SUPPLEMENTARY MATERIAL

SYNTHESIS OF BENZO[*d*]PYRROLO[1,2-*a*]IMIDAZOLES BY IMINOCYCLOPROPANE REARRANGEMENT OF C-CYCLOPROPYL BENZIMIDAZOLES

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Dedicated with respect and friendship to Professor Somsak Ruchirawat on the occasion of his 80th birthday.

Table of Contents

EXPERIMENTAL

All reactions were performed under N_2 that had been passed through a column of drierite®. All glassware was either flame-dried under high vacuum or dried in an oven overnight prior to use and allowed to cool under a stream of N_2. Reactions were stirred magnetically using teflon-coated magnetic stirring bars, and syringe needles were dried in an oven and cooled in a desiccator cabinet over drierite®. CH_2Cl_2 was freshly distilled over CaH_2, THF was freshly distilled over benzophenone ketyl radical anion, DMF was freshly distilled over BaO, and DMSO was dried over 4 Å molecular sieves. All other materials were obtained from commercial sources and used as received. Reactions were monitored by thin-layer chromatography (TLC) analysis on pre-coated silica gel 60 F254 plates (250 μm layer thickness); visualization was accomplished by UV light (254 nm). Flash chromatography was carried out on silica gel 60 (230–400 mesh). Melting points were determined in open capillary tubes, recorded on a Mel-Temp II apparatus fitted with a Fluke 51 II digital thermometer, and are uncorrected. Microwave reactions were carried out using a Biotage Initiator. Nuclear Magnetic Resonance (NMR) spectra were acquired at ambient temperatures on Bruker instruments operating at 400, 500 and 600 MHz for ^{1}H, and at 100, 125 and 151 MHz for ^{13}C. Chemical shifts (δ) were reported in parts per million (ppm) with the residual solvent peak used as an internal standard ($CDCl_3$: 7.26 ppm for ^{1}H NMR and 77.16 ppm for ^{13}C NMR; DMSO-d_6: 2.50 ppm for ^{1}H NMR and 39.5 ppm for ^{13}C NMR). High resolution mass spectra (HRMS) were obtained on a Thermo Scientific Exactive Orbitrap LC-MS (ESI positive ion mode) coupled to a Thermo Scientific Accela HPLC system.

2-(1*H*-Benzo[*d*]imidazol-2-yl)-3-(quinoxalin-2-yl)acrylonitrile (**4**, **5**). To a solution of diisopropylamine (3.99 mL, 28.3 mmol) in anhydrous THF (70 mL) at -78 °C was added a 2.5 M solution of *n*-BuLi in hexanes (10.4 mL, 25.9 mmol). After 1 min, a solution of **3** (6.06 g, 23.6 mmol) in THF (47 mL) was added dropwise via addition funnel. After 15 min, a solution of **2** (4.47 g, 28.3 mmol) in THF (47 mL) was added dropwise by addition funnel. After another 15 min, the reaction temperature was raised to 0 °C for 1 h, then gradually to rt. The resulting suspension was quenched with saturated aqueous ammonium chloride solution (165 mL), and diluted with EtOAc (165 mL) and water to dissolve the salts in the aqueous layer. The solids in the organic layer were isolated by filtration and dried under vacuum to give **5** (2.94 g, 9.89 mmol, 42%,) as a yellow solid. The aqueous layer was further extracted with EtOAc (2 x 165 mL), and the combined organic

layers were washed with brine (1 x 165 mL), dried (Na_2SO_4) and concentrated under reduced pressure. The resulting residue was triturated with hot absolute EtOH to give **4** (1.06 g, 3.57 mmol, 15%,) as a bright orange solid.

4: Mp 246 °C (dec.); IR (neat) 3276, 3055, 2232, 1732, 1612, 1536, 1488, 1441, 1423, 1377, 1317, 1225, 1183, 1126, 1088, 885, 913, 756 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 7.28-7.37 (m, 2H), 7.63 (d, J = 7.9 Hz, 1H), 7.77 (d, J = 7.9 Hz, 1H), 7.97-8.01 (m, 2H), 8.15-8.20 (m, 2H), 8.66 (s, 1H), 9.30 (s, 1H), 13.35 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 108.3, 115.7, 123.1, 129.5, 129.8, 131.9, 132.4, 140.3, 141.7, 142.3, 147.2, 147.4, 147.5; HRMS *m/z* calcd for $C_{18}H_{12}N_5$ $[M+H]^+$ 298.1087, found 298.1098.

5: Mp 236 °C (dec.); IR (neat) 3271, 3053, 2234, 1777, 1615, 1489, 1432, 1369, 1318, 1277, 1195, 1118, 1015, 939, 755, 766 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 7.30-7.32 (m, 2H), 7.68-7.70 (m, 2H), 7.97-7.99 (m, 2H), 8.15-8.19 (m, 2H), 8.78 (s, 1H), 9.28 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 108.3, 115.7, 124.0, 129.5, 129.8, 131.9, 132.4, 140.3, 141.7, 142.3, 147.2, 147.4, 147.5; HRMS *m/z* calcd for $C_{18}H_{12}N_5$ $[M+H]^+$ 298.1087, found 298.1099.

General Procedure A for the Preparation of Acrylonitriles 10, 12, and 14: (*E*)-2-(1-Allyl-1*H*-benzo[*d*]imidazol-2-yl)-3-phenylacrylonitrile (**10**). A solution of **9** (1.00 g, 5.07 mmol) and benzaldehyde (0.57 mL, 5.6 mmol) in DMF (8 mL) was stirred at rt and treated dropwise with TMSCl (1.3 mL, 10 mmol). After 16 h, the reaction mixture was slowly diluted with water (40 mL) and stirred until a fine suspension formed. The precipitate was collected by filtration, rinsed with water and dried under vacuum to give **10** (1.20 g, 4.21 mmol, 82%,) as a light yellow powder: Mp 98-100 °C; IR (neat) 3068, 3012, 2933, 2223, 1615, 1495, 1457, 1446, 1407, 1332, 1162, 1082, 975, 938, 760, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.09-5.10 (m, 2H), 5.14 (d, J = 17.1 Hz, 1H), 5.31 (d, J = 10.4 Hz, 1H), 6.02-6.11 (m, 1H), 7.33-7.42 (m, 3H), 7.50-7.52 (m, 3H), 7.82-7.84 (m, 1H), 7.98-8.00 (m, 2H), 8.16 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 47.1, 99.9, 110.4, 116.5, 118.3, 120.0, 123.4, 124.0, 129.2, 130.2, 131.6, 132.1, 132.7, 136.2, 147.2, 151.8; HRMS *m/z* calcd for $C_{19}H_{16}N_3$ $[M+H]^+$ 286.1339, found 286.1330.

(*E*)-2-(1-Allyl-1*H*-benzo[*d*]imidazol-2-yl)-3-(thiophen-2-yl)acrylonitrile (**12**). According to General Protocol A, **12** was obtained as a light yellow solid: Mp 110-112 °C; IR (neat) 3103, 3047, 2216, 1920, 1863, 1683, 1571, 1478, 1409, 1393, 1357, 1331, 1316, 1264, 1214, 1164, 1050, 992, 927, 858, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.15-5.21 (m, 3H), 5.36 (d, J = 10.5 Hz, 1H), 6.02-6.12 (m, 1H), 7.24-7.25 (m, 1H), 7.42-7.47 (m, 3H), 7.80 (d, J = 5.0 Hz, 1H), 7.92-7.95 (m,

2H), 8.93 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 47.4, 110.9, 115.9, 118.0, 119.3, 125.3, 128.7, 130.5, 135.3, 136.7; HRMS *m/z* calcd for $C_{17}H_{14}N_3S$ $[M+H]^+$ 292.0903, found 292.0898.

(*E*)-2-(1-Allyl-1*H*-benzo[*d*]imidazol-2-yl)-3-(furan-3-yl)acrylonitrile (**14**). According to General Protocol A, **14** was obtained as a light yellow powder: Mp 73 °C (dec.); IR (neat) 3096, 2218, 1587, 1479. 1460, 1397, 1332, 1096, 993, 931, 869, 816, 752 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.15-5.19 (m, 3H), 5.37 (d, *J* =10.5 Hz, 1H), 6.02-6.11 (m, 1H), 7.32 (d, *J* = 1.9 Hz, 1H), 7.43-7.47 (m, 3H), 7.59 (s, 1H), 7.93-7.95 (m, 1H), 8.21 (s, 1H), 8.69 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 47.4, 108.2, 111.0, 115.7, 118.0, 119.4, 121.6, 125.5, 130.3, 134.3, 145.4, 146.5, 150.9; HRMS *m/z* calcd for $C_{17}H_{14}ON_3$ $[M+H]^+$ 276.1131, found 276.1127.

General Procedure B for the Preparation of Cyclopropanes 6, 15, 16, 17, 18, 19, 20, 21, 22, 24, 25 and 27: *trans*-1-(1*H*-Benzo[*d*]imidazol-2-yl)-2-(quinoxalin-2-yl)cyclopropane-1-carbonitrile (**6**). A mixture of trimethylsulfoxonium iodide (296 mg, 1.35 mmol) and 60% sodium hydride in mineral oil (59.2 mg, 1.48 mmol) in dry DMSO (3.2 mL) was stirred at room temperature for 30 min until bubbling of H_2 subsided, treated with **5** (200 mg, 0.670 mmol) and after 2.5 h diluted with saturated ammonium chloride solution (18 mL) and extracted with EtOAc (3 x 8 mL). The combined organic layers were dried (Na_2SO_4) and the residue was purified by chromatography on SiO_2 (3:2, Hexanes/EtOAc) to give **6** (190 mg, 0.61 mmol, 91%,) as a tan powder: Mp 220 °C (dec.); IR (neat) 3011, 2247, 1557, 1493, 1419, 1281, 1179, 1153, 1126, 1019, 928, 764, 678 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-*d*$_6$) 2.64 (dd, *J* = 8.7, 5.4 Hz, 1H), 2.98 (dd, *J* = 7.6, 5.4 Hz, 1H), 3.88 (t, *J* = 8.7 Hz, 1H), 7.23-7.24 (m, 2H), 7.53 (br s, 1H), 7.63 (br s, 1H), 7.88-7.94 (m, 2H), 8.11-8.17 (m, 2H), 9.25 (s, 1H), 12.91 (s, 1H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 21.1, 21.5, 34.0, 112.0, 117.7, 119.1, 122.4, 123.2, 129.4, 129.5, 130.7, 131.3, 141.3, 141.8, 147.4, 149.2, 150.3; HRMS *m/z* calcd for $C_{19}H_{14}N_5$ $[M+H]^+$ 312.1244, found 312.1242.

1-(1*H*-Benzo[*d*]imidazol-2-yl)-2-methyl-3-(quinoxalin-2-yl)cyclopropane-1-carbonitrile (**15**, **16**). According to General Protocol B, a 5:4 mixture of **15** and **16** was obtained as a tan powder: Mp 190 °C (dec.); IR (neat) 3066, 2240, 1623, 1532, 1494, 1454, 1422, 1368, 1328, 1275, 1183, 1130, 1110,1054, 997, 914, 763 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 1.42 (d, *J* = 6.6 Hz, 3H), 1.66 (d, *J* = 6.6 Hz, 3H), 3.00 (dq, *J* = 9.7, 6.6 Hz, 1H), 3.28 (dq, *J* = 7.7, 6.6 Hz, 1H), 3.91 (d, *J* = 9.7 Hz, 1H), 4.08 (d, *J* = 7.7 Hz, 1H), 7.26-7.31 (m, 4H), 7.56-7.62 (m, 4H), 7.74-7.78 (m, 4H), 8.08-8.14 (m, 4H), 8.91 (s, 1H), 9.09 (s, 1H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 10.1, 11.4, 23.5, 24.9, 32.4, 33.3, 36.3, 37.7, 115.0, 116.3, 117.7, 123.6, 123.7, 129.3, 129.31, 129.34, 130.0, 130.2,

130.5, 137.4, 141.5, 141.6, 141.8, 142.0, 145.3, 145.9, 146.2, 148.9, 149.2, 149.4; HRMS *m/z* calcd for $C_{20}H_{14}N_5$ $[M-H]^-$ 324.1252, found 324.1252.

Diethyl *trans*-2-(1*H*-benzo[*d*]imidazol-2-yl)-2-cyano-3-(quinoxalin-2-yl)cyclopropane-1,1-dicarboxylate (**17**). According to General Protocol B, **17** was obtained as a tan powder: Mp 180 °C (dec.); IR (neat) 2985, 2249. 1732, 1495, 1422, 1368, 1280, 1229, 1147, 1066, 1002, 932, 858, 764 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 0.87 (t, J = 7.3 Hz, 3H), 1.14 (t, J = 7.3 Hz, 3H), 3.99 (q, J = 7.3 Hz, 2H), 4.22-4.37 (m, 2H), 4.08 (s, 1H), 7.23-7.32 (m, 2H), 7.57-7.66 (m, 2H), 7.92-7.96 (m, 2H), 7.99-8.03 (m, 1H), 8.18-8.21 (m, 1H), 9.40 (s, 1H), 13.37 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 13.8, 14.0, 28.2, 36.0, 47.2, 62.8, 63.2, 112.3, 114.3, 119.7, 122.7, 124.0, 129.0, 129.6, 131.3, 131.6, 135.0, 140.6, 141.7, 142.9, 144.7, 147.5, 147.5, 163.0, 163.6; HRMS *m/z* calcd for $C_{25}H_{22}O_4N_5$ $[M+H]^+$ 456.1666, found 456.1654.

***trans*-1-(1*H*-Benzo[*d*]imidazol-2-yl)-2-(quinoxalin-2-yl)spiro[2.2]pentane-1-carbonitrile** (**18**). According to General Protocol B, **18** was obtained as a white powder: Mp 192 °C (dec.); IR (neat) 3011, 2239, 1622, 1538, 1491, 1451, 1417, 1368, 1311, 1275, 1215, 1163, 1128, 1076, 1003, 966, 923, 763 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6) δ 1.32 (br s, 1H), 1.44 (br s, 1H), 1.61 (br s, 1H), 1.72 (br s, 1H), 4.22 (s, 1H), 7.21-7.22 (m, 2H), 7.53 (d, J = 7.1 Hz, 1H), 7.64 (d, J = 7.1 Hz, 1H), 7.88-7.90 (m, 2H), 8.11 (d, J = 7.1 Hz, 1H), 8.15 (d, J = 7.1 Hz, 1H), 9.12 (s, 1H), 12.7 (s, 1H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 6.8, 6.9, 25.8, 30.5, 37.0, 111.6, 116.8, 118.7, 121.8, 122.3, 122.6, 129.0, 130.3, 130.7, 141.1, 141.3, 145.7, 148.2, 150.6; HRMS *m/z* calcd for $C_{21}H_{16},N_5$ $[M+H]^+$ 338.1400, found: 338.1397.

(1*SR*,2*RS*)-1-(1-Allyl-1*H*-benzo[*d*]imidazol-2-yl)-2-phenylcyclopropane-1-carbonitrile (**19**). According to General Protocol B, **19** was obtained as a white crystalline solid: Mp 120-121 °C; IR (neat) 3098, 3023, 2236, 1604, 1512, 1502, 1457, 1449, 1404, 1333, 1283, 1252, 1172, 917, 782, 759, 112 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.32 (dd, J = 8.6, 5.9 Hz, 1H), 2.61 (dd, J = 8.6, 5.9 Hz, 1H), 3.13 (t, J = 8.6 Hz, 1H), 4.99-5.06 (m, 3H), 5.30 (d, J = 11.0, 1H), 6.00-6.09 (m, 1H), 7.31-7.45 (m, 8H), 7.76-7.78 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.7, 20.9, 34.2, 46.5, 110.2, 117.8, 118.2, 120.0, 123.0, 123.7, 128.1, 128.4, 128.9, 131.3, 133.6, 135.9, 141.7, 147.8; HRMS *m/z* calcd for $C_{20}H_{18}N_3$ $[M+H]^+$ 300.1495, found 300.1498.

(1*RS*,2*SR*)-1-(1-Allyl-1*H*-benzo[*d*]imidazol-2-yl)-2-phenylspiro[2.2]pentane-1-carbonitrile (**20**). According to General Protocol B, **20** was obtained as a colorless amorphous solid: IR (neat) 3060, 2980, 2233, 1602, 1497, 1456, 1393, 1330, 1250, 1156, 928, 764, 743 cm^{-1}; ^1H NMR (400

MHz, $CDCl_3$) δ 1.19-1.22 (m, 1H), 1.38-1.41 (m, 1H), 1.58-1.62 (m, 2H), 3.76 (s, 1H), 4.85-4.97 (m, 2H), 5.10 (d, *J* = 17.1 Hz, 1H), 5.30 (d, *J* = 10.4 Hz, 1H), 5.95-6.04 (m, 1H), 7.30-7.52 (m, 8H), 1.78-7.80 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 5.9, 7.2, 22.9, 30.0, 37.1, 46.5, 110.2, 117.2, 118.3, 120.2, 122.8, 123.5, 128.2, 128.4, 128.6, 131.5, 133.9, 135.5, 142.1, 147.4; HRMS *m/z* calcd for $C_{22}H_{20}N_3$ $[M+H]^+$ 326.1652, found 326.1634.

(1*SR*,2*SR*)-1-(1-Allyl-1*H*-benzo[*d*]imidazol-2-yl)-2-(thiophen-2-yl)cyclopropane-1-carbonitrile (**21**). According to General Protocol B, **21** was obtained as a colorless amorphous solid: IR (neat) 3086, 2922, 2238, 1645, 1614, 1509, 1458, 1402, 1331, 1285, 1249, 1171, 985, 928, 851, 743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.28 (dd, *J* = 8.5, 5.9 Hz, 1H), 2.73 (dd, *J* = 8.5, 5.9 Hz, 1H), 3.18 (t, *J* = 8.5 Hz, 1H), 4.98 (d, *J* = 17.2 Hz, 1H), 5.07- 5.11 (m, 2H), 5.32 (d, *J* = 10.8 Hz, 1H), 6.03-6.13 (m, 1H), 7.05-7.09 (m, 2H), 7.29-7.37 (m, 4H), 7.74-7.76 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.6, 22.4, 29.3, 46.5, 110.2, 117.6, 118.1, 120.0, 123.0, 123.8, 126.0, 126.6, 127.4, 131.3, 135.9, 137.1, 141.7, 147.1; HRMS *m/z* calcd for $C_{18}H_{16}N_3S$ $[M+H]^+$ 306.1059, found 306.1064.

(1*SR*,2*SR*)-1-(1-Allyl-1*H*-benzo[*d*]imidazol-2-yl)-2-(furan-3-yl)cyclopropane-1-carbonitrile (**22**). According to General Protocol B, **22** was obtained as a colorless amorphous solid: IR (neat) 3087, 2927, 2238, 1614, 1508, 1459, 1403, 1331, 1252, 1165, 1025, 926, 872, 791, 720 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.03 (dd, *J* = 8.5, 5.6 Hz, 1H), 2.56 (dd, *J* = 8.5, 5.6 Hz, 1H), 2.92 (t, *J* = 8.5 Hz, 1H), 5.00-5.07 (m, 3H), 5.31 (d, *J* = 11.0 Hz, 1H), 6.00-6.09 (m, 1H), 6.47 (s, 1H), 7.28-7.36 (m, 3H), 7.47-7.48 (m, 1H), 7.54 (s, 1H), 7.74-7.76 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.8, 21.9, 25.5, 46.4, 109.8, 110.1, 118.1, 118.2, 119.8, 120.0, 122.9, 123.7, 131.3, 135.9, 141.3, 141.7, 143.8, 147.4; HRMS *m/z* calcd for $C_{18}H_{16}N_3O$ $[M+H]^+$ 290.1288, found 290.1283.

(2*SR*,3*SR*)-1-(1-Allyl-1*H*-benzo[*d*]imidazol-2-yl)-2,3-diphenylcyclopropane-1-carbonitrile (**24**). A suspension of **10** (400 mg, 1.40 mmol) and **23** (625 mg, 1.68 mmol) in DMSO (6.4 mL) at rt was treated with a suspension of 60% sodium hydride in mineral oil (73 mg, 1.8 mmol) in one portion. After 20 h, the reaction mixture was diluted with water (30 mL) and extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with brine (1 x 20 mL), dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by chromatography on SiO_2 (Hexanes/EtOAc, 6:1) to give a 4:1 mixture of **24** and **25** (453 mg, 1.21 mmol, 86%) as a white crystalline solid. Recrystallization of the mixture from hexanes/EtOAc gave pure **24** (239 mg, 0.64

mmol, 45%) as a white crystalline solid: Mp 163-165 °C; IR (neat) 3062, 2926, 2228, 1643, 1604, 1501, 1458, 1405, 1332, 1284, 1250, 1172, 1064, 986, 932, 782, 756, 740 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.61 (d, *J* = 8.5 Hz, 1H), 4.48 (d, *J* = 8.5 Hz, 1H), 4.50-4.56 (ddt, *J* = 16.6, 5.6, 1.6 Hz, 1H), 4.70-4.77 (ddt, *J* = 16.6, 5.6, 1.6 Hz, 1H), 5.02-5.14 (m, 2H), 5.32-5.42 (m, 1H), 7.04-7.29 (m, 8H), 7.38-7.42 (m, 1H), 7.45-7.49 (m, 2H), 7.64 (d, *J* = 7.3 Hz, 2H), 7.81 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.2, 35.2, 39.9, 47.1, 110.9, 117.9, 118.8, 120.2, 122.8, 123.6, 127.6, 128.3, 128.5, 128.8, 128.9, 129.0, 131.1, 132.5, 134.0, 135.7. 142.1, 144.5; HRMS *m/z* calcd for $C_{26}H_{22}N_3$ $[M+H]^+$ 376.1808, found 376.1799. The structure of cyclopropane **24** was secured by an x-ray analysis.

(1*SR*,2*RS*)-1-(1-Allyl-1*H*-benzo[*d*]imidazol-2-yl)-2-phenyl-3-((*E*)-styryl)cyclopropane-1-carbonitrile (**27**). According to General Protocol B, **27** was obtained as a colorless solid mixture of diastereomers (2:1): Mp 65-68 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 3.08 (t, *J* = 9.8 Hz, 0.3H), 3.27 (t, *J* = 16.9 Hz, 0.7H), 3.92 (d, *J* = 9.5 Hz, 0.3H), 4.13 (br s, 0.7H), 4.94-5.31 (m, 4H), 5.45 (dd, *J* = 16.0, 9.0 Hz, 0.7H), 5.90-6.00 (m, 1H), 6.03-6.10 (m, 0.3H), 6.81 (d, *J* = 15.8 Hz, 0.7H), 6.86 (d, *J* = 15.8 Hz, 0.3H), 7.11 (dd, *J* = 7.8, 1.3 Hz, 1.4H), 7.17-7.47 (m, 9.6H), 7.52 (d, *J* = 8.0 Hz, 0.6H), 7.56 (d, *J* = 7.5 Hz, 1.4H), 7.79 (d, *J* = 7.5 Hz, 0.3H), 7.85 (d, *J* = 7.5 Hz, 0.7H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 36.6, 37.6, 39.3, 46.6, 47.0, 110.3, 110.8, 119.1, 120.0, 122.0, 123.1, 126.3, 126.5, 128.2, 128.4, 128.6, 128.7, 128.8, 130.3, 131.2, 135.7, 135.8; HRMS *m/z* calcd for $C_{28}H_{24}N_3$ $[M+H]^+$ 402.1965, found 402.1970.

General Protocol C for Iminocyclopropane Rearrangements: 1-(Quinoxalin-2-yl)-2,3-dihydro-1*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole-3-carbonitrile (**7**). A suspension of **6** (75 mg, 0.24 mmol) and magnesium iodide (29 mg, 0.10 mmol) in trifluorotoluene (1.25 mL) was heated in a Biotage microwave reactor at 110 °C for 30 min. The reaction mixture was cooled to rt and diluted with a mixture of water and EtOAc (5 mL, 1:1). The organic layer was washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by chromatography on SiO_2 (Hexanes/EtOAc, 1:1) to give **7** (44 mg, 59%, *dr* 4:1) as a tan powder: Mp 215 °C (dec.); IR (neat) 2912, 2251, 1620, 1531, 1494, 1457, 1422, 1365, 1318, 1281, 1121, 1021, 808, 775 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 3.15-3.21 (m, 1H), 3.38-3.42 (m, 0.3H), 3.60-3.42 (m, 0.3H), 3.67-3.75 (m, 1H), 5.08 (dd, *J* = 9.3, 5.8 Hz, 1H), 5.27 (t, *J* = 8.3 Hz, 0.3H), 6.17 (dd, *J* = 7.7, 5.3 Hz, 1H), 6.30 (dd, *J* = 8.4, 3.1 Hz, 0.3H), 7.09-7.30 (m, 3.8H), 7.68-7.70 (m, 1.3H), 7.83-7.98 (m, 3.8H), 8.12-8.17 (m, 1.3H), 9.16 (s, 0.3H), 9.25 (s, 1H); ^{13}C NMR (100 MHz,

DMSO-d_6) δ 26.45, 26.49, 57.3, 57.8, 111.2, 111.3, 118.6, 118.8, 120.26, 120.27, 122.68, 122.73, 123.15, 123.23, 129.39, 129.45, 129.49, 131.1, 131.2, 131.29, 131.33, 132.2, 132.3, 141.6, 141.7, 142.3, 142.4, 145.0, 145.3, 148.5, 148.6, 153.2, 153.7, 155.09, 155.13; HRMS *m/z* calcd for $C_{19}H_{14}N_5$ $[M+H]^+$ 312.1244, found 312.1242.

(1*SR*,2*RS*)-2-Methyl-1-(quinoxalin-2-yl)-2,4-dihydro-1*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole-3-carbonitrile (**28**). A mixture of **15** and **16** (0.024 g, 0.074 mmol), NH_4I (0.012g, 0.083 mmol) in 1,2-dichlorobenzene (1.5 mL) was degassed (3-cycles-freeze/pump/thaw) and heated at 150 °C under microwave irradiation. The reaction solution was purified by chromatography on SiO_2 (0-75% EtOAc/Hexanes) to give **28** (0.014 g, 58% containing ca. 10% impurities, *dr* 1:1) as an orange oil: IR (neat) 3058, 2927, 2228, 1733, 1619, 1535, 1493, 1451, 1366, 1282, 1218, 1127, 978, 907, 762 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.62 (d, *J* = 6.9 Hz, 1.5H), 1.65 (d, *J* = 7.1 Hz, 1.5H), 3.64-3.70 (m, 1H), 4.15 (d, *J* = 8.5 Hz, 0.5H), 4.80 (d, *J* = 7.9 Hz, 0.5H), 5.36 (d, *J* = 7.4 Hz, 0.5H), 5.50 (d, *J* = 5.9 Hz, 0.5H), 6.68 (d, *J* = 8.0 Hz, 0.5H), 6.80 (d, *J* = 7.9 Hz, 0.5H), 7.06-7.12 (m, 1H), 7.81-7.87 (m, 3H), 8.02-8.04 (m, 0.5H), 8.10-8.12 (m, 0.5H), 8.16-8.19 (m, 1H), 8.84 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 15.8, 17.1 33.5, 35.0, 47.1, 51.1, 65.2, 65.9, 110.1, 110.2, 114.6, 116.1, 121.06, 121.08, 123.19, 123.24, 123.7, 129.64, 129.66, 129.68, 131.19, 131.22, 131.3, 142.20, 142.28, 143.02, 143.05, 143.2, 150.2, 150.7; LCMS *m/z* calcd for $C_{20}H_{16}N_5$ $[M+H]^+$ 326.14, found 326.10.

1-Phenyl-2,3-dihydro-1*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole-3-carbonitrile (**30**). According to General Protocol B, 1-(1*H*-benzo[*d*]imidazol-2-yl)-2-phenylcyclopropane-1-carbonitrile (**29**) was obtained from (*E*)-2-(1*H*-benzo[*d*]imidazol-2-yl)-3-phenylacrylonitrile[1] as a light tan solid (0.141 g, 74%) by treatment of the crude product with Et_2O/Hexanes (1:1) and filtration: Mp 186-188 °C; IR (neat) 2891, 2346, 1541, 1498, 1456, 1425, 1320, 1278, 1227, 1154, 1084, 997, 972, 778, 746, 701 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 2.42 (dd, *J* = 6.0, 9.2 Hz, 1H), 2.64 (dd, *J* = 6.0, 8.1 Hz, 1H), 3.34 (t, *J* = 8.7 Hz, 1H), 7.17-7.23 (m, 2H), 7.34-7.49 (m, 6H), 7.59 (d, *J* = 7.2 Hz, 1H), 12.77 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 19.6, 21.3, 35.1, 111.4, 118.1, 121.7, 122.6, 127.9, 128.3, 128.5, 134.3, 142.7, 149.4; LCMS *m/z* calcd for $C_{17}H_{12}N_3$ $[M-H]^+$ 258.10, found 258.11.

[1] Hranjec, M.; Karminski-Zamola, G. *Molecules* **2007**, *12*, 1817-1828.

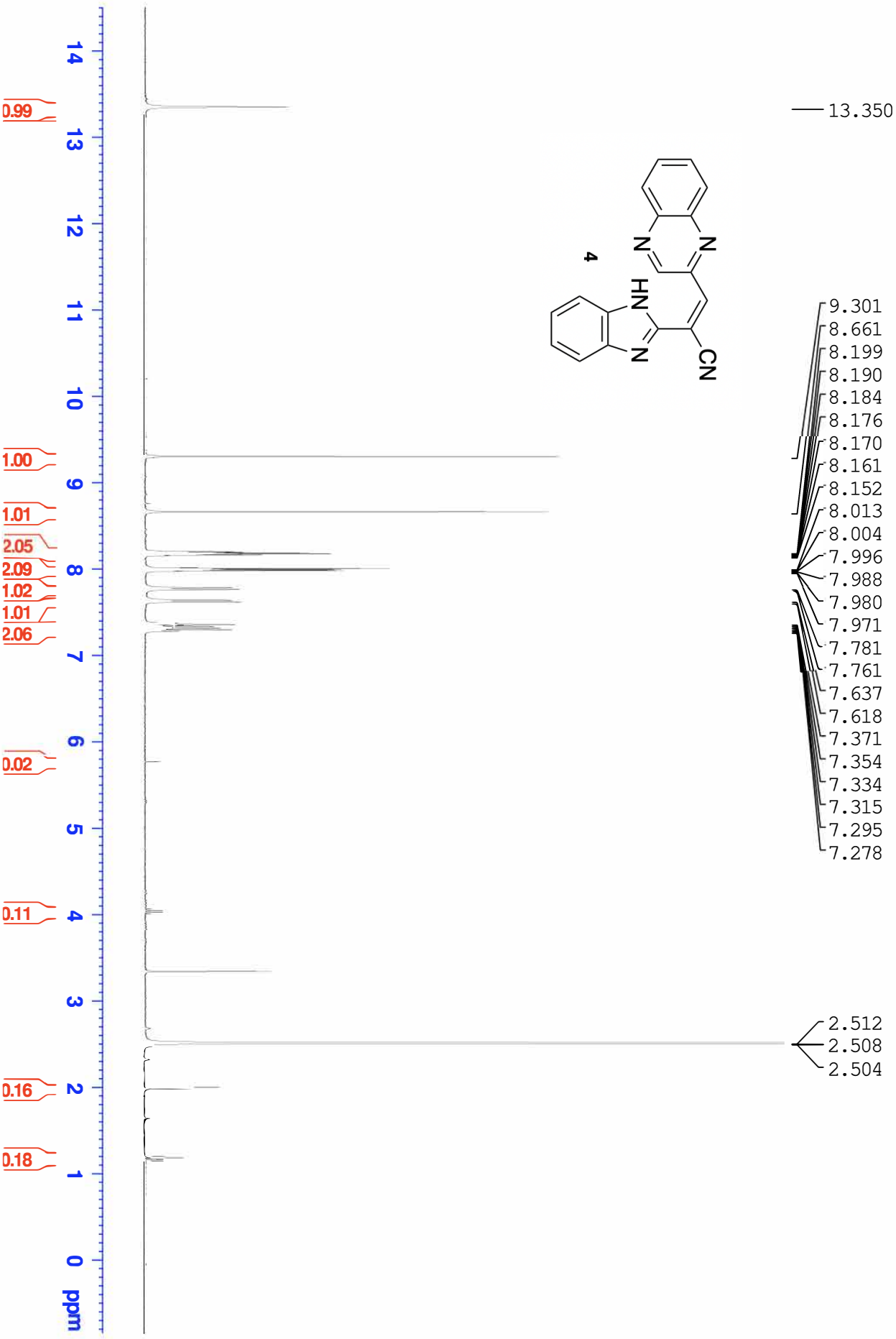
A suspension of **29** (74 mg, 0.28 mmol) and magnesium iodide (33 mg, 0.12 mmol) in trifluorotoluene (1.50 mL) was heated in a Biotage microwave reactor at 110 °C for 30 min. The reaction mixture was cooled to rt, extracted with EtOAc and washed with water (2x). The combined organic layers were washed with brine, dried (Na_2SO_4) and concentrated under reduced pressure. The residual oil was purified by chromatography on SiO_2 (ISCO-Rf, 0-100% EtOAc/Hexanes) to give recovered **29** (12 mg, 16%) and **30** (39 mg, 53%) as a tan powder (dr = 1:1): Mp 72 °C (dec.); IR (neat) 3036, 2245, 1619, 1531, 1494, 1449, 1412, 1359, 1322, 1281, 1217, 1030, 831, 775, 699 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 2.92-2.97 (m, 1H), 2.99-3.04 (m, 1H), 3.43-3.48 (m, 1H), 3.56-3.61 (m, 1H), 4.43 (app t, *J* = 8.4 Hz, 1H), 4.50 (dd, *J* = 4.9, 8.8 Hz, 1H), 5.45 (t, *J* = 7.2 Hz, 1H), 5.68 (t, *J* = 6.9 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 8.1 Hz, 1H), 7.11-7.18 (m, 4H), 7.26-7.31 (m, 4H), 7.41-7.45 (m, 6H), 7.82 (app t, *J* = 7.6 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 26.6, 26.9, 42.5, 42.8, 58.9, 59.3, 110.79, 110.82, 116.85, 116.87, 120.7, 120.8, 122.98, 123.0, 123.3, 123.5, 126.2, 126.6, 129.3, 129.4, 129.6, 131.9, 137.1, 137.4, 148.6, 153.07, 153.1; LCMS *m/z* calcd for $C_{17}H_{14}N_3$ $[M+H]^+$ 261.11, found 261.05.

4-Allyl-1-phenyl-4*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole-3-carbonitrile (**31**). A mixture of **19** (20 mg, 0.067 mmol) and NH_4I (13 mg, 0.089 mmol) in 1,2-dichlorobenzene (1.5 mL) was heated at 150 °C under microwave conditions for 1 h. The solvent was removed by evaporation under vacuum, and the residue was purified by chromatography on SiO_2 (0-25% Et_2O/Hexanes) to yield **31** (7 mg, 35%) as a light brown solid: Mp 112 °C (dec); IR (neat) 2922, 2198, 1618, 1592, 1542, 1484, 1450, 1417, 1324, 1203, 1172, 1157, 1045, 991, 940, 921, 792, 764, 705, 698 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 4.92-4.93 (m, 2H), 5.34-5.39 (m, 2H), 6.03-6.08 (m, 1H), 6.59 (s, 1H), 7.07-7.10 (m, 1H), 7.28-7.33 (m, 2H), 7.40-7.43 (m, 1H), 7.49 (app t, *J* = 7.4 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.59-7.61 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 46.4, 63.8, 109.7, 112.8, 114.1, 117.5, 119.2, 120.5, 122.4, 124.0, 126.6, 128.0, 128.1, 128.9, 130.9, 131.4, 136.5, 143.6; LCMS *m/z* calcd for $C_{20}H_{16}N_3$ $[M+H]^+$ 298.13, found 298.05.

(*RS*)-4-Allyl-1-phenyl-1*H*,4*H*-spiro[benzo[*d*]pyrrolo[1,2-*a*]imidazole-2,1'-cyclopropane]-3-carbonitrile (**32**). According to General Protocol C, **32** (12%) was obtained as a yellow amorphous solid: IR (neat) 2922, 2224, 1595, 1493, 1455, 1394, 1331, 1286, 1253, 1154, 1029, 930, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.29-2.38 (m, 1H), 2.68-2.77 (m, 1H), 3.31-3.36 (m, 2H), 4.53-4.58 (m, 1H), 4.93-4.95 (m, 2H), 5.04 (d, *J* = 17.1 Hz, 1H), 5.24 (d, *J* = 10.3 Hz, 1H), 5.92-6.01 (m, 1H), 7.30-7.40 (m, 8H), 7.77-7.80 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 26.6,

29.7, 32.4, 46.6, 50.6, 98.5, 110.2, 114.1, 118.0, 120.1, 122.9, 123.6, 127.5, 127.7, 128.9, 131.7, 135.1, 139.5, 142.8, 144.5; LC-MS *m/z* calcd for $C_{22}H_{20}N_3$ $[M+H]^+$ 326.2, found 326.1.

4-Allyl-1,2-diphenyl-4*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole-3-carbonitrile (**33**). According to General Protocol C, **33** (60%) was obtained as a colorless amorphous solid: Mp 103-104 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.97-4.99 (m, 2H), 5.30-5.44 (m, 2H), 6.04-6.12 (m, 1H), 7.00-7.04 (m, 1H), 7.18-7.44 (m, 13H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 46.2, 109.5, 112.4, 119.1, 120.5, 123.8, 127.0, 127.2, 128.3, 128.4, 128.7, 129.5, 130.6, 130.8, 130.9, 133.1, 136.1, 142.9.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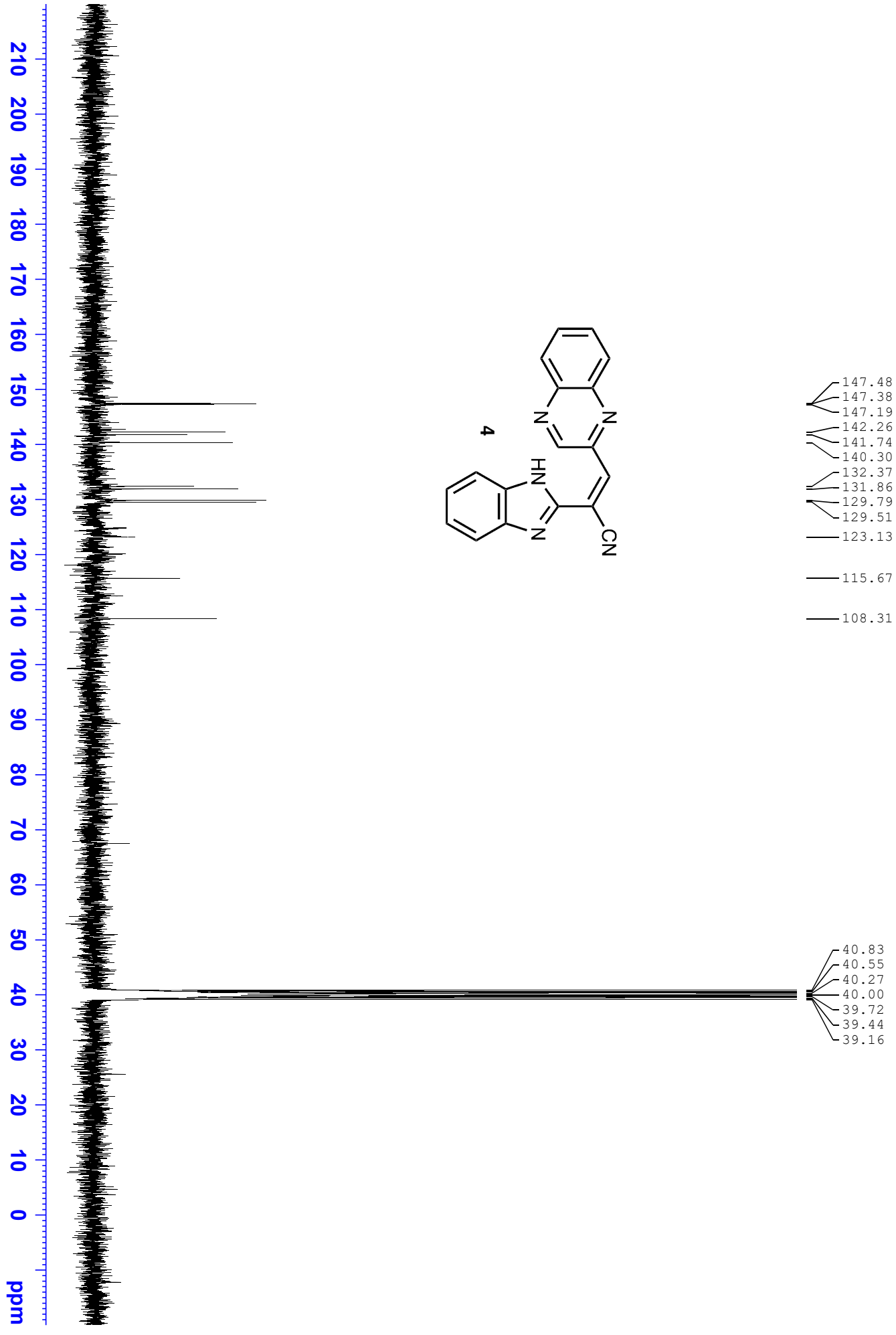
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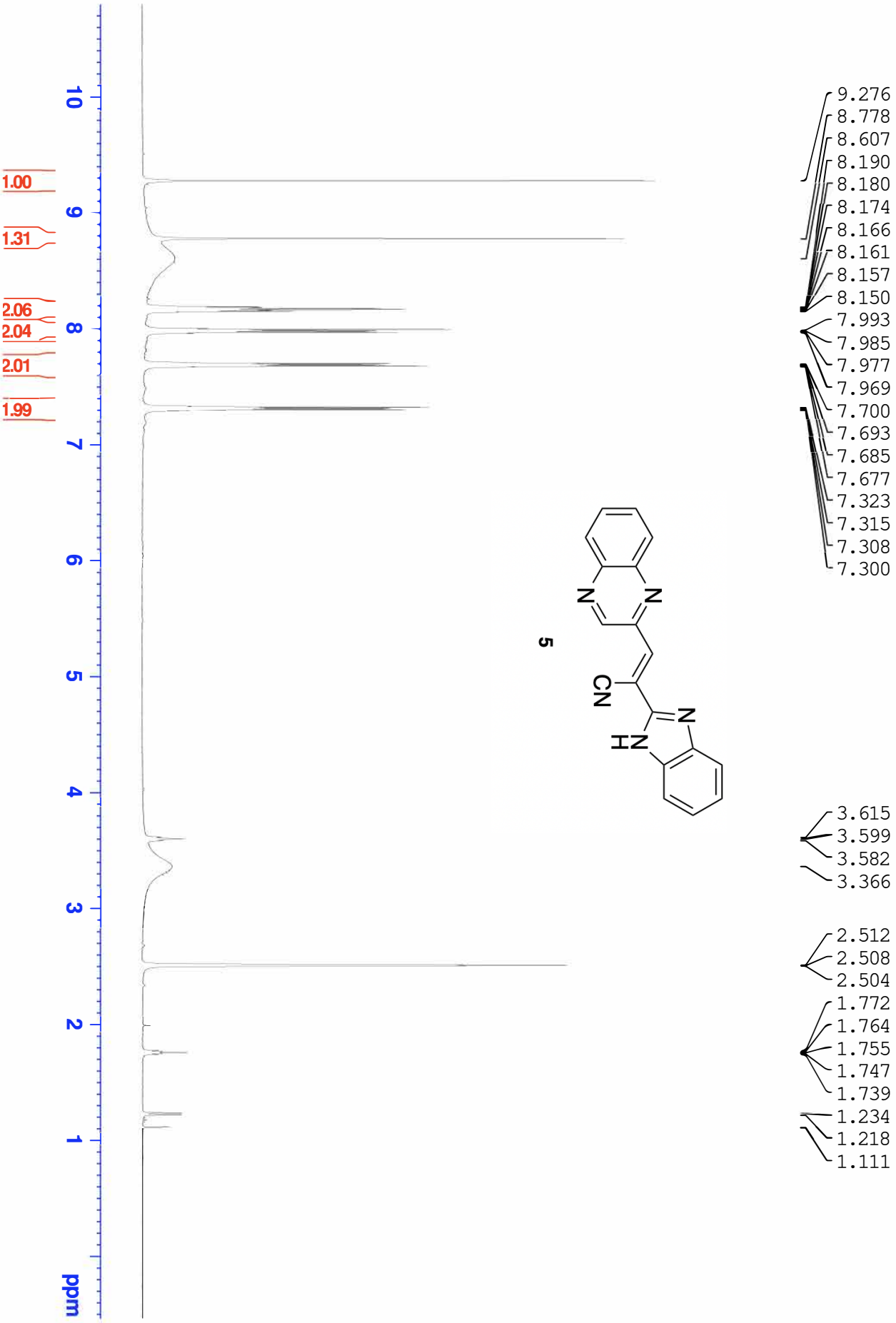
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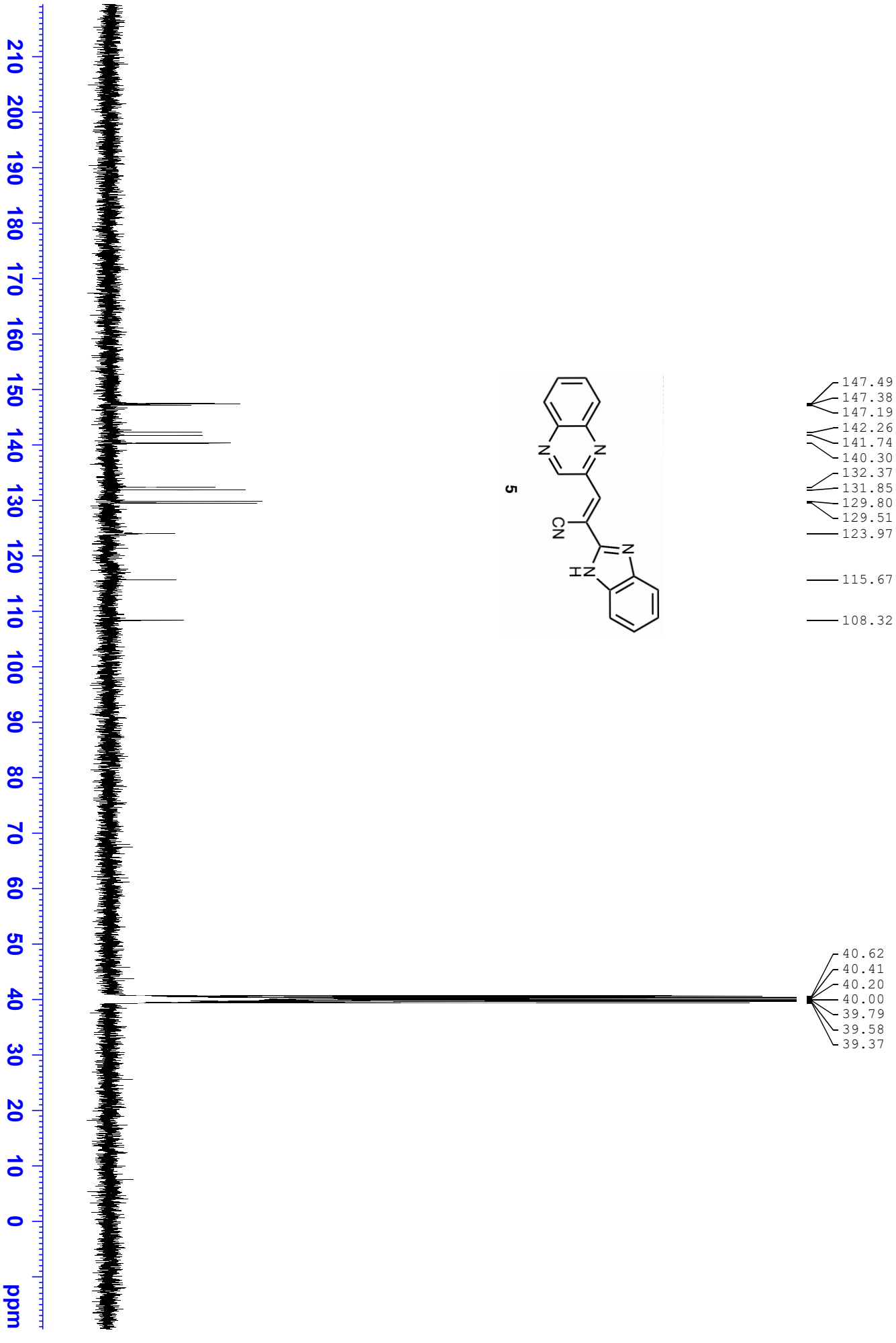
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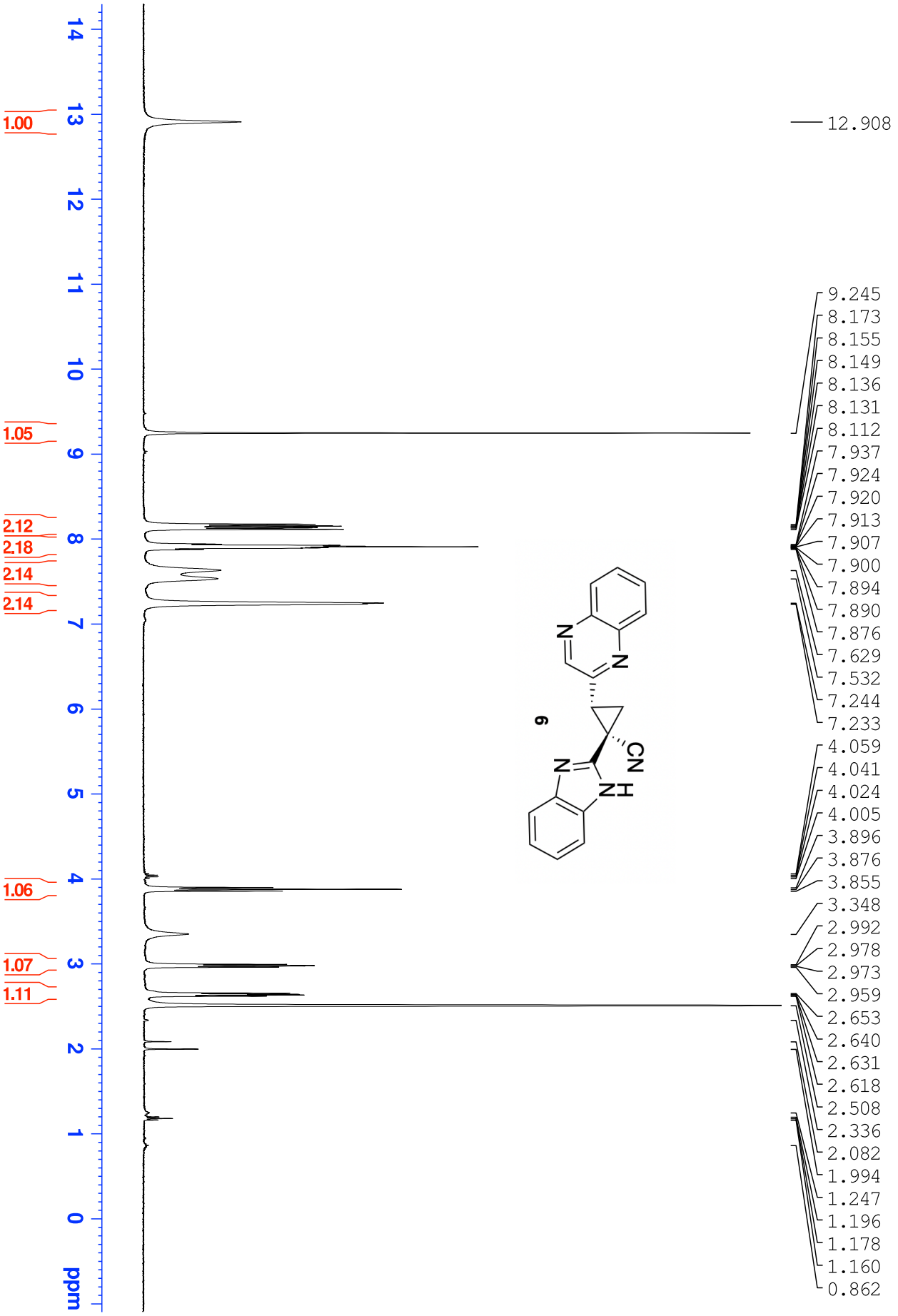
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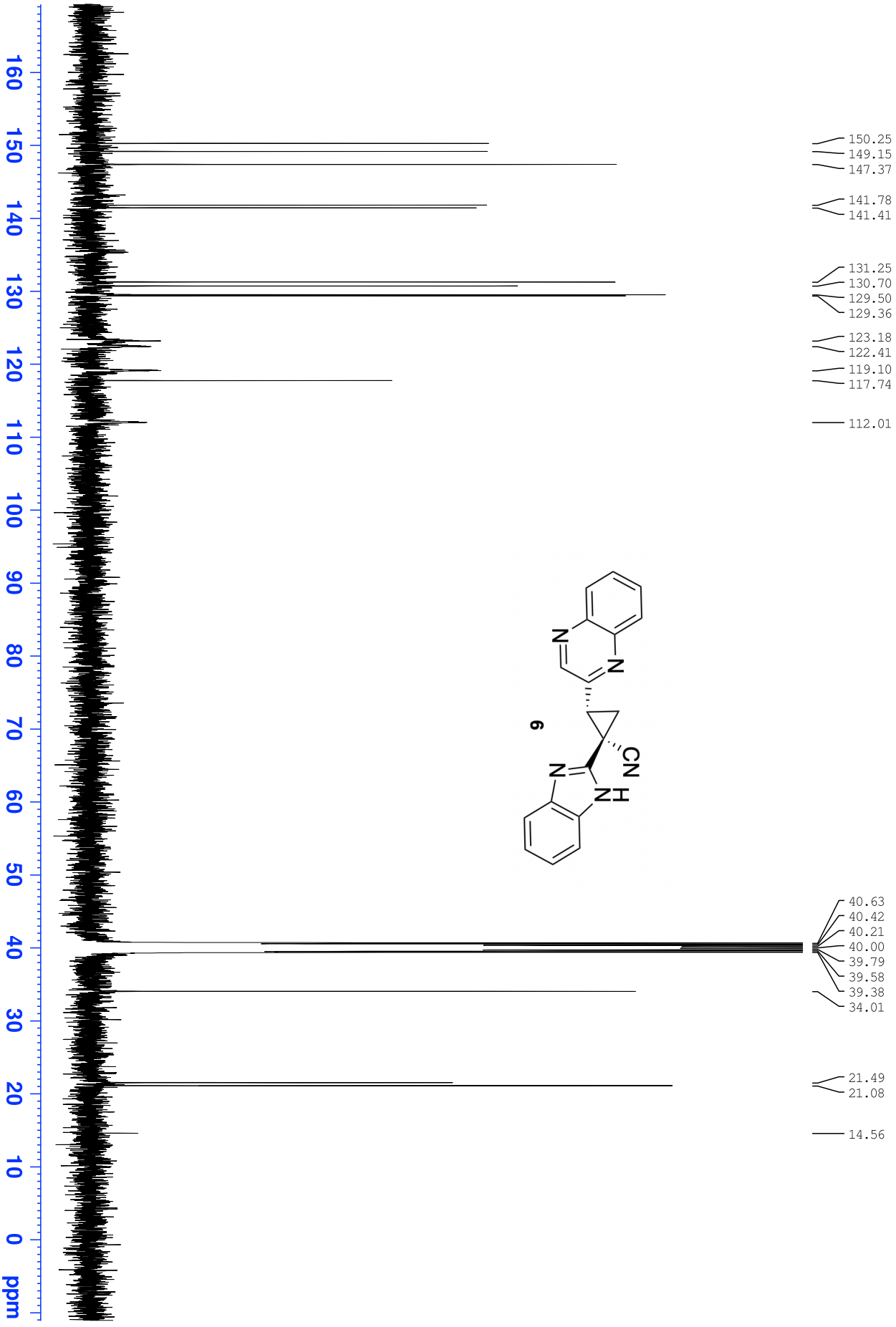
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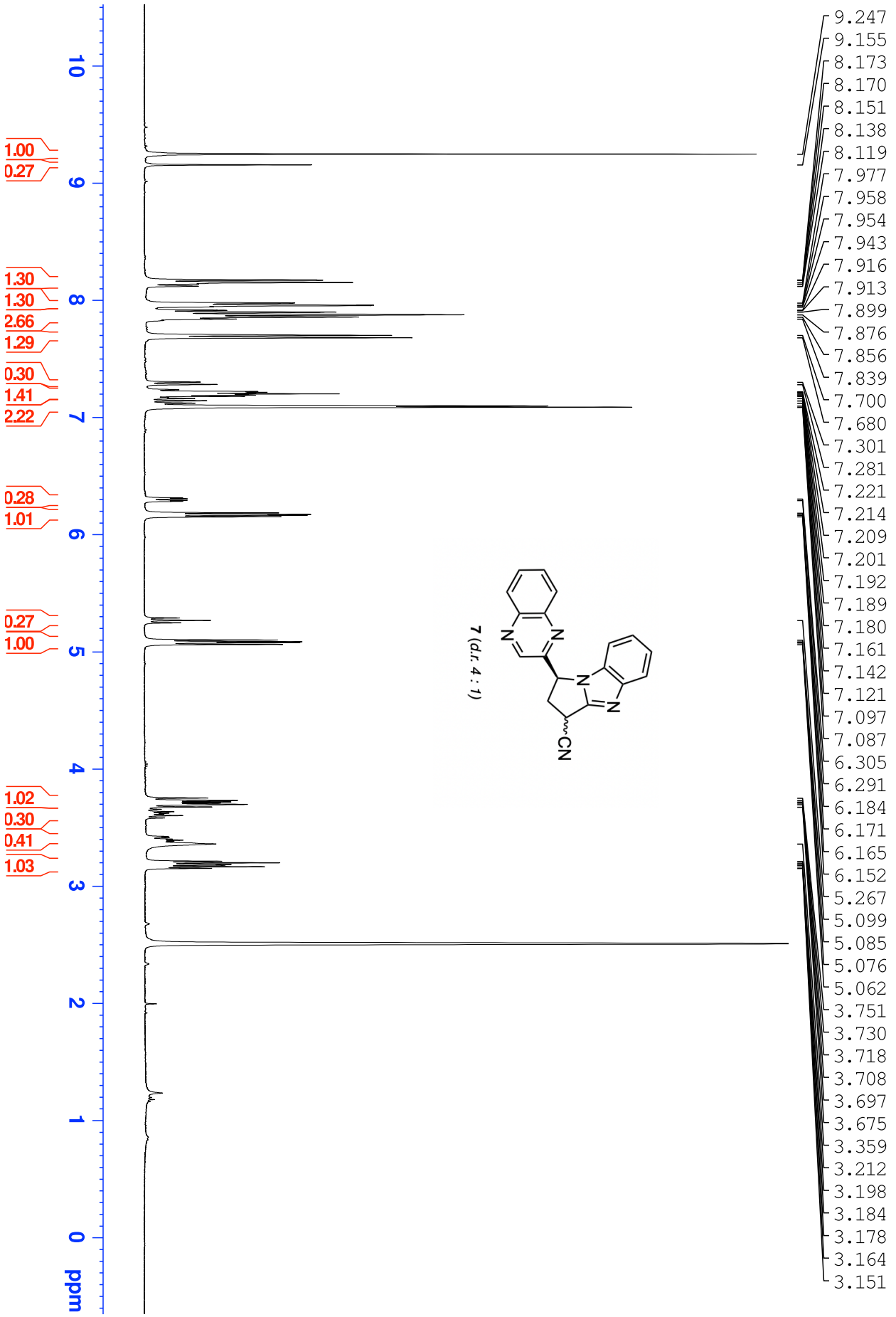
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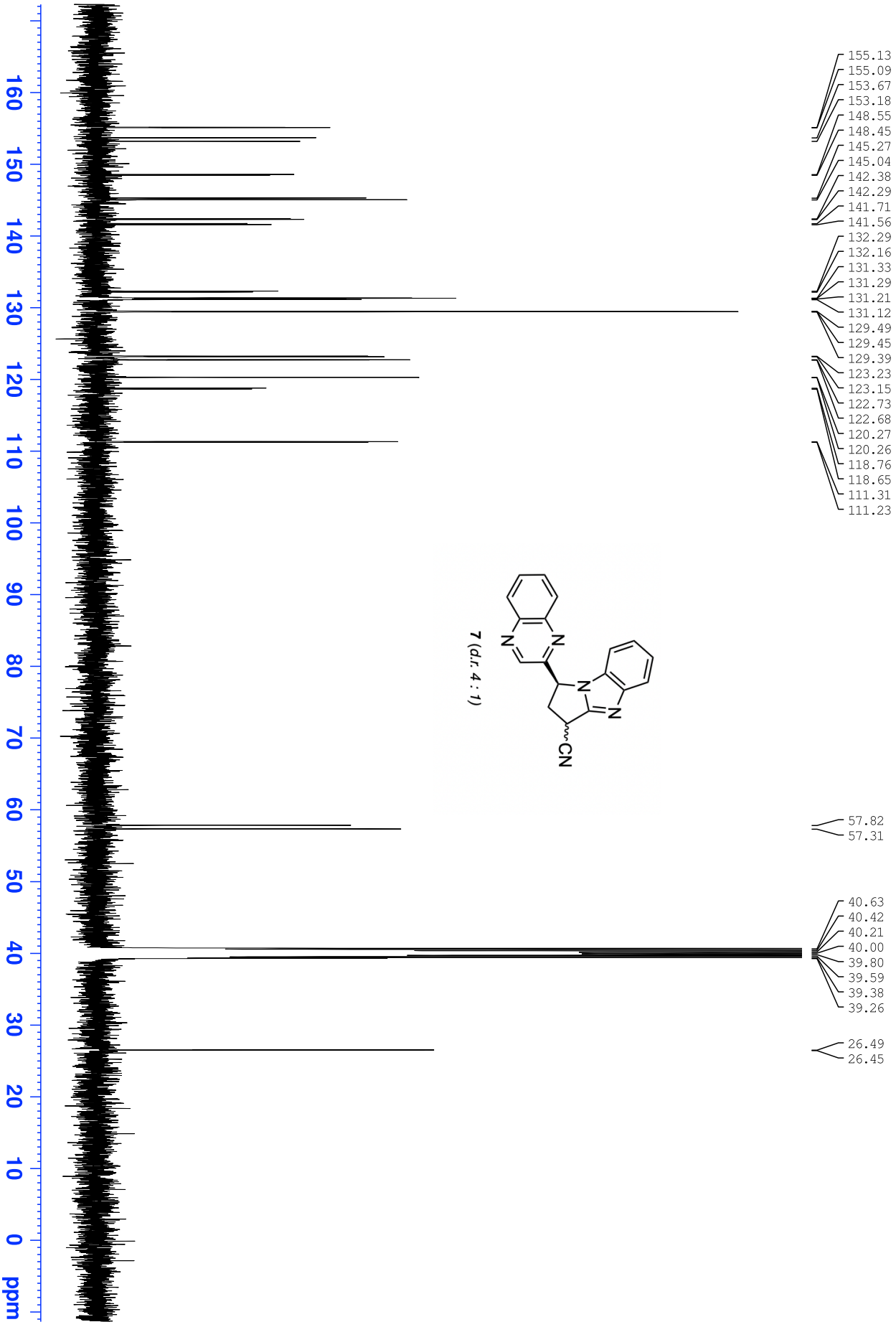
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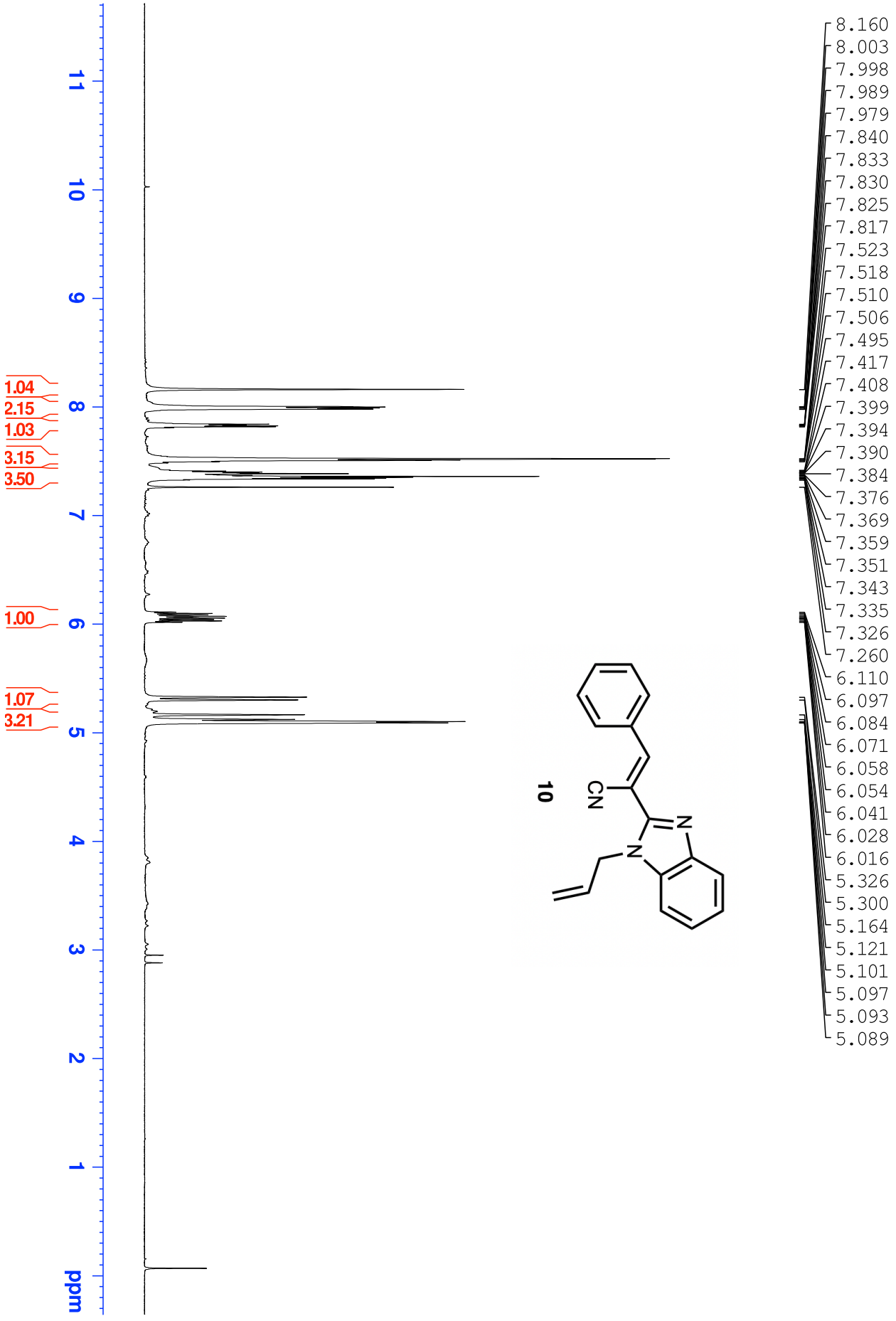
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5.093
5.089
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1.03
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1.07
3.21
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CN
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N
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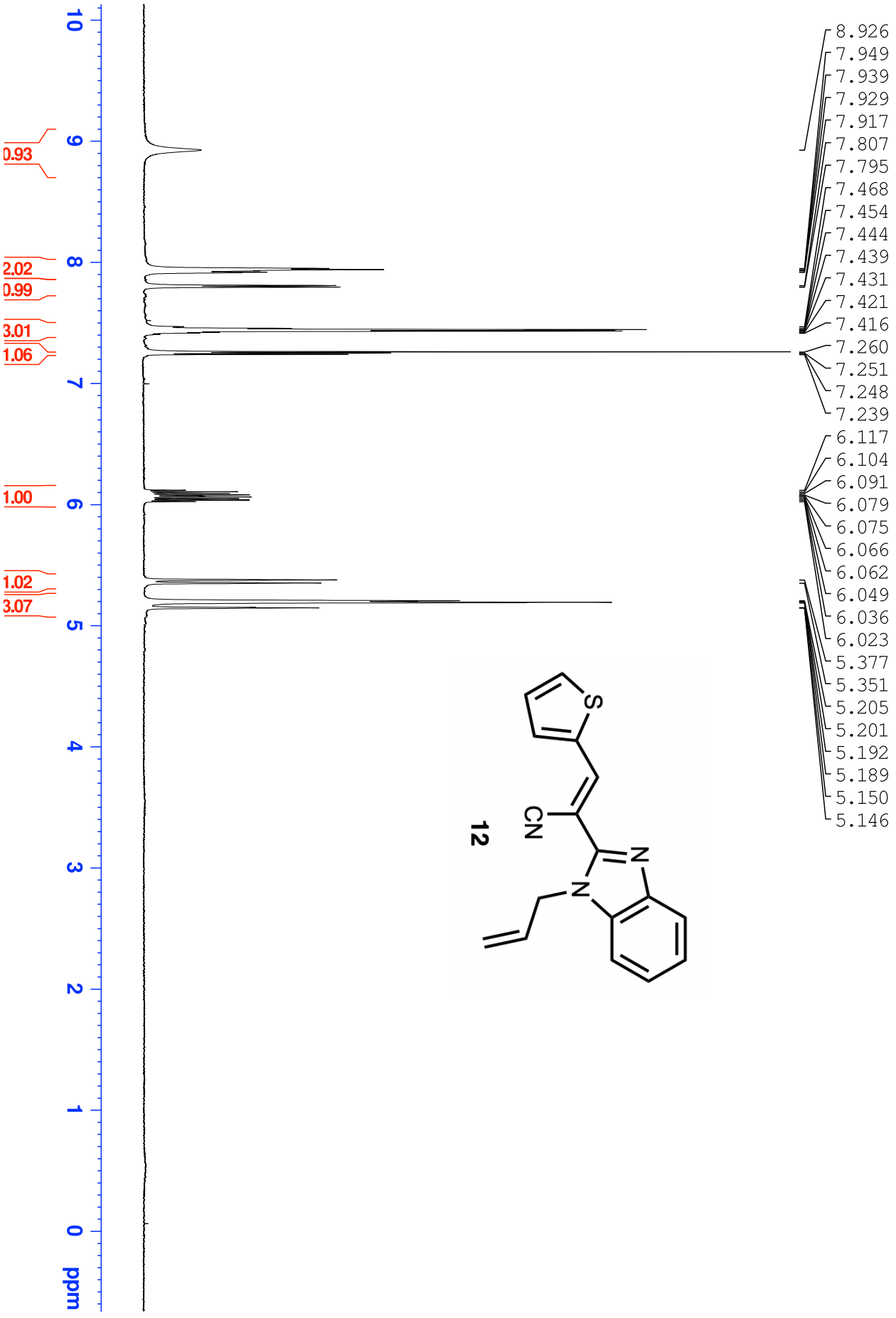
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7.416
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7.248
7.239
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6.075
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6.062
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6.036
6.023
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5.351
5.205
5.201
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5.189
5.150
5.146
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1.00
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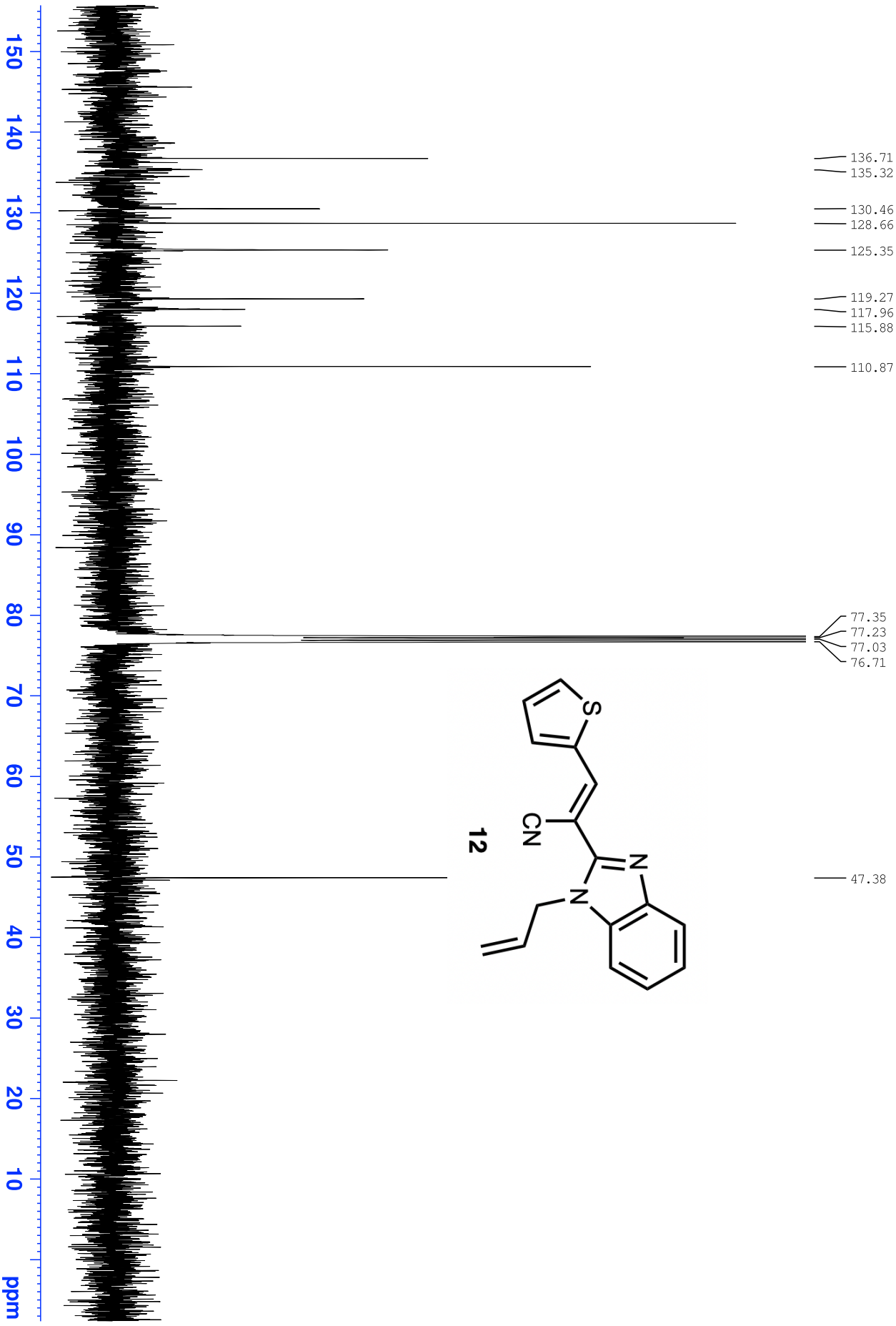
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128.66
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76.71
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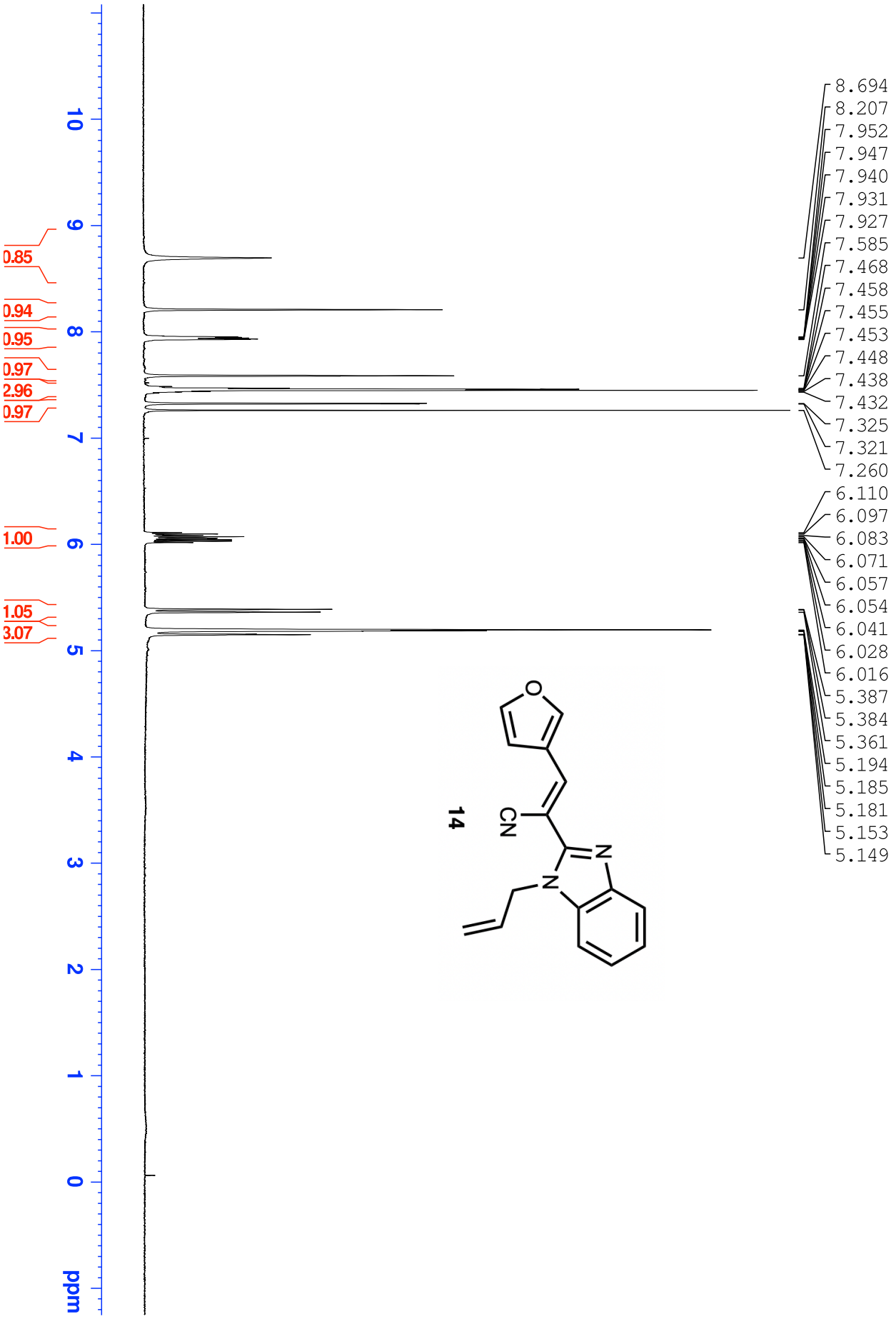
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7.453
7.448
7.438
7.432
7.325
7.321
7.260
6.110
6.097
6.083
6.071
6.057
6.054
6.041
6.028
6.016
5.387
5.384
5.361
5.194
5.185
5.181
5.153
5.149
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0.97
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0.97
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3.07
ppm
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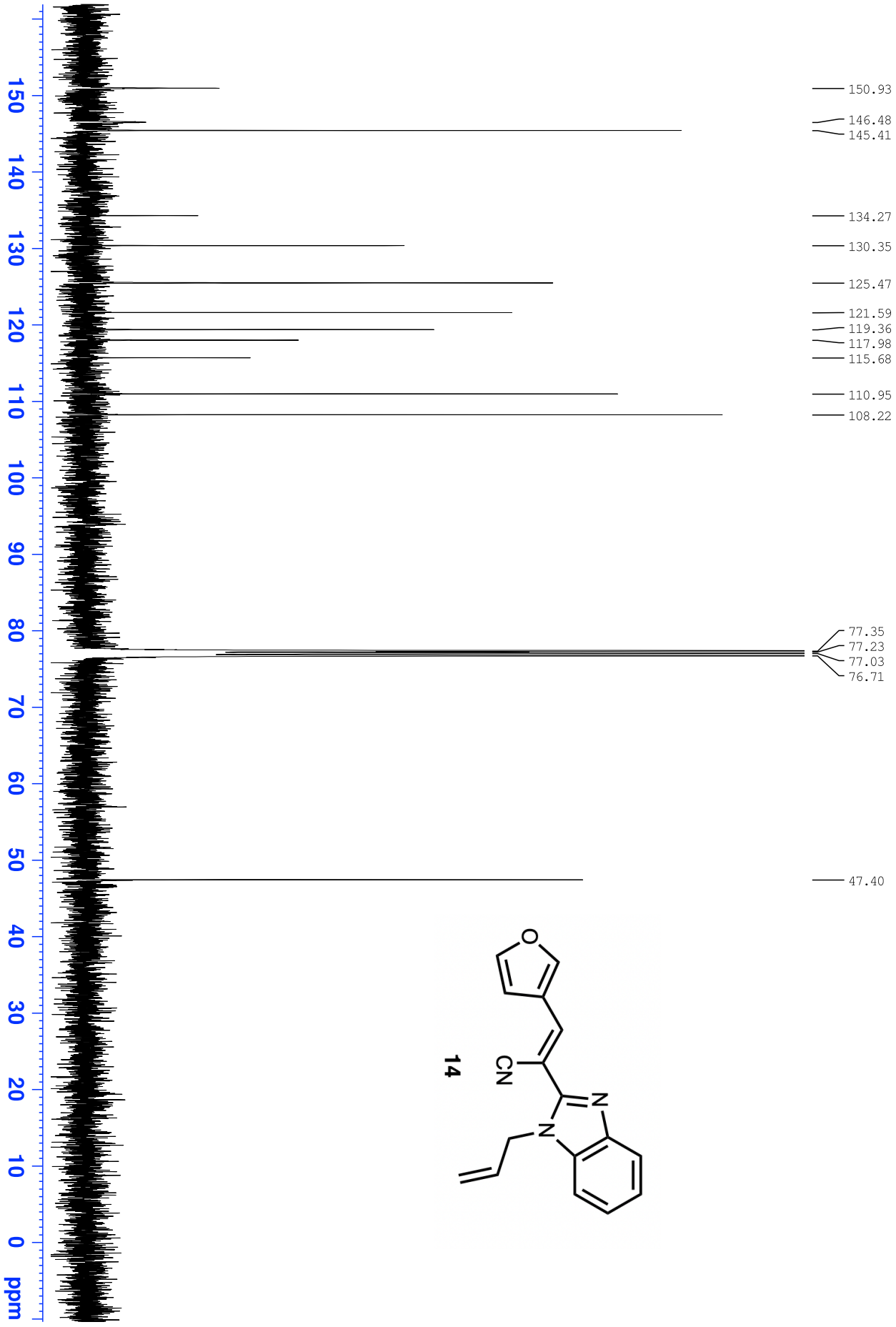
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77.03
76.71
47.40
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N

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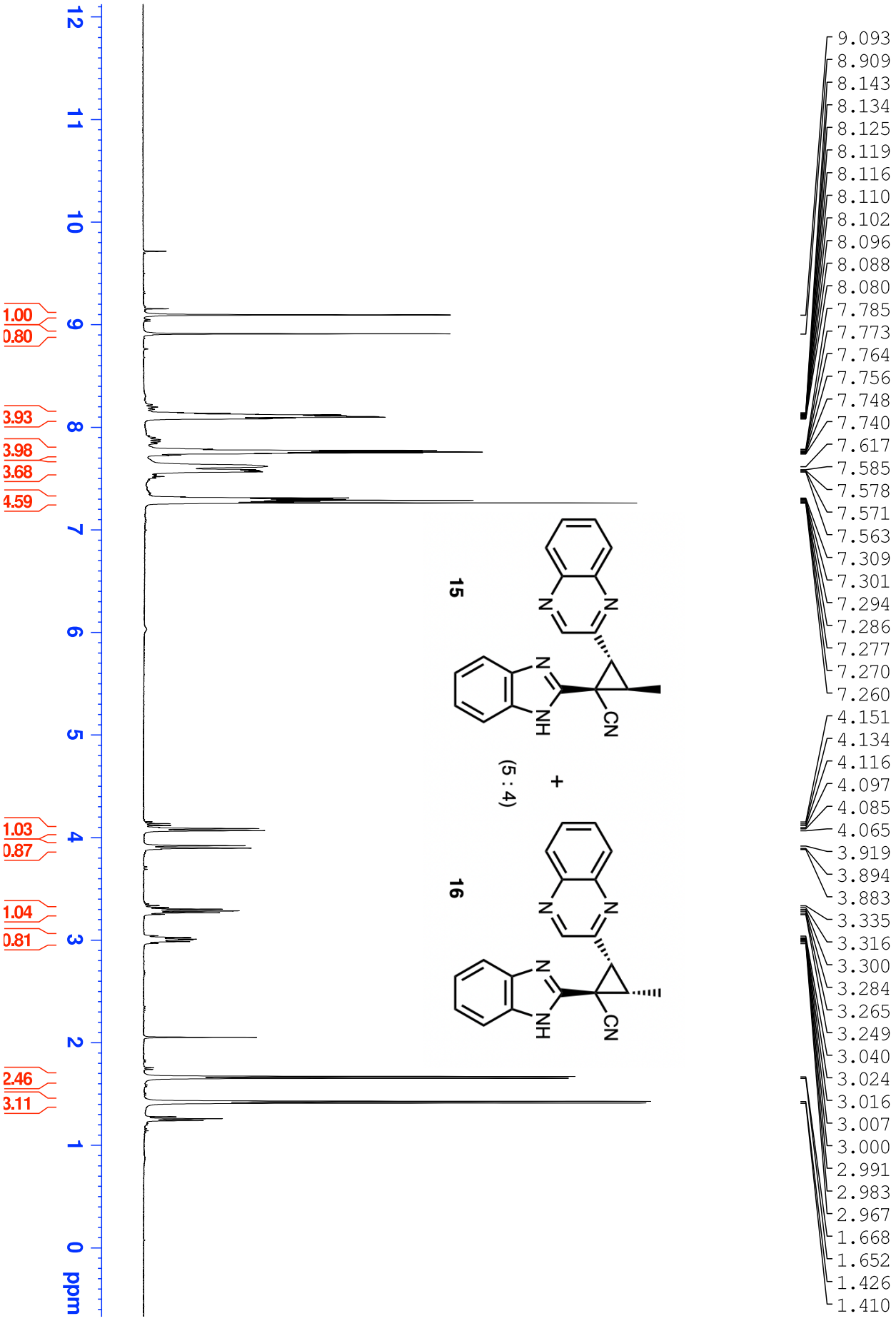
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3.68
4.59
1.03
0.87
1.04
0.81
2.46
3.11
15
16
(5 : 4)
+
N
NH
CN
9.093
8.909
8.143
8.134
8.125
8.119
8.116
8.110
8.102
8.096
8.088
8.080
7.785
7.773
7.764
7.756
7.748
7.740
7.617
7.585
7.578
7.571
7.563
7.309
7.301
7.294
7.286
7.277
7.270
7.260
4.151
4.134
4.116
4.097
4.085
4.065
3.919
3.894
3.883
3.335
3.316
3.300
3.284
3.265
3.249
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3.007
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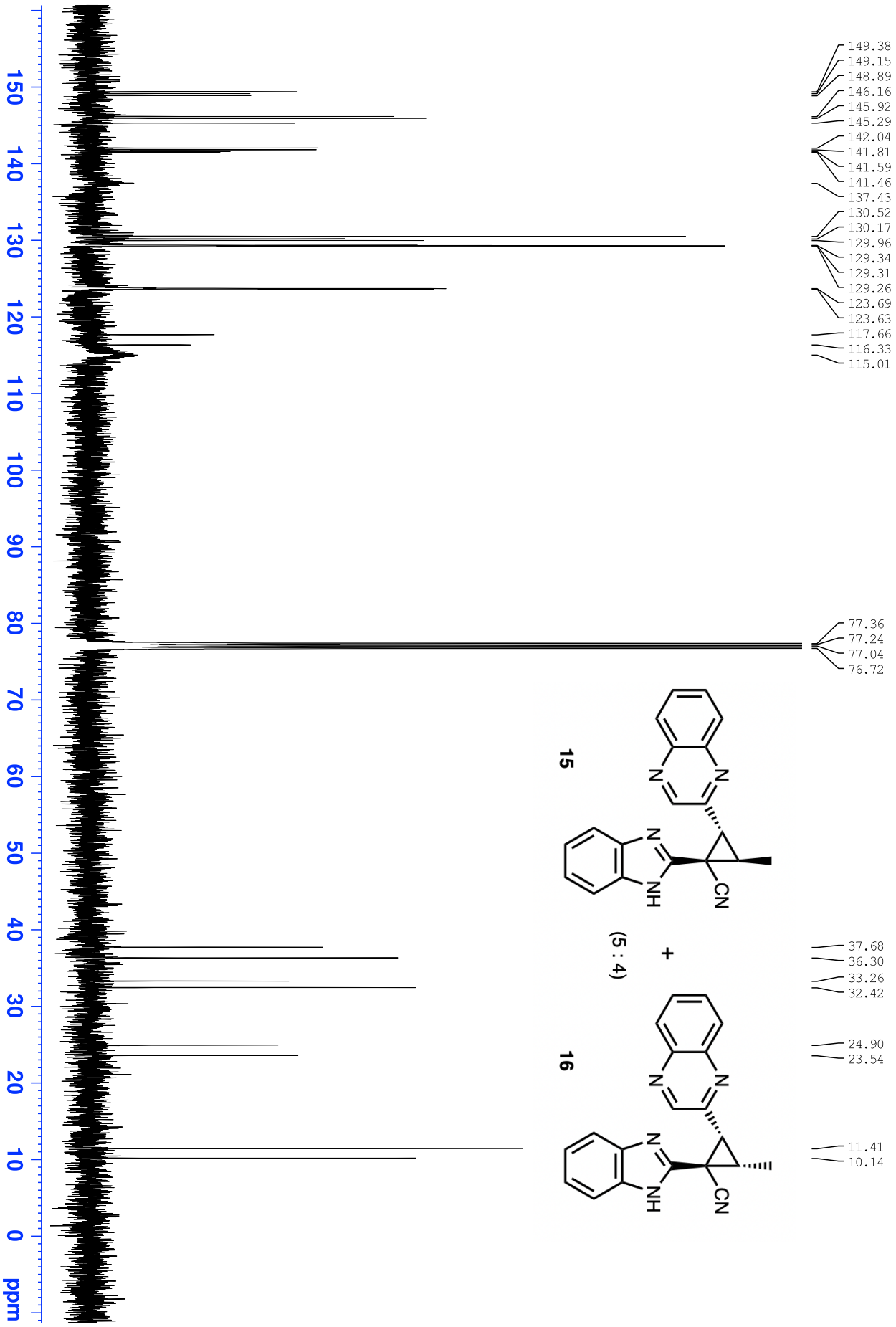
1.426
1.410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130.17
129.96
129.34
129.31
129.26
123.69
123.63
117.66
116.33
115.01
77.36
77.24
77.04
76.72
37.68
36.30
33.26
32.42
24.90
23.54
11.41
10.14
150
140
130
120
110
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60
50
40
30
20
10
0
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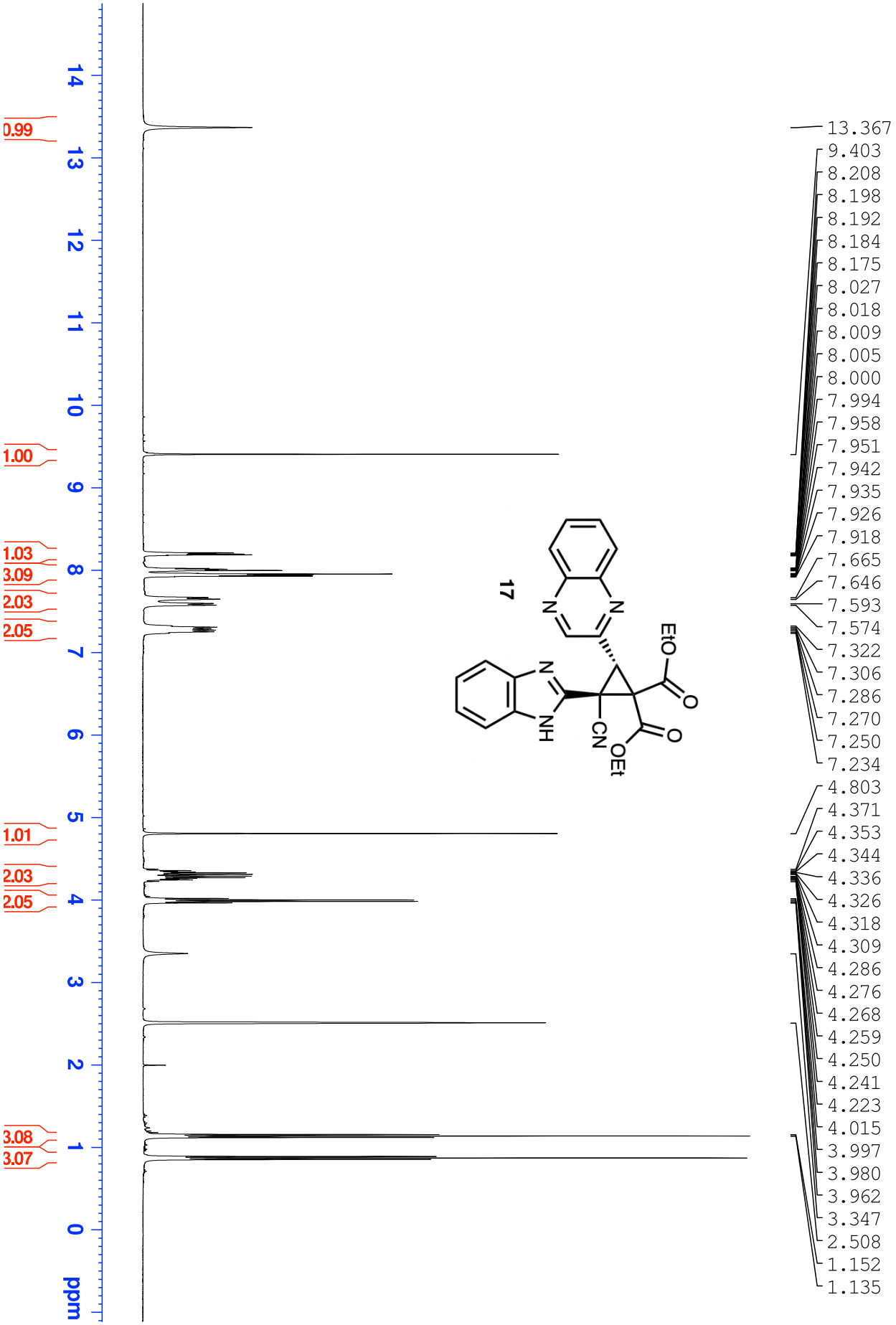
15
(5 : 4)
+
16
N
NH
CN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2.05
3.08
3.07
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13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
17
N
N
NH
CN
EtO
O
O
OEt
13.367
9.403
8.208
8.198
8.192
8.184
8.175
8.027
8.018
8.009
8.005
8.000
7.994
7.958
7.951
7.942
7.935
7.926
7.918
7.665
7.646
7.593
7.574
7.322
7.306
7.286
7.270
7.250
7.234
4.803
4.371
4.353
4.344
4.336
4.326
4.318
4.309
4.286
4.276
4.268
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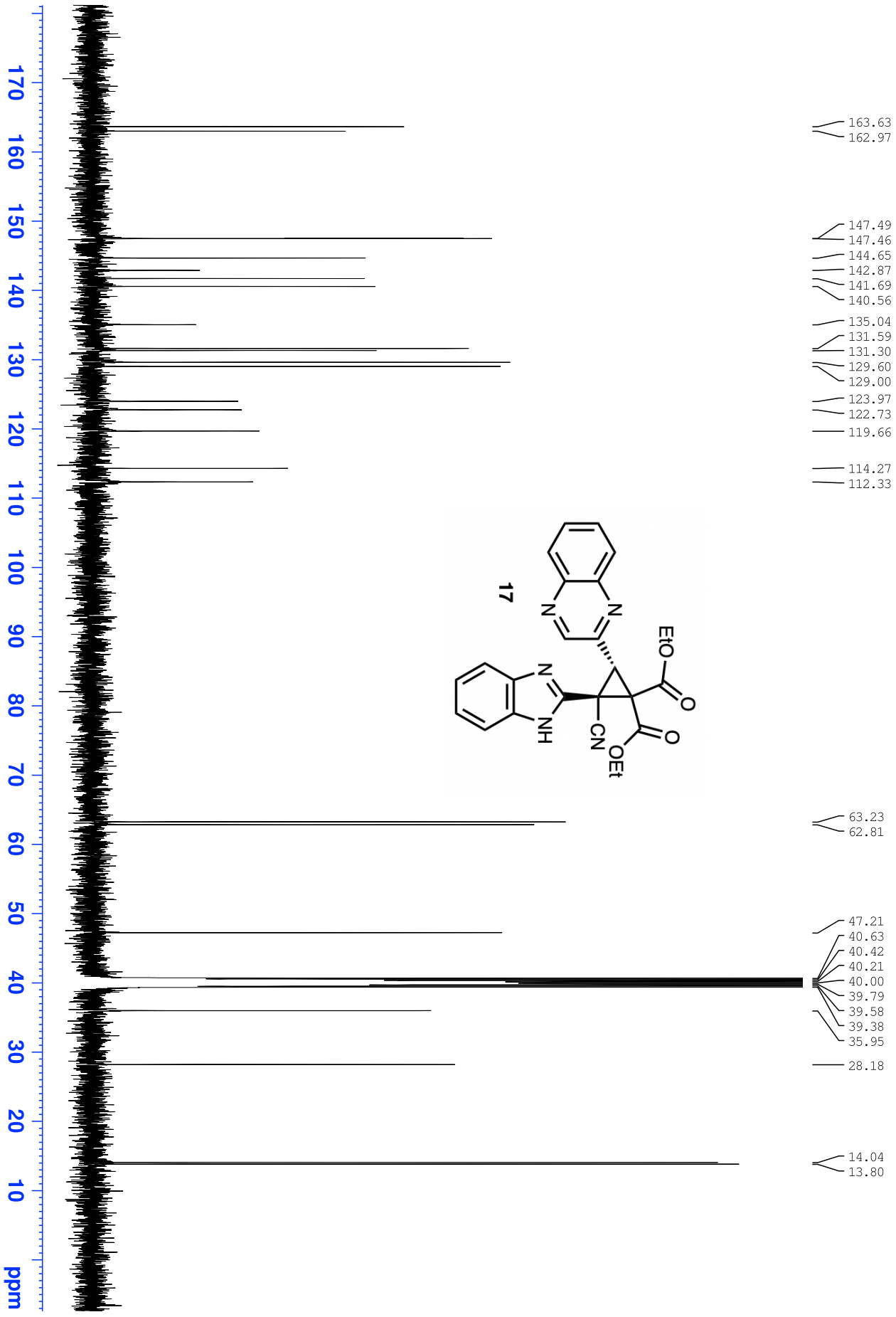
1.135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131.30
129.60
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122.73
119.66
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112.33
63.23
62.81
47.21
40.63
40.42
40.21
40.00
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39.58
39.38
35.95
28.18
14.04
13.80
170
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150
140
130
120
110
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ppm
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NH
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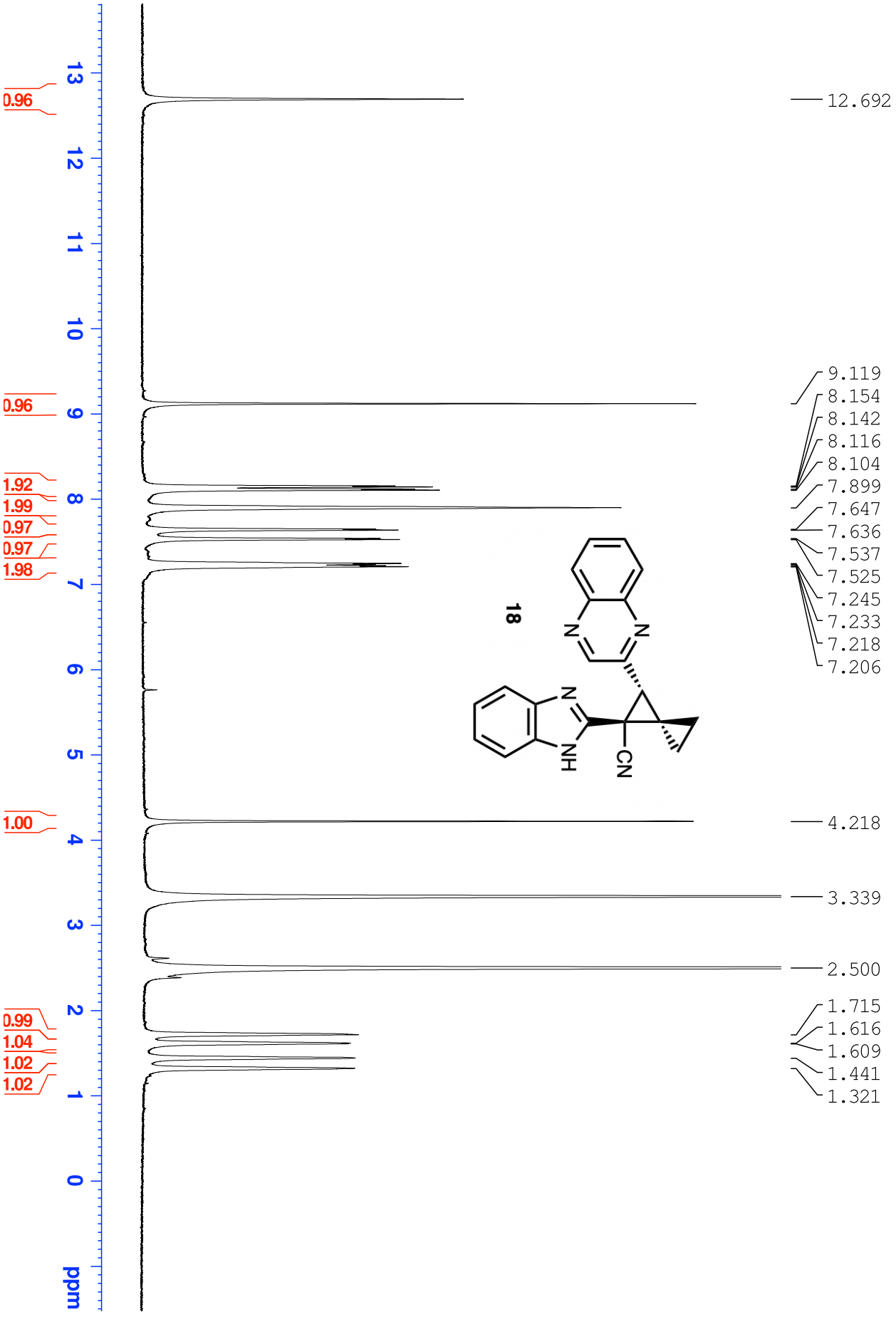
EtO
O
O
OEt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1.02
13
12
11
10
9
8
7
6
5
4
3
2
1
0
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8.142
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8.104
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7.636
7.537
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7.245
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1.616
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1.441
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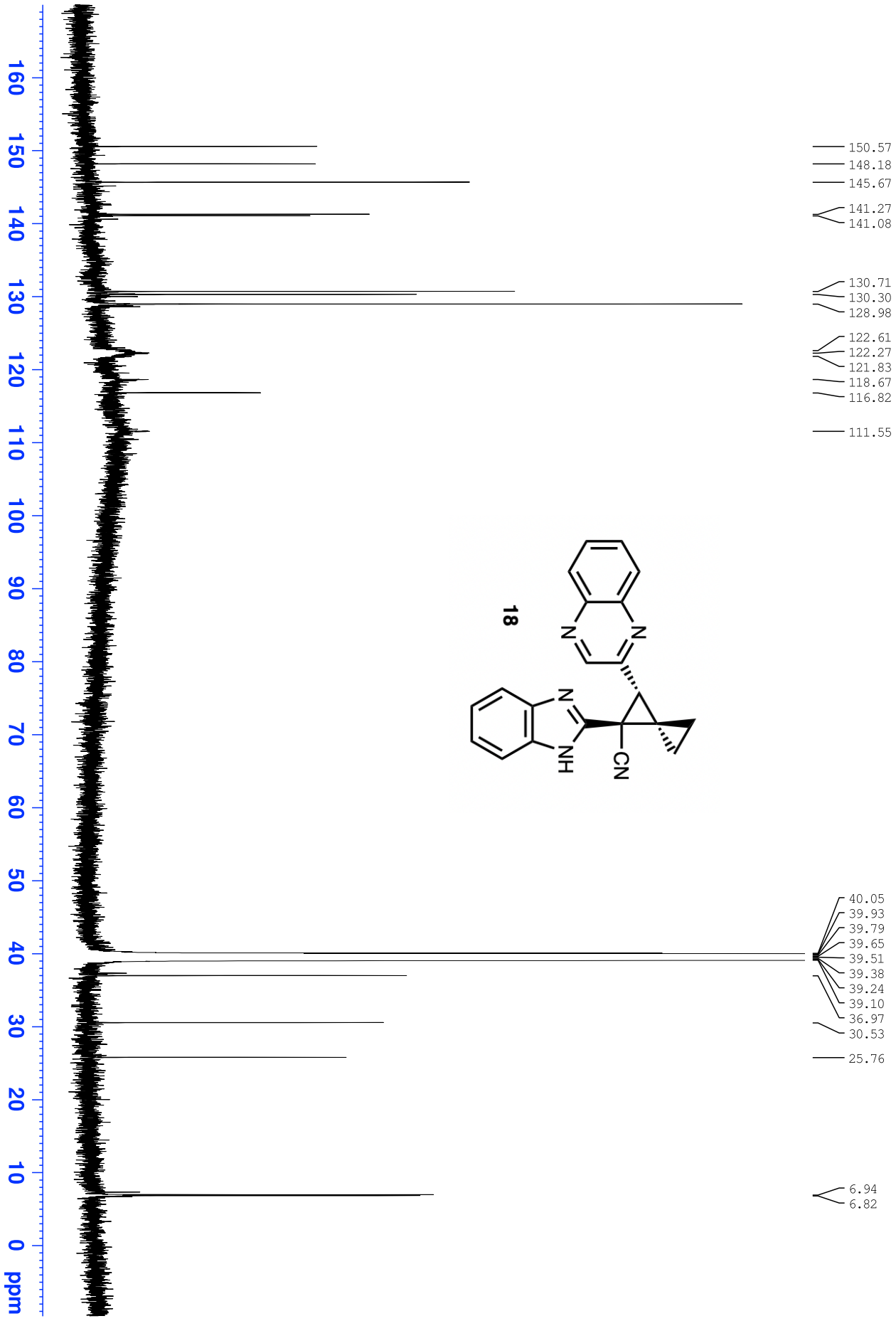
NH
CN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116.82
111.55
40.05
39.93
39.79
39.65
39.51
39.38
39.24
39.10
36.97
30.53
25.76
6.94
6.82
160
150
140
130
120
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80
70
60
50
40
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20
10
0
ppm

18

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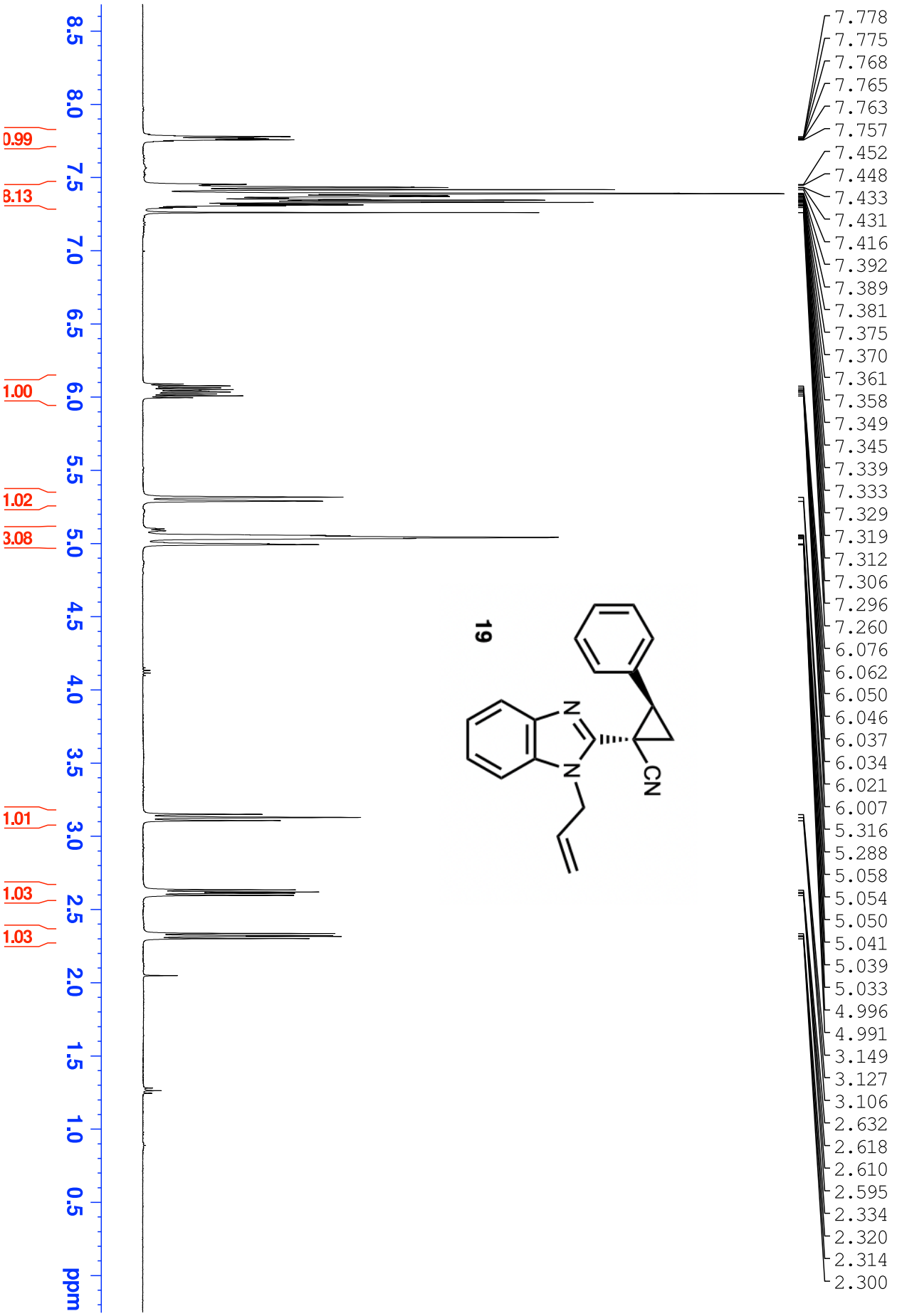
N
NH
CN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5.0
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4.0
3.5
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2.5
2.0
1.5
1.0
0.5
ppm
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8.13
1.00
1.02
3.08
1.01
1.03
1.03
19
N
N
CN
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7.433
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7.416
7.392
7.389
7.381
7.375
7.370
7.361
7.358
7.349
7.345
7.339
7.333
7.329
7.319
7.312
7.306
7.296
7.260
6.076
6.062
6.050
6.046
6.037
6.034
6.021
6.007
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5.288
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5.050
5.041
5.039
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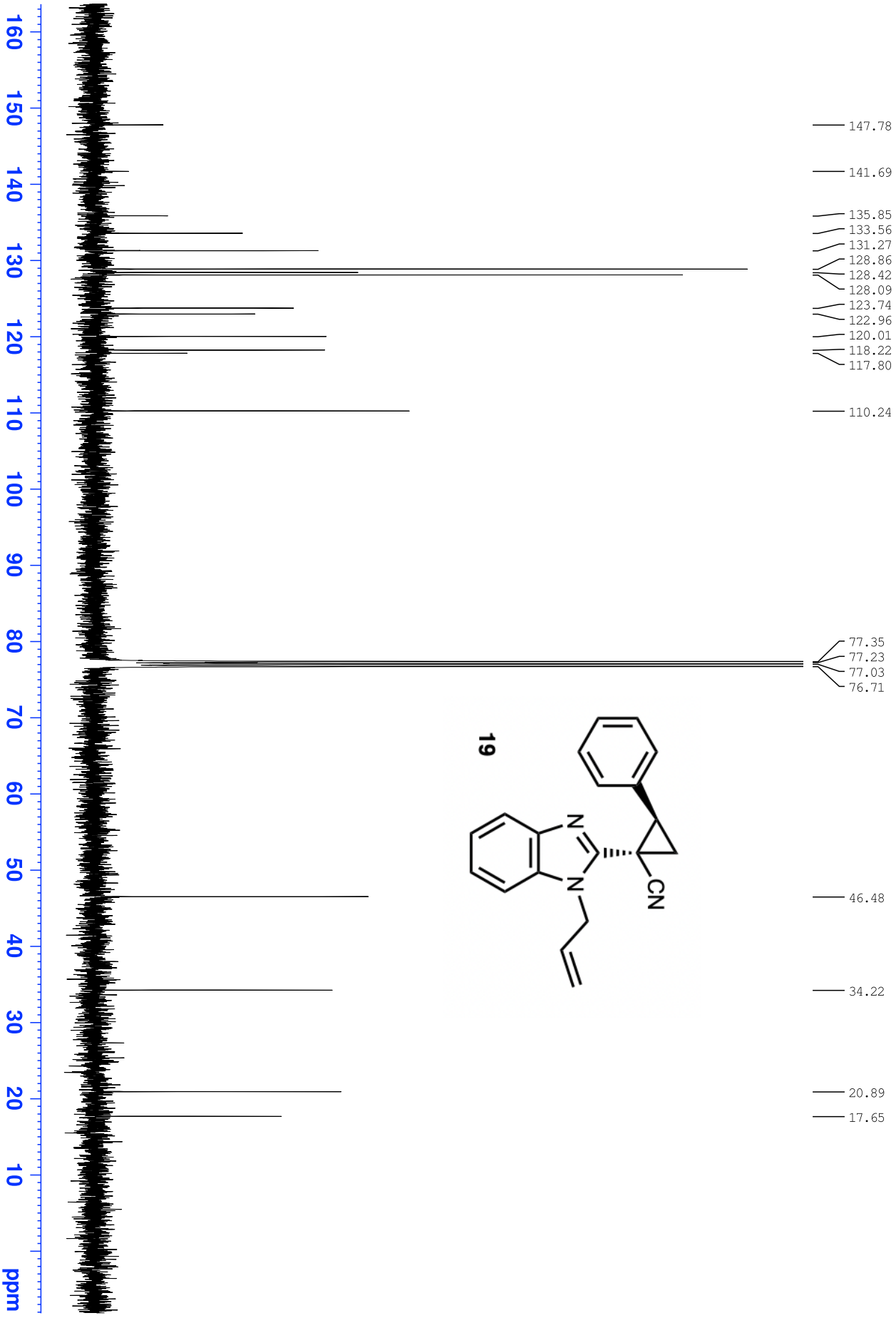
2.314
2.300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117.80
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77.35
77.23
77.03
76.71
46.48
34.22
20.89
17.65
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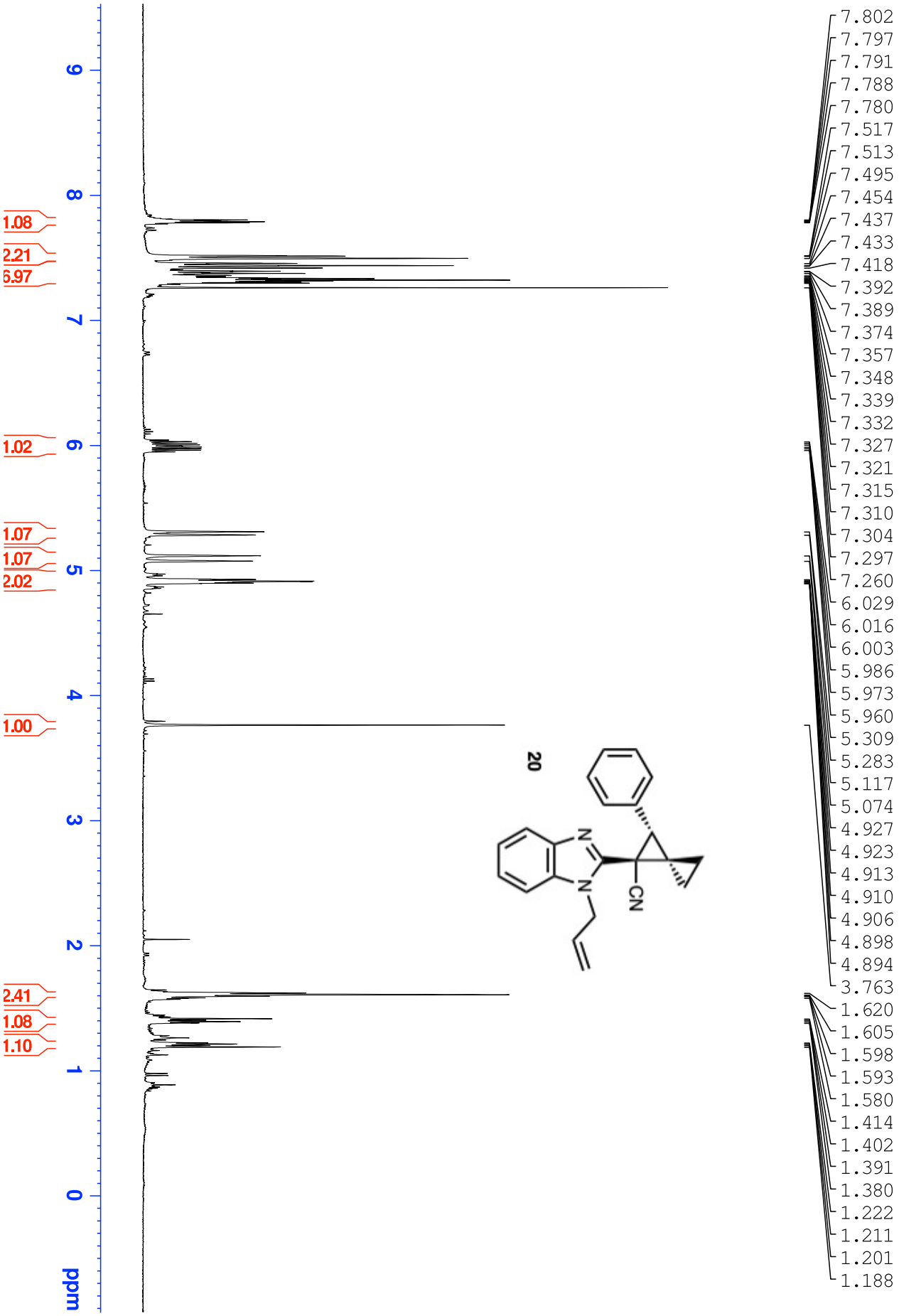
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1.07
2.02
1.00
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1.08
1.10
20
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N
CN
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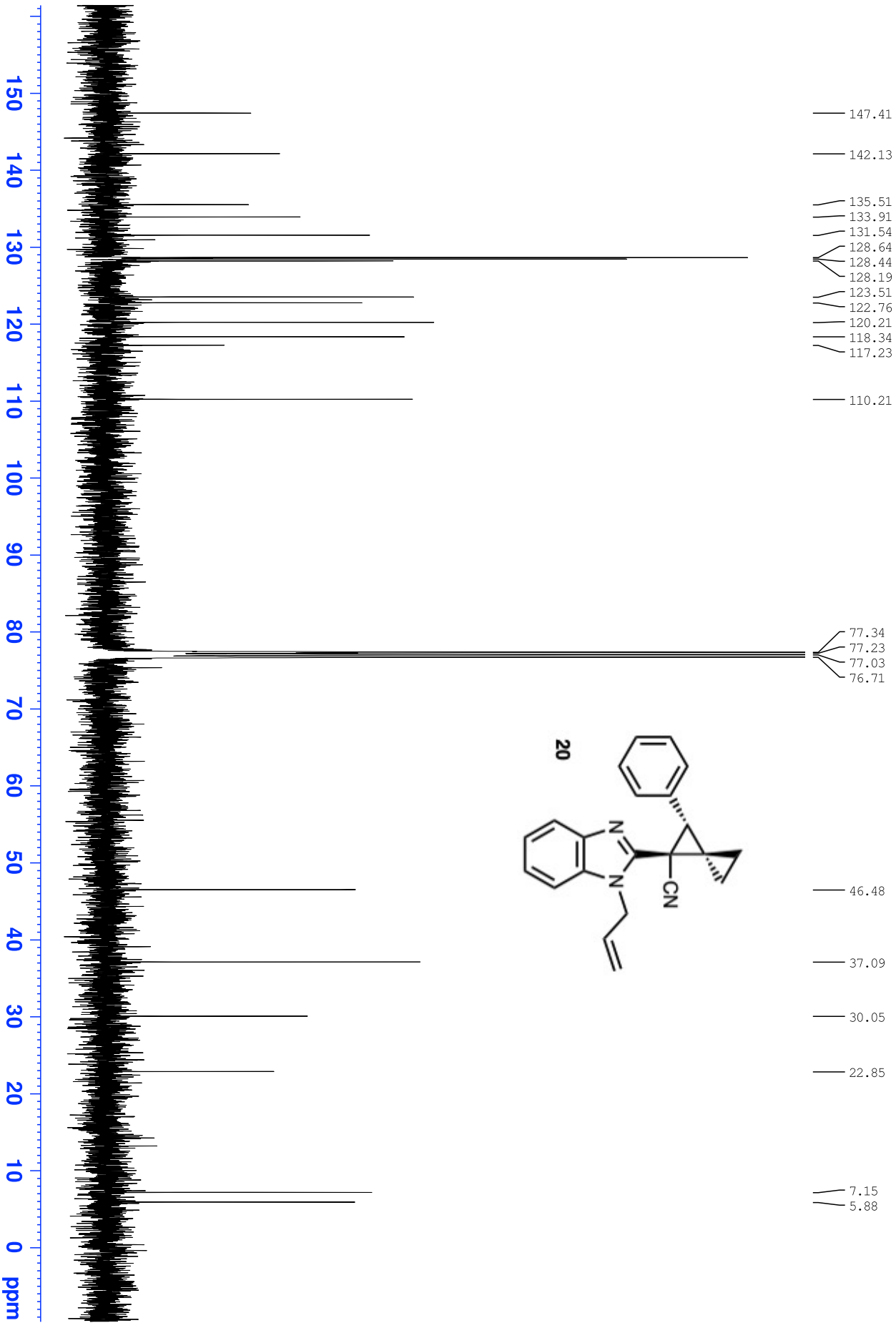
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77.34
77.23
77.03
76.71
46.48
37.09
30.05
22.85
7.15
5.88
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N
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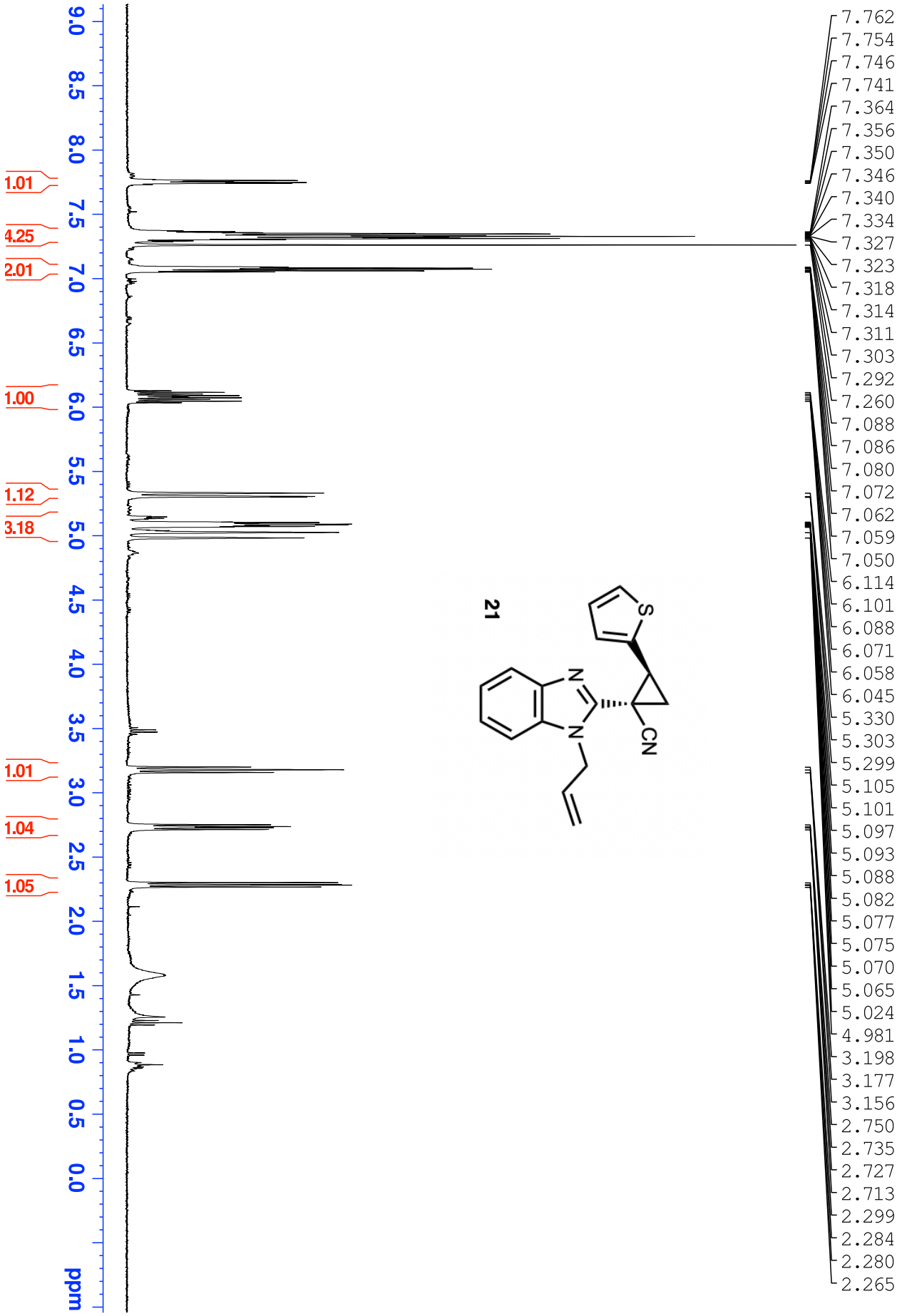
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1.0
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7.086
7.080
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5.303
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5.101
5.097
5.093
5.088
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5.077
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5.070
5.065
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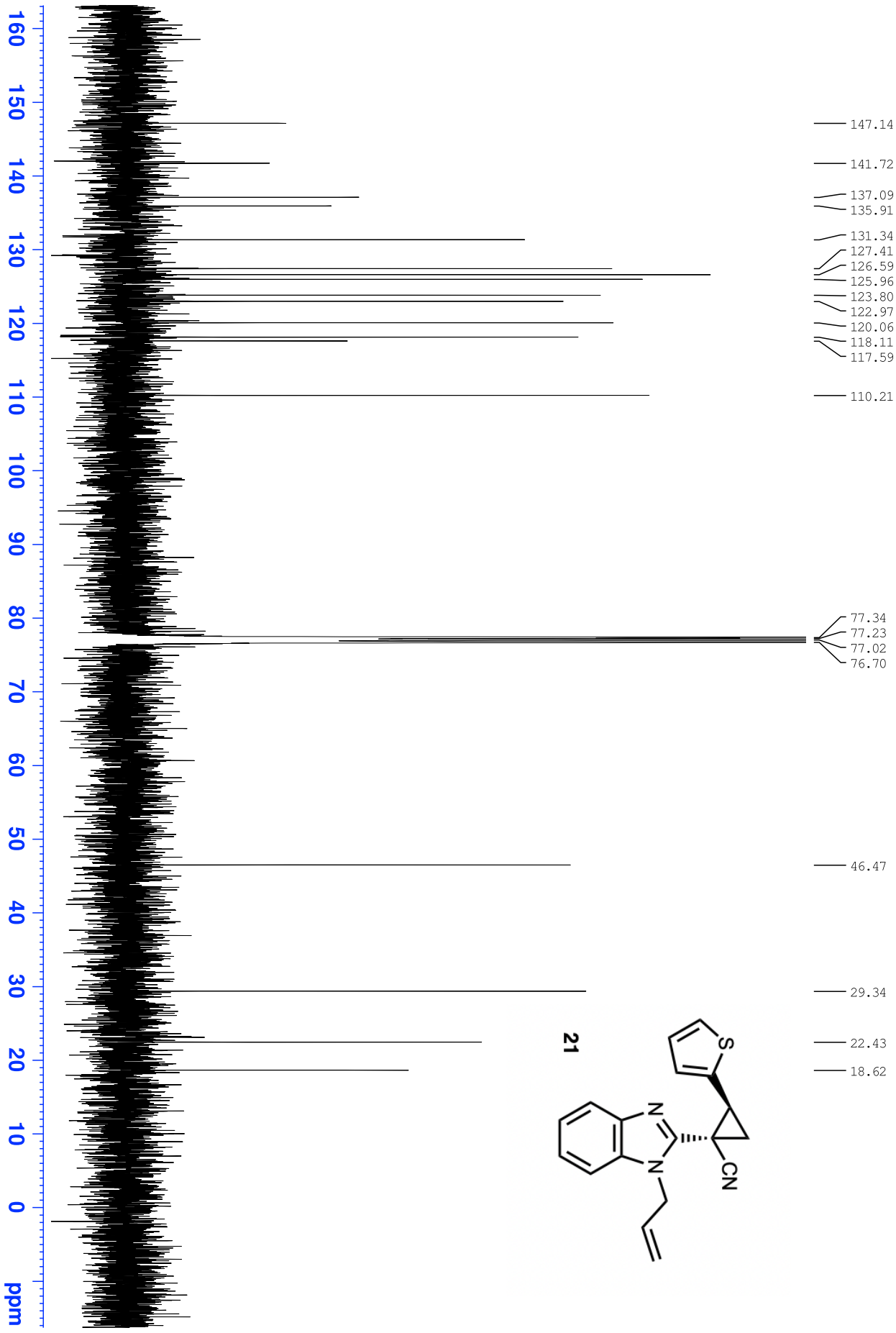
N
CN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110.21
77.34
77.23
77.02
76.70
46.47
29.34
22.43
18.62
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150
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90
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50
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10
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S
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N
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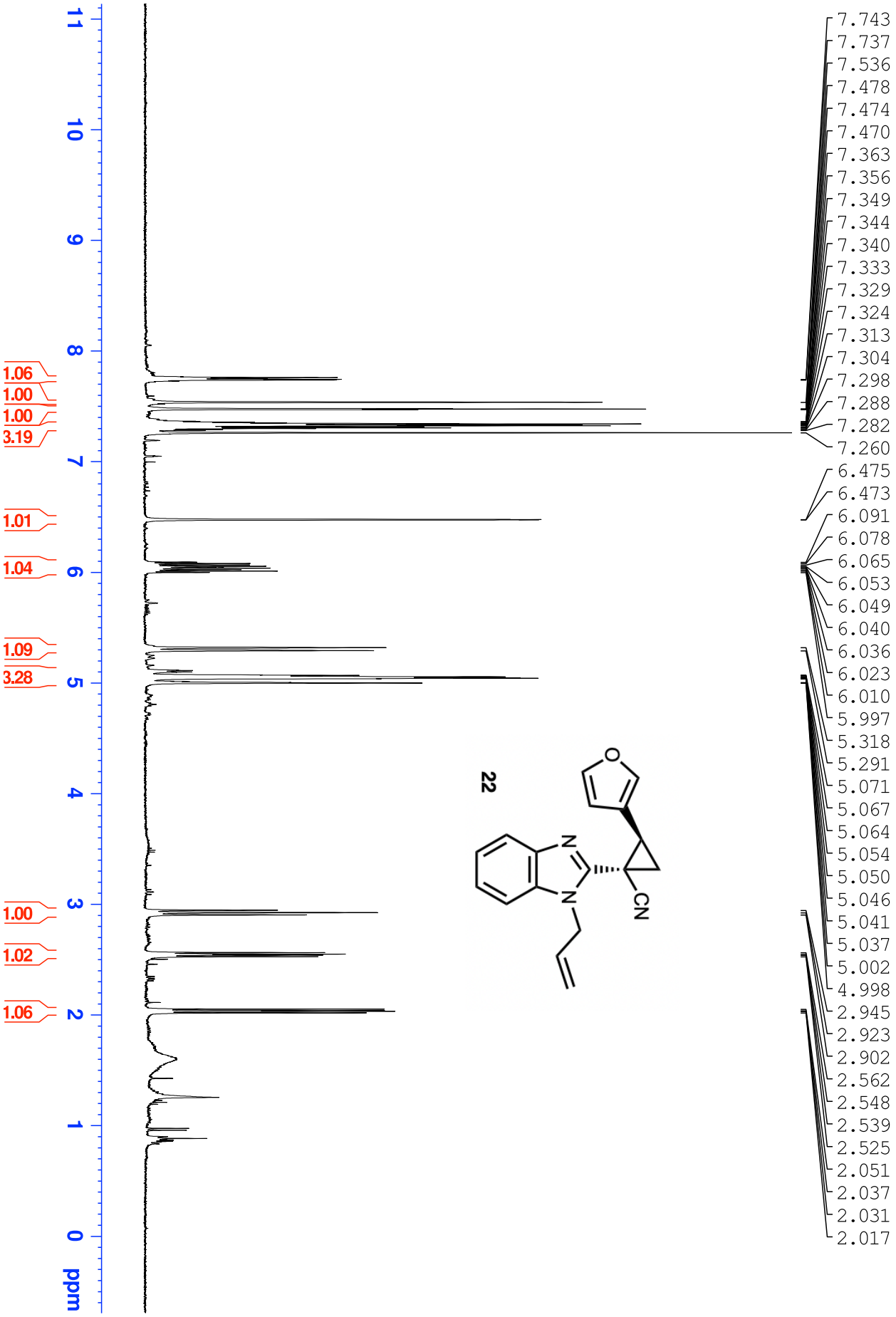
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10
9
8
7
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2
1
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1.00
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1.01
1.04
1.09
3.28
1.00
1.02
1.06
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7.474
7.470
7.363
7.356
7.349
7.344
7.340
7.333
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7.313
7.304
7.298
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7.282
7.260
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6.473
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6.053
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6.023
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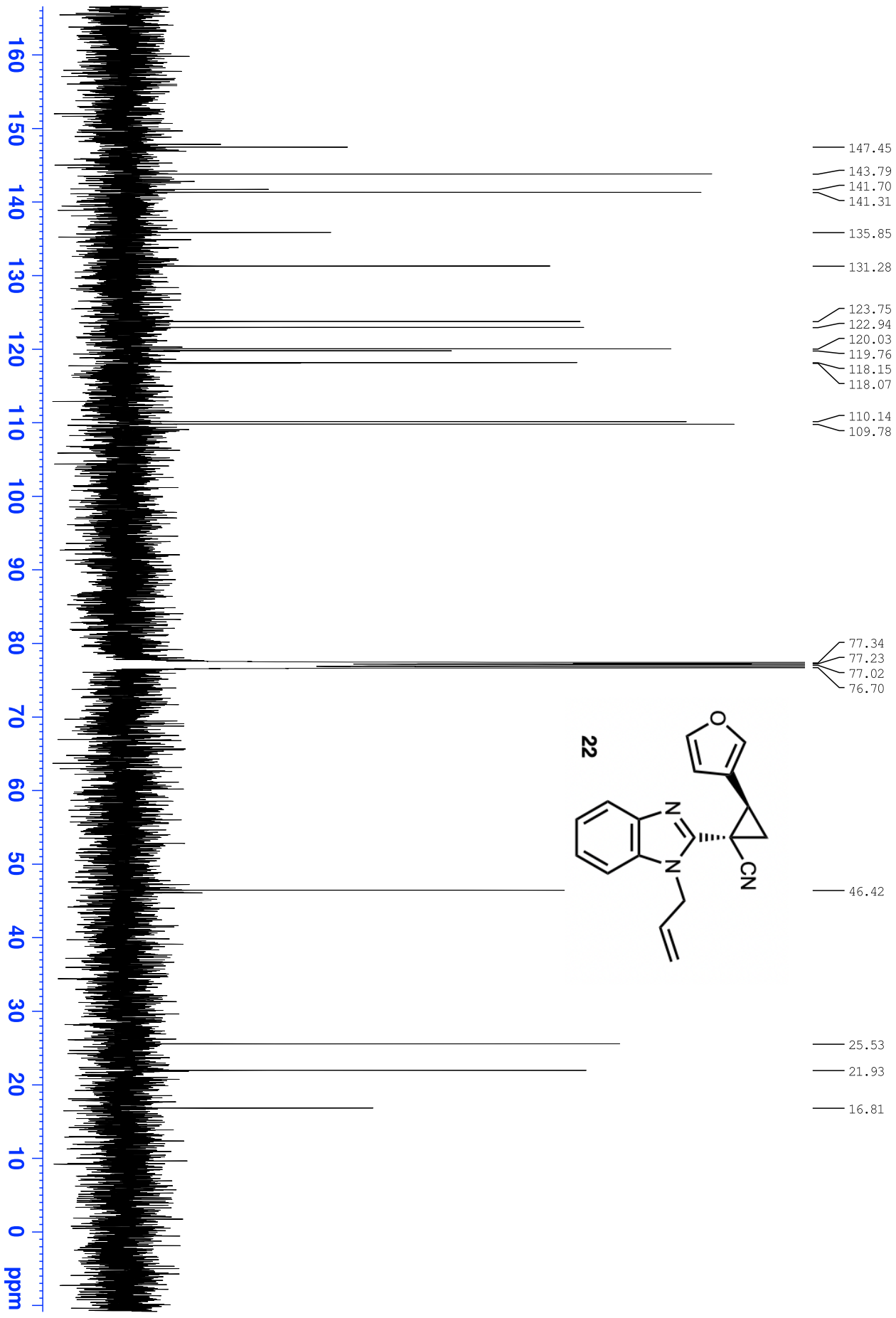
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109.78
77.34
77.23
77.02
76.70
46.42
25.53
21.93
16.81
22
N
N
CN
O
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120
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100
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60
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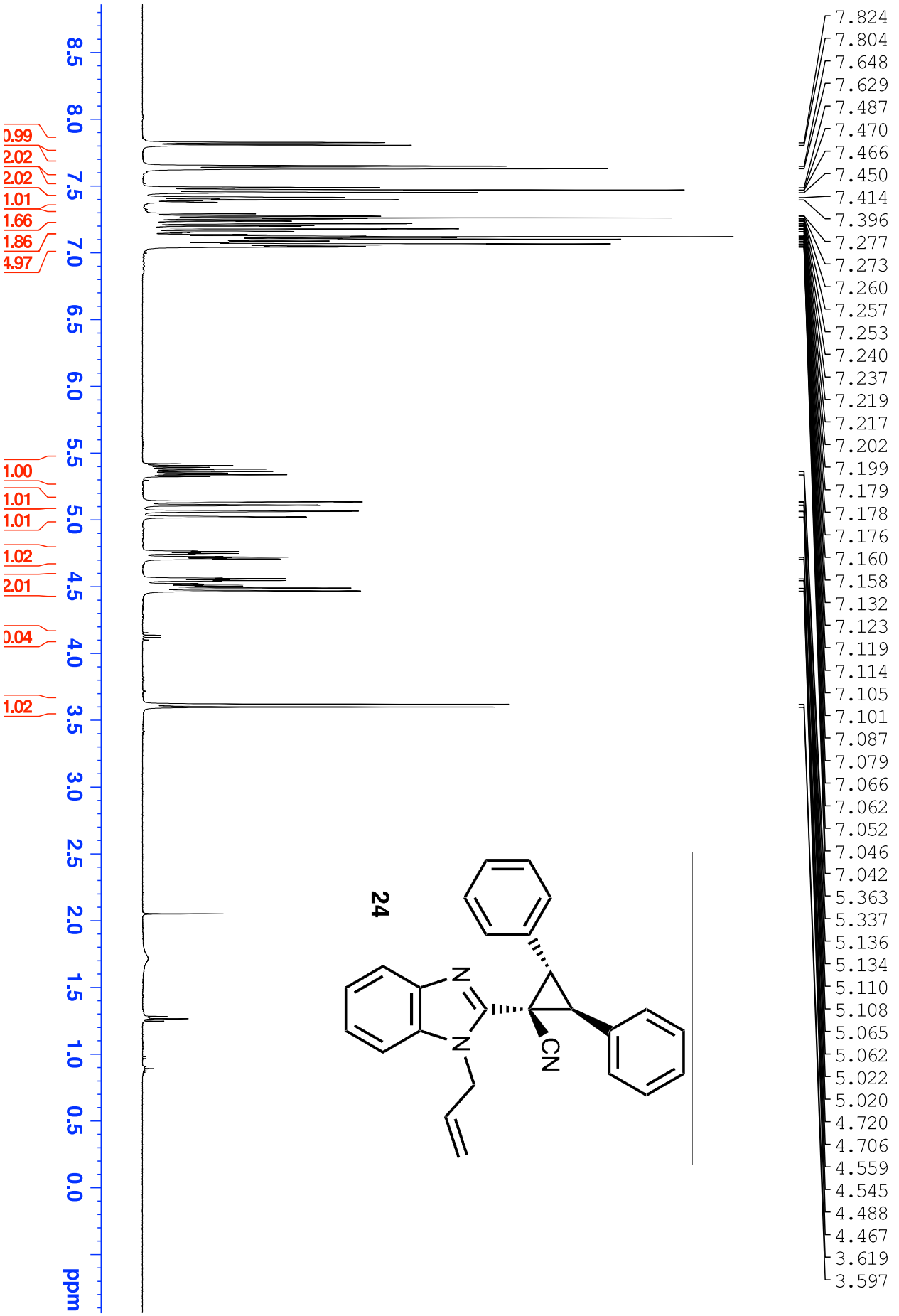
0
ppm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1.01
1.02
2.01
0.04
1.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
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7.253
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7.237
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7.217
7.202
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4.467
3.619
3.597
24
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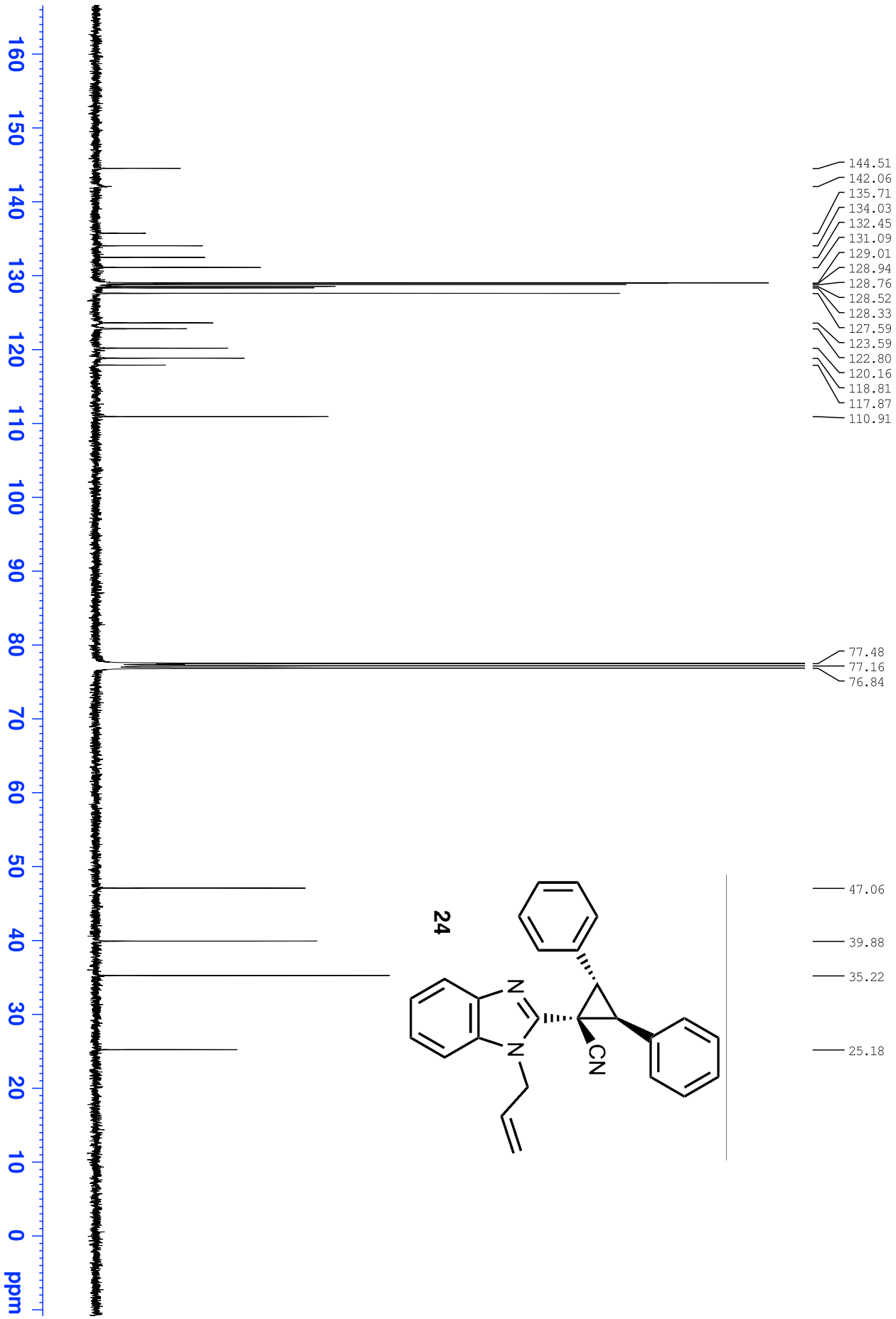
N
CN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142.06
135.71
134.03
132.45
131.09
129.01
128.94
128.76
128.52
128.33
127.59
123.59
122.80
120.16
118.81
117.87
110.91
77.48
77.16
76.84
47.06
39.88
35.22
25.18
160
150
140
130
120
110
100
90
80
70
60
50
40
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20
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0
ppm
24
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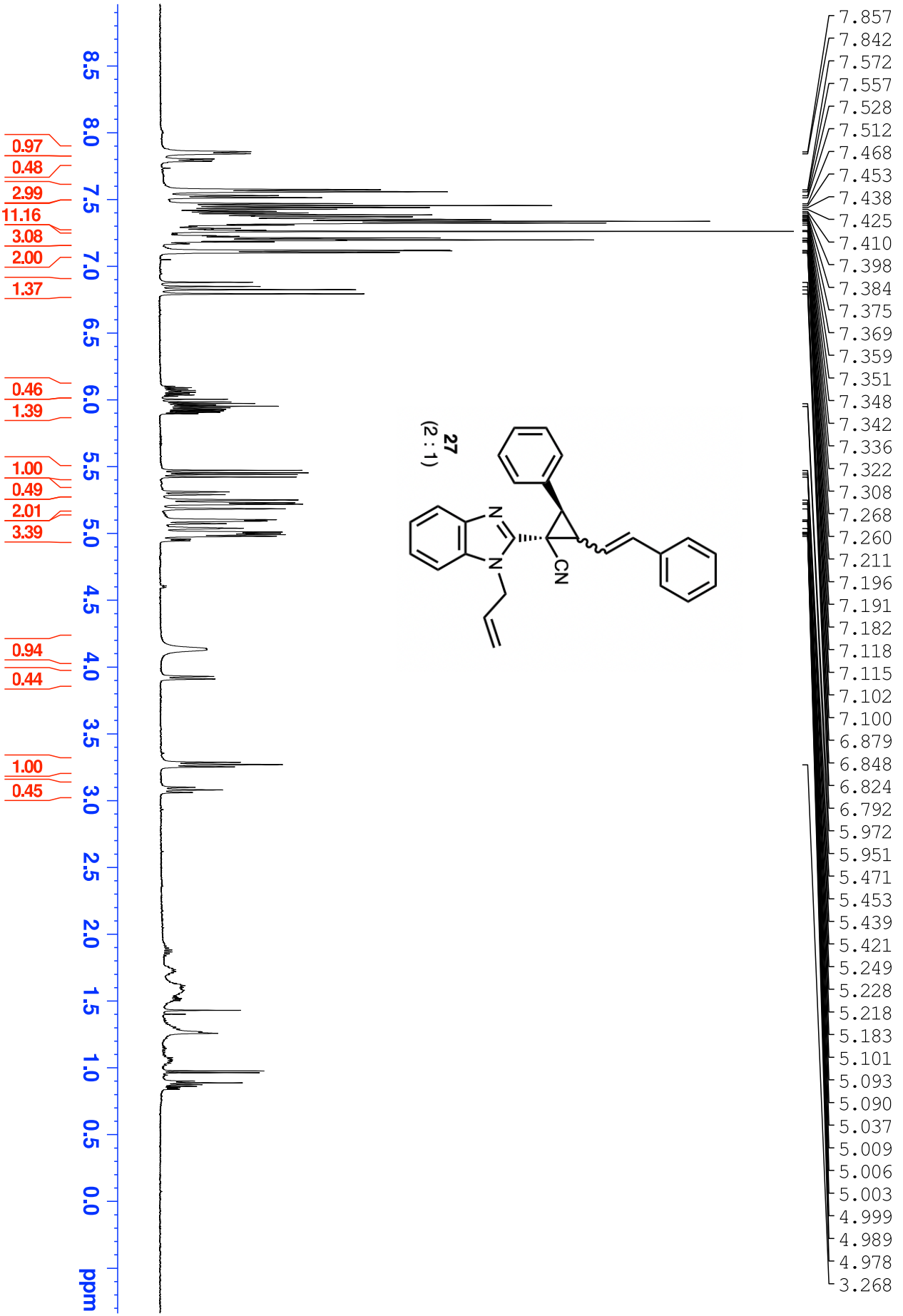
N
CN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2.99
11.16
3.08
2.00
1.37
0.46
1.39
1.00
0.49
2.01
3.39
0.94
0.44
1.00
0.45
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
27
(2 : 1)
N
N
CN
7.857
7.842
7.572
7.557
7.528
7.512
7.468
7.453
7.438
7.425
7.410
7.398
7.384
7.375
7.369
7.359
7.351
7.348
7.342
7.336
7.322
7.308
7.268
7.260
7.211
7.196
7.191
7.182
7.118
7.115
7.102
7.100
6.879
6.848
6.824
6.792
5.972
5.951
5.471
5.453
5.439
5.421
5.249
5.228
5.218
5.183
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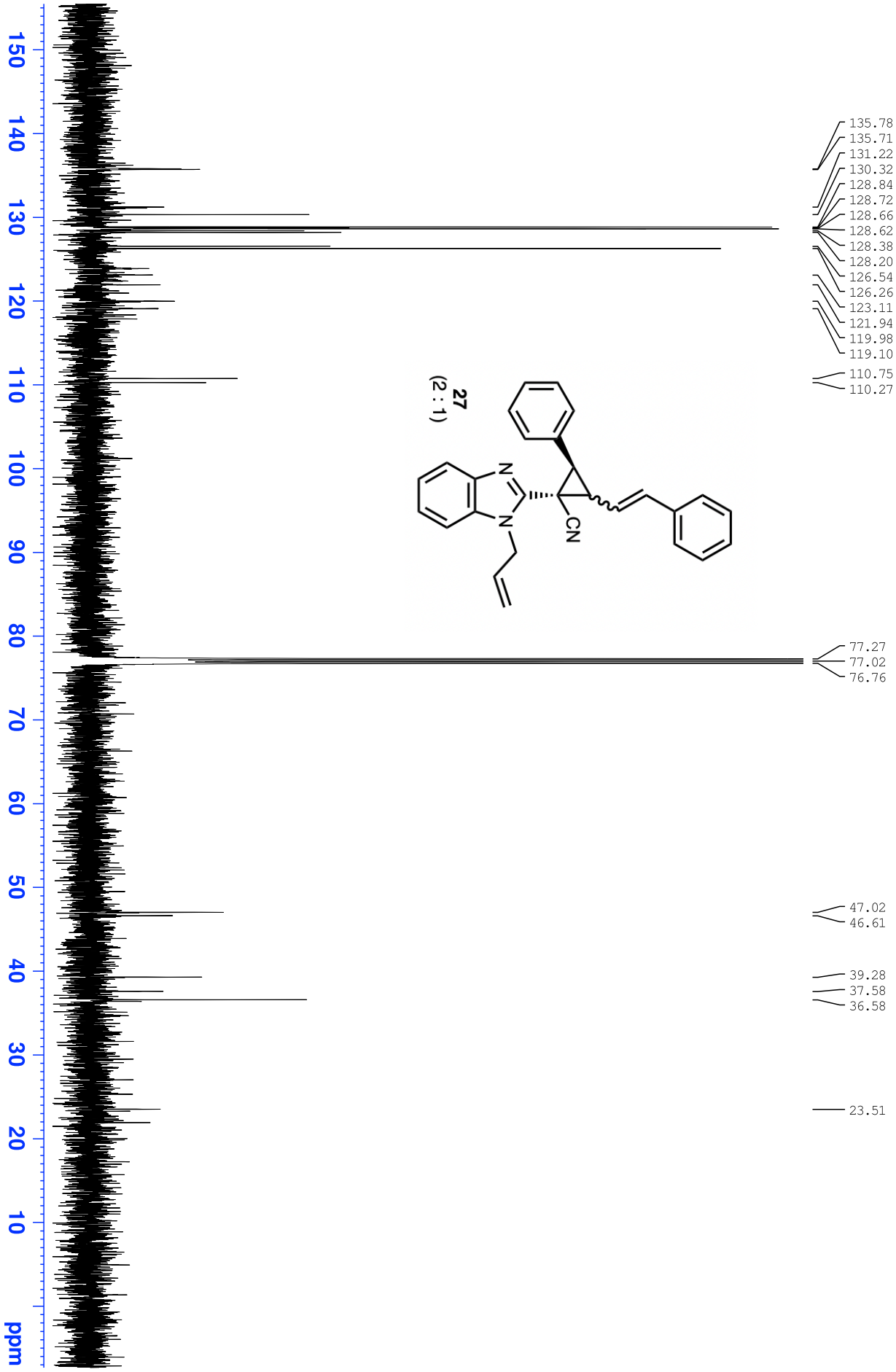
5.093
5.090
5.037
5.009
5.006
5.003
4.999
4.989
4.978
3.268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131.22
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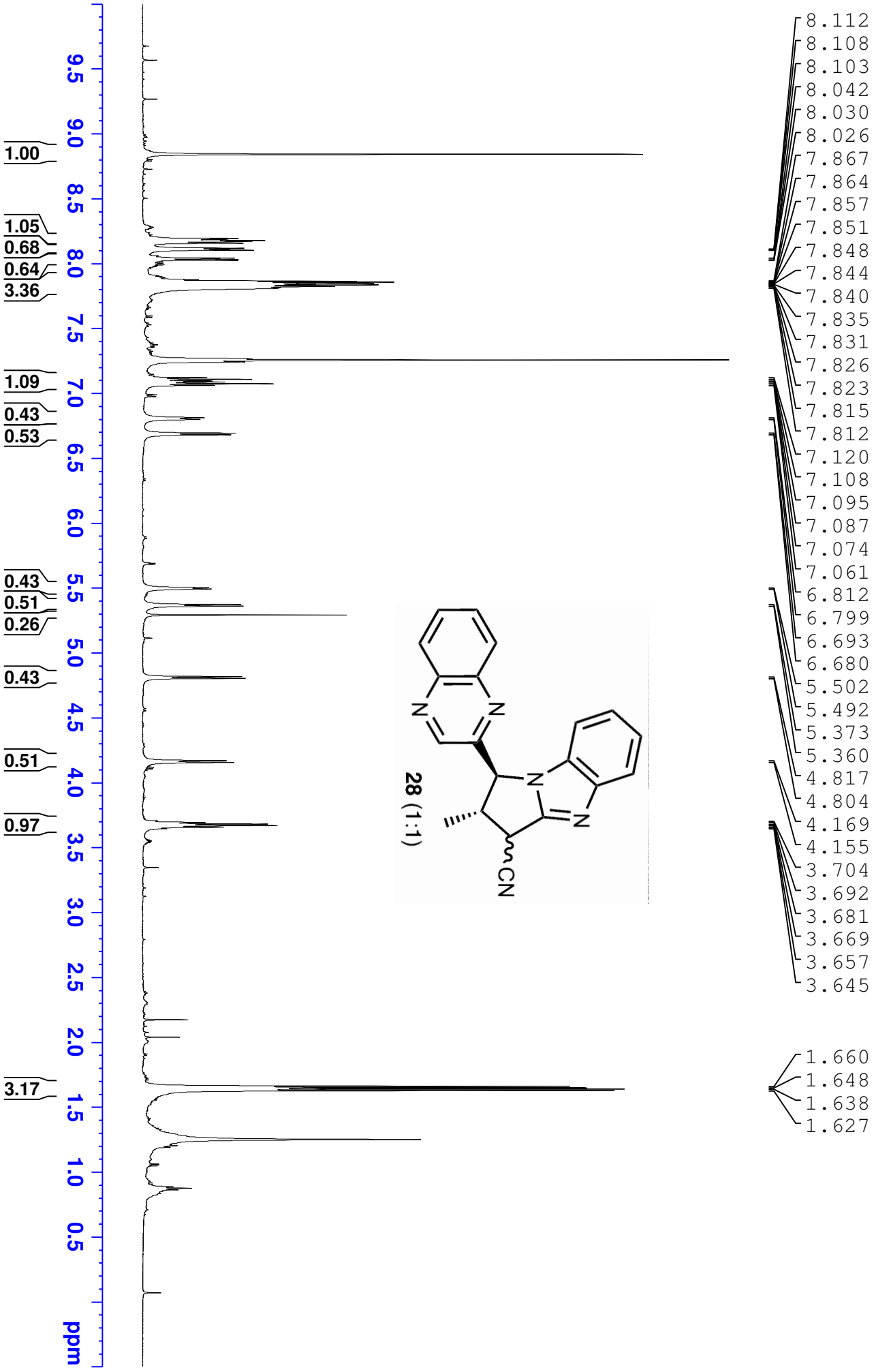
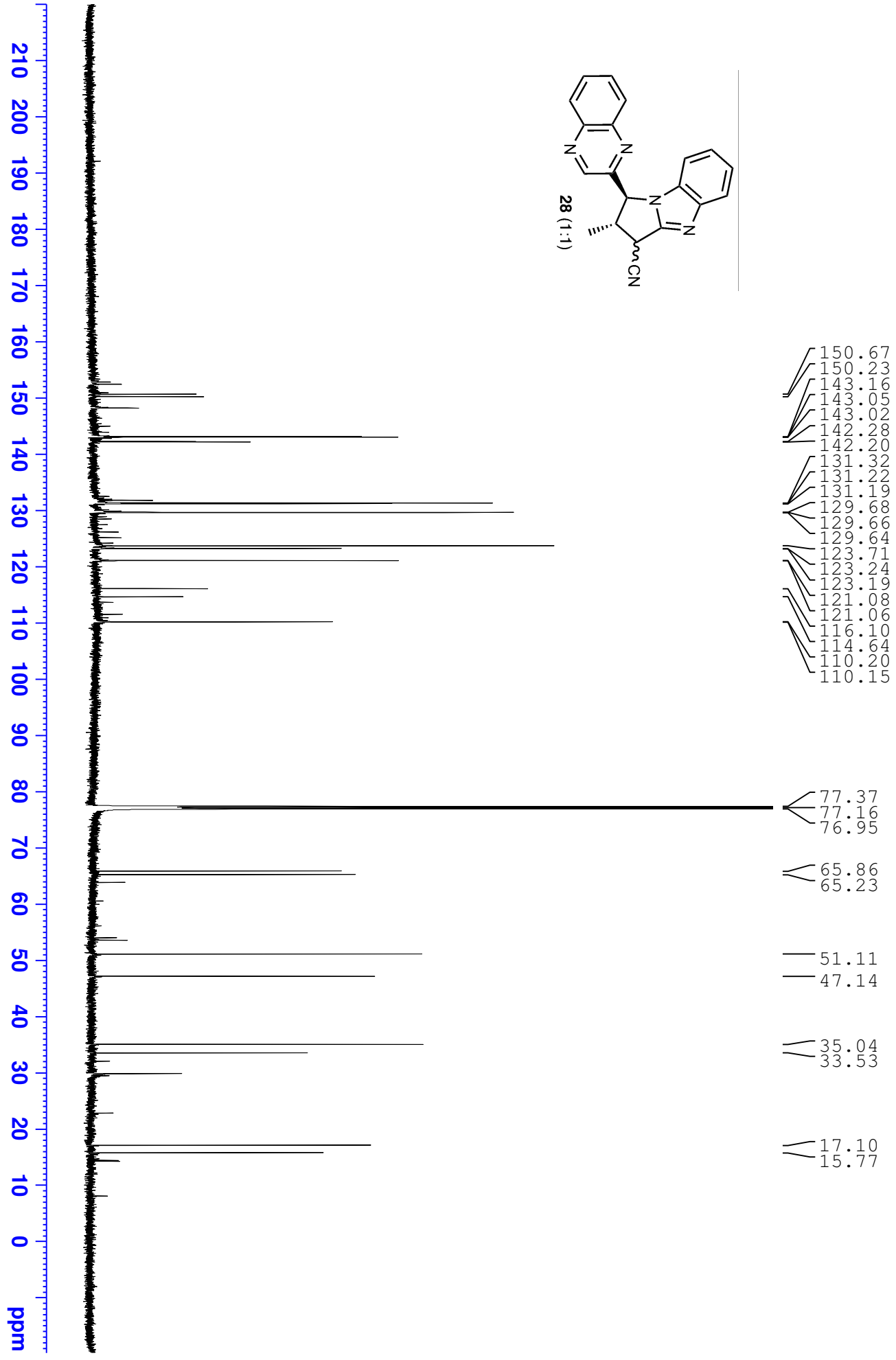
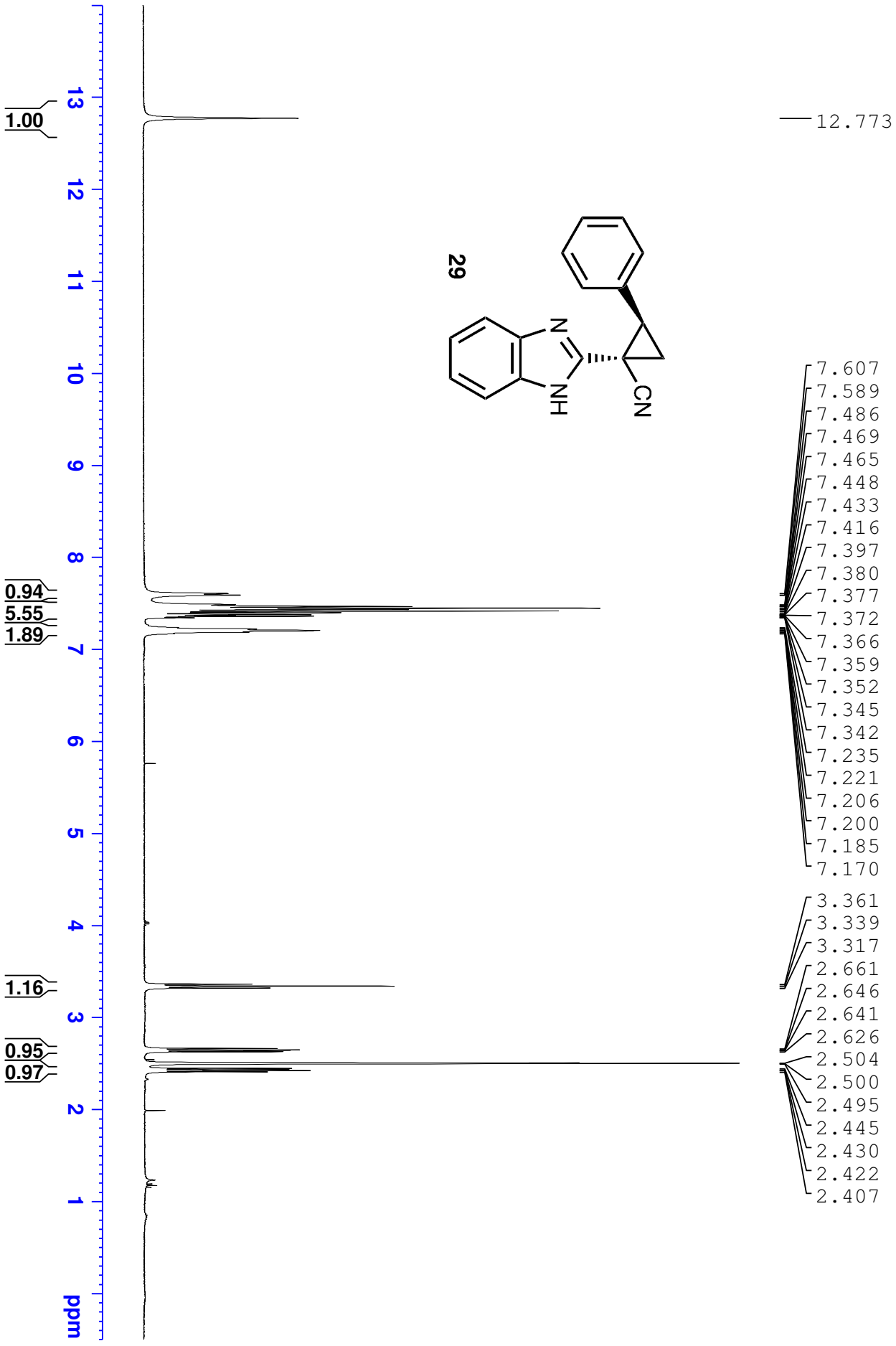
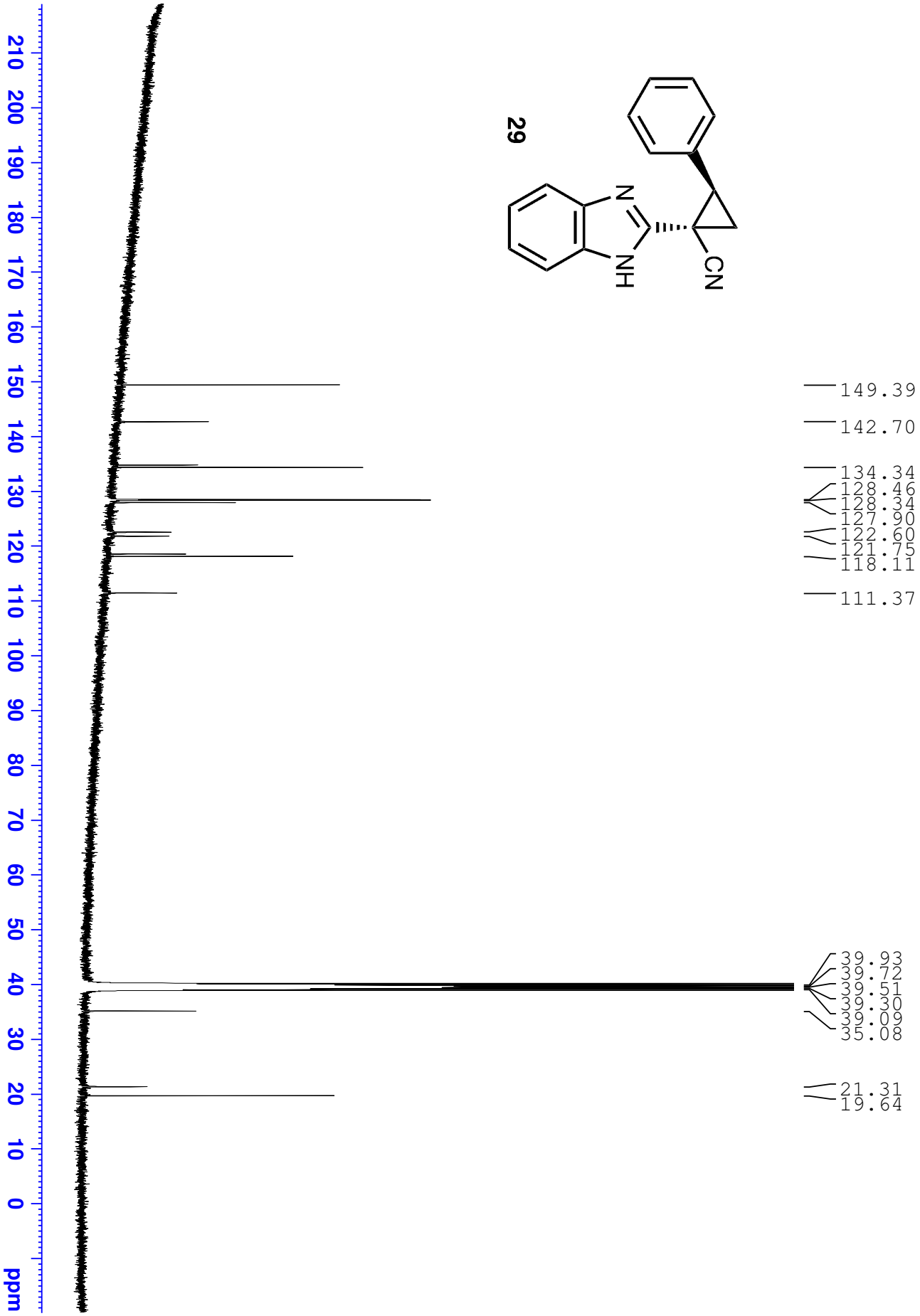
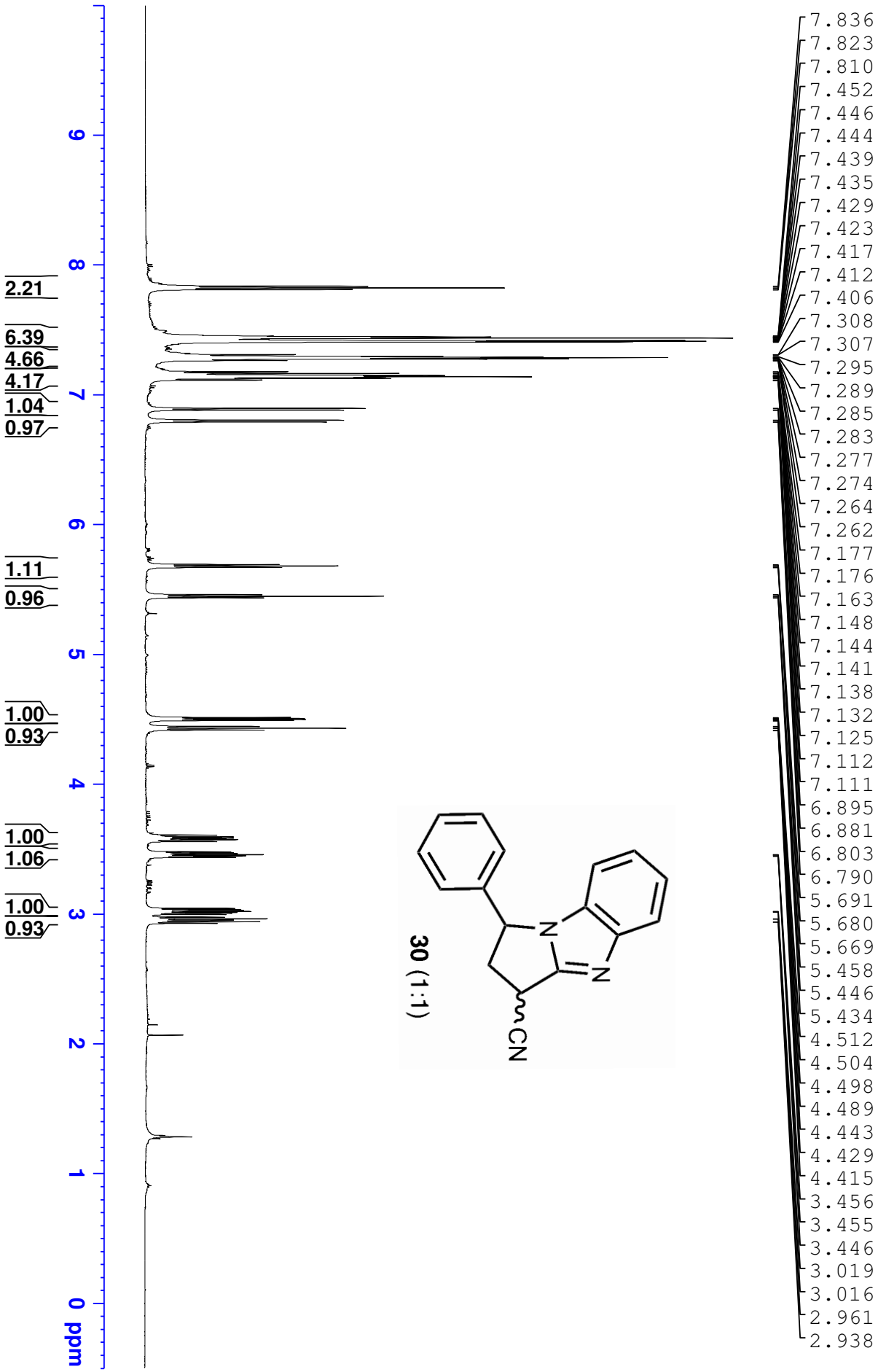
128.84
128.72
128.66
128.62
128.38
128.20
126.54
126.26
123.11
121.94
119.98
119.10
110.75
110.27
77.27
77.02
76.76
47.02
46.61
39.28
37.58
36.58
23.51
27
(2 : 1)
N
N
CN
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.112
8.108
8.103
8.042
8.030
8.026
7.867
7.864
7.857
7.851
7.848
7.844
7.840
7.835
7.831
7.826
7.823
7.815
7.812
7.120
7.108
7.095
7.087
7.074
7.061
6.812
6.799
6.693
6.680
5.502
5.492
5.373
5.360
4.817
4.804
4.169
4.155
3.704
3.692
3.681
3.669
3.657
3.645
1.660
1.648
1.638
1.627
1.00
1.05
0.68
0.64
3.36
1.09
0.43
0.53
0.43
0.51
0.26
0.43
0.51
0.97
3.17
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
ppm
28 (1:1)
N
N
N
N
CN


28 (1:1)
CN
150.67
150.23
143.16
143.05
143.02
142.28
142.20
131.32
131.22
131.19
129.68
129.66
129.64
123.71
123.24
123.19
121.08
121.06
116.10
114.64
110.20
110.15
77.37
77.16
76.95
65.86
65.23
51.11
47.14
35.04
33.53
17.10
15.77
ppm


29
N
NH
CN
12.773
7.607
7.589
7.486
7.469
7.465
7.448
7.433
7.416
7.397
7.380
7.377
7.372
7.366
7.359
7.352
7.345
7.342
7.235
7.221
7.206
7.200
7.185
7.170
3.361
3.339
3.317
2.661
2.646
2.641
2.626
2.504
2.500
2.495
2.445
2.430
2.422
2.407
1.00
0.94
5.55
1.89
1.16
0.95
0.97
ppm


29
N
NH
CN
149.39
142.70
134.34
128.46
128.34
127.90
122.60
121.75
118.11
111.37
39.93
39.72
39.51
39.30
39.09
35.08
21.31
19.64
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.823
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7.446
7.444
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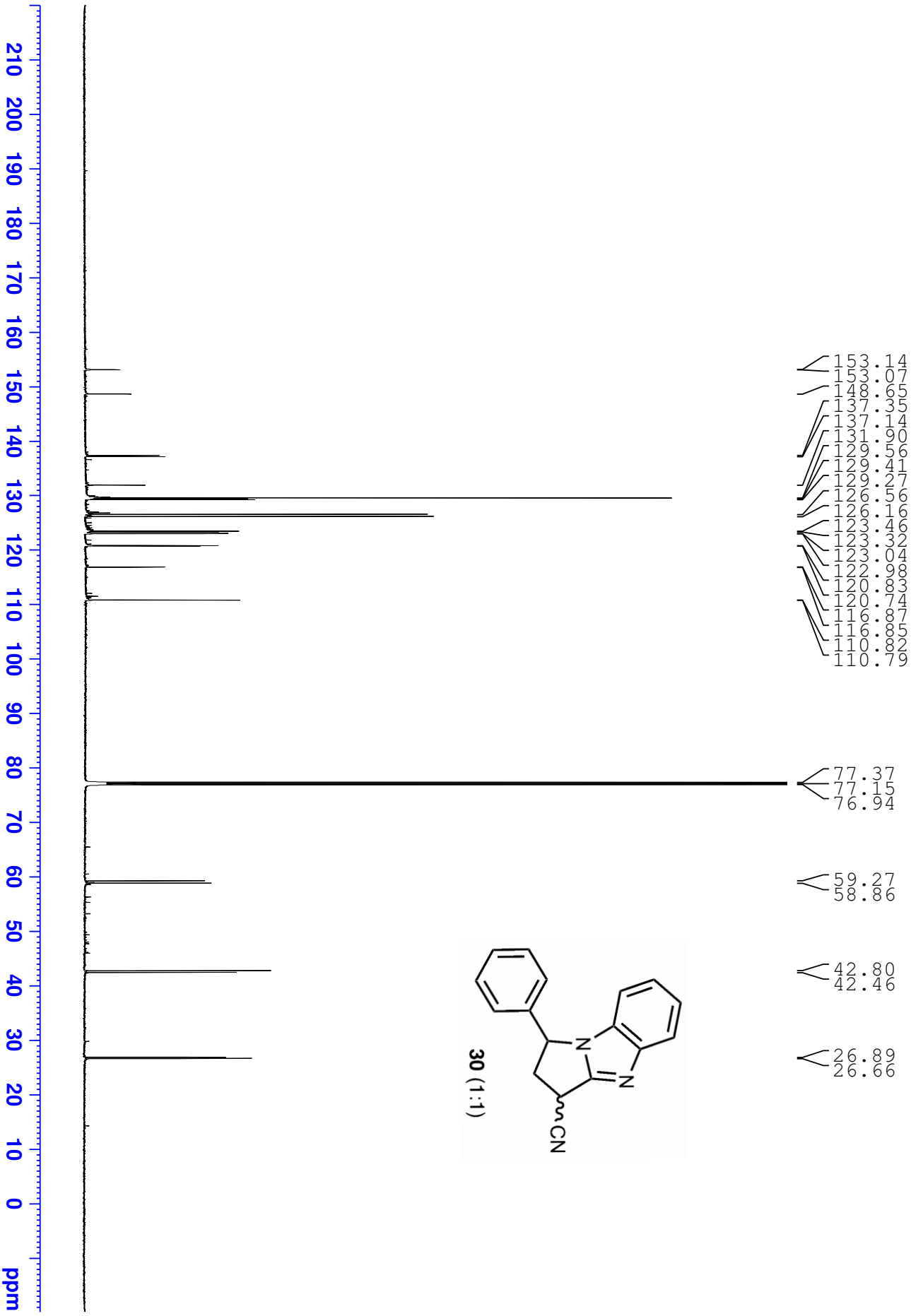
7.435
7.429
7.423
7.417
7.412
7.406
7.308
7.307
7.295
7.289
7.285
7.283
7.277
7.274
7.264
7.262
7.177
7.176
7.163
7.148
7.144
7.141
7.138
7.132
7.125
7.112
7.111
6.895
6.881
6.803
6.790
5.691
5.680
5.669
5.458
5.446
5.434
4.512
4.504
4.498
4.489
4.443
4.429
4.415
3.456
3.455
3.446
3.019
3.016
2.961
2.938
2.21
6.39
4.66
4.17
1.04
0.97
1.11
0.96
1.00
0.93
1.00
1.06
1.00
0.93
9
8
7
6
5
4
3
2
1
0 ppm
30 (1:1)
N
N
CN


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
153.14
153.07
148.65
137.35
137.14
131.90
129.56
129.41
129.27
126.56
126.16
123.46
123.32
123.04
122.98
120.83
120.74
116.87
116.85
110.82
110.79
77.37
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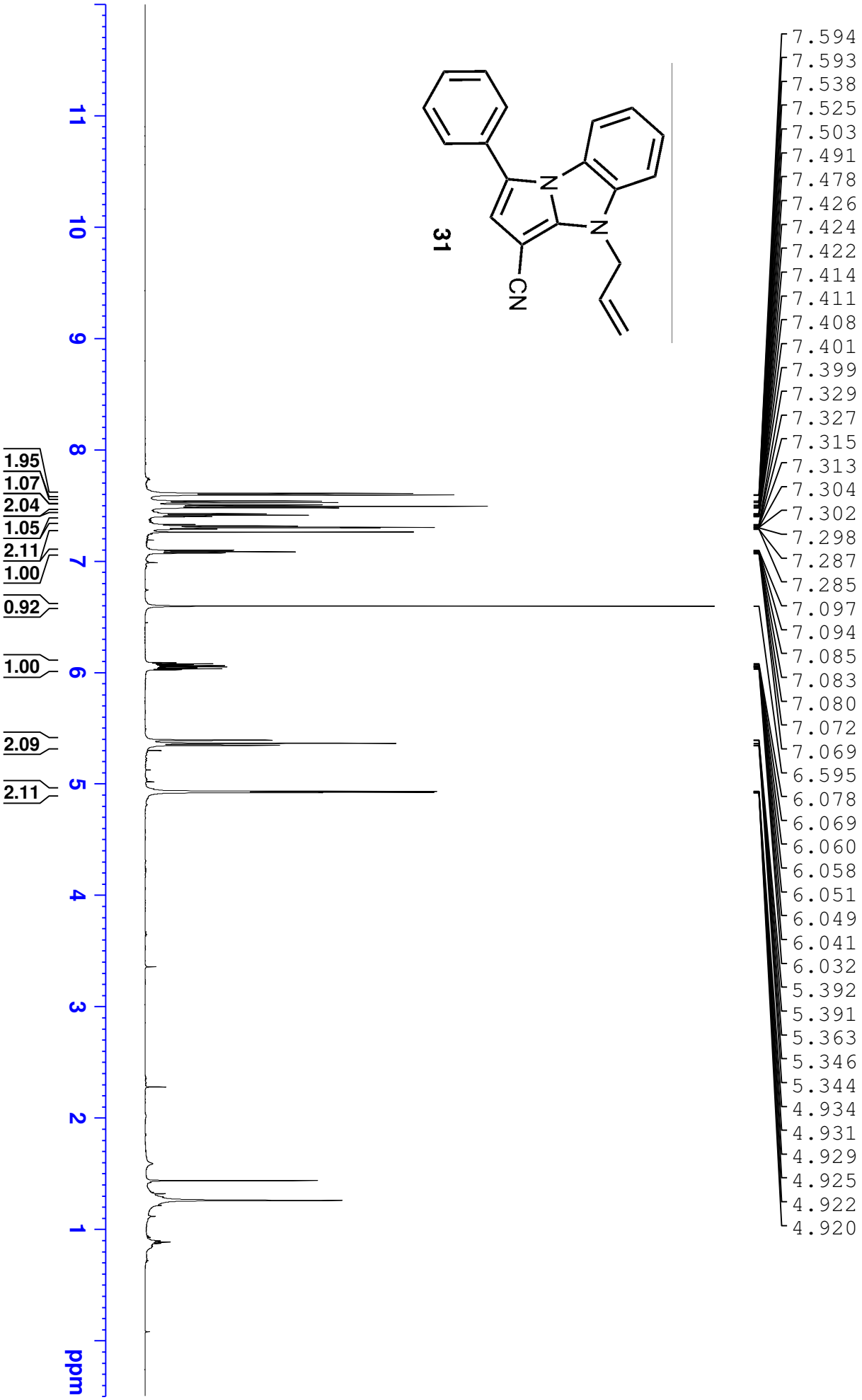
76.94
59.27
58.86
42.80
42.46
26.89
26.66
N
N
CN
30 (1:1)


31
CN
N
N
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7.593
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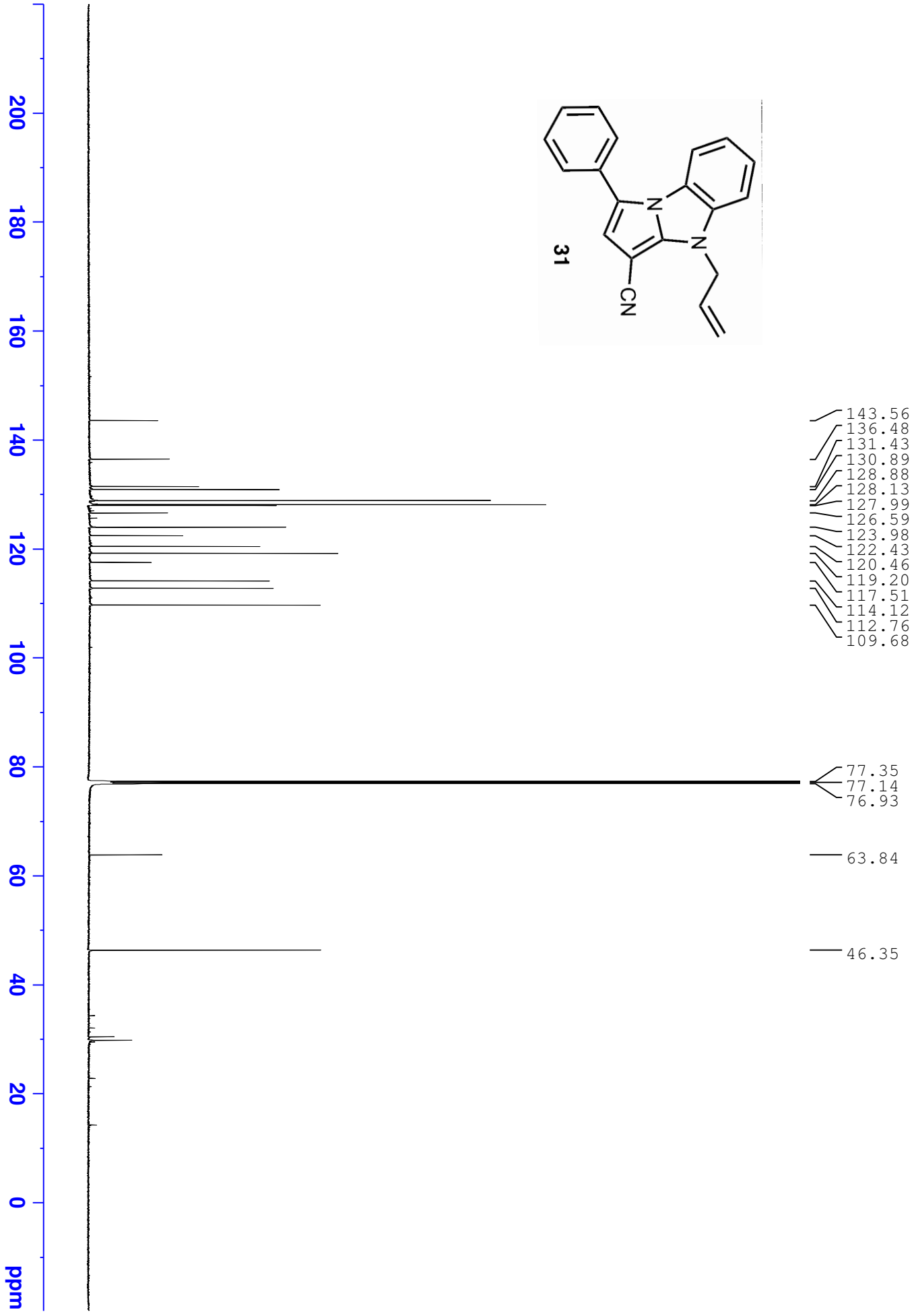
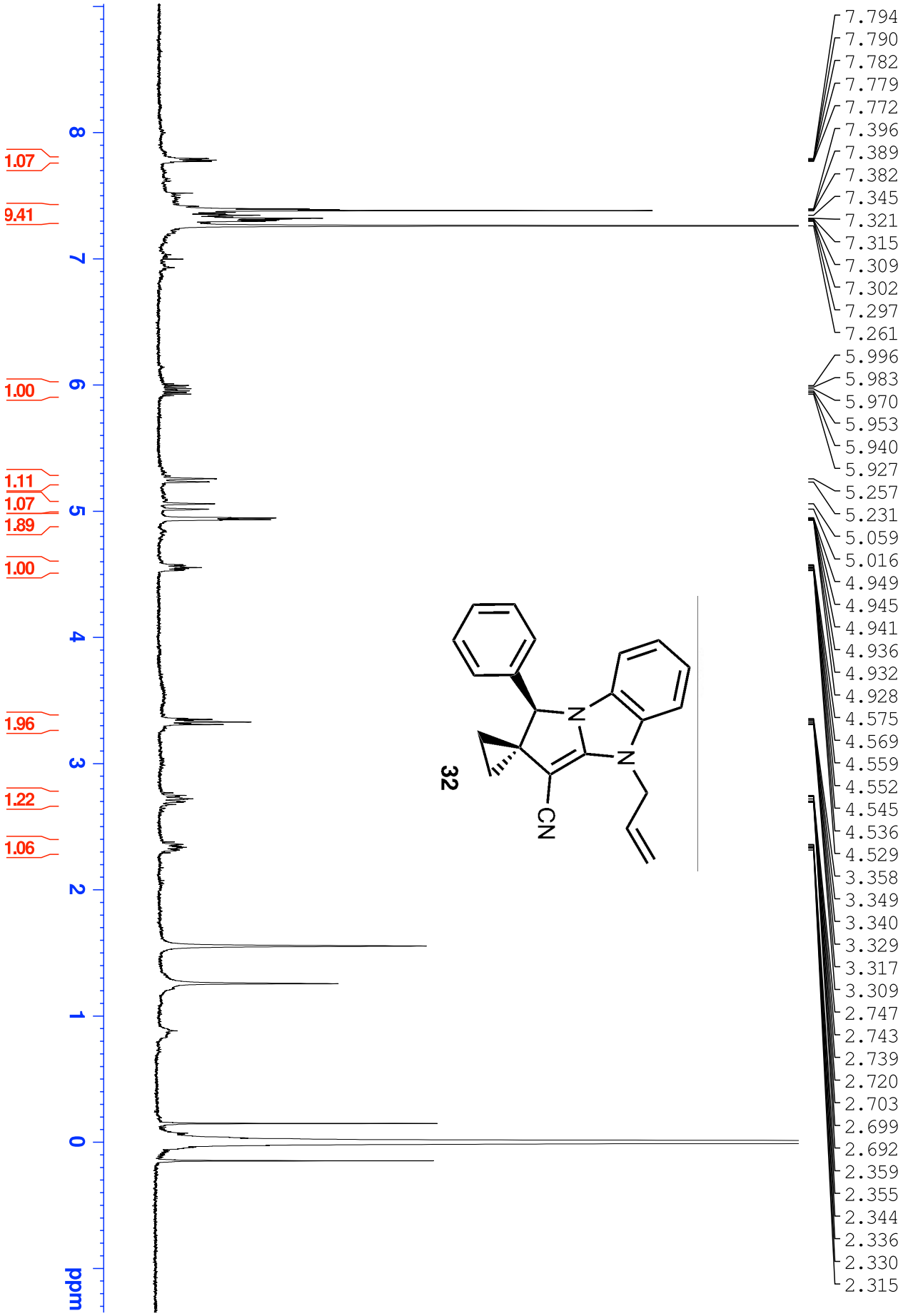
7.525
7.503
7.491
7.478
7.426
7.424
7.422
7.414
7.411
7.408
7.401
7.399
7.329
7.327
7.315
7.313
7.304
7.302
7.298
7.287
7.285
7.097
7.094
7.085
7.083
7.080
7.072
7.069
6.595
6.078
6.069
6.060
6.058
6.051
6.049
6.041
6.032
5.392
5.391
5.363
5.346
5.344
4.934
4.931
4.929
4.925
4.922
4.920
1.95
1.07
2.04
1.05
2.11
1.00
0.92
1.00
2.09
2.11
11
10
9
8
7
6
5
4
3
2
1
ppm


31
CN
N
N
143.56
136.48
131.43
130.89
128.88
128.13
127.99
126.59
123.98
122.43
120.46
119.20
117.51
114.12
112.76
109.68
77.35
77.14
76.93
63.84
46.35
200
180
160
140
120
100
80
60
40
20
0
ppm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7.382
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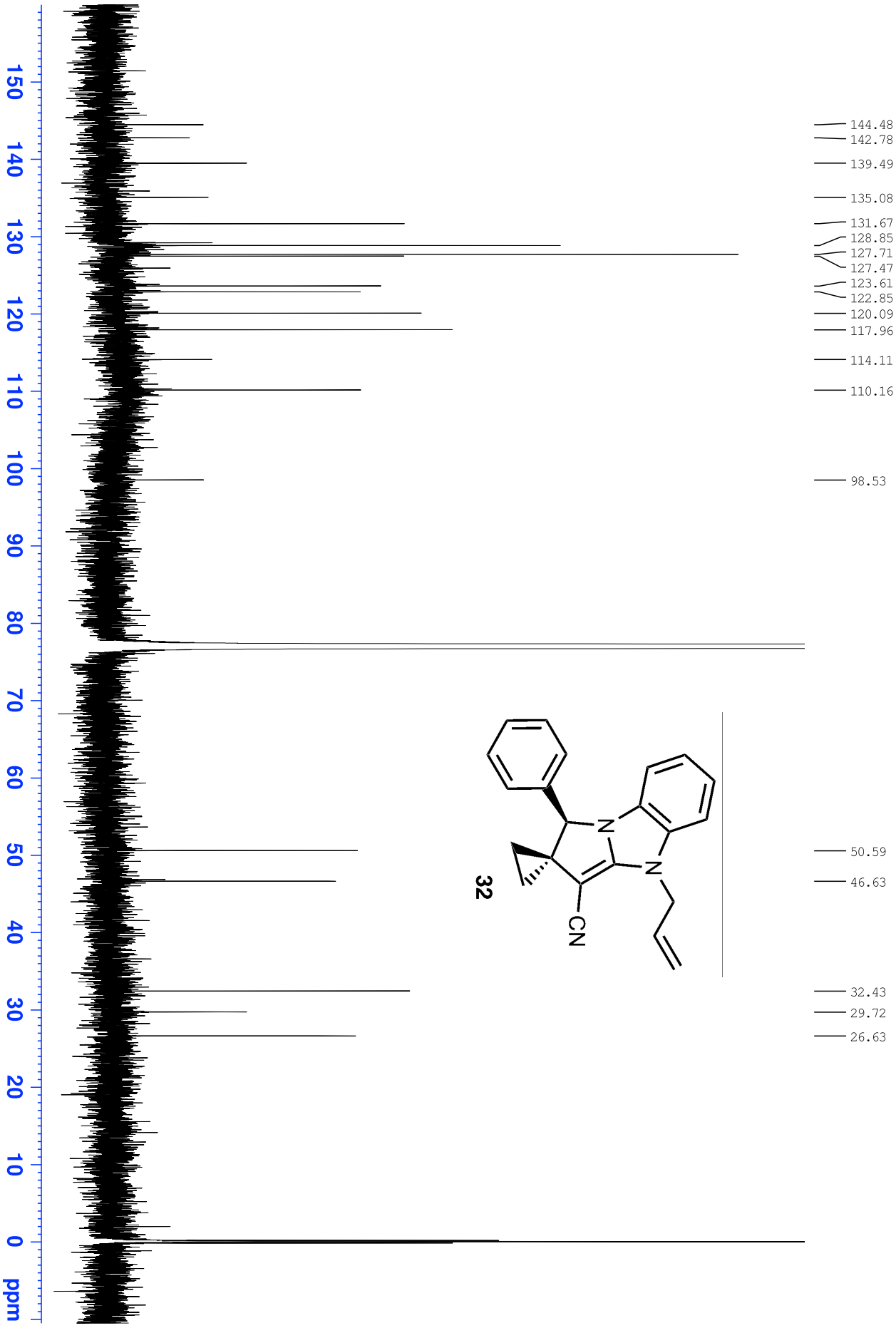
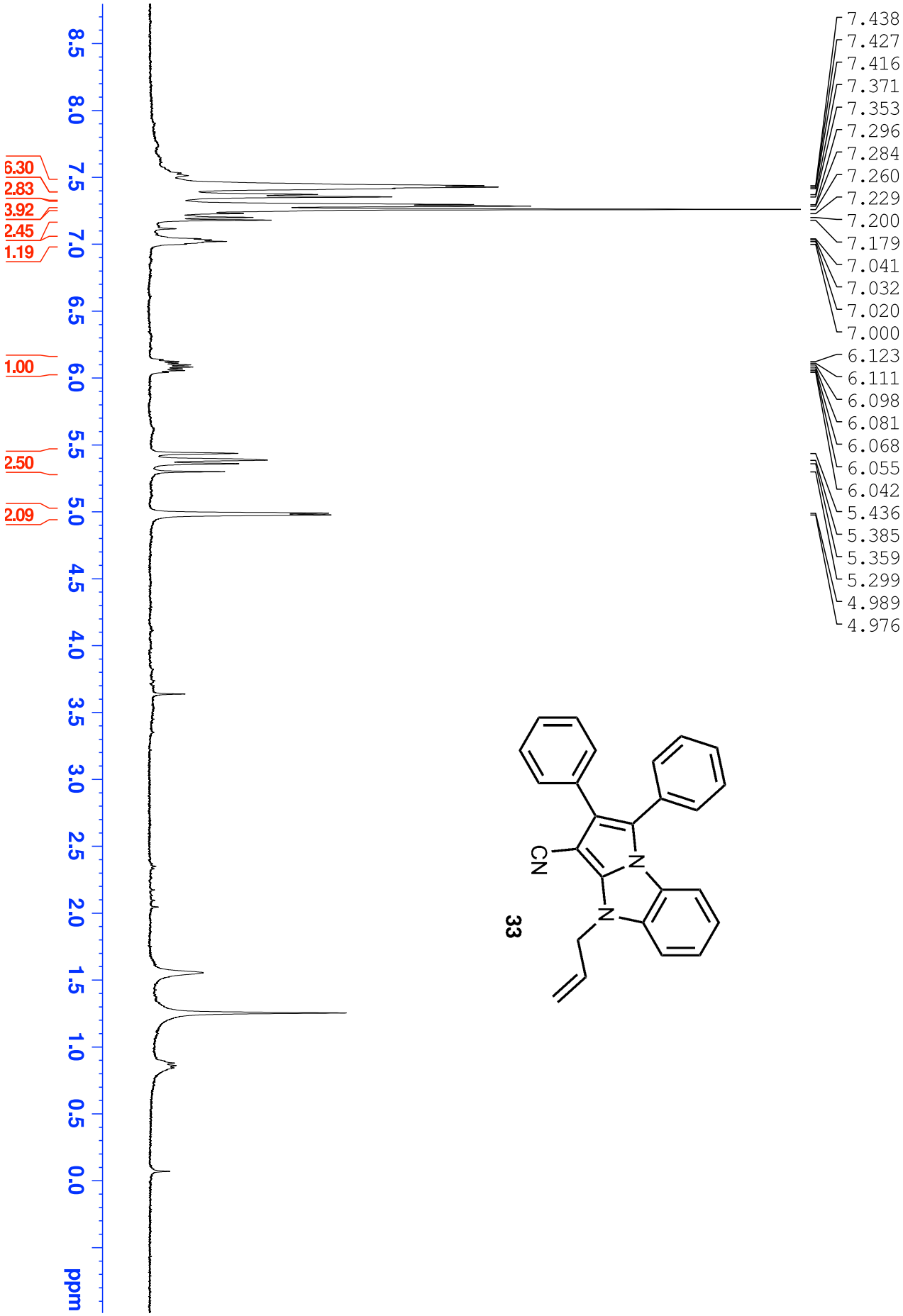
7.309
7.302
7.297
7.261
5.996
5.983
5.970
5.953
5.940
5.927
5.257
5.231
5.059
5.016
4.949
4.945
4.941
4.936
4.932
4.928
4.575
4.569
4.559
4.552
4.545
4.536
4.529
3.358
3.349
3.340
3.329
3.317
3.309
2.747
2.743
2.739
2.720
2.703
2.699
2.692
2.359
2.355
2.344
2.336
2.330
2.315
1.07
9.41
1.00
1.11
1.07
1.89
1.00
1.96
1.22
1.06
8
7
6
5
4
3
2
1
0
ppm
32
N
N
CN


144.48
142.78
139.49
135.08
131.67
128.85
127.71
127.47
123.61
122.85
120.09
117.96
114.11
110.16
98.53
50.59
46.63
32.43
29.72
26.63
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
N
N
CN

32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7.416
7.371
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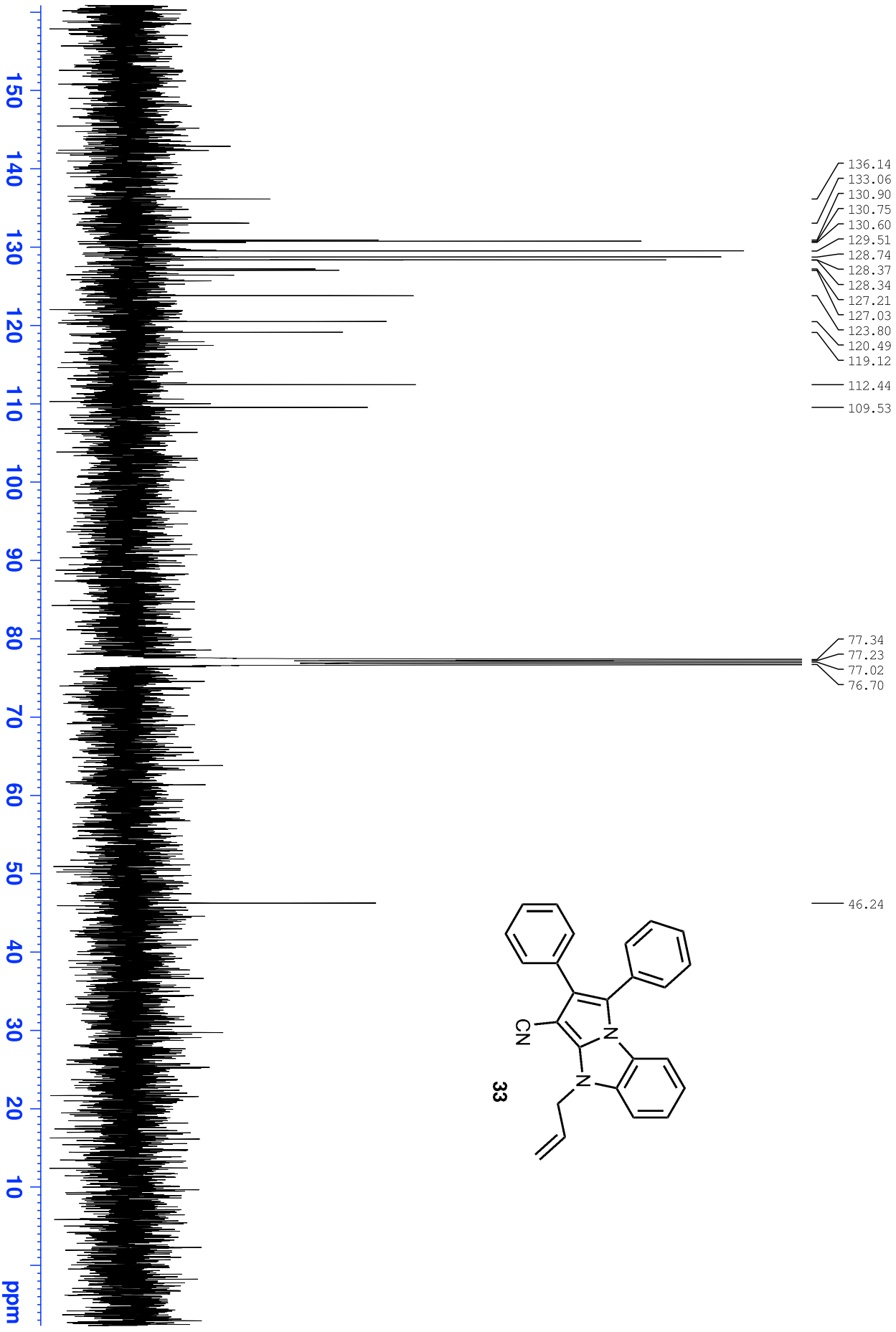
7.284
7.260
7.229
7.200
7.179
7.041
7.032
7.020
7.000
6.123
6.111
6.098
6.081
6.068
6.055
6.042
5.436
5.385
5.359
5.299
4.989
4.976
6.30
2.83
3.92
2.45
1.19
1.00
2.50
2.09
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
CN
N
N
33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128.37
128.34
127.21
127.03
123.80
120.49
119.12
112.44
109.53
77.34
77.23
77.02
76.70
46.24
CN
N
N
33
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm