

An Efficient Synthesis of Fluoren-9-ones by the Palladium-Catalyzed Annulation of Arynes by 2-Haloarenecarboxaldehydes

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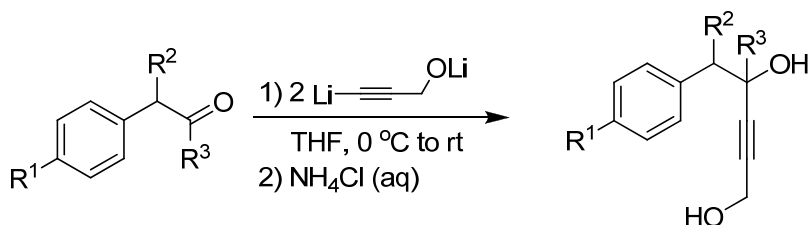
General. The ^1H and ^{13}C NMR spectra were recorded at 300 and 75.5 MHz or 400 and 100 MHz respectively. Thin layer chromatography was performed using commercially prepared 60-mesh silica gel plates (Whatman K6F), and visualization was effected with short wavelength UV light (254 nm) and/or a basic KMnO_4 solution [3 g of KMnO_4 + 20 g of K_2CO_3 + 5 mL of NaOH (5%) + 300 mL of H_2O]. All melting points are uncorrected. High resolution mass spectra were recorded on a Kratos MS50TC double focusing magnetic sector mass spectrometer using EI at 70 eV. Toluene, CH_2Cl_2 and MeCN were distilled from CaH_2 under an atmosphere of argon prior to use and stored over 4\AA molecular sieves. Anhydrous CsF and $\text{Pd}(\text{dba})_2$ were stored in a glove box under an atmosphere of N_2 . All glassware and stirring bars were oven dried prior to use. All reagents were used directly as obtained commercially unless otherwise noted. Compounds **3**, **7-12**, **18**, **19**, and **34-36** have been reported in our previous communication.¹

Synthesis of Starting Materials. Compounds **14**,² **16**³ and benzyne precursors **2a-e**⁴ were prepared according to literature procedures.

Procedure for the Synthesis of 2-(Thiophen-3-yl)acetaldehyde. 2-(Thiophen-3-yl)ethanol (20 mmol, 2.56 g) was dissolved in CH_2Cl_2 (200 mL) and cooled to 0 °C. PCC (26 mmol, 5.59 g) was added slowly. The solution was allowed to slowly warm to room temperature and stirred for 18 h. The resulting brown suspension was filtered through a

plug of silica gel and the solvent concentrated to give the product as an orange oil. The resulting product was taken on to the next step immediately. The resulting aldehyde was unstable and should be used immediately.

General Procedure for the Synthesis of Alkynediols.



Propargyl alcohol (16.6 mmol, 930 mg, 0.98 mL) was dissolved in THF (100 mL) and cooled to 0 °C. Under an atmosphere of argon, *n*-BuLi (2.5 M in hexanes, 33.2 mmol, 13.3 mL) was added slowly and the resulting solution allowed to stir at 0 °C for 1 h. A solution of the appropriate arylacetaldehyde or arylacetone (8.3 mmol) in THF (10 mL) was added slowly, and the solution was allowed to warm to room temperature over a period of 12 h. The solution was quenched with a satd aq NH₄Cl solution and extracted with EtOAc (3 x 20 mL). The organic layers were combined, dried (MgSO₄) and concentrated under reduced pressure. The crude products were isolated by flash column chromatography on silica gel (2:1 hexanes:EtOAc).

5-Phenylpent-2-yne-1,4-diol. This compound was isolated as a pale yellow oil: ¹H NMR (CDCl₃, 400 MHz) δ 2.94-2.95 (d, *J* = 6.6 Hz, 2H), 3.66 (br s, 2H), 4.16 (s, 2H), 4.52-4.55 (t, *J* = 6.5 Hz, 1H), 7.21-7.30 (m, 5H); ¹³C NMR (CDCl₃) δ 44.0, 50.7, 63.2, 84.0, 86.1, 127.0, 128.5, 129.8, 136.8; HRMS Calcd for C₁₁H₁₂O₂: 176.0837. Found: 176.0840.

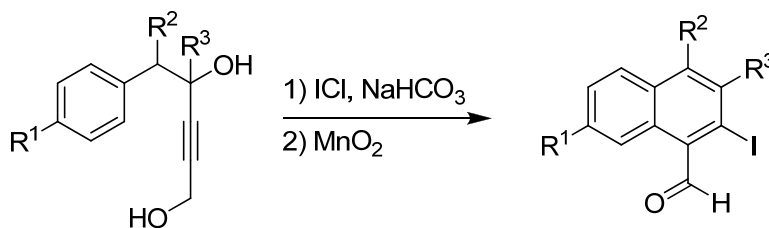
5-Phenylhex-2-yne-1,4-diol. This compound was isolated as a pale yellow oil: ^1H NMR (CDCl_3 , 400 MHz) δ 1.39-1.38 (d, $J = 7.1$ Hz, 3H), 2.96-3.04 (m, 1H), 3.38-3.39 (d, $J = 5.3$ Hz, 1H), 3.56 (br s, 1H), 4.12 (s, 2H), 4.45 (br s, 1H), 7.22-7.34 (m, 5H); ^{13}C NMR (CDCl_3) δ 16.5, 45.9, 50.8, 67.2, 84.7, 85.5, 127.2, 128.5, 128.7, 142.3; HRMS Calcd for $\text{C}_{12}\text{H}_{14}\text{O}_2$: 190.0994. Found: 190.0997.

5,5-Diphenylpent-2-yne-1,4-diol. This compound was isolated as a colorless oil that solidified upon standing: mp 106-108 $^\circ\text{C}$; ^1H NMR ($\text{DMSO}-d_6$, 400 MHz) δ 3.97-3.99 (d, $J = 5.8$ Hz, 2H), 4.12-4.14 (d, $J = 9.0$ Hz, 1H), 5.03-5.07 (m, 1H), 5.09-5.12 (t, $J = 5.7$ Hz, 1H), 5.61-5.63 (d, $J = 6.1$ Hz, 1H), 7.14-7.18 (m, 2H), 7.24-7.28 (t, $J = 7.4$ Hz, 4H), 7.37-7.40 (t, $J = 6.6$ Hz, 4H); ^{13}C NMR ($\text{DMSO}-d_6$) δ 49.0, 57.9, 63.5, 84.7, 85.8, 126.0, 126.3, 128.0, 128.1, 128.6, 128.7, 142.2, 142.3; HRMS Calcd for $\text{C}_{17}\text{H}_{16}\text{O}_2$: 252.1150. Found: 252.1154.

4-Methyl-5-*p*-tolylpent-2-yne-1,4-diol. This compound was isolated as a pale yellow oil: ^1H NMR (CDCl_3 , 400 MHz) δ 1.48 (s, 3H), 2.31 (s, 3H), 2.86-2.93 (m, 2H), 3.03 (br s, 1H), 3.13 (br s, 1H), 7.09-7.11 (d, $J = 7.8$ Hz, 2H), 7.17-7.19 (d, $J = 7.9$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 21.2, 29.3, 49.1, 50.8, 68.2, 82.8, 89.2, 128.9, 130.7, 133.2, 136.6; HRMS Calcd for $\text{C}_{13}\text{H}_{16}\text{O}_2$: 204.1150. Found: 204.1174.

5-(Thiophen-3-yl)pent-2-yne-1,4-diol. This compound was isolated as an orange oil: ^1H NMR (CDCl_3 , 400 MHz) δ 2.98-3.00 (d, $J = 6.2$ Hz, 2H), 3.73 (br s, 2H), 4.19 (s, 2H), 5.49 (br s, 1H), 7.00-7.01 (d, $J = 4.2$ Hz, 1H), 7.09 (s, 1H), 7.23-7.28 (m, 1H); ^{13}C NMR

(CDCl₃) δ 38.4, 50.7, 62.6, 83.9, 86.3, 123.0, 125.6, 129.0, 137.0; HRMS Calcd for C₉H₁₀O₂S: 182.0402. Found: 182.0404.



General Procedure for the Electrophilic Cyclization of Alkynediols by ICl, Followed by Oxidation with MnO₂. A 1.2 mmol portion of the alkynediol, 2 equiv of NaHCO₃, and 8 mL of CH₃CN were placed in a vial and stirred for 1 min at room temperature. Two equiv of ICl in 2 mL of CH₃CN was added dropwise to the vial. The reaction mixture was stirred at room temperature for 10 min. The reaction mixture was then diluted with 25 mL of EtOAc and washed with 20 mL of satd aq Na₂S₂O₃. The organic layer was separated, and the aqueous layer was extracted with another 25 mL of EtOAc. The combined organic layers were dried over MgSO₄ and filtered. The solvent was evaporated under reduced pressure and the crude residue was filtered through a plug of silica gel rinsed with 25% EtOAc in hexanes. The solvent was evaporated under reduced pressure and the residue was dissolved in CHCl₃ (50 mL). The solution was cooled to 0 °C and MnO₂ (6.0 equiv based on the alkynediol) was added. The solution was warmed to room temperature and stirred for 18 h. The suspension was filtered through a plug of celite and the solvent evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel using a gradient solvent system (40:1 hexanes:EtOAc to 9:1 hexanes:EtOAc).

2-Iodonaphthalene-1-carboxaldehyde (20). This product was isolated as a yellow solid: mp 77-79 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 7.55-7.59 (dt, $J = 1.1, 7.5$ Hz, 1H), 7.62-7.67 (m, 2H), 7.80-7.82 (d, $J = 8.1$ Hz, 1H), 7.94-7.96 (d, $J = 8.7$ Hz, 1H), 9.01-9.03 (d, $J = 8.7$ Hz, 1H), 10.39 (s, 1H); ^{13}C NMR (CDCl_3) δ 105.6, 124.2, 127.5, 128.5, 129.4, 130.6, 131.7, 133.8, 135.1, 137.1, 199.0; HRMS Calcd for $\text{C}_{11}\text{H}_7\text{IO}$: 281.9542. Found: 281.9546.

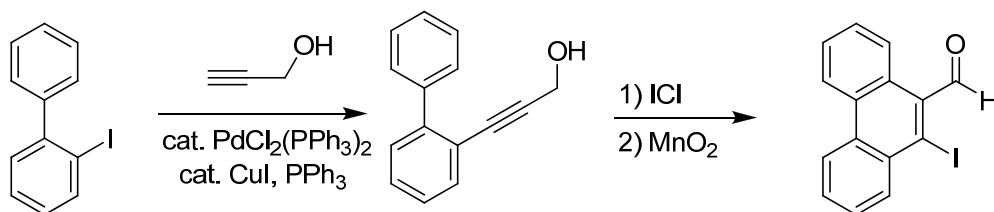
2-Iodo-4-methylnaphthalene-1-carboxaldehyde (22). This product was isolated as a yellow solid: mp 100-102 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 2.60 (s, 3H), 7.53-7.61 (m, 2H), 7.79 (s, 1H), 7.88-7.90 (d, $J = 8.0$ Hz, 1H), 9.06-9.08 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 19.8, 106.8, 125.5, 124.6, 127.3, 128.9, 129.0, 131.5, 132.9, 137.9, 142.9, 198.9; HRMS Calcd for $\text{C}_{12}\text{H}_9\text{IO}$: 295.9698. Found: 295.9704.

2-Iodo-4-phenylnaphthalene-1-carboxaldehyde (24). This product was isolated as a yellow solid: mp 123-125 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 7.38-7.49 (m, 6H), 7.60-7.64 (t, $J = 7.8$ Hz, 1H), 7.83-7.85 (d, $J = 8.3$ Hz, 1H), 7.95 (s, 1H), 9.13-9.15 (d, $J = 8.7$ Hz, 1H), 10.40 (s, 1H); ^{13}C NMR (CDCl_3) δ 105.8, 124.5, 127.1, 127.6, 128.7, 128.8, 129.3, 129.8, 130.0, 132.3, 132.4, 138.1, 138.4, 147.5, 199.0 (one carbon missing due to overlap); HRMS Calcd for $\text{C}_{17}\text{H}_{11}\text{IO}$: 357.9855. Found: 357.9561.

2-Iodo-3,7-dimethylnaphthalene-1-carboxaldehyde (26). This product was isolated as a yellow solid: mp 63-65 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 2.51 (s, 3H), 2.60 (s, 3H), 7.32-7.34 (d, $J = 8.3$ Hz, 1H), 7.58-7.60 (d, $J = 8.3$ Hz, 1H), 7.70 (s, 1H), 8.54 (s, 1H), 10.39 (s, 3H); ^{13}C NMR (CDCl_3) δ 22.5, 29.2, 111.9, 122.8, 127.5, 129.5, 130.1, 131.6,

132.0, 132.6, 137.2, 138.5, 199.4; HRMS Calcd for C₁₃H₁₁IO: 309.9855. Found: 309.9859.

6-Iodothiophene-7-carboxaldehyde (28). This product was isolated as a brown solid: mp 102-105 °C; ¹H NMR (CDCl₃, 400 MHz) δ 7.34-7.35 (d, *J* = 5.5 Hz, 1H), 7.54-7.56 (d, *J* = 5.5 Hz, 1H), 7.70-7.72 (d, *J* = 8.2 Hz, 1H), 7.89-7.91 (d, *J* = 8.2 Hz, 1H), 10.29 (s, 1H); ¹³C NMR (CDCl₃) δ 99.6, 122.8, 128.6, 130.5, 131.0, 136.3, 140.1, 141.3, 196.4; HRMS Calcd for C₉H₅IOS: 287.9106. Found: 287.9110.



Procedure for the Cross-Coupling of 2-Iodobiphenyl and Propargyl Alcohol to form 3-(Biphenyl-2-yl)prop-2-yn-1-ol. To a microwave vial were added 2-iodobiphenyl (1.79 mmol, 0.5 g), propargyl alcohol (1.96 mmol, 110 mg), PdCl₂(PPh₃)₂ (35.7 μmol, 25.1 mg), CuI (71.6 μmol, 13.6 mg), PPh₃ (0.36 mmol, 94.0 mg), DMF (0.5 mL) and Et₂NH (1.5 mL). The vial was capped and the solution was heated in a microwave reactor for 10 min at 100 °C. The solution was diluted with EtOAc (25 mL) and the organic layer washed with water and brine, and dried. The solvent was evaporated under reduced pressure and the product was purified by chromatography on a silica gel column to afford 240 mg (64%) of the product as a yellow-orange oil: ¹H NMR (CDCl₃, 400 MHz) δ 1.88 (br s, 1H), 4.28 (s, 2H), 7.24-7.28 (m, 1H), 7.33-7.41 (m, 5H), 7.52-7.57 (m,

3H); ^{13}C NMR (CDCl_3) δ 51.7, 85.4, 90.2, 121.0, 127.2, 127.7, 128.1, 128.8, 129.7, 133.3, 140.5, 144.0; HRMS Calcd for $\text{C}_{15}\text{H}_{12}\text{O}$: 208.0888. Found: 208.0891.

Procedure for the Cyclization of 3-(Biphenyl-2-yl)prop-2-yn-1-ol by ICl and Oxidation by MnO_2 to form 10-Iodophenanthrene-9-carbaldehyde (30). To a solution of 3-(biphenyl-2-yl)prop-2-yn-1-ol (0.96 mmol) in CH_2Cl_2 (10 mL) under N_2 was added ICl (1.2 equiv) in CH_2Cl_2 (2 mL) at -78°C . The reaction mixture was stirred at -78°C for 0.5 h. The reaction mixture was then diluted with 25 mL of EtOAc and washed with 20 mL of satd aq $\text{Na}_2\text{S}_2\text{O}_3$. The organic layer was separated, and the aqueous layer was extracted with another 25 mL of EtOAc. The combined organic layers were dried over MgSO_4 and filtered. The solvent was evaporated under reduced pressure, and the crude residue was filtered through a plug of silica gel and rinsed with 25% EtOAc in hexanes. The solvent was evaporated under reduced pressure and the residue was dissolved in CHCl_3 (50 mL). The solution was cooled to 0°C and MnO_2 (6.0 equiv) was added. The solution was warmed to room temperature and stirred for 18 h. The suspension was filtered through a plug of celite and the solvent evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using a gradient solvent system (40:1 hexanes:EtOAc to 9:1 hexanes:EtOAc) to afford 243 mg (76%) of the product as a yellow oil that solidified upon standing: mp $80\text{--}82^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz) δ 7.34-7.41 (m, 5H) 7.43-7.47 (m, 2H) 7.50-7.54 (dt, $J = 1.5, 7.5$ Hz, 1H), 9.26 (s, 1H); ^{13}C NMR (CDCl_3) δ 106.5, 127.8, 128.1, 128.6, 128.8, 128.9, 130.7, 130.8, 139.6, 140.2, 150.4, 185.9; HRMS Calcd for $\text{C}_{15}\text{H}_9\text{IO}$: 331.9698. Found: 331.9700.

General Procedure for the Palladium-Catalyzed Synthesis of Fluoren-9-ones.

The 2-iodoarene-carboxaldehyde (0.30 mmol), the 2-(trimethylsilyl)aryl triflate (1.50 mmol), CsF (1.50 mmol), Pd(dba)₂ (0.015 mmol), P(*o*-tolyl)₃ (0.015 mmol), 2 mL of toluene, and 2 mL of MeCN were placed in a 4 dram vial and the vial was sealed. The reaction mixture was stirred first at room temperature for 1 min and then heated to 110 °C for 12 h. The mixture was allowed to cool to room temperature (CAUTION: OPENING THE VIAL AT HIGH TEMPERATURE CAN BE DANGEROUS!), diluted with diethyl ether, washed with brine, dried over anhydrous MgSO₄, and concentrated under reduced pressure. The product was isolated by flash chromatography on silica gel. Compounds **6**,⁵ **15**,⁶ **17**⁷ and **31**⁸ were obtained after flash chromatography, and their spectral properties are identical with these previously reported. In some cases, the product was recrystallized from hexanes/CH₂Cl₂ to afford a spectroscopically pure product.

11H-Benzo[*a*]fluoren-11-one (21). This product was obtained as an orange solid: mp 110-112 °C; ¹H NMR (CDCl₃, 400 MHz) δ 7.24-7.28 (apparent triplet merged with CDCl₃, *J* = 7.3 Hz, 1H), 7.41-7.48 (m, 3H), 7.56-7.63 (m, 3H), 7.76-7.78 (d, *J* = 8.2 Hz, 1H), 7.96-7.98 (d, *J* = 8.2 Hz, 1H), 8.93-8.95 (d, *J* = 8.5 Hz, 1H); ¹³C NMR (CDCl₃) δ 118.3, 120.1, 124.0, 124.4, 126.6, 127.0, 128.7, 129.4, 129.6, 130.3, 134.4, 134.6, 134.7, 136.1, 144.0, 146.3, 195.6; HRMS Calcd for C₁₇H₁₀O: 230.0732. Found: 230.0734.

5-Methyl-11H-benzo[*a*]fluoren-11-one (23). This product was obtained as an orange solid: mp 141-143 °C; ¹H NMR (CDCl₃, 400 MHz) δ 2.77 (s, 3H), 7.24-7.27 (apparent unresolved triplet merged with CDCl₃, 1H), 7.40-7.48 (m, 3H), 7.50 (s, 1H), 7.57-7.60 (t, *J* = 6.5 Hz, 2H), 7.92-7.95 (d, *J* = 8.5 Hz, 1H), 8.98-9.00 (d, *J* = 8.2 Hz, 1H); ¹³C NMR (CDCl₃) δ 21.0, 119.5, 119.9, 123.8, 124.8, 125.0, 125.5, 126.4, 129.2, 129.4,

130.5, 133.4, 134.1, 135.0, 143.9, 144.0, 146.1, 195.4; HRMS Calcd for $C_{18}H_{12}O$: 244.0888. Found: 244.0893.

5-Phenyl-11H-benzo[a]fluoren-11-one (25). This product was obtained as an orange solid: mp 205-207 °C; 1H NMR ($CDCl_3$, 400 MHz) δ 7.24-7.28 (apparent doublet of triplets merged with $CDCl_3$, J = 1.1, 7.2 Hz, 1H), 7.33-7.45 (m, 3H), 7.49-7.61 (m, 8H), 7.78-7.79 (d, J = 8.4 Hz, 1H), 9.03-9.05 (d, J = 8.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 119.7, 120.1, 124.0, 124.7, 126.2, 126.6, 127.2, 128.3, 128.7, 129.4, 129.5, 129.9, 131.0, 132.8, 134.4, 135.0, 140.4, 143.8, 145.7, 148.6, 195.4 (one carbon missing due to overlap); HRMS Calcd for $C_{23}H_{14}O$: 306.1045. Found: 306.1051.

2,6-Dimethyl-11H-benzo[a]fluoren-11-one (27). This product was obtained as an orange solid: mp 203-205 °C; 1H NMR ($CDCl_3$, 400 MHz) δ 2.51 (s, 3H), 2.69 (s, 3H), 7.21-7.24 (m, 2H), 7.39-7.42 (t, J = 7.4 Hz, 1H), 7.55-7.57 (d, J = 8.2 Hz, 2H), 7.59-7.61 (d, J = 7.5 Hz, 1H), 7.65 (s, 1H), 8.75 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.2, 22.4, 123.2, 123.3, 123.9, 126.8, 127.5, 128.8, 129.2, 130.5, 133.0, 134.3, 135.3, 136.7, 139.0, 144.8, 145.5, 196.0; HRMS Calcd for $C_{19}H_{14}O$: 258.1045. Found: 258.1050.

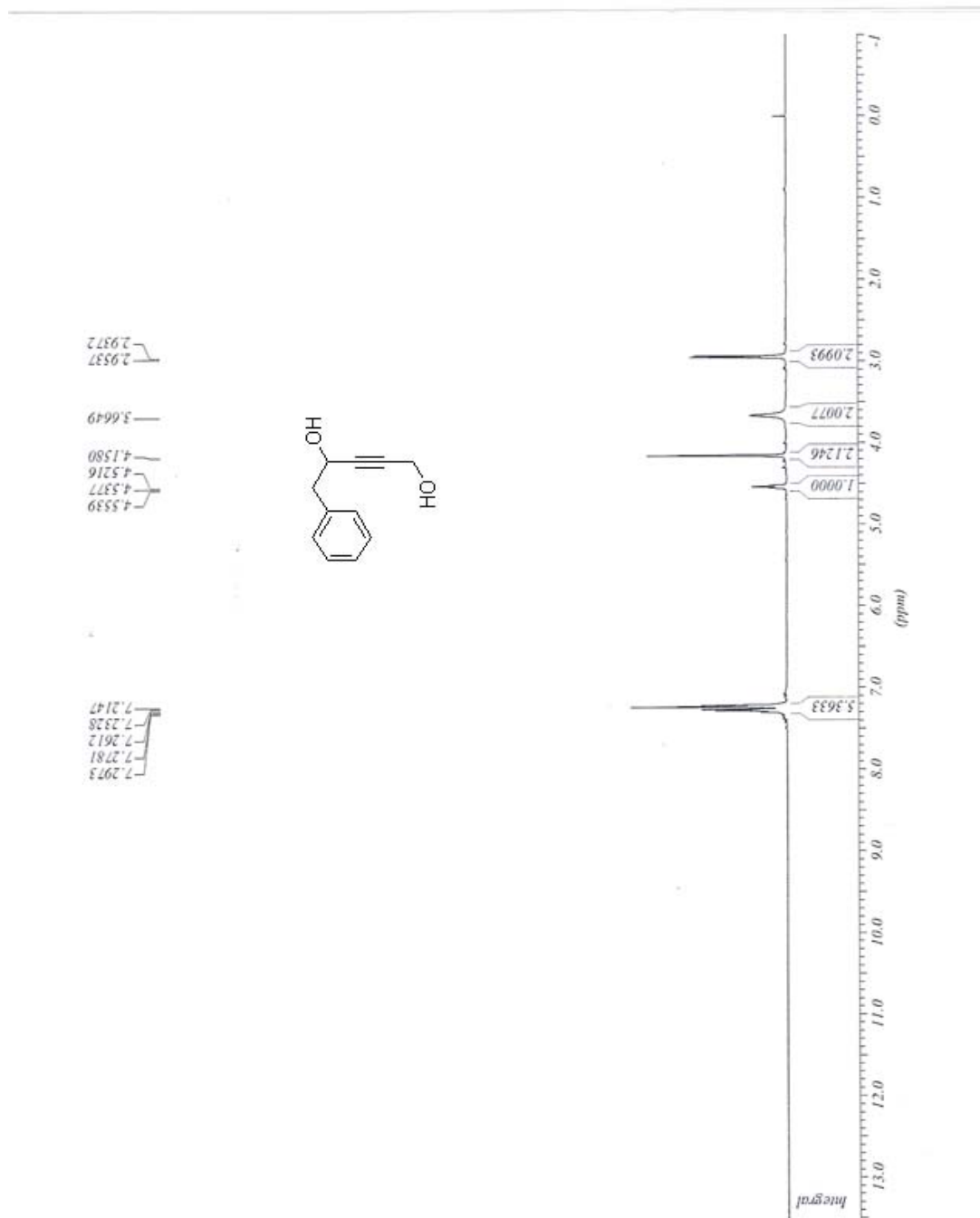
10H-Fluoreno[1,2-b]thiophen-10-one (29). The product was obtained as an orange solid: mp 110-112 °C; 1H NMR ($CDCl_3$, 400 MHz) δ 7.22-7.24 (dd, J = 1.0, 7.3 Hz, 1H), 7.28-7.30 (d, J = 5.4 Hz, 1H), 7.42-7.51 (m, 4H), 7.61-7.63 (d, J = 7.3 Hz, 1H), 7.88-7.90 (d, J = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 116.9, 120.5, 123.3, 124.4, 127.8, 129.1, 129.5, 129.8, 134.4, 134.8, 136.0, 142.5, 144.9, 193.5; HRMS Calcd for $C_{15}H_8OS$: 236.0296. Found: 236.0299.

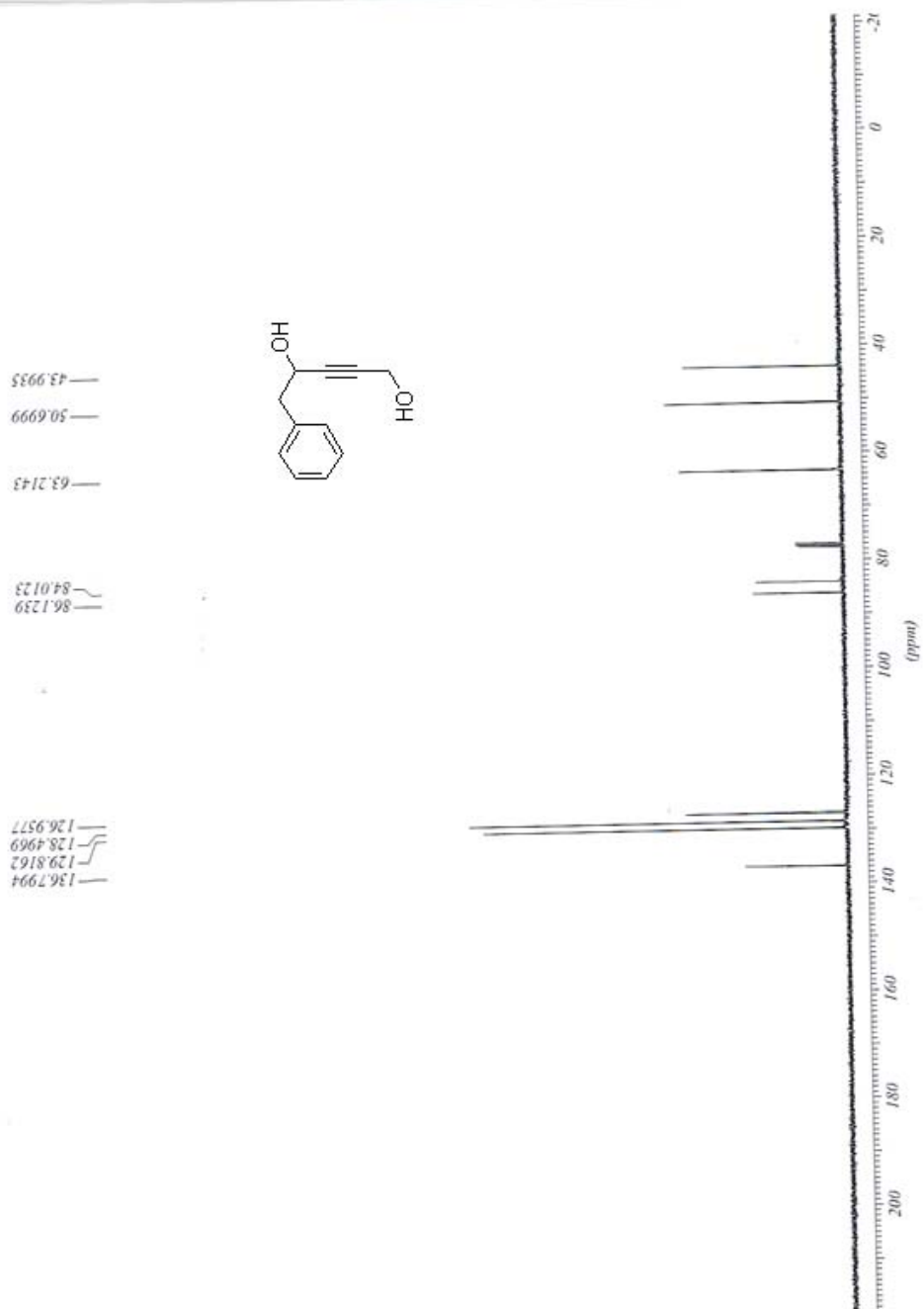
Procedure for the Synthesis of Fluoren-9-one 38 from 2-Bromofluoren-9-one. To a microwave vial was added 2-bromofluoren-9-one (0.20 mmol, 51.8 mg), Pd(PPh₃)₄ (10.0 μmol, 11.6 mg), 3,4,5-trimethoxyphenylboronic acid (0.24 mmol, 50.8 mg), Cs₂CO₃ (1M in H₂O, 0.24 mL), and EtOH (1.5 mL). The microwave vial was capped and heated to 110 °C for 10 min by microwave irradiation. Water (20 mL) was added and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine and dried (MgSO₄). The solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (4:1 hexanes:EtOAc) to afford 66 mg (95%) of the product as a yellow solid: mp 137-139 °C; ¹H NMR (CDCl₃, 400 MHz) δ 3.91 (s, 3H), 3.95 (s, 6H), 6.80 (s, 2H), 7.28-7.32 (m, 1H), 7.48-7.56 (m, 3H), 7.67-7.69 (m, 2H), 7.85-7.86 (d, *J* = 1.7 Hz, 1H); ¹³C NMR (CDCl₃) δ 56.4, 61.2, 91.2, 104.1, 120.6, 120.8, 123.0, 124.6, 129.2, 133.2, 134.6, 135.1, 135.9, 138.2, 142.4, 143.4, 144.4, 153.7, 194.1; HRMS Calcd for C₂₂H₁₈O₄: 346.1205. Found: 346.1210.

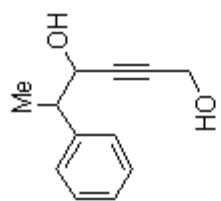
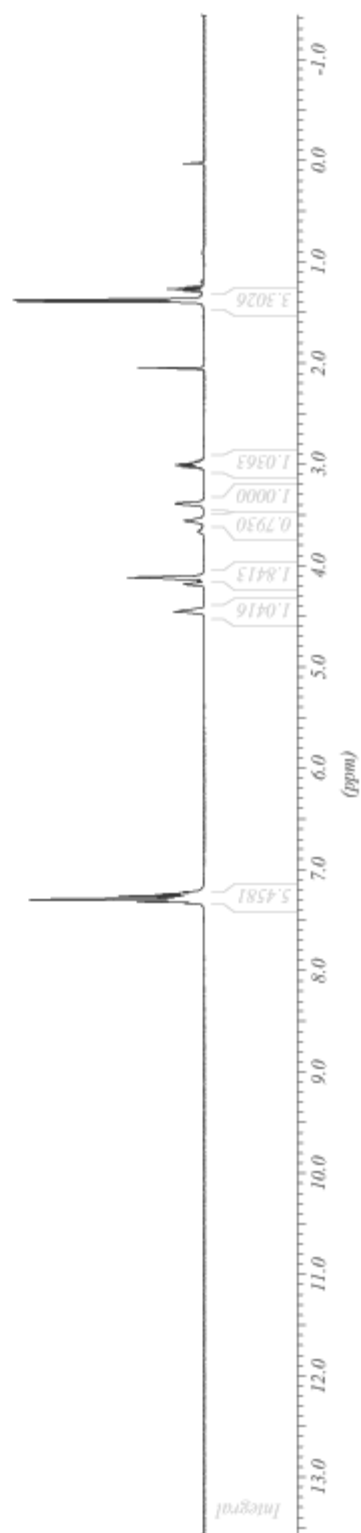
Procedure for the Synthesis of Alkyne 39 from 2-Bromofluoren-9-one. To a microwave vial was added 2-bromofluoren-9-one (0.20 mmol, 51.8 mg), PdCl₂(PPh₃)₂ (4.0 μmol, 2.8 mg), CuI (8.0 μmol, 1.5 mg), PPh₃ (0.04 mmol, 10.5 mg), DMF (0.5 mL) and Et₂NH (1.5 mL). The microwave vial was capped and heated to 120 °C for 15 min by microwave irradiation. Water (20 mL) was added and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine and dried (MgSO₄). The solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (4:1 hexanes:EtOAc) to afford 60 mg (88%) of the product as a yellow solid: mp 145-147 °C; ¹H NMR (CDCl₃, 400 MHz) δ 3.81 (s, 3H), 6.47-6.48

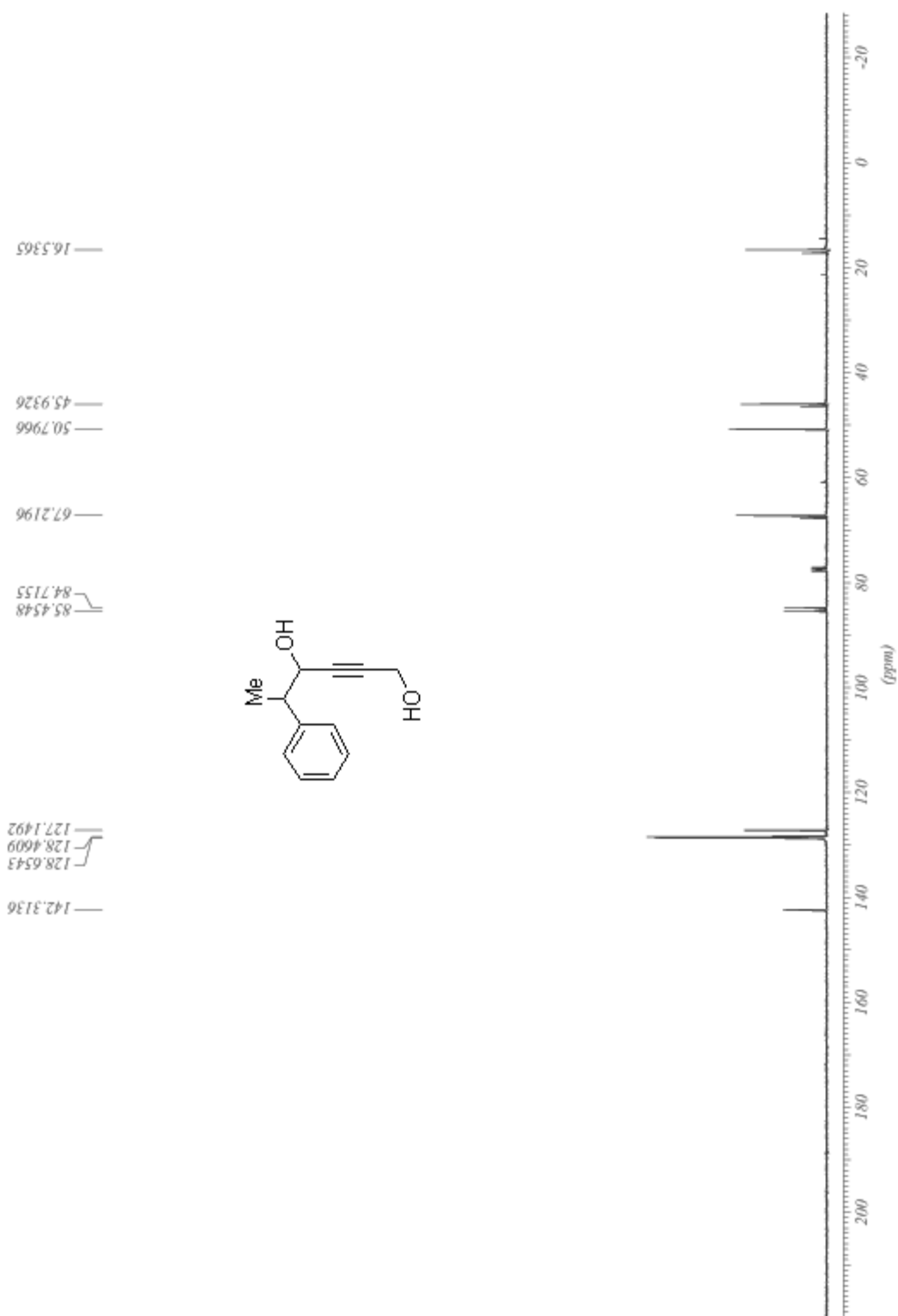
(t, $J = 2.0$ Hz, 1H), 6.68-6.69 (d, $J = 2.4$ Hz, 2H), 7.29-7.33 (dt, $J = 1.8, 7.8$ Hz, 1H), 7.49-7.51 (m, 3H), 7.63-7.68 (m, 2H), 7.79 (s, 1H); ^{13}C NMR (CDCl_3) δ 55.7, 88.4, 91.3, 102.3, 109.5, 120.5, 120.8, 124.2, 124.3, 124.7, 127.5, 129.6, 134.4, 134.5, 135.1, 137.8, 143.9, 144.1, 160.7, 193.2; HRMS Calcd for $\text{C}_{23}\text{H}_{16}\text{O}_3$: 340.1099. Found: 340.1105.

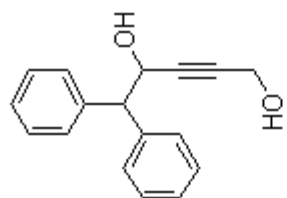
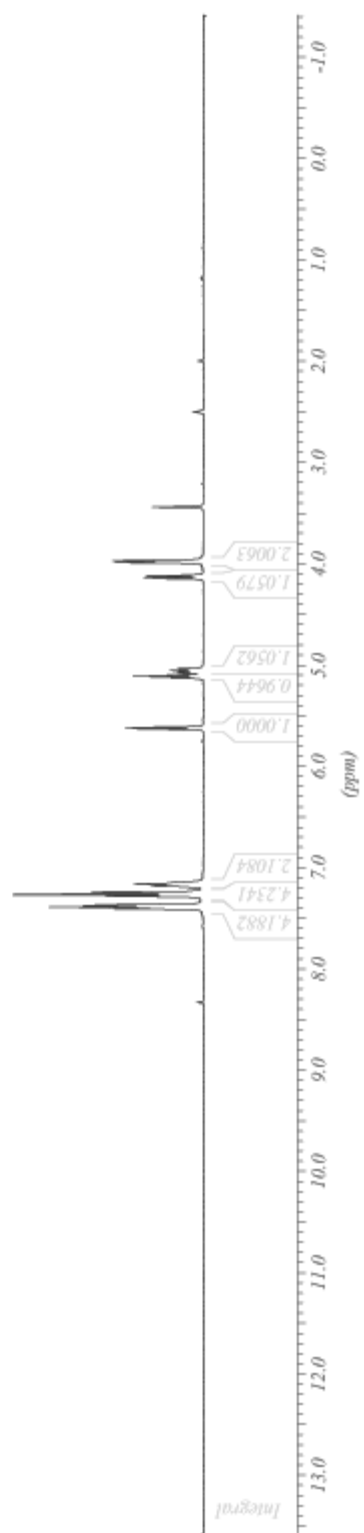
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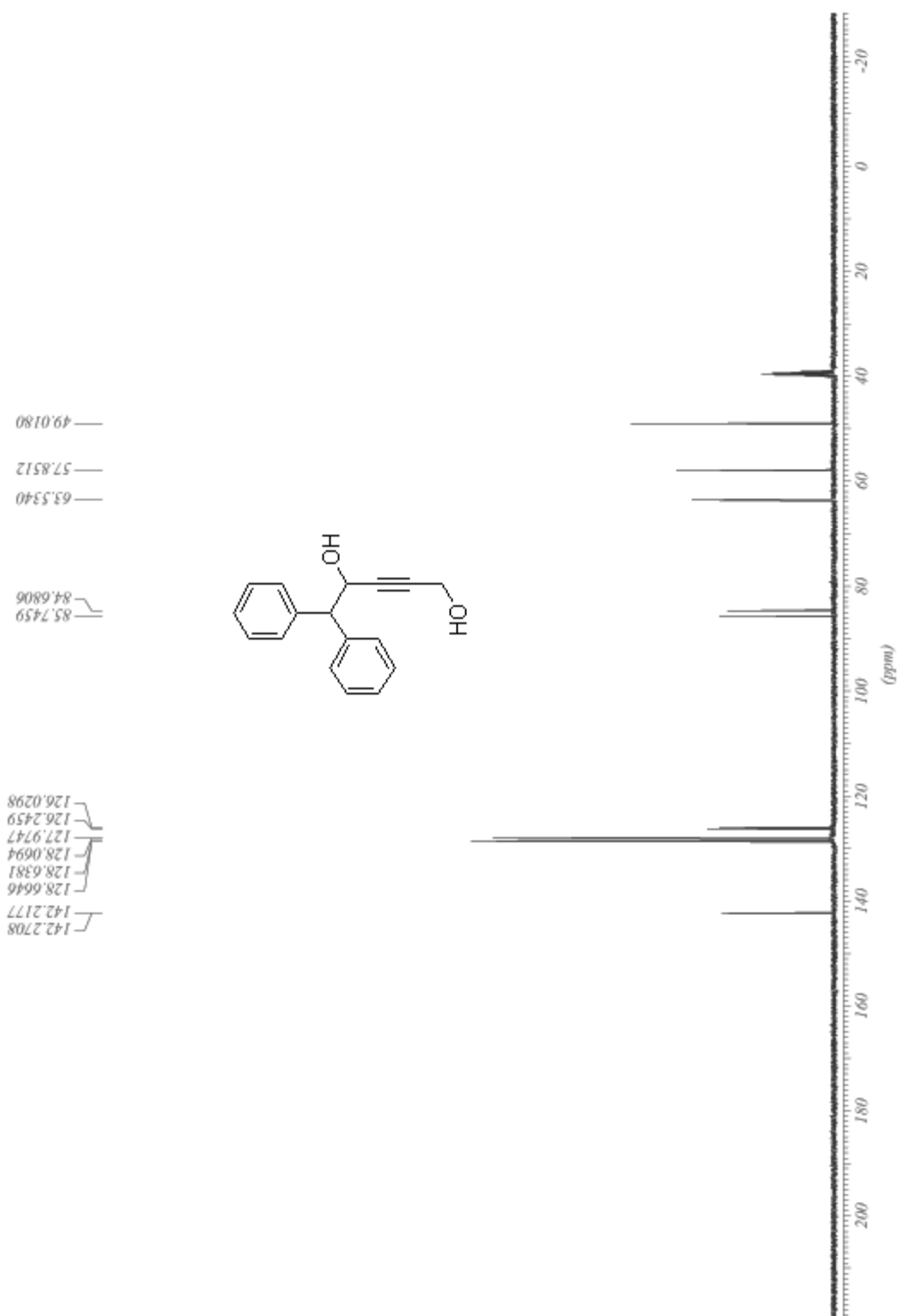




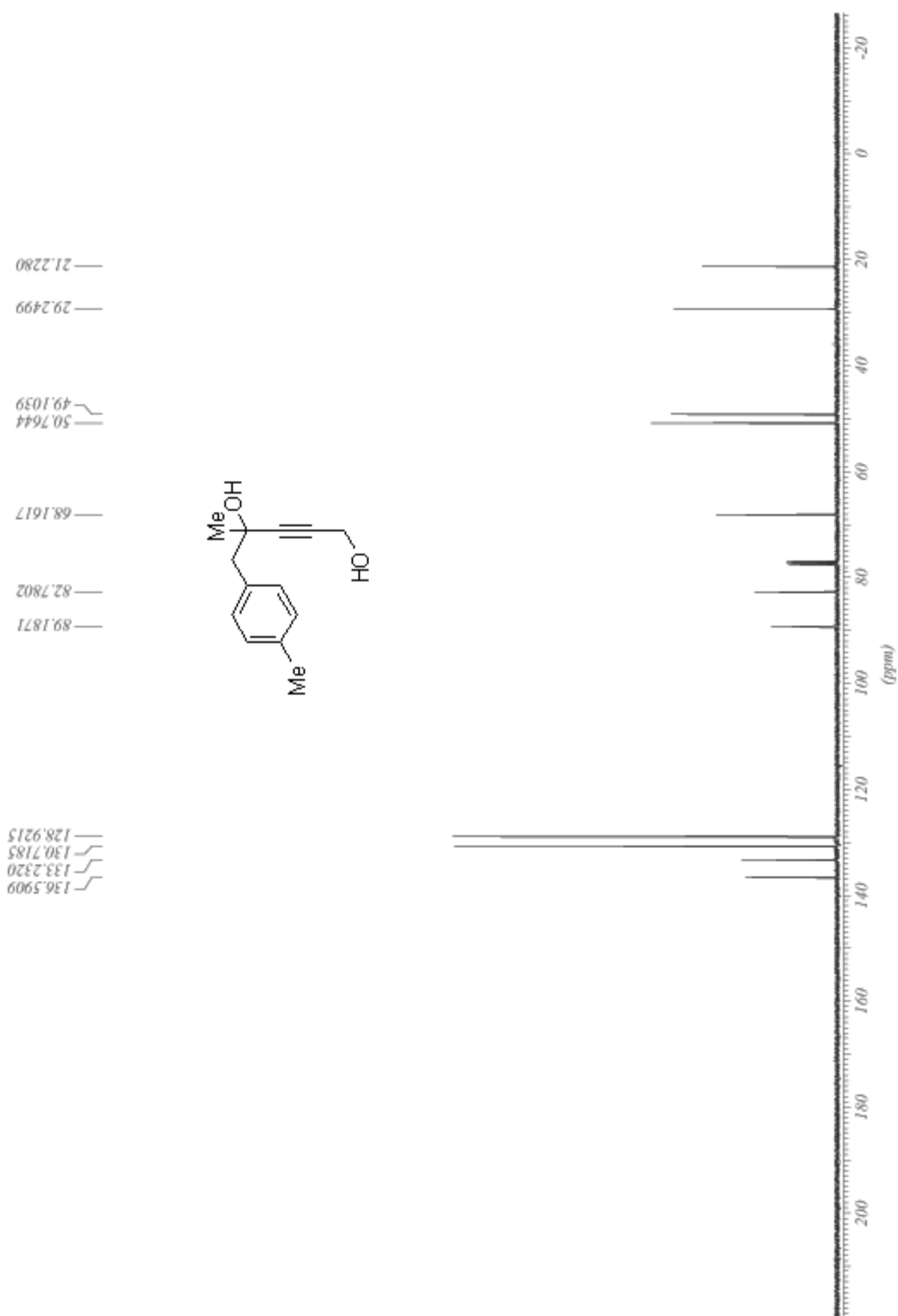


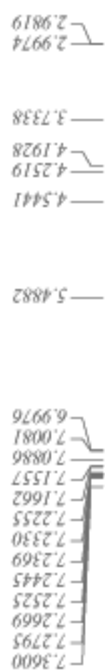
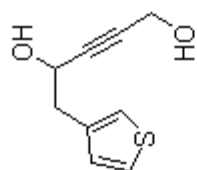
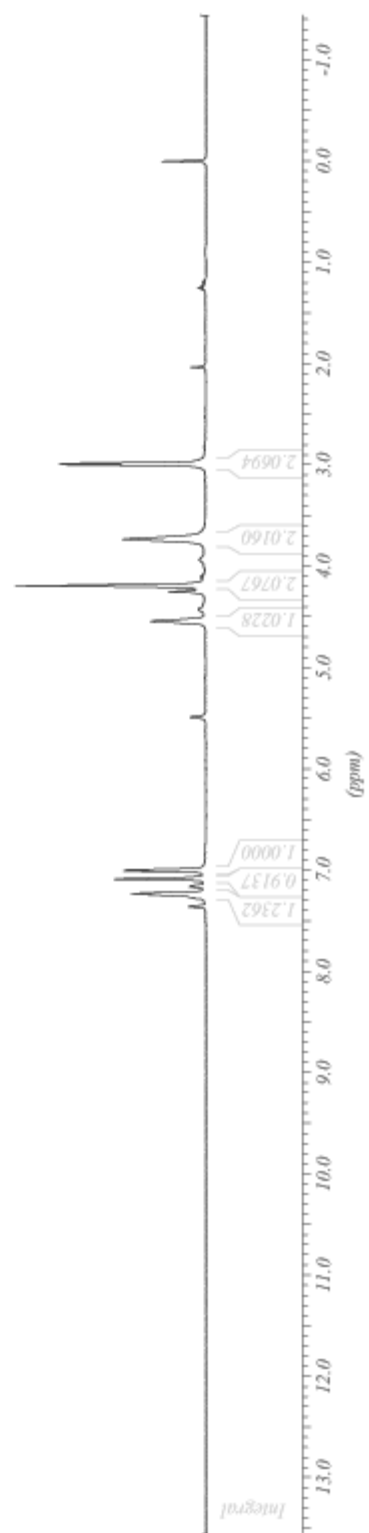


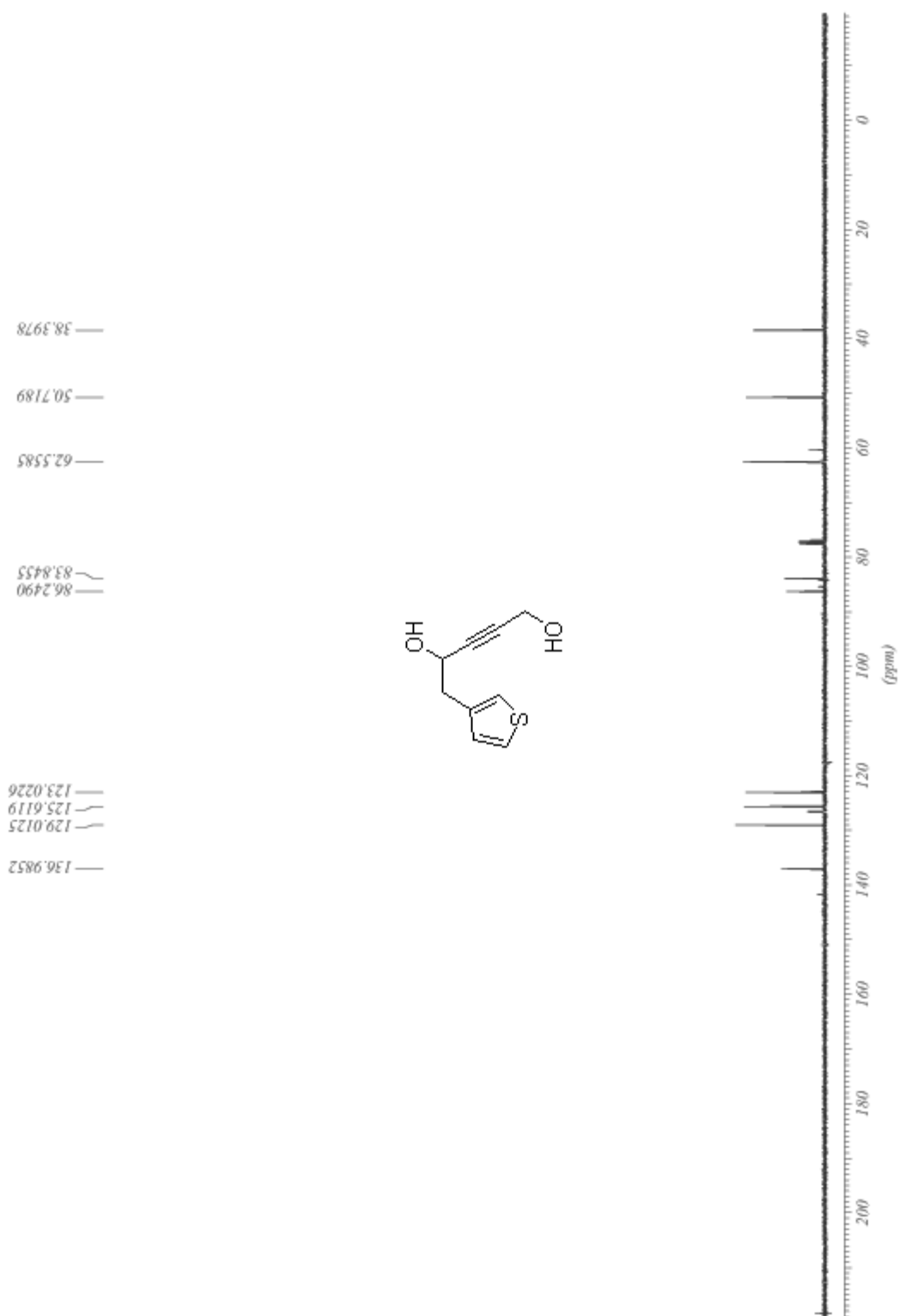
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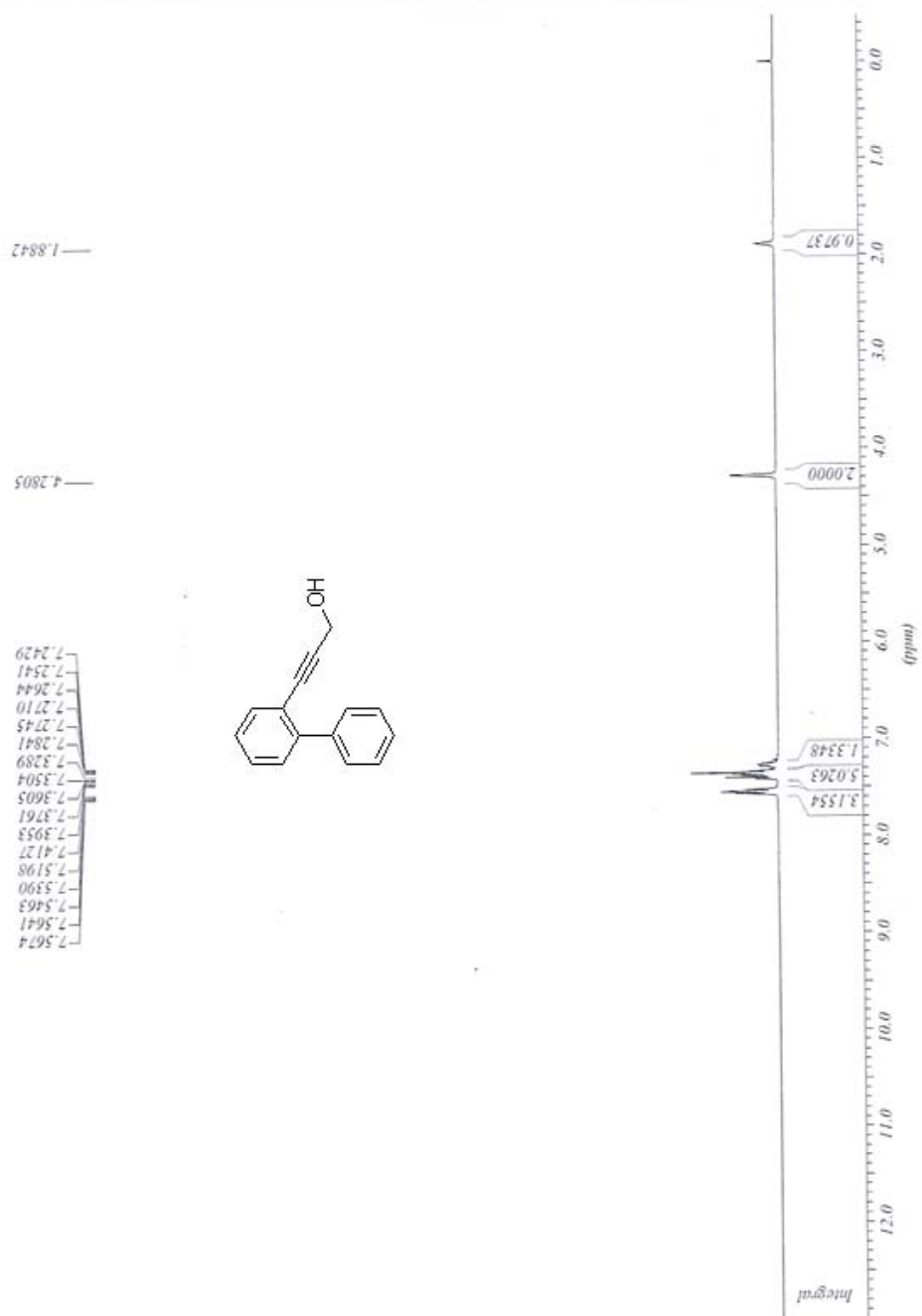


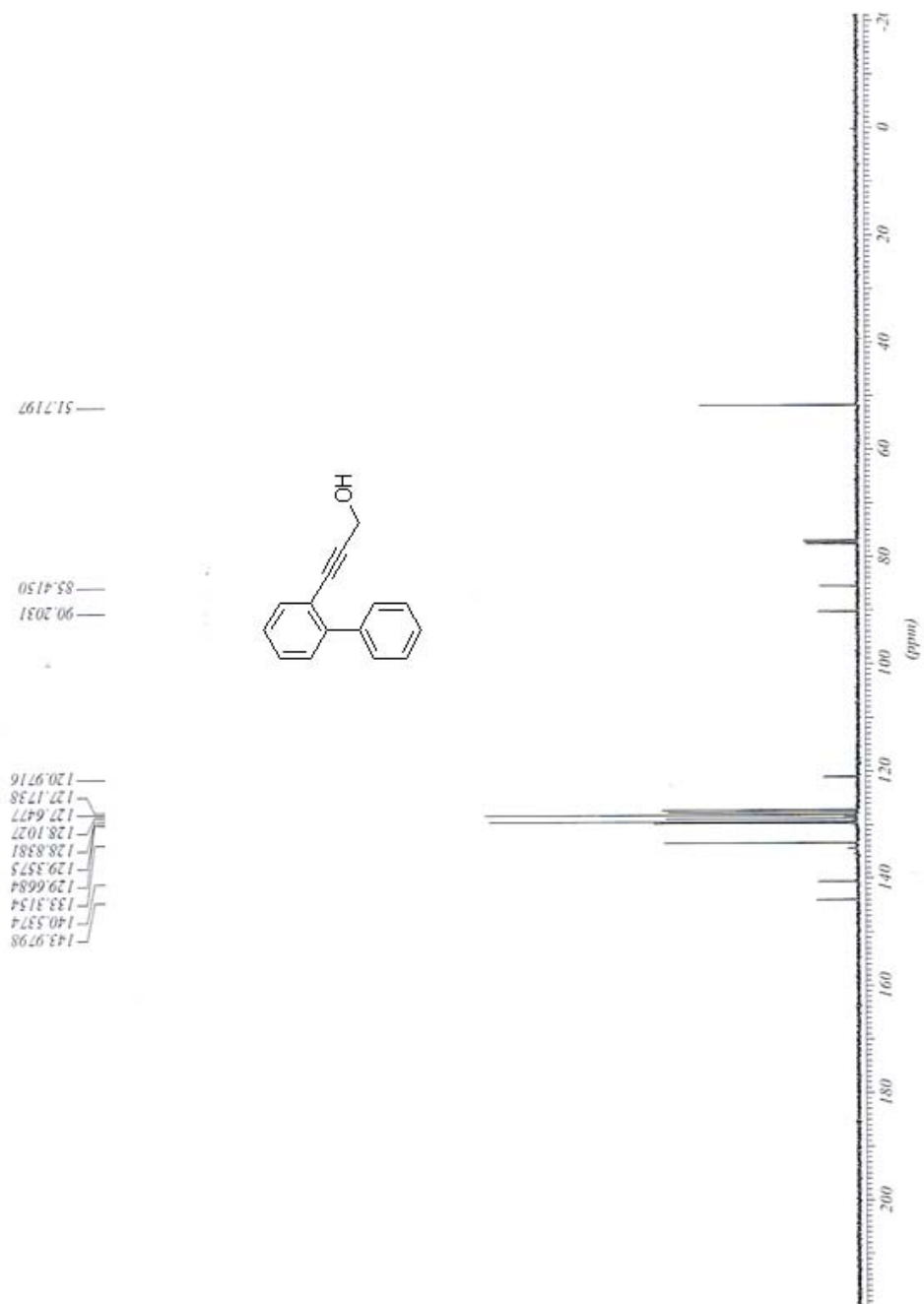


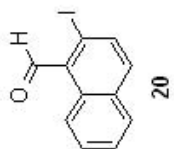
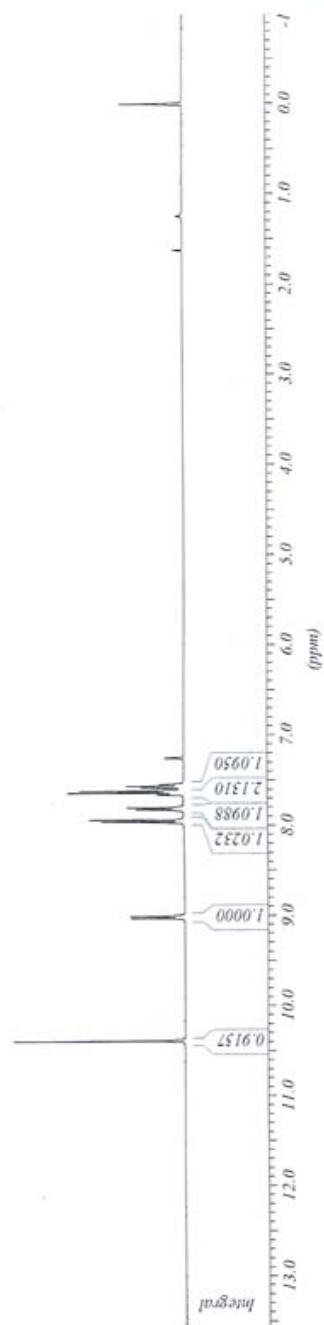


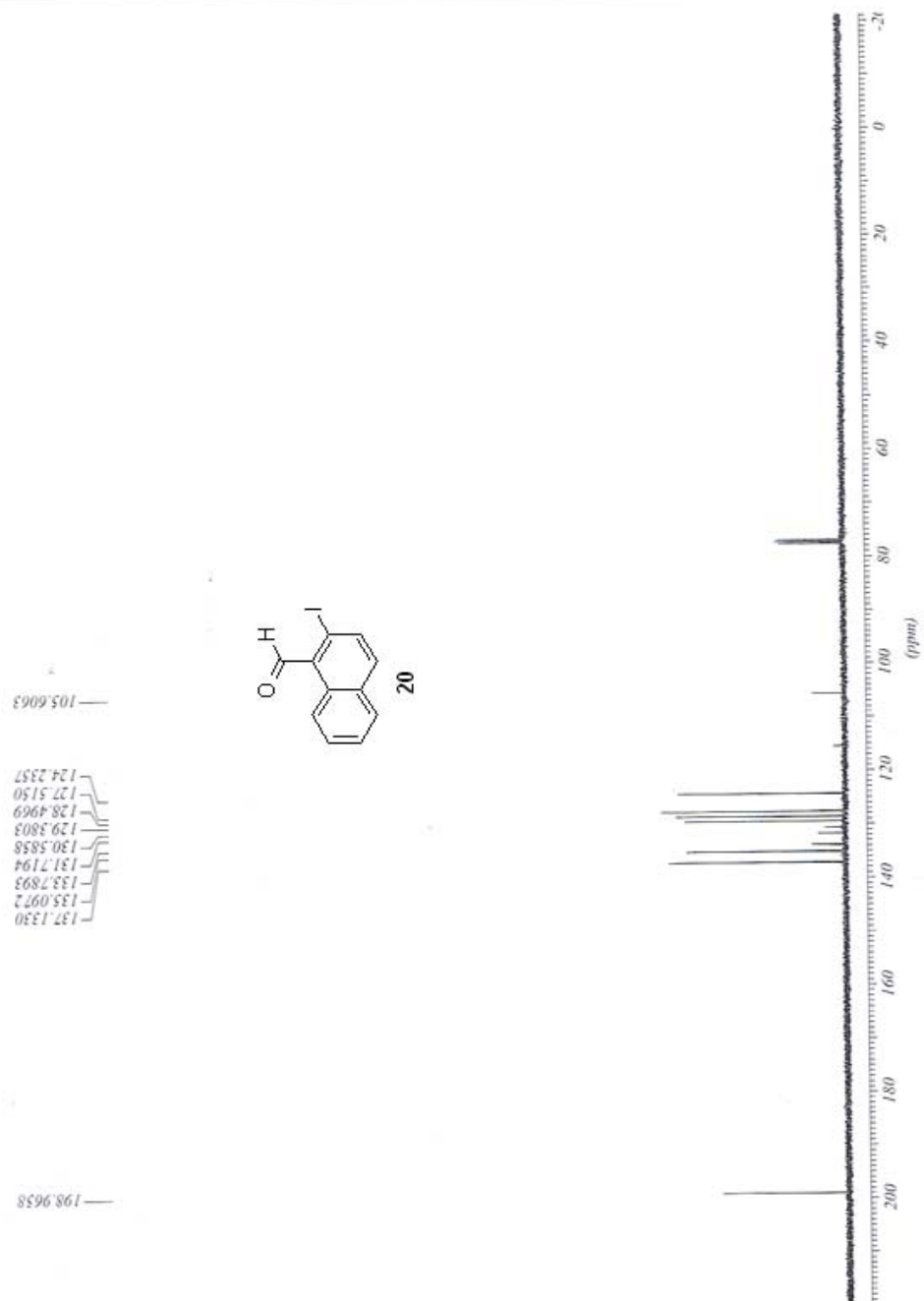










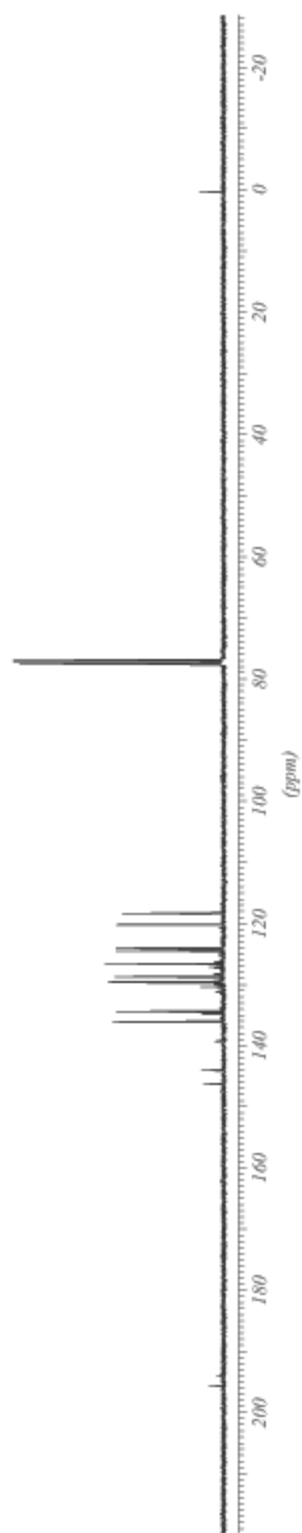
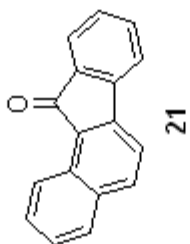




JTH-V-24

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195.5614



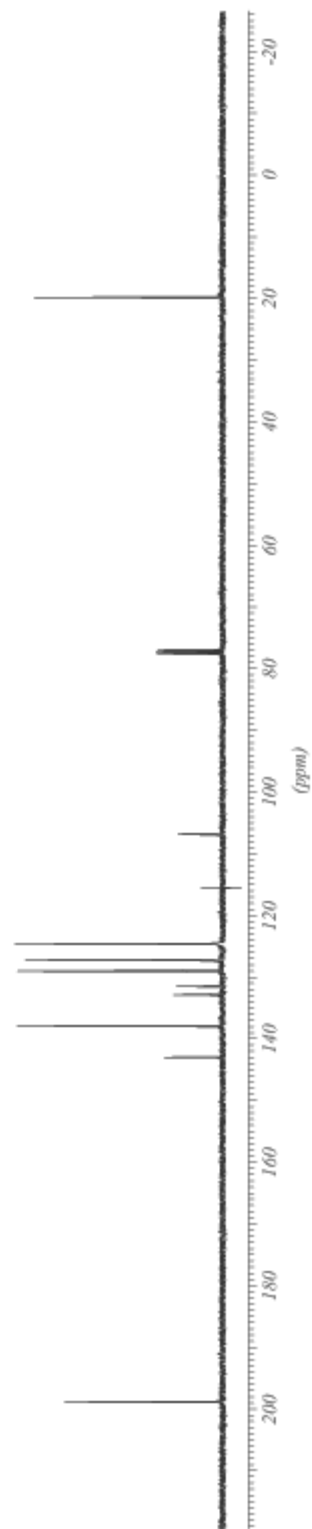
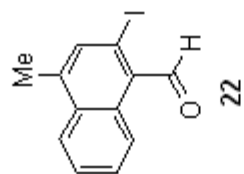


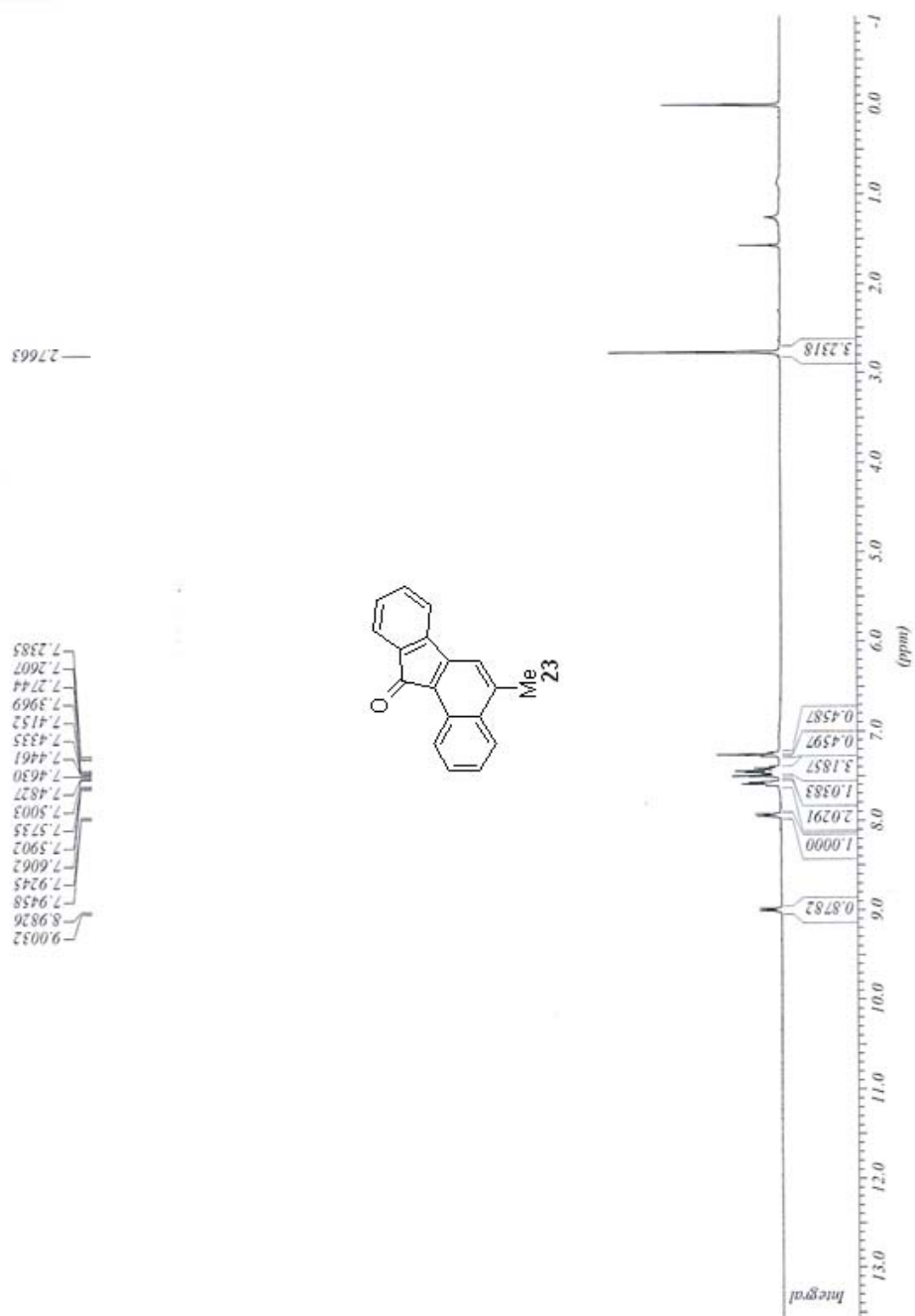
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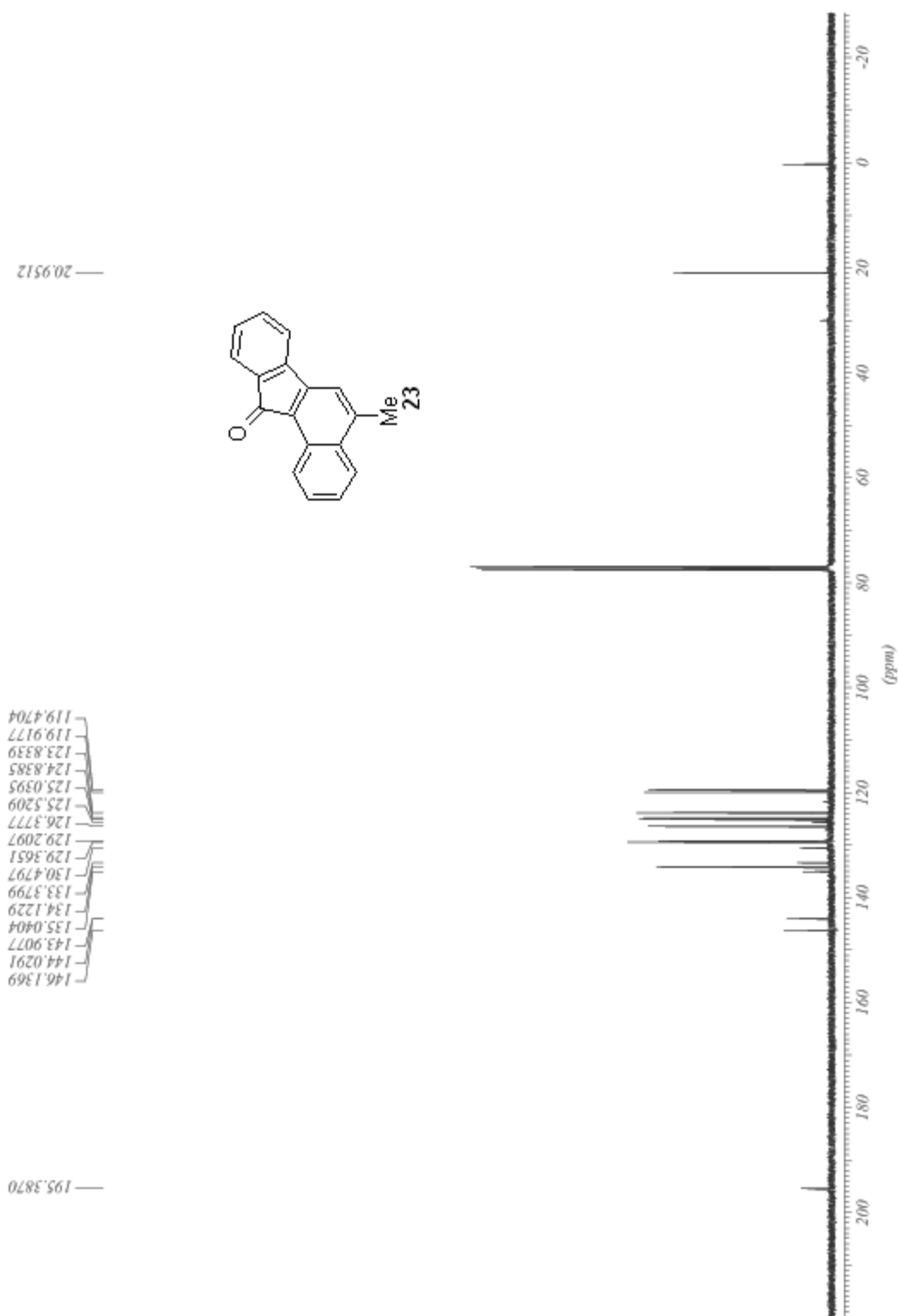
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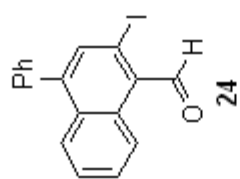
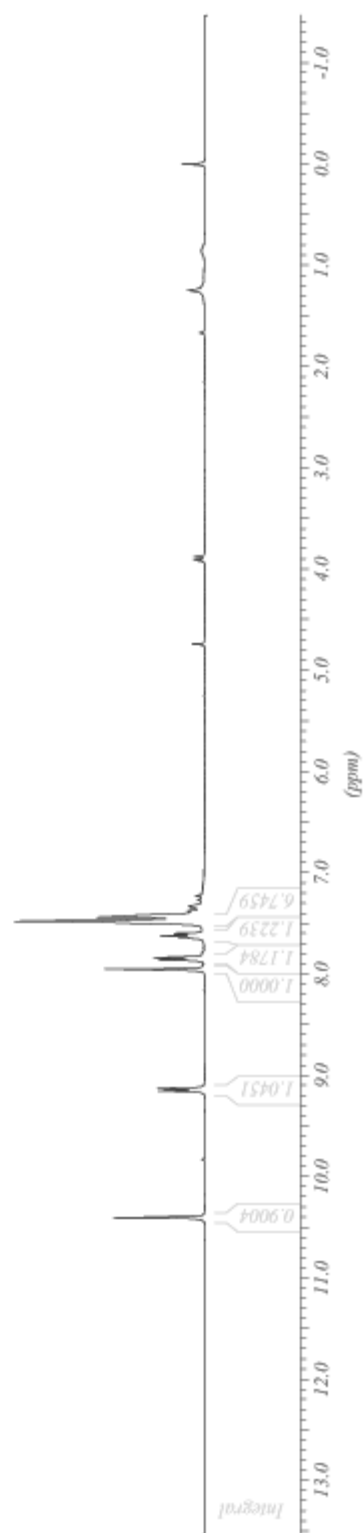
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— 19.7874







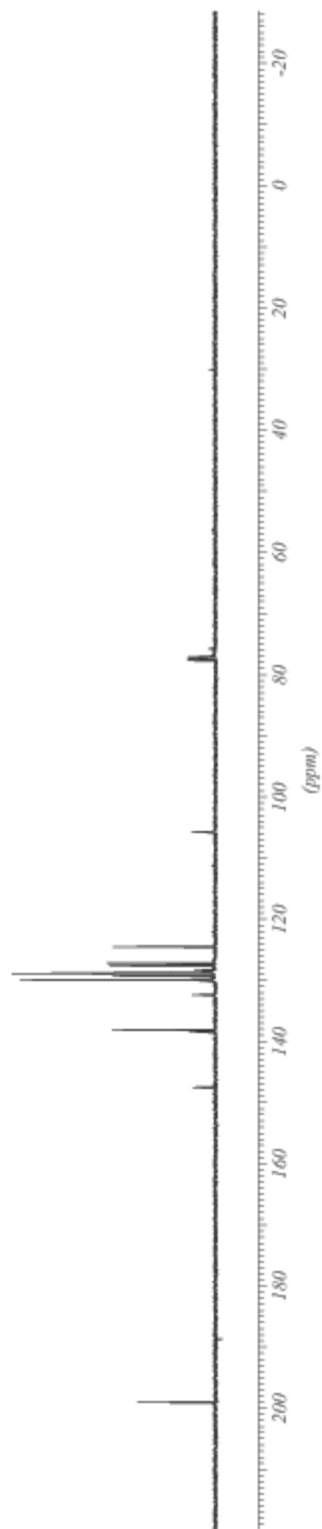
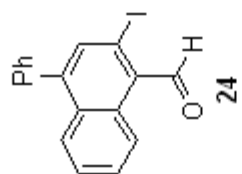


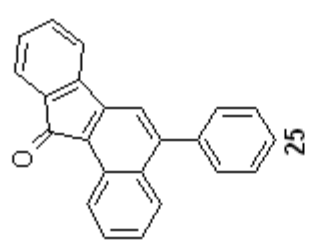
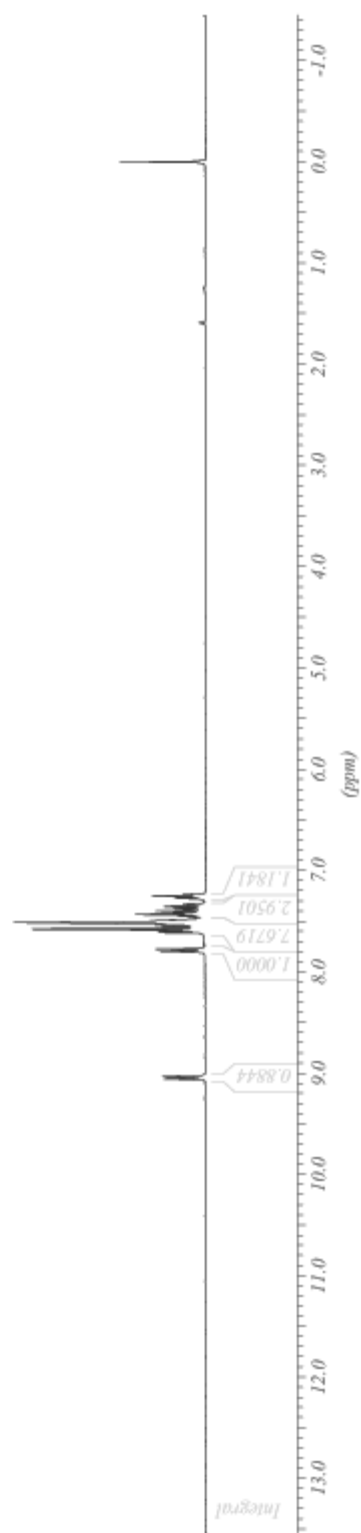
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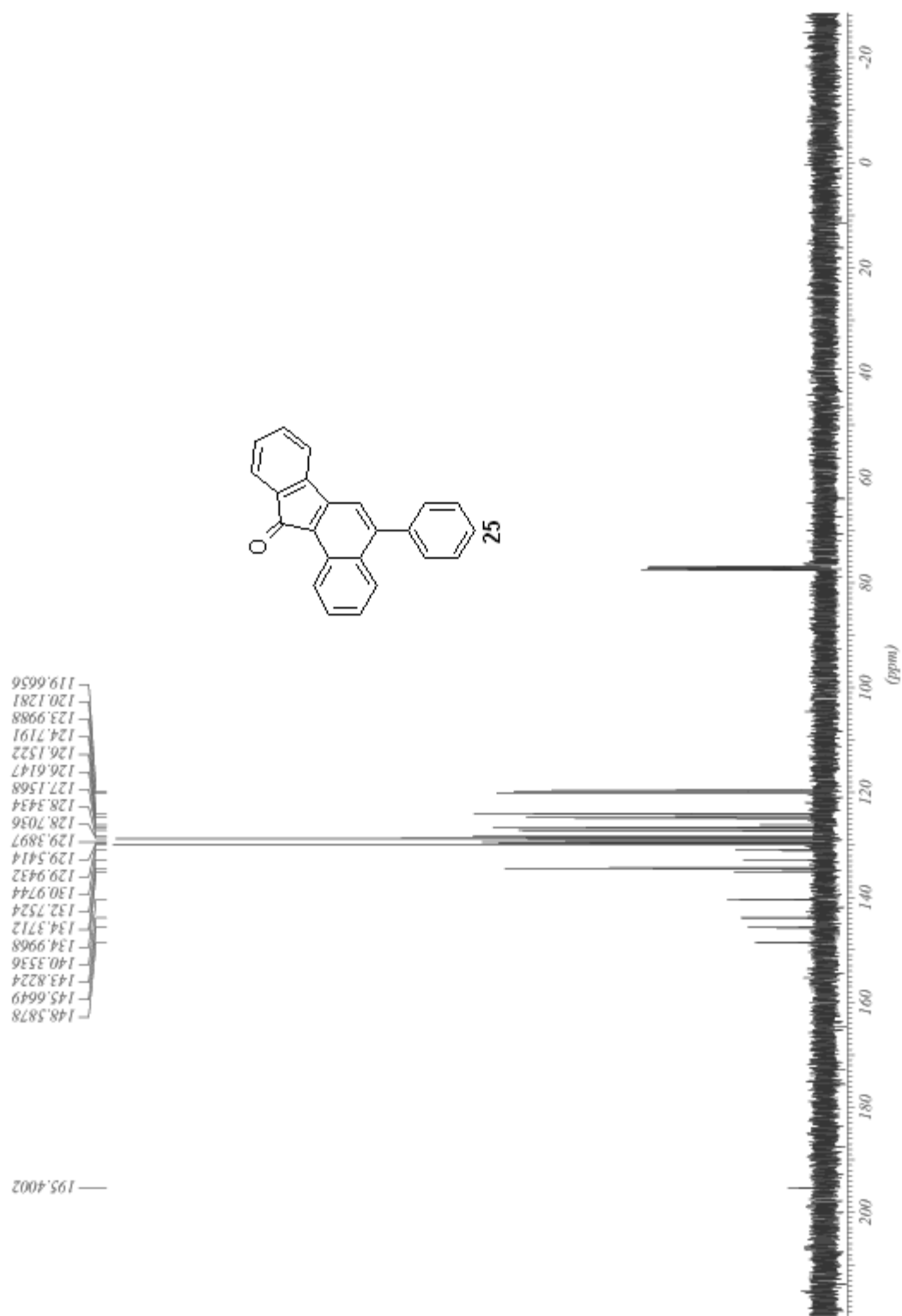
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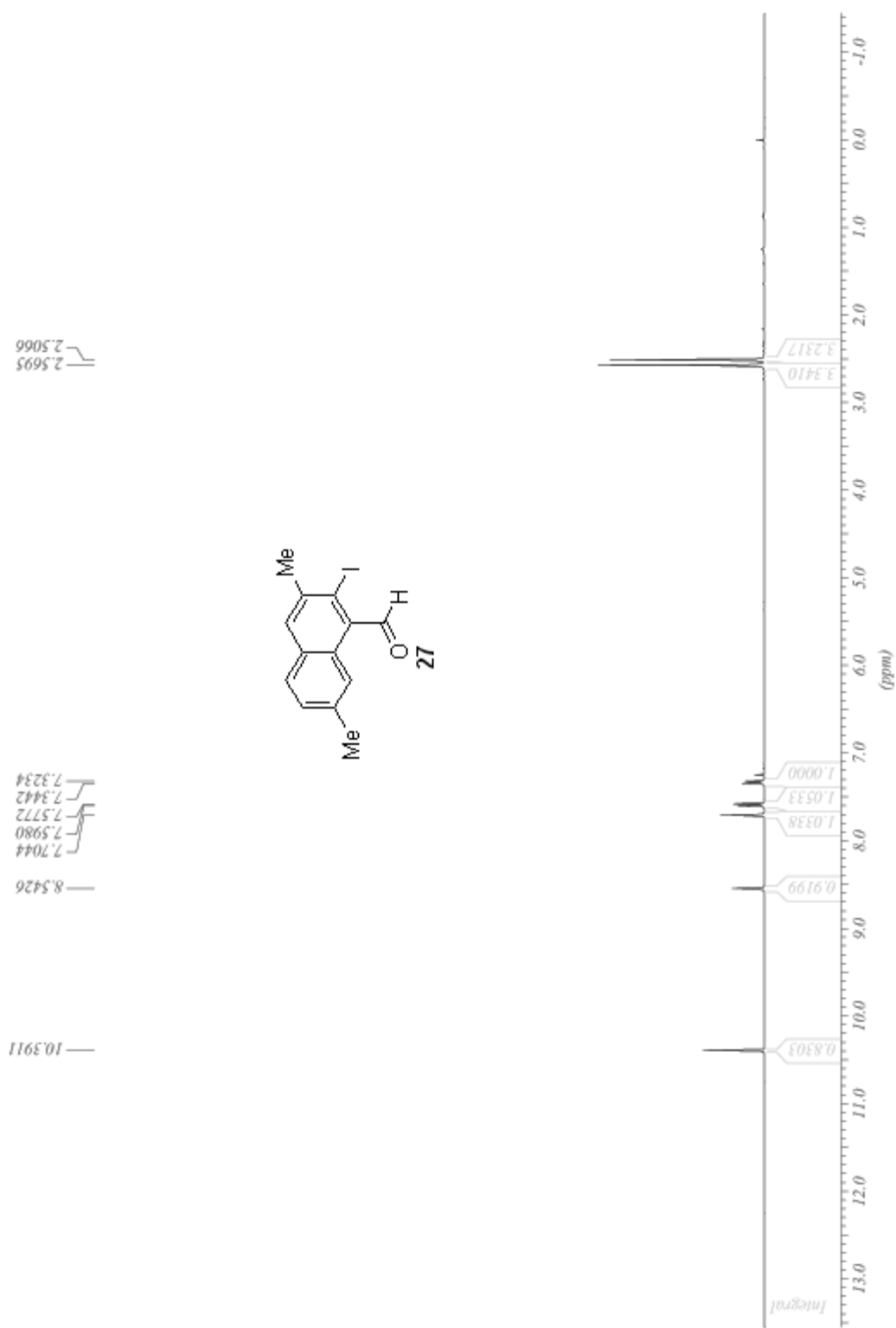
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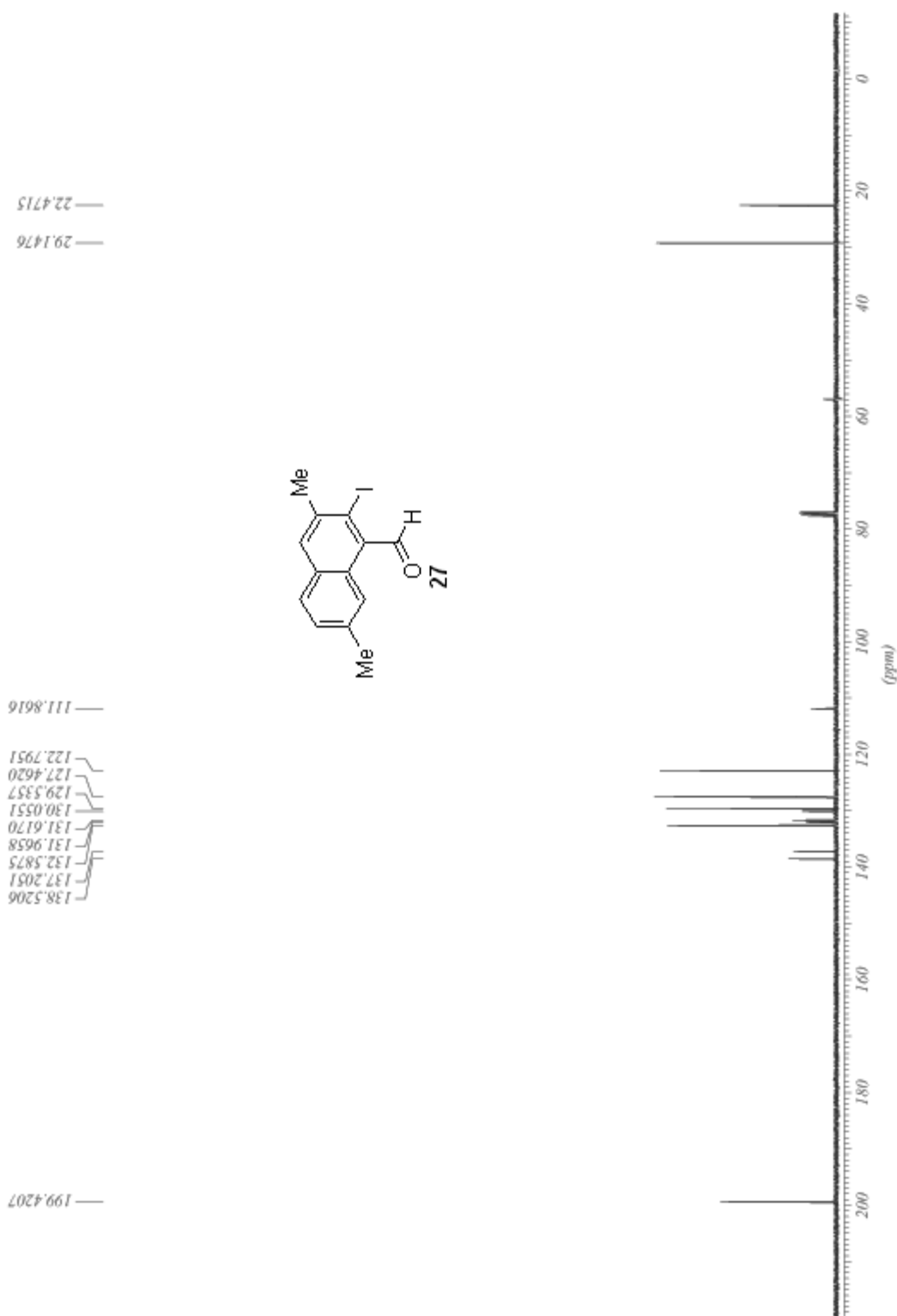


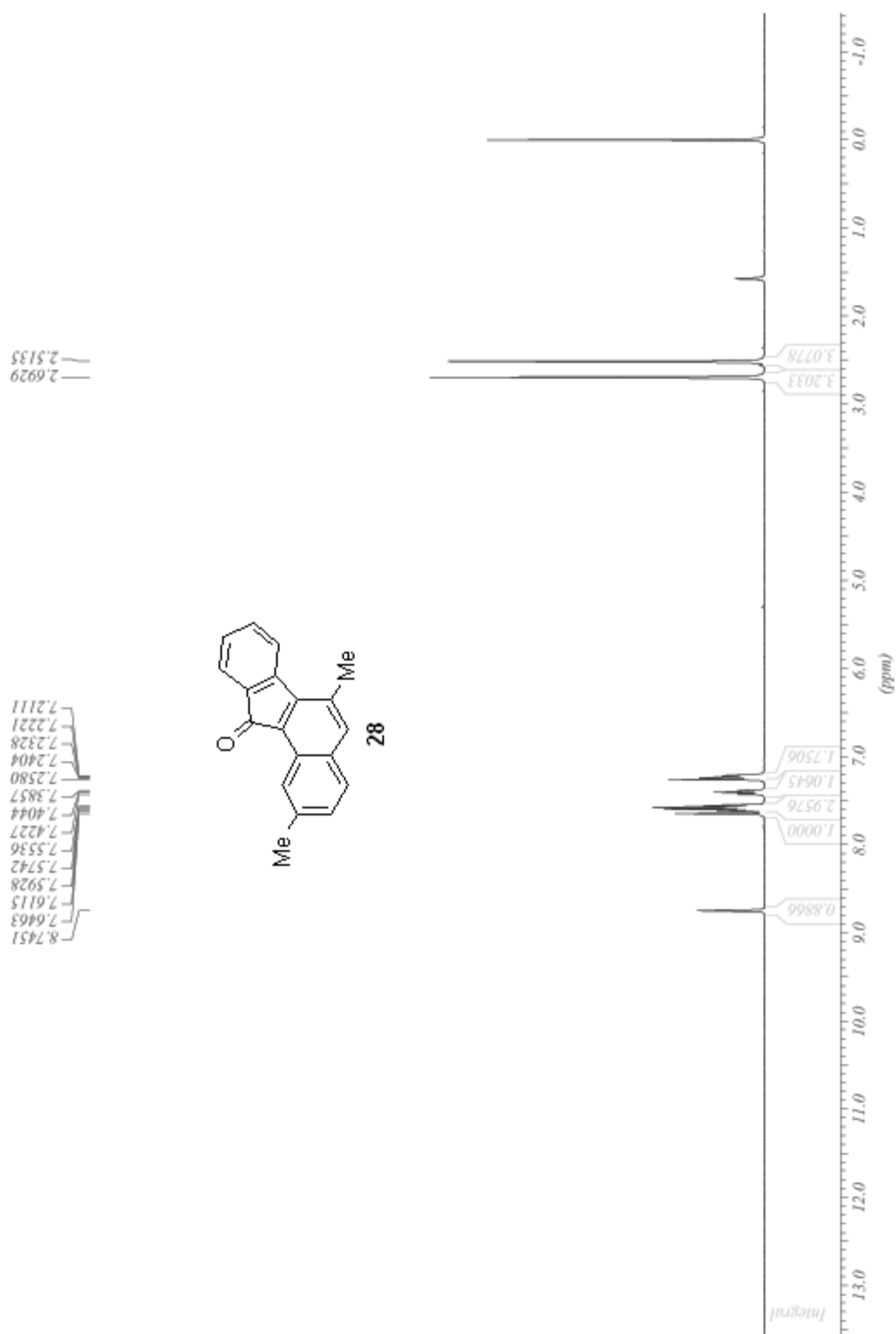


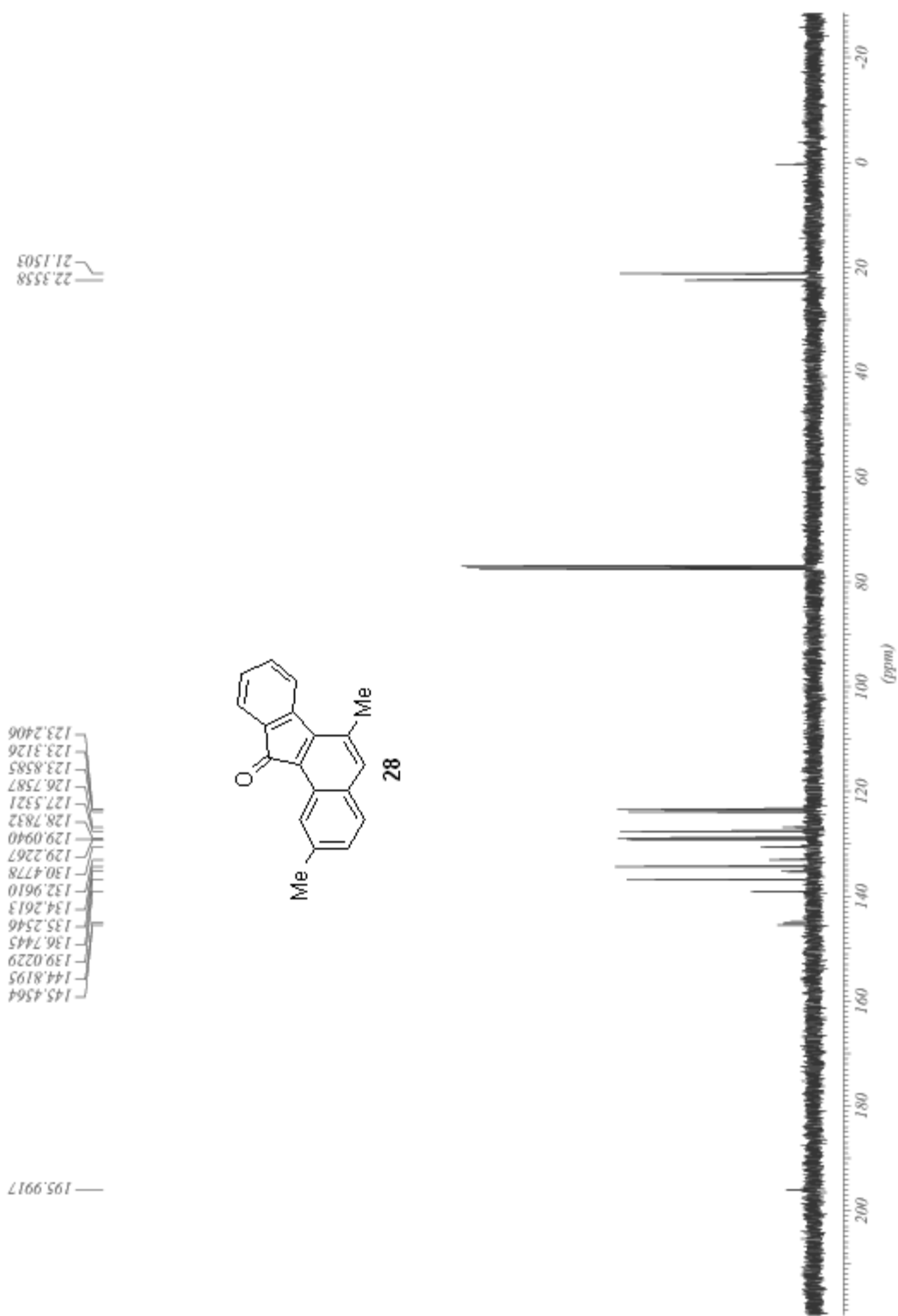
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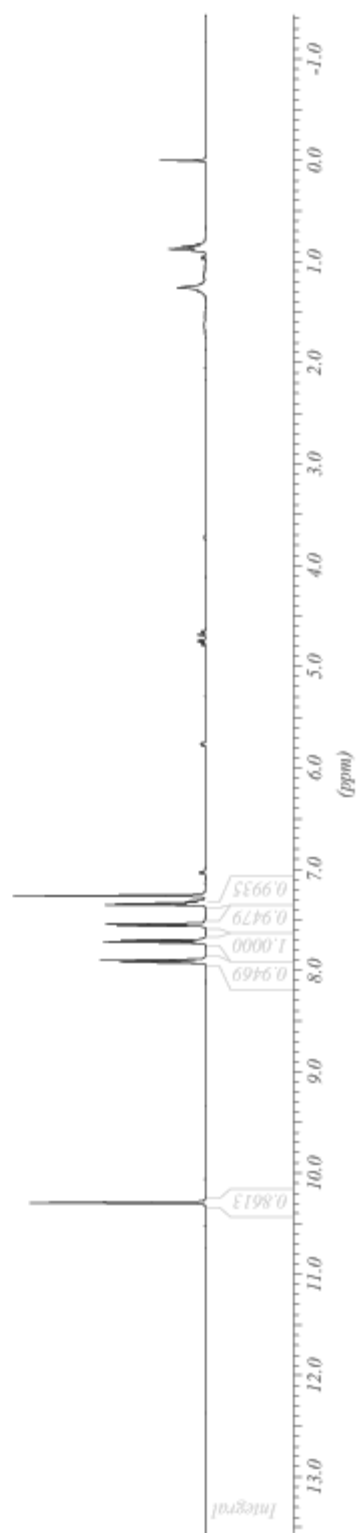
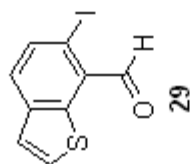


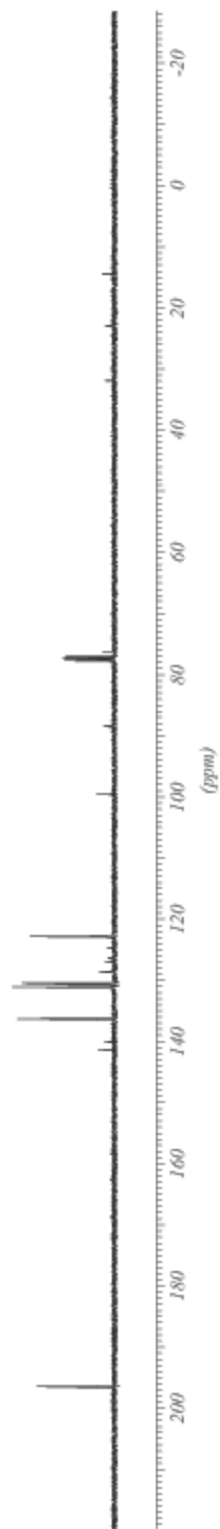


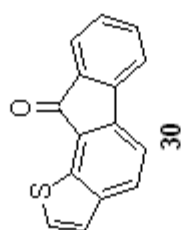
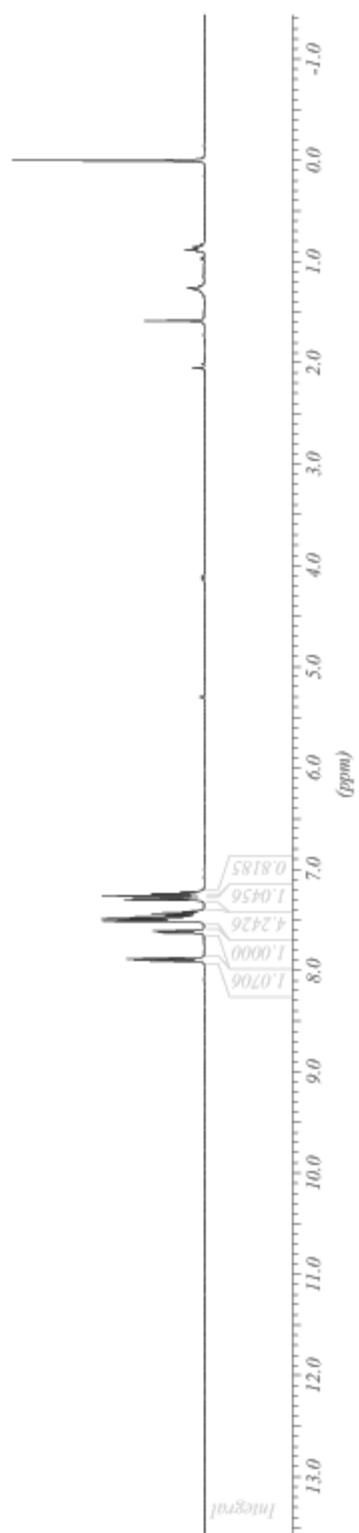


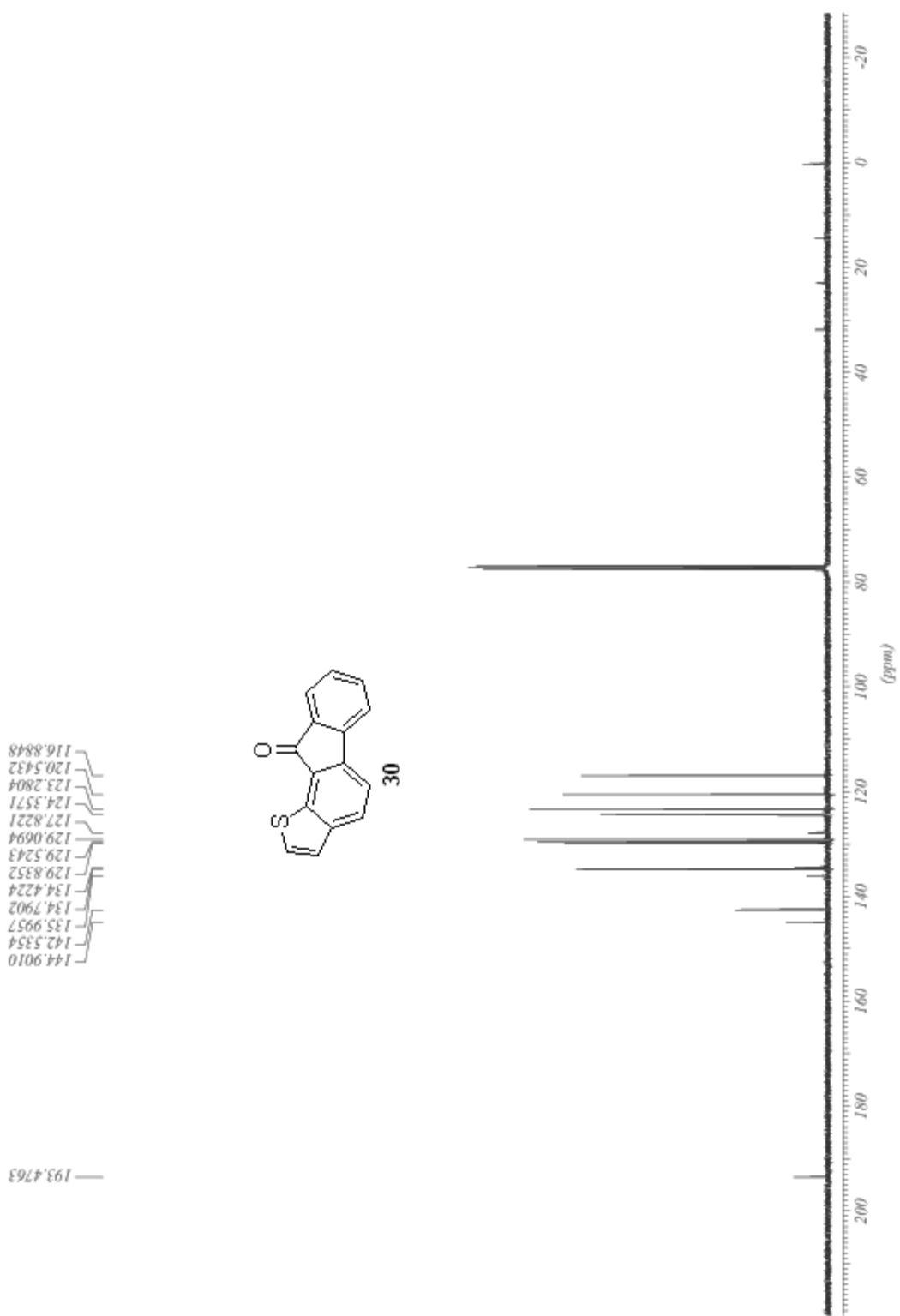
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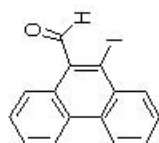
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