Synthesis of Substituted Quinolines by Electrophilic Cyclization of *N*-(2-Alkynyl)anilines

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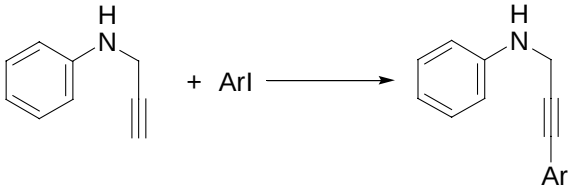
Supporting Information

General. The ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75.5 MHz or 400 and 100 MHz respectively. 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. All reagents were used directly as obtained commercially unless otherwise noted.

Synthesis of Starting Materials. Compounds **1**, **3**, **6**, **8**, and **22** were prepared by the Sonogashiro reaction of *N*-(2-propynyl)aniline with the corresponding aryl halide.



A typical reaction is described below. To a solution of Et_3N (30 mL), $PdCl_2(PPh_3)_2$ (2 mol %), 3.0 mmol of *N*-(2-propynyl)aniline, and 1.2 equiv of aryl iodide (stirring for 3 min beforehand) was added CuI (1 mol %). The reaction mixture was flushed with Ar and the flask was then sealed. The mixture was stirred at room temperature and was monitored by TLC to establish completion of the reaction. The resulting solution was filtered, washed with a satd aq NaCl solution, and extracted with diethyl ether. The

combined ether fractions were dried over $MgSO_4$ and concentrated under vacuum to yield the crude product, which was purified by flash chromatography on silica gel.

***N*-(3-Phenyl-2-propynyl)aniline (1).** The indicated compound was prepared in a 75 % yield as a light yellow oil from the coupling of *N*-(2-propynyl)aniline with iodobenzene. The reaction mixture was chromatographed using 5:1 hexane/EtOAc. The spectral properties were identical with those previously reported. [1]

***N*-[3-(4-Methoxyphenyl)prop-2-ynyl]-*N*-phenylamine (3).** The indicated compound was prepared as a yellow oil from *p*-iodoanisole in a 70 % yield. The reaction mixture was chromatographed using 5:1 hexane/EtOAc. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.67 (s, 3H), 3.92 (s, 1H), 4.04 (s, 2H), 6.66 (d, *J* = 11.6 Hz, 2H), 6.72-6.76 (m, 3H), 7.15-7.21 (m, 2H), 7.31 (d, *J* = 11.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 34.66, 55.36, 83.29, 85.28, 113.69, 114.03, 114.08, 115.14, 118.47, 129.41, 133.32, 147.44, 159.68; IR ($CHCl_3$) 3398, 2929, 2833, 1603, 1504 cm^{-1}; HRMS *m/z* 237.1157 (calcd for $C_{16}H_{15}NO$, 237.1154).

***N*-[3-(4-Fluorophenyl)prop-2-ynyl]-*N*-phenylamine (6).** The indicated compound was prepared as a light orange oil from 4-fluoro-1-iodobenzene in an 81 % yield. The reaction mixture was chromatographed using 5:1 hexane/EtOAc. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.98 (s, 1H), 4.16 (s, 2H), 6.76 (d, *J* = 9.3 Hz, 2H), 6.81-6.85 (m, 1H), 6.97-7.03 (m, 2H), 7.24-7.29 (m, 2H), 7.37-7.42 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 34.73, 82.48, 86.38, 86.40, 113.83, 115.64, 115.93, 118.78, 119.19, 119.23, 129.52, 133.80, 133.91, 147.36, 161.05, 164.36 (the extra peaks are due to ^{19}F splitting); IR ($CHCl_3$) 3407, 1605 cm^{-1}; HRMS *m/z* 225.0957 (calcd for $C_{15}H_{12}FN$, 225.0954).

1-[4-(3-Phenylaminoprop-1-ynyl)phenyl]ethanone (8). The indicated compound was prepared as a pale yellow solid from 4-iodoacetophenone in a 78 % yield. The reaction mixture was chromatographed using 3:1 hexane/EtOAc: mp 95-96 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.58 (s, 3H), 3.9-4.1 (br s, 1H), 4.18 (s, 2H), 6.73-6.83 (m, 3H), 7.21-7.27 (m, 2H), 7.47 (d, *J* = 6.9 Hz, 2H), 7.87 (d, *J* = 6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 26.85, 34.80, 82.79, 90.17, 113.83, 118.90, 128.01, 128.40, 129.51, 132.07, 136.48, 147.15, 197.54; IR ($CHCl_3$) 3375, 2826, 1676, 1602, 1513 cm^{-1}; HRMS *m/z* 249.1156 (calcd for $C_{17}H_{15}NO$, 249.1154).

2-(3-Phenylaminoprop-1-ynyl)aniline (22). The indicated compound was prepared as a light red oil from 2-iodoaniline in a 45 % yield. The reaction mixture was chromatographed using 3:1 hexane/EtOAc. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.96 (s, 3H), 4.14 (s, 2H), 6.56-6.70 (m, 2H), 6.71-6.80 (m, 3H), 7.02-7.08 (m, 1H), 7.10-7.19 (m, 1H), 7.21-7.23 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 35.03, 80.32, 92.18, 114.20, 114.55, 115.40, 118.01, 118.94, 129.58, 129.89, 132.32, 147.38, 148.40; IR ($CHCl_3$) 3374, 3051, 2848 1602, 1500 cm^{-1}; HRMS *m/z* 222.1161 (calcd for $C_{15}H_{14}N_2$, 222.1157).

Compounds **10**, **12**, **17**, and **20** were prepared by the reaction of the appropriate aniline (2 equiv) and the corresponding propargylic mesylate at room temperature in CH_3CN.[2]

***N*-(2-Heptynyl)aniline (10).** To a solution of the methanesulfonate[3] of 2-heptyn-1-ol (950 mg, 5.0 mmol) in 50 mL of CH_3CN was added aniline (930 mg, 10 mmol). After being stirred for 20 h under N_2, the reaction was quenched by adding brine. The reaction mixture was extracted with Et_2O (2 × 30 mL). The extracts were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified

by flash chromatography (10:1 hexane/EtOAc) on silica gel to afford 589 mg of the product in a 63 % yield as a light yellow oil. The spectra properties were identical with those previously reported.[4]

***N*-(3-Cyclohex-1-en-1-yl-1-methylprop-2-ynyl)aniline (12).** Using the procedure used to prepare aniline **10**, aniline and the methanesulfonate of 4-(1-cyclohexen-1-yl)-3-butyn-2-ol were employed to afford the indicated compound in a 35 % yield as a colorless oil. The reaction mixture was chromatographed using 10:1 hexane/EtOAc. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.47-1.58 (m, 7H), 2.00-2.03 (m, 4H), 3.69 (s, 1H), 4.28-4.30 (q, *J* = 6.6 Hz, 1H), 5.99-6.01 (m, 1H), 6.65-6.74 (m, 3H), 7.14-7.19 (m 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.82, 22.61, 22.92, 25.88, 29.60, 41.71, 84.19, 88.55, 114.32, 118.42, 120.67, 129.39, 134.83, 147.05; IR ($CHCl_3$) 3397, 2933, 1605, 1505 cm^{-1}; HRMS *m/z* 225.1520 (calcd for $C_{16}H_{19}N$, 225.1518).

***N*-(3-Phenylprop-2-ynyl)-3-nitroaniline (17).** Using the procedure used to prepare aniline **10**, 3-nitroaniline and the methanesulfonate of 3-phenyl-2-propyn-1-ol were employed to afford the indicated compound in a 55 % yield as an orange oil. The reaction mixture was chromatographed using 10:1 hexane/EtOAc. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.20 (s, 2H), 4.50-5.50 (br s, 1H), 6.96-7.00 (m, 1H), 7.25-7.40 (m, 6H), 7.54-7.61 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 34.33, 84.05, 84.97, 107.39, 113.04, 119.53, 122.48, 128.40, 128.57, 129.82, 131.80; IR ($CHCl_3$) 3060, 1686, 1622, 1528, 1348 cm^{-1}; HRMS *m/z* 252.0902 (calcd for $C_{15}H_{12}N_2O_2$, 252.0899).

***N*-(2-Naphthyl)-*N*-(3-phenylprop-2-ynyl)amine (20).** Using the procedure used to prepare aniline **10**, 2-aminonaphthalene and the methanesulfonate of 3-phenyl-2-propyn-1-ol were employed to afford the indicated compound in a 50 % yield as an light

red oil. The reaction mixture was chromatographed using 10:1 hexane/EtOAc. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.02 (s, 1H), 4.13 (s, 2H), 6.82-6.91 (m, 2H), 7.18-7.24 (m, 4H), 7.33-7.40 (m, 3H), 7.59-7.67 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 34.86, 83.83, 86.68, 106.05, 118.45, 122.83, 123.22, 126.61, 126.75, 128.06, 128.32, 128.65, 128.67, 129.33, 132.10, 135.37, 145.14; IR ($CHCl_3$) 3409, 3054, 1632, 1604, 1519, 1488 cm^{-1}; HRMS *m/z* 257.1204 (calcd for $C_{19}H_{15}N$, 257.1209).

Ethyl 4-[(3-phenylprop-2-ynyl)amino]benzoate (14). To a solution of ethyl 4-aminobenzoate (639 mg, 3.0 mmol) and K_2CO_3 (621 mg, 4.5 mmol) in 30 mL of DMF was added 3-bromo-1-phenylpropyne (1.17 g, 6.0 mmol). The resulting solution was heated at 80 ^{o}C for 24 h. The reaction mixture was quenched with brine and extracted with ethyl acetate. The organic extracts were washed with brine to remove the DMF. The solvent was removed under reduced pressure and the residue was chromatographed using 3:1 hexane/EtOAc. The indicated compound was obtained as a light yellow solid in a 56 % yield: mp 104-105 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.34-1.39 (t, *J* = 7.2 Hz, 3H), 4.19 (s, 2H), 4.32-4.36 (q, *J* = 7.2 Hz, 2H), 4.46 (s, 1H), 6.68 (d, *J* = 8.7 Hz, 2H), 7.26-7.31 (m, 3H), 7.38-7.41 (m, 2H), 7.93 (d, *J* = 6.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.68, 34.22, 60.55, 83.91, 85.53, 112.43, 120.08, 122.80, 128.54, 128.65, 131.65, 131.95, 151.02, 167.05; IR ($CHCl_3$) 3372, 2982, 1693, 1602, 1527, 1280 cm^{-1}; HRMS *m/z* 279.1263 (calcd for $C_{18}H_{11}NO_2$, 279.1259).

General Procedure for the Electrophilic Cyclization of *N*-(2-Alkynyl)anilines by I_2. 0.3 Mmol of the propargylic aniline, 3 equiv of I_2, 2 equiv of $NaHCO_3$, and 3 mL of CH_3CN were placed in a vial. The reaction mixture was stirred at room temperature, and the reaction was monitored by TLC to establish completion. When finely ground

iodine powder was employed, all reactions were complete in 0.5 h. The reaction mixture was then diluted with 25 mL of ether, and washed with 20 mL of satd aq $Na_2S_2O_3$. The organic layer was separated and the aqueous layer was extracted with another 25 mL of ether. The combined organic layers were dried over $MgSO_4$ and filtered. The solvent was evaporated under reduced pressure and the product was isolated by chromatography on a silica gel column.

General Procedure for the Electrophilic Cyclization of *N*-(2-Alkynyl)anilines by ICl and PhSeBr. 0.3 Mmol of the propargylic aniline, 2 equiv of $NaHCO_3$ and 2 mL of CH_3CN were placed in a vial. 2 Equiv of ICl or PhSeBr in 1 mL of CH_3CN were added dropwise to the vial. The reaction mixture was stirred at room temperature for 5 min. The reaction mixture was then diluted with 25 mL of ether, and washed with 20 mL of satd aq $Na_2S_2O_3$ (for the reaction of ICl) or satd aq NaCl (for the reaction of PhSeBr). The organic layer was separated and the aqueous layer was extracted with another 25 mL of ether. The combined organic layers were dried over $MgSO_4$ and filtered. The solvent was evaporated under reduced pressure and the product was isolated by chromatography on a silica gel column.

3-Iodo-4-phenylquinoline (2). The reaction mixture was chromatographed using 5:1 hexane/EtOAc to afford 75 mg (76 %) or 82 mg (83 %) of the product as a white solid from I_2 or ICl, respectively: mp 131-132 ^oC; ^1H NMR ($CDCl_3$) δ 7.25-7.28 (m, 2H), 7.42-7.48 (m, 2H), 7.52-7.55 (m, 3H), 7.69-7.74 (m, 1H), 8.12 (d, J = 8.8 Hz, 1H), 9.24 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 96.4, 126.8, 127.4, 128.7, 129.0, 129.1, 129.5, 140.4, 147.2, 152.4, 156.6 (one sp^2 carbon missing due to overlap); IR ($CHCl_3$) 3061, 2918, 1566, 1501, 1485 cm^{-1}; HRMS *m/z* 330.9864 (calcd for $C_{15}H_{10}IN$, 330.9858).

3-Iodo-4-(4-methoxyphenyl)quinoline (4). The reaction mixture was chromatographed using 5:1 hexane/EtOAc to afford 77 mg (71 %) or 81 mg (73 %) of the product as a light yellow solid from I_2 or ICl, respectively: mp 127-128 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.92 (s, 3H), 7.08 (d, *J* = 8.7 Hz, 2H), 7.21 (d, *J* = 8.7 Hz, 2H), 7.42-7.45 (m, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.68-7.73 (m, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 9.23 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 55.58, 97.29, 114.22, 127.03, 127.52, 129.54, 129.70, 129.85, 130.66, 132.80, 147.49, 152.40, 156.87, 159.99; IR ($CHCl_3$) 2837, 1613, 1513, 1483, 1246 cm^{-1}; HRMS *m/z* 360.9972 (calcd for $C_{16}H_{12}INO$, 360.9964).

4-(4-Methoxyphenyl)-3-(phenylseleno)quinoline (5). The reaction mixture was chromatographed using 3:1 hexane/EtOAc to afford 86 mg (74 %) of the product as a yellow solid: mp 93-94 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.91 (s, 3H), 7.06 (d, *J* = 6.0 Hz, 2H), 7.26-7.32 (m, 5H), 7.43-7.57 (m, 3H), 7.63-7.68 (m, 1H), 7.68-7.73 (m, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 8.67 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 55.57, 114.25, 126.23, 127.22, 127.34, 128.44, 128.47, 129.16, 129.61, 129.70, 129.74, 129.85, 130.87, 134.81, 147.08, 148.27, 152.43, 159.99; IR ($CHCl_3$) 2923, 2851, 1736, 1250 cm^{-1}; HRMS *m/z* 391.0482 (calcd for $C_{22}H_{17}NOSe$, 391.0475).

4-(4-Fluorophenyl)-3-iodoquinoline (7). The reaction mixture was chromatographed using 5:1 hexane/EtOAc to afford 82 mg (78 %) of the product as a white solid: mp 108-109 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.24-7.26 (m, 4H), 7.44-7.45 (m, 2H), 7.70-7.76 (m, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 9.24 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 96.85, 96.86, 115.93, 116.22, 126.65, 127.78, 129.21, 129.81, 130.03, 131.16, 131.27, 136.39, 136.43, 147.41, 151.55, 156.82, 161.41, 164.70; IR ($CHCl_3$) 3067, 1617, 1513, 1494 cm^{-1}; HRMS *m/z* 348.9770 (calcd for $C_{15}H_9FIN$, 348.9764).

1-[4-(3-Iodoquinolin-4-yl)phenyl]ethanone (9). The reaction mixture was chromatographed using 3:1 hexane/EtOAc to afford 64 mg (57 %) of the product as a yellow solid: mp 136-137 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.72 (s, 3H), 7.37-7.47 (m, 4H), 7.72-7.78 (m, 1H), 8.13-8.18 (m, 3H), 9.26 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 26.83, 95.51, 126.25, 127.75, 128.47, 128.78, 129.58, 129.71, 130.00, 137.17, 144.97, 147.12, 151.23, 156.59, 197.62; IR ($CHCl_3$) 3067, 1683, 1268 cm^{-1}; HRMS *m/z* 372.9970 (calcd for $C_{17}H_{12}INO$, 372.9964).

4-Butyl-3-iodoquinoline (11). The reaction mixture was chromatographed using 10:1 hexane/EtOAc to afford 40 mg (43 %) of the product as a colorless oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.00-1.05 (t, *J* = 7.2 Hz, 3H), 1.55-1.67 (m, 4H), 3.20-3.26 (m, 2H), 7.54-7.59 (m, 1H), 7.69-7.74 (m, 1H), 8.03-8.08 (m, 2H), 9.09 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.14, 23.32, 31.65, 37.01, 97.61, 124.23, 127.43, 128.60, 129.62, 130.42, 147.63, 151.41, 157.32; IR ($CHCl_3$) 2956, 2926, 2870, 1505 cm^{-1}; HRMS *m/z* 311.0177 (calcd for $C_{13}H_{14}IN$, 311.0171).

4-(Cyclohex-1-enyl)-3-iodo-2-methylquinoline (13). The reaction mixture was chromatographed using 10:1 hexane/EtOAc to afford 84 mg (80 %) of the product as a white solid: mp 99-100 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.78-1.93 (m, 4H), 2.00-2.14 (m, 1H), 2.30-2.34 (m, 3H), 2.98 (s, 3H), 5.63-5.65 (m, 1H), 7.43-7.47 (m, 1H), 7.66-7.70 (m, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.97, 22.77, 25.25, 28.78, 31.41, 99.43, 125.98, 126.27, 126.33, 128.66, 128.80, 129.67, 139.34, 146.99, 155.78, 159.92; IR ($CHCl_3$) 2927, 1559, 1490, 1436 cm^{-1}; HRMS *m/z* 349.0334 (calcd for $C_{16}H_{16}IN$, 349.0327).

Ethyl 3-iodo-4-phenylquinoline-6-carboxylate (15). The reaction mixture was chromatographed using 1:1 hexane/EtOAc to afford 106 mg (88 %) of the product as a yellow solid: mp 150-151 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.33-1.36 (t, *J* = 7.2 Hz, 3H), 4.32-4.37 (q, *J* = 7.2 Hz, 2H), 7.26-7.29 (m, 2H), 7.56-7.28 (m, 3H), 8.14 (d, *J* = 8.8 Hz, 1H), 8.22 (m, 1H), 8.28-8.31 (m, 1H), 9.30 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.28, 61.46, 97.28, 128.22, 128.83, 129.08, 129.23, 129.26, 129.71, 129.84, 139.61, 148.97, 153.67, 158.64, 165.82; IR ($CHCl_3$) 2974, 1724 cm^{-1}; HRMS *m/z* 403.0075 (calcd for $C_{18}H_{14}INO_2$, 403.0069).

Ethyl 4-phenyl-3-(phenylseleno)quinoline-6-carboxylate (16). The reaction mixture was chromatographed using 1:1 hexane/EtOAc to afford 67 mg (56 %) of the product as a yellow solid: mp 125-127 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.33-1.37 (m, *J* = 7.2 Hz, 3H), 4.32-4.36 (m, *J* = 7.2 Hz, 2H), 7.26-7.36 (m, 5H), 7.50-7.57 (m, 5H), 8.08-8.10 (m, 1H), 8.22-8.26 (m, 2H), 8.70 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.29, 61.36, 127.22, 128.23, 128.46, 128.63, 128.78, 128.87, 128.95, 129.01, 129.04, 129.34, 129.82, 135.07, 136.48, 148.50, 149.01, 153.81, 166.14 (one sp^2 carbon missing due to overlap); IR ($CHCl_3$) 2974, 1721 cm^{-1}; HRMS *m/z* 433.0589 (calcd for $C_{24}H_{19}NOSe$, 433.0581).

3-Iodo-7-nitro-4-phenylquinoline (18) and 3-iodo-5-nitro-4-phenylquinoline (19). The reaction mixture was chromatographed using 3:1 hexane/EtOAc to afford 9 mg of **18** (8 %) and 80 mg of **19** (71 %). Quinoline **18** was obtained as a light yellow solid: mp 157-158 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.26-7.28 (m, 2H), 7.58-7.64 (m, 4H), 8.16-8.19 (m, 1H), 9.02 (m, 1H), 9.41 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 100.47, 120.91, 125.86, 128.65, 128.87, 129.07, 131.77, 139.30, 146.50, 147.98, 159.29 (one sp^2

carbon missing due to overlap); IR ($CHCl_3$) 2930, 1544, 1352 cm^{-1}; HRMS *m/z* 375.9715 (calcd $C_{15}H_9IN_2O_2$, 375.9709). Quinoline **19** was obtained as a light yellow solid: mp 157-158 ^oC; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.16-7.19 (m, 2H), 7.41-7.48 (m, 3H), 7.67-7.69 (m, 1H), 7.73-7.77 (m, 1H), 8.29-8.32 (m, 1H), 9.36 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 102.44, 120.09, 123.86, 128.22, 128.27, 129.46, 134.13, 139.42, 148.00, 148.20, 148.97, 158.56; IR ($CHCl_3$) 2922, 2855, 1527 cm^{-1}; HRMS *m/z* 375.9715 (calcd for $C_{15}H_9IN_2O_2$, 375.9709).

3-Iodo-4-phenylbenzo[*g*]quinoline (21). The reaction mixture was chromatographed using 3:1 hexane/EtOAc to afford 86 mg (75 %) as a white solid: mp 217-219 ^oC; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.13-7.16 (m, 1H), 7.23-7.26 (m, 2H), 7.38 (d, *J* = 8.7 Hz, 1H), 7.44-7.47 (m, 1H), 7.58-7.61 (m, 3H), 7.85 (d, *J* = 9.0 Hz, 1H), 7.99 (s, 1H), 9.33 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 101.09, 126.23, 126.40, 127.27, 128.53, 128.59, 128.79, 128.99, 129.10, 129.60, 129.98, 132.44, 133.31, 145.49, 149.10, 151.56, 156.08; IR ($CHCl_3$) 3063, 3045, 1629, 1598, 1440 cm^{-1}; HRMS *m/z* 381.0019 (calcd for $C_{19}H_{12}IN$, 381.0015).

4-(2-Aminophenyl)-3-iodoquinoline (23). The reaction mixture was chromatographed using 3:1 hexane/EtOAc to afford 57 mg (55 %) of quinoline **23** as a light yellow solid: mp 145-146 ^oC; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.44 (s, 2H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.94-6.98 (m, 2H), 7.26-7.36 (m, 1H), 7.45-7.47 (m, 1H), 7.51-7.54 (m, 1H), 7.71-7.75 (m, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 9.24 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 97.64, 116.05, 118.79, 125.67, 126.48, 127.86, 128.83, 129.69, 129.81, 130.12, 130.14, 143.07, 147.38, 150.16, 156.94; IR ($CHCl_3$) 3100, 2923, 2851, 1736, 1451 cm^{-1}; HRMS *m/z* 345.9974 (calcd for $C_{15}H_{11}IN_2$, 345.9967).

Synthesis of 3-iodo-4-phenylquinoline (2) from *N*-phenyl-*N*-(3-phenyl-2-propyn-1-yl)methanesulfonamide (25) and 3-iodo-1-methanesulfonyl-4-phenyl-1,2-dihydroquinoline (26). To a solution of *N*-phenylmethanesulfonamide[5] (0.513 g, 3.0 mmol), PPh_3 (1.18 g, 4.5 mmol) and 3-phenyl-2-propyn-1-ol (0.594 g, 4.5 mmol) in anhydrous THF (30 mL) at 0 ^oC was added DEAD (0.784 g, 4.5 mmol). The resulting solution was stirred at 0 ^oC for 1 h and an additional 3 h at room temperature. The mixture was washed with brine (30 mL) and the organic layer was dried over Na_2SO_4, filtered, and the solvent removed under reduced pressure. The residue was purified by chromatography on a silica gel column using 3:1 hexane/ethyl acetate to obtain 0.534 g (63 %) of *N*-phenyl-*N*-(3-phenyl-2-propyn-1-yl)methanesulfonamide (**25**) as a white solid: mp 76-77 ^oC; ^1H NMR ($CDCl_3$) δ 3.08 (s, 3H), 4.67 (s, 2H), 7.34-7.46 (m, 8H), 7.62-7.66 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 39.2, 42.3, 84.4, 86.3, 122.3, 127.7, 128.4, 128.7, 129.1, 129.7, 131.9, 140.5. To a solution of *N*-phenyl-*N*-(3-phenyl-2-propyn-1-yl)methanesulfonamide (71.2 mg, 0.25 mmol) in CH_2Cl_2 (3.0 mL) at –78 ^oC was added ICl (48.7 mg, 0.3 mmol) in CH_2Cl_2 (0.5 mL) and the resulting solution was stirred at this temperature for 1 h. The reaction mixture was washed with satd aq $Na_2S_2O_3$ (20 mL) and the organic layer dried over Na_2SO_4, filtered and the solvent removed under reduced pressure. The residue was purified by chromatography on a silica gel column using 5:1 hexane/ethyl acetate to obtain 82.2 mg (80 %) of 3-iodo-1-methanesulfonyl-4-phenyl-1,2-dihydroquinoline (**26**) as a white solid: mp 173-175 ^oC; ^1H NMR ($CDCl_3$) δ 2.89 (s, 3H), 4.82 (s, 2H), 6.80 (dd, J = 7.8, 1.2 Hz, 1H), 7.11-7.16 (m, 3H), 7.30-7.33 (m, 1H), 7.44-7.48 (m, 3H), 7.62 (dd, J = 8.1, 0.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 38.6, 56.7, 92.0, 126.9, 127.2, 127.2 128.6, 128.8, 129.0, 129.2, 130.7, 134.5, 140.3, 143.9. A solution of

3-iodo-1-methanesulfonyl-4-phenyl-1,2-dihydroquinoline (0.103 g, 0.25 mmol) and NaOH (0.10 g, 2.5 mmol) in EtOH (10 mL) was stirred at 50 ^{o}C under O_2 (1 atm) for 12 h. The reaction mixture was diluted with diethyl ether (50 mL) and washed with brine (50 mL). The organic layer was dried (Na_2SO_4), filtered, and the solvent removed under reduced pressure. The residue was purified by column chromatography on a silica gel column using 5:1 hexanes/ethyl acetate to afford 76.1 mg (92 %) of the desired compound **2**.

4-(4-Fluorophenyl)-3-[(*E*)-2-phenylethenyl]quinoline (27). To a solution of 4-(4-fluorophenyl)-3-iodoquinoline (0.15 mmol) and β-styreneboronic acid (0.23 mmol, 1.5 equiv) in 10 mL of DMF/H_2O (V/V = 4/1) were added $PdCl_2(PPh_3)_2$ (2.0 mg, 5 mol %) and K_2CO_3 (0.30 mmol, 2.0 equiv). The resulting mixture was heated under an N_2 atmosphere at 100 ^{o}C for 2 h. The mixture was cooled to room temperature and diluted with 25 ml of ether, washed with 25 mL of satd aq NaCl, dried over $MgSO_4$ and filtered. The solvent was evaporated under reduced pressure. The reaction mixture was chromatographed using 3:1 hexane/EtOAc to afford 35.4 mg (73 %) of the product as a light yellow solid: mp 178-180 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.91 (d, *J* = 16.5 Hz, 1H), 7.23-7.38 (m, 11H), 7.45-7.52 (m, 2H), 7.65-7.70 (m, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 9.33 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) 115.68, 115.89, 124.38, 126.26, 126.72, 127.10, 127.45, 128.15, 128.24, 128.80, 129.04, 129.61, 131.44, 131.72, 131.76, 131.94, 132.02, 136.92, 144.02, 147.31, 148.47, 161.49, 163.96; IR ($CHCl_3$) 2922, 1605, 1514, 1499 cm^{-1}; HRMS *m/z* 325.1272 (calcd for $C_{23}H_{16}FN$, 325.1267).

7H-Indolo[2,3-*c*]quinoline (28). To a solution of 4-(2-aminophenyl)-3-iodoquinoline (0.15 mmol) in 4 mL of toluene/DMF (V/V = 3/1) in a vial was added

$PdCl_2$(dppf) (4.9 mg, 5 mol %), dppf (4.2 mg, 5 mol %), and *t*-BuOK (0.30 mmol, 2.0 equiv). Then the vial was flushed with N_2 gas and closed. The reaction mixture was heated to 100 ^oC for 36 h, cooled to room temperature, diluted with 25 ml of ether, washed with 25 mL of satd aq NaCl, dried over $MgSO_4$ and filtered. The solvent was evaporated under reduced pressure. The reaction mixture was chromatographed using 1:1 hexane/EtOAc to afford 21 mg (65 %) of the product as a light yellow solid**:** mp 247-248 ^oC (lit. mp 249 ^oC);[6] ^1H NMR (*d*-acetone, 400 MHz) δ 7.45-7.48 (m, 1H), 7.60-7.63 (m, 1H), 7.68-7.72 (m, 2H), 7.75-7.79 (m, 1H), 8.33 (d, *J* = 8.0 Hz, 1H), 8.60 (d, *J* = 8.0 Hz, 1H), 8.74 (d, *J* = 8.0 Hz, 1H), 9.15 (s, 1H), 9.29 (s, 1H); ^{13}C NMR (*d*-acetone, 100 MHz) 112.55, 112.60, 120.51, 123.03, 123.32, 124.80, 125.20, 126.72, 126.94, 130.45, 138.63, 138.68, 143.10 (two sp^2 carbons missing due to overlap); IR ($CHCl_3$) 3135, 3075, 2849, 1922, 1736, 1564 cm^{-1}; HRMS *m/z* 218.0847 (calcd for $C_{15}H_{10}N_2$, 218.0844).

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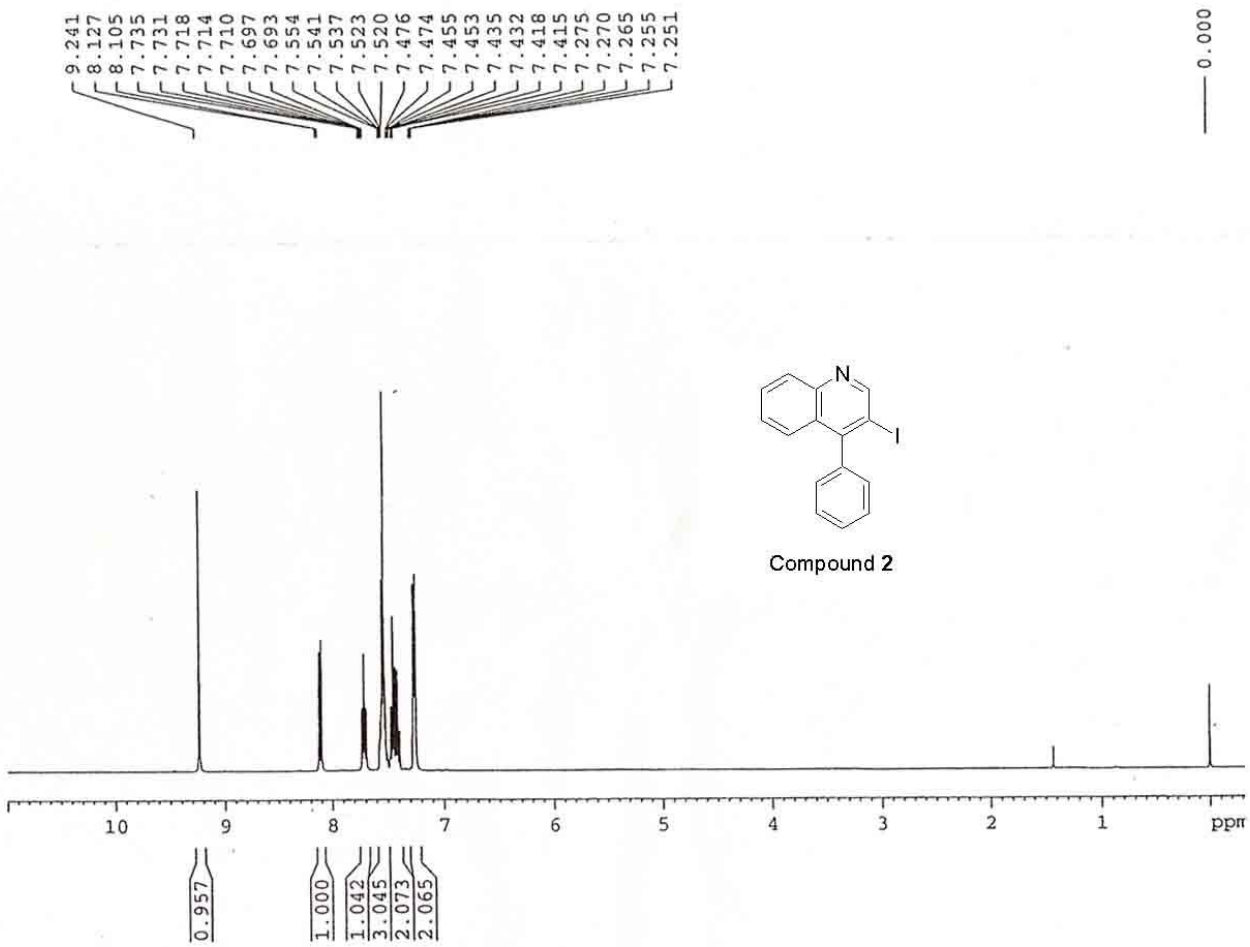
(6) Clemo, G. R.; Felton, D. G. I. *J. Chem. Soc.* **1951**, 671.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I
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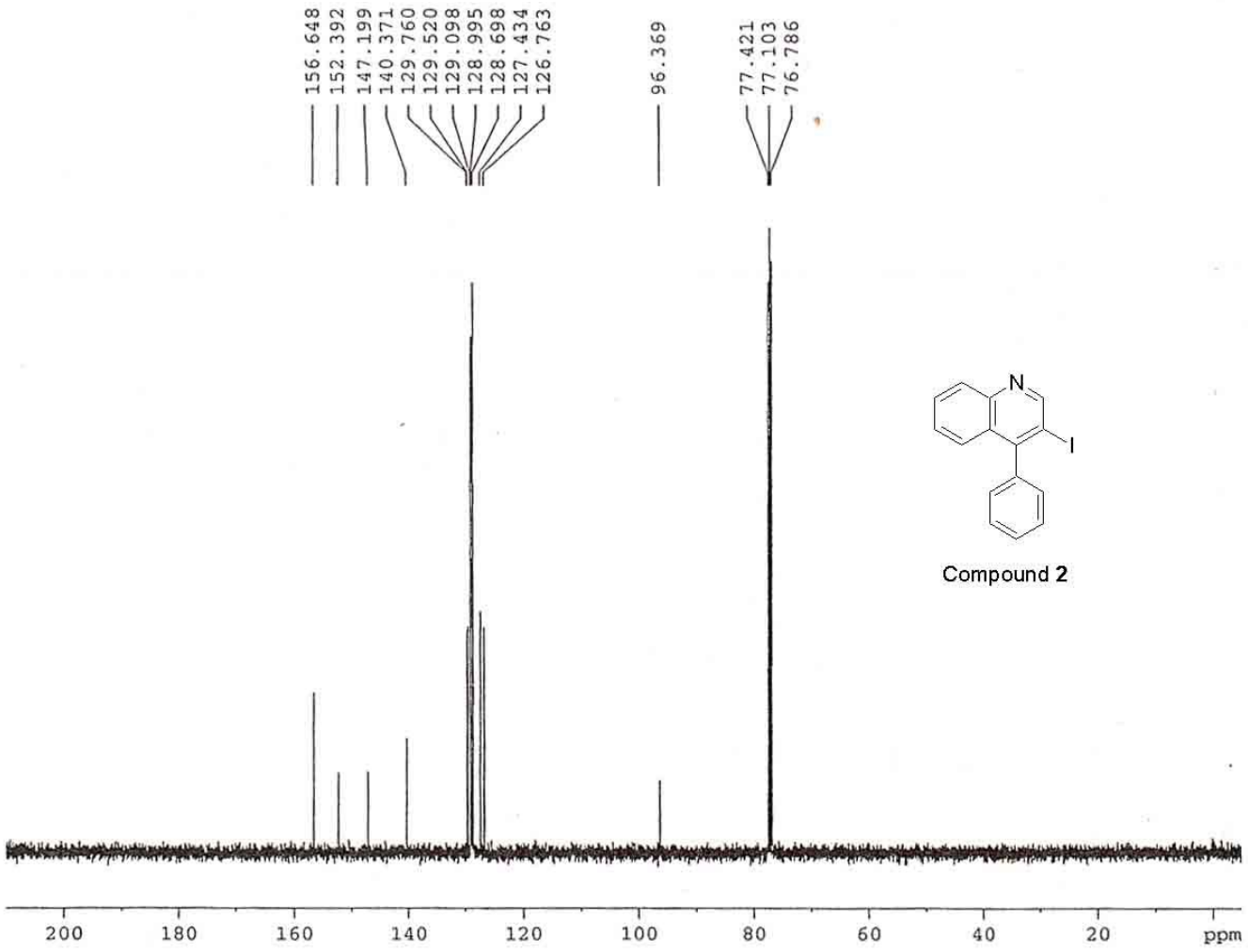
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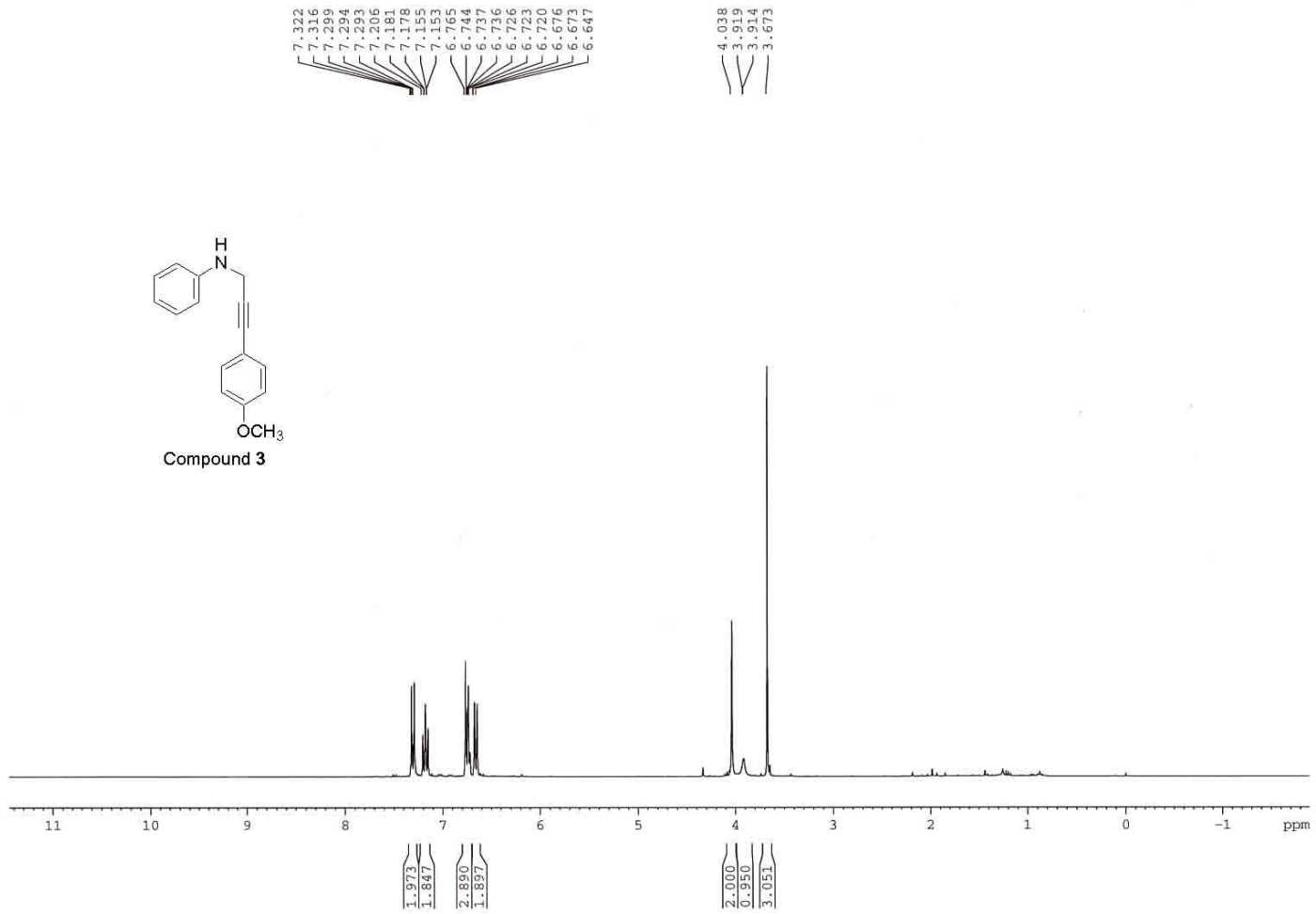
20
ppm

Compound **2**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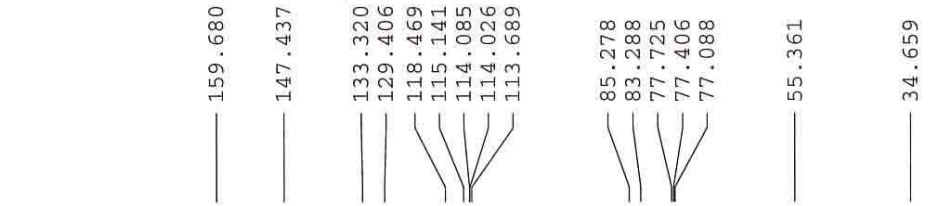
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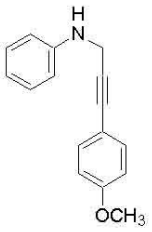
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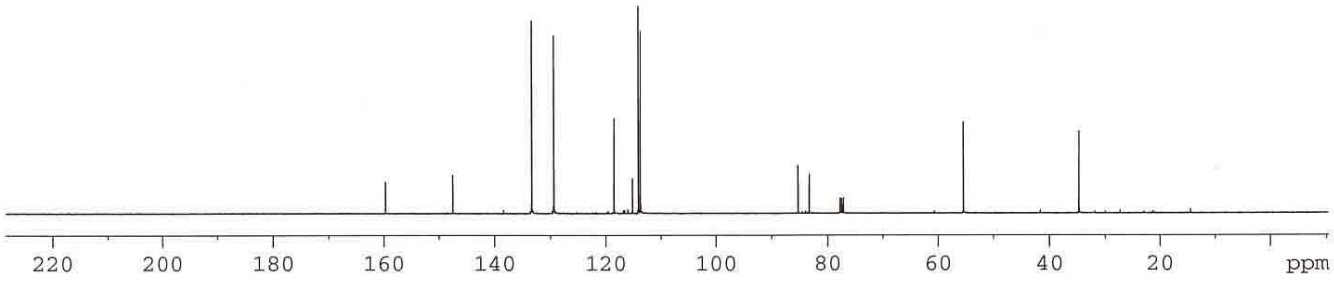
Compound **3**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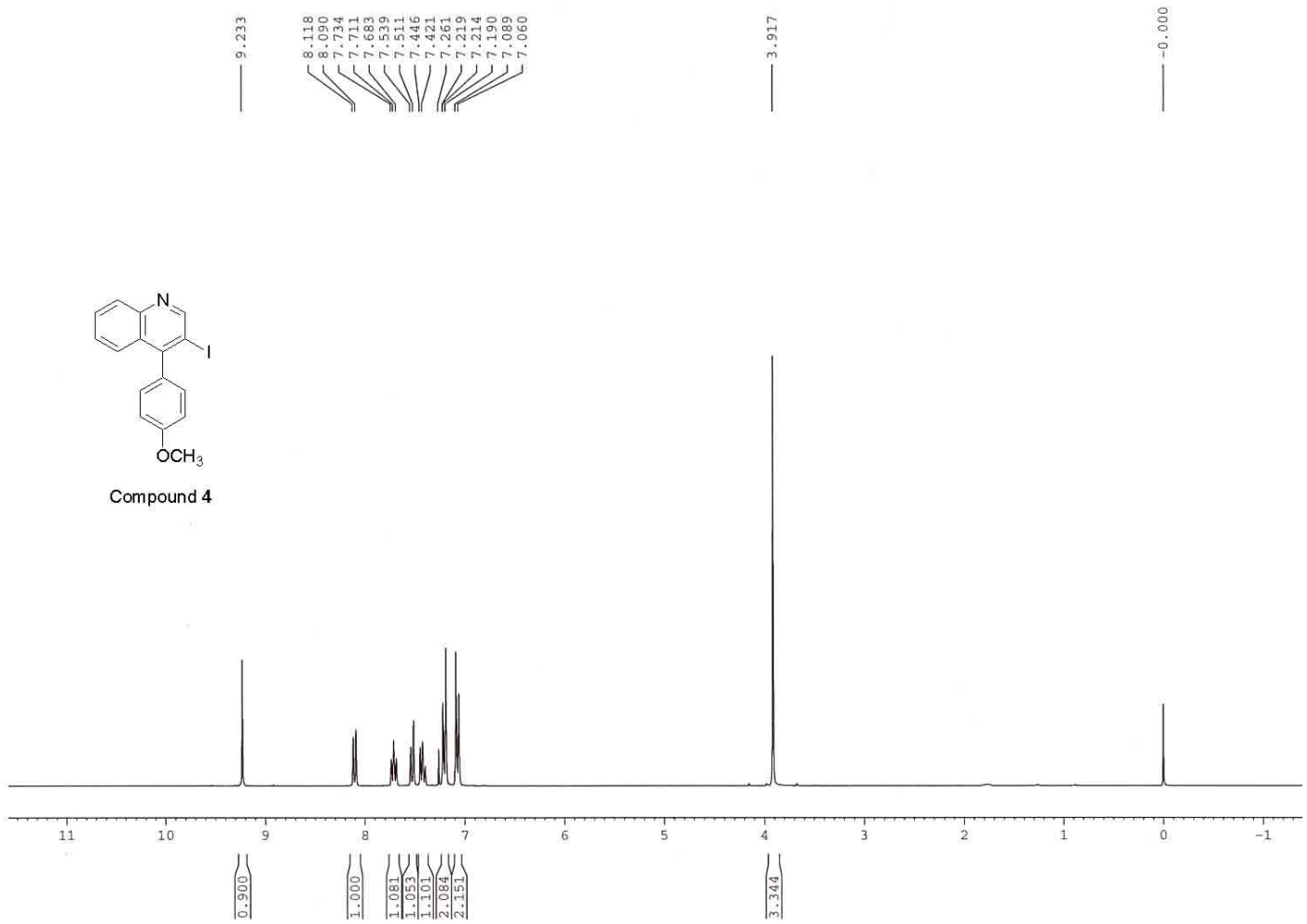
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I
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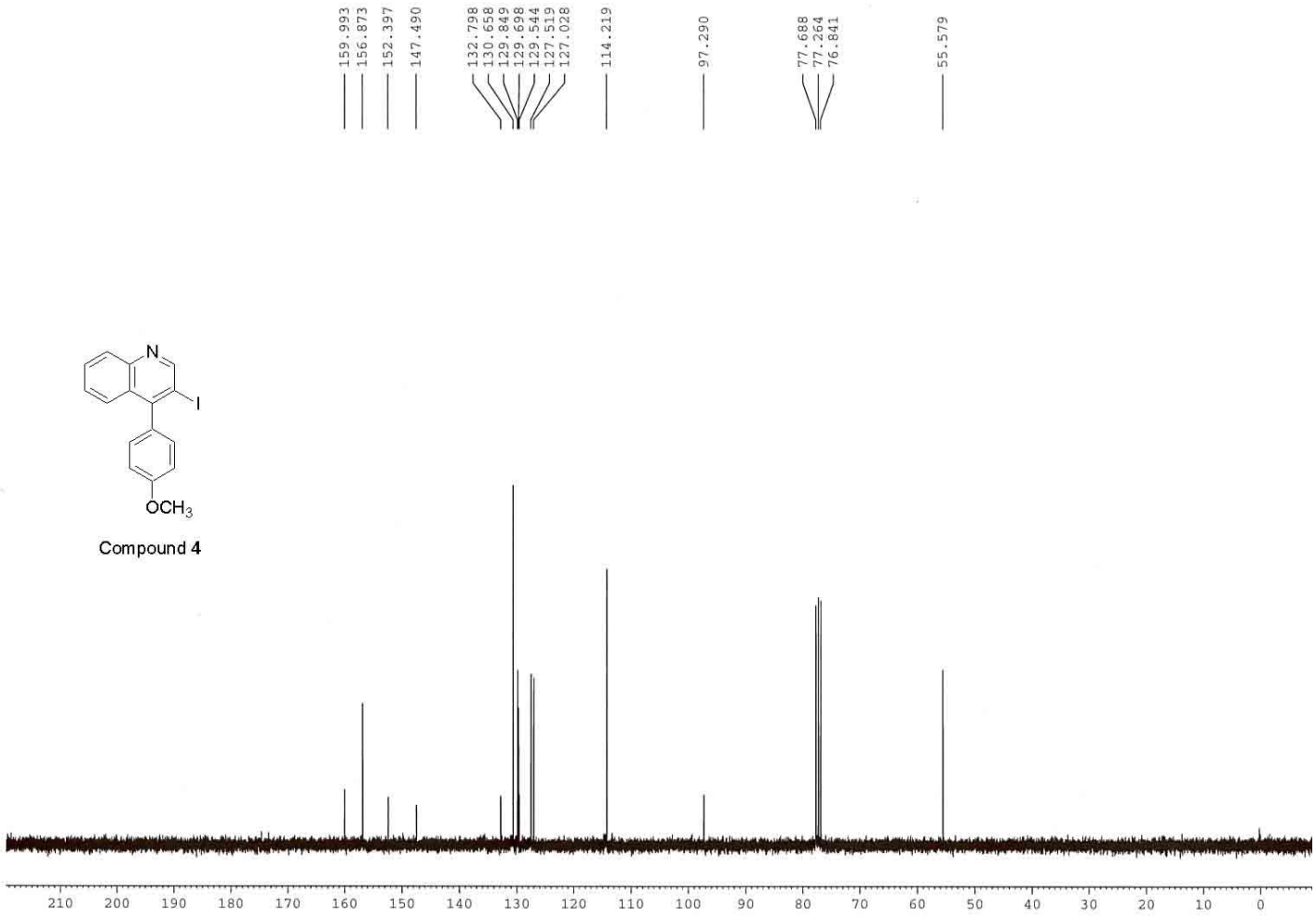
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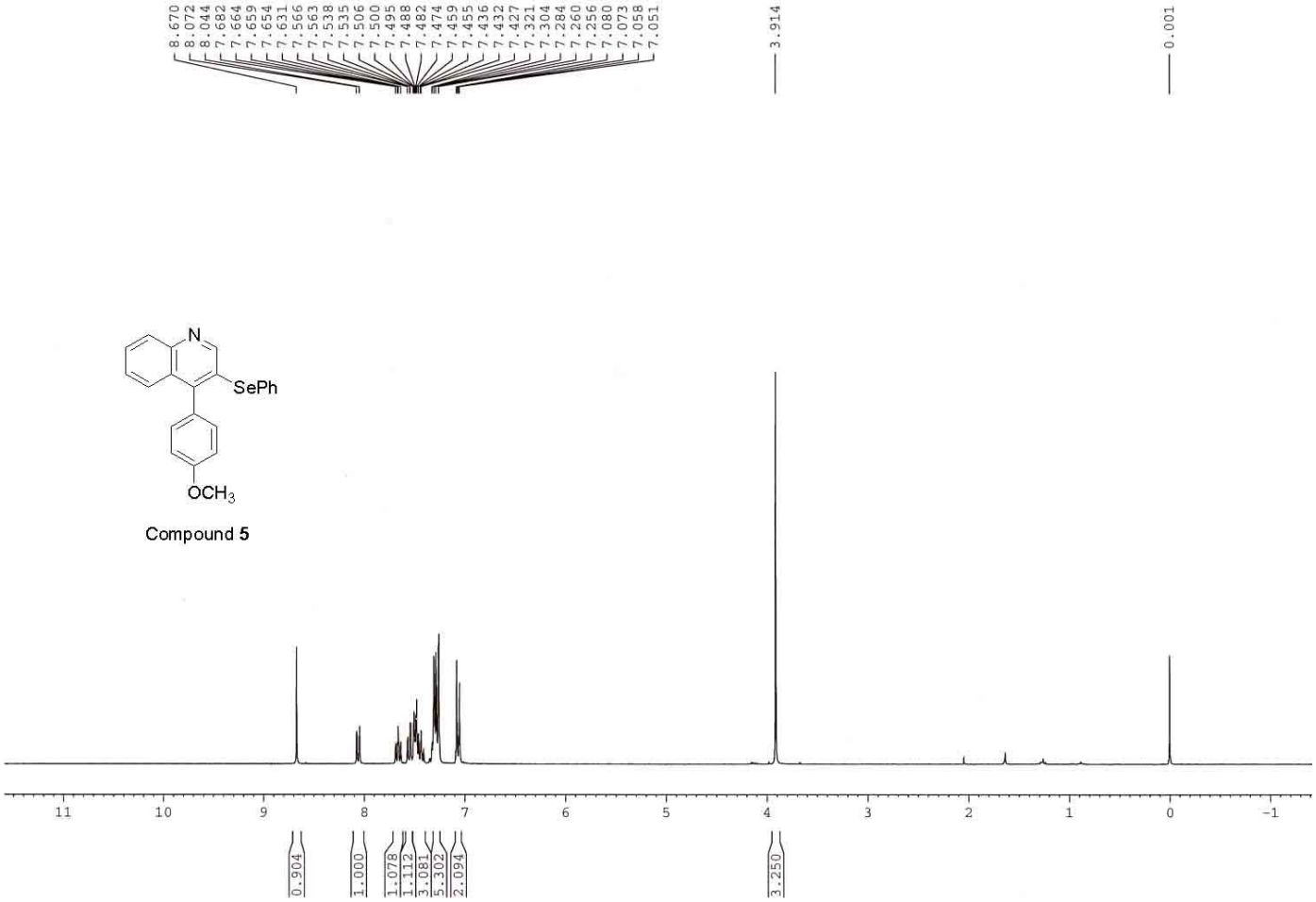
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7.506
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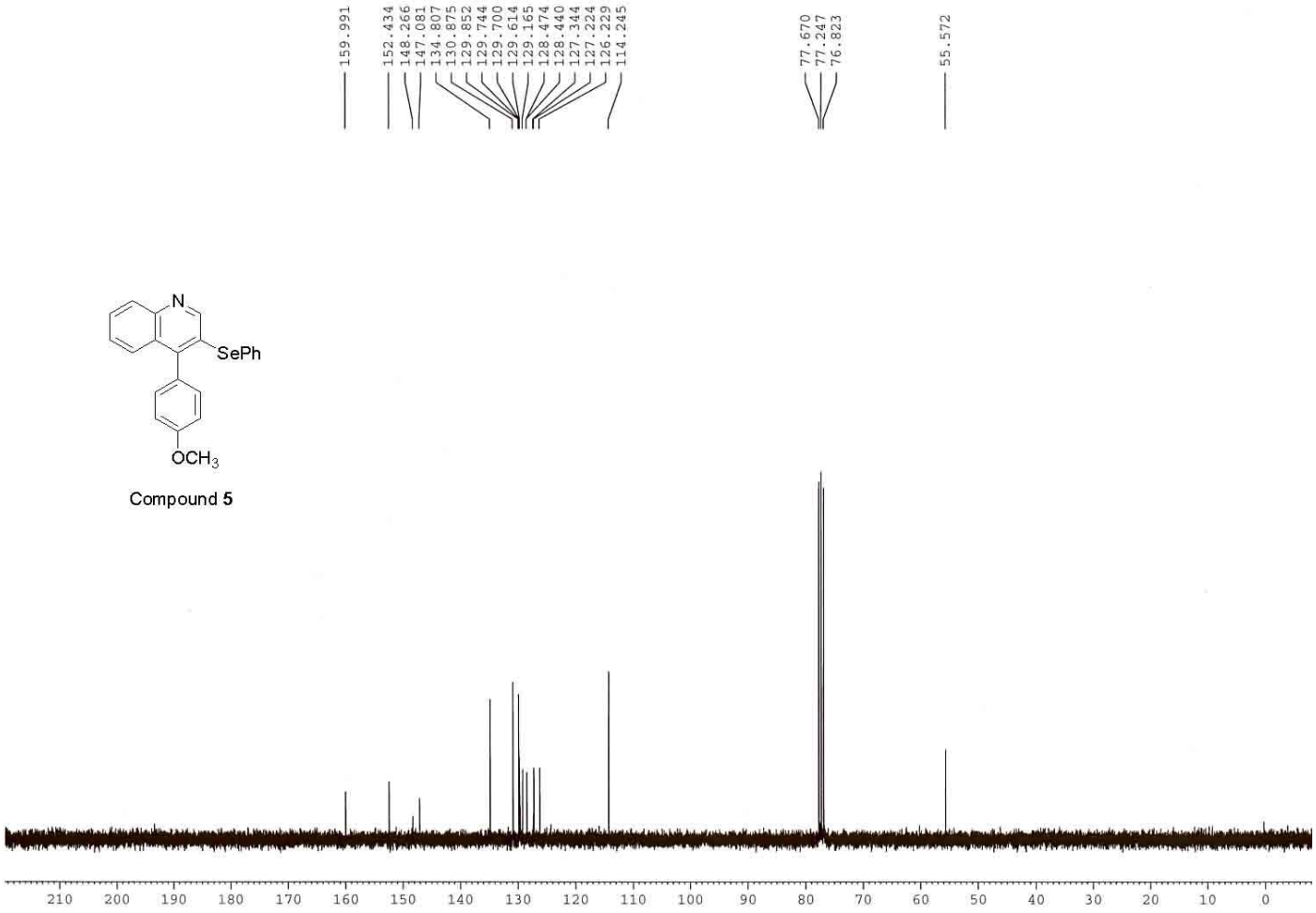
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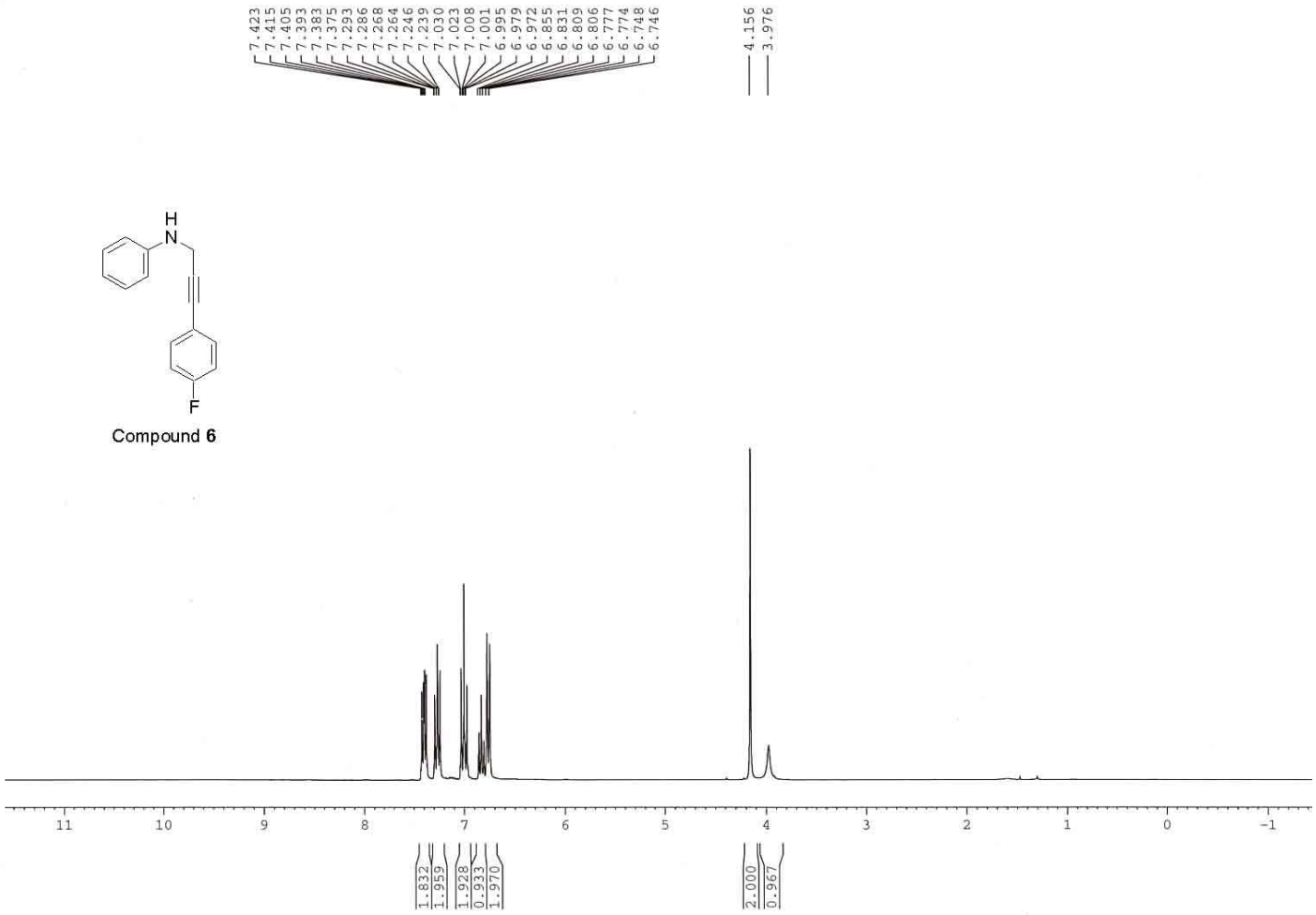
Compound **5**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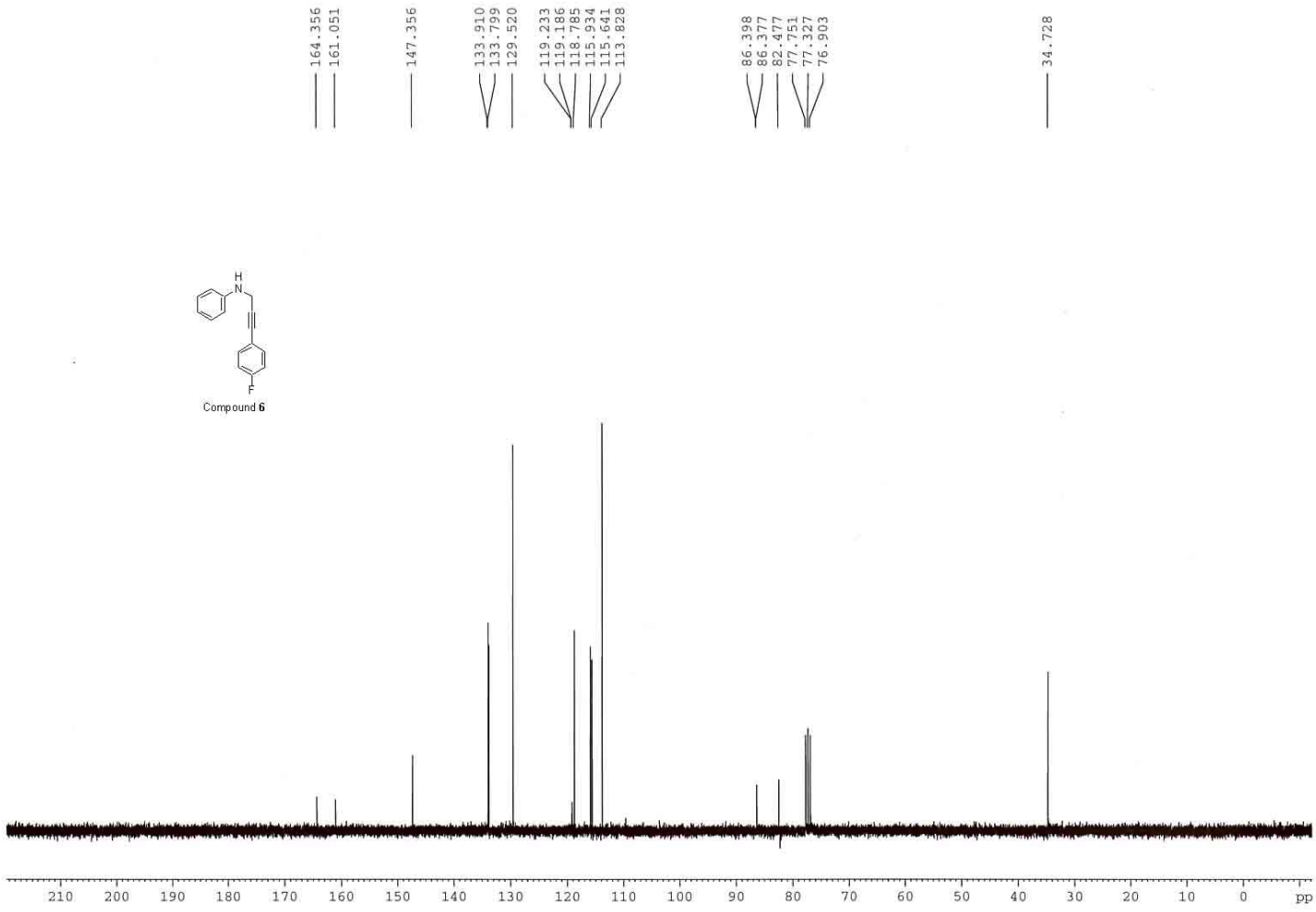
Compound **6**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Compound 6
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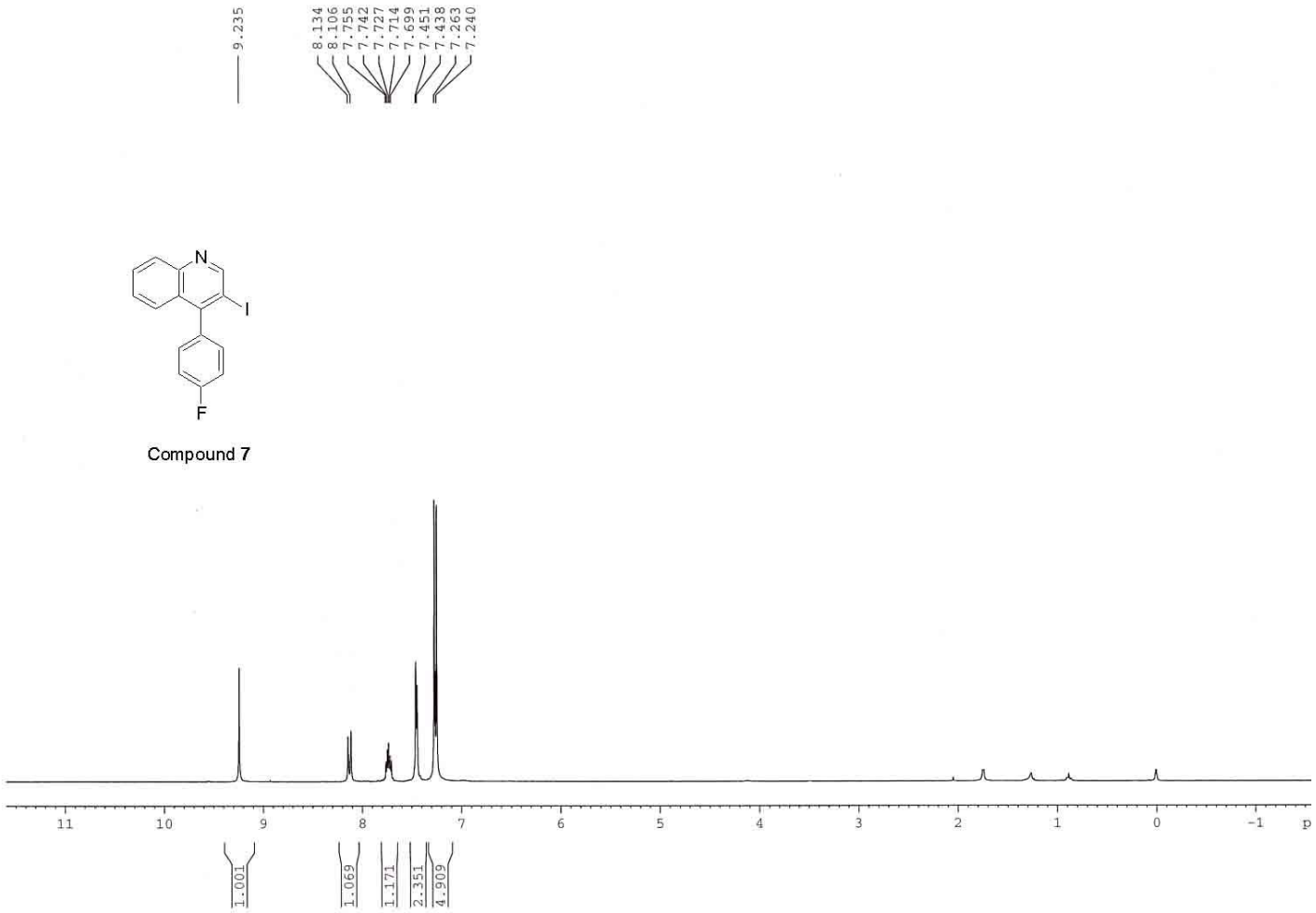
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8
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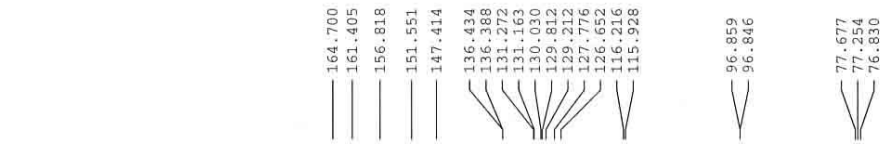
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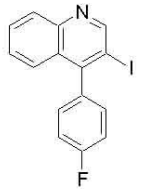
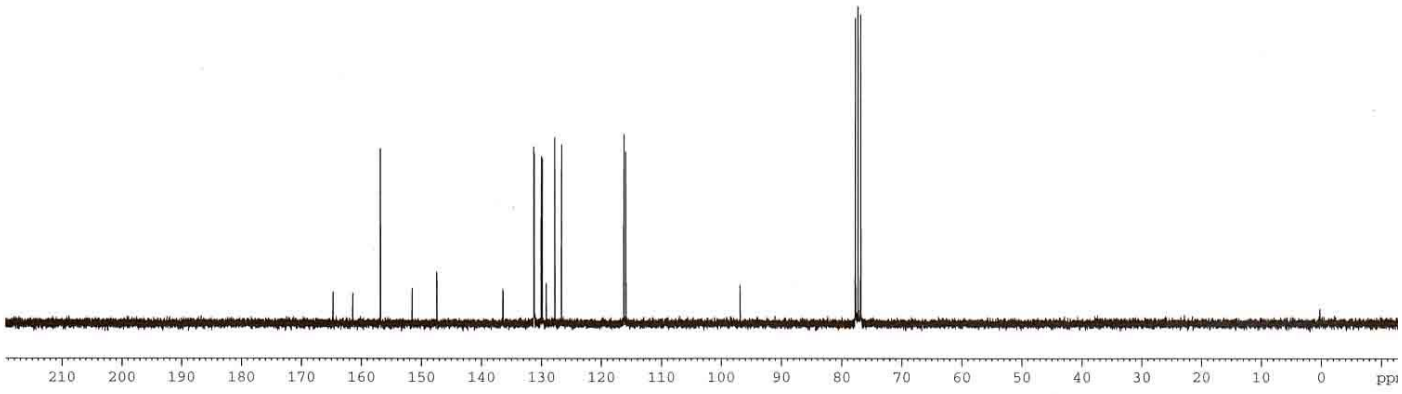

N
I
F

Compound **7**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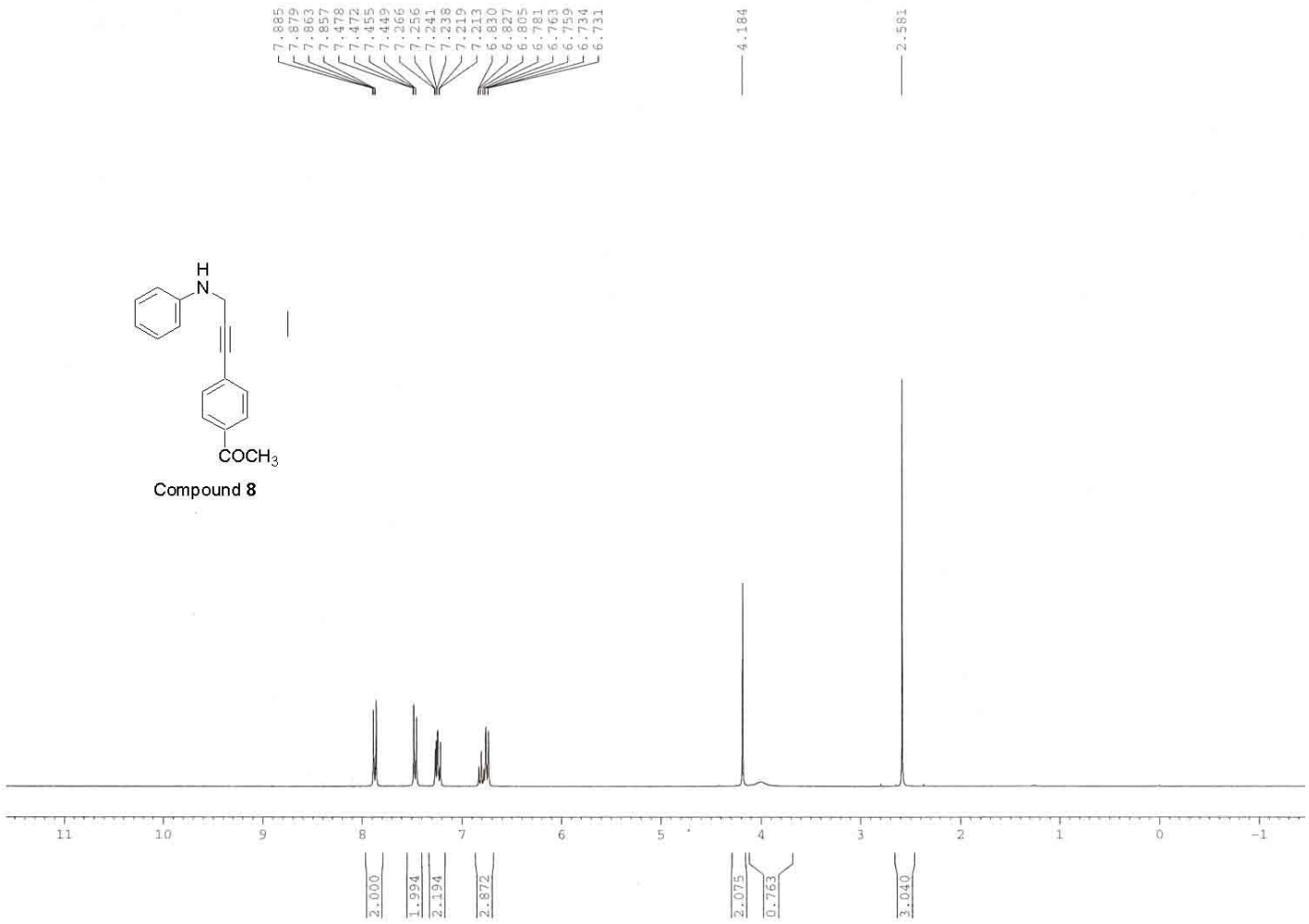
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9
8
7
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5
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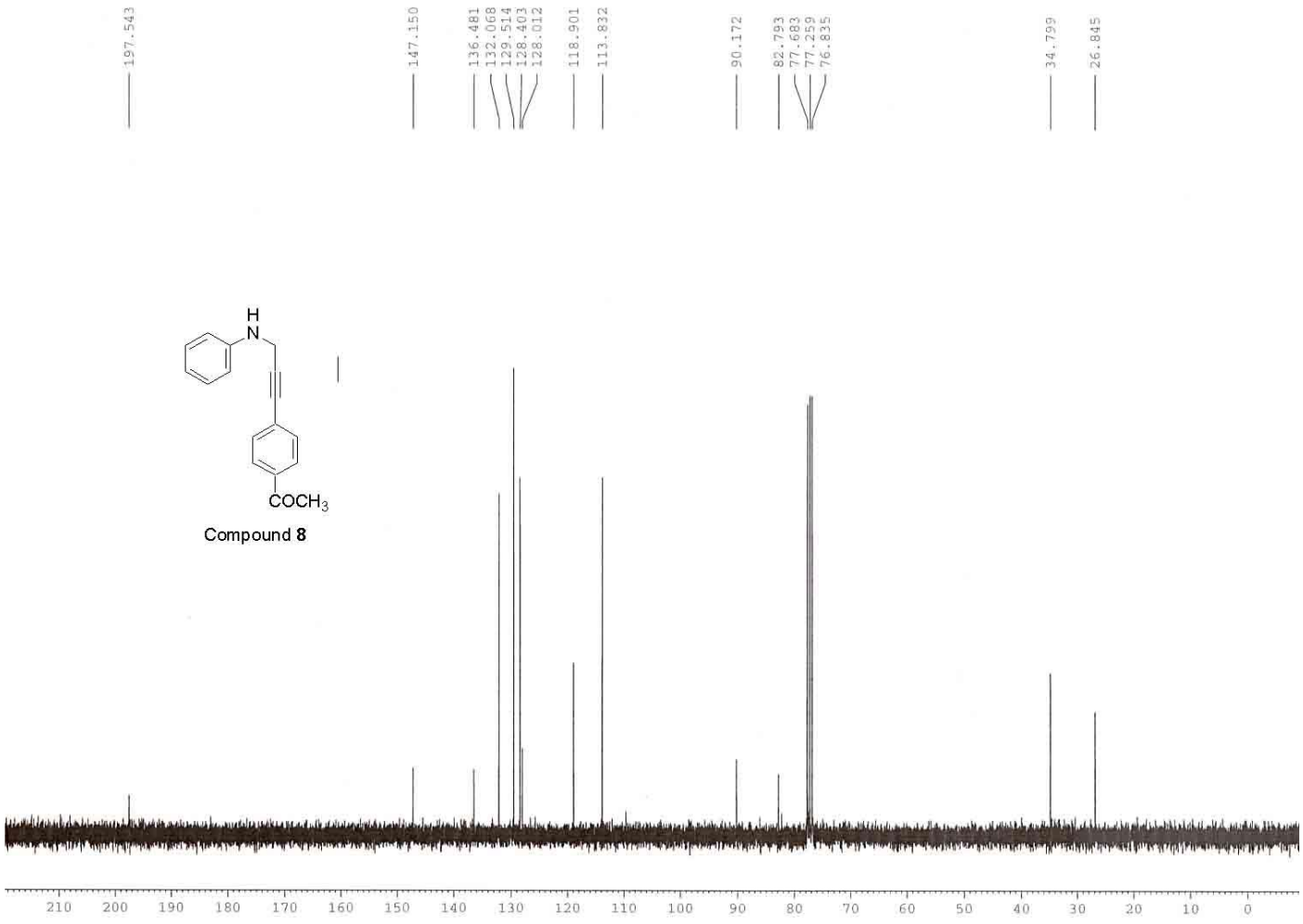
Compound **8**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180
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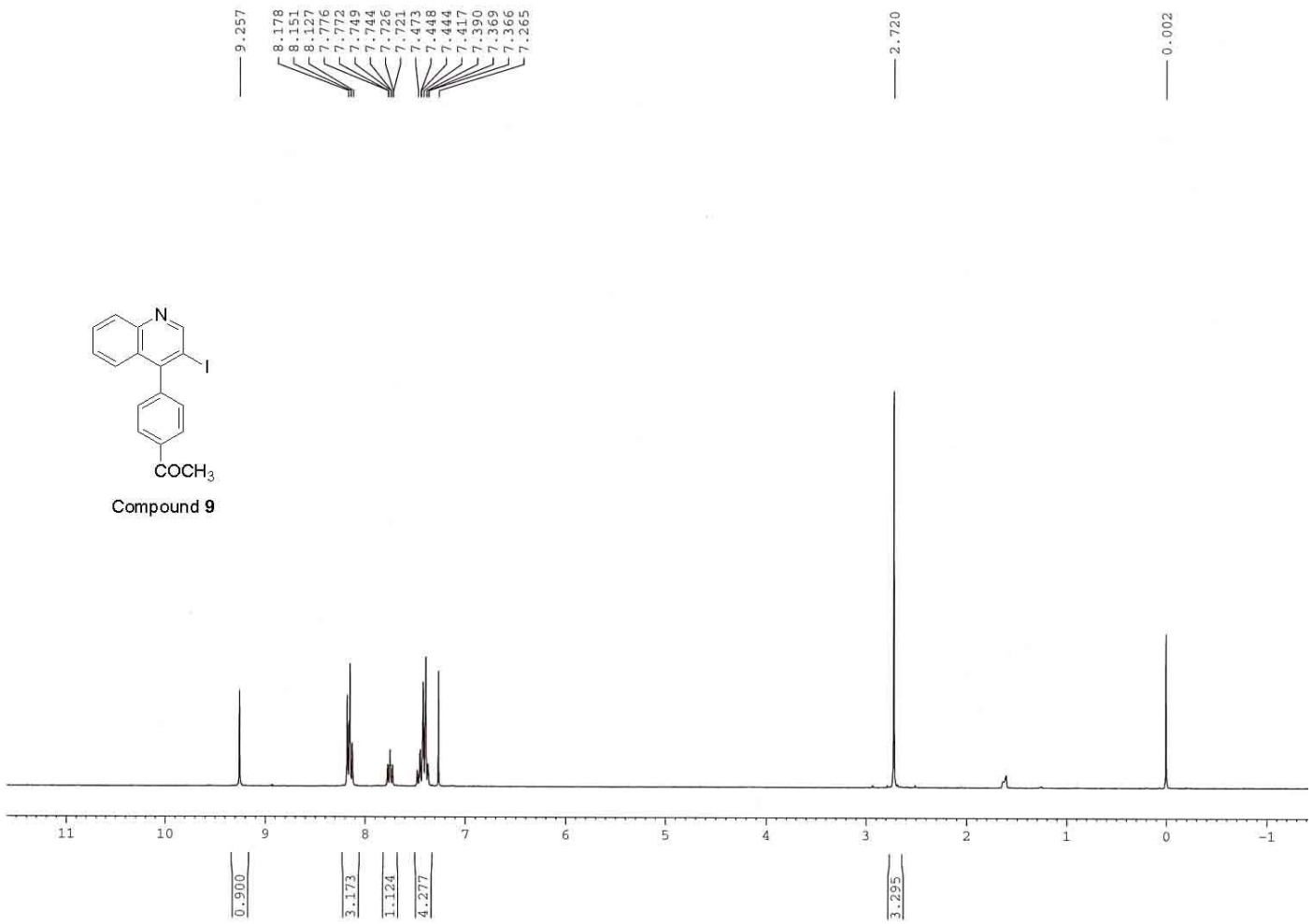
Compound **8**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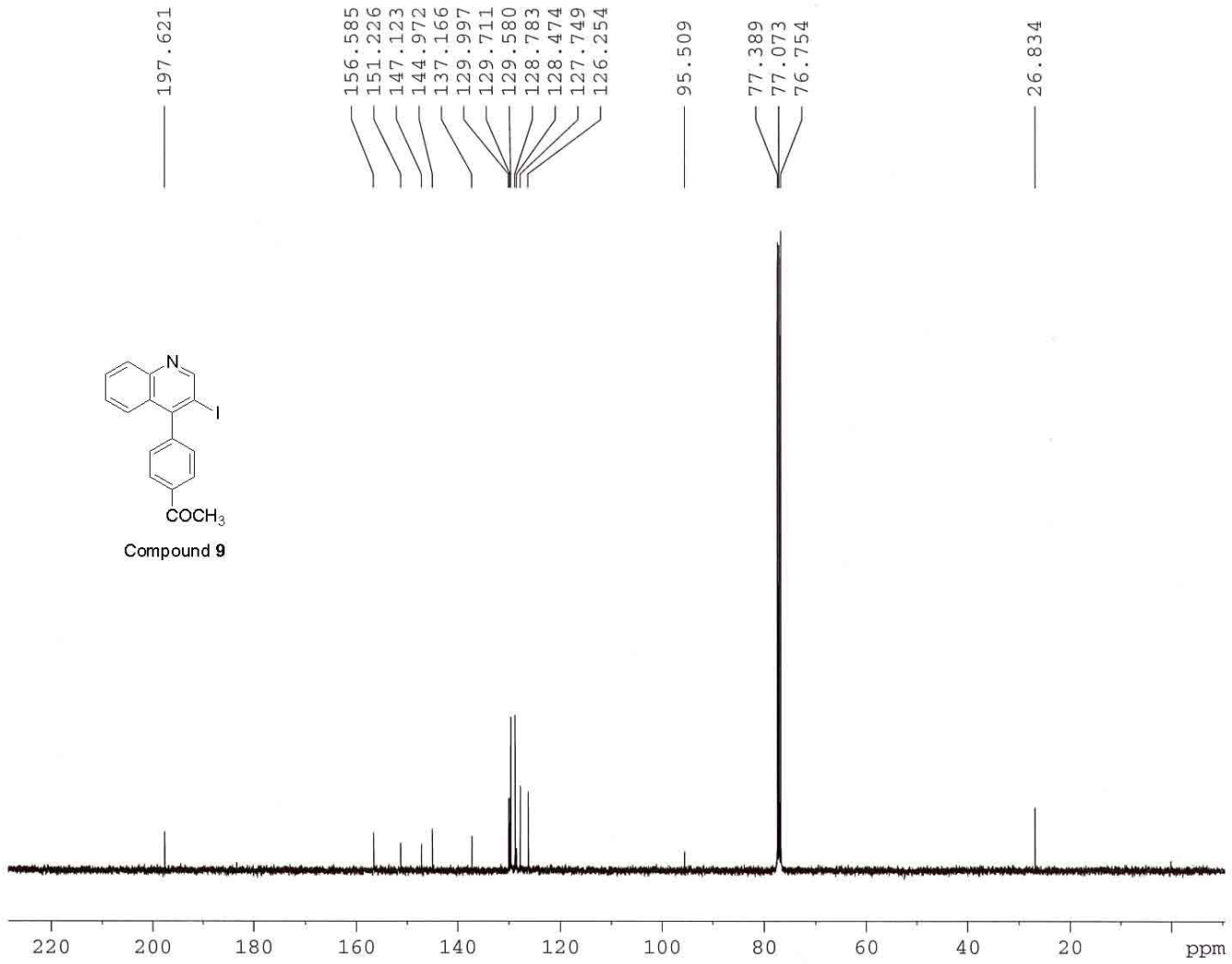
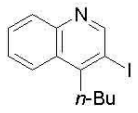
2.720
0.002
N
I
COCH3
11
10
9
8
7
6
5
4
3
2
1
0
−1
0.900
3.173
1.124
4.277
3.295

Compound **9**

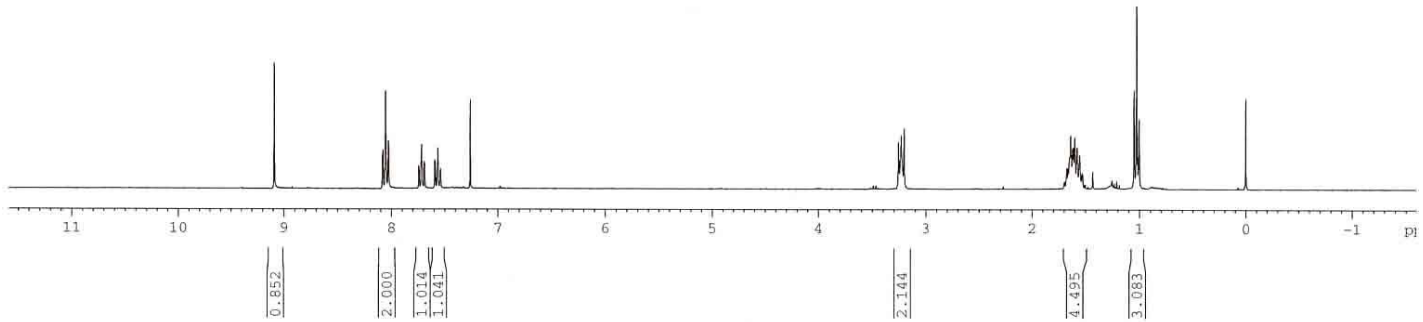

197.621
156.585
151.226
147.123
144.972
137.166
129.997
129.711
129.580
128.783
128.474
127.749
126.254
95.509
77.389
77.073
76.754
26.834
N
I
COCH3
220
200
180
160
140
120
100
80
60
40
20
ppm

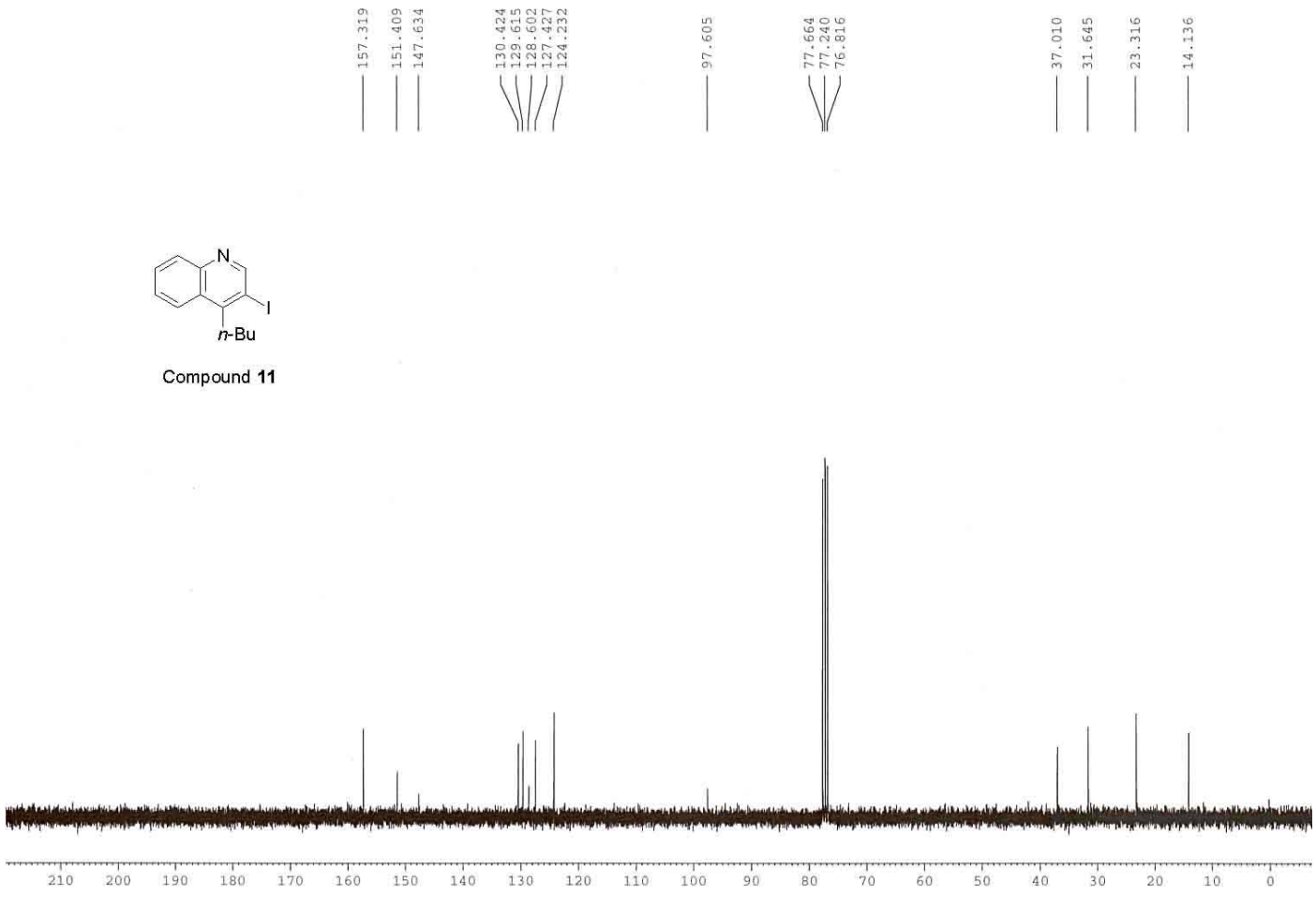
Compound **9**


9.088
8.079
8.077
8.052
8.026
7.742
7.738
7.719
7.715
7.691
7.686
7.592
7.588
7.569
7.564
7.541
7.537
7.259
3.255
3.230
3.202
1.671
1.661
1.635
1.629
1.618
1.608
1.597
1.576
1.551
1.047
1.023
1.000
-0.003

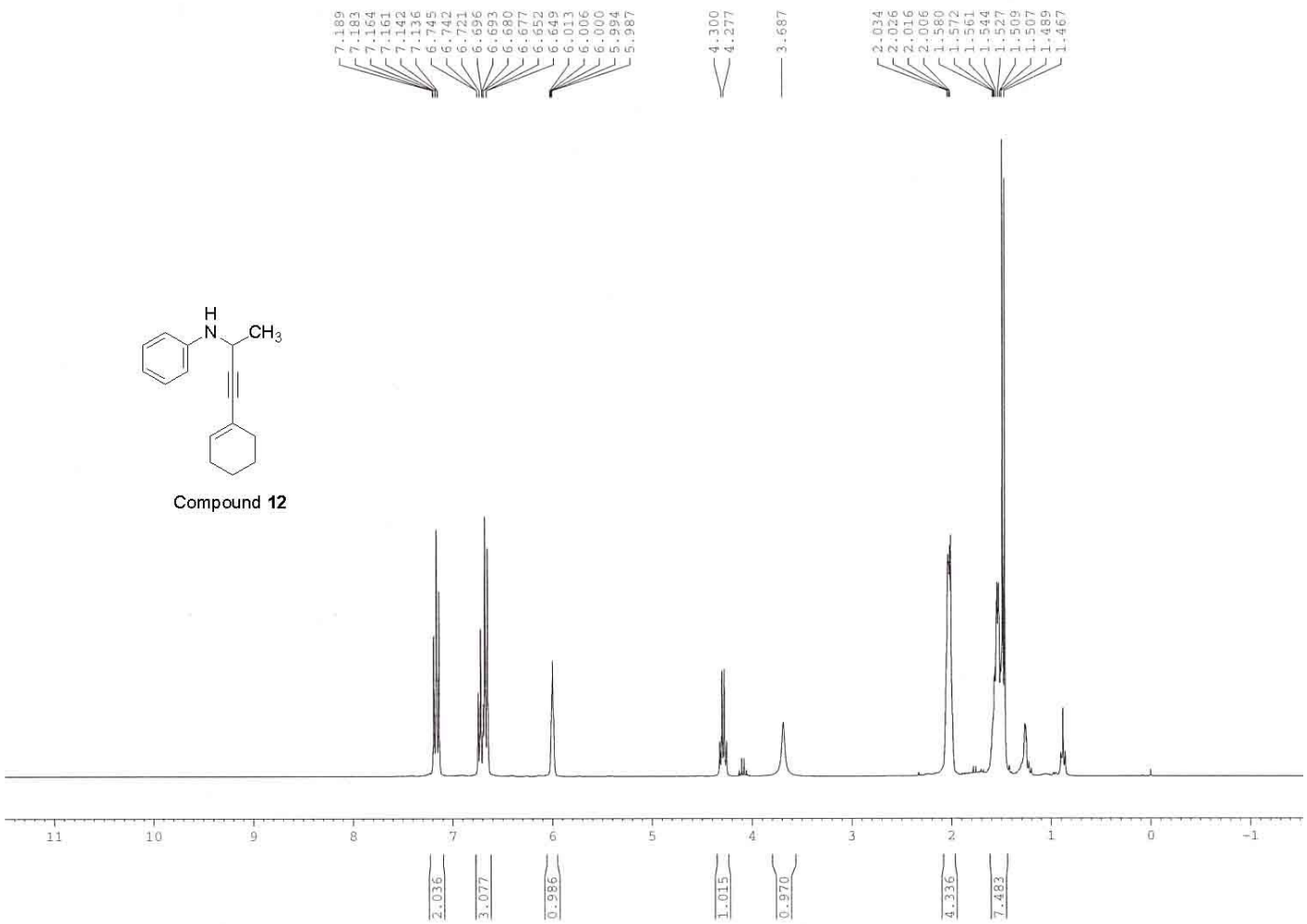

N
I
n-Bu

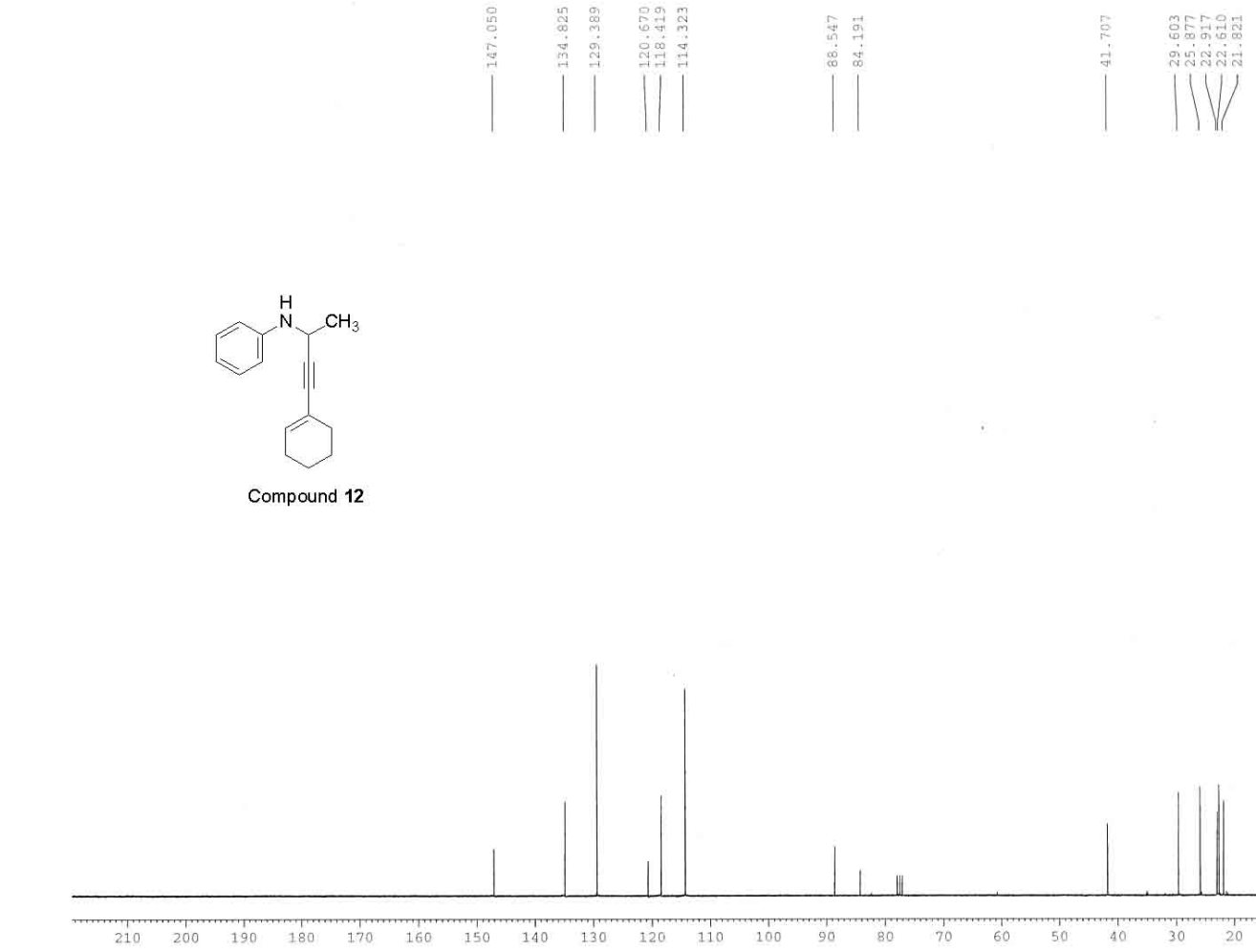
Compound **11**


11
10
9
8
7
6
5
4
3
2
1
0
-1
0.852
2.000
1.014
1.041
2.144
4.495
3.083

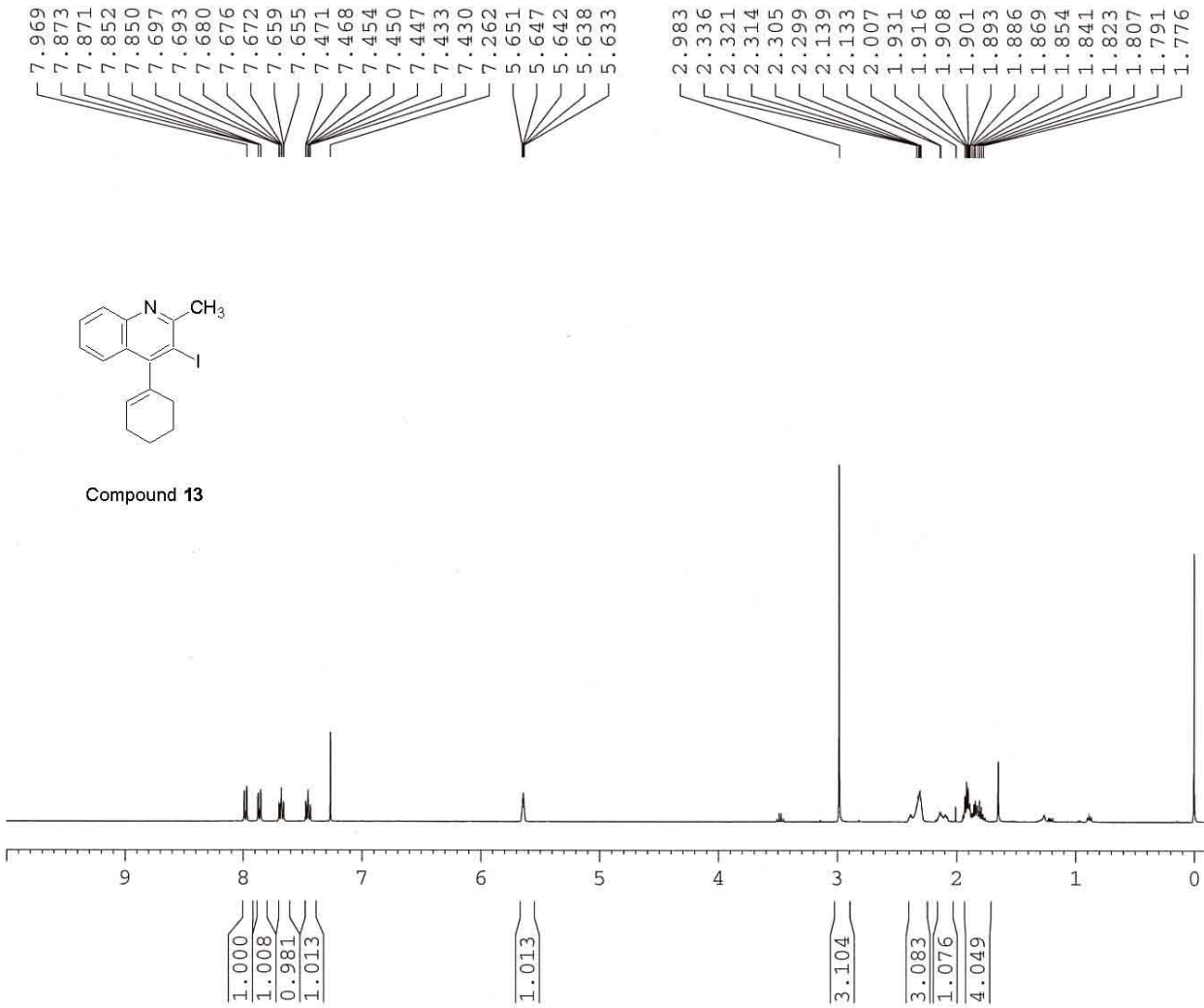

157.319
151.409
147.634
130.424
129.615
128.602
127.427
124.232
97.605
77.664
77.240
76.816
37.010
31.645
23.316
14.136
N
I
n-Bu
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Compound **11**

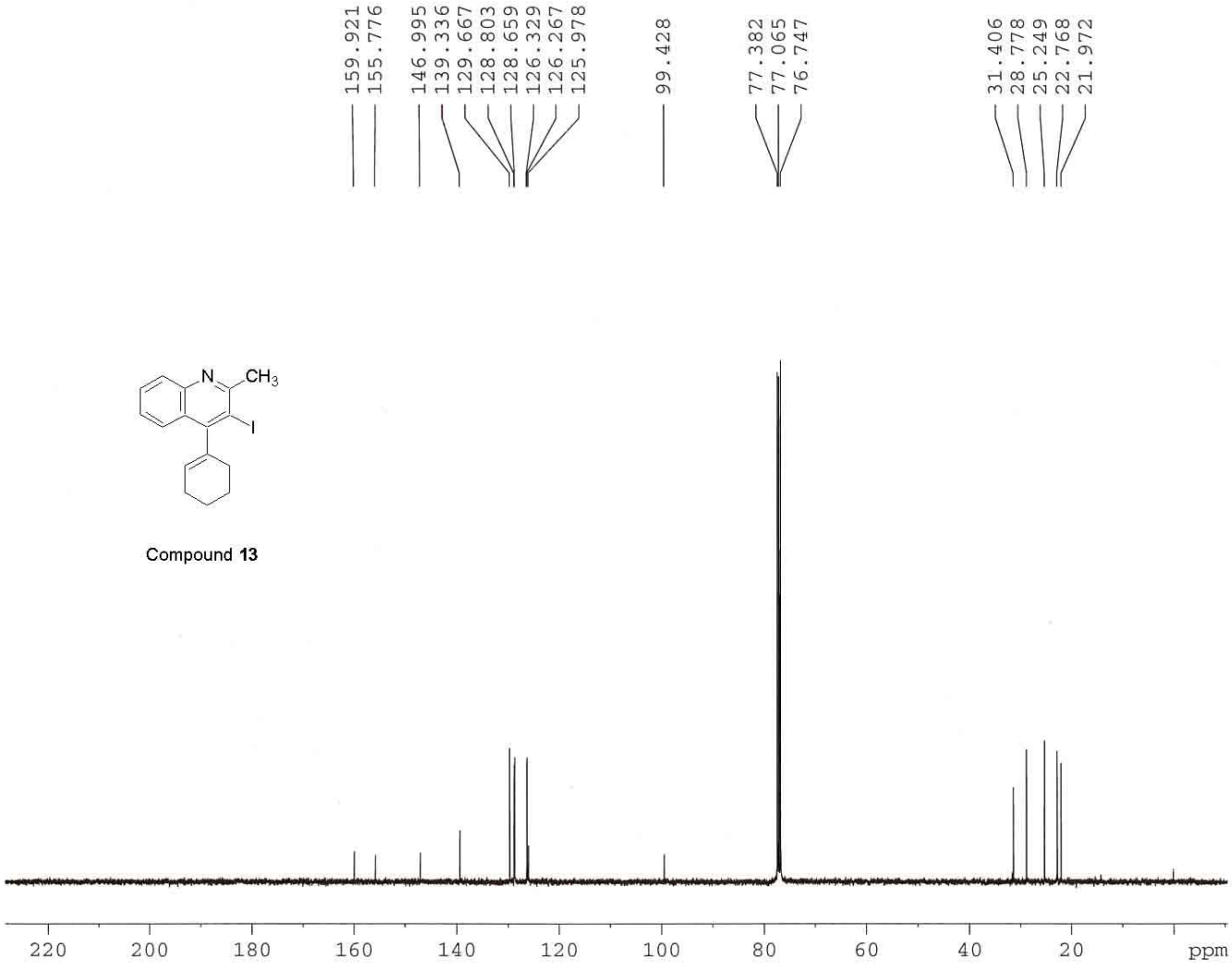

7.189
7.183
7.164
7.161
7.142
7.136
6.745
6.742
6.721
6.696
6.693
6.680
6.677
6.652
6.649
6.013
6.006
6.000
5.994
5.987
4.300
4.277
3.687
2.034
2.026
2.016
2.006
1.580
1.572
1.561
1.544
1.527
1.509
1.507
1.489
1.467
H
N
CH3
Compound 12
11
10
9
8
7
6
5
4
3
2
1
0
-1
2.036
3.077
0.986
1.015
0.970
4.336
7.483


147.050
134.825
129.389
120.670
118.419
114.323
88.547
84.191
41.707
29.603
25.877
22.917
22.610
21.821
H
N
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
pp

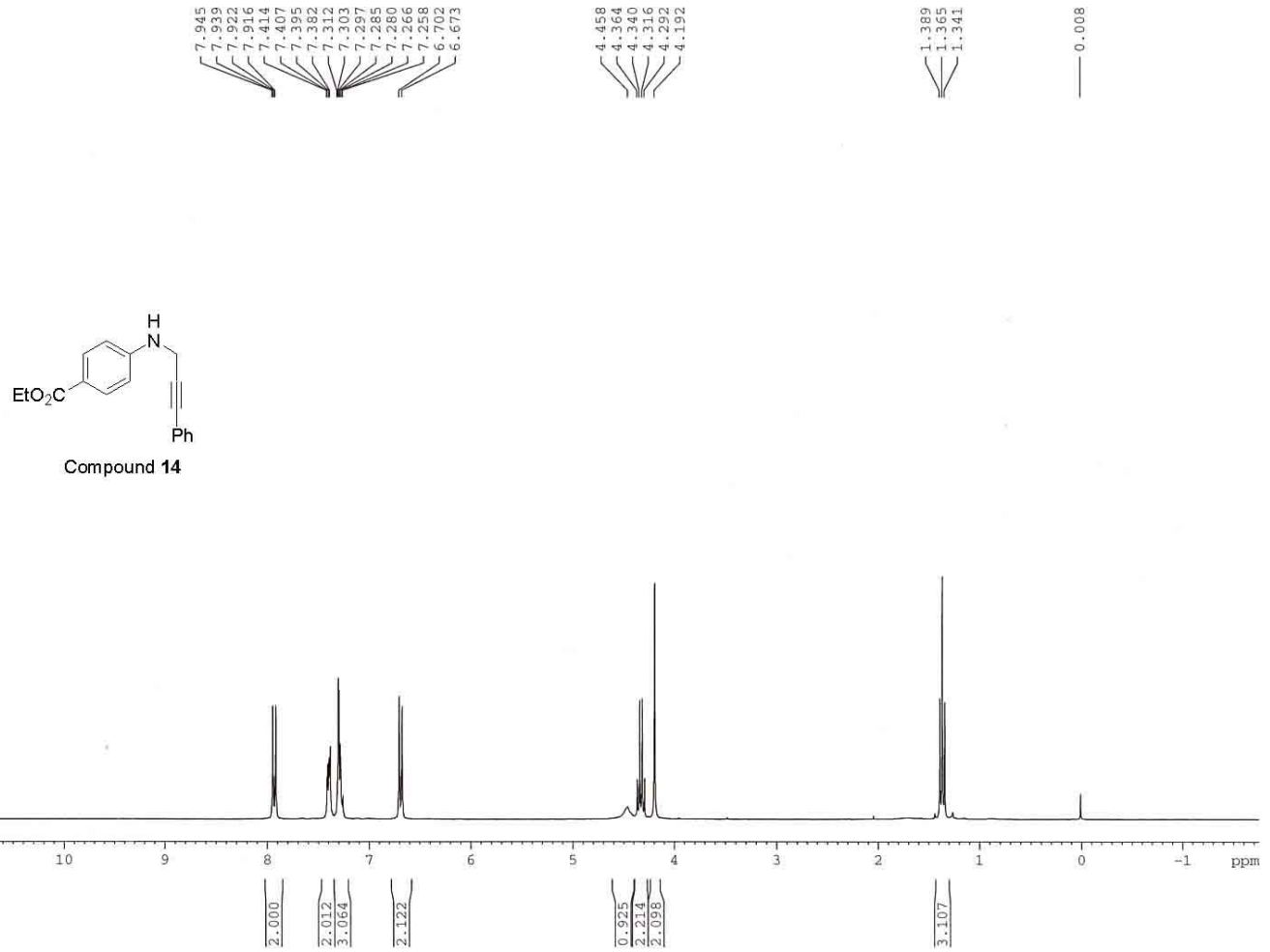
Compound **12**


7.969
7.873
7.871
7.852
7.850
7.697
7.693
7.680
7.676
7.672
7.659
7.655
7.471
7.468
7.454
7.450
7.447
7.433
7.430
7.262
5.651
5.647
5.642
5.638
5.633
2.983
2.336
2.321
2.314
2.305
2.299
2.139
2.133
2.007
1.931
1.916
1.908
1.901
1.893
1.886
1.869
1.854
1.841
1.823
1.807
1.791
1.776
N
CH3
I
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.008
0.981
1.013
1.013
3.104
3.083
1.076
4.049

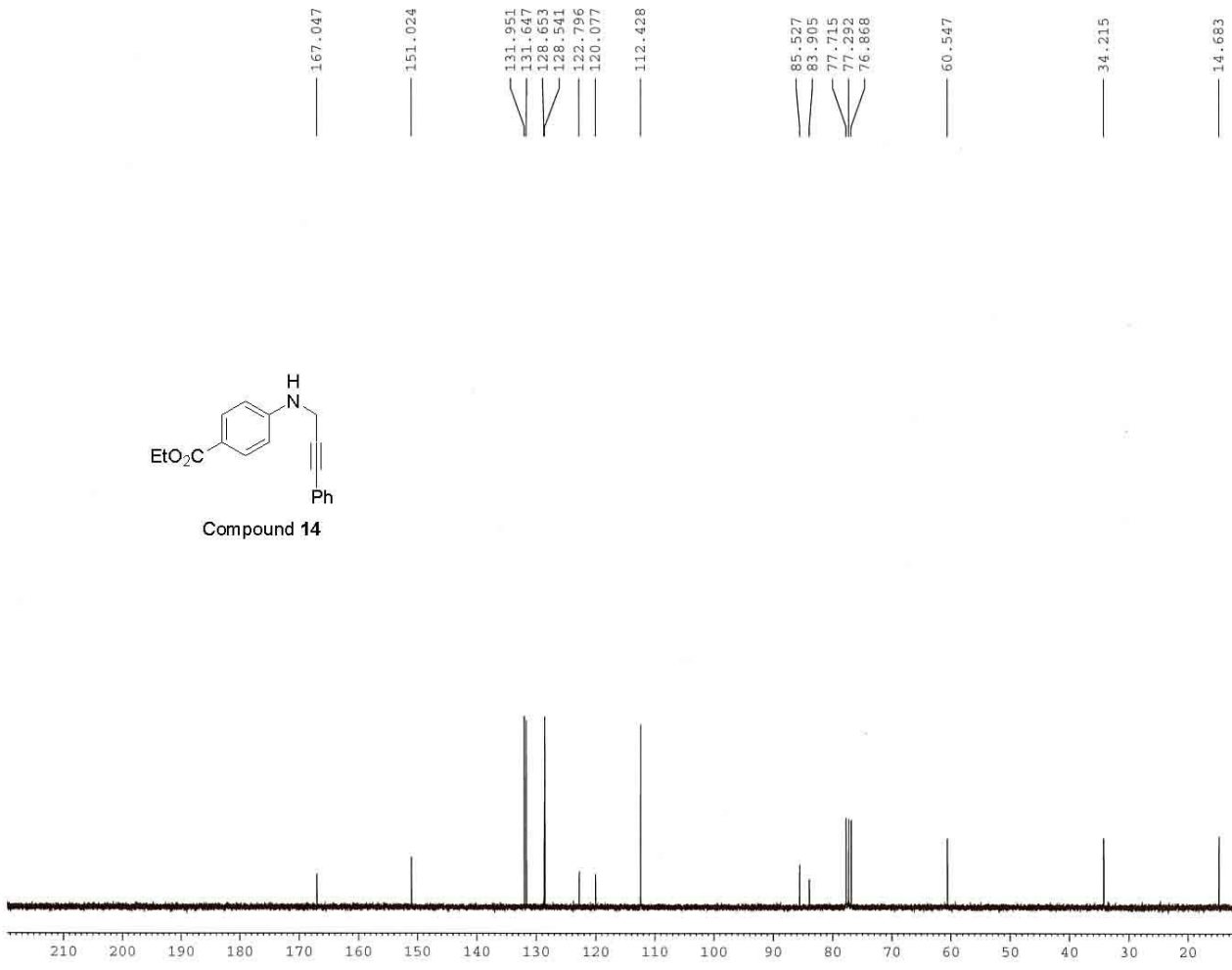
Compound **13**


159.921
155.776
146.995
139.336
129.667
128.803
128.659
126.329
126.267
125.978
99.428
77.382
77.065
76.747
31.406
28.778
25.249
22.768
21.972
N
CH3
I
220
200
180
160
140
120
100
80
60
40
20
ppm

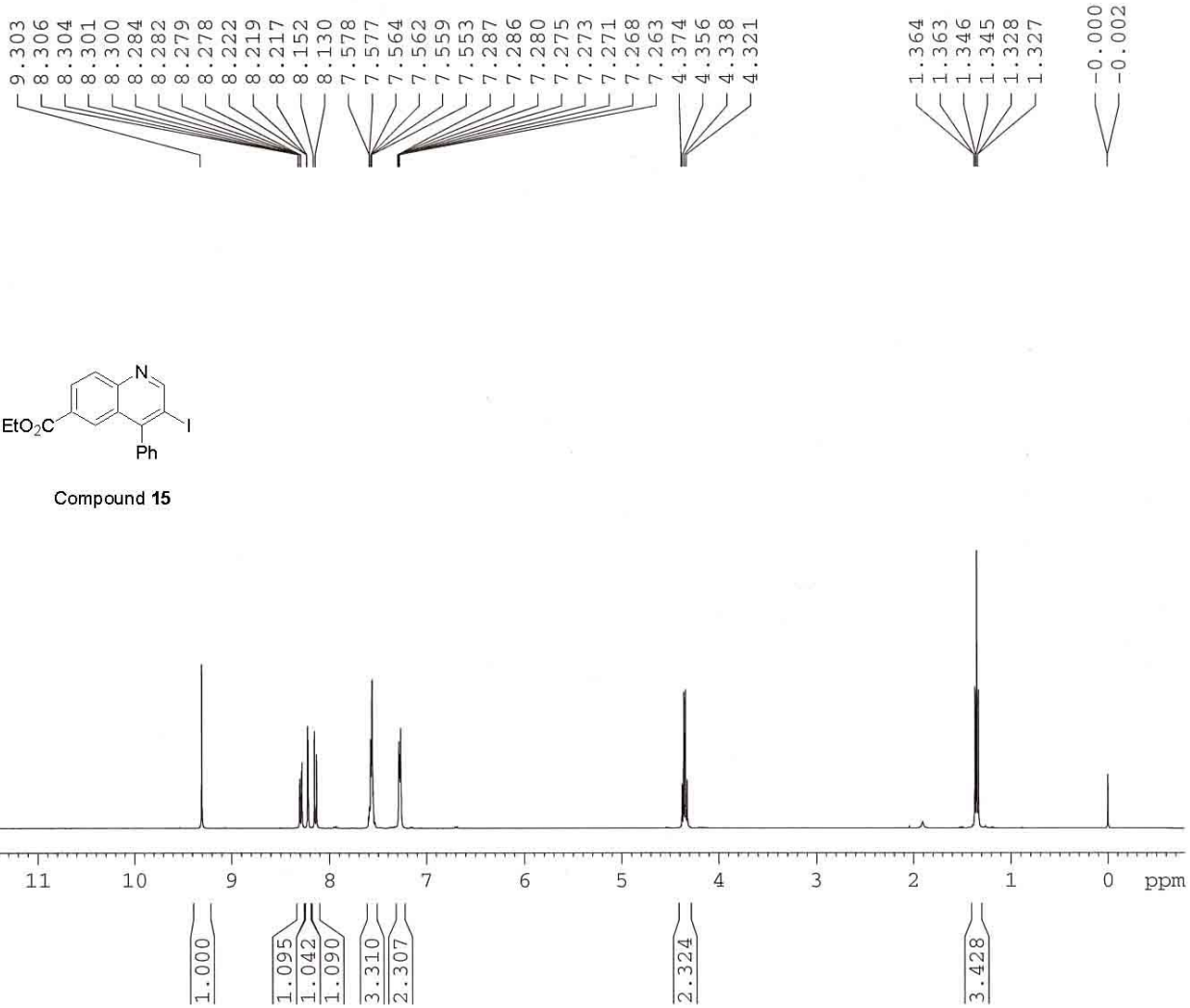
Compound **13**


7.945
7.939
7.922
7.916
7.414
7.407
7.395
7.382
7.312
7.303
7.297
7.285
7.280
7.266
7.258
6.702
6.673
4.458
4.364
4.340
4.316
4.292
4.192
1.389
1.365
1.341
0.008
H
N
EtO2C
Ph
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
2.000
2.012
3.064
2.122
0.925
2.214
2.098
3.107

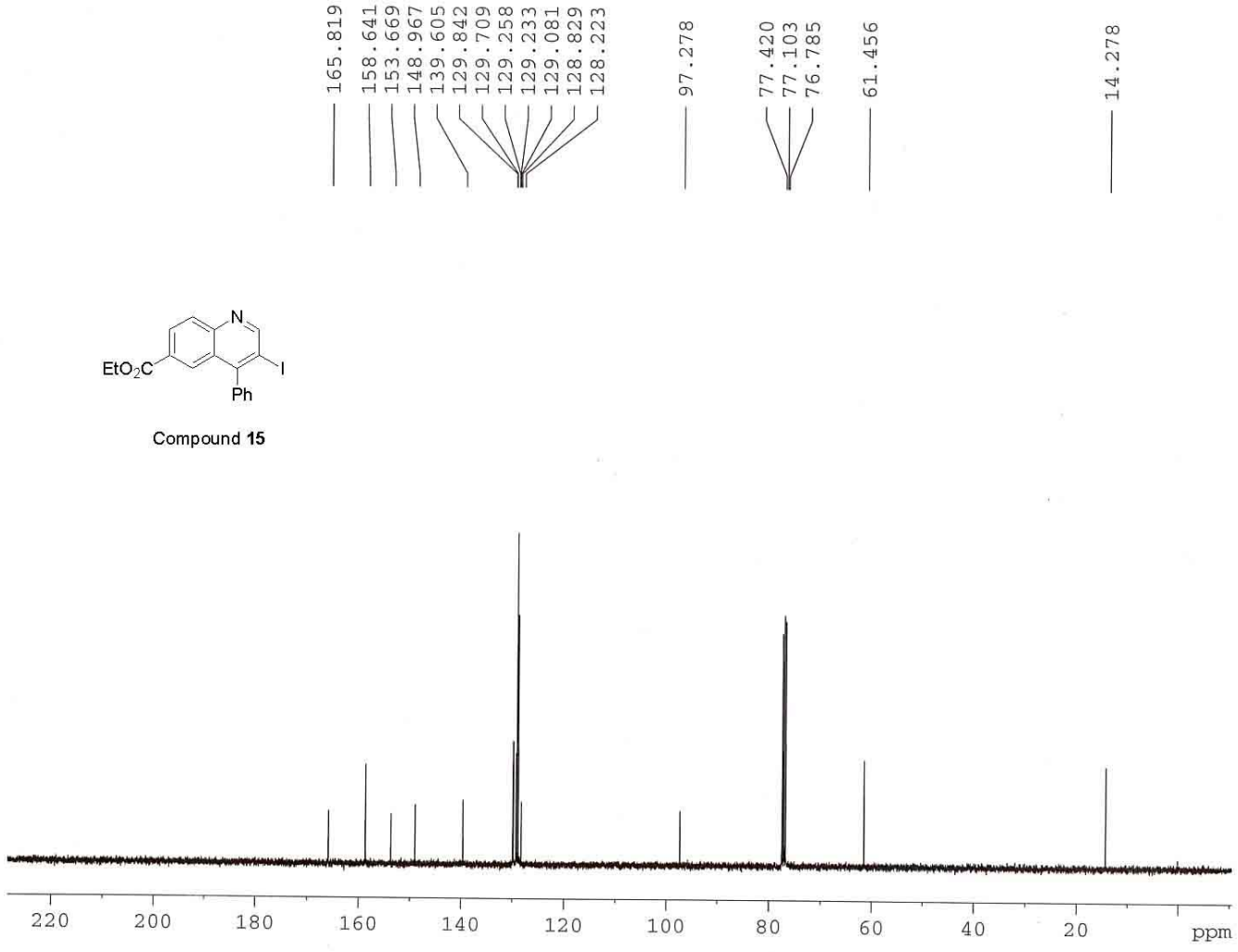
Compound **14**


167.047
151.024
131.951
131.647
128.653
128.541
122.796
120.077
112.428
85.527
83.905
77.715
77.292
76.868
60.547
34.215
14.683
H
N
EtO2C
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

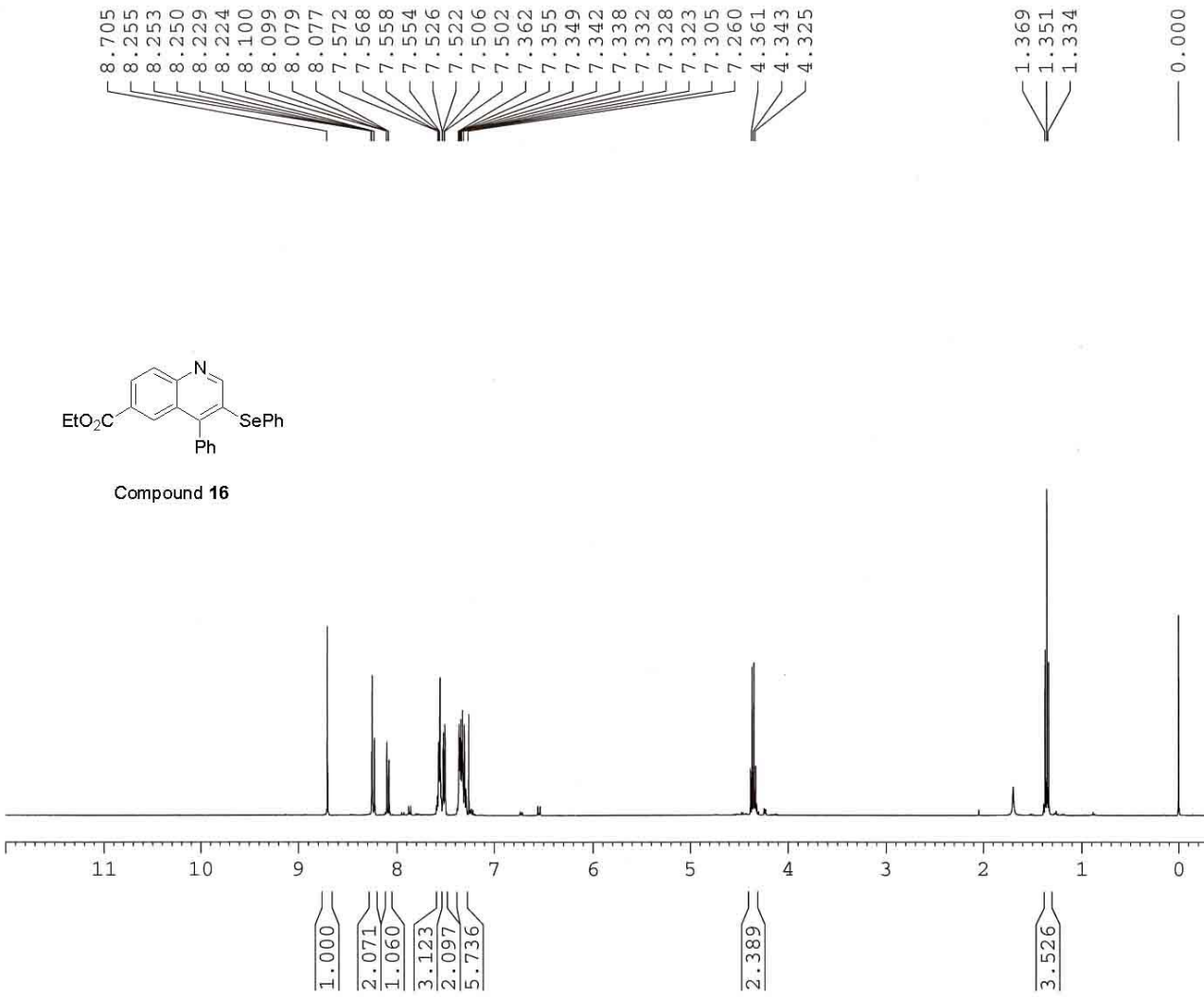
Compound **14**


9.303
8.306
8.304
8.301
8.300
8.284
8.282
8.279
8.278
8.222
8.219
8.217
8.152
8.130
7.578
7.577
7.564
7.562
7.559
7.553
7.287
7.286
7.280
7.275
7.273
7.271
7.268
7.263
4.374
4.356
4.338
4.321
1.364
1.363
1.346
1.345
1.328
1.327
-0.000
-0.002
N
EtO2C
I
Ph
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.095
1.042
1.090
3.310
2.307
2.324
3.428

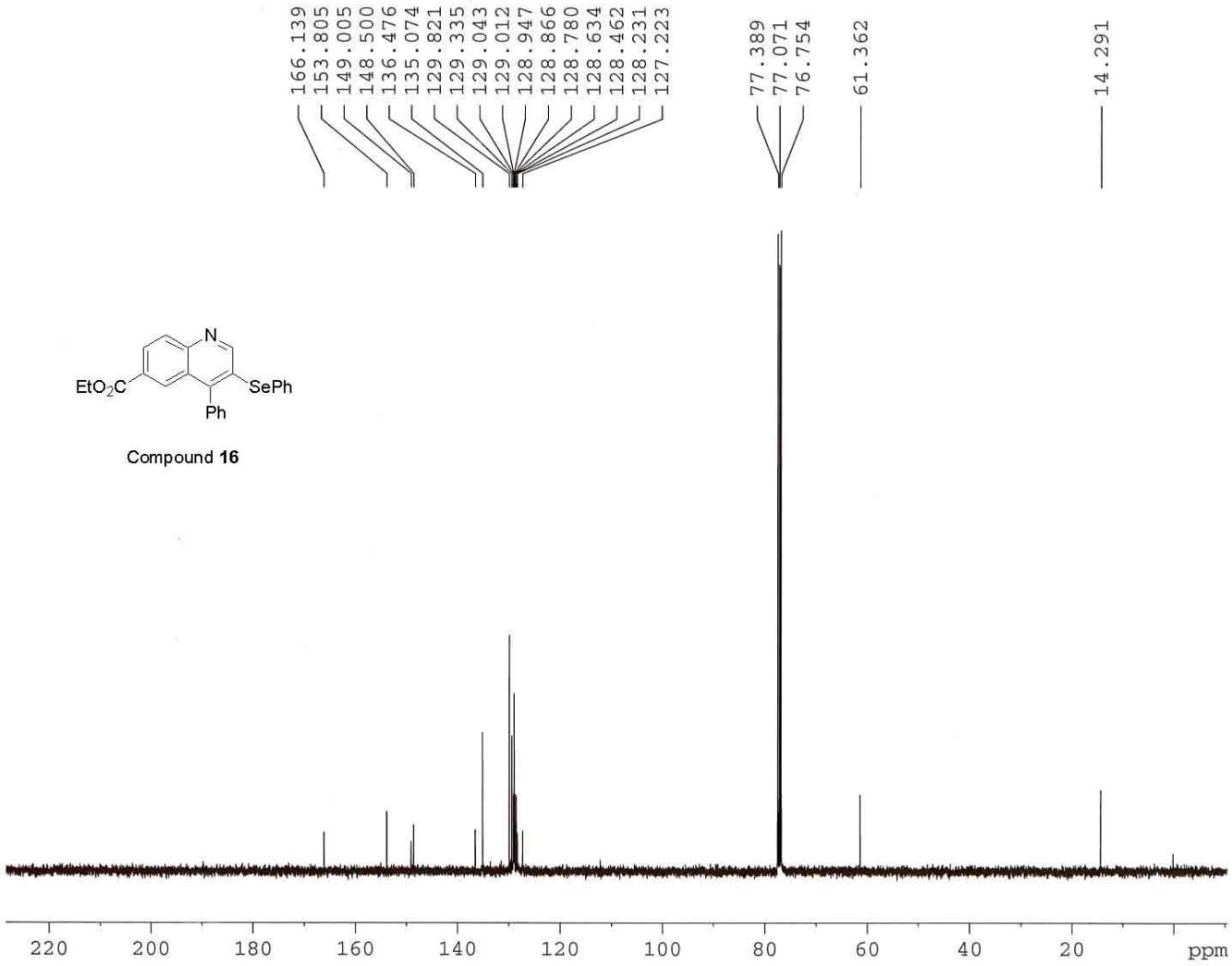
Compound **15**


165.819
158.641
153.669
148.967
139.605
129.842
129.709
129.258
129.233
129.081
128.829
128.223
97.278
77.420
77.103
76.785
61.456
14.278
N
EtO2C
I
Ph
220
200
180
160
140
120
100
80
60
40
20
ppm

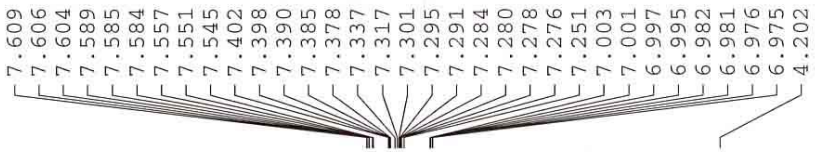
Compound **15**

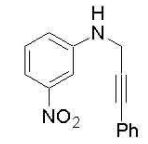

8.705
8.255
8.253
8.250
8.229
8.224
8.100
8.099
8.079
8.077
7.572
7.568
7.558
7.554
7.526
7.522
7.506
7.502
7.362
7.355
7.349
7.342
7.338
7.332
7.328
7.323
7.305
7.260
4.361
4.343
4.325
1.369
1.351
1.334
0.000
N
EtO2C
SePh
Ph
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
2.071
1.060
3.123
2.097
5.736
2.389
3.526

Compound **16**

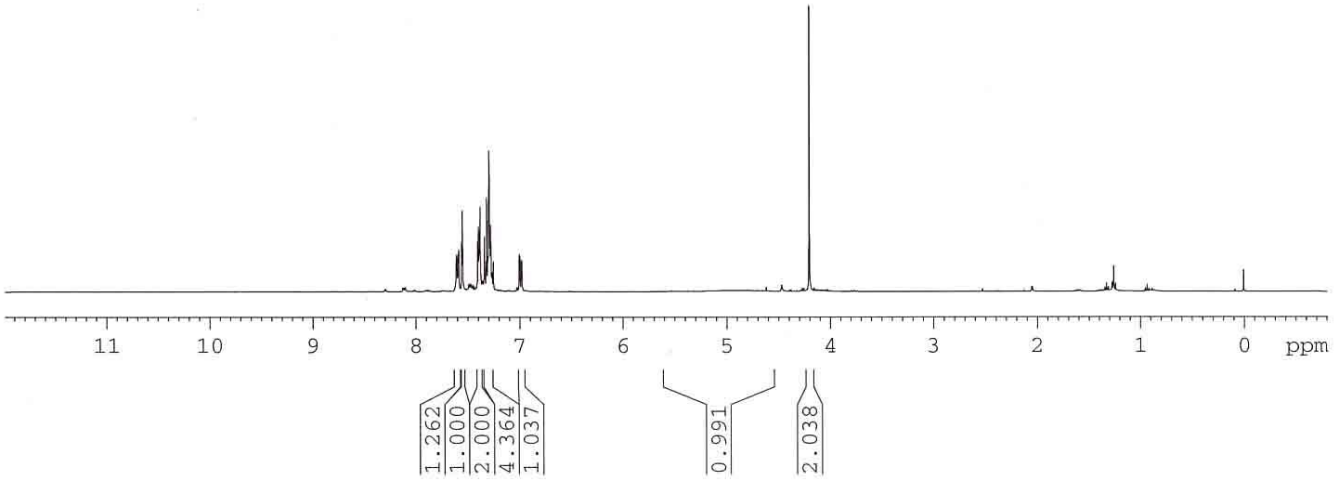

166.139
153.805
149.005
148.500
136.476
135.074
129.821
129.335
129.043
129.012
128.947
128.866
128.780
128.634
128.462
128.231
127.223
77.389
77.071
76.754
61.362
14.291
N
EtO2C
SePh
Ph
220
200
180
160
140
120
100
80
60
40
20
ppm

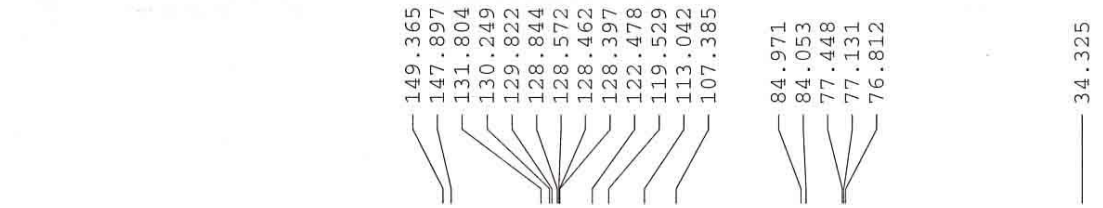
Compound **16**

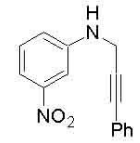

7.609
7.606
7.604
7.589
7.585
7.584
7.557
7.551
7.545
7.402
7.398
7.390
7.385
7.378
7.337
7.317
7.301
7.295
7.291
7.284
7.280
7.278
7.276
7.251
7.003
7.001
6.997
6.995
6.982
6.981
6.976
6.975
4.202


H
N
NO2
Ph

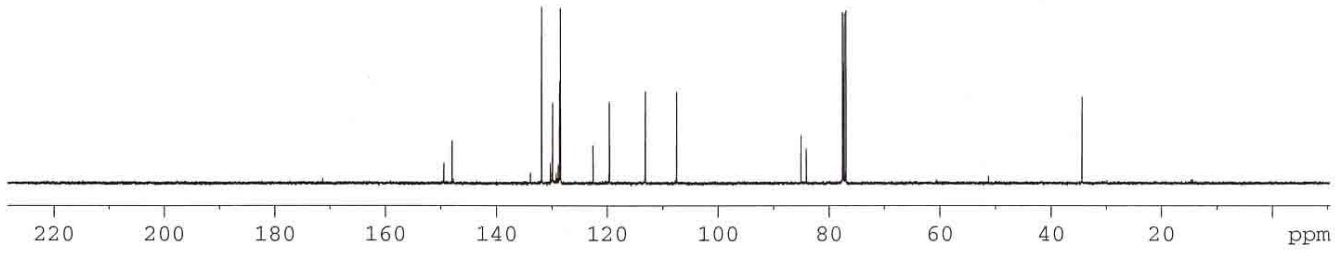
Compound **17**

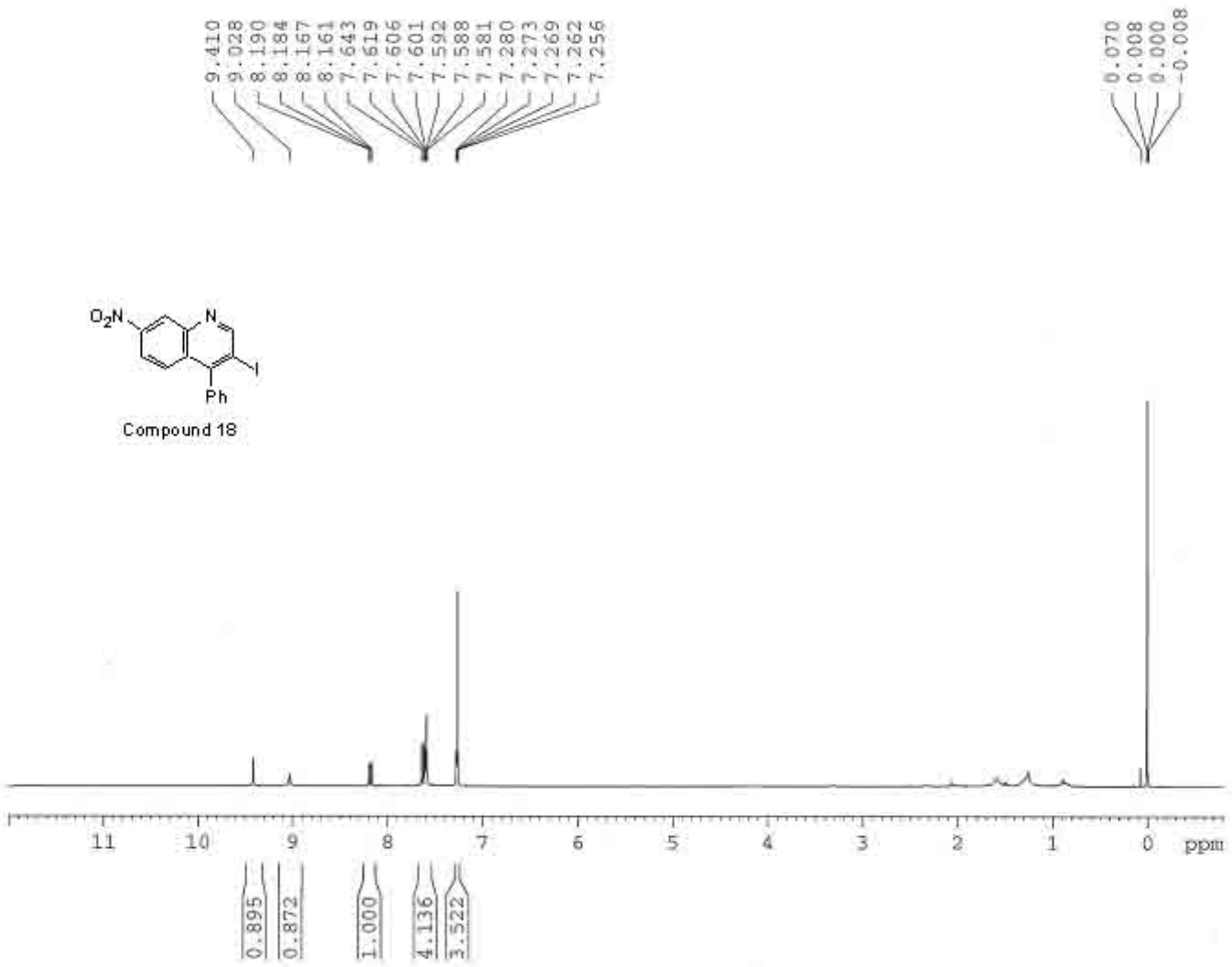

11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.262
1.000
2.000
4.364
1.037
0.991
2.038

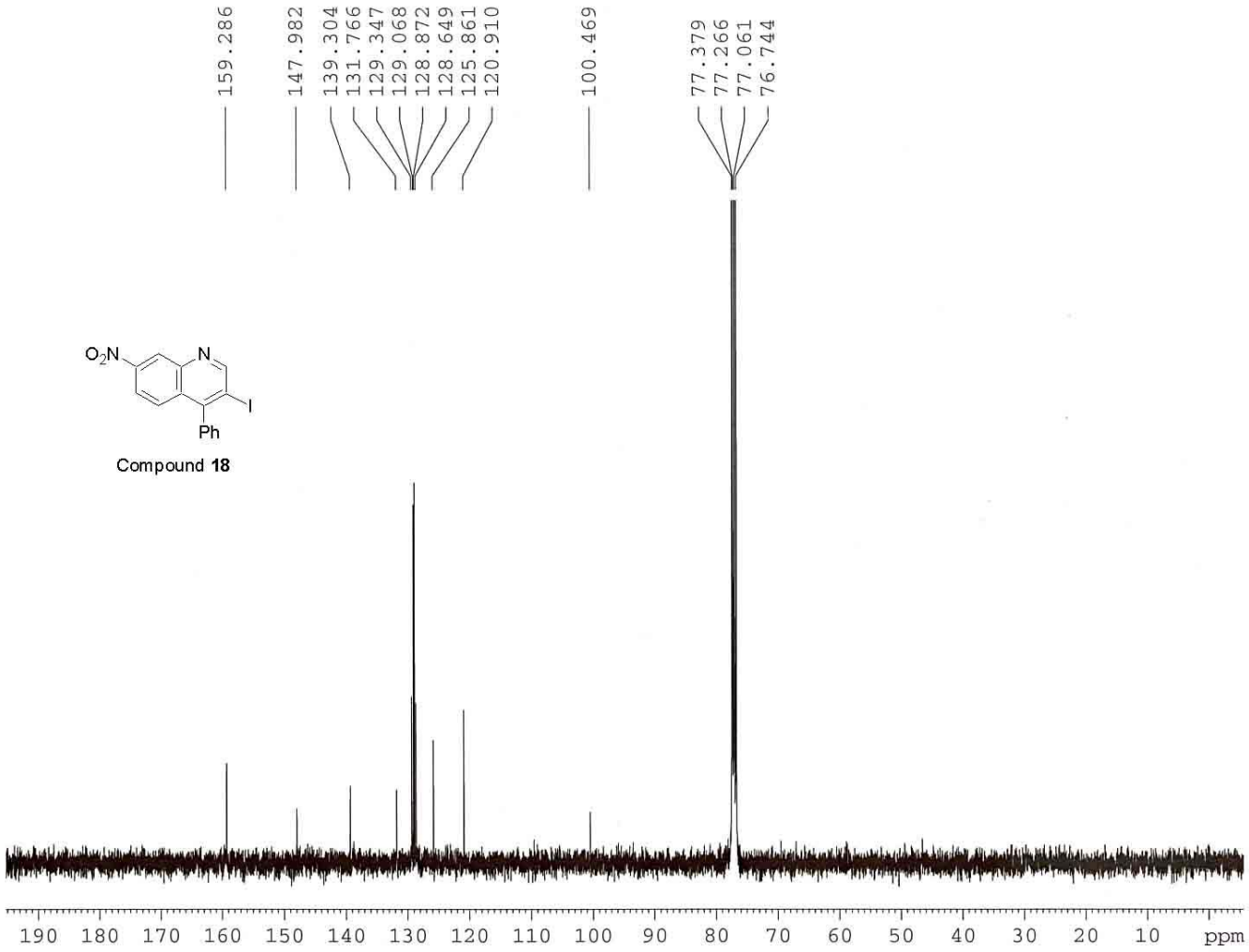

149.365
147.897
131.804
130.249
129.822
128.844
128.572
128.462
128.397
122.478
119.529
113.042
107.385
84.971
84.053
77.448
77.131
76.812
34.325

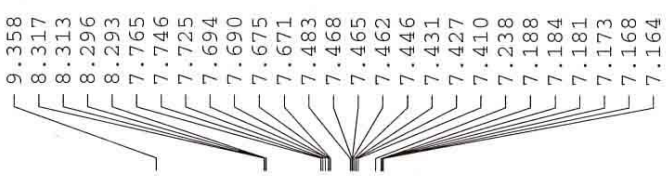

H
N
NO2
Ph

Compound **17**

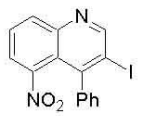

220
200
180
160
140
120
100
80
60
40
20
ppm


9.410
9.028
8.190
8.184
8.167
8.161
7.643
7.619
7.606
7.601
7.592
7.588
7.581
7.280
7.273
7.269
7.262
7.256
0.070
0.008
0.000
-0.008
O2N
N
I
Ph
Compound 18
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.895
0.872
1.000
4.136
3.522

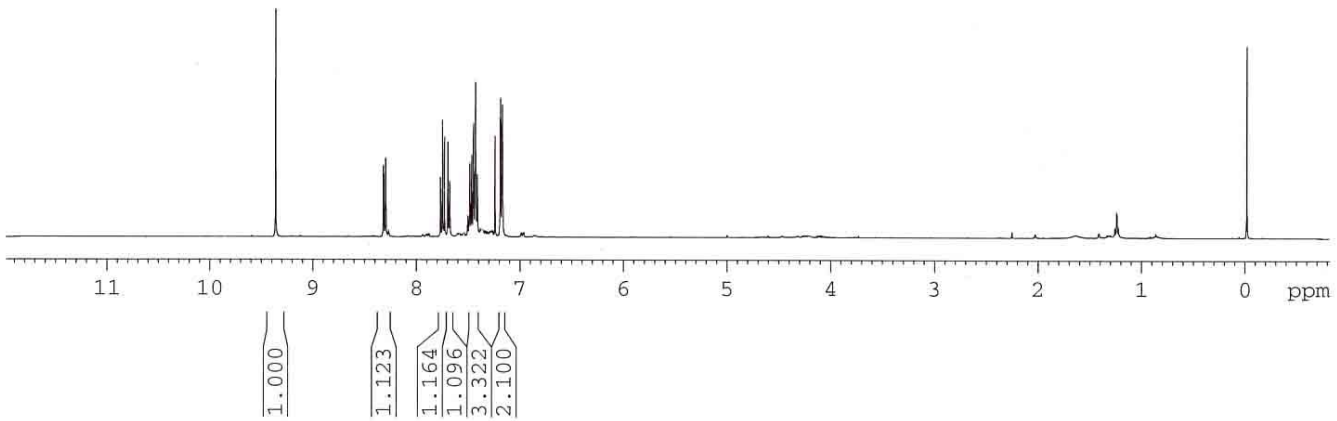

159.286
147.982
139.304
131.766
129.347
129.068
128.872
128.649
125.861
120.910
100.469
77.379
77.266
77.061
76.744
O2N
N
I
Ph
Compound 18
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

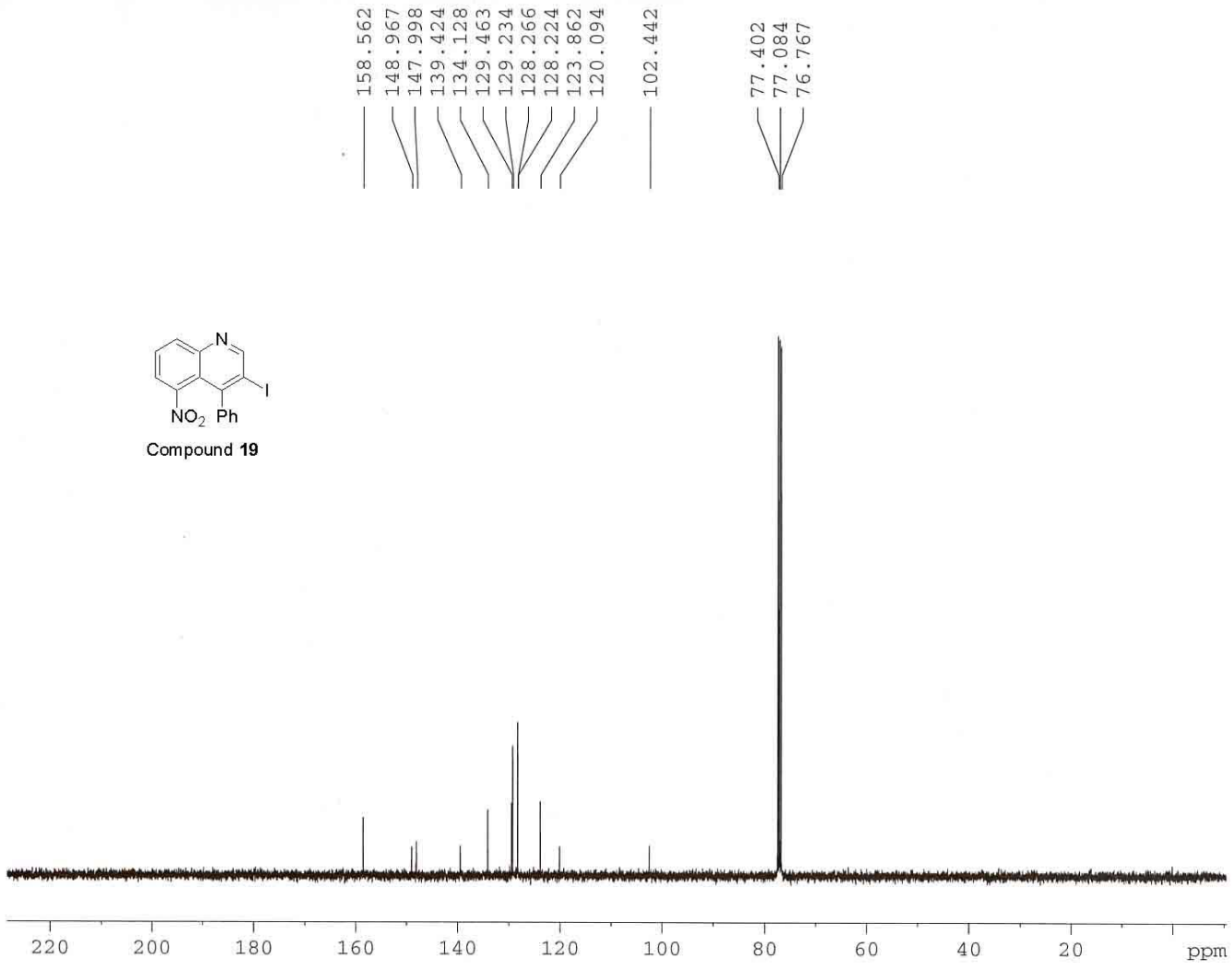

9.358
8.317
8.313
8.296
8.293
7.765
7.746
7.725
7.694
7.690
7.675
7.671
7.483
7.468
7.465
7.462
7.446
7.431
7.427
7.410
7.238
7.188
7.184
7.181
7.173
7.168
7.164


-0.022

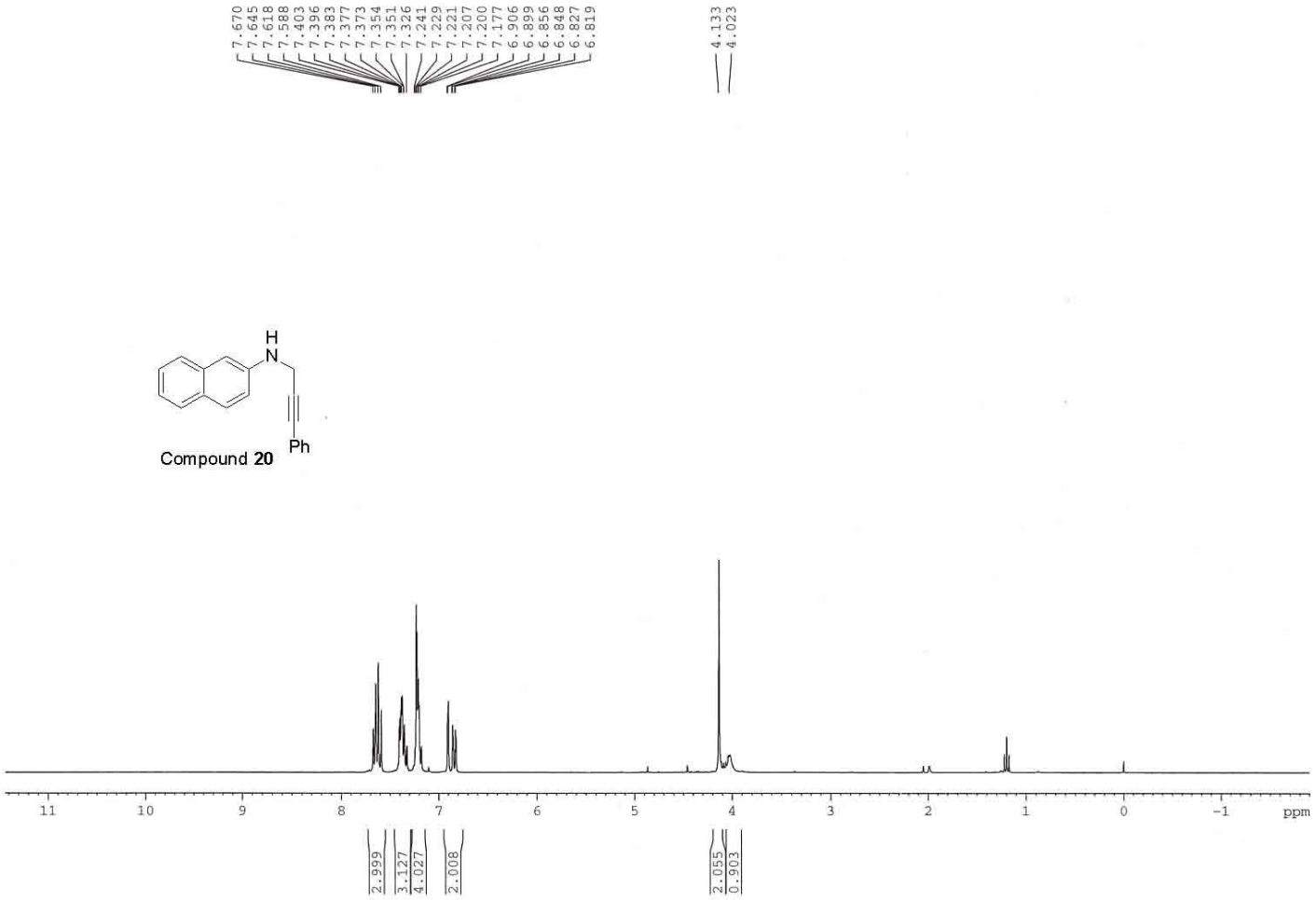

N
I
NO2
Ph

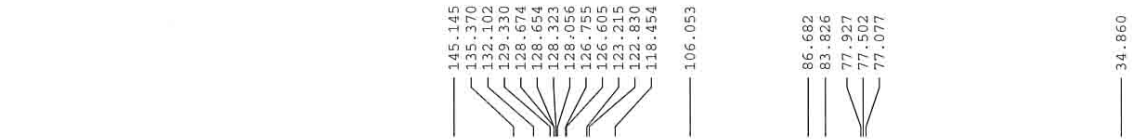
Compound **19**

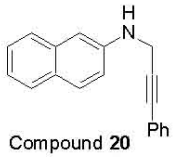

11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.123
1.164
1.096
3.322
2.100


158.562
148.967
147.998
139.424
134.128
129.463
129.234
128.266
128.224
123.862
120.094
102.442
77.402
77.084
76.767
N
I
NO2
Ph
220
200
180
160
140
120
100
80
60
40
20
ppm

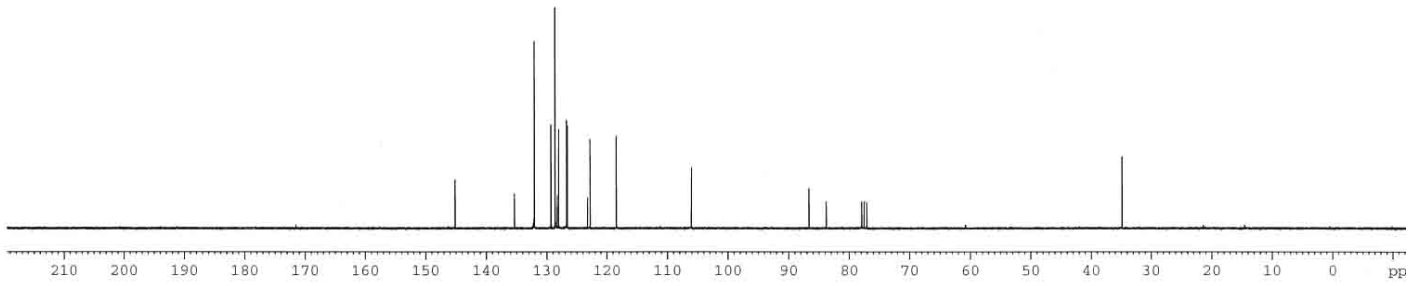
Compound **19**

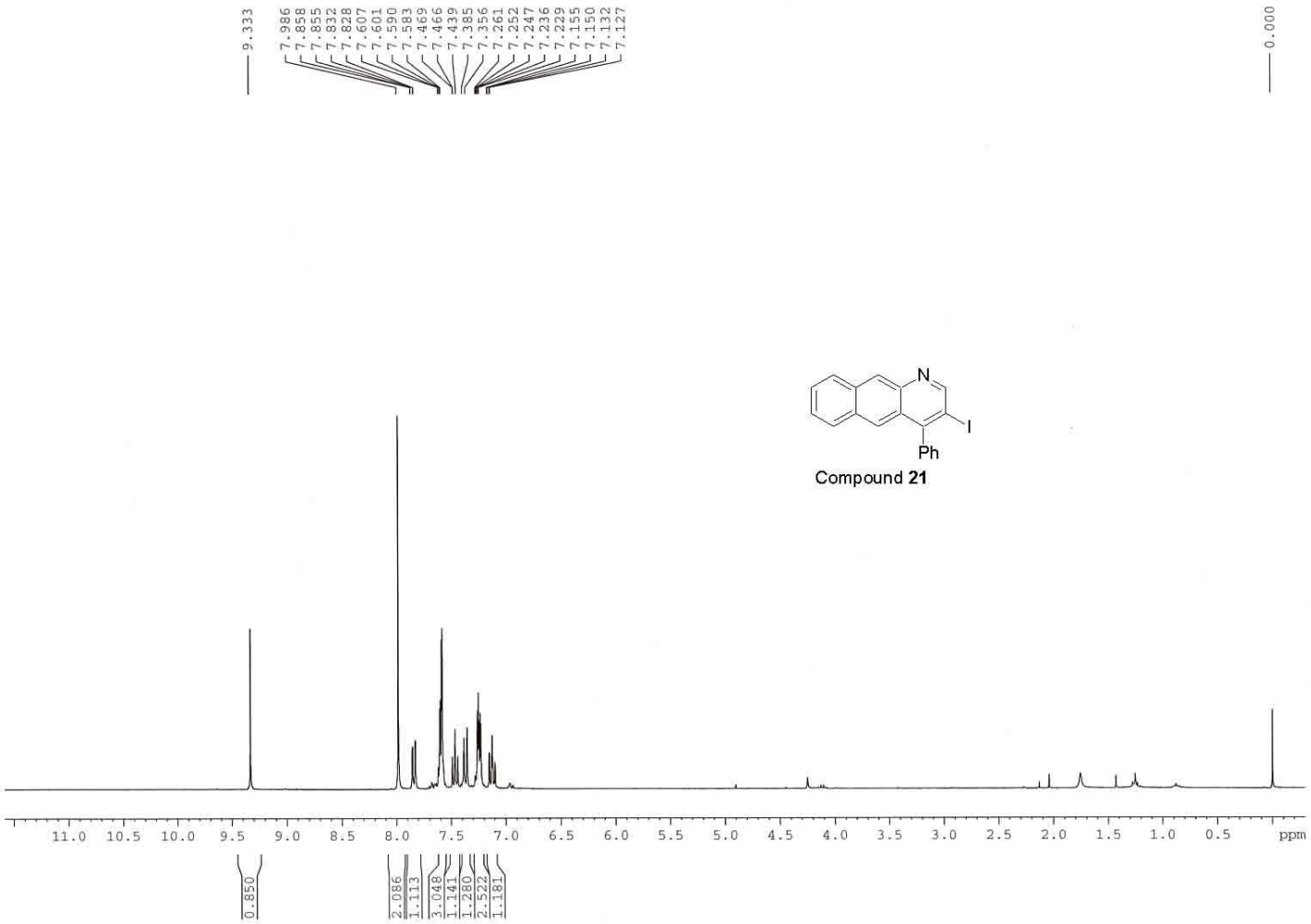

7.670
7.645
7.618
7.588
7.403
7.396
7.383
7.377
7.373
7.354
7.351
7.326
7.241
7.229
7.221
7.207
7.200
7.177
6.906
6.899
6.856
6.848
6.827
6.819
4.133
4.023
H
N
Ph
Compound 20
11
10
9
8
7
6
5
4
3
2
1
0
−1
ppm
2.999
3.127
4.027
2.008
2.055
0.903


145.145
135.370
132.102
129.330
128.674
128.654
128.323
128.056
126.755
126.605
123.215
122.830
118.454
106.053
86.682
83.826
77.927
77.502
77.077
34.860

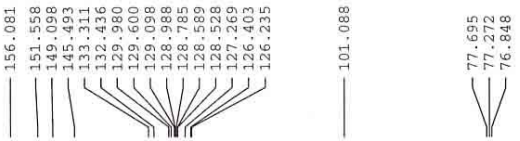

H
N
Ph

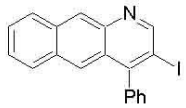
Compound **20**


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
pp

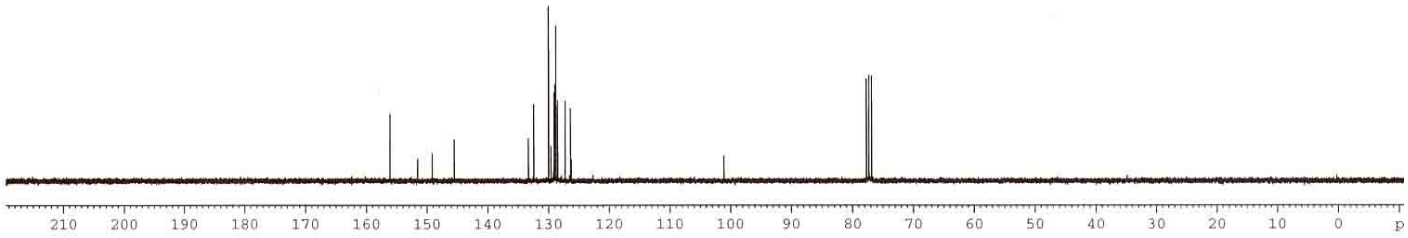

9.333
7.986
7.858
7.855
7.832
7.828
7.607
7.601
7.590
7.583
7.469
7.466
7.439
7.385
7.356
7.261
7.252
7.247
7.236
7.229
7.155
7.150
7.132
7.127
0.000
N
I
Ph
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.850
2.086
1.113
3.048
1.141
1.280
2.522
1.181

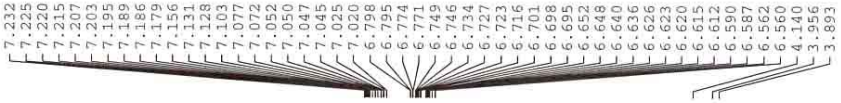
Compound **21**

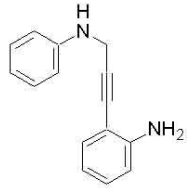

156.081
151.558
149.098
145.493
133.311
132.436
129.980
129.600
129.098
128.988
128.785
128.589
128.528
127.269
126.403
126.235
101.088
77.695
77.272
76.848


N
I
Ph

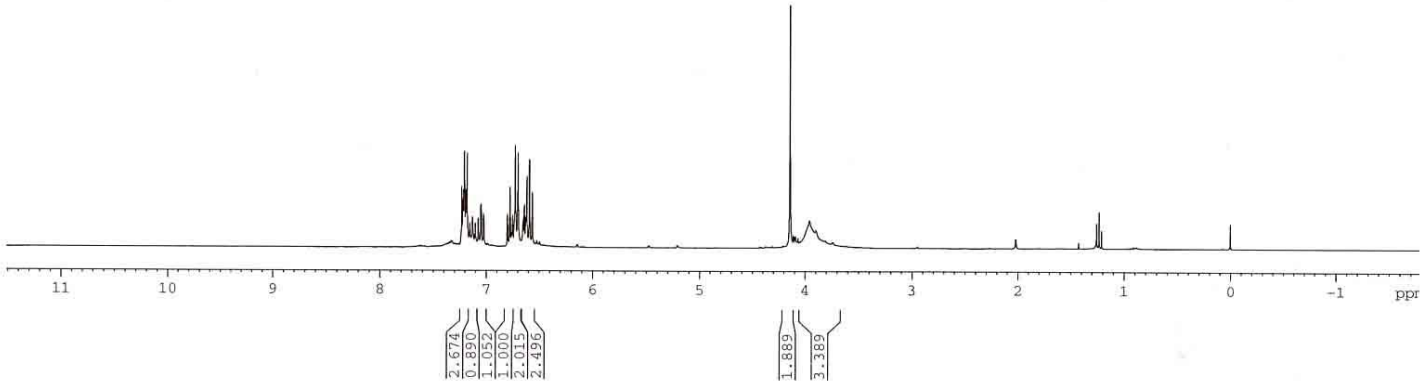
Compound **21**

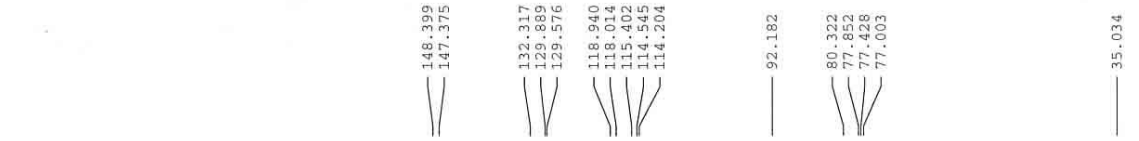

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
p

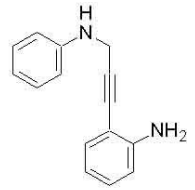

7.232
7.225
7.220
7.215
7.207
7.203
7.195
7.189
7.186
7.179
7.156
7.131
7.128
7.103
7.077
7.072
7.052
7.050
7.047
7.045
7.025
7.020
6.798
6.795
6.774
6.771
6.749
6.746
6.734
6.727
6.723
6.716
6.701
6.698
6.695
6.652
6.648
6.640
6.636
6.626
6.623
6.620
6.615
6.612
6.590
6.587
6.562
6.560
4.140
3.956
3.893
0.001


H
N
NH2

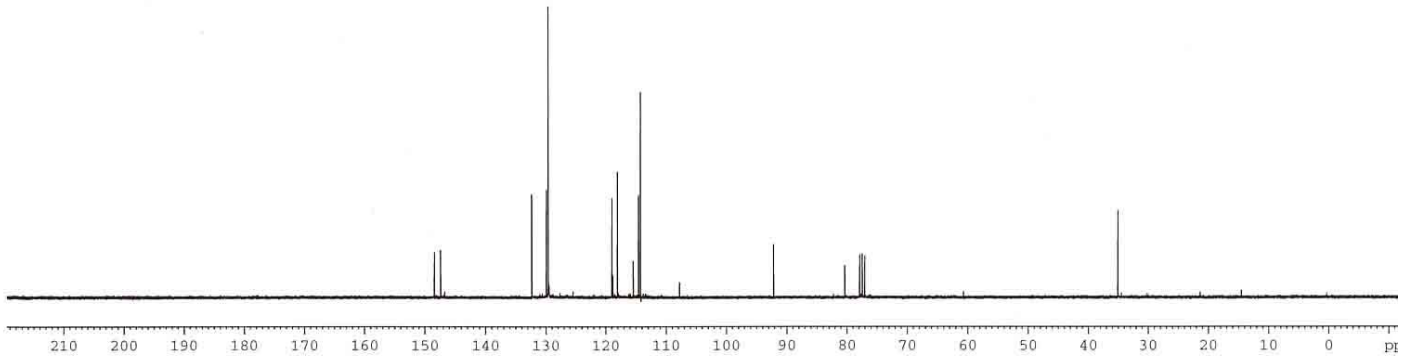
Compound **22**

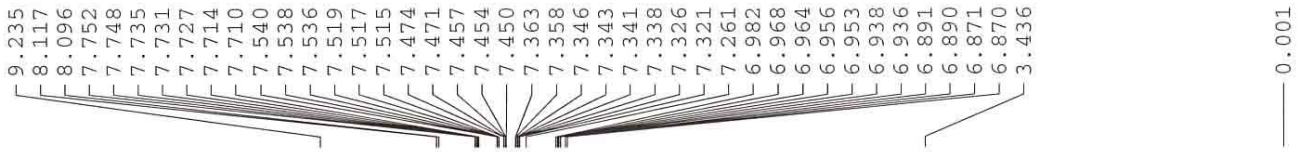

11
10
9
8
7
6
5
4
3
2
1
0
−1
ppm
2.674
0.890
1.052
1.000
2.015
2.496
1.889
3.389


148.399
147.375
132.317
129.889
129.576
118.940
118.014
115.402
114.545
114.204
92.182
80.322
77.852
77.428
77.003
35.034


H
N
NH2

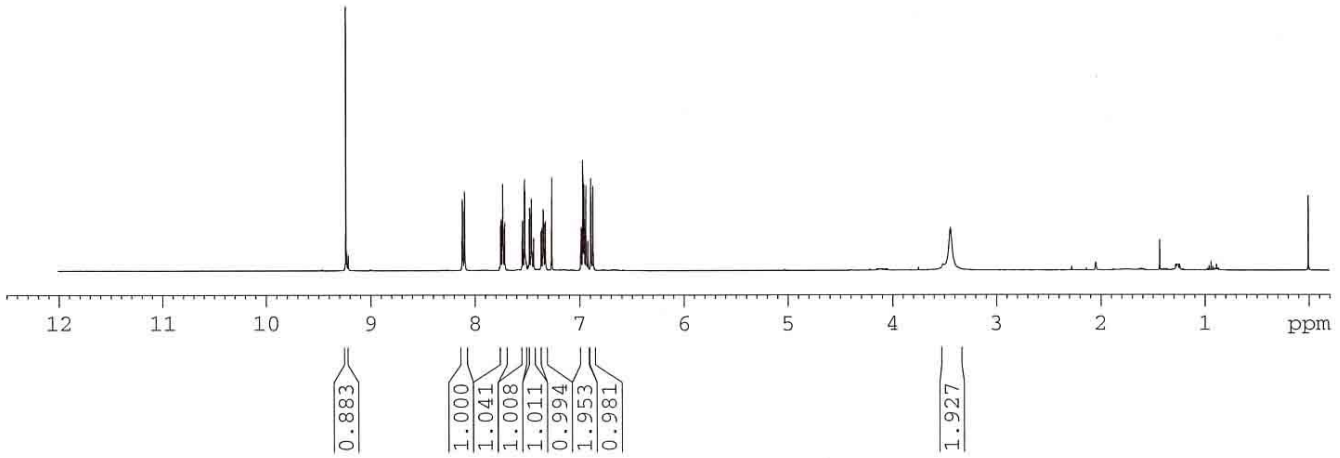
Compound **22**

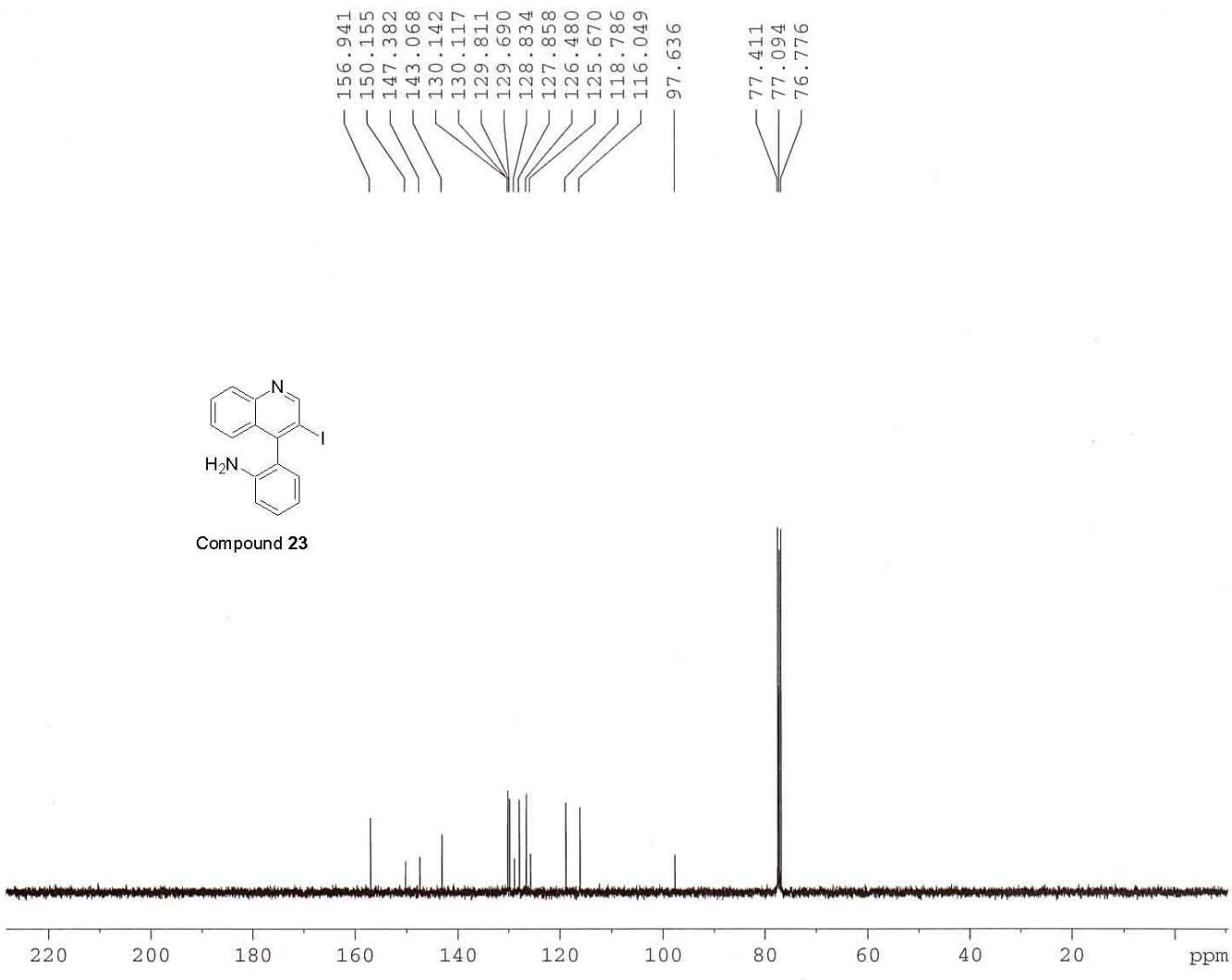

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


9.235
8.117
8.096
7.752
7.748
7.735
7.731
7.727
7.714
7.710
7.540
7.538
7.536
7.519
7.517
7.515
7.474
7.471
7.457
7.454
7.450
7.363
7.358
7.346
7.343
7.341
7.338
7.326
7.321
7.261
6.982
6.968
6.964
6.956
6.953
6.938
6.936
6.891
6.890
6.871
6.870
3.436
0.001

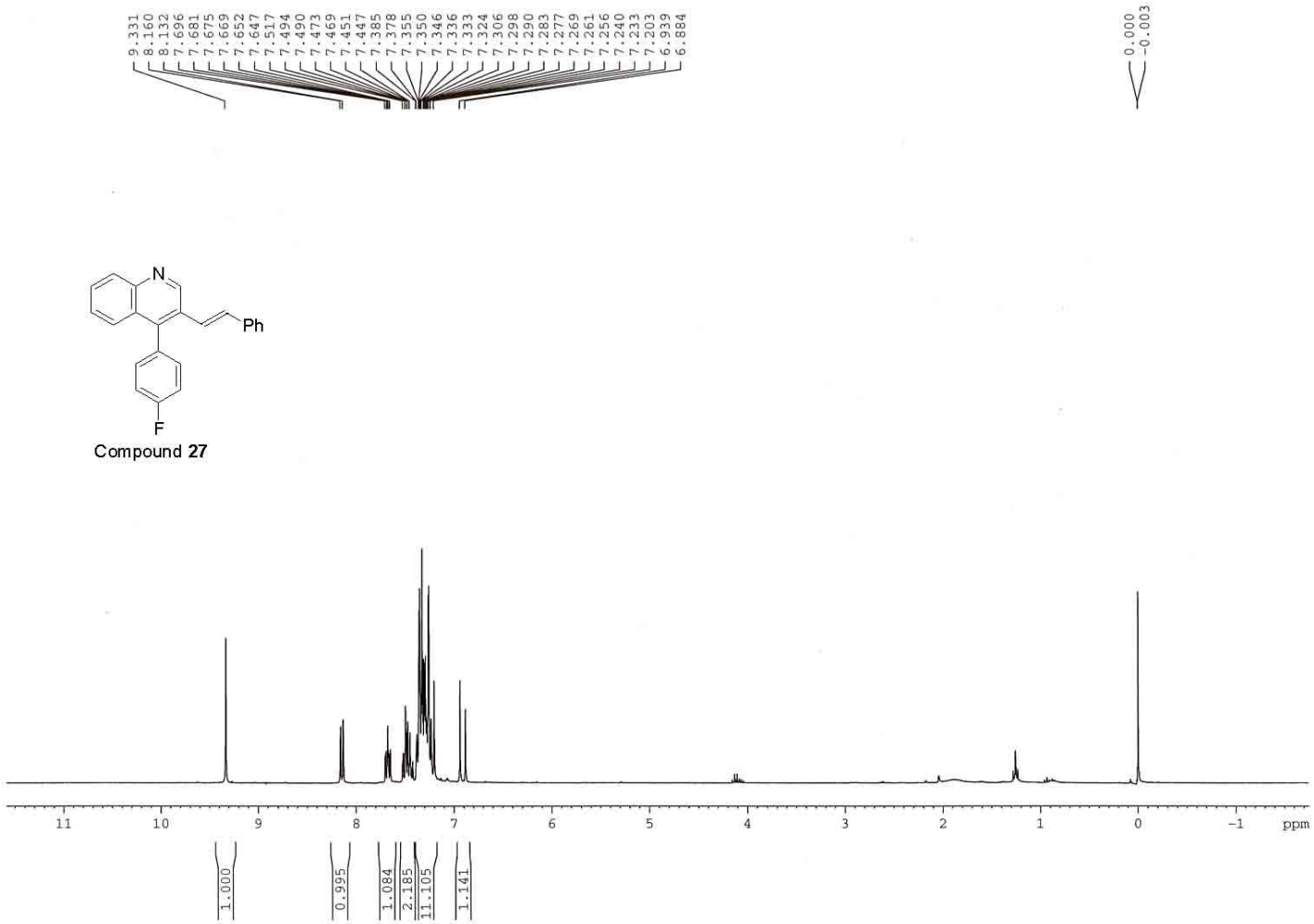

N
I
H2N

Compound **23**

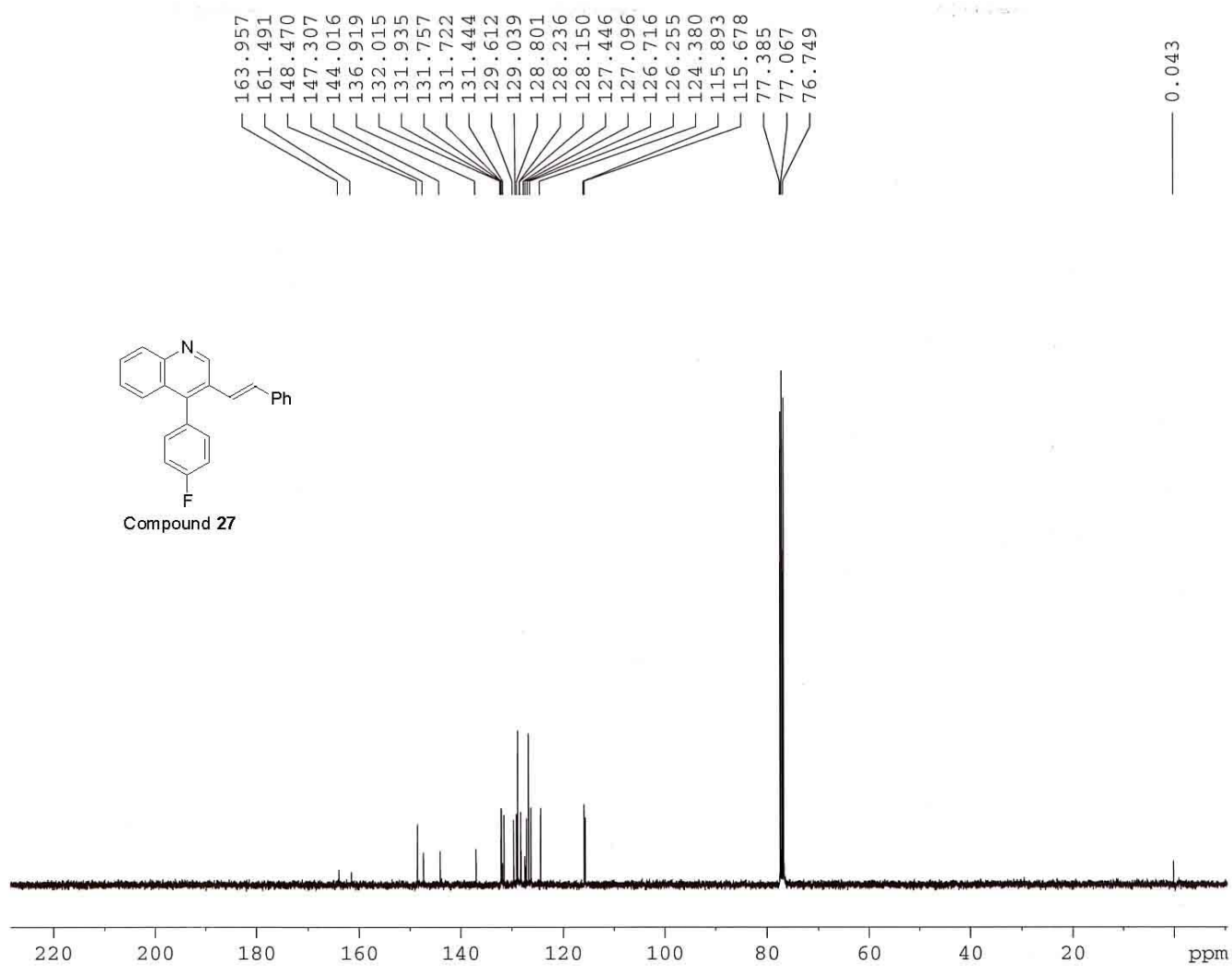

12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.883
1.000
1.041
1.008
1.011
0.994
1.953
0.981
1.927

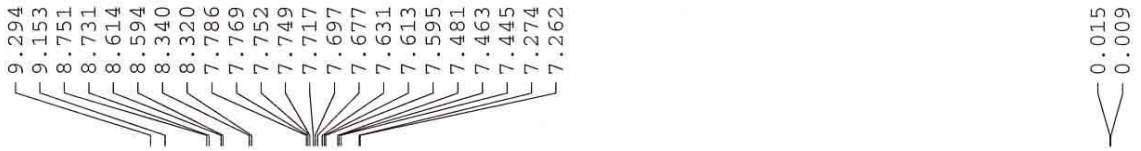

156.941
150.155
147.382
143.068
130.142
130.117
129.811
129.690
128.834
127.858
126.480
125.670
118.786
116.049
97.636
77.411
77.094
76.776
N
I
H2N
220
200
180
160
140
120
100
80
60
40
20
ppm

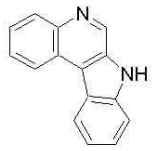
Compound **23**


9.331
8.160
8.132
7.696
7.681
7.675
7.669
7.652
7.647
7.517
7.494
7.490
7.473
7.469
7.451
7.447
7.385
7.378
7.355
7.350
7.346
7.336
7.333
7.324
7.306
7.298
7.290
7.283
7.277
7.269
7.261
7.256
7.240
7.233
7.203
6.939
6.884
0.000
-0.003
N
Ph
F
11
10
9
8
7
6
5
4
3
2
1
0
−1
ppm
1.000
0.995
1.084
2.185
11.105
1.141

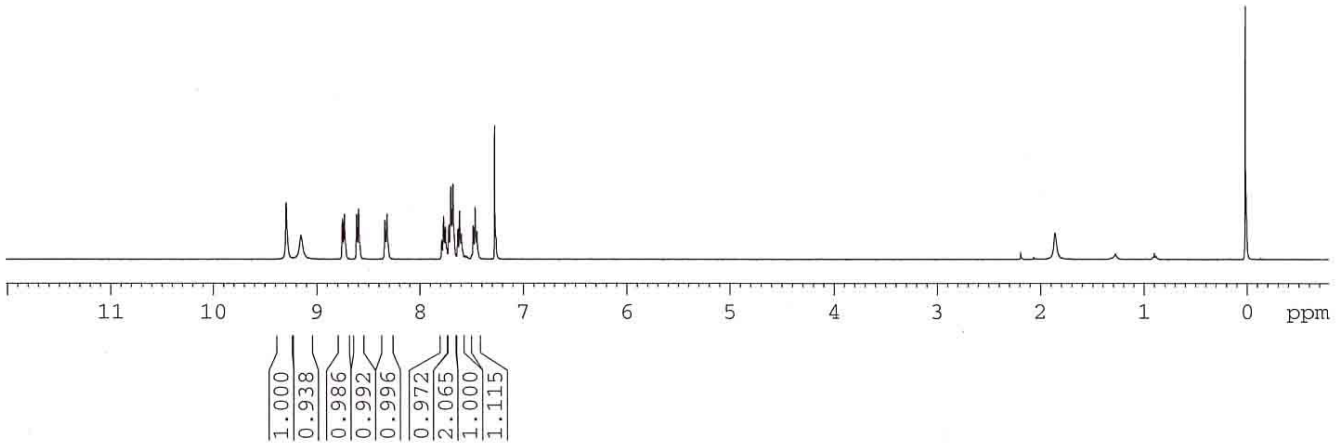
Compound **27**

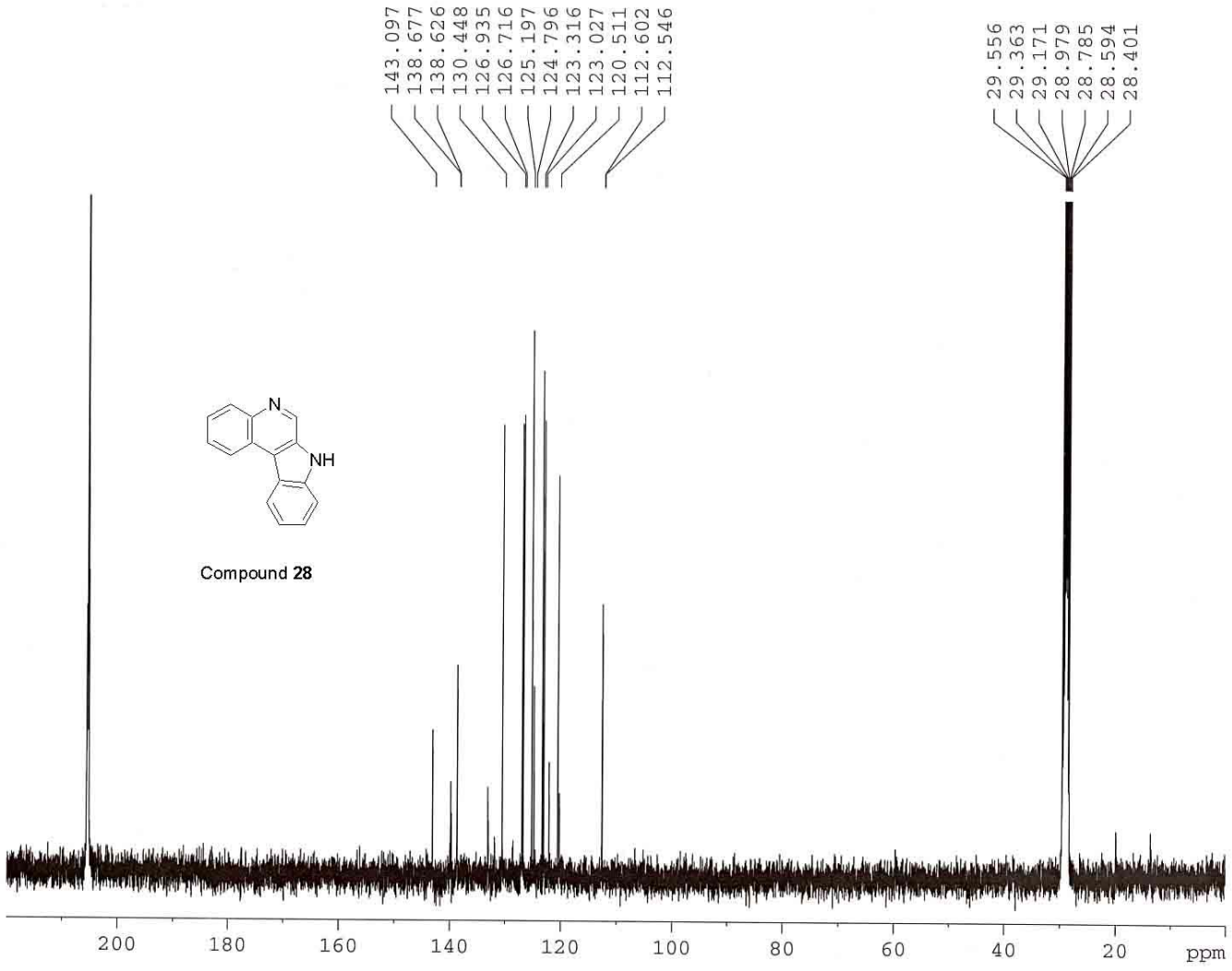

163.957
161.491
148.470
147.307
144.016
136.919
132.015
131.935
131.757
131.722
131.444
129.612
129.039
128.801
128.236
128.150
127.446
127.096
126.716
126.255
124.380
115.893
115.678
77.385
77.067
76.749
0.043
N
Ph
F
Compound 27
220
200
180
160
140
120
100
80
60
40
20
ppm


9.294
9.153
8.751
8.731
8.614
8.594
8.340
8.320
7.786
7.769
7.752
7.749
7.717
7.697
7.677
7.631
7.613
7.595
7.481
7.463
7.445
7.274
7.262
0.015
0.009


N
NH

Compound **28**


11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
0.938
0.986
0.992
0.996
0.972
2.065
1.000
1.115


143.097
138.677
138.626
130.448
126.935
126.716
125.197
124.796
123.316
123.027
120.511
112.602
112.546
29.556
29.363
29.171
28.979
28.785
28.594
28.401
N
NH
Compound 28
200
180
160
140
120
100
80
60
40
20
ppm