

Supporting Information

Facile Synthesis of Carbazoles via a Tandem Iodocyclization with 1,2-Alkyl Migration and Aromatization

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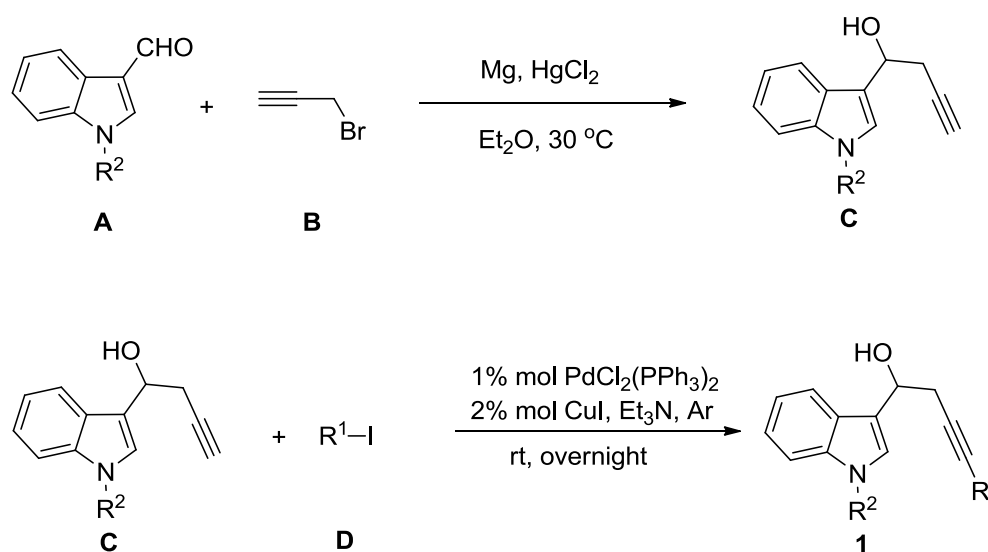
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General Remarks

Column chromatography was carried out on silica gel. ^1H NMR spectra were recorded on 400 MHz in $\text{CDCl}_3/\text{DMSO}$ and ^{13}C NMR spectra were recorded on 100 MHz in $\text{CDCl}_3/\text{DMSO}$. IR spectra were recorded on a FT-IR spectrometer and only major peaks are reported in cm^{-1} . All products were further characterized by high resolution mass spectra (HRMS); Copies of their ^1H NMR and ^{13}C NMR spectra are provided in the Supporting Information. Room temperature is 23–25 °C. The ICl was 1 M in CH_2Cl_2 . THF were distilled over Na/benzophenone, dichloromethane, *i*PrOH, CH_3CN , CH_3NO_2 and CH_3COCH_3 were distilled over CaH_2 , and other solvents were used without further purification.

Synthetic Procedures and Spectral Data

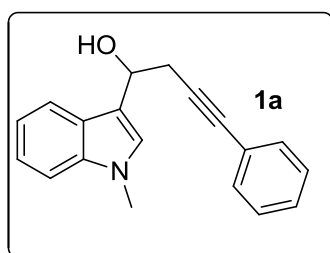
General procedure for synthesis of 1-(1-methyl-1*H*-indol-3-yl)-4-phenylbut-3-yn-1-ol derivatives (1a-1j, 1l-1n and 1s-1t)



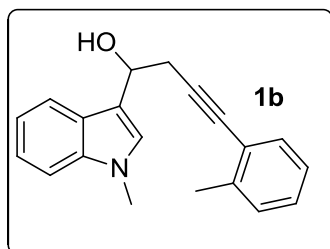
A mixture of Mg powders (15 mmol, 360 mg) and HgCl_2 (0.12 mmol, 32.4 mg, 0.8 mol %) in Et_2O (30 mL) was stirred vigorously for 15 min at room temperature. After that, a small amount of a solution of the corresponding propargylic bromide (18 mmol) was added. Then, the reaction mixture was stirred at $30\text{ }^\circ\text{C}$. When the reaction mixture started to bubble and became turbid, continuing to stir for 15 min. Subsequently, the reaction mixture was stirred for 30 min at room temperature. Then, a solution of indole-3-carboxaldehyde derivatives **A** (10 mmol) in THF (5 mL) were added dropwise through a syringe. The resulting solution was stirred at room temperature for 2 h. When the reaction was considered complete as determined by TLC analysis, the mixture was quenched by water, and extracted with ethyl acetate (3 x 40 mL). The combined organic layers were washed with water, brine, dried over

Na₂SO₄, and concentrated under reduced pressure. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 4/1) to give **C**.

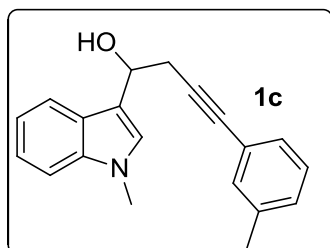
To a solution of **C** in Et₃N (10 mL) was added PdCl₂(PPh₃)₂ (1 mol %) and CuI (2 mol %) and the reaction vial was flushed with Ar and the reaction mixture was stirred for 5 minutes. A solution of **D** in Et₃N (5 mL) were then added dropwise through a syringe for 5 minutes. The resulting solution was stirred at room temperature overnight. When the reaction was considered complete as determined by TLC analysis, the mixture was quenched by addition of saturated aqueous ammonium chloride (10 mL) and extracted with ethyl acetate (3 x 40 mL). The combined organic layers were washed with water, brine, dried over Na₂SO₄, and concentrated under reduced pressure. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 4/1) to give the substrate **1**.



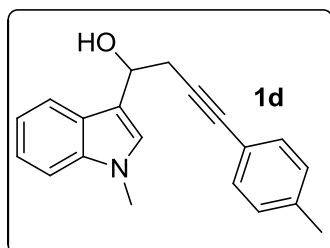
1-(1-methyl-1*H*-indol-3-yl)-4-phenylbut-3-yn-1-ol **1a** Yellow solid, ¹H NMR (400 MHz, CDCl₃) δ ppm 7.73 (d, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 2.8 Hz, 2H), 7.26-7.20 (m, 5H), 7.11 (t, *J* = 7.2 Hz, 1H), 7.06 (s, 1H), 5.23 (t, *J* = 6.4 Hz, 1H), 3.66 (s, 3H), 3.02 (d, *J* = 6.4 Hz, 2H), 2.53 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ ppm 137.1, 131.6, 128.1, 127.7, 126.1, 126.0, 123.4, 121.8, 119.5, 119.2, 116.6, 109.3, 86.9, 82.9, 66.8, 32.6, 29.3.



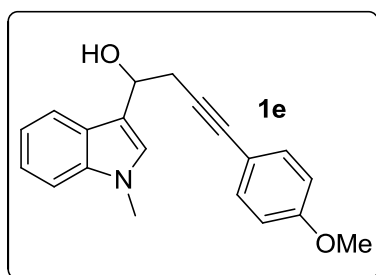
1-(1-methyl-1*H*-indol-3-yl)-4-(*o*-tolyl)but-3-yn-1-ol **1b** Yellow solid, ¹H NMR (400 MHz, CDCl₃) δ ppm 7.73 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.26-7.19 (m, 3H), 7.14-7.10 (m, 3H), 7.06 (d, *J* = 7.2 Hz, 2H), 5.22 (t, *J* = 6.0 Hz, 1H), 3.65 (s, 3H), 3.07 (d, *J* = 6.0 Hz, 2H), 2.51 (s, 1H), 2.31 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ ppm 139.9, 137.1, 131.8, 129.2, 127.7, 126.1, 125.3, 123.2, 121.8, 119.5, 119.2, 116.5, 109.3, 90.6, 81.8, 66.9, 32.5, 29.3, 20.6.



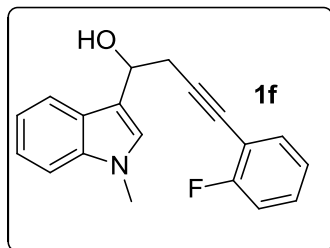
1-(1-methyl-1*H*-indol-3-yl)-4-(*m*-tolyl)but-3-yn-1-ol **1c** Yellow solid, ^1H NMR (400 MHz, CDCl_3) δ ppm 7.75 (d, $J = 7.6$ Hz, 1H), 7.29-7.18 (m, 4H), 7.15-7.10 (m, 2H), 7.06 (d, $J = 9.2$ Hz, 2H), 5.24 (t, $J = 6.4$ Hz, 1H), 3.69 (s, 3H), 3.03 (d, $J = 6.4$ Hz, 2H), 2.50 (s, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 137.7, 137.1, 132.2, 128.7, 128.6, 128.0, 126.1, 126.0, 123.2, 121.8, 119.5, 119.3, 116.6, 109.3, 86.4, 83.1, 66.8, 32.6, 29.3, 21.1.



1-(1-methyl-1*H*-indol-3-yl)-4-(*p*-tolyl)but-3-yn-1-ol **1d** Pale yellow solid, ^1H NMR (400 MHz, CDCl_3) δ ppm 7.74 (d, $J = 8.0$ Hz, 1H), 7.28-7.20 (m, 4H), 7.13-7.08 (m, 2H), 7.06 (d, $J = 7.6$ Hz, 2H), 5.23 (t, $J = 6.4$ Hz, 1H), 3.69 (s, 3H), 3.02 (d, $J = 6.4$ Hz, 2H), 2.48 (s, 1H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 137.8, 137.1, 131.5, 128.9, 126.2, 126.0, 121.8, 120.3, 119.5, 119.3, 116.6, 109.3, 86.0, 83.0, 66.9, 32.6, 29.4, 21.3.

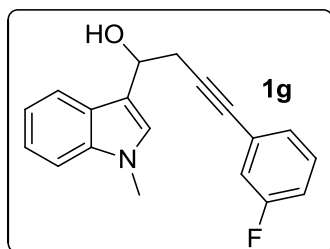


4-(4-methoxyphenyl)-1-(1-methyl-1*H*-indol-3-yl)but-3-yn-1-ol **1e** Yellow solid, ^1H NMR (400 MHz, CDCl_3) δ ppm 7.73 (d, $J = 8.0$ Hz, 1H), 7.31-7.18 (m, 4H), 7.12-7.08 (m, 1H), 7.06 (s, 1H), 6.76 (d, $J = 8.8$ Hz, 2H), 5.22 (t, $J = 6.0$ Hz, 1H), 3.73 (s, 3H), 3.67 (s, 3H), 3.00 (d, $J = 6.0$ Hz, 2H), 2.55 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 159.2, 137.1, 132.9, 126.1, 126.0, 121.8, 119.5, 119.2, 116.7, 115.5, 113.8, 109.3, 85.2, 82.7, 66.8, 55.1, 32.6, 29.4.

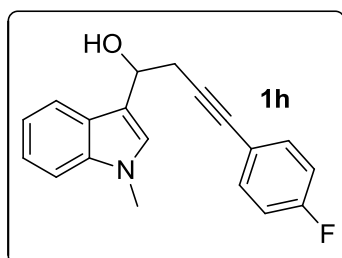


4-(2-fluorophenyl)-1-(1-methyl-1*H*-indol-3-yl)but-3-yn-1-ol **1f** Yellow solid, ^1H NMR (400 MHz, CDCl_3) δ ppm 7.72 (d, $J = 7.6$ Hz, 1H), 7.36-7.32 (m, 1H), 7.27-7.17 (m, 3H), 7.12-7.09 (m, 2H), 7.22-6.98 (m, 2H), 5.24 (t, $J = 6.0$ Hz, 1H), 3.68 (s, 3H), 3.05 (d, $J = 5.6$ Hz, 2H), 2.54 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 164.1, 161.6, 137.0, 133.5, 129.4, 129.4, 126.2, 126.1, 123.8, 123.7, 121.8, 119.4,

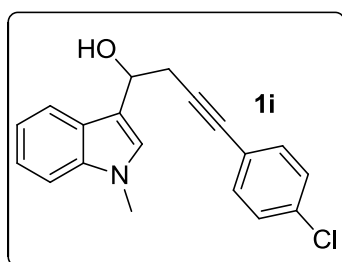
119.2, 116.3, 115.3, 115.1, 112.0, 111.9, 109.3, 92.4, 92.4, 76.3, 66.6, 32.6, 29.4.



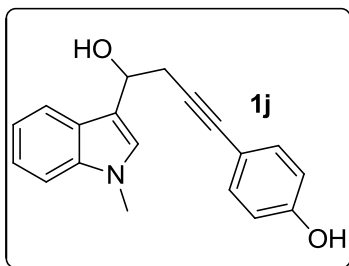
4-(3-fluorophenyl)-1-(1-methyl-1*H*-indol-3-yl)but-3-yn-1-ol **1g** Yellow solid, ^1H NMR (400 MHz, CDCl_3) δ ppm 7.74 (d, $J = 8.0$ Hz, 1H), 7.29 (d, $J = 8.4$ Hz, 1H), 7.26-7.18 (m, 2H), 7.13 (t, $J = 8.0$ Hz, 2H), 7.09-7.05 (m, 2H), 6.98-6.94 (m, 1H), 5.25 (t, $J = 6.0$ Hz, 1H), 3.72 (s, 3H), 3.03 (d, $J = 5.6$ Hz, 2H), 2.40 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 163.5, 161.0, 137.1, 129.7, 129.6, 127.5, 127.5, 126.0, 125.4, 125.3, 121.9, 119.5, 119.4, 118.5, 118.3, 116.5, 115.2, 115.0, 109.4, 88.0, 81.7, 66.8, 32.7, 29.2.



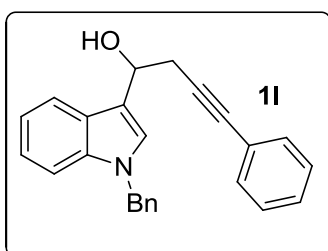
4-(4-fluorophenyl)-1-(1-methyl-1*H*-indol-3-yl)but-3-yn-1-ol **1h** Yellow solid, ^1H NMR (400 MHz, CDCl_3) δ ppm 7.73 (d, $J = 7.6$ Hz, 1H), 7.34-7.31 (m, 2H), 7.29-7.19 (m, 2H), 7.14-7.10 (m, 1H), 7.07 (s, 1H), 6.93 (t, $J = 8.8$ Hz, 2H), 5.23 (t, $J = 6.0$ Hz, 1H), 3.69 (s, 3H), 3.01 (d, $J = 5.6$ Hz, 2H), 2.51 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 163.4, 160.9, 137.1, 133.4, 133.4, 126.1, 126.0, 121.9, 119.5, 119.3, 116.6, 115.4, 115.2, 109.4, 86.5, 81.7, 66.8, 32.6, 29.2.



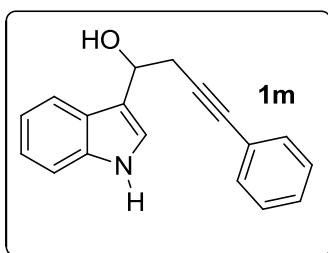
4-(4-chlorophenyl)-1-(1-methyl-1*H*-indol-3-yl)but-3-yn-1-ol **1i** Yellow solid, ^1H NMR (400 MHz, CDCl_3) δ ppm 7.73 (d, $J = 8.0$ Hz, 1H), 7.28-7.25 (m, 3H), 7.23-7.19 (m, 3H), 7.14-7.10 (m, 1H), 7.06 (s, 1H), 5.23 (t, $J = 6.4$ Hz, 1H), 3.69 (s, 3H), 3.02-3.00 (m, 2H), 2.47 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 137.1, 133.7, 132.8, 128.4, 126.1, 126.0, 121.9, 121.9, 119.5, 119.3, 116.6, 109.4, 88.2, 81.7, 66.8, 32.6, 29.3.



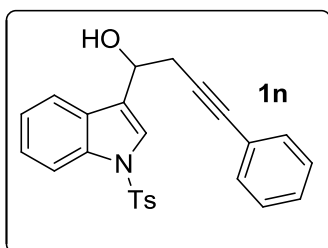
4-(4-hydroxy-4-(1-methyl-1*H*-indol-3-yl)but-1-yn-1-yl)phenol **1j** Yellow solid, ^1H NMR (400 MHz, CDCl_3) δ ppm 7.70 (d, $J = 8.0$ Hz, 1H), 7.26-7.20 (m, 2H), 7.14 (d, $J = 8.4$ Hz, 2H), 7.12-7.09 (m, 1H), 7.03 (s, 1H), 6.64 (d, $J = 8.8$ Hz, 2H), 5.23 (t, $J = 6.4$ Hz, 1H), 4.81 (s, 2H), 3.64 (s, 3H), 3.01-2.99 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 155.9, 137.0, 133.1, 126.2, 126.1, 121.9, 119.4, 119.4, 116.0, 115.5, 114.9, 109.4, 84.6, 83.0, 67.0, 32.6, 29.1.



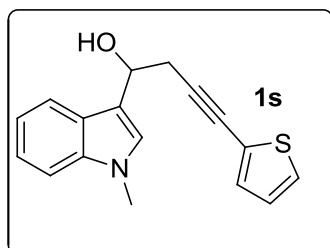
1-(1-benzyl-1*H*-indol-3-yl)-4-phenylbut-3-yn-1-ol **1l** Pale yellow solid, ^1H NMR (400 MHz, DMSO) δ ppm 7.78 (d, $J = 8.0$ Hz, 1H), 7.53 (s, 1H), 7.44 (d, $J = 8.0$ Hz, 1H), 7.32 (s, 5H), 7.23 (s, 5H), 7.13 (t, $J = 7.6$ Hz, 1H), 7.05 (t, $J = 7.6$ Hz, 1H), 5.46 (d, $J = 4.4$ Hz, 1H), 5.40 (s, 2H), 5.17 (s, 1H). ^{13}C NMR (100 MHz, DMSO) δ ppm 138.2, 136.2, 131.2, 128.4, 127.8, 127.2, 127.0, 126.4, 126.2, 123.4, 121.2, 119.8, 118.7, 118.0, 110.0, 88.7, 81.7, 65.8, 49.0, 29.1.



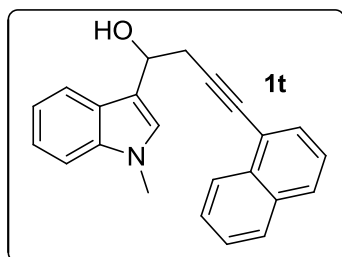
1-(1*H*-indol-3-yl)-4-phenylbut-3-yn-1-ol **1m** Yellow oil, ^1H NMR (400 MHz, CDCl_3) δ ppm 8.19 (s, 1H), 7.73 (d, $J = 8.0$ Hz, 1H), 7.38-7.36 (m, 2H), 7.26-7.23 (m, 4H), 7.19-7.15 (m, 1H), 7.11 (t, $J = 7.2$ Hz, 1H), 7.05 (s, 1H), 5.24-5.21 (m, 1H), 3.02-3.00 (m, 2H), 2.63 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 136.3, 131.6, 128.2, 127.8, 125.6, 123.3, 122.2, 121.6, 119.7, 119.3, 117.6, 111.3, 86.8, 83.0, 66.9, 29.1.



4-phenyl-1-(1-tosyl-1*H*-indol-3-yl)but-3-yn-1-ol **1n** Yellow oil, ^1H NMR (400 MHz, CDCl_3) δ ppm 7.96 (d, $J = 8.4$ Hz, 1H), 7.69-7.64 (m, 4H), 7.36-7.34 (m, 2H), 7.31-7.24 (m, 4H), 7.21 (d, $J = 9.2$ Hz, 1H), 6.98 (d, $J = 8.0$ Hz, 2H), 5.14 (t, $J = 5.6$ Hz, 1H), 3.00 (t, $J = 6.0$ Hz, 2H), 2.77 (s, 1H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 144.8, 135.3, 134.9, 131.6, 129.7, 128.8, 128.2, 128.0, 126.7, 124.8, 123.9, 123.2, 123.1, 120.3, 113.6, 85.5, 83.6, 66.3, 28.5, 21.4.

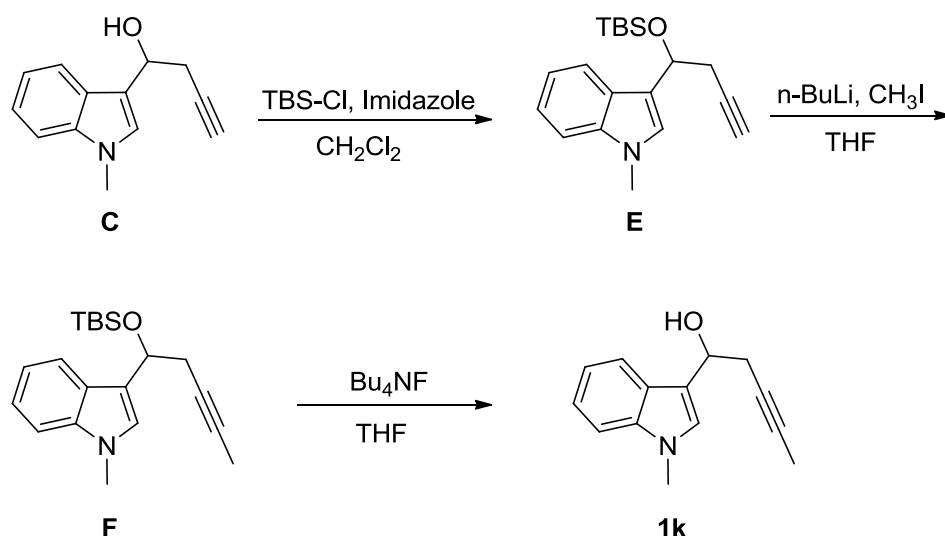


1-(1-methyl-1*H*-indol-3-yl)-4-(thiophen-2-yl)but-3-yn-1-ol **1s** Yellow solid, ^1H NMR (400 MHz, CDCl_3) δ ppm 7.71 (d, $J = 8.0$ Hz, 1H), 7.26-7.19 (m, 2H), 7.16-7.10 (m, 3H), 7.03 (s, 1H), 6.88 (t, $J = 4.4$ Hz, 1H), 5.20 (t, $J = 6.0$ Hz, 1H), 3.65 (s, 3H), 3.01 (d, $J = 6.4$ Hz, 2H), 2.53 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 137.1, 131.4, 126.7, 126.2, 126.0, 123.5, 121.8, 119.5, 119.3, 116.4, 109.3, 91.1, 76.0, 66.7, 32.6, 29.5.



1-(1-methyl-1*H*-indol-3-yl)-4-(naphthalen-1-yl)but-3-yn-1-ol **1t** Pale yellow solid, ^1H NMR (400 MHz, CDCl_3) δ ppm 8.11 (d, $J = 7.6$ Hz, 1H), 7.78-7.75 (m, 2H), 7.72 (d, $J = 8.8$ Hz, 1H), 7.60 (d, $J = 7.2$ Hz, 1H), 7.45-7.38 (m, 2H), 7.35-7.31 (m, 1H), 7.28-7.21 (m, 2H), 7.15-7.11 (m, 1H), 7.09 (s, 1H), 5.32 (t, $J = 6.4$ Hz, 1H), 3.63 (s, 3H), 3.19 (d, $J = 6.4$ Hz, 2H), 2.54 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 137.2, 133.4, 133.1, 130.1, 128.2, 128.1, 126.4, 126.3, 126.2, 126.1, 125.1, 121.9, 121.1, 119.5, 119.3, 116.6, 109.4, 91.8, 80.9, 67.0, 32.6, 29.5.

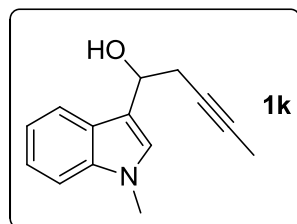
Synthesis of 1k



To a solution of 1-(1-methyl-1*H*-indol-3-yl)but-3-yn-1-ol **C** (10 mmol) in dry CH_2Cl_2 , was added imidazole (22 mmol, 2.2 equiv), TBS-Cl (*tert*-butylchlorodimethylsilane, 15 mmol, 1.5 equiv), in sequence at 0 °C. After stirring 30 minutes at 0 °C, the resulting solution was stirred at room temperature overnight. The mixture was quenched by addition of water (30 mL) and extracted with CH_2Cl_2 (3 x 40 mL). The combined organic layers were washed with water, brine, dried over Na_2SO_4 , and concentrated under reduced pressure. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 30/1) to give **E**.

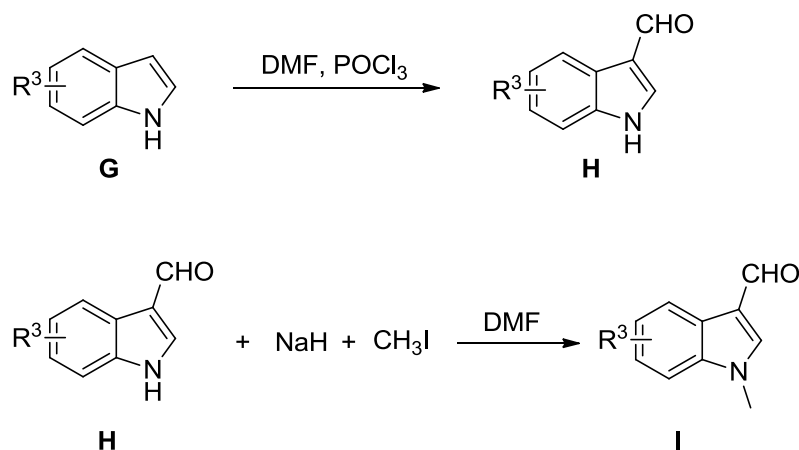
To a solution of **E** in THF with Ar was cooled to -40 °C and $n\text{-BuLi}$ (1.1 equiv) was added dropwise, followed by dropwise addition of CH_3I (1.5 equiv) and the resulting mixture was removed to room temperature. After 2 h, the mixture was quenched by water, and extracted with ethyl acetate (3 x 40 mL). The combined organic layers were washed with water, brine, dried over Na_2SO_4 , and concentrated under reduced pressure. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 30/1) to give **F**.

To a solution of **F** in THF was added tetrabutylammonium fluoride (2.0 equiv) and the resulting solution was stirred at room temperature for 4 h. When the reaction was considered complete as determined by TLC analysis, the mixture was quenched by water, and extracted with ethyl acetate (3 x 40 mL). The combined organic layers were washed with water, brine, dried over Na_2SO_4 , and concentrated under reduced pressure. The crude material was purified by flash column chromatography (petroleum ether/EtOAc = 10/1) to give **1k**.



1-(1-methyl-1*H*-indol-3-yl)pent-3-yn-1-ol **1k** Yellow solid, ^1H NMR (400 MHz, CDCl_3) δ ppm 7.69 (d, $J = 7.6$ Hz, 1H), 7.24 (t, $J = 8.0$ Hz, 1H), 7.20 (d, $J = 8.0$ Hz, 1H), 7.10 (d, $J = 7.6$ Hz, 1H), 7.02 (s, 1H), 5.10 (t, $J = 6.4$ Hz, 1H), 3.68 (s, 3H), 2.75-2.73 (m, 2H), 2.47 (s, 1H), 1.79 (t, $J = 6.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 137.0, 126.1, 125.9, 121.7, 119.4, 119.1, 116.6, 109.3, 78.2, 76.9, 66.8, 32.6, 28.5, 3.5.

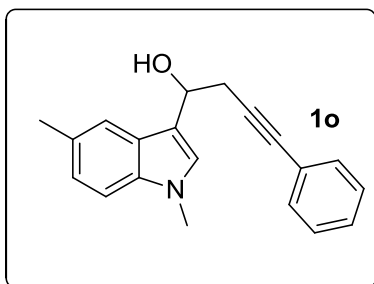
Synthesis of 1o-1r



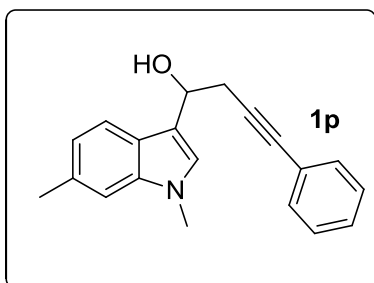
To a well-stirred solution of indole derivatives **G** (20 mmol) in anhydrous DMF (24ml) under dry argon atmosphere, phosphorus chloride oxide (60 mmol, 5.6 ml, 3.0 equiv) was added at 0 $^{\circ}\text{C}$ and the resulting mixture was stirred at room temperature. After being stirred for 1h, the reaction mixture was poured into cold saturated NaHCO_3 solution (aqueous) and stirred for 30 min. The reaction mixture was extracted by ethyl acetate for several times. The combined organic layer was dried over anhydrous Na_2SO_4 , concentrated under reduced pressure and purified by silica gel flash column chromatography (petroleum ether/EtOAc = 2/1) to provide desired products **H**.

To a solution of **H** in DMF was added NaH (60%, 2 equiv) slowly at 0 $^{\circ}\text{C}$. The resulting solution was stirred 2h at 0 $^{\circ}\text{C}$. Then, the CH_3I (2 equiv) was added dropwise through a syringe. The reaction mixture was stirred at room temperature for another 2h. When the reaction was considered complete as determined by TLC analysis, the mixture was quenched by water and extracted by ethyl acetate for three times. The combined organic layer was dried over anhydrous Na_2SO_4 , concentrated under reduced pressure and purified by silica gel flash column chromatography (petroleum ether/EtOAc = 2/1) to provide desired products **I**.

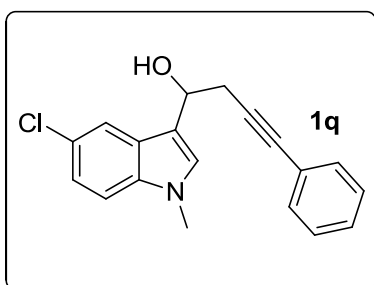
The substrate **1o-1r** was synthesized from **I** according to general procedure as mentioned above.



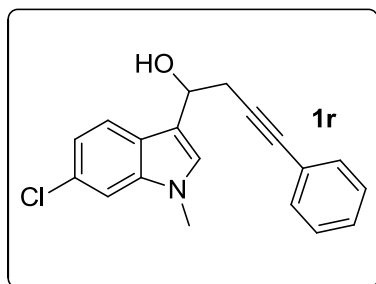
1-(1,5-dimethyl-1*H*-indol-3-yl)-4-phenylbut-3-yn-1-ol **1o** Yellow solid, ^1H NMR (400 MHz, CDCl_3) δ ppm 7.54 (s, 1H), 7.39-7.37 (m, 2H), 7.25-7.24 (m, 3H), 7.16 (d, $J = 8.0$ Hz, 1H), 7.05 (d, $J = 12.4$ Hz, 1H), 5.22 (t, $J = 6.0$ Hz, 1H), 3.66 (s, 3H), 3.03 (d, $J = 6.8$ Hz, 2H), 2.44 (s, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 135.6, 131.6, 128.5, 128.1, 127.8, 126.3, 126.1, 123.5, 119.2, 116.0, 109.1, 86.9, 82.9, 66.9, 32.6, 29.3, 21.4.



1-(1,6-dimethyl-1*H*-indol-3-yl)-4-phenylbut-3-yn-1-ol **1p** Yellow solid, ^1H NMR (400 MHz, CDCl_3) δ ppm 7.59 (d, $J = 7.6$ Hz, 1H), 7.37-7.35 (m, 2H), 7.22-7.20 (m, 3H), 7.03 (s, 1H), 6.93 (d, $J = 5.6$ Hz, 2H), 5.17 (t, $J = 6.0$ Hz, 1H), 3.58 (s, 3H), 2.98 (d, $J = 6.0$ Hz, 2H), 2.65 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 137.5, 131.5, 131.5, 128.0, 127.6, 125.4, 123.9, 123.4, 120.9, 119.1, 116.4, 109.2, 87.0, 82.7, 66.8, 32.4, 29.2, 21.7.

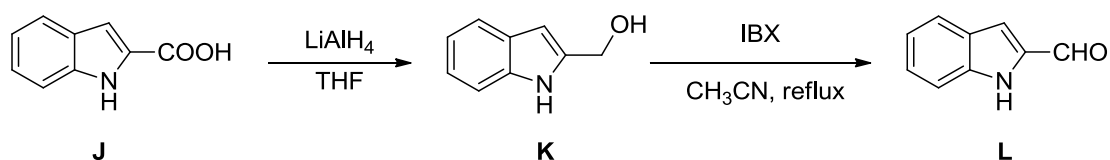


1-(5-chloro-1-methyl-1*H*-indol-3-yl)-4-phenylbut-3-yn-1-ol **1q** Yellow solid, ^1H NMR (400 MHz, CDCl_3) δ ppm 7.72 (s, 1H), 7.38-7.36 (m, 2H), 7.27-7.25 (m, 3H), 7.14 (s, 2H), 7.08 (s, 1H), 5.15 (t, $J = 5.6$ Hz, 1H), 3.66 (s, 3H), 2.98 (d, $J = 5.6$ Hz, 2H), 2.57 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 135.5, 131.6, 128.2, 127.9, 127.3, 127.1, 125.1, 123.3, 122.1, 119.1, 116.3, 110.4, 86.4, 83.1, 66.6, 32.8, 29.4.



1-(6-chloro-1-methyl-1*H*-indol-3-yl)-4-phenylbut-3-yn-1-ol **1r** Yellow solid, ^1H NMR (400 MHz, CDCl_3) δ ppm 7.60 (d, J = 8.8 Hz, 1H), 7.37-7.34 (m, 2H), 7.25-7.23 (m, 4H), 7.07-7.04 (m, 1H), 7.02 (s, 1H), 5.18-5.14 (m, 1H), 3.60 (s, 3H), 2.97 (d, J = 6.0 Hz, 2H), 2.62 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 137.5, 131.5, 128.2, 127.9, 126.7, 124.7, 123.3, 120.5, 119.9, 116.8, 109.4, 86.5, 83.0, 66.6, 32.7, 29.3.

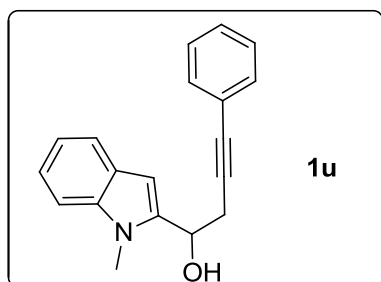
Synthesis of **1u** and **1v**



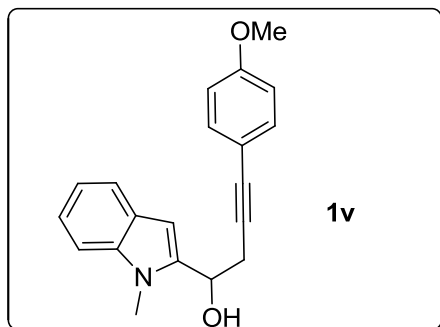
To a solution of indole-2-carboxylic acid **J** (50 mmol) in dry THF (150 mL) was added LiAlH_4 (100 mmol, 2.0 equiv) slowly at 0 °C and the resulting mixture was stirred at room temperature. After being stirred for 4h, the reaction was quenched with water at 0 °C then filtered through a sand core funnel and washed with ethyl acetate (5 x 20 mL). The filtrate was extracted by ethyl acetate for several times and the combined organic layers were washed with water, brine, dried over Na_2SO_4 . Concentration led to the yellow product **K**, which was used directly in the next reaction.

To a solution of (1*H*-indol-2-yl)methanol **K** (20 mmol) in anhydrous CH_3CN (40 mL) was added 2-iodoxybenzoic acid (26 mmol, 1.3 equiv), then the mixture was refluxed. After 2 hours, the reaction was cooled to room temperature and filtered through a sand core funnel, washed with ethyl acetate (3 x 20 mL). The combined organic layers were directly concentrated under reduced pressure. Purification of the residue by column chromatography on silica gel (petroleum ether/ EtOAc = 10/1) gave white product compound **L**.

The substrate **1u** and **1v** were synthesized from **L** according to general procedure as mentioned above.

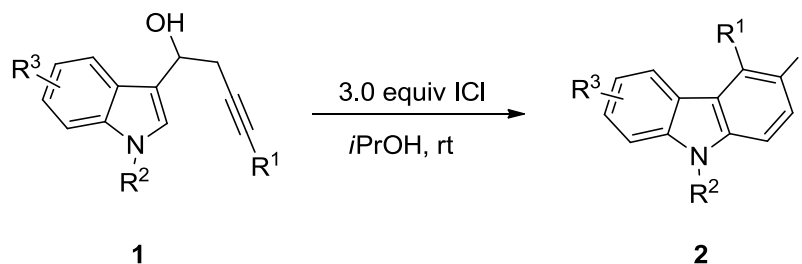


1-(1-methyl-1*H*-indol-2-yl)-4-phenylbut-3-yn-1-ol **1u** Pale yellow solid, ^1H NMR (400 MHz, CDCl_3) δ ppm 7.57 (d, $J = 7.6$ Hz, 1H), 7.39-7.37 (m, 2H), 7.25-7.18 (m, 5H), 7.08 (d, $J = 7.6$ Hz, 1H), 6.50 (s, 1H), 4.98 (q, $J = 6.0$ Hz, 1H), 3.67 (s, 3H), 3.05-3.04 (m, 2H), 2.55 (d, $J = 6.0$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 139.9, 137.8, 131.6, 128.2, 128.0, 127.0, 123.0, 121.9, 120.8, 119.5, 109.1, 99.2, 85.6, 83.5, 65.3, 29.9, 27.5.

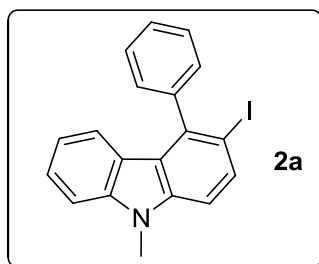


4-(4-methoxyphenyl)-1-(1-methyl-1*H*-indol-2-yl)but-3-yn-1-ol **1v** Pale yellow solid, ^1H NMR (400 MHz, CDCl_3) δ ppm 7.58 (d, $J = 7.6$ Hz, 1H), 7.31 (d, $J = 8.8$ Hz, 2H), 7.27 (d, $J = 8.0$ Hz, 1H), 7.21 (t, $J = 7.2$ Hz, 1H), 7.09 (t, $J = 7.2$ Hz, 1H), 6.76 (d, $J = 8.8$ Hz, 2H), 6.53 (s, 1H), 5.02 (q, $J = 6.0$ Hz, 1H), 3.73 (s, 6H), 3.08-3.06 (m, 2H), 2.52 (d, $J = 5.6$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 159.3, 140.0, 137.8, 133.0, 127.0, 121.9, 120.8, 119.5, 115.1, 113.8, 109.1, 99.2, 83.9, 83.4, 65.4, 55.2, 30.0, 27.5.

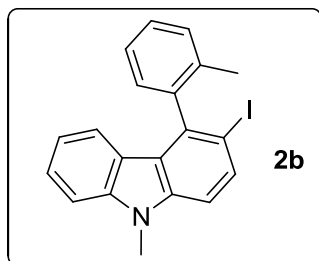
General procedure for synthesis of iodocarbazole compounds



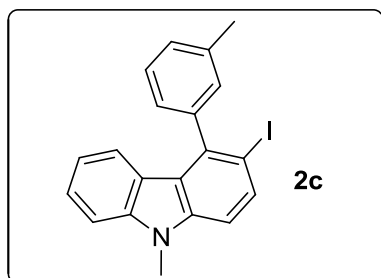
To a solution of **1** (0.20 mmol) in *i*PrOH (4.0 mL) was added ICl (0.6 mmol, 3.0 equiv) at room temperature. When the reaction was considered complete as determined by TLC analysis, the reaction mixture was quenched by addition of saturated aqueous sodium thiosulfate and diluted with ethyl acetate (3 x 15 mL), washed with water, saturated brine, dried over Na_2SO_4 and evaporated under reduced pressure. The residue was purified by chromatography on silica gel (petroleum ether/EtOAc = 30/1) to afford corresponding iodocarbazole derivatives **2**.



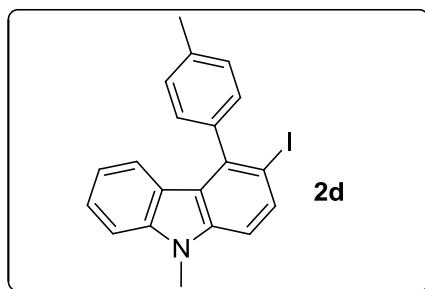
3-iodo-9-methyl-4-phenyl-9*H*-carbazole **2a** Pale yellow solid (68.2 mg, 89%), mp: 132-134 °C ^1H NMR (400 MHz, CDCl_3) δ ppm 7.92 (d, J = 8.4 Hz, 1H), 7.54-7.52 (m, 3H), 7.37-7.29 (m, 4H), 7.10 (d, J = 8.8 Hz, 1H), 6.89 (t, J = 8.0 Hz, 1H), 6.64 (d, J = 8.0 Hz, 1H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 143.4, 141.0, 140.9, 140.7, 135.0, 129.2, 128.7, 128.0, 126.0, 122.4, 122.3, 122.1, 119.1, 109.5, 108.2, 88.2, 29.1. IR (neat, cm^{-1}): 2923, 1688, 1583, 1450, 1385, 1029, 740, 700. HRMS (ESI) m/z Calcd for $\text{C}_{19}\text{H}_{15}\text{IN}$: $[\text{M}+\text{H}]^+ = 384.0244$. Found: 384.0229.



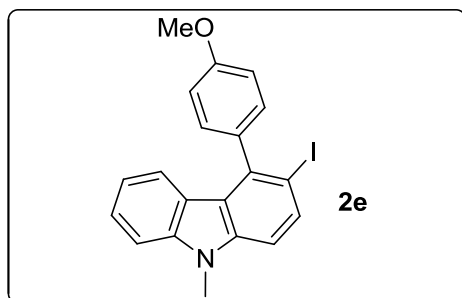
3-iodo-9-methyl-4-(*o*-tolyl)-9*H*-carbazole **2b** White solid (70.7 mg, 89%), mp: 128-130 °C ^1H NMR (400 MHz, CDCl_3) δ ppm 7.94 (d, J = 8.4 Hz, 1H), 7.47-7.43 (m, 1H), 7.41-7.31 (m, 4H), 7.14 (t, J = 8.4 Hz, 2H), 6.92-6.88 (m, 1H), 6.55 (d, J = 8.0 Hz, 1H), 3.80 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 142.7, 140.8, 140.7, 140.6, 136.0, 135.0, 130.2, 129.0, 128.3, 126.4, 126.0, 122.3, 122.2, 121.8, 119.3, 109.4, 108.2, 88.4, 29.1, 19.5. IR (neat, cm^{-1}): 2925, 1583, 1448, 1312, 1156, 1024, 796, 749. HRMS (ESI) m/z Calcd for $\text{C}_{20}\text{H}_{17}\text{IN}$: $[\text{M}+\text{H}]^+ = 398.0400$. Found: 398.0385.



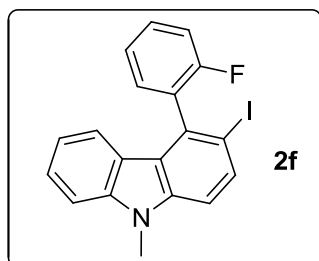
3-iodo-9-methyl-4-(*m*-tolyl)-9*H*-carbazole **2c** Pale yellow solid (72.3 mg, 91%), mp: 112-114 °C ^1H NMR (400 MHz, CDCl_3) δ ppm 7.92 (d, J = 8.8 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.38-7.29 (m, 3H), 7.14-7.09 (m, 3H), 6.92-6.88 (m, 1H), 6.98 (d, J = 8.0 Hz, 1H), 3.78 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 143.3, 141.2, 140.9, 140.6, 138.3, 135.0, 129.7, 128.7, 128.6, 126.1, 125.9, 122.4, 122.3, 122.1, 119.0, 109.4, 108.2, 88.3, 29.1, 21.6. IR (neat, cm^{-1}): 2925, 1584, 1450, 1351, 1122, 1024, 790, 743. HRMS (ESI) m/z Calcd for $\text{C}_{20}\text{H}_{17}\text{IN}$: $[\text{M}+\text{H}]^+ = 398.0400$. Found: 398.0384.



3-iodo-9-methyl-4-(p-tolyl)-9H-carbazole **2d** Pale yellow solid (72.3 mg, 91%), mp: 154-156 °C ^1H NMR (400 MHz, CDCl_3) δ ppm 7.92 (d, J = 8.4 Hz, 1H), 7.38-7.29 (m, 4H), 7.21 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.4 Hz, 1H), 6.91 (t, J = 7.6 Hz, 1H), 6.72 (d, J = 8.0 Hz, 1H), 3.78 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 141.1, 140.9, 140.7, 140.5, 137.6, 135.0, 129.5, 129.0, 125.9, 122.5, 122.3, 122.2, 119.0, 109.4, 108.2, 88.7, 29.1, 21.5. IR (neat, cm^{-1}): 2924, 1584, 1449, 1329, 1123, 1023, 790, 746. HRMS (ESI) m/z Calcd for $\text{C}_{20}\text{H}_{17}\text{IN}$: $[\text{M}+\text{H}]^+ = 398.0400$. Found: 398.0382.

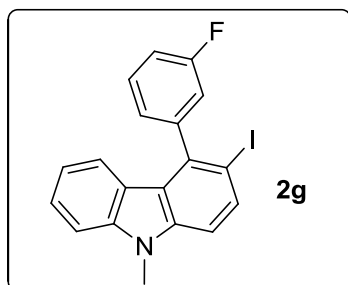


3-iodo-4-(4-methoxyphenyl)-9-methyl-9H-carbazole **2e** Pale yellow solid (76.0 mg, 92%), mp: 130-132 °C ^1H NMR (400 MHz, CDCl_3) δ ppm 7.91 (d, J = 8.8 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.30 (d, J = 8.4 Hz, 1H), 7.23-7.20 (m, 2H), 7.09-7.06 (m, 3H), 6.92 (t, J = 7.6 Hz, 1H), 6.76 (d, J = 8.0 Hz, 1H), 3.91 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 159.3, 140.8, 140.8, 140.7, 135.9, 134.9, 130.3, 125.9, 122.7, 122.3, 122.2, 119.0, 114.1, 109.4, 108.2, 89.3, 55.2, 29.1. IR (neat, cm^{-1}): 2954, 2932, 1513, 1450, 1312, 1029, 792, 747. HRMS (ESI) m/z Calcd for $\text{C}_{20}\text{H}_{17}\text{INO}$: $[\text{M}+\text{H}]^+ = 414.0349$. Found: 414.0332.

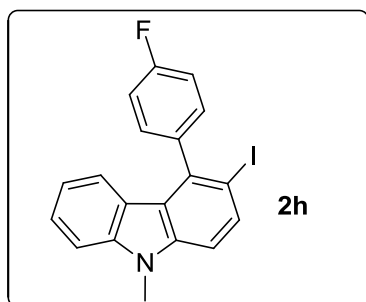


4-(2-fluorophenyl)-3-iodo-9-methyl-9H-carbazole **2f** Pale yellow solid (56.9 mg, 71%), mp: 130-132 °C ^1H NMR (400 MHz, CDCl_3) δ ppm 7.93 (d, J = 8.8 Hz, 1H), 7.57-7.52 (m, 1H), 7.40-7.27 (m, 5H), 7.13 (d, J = 8.8 Hz, 1H), 6.93 (t, J = 7.6 Hz, 1H), 6.73 (d, J = 7.6 Hz, 1H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 160.7, 158.3, 140.9, 140.6, 135.0, 134.9, 131.5, 131.5, 130.8, 130.7, 130.4, 130.3, 126.2,

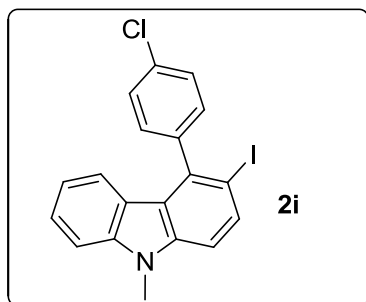
124.6, 124.6, 122.8, 121.8, 121.6, 119.3, 116.3, 116.1, 110.1, 108.4, 88.5, 29.1. IR (neat, cm^{-1}): 2924, 1583, 1450, 1314, 1103, 1026, 795, 747. HRMS (ESI) m/z Calcd for $\text{C}_{19}\text{H}_{14}\text{FIN}$: $[\text{M}+\text{H}]^+ = 402.0149$. Found: 402.0136.



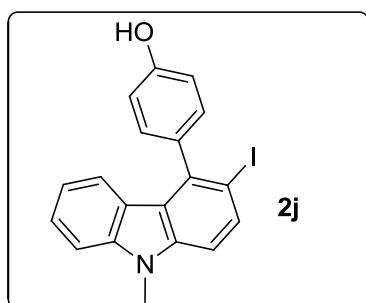
4-(3-fluorophenyl)-3-iodo-9-methyl-9*H*-carbazole **2g** Pale yellow solid (58.5 mg, 73%), mp: 116-118 °C ^1H NMR (400 MHz, CDCl_3) δ ppm 7.93 (d, $J = 8.8$ Hz, 1H), 7.52 (q, $J = 7.2$ Hz, 1H), 7.39 (t, $J = 7.2$ Hz, 1H), 7.31 (d, $J = 8.0$ Hz, 1H), 7.26-7.21 (m, 1H), 7.14 (d, $J = 8.8$ Hz, 1H), 7.10 (d, $J = 7.6$ Hz, 1H), 7.06 (d, $J = 9.6$ Hz, 1H), 6.95-6.91 (m, 1H), 6.70-6.68 (m, 1H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 164.2, 161.7, 145.4, 145.3, 140.9, 140.6, 139.6, 135.1, 130.5, 130.4, 126.2, 125.1, 122.3, 122.1, 121.7, 119.2, 116.6, 116.4, 115.1, 114.9, 109.8, 108.4, 87.6, 29.1. IR (neat, cm^{-1}): 2927, 1583, 1450, 1350, 1121, 1024, 787, 746. HRMS (ESI) m/z Calcd for $\text{C}_{19}\text{H}_{14}\text{FIN}$: $[\text{M}+\text{H}]^+ = 402.0149$. Found: 402.0134.



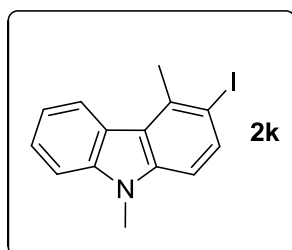
4-(4-fluorophenyl)-3-iodo-9-methyl-9*H*-carbazole **2h** yellow solid (56.9 mg, 71%), mp: 188-190 °C ^1H NMR (400 MHz, CDCl_3) δ ppm 7.91 (d, $J = 8.8$ Hz, 1H), 7.38 (t, $J = 7.6$ Hz, 1H), 7.32 (d, $J = 8.0$ Hz, 1H), 7.28-7.20 (m, 4H), 7.11 (d, $J = 8.4$ Hz, 1H), 6.93 (t, $J = 7.6$ Hz, 1H), 6.68 (t, $J = 8.0$ Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 163.8, 161.3, 140.9, 140.7, 139.9, 139.3, 139.3, 135.0, 131.1, 131.0, 126.1, 122.5, 122.1, 121.9, 119.1, 115.9, 115.7, 109.7, 108.4, 88.5, 29.1. IR (neat, cm^{-1}): 2925, 1510, 1449, 1315, 1092, 1026, 794, 745. HRMS (ESI) m/z Calcd for $\text{C}_{19}\text{H}_{14}\text{FIN}$: $[\text{M}+\text{H}]^+ = 402.0149$. Found: 402.0131.



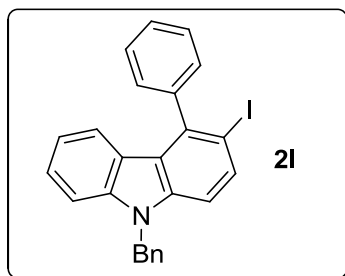
4-(4-chlorophenyl)-3-iodo-9-methyl-9*H*-carbazole **2i** Pale yellow solid (63.4 mg, 76%), mp: 166-168 °C ¹H NMR (400 MHz, CDCl₃) δ ppm 7.92 (d, *J* = 8.8 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.41-7.37 (m, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.25-7.21 (m, 2H), 7.13 (d, *J* = 8.4 Hz, 1H), 6.96-6.92 (m, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 3.81 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ ppm 141.7, 140.9, 140.6, 139.6, 135.0, 134.0, 130.7, 129.1, 126.2, 122.3, 122.1, 121.8, 119.2, 109.8, 108.4, 88.1, 29.2. IR (neat, cm⁻¹): 2925, 1584, 1448, 1313, 1087, 1016, 791, 747. HRMS (ESI) *m/z* Calcd for C₁₉H₁₄ClIN: [M+H]⁺ = 417.9854. Found: 417.9835.



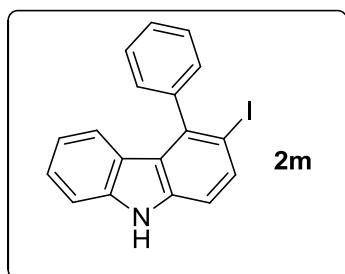
4-(3-iodo-9-methyl-9*H*-carbazol-4-yl)phenol **2j** Pale yellow solid (66.2 mg, 83%), mp: 76-78 °C ¹H NMR (400 MHz, CDCl₃) δ ppm 7.90 (d, *J* = 8.4 Hz, 1H), 7.38-7.34 (m, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.20-7.16 (m, 2H), 7.08 (d, *J* = 8.8 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 5.05 (s, 1H), 3.77 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ ppm 155.4, 140.8, 140.7, 140.6, 135.9, 134.9, 130.5, 125.9, 122.7, 122.3, 122.1, 119.0, 115.7, 109.4, 108.2, 89.2, 29.1. IR (neat, cm⁻¹): 3368, 2927, 1585, 1449, 1311, 1023, 791, 747. HRMS (ESI) *m/z* Calcd for C₁₉H₁₅INO: [M+H]⁺ = 400.0193. Found: 400.0179.



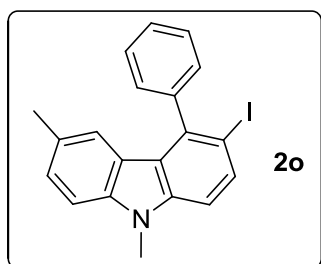
3-iodo-4,9-dimethyl-9*H*-carbazole **2k** Yellow solid (23.8 mg, 37%), mp: 88-90 °C ¹H NMR (400 MHz, CDCl₃) δ ppm 8.15 (d, *J* = 7.6 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.50-7.46 (m, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 3.76 (s, 3H), 2.97 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ ppm 140.7, 140.7, 136.0, 135.5, 125.6, 122.8, 122.8, 122.0, 119.2, 108.4, 108.1, 90.2, 29.0, 25.8. IR (neat, cm⁻¹): 2924, 1586, 1459, 1311, 1276, 1124, 740, 720. HRMS (ESI) *m/z* Calcd for C₁₄H₁₃IN: [M+H]⁺ = 322.0087. Found: 322.0081.



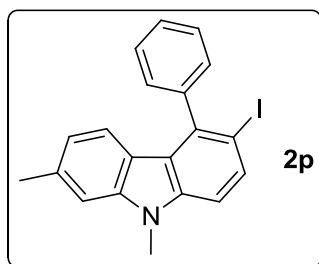
9-benzyl-3-iodo-4-phenyl-9*H*-carbazole **2l** White solid (76.2 mg, 83%), mp: 168-170 °C ^1H NMR (400 MHz, CDCl_3) δ ppm 7.88 (d, $J = 8.4$ Hz, 1H), 7.56-7.53 (m, 3H), 7.36-7.34 (m, 2H), 7.29 (d, $J = 6.0$ Hz, 2H), 7.24-7.21 (m, 3H), 7.11-7.07 (m, 3H), 6.92-6.88 (m, 1H), 6.68 (d, $J = 8.0$ Hz, 1H), 5.44 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 143.3, 141.2, 140.5, 140.3, 136.6, 135.1, 129.2, 128.8, 128.8, 128.1, 127.6, 126.3, 126.1, 122.7, 122.4, 122.3, 119.4, 109.9, 108.7, 88.8, 46.5. IR (neat, cm^{-1}): 3058, 2923, 1582, 1447, 1329, 1027, 797, 747. HRMS (ESI) m/z Calcd for $\text{C}_{25}\text{H}_{19}\text{IN}$: $[\text{M}+\text{H}]^+ = 460.0557$. Found: 460.0537.



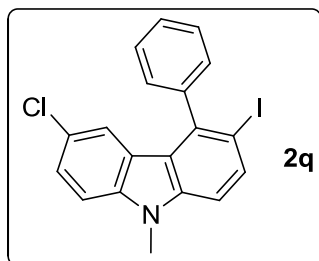
3-iodo-4-phenyl-9*H*-carbazole **2m** yellow solid (55.4 mg, 75%), mp: 96-98 °C ^1H NMR (400 MHz, CDCl_3) δ ppm 8.00 (s, 1H), 7.88 (d, $J = 8.4$ Hz, 1H), 7.54 (s, 3H), 7.33-7.29 (m, 4H), 7.09 (d, $J = 8.4$ Hz, 1H), 6.91-6.88 (m, 1H), 6.63 (d, $J = 8.0$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 143.3, 141.1, 139.4, 139.1, 135.2, 129.1, 128.8, 128.1, 126.1, 123.0, 122.6, 122.3, 119.5, 111.6, 110.4, 88.8. IR (neat, cm^{-1}): 3417, 1595, 1443, 1317, 1121, 1024, 802, 736. HRMS (ESI) m/z Calcd for $\text{C}_{18}\text{H}_{13}\text{IN}$: $[\text{M}+\text{H}]^+ = 370.0087$. Found: 370.0074.



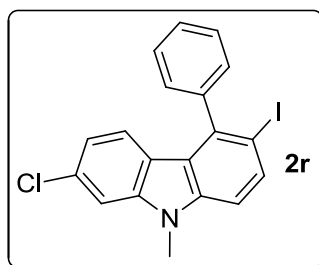
3-iodo-6,9-dimethyl-4-phenyl-9*H*-carbazole **2o** Pale yellow solid (61.9 mg, 78%), mp: 80-82 °C ^1H NMR (400 MHz, CDCl_3) δ ppm 7.90 (d, $J = 8.4$ Hz, 1H), 7.55-7.53 (m, 3H), 7.32-7.30 (m, 2H), 7.21-7.16 (m, 2H), 7.08 (d, $J = 8.8$ Hz, 1H), 6.39 (s, 1H), 3.76 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 143.5, 141.0, 140.8, 139.2, 134.7, 129.2, 128.7, 128.2, 127.9, 127.3, 122.3, 122.2, 122.1, 109.4, 107.9, 87.8, 29.1, 21.4. IR (neat, cm^{-1}): 3056, 2920, 1586, 1449, 1302, 1027, 796, 737. HRMS (ESI) m/z Calcd for $\text{C}_{20}\text{H}_{17}\text{IN}$: $[\text{M}+\text{H}]^+ = 398.0400$. Found: 398.0383.



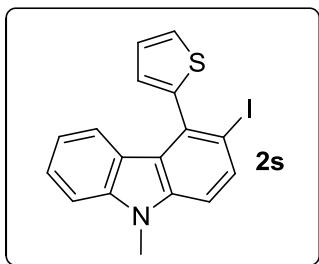
6-iodo-2,9-dimethyl-5-phenyl-9*H*-carbazole **2p** Yellow solid (61.9 mg, 78%), mp: 170-172 °C ^1H NMR (400 MHz, CDCl_3) δ ppm 7.89 (d, $J = 8.4$ Hz, 1H), 7.56-7.51 (m, 3H), 7.32-7.30 (m, 2H), 7.10-7.06 (m, 2H), 6.72 (d, $J = 8.0$ Hz, 1H), 6.51 (d, $J = 8.0$ Hz, 1H), 3.74 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 143.5, 141.3, 140.7, 140.6, 136.3, 134.5, 129.2, 128.7, 127.9, 122.6, 121.9, 120.6, 119.8, 109.4, 108.4, 88.1, 29.0, 22.1. IR (neat, cm^{-1}): 2923, 1587, 1449, 1305, 1127, 1026, 796, 738. HRMS (ESI) m/z Calcd for $\text{C}_{20}\text{H}_{17}\text{IN}$: $[\text{M}+\text{H}]^+ = 398.0400$. Found: 398.0385.



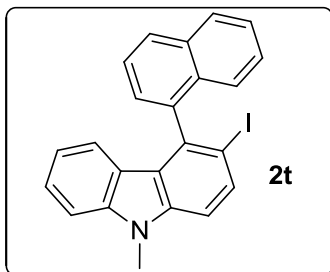
6-chloro-3-iodo-9-methyl-4-phenyl-9*H*-carbazole **2q** Yellow solid (67.6 mg, 81%), mp: 116-118 °C ^1H NMR (400 MHz, CDCl_3) δ ppm 7.96 (d, $J = 8.4$ Hz, 1H), 7.59-7.57 (m, 3H), 7.30-7.22 (m, 4H), 7.14 (d, $J = 8.4$ Hz, 1H), 6.53 (d, $J = 1.6$ Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 142.8, 141.3, 141.1, 139.2, 135.7, 128.9, 128.3, 126.0, 124.4, 123.1, 121.9, 121.6, 109.7, 109.2, 88.5, 29.3. IR (neat, cm^{-1}): 2926, 1582, 1445, 1297, 1075, 1018, 795, 760. HRMS (ESI) m/z Calcd for $\text{C}_{19}\text{H}_{14}\text{ClIN}$: $[\text{M}+\text{H}]^+ = 417.9854$. Found: 417.9836.



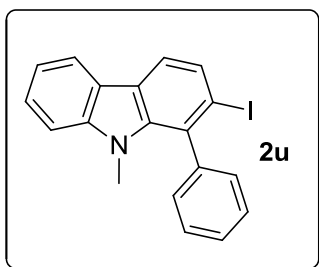
2-chloro-6-iodo-9-methyl-5-phenyl-9*H*-carbazole **2r** White solid (66.7 mg, 80%), mp: 180-182 °C ^1H NMR (400 MHz, CDCl_3) δ ppm 7.93 (d, $J = 8.4$ Hz, 1H), 7.54-7.53 (m, 3H), 7.28-7.25 (m, 3H), 7.09 (d, $J = 8.4$ Hz, 1H), 6.84 (d, $J = 8.4$ Hz, 1H), 6.49 (d, $J = 8.4$ Hz, 1H), 3.74 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 143.0, 141.4, 141.0, 140.9, 135.4, 131.9, 129.0, 128.8, 128.2, 123.0, 122.0, 120.6, 119.6, 109.7, 108.4, 88.8, 29.2. IR (neat, cm^{-1}): 2928, 1582, 1447, 1299, 1073, 1025, 796, 762. HRMS (ESI) m/z Calcd for $\text{C}_{19}\text{H}_{14}\text{ClIN}$: $[\text{M}+\text{H}]^+ = 417.9854$. Found: 417.9837.



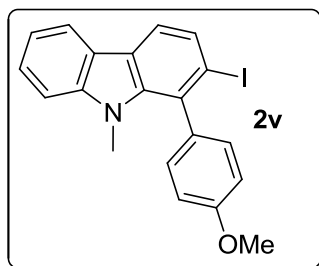
3-iodo-9-methyl-4-(thiophen-2-yl)-9H-carbazole **2s** White solid (63.8 mg, 82%), mp: 140-142 °C ^1H NMR (400 MHz, CDCl_3) δ ppm 7.90 (d, $J = 8.4$ Hz, 1H), 7.55-7.54 (m, 1H), 7.41-7.37 (m, 1H), 7.30-7.24 (m, 2H), 7.11-7.05 (m, 2H), 6.98 (t, $J = 7.6$ Hz, 1H), 6.80 (d, $J = 8.0$ Hz, 1H), 3.73 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 144.1, 140.9, 140.4, 134.8, 133.4, 127.4, 127.2, 126.3, 126.3, 124.0, 122.3, 121.8, 119.3, 110.4, 108.3, 90.9, 29.1. IR (neat, cm^{-1}): 2926, 1584, 1447, 1276, 1182, 1023, 791, 746. HRMS (ESI) m/z Calcd for $\text{C}_{17}\text{H}_{13}\text{INS}$: $[\text{M}+\text{H}]^+ = 389.9808$. Found: 389.9803.



3-iodo-9-methyl-4-(naphthalen-1-yl)-9H-carbazole **2t** White solid (76.2 mg, 88%), mp: 174-176 °C ^1H NMR (400 MHz, CDCl_3) δ ppm 8.01 (d, $J = 8.8$ Hz, 2H), 7.95 (d, $J = 8.0$ Hz, 1H), 7.63 (t, $J = 7.6$ Hz, 1H), 7.43 (t, $J = 7.6$ Hz, 2H), 7.32 (d, $J = 7.6$ Hz, 1H), 7.27-7.24 (m, 3H), 7.21 (t, $J = 7.6$ Hz, 1H), 6.70-6.66 (m, 1H), 6.20 (d, $J = 8.0$ Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 140.9, 140.8, 140.7, 139.2, 135.1, 133.7, 131.3, 128.4, 128.3, 126.9, 126.3, 126.1, 125.9, 125.8, 125.5, 123.3, 122.1, 121.9, 119.4, 109.7, 108.2, 89.3, 29.2. IR (neat, cm^{-1}): 3053, 2927, 1582, 1448, 1257, 1023, 791, 746. HRMS (ESI) m/z Calcd for $\text{C}_{23}\text{H}_{17}\text{IN}$: $[\text{M}+\text{H}]^+ = 434.0400$. Found: 434.0392.



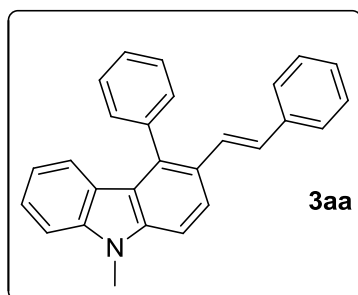
2-iodo-9-methyl-1-phenyl-9H-carbazole **2u** Pale yellow solid (52.1 mg, 68%), mp: 80-82 °C ^1H NMR (400 MHz, CDCl_3) δ ppm 8.06 (d, $J = 7.6$ Hz, 1H), 7.76 (s, 2H), 7.49-7.47 (m, 3H), 7.44 (d, $J = 8.0$ Hz, 1H), 7.32-7.29 (m, 2H), 7.26-7.21 (m, 2H), 3.09 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 142.5, 141.5, 138.6, 130.8, 129.6, 129.2, 128.2, 128.1, 126.3, 123.6, 122.0, 120.7, 120.0, 119.5, 108.9, 99.1, 31.9. IR (neat, cm^{-1}): 2924, 1579, 1435, 1397, 1232, 1052, 733, 700. HRMS (ESI) m/z Calcd for $\text{C}_{19}\text{H}_{15}\text{IN}$: $[\text{M}+\text{H}]^+ = 384.0244$. Found: 384.0247.



2-iodo-1-(4-methoxyphenyl)-9-methyl-9*H*-carbazole **2v** Pale yellow solid (67.7 mg, 82%), mp: 122-124 °C ¹H NMR (400 MHz, CDCl₃) δ ppm 8.04 (d, *J* = 7.6 Hz, 1H), 7.74 (s, 2H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.22-7.18 (m, 3H), 7.00 (d, *J* = 8.4 Hz, 1H), 3.88 (s, 3H), 3.12 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ ppm 159.4, 141.4, 138.9, 134.8, 131.8, 129.3, 129.1, 126.2, 123.6, 122.0, 120.6, 120.0, 119.4, 113.4, 108.8, 100.2, 55.2, 32.0. IR (neat, cm⁻¹): 2930, 1609, 1511, 1397, 1246, 1031, 833, 736. HRMS (ESI) *m/z* Calcd for C₂₀H₁₇INO: [M+H]⁺ = 414.0349. Found: 414.0353.

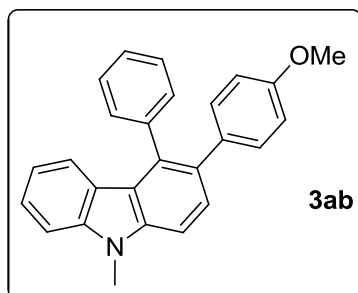
Typical Procedure for 3aa and 3ab Synthesis and Characterization

Data of 3aa and 3ab

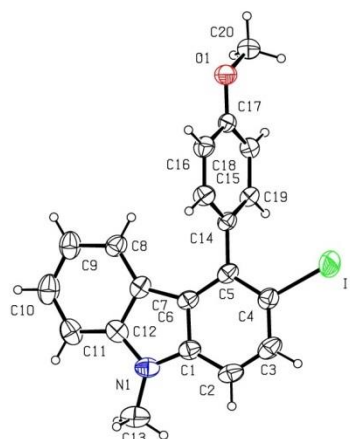
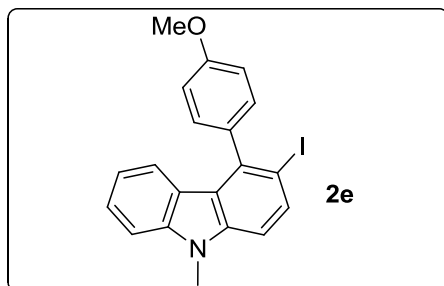


(*E*)-9-methyl-4-phenyl-3-styryl-9*H*-carbazole 3aa To a solution of 3-iodo-9-methyl-4-phenyl-9*H*-carbazole **2a** (76.6 mg, 0.20 mmol) in DMF (2 mL) was added K₂CO₃ (138.0 mg, 5.0 equiv), tetrabutylammonium bromide (128.8 mg, 2.0 equiv), Pd(OAc)₂ (1.34 mg, 3 mol %). The reaction vial was flushed with Ar and the reaction mixture was stirred for 5 minutes at room temperature. A solution of styrene (208 mg, 10 equiv) in DMF (2 mL) was then added dropwise through a syringe. The resulting solution was stirred at 100 °C for 12 h. When the reaction was considered complete as determined by TLC analysis, the mixture was quenched slowly by addition of aqueous 1M HCl (5 mL) and extracted with ethyl acetate (3 x 20 mL). The combined organic layers were washed with water, brine, dried over Na₂SO₄, and concentrated under reduced pressure. The crude material was purified by flash column chromatography to give **3aa** in 77% yield. White solid, mp: 162-164 °C ¹H NMR (400 MHz, CDCl₃) δ ppm 7.94 (d, *J* = 8.8 Hz, 1H), 7.57-7.53 (m, 3H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 6.0 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.25 (t, *J* = 7.6 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.11-6.97 (m, 2H), 6.92-6.88 (m, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 3.84 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ ppm 141.3, 140.4, 139.2, 138.1, 136.3, 129.9, 128.7, 128.5, 127.6, 127.5, 126.8,

126.6, 126.2, 125.4, 122.9, 122.2, 121.4, 118.9, 108.3, 108.0, 29.1. IR (neat, cm^{-1}): 3054, 2926, 1585, 1462, 1312, 1026, 796, 746. HRMS (ESI) m/z Calcd for $\text{C}_{27}\text{H}_{22}\text{N}$: $[\text{M}+\text{H}]^+ = 360.1747$. Found: 360.1741.



3-(4-methoxyphenyl)-9-methyl-4-phenyl-9H-carbazole 3ab To a solution of 3-iodo-9-methyl-4-phenyl-9H-carbazole **2a** (76.6 mg, 0.20 mmol) in dioxane/ H_2O (2:0.5 mL) was added 4-Methoxyphenylboronic acid (60.8 mg, 2.0 equiv), $\text{Pd}(\text{PPh}_3)_4$ (23.12 mg, 10 mol %), Na_2CO_3 (106 mg, 5.0 equiv). The reaction vial was flushed with Ar and the reaction mixture was stirred at 80 $^\circ\text{C}$ for 12 h. On completion, the reaction mixture was quenched with H_2O (10 mL) and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with water, brine, dried over Na_2SO_4 , and concentrated under reduced pressure. The crude material was purified by flash column chromatography to give **3a** (yield 90%) as a white solid. mp: 206-208 $^\circ\text{C}$ ^1H NMR (400 MHz, CDCl_3) δ ppm 7.52 (d, $J = 8.4$ Hz, 1H), 7.40 (d, $J = 8.4$ Hz, 1H), 7.35-7.29 (m, 7H), 7.09 (d, $J = 8.4$ Hz, 2H), 6.92-6.86 (m, 2H), 6.70 (d, $J = 8.8$ Hz, 2H), 3.83 (s, 3H), 3.71 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 157.6, 141.5, 140.2, 139.9, 135.4, 134.3, 131.8, 131.4, 130.4, 128.2, 128.0, 126.9, 125.4, 122.8, 122.4, 121.3, 118.5, 112.9, 108.1, 107.4, 55.0, 29.0. IR (neat, cm^{-1}): 3051, 2930, 1588, 1463, 1246, 1024, 806, 750. HRMS (ESI) m/z Calcd for $\text{C}_{26}\text{H}_{22}\text{NO}$: $[\text{M}+\text{H}]^+ = 364.1696$. Found: 364.1691.



structure of 2e

Datablock

Bond precision: C-C = 0.0093 Å Wavelength=0.71073

Cell: a=10.699(1) b=11.7260(11) c=22.2683(12)
 alpha=94.284(6) beta=101.795(6) gamma=109.369(8)

Temperature: 292 K

	Calculated	Reported
Volume	2549.0(4)	2549.0(4)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C20 H16 I N O	C20 H16 I N O
Sum formula	C20 H16 I N O	C20 H16 I N O
Mr	413.24	413.24
Dx, g cm ⁻³	1.615	1.615
Z	6	6
Mu (mm ⁻¹)	1.888	1.888
F000	1224.0	1224.0
F000'	1221.57	
h, k, lmax	13, 14, 27	13, 14, 27
Nref	10042	10025
Tmin, Tmax	0.573, 0.636	0.793, 1.000
Tmin'	0.521	

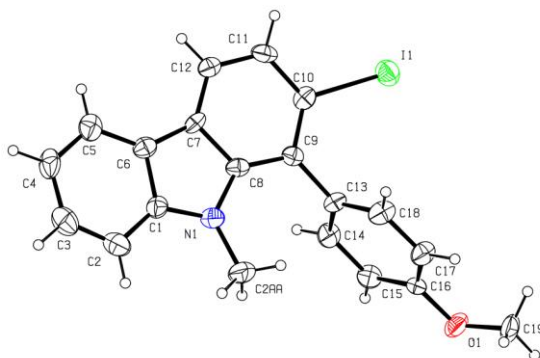
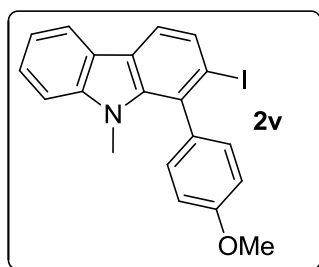
Correction method= # Reported T Limits: Tmin=0.793 Tmax=1.000

AbsCorr = MULTI-SCAN

Data completeness= 0.998 Theta(max)= 26.022

R(reflections)= 0.0555(5787) wR2(reflections)= 0.1481(10025)

S = 1.032 Npar= 628



structure of 2v

Datablock

Bond precision: C-C = 0.0098 Å Wavelength=0.71073

Cell: a=7.2355(5) b=20.9295(19) c=23.0167(15)

alpha=90 beta=90 gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	3485.5(5)	3485.5(5)
Space group	P b c a	P b c a
Hall group	-P 2ac 2ab	-P 2ac 2ab
Moiety formula	C20 H16 I N O	C20 H16 I N O
Sum formula	C20 H16 I N O	C20 H16 I N O
Mr	413.24	413.24
Dx, g cm ⁻³	1.575	1.575
Z	8	8
Mu (mm ⁻¹)	1.841	1.841
F000	1632.0	1632.0
F000'	1628.76	
h, k, lmax	8, 25, 28	8, 25, 28
Nref	3432	3426
Tmin, Tmax	0.550, 0.597	0.804, 1.000
Tmin'	0.539	

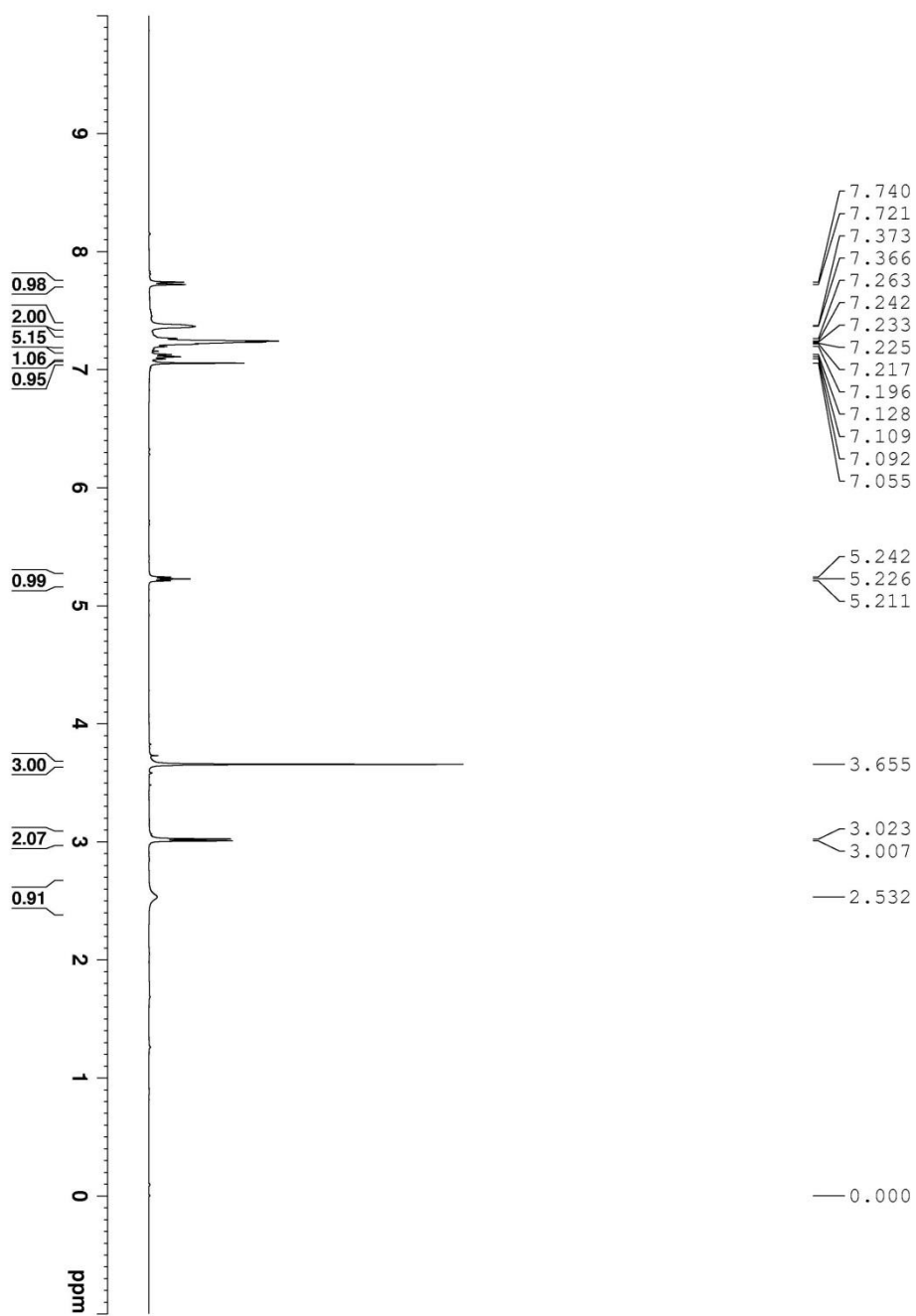
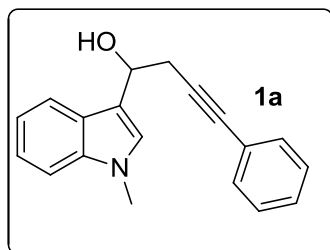
Correction method= # Reported T Limits: Tmin=0.804 Tmax=1.000

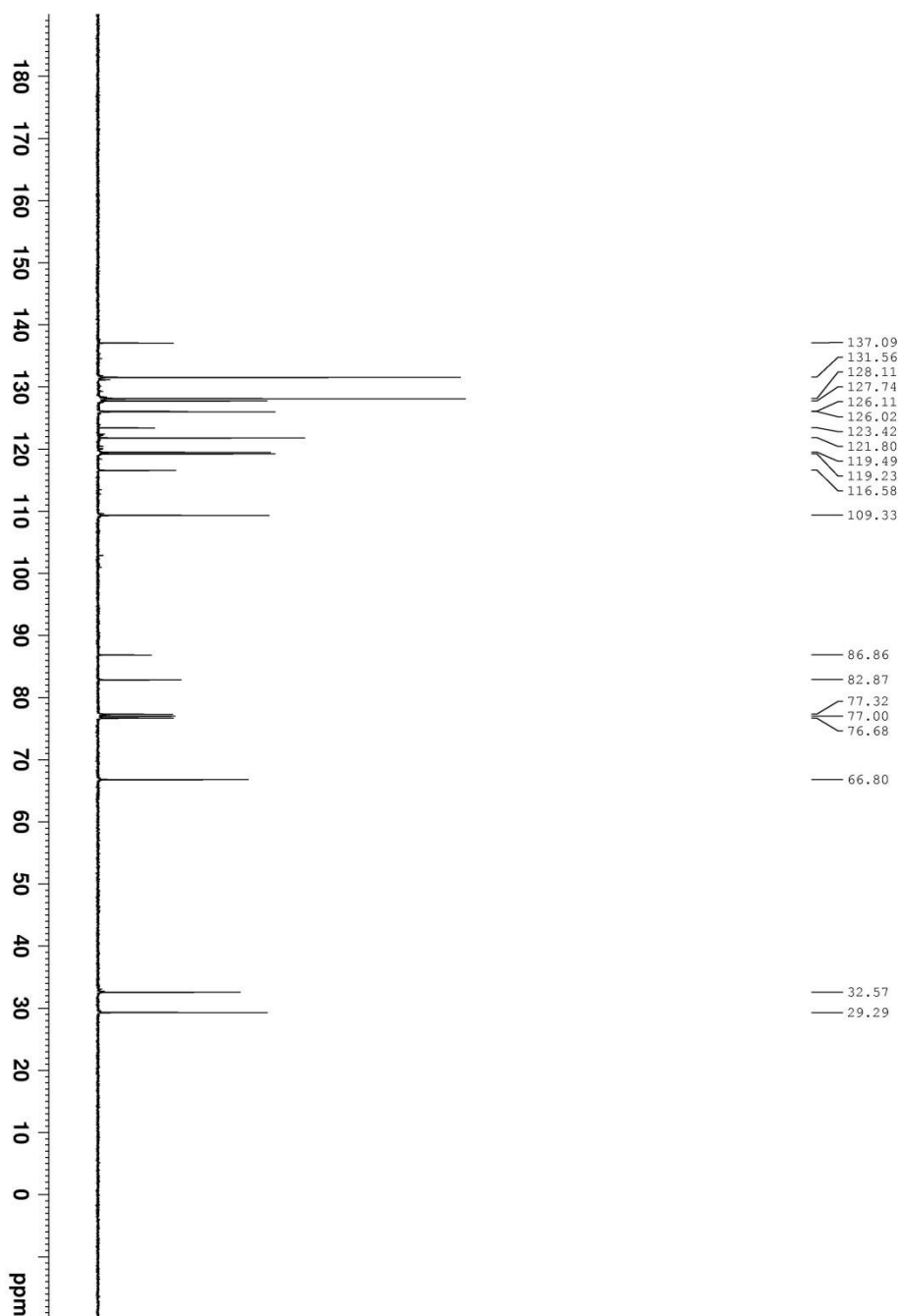
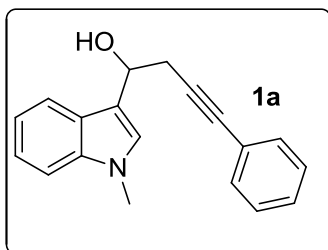
AbsCorr = MULTI-SCAN

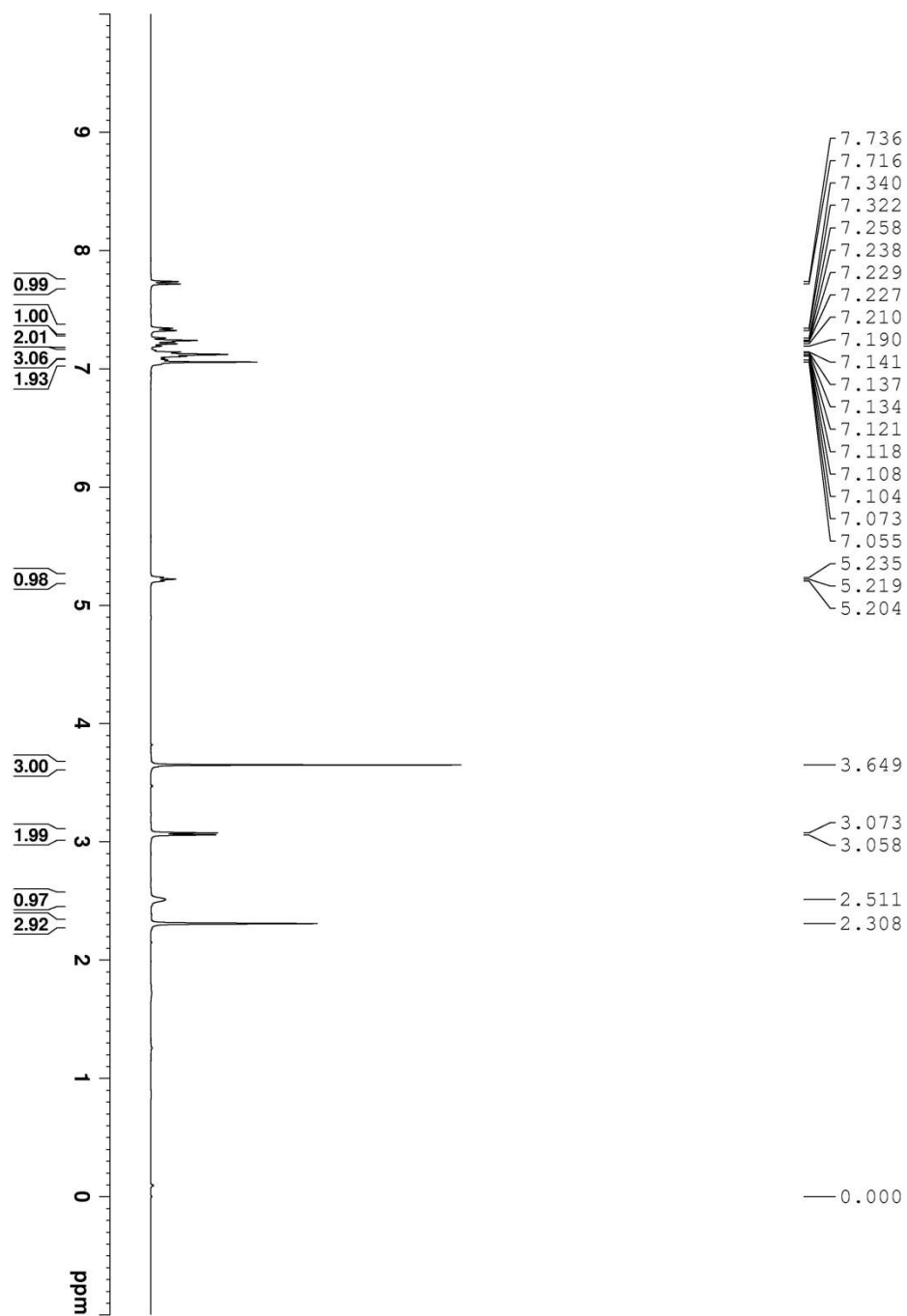
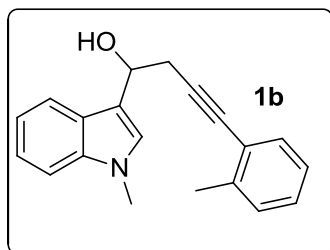
Data completeness= 0.998 Theta(max)= 26.020

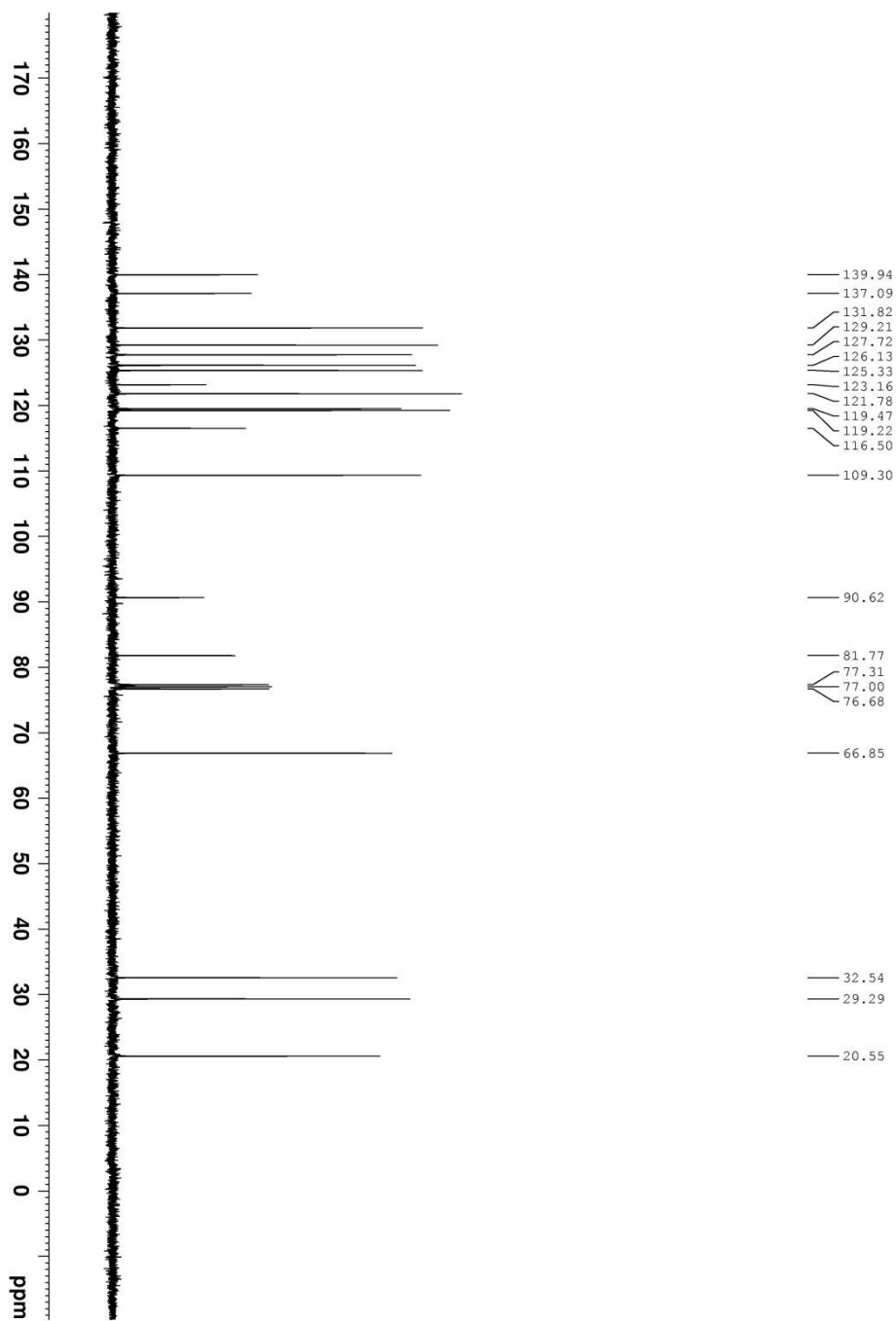
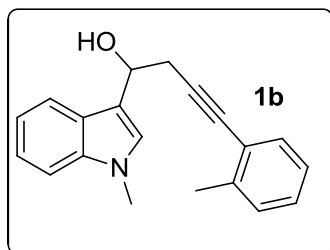
R(reflections)= 0.0639(1933) wR2(reflections)= 0.1839(3426)

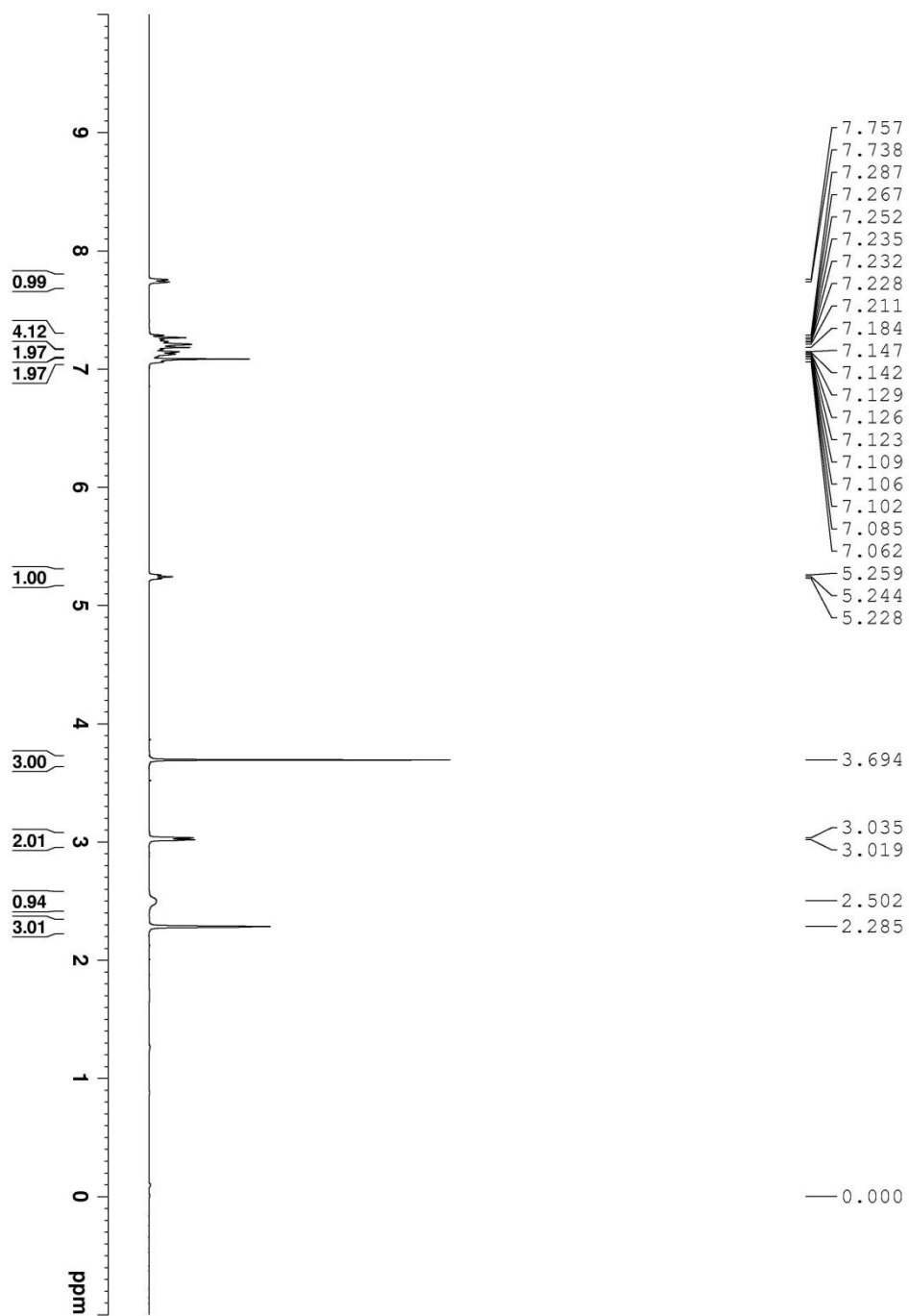
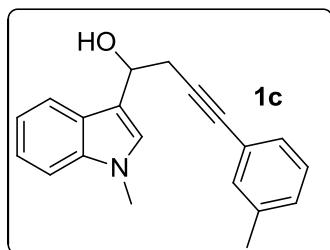
S = 1.032 Npar= 210

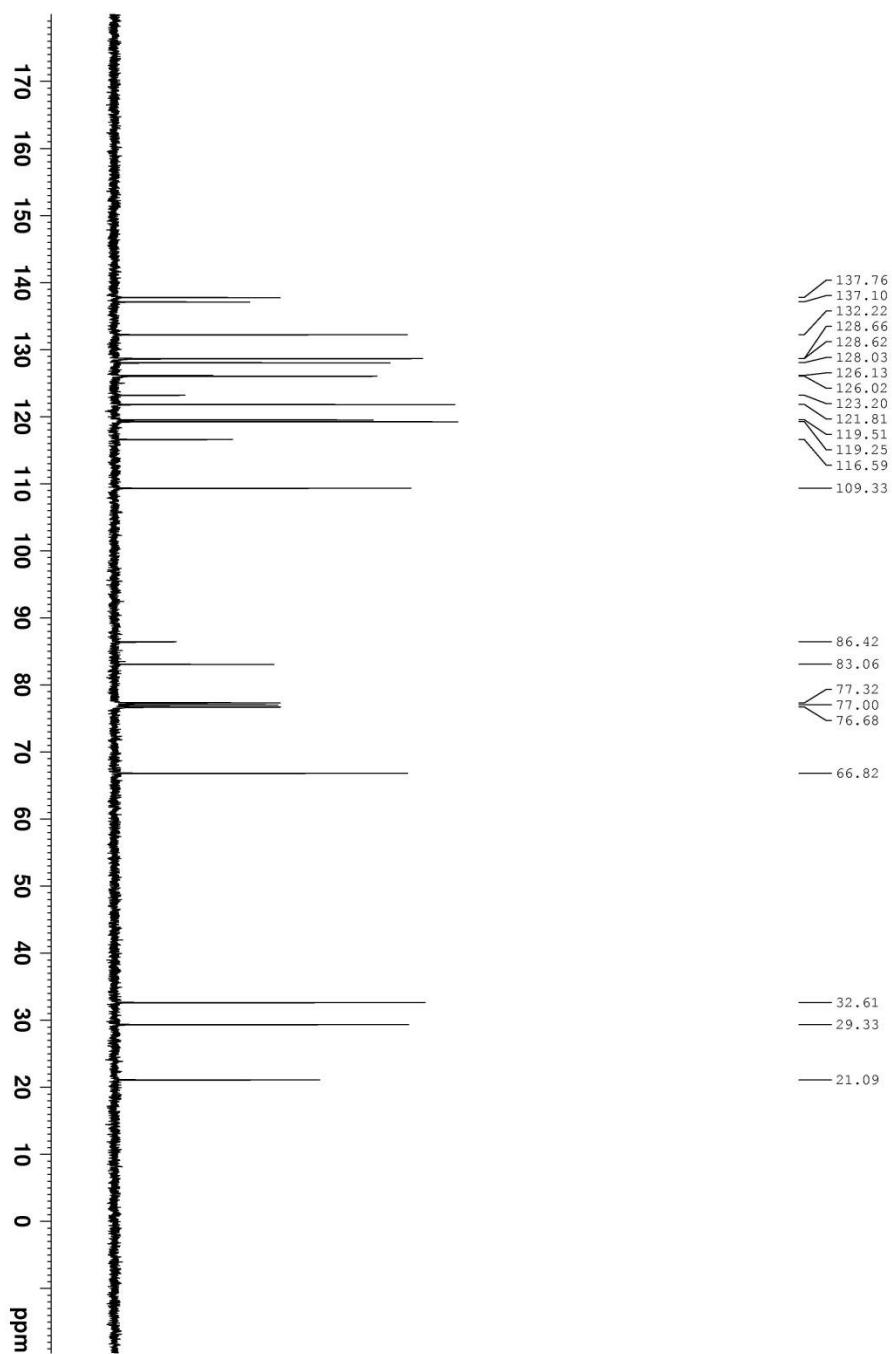
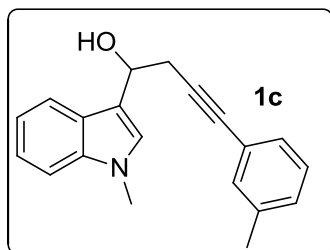


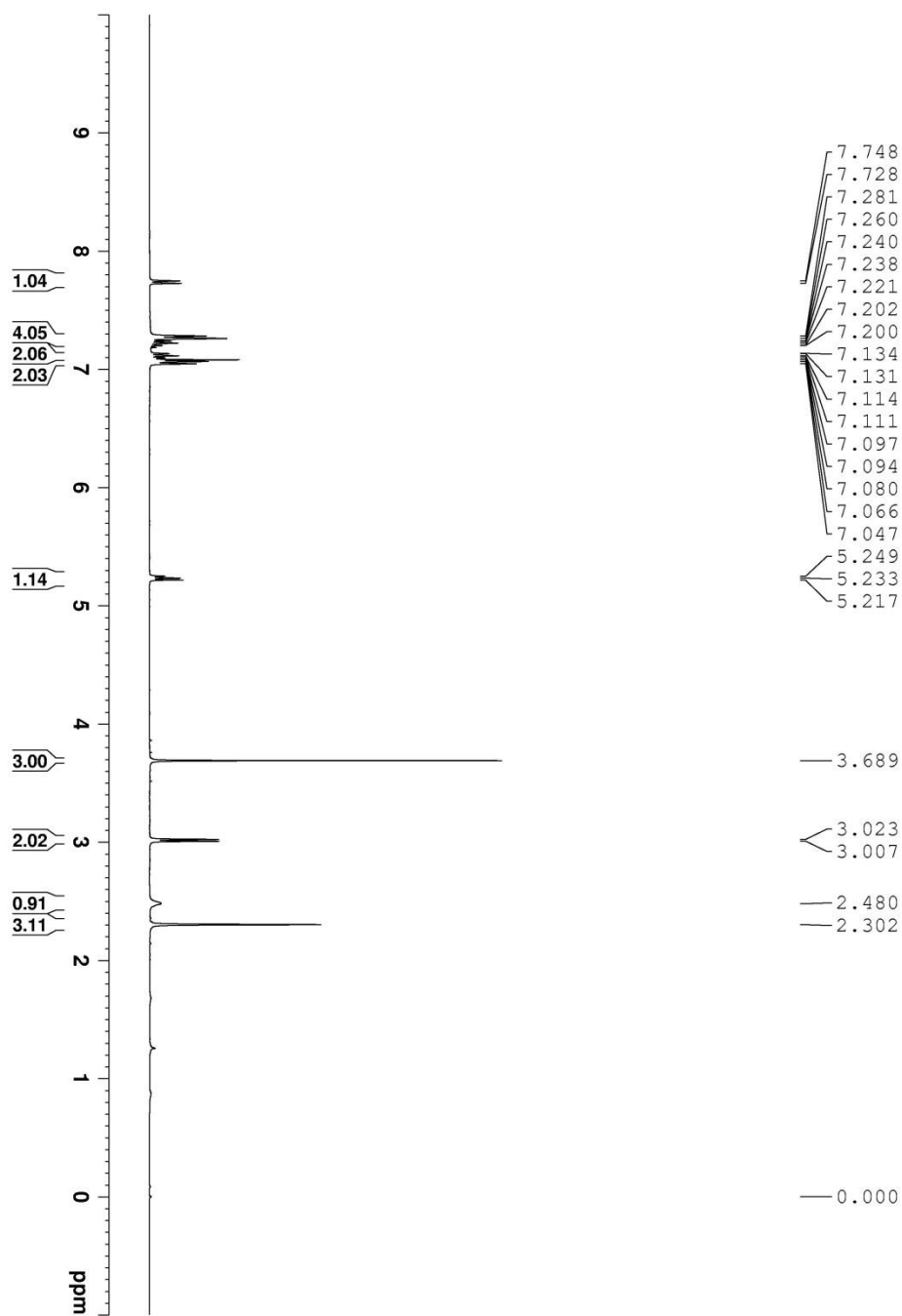
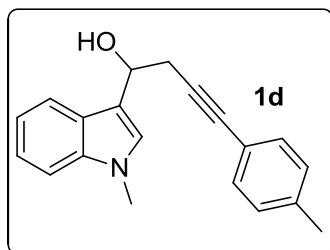


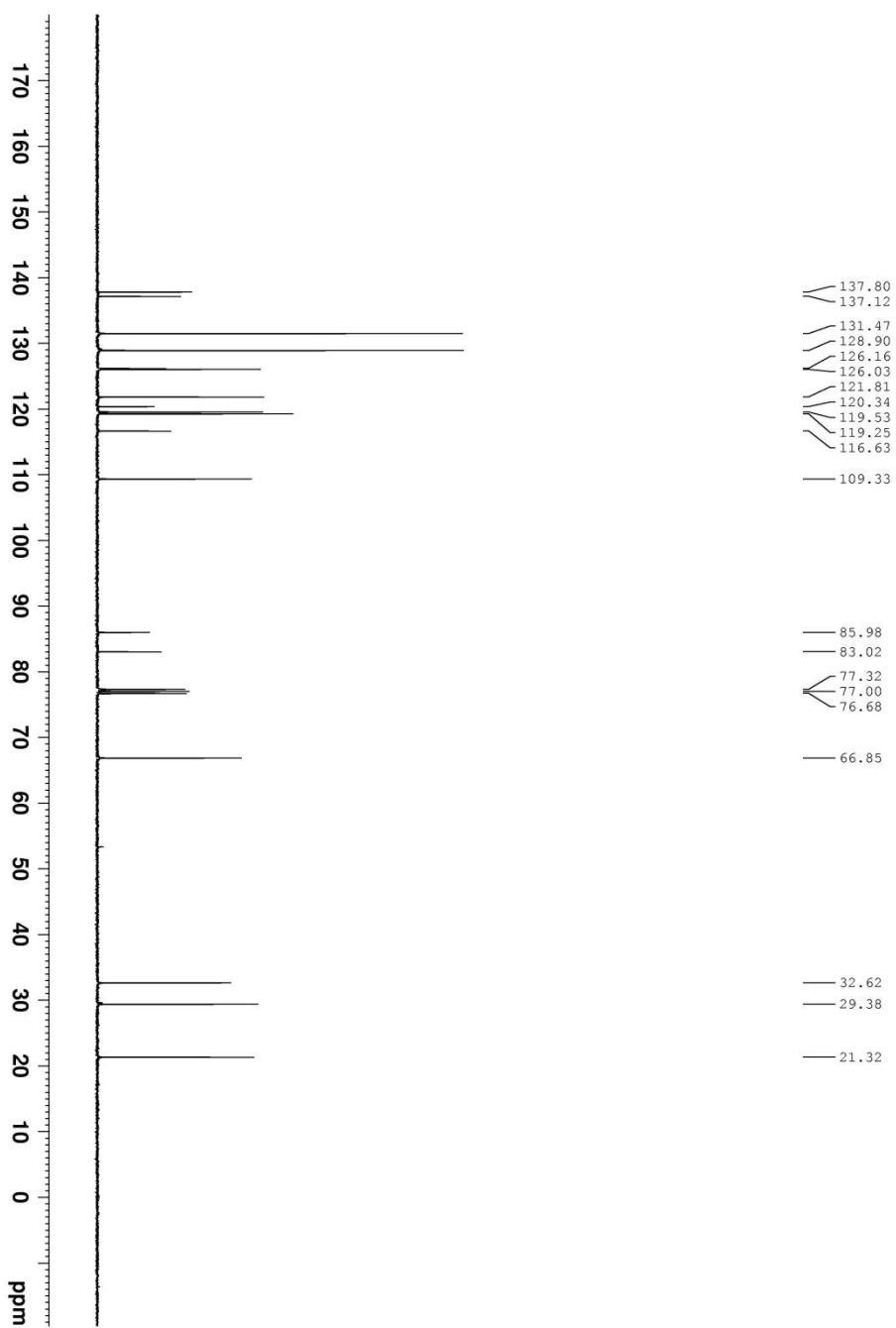
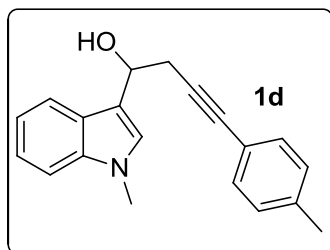


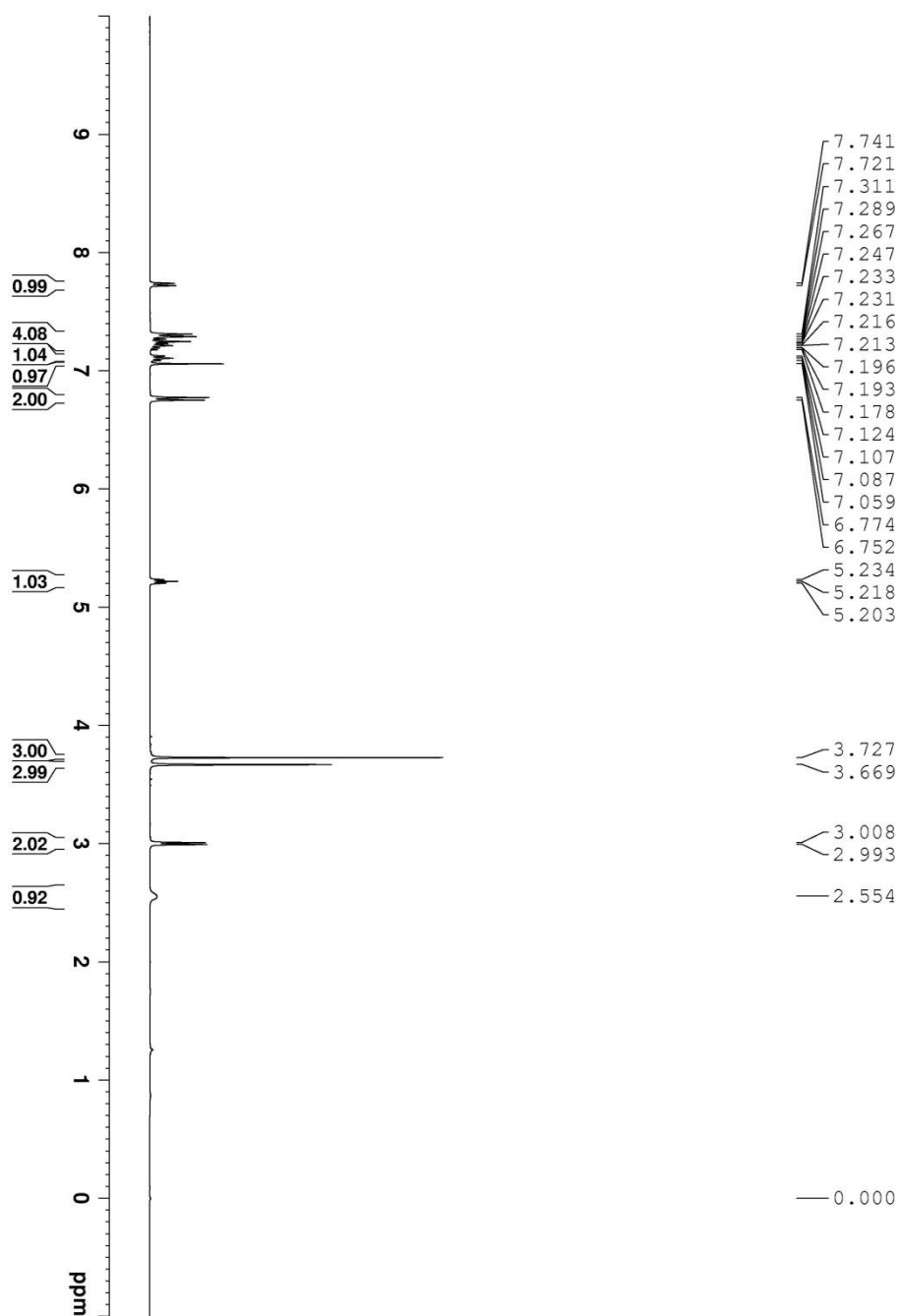
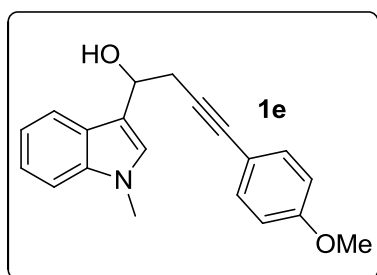


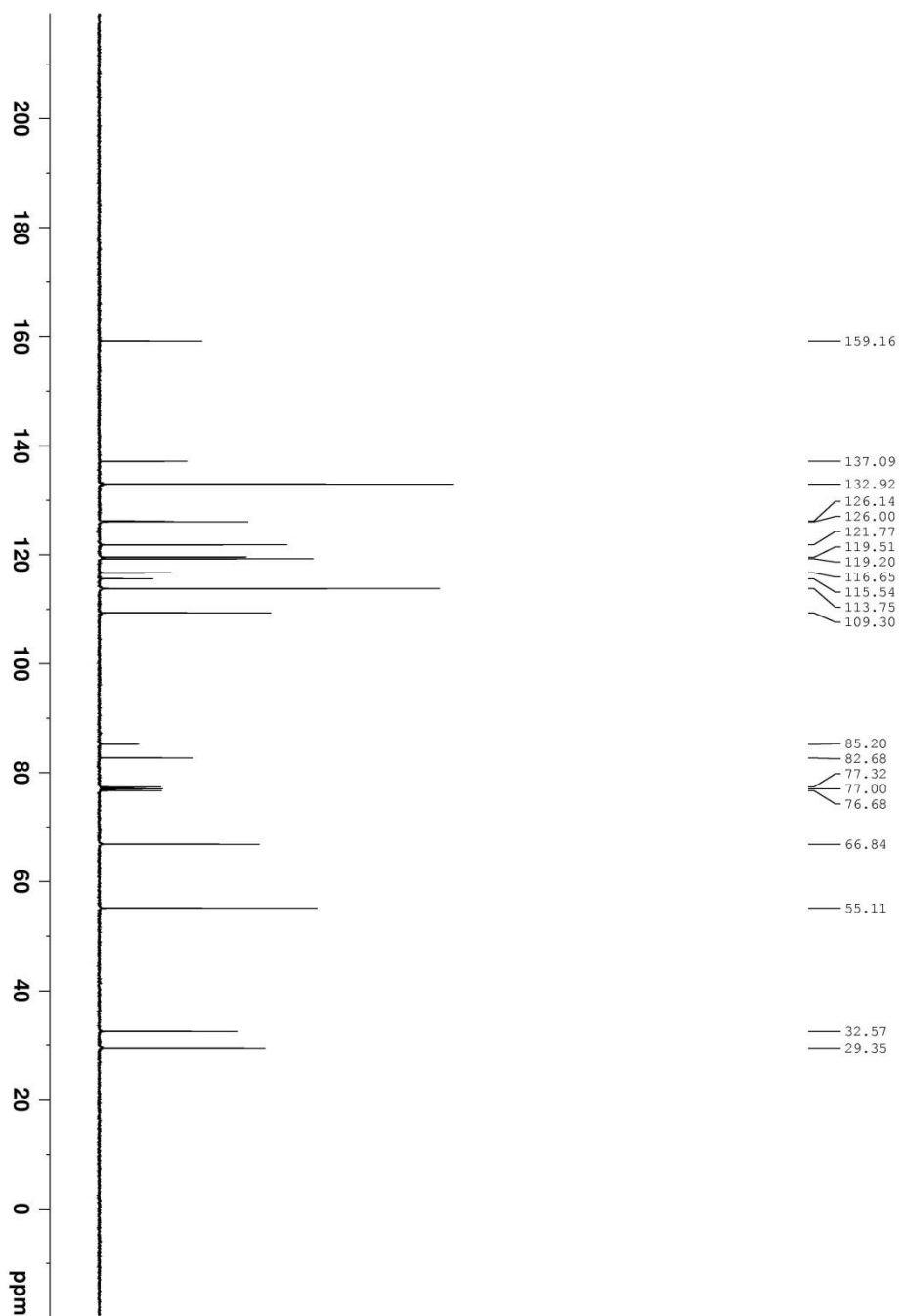
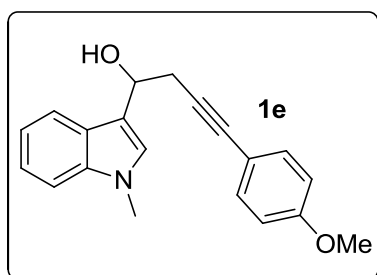


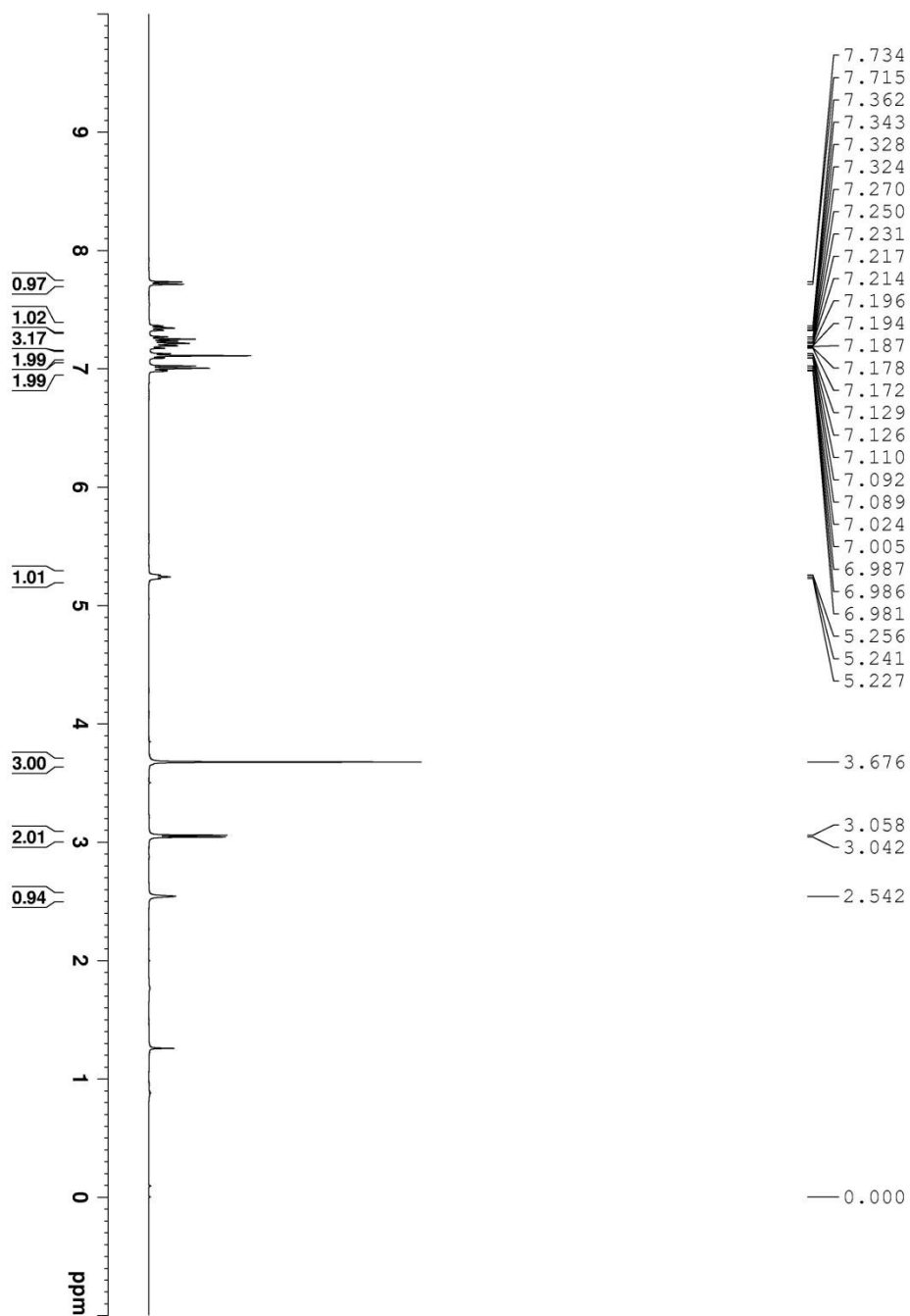
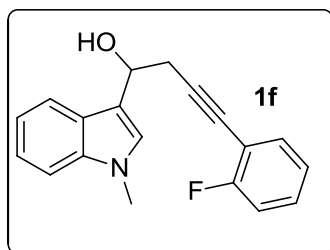


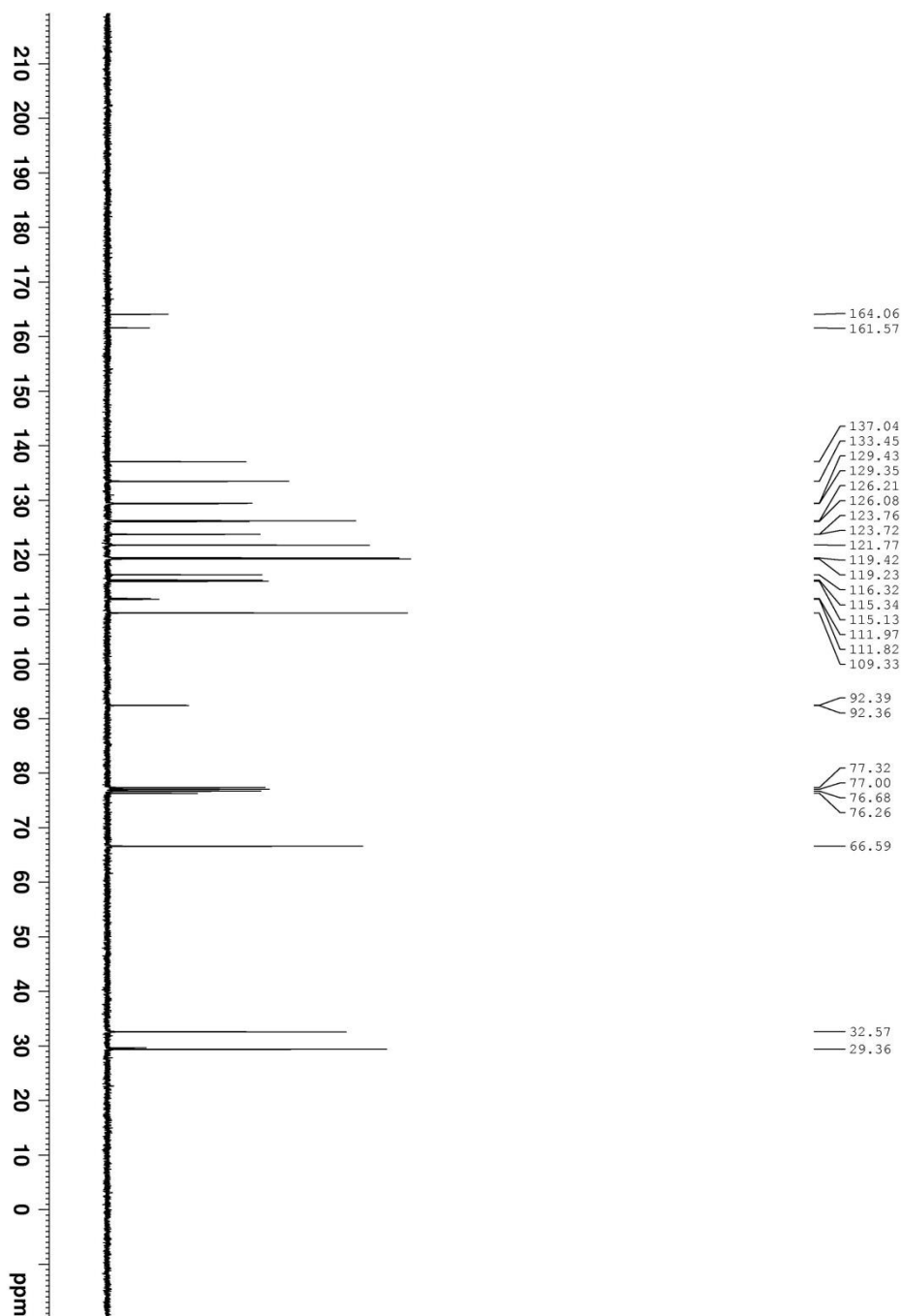
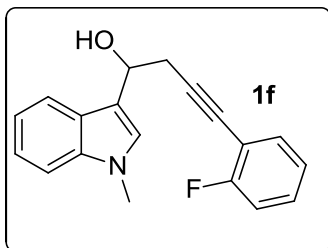


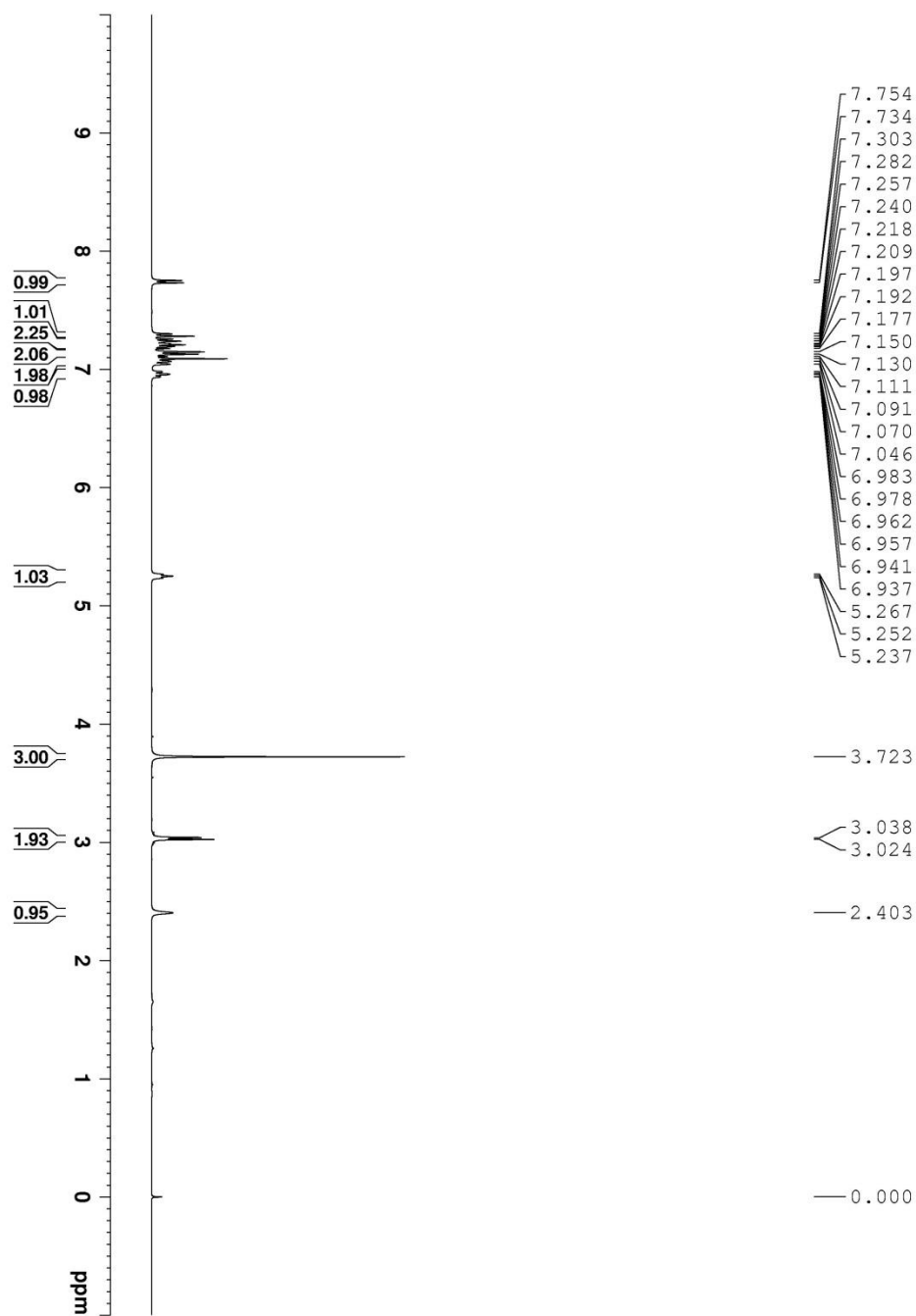
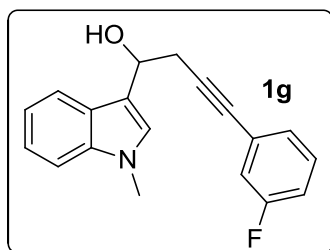


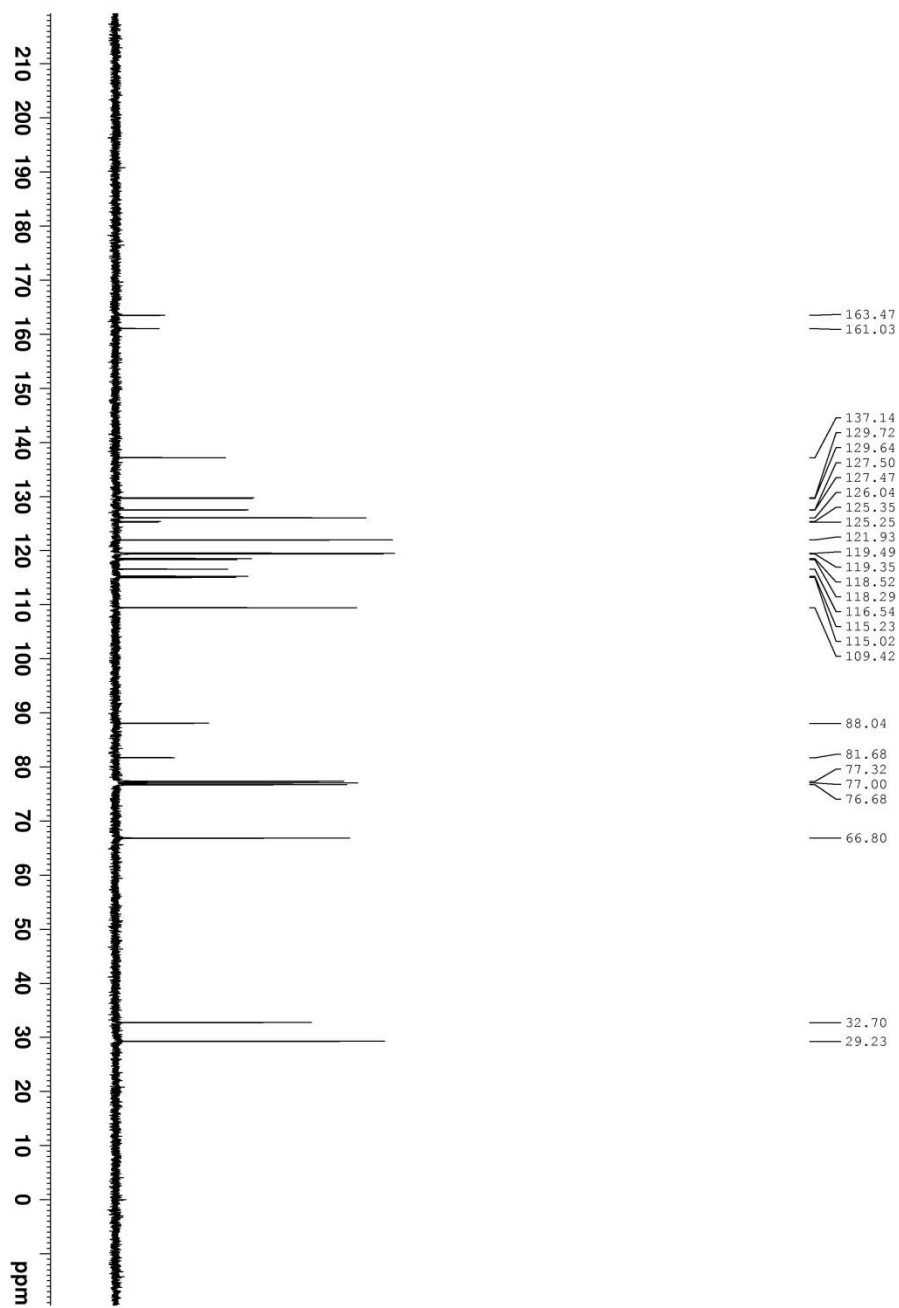
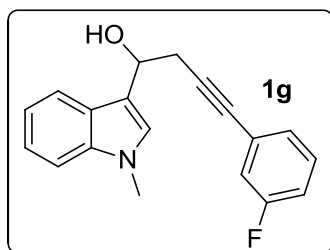


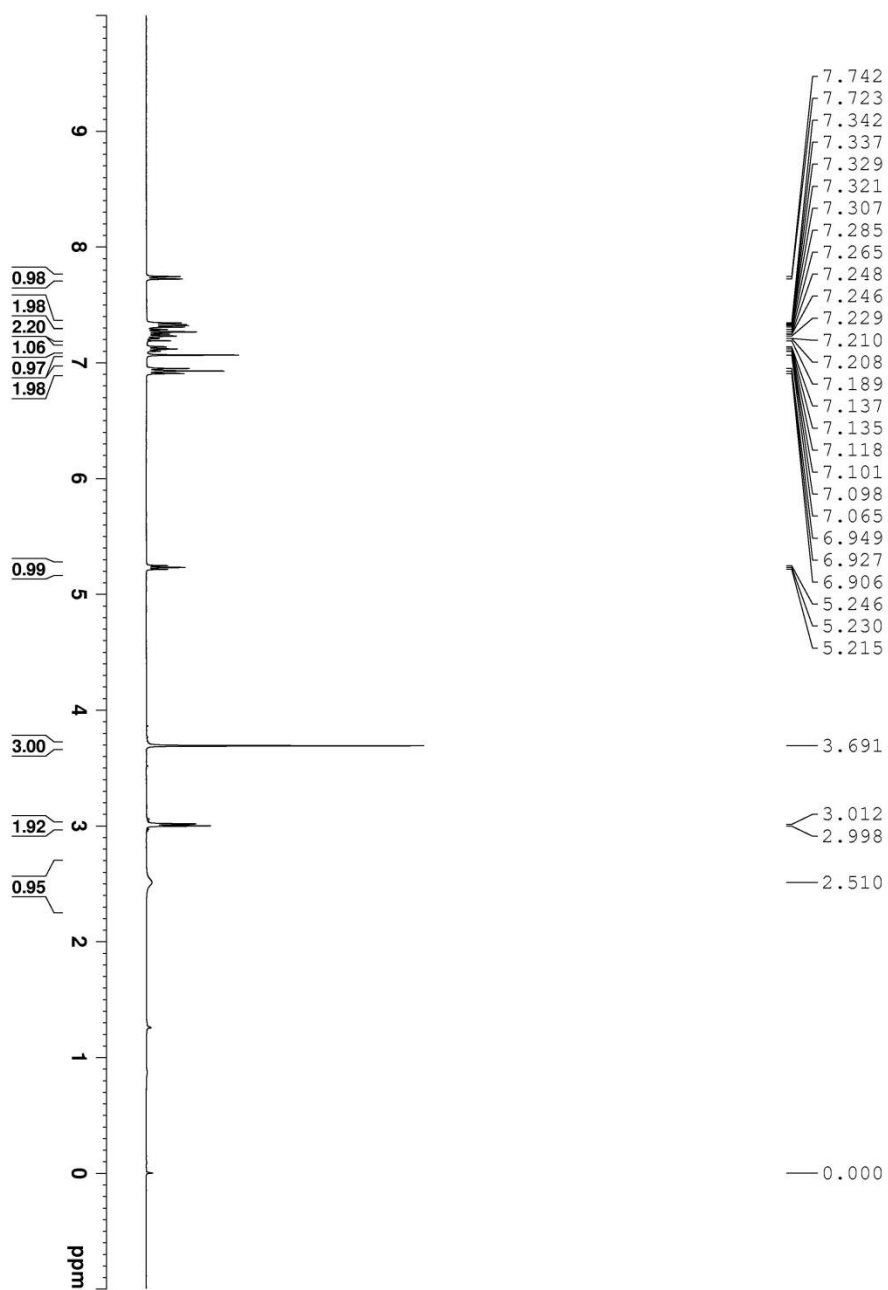
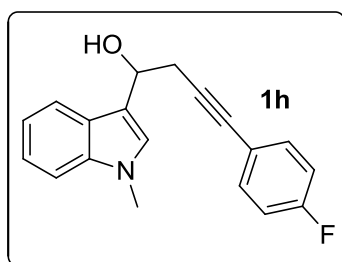


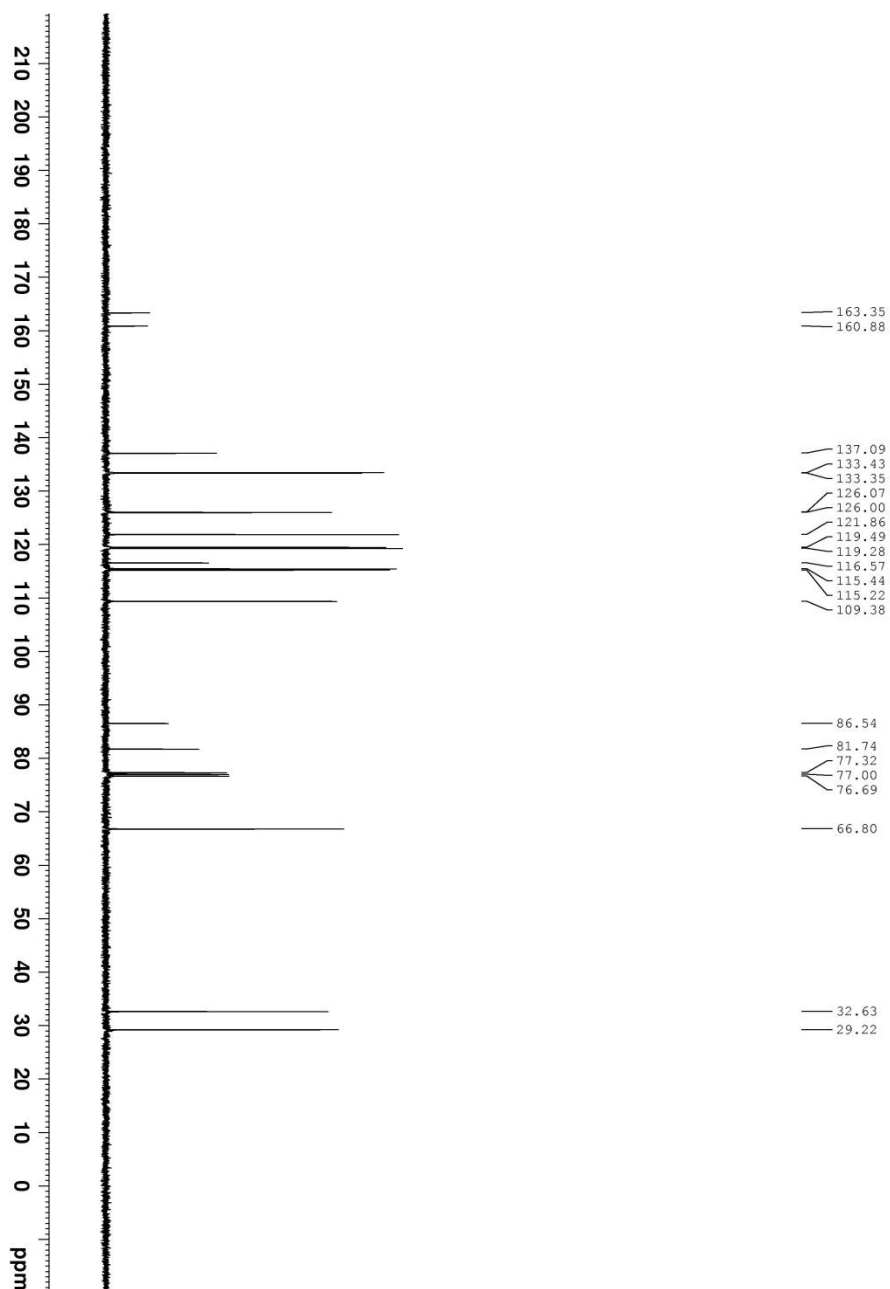
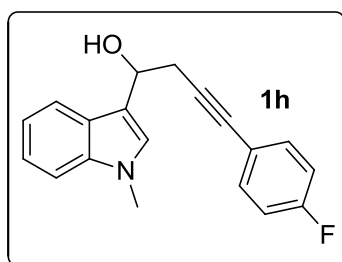


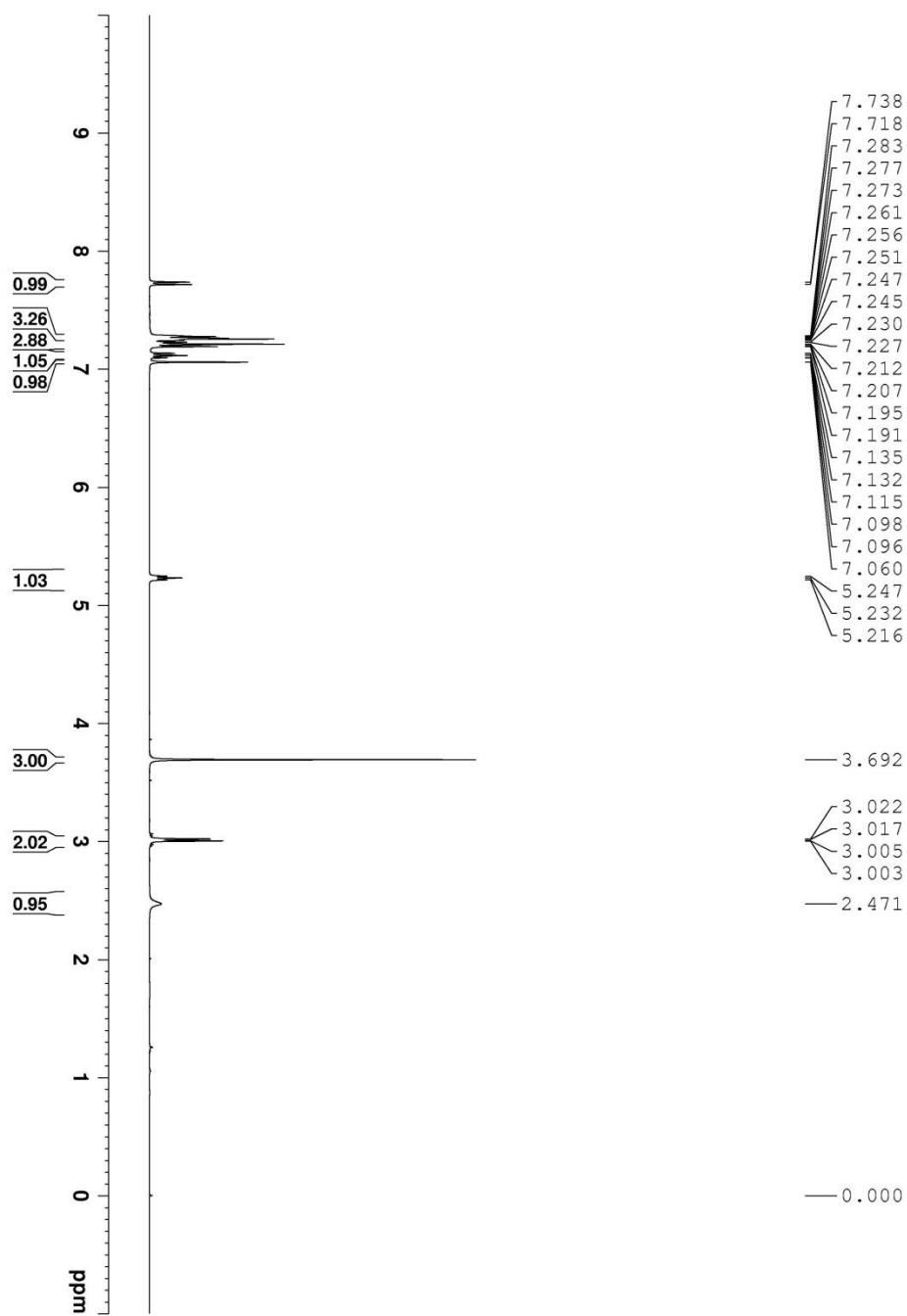
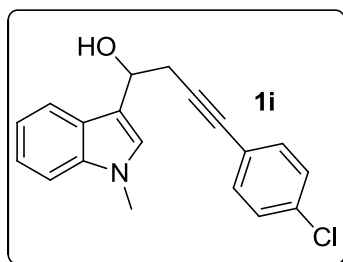


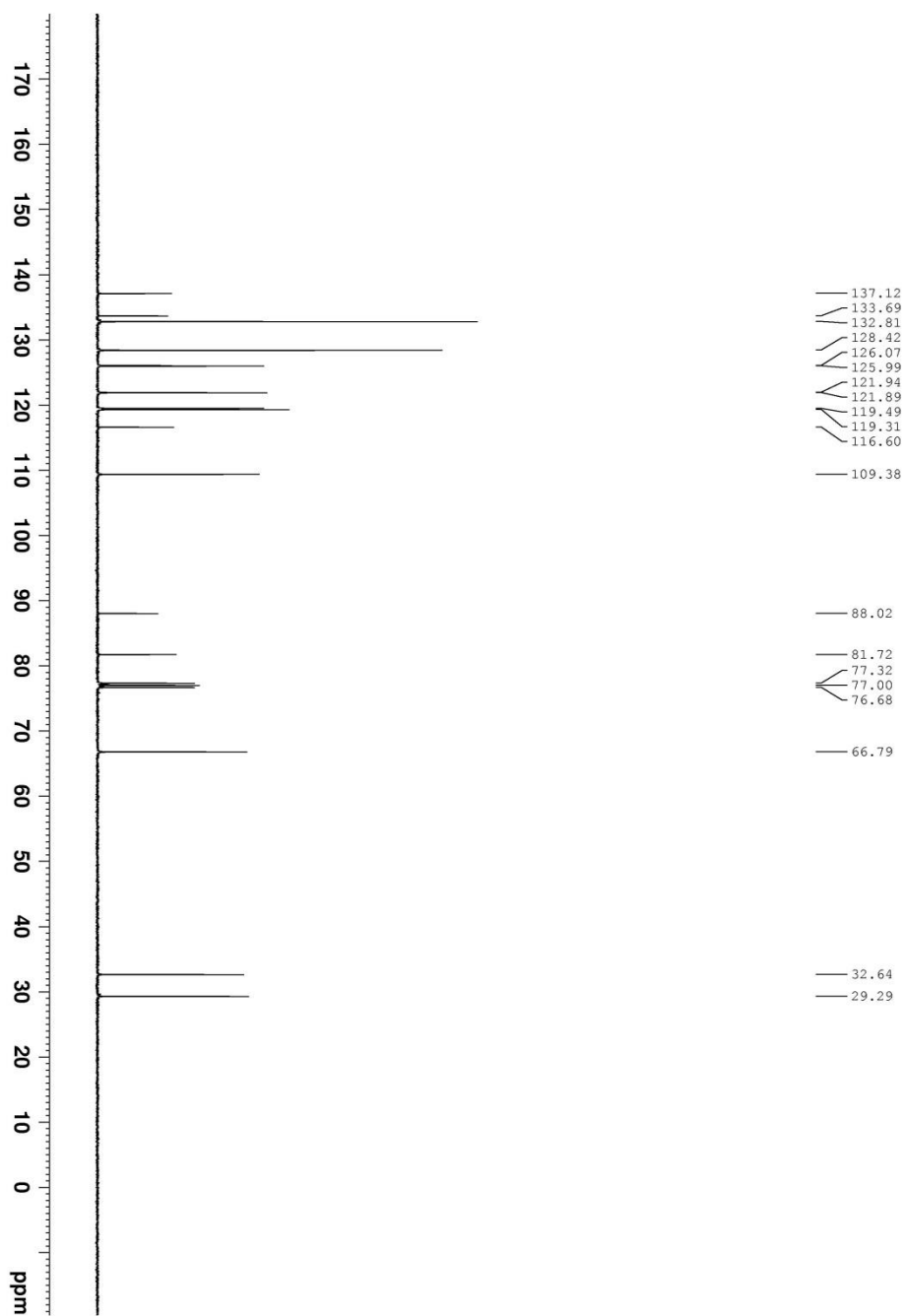
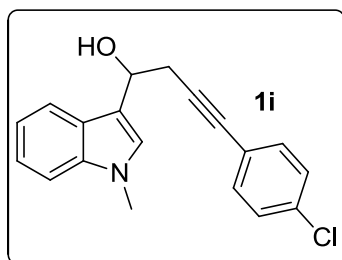


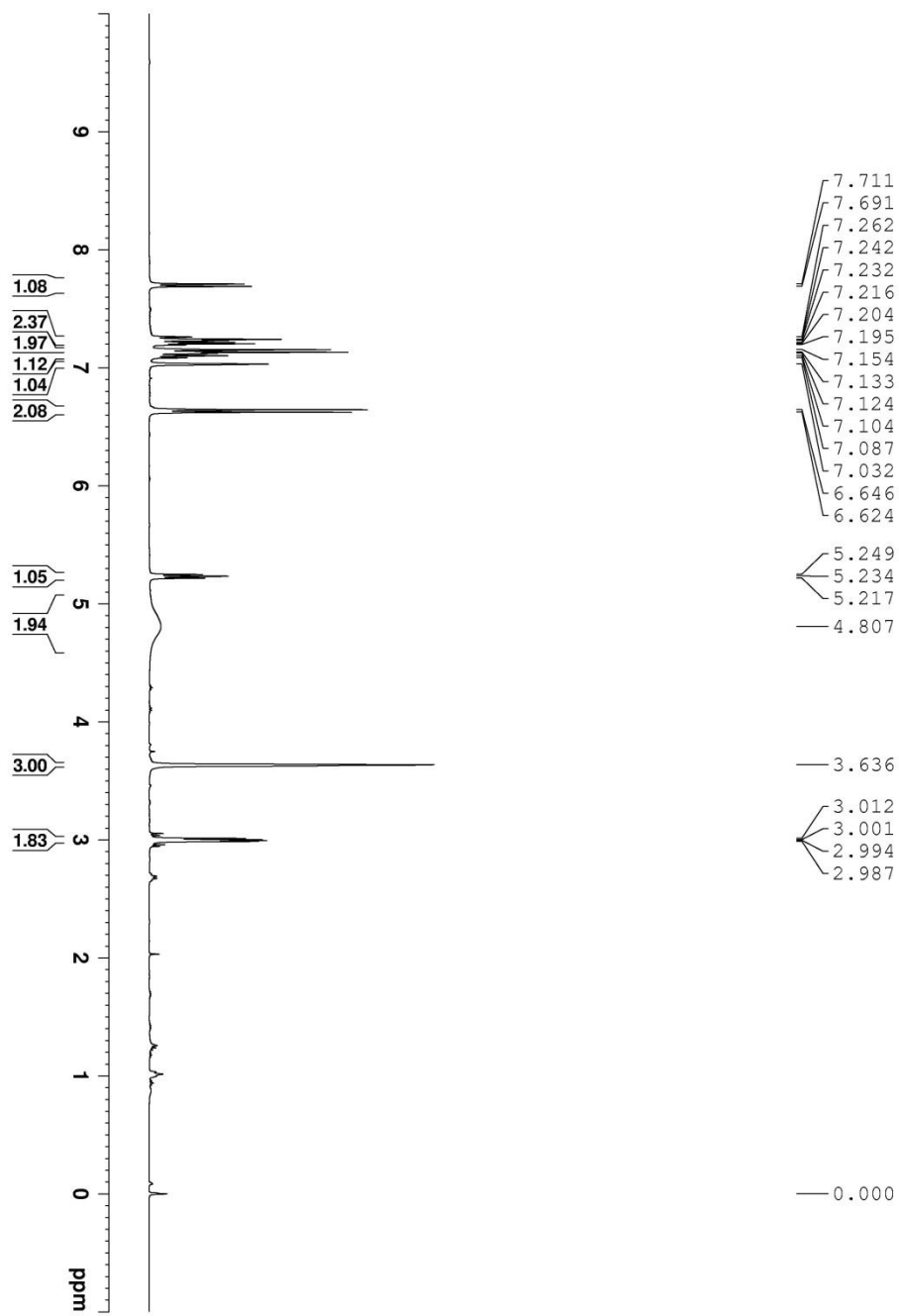
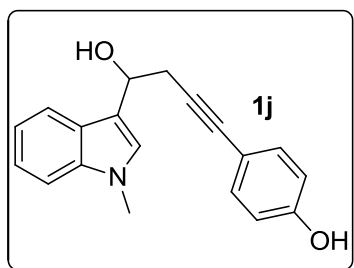


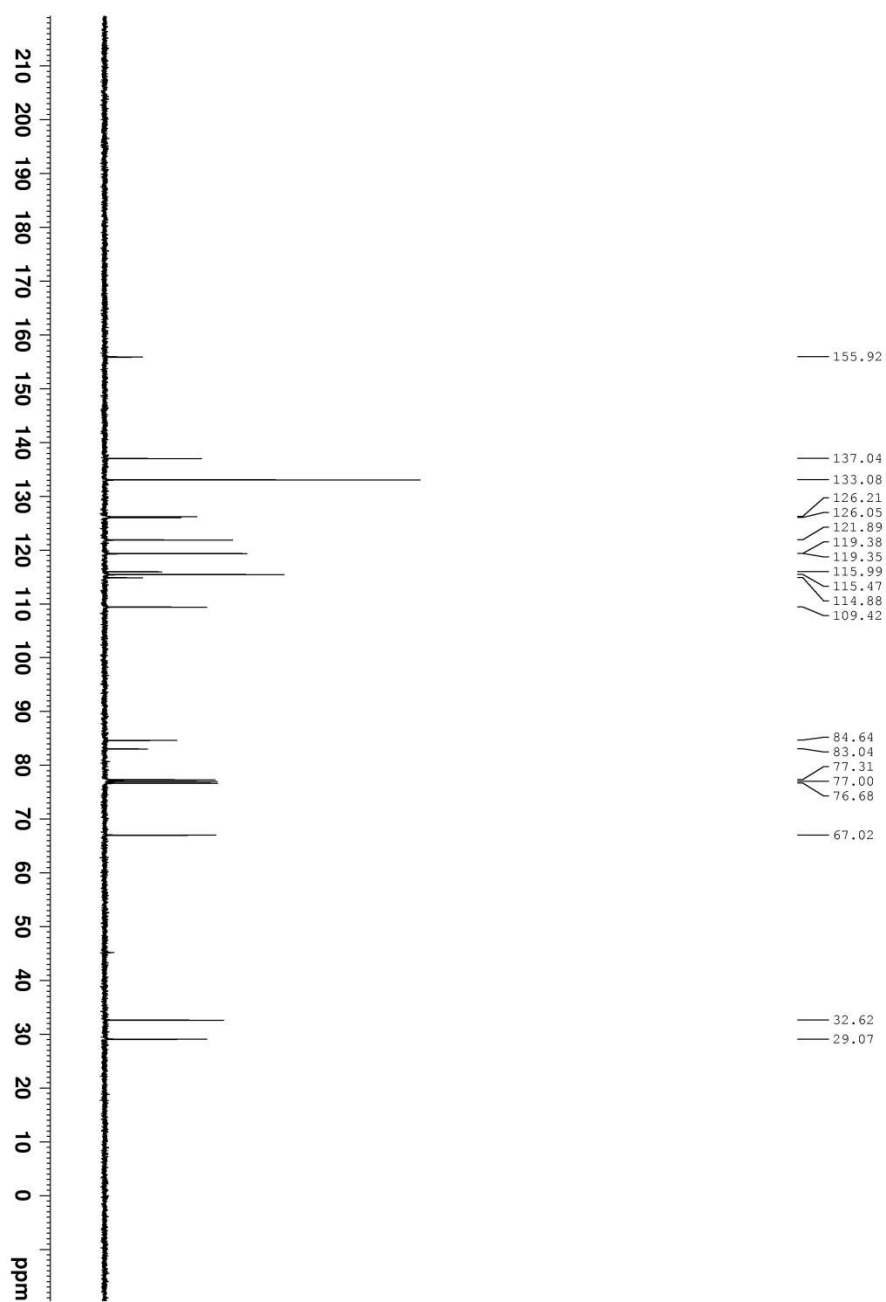
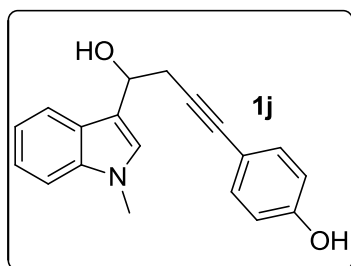


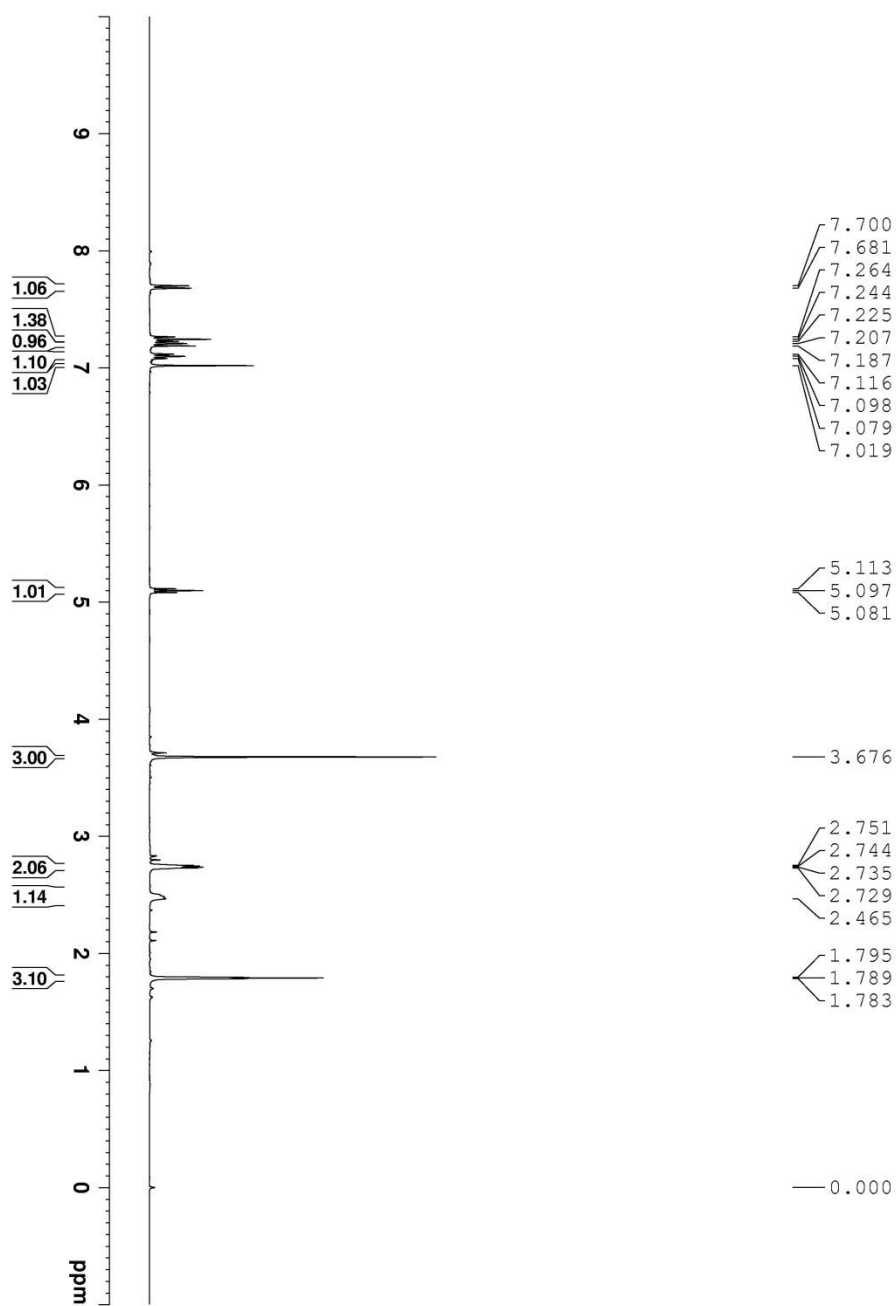
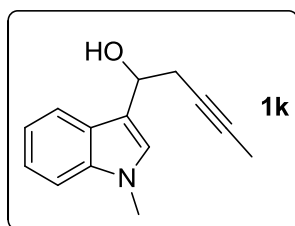


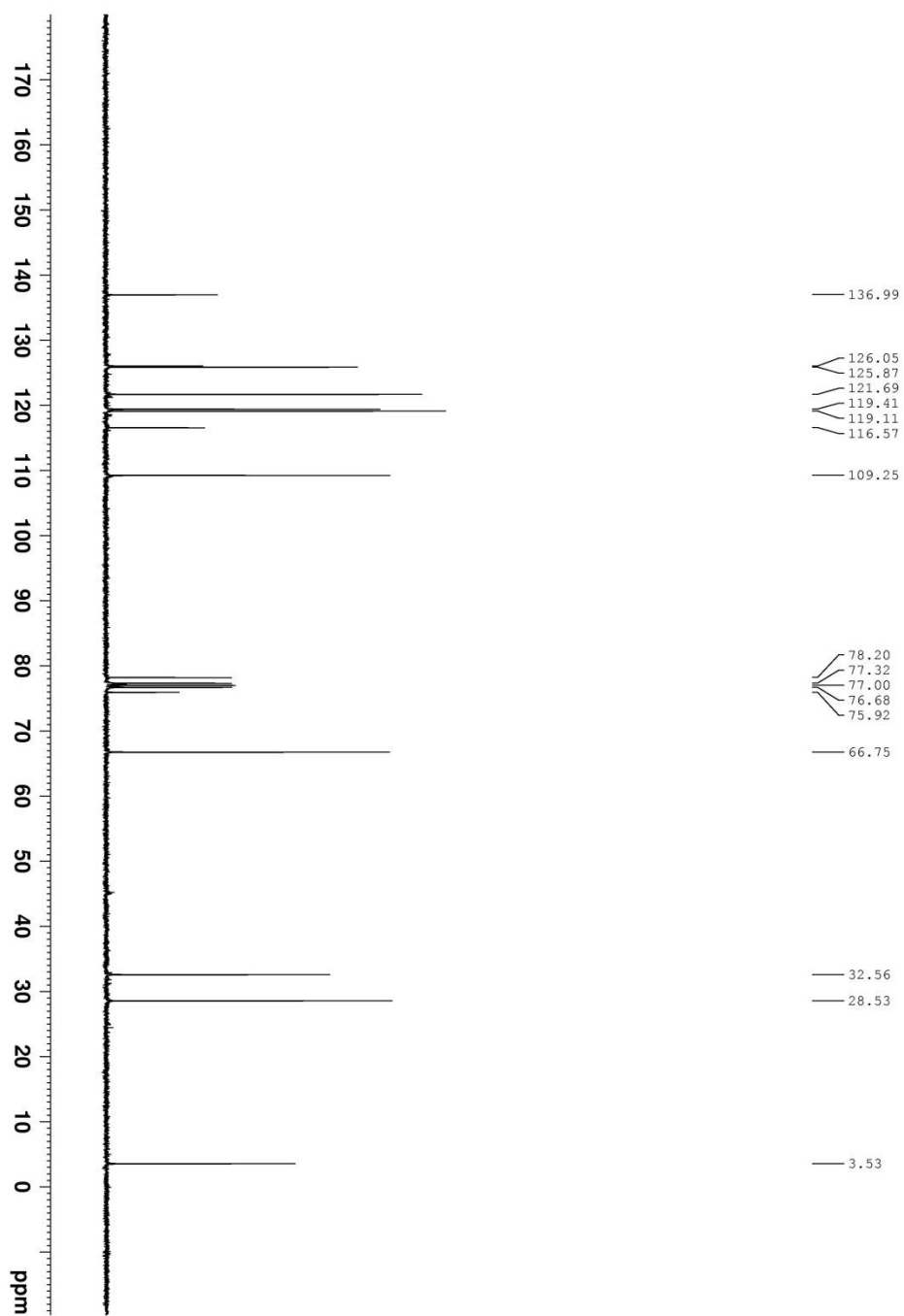
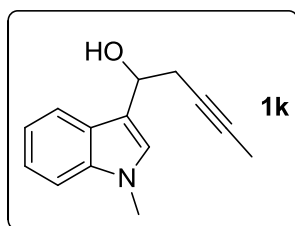


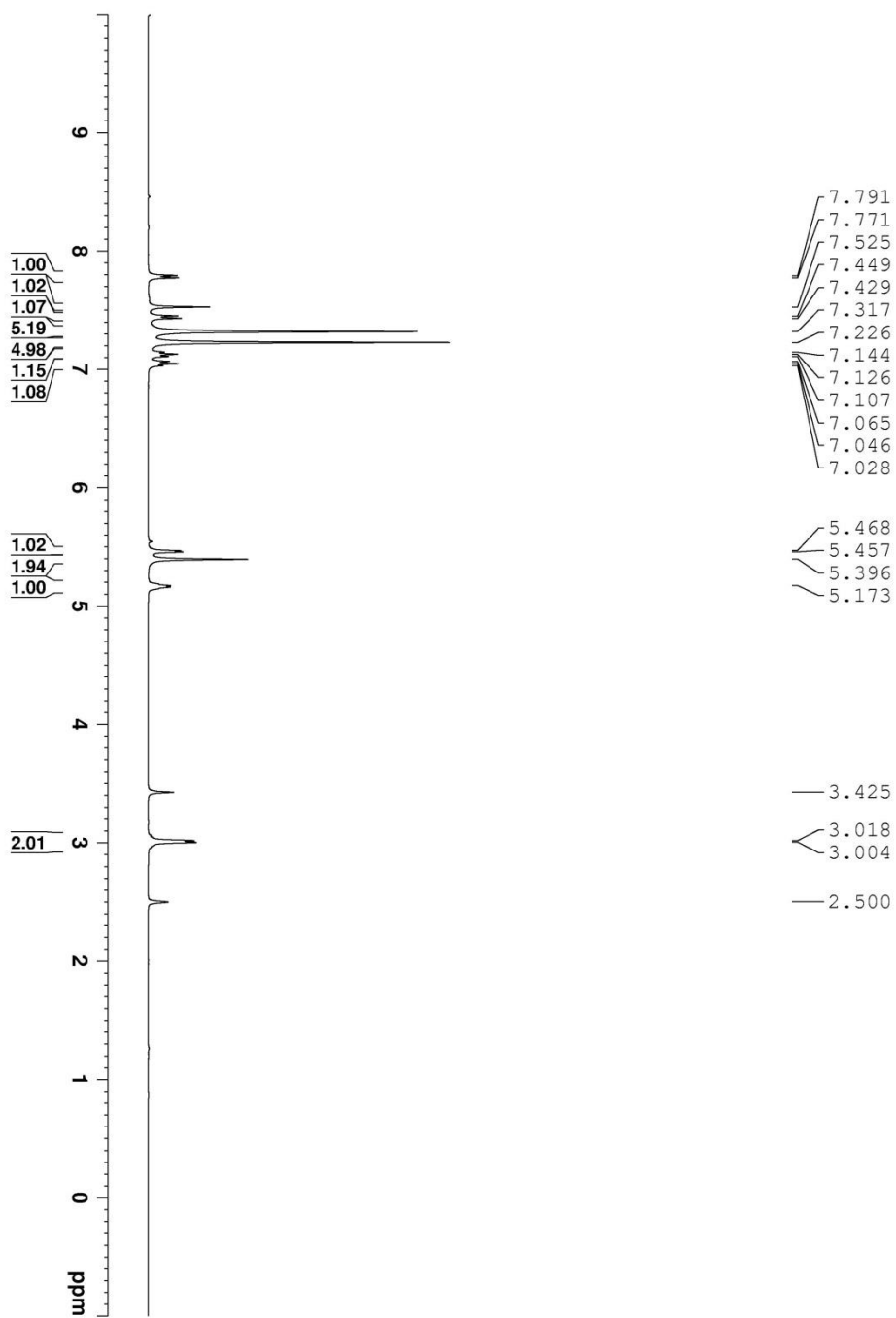
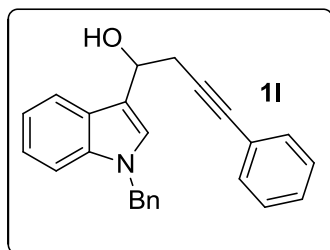


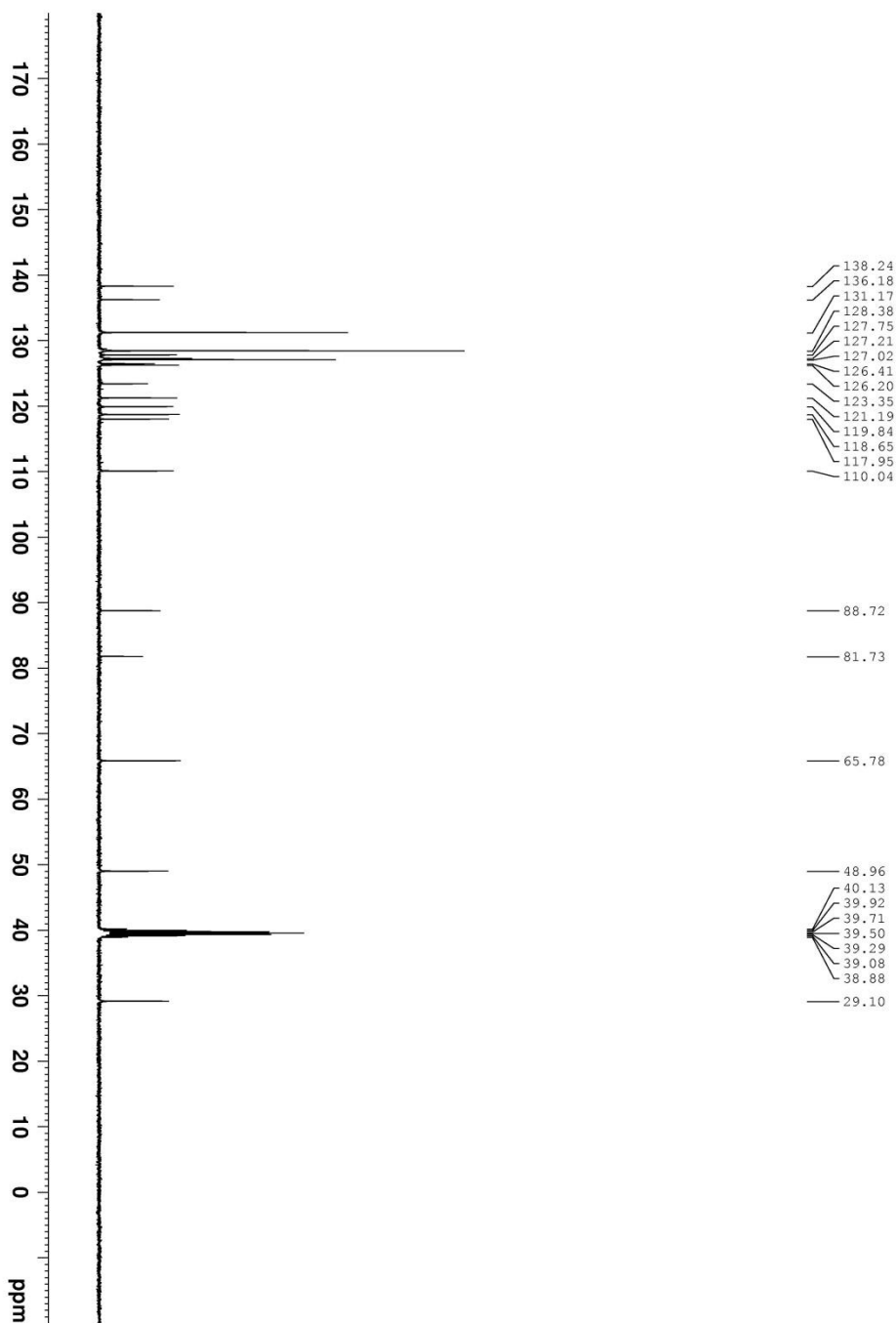
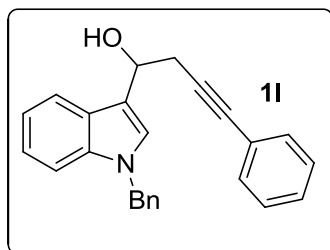


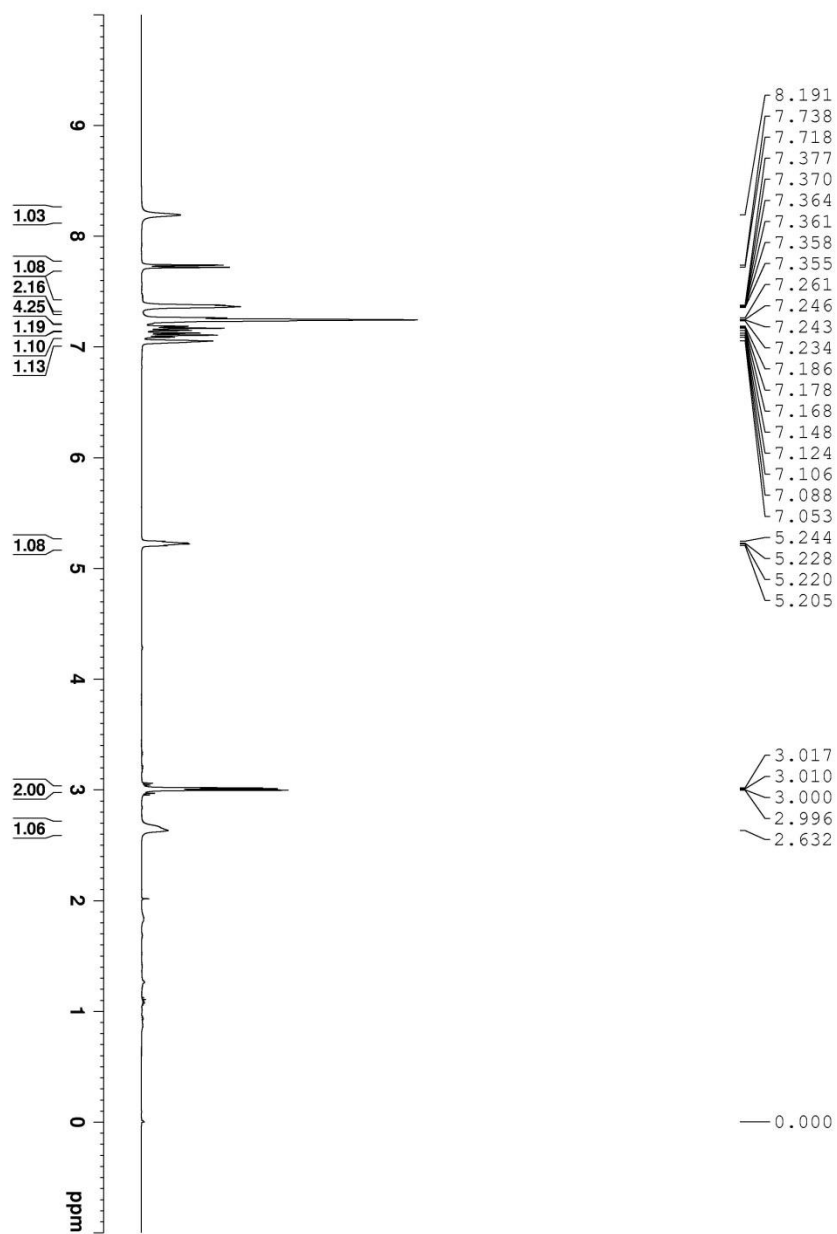
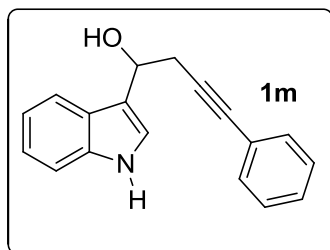


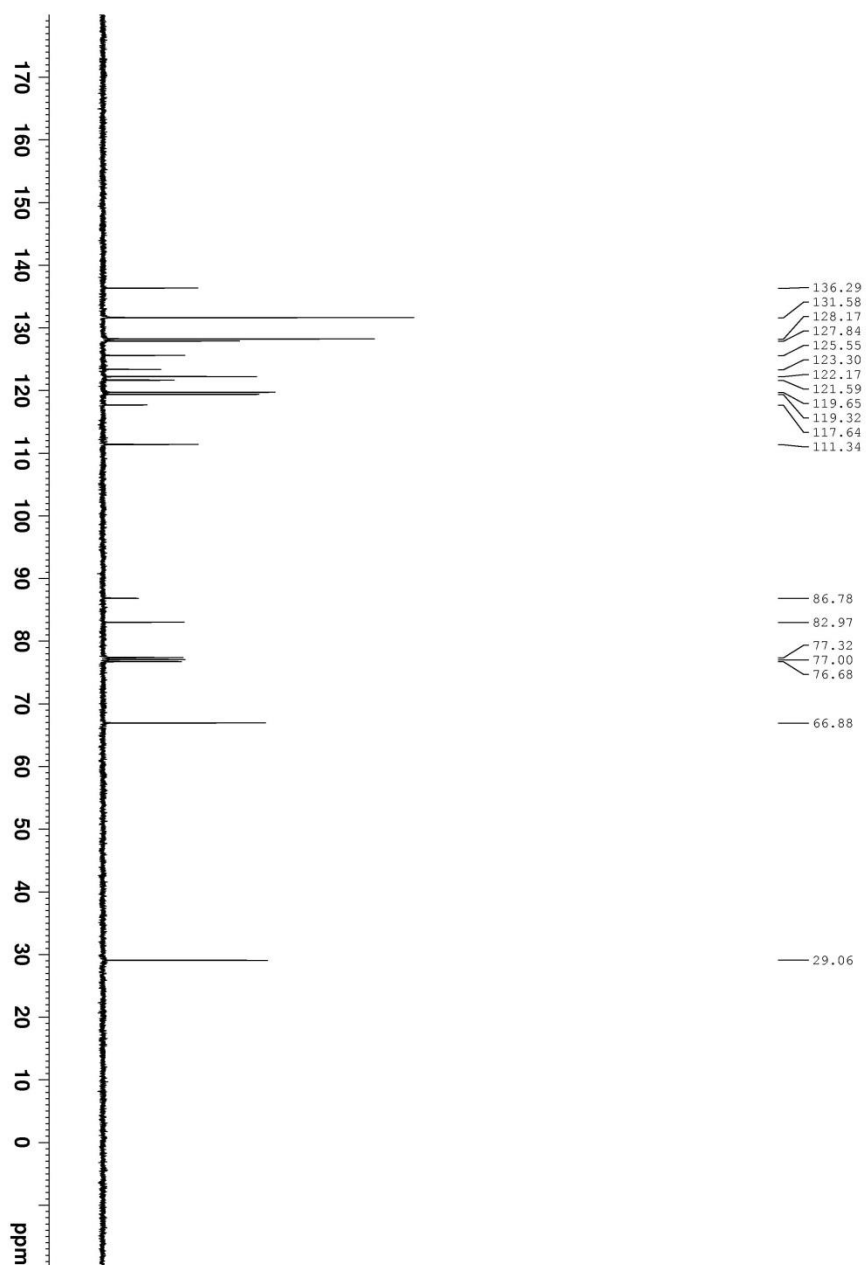
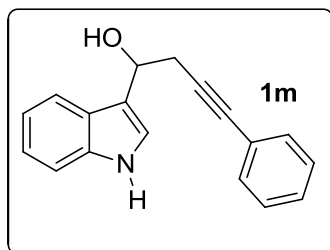


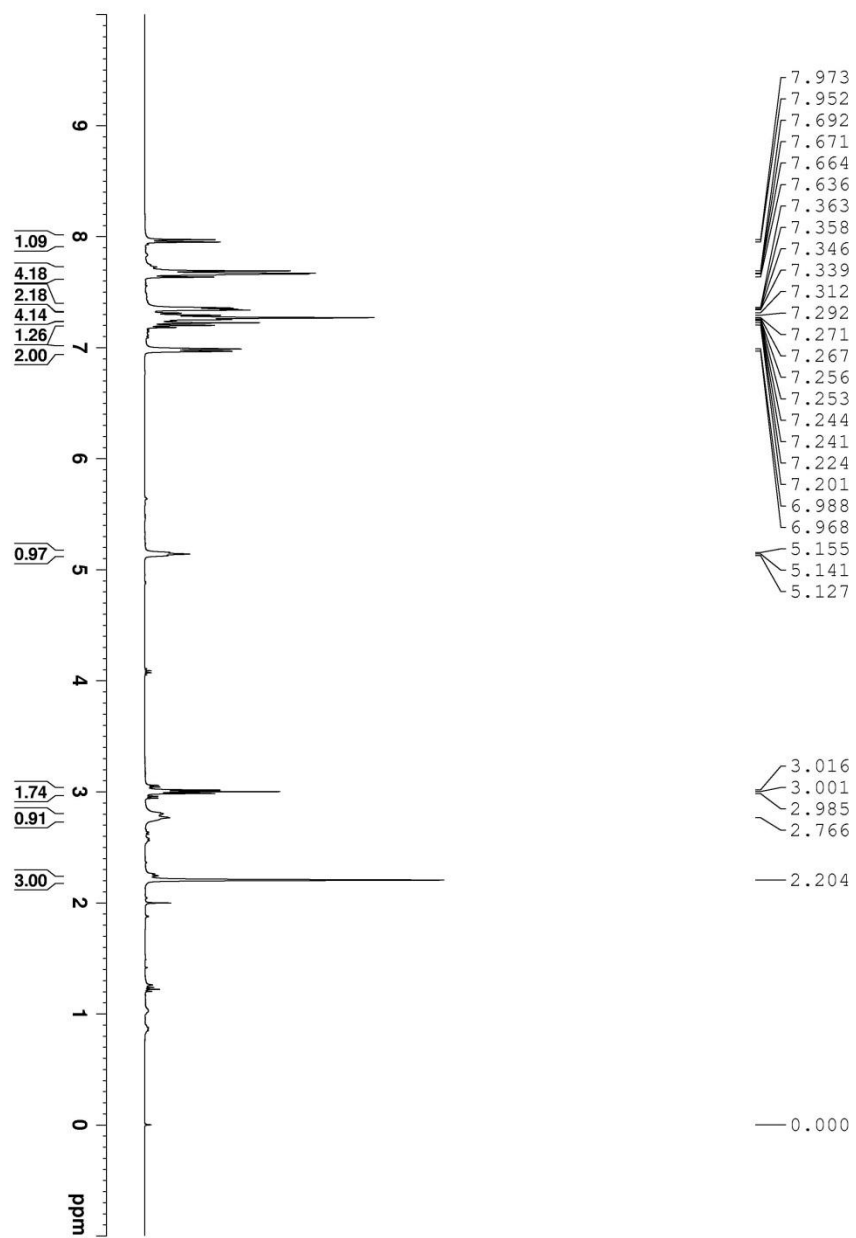
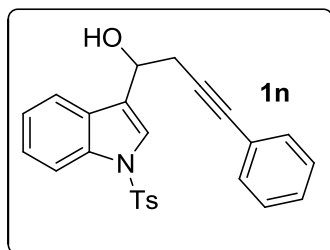


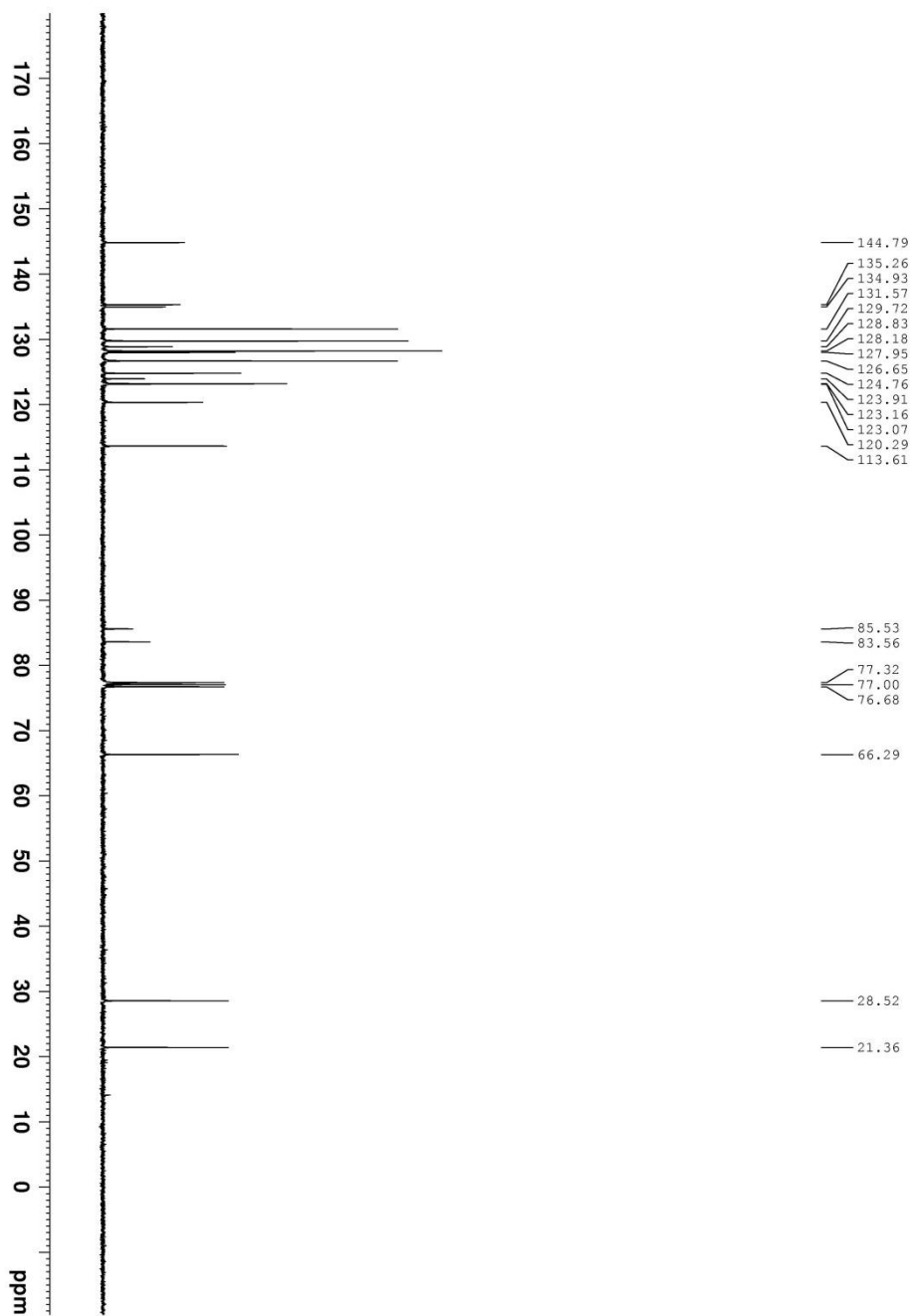
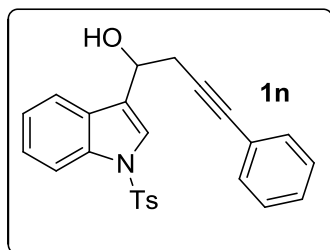


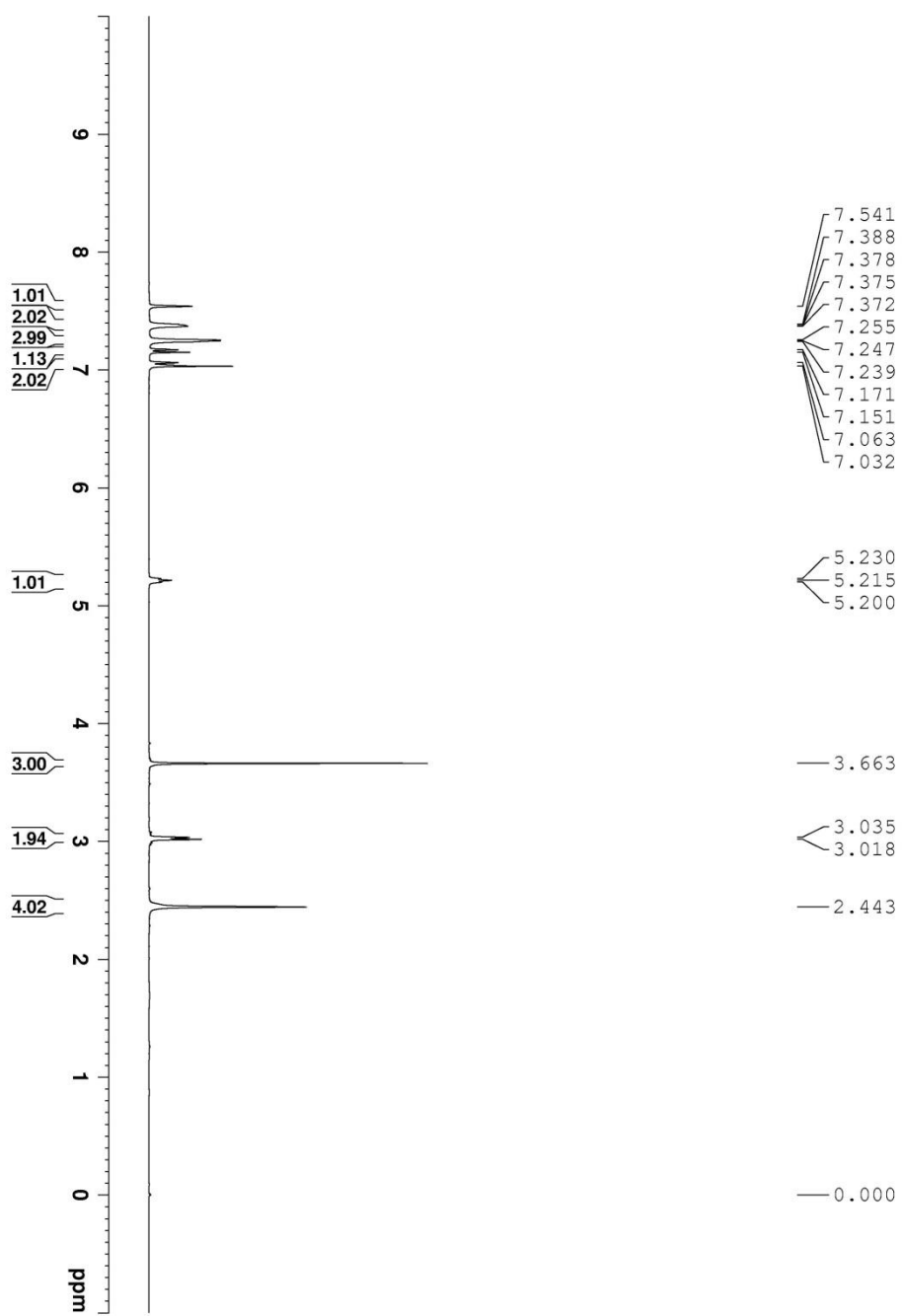
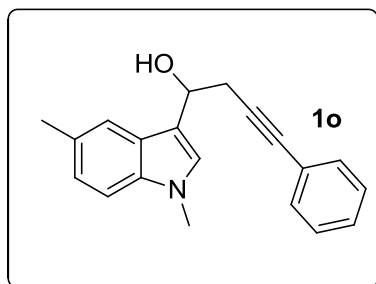


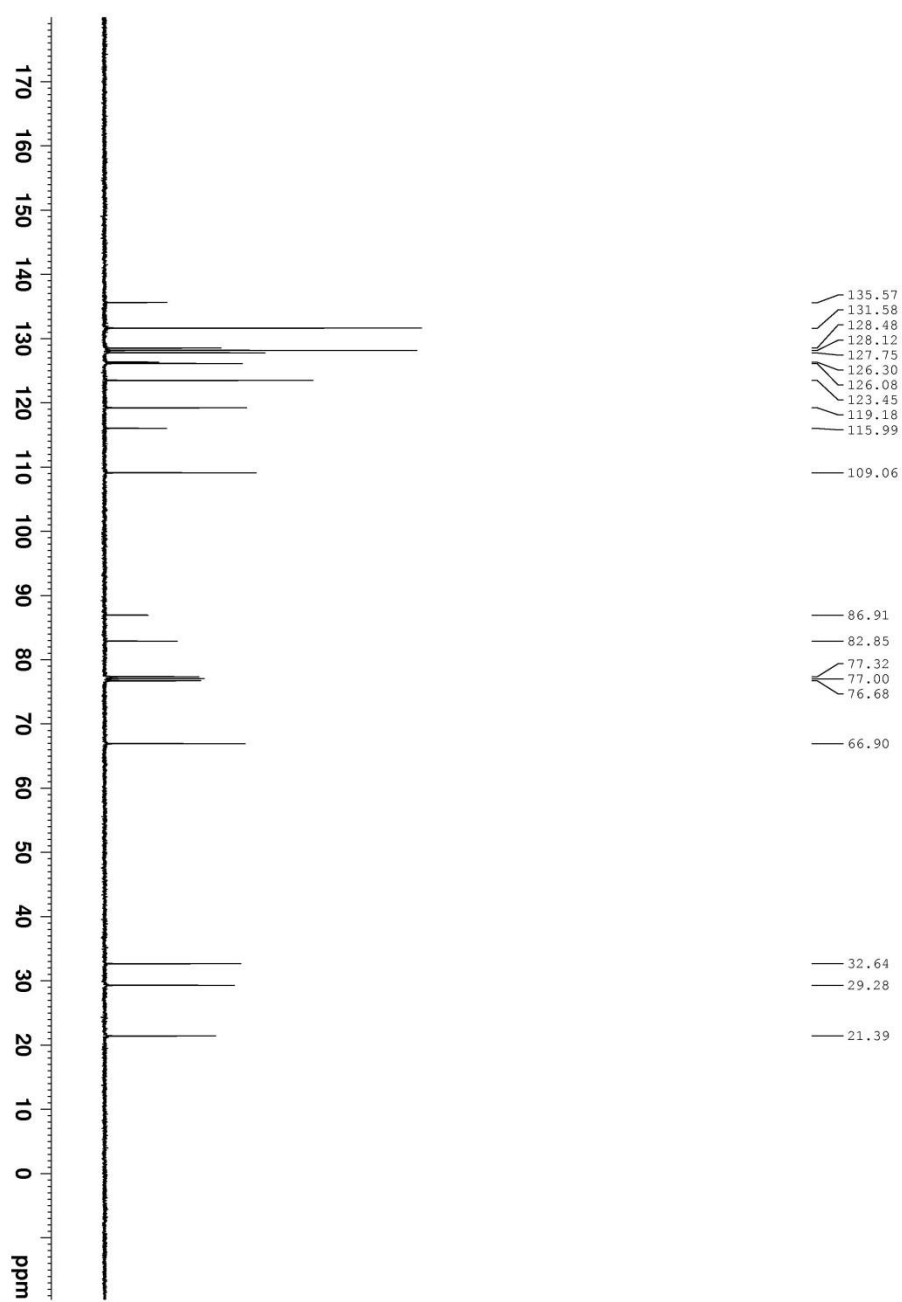
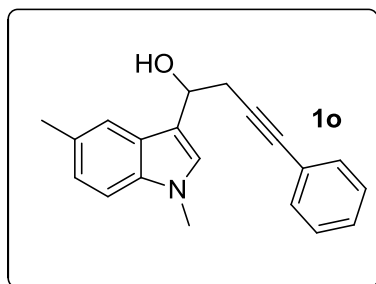


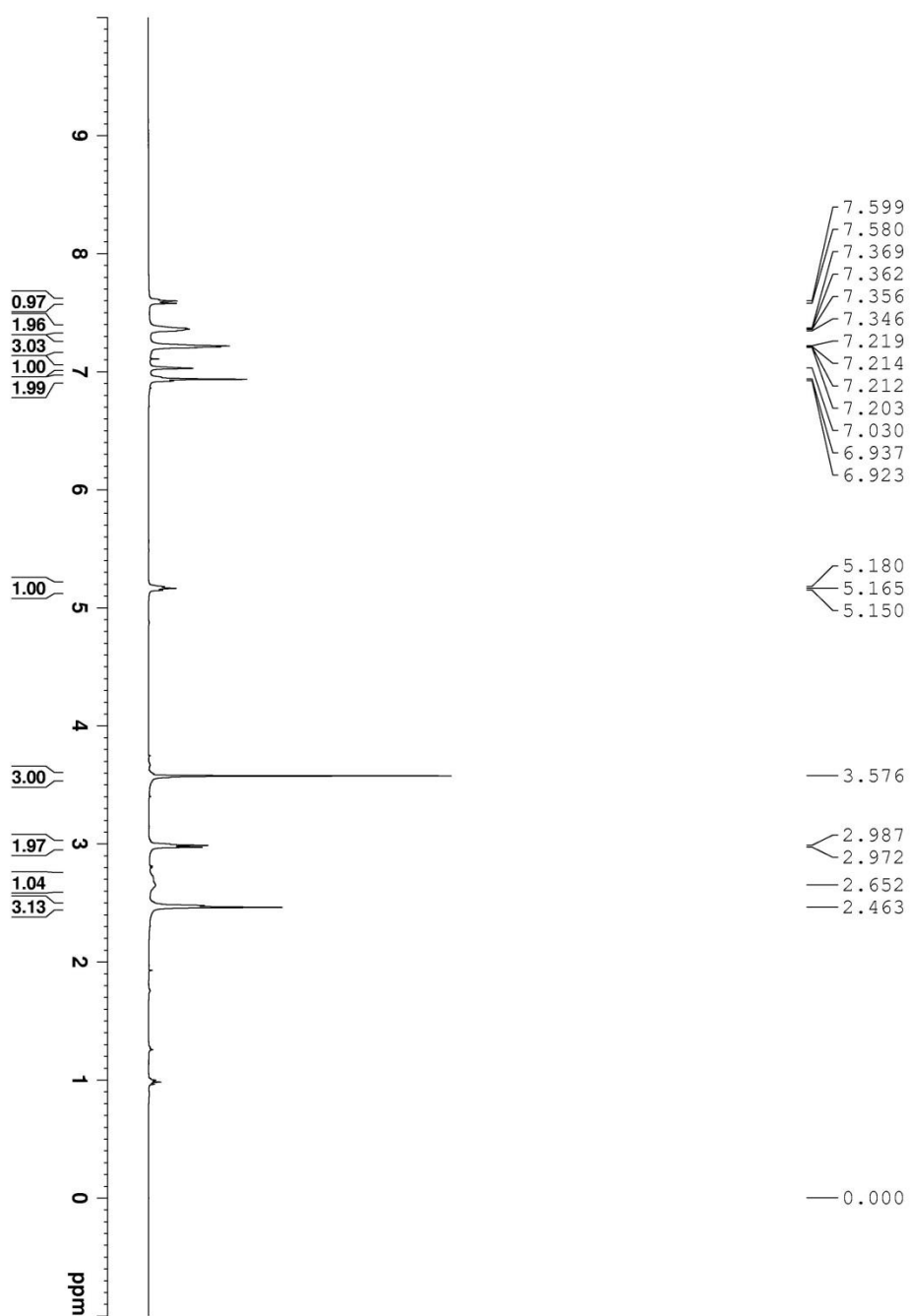
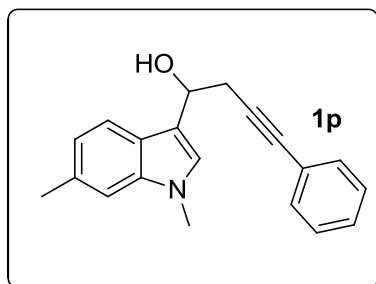


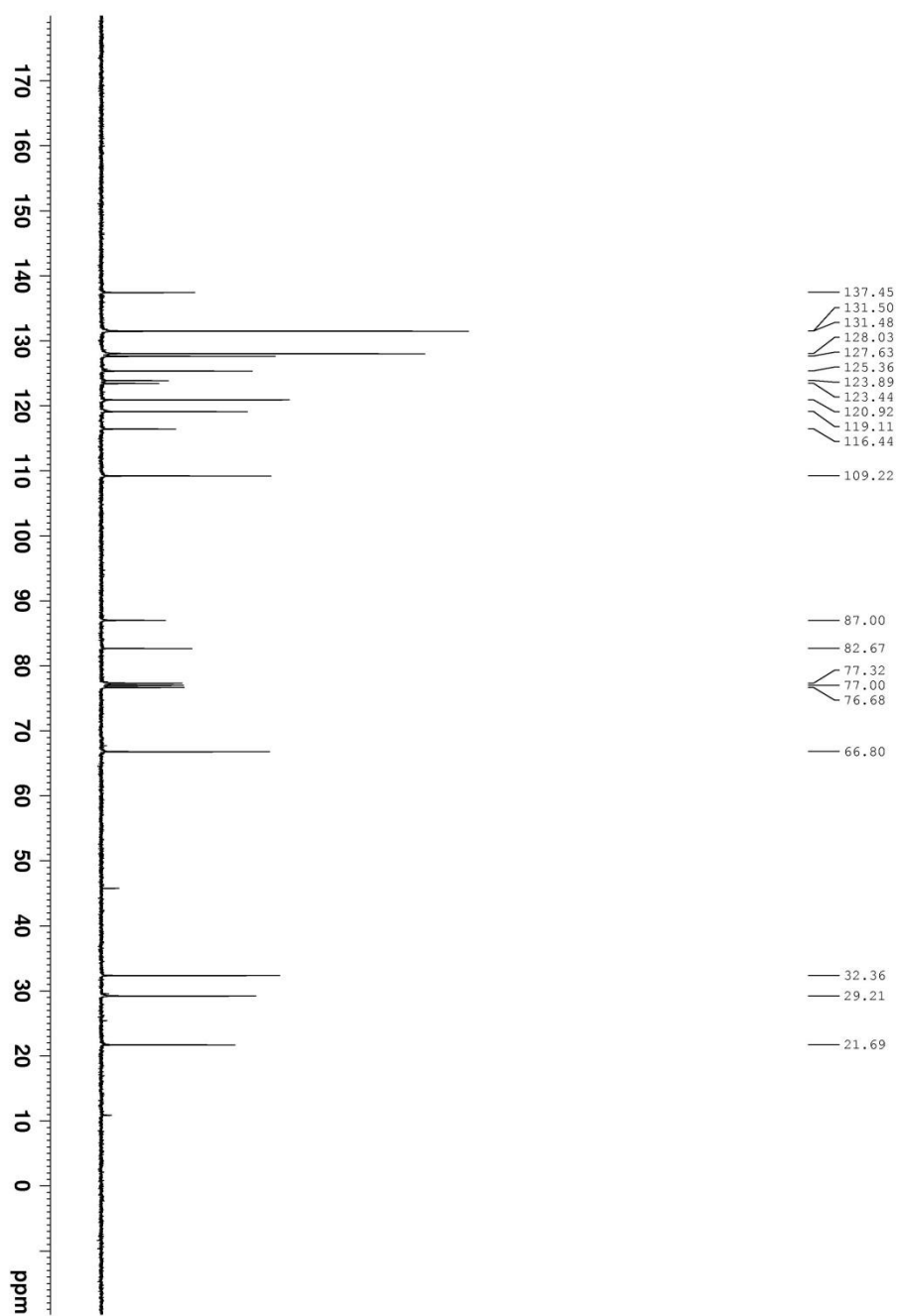
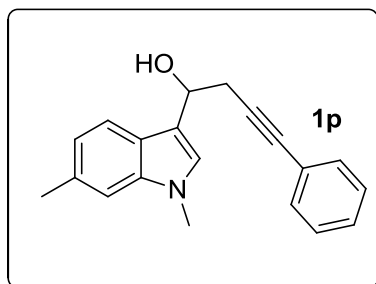


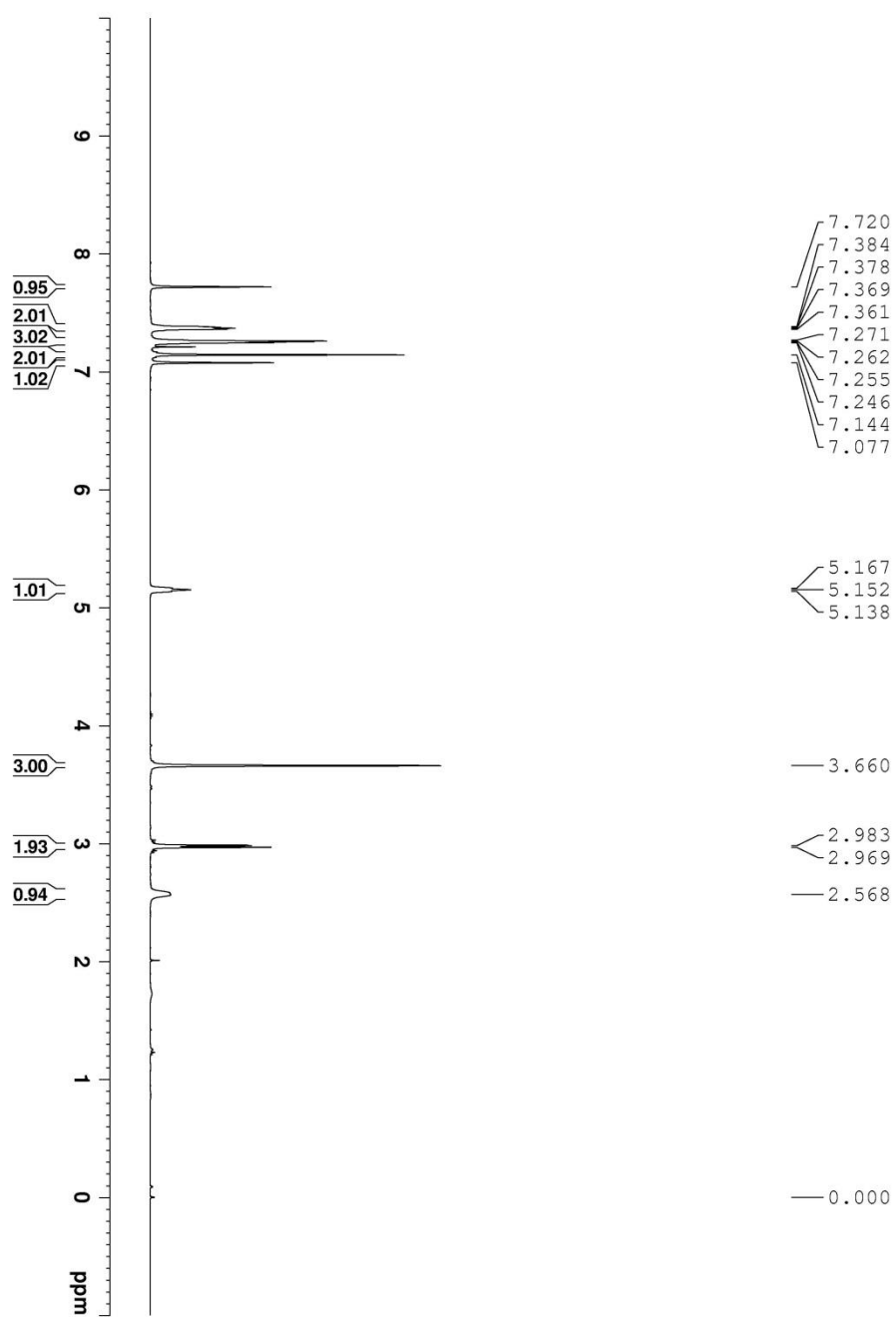
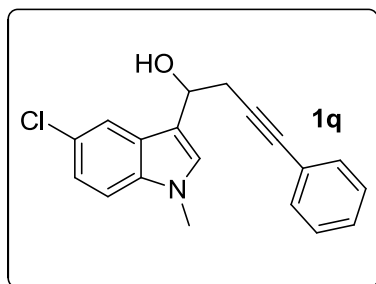


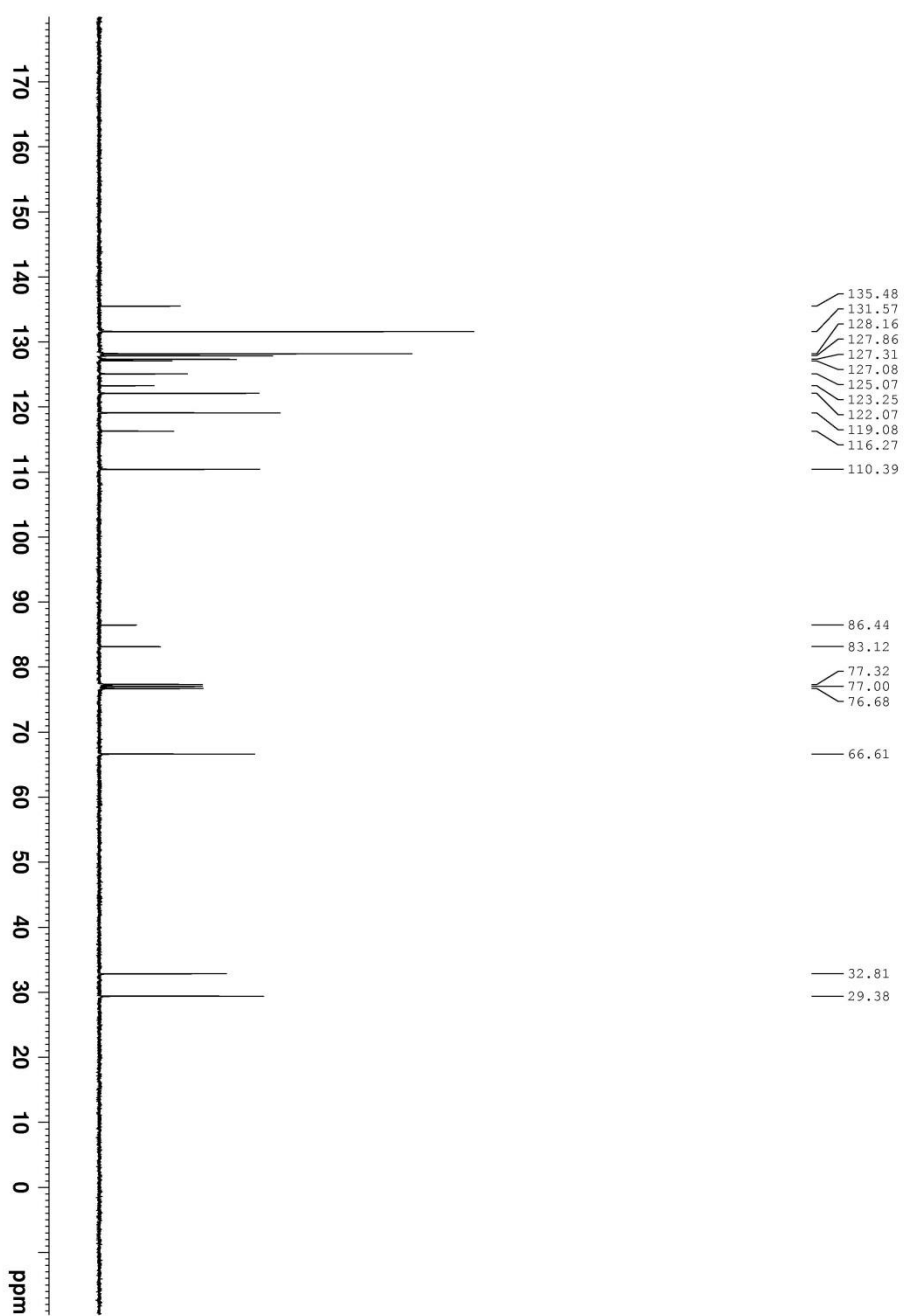
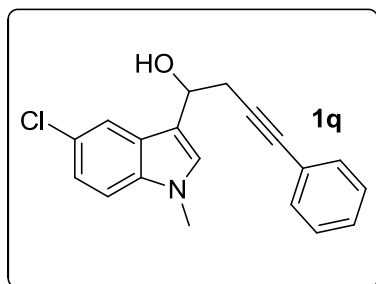


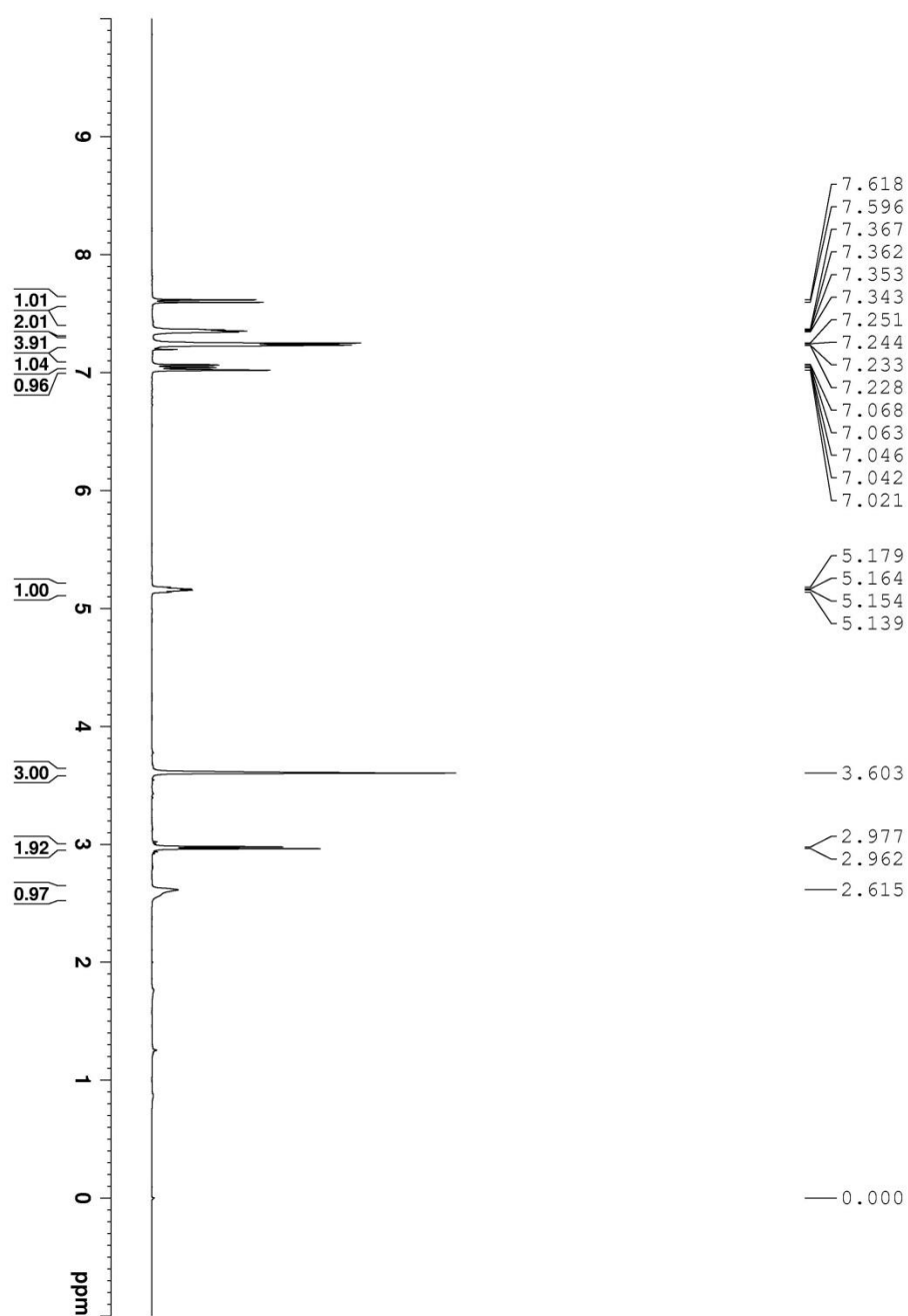
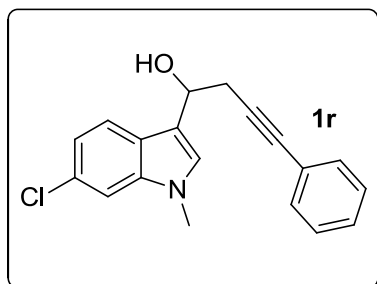


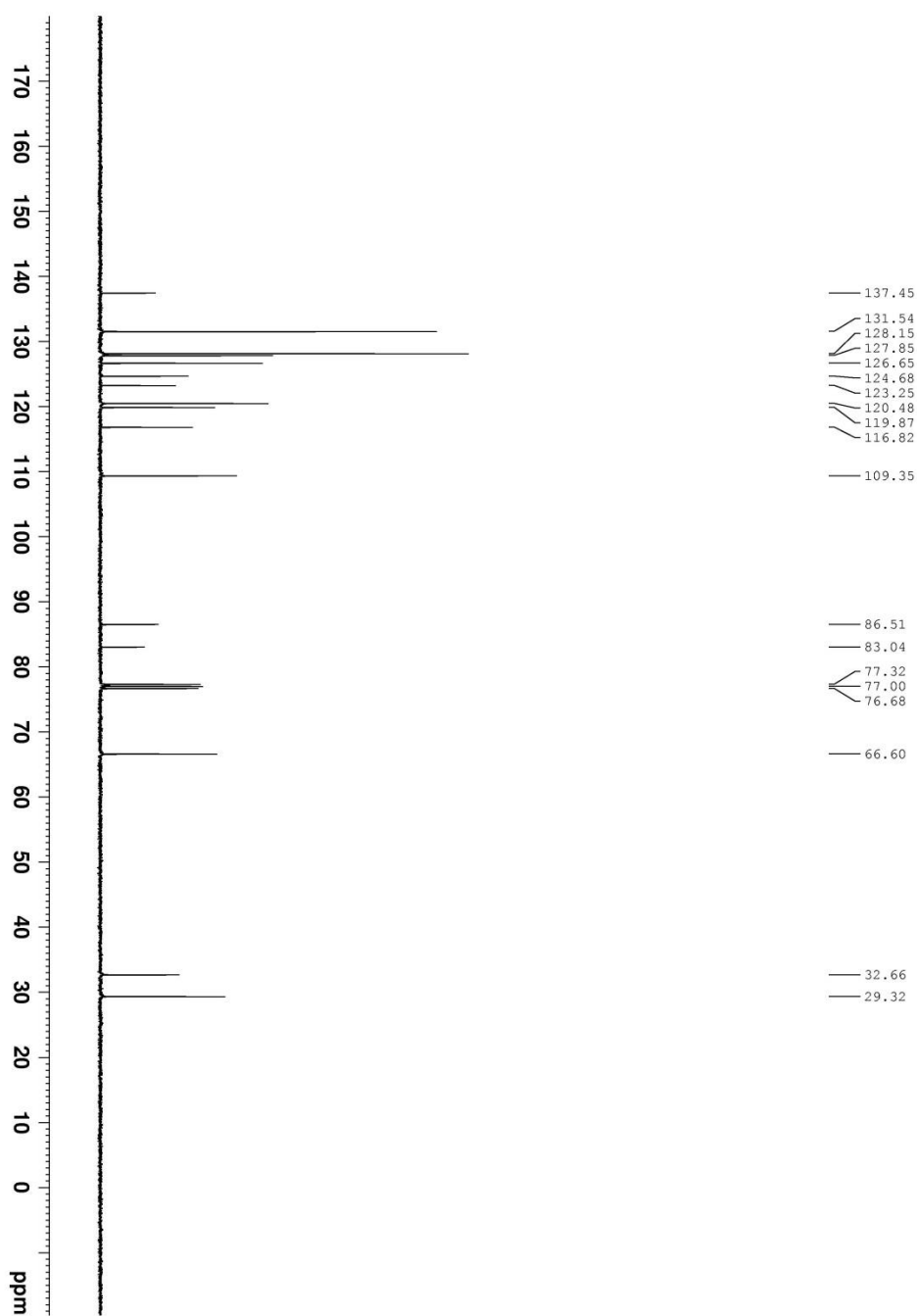
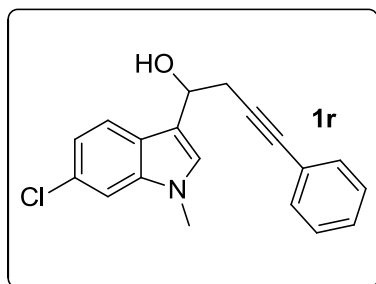


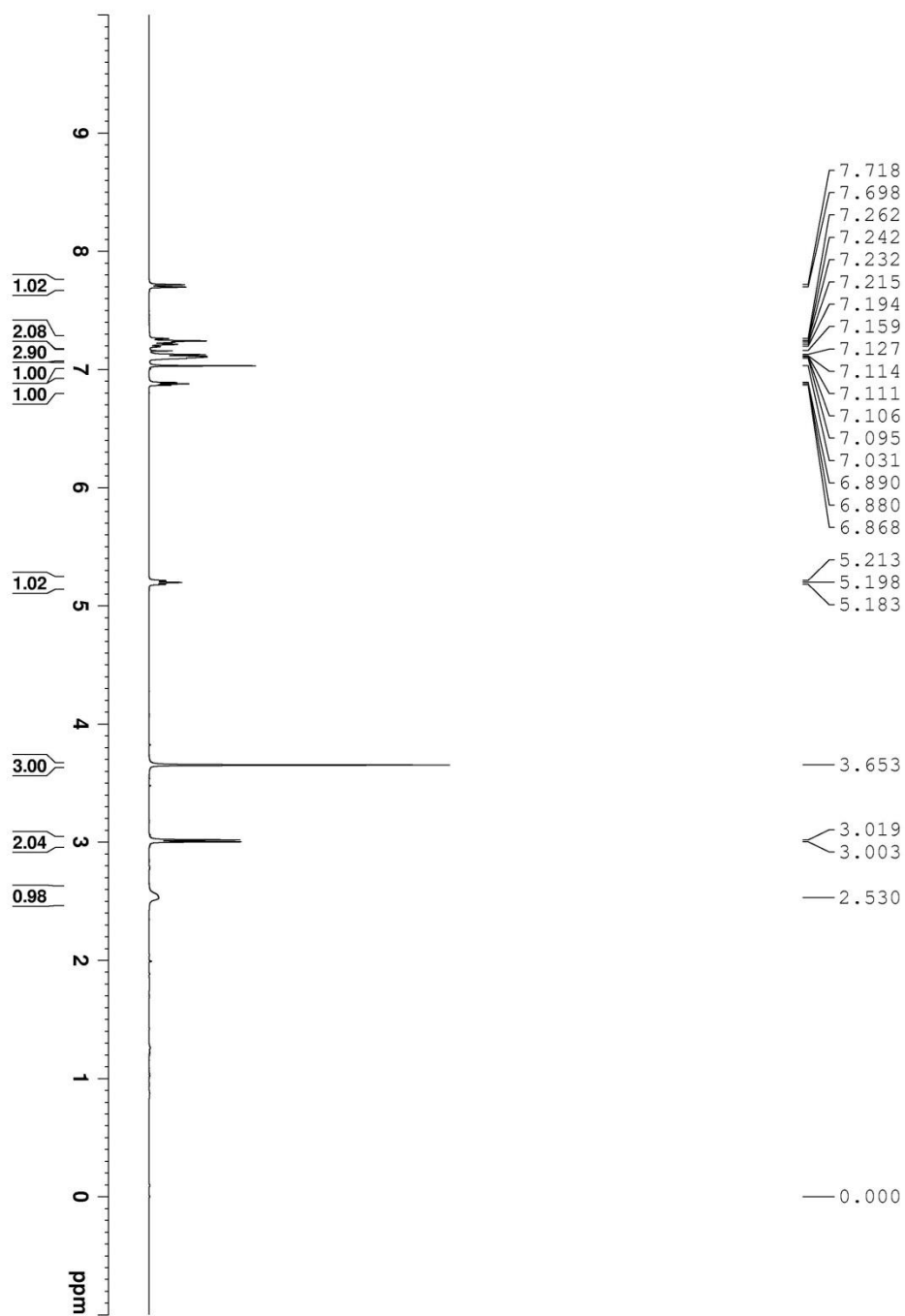
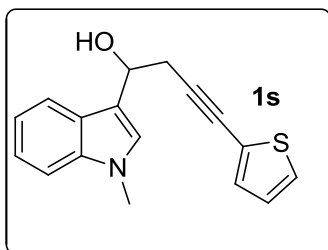


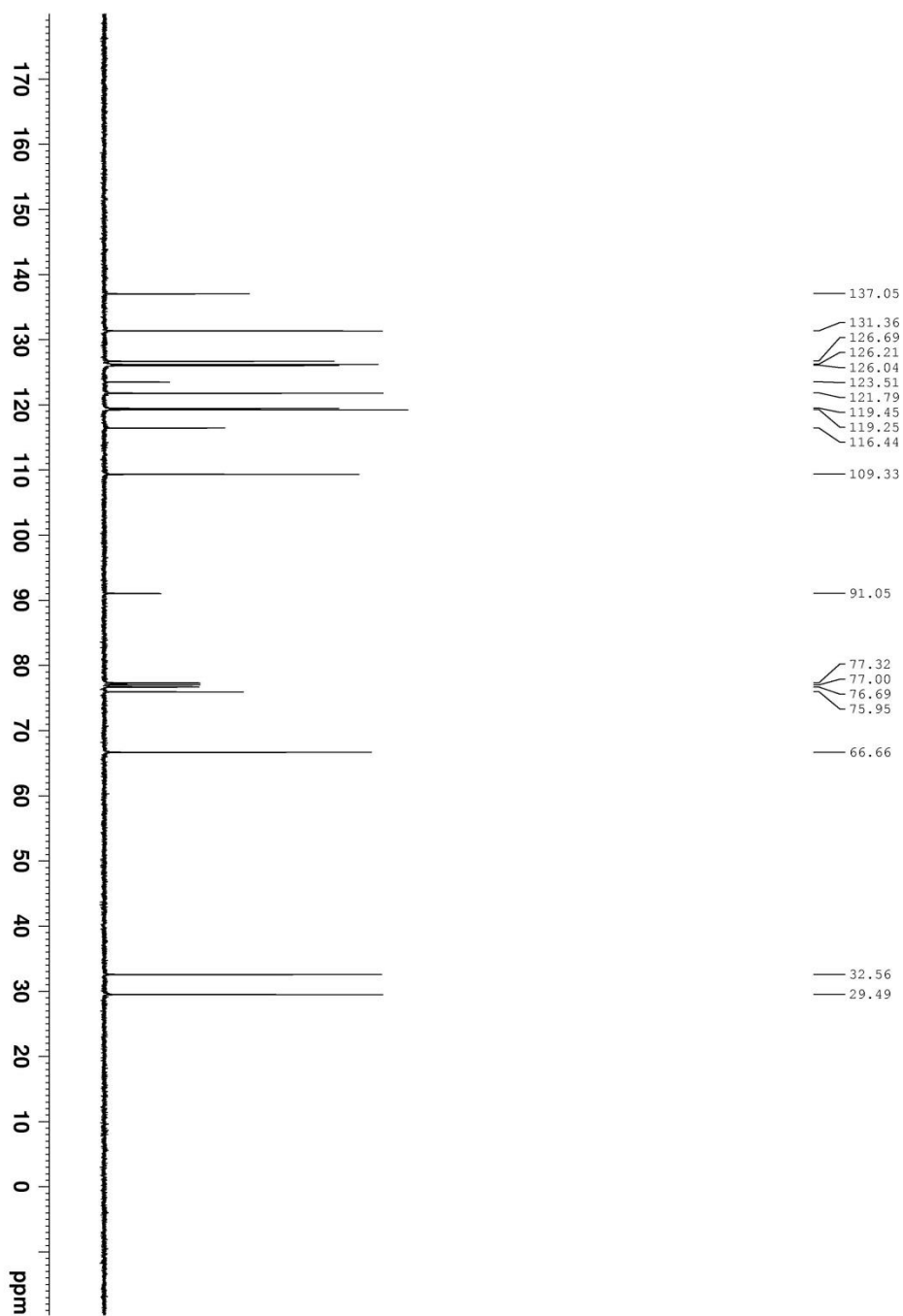
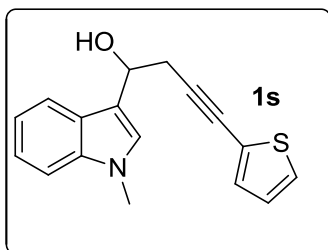


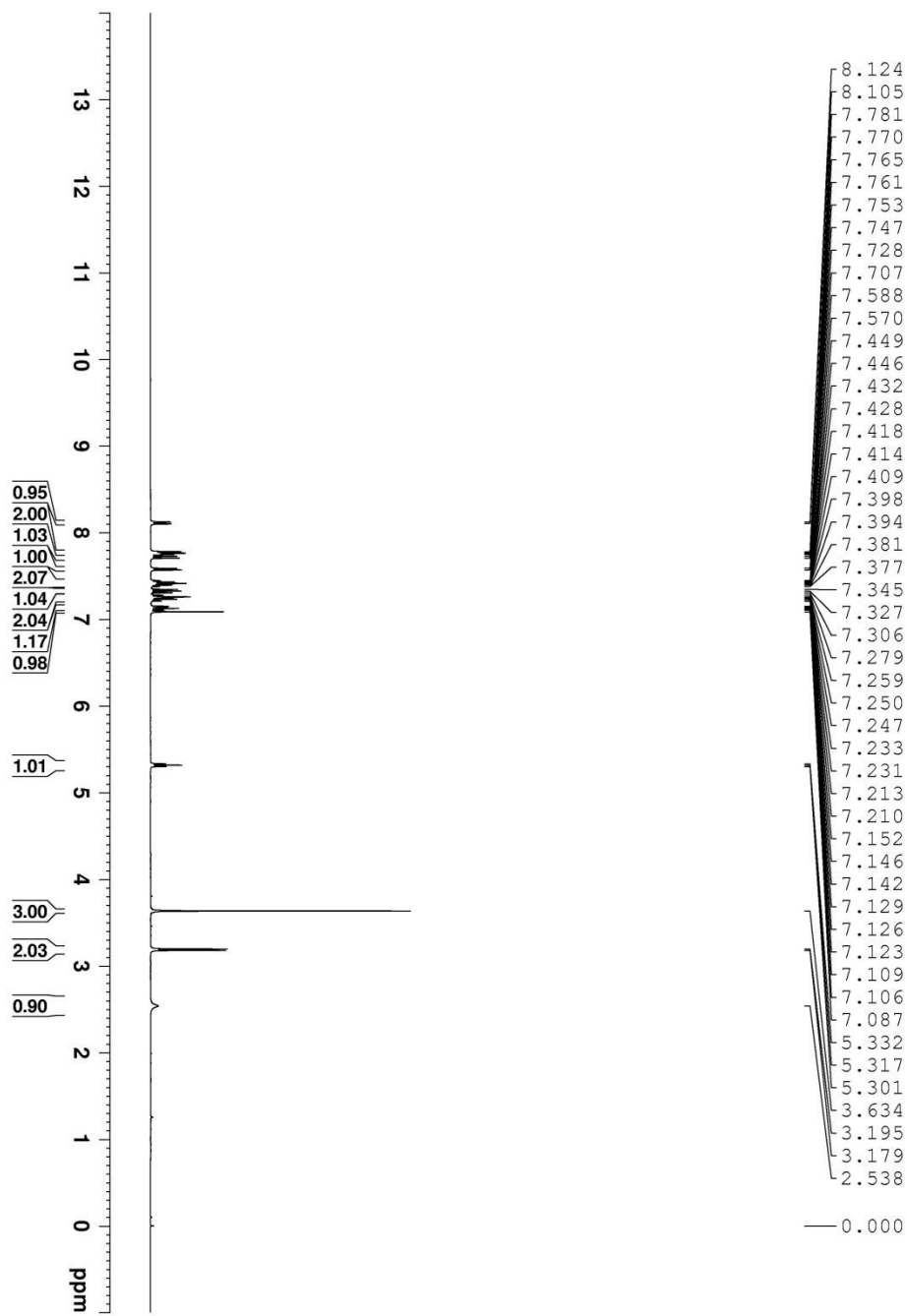
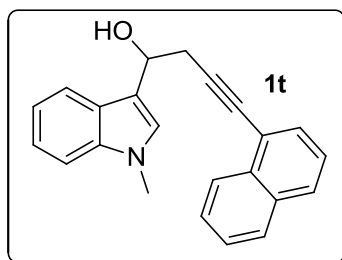


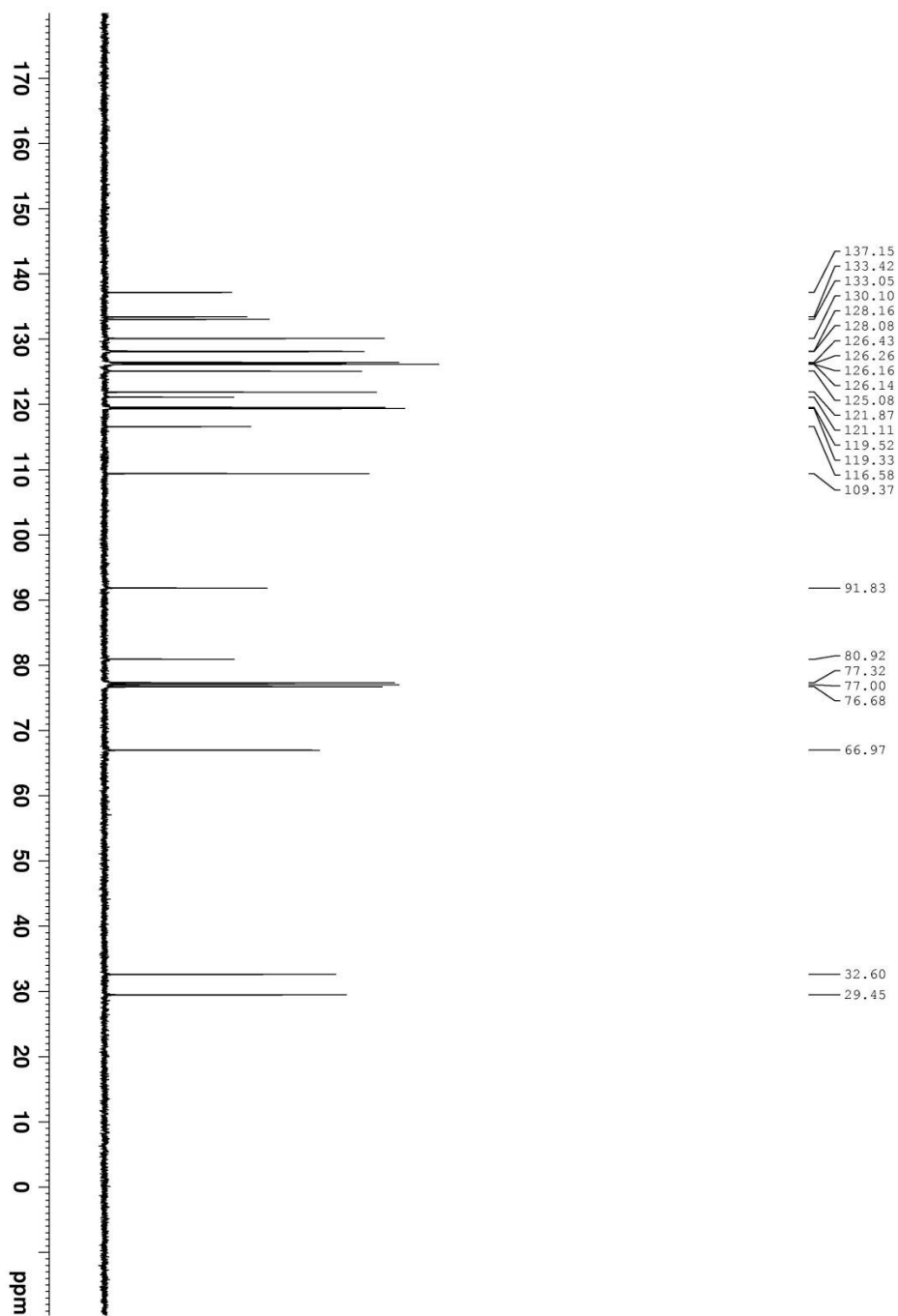
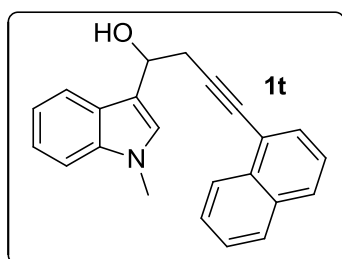


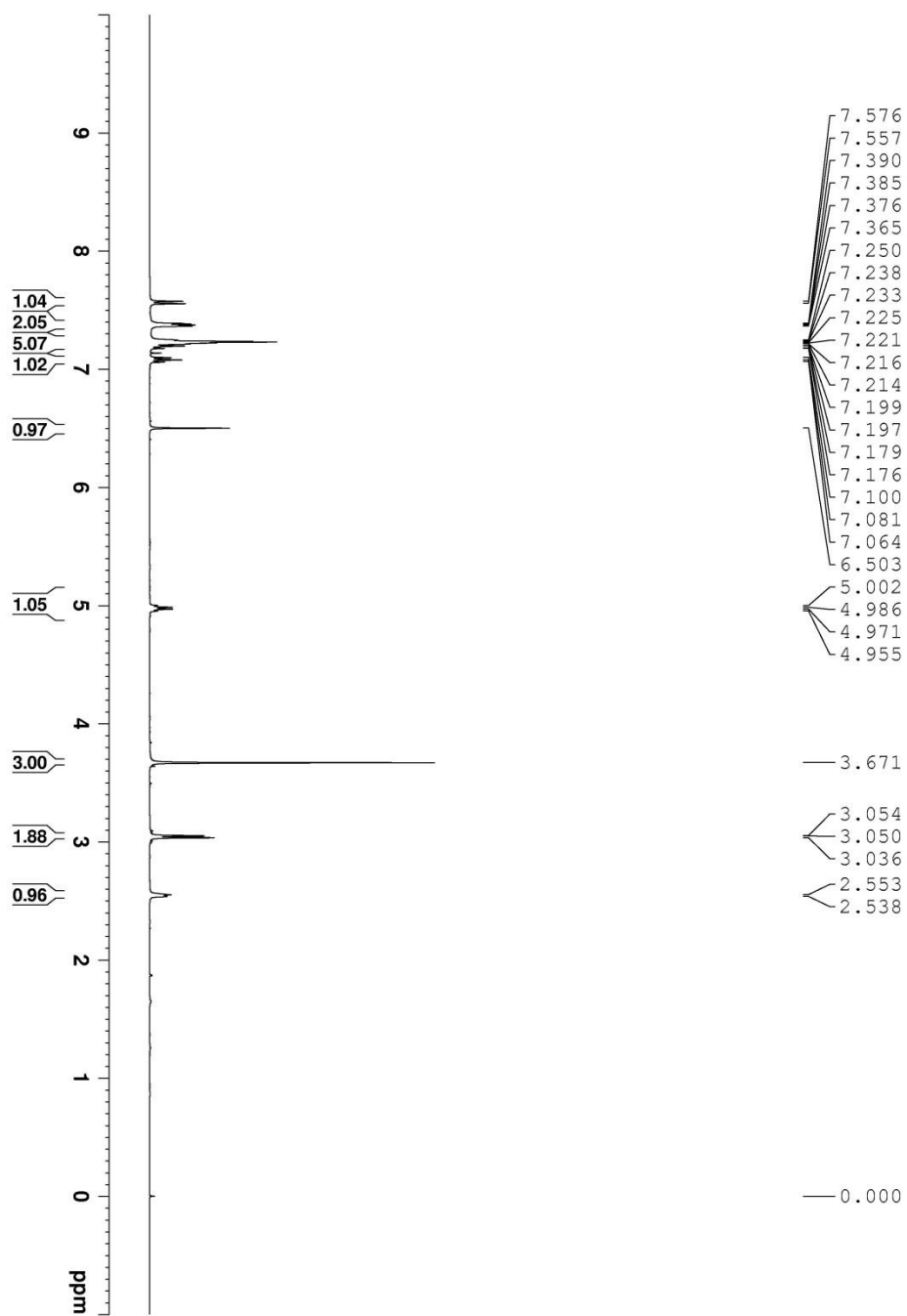
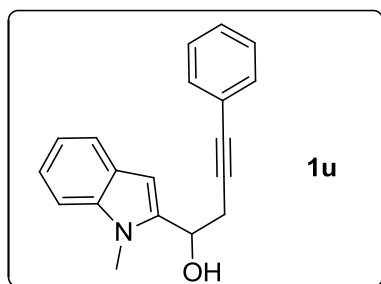


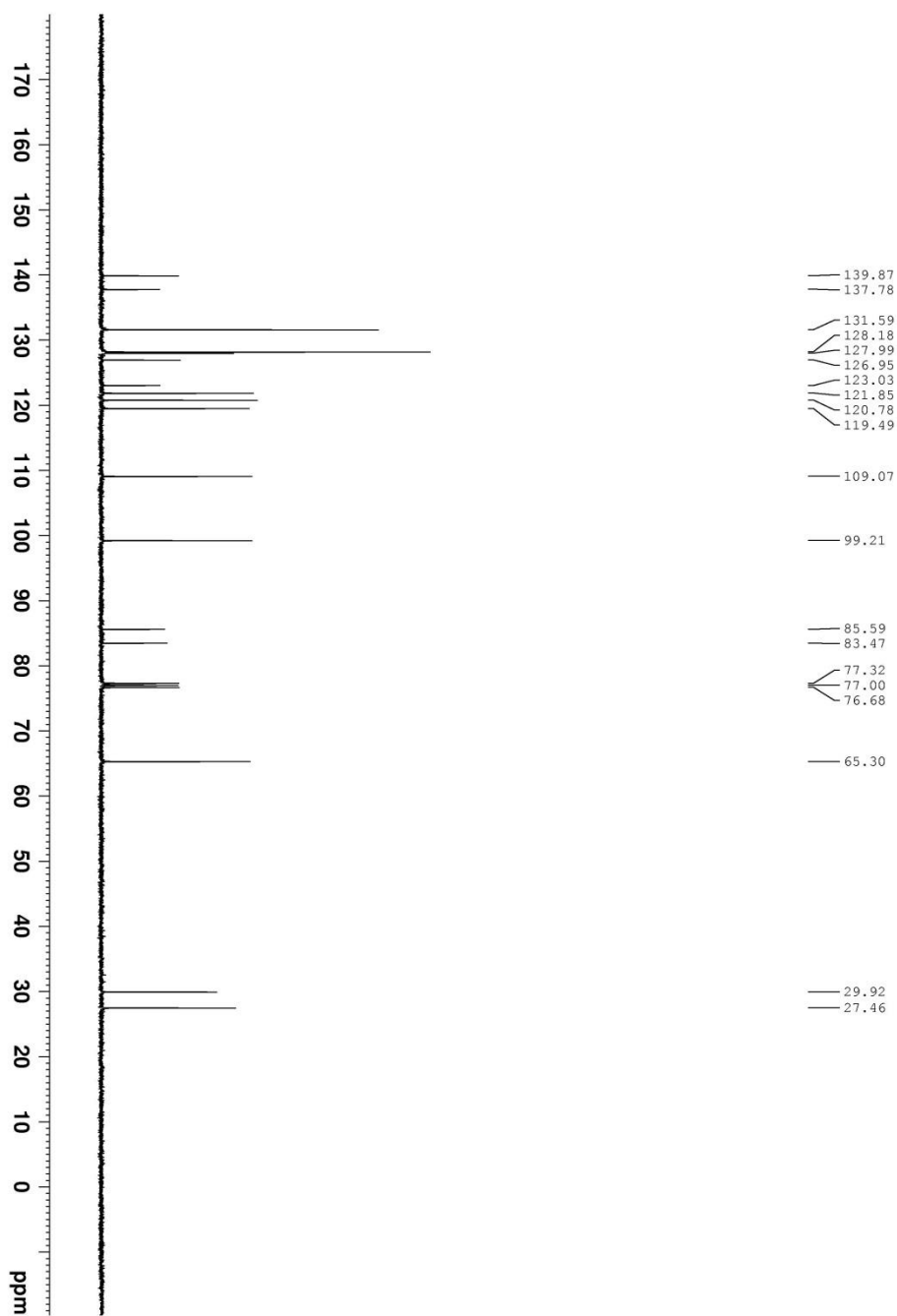
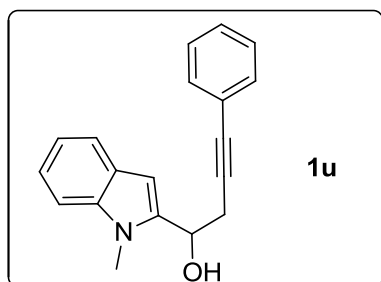


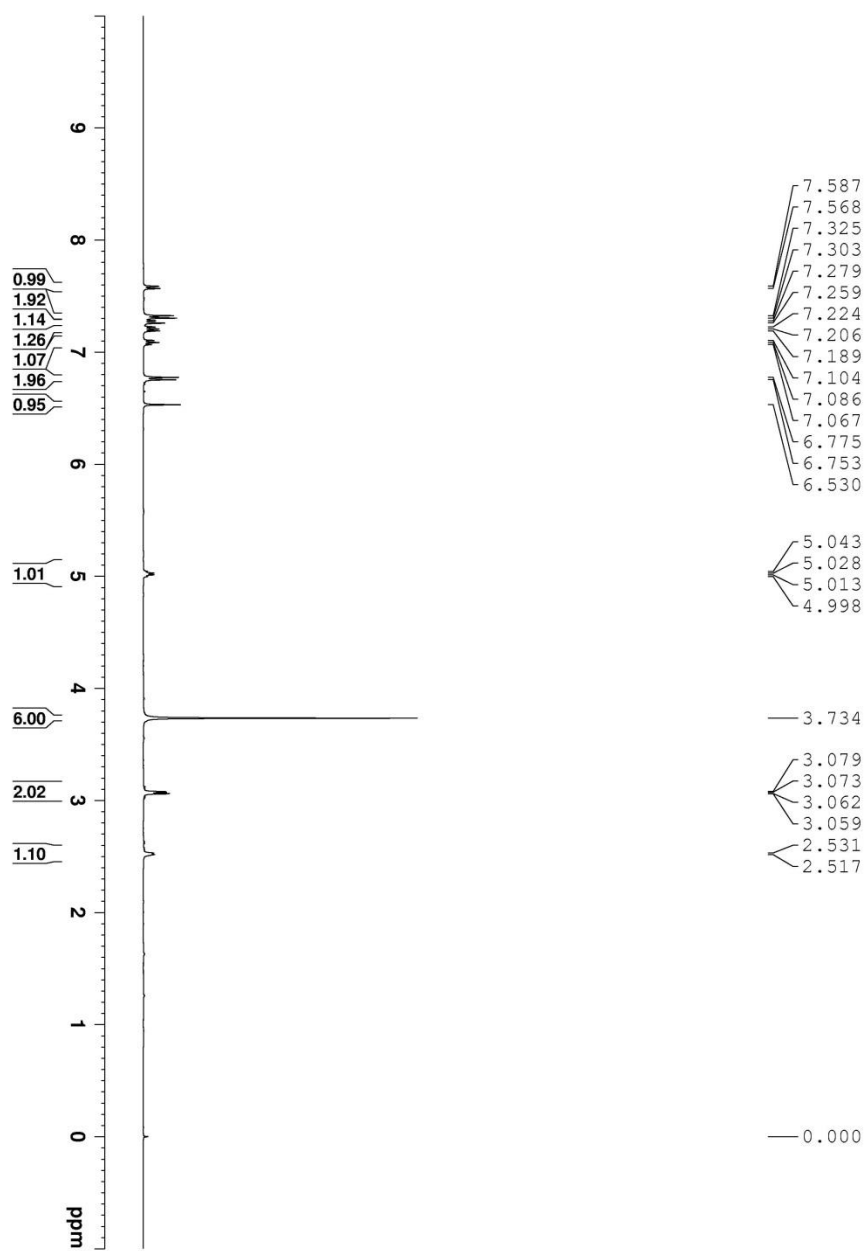
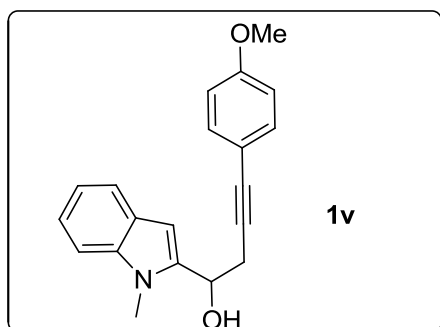


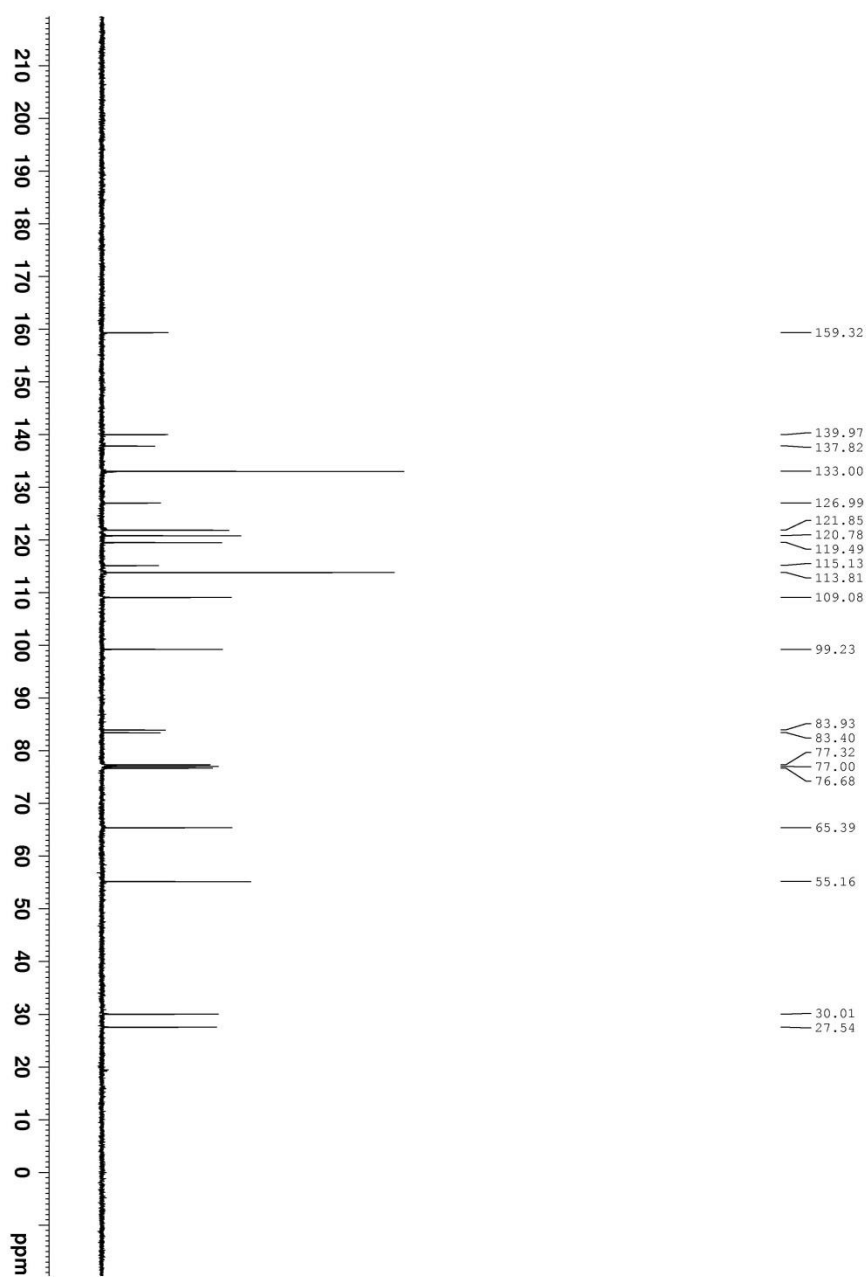
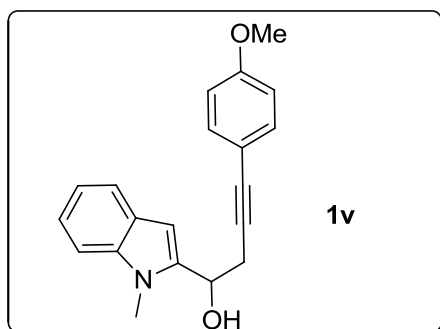


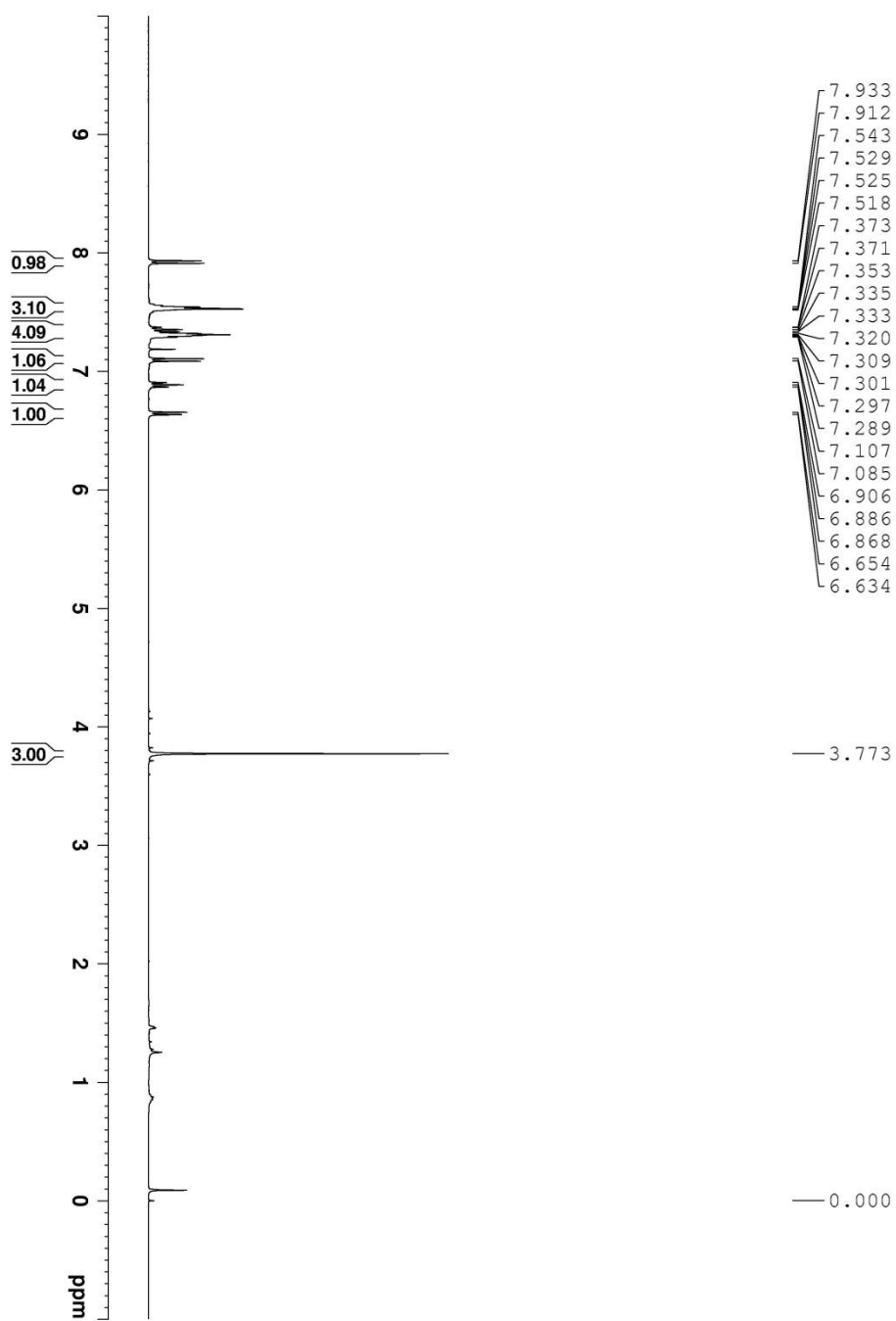
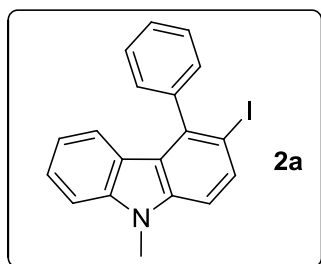


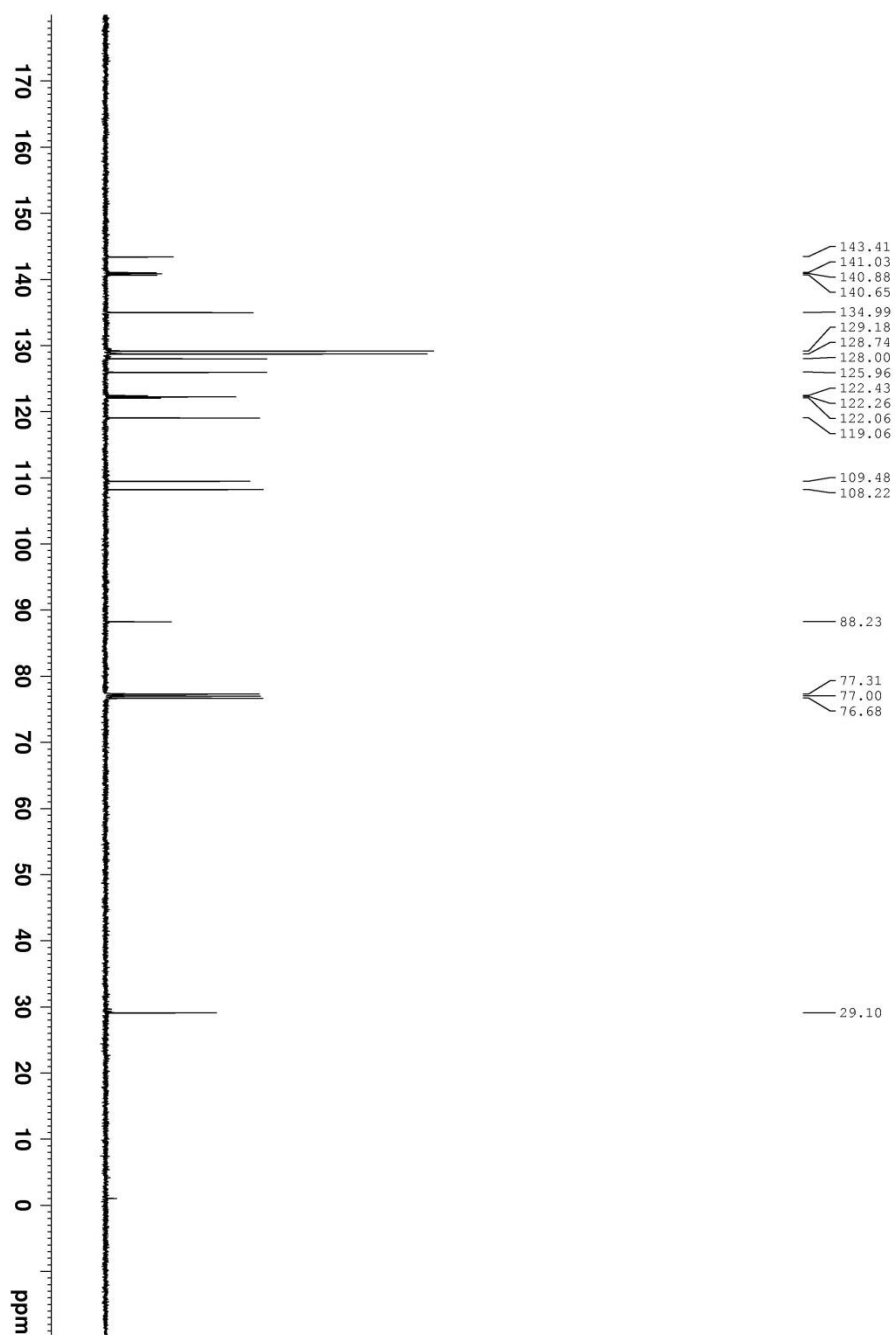
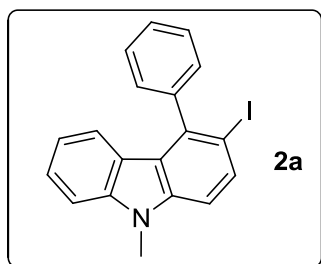


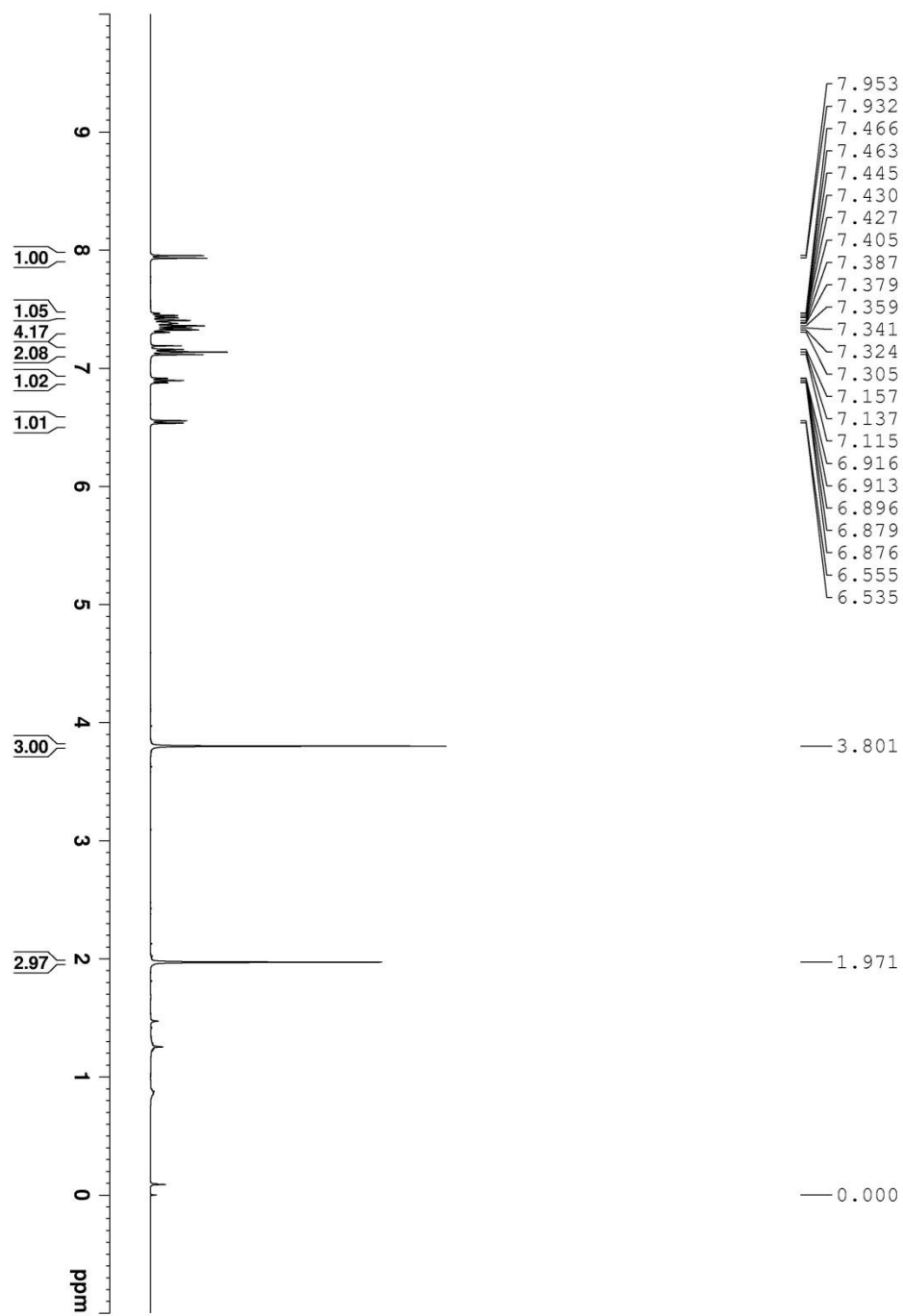
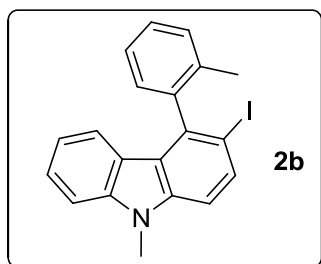


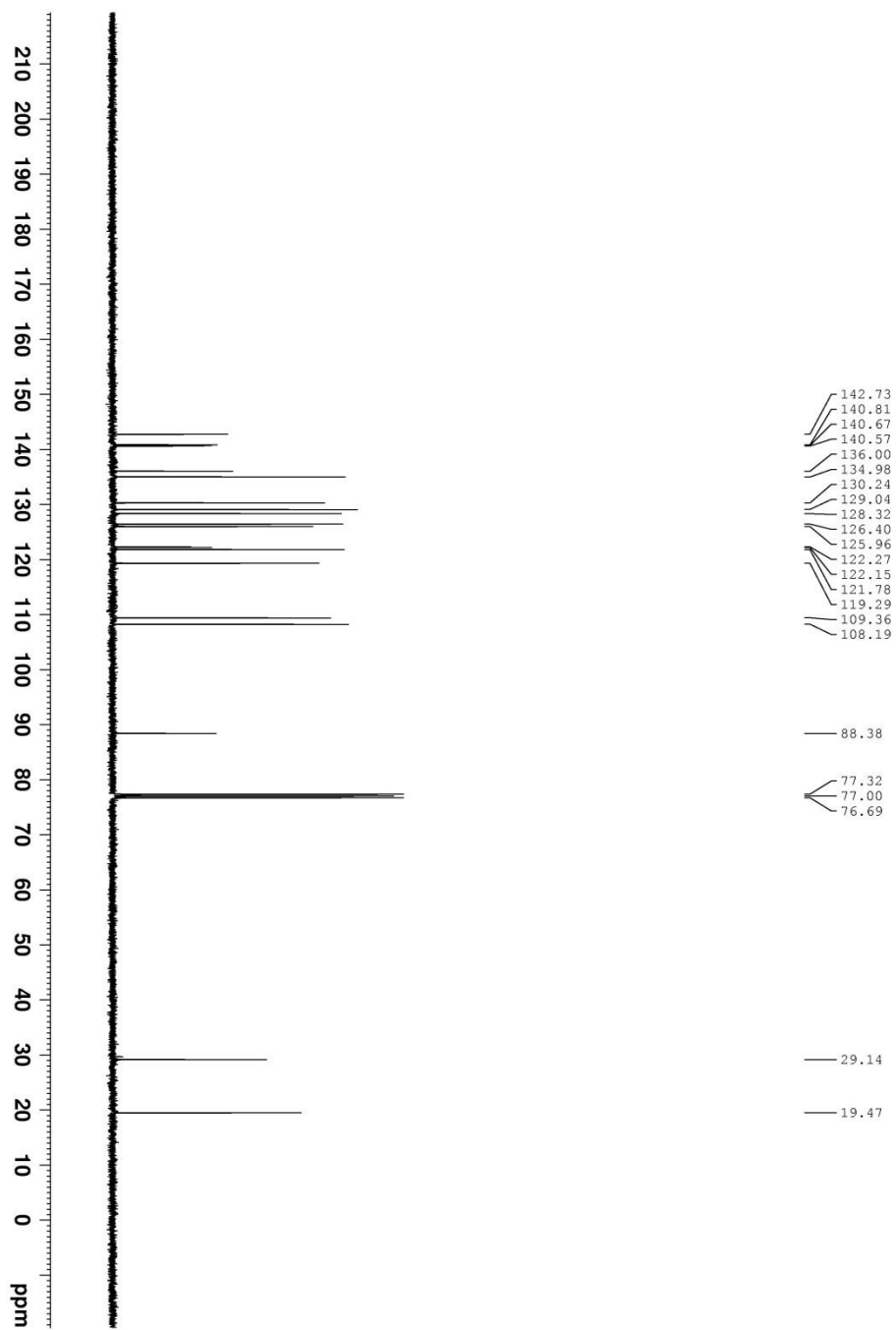
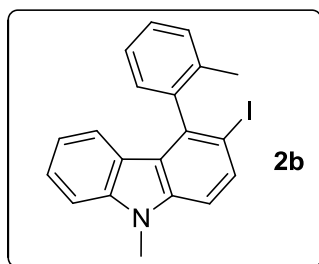


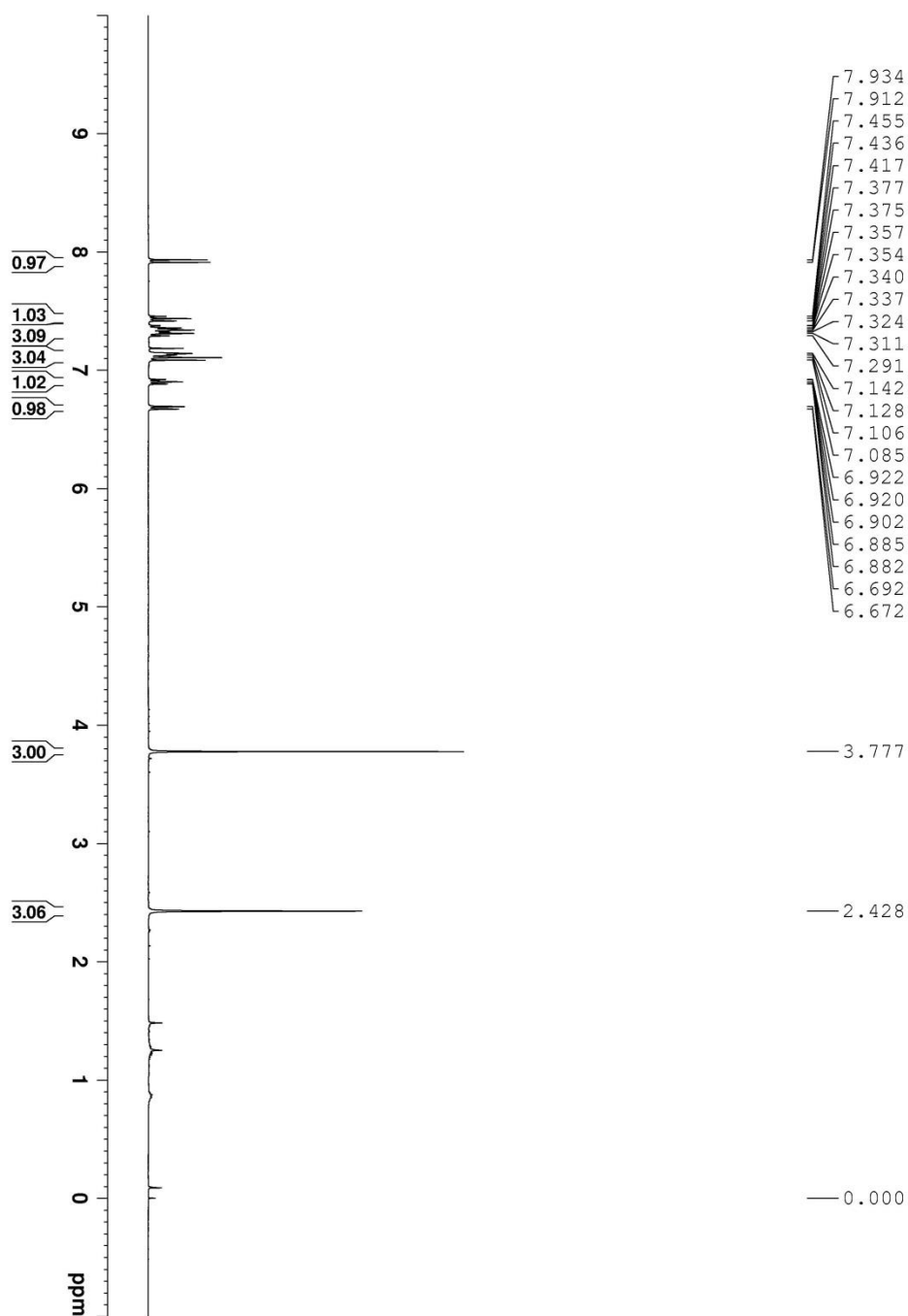
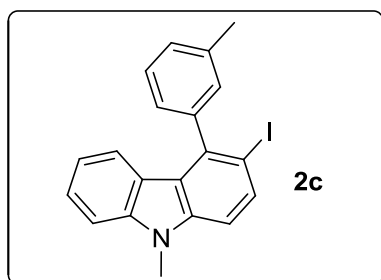


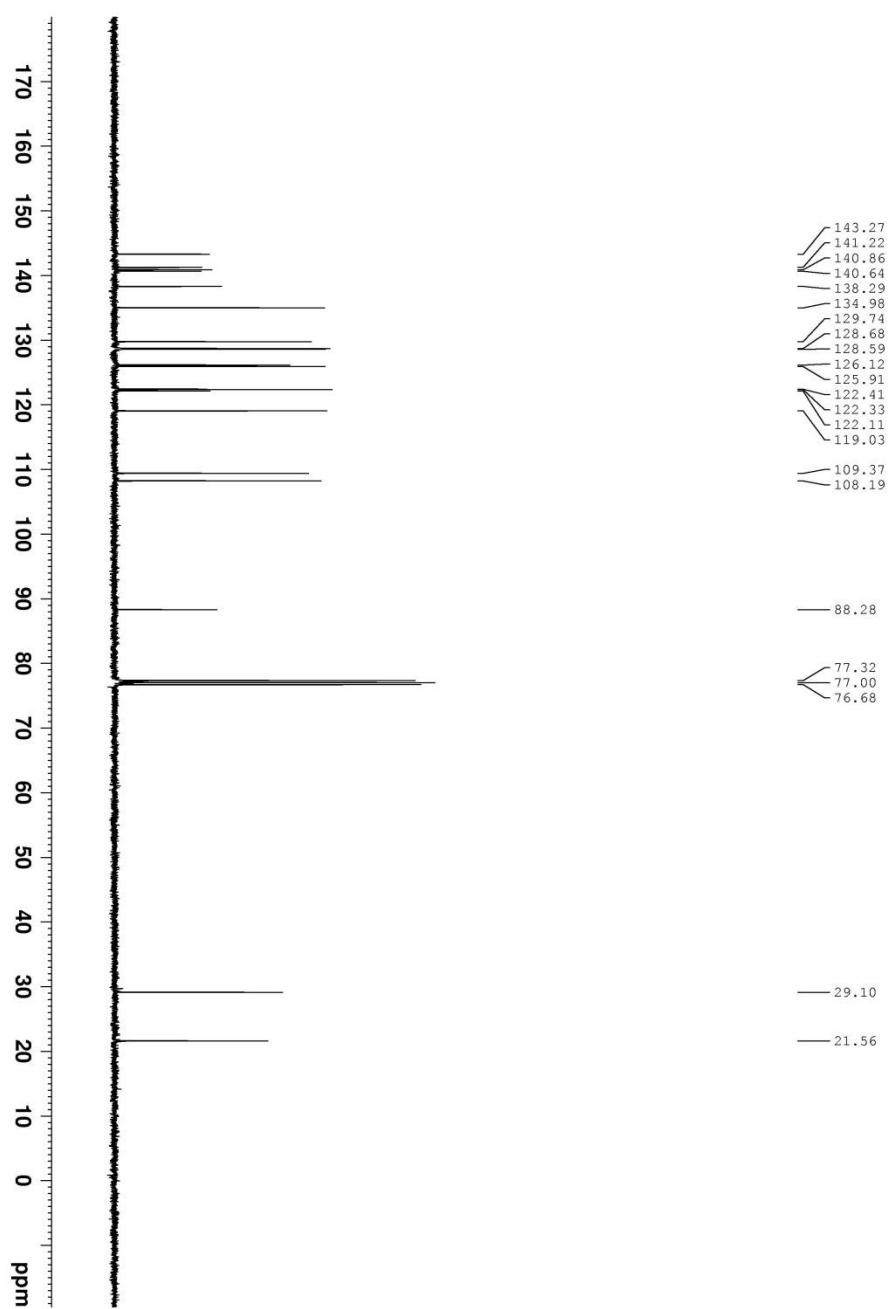
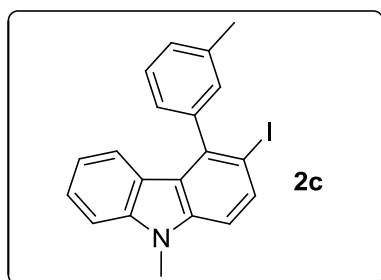


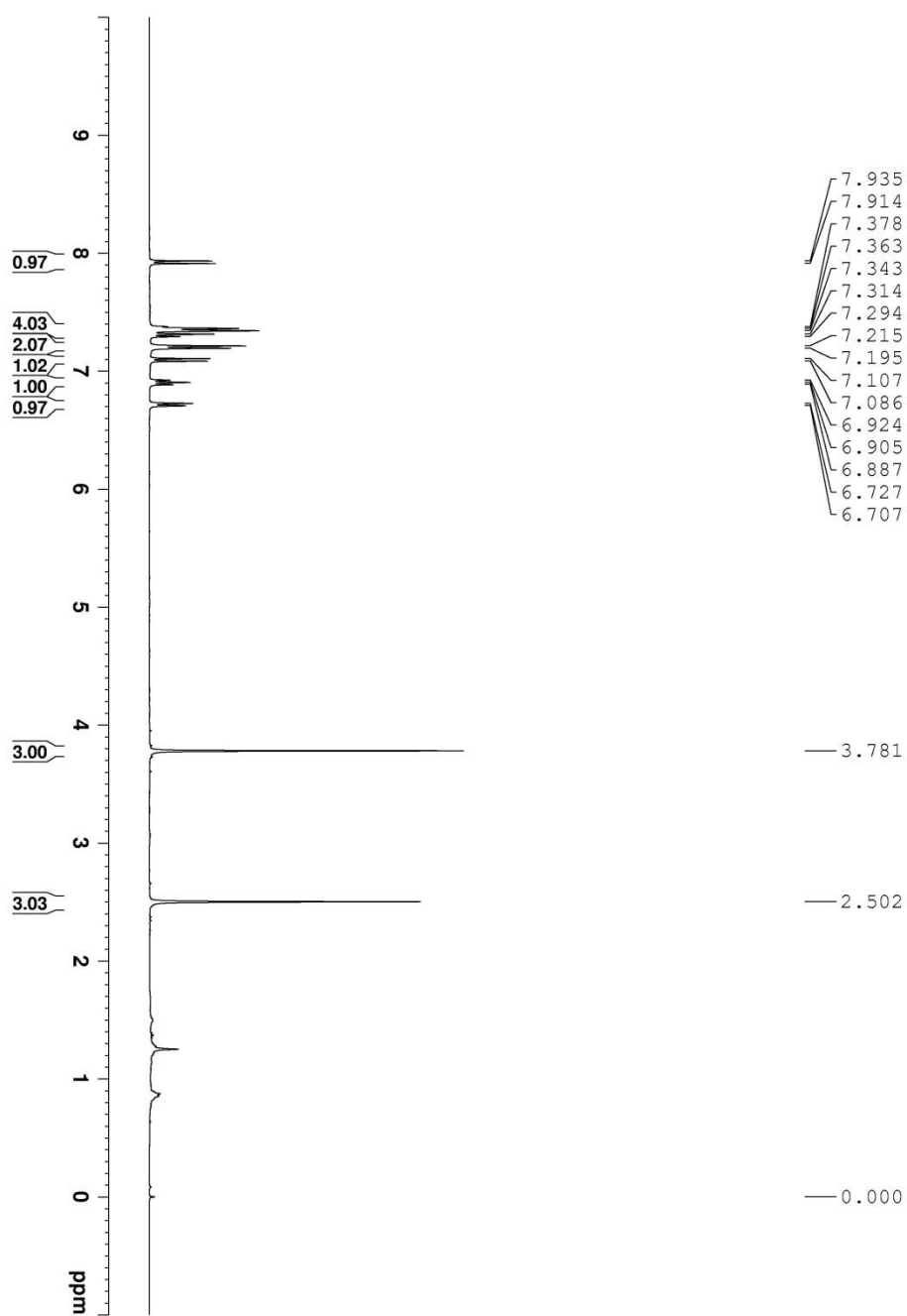
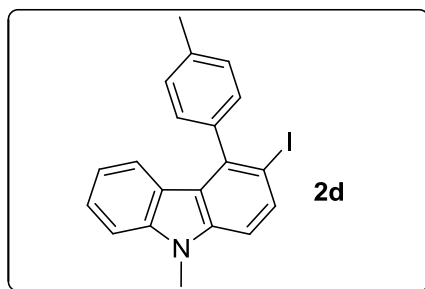


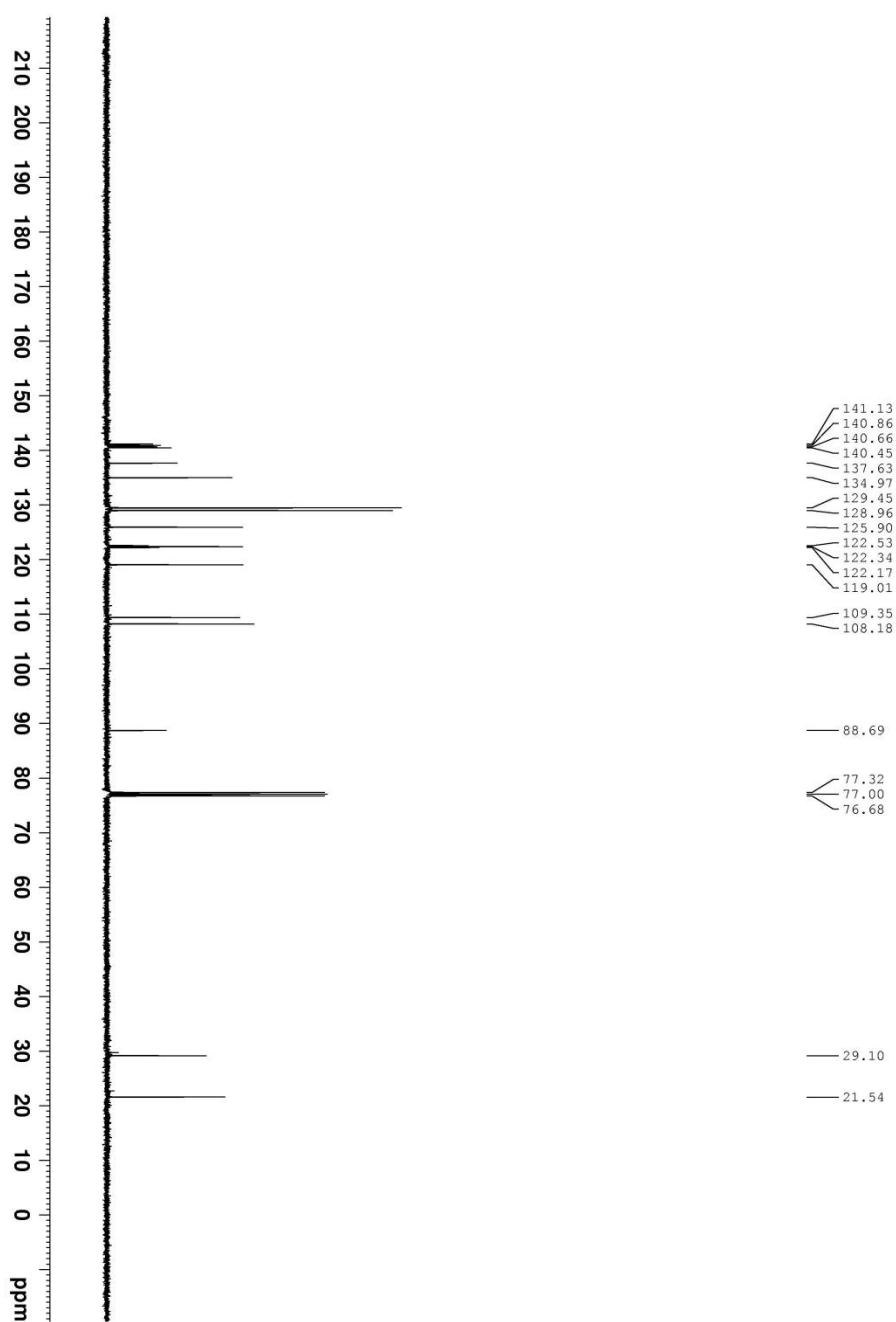
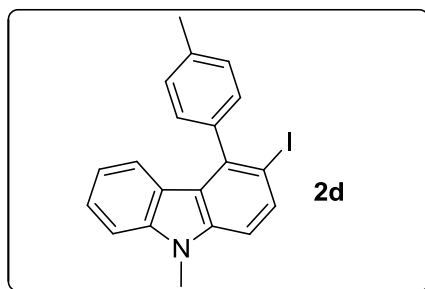


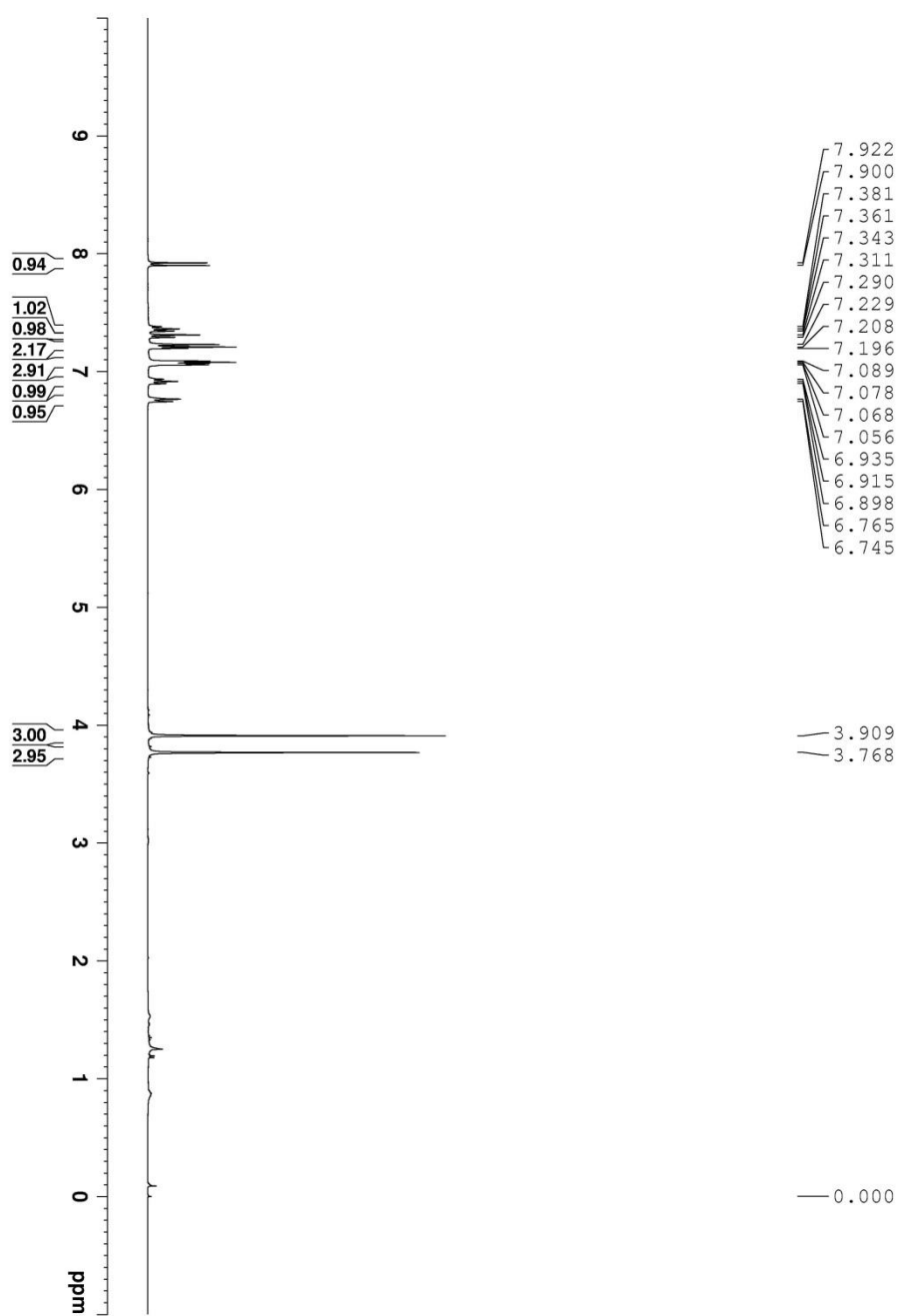
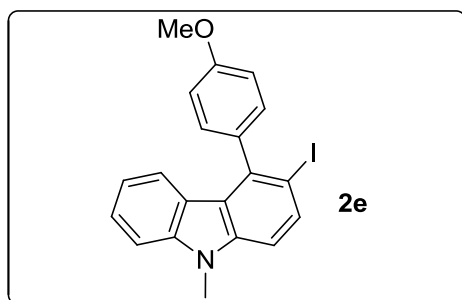


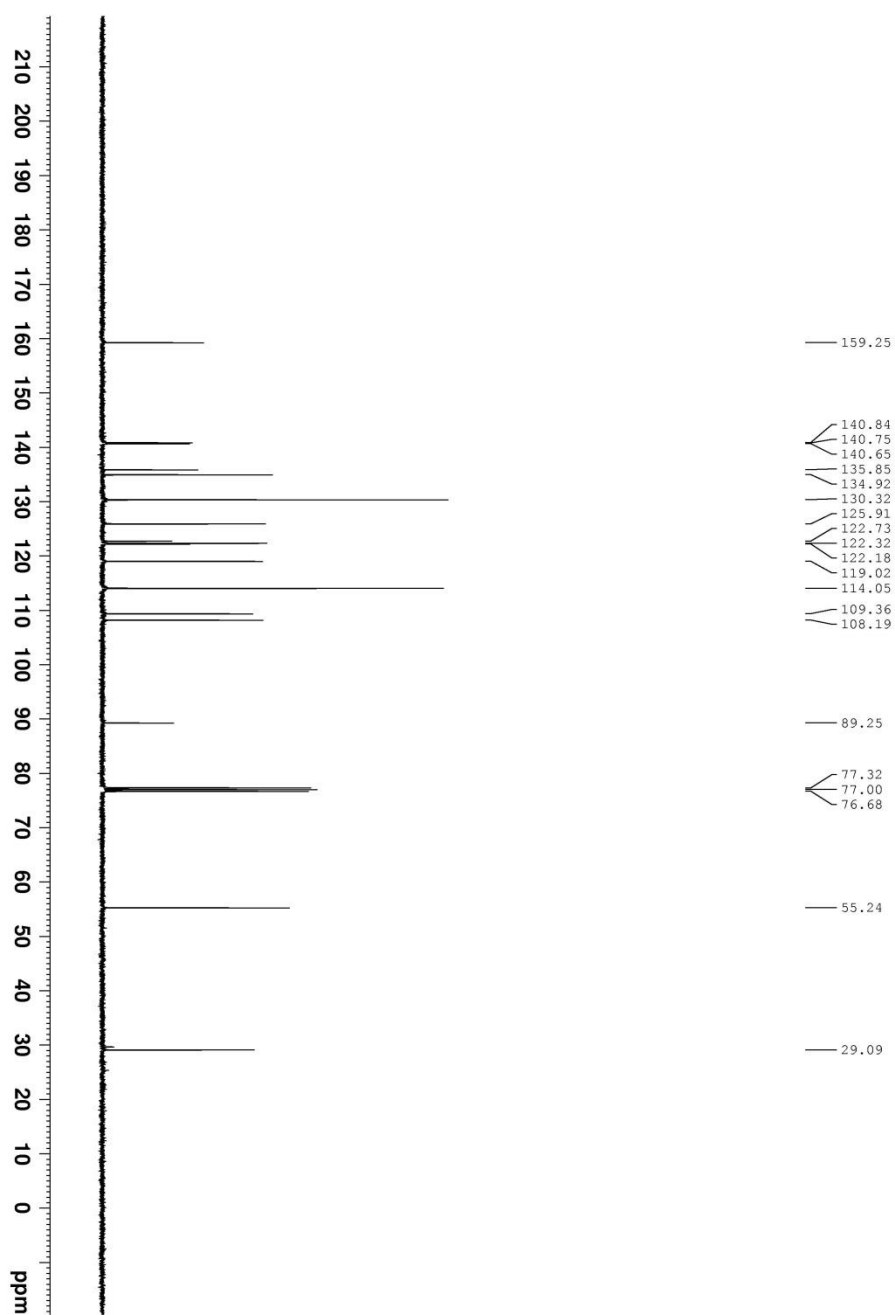
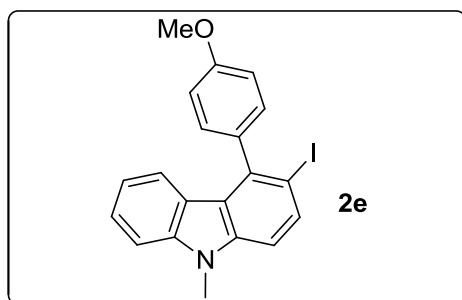


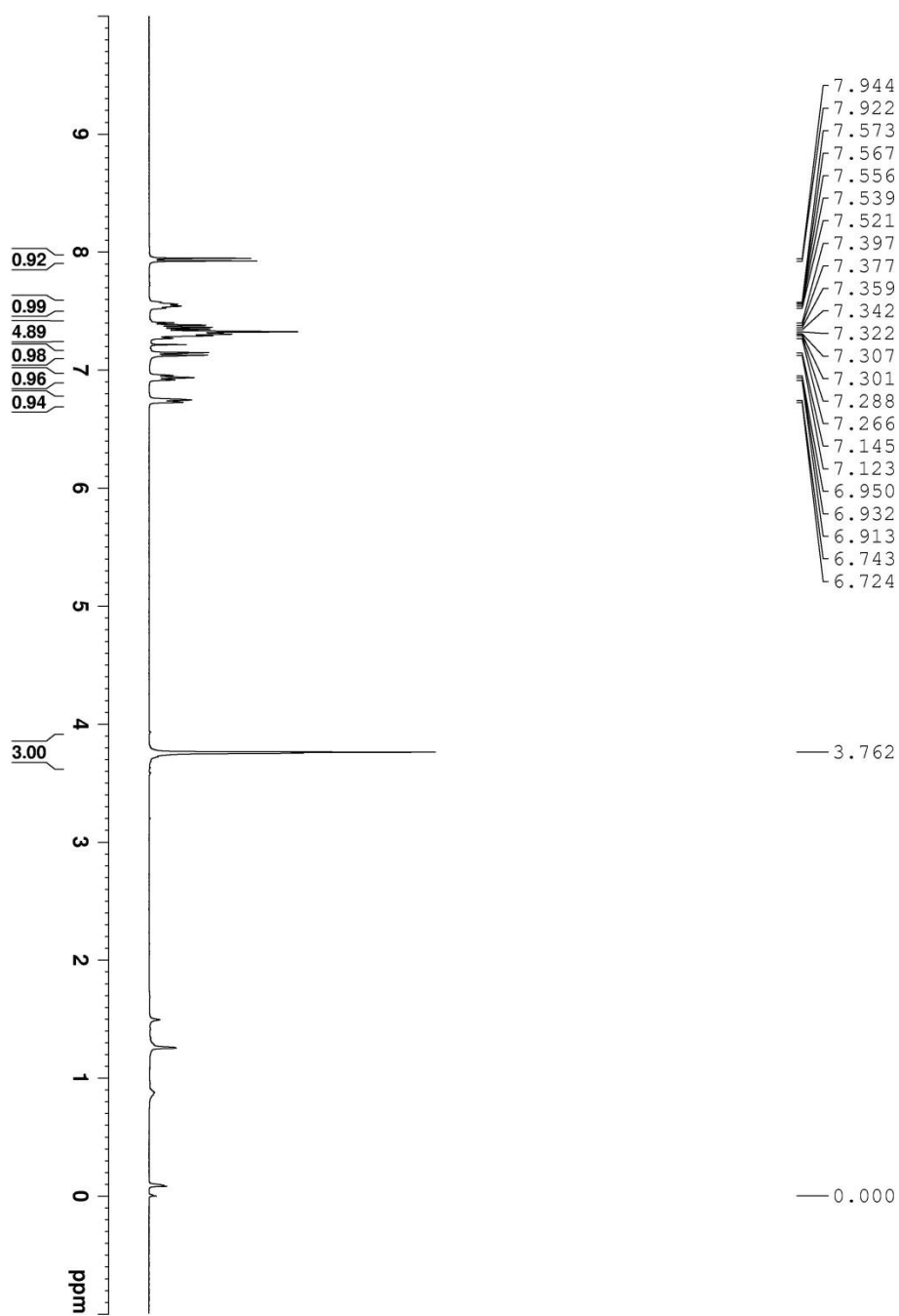
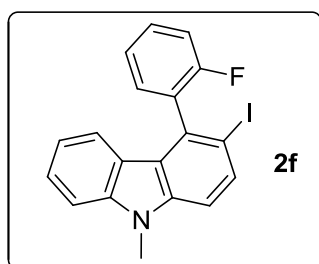


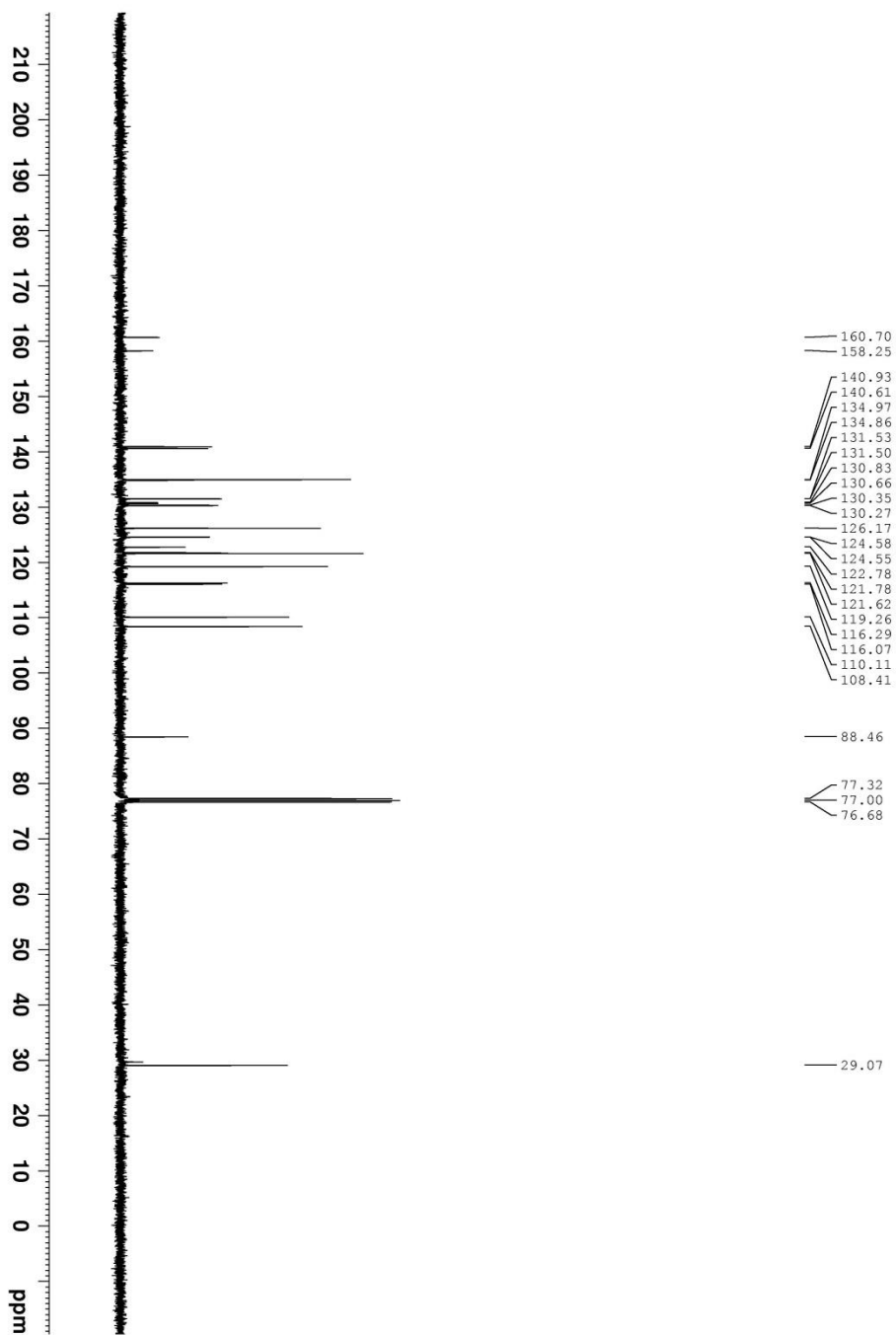
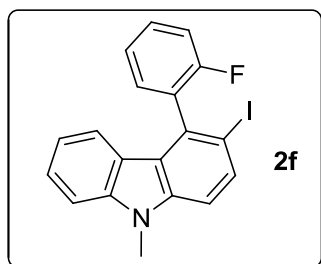


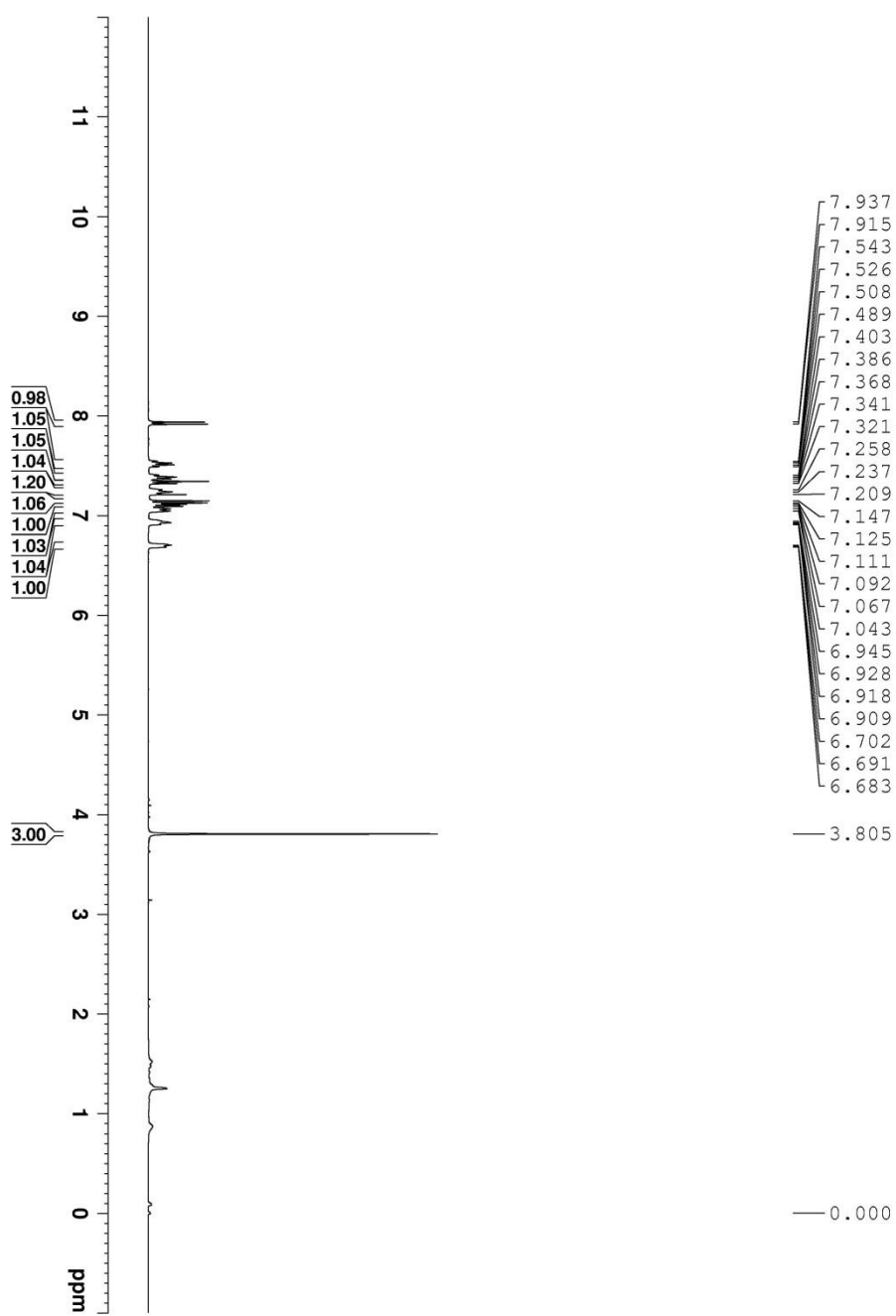
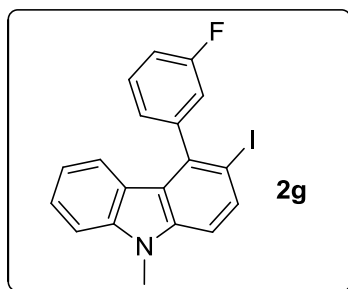


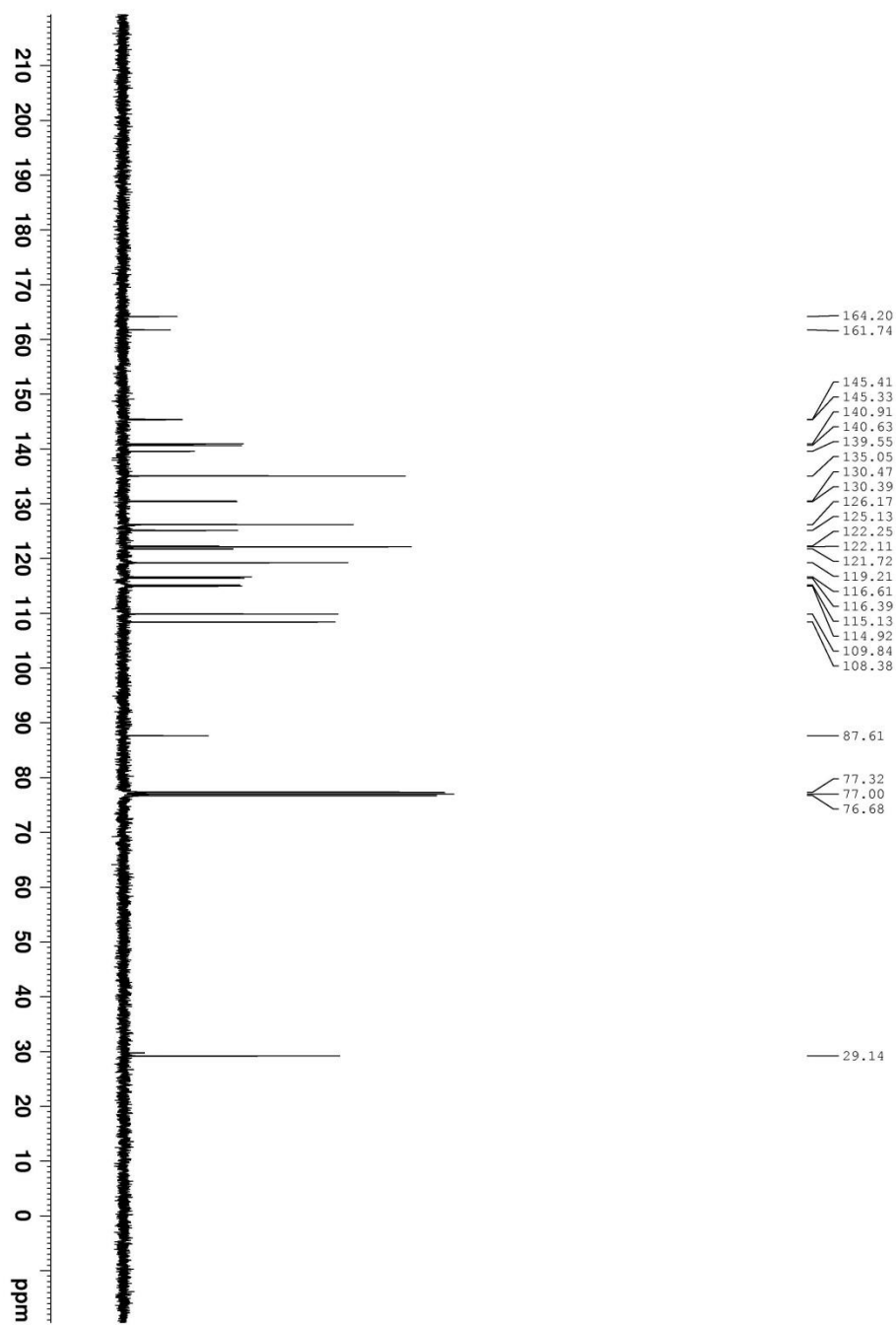
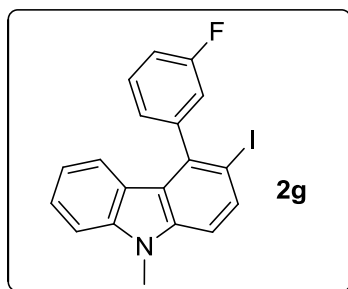


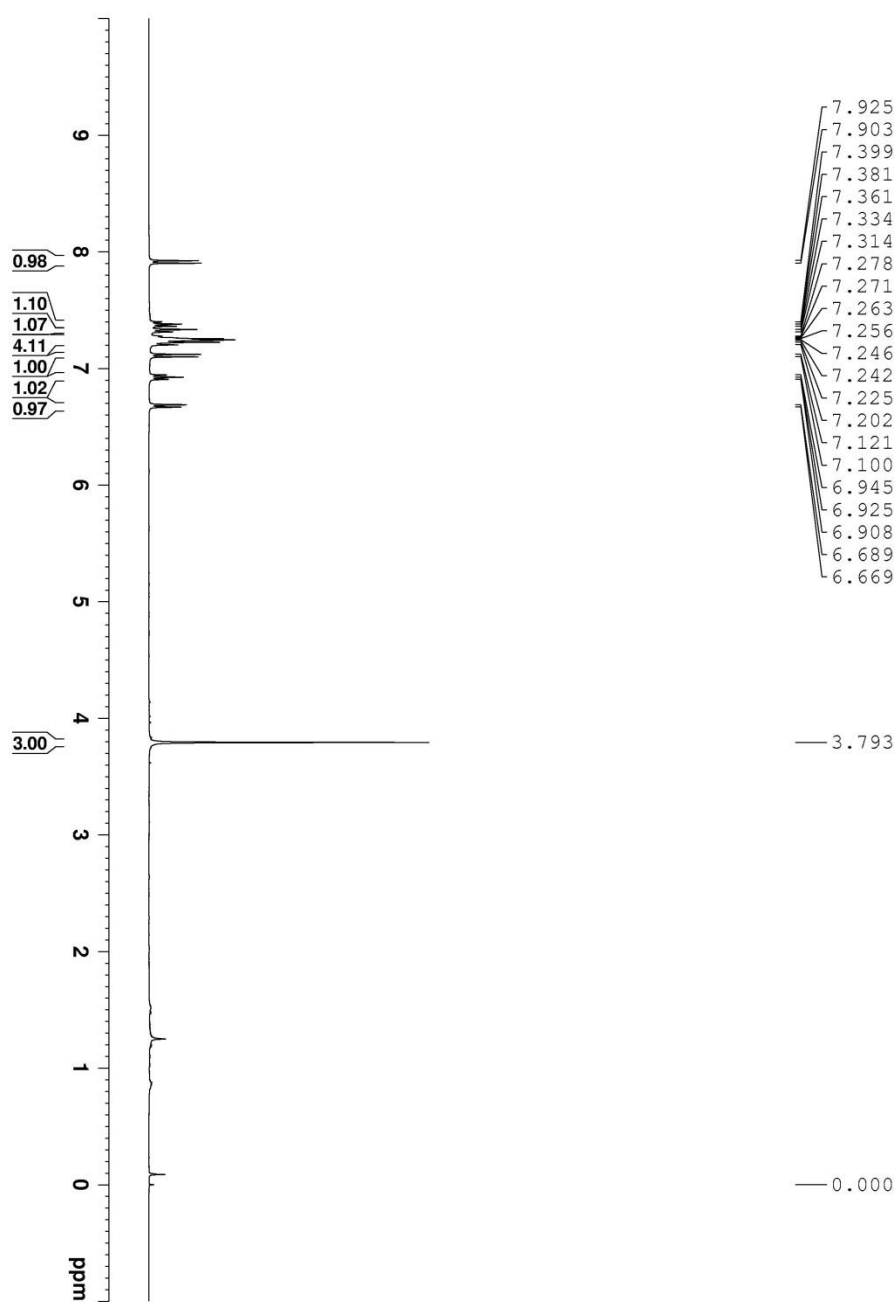
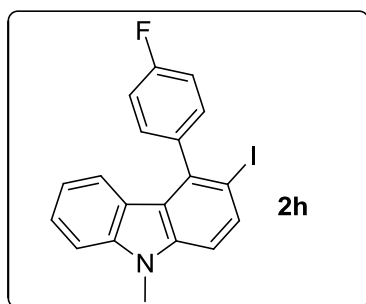


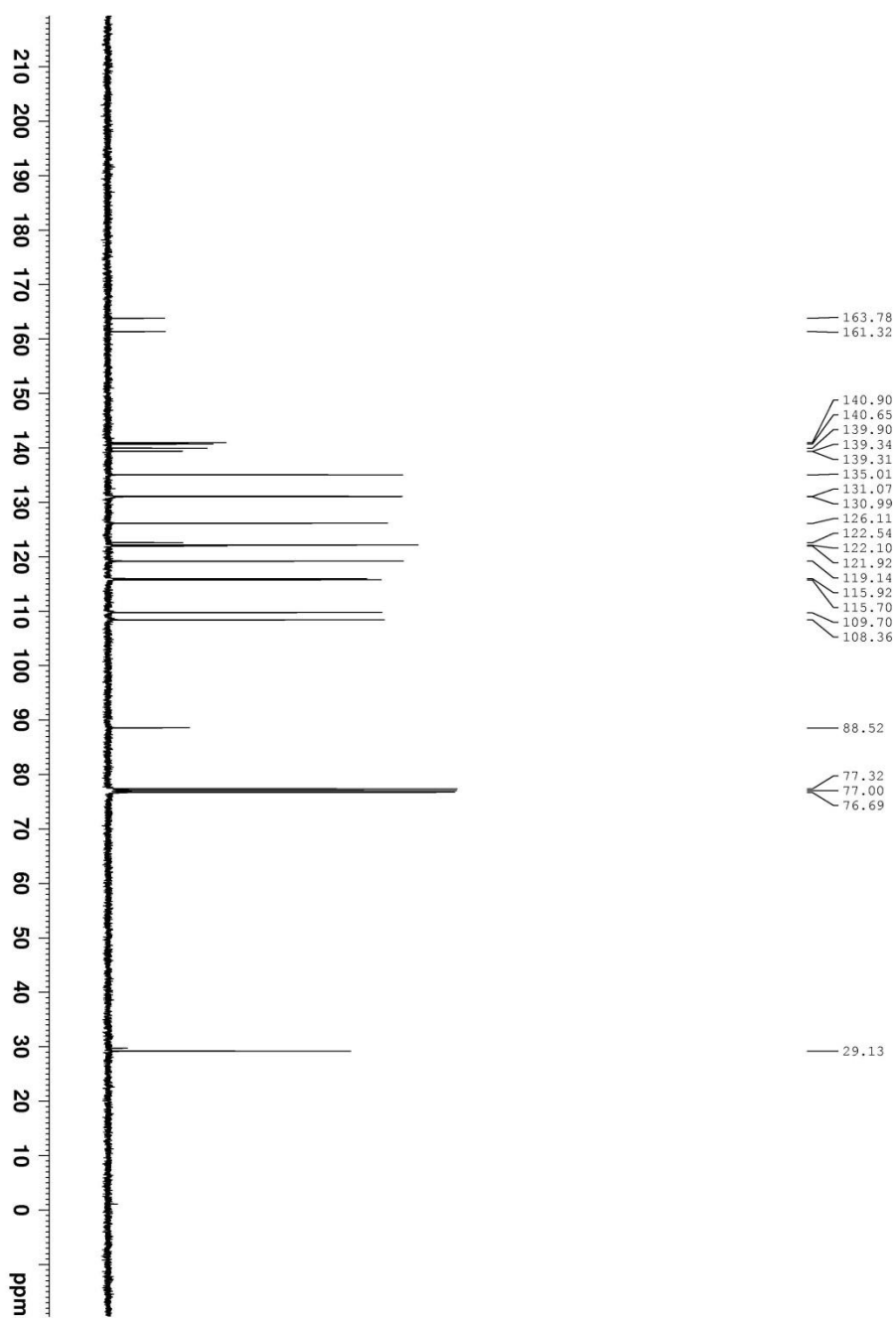
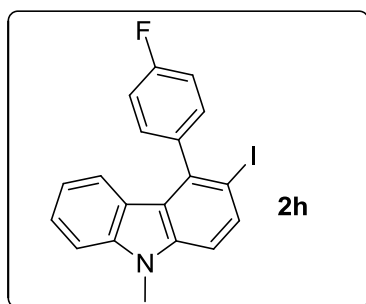


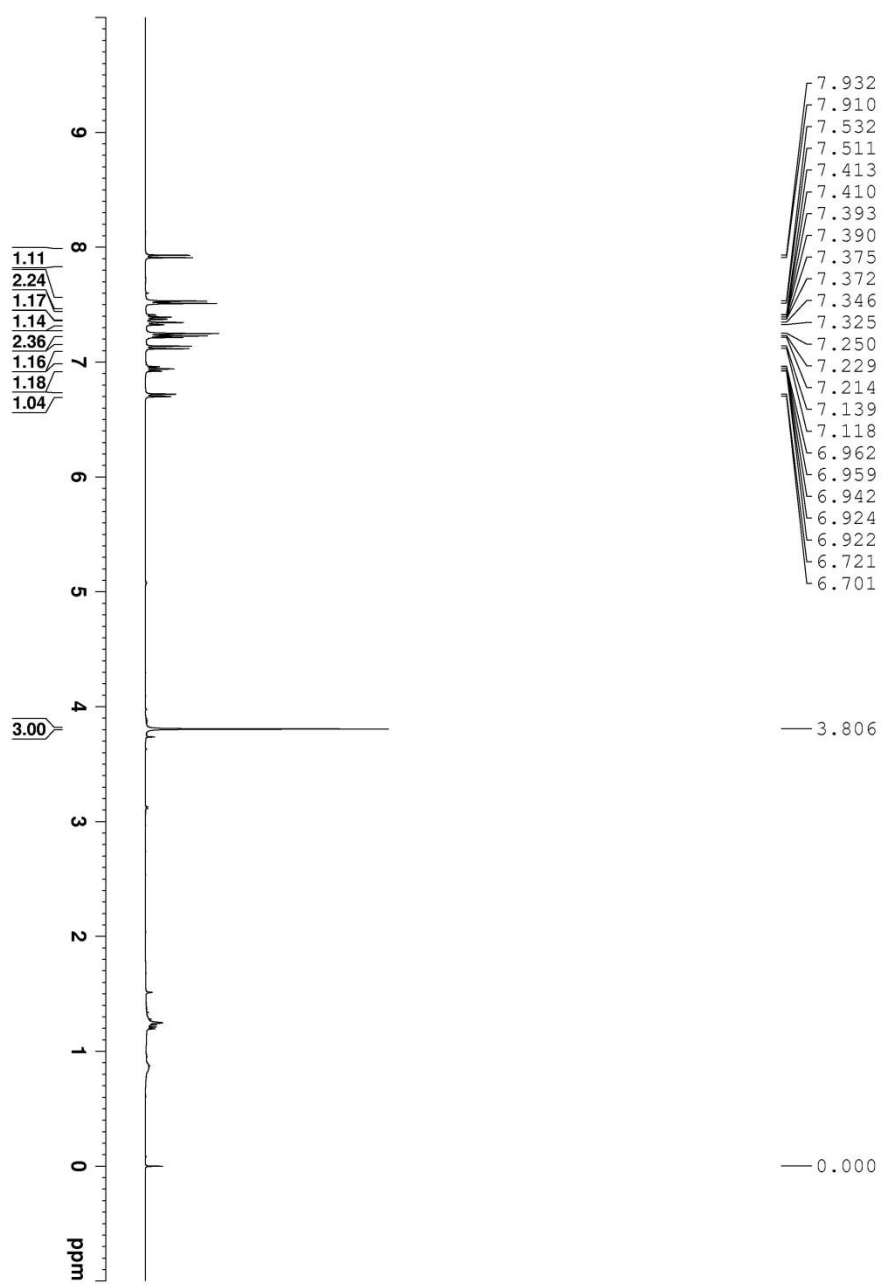
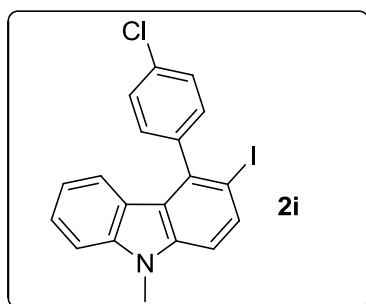


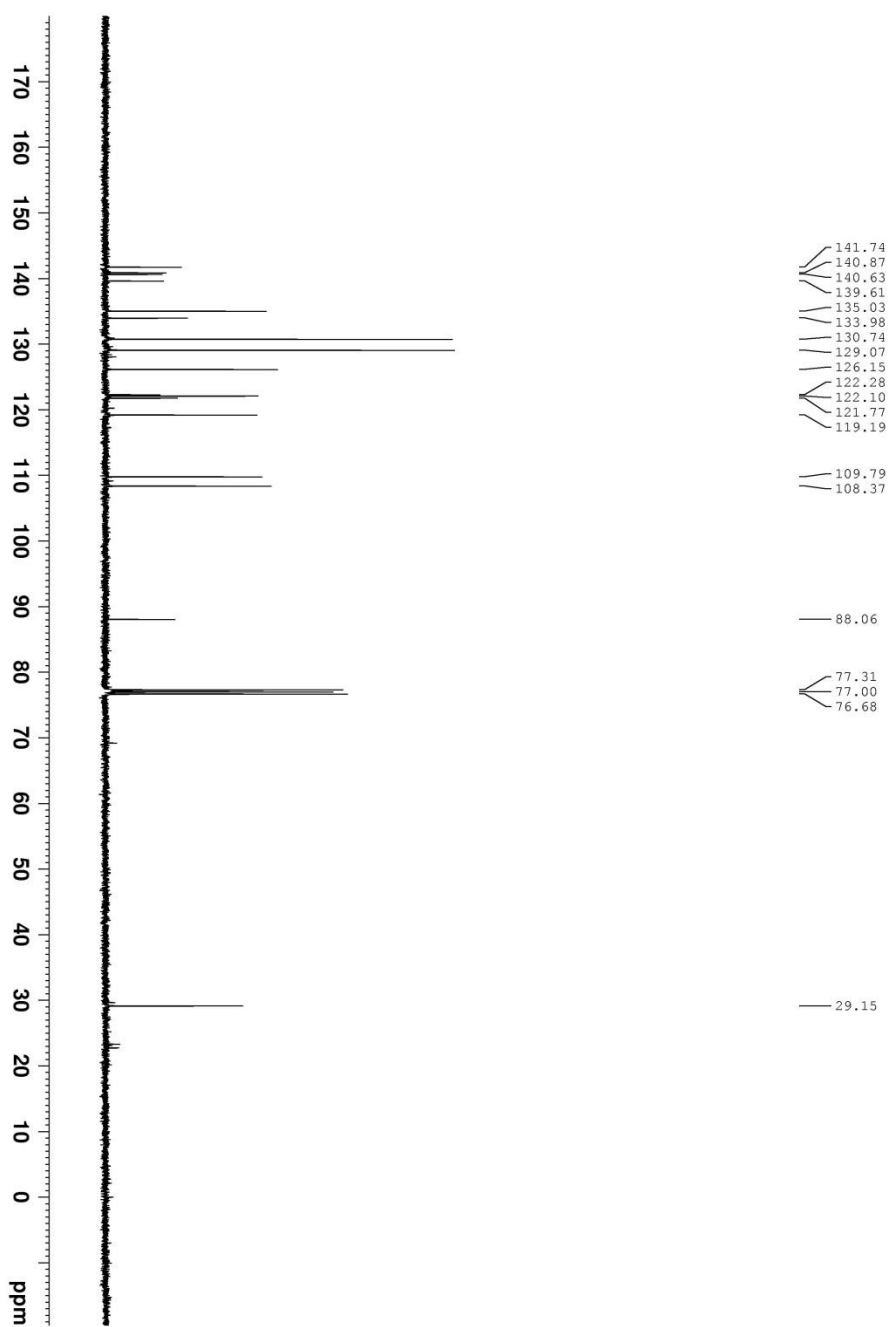
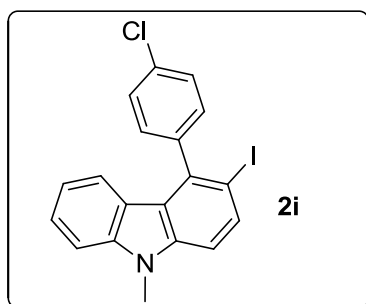


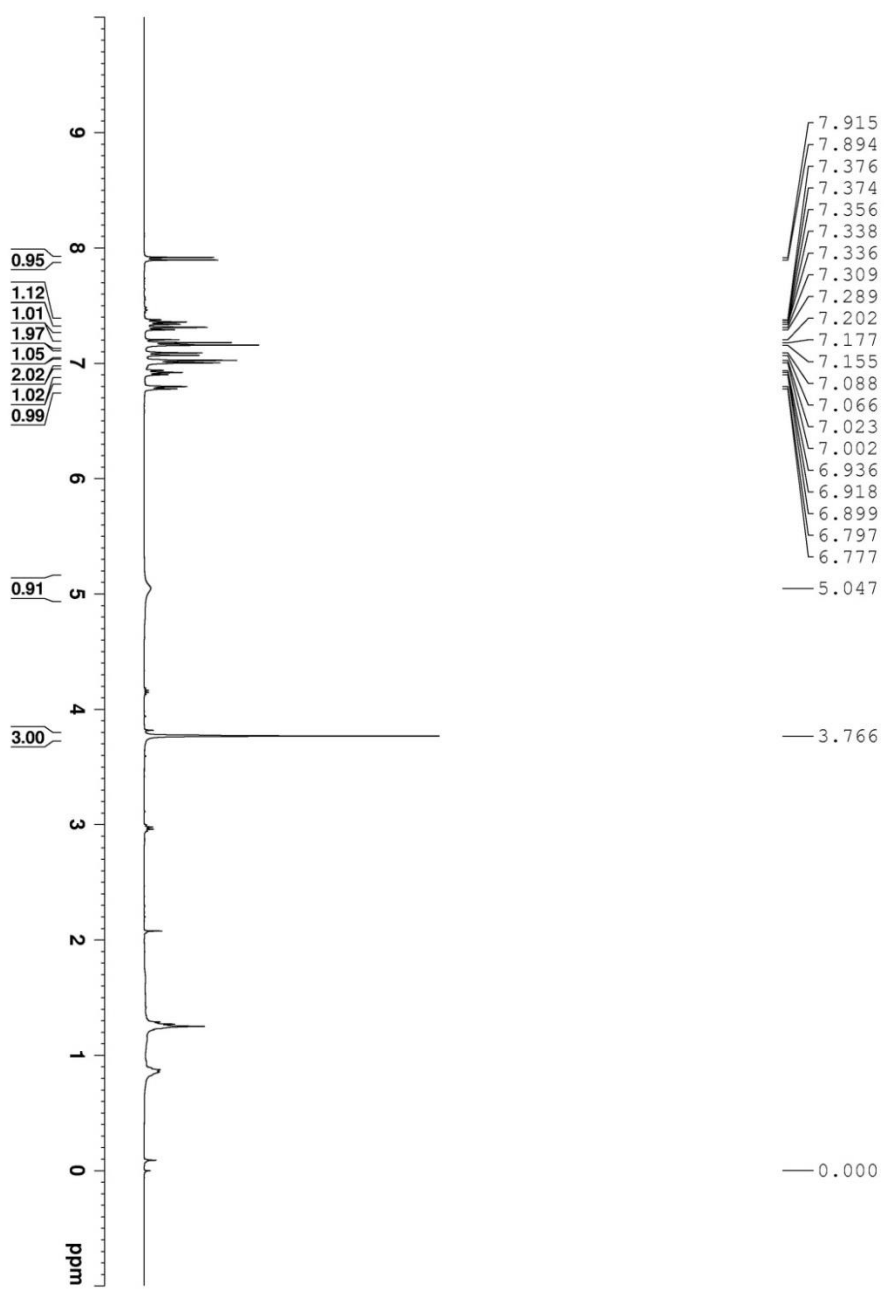
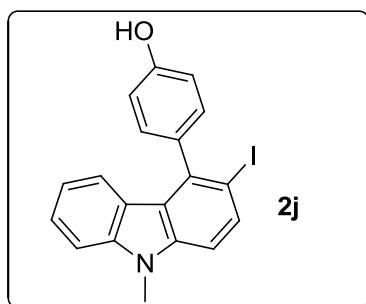


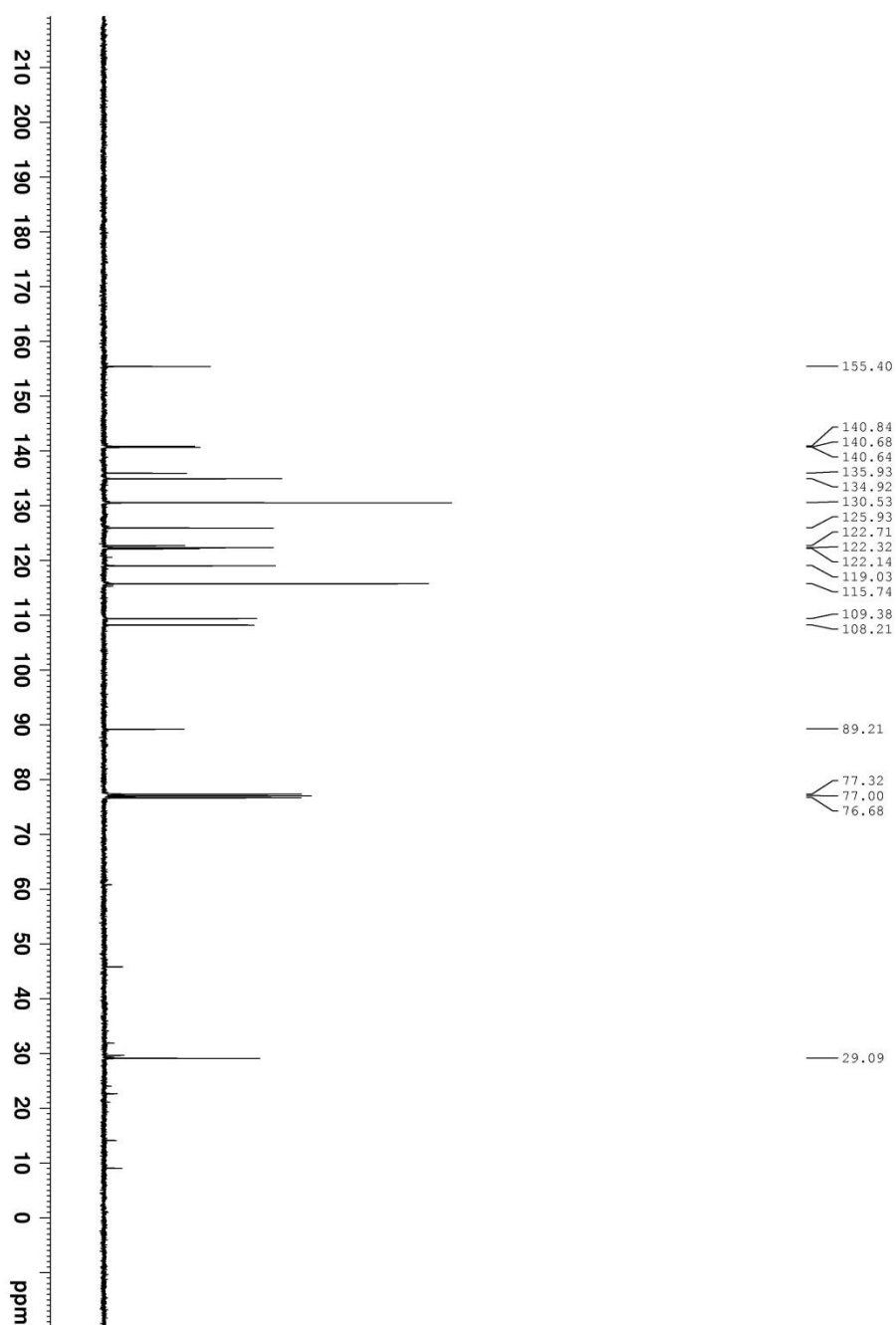
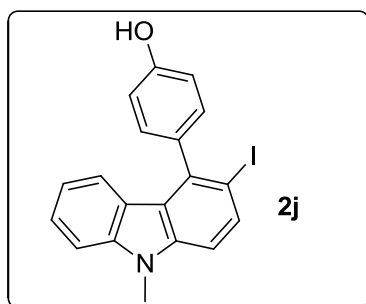


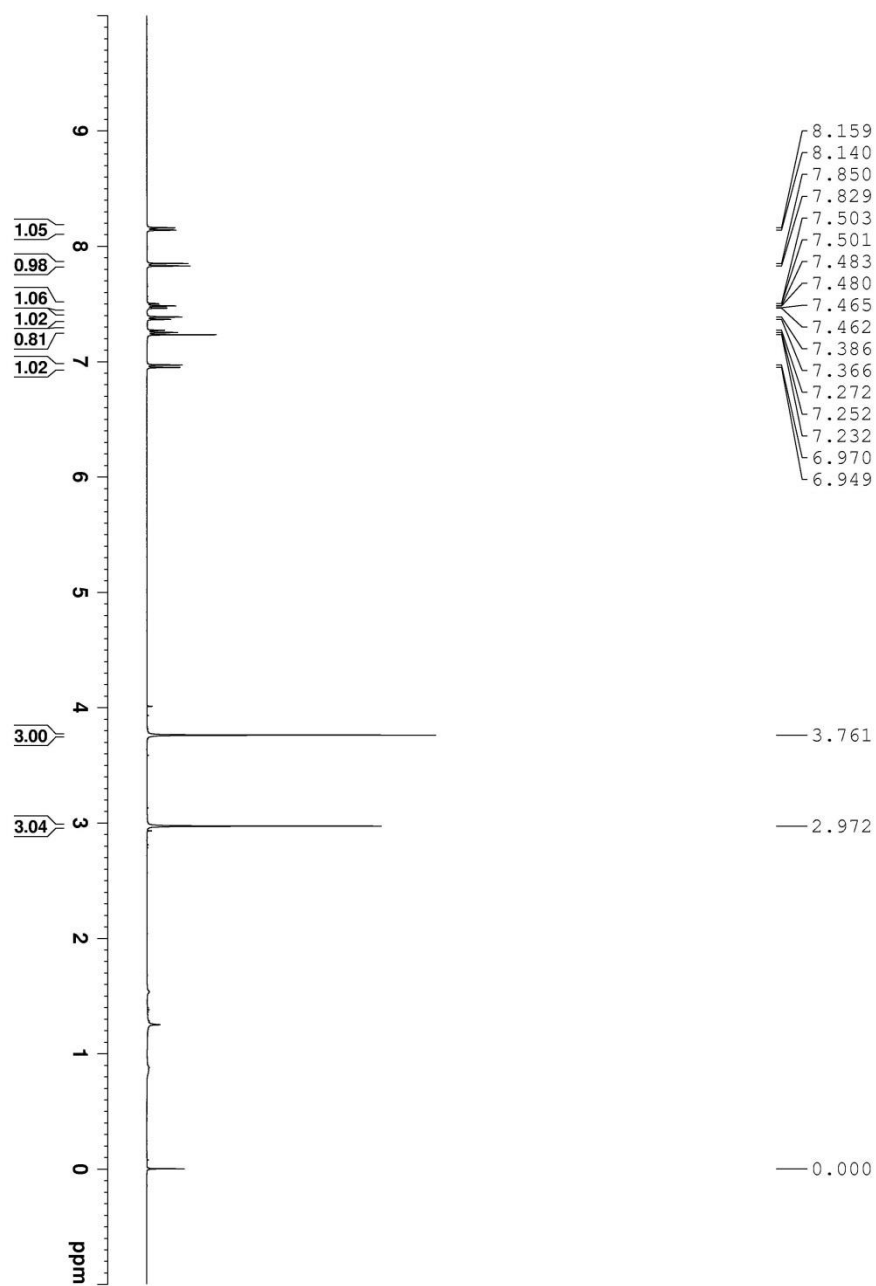
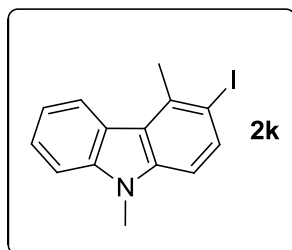


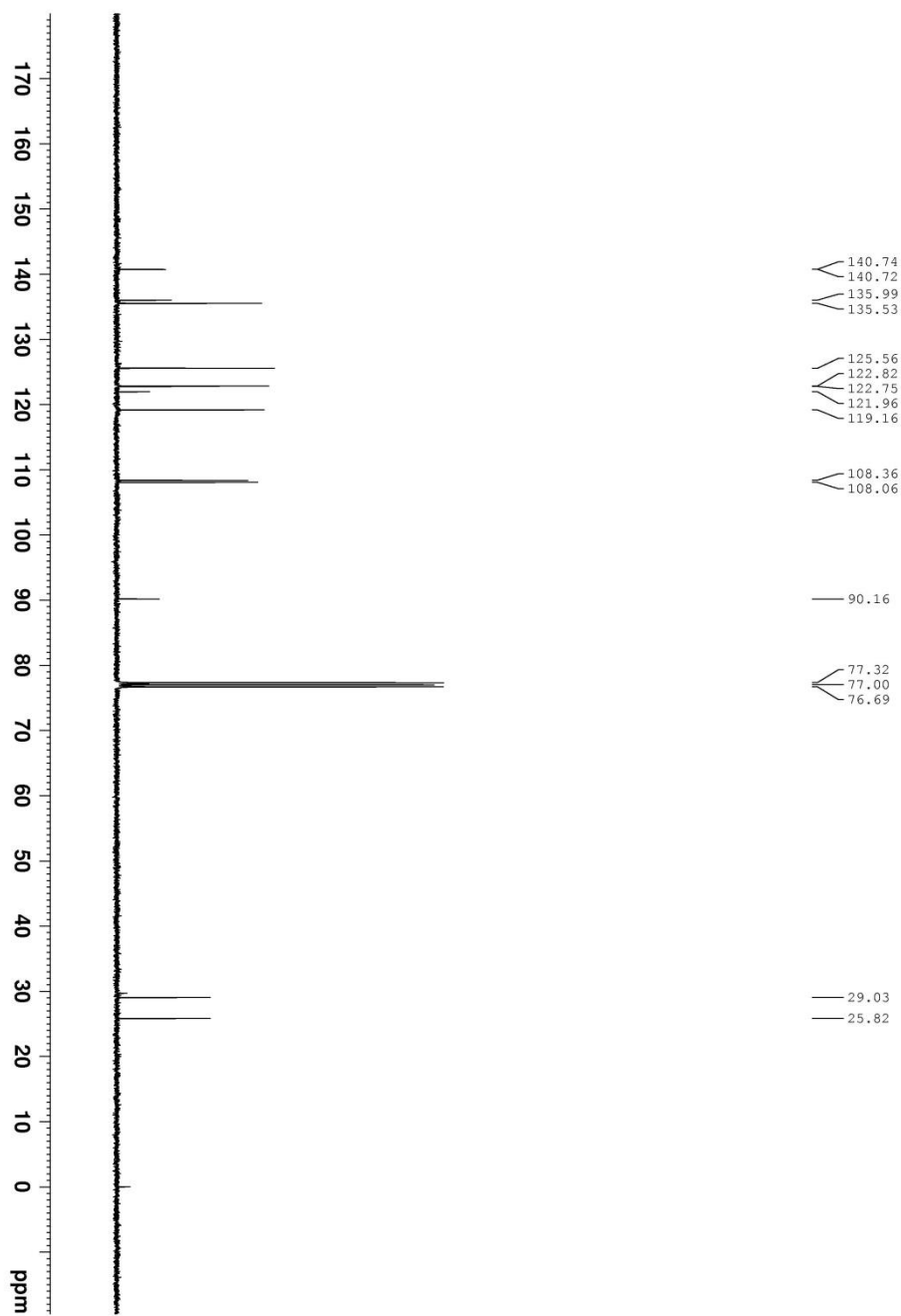
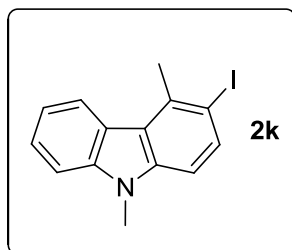


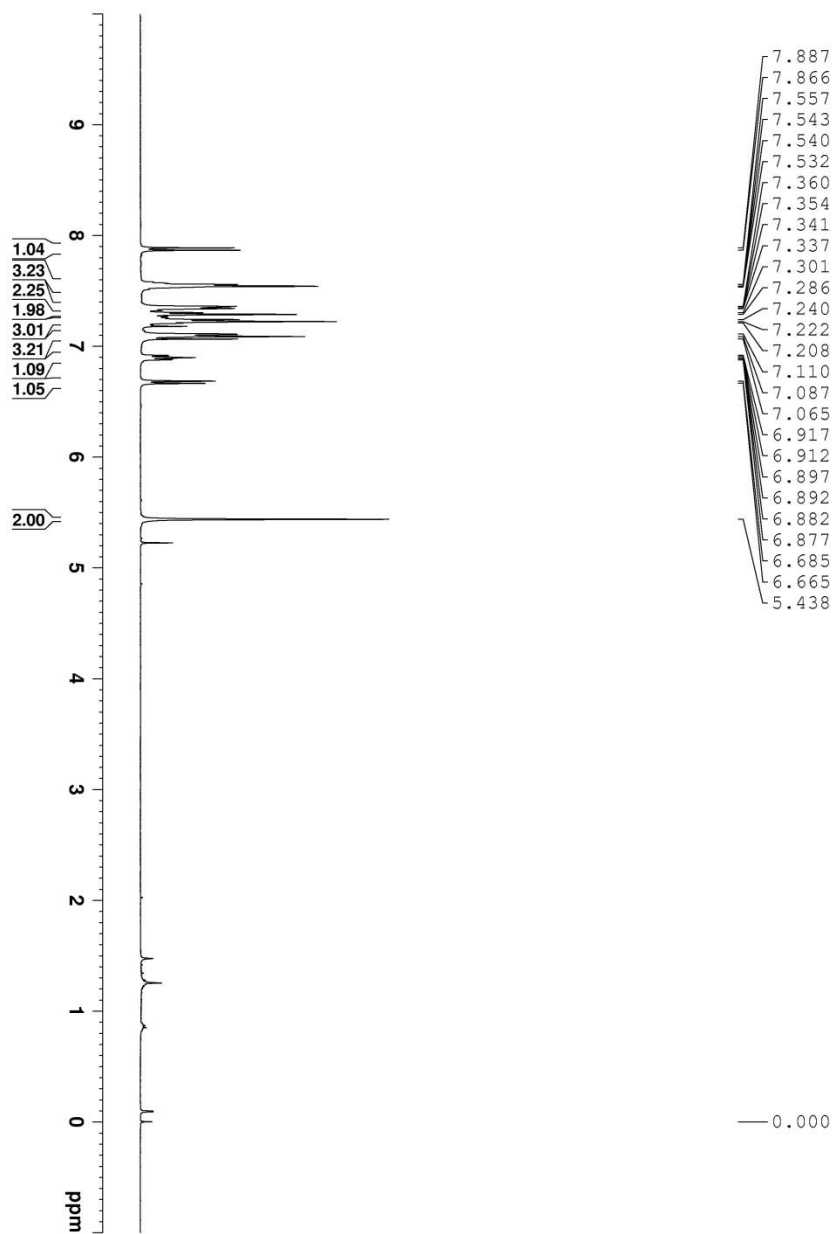
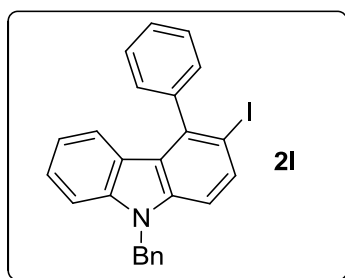


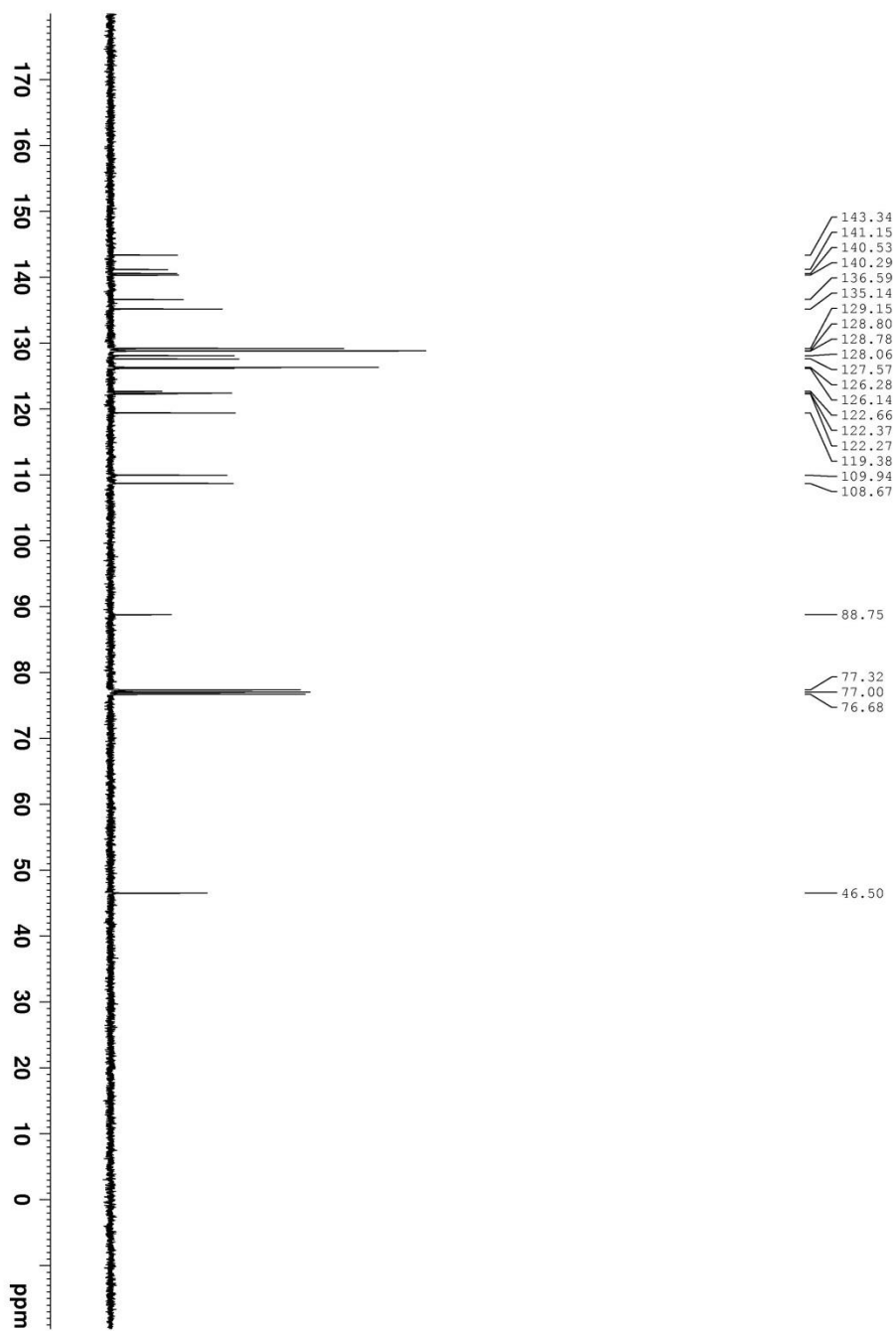
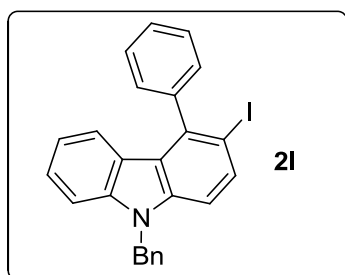


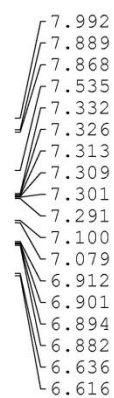
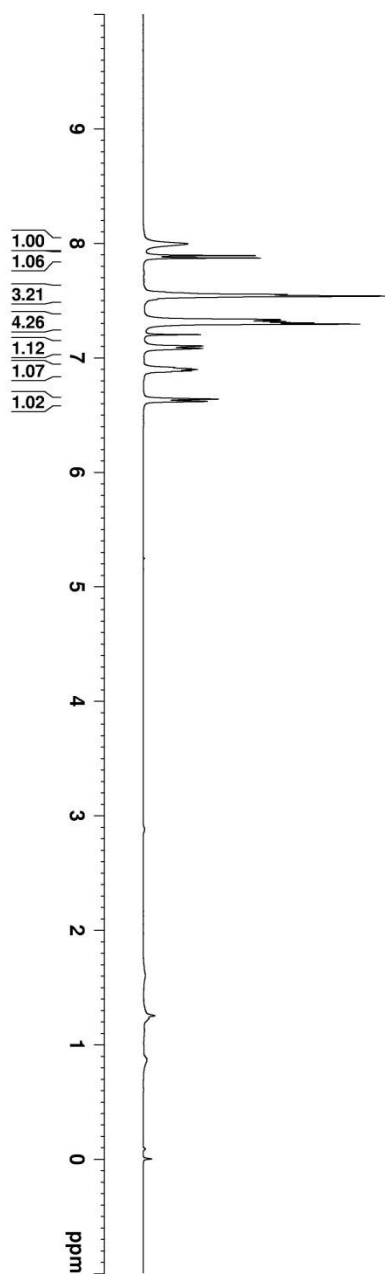
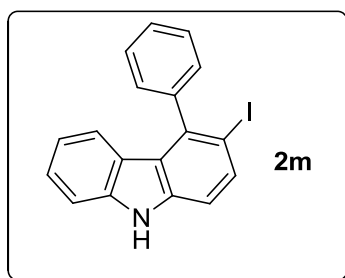




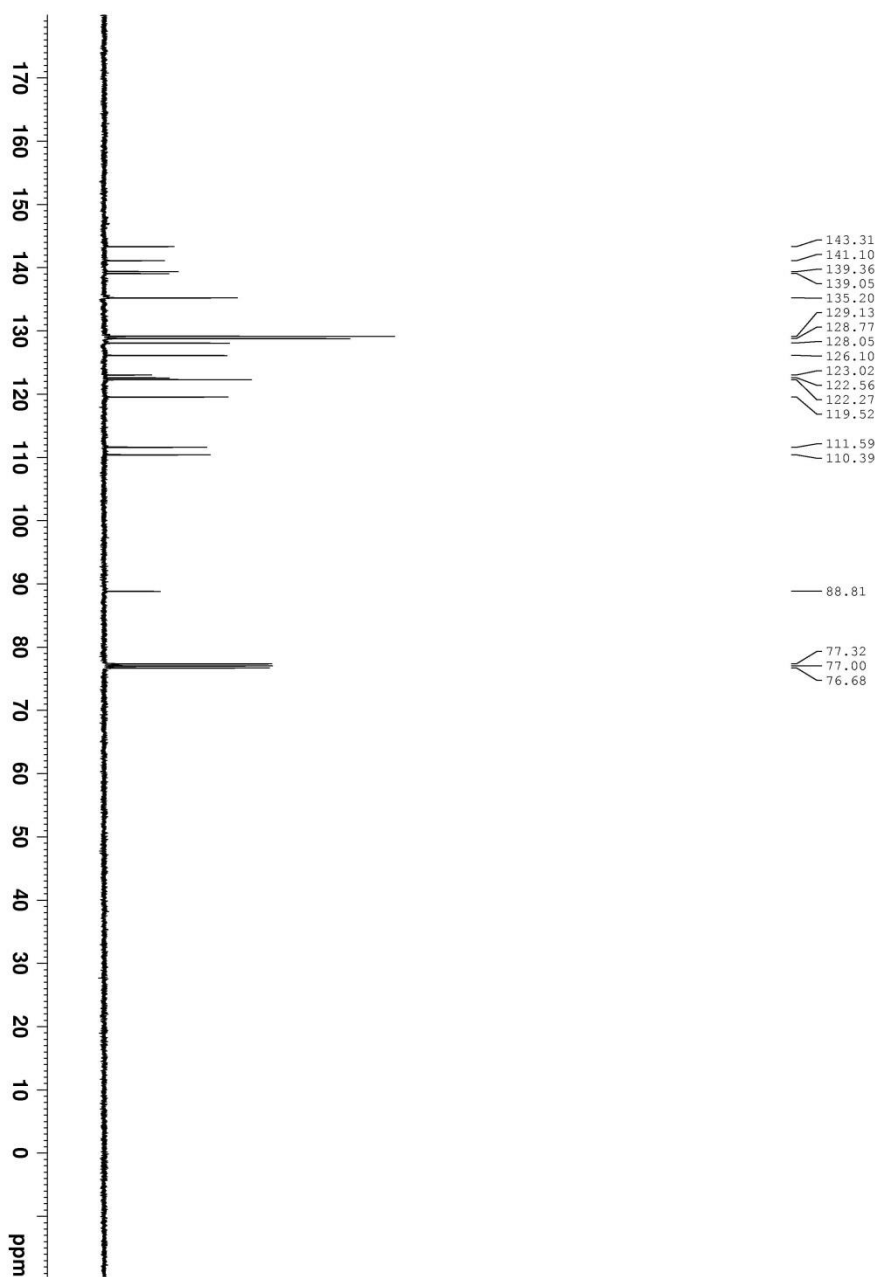
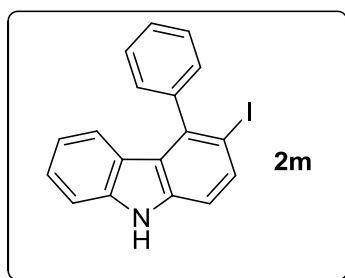


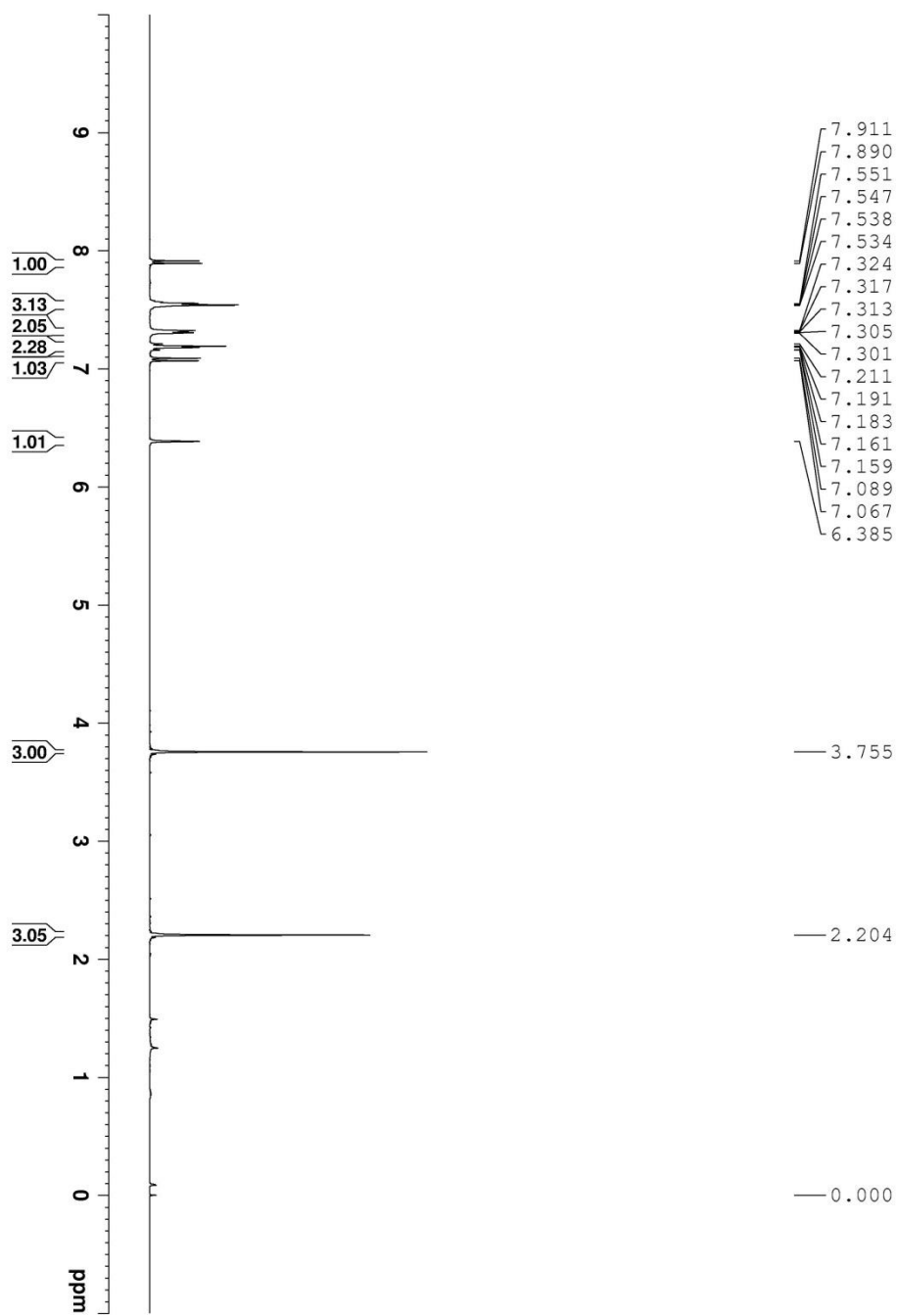
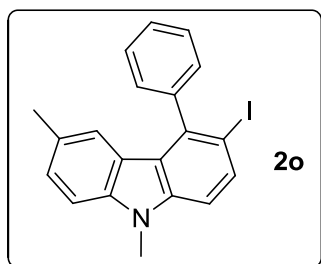


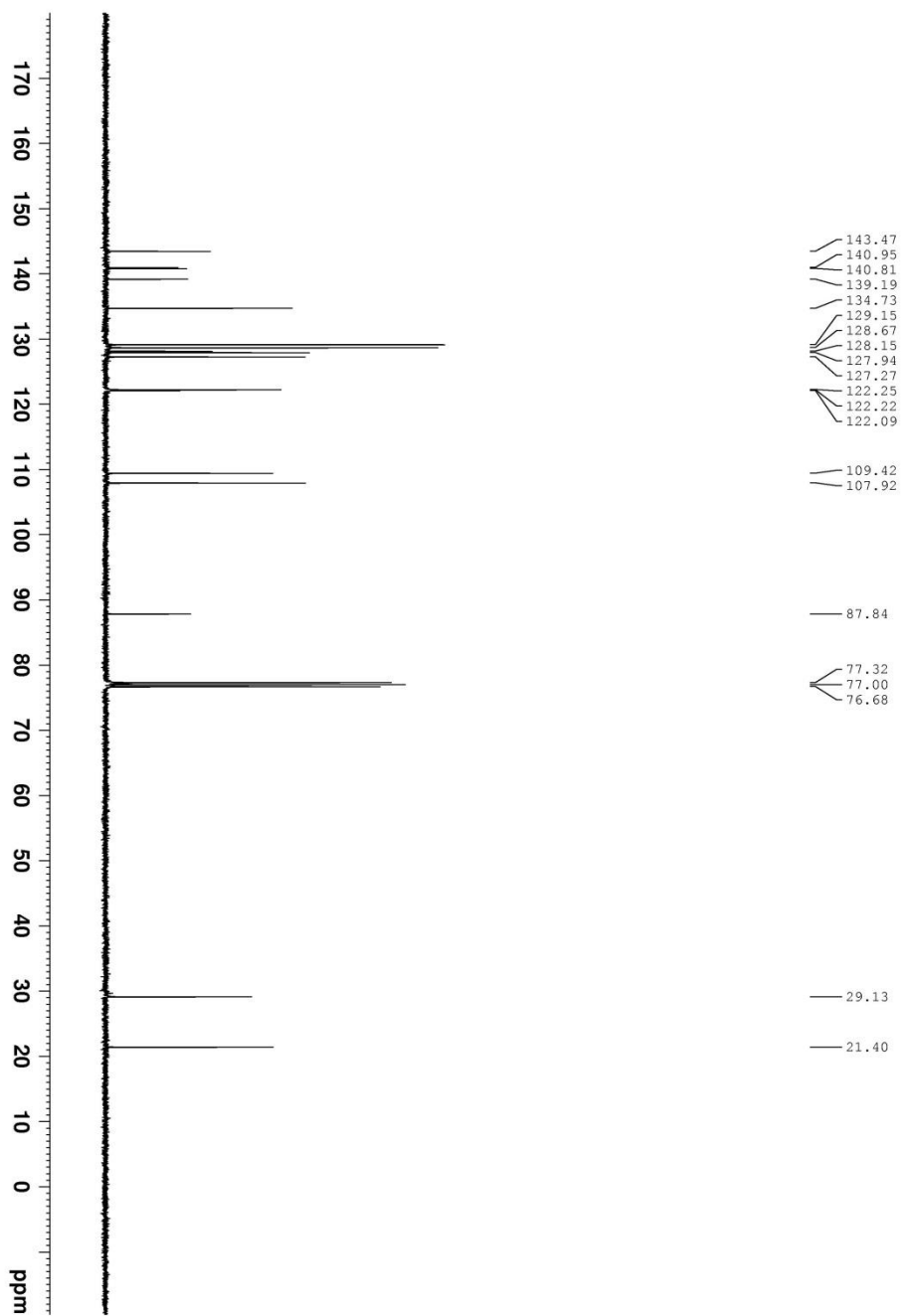
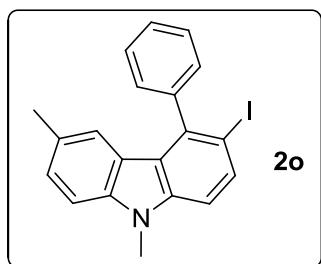


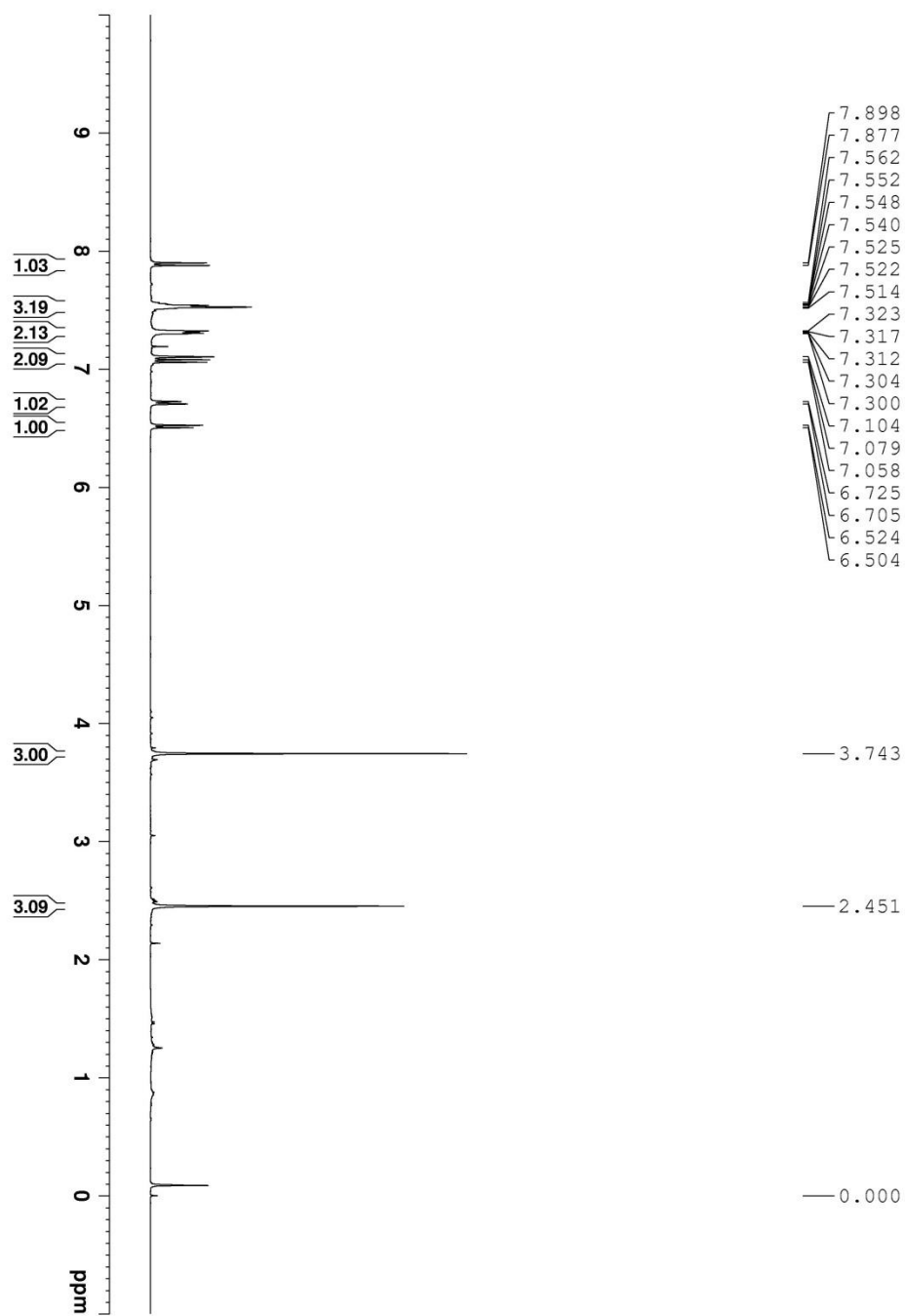
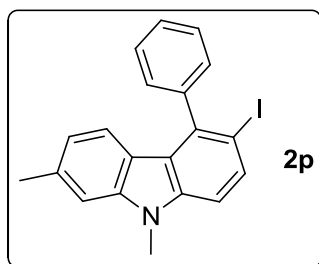


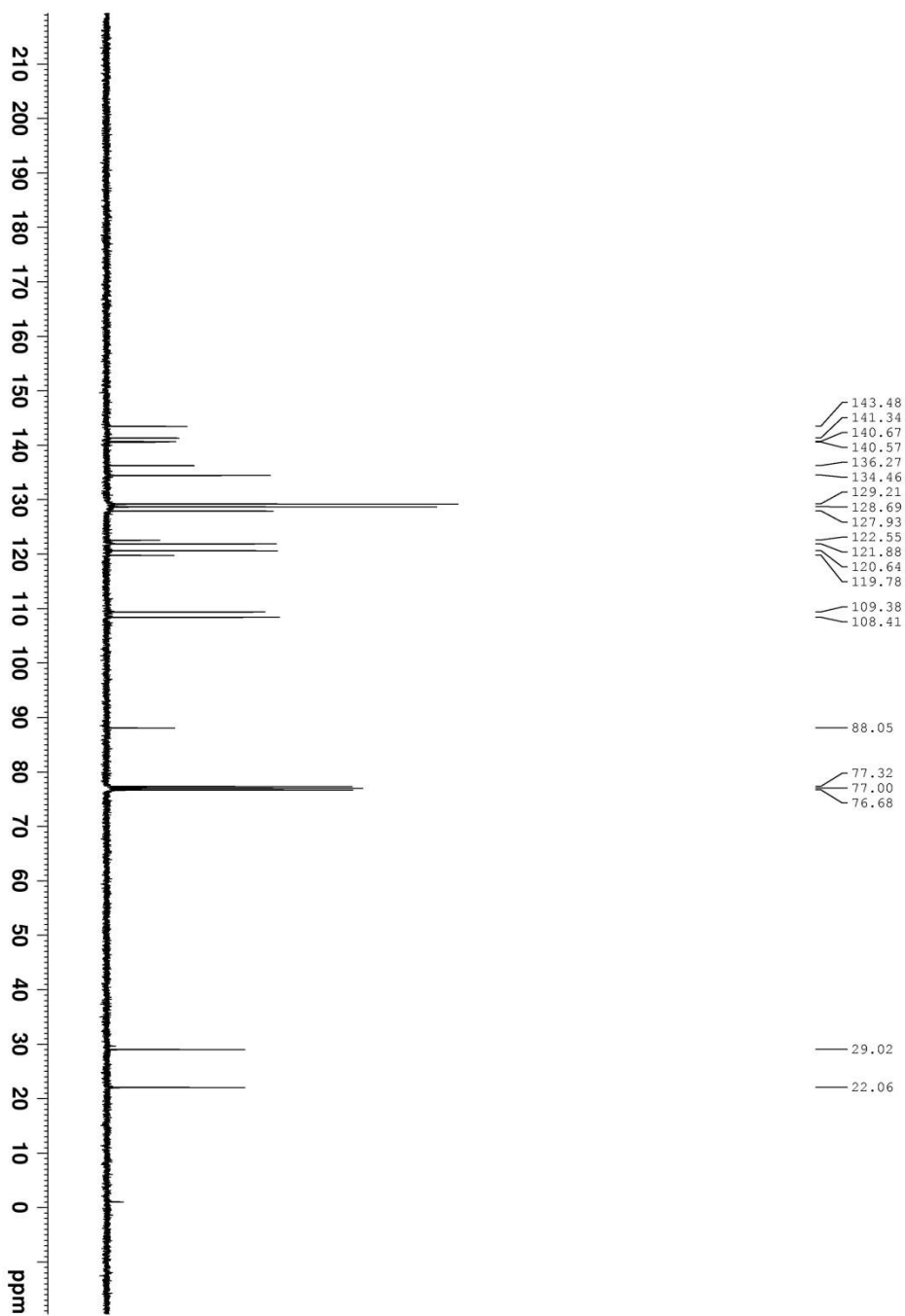
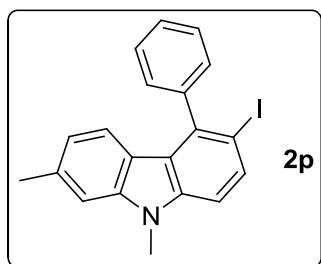
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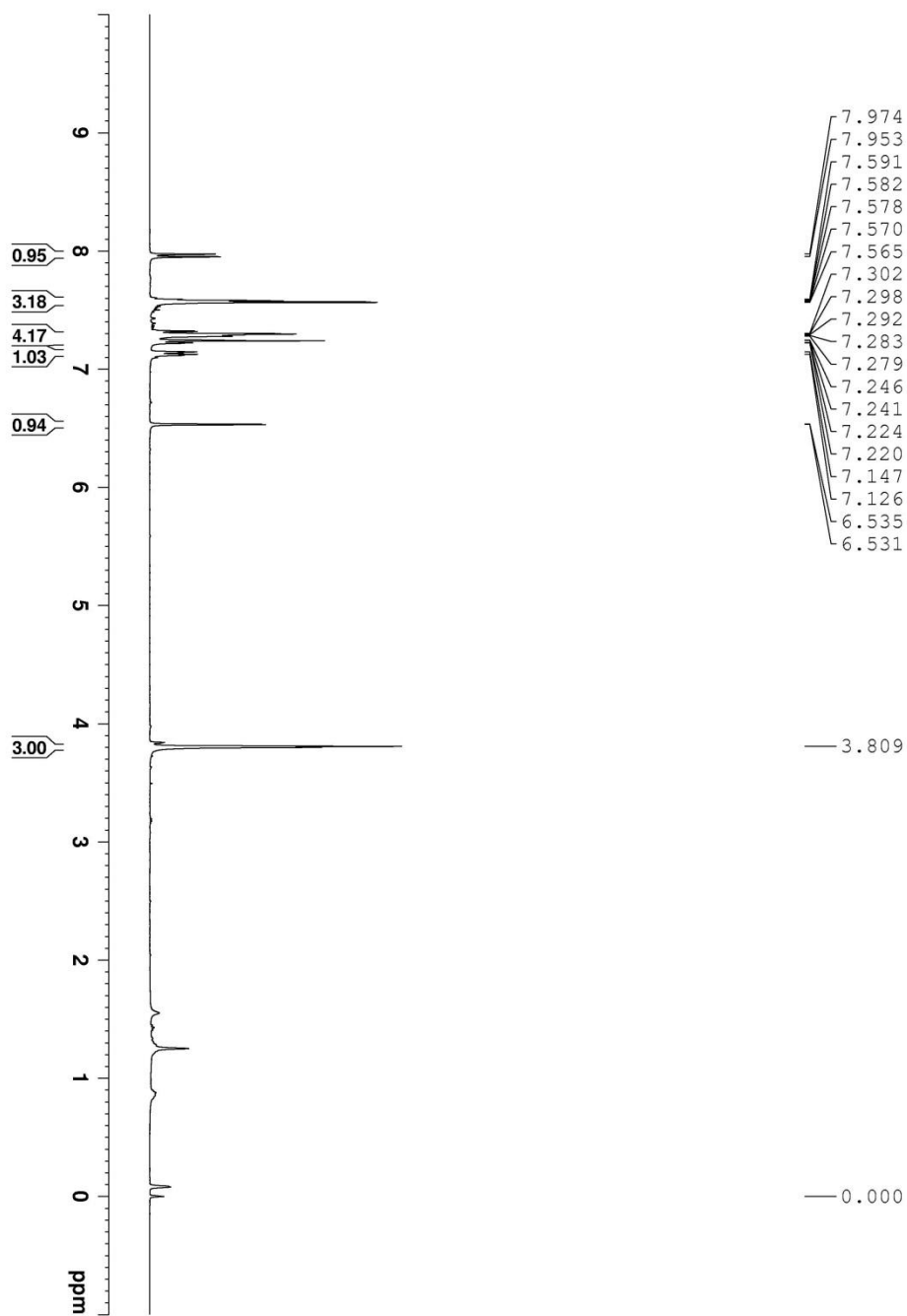
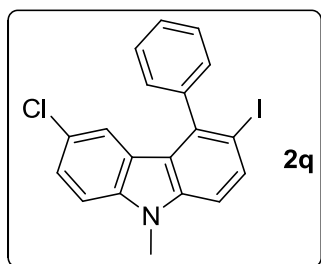


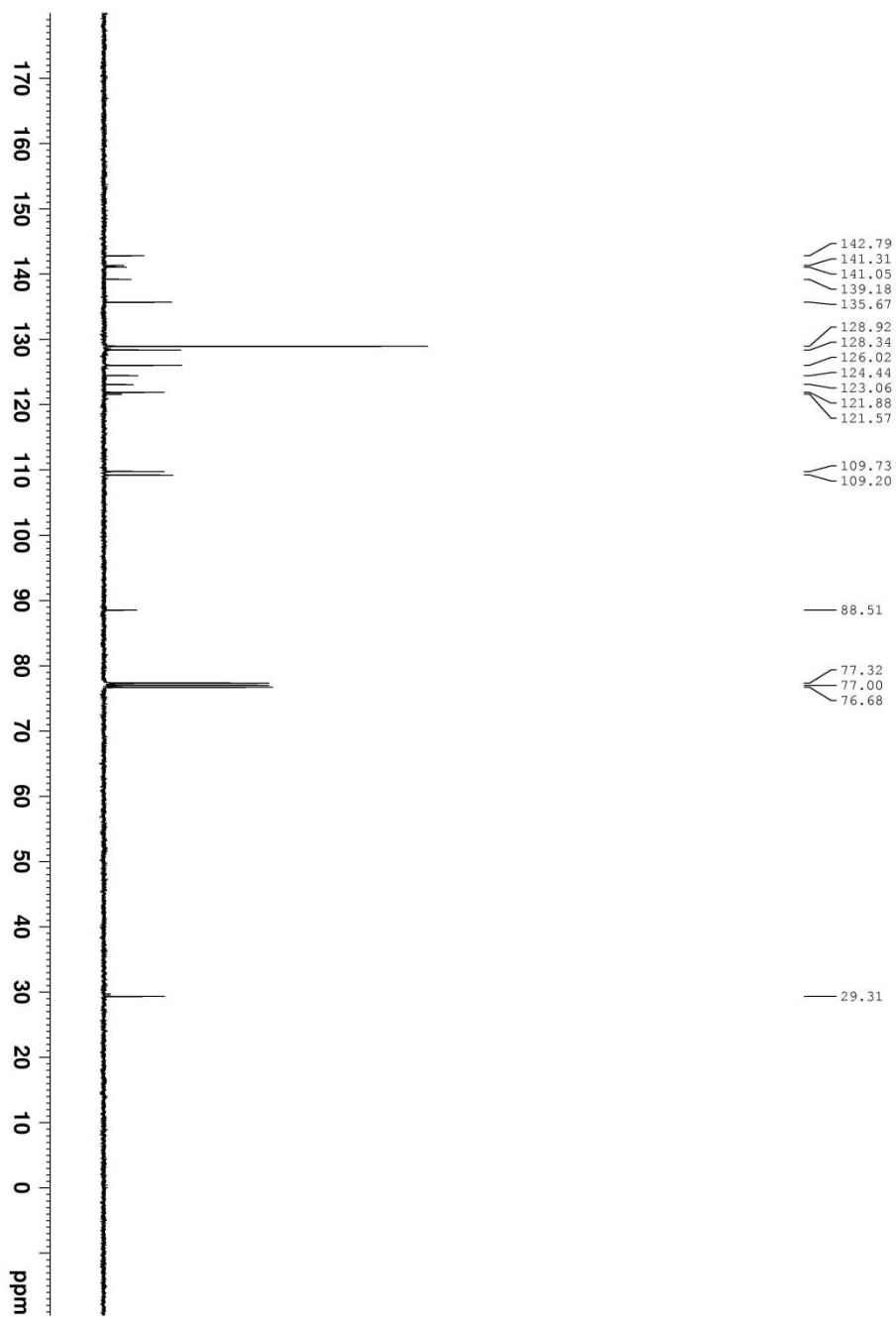
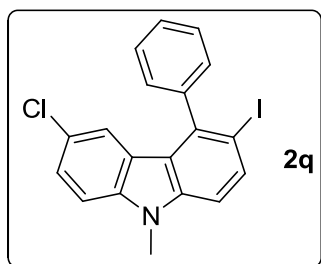


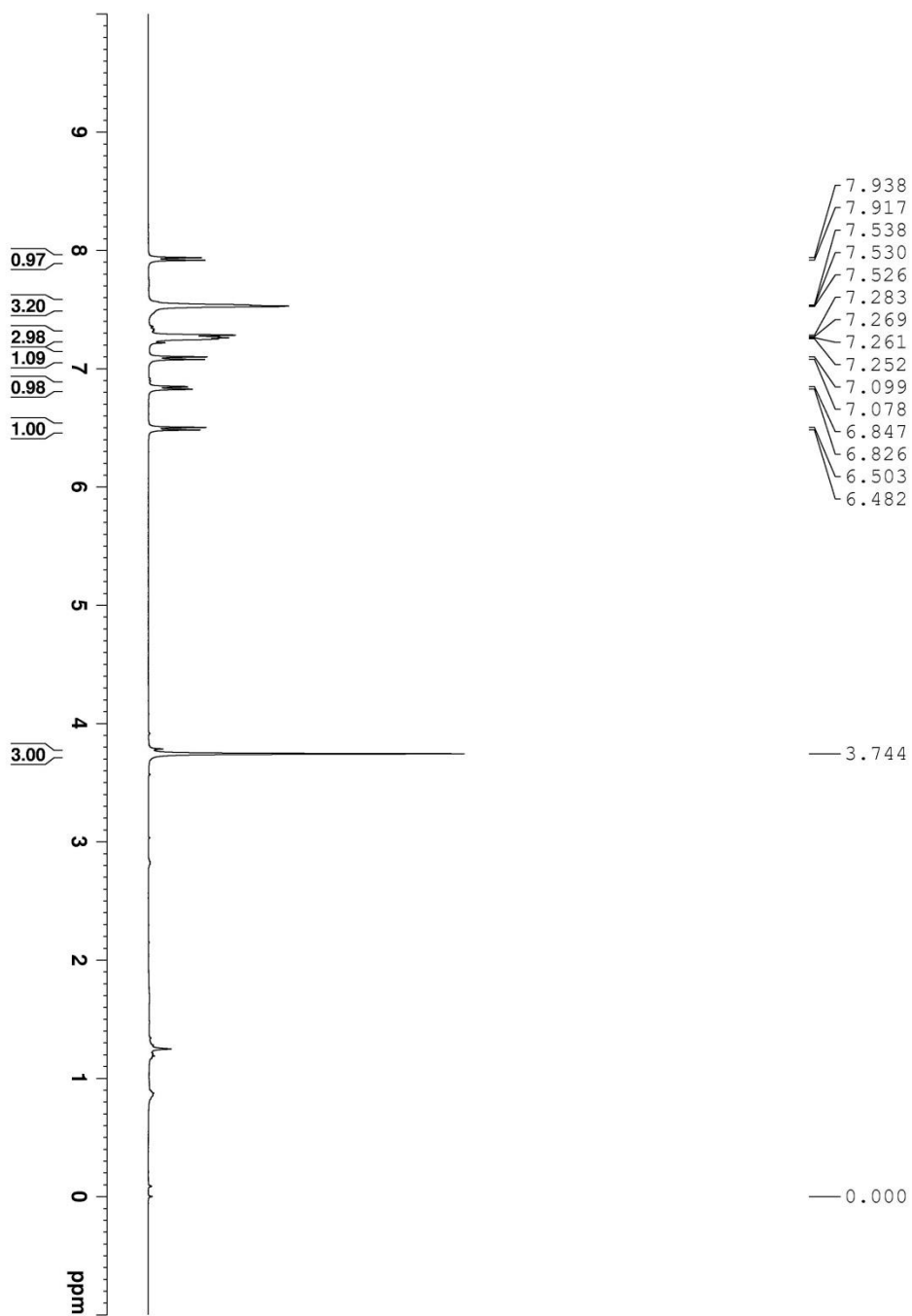
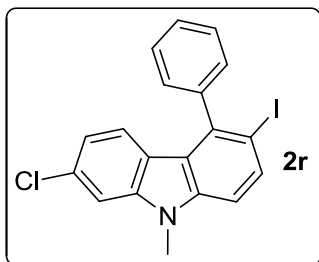


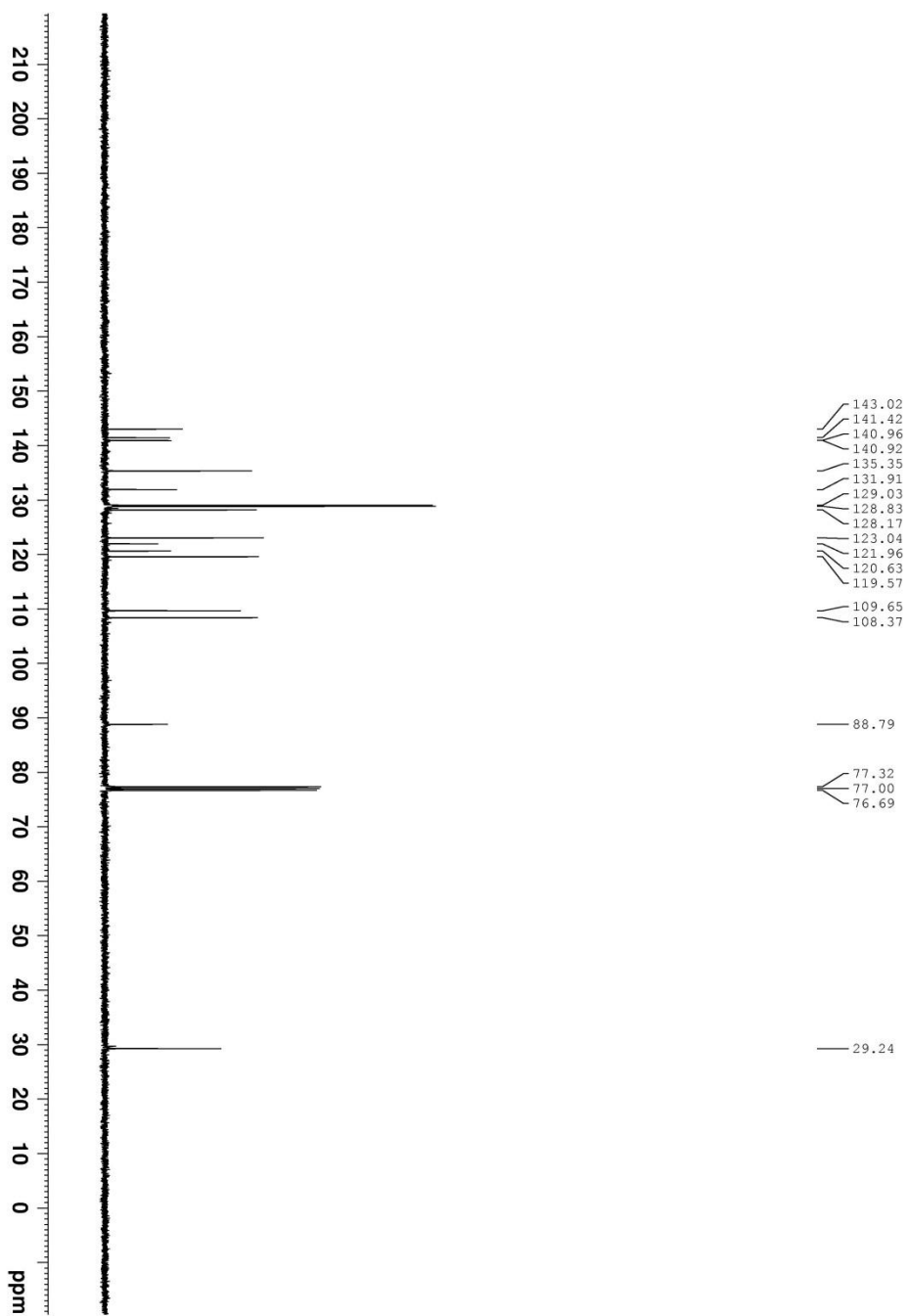
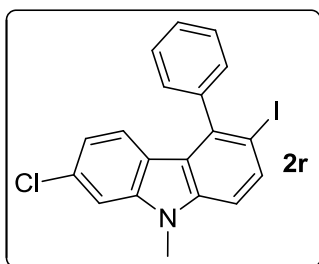


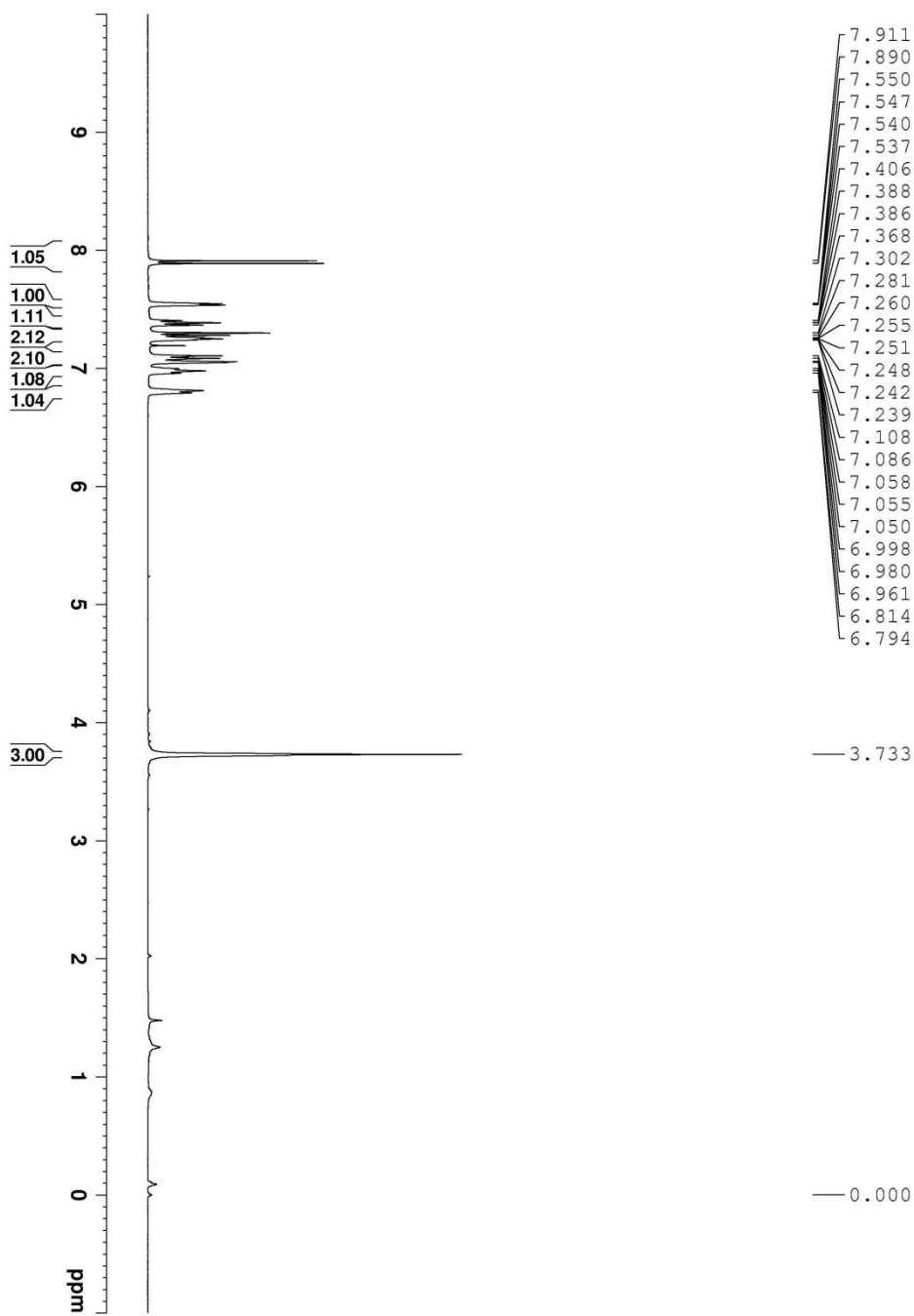
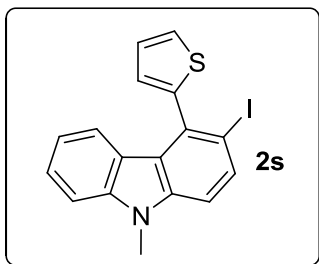


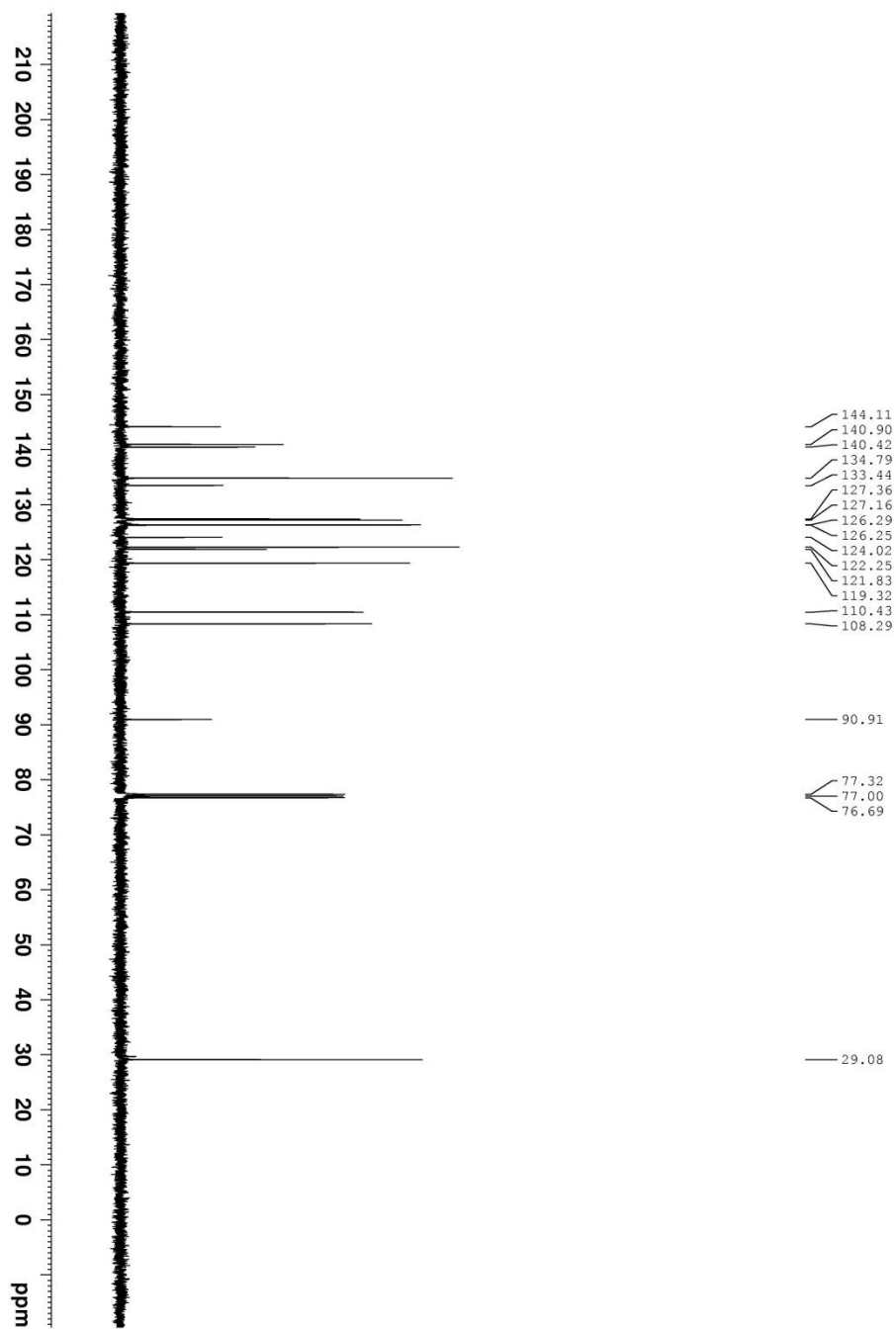
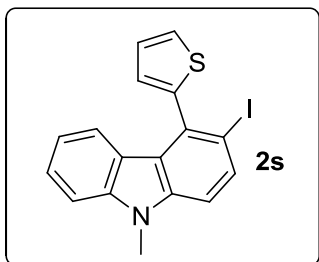


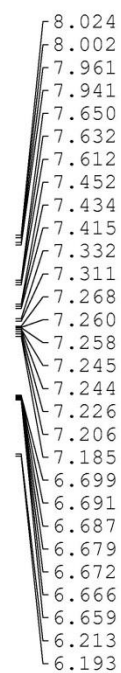
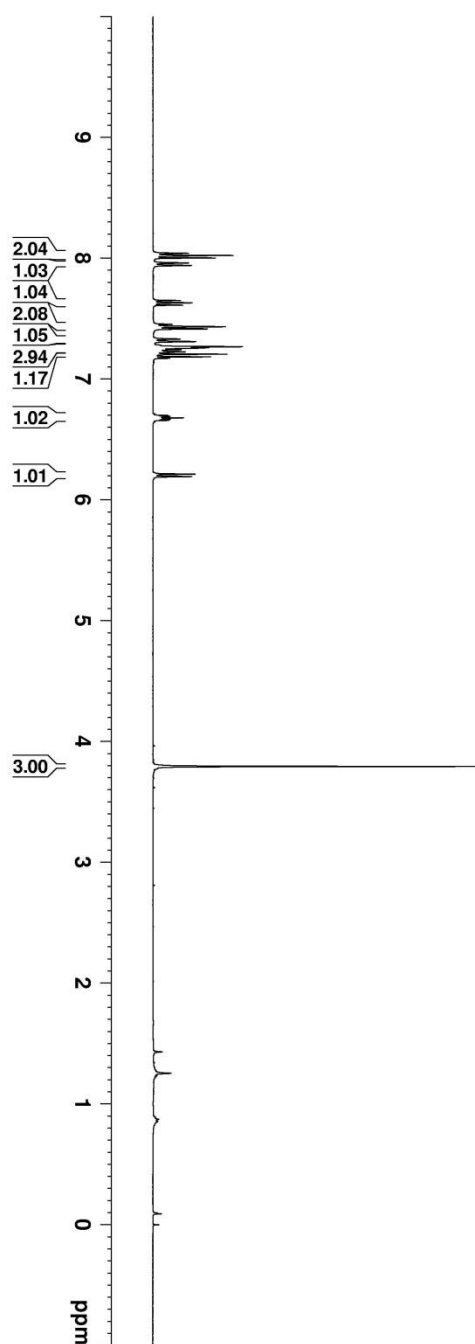
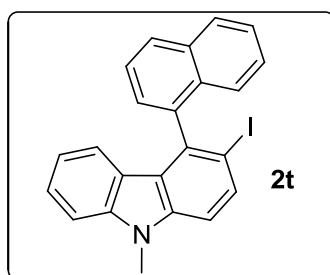






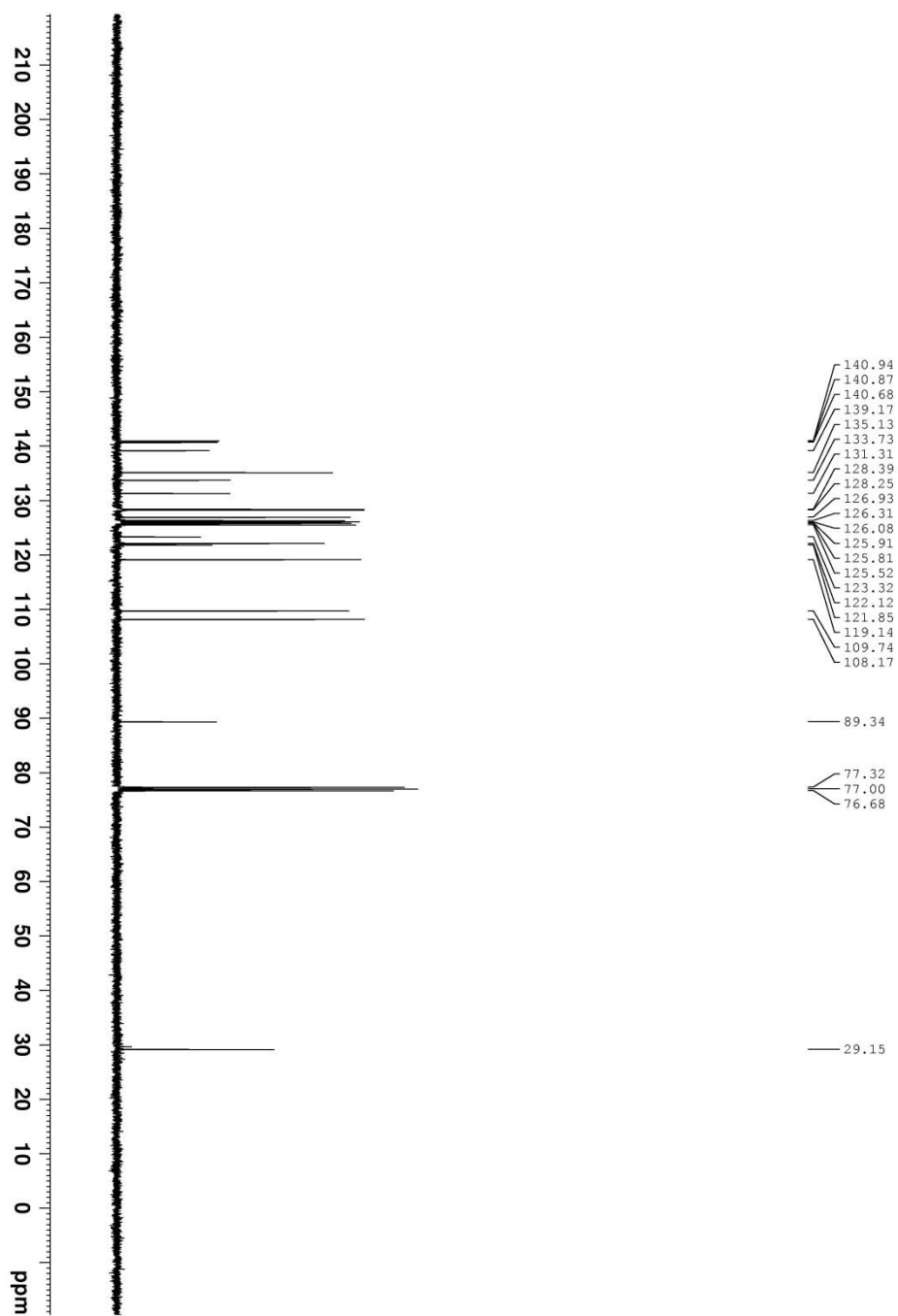
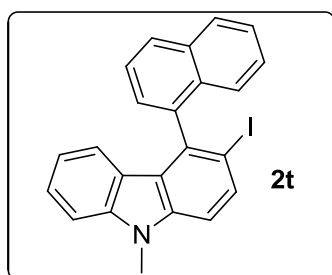


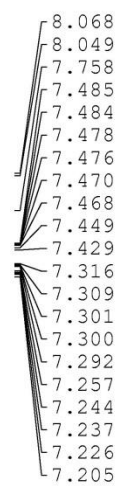
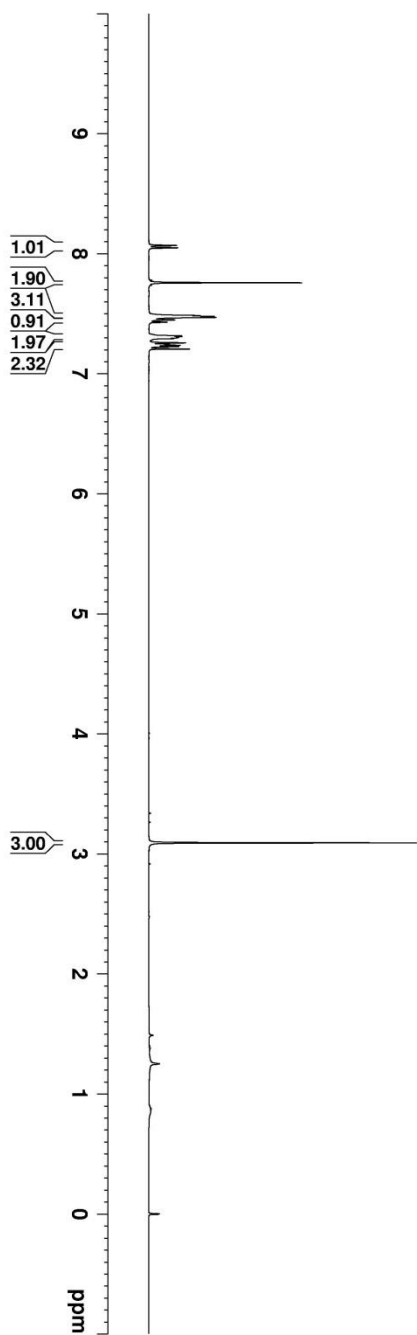
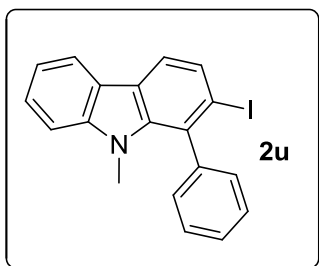




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