Supporting Information

Acid Mediated Coupling of Aliphatic Amines and Nitrosoarenes to Indoles

Subhra Kanti Roy, Anisha Purkait, Sk Md Tarik Aziz and Chandan K. Jana*[a]

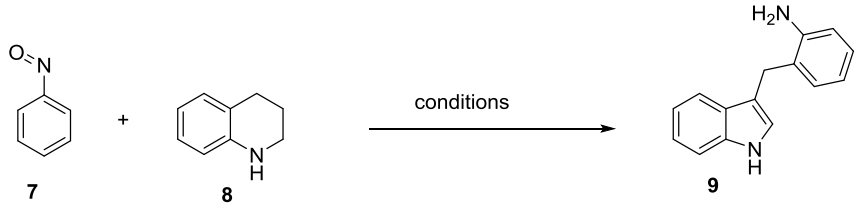
Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati, India- 781039

E-mail: ckjana@iitg.ac.in

Experimental:

General: All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in oven-dried glassware under an argon atmosphere. Toluene was freshly distilled from phosphorus (V) oxide (P_2O_5). Commercial grade xylene, benzene and toluene were distilled over CaH_2 before use. All other solvents and reagents were purified according to standard procedures or were used as received from Aldrich, Acros, Merck and Spectrochem. ^1H, ^{13}C NMR spectroscopy: *Varian Mercury plus 400 MHz, Bruker 600 MHz* (at 298 K). Chemical shifts, δ (in ppm), are reported relative to TMS δ (^1H) 0.0 ppm, δ (^{13}C) 0.0 ppm) which was used as the inner reference. Otherwise the solvents residual proton resonance and carbon resonance ($CHCl_3$, δ (^1H) 7.26 ppm, δ (^{13}C) 77.2 ppm; CD_3OD, (^1H) 3.31 ppm, δ (^{13}C) 49.0 ppm) were used for calibration. Column chromatography: Merck or Spectrochem silica gel 60-120 under gravity. IR: spectra were recorded on Perkin Elmer Instrument at normal temperature making KBr pellet grinding the sample with KBr (IR Grade). MS (ESI-HRMS): Mass spectra were recorded on an Agilent Accurate-Mass Q-TOF LC/MS 6520, and peaks are given in *m/z* (% of basis peak). Nitrosoarene derivatives were synthesized by literature procedures.[1]

Table S1: Variation of reagents and reaction conditions to obtained the best yields of the desired product.



Variation of equivalence of nitrosobenzene.

Entry	Acids (equiv.)	Equiv. of PhNO	Solvent (reflux)	Yield (%)
1	4-NO_2PhCO_2H (1.0)	1	toluene	40
2 [a]	4-NO_2PhCO_2H (1.0)	1	toluene	54
3	4-NO_2PhCO_2H (1.0)	1.5	toluene	51
4	4-NO_2PhCO_2H (1.0)	2	toluene	58
5	4-NO_2PhCO_2H (1.0)	2.5	toluene	49

Screening of the solvent of the reaction.

Entry	Acids (equiv.)	Equiv. of PhNO	Solvent (reflux)	Yield (%)
6	4-NO_2-PhCOOH (1)	2	DCE	45
7	4-NO_2-PhCOOH (1)	2	benzene	46
8	4-NO_2-PhCOOH (1)	2	xylene	40
9	4-NO_2-PhCOOH (1)	2	DMSO	31
10	4-NO_2-PhCOOH (1)	2	DMF	24

Variation of acid source.

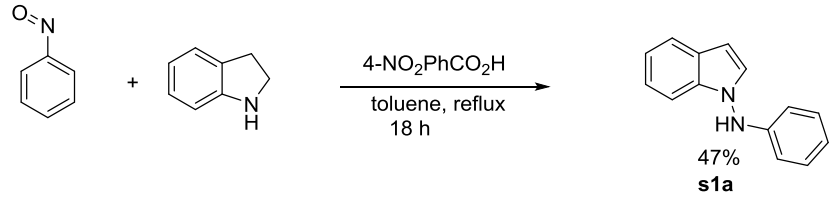
Entry	Acids (equiv.)	Equiv. of PhNO	Solvent (reflux)	Yield (%)
11	$PhCO_2H$ (1.0)	2	toluene	42
12	4-Cl-$PhCO_2H$ (1.0)	2	toluene	40
13	3, 5-di-NO_2PhCO_2H (1.0)	2	toluene	40
14	2, 5-di-Cl-$PhCO_2H$ (1.0)	2	toluene	37
15	CF_3CO_2H (1.0)	2	toluene	ND
16	1-NO_2PhCO_2H (1.0)	2	toluene	28

17	AcOH (1.0)	2	toluene	ND
18	PTSA(1.0)	2	toluene	ND
19	No acid	2	toluene	trace

Addition of nitrosobenzene.

Entry	Acids (equiv.)	Equiv. of PhNO	Solvent (reflux)	Yield (%)
20[b]	4-NO_2-PhCOOH (1)	2	toluene	70
21[c]	4-NO_2-PhCOOH (1)	2	toluene	68
22[b]	4-NO_2PhCO_2H (0.2)	2	toluene	54
23[b]	4-NO_2PhCO_2H (0.5)	2	toluene	60
24[b]	4-NO_2PhCO_2H (2)	2	toluene	41
25[d]	4-NO_2PhCO_2H (1)	2	toluene	66

All reactions were performed with of THQ (0.30 mmol), nitrosobenzene (0.60 mmol) in solvent (4 mL) for 18 h. [a]1.5 equiv. of THQ was used, [b] addition of nitrosobenzene over 2 h and [c]addition of nitrosobenzene in toluene was carried out over 2 h by syringe pump. [d]addition of nitrosobenzene over 3 h.



Scheme S1: Reaction with indoline.

General procedure for the synthesis of 3-benzyl indole derivatives (GP-1): Nitrosoarene (1 equiv.) and 4-nitrobenzoic acid (1 equiv.) were added to a solution of tetrahydroquinoline derivative (0.19 – 0.48 mmol) in dry toluene (4 – 5 mL). After 1 h, additional 1 equiv. of nitrosoarene was added portion wise over a period of 2 h. Then the reaction mixture was refluxed for another 15 h under argon atmosphere. The reaction mixture was allowed to cool to room temperature. Saturated $NaHCO_3$ solution (15 – 20 mL) was added to the reaction mixture and extracted with DCM (3 ×15 mL). Organic layer was dried over Na_2SO_4 and the solvent was evaporated under reduced pressure to obtain brown residue which was purified by column chromatography to afford analytically pure 3-benzyl indole derivatives.

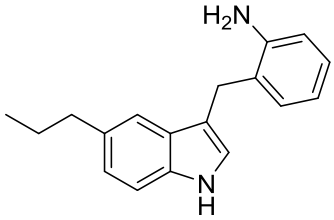
2-((1*H*-indol-3-yl)methyl)aniline (9): According to GP-1: nitrosobenzene (64 mg, 0.60 mmol), 1,2,3,4-tetrahydroquinoline (38 µL, 0.30 mmol) and 4-nitrobenzoic acid (50 mg, 0.30 mmol) were reacted for 18 h in dry toluene (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:5) of the crude gave **9** as a colorless solid (47 mg, 70%). FTIR (KBr): $\tilde{\nu}$ = 3429, 3344, 2962, 2922, 1700, 1611, 1493, 1456, 1262, 1051, 802, 748 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (br.s, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.23 – 7.17 (m, 2H), 7.13 – 7.09 (m, 2H), 6.83 – 6.82 (m, 1H), 6.81 – 6.77 (m, 1H), 6.72 – 6.70 (m, 1H), 4.03 (s, 2H), 3.35 (br.s, 2H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 145.0, 136.7, 130.6, 127.6, 127.5, 125.4, 122.5, 122.4, 119.7, 119.3, 118.9, 116.0, 113.9, 111.3, 28.4 ppm. HRMS (ESI) exact mass calculated for $C_{15}H_{15}N_2$+ ([M + H]+): 223.1230; Found: 223.1238.

2-((5-methyl-1*H*-indol-3-yl)methyl)aniline (12a): According to GP-1: 1-methyl-4-nitrosobenzene (73 mg, 0.60 mmol), 1,2,3,4-tetrahydroquinoline (38 µL, 0.30 mmol) and 4-nitrobenzoic acid (50 mg, 0.30 mmol) were reacted for 18 h in dry toluene (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:5) of the crude gave **12a** as a colorless solid (42 mg, 59%). FTIR (KBr): $\tilde{\nu}$ = 3416, 3333, 3218, 3218, 2917, 2851, 1614, 1582, 1493, 1455, 1442, 1317, 1264, 1095, 1034, 802, 752, 715 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 (br.s, 1H), 7.37 – 7.36 (m, 1H), 7.24 (s, 1H), 7.16 – 7.14 (m, 1H), 7.11 – 7.06 (m, 1H), 7.03 – 7.01 (m, 1H), 6.78 – 6.74 (m, 2H), 6.69 – 6.67 (m, 1H), 3.97 (s, 2H), 3.21 (br.s, 1H), (2.43 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 145.0, 135.1, 130.6, 128.9, 127.8, 127.5, 125.6, 124.0, 122.6, 118.9, 118.9, 116.0, 113.4, 111.0, 28.3, 21.7 ppm. HRMS (ESI) exact mass calculated for $C_{16}H_{17}N_2^+$ ([M + H]+): 237.1386 ; Found: 237.1390.

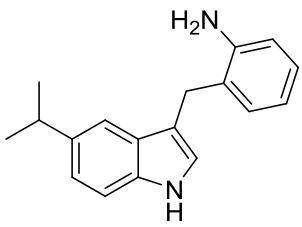
2-((5-ethyl-1H-indol-3-yl)methyl)aniline (12b): According to GP-1: 1-ethyl-4-nitrosobenzene (81 mg, 0.60 mmol), 1,2,3,4-tetrahydroquinoline (38 µL, 0.30 mmol) and 4-nitrobenzoic acid (50 mg, 0.30 mmol) were reacted for 18 h in dry toluene (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:5) of the crude gave **12b** as a brown solid (46 mg, 61%). FTIR (KBr): $\tilde{\nu}$ = 3428, 2962, 2925, 2854, 1623, 1523, 1341, 1317, 1262, 1102, 1014, 800, 753, 723 cm^{-1}. ^{1}H NMR (400 MHz, CD_3OD) δ = 7.25 – 7.23 (m, 2H), 7.06 (d, *J* = 7.6 Hz, 1H),

7.02 – 6.98 (m, 1H), 6.96 – 6.94 (m, 1H), 6.86 (s, 1H), 6.74 – 6.72 (m, 1H), 6.70 – 6.64 (m, 1H), 3.95 (s, 2H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H) ppm. ^{13}C NMR (101 MHz, CD_3OD) δ = 146.7, 137.4, 136.1, 131.5, 129.4, 128.5, 128.3, 124.5, 123.5, 120.2, 118.6, 117.8, 113.93, 112.5, 30.6, 29.3, 17.6 ppm. HRMS (ESI) exact mass calculated for $C_{17}H_{19}N_2$+ ([M + H]+): 251.1543 ; Found: 251.1543.

2-((5-propyl-1*H*-indol-3-yl)methyl)aniline (12c): According to GP-1: 1-nitroso-4-propylbenzene (67 mg, 0.45 mmol), 1,2,3,4-tetrahydroquinoline (28 µL, 0.23 mmol) and 4-nitrobenzoic acid (38 mg, 0.23 mmol) were reacted for 18 h in dry toluene (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:5) of the crude gave **12c** as a colorless solid (43 mg, 54%). FTIR (KBr): $\tilde{\nu}$ = 3442, 3387, 3311, 3210, 3036, 2960, 2922, 2857, 1615, 1589, 1492, 1458, 1260, 1097, 1023, 865, 798, 751 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.87 (br.s, 1H), 7.37 (s, 1H), 7.24 (s, 1H), 7.16 – 7.14 (m, 1H), 7.10 – 7.06 (m, 1H), 7.05 – 7.02 (m, 1H), 6.77 – 6.74 (m, 2H), 6.69 – 6.66 (m, 1H), 3.98 (s, 2H), 2.68 – 2.64 (m, 2H), 1.69 – 1.63 (m, 2H), 0.95 (t, *J* = 7.6 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 145.0, 135.3, 134.1, 130.6, 127.7, 127.5, 125.6, 123.5, 122.6, 118.9, 118.3, 116.0, 113.6, 111.0, 38.5, 28.3, 25.6, 14.2 ppm. HRMS (ESI) exact mass calculated for $C_{17}H_{19}N_2^+$ ([M + H]$^+$): 265.1699; Found: 265.1700.



2-((5-isopropyl-1*H*-indol-3-yl)methyl)aniline (12d): According to GP-1: 1-isopropyl-4-nitrosobenzene (89 mg, 0.60 mmol), 1,2,3,4-tetrahydroquinoline (38 µL, 0.30 mmol) and 4-nitrobenzoic acid (50 mg, 0.30 mmol) were reacted for 18 h in dry toluene (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:5) of the crude gave **12d** as a brown solid (51 mg, 64%). FTIR (KBr): $\tilde{\nu}$ = 3383, 3307, 3188, 3036, 2958, 2925, 2870, 1616, 1586, 1491, 1458, 1353, 1256, 1228, 1100, 799, 753, 726, 653 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 (br.s, 1H), 7.44 (s, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.20 – 7.18 (m, 1H), 7.13 – 7.08 (m, 2H), 6.80 – 6.76 (m, 2H), 6.71 – 6.69 (m, 1H), 4.01 (s, 2H), 3.01 (sept, *J* = 6.8 Mz, 1H), 1.31 (d, *J* = 7.2 Hz, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 145.0, 140.4, 135.4, 130.7, 127.7, 127.6, 125.6, 122.6, 121.6, 118.9, 116.1, 116.0, 113.7, 111.1, 34.4, 28.4, 24.9 ppm. HRMS (ESI) exact mass calculated for $C_{18}H_{21}N_2$+ ([M + H]+): 265.1699; Found: 265.1697.



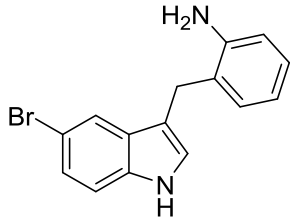
2-((5-(tert-butyl)-1*H*-indol-3-yl)methyl)aniline (12e): According to GP-1: 1-(*tert*-butyl)-4-nitrosobenzene (73 mg, 0.45 mmol), 1,2,3,4-tetrahydroquinoline (28 µL, 0.23 mmol) and 4-nitrobenzoic acid (38 mg, 0.23 mmol) were reacted for 18 h in dry toluene (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:5) of the crude gave **12e** as a brown solid (42 mg, 67%). FTIR (KBr): $\tilde{\nu}$ = 3386, 3315, 2959, 2858, 1615, 1490, 1458, 1259, 1226, 1101, 1021, 802, 757 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86 (br.s, 1H), 7.56 (s, 1H), 7.29 – 7.28 (m, 2H), 7.20 – 7.19 (m, 1H), 7.11 – 7.07 (m, 1H), 6.79 – 6.74 (m, 2H), 6.69 – 6.67 (m, 1H), 4.01 (s, 2H), (1.37 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 145.1, 142.6, 135.0, 130.8, 127.6, 127.3, 125.6, 122.5, 120.7, 118.9, 116.0, 115.0, 113.9, 110.8, 34.8, 32.2, 28.5 ppm. HRMS (ESI) exact mass calculated for $C_{19}H_{23}N_2$+ ([M + H]+): 279.1856; Found: 279.1856.

2-((5-fluoro-1*H*-indol-3-yl)methyl)aniline (12f): According to GP-1: 1-fluoro-4-nitrosobenzene (75 mg, 0.60 mmol), 1,2,3,4-tetrahydroquinoline (38 µL, 0.30 mmol) and 4-nitrobenzoic acid (50 mg, 0.30 mmol) were reacted for 18 h in dry toluene (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:5) of the crude gave **12f** as a brown solid (50 mg, 69%). FTIR (KBr): $\tilde{\nu}$ = 3474, 3397, 3018, 2961, 2920, 2852, 1618, 1578, 1487, 1452, 1312, 1262, 1159, 1091, 1029, 932, 857, 790, 754 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91 (br.s, 1H), 7.16 – 7.08 (m, 2H), 7.07 – 7.05 (m, 1H), 7.03 – 6.99 (m, 1H), 6.87 – 6.82 (m, 1H), 6.78 – 6.77 (m, 1H), 6.71 – 6.67 (m, 1H), 6.61 – 6.59 (m, 1H), 3.86 (s, 2H), 3.12 (br.s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 157.9 (d, J = 235.5 Hz), 144.9, 133.2, 130.6, 128.0, 127.9 (d, J = 9.8 Hz), 125.1, 124.3, 119.1, 116.1, 114.1 (d, J = 4.8 Hz), 111.9 (d, J = 9.7 Hz), 110.9 (d, J = 26.5 Hz), 104.2 (d, J = 23.5), 28.3 ppm. HRMS (ESI) exact mass calculated for $C_{15}H_{14}FN_2$+ ([M + H]+): 241.1136 ; Found: 241.1138.

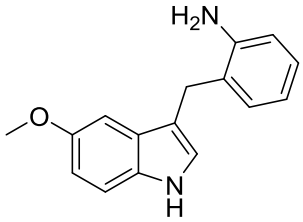
2-((5-chloro-1*H*-indol-3-yl)methyl)aniline (12g): According to GP-1: 1-chloro-4-nitrosobenzene (85 mg, 0.60 mmol), 1,2,3,4-tetrahydroquinoline (38 µL, 0.30 mmol) and 4-nitrobenzoic acid (50 mg, 0.30 mmol) were reacted for 18 h in dry toluene (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:5) of the crude gave **12g** as a light green solid (55 mg, 71%). FTIR (KBr): $\tilde{\nu}$ = 3392, 2929, 1629, 1493, 1459, 1315, 1096, 795, 753

cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.07 (br.s, 1H), 7.56 – 7.55 (m, 1H), 7.23 (d, *J* = 8.8 Hz, 1H), 7.16 – 7.11 (m, 3H), 6.82 – 6.81 (m, 1H), 6.79 – 7.77 (m, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 3.95 (s, 2H), 3.48 (br.s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 144.8, 135.0, 130.5, 128.6, 127.7, 125.4, 125.0, 123.9, 122.7, 119.1, 118.7, 116.1, 113.7, 112.4, 28.0 ppm. HRMS (ESI) exact mass calculated for $C_{15}H_{14}ClN_2$+ ([M + H]+): 257.0840; Found: 257.0846.

2-((5-bromo-1*H*-indol-3-yl)methyl)aniline (12h): According to GP-1: 1-bromo-4-nitrosobenzene (0.10 g, 0.60 mmol), 1,2,3,4-tetrahydroquinoline (38 µL, 0.30 mmol) and 4-nitrobenzoic acid (50 mg, 0.30 mmol) were reacted for 18 h in dry toluene (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:5) of the crude gave **12h** as a brown solid (53 mg, 59%). FTIR (KBr): $\tilde{\nu}$ = 3421, 3027, 2964, 2922, 2855, 1618, 1587, 1492, 1457, 1275, 1262, 1244, 1093, 881, 751 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.06 (br.s, 1H), 7.71 (s, 1H), 7.28 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.18 (d, *J* = 9.0 Hz, 1H), 7.14 – 7.113 (m, 2H), 6.81 – 6.78 (m, 2H), 6.72 – 6.72 (m, 1H), 3.94 (s, 2H), 3.49 (br.s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 144.8, 135.3, 130.5, 129.3, 127.8, 125.2, 125.0, 123.7, 121.8, 119.1, 116.1, 113.6, 112.9, 112.8, 28.0 ppm. HRMS (ESI) exact mass calculated for $C_{15}H_{14}BrN_2$+ ([M + H]+): 301.0335; Found: 301.0341.



2-((5-methoxy-1*H*-indol-3-yl)methyl)aniline (12i): According to GP-1: 1-methoxy-4-nitrosobenzene (0.10 g, 0.75 mmol), 1,2,3,4-tetrahydroquinoline (44 µL, 0.37 mmol) and 4-nitrobenzoic acid (63 mg, 0.37 mmol) were reacted for 18 h in dry toluene (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:5) of the crude gave **12i** colorless solid (47 mg, 50%). FTIR (KBr): $\tilde{\nu}$ = 3386, 3308, 3162, 3040, 2992, 2899, 2825, 1617, 1585, 1489, 1458, 1253, 1214, 1047, 760 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.93 (br.s, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.19 – 7.18 (m, 1H), 7.12 – 7.09 (m, 1H), 6.99 – 6.98 (s, 1H), 6.86 – 6.85 (m, 1H), 6.81 – 6.79 (m, 2H), 6.75 – 6.74 (m, 1H), 4.00 (s, 2H), 3.81 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 154.1, 144.1, 131.8, 130.6, 127.9, 127.6, 126.0, 123.3, 119.5, 116.5, 113.4, 112.6, 112.1, 100.9, 56.0, 28.4 ppm. HRMS (ESI) exact mass calculated for $C_{16}H_{17}N_2O^+$ ([M + H]+): 253.1335; Found: 253.1331.

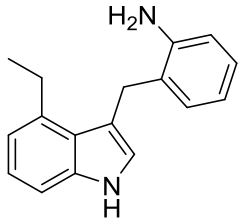


2-((5-(trifluoromethoxy)-1*H*-indol-3-yl)methyl)aniline (12j): According to GP-1: 1-nitroso-4-(trifluoromethoxy)benzene (0.12 g, 0.60 mmol), 1,2,3,4-tetrahydroquinoline (38 µL, 0.30 mmol) and 4-nitrobenzoic acid (50 mg, 0.30 mmol) were reacted for 18 h in dry toluene (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:5) of the crude gave **12j** as a colorless solid (55 mg, 60%). FTIR (KBr): $\tilde{\nu}$ = 3426, 3344, 3220, 2923, 2853, 1603, 1521, 1460, 1346, 1257, 1216, 1177, 1096, 887, 753, 722 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08 (br.s, 1H), 7.42 (s, 1H), 7.33 (d, *J* = 8.8 Hz, 1H), 7.15 – 7.07 (m, 3H), 6.91–6.90 (m, 1H), 6.80 – 6.76 (m, 1H), 6.72 – 6.70 (m, 1H), 3.98 (s, 2H), 3.57 (br.s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 144.8, 143.07, 143.05, 143.03, 143.01, 135.0, 130.6, 127.8, 127.8, 124.8, 124.4, 122.8, 122.3, 119.7, 119.1, 116.4, 116.2, 114.5, 111.9, 111.8, 28.1 ppm. HRMS (ESI) exact mass calculated for $C_{16}H_{14}F_3N_2O^+$ ([M + H]+): 307.1053; Found: 307.1054.

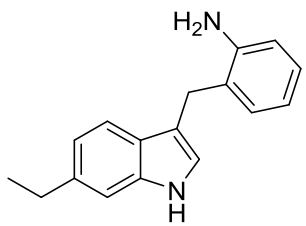
2-((4,6-dimethyl-1*H*-indol-3-yl)methyl)aniline (12k): According to GP-1: 1,3-dimethyl-5-nitrosobenzene (0.10 g, 0.75 mmol), 1,2,3,4-tetrahydroquinoline (47 µL, 0.37 mmol) and 4-nitrobenzoic acid (63 mg, 0.37 mmol) were reacted for 18 h in dry toluene (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:5) of the crude gave **12k** as a colorless solid (52 mg, 55%). FTIR (KBr): $\tilde{\nu}$ = 3389, 3311, 3225, 2917, 2853, 1614, 1588, 1494, 1456, 1257, 1112, 804, 751, 700 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.80 (br.s, 1H), 7.14 – 7.10 (m, 1H), 7.06 – 7.04 (m, 1H), 6.98 (s, 1H), 6.78 – 6.73 (m, 3H), 6.57 – 6.56 (m, 1H), 4.17 (s, 2H), 3.43 (br.s, 2H), 2.65 (s, 3H), 2.43 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 144.6, 137.8, 132.3, 131.0, 130.4, 127.4, 126.3, 124.1, 123.1, 122.2, 119.0, 115.8, 114.4, 109.1, 30.1, 21.6, 20.3 ppm. HRMS (ESI) exact mass calculated for $C_{17}H_{19}N_2^+$ ([M + H]+): 251.1543; Found: 251.1549.

2-((4-ethyl-1*H*-indol-3-yl)methyl)aniline and **2-((6-ethyl-1*H*-indol-3-yl)methyl)aniline (12l** and **12m**: According to GP-1: 1-ethyl-3-nitrosobenzene (0.12 g, 0.90 mmol), 1,2,3,4-tetrahydroquinoline (57 µL, 0.45 mmol) and 4-nitrobenzoic acid (75 mg, 0.45 mmol) were reacted for 18 h in dry toluene (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:6) of the crude gave **12l** as a light yellow solid (37 mg, 33%) and **12m** as a colorless solid (41 mg, 36%).

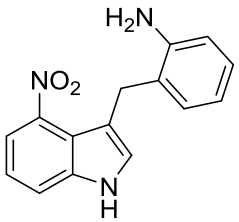
12l: FTIR (KBr): $\tilde{\nu}$ = 3384, 3308, 3208, 3186, 2963, 2920, 1616, 1585, 1491, 1455, 1255, 1229, 1050, 855, 813, 750 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95 (br.s, 1H), 7.21 – 7.19 (m, 1H), 7.15 – 7.09 (m, 2H), 7.08 – 7.04 (m, 1H), 6.92 (d, *J* = 7.0 Hz, 1H), 6.83 – 6.77 (m, 2H), 6.61 (s, 1H), 4.20 (s, 2H), 3.05 (q, *J* = 7.6 Hz, 2H), 1.33 (t, *J* = 7.6 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 143.9, 137.9, 137.6, 130.7, 127.6, 126.6, 125.4, 123.0, 122.6, 119.7, 119.4, 116.4, 114.1, 109.3, 30.4, 26.6, 16.6 ppm. HRMS (ESI) exact mass calculated for $C_{17}H_{19}N_2^+$ ([M + H]+): 251.1543; Found: 251.1549.

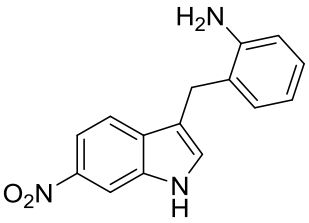


12m: FTIR (KBr): $\tilde{\nu}$ = 3435, 2957, 2925, 2869, 1624, 1457, 1377, 1155, 812, 750 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91 (br.s, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.19 – 7.17 (m, 2H), 7.12 – 7.07 (m, 1H), 6.98 (d, *J* = 7.2 Hz, 1H), 6.79 – 6.75 (m, 2H), 6.68 (d, *J* = 8.4 Hz, 1H), 4.00 (s, 2H), 2.76 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 4H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 145.0, 138.9, 137.2, 130.6, 127.5, 125.7, 125.6, 121.9, 120.4, 119.0, 118.9, 116.0, 113.8, 110.0, 29.3, 28.5, 16.4 ppm. HRMS (ESI) exact mass calculated for $C_{17}H_{19}N_2^+$ ([M + H]+): 251.1543; Found: 251.1544.

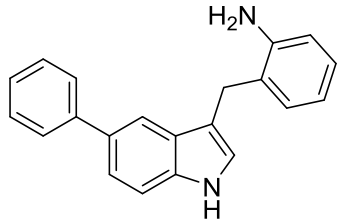


2-((4-nitro-1*H*-indol-3-yl)methyl)aniline and **2-((6-nitro-1*H*-indol-3-yl)methyl)aniline (12n and 12o)**: According to GP-1: 1-nitro-3-nitrosobenzene (91mg, 0.60 mmol), 1,2,3,4-tetrahydroquinoline (38 µL, 0.30 mmol) and 4-nitrobenzoic acid (50 mg, 0.30 mmol) were reacted for 18 h in dry toluene (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:5) of the crude gave 1:1 inseparable mixture of **12n** and **12o** as a as a yellow gum (39 mg, 49%). HRMS (ESI) exact mass calculated for $C_{15}H_{14}N_3O_2^+$ ([M + H]+): 268.1081 ; Found: 268.1084.

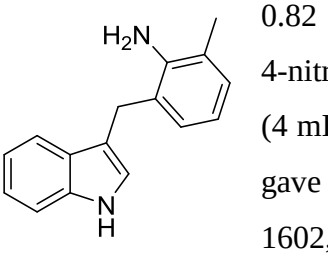




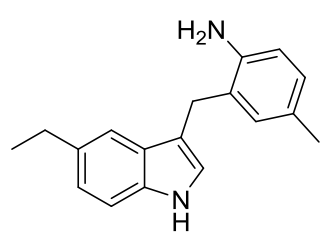
2-((5-phenyl-1*H*-indol-3-yl)methyl)aniline (12p): According to GP-1: 4-nitroso-1,1'-biphenyl (69 mg, 0.38 mmol), 1,2,3,4-tetrahydroquinoline (24 µL, 0.19 mmol) and 4-nitrobenzoic acid (32 mg, 0.19 mmol) were reacted for 18 h in dry toluene (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:5) of the crude gave **12p** as a colorless solid (28 mg, 50%). FTIR (KBr): $\tilde{\nu}$ = 3436, 2962, 2924, 2852, 1635, 1271, 1260, 1097, 749 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 (br.s, 1H), 7.80 (s, 1H), 7.64 – 7.62 (m, 2H), 7.49 – 7.42 (m, 4H), 7.33 – 7.29 (m, 1H), 7.20 – 7.18 (m, 1H), 7.12 – 7.09 (m, 1H), 6.87 – 6.86 (s, 1H), 6.80 – 6.76 (m, 1H), 6.72 – 6.70 (m, 1H), 4.05 (s, 2H), 3.64 (br.s, 1H) ppm. ^{13}C NMR (101 MHz, CDCl3) δ = 144.9, 142.7, 136.3, 133.3, 130.7, 128.8, 128.1, 127.7, 127.6, 126.5, 125.4, 123.2, 122.3, 119.0, 117.8, 116.1, 114.4, 111.6, 28.3 ppm. HRMS (ESI) exact mass calculated for $C_{21}H_{19}N_2^+$ ([M + H]+): 299.1543; Found: 299.1550.



2-((1*H*-indol-3-yl)methyl)-6-methylaniline (12q): According to GP-1: nitrosobenzene (87 mg, 0.82 mmol), 8-methyl-1,2,3,4-tetrahydroquinoline (56 µL, 0.41 mmol) and 4-nitrobenzoic acid (68 mg, 0.41 mmol) were reacted for 18 h in dry toluene (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:5) of the crude gave **12q** as a brown solid (58 mg, 60%). FTIR (KBr): $\tilde{\nu}$ = 3354, 2987, 1676, 1602, 1569, 1514, 1482, 1456, 1384, 1283, 1173, 1119, 769, 752 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (br.s, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.23 – 7.19 (m, 1H), 7.13 – 7.09 (m, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.84 – 6.83 (m, 1H), 6.71 (t, *J* = 7.8 Hz, 1H), 4.03 (s, 2H), 2.18 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 142.9, 136.8, 128.9, 128.6, 127.7, 125.0, 122.7, 122.6, 122.4, 119.7, 119.3, 118.5, 114.1, 111.3, 28.6, 17.8 ppm. HRMS (ESI) exact mass calculated for $C_{16}H_{17}N_2$+ ([M + H]+): 237.1386 ; Found: 237.1387.

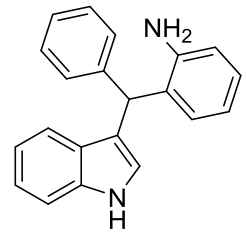


2-((5-ethyl-1*H*-indol-3-yl)methyl)-4-methylaniline (12r): According to GP-1: 1-ethyl-4-nitrosobenzene (55 mg, 0.40 mmol), 6-methyl-1,2,3,4-tetrahydroquinoline (30 mg, 0.20 mmol) and 4-nitrobenzoic acid (34 mg, 0.20 mmol) were reacted for 18 h in dry toluene (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:5) of the crude gave **12r** as a colorless solid (24 mg, 45%). FTIR (KBr): $\tilde{\nu}$ = 3354, 2987, 1675,

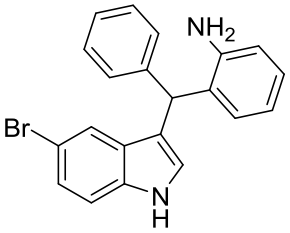


1602, 1569, 1514, 1482, 1457, 1384, 1309, 1283, 1173, 1119, 1105, 769, 752 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.90 (br.s, 1H), 7.42 (s, 1H), 7.28 – 7.26 (m, 1H), 7.08 – 7.06 (m, 1H), 7.01 – 7.00 (m, 1H), 6.92 – 6.90 (m, 1H), 6.77 – 6.76 (m, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 3.97 (s, 2H), 2.75 (q, *J* = 7.6 Hz, 2H), 2.26 (s, 3H), 1.29 (t, *J* = 7.6 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 142.4, 135.6, 135.3, 131.3, 128.1, 128.0, 127.8, 125.7, 123.0, 122.6, 117.6, 116.2, 113.8, 111.1, 29.2, 28.3, 20.7, 16.7 ppm. HRMS (ESI) exact mass calculated for $C_{18}H_{21}N_2^+$ ([M + H]+): 265.1699; Found: 265.1702.

2-((1*H*-indol-3-yl)(phenyl)methyl)aniline (12s): According to GP-1: nitrosobenzene (48 mg, 0.45 mmol), 4-phenyl-1,2,3,4-tetrahydroquinoline[2] (47 mg, 0.22 mmol) and 4-nitrobenzoic acid (37 mg, 0.22 mmol) were reacted for 18 h in dry toluene (4 mL) under argon atmosphere. Column chromatography (silica; EtOAc : Hexane, 1:7) of the crude gave **12s** as a brown gum (38 mg, 57%). FTIR (KBr): $\tilde{\nu}$ = 3437, 2957, 2925, 2869, 1623, 1599, 1488, 1455, 1089, 1015, 823, 765 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01 (br.s, 1H), 7.38 – 7.36 (m, 1H), 7.31 – 7.28 (m, 3H), 7.26 – 7.24 (m, 3H), 7.20 – 7.16 (m, 1H), 7.10 – 7.06 (m, 1H), 7.03 – 6.99 (m, 1H), 6.81 – 6.79 (m, 1H), 6.73 – 6.67 (m, 2H), 6.63 – 6.62 (m, 1H), 5.67 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 144.0, 142.5, 136.8, 129.6, 129.2, 129.1, 128.5, 127.3, 127.1, 126.5, 124.0, 122.3, 119.9, 119.6, 118.8, 118.1, 116.3, 111.1, 43.8 ppm. HRMS (ESI) exact mass calculated for $C_{21}H_{19}N_2^+$ ([M + H]+): 299.1543; Found: 299.1550.

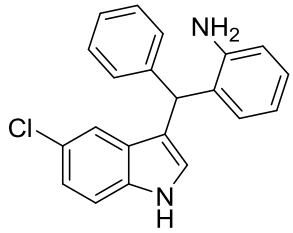


2-((5-bromo-1*H*-indol-3-yl)(phenyl)methyl)aniline (12t): According to GP-1: 1-bromo-4-nitrosobenzene (89 mg, 0.48 mmol), 4-phenyl-1,2,3,4-tetrahydroquinoline (50 mg, 0.24 mmol) and 4-nitrobenzoic acid (40 mg, 0.24 mmol) were reacted for 18 h in dry toluene (4 mL) under argon atmosphere. Column chromatography (silica; EtOAc : Hexane, 1:7) of the crude gave **12t** as a brown gum (45 mg, 50%). FTIR (KBr): $\tilde{\nu}$ = 3445, 2956, 2925, 2869, 1620, 1598, 1584, 1488, 1389, 1089, 1015, 834, 765, 744 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01 (br.s, 1H), 7.36 –7.35 (m, 1H), 7.25 – 7.21 (m 2H), 7.20 – 7.13 (m, 5H), 7.03 – 6.99 (m, 1H), 6.69 – 6.67 (m, 1H), 6.64 – 6.59 (m, 2H), 6.55 –6.54 (s, 1H), 5.50 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 144.4, 142.4, 135.6, 129.6, 129.2, 129.0, 128.8, 128.7, 127.7, 126.9, 125.5, 125.4,

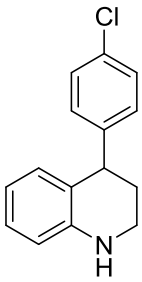


122.4, 118.9, 118.1, 116.5, 113.1, 112.8, 43.8 ppm. HRMS (ESI) exact mass calculated for $C_{21}H_{18}BrN_2^+$ ([M + H]+): 377.0648; Found: 377.0641.

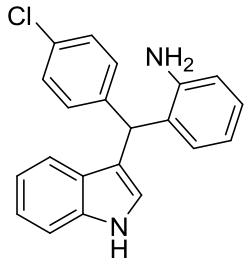
2-((5-chloro-1*H*-indol-3-yl)(phenyl)methyl)aniline (12u): According to GP-1: 1-chloro-4-nitrosobenzene (94 mg, 0.67 mmol), 4-phenyl-1,2,3,4-tetrahydroquinoline (70 mg, 0.33 mmol) and 4-nitrobenzoic acid (56 mg, 0.33 mmol) were reacted for 24 h in dry toluene (4 mL) under argon atmosphere. Column chromatography (silica; EtOAc : Hexane, 1:7) of the crude gave **12u** as a brown gum (49 mg, 51%). FTIR (KBr): $\tilde{\nu}$ = 3412, 2963, 2925, 2853, 1634, 1491, 1451, 1261, 1095, 795, 749 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.02 (br.s, 1H), 7.25 – 7.17 (m, 5H), 7.15 – 7.12 (d, *J* = 8.4 Hz, 2H), 7.05 – 6.99 (m, 2H), 6.70 – 6.60 (m, 3H), 6.55 (s, 1H), 5.52 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 144.0, 142.3, 135.3, 129.6, 129.3, 128.9, 128.8, 128.3, 127.7, 126.9, 125.6, 125.5, 122.8, 119.4, 119.2, 118.1, 116.7, 112.3, 43.8 ppm. HRMS (ESI) exact mass calculated for $C_{21}H_{18}ClN_2^+$ ([M + H]+): 333.1153; Found: 333.1145.



Preparation of 4-(4-chlorophenyl)-1,2,3,4-tetrahydroquinoline (11v): Benzyl azide (0.24 g, 1.8 mmol) in dichloromethane (2 mL) was cooled to 0 °C. TfOH (0.18 mL, 2.0 mmol) was added to the solution at 0 °C and the reaction mixture was allowed to stir at room temperature for 10 min. 4-chlorostyrene (0.44 mL, 3.6 mmol) was added to the reaction mixture and the reaction mixture was stirred at room temperature for 1 h. The reaction mixture was quenched by saturated aqueous Na_2CO_3 solution and extracted with dichloromethane (3 x 15 mL). The combine organic layer was washed with brine solution (3 x 10 mL) and dried over Na_2SO_4. The organic layer was concentrated under vacuo to give brown gum which was purified by column chromatography (silica, EtOAc : Hexane; 1:20) to afford **11v** (0.25 g, 56%). FTIR (KBr): $\tilde{\nu}$ = 3409, 3020, 2921, 2850, 1605, 1584, 1483, 1467, 1312, 1262, 1089, 1013, 822, 723 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.31 – 7.29 (m, 2H), 7.12 – 7.10 (m, 2H), 7.09 – 7.05 (m, 1H), 6.78 – 6.76 (m, 1H), 6.64 – 6.58 (m, 2H), 4.18 – 4.15 (m, 1H), 3.68 (br.s, 1H), 3.35 – 3.29 (m, 1H), 3.26 – 3.21 (m, 1H), 2.27 – 2.20 (m, 1H), 2.08 – 2.00 (m, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 145.3, 145.0, 131.9, 130.4, 130.1, 128.5, 127.7, 122.9, 117.2, 114.4, 42.4, 39.1, 31.2 ppm. HRMS (ESI) exact mass calculated for $C_{15}H_{15}ClN^+$ ([M + H]+): 244.0888; Found: 244.0890.

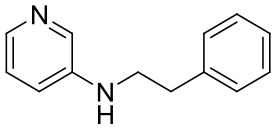


2-((4-chlorophenyl)(1*H*-indol-3-yl)methyl)aniline (12v): According to GP-1: nitrosobenzene



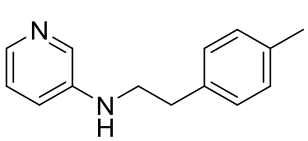
(66 mg, 0.60 mmol), 4-(4-chlorophenyl)-1,2,3,4-tetrahydroquinoline (75 mg, 0.31 mmol) and 4-nitrobenzoic acid (51 mg, 0.31 mmol) were reacted for 24 h in dry toluene (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:6) of the crude gave **12v** as a brown gum (47 mg, 46%). FTIR (KBr): $\tilde{\nu}$ = 3415, 3331, 3053, 2961, 2924, 2868, 1591, 1476, 1451, 1240, 1013, 850, 811, 756, 725 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.98 (br.s, 1H), 7.28 – 7.26 (m, 1H), 7.18 – 7.16 (m, 3H), 7.11 – 7.06 (m, 3H), 7.11 – 6.99 (m, 1H), 6.92 – 6.89 (m, 1H), 6.69 – 6.62 (m, 3H), 6.51 (s, 1H), 5.59 (s, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 143.2, 141.1, 136.8, 132.3, 130.6, 129.5, 129.1, 128.6, 127.5, 126.9, 124.0, 122.4, 119.7, 119.7, 119.5, 117.3, 116.9, 111.2, 43.1 ppm. HRMS (ESI) exact mass calculated for $C_{21}H_{18}ClN_2^+$ ([M + H]+): 333.1153; Found: 333.1146.

***N*-phenethylpyridin-3-amine (13a):** 3-bromopyridine (0.30 mL, 3.16 mmol) was added to a



solution of phenethylamine (0.40 mL, 3.16 mmol), K_2CO_3 (0.87 g, 6.32 mmol), CuI (58 mg, 0.32 mmol) and L-proline (73 mg, 0.63 mmol) in dry DMSO (4 mL) under argon atmosphere. The mixture was stirred at 90 °C for 18 h. After completion of the reaction the reaction mixture was diluted with cooled water and the resulting mixture was extracted with dichloromethane (3×90 mL). The combined organic layers were washed with brine (3×15 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (30% EtOAc in hexane) to give **13a** as a brown gum (0.25 g, 40%). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.85 (s, 1H), 7.80 – 7.79 (m, 1H), 7.19 – 7.15 (m, 2H), 7.11 – 7.05 (m, 3H), 6.93 – 6.90 (m, 1H), 6.72 – 6.69 (m, 1H), 3.98 (br.s, 1H), 3.22 (t, *J* = 7.2 Hz, 2H), 2.75 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 144.1, 138.9, 138.3, 135.9, 128.7, 128.6, 126.4, 123.7, 118.4, 44.5, 35.2.

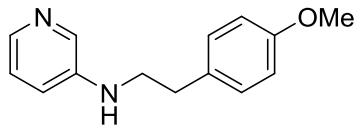
***N*-(4-methylphenethyl)pyridin-3-amine** (**13b**) : 3-bromopyridine (0.15 mL, 1.58 mmol) was



added to a solution of 4-Methylphenethylamine (0.23 mL, 1.58 mmol), K_2CO_3 (0.44 g, 3.2 mmol), CuI (29 mg, 0.16 mmol) and L-proline (36 mg, 0.32 mmol) in dry DMSO (2 mL) under argon atmosphere. The mixture was stirred at 90 °C for 18 h. After completion of the reaction the reaction mixture was diluted with cooled water and the resulting mixture was extracted with dichloromethane (3×90

mL). The combined organic layers were washed with brine (3×15 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (30% EtOAc in hexane) to give **13b** as a brown gum (73 mg, 22%). FTIR (KBr): $\tilde{\nu}$ = 3276, 3031, 2933, 2853, 1671, 1611, 1586, 1510, 1483, 1300, 1242, 1177, 1113, 828, 708 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.01 – 7.94 (m, 2H), 7.15 – 7.08 (m, 5H), 6.89 – 6.87 (m, 1H), 3.87 (br.s, 1H), 3.38 (t, *J* = 6.8 Hz, 2H), 2.89 (t, *J* = 6.8 Hz, 2H), 2.34 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 144.3, 138.4, 136.4, 135.9, 135.8, 129.6, 128.8, 124.0, 119.1, 44.8, 35.0, 21.2 ppm. HRMS (ESI) exact mass calculated for $C_{14}H_{17}N_2^+$ ($[M + H]^+$): 213.1386; Found: 213.1388.

***N*-(4-methoxyphenethyl)pyridin-3-amine** (**13c**) : 3-bromopyridine (0.18 mL, 1.9 mmol) was added to a solution of 3-Methoxylphenethylamine (0.27 mL, 1.9 mmol), K_2CO_3 (0.52 g, 3.8 mmol), CuI (35 mg, 0.19 mmol) and L-proline (44 mg, 0.38 mmol) in dry DMSO (2 mL) under argon atmosphere. The mixture was stirred at 90 ^oC for 18 h. After completion of the reaction the reaction mixture was diluted with cooled water and the resulting mixture was extracted with dichloromethane (3×90 mL). The combined organic layers were washed with brine (3×15 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by flash chromatography (30% EtOAc in hexane) to give **13c** as a brown gum (0.14 g, 31%). FTIR (KBr): $\tilde{\nu}$ = 3299, 3021, 2923, 2860, 1666, 1611, 1588, 1513, 1483, 1417, 1302, 1245, 1115, 1036, 807 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ = 7.97 (s, 1H), 7.91 – 7.90 (m, 1H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.06 – 7.04 (m, 1H), 6.85 – 6.83 (m, 3H), 3.96 (br.s, 1H), 3.76 (s, 3H), 3.33 (t, *J* = 7.2 Hz, 2H), 2.83 (t, *J* = 7.2 Hz, 2H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 158.3, 144.2, 138.4, 135.9, 130.8, 129.7, 123.8, 118.7, 114.1, 55.3, 44.8, 34.3 ppm. HRMS (ESI) exact mass calculated for $C_{14}H_{17}N_2O^+$ ($[M + H]^+$): 229.1335; Found: 229.1338.

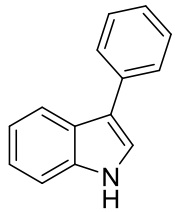


General procedure for the synthesis of 3-aryl indoles and 2, 3 diaryl indole (GP-2):

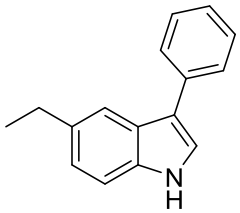
Nitrosoarene (2 equiv.) and 4-nitrobenzoic acid (1 equiv. for *N*-phenethylaniline derivatives or 2 equiv. for *N*-phenethylpyridin-3-amine derivatives) were added to a solution of *N*-phenethylaniline derivative or *N*-phenethylpyridin-3-amine derivative in dry toluene (4 – 5 mL) and reflux for 14 h. Another 1 equiv. of nitrosoarene was added and further the reaction was refluxed for 24 h. The reaction mixture was allowed to cool to room temperature and the solvent was evaporated under

reduced pressure to obtain brown gummy residue which was purified by column chromatography to afford analytically pure indole derivatives.

3-phenyl-1*H*-indole (14a):[3] According to GP-2: nitrosobenzene (97 mg, 0.91 mmol), *N*-phenethylaniline (60 mg, 0.30 mmol) and 4-nitrobenzoic acid (50 mg, 0.30 mmol) were reacted for 38 h in dry toluene (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:7) of the crude gave **14a** as a colorless gum (27 mg, 45%, 62% brsm). **14a** (28 mg, 57%) was isolated from the reaction with *N*-phenethylpyridin-3-amine (50 mg, 0.25 mmol). FTIR (KBr): $\tilde{\nu}$ = 2956, 2923, 2853, 1629, 1597, 1455, 1379, 1355, 746, 696 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.24 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.48 – 7.43 (m, 3H), 7.38 – 7.37 (m, 1H), 7.32 –7.27 (m, 2H), 7.25 – 7.19 (m, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 136.8, 135.7, 129.0, 127.7, 126.2, 126.0, 122.6, 121.9, 120.5, 120.0, 118.6, 111.6 ppm. HRMS (ESI) exact mass calculated for $C_{14}H_{12}N^+$ ([M + H]+): 194.0964; Found: 194.0967.



5-ethyl-3-phenyl-1*H*-indole (14b):[4] According to GP-2: 1-ethyl-4-nitrosobenzene (0.10 g, 0.75 mmol), *N*-phenethylaniline (50 mg, 0.25 mmol) and 4-nitrobenzoic acid (42 mg, 0.25 mmol) were reacted for 38 h in dry toluene (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:7) of the crude gave **14b** as a colorless gum (21 mg, 38%, 52% brsm). **14b** (26 mg, 47%) was isolated from the reaction with *N*-phenethylpyridin-3-amine (50 mg, 0.25 mmol). FTIR (KBr): $\tilde{\nu}$ = 3053, 2960, 2921, 2852, 1636, 1600, 1539, 1275, 748, 695 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.17 (br.s, 1H), 7.75 (s, 1H), 7.69 – 7.68 (m, 2H), 7.48 – 7.44 (m, 2H), 7.37 – 7.34 (m, 2H), 7.31 – 7.27 (m, 1H), 7.13 – 7.11 (m, 1H), 2.81 – 2.74 (m, 2H), 1.29 (t, *J* = 7.6 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 136.6, 136.0, 135.3, 128.9, 127.7, 126.2, 126.1, 123.2, 122.1, 118.4, 118.3, 111.4, 29.4, 16.9 ppm. HRMS (ESI) exact mass calculated for $C_{16}H_{16}N^+$ ([M + H]+): 222.1277; Found: 222.1282.



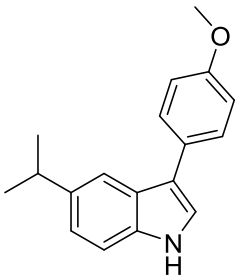
3-(4-methoxyphenyl)-1*H*-indole (14c):[5] According to GP-2: Nitrosobenzene (86 mg, 0.81 mmol), *N*-(4-methoxyphenethyl)aniline (60 mg, 0.26 mmol) and 4-nitrobenzoic acid (45 mg, 0.27 mmol) were reacted for 38 h in dry toluene (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:7) of the crude gave **14c** as a brown gum (24 mg, 41%). **14c** (46 mg, 50%) was isolated from the reaction with *N*-(4-methoxyphenethyl)pyridin-3-amine (88 mg, 0.41 mmol). FTIR (KBr): $\tilde{\nu}$ = 2963, 2924, 2853, 1637, 1545, 1495, 1450, 1260, 745, 696 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.21 (br.s, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.44 – 7.42 (m, 1H), 7.30 (d, *J* = 2.4 Hz, 1H), 7.24 – 7.16 (m, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 158.3, 136.8, 128.8, 128.3, 126.1, 122.5, 121.3, 120.3, 119.9, 118.3, 114.4, 111.5, 55.6 ppm. HRMS (ESI) exact mass calculated for $C_{15}H_{14}NO^+$ ([M + H]+): 224.1070; Found: 224.1079.

3-(p-tolyl)-1*H*-indole (14d):[5] According to GP-2: nitrosobenzene (0.10 g, 1.0 mmol), *N*-(4-methylphenethyl)aniline (70 mg, 0.33 mmol) and 4-nitrobenzoic acid (55 mg, 0.33 mmol) were reacted for 38 h in dry toluene (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:6) of the crude gave **14d** as a colorless gum (25 mg, 36%). **14d** (29 mg, 49%) was isolated from the reaction with *N*-(4-methylphenethyl)pyridin-3-amine (60 mg, 0.28 mmol). FTIR (KBr): $\tilde{\nu}$ = 2922, 2853, 1638, 1660, 1543, 1493, 1450, 1260, 1175, 1099, 805, 746 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.21 (br.s, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.35 – 7.34 (m, 1H), 7.28 – 7.25 (m, 3H), 7.23 – 7.17 (m, 1H), 2.41 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 136.8, 135.8, 132.8, 129.7, 127.6, 126.1, 122.5, 121.7, 120.4, 120.1, 118.5, 111.5, 21.4 ppm. HRMS (ESI) exact mass calculated for $C_{15}H_{14}N^+$ ([M + H]+): 208.1121; Found: 208.1124.

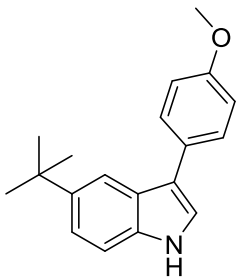
3-(3,4-dimethoxyphenyl)-1*H*-indole (14e):[6] According to GP-2: Nitrosobenzene (62 mg, 0.58 mmol), *N*-(3,4-dimethoxyphenethyl)aniline (50 mg, 0.19 mmol) and 4-nitrobenzoic acid (32 mg, 0.19 mmol) were reacted for 38 h in dry toluene (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:7) of the crude gave **14e** as a brown gum (21 mg, 43%). FTIR (KBr): $\tilde{\nu}$ = 2923, 2853, 1637, 1456, 1261, 1098, 749 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.23 (s, 1H),

7.91 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.33 – 7.32 (m, 1H), 7.27 – 7.23 (m, 2H), 7.22 – 7.17 (m, 3H), 6.98 (d, *J* = 8.0 Hz, 1H), 3.96 (s, 3H), 3.94 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 149.2, 147.6, 136.6, 128.5, 125.9, 122.4, 121.2, 120.2, 119.8, 119.7, 118.3, 111.7, 111.4, 111.2, 56.0, 55.9 ppm. HRMS (ESI) exact mass calculated for $C_{16}H_{16}NO_2^+$ ([M + H]+): 254.1176; Found: 254.1178.

5-isopropyl-3-(4-methoxyphenyl)-1*H*-indole (14f): According to GP-2: 1-isopropyl-4-nitrosobenzene (0.12 g, 0.81 mmol), *N*-(4-methoxyphenethyl)aniline (60 mg, 0.27 mmol) and 4-nitrobenzoic acid (45 mg, 0.27 mmol) were reacted for 38 h in dry toluene (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:7) of the crude gave **14f** as a brown gum (28 mg, 39%, 53% brsm). **14f** (31 mg, 44%) was isolated from the reaction with *N*-(4-methoxyphenethyl)pyridin-3-amine (60 mg, 0.26 mmol). FTIR (KBr): $\tilde{\nu}$ = 2961, 2924, 2854, 1637, 1493, 1452, 1261, 747, 695 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 (s, 1H), 7.64 (s, 1H), 7.53 – 7.50 (m, 2H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.19 – 7.18 (m, 1H), 7.07 (d, *J* = 9.6 Hz, 1H), 6.96 – 6.94 (m, 2H), 3.80 (s, 3H), 2.97 (sept, *J* = 6.8 Hz, 1H), 1.24 (d, *J* = 6.8 Hz, 6H) ppm.^{13}C NMR (101 MHz, $CDCl_3$) δ = 158.2, 141.1, 135.3, 128.9, 128.5, 126.2, 121.7, 121.6, 118.0, 116.8, 114.4, 111.3, 55.6, 34.6, 24.9 ppm. HRMS (ESI) exact mass calculated for $C_{18}H_{20}NO^+$ ([M + H]+): 266.1539; Found: 266.1539.

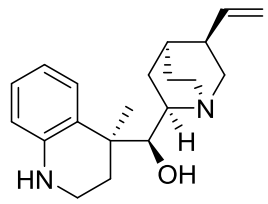


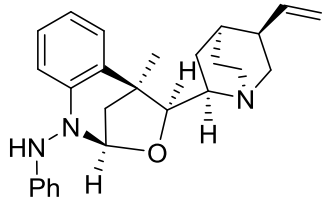
5-(tert-butyl)-3-(4-methoxyphenyl)-1*H*-indole (14g): According to GP-2: 1-(*tert*-butyl)-4-nitrosobenzene (0.15 g, 0.92 mmol), *N*-(4-methoxyphenethyl)aniline (70 mg, 0.31 mmol) and 4-nitrobenzoic acid (51 mg, 0.31 mmol) were reacted for 38 h in dry toluene (4 mL). Column chromatography (silica; EtOAc : Hexane, 1:7) of the crude gave **14g** as a brown gum (30 mg, 35%, 62% brsm). **14g** (36 mg, 36%) was isolated from the reaction with *N*-(4-methoxyphenethyl)pyridin-3-amine (80 mg, 0.35 mmol). FTIR (KBr): $\tilde{\nu}$ = 2963, 2924, 2853, 1637, 1495, 1260, 797, 745, 696 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.10 (br.s, 1H), 7.87 (s, 1H), 7.58 (d, *J* = 8.8 Hz, 2H), 7.37 – 7.32 (m, 2H), 7.26 – 7.25 (m, 1H), 7.02 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 1.40 (s, 9H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 158.2, 143.3, 134.9, 128.9, 128.5, 125.8, 121.6, 120.8, 118.3, 115.5, 114.5, 111.0, 55.6, 34.9, 32.2 ppm. HRMS (ESI) exact mass calculated for $C_{19}H_{22}NO^+$ ([M + H]+): 280.1696; Found: 280.1695.



2,3-diphenyl-1*H*-indole (14h):[7] According to GP-2: nitrosobenzene (0.12 g, 1.1 mmol), *N*-(1,2-diphenylethyl)aniline (0.10 g, 0.37 mmol) and 4-nitrobenzoic acid (62 mg, 0.37 mmol) were reacted for 38 h in dry toluene (5 mL). Column chromatography (silica; EtOAc : Hexane, 1:7) of the crude gave **14h** as a colorless gum (41mg, 41%, 60% brsm). FTIR (KBr): $\tilde{\nu}$ = 3062, 3027, 2923, 2853, 1955, 1894, 1670, 1600, 1478, 1323, 1274, 1072, 762, 687 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.26 (br.s, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.45 – 7.42 (m, 4H), 7.40 – 7.35 (m, 2H), 7.33 – 7.28 (m, 4H), 7.27 – 7.23 (m, 2H), 7.17 – 7.14 (m, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 136.1, 135.3, 134.3, 132.9, 130.4, 129.0, 128.9, 128.7, 128.4, 127.9, 126.4, 122.9, 120.6, 119.9, 115.3, 111.1 ppm. HRMS (ESI) exact mass calculated for $C_{20}H_{16}N^{+}$ ([M + H]+): 270.1277; Found: 270.1287.

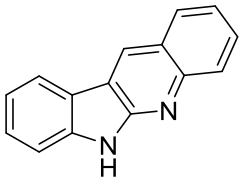
(*2R,4S,5S*)-5-methyl-4-((*1S,2R,4S,5R*)-5-vinylquinuclidin-2-yl)-1,2,4,5-tetrahydro-2,5-methanobenzo[d][1,3]oxazepine (24): Methylmagnesium bromide (4.69 mL, 3.0 M in diethylether, 14.1 mmol) was added to a solution of cinchonine **23** (1.2 g, 4.08 mmol) in dry toluene (15 mL). The reaction mixture was stirred for overnight at 70 °C and then cooled to 0 °C. The mixture was diluted with diethylether and the reaction was quenched by addition of saturated solution of aq. NH_4Cl (30 mL). The organic layer was separated and dried over Na_2SO_4 and evaporated under reduced pressure to give white solid residue which was purified by column chromatography (silica; EtOAc: MeOH: NEt_3, 50:1:1) to give **24** as colorless gum (0.53 g, 42%). FTIR (KBr): $\tilde{\nu}$ = 2962, 2935, 2871, 1637, 1608, 1489, 1454, 1307, 1011, 749 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.03 (d, *J* = 7.8 Hz, 1H), 6.99 – 6.71 (m, 1H), 6.70 – 6.67 (m, 1H), 6.44 – 6.42 (m, 1H), 5.96 – 5.91 (m, 1H), 5.07 – 5.06 (m, 1H), 4.97 – 4.94 (m, 2H), 4.91 – 4.87 (m, 1H), 3.91 (d, *J* = 6.0 Hz, 1H), 2.81 – 2.77 (m, 1H), 2.64 – 2.58 (m, 2H), 2.57 – 2.51 (m, 1H), 2.31 – 2.72 (m, 1H), 2.20 (d, *J* = 10.8 Hz, 1H), 2.17 – 2.09 (m, 2H), 1.59 – 1.56 (m, 1H), 1.50 (s, 3H), 1.49 – 1.47 (m, 1H) 1.35 – 1.31 (m, 2H), 0.86 – 0.81 (m, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 141.9, 141.1, 129.3, 127.4, 125.7, 118.4, 114.5, 114.0, 95.3, 83.0, 56.6, 48.8, 48.7, 43.5, 40.7, 40.4, 27.5, 26.7, 24.0, 19.2 ppm. HRMS (ESI) exact mass calculated for $C_{20}H_{27}N_2O^{+}$ ([M + H]+): 311.2118; Found: 311.2110.

(*S*)-((*S*)-4-methyl-1,2,3,4-tetrahydroquinolin-4-yl)((*1S,2R,4S,5R*)-5-vinylquinuclidin-2-yl)methanol (25):  $NaBH_3CN$ (0.11 g, 1.68 mmol) was added to a solution of **24** (0.26 g, 0.84 mmol) in AcOH (0.25 mL) and methanol (2 mL) at 0 ^oC. The reaction mixture was stirred at room temperature. After 2.5 h, concentrated HCl (0.6 mL) was added to the reaction mixture and stirred for additional 12 h at room temperature. The reaction was quenched by the addition of 2 M sodium hydroxide until pH >9. The reaction mixture was extracted with ethyl acetate (3 x 15 mL). The combine organic layers were washed with brine (3 x 10 mL), dried with Na_2SO_4 and concentrated under reduced pressure. The crude oil was purified by column chromatography (silica; EtOAc: MeOH: NEt_3, 50:1:1) to give **25** as colorless oil (0.13 g, 50%). FTIR (KBr): $\tilde{\nu}$ = 2968, 2935, 2869, 1636, 1604, 1500, 1452, 1345, 746, 702 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.06 (d, *J* = 8.0 Hz, 1H), 6.92 – 6.88 (m, 1H), 6.54 (t, *J* = 7.6 Hz, 1H), 6.39 (d, *J* = 8.0 Hz, 1H), 5.97 – 5.89 (m, 1H), 5.00 – 4.87 (m, 2H), 3.92 (d, *J* = 3.6 Hz, 1H), 3.85 (br.s, 1H), 3.36 – 3.29 (m, 1H), 3.20 – 3.15 (m, 1H), 2.91 – 2.86 (m, 1H), 2.80 – 2.61 (m, 4H), 2.13 – 2.03 (m, 2H), 1.97 – 1.90 (m, 1H), 1.66 – 1.59 (m, 2H), 1.50 – 1.45 (m, 2H), 1.31 – 1.27 (m, 1H), 1.22 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 144.2, 141.2, 127.8, 127.5, 126.4, 116.6, 114.4, 114.2, 77.1, 56.5, 49.2, 49.2, 40.4, 40.2, 38.5, 31.4, 28.3, 27.0, 23.7, 23.3 ppm. HRMS (ESI) exact mass calculated for $C_{20}H_{29}N_2O^+$ ([M + H]+): 313.2274; Found: 313.2276.

(*2R,4S,5S*)-5-methyl-N-phenyl-4-((*1S,2R,4S,5R*)-5-vinylquinuclidin-2-yl)-4,5-dihydro-2,5-methanobenzo[d][1,3]oxazepin-1(2H)-amineoxazepin-1(2*H*)-amine (27):  According to GP-1: nitrosobenzene (21 mg, 0.19 mmol), **25** (30 mg, 0.10 mmol) and 4-nitrobenzoic acid (16 mg, 0.10 mmol) were reacted for 36 h in dry toluene (4 mL). Column chromatography (silica; EtOAc: MeOH: NEt_3, 40:1:1) of the crude gave **27** colorless gum (20 mg, 52%). FTIR (KBr): $\tilde{\nu}$ = 3376, 3019, 2958, 2925, 2867, 1650, 1611, 1499, 1474, 1380, 1257, 1160, 811, 647 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ = 7.26 – 7.22 (m, 2H), 7.09 – 7.06 (m, 1H), 7.04 – 7.03 (m, 1H), 6.94 –6.93 (m, 1H), 6.90 –6.89 (m, 2H), 6.86 –6.82 (m, 2H), 6.07 (s, 1H), 5.97 –5.91 (m, 1H), 5.08 – 5.03 (m, 3H), 4.01 (d, *J* = 5.4 Hz, 1H), 2.86 –2.82 (m, 1H), 2.76 –2.73 (m, 1H), 2.67 – 2.62 (m, 1H), 2.59 – 2.55 (m, 1H), 2.48 (d, *J* = 11.4 Hz, 1H), 2.34 – 2.30 (m, 1H), 2.25 – 2.23 (m, 1H), 2.19 – 2.15 (m, 1H), 1.60 – 1.58 (m, 1H), 1.55 (s, 3H), 1.49 – 1.46 (m, 1H), 1.44 – 1.35

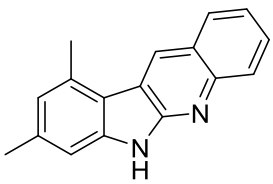
(m, 2H), 0.82 – 0.78 (m, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 148.4, 146.1, 141.2, 130.4, 129.5, 128.1, 125.3, 120.8, 120.0, 116.0, 114.3, 112.9, 94.6, 89.5, 56.6, 49.1, 48.8, 44.0, 42.8, 40.0, 27.6, 26.9, 24.1, 19.5 ppm. HRMS (ESI) exact mass calculated for $C_{26}H_{32}N_3O^+$ ([M + H]+): 402.2540; Found: 402.2542.

6H-indolo[2,3-*b*]quinoline (28a): A mixture of **9** (30 mg, 0.13 mmol), iodine (41 mg, 0.16 mmol),



Cs_2CO_3 (88 mg, 0.27 mmol) in dry CH_3CN (2 mL) was heated at 60 ºC for 4 h under argon atmosphere. The solvent was removed under vacuum and the reaction mixture was diluted with aq. $Na_2S_2O_3$ solution (10 mL) and the reaction mixture was extracted with dichloromethane (3x10 mL). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated in vacuum to give brown gum which was purified by column chromatography (silica; EtOAc : Hexane, 1:3) to give **28a** as a colorless solid (22 mg, 74%). FTIR (KBr): $\tilde{\nu}$ = 3144, 3055, 2956, 2922, 2851, 1659, 1613, 1580, 1479, 1459, 1406, 1255, 1230, 1123, 908, 737 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.70 (s, 1H), 9.04 (s, 1H), 8.26 (d, *J* = 7.6 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.74 – 7.70 (m, 1H), 7.55 – 7.46 (m, 3H), 7.28 – 7.24 (m, 1H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 153.0, 146.4, 141.5, 128.8, 128.8, 128.3, 127.7, 127.1, 123.8, 122.9, 121.9, 120.4, 119.8, 118.0, 111.0 ppm. The ^{1}H NMR and ^{13}C NMR data matched with the literature.[8] HRMS (ESI) exact mass calculated for $C_{15}H_{11}N_2^+$ ([M + H]+): 219.0917; Found: 219.0913.

8,10-dimethyl-6*H*-indolo[2,3-*b*]quinoline (28b): A mixture of **12k** (40 mg, 0.16 mmol), Iodine



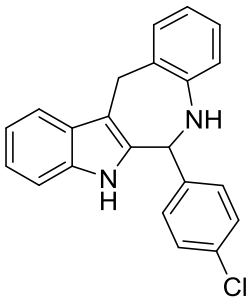
(48 mg, 0.19 mmol), Cs_2CO_3 (0.10 g, 0.32 mmol) in dry CH_3CN (3 mL) was heated at 60 ºC for 4 h under argon atmosphere. The solvent was removed under vacuum and the reaction mixture was diluted with aq. $Na_2S_2O_3$ solution (10 mL) and the reaction mixture was extracted with dichloromethane (3x10 mL). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated in vacuum to give brown gum which was purified by column chromatography (silica; EtOAc : Hexane, 1:3) to give **28b** as a colorless solid (27 mg, 69%). FTIR (KBr): $\tilde{\nu}$ =2922, 2851, 1675, 1606, 1480, 1260, 795, 745 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ =11.62 (s, 1H), 8.90 (s, 1H), 8.16 – 8.14 (m, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.71 – 7.67 (m, 1H), 7.48 – 7.45 (m, 1H), 7.14 (s, 1H), 6.89 (s, 1H), 2.82 (s, 3H), 2.45 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 153.4, 145.9, 142.3, 138.4, 134.4, 129.2, 128.8, 128.8, 127.2, 124.3, 122.9, 118.9, 116.9, 109.1, 22.2,

20.6 ppm. Total count of ^{13}C is less because of overlap in the aromatic region. HRMS (ESI) exact mass calculated for $C_{17}H_{15}N_2^+$ ([M + H]+): 247.1230; Found: 247.1232.

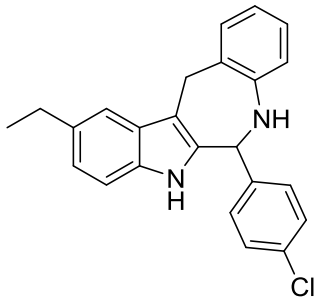
Neocryptolepine (29a): CH_3I (0.11 mL, 1.80 mmol) was added drop-wise to a solution of **28a** (40 mg, 0.18 mmol) in dry THF (2 mL) and the reaction mixture was reflux for 12 h. The reaction mixture was neutralized with aq. NH_3 solution and the mixture was extracted with dichloromethane (3x15 mL). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated in vacuum to give yellow residue which was purified by column chromatography (silica; EtOAc : Hexane, 1:3) to give **29a** as a light orange solid (31 mg, 74%). FTIR (KBr): $\tilde{\nu}$ = 2962, 2924, 2853, 1646, 1615, 1576, 1496, 1452, 1299, 1100, 799, 747 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.55 (s, 1H), 8.06 (d, *J* = 7.6 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.78 – 7.75 (m, 3H), 7.58 – 7.54 (m, 1H), 7.48 – 7.44 (m, 1H), 7.26 – 7.23 (m, 1H), 4.39 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.2, 155.2, 137.1, 130.7, 130.2, 129.6, 128.5, 128.2, 124.0, 122.2, 121.2, 121.1, 120.2, 117.8, 114.4, 33.4 ppm. The ^1H NMR and ^{13}C NMR data matched with the literature.[2] HRMS (ESI) exact mass calculated for $C_{16}H_{13}N_2^+$ ([M + H]+): 233.1073; Found: 233.1075.

5,8,10-trimethyl-5*H*-indolo[2,3-*b*]quinoline (29b): CH_3I (0.10 mL, 1.62 mmol) was added dropwise to a solution of **28b** (40 mg, 0.16 mmol) in dry THF (2 mL) and the reaction mixture was reflux for 12 h. The reaction mixture was neutralized with NH_3 solution and the mixture was extracted with dichloromethane (3x15 mL). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated in vacuum to give yellow gum residue which was purified by column chromatography (silica; EtOAc : Hexane, 1:3) to give **29b** as a light orange solid (30 mg, 71%). FTIR (KBr): $\tilde{\nu}$ = 2963, 2925, 2852, 1634, 1261, 1096, 1021, 864, 748, 691 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.43 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.75 – 7.74 (m, 2H), 7.45 – 7.42 (m, 2H), 6.87 (s, 1H), 4.36 (s, 3H), 2.79 (s, 3H), 2.52 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.4, 155.5, 139.8, 136.4, 133.9, 130.2, 130.1, 129.1, 128.8, 123.3, 122.0, 121.4, 120.1, 116.0, 114.2, 33.3, 22.5, 20.4 ppm. HRMS (ESI) exact mass calculated for $C_{18}H_{17}N_2^+$ ([M + H]+): 261.1386; Found: 261.1393.

6-(4-chlorophenyl)-5,6,7,12-tetrahydrobenzo[6,7]azepino[3,4-*b*]indole (30a): TFA (40 μL) was added drop wise to a solution of **9** (30 mg, 0.13 mmol) and 4-chlorobenzaldehyde (23 mg, 0.16 mmol) in dry dichloromethane (2 mL) and the reaction mixture was stirred at room temperature. After 1 h the reaction mixture was quenched with saturated aqueous solution of $NaHCO_3$ (10 mL) and the reaction mixture was extracted with dichloromethane (3x10 mL). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated under reduced pressure to give brown gum residue which was purified by column chromatography (silica; EtOAc : Hexane, 1:7) to give **30a** as a yellow solid (43 mg, 92%). FTIR (KBr): $\tilde{\nu}$ = 2961, 1593, 1477, 1453, 1323, 1240, 1013, 811, 756 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.71 – 7.69 (m, 1H), 7.31 – 7.29 (m, 4H), 7.21 – 7.19 (m, 2H), 7.16 – 7.12 (m, 3H), 7.10 – 7.06 (m, 1H), 7.03 – 6.99 (m, 1H), 6.73 – 6.72 (m, 1H), 5.49 (s, 1H), 4.32 (d, *J* = 15.2 Hz, 1H), 4.12 (d, *J* = 15.2 Hz, 1H) ppm.^{13}C NMR (101 MHz, $CDCl_3$) δ = 145.6, 140.7, 138.0, 135.6, 134.3, 134.1, 133.9, 129.8, 129.1, 129.0, 127.8, 127.2, 123.9, 123.7, 122.6, 116.8, 111.0, 110.5, 61.7, 29.3, 28.9, 16.8 ppm. HRMS (ESI) exact mass calculated for $C_{22}H_{18}ClN_2^+$ ([M + H]+): 345.1153; Found: 345.1164.

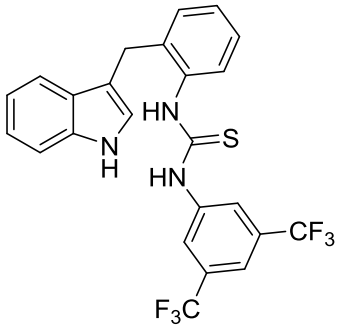


6-(4-chlorophenyl)-2-ethyl-5,6,7,12-tetrahydrobenzo[6,7]azepino[3,4-*b*]indole (30b): TFA (40 μL) was added drop wise to a solution of **12b** (30 mg, 0.12 mmol) and 4-chlorobenzaldehyde (20 mg, 0.14 mmol) in dry dichloromethane (2 mL) and the reaction was stirred at room temperature. After 1 h the reaction mixture was quenched with saturated aqueous solution of $NaHCO_3$ (10 mL) and the reaction mixture was extracted with dichloromethane (3x10 mL). The combined organic layer was dried over Na_2SO_4. The solvent was evaporated under reduced pressure to give brown gum which was purified by column chromatography (silica; EtOAc : Hexane, 1:7) to give **30b** as a yellow solid (40 mg, 89%). FTIR (KBr): $\tilde{\nu}$ = 2963, 2929, 1636, 1486, 1261, 1095, 1023, 801, 656 cm^{-1}.^1H NMR (400 MHz, $CDCl_3$) δ = 7.50 (s, 1H), 7.32 – 7.27 (m, 3H), 7.22 (br.s, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.09 – 7.05 (m, 2H), 7.04 – 6.97 (m, 2H), 6.73 – 6.71 (m, 1H), 5.50 (s, 1H), 4.29 (d, *J* = 15.5 Hz, 1H), 4.13 (d, *J* = 15.6 Hz, 1H), 2.79 (q, *J* = 7.6 Hz, 2H), 1.33 (t, *J* = 7.6 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 145.6, 140.7, 138.0, 135.6, 134.3, 134.1, 133.9, 129.8, 129.1, 129.0,

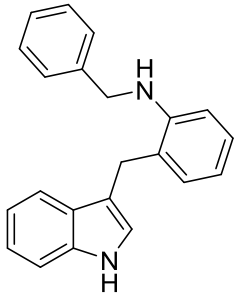


127.8, 127.2, 123.9, 123.7, 122.6, 116.8, 111.0, 110.5, 61.7, 29.3, 28.9, 16.8 ppm. HRMS (ESI) exact mass calculated for $C_{24}H_{22}ClN_2^+$ ([M + H]+): 373.1466; Found: 373.1475.

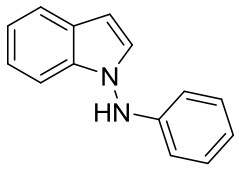
1-(2-((1*H*-indol-3-yl)methyl)phenyl)-3-(3,5-bis(trifluoromethyl)phenyl)thiourea (31): 3,5-Bis(trifluoromethyl)phenyl isothiocyanate (25 μL, 0.13 mmol) was added to a solution of **9** (30 mg, 0. 13 mmol) in dry THF (2 mL) under argon atmosphere. The reaction mixture was stirred at room temperature for 12 h. The solvent was evaporated in vacuum to give brown solid which was purified by column chromatography (silica; EtOAc : Hexane, 1:5) to give **31** as a yellow solid (65 mg, 97%). FTIR (KBr): $\tilde{\nu}$ = 3433, 2925, 2854, 1631, 1487, 1455, 1381, 1343, 1277, 1176, 1133, 1095, 850, 794, 745 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.35 (s, 1H), 7.89 (s, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.45 (s, 1H), 7.36 – 7.33(m, 3H), 7.31 – 7.24 (m, 2H), 7.19 – 7.16 (m, 1H), 7.14 – 7.12 (m, 1H), 7.04 – 7.03 (m, 2H), 6.93 – 6.89 (m, 1H), 6.86 (br.s, 1H), 4.09 (s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 180.1, 139.6, 139.1, 136.5, 134.4, 132.2, 131.8, 131.5, 131.2, 129.6, 128.8, 128.5, 127.2, 126.8, 124.4, 124.1, 124.1, 123.0, 122.6, 121.7, 119.8, 119.08, 119.01, 119.01, 119.0, 118.9, 118.8, 113.0, 111.7, 29.7 ppm. HRMS (ESI) exact mass calculated for $C_{24}H_{18}F_6N_3S^+$ ([M + H]+): 494.1120; Found: 494.1119.



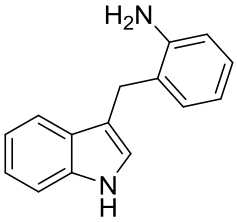
2-((1*H*-indol-3-yl)methyl)-N-benzylaniline (32): A mixture of compound **9** (25 mg, 0.11 mmol), benzyl alcohol (36 μL, 0.34 mmol) and KOH (18 mg, 0.34 mmol) in toluene (1.5 mL) were heated at 150 ^oC for 24 h. After the reaction the brown residue was purified by column chromatography (silica; EtOAc : Hexane, 1:7) to give **32** as a colorless gum (27 mg, 77%). FTIR (KBr): $\tilde{\nu}$ = 2958, 2923, 2853, 1628, 1604, 1510, 1453, 1330, 1261, 1090, 800, 742 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$) δ = 7.98 (s, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.24 –7.19 (m, 5H), 7.15 – 7.12 (m, 3H), 7.09 (t, *J* = 7.2 Hz, 1H), 6.85 (s, 1H), 6.73 (t, *J* = 7.2 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 4.27 (s, 2H), 4.04 (s, 2H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 146.2, 139.5, 136.8, 130.3, 128.7, 127.7, 127.6, 127.4, 127.2, 125.1, 122.5, 122.4, 119.7, 119.4, 117.6, 113.8, 111.3, 111.2, 48.2, 28.6 ppm. HRMS (ESI) exact mass calculated for $C_{22}H_{21}N_2^+$ ([M + H]+): 313.1699; Found: 313.1709.



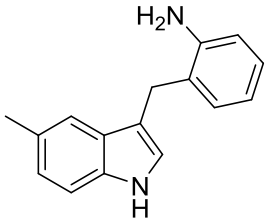
***N*-phenyl-1*H*-indol-1-amine (s1a):**[9] According to GP-1: nitrosobenzene (74 mg, 0.67 mmol), indoline (38 µL, 0.36 mmol) and 4-nitrobenzoic acid (56 mg, 0.34 mmol) were reacted for 24 h in dry toluene (4 mL) under argon atmosphere. Column chromatography (silica; EtOAc : Hexane, 1:15) of the crude gave **s1a** as a brown gum (33 mg, 47%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.2 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.22 – 7.19 (m, 3H), 7.18 – 7.12 (m, 2H), 6.92 –6.88 (m, 1H), 6.65 (s, 1H), 6.55 – 6.51 (m, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 147.3, 135.9 129.4, 128.6, 126.6, 122.4, 121.2, 121.1, 120.4, 112.7, 109.4, 100.8 ppm.



Crystal of **9** (CCDC 1947126):

	
Empirical formula	$C_{15}H_{14}N_2$
Formula weight	222.28
Crystal habit, colour	Block, colorless
Crystal size, mm^3	0.38X 0.33X 0.31
Temperature, *T*	293(2)
Wavelength, λ(Å)	0.71073
Crystal system	orthorhombic
Space group	*P c c n*
Unit cell dimensions	*a* = 20.3252(11)Å *b* = 17.4919(13)Å *c* = 7.6118(3)Å α = 90°, β = 90°, γ = 90°,
Volume, *V*($Å^3$)	2706.2(3)
Z	8
Calculated density, $Mg\cdot m^{-3}$	1.091
Absorption coefficient, μ(mm^{-1})	0.065
F(000)	944
θ range for data collection	3.09 ° to 24.99°
Limiting indices	$-24 \le h \le 22$, $-20 \le k \le 13$, $-8 \le l \le 9$
Reflection collected / unique	7432/ 1387 [*R*(int) = 0.0286]
Completeness to θ	99.8% (θ = 24.99°)
Refinement method	'SHELXL–97'(Sheldrick, 1997)
Data / restraints / parameters	1387 / 0 / 155
Goodness–of–fit on F^2	1.346
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.1227, *wR*2 = 0.3538
R indices (all data)	*R*1 = 0.1657, *wR*2 = 0.3975
Largest diff. peak and hole	0.956 and –0. 0.335 $eÅ^{-3}$

Crystal of **12a** (CCDC 1947123):

	
Empirical formula	$C_{16}H_{16}N_2$
Formula weight	236.31
Crystal habit, colour	Block, colorless
Crystal size, mm^3	0.39X 0.37X 0.35
Temperature, T	293(2)
Wavelength, λ(Å)	0.71073
Crystal system	monoclinic
Space group	*C 2/c*
Unit cell dimensions	a = 20.126(4)Å b = 7.6043(4)Å c = 19.1043(19)Å α = 90°, β = 114.182(10)°, γ = 90°,
Volume, V($Å^3$)	2667.2(6)
Z	8
Calculated density, $Mg \cdot m^{-3}$	1.177
Absorption coefficient, μ(mm^{-1})	0.070
F(000)	1008
θ range for data collection	2.34 ° to 25.00°
Limiting indices	$-23 \leq h \leq 23$, $-9 \leq k \leq 8$, $-13 \leq l \leq 22$
Reflection collected / unique	5096 / 1614 [R(int) = 0.0262]
Completeness to θ	99.9% (θ = 25.00 °)
Refinement method	'SHELXL–97'(Sheldrick, 1997)
Data / restraints / parameters	1614 / 0 / 165
Goodness–of–fit on F^2	1.076
Final R indices [I>2sigma(I)]	$R1$ = 0.0559, $wR2$ = 0.1357
R indices (all data)	$R1$ = 0.0861, $wR2$ = 0.1603
Largest diff. peak and hole	0.190 and $-0.305 \cdot Å^{-3}$

References:

[1] (a) B. Priewisch, K. Rück-Braun, *J. Org. Chem.* **2005**, ***70***, 2350.

(b) B. Priewisch, K. Rück-Braun, *Science of Synthesis* **2007**, *31b*, 1321.

(c) E. Ishow, A. Brosseau, G. Clavier, K. Nakatani, R. B. Pansu, J. -J. Vachon, P. Tauc, D. Chauvat, C. R. Mendonça, E. Piovesan, *J. Am. Chem. Soc.* **2007**, *129*, 8970.

(d) J. L. Jeffrey, S. P. McClintock, M. M. Haley, *J. Org. Chem.* **2008**, *73*, 3288.

(e) M. Min, G. S. Bang, H. Lee, B.-C. Yu, *Chem. Commun*. **2010**, *46*, 5232.

(f) D. Takamatsu, K. Fukui, S. Aroua, Y. Yamakoshi, *Org. Biomol. Chem*. **2010**, *8*, 3655.

(g) A. Yanagisawa, T. Fujinami, Y. Oyokawa, T. Sugita, K. Yoshida, *Org. Lett.* **2012**, *14*, 2434.

(h) X. Tian, C. Zhang, Q. Xu, Z. Li, X. Shao, *Org. Biomol. Chem*. **2017**, *15*, 3320.

(i) A. Purkait, S. K. Roy, H. K. Srivastava, C. K. Jana, *Org. Lett.* **2017**, *19*, 2540.

(j) W. Hu, Q. Zheng, S. Sun, J. Cheng, *Chem. Commun*. **2017**, *53*, 6263.

(k) G. A. Molander, L. N. Cavalcanti, *J. Org. Chem*. **2012**, *77*, 4402.

[2] D. Jung, M. H. Kim, J. Kim, *Org. Lett*. **2016**, *18*, 6300.

[3] L. Bering, F. M. Paulussen, A.P. Antonchick, *Org. Lett.* **2018**, *20*, 1978.

[4] J. Zhang, Z. Yin, P. Leonard, J. Wu, K. Sioson, C. Liu, R. Lapo, S. Zheng, *Angew. Chem. Int. Ed*. **2013**, *52*, 1753.

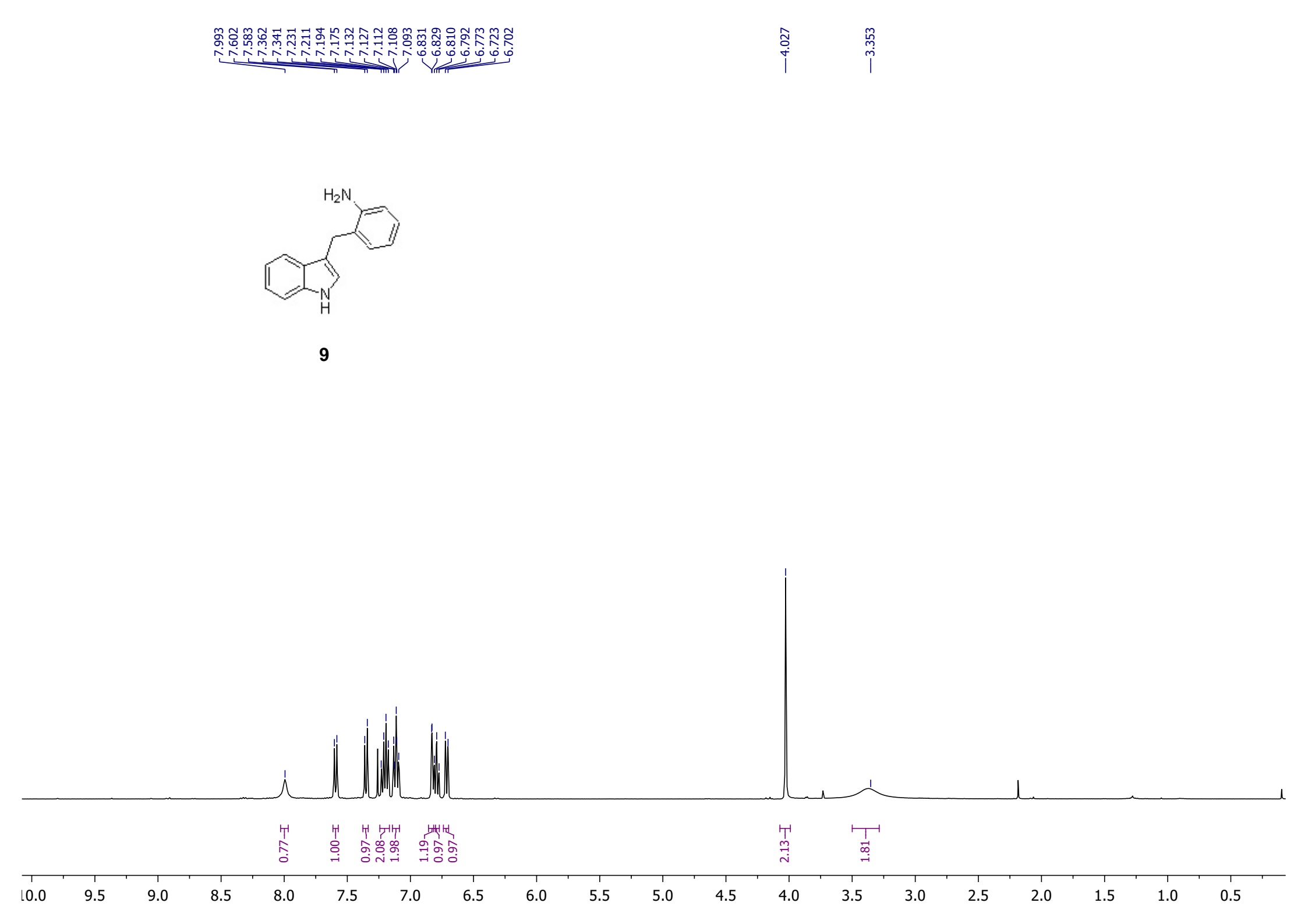
[5] Y. Nagase, H. Shirai, M. Kaneko, E. Shirakawa, T. Tsuchimoto, *Org. Biomol. Chem.* **2013**, *11*, 1456.

[6] A. A. Lamar, K. M. Nicholas, *Tetrahedron* **2009**, *65*, 3829.

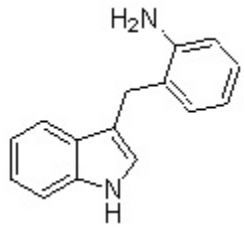
[7] W. Song, L. Ackermann, *Chem. Commun.* **2013**, ***49***, 6638.

[8] I. El Sayed, P. Van der Veken, K. Steert, L. Dhooghe, S. Hostyn; G. Van Baelen, G. Lemière, B. U. W. Maes, P. Cos, L. Maes, J. Joossens, A. Haemers, L. Pieters, K. Augustyns, *J. Med. Chem*. **2009**, *52*, 2979.

[9] K. Ramakumar, J. A. Tunge, *Chem. Commun*. **2014**, *50*, 13056.

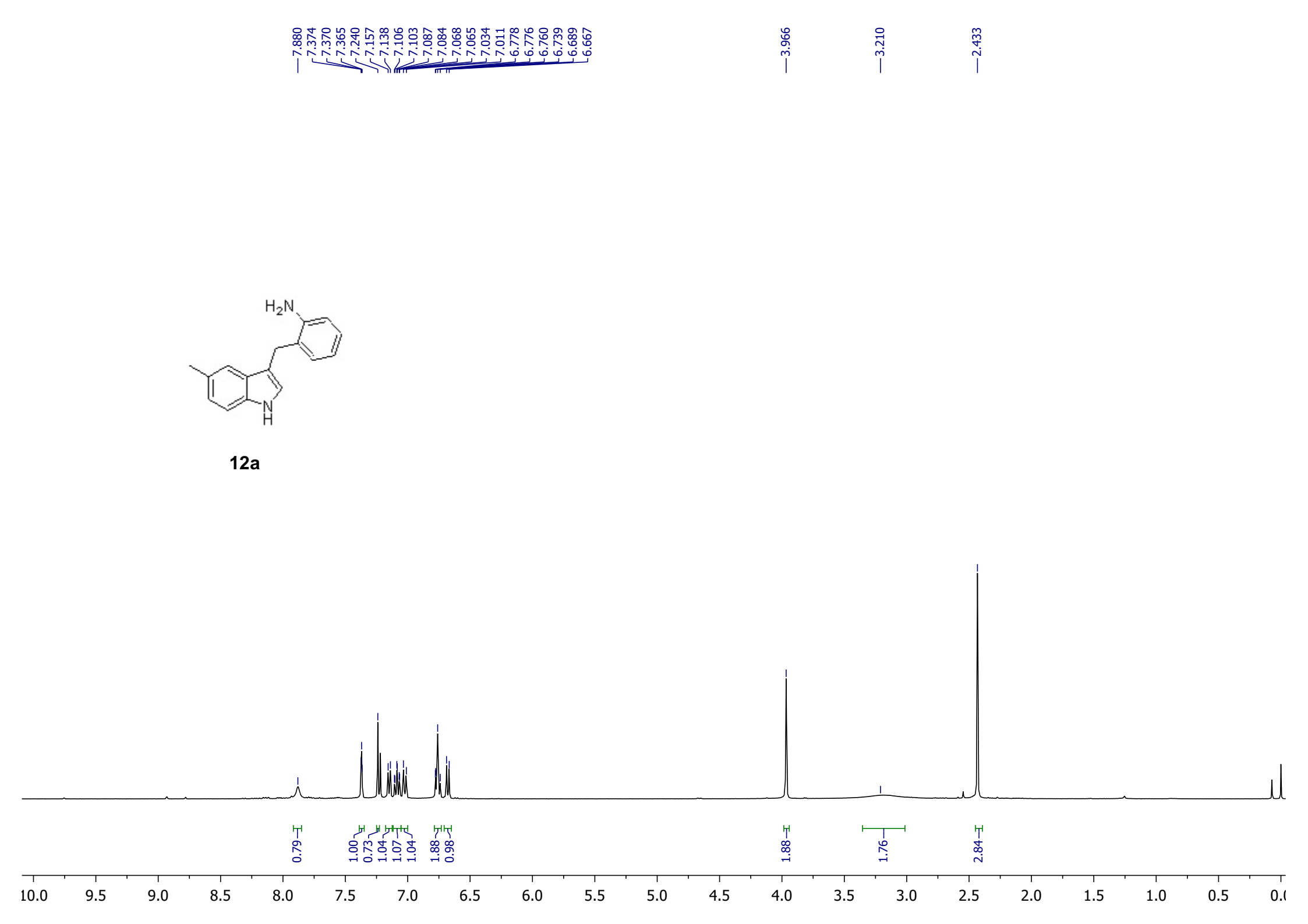

7.993
7.602
7.583
7.362
7.341
7.231
7.211
7.194
7.175
7.132
7.127
7.112
7.108
7.093
6.831
6.829
6.810
6.792
6.773
6.723
6.702
4.027
3.353
H2N
N
H
0.77
1.00
0.97
2.08
1.98
1.19
0.97
0.97
2.13
1.81
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

9

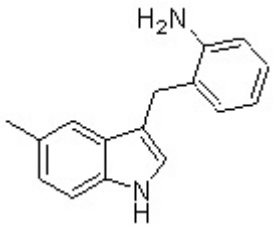

H2N
N
H

9

144.98
136.75
130.65
127.60
127.55
125.45
122.46
122.41
119.66
119.29
118.94
116.02
113.93
111.34
28.39
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

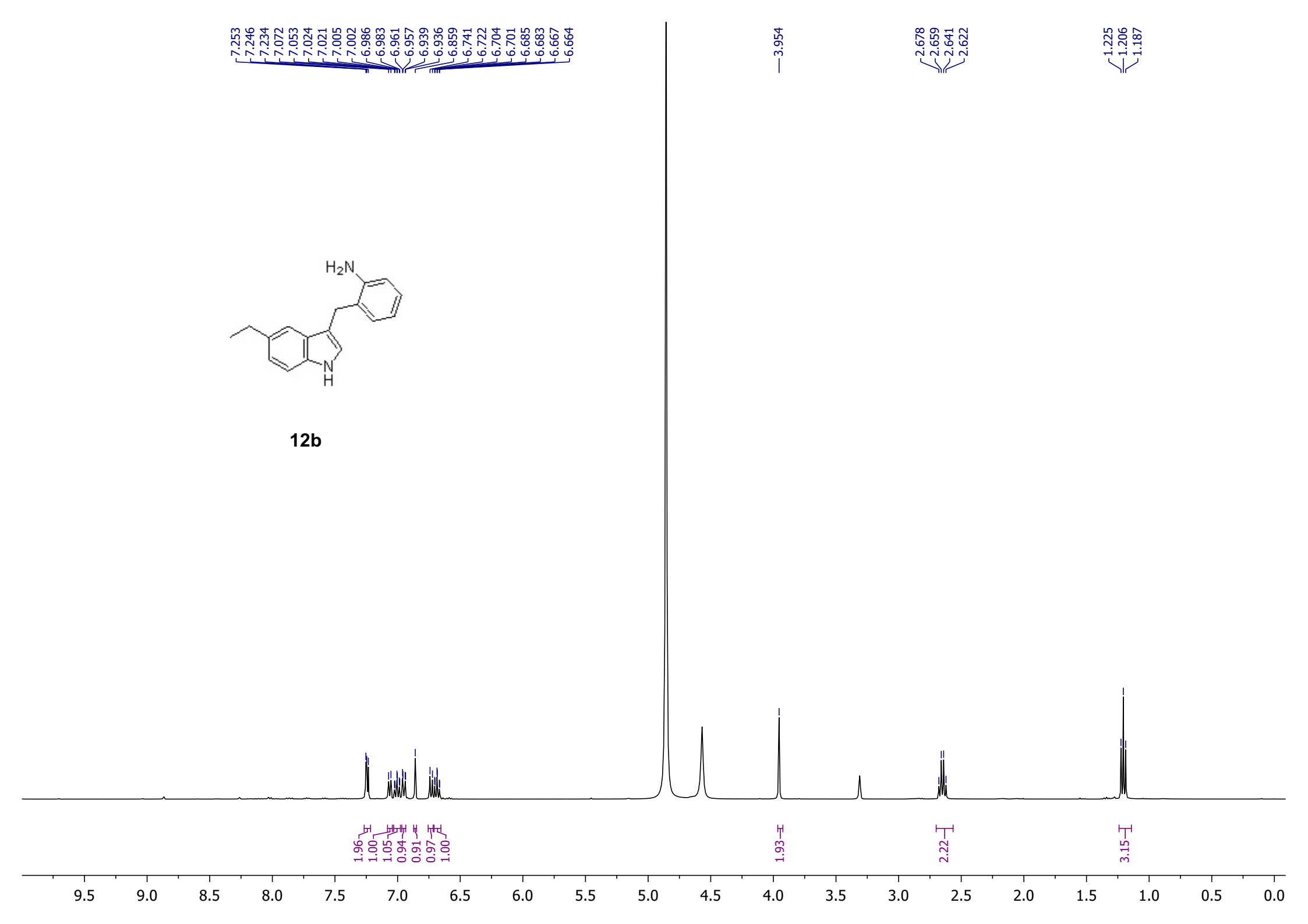

7.880
7.374
7.370
7.365
7.240
7.157
7.138
7.106
7.103
7.087
7.084
7.068
7.065
7.034
7.011
6.778
6.776
6.760
6.739
6.689
6.667
3.966
3.210
2.433
H2N
N
H
0.79
1.00
0.73
1.04
1.07
1.04
1.88
0.98
1.88
1.76
2.84
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

12a

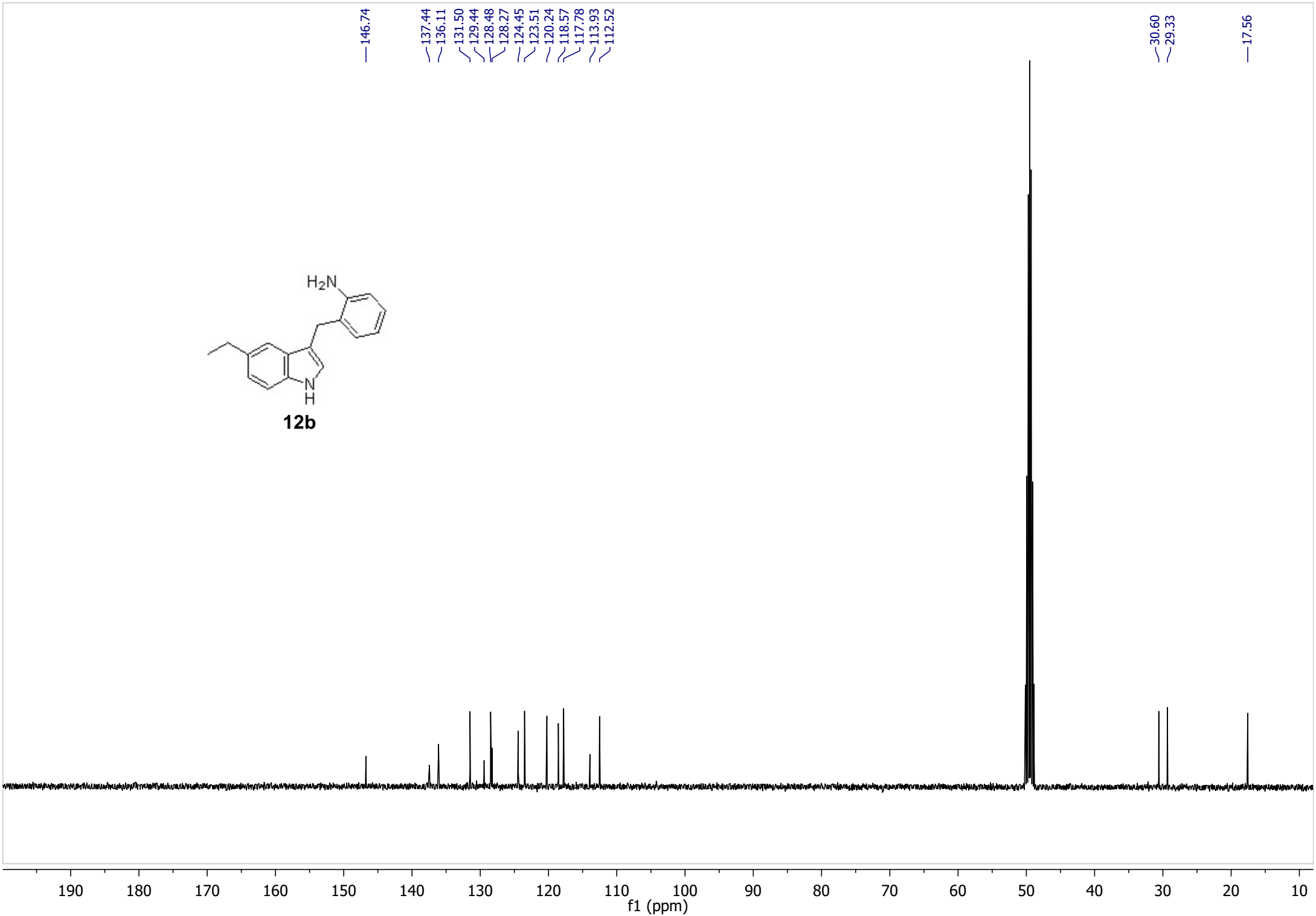

H2N
N
H

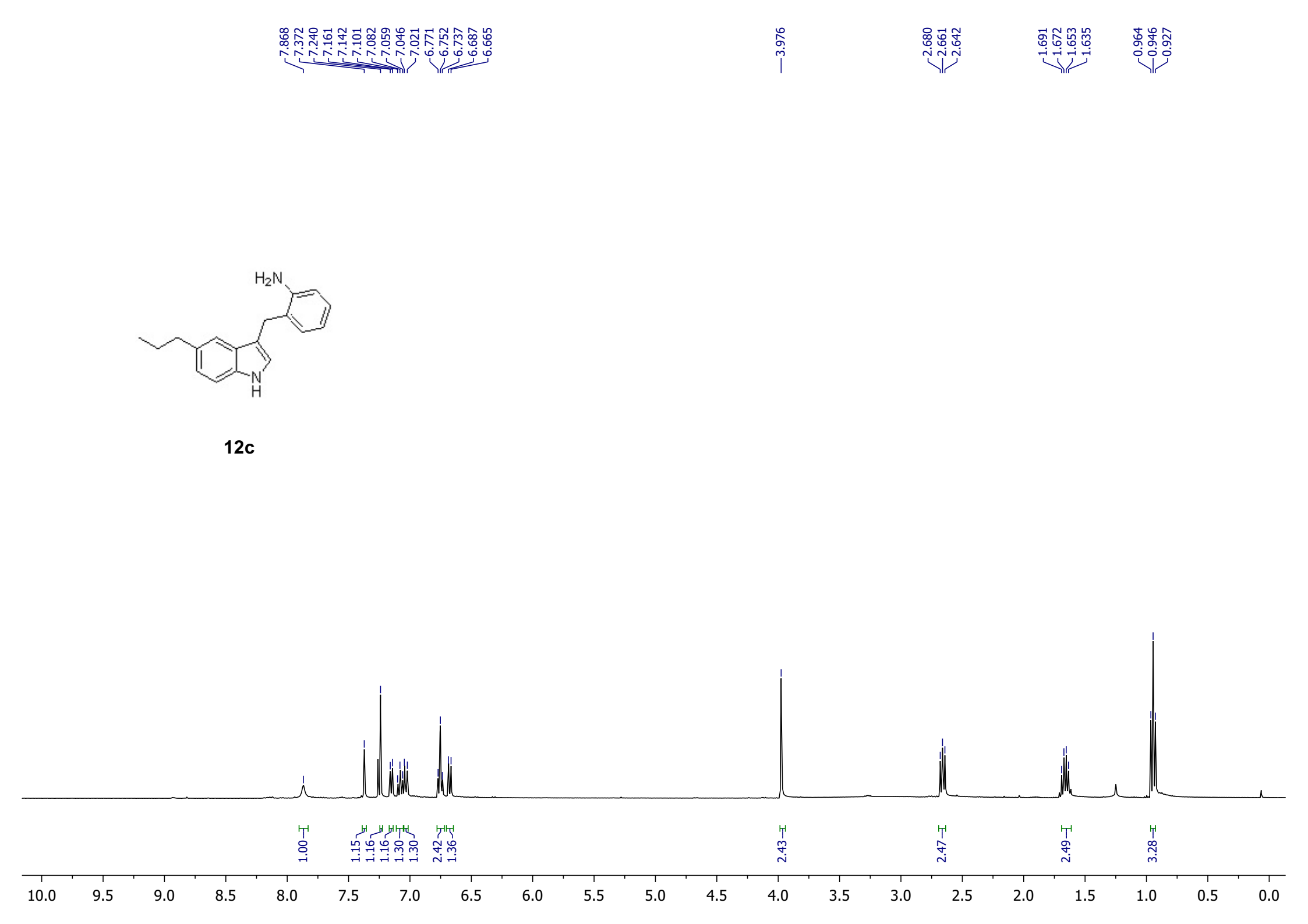
12a

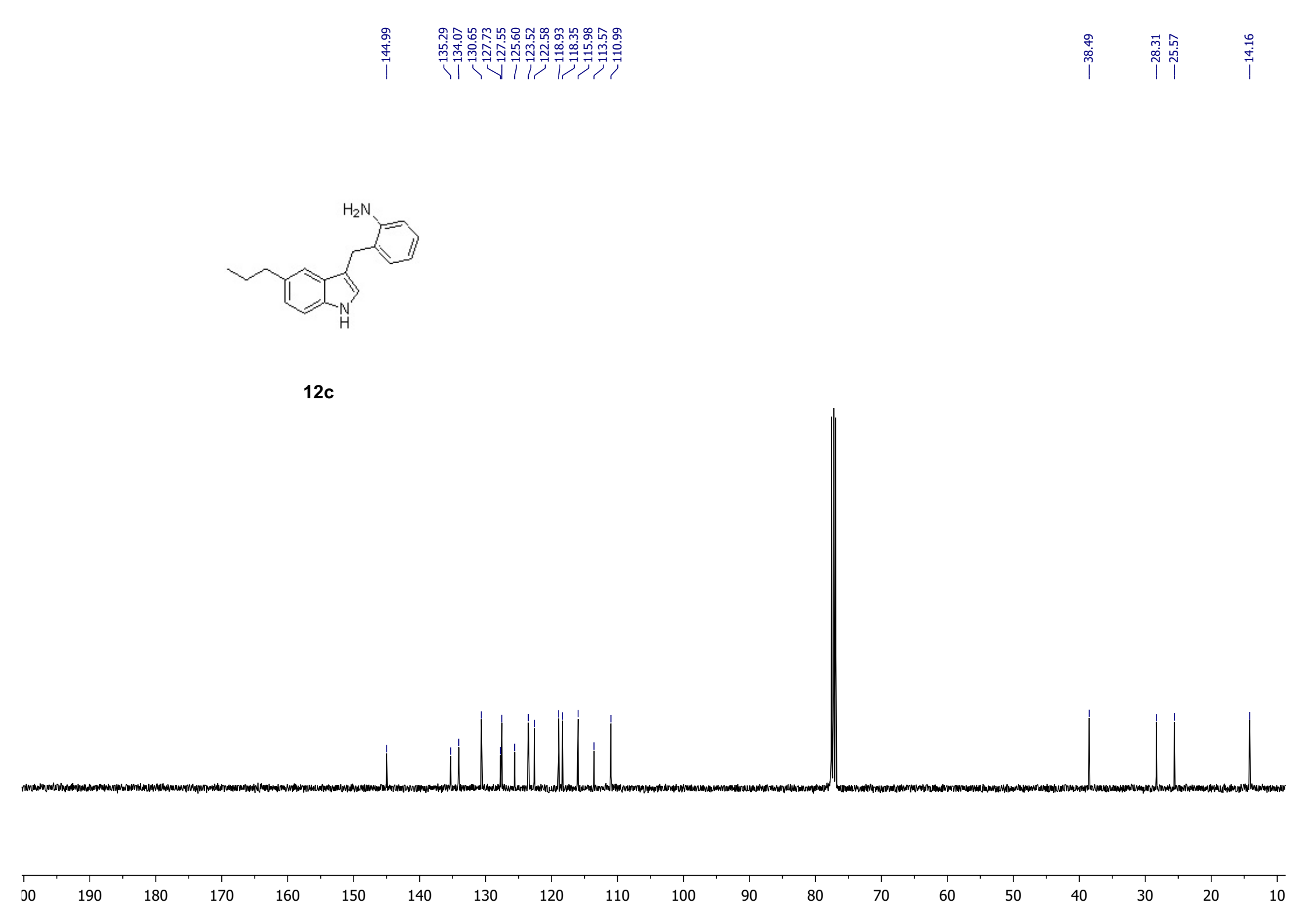
144.97
135.09
130.60
128.92
127.84
127.54
125.61
124.02
122.64
118.93
118.86
115.98
113.41
111.01
28.28
21.72
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

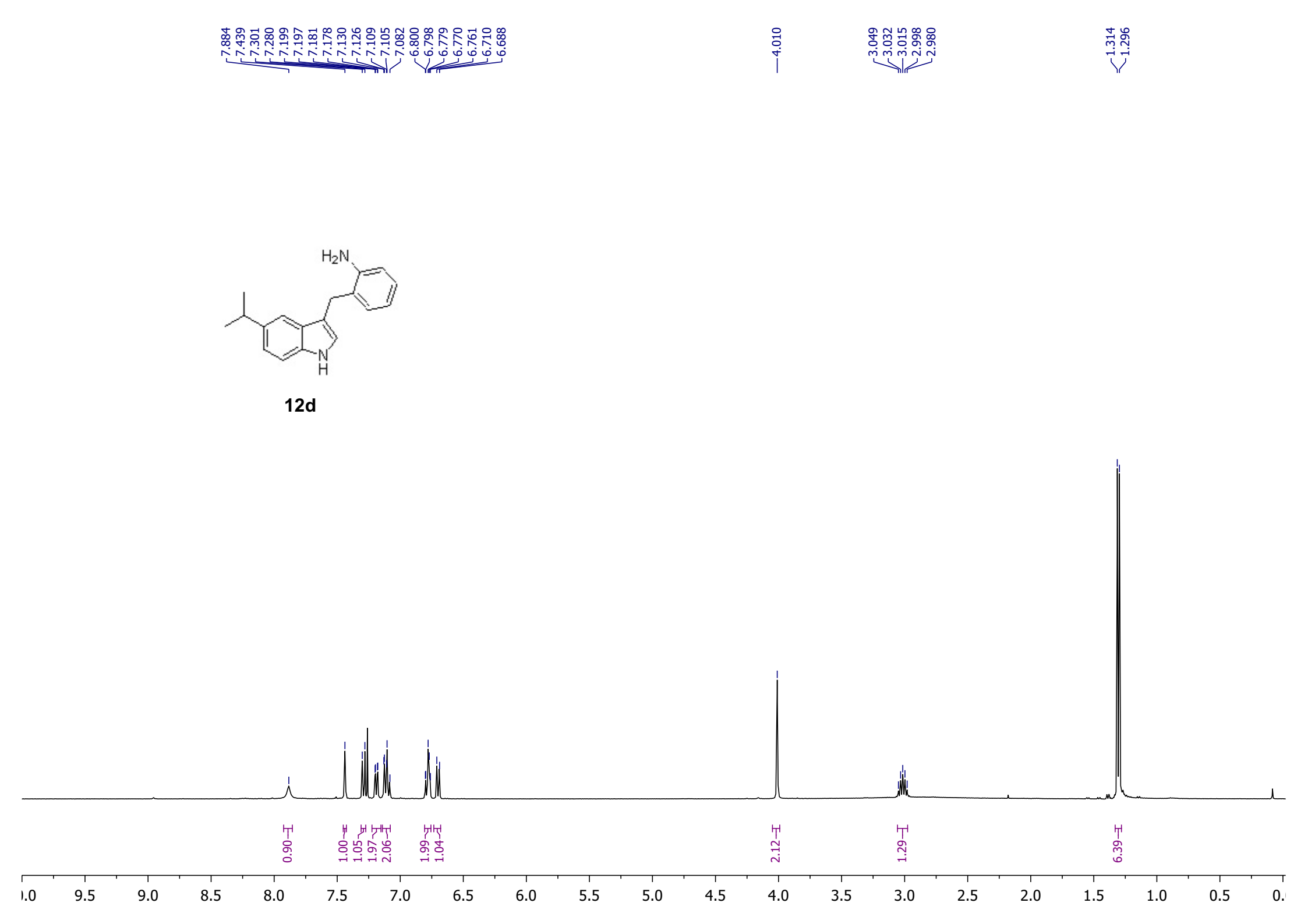

7.253
7.246
7.234
7.072
7.053
7.024
7.021
7.005
7.002
6.986
6.983
6.961
6.957
6.939
6.936
6.859
6.741
6.722
6.704
6.701
6.685
6.683
6.667
6.664
3.954
2.678
2.659
2.641
2.622
1.225
1.206
1.187
H2N
N
H
1.96
1.00
1.05
0.94
0.91
0.97
1.00
1.93
2.22
3.15
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

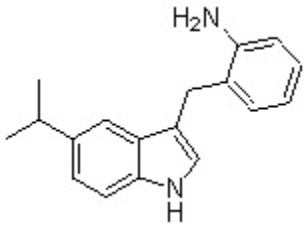
12b


146.74
137.44
136.11
131.50
129.44
128.48
128.27
124.45
123.51
120.24
118.57
117.78
113.93
112.52
30.60
29.33
17.56
H2N
N
H
12b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.868
7.372
7.240
7.161
7.142
7.101
7.082
7.059
7.046
7.021
6.771
6.752
6.737
6.687
6.665
3.976
2.680
2.661
2.642
1.691
1.672
1.653
1.635
0.964
0.946
0.927
H2N
N
H
12c
1.00
1.15
1.16
1.16
1.30
1.30
2.42
1.36
2.43
2.47
2.49
3.28
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
0.0

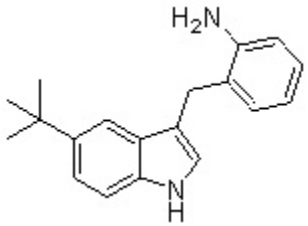

144.99
135.29
134.07
130.65
127.73
127.55
125.60
123.52
122.58
118.93
118.35
115.98
113.57
110.99
38.49
28.31
25.57
14.16
H2N
N
H
12c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


7.884
7.439
7.301
7.280
7.199
7.197
7.181
7.178
7.130
7.126
7.109
7.105
7.082
6.800
6.798
6.779
6.770
6.761
6.710
6.688
4.010
3.049
3.032
3.015
2.998
2.980
1.314
1.296
H2N
N
H
12d
0.90
1.00
1.05
1.97
2.06
1.99
1.04
2.12
1.29
6.39
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

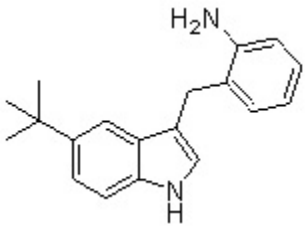

H2N
N
H

12d

145.02
140.43
135.38
130.73
127.66
127.57
125.59
122.62
121.64
118.94
116.13
116.02
113.74
111.11
34.45
28.38
24.90
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

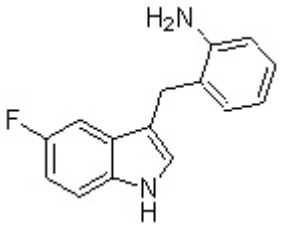


12e


H2N
N
H

12e

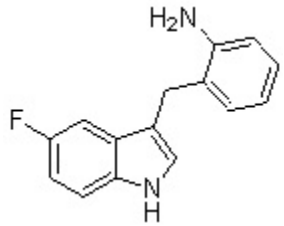
145.08
142.60
134.97
130.81
127.59
127.32
125.57
122.55
120.73
118.93
116.05
115.00
113.95
110.83
34.84
32.16
28.50
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


H2N
F
N
H

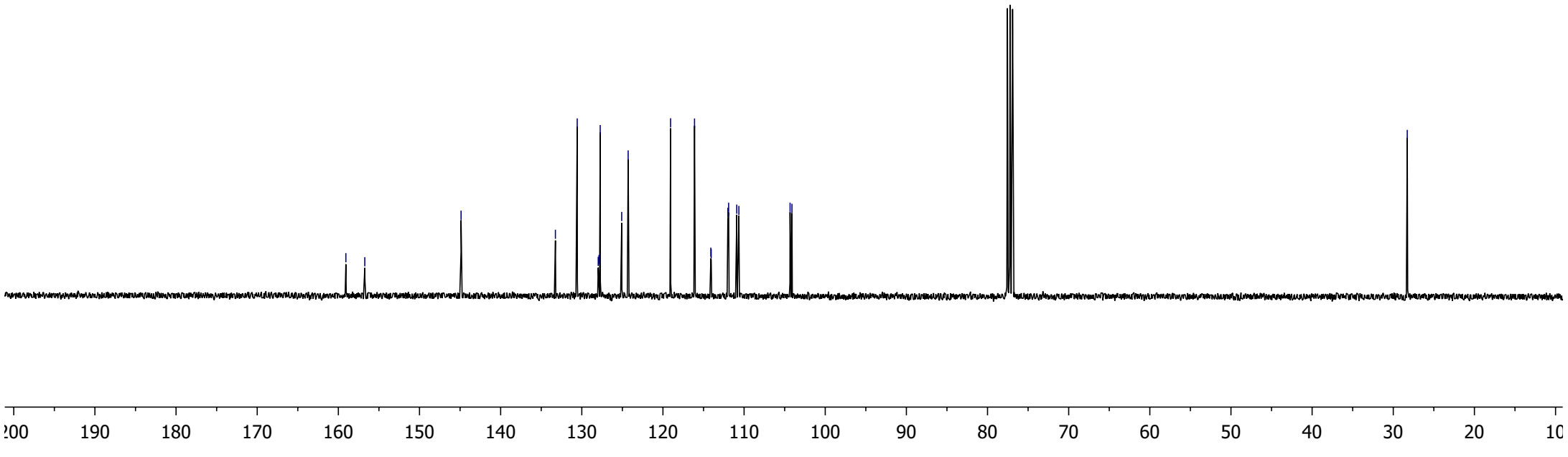
12f

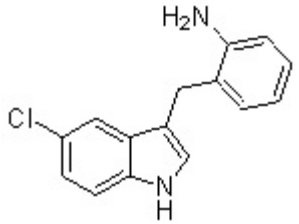
7.914
7.150
7.139
7.128
7.120
7.114
7.096
7.090
7.071
7.067
7.051
7.048
7.037
7.033
7.018
7.014
6.999
6.995
6.873
6.867
6.851
6.845
6.828
6.822
6.781
6.778
6.709
6.706
6.690
6.687
6.672
6.669
6.615
6.613
6.596
6.593
3.858
3.124
0.88
1.87
1.49
1.07
1.08
1.16
1.02
0.97
2.02
1.74
0.0
9.5
9.0
8.5
8.0
7.5
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
0.0

159.08
156.74
144.88
133.25
130.56
127.98
127.88
127.73
125.08
124.29
119.06
116.11
114.10
114.05
112.00
111.90
110.91
110.64
104.33
104.10
28.28



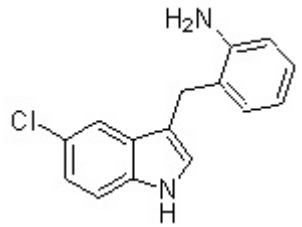
12f




H2N
Cl
N
H

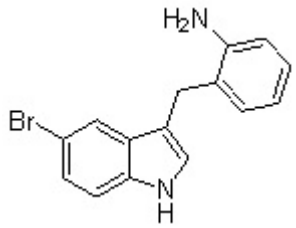
12g

8.073
7.553
7.549
7.240
7.218
7.160
7.153
7.127
7.108
6.823
6.818
6.793
6.775
6.722
6.702
3.949
3.483
0.89
1.00
1.06
3.12
1.32
0.75
1.01
2.14
1.50
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
0.0


H2N
Cl
N
H

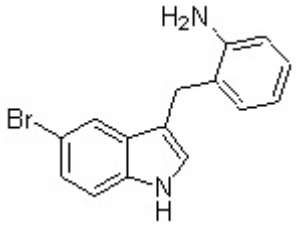
12g

144.79
135.05
130.52
128.64
127.75
125.37
125.01
123.92
122.66
119.07
118.71
116.10
113.69
112.36
28.04
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


H2N
Br
N
H

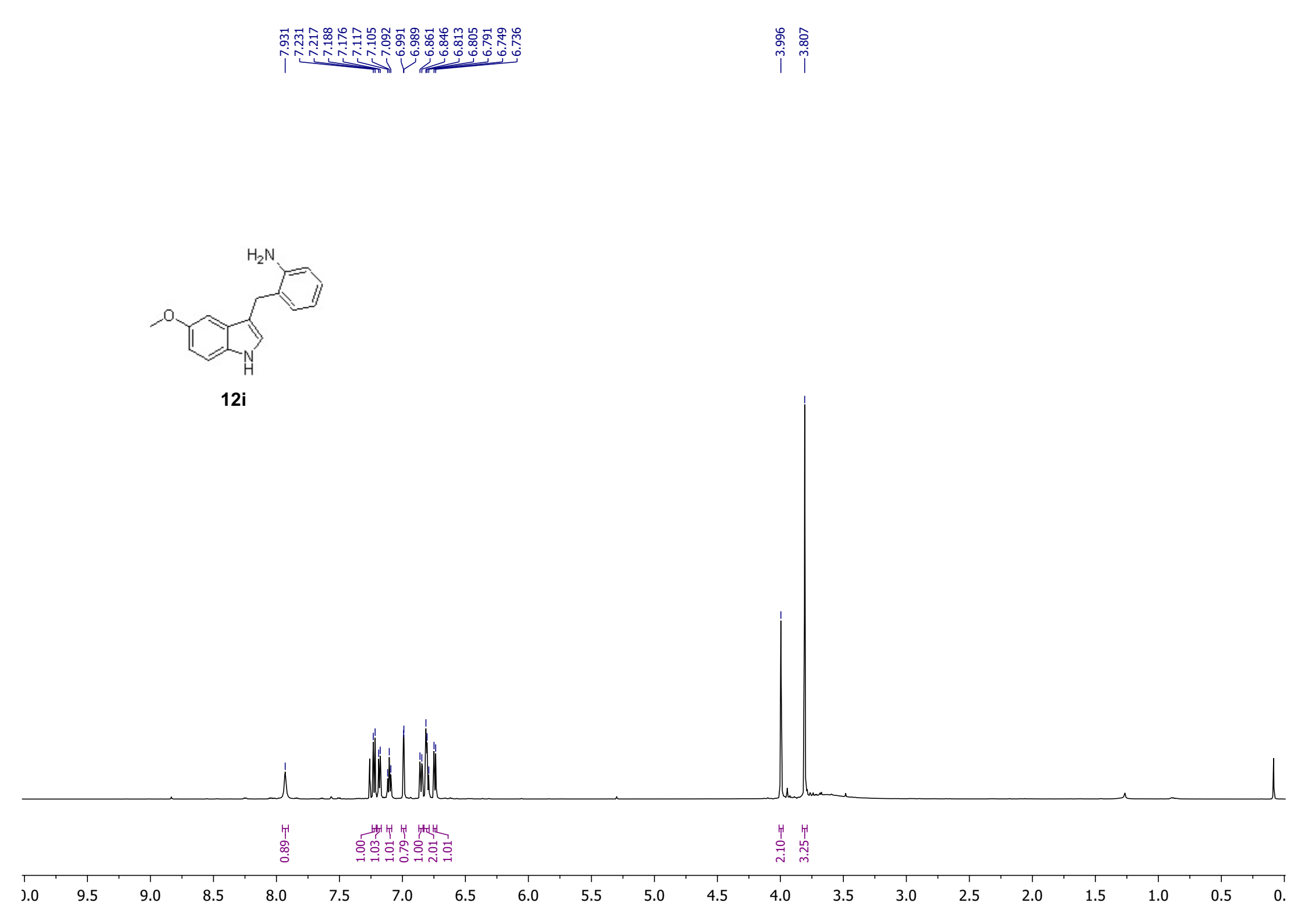
12h

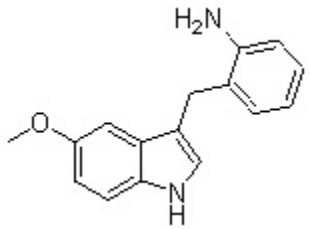
8.065
7.711
7.287
7.284
7.273
7.270
7.189
7.174
7.144
7.141
7.138
7.130
7.128
7.125
7.115
7.113
6.807
6.797
6.795
6.790
6.788
6.786
6.784
6.782
6.722
6.720
6.709
6.707
3.939
3.492
0.99
1.05
1.12
2.04
2.09
1.06
2.16
2.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


H2N
Br
N
H

12h

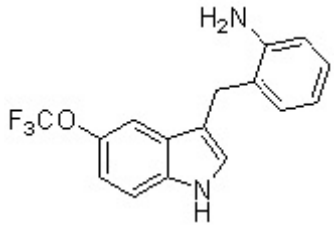
144.77
135.32
130.52
129.32
127.76
125.22
124.98
123.75
121.81
119.08
116.10
113.65
112.93
112.81
28.00
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


7.931
7.231
7.217
7.188
7.176
7.117
7.105
7.092
6.991
6.989
6.861
6.846
6.813
6.805
6.791
6.749
6.736
3.996
3.807
H2N
O
N
H
12i
0.89
1.00
1.03
1.01
0.79
1.00
2.01
1.01
2.10
3.25
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


H2N
O
N
H

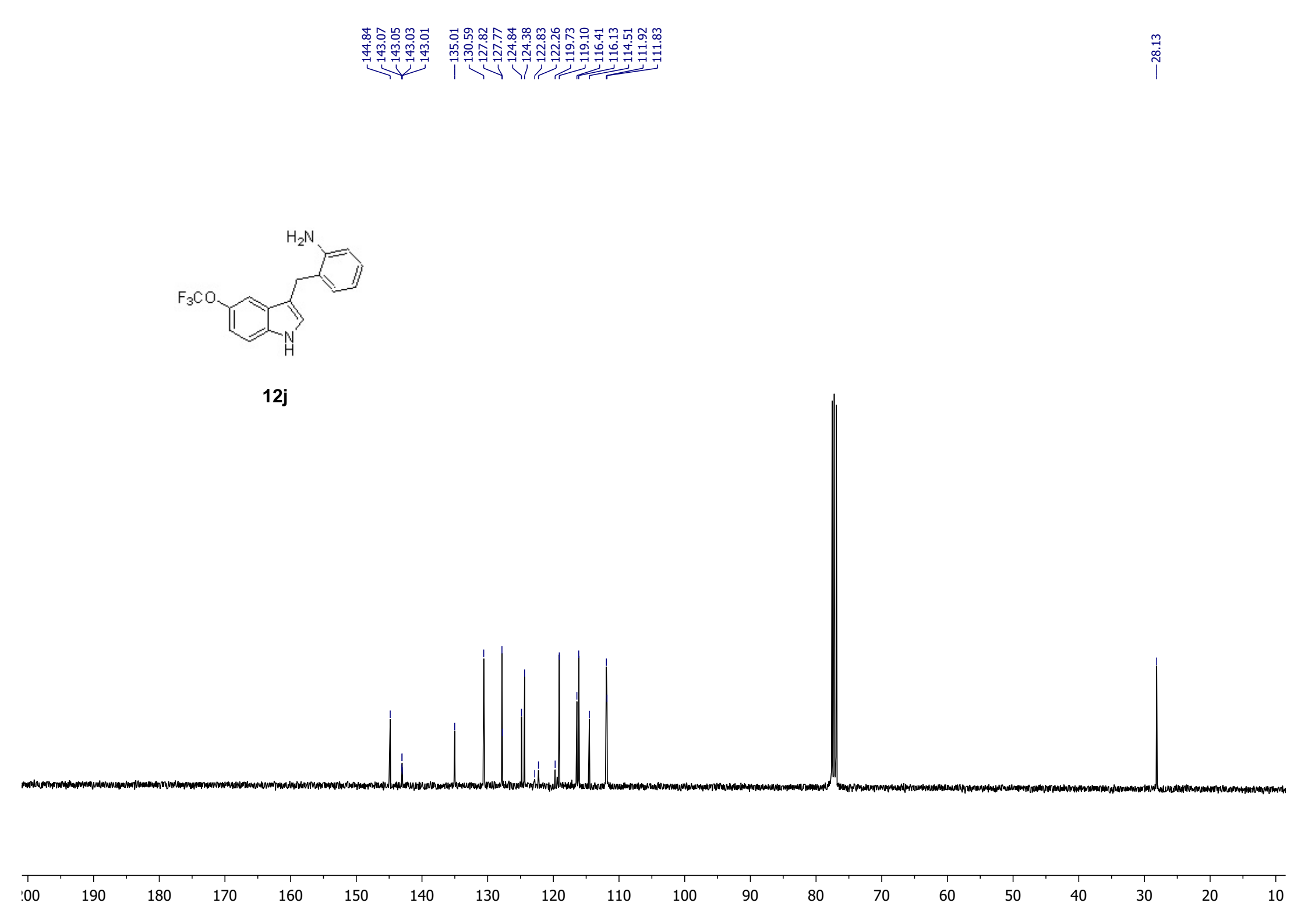
12i

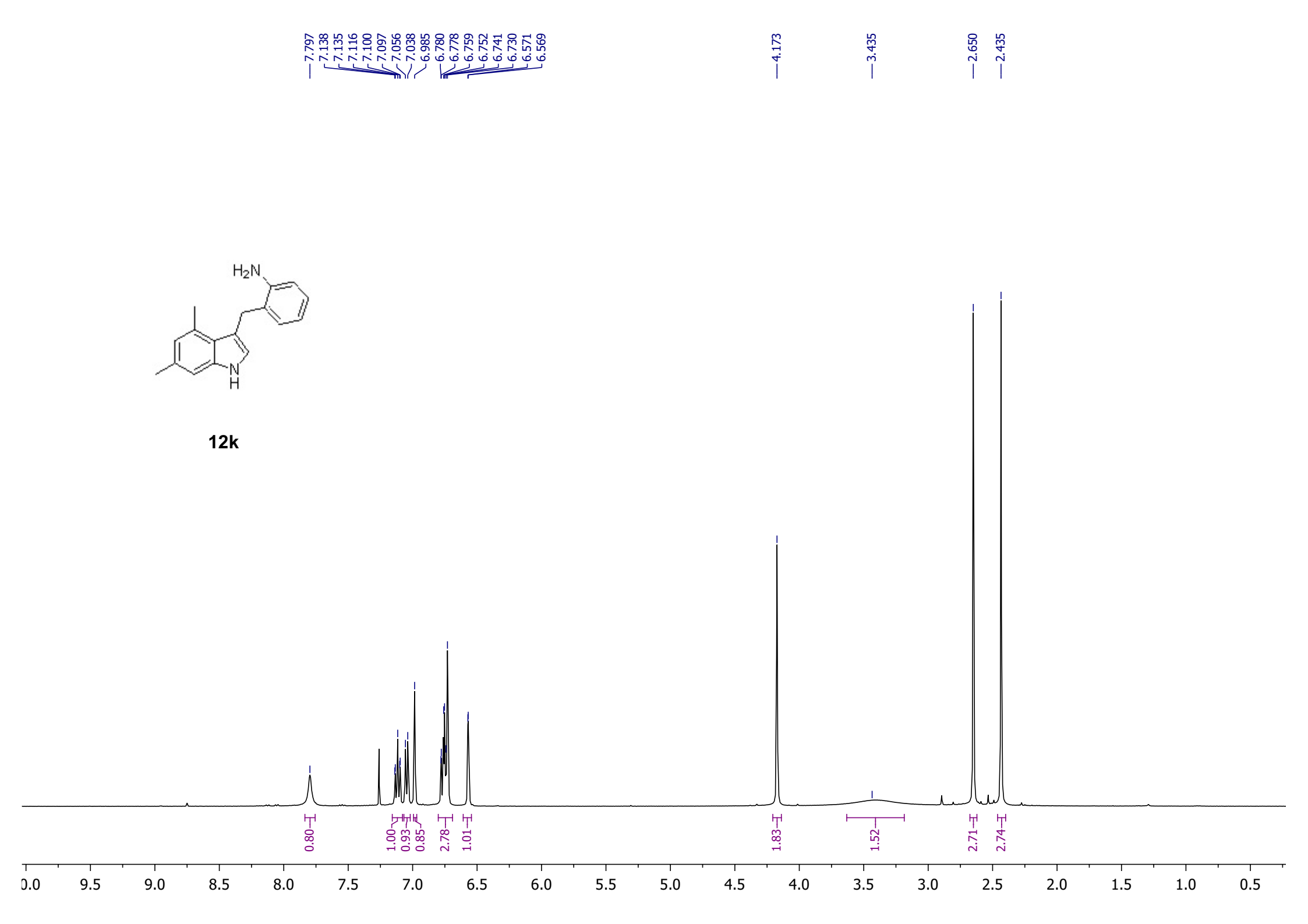
154.11
144.13
131.82
130.62
127.90
127.61
125.98
123.33
119.51
116.49
113.37
112.61
112.08
100.92
56.01
28.43
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

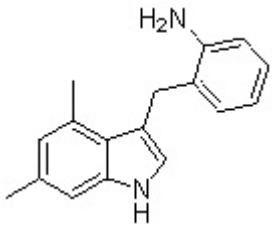

H2N
F3CO
N
H

12j

8.076
7.420
7.338
7.316
7.152
7.133
7.111
7.089
7.067
6.909
6.908
6.905
6.797
6.778
6.760
6.719
6.699
3.978
3.570
1.02
1.00
1.05
3.11
1.13
1.07
1.01
2.08
1.13
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

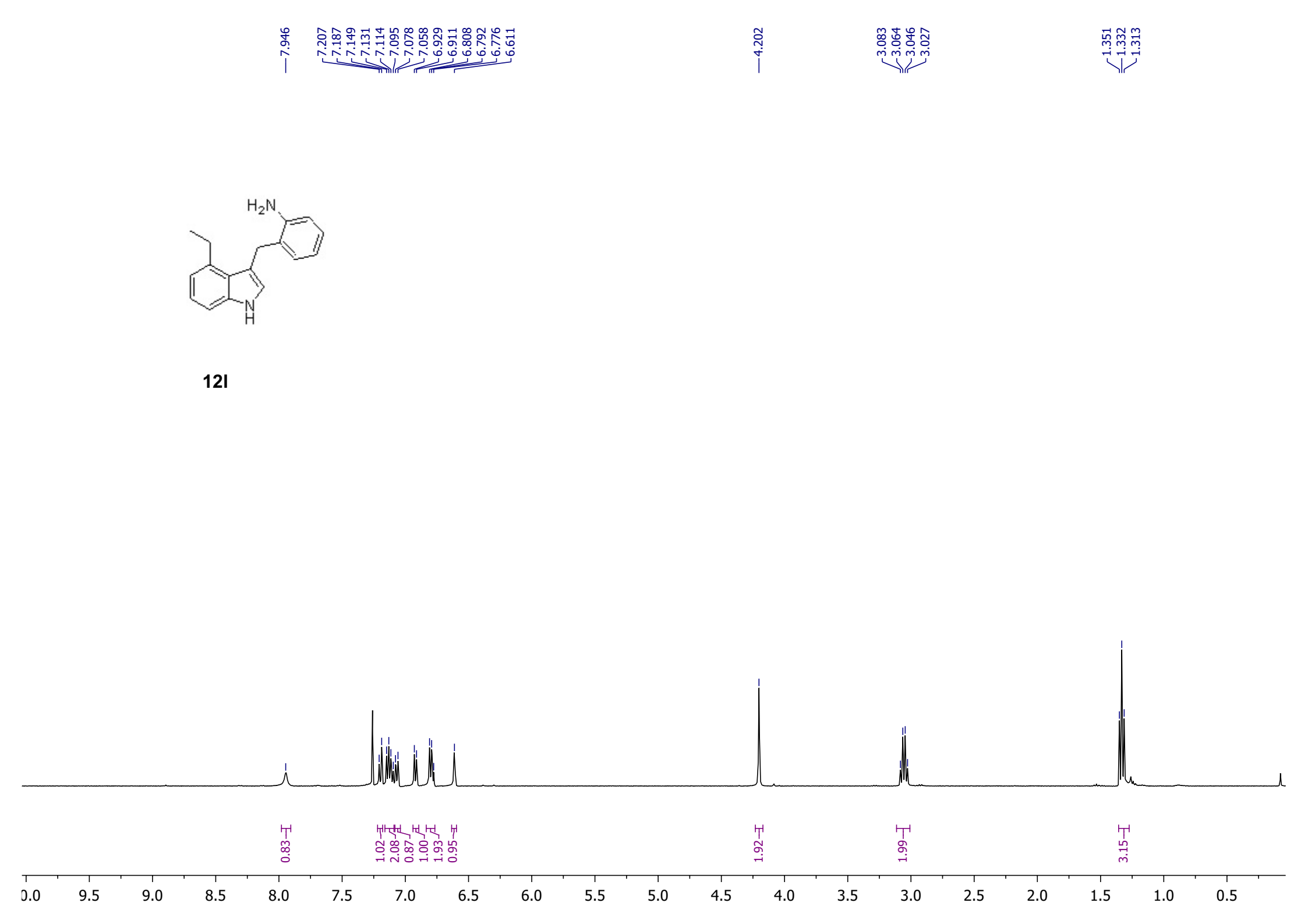

144.84
143.07
143.05
143.03
143.01
135.01
130.59
127.82
127.77
124.84
124.38
122.83
122.26
119.73
119.10
116.41
116.13
114.51
111.92
111.83
28.13
H2N
F3CO
N
H
12j
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


7.797
7.138
7.135
7.116
7.100
7.097
7.056
7.038
6.985
6.780
6.778
6.759
6.752
6.741
6.730
6.571
6.569
4.173
3.435
2.650
2.435
H2N
N
H
12k
0.80
1.00
0.93
0.85
2.78
1.01
1.83
1.52
2.71
2.74
0.0
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

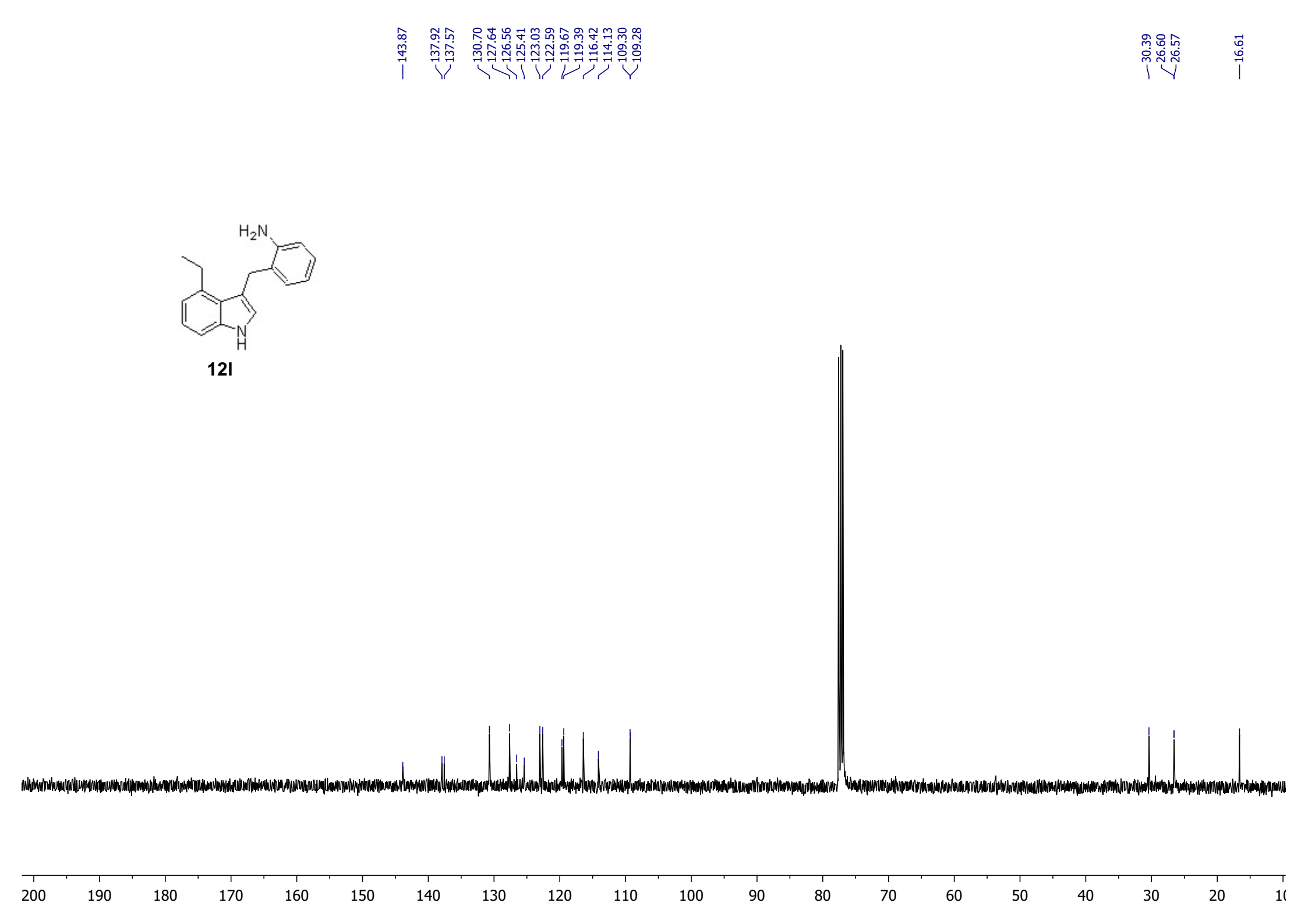

H2N
N
H

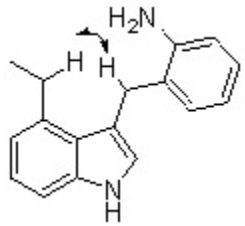
12k

144.57
137.81
132.26
130.98
130.44
127.45
126.26
124.15
123.13
122.16
119.05
115.82
114.40
109.14
30.12
21.65
20.29
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


7.946
7.207
7.187
7.149
7.131
7.114
7.095
7.078
7.058
6.929
6.911
6.808
6.792
6.776
6.611
4.202
3.083
3.064
3.046
3.027
1.351
1.332
1.313
H2N
N
H
0.83
1.02
2.08
0.87
1.00
1.93
0.95
1.92
1.99
3.15
0.0
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

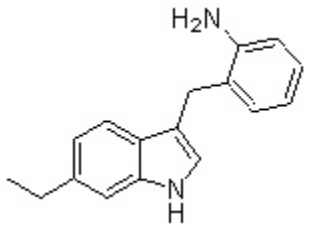
12l


143.87
137.92
137.57
130.70
127.64
126.56
125.41
123.03
122.59
119.67
119.39
116.42
114.13
109.30
109.28
30.39
26.60
26.57
16.61
H2N
N
H
12l
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20


H2N
H
H
N
H

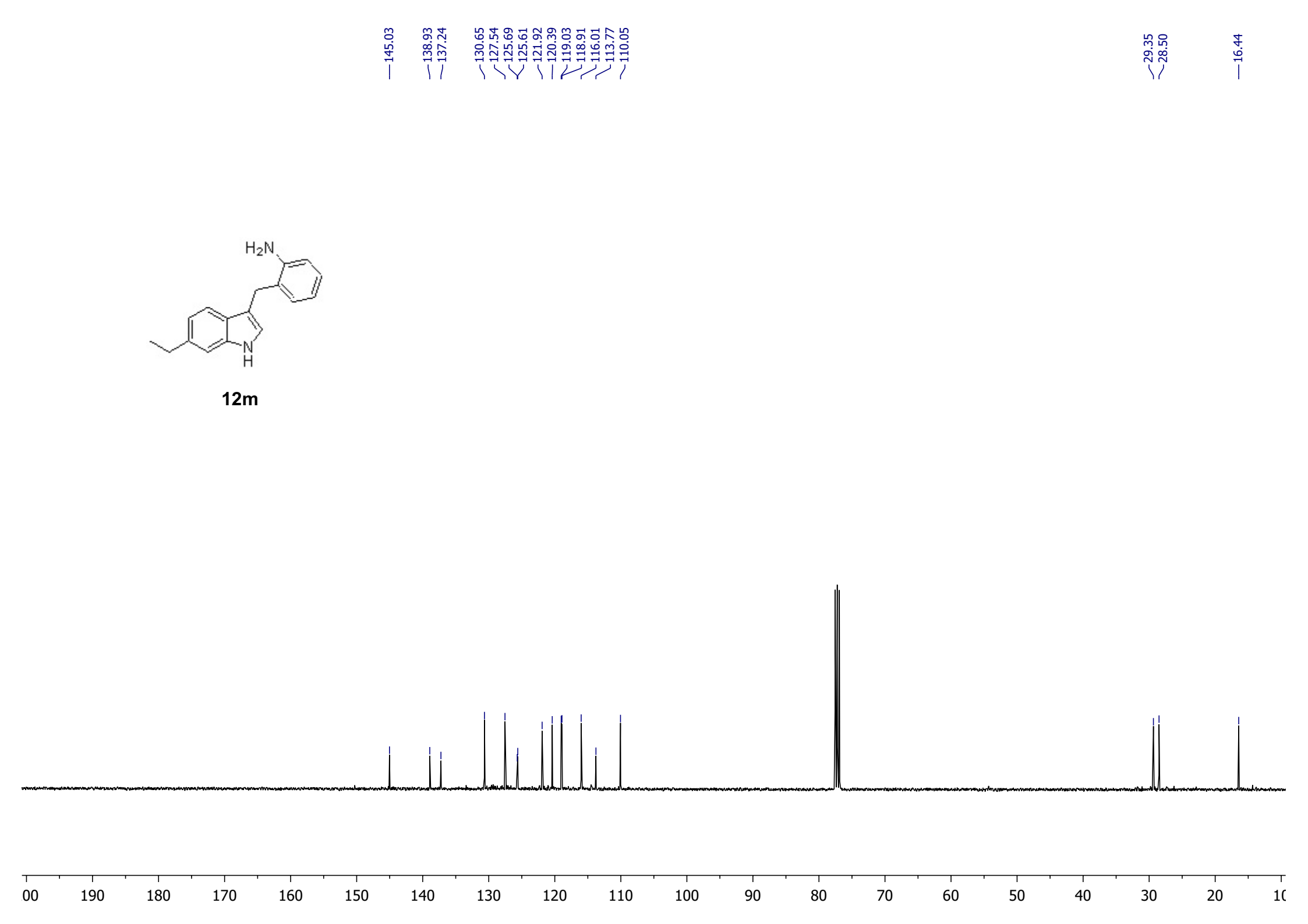
12l

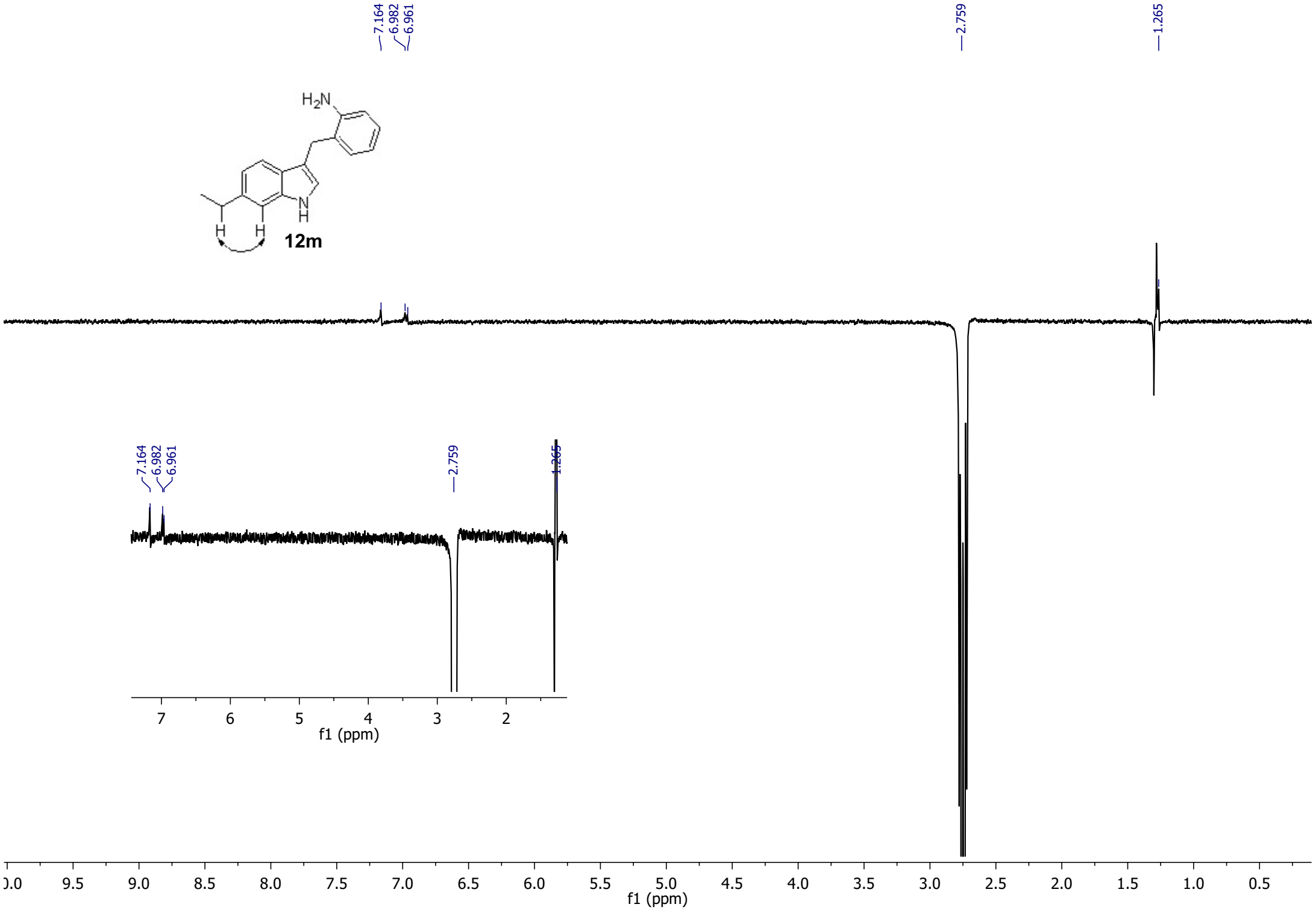
6.905
4.180
4.180
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

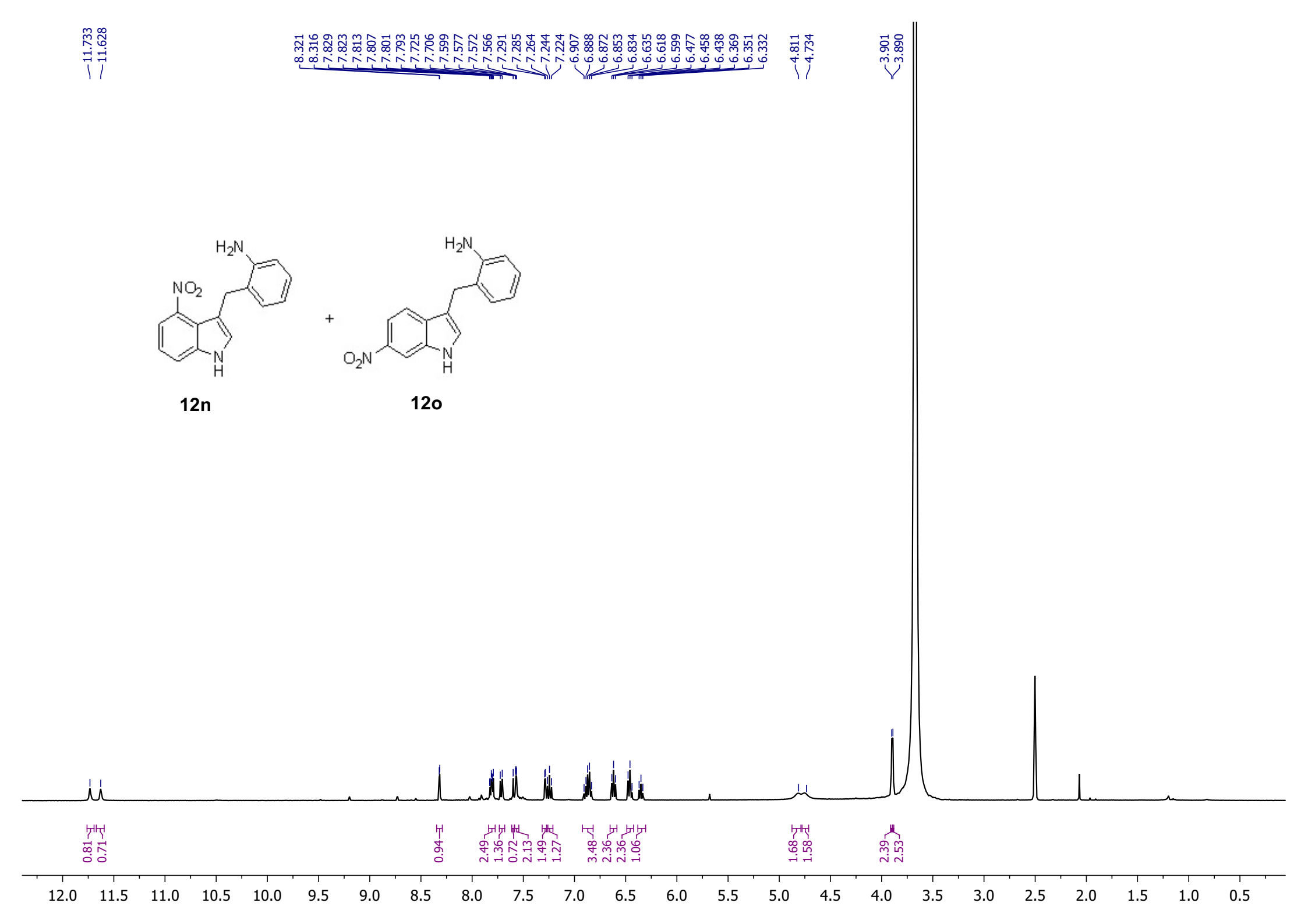

H2N
N
H

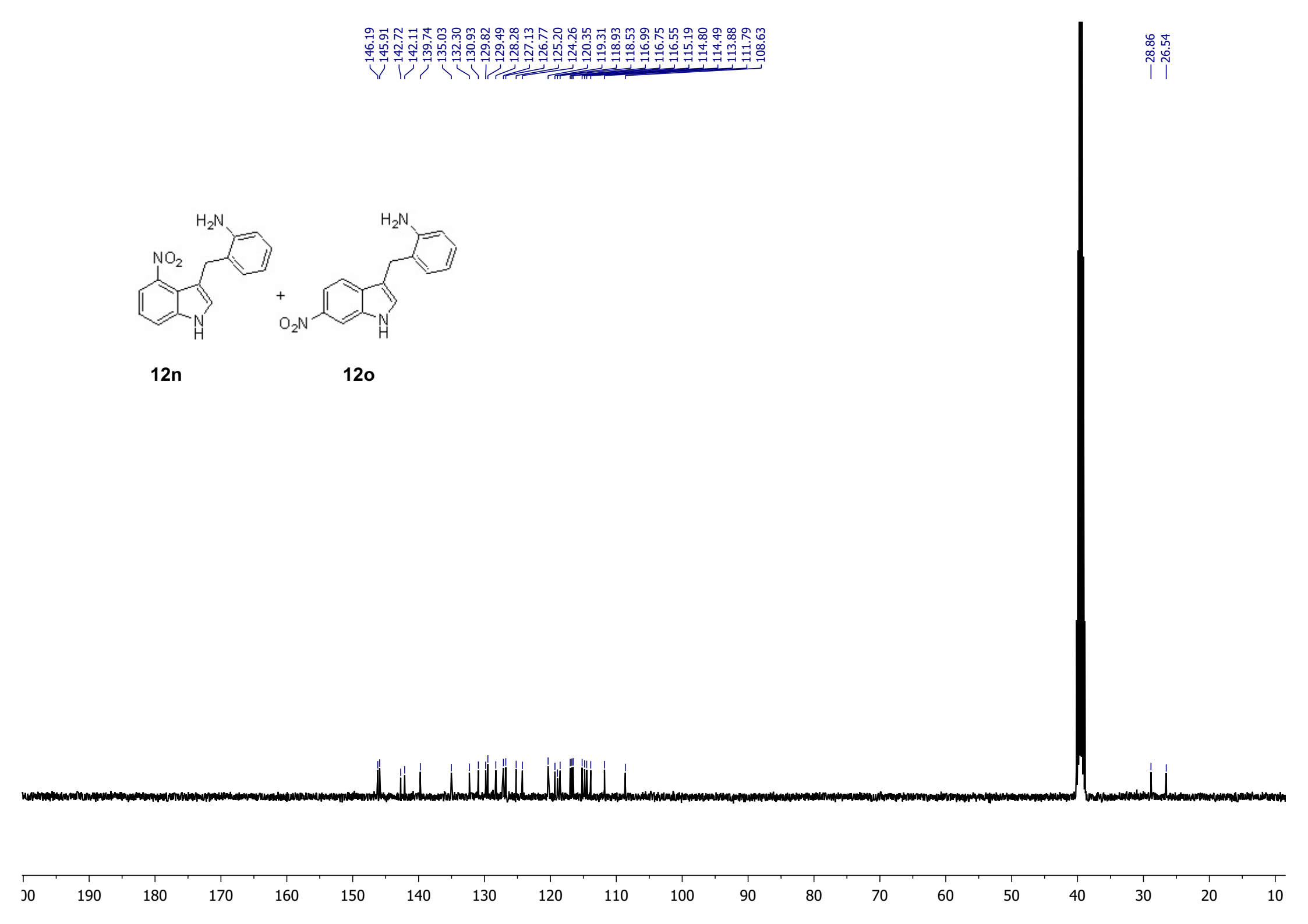
12m

7.907
7.497
7.477
7.191
7.172
7.116
7.078
7.074
6.989
6.971
6.794
6.776
6.754
6.693
6.672
3.998
2.787
2.768
2.749
2.730
1.310
1.291
1.272
0.70
1.00
1.88
1.10
1.03
1.97
1.00
1.92
2.06
3.67
0.0
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

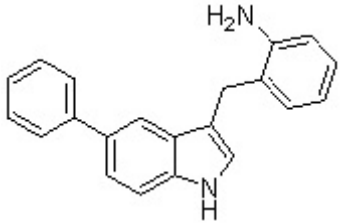

145.03
138.93
137.24
130.65
127.54
125.69
125.61
121.92
120.39
119.03
118.91
116.01
113.77
110.05
29.35
28.50
16.44
H2N
N
H
12m
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


7.164
6.982
6.961
2.759
1.265
H2N
N
H
H
H
12m
7.164
6.982
6.961
2.759
1.265
7
6
5
4
3
2
f1 (ppm)
f1 (ppm)

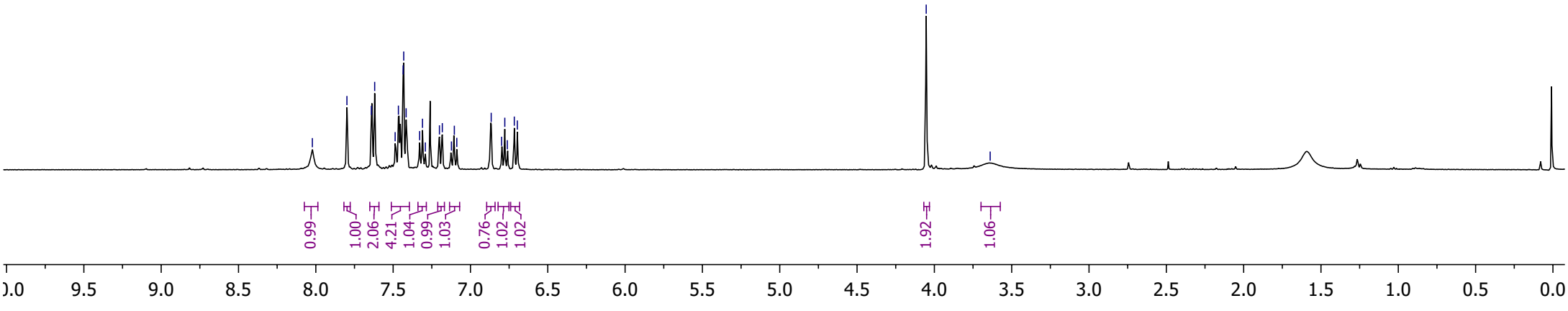

11.733
11.628
8.321
8.316
7.829
7.823
7.813
7.807
7.801
7.793
7.725
7.706
7.599
7.577
7.572
7.566
7.291
7.285
7.264
7.244
7.224
6.907
6.888
6.872
6.853
6.834
6.635
6.618
6.599
6.477
6.458
6.438
6.369
6.351
6.332
4.811
4.734
3.901
3.890
H2N
NO2
N
H
+
H2N
O2N
N
H
12n
12o
0.81
0.71
0.94
2.49
1.36
0.72
2.13
1.49
1.27
3.48
2.36
2.36
1.06
1.68
1.58
2.39
2.53
12.0
11.5
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

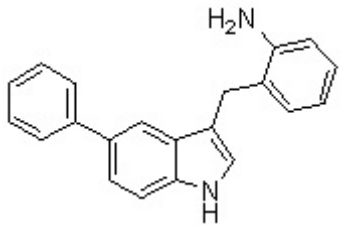

146.19
145.91
142.72
142.11
139.74
135.03
132.30
130.93
129.82
129.49
128.28
127.13
126.77
125.20
124.26
120.35
119.31
118.93
118.53
116.99
116.75
116.55
115.19
114.80
114.49
113.88
111.79
108.63
28.86
26.54
H2N
NO2
N
H
+
O2N
H2N
N
H
12n
12o
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


8.022
7.799
7.640
7.619
7.487
7.466
7.435
7.432
7.416
7.329
7.310
7.292
7.201
7.182
7.123
7.104
7.088
6.866
6.799
6.778
6.762
6.716
6.697
4.053
3.639


H2N
N
H

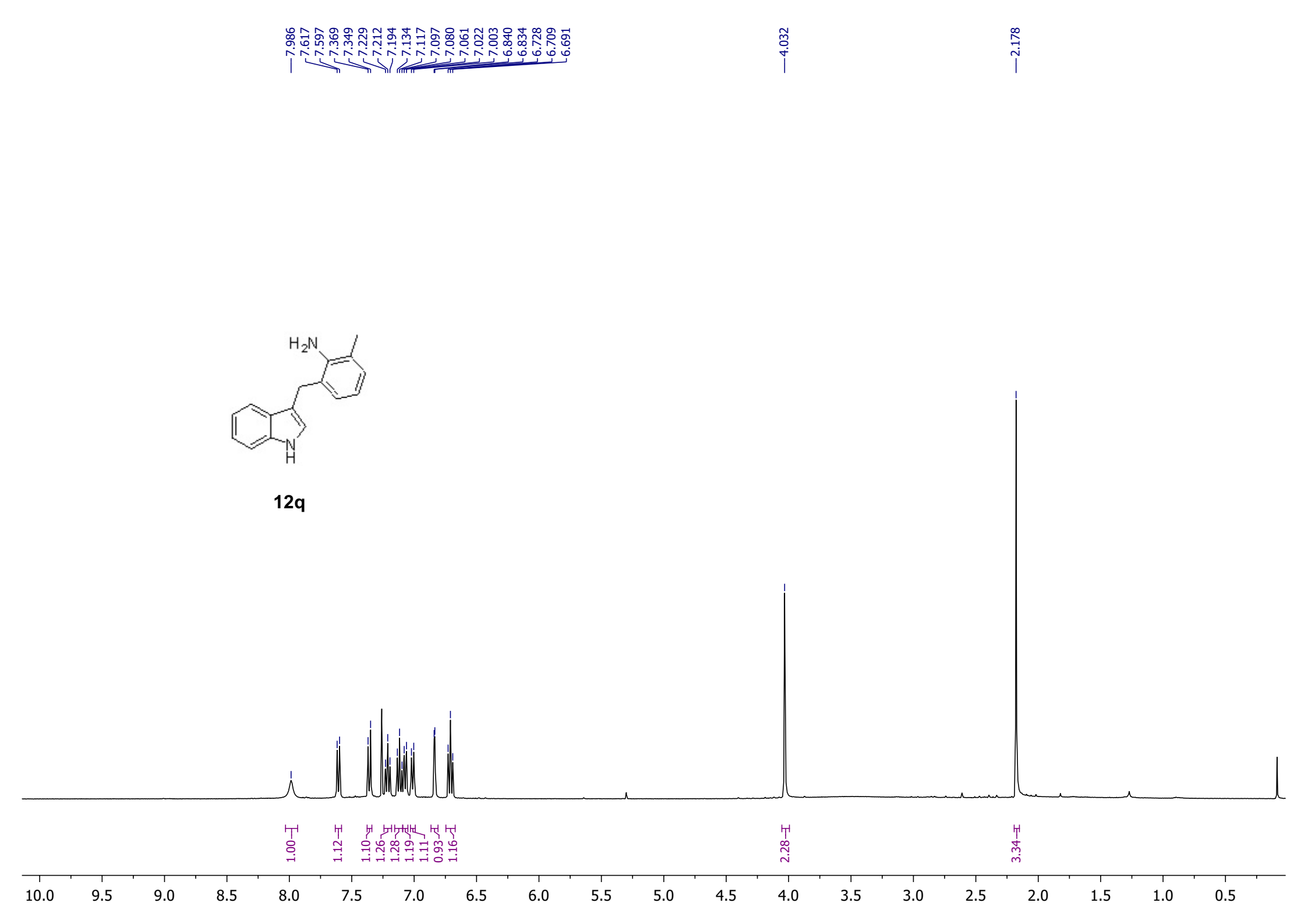
12p

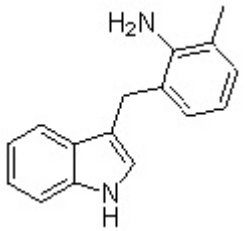

0.99
1.00
2.06
4.21
1.04
0.99
1.03
0.76
1.02
1.02
1.92
1.06
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


H2N
N
H

12p

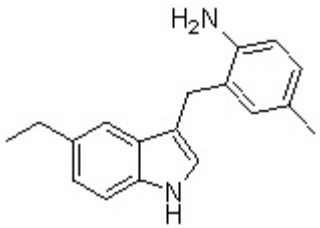
144.93
142.67
136.31
133.33
130.66
128.85
128.13
127.67
127.59
126.55
125.41
123.20
122.30
119.03
117.77
116.08
114.41
111.59
28.31
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.986
7.617
7.597
7.369
7.349
7.229
7.212
7.194
7.134
7.117
7.097
7.080
7.061
7.022
7.003
6.840
6.834
6.728
6.709
6.691
4.032
2.178
H2N
N
H
12q
1.00
1.12
1.10
1.26
1.28
1.19
1.11
0.93
1.16
2.28
3.34
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

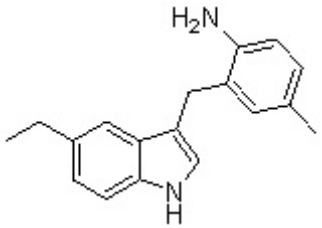

H2N
N
H

12q

142.93
136.81
128.92
128.57
127.66
125.01
122.71
122.57
122.41
119.68
119.32
118.46
114.07
111.35
28.59
17.84
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10



12r

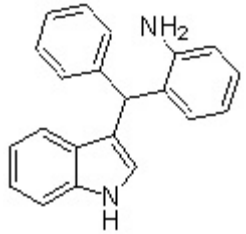


12r

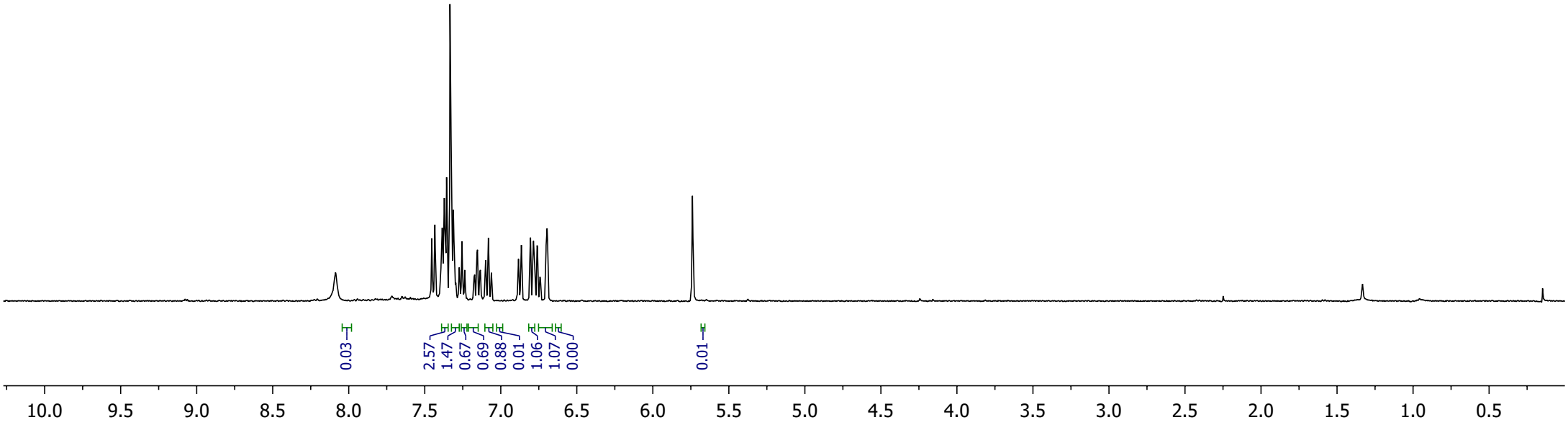
142.42
135.65
135.26
131.32
128.12
127.98
127.80
125.74
122.98
122.60
117.61
116.16
113.79
111.09
29.25
28.30
20.74
16.70

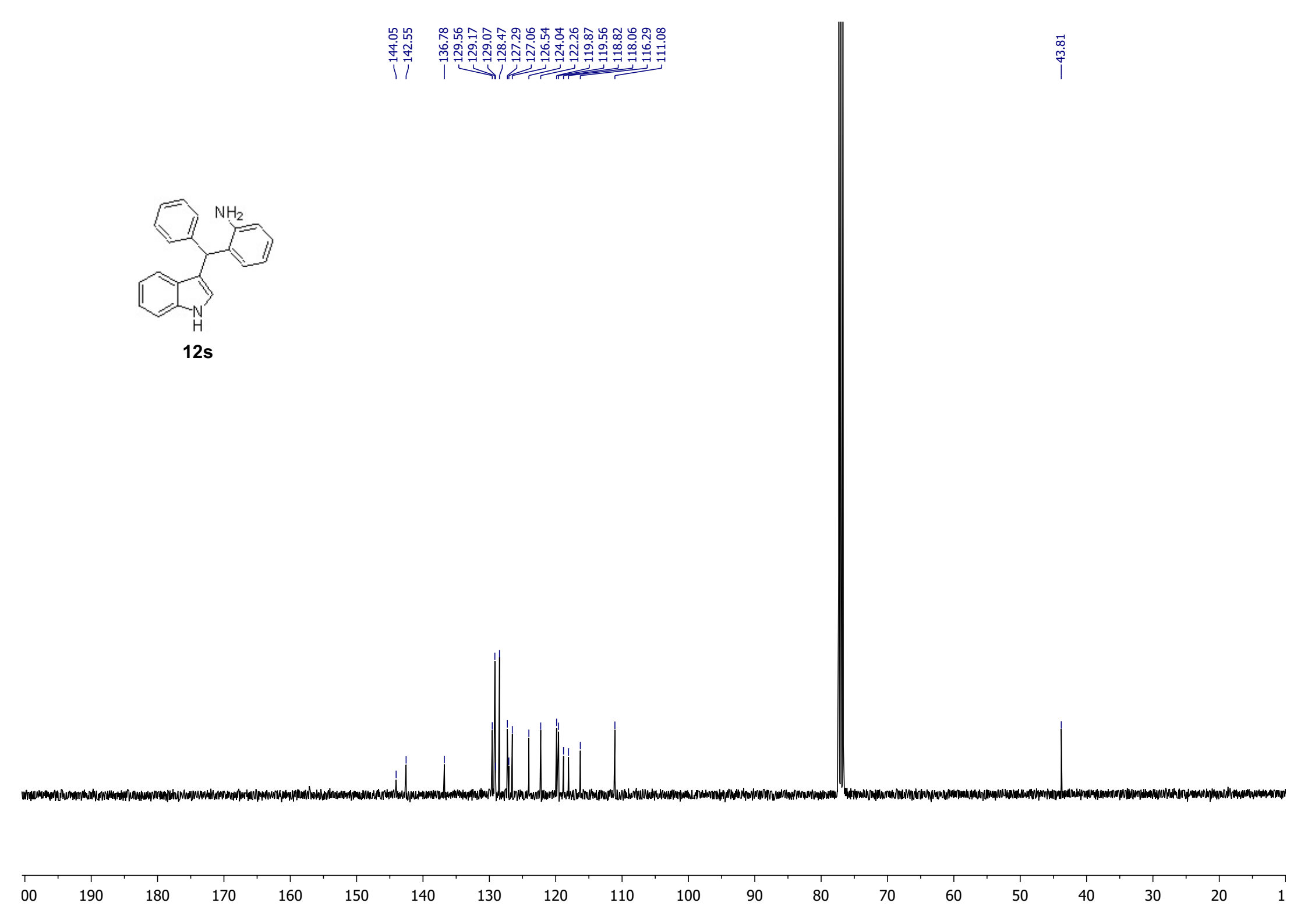
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10


8.086
7.454
7.433
7.385
7.372
7.366
7.356
7.334
7.329
7.312
7.275
7.255
7.235
7.175
7.153
7.134
7.101
7.081
7.063
6.886
6.865
6.805
6.785
6.761
6.740
6.695
6.625
6.621
5.739

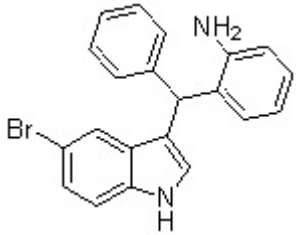

NH2
N
H

12s

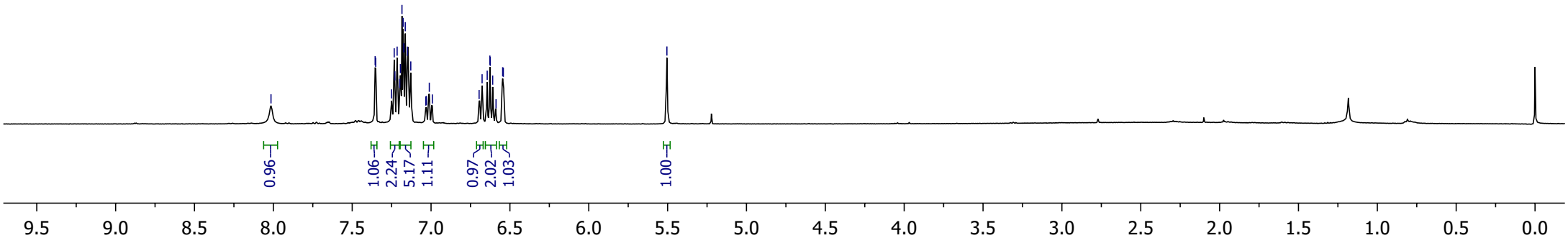

0.03
2.57
1.47
0.67
0.69
0.88
0.01
1.06
1.07
0.00
0.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

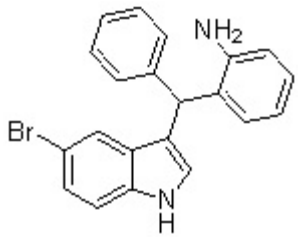

144.05
142.55
136.78
129.56
129.17
129.07
128.47
127.29
127.06
126.54
124.04
122.26
119.87
119.56
118.82
118.06
116.29
111.08
43.81
NH2
N
H
12s
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
1


8.015
7.355
7.351
7.250
7.234
7.230
7.215
7.198
7.194
7.184
7.177
7.173
7.164
7.149
7.129
7.033
7.030
7.011
6.992
6.695
6.676
6.644
6.627
6.625
6.609
6.588
6.546
6.542
5.505


NH2
Br
N
H

12t


0.96
1.06
2.24
5.17
1.11
0.97
2.02
1.03
1.00
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
0.0

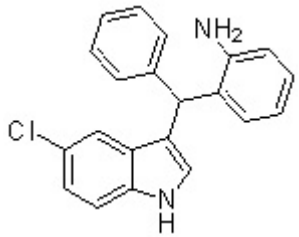


12t

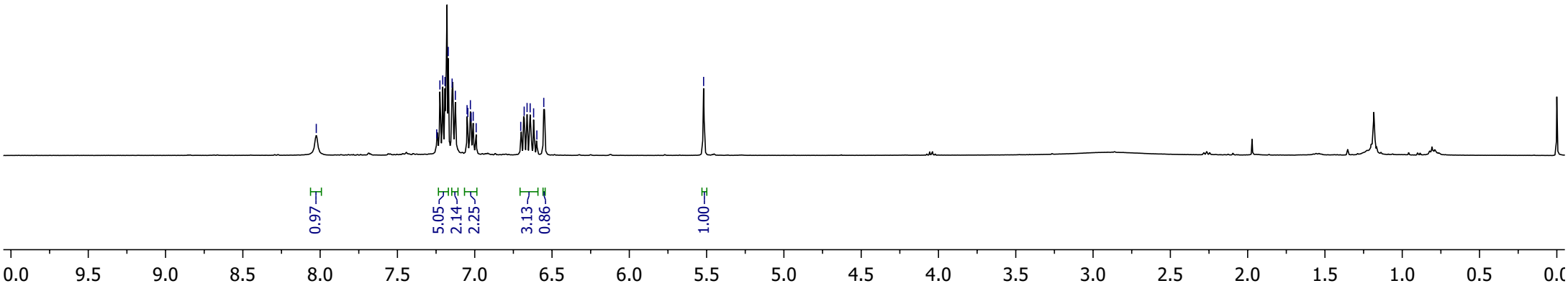
144.36
142.36
135.57
129.59
129.24
128.98
128.79
128.69
127.67
126.93
125.49
125.40
122.43
118.95
118.09
116.50
113.09
112.79
43.78

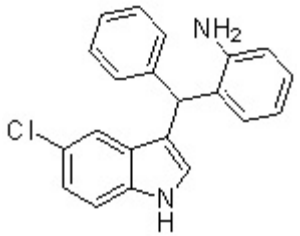
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10


8.025
7.246
7.225
7.207
7.192
7.171
7.146
7.125
7.050
7.045
7.028
7.023
7.010
6.991
6.702
6.680
6.661
6.641
6.619
6.598
6.553
5.519


NH2
Cl
N
H

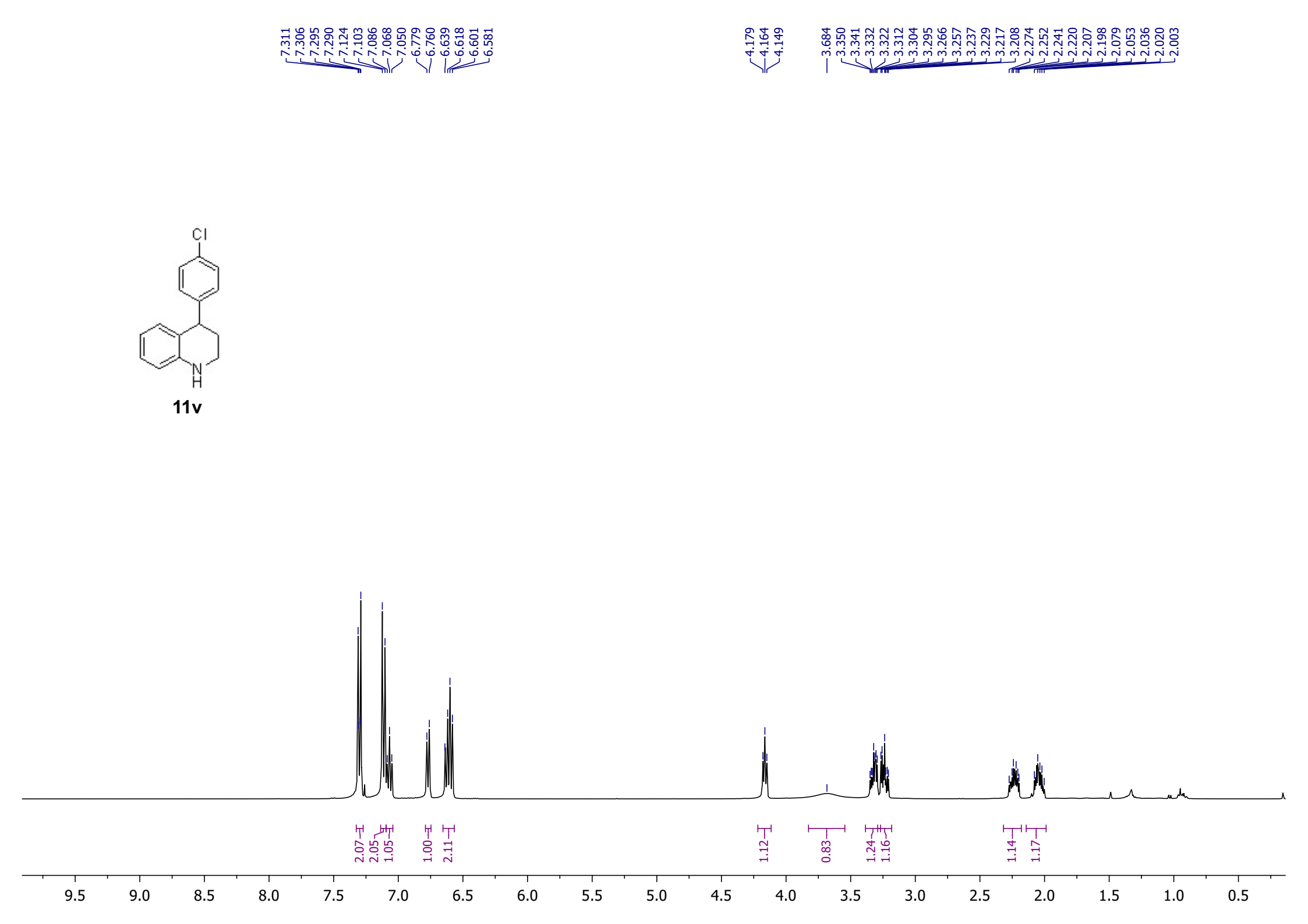
12u

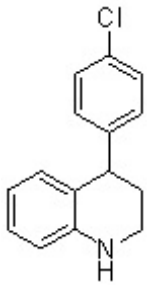

0.97
5.05
2.14
2.25
3.13
0.86
1.00
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


NH2
Cl
N
H

12u

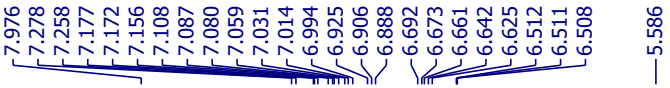
144.01
142.35
135.31
129.63
129.26
128.93
128.78
128.33
127.68
126.93
125.66
125.50
122.83
119.38
119.22
118.11
116.71
112.35
43.82
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

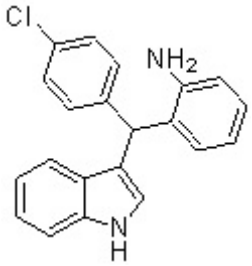

7.311
7.306
7.295
7.290
7.124
7.103
7.086
7.068
7.050
6.779
6.760
6.639
6.618
6.601
6.581
4.179
4.164
4.149
3.684
3.350
3.341
3.332
3.322
3.312
3.304
3.295
3.266
3.257
3.237
3.229
3.217
3.208
2.274
2.252
2.241
2.220
2.207
2.198
2.079
2.053
2.036
2.020
2.003
Cl
N
H
11v
2.07
2.05
1.05
1.00
2.11
1.12
0.83
1.24
1.16
1.14
1.17
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


Cl
N
H

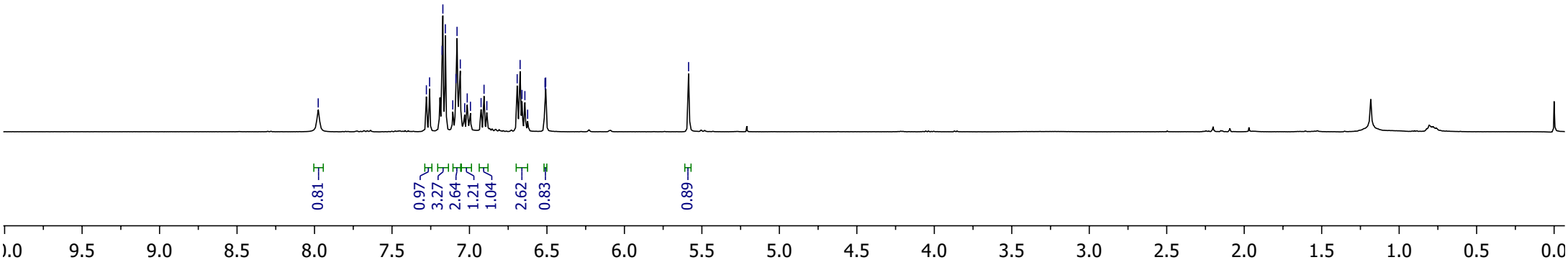
11v

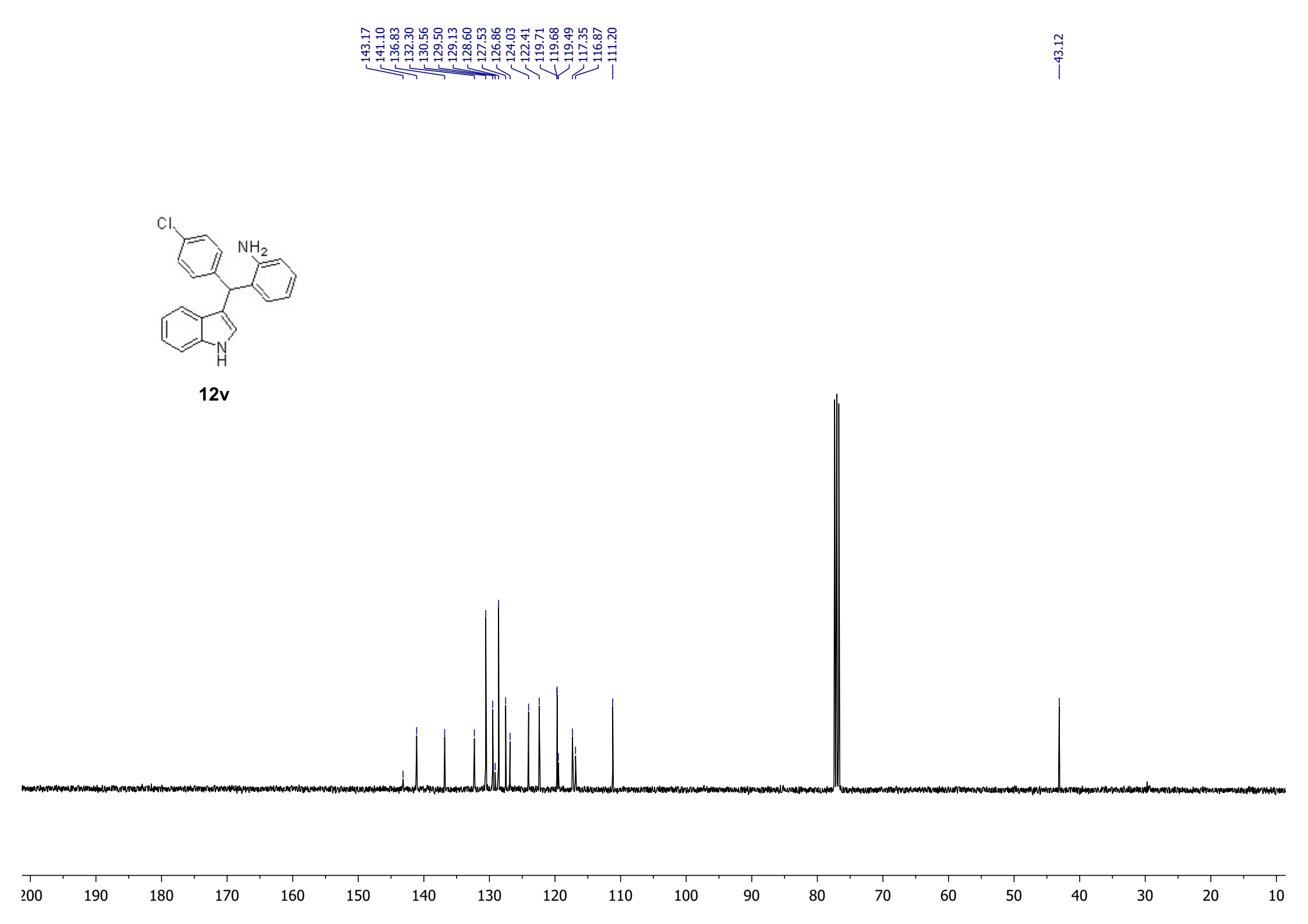
145.30
145.01
131.94
130.45
130.14
128.53
127.66
122.87
117.22
114.44
42.36
39.14
31.16
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

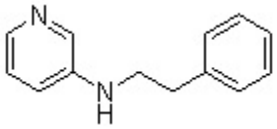

7.976
7.278
7.258
7.177
7.172
7.156
7.108
7.087
7.080
7.059
7.031
7.014
6.994
6.925
6.906
6.888
6.692
6.673
6.661
6.642
6.625
6.512
6.511
6.508
5.586


Cl
NH2
N
H

12v

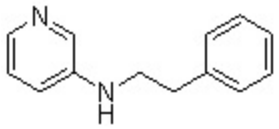

0.81
0.97
3.27
2.64
1.21
1.04
2.62
0.83
0.89
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


143.17
141.10
136.83
132.30
130.56
129.50
129.13
128.60
127.53
126.86
124.03
122.41
119.71
119.68
119.49
117.35
116.87
111.20
43.12
Cl
NH2
N
H
12v
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10



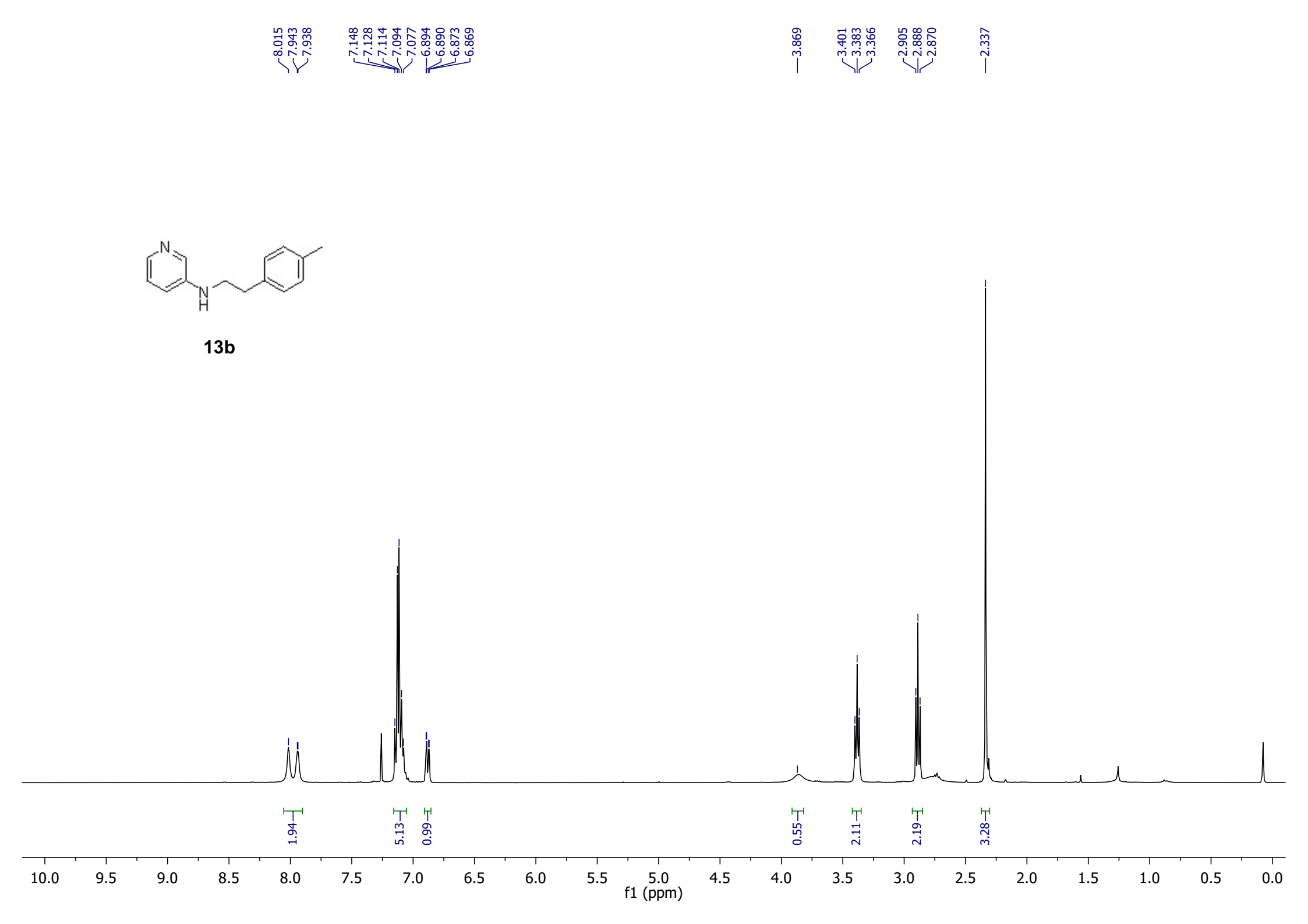
13a

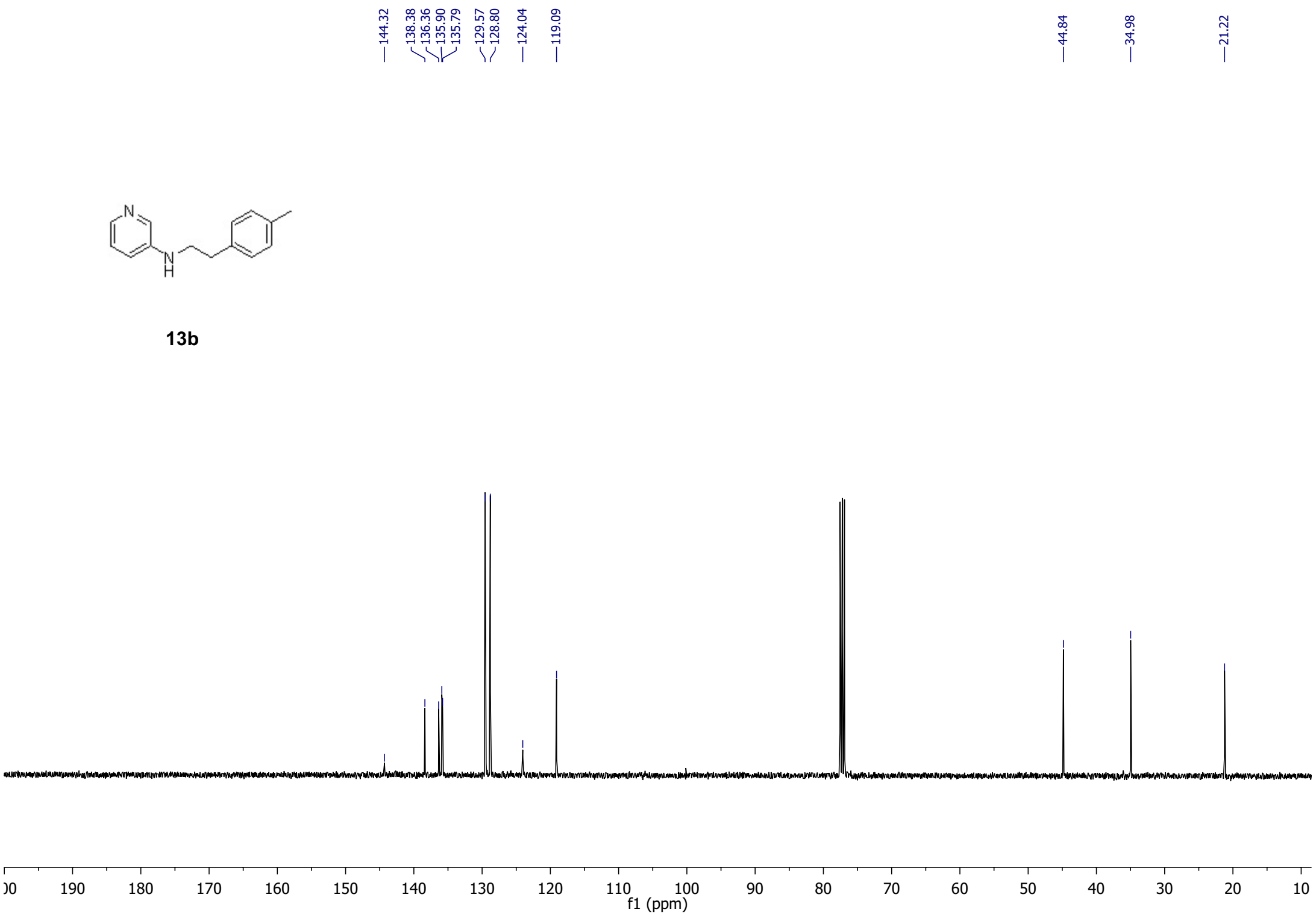
7.849
7.799
7.789
7.188
7.171
7.152
7.107
7.089
7.071
7.069
7.051
6.928
6.916
6.908
6.896
6.716
6.713
6.709
6.695
6.689
3.984
3.240
3.222
3.204
2.764
2.747
2.729
1.00
0.98
2.01
3.06
0.97
1.03
1.07
2.17
2.19
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



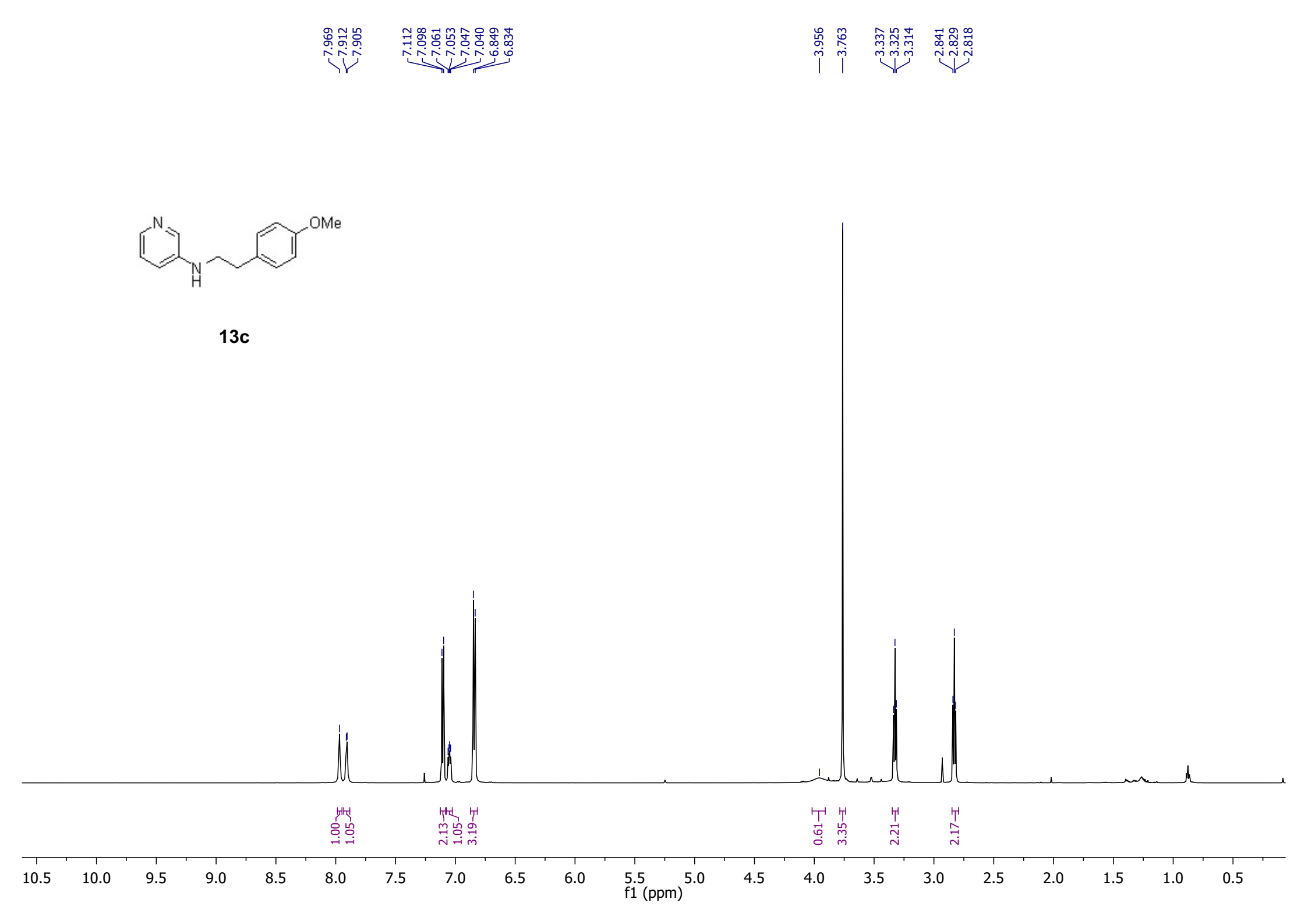
13a

144.08
138.87
138.27
135.87
128.67
128.56
126.45
123.71
118.44
44.48
35.16
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

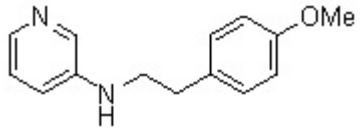

8.015
7.943
7.938
7.148
7.128
7.114
7.094
7.077
6.894
6.890
6.873
6.869
3.869
3.401
3.383
3.366
2.905
2.888
2.870
2.337
N
N
H
13b
1.94
5.13
0.99
0.55
2.11
2.19
3.28
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


144.32
138.38
136.36
135.90
135.79
129.57
128.80
124.04
119.09
44.84
34.98
21.22
N
N
H
f1 (ppm)

13b

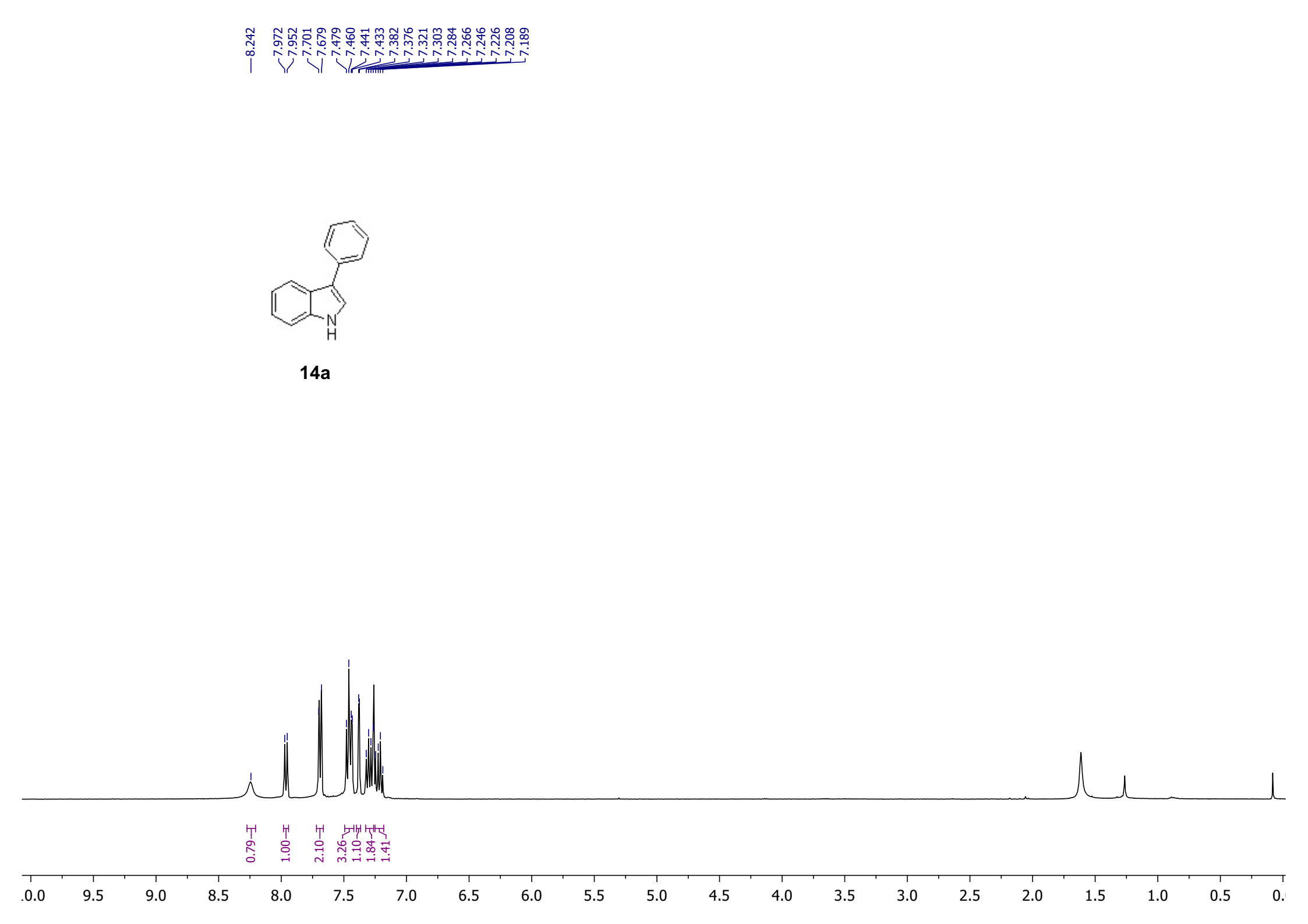

7.969
7.912
7.905
7.112
7.098
7.061
7.053
7.047
7.040
6.849
6.834
3.956
3.763
3.337
3.325
3.314
2.841
2.829
2.818
N
OMe
N
H
1.00
1.05
2.13
1.05
3.19
0.61
3.35
2.21
2.17
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

13c

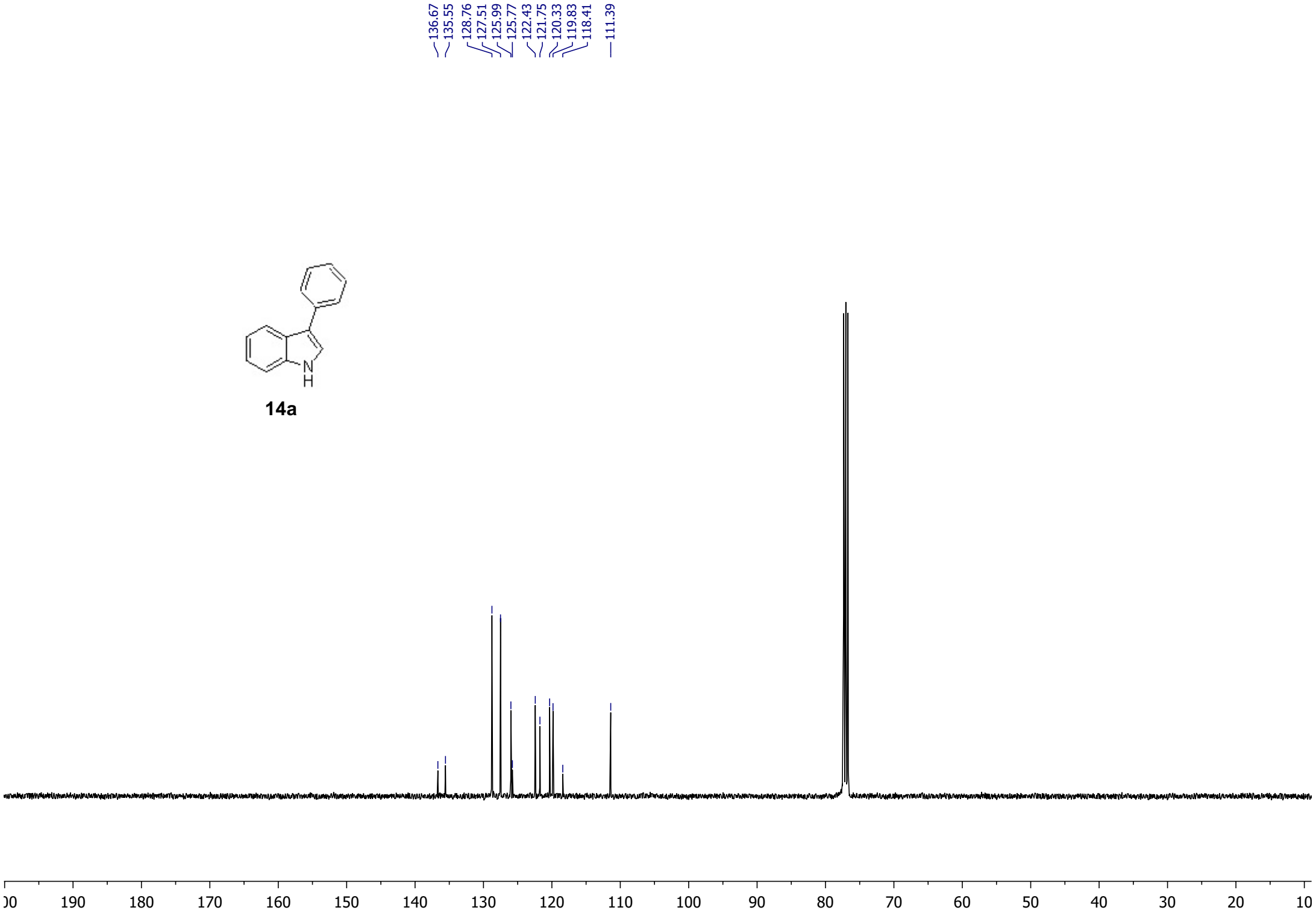

N
OMe
N
H

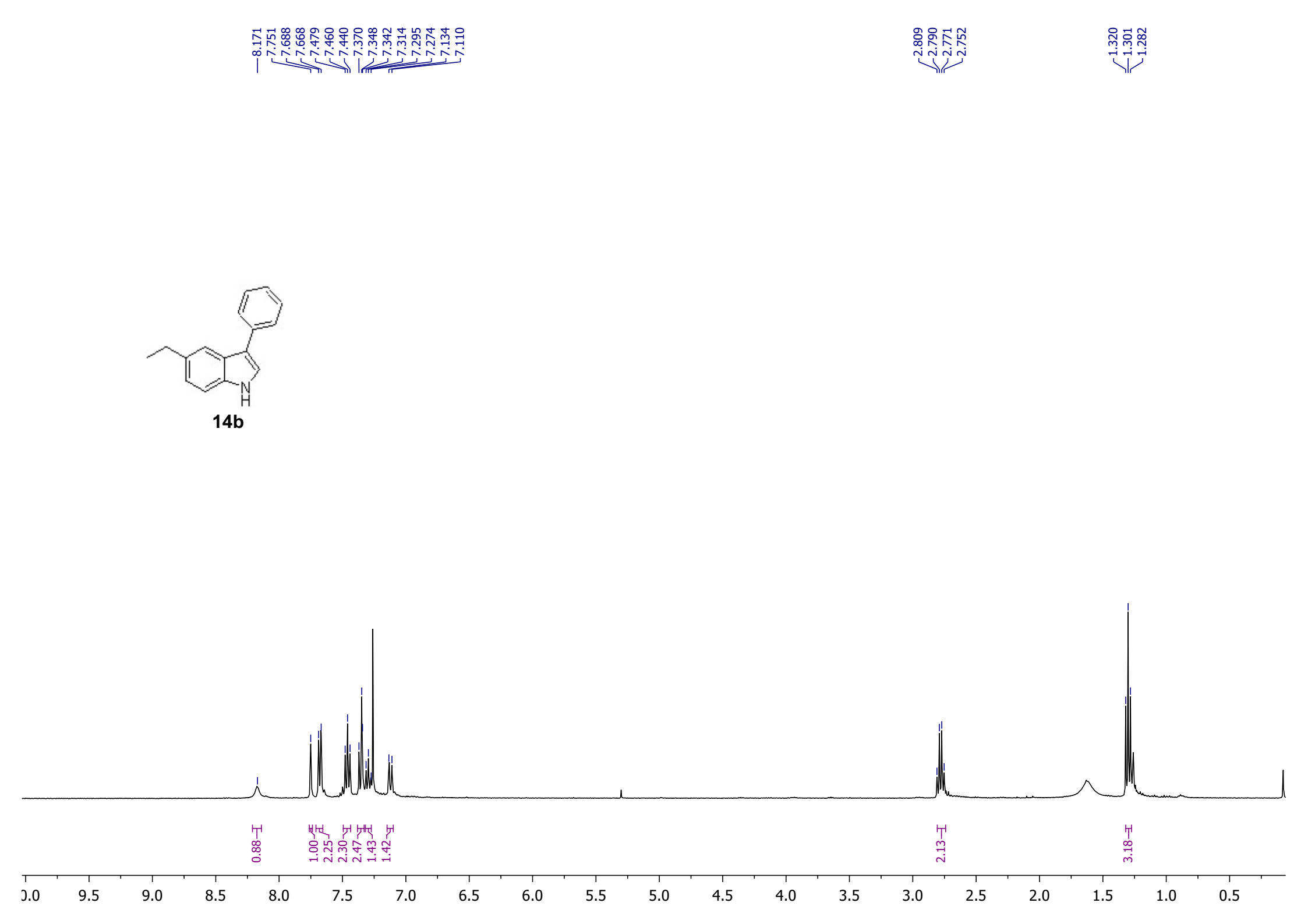
13c

158.29
144.16
138.39
135.93
130.83
129.72
123.84
118.70
114.09
55.28
44.76
34.33
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

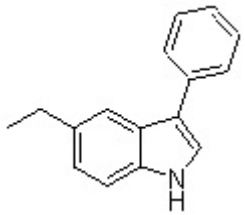

8.242
7.972
7.952
7.701
7.679
7.479
7.460
7.441
7.433
7.382
7.376
7.321
7.303
7.284
7.266
7.246
7.226
7.208
7.189
N
H
0.79
1.00
2.10
3.26
1.10
1.84
1.41
.0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.

14a


136.67
135.55
128.76
127.51
125.99
125.77
122.43
121.75
120.33
119.83
118.41
111.39
N
H
14a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

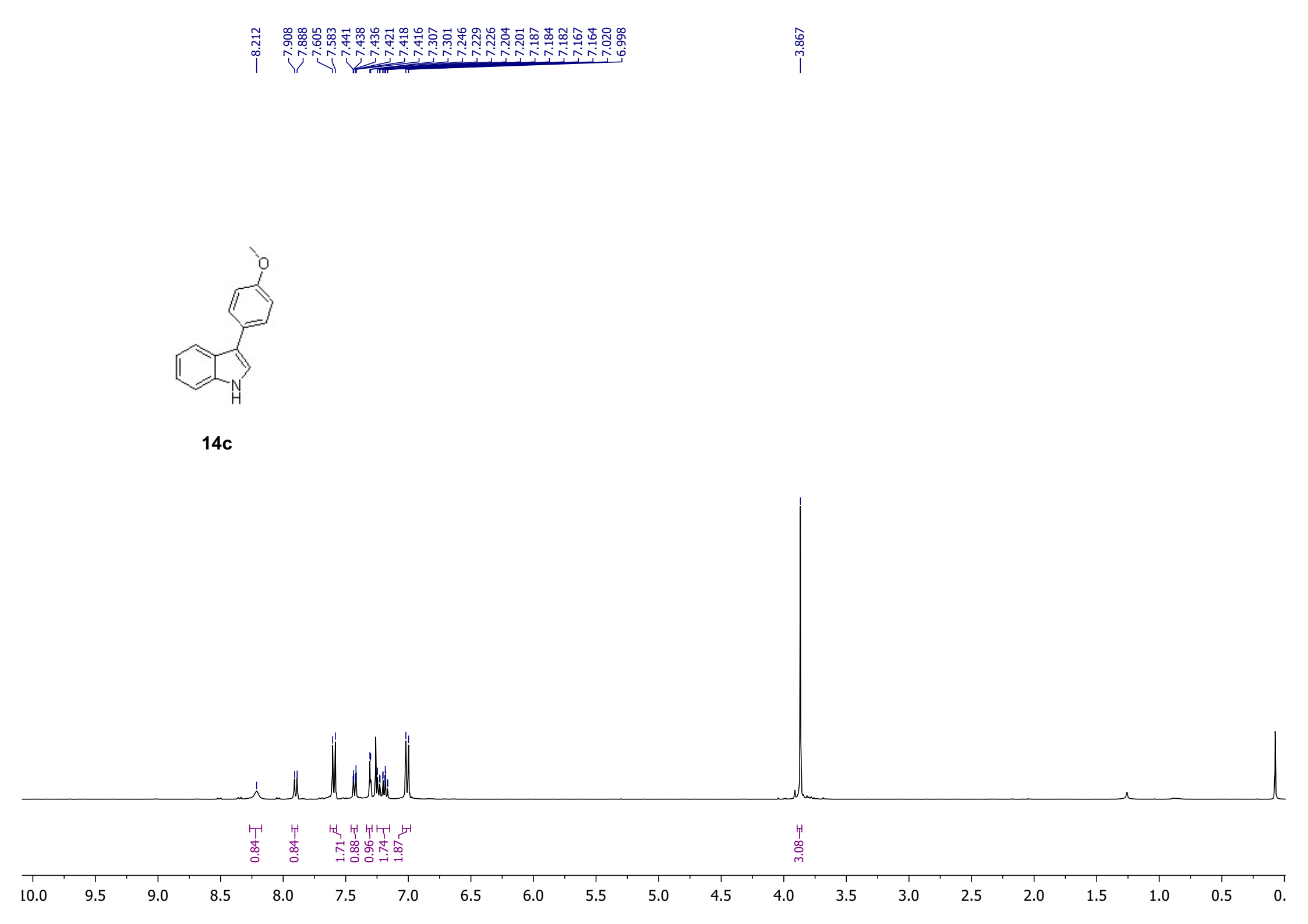

8.171
7.751
7.688
7.668
7.479
7.460
7.440
7.370
7.348
7.342
7.314
7.295
7.274
7.134
7.110
2.809
2.790
2.771
2.752
1.320
1.301
1.282
0.88
1.00
2.25
2.30
2.47
1.43
1.42
2.13
3.18
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

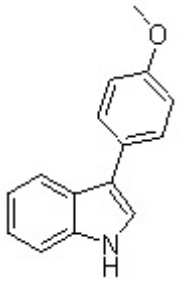
14b



14b

136.62
135.96
135.35
128.93
127.73
126.16
126.08
123.21
122.13
118.43
118.29
111.36
29.43
16.86
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

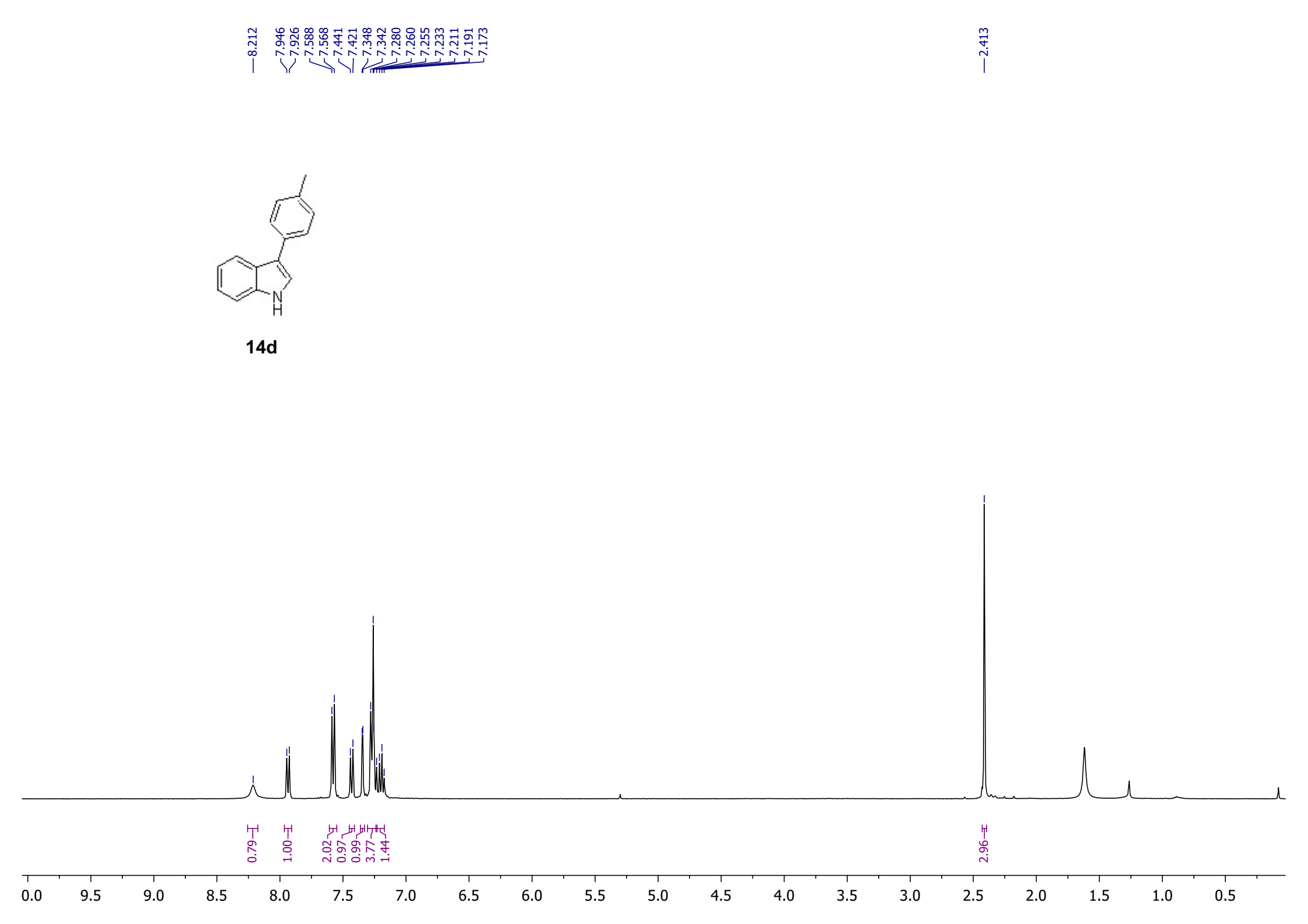

8.212
7.908
7.888
7.605
7.583
7.441
7.438
7.436
7.421
7.418
7.416
7.307
7.301
7.246
7.229
7.226
7.204
7.201
7.187
7.184
7.182
7.167
7.164
7.020
6.998
3.867
O
NH
14c
0.84
0.84
1.71
0.88
0.96
1.74
1.87
3.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.



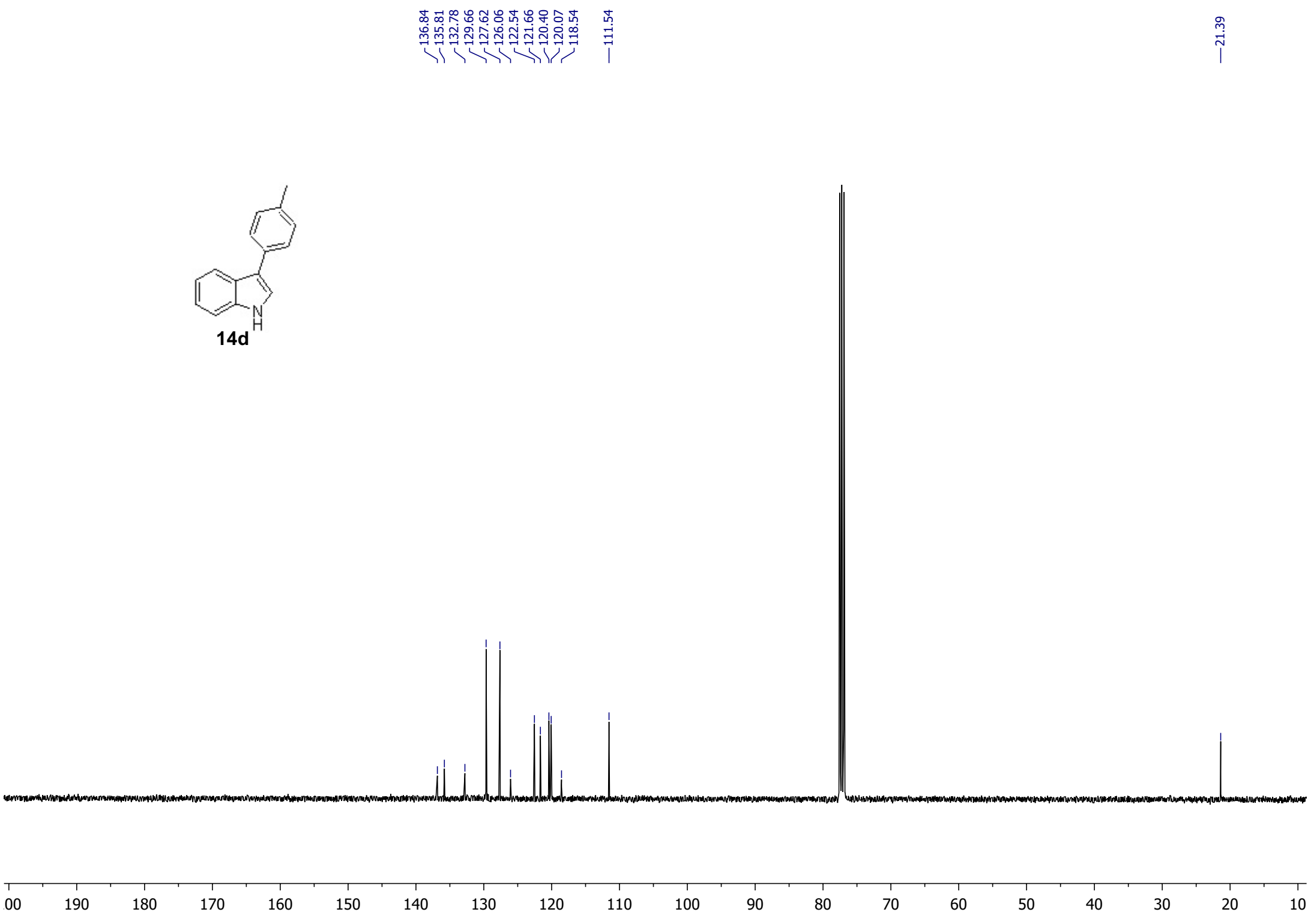
14c

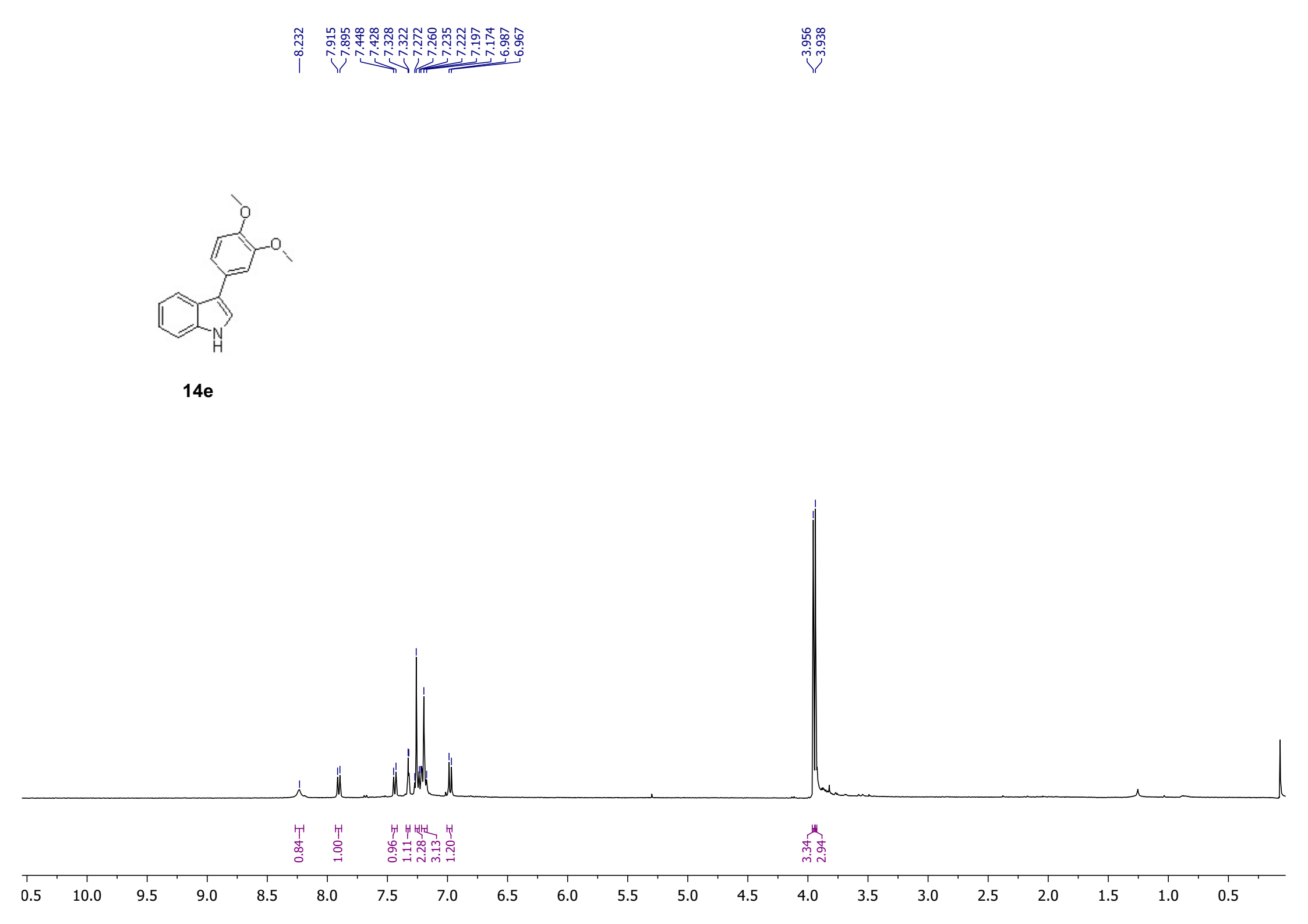
158.29
136.78
128.83
128.30
126.11
122.52
121.32
120.34
119.95
118.26
114.44
111.53
55.58

00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

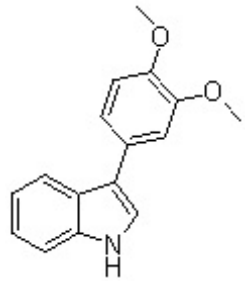

8.212
7.946
7.926
7.588
7.568
7.441
7.421
7.348
7.342
7.280
7.260
7.255
7.233
7.211
7.191
7.173
2.413
0.79
1.00
2.02
0.97
0.99
3.77
1.44
2.96
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

14d


136.84
135.81
132.78
129.66
127.62
126.06
122.54
121.66
120.40
120.07
118.54
111.54
21.39
14d
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

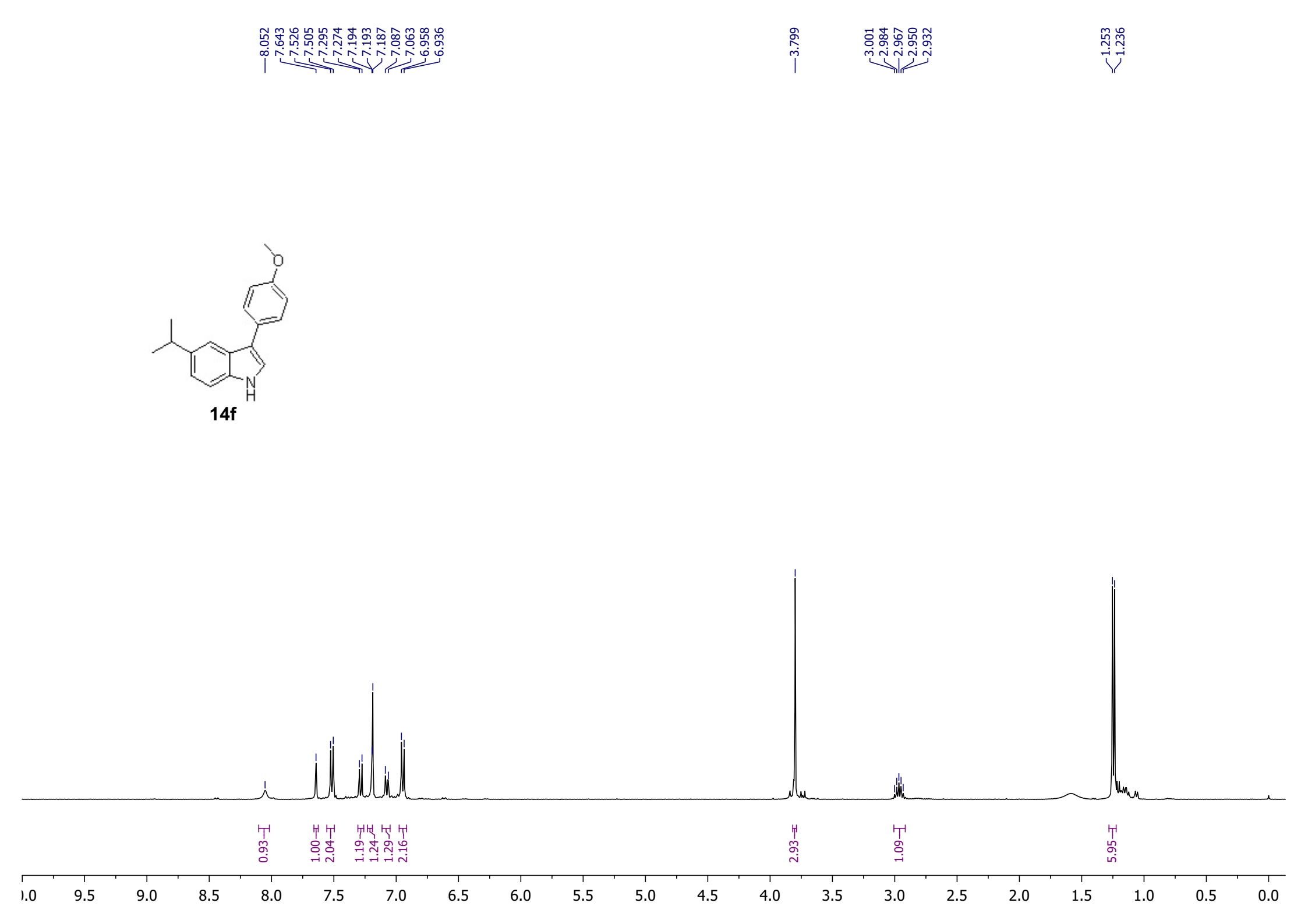

8.232
7.915
7.895
7.448
7.428
7.328
7.322
7.272
7.260
7.235
7.222
7.197
7.174
6.987
6.967
3.956
3.938
O
O
N
H
0.84
1.00
0.96
1.11
2.28
3.13
1.20
3.34
2.94
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

14e

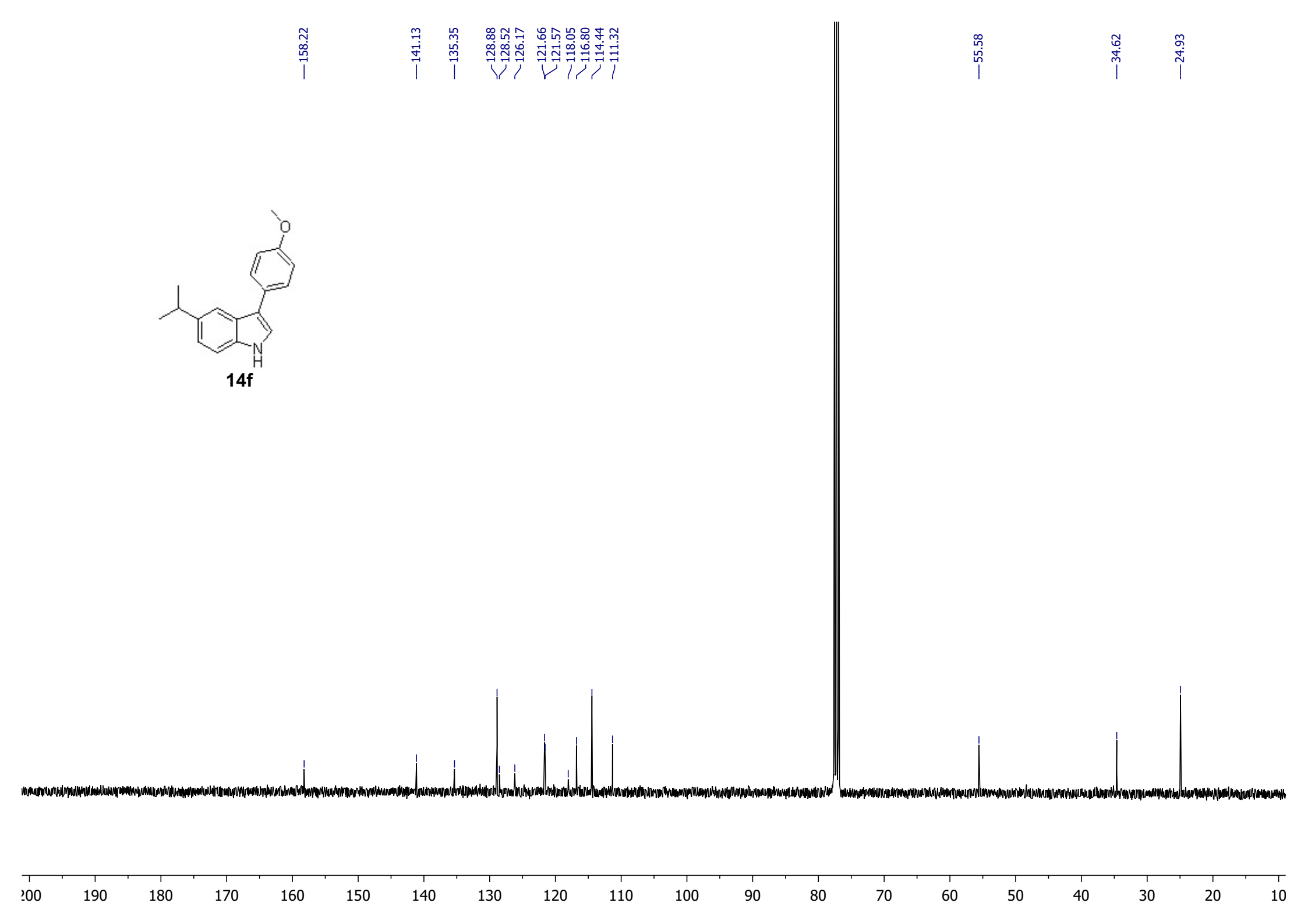


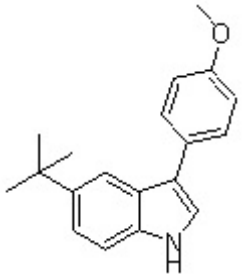
14e

149.18
147.62
136.60
128.48
125.91
122.40
121.24
120.22
119.79
119.69
118.31
111.76
111.38
111.21
56.04
55.97
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


8.052
7.643
7.526
7.505
7.295
7.274
7.194
7.193
7.187
7.087
7.063
6.958
6.936
3.799
3.001
2.984
2.967
2.950
2.932
1.253
1.236
0.93
1.00
2.04
1.19
1.24
1.29
2.16
2.93
1.09
5.95
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
0.0

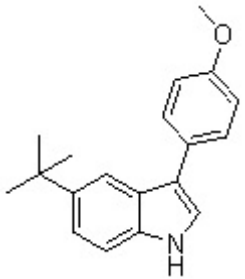
14f


158.22
141.13
135.35
128.88
128.52
126.17
121.66
121.57
118.05
116.80
114.44
111.32
55.58
34.62
24.93
O
N
H
14f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10



14g

8.101
7.866
7.593
7.571
7.371
7.350
7.316
7.256
7.254
7.251
7.031
7.009
3.869
1.398
0.87
1.00
2.00
2.03
1.39
2.10
2.85
9.00
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
0.0
f1 (ppm)

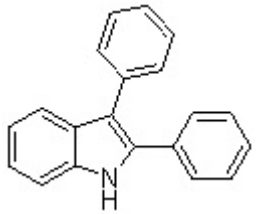


14g

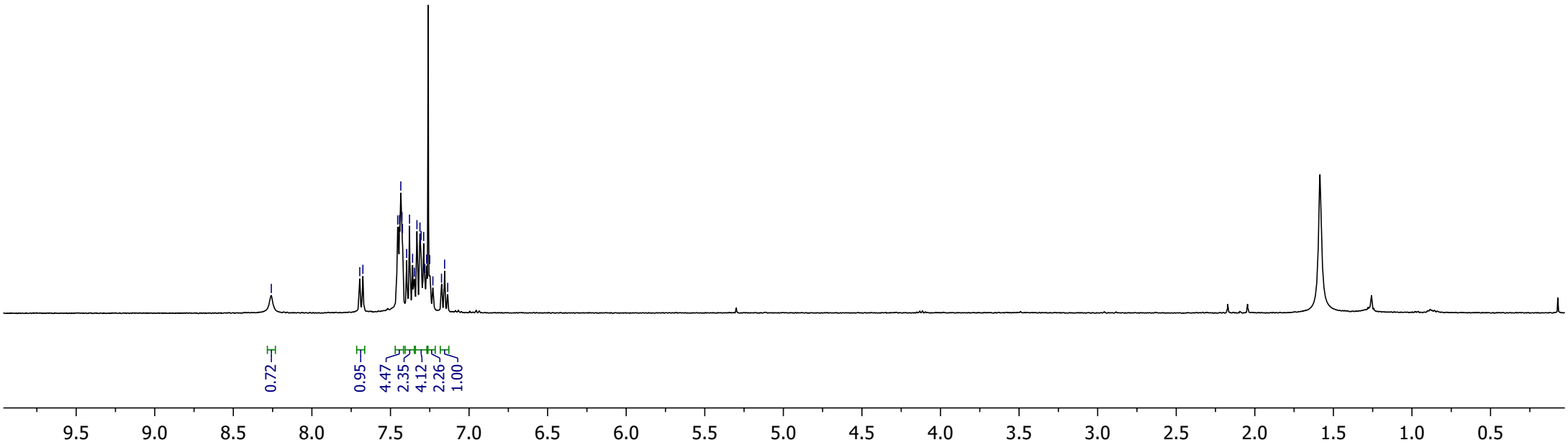
158.20
143.29
134.89
128.89
128.53
125.84
121.60
120.85
118.29
115.50
114.47
111.01
55.57
34.92
32.18

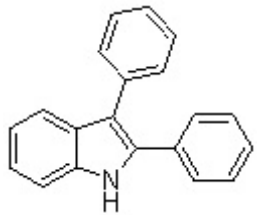
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10


8.258
7.695
7.676
7.454
7.443
7.434
7.427
7.424
7.397
7.379
7.359
7.348
7.332
7.312
7.309
7.305
7.289
7.281
7.270
7.250
7.230
7.175
7.155
7.136


N
H

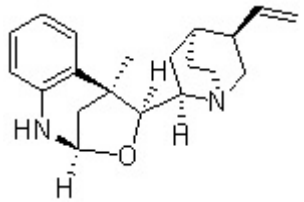
14h


0.72
0.95
4.47
2.35
4.12
2.26
1.00
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

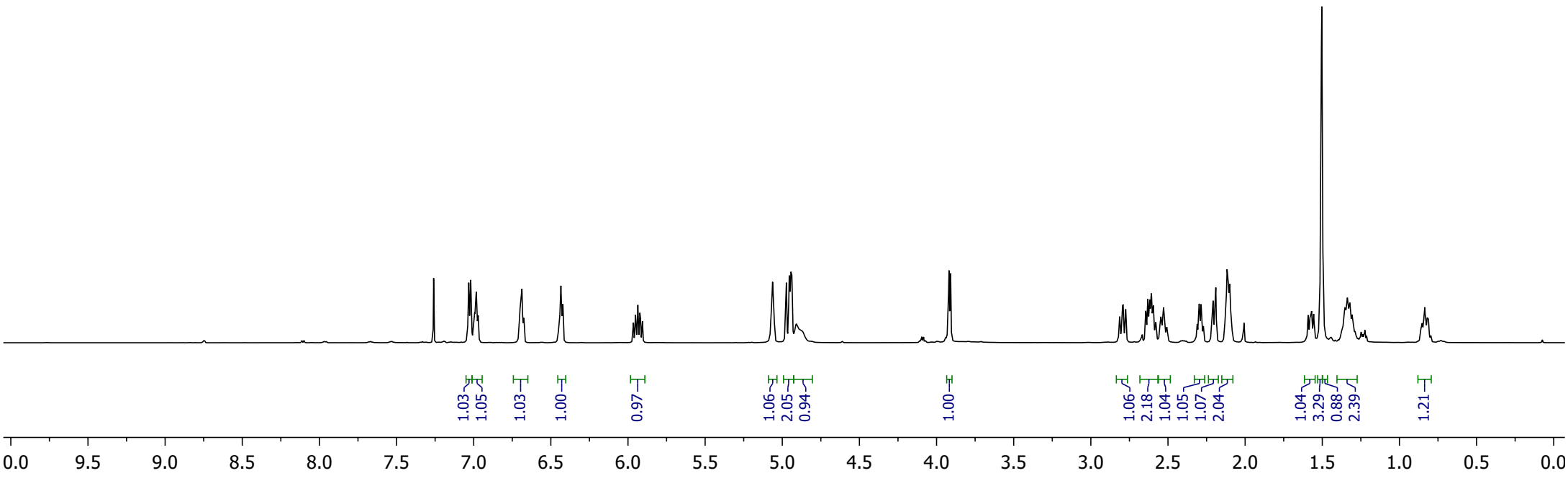


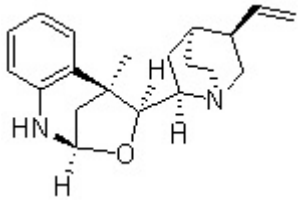
14h

136.12
135.27
134.29
132.94
130.38
129.00
128.91
128.73
128.38
127.91
126.45
122.93
120.65
111.08
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


HN
O
H
H
N
H

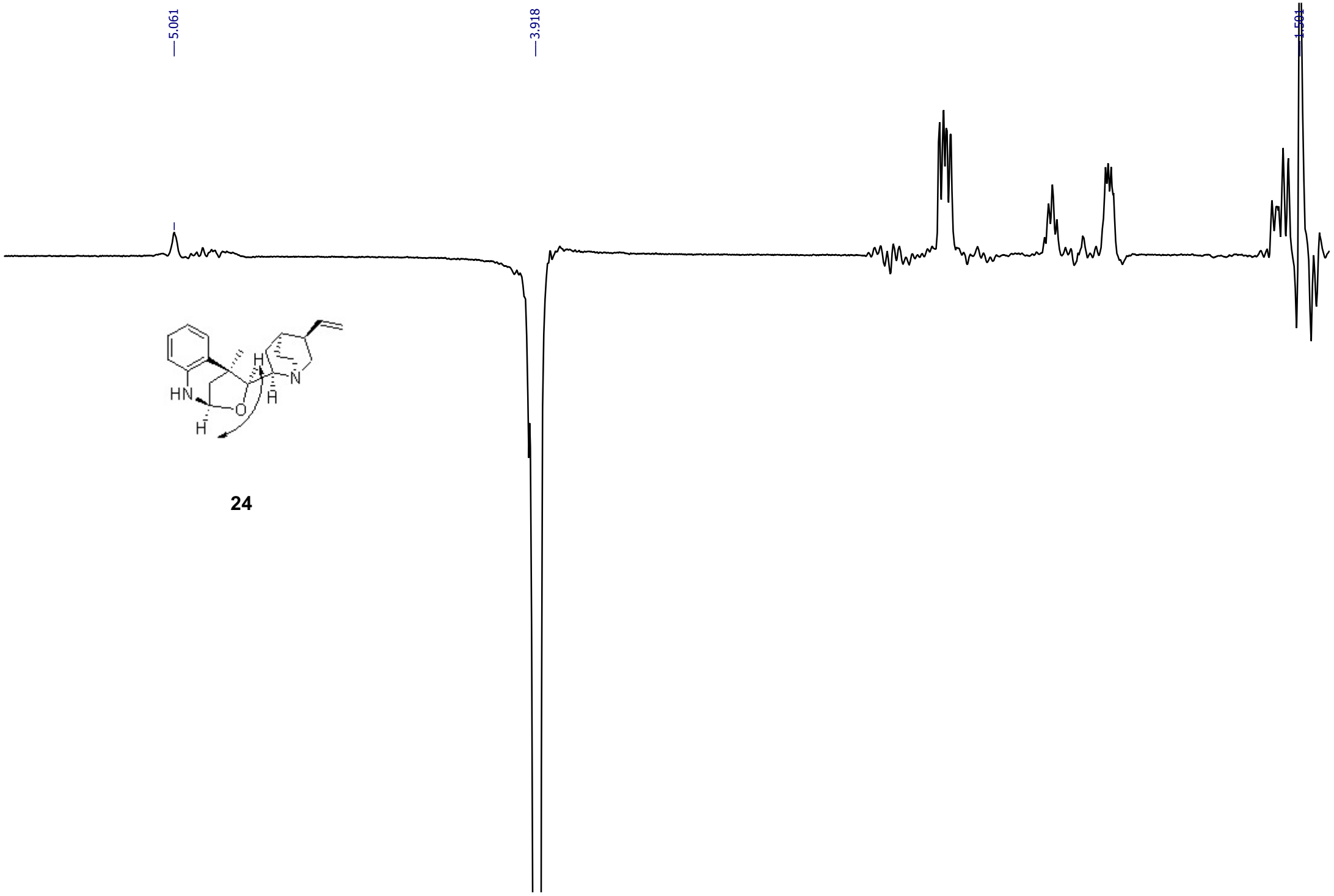
24


7.032
7.019
6.996
6.983
6.971
6.700
6.687
6.675
6.442
6.435
6.422
5.965
5.951
5.936
5.919
5.906
5.073
5.063
5.056
4.973
4.955
4.944
4.938
4.909
4.870
3.919
3.909
2.813
2.794
2.774
2.644
2.618
2.608
2.595
2.579
2.546
2.529
2.508
2.311
2.297
2.285
2.272
2.208
2.190
2.117
2.100
2.091
1.592
1.578
1.556
1.503
1.353
1.337
1.321
1.307
0.858
0.836
0.812
1.03
1.05
1.03
1.00
0.97
1.06
2.05
0.94
1.00
1.06
2.18
1.04
1.05
1.07
2.04
1.04
3.29
0.88
2.39
1.21
0.0
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
0.0


HN
O
H
H
N
H

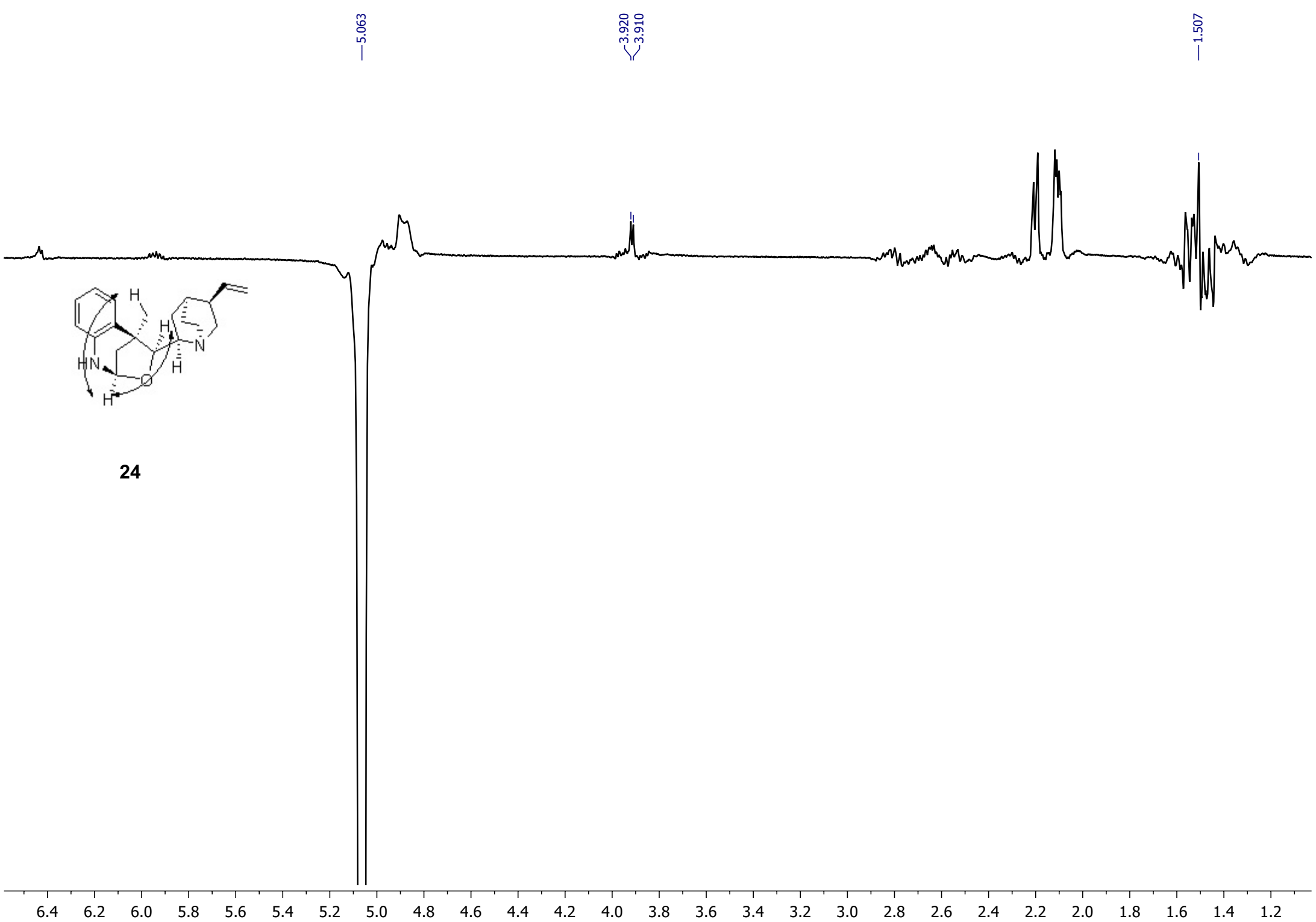
24

141.93
141.11
129.27
127.45
125.71
118.36
114.47
113.99
95.31
82.99
56.61
48.77
48.71
43.55
40.69
40.42
27.52
26.74
23.96
19.16
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

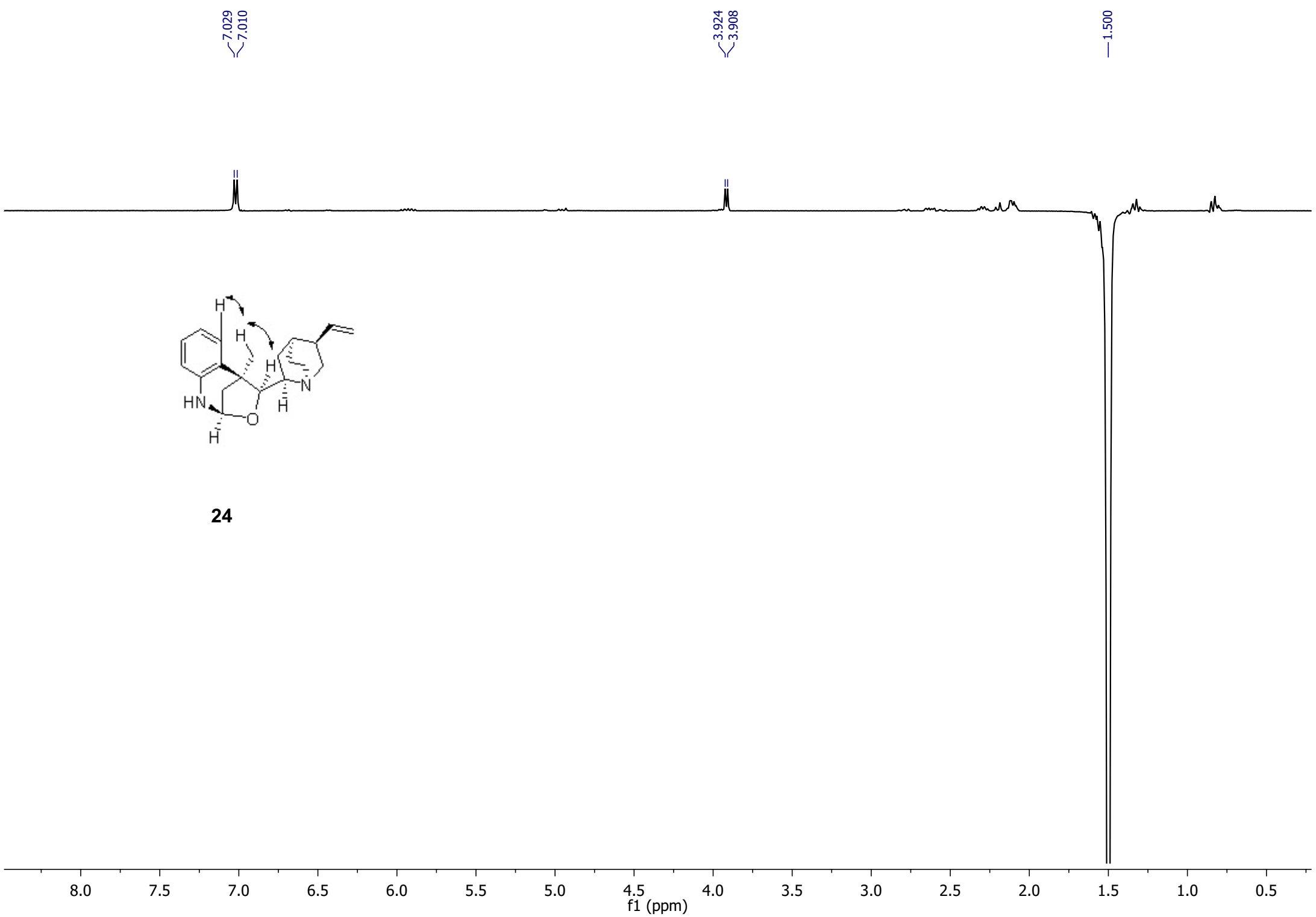


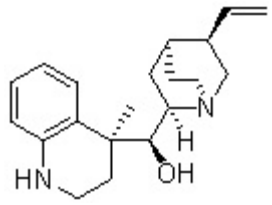
24

5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5

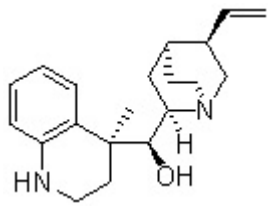

5.063
3.920
3.910
1.507
H
H
HN
O
H
H
N
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2

24


7.029
7.010
3.924
3.908
1.500
H
H
H
HN
O
H
N
H
24
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
f1 (ppm)

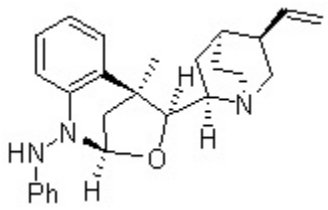


25

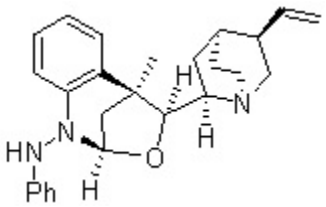

HN
OH
H
N

25

144.21
141.23
127.81
127.46
126.36
116.64
114.39
114.25
77.07
56.53
49.21
49.16
40.39
40.20
38.47
31.44
28.27
27.04
23.72
23.26
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10



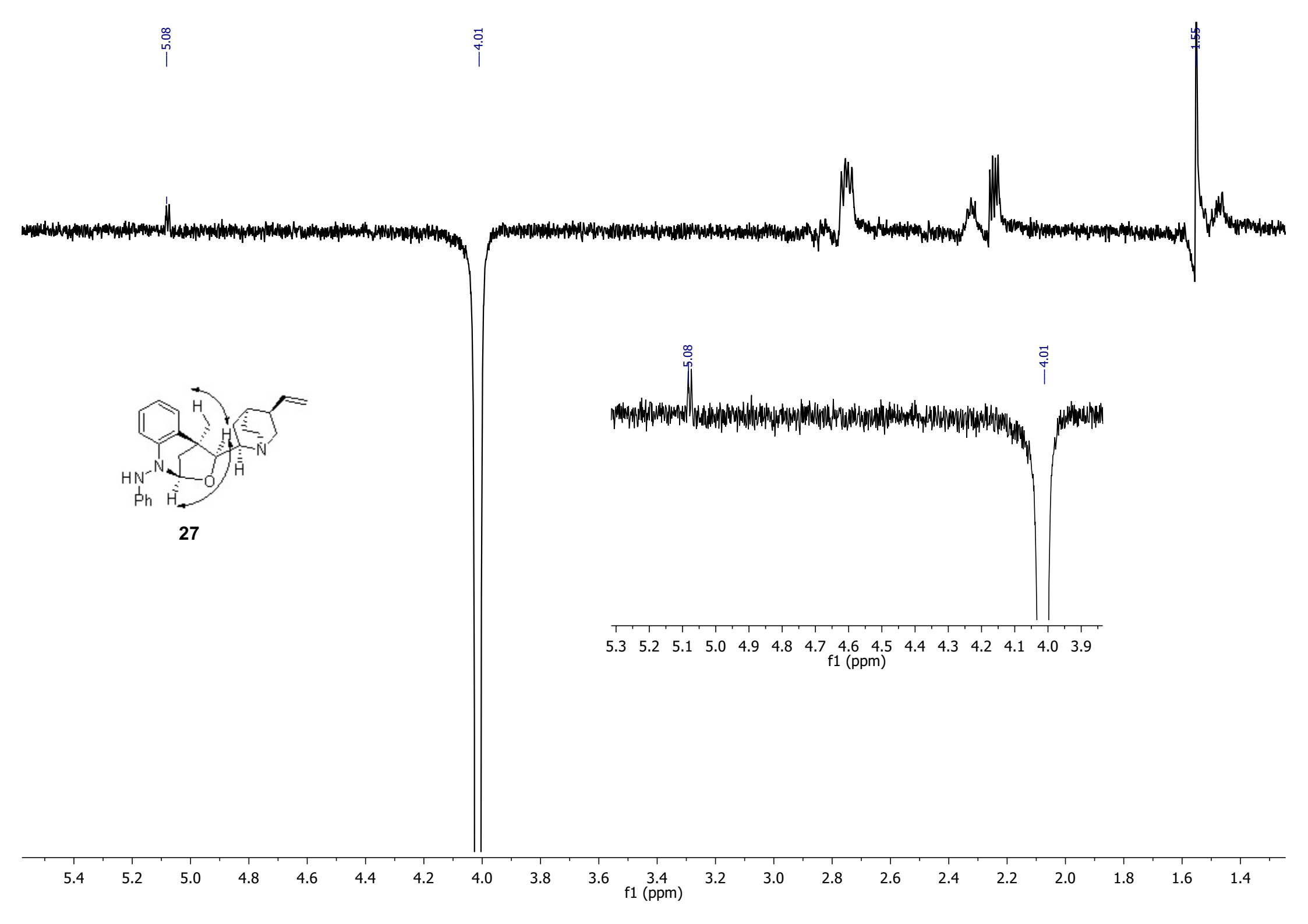
27



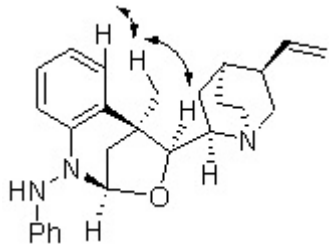
27

148.40
146.08
141.36
130.40
129.54
128.08
125.32
120.85
120.02
116.03
114.26
112.89
94.60
89.50
56.59
49.08
48.78
44.05
42.80
40.02
27.57
26.89
24.13
19.49

f1 (ppm)

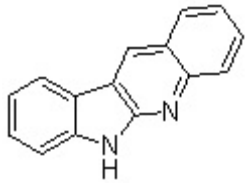

5.08
4.01
1.55
5.08
4.01
5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9
f1 (ppm)
5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4
f1 (ppm)

27


H
H
H
N
HN
Ph
H
O
H
N

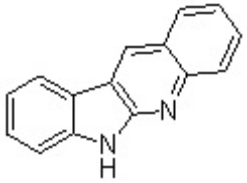
27

7.08
7.06
4.04
4.02
1.57
.0.0
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
f1 (ppm)



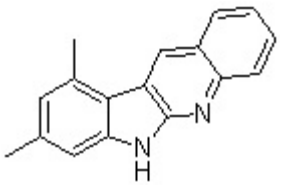
28a

11.698
9.043
8.266
8.247
8.115
8.095
7.983
7.962
7.737
7.716
7.696
7.550
7.531
7.512
7.501
7.475
7.457
7.281
7.262
7.245
1.02
1.00
1.05
1.08
1.04
1.15
3.34
1.18
12.5
12.0
11.5
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
0.

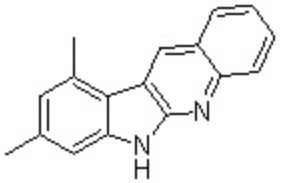

N
H
N

28a

152.97
146.39
141.54
128.82
128.77
128.33
127.68
127.06
123.78
122.87
121.94
120.38
119.81
118.01
111.05
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

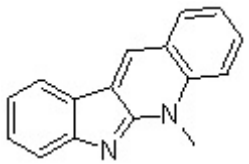


28b


N
N
H

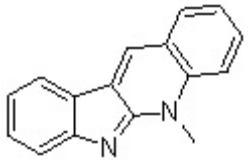
28b

153.40
145.88
142.35
138.36
134.44
129.22
128.82
128.79
127.17
124.28
122.95
118.86
116.87
109.13
22.16
20.56
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10



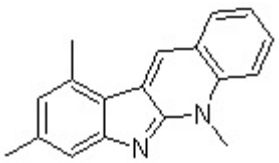
29a

8.554
8.067
8.048
8.013
7.993
7.784
7.776
7.753
7.577
7.558
7.539
7.482
7.474
7.462
7.453
7.442
7.260
7.246
7.228
4.390
0.93
1.00
1.01
2.85
1.06
1.04
1.22
2.78
0.0
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



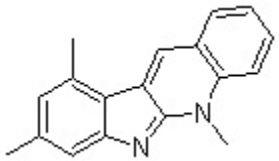
29a

156.22
155.17
137.14
130.69
130.21
129.57
128.50
128.24
124.05
122.25
121.22
121.09
120.18
117.79
114.41
33.42
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20



29b

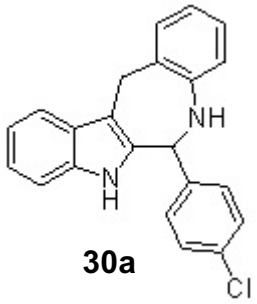
8.430
7.986
7.966
7.746
7.736
7.456
7.448
7.435
7.428
7.416
6.870
4.357
2.792
2.518
1.00
1.07
1.97
1.89
0.94
2.89
2.95
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.



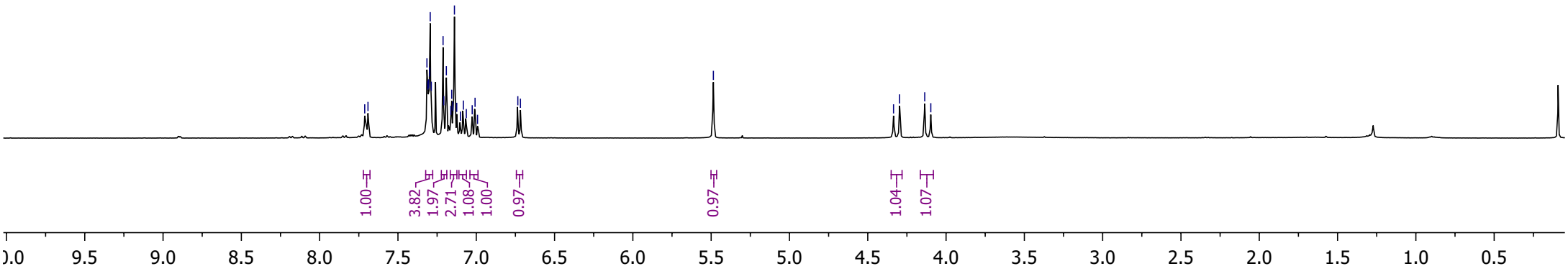
29b

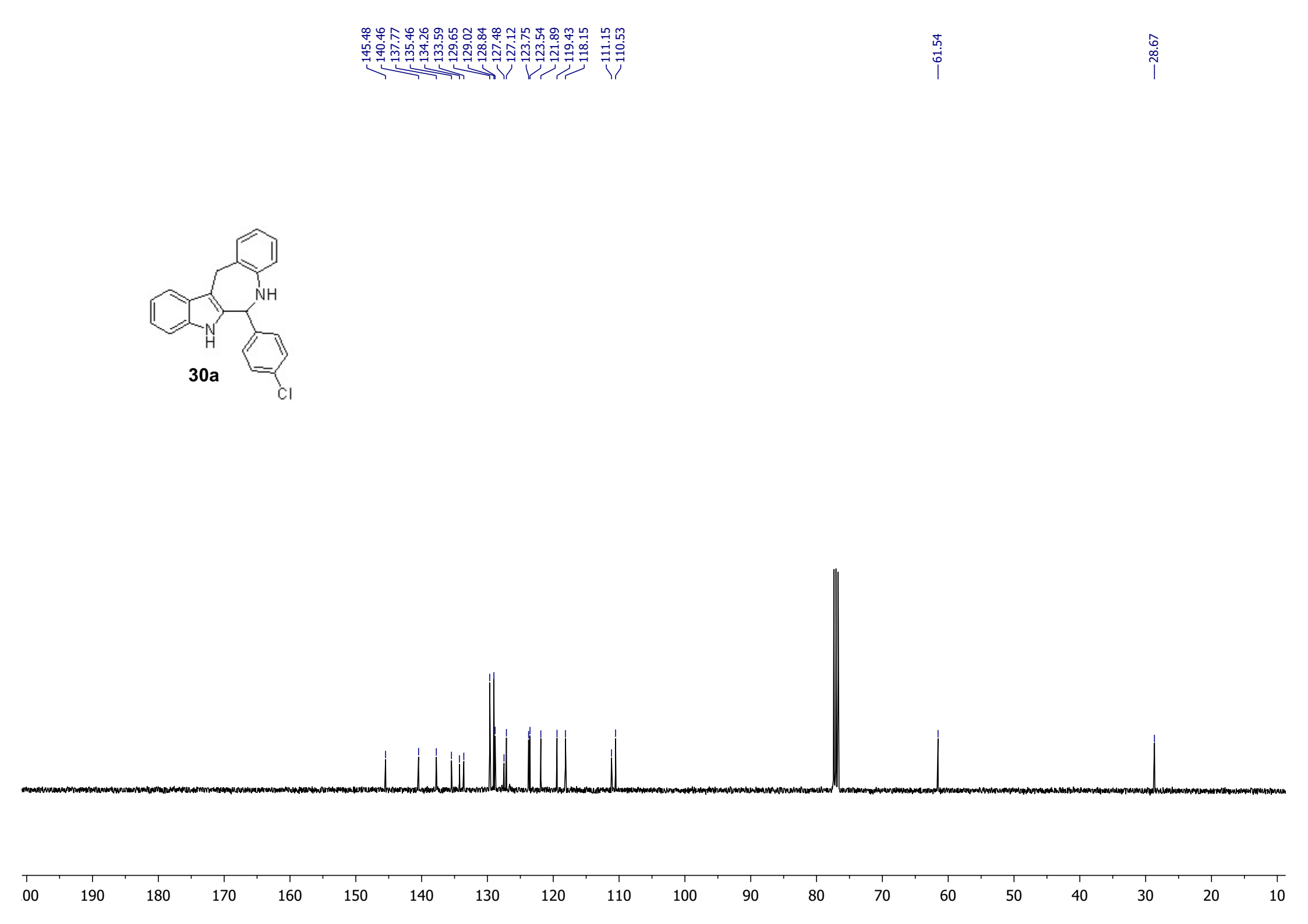
156.41
155.52
136.48
133.87
130.16
130.09
129.14
128.76
123.33
122.02
121.39
120.09
115.99
114.22
33.33
22.48
20.36
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

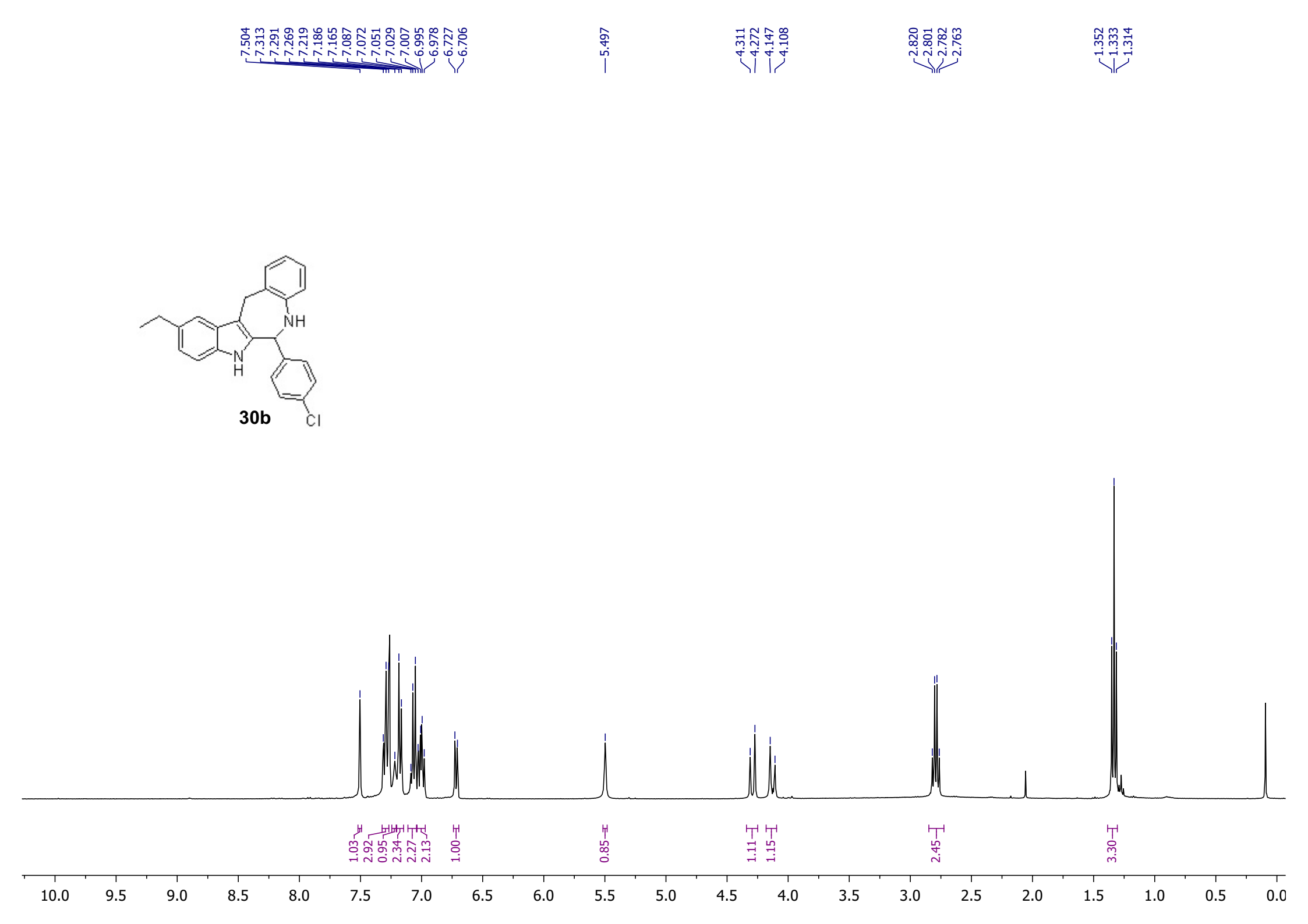

7.712
7.691
7.315
7.309
7.304
7.298
7.294
7.287
7.212
7.207
7.191
7.162
7.157
7.150
7.139
7.125
7.101
7.082
7.064
7.026
7.008
6.992
6.735
6.718
5.486
4.335
4.297
4.136
4.097

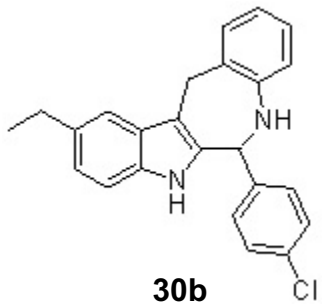

NH
N
H
Cl

30a


1.00
3.82
1.97
2.71
1.08
1.00
0.97
0.97
1.04
1.07
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

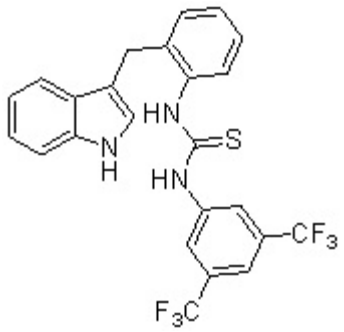

145.48
140.46
137.77
135.46
134.26
133.59
129.65
129.02
128.84
127.48
127.12
123.75
123.54
121.89
119.43
118.15
111.15
110.53
61.54
28.67
NH
N
H
Cl
30a
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


7.504
7.313
7.291
7.269
7.219
7.186
7.165
7.087
7.072
7.051
7.029
7.007
6.995
6.978
6.727
6.706
5.497
4.311
4.272
4.147
4.108
2.820
2.801
2.782
2.763
1.352
1.333
1.314
NH
N
H
Cl
30b
1.03
2.92
0.95
2.34
2.27
2.13
1.00
0.85
1.11
1.15
2.45
3.30
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
0.0


NH
N
H
Cl

30b

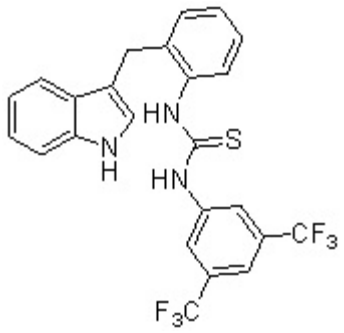
145.62
140.70
137.98
135.63
134.33
134.12
133.89
129.81
129.11
129.02
127.79
127.23
123.87
123.70
122.57
116.83
111.00
110.51
61.68
29.33
28.86
16.81
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


HN
S
HN
N
H
CF3
F3C

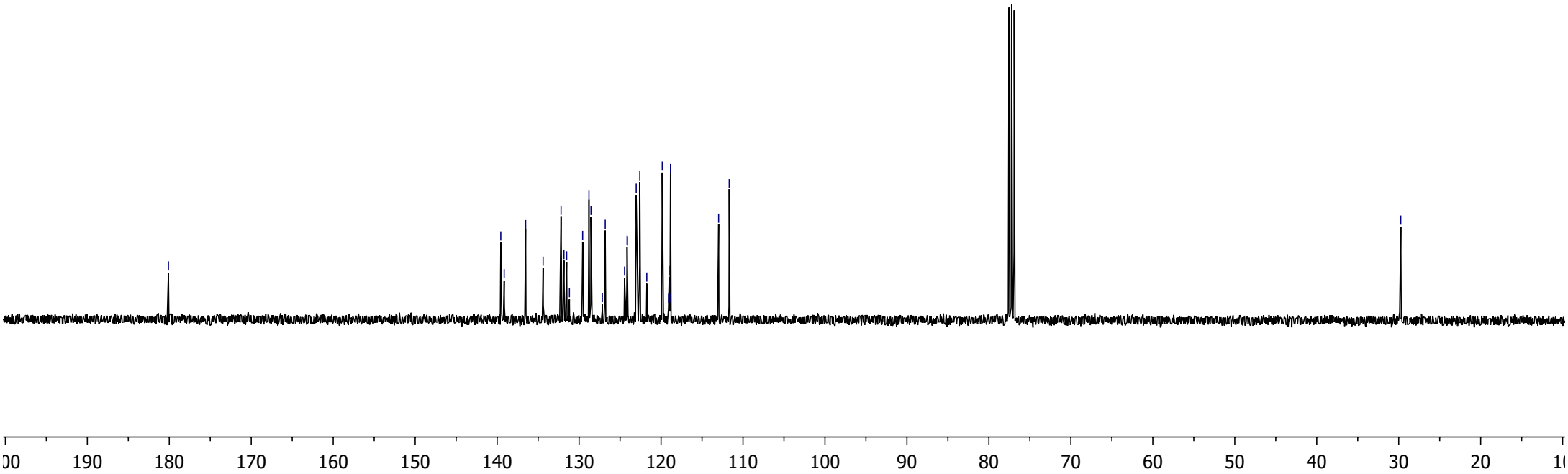
31

8.352
7.894
7.590
7.571
7.451
7.363
7.339
7.329
7.307
7.286
7.266
7.244
7.193
7.174
7.160
7.143
7.123
7.048
7.031
6.929
6.910
6.891
6.860
4.093
1.00
1.09
1.18
1.18
3.40
2.38
1.30
1.21
2.00
1.38
0.54
2.17
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

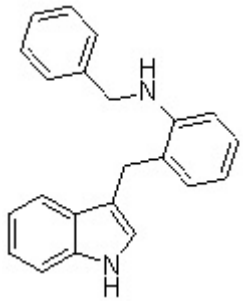

180.10
139.56
139.14
136.52
134.39
132.20
131.85
131.51
131.18
129.57
128.80
128.55
127.16
126.81
124.45
124.14
124.11
123.03
122.59
121.74
119.85
119.08
119.01
118.97
118.93
118.85
112.98
111.68
29.75


HN
S
N
H
HN
CF3
F3C

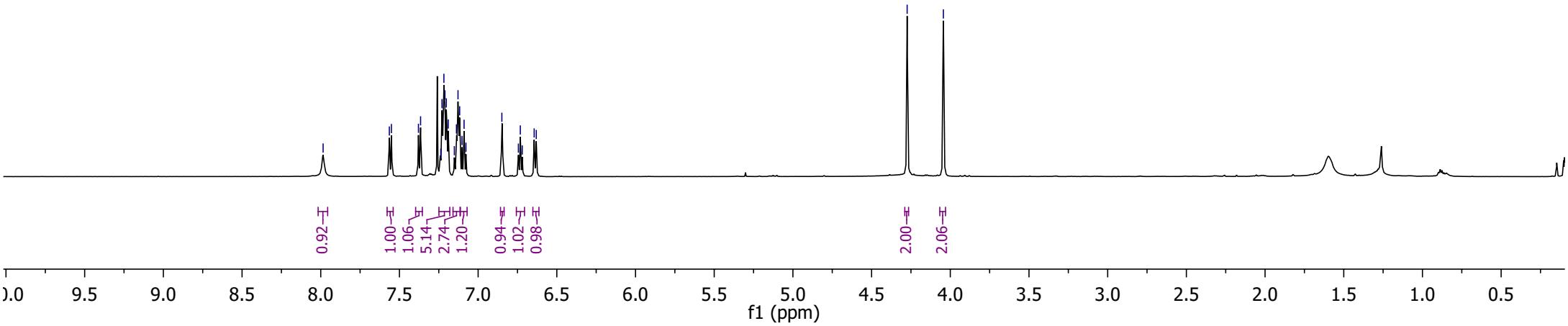
31

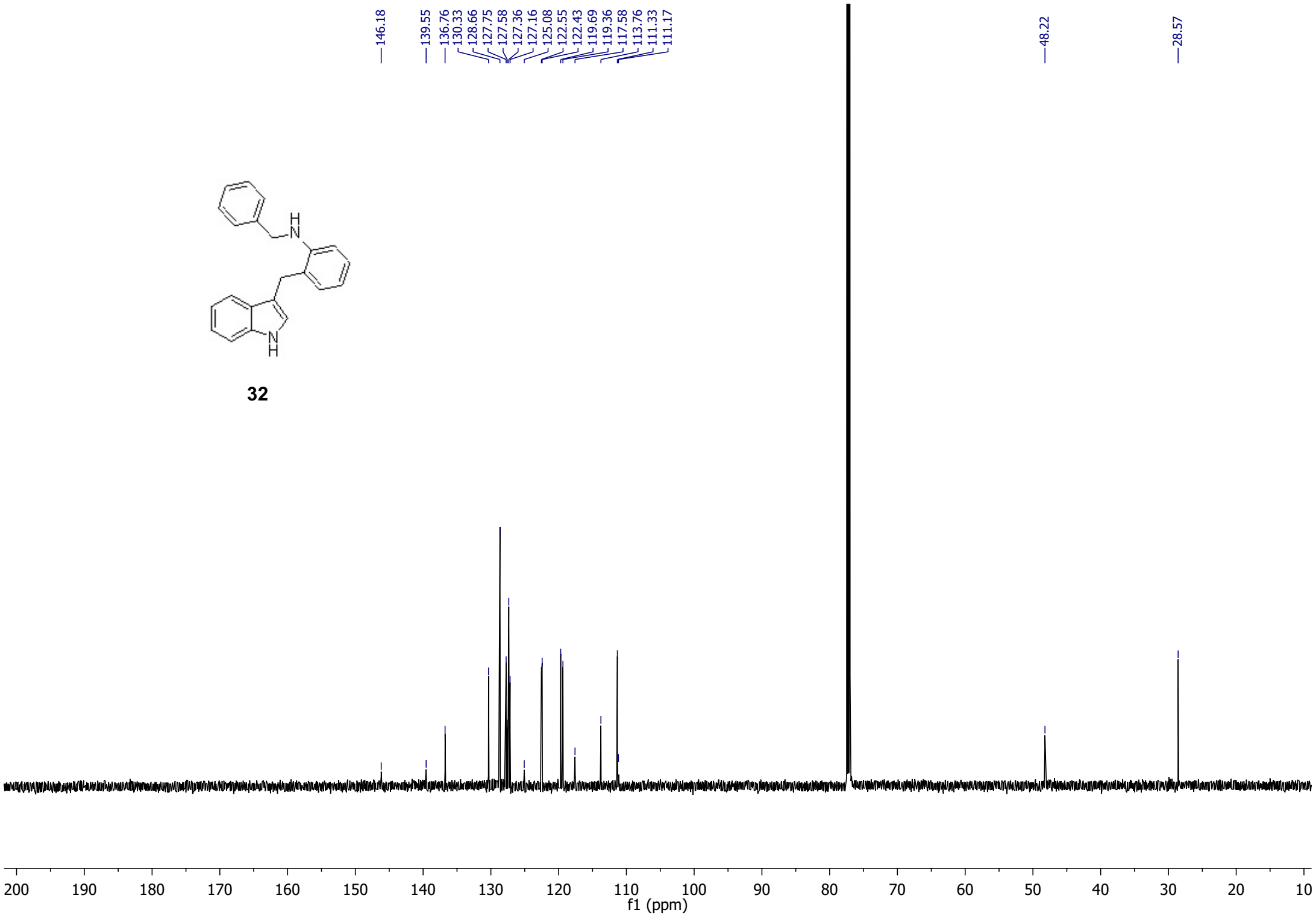

00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


7.985
7.564
7.551
7.379
7.366
7.237
7.230
7.218
7.211
7.202
7.190
7.151
7.138
7.128
7.117
7.102
7.089
7.077
6.849
6.744
6.732
6.720
6.644
6.631
4.274
4.044



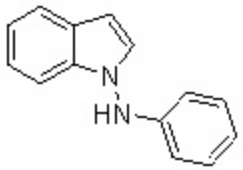
32


0.92
1.00
1.06
5.14
2.74
1.20
0.94
1.02
0.98
2.00
2.06
f1 (ppm)

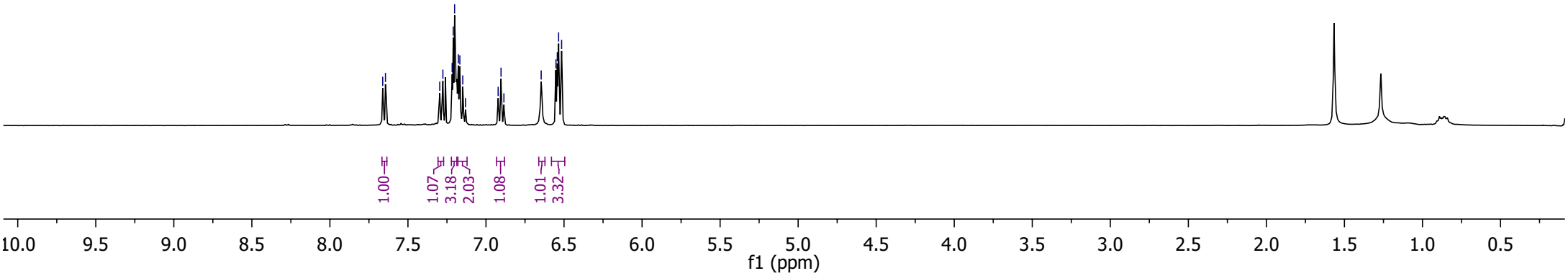

146.18
139.55
136.76
130.33
128.66
127.75
127.58
127.36
127.16
125.08
122.55
122.43
119.69
119.36
117.58
113.76
111.33
111.17
48.22
28.57
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

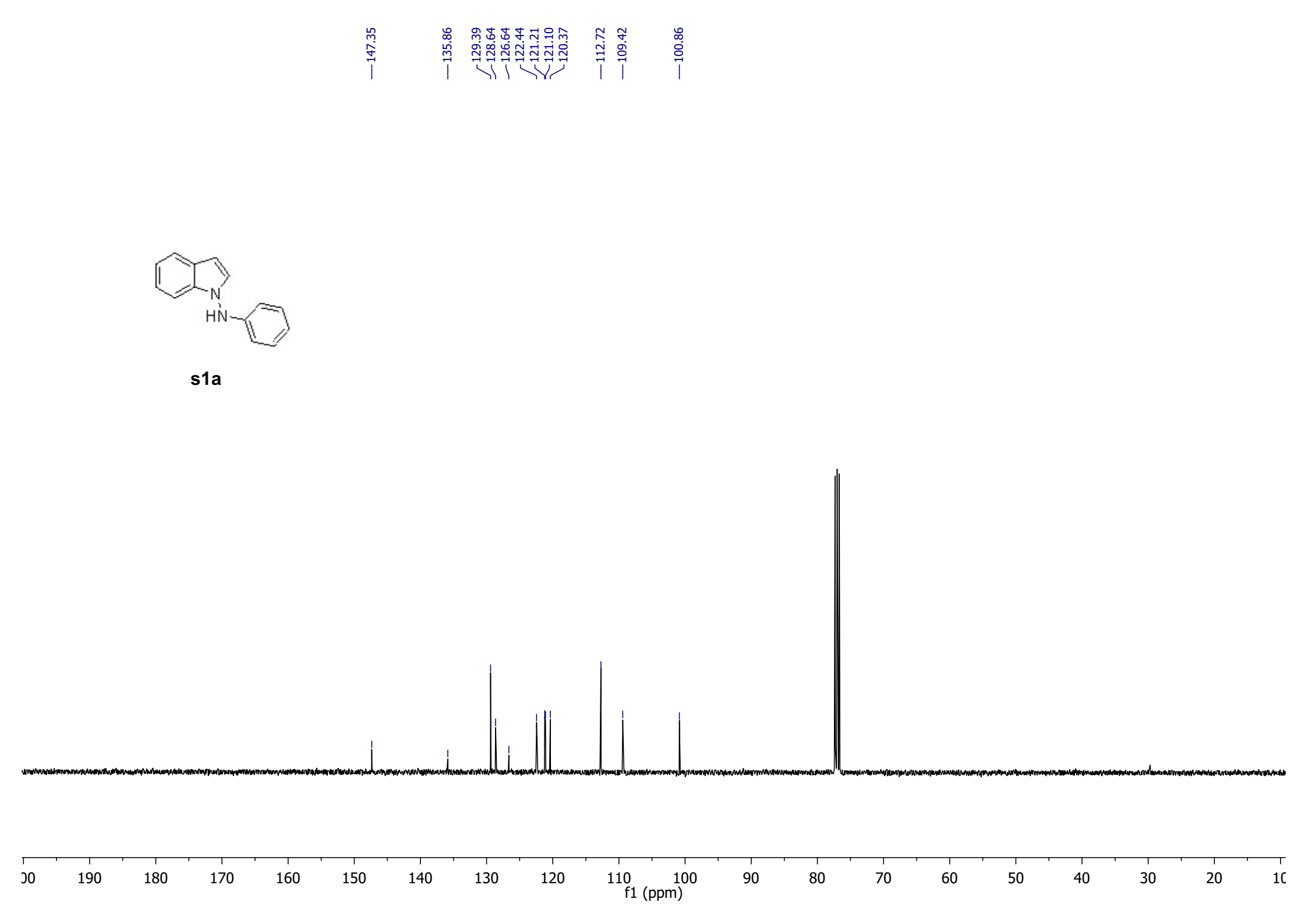
32


7.662
7.644
7.296
7.276
7.217
7.210
7.201
7.177
7.167
7.149
7.131
6.922
6.904
6.885
6.646
6.552
6.543
6.535
6.515


N
HN

s1a


1.00
1.07
3.18
2.03
1.08
1.01
3.32
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
f1 (ppm)


147.35
135.86
129.39
128.64
126.64
122.44
121.21
121.10
120.37
112.72
109.42
100.86
N
HN
s1a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)