Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry

Supporting Information

Luminescent bichromophoric spiroindolones - synthesis and electronic properties

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General Informations:

The catalyses were performed in degassed THF which was dried using MBraun system MB-SPS-800. All reactions were carried out in oven-dried Schlenk glassware using septa and syringes under argon atmosphere. The purification of products was performed on silica gel 60 (0.015-0.040 mm) of Macherey Nagel using flash technique and under pressure of 2 bar. The crude mixtures were adsorbed on Celite 545 (0.02-0.10 mm) before chromatographic purification. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX 500 spectrometer and the resonance of the solvent was locked as internal standard. The multiplicities of signals were abbreviated as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), m (multiplet) and corresponding combinations. The type of carbon atoms (CH_3 , CH_2 , CH, C_{quat}) was determined on the basis of DEPT-135 NMR spectra. EI mass spectra were measured on Finnigan MAT 8200 spectrometer. IR spectra were obtained on a Bruker Vector 22 FT-IR. The solids were measured as KBr pellets and the oils in the form of films on KBr plates. The intensity of signals is abbreviated as s (strong), m (medium) and w (weak). The UV/Vis Spectra were recorded on a Hewlett Packard 84252 A Diode Array Spectrophotometer (c ~ 0.5 µM) and the Emission spectra were recorded on a Perkin Elmer LS55 spectrometer. Combustion analyses were carried out on a Perkin Elmer Series II Analyser 2400 in the microanalytical laboratory of the Institut für Pharmazeutische und Medizinische Chemie der Heinrich-Heine-Universität Düsseldorf. Compounds **1a-e** and **2a-c** were prepared as previously reported.[1]

Synthesis of Starting Materials 1a-e:

1a: See Reference 1) and 2) within this Supporting Information.

1b: M. p. 140 °C; ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 1.39 (s, 9H), 7.05 (t, $^{3}J_{H,H}$ = 7.5 Hz, 1H), 7.25 (m, 3H), 7.35 (m, 4H), 7.86 (d, $^{3}J_{H,H}$ = 8.0 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 126 MHz): δ 28.1 (CH_3), 83.3 ($C_{quart.}$), 84.4 ($C_{quart.}$), 94.0 ($C_{quart.}$), 100.1 ($C_{quart.}$), 120.3 ($C_{quart.}$), 128.7 (CH), 129.4 (CH), 130.0 (CH), 130.2 (CH), 133.2 (CH), 139.7 (CH), 141.0 ($C_{quart.}$), 150.1 ($C_{quart.}$), 153.0 ($C_{quart.}$); EI MS (70 eV, *m/z* (%)): 347 ([M-Boc]$^{+\cdot}$, 4), 245 (14), 220 (38), 129 (100), 101 (11), 75 (26), 57 (78); IR (KBr, [cm^{-1}]): $\tilde{\nu}$ = 3066 (w), 2981 (m), 2932 (w), 2207 (s), 1747 (s), 1659 (s), 1578 (w), 1489 (w), 1468 (m), 1443 (w), 1393 (w), 1328 (m), 1280 (s), 1254 (m), 1152 (s), 1119 (m), 1096 (m), 1040 (w), 1022 (w), 952 (m), 847 (m), 787 (w), 755 (m), 731 (m), 706 (w), 690 (m), 671 (w), 627 (w), 538 (w), 516 (w); Combustion Analysis: Calcd. for $C_{20}H_{18}INO_3$ (447.3): C 53.71, H 4.06, N 3.13: Found: C 53.87, H 4.18, N 3.09.

1c: M. p. 80 °C; ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 2.91 (s, 6H), 7.06 (d, $^{3}J_{H,H}$ = 7.2 Hz, 2H), 7.24 (m, 4H), 7.36 (t, $^{3}J_{H,H}$ = 7.5 Hz, 1H), 7.47 (m, 3H), 7.64 (t, $^{3}J_{H,H}$ = 8.5 Hz, 1H), 8.06 (dd, $^{3}J_{H,H}$ = 8.0 Hz, $J_{H,H}$ = 1.2 Hz, 1H), 8.36 (d, $^{3}J_{H,H}$ = 8.5 Hz, 1H), 8.69 (t, $^{3}J_{H,H}$ = 8.0 Hz, 2H); ^{13}C-NMR ($CDCl_3$, 126 MHz): δ 45.7 (CH_3), 82.2 ($C_{quart.}$), 93.6 ($C_{quart.}$), 103.5 ($C_{quart.}$), 115.5 (CH), 119.3 ($C_{quart.}$), 120.1 (CH), 123.4 (CH), 128.6 (CH), 128.7 (CH), 129.1 (CH), 130.1 ($C_{quart.}$), 130.5 ($C_{quart.}$), 131.1 (CH), 131.5 (CH), 132.5 (CH), 133.1 (CH), 133.1 (CH), 134.3 ($C_{quart.}$), 134.4 (CH), 139.6 ($C_{quart.}$), 140.6 (CH), 152.2 ($C_{quart.}$); EI MS (70 eV, *m/z* (%)): 580 ([M]$^{+\cdot}$, 66), 330 (90), 271 (29), 220 (22), 170 (76) 129 (100); IR (KBr, [cm^{-1}]): $\tilde{\nu}$ = 2942 (w), 2832 (w), 2788 (w), 2215 (s), 1683 (s), 1572 (m), 1489 (w), 1462 (m), 1365 (m), 1287 (m), 1234 (w), 1202 (w), 1149 (s), 1058 (m), 1021 (w), 973 (w), 918 (w), 837 (w), 793 (m), 758 (m), 722 (w), 694 (m), 626 (s), 584 (s), 566 (m), 535 (m); UV/Vis (CH_2Cl_2): λ_{abs} (ε): 362 nm (25000); Combustion Analysis: Calcd. for $C_{27}H_{21}IN_2O_3S$ (580.4): C 55.87, H 3.65, N 4.83: Found: C 55.62, H 3.50, N 4.74.

1d: M. p. 101 °C; ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 2.87 (s, 6H), 6.94 (d, $^{3}J_{H,H}$ = 8.5 Hz, 2H), 7.19 (m, 4H), 7.39 (d, $^{3}J_{H,H}$ = 7.0 Hz, 1H), 7.44 (m, 2H), 7.60 (t, $^{3}J_{H,H}$ = 8.0 Hz, 1H), 8.02

(d, $^{3}J_{H,H}$ = 8.0 Hz, 1H), 8.30 (d, $^{3}J_{H,H}$ = 8.5 Hz, 1H), 8.64 (d, $^{3}J_{H,H}$ = 7.5 Hz, 2H); ^{13}C-NMR ($CDCl_3$, 126 MHz): δ 45.7 (CH_3), 83.9 (C $_{quart.}$), 92.2 (C $_{quart.}$), 103.5 (C $_{quart.}$), 115.5 (CH), 117.8 (C $_{quart.}$), 120.0 (CH), 123.4 (CH), 128.7 (CH), 129.1 (CH), 129.2 (CH), 130.1 (C $_{quart.}$), 130.5 (C $_{quart.}$), 131.6 (CH), 132.6 (CH), 133.1 (CH), 134.2 (CH), 134.5 (CH), 137.5 (C $_{quart.}$), 139.5 (C $_{quart.}$), 140.6 (CH), 152.0 (C $_{quart.}$), 152 .1 (C $_{quart.}$); EI MS (70 eV, *m/z* (%)): 614 ([M]$^{+\cdot}$, 21), 264 (100), 305 (15), 216 (13), 170 (72), 163 (80), 154 (29), 127 (24), 99 (11); IR (KBr, [cm^{-1}]): $\tilde{\nu}$ = 2939 (w), 2222 (s), 1676 (s), 1637 (w), 1571 (w), 1543 (w), 1508 (w), 1476 (m), 1465 (m), 1400 (w), 1362 (s), 1298 (s), 1182 (m), 1163 (s), 1089 (m), 1053 (m), 1013 (w), 975 (w), 946 (w), 917 (w), 868 (w), 831 (m), 787 (w), 756 (w), 725 (w), 695 (m), 620 (s), 588 (s), 564 (m), 533 (m); UV/Vis (CH_2Cl_2): λ_{abs} (ε): 366 nm (25500); Combustion Analysis: Calcd. for $C_{27}H_{20}ClIN_2O_3S$ (614.9): C 52.74, H 3.28, N 4.56: Found: C 52.46, H 3.24, N 4.51.

1e: M. p. 82 °C; ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 2.88 (s, 6H), 3.74 (s, 3H), 6.71 (d, $^{3}J_{H,H}$ = 8.8 Hz, 2H), 6.95 (d, $^{3}J_{H,H}$ = 8.8 Hz, 2H), 7.20 (m, 3H), 7.43 (m, 3H), 7.61 (t, $^{3}J_{H,H}$ = 8.0 Hz, 1H), 8.02 (d, $^{3}J_{H,H}$ = 7.8 Hz, 1H), 8.35 (d, $^{3}J_{H,H}$ = 8.5 Hz, 1H), 8.66 (d, $^{3}J_{H,H}$ = 7.5 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 126 MHz): δ 45.7 (CH_3), 55.6 (CH_3), 82.0 ($C_{quart.}$), 94.8 ($C_{quart.}$), 103.7 ($C_{quart.}$), 111.1 ($C_{quart.}$), 114.4 (CH), 115.5 (CH), 128.5 (CH), 129.0 (CH), 130.5 ($C_{quart.}$), 131.4 (CH), 132.3 (CH), 133.6 (CH), 134.4 (CH), 134.5 ($C_{quart.}$), 135.1 (CH), 139.8 ($C_{quart.}$), 140.6 (CH), 152.4 ($C_{quart.}$), 161.2 ($C_{quart.}$); EI MS (70 eV, *m/z* (%)): 610 ([M]$^{\cdot+}$, 32), 360 (31), 349 (16), 334 (16), 302 (34), 250 (15), 222 (11), 170 (22), 159 (100), 71 (12); IR (KBr, [cm^{-1}]): $\tilde{\nu}$ = 2938 (w), 2190 (b), 1774 (w), 1719 (w), 1676 (s), 1601 (s), 1570 (s), 1508 (s), 1459 (m), 1398 (w), 1363 (m), 1289 (m), 1254 (s), 1145 (s), 1056 (w), 1021 (m), 973 (w), 917 (w), 834 (m), 791 (m), 721 (w), 699 (m), 622 (s), 592 (m), 858 (m), 537 (m); UV/Vis (CH_2Cl_2): λ_{abs} (ε): 367 nm (28200); Combustion Analysis: Calcd. for $C_{27}H_{20}ClIN_2O_3S$ (610.5): C 55.09, H 3.80, N 4.59: Found: C 54.81, H 3.67, N 4.59.

2a:[1]

2b:[1]

2c:[1]

2d: ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.51 (s, 3H), 1.74 (s, 3H), 2.65 (d, $^{2}J_{H,H}$ = 2.4 Hz, 1H), 4.15 (m, 2H), 5.40 (m, 1H), 6.65 (d, $^{4}J_{H,H}$ = 2.4 Hz, 1H), 7.49 (m, 4H), 8.00 (d, $^{3}J_{H,H}$ = 8.4 Hz, 2H), 8.46 (s, 1H), 8.65 (d, $^{3}J_{H,H}$ = 8.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 18.2 (CH_3), 26.1 (CH_3), 64.4 (CH), 65.3 (CH_2), 75.8 (CH), 83.0 ($C_{quart.}$), 120.8 (CH), 124.9 (CH), 125.1 (CH), 126.2 (CH), 129.1 ($C_{quart.}$), 129.3 (CH), 129.9 ($C_{quart.}$), 131.8 ($C_{quart.}$), 138.9 ($C_{quart.}$); EI Ms (70eV, m/z, (%)): 300 ($[M]^{+}\cdot$, 24), 215 ($[M\text{-}C_5H_9O]^{+}\cdot$,100), 69 ($[M\text{-}C_{17}H_{11}O]^{+}\cdot$, 34), 55 ($[M\text{-}C_{18}H_{13}O]^{+}\cdot$,30); IR (KBr): $\tilde{\nu}$ = 3581 (w), 3733 (w), 3276 (m), 2911 (m), 2116 (m), 1677 (m), 1622 (m), 1524 (m), 1446 (s), 1383 (m), 1341 (m), 1302 (w), 1288 (m), 1251 (w), 1229 (w), 1202 (w), 1182 (w), 1159 (w), 1122 (w), 1054 (s), 993 (w), 967 (m), 920 (m), 893 (s), 870 (m), 849 (m), 788 (s), 757 (w), 729 (s), 711 (s), 676 (s), 656 (w), 643 (s), 596 (m), 545 (m); Combustion Analysis: Calcd. for $C_{22}H_{20}O\cdot 0.05\ C_4H_{10}O$ (300.2+3.7): C 86.80, H 7.06: Found: C 87.06, H 7.36.

General Procedure for the Synthesis of Spirocyclic Chromophores and Bichromophores:

In an argon flushed oven-dried screw-cap vessel, 2-iodophenylalkynylamide **1** (1.50 mmol), and propargyl prenyl ether **2** (1.65 mmol) were dissolved in a mixture of dry THF (6 mL) and dry triethylamine (6 mL). Then the reaction mixture was degassed with Argon for 5 min before $PdCl_2(PPh_3)_2$ (5 mol%) and CuI (5 mol%) were subsequently added. First, the reaction was stirred at room temperature for 1 h and was then heated to 130 °C for 16 h. After cooling to room temperature the solvents were removed in vacuo and the residue was chromatographed on silica gel (*n*-hexane/ethyl acetate + 5 vol% of triethylamine). After recrystallization from dichloromethane/*n*-hexane the spirocyclic chromophores were obtained as pale yellow powders.

3:[1]

4a: M. p. 186 °C; ^{1}H NMR (500 MHz, CDCl3): δ 0.63 (s, 3H), 1.23 (s, 3H), 1.55 (s, 9H), 3.94 (m, 1H), 4.22 (m, 1H), 4.50 (t, $^3J_{H,H}$ = 9.0 Hz, 1H), 6.78 (m, 2H), 7.06 (s, 1H), 7.10 (m, 3H), 7.19 (t, $^3J_{H,H}$ = 7.5 Hz, 1H), 7.30 (d, $^3J_{H,H}$ = 7.5 Hz, 1H), 7.38 (m, 4H), 7.68 (d, $^3J_{H,H}$ = 8.0 Hz, 2H), 7.88 (d, $^3J_{H,H}$ = 8.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 17.2 (CH_3), 22.3 (CH_3), 28.3 (CH_3), 40.1 ($C_{quat.}$), 48.1 (CH), 62.8 ($C_{quat.}$), 70.4 (CH_2), 84.3 ($C_{quat.}$), 110.2 ($C_{quat.}$), 114.8 (CH), 122.9 (CH), 124.3 (CH), 125.9 (CH), 126.6 (CH), 127.1 (CH), 127.5 (CH), 128.9 (CH), 128.8 (CH), 128.9 (CH), 129.2 (CH), 131.2 ($C_{quat.}$),131.6 ($C_{quat.}$), 135.4 ($C_{quat.}$), 140.0 ($C_{quat.}$), 141.8 ($C_{quat.}$), 149.5 ($C_{quat.}$), 152.7 ($C_{quat.}$), 174.9 ($C_{quat.}$); EI Ms (70 eV, m/z, (%)): 519 ($[M]^+\cdot$,46), 419 ($[M\text{-Boc}]^+\cdot$,59), 330 (16), 314 (17), 261 (21), 105 (100), 77 (23), 57 (50); IR (KBr): $\tilde{\nu}$ = 2978 (w), 1769 (m), 1733 (s), 1628 (w), 1601 (w), 1491 (w), 1476 (m), 1463 (m), 1395 (w), 1370 (w), 1348 (m), 1290 (m), 1252 (m), 1149 (s), 1091 (m), 1067 (w), 1027 (w), 1001 (w), 957 (w), 921 (w), 844 (w), 768 (s), 697 (m), 672 (w), 635 (w), 598 (w); UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (ε) 348 (38300); Combustion Analysis: Calcd. for $C_{34}H_{33}NO_4$ (519.6): C 78.59, H 6.40, N 2.70. Found: C 78.38, H 6.26, N 2.67.

4b: M. p. 123 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.63 (s, 3H), 1.22 (s, 3H), 1.55 (s, 9H), 3.93 (m, 1H), 4.20 (dd, $^3J_{H,H}$ = 8.5 Hz, $^2J_{H,H}$ = 12.5 Hz, 1H), 4.49 (m, 1H), 6.77 (m, 2H), 7.00 (s, 1H), 7.10 (m, 3H), 7.19 (d, $^3J_{H,H}$ = 7.5 Hz, 1H), 7.28 (d, $^3J_{H,H}$ = 7.0 Hz, 1H), 7.37

(d, $^{3}J_{H,H}$ = 8.5 Hz, 3H), 7.61 (d, $^{3}J_{H,H}$ = 8.5 Hz, 2H), 7.88 (d, $^{3}J_{H,H}$ = 8.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 17.2 (CH_3), 22.3 (CH_3), 22.8 (CH_3), 28.3 (CH_3), 40.1 ($C_{quat.}$), 48.1 (CH), 62.7 ($C_{quat.}$), 70.5 (CH_2), 84.4 ($C_{quat.}$), 110.7 ($C_{quat.}$), 114.9 (CH), 122.5 (CH), 124.3 (CH), 125.9 (CH), 126.6 (CH), 127.3 (CH), 128.6 (CH), 128.7 (CH), 129.0 (CH), 129.0 (CH), 129.6 ($C_{quat.}$), 131.4 ($C_{quat.}$), 134.9 ($C_{quat.}$), 136.1 ($C_{quat.}$), 140.0 ($C_{quat.}$), 141.7 ($C_{quat.}$), 149.4 ($C_{quat.}$), 151.5 ($C_{quat.}$), 174.8 ($C_{quat.}$); EI Ms: (70 eV, m/z, (%)): 553 ($[M]^{+}\cdot$, 6), 453 ($[M\text{-}Boc]^{+}\cdot$,10), 86 (11), 84 (23), 71 (16), 69 (24), 67 (11), 57 ($[C_4H_9]^{+}\cdot$, 95), 56 (97), 55 (30), 43 (84), 42 (59), 41 (100); IR (KBr): $\tilde{\nu}$ = 2954 (w), 1769 (s), 1728 (s), 1599 (w), 1489 (m), 1475 (m), 1465 (m), 1394 (w), 1370 (w), 1345 (m), 1289 (s), 1252 (m), 1148 (s), 1091 (m), 1078 (m), 1010 (w), 959 (w), 835 (w), 769 (w), 698 (w), 600 (w); UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (ε) 350 (17300); Combustion Analysis: Calcd. for $C_{34}H_{32}ClNO_4$ (554.1): C 73.70, H 5.82, N 2.53: Found.: C 73.78, H 6.76, N 2.31.

4c: M. p. 157 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.90 (s, 3H), 1.39 (s, 3H), 1.55 (s, 9H), 3.85 (s, 3H), 3.85 (m, 1H), 4.58 (m, 1H), 4.88 (m, 1H), 6.45 (s, 1H), 6.82 (d, $^{3}J_{H,H}$ = 7.5 Hz, 2H), 6.87 (d, $^{3}J_{H,H}$ = 8.5 Hz, 2H), 6.91 (m, 2H), 7.18 (m, 2H), 7.34 (d, $^{3}J_{H,H}$ = 7.5 Hz, 1H), 7.45 (t, $^{3}J_{H,H}$ = 8.0 Hz, 1H), 7.89 (d, $^{3}J_{H,H}$ = 8.5 Hz, 2H), 7.94 (d, $^{3}J_{H,H}$ = 8.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 19.1 (CH_3), 22.4 (CH_3), 28.2 (CH_3), 46.0 ($C_{quat.}$), 51.6 (CH), 55.6 (CH_3), 60.2 (CH_2), 62.9 ($C_{quat.}$), 85.0 ($C_{quat.}$), 113.8 (CH), 115.9 (CH), 122.6 ($C_{quat.}$), 124.9 (CH), 125.1 (CH), 126.5 (CH), 129.0 (CH), 129.4 (CH), 129.7 (CH), 130.1 (CH), 131.8 (CH), 138.5 ($C_{quat.}$), 140.6 ($C_{quat.}$), 149.0 ($C_{quat.}$), 157.2 ($C_{quat.}$), 163.6 ($C_{quat.}$), 173.5 ($C_{quat.}$); EI Ms: (70 eV, m/z, (%)): 549 ($[M]^{+}\cdot$, 3), 449 ($[M\text{-}Boc]^{+}\cdot$, 19), 261 (13), 233 (12), 204 (11), 152 (25), 135 (100), 105 (11); IR (KBr): $\tilde{\nu}$ = 2972 (w), 1719 (w), 1655 (w), 1605 (m), 1543 (w), 1510 (w), 1460 (m), 1343 (w), 1255 (m), 1150 (bs), 1100 (m), 1029 (w), 843 (w), 770 (w), 698 (w); UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (ε) 350 (18900); Combustion Analysis: Calcd. for $C_{35}H_{35}NO_5 \cdot 0.1\ CH_2Cl_2$ (549.7+8.5): C 69.62, H 5.97, N 2.27: Found.: C 69.75, H 5.67, N 2.20.

4d: M. p. 248 °C; ^{1}H-NMR ($CDCl_3$, 500 MHz): *δ* 0.60 (s, 3 H), 1.11 (s, 3H), 2.88 (s, 6H), 3.87 (m, 1H), 4.15 (m, 1H), 4.47 (t, $^{3}J_{H,H}$ = 9.0 Hz, 1H), 6.28 (t, $^{3}J_{H,H}$ = 7.5 Hz, 2H), 6.43 (d, $^{3}J_{H,H}$ = 8.0 Hz, 2H), 6.64 (t, $^{3}J_{H,H}$ = 7.5 Hz, 1H), 6.90 (s, 1H), 7.16 (d, $^{3}J_{H,H}$ = 7.5 Hz, 1H), 7.25 (d, $^{3}J_{H,H}$ = 8.5 Hz, 2H), 7.34 (d, $^{3}J_{H,H}$ = 8.5 Hz, 2H), 7.44 (m, 2H), 7.51 (m, 1H), 7.57 (d, $^{3}J_{H,H}$ = 8.5 Hz, 2H), 8.25 (m, 2H), 8.47 (m, 2H); ^{13}C-NMR ($CDCl_3$, 126 MHz): *δ* 16.6

(CH_3), 21.8 (CH_3), 40.3 ($C_{quat.}$), 45.4 (CH_3), 47.7 (CH), 62.1 ($C_{quat.}$), 70.3 (CH_2), 110.3 ($C_{quat.}$), 113.2 (CH), 115.8 (CH), 118.1 (CH), 112.5 (CH), 123.1 (CH), 124.3 (CH), 127.7 (CH), 126.1 (CH), 126.5 (CH), 127.7 (CH), 128.5 (CH), 128.7 ($C_{quat.}$), 128.8 (CH), 129.1 (CH), 129.6 (CH), 130.2 (CH), 131.4 (CH), 131.8 (CH), 133.0 (CH), 133.2 ($C_{quat.}$), 134.7 ($C_{quat.}$), 134.8 ($C_{quat.}$), 139.7 ($C_{quat.}$), 140.3 ($C_{quat.}$), 151.6 ($C_{quat.}$), 152.2 ($C_{quat.}$), 174.6 ($C_{quat.}$); EI MS (70 eV, *m/z* (%)): 686 ($[M]^+$, 12), 452 ($[M\text{-Dansyl}]^+$, 17), 307 (17), 293 (61), 170 (41), 149 (100); IR (KBr): $\tilde{\nu}$ = 2942 cm^{-1} (s), 2832 (s), 2788 (s), 2215 (m), 1683 (w), 1572 (s), 1462 (m), 1365 (m), 1287 (m), 1149 (w), 1058 (s), 793 (s), 758 (s), 626 (m), 584 (m); UV/VIS (CH_2Cl_2): λ_{max} (ε) 353 (18849); Combustion Analysis: Calcd. for $C_{41}H_{35}ClN_2O_4S$ (687.3): C 71.65, H 5.13, N 4.08; Found.: C 71.53, H 4.95, N 3.83.

4e: M. p. 268 °C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.64 (s, 3H), 1.09 (s,3H), 2.90 (s, 6H), 3.85 (m, 1H), 4.16 (dd, $^3J_{H,H}$ = 8.8 Hz, 1H), 4.47 (t, $^3J_{H,H}$ = 9.3 Hz, 1H), 6.16 (d, $^3J_{H,H}$ = 8.5 Hz, 2H), 6.32 (d, $^3J_{H,H}$ = 8.5 Hz, 2H), 6.89 (s, 1H), 7.18 (d, $^3J_{H,H}$ = 7.5 Hz, 1H), 7.24 (m, 2H), 7.34 (d, $^3J_{H,H}$ = 8.5 Hz, 2H), 7.43 (m, 2H), 7.51 (m, 1H), 7.55 (d, $^3J_{H,H}$ = 8.5 Hz, 2H), 8.15 (d, $^3J_{H,H}$ = 8.5 Hz, 1H), 8.24 (d, $^3J_{H,H}$ = 8.5 Hz, 1H), 8.46 (d, $^3J_{H,H}$ = 7.5 Hz, 1H), 8.55 (d, $^3J_{H,H}$ = 8.5 Hz, 1H); ^{13}C-NMR (128 MHZ, $CDCl_3$): δ 16.9 (CH_3), 22.1 (CH_3), 40.6 (C_{quat}), 45.6 (CH_3), 47.9 (CH), 62.3 (C_{quat}), 70.6 (CH_2), 110.3 (C_{quat}), 113.5 (CH), 115.3 (CH), 117.9 (CH), 122.8 (CH), 123.3 (CH), 124.6 (CH), 126.3 (CH), 127.3 (CH), 128.1 (CH), 128.7 (CH), 128.9 (CH), 129.1 (CH), 129.3 (C_{quat}), 129.5 (CH), 129.9 (C_{quat}), 130.4 (C_{quat}), 131.4 (C_{quat}), 132.4 (CH), 132.5 (C_{quat}), 133.3 (CH), 133.3 (C_{quat}), 133.6 (C_{quat}), 135.2 (C_{quat}), 139.0 (C_{quat}), 139.8 (C_{quat}), 152.4 (C_{quat}); EI Ms: (70 eV, *m/z*, (%)): 720 ($[M]^+$, 11), 486 ($[M\text{-Dansyl}]^+$, 7), 460 (31), 366 (10), 277 (21), 170 (63), 154 (11), 139 (100), 111 (25), 69 (10); IR (KBr): $\tilde{\nu}$ = 2955 (b), 2346 (w), 1757 (s), 1719 (w), 1701 (w), 1686 (w), 1676 (w), 1655 (w), 1638 (w), 1599 (w), 1561 (w), 1544 (w), 1524 (w), 1509 (w), 1490 (m), 1459 (s), 1399 (w), 1364 (m), 1262 (w), 1237 (m), 1204 (w), 1174 (m), 1148 (m), 1092 (s), 1013 (w), 968 (w), 831 (w), 790 (s), 757 (w), 689 (w), 623 (m), 578 (s); UV/VIS (CH_2Cl_2): λ_{max} (ε) 356 (15188); Combustion Analysis: Calcd. for $C_{41}H_{34}Cl_2N_2O_4S \cdot 0.05\ CH_2Cl_2$ (720.2+4.3): C 65.23, H 4.62, N 3.67; Found: C 65.16, H 4.75, N 3.42.

4f: M. p. 161 °C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.52 (s, 3H) 1.02 (s, 3H), 2.81 (s, 6H), 3.43 (s, 3H), 3.78 (t, $^3J_{H,H}$ = 11 Hz, 1H), 4.07 (m, 1H), 4.39 (m, 1H), 5.82 (d, $^3J_{H,H}$ = 8.72 Hz, 2H), 6.32 (d, $^3J_{H,H}$ = 8.71 Hz, 2H), 6.80 (s, 1H), 7.09 (d, $^3J_{H,H}$ = 7.63 Hz, 1H), 7.20 (m, 1H),

7.29 (d, $^{3}J_{H,H}$ = 8.58 Hz, 2H), 7.46 (m, 4H), 7.50 (d, $^{3}J_{H,H}$ = 8.60 Hz, 2H), 8.16 (d, $^{3}J_{H,H}$ = 8.72 Hz, 1H), 8.20 (d, $^{3}J_{H,H}$ = 8.19 Hz, 1H), 8.41 (d, $^{3}J_{H,H}$ = 7.42 Hz, 1H), 8.46 (d, $^{3}J_{H,H}$ = 7.56 Hz, 1H); ^{13}C-NMR (126 MHz, $CDCl_3$): δ 16.6 (CH_3), 21.9 (CH_3), 40.3 ($C_{quat.}$), 45.3 (CH_3), 47.8 (CH), 54.9 (CH_3), 62.2 ($C_{quat.}$), 70.2 (CH_2), 110.4 ($C_{quat.}$), 113.2 (CH), 113.2 (CH), 114.9 (CH), 120.9 (CH), 123.2 (CH), 124.3 (CH), 126.2 (CH), 126.4 (CH), 126.9 (CH), 127.0 (CH), 128.4 (CH), 128.6 (CH), 128.8 (CH), 129.0 (CH), 129.1 (CH), 129.3 ($C_{quat.}$), 130.3 ($C_{quat.}$), 131.4 ($C_{quat.}$), 131.8 (CH), 132.8 ($C_{quat.}$), 133.0 (CH), 133.3 ($C_{quat.}$), 134.5 ($C_{quat.}$), 134.6 ($C_{quat.}$), 139.6 ($C_{quat.}$), 151.0 ($C_{quat.}$), 158.3 ($C_{quat.}$), 174.8 ($C_{quat.}$); EI Ms (70 eV, m/z, (%)): 716 ($[M]^{+}\cdot$, 100), 717 ($M]^{+}\cdot$, 47), 718 ($[M]^{+}\cdot$, 44), 482 ($[M\text{-}C_{12}H_{12}NO_2S]^{+}\cdot$, 28), 170 (19), 139 (46); IR (KBr): $\tilde{\nu}$ = 3651 (m), 2953 (m), 2835 (m), 1756 (s), 1599 (m), 1570 (m), 1502 (s), 1489 (s), 1458 (s), 1396 (m), 1364 (s), 1285 (m), 1245 (s), 1203 (m), 1173 (s), 1145 (s), 1058 (s), 991 (m), 966 (m), 943 (m), 831 (m), 800 (m), 785 (m), 759 (m), 688 (m), 623 (m), 596 (w), 579 (s), 566 (m); UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (ε) 358 (24900); HR-MS: Calcd. for $C_{42}H_{37}NaClN_2O_5S$: 739.200391; Found: 739.200742.

4g: M. p. 263 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.81 (s, 3H), 1.47 (s, 3H), 2.38 (s, 3H), 4.19 (t, $^{3}J_{H,H}$ = 11.0 Hz, 1H), 4.56 (m, 1H), 4.75 (t, $^{3}J_{H,H}$ = 9.5 Hz, 1H), 6.15 (s, 1H), 6.20 (d, $^{3}J_{H,H}$ = 8.0 Hz, 2H), 6.47 (t, $^{3}J_{H,H}$ = 7.5 Hz, 2H), 6.72 (t, $^{3}J_{H,H}$ = 7.5 Hz, 1H), 7.14 (d, $^{3}J_{H,H}$ = 8.5 Hz, 2H), 7.29 (t, $^{3}J_{H,H}$ = 7.5 Hz, 1H), 7.37 (d, $^{3}J_{H,H}$ = 7.5 Hz, 1H), 7.50 (m, 5H), 7.82 (d, $^{3}J_{H,H}$ = 8.0 Hz, 2H), 7.99 (d, $^{3}J_{H,H}$ = 8.5 Hz, 1H), 8.04 (dd, $^{3}J_{H,H}$ = 8.5 Hz, $^{4}J_{H,H}$ = 3.0 Hz, 2H), 8.14 (d, $^{3}J_{H,H}$ = 8.5 Hz, 1H), 8.20 (d, $^{3}J_{H,H}$ = 8.5 Hz, 1H), 8.51 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 17.5 (CH_3), 21.9 (CH_3), 22.2 (CH_3), 40.8 ($C_{quat.}$), 47.7 (CH), 62.8 ($C_{quat.}$), 71.4 (CH_2), 113.2 (CH), 114.7 ($C_{quat.}$), 122.5 (CH), 124.5 ($C_{quat.}$), 124.8 (CH), 125.5 (CH), 125.7 (CH), 125.9 (CH), 126.2 (CH), 126.3 (CH), 126.5 (CH), 126.8 (CH), 128.0 (CH), 128.2 (CH), 128.9 (CH), 129.9 (CH), 129.5 (CH), 129.8 (CH), 130.8 ($C_{quat.}$),131.0 ($C_{quat.}$),131.5 ($C_{quat.}$), 131.6 ($C_{quat.}$), 132.0 ($C_{quat.}$), 134.0 ($C_{quat.}$), 135.2 ($C_{quat.}$), 139.4 ($C_{quat.}$), 140.8 ($C_{quat.}$), 145.4 ($C_{quat.}$), 150.9 ($C_{quat.}$); EI Ms: (70 eV, m/z, (%)) 673 ($[M]^{+}\cdot$, 37), 518 (21), 340 (17), 299 (12), 252 (28), 205 (64), 177 (57), 135 (56), 91 (81), 57 (67), 43 (100); IR (KBr): $\tilde{\nu}$ = 3053 (w), 2976 (w), 1760 (s), 1655 (w), 1598 (m), 1492 (w), 1459 (m), 1377 (m), 1324 (w), 1295 (w), 1238 (m), 1179 (s), 1145 (m), 1092 (w), 1059 (m), 978 (w), 888 (w), 847 (w), 814 (w), 762 (m), 691 (m), 660 (m), 593 (w), 572 (s), 545 (m); UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (ε) 387 (10500), 368 (10600), 321 nm (17200); Combustion

Analysis: Calcd. for $C_{44}H_{35}NO_4S$ (673.8): C 78.43, H 5.24, N 2.08: Found: C 78.18, H 5.39, N 2.00.

4h: M. p. 189 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.74 (s, 3H), 1.51 (s, 3H), 1.57 (s, 9H), 4.24 (t, $^3J_{H,H}$ = 11.0 Hz, 1H), 4.57 (m, 1H), 4.75 (t, $^3J_{H,H}$ = 9.5 Hz, 1H), 6.23 (s, 1H), 6.56 (d, $^3J_{H,H}$ = 7.5 Hz, 2H), 6.93 (m, 3H), 7.29 (t, $^3J_{H,H}$ = 7.5 Hz, 1H), 7.41 (d, $^3J_{H,H}$ = 7.5 Hz, 2H), 7.46 (m, 1H), 7.52 (m, 2H), 7.57 (t, $^3J_{H,H}$ = 7.5 Hz, 1H), 7.91 (d, $^3J_{H,H}$ = 8.0 Hz, 1H), 8.01 (d, $^3J_{H,H}$ = 8.5 Hz, 1H), 8.05 (d, $^3J_{H,H}$ = 8.5 Hz, 1H), 8.18 (d, $^3J_{H,H}$ = 8.5 Hz, 1H), 8.25 (d, $^3J_{H,H}$ = 8.5 Hz, 1H), 8.53 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 17.7 (CH_3), 22.1 (CH_3), 28.3 (CH_3), 40.7 ($C_{quat.}$), 47.6 (CH), 62.9 ($C_{quat.}$), 71.3 (CH_2), 84.3 ($C_{quat.}$), 109.6 ($C_{quat.}$), 115.0 (CH), 124.6 ($C_{quat.}$), 125.9 (CH), 126.2 (CH), 126.6 (CH), 126.4 (CH), 126.8 (CH), 127.0 (CH), 128.3 (CH), 128.9 (CH), 129.3 (CH), 130.9 ($C_{quat.}$), 131.6 ($C_{quat.}$), 134.0 ($C_{quat.}$), 136.9 ($C_{quat.}$), 140.0 ($C_{quat.}$), 141.2 ($C_{quat.}$), 149.4 ($C_{quat.}$), 150.5 ($C_{quat.}$), 175.0 ($C_{quat.}$); EI Ms: (70 eV, m/z, (%)) 619 ($[M]^+\cdot$, 17), 519 ($[M\text{-Boc}]^+\cdot$, 100), 450 (12), 299 (51), 287 (14), 255 (14), 215 (17), 205 (35), 191 (16), 177 (65), 150 (16), 56 (54), 44 (20), 41 (50); IR (KBr): $\tilde{\nu}$ = 2979 (w), 1767 (m), 1724 (m), 1655 (w), 1602 (w), 1476 (m), 1463 (m), 1395 (w), 1370 (w), 1346 (m), 1303 (m), 1289 (m), 1252 (m), 1148 (s), 1098 (m), 1060 (w), 1003 (w), 936 (w), 891 (w), 844 (w), 750 (m), 735 (m), 699 (m), 645 (m); UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (ε) 387 (10600), 367 (10100), 320 nm (19300); Combustion Analysis: Calcd. for $C_{42}H_{37}NO_4 \cdot 0.02\ CH_2Cl_2$ (619.8+1.7): C 80.26, H 5.96, N 2.22: Found: C 80.03, H 5.93, N 2.20.

4i: M. p. 263 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.72 (s, 3H), 1.36 (s, 3H), 2.86 (s, 6H), 4.18 (t, $^3J_{H,H}$ = 11.0 Hz, 1H), 4.52 (dd, $^3J_{H,H}$ = 9.0 Hz, $^3J_{H,H}$ = 12.0 Hz, 1H), 4.72 (t, $^3J_{H,H}$ = 9.5 Hz, 1H), 6.09 (t, $^3J_{H,H}$ = 8.0 Hz, 2H), 6.13 (s, 1H), 6.22 (d, $^3J_{H,H}$ = 7.5 Hz, 2H), 6.48 (t, $^3J_{H,H}$ = 7.5 Hz, 1H), 7.14 (d, $^3J_{H,H}$ = 7.5 Hz, 1H), 7.46 (m, 9H), 8.00 (m, 3H), 8.10 (d, $^3J_{H,H}$ = 8.5 Hz, 1H), 8.21 (d, $^3J_{H,H}$ = 8.5 Hz, 1H), 8.25 (d, $^3J_{H,H}$ = 9.0 Hz, 1H), 8.29 (d, $^3J_{H,H}$ = 8.0 Hz, 1H), 8.46 (m, 1H), 8.50 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 17.3 (CH_3), 22.1 (CH_3), 41.2 ($C_{quat.}$), 45.7 (CH_3), 47.6 (CH), 62.6 ($C_{quat.}$), 71.4 (CH_2), 113.5 (CH), 114.8 ($C_{quat.}$), 115.3 (CH), 122.2 (CH), 123.4 (CH), 124.4 ($C_{quat.}$), 124.6 (CH), 125.5 (CH), 125.7 (CH), 125.8 (CH), 125.9 (CH), 126.1 (CH), 126.4 (CH), 126.7 (CH), 126.8 (CH), 127.7 (CH), 128.8 (CH), 128.9 (CH), 129.3 (CH), 129.4 (CH), 130.4 ($C_{quat.}$), 130.8 ($C_{quat.}$), 130.9 ($C_{quat.}$), 131.5 ($C_{quat.}$), 131.5 ($C_{quat.}$), 131.9 ($C_{quat.}$), 132.0 (CH), 133.3 (CH), 133.4 ($C_{quat.}$),

133.8 ($C_{quat.}$), 140.0 ($C_{quat.}$), 140.1 ($C_{quat.}$), 150.9 ($C_{quat.}$), 175.1 ($C_{quat.}$); EI Ms (70 eV, m/z, (%)): 752 ($[M]^{+}\cdot$, 100), 590 (10), 519 (32), 518 ($[M\text{-}Ds]^{+}\cdot$,46), 205 (34), 177 (16), 171 (13), 170 (27), 86 (23), 84 (39), 49 (27), 44 (24), 43 (48); IR (KBr): $\tilde{\nu}$ = 3855 (w), 3752 (w), 3651 (w), 3424 (s), 2942 (m), 1753 (s), 1718 (w), 1701 (w), 1655 (m), 1638 (m), 1598 (m), 1543 (w), 1508 (w), 1491 (w), 1458 (s), 1360 (s), 1323 (m), 1237 (s), 1203 (m), 1174 (s), 1145 (s), 1059 (s), 966 (m), 885 (w), 842 (w), 784 (m), 760 (s), 688 (m), 625 (s), 575 (s); UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (ε) 326 nm (10800), 366 nm (7800), 385 nm (6800); Combustion Analysis: Calcd. for $C_{49}H_{40}N_2O_4S$ (752.9): C 78.17, H 5.35, N 3.72 Found: C 78.05, H 5.16, N 3.82.

4j: M. p. 265 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.76 (s, 3H), 1.39 (s, 3H), 2.87 (d, $^{3}J_{H,H}$ = 9.0 Hz, 6H), 4.17 (t, $^{3}J_{H,H}$ = 11.0 Hz, 1H), 4.53 (dd, $^{3}J_{H,H}$ =9.5 Hz, $^{3}J_{H,H}$ = 12.0 Hz, 1H), 4.74 (t, $^{3}J_{H,H}$ = 9.5 Hz, 1H), 5.97 (m, 2H), 6.12 (d, $^{3}J_{H,H}$ = 8.5 Hz, 3H), 7.16 (d, $^{3}J_{H,H}$ = 7.5 Hz, 1H), 7.45 (m, 8H), 8.01 (m, 2H), 8.09 (d, $^{3}J_{H,H}$ = 8.0 Hz, 1H), 8.19 (dd, $^{3}J_{H,H}$ = 5.5 Hz, $^{3}J_{H,H}$ = 8.5 Hz, 2H), 8.27 (d, $^{3}J_{H,H}$ = 8.0 Hz, 1H), 8.48 (d, $^{3}J_{H,H}$ = 7.5 Hz, 1H), 8.51 (s, 1H), 8.54 (d, $^{3}J_{H,H}$ = 8.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 17.3 (CH_3), 22.1 (CH_3), 41.2 ($C_{quat.}$), 45.6 (CH_3), 47.5 (CH), 62.5 ($C_{quat.}$), 71.5 (CH_2), 113.5 (CH), 114.7 ($C_{quat.}$), 115.4 (CH), 122.7 (CH), 123.3 (CH), 124.3 ($C_{quat.}$), 124.7 (CH), 125.6 (CH), 125.7 (CH), 125.9 (CH), 126.0 (CH), 126.3 (CH), 126.8 (CH), 126.8 (CH), 127.1 (CH), 127.8 (CH), 128.9 (CH), 128.9 (CH), 129.4 (CH), 129.6 (CH), 130.4 ($C_{quat.}$), 130.8 ($C_{quat.}$), 130.9 (C_{quat}), 131.5 ($C_{quat.}$), 131.5 ($C_{quat.}$), 131.6 ($C_{quat.}$), 132.2 ($C_{quat.}$), 132.4 (CH), 132.4 ($C_{quat.}$), 133.3 (CH), 138.6 ($C_{quat.}$), 139.9 ($C_{quat.}$), 151.4 ($C_{quat.}$), 175.0 ($C_{quat.}$); EI Ms (70 eV, m/z, (%)): 786 ($[M]^{+}\cdot$,100),554 (13), 553 (14), 552 ($[M\text{-}Dansyl]^{+}\cdot$, 35), 392 (14), 205 (31), 177 (15), 170 ($[M\text{-}C_{37}H_{27}ClNO_4S]^{+}\cdot$, 24), 57 (15), 56 (14), 44 ($[N\text{-}(CH_3)_2]^{+}\cdot$, 11), 43 (76), 42 (16), 41 (21); IR (KBr): $\tilde{\nu}$ = 3855 (w), 3752 (w), 3736 (w), 3713 (w), 3677 (w), 3650 (w), 2938 (m), 1757 (s), 1655 (m), 1543 (m), 1508 (m), 1458 (s), 1364 (s), 1323 (m), 1238 (m), 1174 (s), 1146 (s), 1058 (s), 967 (m), 890 (m), 788 (s), 757 (m), 734 (m), 687 (m), 622 (s), 576 (s); UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (ε) 330 nm (22100), 367 nm (16700), 386 nm (14800); Combustion Analysis: Calcd. for $C_{49}H_{39}ClN_2O_4S$ (787.4): C 74.75, H 4.99, N 3.56: Found: C 74.59, H 5.01, N 3.44.

4k: M. p. 276 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.70 (s, 3H), 1.37 (s, 3H), 2.85 (s, 6H), 3.37 (s, 3H), 4.17 (m, 1H), 4.50 (dd, $^{3}J_{H,H}$ =9.0 Hz, $^{3}J_{H,H}$ = 12.0 Hz, 1H), 4.71 (t, $^{3}J_{H,H}$ = 9.5 Hz, 1H), 5.67 (d, $^{3}J_{H,H}$ = 9.0 Hz, 2H), 6.08 (s, 1H), 6.18 (d, $^{3}J_{H,H}$ = 9.0 Hz, 2H), 7.13 (d,

$^3J_{H,H}$ = 7.5 Hz, 1H), 7.34 (t, $^3J_{H,H}$ = 7.5 Hz, 1H), 7.47 (m, 8H), 8.00 (m, 2H), 8.11 (d, $^3J_{H,H}$ = 8.0 Hz, 1H), 8.22 (m, 2H), 8.28 (d, $^3J_{H,H}$ = 8.0 Hz, 1H), 8.48 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 17.3 (CH_3), 22.1 (CH_3), 41.2 ($C_{quat.}$), 45.5 (CH_3), 47.7 (CH), 55.0 (CH_3), 62.6 ($C_{quat.}$), 71.3 (CH_2), 113.2 (CH), 113.4 (CH), 114.9 ($C_{quat.}$), 115.1 (CH), 118.3 (CH), 121.0 (CH), 123.4 (CH), 124.6 ($C_{quat.}$), 124.6 (CH), 125.5 (CH), 125.7 (CH), 126.0 (CH), 126.2 (CH), 126.5 (CH), 126.7 (CH), 126.7 (CH), 127.0 (CH), 128.8 (CH), 129.0 ($C_{quat.}$), 129.2 (CH), 129.4 (CH), 129.7 ($C_{quat.}$), 130.5 ($C_{quat.}$), 130.8 ($C_{quat.}$), 130.9 ($C_{quat.}$), 131.5 ($C_{quat.}$), 131.5 ($C_{quat.}$), 131.9 ($C_{quat.}$), 132.1 (CH), 132.7 ($C_{quat.}$), 133.2 (CH), 133.5 ($C_{quat.}$), 133.5 ($C_{quat.}$), 139.9 ($C_{quat.}$), 150.2 ($C_{quat.}$), 158.3 ($C_{quat.}$), 175.2 ($C_{quat.}$); EI Ms (70 eV, m/z, (%)): 782 ($[M]^+\cdot$, 100), 552 (13), 549 (20), 548 ($[M\text{-}Ds]^+\cdot$,28), 250 (31), 205 (54), 177 (25), 171 (16), 170 ($[C_{12}H_{12}N]^+\cdot$,44), 169 (11), 168 (13), 149 (12); IR (KBr): $\tilde{\nu}$ = 3855 (w), 3752 (w), 2936 (m), 2833 (m), 1757 (s), 1655 (m), 1606 (m), 1509 (s), 1458 (s), 1409 (m), 1362 (s), 1322 (m), 1306 (m), 1240 (s), 1203 (m), 1175 (s), 1145 (s), 1057 (m), 966 (m), 944 (m), 885 (w), 829 (m), 785 (s), 756 (m), 733 (m), 687 (m); UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (ε) 327 nm (22900), 366 nm (15700), 384 nm (13800); Combustion Analysis: Calcd. for $C_{50}H_{42}N_2O_5S$ (782.9): C 76.70, H 5.41, N 3.58. Found: C 76.48, H 5.17, N 3.43.

General Procedure for the Synthesis of *N*-unsubstituted Spirocyclic Chromophores and Bichromophores:

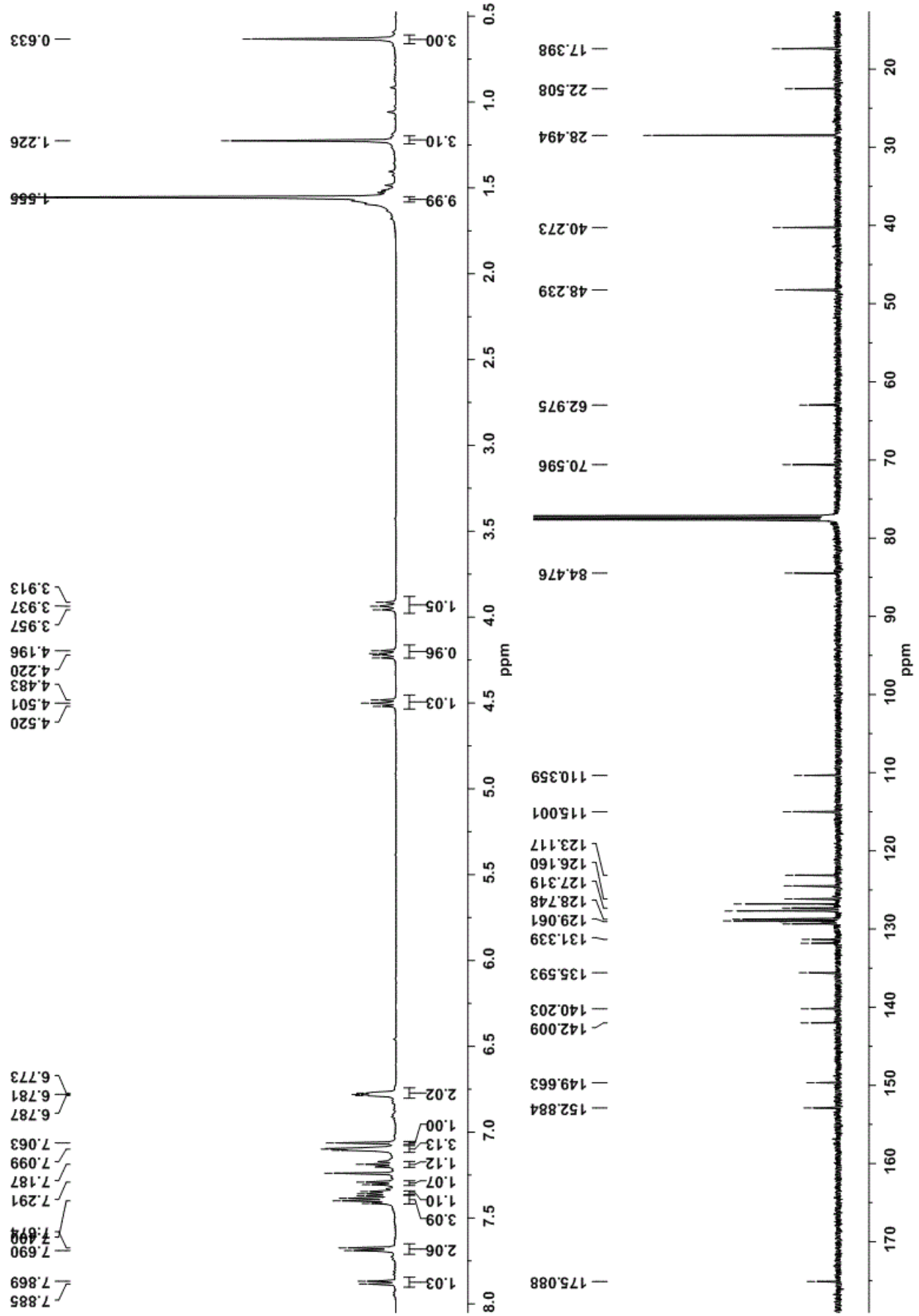
In an argon flushed oven-dried screw-cap vessel, compound **4a** or **4h** (0.2 mmol), respectively, was dissolved in dry dichloromethane (5 mL) and 2 equivalents of dry zinc bromide were added. Then the reaction mixture was stirred for 2 h at room temperature before the solvent was removed in vacuo and the residue was chromatographed on silica gel (*n*-hexane/ethyl acetate + 5 vol% of triethylamine). After recrystallization from dichloromethane/*n*-hexane the spirocyclic chromophores were obtained as pale yellow powders.

4l: M. p. 270 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.66 (s, 3H), 1.24 (s, 3H), 3.97 (dd, $^3J_{H,H}$ = 12.5 Hz, $^3J_{H,H}$ = 9.5 Hz, 1H), 4.23 (dd, $^3J_{H,H}$ = 13.5 Hz, $^3J_{H,H}$ = 8.5 Hz, 1H), 4.52 (m, 1H), 6.76 (d, $^3J_{H,H}$ = 7.5 Hz, 2H), 6.83 (m, 2H), 7.04 (s, 1H), 7.07 (m, 3H), 7.26 (m, 2H), 7.35 (d, $^3J_{H,H}$ = 7.5 Hz, 1H), 7.40 (m, 2H), 7.69 (d, $^3J_{H,H}$ = 8.0 Hz, 2H), 8.33 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 15.7 (CH_3), 20.9 (CH_3), 40.0 ($C_{quat.}$), 47.3 (CH), 61.8 ($C_{quat.}$), 69.2 (CH_2), 108.6 ($C_{quat.}$), 109.3 (CH), 121.3 (CH), 121.4 (CH), 125.1 (CH), 124.4 (CH), 126.0 (CH),

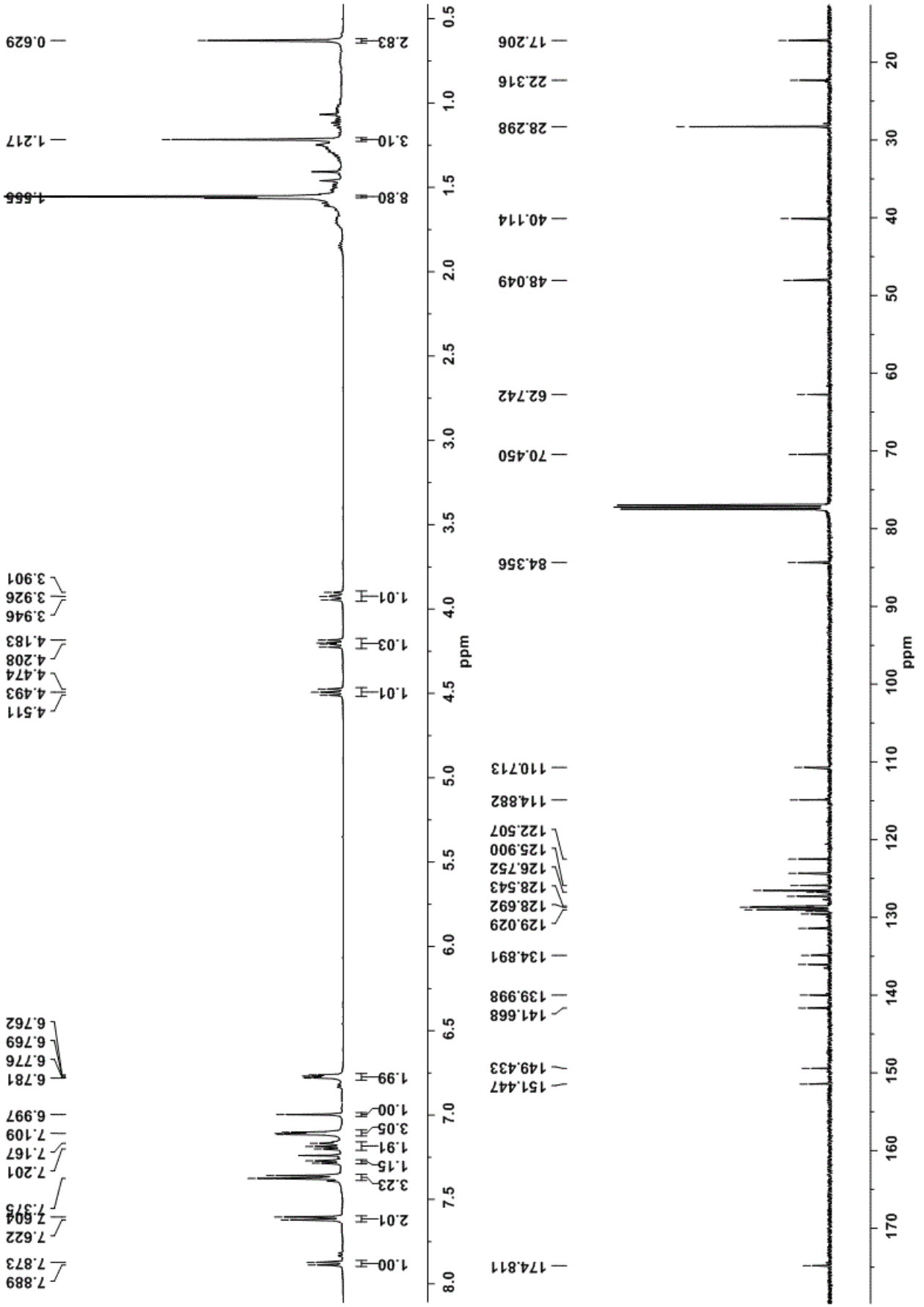
126.3 (CH), 127.2 (CH), 127.3 (CH), 127.5 (CH), 127.9 (CH), 130.0 ($C_{quat.}$), 132.4 ($C_{quat.}$), 134.3 ($C_{quat.}$), 139.8 ($C_{quat.}$), 140.9 ($C_{quat.}$), 151.2 ($C_{quat.}$), 178.8 ($C_{quat.}$); EI Ms (70 eV, m/z, (%)): 419 ($[M]^{+}\cdot$, 69), 314 (28), 246 (14), 185 (10), 165 (15), 132 (12), 115 (13), 105 (100), 91 (11), 77 (53); IR (KBr): $\tilde{\nu}$ = 3056 (w), 2963 (bw), 2892 (w), 1718 (s), 1618 (m), 1597 (w), 1491 (w), 1472 (m), 1445 (w), 1392 (w), 1370 (w), 1326 (w), 1260 (w), 1236 (w), 1179 (w), 1093 (m), 1067 (m), 1024 (w), 954 (w), 802 (w), 766 (m), 698 (m), 674 (w), 630 (w), 559 (w); UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (ε) 347 nm (19100); Combustion Analysis: Calcd. for $C_{29}H_{25}NO_2 \cdot 0.05\ C_4H_8O_2$ (419.5+4.4): C 81.61, H 6.16, N 3.17; Found: C 81.38, H 6.18, N 3.14.

4m: M. P.: 236 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.80 (s, 3H), 1.58 (s, 3H), 4.30 (t, $^{3}J_{H,H}$ = 11.0 Hz, 1H), 4.61 (dd, $^{3}J_{H,H}$ = 9.0 Hz, $^{3}J_{H,H}$ = 11.0 Hz, 1H), 4.79 (t, $^{3}J_{H,H}$ = 9.0 Hz, 1H), 6.23 (s, 1H), 6.64 (d, $^{3}J_{H,H}$ = 7.0 Hz, 2H), 6.81 (d, $^{3}J_{H,H}$ = 7.5 Hz, 1H), 6.94 (m, 3H), 7.17 (t, $^{3}J_{H,H}$ = 7.5 Hz, 1H), 7.31 (t, $^{3}J_{H,H}$ = 7.0 Hz, 1H), 7.41 (d, $^{3}J_{H,H}$ = 7.5 Hz, 1H), 7.48 (m, 1H), 7.48 (m, 1H), 7.54 (m, 2H), 7.59 (m, 1H), 8.03 (d, $^{3}J_{H,H}$ = 8.5 Hz, 1H), 8.07 (d, $^{3}J_{H,H}$ = 8.0 Hz, 1H), 8.23 (d, $^{3}J_{H,H}$ = 8.5 Hz, 1H), 8.28 (d, $^{3}J_{H,H}$ = 9.0 Hz, 1H), 8.55 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 17.6 (CH_3), 22.4 (CH_3), 40.0 ($C_{quat.}$), 48.4 (CH), 63.4 ($C_{quat.}$), 71.6 (CH_2), 110.1 (CH), 115.5 ($C_{quat.}$), 122.2 (CH), 122.7 (CH), 125.8 (CH), 125.9 (CH), 126.3 (CH), 126.5 (CH), 126.5 (CH), 126.6 (CH), 126.9 (CH), 127.3 (CH), 127.7 (CH), 128.4 (CH), 128.9 (CH), 129.0 (CH), 129.1 (CH), 129.4 (CH), 131.1 ($C_{quat.}$), 131.2 ($C_{quat.}$),131.7 ($C_{quat.}$),131.8 ($C_{quat.}$), 133.9 ($C_{quat.}$), 134.0 ($C_{quat.}$), 134.9 (CH), 135.2 ($C_{quat.}$), 141.3 ($C_{quat.}$),141.8 ($C_{quat.}$), 150.4 ($C_{quat.}$), 180.2 ($C_{quat.}$); EI Ms (70 eV, m/z, (%)): 519 ($[M]^{+}\cdot$, 100), 299 (62), 205 (27), 191 (11), 177 (42), 151 (12), 86 (25), 84 (31), 74 (39), 69 (22), 56 (66), 45 (30); IR (KBr): $\tilde{\nu}$ = 2951 (w), 1705 (s), 1655 (m), 1616 (m), 1508 (w), 1491 (w), 1468 (m), 1389 (w), 1318 (w), 1178 (m), 1136 (w), 1037 (w), 976 (w), 845 (w), 749 (m), 698 (m), 635 (w), 548 (w); UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (ε) 386 (9200), 367 (9500), 318 (18500); Combustion Analysis: Calcd. for $C_{37}H_{29}NO_2 \cdot 0.05\ CH_2Cl_2$ (519.6+4.3): C 81.83, H 5.46, N 2.56; Found: C 81.69, H 5.60, N 2.32.

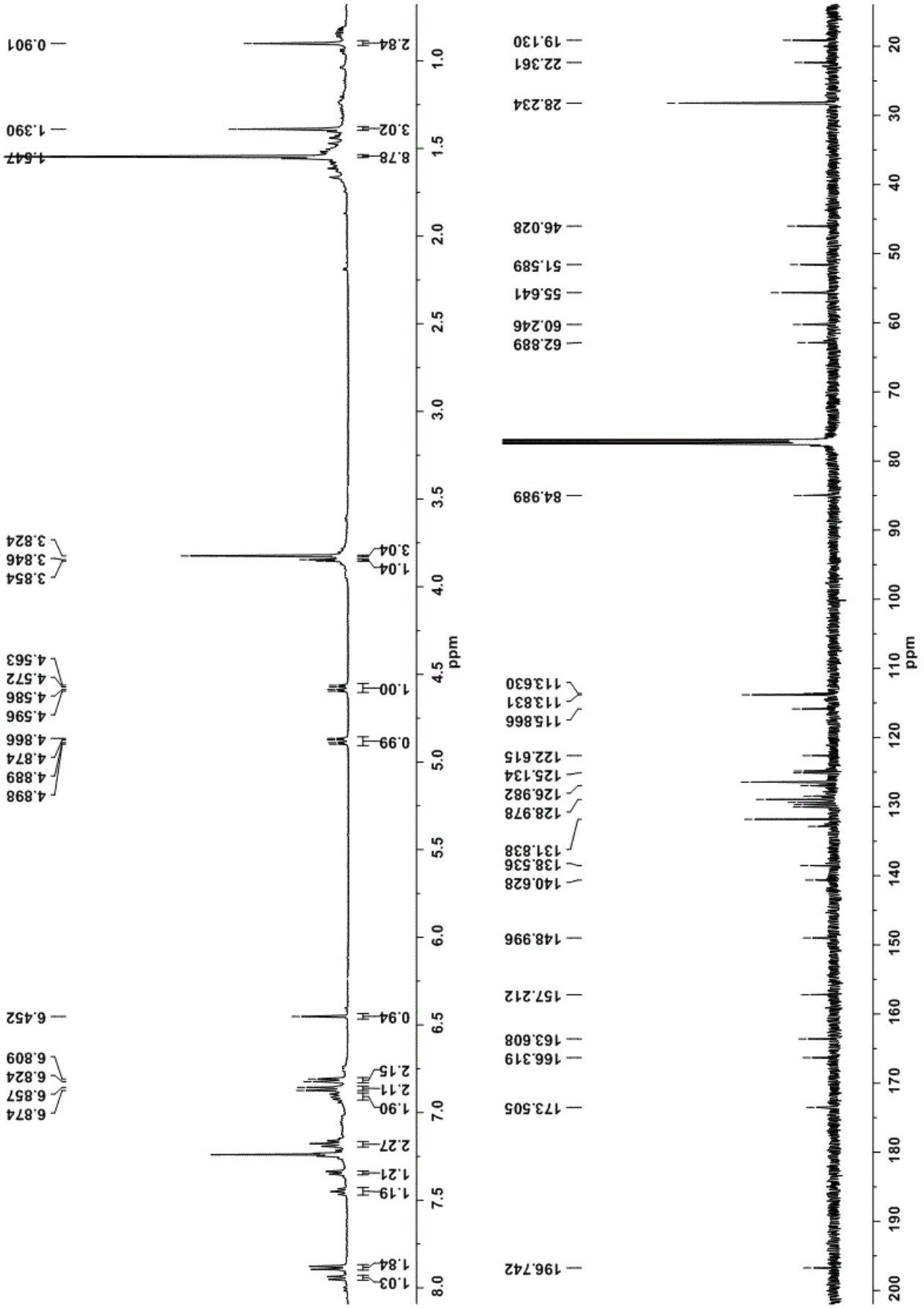
NMR-Spectra of **4a**:



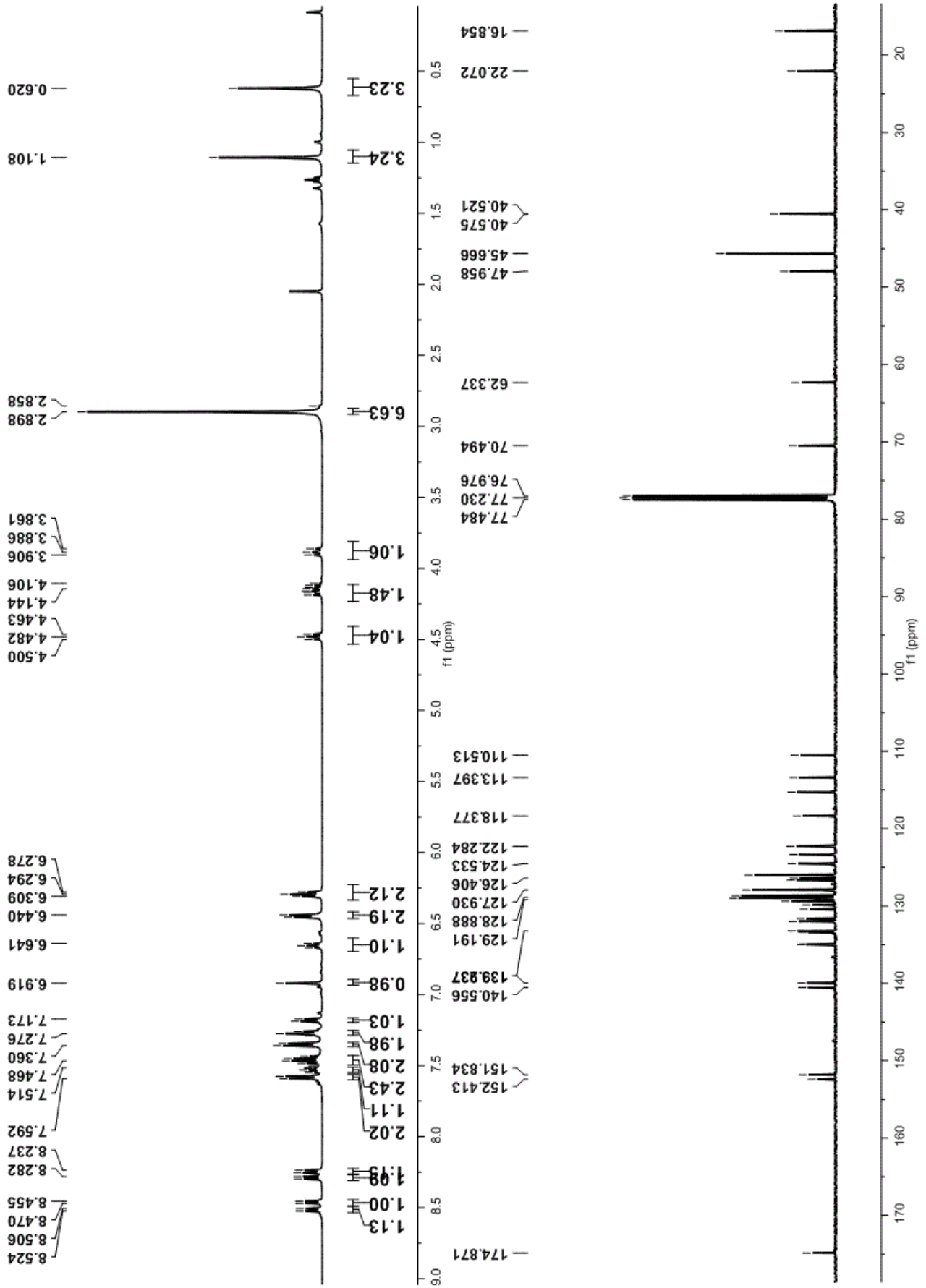
NMR-Spectra of **4b**:



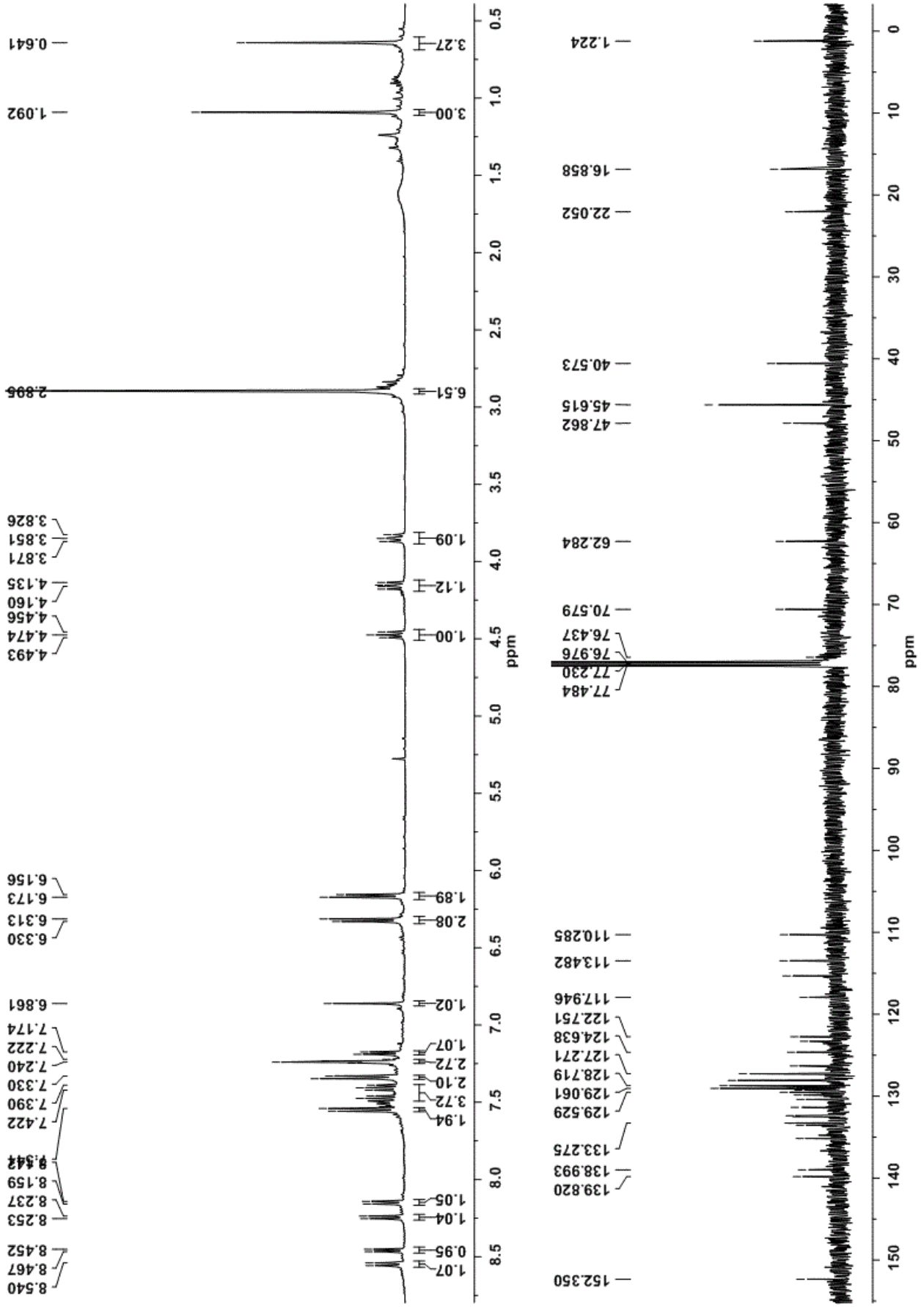
NMR-Spectra of **4c**:



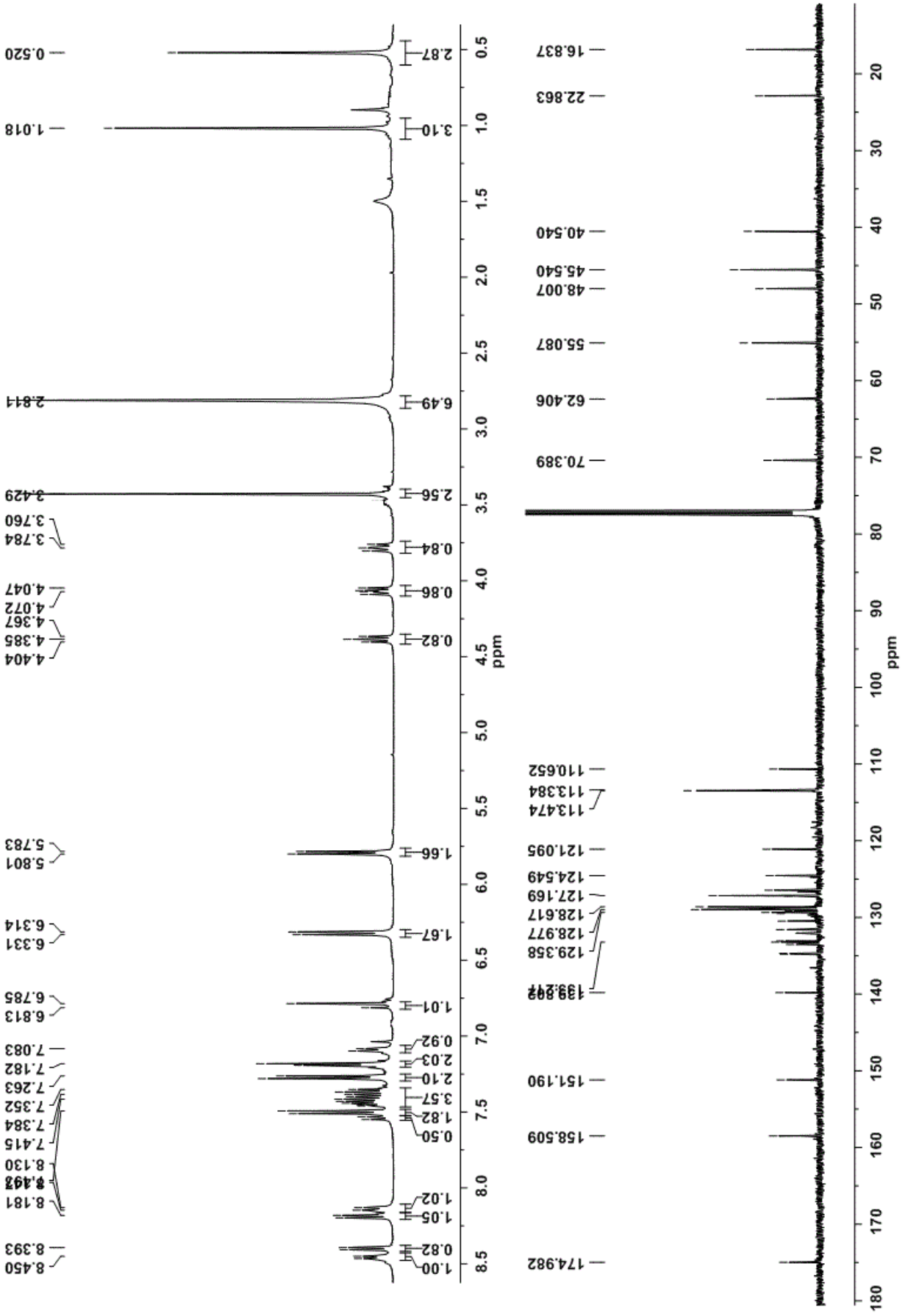
NMR-Spectra of **4d**:



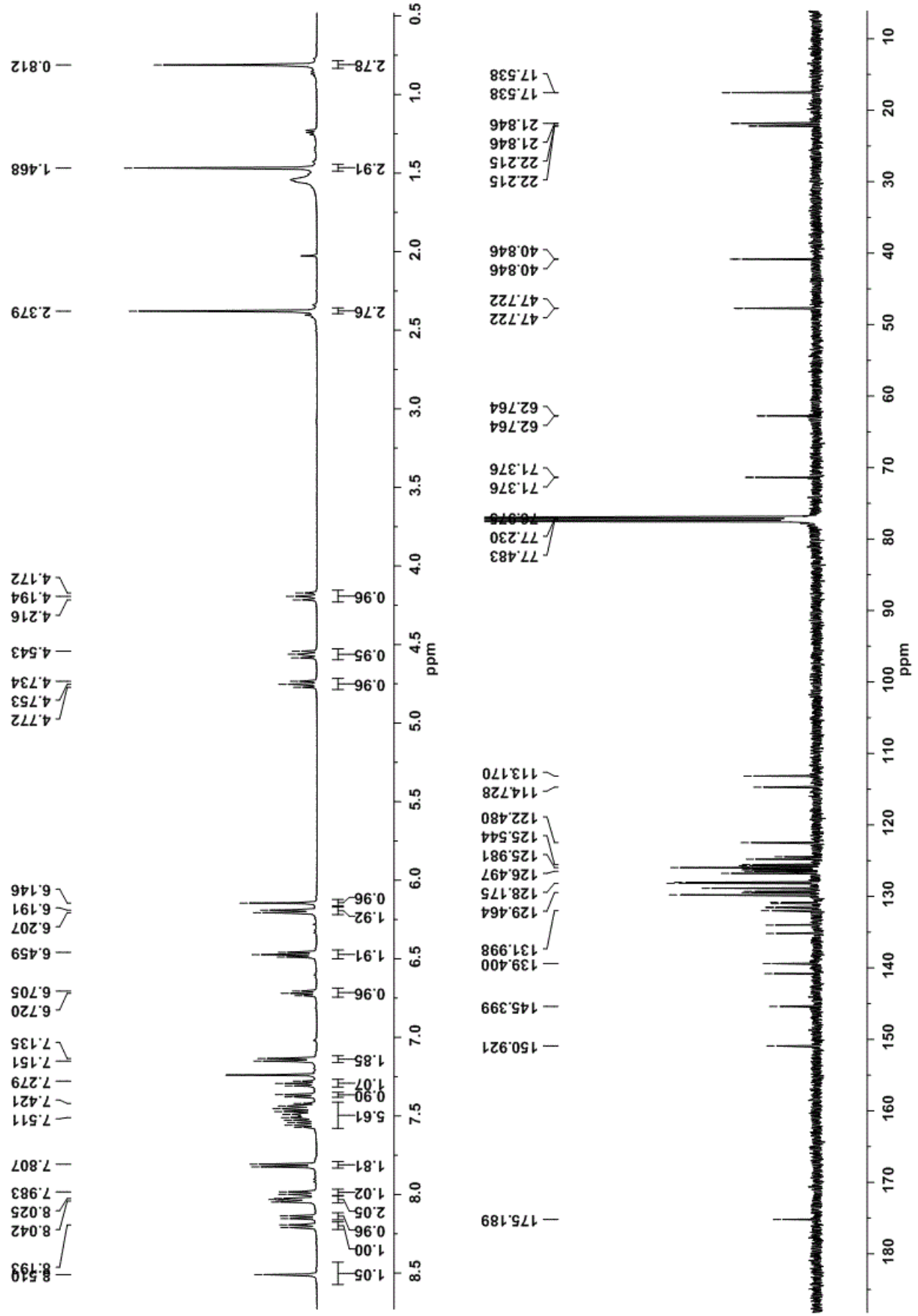
NMR-Spectra of **4e**:



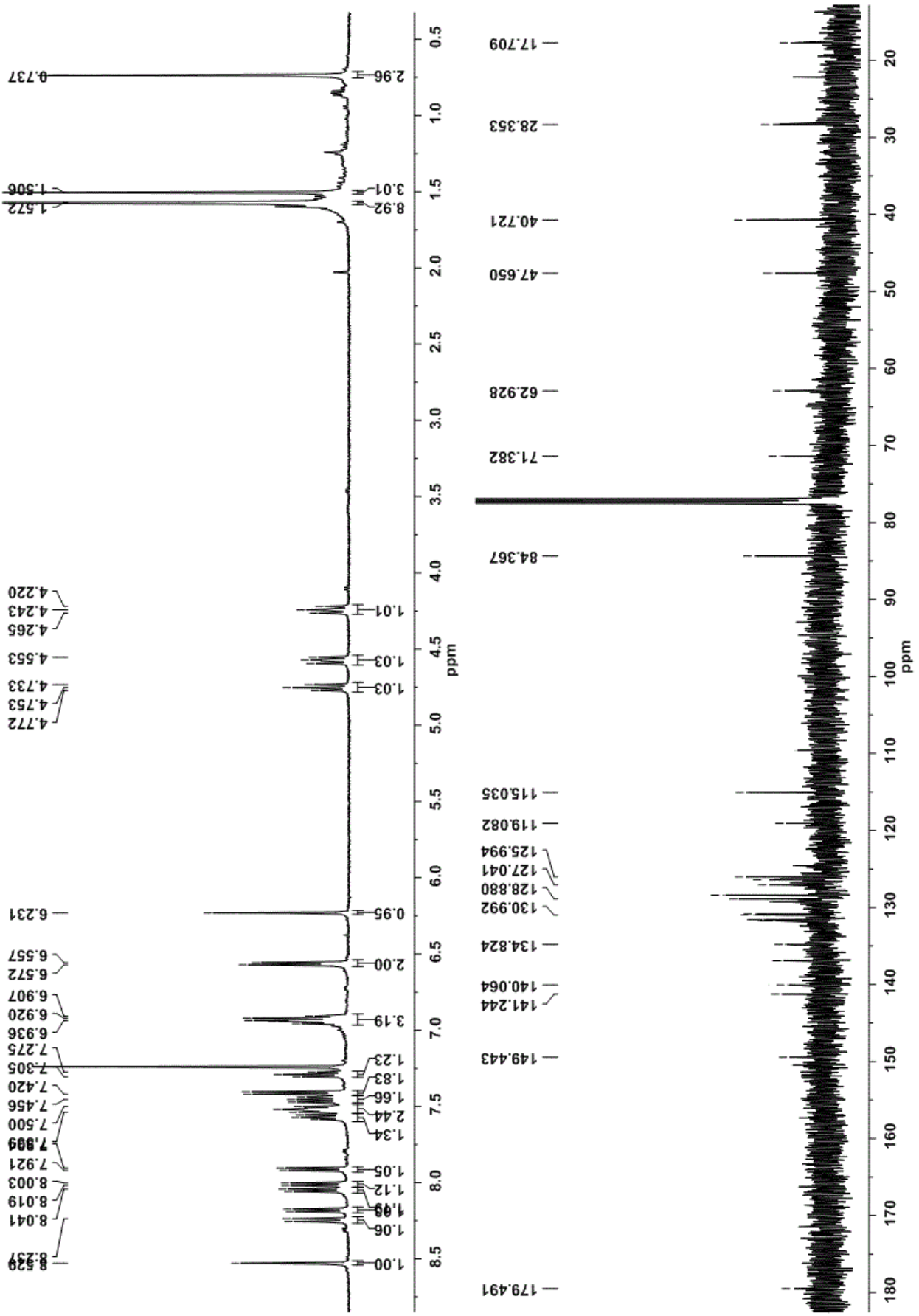
NMR-Spectra of **4f**:



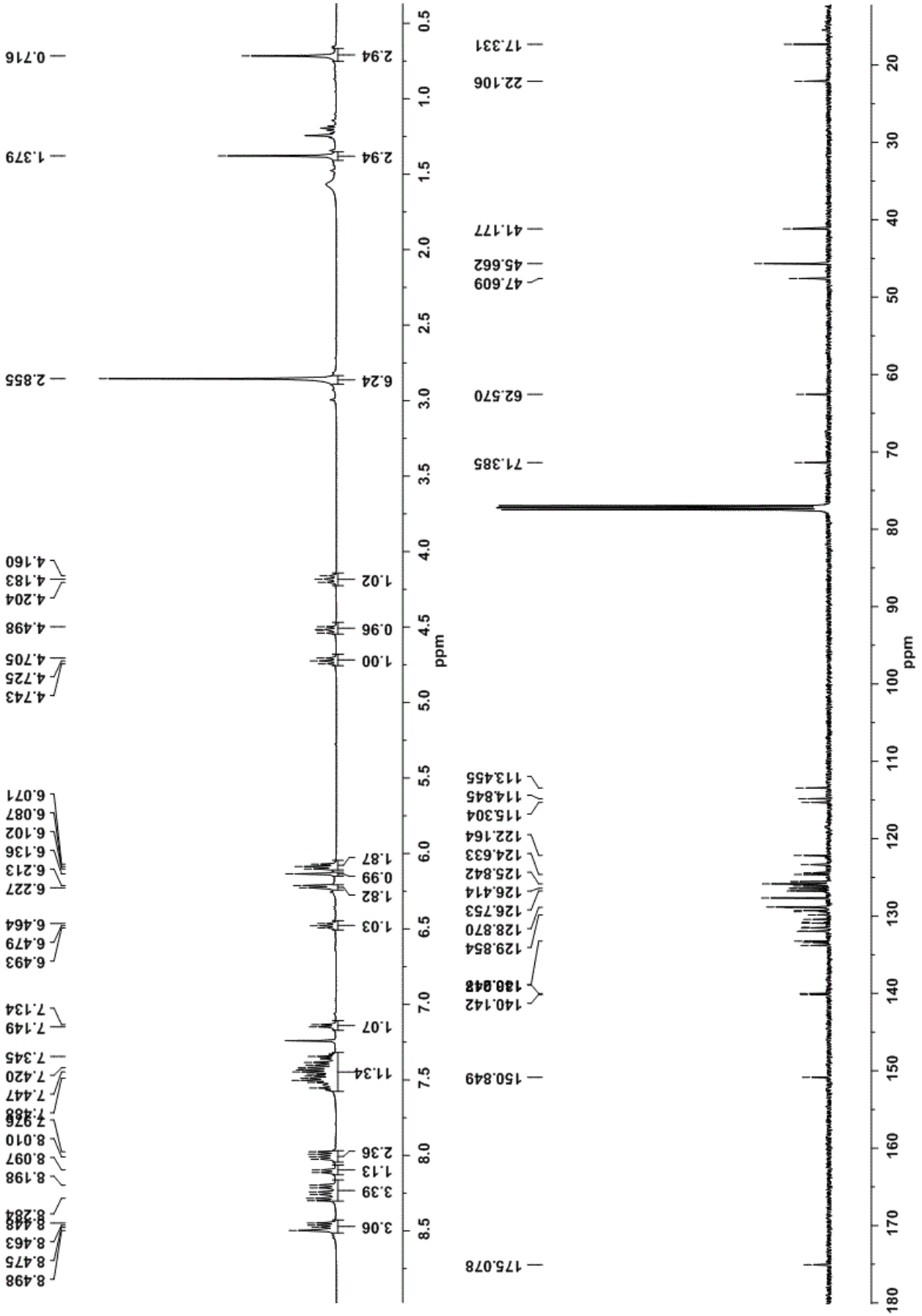
NMR-Spectra of **4g**:



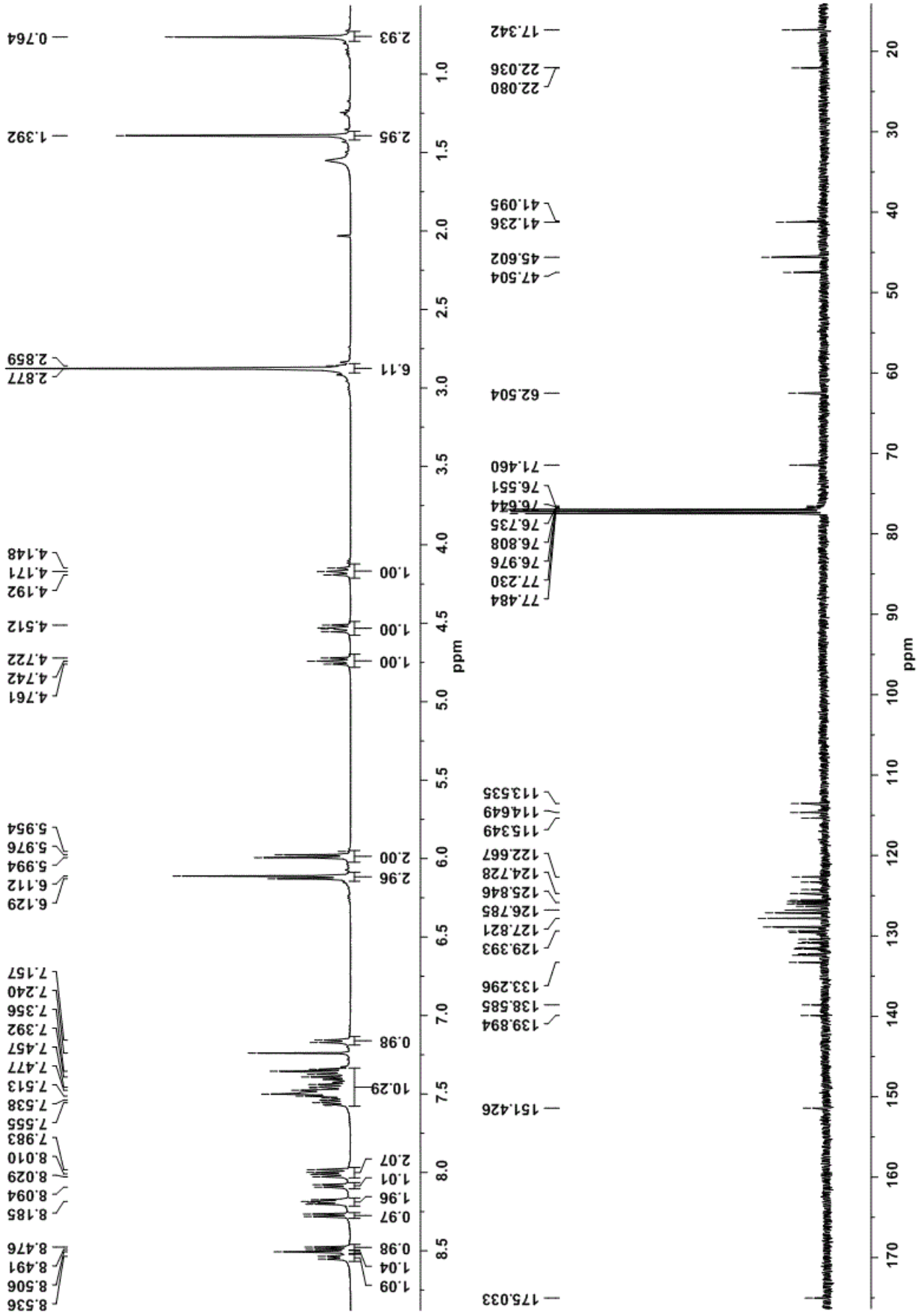
NMR-Spectra of **4h**:



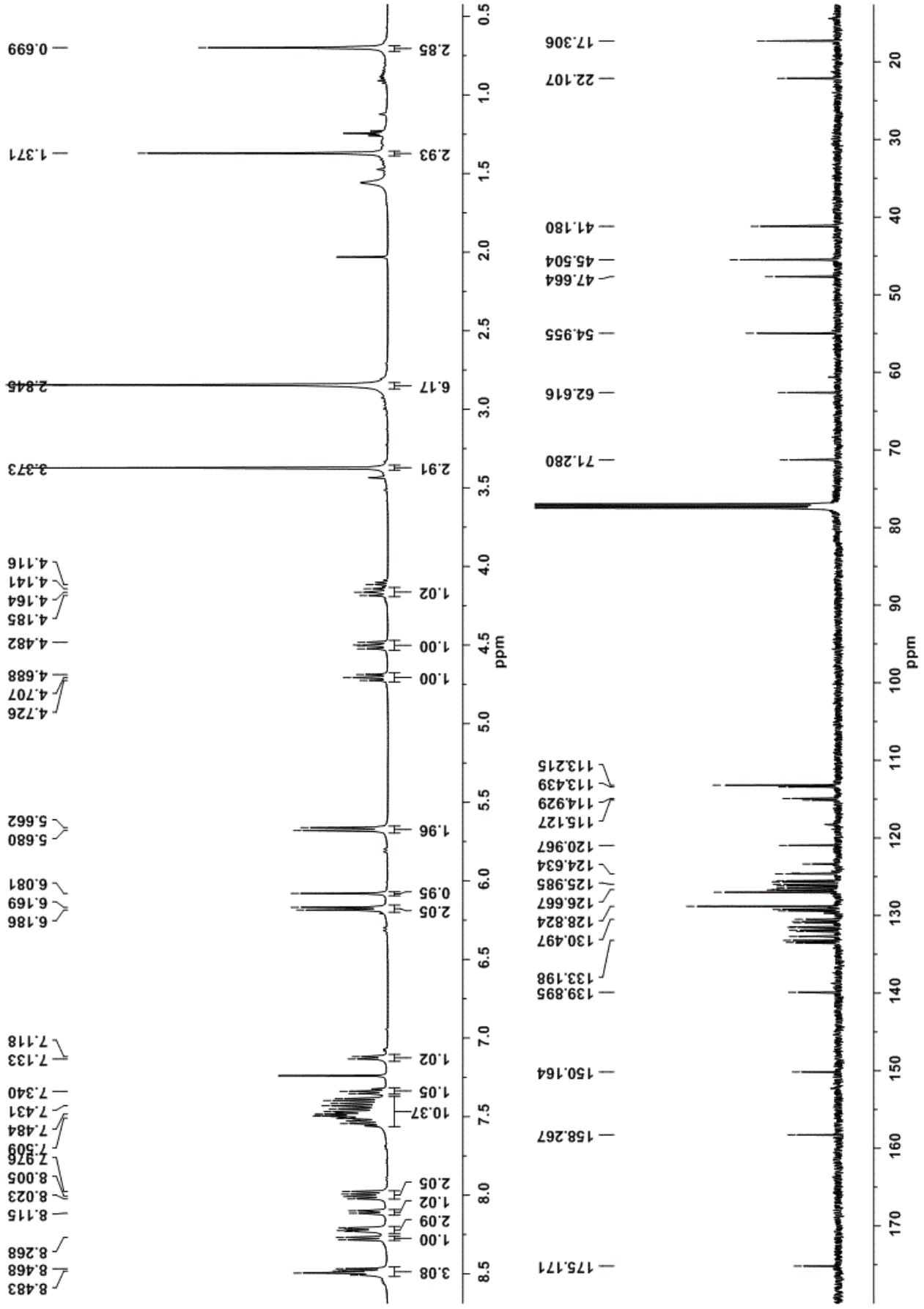
NMR-Spectra of **4i**:



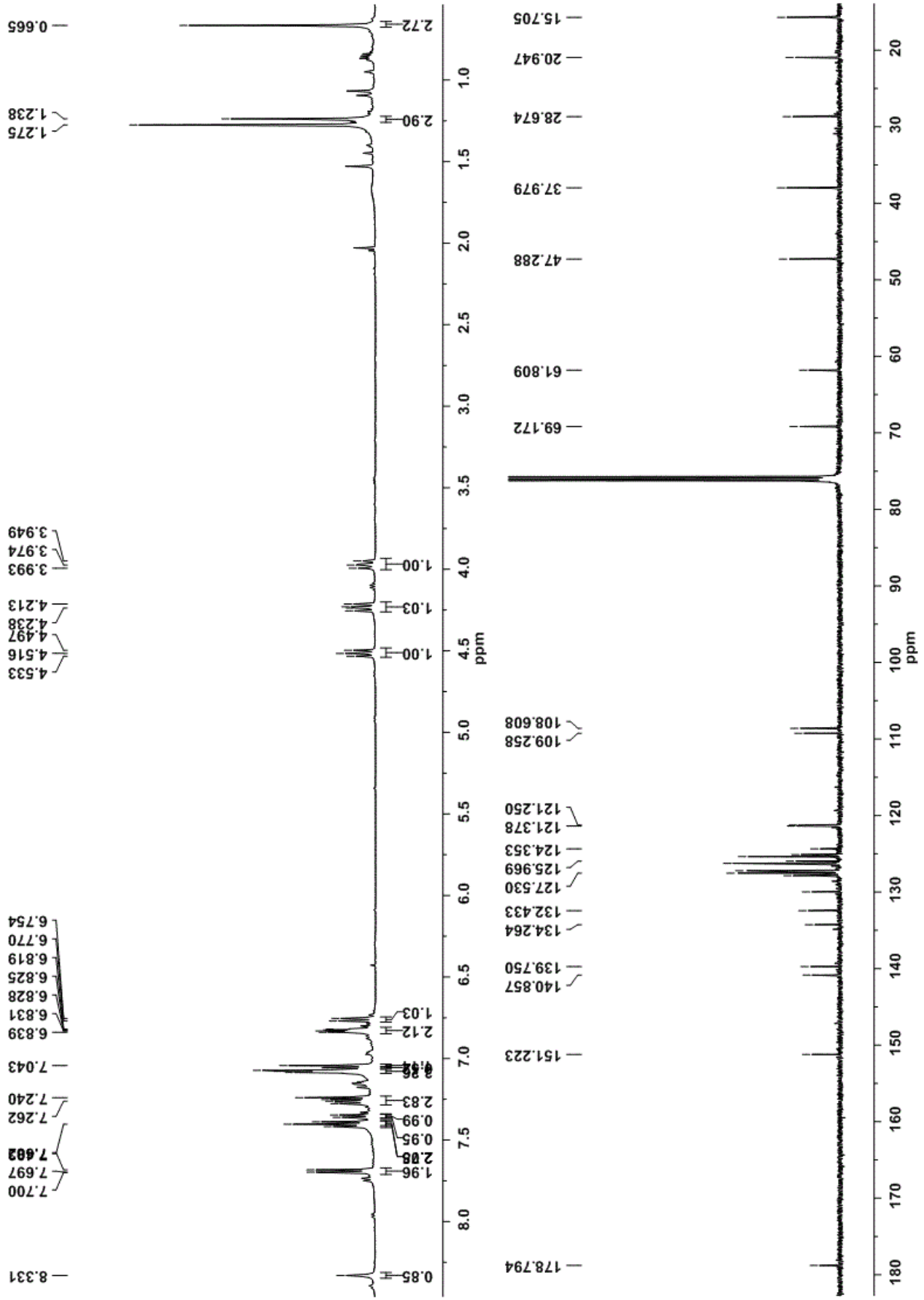
NMR-Spectra of **4j**:



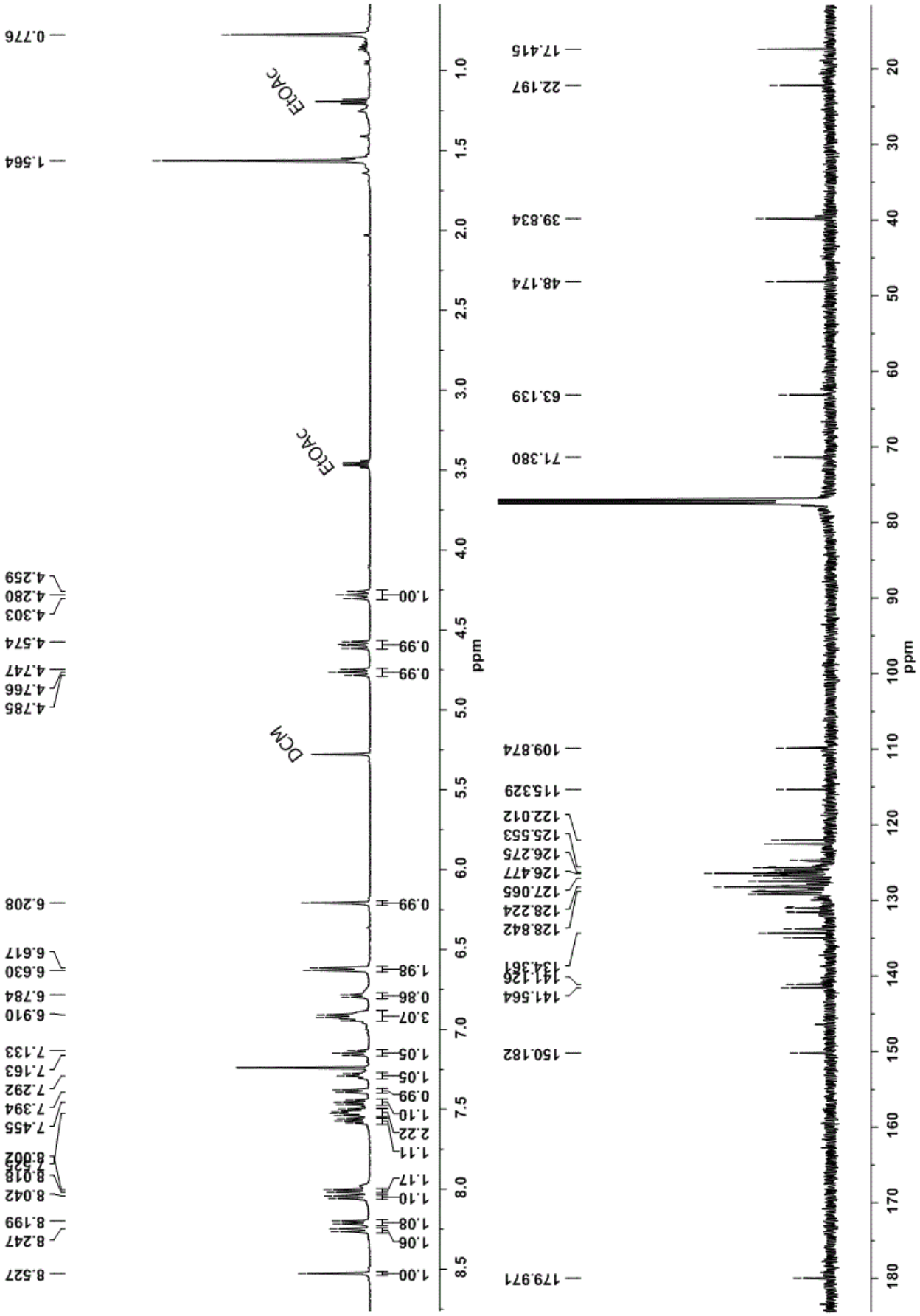
NMR-Spectra of **4k**:



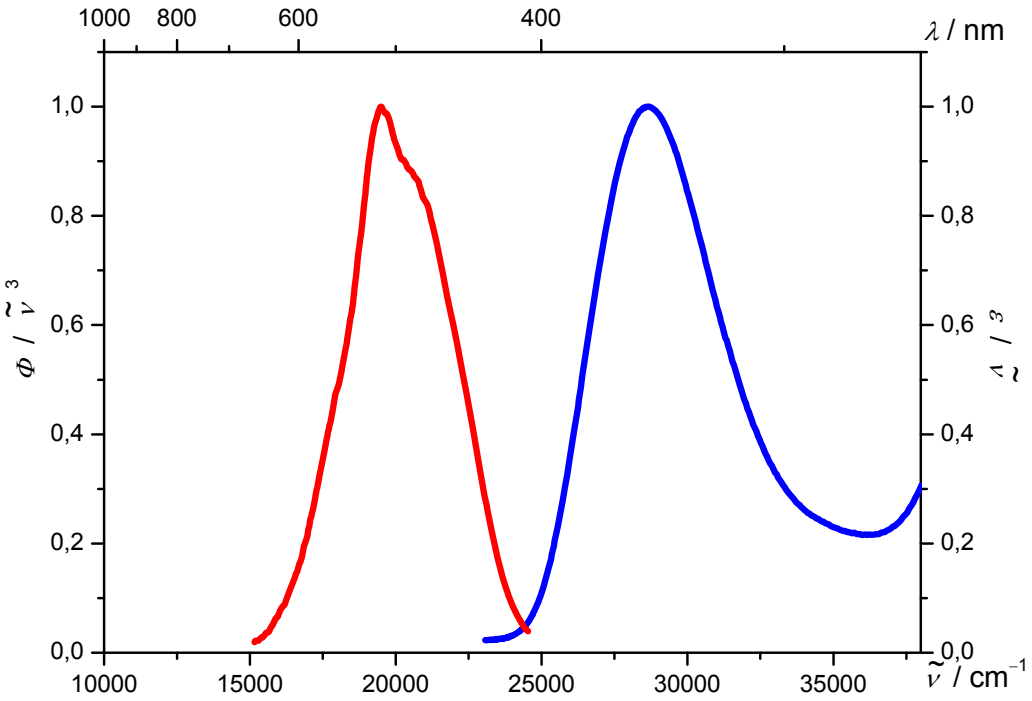
NMR-Spectra of **4l**:



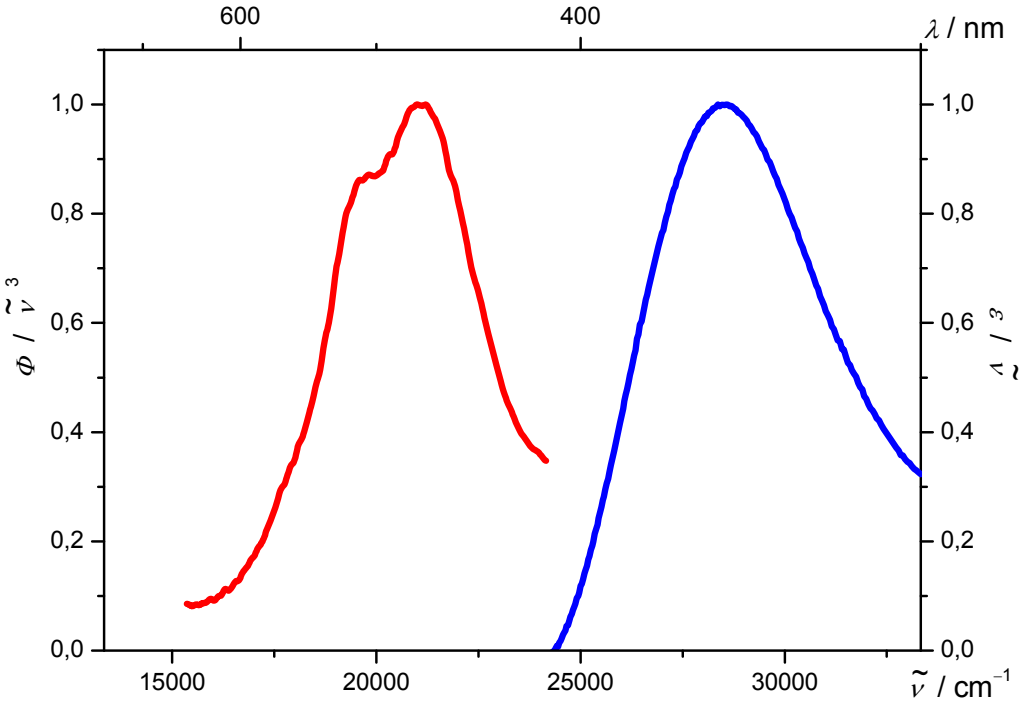
NMR-Spectra of **4m**:



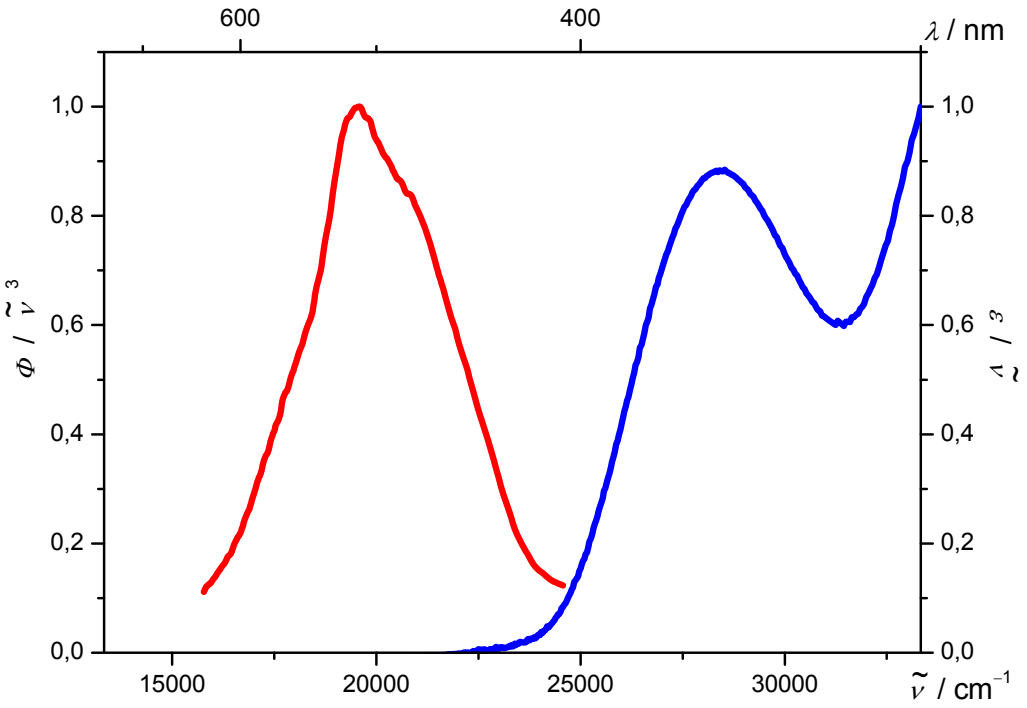
UV/VIS (blue) and Fluorescence (red) Spectra of **4a**:



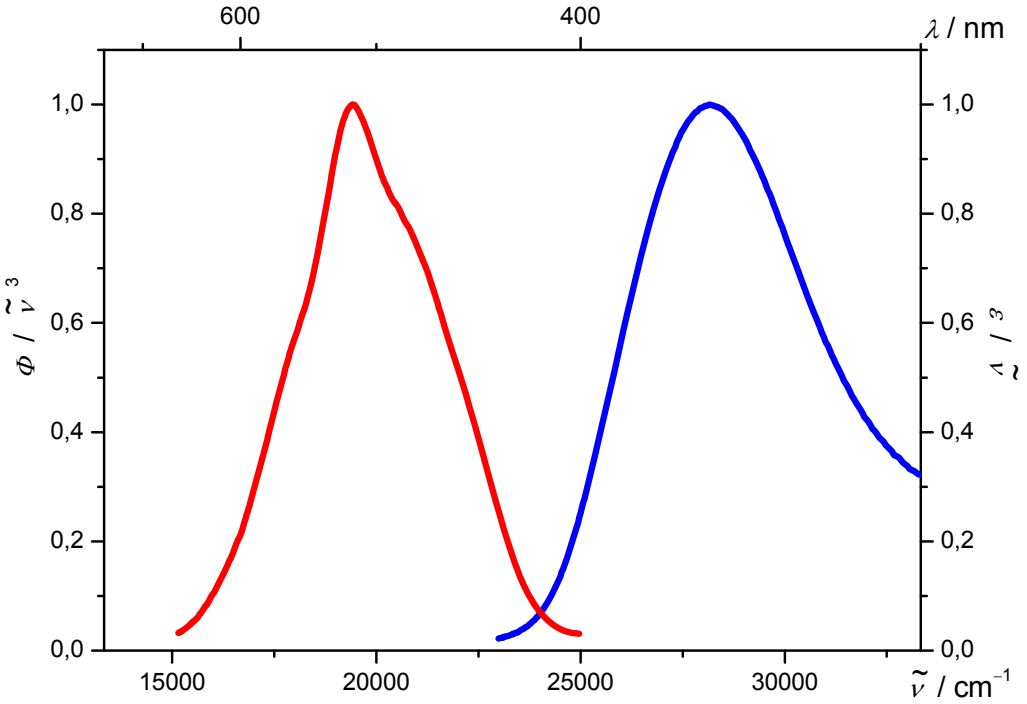
UV/VIS (blue) and Fluorescence (red) Spectra of **4b**:



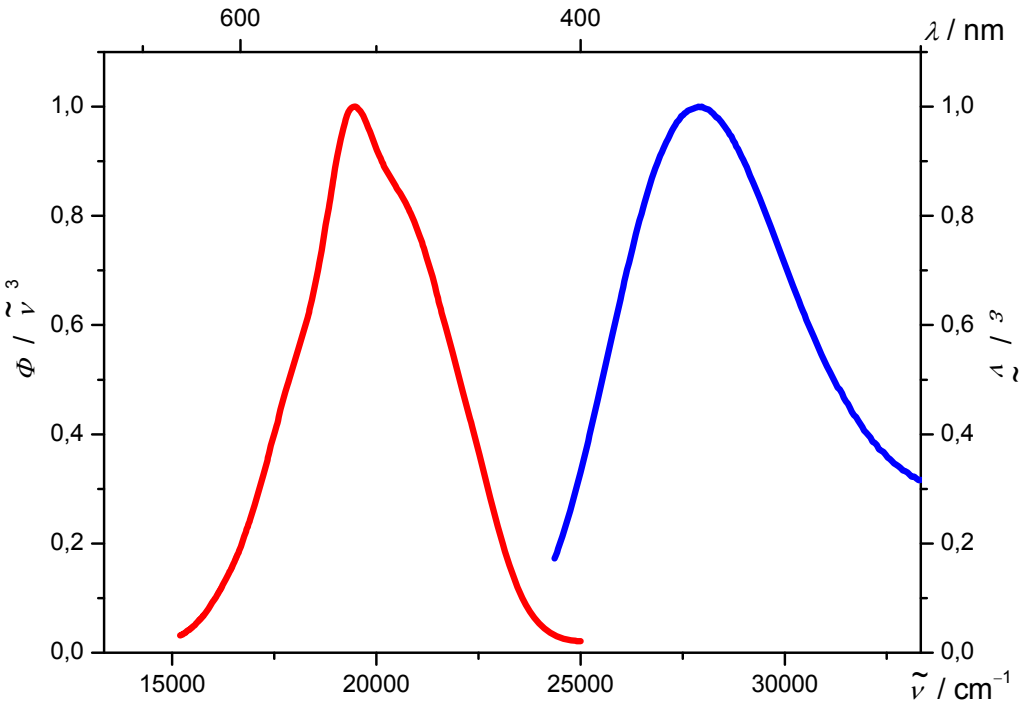
UV/VIS (blue) and Fluorescence (red) Spectra of **4c**:



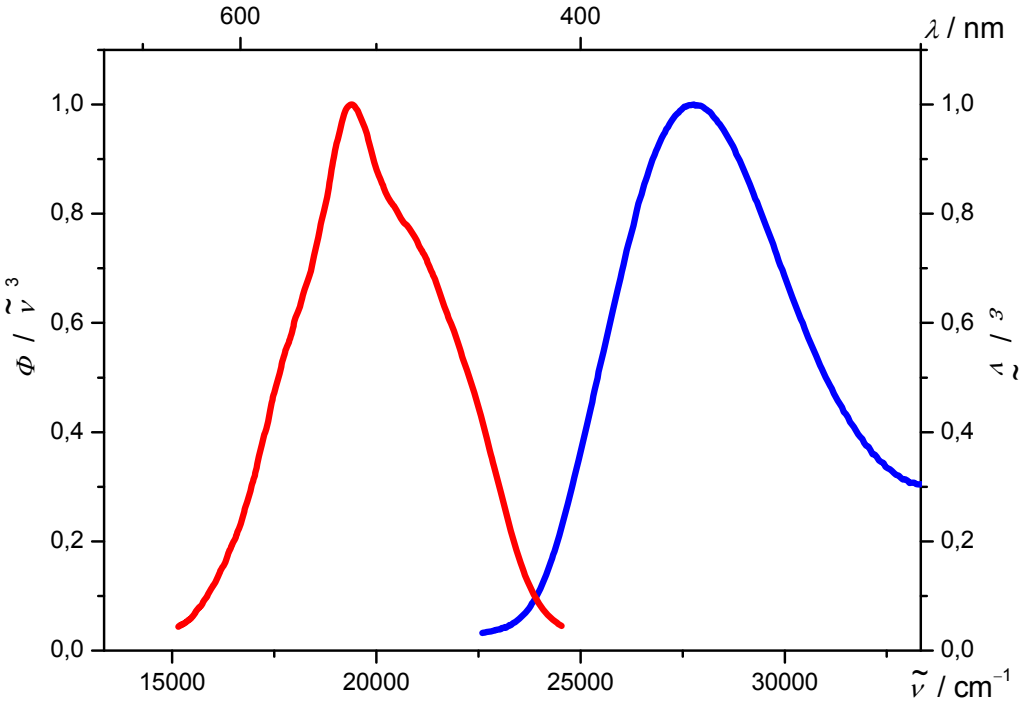
UV/VIS (blue) and Fluorescence (red) Spectra of **4d**:



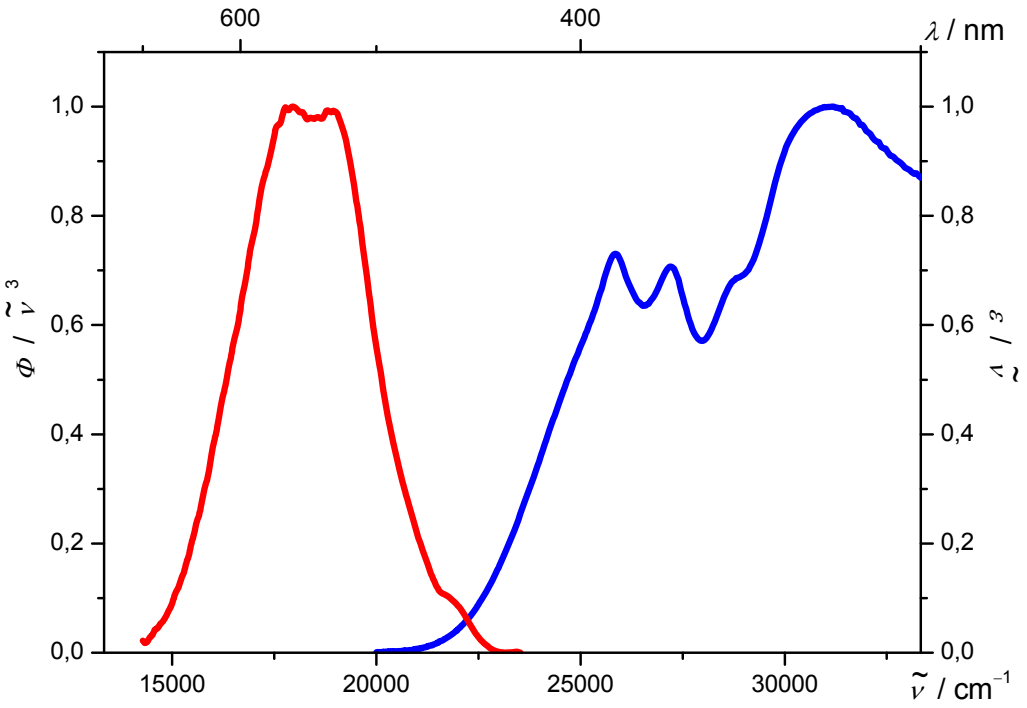
UV/VIS (blue) and Fluorescence (red) Spectra of **4e**:



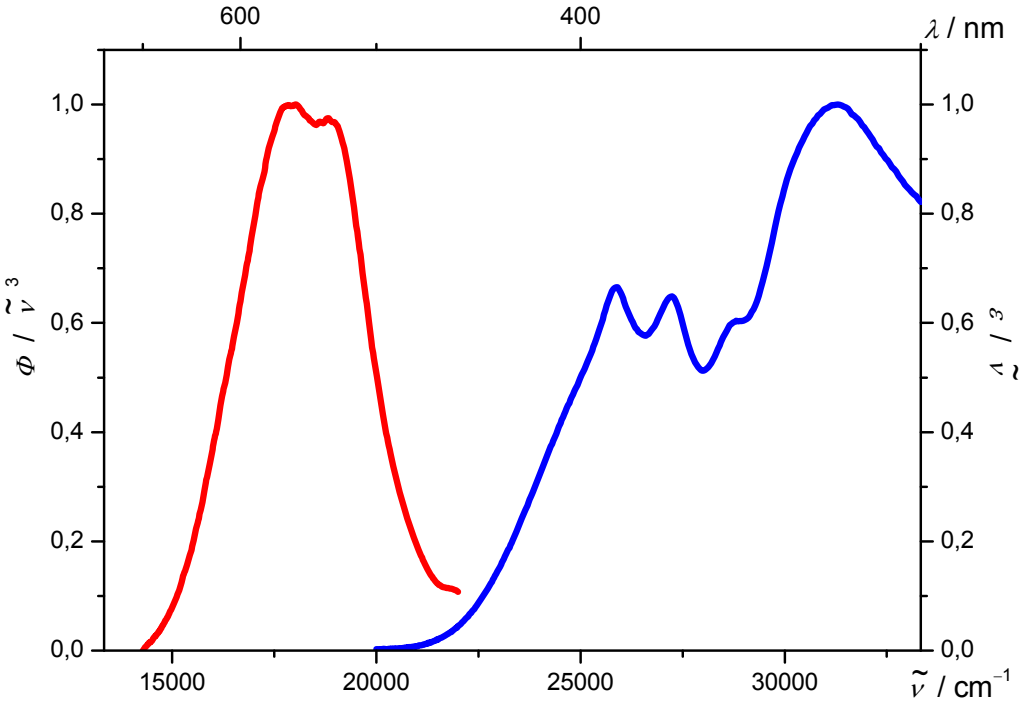
UV/VIS (blue) and Fluorescence (red) Spectra of **4f**:



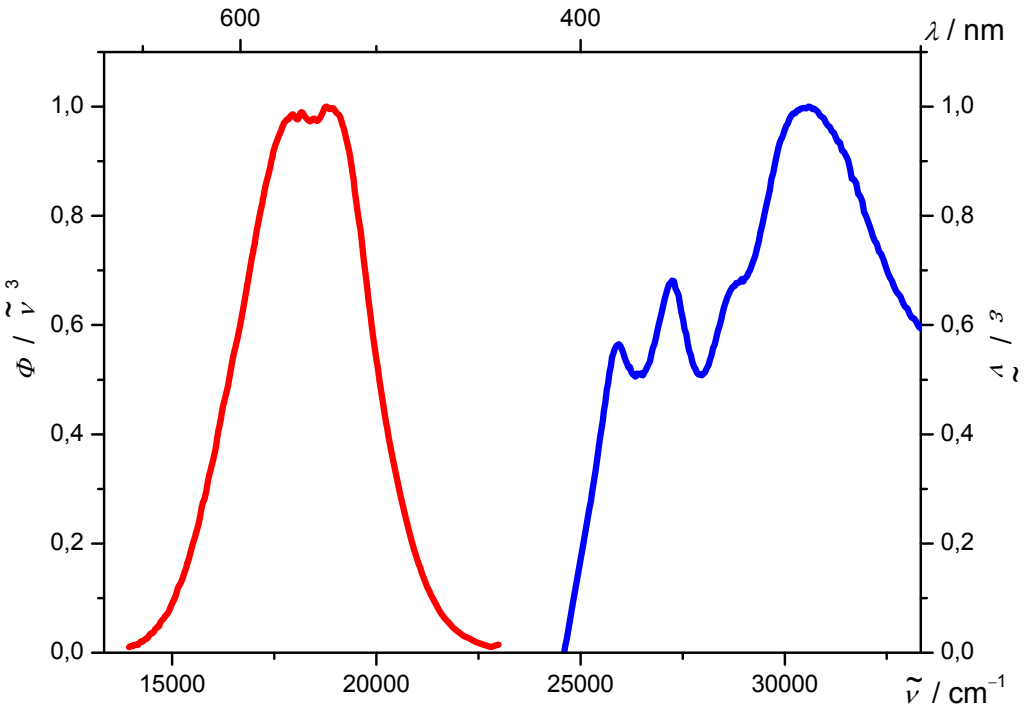
UV/VIS (blue) and Fluorescence (red) Spectra of **4g**:



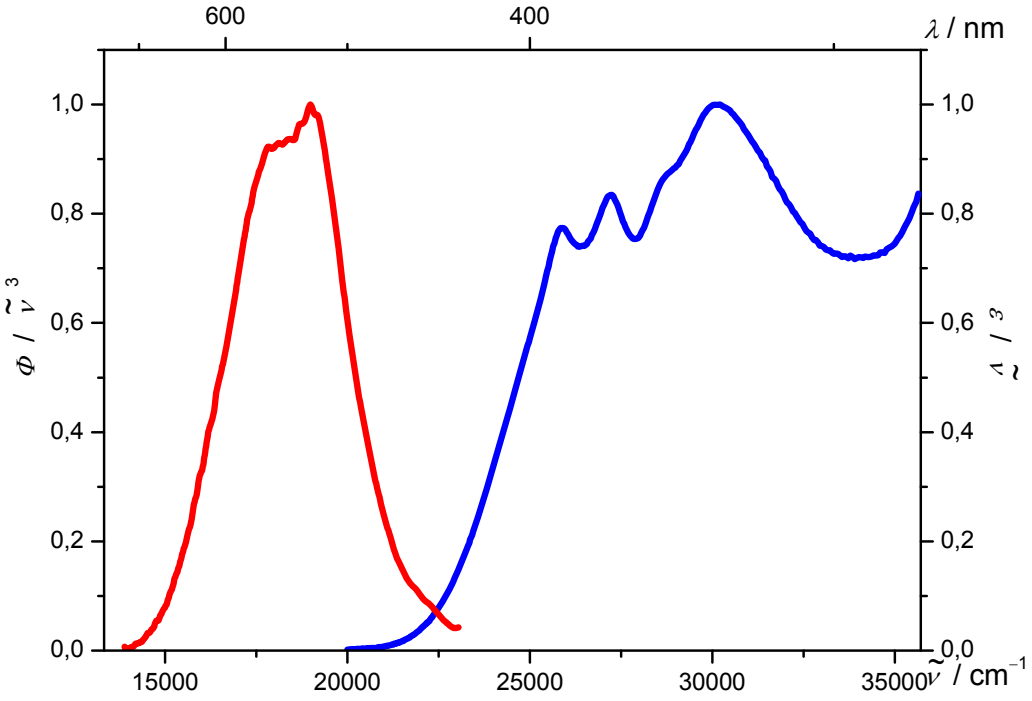
UV/VIS (blue) and Fluorescence (red) Spectra of **4h**:



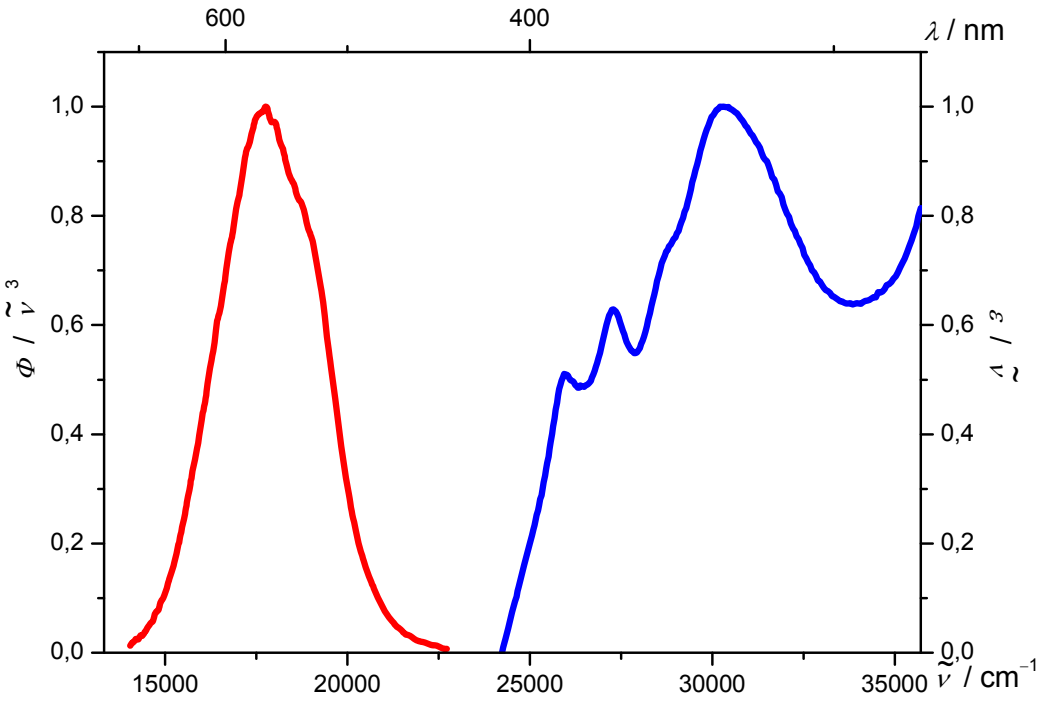
UV/VIS (blue) and Fluorescence (red) Spectra of **4i**:



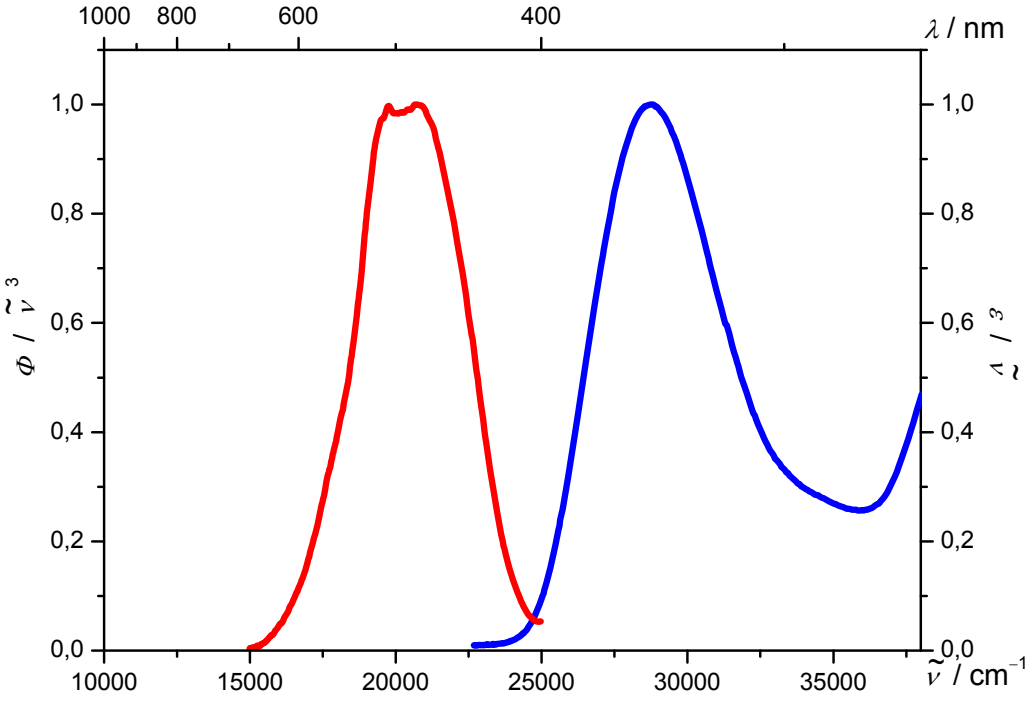
UV/VIS (blue) and Fluorescence (red) Spectra of **4j**:



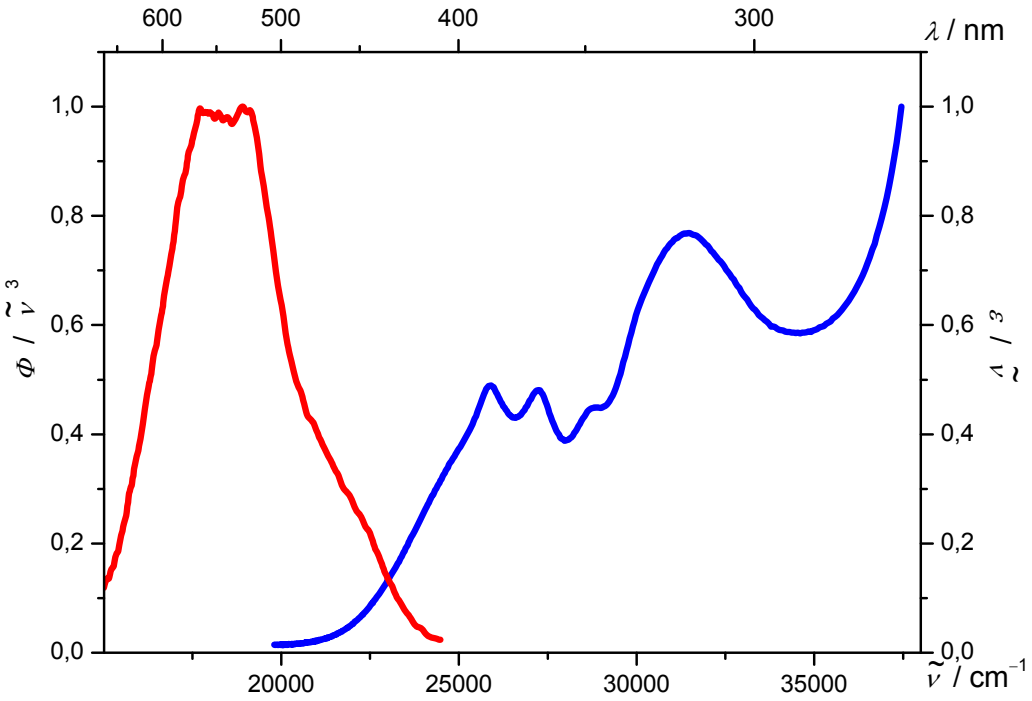
UV/VIS (blue) and Fluorescence (red) Spectra of **4k**:



UV/VIS (blue) and Fluorescence (red) Spectra of **4l**:



UV/VIS (blue) and Fluorescence (red) Spectra of **4m**:



Computational Details of the Computed Model System

Optimized ground state geometry coordinates:

C	0.827787	3.213501	0.562717
C	1.085317	1.883553	0.944669
C	2.004829	1.653478	1.985591
C	2.633199	2.720663	2.627306
C	2.361373	4.036665	2.244391
C	1.455816	4.278314	1.208262
C	0.382700	0.767058	0.257599
C	1.179102	-0.479467	-0.141233
C	0.504009	-1.233725	-1.390369
C	-0.964266	-1.498899	-0.973476
C	-1.684997	-0.185149	-0.659316
C	-0.955590	0.839583	0.032813
C	1.380362	-1.405147	1.063668
C	2.755553	-1.690068	1.199095
N	3.482258	-0.975536	0.240021
C	2.652831	-0.152610	-0.530507
C	3.231350	-2.529073	2.199448
C	2.305373	-3.078690	3.098027
C	0.948166	-2.770605	3.003697
C	0.481692	-1.920096	1.985770
C	-1.908257	-2.134717	-2.022750
O	-3.224637	-1.459600	-1.806910
C	-2.957843	-0.252538	-1.131190
O	3.073516	0.621747	-1.393831
C	-4.109112	0.647501	-1.052051
C	-3.997702	2.021169	-0.768069
C	-5.137435	2.820232	-0.689889
C	-6.404552	2.269686	-0.900412
C	-6.523682	0.910781	-1.205795
C	-5.389334	0.108071	-1.288348

C	1.228711	-2.568903	-1.672295
C	0.552336	-0.337941	-2.653228
H	-7.287470	2.895381	-0.837954
H	4.288158	-2.746034	2.293169
H	2.656386	-3.736151	3.885195
H	0.248703	-3.177907	3.723841
H	-0.564701	-1.643756	1.946325
H	-1.485122	1.710597	0.400657
H	-1.590286	-1.921884	-3.046944
H	-2.068613	-3.203509	-1.881951
H	-0.954242	-2.129495	-0.076647
H	1.216489	-3.218515	-0.792000
H	2.268656	-2.393783	-1.967892
H	0.728012	-3.086274	-2.499526
H	-0.129513	0.509643	-2.549506
H	0.253817	-0.921838	-3.531228
H	1.560343	0.046795	-2.809035
H	-3.023588	2.473785	-0.644060
H	-5.034908	3.877961	-0.475040
H	-7.501848	0.477856	-1.382668
H	-5.467247	-0.942395	-1.532934
H	2.199381	0.639135	2.307725
H	3.329402	2.524339	3.435354
H	2.853210	4.863685	2.743783
H	1.250937	5.295195	0.892171
H	0.156401	3.401183	-0.267337
C	4.939023	-0.944050	0.107272
H	5.328474	-1.933287	-0.156144
H	5.152854	-0.233627	-0.694867
H	5.408422	-0.602288	1.036837

Total energy = -1356.3301792299 a.u.

Optimized excited state geometry coordinates:

C	0.666439	3.354338	0.356018
C	1.181793	2.043590	0.586210
C	2.332802	1.940225	1.416197
C	2.922040	3.066028	1.974558
C	2.397839	4.343109	1.732049
C	1.266385	4.473468	0.916396
C	0.535834	0.880249	0.012260
C	1.260775	-0.446343	-0.201018
C	0.673060	-1.196540	-1.500617
C	-0.823666	-1.459504	-1.205076
C	-1.538600	-0.184611	-0.788493
C	-0.844180	0.903841	-0.271516
C	1.197648	-1.311151	1.061833
C	2.501564	-1.733544	1.395443
N	3.422212	-1.176760	0.495969
C	2.798839	-0.332833	-0.428842
C	2.747161	-2.549098	2.493286
C	1.657250	-2.935828	3.286141
C	0.365701	-2.495968	2.989454
C	0.131872	-1.673819	1.875045
C	-1.706072	-1.919626	-2.390942
O	-3.059700	-1.339278	-2.087956
C	-2.906944	-0.291698	-1.188545
O	3.409975	0.291565	-1.301680
C	-4.061727	0.450844	-0.838332
C	-4.084223	1.328937	0.293700
C	-5.230200	2.047596	0.597890
C	-6.384902	1.935631	-0.193390
C	-6.383761	1.056588	-1.297516
C	-5.257329	0.322616	-1.614319
C	1.405404	-2.538148	-1.729128
C	0.849635	-0.286007	-2.742867

H	-7.271137	2.510949	0.046806
H	3.751459	-2.872385	2.737988
H	1.826738	-3.572210	4.147096
H	-0.463089	-2.783930	3.625208
H	-0.864960	-1.304856	1.666818
H	-1.392610	1.817250	-0.075786
H	-1.370718	-1.497527	-3.340297
H	-1.847814	-2.997311	-2.463848
H	-0.893304	-2.214951	-0.409098
H	1.381204	-3.156546	-0.826648
H	2.446433	-2.366771	-2.021284
H	0.917173	-3.086907	-2.544028
H	0.152985	0.555232	-2.711557
H	0.670637	-0.863484	-3.657511
H	1.868363	0.104122	-2.767076
H	-3.218980	1.387744	0.942786
H	-5.235161	2.698638	1.466112
H	-7.277913	0.955172	-1.903390
H	-5.252715	-0.353806	-2.459529
H	2.727206	0.962590	1.653650
H	3.789315	2.952024	2.615725
H	2.863229	5.219105	2.168681
H	0.861292	5.457692	0.707471
H	-0.178117	3.484591	-0.309659
C	4.872480	-1.372615	0.509885
H	5.124318	-2.426579	0.349802
H	5.267226	-0.767404	-0.309755
H	5.303536	-1.035695	1.459226

total energy = -1356.31961252100 a.u.

[1] D. M. D'Souza, F. Rominger and T. J. J. Müller, *Angew. Chem. Int. Ed.*, 2005, **44**, 153; D. M. D'Souza, A. Kiel, D.-P. Herten, F. Rominger and T. J. J. Müller, *Chem. Eur. J.*, 2008, **14**, 529.