Supplementary Information

Clathrochelate-Based Bipyridyl Ligands of Nanoscale Dimensions: Esay-to-Access Building Blocks for Supramolecular Chemistry

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1. General

All chemicals were obtained from commercial sources and used without further purification except octadecane-9,10-dione[1] and $ReCl(CO)_3(CH_3CN)_2$,[2] which were prepared according to literature procedures. Solvents were dried using a solvent purification system from Innovative Technologies, Inc. Reactions were carried out under an atmosphere of dry N_2 using standard Schlenk techniques, whilst chromatographic separations were performed in air. ^1H and ^{13}C NMR spectra were obtained on a Bruker Avance (^1H: 400 MHz, ^{13}C: 100 MHz). ^1H chemical shifts are reported in parts per million δ (ppm) referenced to the internal solvent. ^{13}C chemical shifts are reported in ppm and referenced to internal $CHCl_3$ (77.16 ppm). All spectra were recorded at RT. Electrospray-ionisation MS data were acquired on a Q-Tof Ultima mass spectrometer (Waters) operated in the positive 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 FT/IR spectrometer. Combustion analysis was performed with a Thermo Scientific Flash 2000 Organic Elemental Analyzer. Thermogravimetric analysis was performed on a Mettler-Toledo TGA/SDTA851^e equipped with a TSO800GC1 gas control unit. Data were collected using the STAR^e software and processed in Microsoft Excel. The sample was heated from 35°C to 750°C at a rate of 2°C per minute in an alumina crucible under a 60 $mLmin^{-1}$ flow of N_2.

2. Synthetic Procedures

Ligand 1

Nioxime (750 mg, 5.28 mmol), pyridin-4-ylboronic acid (541 mg, 4.40 mmol) and anhydrous $FeCl_2$ (335 mg, 2.64 mmol) were dissolved in MeOH (35 mL) and heated under reflux for 3 h under N_2. The deep red reaction mixture was concentrated to dryness on a rotary evaporator before being redissolved in a minimum volume of CH_2Cl_2 and passed through a silica plug (10% MeOH in CH_2Cl_2, approximately 100 mL). The resulting red

solution was transferred to a separatory funnel and washed with saturated aqueous $NaHCO_3$ (3 x 100 mL) and water (100 mL), dried ($MgSO_4$) and filtered before solvent was removed in vacuum to give an orange powder (1.610 g, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.56 (d, ^3J(H,H) = 6 Hz, 4H; Ar-NC*H*), 7.56 (d, ^3J(H,H) = 6 Hz, 4H; Ar-NCHC*H*), 2.94 (broad s, 12H; –C(NO)CH_2), 1.82 (broad s, 12H; –C(NO)CH_2CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ=152.52, 148.73, 126.95, 26.41, 21.66 (C-B not detected); HRMS (ESI): *m/z* calculated for $C_{28}H_{34}B_2FeN_8O_6$ $[M+2H]^{++}$ 328.1074, found 328.1060. X-ray quality single crystals of **1** were obtained by slow cooling of a concentrated toluene solution.

Ligand 2

Nioxime (850 mg, 6.09 mmol), pyridin-4-ylboronic acid (250 mg, 2.03 mmol), benzene-1,4-diboronic acid (165 mg, 1.01 mmol) and anhydrous $FeCl_2$ (258 mg, 2.03 mmol) were dissolved in MeOH (40 mL) and heated under reflux for 3 h under N_2 during which time a red precipitate of **2**·2HCl formed. The reaction mixture was allowed to cool to RT and the red precipitate isolated from the red solution by centrifugation. The pellet was washed repeatedly with MeOH to remove byproduct **1**·2HCl. Subsequently, the pellet was dissolved in $CHCl_3$ (100 mL), transferred to a separatory funnel and washed with saturated aqueous $NaHCO_3$ (3 x 100 mL) and water (100 mL), dried ($MgSO_4$) and filtered before solvent was removed in vacuum to give a red powder (385 mg, 31%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, ^3J(H,H) = 6 Hz, 4H; Ar-NC*H*), 7.70 (s, 4H; Ar-CH), 7.57 (d, ^3J(H,H) = 6 Hz, 4H; Ar-NCHC*H*), 2.97 (broad s, 24H; –C(NO)CH_2), 1.81 (broad s, 24H; –C(NO)CH_2CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.30, 151.82, 148.70, 130.85, 127.02, 26.44, 26.37, 21.75 (C-B not detected); HRMS (ESI): *m/z* calculated for $C_{52}H_{62}B_4Fe_2N_{14}O_{12}$ $[M+2H]^{++}$ 615.1888, found 615.1890. X-ray quality single crystals of **2**·2HCl were obtained by slow evaporation of a saturated CH_2Cl_2 solution of a sample which had not been washed with $NaHCO_3$.

Ligand 3

Nioxime (352 mg, 2.48 mmol), pyridin-4-ylboronic acid (100 mg, 0.82 mmol), 4,4'-biphenyldiboronic acid (100 mg, 0.42 mmol) and anhydrous $FeCl_2$ (104 mg, 0.82 mmol) were dissolved in MeOH (20 mL) and heated under reflux for 5 h under N_2 during which time a fine orange precipitate of **3**·2HCl formed. The reaction mixture was allowed to cool to RT and the precipitate isolated from the red solution by centrifugation. The pellet was

washed with MeOH to remove byproduct **1**·2HCl. Subsequently, a suspension of the pellet in a little MeOH was dissolved in $CHCl_3$ (250 mL), transferred to a separatory funnel and washed with saturated aqueous $NaHCO_3$ (3 x 250 mL) and water (250 mL), dried ($MgSO_4$) and filtered before solvent was removed in vacuum to give a red powder (148 mg, 27%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, ^3J(H,H) = 5 Hz, 4H; Ar-NC*H*), 7.77 (d, ^3J(H,H) = 8 Hz, 4H; Ar-CHC*H*), 7.62 (d, ^3J(H,H) = 8 Hz, 4H; Ar-C*H*), 7.58 (d, ^3J(H,H) = 5 Hz, 4H; Ar-NCHC*H*), 2.96 (24H, m, –C(NO)CH_2), 1.81 (broad s, 24H; –C(NO)CH_2CH_2); ^{13}C NMR ($CDCl_3$) δ 152.40, 152.04, 148.47, 141.21, 132.21, 127.11, 126.28, 26.46, 26.39, 21.69 (C-B not detected); HRMS (ESI): *m/z* calculated for $C_{58}H_{66}B_4Fe_2N_{14}O_{12}$ $[M+2H]^{++}$ 653.2046, found 653.2053.

Octadecane-9,10-dione dioxime

Octadecane-9,10-dione (2 g, 7.1 mmol) was dissolved in EtOH (100 mL) before addition of NaOH (848 mg, 21.2 mmol) and hydroxylamine (50% in water, 868 µL, 14 mmol). The resulting mixture was heated under reflux overnight. The reaction mixture was allowed to cool to RT before addition of water (200 mL) led to the formation of white precipitate. This solid was filtered, washed with water and pentane and dried under vacuum (1.1 g, 50%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (s, 2H; –O*H*), 2.58 (t, ^3J(H,H) = 8 Hz, 4H; –C(NOH)CH_2–), 1.51–1.45 (m, 4H; –C(NOH)CH_2CH_2–), 1.33–1.23 (m, 20 H; –CH_2–), 0.87 (t, ^3J(H,H) = 8 Hz, 6H; –CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.57, 32.02, 30.02, 29.54, 29.40, 26.66, 23.79, 22.82, 14.25 (C-B not detected); HRMS (ESI): *m/z* calculated for $C_{18}H_{37}N_2O_2$ $[M+H]^+$ 313.2855, found 313.2858.

Clathrochelate A

Octadecane-9,10-dione dioxime (500 mg, 1.6 mmol), pyridin-4-ylboronic acid (67 mg, 0.54 mmol), 4-ethynylphenylboronic acid (79 mg, 0.54 mmol) and anhydrous $FeCl_2$ (67 mg, 0.53 mmol) were dissolved in MeOH (50 mL) and heated under reflux overnight under N_2. The reaction mixture was allowed to cool to RT before the solvent was removed under vacuum. The residue was dissolved in $CHCl_3$ (50 mL) and extracted with water (3 x 50 mL). The organic phase was washed with brine (50 mL), dried (Na_2SO_4) and filtered before solvent was removed under vacuum. The resulting solid was purified by silica gel column chromatography (eluent 96:4 pentane: EtOAc) to give clathrochelate **A** as a viscous red oil (189 mg, 30%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, ^3J(H,H) = 5 Hz, 2H; Ar-NC*H*), 7.65

(d, ^{3}J(H,H) = 8 Hz, 2H; Ar-C(C≡CH)C*H*), 7.55 (d, ^{3}J(H,H) = 5 Hz, 2H; Ar-NCHC*H*), 7.47 (d, ^{3}J(H,H) = 8 Hz, 2H; Ar-C(C≡CH)CHC*H*), 3.04 (s, 1H; –C≡C*H*), 2.77 (t, ^{3}J(H,H) = 8 Hz, 12H; –C(NO)CH_2), 1.57–1.53 (m, 12H; –C(NO)CH$_2$CH_2), 1.27–1.21 (m, 60H; –CH_2–), 0.58 (t, ^{3}J(H,H) = 8 Hz, 18H; –CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.47, 157.20, 131.57, 131.09, 126.93, 120.98, 84.71, 31.95, 31.93, 29.44, 29.37, 29.33, 29.30, 27.48, 27.16, 22.78, 14.22 (C-B not detected); HRMS (ESI): *m/z* calculated for $C_{67}H_{112}B_2FeN_7O_6$ [*M*+H]$^{+}$ 1188.8232, found 1188.8208.

Clathrochelates B and C

Octadecane-9,10-dione dioxime (270 mg, 0.86 mmol), 4-iodoboronic acid (71 mg, 0.29 mmol), pyridin-4-ylboronic acid (36 mg, 0.29 mmol) and anhydrous $FeCl_2$ (36 mg, 0.29 mmol) were dissolved in MeOH (50 mL) and heated under reflux for 2 d under N_2. The reaction mixture was allowed to cool to RT before the solvent was removed under vacuum. The residue was dissolved in $CHCl_3$ (50 mL) and extracted with water (3 x 50 mL). The organic phase was washed with brine (50 mL), dried (Na_2SO_4) and filtered before solvent was removed under vacuum. The resulting solid was purified by silica gel column chromatography (eluent 96:4 pentane:EtOAc) to give clathrochelate **C** (first band, 107 mg, 26%) and clathrochelate **B** (second band, 105 mg, 28%) as viscous red oils.

Clathrochelate B

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, ^{3}J(H,H) = 6 Hz, 2H; Ar-NC*H*), 7.69 (d, ^{3}J(H,H) = 8 Hz, 2H; Ar-ClC*H*), 7.56 (d, ^{3}J(H,H) = 6 Hz, 2H; Ar-NCHC*H*), 7.43 (d, ^{3}J(H,H) = 8 Hz, 2H; Ar-ClCHC*H*), 2.78 (t, ^{3}J(H,H) = 8 Hz, 12H; –C(NO)CH_2), 1.59–1.51 (m, 12H; –C(NO)CH$_2$CH_2), 1.28–1.21 (m, 60 H; –CH_2–), 0.87 (t, ^{3}J(H,H) = 4 Hz, 18H; –CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.64, 157.38, 148.72, 136.53, 133.82, 126.99, 31.98, 31.94, 29.84, 29.46, 29.38, 29.35, 29.32, 27.48, 27.17, 22.81, 22.79, 14.27, 14.23 (C-B not detected); HRMS (ESI): *m/z* calculated for $C_{65}H_{111}B_2FeIN_7O_6$ [*M*+H]$^{+}$ 1290.7198, found 1290.7216.

Clathrochelate C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, ^{3}J(H,H) = 8 Hz, 4H; Ar-ClC*H*), 7.42 (d, ^{3}J(H,H) = 8 Hz, 4H; Ar-ClCHC*H*), 2.77 (t, ^{3}J(H,H) = 8 Hz, 12H; –C(NO)CH_2), 1.56–1.51 (m, 12H; –C(NO)CH$_2$CH_2), 1.25–1.21 (m, 60H; –CH_2–), 0.87 (t, ^{3}J(H,H) = 8 Hz, 18 H; –CH_3); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 157.26, 136.53, 133.88, 31.99, 29.84, 29.46, 29.39, 29.34, 27.49, 27.20, 22.85, 14.30 (C-B not detected); HRMS (ESI): *m/z* calculated for $C_{66}H_{111}B_2FeI_2N_6O_6$ $[M+H]^+$ 1415.6212, found 1415.6196.

Ligand 4

Clathrochelate **A** (46 mg, 0.039 mmol), clathrochelate **B** (50 mg 0.039 mmol), $Pd(PPh_3)_2Cl_2$ (6 mg, 8.57 μmol) and CuI (6 mg, 0.030 mmol) were dissolved in of diisopropylamine (10 mL) before DBN (0.5 mL) was added. The mixture was degassed with three cycles of N_2/vacuum and heated under reflux overnight. The reaction mixture was allowed to cool to RT before the solvent was removed under vacuum. The residue was dissolved in $CHCl_3$ (20 mL) and extracted with dilute HCl (3 x 20 mL). The organic phase was washed with brine (20 mL), dried (Na_2SO_4) and filtered before solvent was removed under vacuum. The resulting solid was purified by silica gel column chromatography (eluent 9:1 pentane:acetone) to give **4** as a viscous red oil (25 mg, 27%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, ^3J(H,H) = 5 Hz, 4H; Ar-NC*H*), 7.68 (d, ^3J(H,H) = 8 Hz, 4H; Ar-C(C≡C)C*H*), 7.57 (d, ^3J(H,H) = 5 Hz, 4H; Ar-NCHC*H*), 7.53 (d, ^3J(H,H) = 8 Hz, 4H; Ar-C(C≡C)CHC*H*), 2.80 (t, ^3J(H,H) = 8 Hz, 24H; –C(NO)CH_2), 1.58–1.52 (m, 24H; –C(NO)CH$_2$CH_2), 1.27–1.23 (m, 120H; –CH_2–), 0.90–8.85 (m, 36H; –CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.58, 157.32, 148.61, 131.68, 130.65, 127.03, 122.81, 89.92, 31.99, 31.94, 29.50, 29.46, 29.42, 29.38, 29.37, 29.32, 27.52, 27.47, 27.21, 27.18, 22.81, 22.79, 14.25, 14.22 (C-B not detected); HRMS (APPI): *m/z* calculated for $C_{132}H_{220}B_4Fe_2N_{14}O_{12}$ $[M]^+$ 2349.6280, found 2349.6164.

Ligand 5

Clathrochelate **A** (55 mg, 0.046 mmol), 1,4-diiodobenzene (8 mg, 0.024 mmol), $Pd(PPh_3)_2Cl_2$ (6 mg, 8.57 μmol) and CuI (6 mg, 0.03 mmol) were dissolved in diisopropylamine (10 mL) and DBN (0.5 mL) was added. The mixture was degassed with three cycles of N_2/vacuum and heated under reflux overnight. The reaction mixture was allowed to cool to RT before the solvent was removed under vacuum. The residue was dissolved in $CHCl_3$ (20 mL) and extracted with dilute HCl (3 x 20 mL). The organic phase was washed with brine (20 mL), dried (Na_2SO_4) and filtered before solvent was removed under vacuum. The resulting solid was purified by silica gel column chromatography (9:1 pentane:acetone) to give **5** as a viscous red oil (20 mg, 34%); ^{1}H NMR (400 MHz, $CDCl_3$)

δ 8.57 (d, ^3J(H,H) = 5 Hz, 4H; Ar-NC*H*), 7.69 (d, ^3J(H,H) = 8 Hz, 4H; Ar-C(C≡C)C*H*), 7.57 (d, ^3J(H,H) = 5 Hz, 4H; Ar-NCHC*H*), 7.53 (d, ^3J(H,H) = 8 Hz, 4H; Ar-C(C≡C)CHC*H*), 7.51 (s, 4H; Ar-C*H* middle ring), 2.80 (t, ^3J(H,H) = 8 Hz, 24H; –C(NO)CH_2), 1.59–1.55 (m, 24H; –C(NO)CH$_2$CH_2), 1.27–1.23 (m, 120H; –CH_2–), 0.90–0.85 (m, 36H; –CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.61, 157.35, 148.67, 131.74, 131.57, 130.66, 126.99, 123.52, 121.14, 92.45, 88.72, 32.00, 31.96, 29.49, 29.46, 29.41, 29.39, 29.37, 29.32, 27.53, 27.49, 27.22, 27.19, 22.82, 22.79, 14.26, 14.23 (C-B not detected); HRMS (APPI): *m/z* calculated for $C_{140}H_{226}B_4Fe_2N_{14}O_{12}$ $[M]^+$ 2449.64725, found 2449.65214.

Ligand 6

Clathrochelates **A** (46 mg, 0.039 mmol) and **C** (24 mg, 0.017 mmol), $PdCl_2(PPh_3)_2$ (6 mg, 8.57 μmol) and CuI (6 mg, 0.03 mmol) were dissolved in diisopropylamine (10 mL) before DBN (0.5 mL) was added. The mixture was degassed with three cycles of N_2/vacuum and heated under reflux overnight. The reaction mixture was allowed to cool to RT before the solvent was removed under vacuum. The residue was dissolved in $CHCl_3$ (20 mL) and extracted with dilute HCl (3 x 20 mL). The organic phase was washed with brine (20 mL), dried (Na_2SO_4) and filtered before solvent was removed under vacuum. The resulting solid was purified by silica gel column chromatography (eluent 9:1 pentane:acetone) to give **6** as a viscous red oil (23 mg, 38%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, ^3J(H,H) = 6 Hz, 4H; Ar-NC*H*), 7.64–7.62 (m, 8H; Ar-C(C≡C)C*H*), 7.50 (d, ^3J(H,H) = 6 Hz, 4H; Ar-NCHC*H*), 7.46 (d, ^3J(H,H) = 8 Hz, 8H; Ar-C(C≡C)CHC*H*), 2.74 (t, ^3J(H,H) = 8 Hz, 36H; –C(NO)CH_2), 1.53–1.50 (m, 36 H; –C(NO)CH$_2$CH_2), 1.20–1.17 (m, 180 H; –CH_2–), 0.83–0.80 (m, 54H; –CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.59, 157.31, 157.17, 148.52, 131.72, 131.69, 130.65, 127.06, 122.86, 122.74, 89.96, 89.84, 32.00, 31.94, 29.84, 29.51, 29.46, 29.43, 29.38, 29.33, 27.53, 27.49, 27.22, 27.19, 22.82, 22.80, 14.26, 14.23 (C-B not detected); HRMS (APPI): *m/z* calculated for $C_{200}H_{330}B_6Fe_3N_{20}O_{18}$ $[M]^+$ 3535.4274, found 3535.4234.

Complex 7

$ReCl(CO)_3(CH_3CN)_2Cl$ (38 mg, 0.967 mmol) and **1** (63 mg, 0.967 mmol) were dissolved in dry $CHCl_3$ (20 mL) and heated under reflux in the dark for 2 h under N_2. The volume of solvent was reduced under vacuum to 5 mL before, upon addition of petroleum ether, a

dark orange precipitate formed. The crude solid was dissolved in CH_2Cl_2 and purified by silica gel column chromatography (eluent 95:5 CH_2Cl_2:acetone). The orange fraction was collected and after the evaporation of the solvent an orange crystalline material was obtained. The fraction collected contains a mixture of two isomers. (65 mg, 70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (dd, J = 5, 1.7 Hz, 8H, Ar-NCH_{isomer1}), 8.65 (d, J = 6.5 Hz, 8H, Ar-NC$H_{isomer2}$), 7.54 (dd, J = 6.5, 5.0 Hz, 16H; Ar-NCHC$H_{isomer1+2}$), 2.91 (broad s, 48H; –C(NO)CH_2), 1.82 (broad s, 48H; –C(NO)CH_2CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.13, 193.25, 153.01, 152.25, 152.18, 128.81, 128.66, 26.46, 21.56 (C-B not detected); FT-IR υ_{max}/cm^{-1}: 2939(m), 2866(m), 2020(vs), 1908(vs), 1873(vs), 1615(m), 1584(m), 1434(s), 1389(s), 1233(s), 1201(vs), 1058(vs), 985(s), 939(vs), 860(s), 823(s), 808(s), 688(s), 582(m); Anal. calc. (%) for $Re_4Fe_4C_{124}H_{128}B_8Cl_4N_{32}O_{36}\times 1CH_2Cl_2$ (3923.97): C 38.1, H 3.3, N 11.3, found: C 38.2, H 3.3, N 11.4. X-ray quality, dark orange crystals were obtained by slow diffusion of diisopropyl ether into a solution of the complex in $CHCl_3$.

Coordination Polymer 8

The coordination polymer **8** was prepared in batches of multiple small reaction vessels in order to maximise the effective yield. These individual reactions were carried out as follows in a sealed vial. To a suspension of 4,4'-biphenyldicarboxylic acid (bpda, 32 mg, 0.132 mmol) and **1** (44 mg, 0.0672 mmol) in 20 mL of a 1:1 mixture of dimethylacetamide (DMA) and xylenes was added $Zn(NO_3)_2.6H_2O$ (0.800 mL of a 0.168 M solution in DMA). The resulting suspension was briefly sonicated before the vial was placed into an oil bath at 100°C and heated for 72h, after which time a red crystalline solid had formed. The vial was subsequently removed from the oil and allowed to cool to RT before the solvent was decanted off along with some loose amorphous precipitate. The crystals were washed with DMA (3 x 5 mL) before being isolated by filtration and dried in air to give [Zn_2(bpda)$_2$**1**(solv.)$_n$]. In order to obtain a solvent-free sample of **8** suitable for elemental analysis and calculation of yield, the crystals isolated from a single reaction vial were suspended in $CHCl_3$ for 4 d, the $CHCl_3$ being decanted off and replenished every 24 h. This sample was then dried under high vacuum for 3 d (94 mg, 72%); Anal. calc. (%) for $C_{56}H_{48}B_2FeN_8O_{14}Zn_2$ (1265.23): C 53.2, H 3.8, N 8.9, found: C 53.0, H 3.6, N 8.7. A sample of this dried material was digested in a 35% solution of DCl in D_2O (12 µL) in DMSO-d_6 (0.6 mL) and analyzed by ^{1}H NMR to confirm the stoichiometry and corroborate the elemental analysis (Figure S23); ^{1}H NMR (400 MHz) δ 8.86 (d, ^3J(H,H) = 7 Hz, 4H,

Ar-NC*H*), 8.15 (d, ^3J(H,H) = 7 Hz, 4H, Ar-NCHC*H*), 8.03 (d, ^3J(H,H) = 8 Hz, 8H, Ar-C(COOH)C*H*), 7.85 (d, ^3J(H,H) = 8 Hz, 8H, Ar–C(COOH)CHC*H*), 2.87 (broad s, 12H, –C(NO)CH_2), 1.74 (broad s, 12H, –C(NO)CH_2CH_2). X-ray quality single crystals of **8** were obtained by placing a vial prepared as above into an oil bath at RT before increasing the temperature to 100°C, removing the vial after 24h and immediately decanting off the supernatant solution before washing with fresh DMA.

3. Computational Modeling

Computational models were obtained by conformational search with molecular mechanics (MMFF force field) implemented in the software SciGress. A boron–boron distance across the clathrochelate complex of 5.978 Å (obtained from crystal structures of compounds **1** and **2**) was used as geometrical constraint. In order to decrease the computational cost, the octyl moieties of compounds **4–6** were replaced with methyl groups. The computational method was validated by using the crystal structures of **1** and **2** as a benchmark, comparing the calculated molecules' length with the length observed from X-ray diffractometry. In both these cases it was found that the difference between calculated and measured values was less than ±1%.

4. Single Crystal X-ray Analyses

Intensity data were collected using a Bruker APEX II CCD system (**1, 8**), or a marμx system (**2**, **7**), using graphite monochromatized Mo-K_α radiation (λ = 0.71073 Å) at low temperature. A summary of the crystallographic data, the data collection parameters, and the refinement parameters are given in Table S1. Data reduction was carried out with EvalCCD[3] and automar.[4] Structure solutions and refinements were performed by SHELX.[5] The structures were refined using the full-matrix least-squares routines on F^2. Additional electron density (due to highly disordered solvent molecules) found in the difference Fourier map was treated by the SQUEEZE algorithm of PLATON.[6] All non-hydrogen atoms were refined with anisotropic displacement parameters. H atoms were included to the models in calculated positions using the riding model. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Center (CCDC) as Supplementary Publication No. CCDC 899212 (**1**), 899213 (**2**), and 899211 (**7**), 919266 (**8**). Copies of the data can be

obtained free of charge on application to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. (fax, (internat.) +44-1223-336033; E-mail, deposit@ccdc.cam.ac.uk).

Complex	**1•2$C_6H_5CH_3$**	**2.2HCl•4CH_2Cl_2**	**7•8$CHCl_3$**	**8**
Empirical formula	$C_{42}H_{48}B_2FeN_8O_6$	$C_{56}H_{70}B_4Cl_{10}Fe_2N_{14}O_{12}$	$C_{132}H_{136}B_8Cl_{28}Fe_4N_{32}O_{36}Re_4$	$C_{56}H_{48}B_2FeN_8O_{14}Zn_2$
Mol. Weight / g mol^{-1}	838.35	1640.70	4794.01	1265.23
Crystal size / mm^3	0.44 x 0.12 x 0.12	0.32 x 0.25 x 0.20	0.40 x 0.35 x 0.16	0.41 x 0.33 x 0.23
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	*C*2/*c*	*P*-1	*P*-1	*C*2/*m*
a / Å	23.705(5)	10.235(5)	16.163(3)	24.166(4)
b / Å	9.3657(12)	10.862(4)	20.152(4)	18.520(4)
c / Å	20.454(3)	16.008(6)	20.252(4)	21.805(3)
α / °	90	97.163(18)	93.07(3)	90
β / °	118.680(9)	98.93(2)	90.55(3)	105.600(18)
γ / °	90	93.02(2)	110.44(3)	90
Volume / $Å^3$	3983.8(11)	1739.6(12)	6169(2)	9399(3)
Z	4	1	1	4
Density / g cm^{-3}	1.398	1.566	1.290	0.894
Temperature / *K*	100(2)	140(2)	140(2)	100(2)
Absorption Coeff. / mm^{-1}	0.439	0.870	2.542	0.703
Θ range / °	3.38 to 27.50	2.44 to 27.66	2.23 to 22.21	3.01 to 27.07
Index ranges	-30 → 30, -12 → 12, -26 → 26	-12 → 13, -14 → 14, -20 → 20	-17 → 17, -21 → 20, -21 → 21	-30 → 30, -23 → 23, -27 → 27
Reflections collected	23221	12176	24238	52494
Independent reflections	4570 (R_{int} = 0.0514)	7357 (R_{int} = 0.0594)	14339 (R_{int} = 0.0536)	10528 (R_{int} = 0.0894)
Absorption correction	Semi-empirical	None	None	Semi-empirical from equivalents
Max. & min. transmission	0.7456 and 0.5087			0.7455 and 0.5097
Data / restraints / param.	4570 / 0 / 267	7357 / 0 / 461	14339 / 714 / 1037	10528 / 0 / 478
Goodness-of-fit on F^2	1.110	1.111	0.973	1.067
Final *R* indices [I > 2 s (I)]	*R*1 = 0.0406, w*R*2 = 0.0794	*R*1 = 0.0728, w*R*2 = 0.1814	*R*1 = 0.0923, w*R*2 = 0.2546	*R*1 = 0.0954, w*R*2 = 0.2456
R indices (all data)	*R*1 = 0.0572, w*R*2 = 0.0865	*R*1 = 0.1076, w*R*2 = 0.2018	*R*1 = 0.1296, w*R*2 = 0.2787	*R*1 = 0.1093, w*R*2 = 0.2541
Larg. diff. peak/hole / e$Å^{-3}$	0.379 and -0.522	0.539 and -0.578	1.805 and -1.015	1.706 and -2.815

Table S1. Crystallographic data for **1**, **2**, **7** and **8**.

5. NMR Spectra

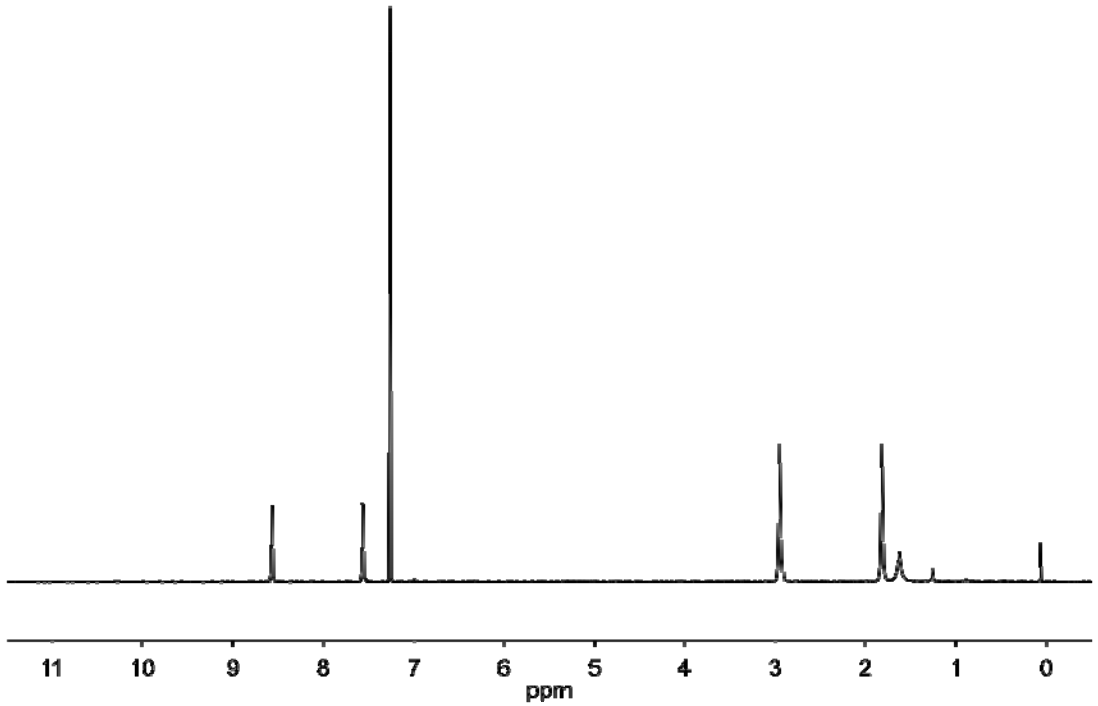

Figure S1. ^{1}H NMR spectrum of **1**.

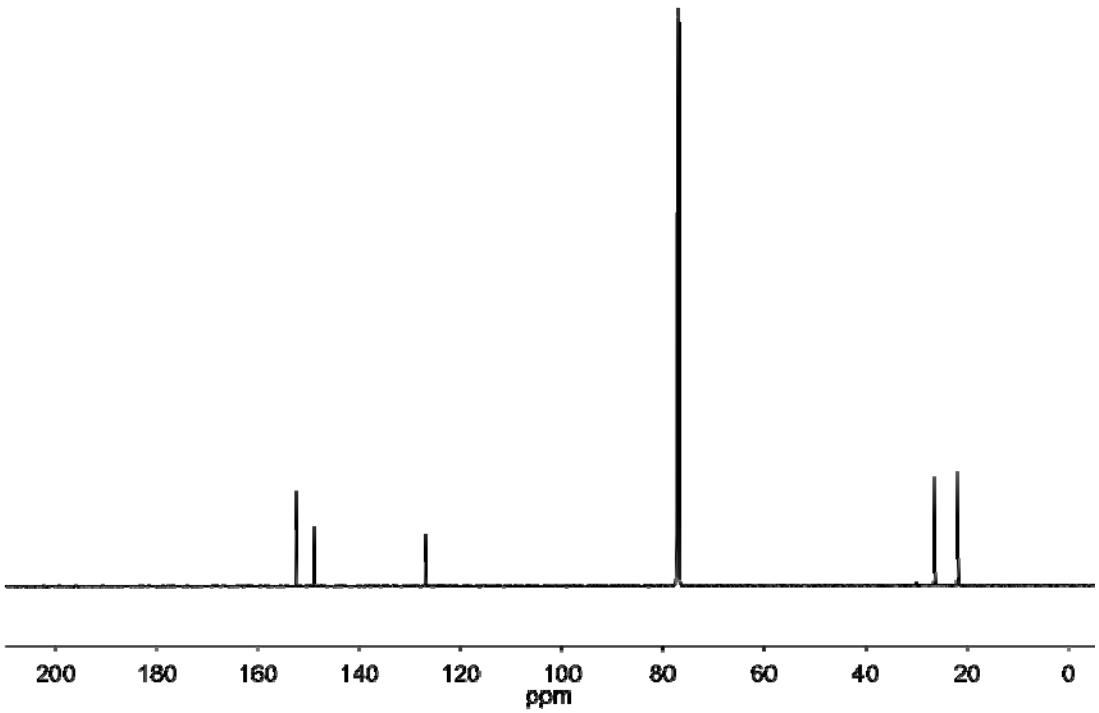

Figure S2. ^{13}C NMR spectrum of **1**.

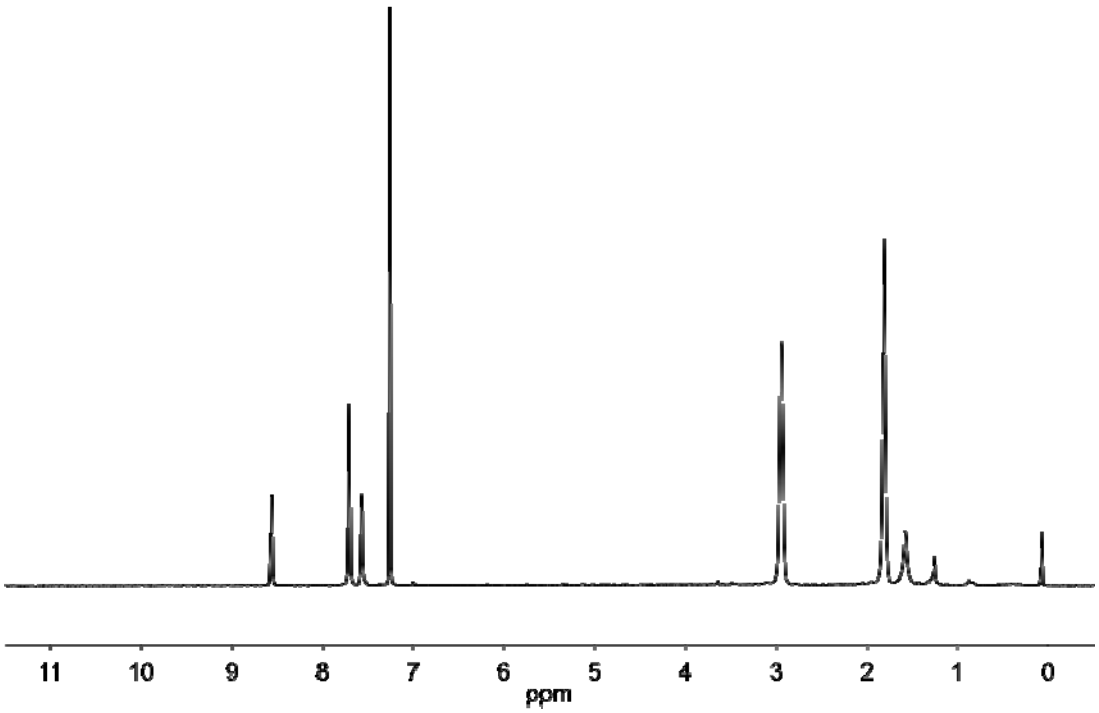

Figure S3. ^{1}H NMR spectrum of **2**.

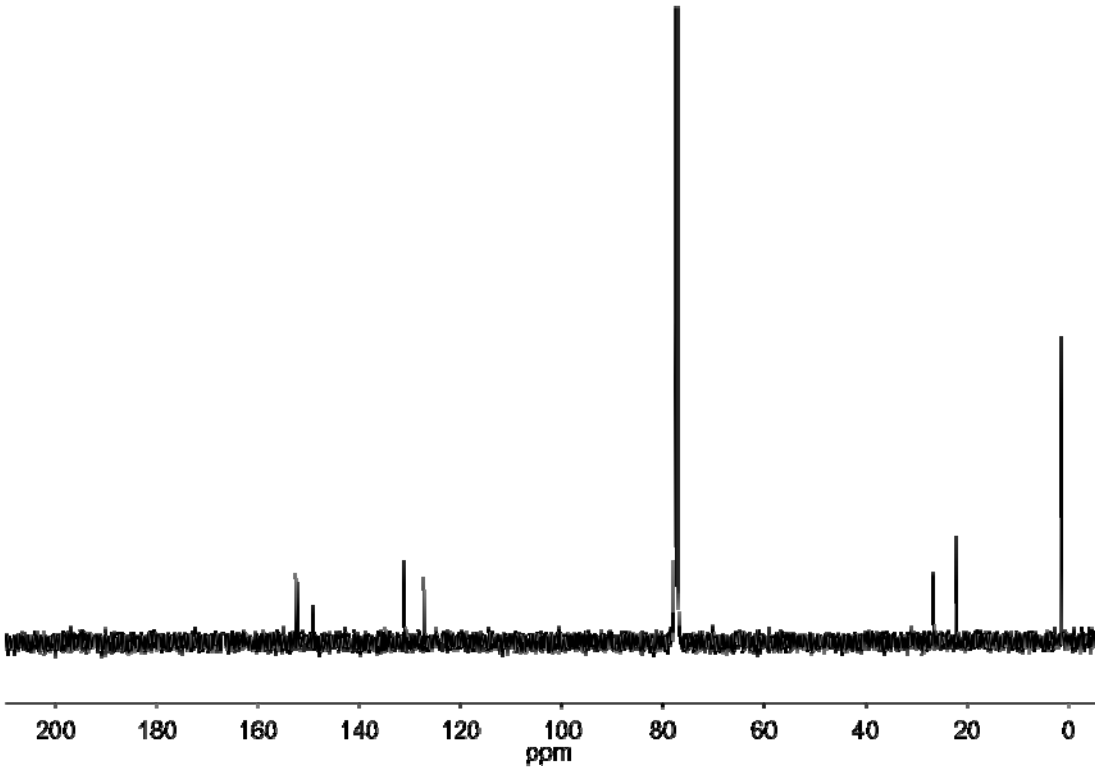

Figure S4. ^{13}C NMR spectrum of **2**.

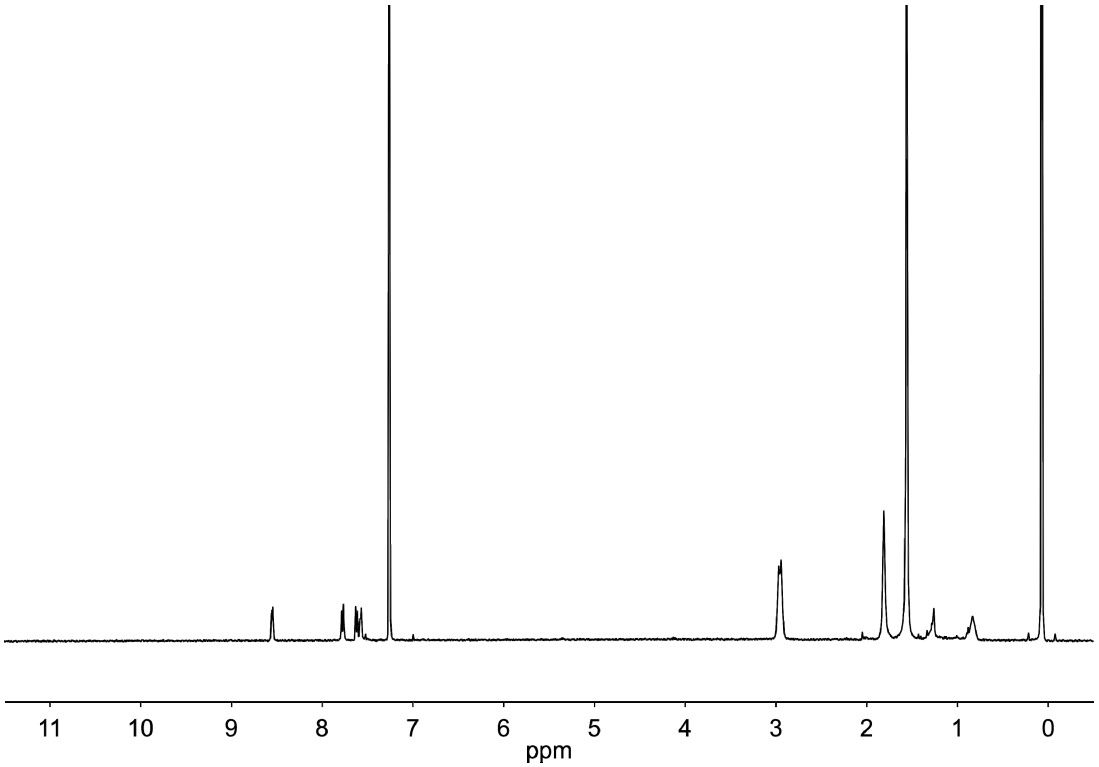

Figure S5. ^{1}H NMR spectrum of **3**.

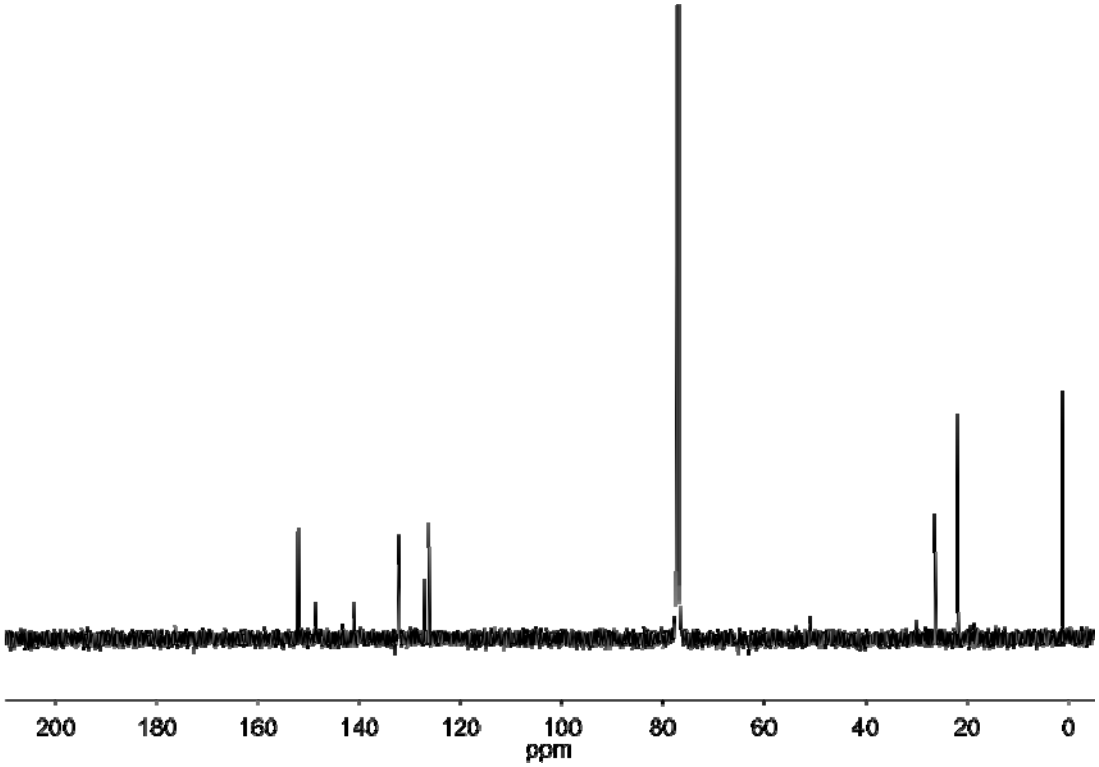

Figure S6. ^{13}C NMR spectrum of **3**.

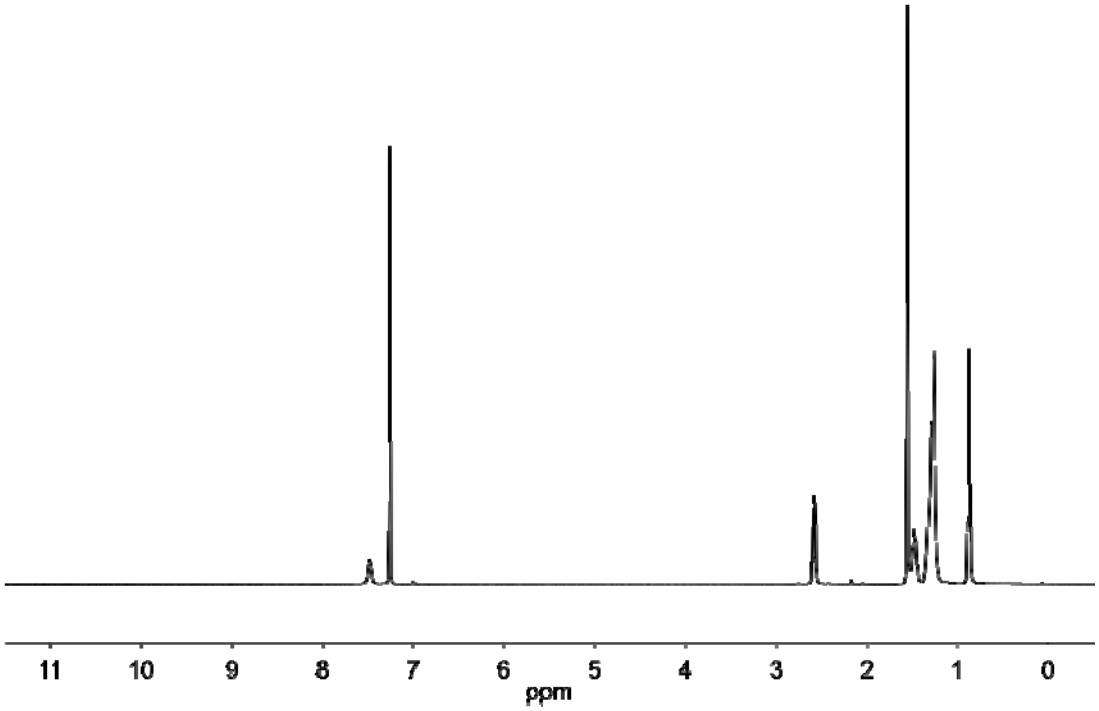

Figure S7. ^{1}H NMR spectrum of octadecane-9,10-dione dioxime.

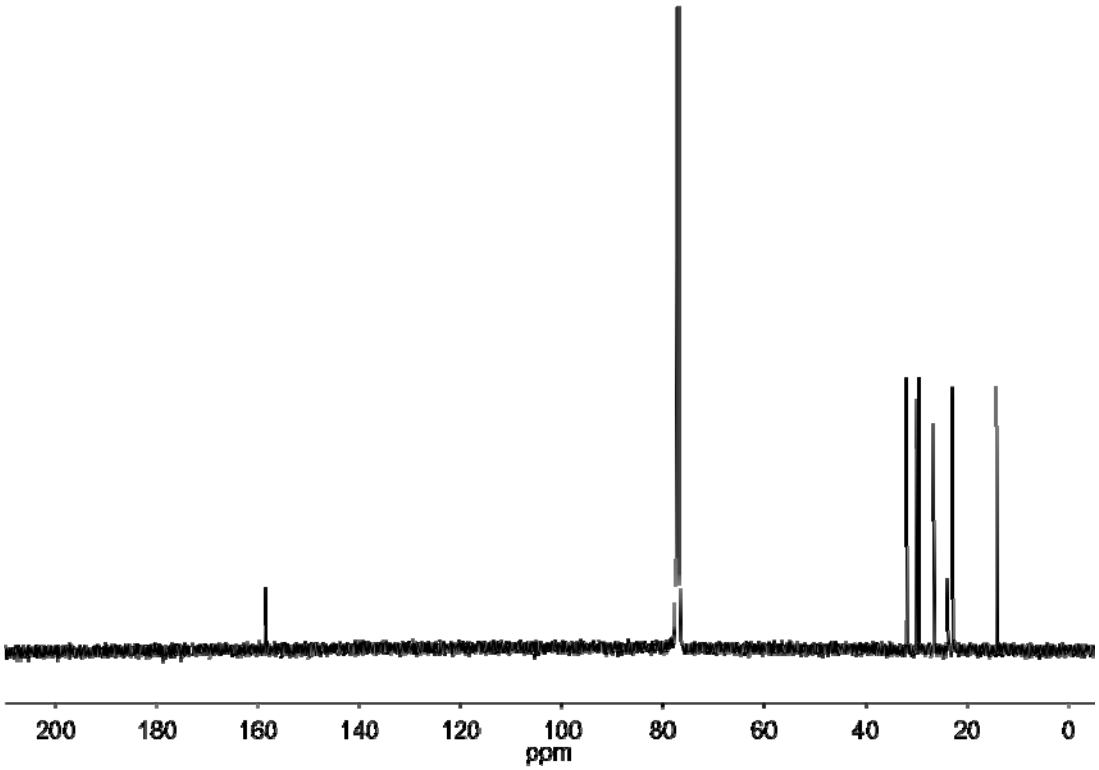

Figure S8. ^{13}C NMR spectrum of octadecane-9,10-dione dioxime.

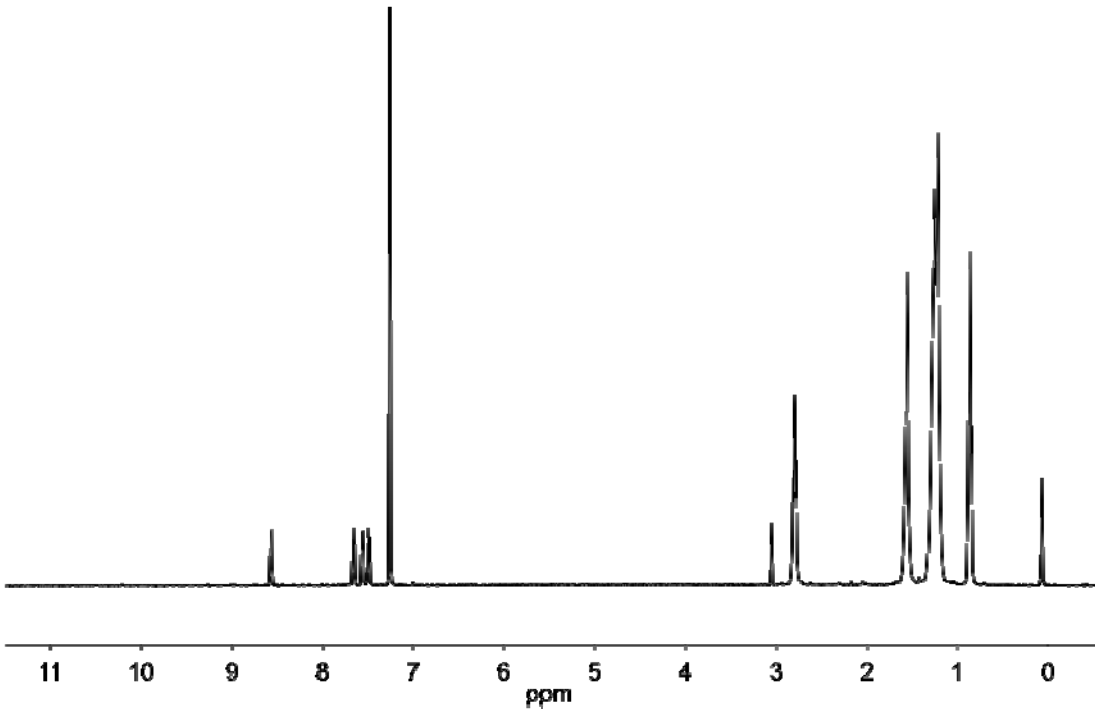

Figure S9. ^{1}H NMR spectrum of clathrochelate **A**.

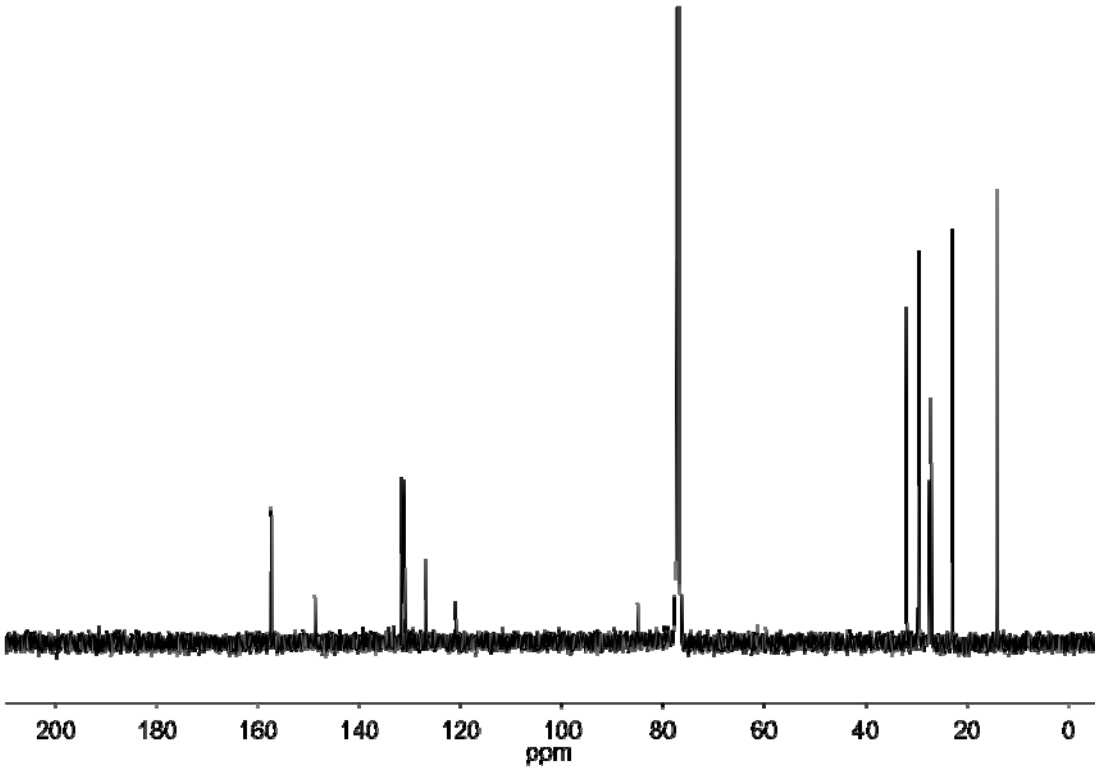

Figure S10. ^{13}C NMR spectrum of clathrochelate **A**.

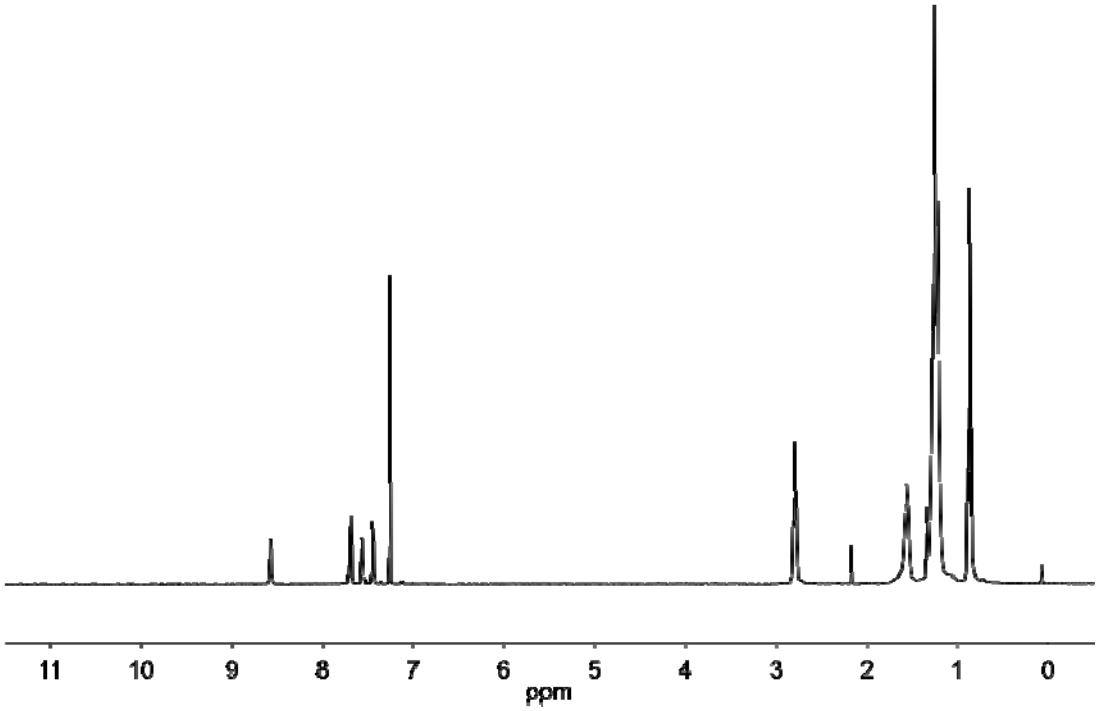

Figure S11. ^{1}H NMR spectrum of clathrochelate **B**.

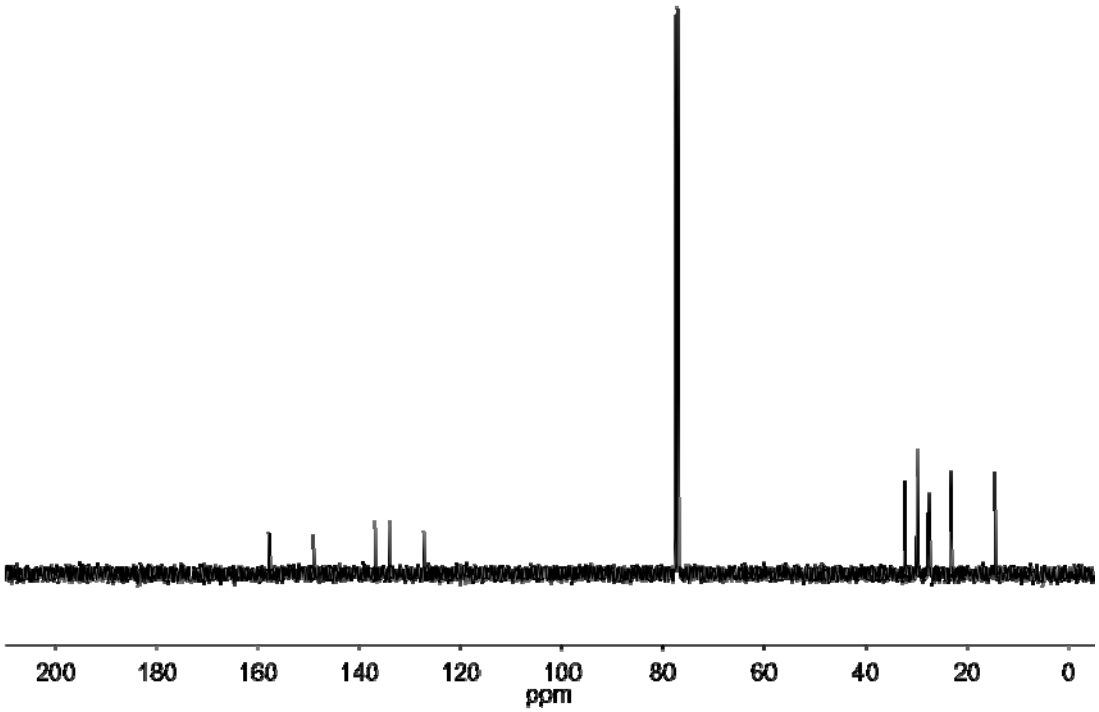

Figure S12. ^{13}C NMR spectrum of clathrochelate **B**.

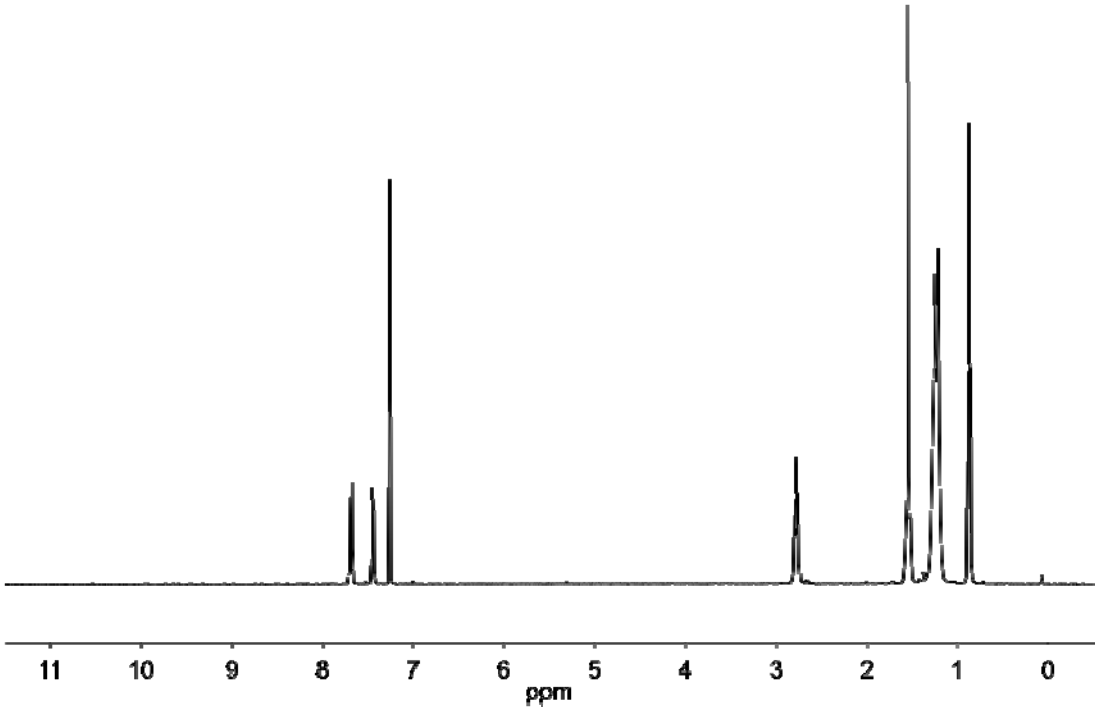

Figure S13. ^{1}H NMR spectrum of clathrochelate **C**.

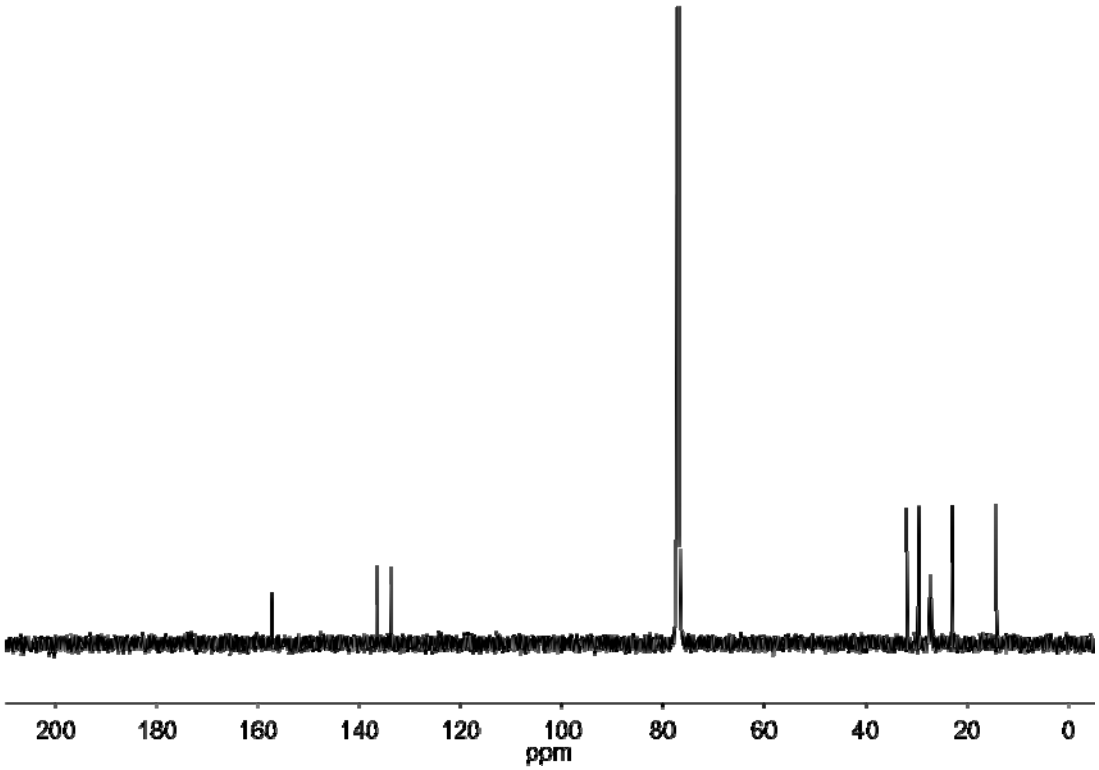

Figure S14. ^{13}C NMR spectrum of clathrochelate **C**.

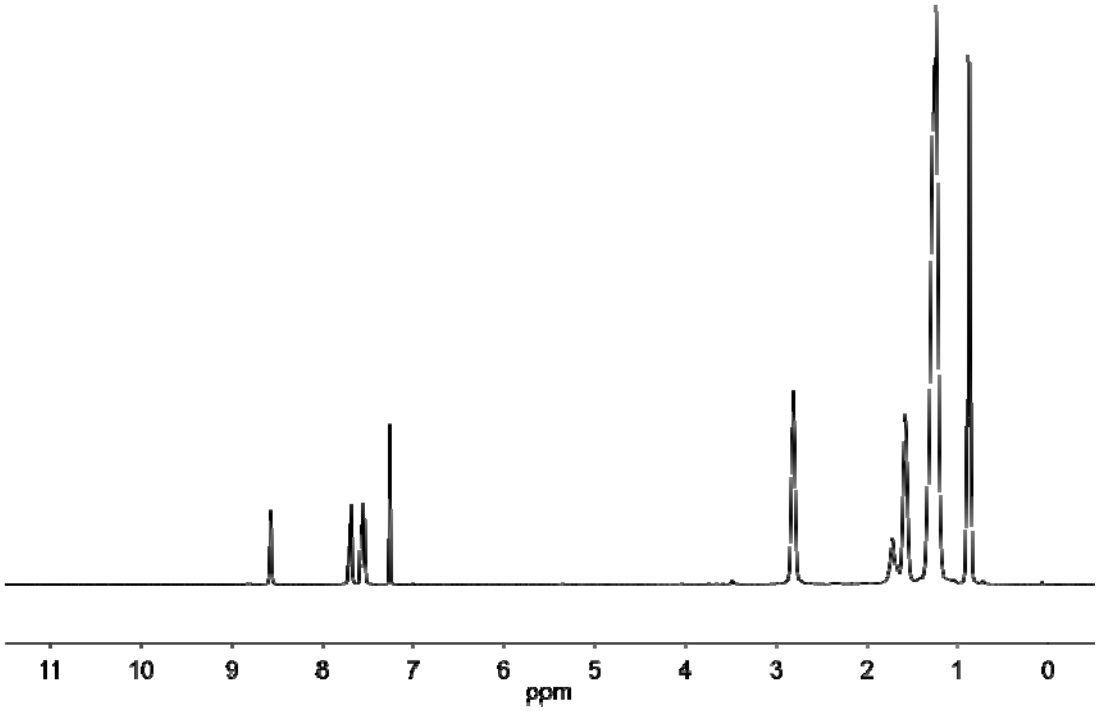

Figure S15. ^{1}H NMR spectrum of **4**.

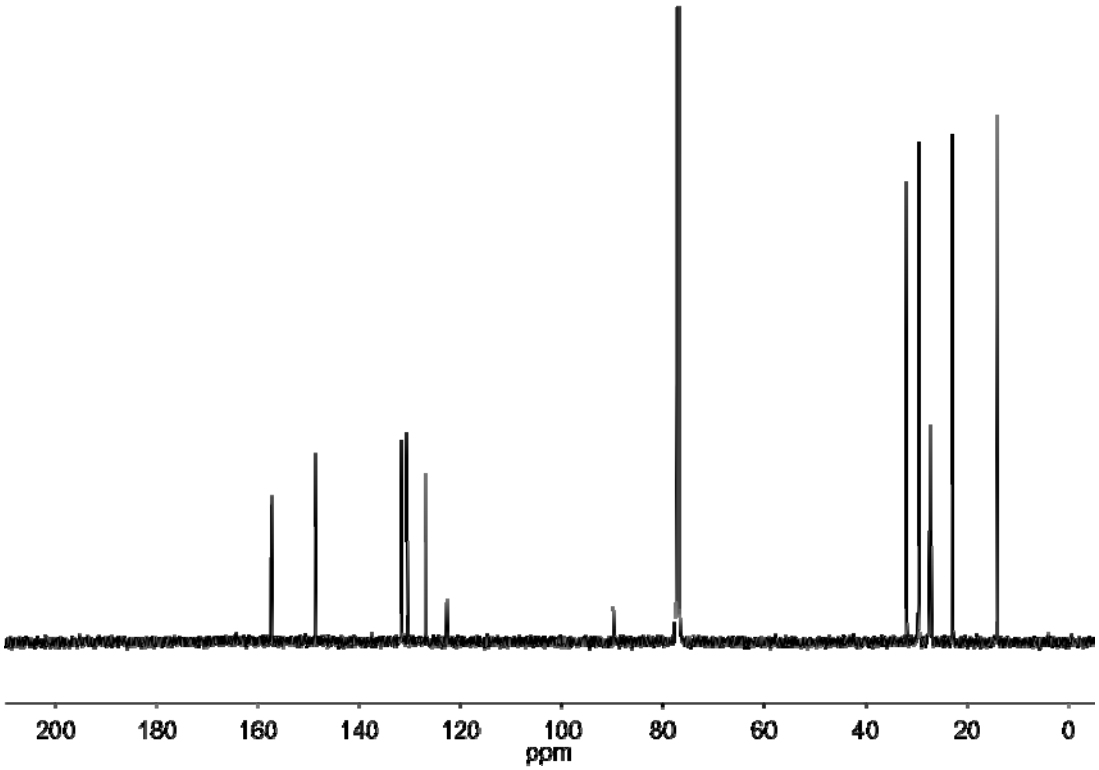

Figure S16. ^{13}C NMR spectrum of **4**.

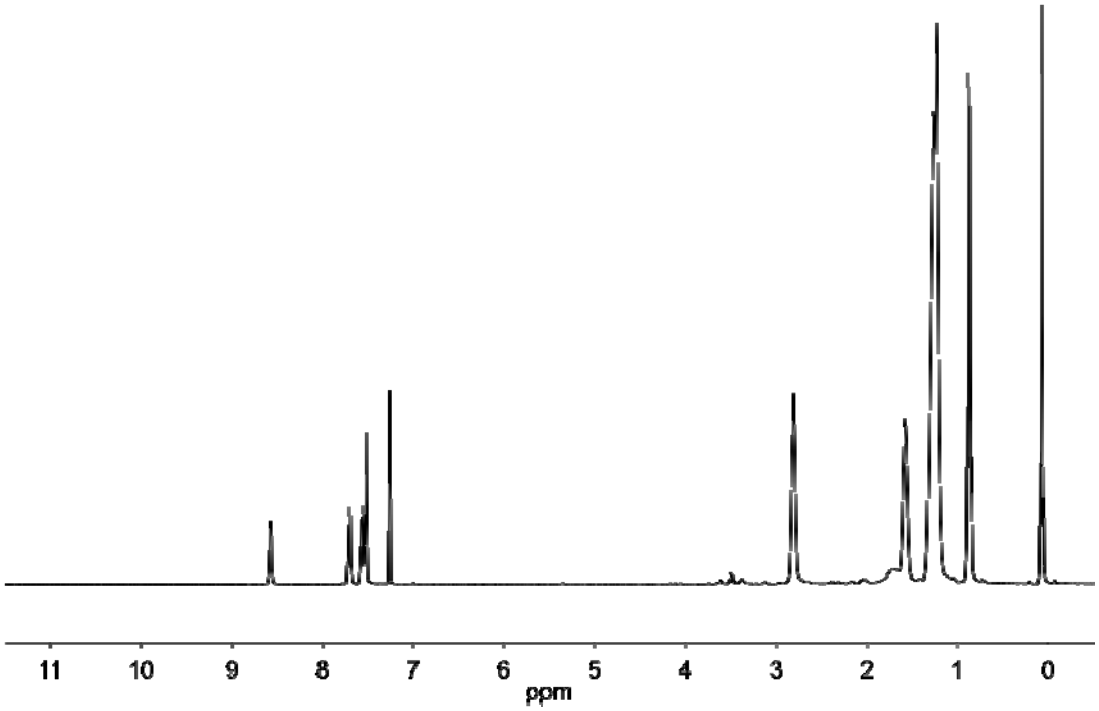

Figure S17. ^{1}H NMR spectrum of **5**.

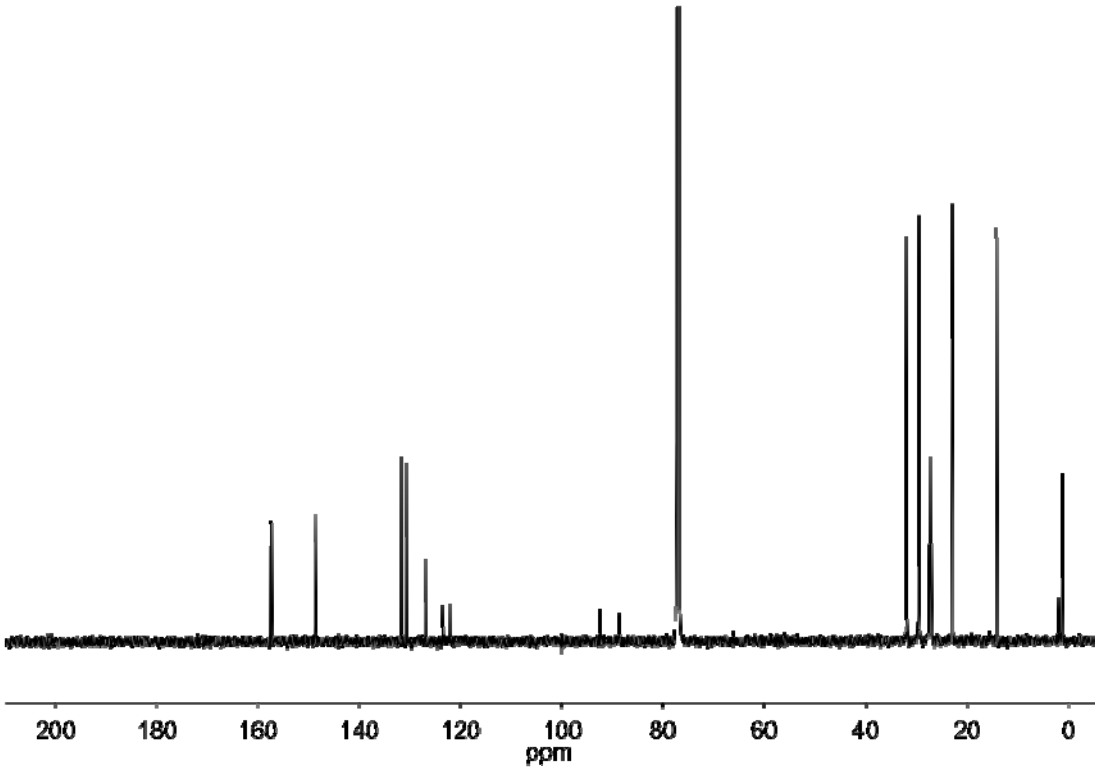

Figure S18. ^{13}C NMR spectrum of **5**.

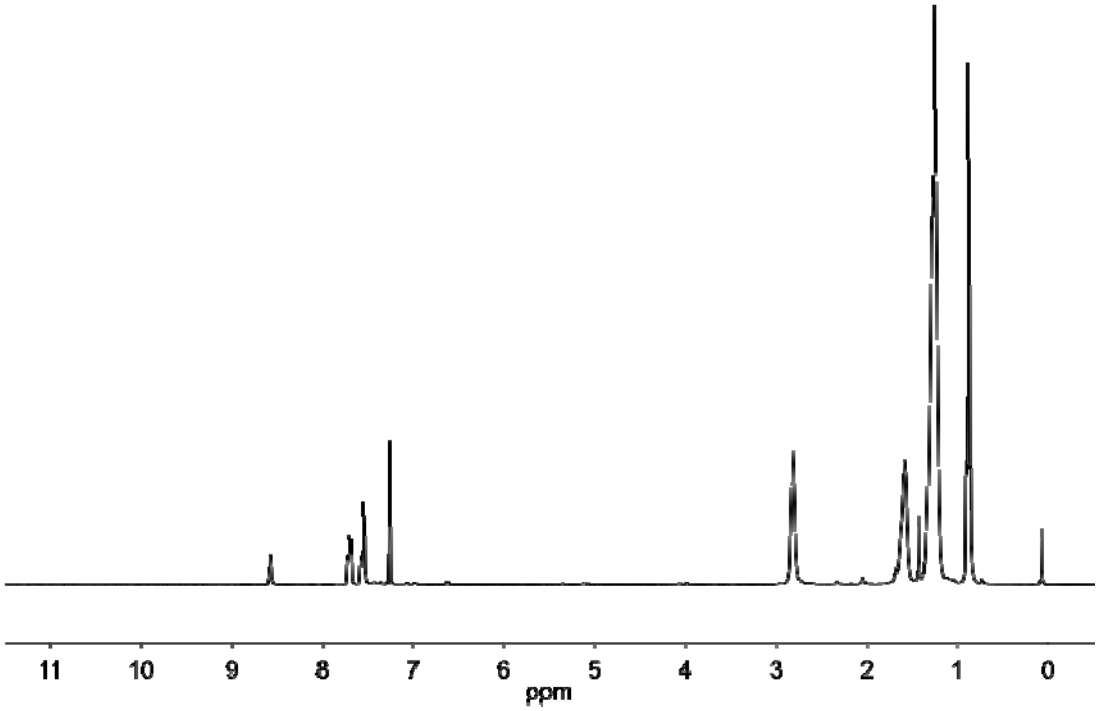

Figure S19. ^{1}H NMR spectrum of **6**.

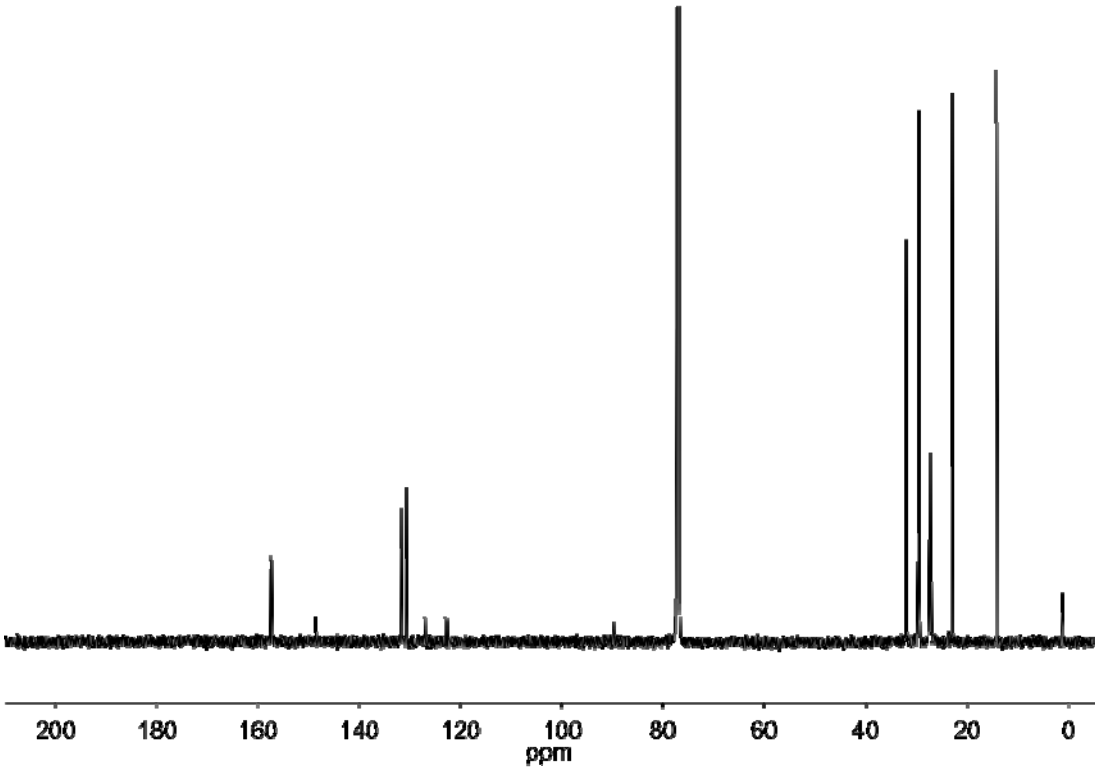

Figure S20. ^{13}C NMR spectrum of **6**.

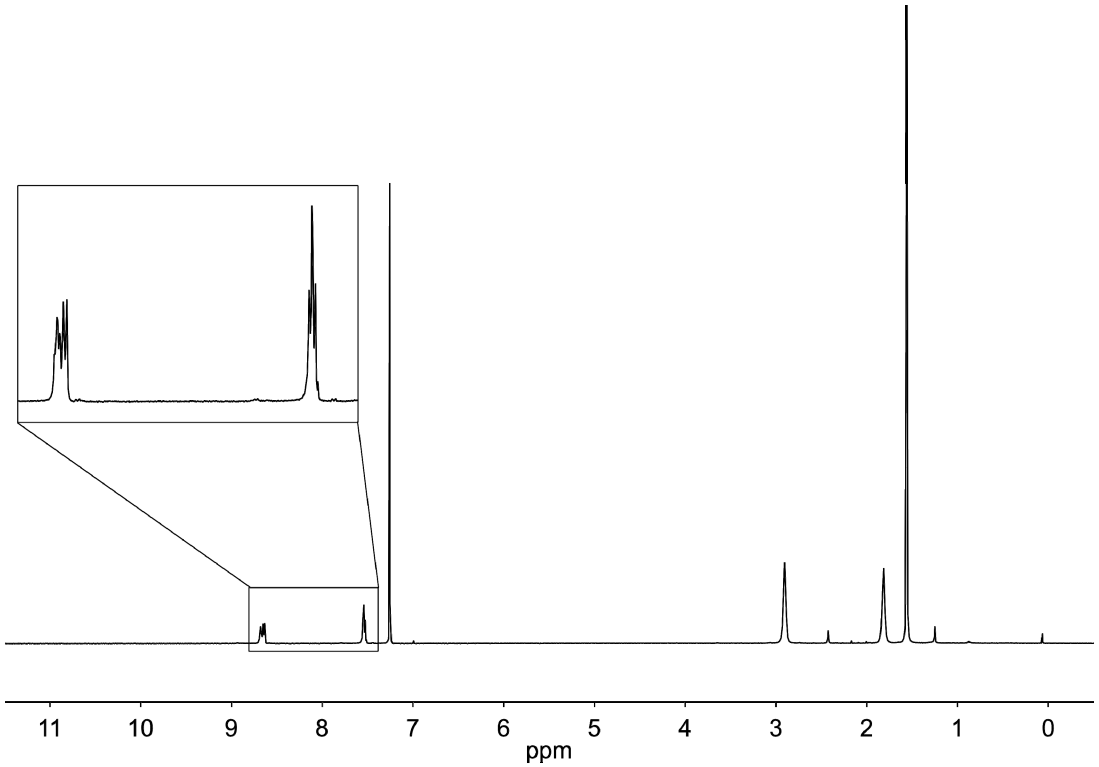

Figure S21. ^{1}H NMR spectrum of complex **7**. The inset shows a detailed view of the signals of the pyridyl protons, which reveal the presence of isomers.

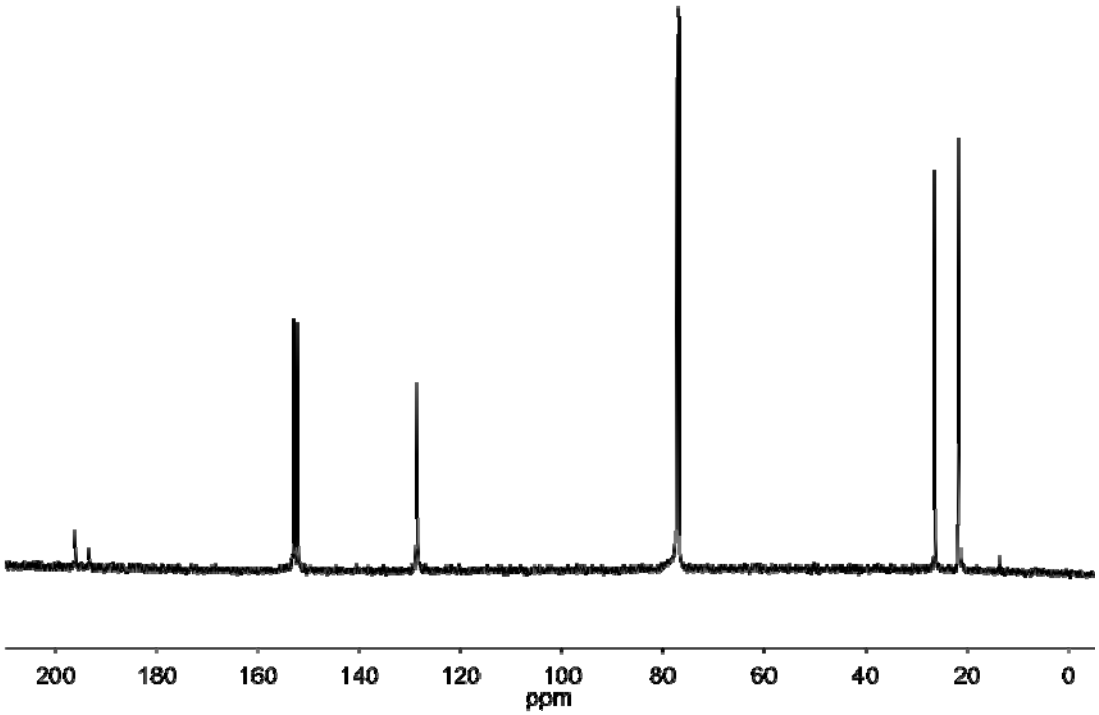

Figure S22. ^{13}C NMR spectrum of complex **7**.

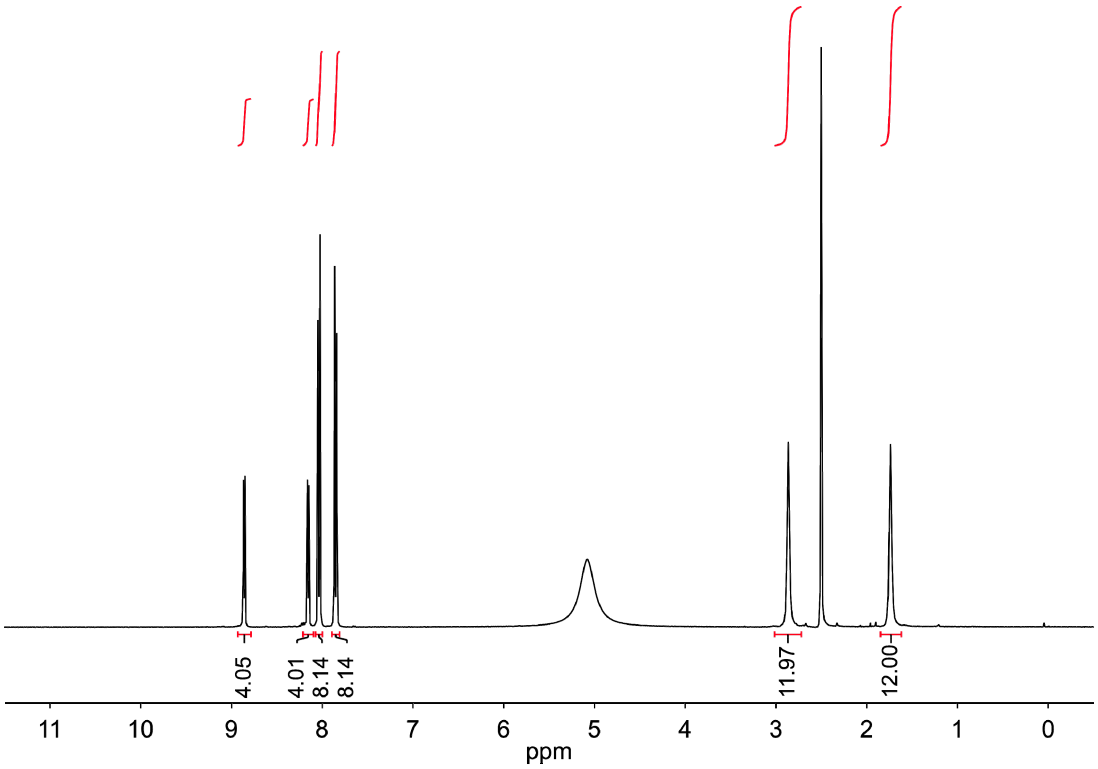

Figure S23. ^{1}H NMR (DMSO-d_6) spectrum of an acid-digested sample of **8** confirming the 1:2 ratio of **1**:bpda, as well as the absence of intercalated solvent, corroborating the elemental analysis results.

6. Thermogravimetric Analysis

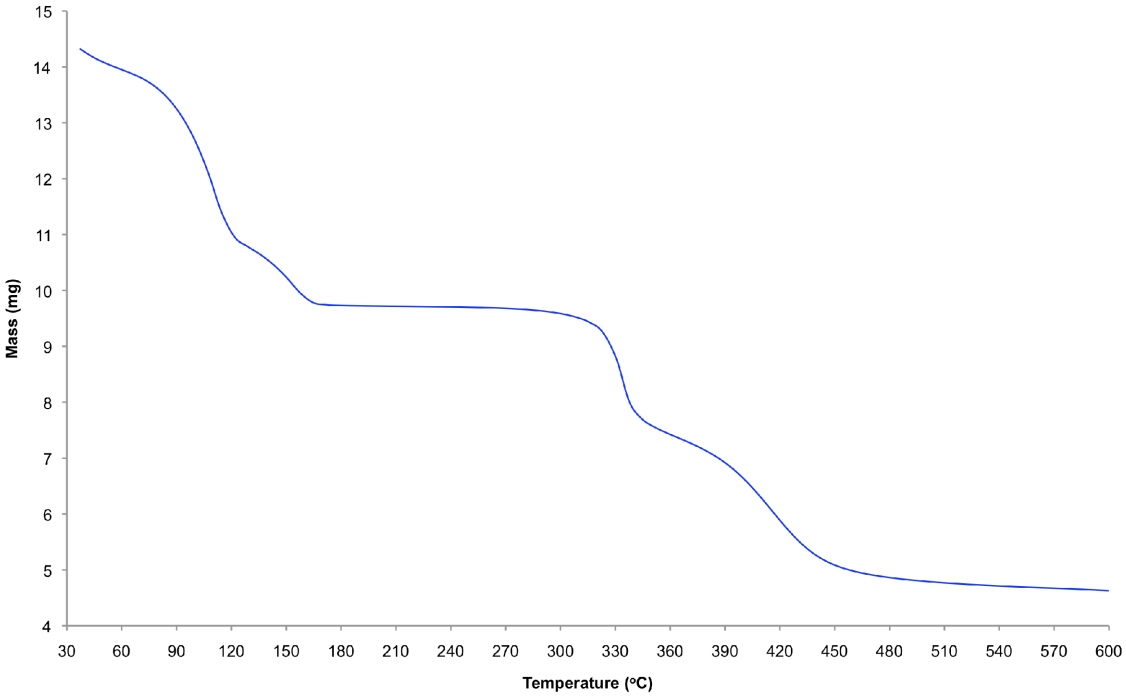

Figure S23. TGA trace for an as-made sample of **8** washed with DMA showing loss of volatile components (extrinsic and intercalated solvent) at 35<T<165°C and framework decomposition at T>300°C.

7. References

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