ChemistryOPEN

Supporting Information

Core-Substituted Naphthalenediimides: LUMO Levels Revisited, in Comparison with Preylenediimides with Sulfur Redox Switches in the Core

François N. Miros and Stefan Matile*[a]

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1. Supplementary Methods

1.1. Materials and Methods

Reagents for synthesis were purchased from SigmaAldrich, Fluka, Acros, Apollo Scientific and Bachem. All reactions were performed under N_2 or Ar atmosphere. Unless stated otherwise, column chromatography was carried out on silica gel 60 (SiliaFlash P60, 40-63 μm). Analytical (TLC) and preparative thin layer chromatography (PTLC) were performed on silica gel 60 (Fluka, 0.2 mm) and silica gel GF (SiliCycle, 1000 μm), respectively. Where indicated, flash purification was performed using Biotage Isolera system. A purification gradient was used which was automatically generated by the machine software by inputting the TLC parameters and values listed in the synthesis section for each respective compound. Semi-preparative HPLC was performed using JASCO LC-2000 Plus system equipped with quaternary pump (JASCO PU-2089) and UV/Vis detector (JASCO UV-2077 Plus). Melting points (Mp) were measured on a Melting Point M-565 (BUCHI). UV-Vis spectra were recorded on a JASCO V-650 spectrophotometer equipped with a stirrer and a temperature controller (25 ºC) and are reported as maximal absorption wavelength λ in nm (extinction coefficient ε in M^{-1} cm^{-1}). IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer (ATR, Golden Gate, unless stated) and are reported as wavenumbers ν in cm^{-1} with band intensities indicated as s (strong), m (medium), w (weak). ^{1}H and ^{13}C spectra were recorded (as indicated) either on a Bruker 300 MHz, 400 MHz or 500 MHz spectrometer and are reported as chemical shifts (δ) in ppm relative to TMS ($\delta = 0$). Spin multiplicities are reported as a singlet (s), broad singlet (br s), doublet (d), triplet (t), quartet (q) and quintet (quint) with coupling constants (J) given in Hz,

or multiplet (m). ^{1}H and ^{13}C resonances were assigned with the aid of additional information from 1D and 2D NMR spectra (H,H-COSY, DEPT 135, HSQC and HMBC). ESI-MS were performed on a Finnigan MAT SSQ 7000 instrument or a ESI API 150EX and are reported as *m/z* (%). Accurate mass determinations using ESI (HR ESI-MS) were performed on a Sciex QSTAR Pulsar mass spectrometer.

Abbreviations. DMF: *N*,*N*-Dimethylformamide; mCPBA: 3-Chloroperoxybenzoic acid; NDA: 1,4,5,8-Naphthalenetetracarboxylic dianhydride; rt: Room temperature.

1.2. Synthesis

Compounds 4, 5. These compounds were prepared following the literature procedure.[S1]

Compounds 31, 32. These compounds were prepared following the literature procedure.[S2]

Compound 33. This compound was prepared following the literature procedure.[S3]

Compound 34. A solution of **33** (2.0 g, 2.8 mmol), octylthiol (24.5 mL, 199 mmol), K_2CO_3 (7.78 g, 41.6 mmol) and 18-crown-6 (150 mg, 0.57 mmol) in $CHCl_3$ (200 mL) was heated to 85 °C for 48 hours in a pressure-resistant vessel. The dark purple solution was extracted three times with petroleum ether/water. The combined organic phases were dried over Na_2SO_4 and filtered. The solid was concentrated and purified by column chromatography (SiO_2, CH_2Cl_2/petroleum ether 1:1) to obtain **34** as a dark purple solid (2.3 g, 96%). R_f (CH_2Cl_2/petroleum ether 1:1): 0.36; Mp: 176.2 - 177.0 °C; IR (neat): 2922 (m), 2853 (m), 1739 (w), 1693 (m), 1653 (m), 1585 (m), 1553 (m), 1502 (w), 1454 (m), 1397 (m), 1383 (s), 1344 (m), 1325 (s), 1255 (m), 1240 (s), 1188 (m), 1161 (m), 1146 (m), 1120 (m), 1081 (m), 1043 (m), 983 (m), 890 (m), 858 (m), 845 (m), 807 (m), 783 (m), 770 (m), 748 (m), 721 (m), 696 (s), 660 (m), 636 (m), 615 (m), 584 (m), 559 (m), 537 (m); ^{1}H NMR (400 MHz, $CDCl_3$): 8.73 (d, ^3J = 8.1 Hz, 2H), 8.68 (s, 2H), 8.59 (d, ^3J = 8.1 Hz, 2H), 5.11 - 5.01 (m, 2H), 3.15 (t, ^3J = 7.4 Hz, 4H), 2.62 - 2.54 (m, 4H), 1.95 - 1.91 (m, 4H), 1.83 - 1.73 (m, 8H), 1.70 - 1.57 (m, 8H), 1.54 - 1.43 (m, 4H), 1.43 - 1.33 (m, 4H), 1.27 - 1.21 (m, 16H), 0.84 (t, ^3J = 6.9 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): 163.9 (C), 138.5 (C), 132.5 (C), 132.3 (C), 130.7 (C), 128.9 (CH), 128.3 (CH), 125.4 (C), 122.5 (C), 122.0 (C), 54.1

(CH), 39.3 (CH_2), 36.0 (CH_2), 31.8 (CH_2), 29.2 (CH_2), 28.9 (CH_2), 28.5 (CH_2), 26.6 (CH_2), 25.5 (CH_2), 22.6 (CH_2), 14.1 (CH_3); MS (ESI, -ve): 843 (66, $[M]^-$), 565 (100).

Compound 21. A solution of **34** (308 mg, 0.36 mmol) and KOH (1.7 g, 27 mmol) in *i*-PrOH (40 mL) was refluxed at 80 °C for four hours. After cooling to rt, AcOH (20 mL) was added and heating continued at 80 °C for eight hours. The dark solution was precipitated in water and filtered. Impurities were removed via solid-liquid extraction with MeOH followed by drying *in vacuo* to yield a crude black powder. This powder and octylamine (20 μL, 2.9 mmol) were combined in 20 mL DMF and refluxed at 140 °C for 8 hours. The dark purple solution was precipitated in 1.0 M HCl and filtered. The precipitation was filtered and DMF was removed with water, 5% LiCl solution, and brine solution. The dark purple crude was purified by column chromatography (SiO_2, CH_2Cl_2/petroleum ether) to yield **21** as dark purple solid (210 mg, 79%). R_f (CH_2Cl_2/petroleum ether 15:8): 0.13; Mp: 224.0 - 224.5 °C; IR (neat): 3670 (w), 3390 (w), 2924 (m), 2853 (m), 2252 (w), 1692 (s), 1651 (s), 1585 (s), 1552 (m), 1525 (w), 1503 (w), 1453 (m), 1385 (m), 1339 (m), 1325 (s), 1255 (m), 1241 (s), 1205 (m), 1193 (m) 1161 (m), 1161 (m), 1147 (m), 1120 (m), 1079 (m), 1045 (m), 984 (m), 907 (m), 859 (m), 845 (m), 807 (m), 784 (m), 770 (m), 730 (s), 697 (m), 648 (m), 618 (m), 585 (m), 560 (m), 523 (m); ^{1}H NMR (500 MHz, $CDCl_3$): 8.73 (d, ^3J = 8.0 Hz, 2H), 8.67 (s, 2H), 8.58 (d, ^3J = 8.0 Hz, 2H), 4.15 (t, ^3J = 7.4 Hz, 4H), 3.11 (t, ^3J = 7.4 Hz, 4H), 1.70 (quint, ^3J = 7.4 Hz, 4H), 1.59 (quint, ^3J = 7.4 Hz, 4H), 1.44 - 1.29 (m, 6H), 1.29 - 1.08 (m, 16H), 0.84 - 0.79 (m, 6H), 0.77 (t, ^3J = 6.9 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): 163.5 (C), 163.4 (C), 138.6 (C), 132.8 (C), 130.9 (C), 129.0 (CH), 128.4 (CH), 125.4 (CH), 122.0 (C), 121.6 (C), 40.8 (CH_2), 36.0 (CH_2), 31.9 (CH_2), 31.8 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.1 (CH_2), 28.9 (CH_2), 28.9 (CH_2), 28.5 (CH_2), 28.4 (CH_2), 28.2 (CH_2), 28.2 (CH_2),

27.2 (CH_2), 22.7 (CH_2), 14.2 (CH_3), 14.1 (CH_3); MS (ESI, -ve): 903 (100, $[M]^-$), 789 (80, $[M - C_8H_{17}]^-$).

Compound 22. A solution of **21** (175 mg, 0.20 mmol) was prepared in 25 mL CH_2Cl_2 and cooled to 0 °C. mCPBA (101 mg, 0.60 mmol) was then added and the reaction was followed by TLC. After 10 minutes the reaction was stopped by diluting with water and extracting with $Na_2S_2O_5$ and $NaHCO_3$ solution, three times each. The organic phase was dried with Na_2SO_4, filtered and concentrated *in vacuo*. The red solid was purified by column chromatography (SiO_2, CH_2Cl_2) to yield dark red **22** (70 mg, 30%). R_f (CH_2Cl_2/EtOAc 30:1): 0.78; Mp: 158.6 (decomposition); IR (neat): 3056 (w), 2934 (m), 2854 (m), 1727 (w), 1698 (s), 1658 (s), 1587 (m), 1501 (w), 1453 (m), 1417 (m), 1396 (m), 1386 (m), 1325 (s), 1304 (m), 1254 (m), 1240 (s), 1189 (m), 1142 (m), 1117 (m), 1059 (m), 982 (m), 944 (m), 923 (m), 896 (m), 878 (m), 848 (m), 833 (m), 811 (m), 781 (m), 749 (m), 719 (m), 698 (m), 667 (m), 640 (m), 614 (m); ^{1}H NMR (400 MHz, $CDCl_3$): 9.54 (s, 1H), 9.30 (s, 1H), 9.13 (d, ^3J = 7.9 Hz, 1H), 8.84 (2d, ^3J = 7.9 Hz, 2H), 8.45 (d, ^3J = 7.9 Hz, 1H), 4.34 - 4.19 (m, 4H), 3.48 - 3.33 (m, 2H), 3.06 - 2.93 (m, 2H), 2.10 - 1.93 (m, 2H), 1.86 - 1.74 (m, 6H), 1.74 - 1.61 (m, 2H), 1.54 - 1.19 (m, 36H), 1.19 - 1.12 (m, 6H), 0.93 - 0.86 (m, 9H), 0.84 (t, ^3J = 7.1 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$): 163.1 (C), 162.7 (C), 146.8 (C), 133.1 (C), 132.4 (C), 131.8 (CH), 131.2 (CH), 130.5 (CH), 129.3 (C), 128.1 (C), 127.9 (CH), 124.5 (C), 55.7 (CH_2), 54.4 (CH_2), 31.7 (CH_2), 29.7 (CH_2), 29.1 (CH_2), 28.5 (CH_2), 26.5 (CH_2), 25.4 (CH_2), 23.3 (CH_2), 22.6 (CH_2), 14.1 (CH_3); MS (ESI, -ve): 919 (100, $[M]^-$).

Compound 23 (Two Diastereomers). A solution of **21** (105 mg, 0.12 mmol) and BF_3Et_2O (44 µL, 0.36 mmol) was prepared in 10 mL CH_2Cl_2 and cooled to -20 °C. mCPBA (48 mg, 0.28 mmol) was then added and allowed to react for two hours. The reaction was stopped by diluting with water and extracting with $Na_2S_2O_5$ and $NaHCO_3$ solution, three times each. The organic phase was dried with Na_2SO_4, filtered and concentrated *in vacuo*. The red solid was purified by column chromatography (SiO_2, CH_2Cl_2/EtOAc 30:1) to yield dark red diastereomers **23a** (9 mg, 9%) and **23b** (10 mg, 10%). **23a:** R_f (CH_2Cl_2/EtOAc 30:1): 0.59; Mp: 156.1 (decomposition); IR (neat): 3054 (w), 2955 (m), 2921 (m), 2853 (m), 1697 (m), 1656 (s), 1592 (s), 1555 (w), 1508 (w), 1460 (m), 1450 (m), 1432 (m), 1411 (m), 1394 (m), 1372 (m), 1353 (m), 1328 (s), 1254 (m), 1242 (m), 1199 (m), 1176 (w), 1148 (w), 1099 (m), 1060 (s), 972 (w), 952 (m), 908 (w), 861 (w), 810 (m), 779 (w), 752 (m), 721 (m), 698 (m), 682 (m), 639 (w), 614 (w), 589 (m), 559 (m), 534 (m); ^{1}H NMR (400 MHz, $CDCl_3$): 9.47 (s, 2H), 8.73 (d, ^3J = 7.9 Hz, 2H), 8.12 (d, ^3J = 7.9 Hz, 2H), 4.17 (t, ^3J = 7.6 Hz, 4H), 3.09 - 2.88 (m, 4H), 2.01 - 1.87 (m, 2H), 1.82 - 1.65 (m, 6H), 1.40 - 1.15 (m, 40H), 0.80 (t, ^3J = 7.4 Hz, 12H); ^{13}C NMR (126 MHz, $CDCl_3$): 162.8 (C), 162.3 (C), 146.7 (C), 132.9 (C), 132.8 (C), 131.2 (CH), 130.9 (CH), 129.0 (C), 128.5 (C), 127.8 (C), 124.2 (CH), 124.0 (CH), 56.0 (CH_2), 41.0 (CH_2), 31.9 (CH_2), 31.8 (CH_2), 29.8 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 28.7 (CH_2), 28.2 (CH_2), 27.2 (CH_2), 23.4 (CH_2), 22.7 (CH_2), 22.6 (CH_2), 14.2 (CH_2), 14.1 (CH_3); MS (ESI, -ve): 1768 (40, $[2M - OC_6H_{12}]^-$, 935 (50, $[M]^-$), 833 (100, $[M - OC_6H_{12}]^-$). **23b:** R_f (CH_2Cl_2/EtOAc 30:1): 0.16; Mp: 158.8 (decomposition); IR (neat): 3052 (w), 2958 (m), 2922 (m), 2853 (m), 1699 (m), 1657 (s), 1588 (m), 1504 (w), 1454 (m), 1433 (m), 1413 (w), 1395 (m), 1331 (s), 1253 (m), 1240 (m), 1194 (m), 1171 (w), 1143 (w), 1099 (m), 1056 (m), 981 (m), 942 (w), 867 (m), 830 (w), 811 (m), 768 (m), 749 (m), 723 (m), 700 (m), 665 (m), 636 (m), 610 (m), 585 (w), 551 (m), 527 (m), 516 (w); ^{1}H

NMR (400 MHz, $CDCl_3$): 9.47 (s, 2H), 8.71 (d, ^3J = 8.0 Hz, 2H), 8.44 (d, ^3J = 8.0 Hz, 2H), 4.16 (t, ^3J = 7.6 Hz, 4H), 2.85 - 2.95 (m, 2H), 2.80 - 2.70 (m, 2H), 1.86 (t, ^3J = 7.6 Hz, 4H), 1.77 - 1.61 (m, 8H), 1.47 - 1.07 (m, 32H), 0.84 - 0.79 (t, ^3J = 6.7 Hz, 6H), 0.80 - 0.75 (t, ^3J = 6.7 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): 162.7 (C), 162.3 (C), 147.0 (C), 133.3 (C), 132.7 (C), 131.3 (CH), 130.5 (CH), 129.2 (C), 128.0 (C), 124.1 (CH), 55.8 (CH_2), 41.0(CH_2), 31.9 (CH_2), 29.0 (CH_2), 28.6 (CH_2), 28.2 (CH_2), 27.2 (CH_2), 23.4 (CH_2), 22.7 (CH_2), 14.2 (CH_3); MS (ESI, -ve): 1768 (33, $[2M - OC_6H_{12}]^-$, 935 (100, $[M]^-$), 833 (90, $[M - OC_6H_{12}]^-$), 821 (80, $[M - OC_7H_{14}]^-$.

Compound 24. A solution of **21** (35.6 mg, 39.2 μmol) was prepared in 25 mL CH_2Cl_2 and mCPBA (61.2 mg, 392 μmol) was then added and reaction was allowed to progress for one hour. The reaction was diluted with water and extracted with $Na_2S_2O_3$ and K_2CO_3 solutions, three times each. The organic layer was dried with Na_2SO_4, filtered and concentrated *in vacuo*. The red solid was purified by column chromatography (SiO_2, CH_2Cl_2/acetone 98:2) to yield **24** as a red solid (11 mg, 41%). R_f (CH_2Cl_2/EtOAc 20:3): 0.84; Mp: 180.6 (decomposition); IR (neat): (2923 (m), 2853 (m), 1730 (w), 1701 (m), 1659 (s), 1591 (m), 1454 (m), 1400 (m), 1328 (s), 1303 (m), 1257 (m), 1240 (m), 1193 (m), 1165 (m), 1131 (s), 1080 (m), 1039 (m), 1019 (m), 984 (m), 921 (w), 892 (m), 879 (m), 848 (w), 811 (m), 773 (m), 747 (m), 720 (m), 698 (m), 661 (m), 632 (m), 614 (m), 591 (m), 575 (m), 555 (m); ^{1}H NMR (500 MHz, $CDCl_3$): 9.11 (s, 2H), 8.96 (d, ^3J = 7.9 Hz, 2H), 8.74 (d, ^3J = 7.9 Hz, 2H), 5.07 - 4.88 (m, 4H), 3.42 - 3.26 (m, 4H), 2.53 - 2.46 (m, 4H), 1.82 - 1.78 (m, 4H), 1.76 - 1.70 (m, 4H), 1.66 - 1.57 (m, 4H), 1.46 - 1.36 (m, 4H), 1.30 - 1.18 (m, 12H), 1.17 - 1.04 (m, 16H), 0.82 (t, ^3J = 7.1 Hz, 6H), 0.75 (t, ^3J = 7.1 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): 173.6 (C), 162.9 (C), 139.0 (C), 135.7 (C), 134.2 (C), 131.7 (CH), 131.5 (CH), 129.9 (C), 128.3 (C), 128.0 (C), 124.6 (C), 123.6 (C), 66.9 (C), 55.3 (CH_2), 54.6 (CH_2), 38.8

(CH_2), 34.1 (CH_2), 31.6 (CH_2), 30.5 (CH_2), 29.2 (CH_2), 28.9 (CH_2), 28.2 (CH_2), 26.5 (CH_2), 25.4 (CH_2), 24.5 (CH_2), 23.8 (CH_2), 23.0 (CH_2), 22.6 (CH_2), 14.1 (CH_3), 11.0 (CH_3); MS (ESI, +ve): 968 $[M+H]^+$.

Compound 25. A solution of **34** (2.30 g, 2.70 mmol) and KOH (13.0 g, 203 mmol) in *i*-PrOH (250 mL) was refluxed at 80 °C for four hours. After cooling to rt, AcOH (150 mL) was added and heating continued at 80 °C for eight hours. The dark solution was precipitated in water and filtered. Impurities were removed via solid-liquid extraction with MeOH followed by drying *in vacuo* to yield a crude black powder. This powder and 2-amino-4-tertbutylphenol (1.27 g, 7.61 mmol) were combined in DMF (120 mL) and refluxed at 140 °C for 10 hours. The dark purple solution was precipitated in 1.0 M HCl and filtered. DMF and impurities were removed with water, 5% LiCl solution and brine solution. The dark purple crude was purified by column chromatography (SiO_2, CH_2Cl_2/EtOAc 20:1) to yield **25** as a dark purple solid (1.91 g, 94%). R_f (CH_2Cl_2/EtOAc 20:3): 0.47; Mp: 138.4 °C (decomposition); IR (neat): 3366 (w), 2954 (m), 2924 (m), 2855 (m), 2210 (w), 2033 (w), 1704 (s), 1658 (s), 1587 (s), 1552 (m), 1513 (m), 1481 (w), 1460 (m), 1422 (m), 1391 (s), 1335 (s), 1289 (m), 1246 (s), 1200 (s), 1162 (m), 1124 (m), 1095 (m), 1021 (m), 980 (m), 910 (m), 873 (m), 845 (m), 823 (m), 807 (s), 769 (m), 748 (m), 723 (m), 704 (m), 665 (m), 614 (m), 590 (m), 573 (m); ^{1}H NMR (500 MHz, $CDCl_3$, mixture of atropisomers): 8.75 - 8.65 (m, 2H), 8.63 - 8.51 (m, 2H), 8.44 - 8.28 (m, 2H), 7.49 - 7.40 (m, 2H), 7.21 - 7.13 (m, 2H), 7.07 - 6.99 (m, 2H), 3.25 - 3.00 (m, 4H), 1.79 - 1.57 (m, 12H), 1.49 - 1.35 (m, 18H), 1.35 - 1.19 (m, 12H), 0.91 - 0.84 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$, mixture of atropisomers): 163.5 (C), 149.5 (C), 149.1 (C), 144.5 (C), 139.1 (C), 132.7 (C), 132.1 (C), 132.0 (C), 130.8 (C), 130.6 (C), 129.1 (C), 128.9 (C), 128.7 (C), 128.5 (C), 128.3 (C), 128.2 (C), 127.7

(CH), 127.6 (CH), 126.7 (CH), 126.0 (CH), 125.5 (CH), 125.4 (C), 122.1 (CH), 121.9 (CH), 121.8 (C), 121.6 (C), 121.5 (C), 121.5 (C), 118.3 (CH), 117.4 (CH), 35.9 (CH_2), 34.3 (CH_2), 31.7 (CH_2), 31.5 (CH_3), 29.7 (CH_2), 29.1 (CH_2), 28.9 (CH_2), 28.4 (CH_2), 22.6 (CH_2), 14.1 (CH_3); MS (ESI, -ve): 975 (100, $[M]^-$).

Compound 1. A solution of **35** (1.0 g, 3.7 mmol) and ethylhexylamine (450 μL, 7.5 mmol) was made in DMF (25 mL) and heated at 140 °C for eight hours. The reaction was precipitated in 1.0 M HCl solution and filtered. The solid was purified with H_2O, 5% LiCl solution, and brine solution. The beige solid was further purified by column chromatography (SiO_2, CH_2Cl_2) to yield **1** as a colorless powder (1.27 g, 70%). R_f (CH_2Cl_2): 0.63; Mp: 298.7 - 299.1; IR (neat): 3350 (w), 3316 (w), 3081 (w), 3043 (w), 2961 (m), 2930 (m), 2860 (w), 1982 (w), 1782 (w), 1699 (m), 1640 (s), 1580 (m), 1517 (w), 1496 (w), 1453 (m), 1374 (m), 1332 (s), 1289 (m), 1241 (s), 1223 (m), 1182 (m), 1155 (m), 1089 (m), 1060 (m), 1013 (w), 994 (m), 977 (m), 946 (w), 930 (w), 893 (m), 829 (w), 808 (w), 769 (s), 718 (m), 657 (w), 616 (m), 564 (m); ^{1}H NMR (500 MHz, $CDCl_3$): 9.05 - 8.70 (s, 4H), 4.24 - 4.18(m, 4H), 2.04 - 1.92 (m, 2H), 1.52 - 1.43 (m, 8H), 1.43 - 1.30 (m, 8H), 1.10 - 1.00 (m, 6H), 0.98 (t, ^3J = 7.8 Hz, 3H), 0.93 (t, ^3J = 7.8 Hz ,6H); ^{13}C NMR (126 MHz, $CDCl_3$): 163.3 (C), 131.1 (CH), 126.8 (C), 126.6 (C),44.7 (CH_2), 38.0 (CH), 30.7 (CH_2), 28.7 (CH_2), 24.2 (CH_2), 24.1 (CH_2), 23.1 (CH_2), 14.1 (CH_3), 10.7 (CH_3); MS (ESI, +ve): 491 (100, $[M+H]^+$).

Compound 18. A solution of **32** (305 mg, 0.83 mmol) and octylamine (415 μL, 2.49 mmol) was made in 25 mL AcOH and heated at 80 °C for eight hours. The reaction was precipitated in 1.0 M HCl solution and filtered. The solid was purified by solid-liquid extraction with H_2O, 5%

LiCl solution, brine solution and petroleum ether. The yellow solid was purified by column chromatography (SiO_2, CH_2Cl_2/EtOAc 20:3) to yield **18** as a yellow solid (280 mg, 58%). R_f (CH_2Cl_2/EtOAc 20:3): 0.71; Mp: 167.8 - 168.9; IR (neat): 2987 (w), 2952 (m), 2919 (m), 2851 (m), 1779 (w), 1744 (m), 1704 (m), 1657 (s), 1573 (s), 1497 (m), 1449 (m), 1409 (m), 1376 (m), 1358 (m), 1326 (m), 1295 (m), 1279 (s), 1253 (m), 1233 (m), 1220 (m), 1185 (s), 1108 (m), 1073 (m), 1023 (m), 1011 (m), 991 (m), 948 (m), 927 (m), 898 (m), 873 (m), 863 (m), 833 (w), 788 (s), 763 (m), 738 (m), 724 (m), 663 (m), 626 (w), 613 (w); ^{1}H NMR (500 MHz, $CDCl_3$): 8.48 (s, 2H), 4.52 (q, ^3J = 7.0 Hz, 4H), 4.16 (t, ^3J = 7.4 Hz, 4H), 1.76 - 1.69 (m, 4H), 1.66 (t, ^3J = 6.9 Hz, 6H), 1.45 - 1.39 (m, 4H), 1.39 - 1.22 (m, 16H), 0.87 (t, ^3J = 7.4 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): 162.5 (C), 161.3 (C), 160.1 (C), 127.3 (CH), 123.7 (CH), 121.5 (CH), 119.6 (CH), 111.0 (C), 66.3 (CH_2), 40.9 (CH_2), 31.9 (CH_2), 29.4 (CH_2), 28.1 (CH_2), 27.2 (CH_2), 22.7 (CH_2), 14.9 (CH_3), 14.1 (CH_3); MS (ESI, +ve): 579 (100, $[M+H]^+$).

Compound 20. A solution of **18** (60 mg, 10.3 mmol) is made in 2 mL CH_2Cl_2 to which pyrrolidine was added (2 mL). The mixture was allowed to react for two hours. The purple solution was extracted with 10% $NaHCO_3$ solution three times to remove excess pyrrolidine. The organic layer was dried with Na_2SO_4, filtered and concentrated *in vacuo*. The purple solid was purified by column chromatography (SiO_2, CH_2Cl_2/EtOAc 20:3) to yield **20** as a purple powder (31 mg, 48%). R_f (CH_2Cl_2/EtOAc 20:3): 0.63; Mp: 160.1 - 160.9; IR (neat): 2955 (m), 2921 (m), 2869 (m), 2853 (m), 1781 (w), 1767 (w), 1740 (w), 1734 (w), 1701 (m), 1679 (m), 1658 (m), 1637 (s), 1579 (m), 1564 (m), 1489 (m), 1441 (s), 1397 (w), 1377 (m), 1341 (m), 1324 (m), 1305 (s), 1260 (m), 1220 (m), 1203 (m), 1191 (m), 1127 (m), 1107 (m), 1072 (m), 1014 (m), 991 9m), 952 (m), 930 (m), 890 (m), 890 (m), 873 (m), 813 (w), 786 (m), 762 (m), 734 (m), 723 (m), 661

(m), 637 (w), 600 (m); ^{1}H NMR (400 MHz, $CDCl_3$): 8.48 (s, 1H), 8.37 (s, 1H), 4.48 (q, ^{3}J = 7.0 Hz, 2H), 4.28 - 4.11 (m, 4H), 3.54 (m, 4H), 2.19 - 2.00 (m, 4H), 1.79 - 1.70 (m, 4H), 1.67 (t, ^{3}J = 7.0 Hz, 3H), 1.49 - 1.23 (m, 20H), 0.89 (t, ^{3}J = 6.7 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): 163.3 (C), 161.9 (C), 161.5 (C), 158.0 (C), 148.7 (CH), 126.1 (C), 125.3 (C), 124.6 (C), 124.1 (C), 122.1 (CH), 117.4 (C), 111.6 (C), 103.8 (C), 65.9 (CH_2), 52.9 (CH_2), 40.8 (CH_2), 31.9 (CH_2), 29.4 (CH_2), 28.4 (CH_2), 28.1 (CH_2), 27.2 (CH_2), 25.9 (CH_2), 22.7 (CH_2), 14.9 (CH_3), 14.2 (CH_3); MS (ESI, +ve): 626 (24, $[M+Na]^+$), 605 (100, $[M+H]^+$).

Compound 19. A solution of **18** (60 mg, 10.3 mmol) was made in pyrrolidine (4 mL) and allowed to react for one hour at 50 °C. The dark blue solution was extracted with 10% $NaHCO_3$ solution three times to remove excess pyrrolidine. The organic layer was dried with Na_2SO_4, filtered and concentrated *in vacuo*. The dark blue solid was purified by column chromatography (SiO_2, CH_2Cl_2/EtOAc 20:3) to yield **19** as a dark blue powder (19 mg, 32%). R_f (CH_2Cl_2/EtOAc 20:3): 0.77; Mp: 155.4 - 156.0; IR (neat): 2958 (m), 2924 (m), 2851 (m), 1912 (w), 1860 (w), 1774 (w), 1736 (w), 1698 (w), 1678 (m), 1612 (s), 1562 (s), 1512 (w), 1481 (m), 1461 (s), 1435 (s), 1376 (m), 1350 (m), 1342 (m), 1323 (m), 1308 (s), 1291 (s), 1267 (m), 1225 (m), 1195 (s), 1150 (m), 1128 (s), 1080 (m), 1051 (m), 1033 (m), 1011 (m), 994 (m), 972 (m), 956 (m), 937 (m), 928 (m), 897 (m), 875 (m), 819 (m), 781 (m), 764 (m), 738 (m), 723 (m), 659 (m), 641 (w), 600 (m); ^{1}H NMR (400 MHz, $CDCl_3$): 8.39 (s, 2H), 4.28 - 4.13 (m, 4H), 3.56 - 3.48 (m, 8H), 2.21 - 2.04 (m, 8H), 1.73 (quint, ^{3}J = 6.7 Hz, 4H), 1.53 - 1.18 (m, 20H), 0.93 - 0.83 (t, ^{3}J = 6.4 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): 163.8 (C), 161.9 (C), 147.5 (CH), 124.9 (CH), 122.5 (C), 121.4 (C), 117.4 (C), 105.4 (C), 52.7 (CH_2), 40.9 (CH_2), 31.9 (CH_2), 29.3 (CH_2), 28.4 (CH_2), 27.2 (CH_2), 26.0 (CH_2), 22.7 (CH_2), 14.2 (CH_3); MS (ESI, +ve): 629 (100, $[M+H]^+$).

Compound 6. A solution of **31** (35 mg, 90 μmol) and ethylhexylamine (31 μL, 180 μmol) was made in DMF (25 mL) and heated at 140 °C for eight hours. The solution was precipitated in 1.0 M HCl solution and filtered. Impurities were removed with H_2O, 5% LiCl solution, brine solution and petroleum ether. The red solid was purified by column chromatography (SiO_2, CH_2Cl_2/petroleum ether 2:1) to yield **6** as a red powder (39 mg, 70%). R_f (CH_2Cl_2/petroleum ether 2:1): 0.37; Mp: 217.5 (decomposition); IR (neat): 2959 (m), 2926 (m), 2858 (m), 1690 (m) 1620 (s), 1854 (w), 1546 (m), 1492 (w), 1444 (s), 1374 (m), 1314 (m), 1258 (m), 1240 (m), 1200 (s), 1161 (m), 1101 (m), 1079 (m), 1052 (m), 1023 (m), 973 (m), 959 (m), 938 (m), 894 (m), 786 (s), 762 (m), 723 (m), 684 (m), 641 (m), 628 (m); ^{1}H NMR (500 MHz, $CDCl_3$): 8.71 (s, 2H), 4.21 - 4.12 (m, 4H), 3.30 - 3.22 (m, 4H), 2.06 - 1.96 (m, 2H), 1.54 (t, ^3J = 7.4 Hz, 6H), 1.46 - 1.34 (m, 8H), 1.35 - 1.23 (m, 8H), 0.93 (t, ^3J = 7.4 Hz, 6H), 0.88 (t, ^3J = 7.1 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): 163.8 (C), 162.9 (C), 148.5 (C), 128.3 (CH), 125.1 (C), 123.8 (C), 119.2 (C), 44.8 (CH_2), 37.8 (CH), 30.7 (CH_2) , 28.6 (CH_2), 26.4 (CH_2), 24.0 (CH_2), 23.2 (CH_2), 14.1 (CH_3), 12.9 (CH_3), 10.7 (CH_3); MS (ESI, +ve): 611 (100, $[M+H]^+$); HRMS (ESI, +ve) calcd for $C_{45}H_{46}N_2O_{12}S_2$: 611.2976, found: 611.2972.

Compounds 13 and 14. A solution of **6** (70.0 mg, 81.0 μmol) was made in CH_2Cl_2 (20 mL) at 0 °C followed by mCPBA (39.5 mg, 243 μmol) addition. After one hour, the reaction was stopped via addition of brine solution. The mixture was liquid/liquid extracted with CH_2Cl_2. The organic layer was dried with Na_2SO_4, filtered and concentrated *in vacuo*. The orange powder was purified by column chromatography (SiO_2, CH_2Cl_2/EtOAc 20:3) to yield **13** (20.0 mg, 32%) as well as **14** (38.3 mg, 62%) as orange powders. **13:** R_f (CH_2Cl_2/EtOAc 20:3): 0.69; Mp: 171.6

(decomposition); IR (neat): 3071 (w), 2959 (m), 2929 (m), 2859 (m), 1696 (m), 1645 (s) 1612 (m), 1586 (w), 1554 (m), 1493 (w), 1446 (m), 1407 (m), 1374 (m), 1316 (m), 1304 (m), 1265 (m), 1240 (s), 1198 (s), 1162 (m), 1130 (w), 1102 (m), 1051 (m), 1023 (m), 985 (w), 948 (m), 931 (m), 903 (m), 883 (m), 848 (w), 806 (m), 788 (m), 763 (m), 724 (m), 689 (w), 639 (m), 601 (w), 573 (m), 538 (m); ^{1}H NMR (400 MHz, $CDCl_3$): 9.43 (s, 1H), 8.71 (s, 1H), 4.17 - 4.09 (m, 2H), 4.09 - 3.99 (m, 2H), 3.28 - 3.18 (m, 3H), 2.91 - 2.82 (m, 1H), 1.98 - 1.89 (m, 1H), 1.88 - 1.80 (m, 1H), 1.50 (t, ^{3}J = 7.5 Hz, 3H), 1.38 - 1.15 (m, 22H), 0.90 - 0.84 (m, 6H), 0.84 - 0.78 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): 163.7 (C), 163.3 (C), 162.7 (C), 162.0 (C), 152.5 (C), 151.0 (C), 129.3 (C), 128.8 (CH), 128.1 (C), 125.4 (CH), 124.5 (C), 124.0 (C), 122.3 (C), 119.2 (C), 49.26 (CH_2), 44.8 (CH_2), 38.0 (CH_2), 30.7 (CH_2), 28.6 (CH_2), 26.7 (CH_2), 24.1 (CH_2), 23.1 (CH_2), 14.1 (CH_3), 12.9 (CH_3), 10.7 (CH_3), 10.5 (CH_3), 7.3 (CH_3); MS (ESI, +ve): 1255 (92, $[2M+H]^+$), 628 (100, $[M+H]^+$). **14:** R_f (CH_2Cl_2/EtOAc 20:3): 0.30; Mp: 281.5 (decomposition); IR (neat): 3056 (w), 2955 (m), 2929 (m), 2855 (m), 1877 (w), 1731 (w), 1698 (m), 1651 (s), 1564 (m), 1448 (m), 1403 (w), 1374 (m), 1338 (m), 1312 (m), 1279 (m), 1246 (s), 1191 (m), 1150 (m), 1105 (m), 1050 (s), 1026 (s), 967 (m), 940 (m), 921 (m), 877 (w), 854 (m), 791 (m), 767 (m), 725 (m), 650 (m), 633 (m), 574 (m); ^{1}H NMR (500 MHz, $CDCl_3$): 9.47 (s, 2H), 4.16 - 4.06 (m, 4H), 3.94 (q, ^{3}J = 7.5 Hz, 4H), 1.87 (m, 2H), 1.35 (m, 6H), 1.33 - 1.28 (m, 8H), 1.26 - 1.17 (m, 8H), 0.87 (t, ^{3}J = 7.4 Hz, 6H), 0.82 (t, ^{3}J = 7.0 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): 160.9 (C), 145.8 (C), 133.9 (C), 129.3 (CH), 127.4 (C), 126.8 (C), 50.7 (CH_2), 45.3 (CH), 37.9 (CH_2), 30.6 (CH_2), 28.5 (CH_2), 23.9 (CH_2), 23.1 (CH_2), 14.1 (CH_3), 10.5 (CH_3), 7.6 (CH_3); MS (ESI, +ve): 643 (100, $[M+H]^+$).

Compound 3. A solution of **35** (3.00 g, 7.91 mmol), octylamine (1.3 mL, 7.91 mmol), 2-aminobenzyl alcohol (1.95 g, 15.8 mmol) in DMF (30 mL) was heated to 140 °C for 10 hours. After cooling to rt, 1.0 M HCl was added and the precipitate was filtered off. Impurities were removed by solid-liquid extraction with water. The solid was dried *in vacuo* to yield a crude brown solid. The solid was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 10:1) to yield **3** as a brown powder (438.3 mg, 12%). R_f (CH_2Cl_2/MeOH 50:1): 0.40; Mp: 116.9 - 117.5; IR (neat): 3513 (w), 3070 (w), 2957 (w), 2925 (m), 2855 (w), 2247 (w), 1979 (w), 1703 (m), 1658 (s), 1609 (w), 1579 (m), 1550 (w), 1516 (w), 1491 (w), 1450 (m), 1411 (w), 1392 (w), 1333 (s), 1242 (s), 1195 (m), 1166 (m), 1128 (w), 1091 (m), 1045 (m), 1017 (m), 977 (m), 945 (w), 919 (m), 908 (m), 878 (m), 850 (m), 829 (w), 814 (w), 787 (w), 767 (m), 733 (m), 645 (m), 616 (m); ^{1}H NMR (500 MHz, $CDCl_3$): 8.77 (s, 4H), 7.63 (d, ^3J = 7.5 Hz, 1H), 7.55 - 7.51 (m, 1H), 7.51 - 7.47 (m, 1H), 7.23 (d, ^3J = 7.6 Hz, 1H), 4.49 (s, 2H), 4.24 - 4.11 (m, 2H), 1.76-1.70 (m, 2H), 1.49 - 1.16 (m, 12H), 0.85 (t, ^3J = 6.9, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): 163.4 (C), 162.8 (C), 138.4 (C), 133.1 (C), 131.6 (CH), 131.0 (C), 129.9 (C), 129.0 (C), 127.1 (CH), 126.4 (CH), 61.9 (CH_2), 41.1 (CH_2), 31.8 (CH_2), 29.3 (CH_2), 28.1 (CH_2), 27.1 (CH_2), 22.6 (CH_2), 14.1 (CH_3); MS (ESI, +ve): 628 (32, $[M+NH_4+H]^+$), 485 (25, $[M+H]^+$), 467 (100, $[M - OH^-]^+$).

Compound 8. A solution of **31** (100 mg, 0.26 mmol), octylamine (40 µL, 0.26 mmol) and 2-aminobenzyl alcohol (38 mg, 0.32 mmol) was made in DMF (20 mL) and heated at 140 °C for 10 hours. The solution was precipitated in 1.0 M HCl solution and filtered. Impurities were removed by solid extraction with H_2O, 5% LiCl solution, brine solution and petroleum ether. The red solid was purified by column chromatography (SiO_2, CH_2Cl_2/EtOAc 20:3) to yield **8** as a red powder (49 mg, 69%). R_f (CH_2Cl_2/EtOAc 20:3): 0.55; 119.6 - 120.0; IR (neat): 3511 (w), 3071

(w), 3043 (w), 2956 (w), 2926 (m), 2855 (w), 1703 (m), 1658 (s), 1604 (w), 1579 (m), 1546 (w), 1515 (w), 1492 (w), 1450 (m), 1392 (w), 1369 (m), 1332 (s), 1242 (s), 1194 (m), 1166 (m), 1125 (m), 1090 (m), 1044 (m), 1017 (m), 977 (m), 944 (w), 920 (m), 908 (m), 877 (m), 850 (m), 827 (m), 806 (m), 788 (m), 766 (s), 733 (m), 723 (m), 645 (m), 615 (m), 598 (m), 576 (m), 559 (m), 544 (m); ^{1}H NMR (500 MHz, $CDCl_3$): 8.74 (s, 2H), 7.65 (d, ^{3}J = 7.4 Hz, 1H), 7.61 - 7.48 (m, 2H), 7.28 (d, ^{4}J = 1.7 Hz, 1H), 4.52 (s, 2H), 4.22 (t, ^{3}J = 7.4 Hz, 2H), 3.24 (2 q, ^{3}J = 7.4 Hz, 4H), 1.76 (quint, ^{3}J = 7.4 Hz, 2H), 1.54 (t, ^{3}J = 7.4 Hz, 3H), 1.51 (t, ^{3}J = 7.4 Hz, 3H), 1.48 - 1.41 (m, 2H), 1.41 - 1.34 (m, 2H), 1.31 - 1.25 (m, 6H), 0.89 (t, ^{3}J = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): 163.9 (C), 163.4 (C), 163.1 (C), 162.4 (C), 149.7 (C), 148.6 (C), 138.0 (CH), 133.4 (C), 130.3 (C), 129.9 (CH), 129.5 (CH), 129.2 (CH), 128.8 (CH), 128.4 (C), 125.7 (C), 125.2 (C), 124.3 (C), 123.7 (C), 119.7 (C), 118.8 (C), 62.4 (CH_2), 41.3 (CH_2), 31.9 (CH_2), 29.7 (CH_2), 29.3 (CH_2), 29.3 (CH_2), 28.1 (CH_2), 27.2 (CH_2), 26.4 (CH_2), 22.7 (CH_2), 14.2 (CH_3), 12.9 (CH_3), 12.9 (CH_3); MS (ESI, +ve): 628 (40, $[M+Na]^+$), 605 (22, $[M+H]^+$), 587 (100, $[M - OH^-]^+$).

Compound 2. A solution of **35** (200 mg, 0.58 mmol) and 4-*tert*-butyl aniline (223 µL, 1.1 mmol) was made in DMF (20 mL) and heated at 140 °C for eight hours. The solution was precipitated in 1.0 M HCl solution and filtered. Impurities were removed by solid-liquid extraction with H_2O, 5% LiCl solution, brine solution and petroleum ether. The beige solid was purified by column chromatography (SiO_2, CH_2Cl_2/petroleum ether 10:1) to yield **2** as a beige powder (205 mg, 66%). R_f (CH_2Cl_2/petroleum ether 10:1): 0.42; Mp: > 400 °C; IR (neat): 3072 (w), 2958 (m), 2905 (w), 2868 (w), 1978 (w), 1913 (w), 1710 (m), 1664 (s), 1580 (m), 1509 (m), 1476 (w), 1447 (m), 1412 (w), 1393 (w), 1347 (s), 1244 (s), 1215 (m), 1196 (s), 1143 (m), 1117 (m), 1105 (m), 1023 (m), 980 (m), 948 (m), 926 (w), 887 (m), 861 (m), 835 (m), 801 (w), 766

(s), 754 (m), 733 (m), 712 (m), 694 (m), 654 (w), 641 (w), 618 (w); ^{1}H NMR (500 MHz, $CDCl_3$): 8.90 (s, 4H), 7.66 (d, ^{3}J = 9.3 Hz, 4H), 7.33 (d, ^{3}J = 9.3 Hz 4H), 1.46 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$): 163.1 (C), 152.1 (CH), 131.7 (C), 131.5 (C), 127.8 (CH), 127.2 (C), 127.1 (C), 126.8 (C), 126.7 (CH), 34.9 (C), 31.4 (CH_3), 31.4 (CH_3); MS (ESI, +ve): 532 (100, $[M+H]^+$).

Compound 7. A solution of **31** (200 mg, 0.51 mmol) and 4-*tert*-butyl aniline (223 µL, 1.1 mmol) was made in DMF (20 mL) and heated at 140 °C for eight hours. The solution was precipitated in 1.0 M HCl and filtered. Impurities were removed by solid-liquid extraction with H_2O, 5% LiCl solution, brine solution and petroleum ether. The light pink solid was purified by column chromatography (SiO_2, CH_2Cl_2) to yield **7** as a light pink powder (75 mg, 20%). R_f (CH_2Cl_2): 0.68; Mp: 367.8 - 368.1; IR (neat): 2968 (w), 2932 (w), 2903 (w), 2860 (w), 2247 (w), 1979 (w), 1913 (w), 1810 (w), 1703 (m), 1651 (s), 1609 (w), 1582 (w), 1547 (m), 1518 (w), 1597 (w), 1435 (m), 1392 (w), 1362 (m), 1326 (m), 1266 (m), 1226 (s), 1165 (m), 1137 (m), 1106 (m), 1050 (w), 1031 (m), 1018 (m), 983 (w), 949 (w), 919 (m), 907 (m), 852 (w), 828 (m), 801 (m), 788 (m), 758 (m), 729 (m), 718 (s), 644 (m), 628 (m), 599 (w); ^{1}H NMR (500 MHz, $CDCl_3$): 8.84 (s, 2H), 7.65 (d, ^{3}J = 7.2 Hz, 4H), 7.33 (d, ^{3}J = 7.2 Hz, 4H), 3.27 (q, ^{3}J = 7.4 Hz, 4H), 1.55 (t, ^{3}J = 7.4 Hz, 6H), 1.45 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$): 163.7 (C), 162.8 (C), 152.0 (C), 149.4 (C), 131.8 (CH), 128.7 (C), 127.9 (CH), 126.6 (CH), 125.6 (CH), 124.3 (CH), 119.5 (C), 34.9 (C), 31.4 (CH_3), 26.3 (CH_2), 12.9 (CH_3); MS (ESI, +ve): 651 (100, $[M+H]^+$).

1.4. References

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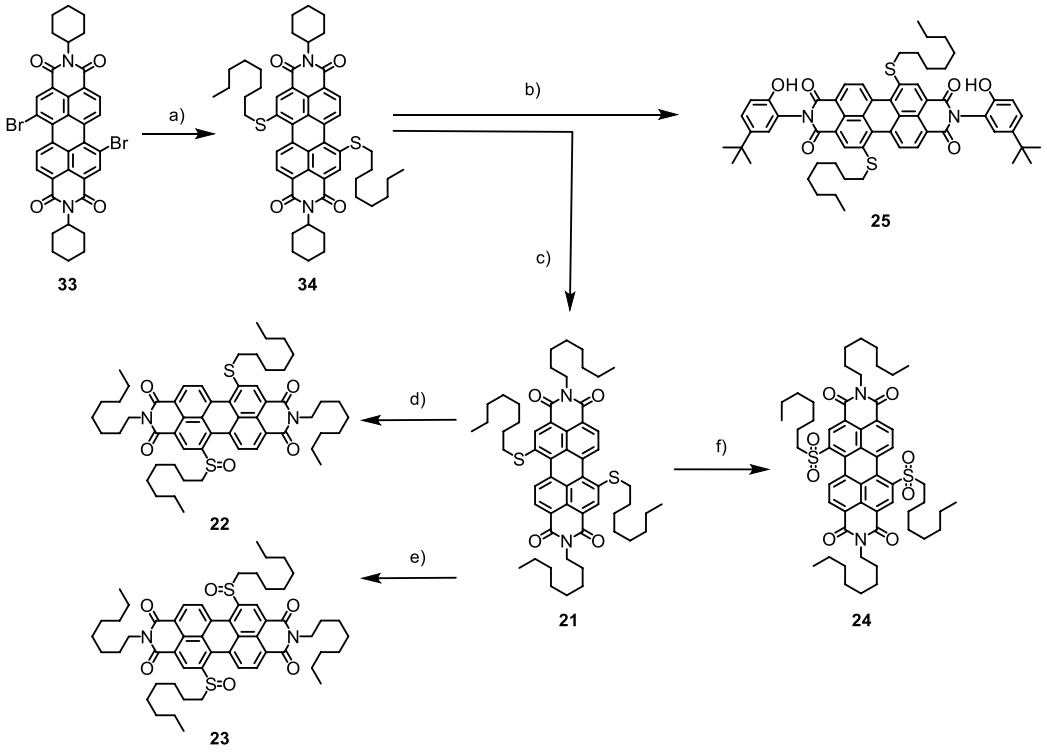
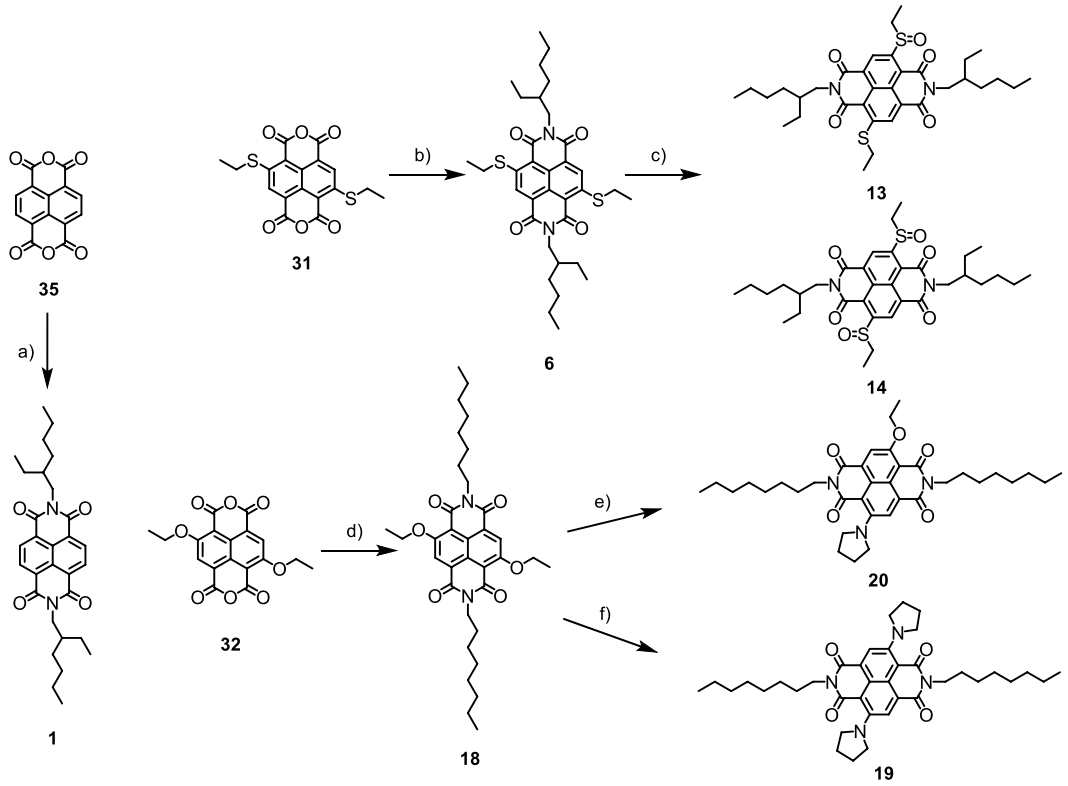
[S2] F. N. Miros, Y. Zhao, G. Sargsyan, M. Pupier, C. Besnard, C. Beuchat, J. Mareda, N. Sakai, S. Matile, *Chem. Eur. J.* **2015**, in press.

[S3] F. Würthner, V. Stepanenko, Z. Chen, Z. C. Saha-Möller, N. Kocher, D. Stalke, *J. Org. Chem.* **2004**, *69*, 7933 - 7939.

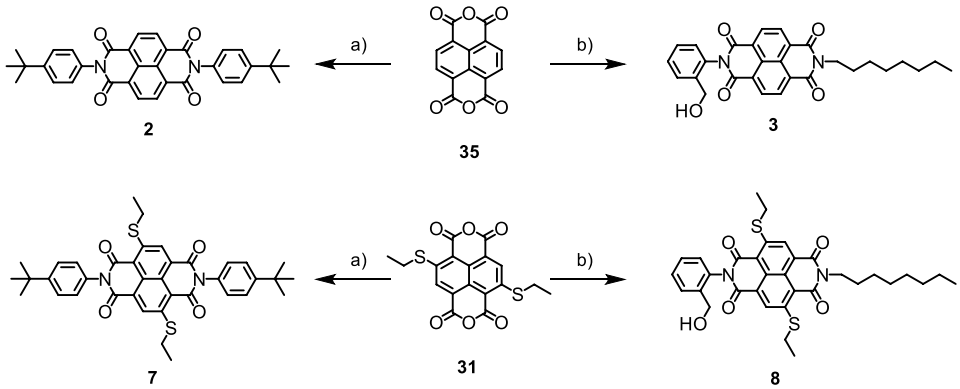
2. Supplementary Figures and Legends



Scheme S1. a) **33**, octylthiol, K_2CO_3, 18-crown-6, $CHCl_3$, 85 °C, 48 h, 96%; b) 1. **34**, KOH, *i*-PrOH, 80 °C, 4 h, 2. AcOH, 80 °C, 8 h, 3. 2-amino-4-*tert*-butylphenol, DMF, 140 °C, 10 h, 83%; c) **34**, KOH, *i*-PrOH, 80 °C, 4 h, 2. AcOH, 80 °C, 8 h, 3. octylamine, DMF, 140 °C, 8 h, 79%; d) **21**, mCPBA, CH_2Cl_2, 0 °C, 10 min, 30%; e) **21**, mCPBA, BF_3Et_2O, CH_2Cl_2, -20 °C, 2 h, 19%; f) **21**, mCPBA, CH_2Cl_2, 1 h, 41%.



Scheme S2. a) **35**, 2-ethylhexylamine, DMF, 140 °C, 8 h, 70%; b) **31**, 2-ethylhexylamine, DMF, 140 °C, 8 h, 70%; c) **6**, mCPBA, CH_2Cl_2, 0 °C, 20 min, 32% (**13**), 62% (**14**); d) **32**, octylamine, AcOH, 80 °C, 8 h, 58%; e) **18**, pyrrolidine, CH_2Cl_2, 2 h, 48%; f) **18**, pyrrolidine, 1 h, 50 °C, 32%.



Scheme S3. a) **31**/**35**, *p-tert*-butyl aniline, DMF, 140 °C, 8 h, 20% (**2**), 66% (**7**); b) **31**/**35**, 2-aminobenzyl alcohol, octylamine, DMF, 10 h, 12% (**3**), 69% (**8**).

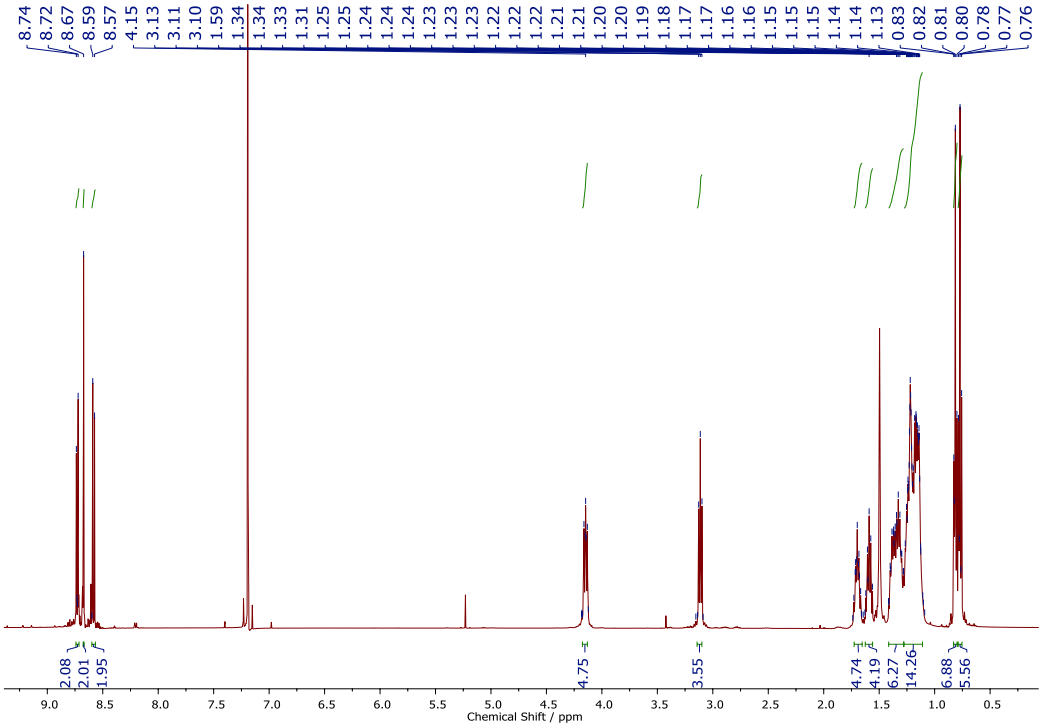


Figure S1. ^{1}H NMR spectrum of **21** in $CDCl_3$.

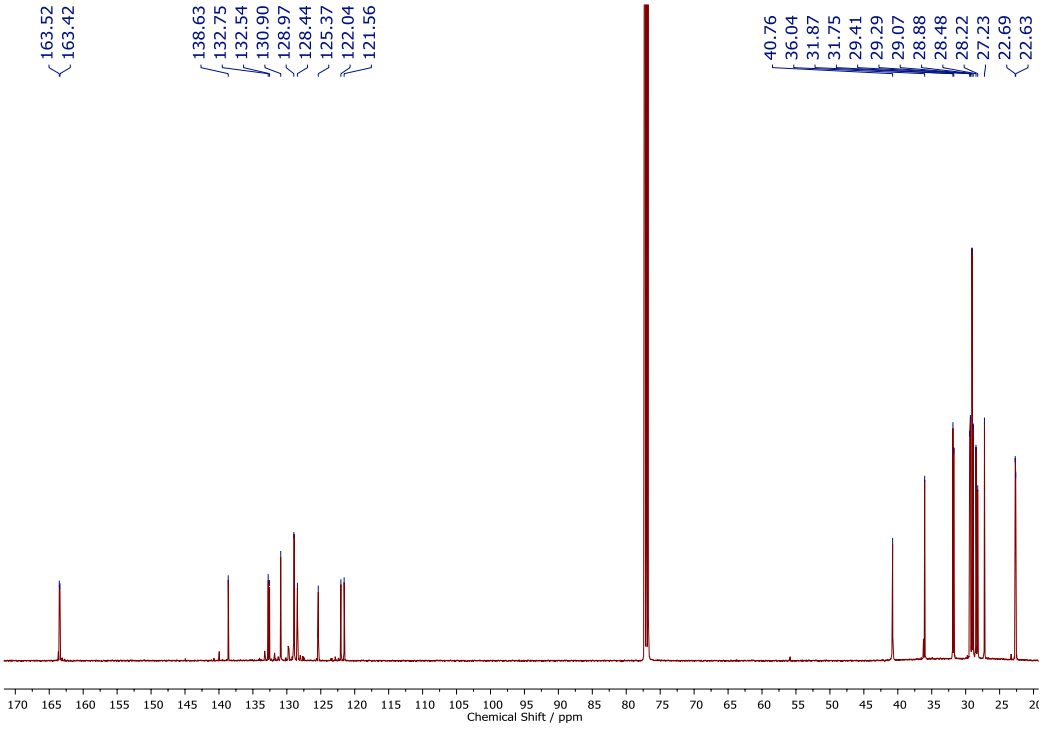


Figure S2. ^{13}C NMR spectrum of **21** in $CDCl_3$.

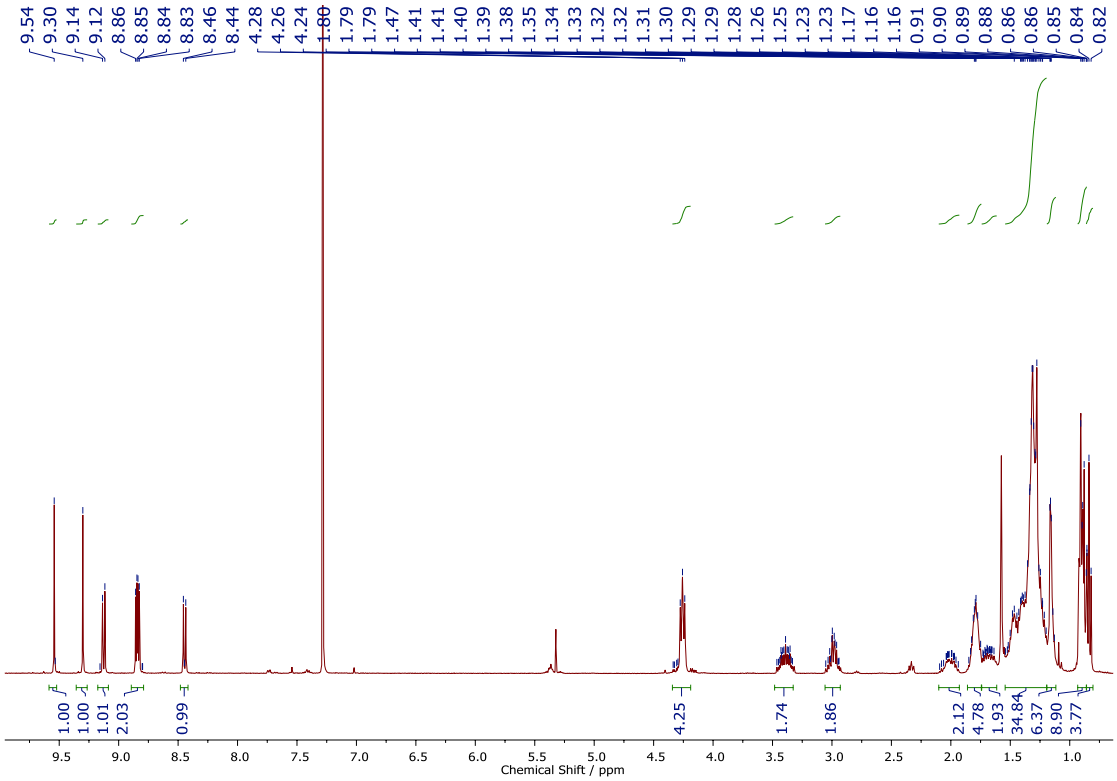


Figure S3. ^{1}H NMR spectrum of **22** in $CDCl_3$.

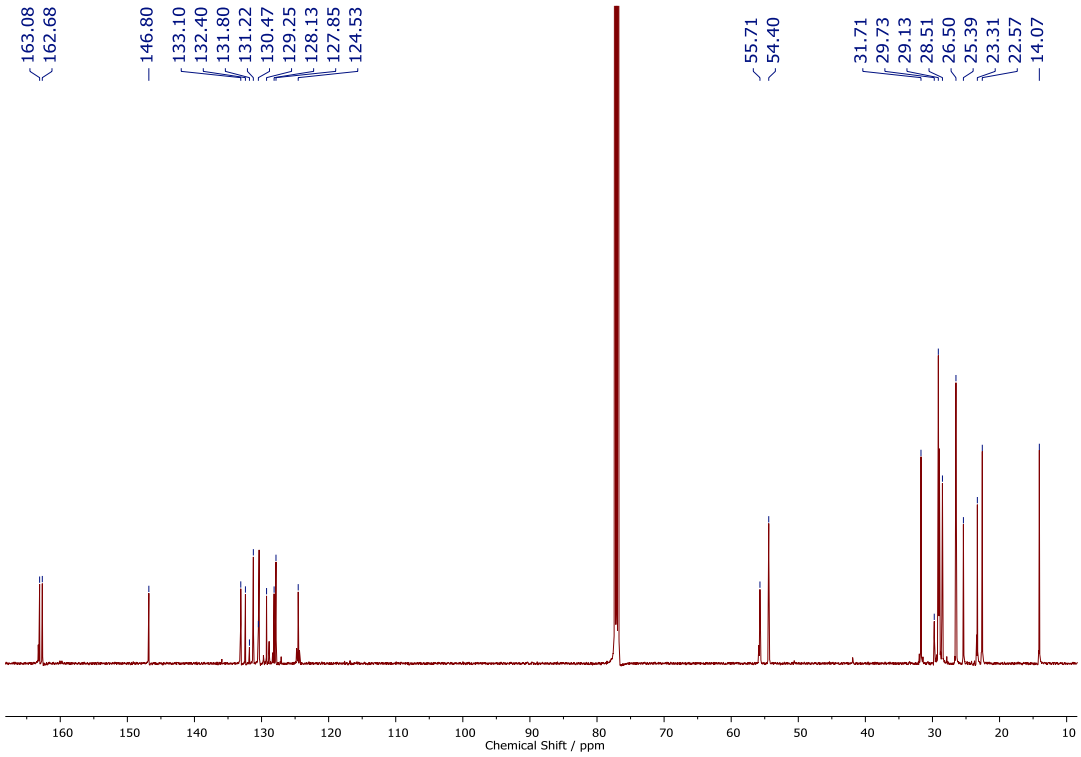


Figure S4. ^{13}C NMR spectrum of **22** in $CDCl_3$.

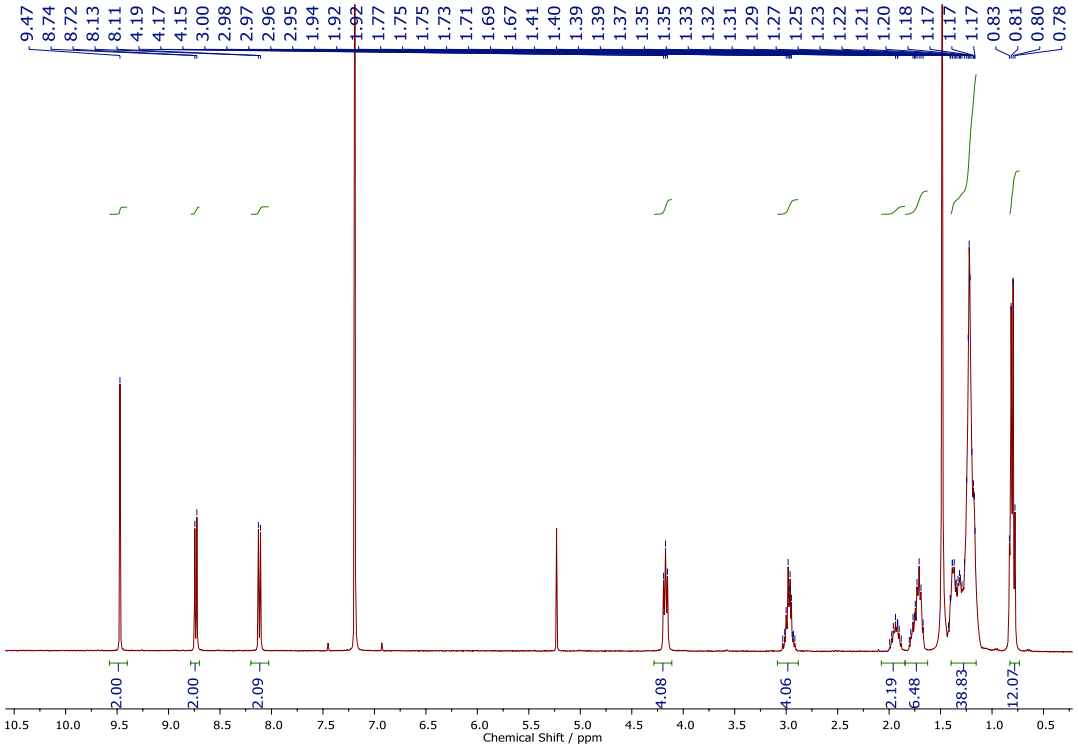


Figure S5. ^{1}H NMR spectrum of **23a** in $CDCl_3$.

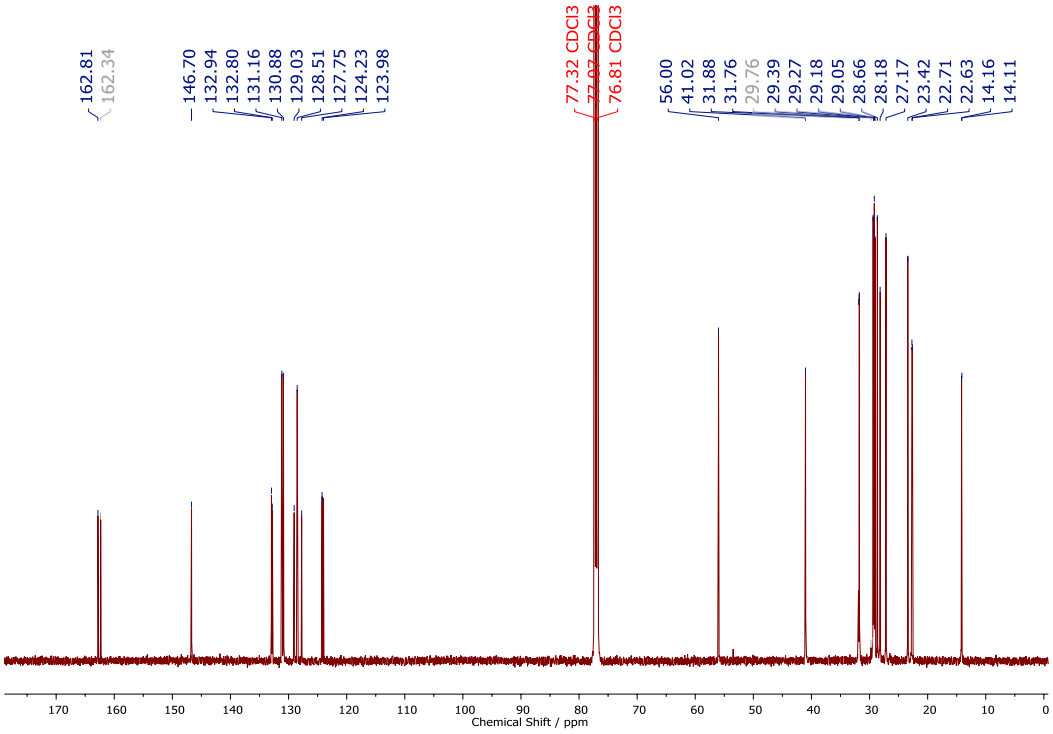


Figure S6. ^{13}C NMR spectrum of **23a** in $CDCl_3$.

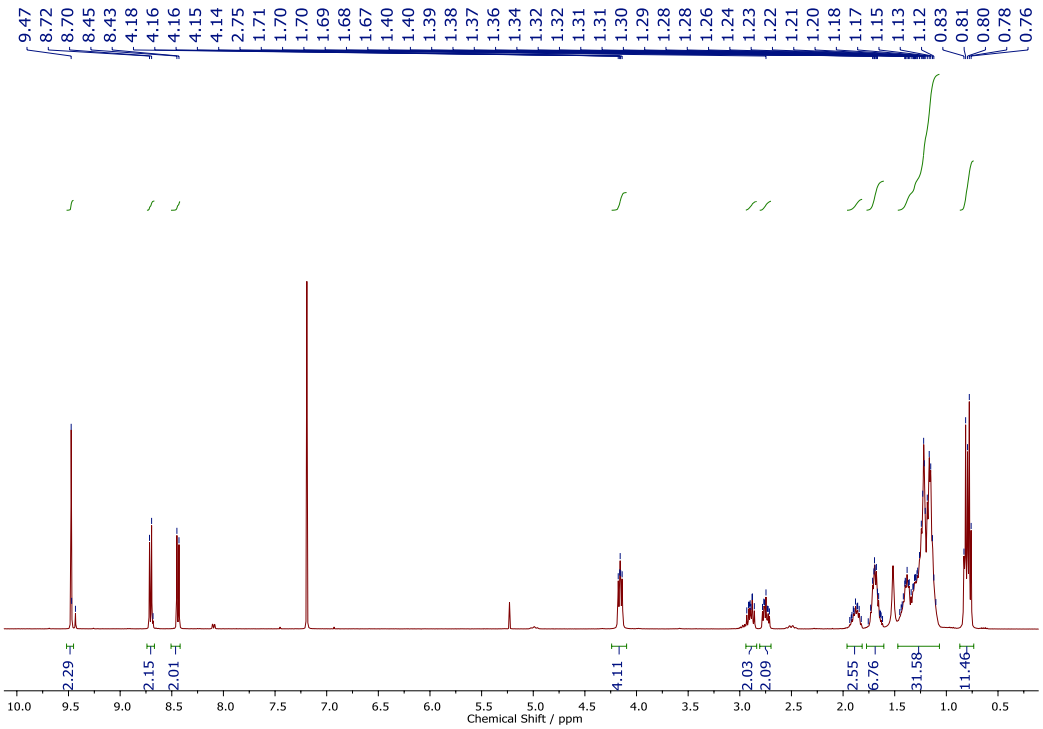


Figure S7. ^{1}H NMR spectrum of **23b** in $CDCl_3$.

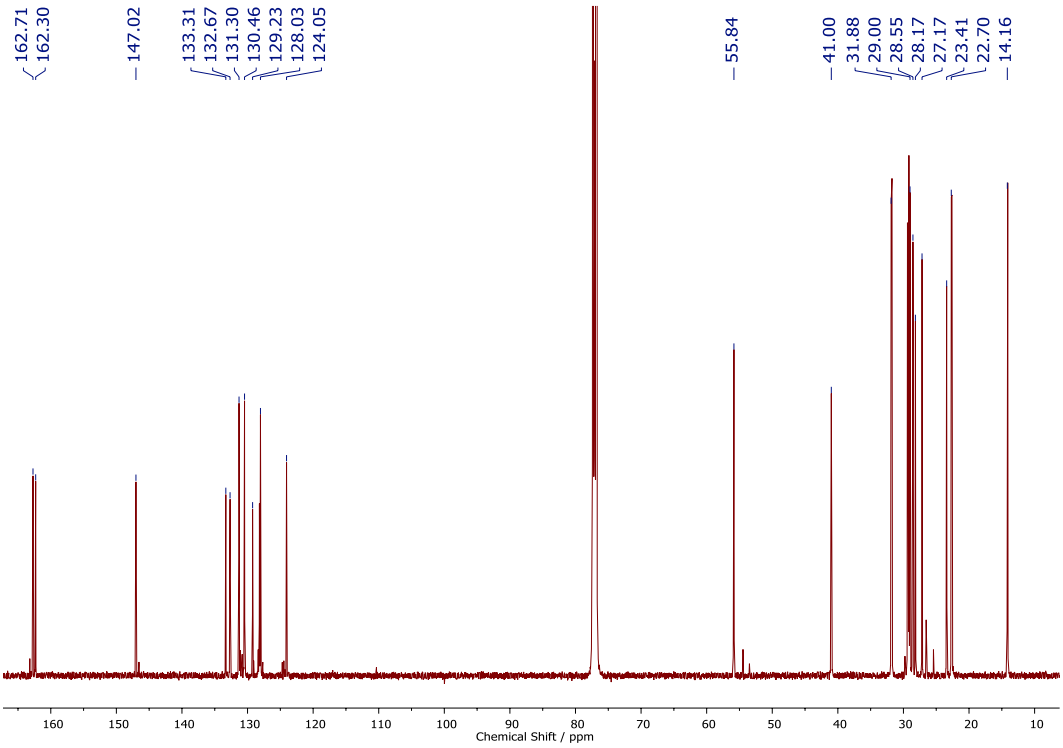


Figure S8. ^{13}C NMR spectrum of **23b** in $CDCl_3$.

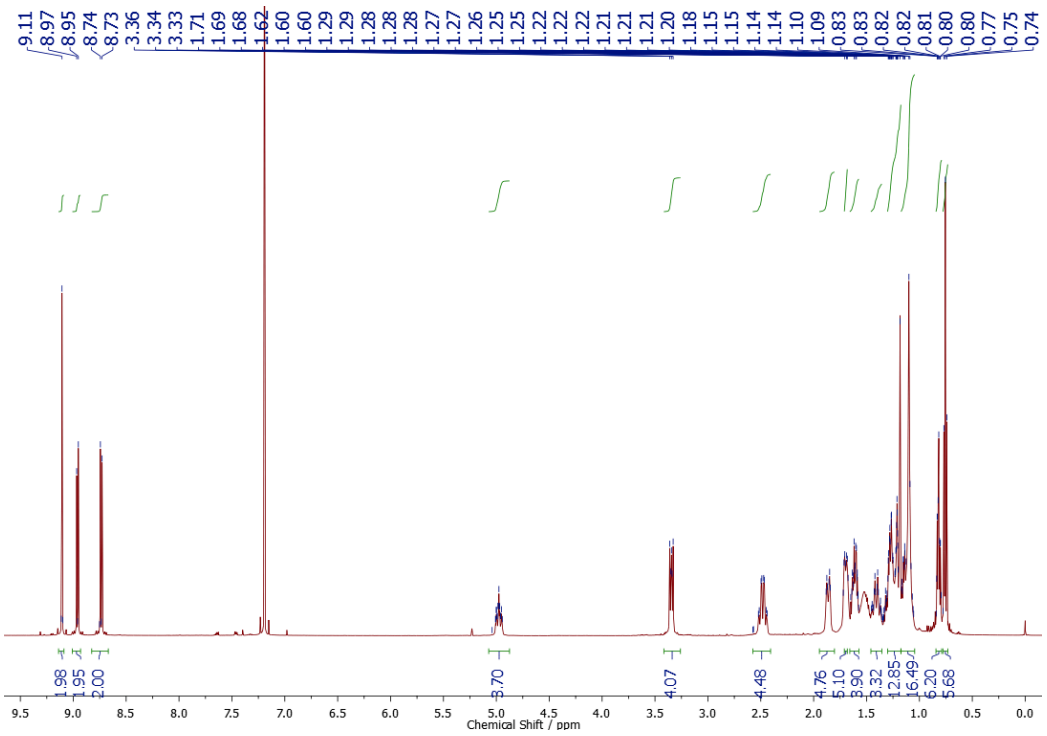


Figure S9. ^{1}H NMR spectrum of **24** in $CDCl_3$.

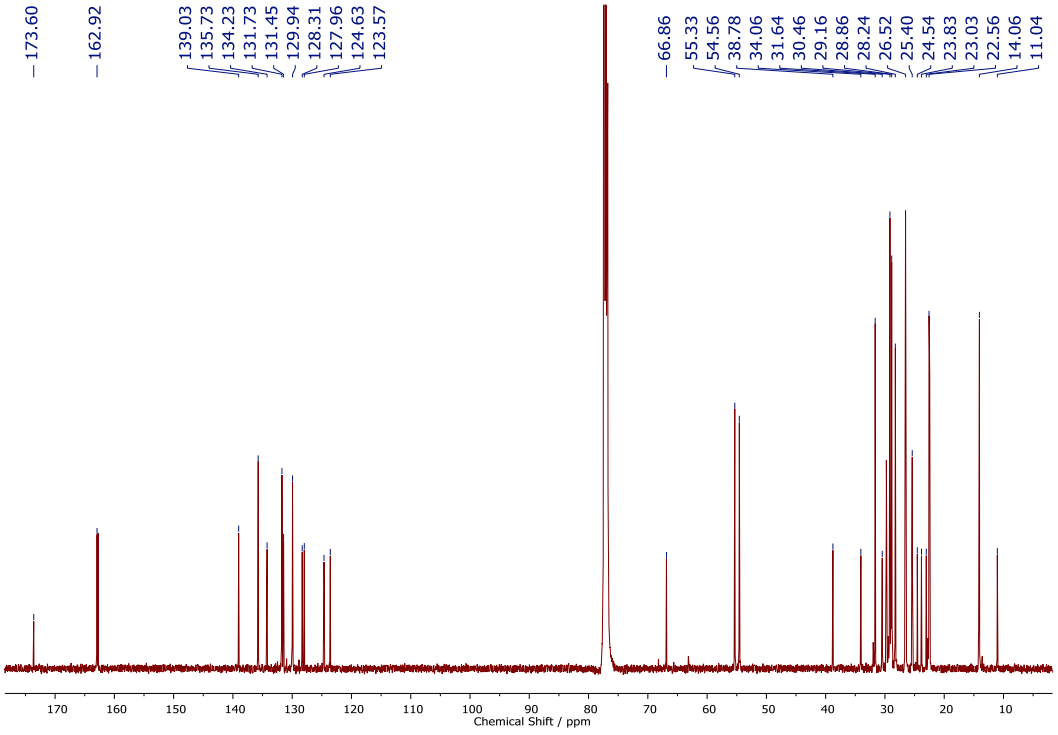


Figure S10. ^{13}C NMR spectrum of **24** in $CDCl_3$.

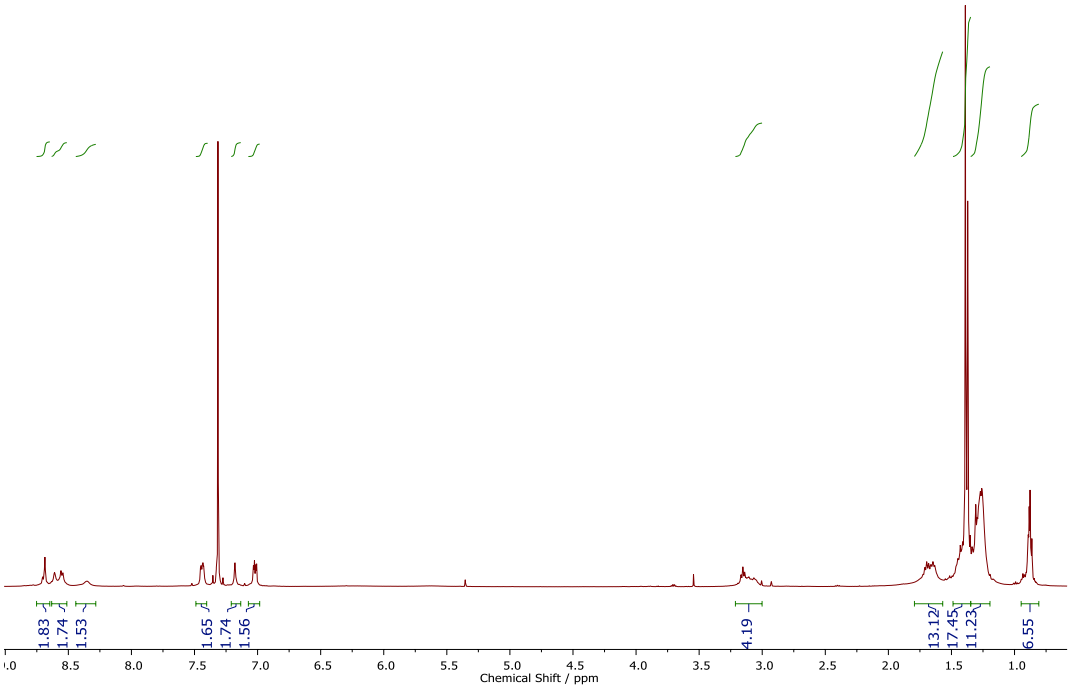


Figure S11. ^{1}H NMR spectrum of atropisomer mixture **25** in $CDCl_3$.

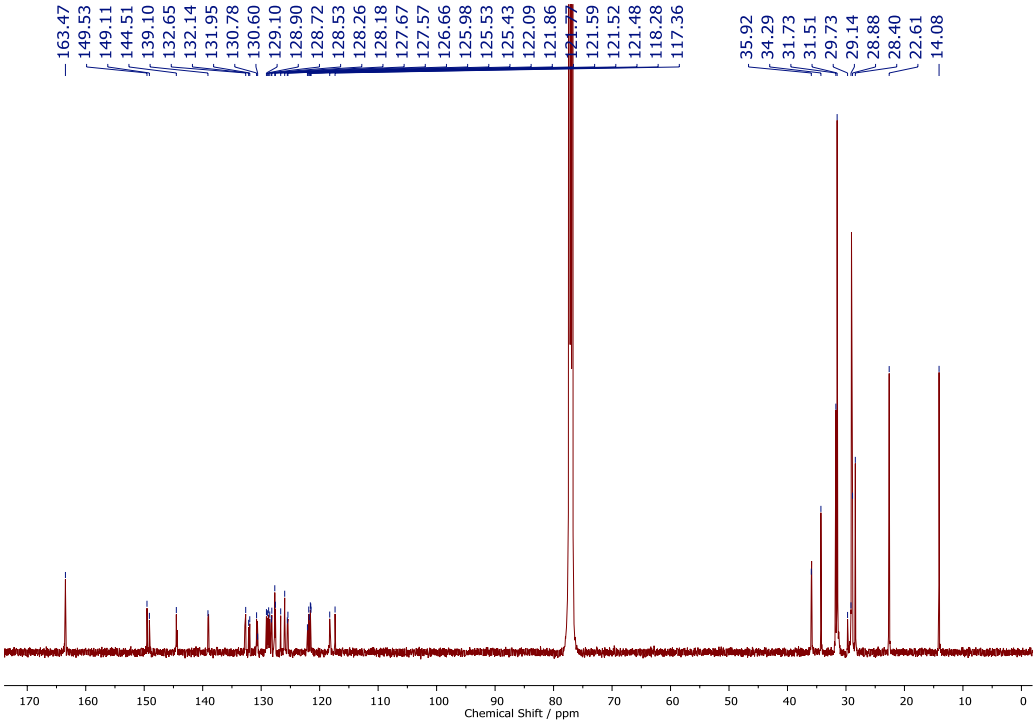


Figure S12. ^{13}C NMR spectrum of atropisomer mixture **25** in $CDCl_3$.

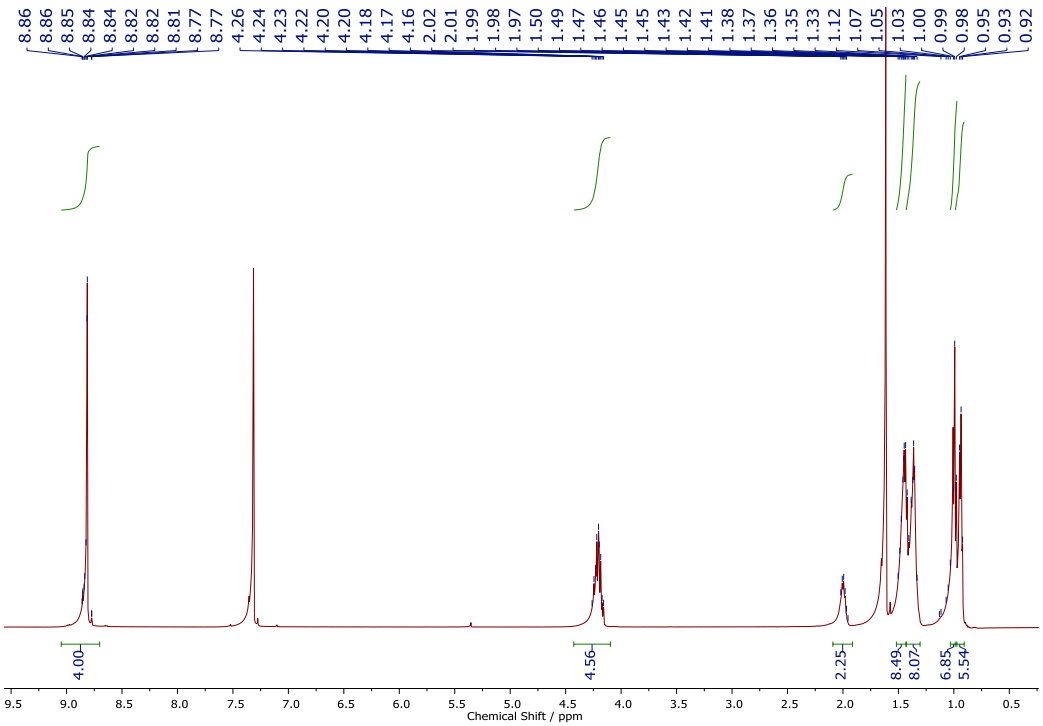


Figure S13. ^{1}H NMR spectrum of **1** in $CDCl_3$.

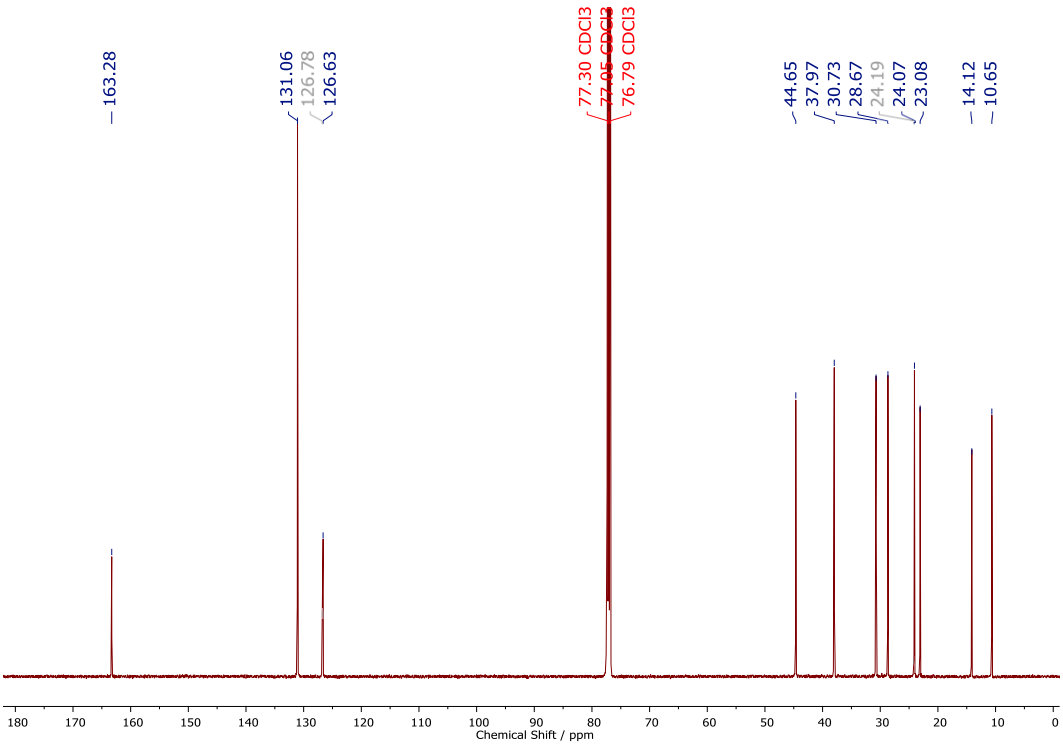


Figure S14. ^{13}C NMR spectrum of **1** in $CDCl_3$.

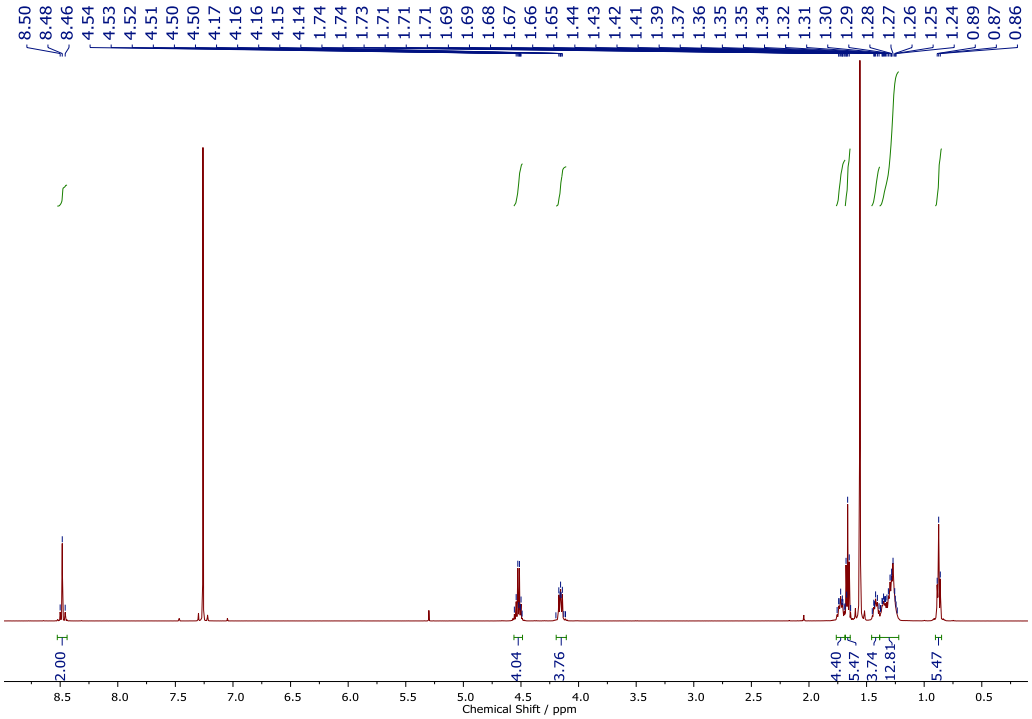


Figure S15. ^{1}H NMR spectrum of **18** in $CDCl_3$.

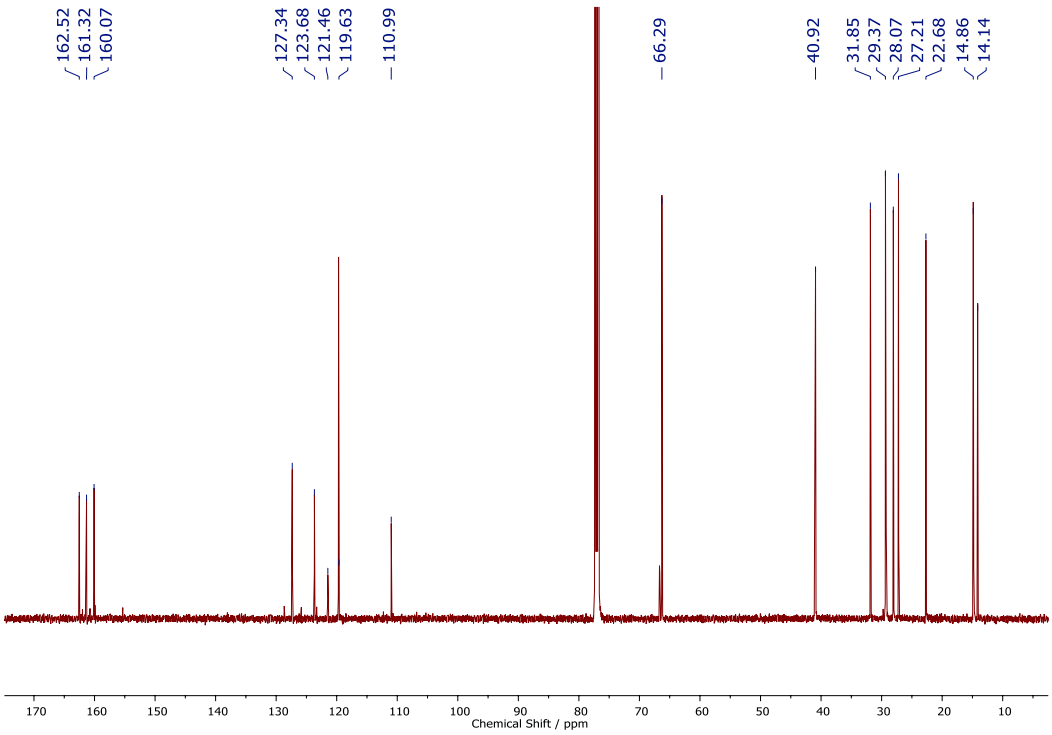


Figure S16. ^{13}C NMR spectrum of **18** in $CDCl_3$.

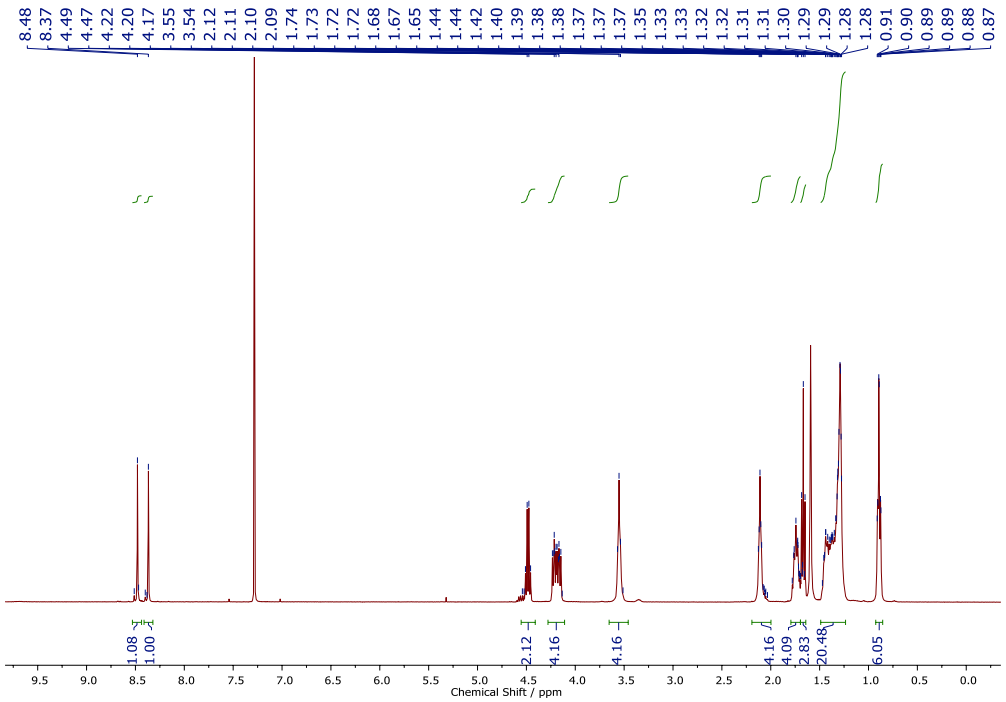


Figure S17. ^{1}H NMR spectrum of **20** in $CDCl_3$.

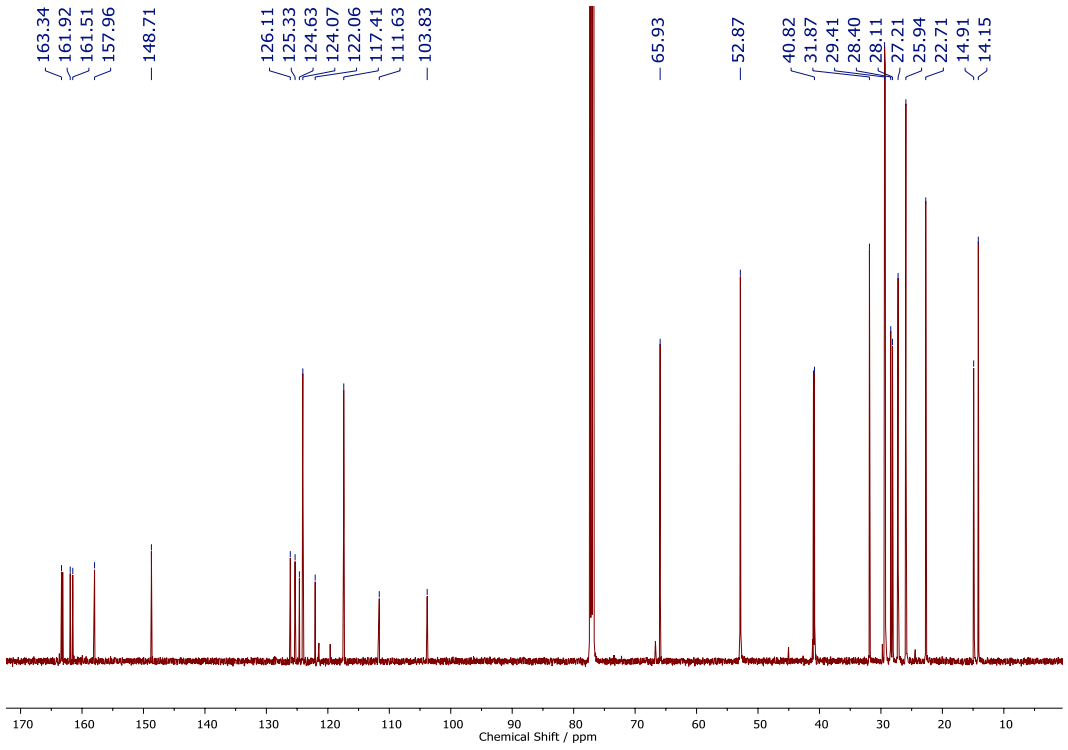


Figure S18. ^{13}C NMR spectrum of **20** in $CDCl_3$.

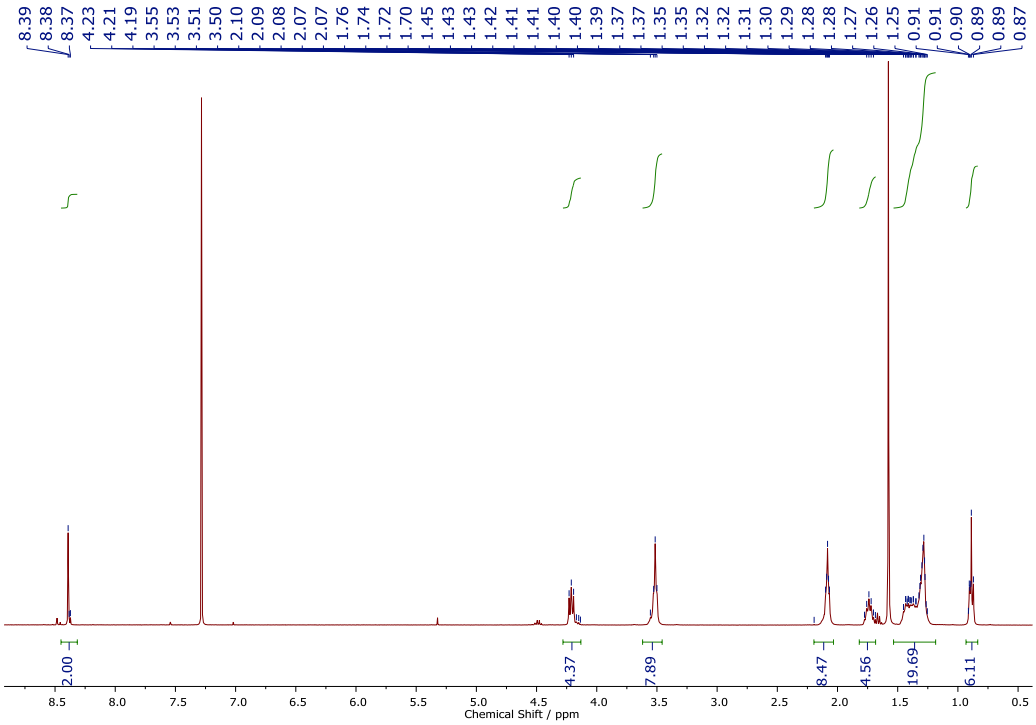


Figure S19. ^{1}H NMR spectrum of **19** in $CDCl_3$.

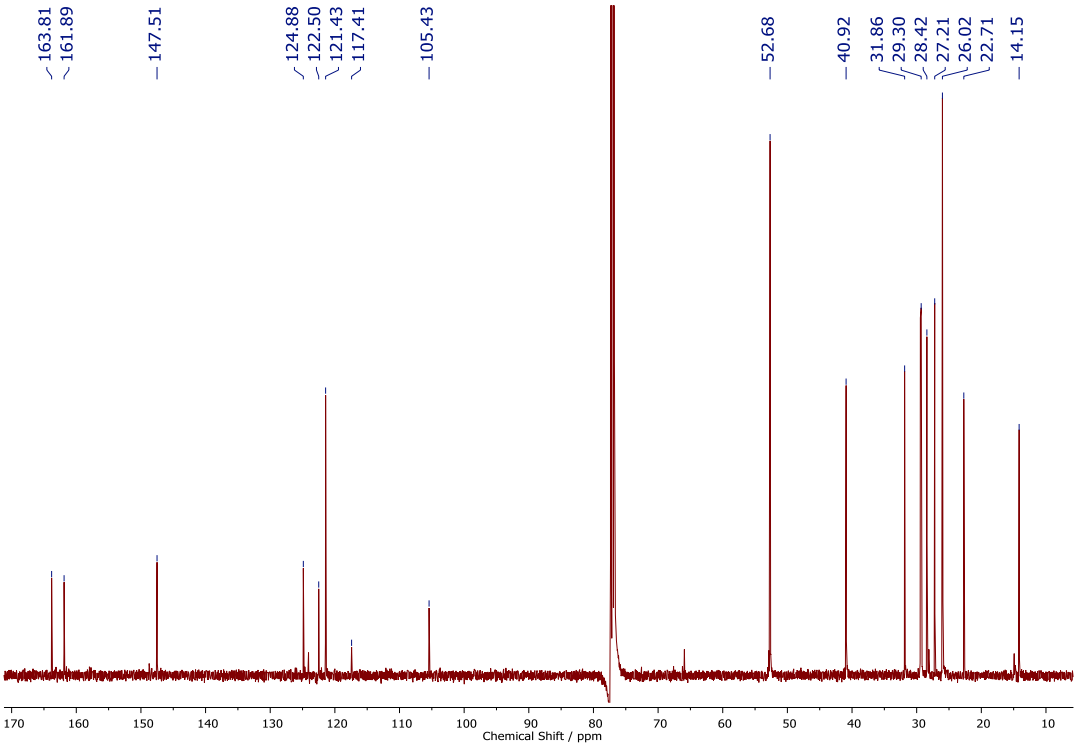


Figure S20. ^{13}C NMR spectrum of **19** in $CDCl_3$.

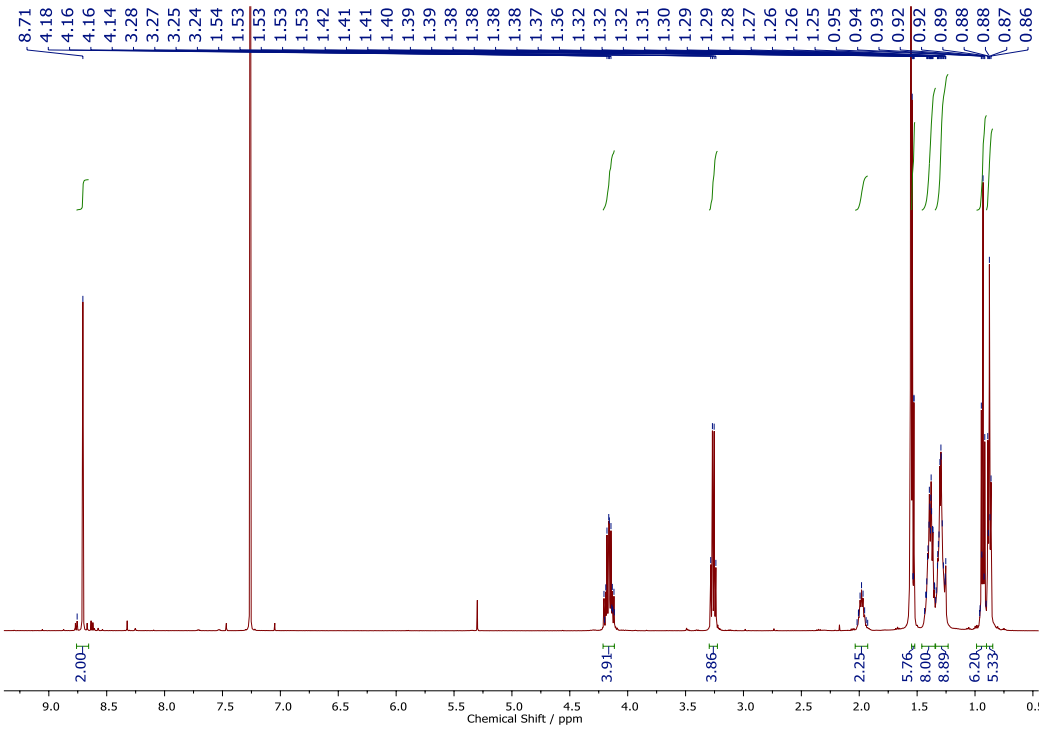


Figure S21. ^{1}H NMR spectrum of **6** in $CDCl_3$.

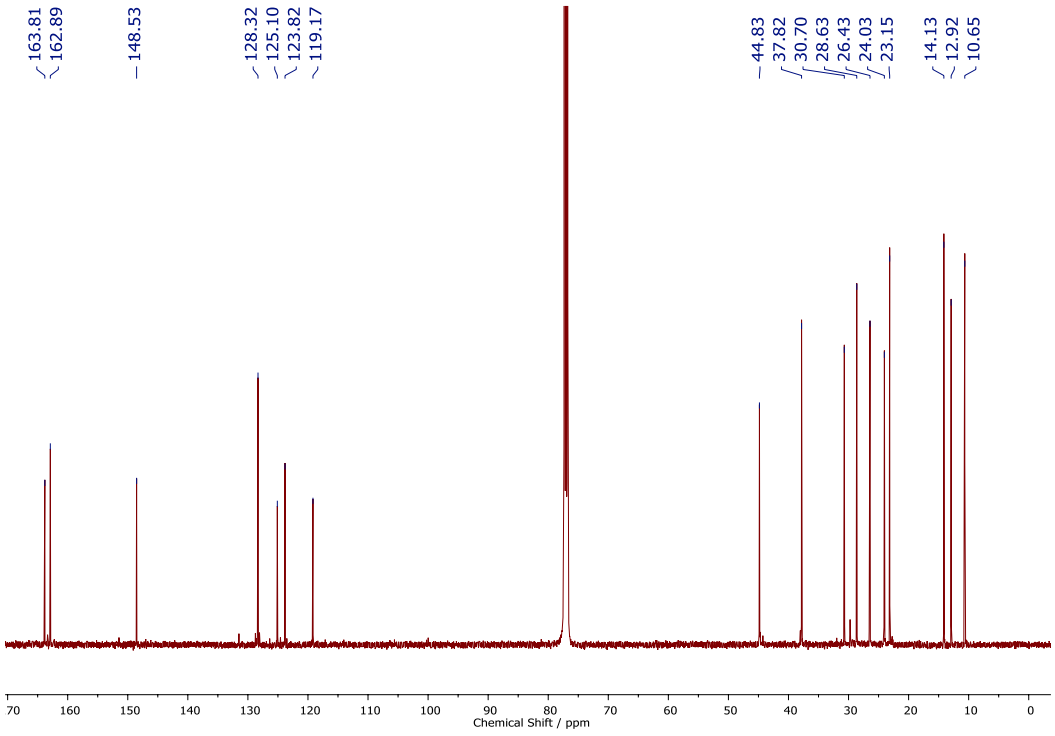


Figure S22. ^{13}C NMR spectrum of **6** in $CDCl_3$.

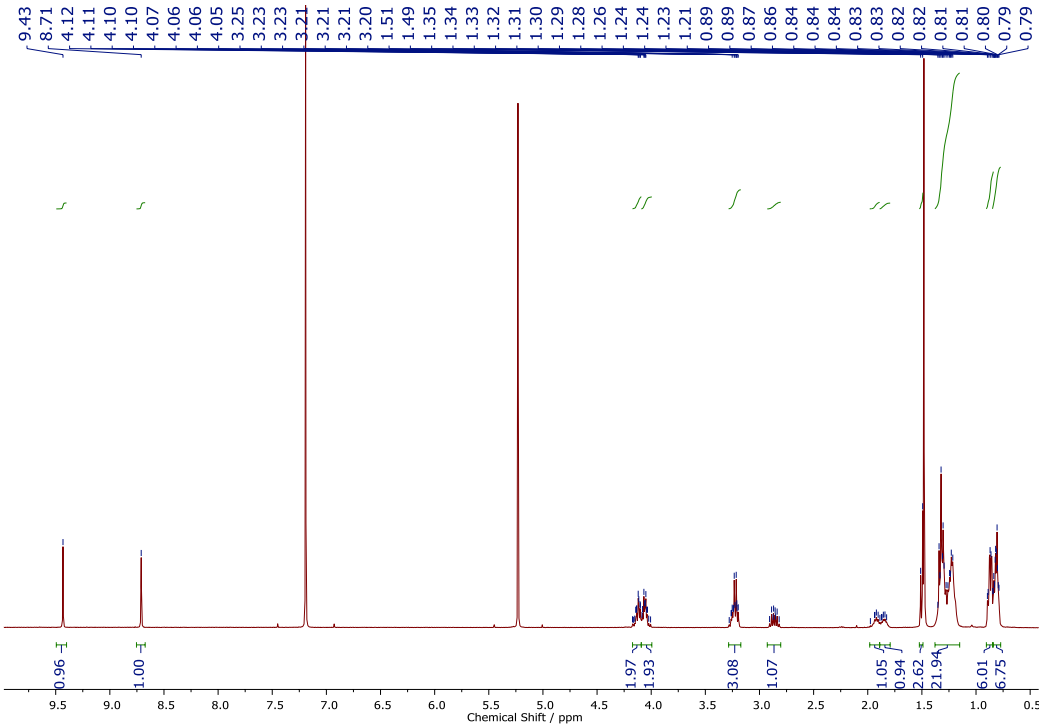


Figure S23. ^{1}H NMR spectrum of **13** in $CDCl_3$.

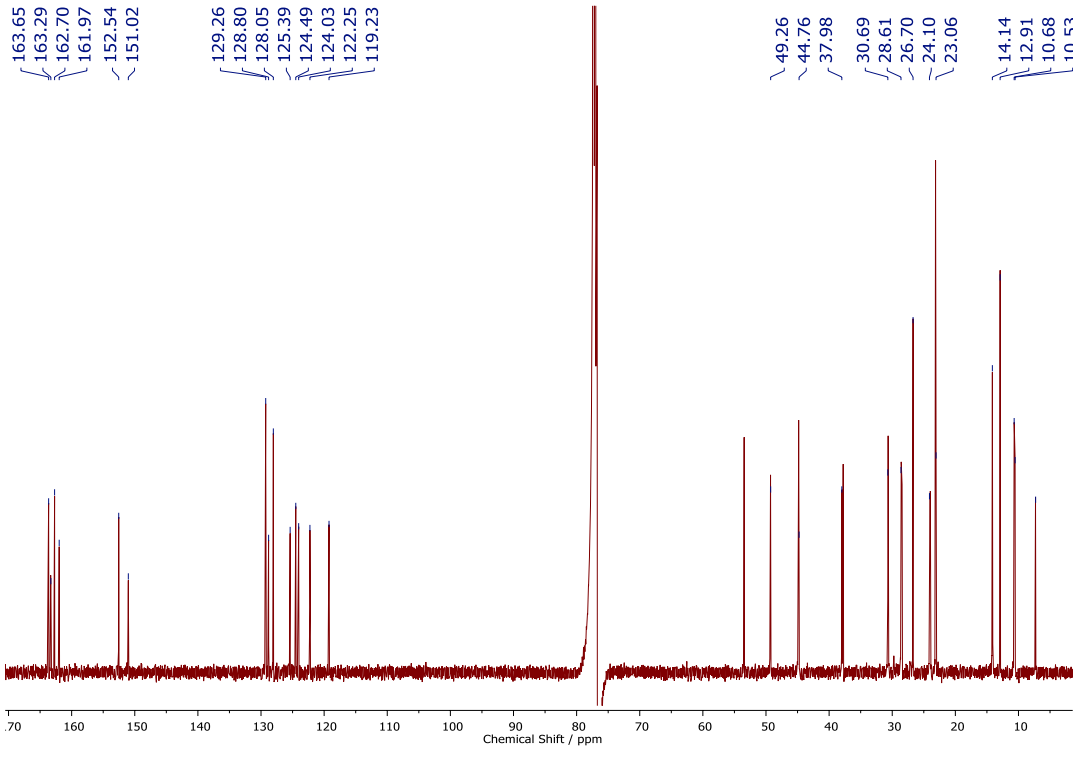


Figure S24. ^{13}C NMR spectrum of **13** in $CDCl_3$.

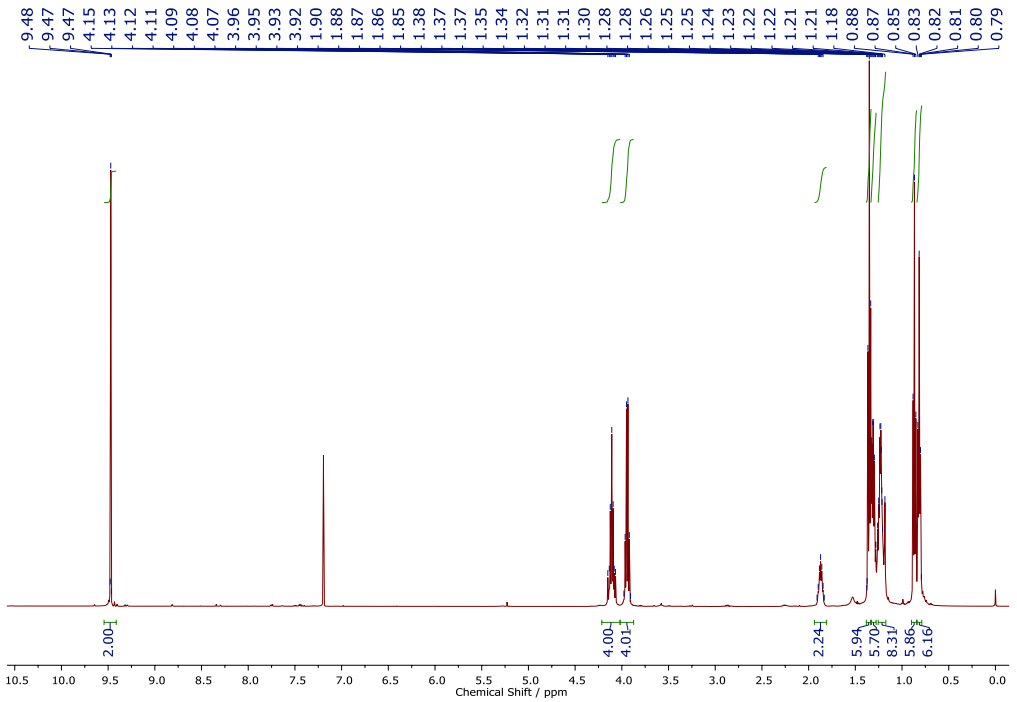


Figure S25. ^{1}H NMR spectrum of **14** in $CDCl_3$.

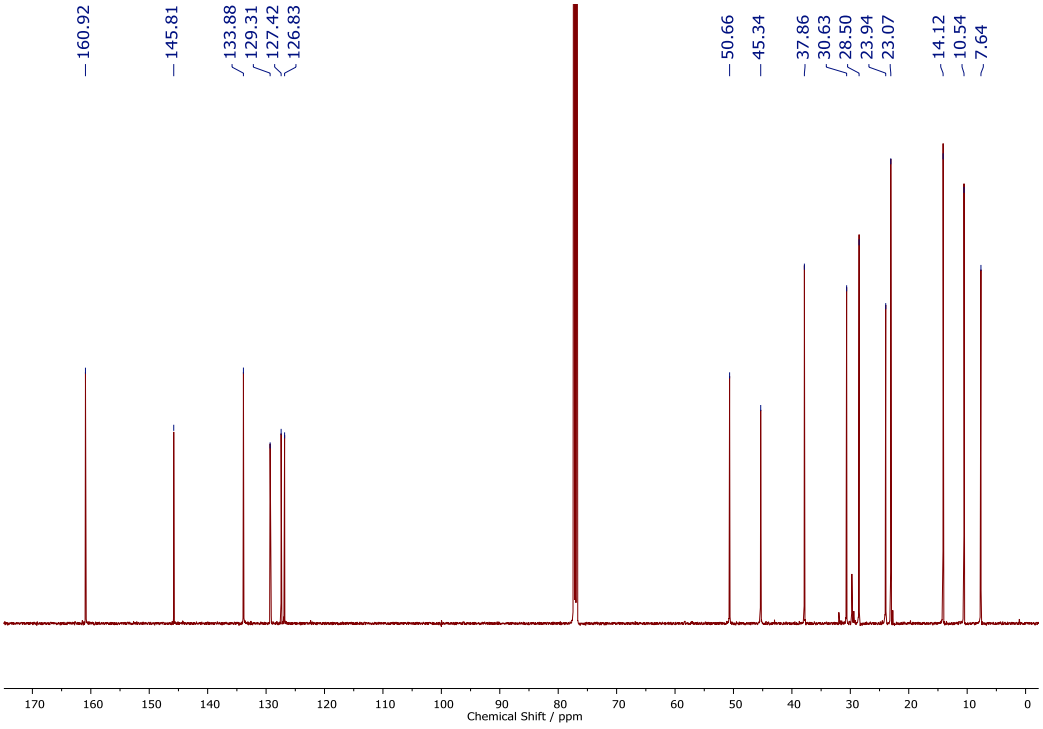


Figure S26. ^{13}C NMR spectrum of **14** in $CDCl_3$.

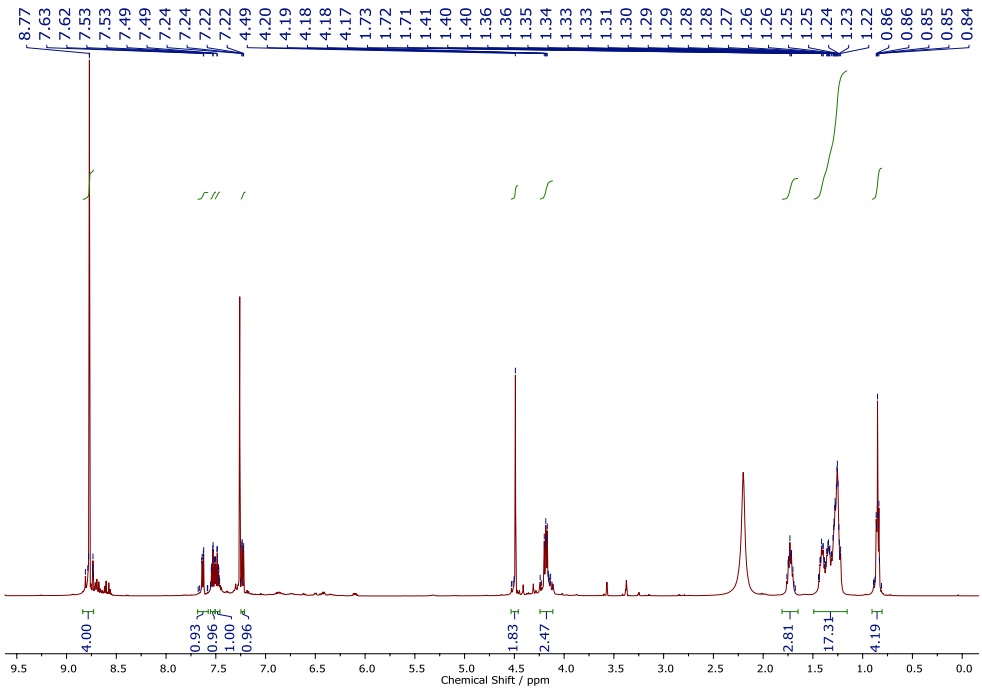


Figure S27. ^{1}H NMR spectrum of **3** in $CDCl_3$.

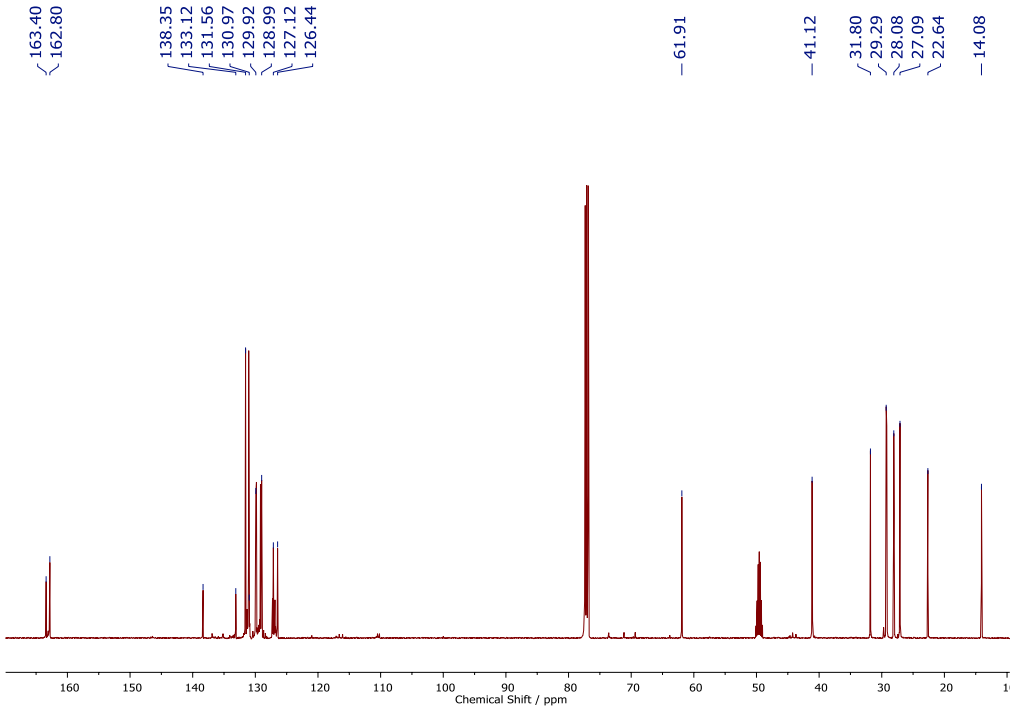


Figure S28. ^{13}C NMR spectrum of **3** in $CDCl_3$.

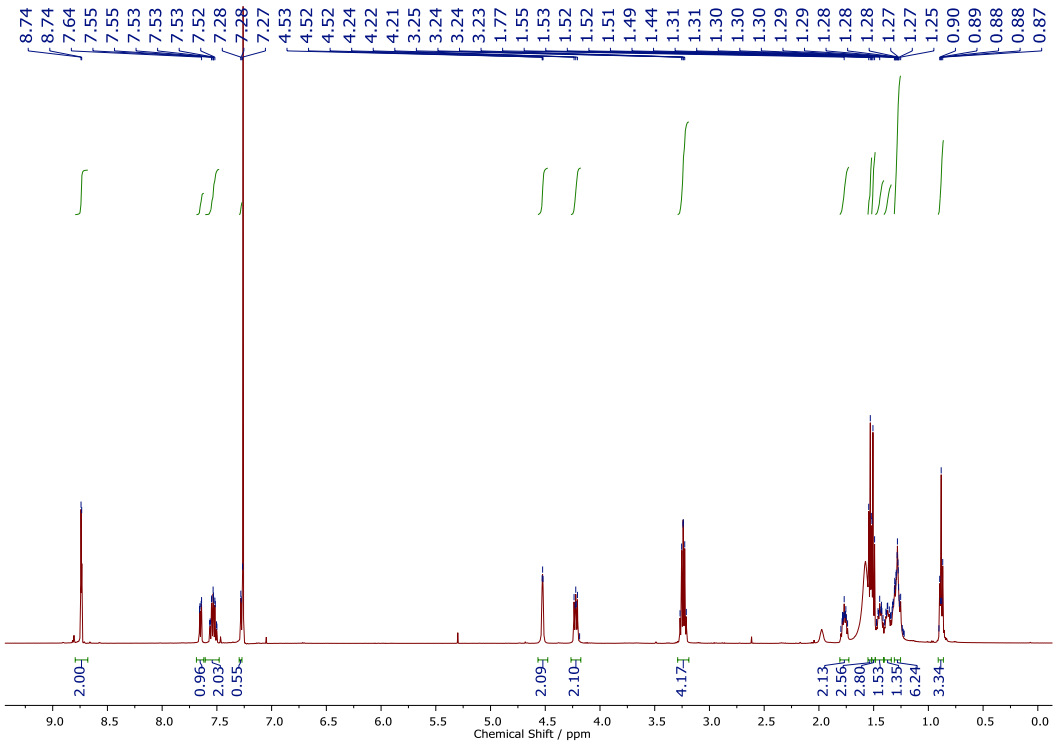


Figure S29. ^{1}H NMR spectrum of **8** in $CDCl_3$.

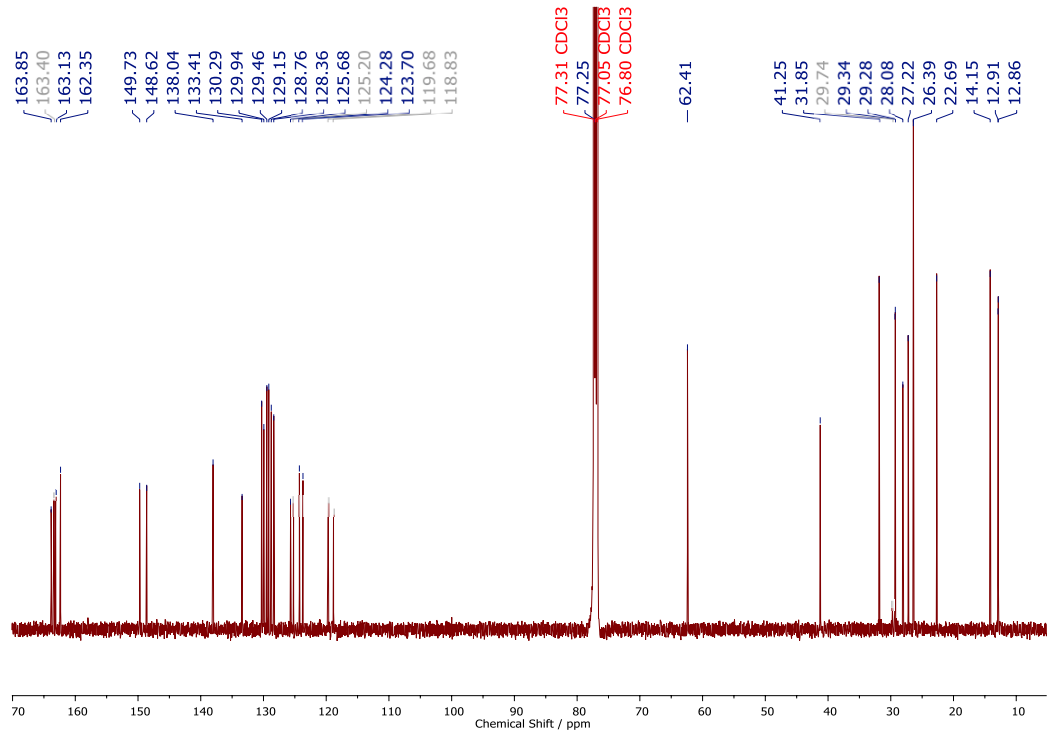


Figure S30. ^{13}C NMR spectrum of **8** in $CDCl_3$.

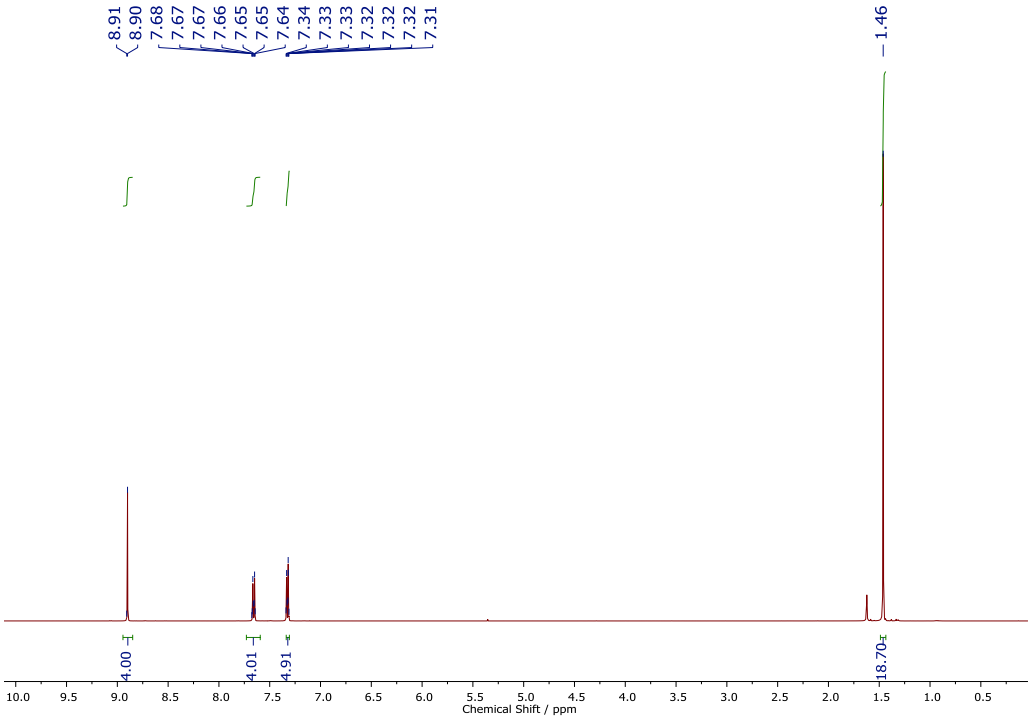


Figure S31. ^{1}H NMR spectrum of **2** in $CDCl_3$.

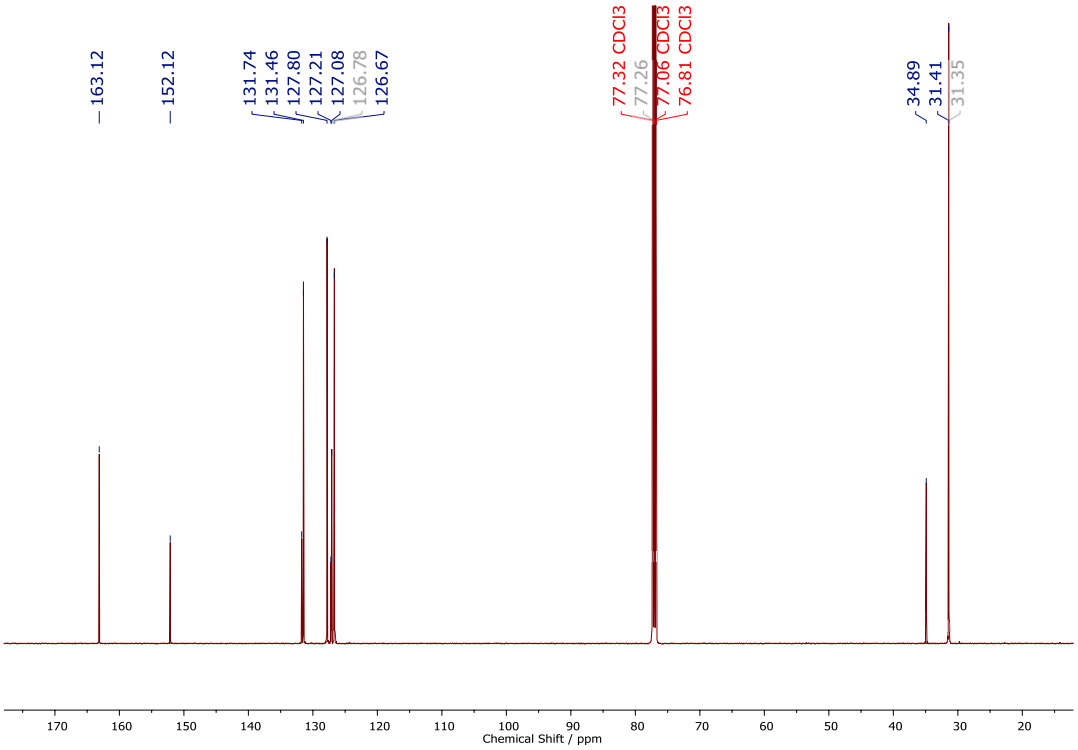


Figure S32. ^{13}C NMR spectrum of **2** in $CDCl_3$.

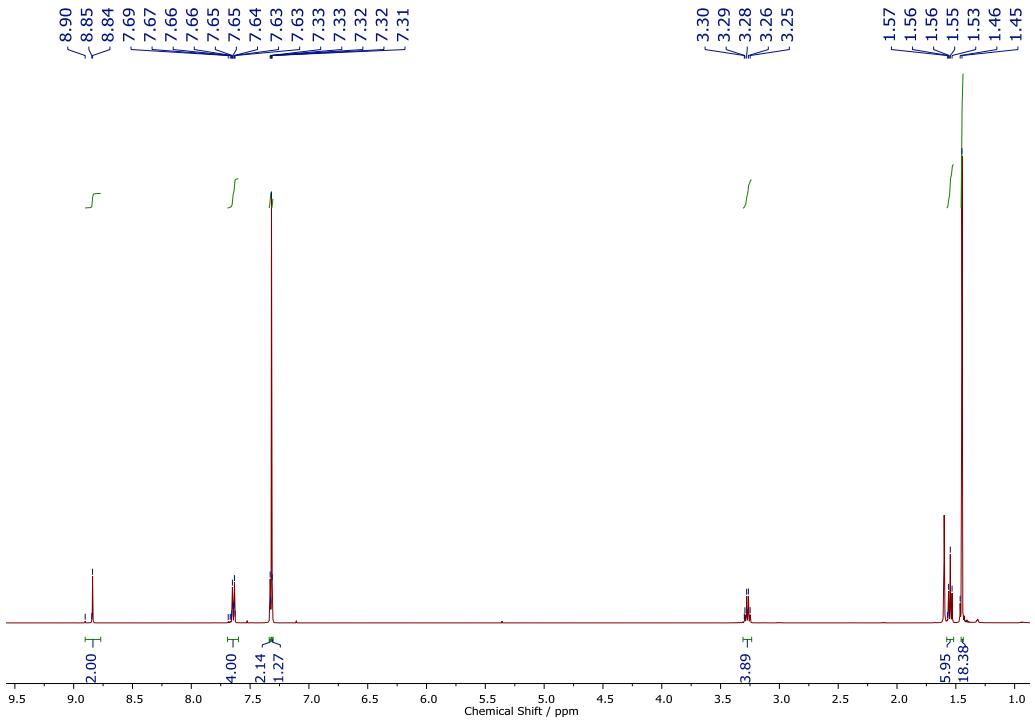


Figure S33. ^{1}H NMR spectrum of **7** in $CDCl_3$.

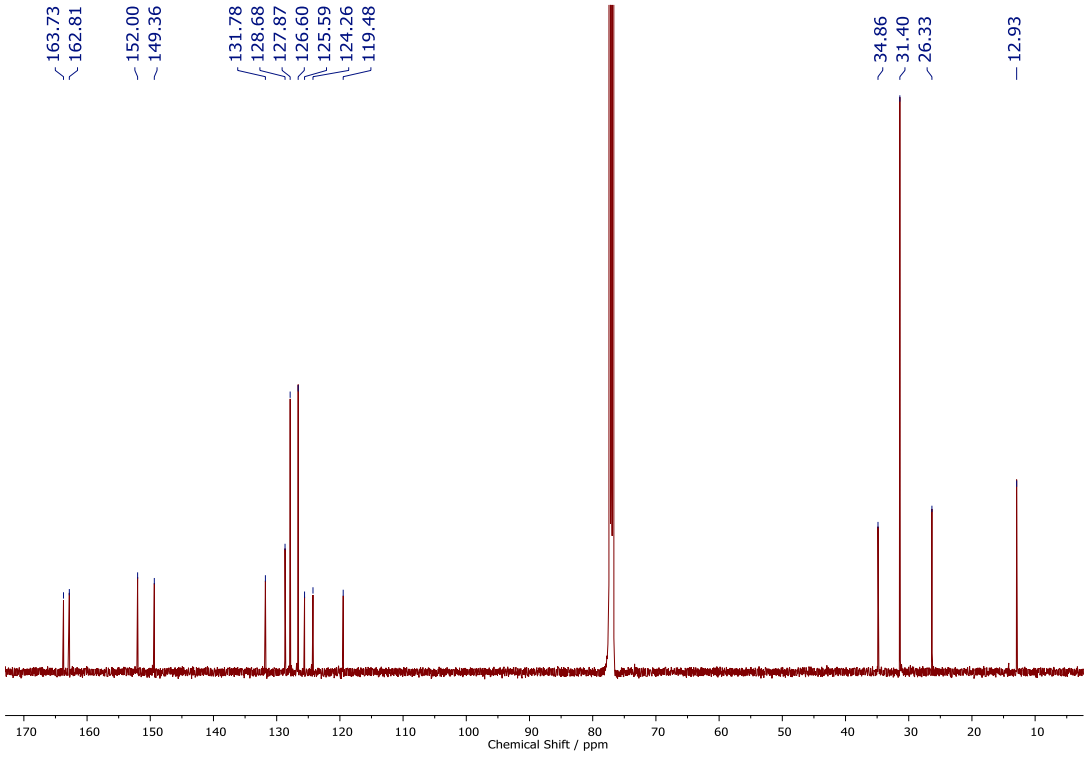


Figure S34. ^{13}C NMR spectrum of **7** in $CDCl_3$.