Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Synthesis of Substituted 8-Aminoquinolines and Phenanthrolines through a Povarov Approach

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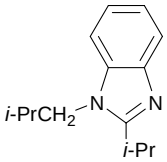
Experimental section

Materials and methods

1,1,1-Trifluoroethanol was purchased from Fluorochem. Melting points were recorded on a Stuart SMP10 apparatus. NMR spectra were recorded on Brucker AC 300 instruments in $CDCl_3$. Chemical shifts are given in parts per million (ppm) from TMS as internal standard. All the reagents received from suppliers were used without further purification.

1-Isobutyl-2-isopropyl-1H-benzo[d]imidazole (2)[1]



To a stirred solution of isobutyraldehyde (2 mmol, 144 mg) in TFE (1 mL), a solution of 1,2-phenylenediamine **1a** (1 mmol, 108 mg) in TFE (1 mL) was added at room temperature. After completion of the reaction (3 h, TLC monitoring), TFE was evaporated under vacuum and the compound was purified by column chromatography on silica gel (cyclohexane/ethyl acetate, 15:85).

Yield 71%, 153 mg; semi solid

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.89 (d, J= 6.8 Hz, 6H), 1.37 (d, J= 6.8 Hz, 6H), 2.11 (sept, J= 6.6 Hz, 1H), 3.16 (sept, J= 6.8 Hz, 1H), 3.86 (d, J= 7.7 Hz, 2H), 7.12-7.15 (m, 2H), 7.45 (dd, J= 3.2, 9.2 Hz, 1H), 7.65 (dd, J= 3.3, 9.2 Hz, 1H);

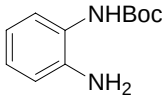
^{13}C NMR (75 MHz, $CDCl_3$): δ 20.2, 21.9, 26.3, 29.3, 50.8, 109.9, 119.1, 121.7, 135.1, 142.5, 160.2

General procedure for the preparation of 1b-c

To a stirred solution of the corresponding 1,2-phenylenediamine (10 mmol) in TFE (10 mL), Boc anhydride (11 mmol) was added at room temperature and the reaction mixture was heated at reflux. After completion of the reaction (4 h, TLC monitoring), TFE was evaporated under vacuum and the compound was purified by column chromatography on silica gel (cyclohexane/ethyl acetate, 15:85).

[1] Cho, C. S.; Kim, J. U. *Bull. Korean Chem. Soc.* **2008**, *29*,1097.

(2-Amino-phenyl)-carbamic acid tert-butyl ester (1b)[2]

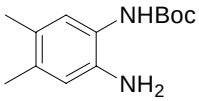


Yield 75%, 1.6 g; white solid: Mp: 114 °C

^{1}H NMR (300 MHz, $CDCl_3$): 1.51 (s, 9H), 3.74 (bs, 2H), 6.31 (bs, 1H), 6.74-6.81 (m, 2H), 6.97-7.02 (m, 1H), 7.27 (d, J= 7.5 Hz, 1H)

^{13}C NMR (75 MHz, $CDCl_3$): 28.3, 80.5, 117.6, 119.6, 124.8, 126.1, 139.9, 153.9

(2-Amino-4,5-dimethyl-phenyl)-carbamic acid tert-butyl ester (1c)[3]



Yield 76%, 1.8 g, white solid: Mp: 146 °C

^{1}H NMR (300 MHz, $CDCl_3$): 1.51 (s, 9H), 2.14(s, 3H), 2.15 (s, 3H), 3.57 (bs, 1H), 6.21 (bs, 1H), 6.56 (s, 1H), 7.02 (s, 1H)

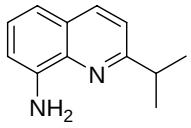
^{13}C NMR (75 MHz, $CDCl_3$): 18.8, 19.2, 28.3, 80.2, 119.1, 122.3, 125.7, 127.5, 134.3, 137.5, 153.9

General procedure for the synthesis of 8-aminoquinolines 4, 5 and 8 via aza-Diels-Alder reaction in TFE

To a stirred solution of aldehyde (2.2 mmol) and ethyl vinyl ether (6 mmol) in TFE (2 mL), a solution of **1b** or **1c** (2.0 mmol) in TFE (2 mL) was added at room temperature. After completion of the reaction (TLC monitoring), TFE was evaporated under vacuum to afford the crude cycloaddition product. Then, this latter product (2.0 mmol) was dissolved in acetonitrile (2 mL), aq HCl (6 N, 0.8 mL) was added and the reaction mixture was placed under oxygen atmosphere (1 atm) and stirred. After 16 h, dichloromethane (50 mL) was added and the reaction mixture was transferred to a separating funnel and washed with saturated aqueous $NaHCO_3$ solution (2×25 mL). The organic layer was separated and the aqueous layer was washed with dichloromethane (3×25 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and the solvents were evaporated under vacuum. The product was purified by column chromatography on silica gel (cyclohexane/ethyl acetate, 90:10).

[2]Varala, R.; Nuvula, S.; Adapa, S.R. *J. Org. Chem.*, **2006**, *71*, 8283
[3] Maggio-Hall, L. A.; Dorrestein, P. C.; Escalante-Semerena, J. C.; Begley, T. P. *Org. Lett*. **2003**, 5, 2211.

2-Isopropyl-quinolin-8-ylamine (4)



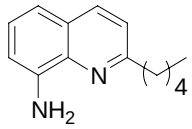
Yield 46%, 171 mg; yellow oil

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.30 (d, J= 6.8 Hz, 6H), 3.13 (sept, J= 6.9 Hz, 1H), 4.91 (bs, 2H), 6.82, (d, J= 7.5 Hz, 1H), 7.03 (d, J= 8.1 Hz, 1H), 7.15- 7.21 (m, 2H), 7.88, (d, J= 8.5 Hz, 1H)

^{13}C NMR (75 MHz, $CDCl_3$): 22.5, 36.8, 104.4, 109.9, 115.8, 120.0, 126.3, 127.2, 136.1, 143.6, 164.5

Anal. calcd. for $C_{12}H_{14}N_2$: C, 77.38; H, 7.58; N, 15.04; found: C, 77.67; H, 7.47; N, 15.27

2-n-Pentyl-quinolin-8-ylamine (5)



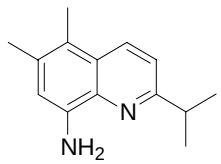
Yield 55%, 235 mg; yellow oil

^{1}H NMR (300 MHz, $CDCl_3$): 0.87-0.92 (m, 3H), 1.35-1.38 (m, 4H), 1.76-1.86 (m, 2H), 2.92 (t, J= 7.8 Hz, 2H), 6.87 (dd, J= 1.2, 7.4 Hz, 1H), 7.08, (dd, J= 1.1, 8.1 Hz, 1H), 7.19-7.24 (m, 2H), 7.92 (d, J= 8.4 Hz, 1H)

^{13}C NMR (75MHz, $CDCl_3$): 14.1, 22.6, 29.3, 31.7, 38.8, 110.1, 115.9, 121.6, 126.4, 127.1, 136.2, 137.7, 143.5, 160.1

Anal. calcd. for $C_{14}H_{18}N_2$: C, 78.46; H, 8.47; N, 13.07; found: C, 78.69; H, 8.49; N, 13.22

2-Isopropyl-5,6-dimethyl-quinolin-8-ylamine (8)



Yield 54%, 231 mg; brown oil;

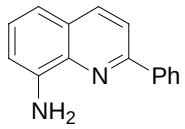
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42 (d, J= 7.0 Hz, 6H), 2.40 (s, 3H), 2.45 (s, 3H), 3.24 (sept, J= 7.0 Hz, 1H), 4.85 (bs, 2H), 6.79 (s, 1H), 7.30 (d, J= 8.7 Hz, 2H), 8.2 (d, J = 8.7 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): 13.2, 20.5, 22.5, 36.4, 113.3, 119.2, 119.3, 126.4, 132.3, 133.2, 136.9, 141.1, 162.8

Anal. calcd. for $C_{14}H_{18}N_2$: C, 78.46; H, 8.47; N, 13.07, found: C 78.67, H 8.27, N 13.45

Procedure for the synthesis of 2-phenyl-quinolin-8-ylamine 7

To a solution of $Yb(OTf)_3$ (0.1 mmol, 62 mg) in acetonitrile (2 mL) was added the imine derived from **1b** and benzaldehyde (2.0 mmol, 593 mg) and ethyl vinyl ether (6 mmol, 426 mg) in acetonitrile (3 mL) at room temperature. The reaction mixture was stirred for 15 min, then a saturated aqueous $NaHCO_3$ solution (20 mL) was added, and the product was extracted with ether (30 mL). The organic layered was dried over $MgSO_4$, filtered and solvents were evaporated under vacuum to afford the crude cycloaddition product. Then, this latter product (2 mmol) was dissolved in acetonitrile (2 mL), aq HCl (6 N, 0.8 mL) was added and the reaction mixture was placed under oxygen atmosphere (1 atm) and stirred. After 16 h, dichloromethane (50 mL) was added and the reaction mixture was transferred to a separating funnel and washed with saturated aqueous $NaHCO_3$ solution (2×25 mL). The organic layer was separated and the aqueous layer was washed with dichloromethane (3×25 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and the solvents were evaporated under vacuum. The product was purified by column chromatography on silica gel (cyclohexane/ethyl acetate, 90:10).



Yield 51%, 224 mg; yellow oil,

^{1}H NMR (300 MHz, $CDCl_3$): 5.01 (bs, 2H), 6.84 (dd, J= 1.2, 7.5 Hz, 1H), 7.18-7.22 (m, 2H), 7.36-7.43 (m, 3H), 7.77 (d, J= 8.6 Hz, 1H), 8.03 (d, J= 8.6 Hz, 1H), 8.10 (dd, J= 1.5, 6.9 Hz, 2H)

^{13}C NMR (75 MHz, $CDCl_3$): 110.2, 115.7, 118.8, 127.2, 127.3, 128.7, 129.0, 136.8, 139.6, 144.1, 154.1

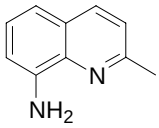
Anal. calcd. for $C_{15}H_{12}N_2$: C, 81.79; H, 5.49; N, 12.72; found: C 81.60, H 5.23, N 12.95

General procedure for the synthesis of 8-aminoquinolines 6 and 9 via domino aza-Diels-Alder reaction in HFIP

To a stirred solution of ethyl vinyl ether (20 mmol) in HFIP (2 mL), a solution of the amine (2.0 mmol) in HFIP (2 mL) was added at 30 °C and the reaction mixture was stirred for an appropriate time. After completion of the reaction (TLC monitoring), HFIP was evaporated under vacuum to afford the crude cycloaddition product. Then, this latter product (2.0 mmol) was dissolved in acetonitrile (2 mL), aq HCl (6 N, 0.8 mL) was added and the reaction mixture was placed under oxygen atmosphere (1 atm) and stirred. After 16 h,

dichloromethane (50 mL) was added and the reaction mixture was transferred to a separating funnel and washed with saturated aqueous $NaHCO_3$ solution (2×25 mL). The organic layer was separated and the aqueous layer was washed with dichloromethane (3×25 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and the solvents were evaporated under vacuum. The product was purified by column chromatography on silica gel (cyclohexane/ethyl acetate, 90:10).

2-Methyl-quinolin-8-ylamine (6)[4]



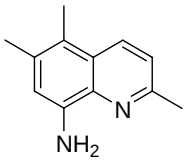
Yield: 50%, 158 mg; yellow oil,

^{1}H NMR (300 MHz, $CDCl_3$): 2.72 (s, 3H), 4.98 (bs, 2H), 6.91 (d, J= 7.4 Hz, 1H), 7.12 (d, J= 8.0 Hz, 1H), 7.22-7.27 (m, 2H), 7.94, (d, J= 8.4 Hz, 1H)

^{13}C NMR (75MHz, $CDCl_3$): 25.2, 110.1, 115.9, 122.1, 126.3, 126.9, 136.1, 137.9, 143.4, 156.1

Anal. calcd. for $C_{10}H_{10}N_2$ C, 75.92; H, 6.37; N, 17.71; found: C 76.33, H 6.21, N 17.32

2,5,6-Trimethyl-quinolin-8-ylamine (9)[5]



Yield 50%, 186 mg; white solid mp: 77 °C (Lit: 80-81 °C),

^{1}H NMR (300 MHz, $CDCl_3$): 2.39 (s, 3H), 2.43 (s, 3H), 2.71 (s, 3H), 4.81 (bs, 2H), 6.77 (s, 1H), 7.23 (d, J= 8.7 Hz, 1H), 8.13 (d, J= 8.7 Hz, 1H)

^{13}C NMR (75 MHz, $CDCl_3$): 13.2, 20.5, 24.8, 113.4, 119.2, 121.5, 126.0, 132.2, 133.2, 137.2, 140.9, 154.3

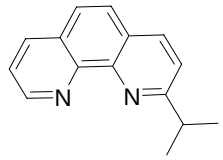
Anal. calcd. for $C_{12}H_{14}N_2$: C, 77.38; H, 7.58; N, 15.04; found: C 77.69, H 7.28, N 15.05

[4] (a) Lund, G.K. *J. Chem. Eng. Dat* **1981**, *26*, 227, Roth, R. *Helv. Chimica Acta*, **1954**, *37*, 1064. (b) Raymond, Z.; Weibel, N.; Charbonnière, L. J. *Synthesis* **2006** , 3127.
[5] Case, F.H. *J. Org. Chem.* **1954**, *19*, 919.

General procedure for the synthesis of phenanthrolines 10, 12, 13, 15 and 16 from 8-aminoquinolines via aza-Diels-Alder reaction in TFE

To a stirred solution of the aldehyde (0.55 mmol) and ethyl vinyl ether (1.5 mmol) in TFE (1 mL), a solution of the 8-aminoquinoline (0.5 mmol) in TFE (1 mL) was added at room temperature and the reaction mixture was stirred for an appropriate time. After completion of the reaction (TLC monitoring), TFE was evaporated under vacuum to afford the crude cycloaddition product. Then, this latter product (0.5 mmol) was dissolved in acetonitrile (0.5 mL), aq HCl (6 N, 0.2 mL) was added and the reaction mixture was placed under oxygen atmosphere (1 atm) and stirred. After 16 h, dichloromethane (25 mL) was added and the reaction mixture was transferred to a separating funnel and washed with saturated aqueous $NaHCO_3$ solution (2×15 mL). The organic layer was separated and the aqueous layer was washed with dichloromethane (3×15 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and the solvents were evaporated under vacuum. The product was purified by column chromatography on silica gel (cyclohexane/ethyl acetate, 95:5 to 85:15).

2-Isopropyl-[1,10]phenanthroline (10)[6]



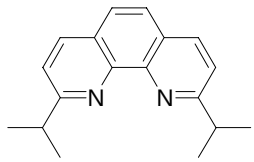
Yield: 49%, 54 mg, yellow oil;

^{1}H NMR (300 MHz, $CDCl_3$): 1.42 (d, J= 7.0 Hz, 6H), 3.64 (sept, J= 7.0 Hz, 1H), 7.54-7.57 (m, 2H), 7.68-7.69 (m, 2H), 8.12-8.19 (m, 2H), 9.19 (dd, J= 1.8, 4.2 Hz, 1H)

^{13}C NMR (75MHz, $CDCl_3$): 23.1, 37.6, 120.0, 122.5, 125.4, 126.3, 127.0, 128.7, 135.9, 136.5, 145.2, 146.0, 150.1, 168.4

Anal. calcd. for $C_{15}H_{14}N_2$: C, 81.05; H, 6.35; N, 12.60; found: C 81.44, H 6.37, N 12.40

2,9-Diisopropyl-[1,10]phenanthroline (12)[6]



Yield 40%, 52 mg; yellow solid, mp: 80 °C (Lit: 98-99 °C),

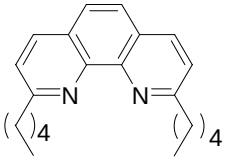
[6] Metallinos, C.; Barrett, F.B.; Wang, Y.; Xu, Shufen.; Taylor, N.J. *Tetrahedron* **2006**, *62*, 11145.

^{1}H NMR (300 MHz, $CDCl_3$): δ1.41 (d, J = 7.0 Hz, 12H), 3.50 (sept, J= 7.0 Hz, 2H), 7.48 (d, J= 8.5 Hz, 2H), 7.62 (s, 2H), 8.08 (d, J= 8.5 Hz, 2H)

^{13}C NMR (75 MHz, $CDCl_3$): 22.9, 37.3, 120.1, 125.5, 127.3, 136.4, 145.2, 167.9

Anal. calcd. for $C_{18}H_{20}N_2$: C, 81.78; H, 7.63; N, 10.60; found: C 81.47, H 7.67, N 10.82

2,9-Dipentyl-[1,10]phenanthroline (13)[7]

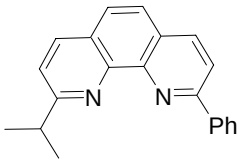


Yield 33%, 53 mg, yellow oil, ^{1}H NMR (300 MHz, $CDCl_3$): 0.94 (t, J= 6.9 Hz, 6H), 1.41-1.51 (m, 8H), 1.94 (pent, J= 7.2 Hz, 4H), 3.19 (t, J= 8.2 Hz, 4H), 7.50, (d, J= 8.3 Hz, 2H), 7.69 (s, 2H), 8.13 (d, J= 8.3 Hz, 2H)

^{13}C NMR (75MHz, $CDCl_3$): 14.1, 22.7, 29.5, 32.1, 39.5, 122.3, 125.4, 127.1, 136.2, 145.4, 163.3

Anal. calcd. for $C_{22}H_{28}N_2$: C, 82.45; H, 8.81; N, 8.74; found: C 82.67, H 8.67, N 8.75

2-Isopropyl-9-phenyl-[1,10]phenanthroline (15)



Yield 50%, 74 mg, yellow oil,

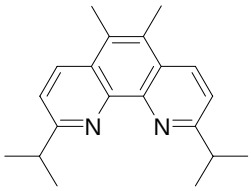
^{1}H NMR (300 MHz, $CDCl_3$): 1.44 (d, J= 7.0 Hz, 6H), 3.50 (sept, J= 7.0 Hz, 1H), 7.44-7.50 (m, 4H), 7.63 (s, 2H), 8.00 (d, J= 8.4 Hz, 1H), 8.07 (d, J= 8.3 Hz, 1H), 8.17 (d, J= 8.4 Hz, 1H), 8.33 (dd, J= 1.5, 7.2 Hz, 2H)

^{13}C NMR (75MHz, $CDCl_3$): 22.8, 37.3, 119.7, 120.6, 125.2, 126.1, 127.7, 128.7, 129.3, 136.3, 136.8, 139.6, 145.9, 156.7, 167.9

Anal. calcd. for $C_{21}H_{18}N_2$: C, 84.53; H, 6.08; N, 9.39; found: C 84.90, H 6.20, N 9.46

[7] Pallenberg, A.J. ; Koenig, K.S. ; Barnhart, D.M. *Inorg. Chem*. **1995**, *34*, 2833.

2,9-Diisopropyl-5,6-dimethyl-[1,10]phenanthroline (16):



Yield: 44%, 47 mg, white solid, mp: 97 °C,

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.49 (d, J= 7.0 Hz, 12H), 2.68 (s, 6H), 3.55 (sept, J= 7.0 Hz, 1H), 7.55 (d, J= 8.7 Hz, 2H), 8.36 (d, J = 8.7 Hz, 2H)

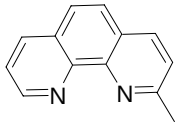
^{13}C NMR (75 MHz, $CDCl_3$): 15.2, 22.9, 36.9, 119.8, 127.4, 128.3, 132.7, 144.3, 166.2

Anal. calcd. for $C_{20}H_{24}N_2$: C, 82.15; H, 8.27; N, 9.58; found: C 82.17, H 8.28, N 9.45

General procedure for the synthesis of phenanthrolines 11, 14 and 17 from 8-aminoquinolines via aza-Diels-Alder reaction in HFIP

To a stirred solution of ethyl vinyl ether (5 mmol) in HFIP (1 mL), a solution of the aminoquinoline (0.5 mmol) in HFIP (1 mL) was added at 30 °C and the reaction mixture was stirred for an appropriate time. After completion of the reaction (TLC monitoring), HFIP was evaporated under vacuum to afford the crude cycloaddition product. Then, this latter product (0.5 mmol) was dissolved in acetonitrile (1 mL), aq HCl (6 N, 0.2 mL) was added and the reaction mixture was placed under oxygen atmosphere (1 atm) and stirred. After 16 h, dichloromethane (25 mL) was added and the reaction mixture was transferred to a separating funnel and washed with saturated aqueous $NaHCO_3$ solution (2×15 mL). The organic layer was separated and the aqueous layer was washed with dichloromethane (3×15 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and the solvents were evaporated under vacuum. The product was purified by column chromatography on silica gel (cyclohexane/ethyl acetate, 85:15).

2-Methyl-[1,10]phenanthroline (11)[8]



Yield 43%, 42 mg, yellow solid, mp: 84 °C (Lit 85-86 °C),

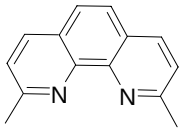
[8] Poole, R.A. ; Bobba, G. ; Cann, M.J. ; Frias, J.C. ; Parker, D., Peacock, R.D. *Org. Biomol. Chem*. **2005**, *3*, 1013.

^{1}H NMR (300 MHz, $CDCl_3$): 2.94 (s, 3H), 7.49 (dd, J= 2.6, 8.2 Hz, 1H), 7.58 (ddd, J= 2.8, 7.2, 12.2 Hz, 1H), 7.70-7.72 (m, 2H), 8.10 (dd, J= 2.6, 8.2 Hz, 1H), 8.20 (ddd, J= 1.7, 2.7, 8.1 Hz, 1H), 9.19 (dd, J= 1.7, 4.3 Hz, 1H)

^{13}C NMR (75MHz, $CDCl_3$): 25.7, 122.6, 123.6, 125.3, 126.3, 126.5, 128.6, 135.8, 136.0, 145.6, 145.8, 150.1, 159.3

Anal. calcd. for $C_{13}H_{10}N_2$: C, 80.39; H, 5.19; N, 14.42; found: C 80.65, H 5.26, N 14.65

2,9-Dimethyl-[1,10]phenanthroline (neo) (14)[9]



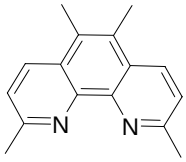
Yield 42%, 43 mg, white solid, mp: 158 °C (Lit: 159-160 °C),

^{1}H NMR (300 MHz, $CDCl_3$): 2.94 (s, 6H), 7.49 (d, J= 8.2 Hz, 2H), 7.70 (s, 2H), 8.12 (d, J= 8.2 Hz, 2H)

^{13}C NMR (75MHz, $CDCl_3$): 25.9, 123.5, 125.4, 126.8, 132.0, 136.2, 145.3, 159.3

Anal. calcd. for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45; found: C 81.97, H 5.77, N 13.32

2,5,6,9-Tetramethyl-[1,10]phenanthroline (17)[17]



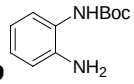
Yield: 40%, 47 mg, white solid, mp: 170 °C (lit: 171 °C),

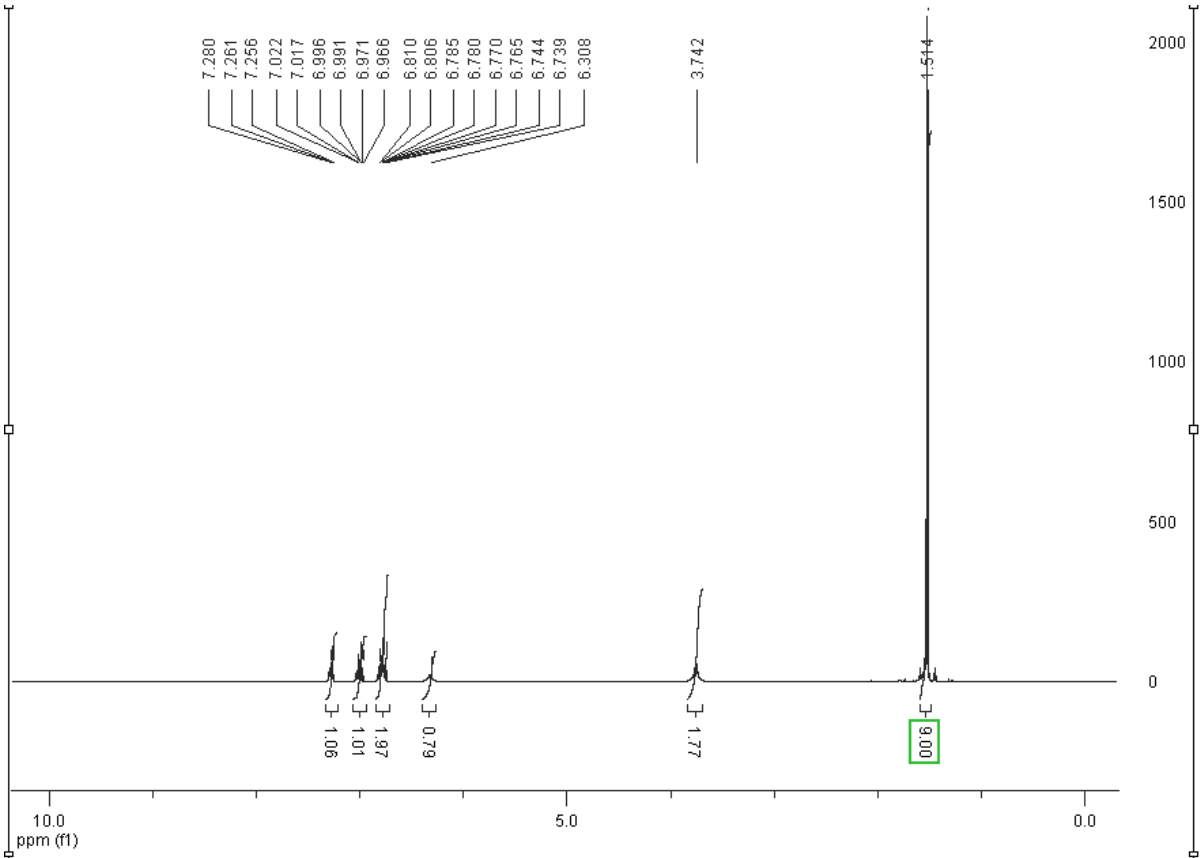
^{1}H NMR (300 MHz, $CDCl_3$): 2.60 (s, 6H), 2.90 (s, 6H), 7.46 (d, J= 8.5 Hz, 2H), 8.28 (d, J= 8.5 Hz, 2H)

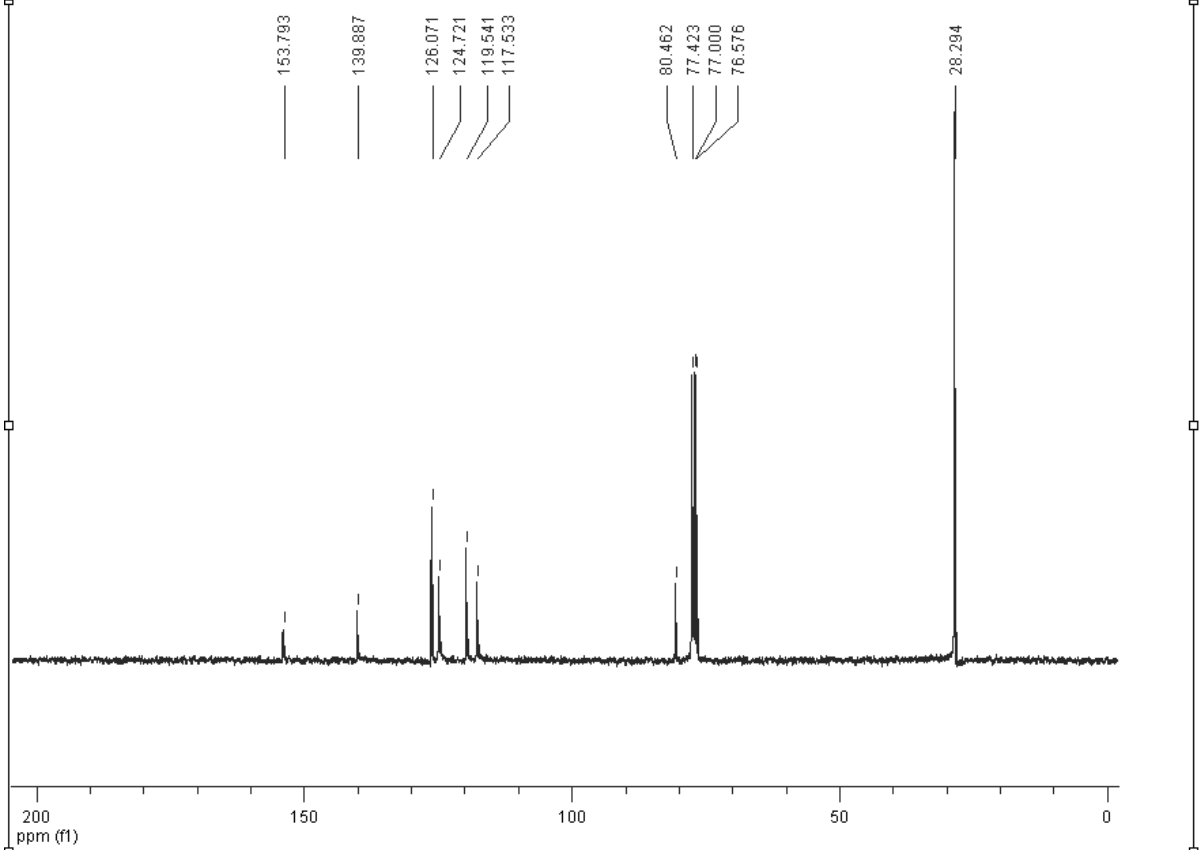
^{13}C NMR (75 MHz, $CDCl_3$): 15.1, 25.5, 123.1, 126.8, 128.2, 132.4, 144.3, 157.6

Anal. calcd. for $C_{16}H_{16}N_2$: C, 81.32; H, 6.82; N, 11.85; found: C 81.44, H 6.63, N 11.95

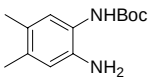
[9] Case, F.H. J. *Am. Chem. Soc*. **1948**, *70*, 3994.

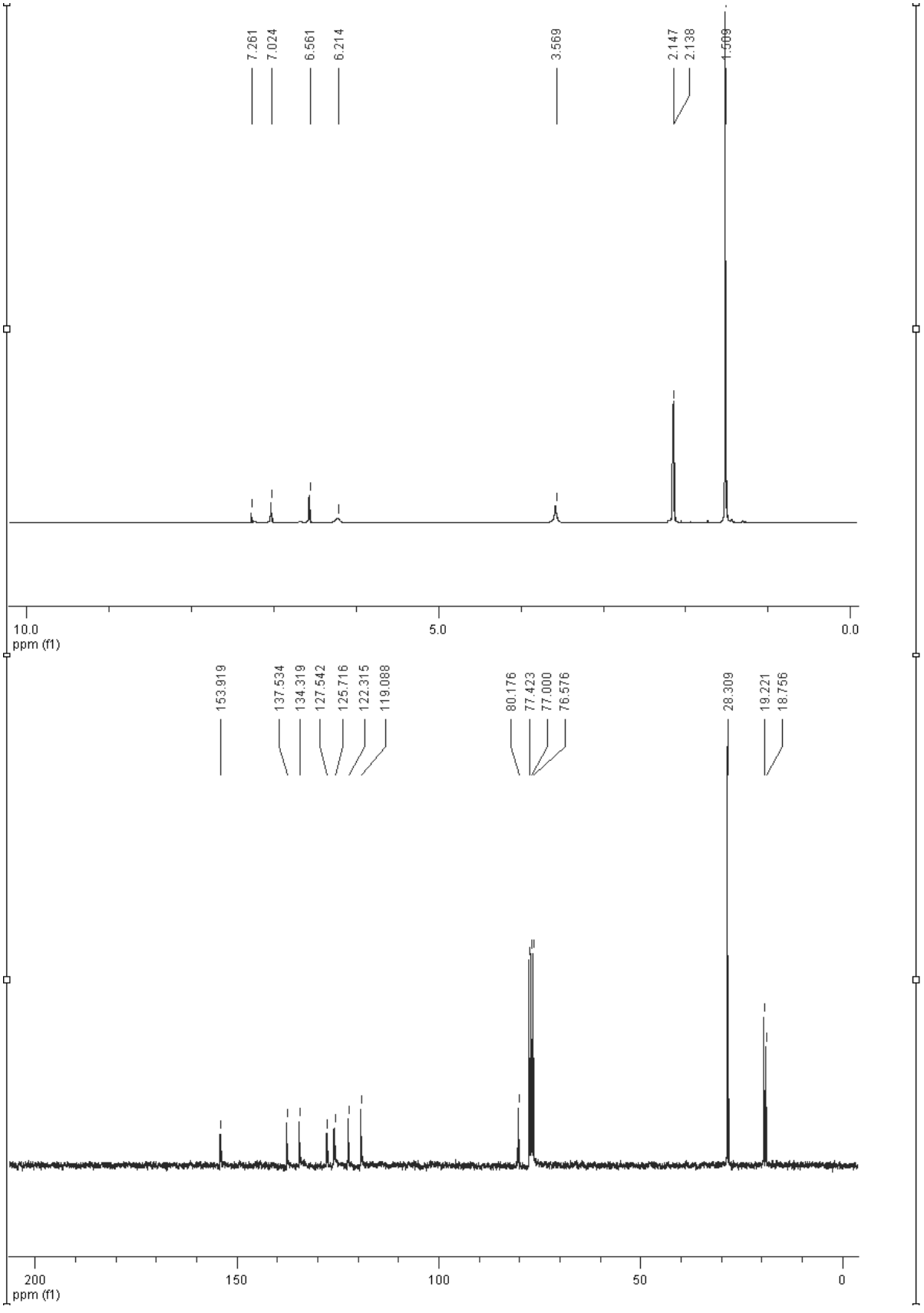
Compound **1b** 
NHBoc
NH2


7.280
7.261
7.256
7.022
7.017
6.996
6.991
6.971
6.966
6.810
6.806
6.785
6.780
6.770
6.765
6.744
6.739
6.308
3.742
1.514
2000
1500
1000
500
0
1.06
1.01
1.97
0.79
1.77
9.00
10.0
5.0
0.0
ppm (f1)

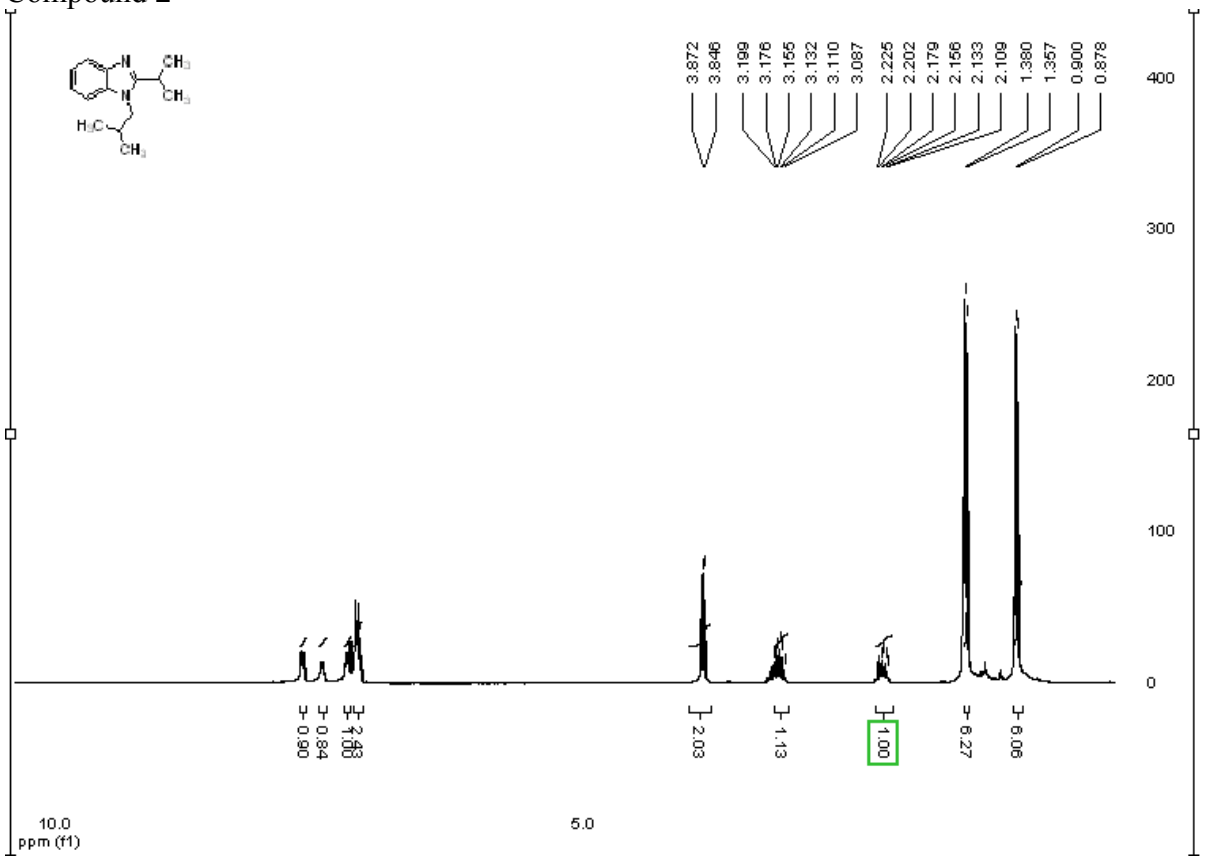

153.793
139.887
126.071
124.721
119.541
117.533
80.462
77.423
77.000
76.576
28.294
200
150
100
50
0
ppm (f1)

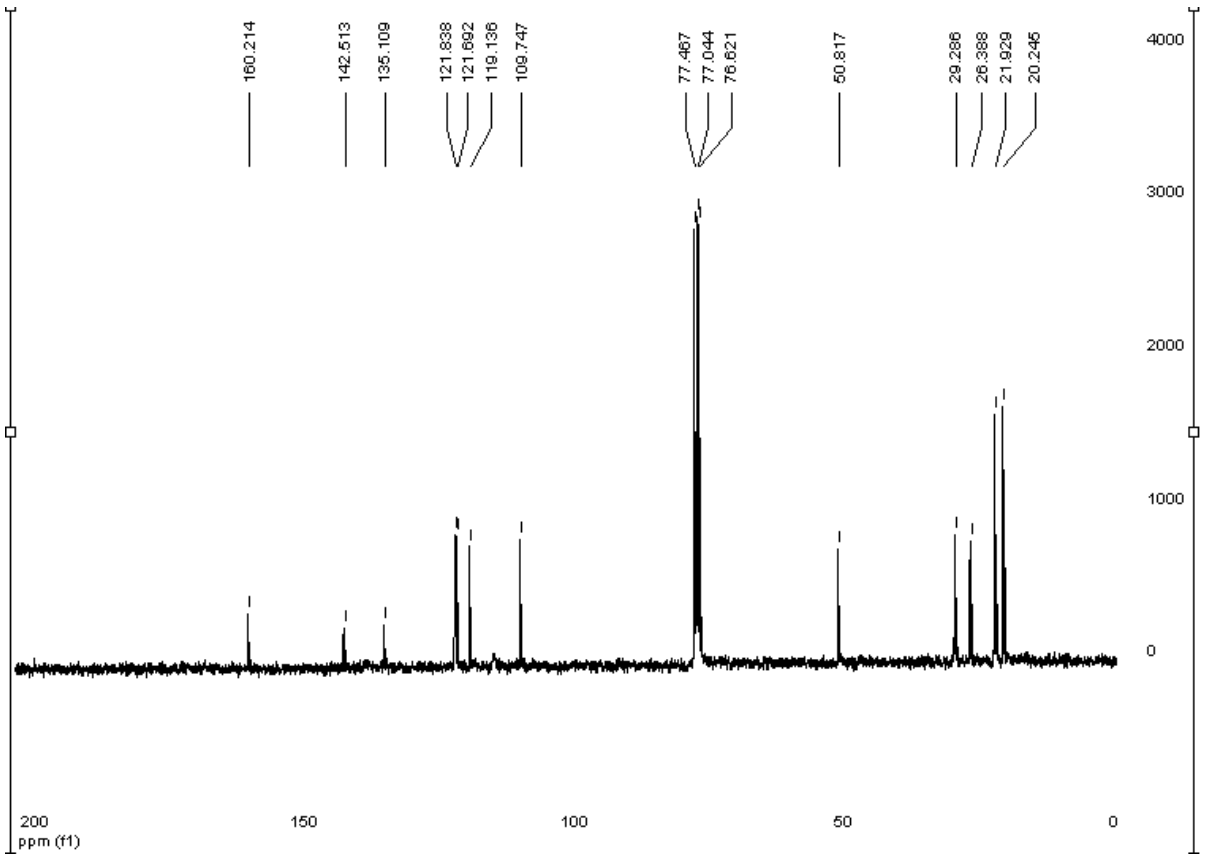
1c


NHBoc
NH2

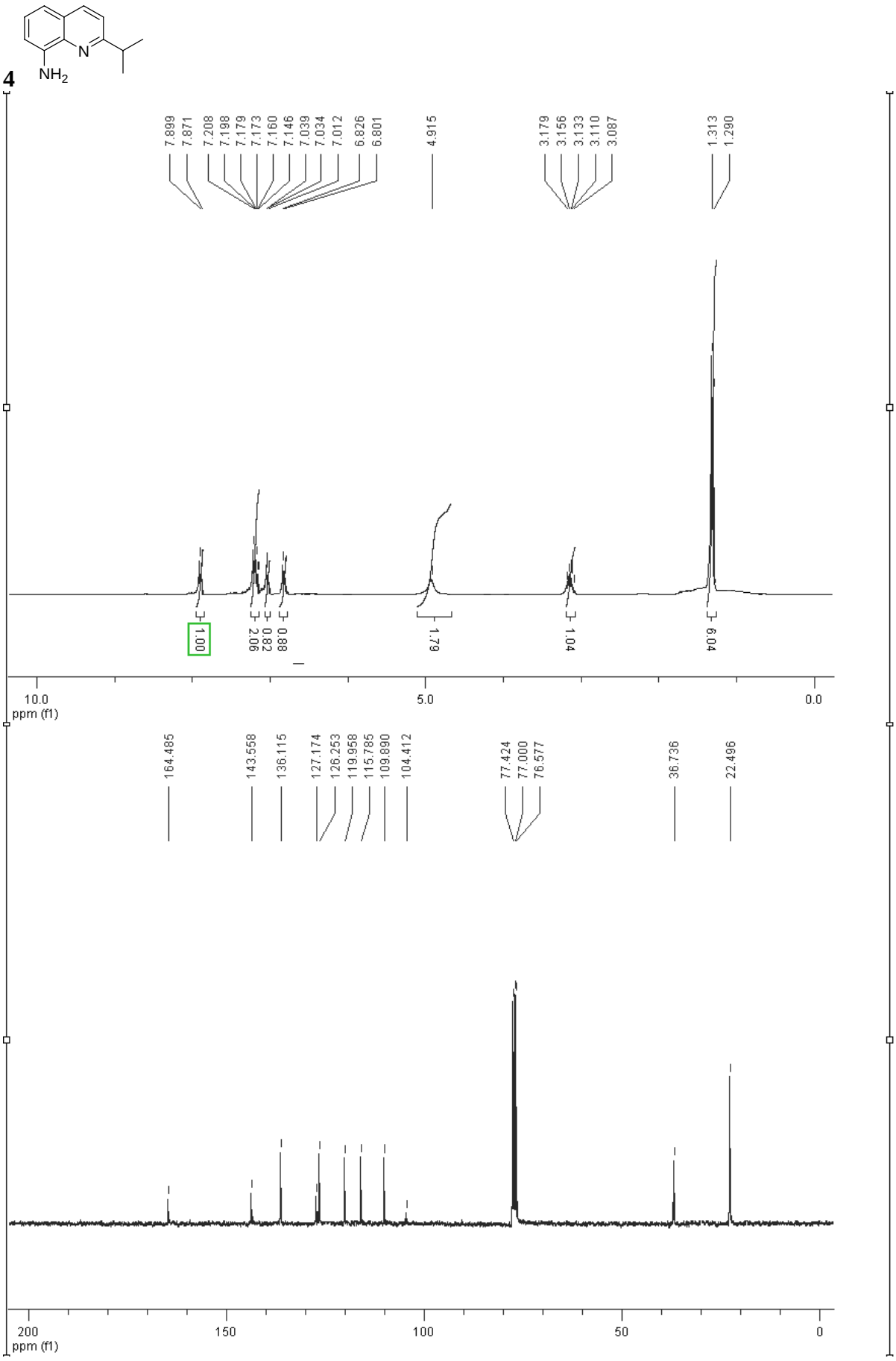

7.261
7.024
6.561
6.214
3.569
2.147
2.138
1.509
10.0
5.0
0.0
ppm (f1)
153.919
137.534
134.319
127.542
125.716
122.315
119.088
80.176
77.423
77.000
76.576
28.309
19.221
18.756
200
150
100
50
0
ppm (f1)

Compound **2**

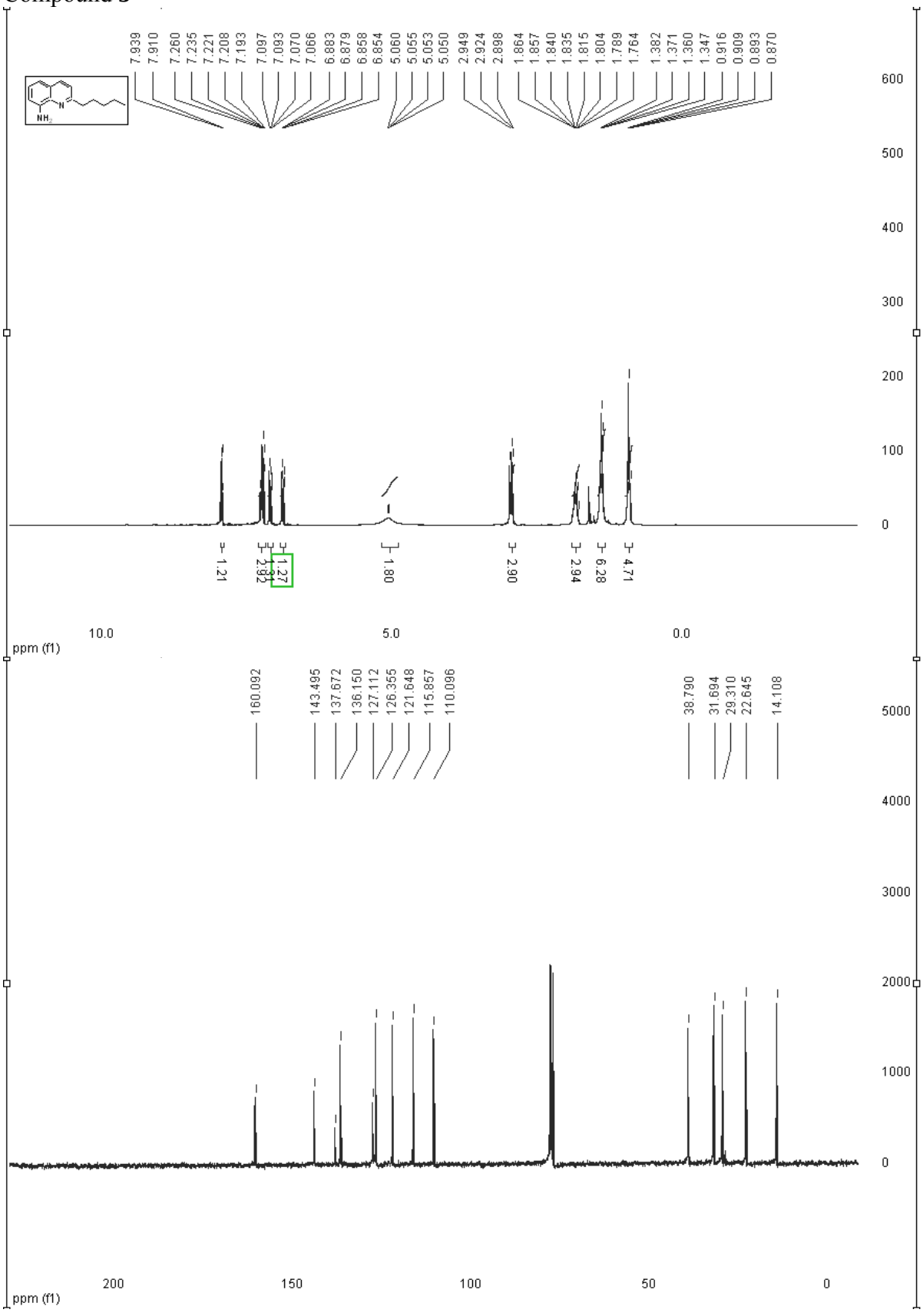

3.872
3.846
3.199
3.176
3.155
3.132
3.110
3.087
2.225
2.202
2.179
2.156
2.133
2.109
1.380
1.357
0.900
0.878
0.90
0.84
2.03
1.13
1.00
6.27
6.06
10.0
ppm (f1)
5.0


160.214
142.513
135.109
121.838
121.692
119.136
109.747
77.467
77.044
76.621
50.817
29.286
26.388
21.929
20.246
200
ppm (f1)
150
100
50
0

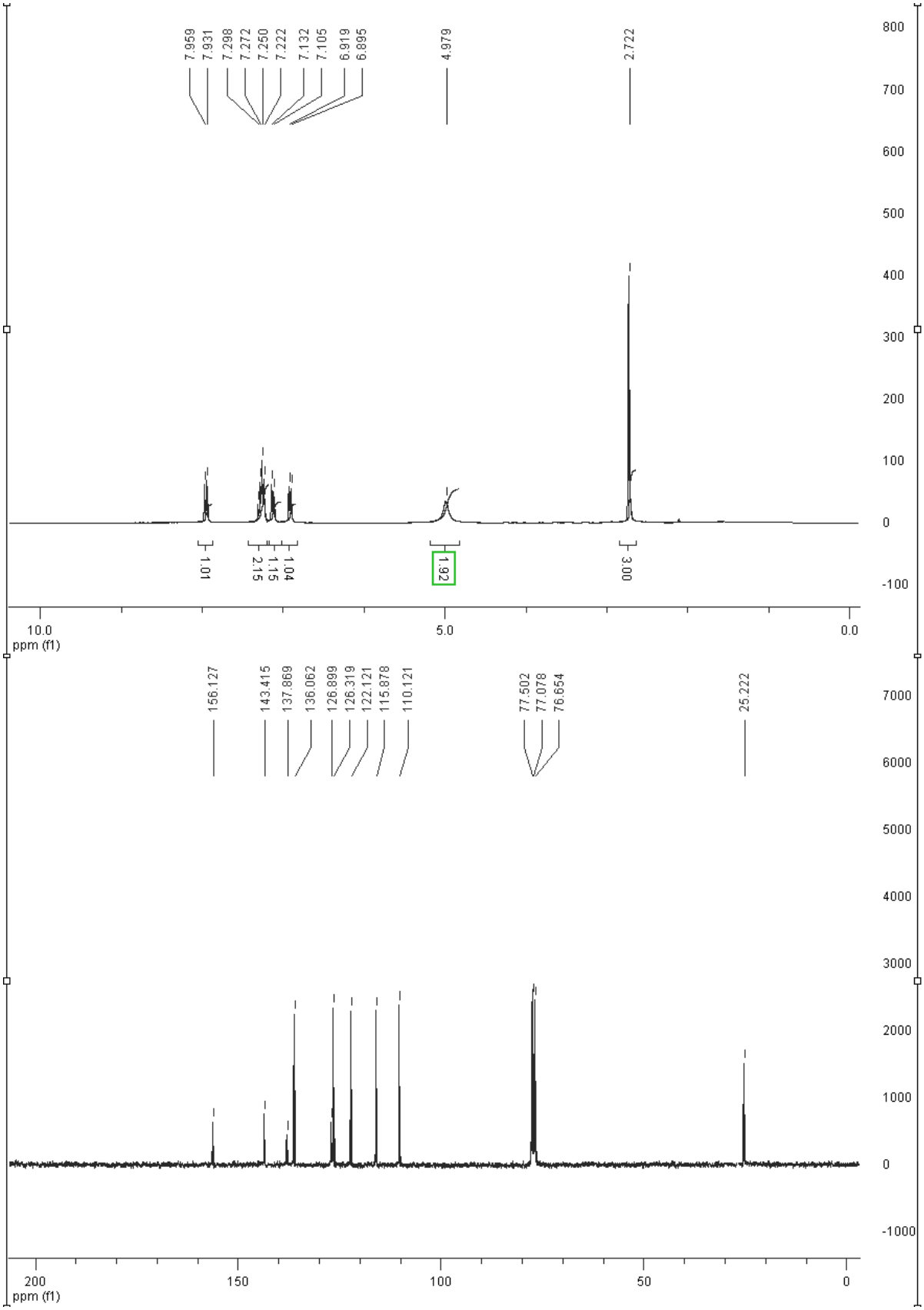
4

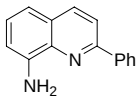

7.899
7.871
7.208
7.198
7.179
7.173
7.160
7.146
7.039
7.034
7.012
6.826
6.801
4.915
3.179
3.156
3.133
3.110
3.087
1.313
1.290
1.00
2.06
0.82
0.88
1.79
1.04
6.04
10.0
5.0
0.0
ppm (f1)
164.485
143.558
136.115
127.174
126.253
119.958
115.785
109.890
104.412
77.424
77.000
76.577
36.736
22.496
200
150
100
50
0
ppm (f1)

Compound **5**

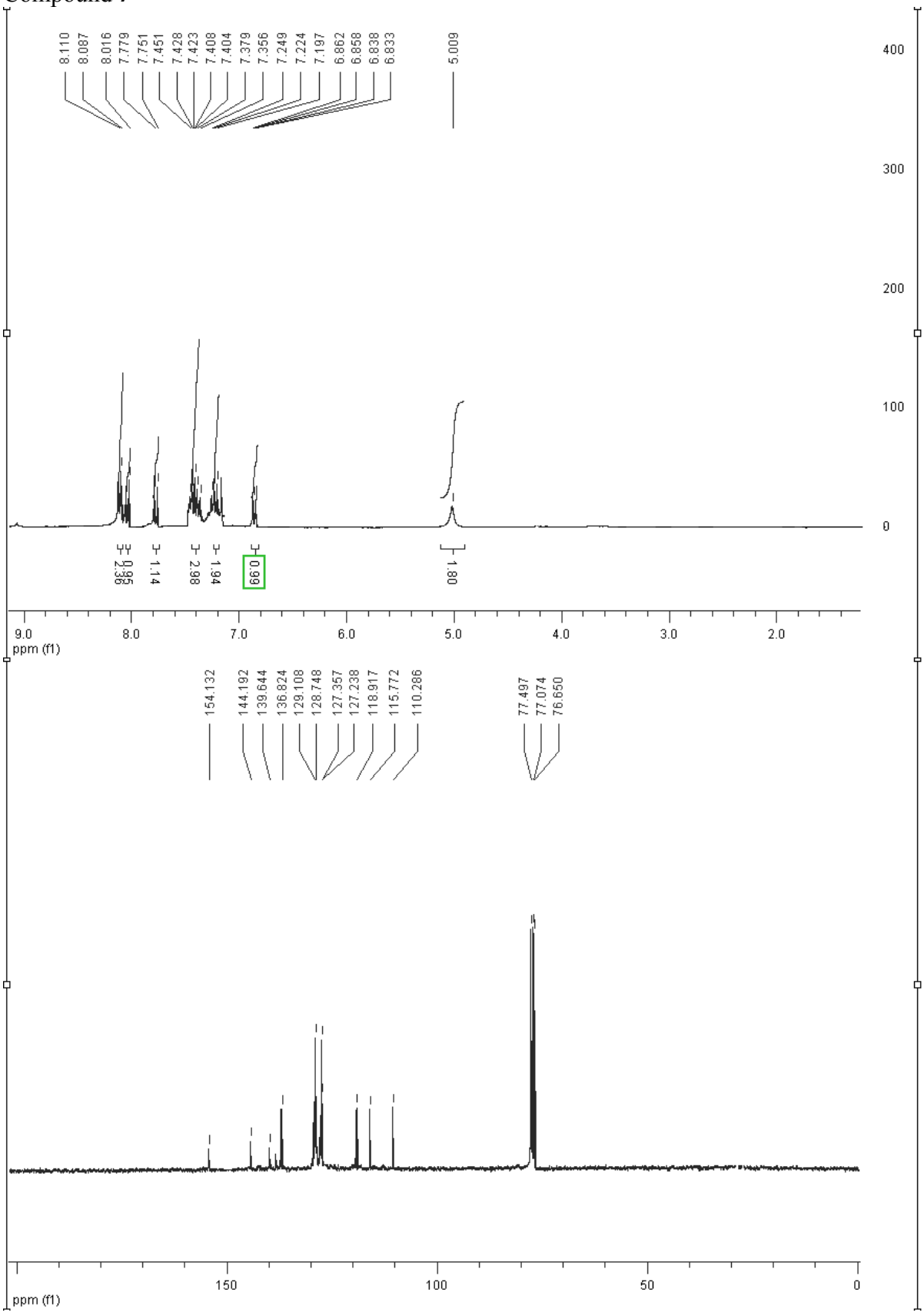

7.939
7.910
7.260
7.235
7.221
7.208
7.193
7.097
7.093
7.070
7.066
6.883
6.879
6.858
6.854
5.060
5.055
5.053
5.050
2.949
2.924
2.898
1.864
1.857
1.840
1.835
1.815
1.804
1.789
1.764
1.382
1.371
1.360
1.347
0.916
0.909
0.893
0.870
NH2
1.21
2.82
1.31
1.27
1.80
2.90
2.94
9.28
4.71
10.0
5.0
0.0
ppm (f1)
160.092
143.495
137.672
136.150
127.112
126.355
121.648
115.857
110.096
38.790
31.694
29.310
22.645
14.108
200
150
100
50
0
ppm (f1)

Compound **6**

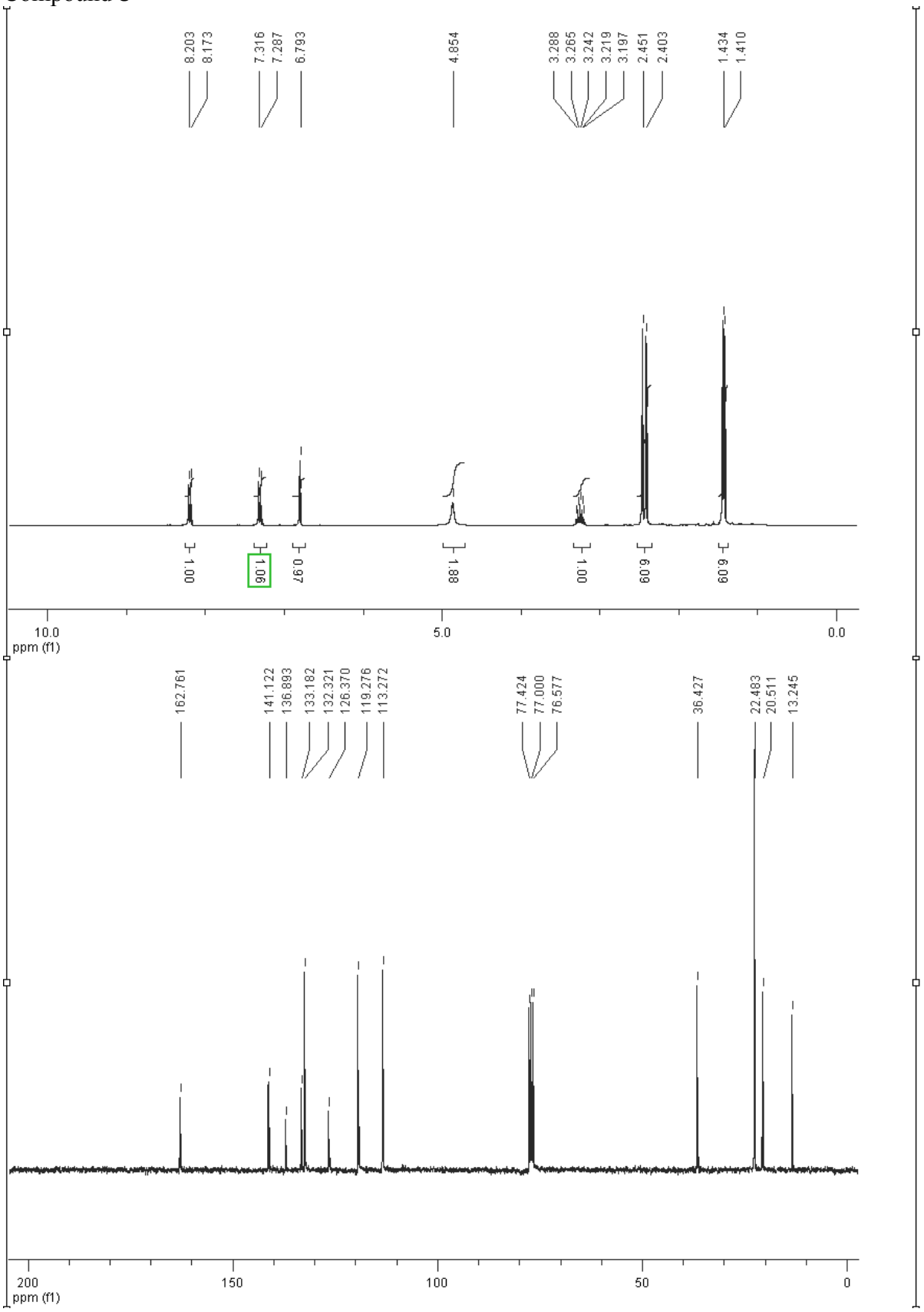

7.959
7.931
7.298
7.272
7.250
7.222
7.132
7.105
6.919
6.895
4.979
2.722
1.01
2.16
1.15
1.04
1.92
3.00
10.0
5.0
0.0
ppm (f1)
156.127
143.415
137.869
136.062
126.899
126.319
122.121
115.878
110.121
77.502
77.078
76.654
25.222
200
150
100
50
0
ppm (f1)

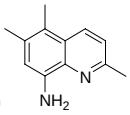

N
Ph
NH2

Compound **7**

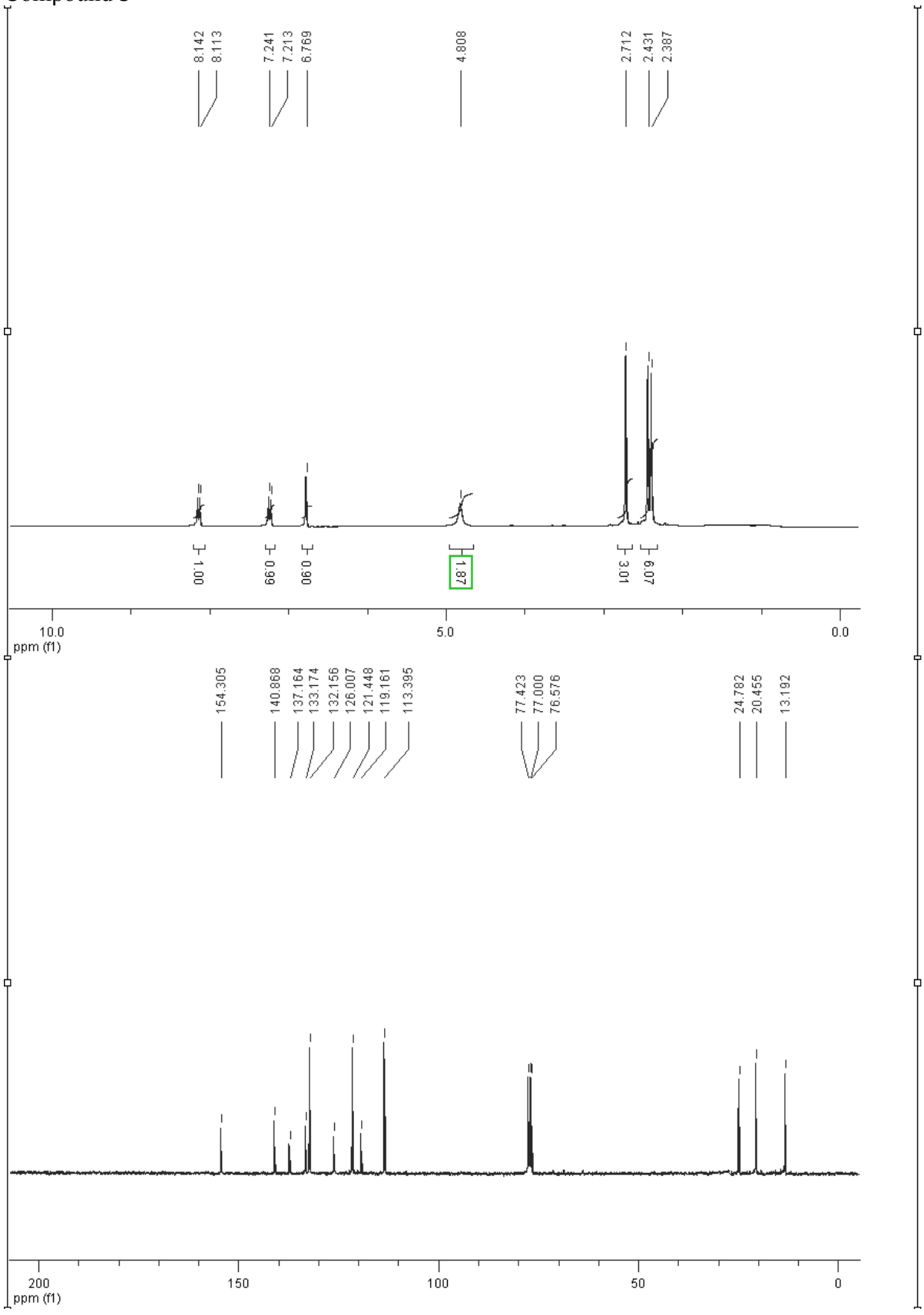

8.110
8.087
8.016
7.779
7.751
7.451
7.428
7.423
7.408
7.404
7.379
7.356
7.249
7.224
7.197
6.862
6.858
6.838
6.833
5.009
2.36
0.95
1.14
2.98
1.94
0.99
1.80
400
300
200
100
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (f1)
154.132
144.192
139.644
136.824
129.108
128.748
127.357
127.238
118.917
115.772
110.286
77.497
77.074
76.650
150
100
50
0
ppm (f1)

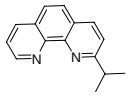
Compound **8**


8.203
8.173
7.316
7.287
6.793
4.854
3.288
3.265
3.242
3.219
3.197
2.451
2.403
1.434
1.410
1.00
1.06
0.97
1.88
1.00
6.09
6.09
10.0
5.0
0.0
ppm (f1)
162.761
141.122
136.893
133.182
132.321
126.370
119.276
113.272
77.424
77.000
76.577
36.427
22.483
20.511
13.245
200
150
100
50
0
ppm (f1)

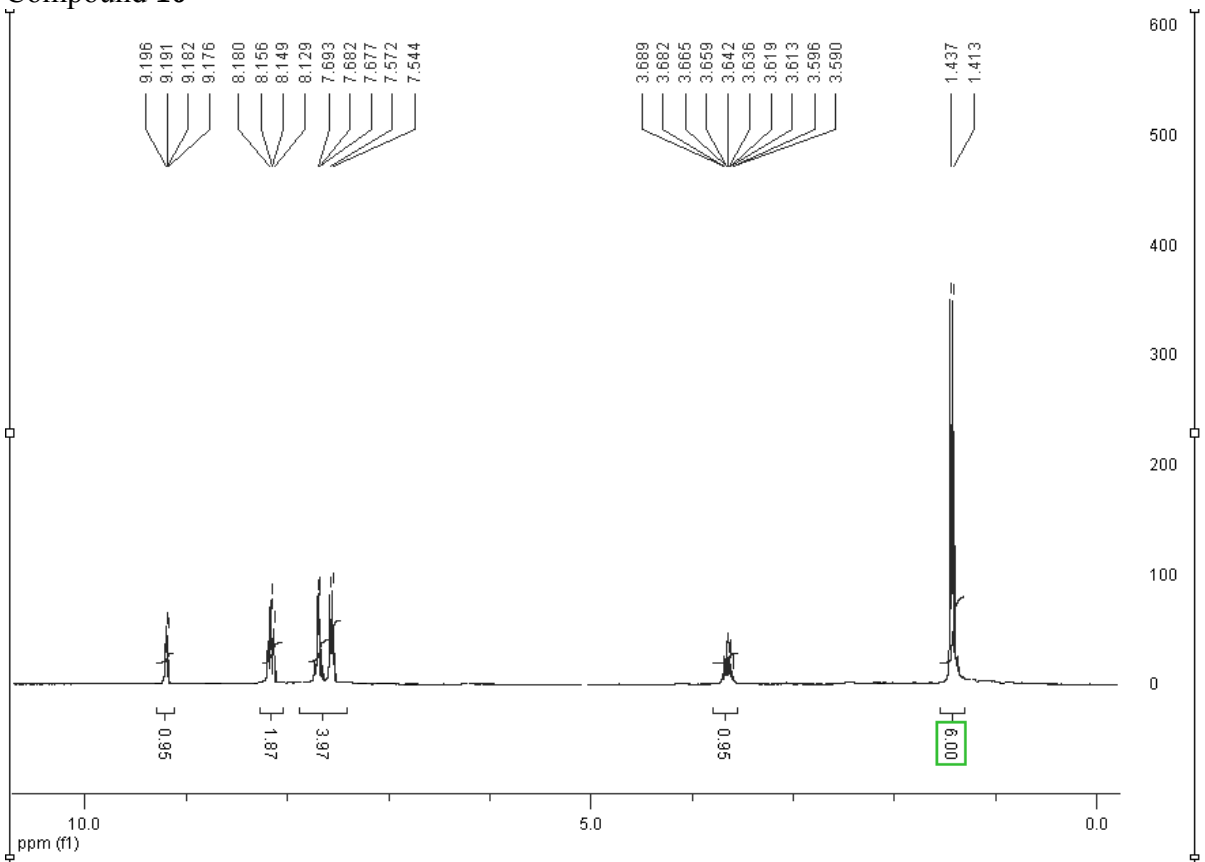

N
NH2

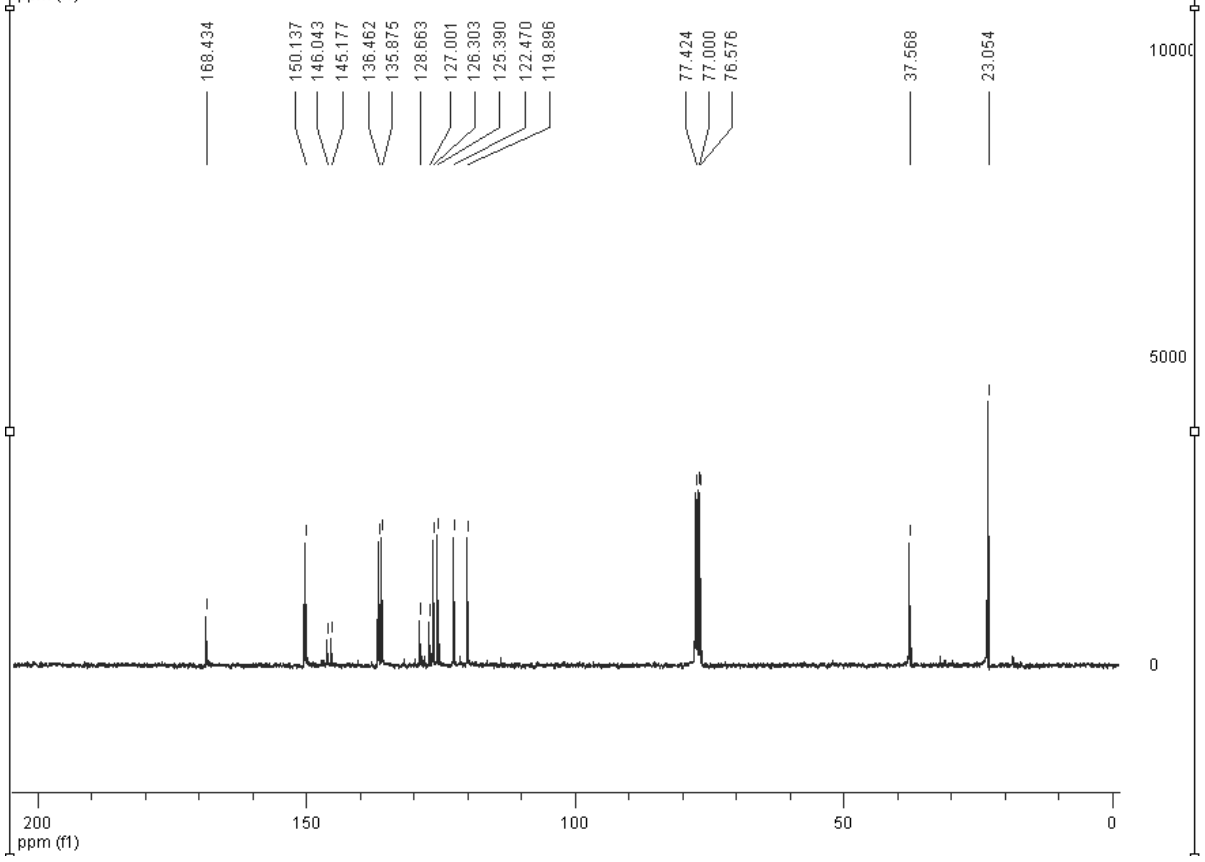
Compound **9**


8.142
8.113
7.241
7.213
6.769
4.808
2.712
2.431
2.387
1.00
0.99
0.90
1.87
3.01
6.07
10.0
5.0
0.0
ppm (f1)
154.305
140.868
137.164
133.174
132.156
126.007
121.448
119.161
113.395
77.423
77.000
76.576
24.782
20.455
13.192
200
150
100
50
0
ppm (f1)

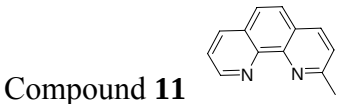


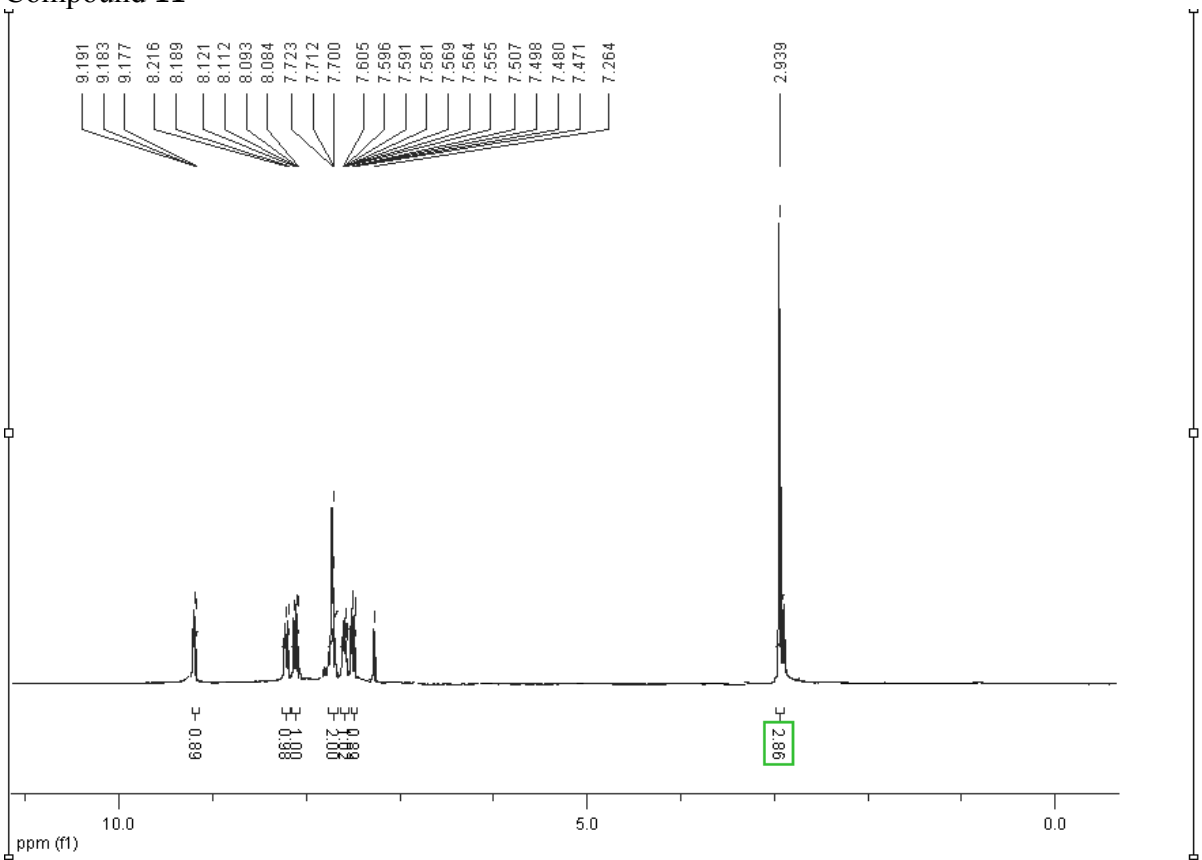
Compound **10**

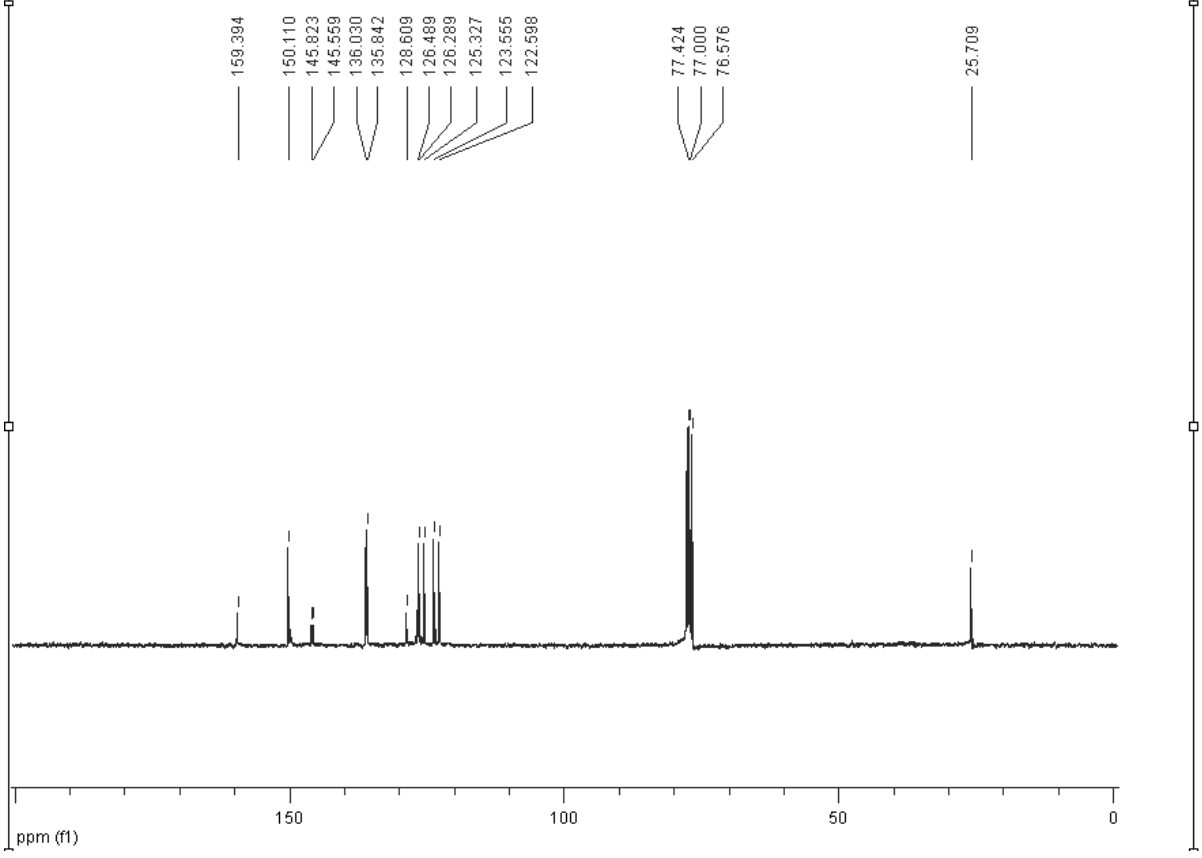

9.196
9.191
9.182
9.176
8.180
8.156
8.149
8.129
7.693
7.682
7.677
7.572
7.544
3.689
3.682
3.665
3.659
3.642
3.636
3.619
3.613
3.596
3.590
1.437
1.413
0.95
1.87
3.97
0.95
6.00
10.0
5.0
0.0
ppm (f1)


168.434
150.137
146.043
145.177
136.462
135.875
128.663
127.001
126.303
125.390
122.470
119.896
77.424
77.000
76.576
37.568
23.054
200
150
100
50
0
ppm (f1)

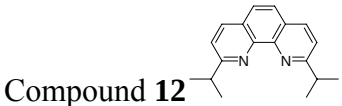
Compound **11**

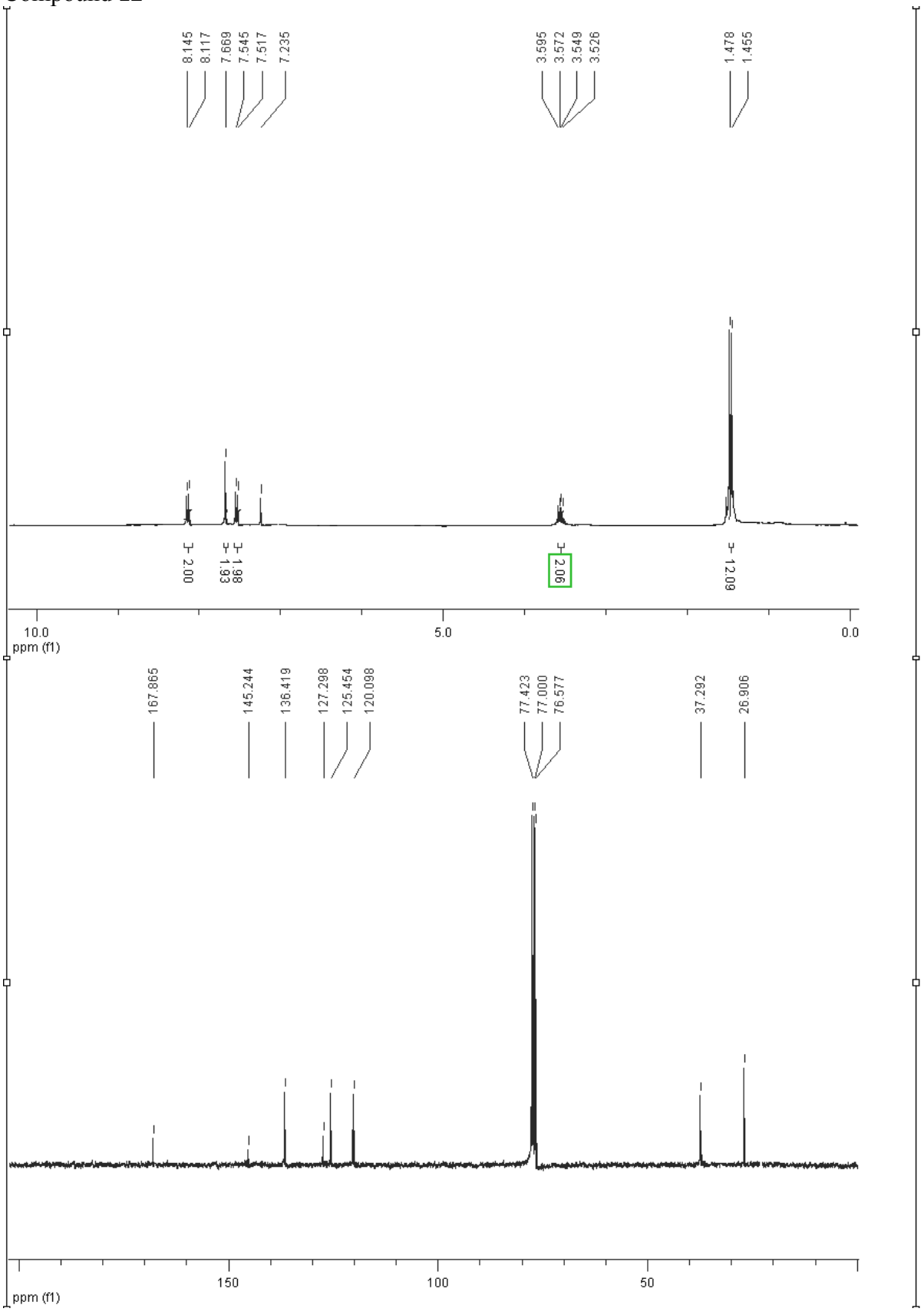


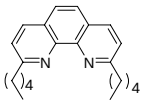

9.191
9.183
9.177
8.216
8.189
8.121
8.112
8.093
8.084
7.723
7.712
7.700
7.605
7.596
7.591
7.581
7.569
7.564
7.555
7.507
7.498
7.480
7.471
7.264
2.939
0.89
0.98
2.00
2.86
10.0
5.0
0.0
ppm (f1)

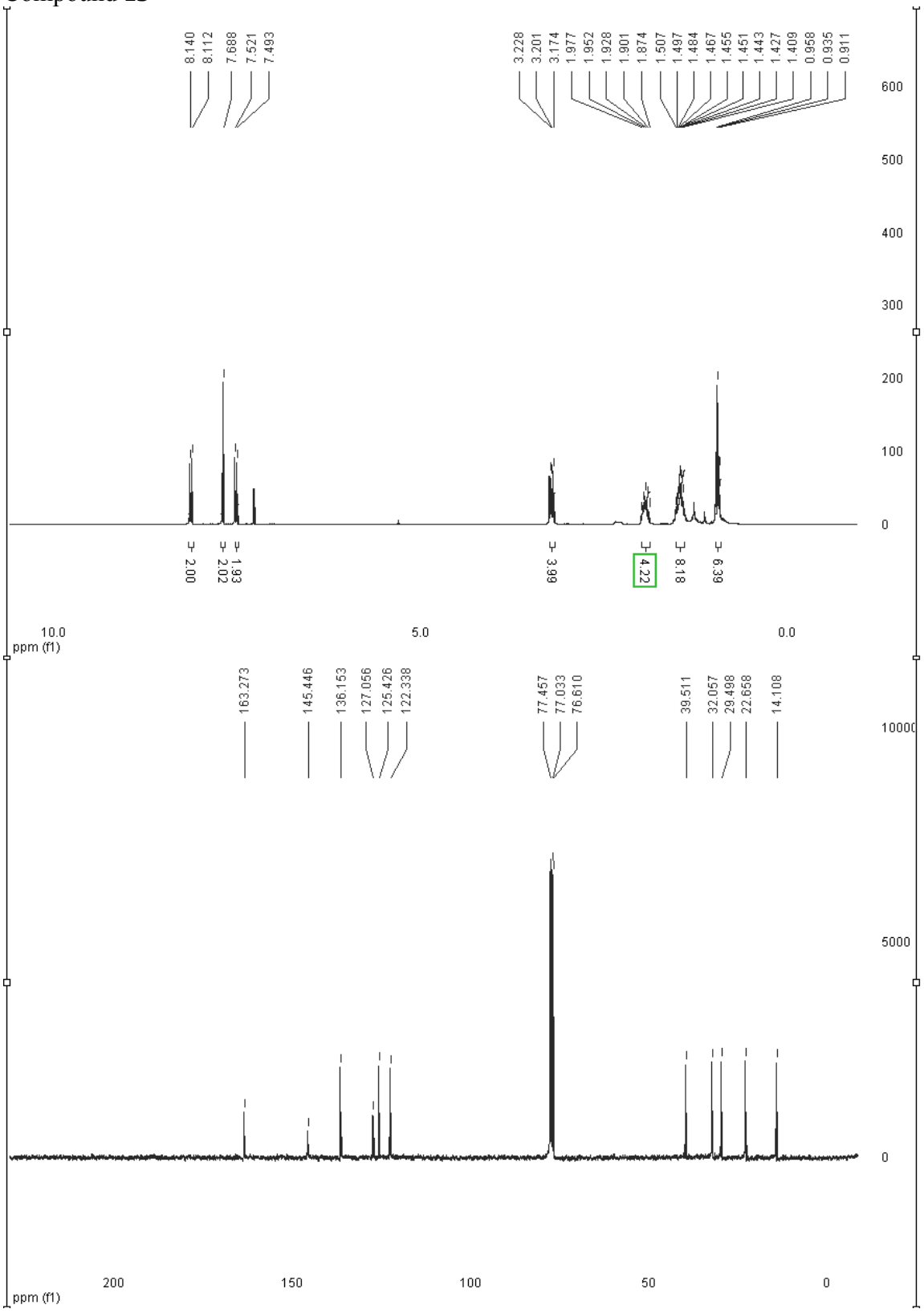

159.394
150.110
145.823
145.559
136.030
135.842
128.609
126.489
126.289
125.327
123.555
122.598
77.424
77.000
76.576
25.709
150
100
50
0
ppm (f1)

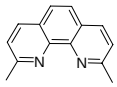
Compound **12**

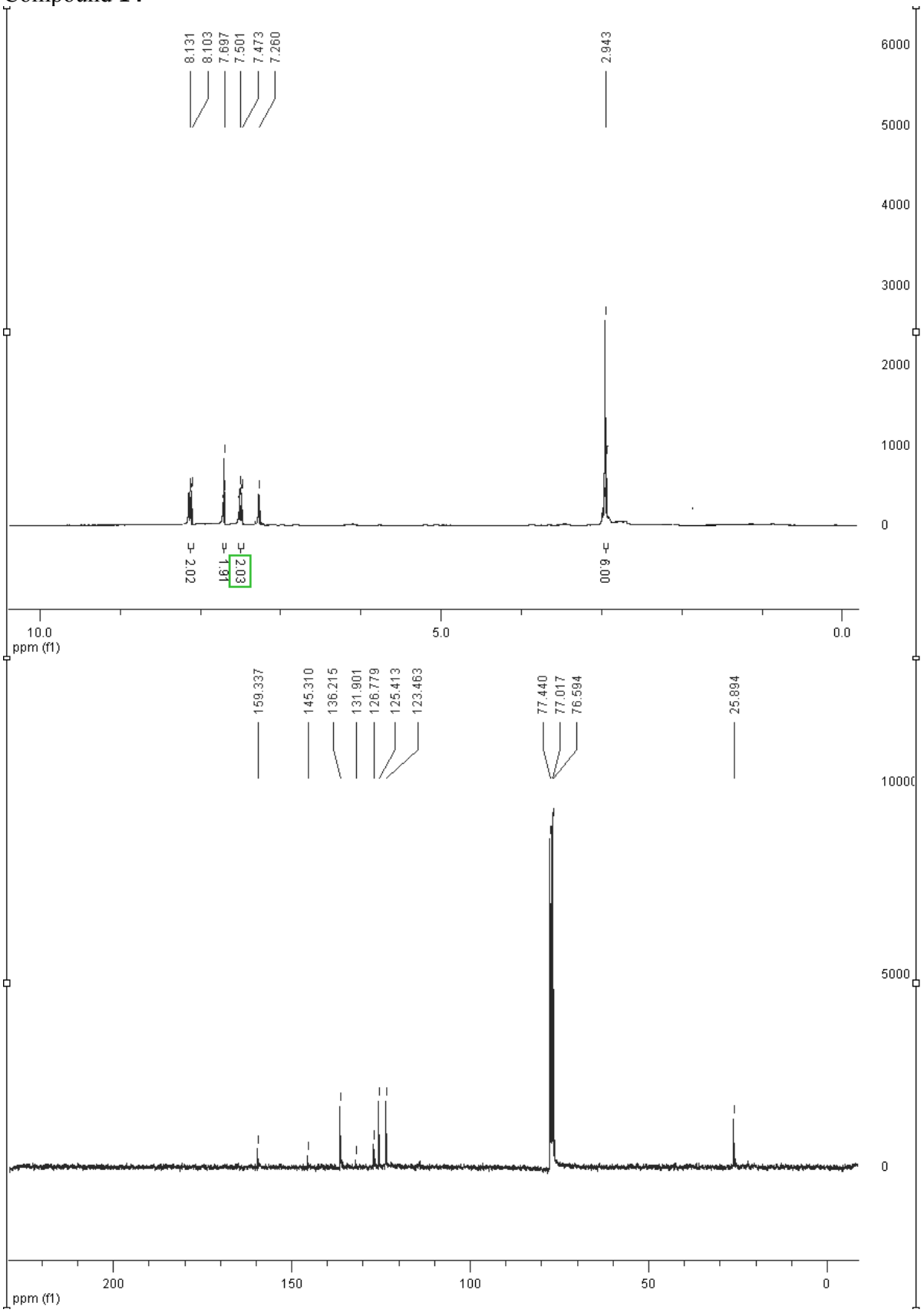



8.145
8.117
7.669
7.545
7.517
7.235
3.595
3.572
3.549
3.526
1.478
1.455
2.00
1.93
1.98
2.06
12.09
10.0
5.0
0.0
ppm (f1)
167.865
145.244
136.419
127.298
125.454
120.098
77.423
77.000
76.577
37.292
26.906
150
100
50
ppm (f1)

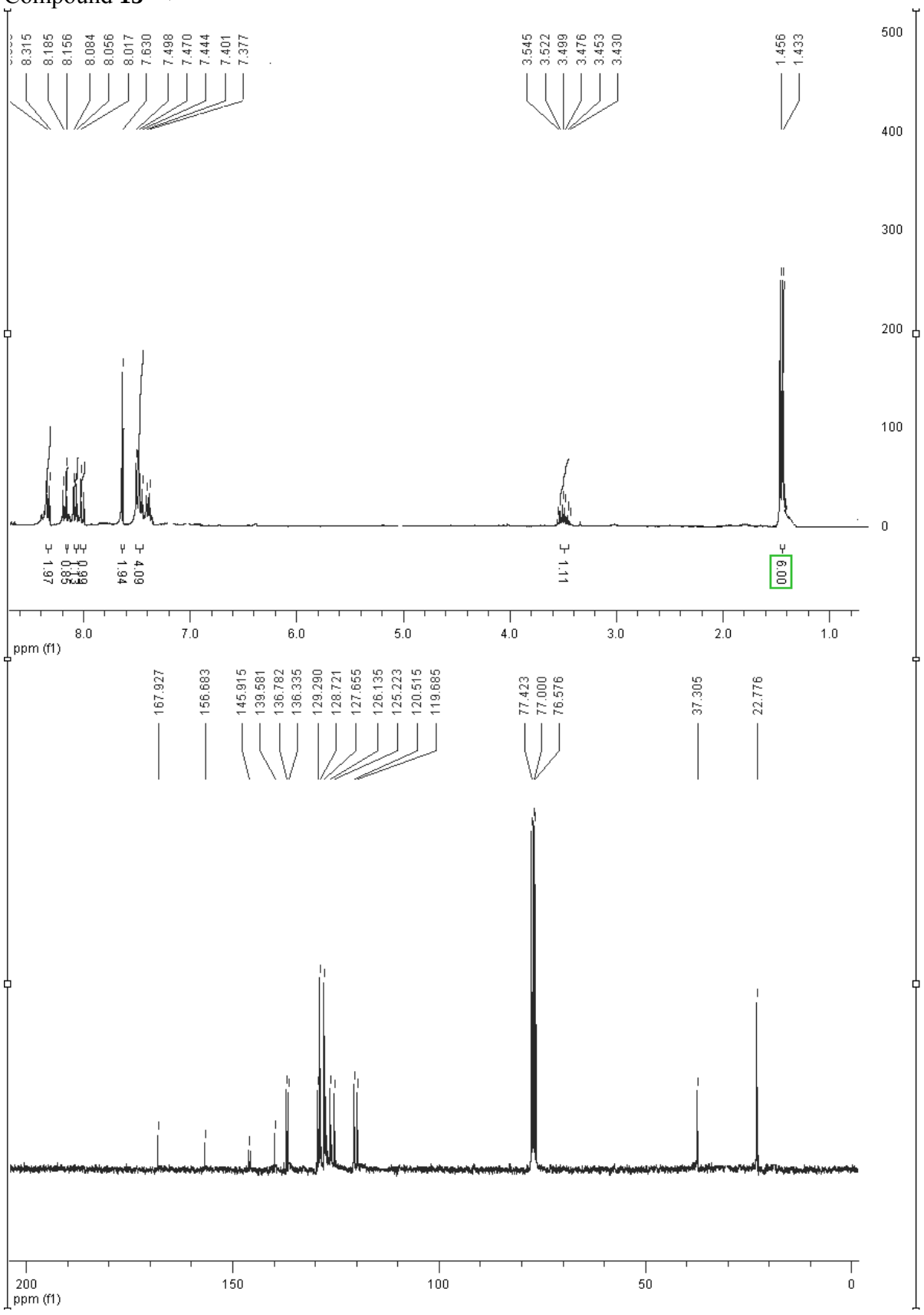
Compound **13** 


8.140
8.112
7.688
7.521
7.493
3.228
3.201
3.174
1.977
1.952
1.928
1.901
1.874
1.507
1.497
1.484
1.467
1.455
1.451
1.443
1.427
1.409
0.958
0.935
0.911
2.00
2.02
1.83
3.99
4.22
8.18
6.39
10.0
5.0
0.0
ppm (f1)
163.273
145.446
136.153
127.056
125.426
122.338
77.457
77.033
76.610
39.511
32.057
29.498
22.658
14.108
200
150
100
50
0
ppm (f1)

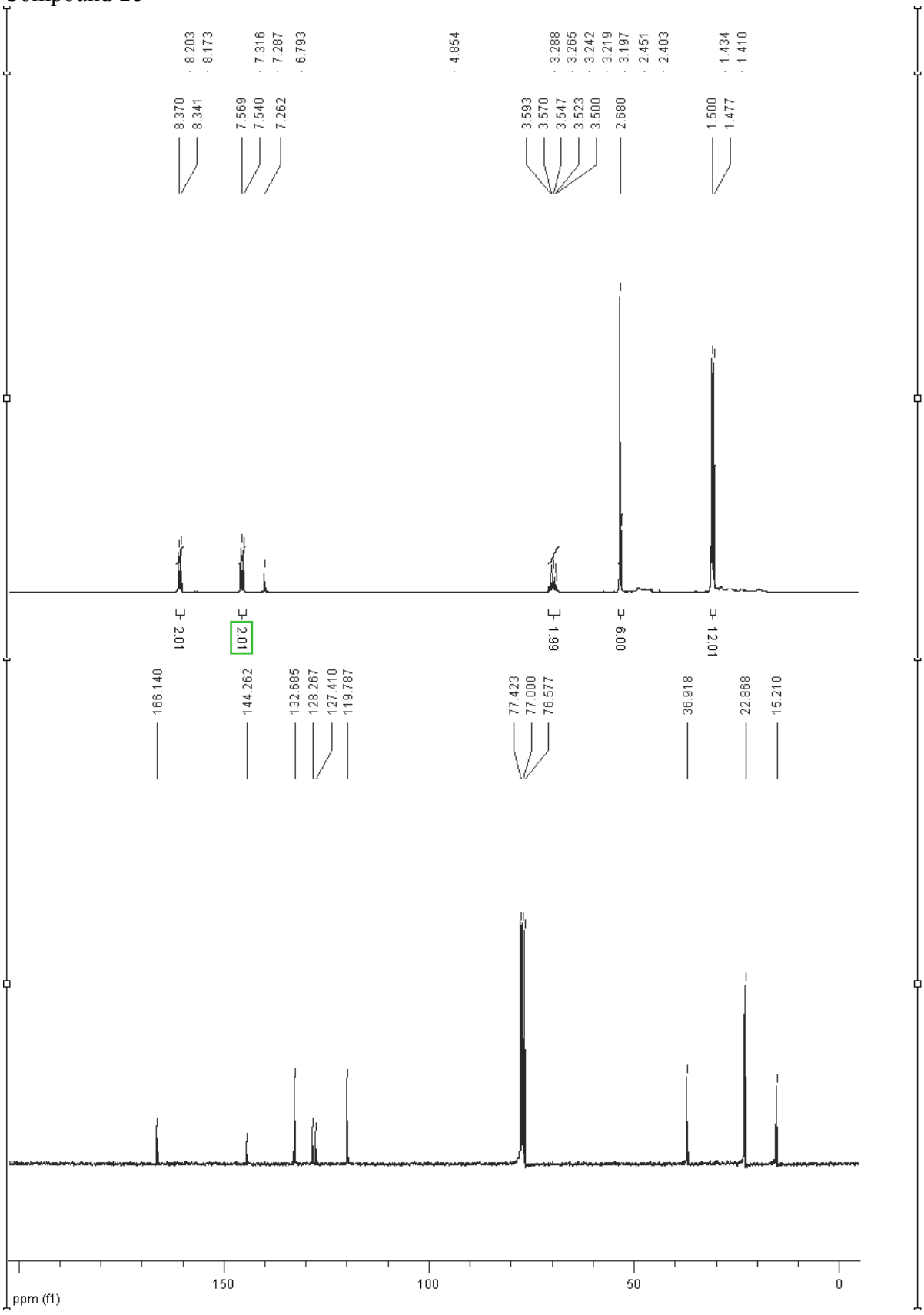
Compound **14** 

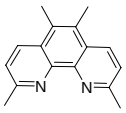

8.131
8.103
7.697
7.501
7.473
7.260
2.943
2.02
1.91
2.03
6.00
10.0
5.0
0.0
ppm (f1)
159.337
145.310
136.215
131.901
126.779
125.413
123.463
77.440
77.017
76.594
25.894
200
150
100
50
0
ppm (f1)

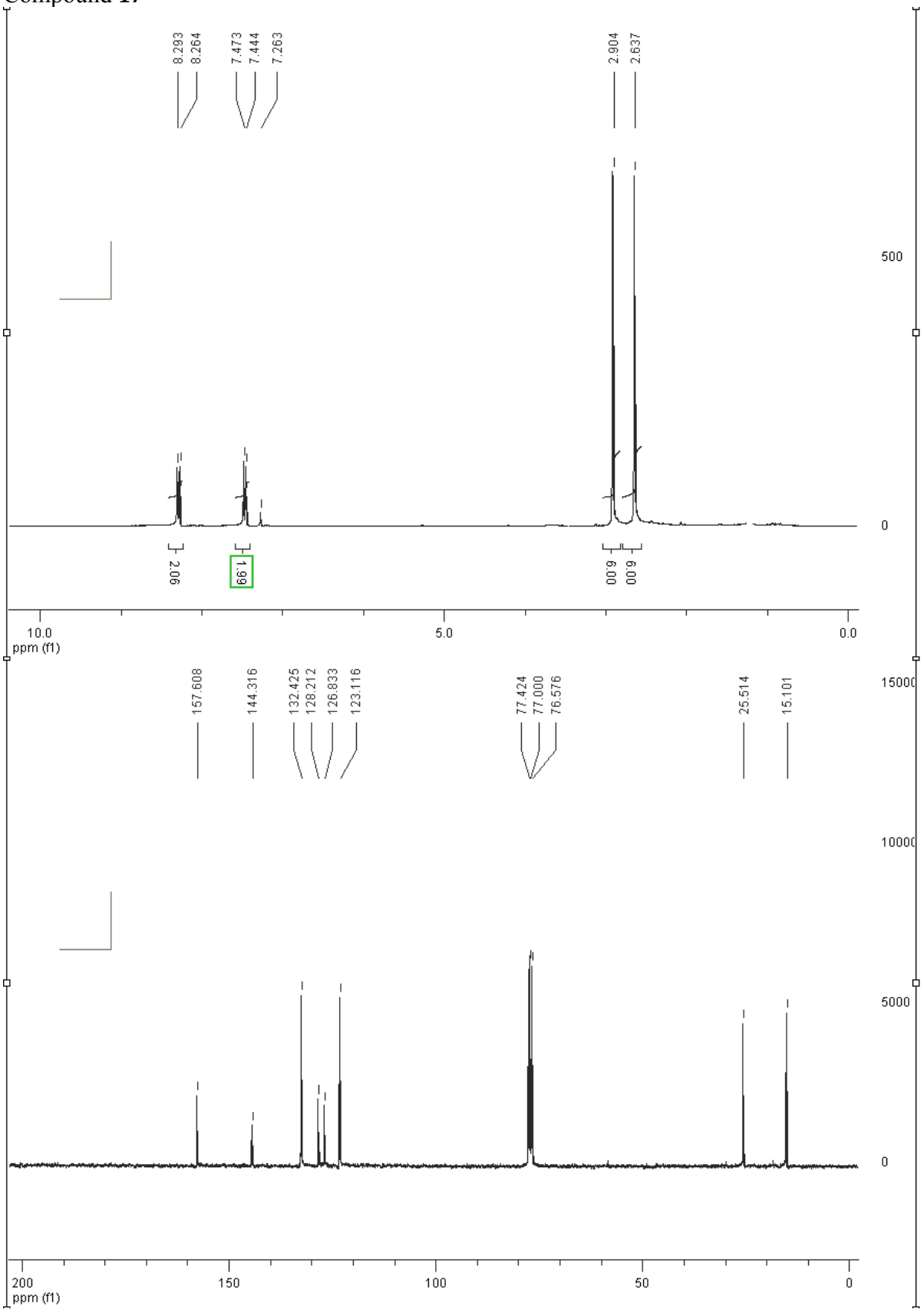
Compound **15**


8.315
8.185
8.156
8.084
8.056
8.017
7.630
7.498
7.470
7.444
7.401
7.377
3.545
3.522
3.499
3.476
3.453
3.430
1.456
1.433
1.97
0.99
1.94
4.09
1.11
6.00
ppm (f1)
167.927
156.683
145.915
139.581
136.782
136.335
129.290
128.721
127.655
126.135
125.223
120.515
119.685
77.423
77.000
76.576
37.305
22.776
ppm (f1)

Compound **16**


8.370
8.341
8.203
8.173
7.569
7.540
7.316
7.287
7.262
6.793
4.854
3.593
3.570
3.547
3.523
3.500
3.288
3.265
3.242
3.219
3.197
2.680
2.451
2.403
1.500
1.477
1.434
1.410
2.01
2.01
1.99
6.00
12.01
166.140
144.262
132.685
128.267
127.410
119.787
77.423
77.000
76.577
36.918
22.868
15.210
150
100
50
0
ppm (f1)

Compound **17** 


8.293
8.264
7.473
7.444
7.263
2.904
2.637
2.06
1.99
6.00
6.00
500
0
10.0
5.0
0.0
ppm (f1)
157.608
144.316
132.425
128.212
126.833
123.116
77.424
77.000
76.576
25.514
15.101
15000
10000
5000
0
200
150
100
50
0
ppm (f1)