SUPPORTING INFORMATION

Synthesis of Annulated γ-Carbolines by Palladium-Catalyzed Intramolecular Iminoannulation

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General. ^{1}H 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 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. All reagents were used directly as obtained commercially unless otherwise noted. 2-Bromo-1*H*-indole-3-carboxaldehyde,[1] 1-bromoundec-4-yne,[2] 6-phenylhex-5-yn-1-ol,[3] 2-(phenylethynyl)benzyl alcohol,[4] and 1-(hydroxymethyl)-2-(trifluoromethanesulfonyloxy)cyclopentene[5] were prepared according to literature procedures. The following starting materials were prepared as described.

5-Chloro-1-phenylpent-1-yne. This compound was prepared by a procedure used to synthesize 6-phenylhex-5-yn-1-ol,[3] but using iodobenzene and 5-chloropent-1-yne. The product was purified using 50:1 hexanes/EtOAc to afford 87% of the indicated compound as a colorless oil whose spectral properties are consistent with those in the literature.[6]

6-Chloro-1-(4-methoxyphenyl)hex-2-yn-1-ol. To 5-chloropent-1-yne (0.513 g, 5.0 mmol) in dry THF (10 mL) was added *n*-BuLi (5.5 mmol, 2.5 M in hexanes) dropwise at -78 °C. The mixture was stirred for 30 min and a solution

of 4-methoxybenzaldehyde (0.885g, 6.5 mmol) in THF (10 mL) was added slowly. The resulting mixture was stirred at -78 °C for another 30 min and at room temperature for 2 h. The reaction was quenched with satd aq NH_4Cl and extracted with ether (3 x 20 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was evaporated. The residue was purified using 2:1 hexanes/EtOAc to afford 1.08 g (91%) of the indicated compound as a pale yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.97 (quintet, J= 6.9 Hz, 2H), 2.45 (dt, J= 2.1, 6.9 Hz, 2H), 3.63 (t, J= 6.9 Hz, 2H), 3.79 (s, 3H), 5.37 (dd, J= 3.9, 1.8 Hz, 1H), 6.88 (dd, J= 6.9, 1.8 Hz, 2H), 7.42 (dd, J= 6.9, 1.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 16.5, 31.5, 43.9, 55.5, 64.5, 81.6, 85.3, 114.1, 128.2, 133.7, 159.8.

Ethyl 3-(5-chloropent-1-ynyl)benzoate. This compound was prepared by a procedure used to synthesize 6-phenylhex-5-yn-1-ol,[3] but using ethyl 3-iodobenzoate and 5-chloropent-1-yne. The product was purified using 10:1 hexanes/EtOAc to afford 99% of the indicated compound as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.39 (t, J= 7.2 Hz, 3H), 2.06 (quintet, J= 6.8 Hz, 2H), 2.62 (t, J= 6.8 Hz, 2H), 3.72 (t, J= 6.8 Hz, 2H), 4.37 (q, J= 7.2 Hz, 2H), 7.36 (t, J= 7.6 Hz, 1H), 7.56 (d, J= 7.6 Hz, 1H), 7.95 (d, J= 7.6 Hz, 1H), 8.07 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.4, 16.9, 31.4, 43.7, 61.2, 80.7, 89.2, 124.0, 128.4, 128.8, 130.7, 132.7, 135.7, 166.0.

5-(5-Chloropent-1-ynyl)pyrimidine. This compound was prepared by a procedure used to synthesize 6-phenylhex-5-yn-1-ol,[3] but using 5-bromopyrimidine and 5-chloropent-1-yne. The product was purified using 2:1 hexanes/EtOAc to afford a 93% yield of the indicated compound as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 2.09 (quintet, J= 6.9 Hz, 2H), 2.68 (t, J= 6.9 Hz, 2H), 3.71 (t, J= 6.9 Hz, 2H), 8.73 (s, 2H), 9.11 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 17.0, 31.0, 43.5, 74.9, 95.9, 120.1, 156.5, 158.8.

1-(Hydroxymethyl)-2-(phenylethynyl)cyclopentene. This compound was prepared by a procedure used to synthesize 6-phenylhex-5-yn-1-ol,[3] but using 1-(hydroxymethyl)-2-(trifluoromethanesulfonyloxy)cyclopentene[5] and phenylacetylene. The product was purified using 2:1 hexanes/EtOAc to afford a

95% yield of the indicated compound as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.94 (quintet, *J* = 5.7 Hz, 2H), 2.57 (m, 4H), 4.42 (s, 2H), 7.30 (m, 3H), 7.42 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 22.6, 34.0, 37.1, 60.9, 85.1, 94.5, 120.0, 123.4, 128.2, 128.4, 131.4, 150.0.

1-(Bromomethyl)-2-(phenylethynyl)cyclopentene. To a solution of 1-(hydroxymethyl)-2-(phenylethynyl)cyclopentene (1.0 mmol, 0.198 g) and CBr_4 (1.3 mmol, 0.431 g) in CH_2Cl_2 (5 mL) at 0 °C was added PPh_3 (1.5 mmol, 0.393 g) portionwise. The mixture was stirred at room temperature for 2 h. The reaction mixture was flushed through a short silica gel column to remove the triphenylphosphine oxide. The solvent was evaporated and the residue was purified using 20:1 hexanes/EtOAc to afford 0.248 g (95%) of the indicated compound as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.97 (quintet, *J* = 7.6 Hz, 2H), 2.61 (t, *J* = 7.6 Hz, 4H), 4.29 (s, 2H), 7.31 (m, 3H), 7.46 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 22.3, 29.7, 34.3, 37.2, 84.6, 96.3, 123.2, 124.0, 128.4, 128.5, 131.6, 145.7.

General Procedure for the Synthesis of *N*-Substituted 2-Bromo-1*H*-indole-3-carboxaldehydes. Method A: 2-bromo-1*H*-indole-3-carboxaldehyde (0.5 mmol), the alkynyl halide (0.6 mmol), NaI (0.75 mmol) and K_2CO_3 (0.75 mmol) were placed in a 4-dram vial and acetone (3 mL) was added. The vial was flushed with Ar and heated in an oil bath at 75 °C for 24 h. The mixture was cooled and diluted with ether (5 mL). The precipitate was removed by filtration and the solvent was evaporated. The residue was purified by chromatography on a silica gel column. Method B: to a mixture of 2-bromo-1*H*-indole-3-carboxaldehyde (0.5 mmol), the alkynyl alcohol (0.6 mmol), and PPh_3 (0.75 mmol) in CH_2Cl_2 (8 mL) was added diethyl azodicarboxylate (0.75 mmol) at 0 °C. The resulting mixture was flushed with Ar and stirred at room temperature for 24 h. The mixture was concentrated and the residue was purified by chromatography on a silica gel column.

***N*-Substituted 2-Bromo-1*H*-indole-3-carboxaldehydes Prepared**

2-Bromo-1-(5-phenylpent-4-ynyl)-1*H*-indole-3-carboxaldehyde (3a). This compound was prepared using 5-chloro-1-phenylpent-1-yne according to method A. The product was purified using 5:1 hexanes/EtOAc to afford 166 mg (91%) of the indicated compound as a yellow solid: mp 74-76 °C; ^{1}H NMR ($CDCl_3$) δ 2.13 (quintet, *J* = 7.2 Hz, 2H), 2.52 (t, *J* = 7.2 Hz, 2H), 4.46 (t, *J* = 7.2 Hz, 2H), 7.25-7.38 (m, 5H), 7.38-7.50 (m, 3H), 8.32 (m, 1H), 10.03 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 17.0, 28.5, 44.3, 82.2, 88.0, 109.9, 115.5, 121.3, 123.3, 123.4, 124.2, 125.4, 125.7, 128.1, 128.4, 131.6, 136.9, 185.5; IR (neat, cm^{-1}) 3055, 2947, 2806, 2228, 1653; HRMS calcd for $C_{20}H_{16}BrNO$: 365.0415. Found: 365.0420.

2-Bromo-1-(undec-4-ynyl)-1*H*-indole-3-carboxaldehyde (3b). This compound was prepared using 1-bromoundec-4-yne according to method A. The product was purified using 3:1 hexanes/EtOAc to afford 172 mg (92%) of the indicated compound as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 0.90 (t, *J* = 7.2 Hz, 3H), 1.25-1.35 (m, 4H), 1.35-1.45 (m, 2H), 1.51 (quintet, *J* = 7.2 Hz, 2H), 1.99 (quintet, *J* = 7.2 Hz, 2H), 2.19 (m, 2H), 2.27 (m, 2H), 4.38 (2H, *J* = 7.2 Hz, 2H), 7.30 (m, 2H), 7.44 (m, 1H), 8.31 (m, 1H), 10.03 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.1, 16.4, 18.8, 22.7, 28.7, 28.8, 29.1, 31.5, 44.4, 78.1, 82.2, 109.9, 115.4, 121.3, 123.4, 124.1, 125.4, 125.7, 136.9, 185.4; IR (neat, cm^{-1}) 3060, 2960, 2855, 1660; HRMS calcd for $C_{20}H_{24}BrNO$: 373.1041. Found: 373.1046.

2-Bromo-1-[6-hydroxy-6-(4-methoxyphenyl)hex-4-ynyl]-1*H*-indole-3-carboxaldehyde (3c). This compound was prepared using 6-chloro-1-(4-methoxyphenyl)hex-2-yn-1-ol according to method A. The product was purified using 4:5 hexanes/EtOAc to afford 180 mg (85%) of the indicated compound as a thick yellow oil: ^{1}H NMR ($CDCl_3$) δ 2.04 (m, 2H), 2.36 (m, 2H), 2.51 (s, 1H), 3.80 (s, 3H), 4.34 (t, *J* = 7.2 Hz, 2H), 5.43 (s, 1H), 6.91 (d, *J* = 8.4 Hz, 2H), 7.20-7.33 (m, 3H), 7.47 (d, *J* = 8.4 Hz, 2H), 8.28 (dd, *J* = 7.6, 1.6 Hz, 1H), 9.96 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 16.4, 28.2, 44.3, 55.4, 64.4, 82.2, 84.9, 109.9, 114.1, 115.4, 121.2, 123.4, 124.2, 125.3, 125.7, 128.0, 133.5, 136.8, 159.7, 185.5; IR (neat,

cm^{-1}) 3386, 2953, 1655; HRMS calcd for $C_{22}H_{20}BrNO_3$: 425.0627. Found: 425.0633.

Ethyl 3-[5-(2-bromo-3-formyl-1*H*-indol-1-yl)pent-1-ynyl]benzoate (3d). This compound was prepared using ethyl 3-(5-chloropent-1-ynyl)benzoate according to method A. The product was purified using 2:1 hexanes/EtOAc to afford 205 mg (94%) of the indicated compound as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.38 (t, *J* = 7.2 Hz, 3H), 2.13 (quintet, *J* = 7.2 Hz, 2H), 2.51 (t, *J* = 7.2 Hz, 2H), 4.37 (q, *J* = 7.2 Hz, 2H), 4.45 (t, *J* = 7.2 Hz, 2H), 7.25-7.33 (m, 2H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 7.2 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 8.08 (s, 1H), 8.30 (d, *J* = 8.0 Hz, 1H), 10.01 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.4, 17.0, 28.4, 44.3, 61.3, 81.3, 89.0, 109.8, 115.5, 121.4, 123.4, 123.7, 124.2, 125.4, 125.6, 128.5, 129.1, 130.8, 132.7, 135.6, 166.0, 185.4; IR (neat, cm^{-1}) 2979, 2232, 1717, 1658; HRMS calcd for $C_{23}H_{20}BrNO_3$: 437.0627. Found: 437.0633.

2-Bromo-1-[5-(pyrimidin-5-yl)pent-4-ynyl]-1*H*-indole-3-carboxaldehyde (3e). This compound was prepared using 5-(5-chloropent-1-ynyl)pyrimidine according to method A. The product was purified using 1:3 hexanes/EtOAc to afford 152 mg (83%) of the indicated compound as a pale yellow solid: mp 116-118 °C; ^{1}H NMR ($CDCl_3$) δ 2.19 (quintet, *J* = 7.2 Hz, 2H), 2.58 (t, *J* = 7.2 Hz, 2H), 4.45 (t, *J* = 7.2 Hz, 2H), 7.28-7.35 (m, 2H), 7.40 (m, 1H), 8.31 (m, 1H), 8.70 (s, 2H), 9.12 (s, 1H), 10.02 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 17.1, 28.0, 44.2, 75.3, 95.6, 109.7, 115.6, 119.9, 121.4, 123.5, 124.3, 125.4, 125.5, 136.8, 156.7, 158.8, 185.4; IR (neat, cm^{-1}) 3036, 2950, 2807, 2231, 1657; HRMS calcd for $C_{18}H_{14}BrN_3O$: 367.0320. Found: 367.0326.

2-Bromo-1-(6-phenylhex-5-ynyl)-1*H*-indole-3-carboxaldehyde (3f). This compound was prepared using 6-phenylhex-5-yn-1-ol according to method B. The product was purified using 4:1 hexanes/EtOAc to afford 170 mg (89%) of the indicated compound as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.70 (quintet, *J* = 7.6 Hz, 2H), 2.05 (quintet, *J* = 7.6 Hz, 2H), 2.49 (t, *J* = 7.6 Hz, 2H), 4.33 (t, *J* = 7.6 Hz, 2H), 7.25-7.31 (m, 5H), 7.31-7.40 (m, 3H), 8.32 (m, 1H), 10.03 (s, 1H); ^{13}C

NMR ($CDCl_3$) δ 19.1, 25.7, 28.5, 45.0, 81.7, 88.8, 109.9, 115.3, 121.3, 123.4, 123.6, 124.1, 125.5, 125.7, 127.9, 128.3, 131.6, 136.8, 185.5; IR (neat, cm^{-1}) 3055, 2942, 2805, 2232, 1653; HRMS calcd for $C_{21}H_{18}BrNO$: 379.0572. Found: 379.0578.

2-Bromo-1-(dec-3-ynyl)-1*H*-indole-3-carboxaldehyde (3g). This compound was prepared using 3-decyn-1-ol according to method B. The product was purified using 6:1 hexanes/EtOAc to afford 180 mg (99%) of the indicated compound as a yellow oil which crystallizes upon standing at 0 °C: mp 52-54 °C; ^1H NMR ($CDCl_3$) δ 0.88 (t, *J* = 7.2 Hz, 3H), 1.18-1.31 (m, 6H), 1.38 (m, 2H), 2.06 (m, 2H), 2.68 (m, 2H), 4.40 (t, *J* = 7.2 Hz, 2H), 7.26-7.32 (m, 2H), 7.40 (m, 1H), 8.31 (m, 1H), 10.04 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.1, 18.7, 19.9, 22.6, 28.6, 31.4, 44.5, 74.9, 83.9, 110.0, 115.5, 121.3, 123.4, 124.1, 125.4, 125.6, 136.8, 185.5; IR (neat, cm^{-1}) 3055, 2929, 2856, 1660; HRMS calcd for $C_{19}H_{22}BrNO$: 359.0890. Found: 359.0890.

2-Bromo-1-[2-(phenylethynyl)benzyl]-1*H*-indole-3-carboxaldehyde (3h). This compound was prepared using 2-(phenylethynyl)benzyl alcohol according to method B. The product was purified using 5:1 hexanes/EtOAc to afford 86 mg (42%) of the indicated compound as a yellow solid: mp 151-152 °C; ^1H NMR ($CDCl_3$) δ 5.76 (s, 2H), 6.59 (d, *J* = 7.8 Hz, 1H), 7.18 (dt, *J* = 1.2, 7.5 Hz, 1H), 7.25-7.34 (m, 4H), 7.36-7.42 (m, 3H), 7.58-7.64 (m, 3H), 8.37 (dt, *J* = 7.2, 1.2 Hz), 10.10 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 47.5, 86.4, 96.0, 110.6, 116.0, 121.5, 121.6, 122.9, 123.8, 124.7, 125.6, 125.7, 126.5, 128.1, 128.8, 129.1, 129.3, 131.8, 132.7, 136.8, 137.4, 185.8; IR (neat, cm^{-1}) 3058, 2808, 2249, 1659; HRMS calcd for $C_{24}H_{16}BrNO$: 413.0415. Found: 413.0423.

2-Bromo-1-{[2-(phenylethynyl)cyclopent-1-en-1-yl]methyl}-1*H*-indole-3-carboxaldehyde (3i). This compound was prepared using 1-(bromomethyl)-2-(phenylethynyl)cyclopentene according to method A. The product was purified using 5:1 hexanes/EtOAc to afford 110 mg (55%) of the indicated compound as a pale yellow solid: mp 162-163 °C; ^1H NMR ($CDCl_3$) δ 1.86 (quintet, *J* = 7.2 Hz, 2H), 2.24 (t, *J* = 7.2 Hz, 2H), 2.63 (t, *J* = 7.2 Hz, 2H), 5.20 (s, 2H), 7.26-7.38 (m,

5H), 7.43-7.55 (m, 3H), 8.31 (m, 1H), 10.04 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 22.2, 33.8, 36.9, 45.0, 84.5, 96.1, 110.4, 115.5, 121.2, 123.0, 123.4, 123.5, 124.3, 125.4, 126.0, 128.5, 128.6, 131.5, 137.1, 143.4, 185.6; IR (neat, cm^{-1}) 3055, 2955, 2252, 1658; HRMS calcd for $C_{23}H_{18}BrNO$: 403.0572. Found: 403.0577.

General Procedure for the Synthesis of Annulated γ-Carbolines by Palladium-Catalyzed Intramolecular Iminoannulation. The *N*-substituted 2-bromo-1*H*-indole-3-carboxaldehyde (0.25 mmol) was placed in a 2-dram vial and *tert*-butylamine (1 mL) was added. The vial was flushed with Ar and carefully sealed. The mixture was heated at 100 °C for 8 h and cooled, diluted with ether, dried over anhydrous Na_2SO_4 and filtered. The solvent was evaporated and the residue was dissolved in DMF (5 mL) and transferred to a 4-dram vial containing $Pd(OAc)_2$ (5 mol %), PPh_3 (10 mol %) and Na_2CO_3 (0.25 mmol). The mixture was flushed with Ar and heated at 100 °C for the indicated time. The completion of the reaction was established by the observation of palladium black. The mixture (except entries 3 and 5 in Table 1, which produce reasonably water soluble products) was diluted with EtOAc (30 mL), washed with satd aq NH_4Cl (3 × 10 mL) and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by chromatography on a silica gel column. The solvent from the reaction mixtures of entries 3 and 5 was directly evaporated and the residue was purified by chromatography on a silica gel column.

Annulated γ-Carbolines Prepared

3-Phenyl-5,6-dihydro-4*H*-indolo[3,2,1-*ij*]-1,6-naphthyridine (4a). The mixture was chromatographed using 1:1 hexanes/EtOAc to afford 66 mg (93%) of the indicated compound as a white solid: mp 172-173 °C; ^{1}H NMR ($CDCl_3$) δ 2.24 (quintet, *J* = 6.0 Hz, 2H), 3.15 (t, *J* = 6.0 Hz, 2H), 4.22 (t, *J* = 6.0 Hz, 2H), 7.31 (dt, *J* = 0.9, 7.8 Hz, 1H), 7.36-7.43 (m, 2H), 7.43-7.52 (m, 3H), 7.69-7.73 (m, 2H), 8.16 (d, *J* = 7.8 Hz, 1H), 9.23 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 22.7, 23.9, 41.0, 108.9, 113.8, 116.9, 120.5, 121.5, 121.6, 126.5, 127.9, 128.4, 129.6, 140.3,

140.5, 140.7, 143.2, 150.8; IR (neat, cm^{-1}) 3055, 2943; HRMS calcd for $C_{20}H_{16}N_2$: 284.1314. Found: 284.1317.

3-Hexyl-5,6-dihydro-4*H*-indolo[3,2,1-*ij*]-1,6-naphthyridine (4b). The mixture was chromatographed using 10:1 $CHCl_3$/MeOH to afford 70 mg (95%) of the indicated compound as a white solid: mp 58-59 °C; ^1H NMR ($CDCl_3$) δ 0.88 (t, *J*= 6.9 Hz, 3H), 1.25-1.48 (m, 6H), 1.75 (m, 2H), 2.32 (quintet, *J*= 6.0 Hz, 2H), 2.89 (t, *J*= 7.8 Hz, 2H), 3.01 (t, *J*= 6.0 Hz, 2H), 4.15 (t, *J*= 6.0 Hz, 2H), 7.26 (dt, *J*= 1.2, 7.8 Hz, 1H), 7.36 (d, *J*= 8.1 Hz, 1H), 7.46 (dt, *J*= 1.2, 7.2 Hz, 1H), 8.09 (d, *J*= 7.8 Hz, 1H), 9.06 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.4, 21.8, 22.4, 22.9, 29.7, 30.2, 32.1, 34.8, 40.7, 108.8, 113.3, 116.3, 120.2, 121.3, 121.8, 126.1, 140.0, 140.4, 143.2, 153.5; IR (neat, cm^{-1}) 3053, 2925, 2854; HRMS calcd for $C_{20}H_{24}N_2$: 292.1940. Found: 292.1945.

5,6-Dihydro-4*H*-indolo[3,2,1-*ij*]-1,6-naphthyridin-3-yl(4-methoxyphenyl)methanol (4c). The mixture was chromatographed using 10:1 $CHCl_3$/MeOH to afford 82 mg (95%) of the indicated compound as a yellow oil, which crystallizes upon standing at 0 °C: mp 131-133 °C; ^1H NMR ($CDCl_3$) δ 2.25 (m, 2H), 2.50 (m, 1H), 2.93 (dt, *J*= 16.4, 4.8 Hz, 1H), 3.76 (s, 3H), 4.03 (m, 1H), 4.23 (m, 1H), 5.86 (s, 1H), 6.82 (d, *J*= 8.4 Hz, 2H), 7.23 (d, *J*= 8.4 Hz, 2H), 7.29 (t, *J*= 8.0 Hz, 1H), 7.33 (d, *J*= 8.0 Hz, 1H), 7.49 (d, *J*= 8.0 Hz, 1H), 8.12 (d, *J*= 8.0 Hz, 1H), 9.11 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 20.9, 21.7, 40.4, 55.3, 71.8, 108.8, 112.4, 113.9, 117.6, 120.4, 121.3, 121.4, 126.6, 128.8, 136.0, 138.2, 140.7, 143.2, 150.9, 159.0; IR (neat, cm^{-1}) 3321, 3005, 2930, 1473; HRMS calcd for $C_{22}H_{20}N_2O_2$: 344.1525. Found: 344.1531.

Ethyl 3-(5,6-dihydro-4*H*-indolo[3,2,1-*ij*]-1,6-naphthyridin-3-yl)benzoate (4d). The mixture was chromatographed using 12:1 $CHCl_3$/MeOH to afford 83 mg (93%) of the indicated compound as a yellow oil: ^1H NMR ($CDCl_3$) δ 1.41 (t, *J* = 7.2 Hz, 3H), 2.27 (quintet, *J*= 6.0 Hz, 2H), 3.17 (t, *J*= 6.0 Hz, 2H), 4.25 (t, *J*= 6.0 Hz, 2H), 4.41 (q, *J*= 7.2 Hz, 2H), 7.33 (t, *J*= 7.2 Hz, 1H), 7.43 (d, *J*= 8.0 Hz, 1H), 7.50-7.58 (m, 2H), 7.94 (d, *J*= 8.0 Hz, 1H), 8.09 (d, *J*= 8.0 Hz, 1H), 8.17 (d, *J*= 8.0 Hz, 1H), 8.39 (s, 1H), 9.24 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.4, 22.5, 23.6,

40.8, 61.1, 108.8, 113.9, 117.0, 120.4, 121.3, 121.4, 126.5, 128.4, 128.5, 128.8, 130.4, 133.9, 140.4, 140.5, 140.6, 143.0, 149.5, 166.7; IR (neat, cm^{-1}) 3055, 2952, 1716; HRMS calcd for $C_{23}H_{20}N_2O_2$: 356.1525. Found: 356.1532.

3-(5-Pyrimidin-5-yl)-5,6-dihydro-4*H*-indolo[3,2,1-*ij*]-1,6-naphthyridine (4e). The mixture was chromatographed using 12:1 $CHCl_3$/MeOH to afford 71 mg (99%) of the indicated compound as a yellow solid: mp 217-218 °C; ^{1}H NMR ($CDCl_3$) δ 2.33 (quintet, *J* = 5.6 Hz, 2H), 3.20 (t, *J* = 5.6 Hz, 2H), 4.29 (t, *J* = 5.6 Hz, 2H), 7.24-7.31 (m, 2H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 8.19 (d, *J* = 7.6 Hz, 1H), 9.14 (s, 2H), 9.26 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 22.4, 23.4, 40.8, 109.0, 114.8, 117.6, 120.8, 121.1, 121.6, 127.0, 133.6, 140.6, 141.1, 142.8, 143.8, 157.0, 157.5; IR (neat, cm^{-1}) 3043, 2958, 2866; HRMS calcd for $C_{18}H_{14}N_4$: 286.1219. Found: 286.1223.

3-Phenyl-4,5,6,7-tetrahydro-2,7-diazacyclohept[1,2,3-*jk*]fluorene (4f). The mixture was chromatographed using 1:1 hexanes/EtOAc to afford 69 mg (90%) of the indicated compound as a yellow solid: mp 164-166 °C; ^{1}H NMR ($CDCl_3$) δ 2.10 (quintet, *J* = 6.0 Hz, 2H), 2.27 (quintet, *J* = 6.0 Hz, 2H), 3.18 (t, *J* = 6.0 Hz, 2H), 4.40 (t, *J* = 6.0 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.37-7.53 (m, 5H), 7.55-7.59 (m, 2H), 8.14 (d, *J* = 7.6 Hz, 1H), 9.20 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 26.9, 28.2, 29.1, 45.0, 109.5, 118.6, 119.2, 120.5, 120.6, 121.6, 126.5, 127.6, 128.1, 129.7, 140.0, 141.6, 141.9, 146.6, 154.2; IR (neat, cm^{-1}) 3056, 2931, 1585; HRMS calcd for $C_{21}H_{18}N_2$: 298.1470. Found: 298.1475.

3-*n*-Hexyl-4,5-dihydrobenzo[*b*]pyrido[3,4,5-*gh*]pyrrolizine (4g). The mixture was chromatographed using 10:1 $CHCl_3$/MeOH to afford 63 mg (91%) of the indicated compound as a yellow solid: mp 76-78 °C; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, *J* = 7.2 Hz, 3H), 1.25-1.45 (m, 6H), 1.79 (quintet, *J* = 7.8 Hz, 2H), 2.87 (t, *J* = 7.5 Hz, 2H), 3.82 (t, *J* = 7.5 Hz, 2H), 4.53 (t, *J* = 7.5 Hz, 2H), 7.25 (m, 1H), 7.35 (dd, *J* = 0.6, 7.5 Hz, 1H), 7.43 (dt, *J* = 1.2, 8.1 Hz, 1H), 8.04 (dd, *J* = 0.6, 8.1 Hz, 1H), 8.93 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.3, 22.9, 29.5, 29.7, 32.0, 32.9, 36.1, 49.0, 110.6, 112.1, 117.2, 120.2, 123.1, 125.9, 126.5, 140.5, 140.7, 151.4, 158.0;

IR (neat, cm^{-1}) 3051, 2953, 2853; HRMS calcd for $C_{19}H_{22}N_2$: 278.1783. Found: 278.1787.

1-Phenyl-9*H*-benzo[*c*]indolo[3,2,1-*ij*]-1,6-naphthyridine (4h). The mixture was chromatographed using 1:1 hexanes/EtOAc to afford 72 mg (88%) of the indicated compound as a white solid: mp 234-235 °C; ^{1}H NMR ($CDCl_3$) δ 5.52 (s, 2H), 7.01 (t, *J* = 8.0 Hz, 1H), 7.19-7.26 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.46-7.52 (m, 4H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.65 (dd, *J* = 1.6, 8.0 Hz, 2H), 8.17 (d, *J* = 8.0 Hz, 1H), 9.15 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 45.7, 109.3, 112.2, 117.3, 121.2, 121.5, 122.0, 126.6, 127.1, 127.5, 127.7, 128.0, 128.3, 128.8, 129.0, 129.2, 129.4, 130.6, 140.5, 140.8, 142.0, 143.6; IR (neat, cm^{-1}) 3057, 2934, 2841; HRMS calcd for $C_{24}H_{16}N_2$: 332.1314. Found: 332.1320.

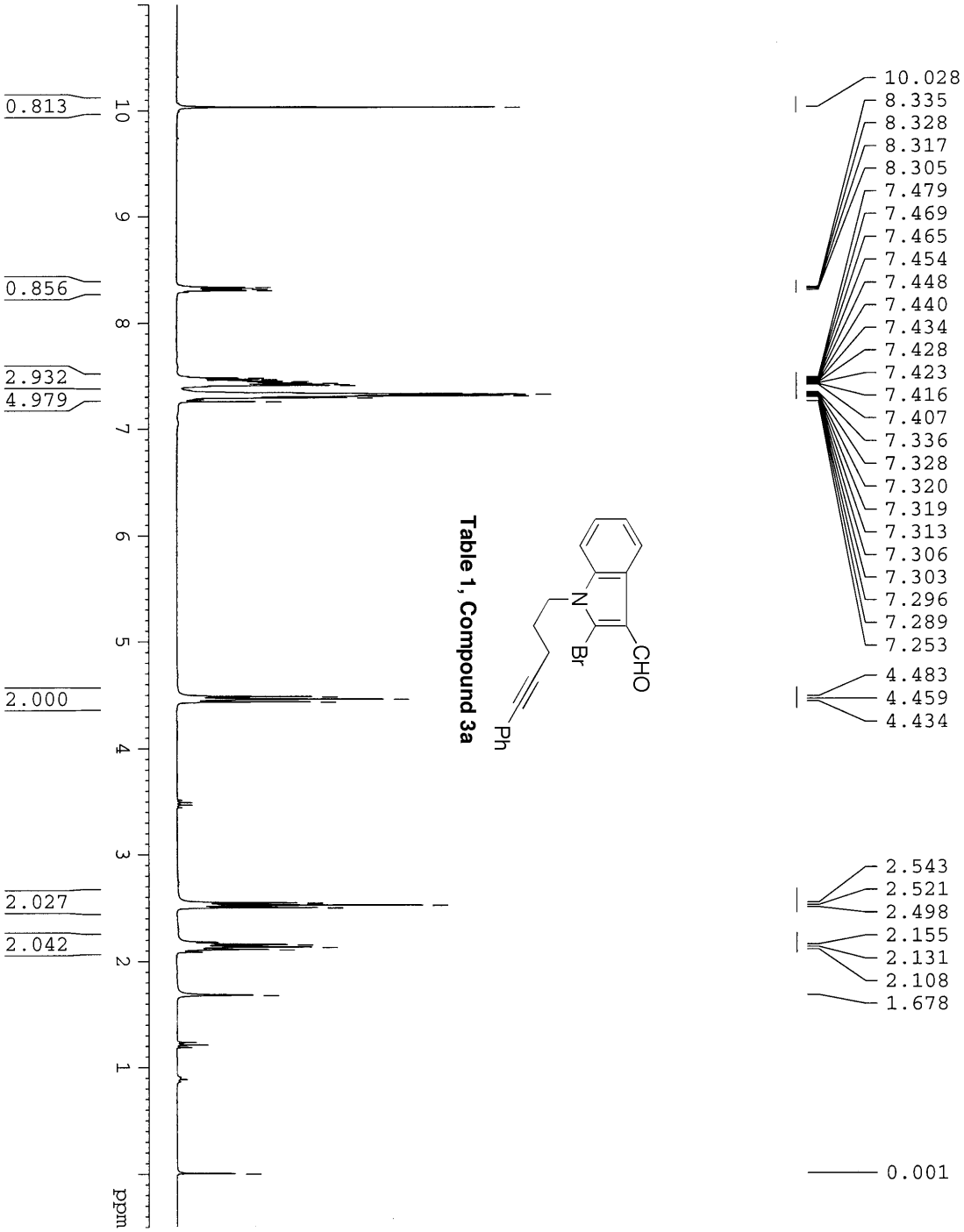
3-Phenyl-4,5,6,7-tetrahydrocyclopenta[*c*]indolo[3,2,1-*ij*]-1,6-naphthyridine (4i). The mixture was chromatographed using 10:1 $CHCl_3$/MeOH to afford 76 mg (94%) of the indicated compound as a yellow solid: mp 184-185 °C; ^{1}H NMR ($CDCl_3$) δ 1.89 (quintet, *J* = 7.2 Hz, 2H), 2.10 (m, 2H), 2.41 (m, 2H), 5.02 (s, 2H), 7.30-7.52 (m, 8H), 8.11 (d, *J* = 7.6 Hz, 1H), 9.03 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 23.0, 33.4, 34.3, 45.4, 109.0, 112.1, 115.6, 120.9, 121.4, 122.3, 126.1, 127.5, 127.7, 129.9, 130.8, 135.5, 140.0, 141.2, 141.6, 142.6, 149.0; IR (neat, cm^{-1}) 3055, 2957, 2841; HRMS calcd for $C_{23}H_{18}N_2$: 322.1470. Found: 322.1476.

2-Phenyl-2,4,5,6-tetrahydro-1*H*-6-azabenzo[*a*]cyclopenta[*cd*]azulen-1-one (5a). To a 4-dram vial were added 2-bromo-1-(6-phenylhex-5-ynyl)-1*H*-indole-3-carboxaldehyde (**3f**, 0.25 mmol), $Pd(OAc)_2$ (5 mol %), *n*-Bu_4NCl (0.25 mmol), Na_2CO_3 (1.0 mmol) and DMA (5 mL). The mixture was flushed with Ar and heated at 100 °C for 8 h. The completion of the reaction was established by the observation of palladium black. The mixture was diluted with EtOAc (30 mL), washed with satd aq NH_4Cl (3 × 10 mL) and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by chromatography on a silica gel column. The mixture was chromatographed using 1:1 hexanes/EtOAc to afford 36 mg (48%) of the indicated compound as an off-white solid: mp 231-233 °C; ^{1}H NMR ($CDCl_3$) δ 2.32 (m, 2H), 2.67 (m, 2H), 4.30 (t, *J* = 5.2 Hz, 2H),

4.50 (s, 1H), 5.78 (t, J = 5.2 Hz, 1H), 7.20-7.36 (m, 8H), 7.97 (d, J = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 25.8, 30.7, 46.7, 62.6, 110.2, 119.7, 121.7, 122.1, 122.6, 124.4, 127.0, 127.9, 128.5, 128.6, 132.0, 138.9, 143.8, 160.9, 192.0; IR (neat, cm^{-1}) 3055, 2923, 1683; HRMS calcd for $C_{21}H_{17}NO$: 299.1310. Found: 299.1314.

References

1. Gilchrist, T. L.; Kemmitt, P. D.; Germain, A. L. *Tetrahedron* **1997**, *53*, 4447. We used ethyl acetate instead of diethyl ether as the extraction solvent and were able to isolate 2-bromo-1*H*-indole-3-carboxaldehyde in 55% yield.
2. Sudo, T.; Asao, N.; Yamamoto, Y. *J. Org. Chem.* **2000**, *65*, 8919.
3. Roesch, K. R.; Larock, R. C. *J. Org. Chem.* **2001**, *66*, 412.
4. Padwa, A.; Krumple, K. E.; Weinggarten, M. D. *J. Org. Chem.* **1995**, *60*, 5595.
5. Saulnier, M. G.; Kadow, J. F.; Tun, M. M.; Langley, D. R.; Vyas, D. M. *J. Am. Chem. Soc.* **1989**, *111*, 8320.
6. Baker, M. V.; Brown, D. H.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **2000**, 4607.



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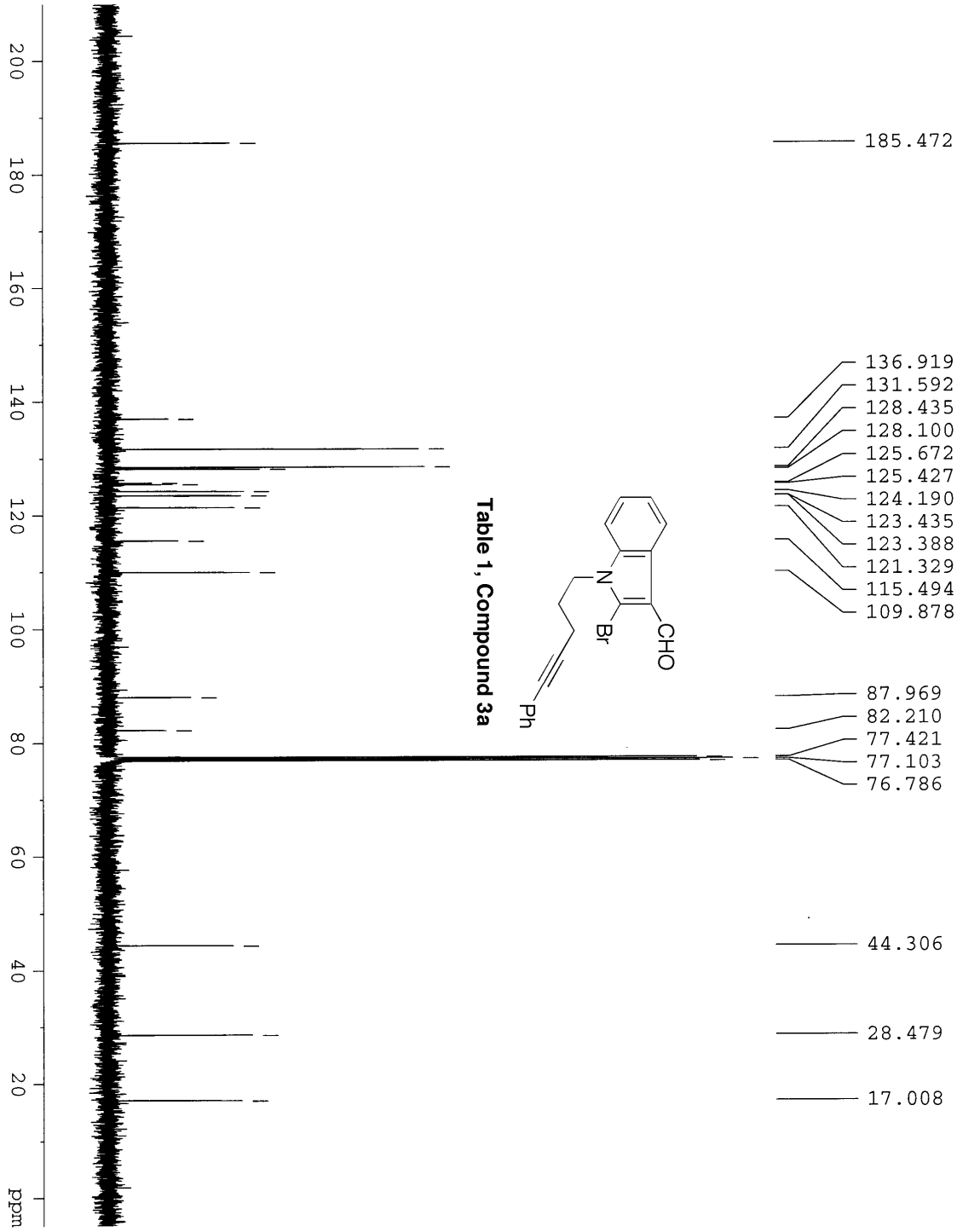
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128.100
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124.190
123.435
123.388
121.329
115.494
109.878
87.969
82.210
77.421
77.103
76.786
44.306
28.479
17.008
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180
160
140
120
100
80
60
40
20
ppm
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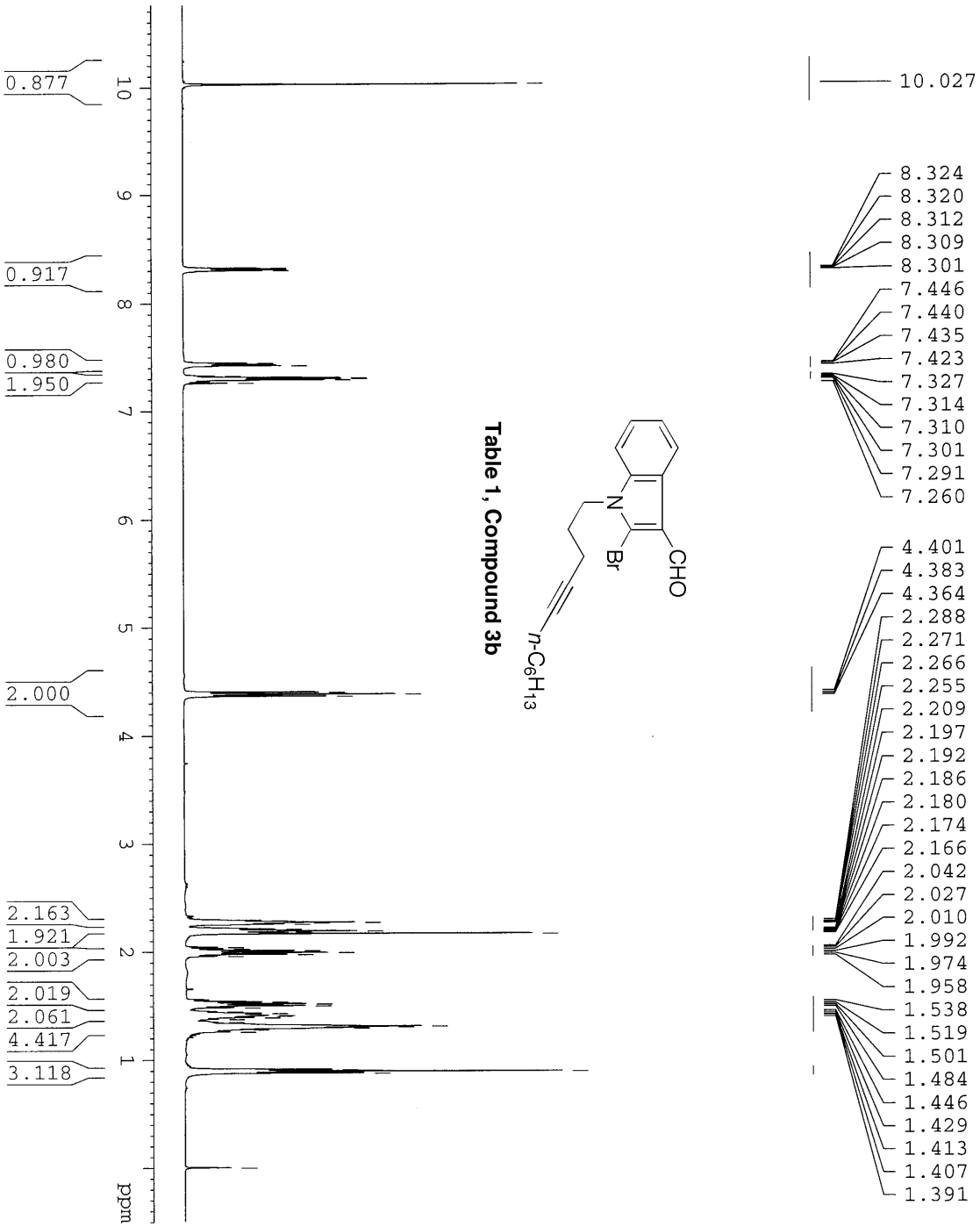
N
Br
CHO
Ph



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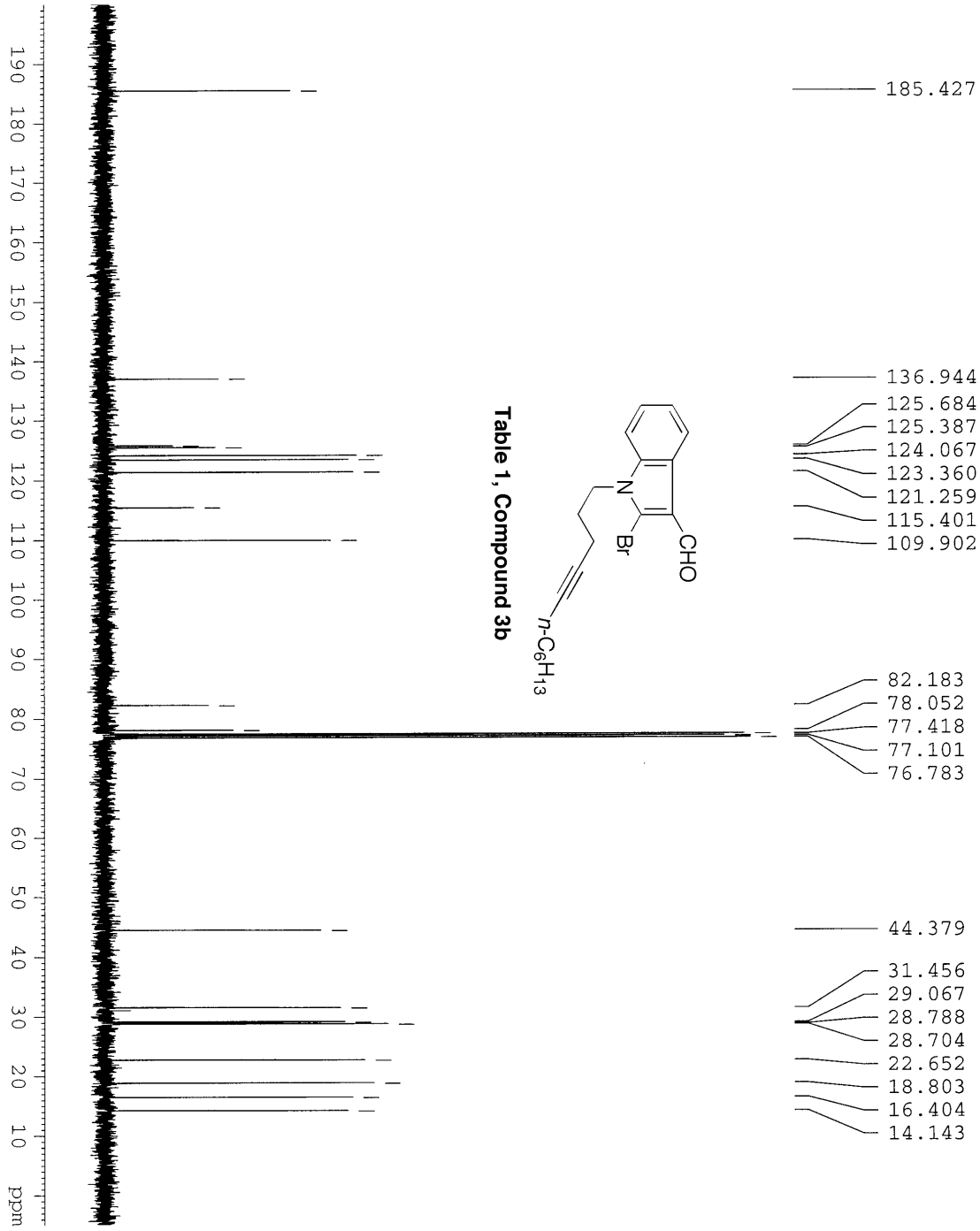

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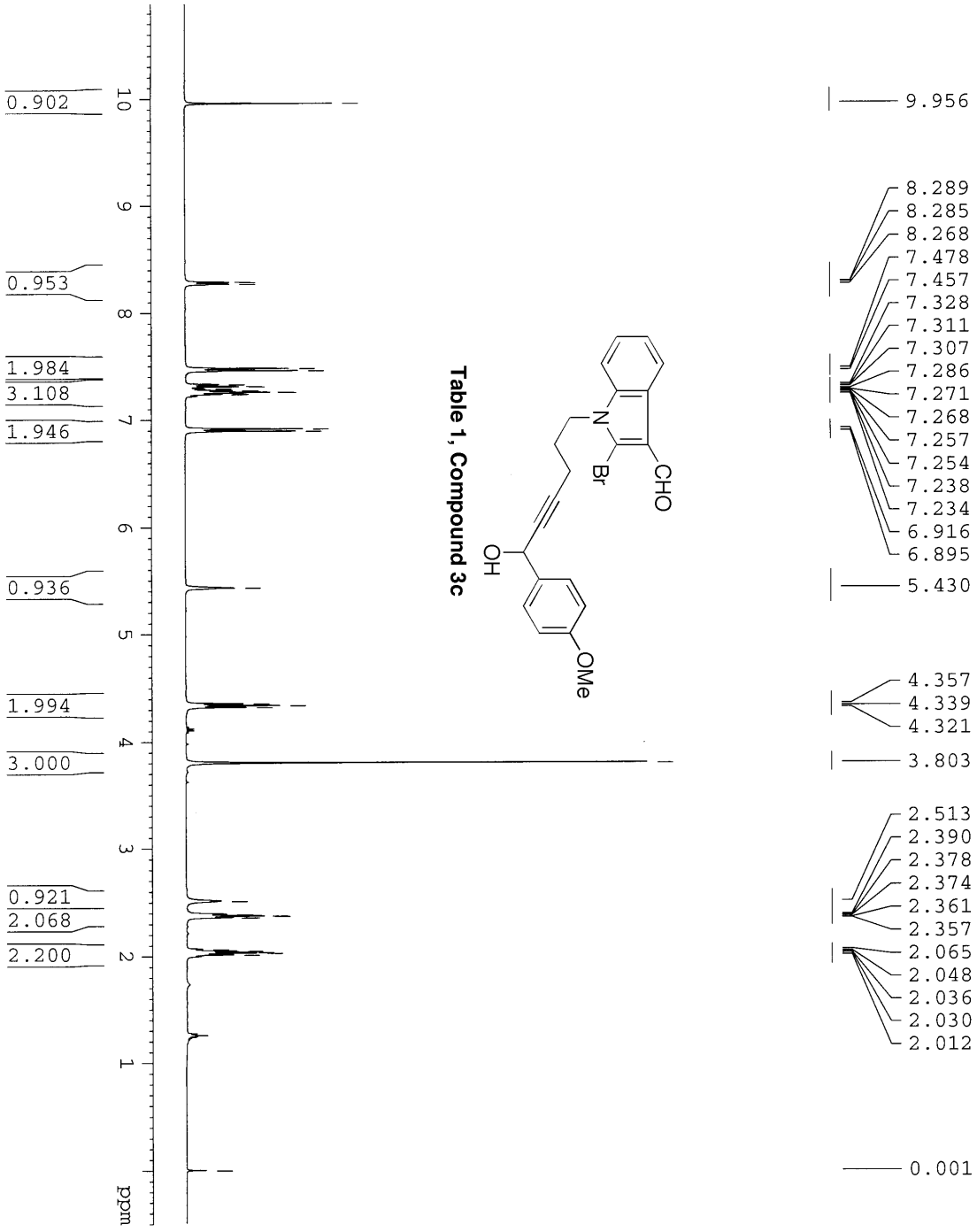
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3.000
0.921
2.068
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10
9
8
7
6
5
4
3
2
1
ppm
9.956
8.289
8.285
8.268
7.478
7.457
7.328
7.311
7.307
7.286
7.271
7.268
7.257
7.254
7.238
7.234
6.916
6.895
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2.374
2.361
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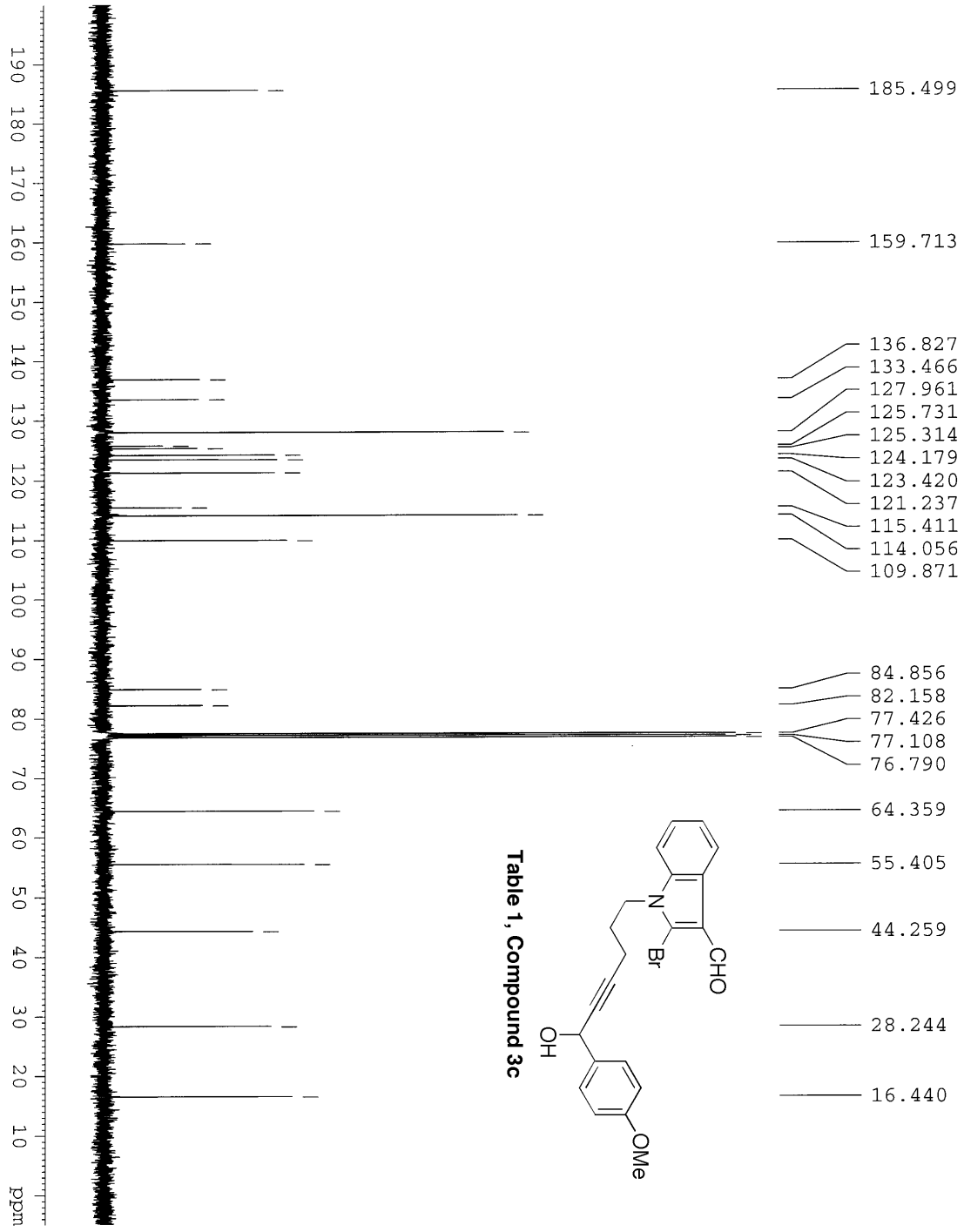

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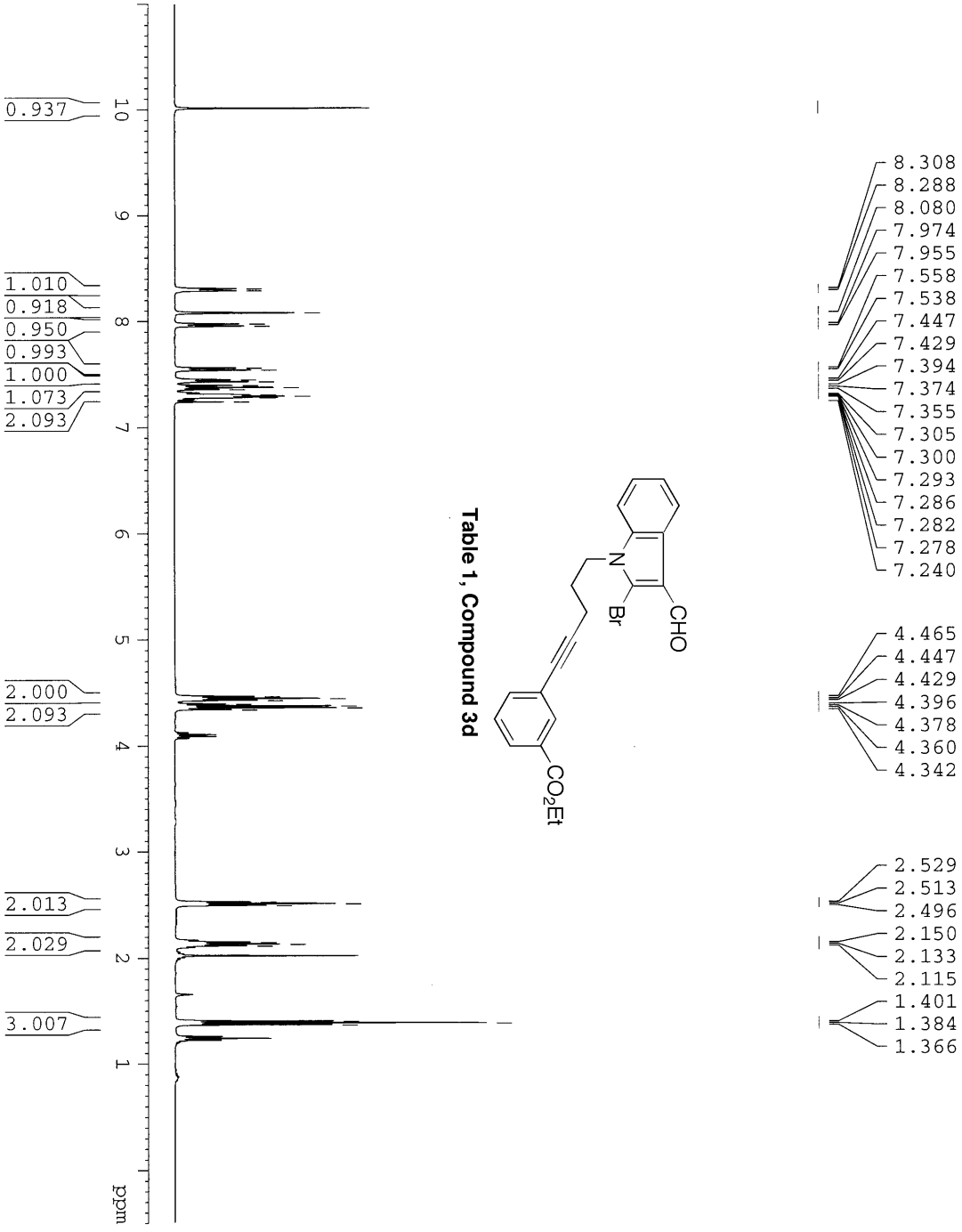

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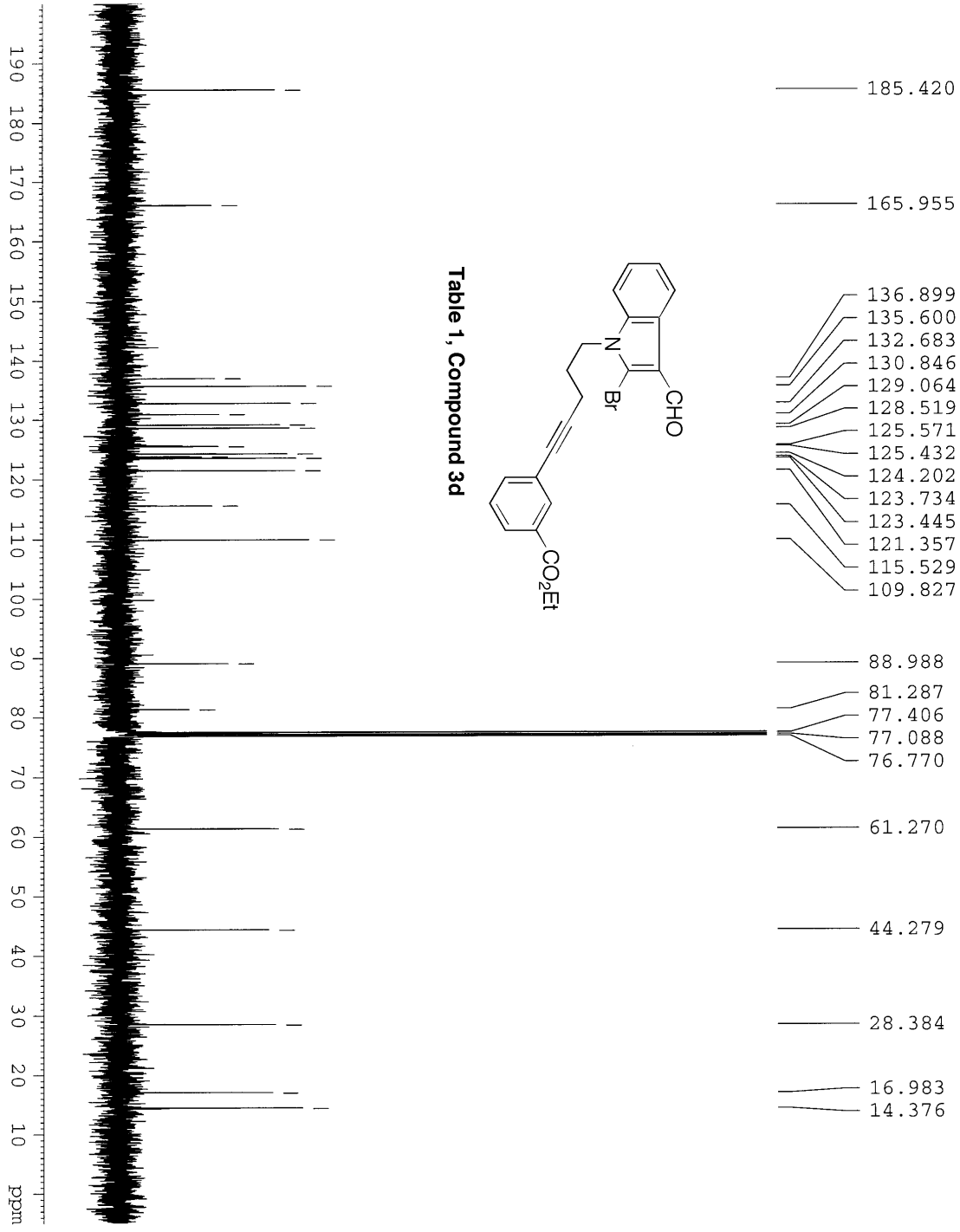
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124.202
123.734
123.445
121.357
115.529
109.827
88.988
81.287
77.406
77.088
76.770
61.270
44.279
28.384
16.983
14.376
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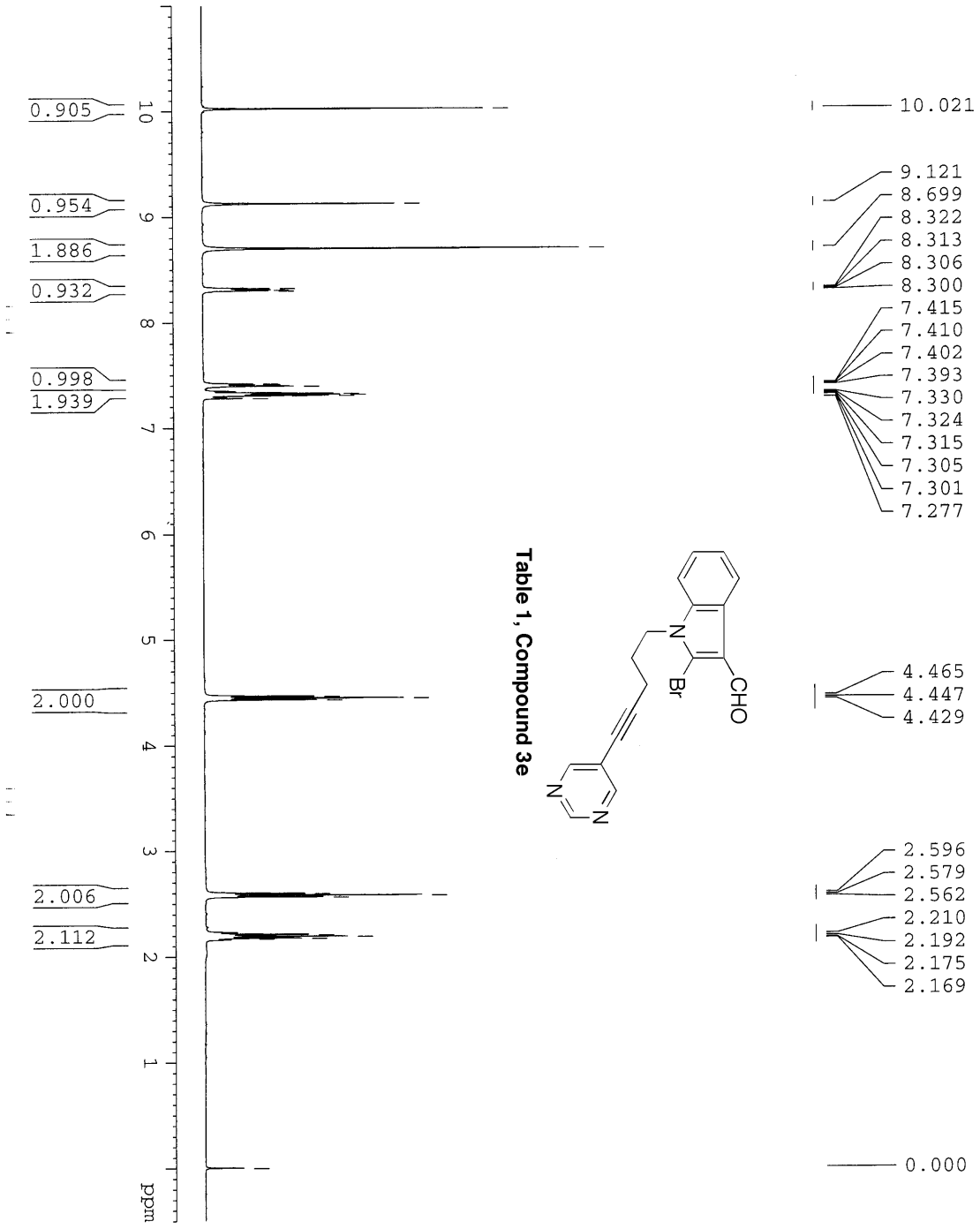

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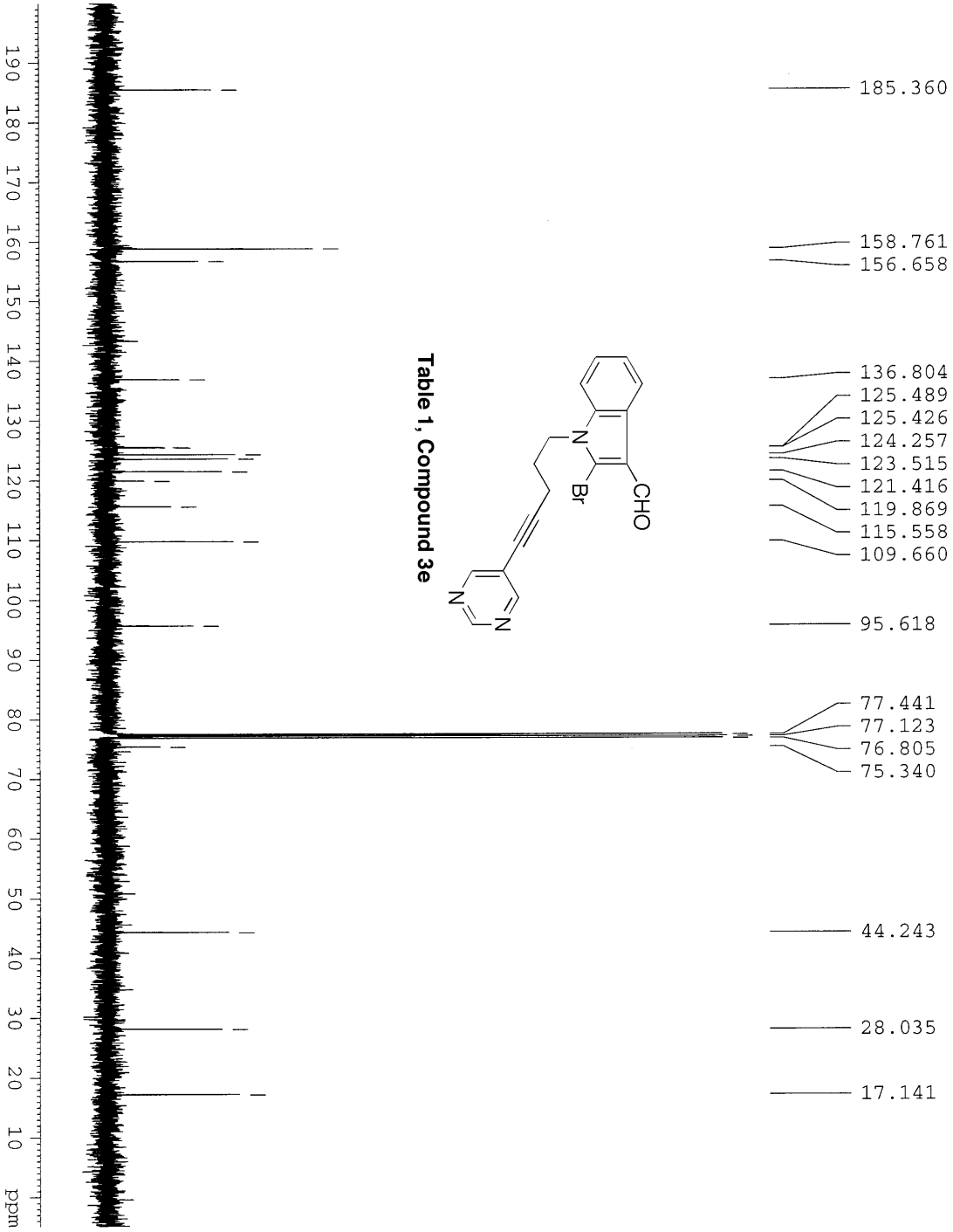

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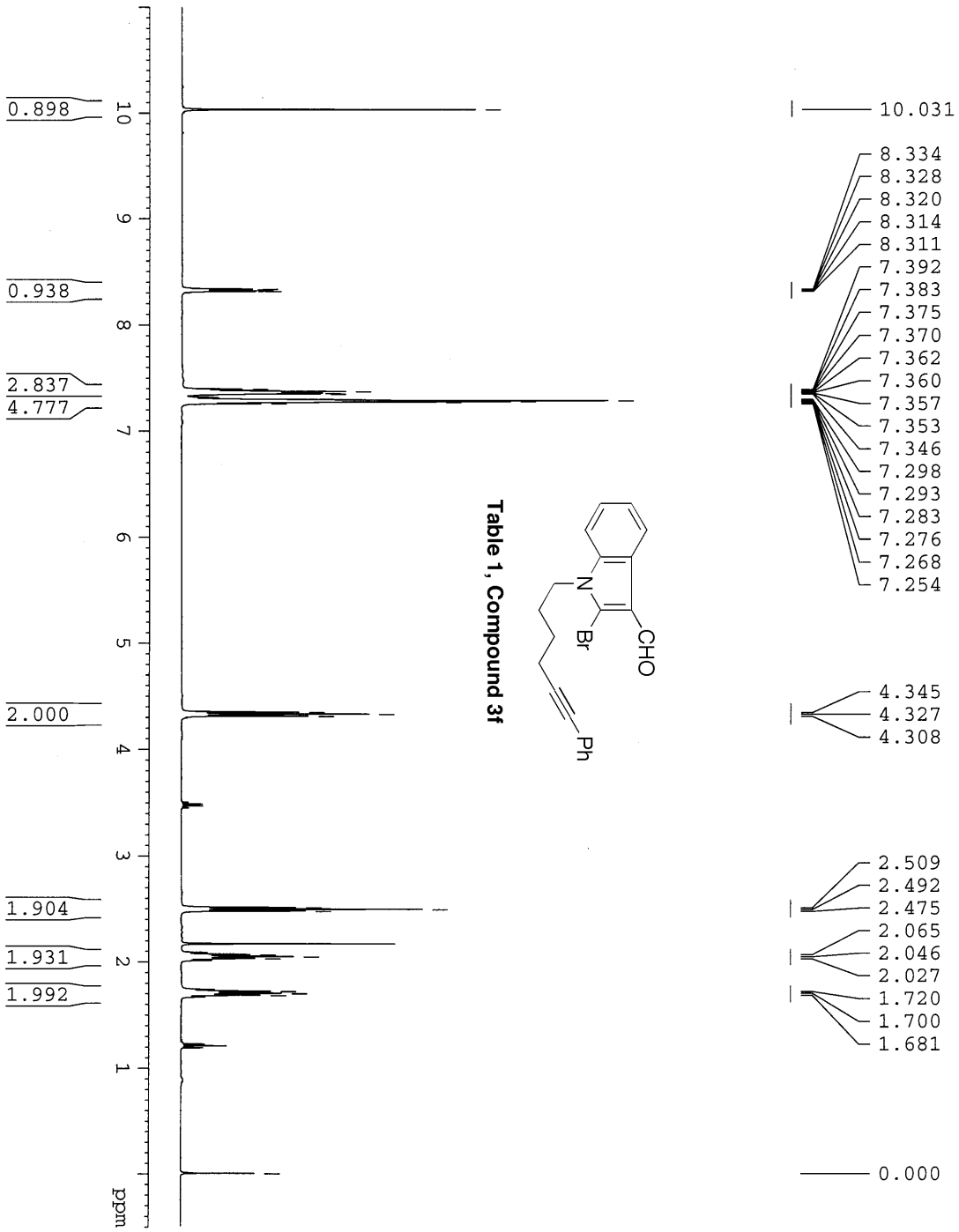

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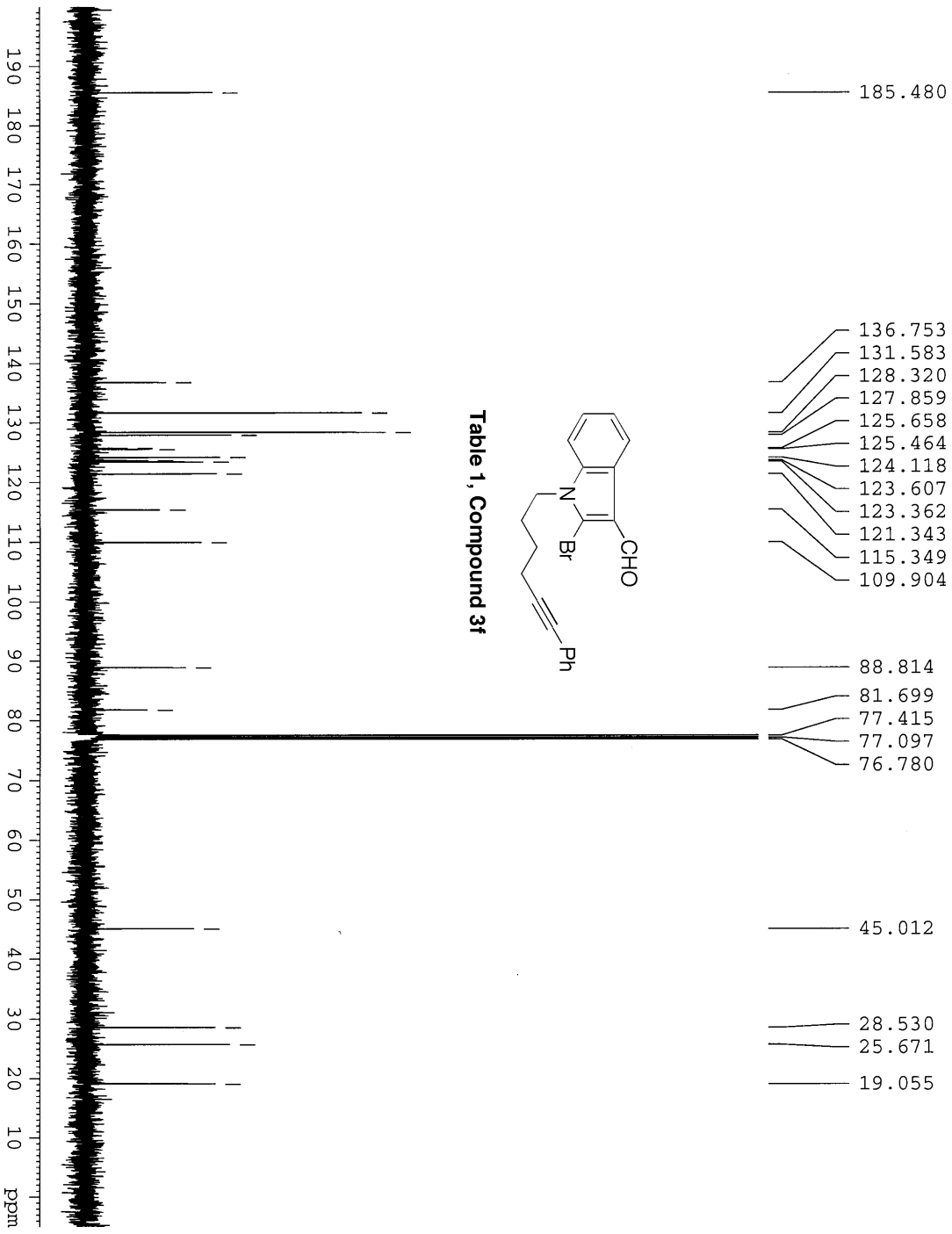

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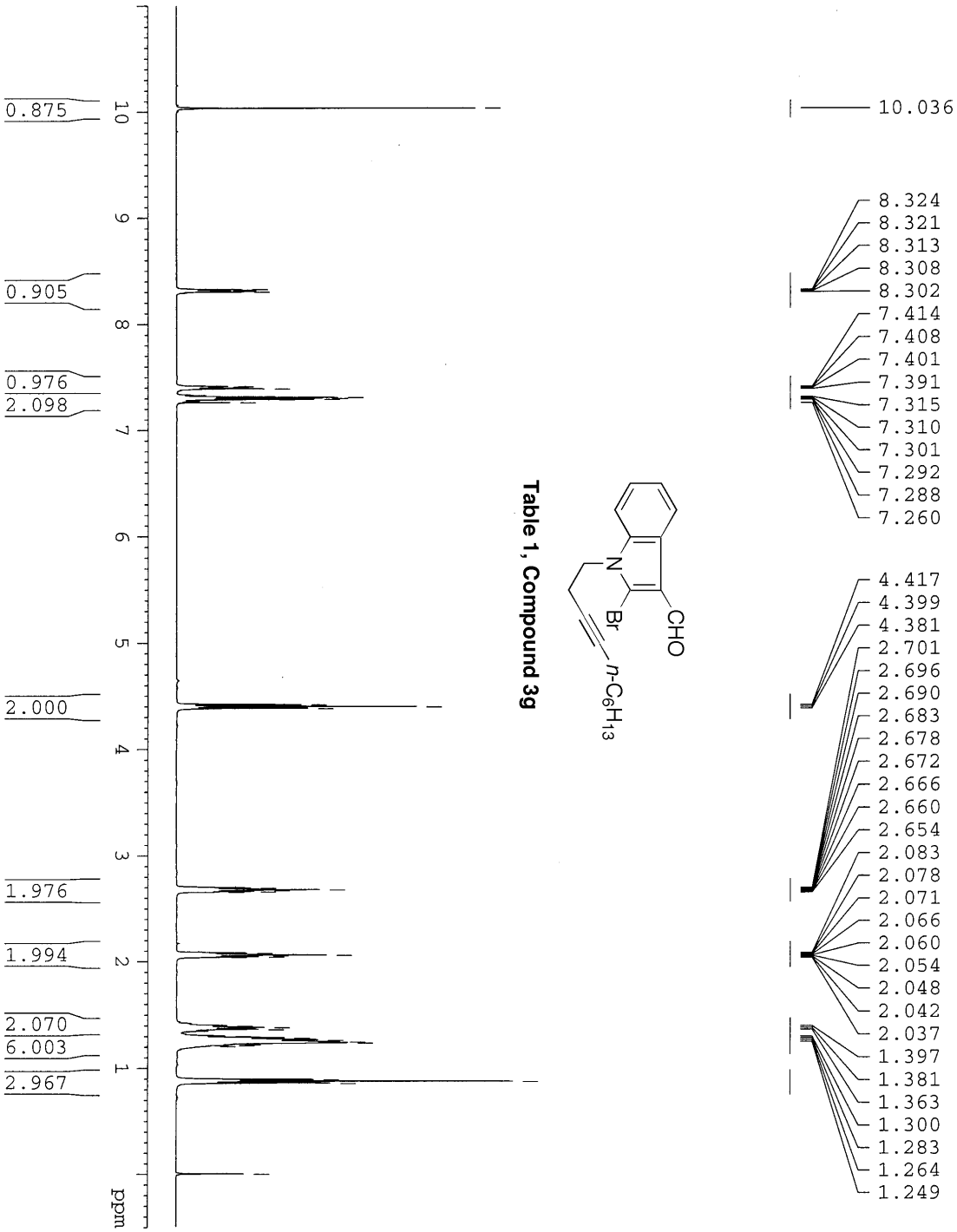

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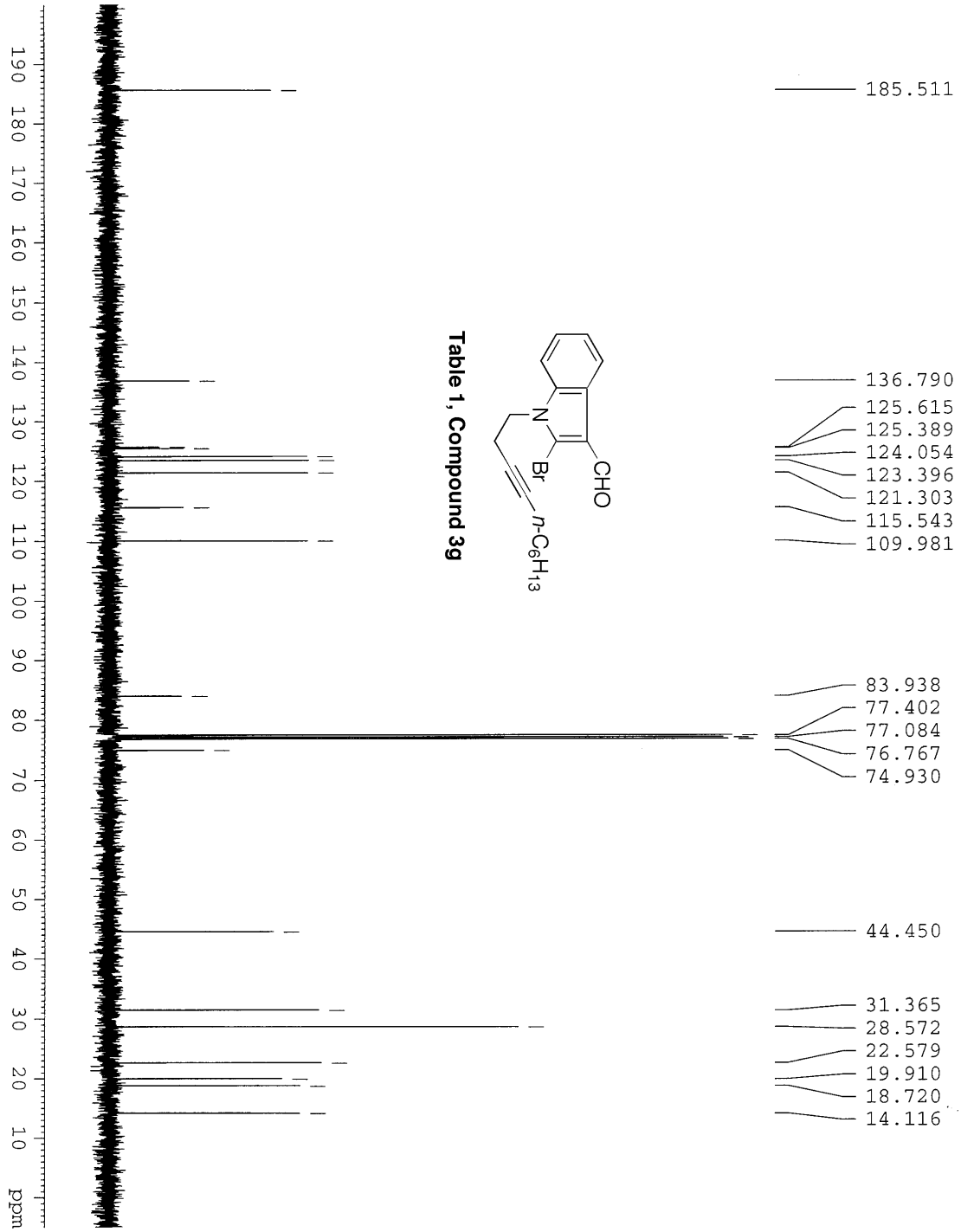

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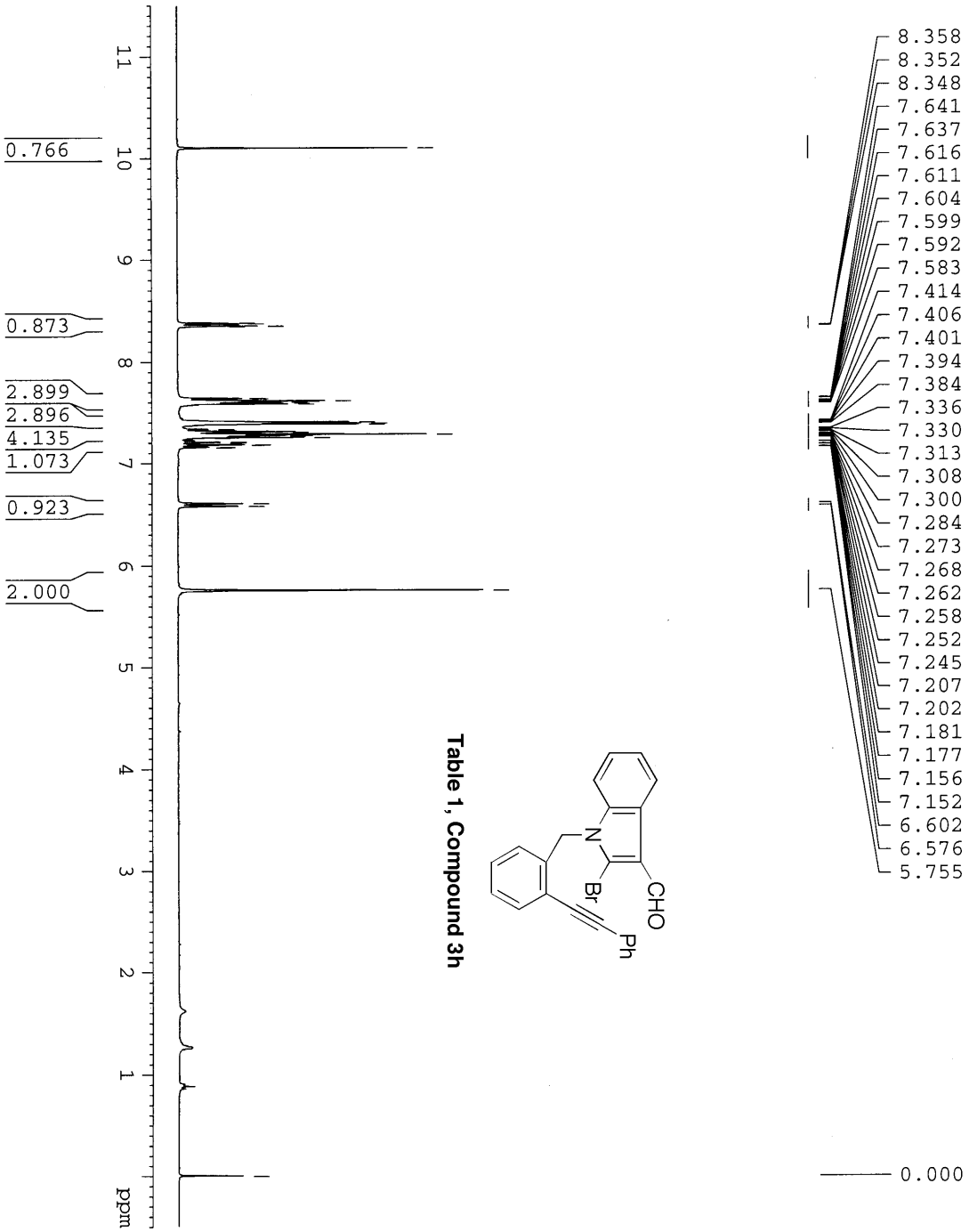

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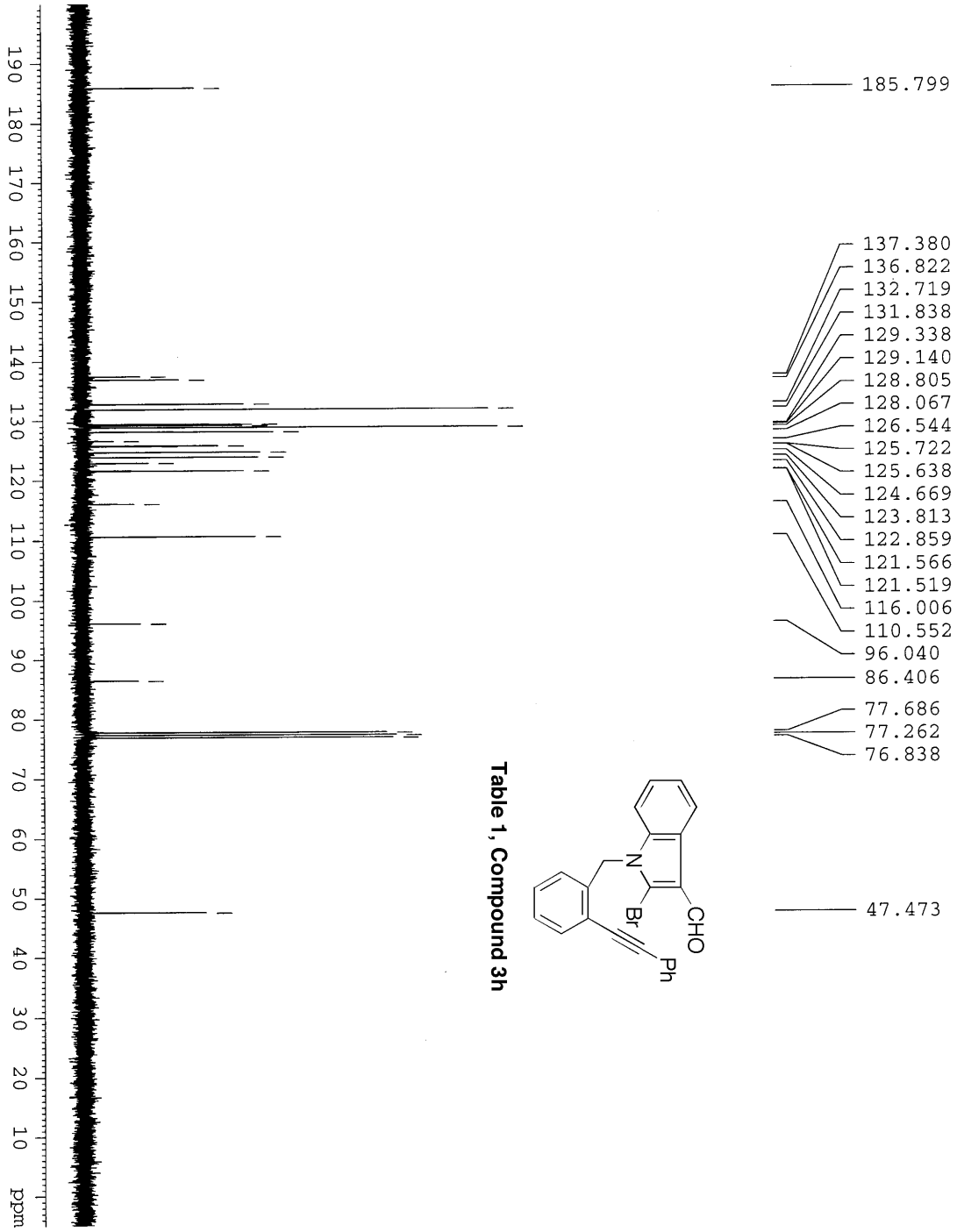

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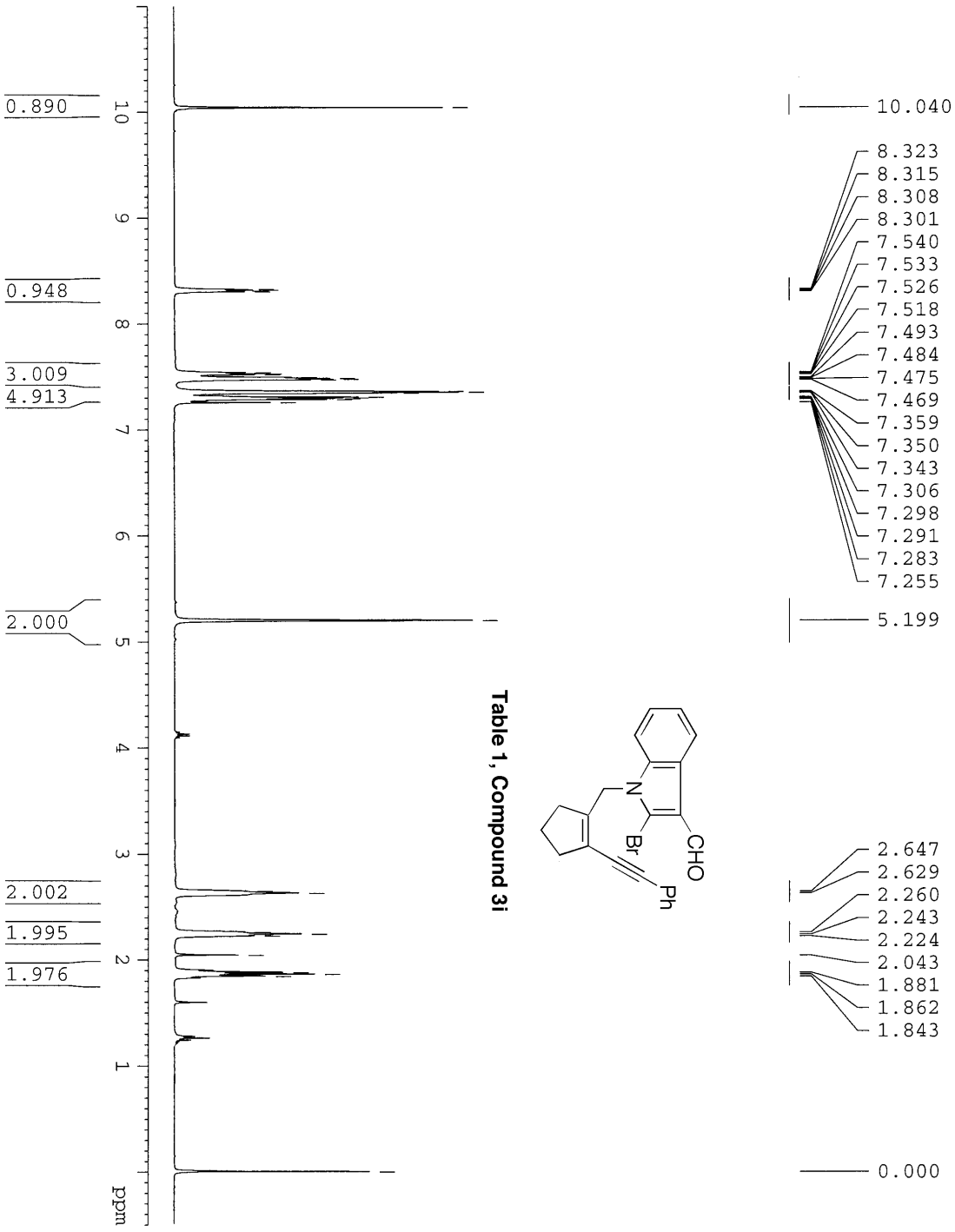

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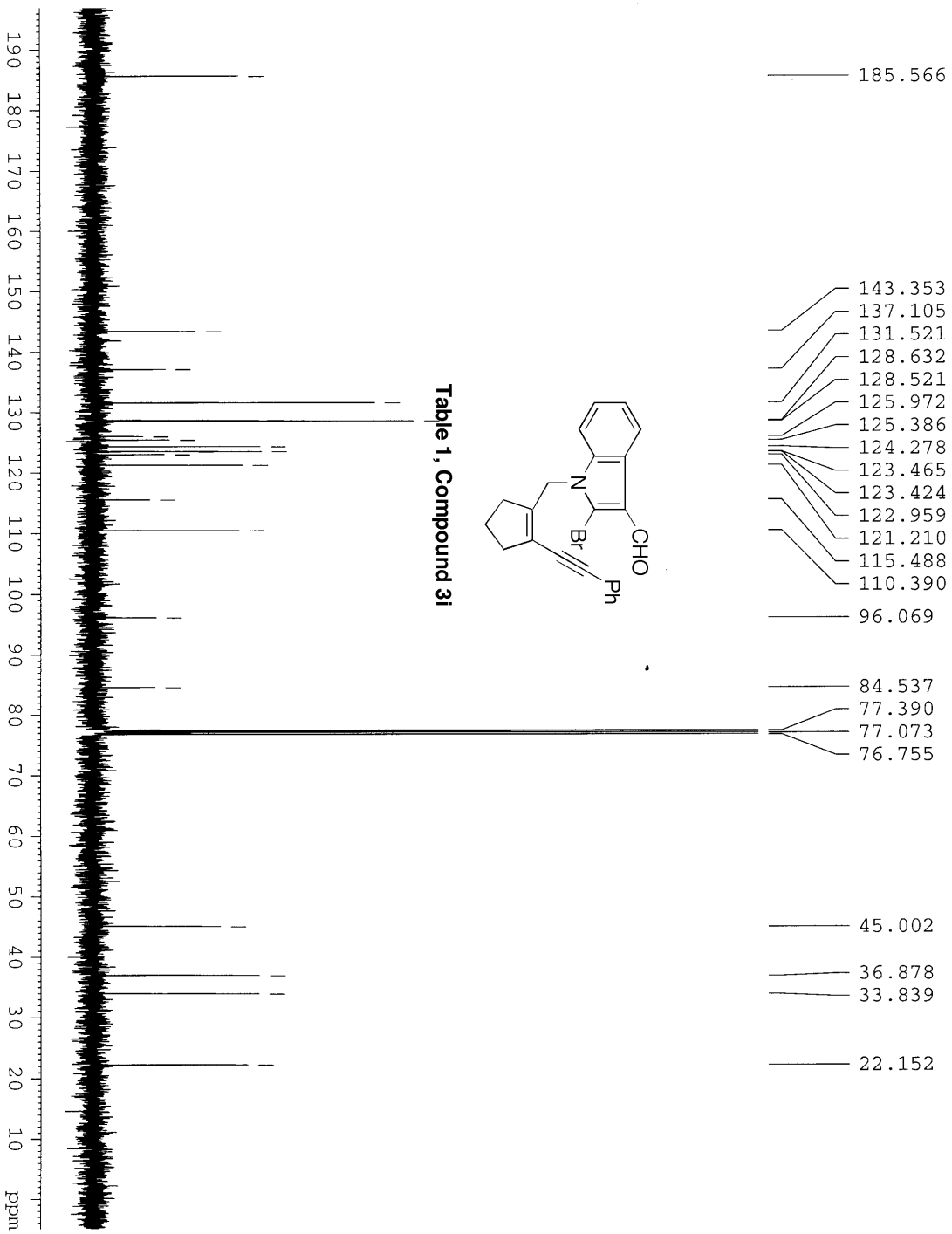
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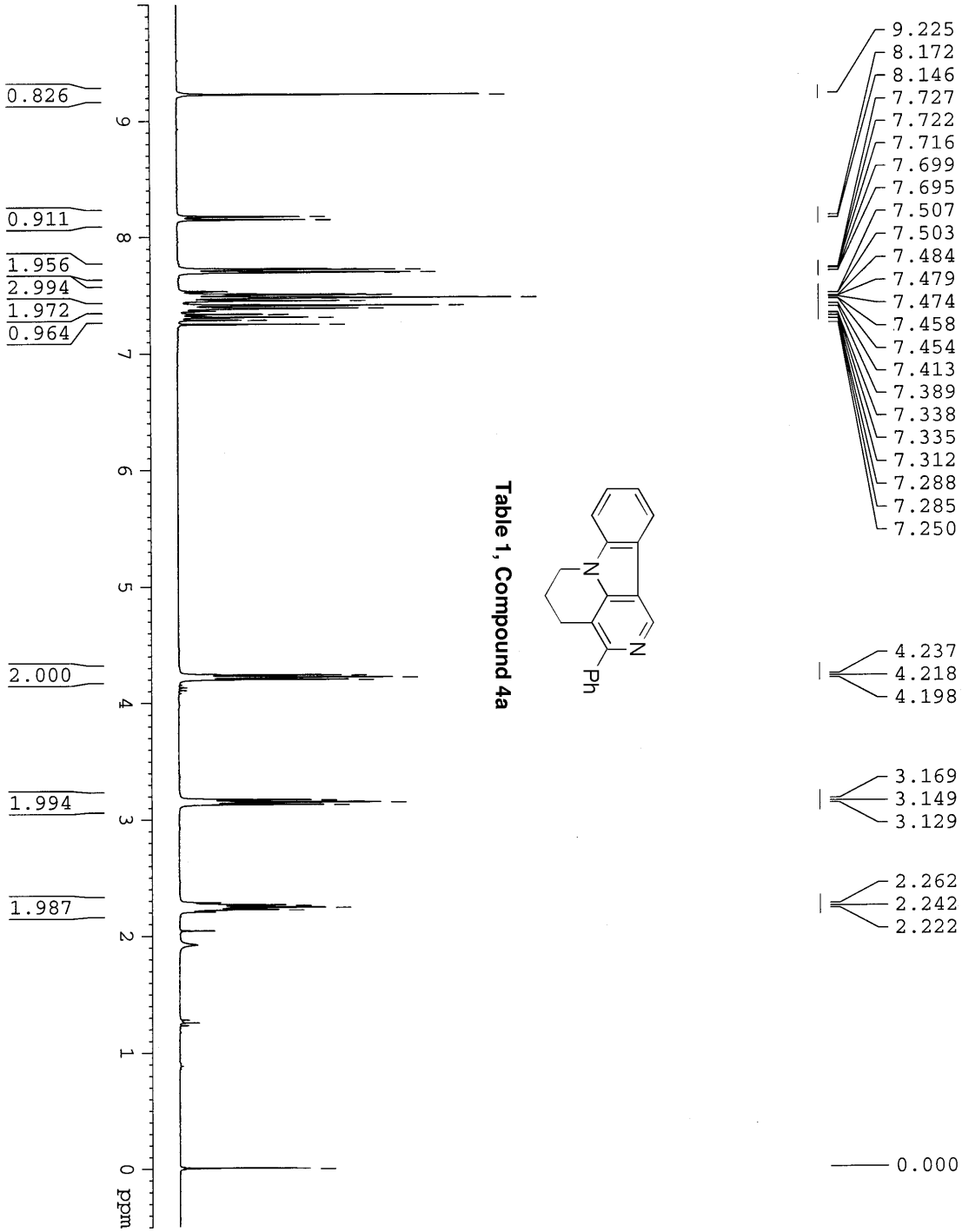

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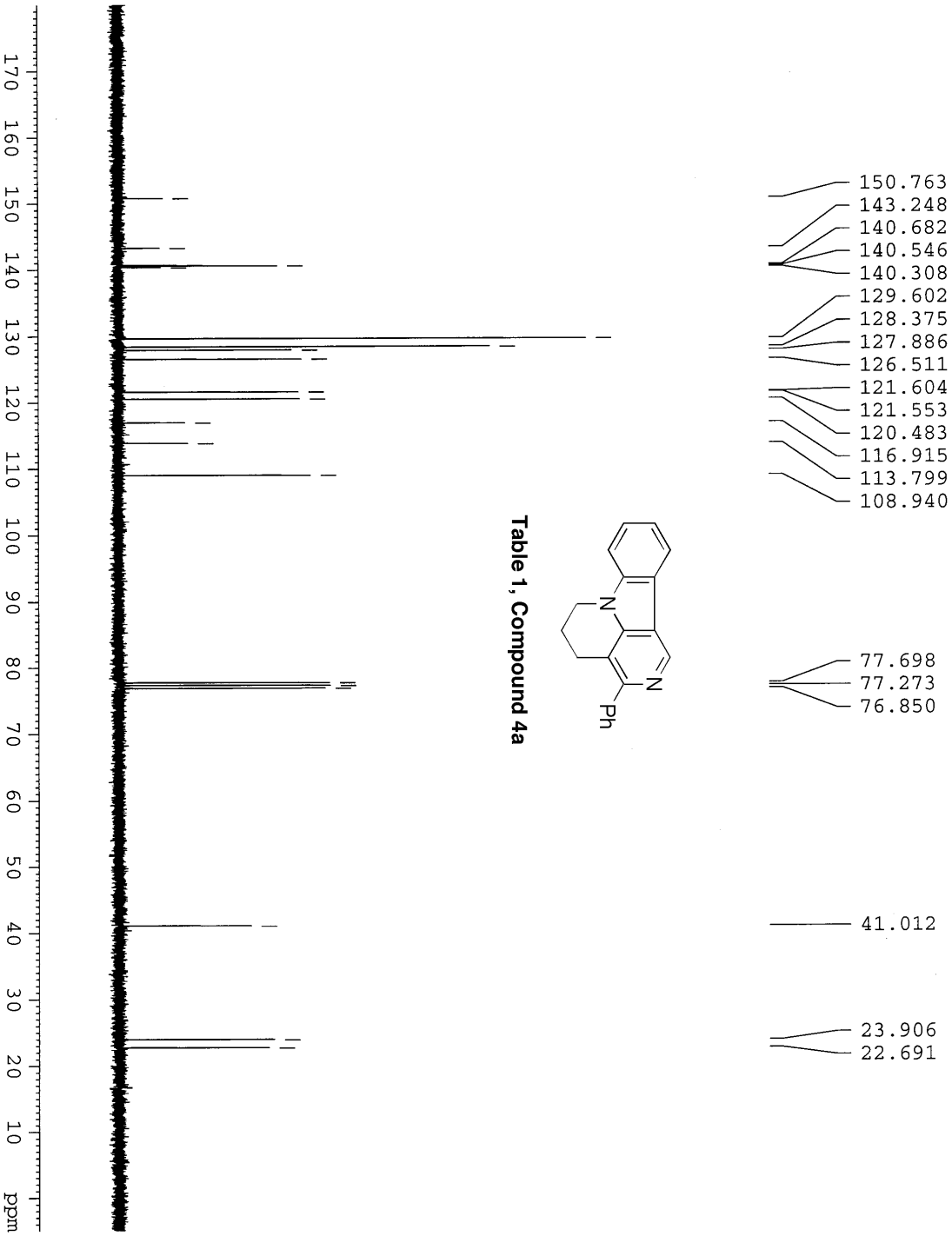

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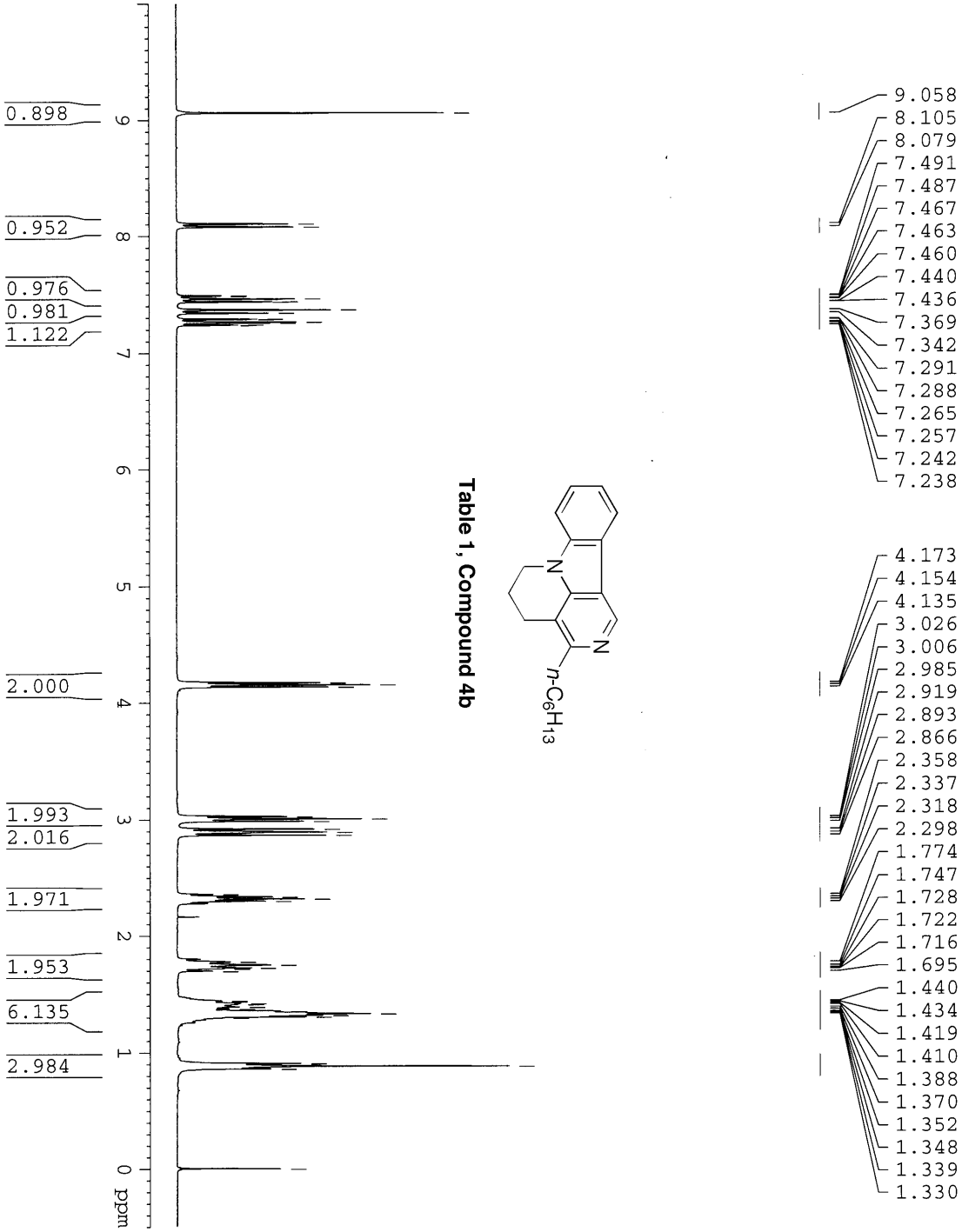

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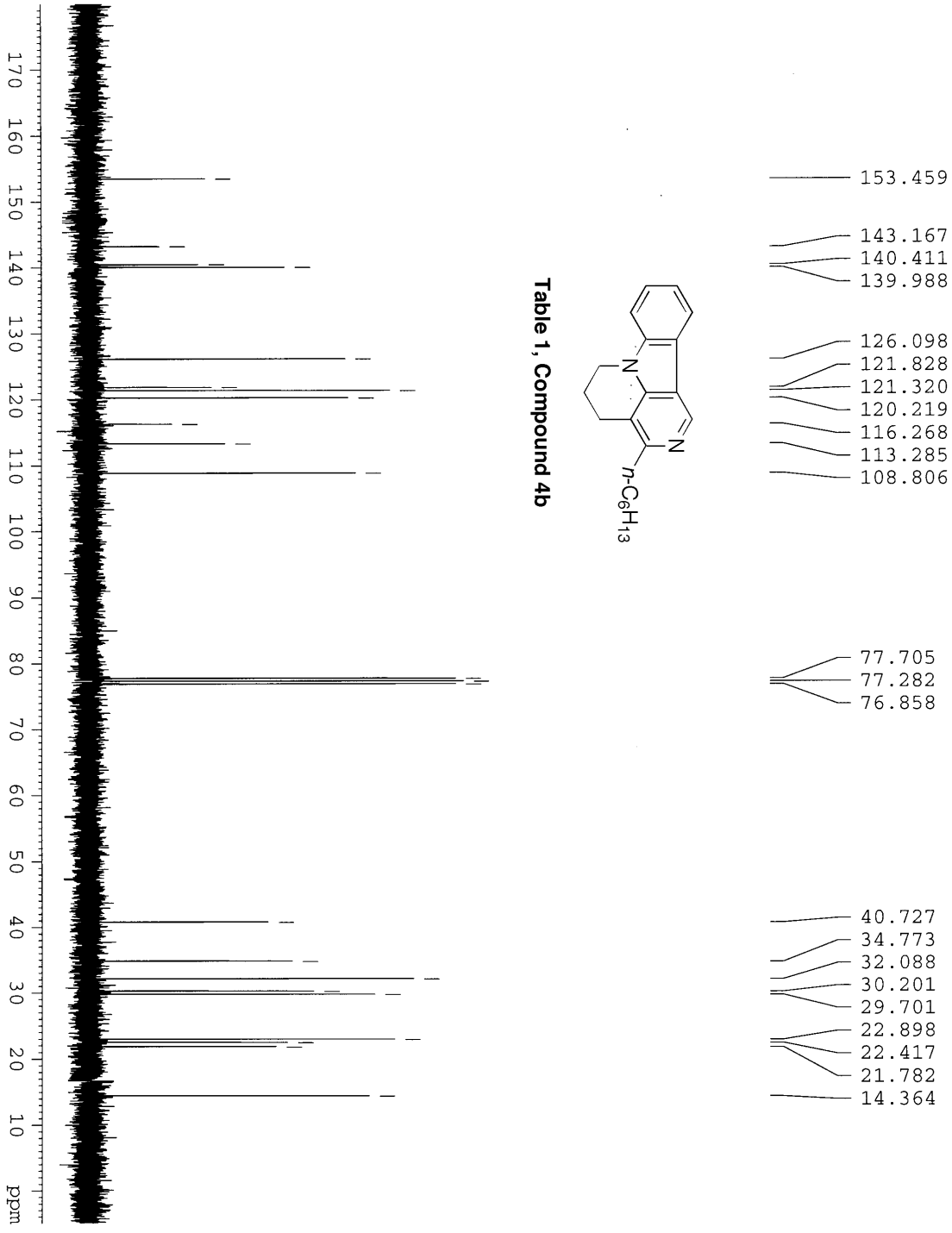

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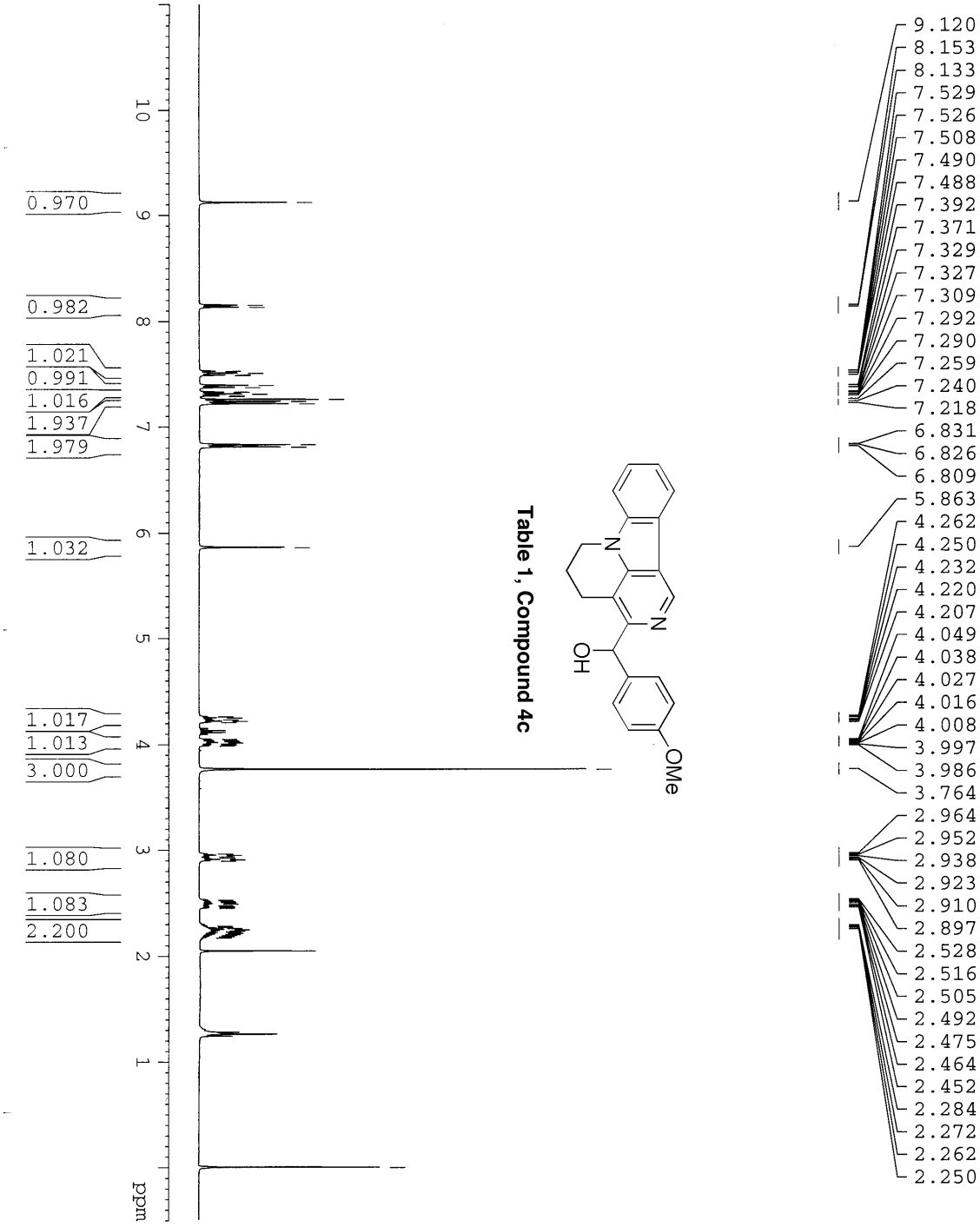

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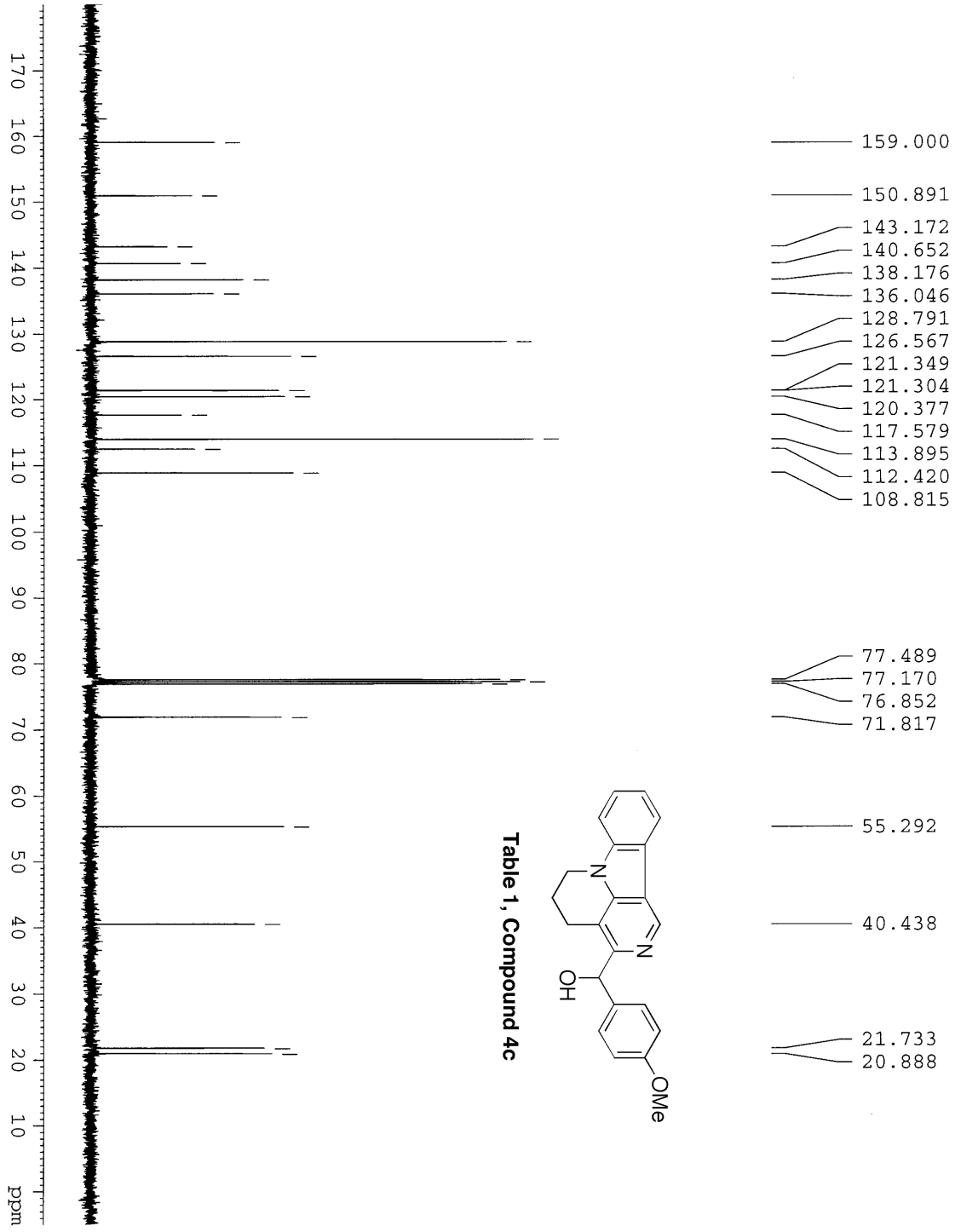

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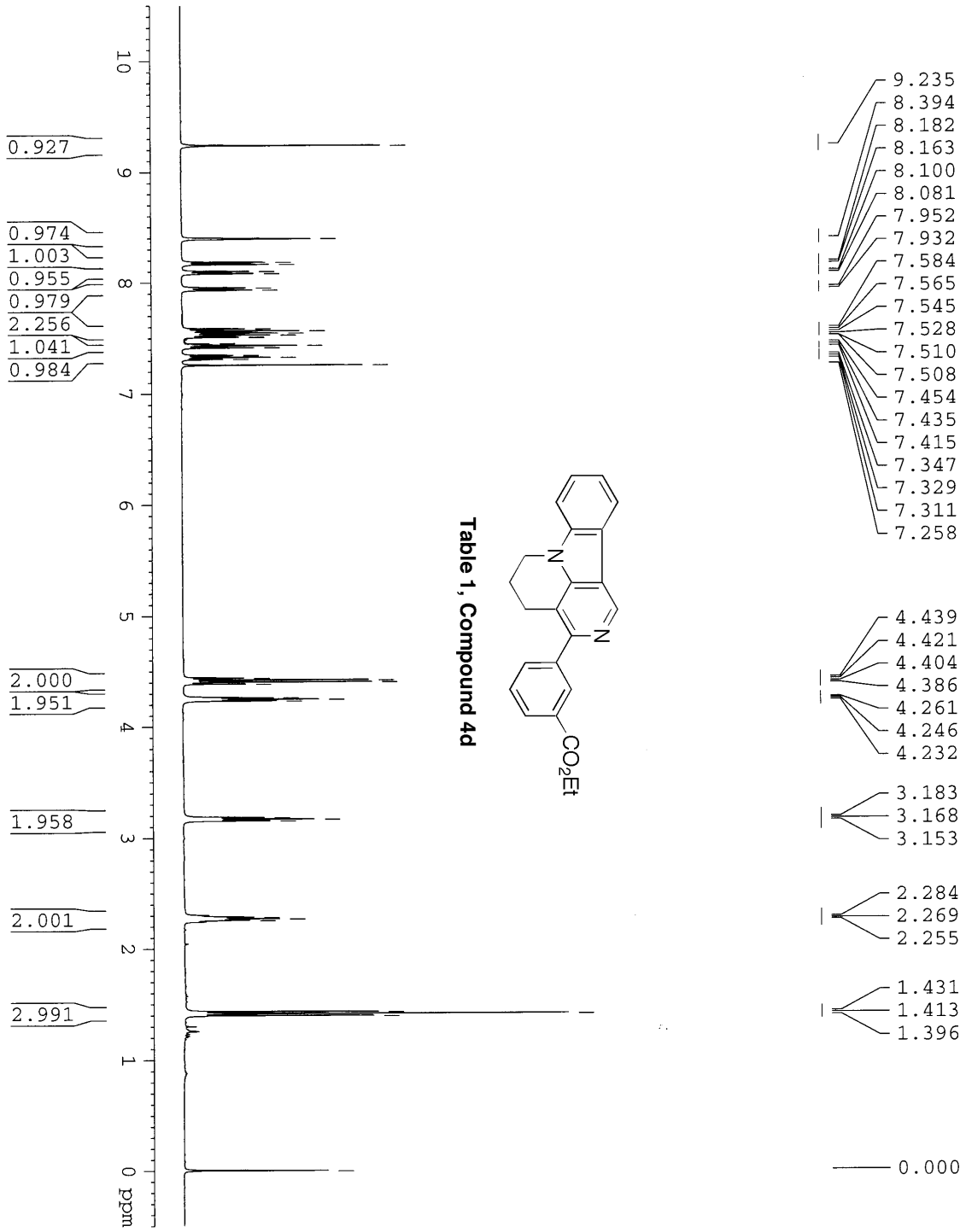

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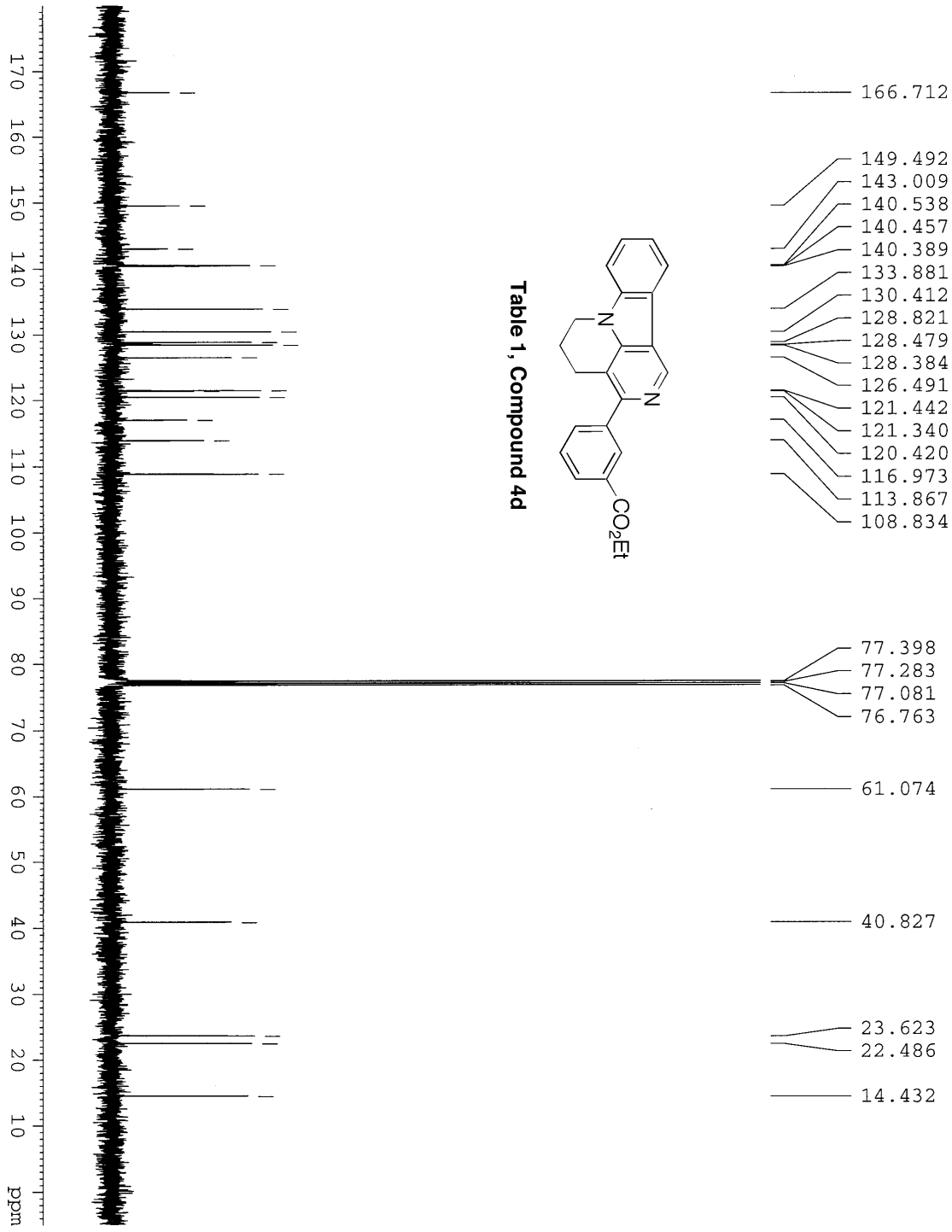

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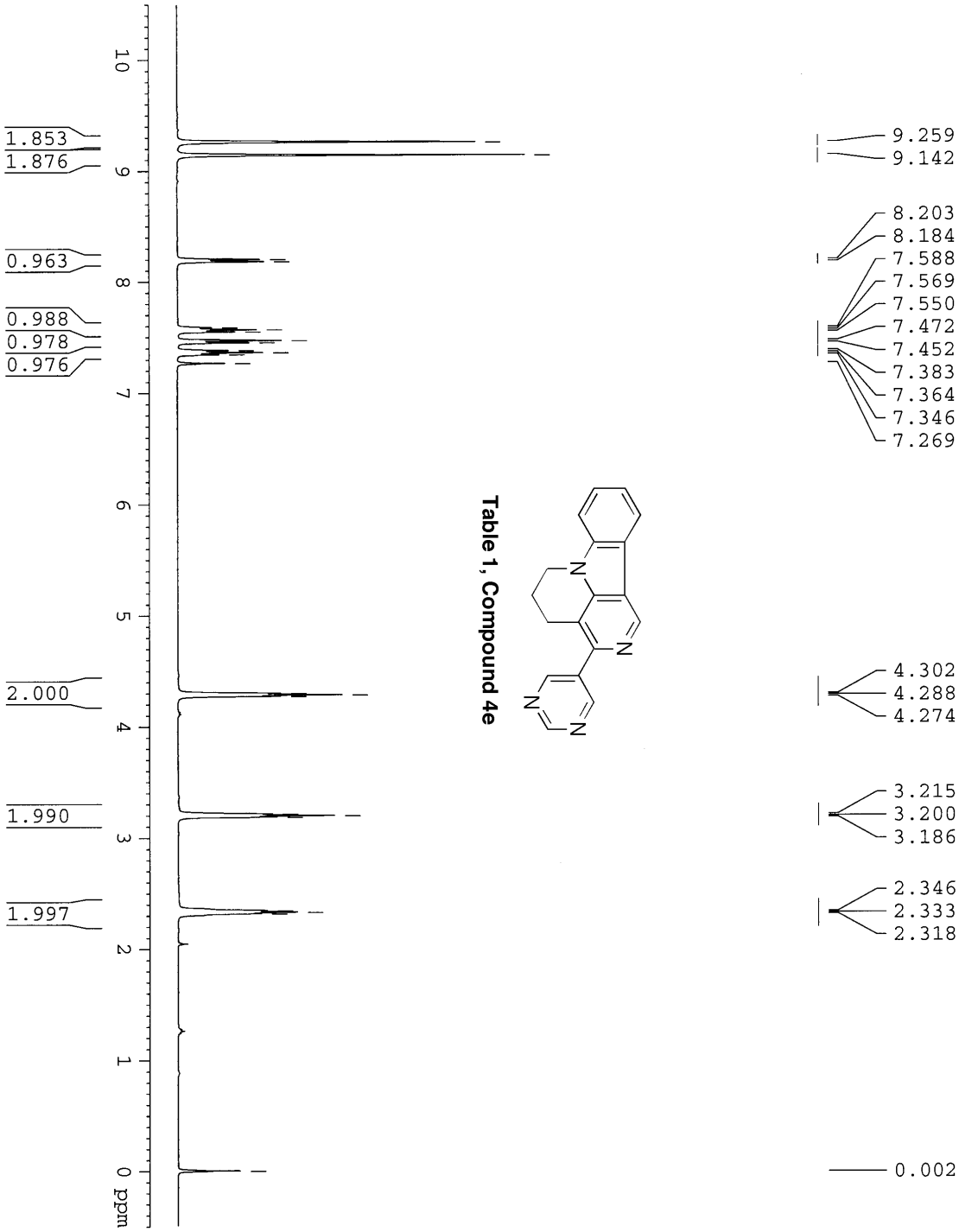

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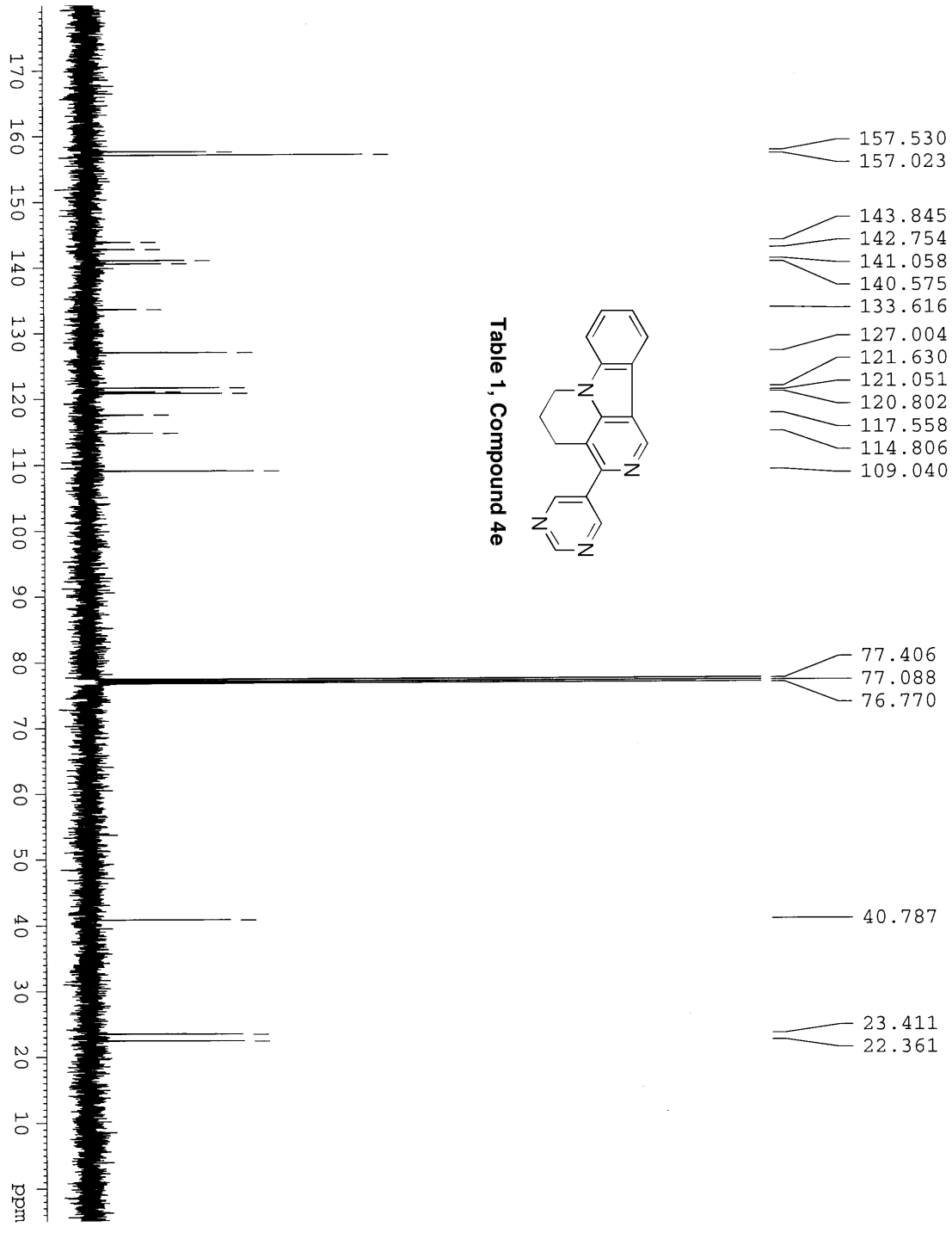

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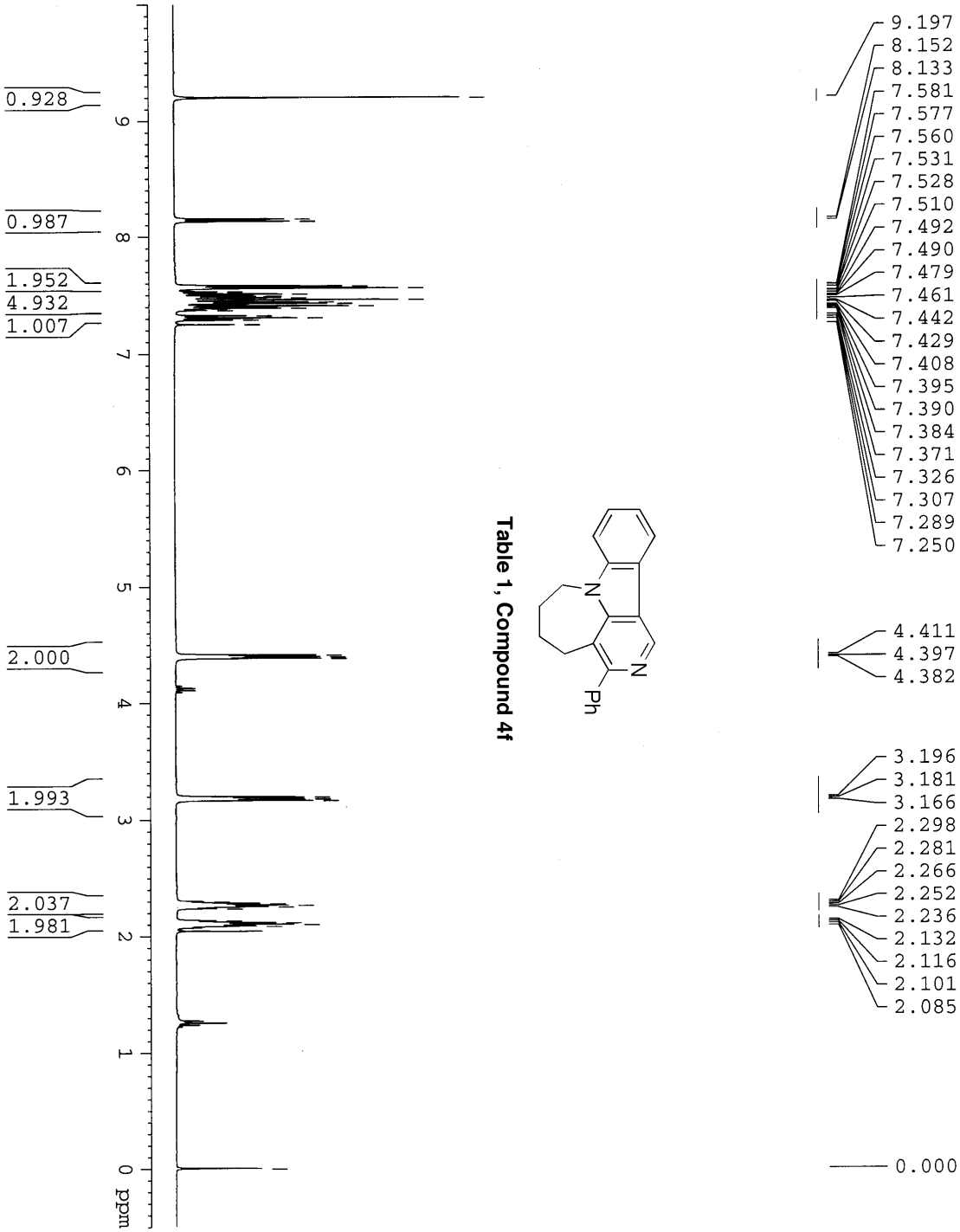

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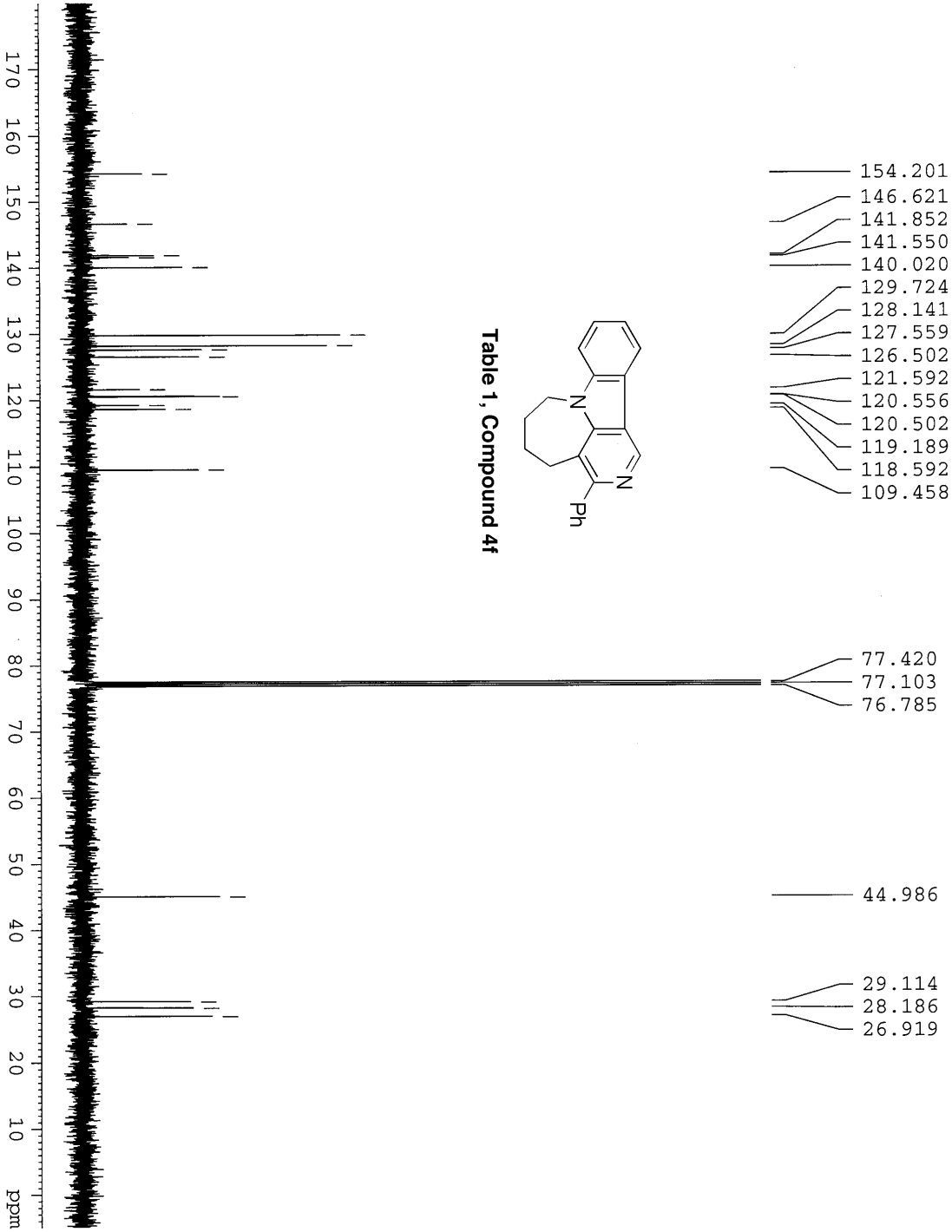

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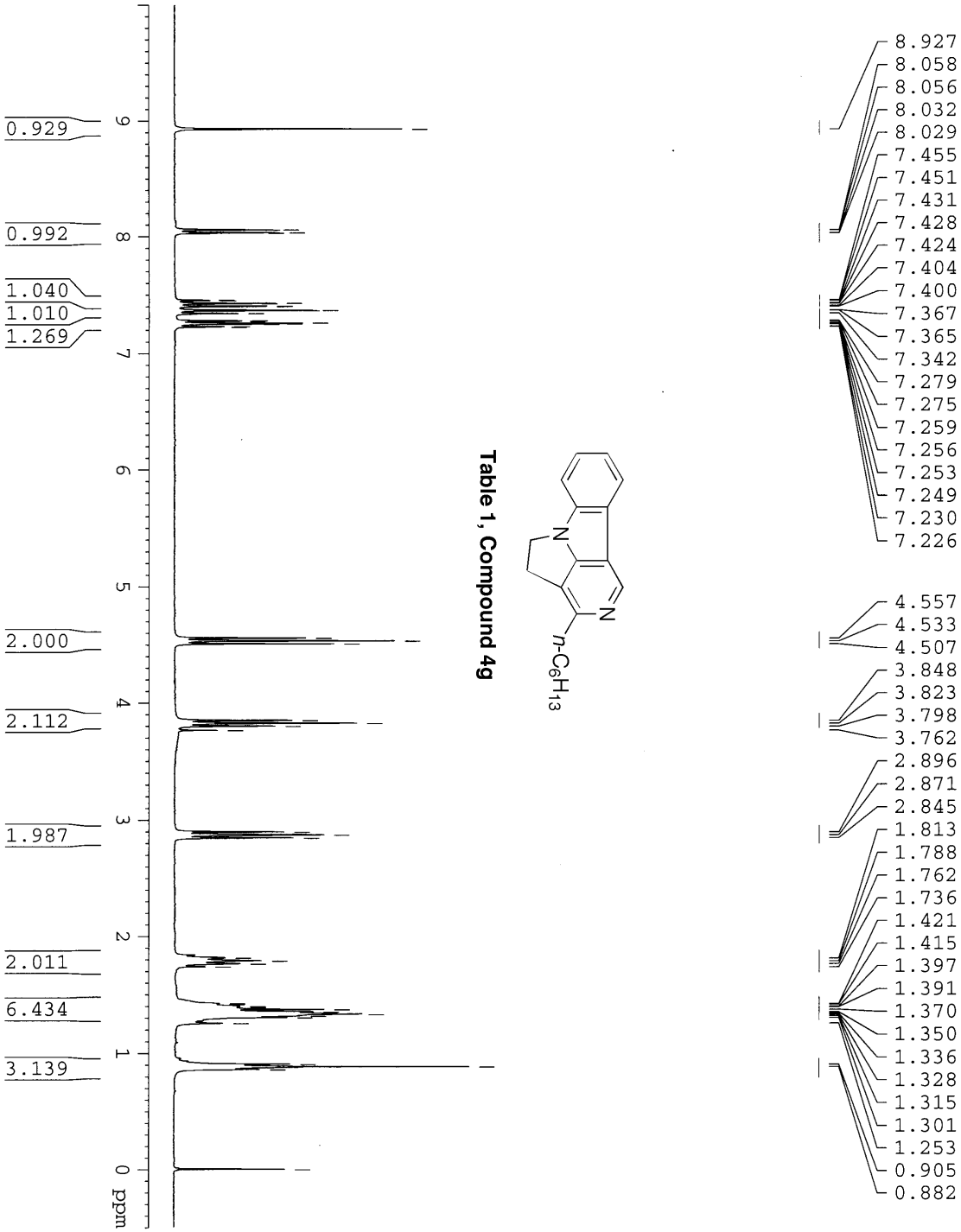

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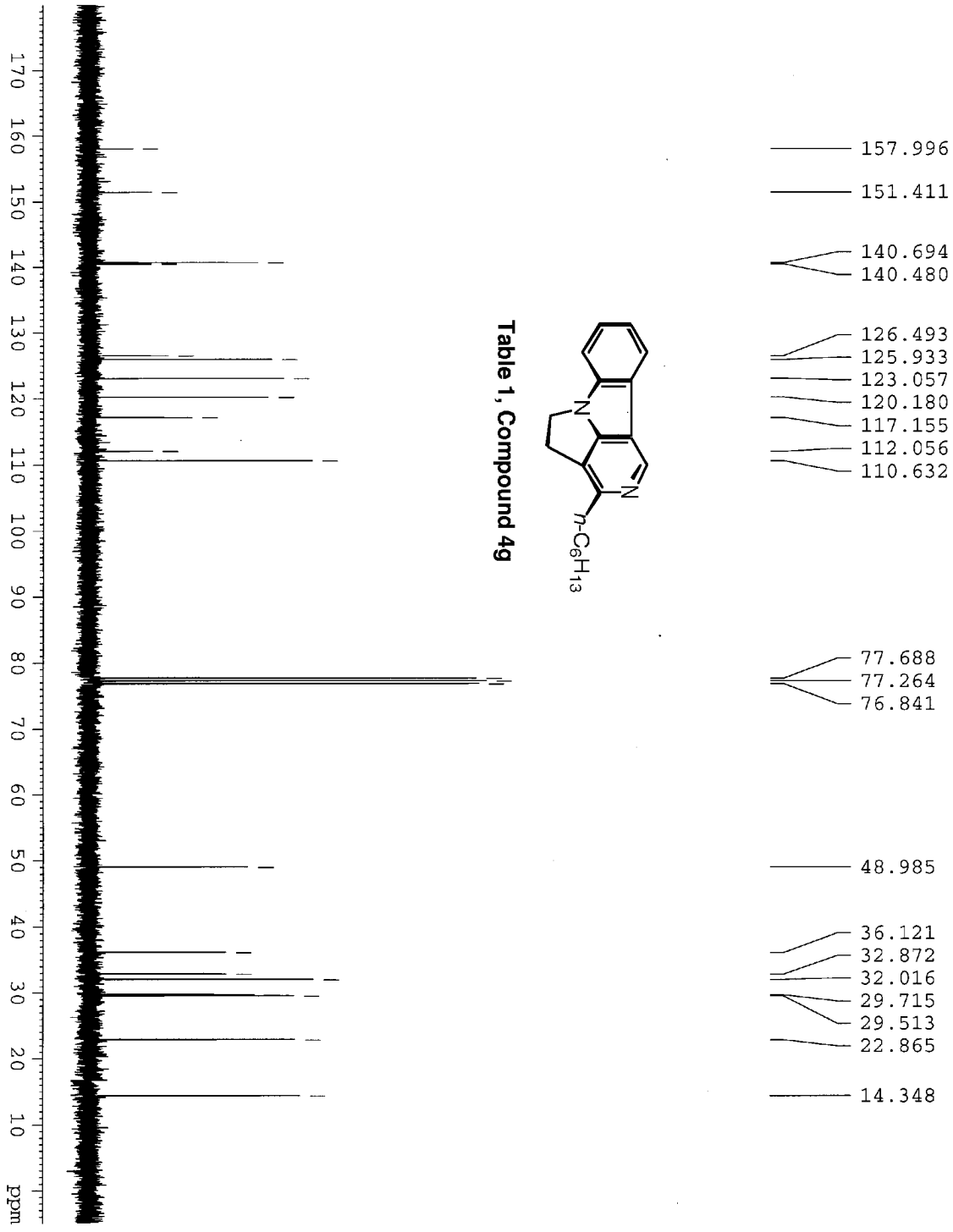


Table 1, Compound 4g

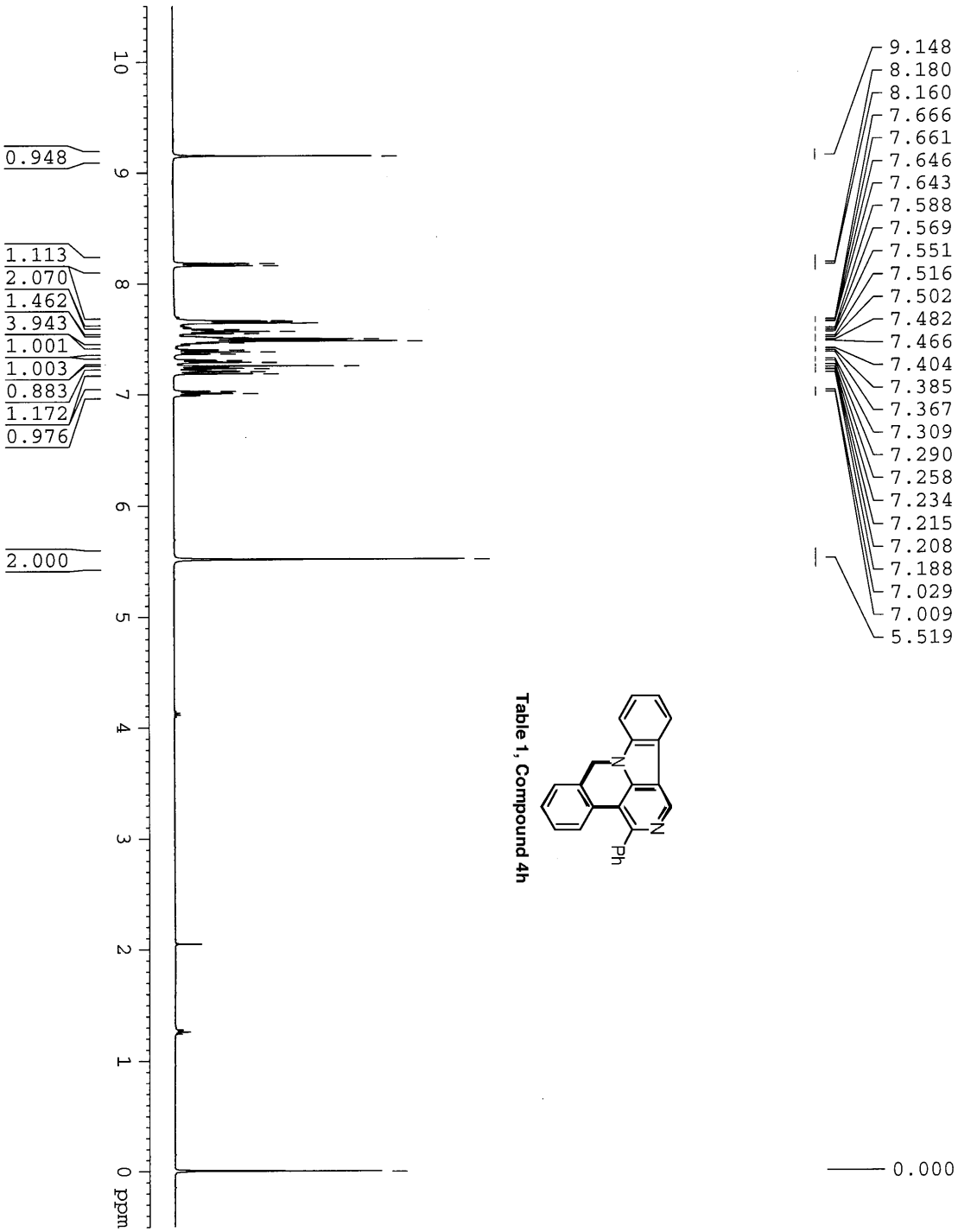
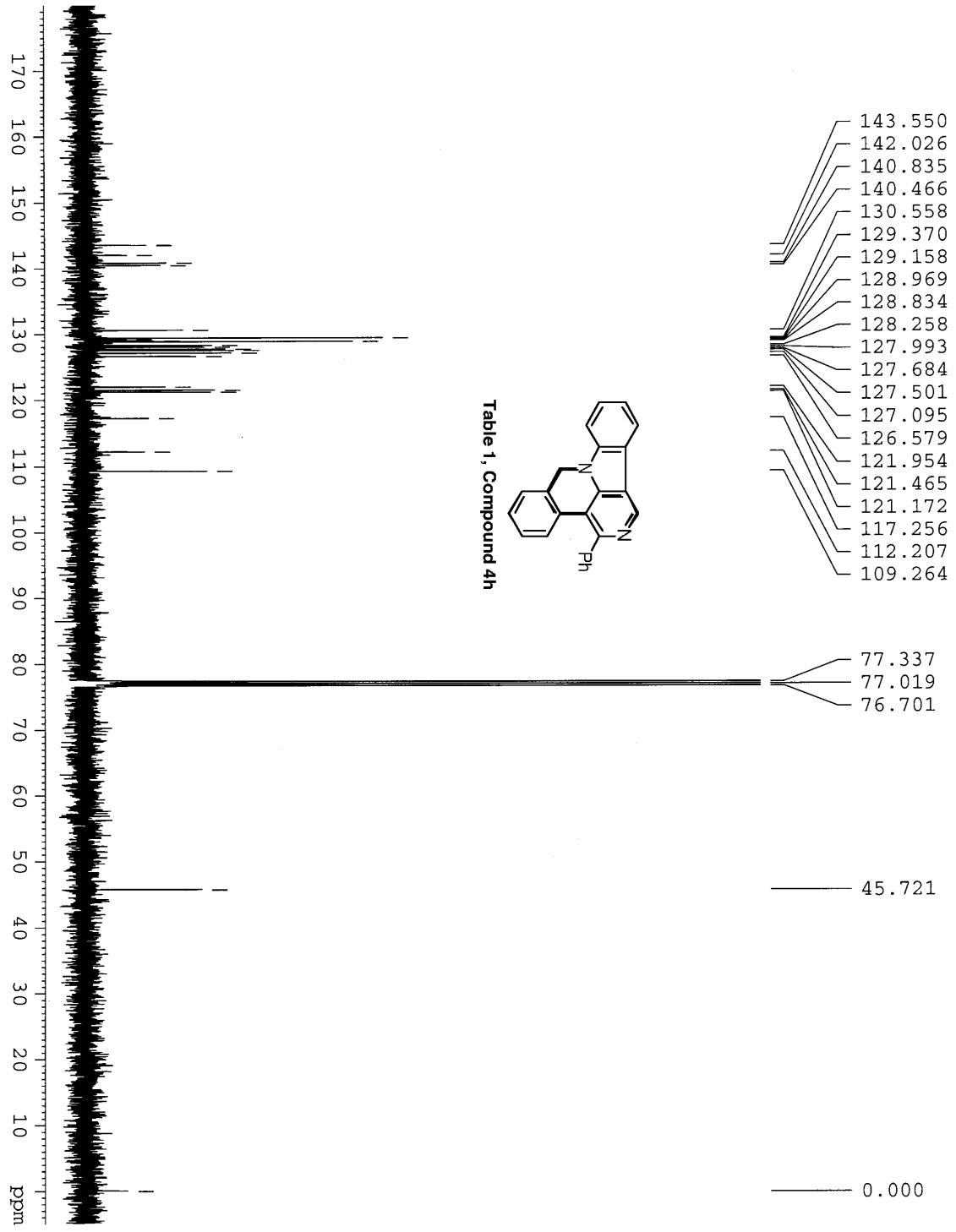


Table 1, Compound 4h


143.550
142.026
140.835
140.466
130.558
129.370
129.158
128.969
128.834
128.258
127.993
127.684
127.501
127.095
126.579
121.954
121.465
121.172
117.256
112.207
109.264
77.337
77.019
76.701
45.721
0.000
Table 1, Compound 4h
N
N
Ph
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

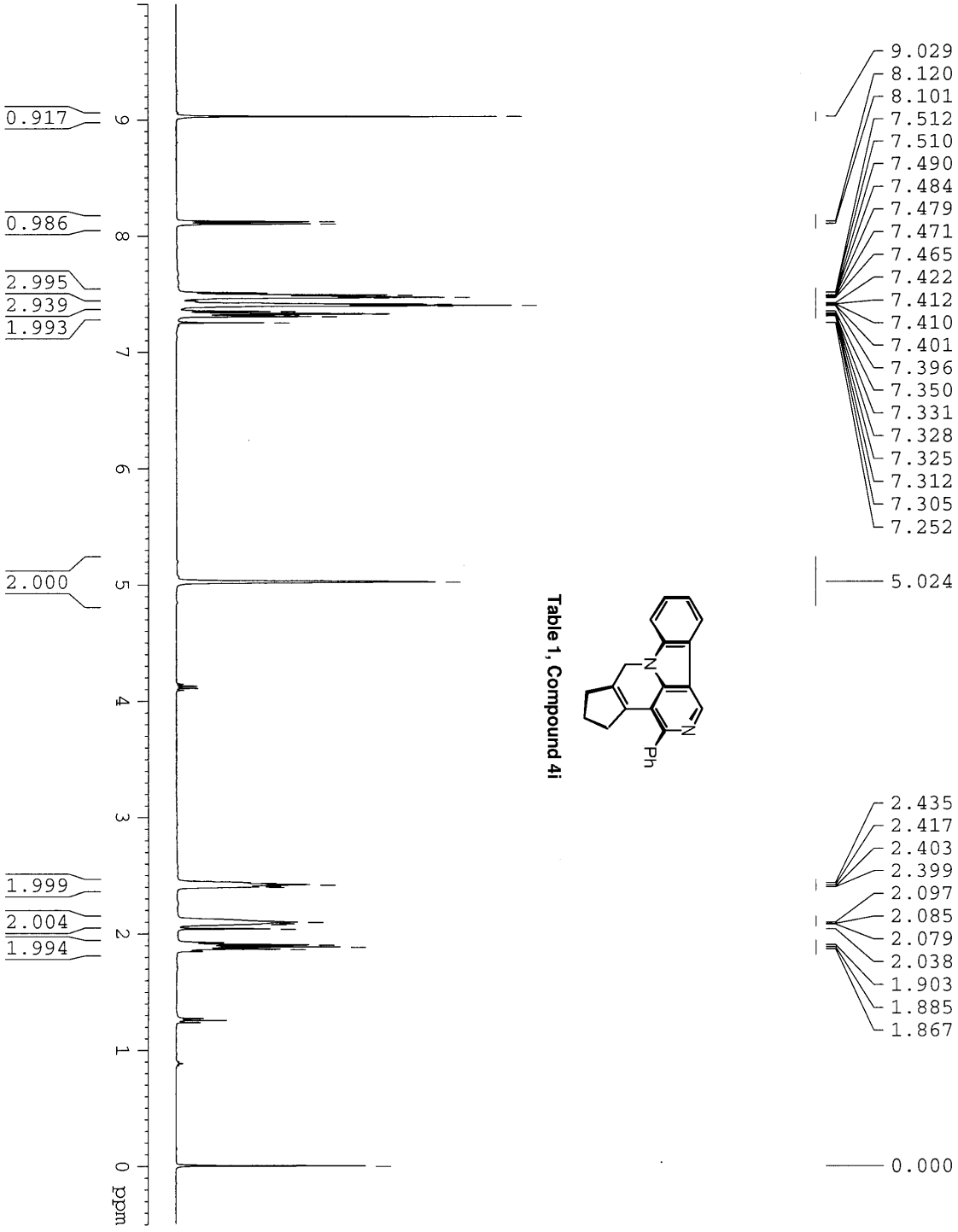
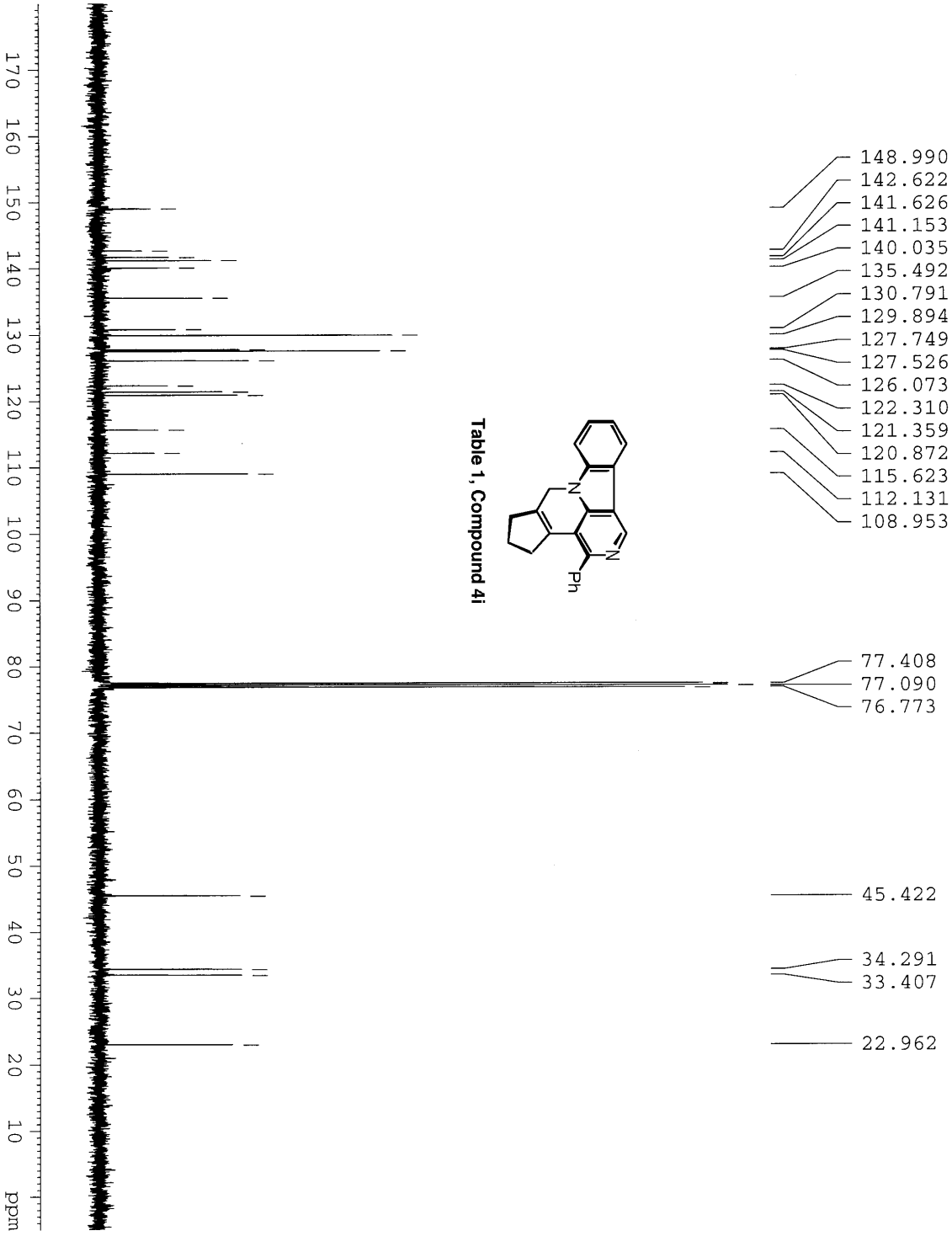


Table 1, Compound 4i


148.990
142.622
141.626
141.153
140.035
135.492
130.791
129.894
127.749
127.526
126.073
122.310
121.359
120.872
115.623
112.131
108.953
77.408
77.090
76.773
45.422
34.291
33.407
22.962
Table 1, Compound 4i
N
N
Ph
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

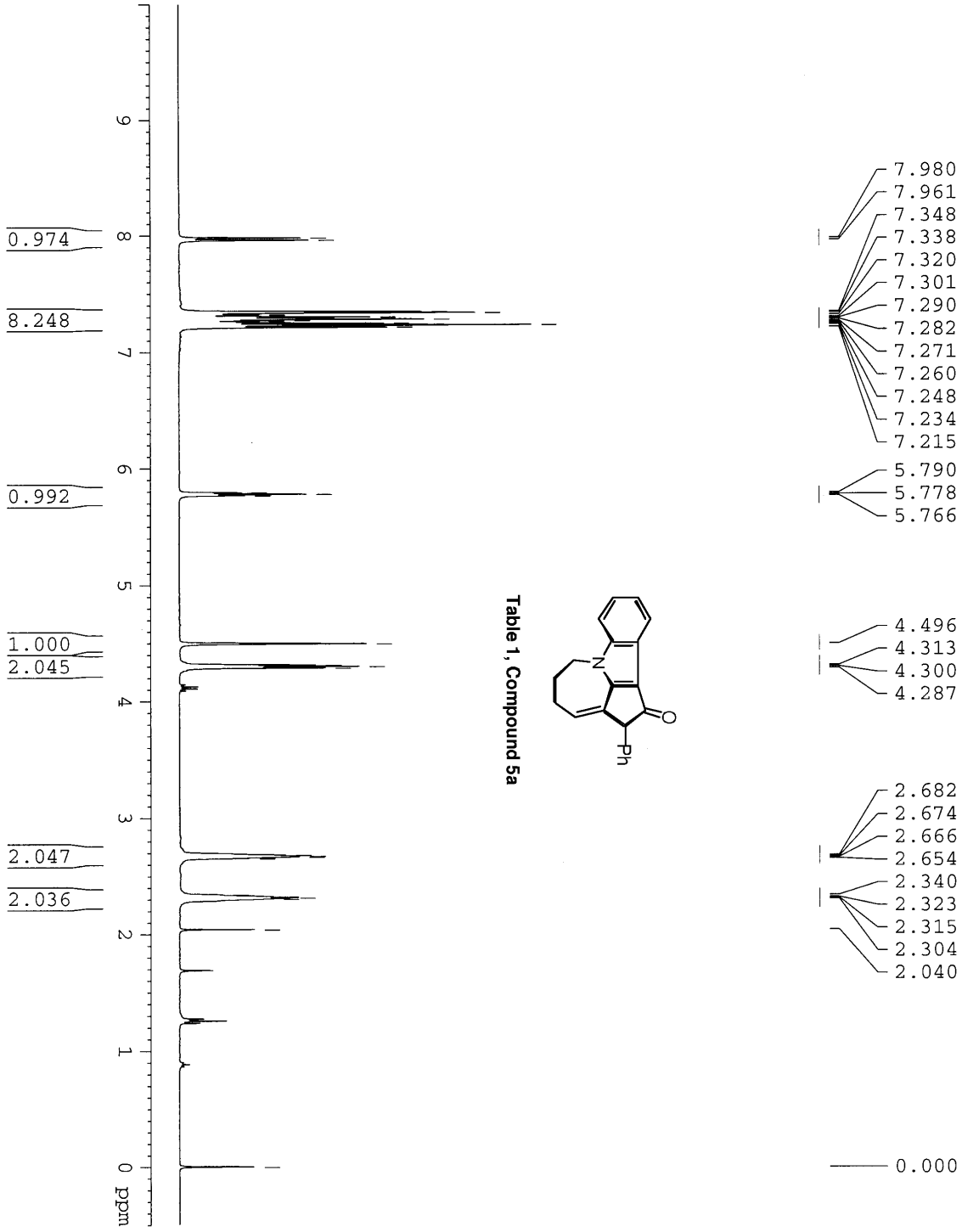
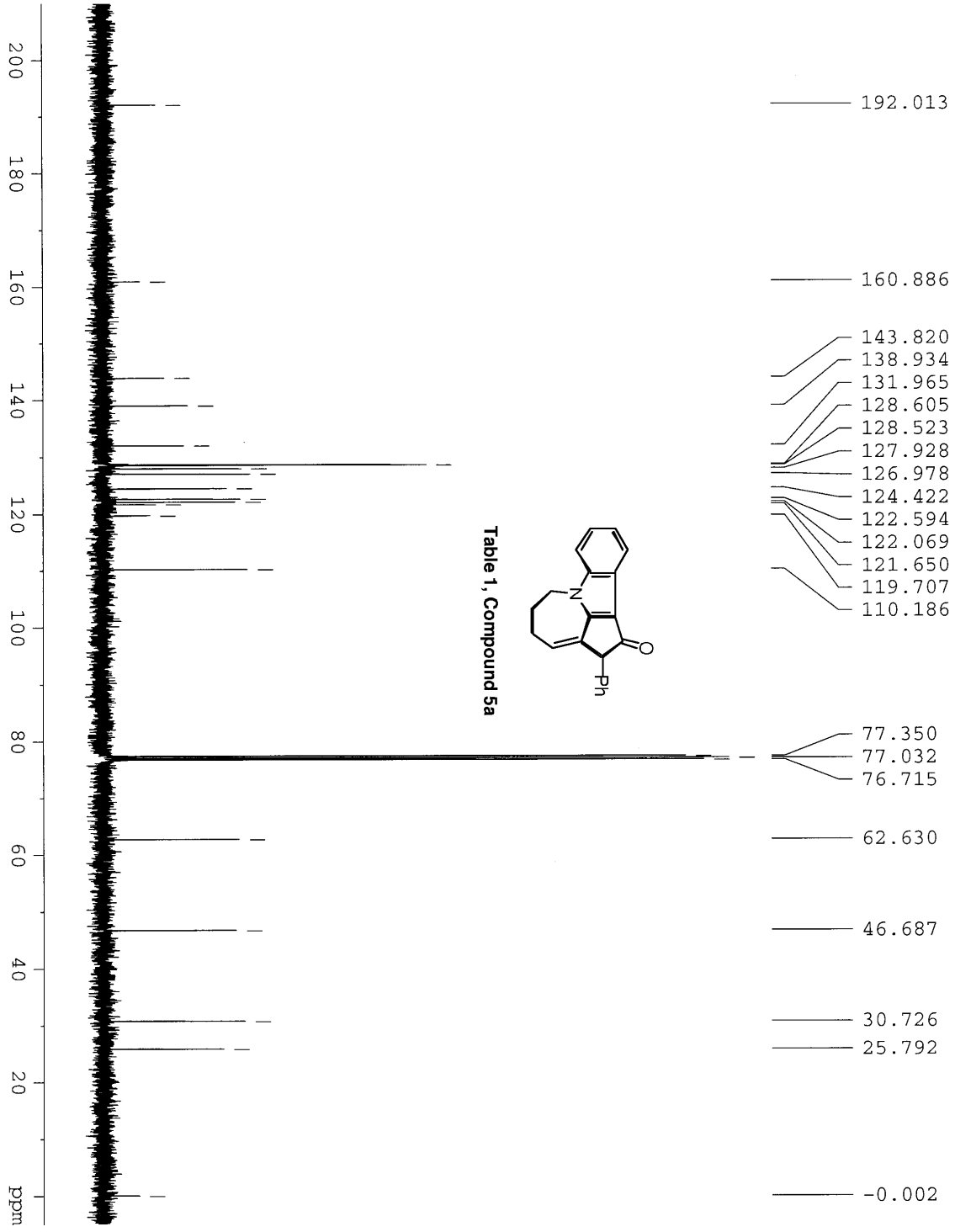


Table 1, Compound 5a


200
180
160
140
120
100
80
60
40
20
ppm
192.013
160.886
143.820
138.934
131.965
128.605
128.523
127.928
126.978
124.422
122.594
122.069
121.650
119.707
110.186
77.350
77.032
76.715
62.630
46.687
30.726
25.792
-0.002
Table 1, Compound 5a
N
O
Ph