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Supporting information

Direct synthesis of a new class of N,N,N ligands based on 1,2-dihydro-1,10-phenanthroline backbone and their coordination to Pd complexes

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Contents

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S1. Synthesis and characterization of the compounds

General procedures: All operations were carried out using standard Schlenk techniques under inert atmosphere. Solvents were dried and freshly distilled prior to use. Toluene was dried by a solvent purification system (SPS-M-Braun). Methanol was purchased from Carlo Erba and distilled over Mg turnings and KI prior to use. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded at room temperature on a Bruker AC 300 MHz instrument. CD_2Cl_2 was purchased from Eurisotop. Chemical shifts are reported in ppm *vs* $SiMe_4$ and were determined by reference to the residual solvent peaks. Assignments are based on ^{1}H, ^{1}H-COSY, ^{1}H, ^{13}C-HMQC and ^{1}H, ^{13}C-HMBC experiments. IR spectra were recorded in the region 4000-450 cm^{-1} on a Perkin-Elmer "Spectrum One" FT-IR spectrometer (ATR mode, ZnSe diamond). Mass spectra were collected with an Agilent 6890 N apparatus with Agilent 5975B inert XL EI/CI MSD mass spectrometer. Elemental analyses were performed by SGS Multilab. Lower C values have systematically been found and applying corrections to a total sum of elements of 100% instead of ca.98% yielded satisfactory results.
2,2-dimethyl-1-pyridin-2-ylpropan-1-one,[1] 2-methyl-8-aminoquinoline,[2] 2-acetyl-6-bromo-pyridine,[1] 2-methoxy-6-bromopyridine[1] were synthesised according to literature procedures. All other reagents were used as received from commercial suppliers.

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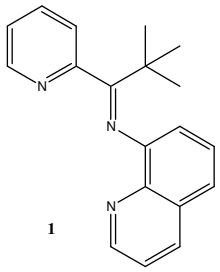
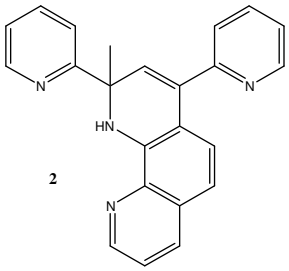
[1] C. Bolm, M. Ewald, M. Felder, and G. Schlingloff, *Chem. Ber.*, 1992, **125**, 1169.

[2] R. Ziessel, N. Weibel, and L. J. Charbonnière, *Synthesis*, 2006, **18**, 3127.



1

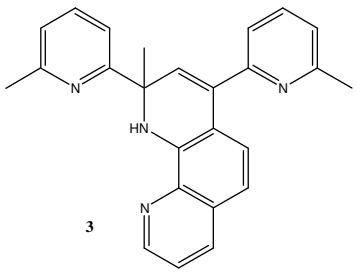
Synthesis of 1. 2,2-Dimethyl-1-pyridin-2-ylpropan-1-one (0.85 g, 5.2 mmol) and 8-aminoquinoline (1.12 g, 7.8 mmol) were dissolved in toluene (15 mL) in a Dean-Stark apparatus full with 3 Å molecular sieves. *p*-Toluenesulfonic acid (0.08 g, 0.4 mmol) was added to the solution. The reaction mixture was heated at 150 °C for 3 days. The solvent was evaporated under vacuum. 8-Aminoquinoline was removed by flash chromatography on alumina (solvent: CH_2Cl_2/AcOEt, 80/20). Product was crystallized from the starting ketone. Crystals were washed with *n*-pentane and dried under vacuum yielding **1** as colorless crystals (0.53 g, 35% yield). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 1.41 (s, 9H), 6.70 (dd, 1H, $^3J_{HH}$ = 7.3 Hz), 6.81 (dt, 1H, $^3J_{HH}$ = 7.8 Hz), 6.93 (ddd, 1H, $^3J_{HH}$ = 7.9 Hz), 7.12-7.24 (m, 2H), 7.28-7.40 (m, 2H), 7.27 (dm, 1H, $^3J_{HH}$ = 7.3 Hz), 8.02 (dd, 1H, $^3J_{HH}$ = 8.4 Hz), 8.41 (ddd, 1H, $^3J_{HH}$ = 5.0 Hz) ppm; ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ 28.7, 40.7, 118.3, 121.4, 122.4, 122.5, 126.5, 128.9, 135.3, 135.9, 141.4, 148.5, 149.3, 149.6, 157.2, 178.7 ppm; IR: 3037w, 2929w, 2968w, 1644m, 1581w, 1560w, 1496w, 1477w, 1462m, 1426w, 1391w, 1363m, 1311m, 1251w, 1217w, 1079w, 1056w, 1033w, 1002m, 986w, 830m, 809w, 791s, 756s, 721m cm^{-1}. MS: EI *m/z* 232, 205, 155, 128, 101, 78, 57.



2

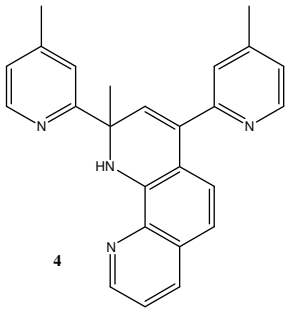
Synthesis of 2. 2-Acetylpyridine (6.90 g, 56.9 mmol) and 8-aminoquinoline (4.1 g, 28.4 mmol) were dissolved in anhydrous methanol (75 mL). Formic acid (1.3 mL) was added to the solution. The reaction mixture was refluxed for 72 h. The solvent was evaporated under reduced pressure and the excess ketone was removed under vacuum at 60 °C. The crude product was purified by flash chromatography on alumina and then on silica (solvent: CH_2Cl_2/AcOEt 80/20), yielding **2** as a yellow solid (2.40 g, 30% yield). ^{1}H NMR (300 MHz,

CD_2Cl_2, 298 K): δ 1.90 (s, 3H), 6.17 (d, 1H, $^4J_{HH}$ = 2.3 Hz), 6.95 (d, 1H, $^3J_{HH}$ = 8.6 Hz), 7.00 (s, 1H), 7.11 (ddd, 1H, $^3J_{HH}$ = 7.3 Hz), 7.29 (ddd, 1H, $^3J_{HH}$ = 7.6 Hz), 7.32 (d, 1H, $^3J_{HH}$ = 8.5 Hz), 7.35 (dd, 1H, $^3J_{HH}$ = 8.2 Hz), 7.49 (dt, 1H, $^3J_{HH}$ = 7.9 Hz), 7.59 (dt, 1H, $^3J_{HH}$ = 7.94 Hz), 7.62 (td, 1H, $^3J_{HH}$ = 7.5 Hz), 7.76 (td, 1H, $^3J_{HH}$ = 7.6 Hz), 8.02 (dd, 1H, $^3J_{HH}$ = 8.3 Hz), 8.60 (dq, 1H, $^3J_{HH}$ = 4.8 Hz), 8.69 (dq, 1H, $^3J_{HH}$ = 4.9 Hz), 8.75 (dd, 1H, $^3J_{HH}$ = 4.2 Hz) ppm; ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ 31.1, 59.1, 113.8, 115.5, 120.3, 121.8, 121.9, 122.7, 123.9, 125.1, 128.9, 130.0, 136.1, 136.5, 136.8, 136.9, 137.7, 140.6, 148.0, 149.61, 149.64, 158.2, 166.6 ppm; IR: 3371brw, 3048w, 2968w, 1632w, 1583s, 1563m, 1508s, 1464s, 1428s, 1378s, 1294w, 1225w, 1100m, 1044w, 991m, 823s, 804s, 783s, 750s cm^{-1}. MS: EI *m/z* 350, 335, 272, 256, 167. Anal. Calcd (%) for $C_{23}H_{18}N_4$: C, 78.83; H, 5.18; N, 15.99. Found: C, 78.78; H, 5.47; N, 15.75.



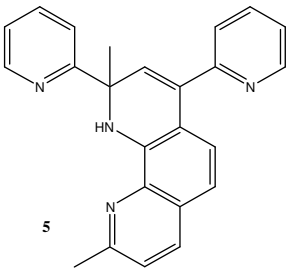
3

Synthesis of 3. 2-Acetyl-6-methylpyridine (1.95 g, 14.4 mmol) and 8-aminoquinoline (2.08 g, 14,4 mmol) were dissolved in anhydrous methanol (30 mL). Formic acid (0.4 mL) are added to the solution. The reaction mixture was refluxed for 96 h. The solvent was evaporated under reduced pressure and the crude product was purified by flash chromatography on silica (solvent: CH_2Cl_2/AcOEt 95/5) yielding **3** as a yellow solid (0.80 g, 17% yield). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 1.87 (s, 3H), 2.54 (s, 3H), 2.59 (s, 3H), 6.12 (d, 1H, $^4J_{HH}$ = 2.3 Hz), 6.93 (d, 1H, $^3J_{HH}$ = 8.7 Hz), 6.94 (s, 1H), 6.97 (dt, 1H, $^3J_{HH}$ = 7.5 Hz), 7.15 (dm, 1H, $^3J_{HH}$ = 7.7 Hz), 7.27 (dm, 1H, $^3J_{HH}$ = 7.3Hz), 7.29-7.38 (m, 3H), 7.50 (t, 1H, $^3J_{HH}$ = 7.7 Hz), 7.64 (t, 1H, $^3J_{HH}$ = 7.7 Hz), 8.01 (dd, 1H, $^3J_{HH}$ = 8.2 Hz), 8.75 (dd, 1H, $^3J_{HH}$ = 4.2 Hz) ppm; ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ 24.69, 24.72, 31.1, 59.1, 113.7, 115.6, 117.1, 120.9, 121.4, 121.7, 122.1, 125.3, 128.9, 129.9, 136.1, 136.3, 137.1, 137.7, 140.6, 147.9, 157.7, 158.36, 158.49, 165.9 ppm; IR: 3373w, 3055w, 2965w, 2920w, 1733w, 1637w, 1586m, 1572m, 1511s, 1478m, 1456s, 1384s, 1256m, 1225w, 1167w, 1124w, 1099w, 1063w, 996w, 856w, 818s, 806s, 798s, 752m, 703m cm^{-1}. MS: EI *m/z* 363, 286, 270, 256, 243, 189, 181. Anal. Calcd (%) for $C_{25}H_{22}N_4$: C, 79.34; H, 5.86; N, 14.80. Found: C, 79.43; H, 5.96; N, 14.61.



4

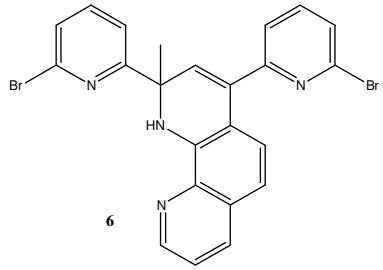
Synthesis of 4. 4-Methyl-2-acetylpyridine (4.00 g, 29.6 mmol) and 8-aminoquinoline (4.27 g, 29.6 mmol) were dissolved in anhydrous methanol (60 mL). Formic acid (0.8 mL) was added to the solution. The reaction mixture was refluxed for 96 h. The solvent was evaporated under reduced pressure and the crude product was purified by flash chromatography on silica (solvent: CH_2Cl_2/AcOEt 80/20), yielding **4** as a yellow solid (1.80 g, 32% yield). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 1.85 (s, 3H), 2.28 (s, 3H), 2.40 (s, 3H), 6.10 (d, 1H, $^4J_{HH}$ = 2.3 Hz), 6.93 (d, 1H, $^3J_{HH}$ = 8.6 Hz), 6.96 (m, 1H), 7.12 (dm, 1H, $^3J_{HH}$ = 5.0 Hz), 7.30-7.40 (m, 4H), 8.01 (dd, 1H, $^3J_{HH}$ = 8.4 Hz), 8.44 (d, 1H, $^3J_{HH}$ = 4.9 Hz), 8.52 (d, 1H, $^3J_{HH}$ = 5.1 Hz), 8.74 (dd, 1H, $^3J_{HH}$ = 4.2 Hz) ppm; ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ 21.2, 21.4, 31.2, 59.1, 113.7, 115.4, 121.2, 121.8, 122.9, 123.7, 124.7, 125.3, 128.9, 129.6, 136.1, 136.4, 137.8, 140.6, 147.9, 148.1, 148.2, 149.31, 149.32, 158.2, 166.4 ppm; IR: 3359w, 2974w, 2921w, 2822w, 1640w, 1599s, 1555m, 1509s, 1467s, 1448m, 1423w, 1378s, 1350w, 1116m, 1090m, 1031m, 991m, 847m, 827vs, 803s, 779s, 711s, 696m cm^{-1}. MS: EI *m/z* 363, 286, 270, 256, 243, 189, 181. Anal. Calcd (%) for $C_{25}H_{22}N_4$: C, 79.34; H, 5.86; N, 14.80. Found: C, 79.47; H, 5.94; N, 14.58.



5

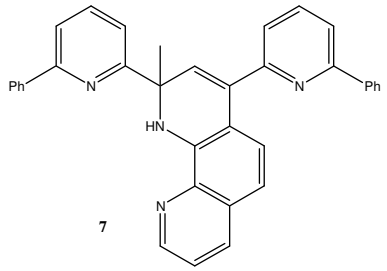
Synthesis of 5. 2-Methyl-8-aminoquinoline (1.00 g, 6.3 mmol) and 2-acetylpyridine (1.53 g, 12.6 mmol) were dissolved in anhydrous methanol (10 mL). Drops of formic acid were added to the solution. The reaction mixture was refluxed for 5 days. The solvent was evaporated under reduced pressure and the crude product was purified by flash chromatography on silica (solvent: CH_2Cl_2/AcOEt 90/10 and AcOEt 100%) yielding **5** as a

yellow brown solid (0.82 g, 43% yield). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 1.89 (s, 3H), 2.72 (s, 3H), 6.12 (d, 1H, $^3J_{HH}$ = 2.3 Hz), 6.89 (d, 1H, $^3J_{HH}$ = 9.3 Hz), 6.93 (s, 1H), 7.12 (ddd, 1H, $^3J_{HH}$ = 7.2 Hz), 7.23 (t, 2H, $^3J_{HH}$ = 7.2 Hz), 7.28 (ddd, 1H, $^3J_{HH}$ = 7.6 Hz), 7.47 (dt, 1H, $^3J_{HH}$ = 7.8 Hz), 7.56-7.66 (m, 2H), 8.75 (td, 1H, $^3J_{HH}$ = 7.7 Hz), 7.90 (d, 1H, $^3J_{HH}$ = 8.4 Hz), 8.60 (ddd, 1H, $^3J_{HH}$ = 4.7 Hz), 8.67 (ddd, 1H, $^3J_{HH}$ = 4.9 Hz) ppm; ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ 25.9, 30.8, 59.1, 113.8, 115.5, 120.4, 121.9, 122.6, 122.7, 123.9, 124.1, 136.2, 136.5, 136.8, 136.9, 137.0, 140.0, 149.6 (2C), 156.9, 158.4, 166.8 ppm; IR: 3373brw, 3051w, 2964w, 2921w, 1633w, 1602w, 1584m, 1564w, 1552s, 1516s, 1646s, 1429s, 1385m, 1369m, 1259s, 1090s, 1044s, 1019s, 993s, 835s, 785s, 746s, 706s, 687s cm^{-1}. SM: EI *m/z*: 364, 349, 286.



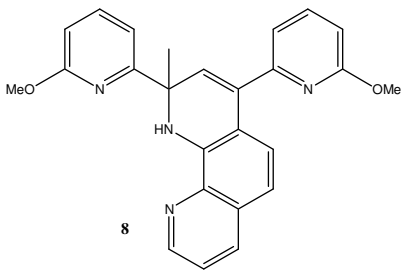
6

Synthesis of 6. 2-Acetyl-6-bromopyridine (0.50 g, 2.5 mmol) and 8-aminoquinoline (0.36 g, 2.5 mmol) were dissolved in anhydrous methanol (4.3 mL). Few drops of formic acid were added to the solution and the reaction mixture was refluxed for 4 days. The reaction mixture was filtered and the precipitate obtained was washed with cold methanol (2×5 mL) and dried under vacuum yielding **6** as a yellow solid (0.35 g, 54% yield). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 1.89 (s, 3H), 6.13 (d, 1H, $^4J_{HH}$ = 2.3 Hz), 6.87 (s, 1H), 7.00 (s, 1H, $^3J_{HH}$ = 8.7 Hz), 7.27-7.33 (m, 2H), 7.39 (dd, 1H, $^3J_{HH}$ = 8.4 Hz), 7.43-7.54 (m, 4H), 7.63 (t, 1H, $^3J_{HH}$ = 7.7 Hz), 8.05 (dd, 1H, $^3J_{HH}$ = 8.3 Hz), 8.76 (dd, 1H, $^3J_{HH}$ = 4.2 Hz) ppm; ^{13}C NMR (75 MHz, CD_2Cl_2, 298K): δ 30.5, 59.1, 114.5, 114.8, 119.5, 122.1, 122.9, 124.6, 126.4, 127.2, 129.4, 130.2, 135.5, 136.2, 137.7, 139.4, 139.6, 140.3, 141.8, 142.2, 148.2, 159.0, 168.1 ppm; IR: 3370w, 3064w, 1635s, 1576m, 1548s, 1508m, 1465m, 1441m, 1417s, 1402m, 1375s, 1363m, 1223w, 1184w, 1164w, 1151m, 1119s, 1090m, 1046w, 1019w, 986m, 922w, 848s, 823s, 797s, 770m, 746s, 705s, 696s, 668m cm^{-1}. MS: EI *m/z* 508, 493, 413, 350, 270. Anal. Calcd (%) for $C_{25}H_{22}N_4$: C, 54.36; H, 3.17; N, 11.02. Found: C, 54.35; H, 3.30; N, 10.94.



7

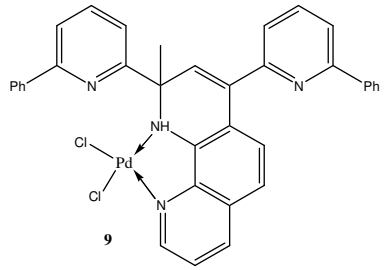
Synthesis of 7. Ligand **6** (1.50 g, 2.94 mmol) and 0.21 g of tetrakis(triphenylphosphine)palladium(0) (0.21 g, 18.0 mmol) were dissolved in toluene (12 mL). A degassed solution of Na_2CO_3 (1.25 g, 11.8 mmol) in distilled water (6mL) and phenylboronic acid (0.86 g, 7.0 mmol) were added to the solution. The reaction mixture was refluxed for 24 h. 4.5 mL of NH_3 aqueous solution (20%) diluted in 30mL of saturated Na_2CO_3 solution were added. The aqueous phase was extracted with dichloromethane (3×50 mL), the combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica (solvent: CH_2Cl_2 100%) yielding **7** as a yellow solid (1.56 g, 44% yield). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 2.01 (s, 3H), 6.37 (d, 1H, $^4J_{HH}$ = 2.2 Hz), 6.99 (d, 1H, $^3J_{HH}$ = 8.6 Hz), 7.22 (bs, 1H), 7.36-7.60 (m, 11H), 7.69-7.85 (m, 3H), 8.02-8.12 (m, 5H), 8.8 (dd, 1H, $^3J_{HH}$ = 4.2 Hz); ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ 31.3, 59.3, 114.0, 115.9, 118.4, 118.8, 119.2, 121.8, 122.4, 125.4, 127.3, 128.9, 128.9, 129.0, 129.2, 129.3, 130.3, 136.1, 136.7, 137.8, 137.9, 139.7, 141.2, 148.0, 156.5, 156.7, 158.1, 166.5 ppm. IR: 3360brw, 3058w, 2964w, 1633w, 1587w, 1564m, 1508m, 1468m, 1441s, 1379m, 1260m, 1158w, 1092m, 1061m, 1026m, 989w, 814s, 800s, 760s, 692s, 659m cm^{-1}. SM: EI *m/z*: 502, 487 , 348, 243. Anal. Calcd (%) for $C_{35}H_{26}N_4$: C, 83.64; H, 5.21; N, 11.15. Found: C, 83.60; H, 5.56; N, 10.84.



8

Synthesis of 8. 2-Acetyl-6-methoxypyridine (0.50 g, 3.3 mmol) and 8-aminoquinoline (0.47 g, 3.3 mmol) were dissolved in anhydrous methanol (6 mL). Formic acid (0.1 mL) was added to the solution. The reaction mixture was refluxed for 4 days. The solvent was

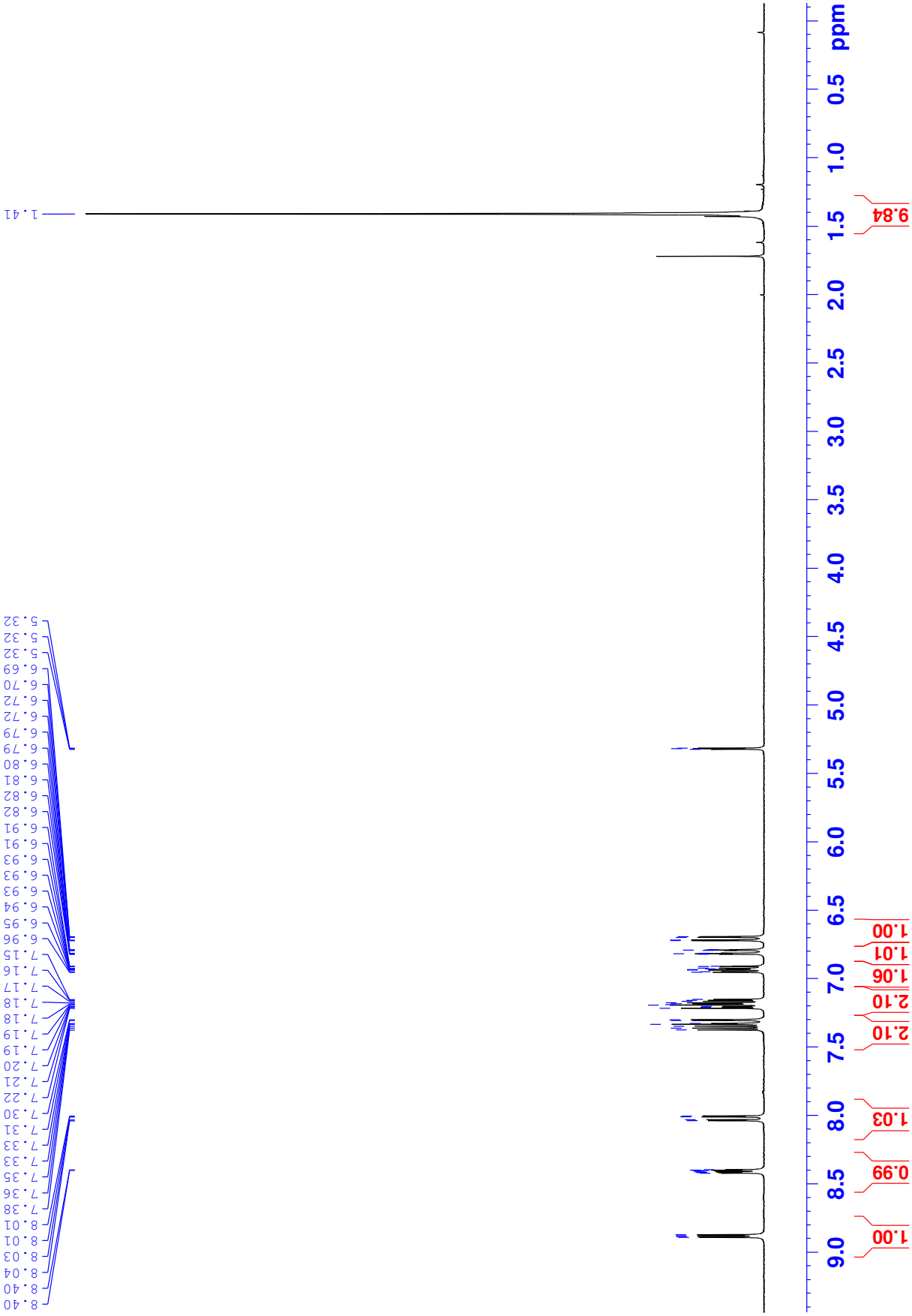
evaporated under reduced pressure and the crude product was purified by flash chromatography on silica (solvent: CH_2Cl_2 100% and CH_2Cl_2/AcOEt 80/20) yielding **8** as a yellow solid (0.41 g, 60% yield) . ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 1.88 (s, 3H), 3.92 (s, 3H), 3.93(s, 3H), 6.23 (d, 1H, $^4J_{HH}$ = 2.3 Hz), 6.52 (dd, 1H, $^3J_{HH}$ = 8.3 Hz), 6.74 (dd, 1H, $^3J_{HH}$ = 8.2 Hz), 6.95 (d, 1H, $^3J_{HH}$ = 8.6 Hz), 7.07 (m, 3H), 7.35 (dd, 1H, $^3J_{HH}$ = 7.4 Hz), 7.41-7.51 (m, 2H), 7.66 (dd, 1H, $^3J_{HH}$ = 8.3 Hz), 8.01 (dd, 1H, $^3J_{HH}$ = 8.3 Hz), 8.73 (dd, 1H, $^3J_{HH}$ = 4.2 Hz) ppm ; ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ 31.0, 53.5, 53.6, 58.6, 108.8, 109.8, 112.5, 113.9 (2C), 116.5, 121.2, 125.4, 128.8, 129.9, 136.0, 136.2, 137.9, 139.3, 139.5, 141.0, 147.9, 155.9, 163.8, 164.0, 164.6 ppm. IR: 3384w, 2972w, 2945w, 1630w, 1575s, 1550m, 1510m, 1457s, 1424m, 1409m, 1375m, 1362m, 1299m, 1257s, 1149w, 1120w, 1032m, 986m, 913w, 820m, 797s, 743m, 704m cm^{-1}. SM: EI *m/z*: 410, 395, 302, 286, 258.



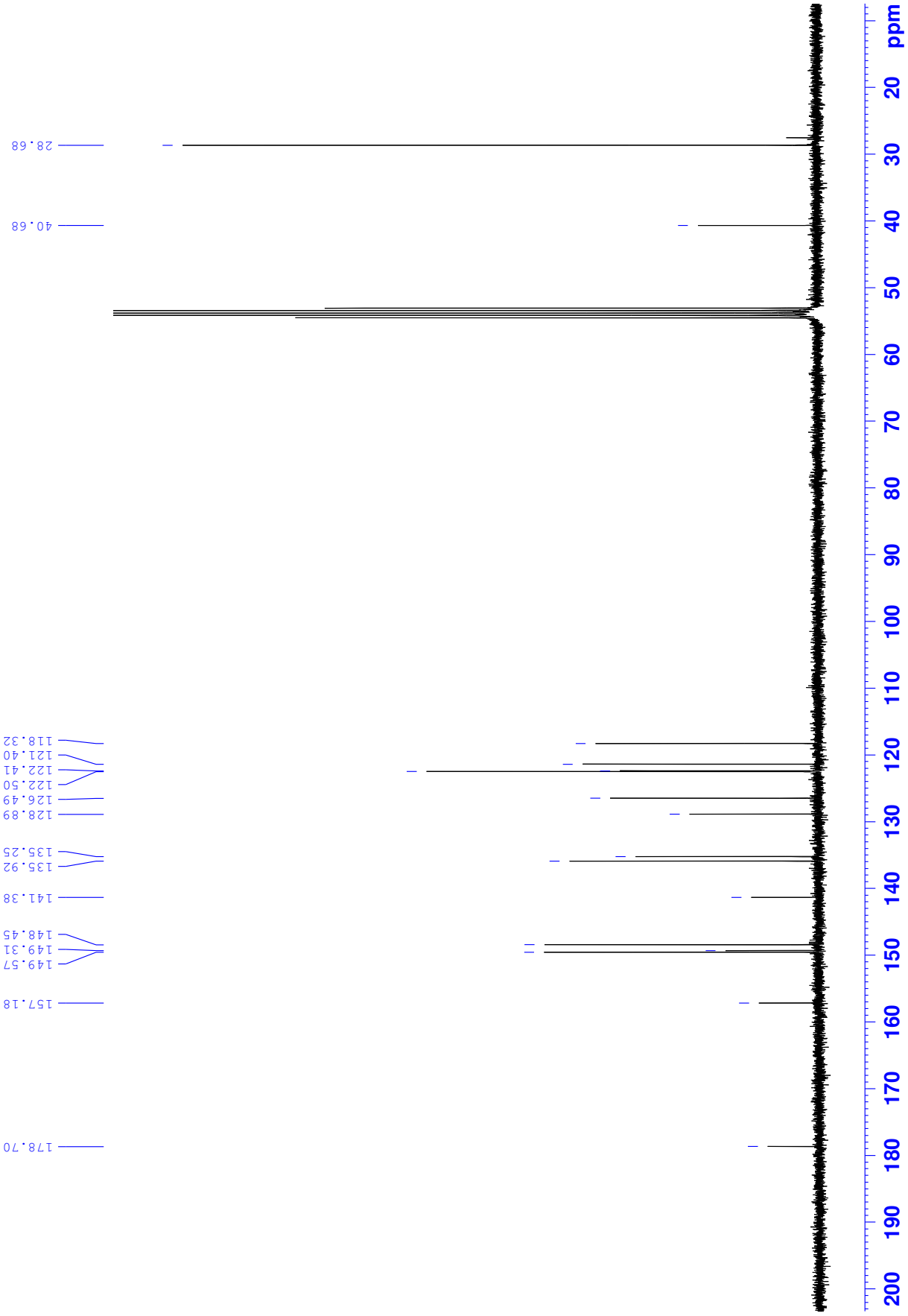
9

Synthesis of 9. Ligand **7** (0.50 g, 1.0 mmol) and [$PdCl_2(NCPh)_2$] (0.38 g, 1.0 mmol) were dissolved in anhydrous CH_2Cl_2 (10 mL). The solution became orange and was stirred at r.t. for 16 h. 5 mL of dry Et_2O were added to precipitate the desired compound and the reaction mixture was filtered. The orange precipitate was washed with Et_2O (3×5 mL) and dried under vacuum yielding **10** as an orange crystalline powder (0.62 g, 95% yield). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 2.39(s, 3H), 6.16 (s, 1H), 7.50-7.39 (m, 7H), 7.60 (m, 2H), 7.70 (dd, 1H, $^3J_{HH}$ = 7.8 Hz), 7.78 (dd, 1H, $^3J_{HH}$ = 7.9 Hz), 7.82-8.08 (m, 8H), 8.43 (dd, 1H, $^3J_{HH}$ = 8.3 Hz), 9.38 (bs, 1H, N-H), 9.52 (dd, 1H, $^3J_{HH}$ = 5.3 Hz) ppm ; ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ 21.5, 65.3, 119.0, 119.7, 120.2, 122.0; 122.9, 126.8, 127.2 (2C), 127.6, 127.7 (2C), 129.1, 129.1 (2C), 129.6, 129.6, 129.9, 131.0, 132.2, 136.4, 138.4, 139.1, 139.2, 139.3, 139.5, 147.8, 151.9, 155.5, 155.8, 157.7, 160.1 ppm. IR: 3038w, 1614w, 1593w, 1565s, 1507w, 1444s, 1375,w 1348m, 1263w, 1223w, 1156w, 1065w, 1024w, 1010w, 842m, 816m, 761s, 703s, 691s, 624m cm^{-1}.

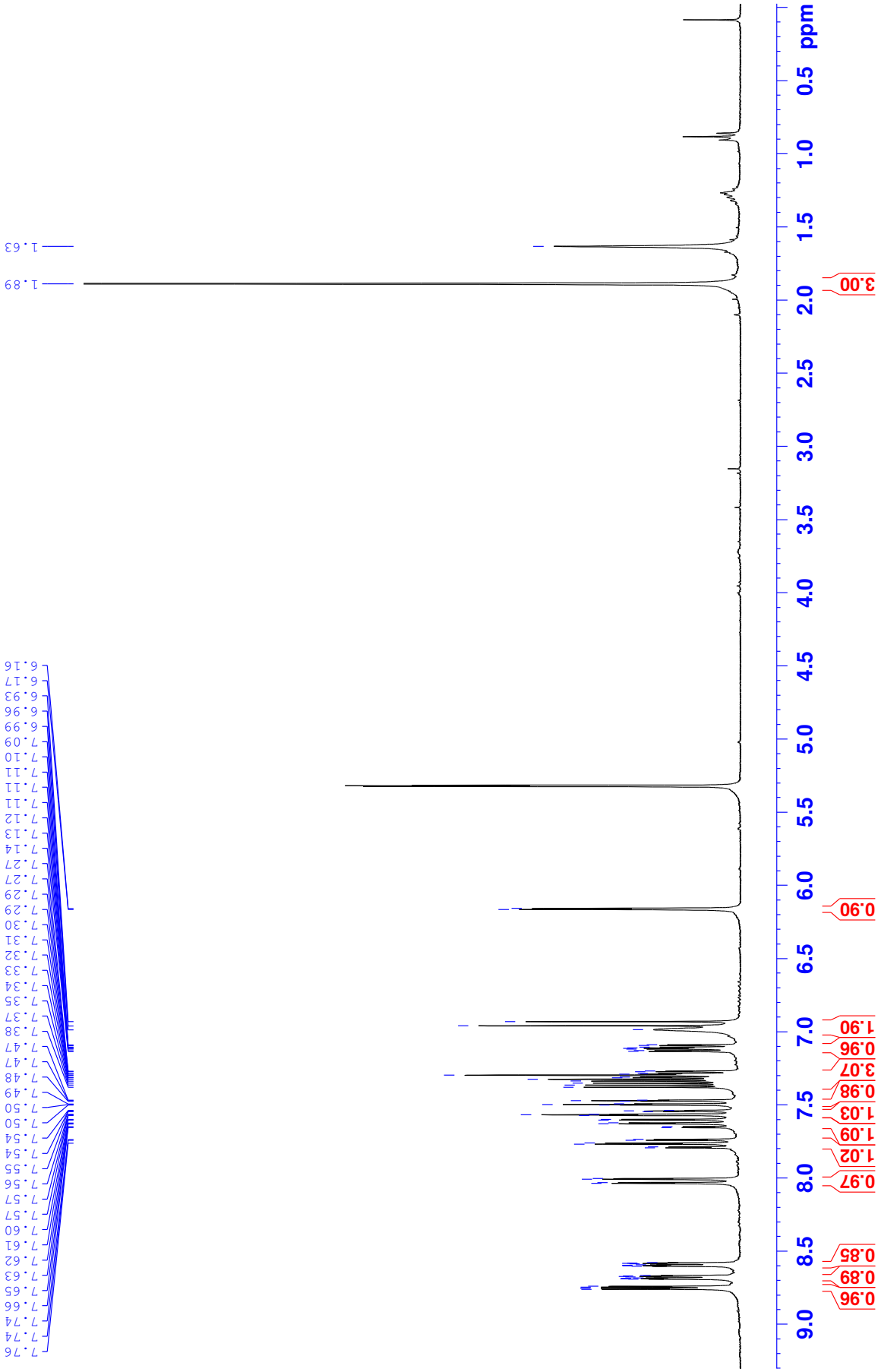
^{1}H RMN of **1** (CD_2Cl_2)



^{13}C RMN of **1** (CD_2Cl_2)



^{1}H RMN of **2** (CD_2Cl_2)



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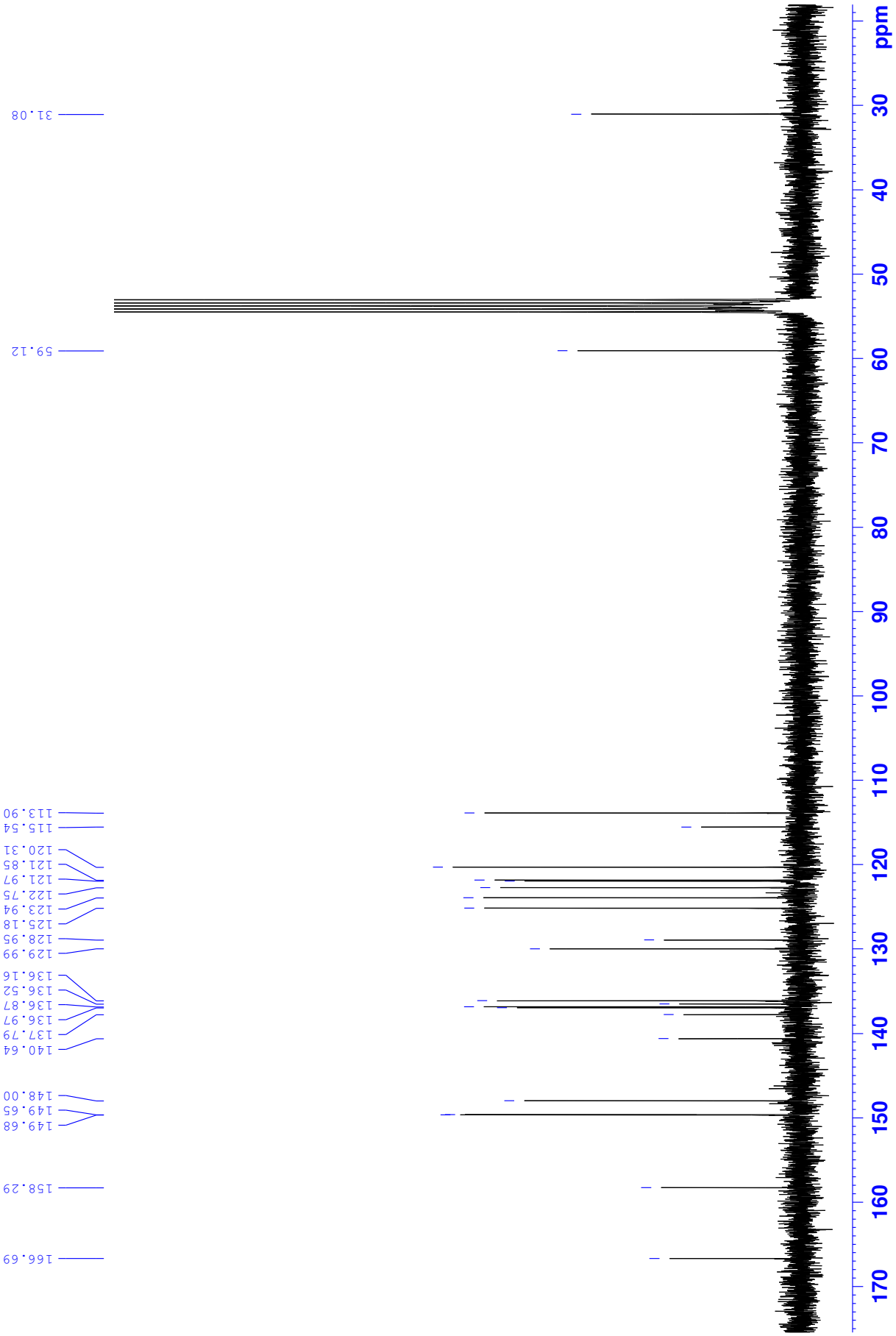

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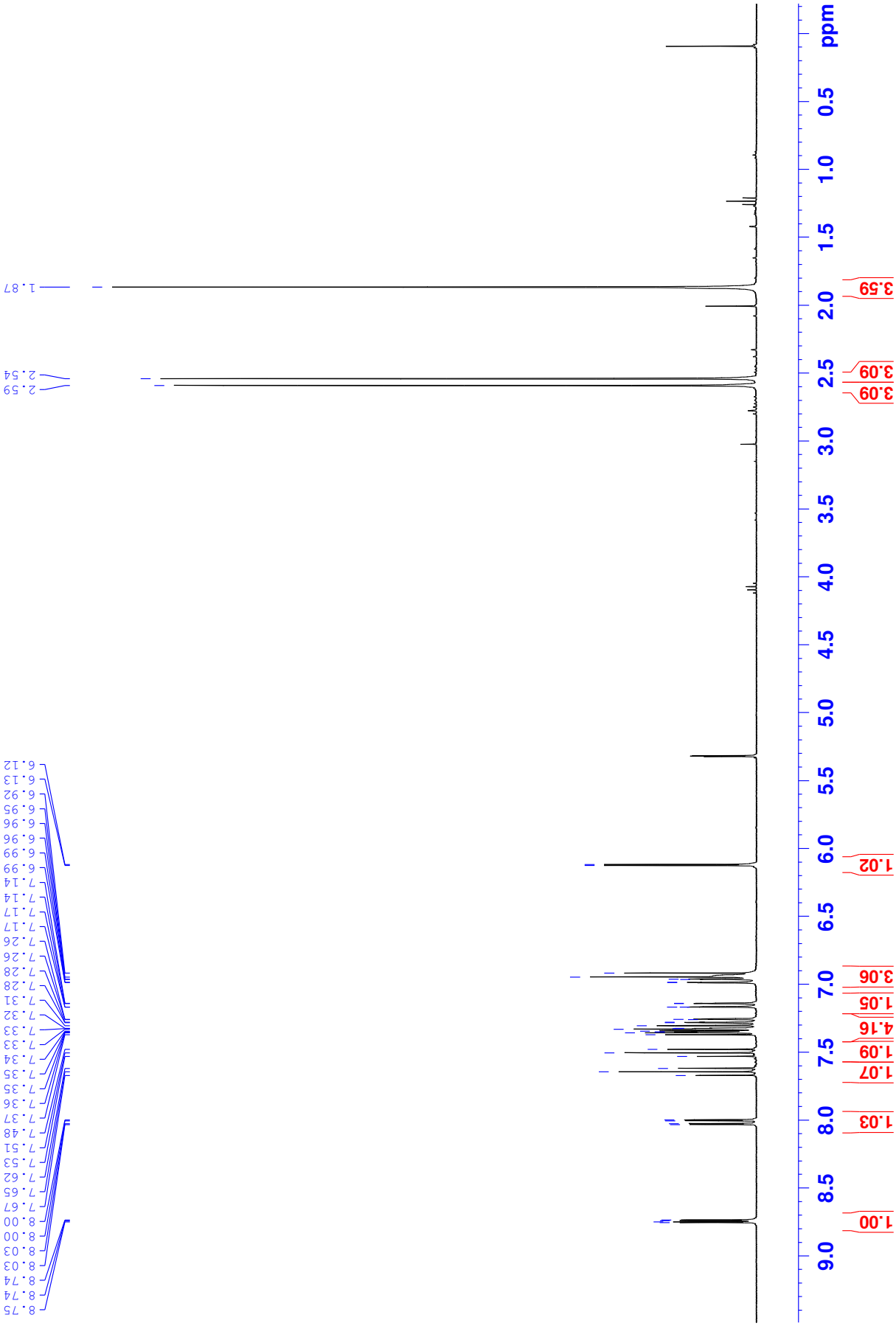
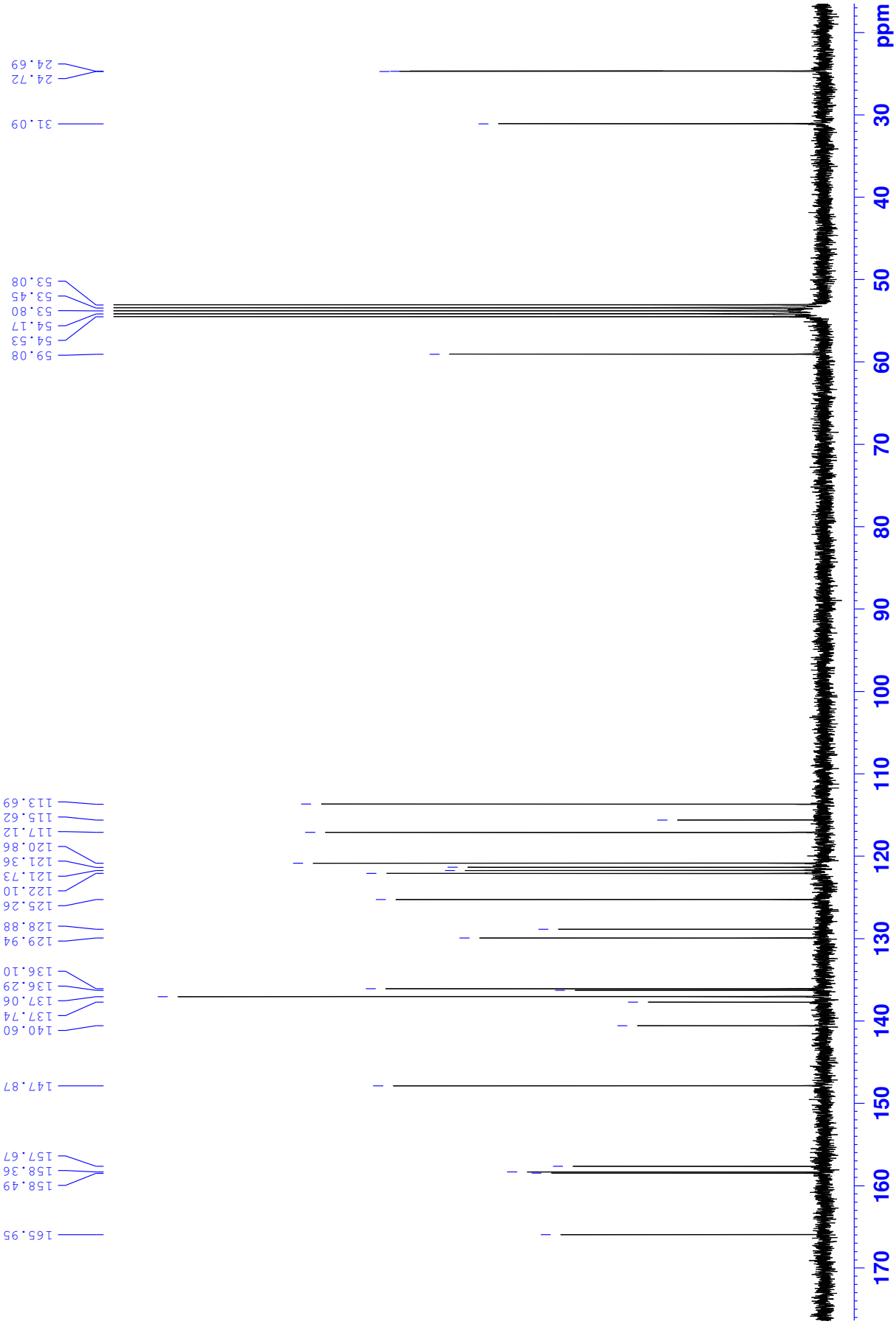
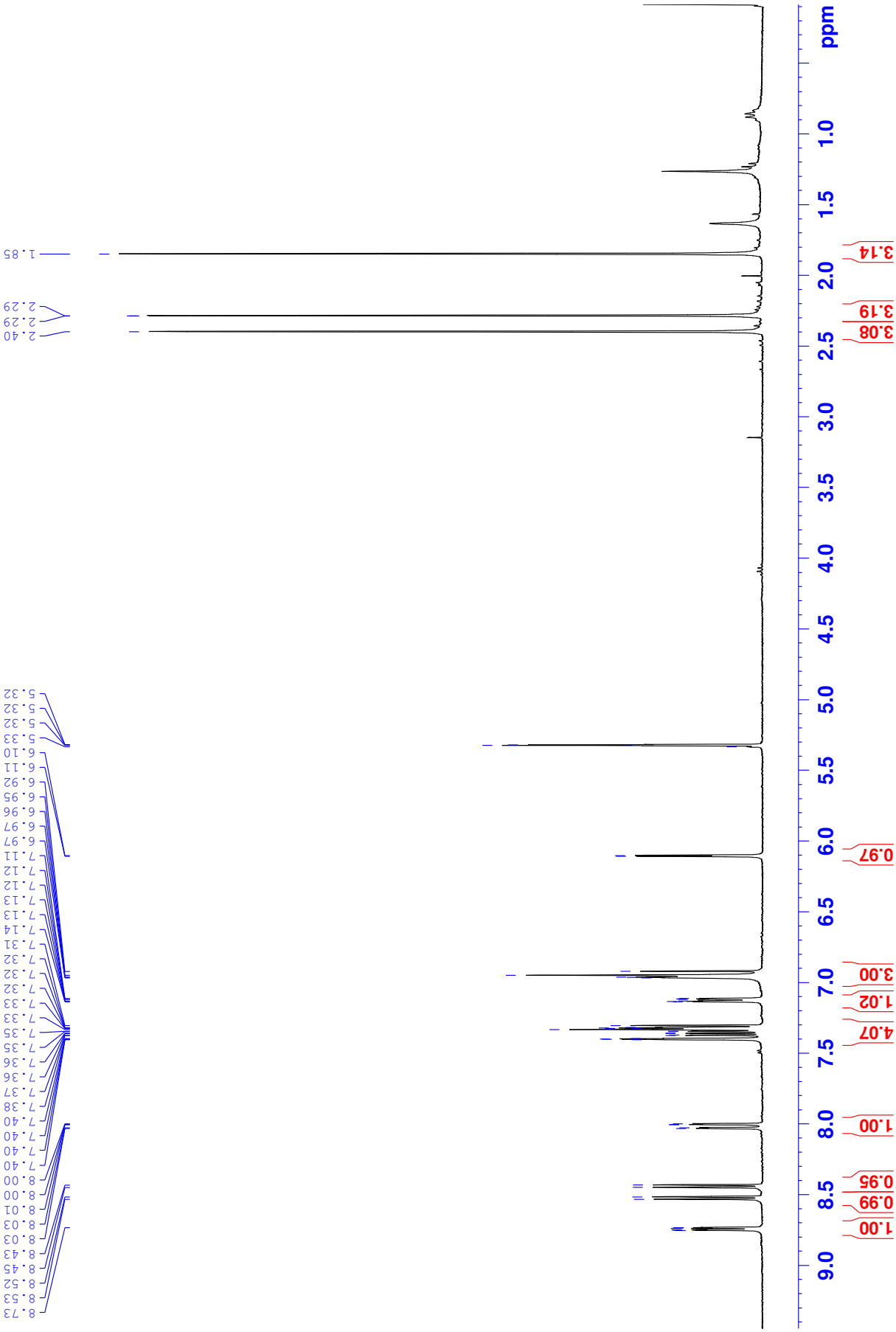


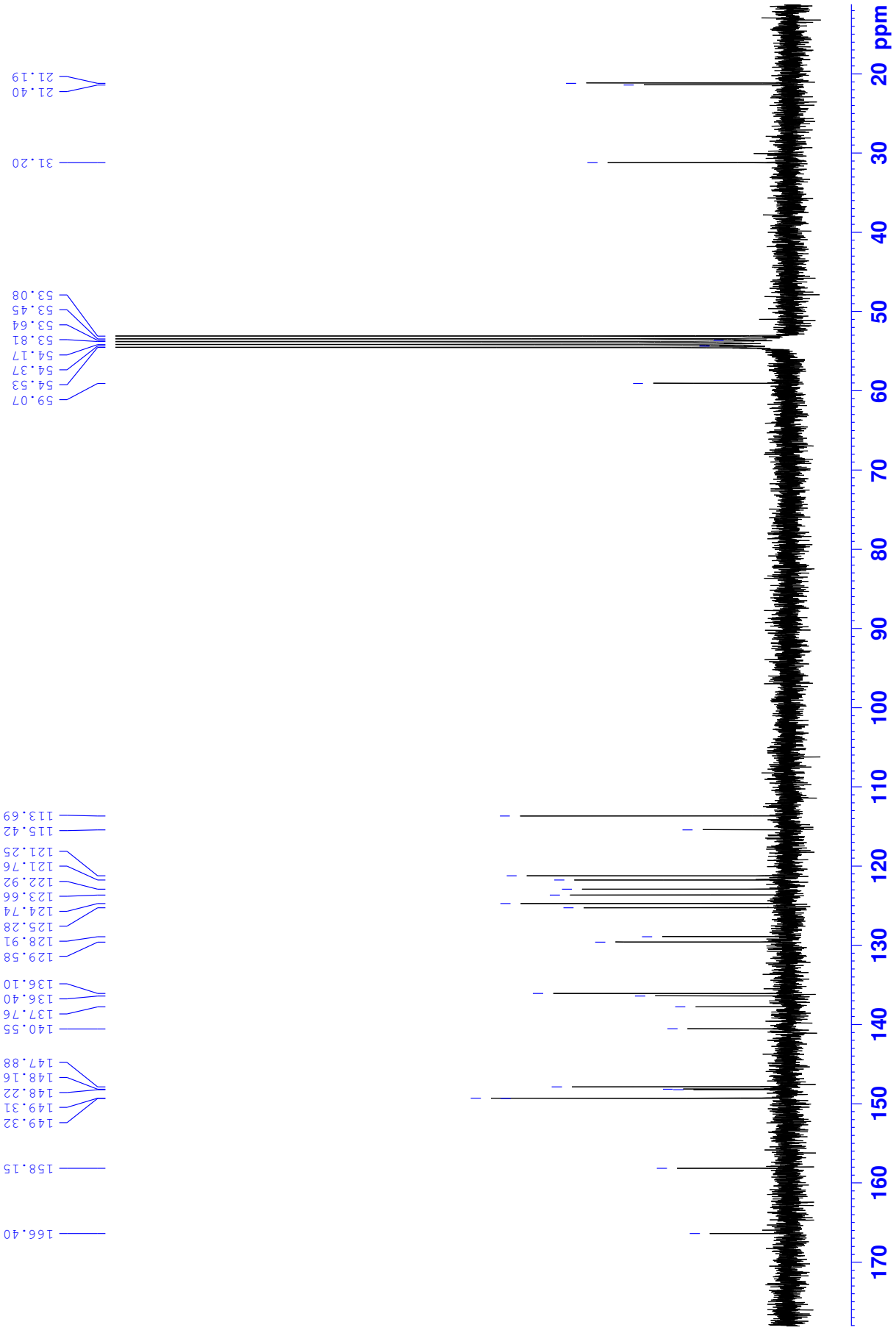
^{13}C RMN of **3** (CD_2Cl_2)



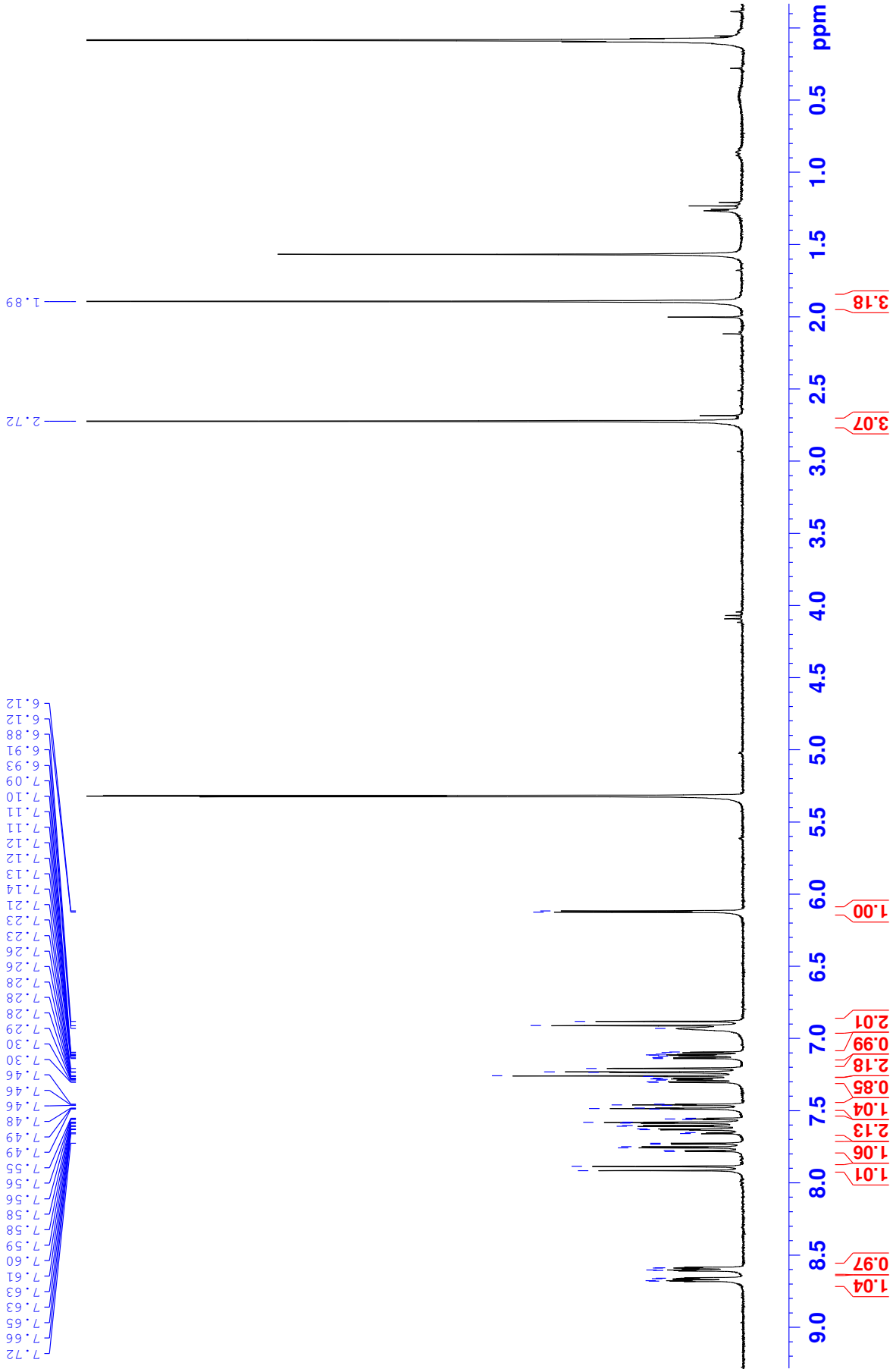
^{1}H RMN of **4** (CD_2Cl_2)



^{13}C RMN of **4** (CD_2Cl_2)



^{1}H RMN of **5** (CD_2Cl_2)



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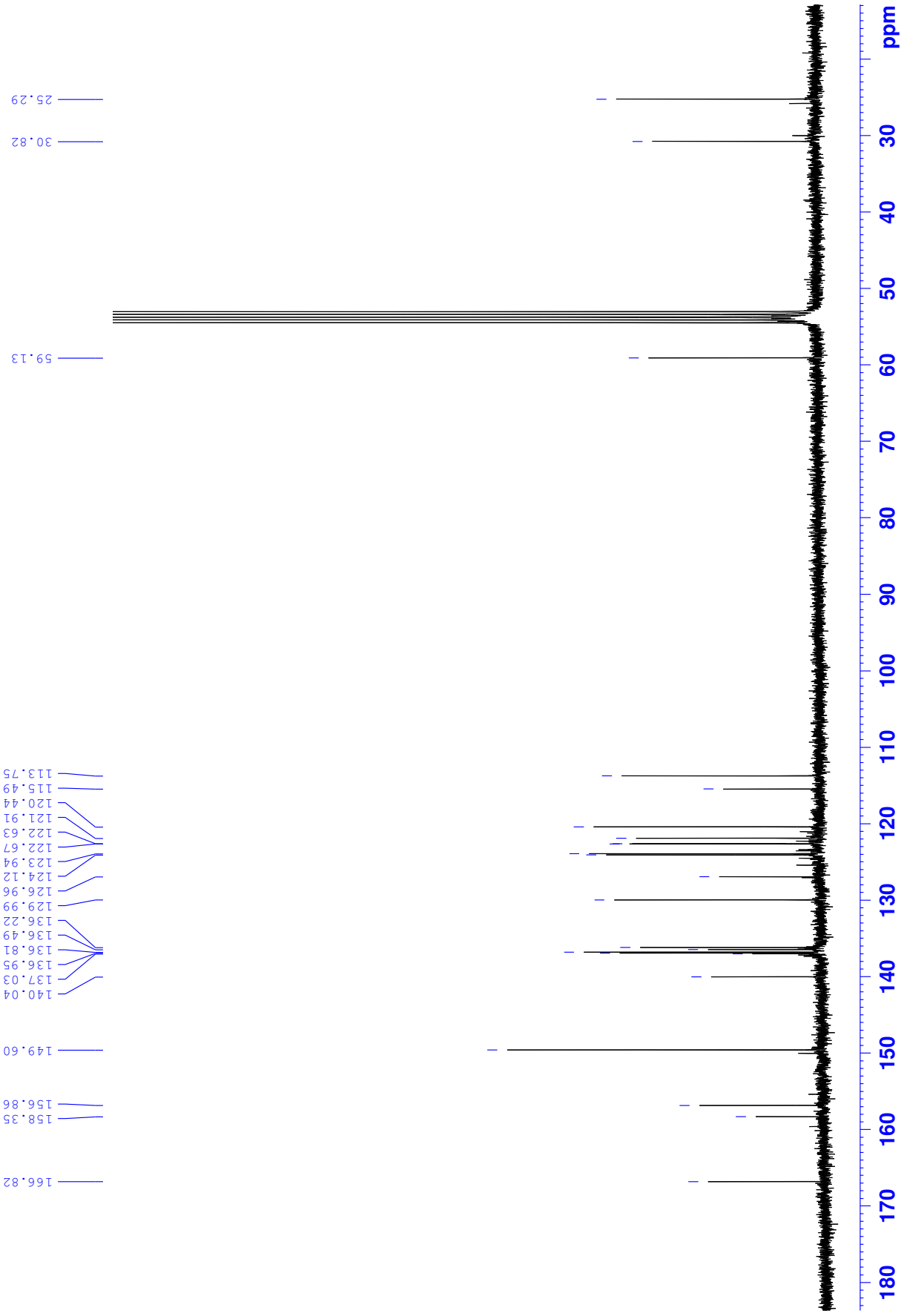

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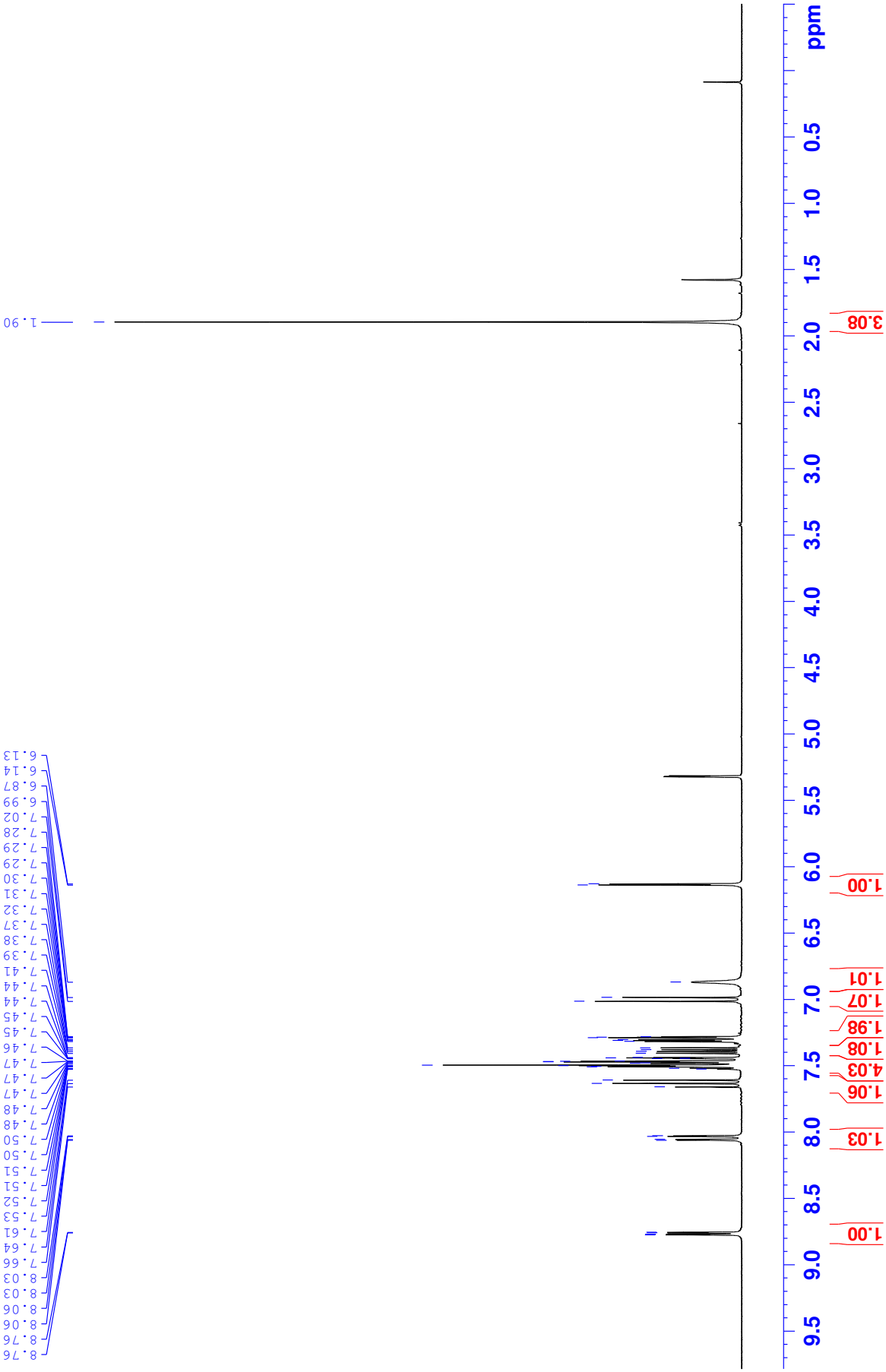
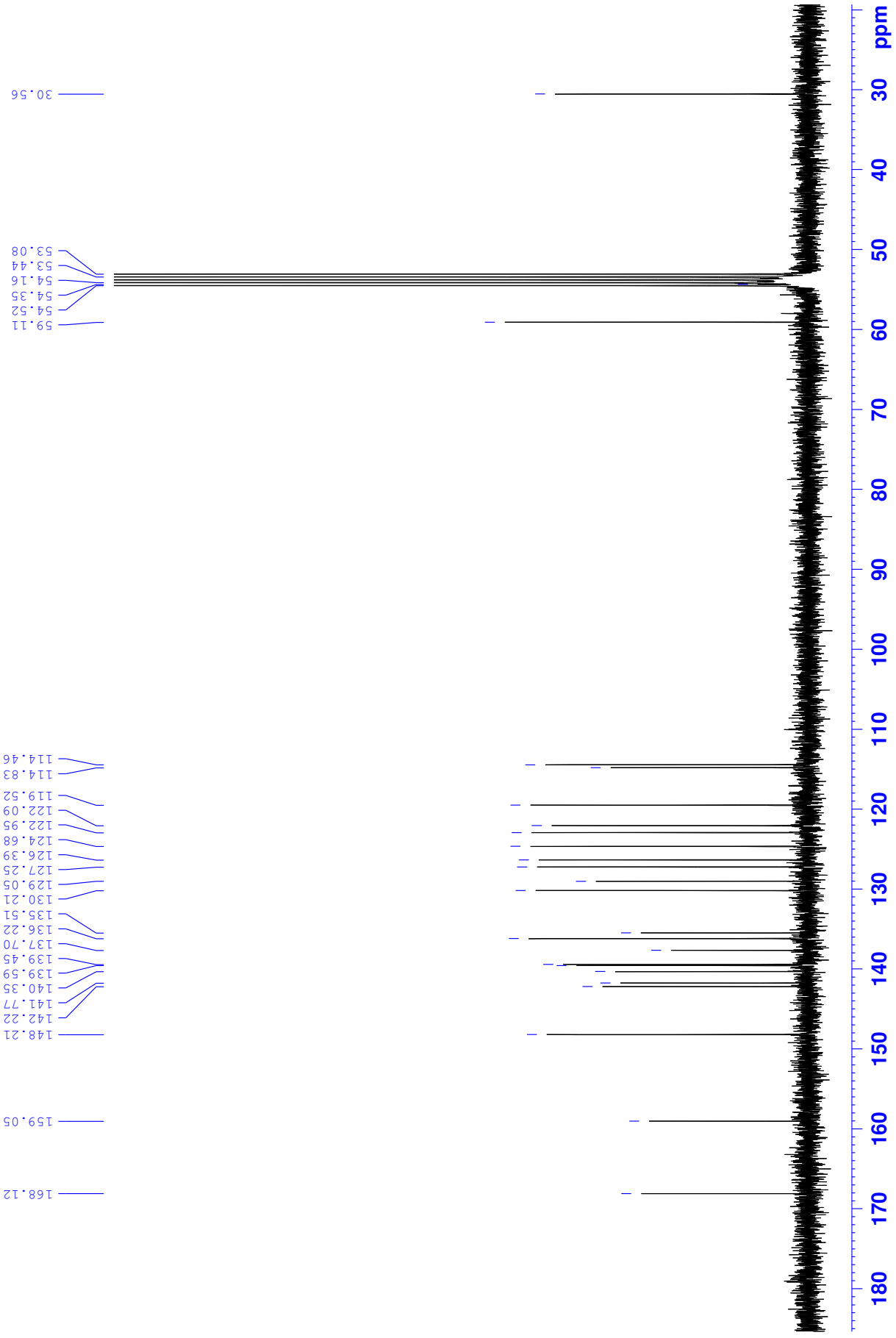
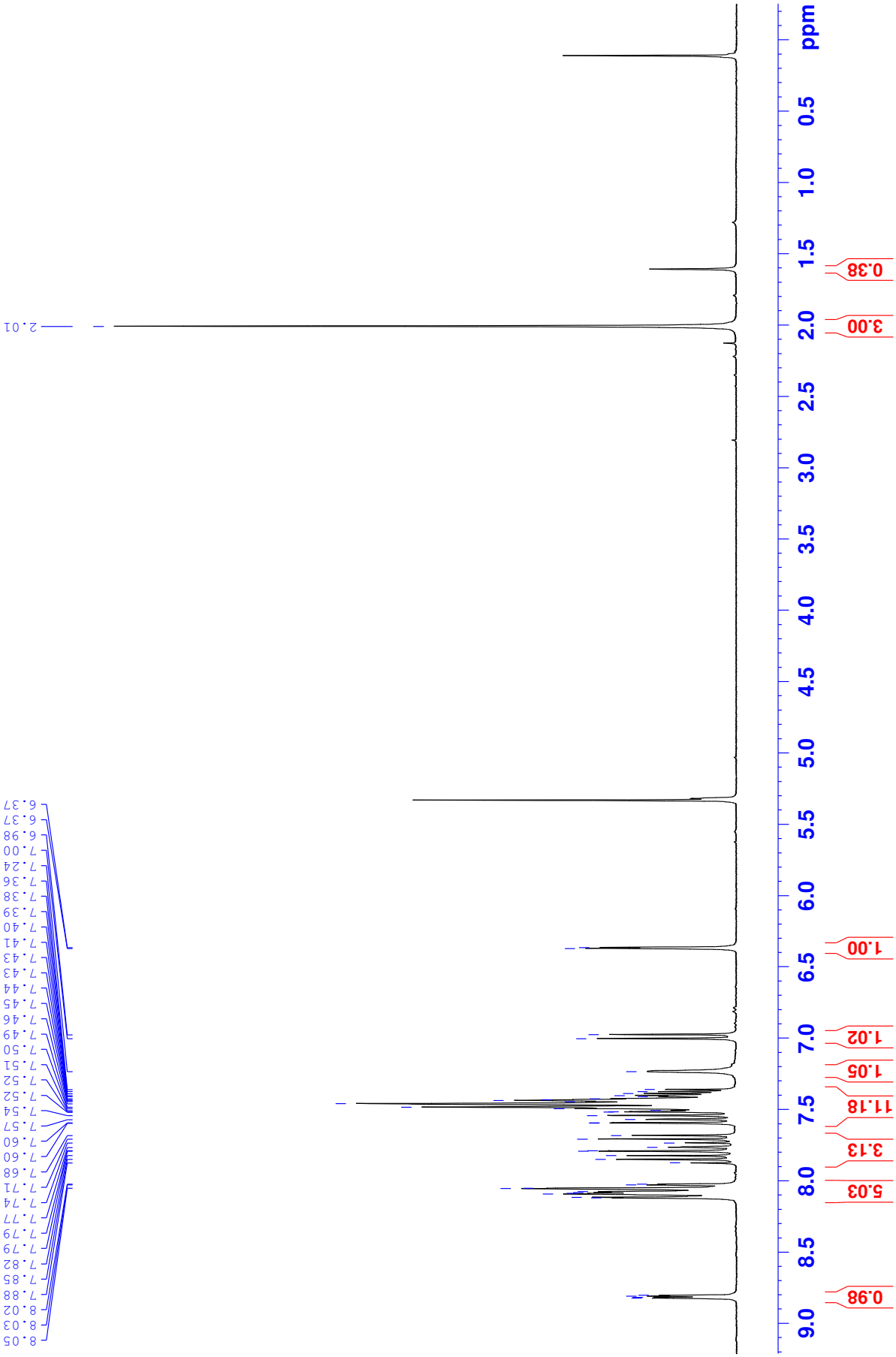


^{13}C RMN of **6** (CD_2Cl_2)



^{1}H RMN of **7** (CD_2Cl_2)



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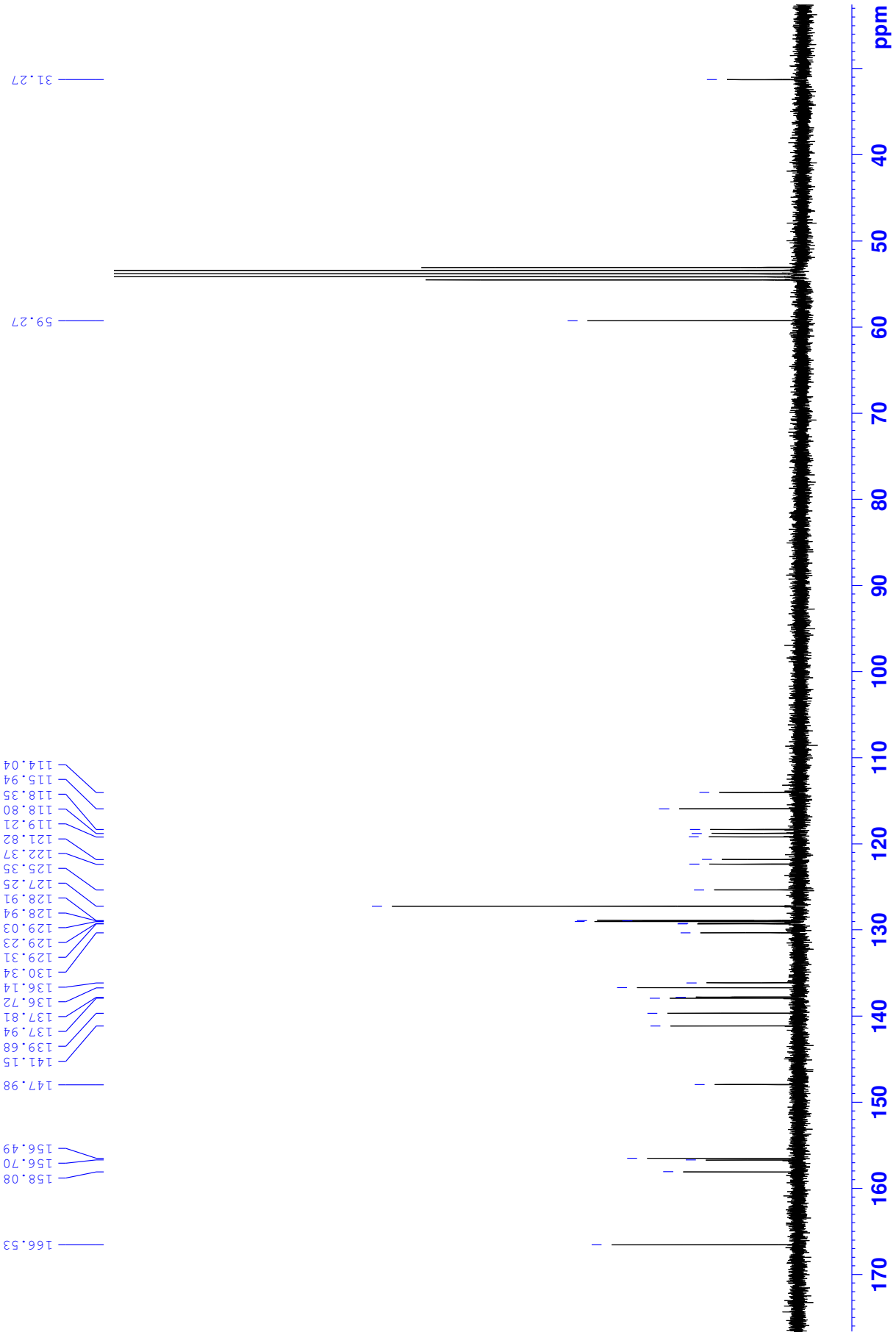
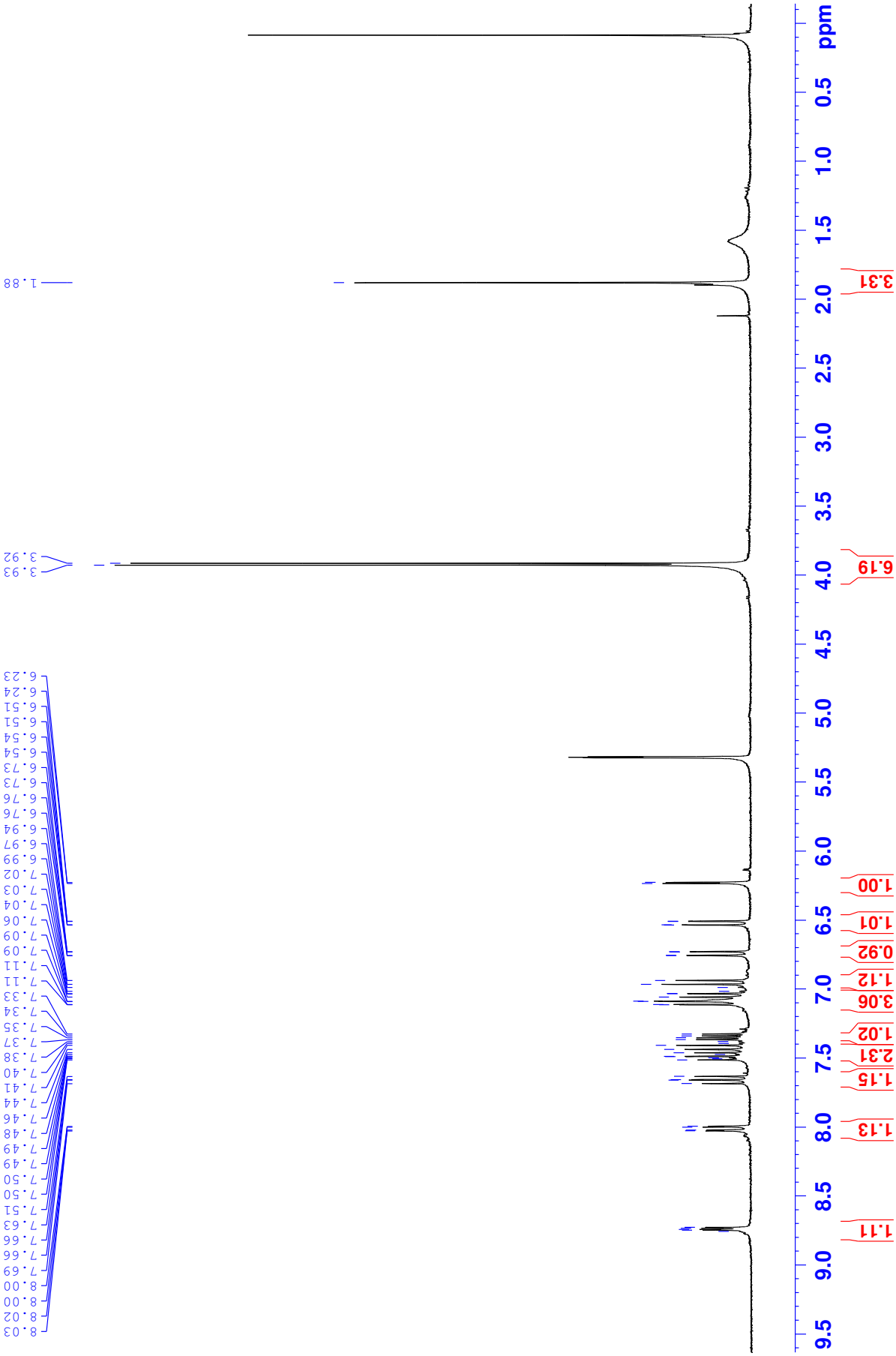


^{1}H RMN of **8** (CD_2Cl_2)



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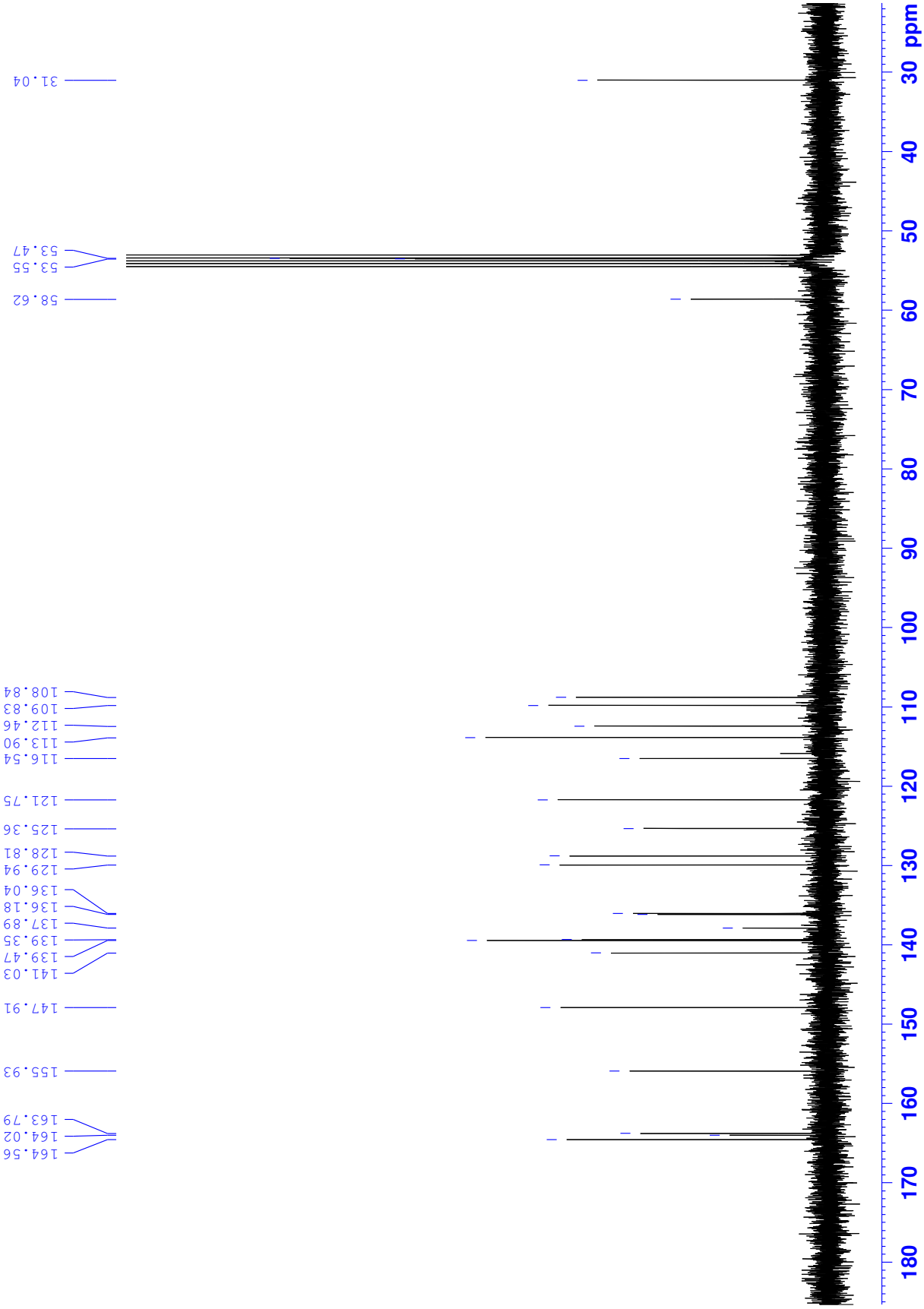
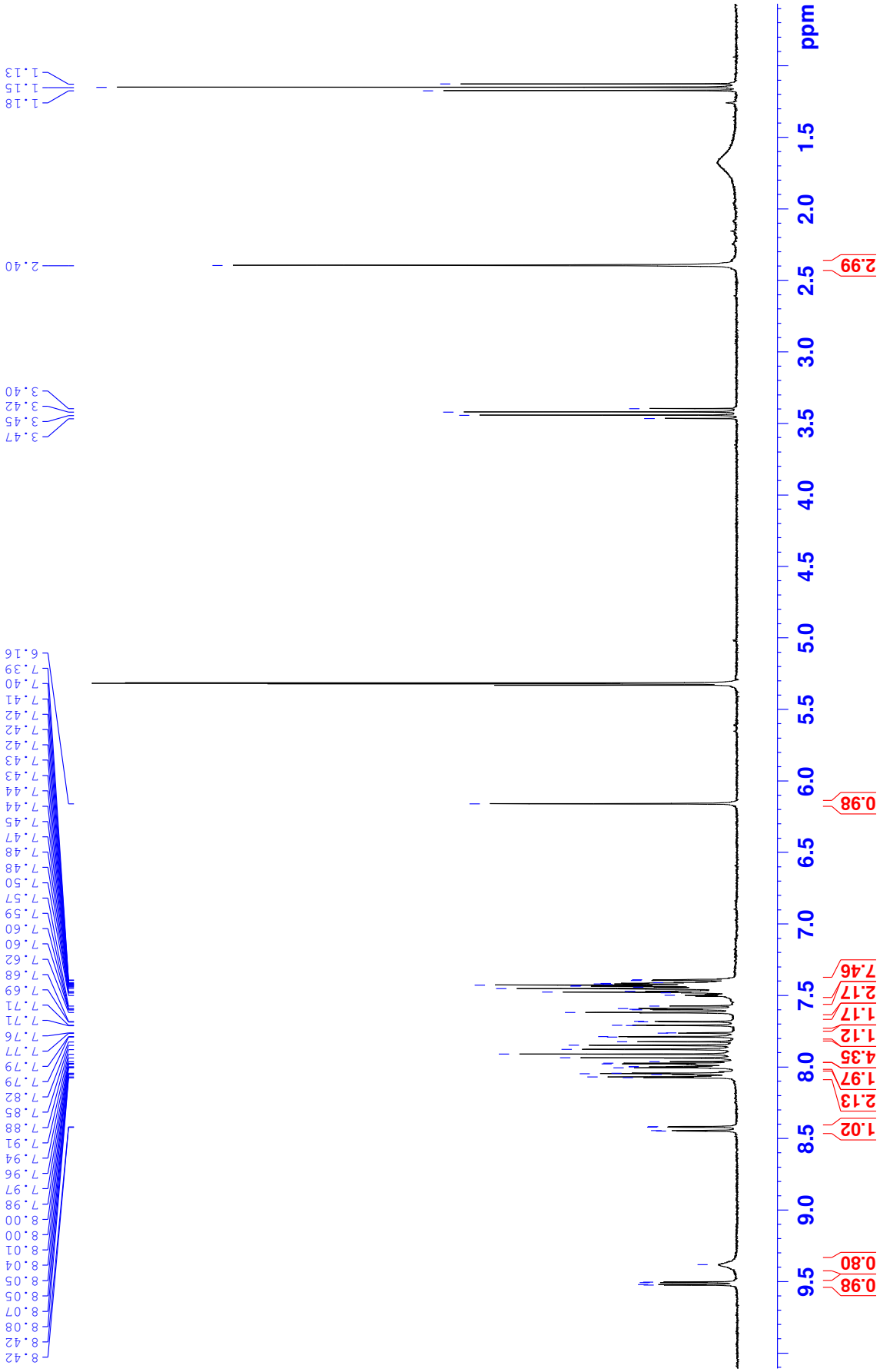
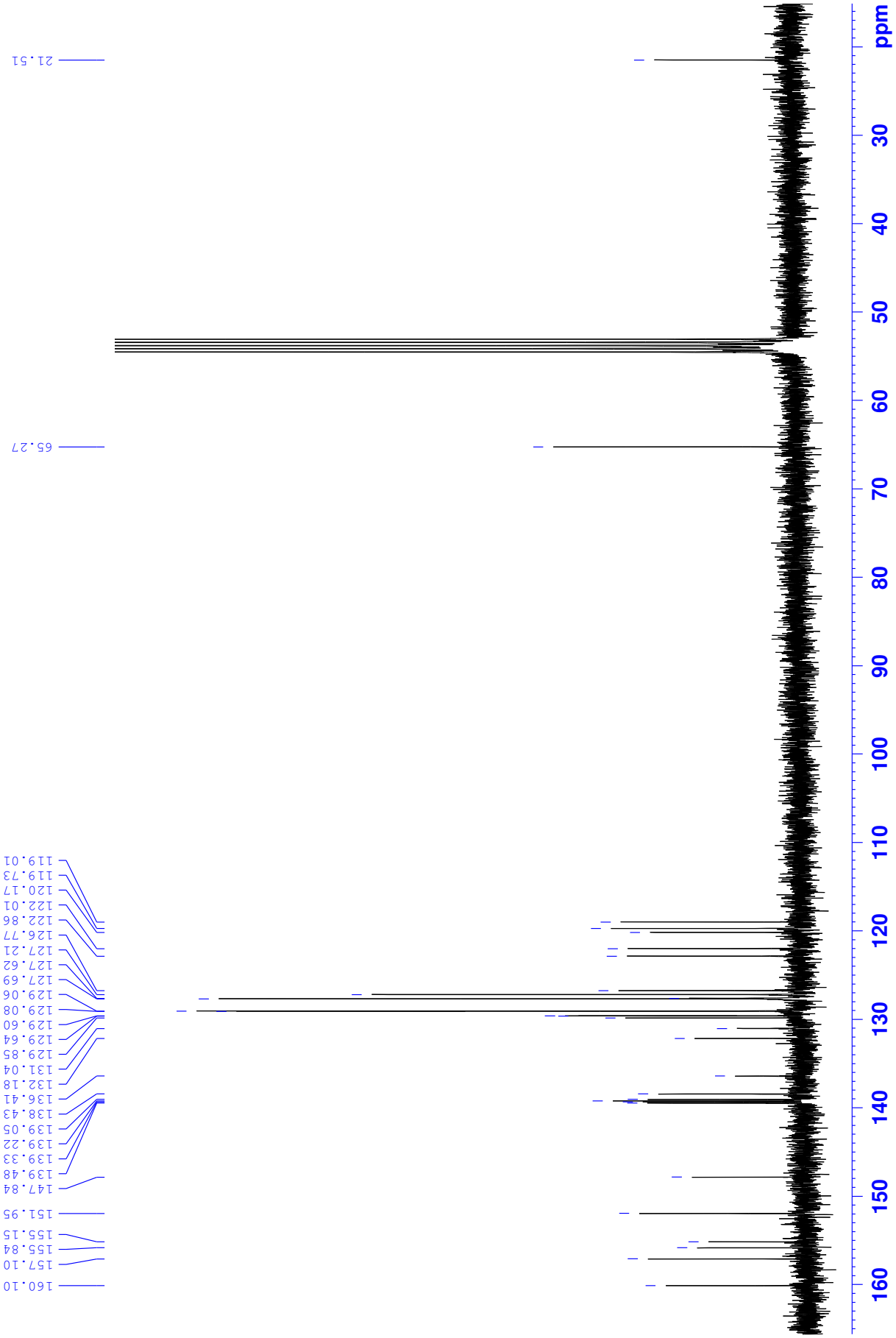


^{1}H RMN of **9** (CD_2Cl_2)



^{13}C RMN of **9** (CD_2Cl_2)



S2. Crystallographic data

Diffraction data of **1**, **4, 6** and **9**·2CH_2Cl_2 were collected on a Kappa CCD diffractometer using graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å).[i] Crystallographic and experimental details are summarized in Table 6. The structures were solved by direct methods (SHELXS-97)[ii] and refined by full-matrix least-squares procedures (based on F^2, SHELXL-97) with anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions (SHELXS-97 procedures) and refined riding on the corresponding parent atoms, with refined torsion angles for the methyl groups. Crystallographic data for all of the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC XXX (**1**), XXX (**4**), XXX (**6**) and XXX (**9**·2CH_2Cl_2). Copies of this information may be obtained free of charge *via* http://www.ccdc.cam.ac.uk

S2.1 Crystallographic data of compound 1

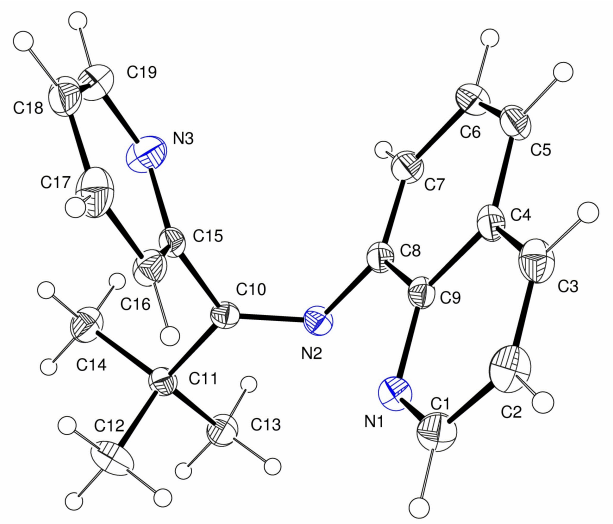


Fig. 1 ORTEP plot of the molecular structure of **1**. Single crystals were grown from CH_2Cl_2. Ellipsoïds are represented at 50% probability level.

S2.2 Crystallographic data of compound 4

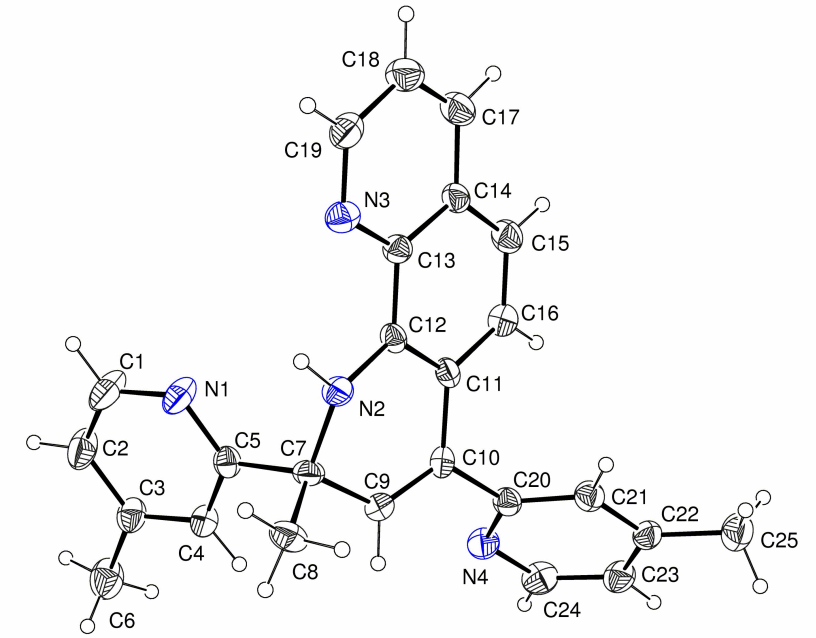


Fig. 2 ORTEP plot of the molecular structure of **4**. Single crystals were grown from CH_2Cl_2. Ellipsoïds are represented at 50% probability level.

S2.3 Crystallographic data of compound 6

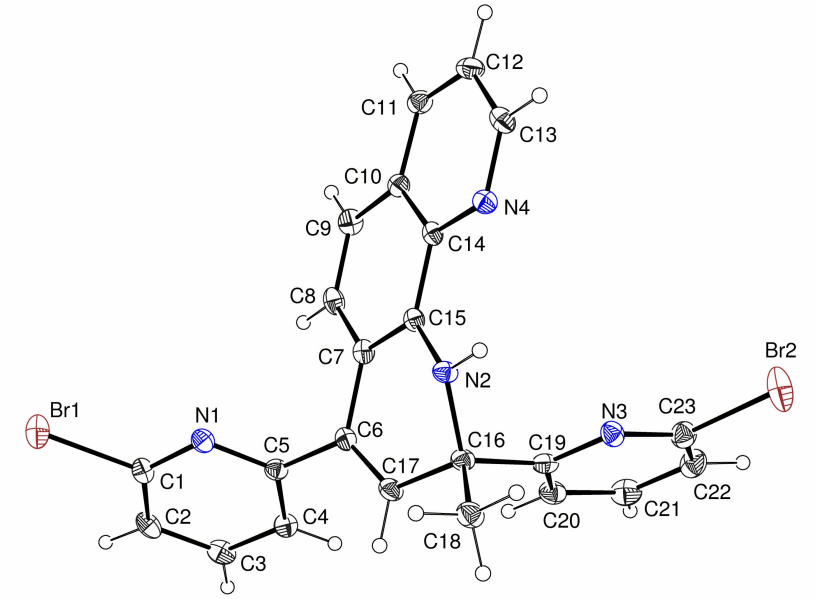


Fig. 3 ORTEP plot of the molecular structure of **6**. Single crystals were grown from CH_2Cl_2. Ellipsoïds are represented at 50% probability level.

S2.4 Crystallographic data of compound **9**·$2CH_2Cl_2$

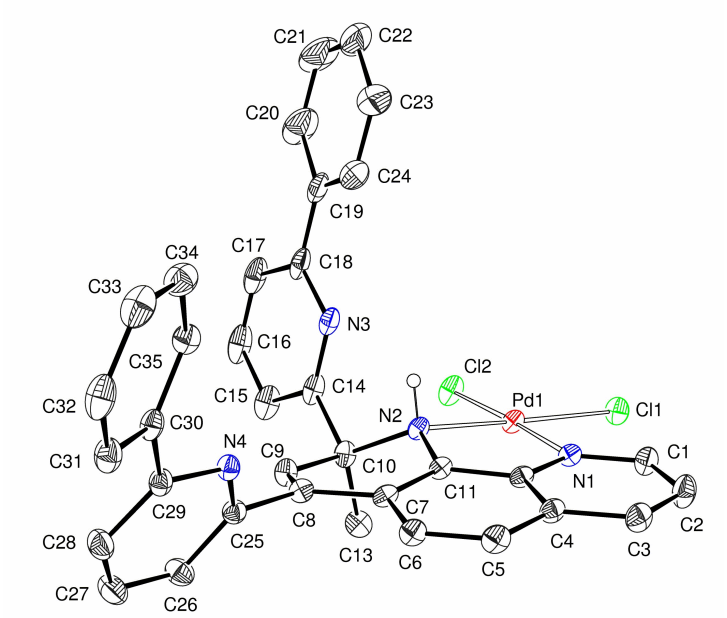


Fig. 3 ORTEP plot of the molecular structure of **9**. Single crystals were grown by slow diffusion of Et_2O in a CH_2Cl_2 solution. Ellipsoïds are represented at 50% probability level.

Table 1. Crystallographic data for **1**, **4, 6** and **9**·$2CH_2Cl_2$ **.**

	1	**9**·$2CH_2Cl_2$	**4**	**6**
Formula	$C_{19}H_{19}N_3$	$C_{35}H_{26}Cl_2N_4Pd$, $2(CH_2Cl_2)$	$C_{25}H_{22}N_4$	$C_{23}H_{16}Br_2N_4$
Formula weight	289.37	849.75	378.47	508.22
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	*P2₁/c*	*P-1*	*C2/c*	*P2₁/c*
a (Å)	8.6143(4)	10.9448(4)	30.417(5)	10.5388(7)
b (Å)	16.7777(9)	12.9038(6)	13.252(2)	19.5573(8)
c (Å)	12.7282(5)	13.8457(6)	10.065(1)	10.6246(7)
α (º)	90.00	80.351(2)	90.00	90.00
β (º)	120.663(3)	86.891(2)	102.944(8)	112.491(2)
γ (º)	90.00	67.035(2)	90.00	90.00
V (Å^3)	1582.38(13)	1774.84(13)	3954.0(10)	2023.3(2)
Z	4	2	8	4
Color	colorless	yellow	yellow	Pale yellow
Crystal size (mm)	0.50×0.40×0.30	0.3×0.2×0.1	0.08×0.02×0.02	0.08×0.06×0.06
D_{calc} (g cm^{-3})	1.215	1.590	1.272	1.668
μ (mm^{-1})	0.073	1.009	0.077	4.024
Max. 2θ	60.02	59.98	51	54
F(000)	616	856	1600	1008
Measd. Refl.	10877	23285	6364	7478
Obsvd. Refl. [$I>2\sigma(I)$]	3097	7839	1171	2917
Parameters	202	438	268	267
$R[I>2\sigma(I)]$	0.0634	0.0727	0.0623	0.0444
$wR2[I>2\sigma(I)]$	0.1654	0.1460	0.0901	0.0892
S	1.037	1.058	0.931	0.979
Largest diff. peak, hole (e Å^{-3})	0.392, -0.299	2.299, -1.899	0.198, -0.224	0.631, -0.758

[i] *Kappa CCD Operation Manual*; Nonius BV, Delft, The Netherlands, 1997.

[ii] G. M. Sheldrick, *SHELX97, Program for the refinement of crystal structures*; University of Göttingen; Göttingen, Germany, 1997.