Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Control over the macrocyclisation pathway and product topology in a copper-templated catenane synthesis

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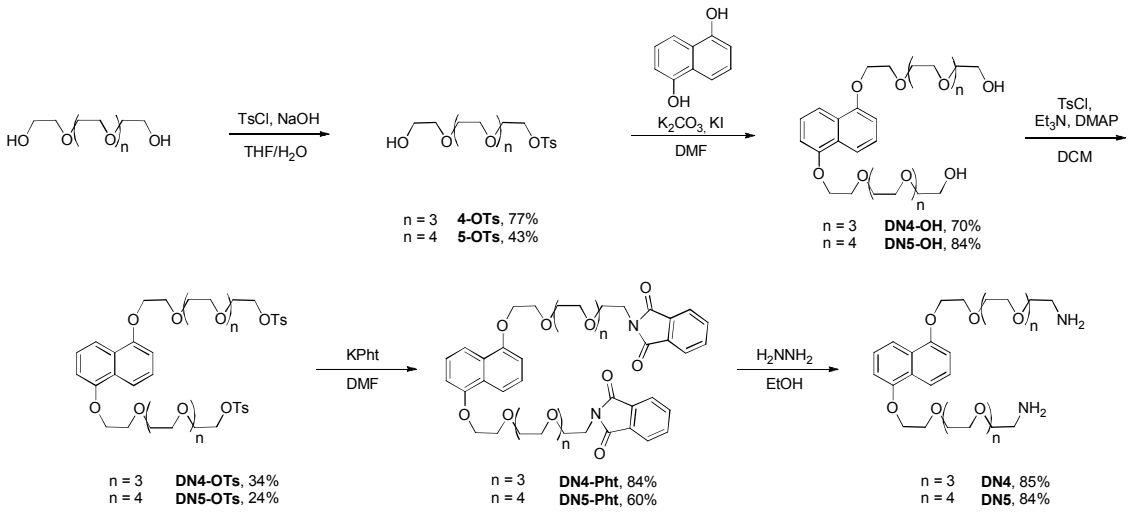
1. Synthesis

General. All reagents were purchased from commercial suppliers (Aldrich, Acros, Dkmchem and J&K) and used without further purification. All the solvents for synthesis were of analytical grade (ACI Labscan and DUKSAN Pure Chemicals). MeCN, $CHCl_3$ and MeOH were distilled over CaH_2 before use. **DN1**,[S1] **DN2**,[S2] **DN3**,[S3] **L**,[S4] **Phen-OTs**,[S4] **S1-OTs**[S5] and cucurbit[6]uril (CB[6])[S6] were synthesized according to literature procedures. Microwave-assisted reactions were carried out using a Discover SP microwave synthesizer (CEM, USA) in the closed vessel mode. Thin layer chromatography (TLC) was performed on silica gel 60 F254 (Merck, Germany, Aluminium sheet) and column chromatography was carried out on silica gel 60F (Silicycle, Canada). HPLC analyses were carried out using a Waters-Alliance e2695 system coupled to a 2489 UV/Vis detector. ESI-MS were carried out using a Waters-Acquity UPLC H-Class system coupled with a QDa MS detector. NMR spectra were recorded on Bruker DPX spectrometers with working frequencies of 300 MHz, 400 MHz, 500 or 600 MHz for ^{1}H, and 75 MHz, 100 MHz, 125 MHz or 150 MHz for ^{13}C, respectively. Chemical shifts are reported in ppm and referenced to solvent residues (For ^{1}H: $CDCl_3$: δ = 7.26 ppm, d_6-DMSO: δ = 2.50 ppm, D_2O: δ = 4.79 ppm, CD_3CN: δ = 1.94 ppm; For ^{13}C: $CDCl_3$: δ = 77.16 ppm, d_6-DMSO: δ = 39.52 ppm, CD_3CN: δ = 118.26 ppm).

A. Building blocks synthesis



Scheme S1. Synthesis of **DN4** and **DN5**.

4-OTs. A mixture of pentaethylene glycol (1.00 g, 4.2 mmol) and NaOH (0.20 g, 5.0 mmol) in THF/H_2O (v:v 5:1, 30 mL) was stirred at room temperature for 10 min. The mixture was then cooled to 0 °C in an ice bath and a solution of TsCl (0.80 g, 4.2 mmol) in THF (30 mL) was added dropwisely over 2 hr and stirred for overnight at room temperature. The solvent was removed by a rotary evaporator and the residue was dissolved in CH_2Cl_2 (50 mL), washed with water and brine, dried over $MgSO_4$, filtered and concentrated to afford a light-yellow oil. The light yellow oil was purified on a silica column (EtOAc/hexane = 3:2) to afford the product. Yield = 1.27 g, 77%. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ = 7.80 (d, *J* = 7.5 Hz, 2 H), 7.34 (d, *J* = 7.5 Hz, 2 H), 4.16 (t, *J* = 6.0 Hz, 2 H), 3.75–3.51 (m, 18 H), 2.44 (s, 3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ = 144.9, 133.0, 129.9, 128.0, 72.7, 70.5, 69.3, 68.7, 61.7, 21.6. ESI-MS: 393.5 $[M+H]^+$.

5-OTs. A mixture of hexaethylene glycol (2.50 g, 8.9 mmol) and NaOH (0.43 g, 10.7 mmol) in THF/H_2O (v:v 5:1, 60 mL) was stirred at room temperature for 10 min. The mixture was then cooled to 0 °C in an ice bath and a solution of TsCl (1.70 g, 8.9 mmol) in THF (60 mL) was added dropwisely over 2 hr and stirred for overnight at room temperature. The solvent was removed by a rotary evaporator and the residue was dissolved in CH_2Cl_2 (50 mL), washed with water and brine, dried over $MgSO_4$, filtered and concentrated to afford a light-yellow oil. The light yellow oil was purified on a silica column (EtOAc/hexane = 3:2) to afford the product. Yield = 1.67 g, 43%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 7.79 (d, *J* = 8.0 Hz, 2 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 4.15 (t, *J* = 6.0 Hz, 2 H), 3.75–3.50 (m, 22 H), 2.44 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ = 144.3, 132.4, 129.4, 127.3, 72.0, 70.0, 69.9, 68.9, 68.0, 60.9, 21.0. ESI-MS: 436.5 $[M+H]^+$.

DN4-OH. A mixture of 1,5-dihydroxynaphthalene (0.18 g, 1.2 mmol), **4-OTs** (1.00 g, 2.6 mmol), K_2CO_3 (0.67 g, 4.8 mmol) and KI (40 mg, 0.24 mmol) in dry DMF (20 mL) was heated at 100 °C for overnight. Insoluble materials were removed by filtration and the solvent was removed by a rotary evaporator. The residue was partitioned between $CHCl_3$ (50 mL) and 0.5 M NaOH (50 mL). The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (2 x 50 mL). The organic fractions were combined, washed by brine, dried over $MgSO_4$, filtered and concentrated to afford a dark oil which was used in the next step

without further purification. Yield = 0.51 g, 70%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 7.85 (d, *J* = 8.0 Hz, 2 H), 7.34 (t, *J* = 8.0 Hz, 2 H), 6.84 (d, *J* = 8.0 Hz, 2 H), 4.29 (t, *J* = 4.0 Hz, 4 H), 3.99 (t, *J* = 4.0 Hz, 4 H), 3.80 (t, *J* = 4.0 Hz, 4 H), 3.71–3.65 (m, 24 H), 3.57 (t, *J* = 4.0 Hz, 4 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ = 154.0, 126.5, 124.9, 114.3, 105.5, 72.5, 71.0, 70.6, 70.3, 70.2, 70.1, 69.8, 69.5, 67.6, 61.2. ESI-MS: 601.3 $[M+H]^+$, 623.1 $[M+Na]^+$.

DN5-OH. A mixture of 1,5-dihydroxynapthalene (0.18 g, 1.2 mmol), **5-OTs** (1.10 g, 2.5 mmol), K_2CO_3 (0.67 g, 4.8 mmol) and KI (0.04 g, 0.24 mmol) in dry DMF (20 mL) was heated at 100 °C for overnight. Insoluble materials were removed by filtration and the solvent was removed by a rotary evaporator. The residue was partitioned between $CHCl_3$ (50 mL) and 0.5 M NaOH (50 mL). The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (2 x 50 mL). The organic fractions were combined, washed by brine, dried over $MgSO_4$, filtered and concentrated to afford a dark oil which was used in the next step without further purification. Yield = 0.69 g, 84%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 7.85 (d, *J* = 8.0 Hz, 2 H), 7.33 (t, *J* = 8.0 Hz, 2 H), 6.83 (d, *J* = 8.0 Hz, 2 H), 4.28 (t, *J* = 4.0 Hz, 4 H), 3.99 (t, *J* = 4.0 Hz, 4 H), 3.79 (t, *J* = 4.0 Hz, 4 H), 3.70–3.67 (m, 8 H), 3.66–3.63 (m, 24 H), 3.57 (t, *J* = 4.0 Hz, 4 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ = 154.3, 126.7, 125.1, 114.6, 105.6, 77.4, 72.5, 71.3, 70.9, 70.7, 70.6, 70.5, 70.5, 70.3, 69.8, 67.9, 61.6. ESI-MS: 688.4 $[M+H]^+$, 710.4 $[M+Na]^+$.

DN4-OTs. A mixture of **DN4-OH** (0.50 g, 0.8 mmol), Et_3N (0.18 g, 1.8 mmol), 4-(dimethylamino)pyridine (5 mg, 0.04 mmol) in CH_2Cl_2 (10 mL) was stirred at 0 °C. A solution of TsCl (0.33 g, 1.8 mmol) in CH_2Cl_2 (20 mL) was added dropwisely over 2 hr at 0 °C. The reaction mixture was stirred for overnight at room temperature. Insoluble materials were removed by filtration and the solvent was removed by a rotary evaporator. The residue was partitioned between CH_2Cl_2 (50 mL) and H_2O (50 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 50 mL). The combined organic fraction was washed with brine (20 mL), dried over $MgSO_4$, filtered and concentrated to afford light-yellow oil. The light yellow oil was purified on a silica column (EtOAc/hexane = 4:1) to afford the product. Yield = 0.26 g, 34%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 7.83 (d, *J* = 8.0 Hz, 2 H), 7.75 (d, *J* = 8.0 Hz), 7.30–7.28 (m, 6 H), 6.81 (d, *J* = 8.0 Hz, 2 H), 4.26 (t, *J* = 4.0 Hz, 4 H),

4.11 (t, *J* = 4.0 Hz, 4 H), 3.96 (t, *J* = 4.0 Hz, 4 H), 3.77 (t, *J* = 4.0 Hz, 4 H), 3.66 (t, *J* = 4.0 Hz, 4 H), 3.63–3.61 (m, 8 H), 3.59 (t, *J* = 4.0 Hz, 4 H), 3.58–3.52 (m, 8 H), 2.39 (s, 6 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) δ = 154.3, 144.8, 133.0, 129.8, 128.0, 126.8, 125.1, 114.6, 105.7, 71.0, 70.7, 70.6, 70.5, 69.8, 69.3, 68.6, 67.9, 21.6. ESI-MS: 909.3 $[M+H]^+$, 931.3 $[M+Na]^+$.

DN5-OTs. A mixture of **DN5-OH** (0.69 g, 1.0 mmol), Et_3N (0.21 g, 2.1 mmol), 4-(dimethylamino)pyridine (5 mg, 0.04 mmol) in CH_2Cl_2 (10 mL) was stirred at 0 °C. A solution of TsCl (0.40 g, 2.1 mmol) in CH_2Cl_2 (20 mL) was added dropwisely over 2 hr at 0 °C. The reaction mixture was stirred for overnight at room temperature. Insoluble materials were removed by filtration and the solvent was removed by a rotary evaporator. The residue was partitioned between CH_2Cl_2 (50 mL) and H_2O (50 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 50 mL). The combined organic fraction was washed with brine (20 mL), dried over $MgSO_4$, filtered and concentrated to afford light-yellow oil. The light yellow oil was purified on a silica column (EtOAc/hexane = 4:1) to afford the product. Yield = 0.24 g, 24%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 7.82 (d, *J* = 8.0 Hz, 2 H), 7.75 (d, *J* = 8.0 Hz, 4 H), 7.33–7.28 (m, 6 H), 6.80 (d, *J* = 8.0 Hz, 2 H), 4.25 (t, *J* = 4.0 Hz, 4 H), 4.11 (t, *J* = 4.0 Hz, 4 H), 3.96 (t, *J* = 4.0 Hz, 4 H), 3.78 (t, *J* = 4.0 Hz, 4 H), 3.75–3.55 (m, 32 H), 2.39 (s, 6 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) δ = 154.3, 144.7, 132.9, 129.8, 127.9, 126.7, 125.1, 114.6, 105.6, 71.0, 70.7, 70.6, 70.5, 69.8, 69.3, 68.6, 67.9, 21.6. ESI-MS: 996.3 $[M+H]^+$, 1018.3 $[M+Na]^+$.

DN4-Pht. A mixture of **DN4-OTs** (0.26 g, 0.3 mmol), potassium phthalimide (0.13 g 0.7 mmol) in dry DMF (10 mL) was heated to 100 °C for overnight. Solvent was removed by a rotary evaporator. The residue was partitioned between CH_2Cl_2 (50 mL) and H_2O (50 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 50 mL). The combined organic fraction was washed with brine (20 mL), dried over $MgSO_4$, filtered and concentrated to afford a deep yellow oil. The deep yellow oil was purified on a silica column (EtOAc/hexane = 4:1) to afford the product as a light-yellow oil. Yield = 0.20 g, 84%. $^{1}HNMR$ (400 MHz, $CDCl_3$, 298 K) δ = 7.83 (d, *J* = 8.0 Hz, 2 H), 7.80 (d, *J* = 8.0 Hz, 4 H), 7.68 (d, *J* = 8.0 Hz, 4 H), 7.32 (t, *J* = 8.0 Hz, 2 H), 6.82 (d, *J* = 8.0 Hz, 2 H), 4.27 (t, *J* = 4.0 Hz, 4 H), 3.97 (t, *J* = 4.0 Hz, 4 H), 3.87 (t, *J* = 4.0 Hz, 4 H), 3.77 (t, *J* = 4.0 Hz, 4 H), 3.71 (t, *J* = 4.0 Hz, 4 H),

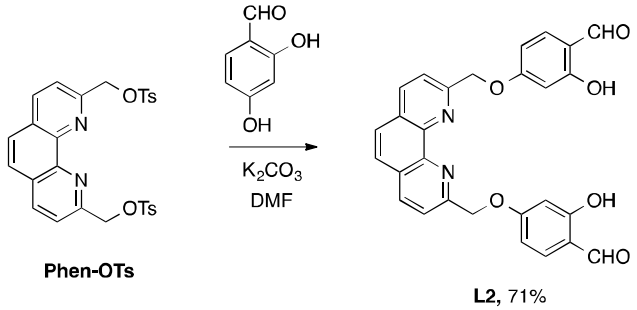
3.67 (t, *J* = 4.0 Hz, 4 H), 3.64–3.59 (m, 16 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) δ = 168.3, 154.4, 134.0, 132.2, 126.8, 125.1, 123.3, 114.7, 105.7, 71.0, 70.7, 70.6, 70.1, 69.9, 68.0, 37.3. ESI-MS: 881.7 $[M+Na]^+$.

DN5-Pht. A mixture of **DN5-OTs** (0.29 g, 0.3 mmol), potassium phthalimide (0.13 g 0.7 mmol) in dry DMF (10 mL) was heated to 100 °C for overnight. Solvent was removed by a rotary evaporator. The residue was partitioned between CH_2Cl_2 (50 mL) and H_2O (50 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 50 mL). The combined organic fraction was washed with brine (20 mL), dried over $MgSO_4$, filtered and concentrated to afford a deep yellow oil. The deep yellow oil was purified on a silica column (EtOAc/hexane = 4:1) to afford the product as a light-yellow oil. Yield = 0.17 g, 60%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 7.79 (d, *J* = 8.0 Hz, 2 H), 7.77 (d, *J* = 8.0 Hz, 4 H), 7.63 (d, *J* = 8.0 Hz, 4 H), 7.28 (t, *J* = 8.0 Hz, 2 H), 6.78 (d, *J* = 8.0 Hz, 2 H), 4.24 (t, *J* = 4.0 Hz, 4 H), 3.95 (t, *J* = 4.0 Hz, 4 H), 3.83 (t, *J* = 4.0 Hz, 4 H), 3.75 (t, *J* = 4.0 Hz, 4 H), 3.69–3.52 (m, 32 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) δ = 168.2, 154.2, 133.7, 132.2, 126.7, 125.1, 123.1, 114.5, 105.6, 70.9, 70.6, 70.5, 70.0, 69.8, 67.8, 37.2. ESI-MS: 969.6 $[M+Na]^+$.

DN4. A mixture of **DN4-Pht** (0.58 g, 0.7 mmol) and hydrazine hydrate (1 mL) in EtOH (50 mL) was heated to reflux for 4 hr. Insoluble materials were removed by filtration and solvent was removed by a rotary evaporator. The residue was dissolved in CH_2Cl_2 (50 mL), filtered, and the organic solvent was removed by a rotary evaporator to afford the product. Yield = 0.34 g, 85%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 7.83 (d, *J* = 8.0 Hz, 2 H), 7.32 (t, *J* = 8.0 Hz, 2 H), 6.82 (d, *J* = 8.0 Hz, 2 H), 4.27 (t, *J* = 4.0 Hz, 4 H), 3.97 (t, *J* = 4.0 Hz, 4 H), 3.78 (t, *J* = 4.0 Hz, 4 H), 3.67 (t, *J* = 4.0 Hz, 4 H), 3.66–3.62 (m, 8 H), 3.60 (t, *J* = 4.0 Hz, 4 H), 3.58 (t, *J* = 4.0 Hz, 4 H), 3.45 (t, *J* = 4.0 Hz, 4 H), 2.81 (t, *J* = 4.0 Hz, 4 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) δ = 154.4, 126.8, 125.2, 114.7, 105.7, 73.3, 71.2, 70.8, 70.7, 70.6, 70.6, 70.3, 69.9, 68.0, 41.7. ESI-MS: 300.2 $[M+2H]^{2+}$, 599.2 $[M+H]^+$.

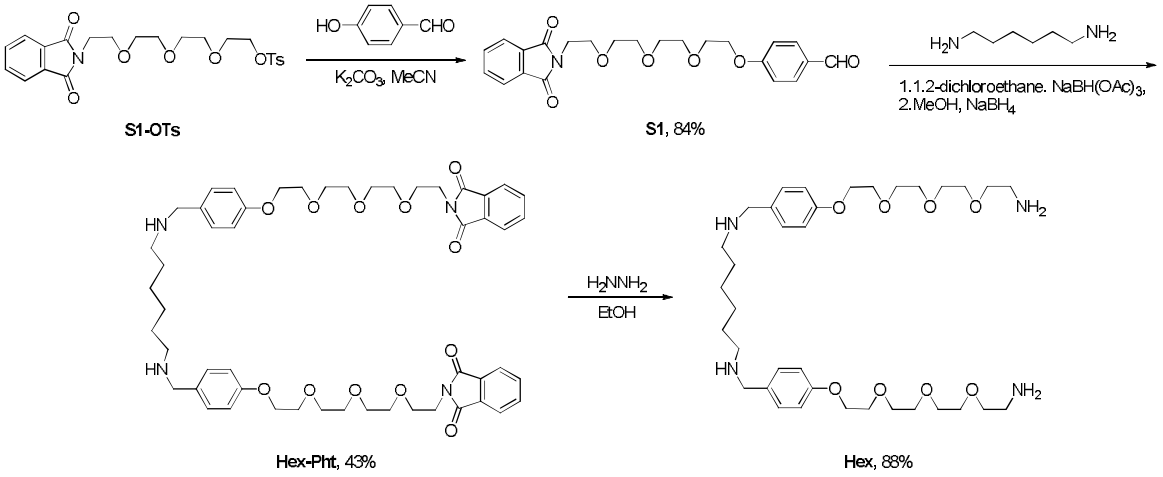
DN5. A mixture of **DN5-Pht** (0.70 g, 0.7 mmol) and hydrazine hydrate (1 mL) in EtOH (50 mL) was heated to reflux for 4 hr. Insoluble materials were removed by filtration and solvent

was removed by a rotary evaporator. The residue was dissolved in CH_2Cl_2 (50 mL), filtered, and the organic solvent was removed by a rotary evaporator to afford the product. Yield = 0.43 g, 84%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 7.80 (d, *J* = 8.0 Hz, 2 H), 7.29 (t, *J* = 8.0 Hz, 2 H), 6.78 (d, *J* = 8.0 Hz, 2 H), 4.23 (t, *J* = 4.0 Hz, 4 H), 3.93 (t, *J* = 4.0 Hz, 4 H), 3.74 (t, *J* = 4.0 Hz, 4 H), 3.64 (t, *J* = 4.0 Hz, 4 H), 3.60–3.50 (m, 24 H), 3.42 (t, *J* = 4.0 Hz, 4 H), 2.78 (t, *J* = 4.0 Hz, 4 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ = 153.7, 126.3, 124.7, 114.3, 105.4, 73.2, 71.0, 70.7, 70.6, 70.6, 70.5, 70.2, 69.8, 67.9, 53.7, 41.9, 30.0. ESI-MS: 344.2 $[M+2H]^{2+}$, 687.4 $[M+H]^+$.



Scheme S2. Synthesis of **L2**.

L2. A mixture of **Phen-OTs** (2.20 g, 4.0 mmol), 2,4-dihydoxylbenzaldehyde (1.16 g, 8.4 mmol), K_2CO_3 (1.64 g, 12.0 mmol) and KI (67 mg, 0.4 mmol) in dry DMF (40 mL) was heated at 100 °C for overnight. Solvent was removed using a rotary evaporator and the residue was partitioned between $CHCl_3$ (60 mL) and water (30 mL). The aqueous layer was extracted with $CHCl_3$ (2 x 50 mL). The organic fractions were combined and washed with brine, dried over $MgSO_4$, concentrated and purified on a silica column ($CHCl_3$/MeOH/Et_3N = 97:3:0.5 to 90:10:0.5) to afford the product as a white solid. Yield = 1.36 g, 71%. ^{1}H NMR (300 MHz, $(CD_3)_2SO$, 298 K) δ = 11.02 (s, 2 H), 10.03 (s, 2 H), 8.57 (d, *J* = 8.2 Hz, 2 H), 8.02 (s, 2 H), 7.89 (d, *J* = 8.2 Hz, 2 H), 7.67 (d, *J* = 8.7 Hz, 2 H), 6.76 (dd, *J* = 8.7, 2.0 Hz, 2 H), 6.66 (d, *J* = 2.0 Hz, 2 H), 5.60 (s, 4 H). ^{13}C{^{1}H} NMR (75 MHz, $(CD_3)_2SO$, 298 K) δ = 191.0, 164.7, 163.0, 156.5, 144.6, 137.5, 132.2, 128.1, 126.6, 121.2, 116.7, 108.0, 102.0, 71.3. ESI-MS: 481.6 $[M+H]^+$.



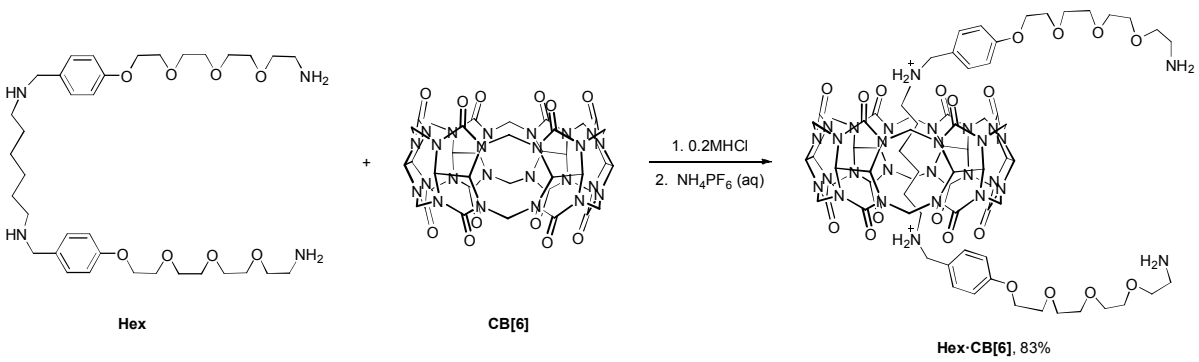
Scheme S3. Synthesis of **Hex**.

S1. A mixture of **S1-OTs** (4.05 g, 8.5 mmol), 4-hydroxylbenzaldehyde (1.14 g, 9.4 mmol) and K_2CO_3 (1.76 g, 12.8 mmol) in dried MeCN (50 mL) was heated to reflux for overnight. Insoluble materials were removed by filtration and the solvent was removed by a rotary evaporator. The residue was partitioned between CH_2Cl_2 (50 mL) and H_2O (50 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 50 mL). The organic fractions were combined, washed by brine, dried over $MgSO_4$, filtered and concentrated to afford a dark oil. The dark oil was purified on a silica column (EtOAc/hexane = 3:2) to afford the product as a light-yellow oil. Yield = 3.02 g, 84%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 9.88 (s, 1 H), 7.84–7.79 (m, 4 H), 7.72–7.69 (m, 2 H), 7.01 (d, *J* = 8.7 Hz, 2 H), 4.19 (t, *J* = 4.0 Hz, 2 H), 3.89 (t, *J* = 5.9 Hz, 2 H), 3.86 (t, *J* = 4.0 Hz, 2 H), 3.74 (t, *J* = 4.0 Hz, 2 H), 3.68–3.59 (m, 8 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ = 191.0, 168.4, 164.0, 134.1, 132.3, 132.1, 123.4, 115.0, 71.0, 70.8, 70.7, 70.3, 69.6, 68.1, 67.9, 37.4. ESI-MS: 428.1 $[M+H]^+$.

Hex-Pht. A mixture of **S1** (3.02 g, 7.1 mmol), 1,6-hexanediamine (0.39 g, 3.4 mmol) and $NaBH(OAc)_3$ (4.50 g, 21.2 mmol) in 1,2-dichloroethane (70 mL) was heated at 80 °C for 2 hr. The reaction mixture was diluted with MeOH (40 mL) and cooled at 0 °C. $NaBH_4$ (0.52 g, 14.1 mmol) was added in portions. The resulting solution was stirred at room temperature for 2 h. The solvent was removed by a rotary evaporator. The residue was partitioned between CH_2Cl_2 (75 mL) and H_2O (75 mL). The organic layer was separated and the aqueous layer was

extracted with CH_2Cl_2 (2 x 75 mL). The organic fractions were combined, washed with brine, dried over $MgSO_4$, filtered and concentrated to afford a dark oil. The dark oil was purified on a silica column (CH_2Cl_2/MeOH/Et_3N, 95:5:0.5) to afford the product as a light-yellow oil. Yield = 1.48 g, 47%. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ = 7.84–7.82 (m, 4 H), 7.71–7.69 (m, 4 H), 7.43 (d, *J* = 8.6 Hz, 4 H), 6.88 (d, *J* = 8.7 Hz, 4 H), 4.07 (t, *J* = 5.9 Hz, 4 H), 3.94 (s, 4 H), 3.89 (t, *J* = 5.9 Hz, 4 H), 3.80 (t, *J* = 5.9 Hz, 4 H), 3.73 (t, *J* = 5.8 Hz, 4 H), 3.67–3.58 (m, 16 H), 2.70 (t, *J* = 7.2 Hz, 4 H), 1.70 (t, *J* = 7.5 Hz, 4 H), 1.37 (t, *J* = 4.2 Hz, 4 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ = 169.1, 158.3, 134.1, 132.3, 130.0, 123.4, 114.8, 70.9, 70.3, 69.9, 68.1, 67.5, 52.8, 48.6, 37.5, 29.8, 27.0. ESI-MS: 940.1 $[M+H]^+$.

Hex. A mixture of **Hex-Pht** (1.48 g, 1.6 mmol) and hydrazine hydrate (2 mL) in EtOH (50 mL) was heated to reflux for 4 hr. Insoluble materials were removed by filtration and solvent was removed by a rotary evaporator. The residue was dissolved in CH_2Cl_2 (50 mL), filtered, and the organic solvent was removed by a rotary evaporator to afford the product as a yellow oil. Yield = 887 mg, 83%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 6.93 (d, *J* = 8.7 Hz, 4 H), 6.58 (d, *J* = 8.7 Hz, 4 H), 3.86–3.78 (m, 4 H), 3.59–3.51 (m, 4 H), 3.47–3.27 (m, 24 H), 3.25–3.16 (m, 4 H), 2.33–2.27 (m, 4 H), 1.28–1.13 (m, 4 H), 1.10–0.96 (m, 4 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K) δ = 157.1, 132.1, 128.6, 113.8, 72.6, 70.1, 69.9, 69.6, 69.1, 66.8, 52.7, 48.6, 41.0, 29.3, 26.6. ESI-MS: 679.6 $[M+H]^+$.



Scheme S4. Synthesis of **Hex**·CB[6]

Hex·CB[6]. A mixture of **Hex** (68 mg, 0.1 mmol) and CB[6] (100 mg, 0.1 mmol) in 0.2 M HCl (50 mL) was heated to 80 °C for 4 hr. Insoluble materials were removed by filtration. The

filtrate was treated with saturated NH_4PF_6 (2 mL) to yield a white precipitate. The product was collected by filtration, washed with water and dried under vacuum as a white solid. Yield = 140 mg, 83%. ^{1}H NMR (500 MHz, CD_3CN, 298 K) δ = 7.59 (d, *J* = 8.4 Hz, 4H), 7.00 (d, *J* = 8.4 Hz, 4H), 6.79 (s, 2H), 5.71 (d, *J* = 15.3 Hz, 12H), 5.35 (s, 12H), 4.21–4.12 (m, 20H), 3.82 (t, *J* = 4.5 Hz, 4H), 3.72–3.55 (m, 20H), 3.09 (t, *J* = 5.2 Hz, 4H), 3.00 (t, *J* = 7.1 Hz, 4H), 0.74 (d, *J* = 7.9 Hz, 4H), 0.45 (dt, *J* = 8.4, 3.7 Hz, 4H). ESI-MS: 838.4 $[M+2H]^+$, 559.2 $[M+3H]^+$.

B. Imine assembly:

General procedure for imine assembly using dioxynaphthalene-derived diamines: A mixture of **L1** (45 mg, 0.10 mmol) and $[Cu(CH_3CN)_4]PF_6$ (19 mg, 0.05 mmol) in $CHCl_3$/MeCN (v/v 7:3, 25 mL) was stirred for 30 min under argon. A solution of **DNn** (n = 1–5, 0.11 mmol) in $CHCl_3$/MeCN (v/v 7:3, 25 mL) was added to reaction mixture. The dark red solution was heated at 80 °C for overnight. The solution was cooled to 0 °C and $NaBH_4$ (10 mg, 0.25 mmol) was added in portions. The resulting solution was stirred at room temperature for 2 hr. Solvents were removed by a rotary evaporator and the residue was partitioned between $CHCl_3$ (30 mL) and a saturated K_2CO_3 solution (10 mL). The organic fraction was separated and the aqueous layer was extracted with $CHCl_3$ (3 × 20 mL). The organic fractions were combined, dried over $MgSO_4$ and filtered. The solution was concentrated and re-dissolved in 8 mL $CHCl_3$/CH_3CN (v/v 1:1). Pure samples of the products were obtained by preparative HPLC.

H1. A pure sample of **H1** was obtained by preparative HPLC using *Method 1.* From 1 mL of the 8 mL $CHCl_3$/CH_3CN solution, 7.2 mg of **H1** was isolated. Isolated yield = 67%. ^{1}H NMR (500 MHz, D_2O, 298 K) δ = 8.18 (d, *J* = 8.5 Hz, 4 H), 7.82–7.74 (m, 12 H), 7.35 (d, *J* = 7.7 Hz, 4 H), 6.46–6.39 (m, 12 H), 5.78 (d, *J* = 8.3 Hz, 8 H), 4.47 (t, *J* = 3.9 Hz, 2 H), 4.10 (d, *J* = 4.0 Hz, 2 H), 4.02 (s, 2 H), 3.98 (t, *J* = 5.0 Hz, 2 H), 3.06 (t, *J* = 4.9 Hz, 2 H). $^{13}C\{^1H\}$ NMR (150 MHz, D_2O, 298 K) δ = 157.3, 154.2, 152.6, 142.3, 137.3, 130.6, 128.2, 126.3, 126.2, 125.5, 125.4, 121.8, 114.5, 112.6, 106.8, 70.3, 69.3, 68.0, 65.9, 48.9, 46.4, 43.2. ESI-MS: 1563.6 $[M]^+$.

H1b. The copper containing **H1** was demetallated to give **H1b** by treating the assembly mixture in $CHCl_3$/MeCN (v/v 1:1, 25mL) with an aqueous solution of NaCN (49 mg, 1.0 mmol, 5 mL) and stirred at room temperature for 4 hr. Volatiles was removed from the mixture and the residue was partitioned between $CHCl_3$ (30 mL) and a saturated K_2CO_3 solution (10 mL). The organic fraction was separated and the aqueous layer was extracted with $CHCl_3$ (3 × 20 mL). The organic fractions were combined, dried over $MgSO_4$ and filtered. The solution was concentrated and re-dissolved in 8 mL $CHCl_3$/CH_3CN (v/v 1:1) by using rotary evaporator. A pure sample of **H1b** was obtained by preparative HPLC using *Method 1*. From 1 mL of the 8 mL $CHCl_3$/CH_3CN solution, 5.0 mg of **H1b** was isolated, isolated yield = 54%. ^{1}H NMR (500 MHz, D_2O, 298 K) δ = 7.68 (d, *J* = 8.3 Hz, 4H), 7.54 (s, 4H), 7.31 (d, *J* = 8.3 Hz, 8H), 7.26 (d, *J* = 8.4 Hz, 4H), 7.11 (d, *J* = 8.2 Hz, 4H), 6.88 (t, *J* = 8.0 Hz, 4H), 6.60 (d, *J* = 8.2 Hz, 8H), 6.25 (d, *J* = 7.5 Hz, 4H), 4.23 (d, *J* = 8.8 Hz, 16H), 3.81 (s, 8H), 3.77 (d, *J* = 5.1 Hz, 8H), 3.16 (t, *J* = 4.9 Hz, 4H). ESI-MS: 1523.6 $[M+Na]^+$, 751.6 $[M+2H]^{2+}$.

F2. A pure sample of **F2** was obtained by preparative HPLC using *Method 1.* From 1 mL of the 8 mL $CHCl_3$/CH_3CN solution, 4.2 mg of **F2** was isolated, isolated yield = 35%. ^{1}H NMR (500 MHz, D_2O, 298 K) δ = 8.45 (d, *J* = 8.1 Hz, 4H), 7.87 (s, 4H), 7.69–7.61 (m, 8H), 7.25 (t, *J* = 8.0 Hz, 4H), 6.88 (d, *J* = 7.6 Hz, 4H), 6.55 (d, *J* = 8.2 Hz, 4H), 5.67 (d, *J* = 8.2 Hz, 8H), 4.52 (d, *J* = 10.0 Hz, 4H), 4.38 (d, *J* = 10.0 Hz, 4H), 4.12 (t, *J* = 4.2 Hz, 8H), 3.96 (s, 8H), 3.82–3.72 (m, 32H), 3.14–3.11 (m, 8H). ESI-MS: 1739.5 $[M]^+$, 870.5 $[M+H]^{2+}$.

H2. A pure sample of **H2** was obtained by preparative HPLC using *Method 1.* From 1 mL of the 8 mL $CHCl_3$/CH_3CN solution, 4.4 mg of **H2** was isolated, isolated yield = 37%. ^{1}H NMR δ 8.13 (d, *J* = 8.2 Hz, 4H), 7.80 (d, *J* = 8.2 Hz, 4H), 7.68 (d, *J* = 8.3 Hz, 4H), 7.38 (s, 4H), 7.28 (t, *J* = 8.0 Hz, 4H), 6.91 (d, *J* = 7.8 Hz, 4H), 6.74 (d, *J* = 8.3 Hz, 8H), 6.09 (d, *J* = 8.2 Hz, 8H), 4.89 (s, 8H), 4.29–4.25 (m, 8H), 4.01–3.96 (m, 8H), 3.92 (s, 8H), 3.85–3.82 (m, 8H), 3.78–3.75 (m, 8H), 3.74–3.70 (m, 8H), 3.08 (t, J = 4.9 Hz, 8H). ESI-MS: 1739.5 $[M]^+$, 870.5 $[M+H]^{2+}$.

F3. A pure sample of **F3** was obtained by preparative HPLC using *Method 1.* From 2 mL of the 8 mL $CHCl_3$/CH_3CN solution, 10.8 mg of **F3** was isolated, isolated yield = 45%. ^{1}H NMR

(500 MHz, D_2O, 298 K) δ = 8.43 (d, *J* = 8.1 Hz, 4H), 7.86 (s, 4H), 7.66 (d, *J* = 8.2 Hz, 8H), 7.24 (t, *J* = 8.0 Hz, 4H), 6.83 (d, *J* = 7.5 Hz, 4H), 6.53 (d, *J* = 8.2 Hz, 8H), 5.68 (d, *J* = 8.4 Hz, 8H), 4.50–4.40 (m, 8H), 4.10–4.04 (m, 8H), 3.94–3.87 (m, 8H), 3.81–3.74 (m, 16H), 3.70–3.64 (m, 32H), 3.15–3.11 (m, 8H). $^{13}C\{^1H\}$ NMR (150 MHz, D_2O, 298 K) δ = 157.5, 153.7, 152.9, 142.5, 137.8, 130.5, 128.6, 126.5, 126.2, 125.7, 125.5, 122.4, 114.4, 112.8, 106.7, 70.2, 69.8, 69.6, 69.6, 69.5, 69.1, 67.6, 65.1, 49.8, 45.9. ESI-MS: 1916.2 $[M]^+$, 958.6 $[M+H]^{2+}$.

H3. A pure sample of **H3** was obtained by preparative HPLC using *Method 1.* From 2 mL of the 8 mL $CHCl_3/CH_3CN$ solution, 5.2 mg of **H3** was isolated. Isolated yield = 20%. ^1H NMR (500 MHz, D_2O, 298 K) δ = 8.28 (d, *J* = 8.1 Hz, 4H), 7.83 (d, *J* = 8.1 Hz, 4H), 7.75 (d, *J* = 8.4 Hz, 4H), 7.59 (s, 4H), 7.32 (t, *J* = 8.1 Hz, 4H), 6.93 (d, *J* = 7.7 Hz, 4H), 6.54 (d, *J* = 8.2 Hz, 8H), 5.95 (d, *J* = 8.2 Hz, 8H), 4.83 (s, 8H), 4.25–4.22 (m, 8H), 3.95–3.90 (m, 8H), 3.82–3.78 (m, 8H), 3.77–3.74 (m, 8H), 3.71–3.65 (m, 32H), 3.64–3.62 (m, 8H), 3.05–3.00 (m, 8H). $^{13}C\{^1H\}$ NMR (150 MHz, D_2O, 298 K) δ = 157.6, 153.8, 153.3, 142.5, 137.9, 130.7, 128.6, 126.3, 126.2, 125.7, 125.3, 122.7, 114.4, 113.3, 106.8, 70.7, 69.8, 69.7, 69.6, 69.5, 69.1, 67.8, 65.2, 49.6, 45.6. ESI-MS: 1916.2 $[M]^+$, 958.6 $[M+H]^{2+}$.

F5. Pure sample of **F5** was obtained by preparative HPLC using *Method 1.* From 1 mL of the 8 mL $CHCl_3/CH_3CN$ solution, 6.5 mg of **H5** was isolated, isolated yield = 43%.^1H NMR (500 MHz, D_2O, 298 K) δ = 8.37 (d, *J* = 8.1 Hz, 4H), 7.77 (s, 4H), 7.73 (d, *J* = 8.1 Hz, 4H), 7.64 (d, *J* = 8.5 Hz, 3H), 7.18 (d, *J* = 7.0 Hz, 4H), 6.77 (d, *J* = 7.9 Hz, 4H), 6.60 (d, *J* = 8.3 Hz, 8H), 5.83 (d, *J* = 8.4 Hz, 8H), 4.58 (d, *J* = 4.6 Hz, 8H), 4.16–4.10 (m, 8H), 3.93–3.87 (m, 8H), 3.86–3.81 (m, 8H), 3.71–3.67 (m, 8H), 3.63–3.60 (m, 16H), 3.59–3.47 (m, 32H), 3.10–3.05 (m, 8H). $^{13}C\{^1H\}$ NMR (125 MHz, D_2O, 298 K) δ = 156.1, 153.8, 153.1, 142.6, 137.9, 136.6, 130.7, 129.5, 126.8, 126.5, 126.2, 125.8, 123.1, 113.0, 111.9, 106.7, 70.3, 69.8, 69.5, 69.5, 69.4, 69.3, 69.3, 69.1, 69.1, 67.8, 67.7, 64.3, 48.7, 45.9. ESI-MS: 1135.6 $[M+H]^{2+}$, 757.4 $[M+2H]^{3+}$, 568.3 $[M+3H]^{4+}$.

H5. Pure sample of **H5** was obtained by preparative HPLC using *Method 1.* From 2 mL of the 8 mL $CHCl_3/CH_3CN$ solution, 3.2 mg of **H5** was isolated, isolated yield = 22%. ^1H NMR (500 MHz, D_2O, 298 K) δ = 8.37 (d, *J* = 8.4 Hz, 4H), 7.82 (d, *J* = 7.9 Hz, 4H), 7.76 (d, 4H), 7.72 (s, 4H),

7.29 (t, 4H), 6.90 (d, 4H), 6.64 (d, 8H), 5.89 (d, 8H), 4.70–4.66 (m, 8H), 4.25–4.20 (m, 8H), 3.96–3.91 (m, 8H), 3.74–3.69 (m, 16H), 3.67–3.63 (m, 16H), 3.63–3.52 (m, 32H), 3.14–3.09 (m, 8H). $^{13}C\{^{1}H\}$ NMR (125 MHz, D_2O, 298 K) δ = 156.2, 153.8, 153.3, 142.6, 138.0, 136.6, 131.0, 129.4, 126.8, 126.5, 126.3, 125.8, 123.3, 113.1, 112.0, 106.5, 70.3, 69.8, 69.5, 69.5, 69.4, 69.3, 69.2, 69.1, 69.0, 67.8, 67.7, 64.4, 48.8, 45.9. ESI-MS: 1135.6 $[M+H]^{2+}$, 757.4 $[M+2H]^{3+}$, 568.3 $[M+3H]^{4+}$.

General procedure of imine assembly using α,ω-diamine with 7 to 12 methylene groups: A mixture of **L1** (45 mg, 0.1 mmol) and $[Cu(CH_3CN)_4]PF_6$ (19 mg, 0.05 mmol) in $CHCl_3$/MeCN (v/v 7:3, 25 mL) was stirred for 30 min under argon. A solution of α,ω-diamine (0.11 mmol) in $CHCl_3$/MeCN (v/v 7:3, 25 mL) was added to reaction mixture. The dark red solution was heated at 80 °C for overnight. The solution was cooled to 0 °C and $NaBH_4$ (10 mg, 0.25 mmol) was added in portions. The resulting solution was stirred at room temperature for 2 hr. Solvents were removed by a rotary evaporator and the residue was partitioned between $CHCl_3$ (30 mL) and a saturated K_2CO_3 solution (10 mL). The organic fraction was separated and the aqueous layer was extracted with $CHCl_3$ (3 × 20 mL). The organic fractions were combined, dried over $MgSO_4$ and filtered. The solution was concentrated and re-dissolved in 8 mL $CHCl_3$/CH_3CN (v/v 1:1) by using rotary evaporator. Pure samples of assembly products were obtained by preparative HPLC.

H6. A pure sample of **H6** was obtained by preparative HPLC using *Method 2.* From 2 mL of the 8 mL $CHCl_3$/CH_3CN solution, 11.6 mg of **H6** was isolated, isolated yield = 72%. ^{1}H NMR (500 MHz, D_2O, 298 K) δ = 8.55 (d, *J* = 8.1 Hz, 4H), 8.10 (d, *J* = 8.1 Hz, 4H), 7.80 (s, 4H), 6.70 (d, *J* = 8.3 Hz, 8H), 5.94 (d, *J* = 8.4 Hz, 8H), 4.98 (s, 8H), 3.82 (s, 8H), 2.89 (t, *J* = 7.6 Hz, 8H), 1.78 (s, 8H), 1.51 (d, *J* = 9.5 Hz, 12H). $^{13}C\{^{1}H\}$ NMR (100 MHz, D_2O, 298 K) δ = 157.6, 153.6, 143.2, 137.8, 130.6, 128.5, 126.5, 126.1, 123.7, 113.6, 70.9, 49.9, 46.3, 27.5, 25.9, 25.4. ESI-MS: 1155.5 $[M]^{+}$, 578.0 $[M+H]^{2+}$.

H7. A pure sample of **H7** was obtained by preparative HPLC using *Method 2.* From 2 mL of the 8 mL $CHCl_3$/CH_3CN solution, 13.4 mg of **H7** was isolated, isolated yield = 81%. ^{1}H NMR

(500 MHz, D_2O, 298 K) δ = 8.50 (d, *J* = 8.2 Hz, 4H), 8.08 (d, *J* = 8.2 Hz, 4H), 7.71 (s, 4H), 6.70 (d, *J* = 8.1 Hz, 8H), 5.97 (d, *J* = 8.2 Hz, 8H), 5.02 (s, 8H), 3.83 (s, 8H), 2.88 (t, *J* = 7.4 Hz, 8H), 1.78 (t, *J* = 7.7 Hz, 8H), 1.61–1.48 (m, 16H). $^{13}C\{^1H\}$ NMR (125 MHz, D_2O, 298 K) δ = 157.6, 153.1, 143.1, 137.7, 130.8, 128.3, 126.3, 126.0, 122.7, 113.1, 70.8, 50.0, 46.7, 27.4, 25.9, 25.2. ESI-MS: 1183.6 $[M]^+$, 592.3 $[M+H]^{2+}$, 395.1 $[M+2H]^{3+}$.

H8. A pure sample of **H8** was obtained by preparative HPLC using *Method 2.* From 2 mL of the 8 mL $CHCl_3/CH_3CN$ solution, 12.4 mg of **H8** was isolated, isolated yield = 73%. ^1H NMR (500 MHz, D_2O, 298 K) δ = 8.56 (d, *J* = 8.1 Hz, 4H), 8.11 (d, *J* = 8.2 Hz, 4H), 7.83 (s, 4H), 6.68 (d, *J* = 8.0 Hz, 8H), 6.04 (d, *J* = 8.1 Hz, 8H), 5.05 (d, *J* = 8.7 Hz, 8H), 3.82 (s, 8H), 2.89 (t, *J* = 7.5 Hz, 8H), 1.88–1.79 (m, 8H), 1.61–1.54 (m, 20H). $^{13}C\{^1H\}$ NMR (100 MHz, D_2O, 298 K) δ = 157.6, 153.4, 143.1, 137.9, 130.5, 128.6, 126.3, 126.0, 123.3, 113.2, 71.1, 49.4, 46.1, 28.1, 27.7, 25.9, 25.5. ESI-MS: 1211.6 $[M]^+$, 605.9 $[M+H]^{2+}$, 404.3 $[M+2H]^{3+}$.

H9. A pure sample of **H9** was obtained by preparative HPLC using *Method 2.* From 2 mL of the 8 mL $CHCl_3/CH_3CN$ solution, 13.2 mg of **H9** was isolated, isolated yield = 76%. ^1H NMR (500 MHz, D2O, 298 K) δ = 8.53 (d, *J* = 8.1 Hz, 4H), 8.09 (d, *J* = 8.1 Hz, 4H), 7.82 (s, 4H), 6.69 (d, *J* = 8.2 Hz, 8H), 6.06 (d, *J* = 8.3 Hz, 8H), 5.05 (s, 8H), 3.82 (s, 8H), 2.83 (t, *J* = 7.3 Hz, 8H), 1.80–1.74 (m, 8H), 1.58–1.52 (m, 24H). $^{13}C\{^1H\}$ NMR (125 MHz, D_2O, 298 K) δ = 157.5, 153.4, 143.0, 137.9, 130.5, 128.6, 126.3, 123.4, 113.1, 71.1, 49.4, 46.2, 28.0, 27.7, 25.7, 25.5. ESI-MS: 1239.6 $[M]^+$, 620.0 $[M+H]^{2+}$, 413.9 $[M+2H]^{3+}$.

H10. A pure sample of **H10** was obtained by preparative HPLC using *Method 2.* From 2 mL of the 8 mL $CHCl_3/CH_3CN$ solution, 13.0 mg of **H10** was isolated, isolated yield = 74%. ^1H NMR (500 MHz, D_2O, 298 K) δ = 8.55 (d, *J* = 8.1 Hz, 4H), 8.09 (d, *J* = 8.1 Hz, 4H), 7.86 (s, 4H), 6.67 (d, *J* = 8.3 Hz, 8H), 6.08 (d, *J* = 8.3 Hz, 8H), 5.05 (s, 8H), 3.84 (s, 8H), 2.87 (t, *J* = 7.8 Hz, 8H), 1.82–1.76 (m, 8H), 1.55–1.50 (m, 28H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 298 K) δ = 156.4, 155.2, 143.1, 137.7, 133.0, 128.8, 128.7, 126.6, 125.4, 113.1, 71.3, 53.0, 49.1, 30.1, 29.6, 29.3, 29.0, 27.3. ESI-MS: 1267.1 $[M]^+$, 634.0 $[M+H]^{2+}$, 423.3 $[M+2H]^{3+}$.

H11. A pure sample of **H11** was obtained by preparative HPLC using *Method 1.* From 2 mL of the 8 mL $CHCl_3/CH_3CN$ solution, 12.8 mg of **H11** was isolated, isolated yield = 71%. ^{1}H NMR (500 MHz, D2O) δ = 8.55 (d, *J* = 8.2 Hz, 4H), 8.08 (d, *J* = 8.1 Hz, 4H), 7.88 (s, 4H), 6.69 (d, *J* = 8.2 Hz, 8H), 6.08 (d, *J* = 8.2 Hz, 8H), 5.05 (s, 8H), 3.87 (s, 8H), 2.85 (t, *J* = 7.6 Hz, 8H), 1.80–1.74 (m, 8H), 1.51–1.48 (m, 32H). $^{13}C\{^1H\}$ NMR (100 MHz, D_2O, 298 K) δ = 157.7, 153.5, 143.0, 138.0, 130.6, 128.7, 126.4, 126.1, 122.9, 113.2, 71.1, 49.0, 45.8, 28.2, 27.8, 27.6, 25.5, 24.6. ESI-MS: 1295.1 $[M]^+$, 648.4 $[M+H]^{2+}$, 432.7 $[M+2H]^{3+}$.

Procedure for imine assembly using **Hex**: A mixture of **L2** (48 mg, 0.1 mmol) and $Cu(CH_3CN)_4PF_6$ (19 mg, 0.05 mmol) in $CHCl_3$/MeCN (v/v 7:3, 25 mL) was stirred for 30 min under argon. A solution of **Hex** (75 mg, 0.11 mmol) in $CHCl_3$/MeCN (v/v 7:3, 25 mL) was added to reaction mixture. The dark red solution was heated at 80 °C for overnight. The solution was cooled to 0 °C and $NaBH_4$ (10 mg, 0.25 mmol) was added in portions. The resulting mixture was stirred at room temperature for 2 hr. Solvents were removed by a rotary evaporator and the residue was partitioned between $CHCl_3$ (30 mL) and a saturated K_2CO_3 solution (10 mL). The organic fraction was separated and the aqueous layer was extracted with $CHCl_3$ (3 × 20 mL). The organic fractions were combined, dried over $MgSO_4$ and filtered. The solvents were removed and re-dissolved in $CHCl_3$/MeCN (v/v 1:1, 25 mL) and treated with a solution of NaCN (50 mg, 1 mmol) in H_2O (5 mL). The resulting mixture was stirred at room temperature for 4 h and partitioned between $CHCl_3$ (30 mL) and a saturated K_2CO_3 solution (10 mL). The organic fraction was separated and the aqueous layer was extracted with $CHCl_3$ (3 × 20 mL). The organic fractions were combined, dried over $MgSO_4$ and filtered. Pure samples of the assembly products were obtained by preparative HPLC.

F12b. Pure sample of **F12b** was obtained by preparative HPLC using *Method 3*. From 2 mL of the 8 mL $CHCl_3/CH_3CN$ solution, 13.0 mg of **F12b** was isolated, isolated yield = 46%. ^{1}H NMR (500 MHz, D_2O, 298 K) δ = 7.99 (d, *J* = 8.3 Hz, 4H), 7.47 (d, *J* = 8.2 Hz, 4H), 7.42 (s, 4H), 7.14 (d, *J* = 8.5 Hz, 4H), 7.10 (d, *J* = 8.2 Hz, 8H), 6.73 (d, *J* = 8.2 Hz, 8H), 6.59 (s, 4H), 6.49–6.45 (m, 4H), 5.02 (s, 8H), 4.07 (s, 8H), 3.89 (d, *J* = 4.9 Hz, 8H), 3.79 (s, 8H), 3.71 (s, 8H), 3.65 (s, 8H), 3.61–3.58 (m, 32H), 3.18 (t, J = 4.9 Hz, 8H), 2.62–2.57 (m, 8H), 1.28 (s, 8H), 0.91 (s, 8H).

$^{13}C\{^{1}H\}$ NMR (125 MHz, D_2O, 298 K) δ = 163.1, 160.0, 158.6, 156.6, 143.2, 137.8, 132.8, 131.3, 127.8, 122.9, 117.6, 115.2, 114.9, 110.6, 106.8, 102.3, 70.2, 69.7, 69.7, 69.6, 69.6, 69.5, 68.8, 67.0, 65.1, 49.5, 46.2, 45.9, 45.5, 24.9, 24.7. ESI-MS: 1128.1 $[M+2H]^{2+}$ 752.4 $[M+3H]^{3+}$, 564.6 $[M+4H]^{4+}$.

H12b. Pure sample of **H12b** was obtained by preparative HPLC using *Method 3.* From 2 mL of the 8 mL $CHCl_3/CH_3CN$ solution, 6.0 mg of **H12** was isolated, isolated yield = 21%. ^{1}H NMR (500 MHz, D_2O, 298 K) δ = 8.41 (d, *J* = 8.3 Hz, 4H), 7.90 (s, 4H), 7.80 (d, *J* = 8.3 Hz, 4H), 7.19 (d, *J* = 8.4 Hz, 4H), 7.11 (d, *J* = 8.4 Hz, 8H), 6.71 (d, *J* = 8.4 Hz, 8H), 6.68–6.63 (m, 8H), 5.42 (s, 8H), 4.84 (s, 8H), 4.11 (s, 8H), 3.90–3.85 (m, 8H), 3.77–3.73 (m, 16H), 3.65–3.61 (m, 32H), 3.23 (t, *J* = 4.9 Hz, 8H), 2.57–2.52 (m, 8H), 1.25 (s, 8H), 0.87 (s, 8H). $^{13}C\{^{1}H\}$ NMR (125 MHz, D_2O, 298 K) δ = 163.2, 159.3, 158.8, 156.9, 143.5, 138.0, 133.0, 131.7, 128.0, 123.0, 117.6, 115.4, 115.0, 110.7, 106.9, 102.6, 70.3, 69.9 69.8, 69.7, 69.6, 69.0, 67.2, 65.3, 49.7, 46.5, 46.1 45.7, 25.0, 24.8. ESI-MS: 1128.1 $[M+2H]^{2+}$, 752.4 $[M+3H]^{3+}$, 564.6 $[M+4H]^{4+}$.

Procedure for imine assembly using **Hex**·CB[6]: A mixture of **L2** (12 mg, 0.025 mmol) and $[Cu(CH_3CN)_4]PF_6$ (4.5 mg, 0.0125 mmol) in $CHCl_3$/MeCN (v/v 7:3, 12 mL) was stirred for 30 min under argon. A solution of **Hex**·CB[6] (68 mg, 0.03 mmol) in MeCN (12 mL) was added to the reaction mixture. Piperidine (2.5 μl, 0.025 mmol) was added. The dark red solution was heated at 80 °C for overnight. The solution was cooled to 0 °C and $NaBH_4$ (4 mg, 0.1 mmol) was added in portions. The resulting mixture was stirred at room temperature for 2 hr and concentrated by a rotary evaporator. The residue was re-dissolved in 4 mL of $CHCl_3$/MeCN (v/v 7:3).

H13. Pure sample of **H13** was obtained by preparative HPLC using *Method 4.* From 1 mL of the 4 mL $CHCl_3/CH_3CN$ solution, 8.4 mg of **H13** was isolated, isolated yield = 52%. ^{1}H NMR (500 MHz, D_2O, 298 K) δ = 8.48 (d, *J* = 8.1 Hz, 4H), 8.00 (d, *J* = 8.2 Hz, 4H), 7.87 (s, 4H), 7.61 (d, *J* = 8.8 Hz, 8H), 6.96 (d, *J* = 8.8 Hz, 8H), 6.39 (d, *J* = 8.5 Hz, 4H), 5.64 (d, *J* = 15.6 Hz, 24H), 5.50 (s, 4H), 5.42 (d, *J* = 4.5 Hz, 4H), 5.37 (s, 24H), 4.29–4.27 (m, 8H), 4.21–4.16 (m, 24H), 4.11–4.04 (m, 8H), 3.88 (s, 8H), 3.75–3.67 (m, 48H), 3.11 (s, 8H), 2.94 (s, 8H), 0.81 (s, 8H),

0.40 (s, 8H). $^{13}C\{^{1}H\}$ NMR (125 MHz, D_2O, 298 K) δ = 159.4, 158.5, 155.9, 142.8, 138.1, 131.4, 128.7, 126.5, 125.7, 124.7, 119.8, 117.5, 115.2, 114.9, 109.9, 109.6, 104.0, 70.2, 70.1, 69.7, 69.6, 69.5, 69.5, 68.9, 68.8, 67.1, 65.0, 51.6, 51.3, 48.0, 46.0, 45.9, 45.8, 26.7, 26.1. ESI-MS: 1107.2 $[M+4H+TFA]^{4+}$, 863.2 $[M+4H]^{5+}$, 719.5 $[M+5H]^{6+}$.

Procedure for imine assembly using **L2** and **Hex**·CB[6]: To a solution of **L2** (12 mg, 0.025 mmol) in $CHCl_3$/MeCN (v/v 7:3, 12 mL) was added **Hex**·CB[6] (68 mg, 0.03 mmol) in MeCN (12 mL) and stirred at room temperature for 30 min. Piperidine (2.5 μl, 0.025 mmol) was added and the yellow solution was heated at 80 °C for overnight under argon. The solution was cooled to 0 °C and $NaBH_4$ (4 mg, 0.1 mmol) was added in portions. The resulting mixture was stirred at room temperature for 2 hr. Solvents were removed and the residue re-dissolved in 4 mL $CHCl_3$/MeCN (v/v 7:3). Pure sample of **M13** was obtained by preparative HPLC using *Method 2.* From 1 mL of the 4 mL $CHCl_3$/CH_3CN solution, 12.4 mg of **M13** was isolated, isolated yield = 82%. ^{1}H NMR (500 MHz, D_2O, 298 K) δ = 8.38 (s, 4H), 7.84 (d, *J* = 8.4 Hz, 4H), 7.79 (s, 4H), 7.49 (d, *J* = 8.8 Hz, 8H), 7.08 (d, *J* = 8.5 Hz, 4H), 6.97 (d, *J* = 8.7 Hz, 8H), 6.54 (s, 4H), 6.52 (d, *J* = 8.4 Hz, 4H), 5.39 (d, *J* = 15.6 Hz, 24H), 5.13 (s, 24H), 4.12–4.06 (m, 8H), 4.00–3.95 (m, 32H), 3.75 (s, 8H), 3.65–3.59 (m, 24H), 3.57–3.54 (m, 16H), 3.53 (s, 16H), 3.08 (t, *J* = 4.9 Hz, 8H), 2.73 (t, *J* = 7.3 Hz, 8H), 0.51 (s, 8H), 0.16 (s, 8H). $^{13}C\{^{1}H\}$ NMR (125 MHz, D_2O, 298 K) δ = 158.6, 157.1, 155.7, 141.6, 138.6, 131.3, 128.6, 127.0, 124.8, 122.9, 118.6, 117.5, 115.0, 112.1, 111.5, 109.6, 102.6, 70.9, 70.3, 70.0 , 69.7, 69.6, 69.5, 69.5, 69.0, 67.3, 65.3, 51.6, 51.2, 48.0, 46.1, 42.9, 39.4, 26.5, 25.8. ESI-MS: 1063.1 $[M+2H]^{2+}$, 709.1 $[M+3H]^{3+}$, 532.1 $[M+4H]^{4+}$.

2. HPLC Analysis

HPLC analyses were carried out using a Waters-Alliance e2695 system coupled to a 2489 UV/Vis detector. HPLC grade H_2O (Scharlau), MeCN (Arkonic Scientific), formic acid (Merck) and trifluoroacetic acid (J&K) were used as received. C18 SunFire preparative columns (5 µm, 10 × 250 mm or 10 µm, 4.6 × 250 mm) were used with gradient elution described below. UV-Vis absorbance was monitored at 280 nm.

Method 1 (flow rate = 1 mL/min)

time/min	H_2O (with 0.05% formic acid)	MeCN (with 0.05% formic acid)
0	90%	10%
2	90%	10%
7	75%	25%
10	60%	40%
11	0%	100%
13	0%	100%

Method 2 (flow rate = 3 mL/min)

time/min	H_2O (with 0.05% formic acid)	MeCN (with 0.05% formic acid)
0	95%	5%
2	95%	5%
13	65%	35%
15	0%	100%
22	0%	100%

Method 3 (flow rate = 3 mL/min)

time/min	H_2O (with 0.1% TFA)	MeCN (with 0.1% TFA)
0	74%	26%
4	72%	28%
13	67%	33%
17	60%	40%
18	20%	80%
23	20%	80%

Method 4 (flow rate = 3 mL/min)

time/min	H_2O (with 0.1% TFA)	MeCN (with 0.1% TFA)
0	78%	22%
2	78%	22%
8	75%	25%
18	70%	30%
19	20%	80%
23	20%	80%

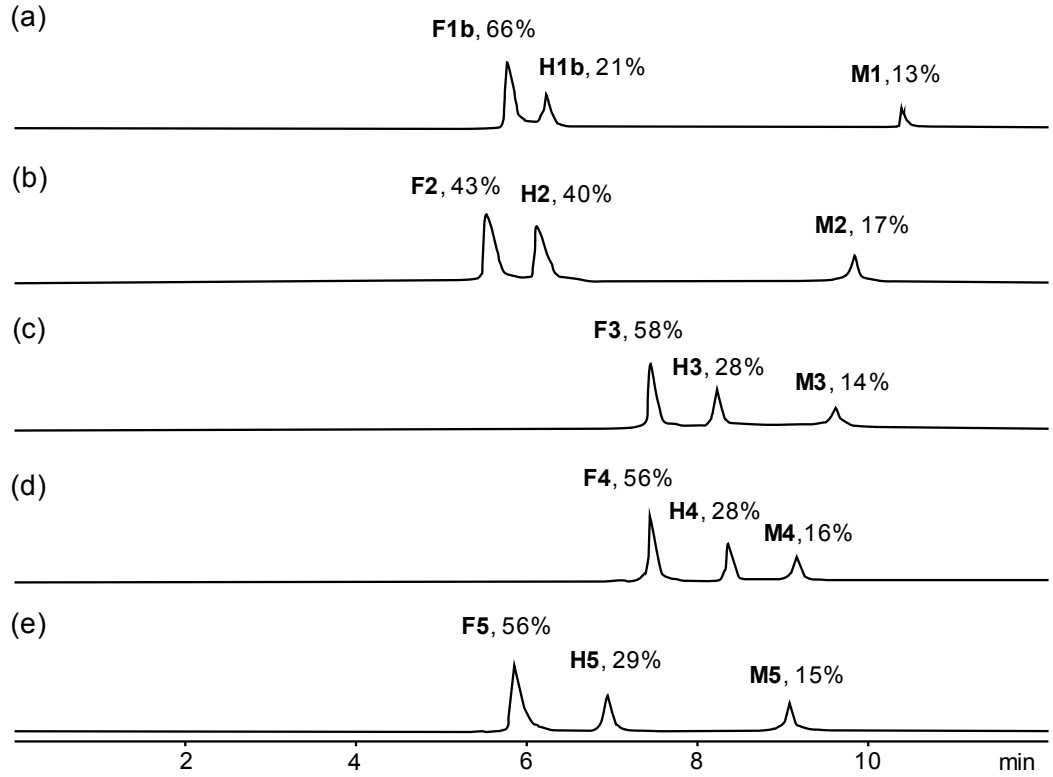


Figure S1. HPLC chromatograms (*Method 1*) of the crude assembly mixture from $[Cu(\mathbf{L1})_2]^+$ and (a) **DN1** (after demetallation), (b) **DN2**, (c) **DN3**, (d) **DN4** and (e) **DN5**.

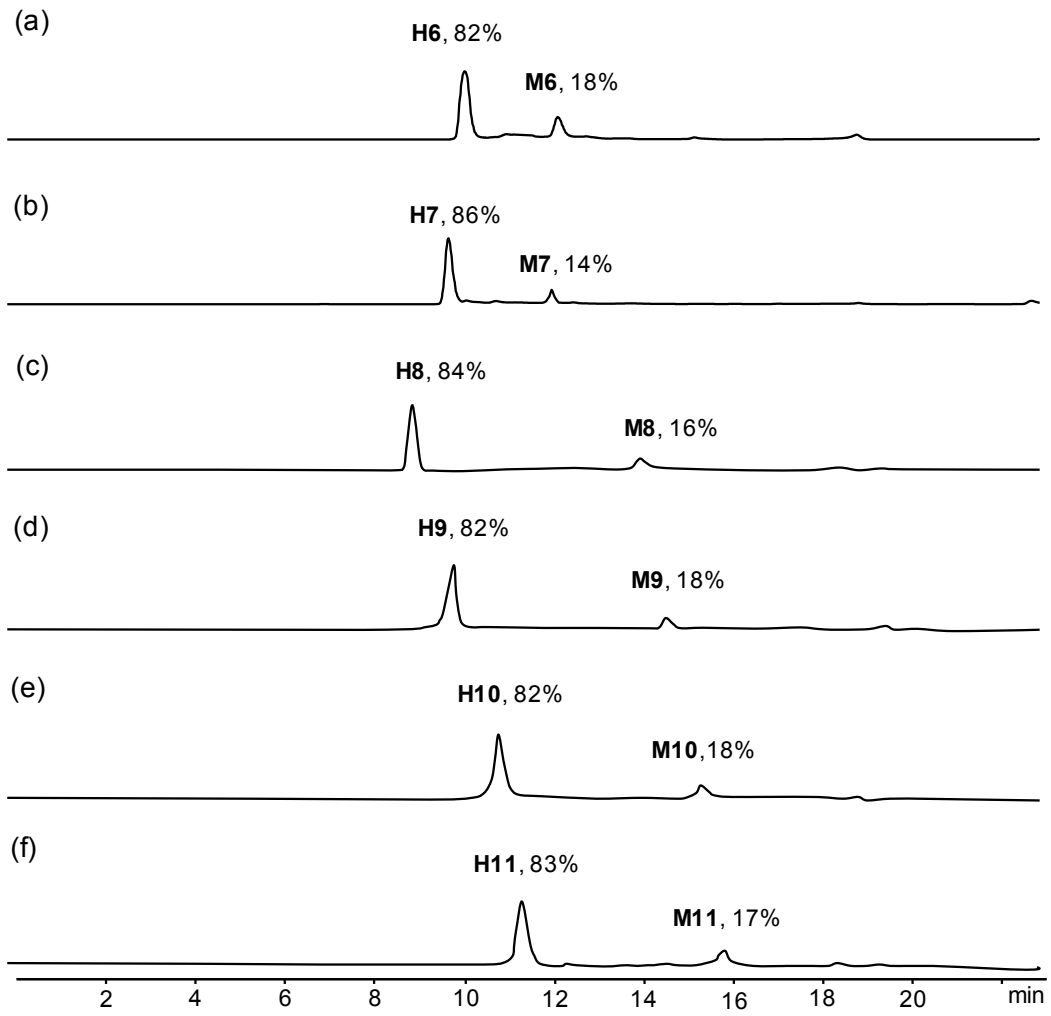


Figure S2. HPLC chromatograms (*Method 2*) of the crude assembly mixture from $[Cu(\mathbf{L1})_2]^+$ and (a) **Alk7**, (b) **Alk8**, (c) **Alk9**, (d) **Alk10**, (e) **Alk11** and (f) **Alk12**.

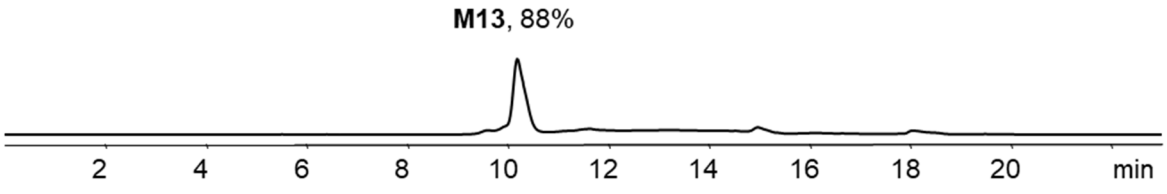


Figure S3. HPLC chromatogram of the crude assembly mixture from **L2** and **Hex**·CB[6]. Separation was achieved using *Method 2.*

3. NMR

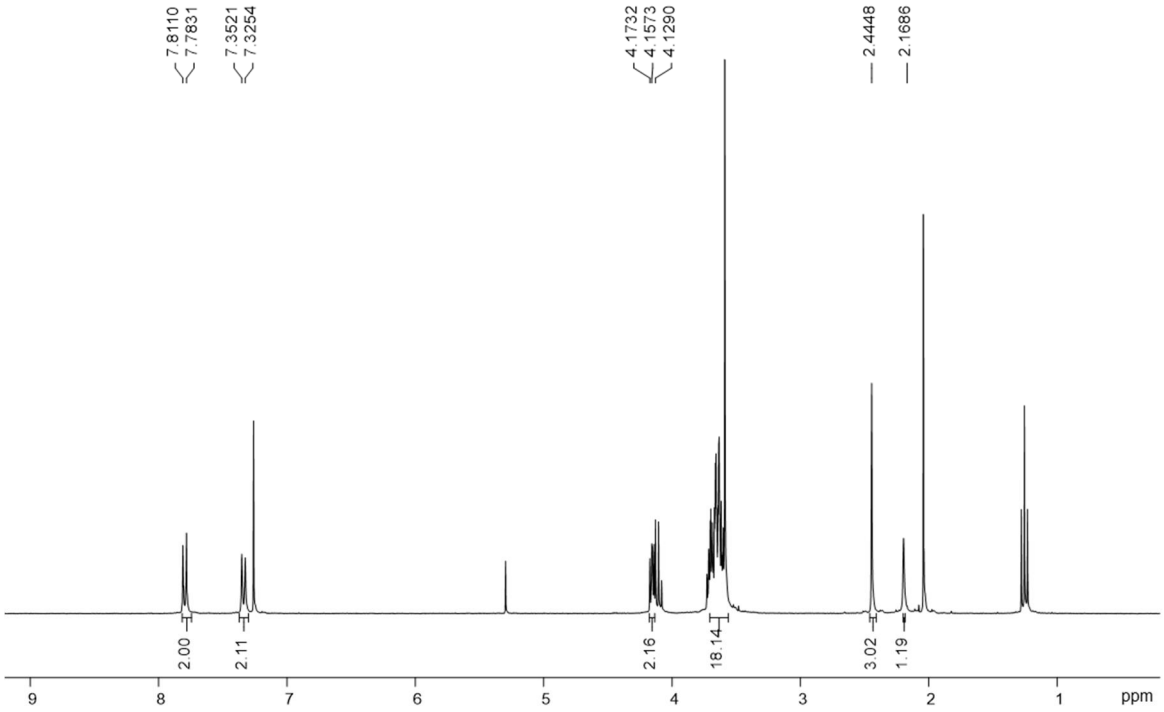


Figure S4. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) of **4-OTs**.

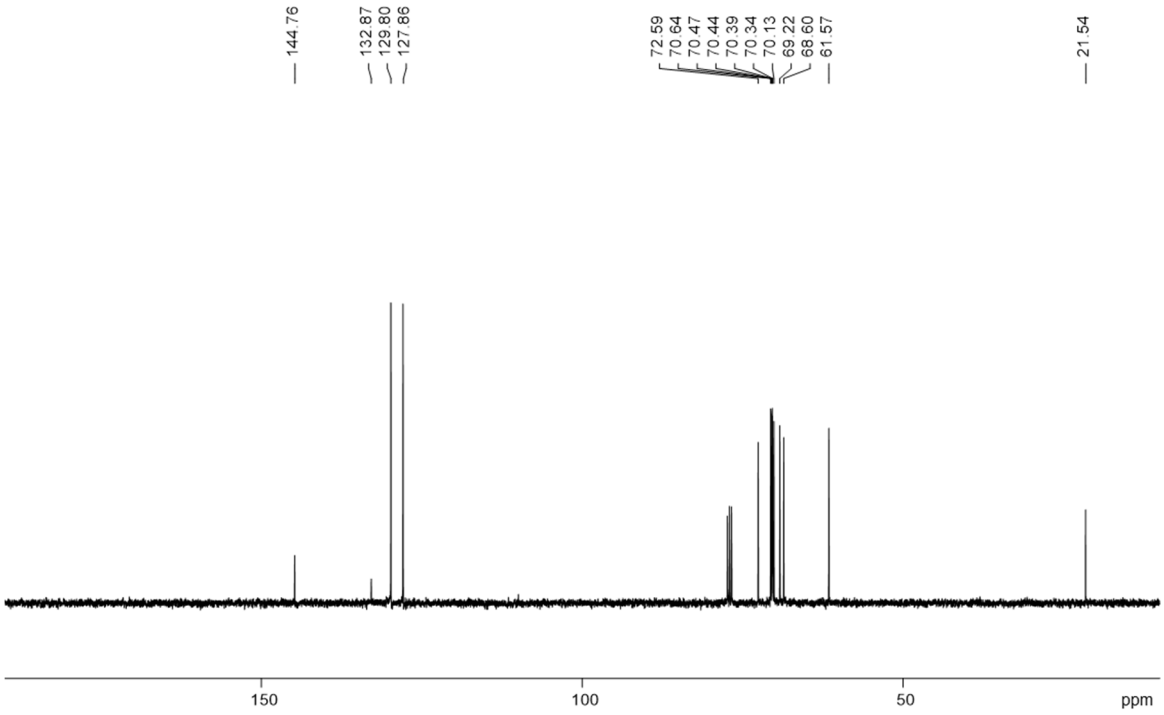


Figure S5. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) of **4-OTs**.

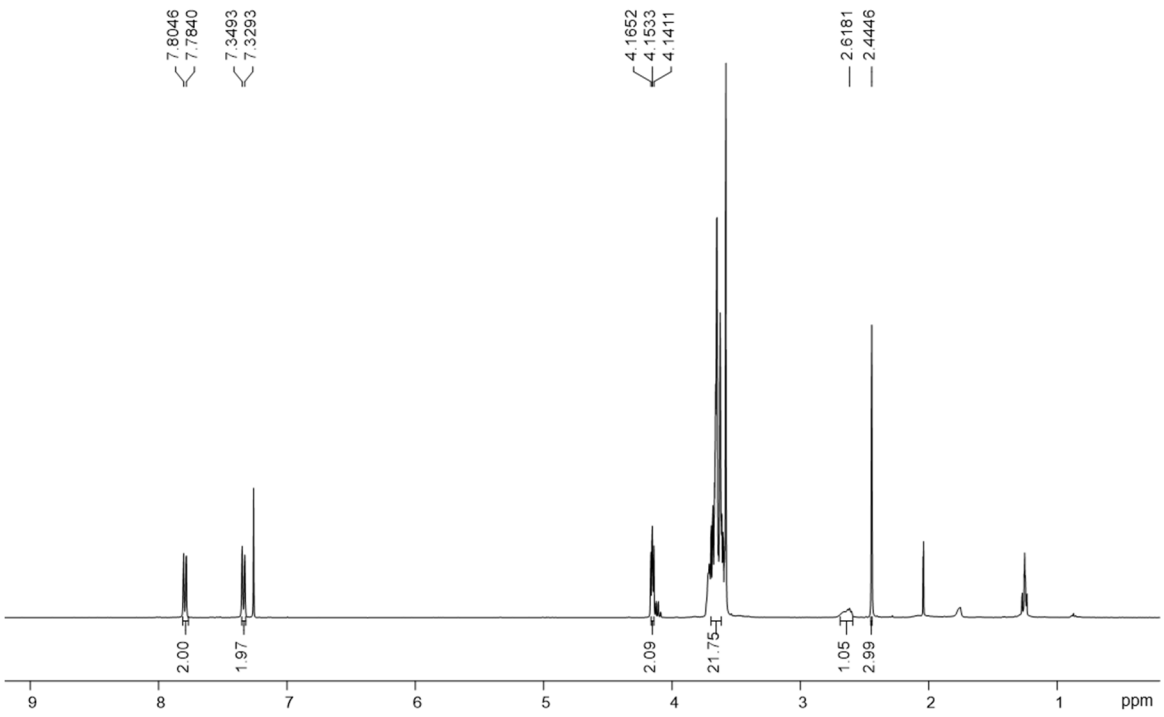


Figure S6. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of **5-OTs**.

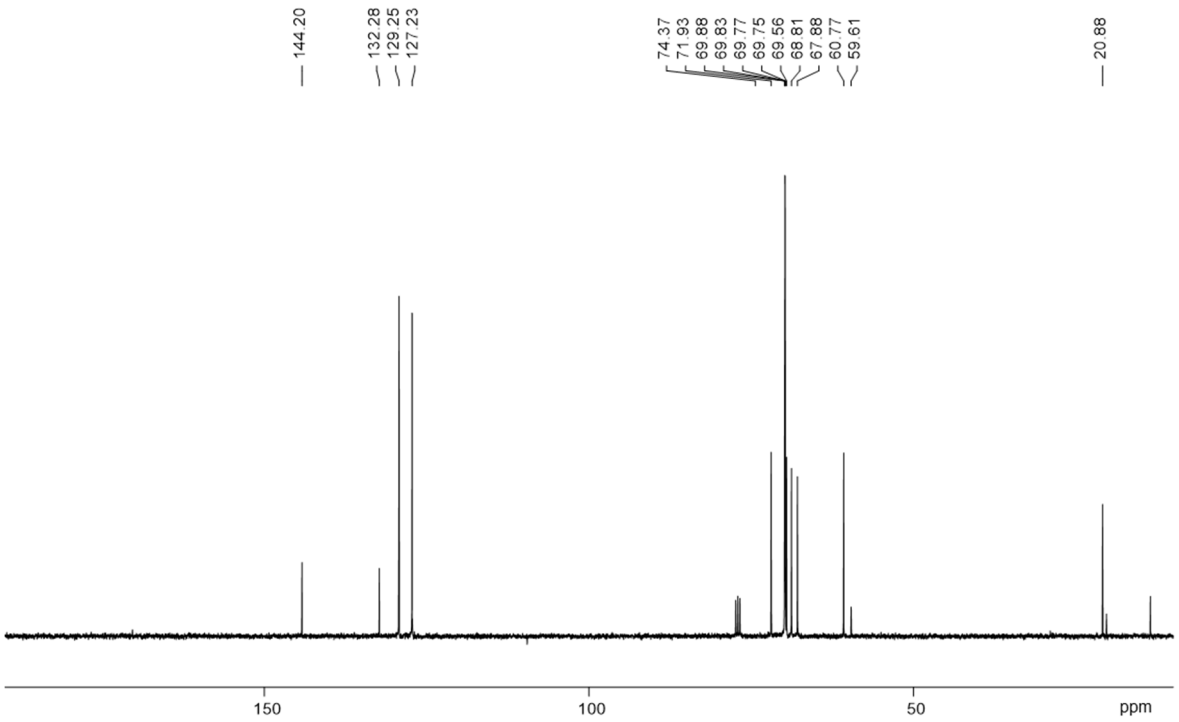


Figure S7. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) of **5-OTs**.

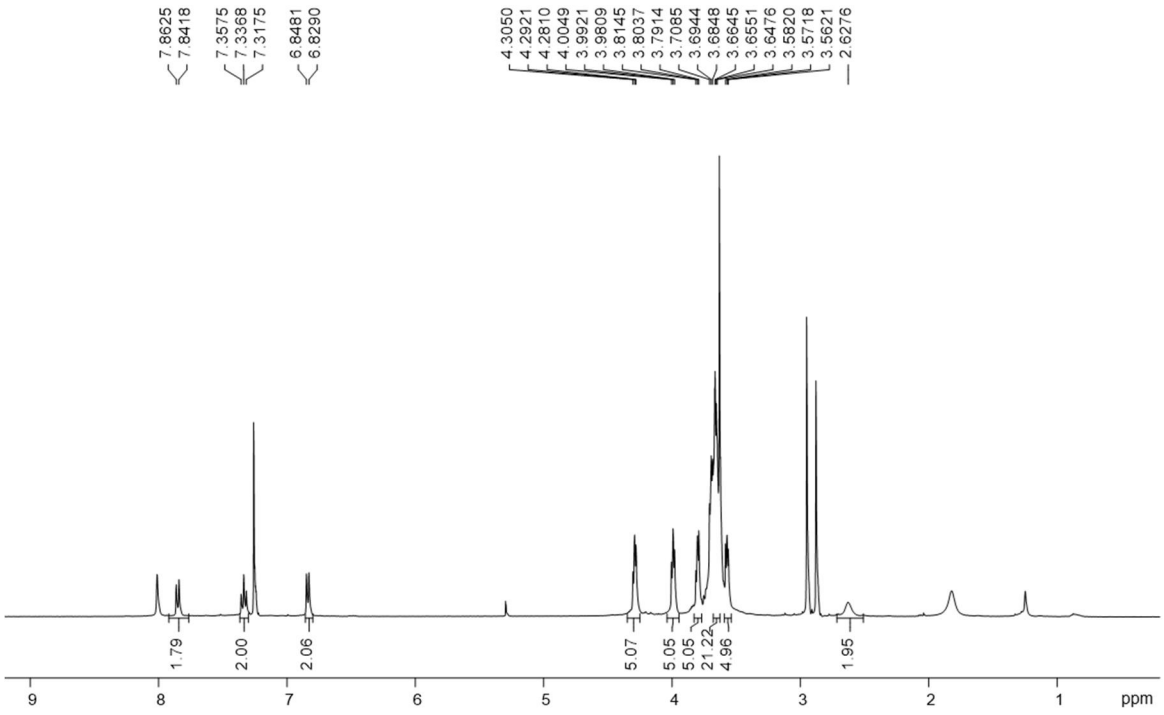


Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of **DN4-OH**.

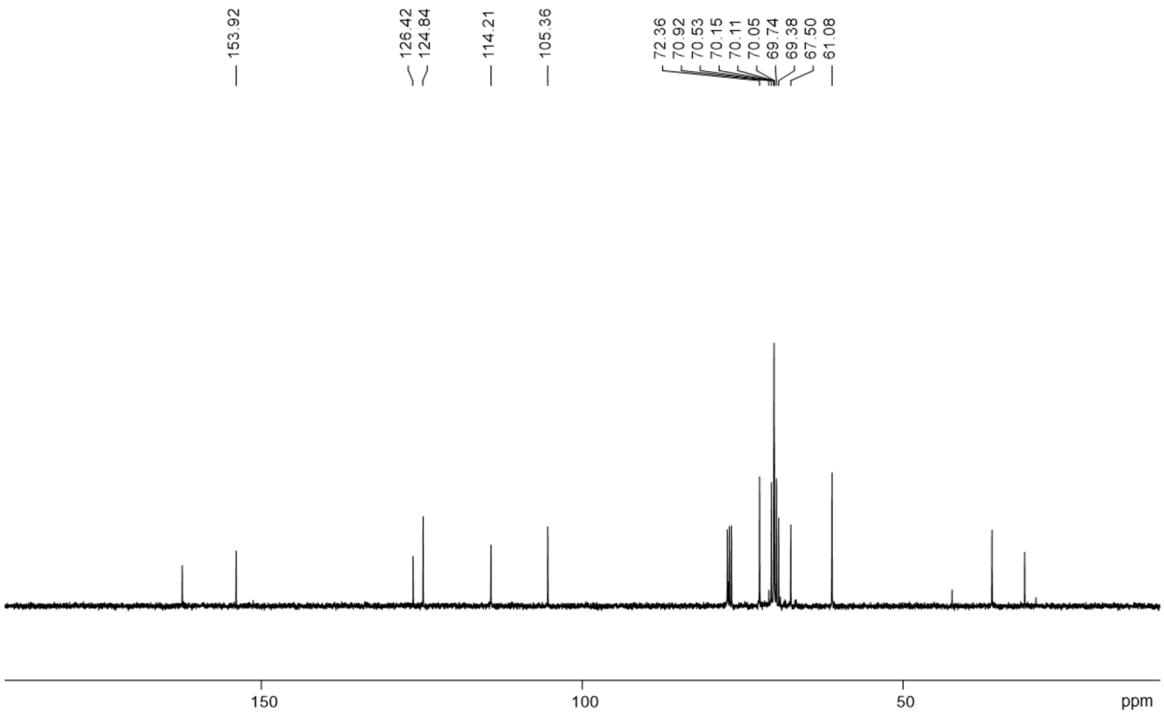


Figure S9. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) of **DN4-OH**.

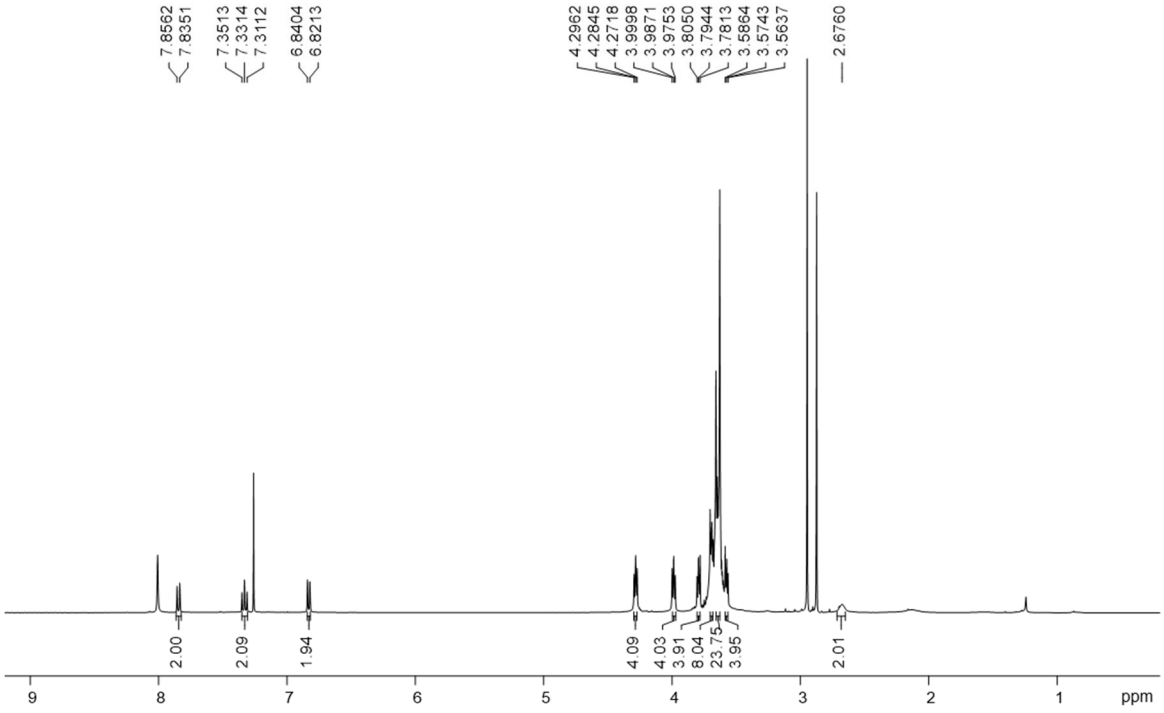


Figure S10. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of **DN5-OH**.

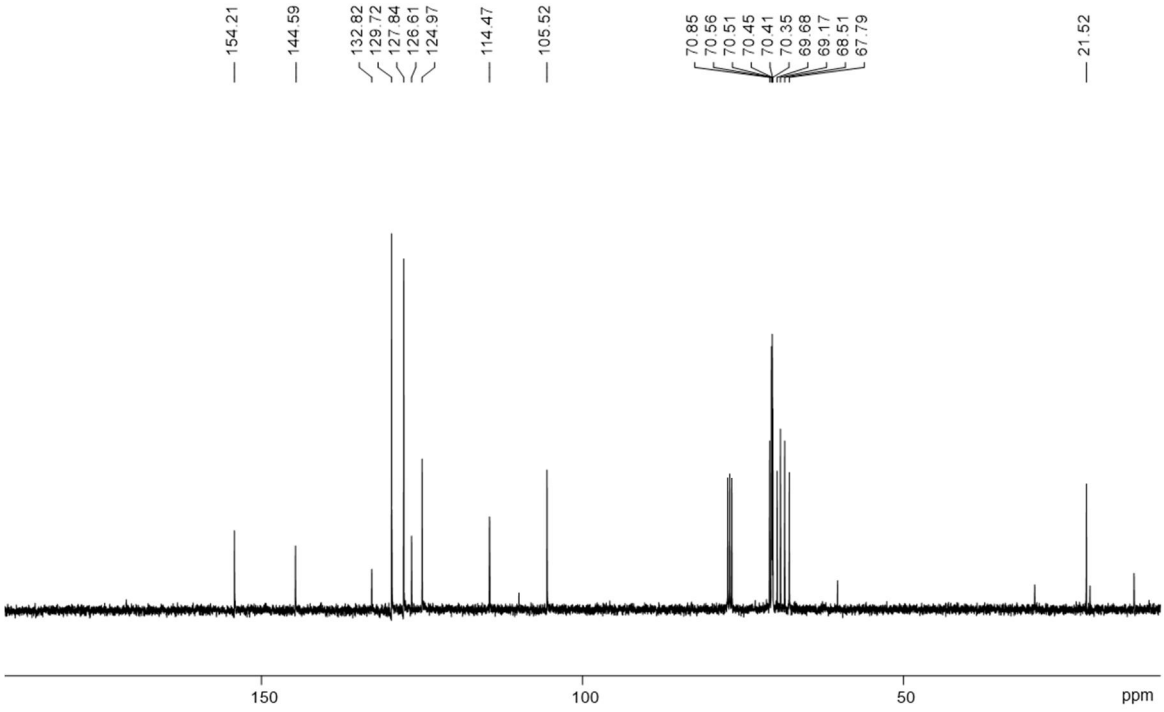


Figure S11. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) of **DN5-OH**.

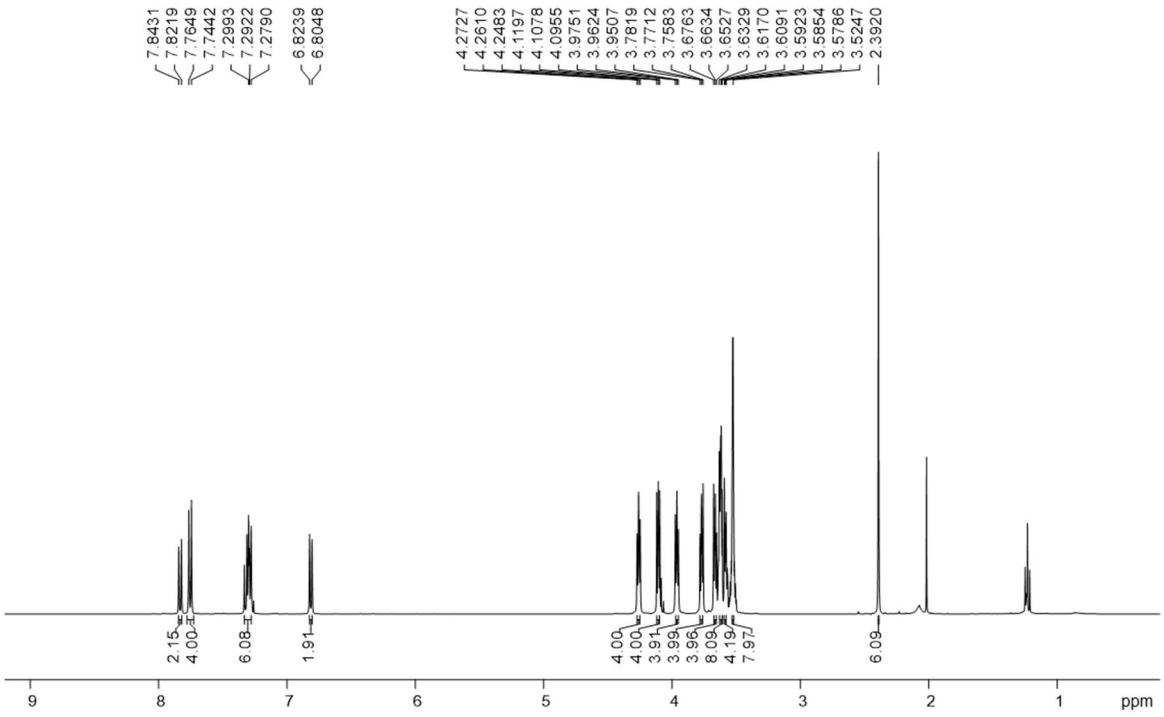


Figure S12. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of **DN4-OTs**.

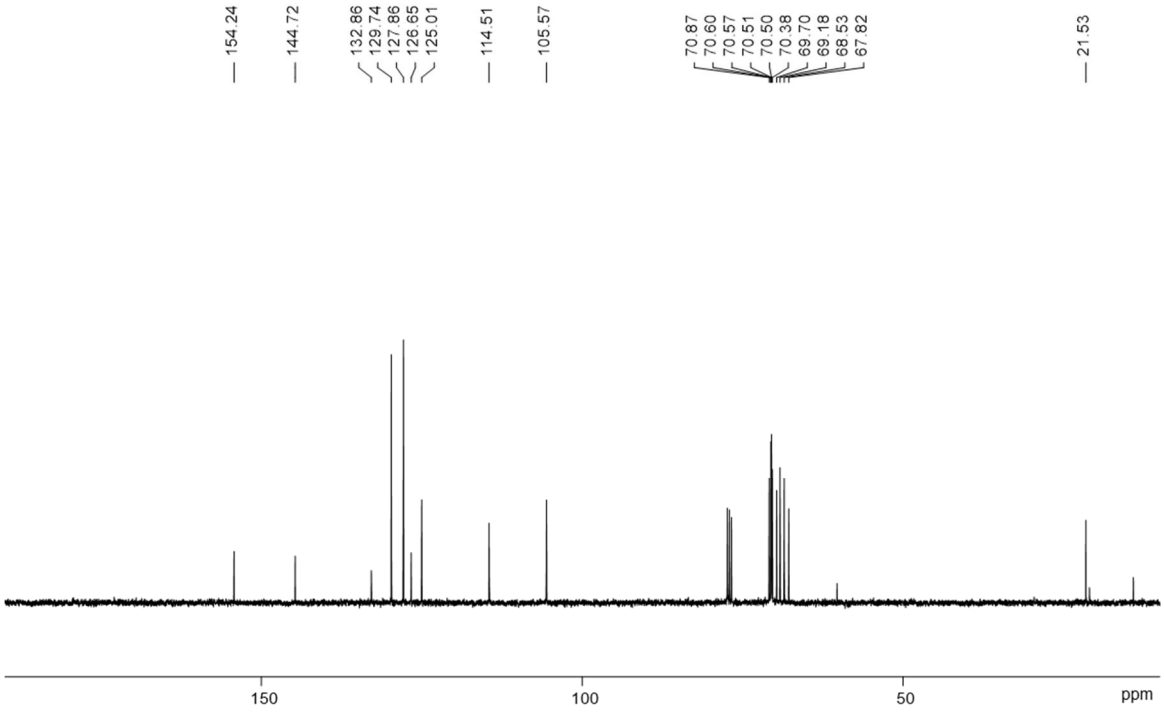


Figure S13. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) of **DN4-OTs**.

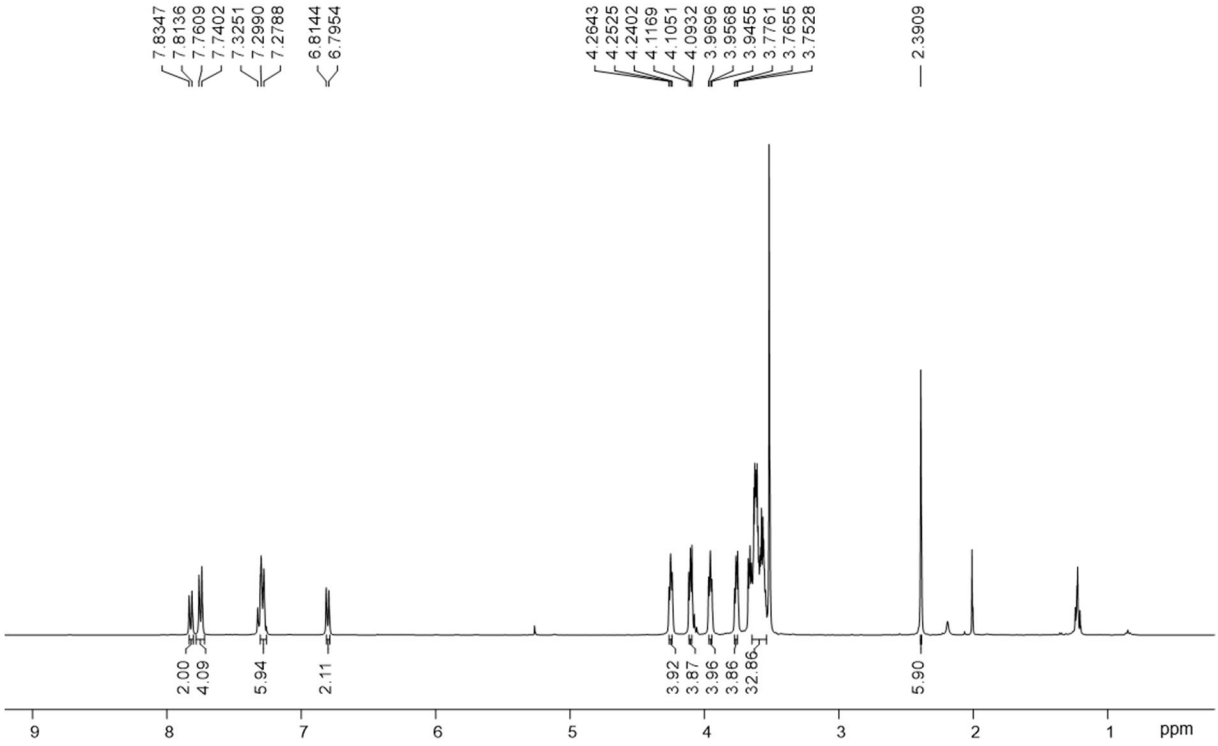


Figure S14. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of **DN5-OTs**.

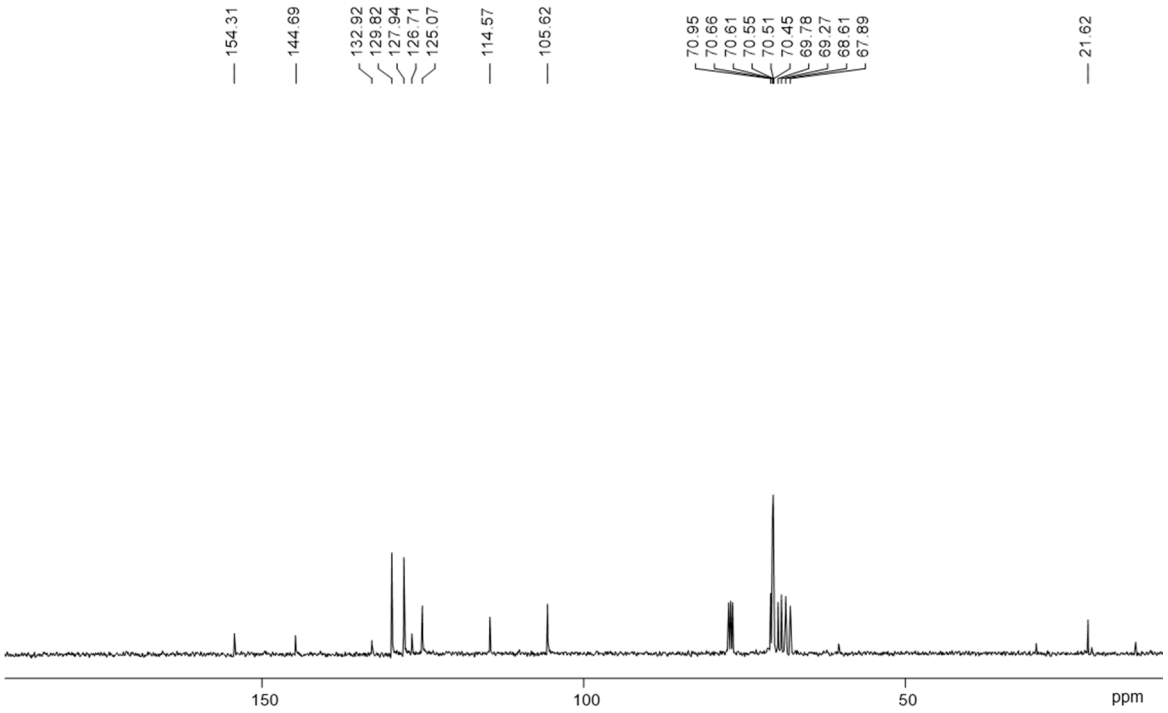


Figure S15. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) of **DN5-OTs**.

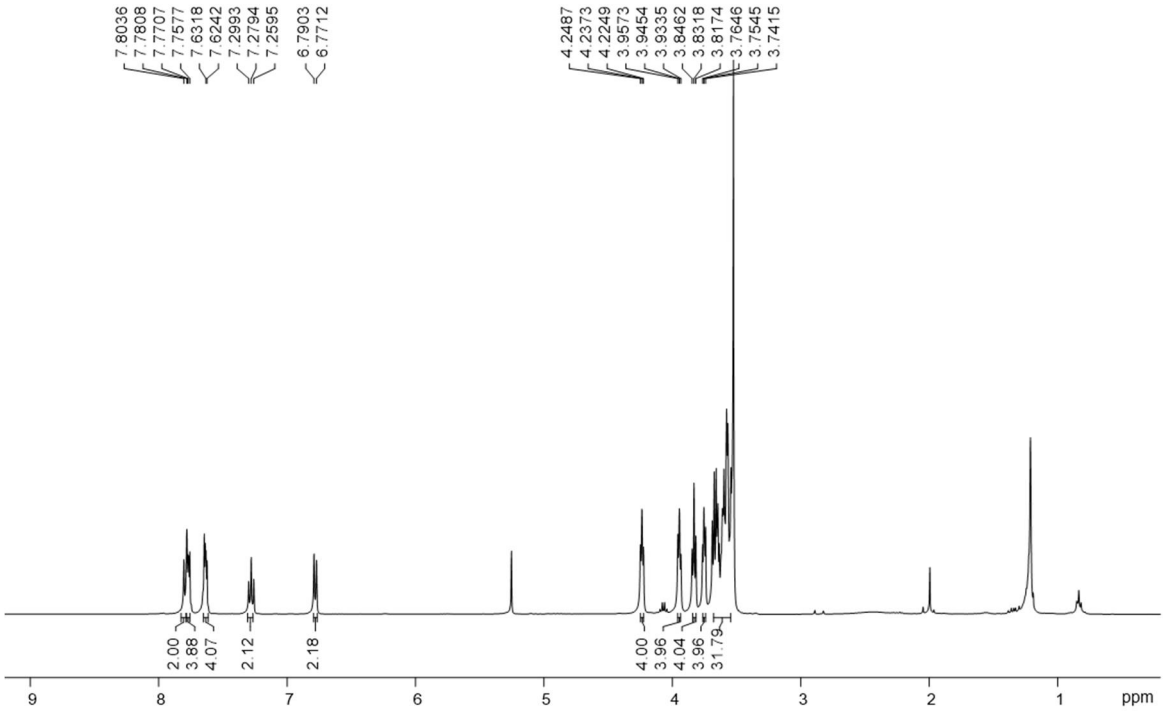


Figure S16. ^{1}HNMR (400 MHz, $CDCl_3$, 298 K) of **DN4-Pht**.

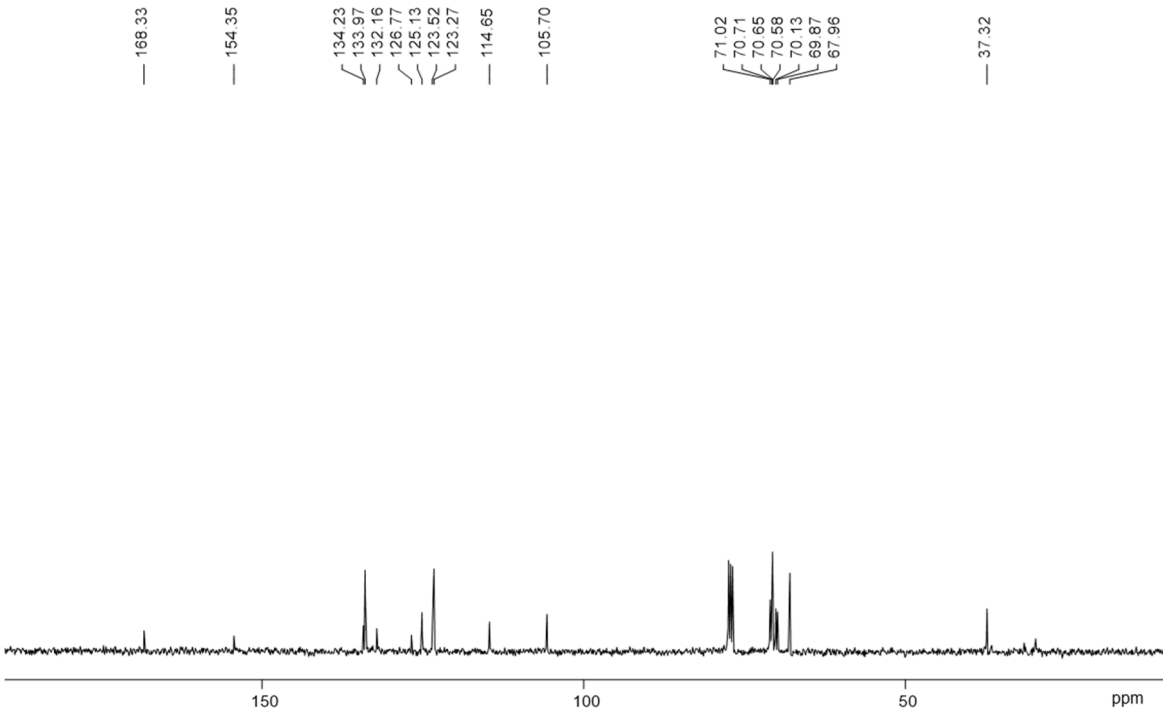


Figure S17. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) of **DN4-Pht**.

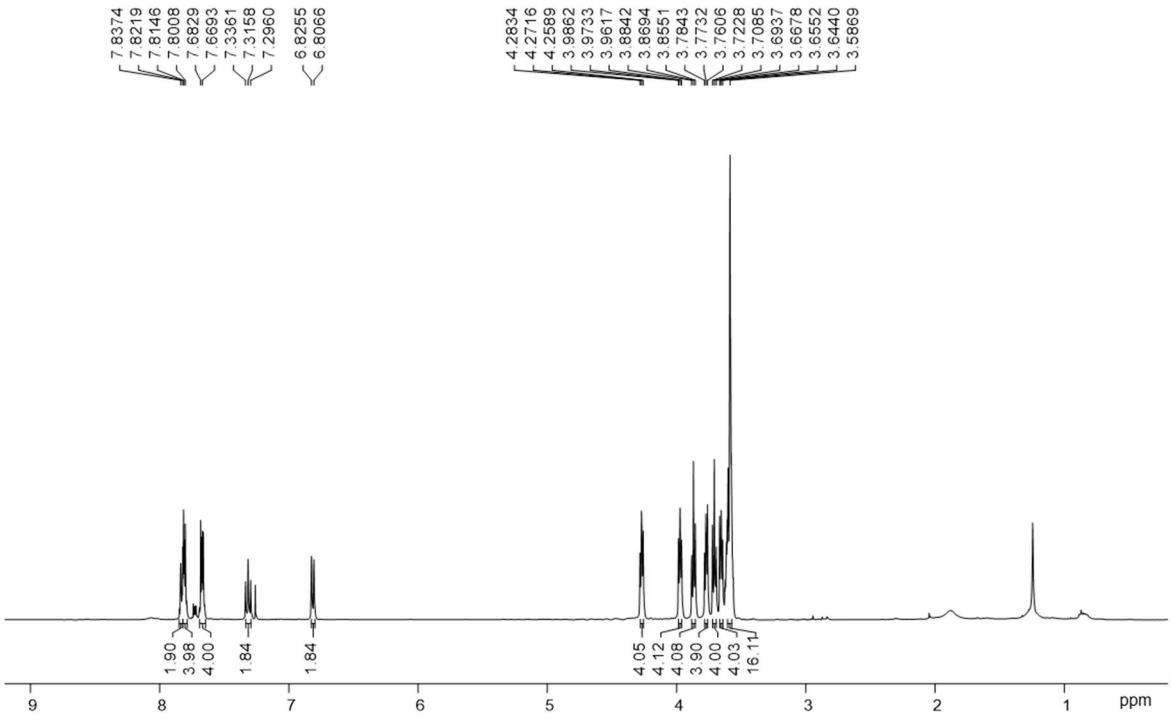


Figure S18. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of **DN5-Pht**.

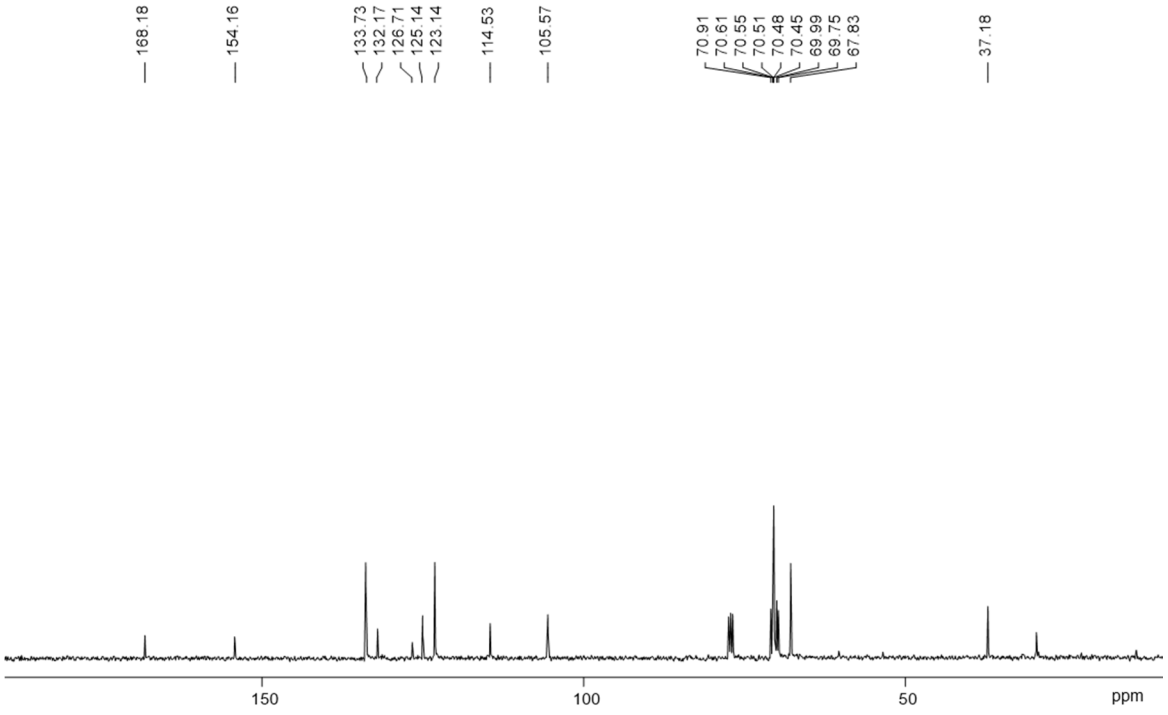


Figure S19. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) of **DN5-Pht**.

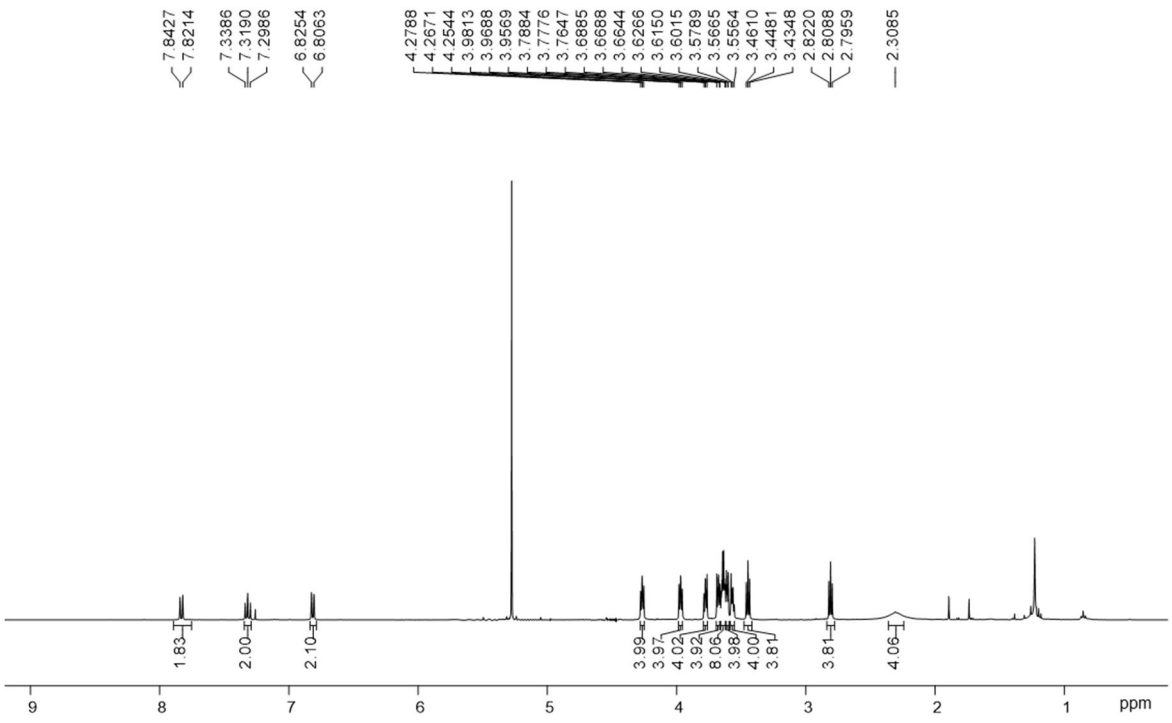


Figure S20. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of **DN4**.

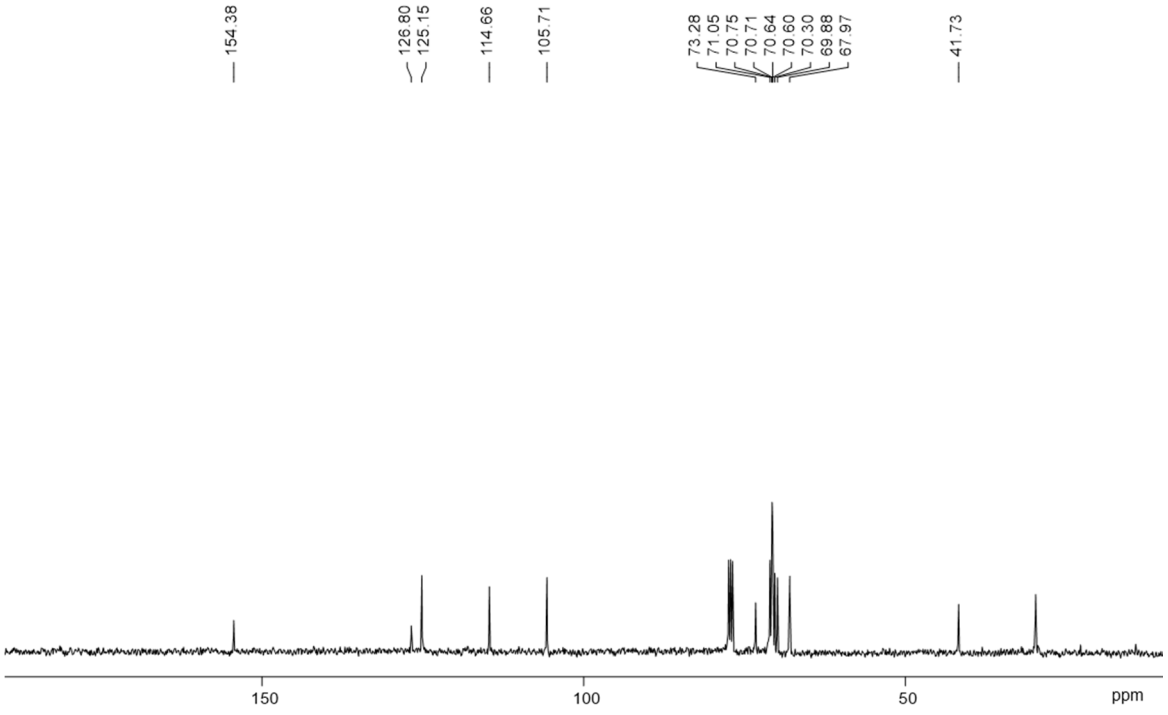


Figure S21. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) of **DN4**.

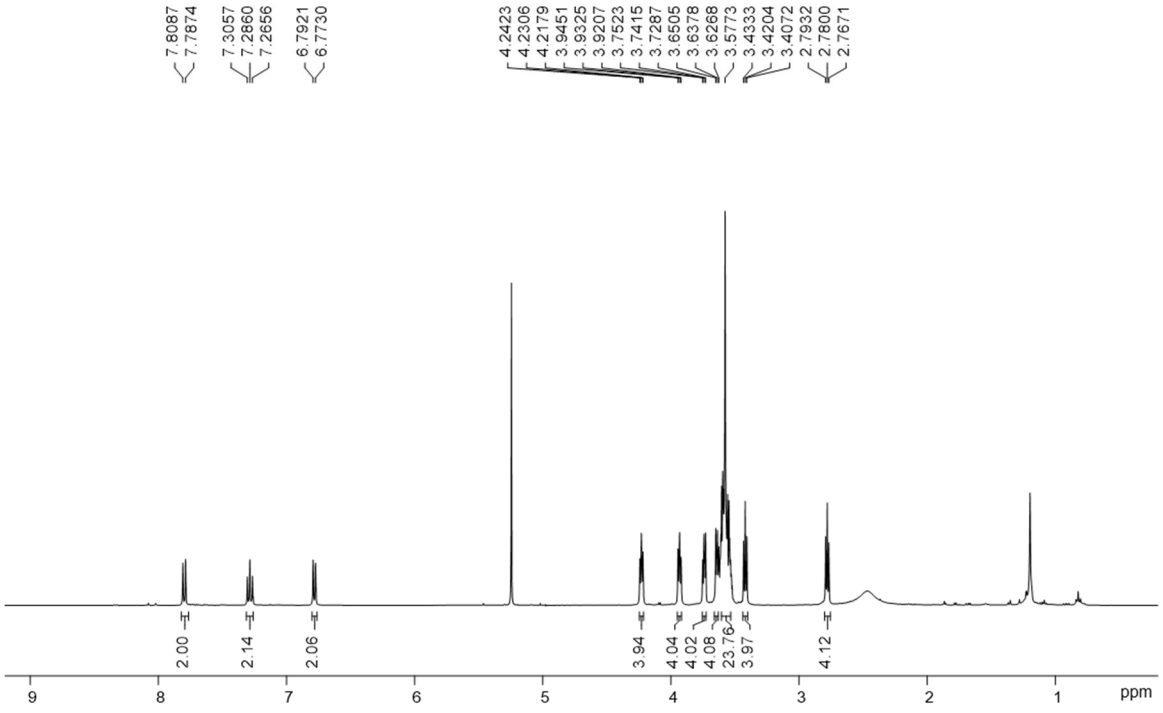


Figure S22. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of **DN5**.

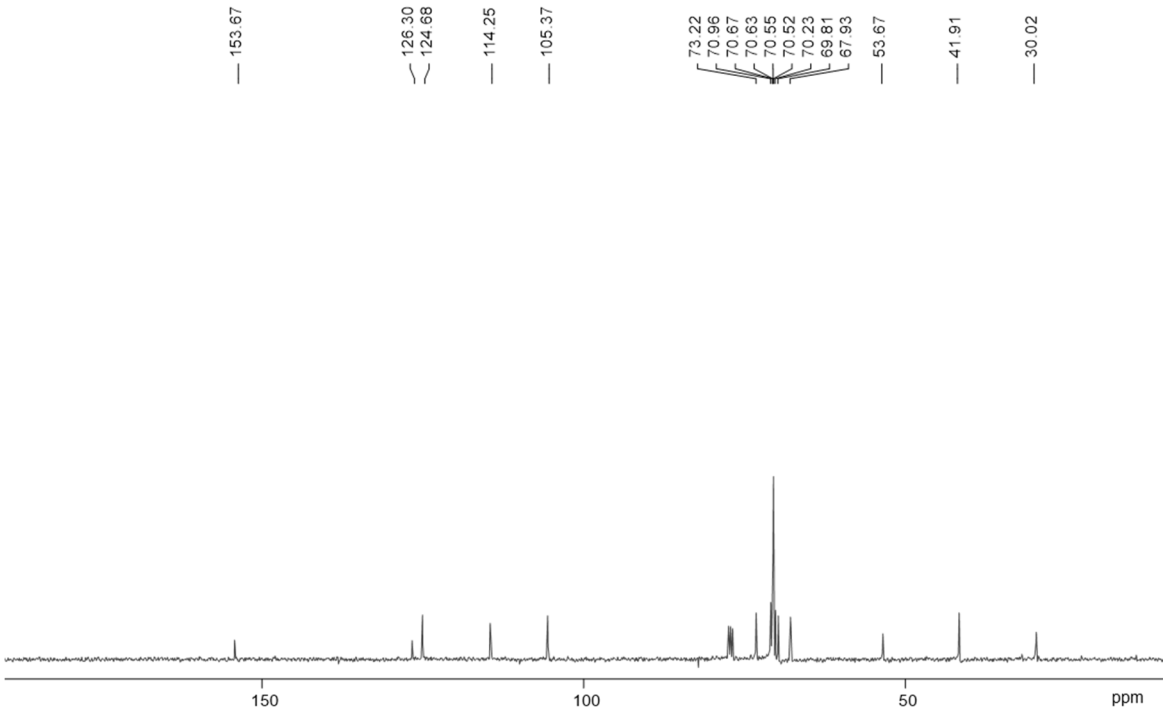


Figure S23. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) of **DN5**.

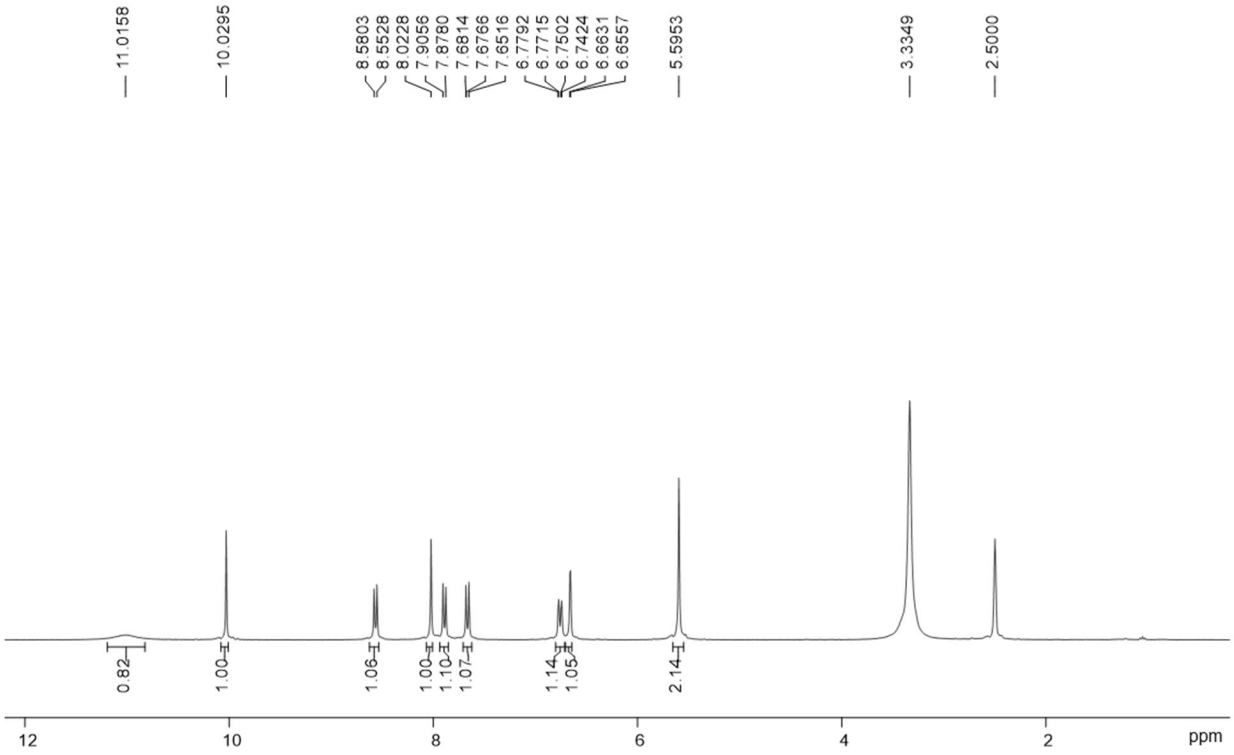


Figure S24. ^{1}H NMR (300 MHz, $(CD_3)_2SO$, 298 K) of **L2**.

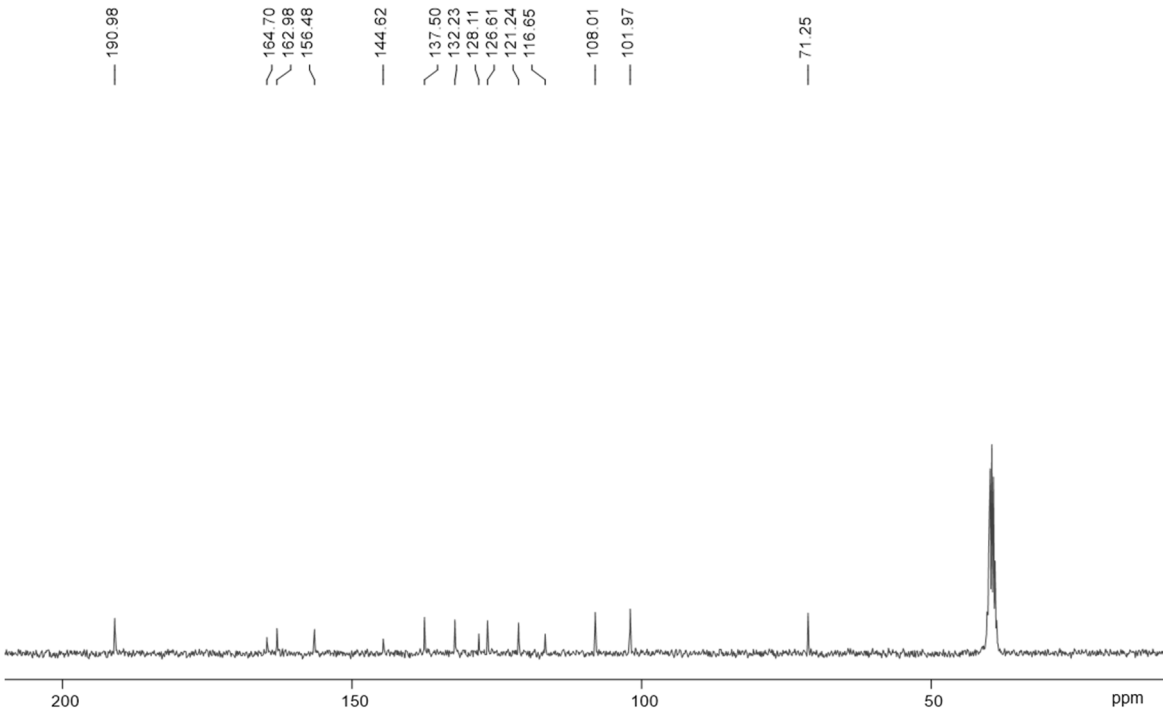


Figure S25. $^{13}C\{^{1}H\}$ NMR (75 MHz, $(CD_3)_2SO$, 298 K) of **L2**.

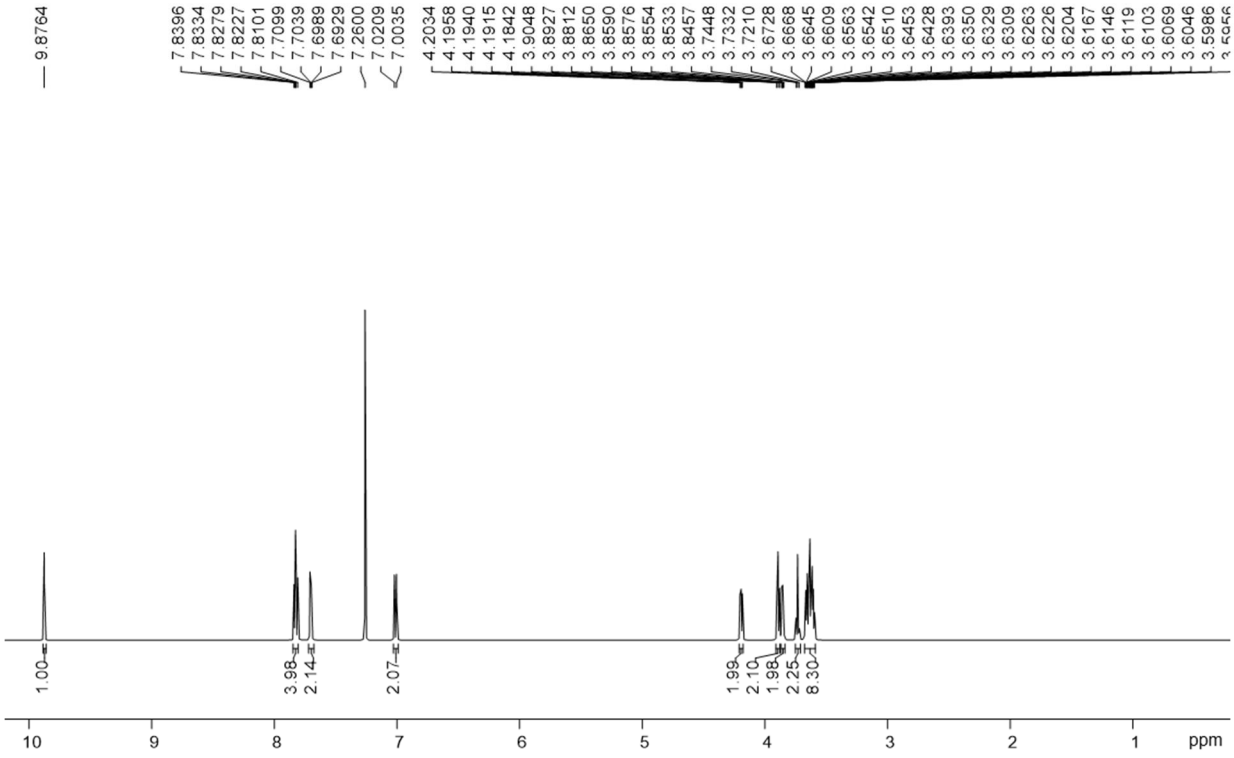


Figure S26. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of **S1**.

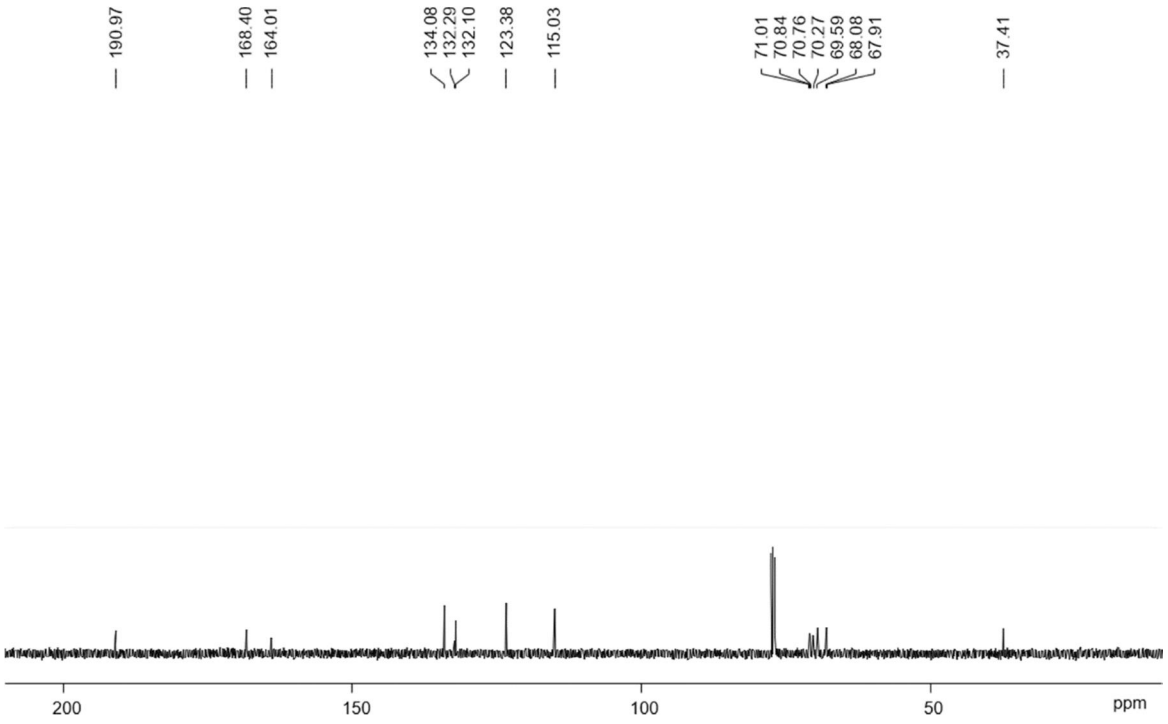


Figure S27. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) of **S1**.

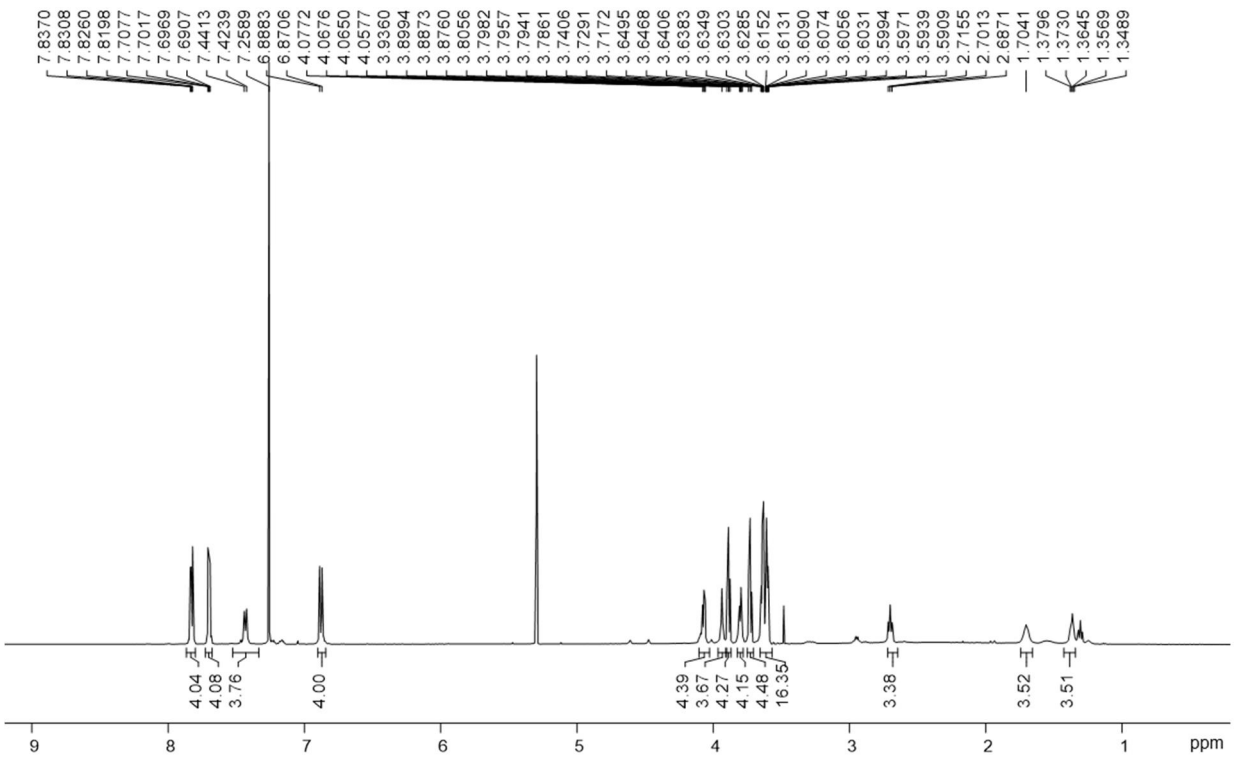


Figure S28. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) of **Hex-Pht**.

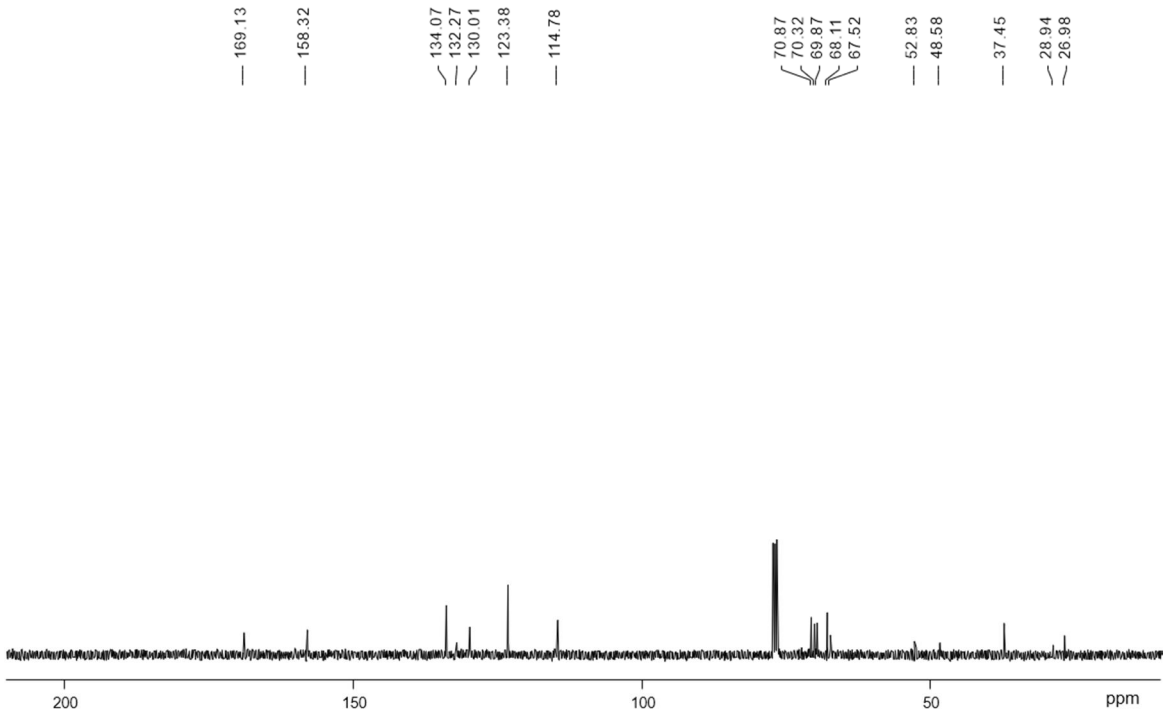


Figure S29. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) of **Hex-Pht**.

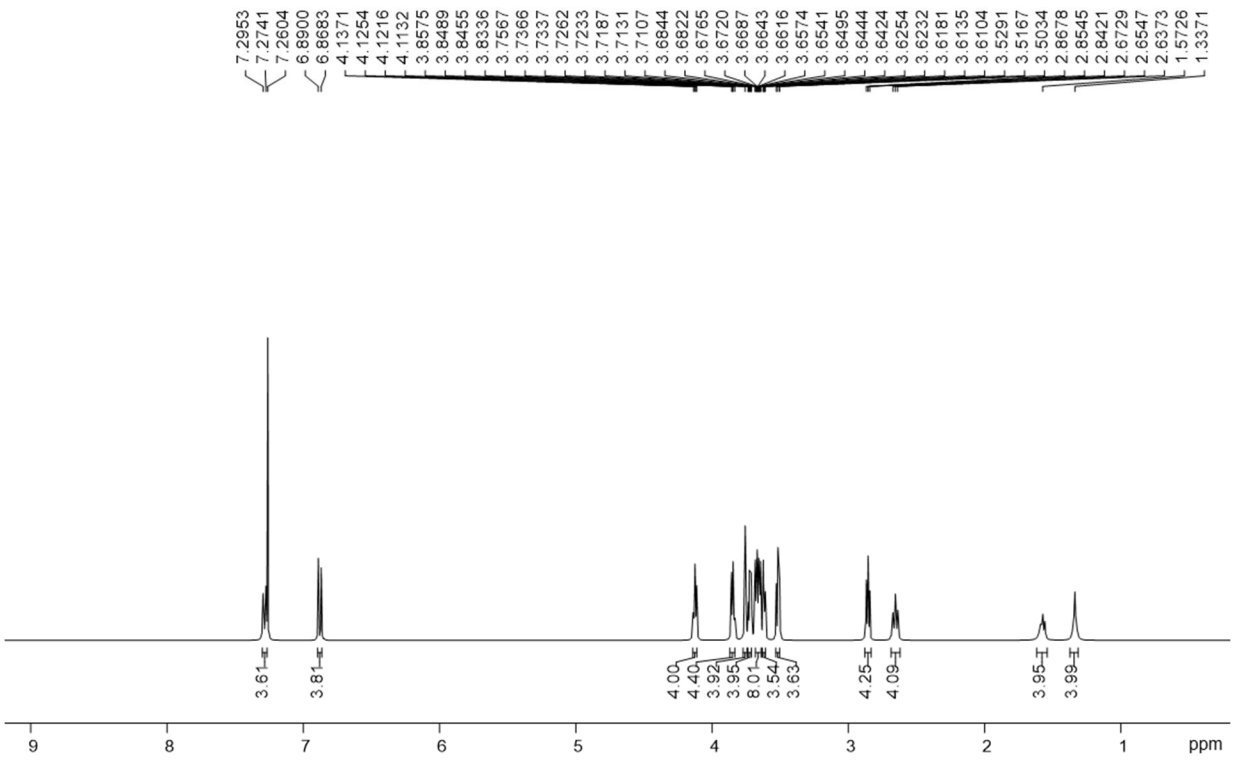


Figure S30. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) of **Hex**.

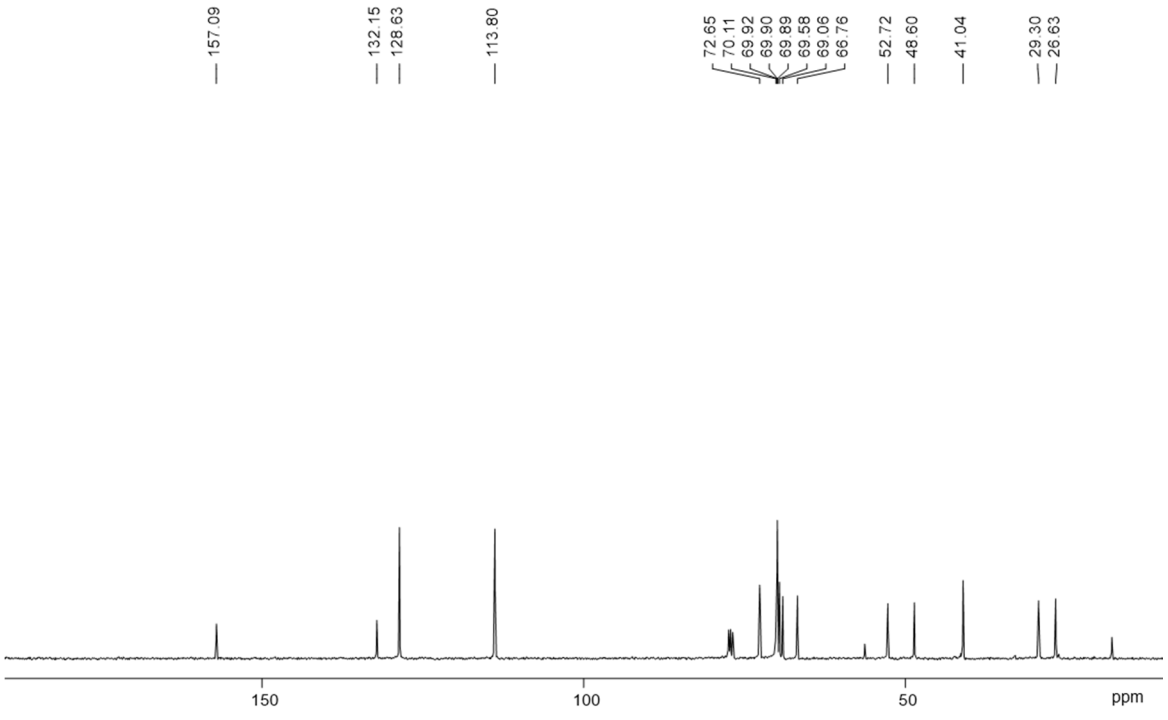


Figure S31. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K) of **Hex**.

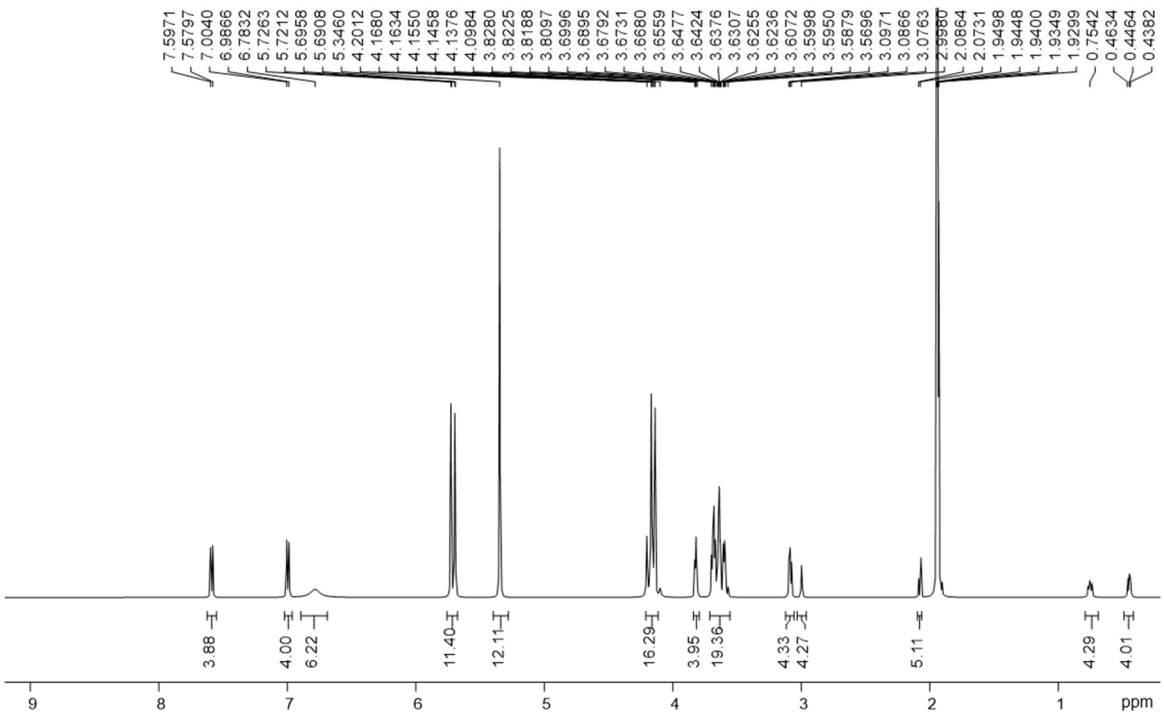


Figure S32. ^{1}H NMR (500 MHz, CD_3CN, 298 K) of **Hex**·CB[6].

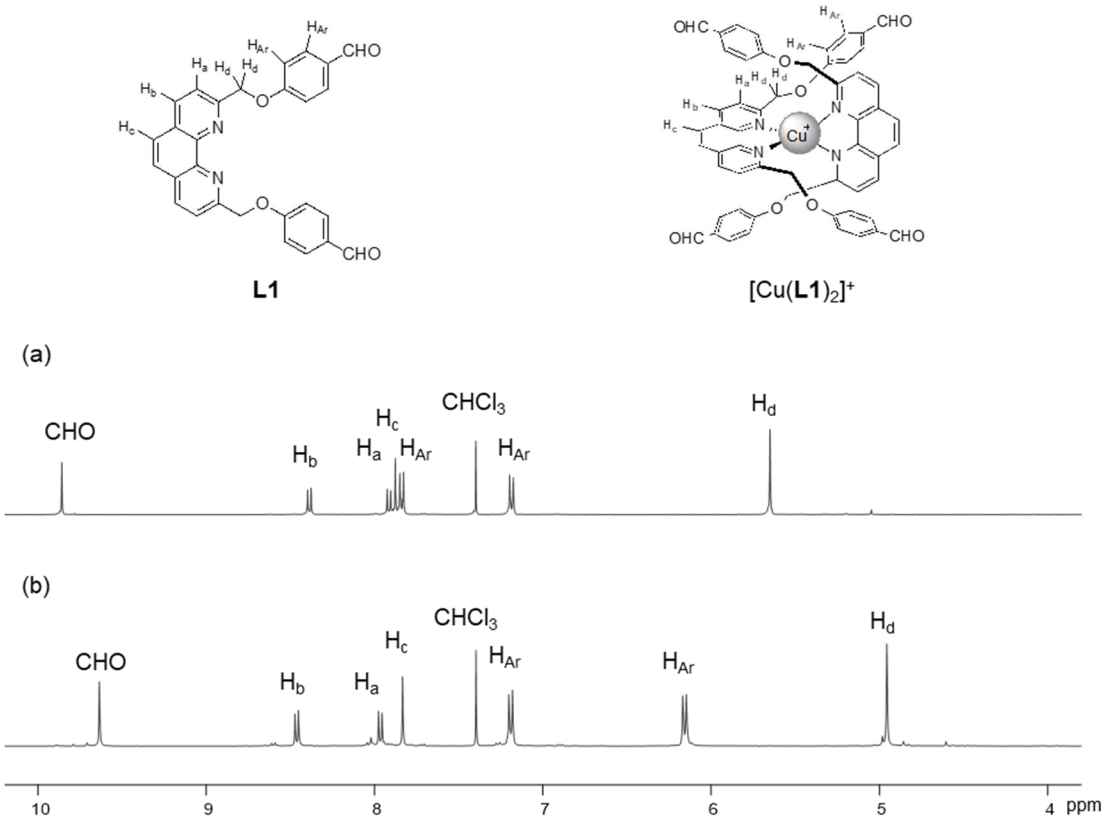


Figure S33. ^{1}H NMR (400 MHz, $CDCl_3/CD_3CN$ = 7/3, 298 K) of (a) **L1** and (b) $[Cu(\mathbf{L1})_2]^+$.

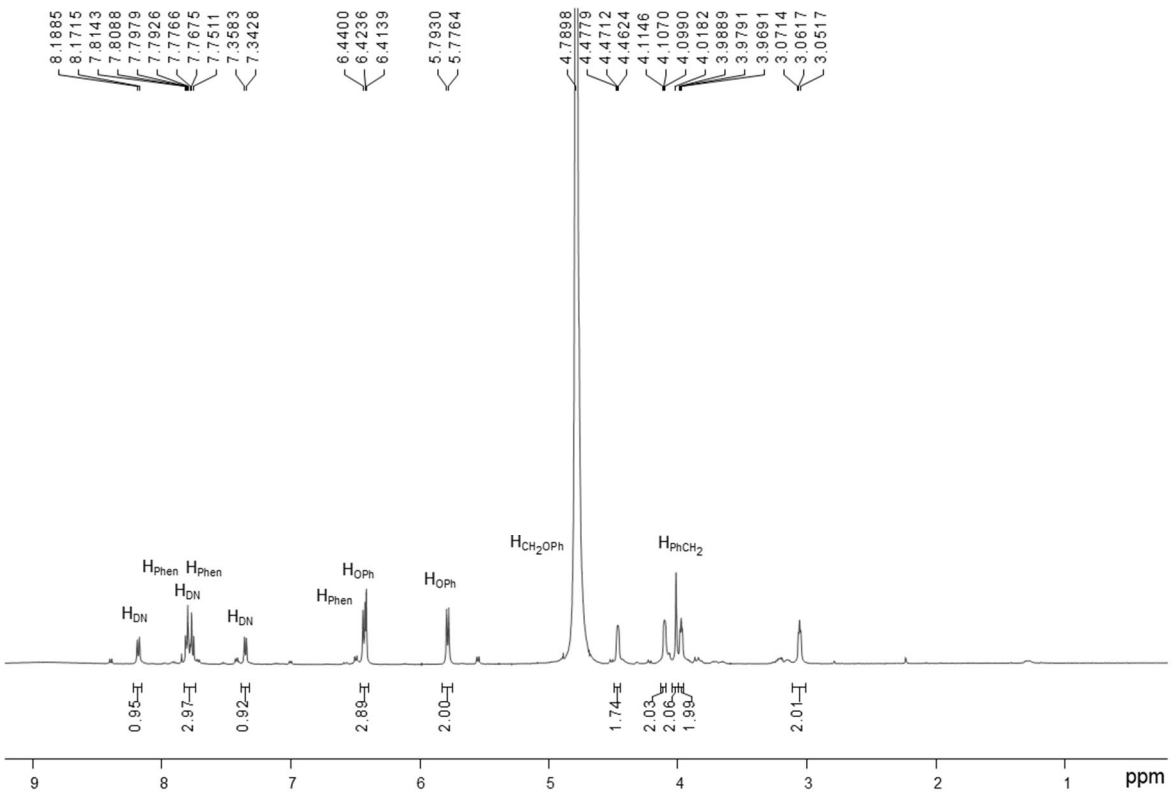


Figure S34. ^{1}H NMR (500 MHz, D_2O, 298 K) of **H1**.

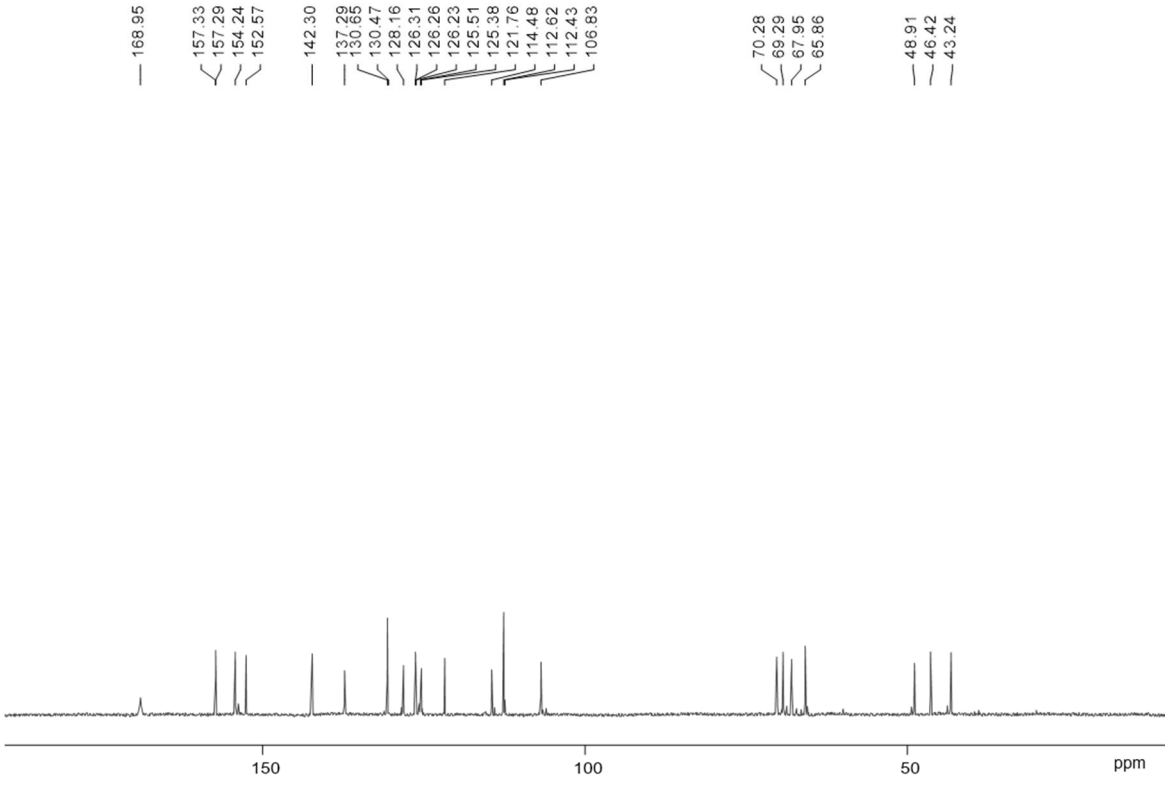


Figure S35. $^{13}C\{^{1}H\}$ NMR (150 MHz, D_2O, 298 K) of **H1**.

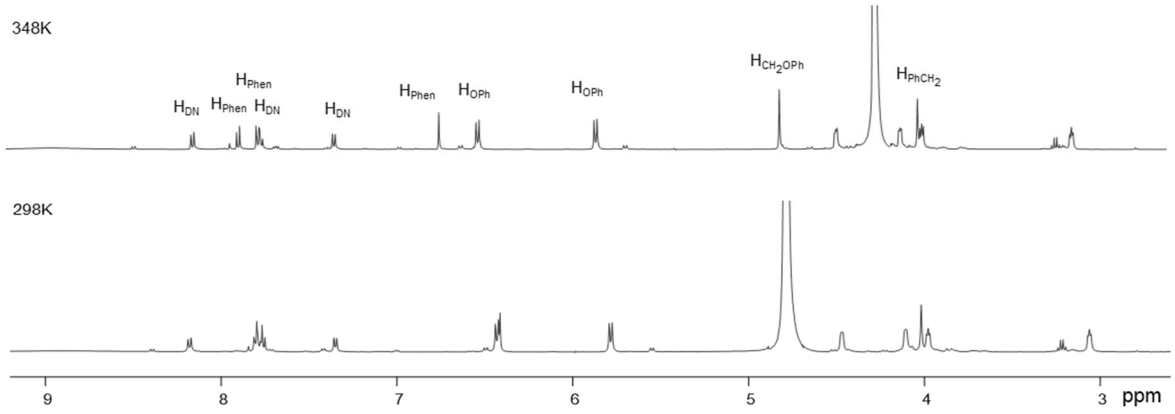


Figure S36. ^{1}H NMR (500 MHz, D_2O) of **H1** at 348 K (top) and 298 K (bottom).

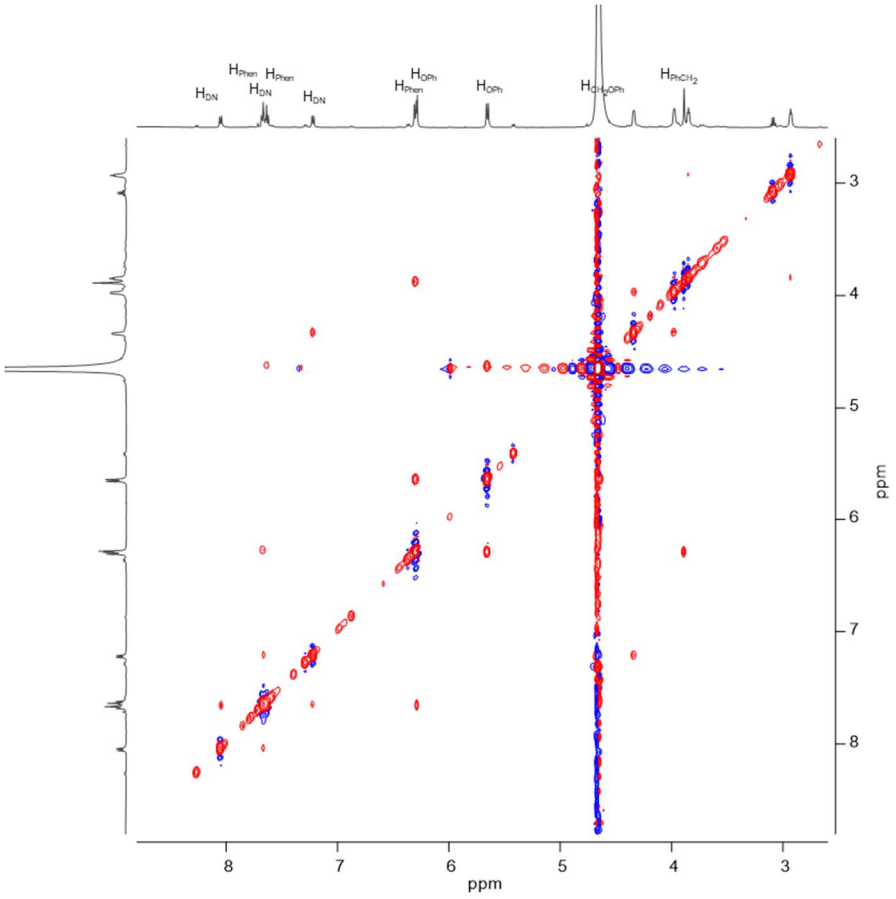


Figure S37. NOESY (500 MHz, D_2O, 298 K, d_8 = 700ms) of **H1**.

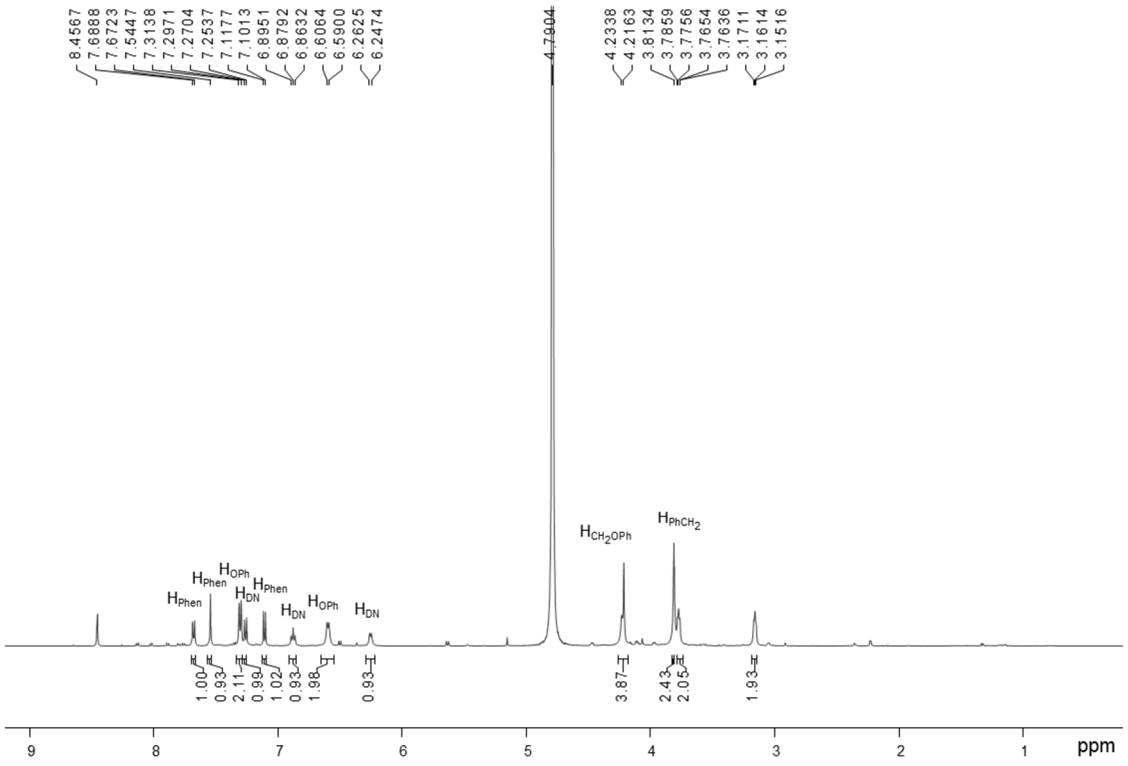


Figure S38. ^{1}H NMR (500 MHz, D_2O, 298 K) of **H1b**.

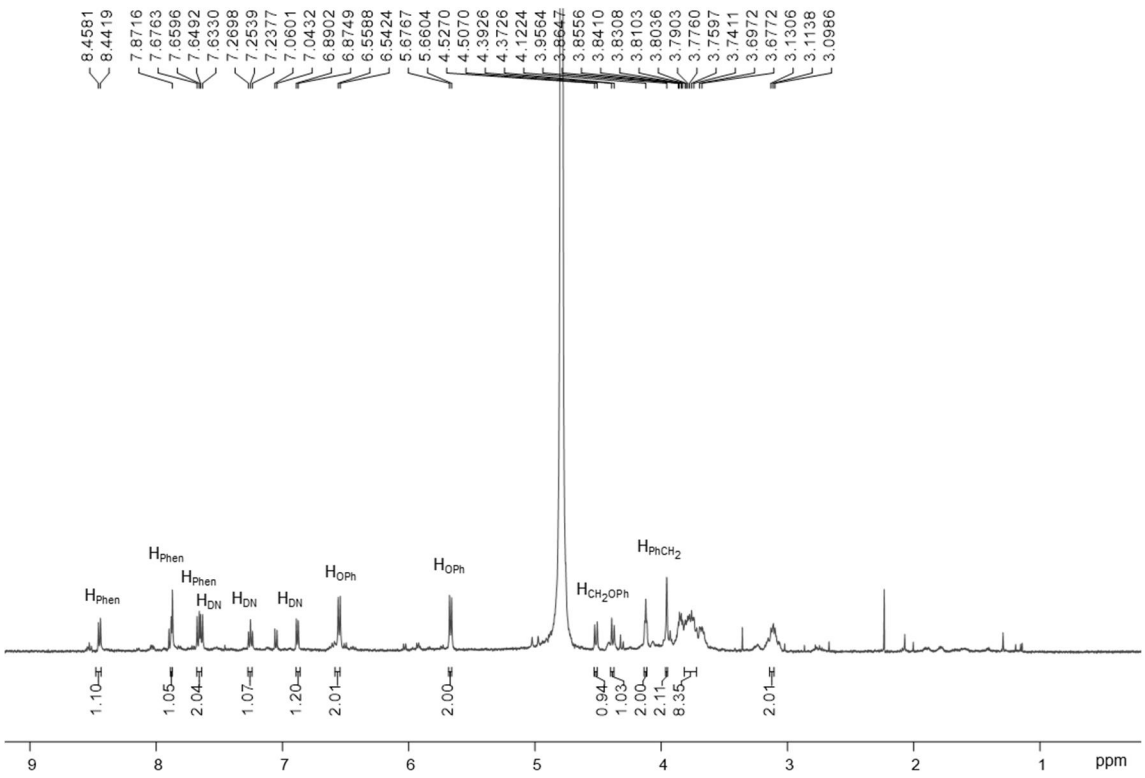


Figure S39. ^{1}H NMR (500 MHz, D_2O, 298 K) of **F2**.

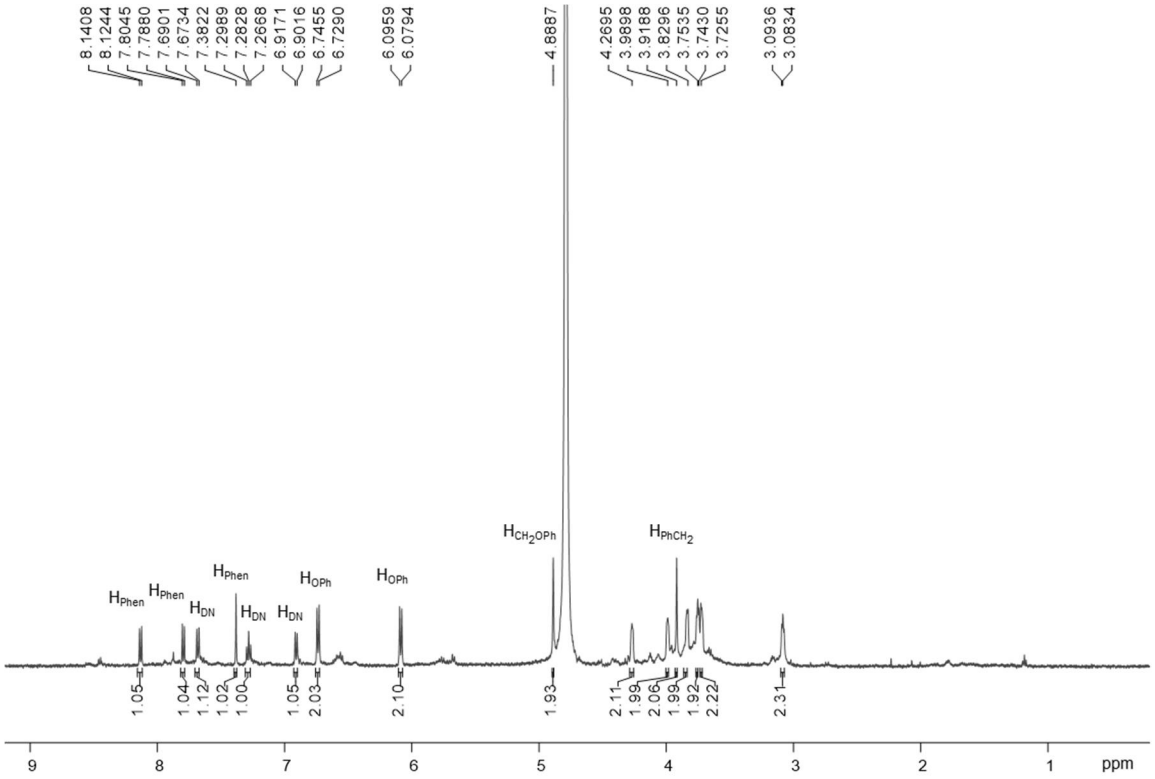


Figure S40. ^{1}H NMR (500 MHz, D_2O, 298 K) of **H2**.

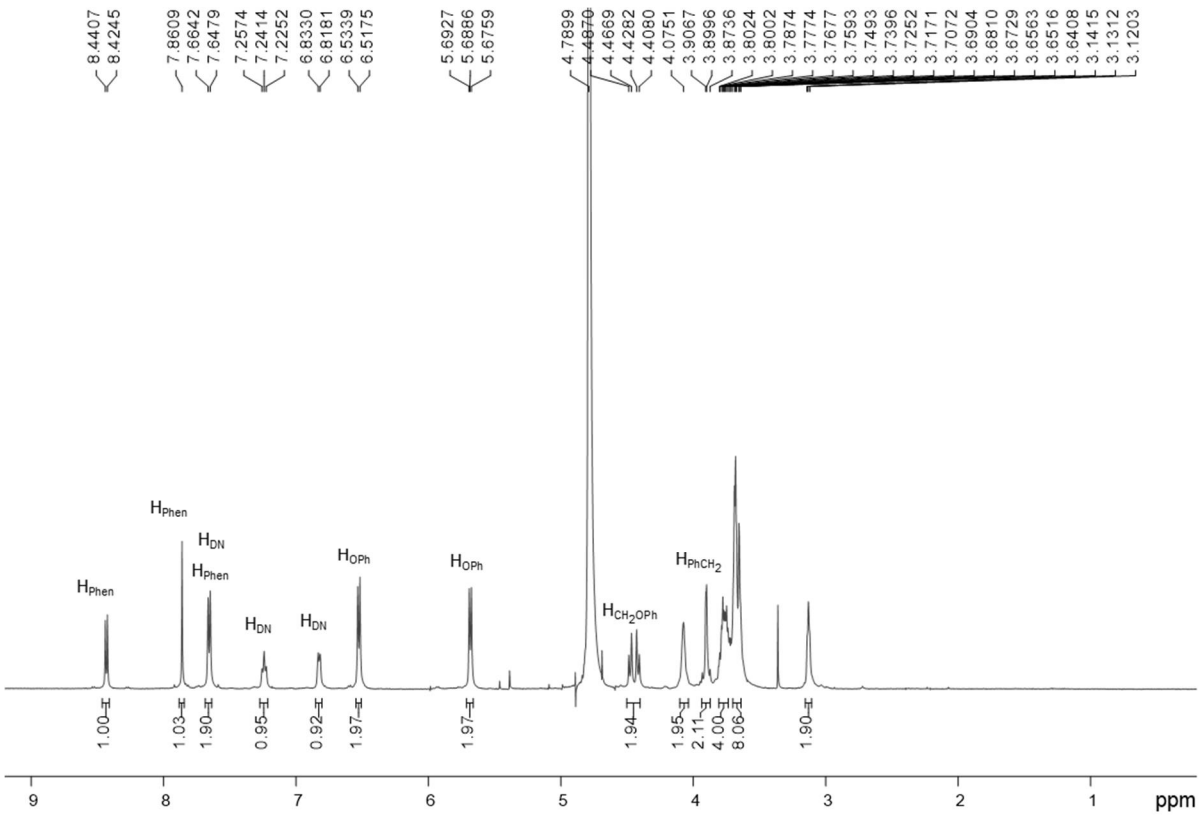


Figure S41. ^{1}H NMR (500 MHz, D_2O, 298 K) of **F3**.

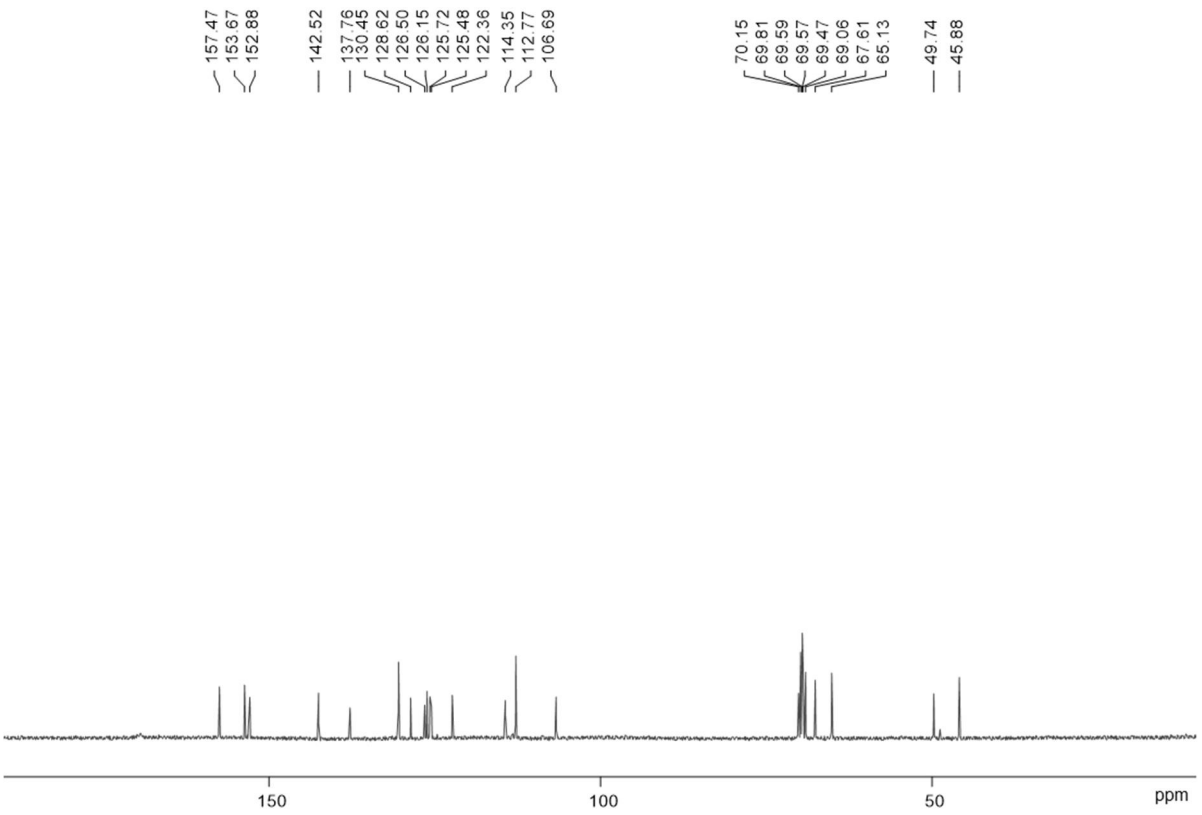


Figure S42. $^{13}C\{^{1}H\}$ NMR (150 MHz, D_2O, 298 K) of **F3**.

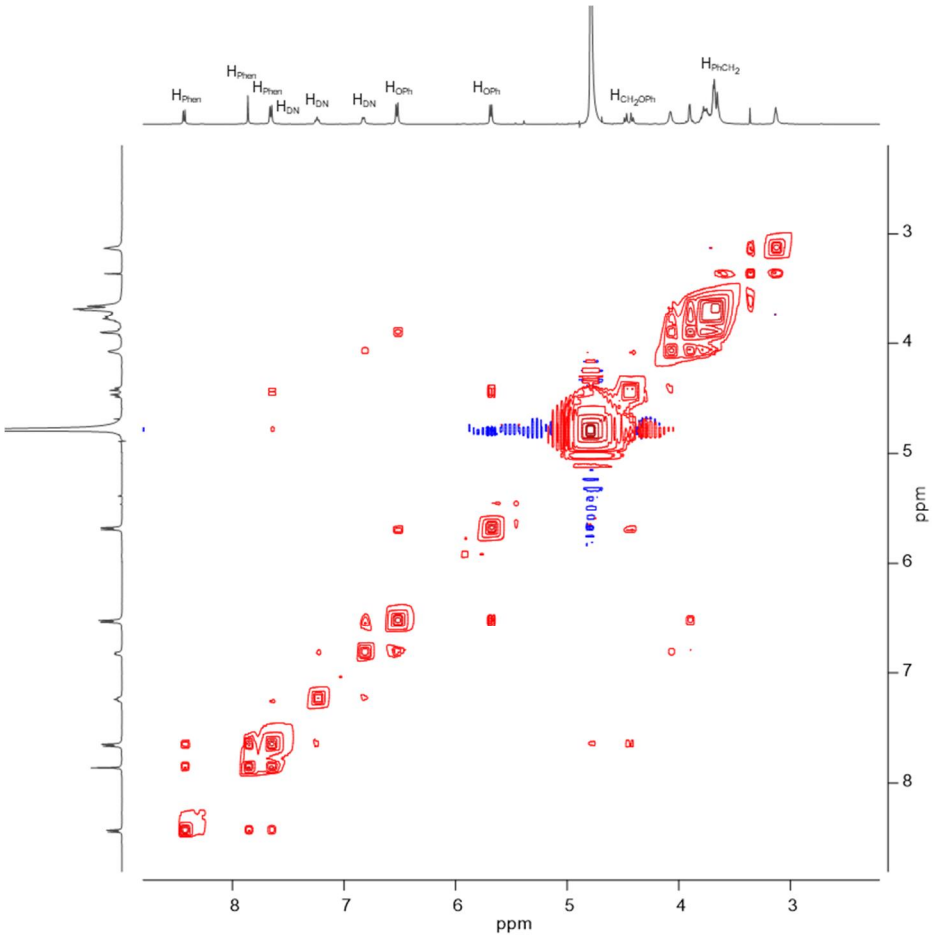


Figure S43. NOESY (500 MHz, D_2O, 298 K, d_8 = 700 ms) of **F3**.

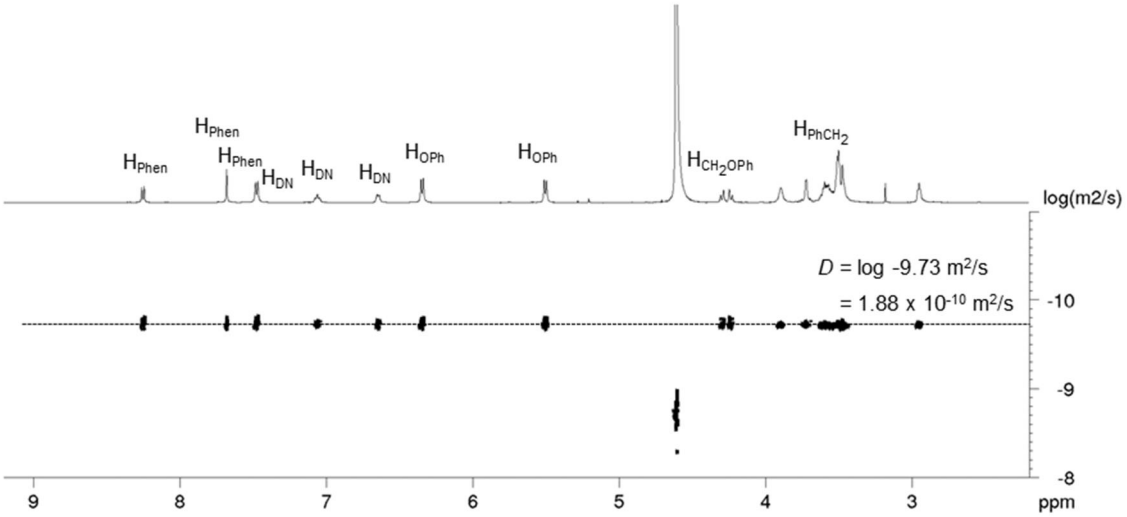


Figure S44. DOSY (500 MHz, D_2O, 298 K) of **F3**.

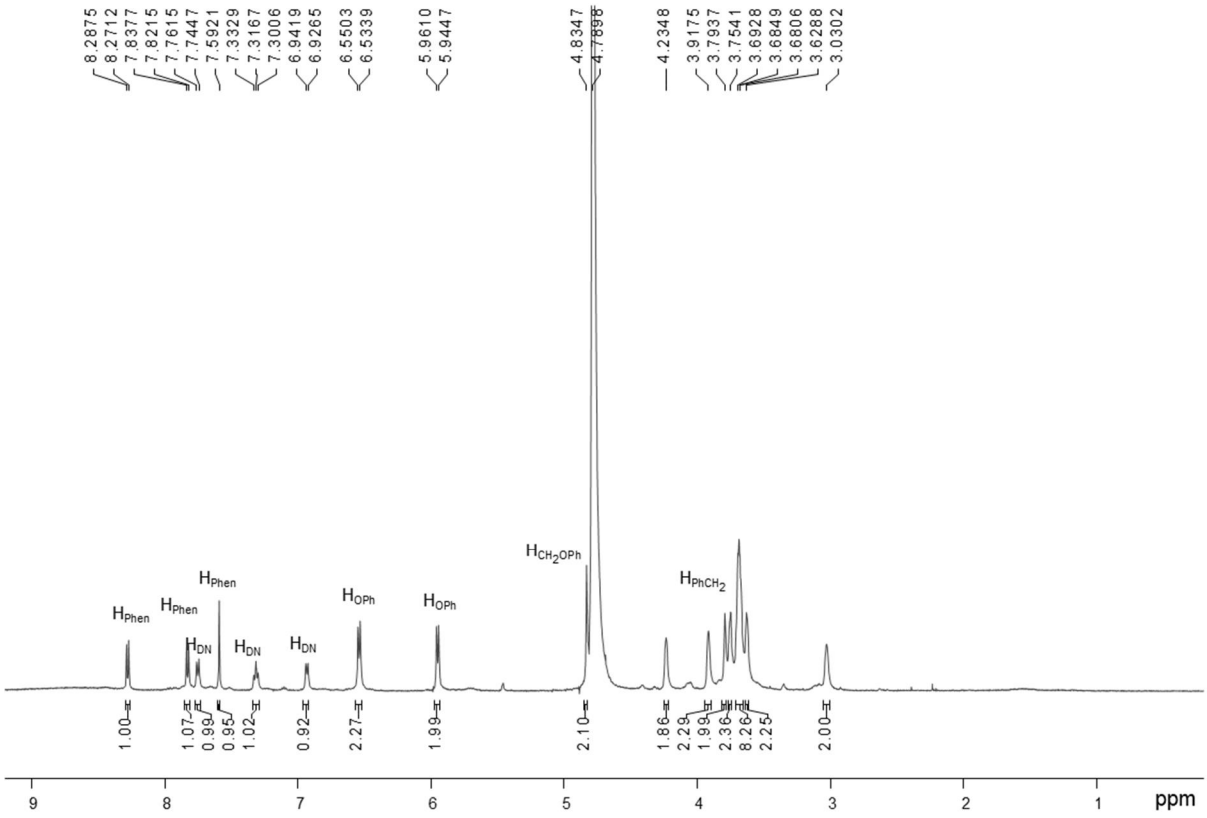


Figure S45. ^{1}H NMR (500 MHz, D_2O, 298 K) of **H3**.

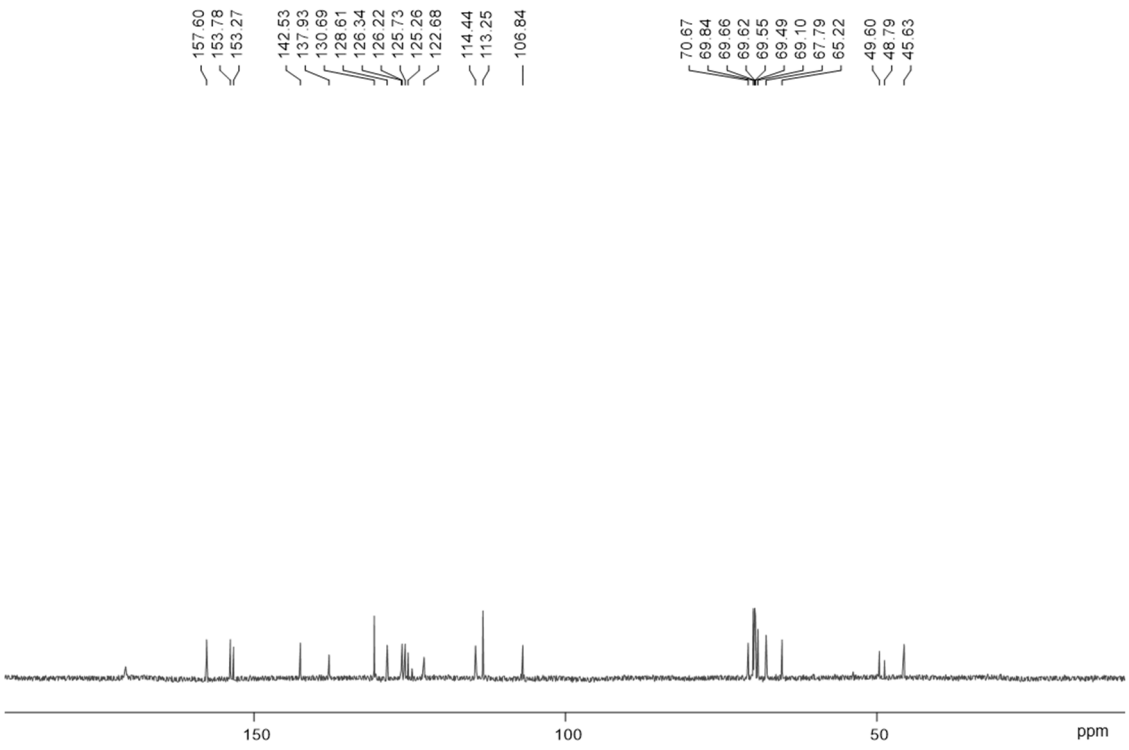


Figure S46. $^{13}C\{^{1}H\}$ NMR (150 MHz, D_2O, 298 K) of **H3**.

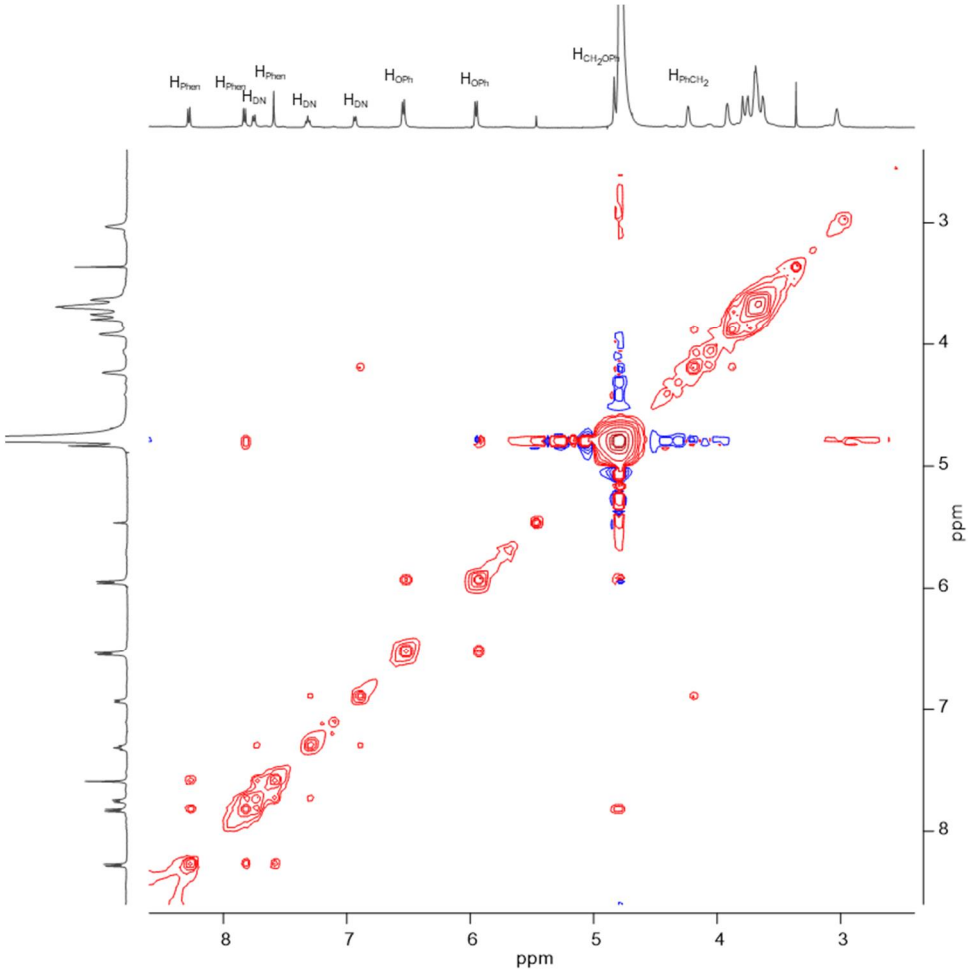


Figure S47. NOESY (500 MHz, D_2O, 298 K, d_8 = 700ms) of **H3**.

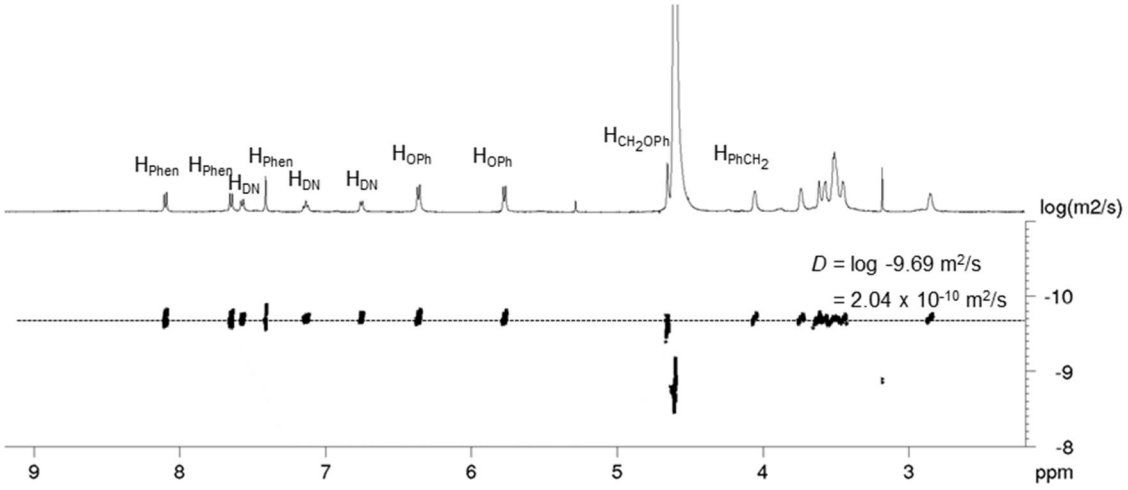


Figure S48. DOSY (500 MHz, D_2O, 298 K) of **H3**.

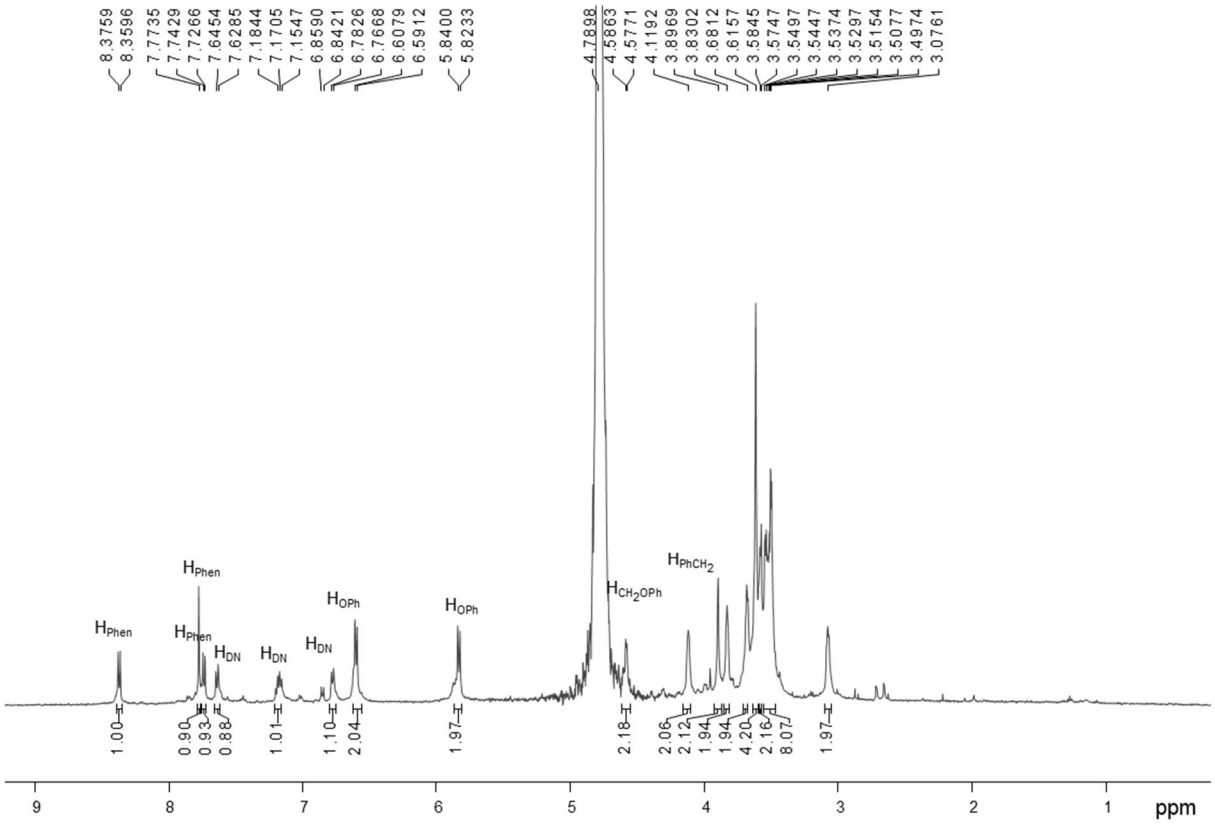


Figure S49. ^{1}H NMR (500 MHz, D_2O, 298 K) of **F5**.

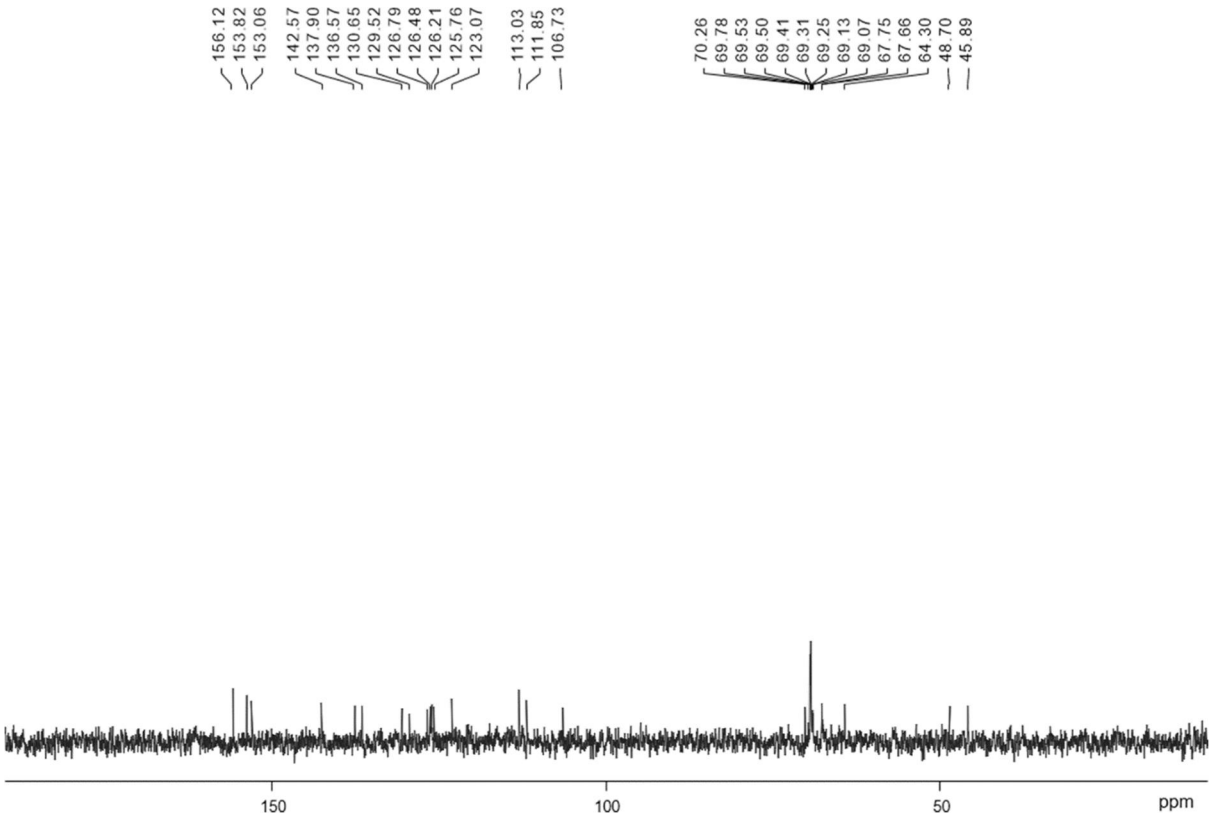


Figure S50. $^{13}C\{^{1}H\}$ NMR (125 MHz, D_2O, 298 K) of **F5**.

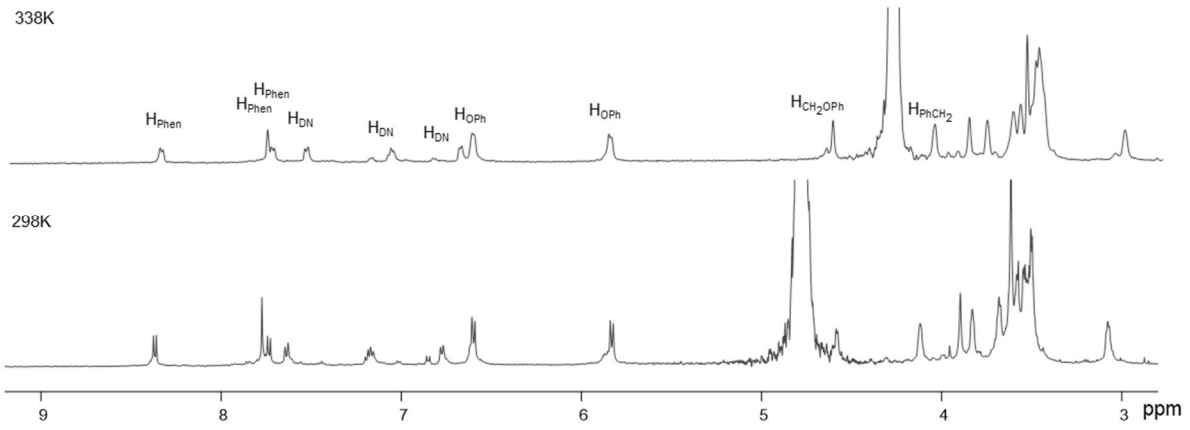


Figure S51. ^{1}H NMR (500 MHz, D_2O) of **F5** at 338 K (top) and 298 K (bottom).

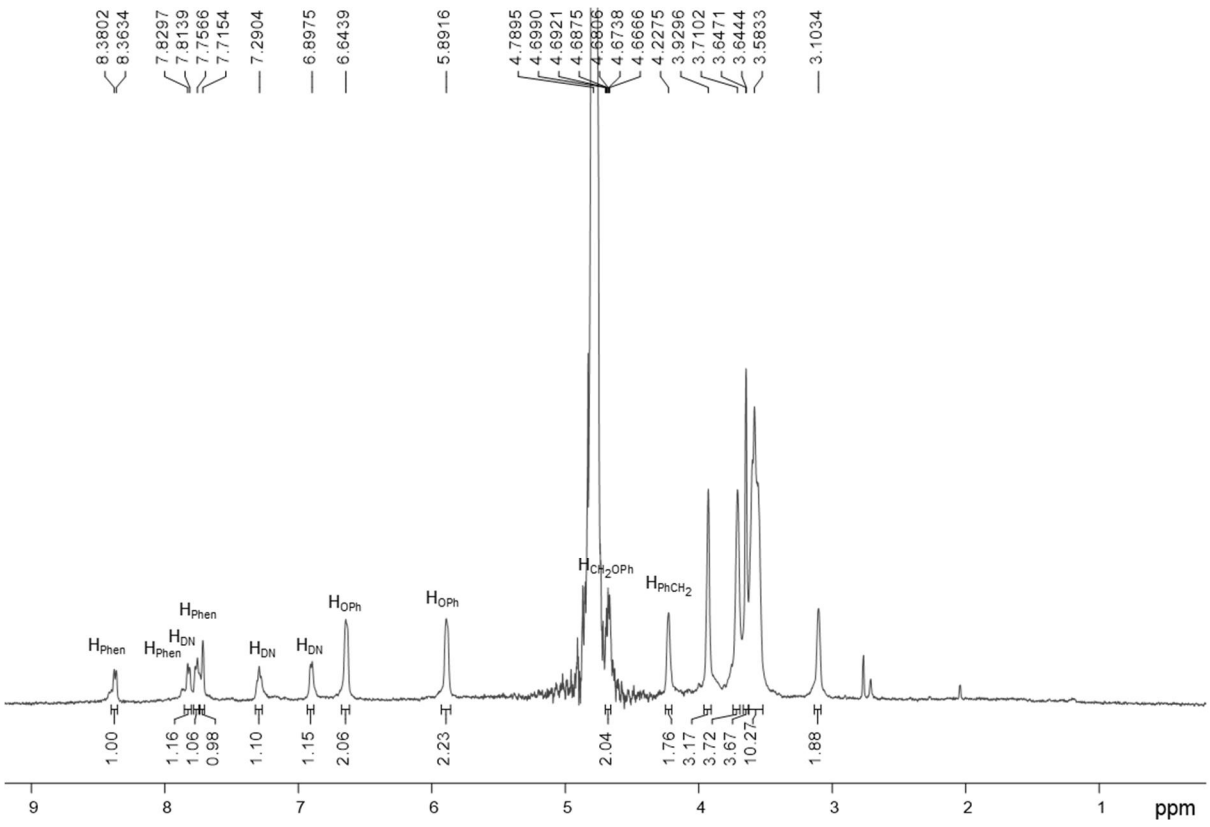


Figure S52. ^{1}H NMR (500 MHz, D_2O, 298 K) of **H5**.

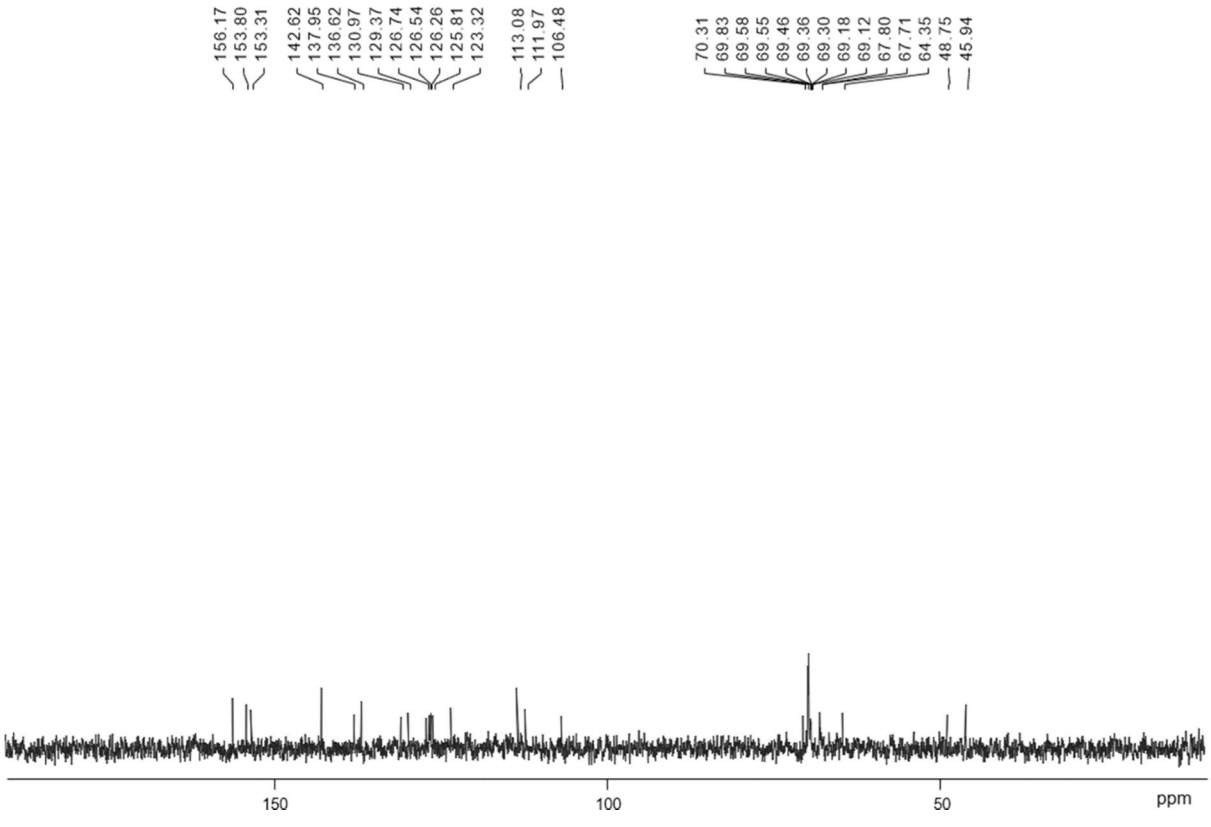


Figure S53. $^{13}C\{^{1}H\}$ NMR (125 MHz, D_2O, 298 K) of **H5**.

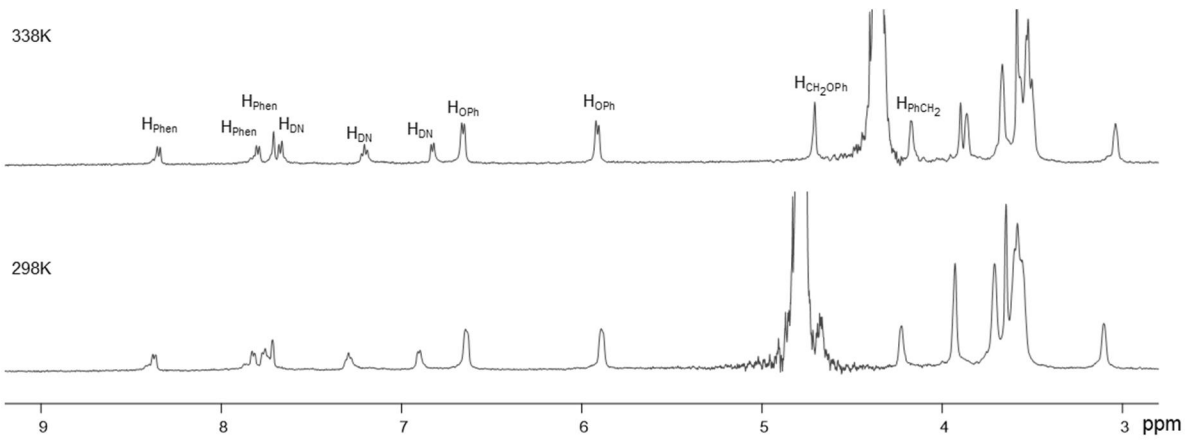


Figure S54. ^{1}H NMR (500 MHz, D_2O) of **H5** at 338 K (top) and 298 K (bottom).

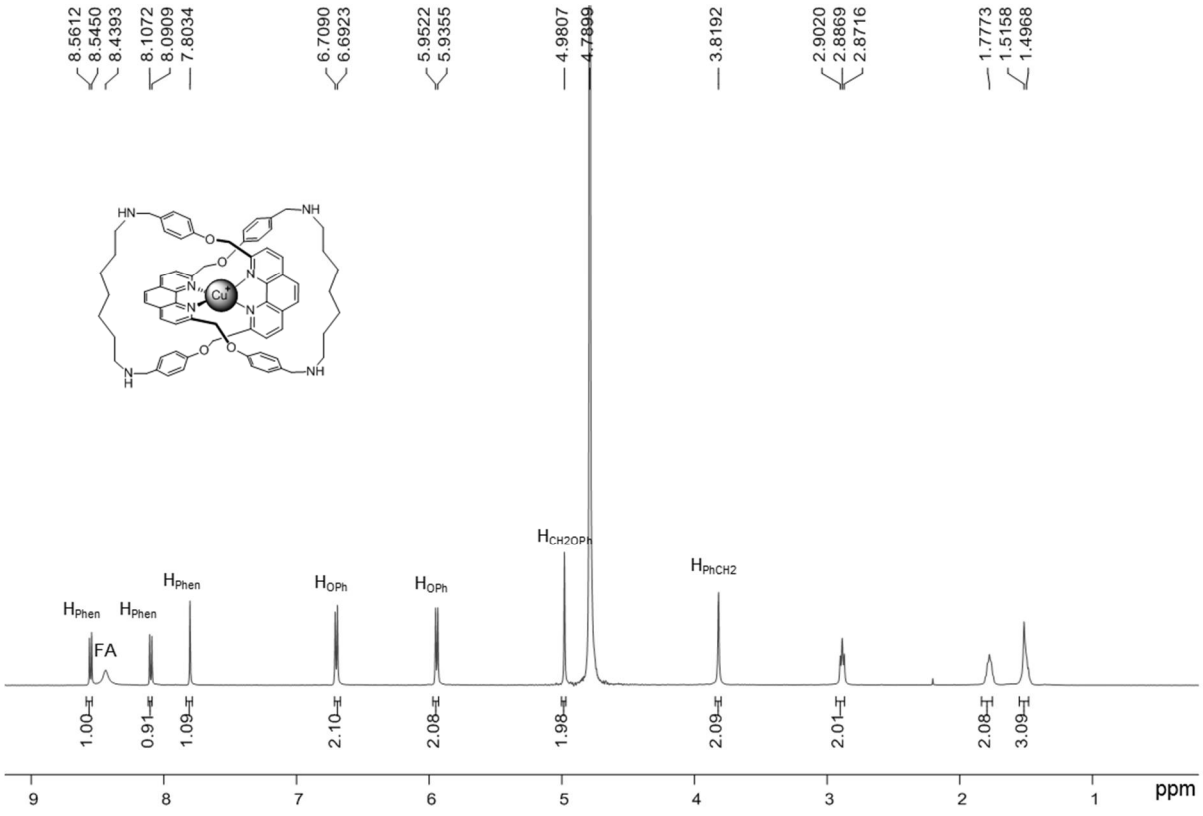


Figure S55. ^{1}H NMR (500 MHz, D_2O, 298 K) of **H6**.

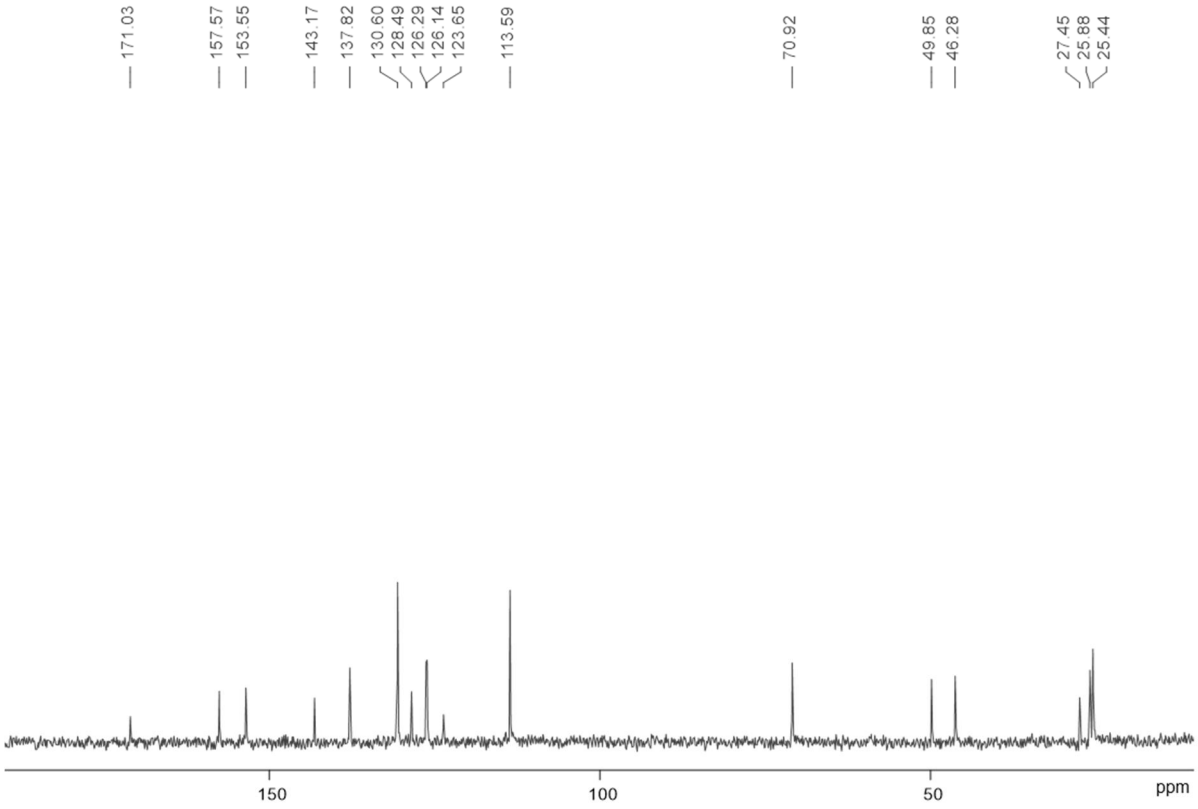


Figure S56. $^{13}C\{^{1}H\}$ NMR (125 MHz, D_2O, 298 K) of **H6**.

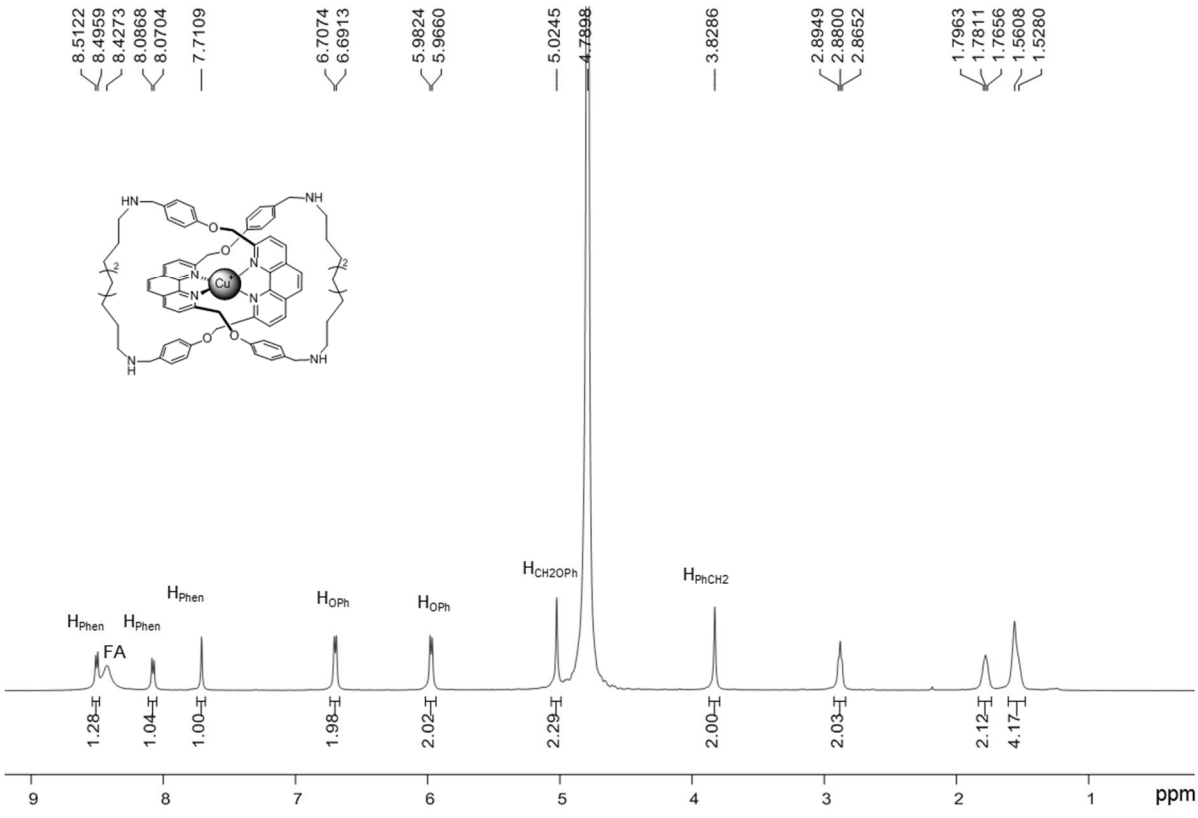


Figure S57. ^{1}H NMR (500 MHz, D_2O, 298 K) of **H7**.

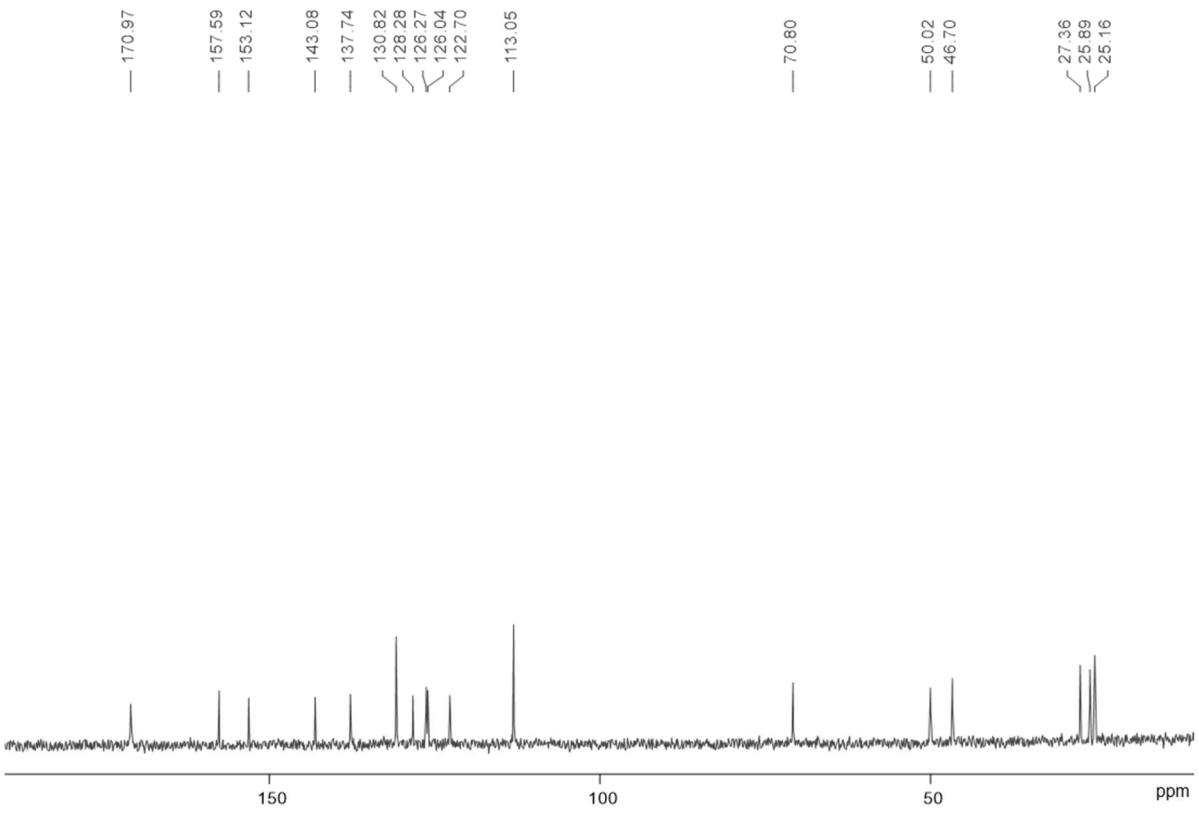


Figure S58. $^{13}C\{^{1}H\}$ NMR (125 MHz, D_2O, 298 K) of **H7**.

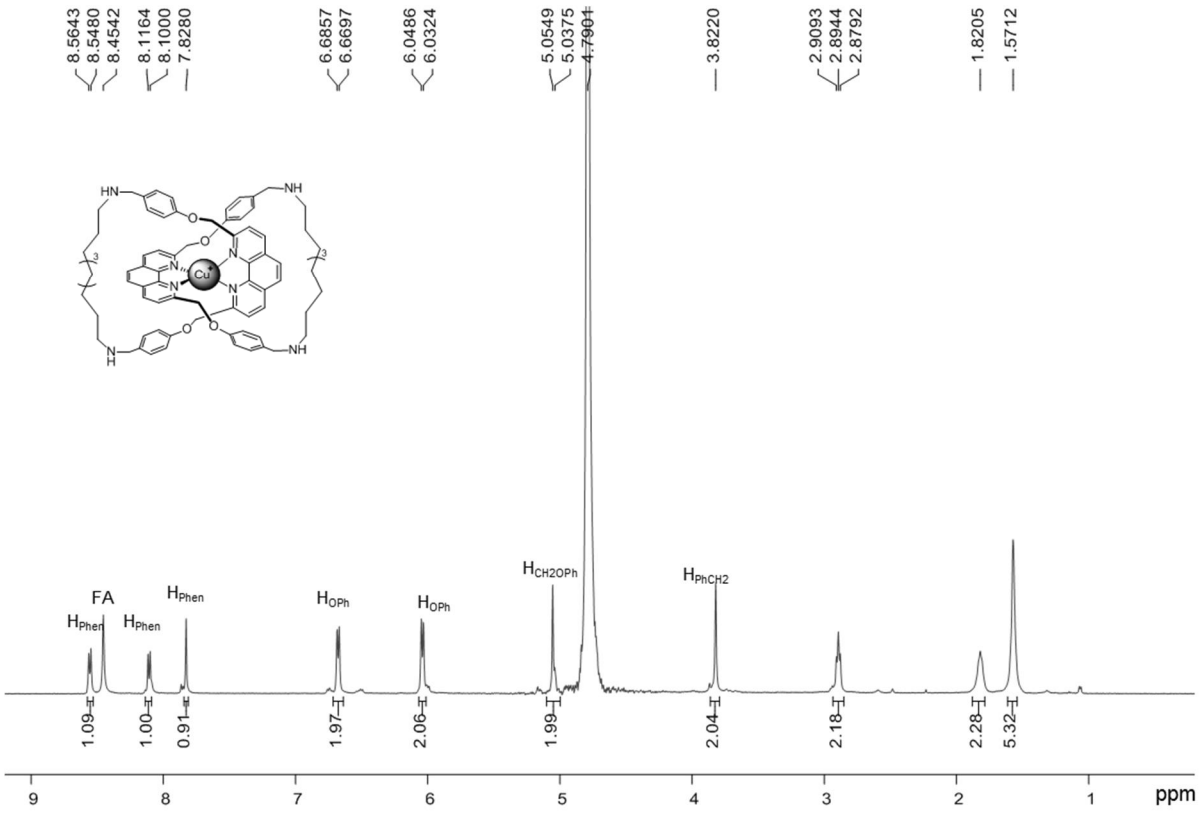


Figure S59. ^{1}H NMR (500 MHz, D_2O, 298 K) of **H8**.

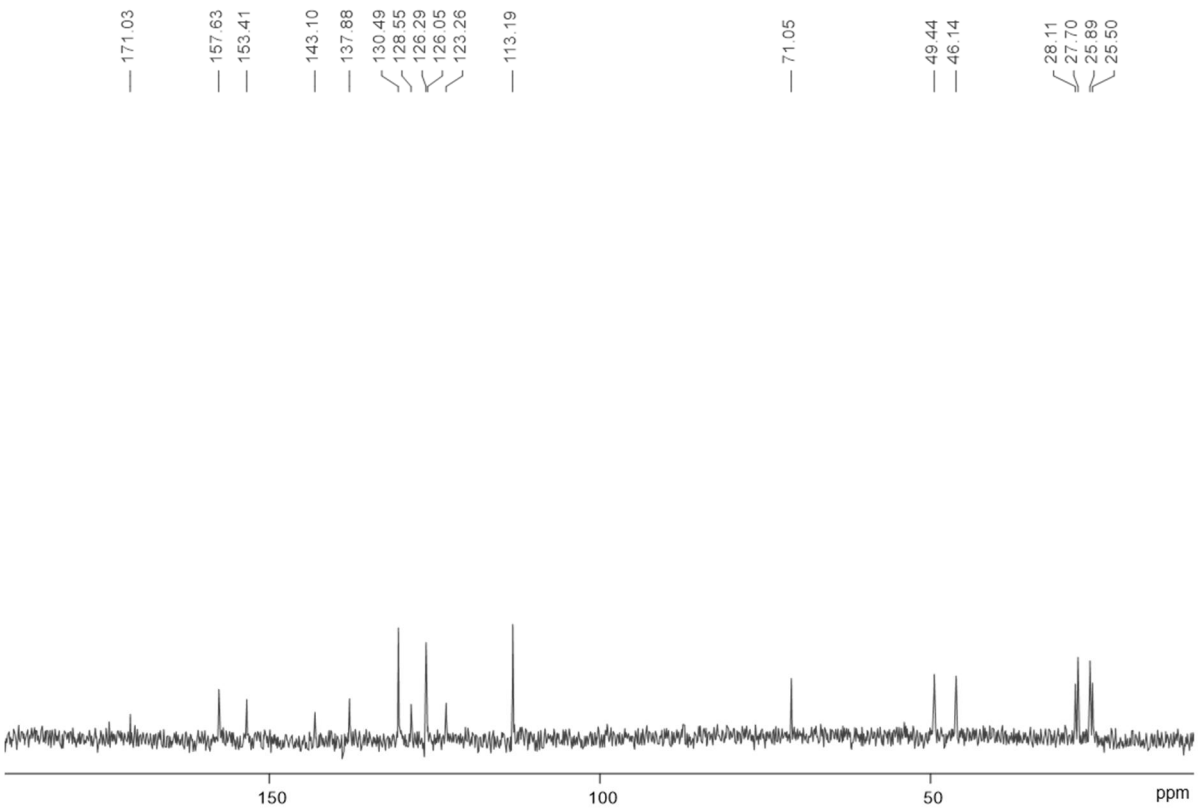


Figure S60. $^{13}C\{^{1}H\}$ NMR (125 MHz, D_2O, 298 K) of **H8**.

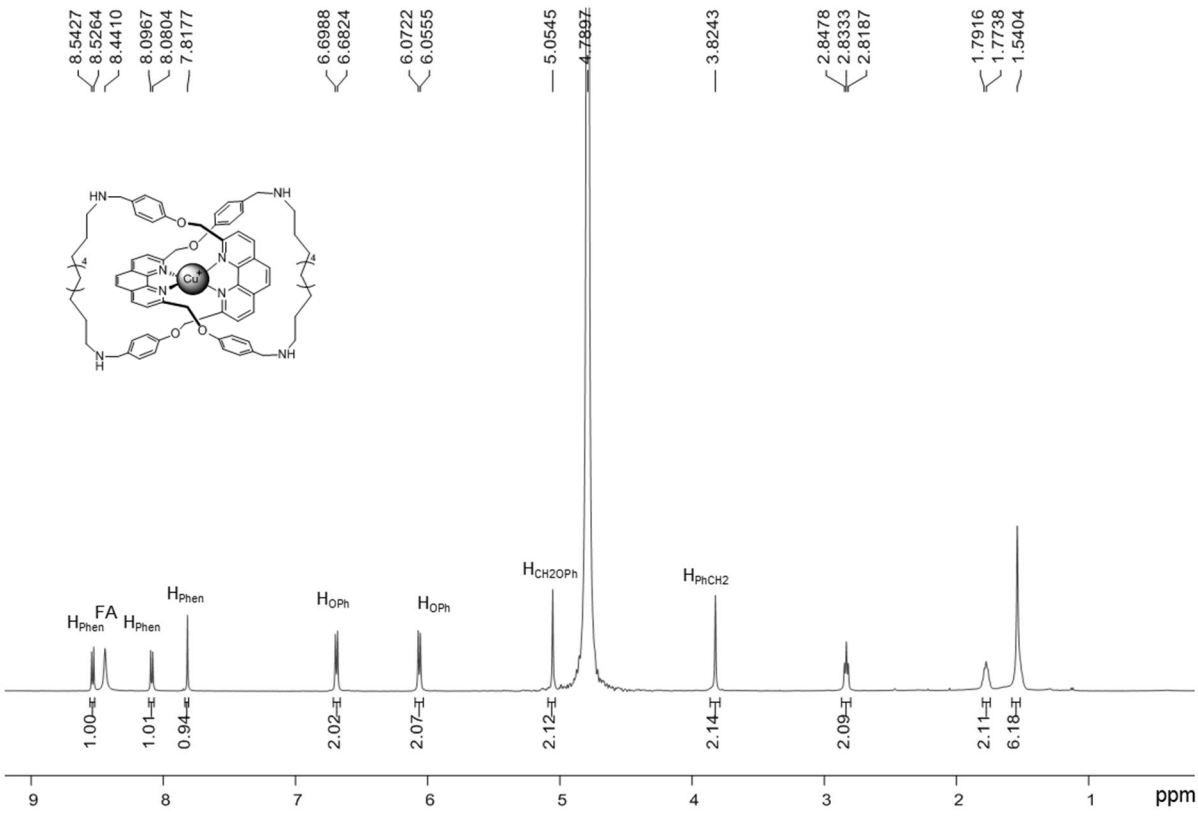


Figure S61. ^{1}H NMR (500 MHz, D_2O, 298 K) of **H9**.

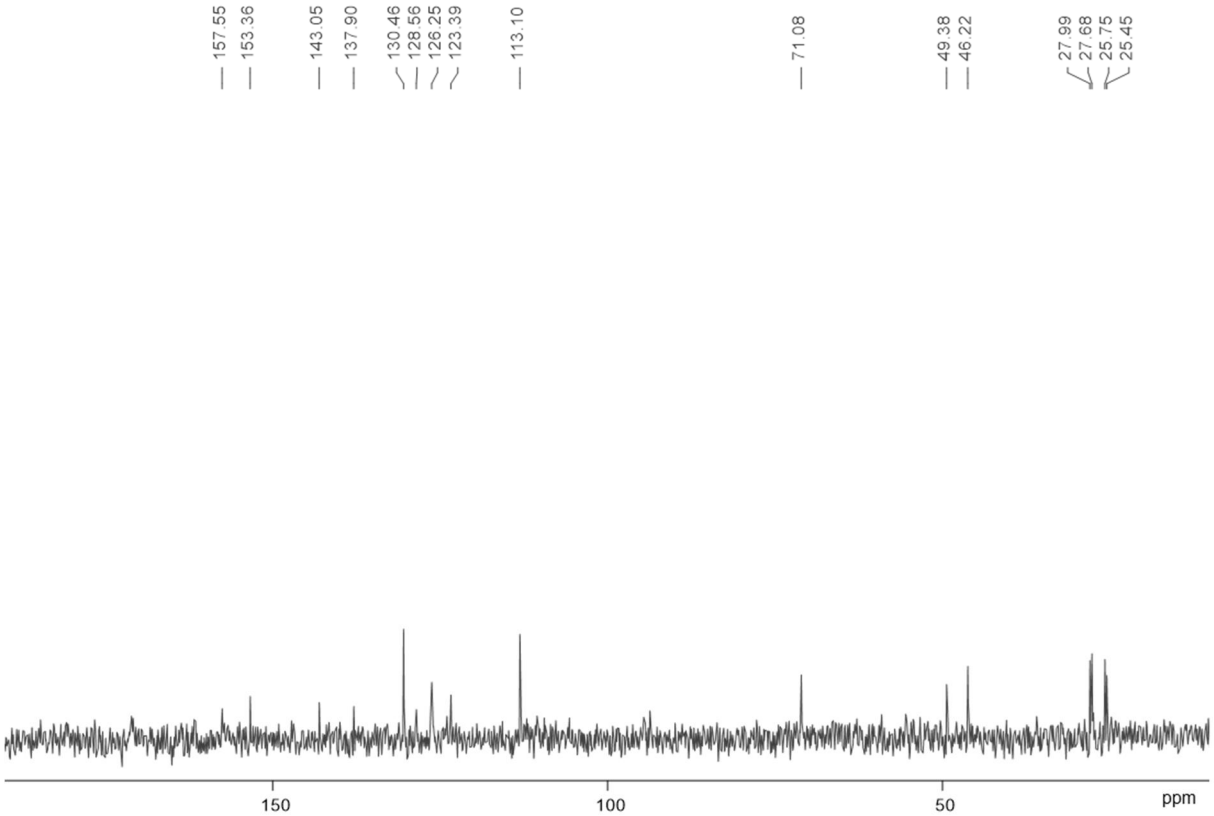


Figure S62. $^{13}C\{^{1}H\}$ NMR (125 MHz, D_2O, 298 K) of **H9**.

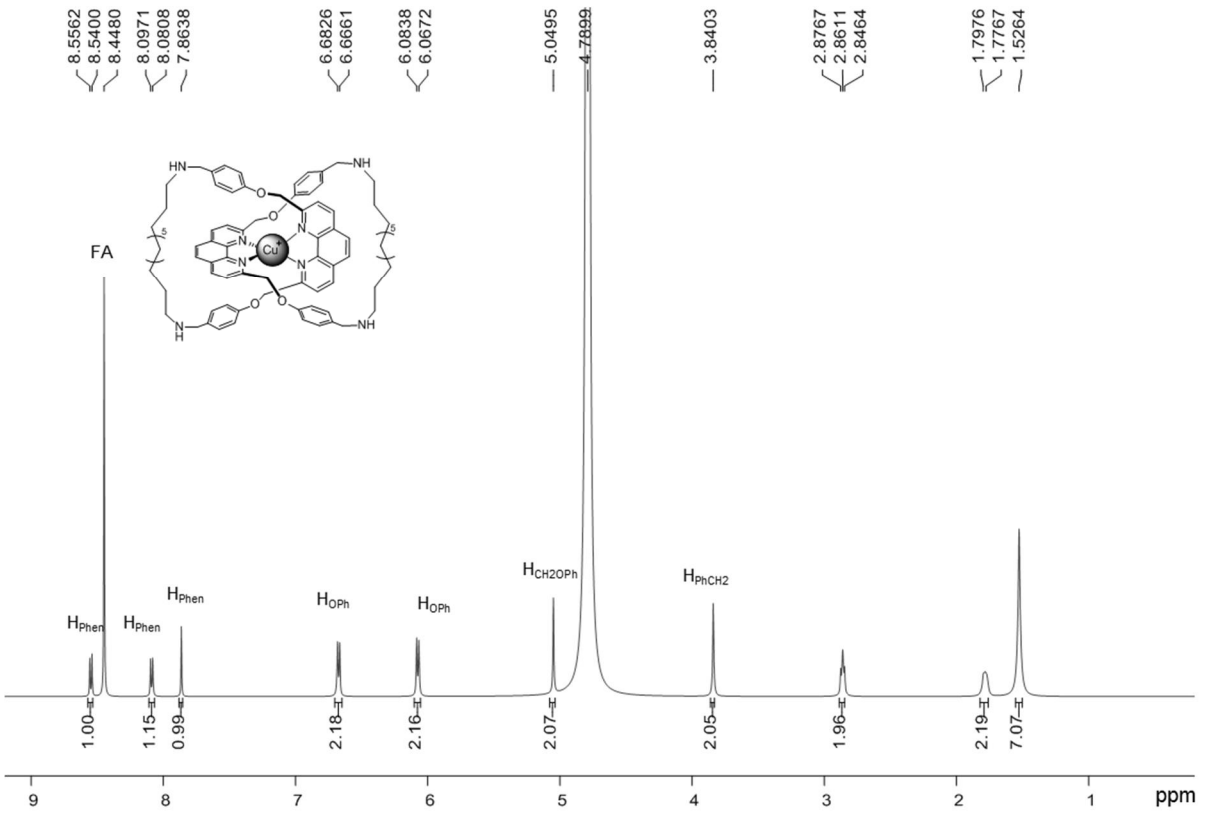


Figure S63. ^{1}H NMR (500 MHz, D_2O, 298 K) of **H10**.

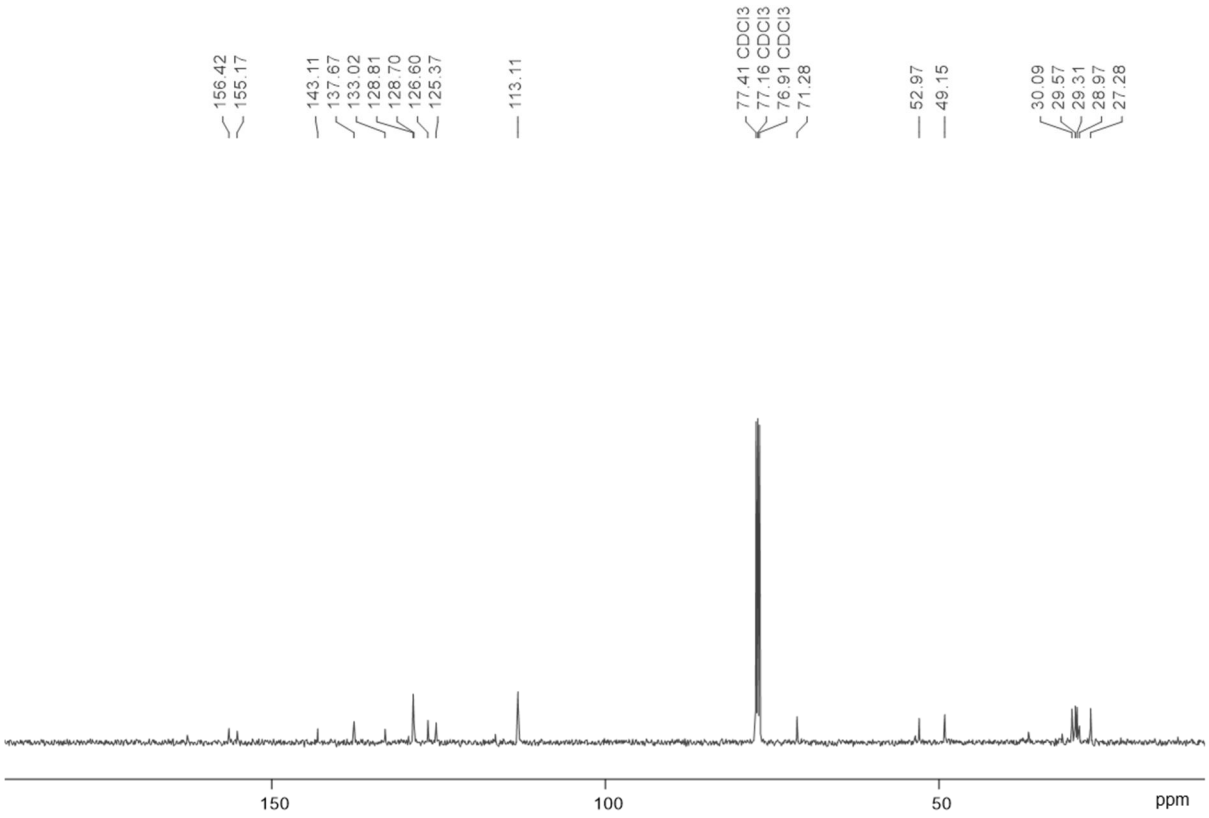


Figure S64. $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, 298 K) of **H10**.

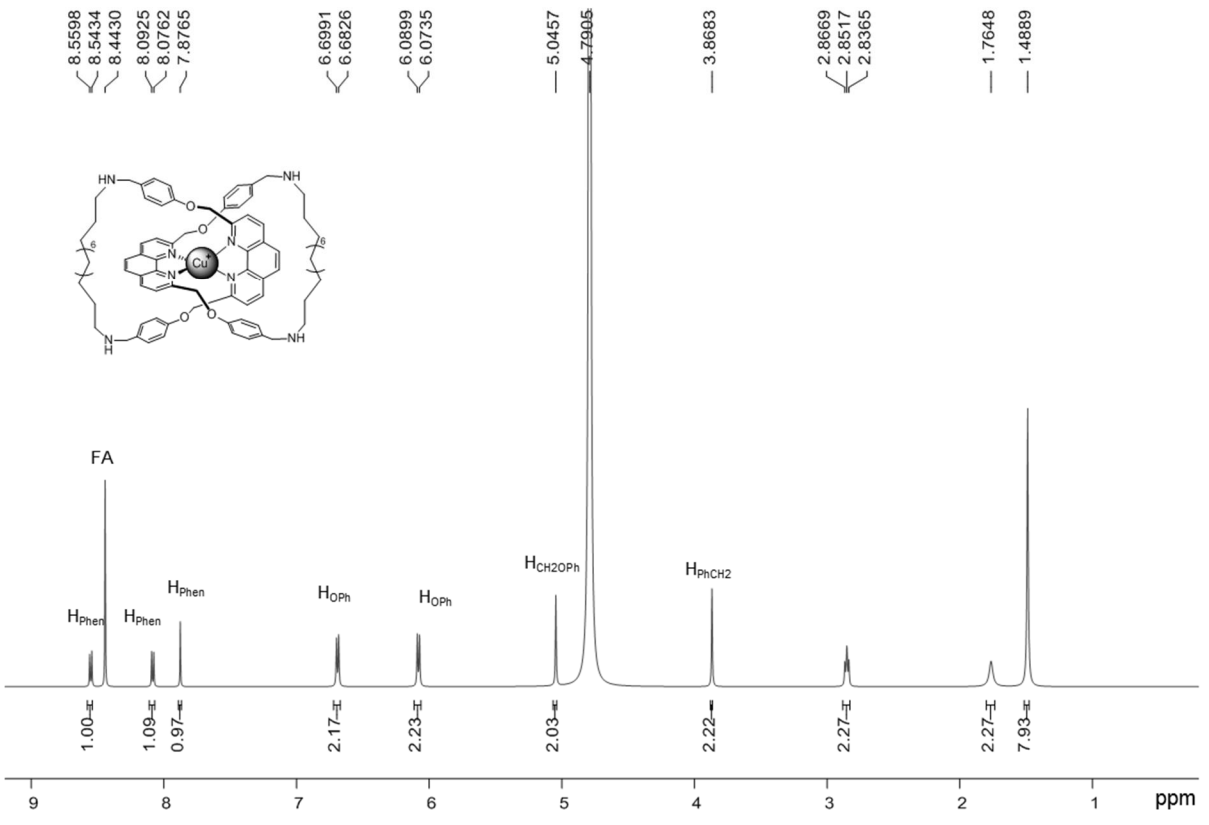


Figure S65. ^{1}H NMR (500 MHz, D_2O, 298 K) of **H11**.

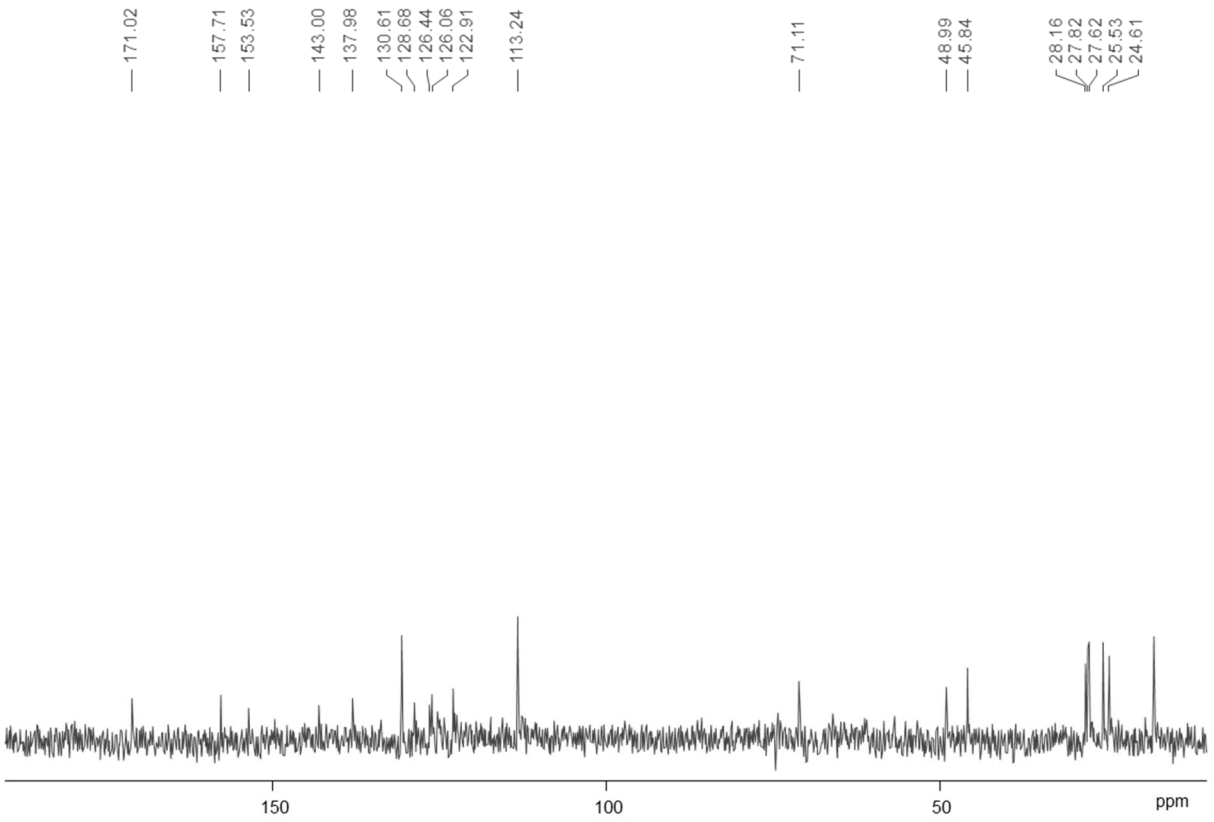


Figure S66. $^{13}C\{^{1}H\}$ NMR (125 MHz, D_2O, 298 K) of **H11**.

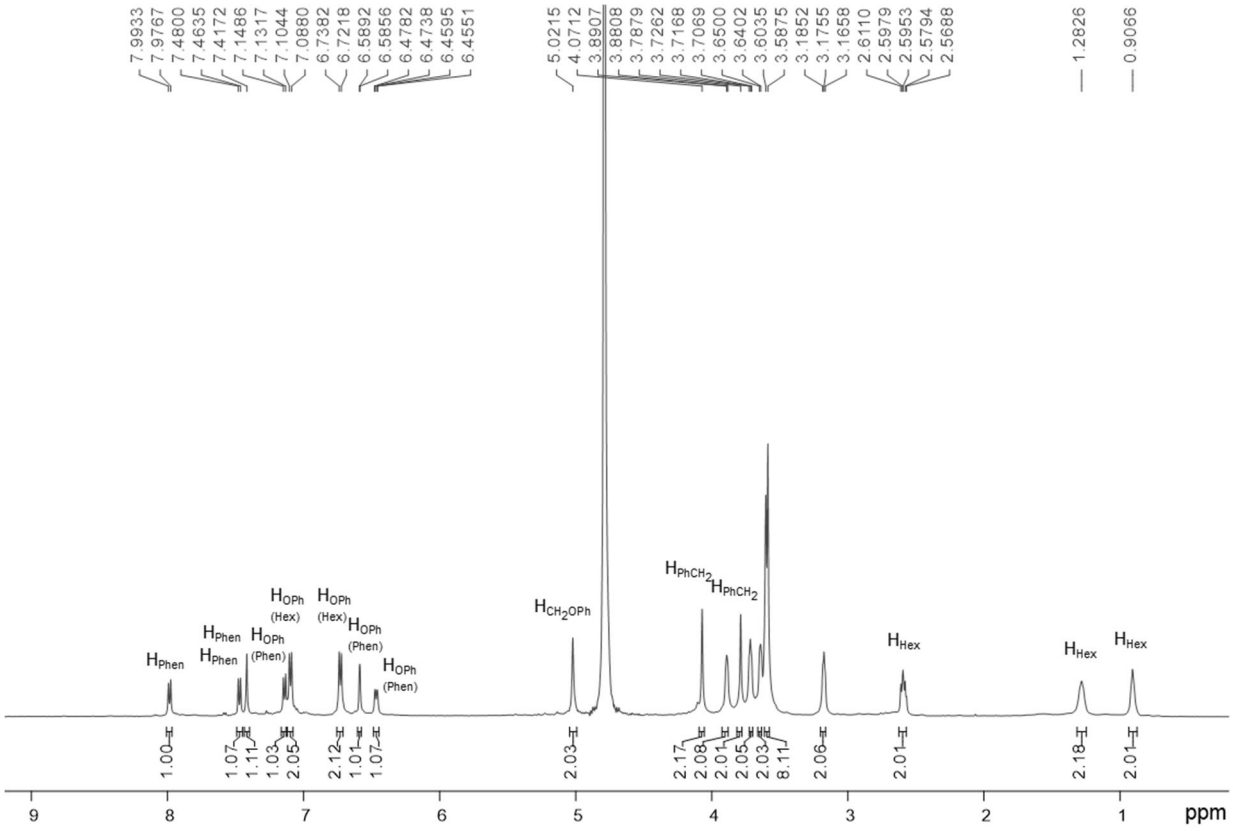


Figure S67. ^{1}H NMR (500 MHz, D_2O, 298 K) of **F12b**.

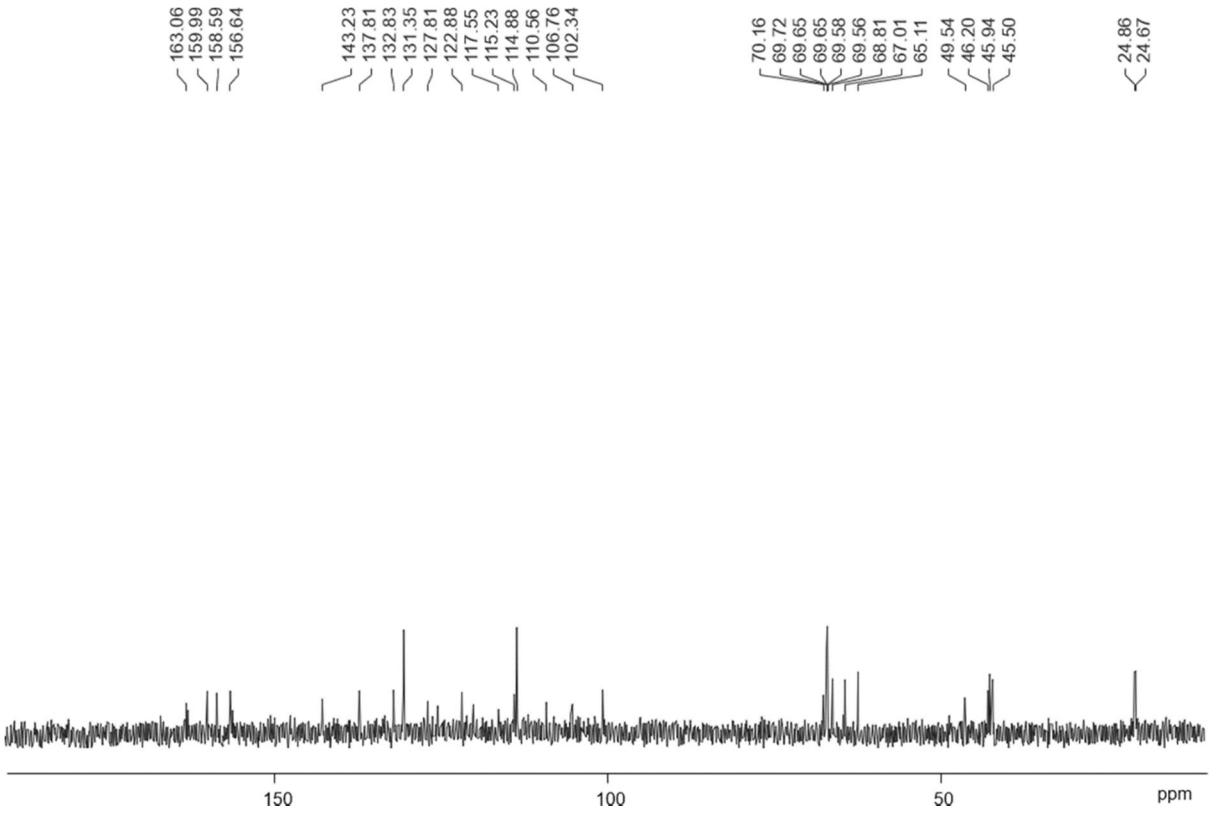


Figure S68. $^{13}C\{^{1}H\}$ NMR (125 MHz, D_2O, 298 K) of **F12b**.

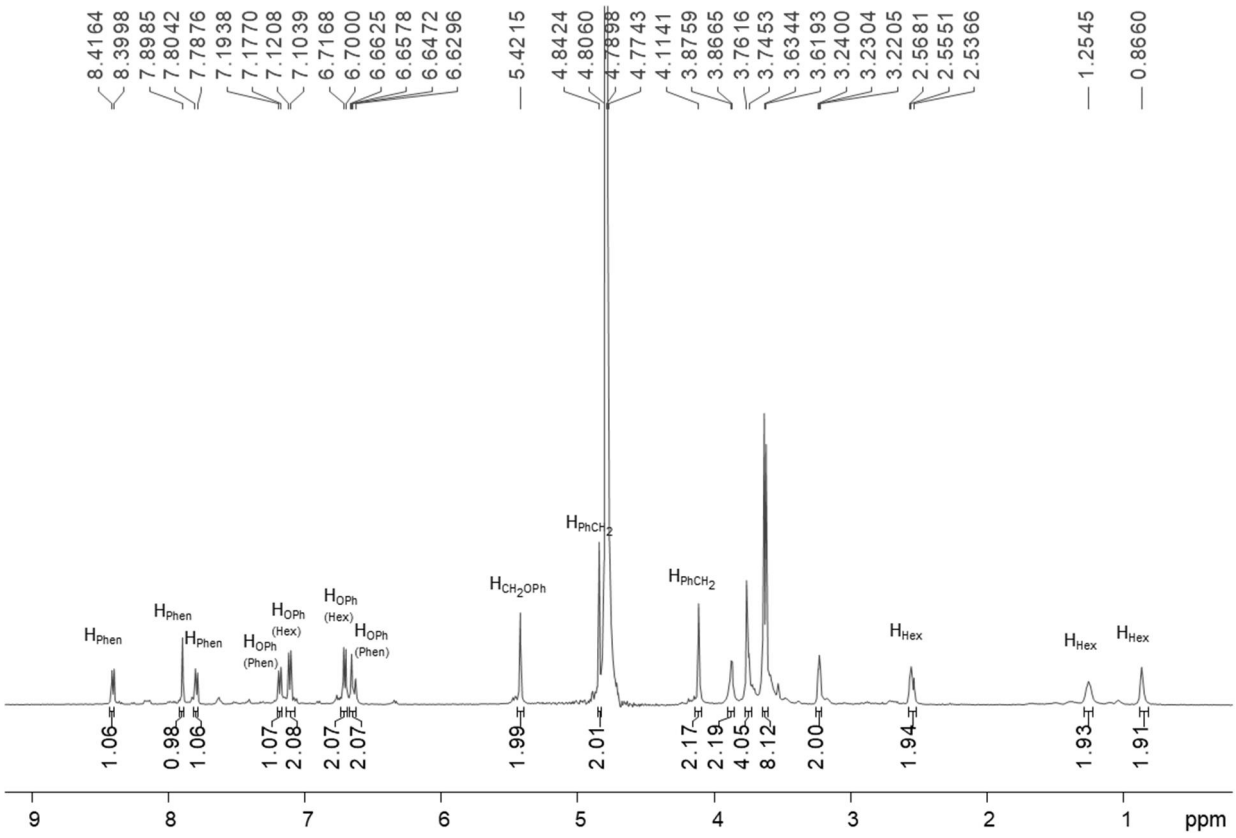


Figure S69. ^{1}H NMR (500 MHz, D_2O, 298 K) of **H12b**.

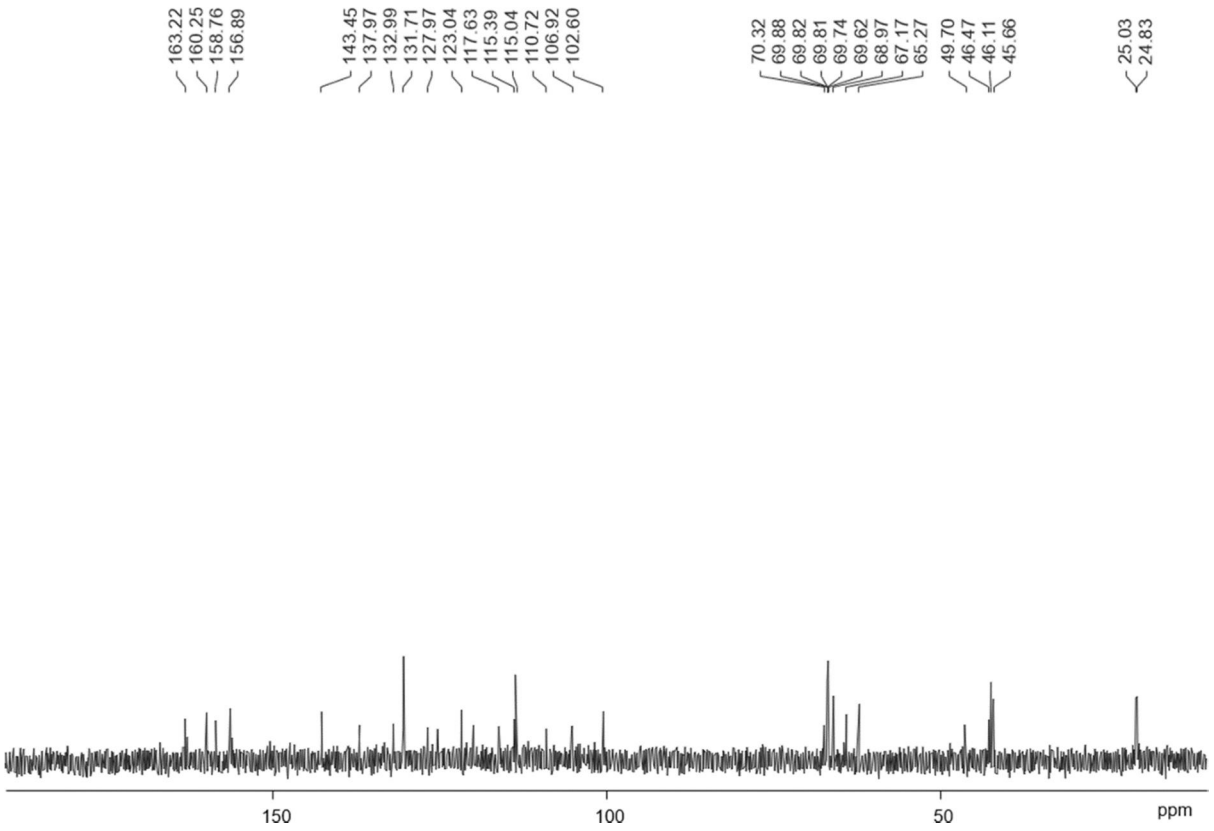


Figure S70. $^{13}C\{^{1}H\}$ NMR (125 MHz, D_2O, 298 K) of **H12b**.

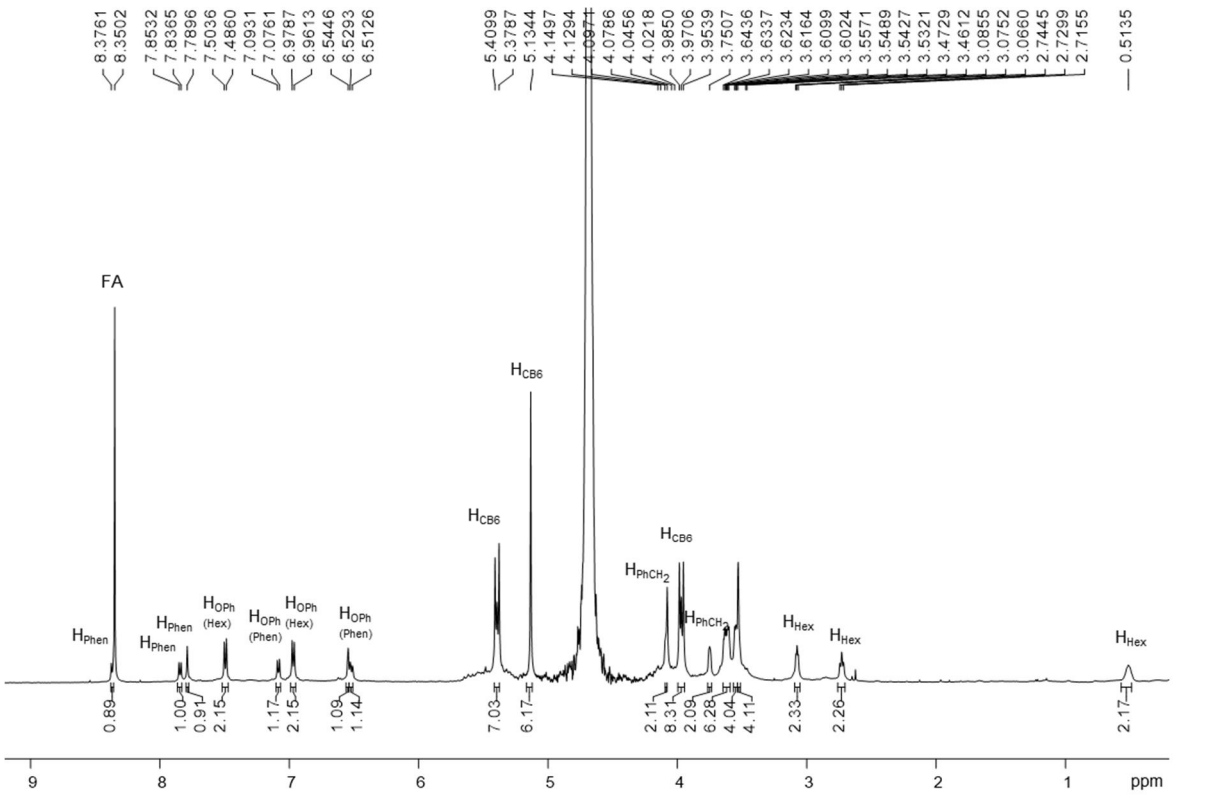


Figure S71. ^{1}H NMR (500 MHz, D_2O, 298 K) of **M13**.

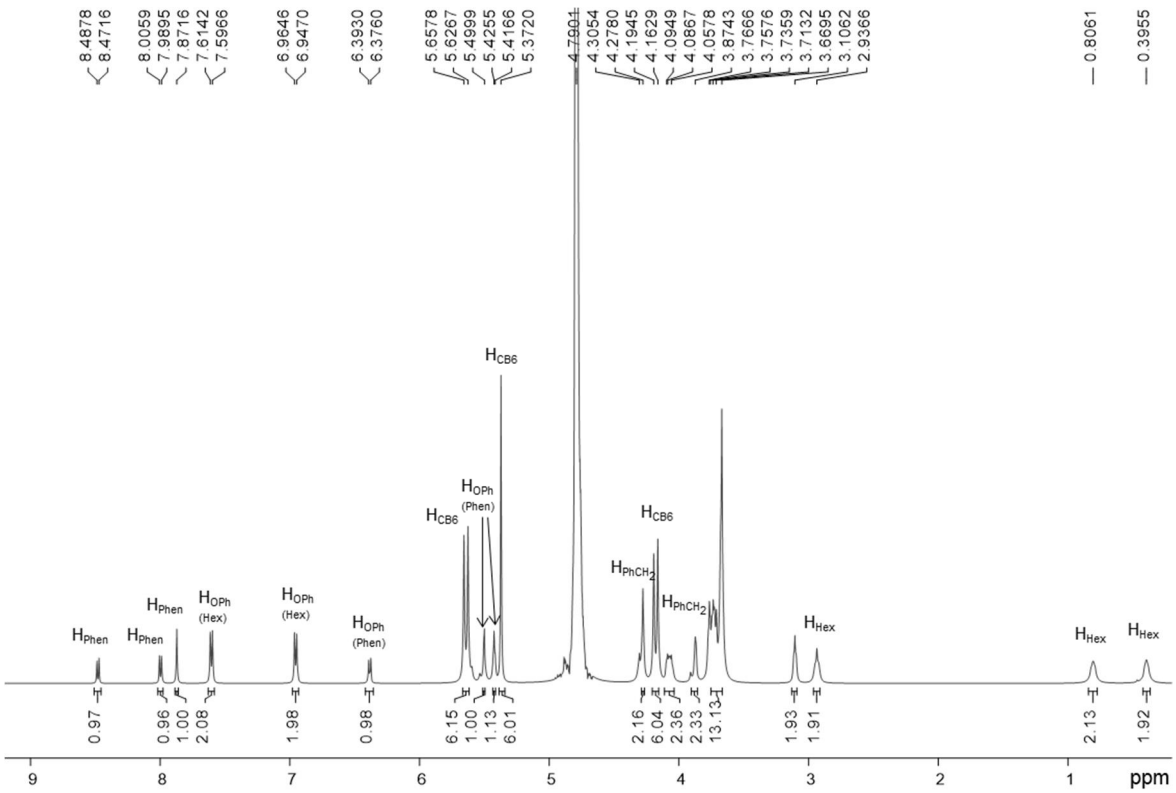


Figure S72. ^{1}H NMR (500 MHz, D_2O, 298 K) of **H13**.

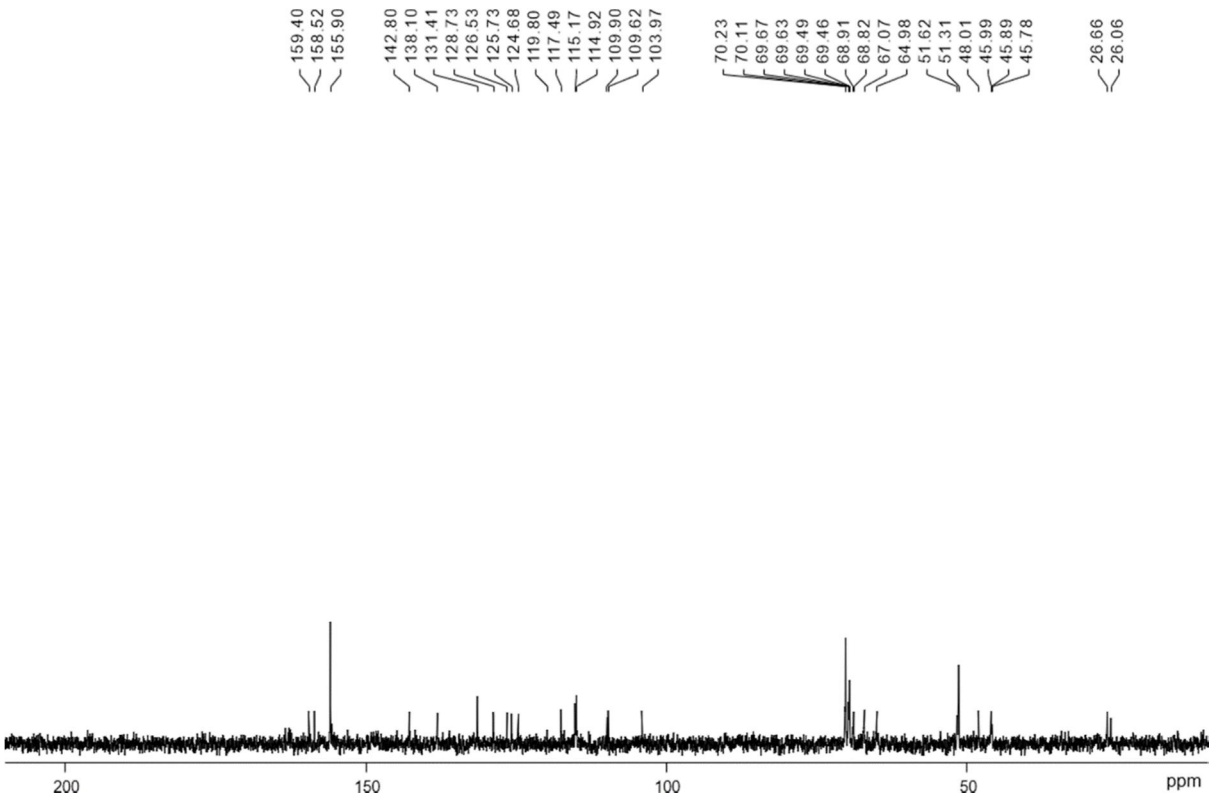


Figure S73. $^{13}C\{^{1}H\}$ NMR (125 MHz, D_2O, 298 K) of **H13**.

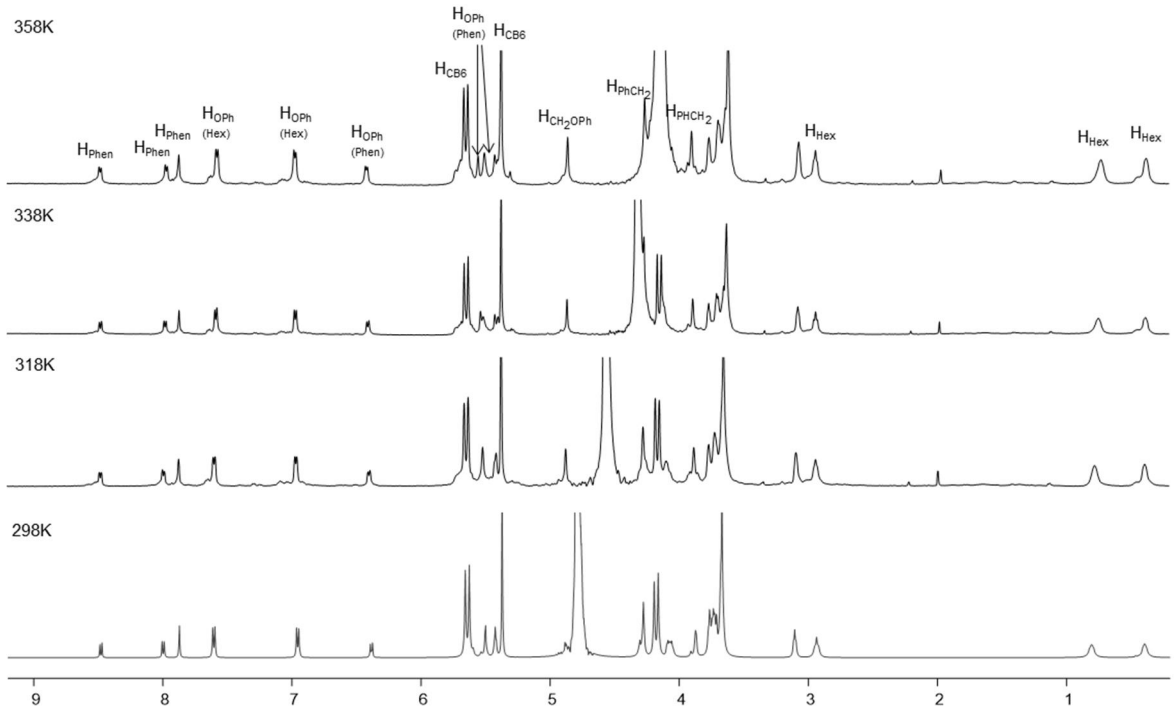


Figure S74. Variable temperature ^{1}H NMR (500 MHz, D_2O) of **H13**.

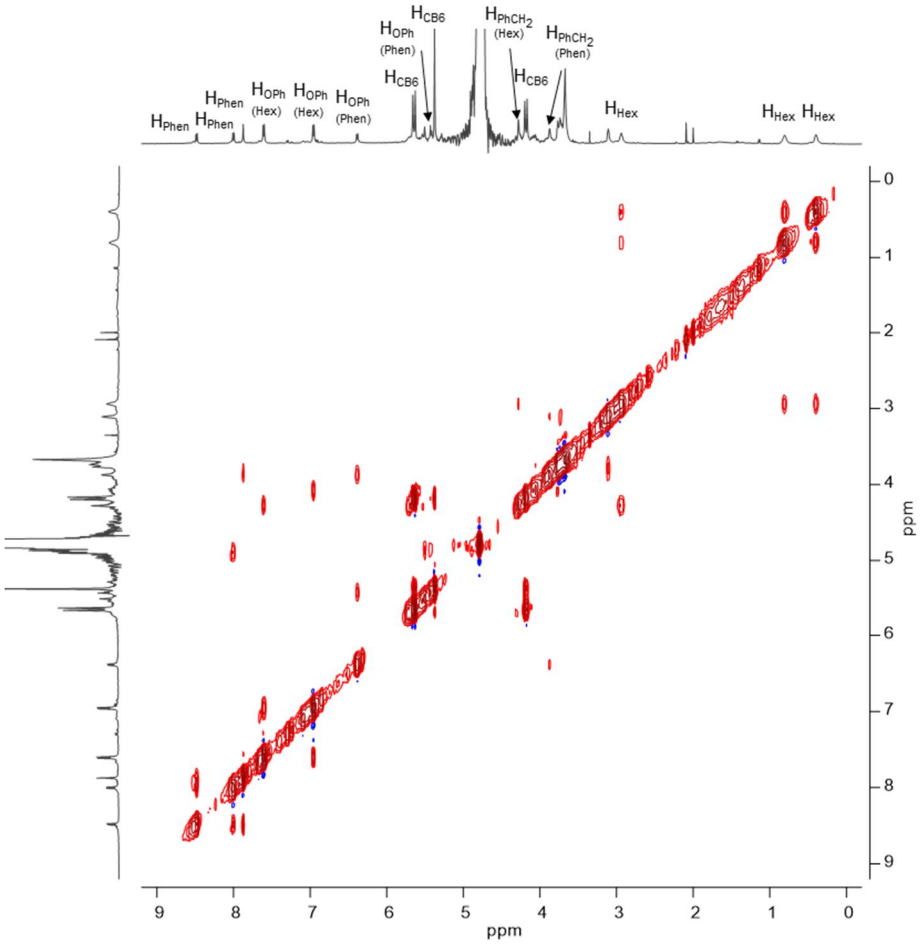


Figure S75. NOESY (500 MHz, D_2O, 298 K, d_8 = 700ms) of **H13**.

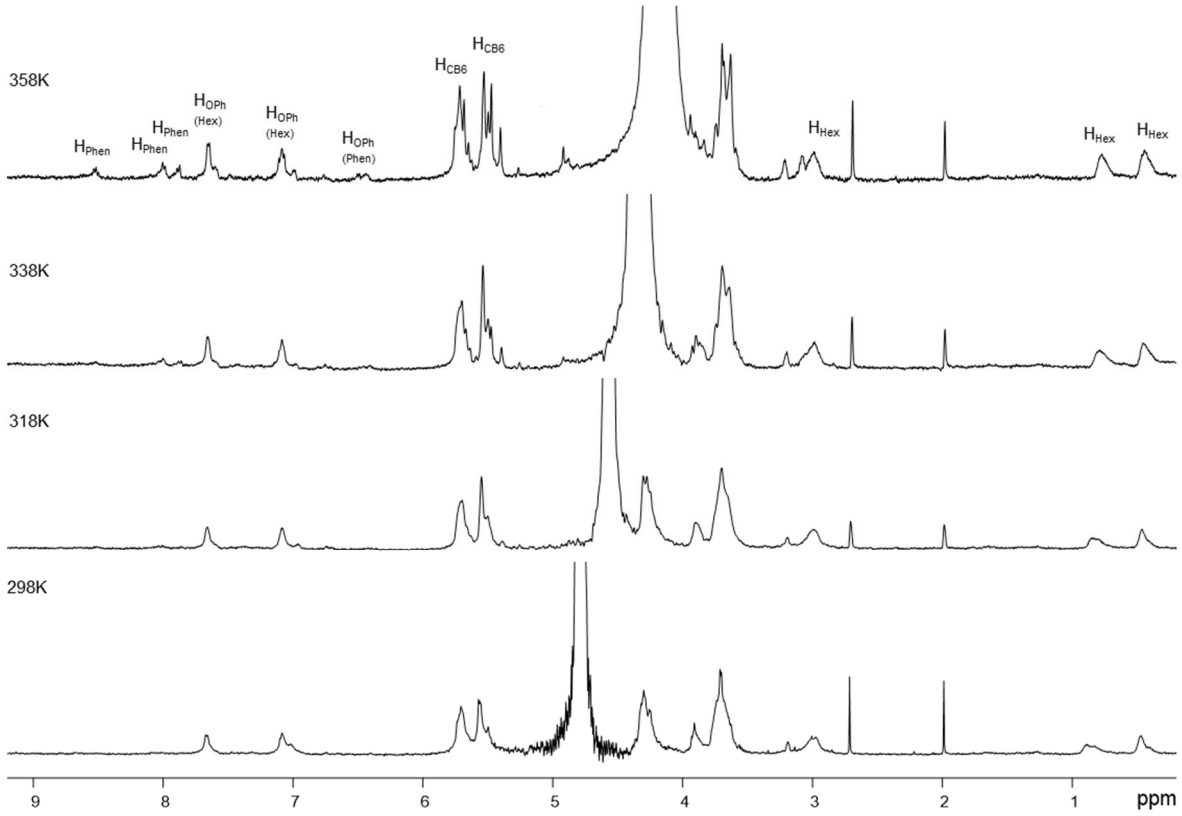


Figure S76. Variable temperature ^{1}H NMR (500 MHz, D_2O) of **F13**.

4. ESI-MS

Mass spectrometry was performed on a Thermo Scientific LTQ FLEET mass spectrometer or a Finnigan LCQ mass spectrometer. HR-ESI-MS were carried out on a Bruker ESI Quadrupole TOF mass spectrometer. MS^2 experiments were carried out on a Thermo Scientific LTQ FLEET mass spectrometer. Isotopic patterns were simulated using IsoPro, version 3.1.

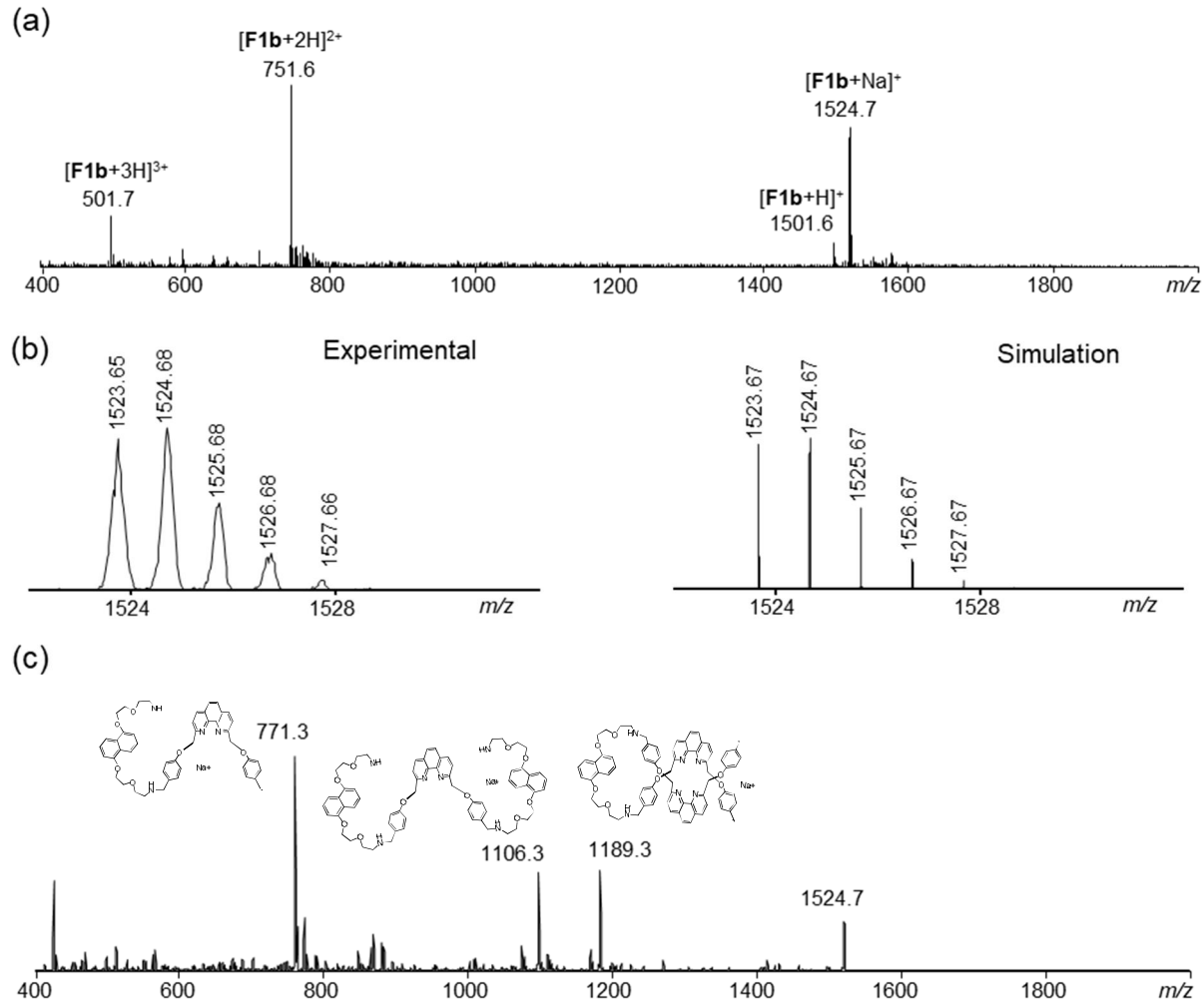


Figure S77. (a) ESI-MS spectrum of **F1b** (after demetallation), (b) HRMS of the peak at *m/z* = 1524.7 (left: experimental; right: simulation) (c) MS^2 spectrum of **F1b** upon fragmentation of the peak at *m/z* = 1524.7.

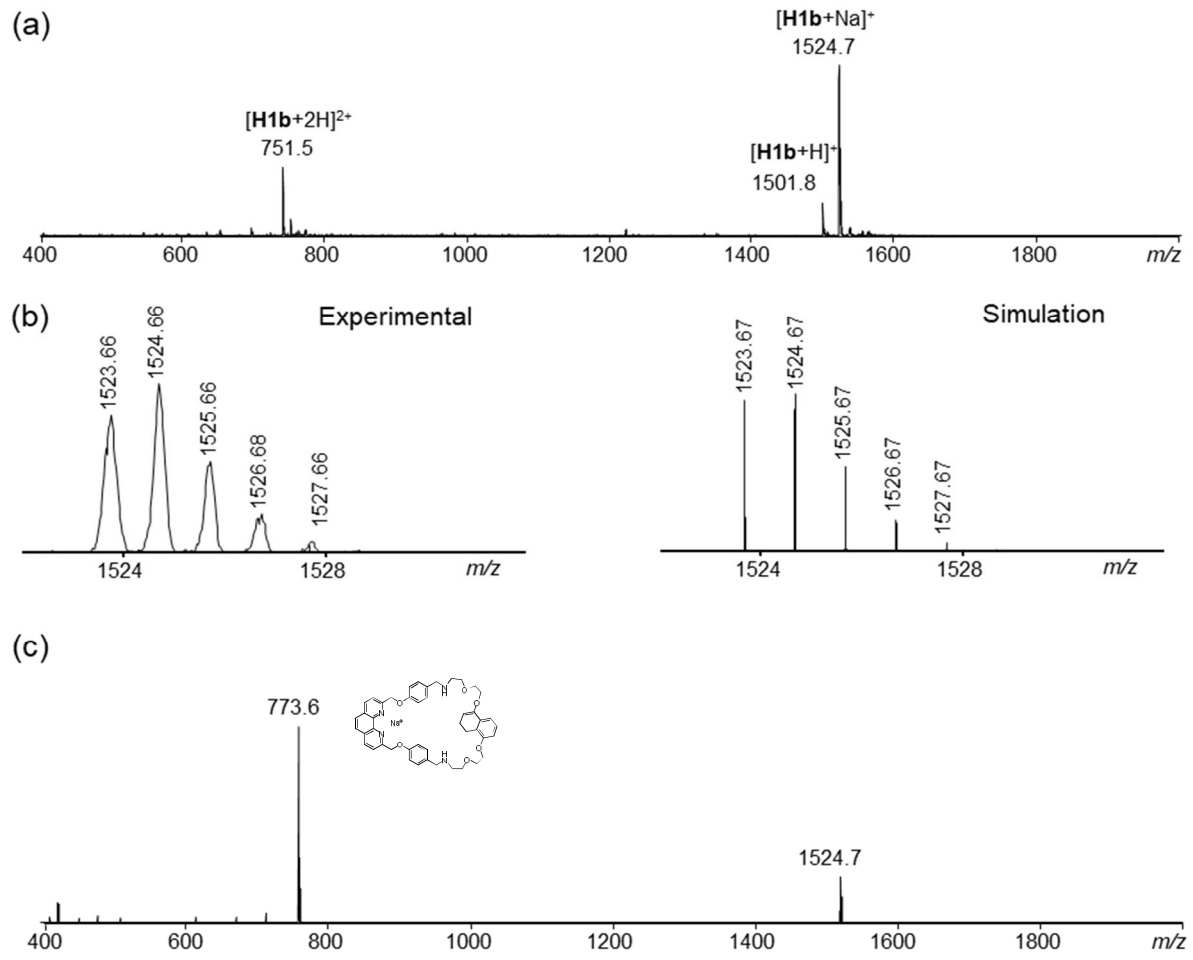


Figure S78. (a) ESI-MS spectrum of **H1b** (after demetallation), (b) HRMS of the peak at *m/z* = 1524.7 (left: experimental; right: simulation) (c) MS^2 spectrum of **H1b** upon fragmentation of the peak at *m/z* = 1524.7.

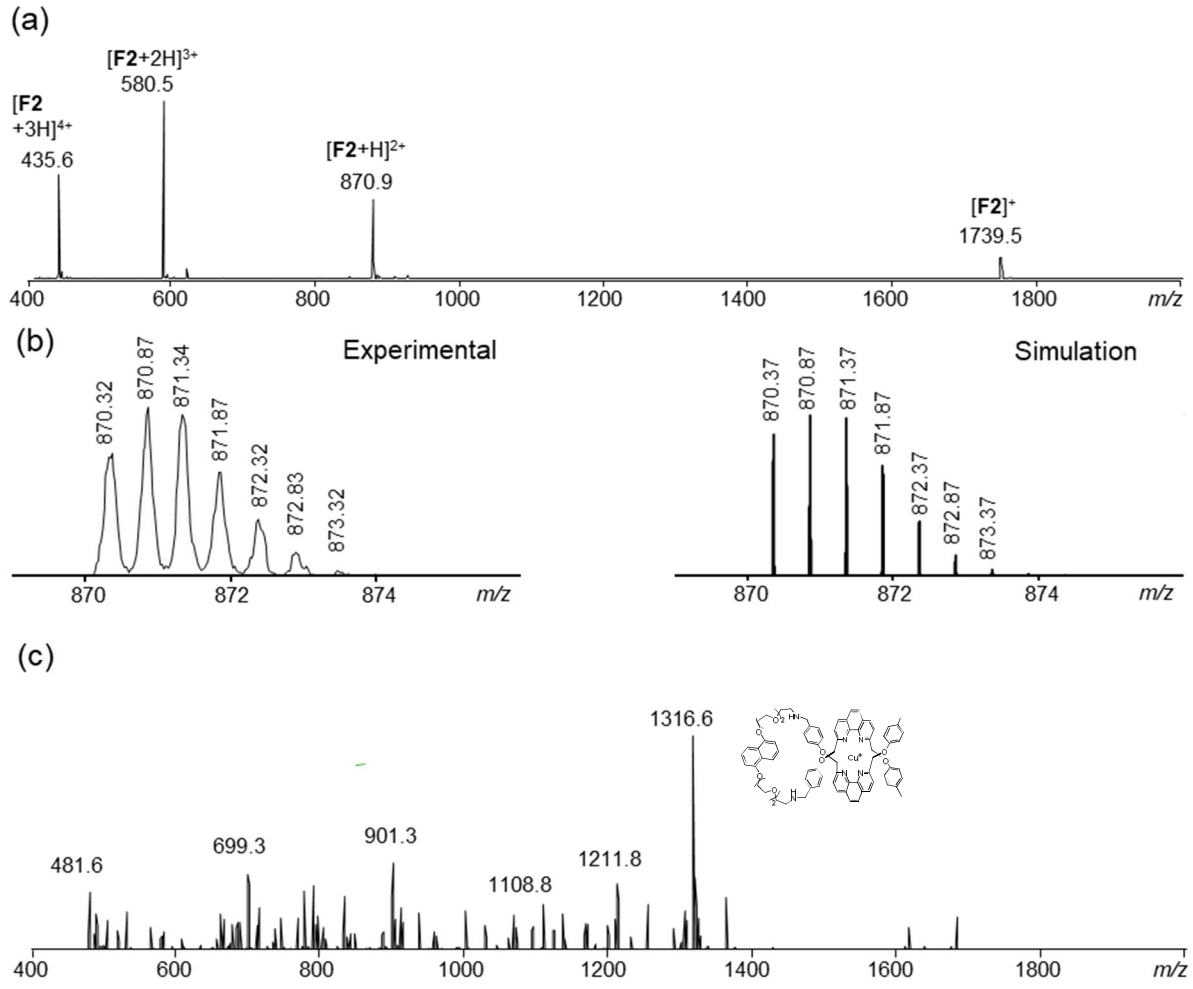


Figure S79. (a) ESI-MS spectrum of **F2**, (b) HRMS of the peak at *m/z* = 870.9 (left: experimental; right: simulation) (c) MS^2 spectrum of **F2** upon fragmentation of the peak at *m/z* = 870.9.

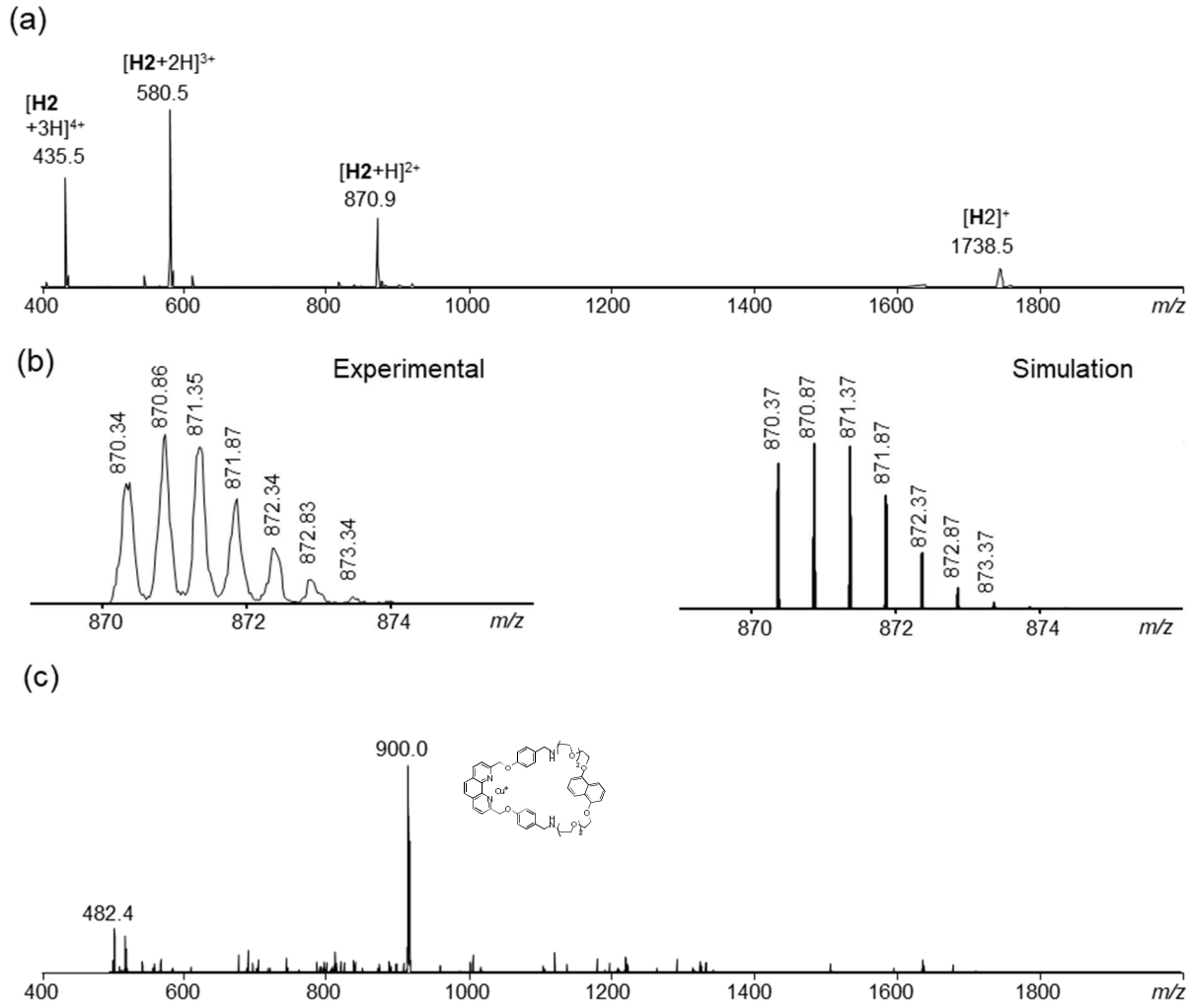


Figure S80. (a) ESI-MS spectrum of **H2**, (b) HRMS of the peak at *m/z* = 870.9 (left: experimental; right: simulation) (c) MS^2 spectrum of **H2** upon fragmentation of the peak at *m/z* = 870.9.

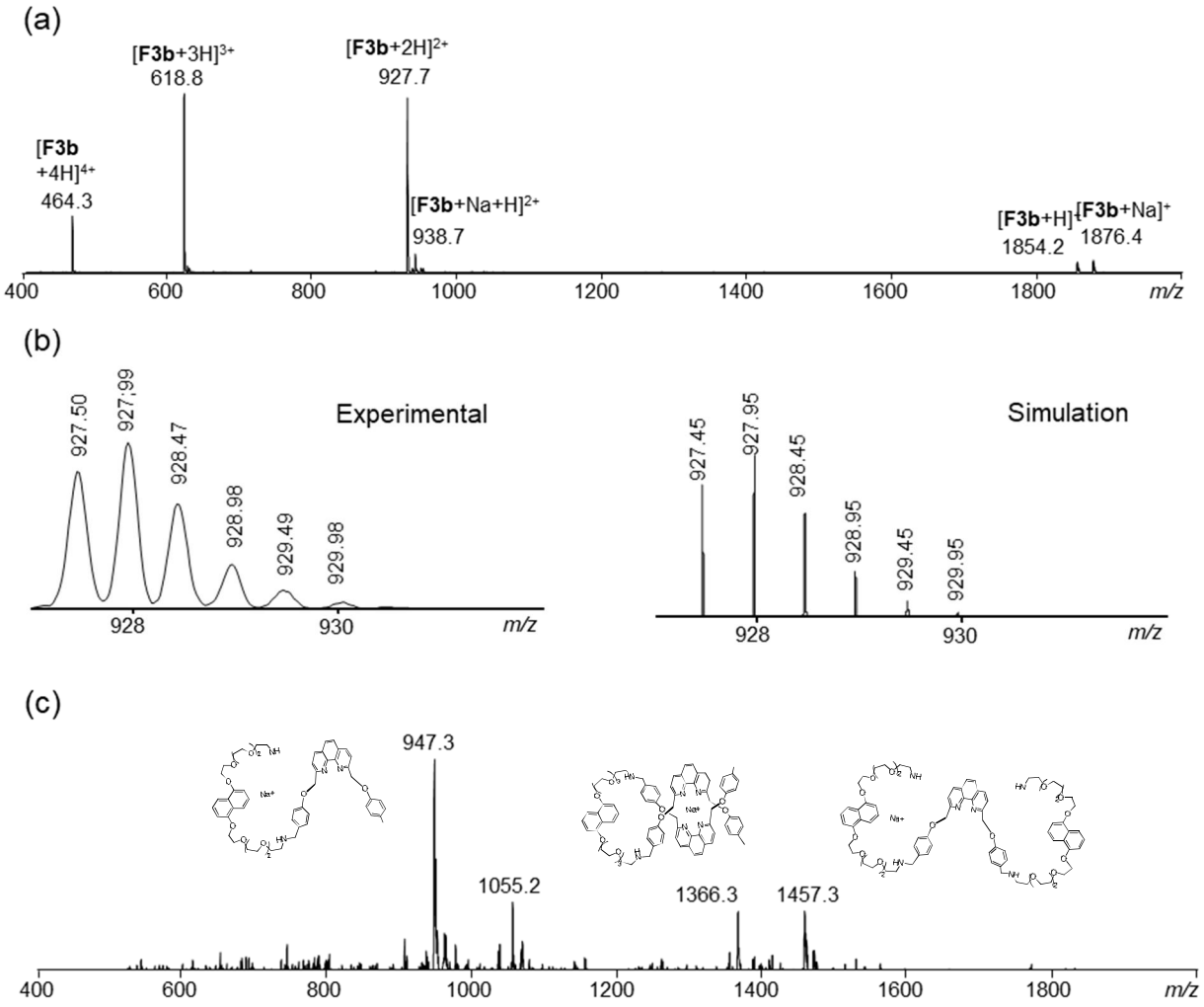


Figure S81. (a) ESI-MS spectrum of **F3b** (after demetallation), (b) HRMS of the peak at *m/z* = 927.7 (left: experimental; right: simulation) (c) MS^2 spectrum of **F3b** upon fragmentation of the peak at *m/z* = 927.7.

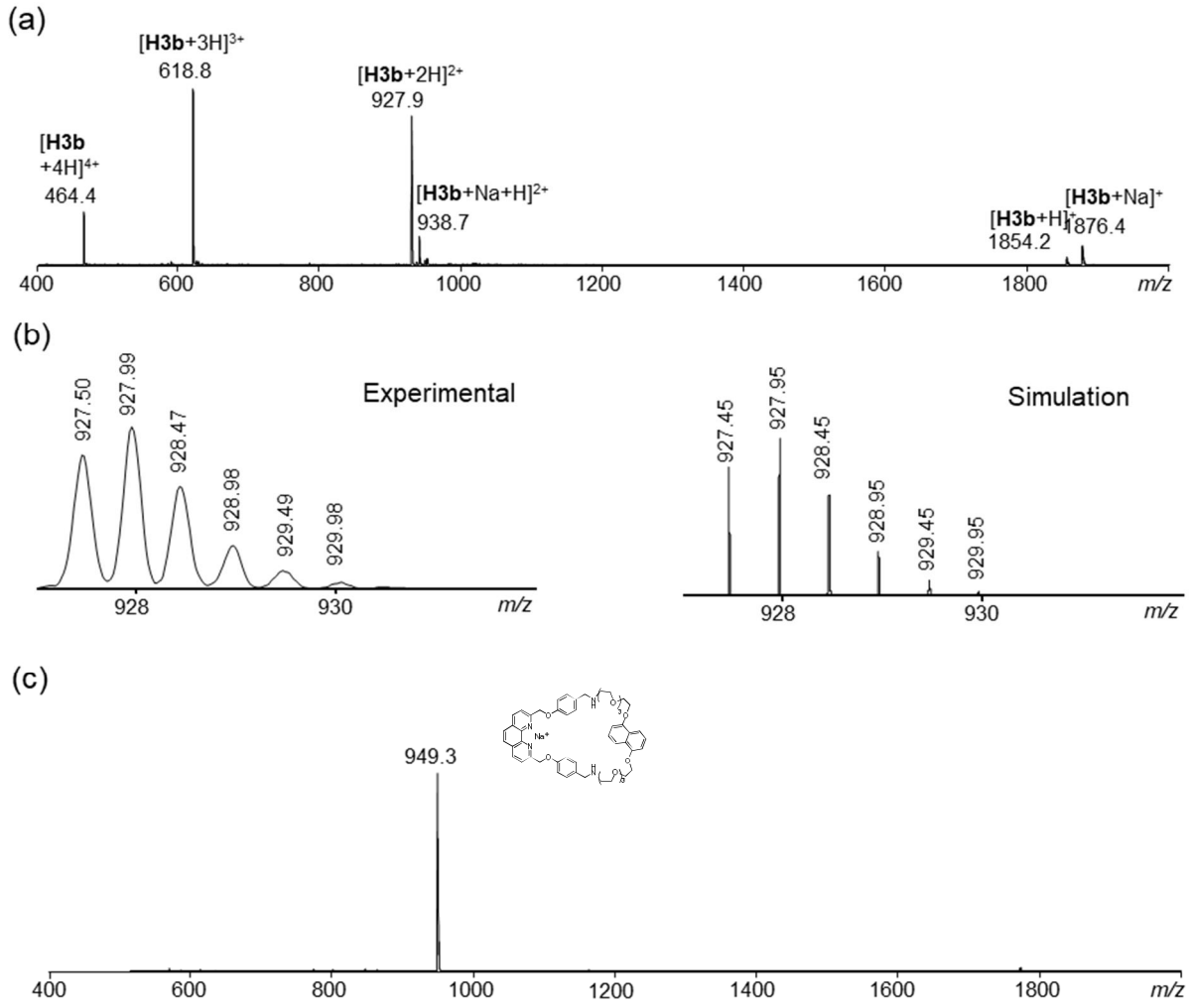


Figure S82. (a) ESI-MS spectrum of **H3b** (after demetallation), (b) HRMS of the peak at *m/z* = 927.9 (left: experimental; right: simulation) (c) MS^2 spectrum of **H3b** upon fragmentation of the peak at *m/z* = 927.9.

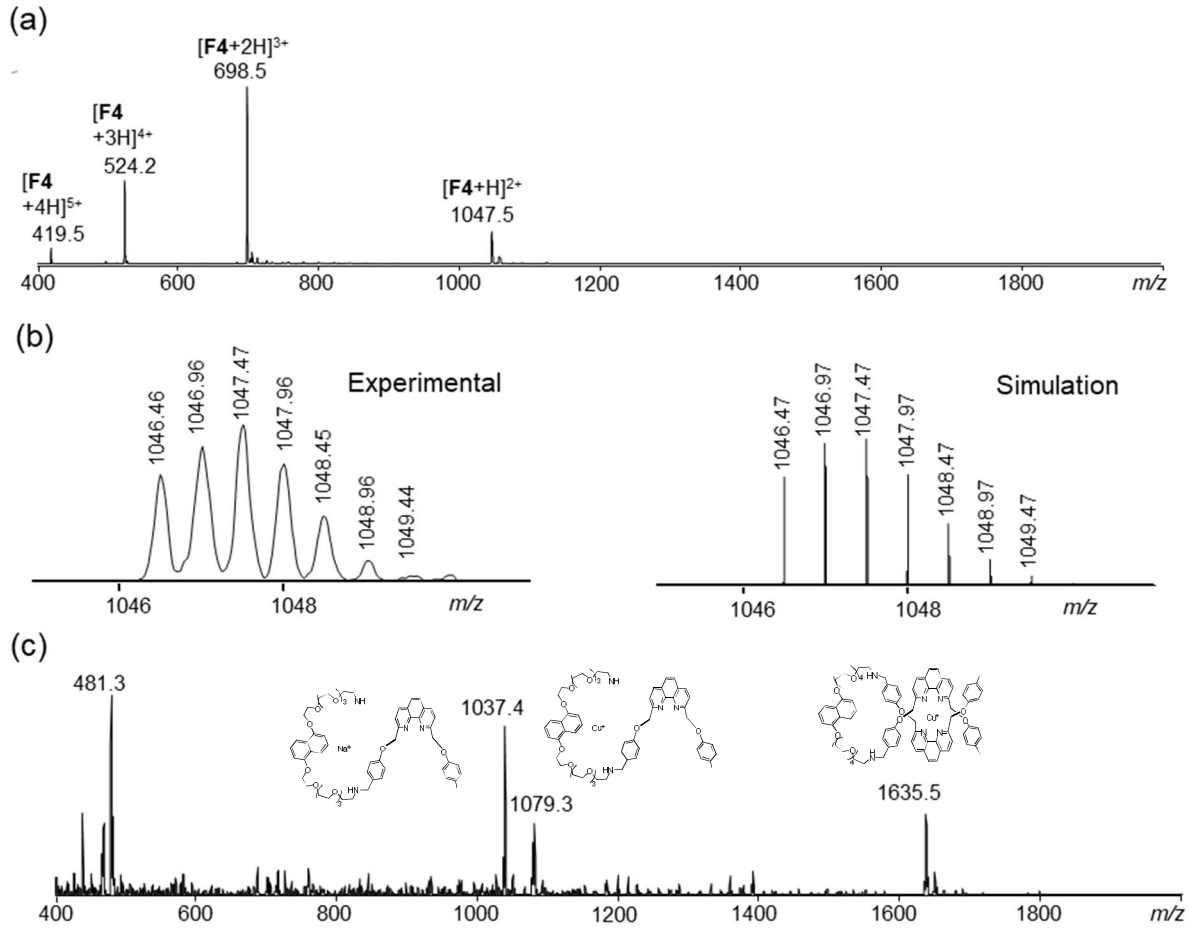


Figure S83. (a) ESI-MS spectrum of **F4**, (b) HRMS of the peak at *m/z* = 1047.5 (left: experimental; right: simulation) (c) MS^2 spectrum of **F4** upon fragmentation of the peak at *m/z* = 1047.5.

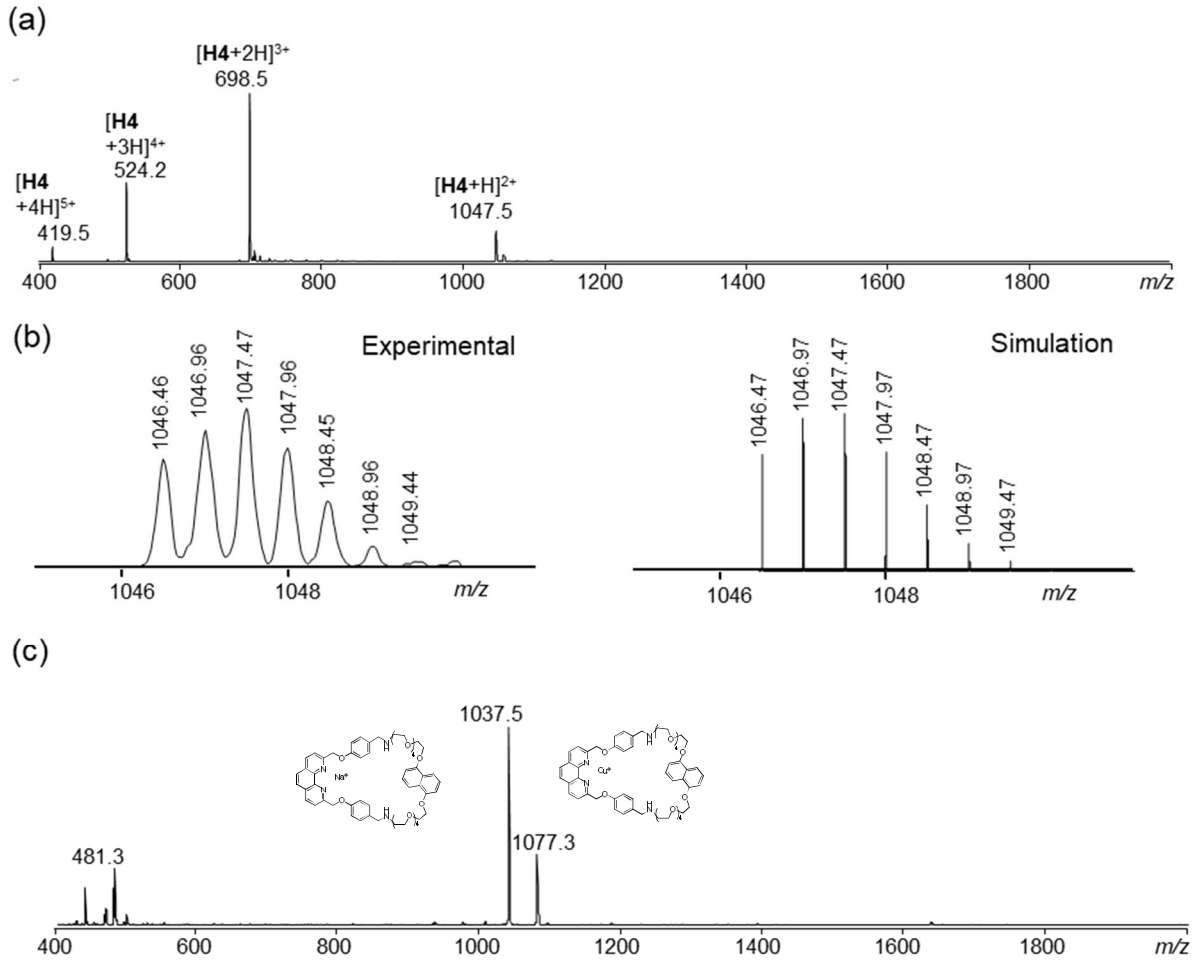


Figure S84. (a) ESI-MS spectrum of **H4**, (b) HRMS of the peak at *m/z* = 1047.5 (left: experimental; right: simulation) (c) MS^2 spectrum of **H4** upon fragmentation of the peak at *m/z* = 1047.5

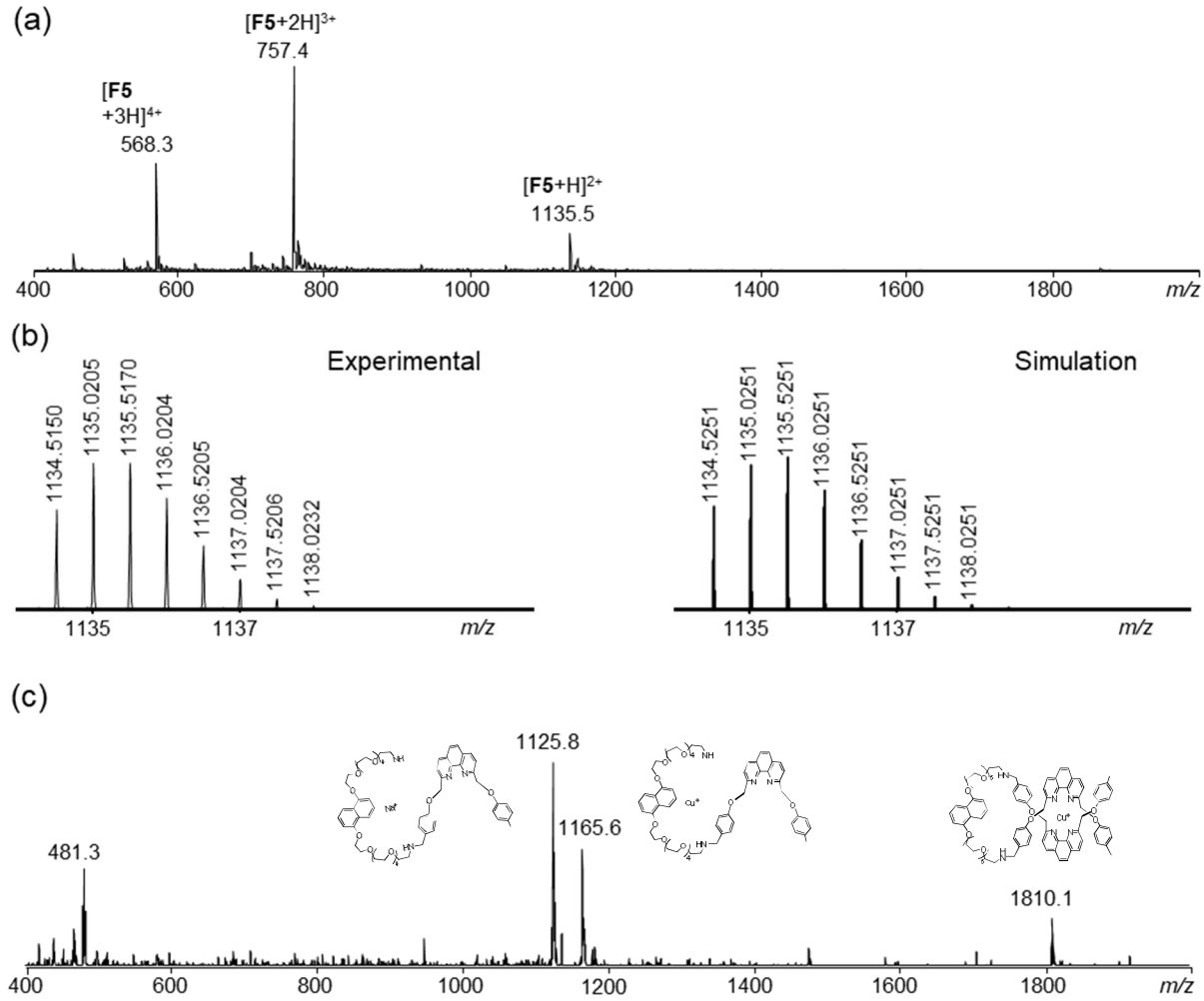


Figure S85. (a) ESI-MS spectrum of **F5**, (b) HRMS of the peak at *m/z* = 1135.5 (left: experimental; right: simulation) (c) MS^2 spectrum of **F5** upon fragmentation of the peak at *m/z* = 1135.5.

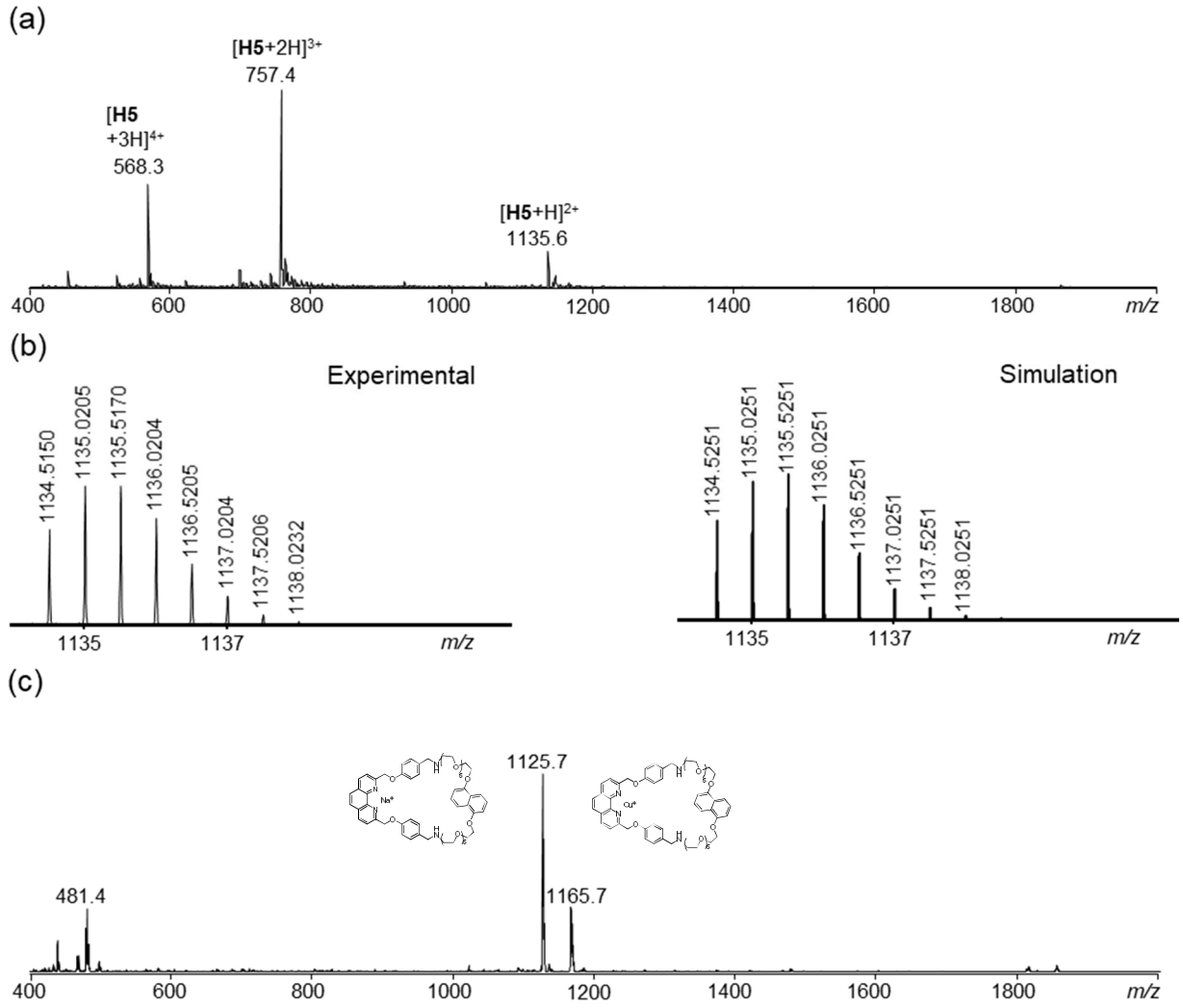


Figure S86. (a) ESI-MS spectrum of **H5**, (b) HRMS of the peak at *m/z* = 1135.6 (left: experimental; right: simulation) (c) MS^2 spectrum of **H5** upon fragmentation of the peak at *m/z* = 1135.6.

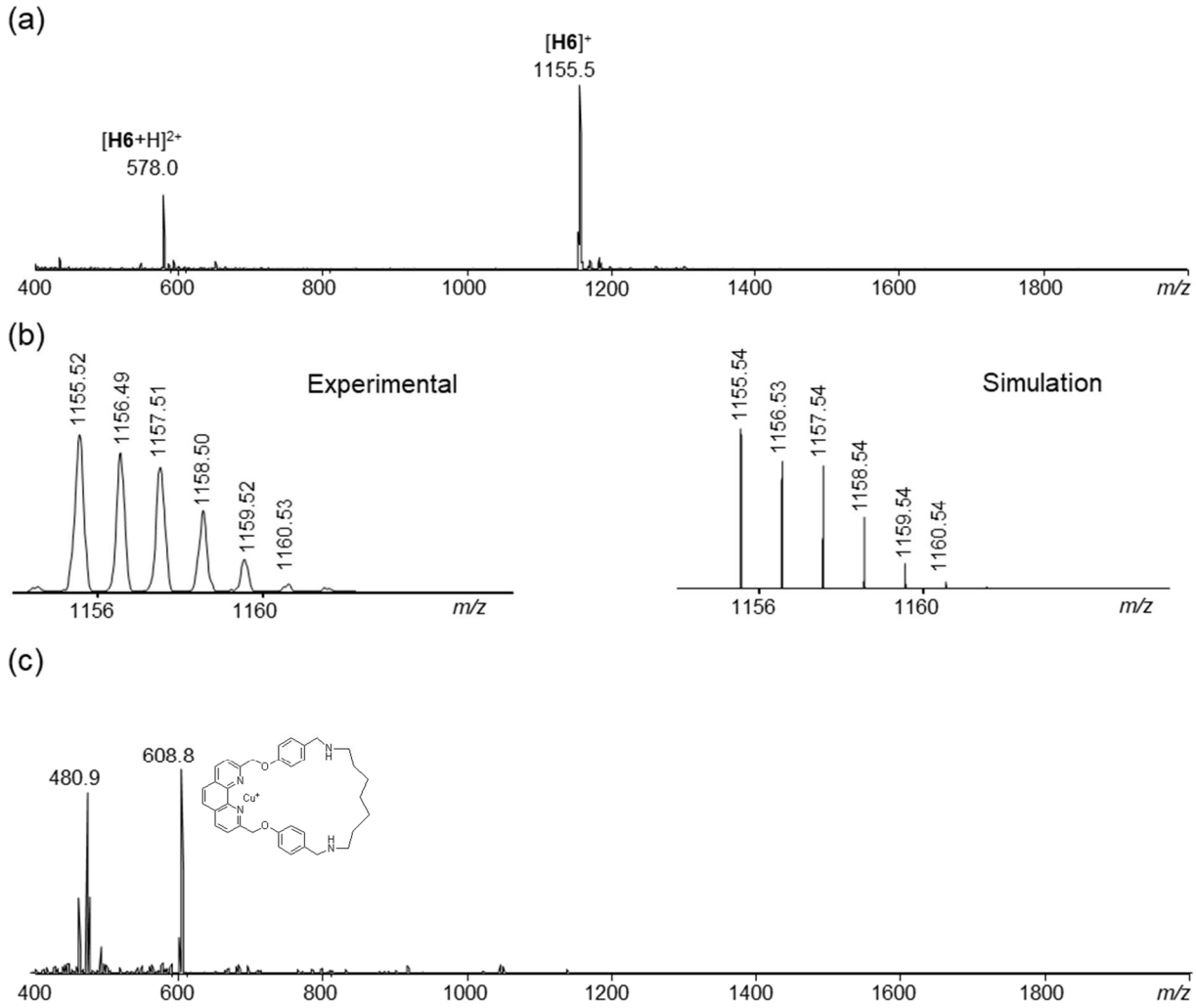


Figure S87. (a) ESI-MS spectrum of **H6**, (b) HRMS of the peak at *m/z* = 1155.5 (left: experimental; right: simulation) (c) MS^2 spectrum of **H6** upon fragmentation of the peak at *m/z* = 1155.5

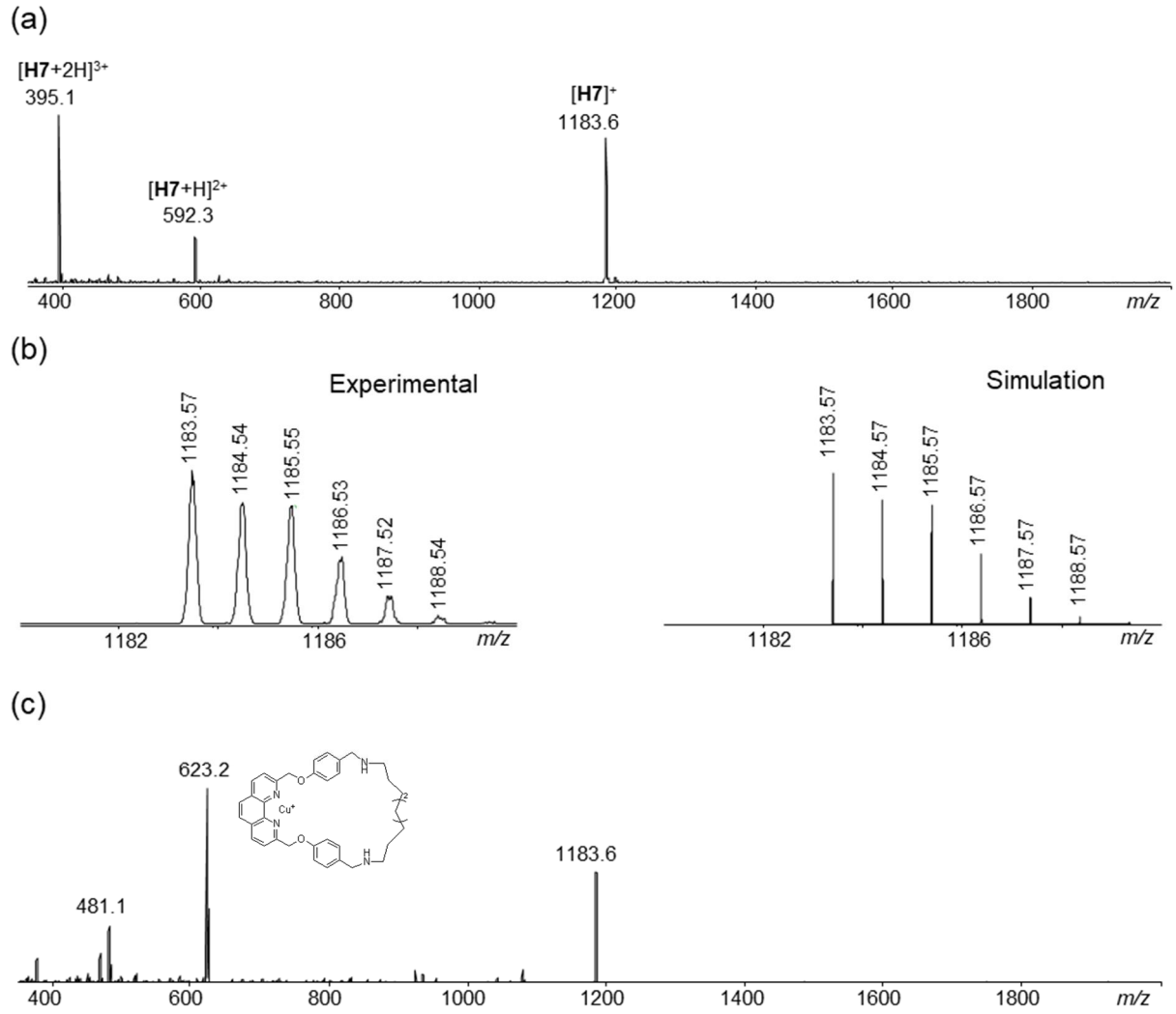


Figure S88. (a) ESI-MS spectrum of **H7**, (b) HRMS of the peak at *m/z* = 1183.6 (left: experimental; right: simulation) (c) MS^2 spectrum of **H7** upon fragmentation of the peak at *m/z* = 1183.6

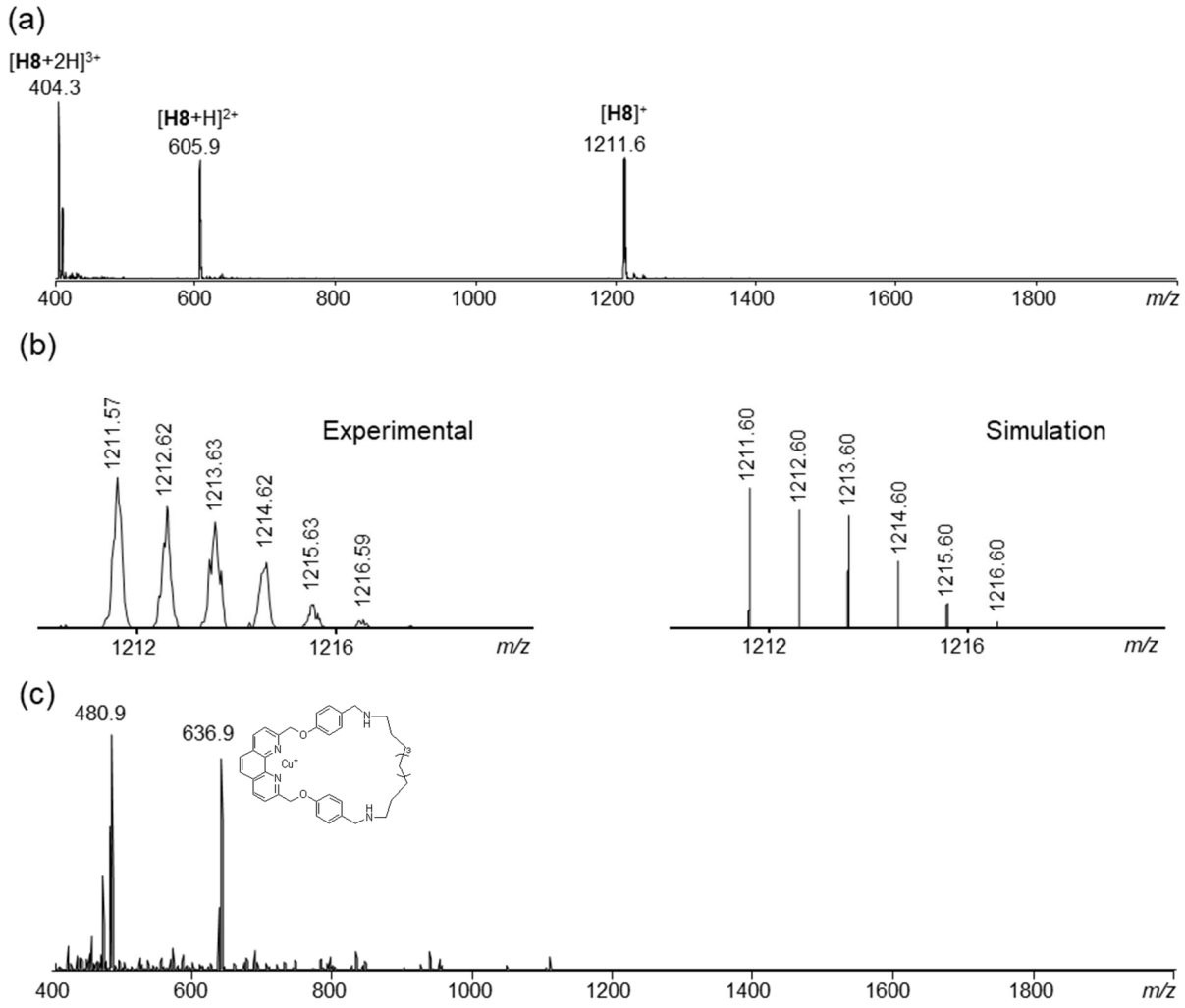


Figure S89. (a) ESI-MS spectrum of **H8**, (b) HRMS of the peak at *m/z* = 1211.6 (left: experimental; right: simulation) (c) MS^2 spectrum of **H8** upon fragmentation of the peak at *m/z* = 1211.6

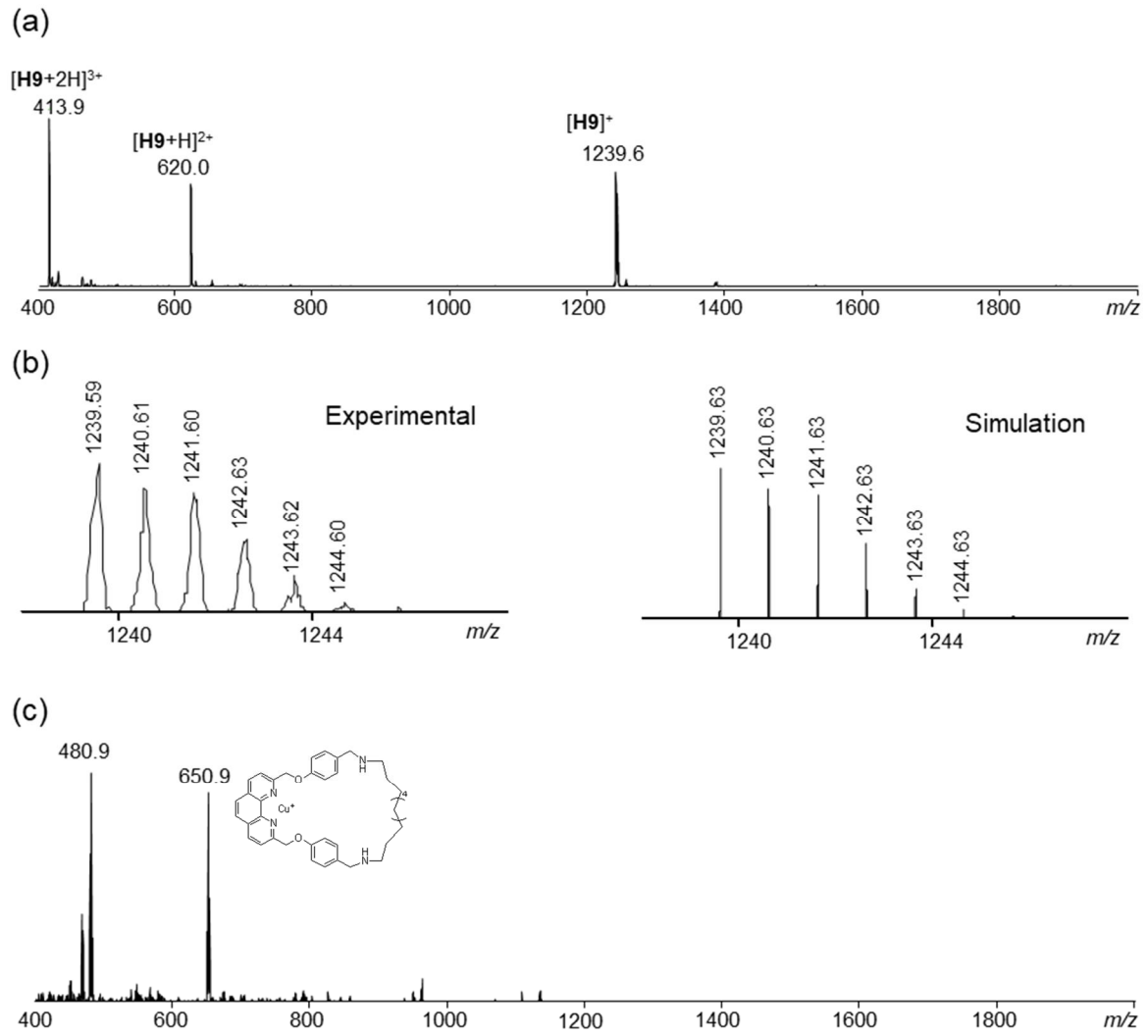


Figure S90. (a) ESI-MS spectrum of **H9**, (b) HRMS of the peak at *m/z* = 1239.6 (left: experimental; right: simulation) (c) MS^2 spectrum of **H9** upon fragmentation of the peak at *m/z* = 1239.6

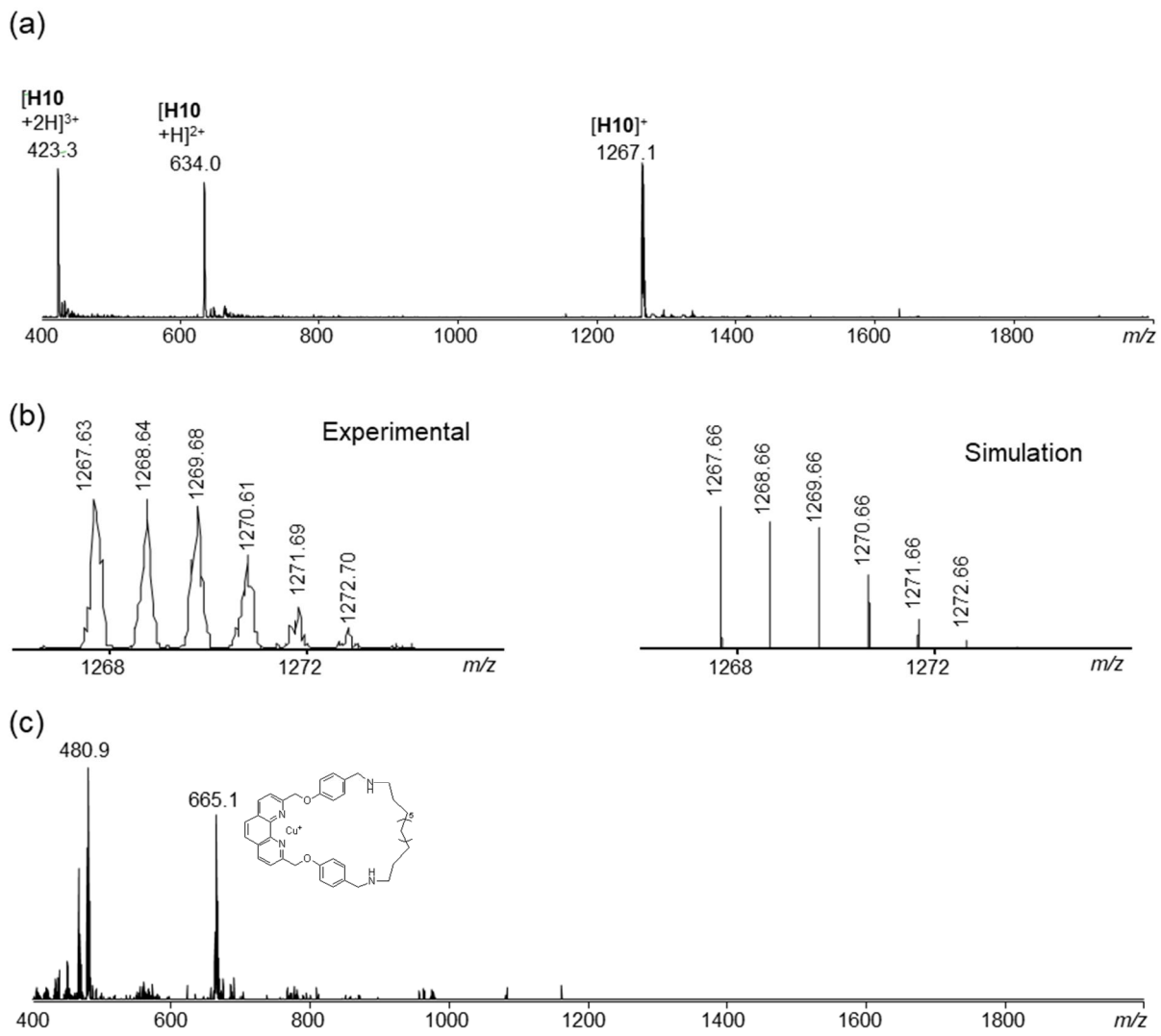


Figure S91. (a) ESI-MS spectrum of **H10**, (b) HRMS of the peak at *m/z* = 1267.1 (left: experimental; right: simulation) (c) MS^2 spectrum of **H10** upon fragmentation of the peak at *m/z* = 1267.1

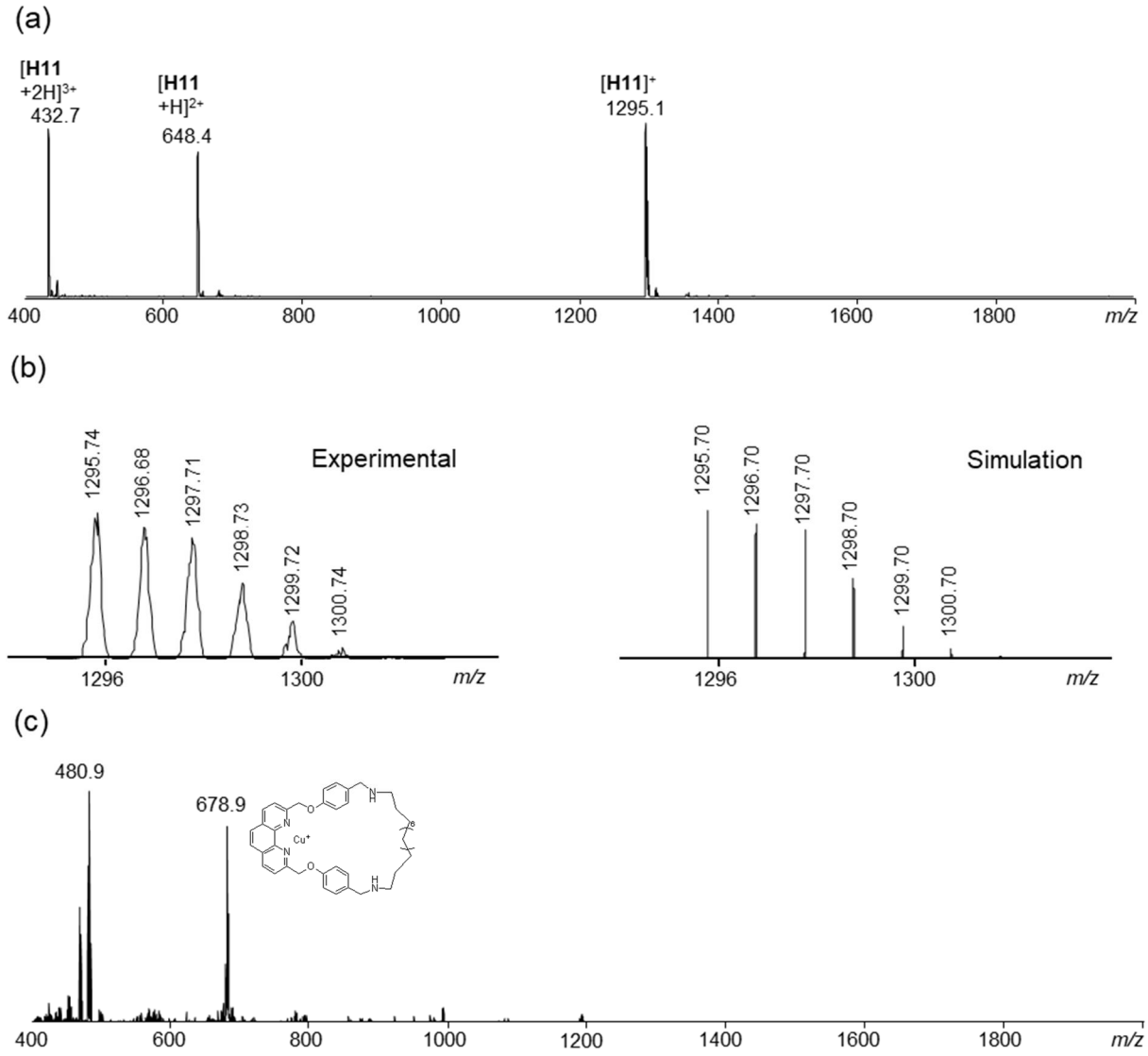


Figure S92. (a) ESI-MS spectrum of **H11**, (b) HRMS of the peak at *m/z* = 1295.1 (left: experimental; right: simulation) (c) MS^2 spectrum of **H11** upon fragmentation of the peak at *m/z* = 1295.1

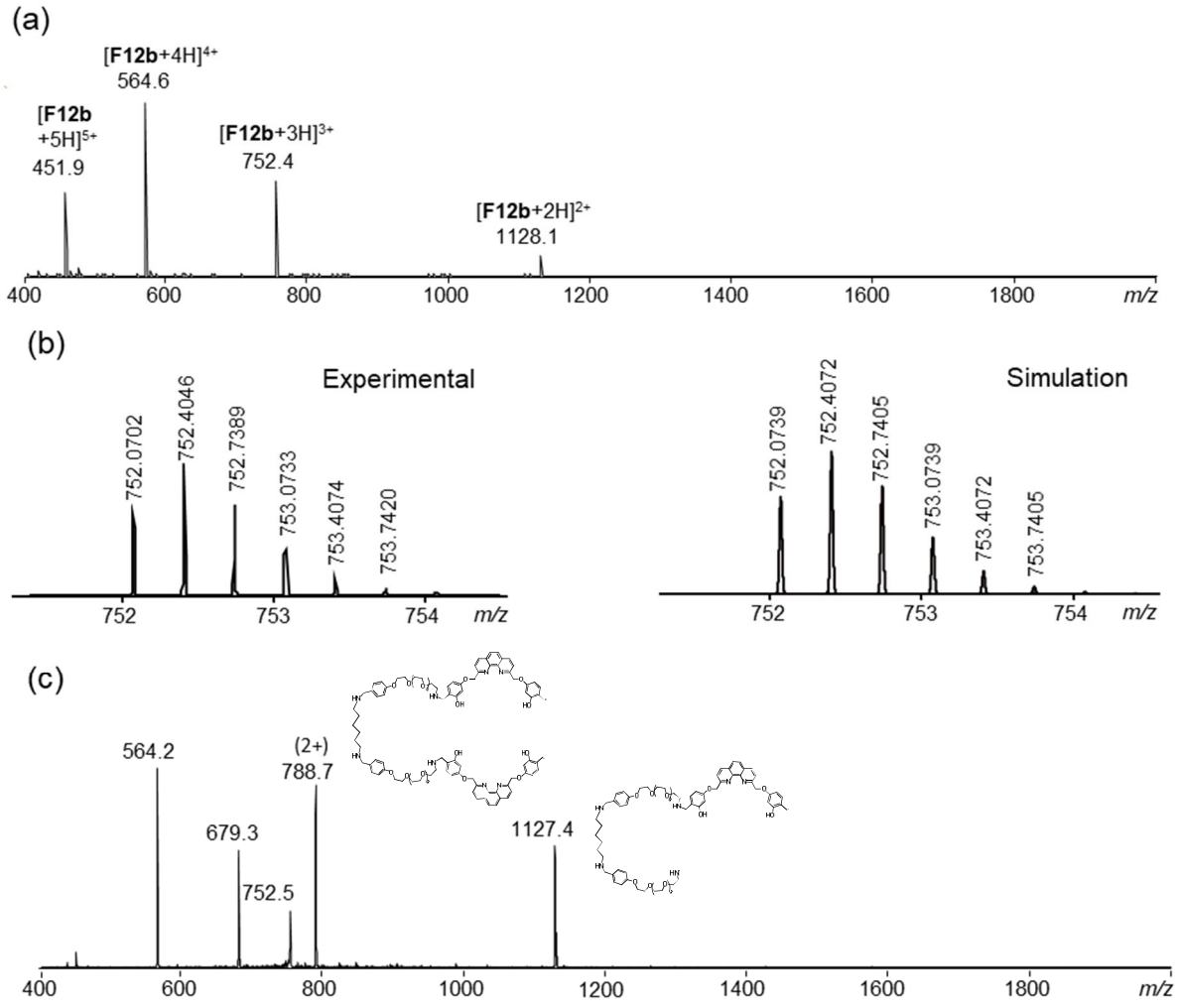


Figure S93. (a) ESI-MS spectrum of **F12b** (after demetallation), (b) HRMS of the peak at *m/z* = 752.4 (left: experimental; right: simulation) (c) MS^2 spectrum of **F12b** upon fragmentation of the peak at *m/z* = 752.4.

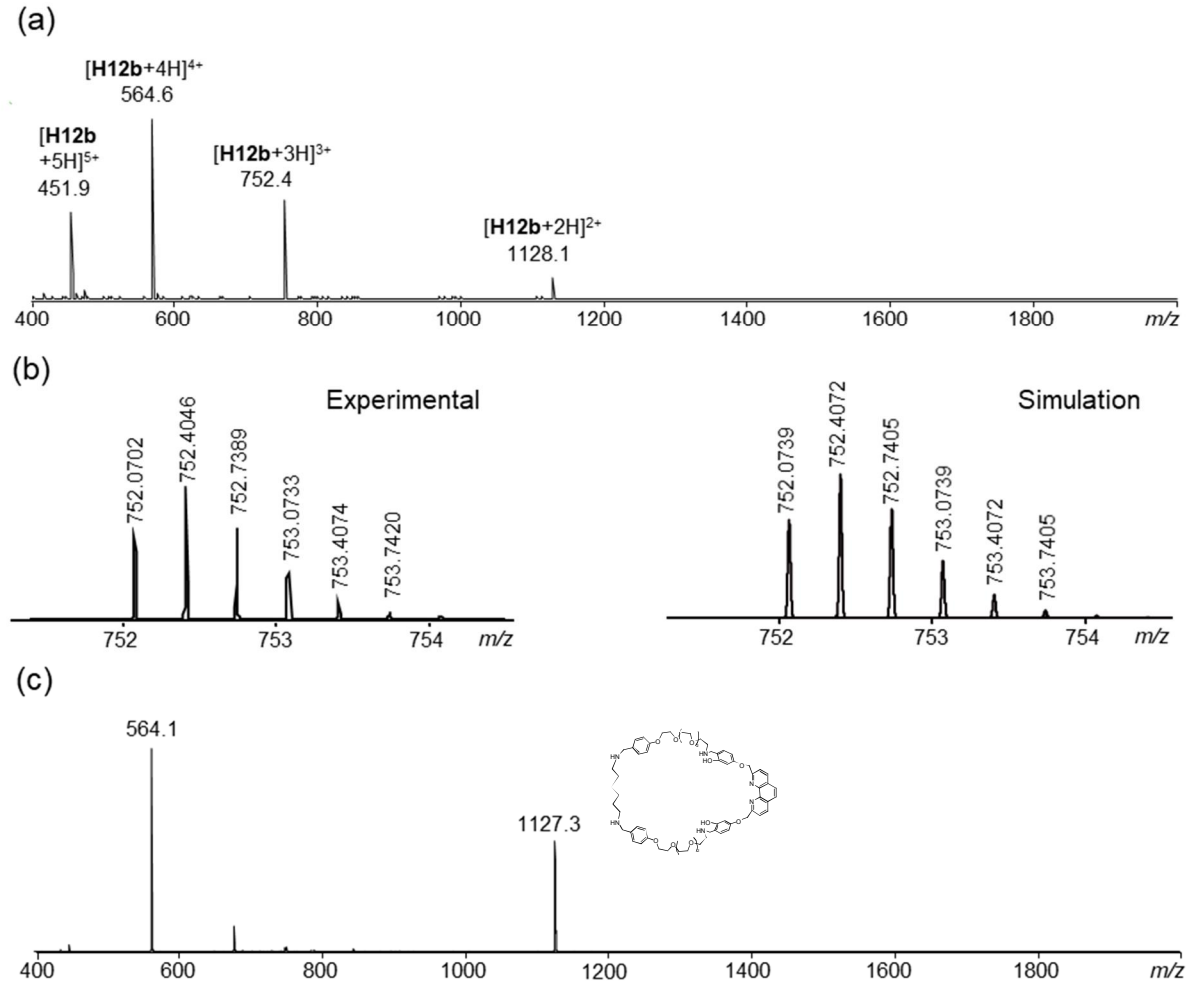


Figure S94. (a) ESI-MS spectrum of **H12b** (after demetallation), (b) HRMS of the peak at *m/z* = 752.4 (left: experimental; right: simulation) (c) MS^2 spectrum of **H12b** upon fragmentation of the peak at *m/z* = 752.4

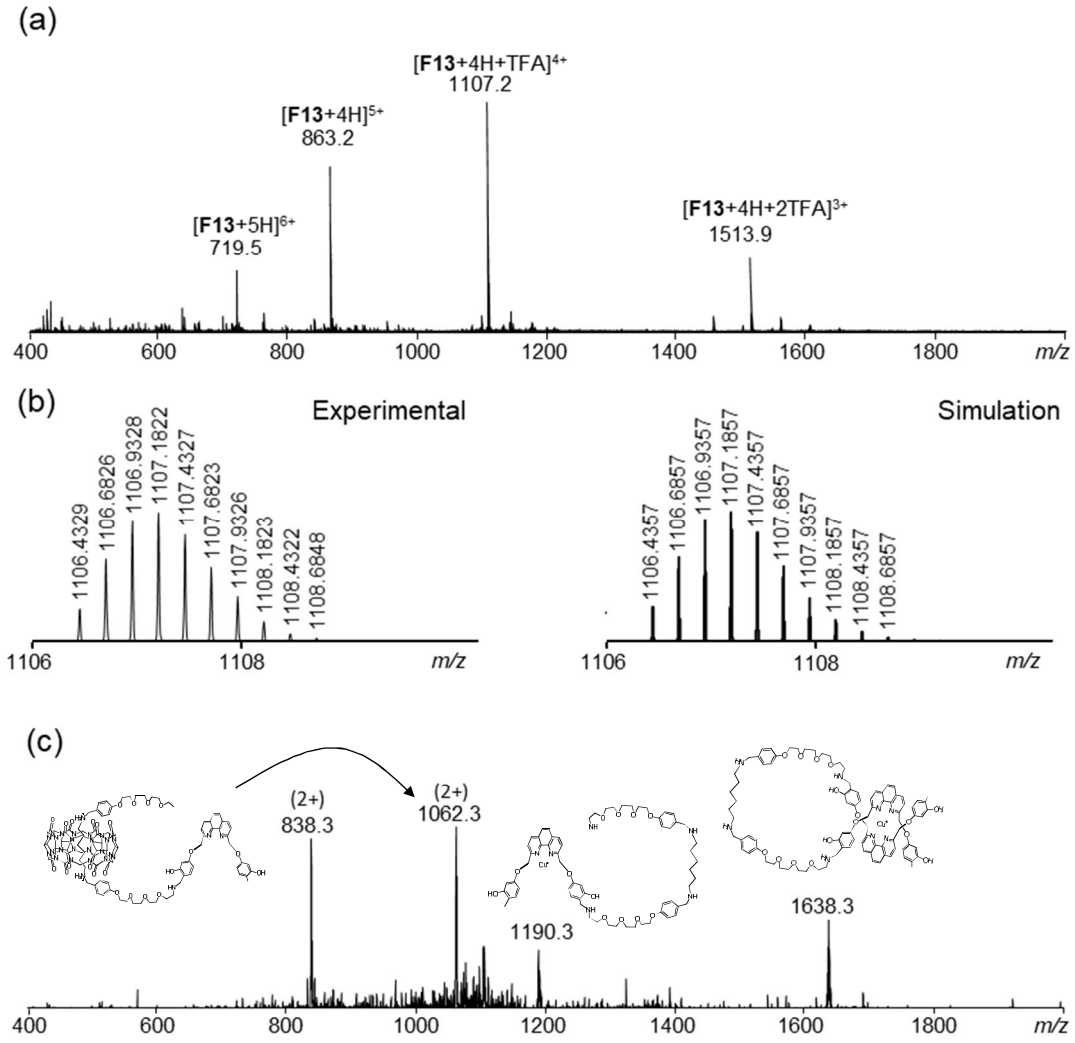


Figure S95. (a) ESI-MS spectrum of **F13**, (b) HRMS of the peak at *m/z* = 1107.2 (left: experimental; right: simulation) (c) MS^2 spectrum of **F13** upon fragmentation of the peak at *m/z* = 1107.2

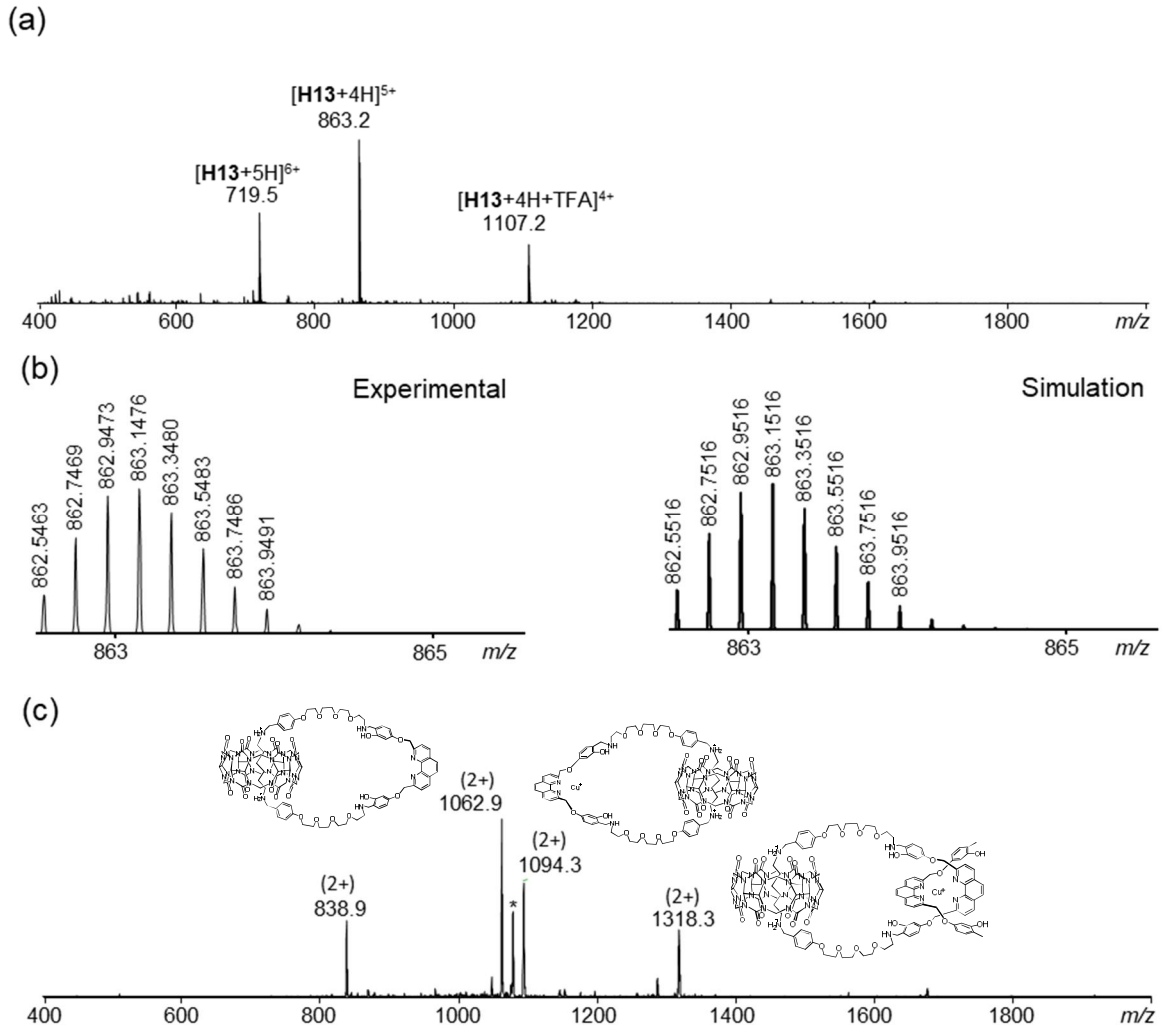


Figure S96. (a) ESI-MS spectrum of **H13**, (b) HRMS of the peak at *m/z* = 863.2 (left: experimental; right: simulation) (c) MS^2 spectrum of **H13** upon fragmentation of the peak at *m/z* = 1107.2

5. X-Ray Diffraction Analysis

Compound		$[Cu(\mathbf{L1})_2]PF_6^-.2CH_3CN$	
Empirical formula		$C_{56}H_{40}CuN_4O_8{\cdot}F_6P{\cdot}2(C_2H_3N)$	
Formula weight		1187.54	
Temperature / K		123(2)	
Wavelength / Å		0.71073	
Crystal system		Monoclinic	
Space group		*C2/c*	
Unit cell dimension			
a / Å	α / degree	27.376(3)	90
b / Å	β / degree	11.9418(12)	94.952(3)
c / Å	γ / degree	16.4539(16)	90
Volume / $Å^3$		5359.1(9)	
Z		4	
Density (calcd) / Mgm^{-3}		1.472	
Absorption coeff. / mm^{-1}		0.522	
F(000)		2440.0	
Crystal size / mm^3		0.076 x 0.131 x 0.392	
θ range for data collection		2.8 to 25.02°	
Index ranges		-32<=h<=32	
		-14<=k<=14	
		-19<=l<=19	
Reflection collected		59902	
Independent reflections		4742 [R(int) = 0.05]	
Completeness to θ		θ = 25.02, 99.9 %	
Absorption correction		Multi-scan	
Max. and min. transmission		0.746 and 0.697	
Refinement method		Full-matrix least-squares on F^2	
Data/ restraints / parameters		4742 / 23 / 439	
Goodness-of-fit on F^2		1.03	
Final R indices [$I \geq 2\sigma(I)$]		R1 = 0.0473, wR2 = 0.1325	
Largest diff. peak and hole		0.850 and -0.35 $eÅ^{-3}$	

The X-ray intensity data were measured on a Bruker *D8 Venture* X-ray Diffractometer equipped with microfocus I□S radiation and Photon100 CMOS detector. The frames were integrated with the

Bruker SAINT software package using a narrow-frame algorithm. The structure was solved and refined using the Bruker SHELXTL Software Package.

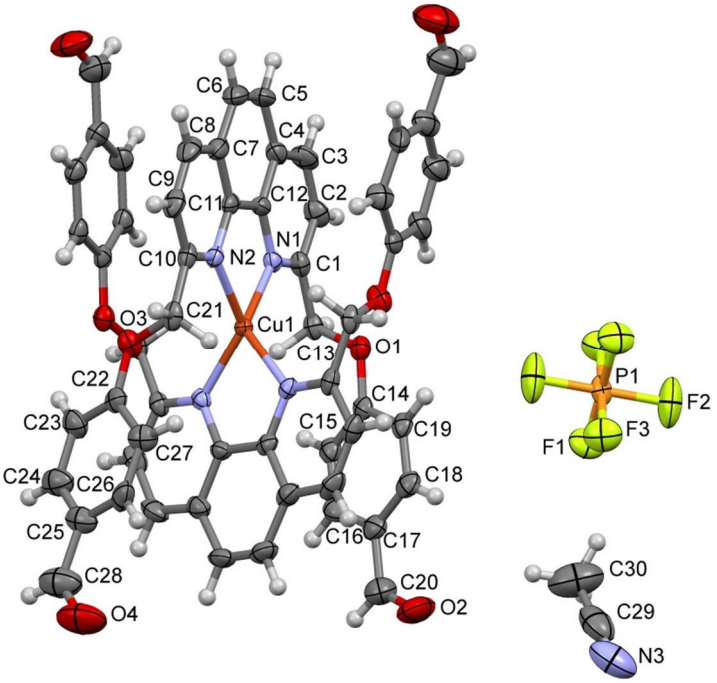


Figure S97. The complex molecule was shown at 50% probability thermal ellipsoids with the atom numbering scheme (only the major component is shown).

6. References:

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