

## Supported Palladium Nanoparticle-Catalyzed Decarboxylative Coupling Approaches for Aryl Alkynes, Indoles and Pyrrolines Synthesis

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### CONTENTS

General method.....	S2
Preparation of Pd@PS catalyst.....	S2
Experimental procedure and characterization data for synthesized compounds.....	S3-S11
2D spectral data for compound <b>9g</b> .....	S11-S16
Mechanistic studies for cyclization reaction.....	S17
ICP-AES analysis of the reaction mixture.....	S18
SEM&SEM-EDS analysis after five runs.....	S18
<sup>1</sup> H, <sup>13</sup> C NMR, GC-MS, HRMS, ESI-MS spectra for the synthesized compounds.....	S19-S109
References.....	S110

## General method

Reagents of high quality were purchased from Sigma Aldrich, LobaChemie and Sd Fine-chem Ltd. Amberlite® IRA 900 Cl<sup>-</sup> resin (PS) used as solid support (Chloride form) was purchased from Acros Organics. Commercial reagents and solvents were of analytical grade and were purified by standard procedures prior to use. Thin layer chromatography was performed using pre coated silica gel plates 60F<sub>254</sub> (Merck) in UV light detector. GC-MS analysis was carried out on a Shimadzu (QP 2010) series GC-MS (Tokyo, Japan), equipped with a FID, AOC 5000 autosampler, DB-5MS capillary column (30 m 9 0.25 mm i.d. with film thickness 0.25 μm). Mass spectra were recorded on an advance Bruker Daltonics (impact HD) UHR -QqTOF (Ultra-High Resolution Qq-Time-Of-Flight). ESI-MS spectra were determined using Waters Micromass Q-TOF Ultima Spectrometer. A SEM image was recorded on E1010 ion sputter Hitachi, Japan. A TEM image was taken using a carbon coated copper grid (Microscopy sciences) in a transmission electron microscope JEOL 2100F and FEI Tecnoi G20, 200 kV, Netherlands. ICP-AES analysis was carried on the instrument, ARCOS Spectro, Germany. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using a Bruker Avance 600 spectrometer operating at 600 MHz (<sup>1</sup>H) and 150 MHz (<sup>13</sup>C) and Bruker Avance 300 spectrometer operating at 300 MHz (<sup>1</sup>H) and 75 MHz (<sup>13</sup>C) spectra were recorded at 25 °C in CDCl<sub>3</sub> [residual CHCl<sub>3</sub> (δ<sub>H</sub> 7.26 ppm) or CDCl<sub>3</sub> (δ<sub>C</sub> 77.00 ppm), Acetone-d<sub>6</sub> [ residual (CH<sub>3</sub>)<sub>2</sub>CO (δ<sub>H</sub> 2.1 ppm) or (CH<sub>3</sub>)<sub>2</sub>CO (δ<sub>C</sub> 205.5 ppm)] Chemical shifts were recorded in δ (ppm) relative to the TMS and NMR solvent signal, coupling constants (J) are given in Hz and multiplicities of signals are reported as follows: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad singlet. Melting points were determined by using melting point apparatus and are uncorrected.

## Preparation of the Pd@PS catalyst

The solution of 120 mg of NaBH<sub>4</sub> in 30 mL of water was added to 4 g of Amberlite IRA 900 resin (chloride form) in a 100 mL flask. The mixture was stirred for 4 h at room temperature. Then the resin was washed with water till pH became neutral and then with acetone to remove water from the solid surface. The resin beads (borohydride exchanged) were dried under reduced pressure. The dried borohydride exchanged resin beads (solid surface) (1 g) was added into the warm (100 °C) solution of palladium acetate (10 mg) in DMF (3 mL) then the mixture was stirred for 1 h or till the dark brown colour of the solution changed into colourless and simultaneously white solid beads were turned into blackish. After cooling, the beads were filtered through a cotton bed, washed with water and acetone, and dried under reduced pressure.

## General procedure for Pd@PS catalyzed decarboxylative coupling of alkynyl carboxylic acids with aryl halides

**1-Methoxy-4-(2-phenylethynyl) benzene (3a)<sup>1</sup>:** 4-iodoanisole (100 mg, 0.42 mmol, 1 equiv.), phenylpropionic acid (75 mg, 0.5 mmol, 1.2 equiv.), DBU (194 mg, 1.2 mmol, 3 equiv.), Pd@PS (286 mg, 3 mol % Pd) and DMF were added to an oven dried reaction tube. Then the solution was stirred at 110 °C for 12 h. as the completion of reaction was monitored by TLC and GC-MS. After the completion of the reaction 3 ml water was added to the mixture and extracted with EtOAc (3 x 3 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, evaporated in vacuum. The residue was purified by column chromatography on silica gel (hexane) to afford the desired product **3a** as light yellow solid (70 mg, 78%) ; mp 57-59 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 3.73 (s, 3H), 6.78-6.80 (m, 2H), 7.22-7.26 (m, 3H), 7.38-7.40 (m, 2H), 7.42-7.44 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 55.2, 88.0, 89.3, 113.9, 115.3, 123.5, 127.9, 128.2, 131.4, 133.0, 159.6.

**1-Methyl-4-(phenylethynyl)benzene (3b)<sup>1</sup>:** Prepared as described for **3a** starting from 4-iodo toluene (0.45mmol), after work up, column chromatography (100% hexane) afforded **3b** as white solid (62 mg, 70%) ; mp 67-69 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 2.37 (s, 3H), 7.15 (d, *J* = 7.8 Hz, 2H), 7.32-7.36 (m, 3H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.52-7.53 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 21.4, 88.7, 89.5, 121.1, 123.4, 128.0, 128.3, 129.1, 131.4, 134.5, 138.3.

**1,2-Diphenylethyne (3c)<sup>1</sup>:** Prepared as described for **3a** starting from iodobenzene (0.49mmol), after work up, column chromatography (100% hexane) afforded **3c** as white solid (58 mg, 66%); mp 60-62°C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 6.08-6.10 (m, 6H), 6.27-6.29 (m, 4H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 89.3, 123.2, 128.2, 128.3, 131.6.

**4-(Phenylethynyl)benzotrile (3d)<sup>1</sup>:** Prepared as described for **3a** starting from 4-iodobenzotrile (0.43mmol), after work up, column chromatography (hexane:ethylacetate = 98:2) afforded **3d** as yellow solid (60 mg, 69%); mp 101-103°C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 7.38-7.39 (m, 3H), 7.54-7.56 (m, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.4Hz, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 87.7, 93.7, 111.4, 118.5, 122.2, 128.2, 128.5, 129.1, 131.7, 132.0, 132.1.

**4-(Phenylethynyl)benzotrile (3d):** Prepared as described for **3a** starting from 4-bromobenzotrile (0.55 mmol) after work up, column chromatography (hexane:ethylacetate = 98:2) afforded **3d** (65 mg, 58%) as yellow solid.

**1-(4-(Phenylethynyl)phenyl)ethanone (3e)<sup>1</sup>:** Prepared as described for **3a** starting from 4-iodoacetophenone (0.3 mmol), after work up, column chromatography (hexane:ethylacetate = 98:2)

afforded **3e** as white solid (67 mg, 75%); mp 95-96 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 2.5 (s, 3H), 7.29 (m, 3H), 7.47 (bs, 2H), 7.52 (d, *J* = 6.6 Hz, 2H), 7.85-7.86 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 26.5, 88.5, 92.6, 122.6, 128.1, 128.2, 128.4, 128.7, 131.6, 131.7, 136.1, 197.3.

**1-(4-(Phenylethynyl)phenyl)ethanone (3e)**: Prepared as described for **3a** starting from 4-bromoacetophenone (0.50 mmol) after work up, column chromatography (hexane:ethylacetate = 98:2) afforded **3e** as white solid (67 mg, 60%).

**4-(Phenylethynyl)benzaldehyde (3f)**<sup>1</sup>: Prepared as described for **3a** starting from 4-iodobenzaldehyde (0.43 mmol), after work up, column chromatography (100% hexane) afforded **3f** as white solid (70 mg, 79%); mp 95-97 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 7.37-7.39 (m, 3H), 7.55-7.57 (m, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.87 (d, *J* = 8.2 Hz, 2H), 10.02 (s, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 88.4, 93.4, 122.4, 128.4, 128.9, 129.5, 129.6, 131.7, 132.0, 135.3, 191.4.

**Methyl 4-(phenylethynyl)benzoate(3g)**<sup>1</sup>: Prepared as described for **3a** starting from 4-iodomethylbenzoate(0.38 mmol), after work up, column chromatography (hexane:ethylacetate = 98:2) afforded **3g** as yellow solid (84 mg, 93%); mp 120-122 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 3.92 (s, 3H), 7.36-7.37 (m, 3H), 7.55-7.56 (m, 2H), 7.58-7.60 (m, 2H), 8.02-8.03 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 52.1, 88.5, 92.3, 122.6, 127.9, 128.3, 128.6, 129.3, 129.4, 131.4, 131.6, 166.4.

**1-(Phenylethynyl)-4-(trifluoromethyl)benzene (3h)**: Prepared as described for **3a** starting from 1-iodo-4-(trifluoromethyl)benzene (0.36 mmol), after work up, column chromatography (100% hexane) afforded **3h** as white solid (87 mg, 96%); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 7.38-7.39 (m, 3H), 7.55-7.57 (m, 2H), 7.60-7.65 (m, 4H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 87.9, 91.7, 122.5, 123.0, 124.8, 125.2, 127.1, 128.4, 128.8, 129.7, 129.9, 131.7, 131.8.

**1-Chloro-4-(phenylethynyl)benzene (3i)**<sup>2</sup>: Prepared as described for **3a** starting from 1-chloro-4-iodobenzene (0.42 mmol), after work up, column chromatography (100% hexane) afforded **3i** as white solid (65 mg, 73%); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 7.26-7.32 (m, 5H), 7.40-7.43 (m, 2H), 7.47-7.51 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 88.2, 90.3, 121.7, 122.8, 128.3, 128.4, 128.6, 131.5, 132.7, 134.1.

**2-(Phenylethynyl)aniline (3j)**<sup>7</sup>: Prepared as described for **3a** starting from 2-iodoaniline (0.45mmol), after work up, column chromatography (hexane:ethylacetate = 98:2) afforded **3j** as light yellow solid (65 mg, 74%); mp 90-92 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 6.62-6.65(m, 2H), 7.04-7.06 (m, 1H), 7.24-7.29 (m,4H),7.44(d, *J*= 6.4 Hz, 2H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 85.8, 94.6, 107.9, 114.3, 118.0, 123.3, 128.1, 128.3, 129.7, 131.4, 132.1, 147.7.

***N*-(2-(Phenylethynyl)phenyl)acetamide (3k)**: Prepared as described for **3a** starting from *N*-(2-iodophenyl)acetamide (0.38mmol), after work up, column chromatography (hexane:ethylacetate = 90:10) afforded **3k** as white solid (68 mg, 76%); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 2.25 (s, 3H), 7.07-7.09 (t, *J* = 7.5 Hz, 1H), 7.34-7.37 (m, 1H), 7.39-7.40 (m, 3H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.54-7.55 (m, 2H), 7.99 (bs, 1H), 8.41 (d, *J* = 8.4 Hz, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 24.9, 84.2, 96.3, 111.7, 119.3, 122.3, 123.3, 128.5, 128.9, 129.7, 131.4, 131.6, 138.8, 168.1.

**(3-(Phenylethynyl)phenyl)methanol (3l)**<sup>3</sup>: Prepared as described for **3a** starting from (3-iodophenyl)methanol (0.42 mmol), after work up, column chromatography (hexane:ethylacetate = 95:5) afforded **3l** as yellowish liquid (76 mg, 86%); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 4.71 (s, 2H), 7.35-7.37 (m, 5H), 7.46-7.47 (m, 1H), 7.53-7.56 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 64.8, 123.1, 123.4, 126.7, 128.3, 128.3, 128.5, 130.0, 130.7, 131.5, 141.0.

**(Phenylethynyl)thiophene(3m)**<sup>1</sup>: Prepared as described for **3a** starting from 2-iodothiophene (0.47 mmol), after work up, column chromatography (100% hexane) afforded **3m** as light grey solid (67 mg, 76%); mp 48-50°C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 7.02-7.03 (t, *J* = 4.3 Hz, 1H), 7.30 (m, 2H), 7.35-7.38 (m, 3H), 7.52-7.54 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 82.5, 92.9, 122.8, 123.2, 127.0, 127.2, 128.3, 128.4, 131.3, 131.8.

**(Phenylethynyl)naphthalene (3n)**<sup>3</sup>: Prepared as described for **3a** starting from 1-iodonaphthalene (0.39 mmol), after work up, column chromatography (100% hexane) afforded **3n** as colourless oil (74 mg, 82%); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 7.43-7.47 (m, 3H), 7.50-7.53 (m, 1H), 7.58-7.60 (m, 1H), 7.61-7.69 (m, 1H), 7.73-7.74 (m, 2H), 7.84 (dd, *J* = 7.1 Hz, 1H), 7.87-7.93 (m, 2H) 8.54 (d, *J* = 8.43 Hz, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 87.5, 94.3, 120.8, 123.3, 125.2, 126.1, 126.3, 126.7, 128.2, 128.3, 128.4, 128.7, 130.3, 131.6, 133.1, 133.2.

**1-Methoxy-4-(phenylethynyl)benzene (3o)**: Prepared as described for **3a** starting from iodobenzene (0.49 mmol), 3-(4-methoxyphenyl)propionic acid (0.58mmol) after work up, column chromatography (100% hexane) afforded **3o** (76 mg, 75%) as white solid. Spectral data same as described for **3a**.

**1,2-Bis(4-methoxyphenyl)ethyne (3p)**<sup>4</sup>: Prepared as described for **3a** starting from 4-iodoanisole (0.42 mmol), 3-(4-methoxyphenyl) propionic acid (0.51 mmol) after work up, column chromatography (100% hexane) afforded **3p** as pale yellow solid (65 mg, 64%); mp 146-148°C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 3.82 (s, 6H), 6.87 (d, *J* = 8.3 Hz, 4H), 7.45 (d, *J* = 8.3 Hz, 4H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 55.3, 87.9, 113.9, 115.7, 132.8, 159.3.

**1-Chloro-4-((4-methoxyphenyl)ethynyl)benzene (3q)<sup>3</sup>:** Prepared as described for **3a** starting from 4-iodoanisole (0.42 mmol), 3-(4-chlorophenyl)propionic acid (0.51 mmol) after work up, column chromatography (100% hexane) afforded **3q** as white solid (70 mg, 68%); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 3.83 (s, 3H), 6.88 (d, *J* = 8.7 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 55.2, 86.9, 90.3, 114.0, 114.9, 122.1, 128.6, 132.6, 133.0, 133.8, 159.7.

**1-Methoxy-4-(prop-1-yn-1-yl)benzene (3r)<sup>1</sup>:** Prepared as described for **3a** starting from 4-iodoanisole (0.42 mmol), 2-butyric acid (0.51 mmol) after work up, column chromatography (100% hexane) afforded **3r** as colourless liquid (36 mg, 58%); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 2.03 (s, 3H), 3.79 (s, 3H), 6.80-6.82 (m, 2H), 7.31-7.33 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 29.6, 55.2, 79.3, 84.0, 113.8, 116.1, 132.7, 158.9.

**1-Chloro-4-(phenylethynyl)benzene (3s):** Prepared as described for **3a** starting from iodobenzene (0.49 mmol), 3-(4-chlorophenyl) propionic acid (0.58 mmol) after work up, column chromatography (100% hexane) afforded **3s** (76 mg, 74%) as solid. Spectral data same as described for **3i**.

**2-(Phenylethynyl)pyridine (3t)<sup>3</sup>:** Prepared as described for **3a** starting from 2-bromopyridine (0.63 mmol), after work up, column chromatography (100% hexane) afforded **3t** as yellowish liquid (63 mg, 55%); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 7.22-7.24 (m, 1H), 7.34-7.36 (m, 3H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.59-7.60 (m, 2H), 7.66-7.68 (m, 1H), 8.61 (d, *J* = 4.4 Hz, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 88.5, 89.2, 122.2, 122.7, 127.1, 128.3, 128.9, 132.0, 136.1, 143.3, 149.9.

**1-Nitro-3-(phenylethynyl)benzene (3u)<sup>1</sup>:** Prepared as described for **3a** starting from 1-bromo-3-nitrobenzene (0.49 mmol) after work up, column chromatography (hexane:ethylacetate = 98:2) afforded **3u** as light yellow solid (63 mg, 57%); mp 67-69°C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 7.38-7.40 (m, 3H), 7.52-7.57 (m, 3H), 7.82 (d, *J* = 7.6 Hz, 1H), 8.17-8.18 (m, 1H), 8.37-8.38 (m, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 86.8, 91.9, 122.1, 122.8, 125.0, 126.3, 128.4, 129.0, 129.3, 131.7, 137.1, 148.0.

**1,2-Bis(phenylethynyl)benzene (5a)<sup>2</sup>:** Prepared as described for **3a** starting from 1,2-diiodobenzene (0.3 mmol), after work up, column chromatography (hexane) afforded **5a** as yellow solid (79 mg, 94%); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 7.22-7.24 (m, 2H), 7.26-7.27 (m, 6H), 7.48-7.50 (m, 6H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 88.3, 93.5, 123.3, 125.8, 127.9, 128.3, 128.4, 131.6, 131.7.

**1,3-Bis(phenylethynyl)benzene (5b)<sup>2</sup>:** Prepared as described for **3a** starting from 1,3-diiodobenzene (0.3 mmol), after work up, column chromatography (100% hexane) afforded **5b** as white solid (65 mg,

77%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.38-7.43 (m, 7H); 7.53-7.79 (m, 6H); 7.79 (s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 88.5, 89.9, 123.0, 123.6, 128.3, 128.4, 131.2, 131.6, 134.5.

**1,4-Bis(phenylethynyl)benzene (5c)<sup>2</sup>:** Prepared as described for **3a** starting from 1,4-diiodobenzene (0.3 mmol), after work up, column chromatography (hexane) afforded **5c** as white solid (60 mg, 72%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.35-7.36 (m, 3H), 7.37-7.38 (m, 3H), 7.53 (s, 4H), 7.54-7.55 (m, 2H), 7.56-7.57 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 89.1, 91.2, 123.0, 123.1, 128.3, 128.4, 131.5, 131.6.

**2-Phenyl-1-tosyl-1H-indole (7a)<sup>5</sup>:** Prepared as described for **3a** starting from N-(2-iodophenyl)-4-methylbenzenesulfonamide (0.26 mmol) after work up, column chromatography (hexane) afforded **7a** as white solid (68 mg, 73%); mp 145-147 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 2.30 (s, 3H), 6.58 (s, 1H), 7.06 (d, *J* = 7.8 Hz, 2H), 7.30-7.42 (m, 4H), 7.47-7.56 (m, 6H), 8.36 (d, *J* = 8.0 Hz, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 21.4, 113.5, 116.5, 120.6, 124.2, 124.7, 126.7, 127.4, 128.5, 129.1, 130.2, 130.5, 132.2, 134.6, 138.2, 142.0, 144.4.

**5-Methyl-2-phenyl-1-tosyl-1H-indole(7b)<sup>5</sup>:** Prepared as described for **3a** starting from N-(4-methyl-2-iodophenyl)-4-methylbenzenesulfonamide (0.25 mmol), after work up, column chromatography (hexane:ethylacetate 98:2) afforded **7b** as solid (67 mg, 72%); mp 110-112 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 2.27 (s, 3H), 2.40 (s, 3H), 6.46 (s, 1H), 7.02 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 1H), 7.21-7.25 (m, 3H), 7.41-7.42 (m, 3H), 7.48-7.50 (m, 2H), 8.16 (d, *J* = 8.5 Hz, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 21.2, 21.5, 113.5, 116.3, 120.6, 126.1, 126.7, 127.4, 128.5, 129.1, 130.2, 130.8, 132.5, 133.9, 142.2, 144.3.

**5-Chloro-2-phenyl-1-tosyl-1H-indole (7c)<sup>5</sup>:** Prepared as described for **3a** starting from N-(4-chloro-2-iodophenyl)-4-methylbenzenesulfonamide (0.24mmol), after work up, column chromatography (hexane) afforded **7c** as white solid (62 mg, 66%); mp 140-142 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 2.18 (s, 3H), 6.36 (s, 1H), 6.93 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.8 Hz, 1H), 7.29-7.37 (m, 6H), 8.12 (d, *J* = 8.8 Hz, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 21.5, 112.5, 117.6, 120.2, 124.8, 126.7, 127.5, 128.9, 129.2, 129.9, 130.3, 131.6, 131.8, 134.4, 136.5, 143.5, 144.8; HRMS (TOF-ESI) *m/z* calcd for C<sub>21</sub>H<sub>17</sub>ClNO<sub>2</sub>S [M + H]<sup>+</sup> 382.0669, found 382.0663.

**2-(4-Chlorophenyl)-1-tosyl-1H-indole (7d):** Prepared as described for **3a** starting from N-(2-iodophenyl)-4-methylbenzenesulfonamide (0.26 mmol) after work up, column chromatography (hexane) afforded **7d** as white solid (61 mg, 65%); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 2.29 (s, 3H), 6.55 (s, 1H), 7.04 (d, *J* = 8.04 Hz, 2H), 7.26-7.29 (m, 3H), 7.36-7.40 (m, 3H), 7.41-7.45 (m, 3H), 8.30 (d, *J* = 8.4Hz, 1H);

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  = 21.5, 114.0, 116.6, 120.7, 124.4, 125.0, 126.6, 127.7, 129.2, 130.4, 130.8, 131.4, 134.4, 134.7, 138.3, 140.7, 144.7.

**5-Chloro-2-(4-chlorophenyl)-1-tosyl-1H-indole (7e):** Prepared as described for **3a** starting from *N*-(4-chloro-2-iodophenyl)-4-methylbenzenesulfonamide (0.24 mmol), after work up, column chromatography (hexane:ethylacetate 98:2) afforded **7e** as solid (71 mg, 70%);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 2.31 (s, 3H), 6.48 (s, 1H), 7.07 (d,  $J$  = 8.1 Hz, 2H), 7.23 (d,  $J$  = 8.1 Hz, 2H), 7.31-7.33 (m, 1H), 7.40-7.43 (m, 5H), 8.23 (d,  $J$  = 8.8 Hz, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  = 21.5, 112.9, 117.6, 120.3, 125.1, 126.6, 127.8, 129.3, 130.1, 130.2, 131.4, 131.5, 134.2, 135.1, 136.6, 142.2, 145.0; HRMS (TOF-ESI)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{16}\text{Cl}_2\text{NO}_2\text{S}$  [ $\text{M} + \text{H}$ ] $^+$  416.0279, found 416.0273.

**5-Chloro-2-methyl-1-tosyl-1H-indole (7f):** Prepared as described for **3a** starting from *N*-(4-chloro-2-iodophenyl)-4-methylbenzenesulfonamide (0.24mmol) after work up, column chromatography (hexane:ethylacetate = 98:2) afforded **7f** as white solid (60 mg, 76%);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 2.35 (s, 3H), 2.58 (s, 3H), 6.28 (s, 1H), 7.19-7.22 (m, 3H), 7.36 (s, 1H), 7.63 (d,  $J$  = 8.2 Hz, 2H), 8.07 (d,  $J$  = 8.8 Hz, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 21.5, 30.9, 108.8, 115.4, 119.5, 123.8, 126.3, 129.1, 129.9, 130.9, 135.3, 136.0, 138.9, 144.9.

**2-Phenyl-1H-indole (7g)<sup>6</sup>:** Prepared as described for **3a** starting from *N*-(2-iodophenyl)methanesulfonamide (0.33 mmol), after work up, column chromatography (hexane:ethylacetate = 98:2) afforded **7g** as white solid (44 mg, 68%);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 6.84 (s, 1H), 7.12-7.14 (m, 1H), 7.19-7.21 (m, 1H), 7.32-7.34 (m, 1H), 7.40 (d,  $J$  = 8.1 Hz, 1H), 7.44-7.46 (m, 2H), 7.63 (d,  $J$  = 7.8 Hz, 1H), 7.67 (d,  $J$  = 7.8 Hz, 2H), 8.34 (bs, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  = 100.0, 110.8, 120.2, 120.6, 122.3, 125.1, 127.7, 129.0, 129.2, 132.4, 136.8, 137.8.

**5-Methyl-2-phenyl-1H-indole (7h):** Prepared as described for **3a** starting from 2,2,2-trifluoro-*N*-(2-iodo-4-methylphenyl)acetamide (0.30 mmol), after work up, column chromatography (hexane:ethylacetate = 98:2) afforded **7h** as white solid (39 mg, 63%);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 2.46 (s, 3H), 6.76 (s, 1H), 7.02 (d,  $J$  = 8.2 Hz, 1H), 7.29-7.33 (m, 2H), 7.43-7.46 (m, 3H), 7.65 (d,  $J$  = 7.5 Hz, 2H), 8.24 (bs, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  = 21.4, 95.5, 110.5, 120.2, 123.9, 125.0, 127.5, 128.9, 129.4, 129.5, 132.5, 135.1, 137.9; HRMS (TOF-ESI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{14}\text{N}$  [ $\text{M} + \text{H}$ ] $^+$  208.1126, found 208.1120.

Important note: Compounds **9a**, **c-f**, **h** are unstable in nature and we became unable to perform HRMS analysis from outside agencies. These compounds are not possible to perform GCMS, so we have provided only HRMS data for compounds **9b**, **9g**. ESI-MS for **9a**, **9h**. Further structure of **9g** was confirmed by 2D NMR.



**(E)-2-Benzyl-3-benzylidene-6,6,8-trimethyl-1,2,3,4,5,6-hexahydrobenzo[3,4]cyclohepta[1,2-c]pyrrole (9a):** Prepared as described for **3a** starting from *N*-benzyl-1-(8-bromo-3,5,5-trimethyl-6,7-dihydro-5H-benzo[7]annulen-9-yl)methanamine (0.26 mmol), after work up, column chromatography (100% Hexane) afforded **9a** as liquid (75 mg, 71%); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 1.35 (s, 6H), 2.00-2.02 (t, *J* = 6.9 Hz, 2H), 2.37 (s, 3H), 2.72-2.75 (t, *J* = 6.9 Hz, 2H), 3.86 (s, 2H), 4.87 (s, 2H), 6.81 (s, 1H), 6.98-7.01 (m, 3H), 7.09 (d, *J* = 7.2 Hz, 2H), 7.18 (d, *J* = 7.3 Hz, 1H), 7.24-7.30 (m, 6H), 7.40 (d, *J* = 7.8 Hz, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 21.3, 22.6, 22.9, 30.1, 37.9, 42.4, 50.6, 117.7, 119.8, 124.7, 126.0, 126.1, 126.4, 126.5, 126.6, 127.2, 127.9, 128.4, 128.5, 128.6, 132.0, 134.2, 138.3, 139.8, 146.3; ESI-MS (Q-TOF) *m/z* calcd for C<sub>30</sub>H<sub>32</sub>N [M + 1]<sup>+</sup> 406.2535, observed 406.2559.

**(E)-3-Benzylidene-6,6,8-trimethyl-2-(3,4,5-trimethoxybenzyl)-1,2,3,4,5,6-hexahydrobenzo[3,4]cyclohepta[1,2-c]pyrrole (9b):** Prepared as described for **3a** starting from 1-(8-bromo-3,5,5-trimethyl-6,7-dihydro-5H-benzo[7]annulen-9-yl)-*N*-(3,4,5-trimethoxybenzyl)methanamine (0.21 mmol) after work up, column chromatography (100% Hexane) afforded **9b** as liquid (69 mg, 66%); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 1.24 (s, 6H), 1.90-1.95 (t, *J* = 6.9 Hz, 2H), 2.28 (s, 3H), 2.61-2.65 (t, *J* = 6.9 Hz, 2H), 3.61 (s, 6H), 3.71 (s, 3H), 3.78 (s, 2H), 4.74 (s, 2H), 6.04 (s, 2H), 6.70 (s, 1H), 6.92-6.94 (d, *J* = 7.7 Hz, 1H), 6.97-7.00 (m, 2H), 7.06-7.08 (m, 1H), 7.11-7.16 (m, 3H), 7.29 (d, *J* = 7.7 Hz, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 21.3, 22.8, 30.0, 37.9, 42.9, 50.6, 55.8, 56.0, 60.7, 103.1, 117.5, 119.8, 125.0, 126.0, 126.2, 126.6, 126.7, 127.9, 128.2, 128.3, 132.1, 134.1, 134.4, 136.8, 139.7, 146.0, 153.3. HRMS (TOF-ESI) *m/z* calcd for C<sub>33</sub>H<sub>38</sub>NO<sub>3</sub> [M + H]<sup>+</sup> 496.2852, found 496.2846.

**(E)-3-Benzylidene-6,6,8-trimethyl-2-(4-methylbenzyl)-1,2,3,4,5,6-hexahydrobenzo[3,4]cyclohepta[1,2-c]pyrrole (9c):** Prepared as described for **3a** starting from 1-(8-bromo-3,5,5-trimethyl-6,7-dihydro-5H-benzo[7]annulen-9-yl)-*N*-(4-methylbenzyl)methanamine (0.12 mmol) after work up, column chromatography (100% Hexane) afforded **9c** as liquid (40 mg, 76%); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 1.28 (s, 6H), 1.99-2.01 (t, *J* = 6.9 Hz, 2H), 2.33 (s, 3H), 2.37 (s, 3H), 2.71-2.74 (t, *J* = 6.9 Hz, 2H), 3.86 (s, 2H), 4.82 (s, 2H), 6.79 (s, 1H), 6.87 (d, *J* = 7.7 Hz, 2H), 6.99 (d, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 4H), 7.17-7.20 (t, *J* = 7.2 Hz, 1H), 7.25-7.27 (m, 3H), 7.40 (d, *J* = 7.7 Hz, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 21.0, 21.3, 22.9, 30.0, 37.9, 42.3, 50.3, 60.3, 117.6, 119.7, 124.6, 125.9, 126.1, 126.5, 126.5, 126.6, 127.9, 128.1, 128.4, 129.2, 132.1, 134.2, 135.3, 136.9, 139.9, 146.3.

**(E)-3-Benzylidene-2-(2-methoxybenzyl)-6,6,8-trimethyl-1,2,3,4,5,6-hexahydrobenzo[3,4]cyclohepta[1,2-c]pyrrole (9d):** Prepared as described for **3a** starting from 1-(8-bromo-3,5,5-trimethyl-6,7-dihydro-5H-benzo[7]annulen-9-yl)-*N*-(2-methoxybenzyl)methanamine

(0.24mmol) after work up, column chromatography (100% Hexane) afforded **9d** as liquid (55 mg, 52%); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 1.32 (s, 6H), 2.01-2.03 (t, *J* = 6.6 Hz, 2H), 2.37 (s, 3H), 2.73-2.74 (t, *J* = 6.0 Hz, 2H), 3.82 (s, 3H), 3.87 (s, 2H), 4.92 (s, 2H), 6.64 (s, 1H), 6.82-6.85 (m, 3H), 7.00 (d, *J* = 7.3 Hz, 1H), 7.10 (d, *J* = 6.8 Hz, 2H), 7.17-7.26 (m, 6H), 7.42 (d, *J* = 7.5 Hz, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ = 21.3, 23.0, 30.0, 37.9, 42.3, 45.5, 55.1, 109.8, 117.7, 119.3, 120.6, 124.5, 125.8, 126.3, 126.5, 126.6, 126.8, 127.5, 127.9, 128.1, 128.2, 128.3, 134.1, 139.9, 146.2, 156.2.

**(E)-3-Benzylidene-6,6,8-trimethyl-2-(naphthalen-1-ylmethyl)-1,2,3,4,5,6-hexahydrobenzo**

**[3,4]cyclohepta[1,2-c]pyrrole (9e):** Prepared as described for **3a** starting from 1-(8-bromo-3,5,5-trimethyl-6,7-dihydro-5H-benzo[7]annulen-9-yl)-*N*-(naphthalen-1-ylmethyl)methanamine (0.23 mmol) after work up, column chromatography (100% hexane) afforded **9e** as liquid (77 mg, 73%); <sup>1</sup>H NMR (600 MHz, Acetone-d<sub>6</sub>) δ = 1.15 (s, 6H), 1.83-1.85 (t, *J* = 6.9 Hz, 2H), 2.12 (s, 3H), 2.59-2.61 (t, *J* = 6.9 Hz, 2H), 3.76 (s, 2H), 5.27 (s, 2H), 6.65 (d, *J* = 7.1 Hz, 1H), 6.68 (s, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 2H), 6.99 (d, *J* = 6.9 Hz, 1H), 7.05-7.07 (m, 3H), 7.13 (d, *J* = 6.8 Hz, 1H), 7.18-7.21 (t, *J* = 7.7 Hz, 1H), 7.30-7.31 (t, *J* = 7.9 Hz, 1H), 7.33-7.35 (t, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 1H); <sup>13</sup>C NMR (150 MHz, Acetone-d<sub>6</sub>) δ = 20.5, 22.8, 29.7, 29.8, 37.7, 42.6, 40.1, 117.6, 119.2, 122.7, 124.2, 124.8, 125.5, 125.8, 125.9, 126.2, 126.4, 126.5, 126.7, 127.8, 128.0, 128.1, 128.3, 128.6, 130.6, 132.3, 133.6, 133.8, 134.2, 140.0, 145.9.

**(E)-3-Benzylidene-6,6,8-trimethyl-2-phenyl-1,2,3,4,5,6-hexahydrobenzo[3,4]cyclohepta[1,2-**

**c]pyrrole (9f):** Prepared as described for **3a** starting from *N*-((8-bromo-3,5,5-trimethyl-6,7-dihydro-5H-benzo[7]annulen-9-yl)methyl)aniline (0.27 mmol) after work up, column chromatography (100% Hexane) afforded **9f** as liquid (64 mg, 60%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 1.38 (s, 6H), 2.02-2.04 (m, 2H), 2.41 (s, 3H), 2.70-2.75 (m, 2H), 3.99 (s, 2H), 7.01 (s, 1H), 7.07-7.09 (m, 3H), 7.21-7.24 (m, 3H), 7.30-7.39 (m, 5H), 7.49-7.52 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 21.3, 22.9, 30.4, 30.8, 37.9, 42.0, 117.9, 120.5, 125.7, 125.9, 126.5, 126.6, 126.7, 126.8, 127.8, 128.2, 128.9, 129.4, 129.7, 130.6, 134.6, 140.2, 146.5.

**(E)-3-Benzylidene-2-cyclohexyl-6,6,8-trimethyl-1,2,3,4,5,6-hexahydrobenzo[3,4]cyclohepta [1,2-**

**c]pyrrole (9g):** Prepared as described for **3a** starting from *N*-((8-bromo-3,5,5-trimethyl-6,7-dihydro-5H-benzo[7]annulen-9-yl)methyl)cyclohexanamine (0.26 mmol), after work up, column chromatography (100% Hexane) afforded **9g** as light yellow liquid (69 mg, 65%); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ = 1.22-1.25 (m, 3H), 1.37 (s, 6H), 1.58-1.60 (m, 2H), 1.70 (m, 1H), 1.77-1.82 (m, 4H), 2.03-2.05 (t, *J* = 6.9 Hz, 2H), 2.41 (s, 3H), 2.78-2.80 (t, *J* = 6.9 Hz, 2H), 3.71 (m, 1H), 4.03 (s, 2H), 6.90 (s, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 2H), 7.22-7.24 (m, 1H), 7.28 (s, 1H), 7.31-7.33 (t, *J* = 7.5 Hz, 2H), 7.48 (d, *J*

= 7.8 Hz, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  = 21.3, 22.9, 25.4, 25.9, 29.9, 30.1, 34.7, 37.8, 42.1, 55.1, 113.0, 118.0, 124.2, 125.4, 125.9, 126.4, 126.5, 127.9, 128.3, 132.2, 133.9, 140.2, 146.3. HRMS (TOF-ESI)  $m/z$  calcd for  $\text{C}_{29}\text{H}_{36}\text{N}$   $[\text{M} + \text{H}]^+$  398.2848, found 398.2841.

**(E)-3-Benzylidene-6,6,8-trimethyl-2-phenethyl-1,2,3,4,5,6-hexahydrobenzo[3,4]cyclohepta [1,2-c]pyrrole (9h):** Prepared as described for **3a** starting from *N*-((8-bromo-3,5,5-trimethyl-6,7-dihydro-5H-benzo[7]annulen-9-yl)methyl)-2-phenylethanamine (0.25 mmol) after work up, column chromatography (100% Hexane) afforded **9h** as liquid (76 mg, 72%);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.22 (s, 6H), 1.87-1.89 (t,  $J$  = 6.9 Hz, 2H), 2.25 (s, 3H), 2.57-2.63 (m, 4H), 3.74-3.77 (m, 4H), 6.58 (s, 1H), 6.81 (d,  $J$  = 7.0 Hz, 2H), 6.88 (d,  $J$  = 7.7 Hz, 1H), 7.01 (d,  $J$  = 7.5 Hz, 2H), 7.06-7.13 (m, 5H), 7.16-7.18 (t,  $J$  = 7.5 Hz, 2H), 7.24 (d,  $J$  = 7.7 Hz, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  = 21.3, 22.9, 29.9, 30.0, 37.9, 38.3, 42.5, 48.4, 116.5, 119.0, 124.5, 125.7, 126.0, 126.4, 126.5, 126.6, 127.9, 128.1, 128.4, 128.5, 128.7, 132.1, 134.1, 138.4, 139.9, 146.2; ; ESI-MS (Q-TOF)  $m/z$  calcd for  $\text{C}_{31}\text{H}_{34}\text{N}$   $[\text{M} + 1]^+$  420.2691, observed 420.2704.

### 2DNMR spectral interpretation of compound 9g

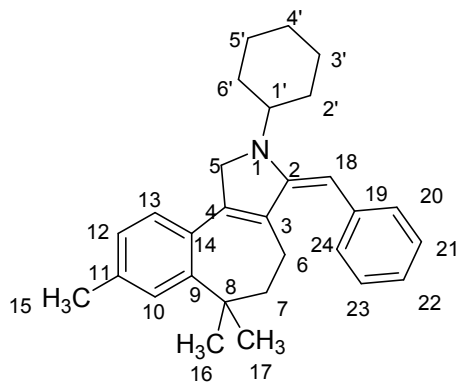
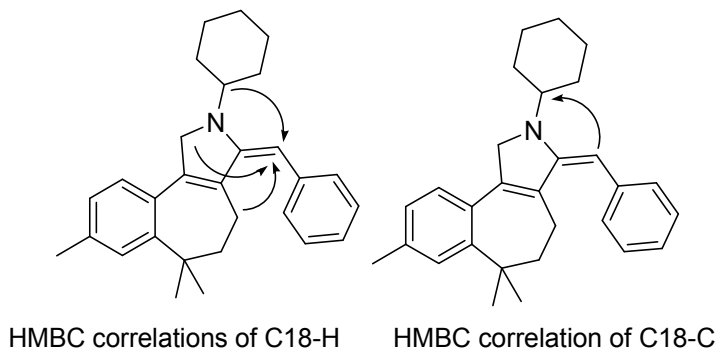


Fig. 1 Structure of 9g



**Fig. 2 Selected HMBC correlations****Table 1. <sup>1</sup>H NMR (600 MHz) and <sup>13</sup>C NMR (150 MHz) of compound 9g in CDCl<sub>3</sub> (δ values)**

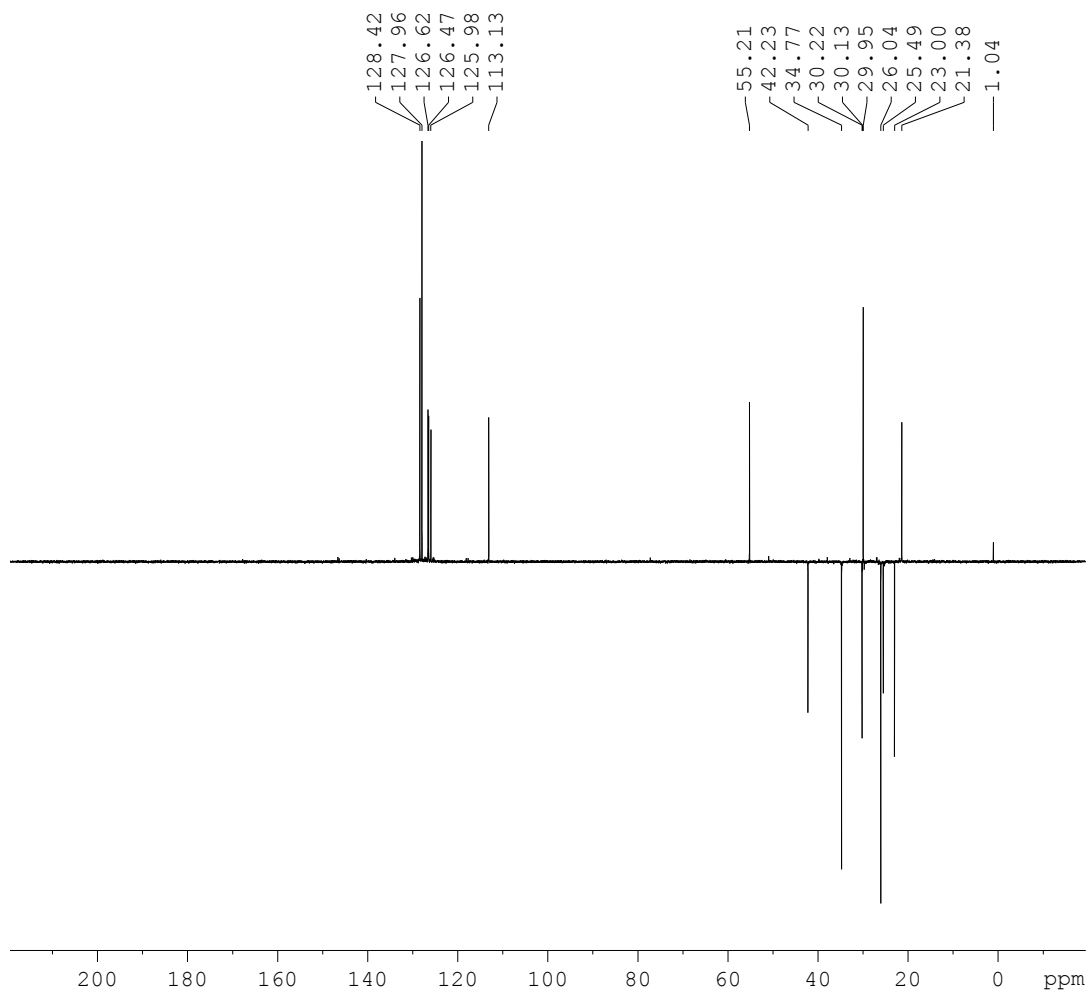
Position	δ <sub>C</sub> (ppm)	δ <sub>H</sub> (ppm) m ( <i>J</i> Hz)
1	-	-
2	140	-
3	118	-
4	125.4	-
5	30.1	3.98 s
6	22.9	2.74 t (6.9)
7	42.2	2.00-1.98 t (6.9)
8	37.9	-
9	146	-
10	126.4	7.23 s
11	133.9	-
12	126.6	7.01 d (7.8)
13	127.9	7.44 d (7.8)
14	132	-
15	21.3	2.36 s
16, 17	29.9	1.31 s
18	113	6.85 s
19	124	-
20, 24	127.9	7.14 d (7.2)
21, 23	128.2	7.29 m
22	125.9	7.19 m
1'	55	3.65 s

2', 6'	26	1.74 m
3', 4', 5'	34.7, 25.4	1.54, 1.17 m

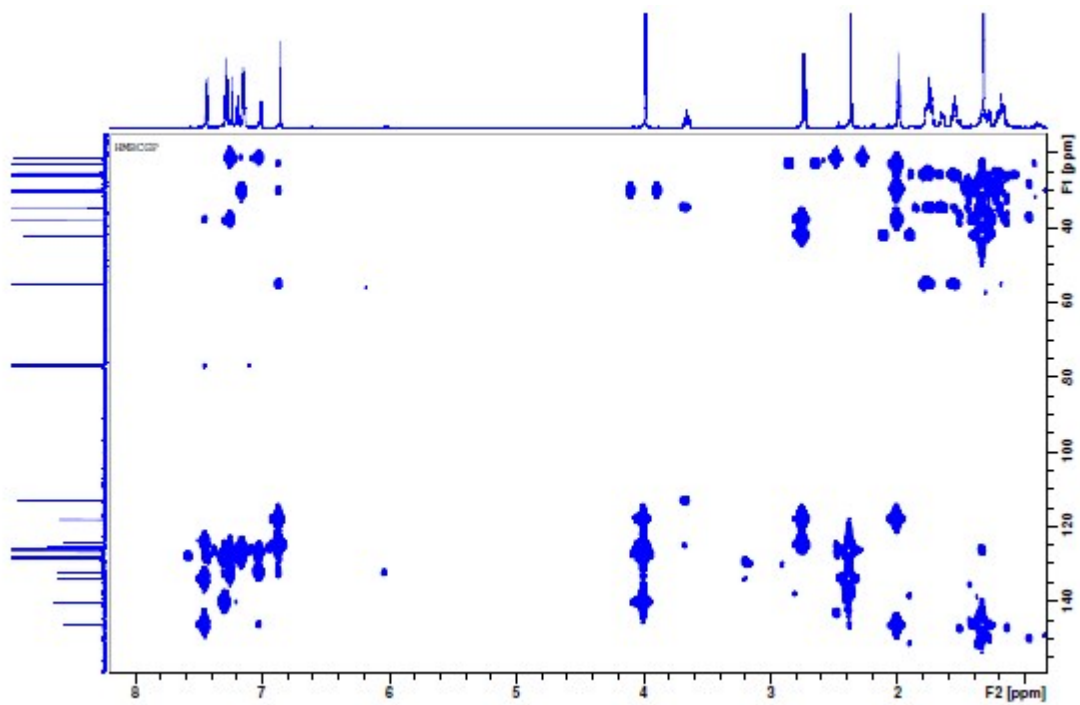
The COSY data revealed the corresponding proton-proton networks as follows H5 → H1', H13, H6 → H7, H12 → H3, H20 → H21.

The long range proton-carbon correlations observed in HMBC spectrum of 9e. The HMBC spectrum disclosed the intense linkage of H18 to C1', C3, C5, C6 and H1' to C18 which was the evidence for the formation of 3-pyrroline ring (**fig 2**). The other HMBC correlations were as following: H5 correlates with C3, C2, C4, and H6 correlates with C7, C8, C3, C19, and H7 correlates with C3, C9, C6, C16, C17, C8 and H10 correlates with C15, C8 and H12 correlates with C15, C14, C9, and H13 correlates with C11, C9.

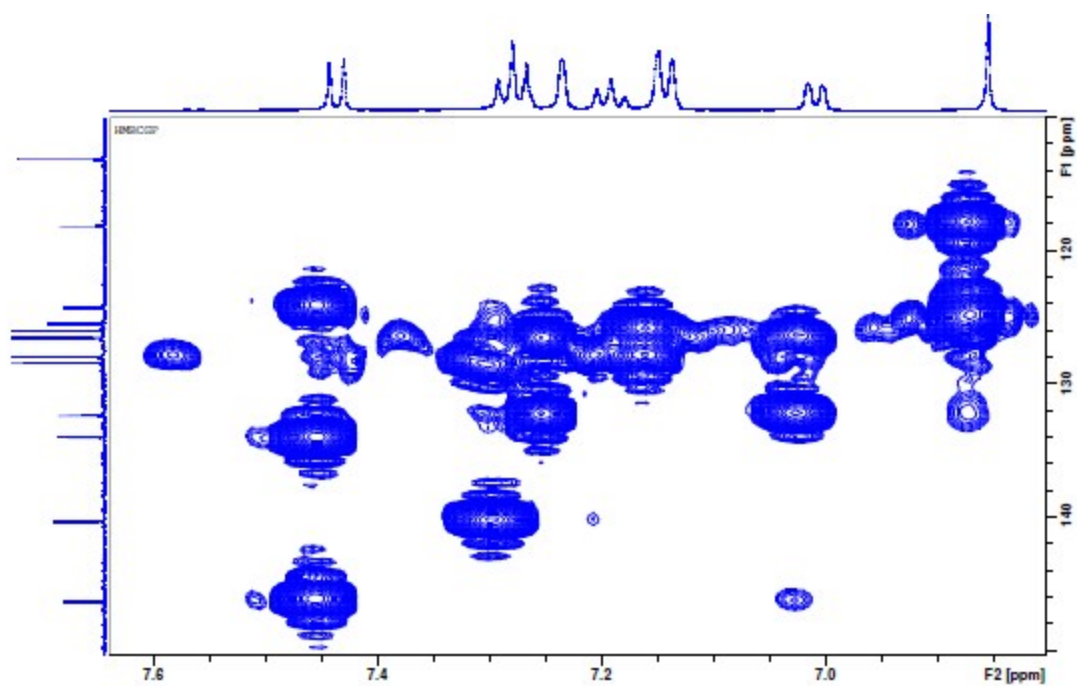
Compound **9g** (DEPT 135 ° in CDCl<sub>3</sub>)



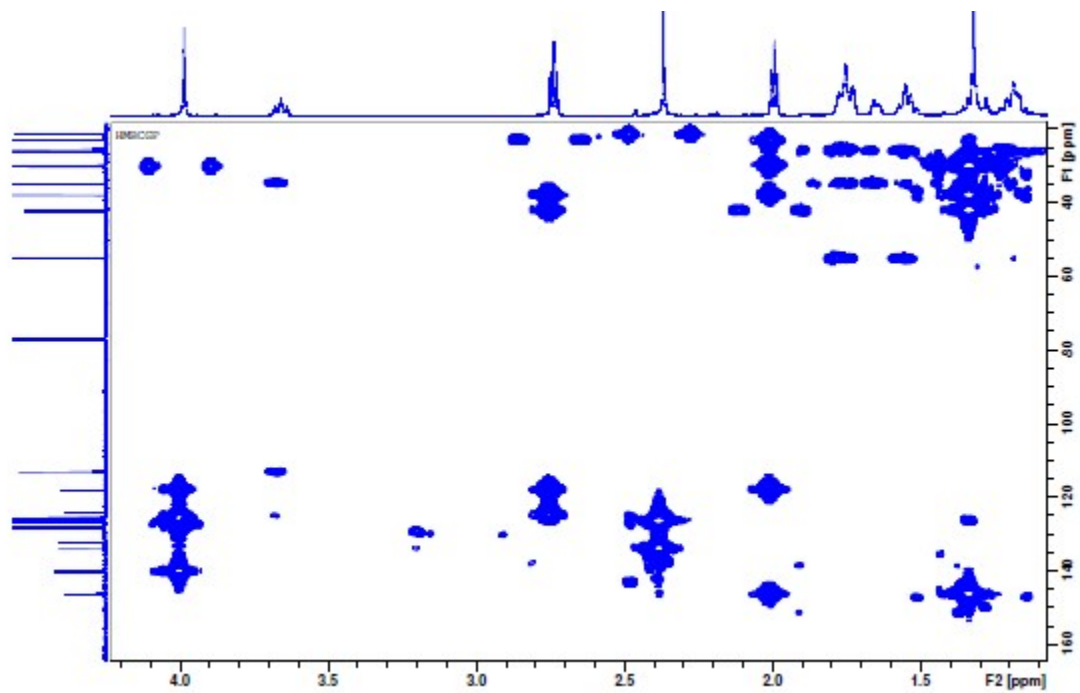
Compound **9g** (HMBC in CDCl<sub>3</sub>)



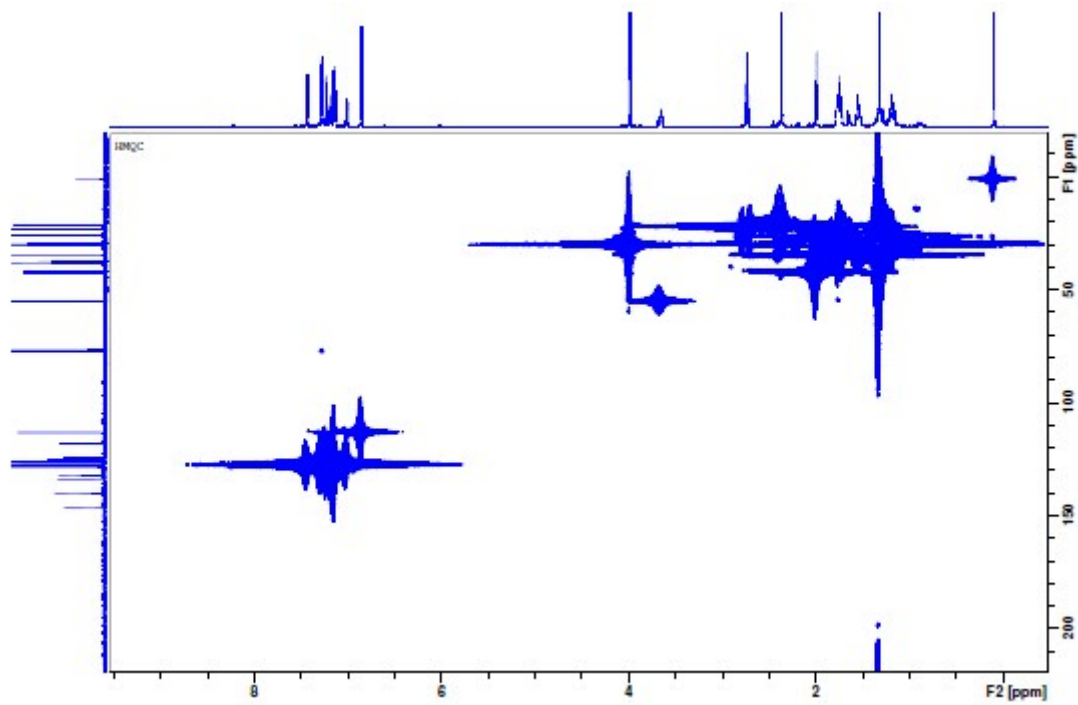
Compound **9g** (HMBC Expanded aromatic region in CDCl<sub>3</sub>)



Compound **9g** (HMBC Expanded aliphatic region in CDCl<sub>3</sub>)

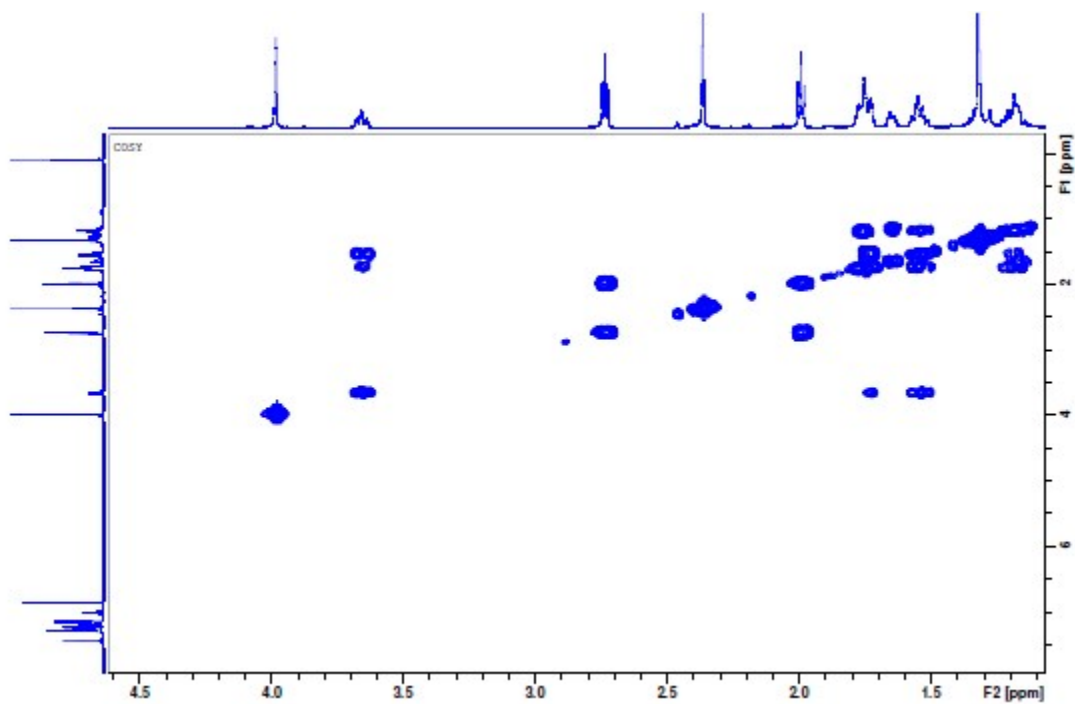


Compound **9g** (HMQC in CDCl<sub>3</sub>)

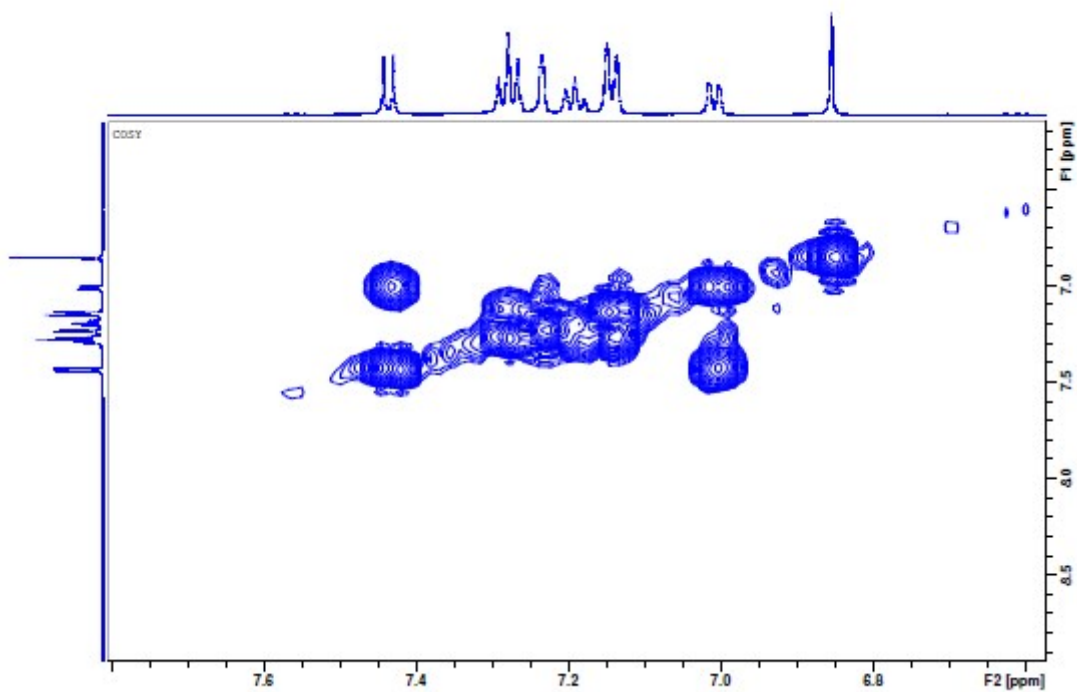


Compound **9g** (COSY aliphatic region in CDCl<sub>3</sub>)



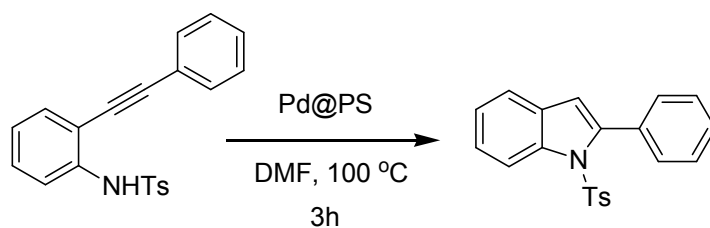


Compound **9g** (COSY aliphatic region in CDCl<sub>3</sub>)



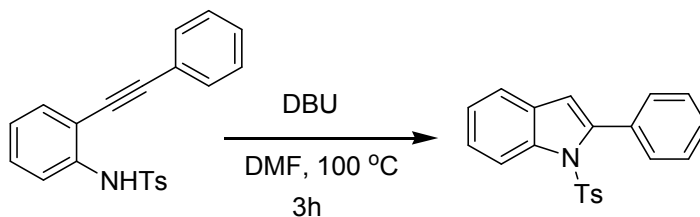
**Mechanistic studies for the cyclization reaction for the synthesis of substituted indoles.**

**i) Cyclization mediated by Pd@PS**



2-(2-phenylethynyl)-N-tosylbenzenamine **10a** (0.5 mmol) was charged in 10 ml reaction tube and Pd@PS (1 equiv) and DMF was added then the reaction mixture was stirred at 100 °C for 3 h. As the completion of the reaction monitored by TLC, 3 ml of H<sub>2</sub>O was added to the reaction mixture and extracted with ethylacetate, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated on vacuum. The crude mixture was purified by column chromatography (hexane:ethylacetate = 98:2) gave the desired product **7a** in 85% yield.

**ii) Cyclization mediated by DBU**



2-(2-phenylethynyl)-N-tosylbenzenamine **10a** (0.5 mmol) was charged in 10 ml reaction tube and DBU (1 equiv) and DMF was added then the reaction mixture was stirred at 100 °C for 3 h. As the completion of the reaction monitored by TLC, 3 ml of H<sub>2</sub>O was added to the reaction mixture and extracted with ethylacetate, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated on vacuum. The crude mixture was purified by column chromatography (hexane:ethylacetate = 98:2) gave the desired product **7a** in 65% yield.

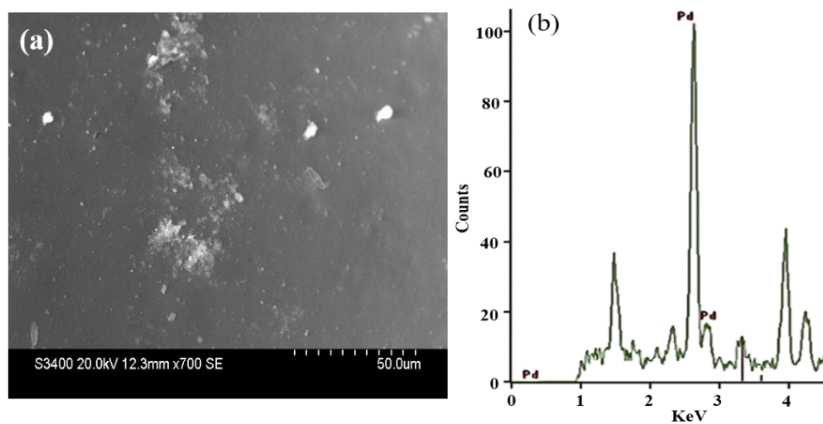
ICP-AES analysis was performed from the reaction mixture using 4-iodoanisole as substrate under optimized reaction condition. The reaction mixture after complete acid digestion was analyzed for ICP-AES analysis and the results are summarized in the following table 2.

**Table 2. ICP-AES analysis**

Cycle	Leaching (ppm)
1 <sup>st</sup>	0.146
3 <sup>rd</sup>	0.14
5 <sup>th</sup>	0.052

### SEM and SEM-EDS analysis after five runs

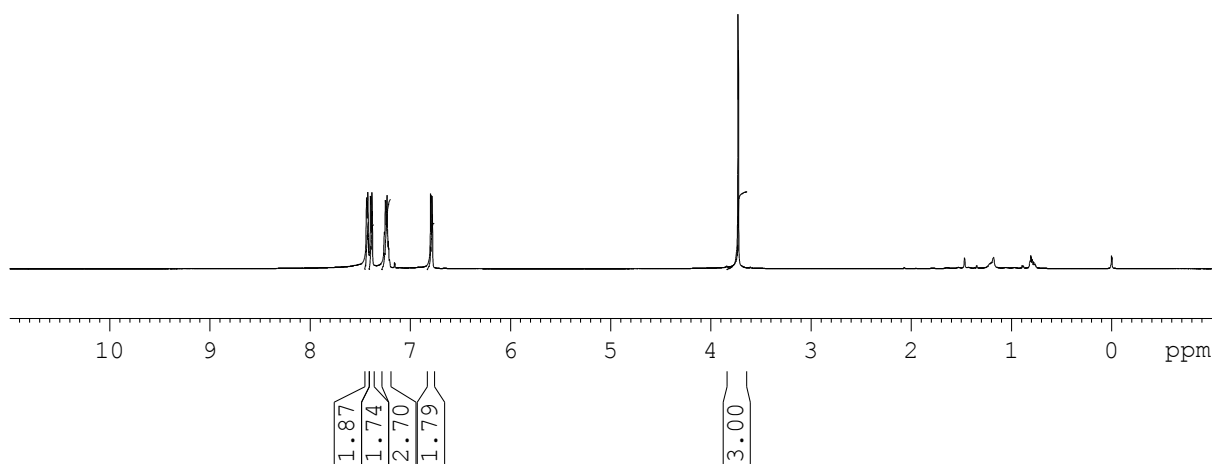
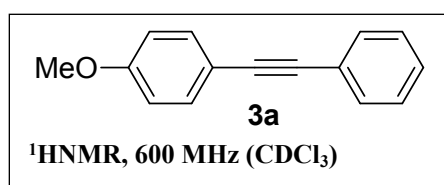
The SEM-EDS analysis of the Pd@PS catalyst was done after five reaction cycles and gratifying to found that the presence of palladium particles on the surface of the catalyst.

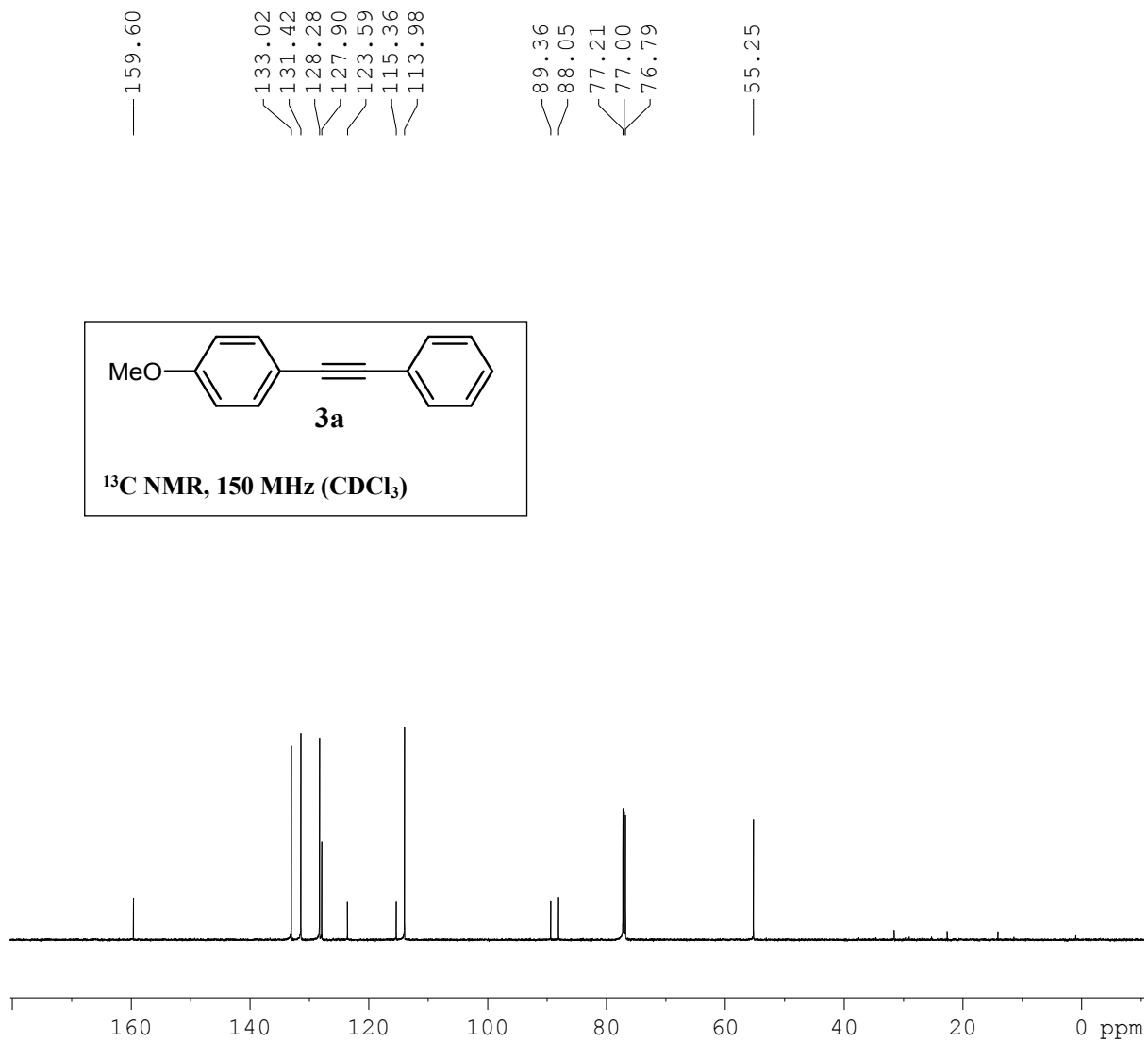


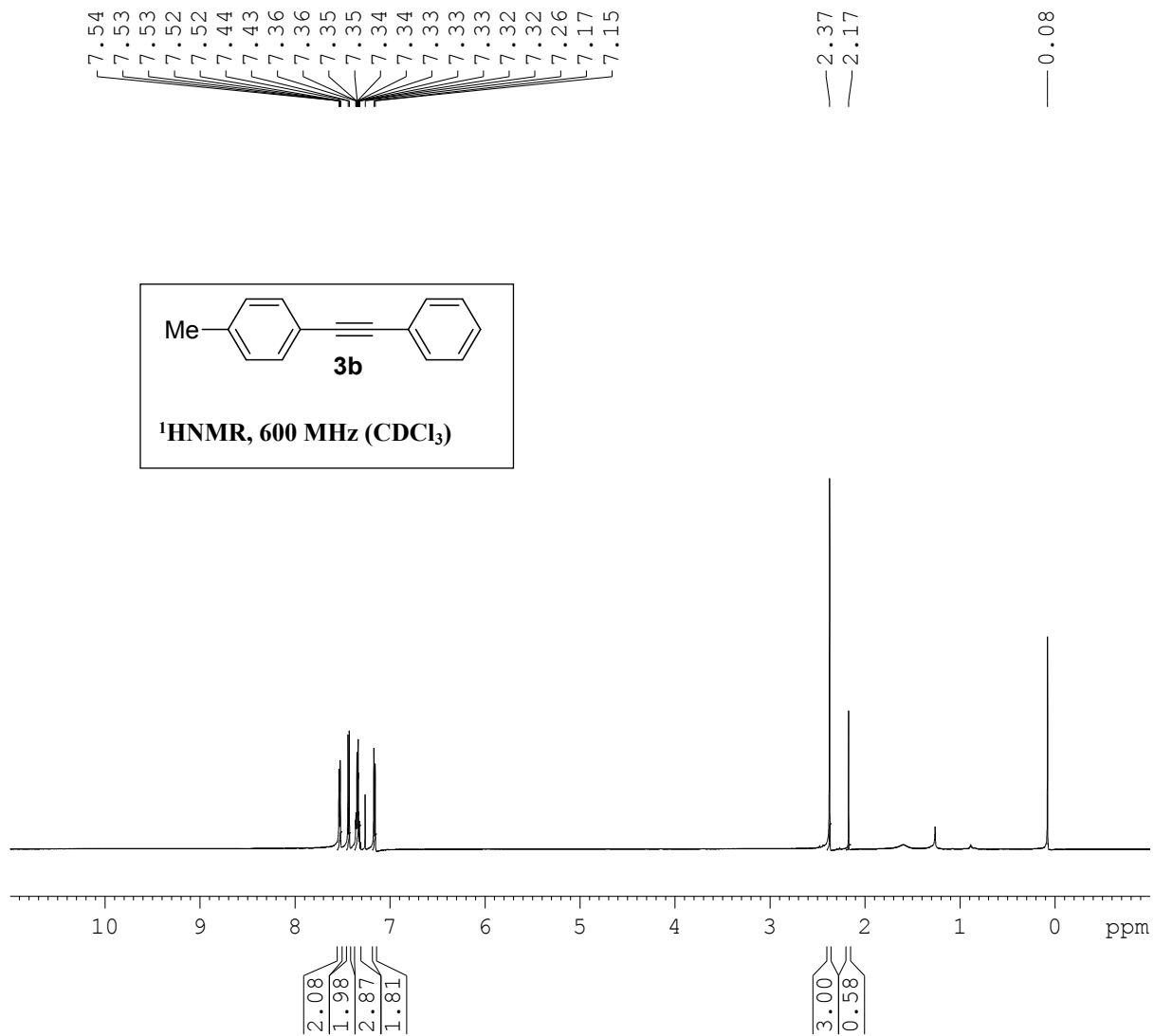
**Fig 3.** a) SEM image of Pd@PS after 5 cycles b) EDS spectra shows presences of Palladium

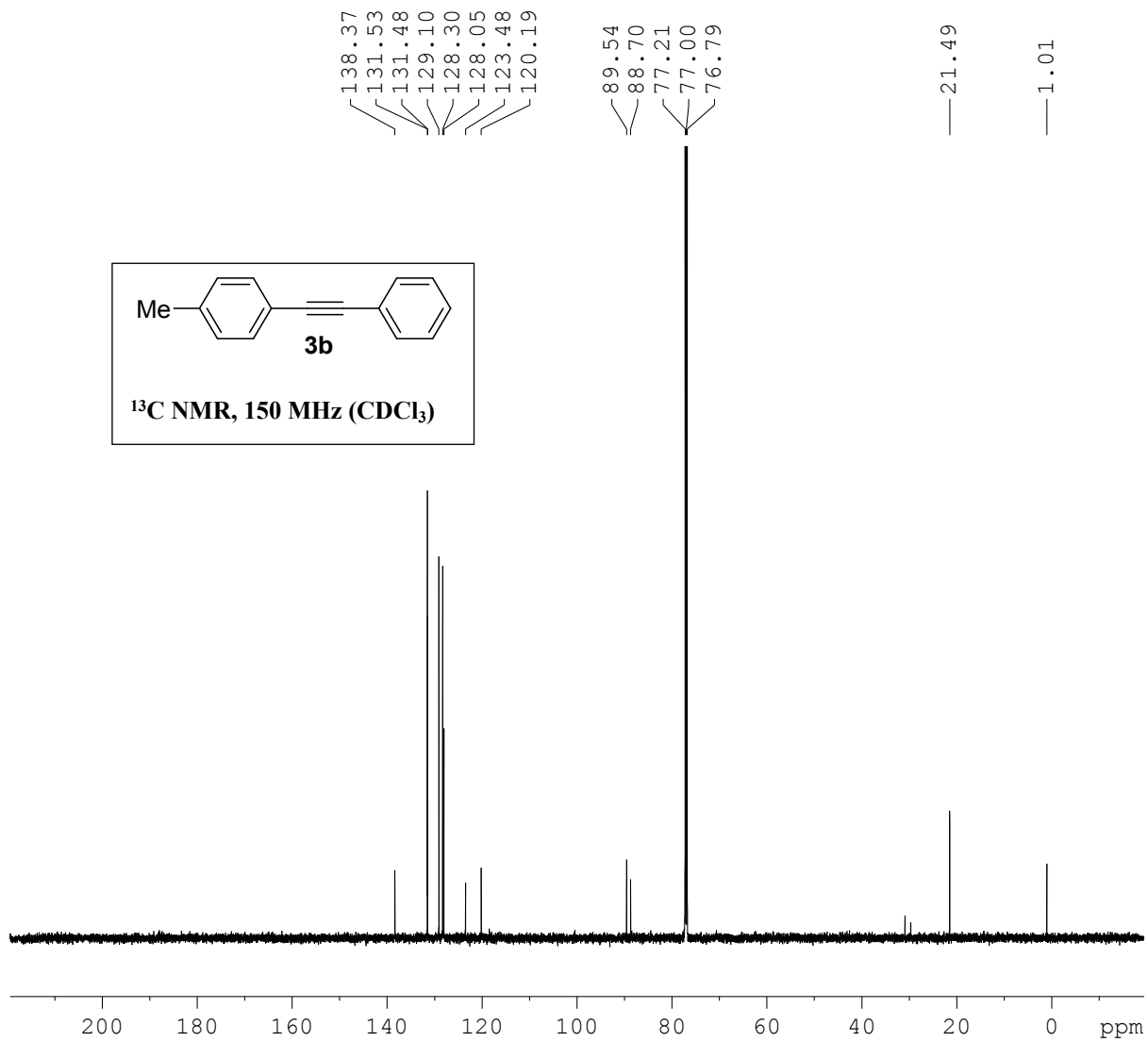
Spectral data for all synthesized compounds ( $^1\text{H}$ NMR,  $^{13}\text{C}$ NMR, GC-MS, ESI-MS)

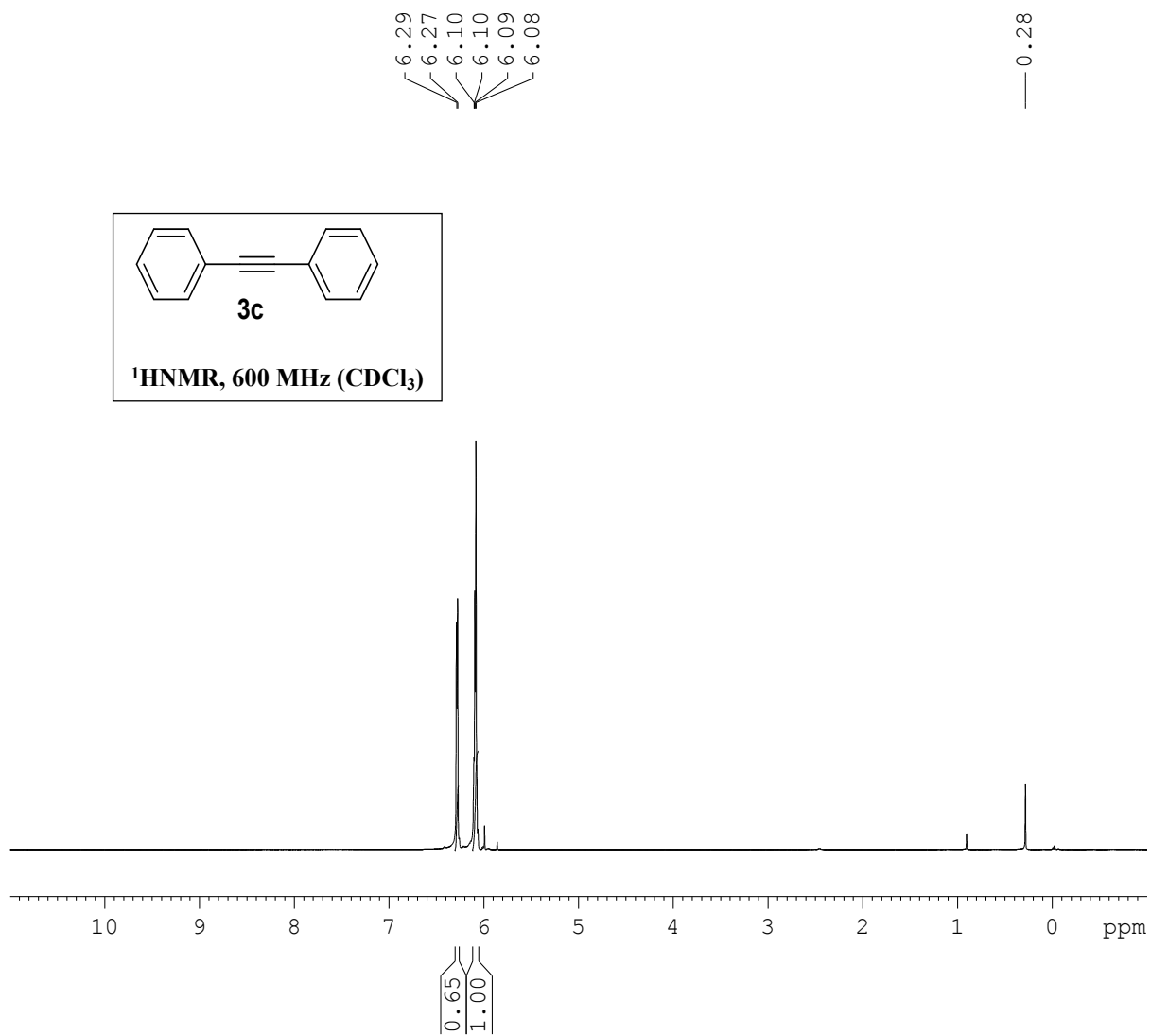
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6.79  
6.78  
6.78  
3.73  
3.72







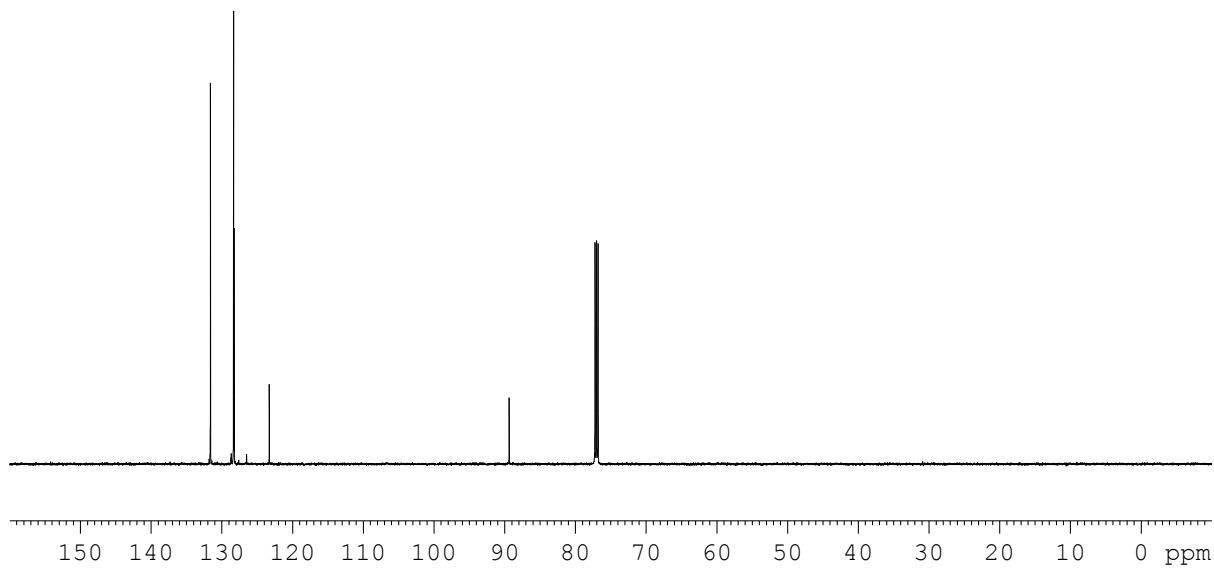
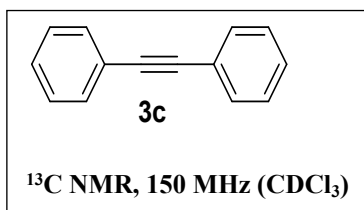


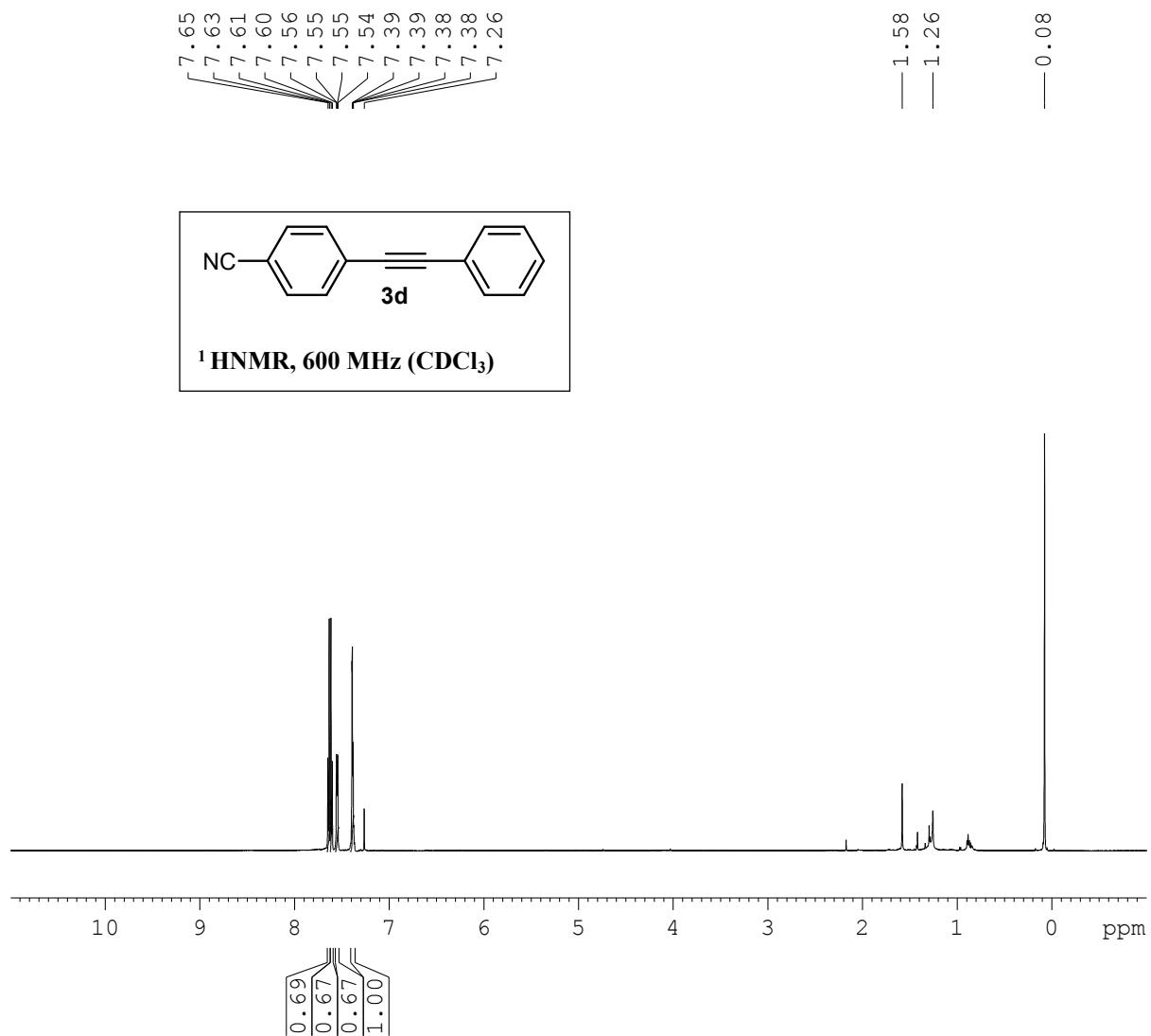


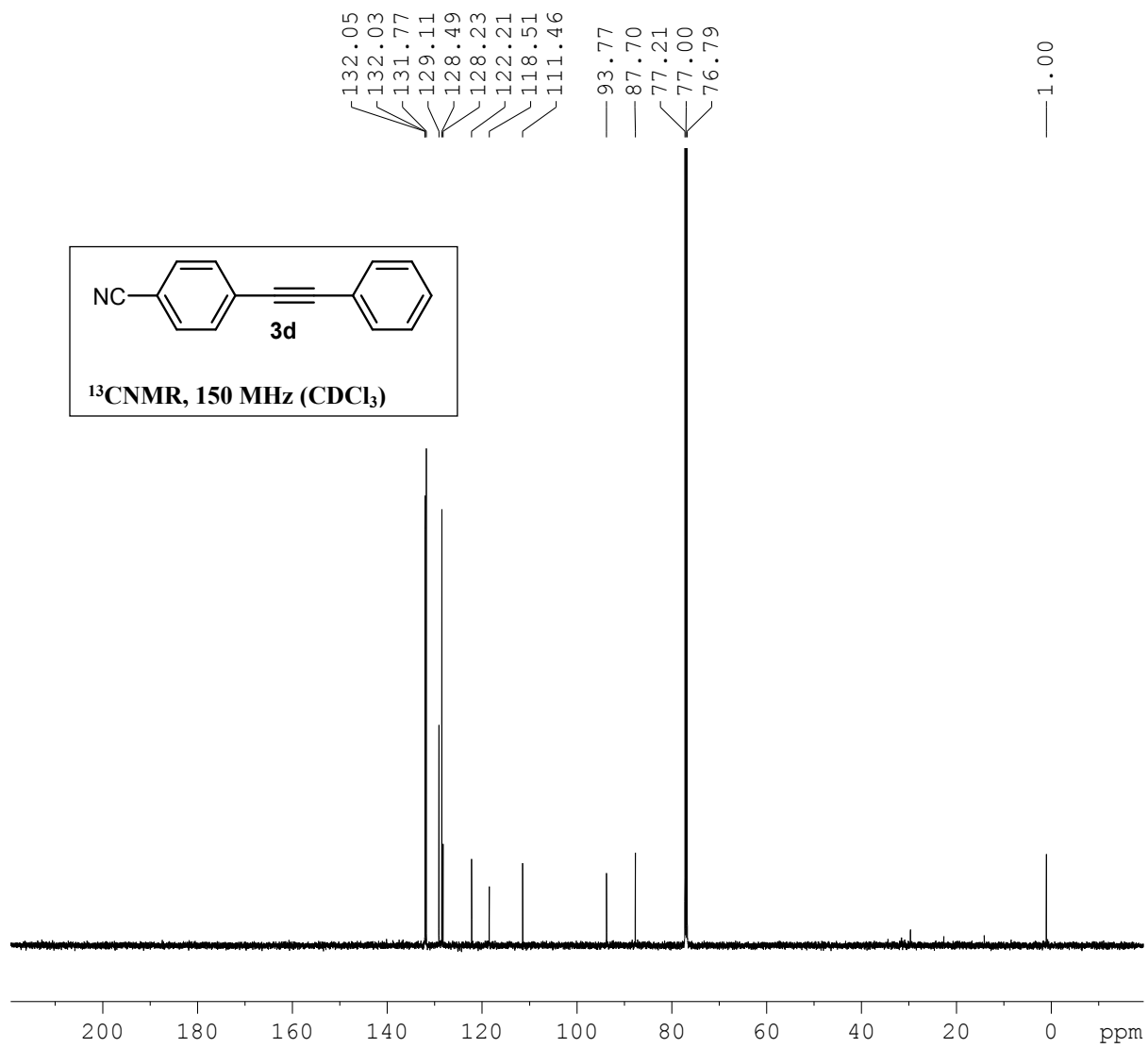


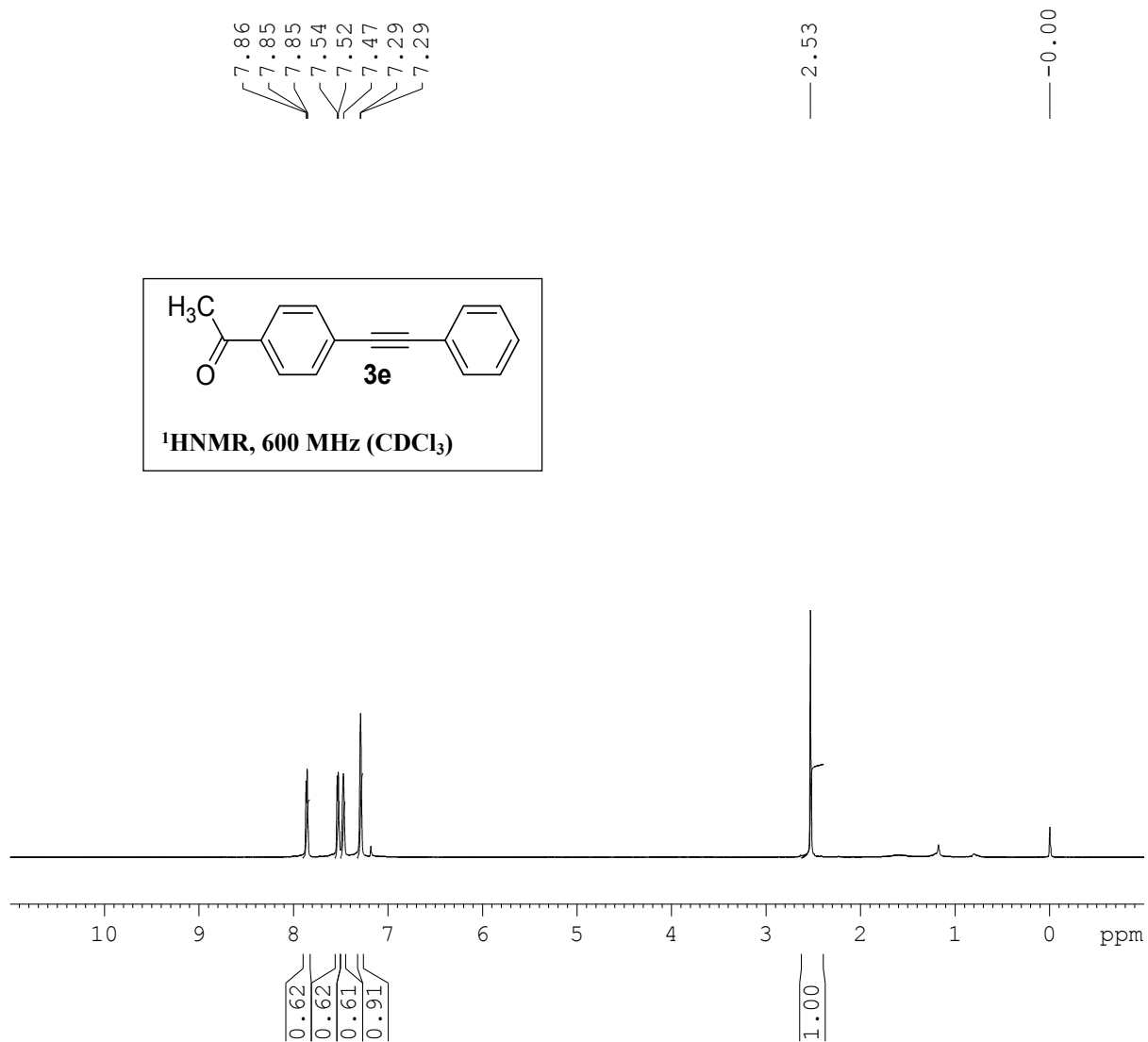
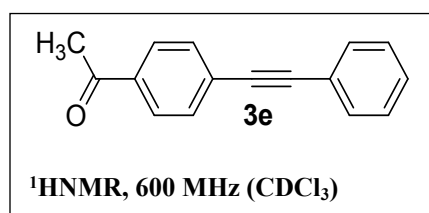
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123.28

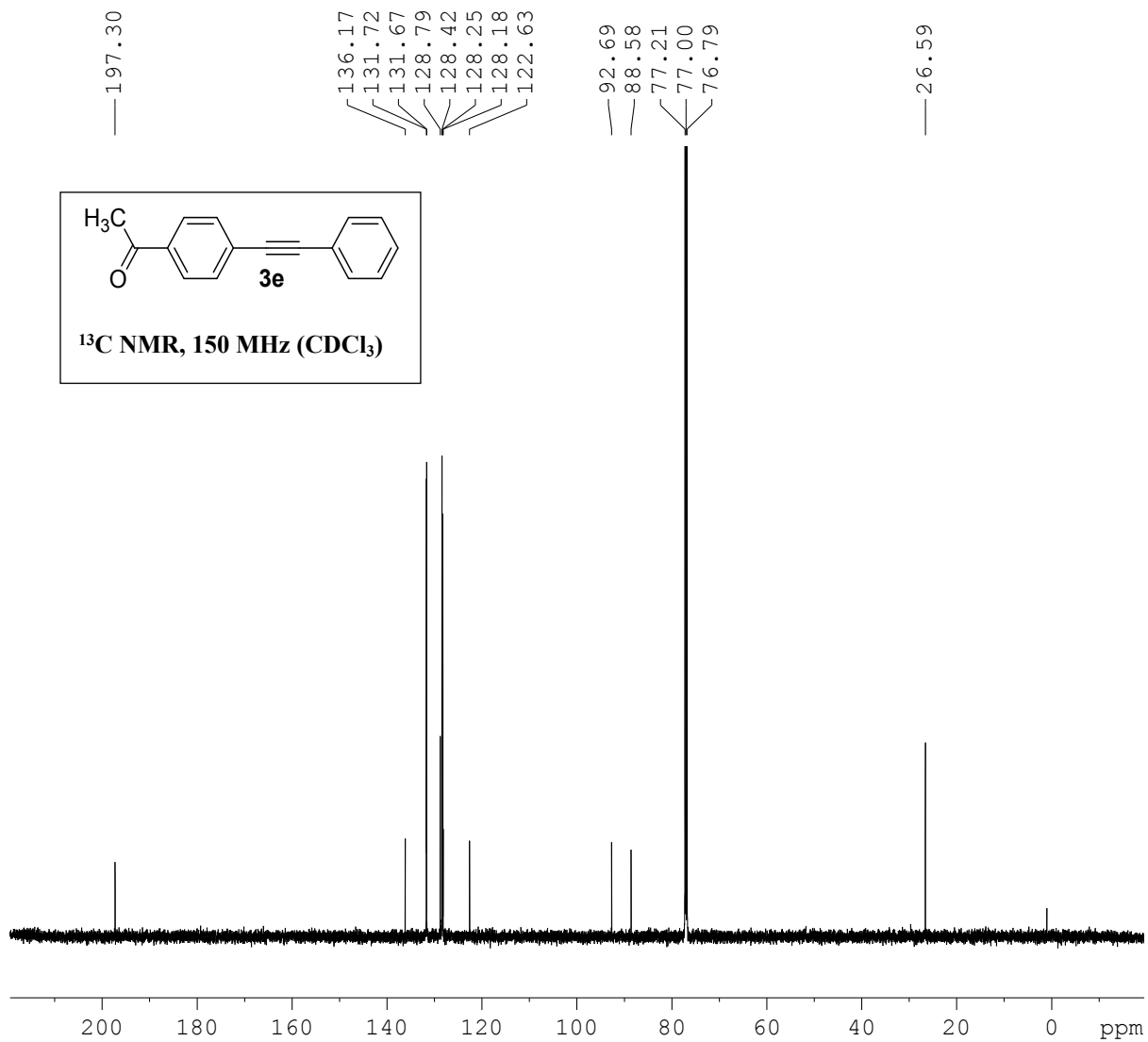
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76.79

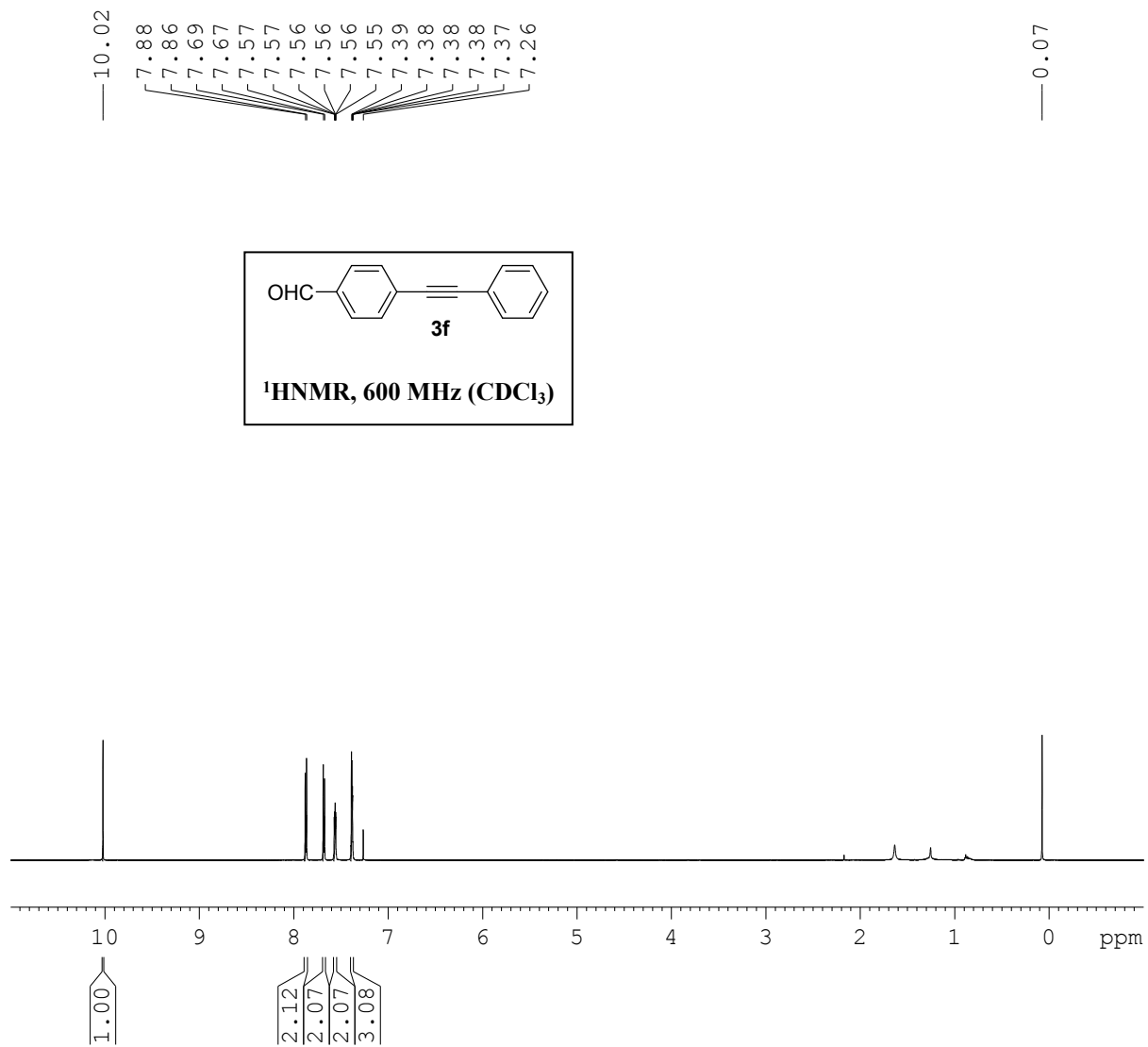


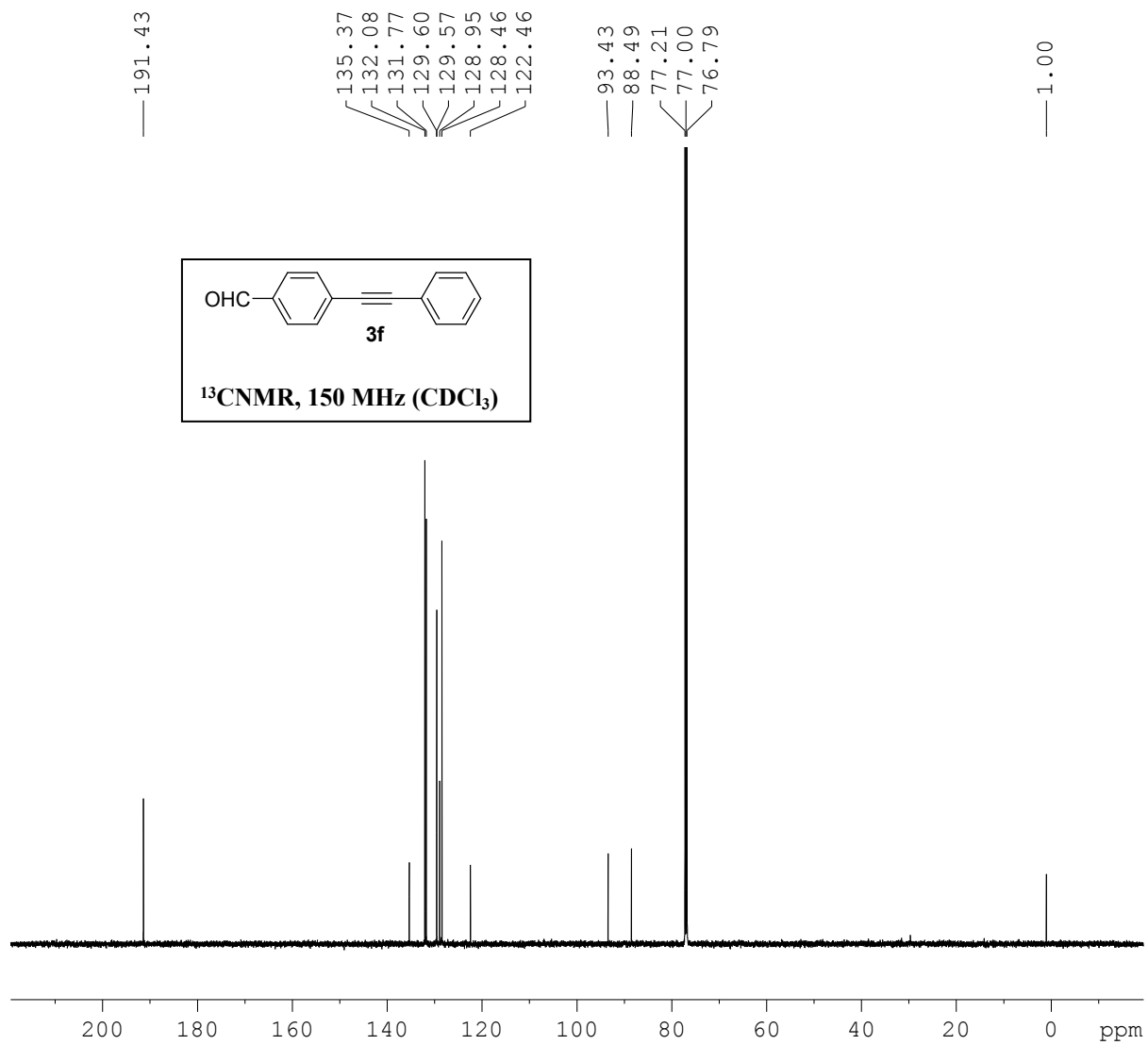


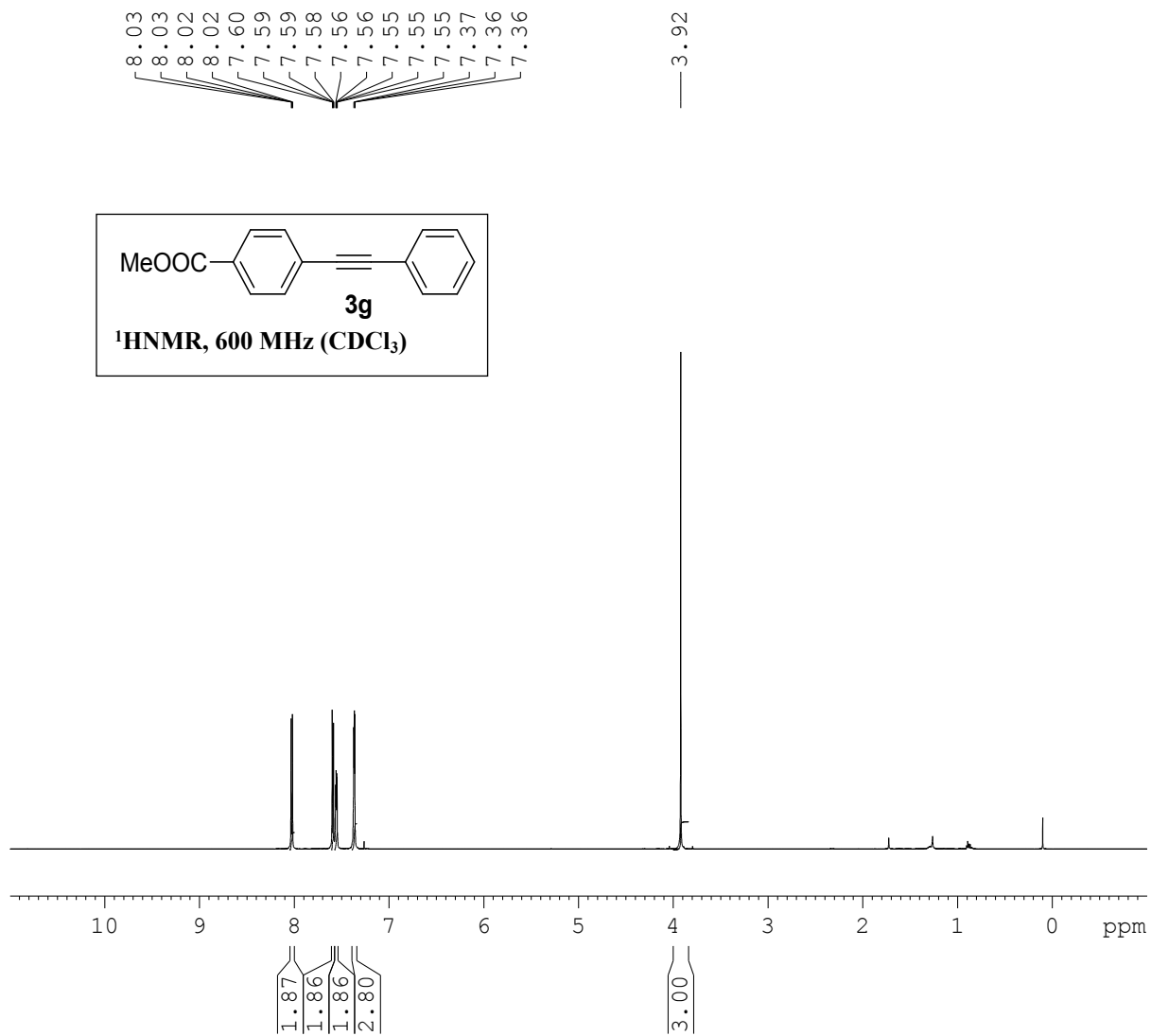




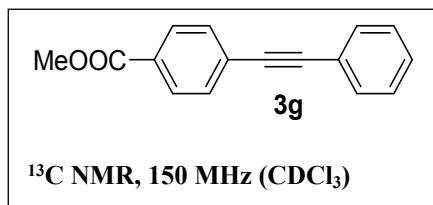










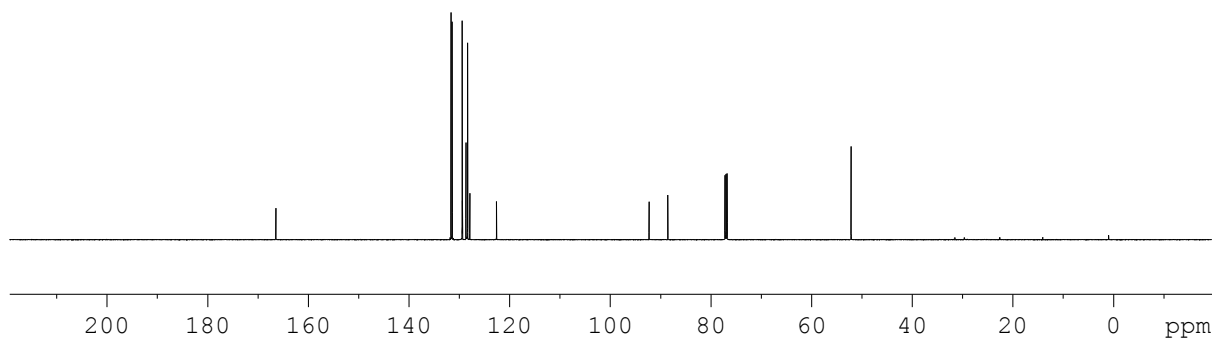


—166.46

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131.43  
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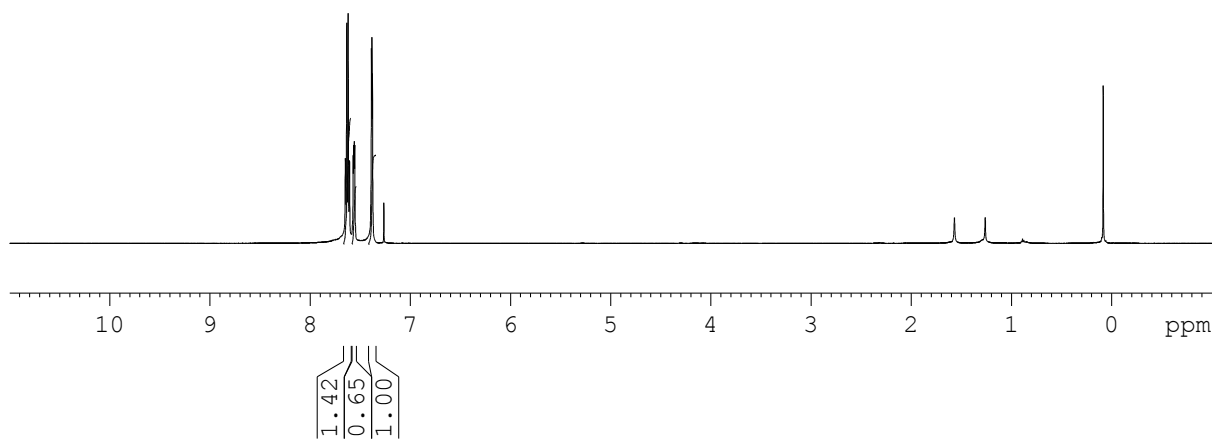
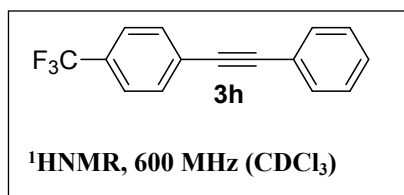
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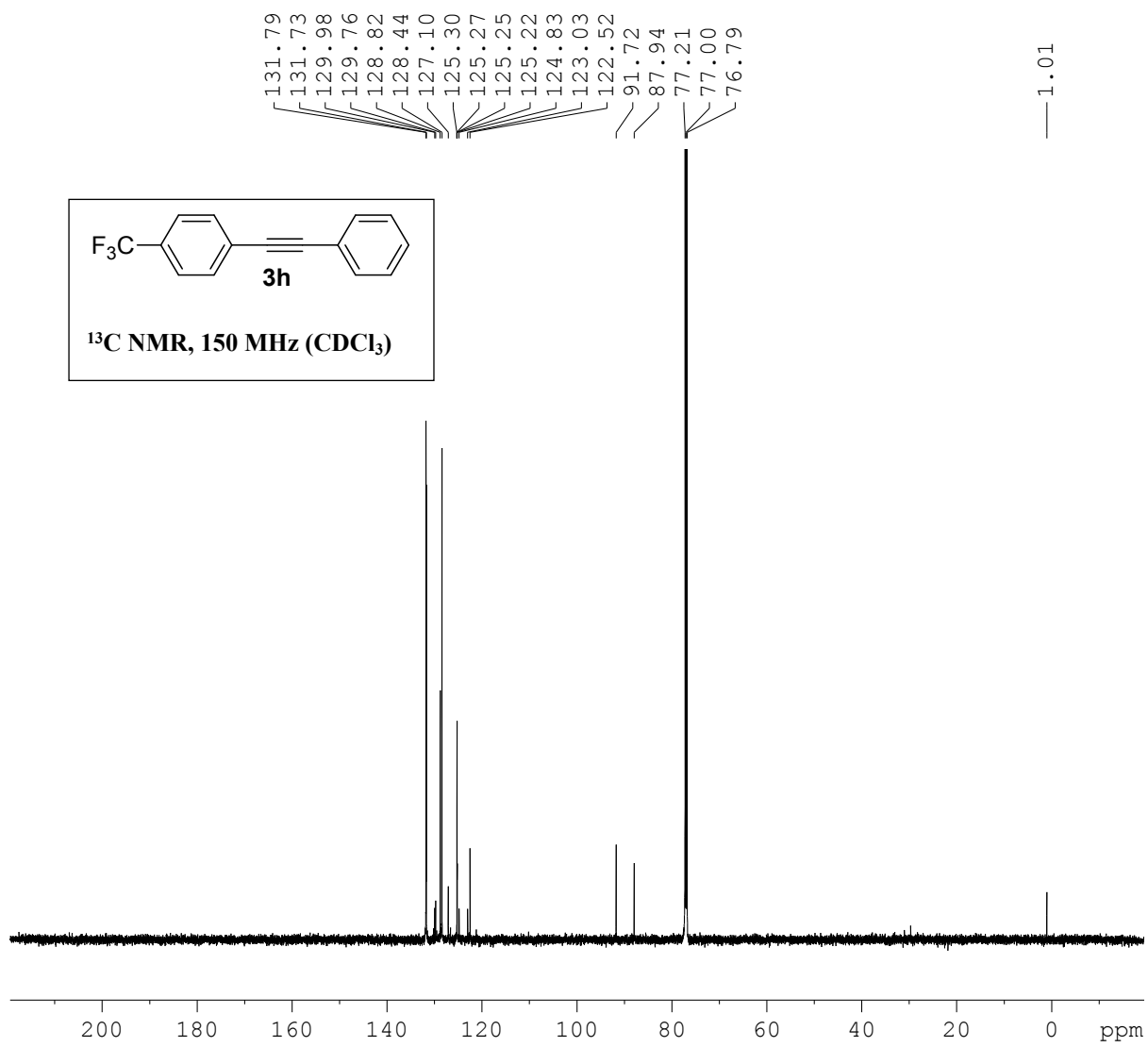


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7.38  
7.26

— 1.57  
— 1.26

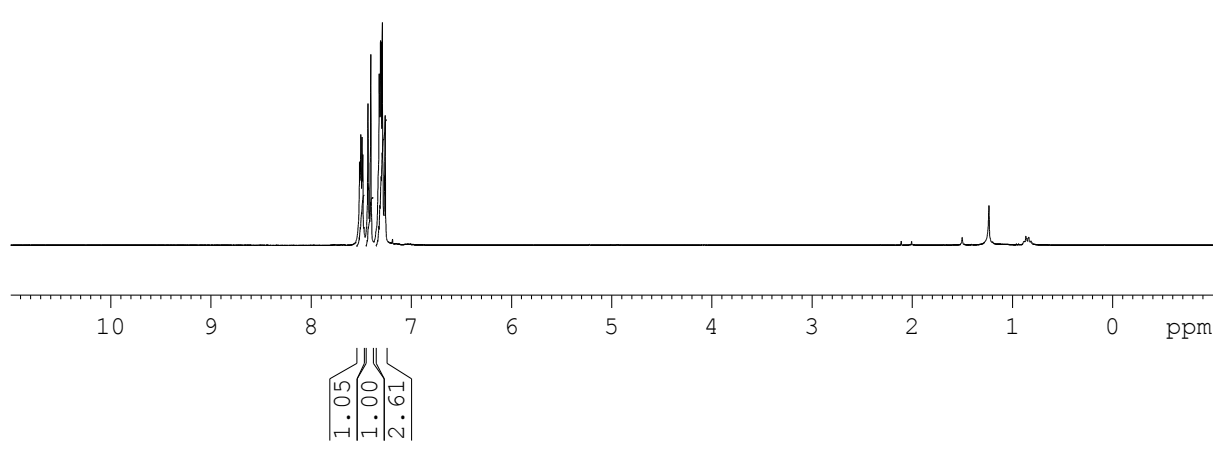
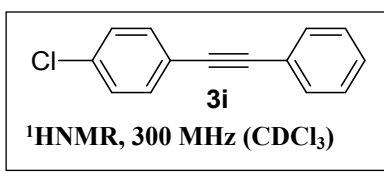
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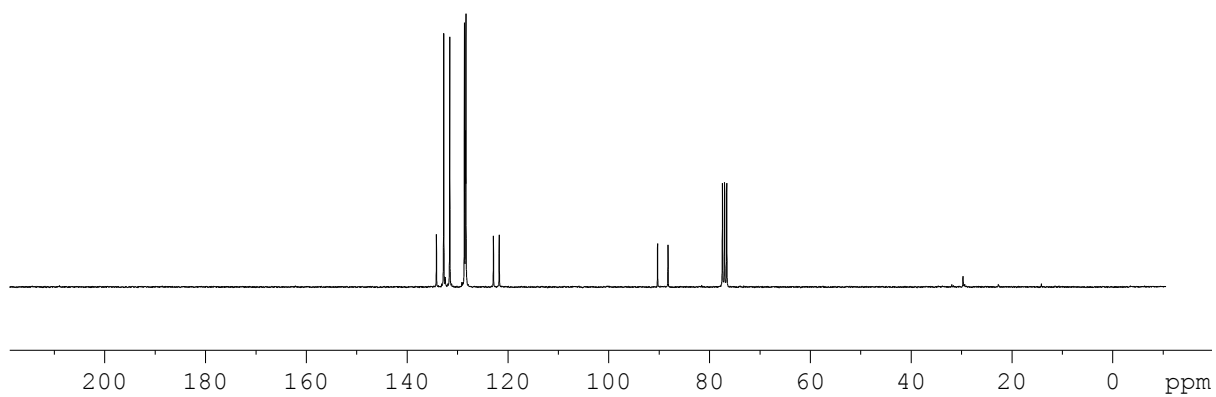
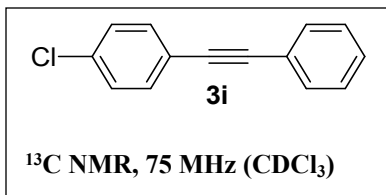
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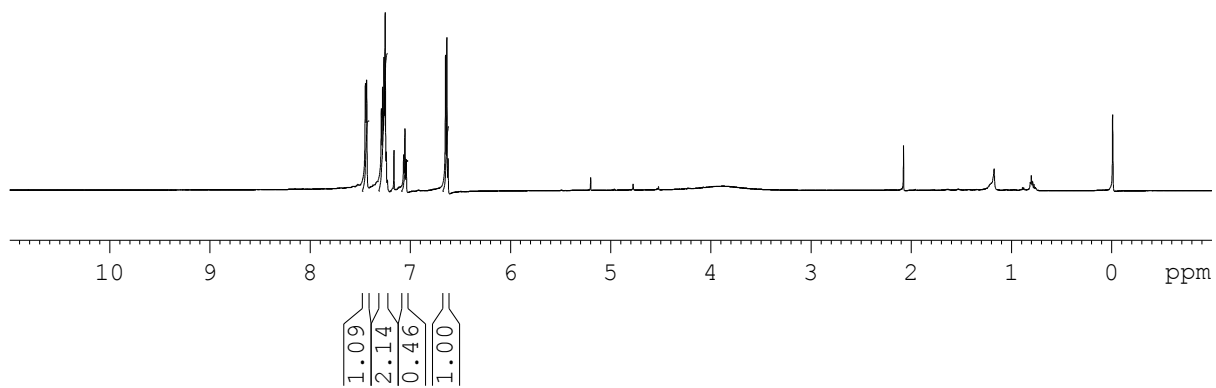
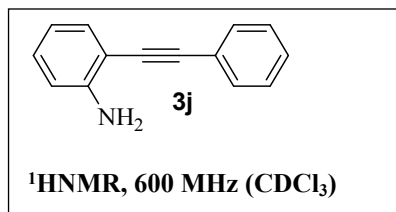
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90.30  
88.23  
77.42  
77.00  
76.58





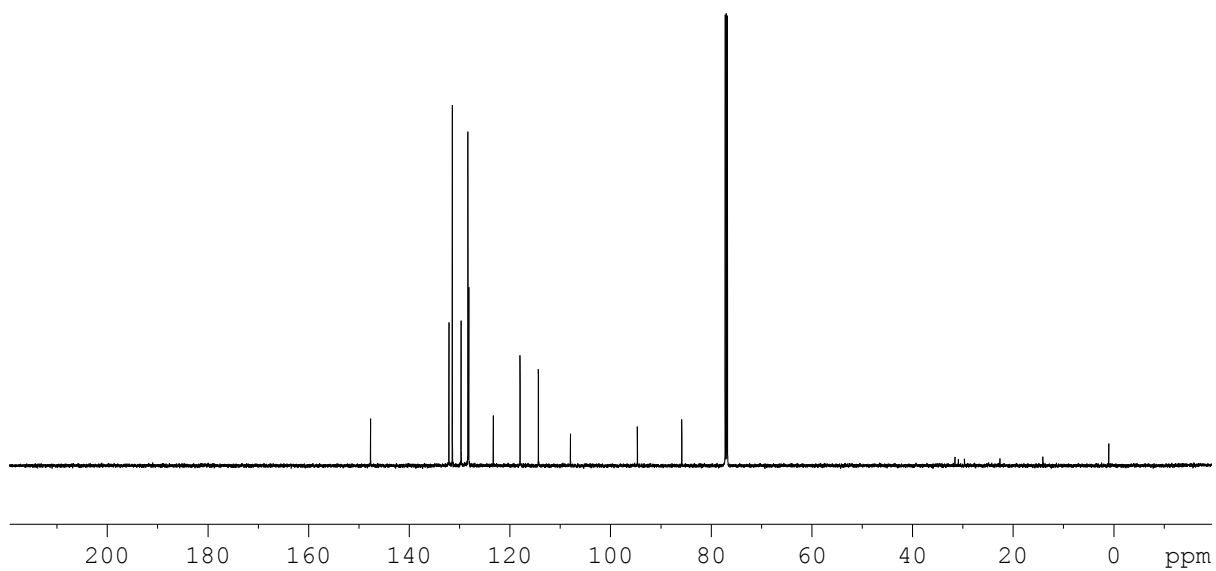
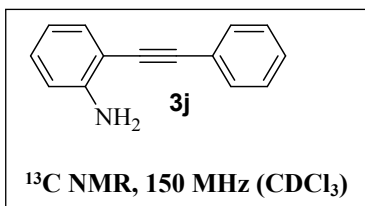
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6.62

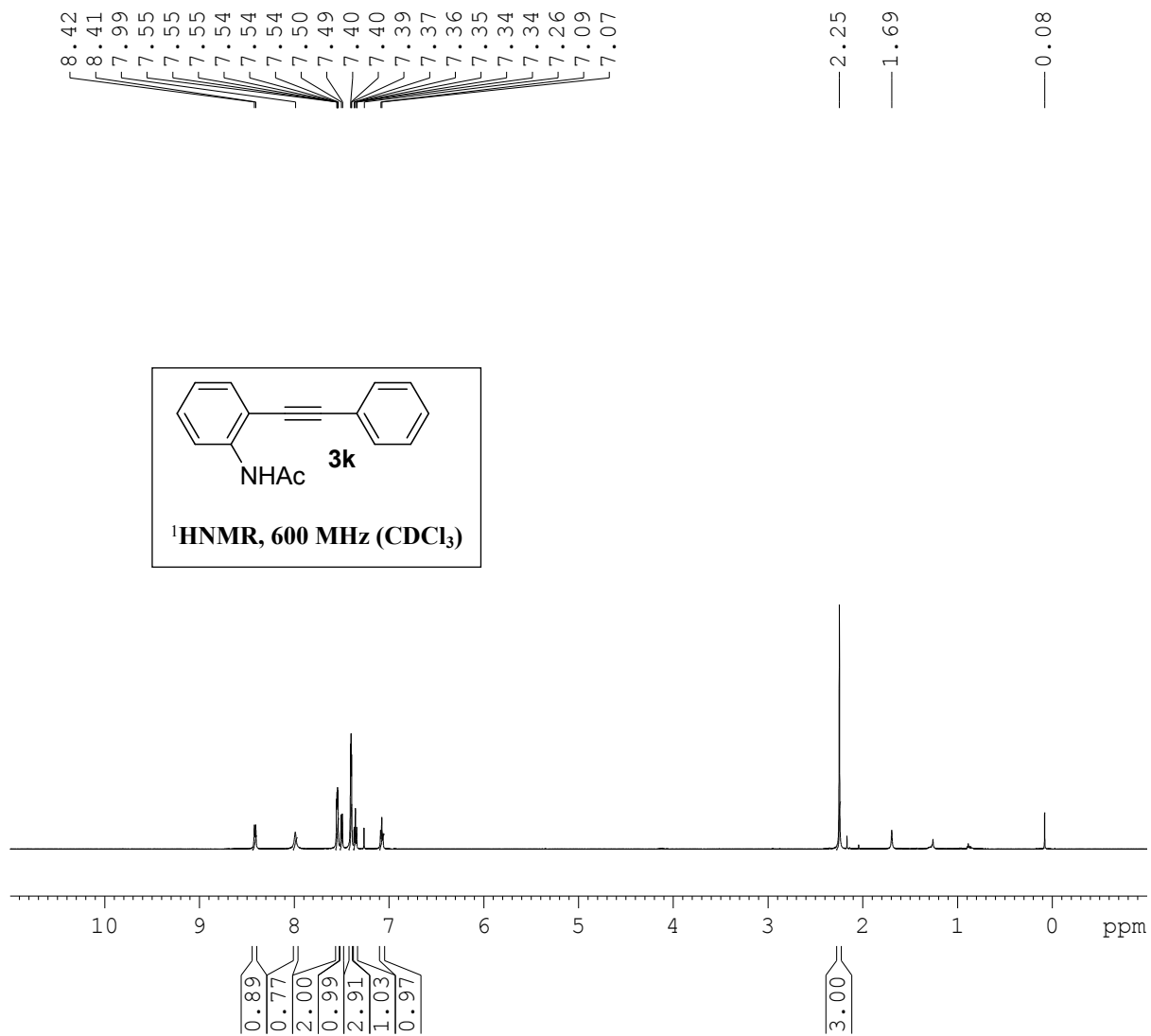
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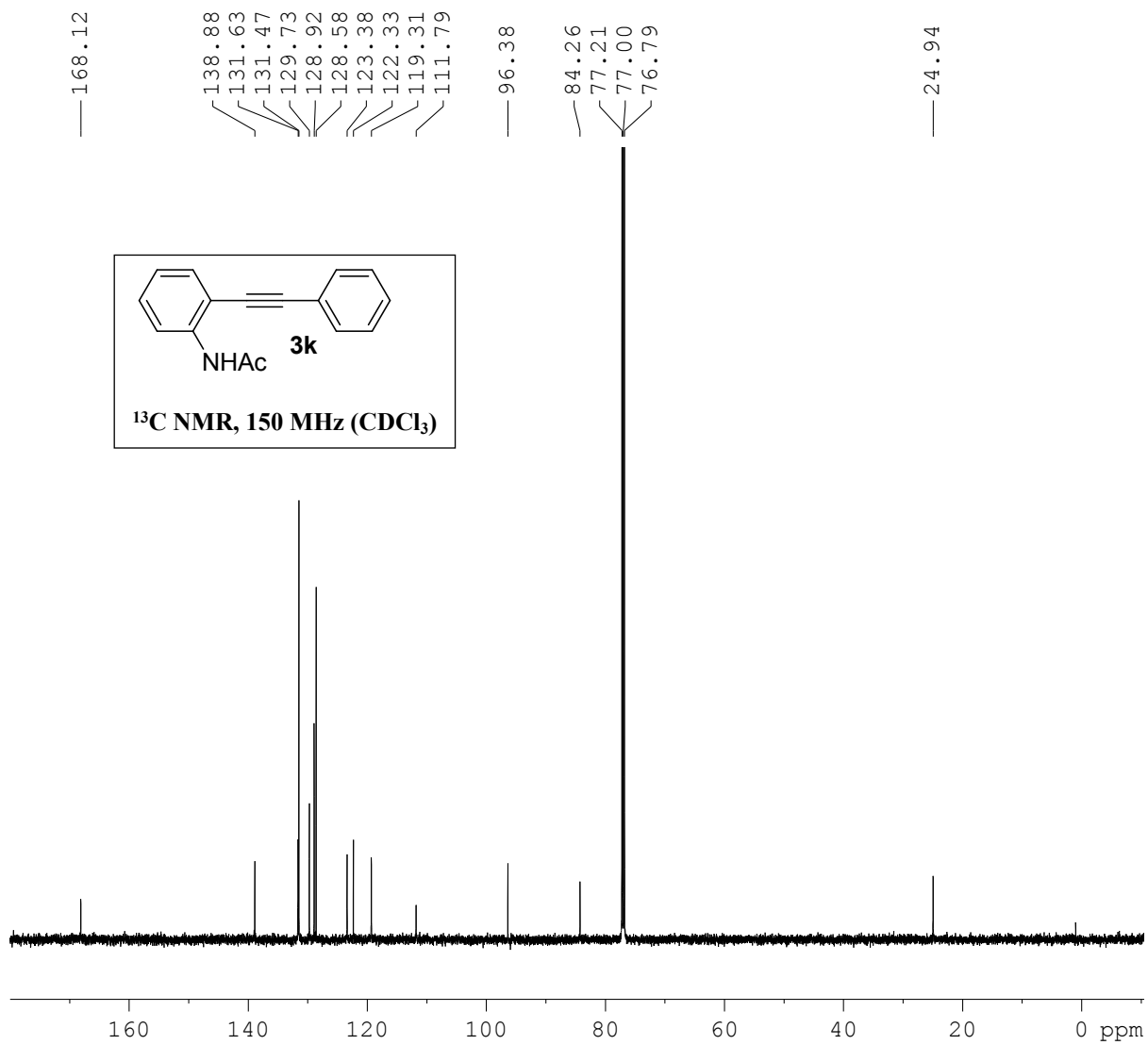
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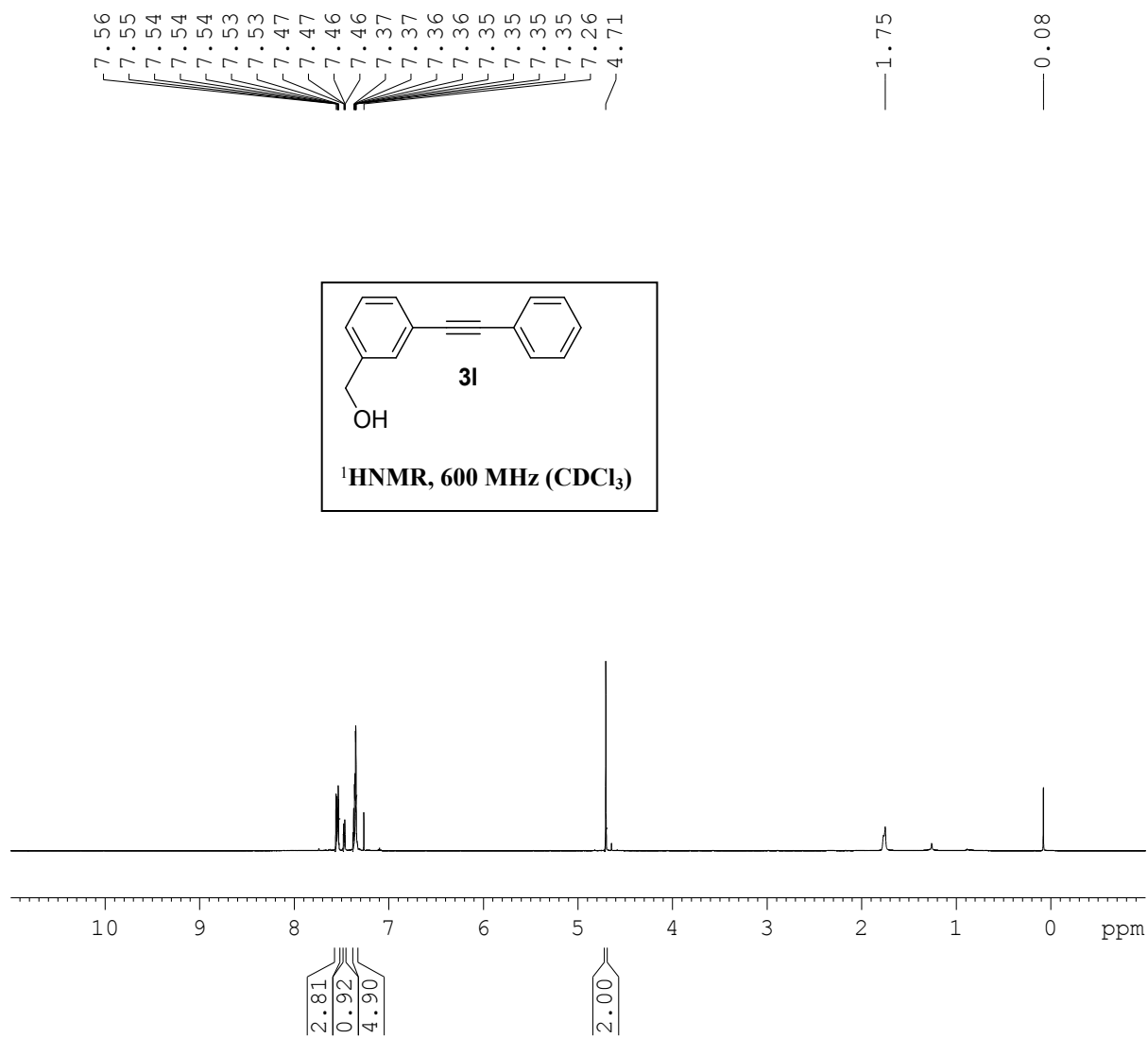
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— 94.68  
85.86  
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77.00  
76.79

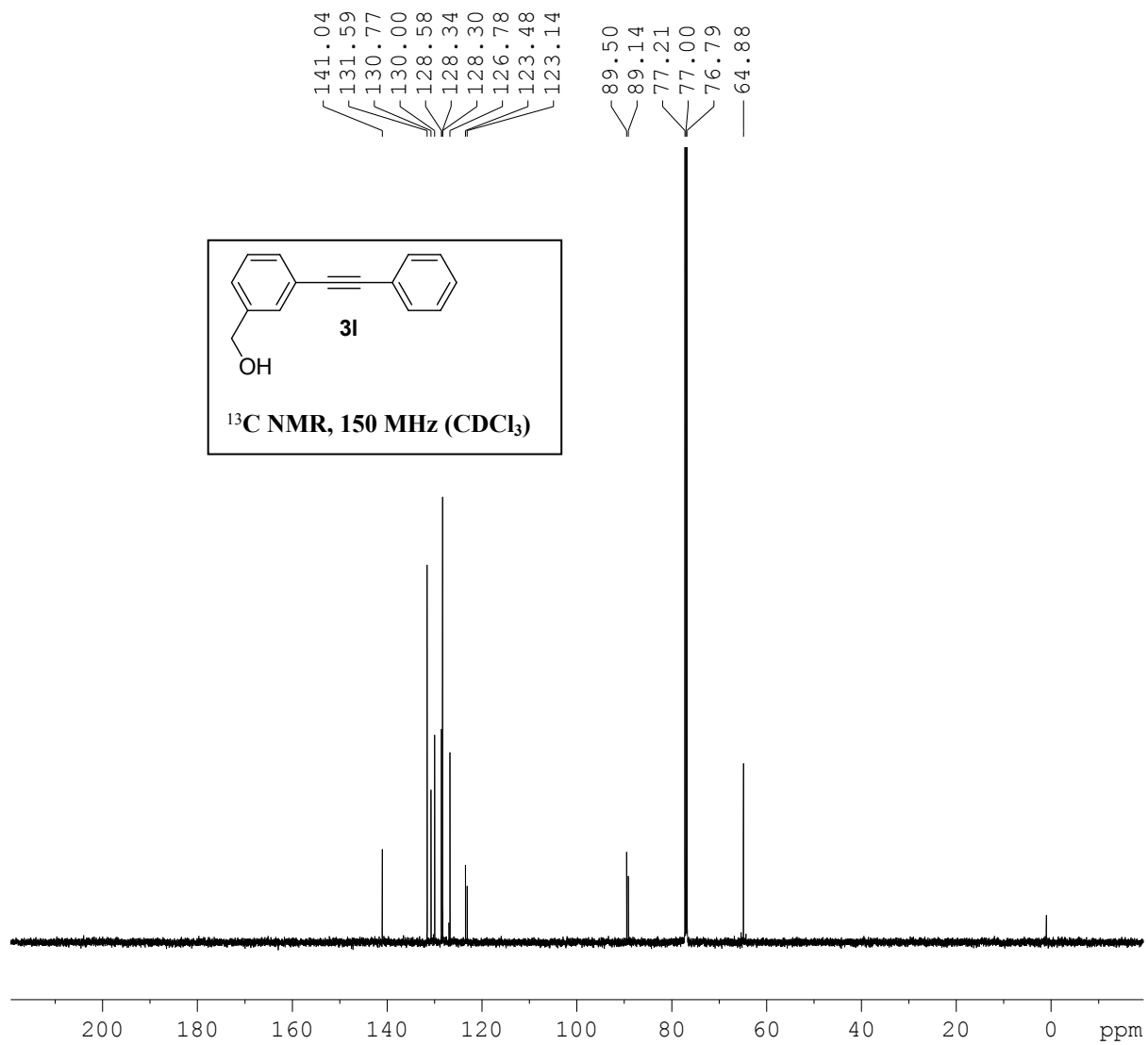








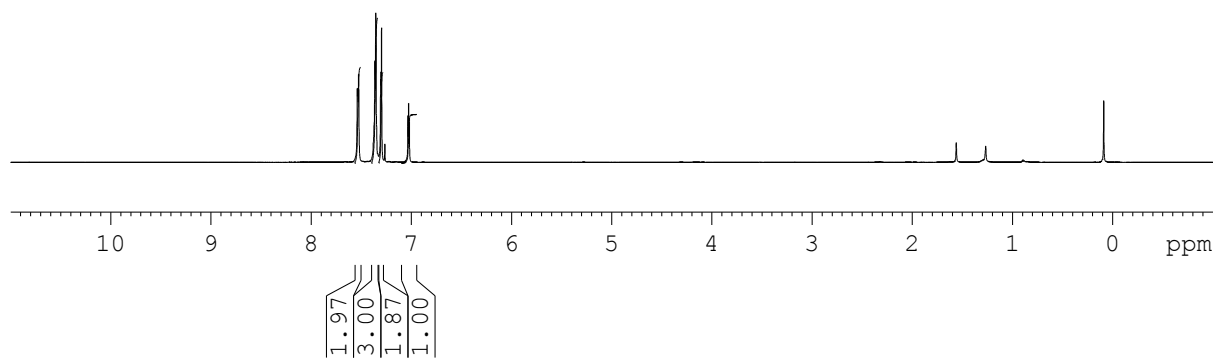
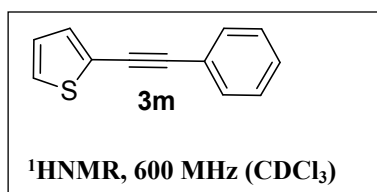




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7.02  
7.02

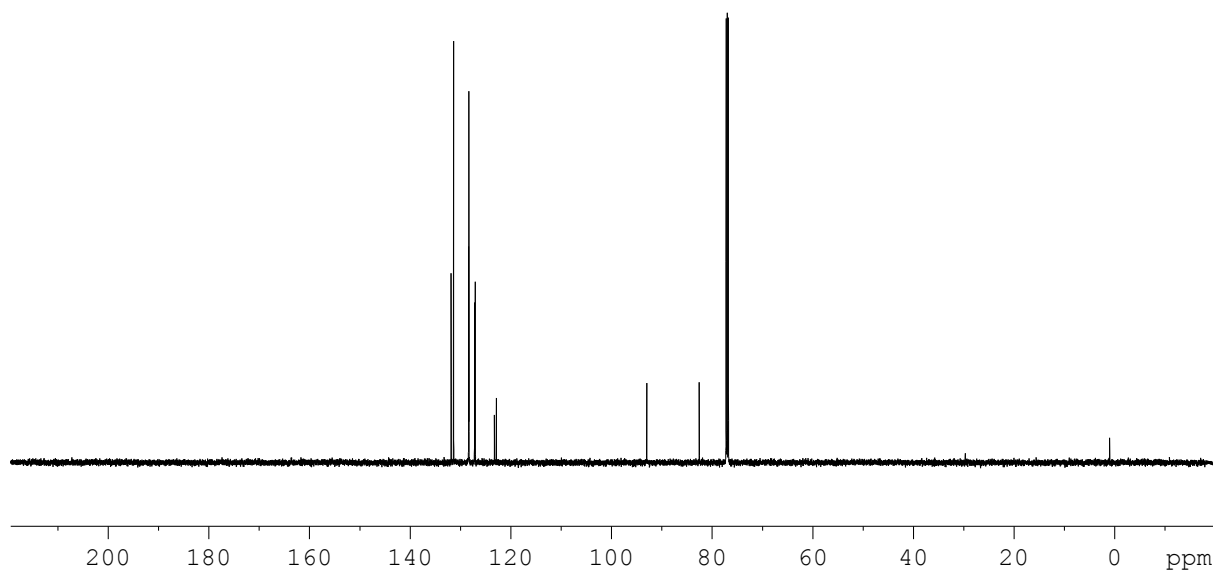
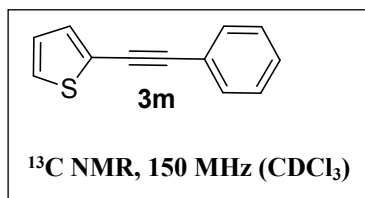
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— 0.09

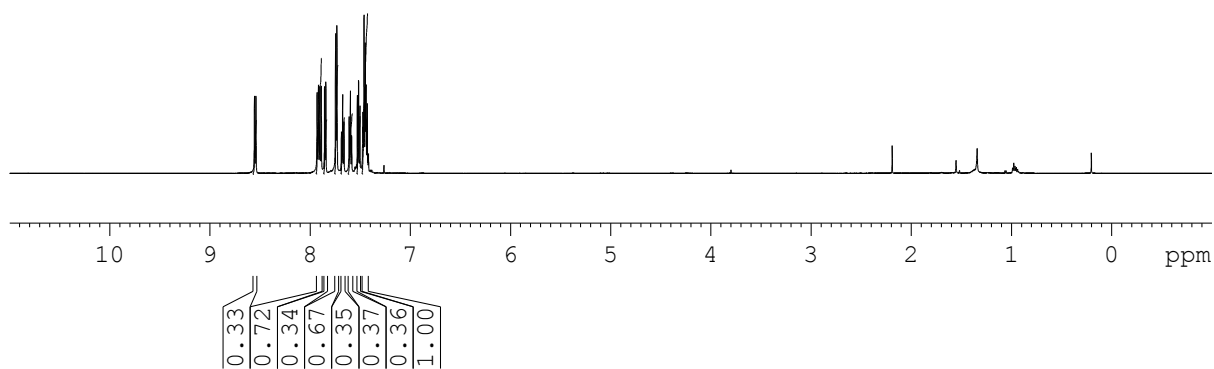
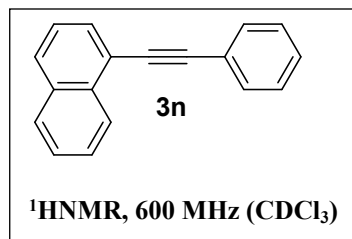


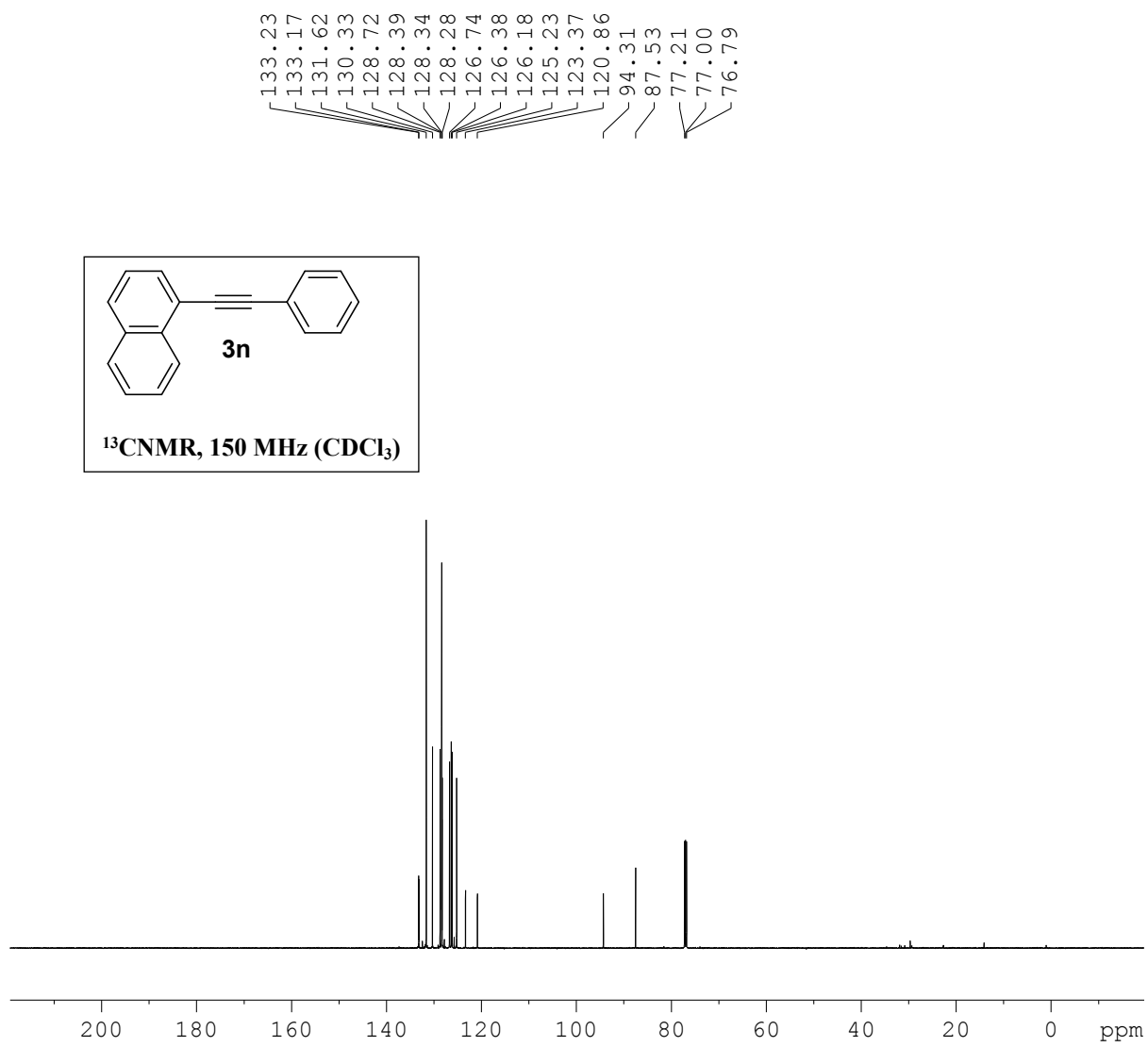
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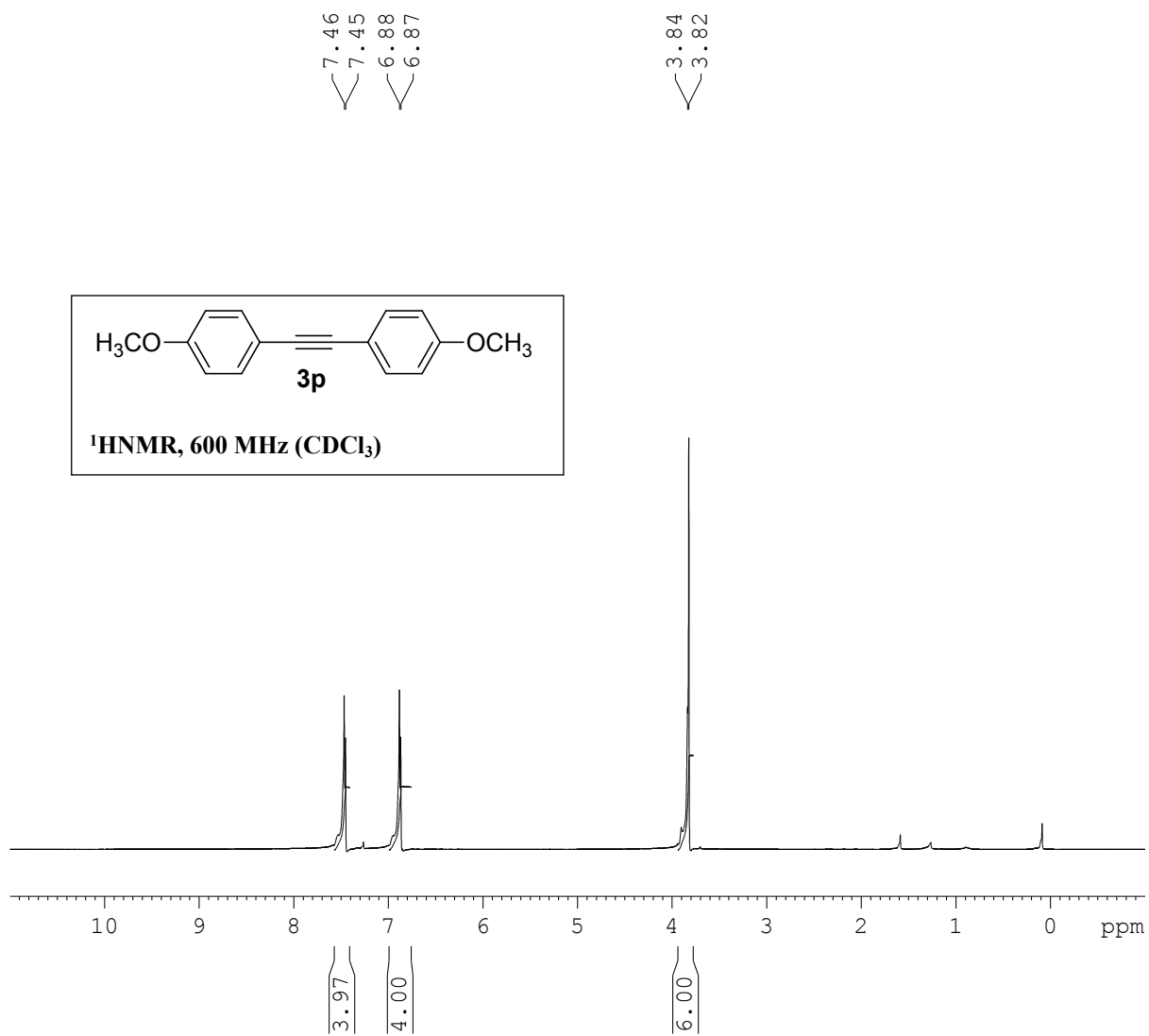
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76.79



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7.73  
7.69  
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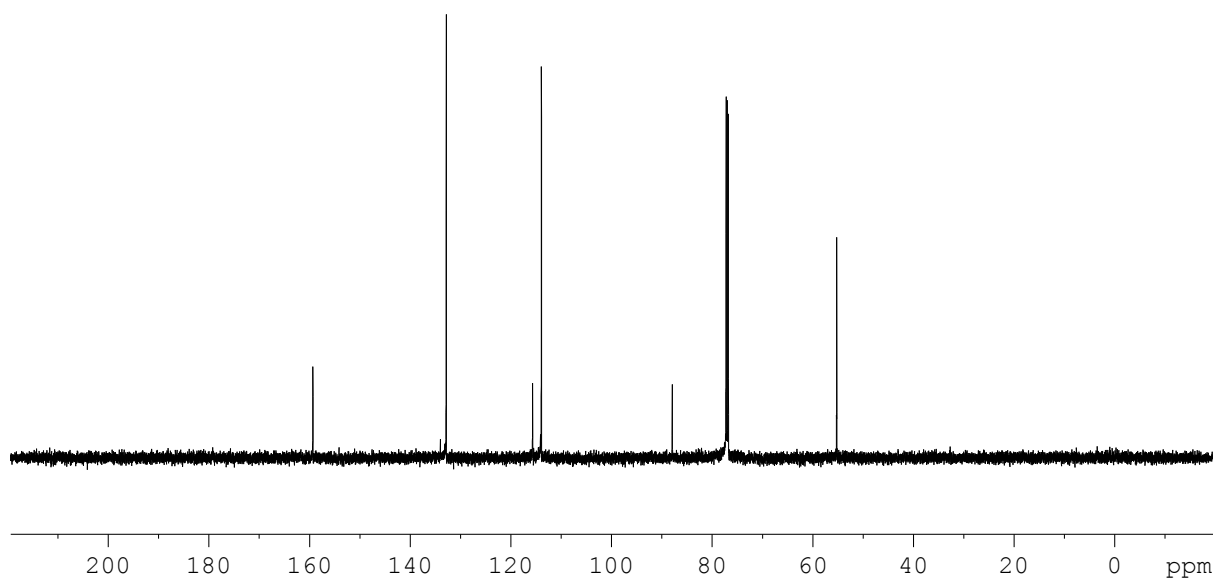
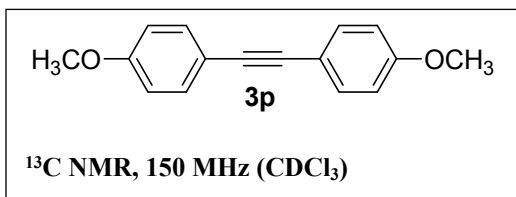


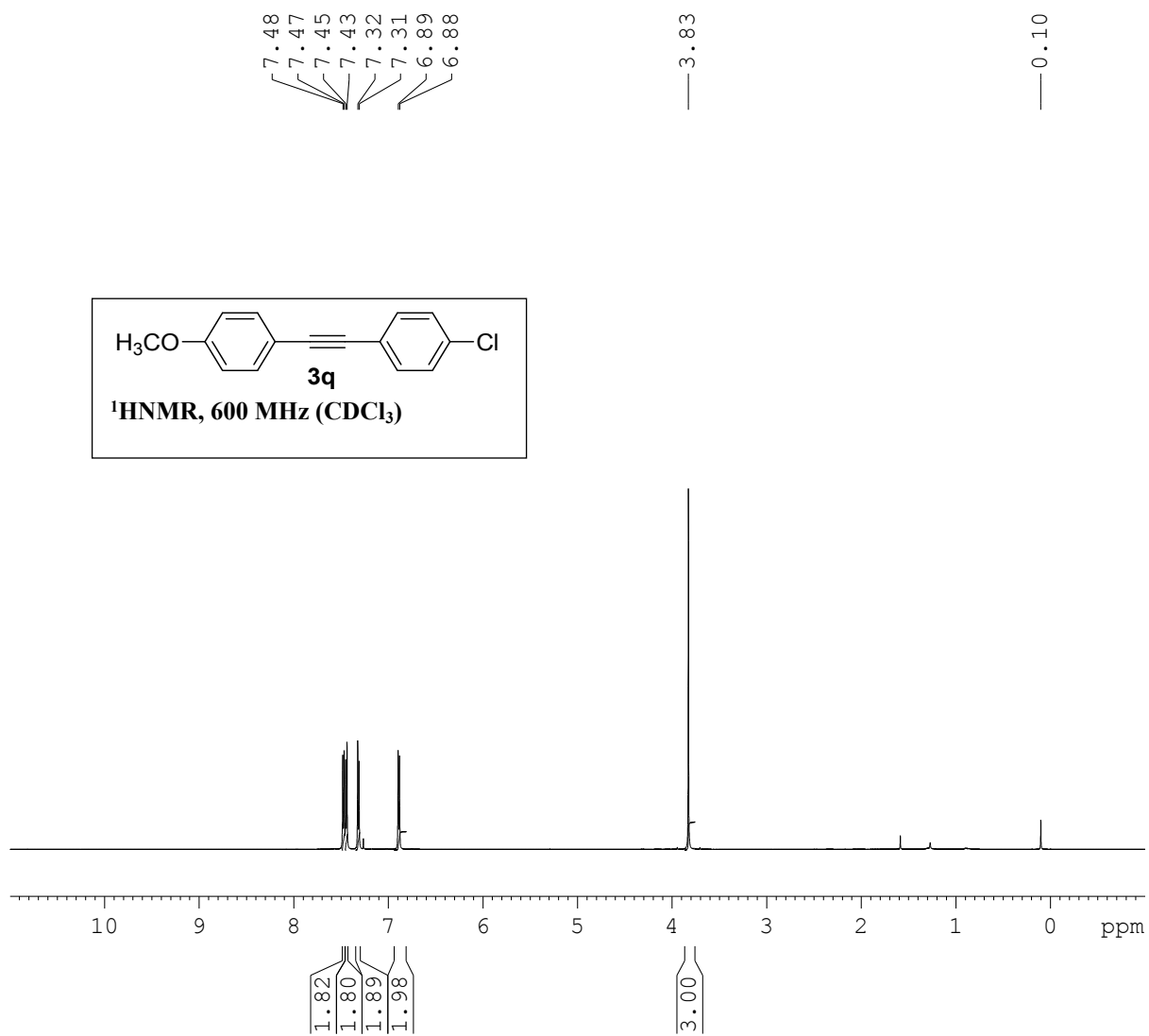


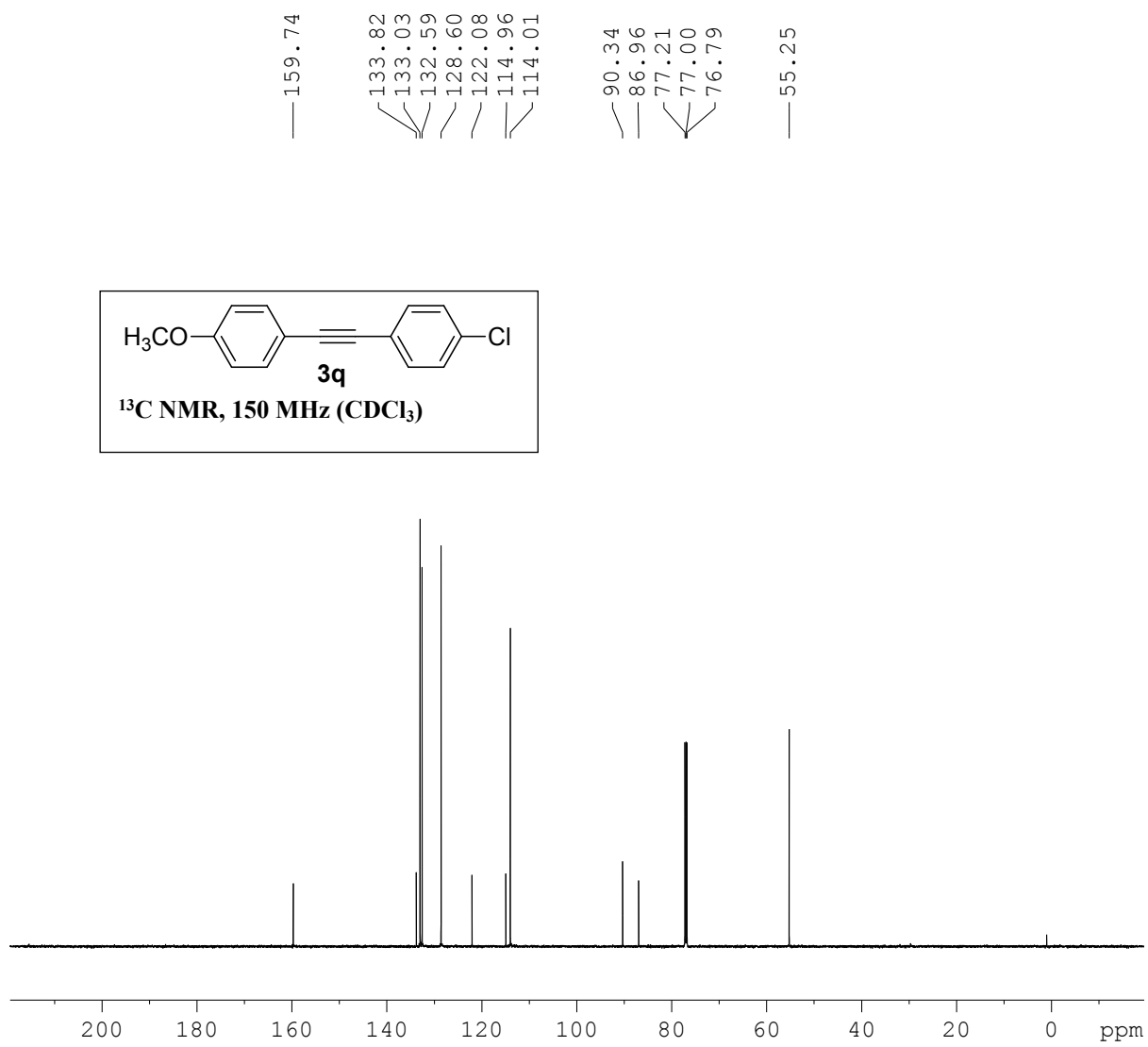


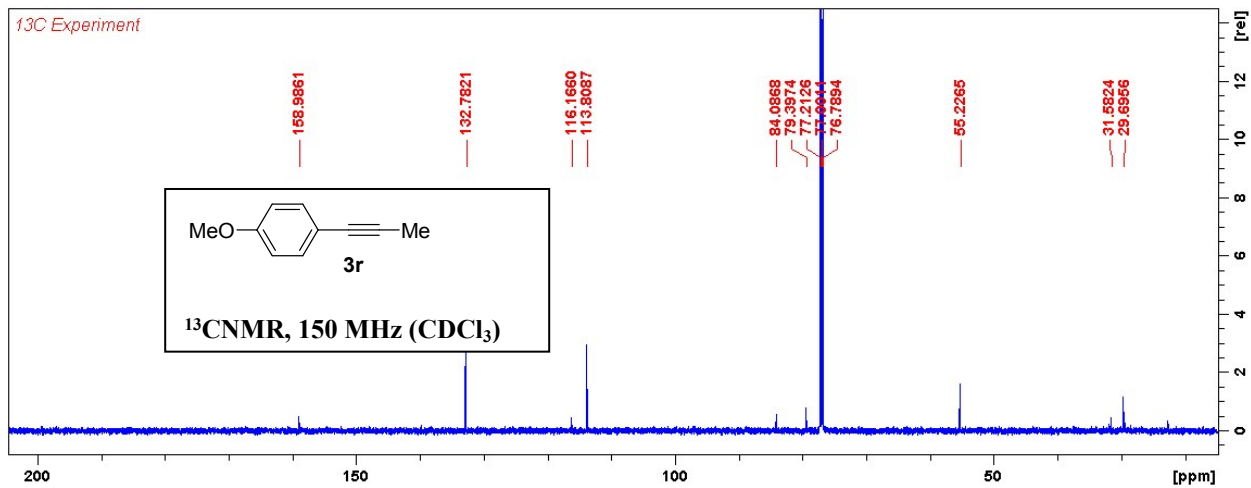
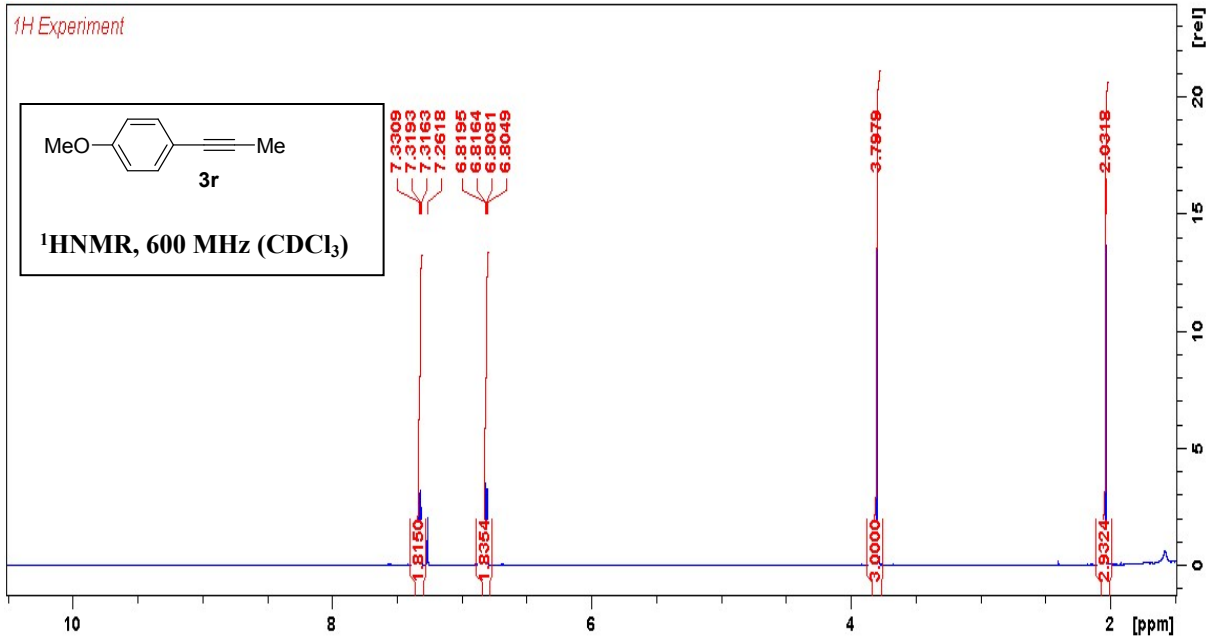


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—55.25





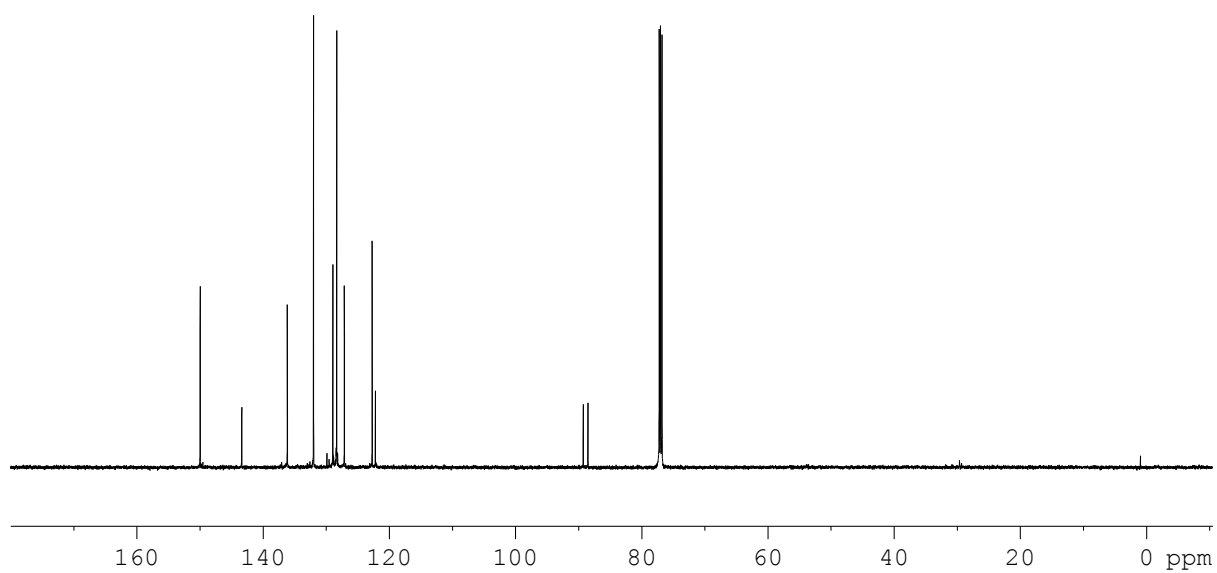
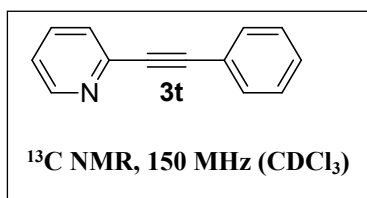






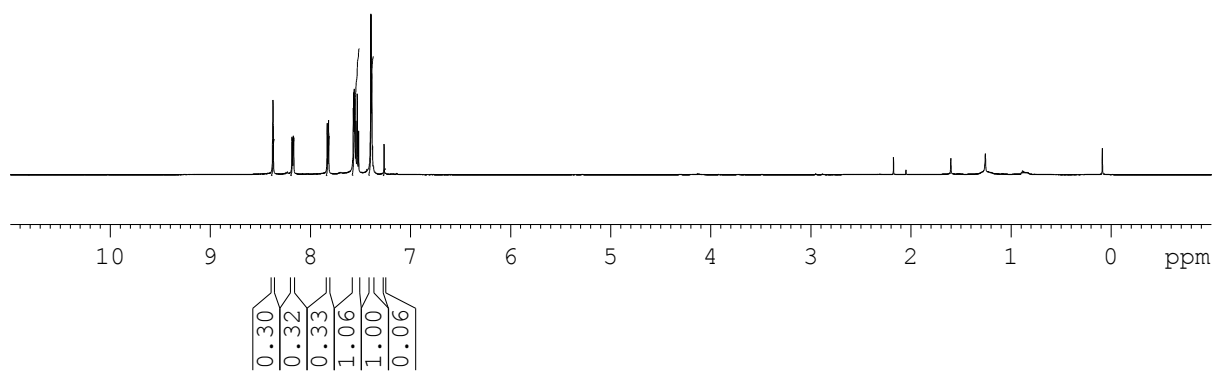
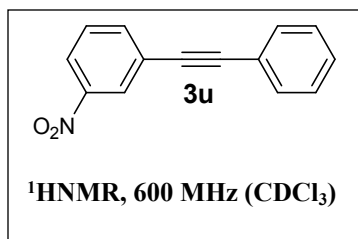
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77.00  
76.79

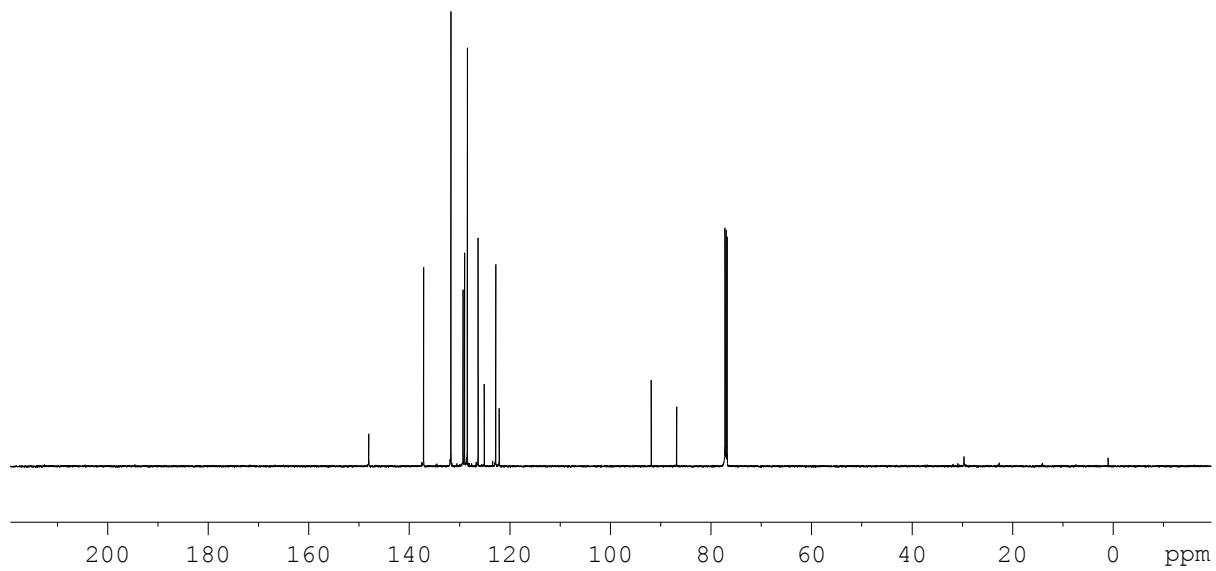
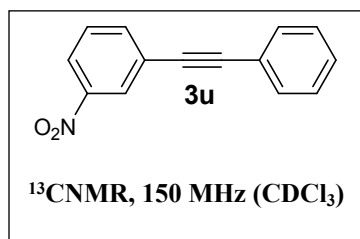


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8.17  
8.17  
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7.82  
7.57  
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7.38  
7.38  
7.26

— 0.09



148.09  
137.17  
131.73  
129.32  
129.02  
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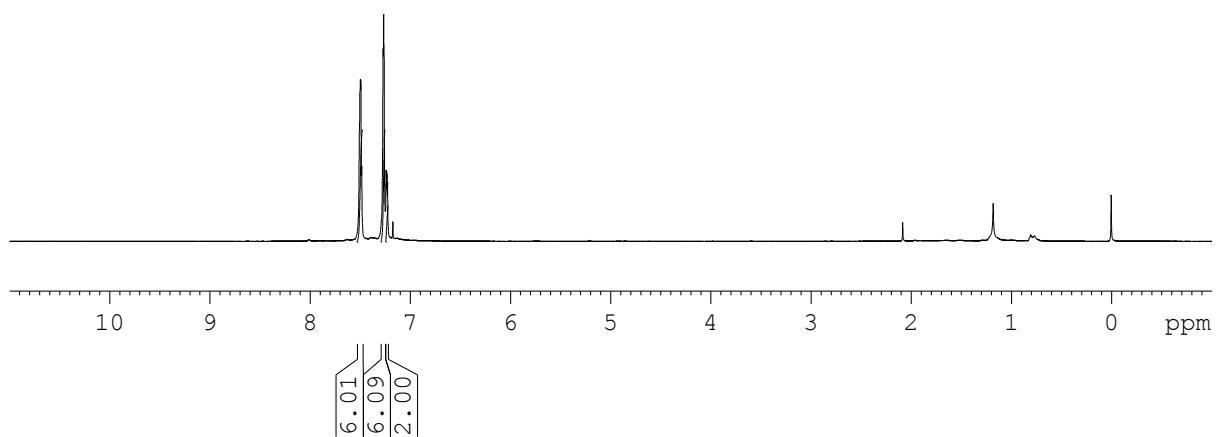
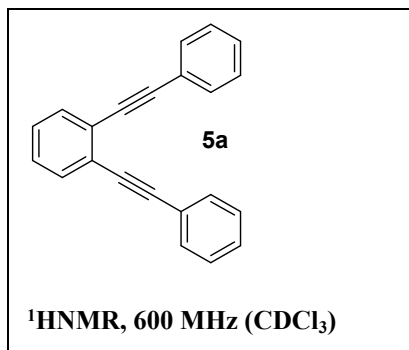




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7.22

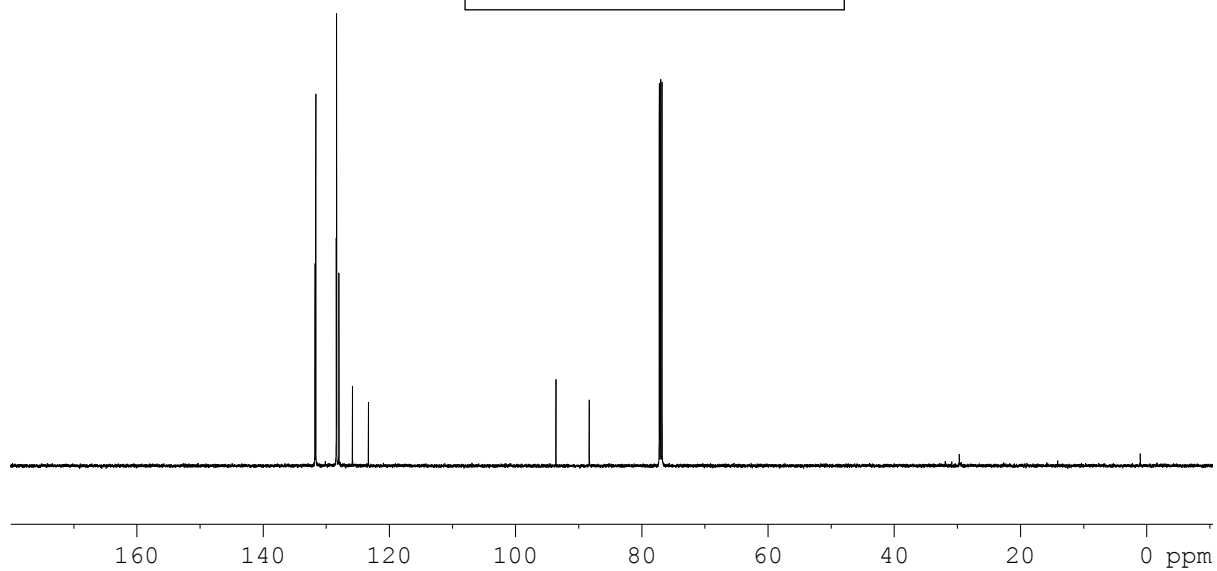
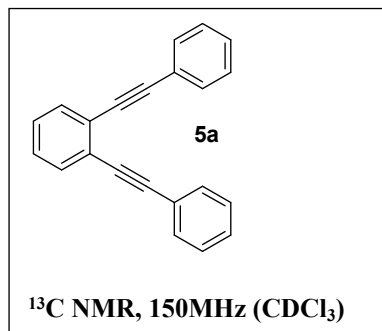
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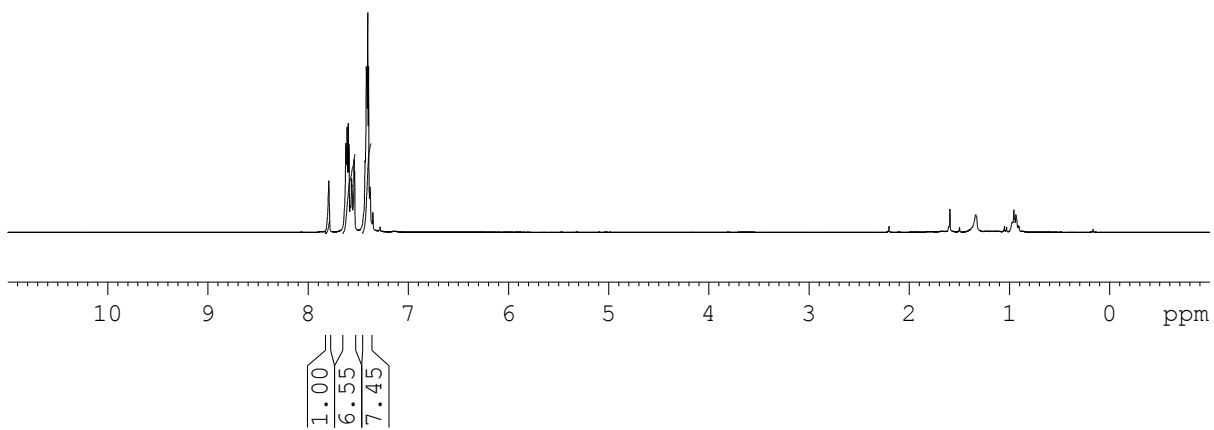
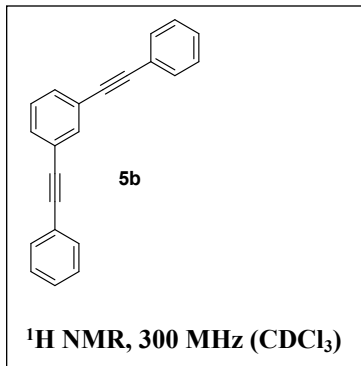


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131.65  
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77.00  
76.79

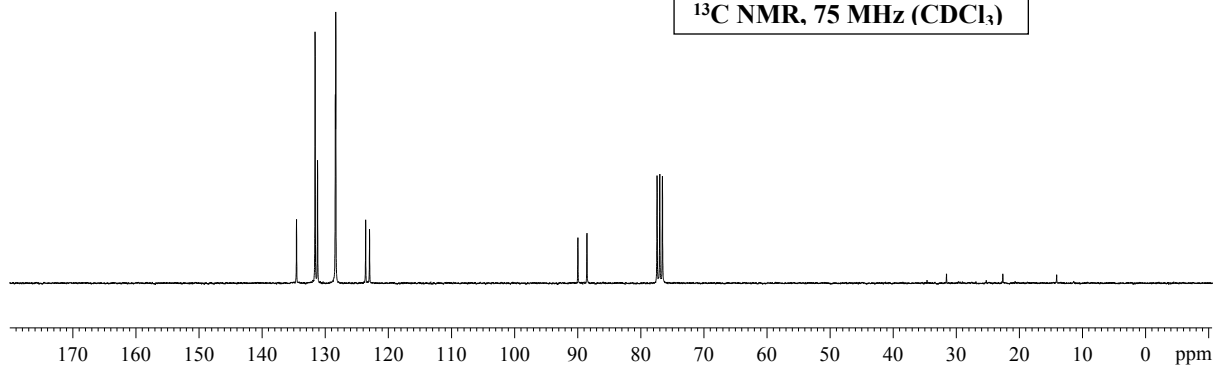
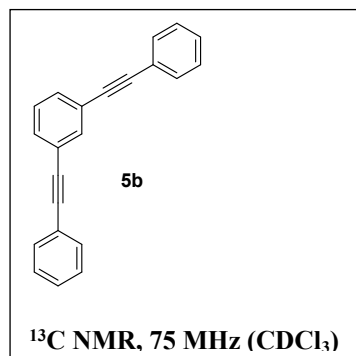


7.79  
7.79  
7.62  
7.61  
7.60  
7.59  
7.56  
7.56  
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7.53  
7.43  
7.42  
7.41  
7.40  
7.39  
7.38

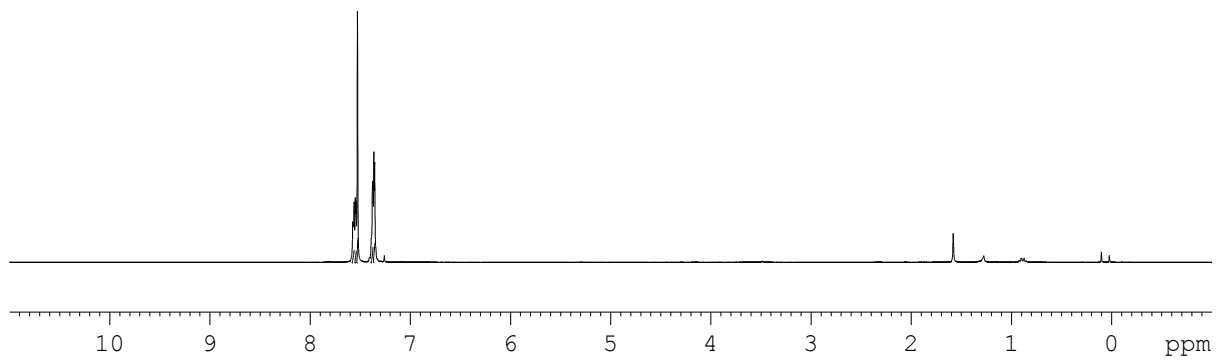
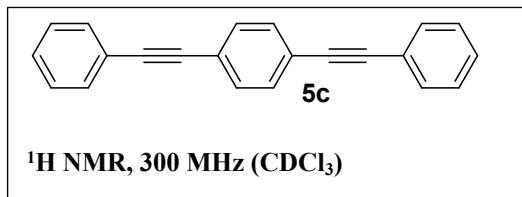


134.57  
131.62  
131.24  
128.41  
128.35  
123.61  
123.00

89.98  
88.54  
77.42  
77.00  
76.58



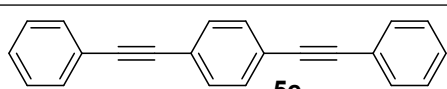
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7.53  
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7.35



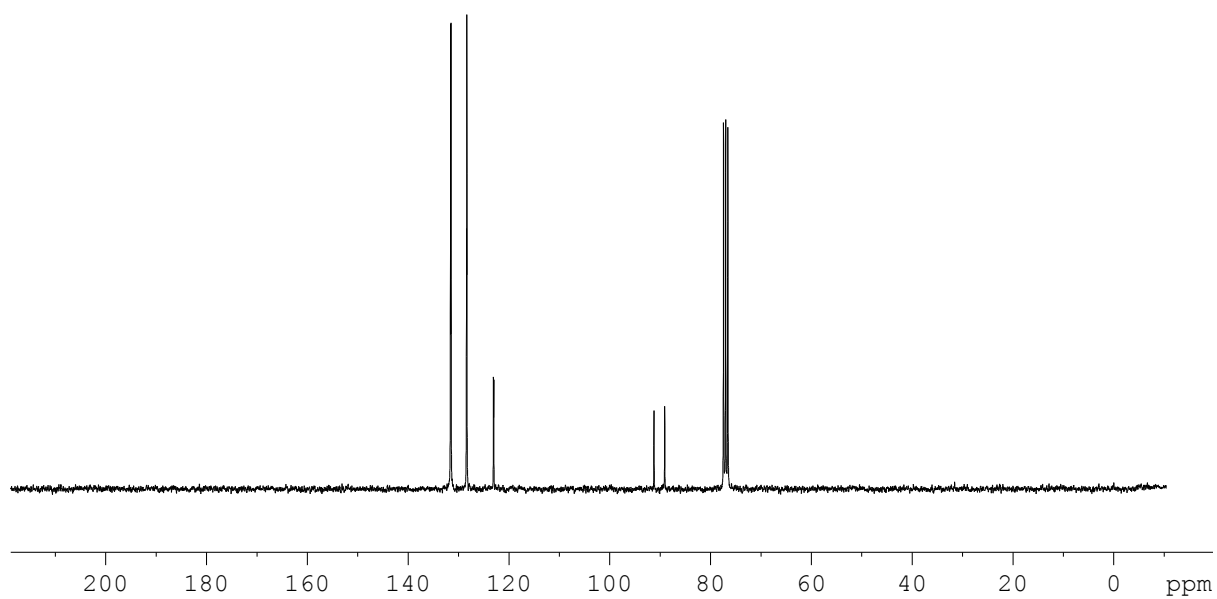
2.24  
2.03  
4.00  
2.73  
3.22

131.60  
131.51  
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128.36  
123.08  
123.03

91.22  
89.10  
77.42  
76.99  
76.57

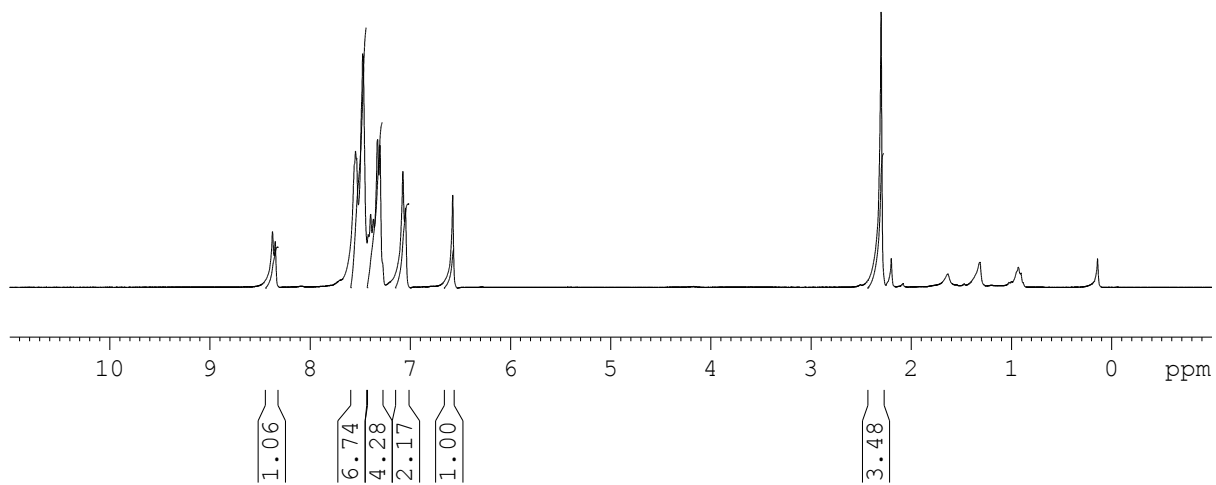
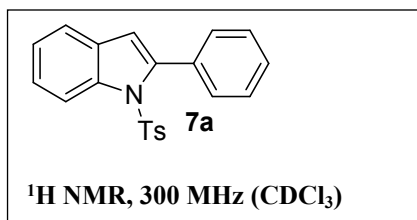


<sup>13</sup>C NMR, 75 MHz (CDCl<sub>3</sub>)



8.38  
8.35  
7.56  
7.54  
7.47  
7.47  
7.42  
7.39  
7.37  
7.32  
7.30  
7.07  
7.05  
6.58

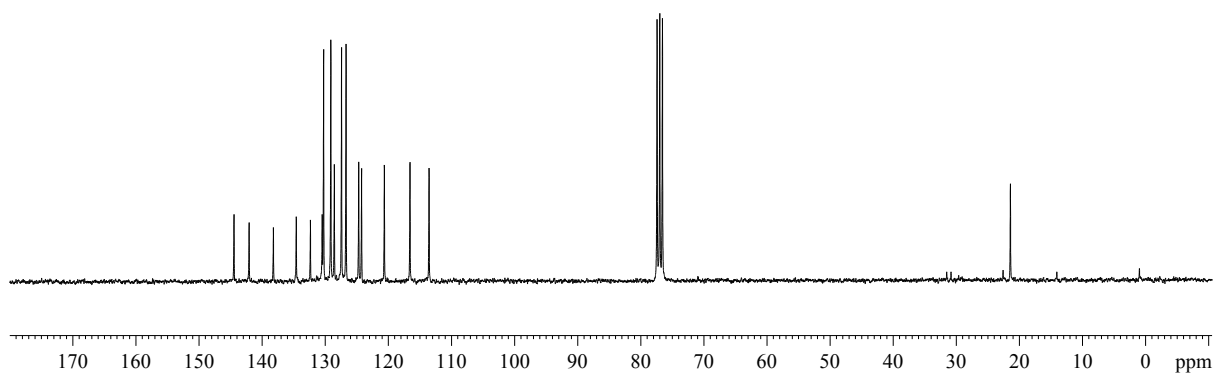
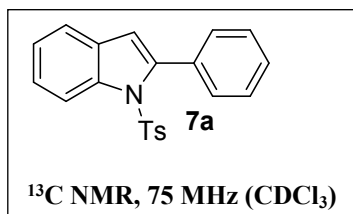
—2.30



144.47  
142.08  
138.23  
134.61  
132.36  
130.50  
130.27  
129.13  
128.57  
127.43  
126.72  
124.71  
124.26  
120.65  
116.59  
113.56

77.42  
77.00  
76.58

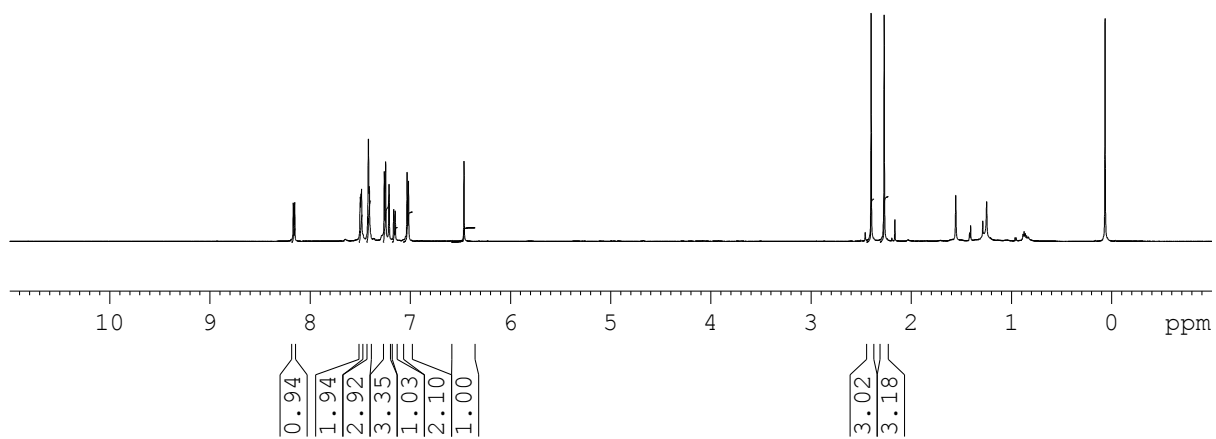
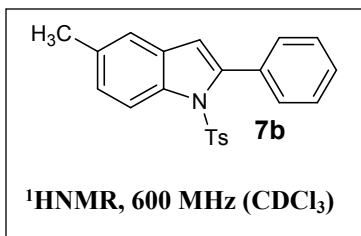
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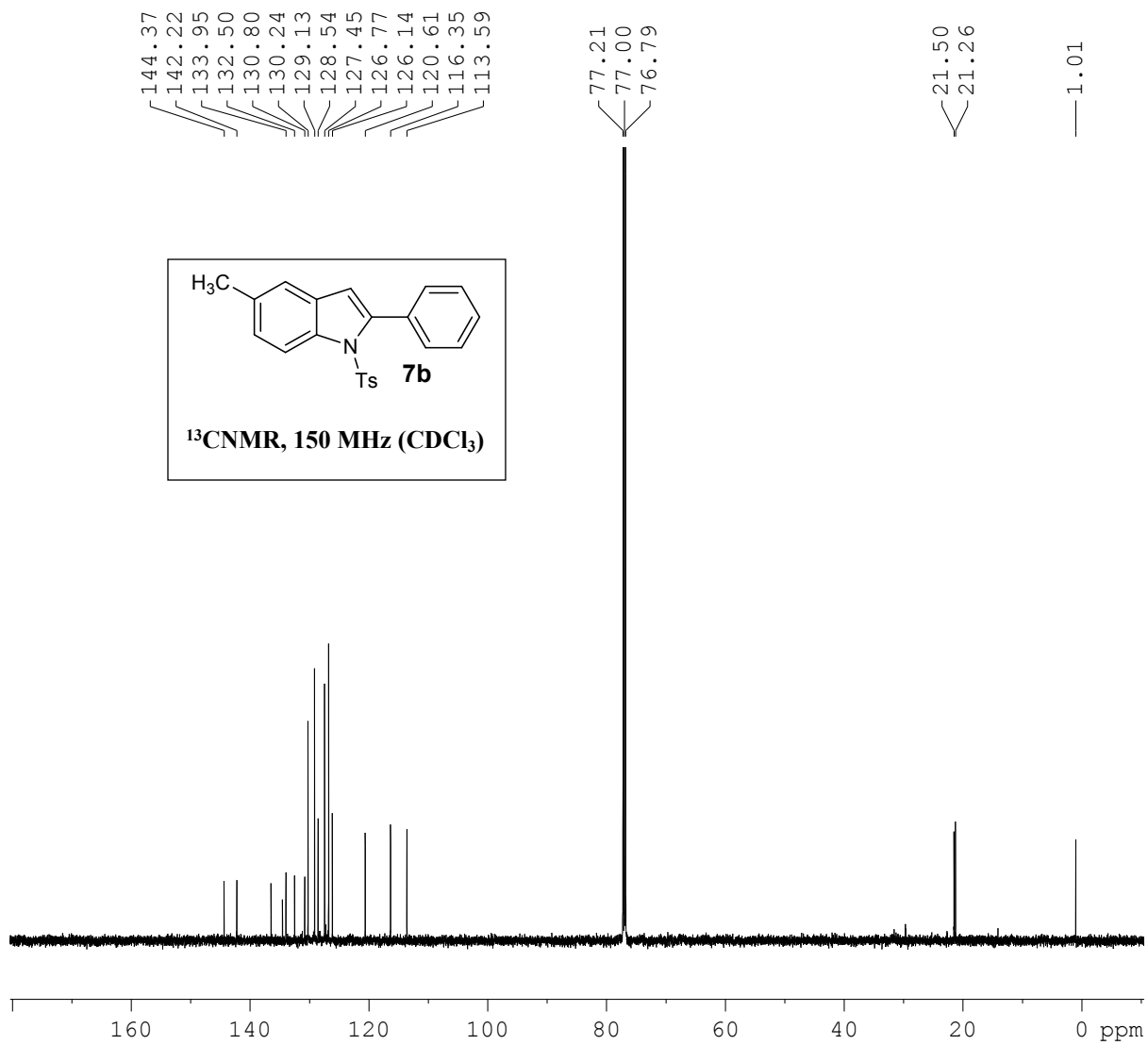


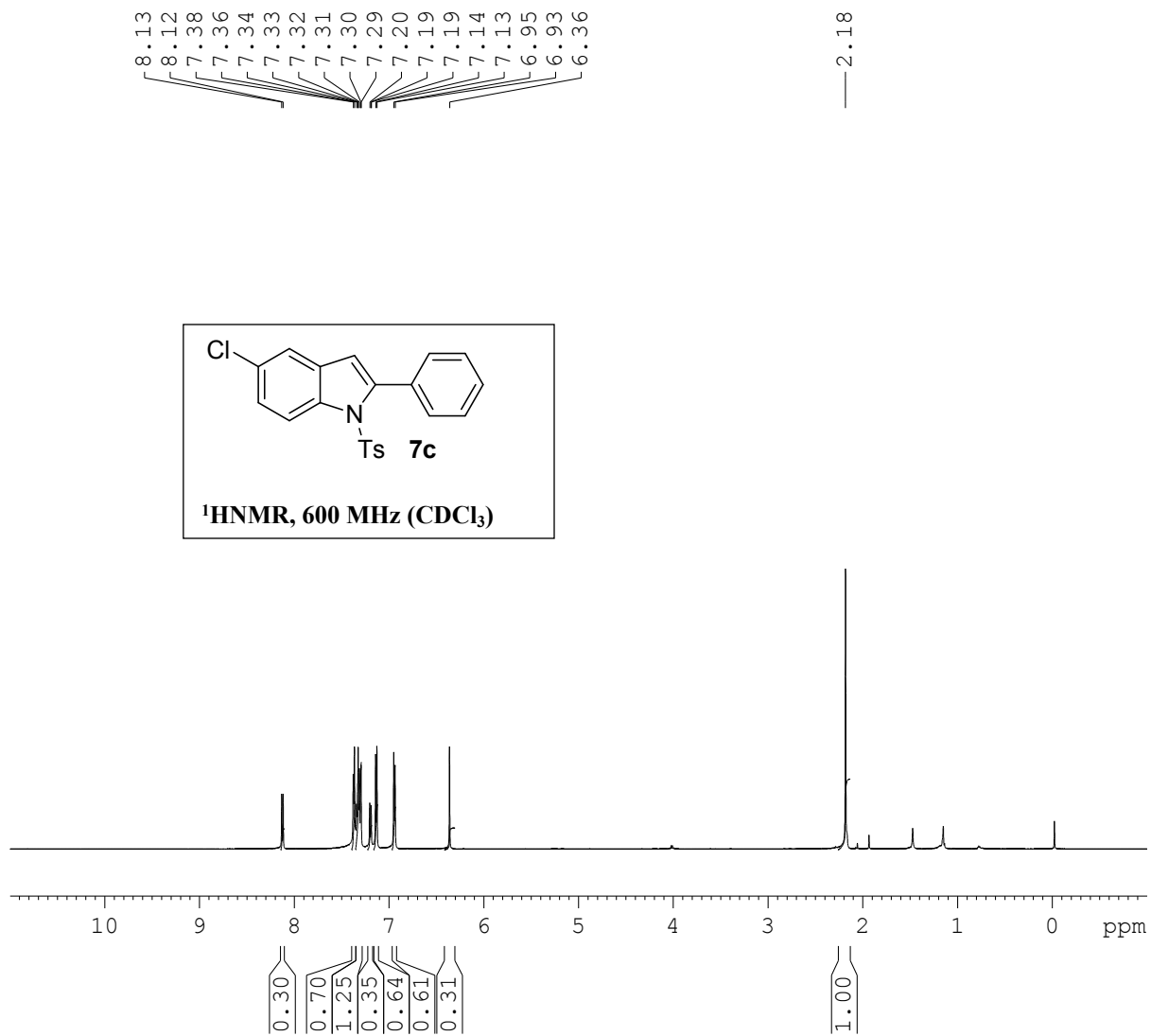


8.17  
8.15  
7.50  
7.49  
7.48  
7.42  
7.41  
7.26  
7.24  
7.21  
7.16  
7.15  
7.03  
7.02  
6.46

2.40  
2.27  
2.16  
1.56  
1.41  
1.29  
1.25  
— 0.07

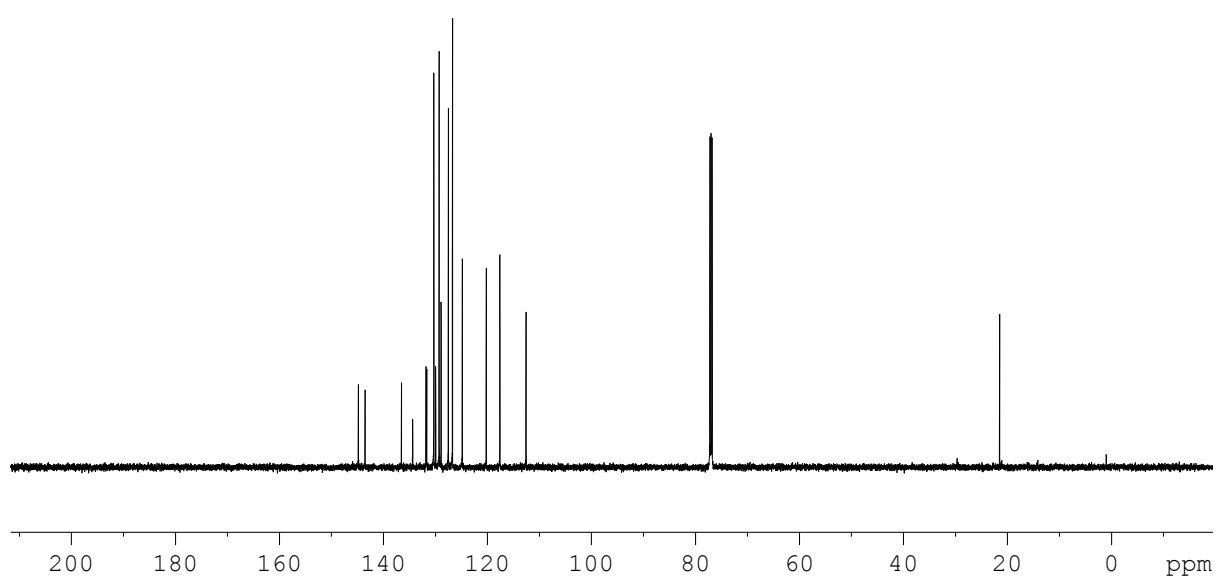
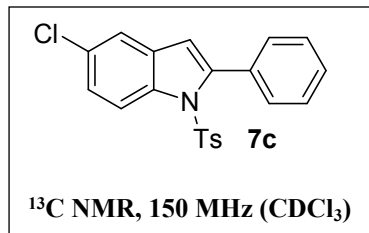


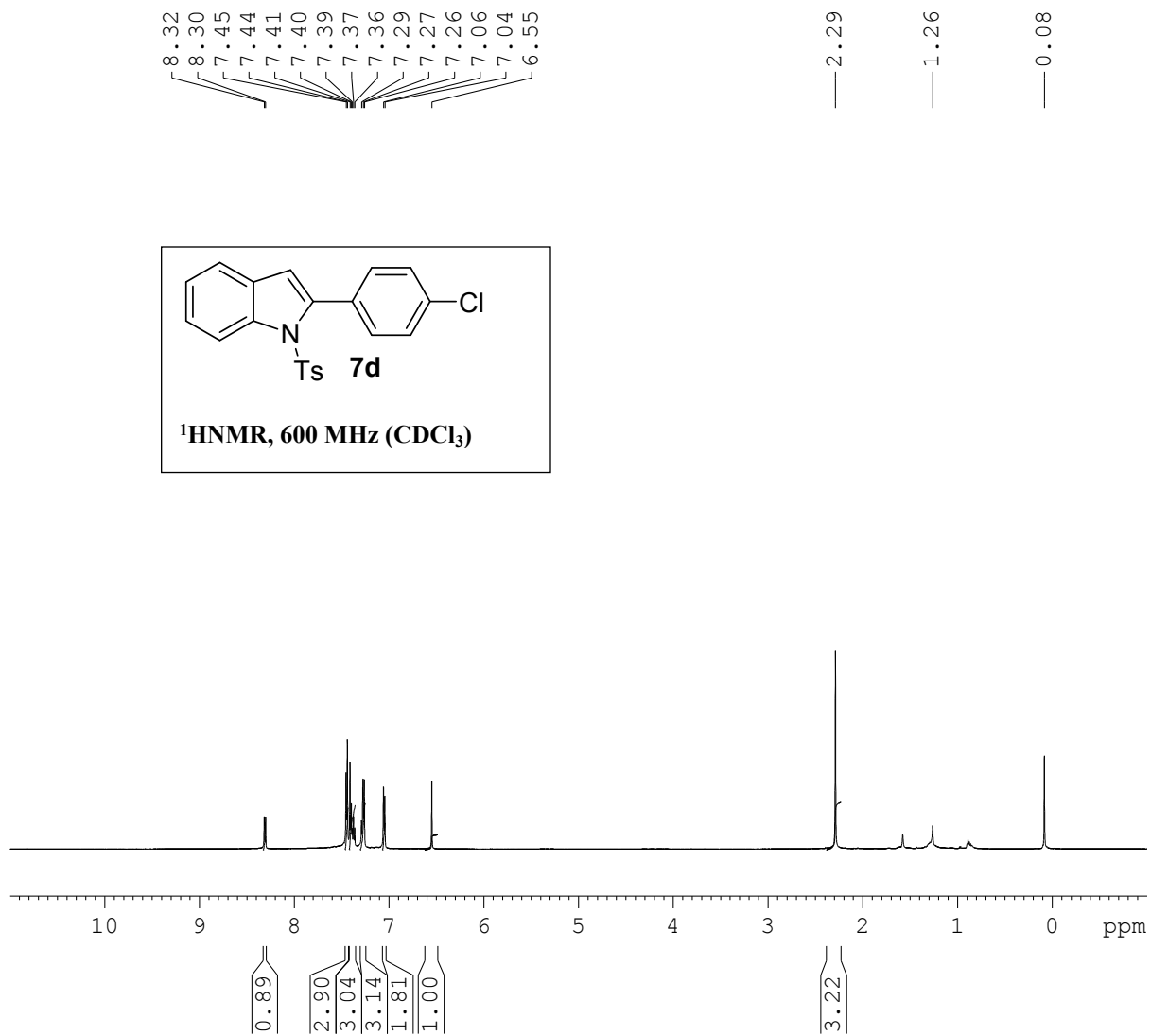




144.82  
143.54  
136.55  
134.40  
131.82  
131.68  
130.33  
129.97  
129.29  
128.92  
127.52  
126.73  
124.84  
120.24  
117.63  
112.57  
77.21  
77.00  
76.79

—21.50

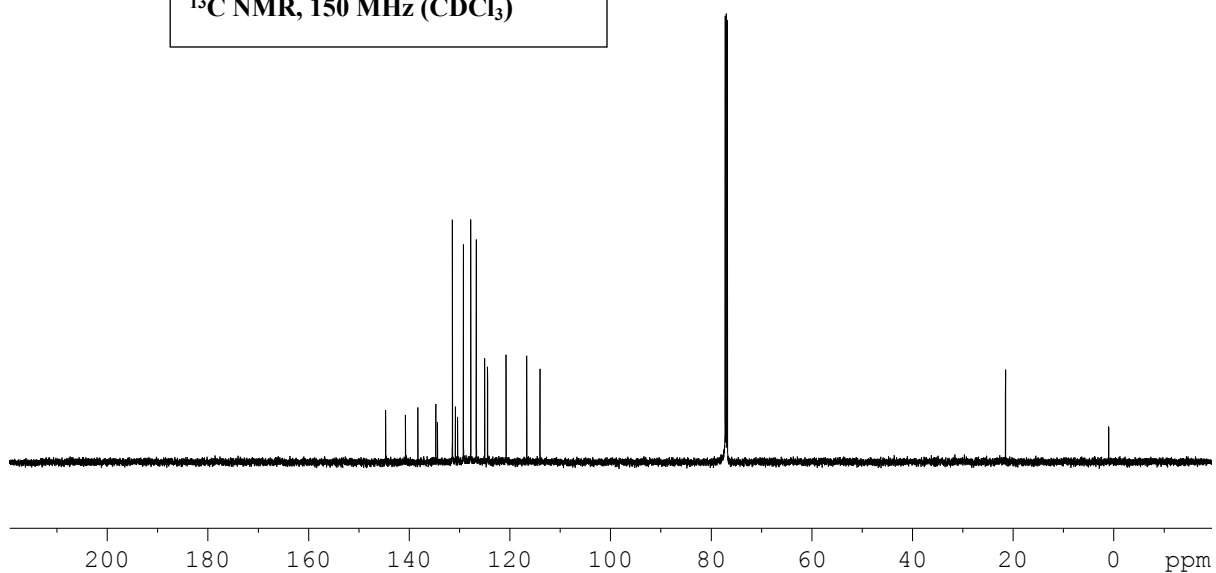
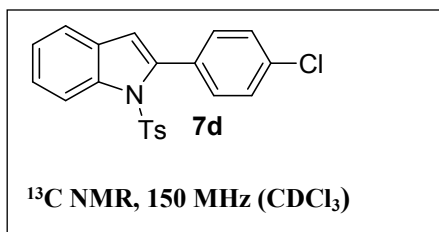




144.70  
140.78  
138.30  
134.73  
134.41  
131.44  
130.84  
130.40  
129.25  
127.79  
126.68  
125.03  
124.45  
120.76  
116.67  
114.01  
77.21  
77.00  
76.79

—21.51

—1.00

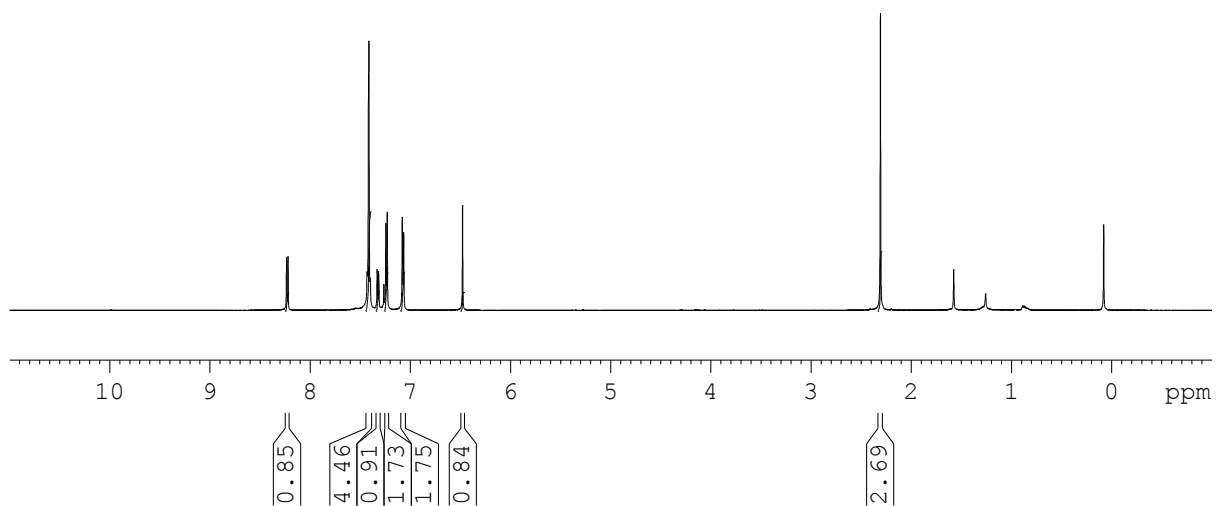
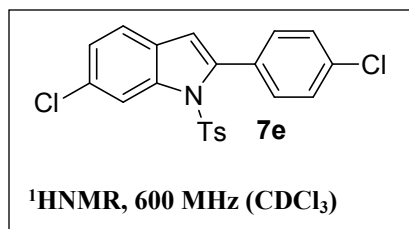


8.24  
8.22  
7.43  
7.41  
7.41  
7.40  
7.33  
7.33  
7.31  
7.31  
7.24  
7.23  
7.08  
7.06  
6.48

— 2.31

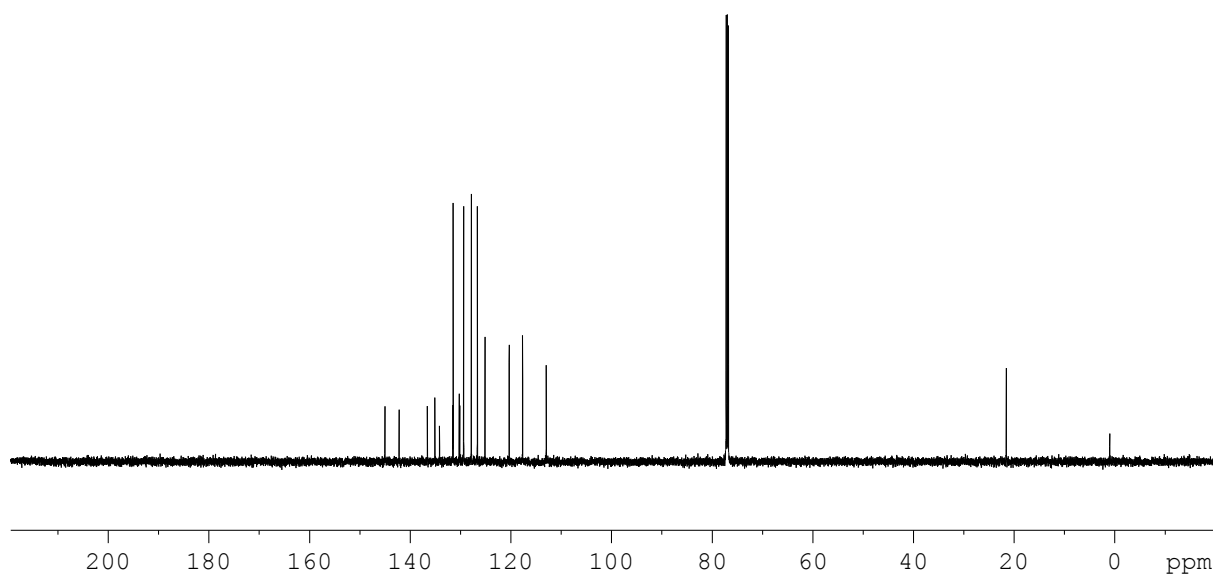
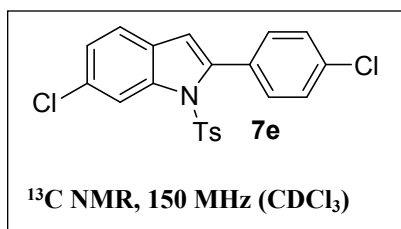
— 1.58

— 0.08

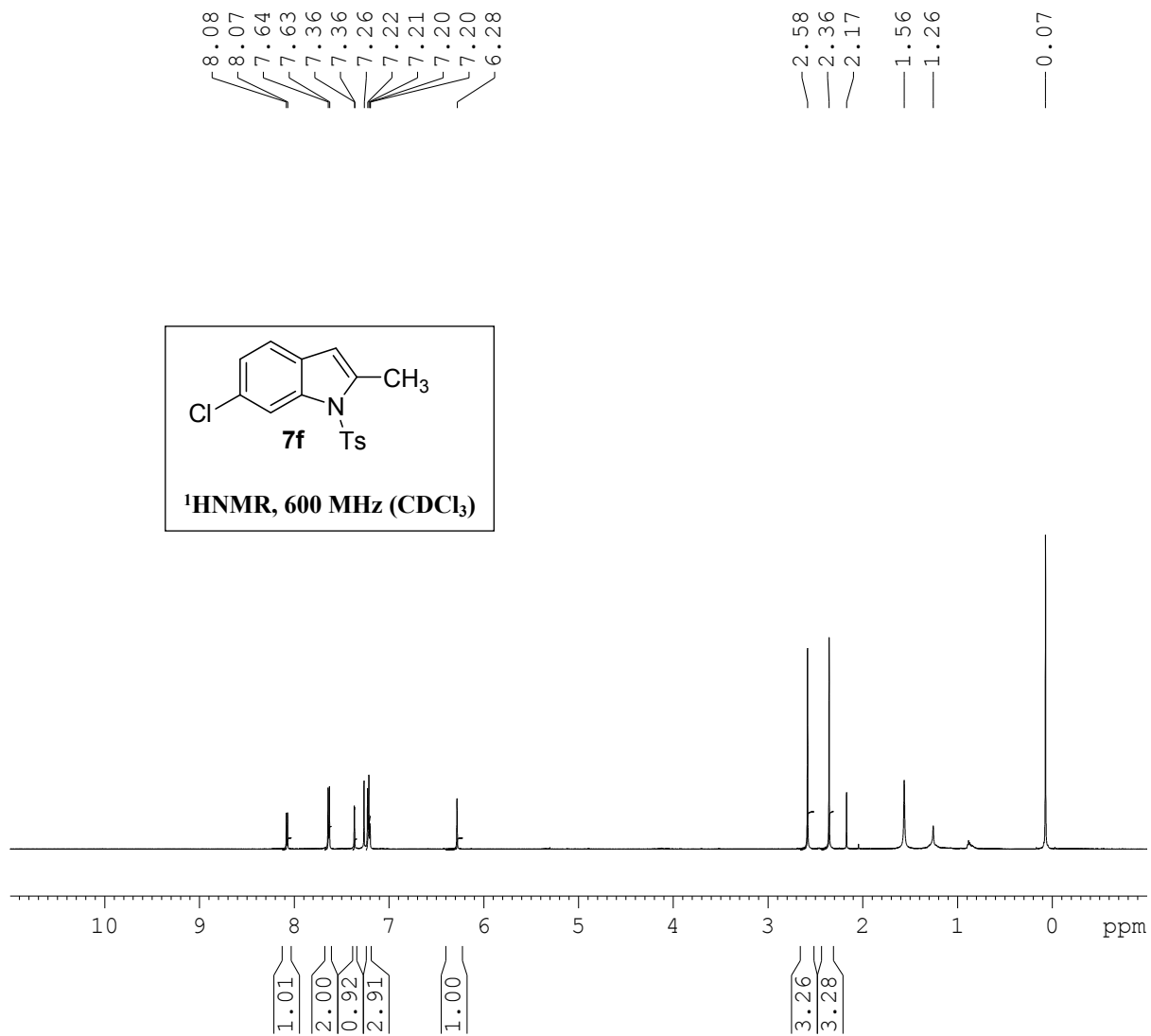


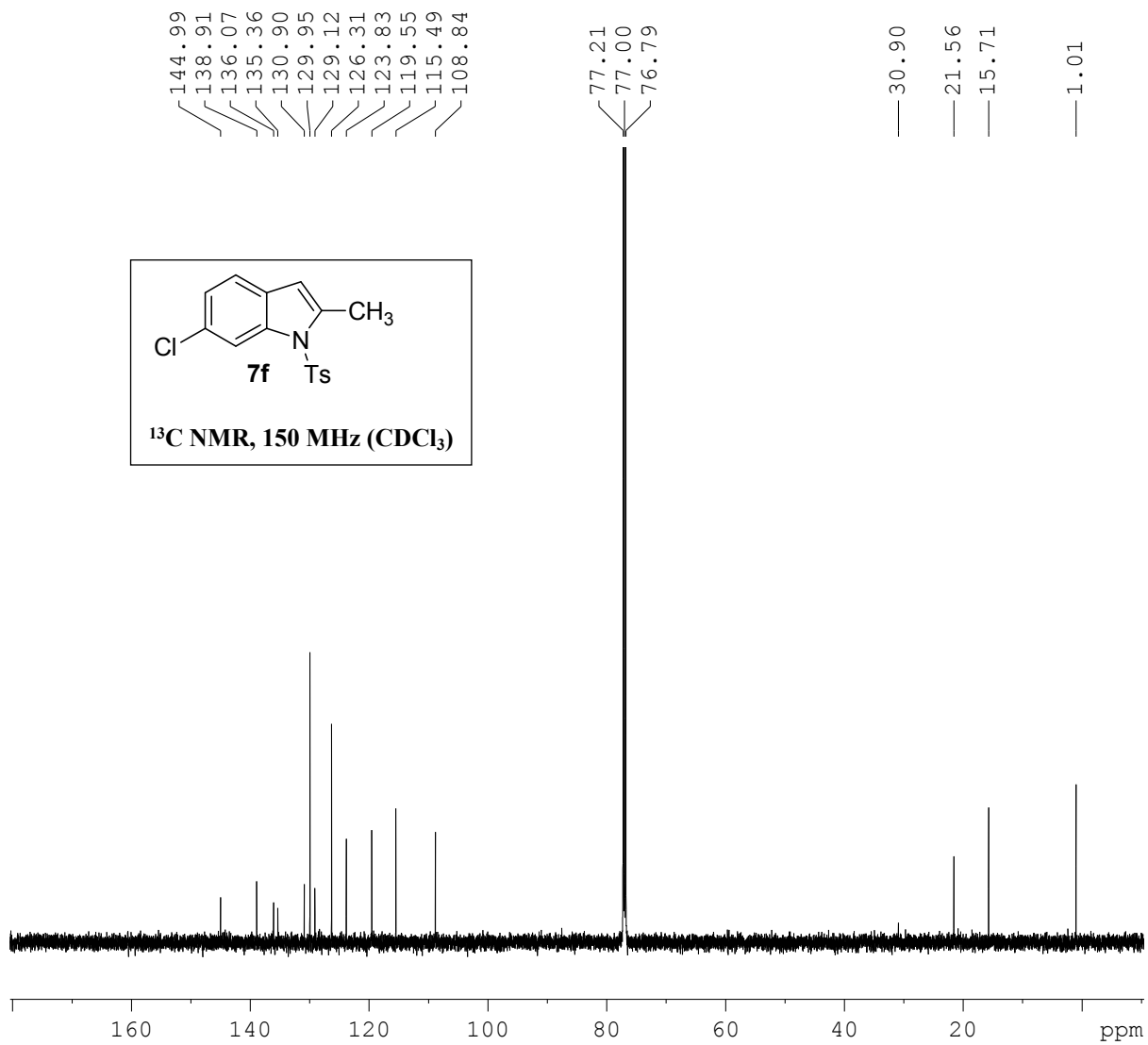
145.03  
142.21  
136.60  
135.11  
134.20  
131.56  
131.48  
130.27  
130.15  
129.39  
127.87  
126.66  
125.15  
120.34  
117.68  
112.98  
77.21  
77.00  
76.78

— 21.54



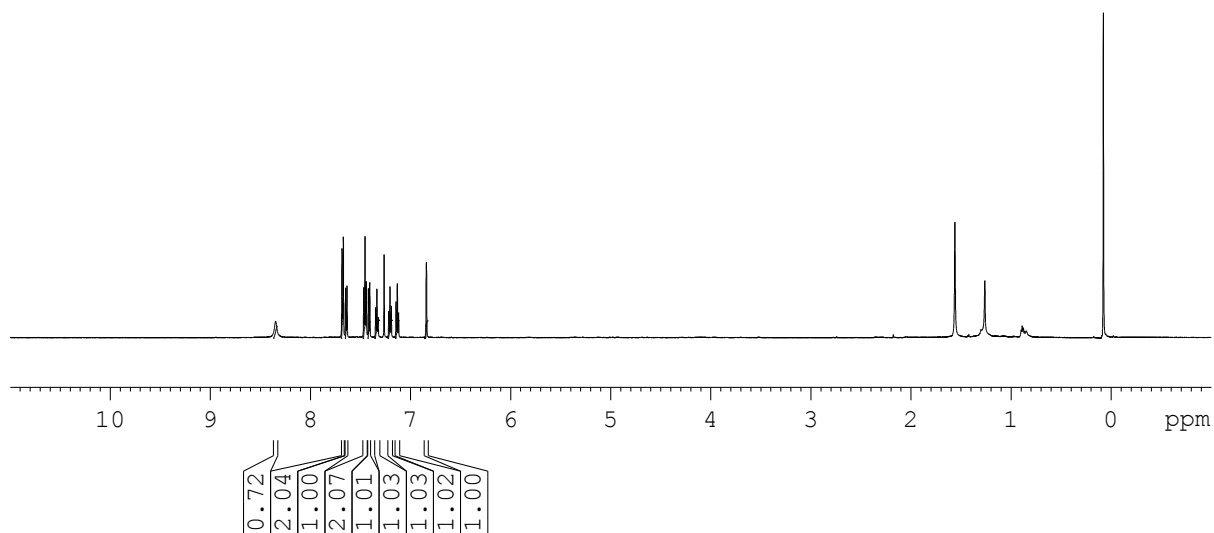
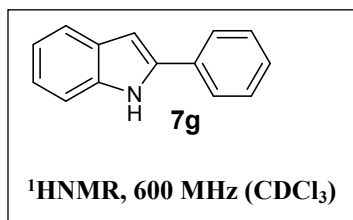




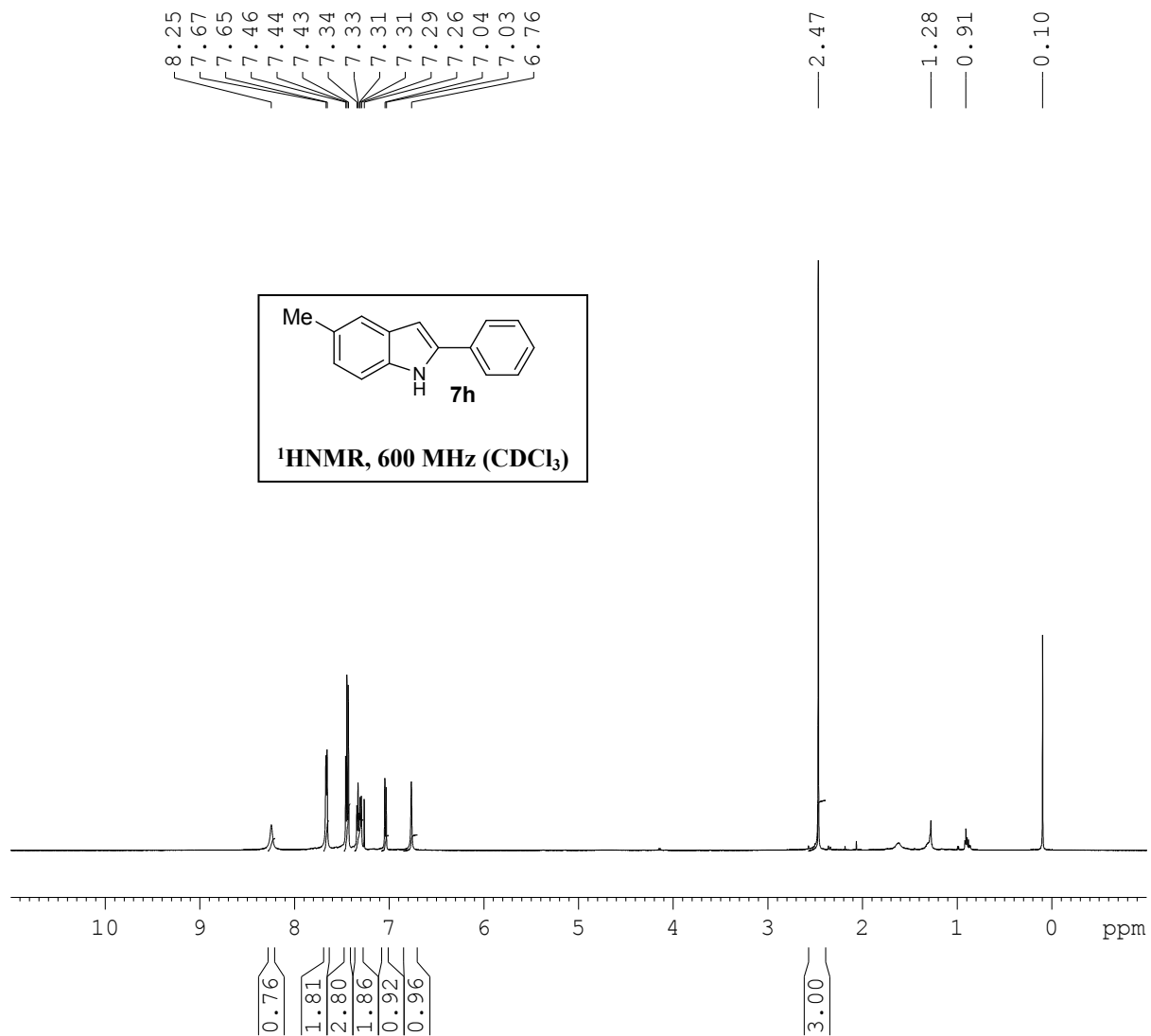


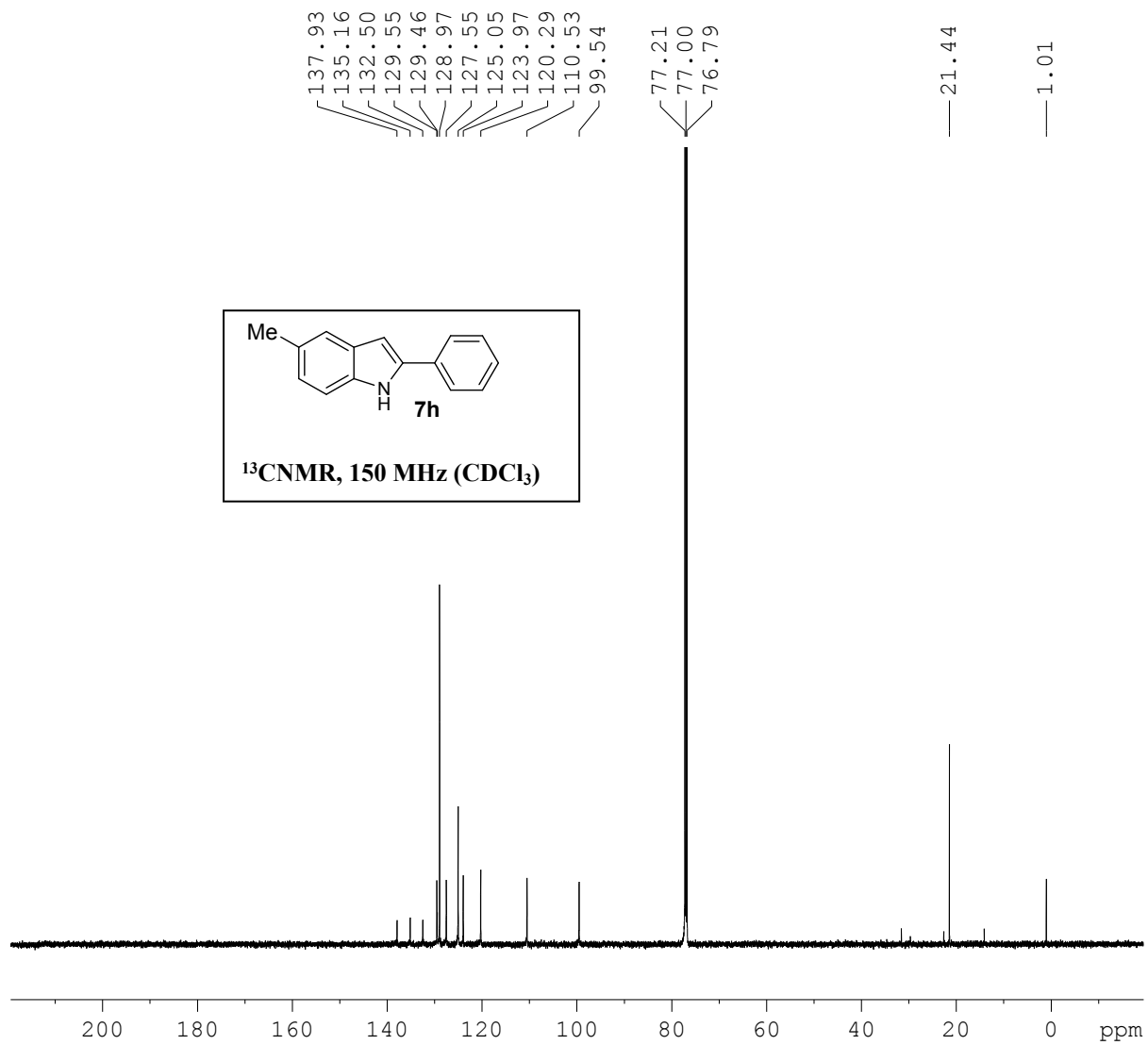
8.35  
7.68  
7.67  
7.65  
7.63  
7.46  
7.45  
7.44  
7.42  
7.41  
7.35  
7.33  
7.32  
7.26  
7.22  
7.20  
7.19  
7.14  
7.13  
7.12  
6.84

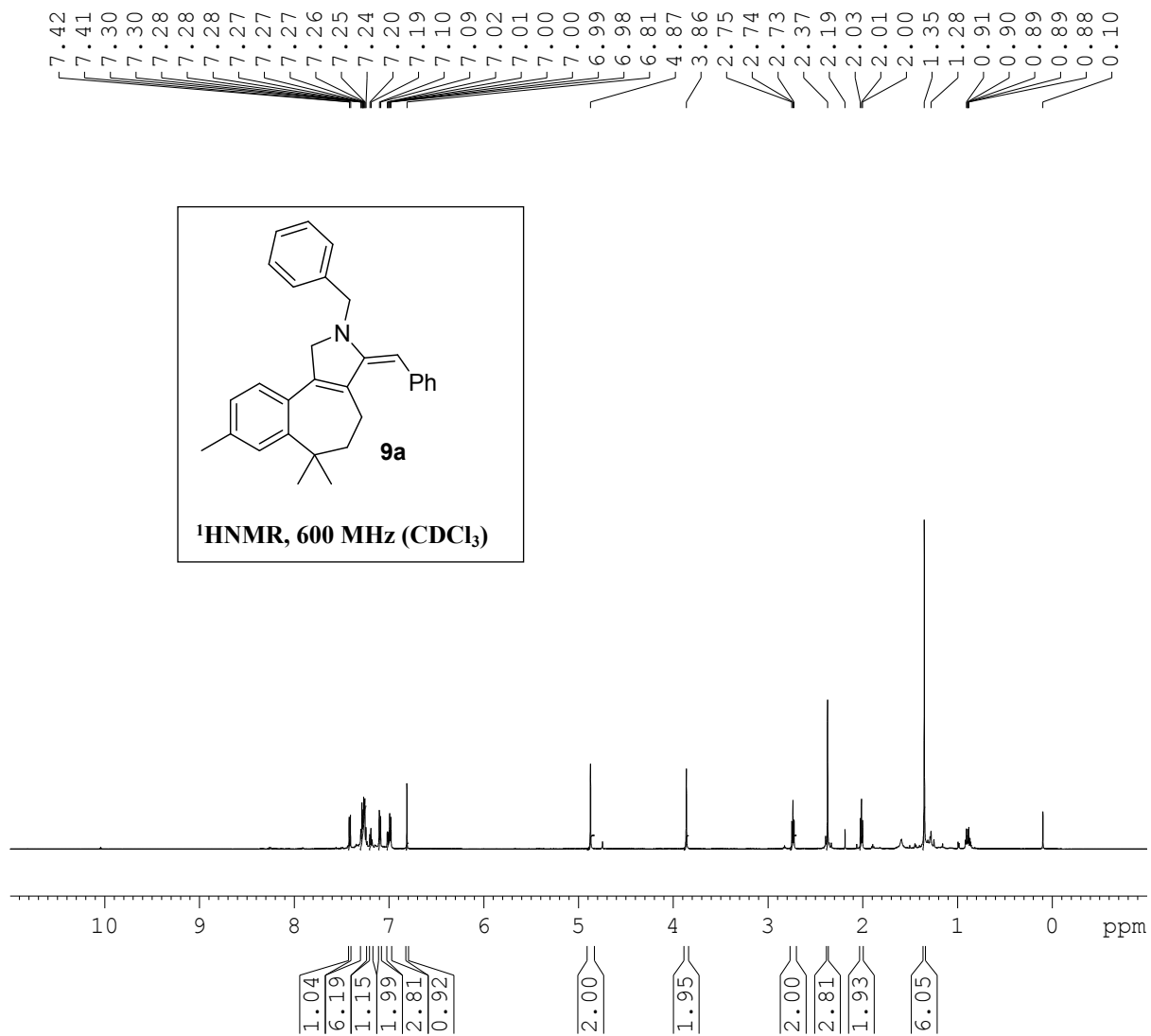
— 1.56  
— 1.26  
— 0.89  
— 0.08







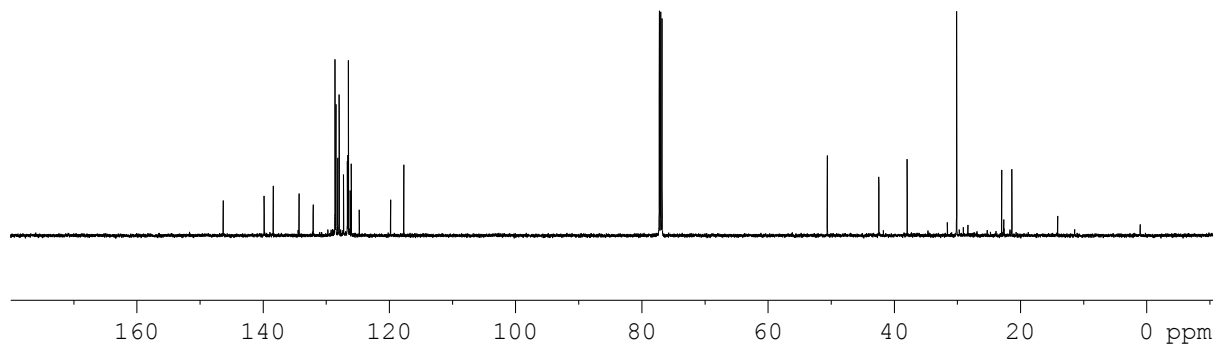
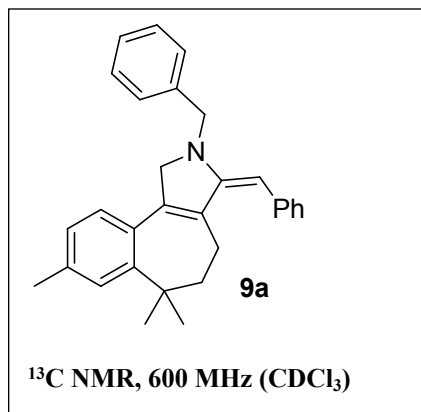




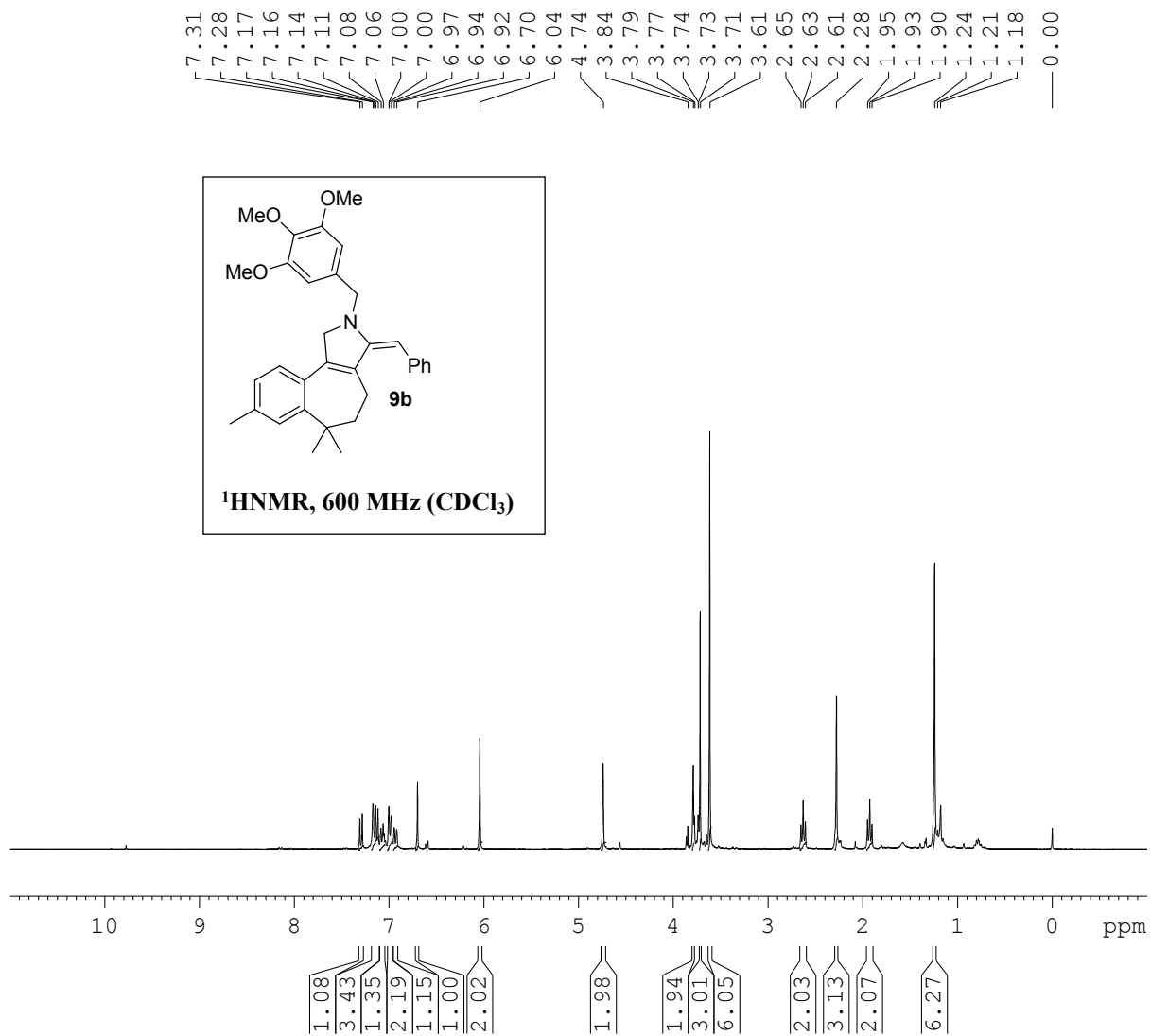
146.32  
139.83  
138.39  
134.29  
132.06  
128.60  
128.49  
128.46  
128.16  
127.94  
127.25  
126.65  
126.57  
126.48  
126.19  
126.02  
124.76  
119.80  
117.71

77.21  
77.00  
76.79

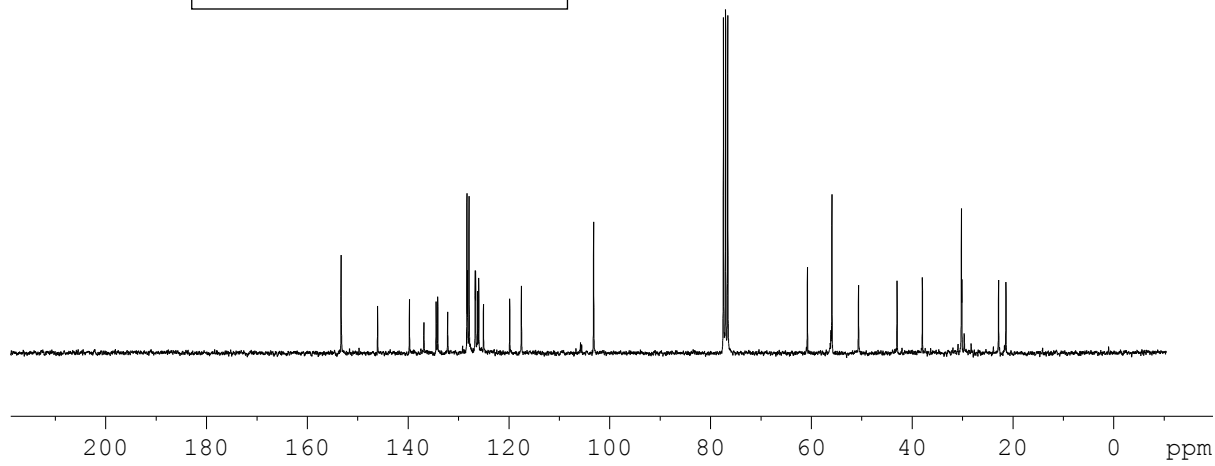
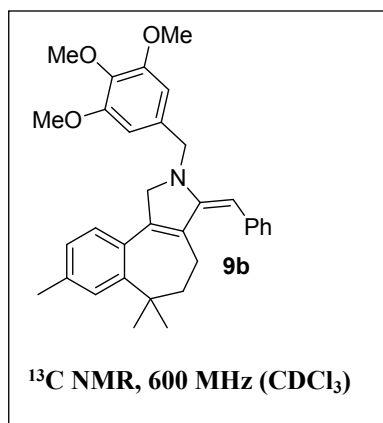
50.60  
42.44  
37.94  
30.11  
22.97  
22.64  
21.36  
14.10

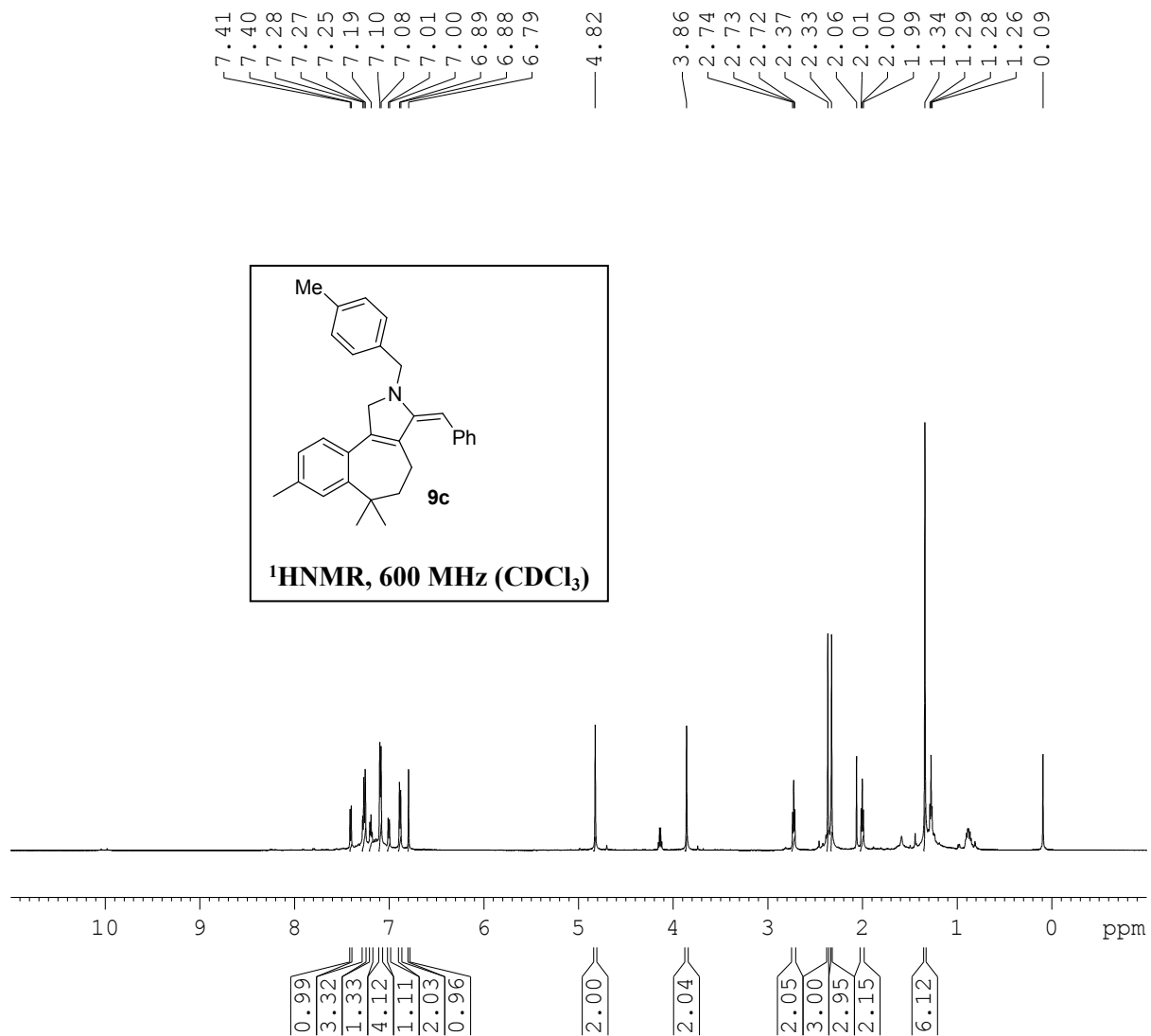


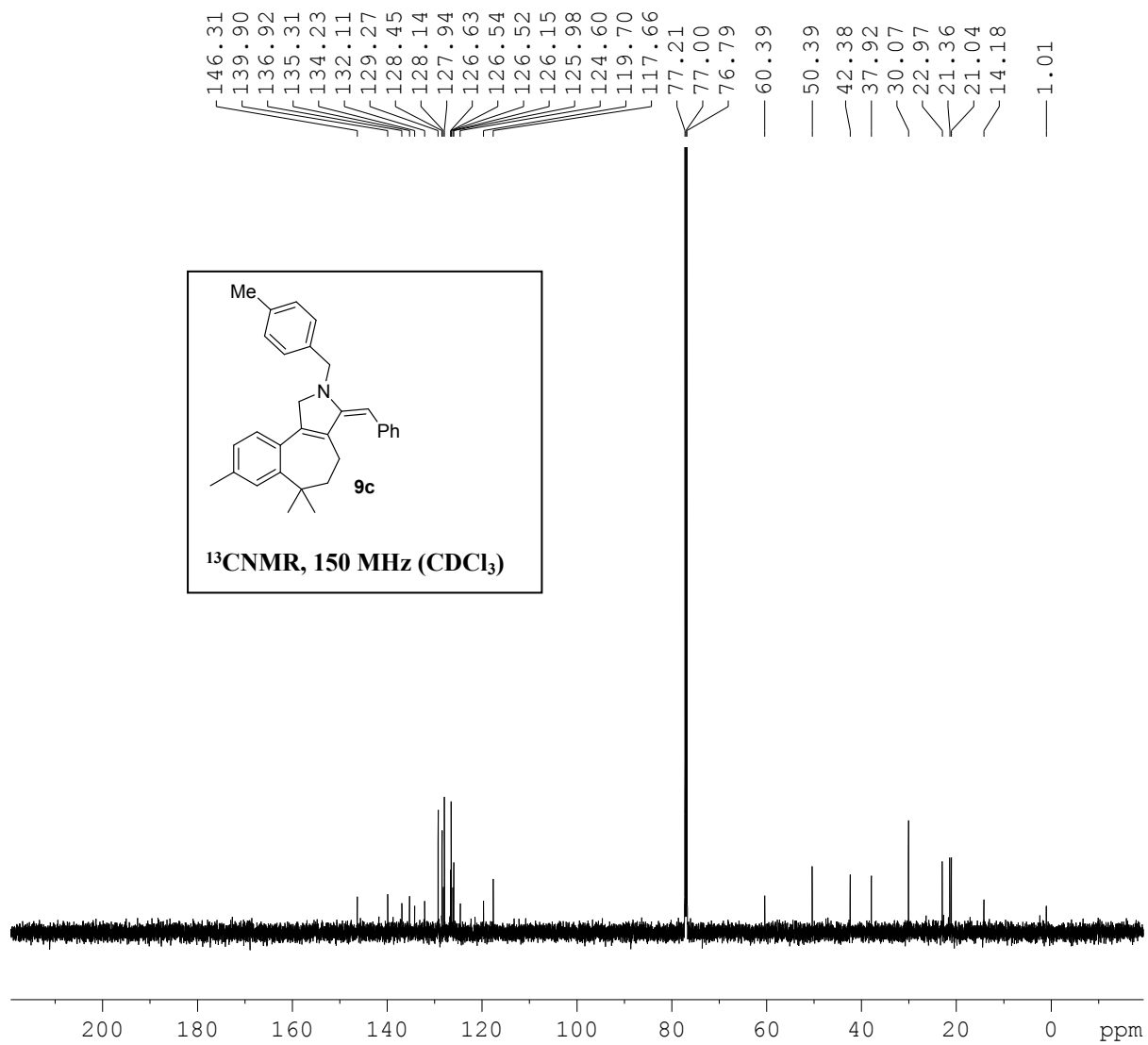




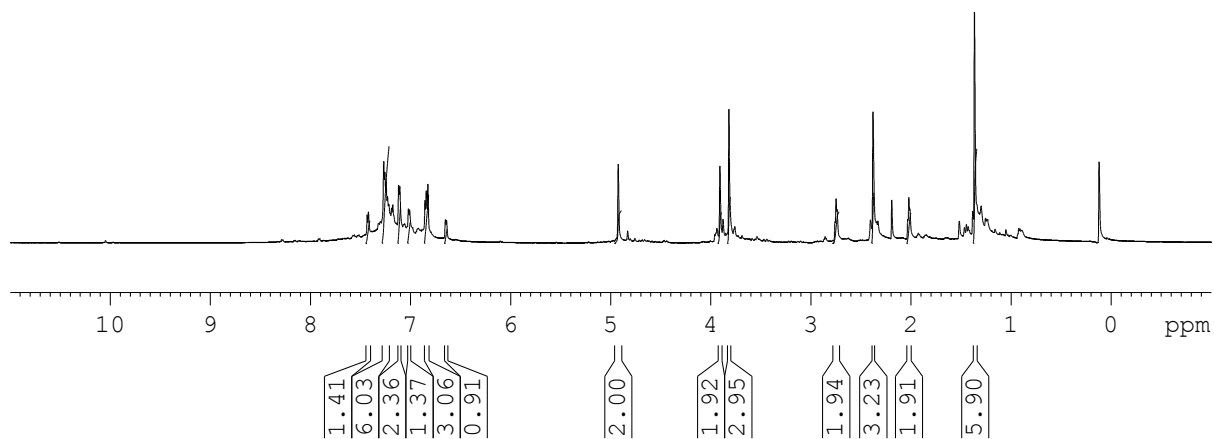
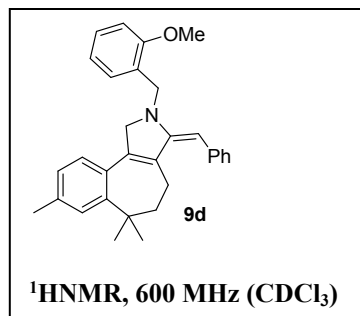
153.31  
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 136.87  
 134.45  
 134.13  
 132.16  
 128.34  
 128.22  
 127.92  
 126.68  
 126.62  
 126.21  
 126.00  
 125.06  
 119.85  
 117.53  
 103.19  
 77.42  
 77.00  
 76.57  
 60.75  
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 30.09  
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 22.81  
 21.35

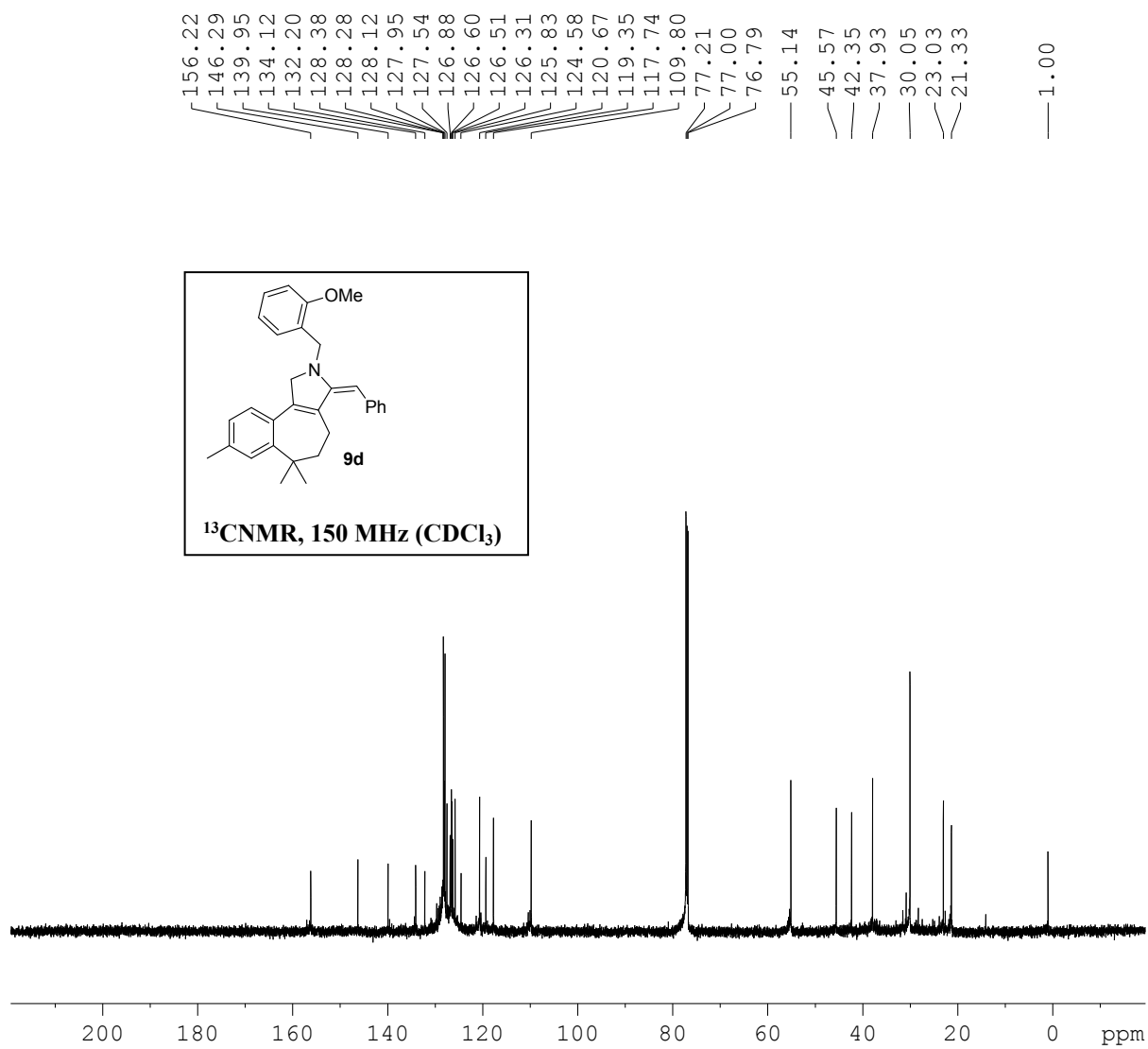




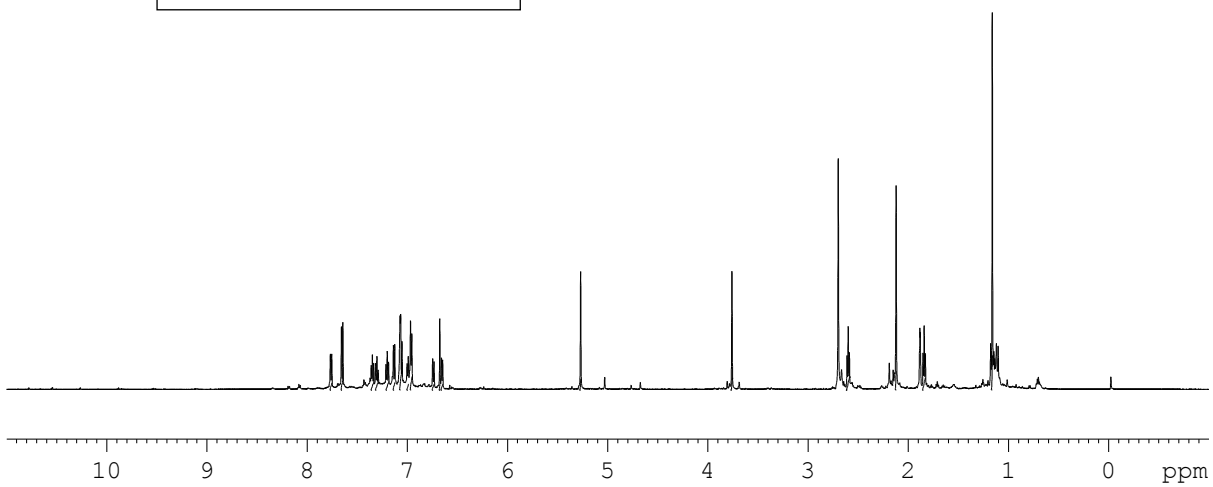
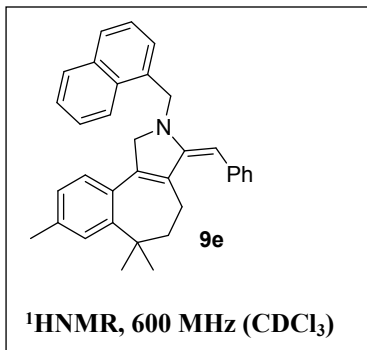


7.43  
7.42  
7.27  
7.25  
7.24  
7.23  
7.21  
7.20  
7.19  
7.18  
7.12  
7.11  
7.02  
7.01  
6.85  
6.84  
6.82  
6.65  
4.93  
3.91  
3.88  
3.82  
2.75  
2.74  
2.38  
2.19  
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2.02  
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1.30  
1.26  
1.24  
0.12



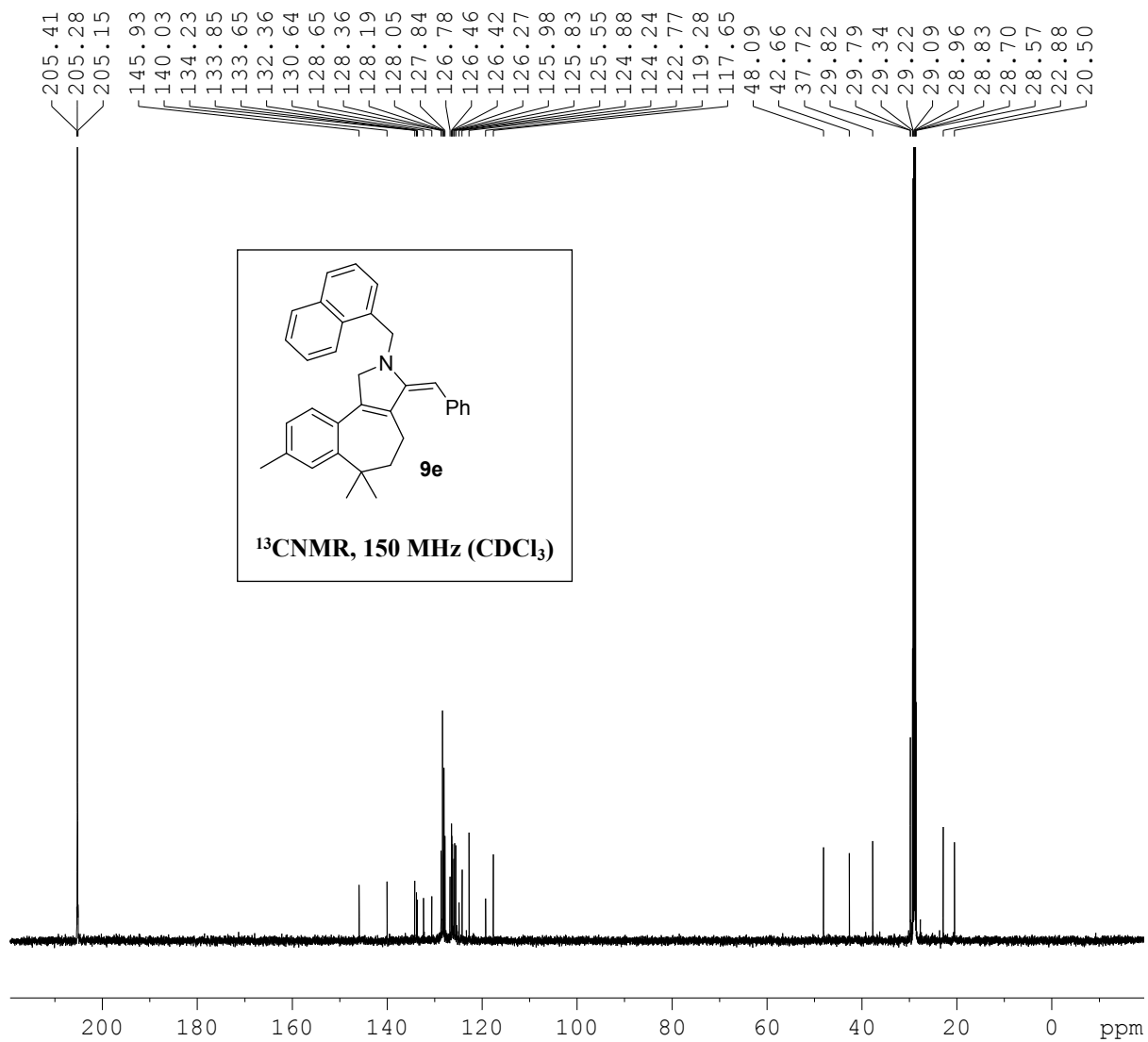


7.77  
7.75  
7.66  
7.64  
7.35  
7.33  
7.31  
7.30  
7.20  
7.19  
7.14  
7.12  
7.07  
7.06  
7.05  
6.99  
6.97  
6.95  
6.75  
6.73  
6.68  
6.66  
6.65  
5.27  
3.76  
2.70  
2.61  
2.60  
2.59  
2.19  
2.12  
1.89  
1.88  
1.88  
1.85  
1.84  
1.83  
1.18  
1.16  
1.15  
1.14  
1.12  
1.10



10 9 8 7 6 5 4 3 2 1 0 ppm

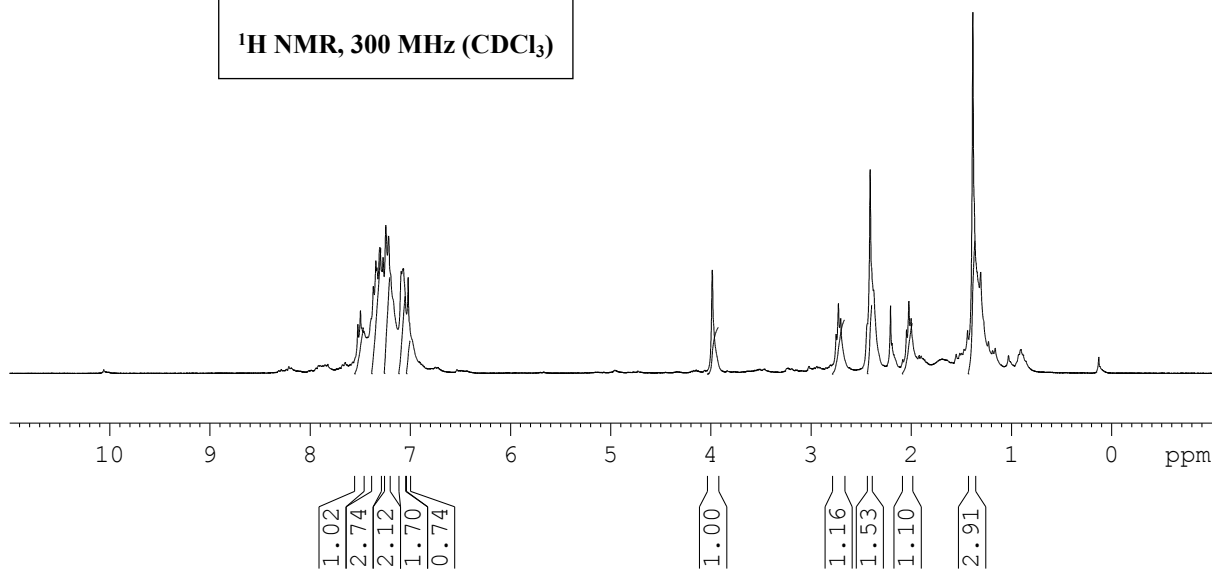
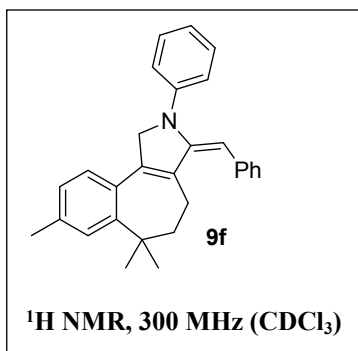
1.26  
2.16  
1.49  
1.47  
1.56  
1.43  
3.53  
1.13  
2.43  
1.05  
1.03  
1.06  
2.00  
2.09  
2.32  
3.47  
2.22  
6.17

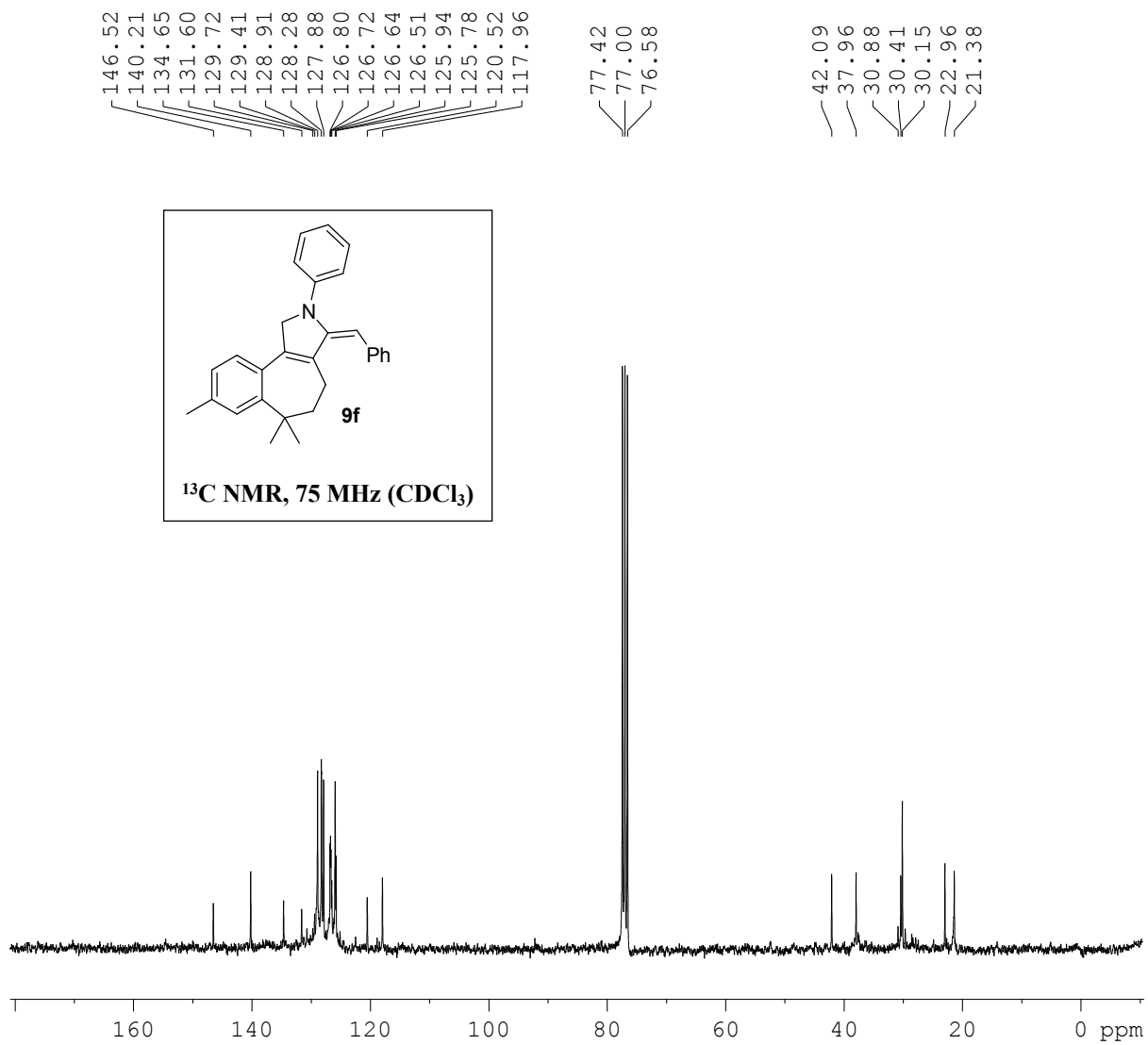


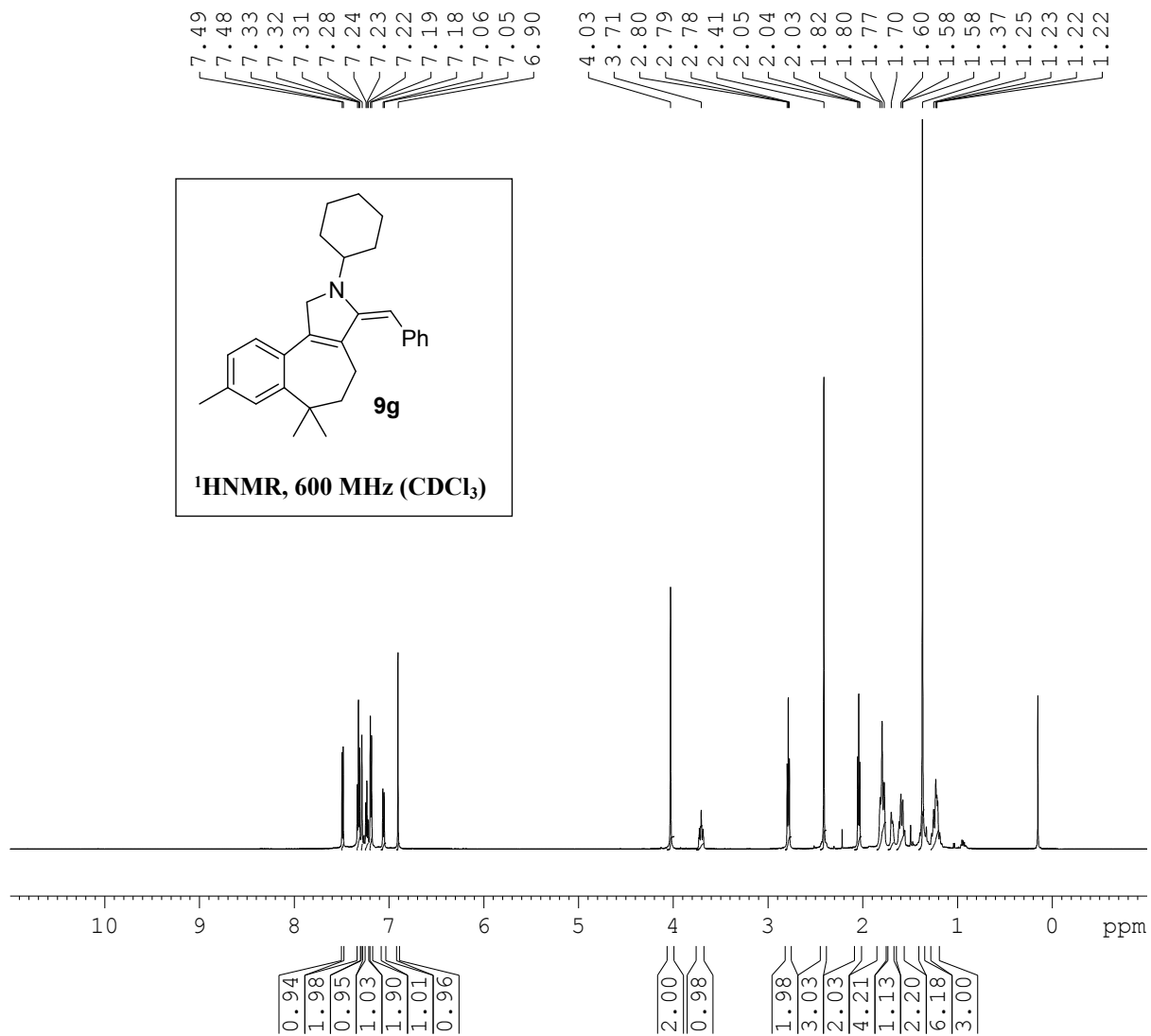


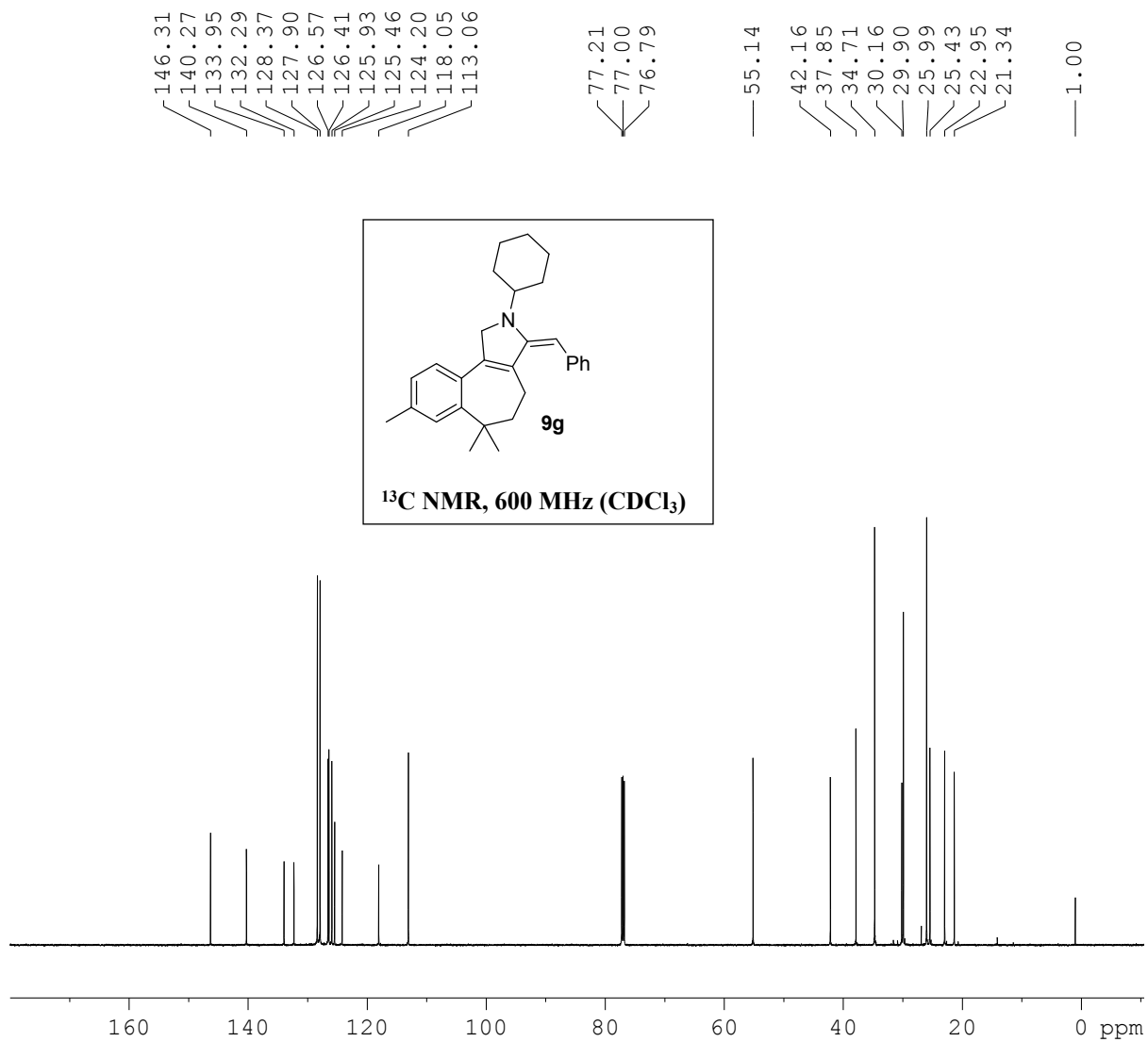
7.52  
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7.37  
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7.33  
7.30  
7.27  
7.24  
7.21  
7.09  
7.07  
7.07  
7.02

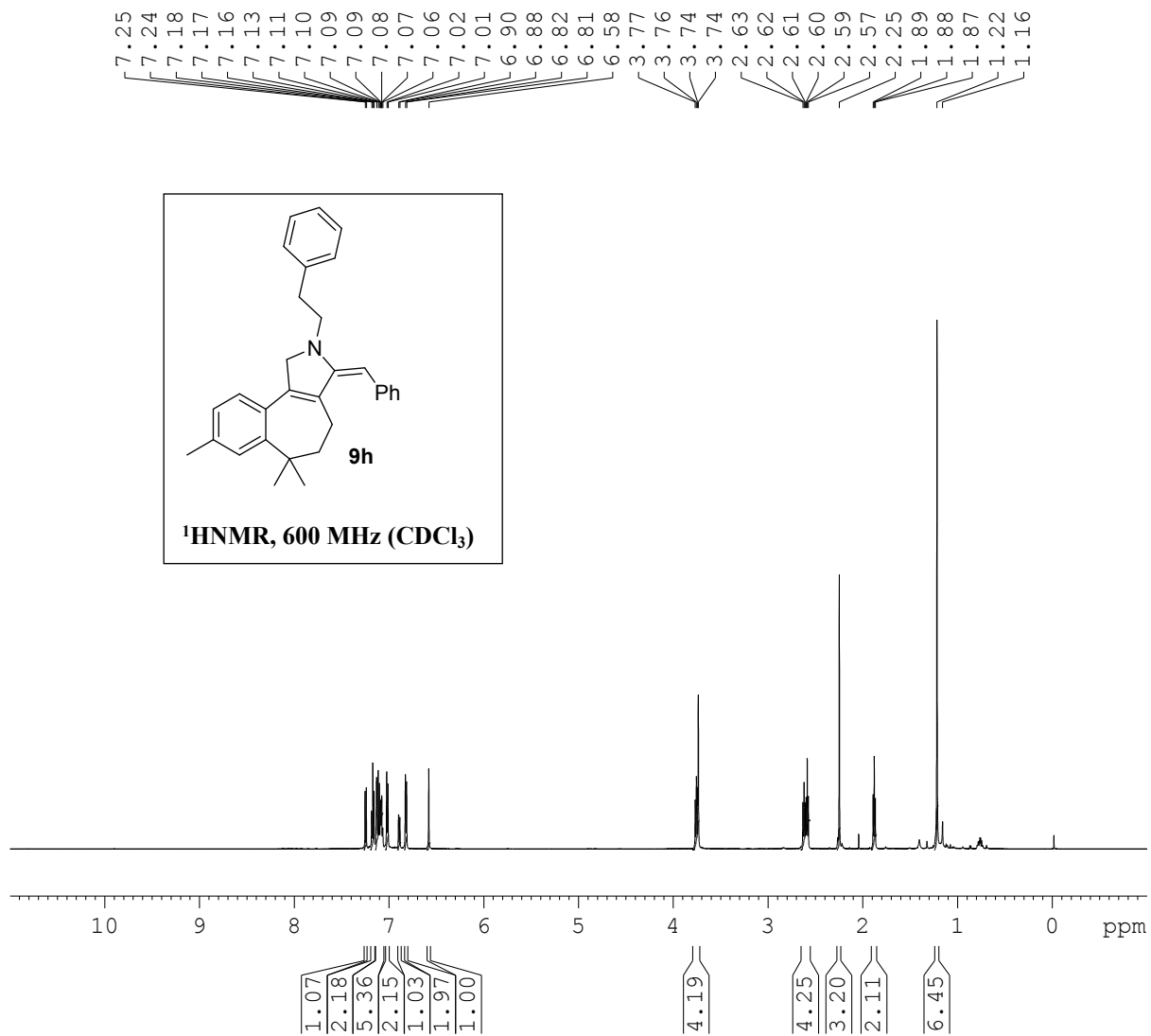
— 3.99  
2.75  
2.73  
2.70  
2.41  
2.38  
2.21  
2.05  
2.02  
2.00  
1.44  
1.39  
1.31

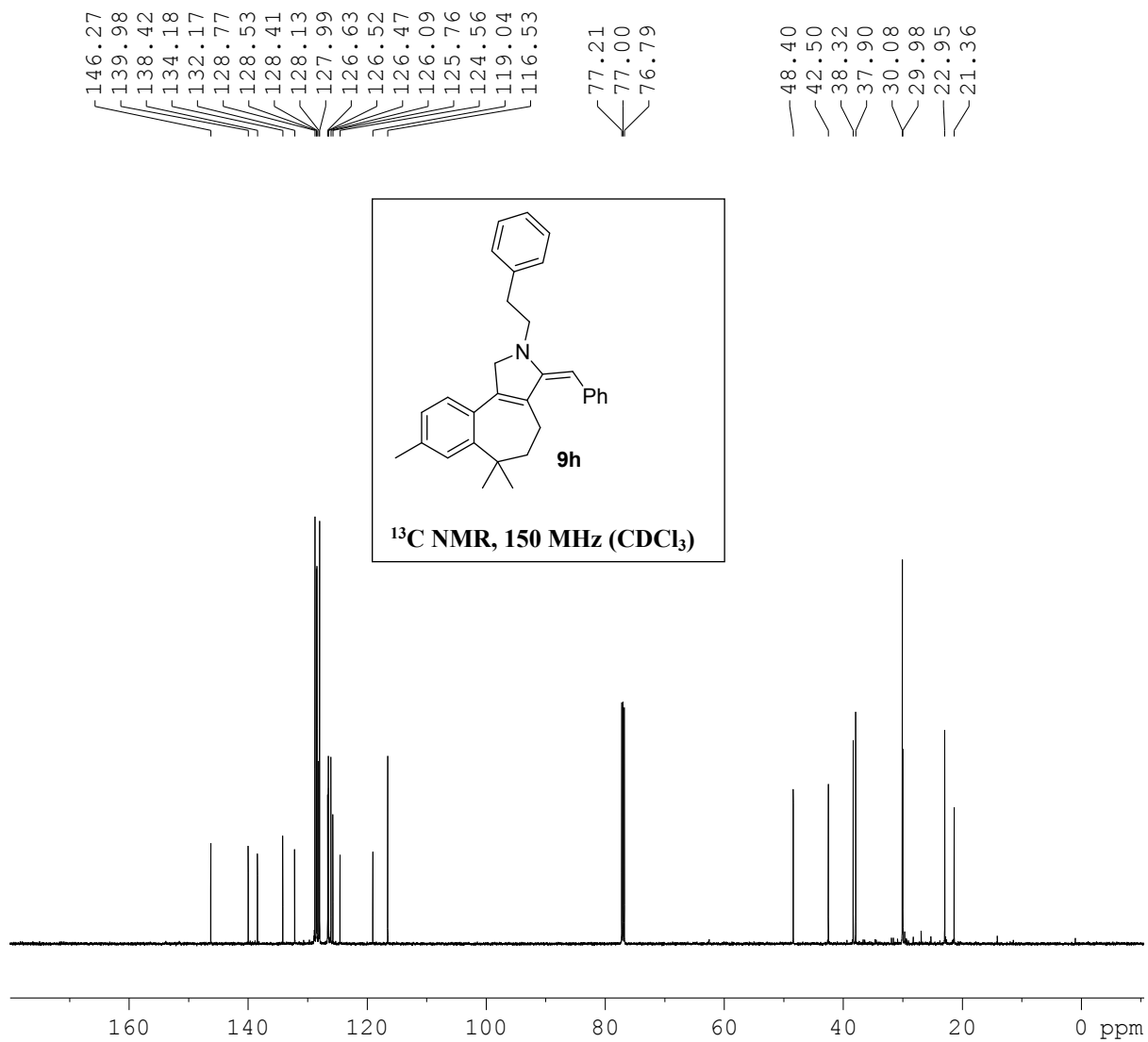


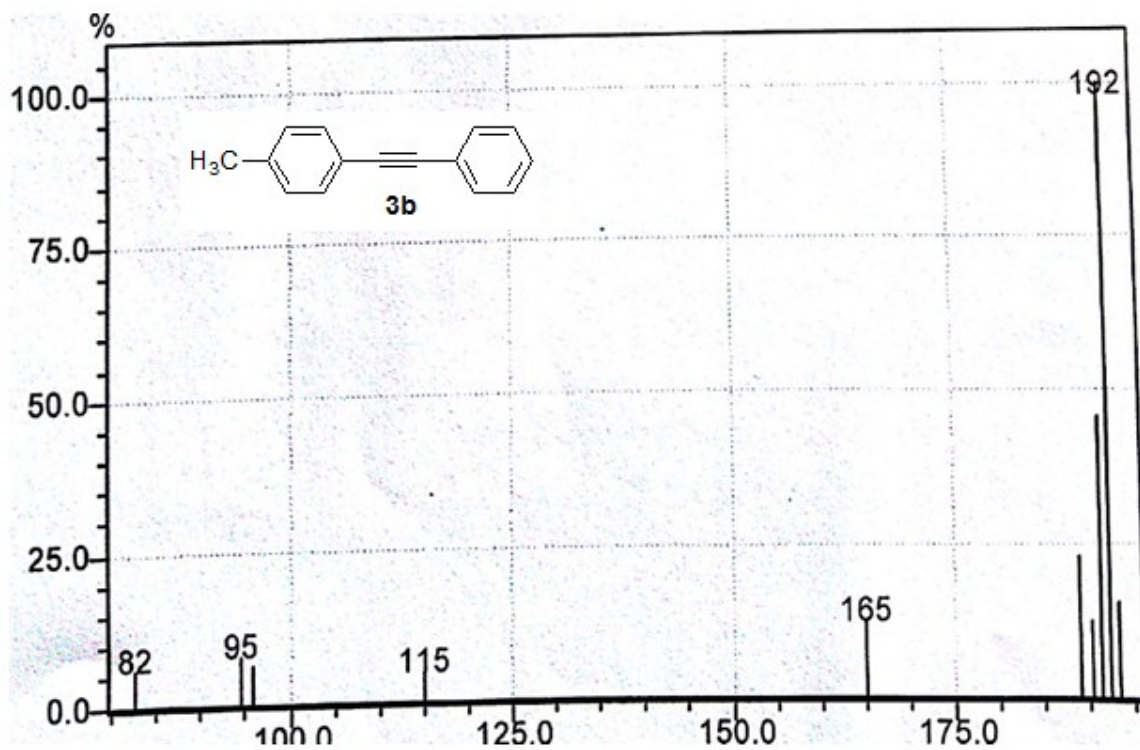
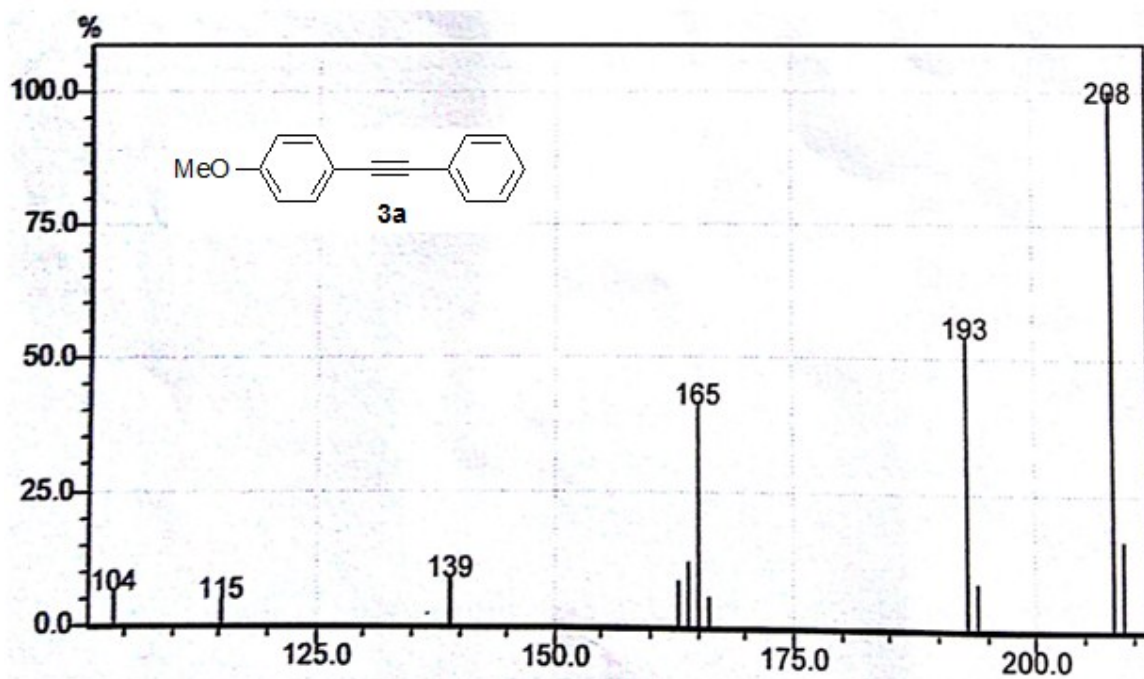


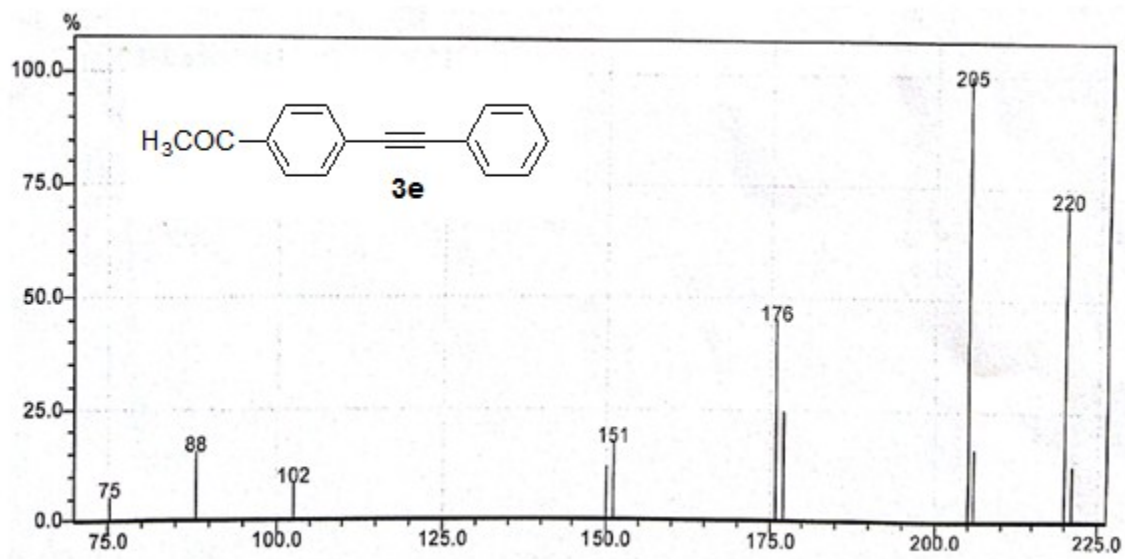
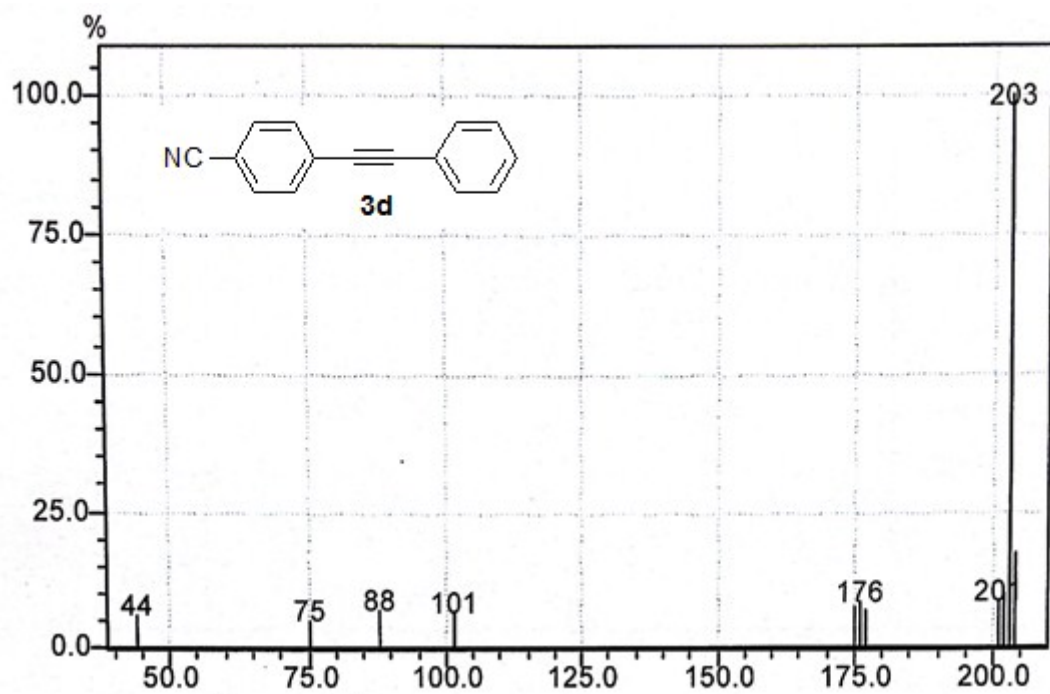




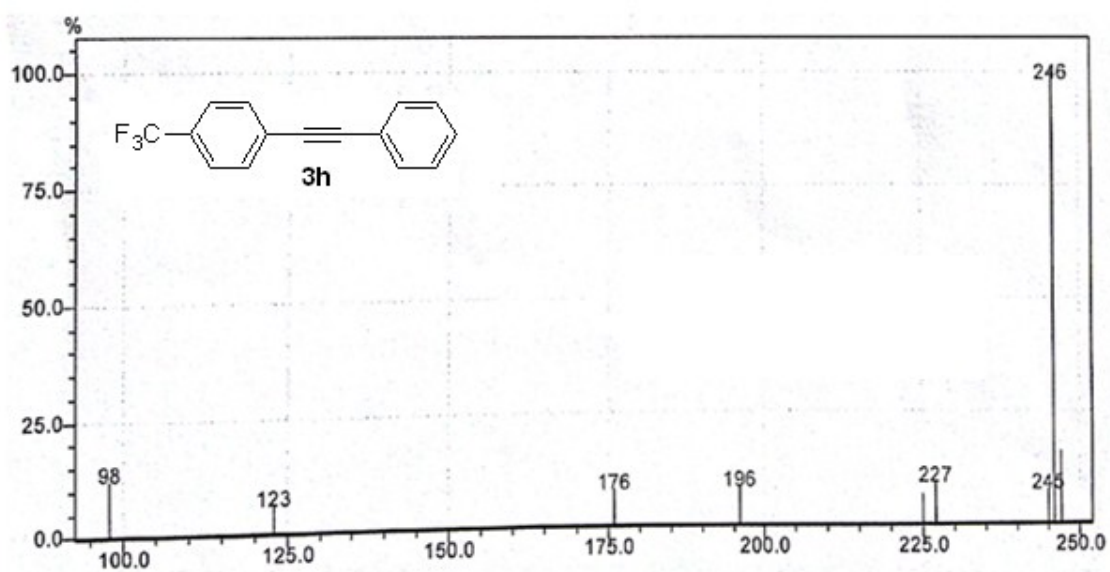
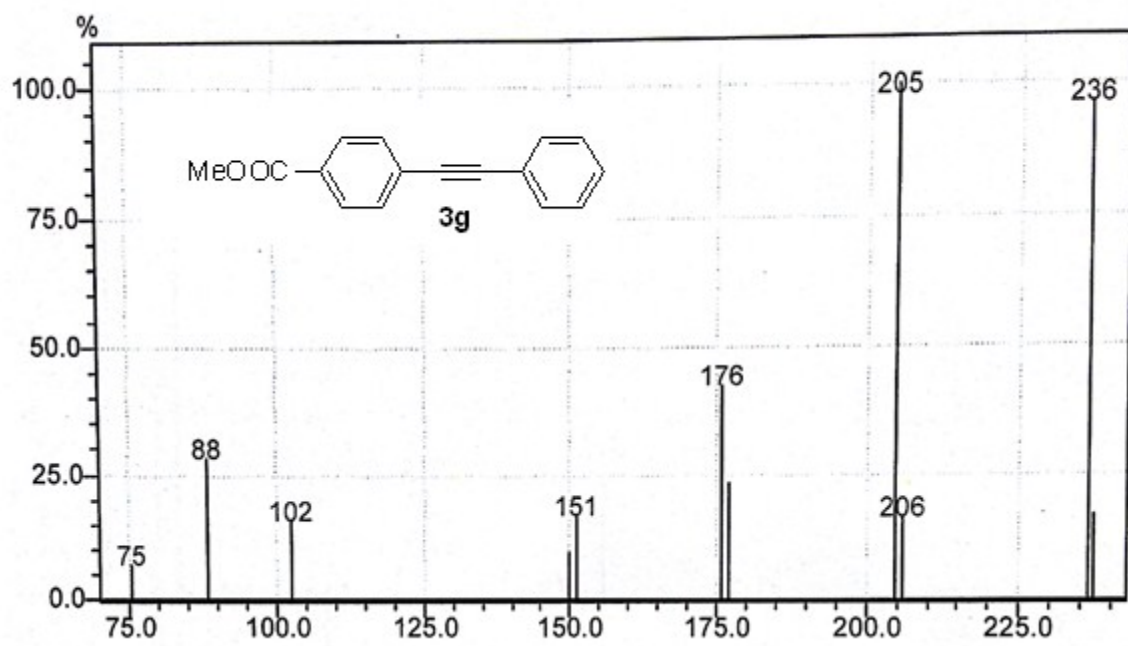


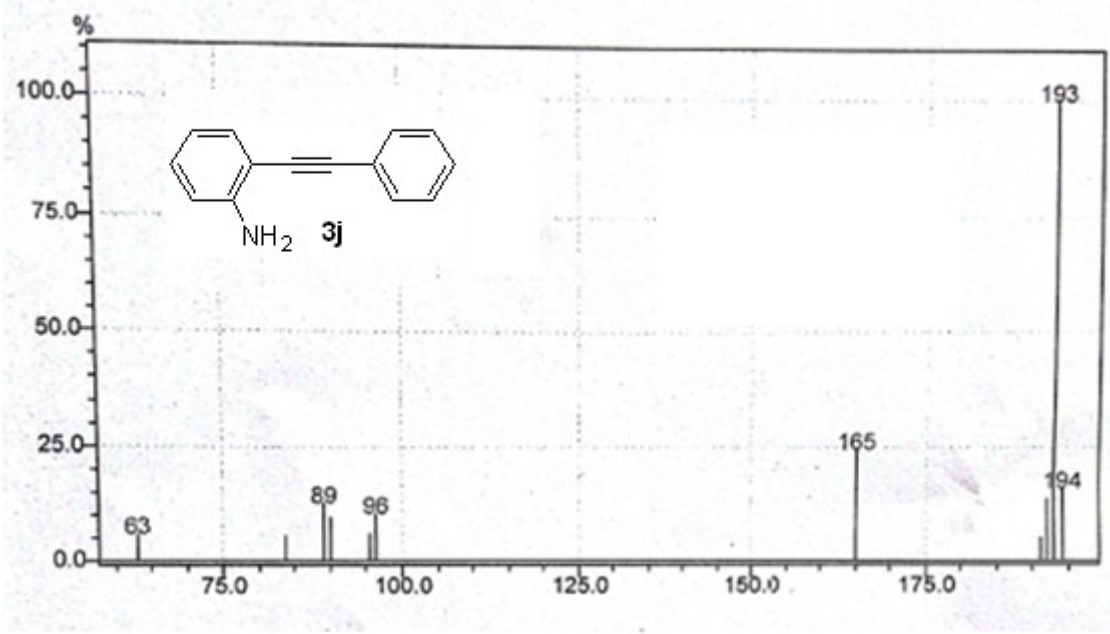
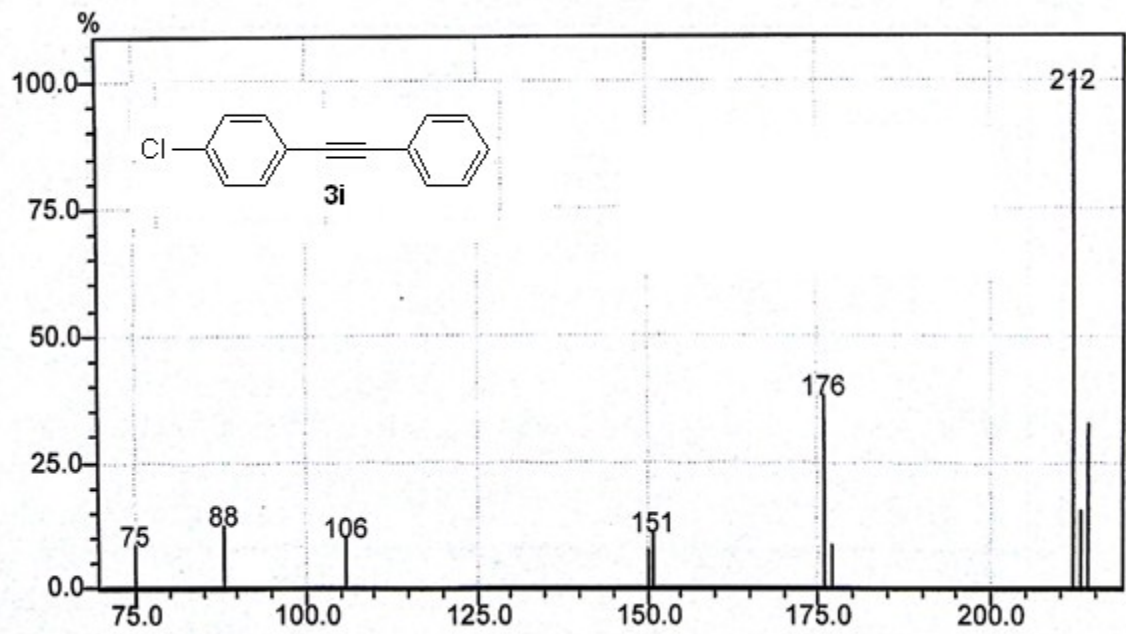


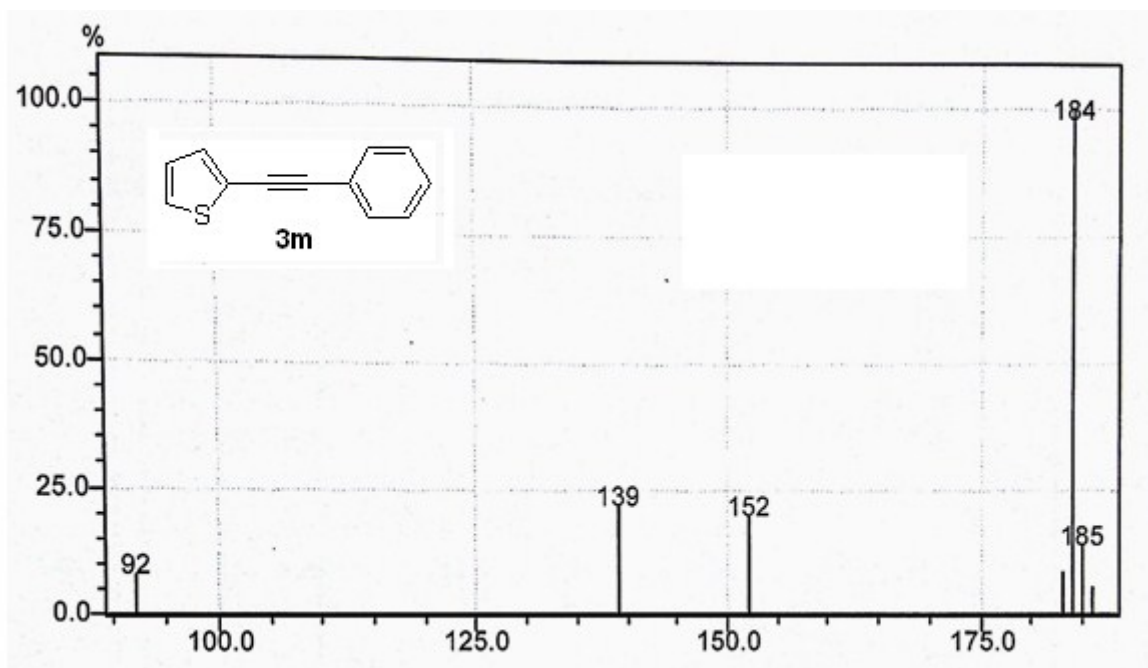
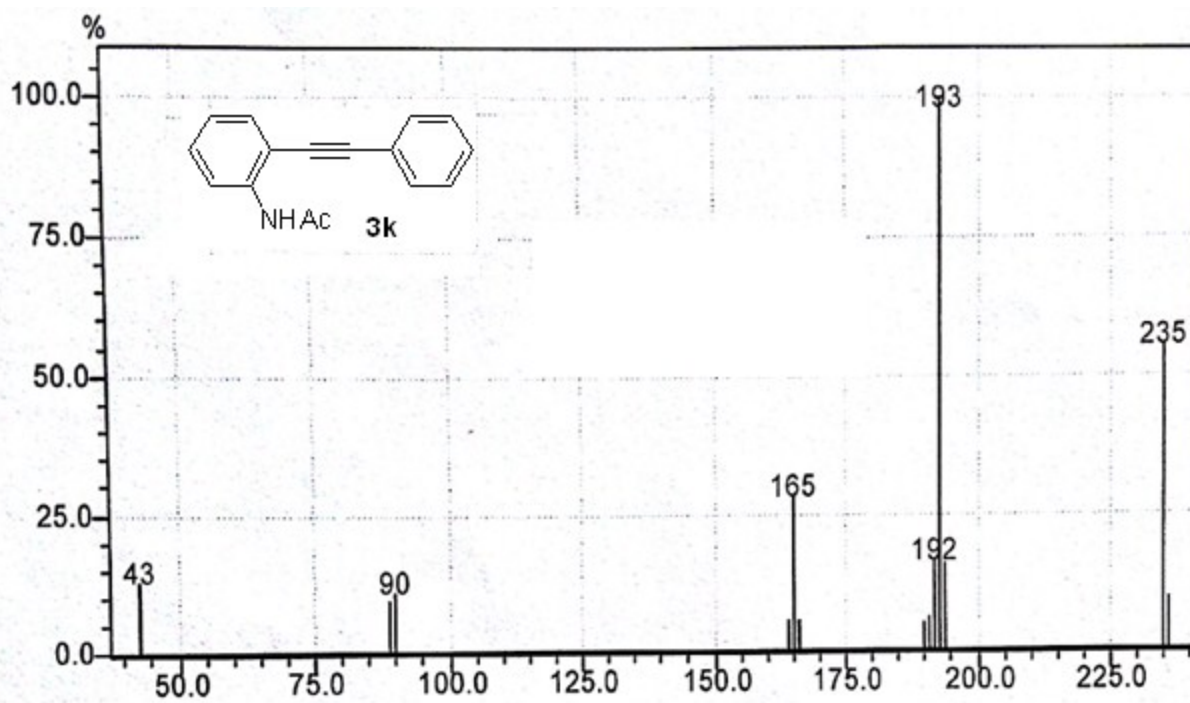


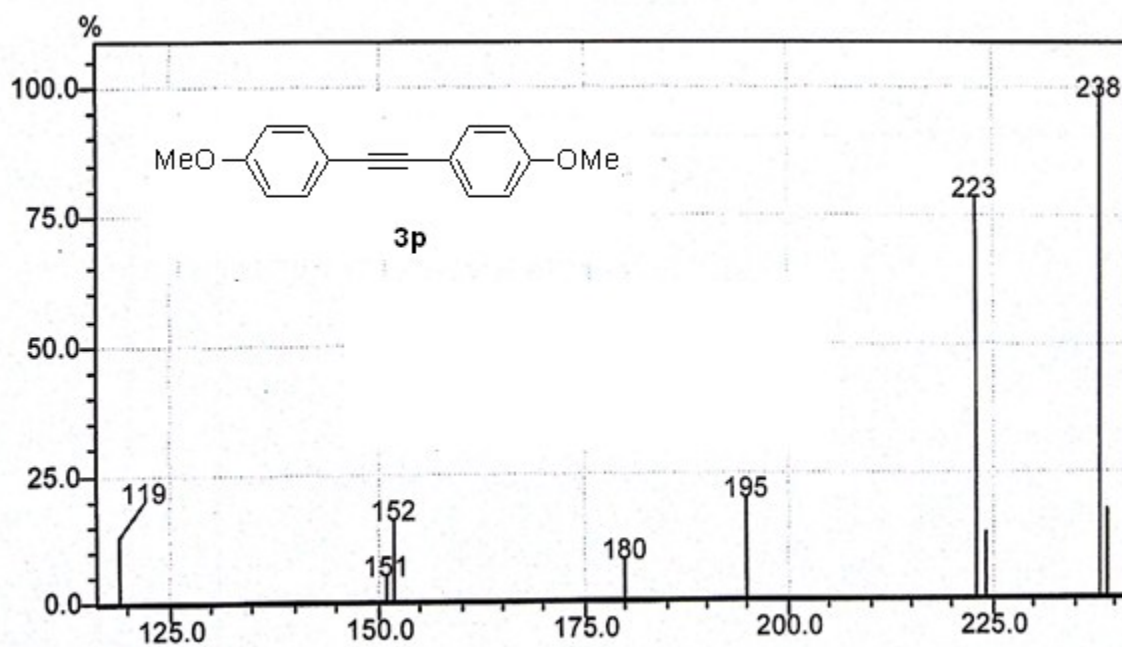
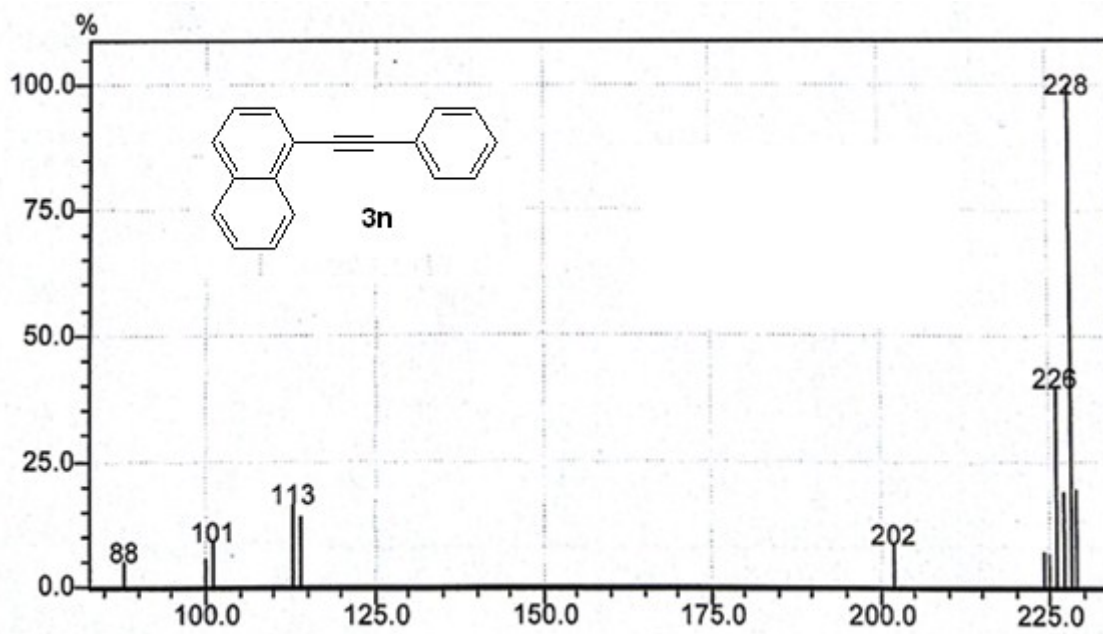


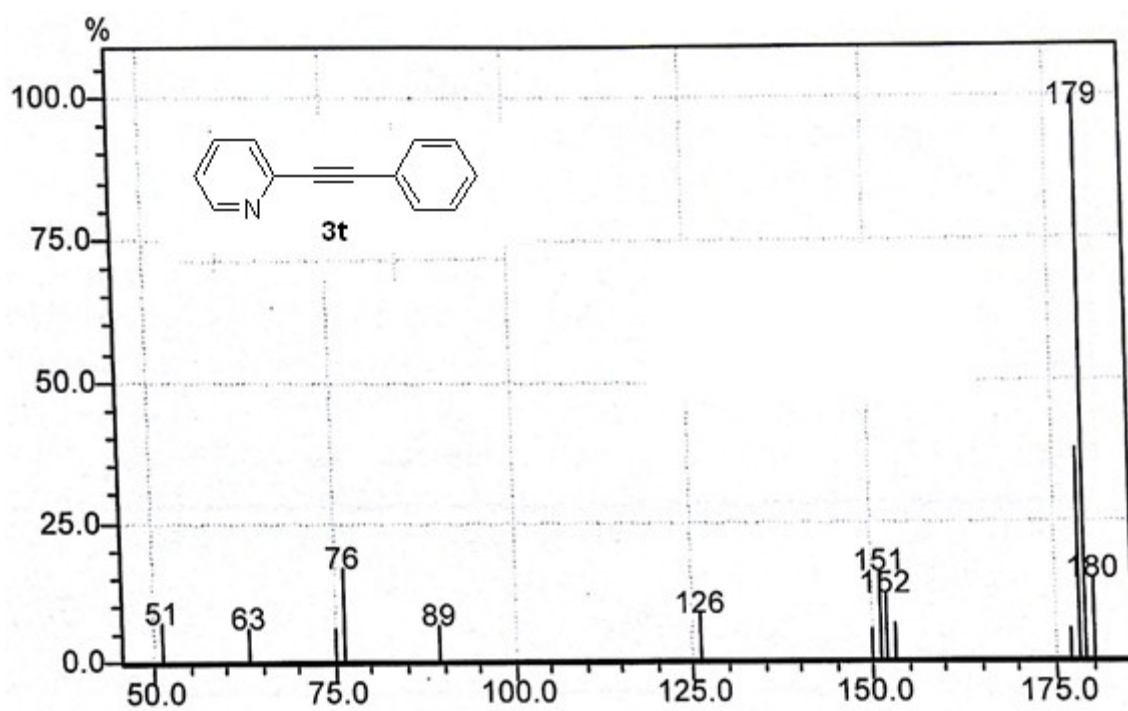
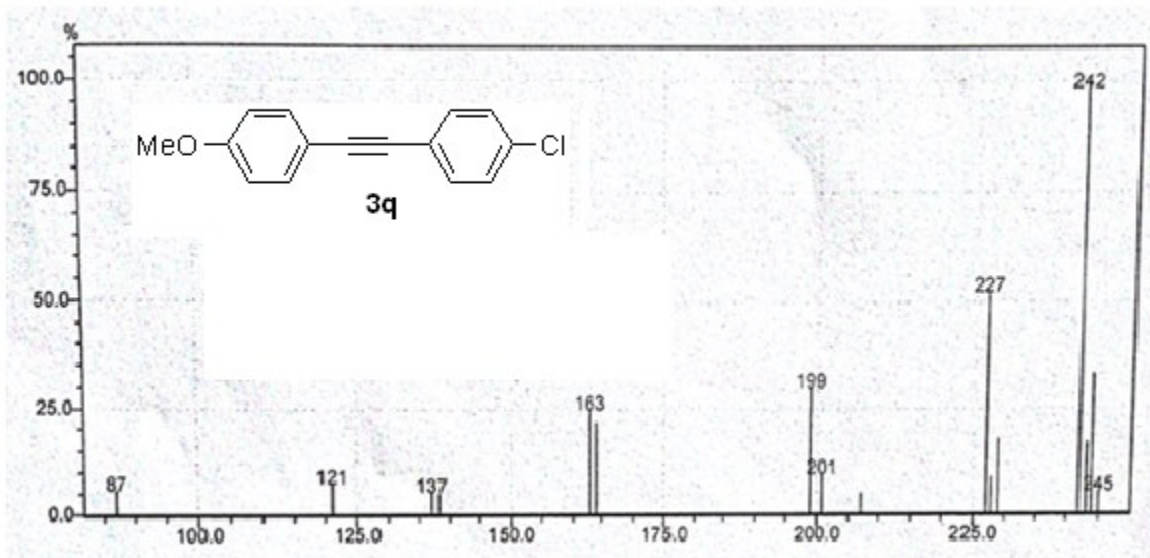




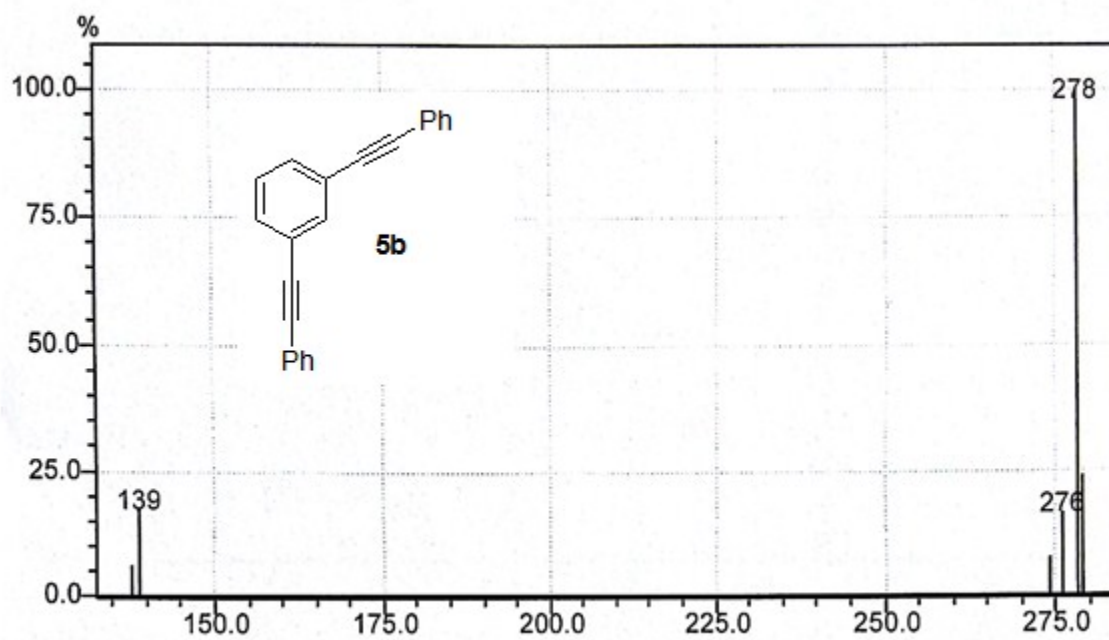
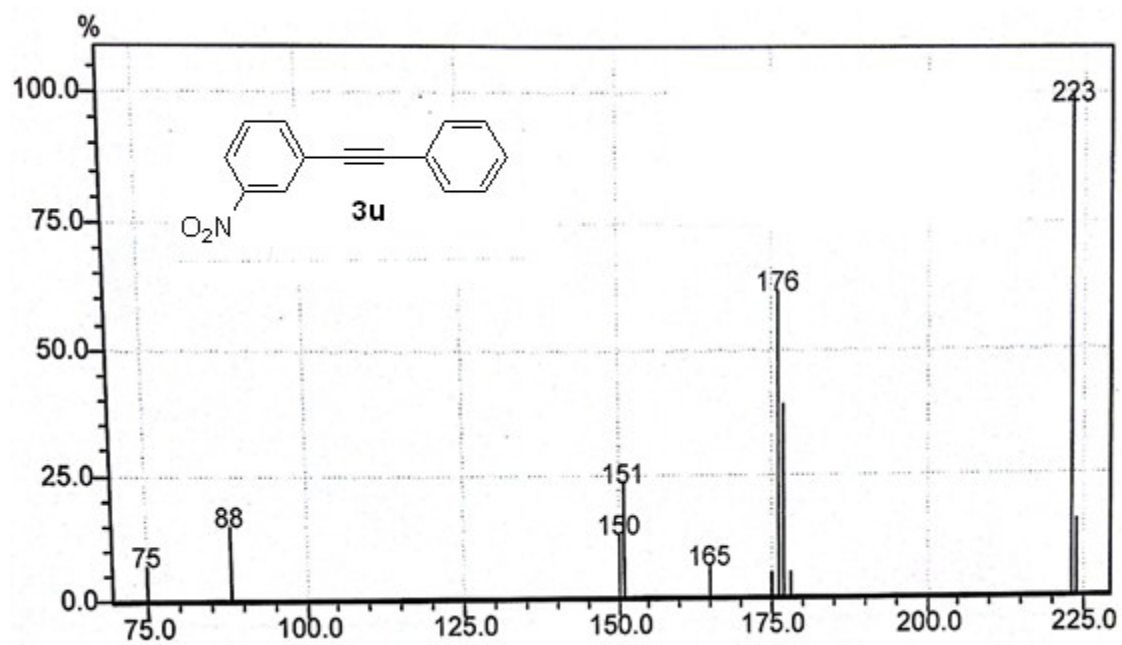


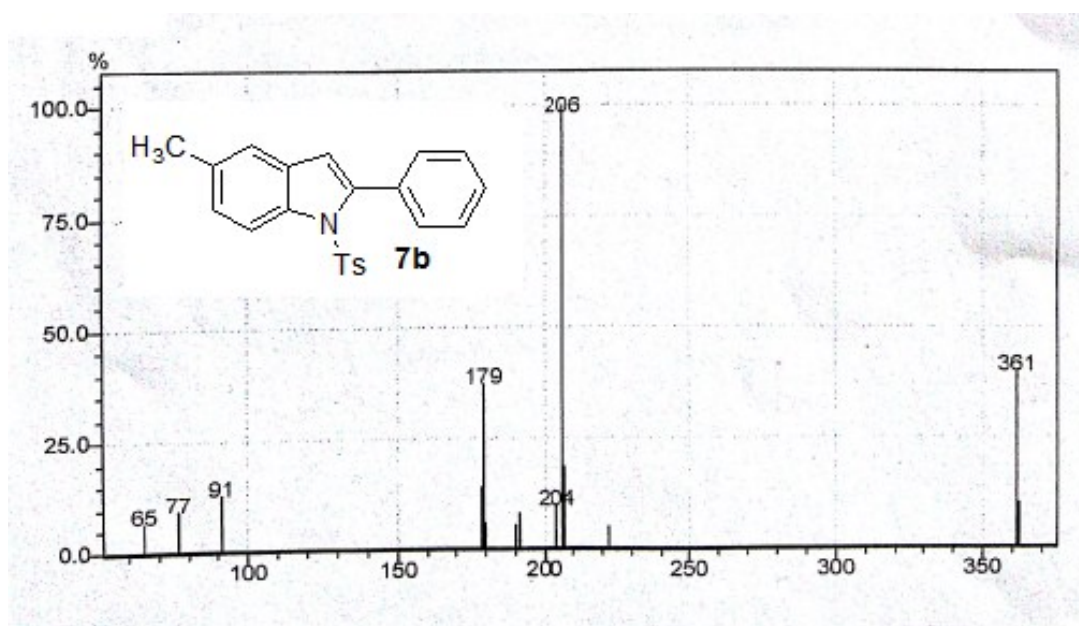
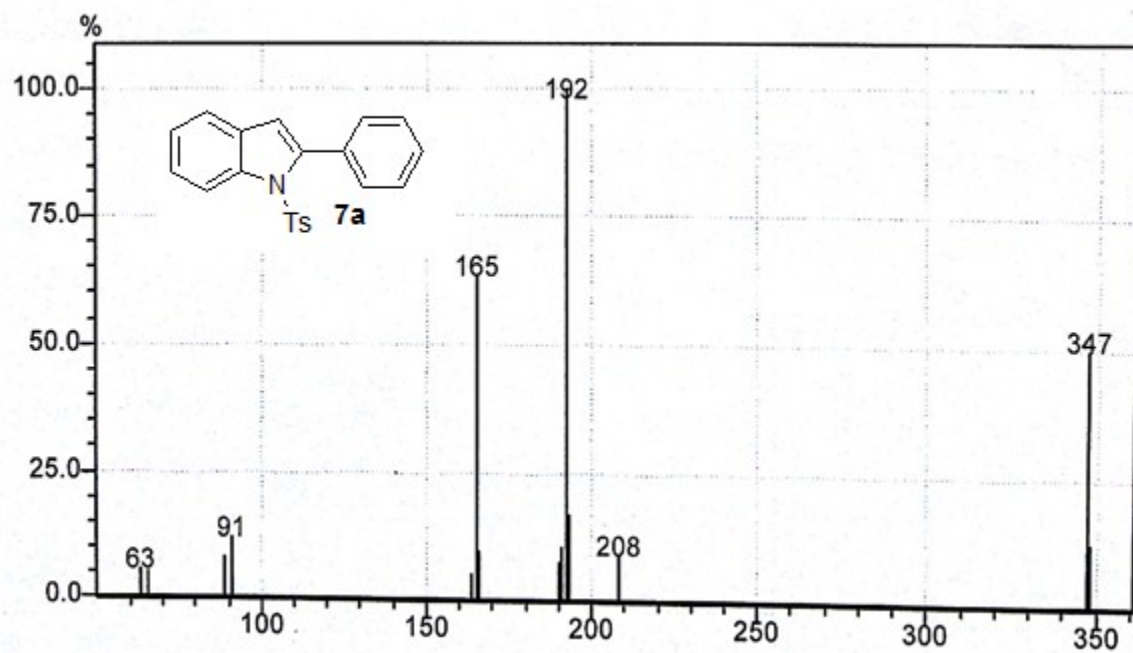


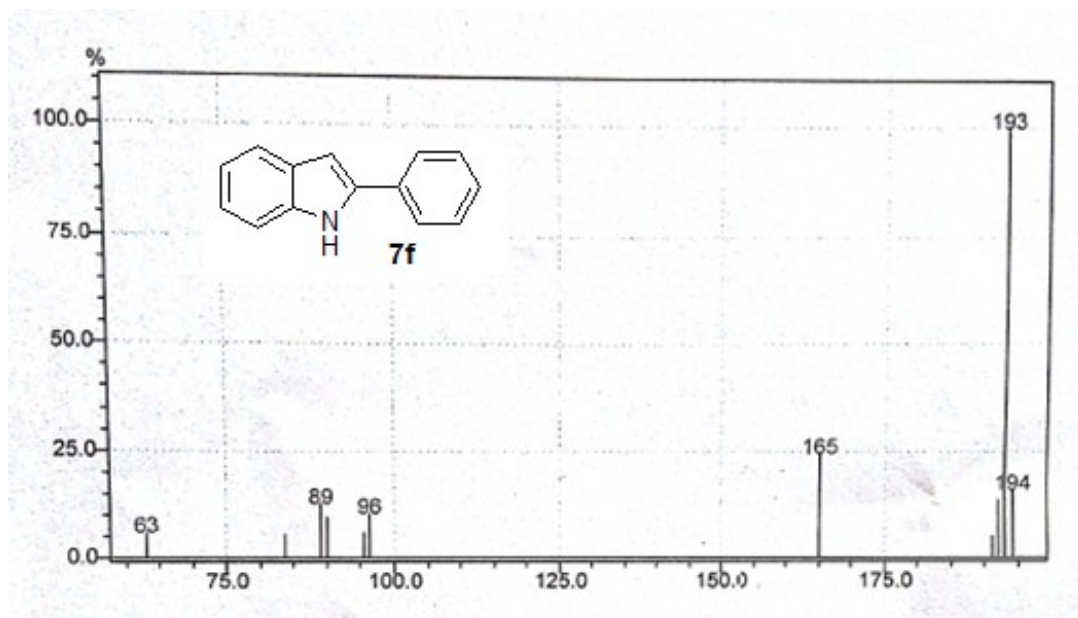
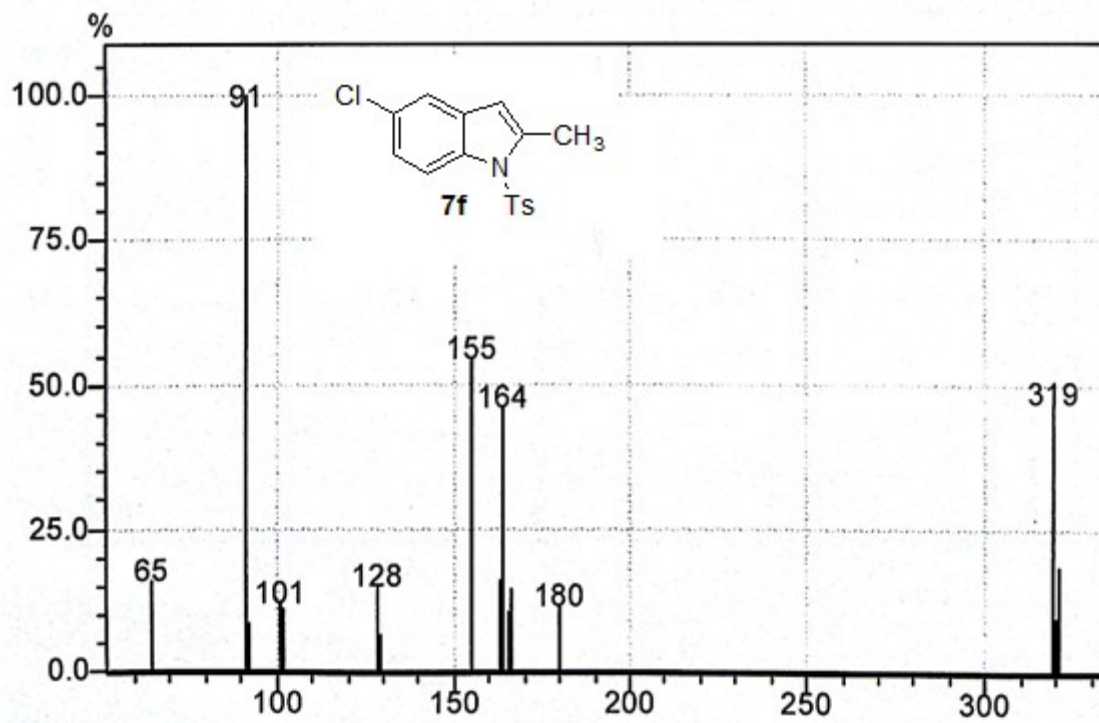






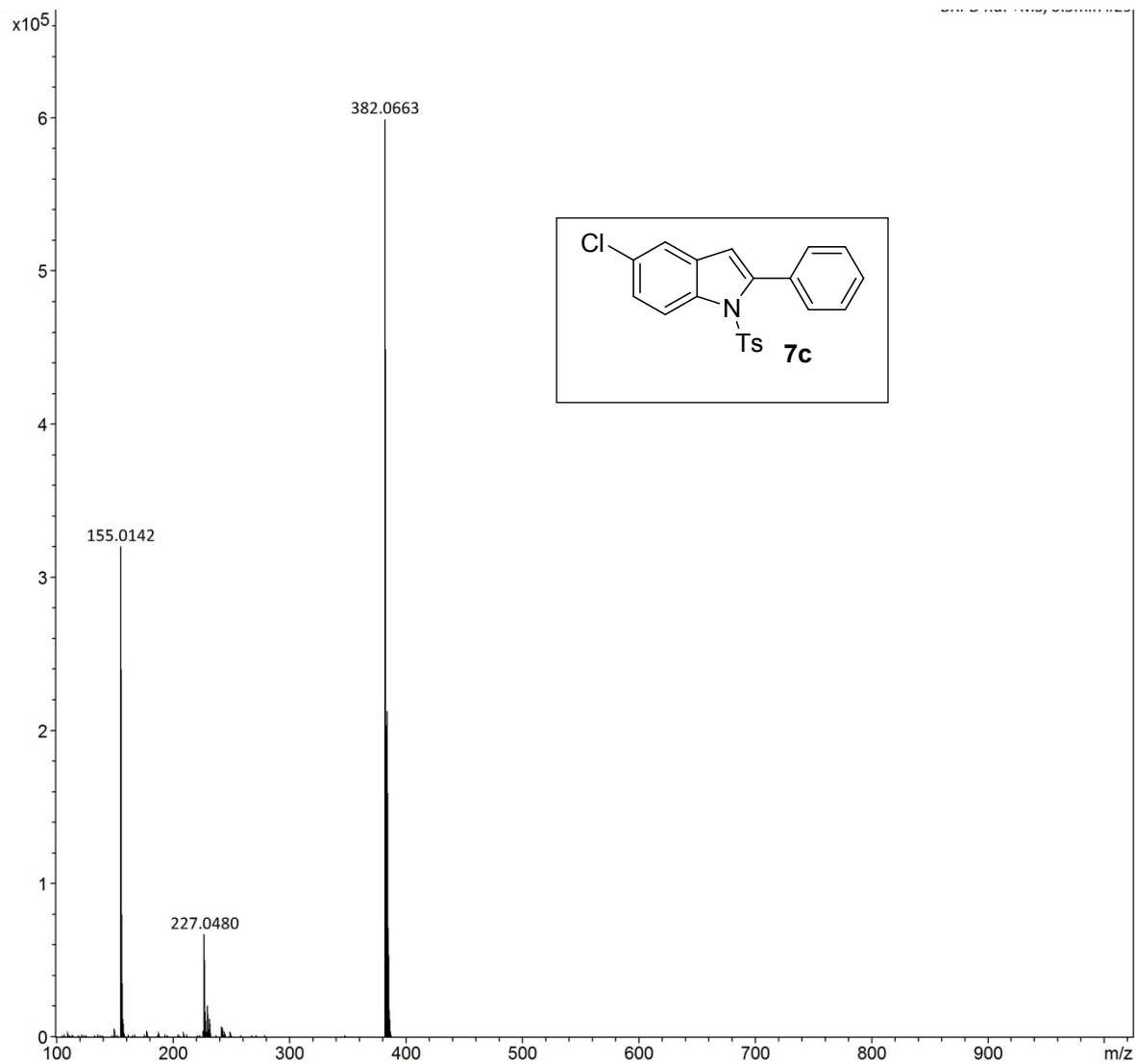


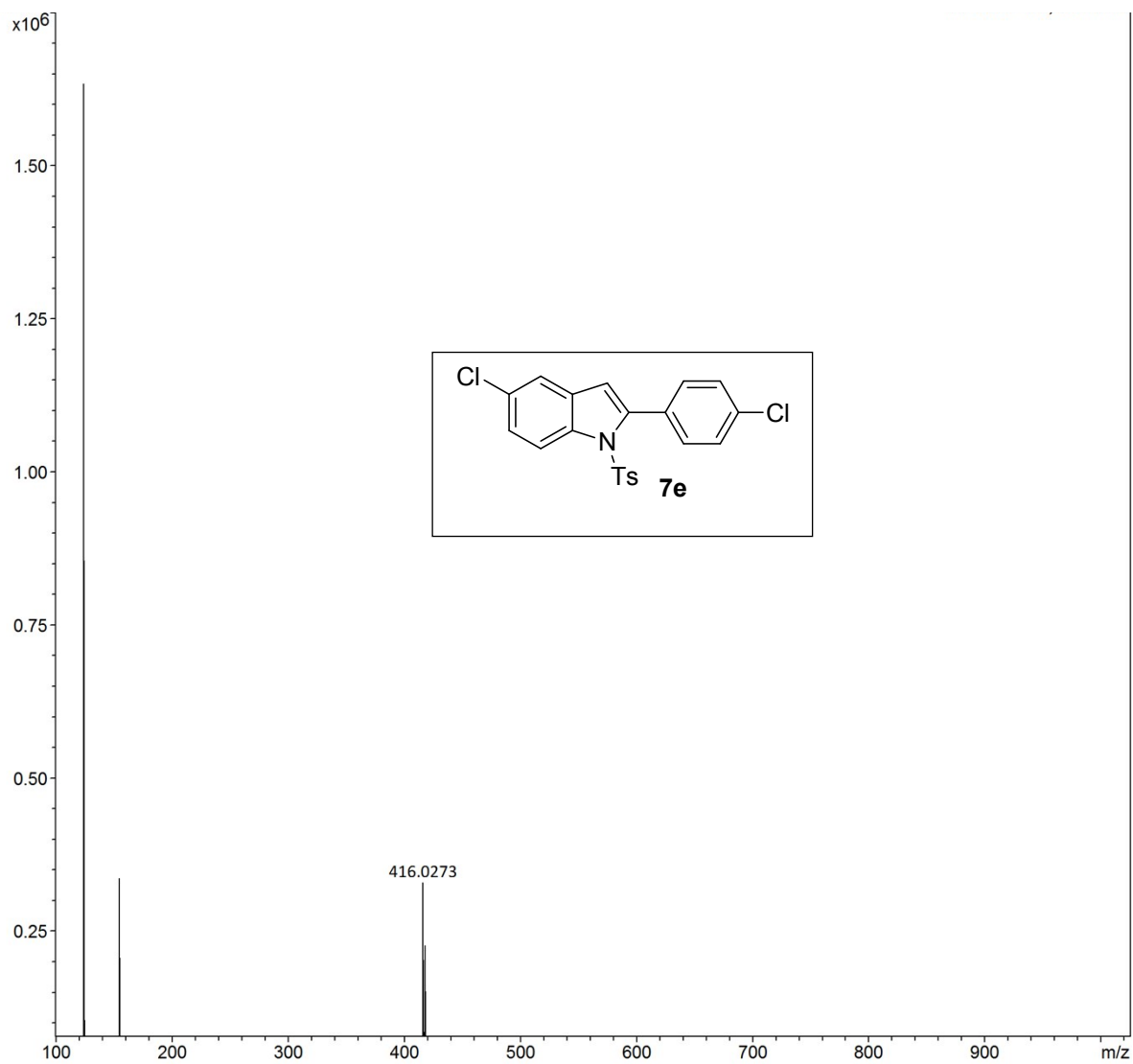


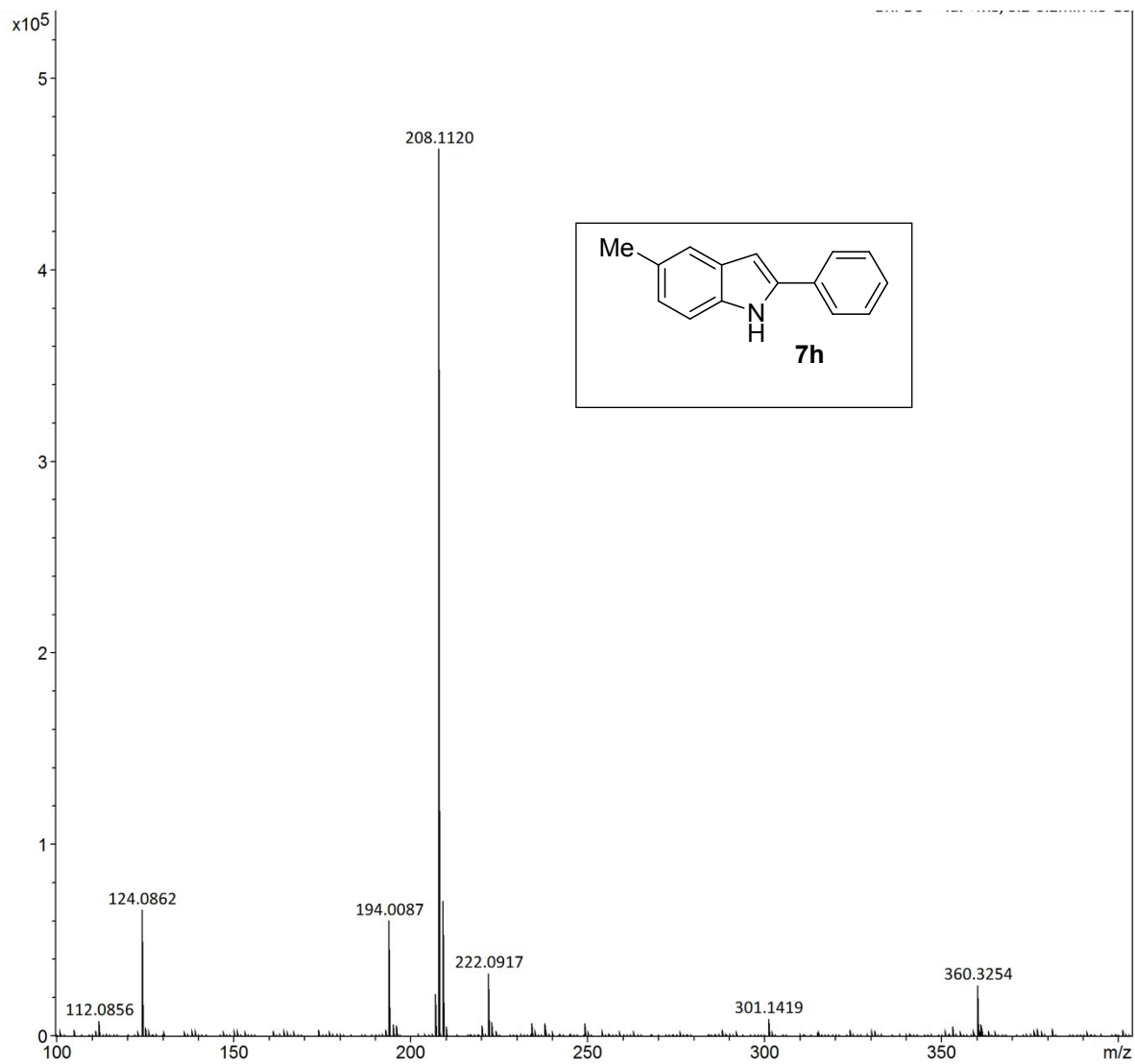


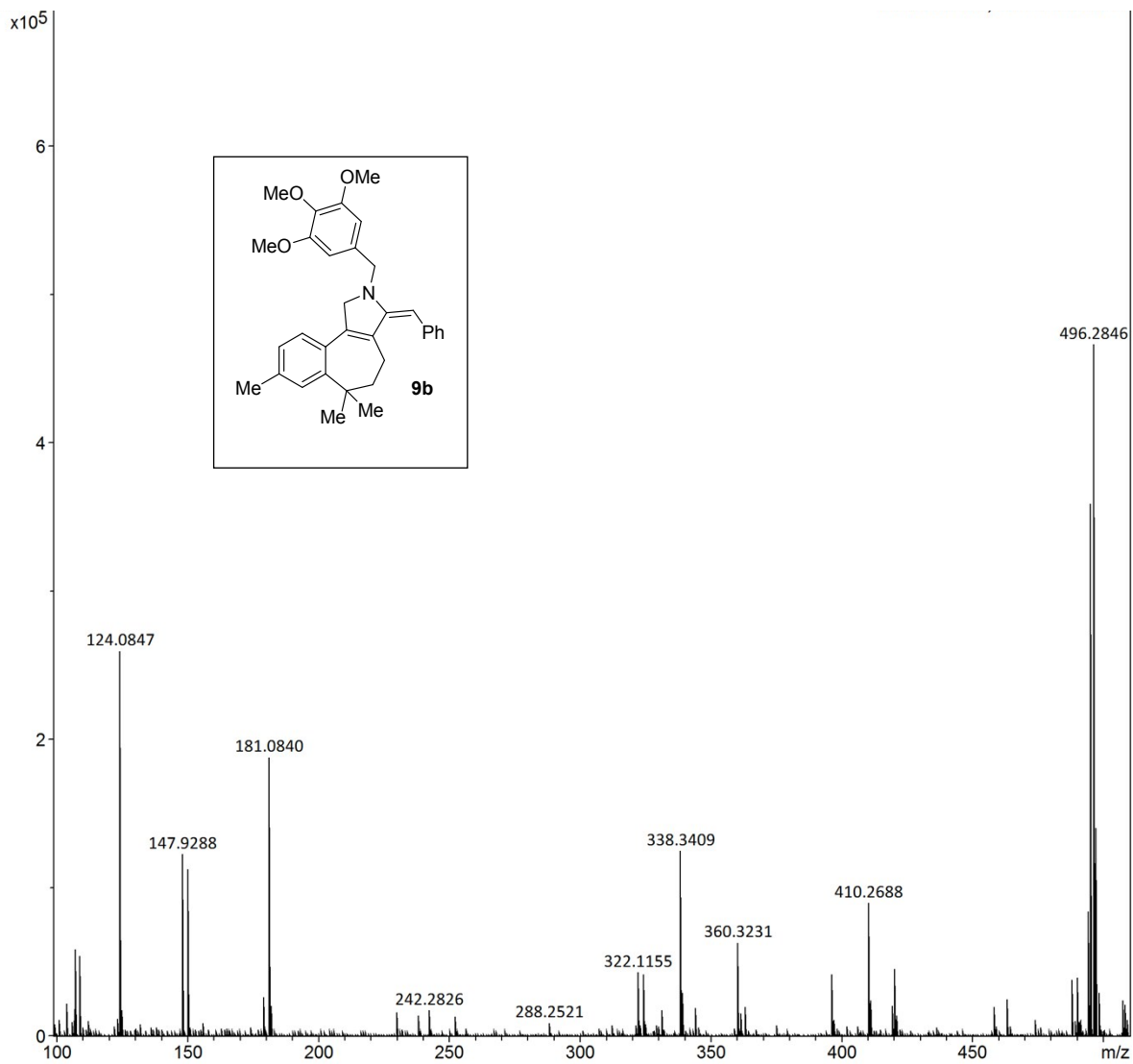


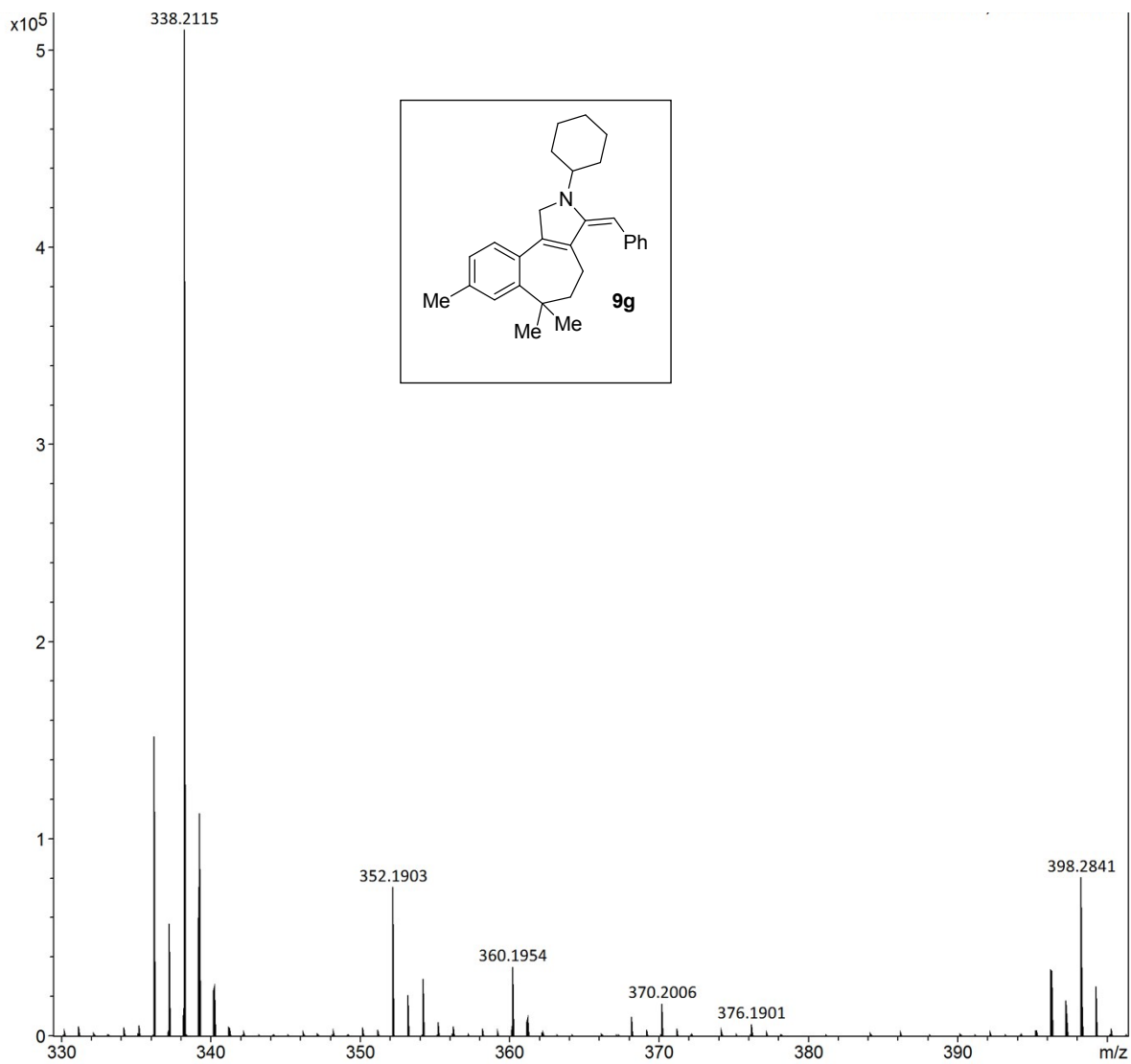
# HRMS Chromatogram



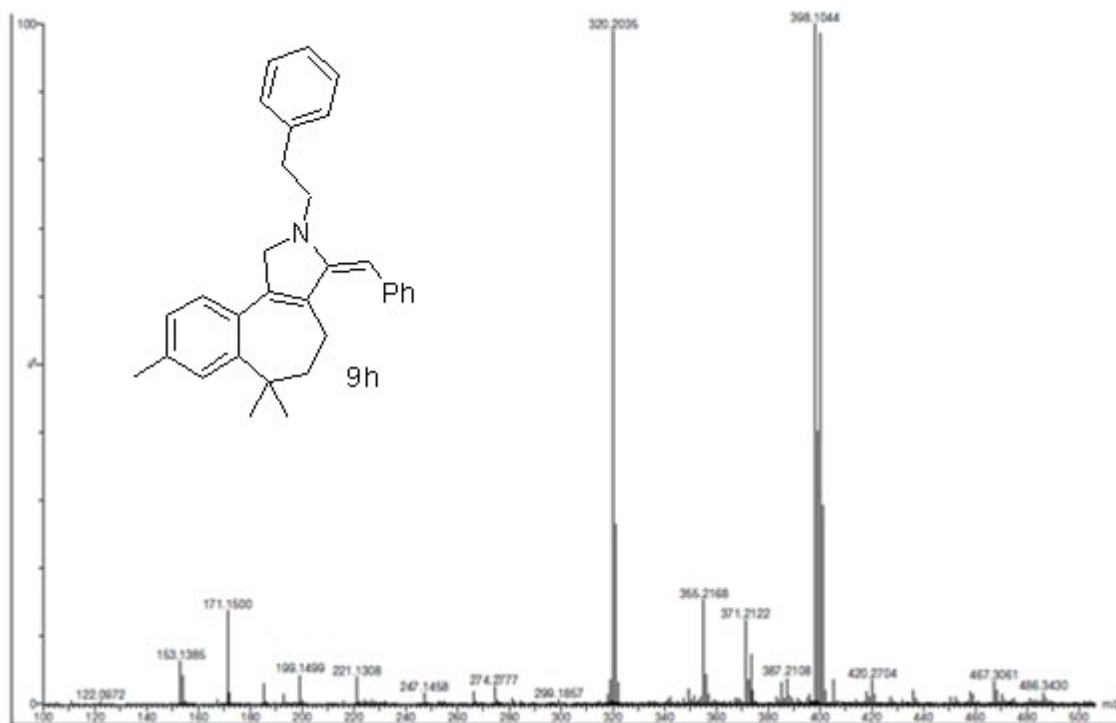
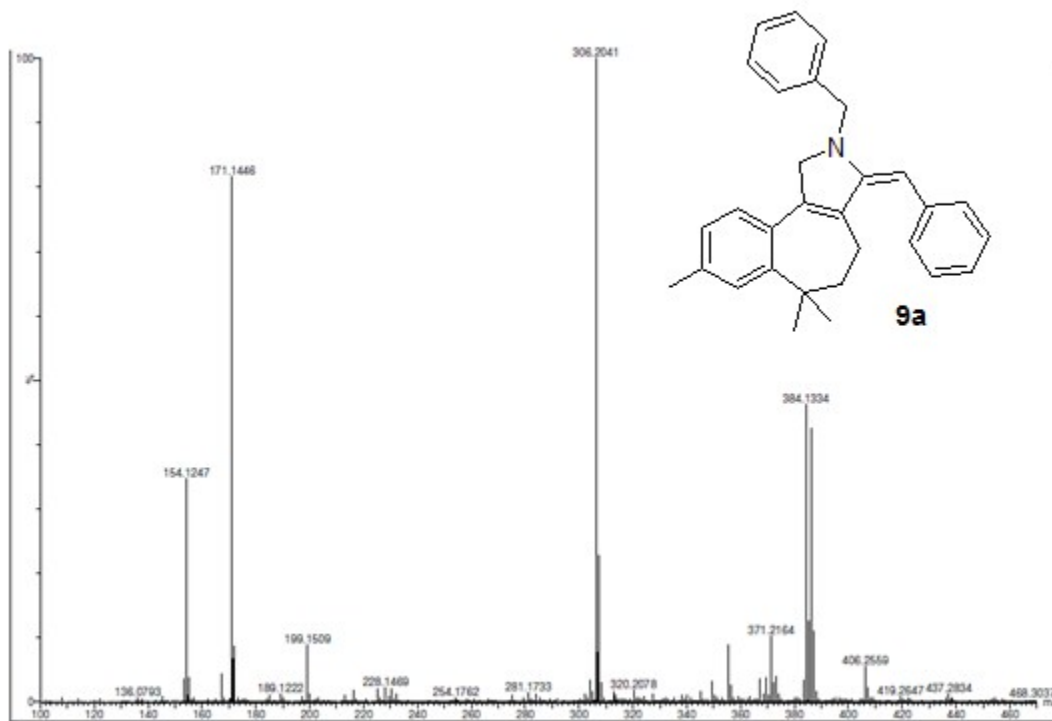








ESI-MS Chromatogram for compounds **9a**, **9h**



## References

- 1) X. Li, F. Yang, Y. Wu, *J. Org. Chem.*, **2013**, 78, 4543.
- 2) X. Qu, T. Li, P. Sun, Y. Zhu, H. Yang, J. Mao. *Org. Biomol. Chem.*, **2011**, 9, 6938
- 3) D. Zhao, C. Gao, X. Su, Y. He, J. You, Y. Xue, *Chem. Commun.*, **2010**, 46, 9049
- 4) W. -W. Zhang, X. -G. Zhang, J.-H. Li, *J. Org. Chem.*, **2010**, 75, 5259
- 5) Y. Yin, W. Ma, Z. Chai, G. Zhao, *J. Org. Chem.*, **2007**, 72, 5731
- 6) F. Liu, D. Ma, *J. Org. Chem.*, **2007**, 72, 4844
- 7) N. Sakai, K. Annaka, A. Fujita, A. Sato, T. Konakahra, *J. Org. Chem.*, **2008**, 73, 4160