the general procedure, using 4-methylbenzaldehyde (0.144 g, 1.2 mmol) as electrophile and workup as described above yielded **11d** (0.228 g, 75%) as a white solid: mp 123-125 °C; ^1H NMR (300 MHz, CDCl_3) δ 8.28 (d, J = 7.7 Hz, 1H), 7.89-7.82 (m, 2H), 7.51-7.35 (m, 3H), 7.29 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 6.78 (d, J = 4.4 Hz, 1H), 2.64 (d, J = 4.3 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 140.1 (C), 139.8 (C), 139.6 (C), 138.8 (C), 137.5 (C), 134.7 (C), 132.8 (C), 129.2 (CH), 127.3 (CH), 126.02 (CH), 125.97 (CH), 125.8 (CH), 124.3 (CH), 123.8 (CH), 122.6 (CH), 122.3 (CH), 73.0 (CH), 21.1 (CH_3); EI-LRMS m/z 304 (M^+ , 100); IR (KBr) 3313, 3047, 1516, 1409, 1301, 1178, 1157, 1030, 758, 753 cm^{-1} ; HRMS calcd for $\text{C}_{20}\text{H}_{16}\text{OS}$, 304.0922; found, 304.0934. Anal. Calcd for $\text{C}_{20}\text{H}_{16}\text{OS}$ (304.4): C, 78.91; H, 5.30. Found: C, 79.14; H, 5.32.

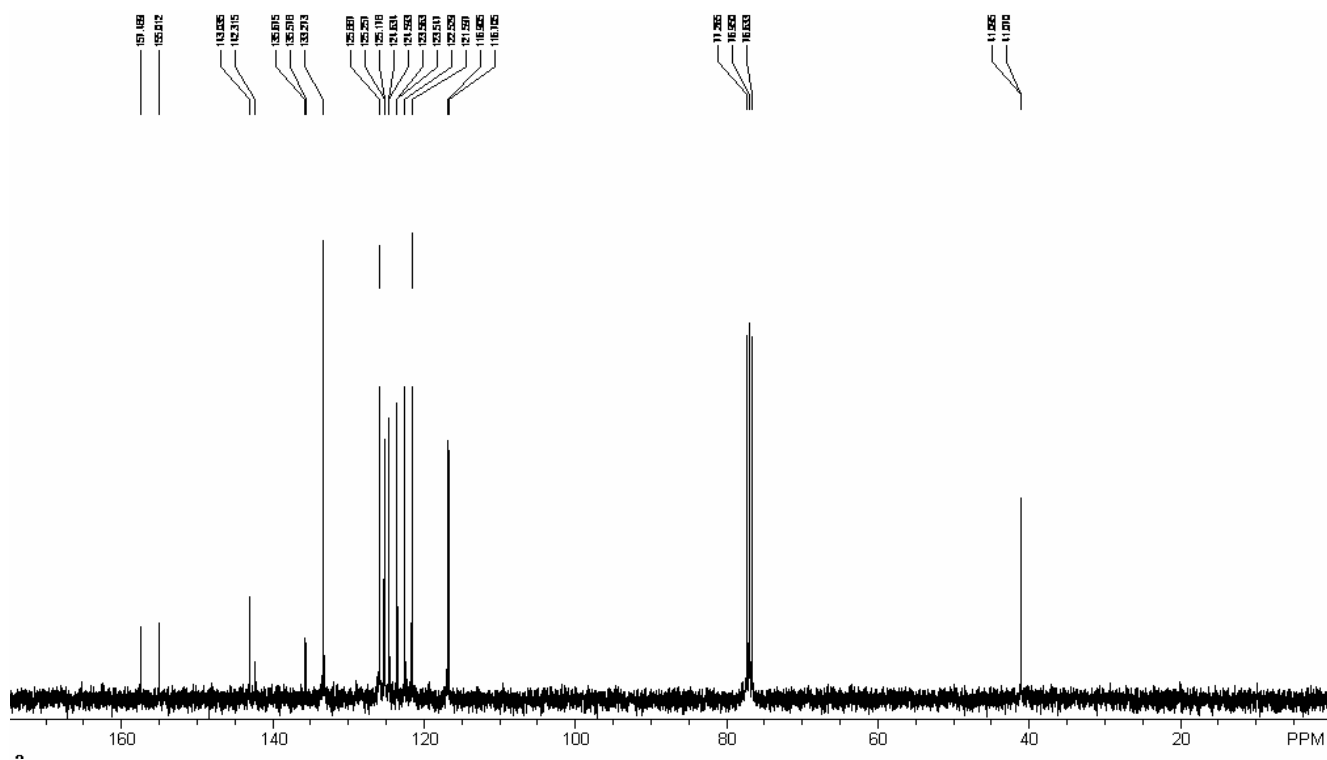


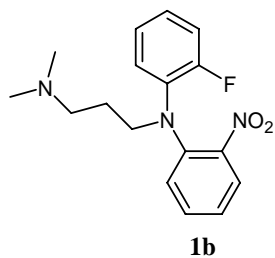
1a

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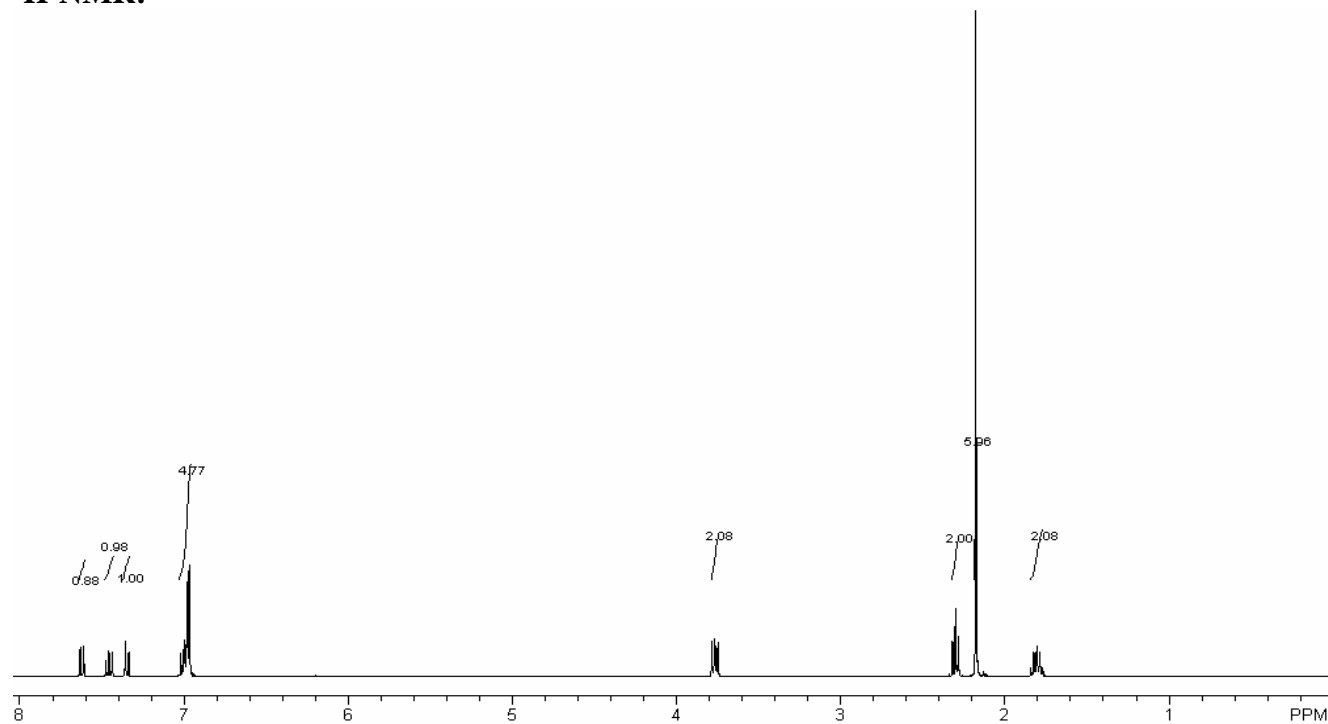


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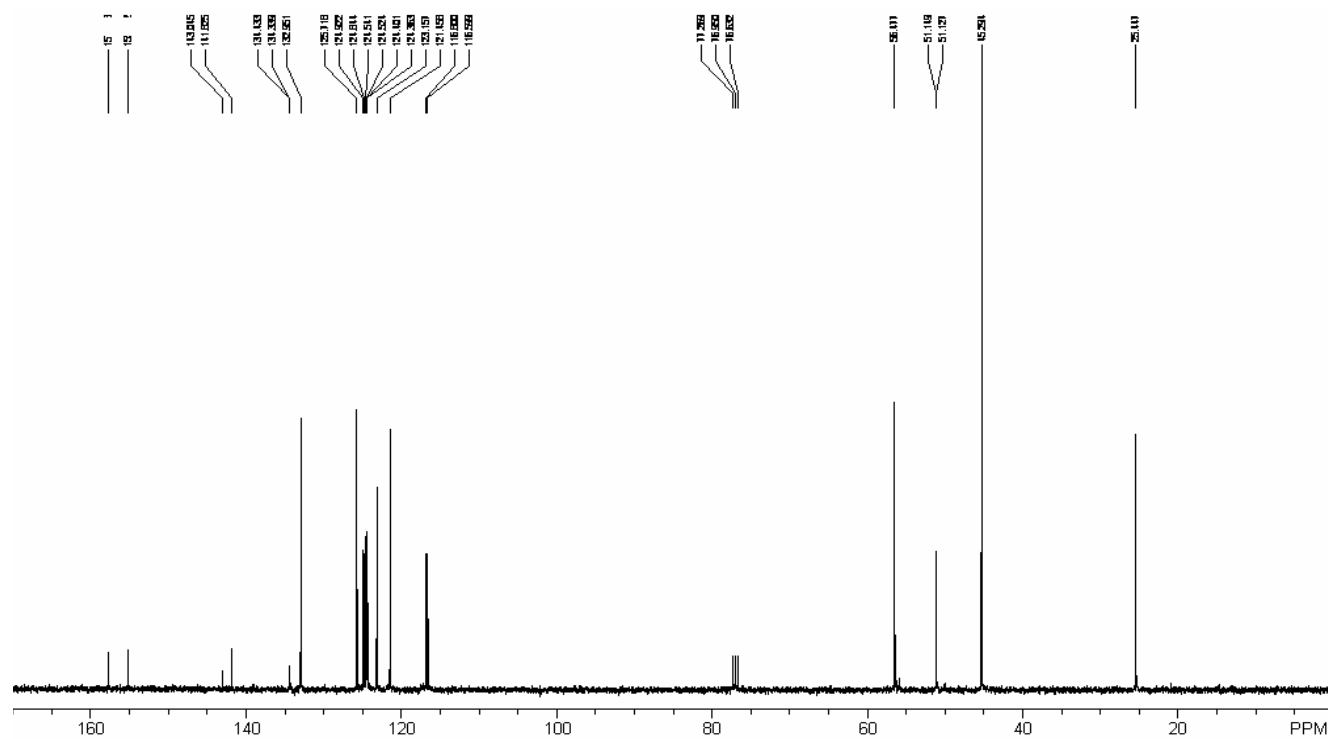


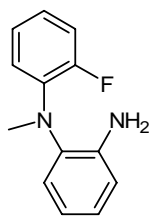


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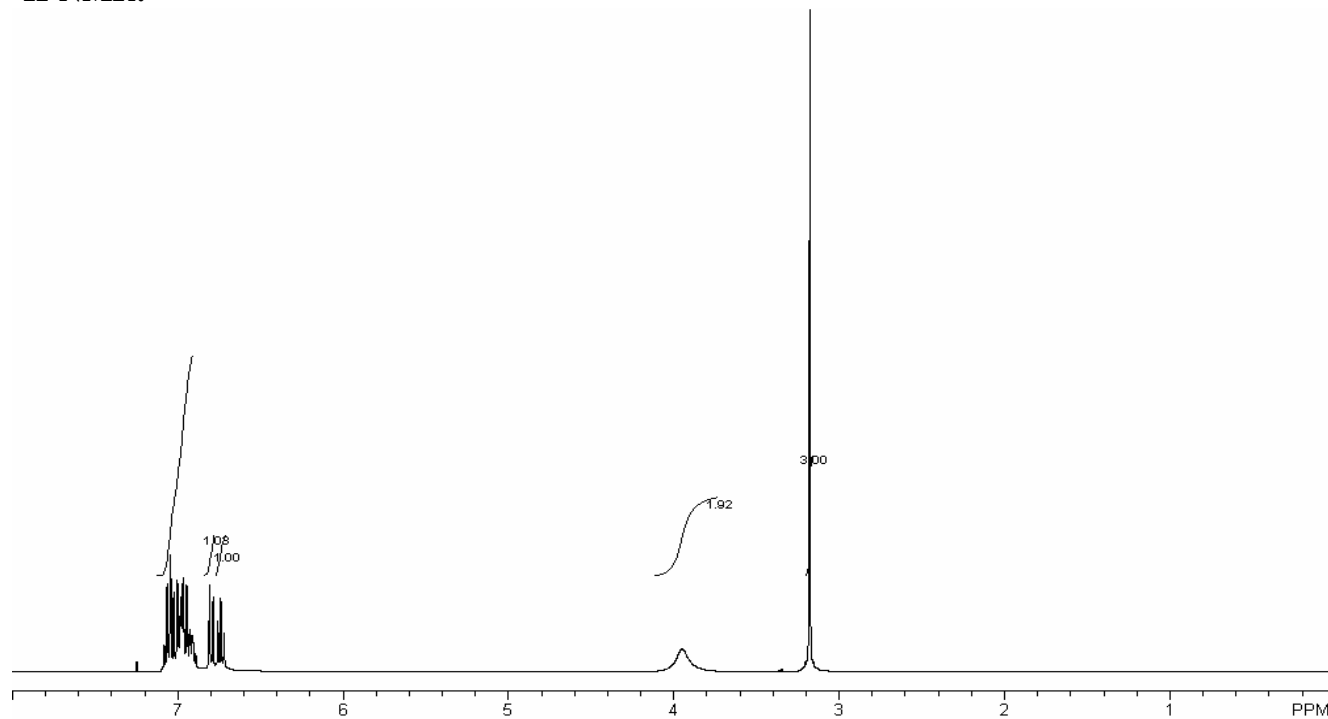
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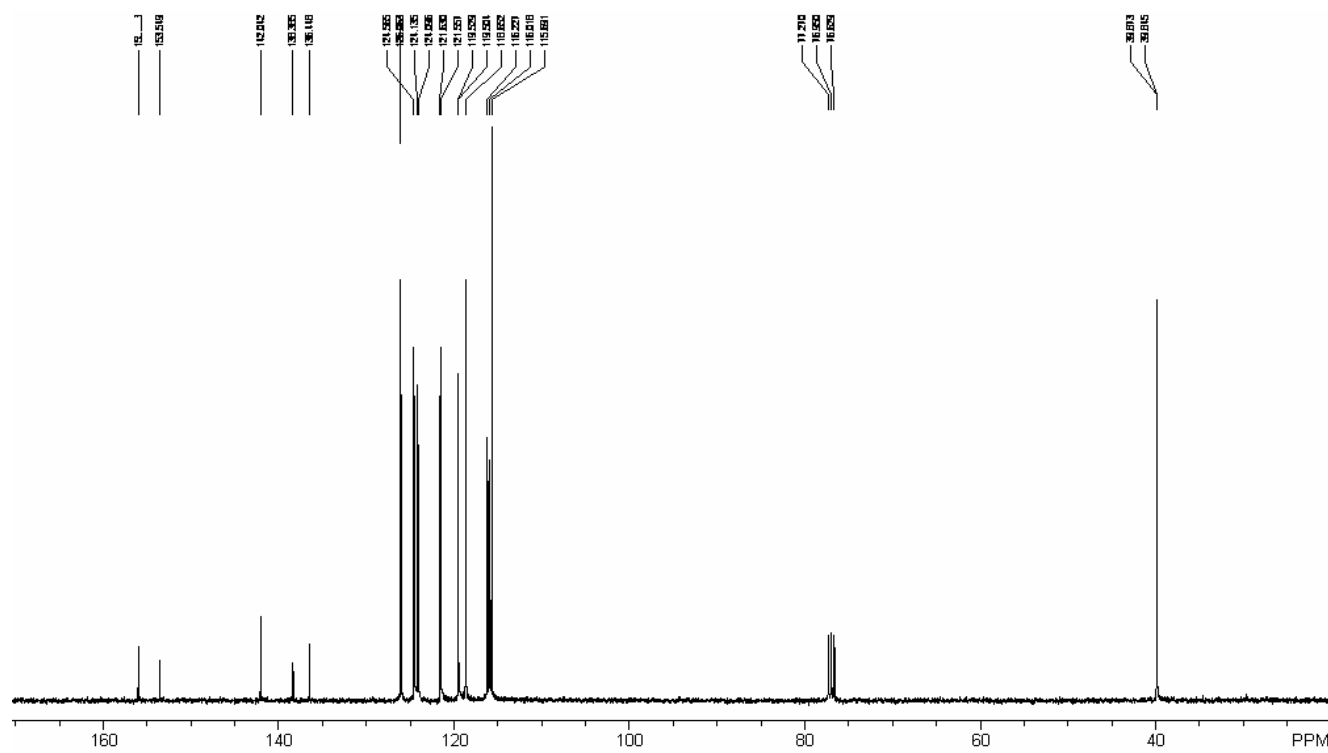


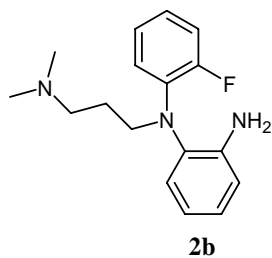
2a

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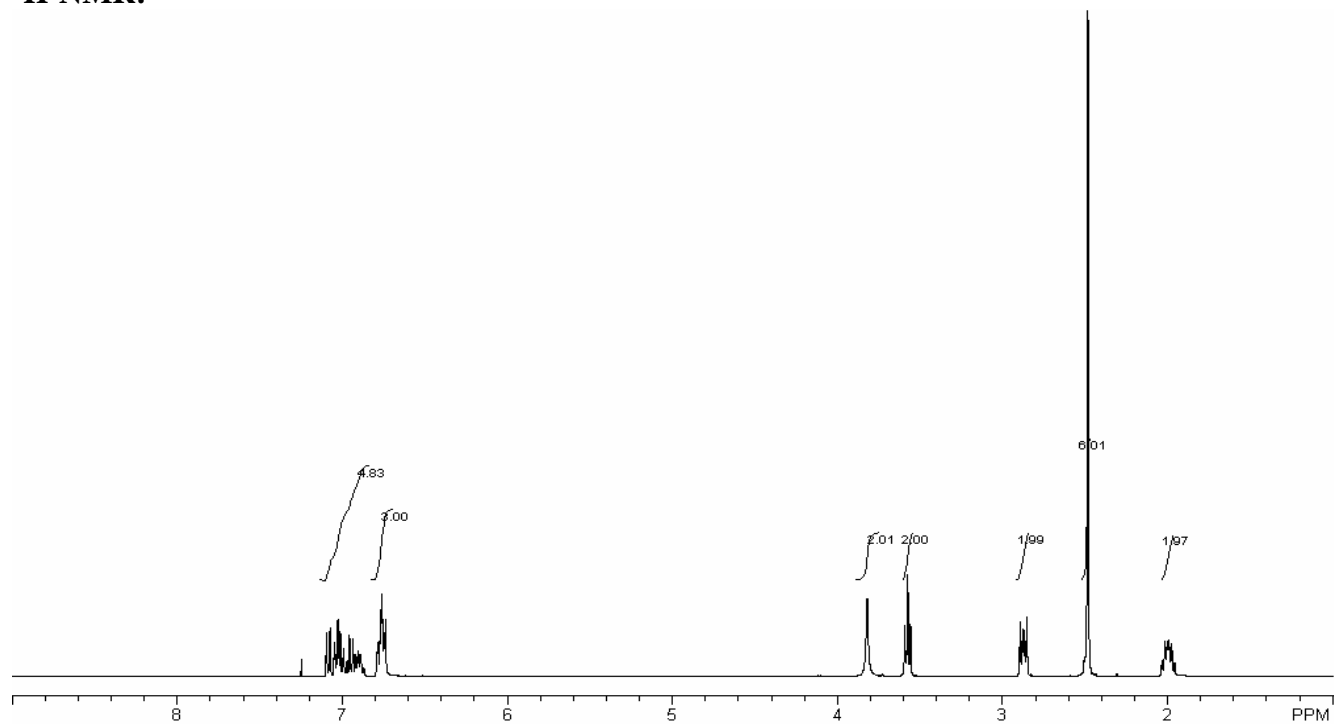


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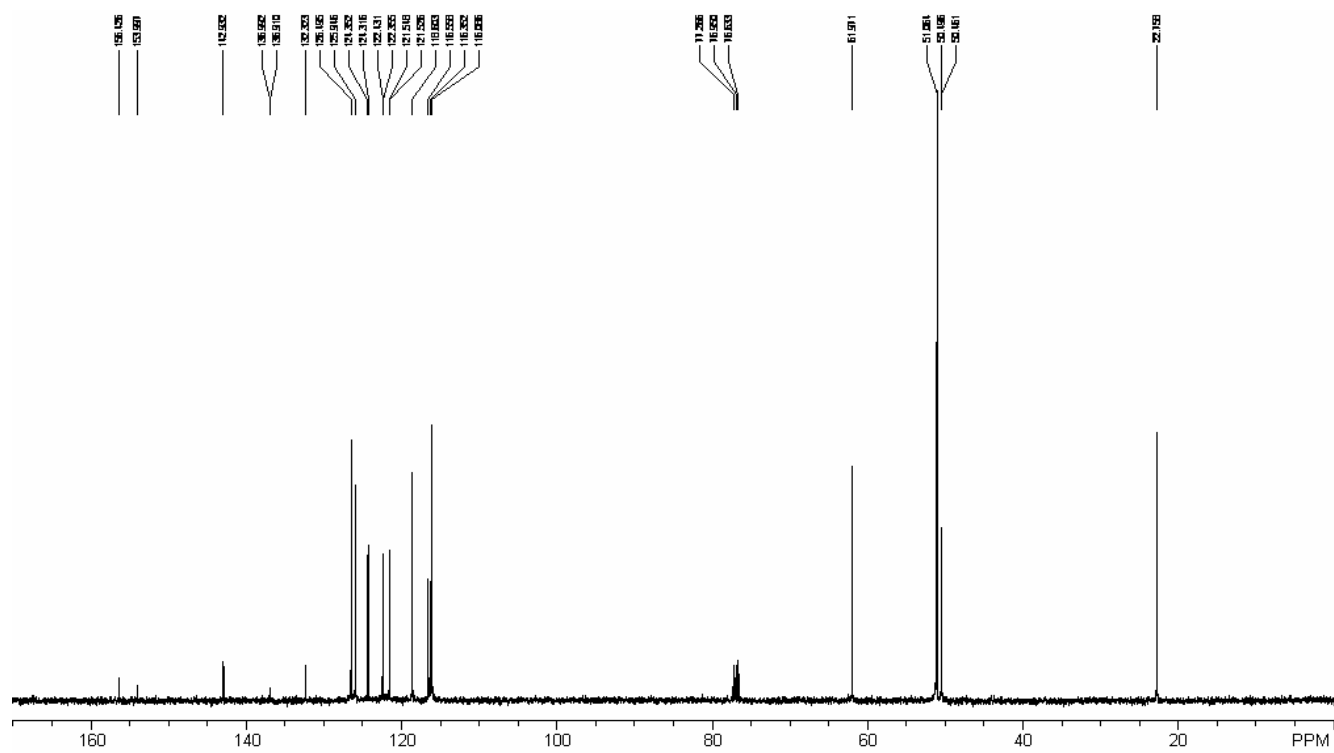


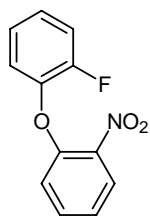


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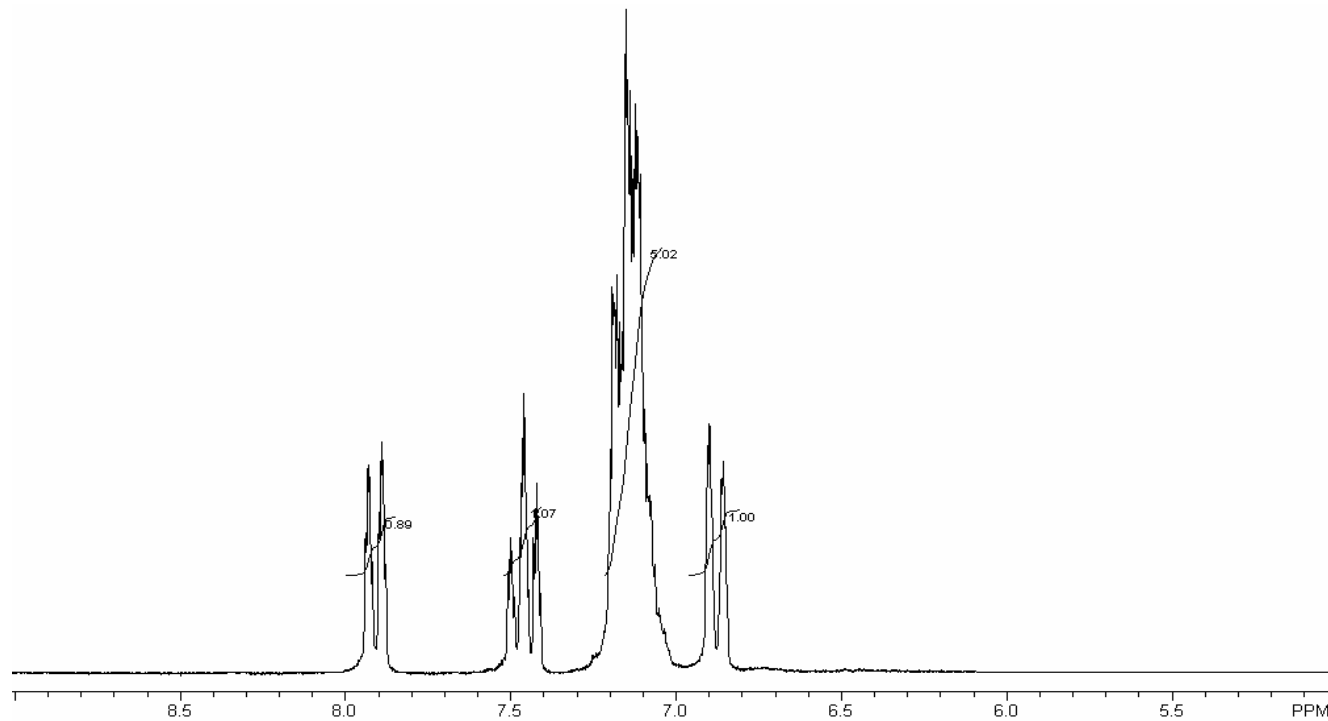
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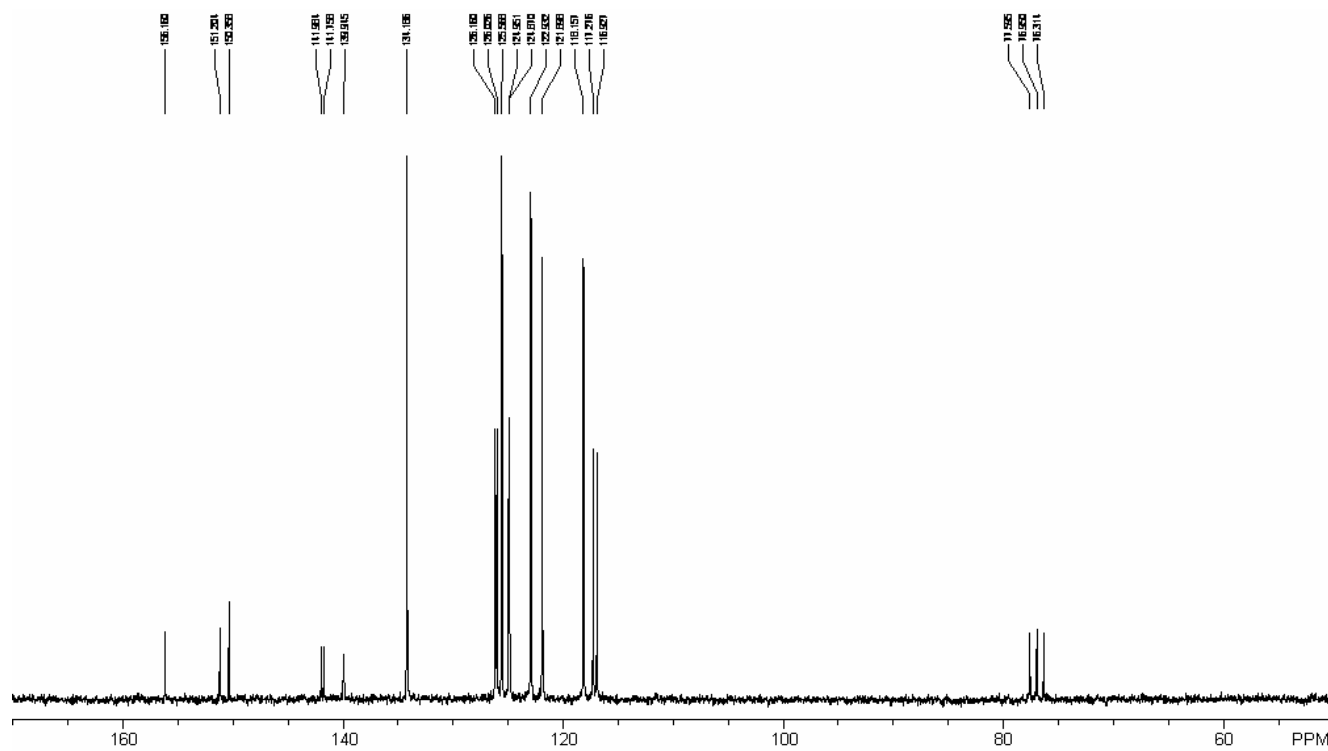


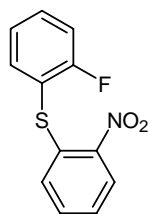
7a

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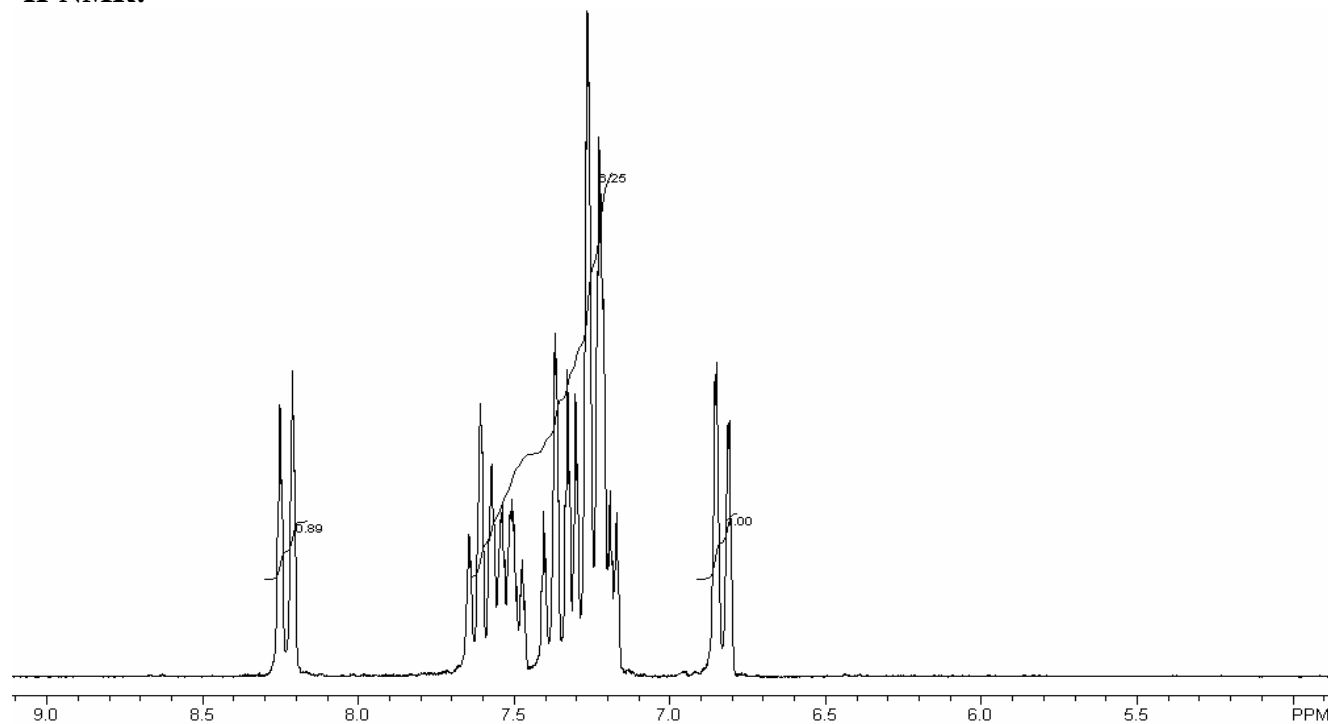
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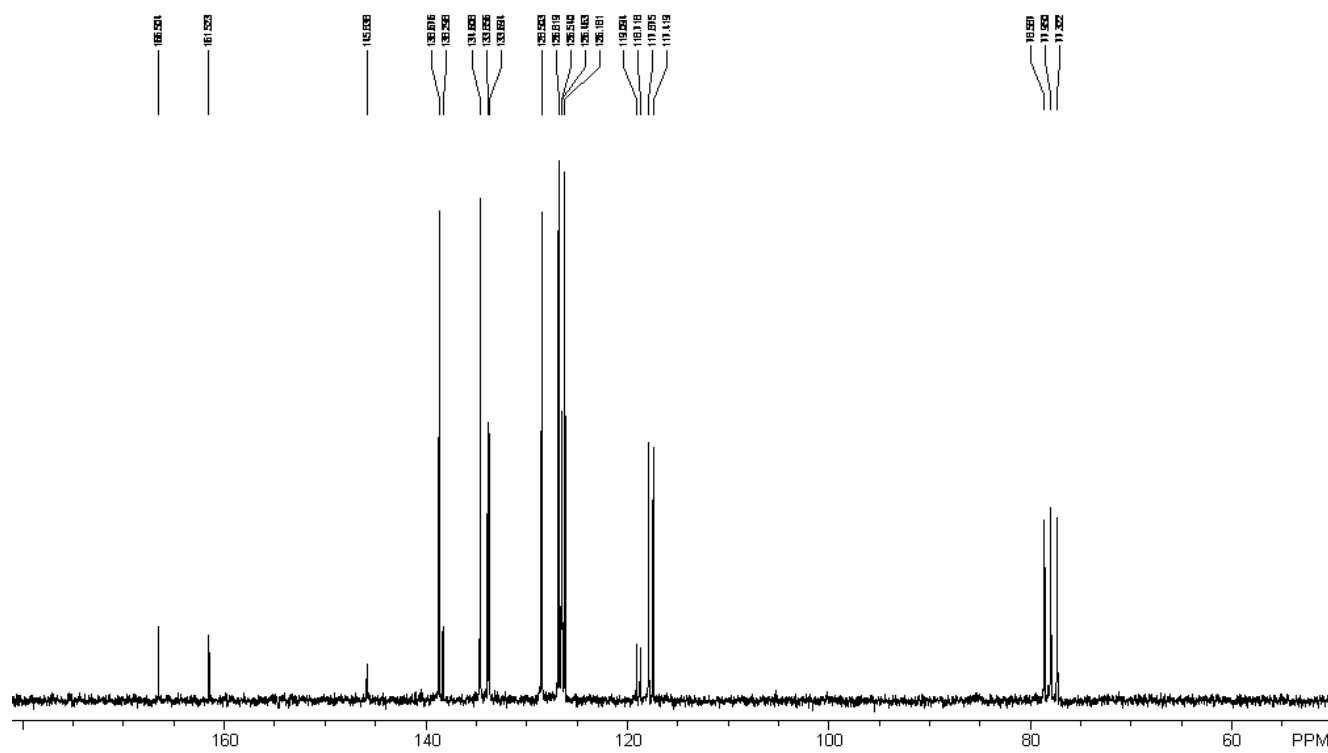


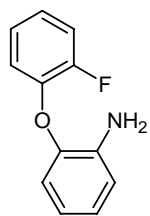
7b

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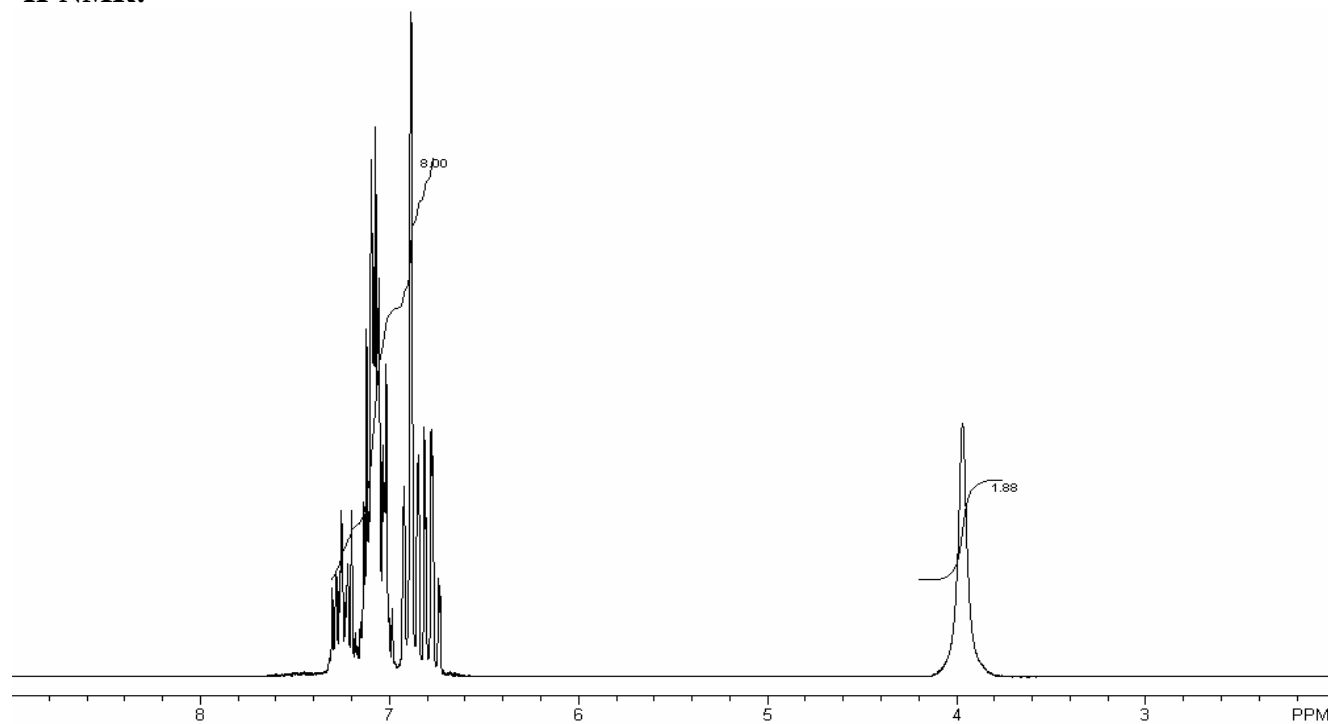
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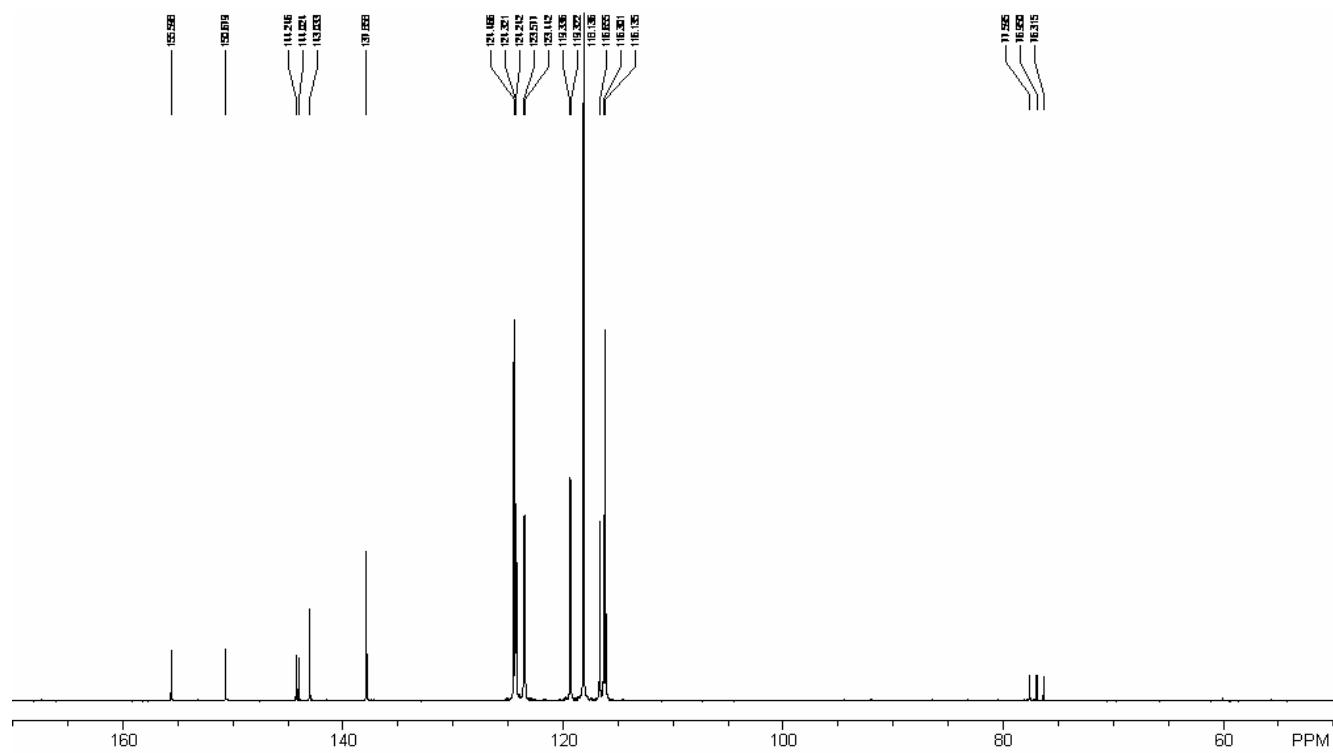


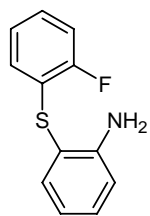
8a

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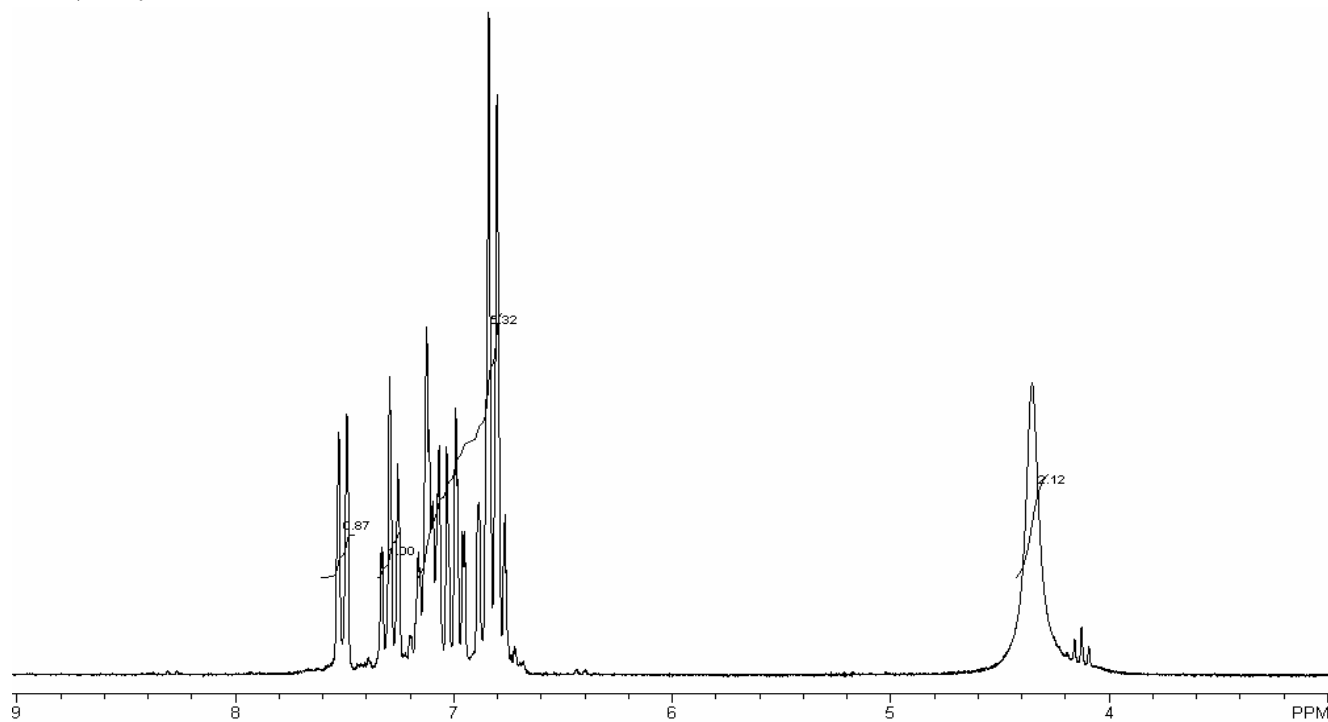
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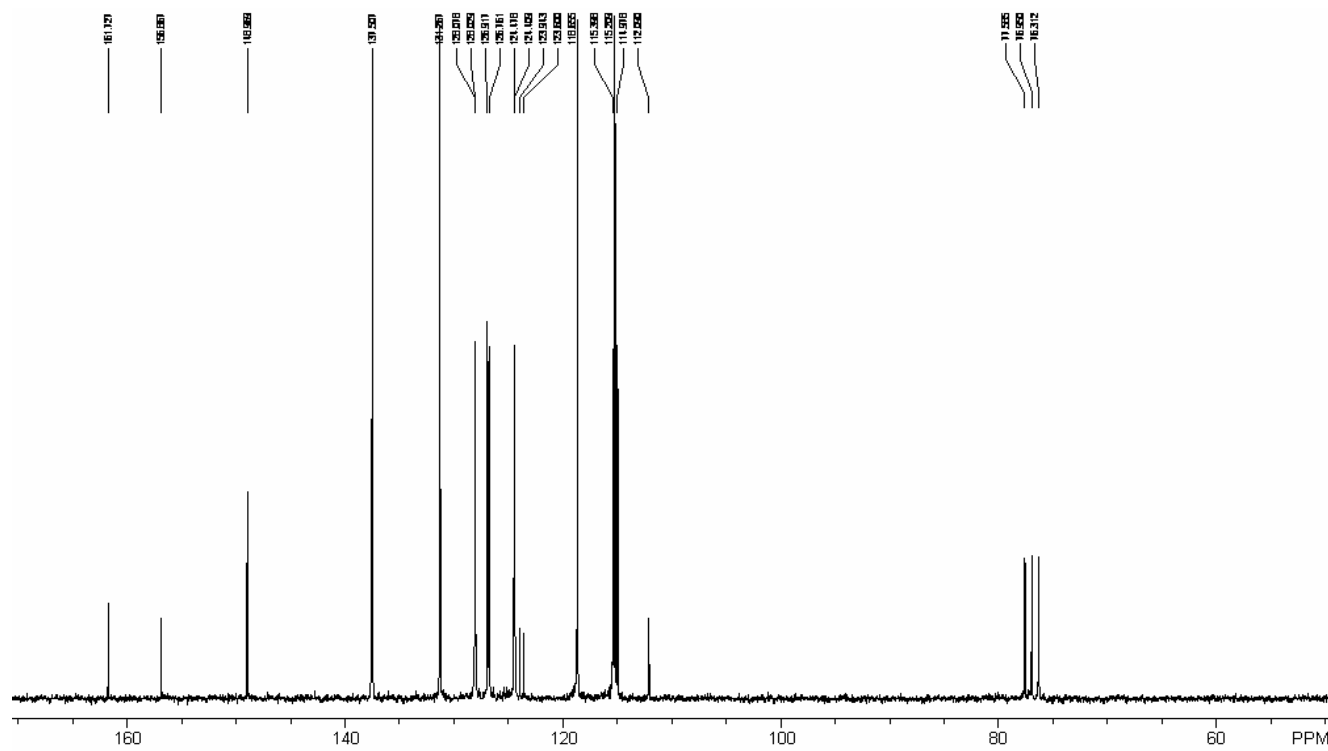


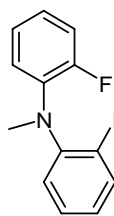
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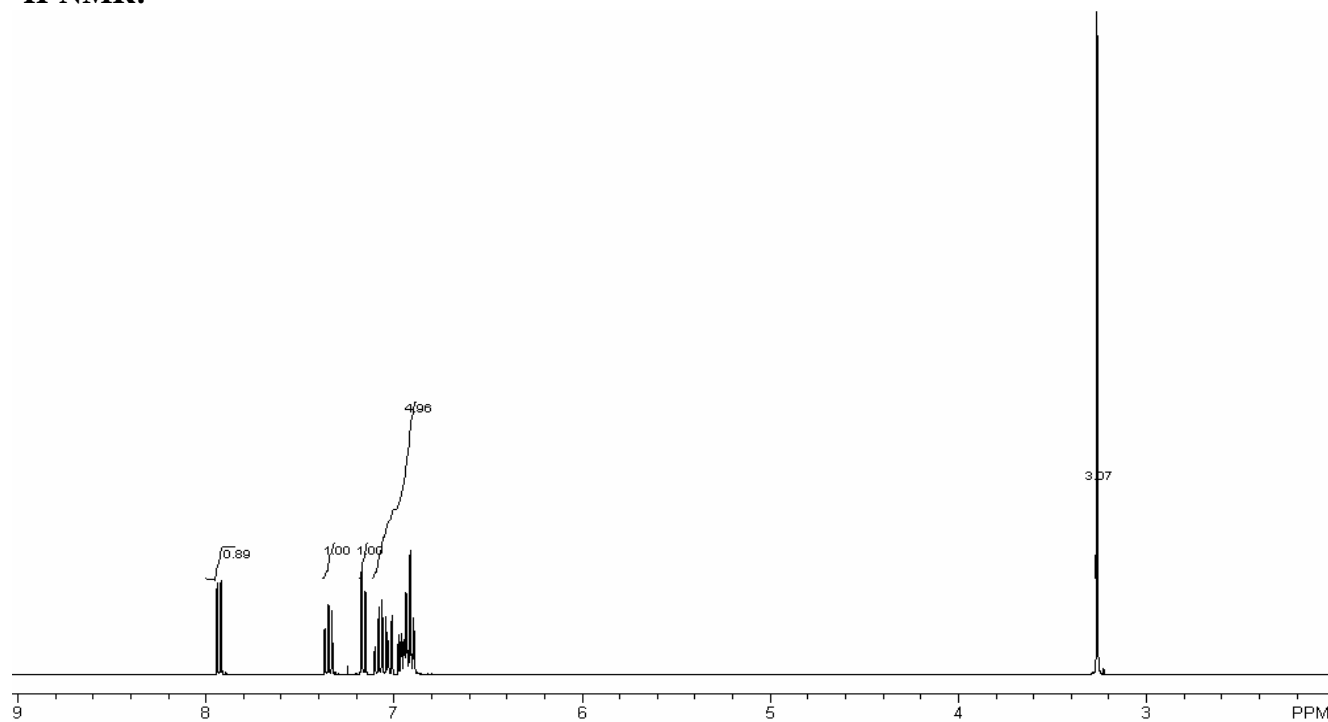
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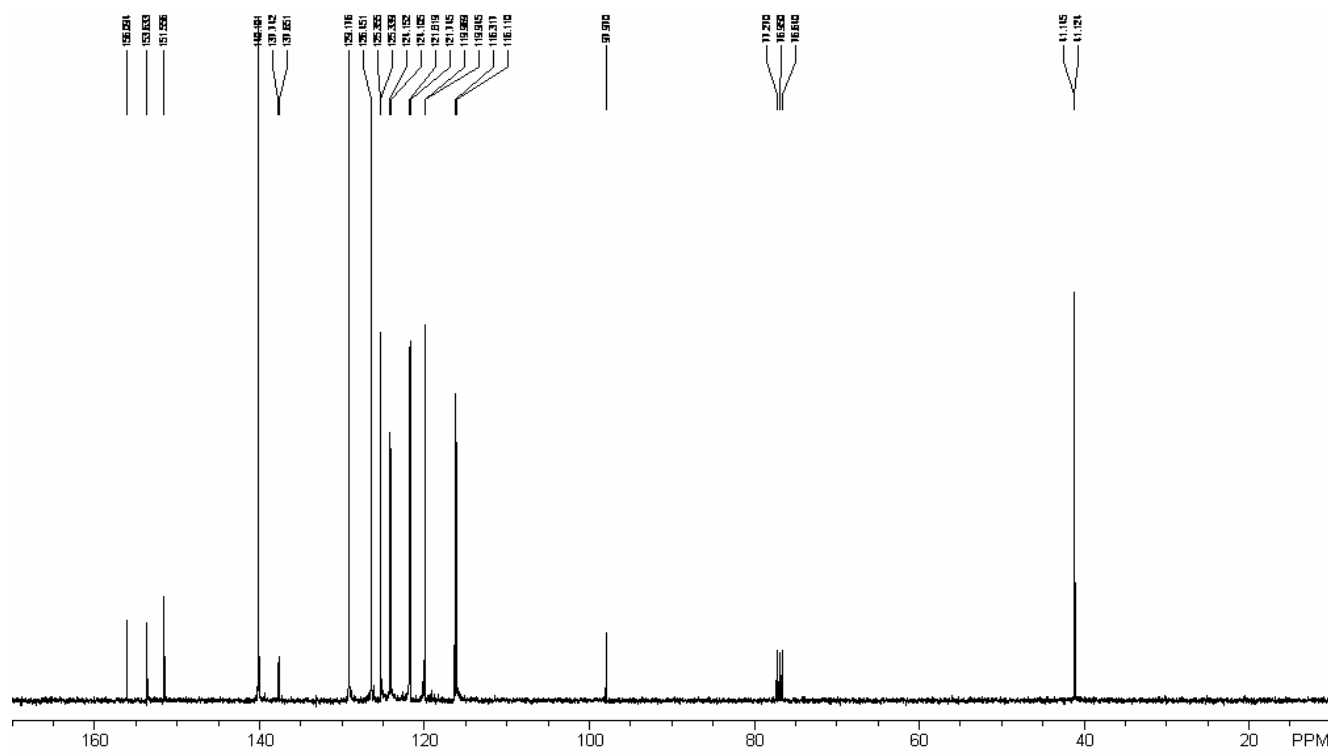


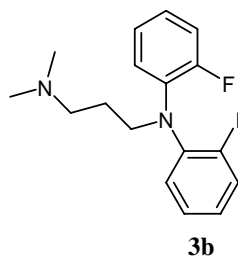
3a

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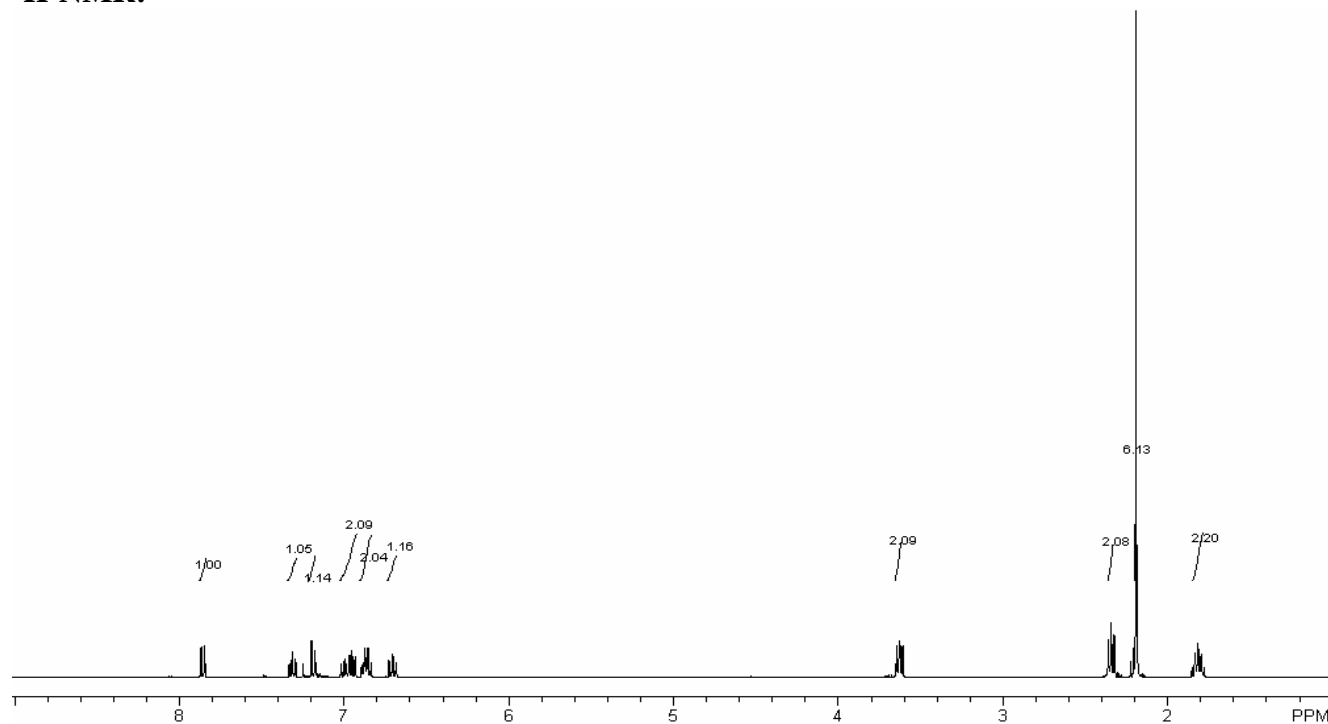


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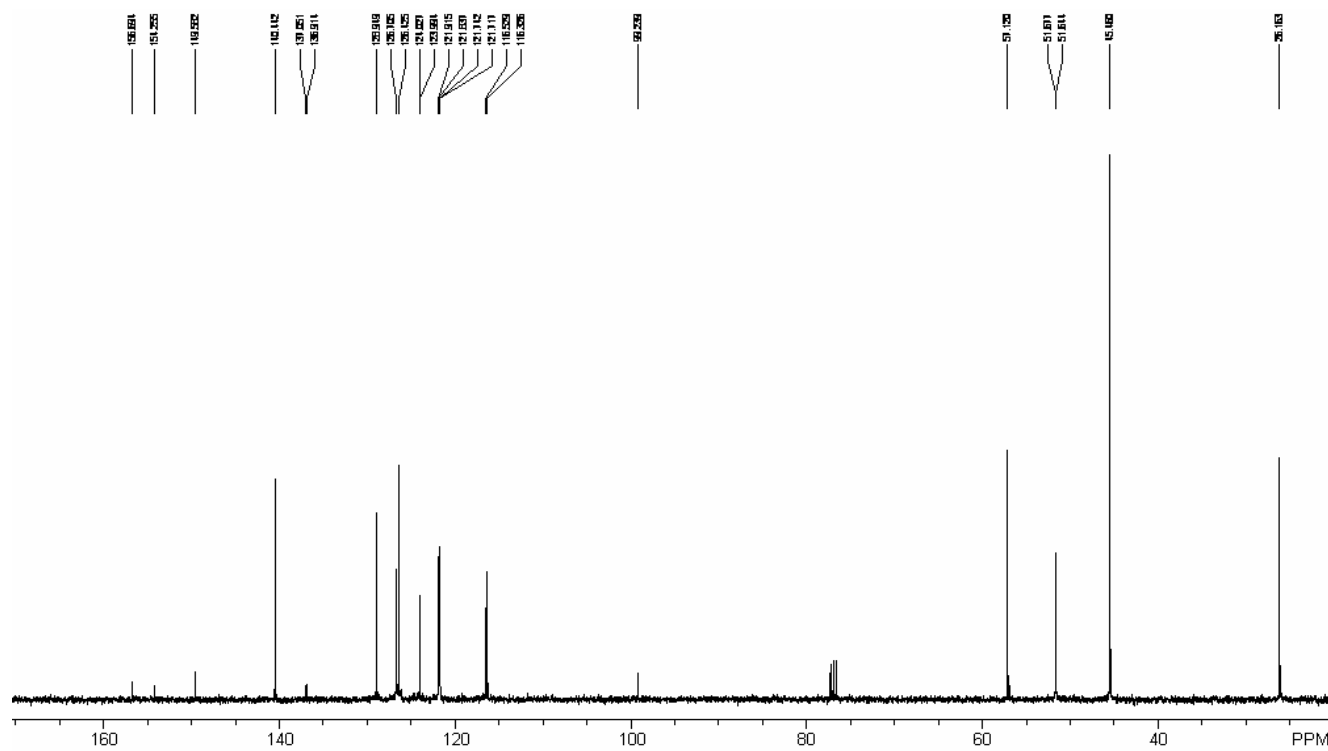


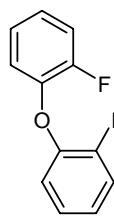


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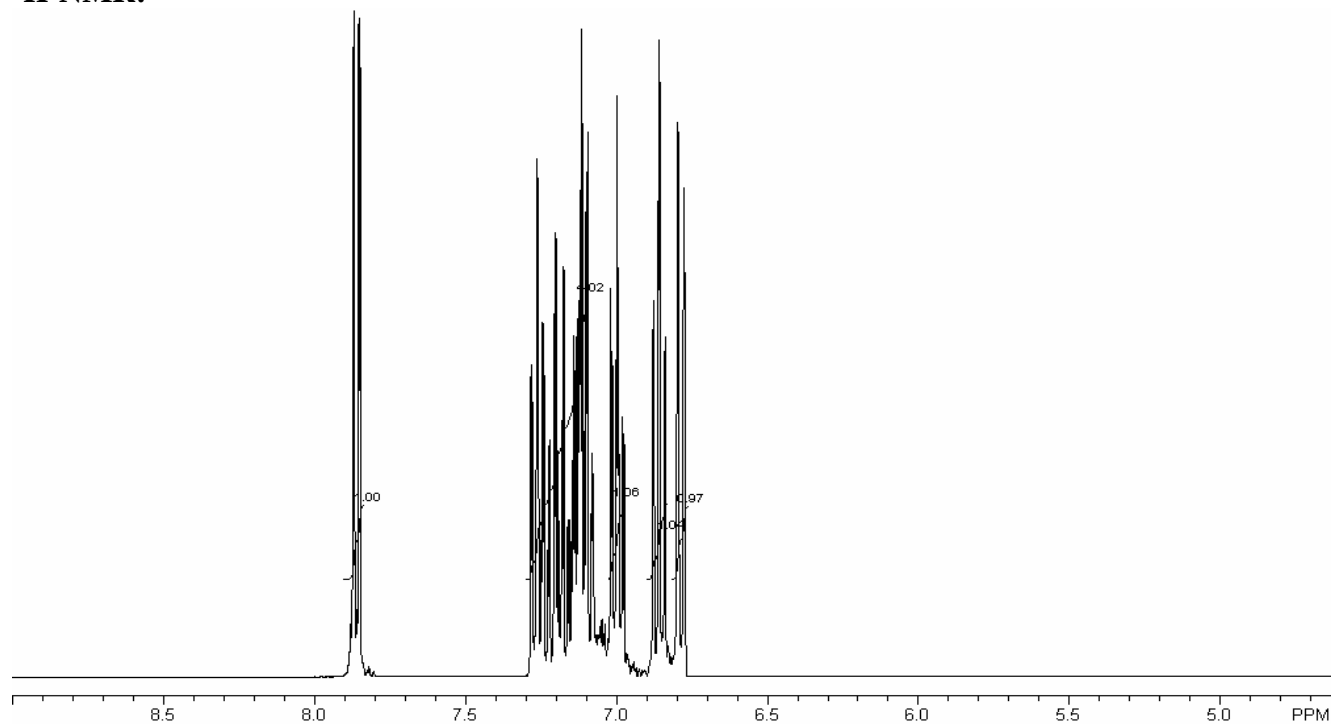
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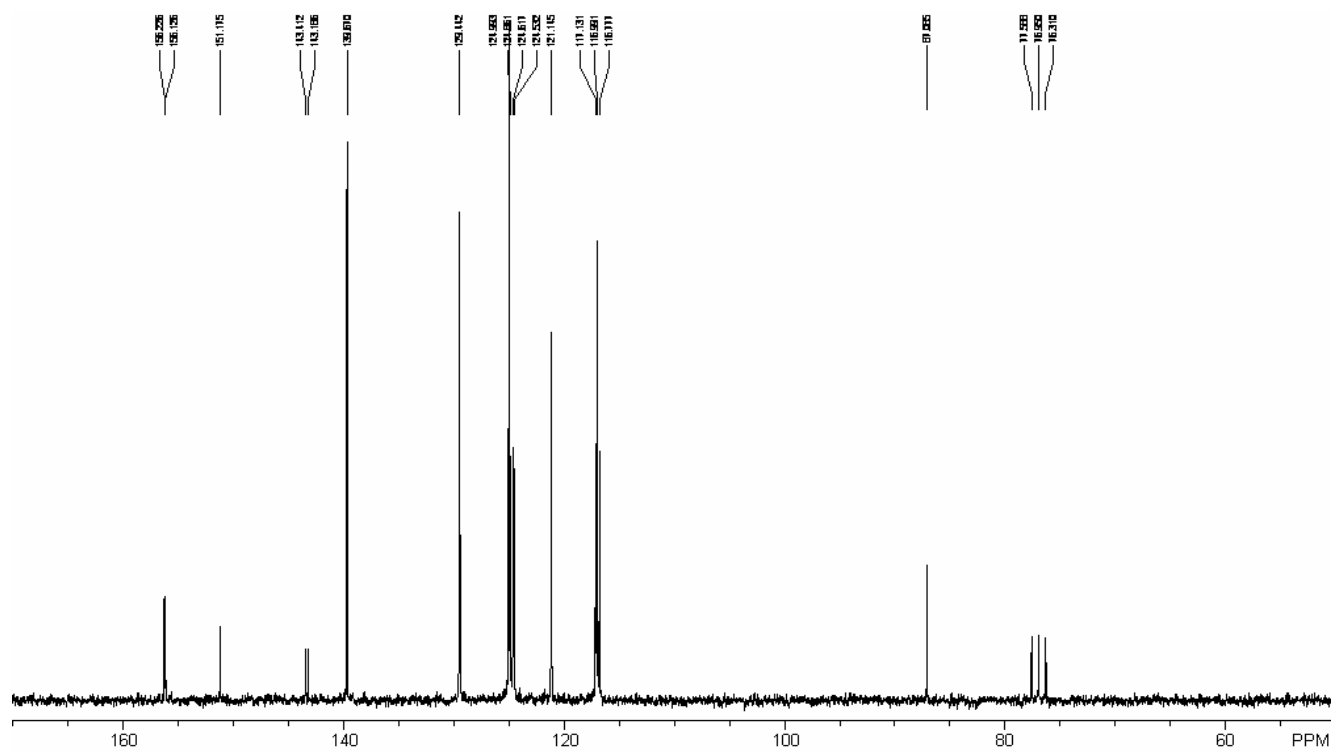


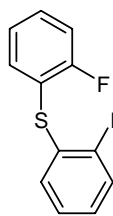
9a

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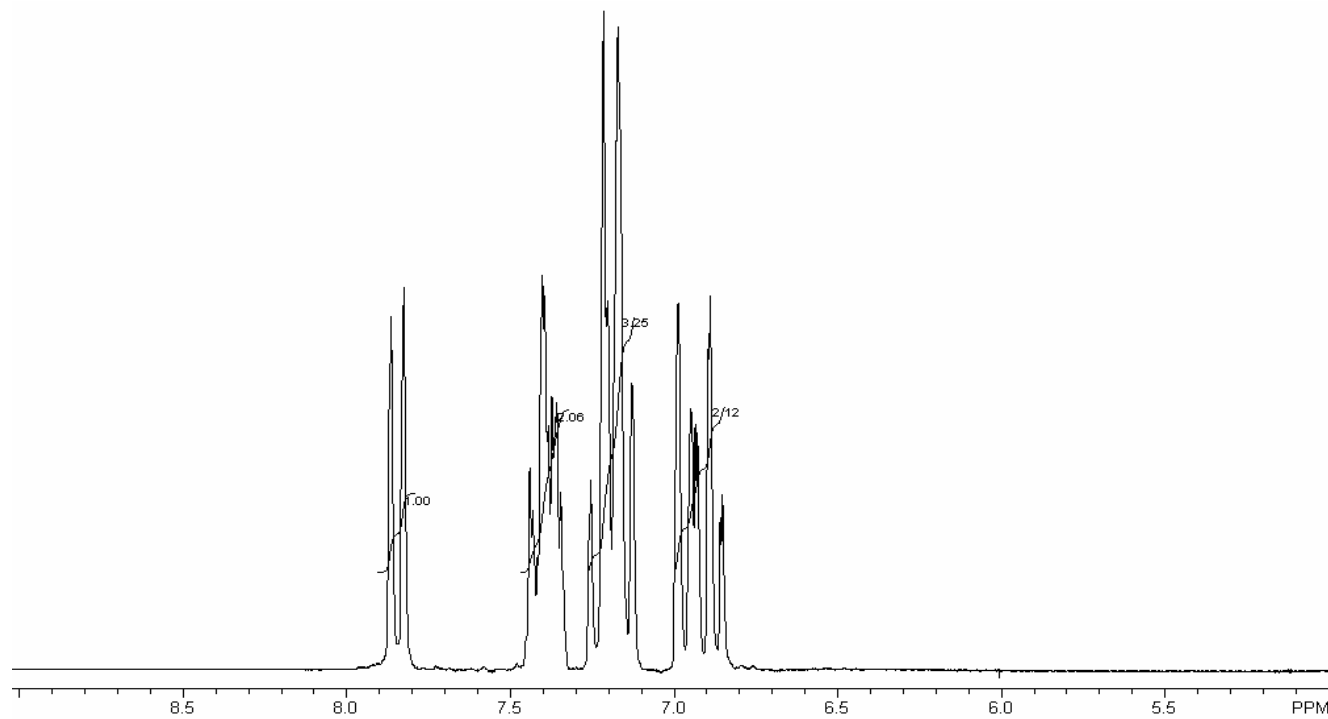
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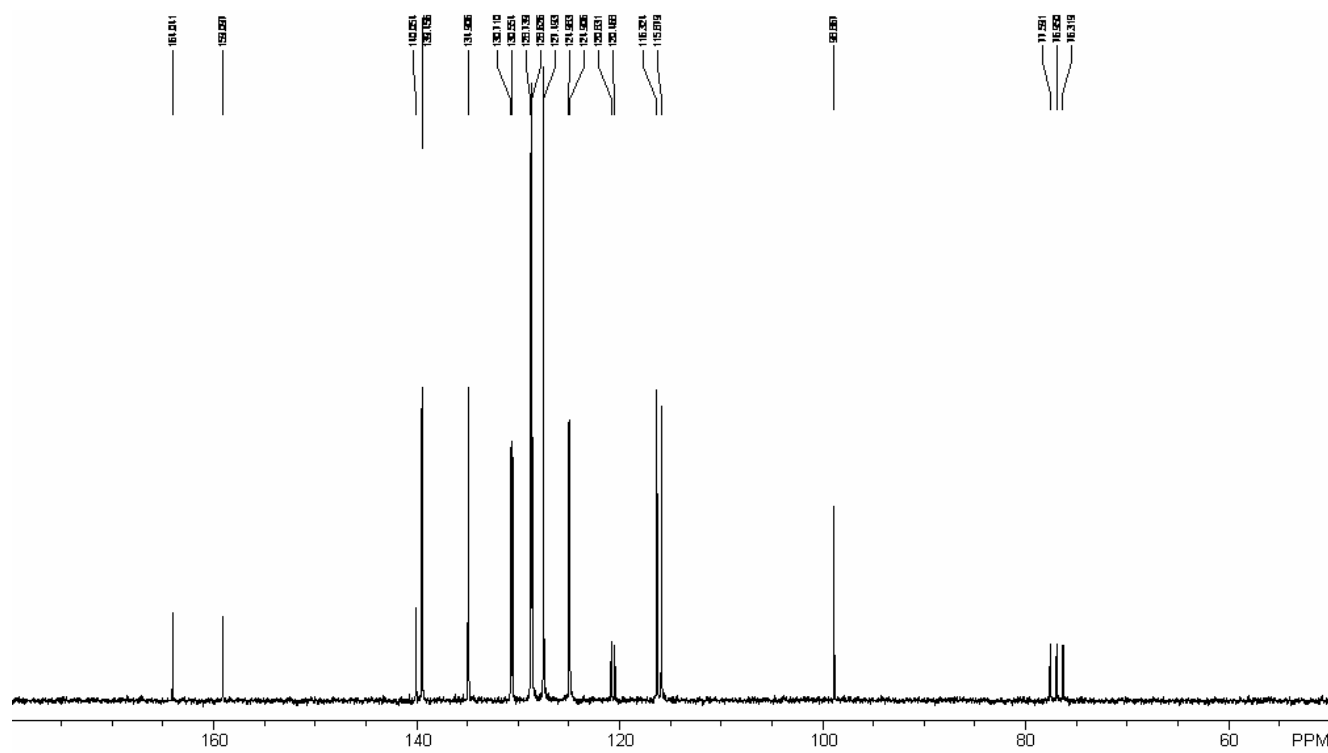


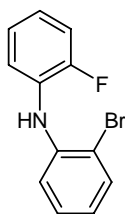
9b

^1H -NMR:



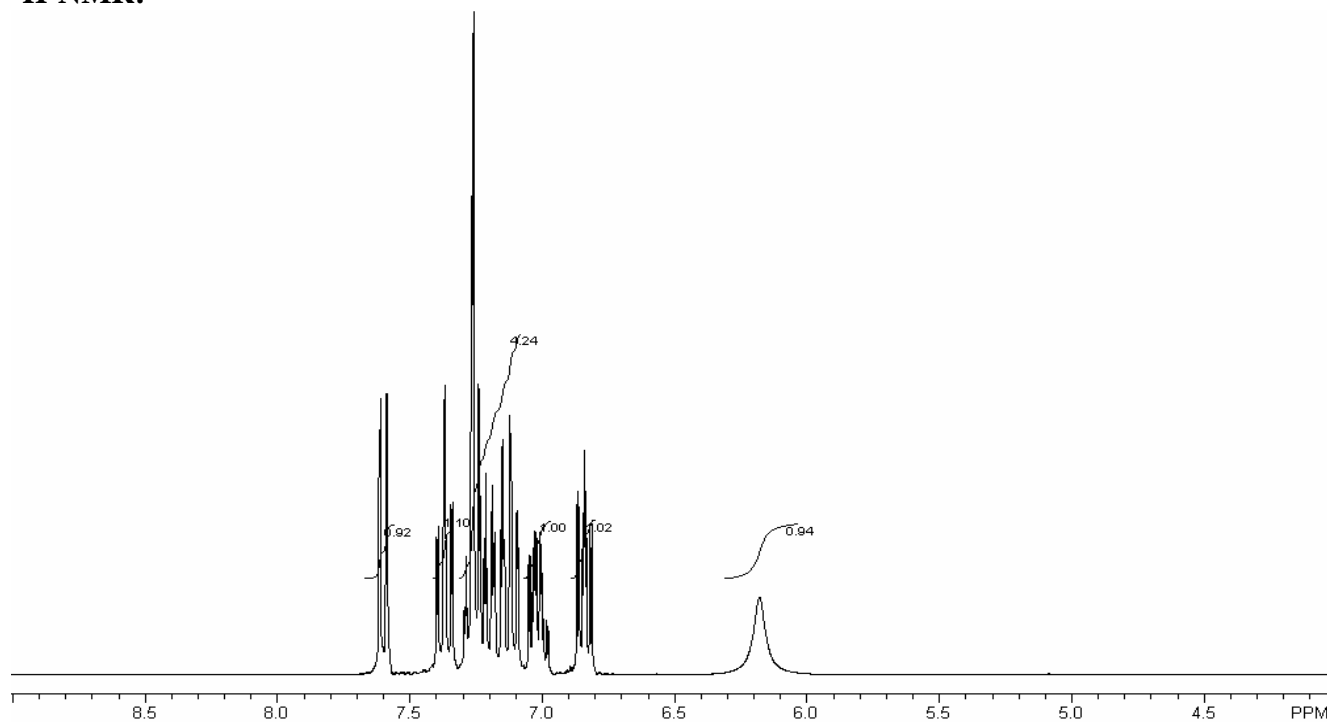
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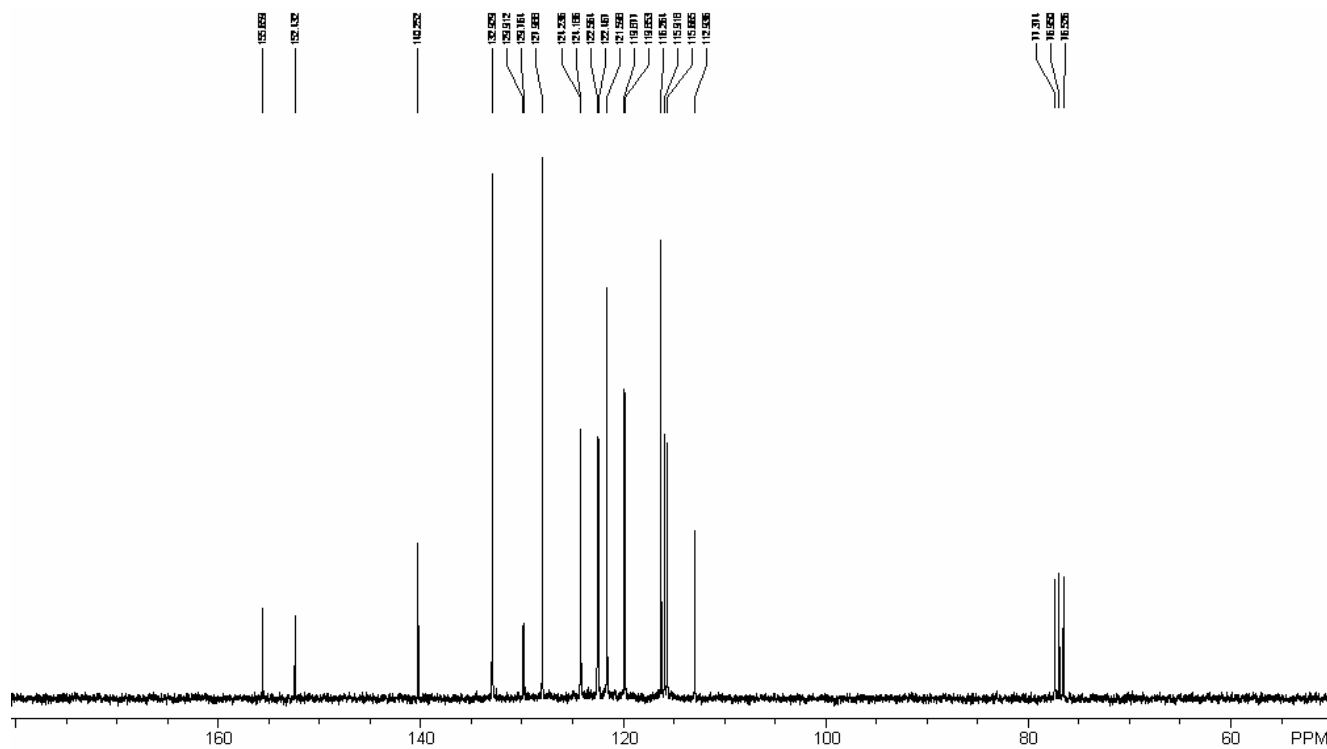


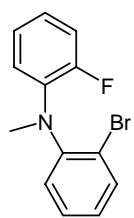
N-(2-Bromophenyl)-2-fluoroaniline

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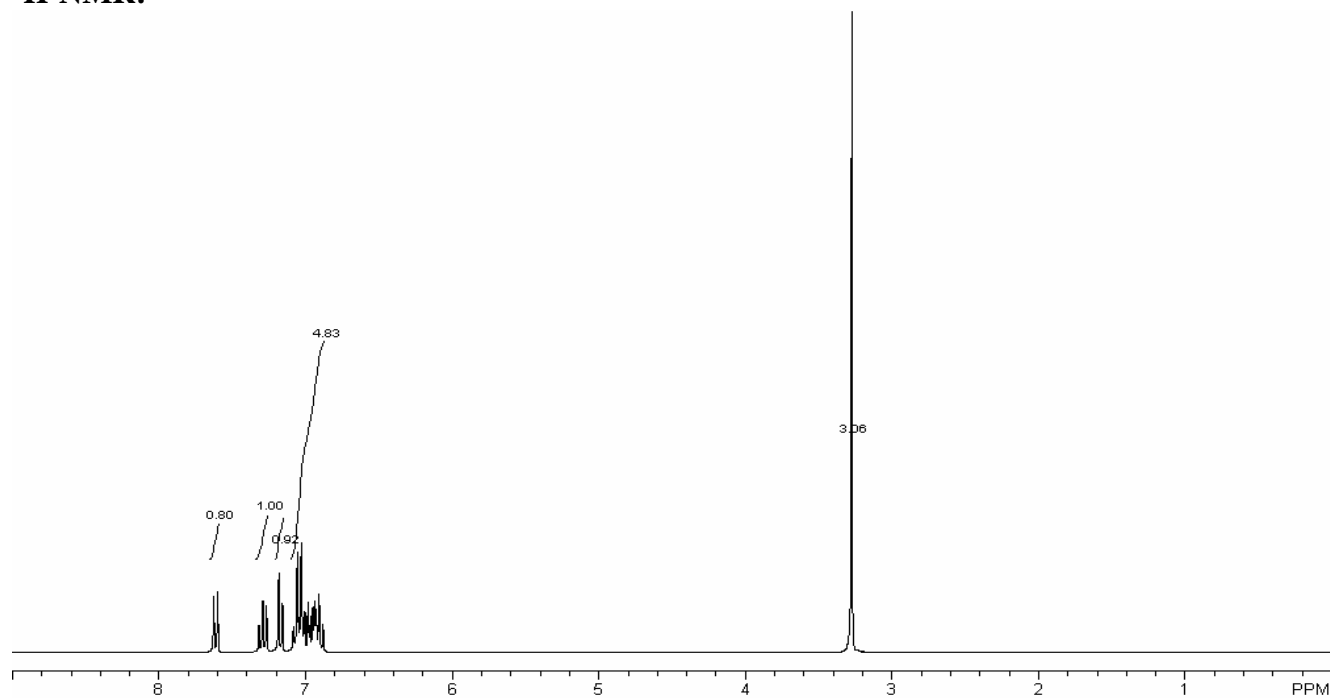
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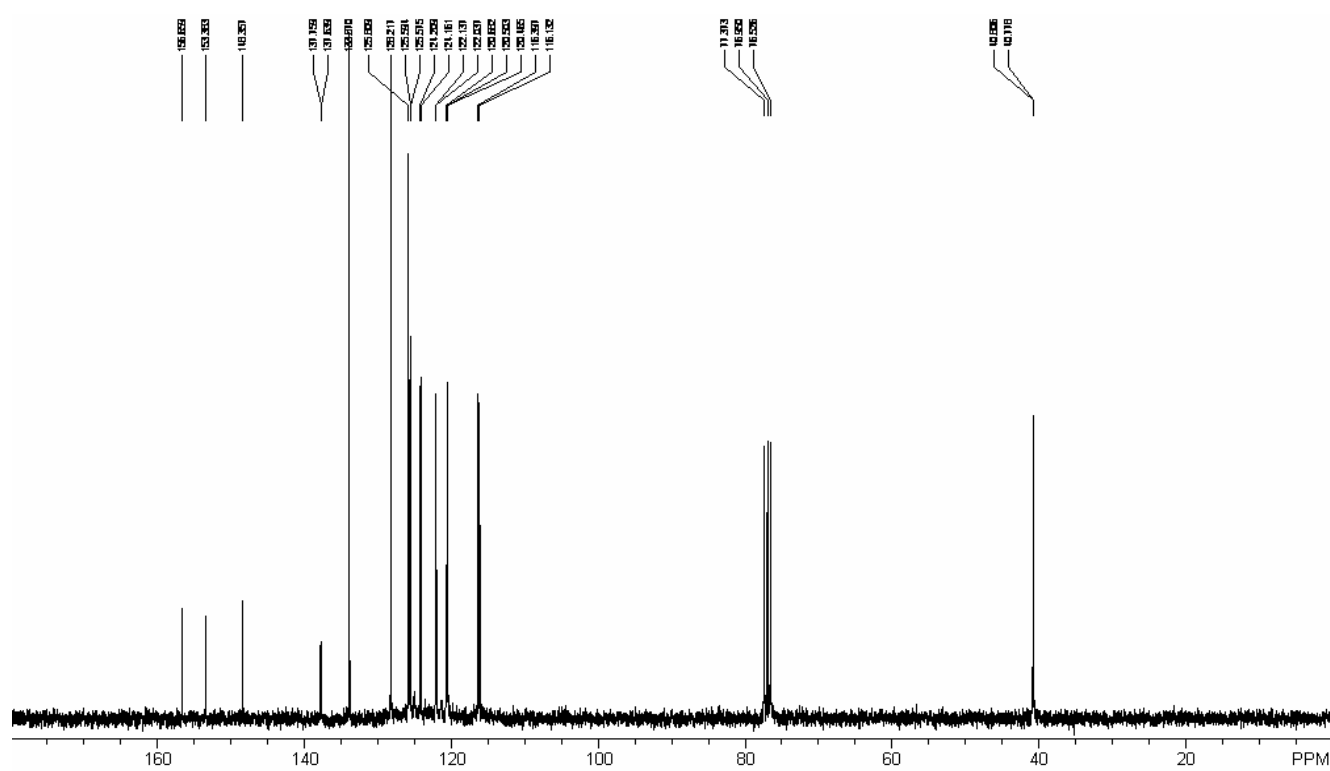


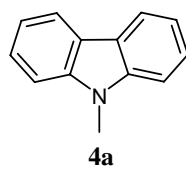
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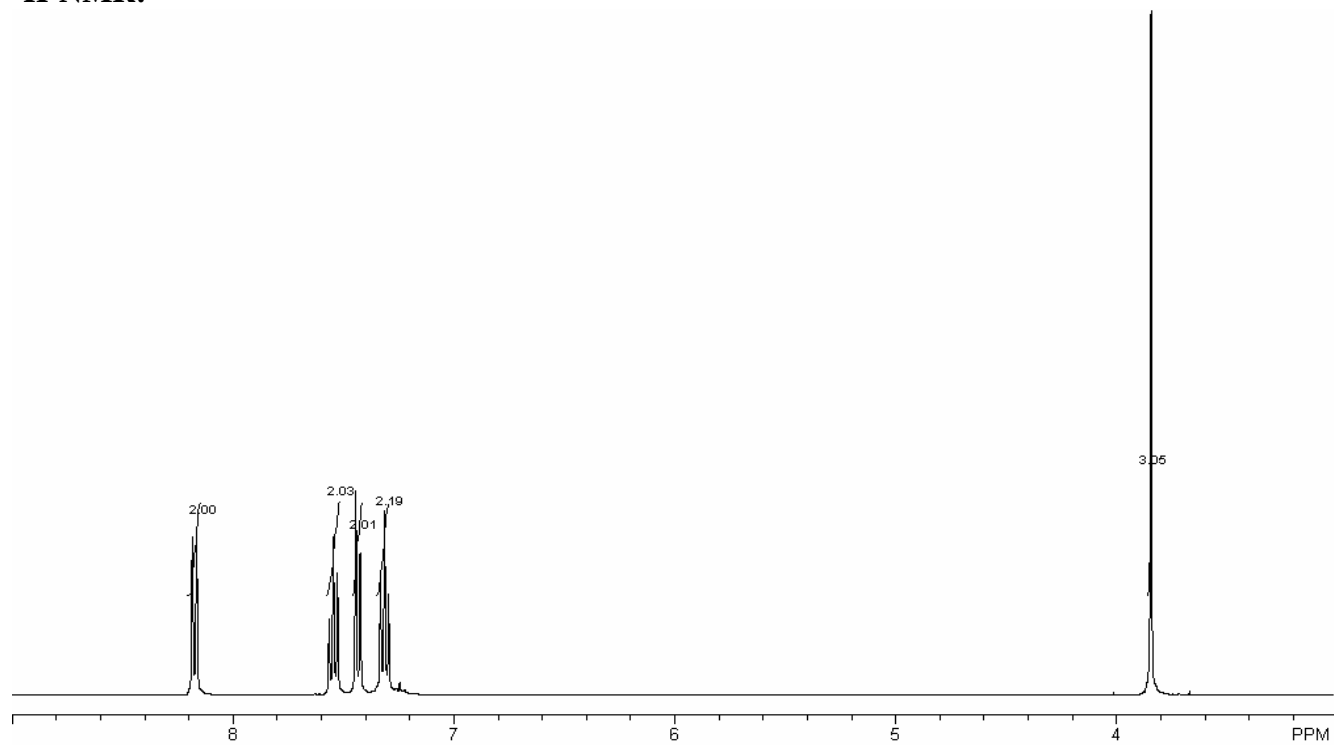


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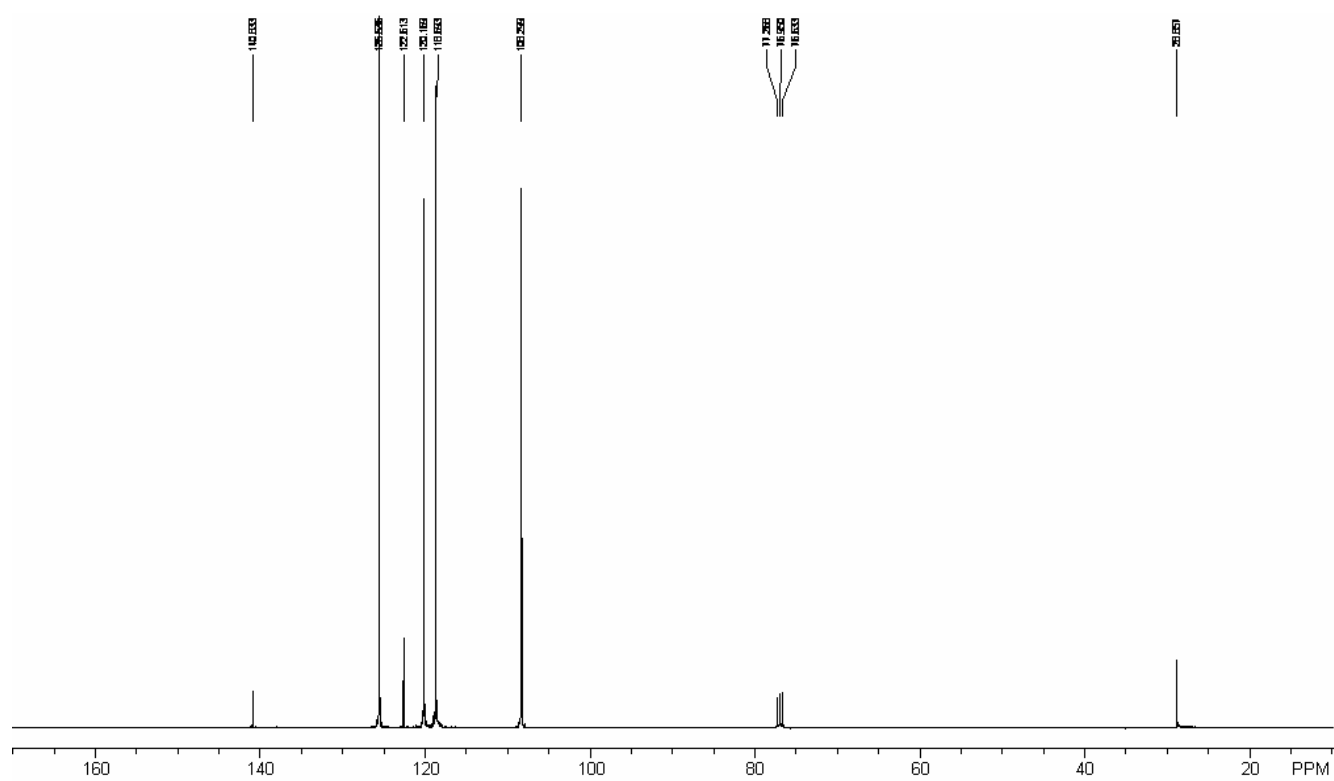


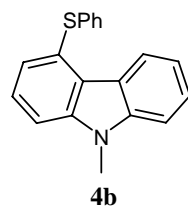


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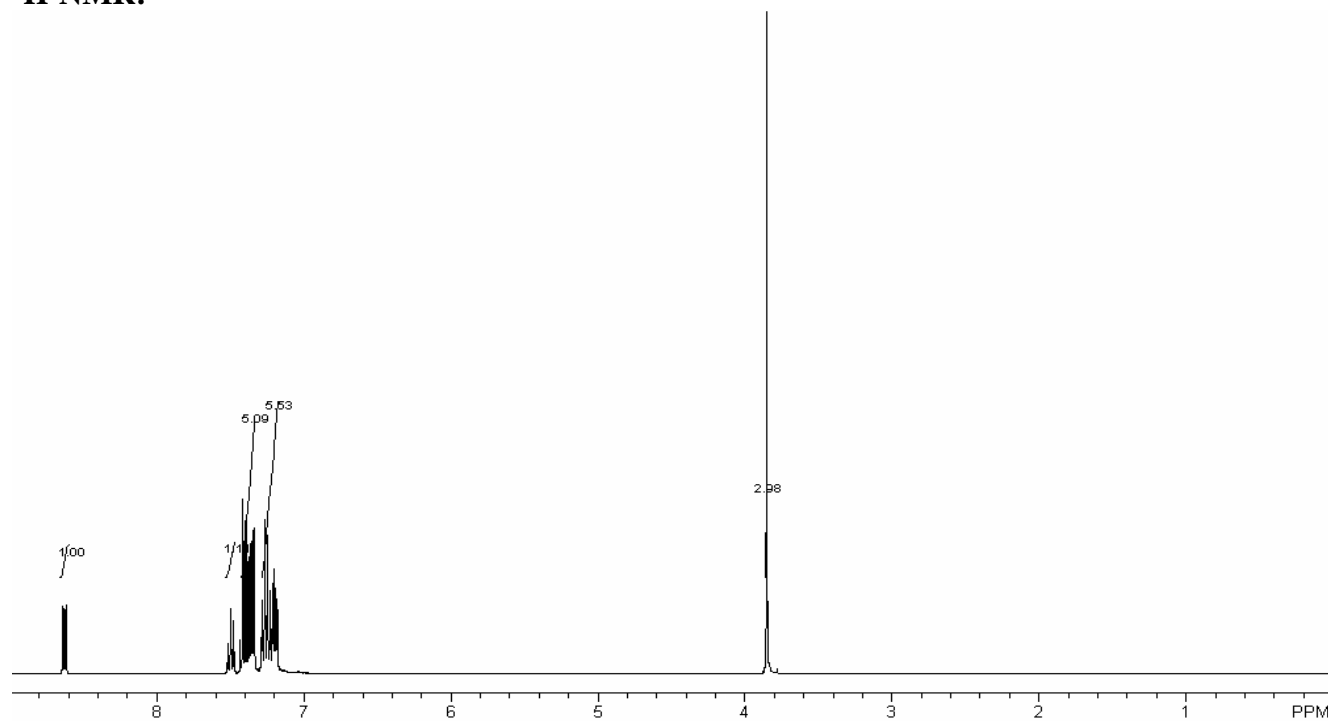


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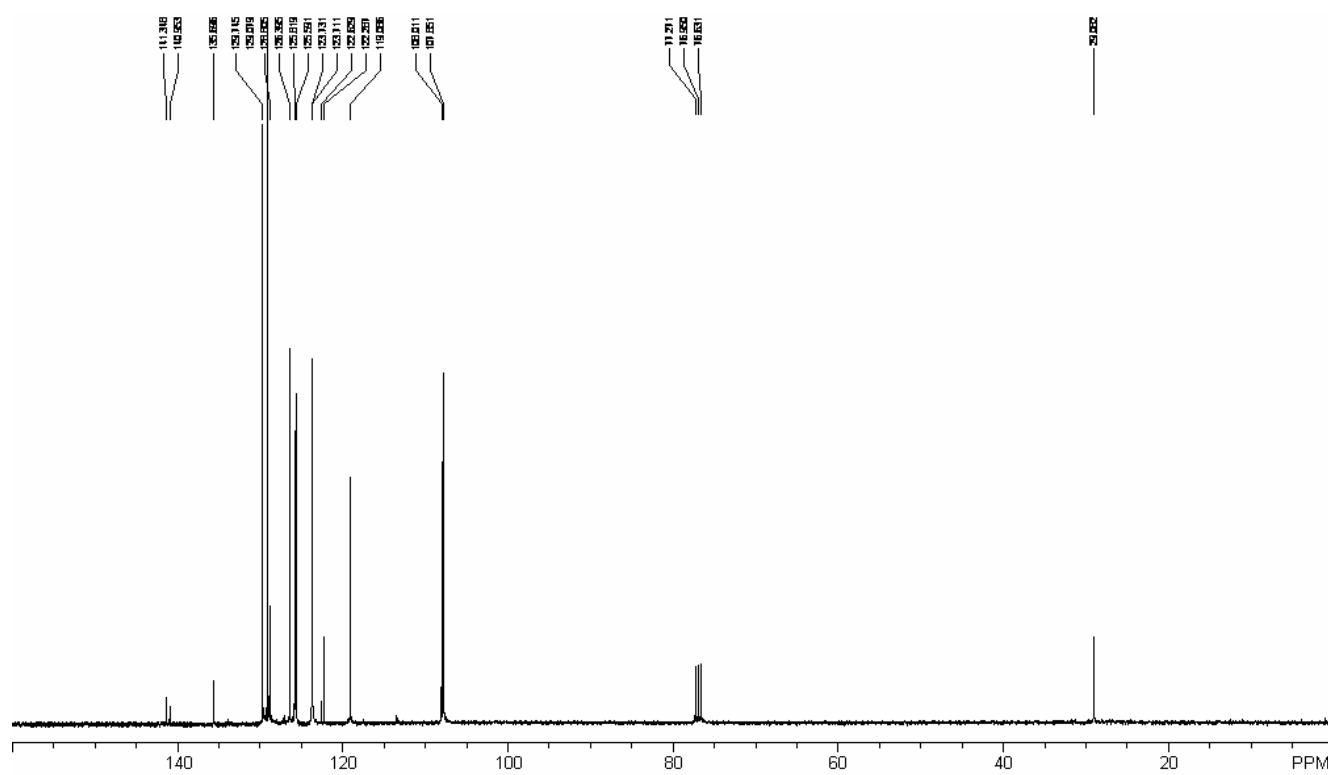


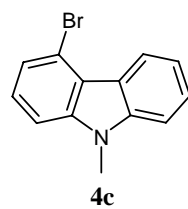


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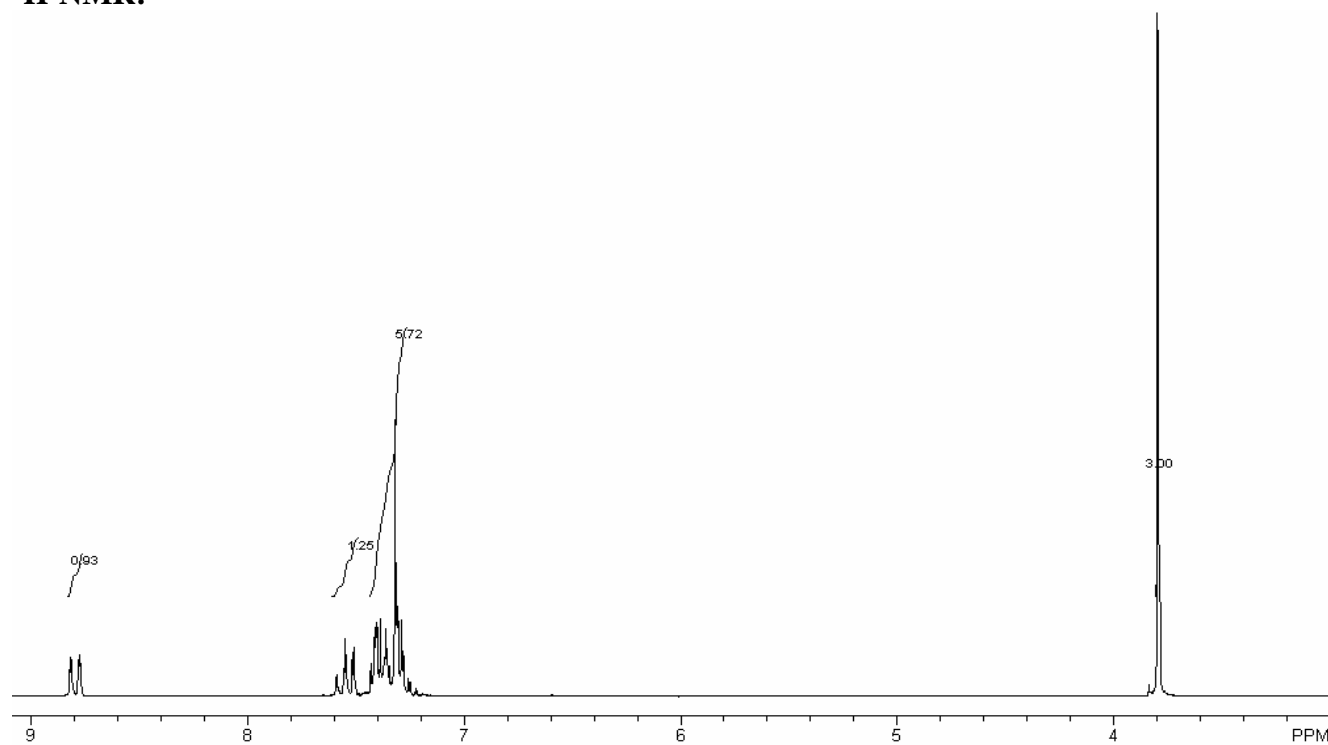


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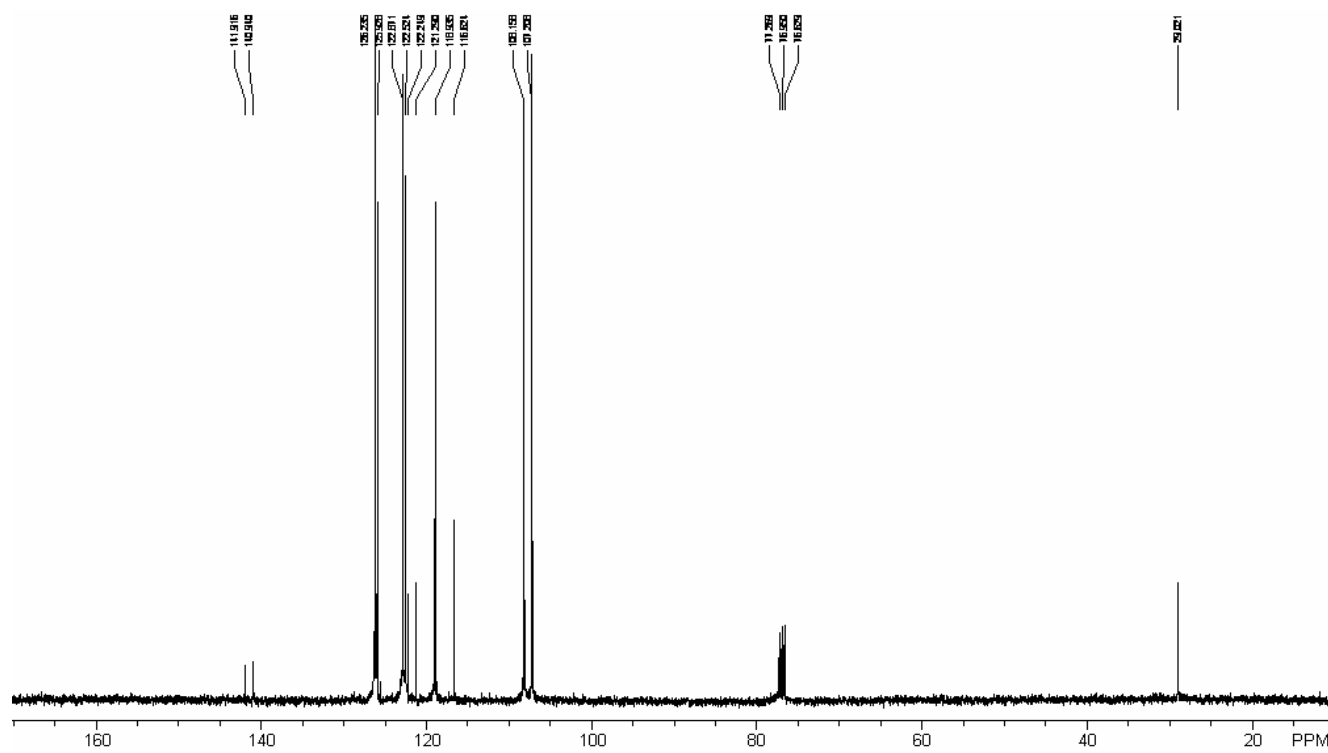


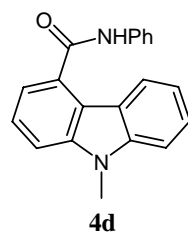


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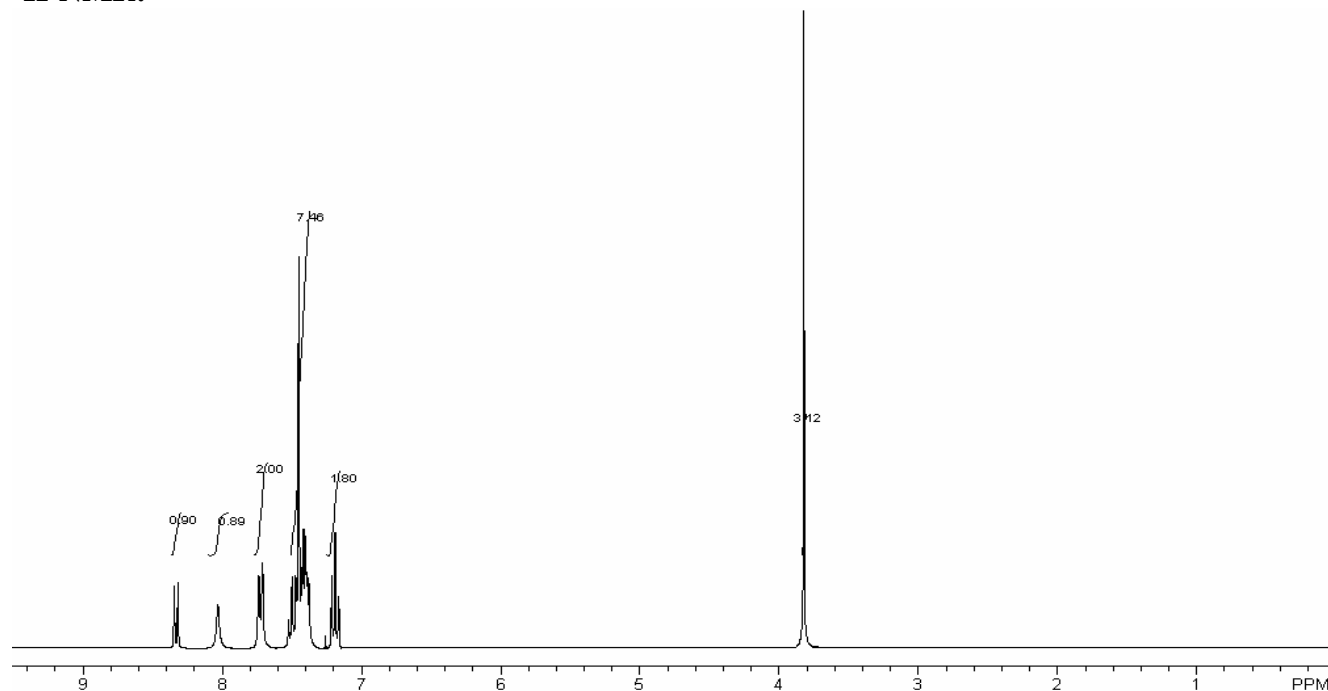


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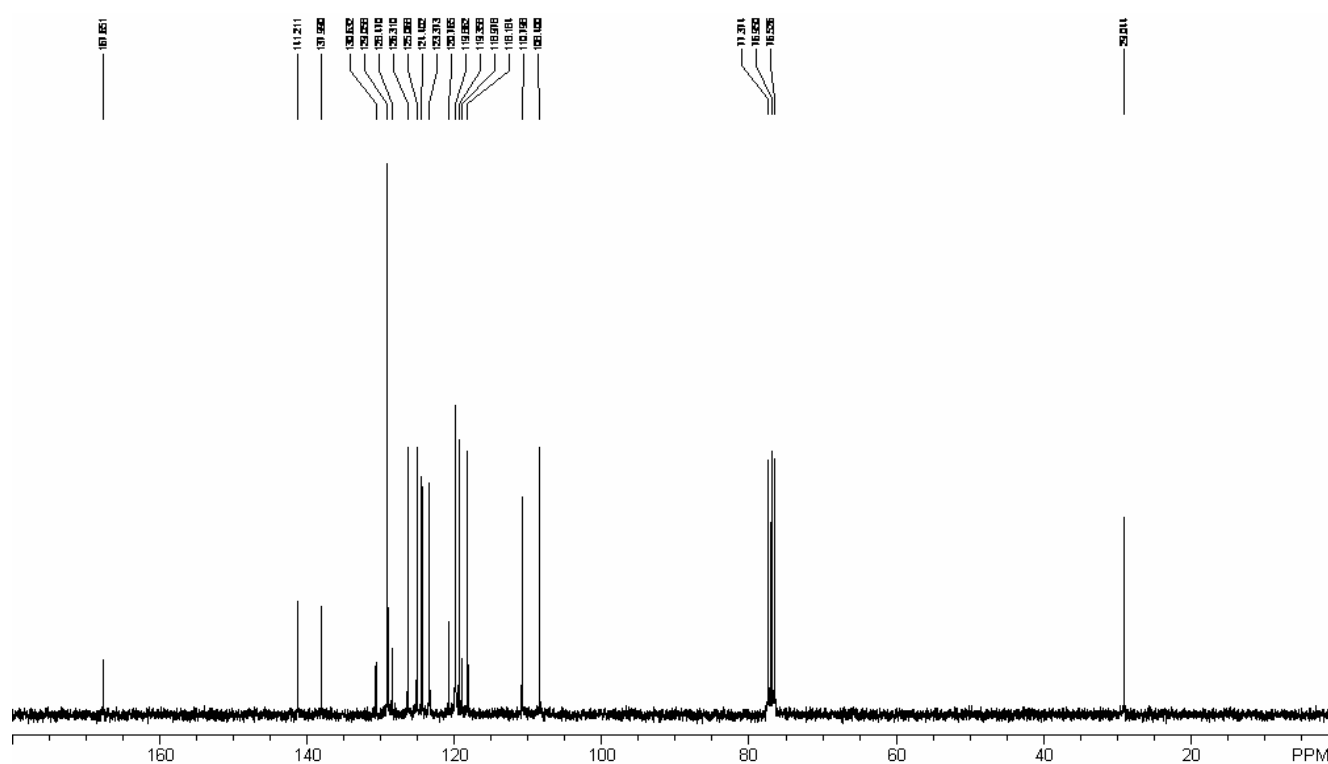


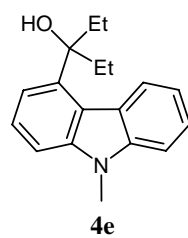


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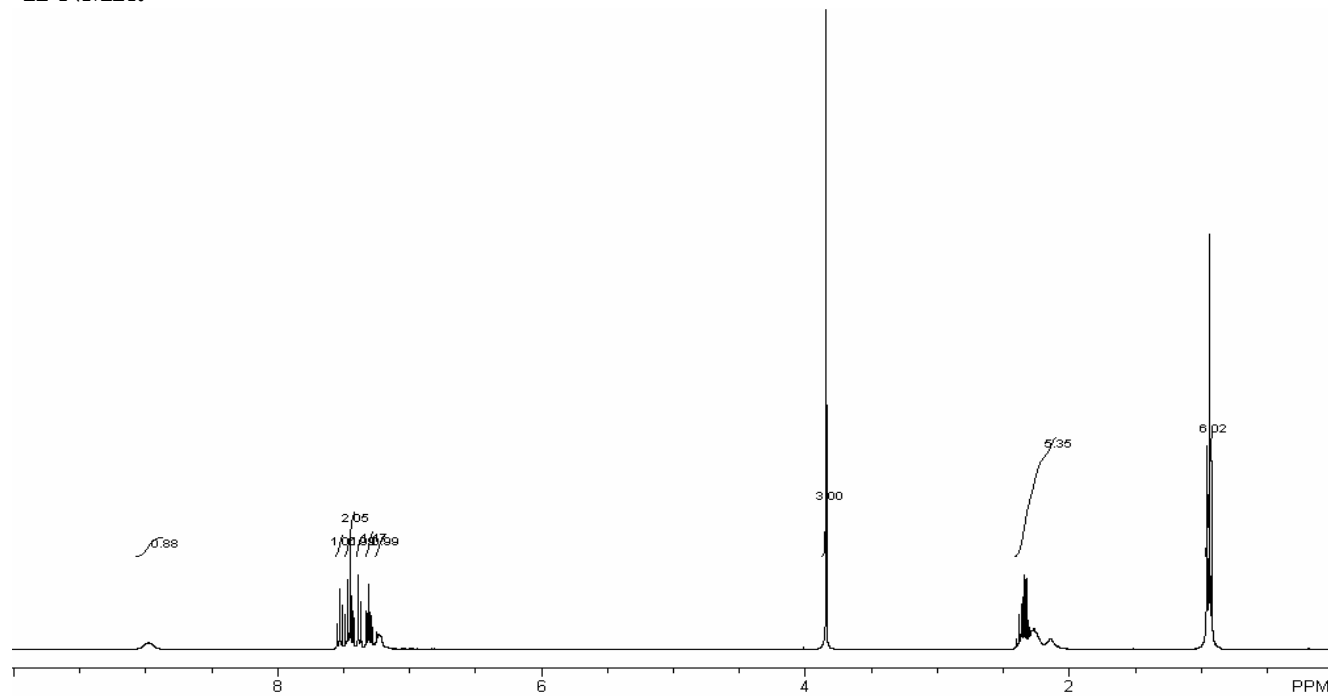


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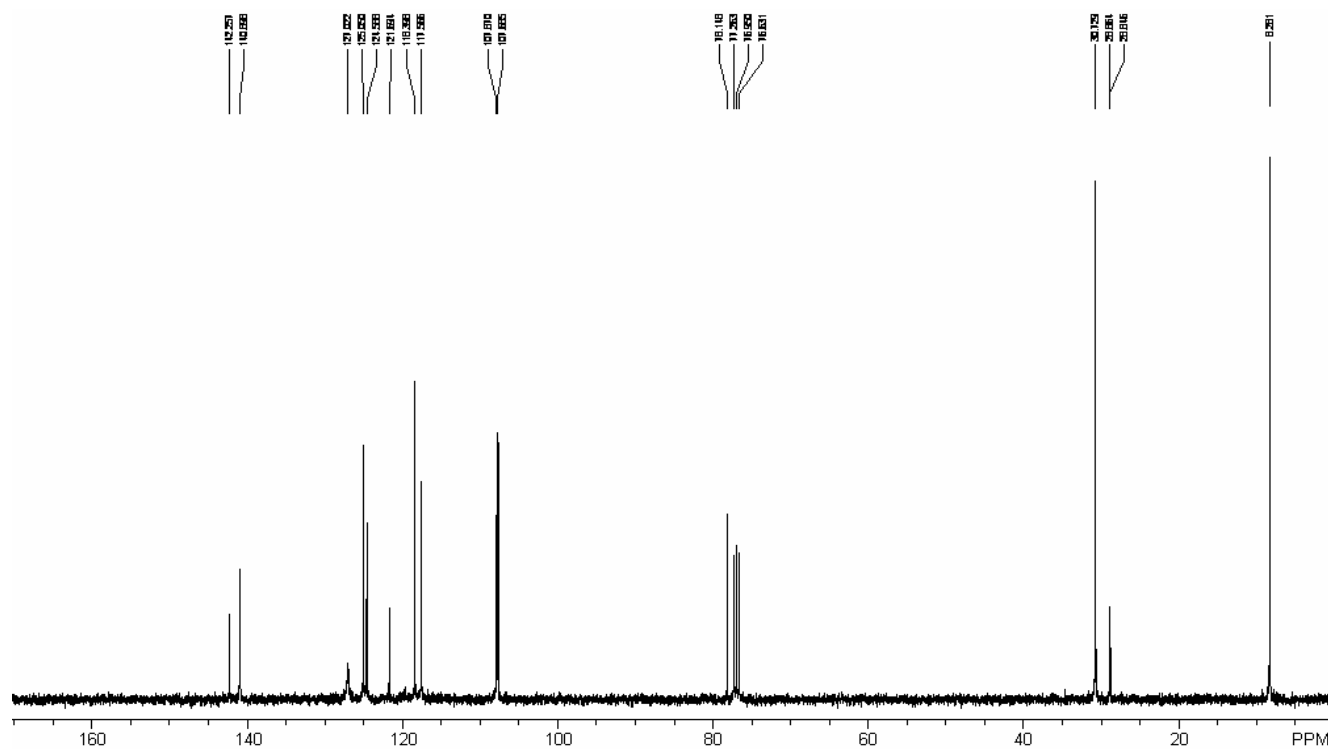


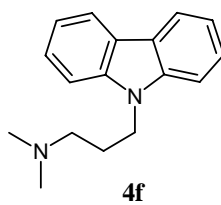


¹H-NMR:

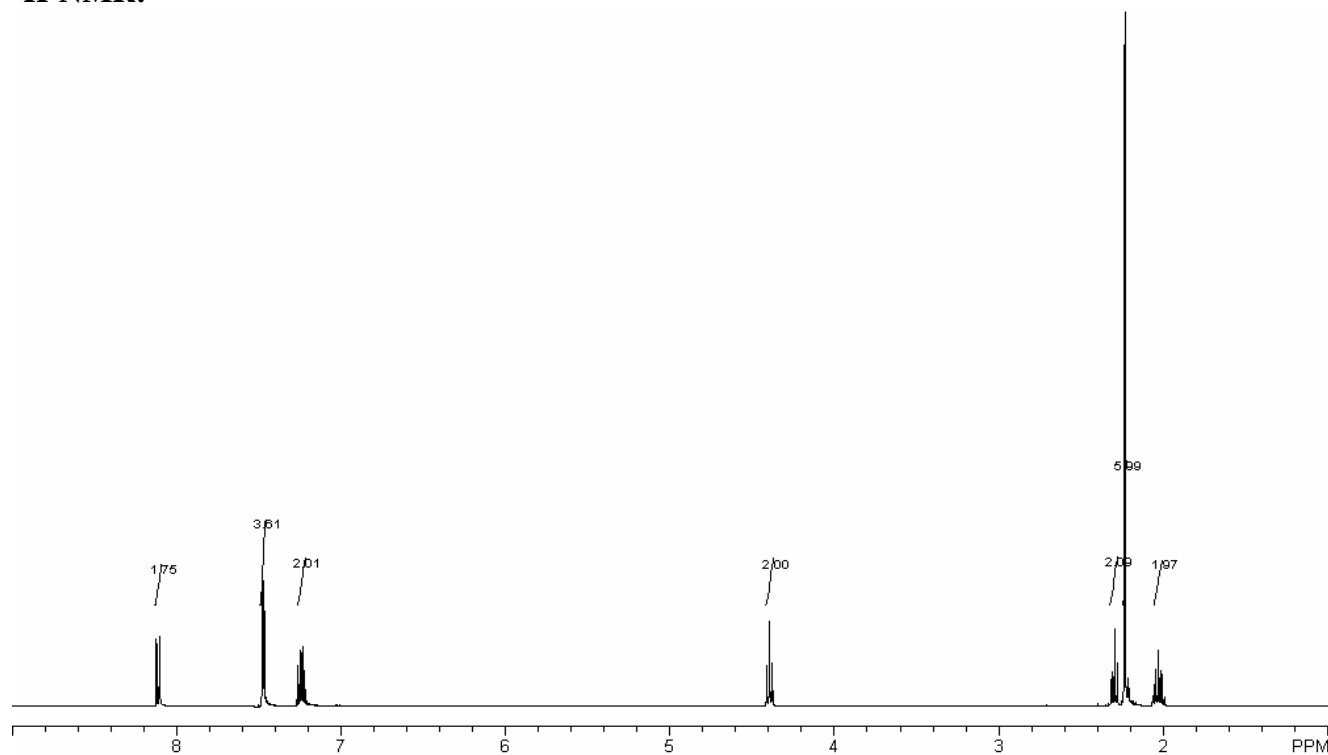


¹³C-NMR:

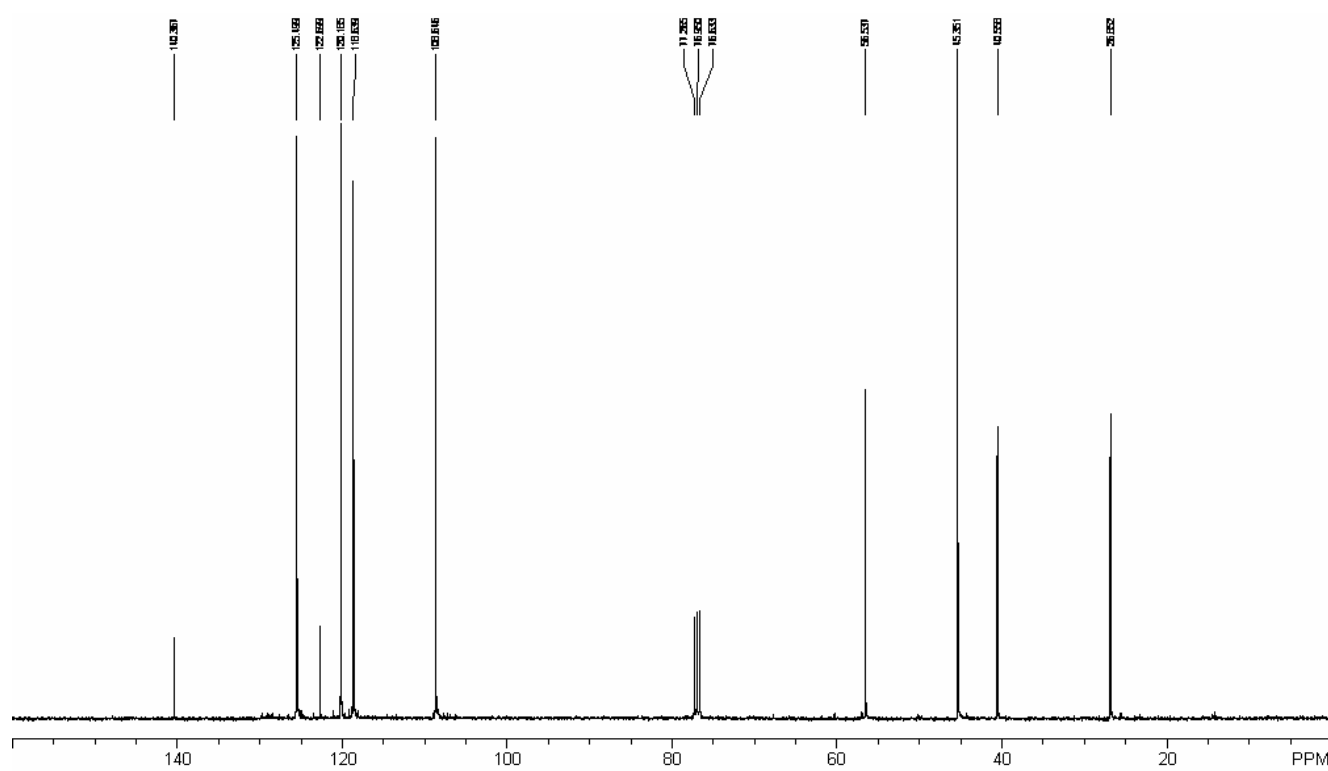


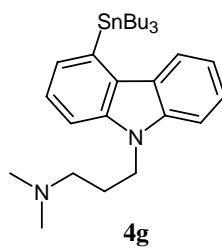


¹H-NMR:

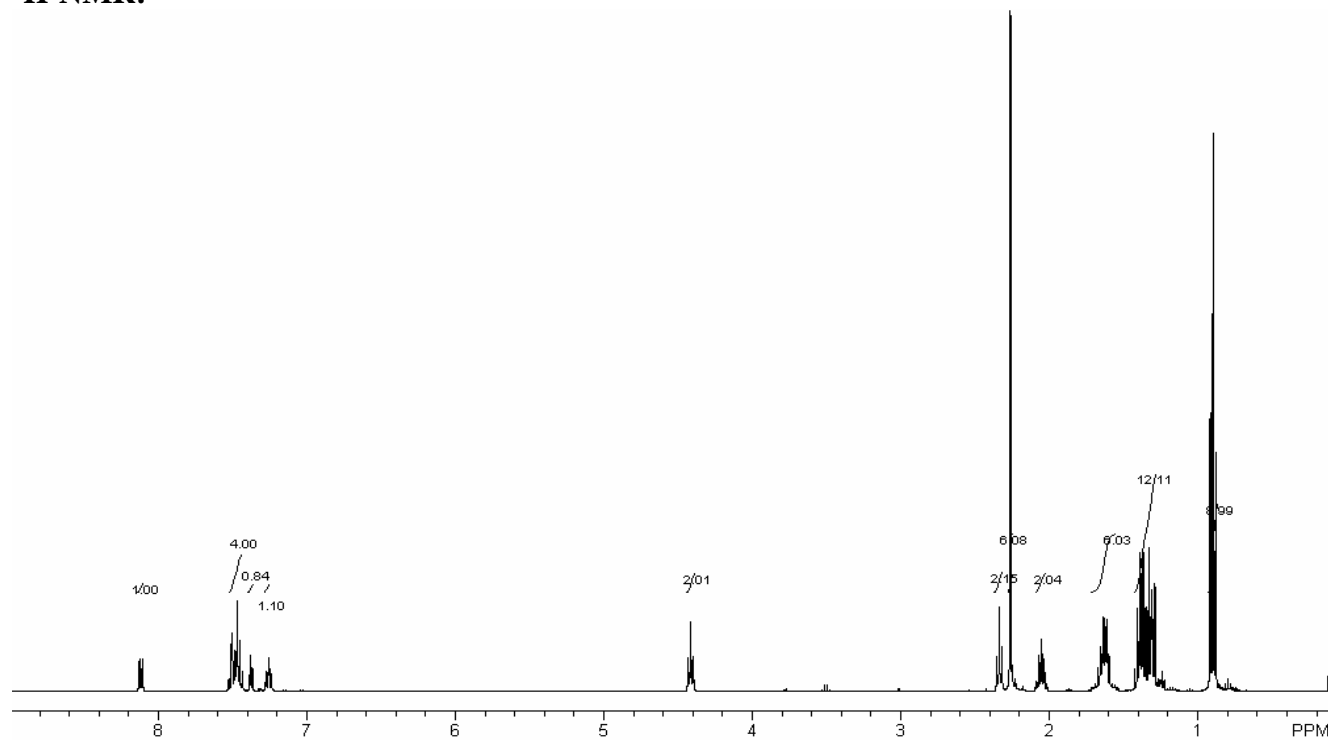


¹³C-NMR:

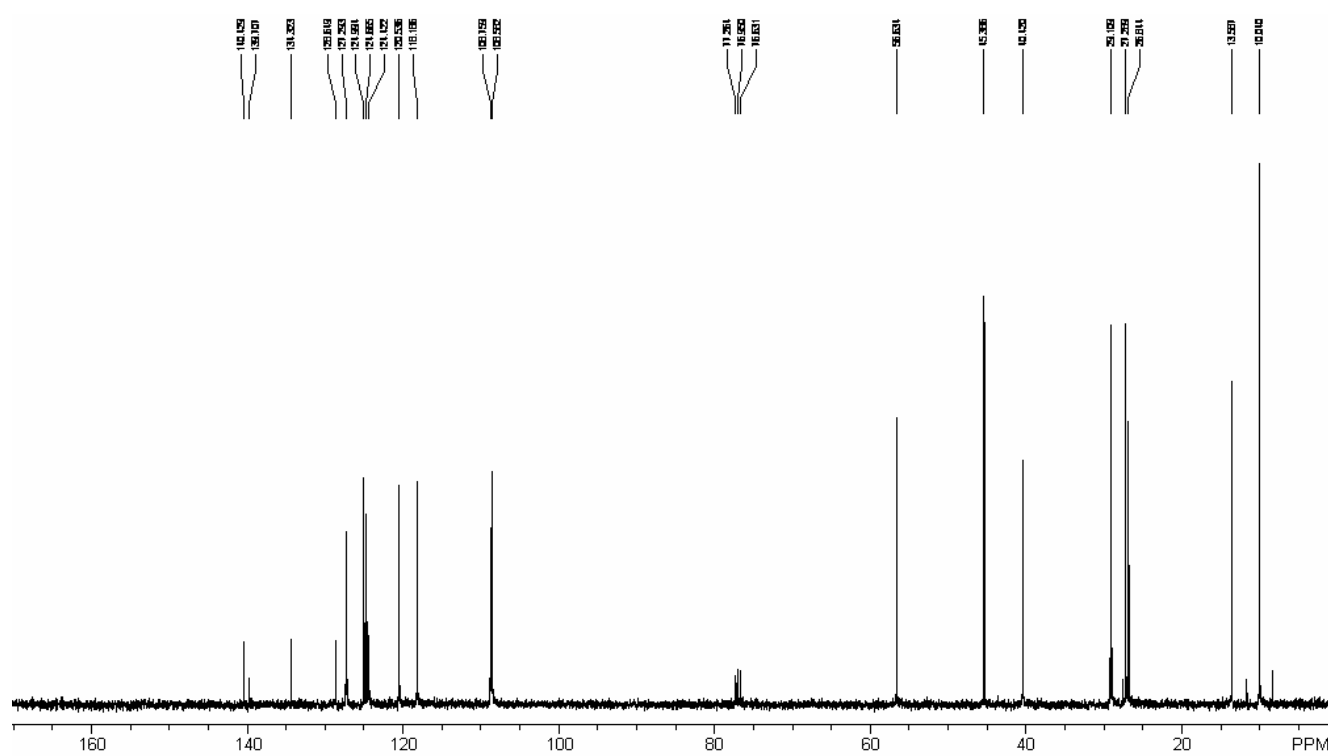


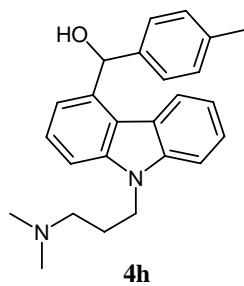


¹H-NMR:

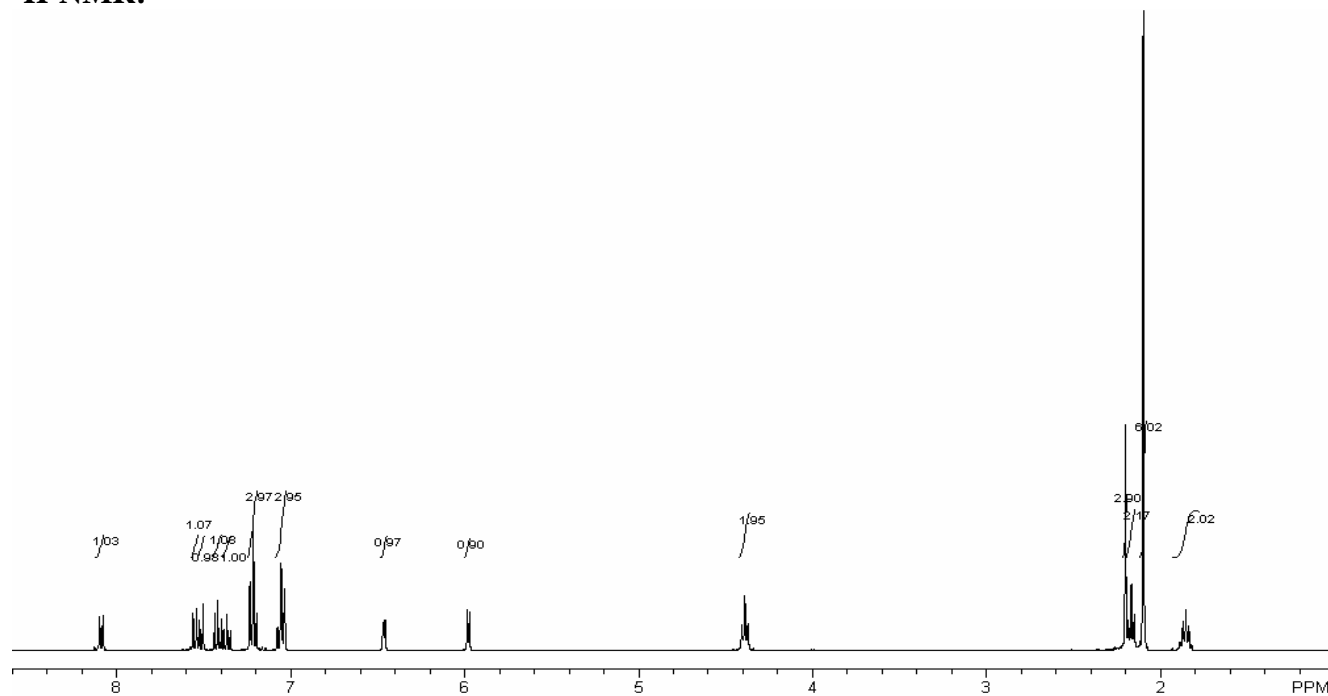


¹³C-NMR:

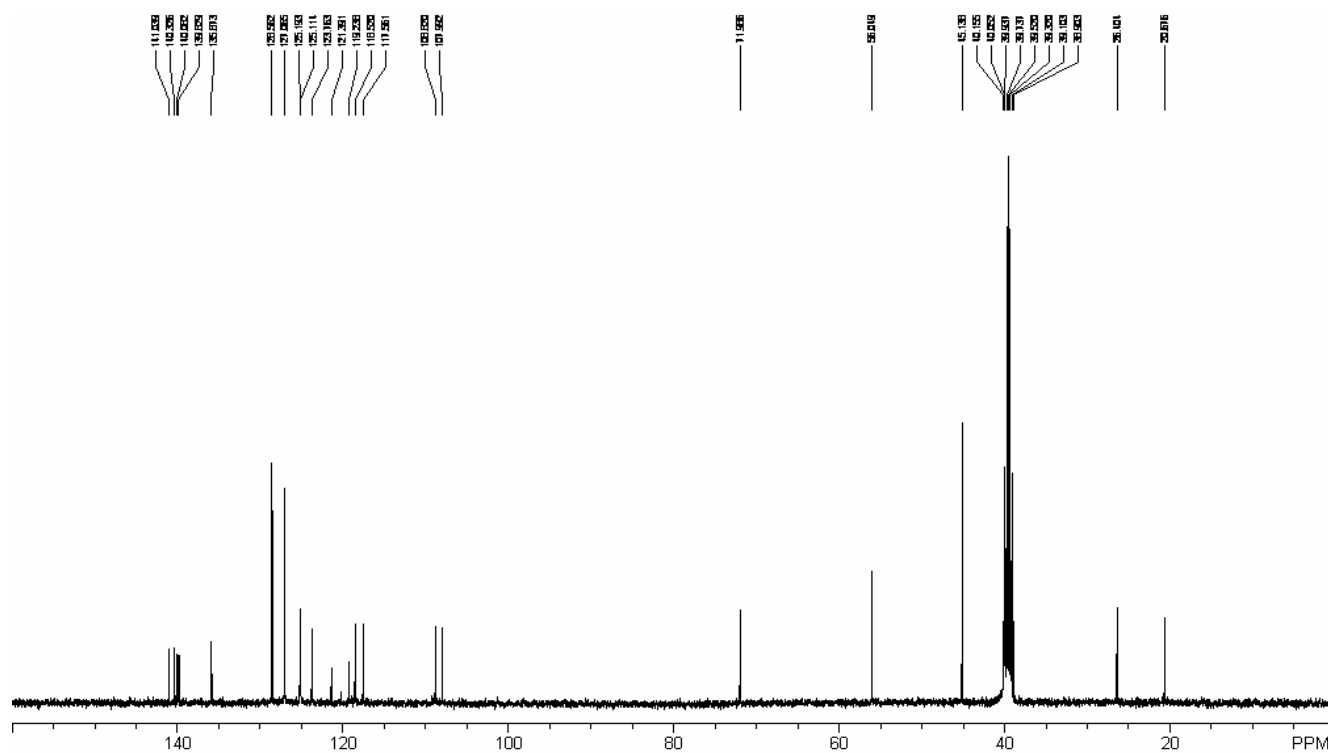


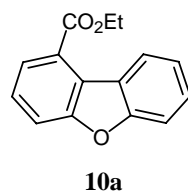


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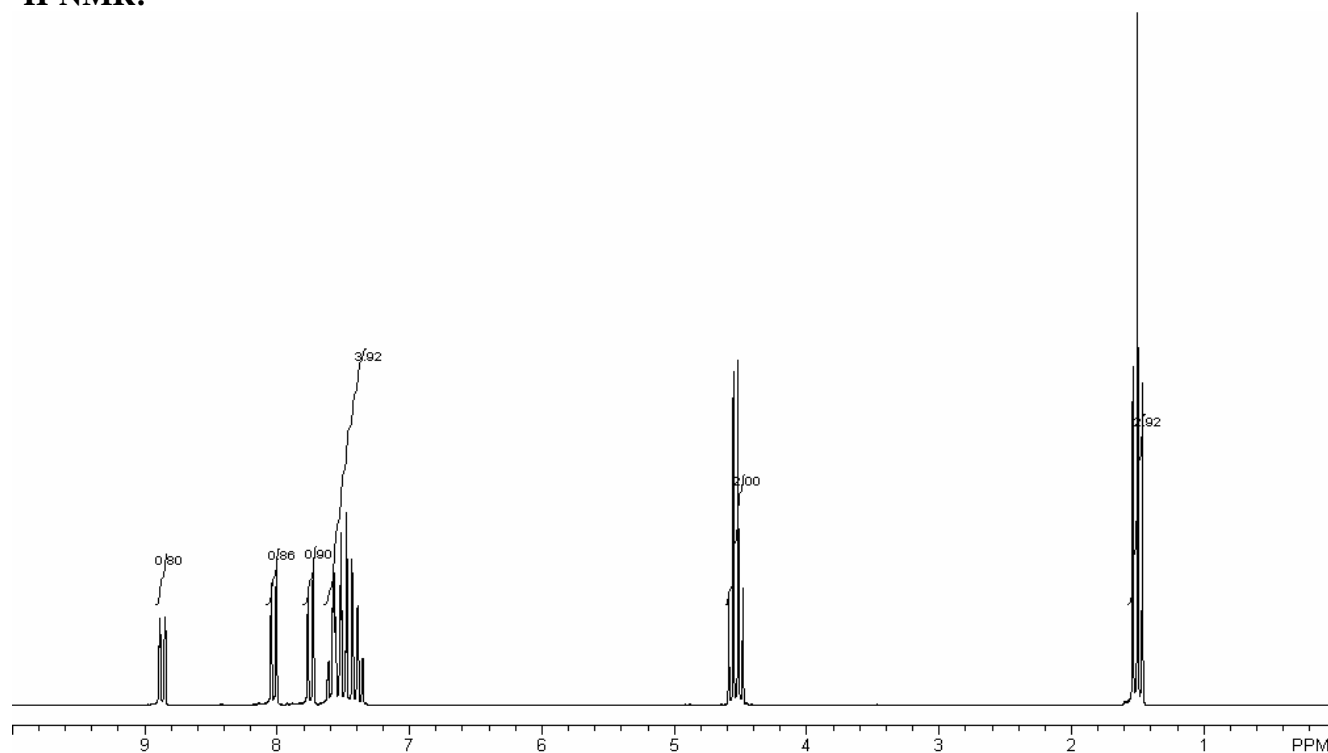


¹³C-NMR:

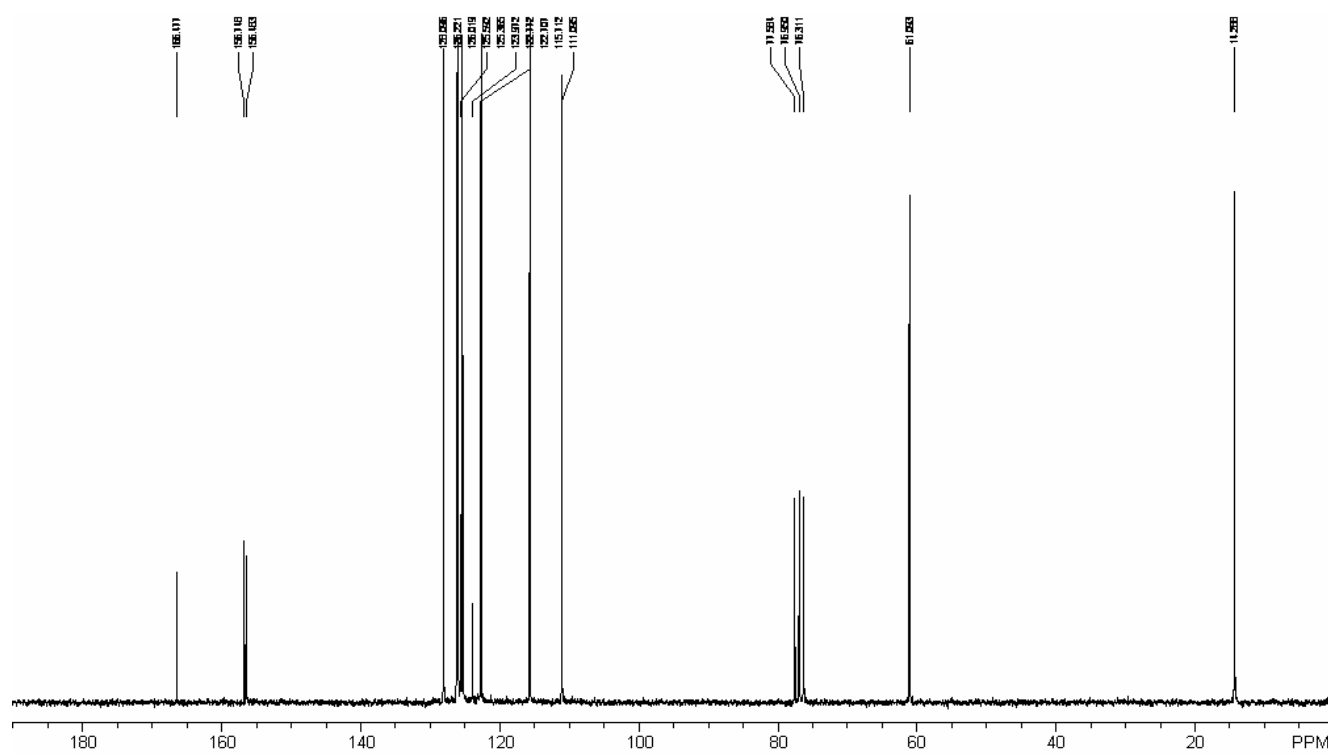


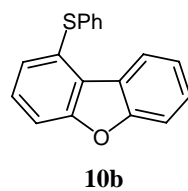


¹H-NMR:

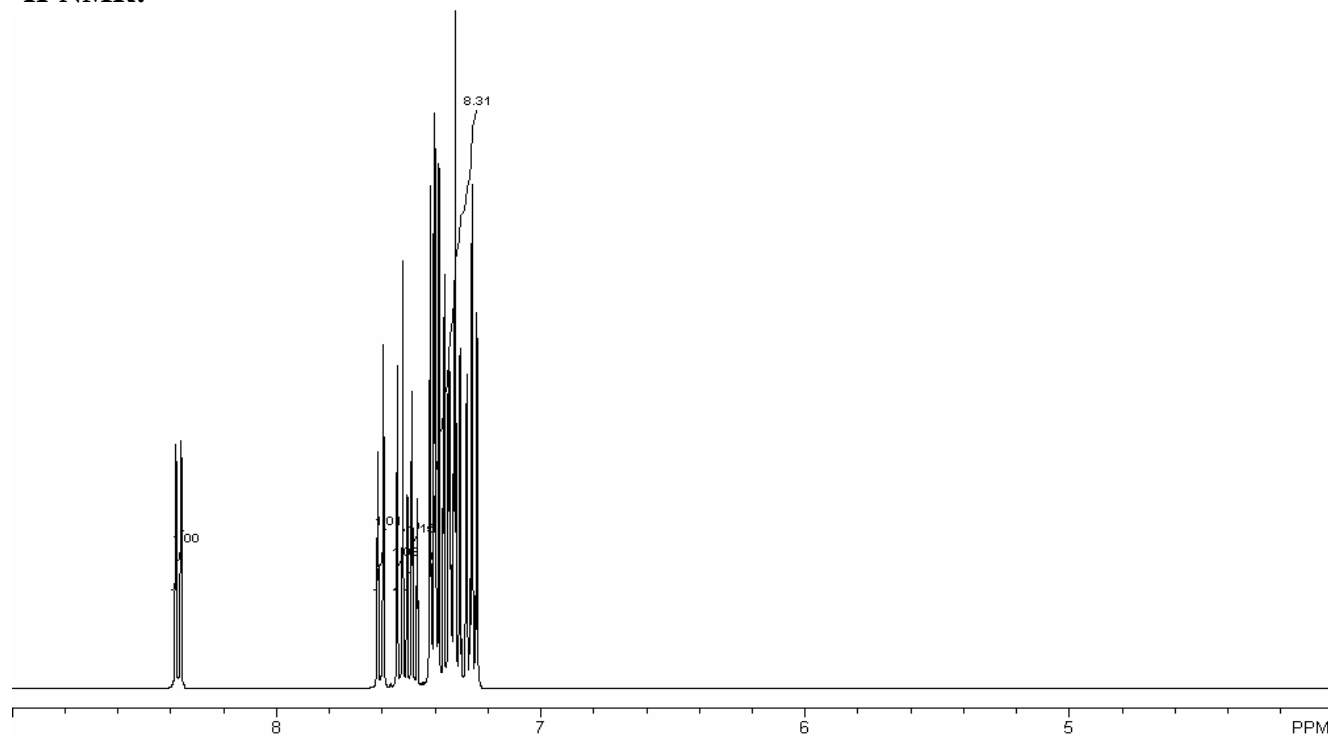


¹³C-NMR:

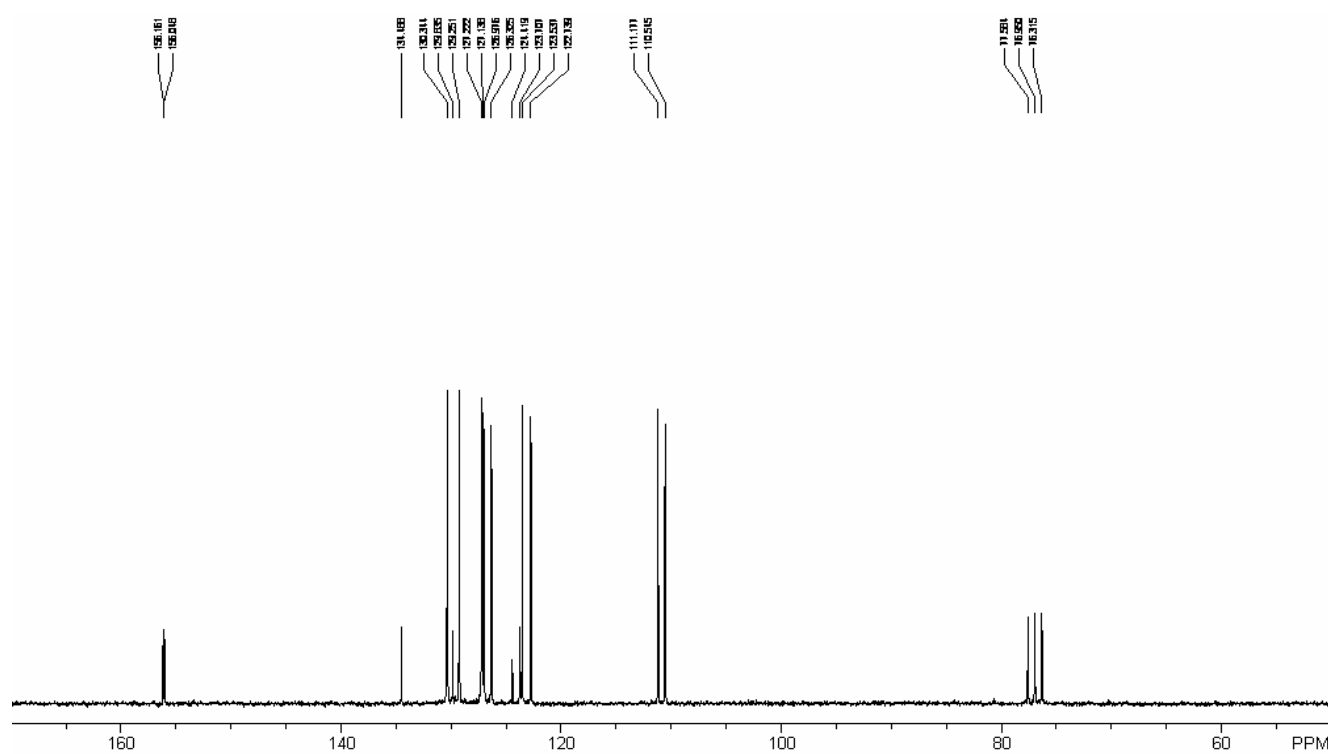


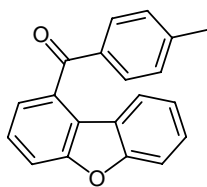


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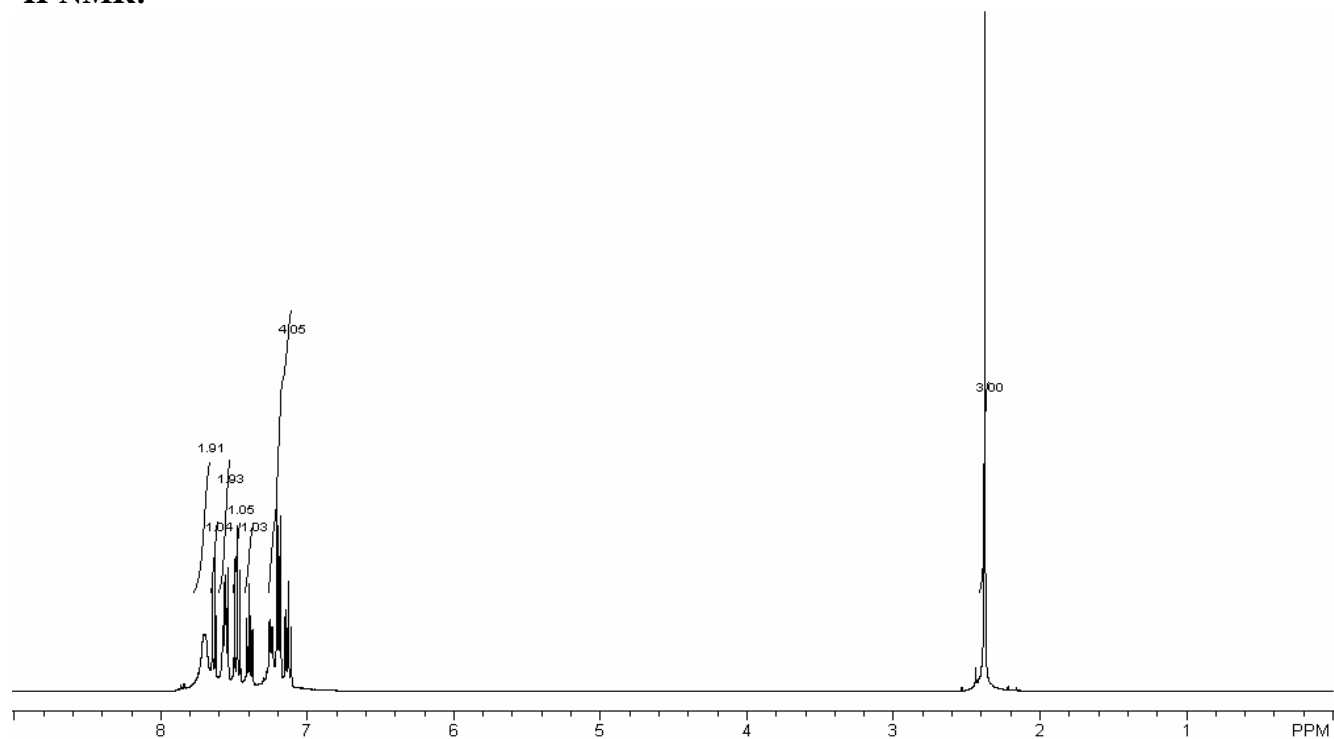
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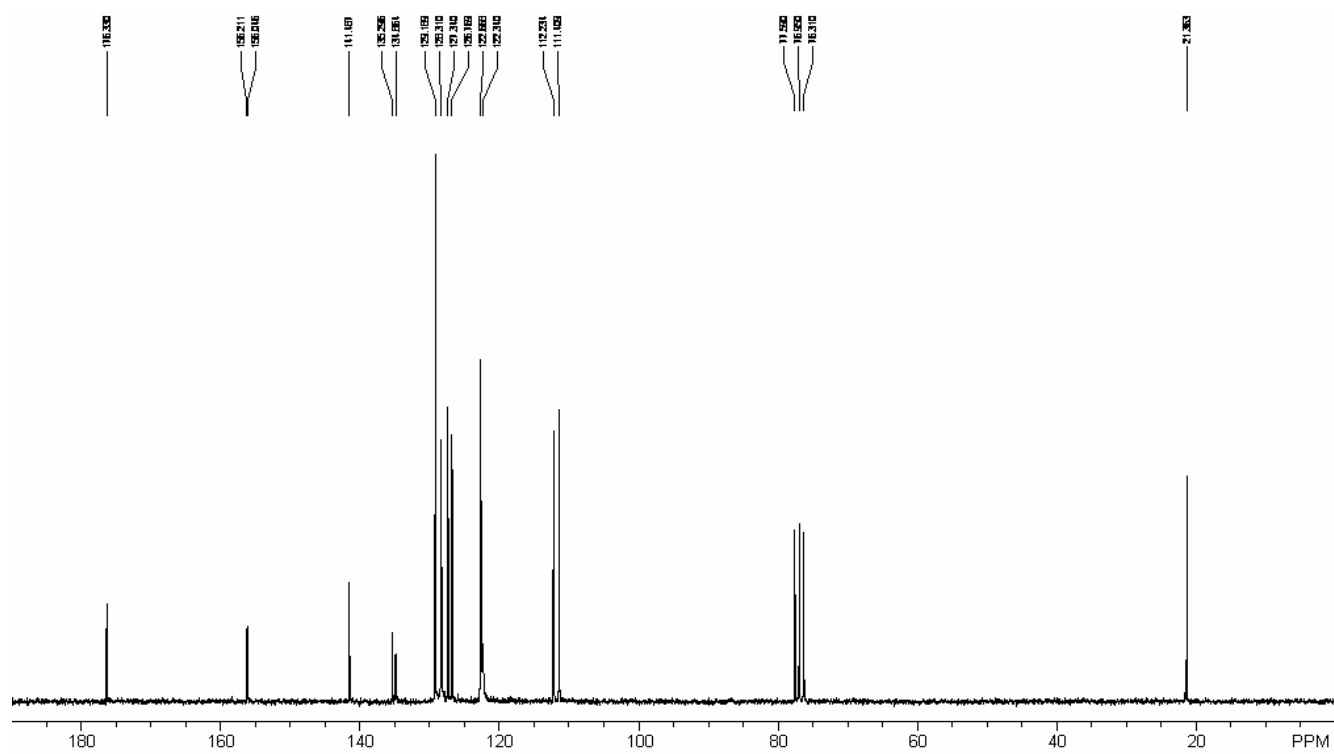


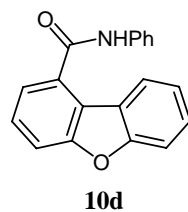
10c

^1H -NMR:

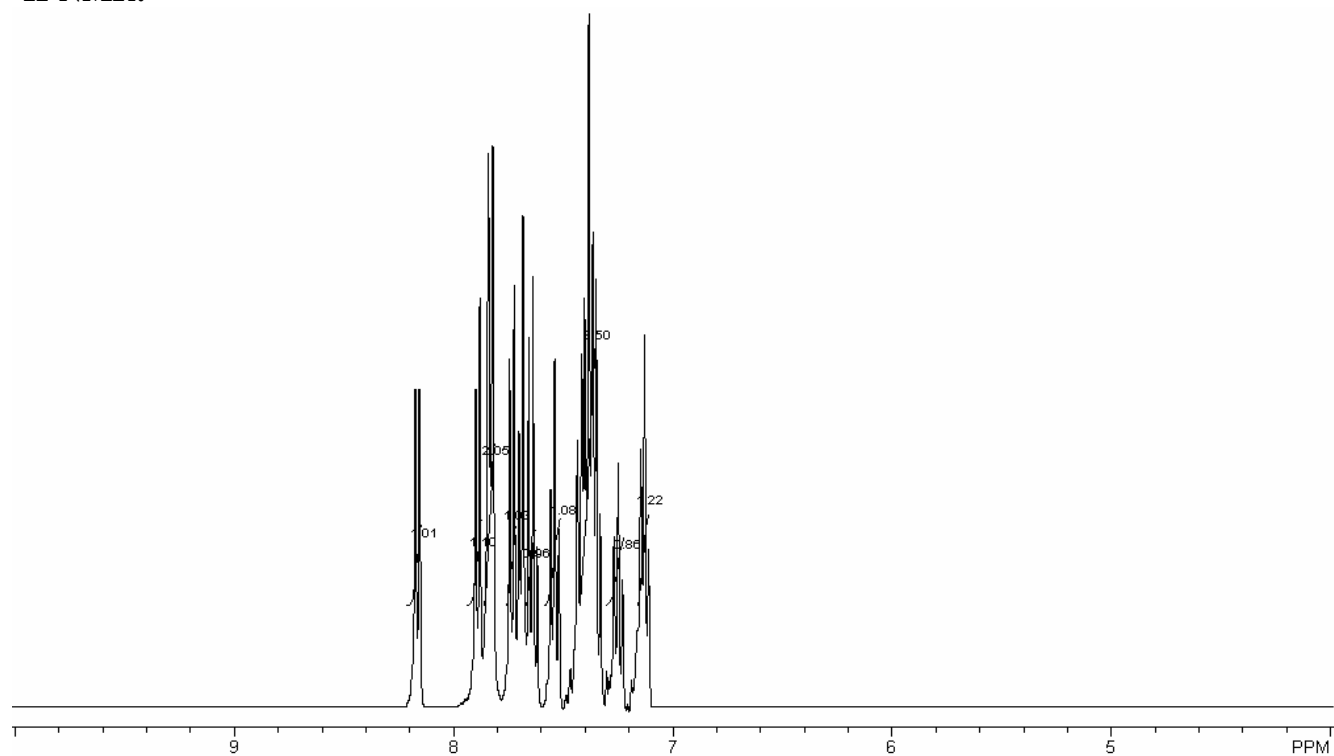


^{13}C -NMR:

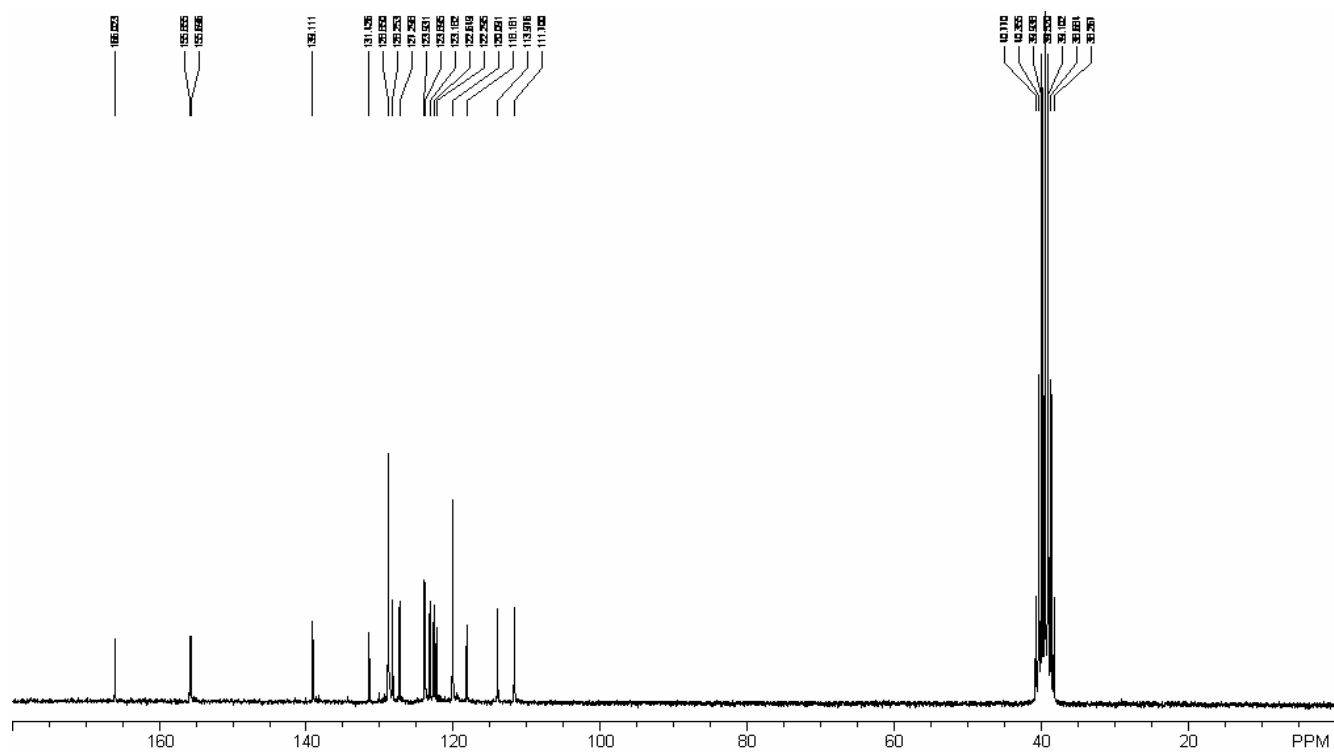


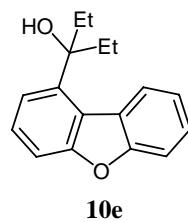


¹H-NMR:

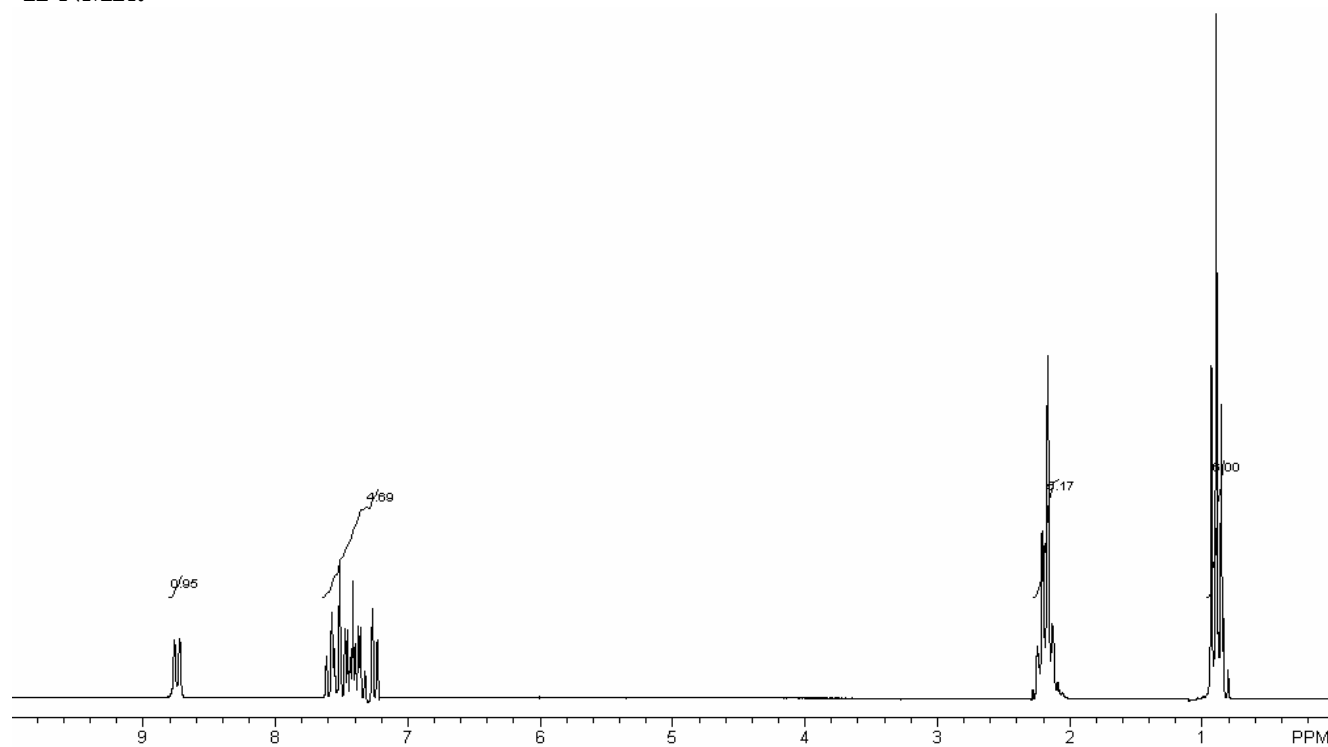


¹³C-NMR:

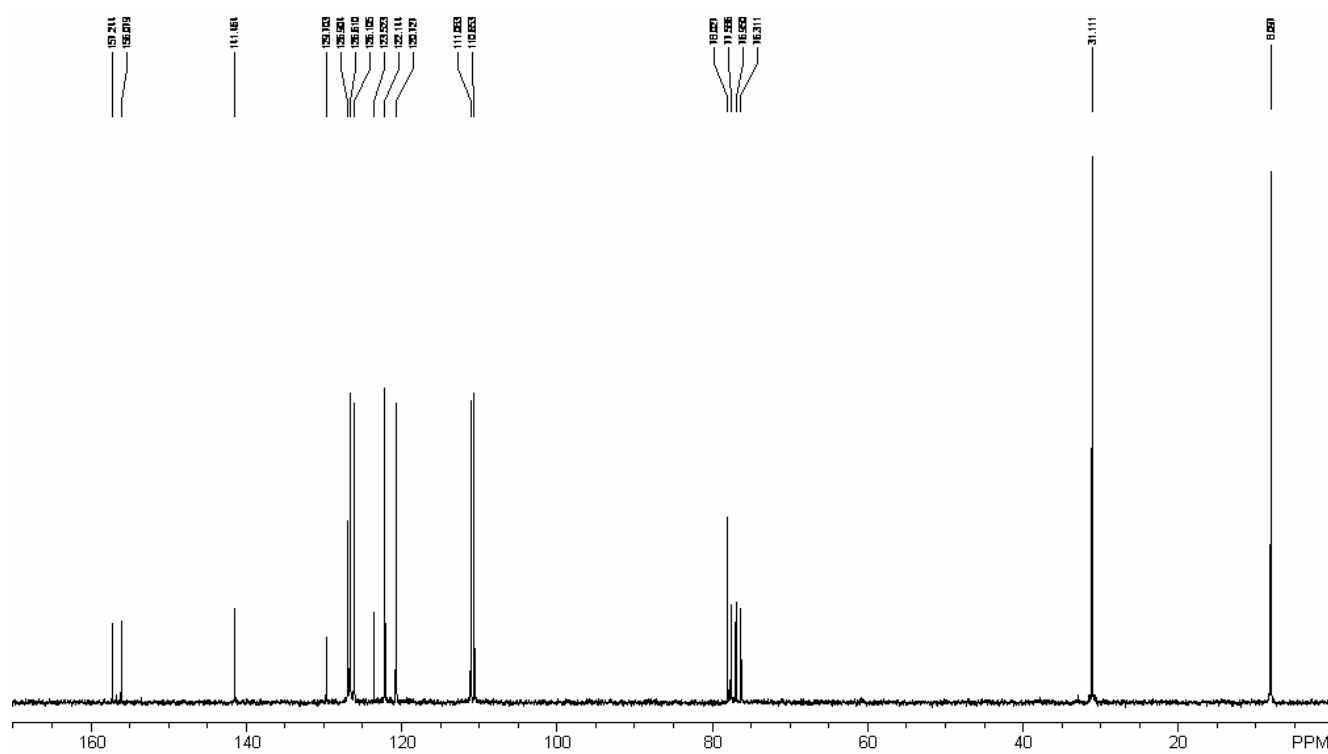


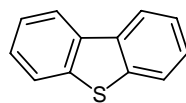


¹H-NMR:



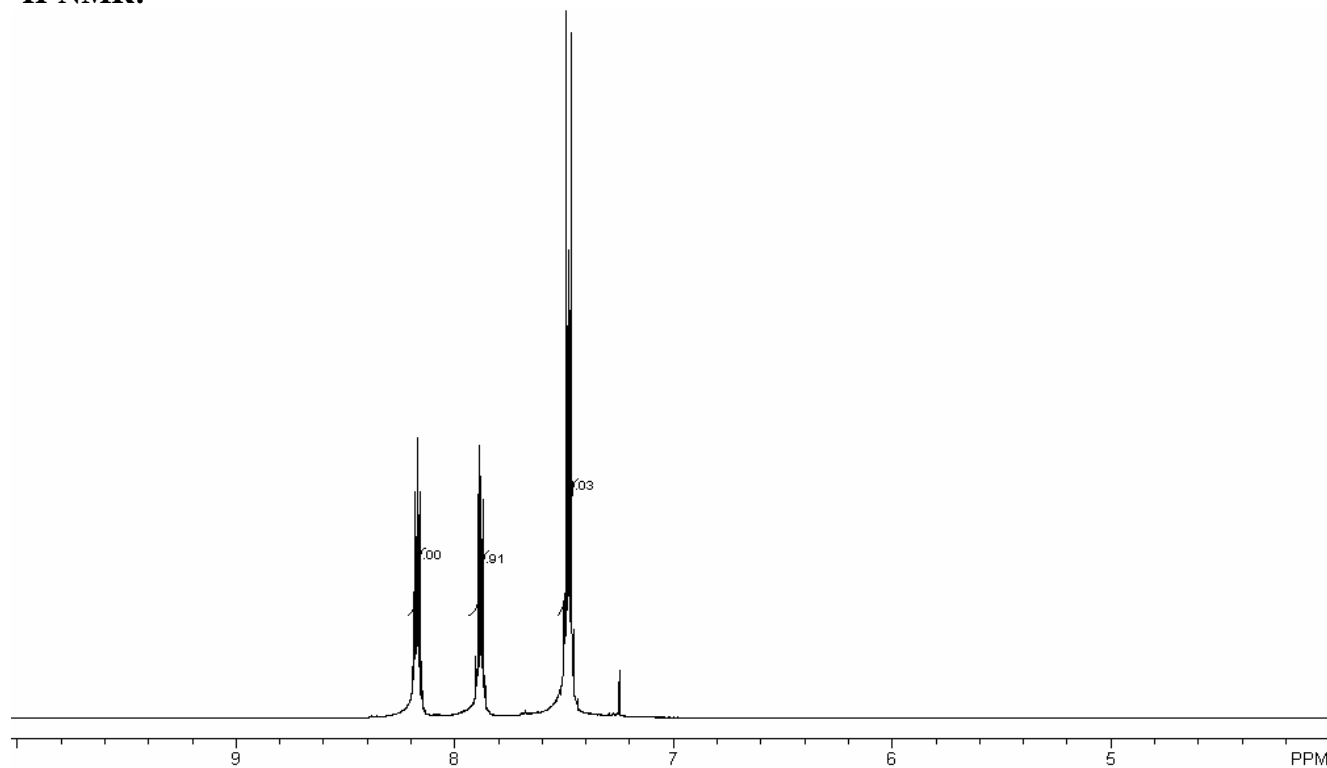
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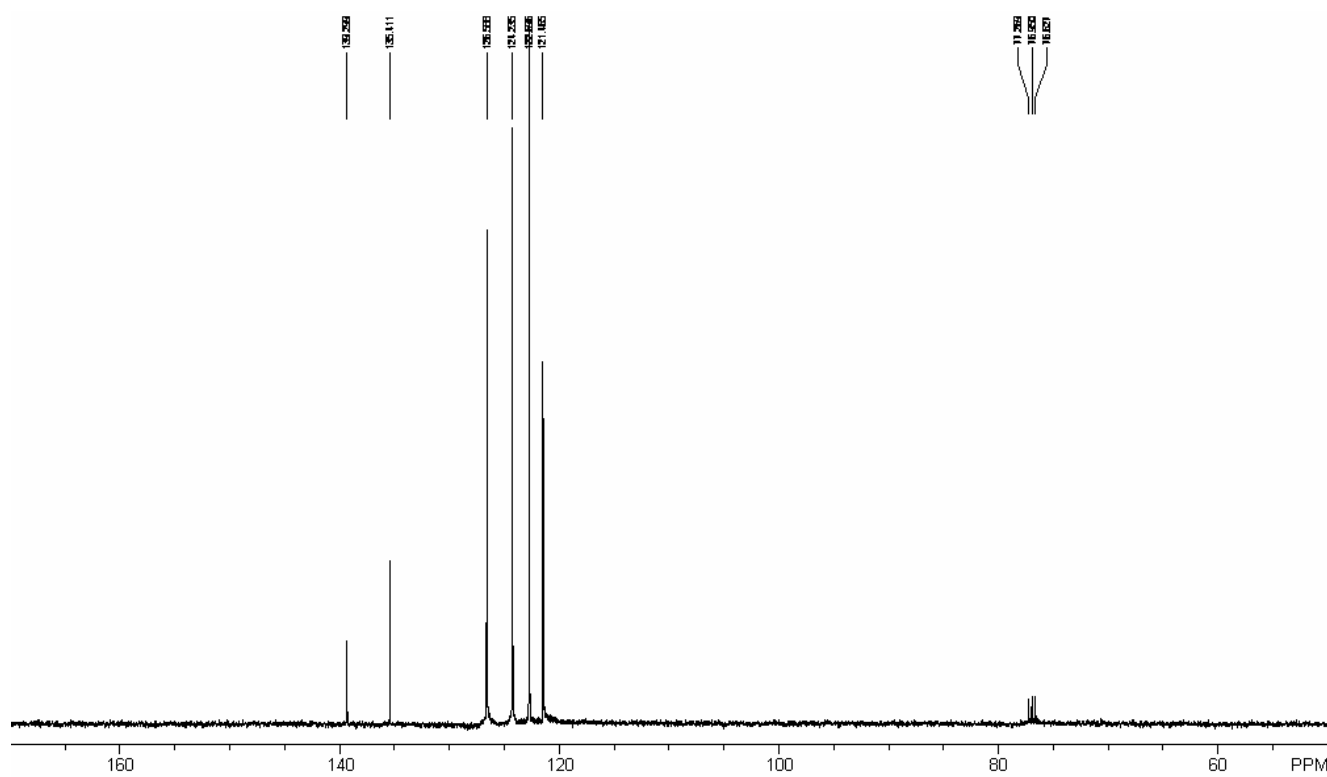


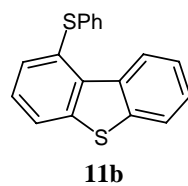
11a

^1H -NMR:

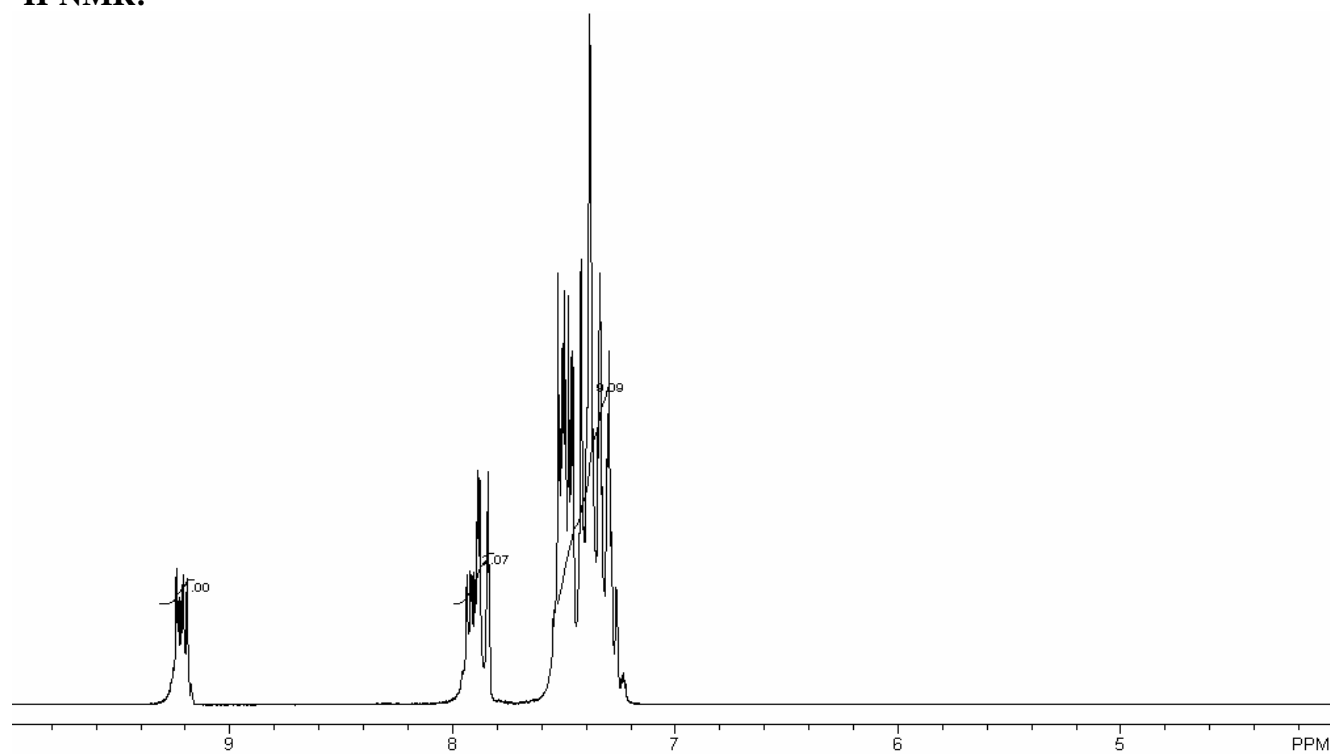


^{13}C -NMR:

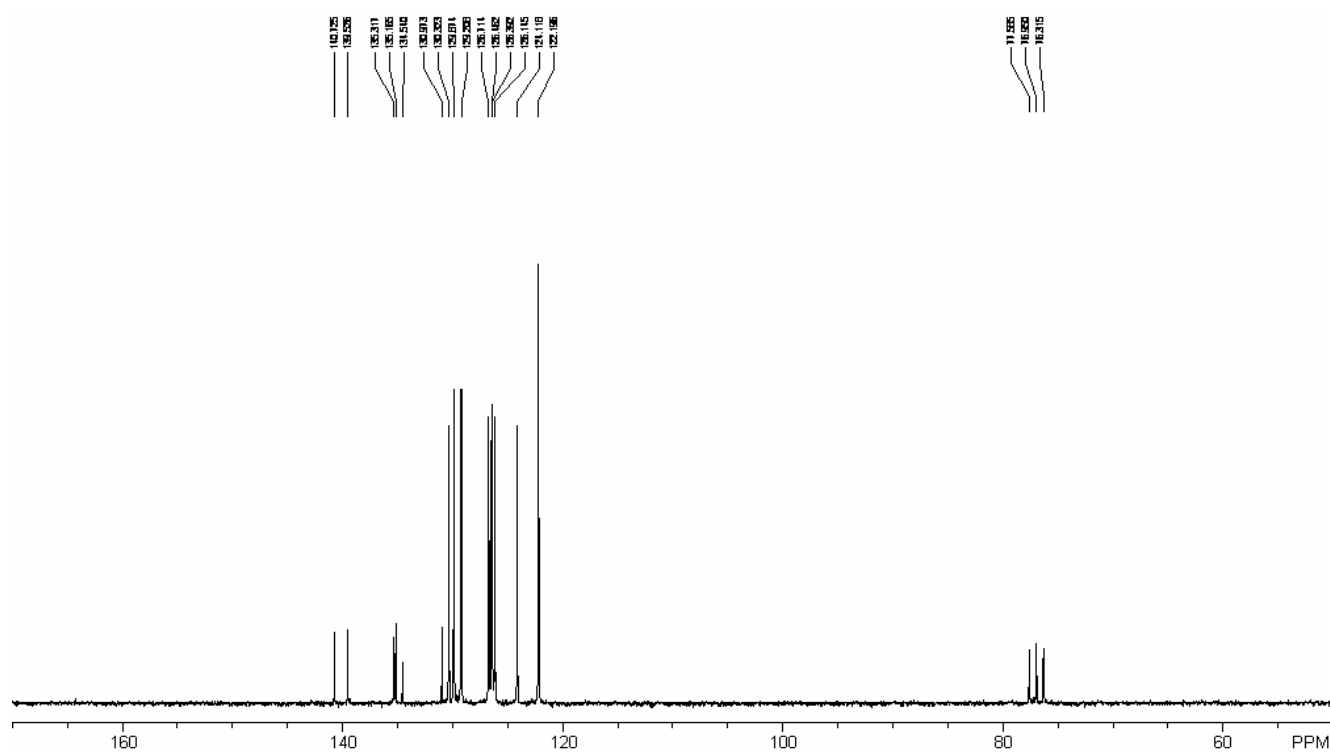


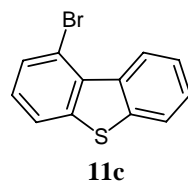


¹H-NMR:

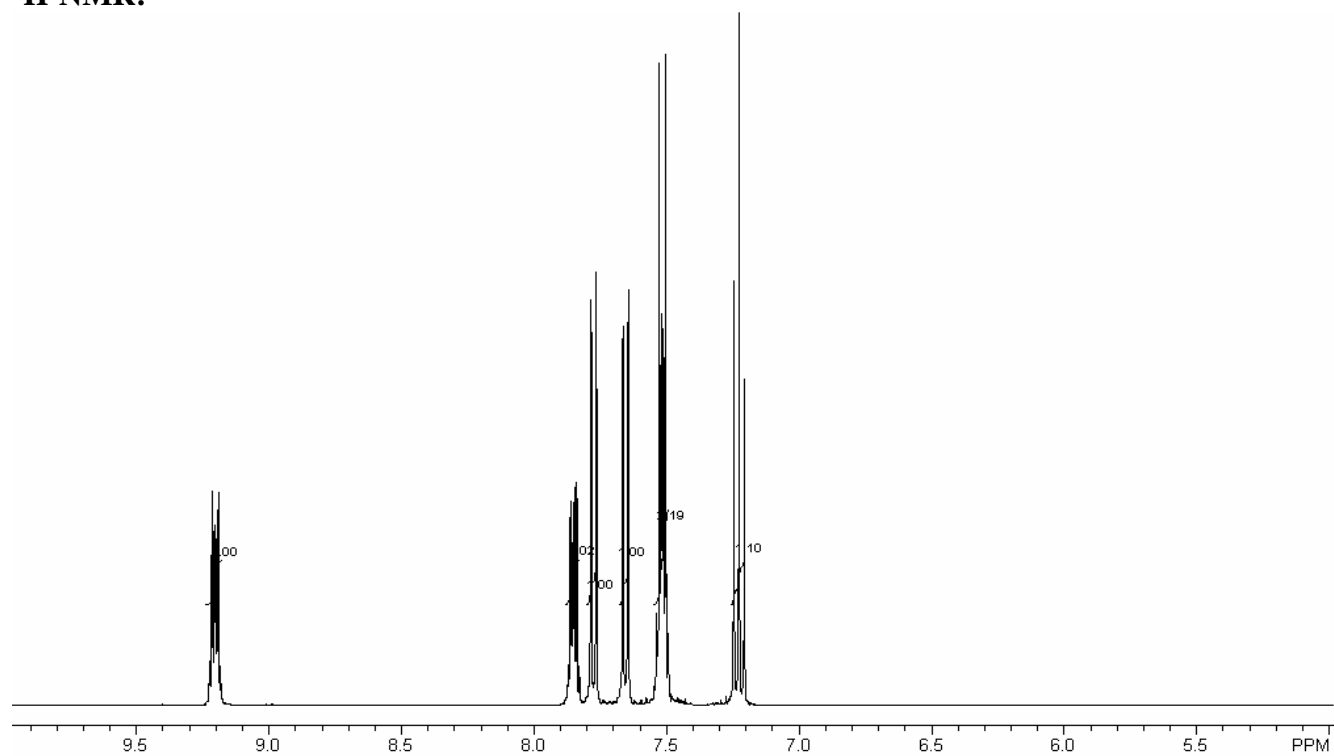


¹³C-NMR:

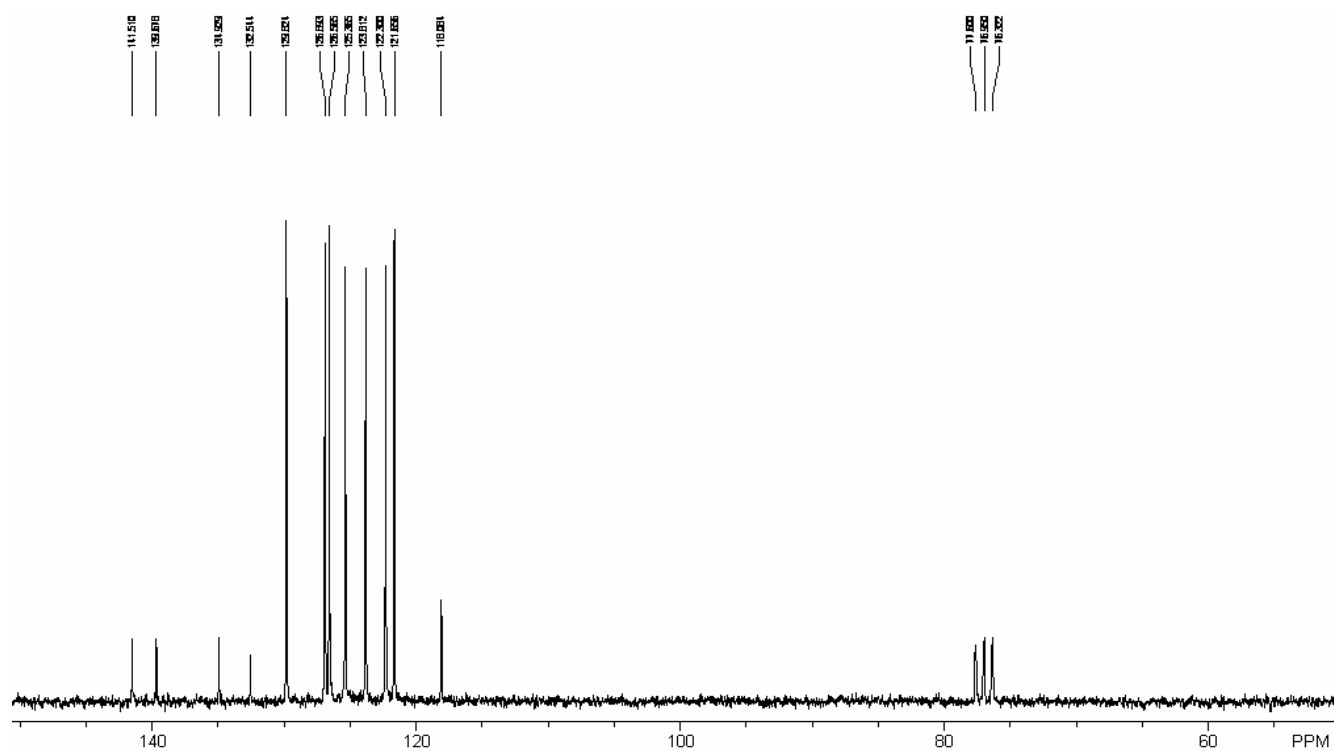


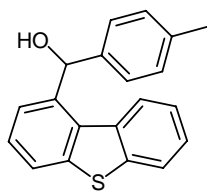


^1H -NMR:



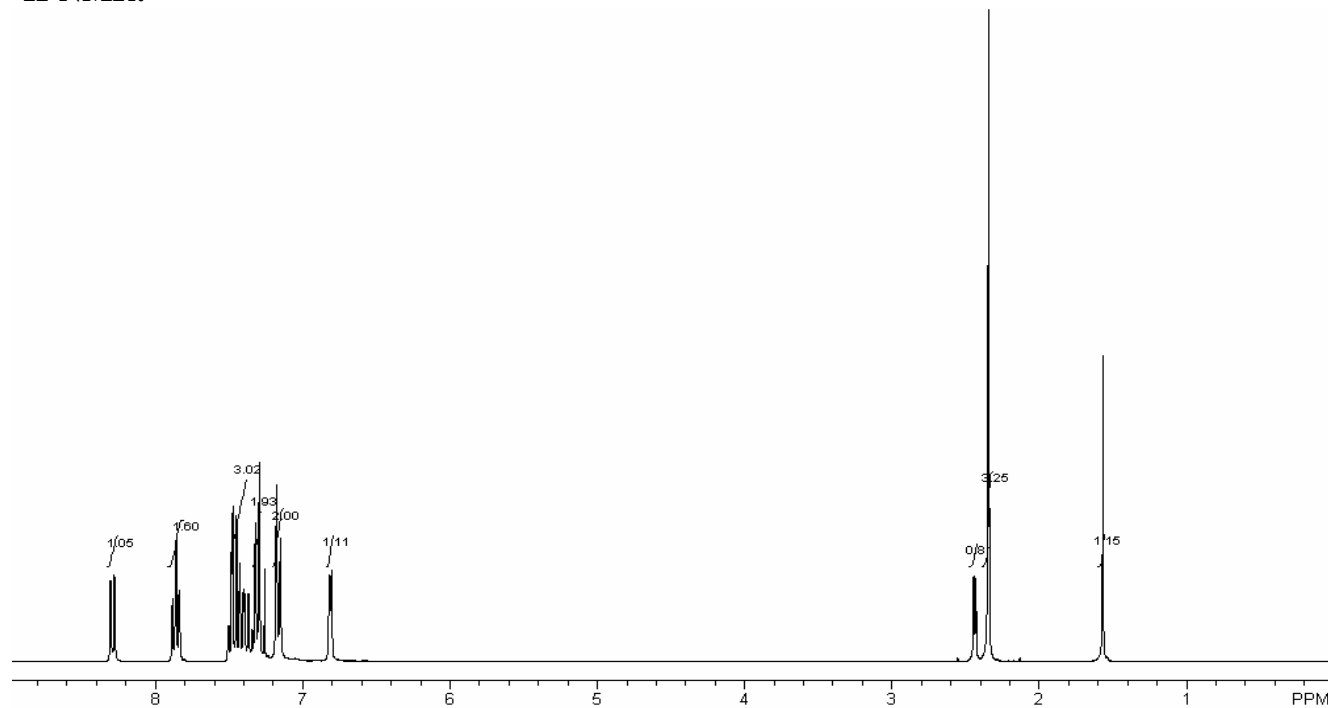
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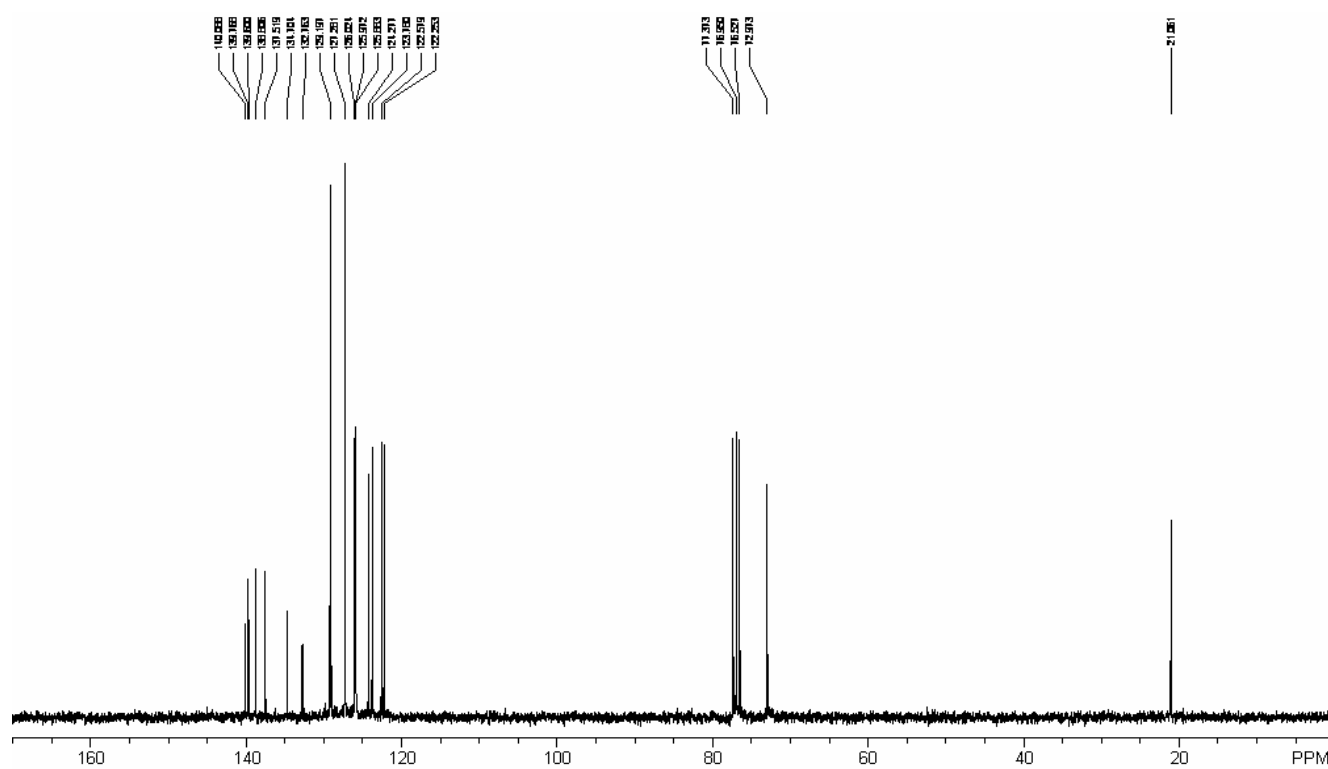


11d

^1H -NMR:



^{13}C -NMR:



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