Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Surface functionalization of dinuclear clathrochelates via Pd catalyzed cross-coupling reactions: facile synthesis of polypyridyl metalloligands

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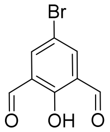
1 Synthetic Procedures

1.1 Materials and General Procedures

2,6-diformyl-4-*tert*-butylphenol dioxime ligand was synthesized according to literature.[1] ^{1}H and ^{13}C NMR spectra were obtained on a Bruker Avance III (^{1}H: 400 MHz, ^{13}C: 100 MHz). ^{1}H and ^{13}C chemical shifts are reported in parts per million δ (ppm) referenced to the internal solvent. All spectra were recorded at RT. Electrospray-ionisation MS data were acquired on a Q-Tof Ultima mass spectrometer (Waters) operated in the negative ionization mode and data were processed using the MassLynx 4.1 software. APPI-FT-ICR experiments were performed on a hybrid linear ion trap Fourier transform ion cyclotron resonance mass spectrometer (LTQ FT-ICR MS, Thermo Scientific, Bremen, Germany) equipped with a 10 T superconducting magnet (Oxford Instruments Nanoscience, Abingdon, UK). Data analysis was carried out using XCalibur software (Thermo Scientific, Bremen, Germany). IR spectra were recorded on a Perkin Elmer Spectrum One Golden Gate FTIR spectrometer. Emission spectra were recorded with a Varian Cary Eclipse spectrofluorimeter, using an excitation wavelength of λ_{ex} = 330 nm. Absorption spectra were recorded on a Cary 60 UV-Vis (Agilent Technologies).

1.2 Synthesis of 2,6-diformyl-4-bromophenol



The procedure described by Lindoy[2] was followed with the following modifications. Urotropine (9.75 g, 69.2 mmol, 4.0 equiv.) was dissolved in TFA (33 ml). 4-bromophenol (3.0 g, 17.3 mmol, 1.0 equiv.) was added in one portion, and the yellow solution was stirred at 120 °C under inert atmosphere for 48 h. The reaction mixture was then cooled down to RT, H_2O (21 ml) and H_2SO_4 50% (10.5 ml) were added and the reaction mixture was stirred 2 h at RT. The mixture was poured into H_2O (210 ml) and the precipitate was isolated by filtration and washed with H_2O (800 ml). The yellow precipitate was then dissolved in EtOAc (100 ml) and dried over $MgSO_4$. Purification by column chromatography (15 to 40% EtOAc in petroleum ether) afforded the dialdehyde in the form of yellow needles (2.11 g, 9.22 mmol, 54%).

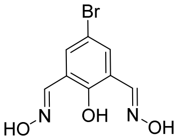
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 11.54 (s, 1H, Ar-O*H*), 10.19 (s, 2H, C*H*O), 8.05 (s, 2H, Ar-*H*).

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 191.03, 162.38, 139.88, 124.74, 112.29.

HRMS-APPI: calcd for $C_8H_5BrO_3$: 228.94948; found: 228.94892.

IR: 3300, 3060, 2875, 1675, 1660, 1600, 1575, 1435, 1400, 1375, 1325, 1280, 1260, 1200, 1120, 1095, 1005, 970, 900, 885, 745, 705, 605 cm^{-1}.

1.3 Synthesis of 2,6-diformyl-4-bromophenol dioxime



2,6-Diformyl-4-bromophenol (2.1 g, 9.2 mmol, 1.0 equiv.) was dissolved in a mixture of MeOH (15 ml) and H_2O (30 ml) and hydroxylamine hydrochloride (1.6 g, 23 mmol, 2.5 equiv.) was added. The solution was heated for 1 h at 85 °C, and H_2O was added until the solution became turbid. The mixture was cooled down to RT, and the product was allowed to crystallize overnight. The white precipitate was isolated by filtration, washed with H_2O (3 x 100 ml) and dried under vacuum to afford the dioxime as an off-white powder (2.0 g, 7.7 mmol, 84%).

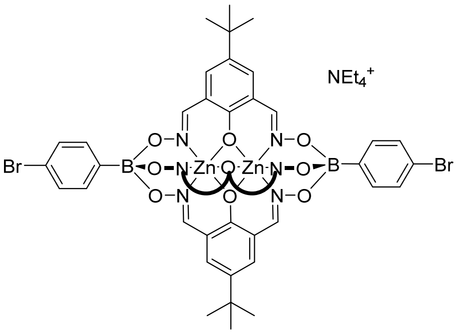
^{1}H-NMR (400 MHz, DMSO-d_6): δ = 11.70 (s, 2H), 10.89 (s, 1H), 8.34 (s, 2H), 7.68 (s, 2H).

^{13}C-NMR (101 MHz, DMSO-d_6): δ = 153.46, 145.78, 130.32, 121.36, 110.87.

HRMS-ESI: calcd. for $C_8H_7BrN_2O_3$: 256.9562; found: 256.9562.

IR: 3240, 3090, 2995, 1620, 1485, 1440, 1385, 1325, 1285, 1255, 1220, 1020, 1000, 930, 870, 690, 650, 585 cm^{-1}.

1.4 Synthesis of 1a



A mixture of 2,6-diformyl-4-*tert*-butylphenol dioxime (400 mg, 1.69 mmol, 3.0 equiv.), 4-bromophenylboronic acid (228 mg, 1.13 mmol, 2.0 equiv.) and $Zn(OTf)_2$ (412 mg, 1.13 mmol, 2.0 equiv.) in MeOH (30 ml) was heated to 70 °C until all solid dissolved. Tetraethylammonium hydroxide (565 µl, 0.84 mmol, 25% in MeOH) was added, and the solution was stirred at 70 °C for 10 min. After a second addition of tetraethylammonium hydroxide (565 µl, 0.84 mmol, 25% in MeOH), the solution was cooled down to RT, and the solvent was removed under reduced pressure. The yellow solid was suspended in EtOH (10 ml), isolated by filtration, washed with EtOH (3 x 10 ml) and Et_2O (2 x 50 ml) and dried under vacuum to afford **1a** as a yellow powder (469 mg, 0.36 mmol, 64%).

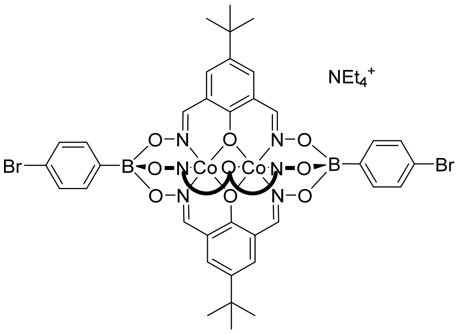
^{1}H-NMR (400 MHz, DMSO-d_6): δ = 8.35 (s, 6H), 7.59 (d, J = 8.0 Hz, 4H), 7.40 (d, J = 8.1 Hz, 4H), 7.31 (s, 6HH), 3.19 (q, J = 7.2 Hz, 8H), 1.21 (s, 27H), 1.15 (t, J = 7.2 Hz, 12H).

^{13}C-NMR (101 MHz, DMSO-d_6): δ = 162.38, 154.00, 136.98, 134.09, 132.21, 129.12, 119.56, 118.24, 51.32, 33.37, 31.13, 7.02 (C-B not detected).

HRMS-ESI: calcd. for $C_{48}H_{47}B_2Br_2N_6O_9Zn_2$: 1163.0518; found: 1163.0504.

IR: 2955, 2860, 1610, 1580, 1550, 1445, 1395, 1365, 1330, 1280, 1240, 1220, 1195, 1080, 1040, 980, 925, 840, 815, 780, 730, 705, 675, 635, 560, 520 cm^{-1}.

1.5 Synthesis of 1b

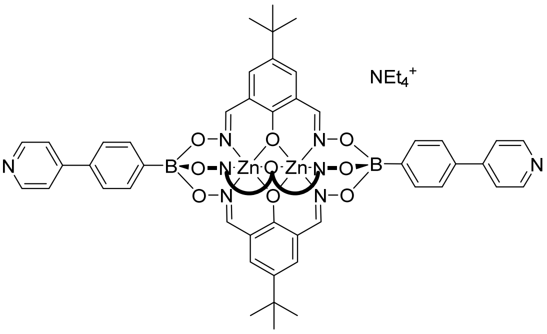


A mixture of 2,6-diformyl-4-*tert*-butylphenol dioxime (300 mg, 1.27 mmol, 3.0 equiv.), 4-bromophenylboronic acid (170 mg, 0.85 mmol, 2.0 equiv.) and $[Co(H_2O)_6](NO_3)_2$ (246 mg, 0.85 mmol, 2.0 equiv.) in MeOH (30 ml) was heated to 70 °C until all solid dissolved. Tetraethylammonium hydroxide (423 µl, 0.64 mmol, 25% in MeOH) was added, and the solution was stirred at 70 °C for 10 min. After a second addition of tetraethylammonium hydroxide (423 µl, 0.64 mmol, 25% in MeOH), the solution was cooled down to RT, and the solvent was removed under reduced pressure. The orange solid was suspended in EtOH (10 ml), isolated by filtration, washed with EtOH (3 x 10 ml) and Et_2O (2 x 50 ml) and dried under vacuum to afford **1b** as a bright orange powder (390 mg, 0.31 mmol, 73%).

HRMS-ESI: calcd. for $C_{48}H_{47}B_2Br_2Co_2N_6O_9$: 1151.0621; found: 1151.0637.

IR: 2960, 2860, 1610, 1580, 1550, 1445, 1390, 1360, 1330, 1285, 1240, 1225, 1195, 1170, 1080, 1040, 1010, 995, 930, 840, 820, 785, 770, 705, 680, 635, 570 cm^{-1}.

1.6 Synthesis of 2a



To a 25 ml pyrex vial containing **1a** (90 mg, 69 µmol, 1.0 equiv.), 4-pyridylboronic acid hydrate (58 mg, 0.41 mmol, 6 equiv.) and K_3PO_4 (44 mg, 0.21 mmol, 3.0 equiv.) under inert atmosphere were added degassed *n*-BuOH (10 ml) and degassed toluene (10 ml). $Pd_2(dba)_3$ (3.21 mg, 3.5 µmol, 0.05 equiv.) and SPhos (2.85 mg, 7 µmol, 0.1 equiv.) were then added and the system was cycled two times with nitrogen, and the sealed vial was heated for 12 h at 120 °C. After cooling to RT, the reaction mixture was filtered through Celite, and washed with *n*-BuOH (5 ml), MeOH (20 ml) and H_2O (200 ml). The filtrate was then concentrated to half its volume and the resulting precipitate was isolated by filtration, washed with H_2O (2 x 50 ml) and Et_2O (100 ml). The crude product was suspended in a mixture of MeOH (10 ml) and acetonitrile (10 ml) and tetraethylammonium hydroxide (46 µl, 69 µmol, 25% in MeOH) was added, leading to a complete dissolution of all material. The solvents were removed under reduced pressure and the solid was suspended in EtOH (8 ml), isolated by filtration, washed with EtOH (2 x 5 ml) and Et_2O (2 x 30 ml) and dried under vacuum to afford **2a** as a pale-yellow powder (60 mg, 47 µmol, 68%). X-ray quality, light yellow crystals were obtained by slow diffusion of Et_2O into a solution of the complex in DCM.

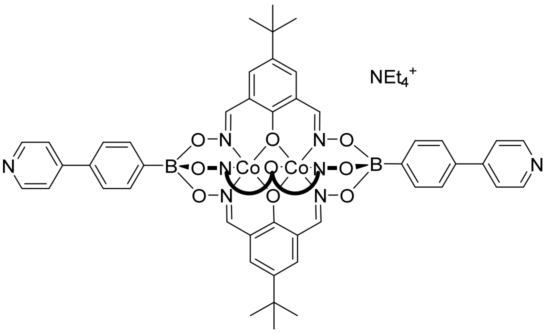
^{1}H-NMR (400 MHz, DMSO-*d*$_6$): *δ* = 8.62 (d, *J* = 5.1 Hz, 4H), 8.39 (s, 6H), 7.81 (d, *J* = 7.7 Hz, 4H), 7.74 (d, *J* = 5.2 Hz, 4H), 7.68 (d, *J* = 7.9 Hz, 4H), 7.33 (s, 6H), 3.18 (q, *J* = 7.2 Hz, 8H), 1.23 (s, 27H), 1.14 (t, *J* = 7.2 Hz, 12H).

^{13}C-NMR (101 MHz, DMSO-*d*$_6$): *δ* = 162.43, 153.98, 150.08, 147.91, 136.97, 134.57, 132.70, 132.18, 124.71, 120.96, 118.30, 51.36, 33.40, 31.16, 7.04 (C-B not detected).

HRMS-ESI: calcd. for $C_{58}H_{55}B_2N_8O_9Zn_2$: 1161.2845; found: 1161.2885.

IR: 2955, 2865, 1610, 1595, 1550, 1445, 1410, 1390, 1365, 1330, 1285, 1225, 1200, 1140, 1075, 1040, 995, 930, 840, 810, 780, 775, 755, 690, 635, 565, 555, 525, 505 cm^{-1}.

1.7 Synthesis of 2b

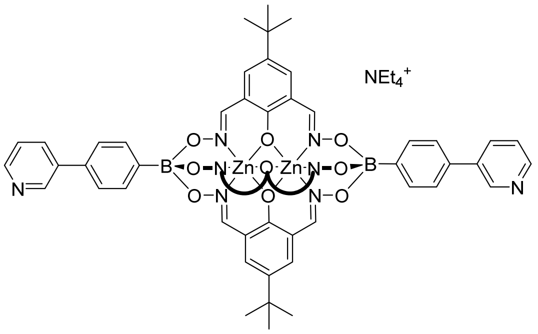


To a 25 ml pyrex vial containing **1b** (100 mg, 78 µmol, 1.0 equiv.), 4-pyridylboronic acid hydrate (65 mg, 0.47 mmol, 6 equiv.) and K_3PO_4 (50 mg, 0.23 mmol, 3.0 equiv.) under inert atmosphere were added degassed *n*-BuOH (10 ml) and degassed toluene (10 ml). $Pd_2(dba)_3$ (3.57 mg, 3.9 µmol, 0.05 equiv.) and SPhos (3.2 mg, 7.8 µmol, 0.1 equiv.) were then added and the system was cycled two times with nitrogen, and the sealed vial was heated for 12 h at 120 °C. After cooling to RT, the reaction mixture was filtered through Celite, and washed with *n*-BuOH (5 ml), MeOH (20 ml) and H_2O (200 ml). The filtrate was then concentrated to half its volume and the resulting precipitate was isolated by filtration, washed with H_2O (2 x 50 ml) and Et_2O (100 ml). The crude product was suspended in a mixture of MeOH (10 ml) and acetonitrile (10 ml) and tetraethylammonium hydroxide (52 µl, 78 µmol, 25% in MeOH) was added, leading to a complete dissolution of all material. The solvents were removed under reduced pressure and the solid was suspended in EtOH (10 ml), isolated by filtration, washed with EtOH (2 x 7 ml) and Et_2O (2 x 30 ml) and dried under vacuum to afford **2b** as an orange powder (77 mg, 60 µmol, 77%).

HRMS-ESI: calcd. for $C_{58}H_{55}B_2Co_2N_8O_9$: 1147.2942 ; found: 1147.2981.

IR: 2965, 2860, 1605, 1595, 1550, 1530, 1450, 1410, 1365, 1330, 1285, 1225, 1200, 1080, 1040, 1025, 995, 935, 880, 840, 810, 785, 770, 755, 695, 635, 570, 535 cm^{-1}.

1.8 Synthesis of 3



To a 25 ml pyrex vial containing **1a** (90 mg, 69 µmol, 1.0 equiv.), 3-pyridylboronic acid hydrate (58 mg, 0.41 mmol, 6 equiv.) and K_3PO_4 (44 mg, 0.21 mmol, 3.0 equiv.) under inert atmosphere were added degassed *n*-BuOH (10 ml) and degassed toluene (10 ml). $Pd_2(dba)_3$ (3.21 mg, 3.5 µmol, 0.05 equiv.) and SPhos (2.85 mg, 7 µmol, 0.1 equiv.) were then added and the system was cycled two times with nitrogen, and the sealed vial was heated for 12 h at 120 °C. After cooling to RT, the reaction mixture was filtered through Celite, and was washed with *n*-BuOH (5 ml), MeOH (20 ml) and H_2O (200 ml). The filtrate was then concentrated to half its volume and the resulting precipitate was isolated by filtration, washed with H_2O (2 x 50 ml) and Et_2O (100 ml). The crude product was suspended in a mixture of MeOH (10 ml) and acetonitrile (10 ml) and tetraethylammonium hydroxide (46 µl, 69 µmol, 25% in MeOH) was added, leading to a complete dissolution of all material. The solvents were removed under reduced pressure and the solid was suspended in EtOH (8 ml), isolated by filtration, washed with EtOH (2 x 5 ml) and Et_2O (2 x 30 ml) and dried under vacuum to afford **3** as a pale-yellow powder (87 mg, 67 µmol, 98%).

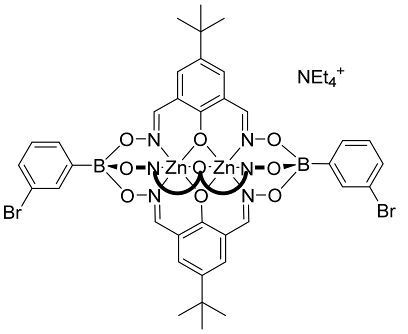
^{1}H-NMR (400 MHz, DMSO-*d*$_6$): δ = 8.93 (s, 2H), 8.56 (d, *J* = 4.0 Hz, 2H), 8.40 (s, 6H), 8.10 (d, *J* = 7.9 Hz, 2H), 7.80 (d, *J* = 7.6 Hz, 4H), 7.60 (d, *J* = 7.7 Hz, 4H), 7.50 (dd, *J* = 7.2, 5.1 Hz, 2H), 7.34 (s, 6H), 3.18 (q, *J* = 7.2 Hz, 8H), 1.24 (s, 27H), 1.14 (t, *J* = 6.4 Hz, 12H).

^{13}C-NMR (101 MHz, DMSO-*d*$_6$): δ = 162.43, 153.95, 147.85, 147.51, 136.98, 136.50, 134.55, 133.78, 132.68, 132.16, 124.85, 123.81, 118.32, 51.35, 33.41, 31.17, 7.03 (C-B not detected).

HRMS-ESI: calcd. for $C_{58}H_{55}B_2N_8O_9Zn_2$: 1161.2845; found: 1161.2844.

IR: 2960, 2870, 1610, 1590, 1550, 1445, 1390, 1365, 1330, 1285, 1225, 1200, 1080, 1040, 1020, 995, 930, 840, 810, 780, 775, 705, 695, 635, 620, 656, 525 cm^{-1}.

1.9 Synthesis of 4



A mixture of 2,6-diformyl-4-*tert*-butylphenol dioxime (400 mg, 1.69 mmol, 3.0 equiv.), 3-bromophenylboronic acid (228 mg, 1.13 mmol, 2.0 equiv.) and $Zn(OTf)_2$ (412 mg, 1.13 mmol, 2.0 equiv.) in MeOH (30 ml) was heated to 70 °C until all solid dissolved. Tetraethylammonium hydroxide (565 µl, 0.84 mmol, 25% in MeOH) was added, and the solution was stirred at 70 °C for 10 min. After a second addition of tetraethylammonium hydroxide (565 µl, 0.84 mmol, 25% in MeOH), the solution was cooled down to RT, and the solvent was removed under reduced pressure. The yellow solid was suspended in EtOH (10 ml), isolated by filtration, washed with EtOH (3 x 10 ml) and Et_2O (2 x 50 ml) and dried under vacuum to afford **4** as a yellow powder (486 mg, 0.38 mmol, 67%).

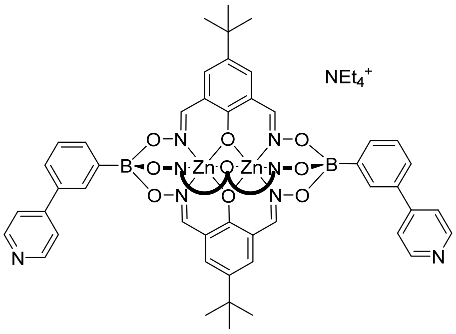
^{1}H-NMR (400 MHz, DMSO-*d*$_6$): δ = 8.39 (s, 6H), 7.78 – 7.75 (m, 2H), 7.62 (d, *J* = 7.2 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.34 (s, 6H), 7.20 (t, *J* = 7.6 Hz, 2H), 3.17 (q, *J* = 7.2 Hz, 8H), 1.22 (s, 27H), 1.14 (t, *J* = 7.2 Hz, 12H).

^{13}C-NMR (101 MHz, DMSO-*d*$_6$): δ = 162.41, 154.15, 137.03, 134.38, 132.31, 130.58, 128.85, 128.64, 120.96, 118.24, 51.35, 33.40, 31.15, 7.02 (C-B not detected).

HRMS-ESI: calcd. for $C_{48}H_{47}B_2Br_2N_6O_9Zn_2$: 1163.0518; found: 1163.0525.

IR: 2955, 2860, 1610, 1550, 1445, 1395, 1365, 1330, 1285, 1240, 1190, 1080, 1035, 990, 960, 930, 890, 835, 775, 715, 640, 560, 520, 510 cm^{-1}.

1.10 Synthesis of 5



To a 25 ml pyrex vial containing **4** (90 mg, 69 µmol, 1.0 equiv.), 4-pyridylboronic acid hydrate (58 mg, 0.41 mmol, 6 equiv.) and K_3PO_4 (44 mg, 0.21 mmol, 3.0 equiv.) under inert atmosphere were added degassed *n*-BuOH (10 ml) and degassed toluene (10 ml). $Pd_2(dba)_3$ (3.21 mg, 3.5 µmol, 0.05 equiv.) and SPhos (2.85 mg, 7 µmol, 0.1 equiv.) were then added and the system was cycled two times with nitrogen, and the sealed vial was heated for 12 h at 120 °C. After cooling to RT, the reaction mixture was filtered through Celite, and was washed with *n*-BuOH (5 ml), MeOH (20 ml) and H_2O (200 ml). The filtrate was then concentrated to half its volume and the resulting precipitate was isolated by filtration, washed with H_2O (2 x 50 ml) and Et_2O (100 ml). The crude product was suspended in a mixture of MeOH (10 ml) and acetonitrile (10 ml) and tetraethylammonium hydroxide (46 µl, 69 µmol, 25% in MeOH) was added, leading to a complete dissolution of all material. The solvents were removed under reduced pressure and the solid was suspended in EtOH (8 ml), isolated by filtration, washed with EtOH (2 x 5 ml) and Et_2O (2 x 30 ml) and dried under vacuum to afford **5** as a pale-yellow powder (81 mg, 62 µmol, 91%).

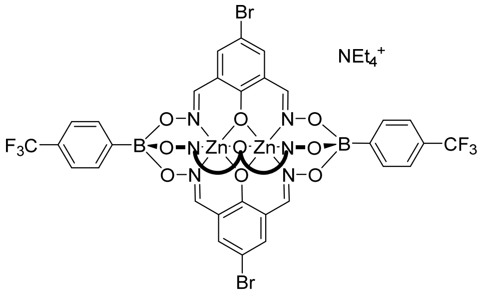
^{1}H-NMR (400 MHz, DMSO-*d*$_6$): δ = 8.64 (d, *J* = 3.6 Hz, 4H), 8.41 (s, 6H), 8.05 (s, 2H), 7.77 (d, *J* = 7.1 Hz, 2H), 7.72 (d, *J* = 4.1 Hz, 4H), 7.61 (d, *J* = 7.1 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.33 (s, 6H), 3.17 (q, *J* = 6.8 Hz, 8H), 1.22 (s, 27H), 1.13 (m, 12H).

^{13}C-NMR (101 MHz, DMSO-*d*$_6$): δ = 162.44, 154.06, 150.09, 148.59, 136.99, 135.12, 133.08, 132.19, 130.13, 127.26, 124.54, 121.21, 118.32, 51.38, 33.41, 31.16, 7.04 (C-B not detected).

HRMS-ESI: calcd. for $C_{58}H_{55}B_2N_8O_9Zn_2$: 1161.2845; found: 1161.2878.

IR: 2955, 2870, 1610, 1605, 1550, 1445, 1395, 1365, 1330, 1285, 1240, 1195, 1080, 1035, 995, 980, 930, 900, 835, 775, 725, 695, 650, 615, 555, 525 cm^{-1}.

1.11 Synthesis of 6



A mixture of 2,6-diformyl-4-bromophenol dioxime (400 mg, 1.54 mmol, 3.0 equiv.), 4-(trifluoromethyl)phenylboronic acid (200 mg, 1.03 mmol, 2.0 equiv.) and $Zn(OTf)_2$ (376 mg, 1.03 mmol, 2.0 equiv.) in MeOH (30 ml) was heated to 70 °C until all solid dissolved. Tetraethylammonium hydroxide (515 µl, 0.77 mmol, 25% in MeOH) was added, and the solution was stirred at 70 °C for 10 min. After a second addition of tetraethylammonium hydroxide (515 µl, 0.77 mmol, 25% in MeOH), the solution was cooled down to RT, and the solvent was removed under reduced pressure. The yellow solid was suspended in EtOH (10 ml), isolated by filtration, washed with EtOH (3 x 10 ml) and Et_2O (2 x 50 ml) and dried under vacuum to afford **6** as a yellow powder (540 mg, 0.40 mmol, 78%).

^{1}H-NMR (400 MHz, DMSO-*d*$_6$): δ = 8.39 (s, 6H), 7.83 (d, *J* = 7.7 Hz, 4H), 7.57 (d, *J* = 7.8 Hz, 4H), 7.53 (s, 6H), 3.19 (q, *J* = 7.2 Hz, 8H), 1.15 (ddt, *J* = 7.3, 5.4, 2.1 Hz, 12H).

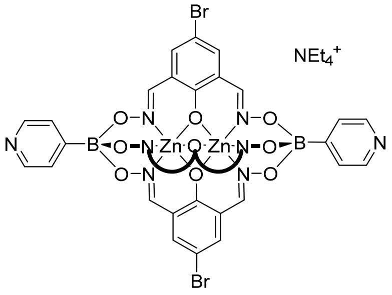
^{13}C-NMR (101 MHz, DMSO-*d*$_6$): δ = 163.32, 153.41, 136.95, 132.27, 127.00, 124.94, 122.99, 120.83, 105.08, 51.36, 7.05 (C-B not detected).

^{19}F-NMR (376 MHz, DMSO-*d*$_6$): δ = -60.51.

HRMS-ESI: calcd. for $C_{38}H_{20}B_2Br_3F_6N_6O_9Zn_2$: 1210.7468; found: 1210.7467.

IR: 1605, 1550, 1515, 1435, 1395, 1320, 1220, 1205, 1155, 1090, 1075, 1060, 1040, 1020, 980, 965, 950, 935, 890, 870, 845, 830, 780, 745, 700, 665, 640, 630, 600, 545, 530, 510 cm^{-1}.

1.12 Synthesis of 7a



A mixture of 2,6-diformyl-4-bromophenol dioxime (200 mg, 0.77 mmol, 3.0 equiv.) and 4-pyridylboronic acid hydrate (72 mg, 0.51 mmol, 2.0 equiv.) were dissolved in MeOH (30 ml). $Zn(OTf)_2$ (187 mg, 0.51 mmol, 2.0 equiv.) was added and the yellow solution was heated at 50 °C for 15 min. The solvent was removed under reduced pressure and the yellow solid was suspended in

EtOH (10 ml), isolated by filtration and washed with EtOH (10 ml) and Et_2O (20 ml). The yellow solid was then suspended in a mixture of MeOH (10 ml) and acetonitrile (10 ml) and tetraethylammonium hydroxide (345 µl, 0.51 mmol, 25% in MeOH) was added, and the solution was stirred at RT for 10 min. After removal of the solvents under reduced pressure the solid was suspended in EtOH (8 ml), isolated by filtration, washed with cold EtOH (3 x 5 ml) and Et_2O (2 x 50 ml) and dried under vacuum to afford **7a** as a yellow powder (270 mg, 0.22 mmol, 87%).

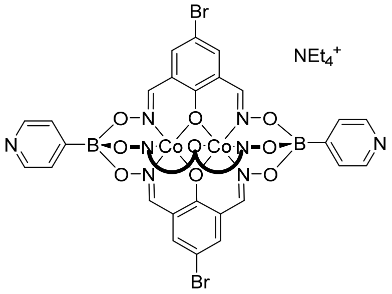
^{1}H-NMR (400 MHz, DMSO-*d*$_6$): δ = 8.41 (d, *J* = 5.7 Hz, 4H), 8.39 (s, 6H), 7.54 (d, *J* = 5.7 Hz, 4H), 7.52 (s, 6H), 3.20 (q, *J* = 7.2 Hz, 8H), 1.20 – 1.10 (m, 12H).

^{13}C-NMR (101 MHz, DMSO-*d*$_6$): δ = 163.32, 153.52, 147.73, 137.00, 127.09, 120.80, 105.09, 51.37, 7.05 (C-B not detected).

HRMS-ESI: calcd. for $C_{34}H_{20}B_2Br_3N_8O_9Zn_2$: 1076.7623; found: 1076.7626.

IR: 1605, 1550, 1485, 1435, 1325, 1205, 1075, 1035, 970, 945, 890, 875, 810, 780, 745, 700, 685, 650, 540, 520, 515 cm^{-1}

1.13 Synthesis of 7b

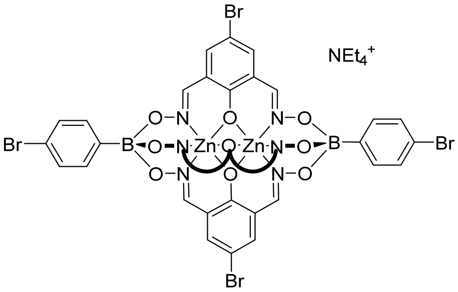


A mixture of 2,6-diformyl-4-bromophenol dioxime (200 mg, 0.77 mmol, 3.0 equiv.) and 4-pyridylboronic acid hydrate (72 mg, 0.51 mmol, 2.0 equiv.) were dissolved in MeOH (30 ml). $[Co(H_2O)_6](NO_3)_2$ (150 mg, 0.51 mmol, 2.0 equiv.) was added and the orange solution was heated at 50 °C for 15 min. The solvent was removed under reduced pressure and the orange solid was suspended in EtOH (10 ml), isolated by filtration and washed with EtOH (10 ml) and Et_2O (20 ml). The orange solid was then suspended in a mixture of MeOH (10 ml) and acetonitrile (10 ml) and tetraethylammonium hydroxide (345 µl, 0.51 mmol, 25% in MeOH) was added, and the solution was stirred at RT for 10 min. After removal of the solvents under reduced pressure the solid was suspended in EtOH (8 ml), isolated by filtration, washed with cold EtOH (3 x 5 ml) and Et_2O (2 x 50 ml) and dried under vacuum to afford **7b** as an orange powder (250 mg, 0.21 mmol, 82%).

HRMS-ESI: calcd. for $C_{34}H_{20}B_2Br_3Co_2N_8O_9$: 1164.7731; found: 1164.7717.

IR: 1600, 1550, 1485, 1435, 1330, 1245, 1210, 1175, 1080, 1035, 970, 945, 895, 870, 810, 780, 770, 750, 700, 690, 650, 540, 520, 510 cm^{-1}.

1.14 Synthesis of 8



A mixture of 2,6-diformyl-4-bromophenol dioxime (400 mg, 1.54 mmol, 3.0 equiv.), 4-bromophenylboronic acid (206 mg, 1.03 mmol, 2.0 equiv.) and $Zn(OTf)_2$ (380 mg, 1.03 mmol, 2.0 equiv.) in MeOH (30 ml) was heated to 70 °C until all solid dissolved. Tetraethylammonium hydroxide (515 µl, 0.77 mmol, 25% in MeOH) was added, and the solution was stirred at 70 °C for 10 min. After a second addition of tetraethylammonium hydroxide (515 µl, 0.77 mmol, 25% in MeOH), the solution was cooled down to RT, and the solvent was removed under reduced pressure. The yellow solid was suspended in EtOH (10 ml), isolated by filtration, washed with EtOH (3 x 10 ml) and Et_2O (2 x 50 ml) and dried under vacuum to afford **8** as a yellow powder (551 mg, 0.40 mmol, 79%).

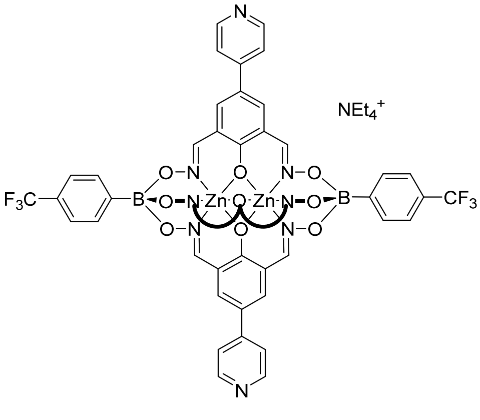
^{1}H-NMR (400 MHz, DMSO-*d*$_6$): δ = 8.37 (s, 6H), 7.56 (d, *J* = 8.0 Hz, 4H), 7.51 (s, 6H), 7.40 (d, *J* = 8.0 Hz, 4H), 3.18 (q, *J* = 7.2 Hz, 8H), 1.15 (t, *J* = 6.2 Hz, 12H).

^{13}C-NMR (101 MHz, DMSO-*d*$_6$): δ = 163.27, 153.23, 136.83, 134.02, 129.25, 120.84, 119.81, 105.02, 51.36, 7.04 (C-B not detected).

HRMS-ESI: calcd. for $C_{36}H_{20}B_2Br_5N_6O_9Zn_2$: 1232.5909; found: 1232.5892.

IR: 1605, 1550, 1480, 1430, 1390, 1325, 1240, 1220, 1200, 1065, 1040, 1010, 975, 950, 930, 890, 855, 820, 780, 700, 670, 560, 535, 510 cm^{-1}.

1.15 Synthesis of 9



To a 25 ml pyrex vial containing **6** (100 mg, 74 µmol, 1.0 equiv.), 4-pyridylboronic acid hydrate (156 mg, 1.12 mmol, 15 equiv.) and K_3PO_4 (118 mg, 0.56 mmol, 7.5 equiv.) under inert atmosphere were added degassed *n*-BuOH (10 ml) and degassed toluene (10 ml). $Pd_2(dba)_3$ (3.41 mg, 3.7 µmol, 0.05 equiv.) and SPhos (3.06 mg, 7.4 µmol, 0.1 equiv.) were then added and the system was cycled two times with nitrogen, and the sealed vial was heated for 12 h at 120 °C. After cooling to RT, the reaction mixture was filtered through Celite, and was washed with *n*-BuOH (5 ml), MeOH (20 ml) and H_2O (200 ml). The filtrate was then concentrated to half its volume and the resulting precipitate was isolated by filtration, washed with H_2O (2 x 50 ml) and Et_2O (100 ml). The crude product was suspended in a mixture of MeOH (10 ml) and acetonitrile (10 ml) and tetraethylammonium hydroxide (50 µl, 74 µmol, 25% in MeOH) was added, leading to a complete dissolution of all material. The solvents were removed under reduced pressure and the solid was suspended in EtOH (8 ml), isolated by filtration, washed with EtOH (2 x 5 ml) and Et_2O (2 x 30 ml) and dried under vacuum to afford **9** as a pale-yellow powder (81 mg, 61 µmol, 82%).

^{1}H-NMR (400 MHz, DMSO-d_6): δ = 8.56 (d, J = 5.9 Hz, 6H), 8.56 (s, 6H), 7.95 (s, 6H), 7.90 (d, J = 7.6 Hz, 4H), 7.65 (d, J = 5.5 Hz, 6H), 7.61 (d, J = 7.8 Hz, 4H), 3.18 (q, J = 7.2 Hz, 8H), 1.14 (t, J = 6.4 Hz, 12H).

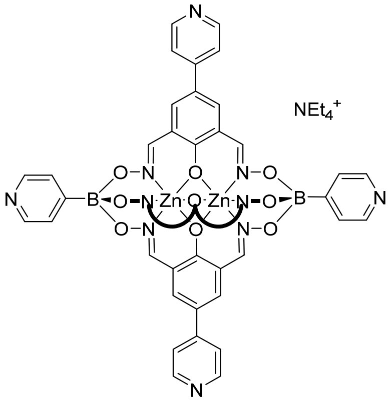
^{13}C-NMR (101 MHz, DMSO-d_6): δ = 165.19, 154.20, 150.10, 145.53, 133.79, 132.28, 123.59, 123.04, 119.73, 119.50, 51.39, 7.06 (C-B, CF_3 and C-CF_3 not detected).

^{19}F-NMR (376 MHz, DMSO-d_6): δ = -60.47.

HRMS-ESI: calcd. for $C_{53}H_{32}B_2F_6N_9O_9Zn_2$: 1206.0978; found: 1206.1001.

IR: 1705, 1595, 1560, 1445, 1395, 1335, 1320, 1305, 1240, 1220, 1205, 1150, 1120, 1080, 1065, 1040, 995, 980, 955, 915, 830, 820, 795, 775, 760, 730, 695, 670, 610, 600, 565, 520 cm^{-1}.

1.16 Synthesis of 10a



To a 25 ml pyrex vial containing **7a** (100 mg, 83 µmol, 1.0 equiv.), 4-pyridylboronic acid hydrate (174 mg, 1.24 mmol, 15 equiv.) and K_3PO_4 (132 mg, 0.62 mmol, 7.5 equiv.) under inert atmosphere were added degassed *n*-BuOH (10 ml) and degassed toluene (10 ml). $Pd_2(dba)_3$ (3.79 mg, 4.1 µmol, 0.05 equiv.) and SPhos (3.40 mg, 8.3 µmol, 0.1 equiv.) were then added and the system was cycled two times with nitrogen, and the sealed vial was heated for 12 h at 120 °C. After cooling to RT, the reaction mixture was filtered through Celite, and was washed with *n*-BuOH (5 ml), MeOH (20 ml) and H_2O (200 ml). The filtrate was then concentrated to half its volume and the resulting precipitate was isolated by filtration, washed with H_2O (2 x 50 ml) and Et_2O (100 ml). The crude product was suspended in a mixture of MeOH (10 ml) and acetonitrile (10 ml) and tetraethylammonium hydroxide (55 µl, 83 µmol, 25% in MeOH) was added, leading to a complete dissolution of all material. The solvents were removed under reduced pressure and the solid was suspended in EtOH (8 ml), isolated by filtration, washed with EtOH (2 x 5 ml) and Et_2O (2 x 30 ml) and dried under vacuum to afford **10a** as a pale-yellow powder (85 mg, 71 µmol, 85%). X-ray quality, light yellow crystals were obtained by slow diffusion of ^{i}Pr$_2$O into a solution of the complex in DCM.

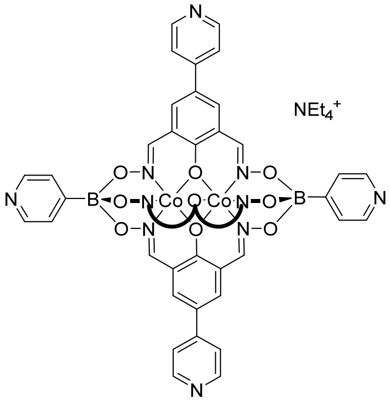
^{1}H-NMR (400 MHz, DMSO-d_6): δ = 8.57 (d, J = 6.0 Hz, 6H), 8.56 (s, 6H), 8.45 (d, J = 5.5 Hz, 4H), 7.94 (s, 6H), 7.65 (d, J = 6.2 Hz, 6H), 7.61 (d, J = 5.5 Hz, 4H), 3.18 (q, J = 7.2 Hz, 8H), 1.19 – 1.10 (m, 12H).

^{13}C-NMR (101 MHz, DMSO-d_6): δ = 165.20, 154.33, 150.12, 147.78, 145.53, 133.85, 127.15, 123.64, 119.74, 119.49, 51.38, 7.06 (C-B not detected).

HRMS-ESI: calcd. for $C_{49}H_{32}B_2N_{11}O_9Zn_2$: 1072.1133; found: 1072.1174.

IR: 1605, 1590, 1560, 1445, 1400, 1340, 1310, 1220, 1205, 1080, 1035, 995, 975, 945, 915, 825, 795, 775, 765, 735, 695, 655, 610, 656, 545, 520, 510 cm^{-1}.

1.17 Synthesis of 10b

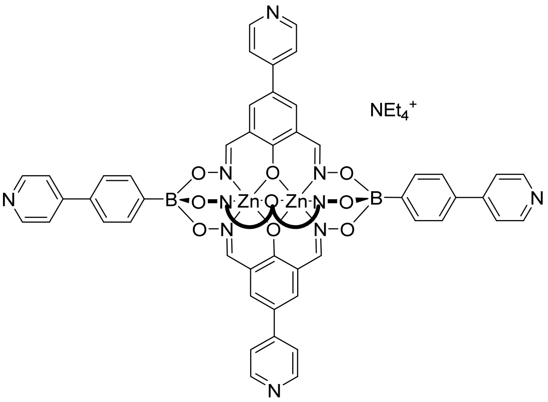


To a 25 ml pyrex vial containing **7b** (100 mg, 84 µmol, 1.0 equiv.), 4-pyridylboronic acid hydrate (175 mg, 1.25 mmol, 15 equiv.) and K_3PO_4 (134 mg, 0.63 mmol, 7.5 equiv.) under inert atmosphere were added degassed *n*-BuOH (10 ml) and degassed toluene (10 ml). $Pd_2(dba)_3$ (3.83 mg, 4.2 µmol, 0.05 equiv.) and SPhos (3.44 mg, 8.4 µmol, 0.1 equiv.) were then added and the system was cycled two times with nitrogen, and the sealed vial was heated for 12 h at 120 °C. After cooling to RT, the reaction mixture was filtered through Celite, and was washed with *n*-BuOH (5 ml), MeOH (20 ml) and H_2O (200 ml). The filtrate was then concentrated to half its volume and the resulting precipitate was isolated by filtration, washed with H_2O (2 x 50 ml) and Et_2O (100 ml). The crude product was suspended in a mixture of MeOH (10 ml) and acetonitrile (10 ml) and tetraethylammonium hydroxide (55 µl, 84 µmol, 25% in MeOH) was added, leading to a complete dissolution of all material. The solvents were removed under reduced pressure and the solid was suspended in EtOH (8 ml), isolated by filtration, washed with EtOH (2 x 5 ml) and Et_2O (2 x 30 ml) and dried under vacuum to afford **10b** as an orange powder (82 mg, 69 µmol, 82%).

HRMS-ESI: calcd. for $C_{49}H_{32}B_2Co_2N_{11}O_9Zn_2$: 1058.1250; found: 1058.1267.

IR: 1600, 1560, 1450, 1405, 1335, 1310, 1220, 1205, 1085, 1035, 995, 975, 915, 825, 800, 775, 740, 700, 670, 655, 615, 570, 550, 530, 510 cm^{-1}.

1.18 Synthesis of 11



To a 25 ml pyrex vial containing **8** (100 mg, 73 µmol, 1.0 equiv.), 4-pyridylboronic acid hydrate (205 mg, 1.47 mmol, 20 equiv.) and K_3PO_4 (156 mg, 0.73 mmol, 10 equiv.) under inert atmosphere were added degassed *n*-BuOH (10 ml) and degassed toluene (10 ml). $Pd_2(dba)_3$ (5.04 mg, 5.5 µmol, 0.075 equiv.) and SPhos (4.52 mg, 11 µmol, 0.15 equiv.) were then added and the system was cycled two times with nitrogen, and the sealed vial was heated for 12 h at 120 °C. After cooling to RT, the reaction mixture was filtered through Celite, and was washed with *n*-BuOH (5 ml), MeOH (20 ml) and H_2O (200 ml). The filtrate was then concentrated to half its volume and the resulting precipitate was isolated by filtration, washed with H_2O (2 x 50 ml) and Et_2O (100 ml). The crude product was suspended in a mixture of MeOH (10 ml) and acetonitrile (10 ml) and tetraethylammonium hydroxide (49 µl, 73 µmol, 25% in MeOH) was added, leading to a complete dissolution of all material. The solvents were removed and the solid was suspended in EtOH (8 ml), isolated by filtration, washed with EtOH (2 x 5 ml) and Et_2O (2 x 30 ml) and dried under vacuum to afford **11** as a pale-yellow powder (81 mg, 60 µmol, 82%). X-ray quality, light yellow crystals were obtained by slow diffusion of Et_2O into a solution of the complex in DCM.

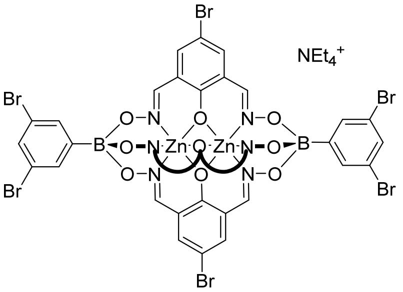
^{1}H-NMR (400 MHz, DMSO-*d*$_6$): δ = 8.63 (d, *J* = 5.4 Hz, 4H), 8.57 (d, *J* = 4.8 Hz, 6H), 8.56 (s, 6H), 7.94 (s, 6H), 7.84 (d, *J* = 8.0 Hz, 4H), 7.75 (d, *J* = 5.9 Hz, 4H), 7.71 (d, *J* = 8.1 Hz, 4H), 7.66 (d, *J* = 6.0 Hz, 6H), 3.19 (q, *J* = 7.2 Hz, 8H), 1.19 – 1.10 (m, 12H).

^{13}C-NMR (101 MHz, DMSO-*d*$_6$): δ = 165.21, 154.02, 150.12, 147.86, 145.58, 134.81, 133.65, 132.68, 124.89, 124.85, 123.55, 121.00, 119.74, 119.59, 51.37, 7.06 (C-B not detected).

HRMS-ESI: calcd. for $C_{61}H_{40}B_2N_{11}O_9Zn_2$: 1224.1765; found: 1224.1733.

IR: 1595, 1560, 1445, 1335, 1305, 1205, 1075, 1040, 995, 970, 935, 910, 815, 795, 775, 755, 690, 610, 565, 530, 520 cm^{-1}.

1.19 Synthesis of 12



A mixture of 2,6-diformyl-4-bromophenol dioxime (438 mg, 1.69 mmol, 3.0 equiv.), 3,5-dibromophenylboronic acid (315 mg, 1.13 mmol, 2.0 equiv.) and $Zn(OTf)_2$ (410 mg, 1.13 mmol, 2.0 equiv.) in MeOH (30 ml) was heated to 70 °C until all solid dissolved. Tetraethylammonium hydroxide (565 µl, 0.84 mmol, 25% in MeOH) was added, and the solution was stirred at 70 °C for 10 min. After a second addition of tetraethylammonium hydroxide (565 µl, 0.84 mmol, 25% in MeOH), the solution was cooled down to RT, and the solvent was removed under reduced pressure. The yellow solid was suspended in EtOH (10 ml), isolated by filtration, washed with EtOH (3 x 10 ml) and Et_2O (2 x 50 ml) and dried under vacuum to afford **12** as a yellow powder (590 mg, 0.39 mmol, 69%).

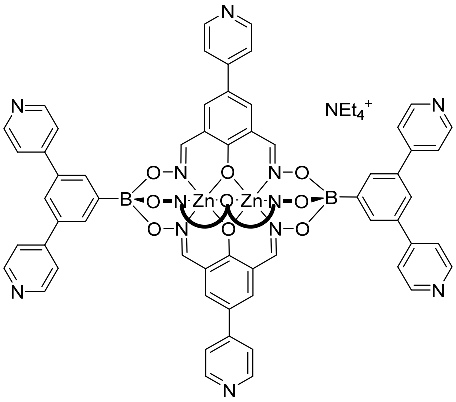
^{1}H-NMR (400 MHz, DMSO-*d*$_6$): δ = 8.43 (s, 6H), 7.70 (d, *J* = 1.6 Hz, 4H), 7.63 (s, 2H), 7.53 (s, 6H), 3.19 (q, *J* = 7.2 Hz, 8H), 1.15 (t, *J* = 7.1 Hz, 12H).

^{13}C-NMR (101 MHz, DMSO-*d*$_6$): δ = 163.27, 153.23, 136.83, 134.02, 129.25, 120.84, 119.81, 105.02, 51.36, 7.04 (C-B not detected).

HRMS-ESI: calcd. for $C_{36}H_{18}B_2Br_7N_6O_9Zn_2$: 1390.4099; found: 1390.4065.

IR: 1605, 1575, 1540, 1480, 1470, 1435, 1390, 1350, 1335, 1325, 1220, 1205, 1190, 1090, 1070, 1045, 990, 980, 950, 895, 870, 850, 780, 730, 715, 675, 550, 520, 510 cm^{-1}.

1.20 Synthesis of 13



To a 25 ml pyrex vial containing **12** (100 mg, 66 µmol, 1.0 equiv.), 4-pyridylboronic acid hydrate (258 mg, 2.3 mmol, 28 equiv.) and K_3PO_4 (195 mg, 0.92 mmol, 14 equiv.) under inert atmosphere were added degassed *n*-BuOH (10 ml) and degassed toluene (10 ml). $Pd_2(dba)_3$ (6.04 mg, 6.6 µmol, 0.1 equiv.) and SPhos (5.41 mg, 13.2 µmol, 0.2 equiv.) were then added and the system was cycled two times with nitrogen, and the sealed vial was heated for 12 h at 120 °C. After cooling to RT, the reaction mixture was filtered through Celite, and was washed with *n*-BuOH (5 ml), MeOH (20 ml) and H_2O (200 ml). The filtrate was then concentrated to half its volume and the resulting precipitate was isolated by filtration, washed with H_2O (2 x 50 ml) and Et_2O (100 ml). The crude product was suspended in a mixture of MeOH (10 ml) and acetonitrile (10 ml) and tetraethylammonium hydroxide (44 µl, 66 µmol, 25% in MeOH) was added, leading to a complete dissolution of all material. The solvents were removed under reduced pressure and the solid was suspended in EtOH (8 ml), isolated by filtration, washed with EtOH (2 x 5 ml) and Et_2O (2 x 30 ml) and dried under vacuum to afford **13** as a pale-yellow powder (84 mg, 56 µmol, 85%).

^{1}H-NMR (400 MHz, DMSO-d_6): δ = 8.70 (d, J = 5.8 Hz, 8H), 8.62 (s, 6H), 8.56 (d, J = 5.8 Hz, 6H), 8.19 – 8.12 (m, 4H), 8.03 (s, 2H), 7.96 (s, 6H), 7.87 (d, J = 5.9 Hz, 8H), 7.65 (d, J = 6.0 Hz, 6H), 3.19 (q, J = 7.2 Hz, 8H), 1.15 (t, J = 7.1 Hz, 12H).

^{13}C-NMR (101 MHz, DMSO-d_6): δ = 165.26, 154.31, 150.19, 150.11, 148.03, 145.56, 136.51, 133.74, 131.18, 123.61, 123.50, 121.54, 119.72, 119.59, 51.37, 7.05 (C-B not detected).

HRMS-ESI: calcd. for $C_{71}H_{46}B_2N_{13}O_9Zn_2$: 1378.2302; found: 1378.2233.

IR: 1595, 1555, 1445, 1400, 1335, 1305, 1215, 1190, 1075, 1035, 970, 915, 885, 820, 795, 775, 750, 685, 635, 615, 585, 565, 530, 520, 510 cm^{-1}.

2 NMR Spectra

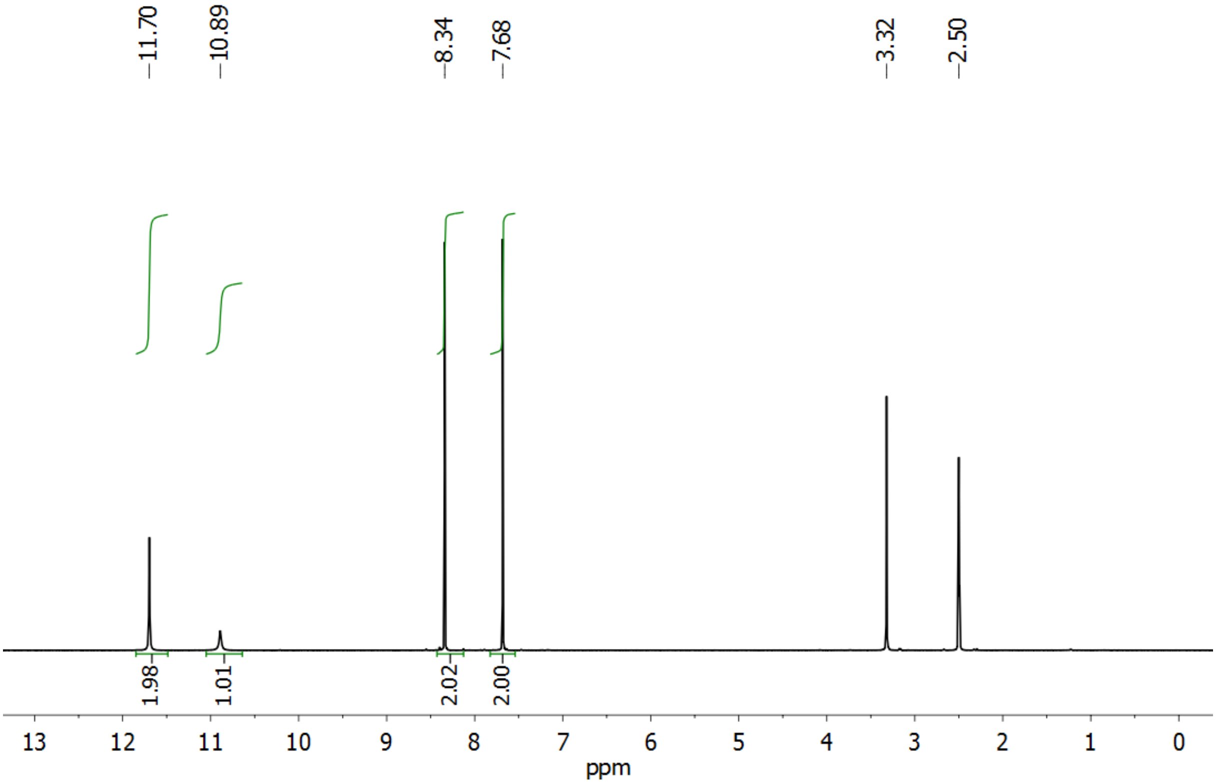


Figure S1 – *^{1}H-NMR spectrum of 2,6-diformyl-4-bromophenol dioxime in DMSO-d$_6$*

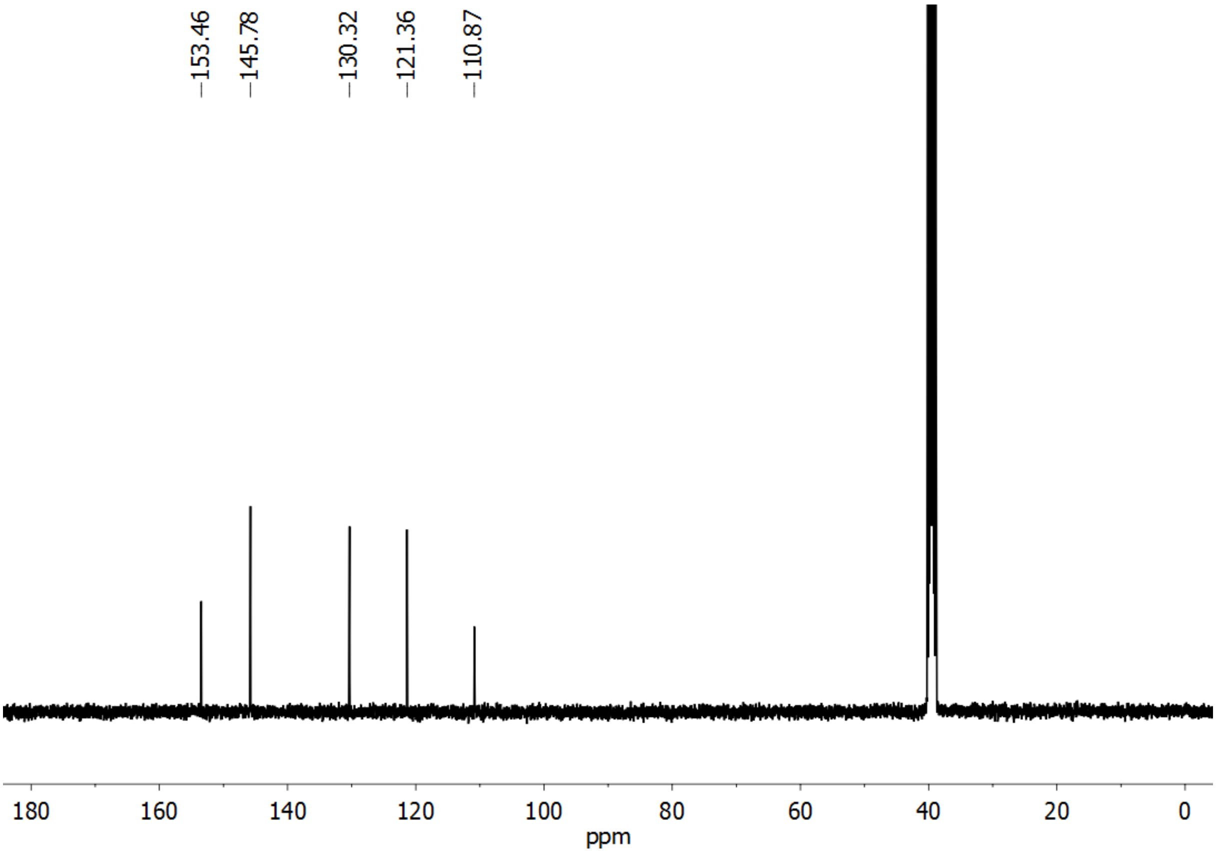


Figure S2 – *^{13}C-NMR spectrum of 2,6-diformyl-4-bromophenol dioxime in DMSO-d$_6$*

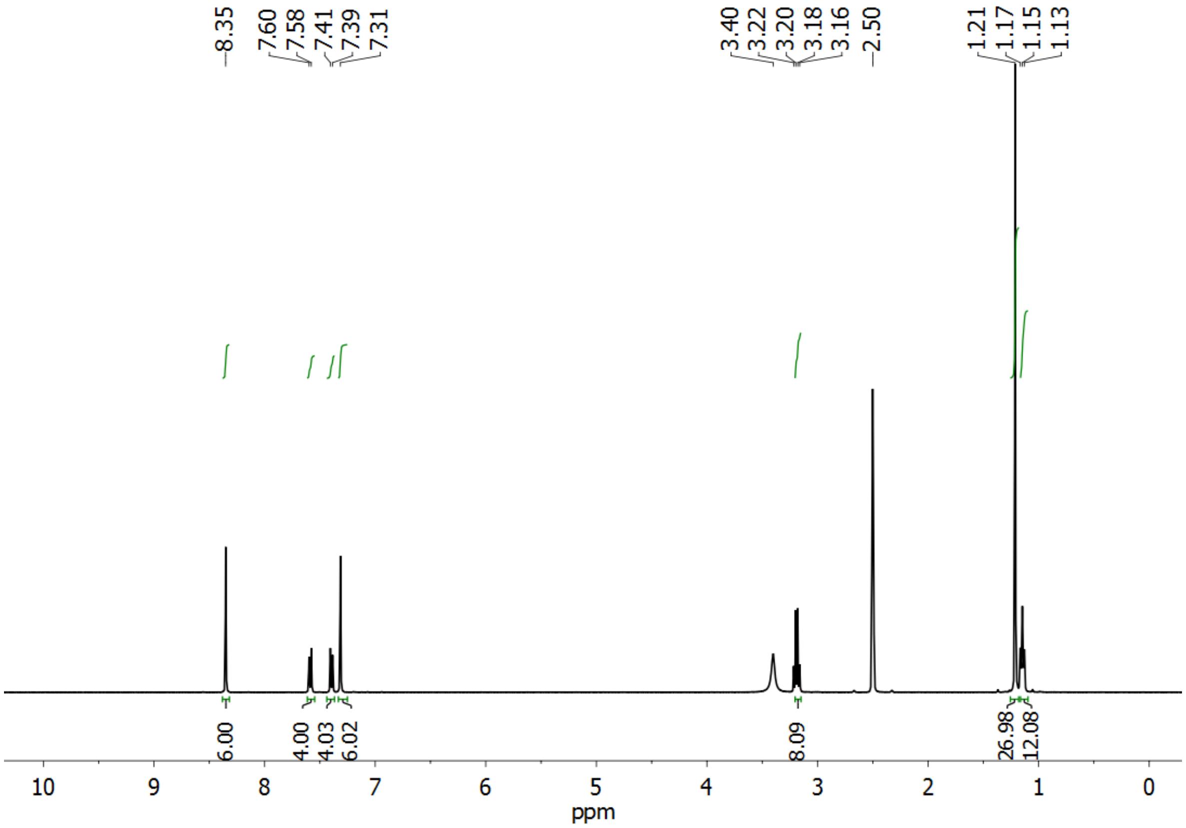


Figure S3 – *^{1}H-NMR spectrum of **1a** in DMSO-d_6*

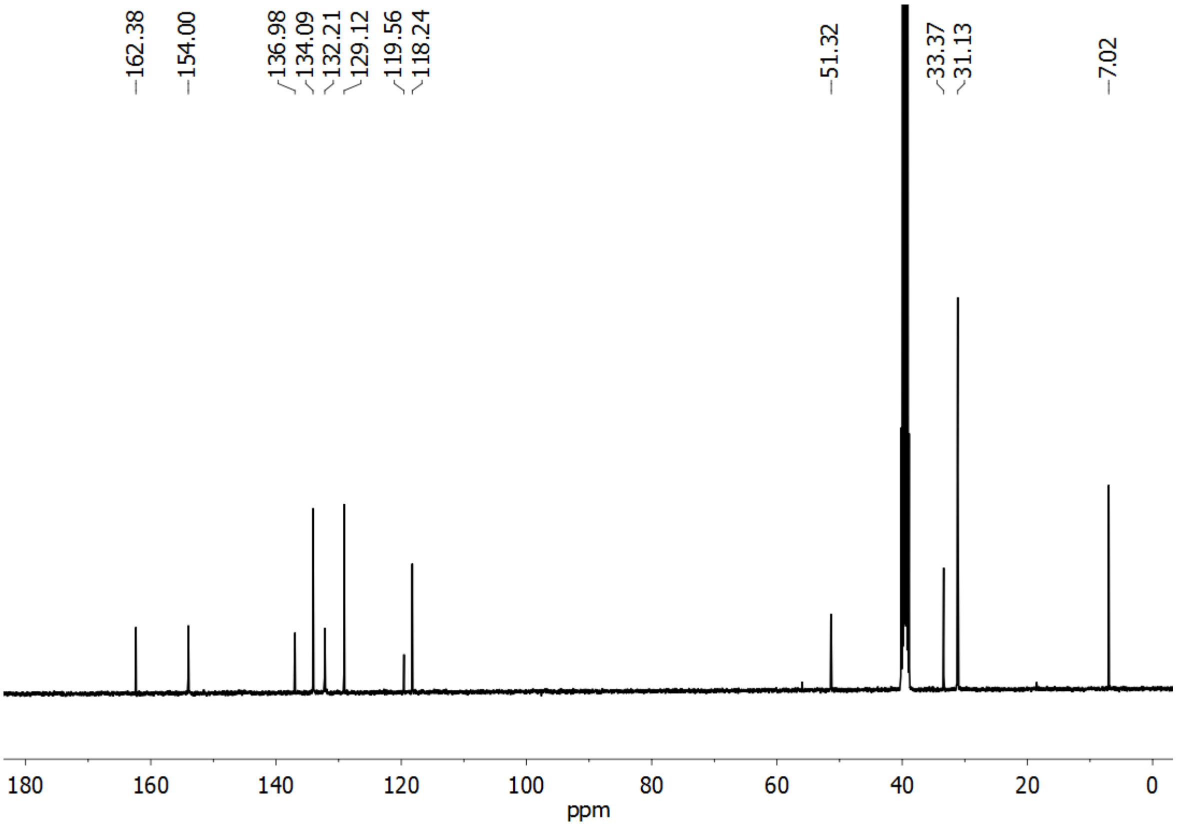


Figure S4 – *^{13}C-NMR spectrum of **1a** in DMSO-d_6*

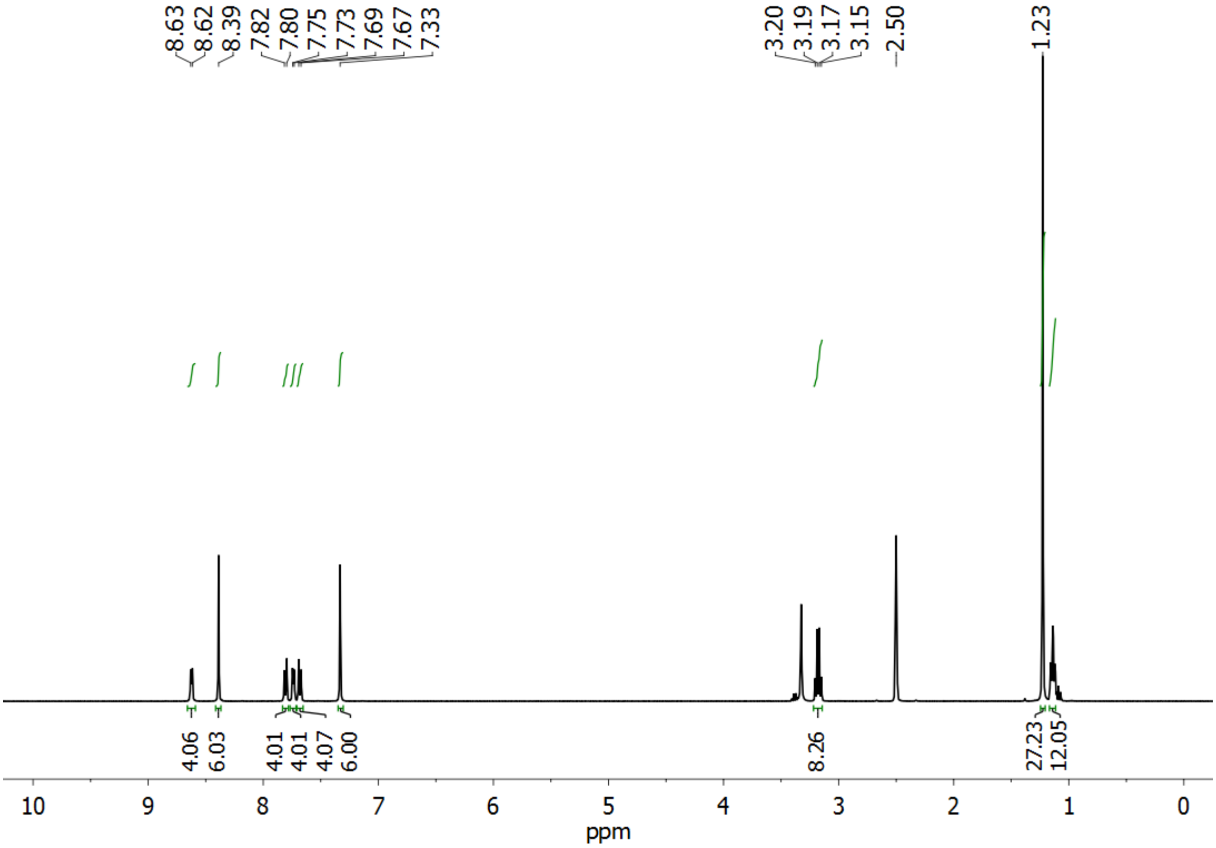


Figure S5 – ^{1}*H-NMR spectrum of **2a** in DMSO-d$_6$*

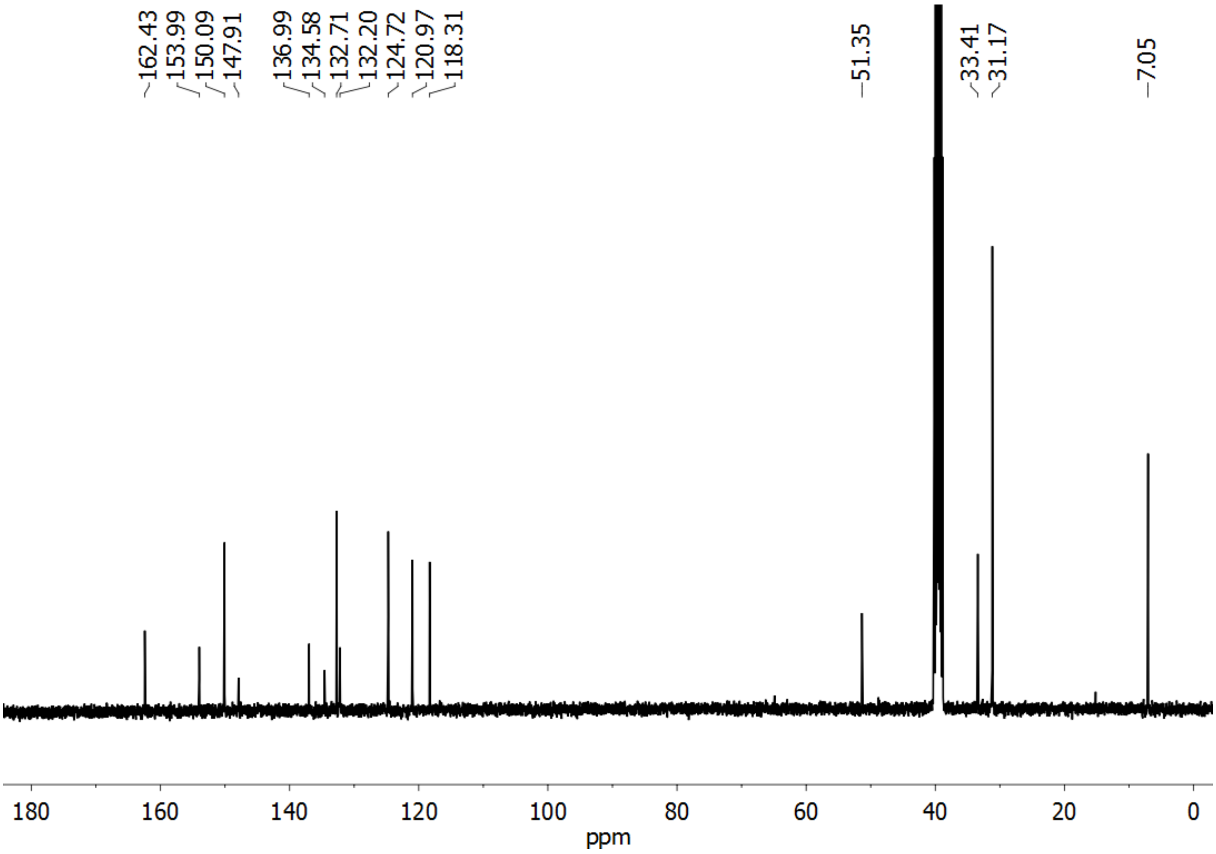


Figure S6 – ^{13}*C-NMR spectrum of **2a** in DMSO-d$_6$*

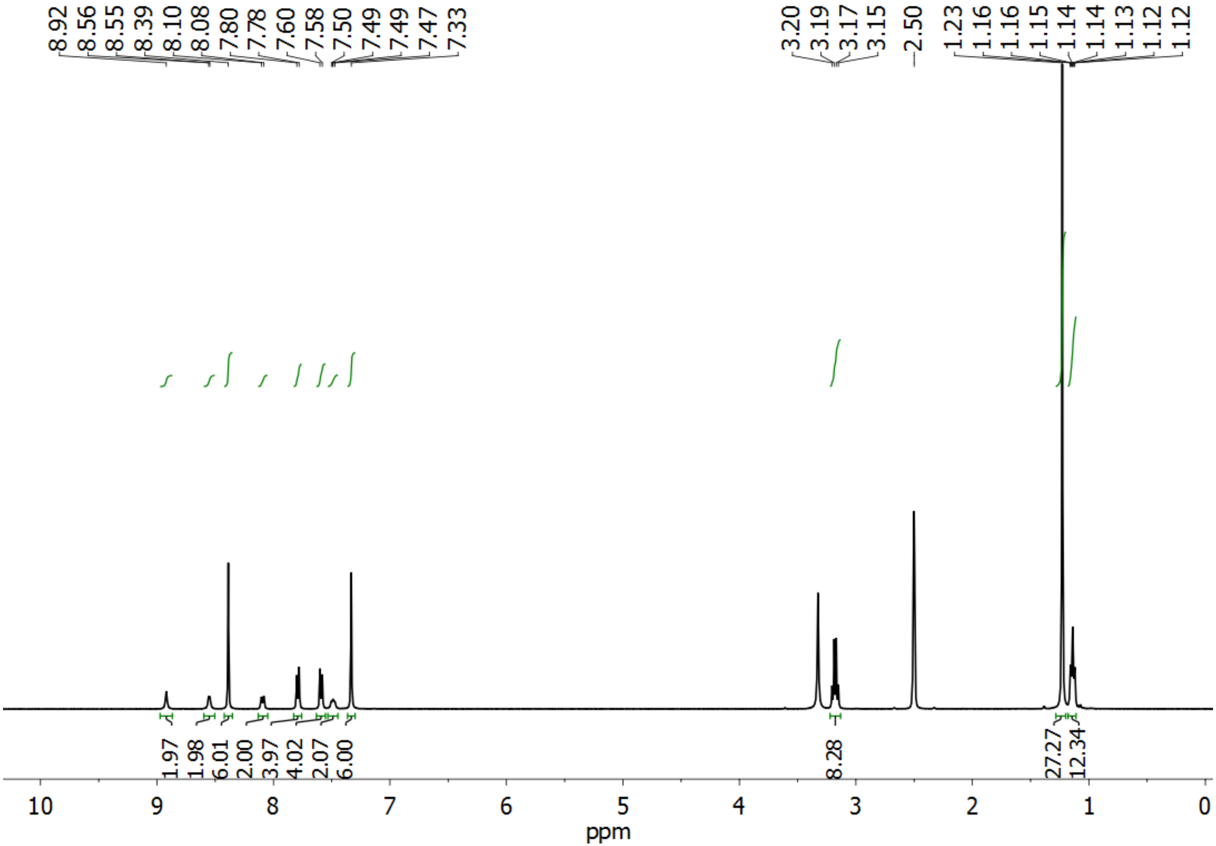


Figure S7 – *^{1}H-NMR spectrum of **3** in DMSO-d_6*

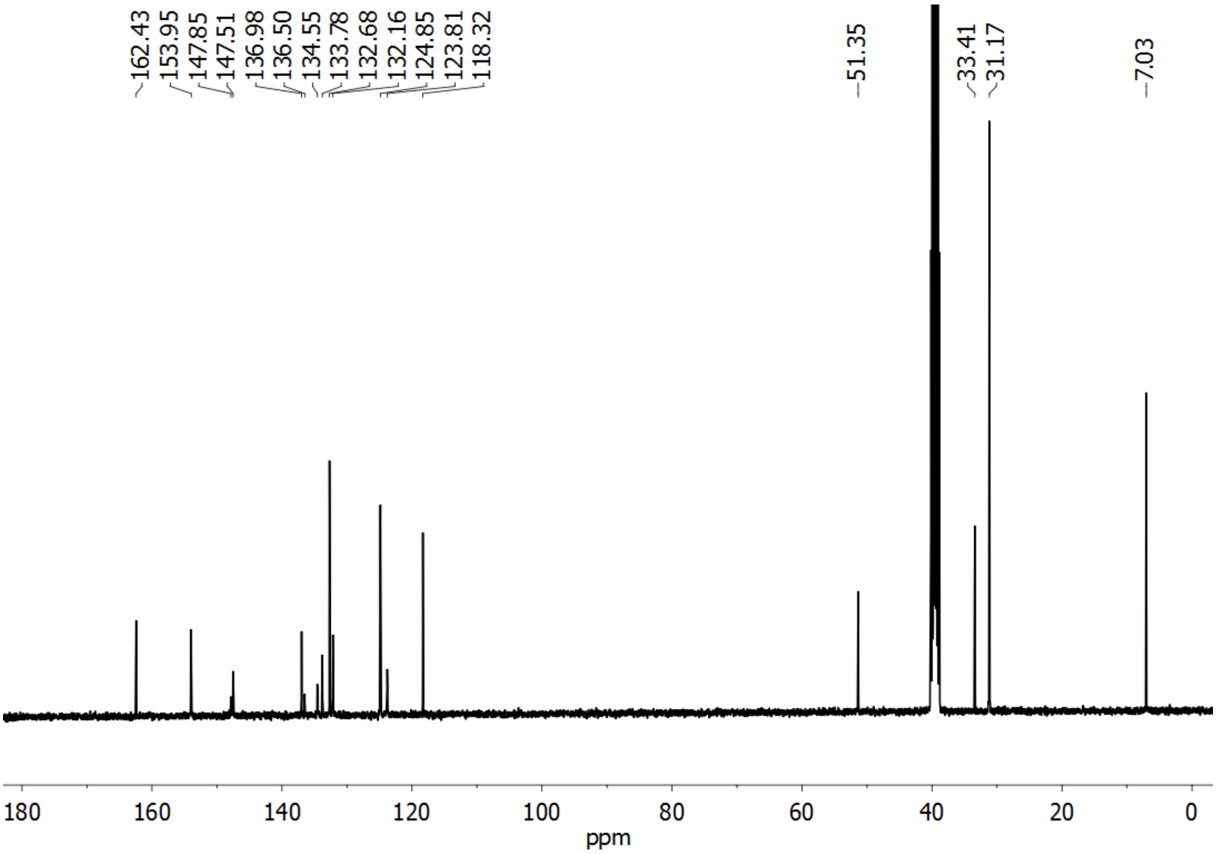


Figure S8 – *^{13}C-NMR spectrum of **3** in DMSO-d_6*

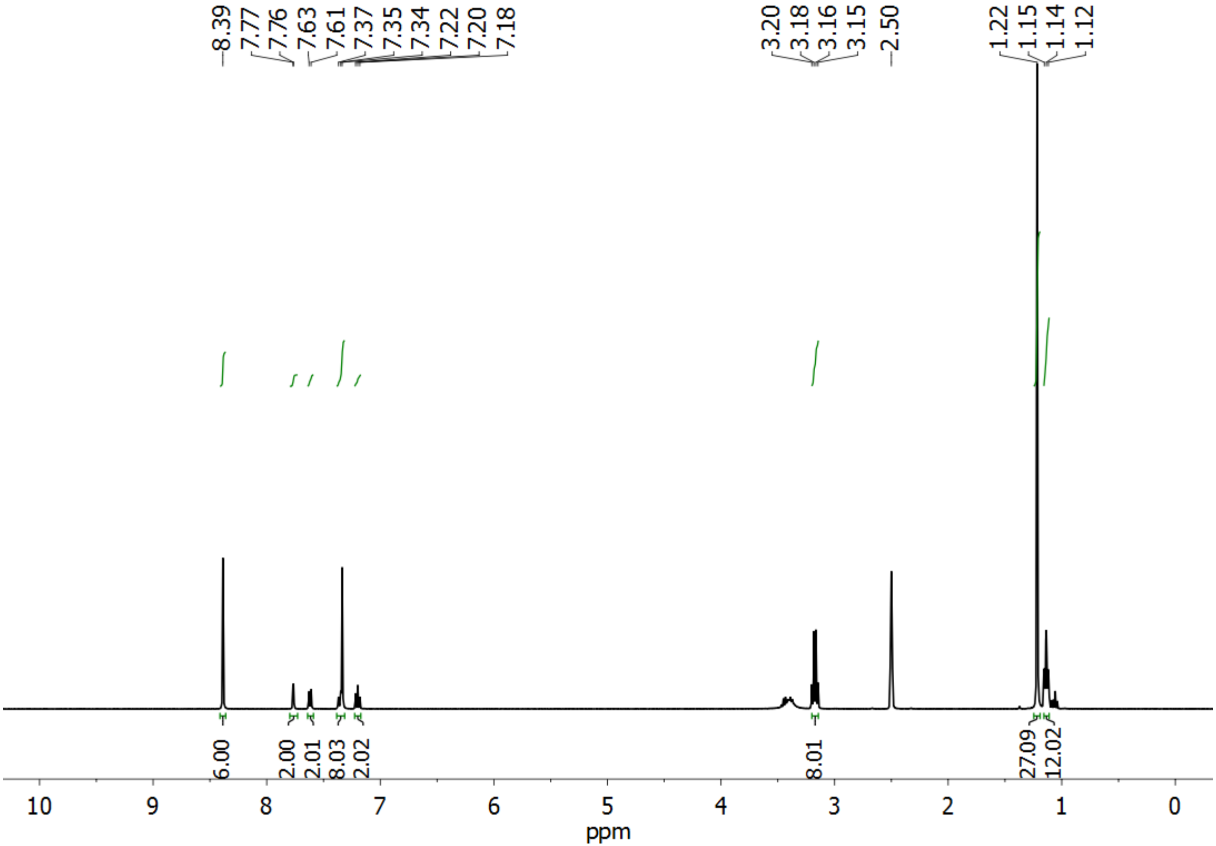


Figure S9 – *^{1}H-NMR spectrum of **4** in DMSO-d_6*

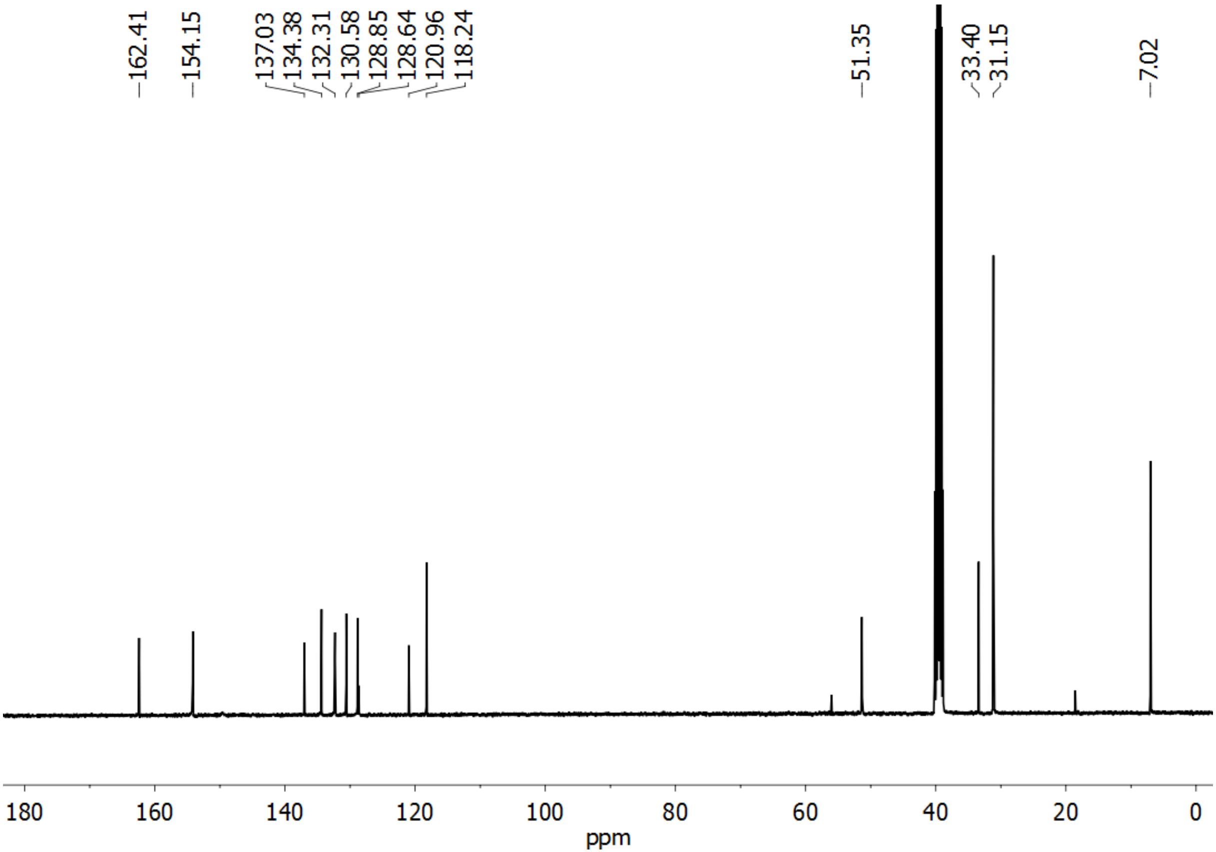


Figure S10 – *^{13}C-NMR spectrum of **4** in DMSO-d_6*

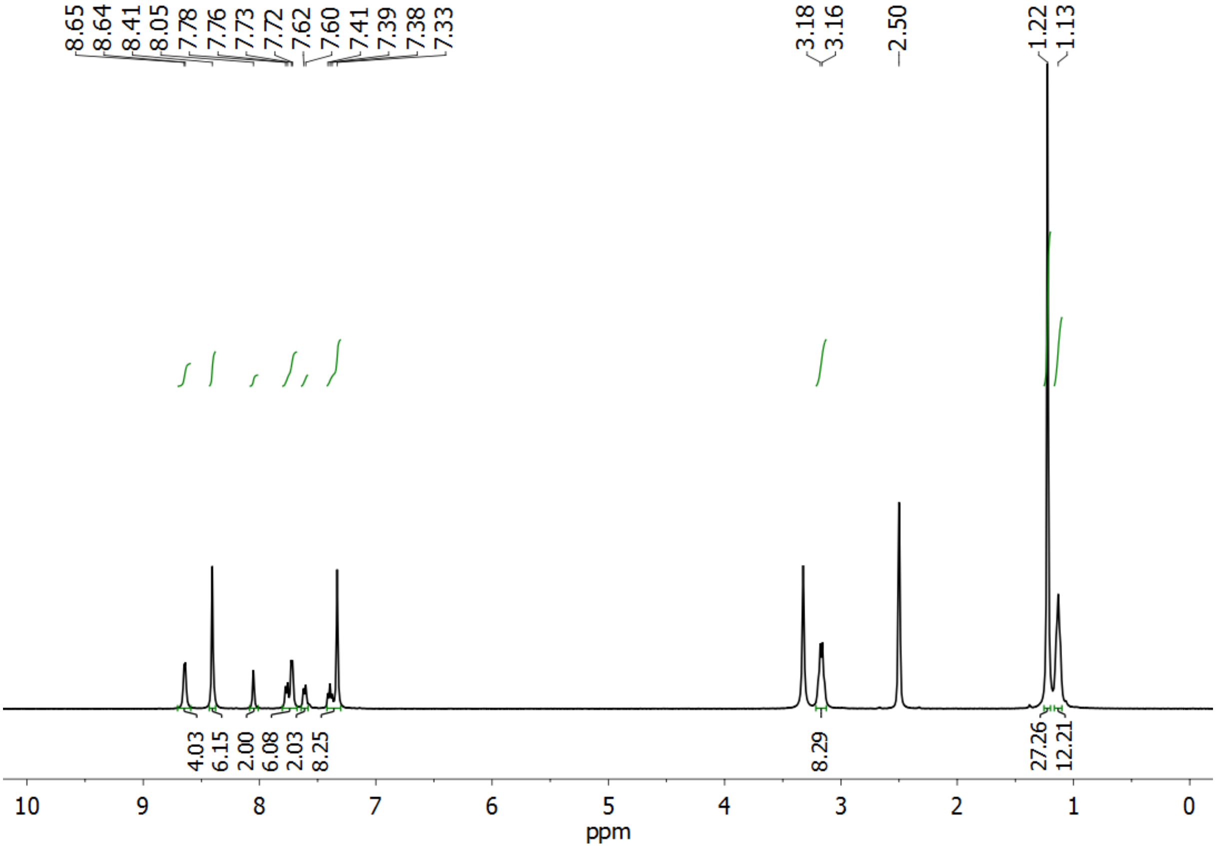


Figure S11 – *^{1}H-NMR spectrum **5** in DMSO-d_6*

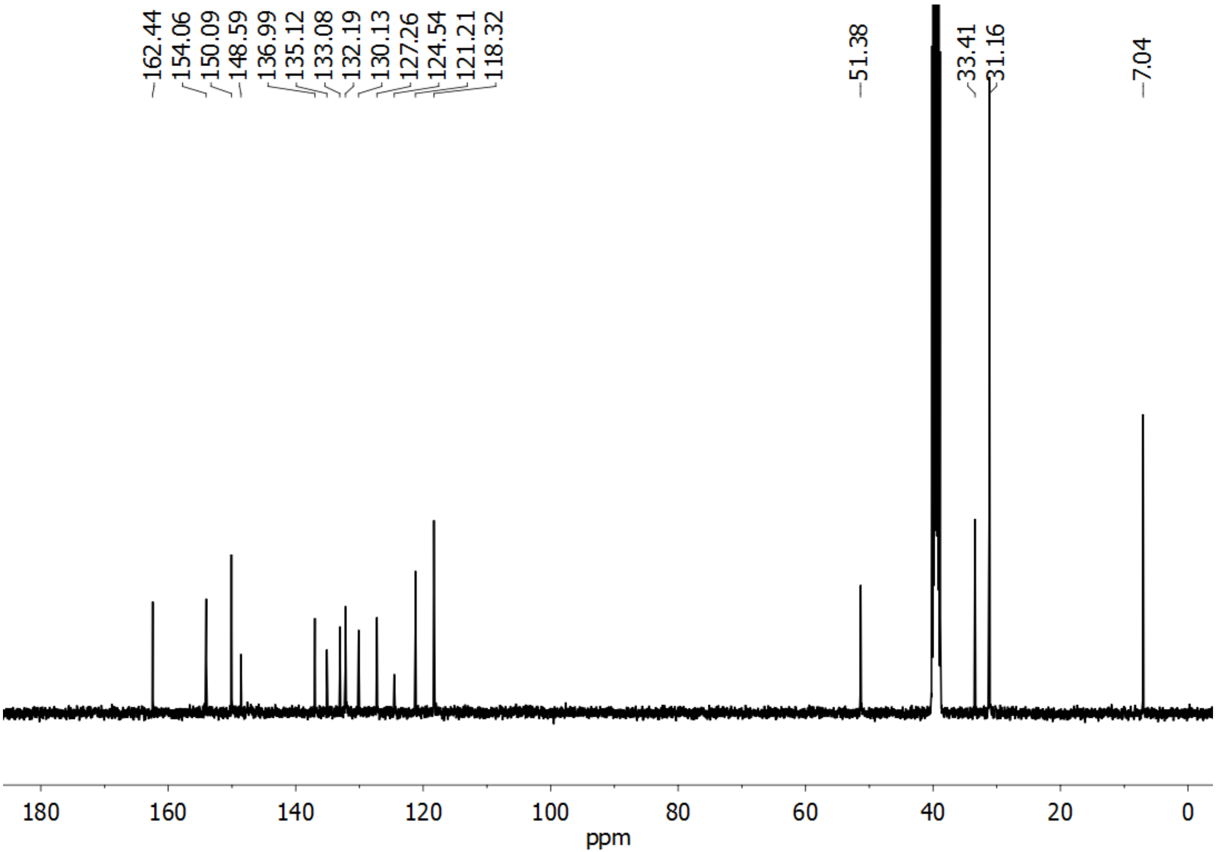


Figure S12 – *^{13}C-NMR spectrum of **5** in DMSO-d_6*

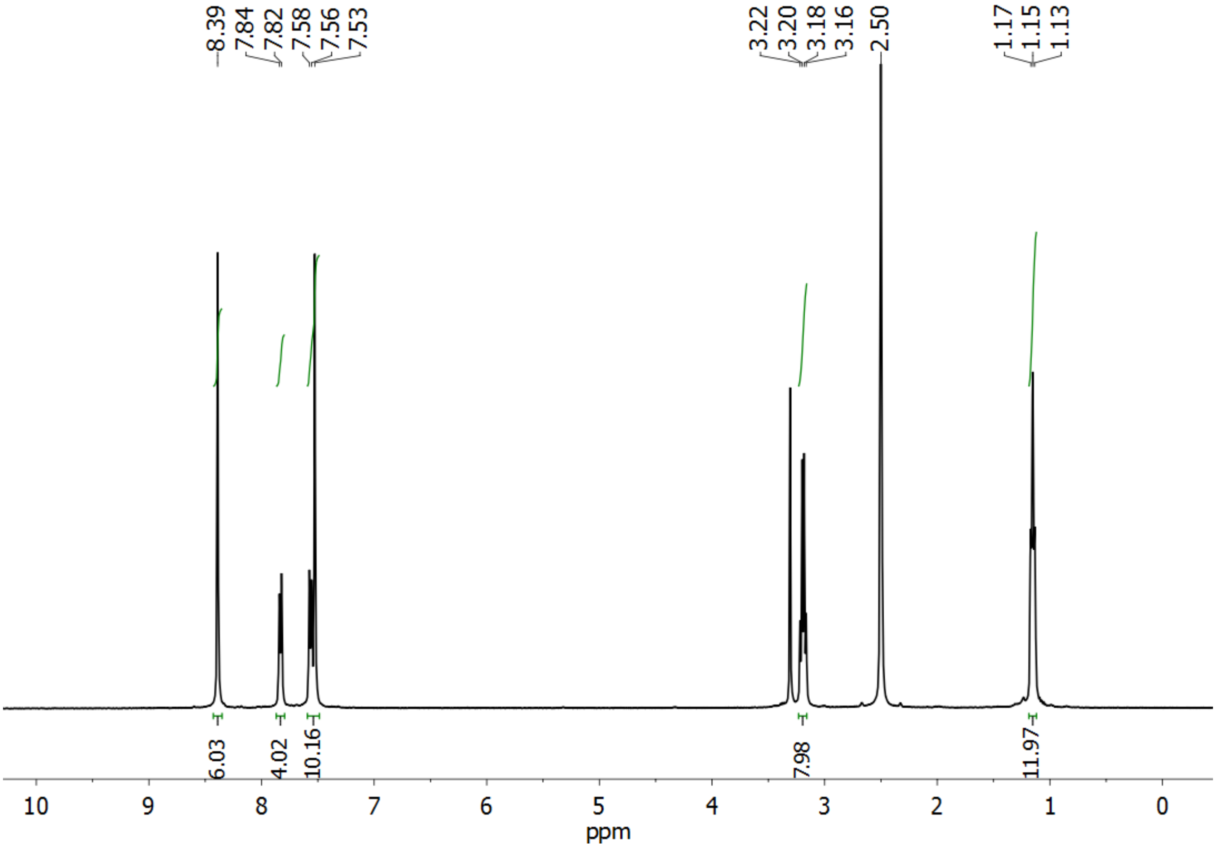


Figure S13 – *^{1}H-NMR spectrum of **6** in DMSO-d_6*

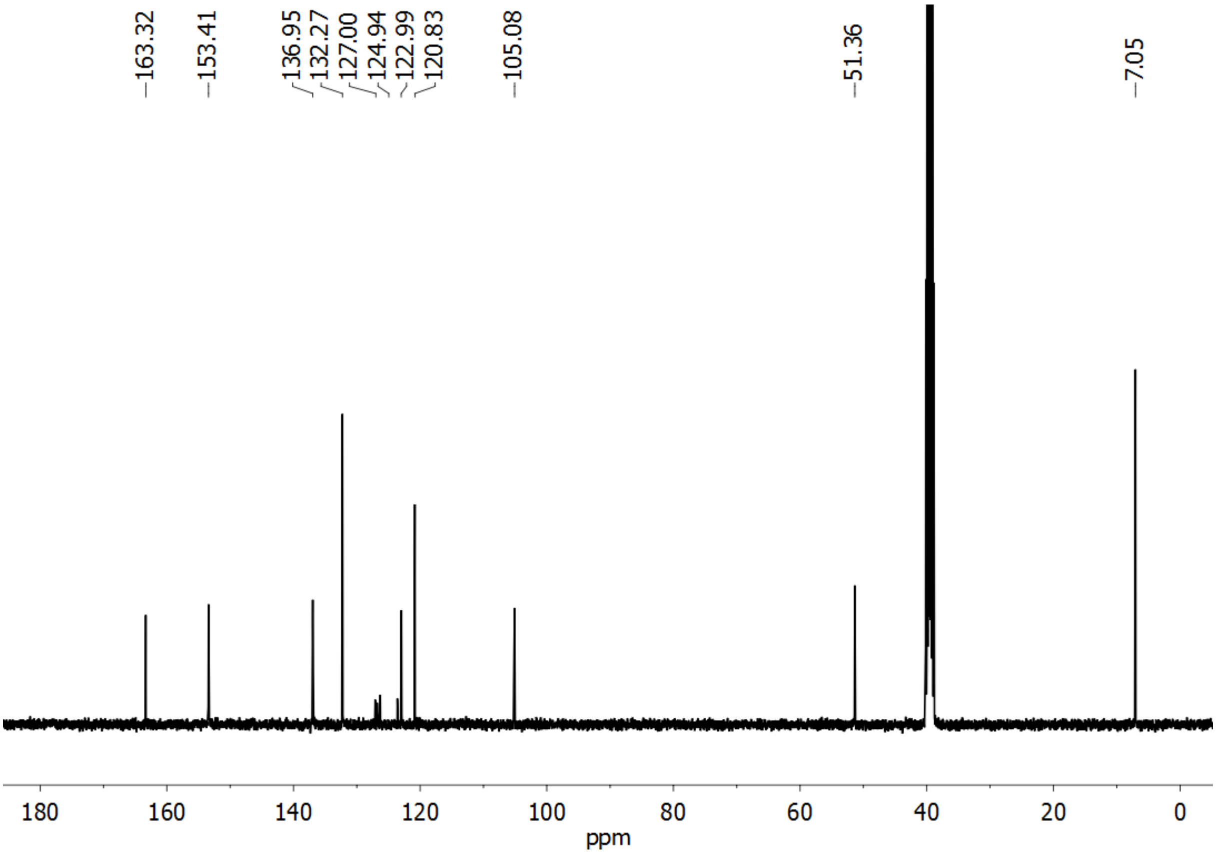


Figure S14 – *^{13}C-NMR spectrum of **6** in DMSO-d_6*

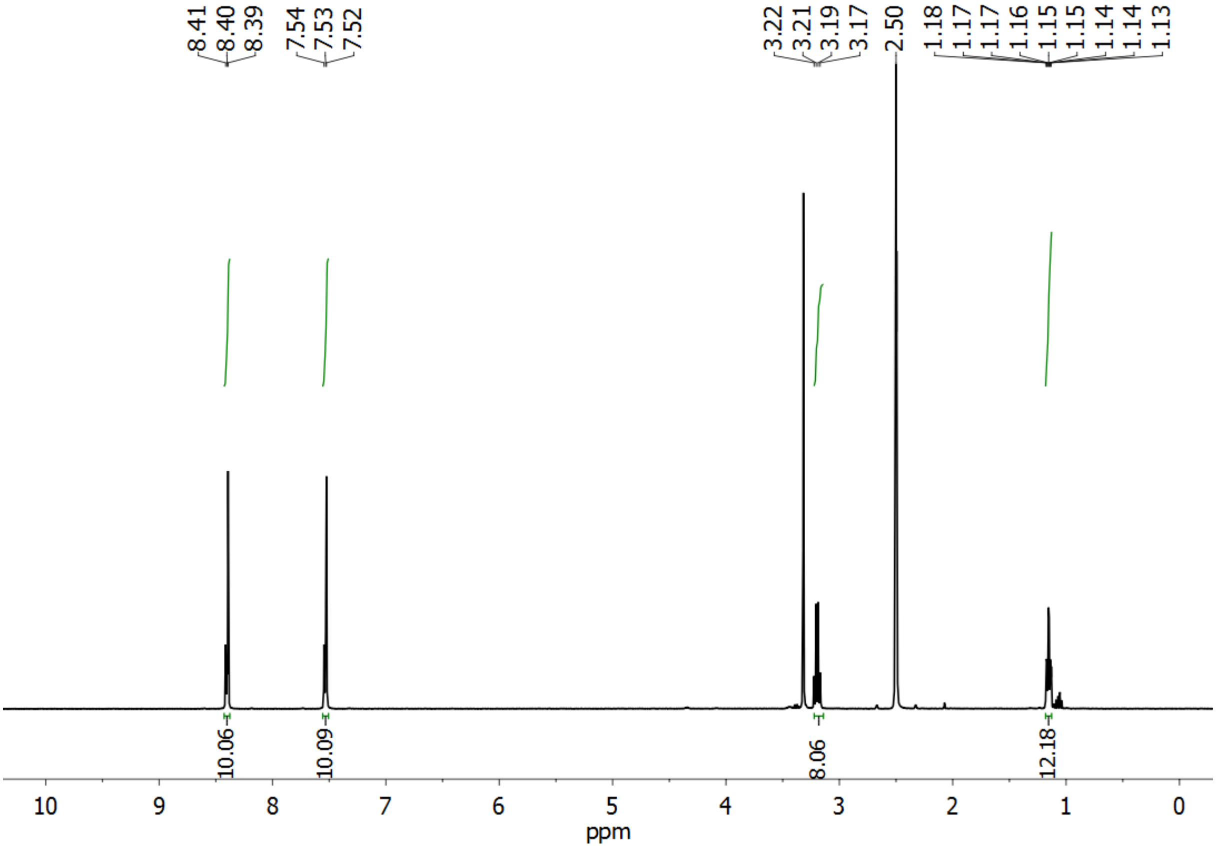


Figure S15 – *^{1}H-NMR spectrum of **7a** in DMSO-d_6*

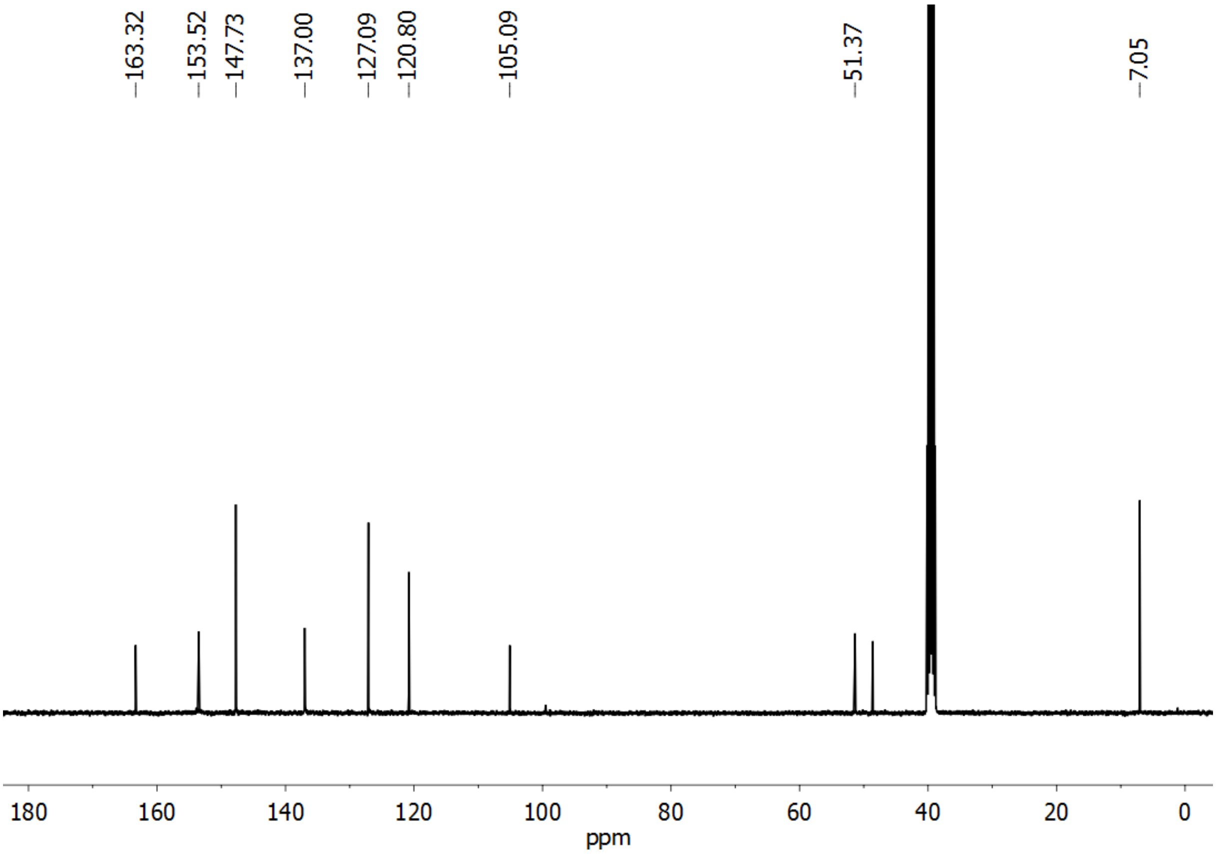


Figure S16 – *^{13}C-NMR spectrum of **7a** in DMSO-d_6*

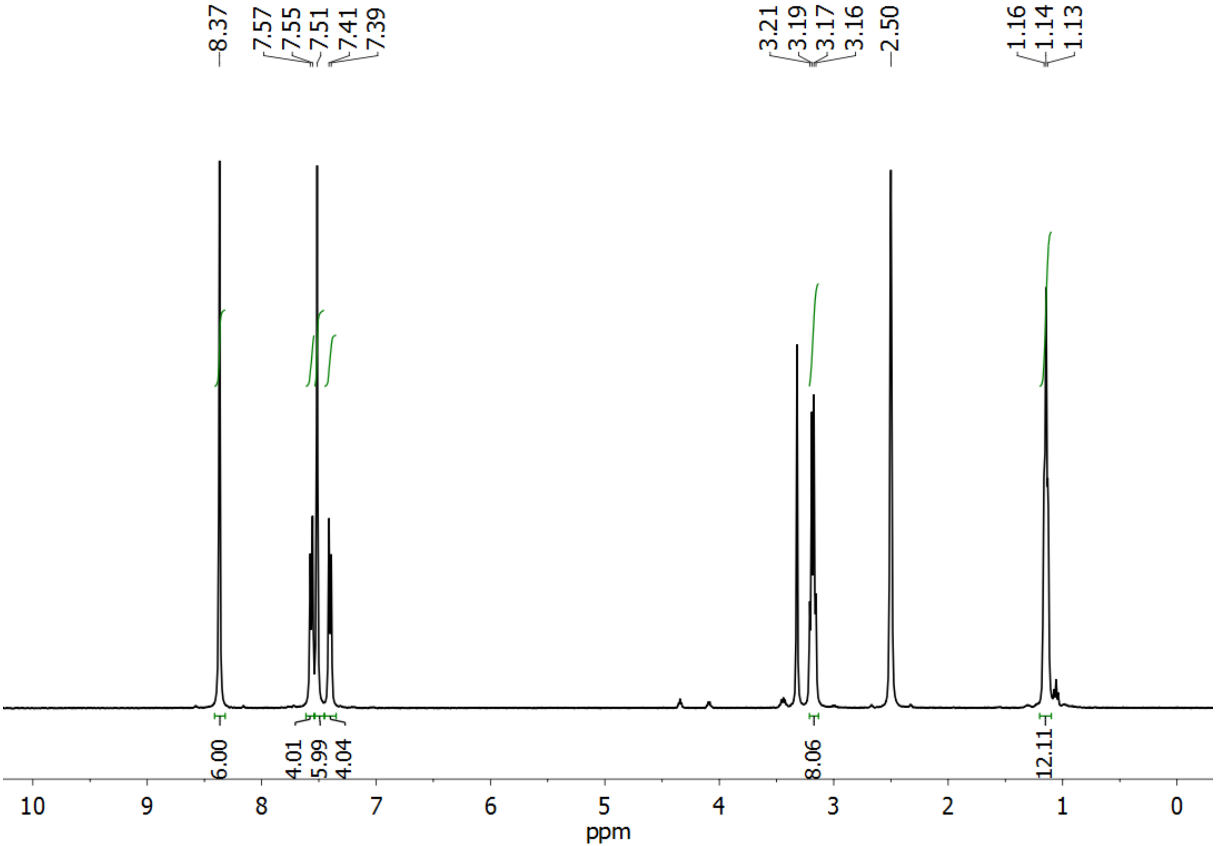


Figure S17 – *^{1}H-NMR spectrum of **8** in DMSO-d$_6$*

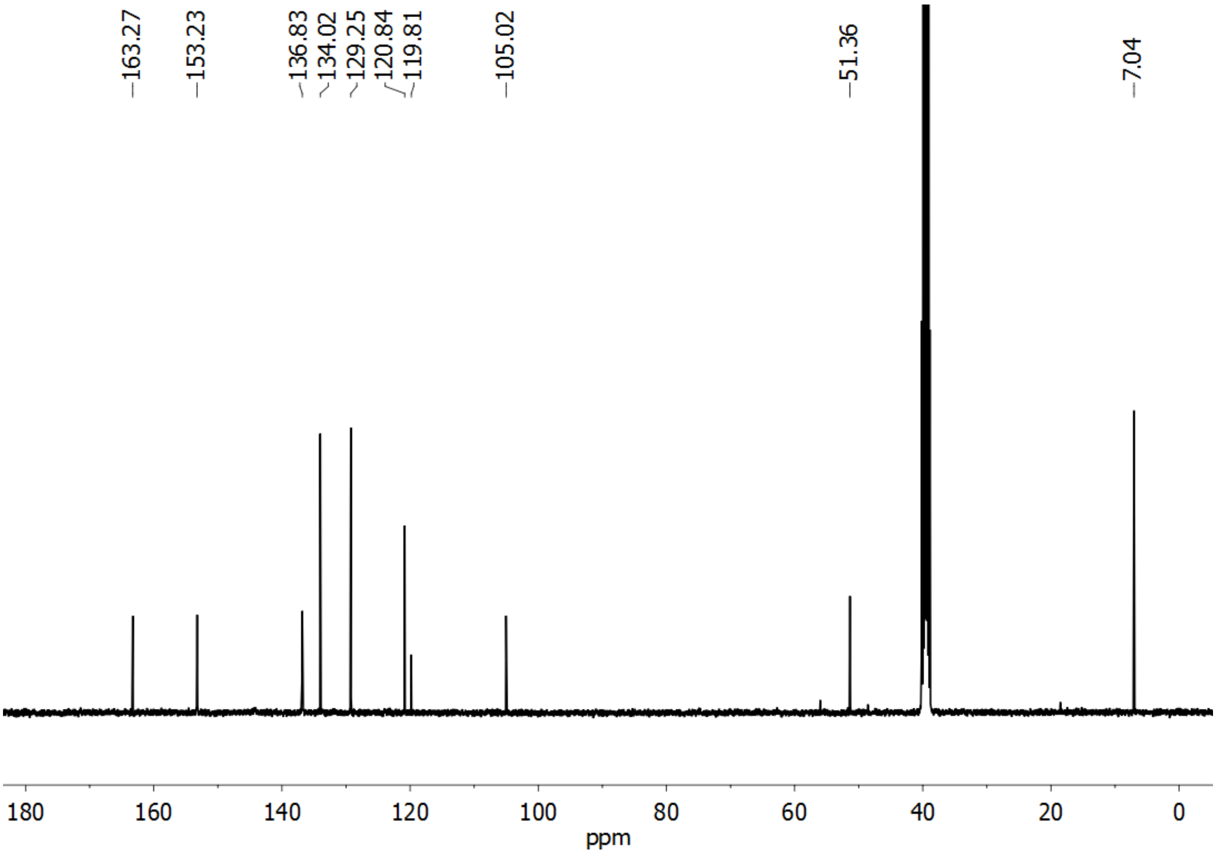


Figure S18 – *^{13}C-NMR spectrum of **8** in DMSO-d$_6$*

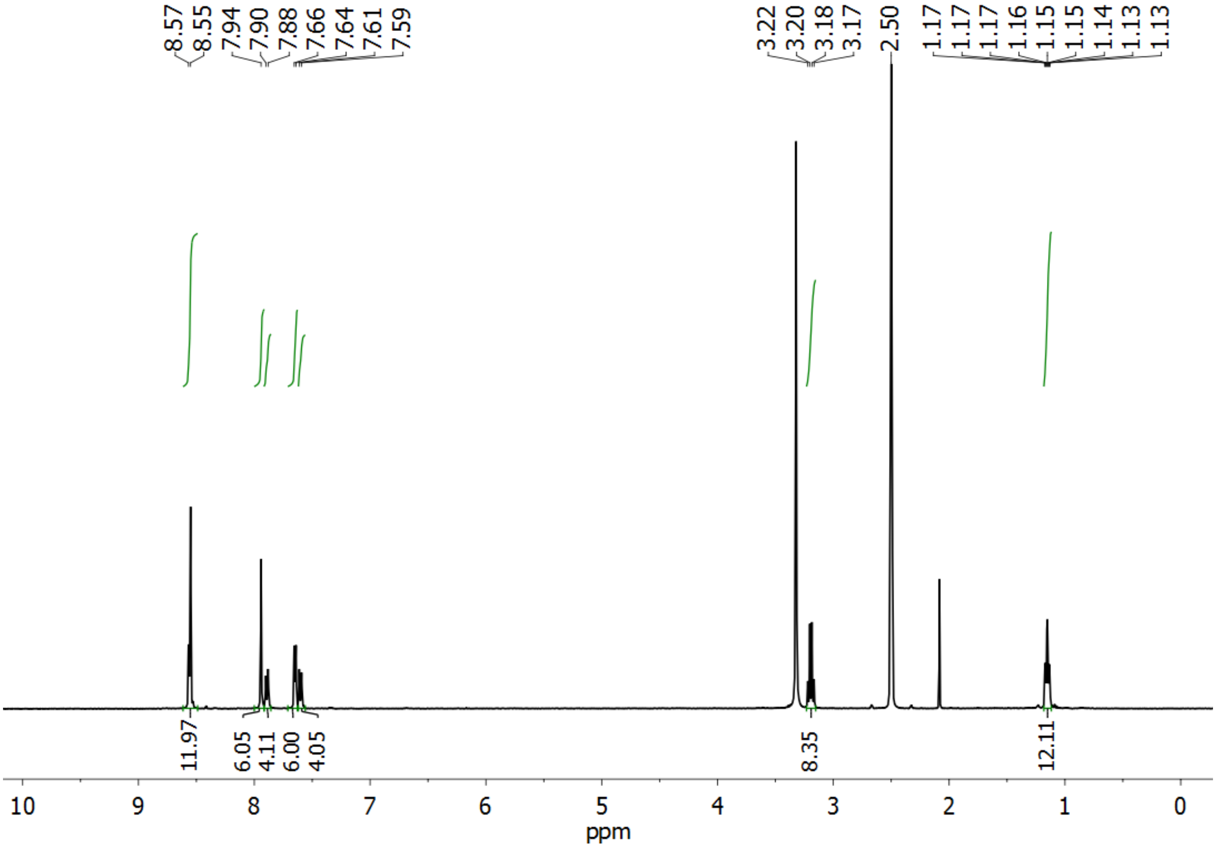


Figure S19 – *^{1}H-NMR spectrum of **9** in DMSO-d_6*

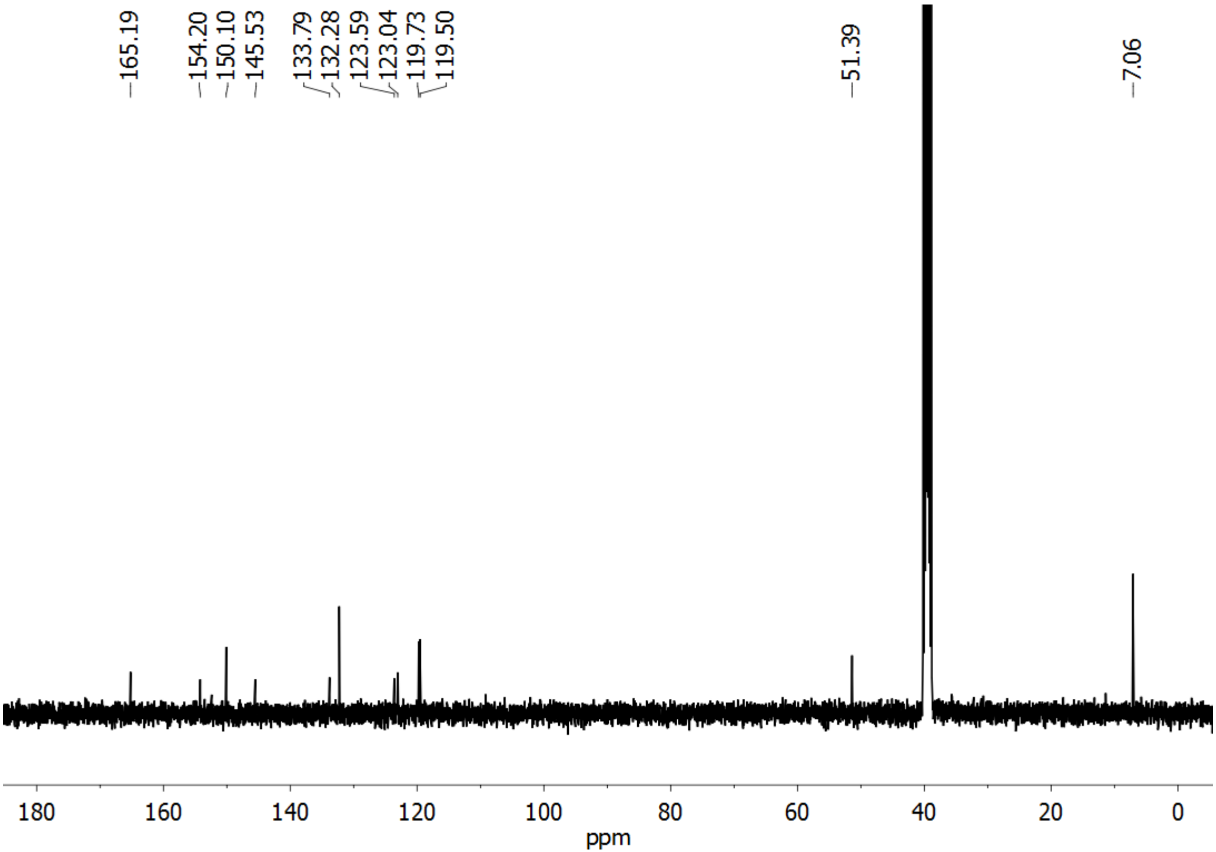


Figure S20 – *^{13}C-NMR spectrum of **9** in DMSO-d_6*

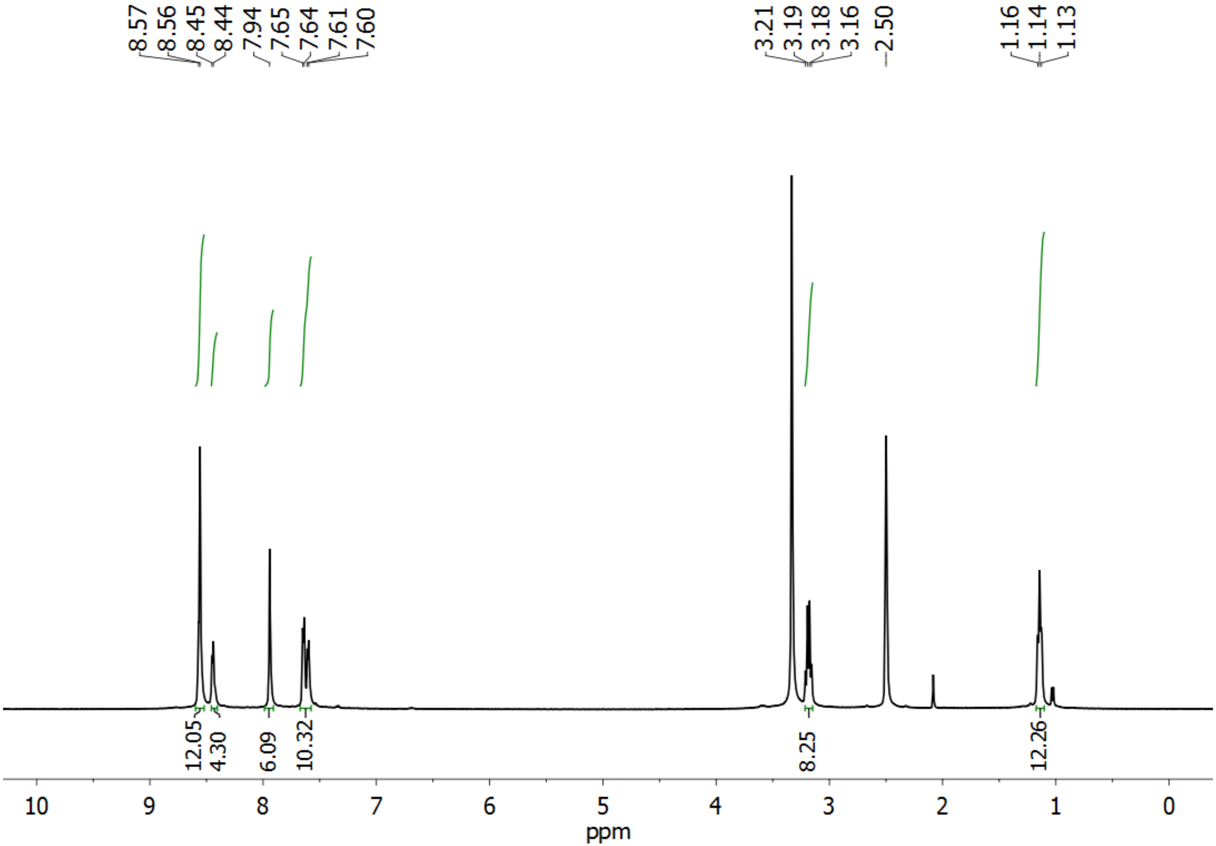


Figure S21 – *^{1}H-NMR spectrum of **10a** in DMSO-d$_6$*

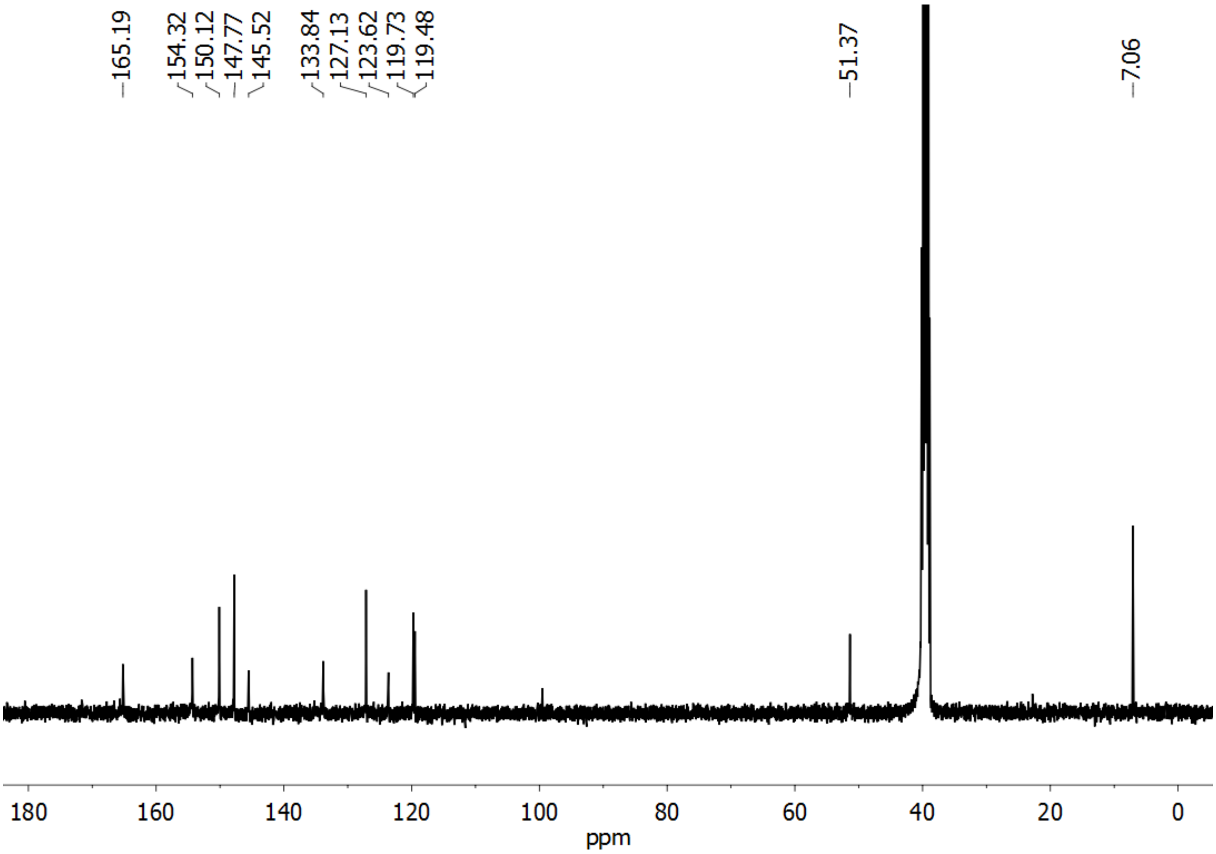


Figure S22 – *^{13}C-NMR spectrum of **10a** in DMSO-d$_6$*

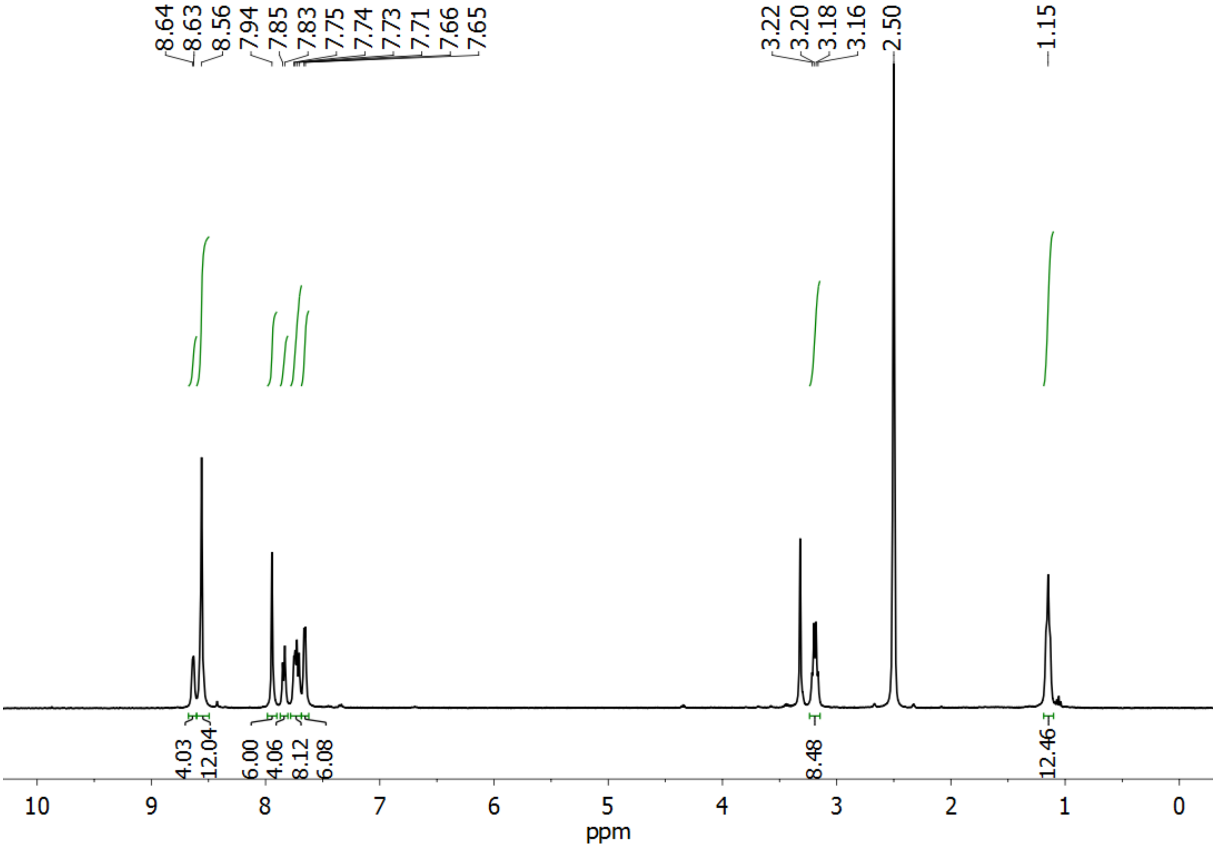


Figure S23 – *^{1}H-NMR spectrum of **11** in DMSO-d_6*

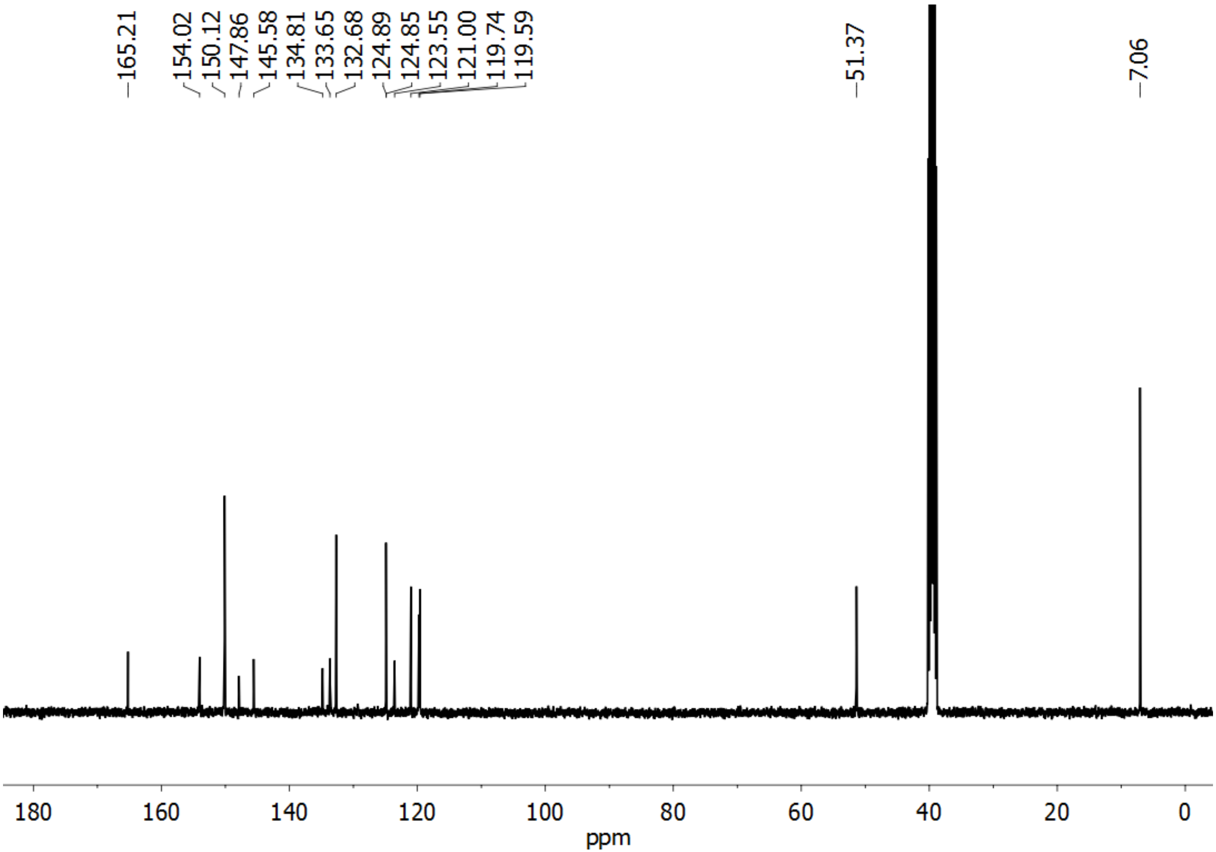


Figure S24 – *^{13}C-NMR spectrum of **11** in DMSO-d_6*

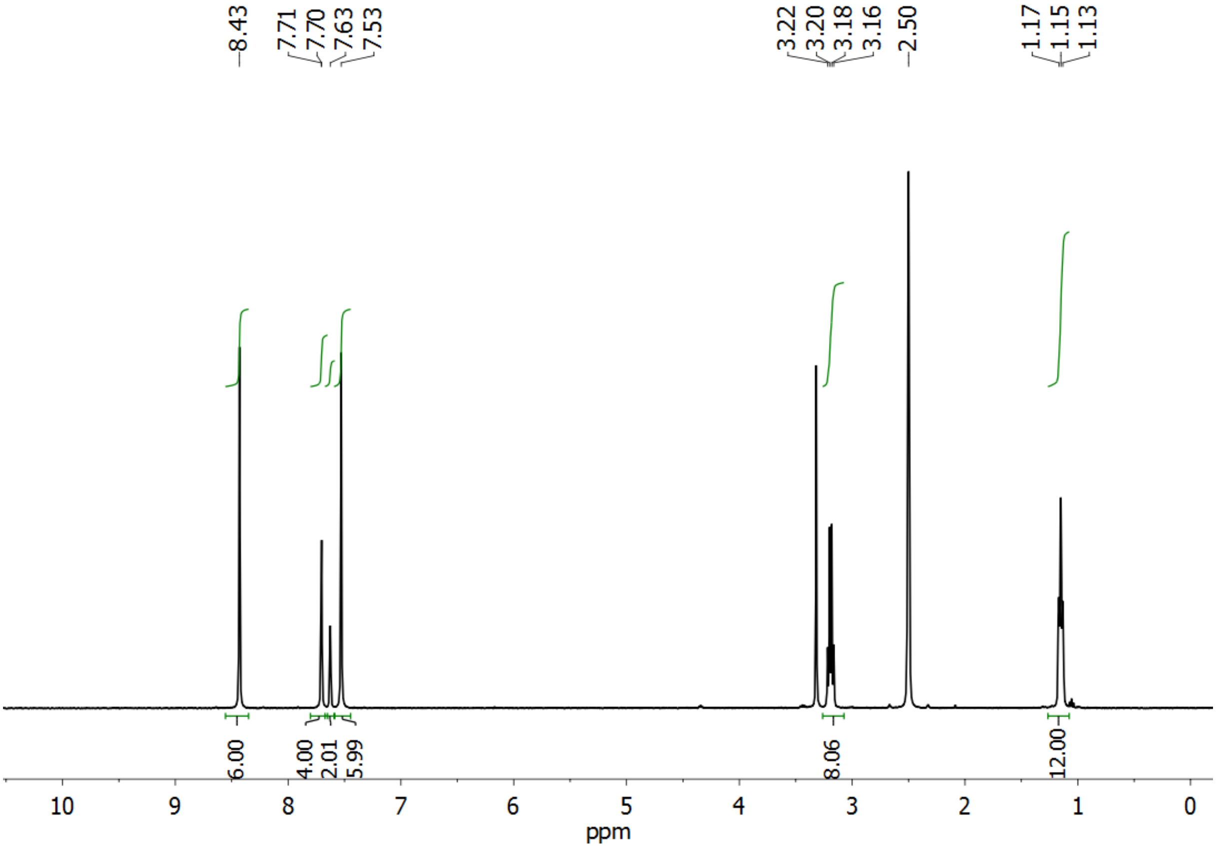


Figure S25 – *^{1}H-NMR spectrum of **12** in DMSO-d$_6$*

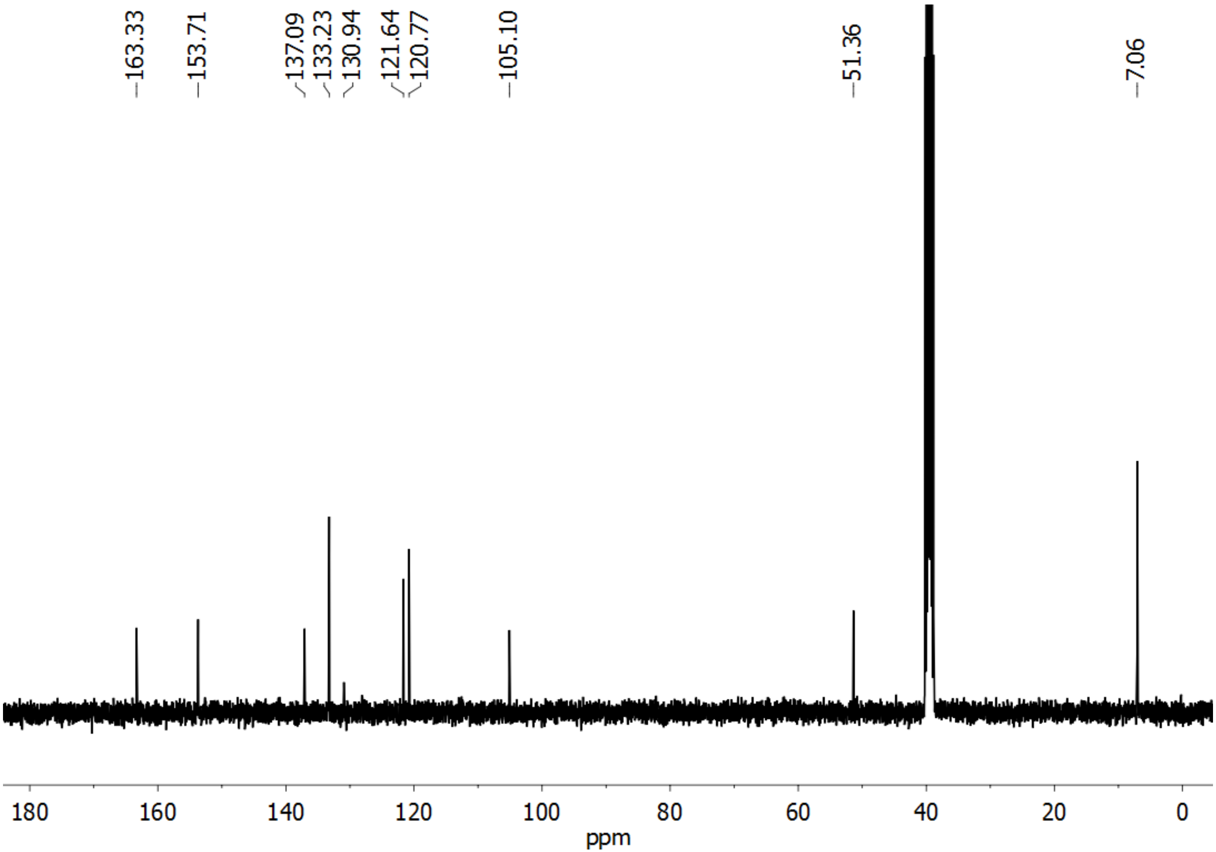


Figure S26 – *^{13}C-NMR spectrum of **12** in DMSO-d$_6$*

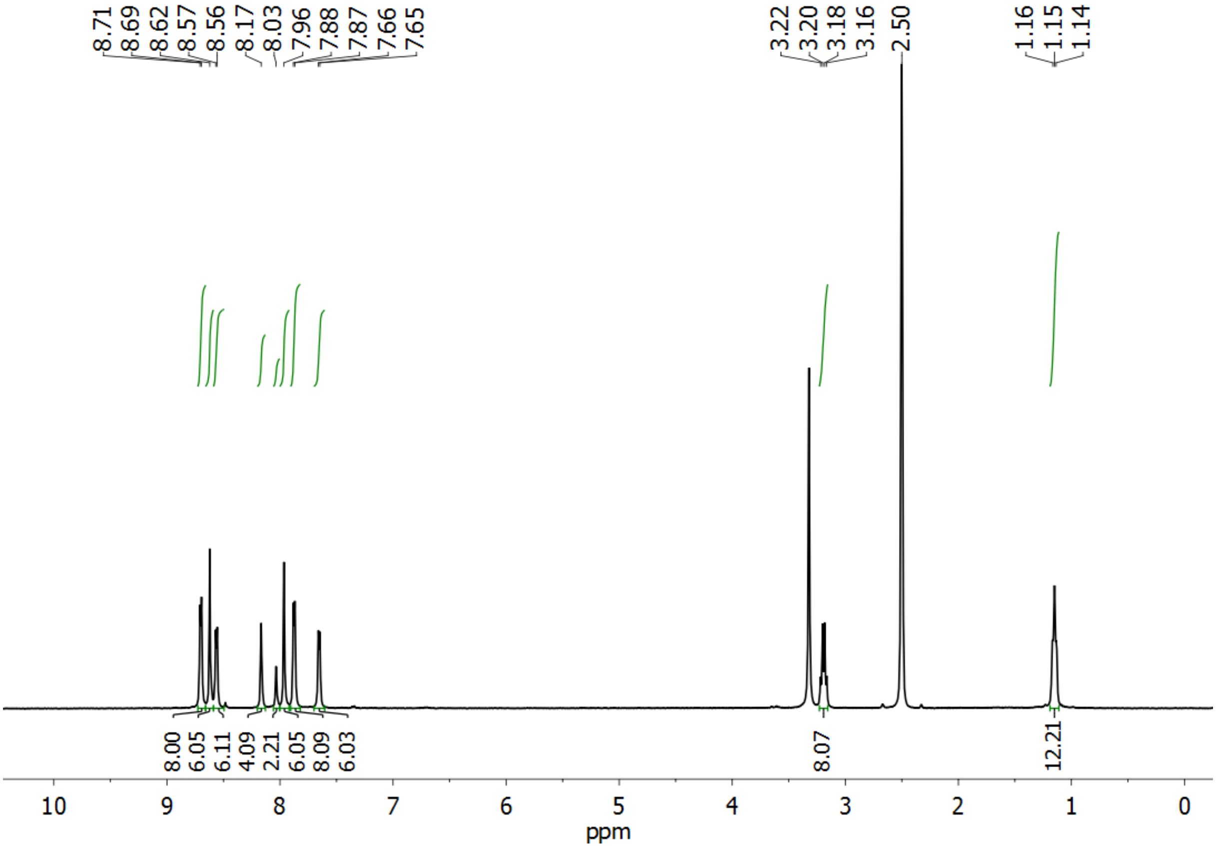


Figure S27 – *^{1}H-NMR spectrum of **13** in DMSO-d$_6$*

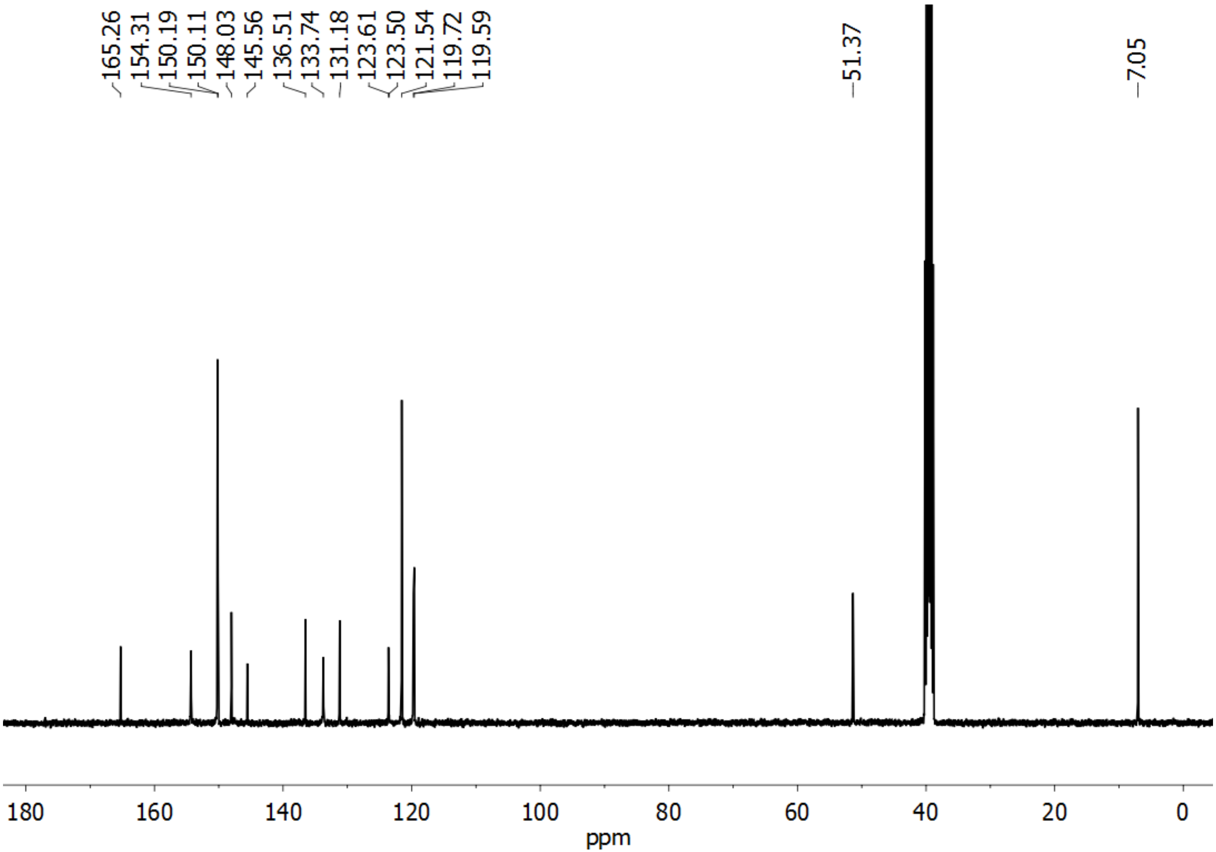


Figure S28 – *^{13}C-NMR spectrum of **13** in DMSO-d$_6$*

3 Absorption and Fluorescence Spectra

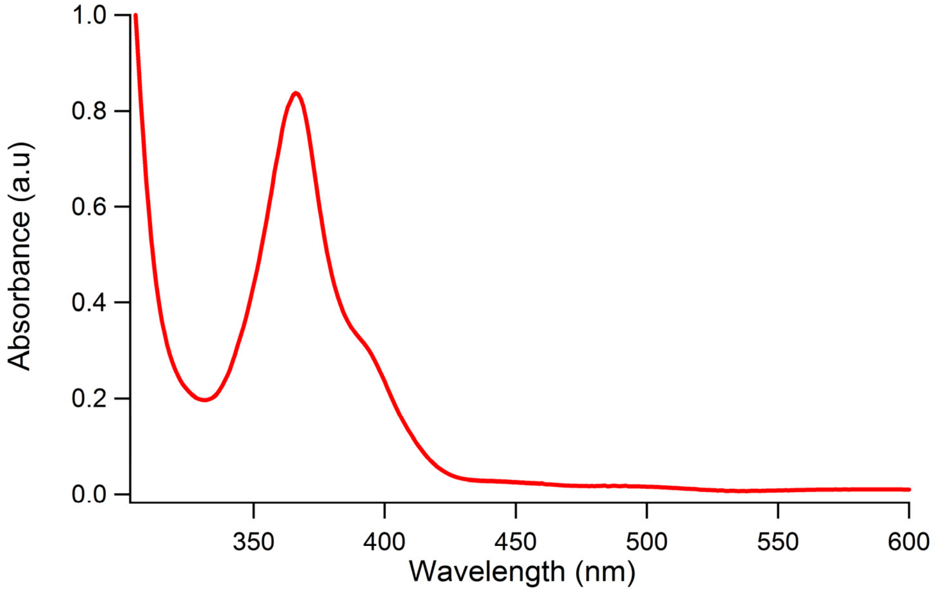


Figure S29 – *Absorption spectrum of clathrochelate **3a** in DMF.*

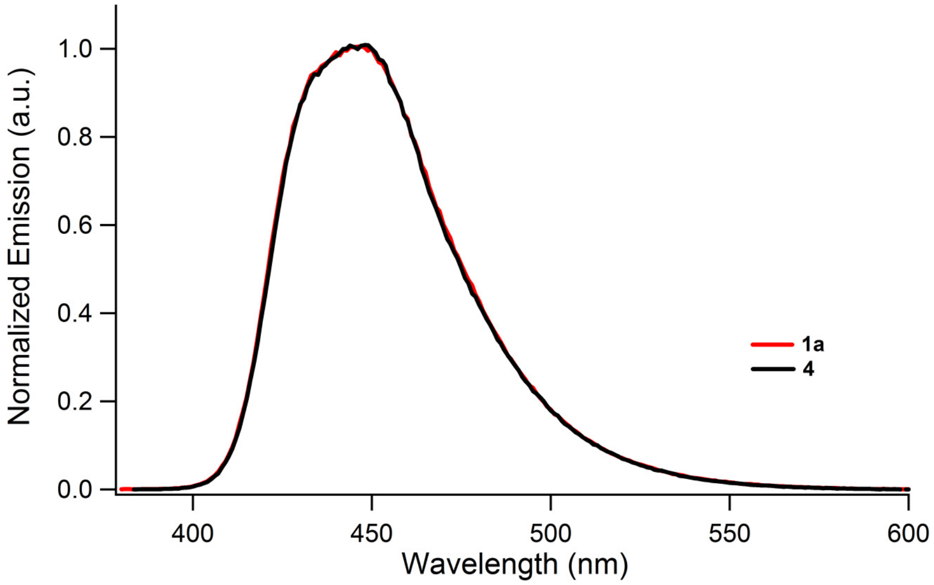


Figure S30 – *Emission spectra in DMF solution of **1a** and **4** (λ_{ex} = 330 nm).*

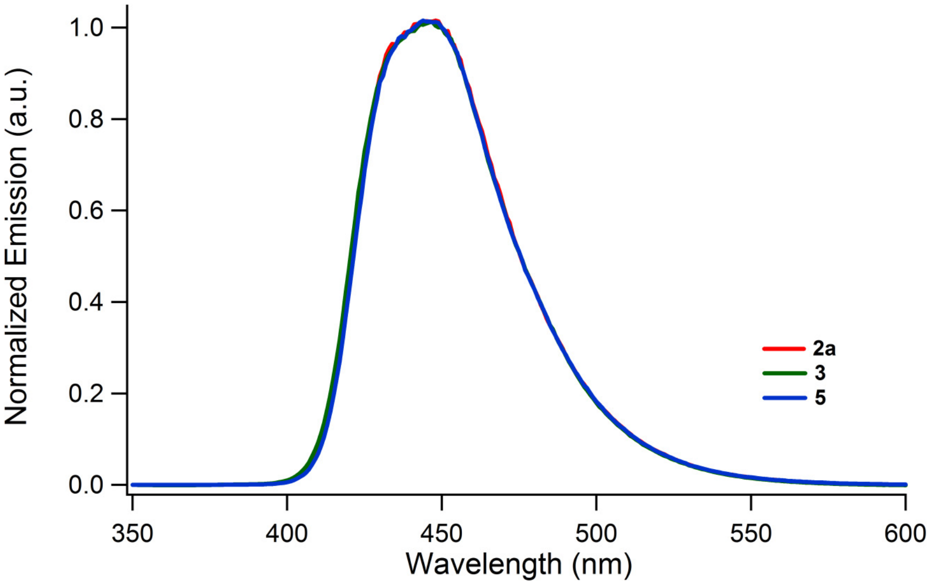


Figure S31– *Emission spectra in DMF solution of **2a**, **3** and **5** (λ_{ex} = 330 nm).*

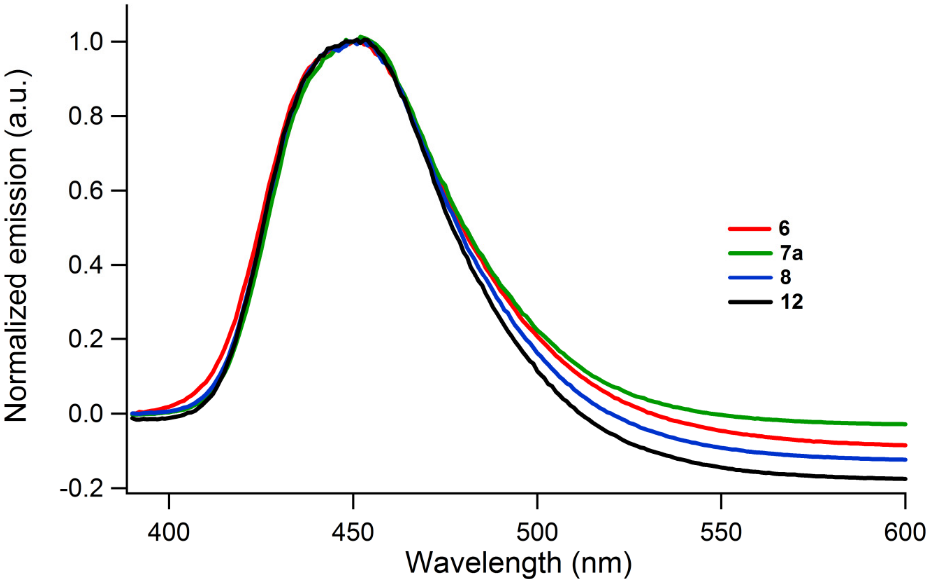


Figure S32– *Emission spectra in DMF solution of **6**, **7a**, **8** and **12** (λ_{ex} = 330 nm).*

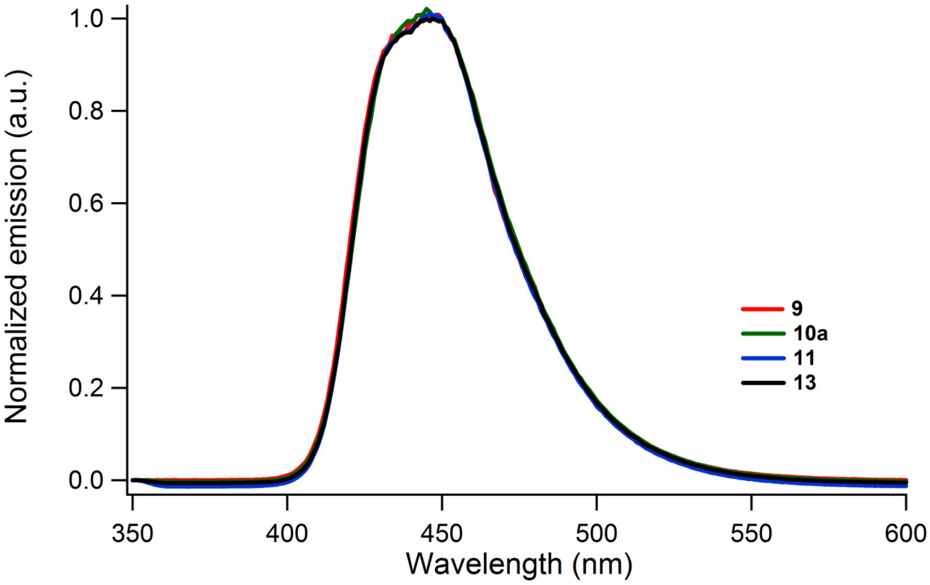


Figure S33– *Emission spectra in DMF solution of **9**, **10a**, **11** and **13** (λ_{ex} = 330 nm).*

4 Computational Details

Full geometry optimization of the clathrochelates **2a** and **13** was performed in gas phase with density functional theory (DFT),[3] using the PBE0 functional[4] and a 6-31G* basis set.[5] Frequency calculations were performed to ensure that the extremum located for each compound is a true minimum of the ground-state potential energy hypersurface. Additional calculations were conducted for compound **13** with the M06 functional,[6] using an ultrafine integration grid, and with the inclusion of Grimme's D3 dispersion correction together with PBE0.[7] All calculations were performed with the Gaussian 09 package.[8]

The DFT/PBE0 optimized geometry agrees well with the crystal structure for clathrochelate **2a** (Tables S1, Figures S34). To validate the theoretical prediction for compound **13**, whose structure could not be measured experimentally, we performed additional tests with different exchange and correlation functionals. M06 – a meta-hybrid functional – and D3-PBE0 – PBE0 with a correction for including dispersion interactions – both provide a minimum-energy geometry that is similar to that obtained with PBE0 (Table S2 and Figure S35).

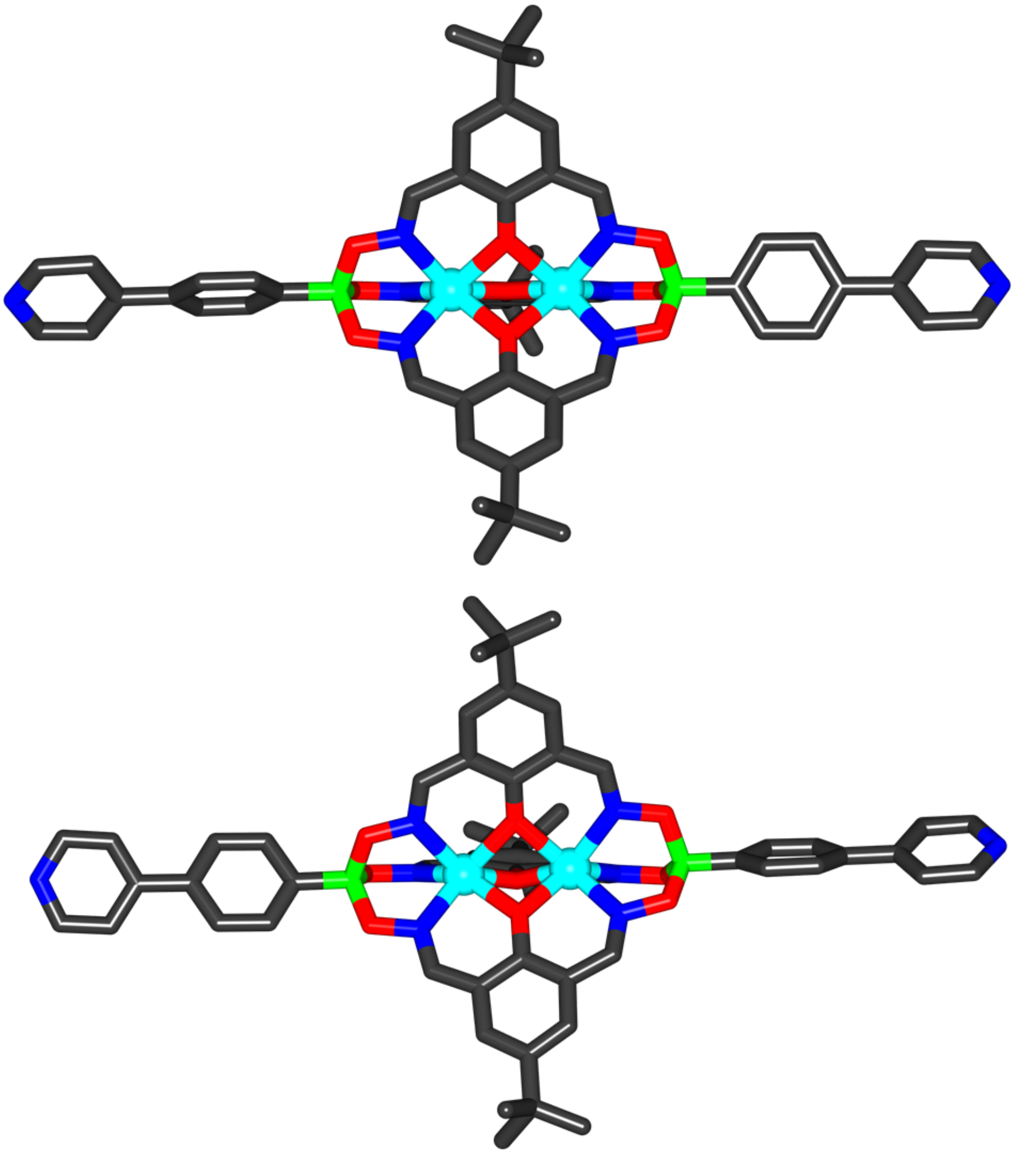


Figure S34– *Comparison between PBE0-optimized structure of* ***2a*** *(top) and its crystal structure (bottom). Hydrogen atoms, solvent molecules and* NEt_4^+ *counterion have been omitted for clarity. Color coding: C: gray; O: red; N: blue; B: green; Zn: cyan.*

	Experimental (XRD)	Calculated (PBE0)
Zn---Zn	2.970(1) Å	3.003 Å
(Zn---N)$_{av}$	2.127 Å	2.105 Å
(Zn---O)$_{av}$	2.121 Å	2.116 Å
B---B	9.217(2) Å	9.096 Å
N$_{py}$---N$_{py}$	26.711(7) Å	26.626 Å

Table S1 – *Comparison of selected bond lengths between PBE0-optimized structure of* ***2a*** *and its crystal structure.*

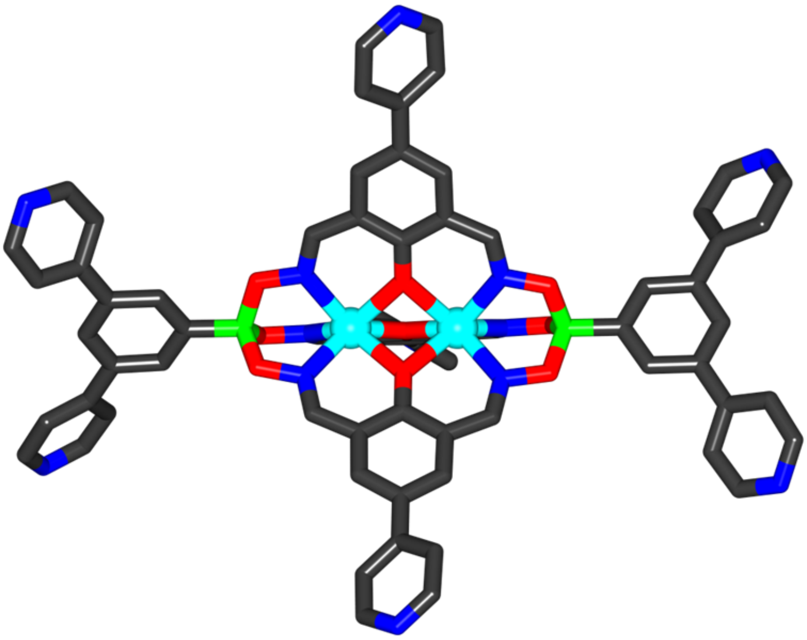


Figure S35– *Graphical representation of the PBE0-optimized structure for compound* ***13****. Hydrogen atoms, solvent molecules and* NEt_4^+ *have been omitted for clarity. Color coding: C: gray; O: red; N: blue; B: green; Zn: cyan*

	M06	**PBE0**	**D3-PBE0**
Zn---Zn	3.010 Å	3.014 Å	3.004 Å
$(Zn---N)_{av}$	2.097 Å	2.098 Å	2.095 Å
$(Zn---O)_{av}$	2.124 Å	2.121 Å	2.116 Å
B---B	9.084 Å	9.094 Å	9.078 Å
$(N_{lateral}---N_{lateral})_{av}$	17.260 Å	17.266 Å	17.254 Å

Table S2– *Comparison of selected bond lengths for the DFT-optimized structure of compound* ***13****, as obtained with three different DFT functionals (M06, PBE0 and D3-PBE0)*

5 Single-Crystal X-Ray Analyses

Intensity data for building block **11** was collected on a Rigaku SuperNova dual system in combination with an Atlas CCD detector and using Mo K_α radiation at 140(2) K. Intensity data for clathrochelates **2a** and **10a** were collected at the Swiss Norwegian beamline BM01A at the ESRF in Grenoble (France) using synchrotron radiation on the Pilatus@SNBL kappa goniometer from Huber Diffraktionstechnik GmbH equipped with a Pilatus2M pixel detector from Dectris Ltd. Data collection was performed at low temperature (100 K) using a Cryostream 700 Series from Oxford Cryosystems Ltd. Data integration was carried out using *CrysAlis Pro*.[9]

The solutions and refinements were performed by *SHELX*.[10] The crystal structures were refined using full-matrix least-squares based on F^2 with all non hydrogen atoms anisotropically defined. Hydrogen atoms were placed in calculated positions by means of the "riding" model. Additional electron density found in the difference Fourier map of compound **2a** and **11** was treated by the SQUEEZE algorithm of *PLATON*.[11] Intense disorder affected several moieties of crystal structure **2a** and tough restraints/constraints (involving SHELX commands: EADP, SIMU and SADI) were used to handle it.

Crystallographic data have been deposited with the CCDC no. 1453506−1453508. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. (fax, (internet.) +44-1223-336033; E-mail, deposit@ccdc.cam.ac.uk) or via www.ccdc.cam.ac.uk/data_request/cif.

Table S3. Crystallographic data of the clathrochelate ligands **2a**, **10a** and **11**

Structure, CCDC no.	**Ligand 2a, 1453506**	**Ligand 10a, 1453507**	**Ligand 11, 1453508**
Empirical formula	$C_{66}H_{75}B_2N_9O_9Zn_2$	$C_{57}H_{52}B_2N_{12}O_9Zn_2$	$C_{65}H_{50}B_2N_{11.50}O_9Zn_2$
Mol. Weight / g mol^{-1}	1290.71	1201.46	1288.52
Temperature / *K*	100(2)	100(2)	140(2)
Wavelength / Å	0.69791	0.69791	0.71073
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$C222_1$	$I2/a$
a / Å	17.9643(4)	16.9652(2)	24.0018(8)
b / Å	22.2539(9)	25.8649(2)	26.4540(8)
c / Å	20.8724(4)	14.10590(10)	25.9813(10))
α / °	90	90	90
β / °	108.065(2)	90	115.749(5)
γ / °	90	90	90
Volume / Å^3	7932.9(4)	6189.71(10)	14858.6(10)
Z	4	4	8
Density / g cm^{-3}	1.081	1.289	1.152
Absorption Coeff. / mm^{-1}	0.656	0.800	0.702
Crystal size / mm^3	0.500 x 0.400 x 0.300	0.500 x 0.150 x 0.150	0.361 x 0.254 x 0.193
Θ range / °	1.569 to 21.549	1.991 to 26.855	3.381 to 29.517
Index ranges	$-18 \leq h \leq 18$ $-22 \leq k \leq 18$ $-21 \leq l \leq 21$	$-21 \leq h \leq 20$ $-33 \leq k \leq 33$ $-18 \leq l \leq 17$	$-32 \leq h \leq 32$ $-34 \leq k \leq 36$ $-30 \leq l \leq 35$
Reflections collected	56549	46615	81462
Independent reflections	9262 [*R*(int) = 0.0901]	6700 [*R*(int) = 0.0536]	18615 [*R*(int) = 0.0396]
Completeness	95.7 % (to Θ = 21.549°)	99.3 % (to Θ = 24.755°)	99.7 % (to Θ = 25.242°)
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Analytical
Max. & min. transmission	1.00000 and 0.43991	0.889 and 0.6916	0.898 and 0.821
Data / restraints / parameters	9262 / 566 / 919	6700 / 0 / 376	18615 / 0 / 809
Goodness-of-fit on F^2	1.039	1.081	1.022
Final *R* indices [I > 2 s (I)]	*R*1 = 0.0834, w*R*2 = 0.2197	*R*1 = 0.0293, w*R*2 = 0.0819	*R*1 = 0.0492, w*R*2 = 0.1314
R indices (all data)	*R*1 = 0.0909, w*R*2 = 0.2267	*R*1 = 0.0293, w*R*2 = 0.0819	*R*1 = 0.0759, w*R*2 = 0.1508
Extinction coefficient	-	-	-
Larg. diff. peak/hole / eÅ^{-3}	1.333 and -1.031	0.32 and -0.34	1.393 and -0.476
Flack x (Parsons)	-	0.051(4)	-

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