Self-Assembly of Supramolecular Fractals from Generation 1 to 5

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1. Experimental section

General Procedures. All reagents were purchased from Sigma-Aldrich, Matrix Scientific, Fisher Scientific, Oakwood Chemicals, and used without further purification. Column chromatography was conducted using neutral Al_2O_3 (Brockman I, 50-200 µm, 60 Å) or SiO_2 (VWR, 40-60 µm, 60 Å) and the separated products were visualized by UV light or testified by ESI-MS. ^1H NMR and ^{13}C NMR spectral data of the organic intermediates and **LA**, ^{13}C NMR spectral data of **LB**, **LC** and **LE** were recorded on a Bruker BioSpin GmbH 400-MHz (probe: Z104450_0395 (PA BBO 400S1 BBF-H-D-05 Z)), Varian 500-MHz (probe: ColdProbe_TR_Z_MR1007_3900B-12). ^1H NMR, 2D NMR and ^{13}C NMR spectral data of the metallic organic intermediates and the supramolecular complexes **G1**-**G5**, ^1H NMR, 2D NMR of the ligands (**LB**-**LE**), ^{13}C NMR spectral data of **LD** were recorded on a Varian 500-MHz (probe: ColdProbe_TR_Z_MR1007_3900B-12) spectrometer. DOSY NMR spectral data of the complexes **G1**-**G5** were recorded on a Varian 600-MHz spectrometer. ESI-MS was conducted on Waters Synapt G2 mass spectrometer with traveling wave ion mobility. The IM-MS experiments for complexes were performed under the following conditions: ESI capillary voltage, 3.0 kV; sample cone voltage, 15 V; extraction cone voltage, 0.5 V; source temperature 100 ºC; desolvation temperature, 100 ºC; cone gas flow, 10 L/h; desolvation gas flow, 700 L/h (N_2); source gas control, 0 mL/min; trap gas control, 2 mL/min; Helium cell gas control, 100 mL/min; ion mobility (IM) cell gas control, 30 mL/min; sample flow rate, 5 µL/min; IM traveling wave height, 25 V; and IM traveling wave velocity, 1000 m/s. Electronic absorption experiments were conducted on a HORIBA FLUOROMAX-4C-L.

CV: Cyclic voltammetry measurements were performed on a WaveDrive 10 potentiostat with a standard three-electrode configuration using a platinum button working electrode, a platinum flag counter electrode and a saturated calomel electrode reference electrode. The electrochemical properties of these five complexes in DMF (10^{-5} M) were studied in a three-electrode electrochemical cell with Bu_4NPF_6 (0.1 M) as electrolyte.

Molecular model: Energy minimization of the macrocycles was conducted with Materials Studio version 4.2, using the Anneal and Geometry Optimization tasks in the Forcite module (Accelrys Software, Inc.). All counterions and alkyl chain were omitted. Geometry optimization used a universal force field with atom-based summation and cubic spline truncation for both the electrostatic and Van der Waals parameters.

TEM: The sample solutions (0.5 mg/mL in DMF) were drop cast on copper grids (carbon coated 400 mesh Cu grids purchased from www.2spi.com) and the extra solution was absorbed by filter paper to avoid aggregation. The grid was then washed with three drops of methanol to remove DMF. The nanostructures were formed by diffusing THF into the sample solution (5.0 mg/mL in DMF) slowly and the mixture were drop cast on copper grids directly. The TEM images were all taken with a FEI Morgagni transmission electron microscope.

STM: The sample solution (0.2 mg/mL in DMSO) was dropped on freshly cleaved HOPG surface. After 30 seconds, the surface was washed slightly with water for three times and spin-coated for 30 minutes to make sure that the molecules were uniformly distributed on the HOPG surface dried in room temperature. The STM images were taken with a PicoPlus SPM system with a PicoScan 3000 Controller. The obtained STM images were processed by WSxM software.

2. Attempts to obtain LB, LC, and LE

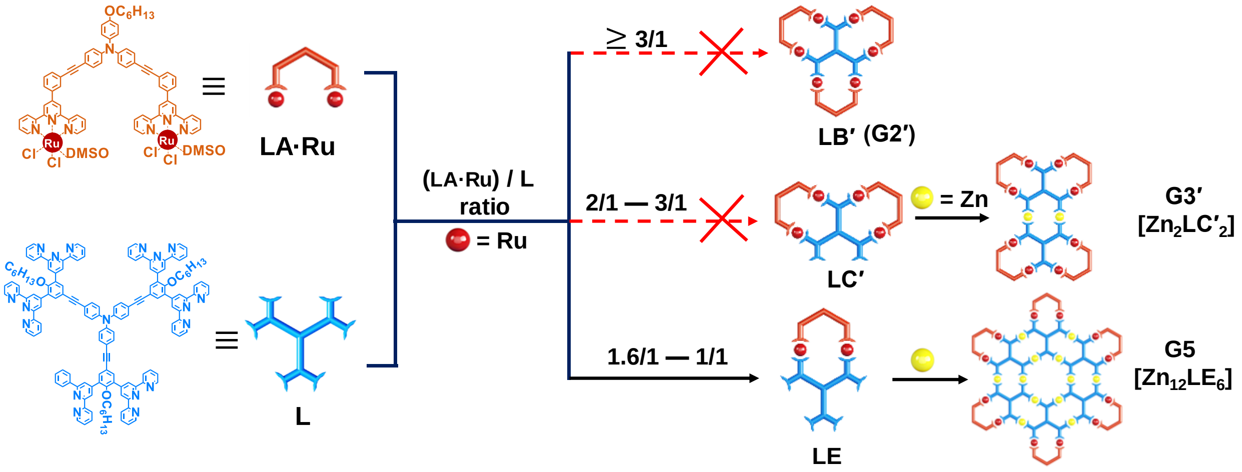


Figure S1. Initial end-capping strategy of approach 2.

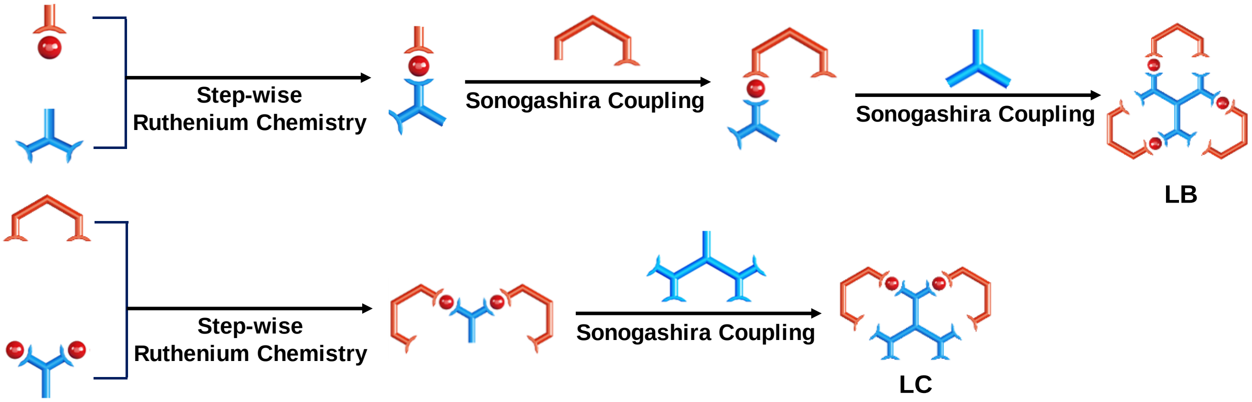
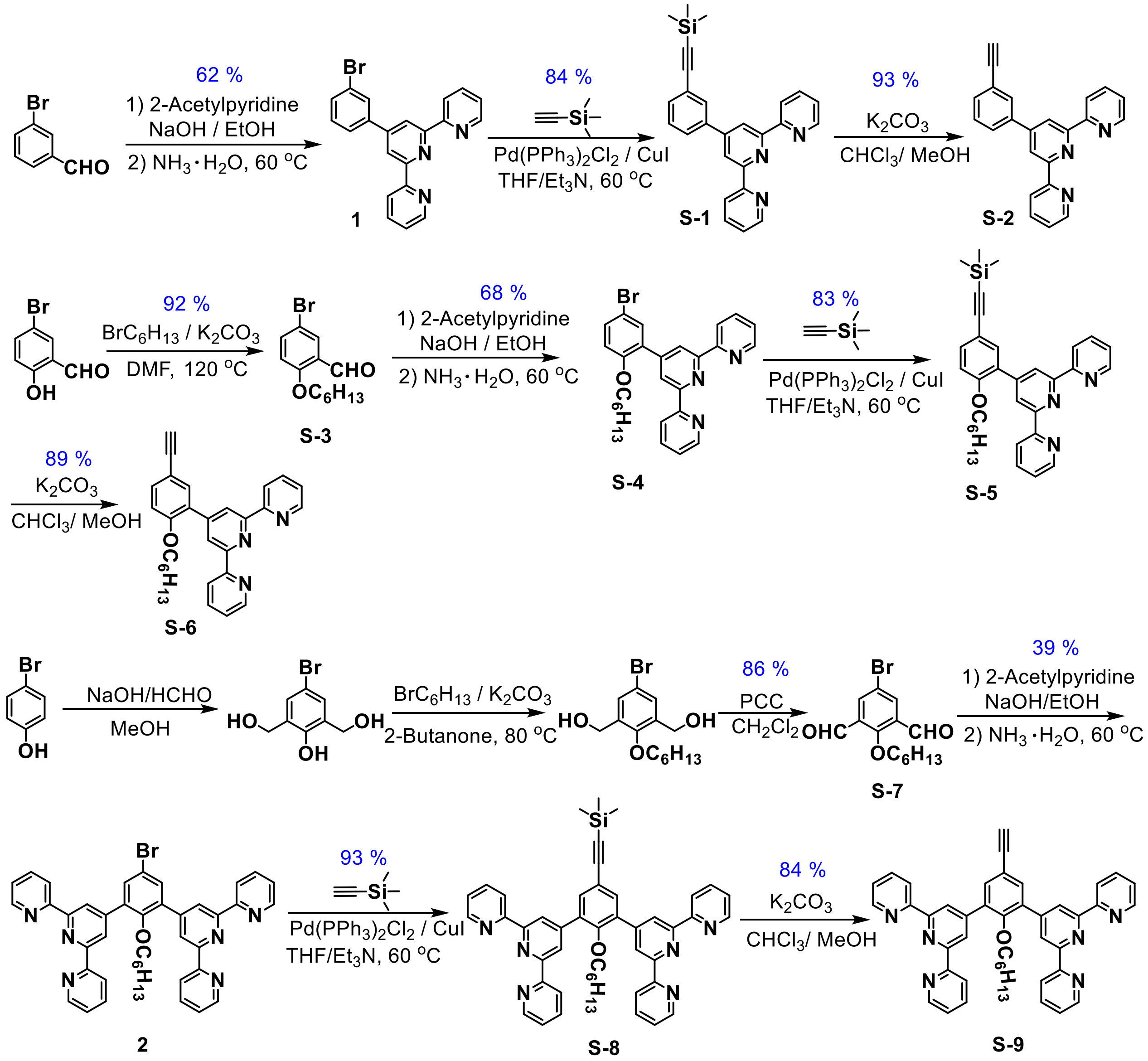
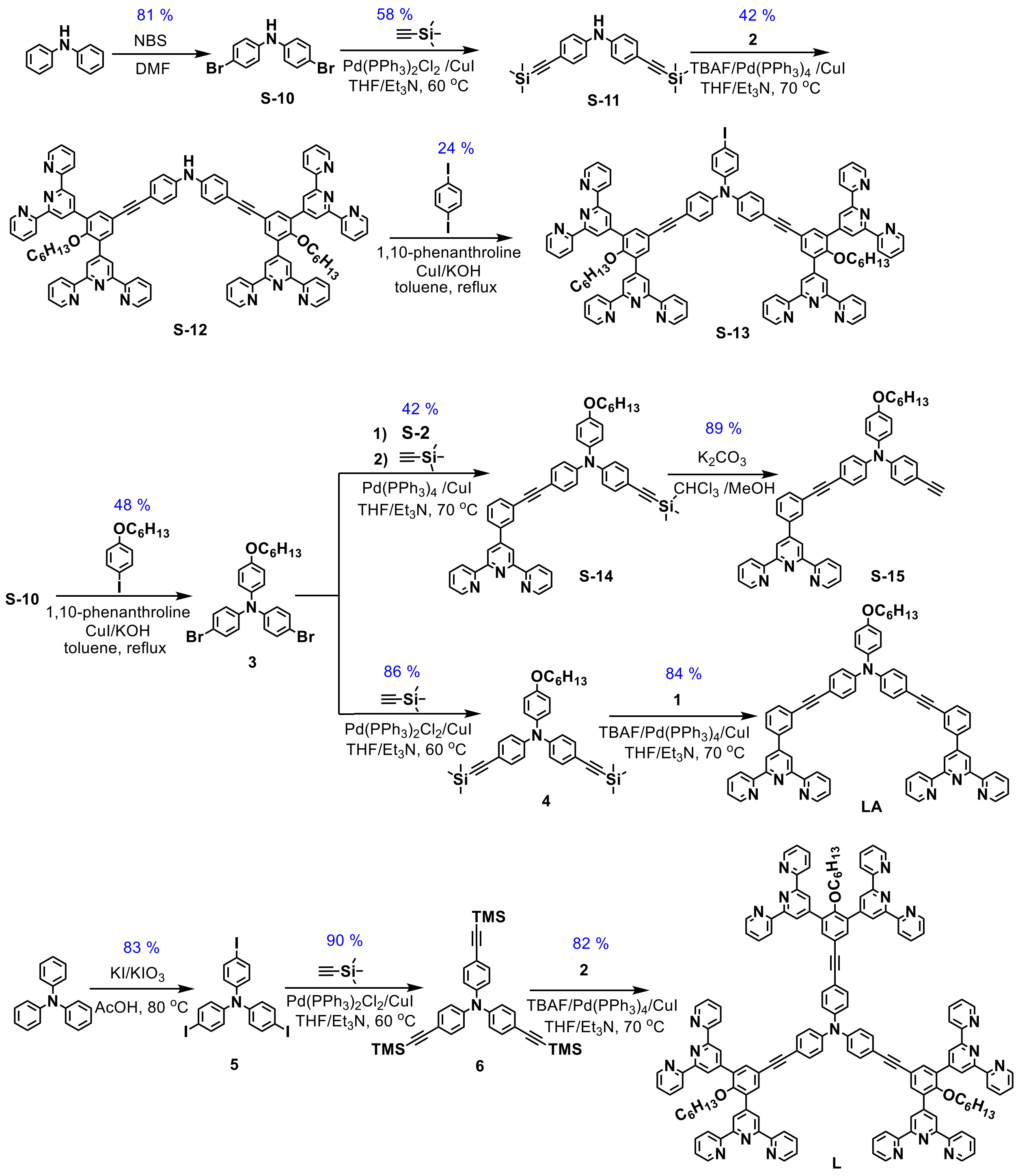


Figure S2. Combination of Ru(II) connectivity and Sonogashira coupling in approach 3.

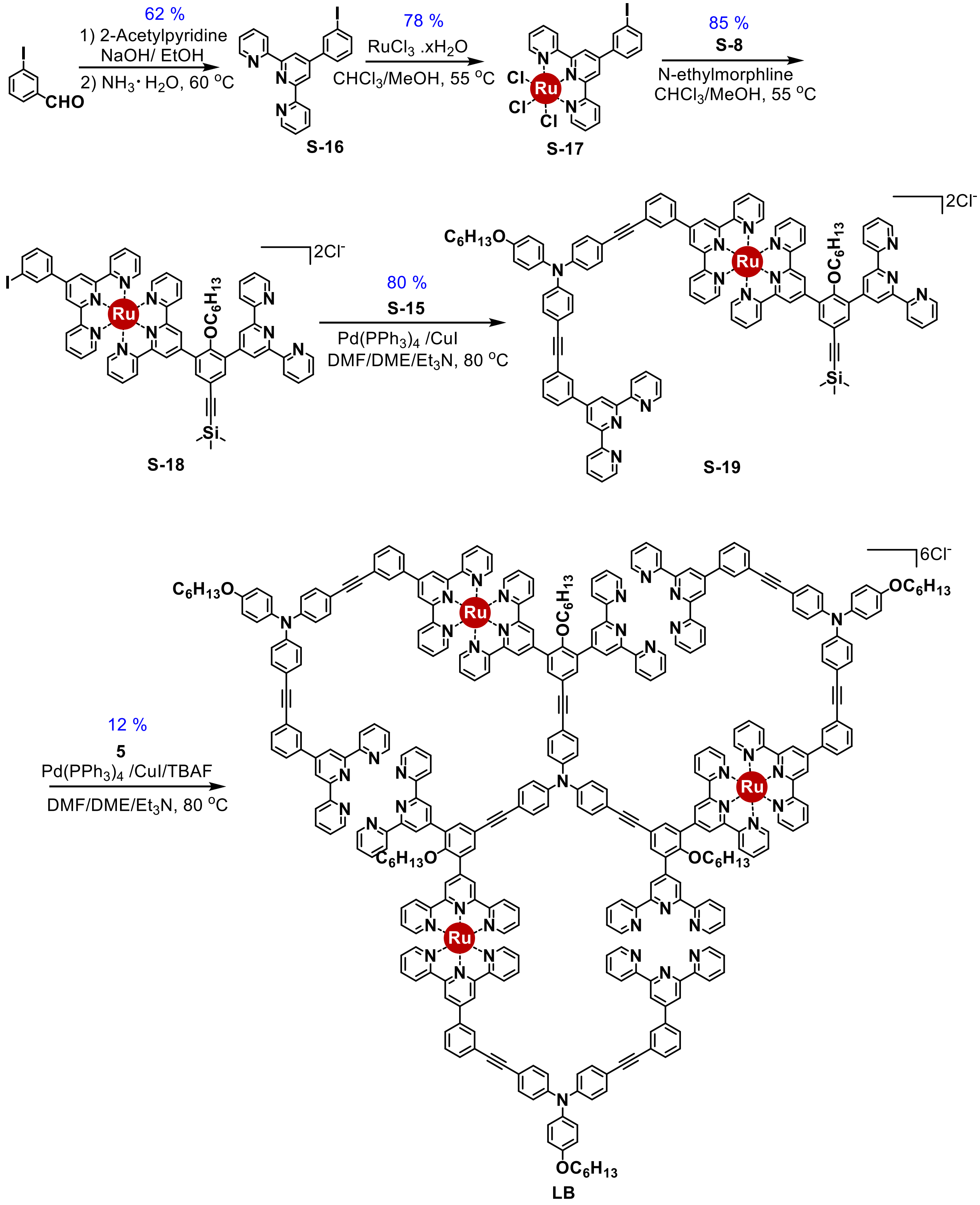
3. Synthetic route to LA-LE



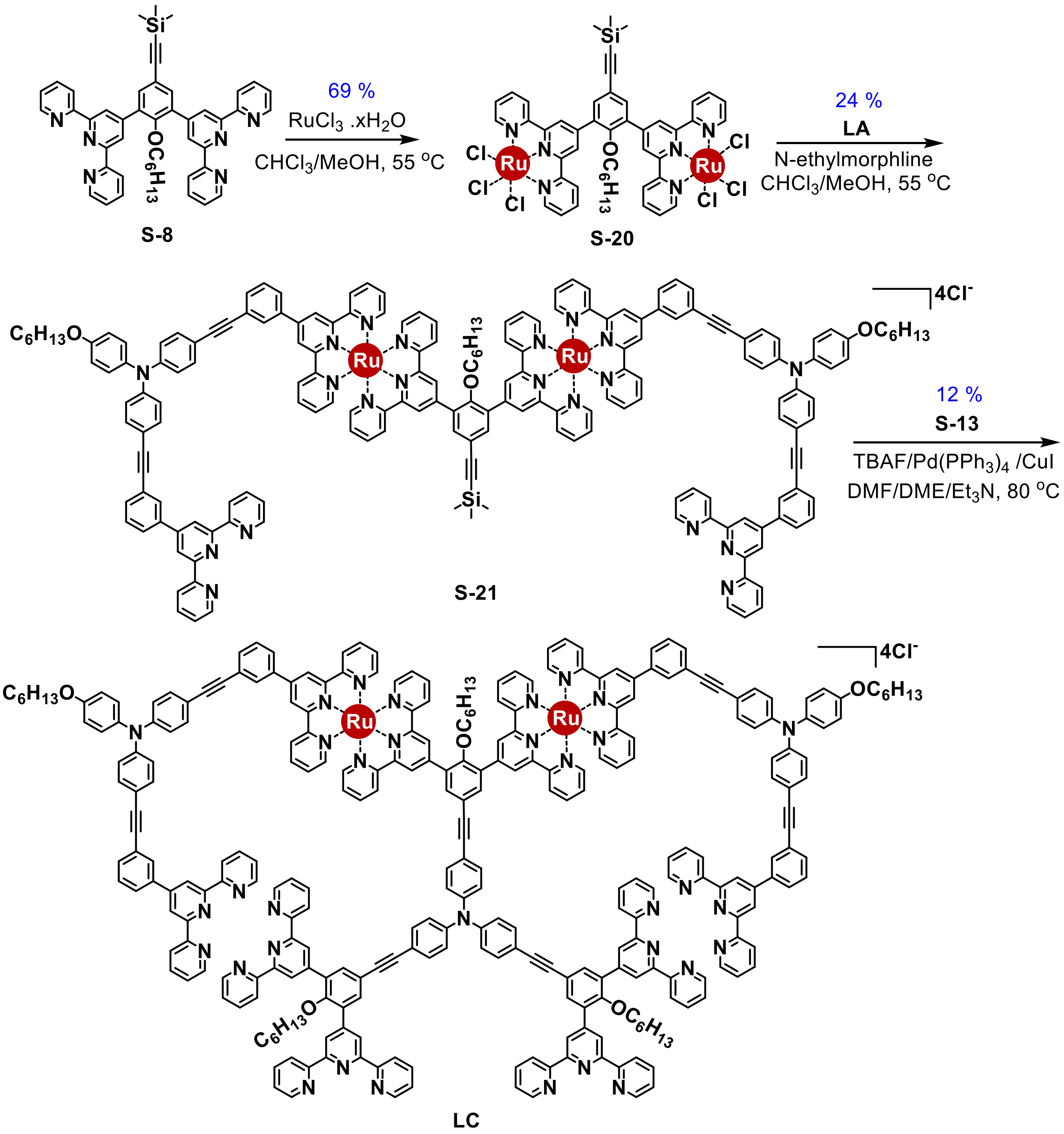
Scheme S1. Synthesis of terpyridine precursors.



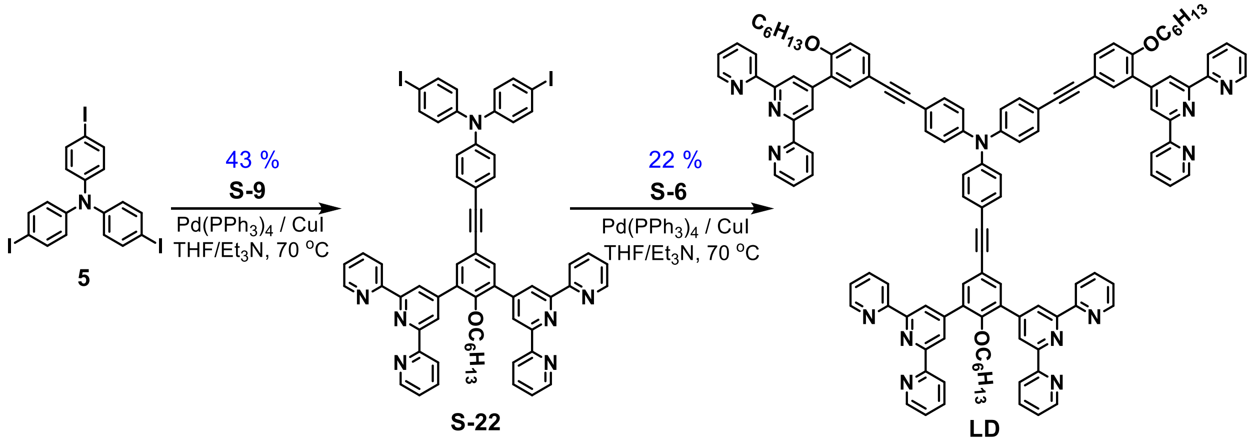
Scheme S2. Synthesis of **LA** and **L**.



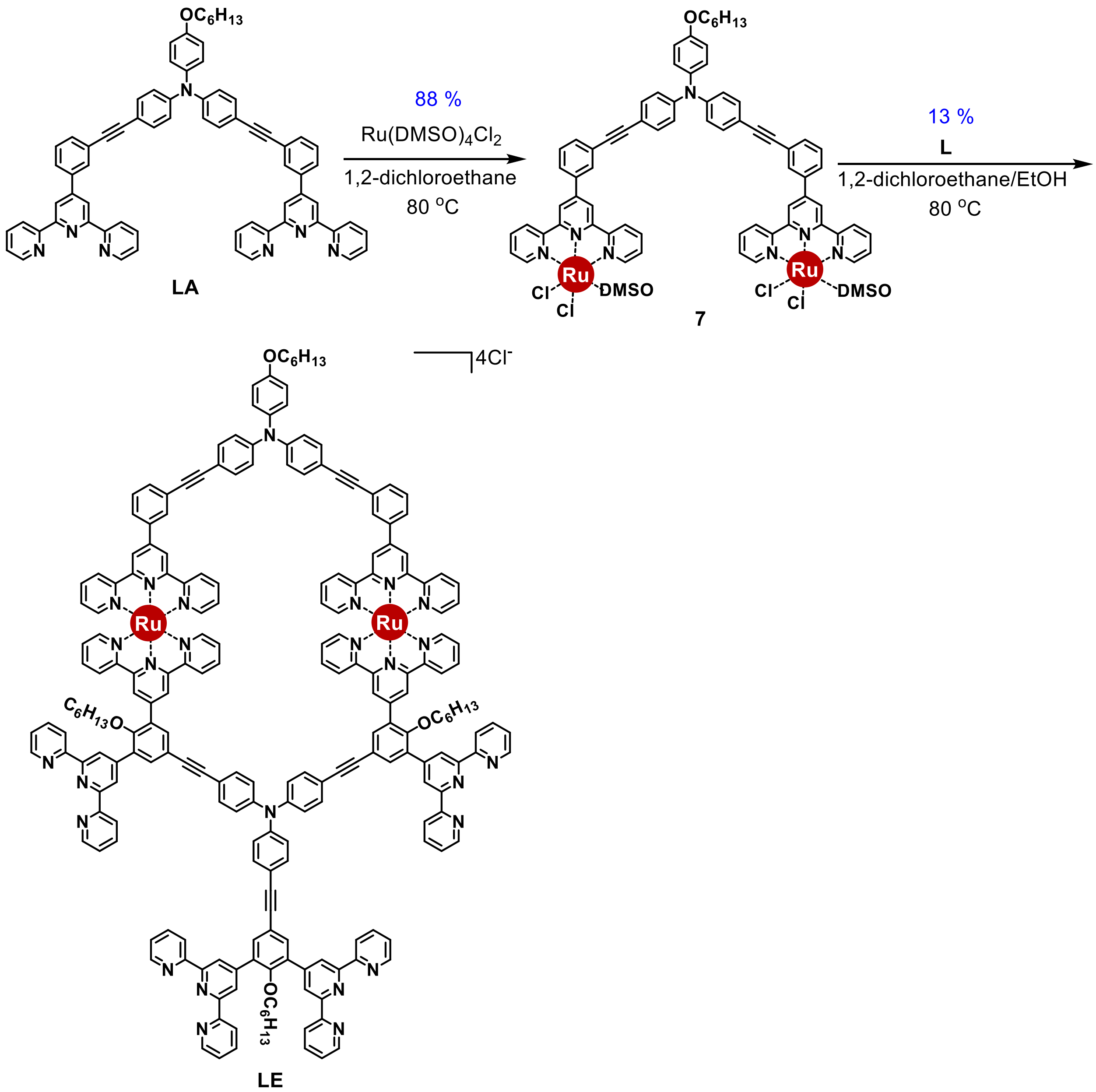
Scheme S3. Synthesis of **LB**.



Scheme S4. Synthesis of **LC**.

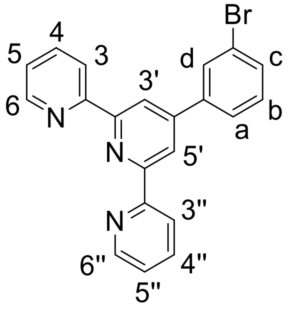


Scheme S5. Synthesis of **LD**.

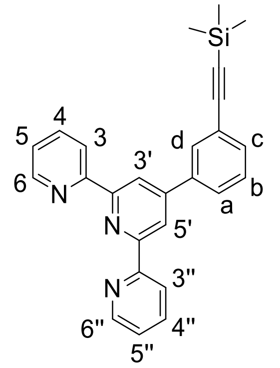


Scheme S6. Synthesis of **LE**.

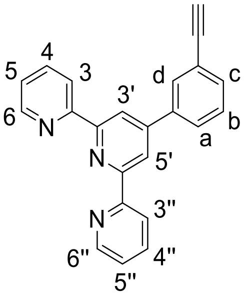
4. Synthesis of ligands and complexes.



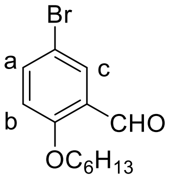
Compound **1**. Compound **1** was synthesized according to a literature method.[1] To a flask containing NaOH (4.8 g, 120 mmol) in EtOH (150 mL), 3-bromobenzaldehyde (3.7 g, 20 mmol) and 2-acetylpyridine (5.3 g, 44 mmol) were subsequently added. After stirring at room temperature overnight, aqueous $NH_3 \cdot H_2O$ (37 %, 150 mL) was added and the mixture was heated at 60 ºC overnight. After cooling down to room temperature, the precipitate was filtered under vacuum and washed with ethanol to give **1** as a white power (4.8 g, 62 % yield). ^1H NMR (500 MHz, CDCl3, 300 K) δ 8.73 (s, 2H, tpy-$H^{3',5'}$), 8.69-8.62 (m, 4H, tpy-$H^{6,6''}$, tpy-$H^{3,3''}$), 8.04 (s, 1H, Ph-H^{d}), 7.90-7.88 (m, 2H, tpy-$H^{4,4''}$), 7.81 (d, J = 7.9 Hz, 1H, Ph-H^{a}), 7.58 (d, J = 8.1 Hz, 1H, Ph-H^{c}), 7.41-7.36 (m, 3H, tpy-$H^{5,5''}$, Ph-H^{b}). ^{13}C NMR (125 MHz, $CDCl_3$, 300 K) δ 156.06, 155.96, 149.13, 148.83, 140.64, 136.89, 131.92, 130.42, 130.26, 126.00, 123.94, 123.10, 121.36, 118.77. ESI-TOF (*m/z*): Calcd. $[C_{21}H_{14}BrN_3 + H]^+$ for: 388.04, found: 388.02.



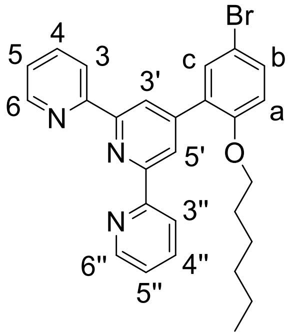
Compound **S-1**. Compound **S-1** was synthesized according to a literature method.[2] A mixture of compound **1** (3.9 g, 10.0 mmol), $Pd(PPh_3)_2Cl_2$ (250 mg, 0.35 mmol) and copper(I) iodide (53 mg, 0.28 mmol) was degassed under nitrogen for three times. After that, 30 mL anhydrous THF, 45 mL anhydrous Et_3N and ethynyltrimethylsilane (2.5 mL, 18 mmol) was added and then the mixture was stirred at 60 ºC overnight. After cooling down to room temperature, solvent was removed, and the residue was extracted with $CHCl_3$. The combined organic phase was washed with brine and dried over Na_2SO_4. After removal of solvent under vacuum, the residue was purified by column chromatography on silica gel with chloroform: ethanol (100:1) as eluent to afford a white solid (3.4 g, 84 % yield). ^{1}H NMR (400 MHz, CDCl3, 300 K) δ 8.76 – 8.73 (m, 2H, tpy-$H^{6,6''}$) δ 8.74 (s, 2H, tpy-$H^{3',5'}$), 8.68 (dq, J = 8.0, 1.3 Hz, 2H, tpy-$H^{3,3''}$), 8.02 (s, 1H, Ph-H^{d}), 7.93-7.80 (m, 3H, tpy-$H^{4,4''}$, Ph-H^{a}), 7.55 (dt, J = 7.7, 1.4 Hz, 1H, Ph-H^{c}), 7.50 – 7.42 (m, 1H, Ph-H^{b}), 7.39 – 7.33 (m, 2H, tpy-$H^{5,5''}$), 0.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, 300 K) δ 156.09, 155.97, 149.52, 149.12, 138.63, 136.91, 132.35, 130.81, 128.84, 127.45, 123.90, 121.39, 118.83, 104.59, 94.91, -0.03. ESI-TOF (*m/z*): Calcd. $[C_{26}H_{23}N_3Si + H]^+$ for: 406.17, found: 406.14.



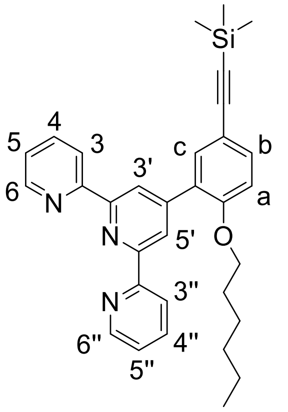
Compound **S-2**. Compound **S-2** was also synthesized according to a literature method.[2] To a flask containing solution of compound **S-1** (3.4 g, 8.4 mmol) in $CHCl_3$ (30 mL) and MeOH (30 mL), K_2CO_3 (4.6 g, 33.5 mmol) was added. The mixture was stirred at room temperature for 4 h and then extracted with $CHCl_3$. The combined organic phase was washed with brine and dried with anhydrous Na_2SO_4. After removal of solvent under vacuum, the crude was purified by column chromatography on silica gel with chloroform: ethanol (100:1) as eluent to afford the product as a light-yellow solid (2.6 g, 93 % yield). ^{1}H NMR (500 MHz, CDCl3, 300 K) δ 8.77 – 8.71 (m, 4H, tpy-$H^{6,6''}$, tpy-$H^{3',5'}$) δ 8.68 (dt, J = 7.9, 1.1 Hz, 2H, tpy-$H^{3,3''}$), 8.05 (s, 1H, Ph-H^{d}), 7.96-7.83 (m, 3H, tpy-$H^{4,4''}$, Ph-H^{a}), 7.58 (dt, J = 7.7, 1.4 Hz, 1H, Ph-H^{c}), 7.47 (t, 1H, Ph-H^{b}), 7.39 – 7.33 (m, 2H, tpy-$H^{5,5''}$), 3.15 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 300 K) δ 156.06, 156.03, 149.31, 149.13, 138.78, 136.88, 132.50, 130.98, 128.96, 127.77, 123.91, 122.87, 121.35, 118.80, 83.25, 77.78. ESI-TOF (*m/z*): Calcd. $[C_{23}H_{15}N_3 + H]^+$ for: 334.13, found: 334.13.



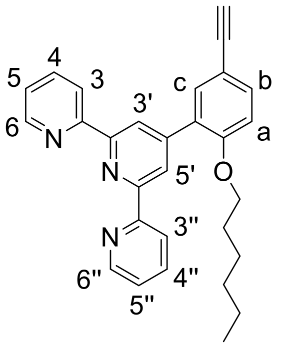
Compound **S-3**. Compound **S-3** was synthesized according to a literature method.[3] 2-hydroxyl-5-bromo benzaldehyde (5.0 g, 25.0 mmol) was dissolved in DMF (25 mL).1-bromohexane (4.5 g, 27.5 mmol), K_2CO_3 (6.9 g, 50.0 mmol) were added and the mixture was heated at 110 °C overnight. The reaction mixture was cooled to room temperature and extracted with ethyl acetate. The crude product was purified by a silica gel column chromatography with ethyl acetate: hexane (1:3) to afford the product as light yellow oil (4.5g, 92 % yield).^{1}H NMR (400 MHz, $CDCl_3$, 300 K) δ 10.42 (s, 1H, CHO-*H*), 7.92 (d, *J* = 2.8 Hz, 1H, Ph-H^{c}), 7.59 (ddd, *J* = 8.9, 2.6, 0.4 Hz, 1H, Ph-H^{a}), 6.87 (d, *J* = 8.9 Hz, 1H, Ph-H^{b}), 4.07 (t, *J* = 6.4 Hz, 2H), 1.85 – 1.76 (m, 2H), 1.55 – 1.43 (m, 2H), 1.38 – 1.32 (m, 4H), 0.90 (t, *J* = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.36, 160.42, 138.21, 130.77, 126.16, 114.58, 113.18, 69.00, 31.45, 28.93, 25.65, 22.53, 13.86.



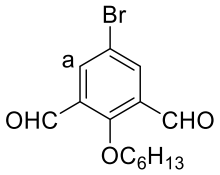
Compound **S-4**. Compound **S-4** was synthesized using the same method as compound **1**. To a flask containing NaOH (3.2 g, 80 mmol) in EtOH (100 mL), compound **S-3** (4.3 g, 15 mmol) and 2-acetylpyridine (5.3 g, 44 mmol) were subsequently added. After stirring at room temperature overnight, aqueous $NH_3{\bullet}H_2O$ (37 %, 60 mL) was added and the mixture was heated at 60 ºC overnight. After cooling down to room temperature, the precipitate was filtered under vacuum and washed with ethanol and ethyl ether to give **S-4** as a yellow power (4.2 g, 68 % yield). ^{1}H NMR (400 MHz, $CDCl_3$, 300K) δ 8.87 – 8.50 (m, 6H, tpy-$H^{6,6''}$, tpy-$H^{3,3''}$, tpy-$H^{3',5'}$), 7.85 (td, *J* = 7.7, 1.8 Hz, 2H, tpy-$H^{4,4''}$), 7.68 (d, *J* = 2.5 Hz, 1H, H^{c}), 7.44 (dd, *J* = 8.7, 2.5 Hz, 1H, H^{b}), 7.32 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 0H), 6.86 (d, *J* = 8.7 Hz, 2H, tpy-$H^{5,5''}$), 3.97 (t, *J* = 6.2 Hz, 2H), 1.69 (dt, *J* = 14.4, 6.3 Hz, 2H), 1.37 (m, 2H), 1.13 (m, 4H), 0.72 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 300K) δ 156.28, 155.46, 155.20, 149.06, 146.98, 136.70, 132.91, 132.37, 130.29, 123.61, 121.59, 121.15, 113.93, 112.81, 68.81, 31.46, 29.02, 25.71, 22.31, 13.88. ESI-TOF (*m/z*): Calcd. $[C_{27}H_{26}BrN_3O + H]^+$ for 488.13, found: 488.12.



Compound **S-5**. Compound **S-5** was synthesized using the same method as compound **S-1**. A mixture of compound **S-4** (4.0 g, 8 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (245 mg, 0.34 mmol) and copper(I) iodide (47 mg, 0.25 mmol) was degassed under nitrogen for three times. After that, 40 mL anhydrous THF, 20 mL anhydrous Et$_3$N and ethynyltrimethylsilane (2.5 mL, 18 mmol) was added and then the mixture was stirred at 60 ºC overnight. After cooling down to room temperature, solvent was removed under vacuum, and the residue was extracted with CH$_2$Cl$_2$. The combined organic phase was washed with brine and dried over Na$_2$SO$_4$. After removal of solvent under vacuum, the residue was purified by column chromatography on silica gel with DCM: methanol (100:1) as eluent to afford a yellow solid (3.2 g, 83 % yield). ^{1}H NMR (400 MHz, CDCl3, 300 K) δ 8.72 – 8.64 (m, 6H, tpy-$H^{6,6''}$, tpy-$H^{3',5'}$, tpy-$H^{3,3''}$), 7.86 (td, J = 7.7, 1.8 Hz, 2H, tpy-$H^{4,4''}$), 7.71 (d, J = 2.1 Hz, 1H, H^c), 7.48 (dd, J = 8.8, 2.1 Hz, 1H, H^b), 7.37 – 7.28 (m, 2H, tpy-$H^{5,5''}$), 6.91 (d, J = 8.5 Hz, 1H, H^a), 4.02 (t, J = 6.2 Hz, 2H), 1.70 (dt, J = 12.0, 6.3 Hz, 2H), 1.44 – 1.29 (m, 2H), 1.21 – 1.03 (m, 4H), 0.72 (t, J = 7.0 Hz, 3H). 0.26 (s, 9H). ^{13}C NMR (100 MHz, CDCl$_3$, 300 K) δ 156.49, 156.35, 155.08, 149.01, 147.47, 136.65, 134.21, 133.67, 128.29, 123.53, 121.68, 121.13, 115.34, 111.87, 104.83, 92.90, 68.54, 31.45, 28.99, 25.70, 22.28, 13.86, 0.03. ESI-TOF (*m/z*): Calcd. [C$_{32}$H$_{35}$N$_3$OSi + H]$^+$ for: 506.26, found: 506.26.

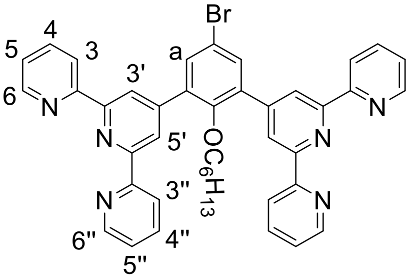


Compound **S-6**. To a flask containing solution of compound **S-5** (2.4 g, 4.8 mmol) in $CHCl_3$ (40 mL) and MeOH (40 mL), K_2CO_3 (2.1 g, 15 mmol) was added. The mixture was stirred at room temperature for 4 h and extracted with $CHCl_3$. The combined organic phase was washed with brine and dried with anhydrous Na_2SO_4. After removal of solvent under vacuum, the crude was purified by column chromatography on silica gel with chloroform: methanol (100:1) as eluent to afford the product as reported[5] as a light-yellow solid (1.6 g, 89 % yield). ^{1}H NMR (400 MHz, $CDCl_3$, 300K) δ 8.72 – 8.68 (m, 2H, , tpy-$H^{6,6''}$), 8.67 (s, 2H, tpy-$H^{3',5}$), 8.66 (dt, J = 8.0, 1.1 Hz, 2H, tpy-$H^{3,3''}$), 7.85 (ddd, J = 8.0, 7.5, 1.8 Hz, 2H, tpy-$H^{4,4''}$), 7.73 (d, J = 2.1 Hz, 1H, H^c), 7.50 (dd, J = 8.5, 2.1 Hz, 1H, H^b), 7.31 (ddd, J = 7.5, 4.8, 1.2 Hz, 2H, tpy-$H^{5,5''}$), 6.93 (d, J = 8.6 Hz, 1H, H^a), 4.01 (t, J = 6.2 Hz, 2H), 3.04 (s, 1H), 1.71 (ddt, J = 9.3, 7.9, 6.2 Hz, 2H), 1.48 – 1.32 (m, 2H), 1.25 – 1.00 (m, 4H), 0.72 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 300K) δ 156.89, 156.53, 155.31, 149.20, 147.53, 136.80, 134.46, 133.97, 128.53, 123.71, 121.84, 121.29, 114.39, 112.18, 83.50, 76.34, 68.76, 31.62, 29.16, 25.86, 22.44, 14.01. ESI-TOF (*m/z*): Calcd. $[C_{29}H_{27}N_3O+H]^+$ for 434.22, found 434.22.

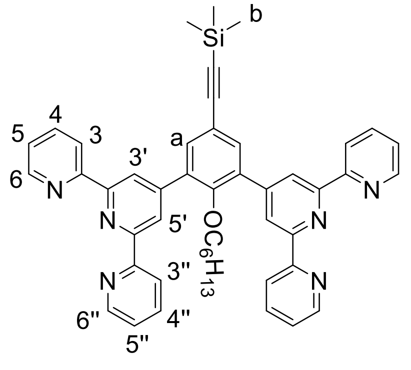


Compound **S-7**. Compound **S-7** was synthesized according to a literature method.[4-5] ρ-bromophenol (34.6 g, 0.2 mol) was dissolved in an aqueous solution of NaOH (25%, 50 mL) and methanol (50 mL) with formaldehyde (38%, 180 mL) was added subsequently. The mixture was stirred for 12 days at room temperature. Then, a mixture of water (100 mL) and acetic acid (30 mL) was added. The reaction mixture was stirred for 8 h at room temperature to give a white precipitate. The precipitate was filtrated and dissolved in 10% aqueous NaOH. After that, the solution was acidified with 2 M HCl to give 4-bromo-2,6-bis(hydroxymethyl)phenol as a white powder. A mixture of the white powder (6.0 g, 26 mmol), 1-bromohexane (5.1 g, 31mmol), K_2CO_3 (7.2 g, 52 mmol) in 200 mL methyl ethyl ketone was refluxed under N_2 overnight. The mixture was then cooled to room temperature and extracted with DCM. After removal of solvent under vacuum, a white residue was obtained. The white residue, PCC (11.8 g, 75 mmol) and celite (10 g) were dissolved in DCM (200 mL), and the mixture was stirred for 4 h at room temperature. The solution was filtered and poured onto silica gel column with DCM as eluent to afford 5-bromo-2-

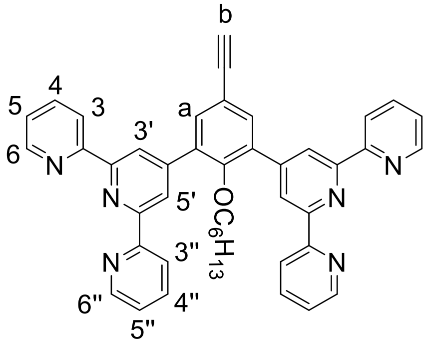
(hexyloxy)benzene-1,3-dialdehyde as a white solid (11.2 g, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 300 K) δ 10.32 (s, 2H, CHO-*H*), 8.16 (s, 2H, Ph-*H*^{a}), 4.11 (t, *J* = 6.4 Hz, 2H), 1.87 (m, 2H), 1.56 – 1.45 (m, 2H), 1.40 – 1.35 (m, 4H), 0.90 (t, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 300 K) δ 187.08, 163.34, 137.24, 131.76, 118.29, 81.04, 31.48, 29.85, 25.45, 22.49, 13.94.



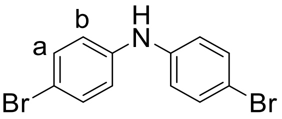
Compound **2**. Compound **2** was synthesized according to a literature method.[4] To a flask containing NaOH (4.8 g, 120 mmol) in EtOH (150 mL), compound **S-7** (3.0 g, 10 mmol) and 2-acetylpyridine (5.3 g, 44 mmol) were subsequently added. After stirring at room temperature for two days, aqueous $NH_3 \cdot H_2O$ (37 %, 150 mL) was added and the mixture was heated at 60 ºC for another two days to give a yellow precipitate. After cooling down to room temperature, the precipitate was filtered under vacuum and washed with ethanol to give **2** as a white power (2.8 g, 39 % yield). ^{1}H NMR (500 MHz, CDCl3, 300 K) δ 8.77 (s, 4H, tpy-*H*$^{3',5'}$), 8.75 (dd, *J* = 4.9, 1.6 Hz, 4H, tpy-*H*$^{6,6''}$), 8.69 (d, *J* = 7.9 Hz, 4H, tpy-*H*$^{3,3''}$), 7.89 (td, *J* = 7.9, 1.8 Hz, 4H, tpy-*H*$^{4,4''}$), 7.77 (s, 2H, Ph-*H*^{a}), 7.36 (ddd, *J* = 7.4, 4.8, 1.2 Hz, 4H, tpy-*H*$^{5,5''}$), 3.34 (t, *J* = 6.0 Hz, 2H), 1.16 (dq, *J* = 11.8, 6.3 Hz, 2H), 0.92-0.89 (m, 2H), 0.74-0.71 (m, 4H), 0.48 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 300 K) δ 156.05, 155.53, 153.93, 149.18, 147.05, 136.80, 135.83, 133.63, 123.81, 121.42, 121.23, 117.02, 74.29, 31.26, 29.67, 25.36, 22.08, 13.74. ESI-TOF (*m/z*): Calcd. $[C_{42}H_{35}BrN_6O + H]^+$ for: 719.21, found: 719.21.



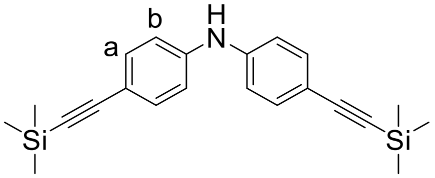
Compound **S-8**. A mixture of compound **2** (2.51 g, 3.5 mmol), $Pd(PPh_3)_2Cl_2$ (125 mg, 0.17 mmol) and copper(I) iodide (26 mg, 0.14 mmol) was degassed under nitrogen for three times. After that, 30 mL anhydrous THF, 15 mL anhydrous Et_3N and ethynyltrimethylsilane (2 mL, 14 mmol) was added and then the mixture was stirred at 60 ºC overnight and then cooled to room temperature. The solvent was removed, and the residue was extracted with $CHCl_3$. The combined organic phase was washed with brine and dried over Na_2SO_4. After removal of solvent under vacuum, the residue was purified by column chromatography on silica gel with chloroform: ethanol (100:1) as eluent to afford a yellow solid (2.4 g, 93 % yield). ^1H NMR (400 MHz, $CDCl_3$, 300 K) δ 8.79 (s, 4H, tpy-$H^{3',5'}$), 8.75 (ddd, J = 4.8, 1.8, 0.9 Hz, 4H, tpy-$H^{6,6''}$), 8.69 (dt, J = 7.9, 1.1 Hz, 4H, tpy-$H^{3,3''}$), 7.88 (ddd, J = 8.0, 7.5, 1.8 Hz, 4H, tpy-$H^{4,4''}$), 7.78 (s, 2H, Ph-H^{a}), 7.35 (ddd, J = 7.5, 4.8, 1.2 Hz, 4H, tpy-$H^{5,5''}$), 3.36 (t, J = 6.1 Hz, 2H), 1.18 (dt, J = 14.5, 6.1 Hz, 2H), 0.91 (p, J = 7.9 Hz, 2H), 0.79 – 0.66 (m, 4H), 0.49 (t, 3H), 0.28 (s, 9H, TMS- H^{b}). ^{13}C NMR (100 MHz, $CDCl_3$, 300 K) δ 156.18, 155.45, 154.99,149.16, 147.67, 136.81, 134.73, 134.07, 123.76, 121.58, 121.27, 119.50, 103.97, 94.73, 74.34, 31.29, 29.71, 25.39, 22.10, 13.75, 0.03. ESI-TOF (*m/z*): Calcd. $[C_{47}H_{44}N_6OSi + H]^+$ for: 737.34, found: 737.30.



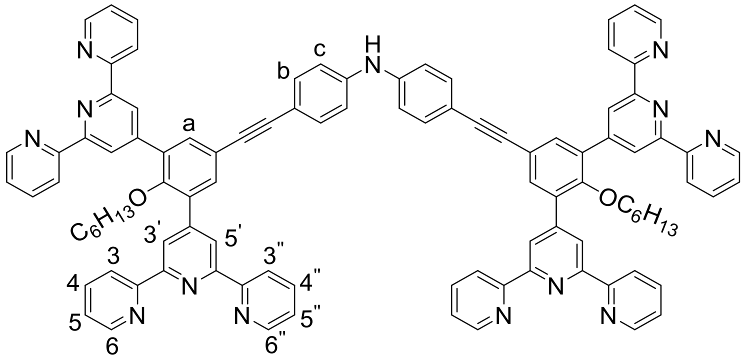
Compound **S-9**. To a flask containing solution of compound **S-8** (2.4 g, 3.4 mmol) in $CHCl_3$ (30 mL) and MeOH (30 mL), K_2CO_3 (1.24 g, 13.6 mmol) was added. The mixture was stirred at room temperature for 4 h. The reaction mixture was extracted with $CHCl_3$, and the combined organic phase was washed with brine and dried with anhydrous Na_2SO_4. After removal of solvent under vacuum, the crude was purified by column chromatography on silica gel with chloroform: ethanol (100:1) as eluent to afford the product as a light-yellow solid (1.9 g, 84% yield). ^1H NMR (400 MHz, $CDCl_3$, 300 K) δ 8.79 (s, 4H, tpy-$H^{3',5'}$), 8.74 (ddd, J = 4.8, 1.8, 0.9 Hz, 4H, tpy-$H^{6,6''}$), 8.69 (dt, J = 7.9, 1.1 Hz, 4H, tpy-$H^{3,3''}$), 7.88 (ddd, J = 8.0, 7.5, 1.8 Hz, 4H, tpy-$H^{4,4''}$), 7.80 (s, 2H, Ph-H^{a}), 7.35 (ddd, J = 7.5, 4.8, 1.2 Hz, 4H, tpy-$H^{5,5''}$), 3.38 (t, J = 6.1 Hz, 2H), 3.12 (s, 1H, yne-H^{b}), 1.28 – 1.09 (m, 2H), 0.91 (p, J = 7.4 Hz, 2H), 0.73 (ddd, J = 6.5, 4.1, 1.7 Hz, 4H), 0.49 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 300 K) δ 156.14, 155.50, 155.27, 149.16, 147.52, 136.78, 134.86, 131.87, 128.52, 123.76, 121.54, 121.23 ,118.36, 77.61, 74.37, 31.28, 29.70, 25.37, 22.09, 13.74. ESI-TOF (*m/z*): Calcd. $[C_{44}H_{36}N_6O + H]^+$ for: 665.30, found: 665.27.



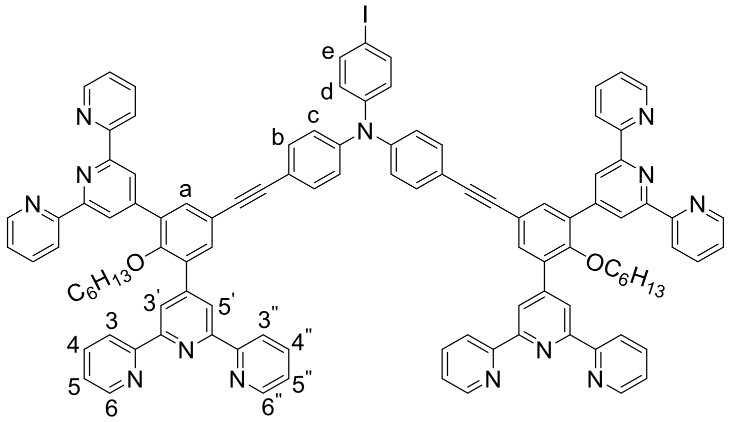
Compound **S-10**. Compound **S-10** was synthesized according to the literature report.[6] A solution of *N*-bromosuccinimide (NBS) (5.3 g, 28.6 mmol) in DMF (30 mL) was added dropwise to a stirred solution of diphenylamine (2.5 g, 14.8 mmol) in DMF (20 mL) at 0 °C. The resulting solution continued to be stirred at 0 °C for 6 h. Water then was added to bring the product out of solution. The precipitate was filtered and dried under vacuum to afford the product as a white powder (3.9 g, 81 % yield). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) δ 7.36 (d, J = 8.8 Hz, 4H, Ph-H^a), 6.92 (d, J = 8.8 Hz, 4H, Ph-H^b). ^{13}C NMR (125 MHz, $CDCl_3$, 300 K) δ 141.67, 132.28, 119.47, 113.36. ESI-TOF (*m/z*): Calcd. $[C_{12}H_9Br_2N + H]^+$ for: 325.92, found: 325.91.



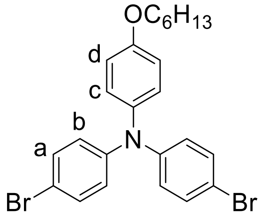
Compound **S-11**. Compound **S-11** was synthesized using the similar method of the reported literature.[7] Compound **S-10** (1.95 g, 6.0 mmol), $Pd(PPh_3)_2Cl_2$ (62 mg, 0.08 mmol) and copper(I) iodide (9.5 mg, 0.05 mmol) was degassed under nitrogen for three times. After that, anhydrous THF (30 mL), anhydrous Et_3N (30 mL) and ethynyltrimethylsilane (3.2 mL, 20 mmol) was added and then the mixture was stirred at 60 ºC for 2 days. The solvent was removed, and the residue was extracted with CH_2Cl_2. The combined organic phase was washed with brine and dried over Na_2SO_4. After removal of solvent under vacuum, the residue was purified by column chromatography on silica gel with CH_2Cl_2: hexane (1:1) as eluent to afford the product as a brown solid (1.25 g, 58 % yield). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) δ 7.37 (d, J = 8.6 Hz, 4H, Ph-H^a), 6.97 (d, J = 8.6 Hz, 4H, Ph-H^b), 0.24 (s, 18H).^{13}C NMR (125 MHz, $CDCl_3$, 300 K) δ 142.32, 133.30, 117.24, 115.53, 105.31, 92.80, 0.07. ESI-TOF (*m/z*): Calcd. $[C_{22}H_{27}NSi_2 + H]^+$ for: 362.18, found: 362.14.



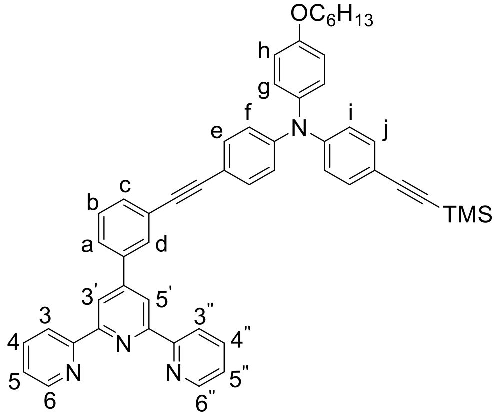
Compound **S-12**. Compound **S-11** (288 mg, 0.8 mmol), Compound **2** (1.44 g, 2.0 mmol), $Pd(PPh_3)_4$ (74.2 mg, 0.06 mmol) and copper(I) iodide (9.5 mg, 0.05 mmol) was degassed under nitrogen for three times. After that, 30 mL anhydrous THF, 30 mL anhydrous Et_3N was added and then the mixture was stirred at 70 ºC for a while. TBAF (2 mmol, 1M in THF, 2 mL) was added and the reaction mixture was stirred at 70 ºC for 2 days. The solvent was removed, and the residue was extracted with $CHCl_3$. The combined organic phase was washed with brine and dried with anhydrous Na_2SO_4. After removal of solvent under vacuum, the crude was purified by column chromatography on silica gel with chloroform: methanol (100:1) as eluent to afford the product as a yellow solid (500 mg, 42 % yield). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) δ 8.82 (s, 8H, tpy-$H^{3',5'}$), 8.78 – 8.74 (m, 8H, tpy-$H^{6,6''}$), 8.70 (d, *J* = 7.9 Hz, 8H, tpy-$H^{3,3''}$), 7.89 (td, *J* = 7.7, 1.8 Hz, 8H, tpy-$H^{4,4''}$), 7.82 (s, 4H, Ph-H^{a}), 7.47 (d, *J* = 8.3 Hz, 4H, Ph-H^{b}), 7.36 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 8H, tpy-$H^{5,5''}$), 7.08 (d, *J* = 8.3 Hz, 4H, Ph-H^{c}), 3.38 (t, *J* = 6.2 Hz, 4H), 1.19 (dq, *J* = 11.5, 6.2 Hz, 4H), 0.92 (m,4H), 0.74 (m, 8H), 0.49 (t, *J* = 6.6 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 300 K) δ 156.16, 155.41, 155.29, 154.49, 149.15, 147.80, 142.29, 136.84, 134.10, 132.93, 123.76, 121.64, 121.28, 120.03, 117.45, 115.44, 90.18, 87.43, 74.33, 31.32, 29.74, 25.43, 22.12, 13.79. ESI-TOF (*m/z*): Calcd. $[C_{100}H_{79}N_{13}O_2 + 2H]^{2+}$ for: 747.83, found: 747.79.



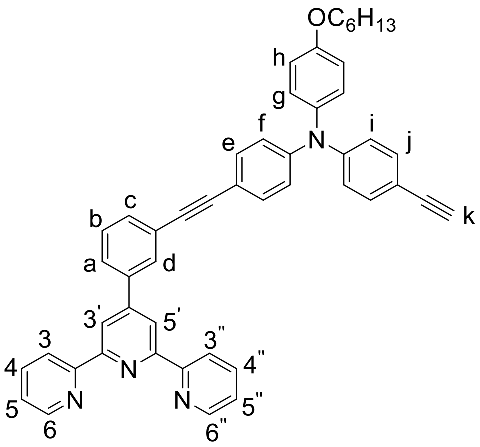
Compound **S-13**. Compound **S-13** was synthesized according to a literature method.[8] To a flask containing solution of compound **S-12** (448 mg, 0.3 mmol) in toluene (25 mL), 1,4-diodobenzene (3.29 mg, 1.0 mmol), 1,10-phenathroline (5.4 mg, 0.03 mmol), copper(I) iodide (5.7 mg, 0.03 mmol), potassium hydroxide (170 mg, 3.2 mmol) were added. The mixture was refluxed for 2 days. Then the reaction mixture was extracted with CH_2Cl_2, and the combined organic phase was washed with brine and dried with anhydrous Na_2SO_4. After removal of solvent under vacuum, the crude was purified by column chromatography on silica gel with with chloroform: methanol (100:1) as eluent to afford the product as a yellow solid (120 mg, 24 % yield). ^1H NMR (500 MHz, $CDCl_3$, 300 K) δ 8.81 (s, 8H, tpy-$H^{3',5'}$), 8.77 – 8.74 (m, 8H, tpy-$H^{6,6''}$), 8.70 (d, J = 8.0 Hz, 8H, tpy-$H^{3,3''}$), 7.89 (td, J = 7.7, 1.8 Hz, 8H, tpy-$H^{4,4''}$), 7.83 (s, 4H, Ph-H^{a}), 7.58 (d, J = 8.7 Hz, 2H, Ph-H^{d}), 7.45 (d, J = 8.7 Hz, 4H, Ph-H^{b}), 7.36 (ddd, J = 7.5, 4.8, 1.2 Hz, 8H, tpy-$H^{5,5''}$), 7.07 (d, J = 8.7 Hz, 4H, Ph-H^{c}), 6.91 (d, J = 8.7 Hz, 2H, Ph-H^{e}), 3.38 (t, J = 6.0 Hz, 4H), 1.19 (dd, J = 9.1, 5.9 Hz, 4H), 0.92 (t, J = 7.7 Hz, 4H), 0.73 (dt, J = 6.5, 2.8 Hz, 8H), 0.49 (t, J = 6.7 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 300 K) δ 156.18, 155.45, 154.67, 149.17, 147.72, 146.66, 146.59, 138.44, 136.78, 134.21, 134.15, 132.79, 126.78, 123.75, 123.69, 121.58, 121.23, 119.73, 117.65, 89.75, 88.29, 86.88, 74.34, 31.30, 29.72, 25.41, 22.11, 13.78. ESI-TOF (*m/z*): Calcd. $[C_{106}H_{82}IN_{13}O_2 + 2H]^{2+}$ for: 848.80, found: 848.76.



Compound **3**. Compound **3** was synthesized according to a literature method.[8-9] To a flask containing solution of compound **S-10** (3.25 g, 10.0 mmol), 1-(hexyloxy)-4-iodobenzene (3.95 g, 13 mmol), 1,10-phenathroline (142 mg, 0.8 mmol), copper(I) chloride (80 mg, 0.8 mmol) in toluene (25 mL), potassium hydroxide (4.82 g, 86 mmol) was added. The mixture was refluxed for 2 days. Then the reaction mixture was extracted with CH_2Cl_2, and the combined organic phase was washed with brine and dried with anhydrous Na_2SO_4. After removal of solvent under vacuum, the crude was purified by column chromatography on silica gel with CH_2Cl_2: hexane (1:3) as eluent to afford the product as a light yellowish oil (2.4 g, 48% yield). ^{1}H NMR (400 MHz, CDCl$_3$, 300 K) δ 7.35 – 7.27 (m, 4H, Ph-H^a), 7.07 – 6.99 (m, 2H, Ph-H^c), 6.95 – 6.87 (m, 4H, Ph-H^b), 6.87 – 6.80 (m, 2H, Ph-H^d), 3.94 (t, J = 6.5 Hz, 2H), 1.79 (dq, J = 7.9, 6.6 Hz, 2H), 1.53 – 1.42 (m, 2H), 1.40 – 1.31 (m, 4H), 0.93 (t, 3H). ^{13}C NMR (100 MHz, CDCl$_3$, 300 K) δ 156.34, 146.81, 139.44, 132.11, 127.39, 124.20, 115.56, 114.45, 68.26, 31.57, 29.26, 25.73, 22.59, 14.02. ESI-TOF (*m/z*): Calcd. $[C_{24}H_{25}Br_2NO + H]^+$ for: 502.04, found: 502.04.

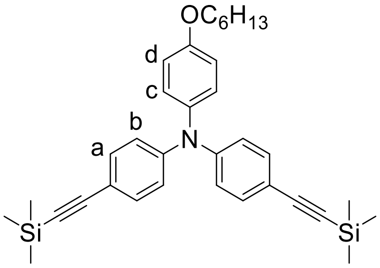


Compound **S-14**. Compound **S-14** (2.2 g, 4.4 mmol), Compound **S-2** (932 mg, 2.8 mmol), $Pd(PPh_3)_4$ (254 mg, 0.22 mmol) and copper(I) iodide (33 mg, 0.18 mmol) was degassed under nitrogen for three times. After that, 50 mL anhydrous THF, 50 mL anhydrous Et_3N was added and then the mixture was stirred at 70 ºC overnight. Ethynyltrimethylsilane (1.8 mL, 12 mmol) was added and the reaction mixture continued to be stirred at 70 ºC for another day. The solvent was removed, and the residue was extracted with $CHCl_3$. The combined organic phase was washed with brine and dried with anhydrous Na_2SO_4. After removal of solvent under vacuum, the crude was purified by column chromatography on silica gel with chloroform: methanol (100:1) as eluent to afford the product as a yellow solid (900 mg, 42 % yield). ^{1}H NMR (500 MHz, CDCl$_3$, 300 K) δ 8.78 – 8.72 (m, 4H, tpy-$H^{3',5'}$, tpy-$H^{6,6''}$), 8.69 (dd, *J* = 8.0, 1.1 Hz, 2H, tpy-$H^{3,3''}$), 8.07 (dt, *J* = 3.4, 1.7 Hz, 1H, Ph-H^{d}), 7.89 (td, *J* = 7.7, 1.8 Hz, 2H, tpy-$H^{4,4''}$), 7.85 (dt, *J* = 7.8, 1.5 Hz, 1H, Ph-H^{a}), 7.59 (dt, *J* = 7.7, 1.3 Hz, 1H, Ph-H^{c}), 7.51 – 7.45 (m, 1H, Ph-H^{b}), 7.41 (d, *J* = 8.6 Hz, 2H, Ph-H^{f}), 7.37 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 2H, tpy-$H^{5,5''}$), 7.32 (d, *J* = 8.7 Hz, 2H, Ph-H^{j}), 7.06 (d, *J* = 8.9 Hz, 2H, Ph-H^{g}), 7.00 (d, *J* = 8.6 Hz, 2H, Ph-H^{i}), 6.97 (d, *J* = 8.6 Hz, 2H, Ph-H^{e}), 6.86 (d, *J* = 8.9 Hz, 2H, Ph-H^{h}), 3.95 (t, *J* = 6.5 Hz, 2H), 1.88 – 1.72 (m, 2H), 1.52 – 1.42 (m, 2H), 1.35 (dq, *J* = 7.6, 3.7 Hz, 4H), 0.92 (t, *J* = 3.7 Hz, 3H), 0.24 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, 300 K) δ 156.56, 155.88, 155.78, 149.64, 148.93, 147.58, 147.52, 139.11, 138.56, 137.11, 132.94, 132.62, 131.88, 130.27, 128.96, 127.93, 126.90, 124.36, 123.95, 122.27, 122.19, 122.16, 121.50, 118.95, 116.20, 116.09, 115.51, 105.29, 93.20, 90.27, 88.39, 68.23, 31.58, 29.26, 25.73, 22.60, 14.03, 0.05. ESI-TOF (*m/z*): Calcd. $[C_{52}H_{48}N_4OSi + H]^+$ for: 773.37, found: 773.33.

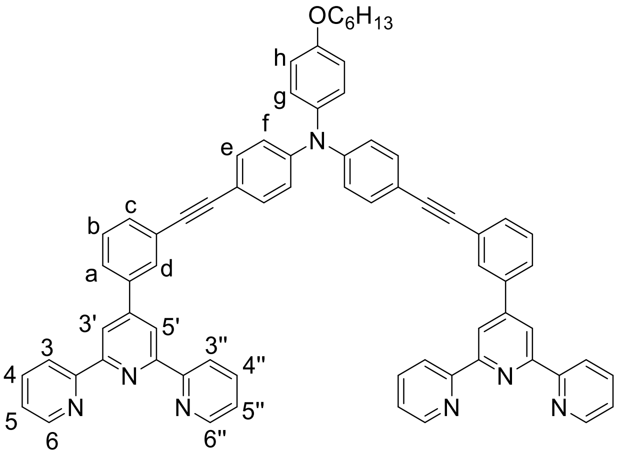


Compound **S-15**. To a flask containing solution of compound **S-14** (800 mg, 1.0 mmol) in $CHCl_3$ (30 mL) and MeOH (30 mL), K_2CO_3 (552 mg, 4 mmol) was added. The mixture was stirred at room temperature for 4 h and then extracted with $CHCl_3$. The combined organic phase was washed with brine and dried with anhydrous Na_2SO_4. After removal of solvent under vacuum, the crude was purified by column chromatography on silica gel with chloroform: ethanol (100:1) as eluent to afford the product as a yellow solid (620 mg, 89 % yield). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) δ 8.78 – 8.72 (m, 1H, tpy-$H^{3',5'}$, tpy-$H^{6,6''}$), 8.69 (dd, *J* = 8.0, 1.1 Hz, 2H, tpy-$H^{3,3''}$), 8.07 (t, *J* = 1.7 Hz, 1H, Ph-H^{d}), 7.89 (td, *J* = 7.7, 1.8 Hz, 2H, tpy-$H^{4,4''}$), 7.86 – 7.82 (m, 1H, Ph-H^{a}), 7.59 (dt, *J* = 7.6, 1.3 Hz, 1H, Ph-H^{c}), 7.49 (m, *1*H, Ph-H^{b}), 7.44 (d, *J* = 8.7 Hz, 2H, Ph-H^{f}), 7.37 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 2H, tpy-$H^{5,5''}$), 7.35 (d, *J* = 8.7 Hz, 2H, Ph-H^{j}), 7.07 (d, *J* = 8.9 Hz, 2H, Ph-H^{g}), 7.02 (d, *J* = 8.7 Hz, 2H, Ph-H^{i}), 6.99 (d, *J* = 8.7 Hz, 2H, Ph-H^{e}), 6.87 (d, *J* = 9.0 Hz, 2H, Ph-H^{h}), 3.95

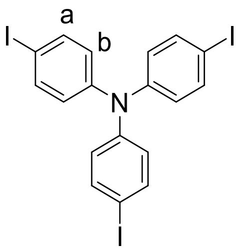
(t, J = 6.5 Hz, 2H), 3.03 (s, 1H), 1.86 – 1.72 (m, 2H), 1.52 – 1.43 (m, 2H), 1.35 (m, 4H), 0.92 (t, J = 3.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 300 K) δ 156.65, 156.13, 156.00, 149.61, 149.14, 147.90, 147.47, 139.08, 138.72, 136.89, 133.08, 132.64, 131.85, 130.31, 128.95, 128.04, 126.91, 124.35, 123.89, 122.32, 122.08, 121.38, 118.84, 116.26, 115.56, 115.00, 90.20, 88.44, 83.84, 76.28, 68.26, 31.59, 29.28, 25.75, 22.61, 14.04. ESI-TOF (*m/z*): Calcd. $[C_{49}H_{40}N_4O + H]^+$ for: 701.33, found: 701.31.



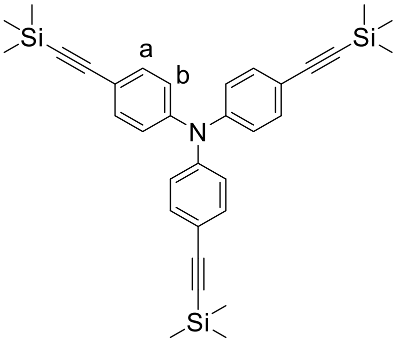
Compound **4**. Compound **3** (2.51 g, 5.0 mmol), $Pd(PPh_3)_2Cl_2$ (62 mg, 0.08 mmol) and copper(I) iodide (9.5 mg, 0.05 mmol) was degassed under nitrogen for three times. After that, 40 mL anhydrous THF, 30 mL anhydrous Et_3N and ethynyltrimethylsilane (3.6 mL, 24 mmol) was added and then the mixture was stirred at 70 ºC for 2 days and then cooled to room temperature. The solvent was removed, and the residue was extracted with CH_2Cl_2. The combined organic phase was washed with brine and dried over Na_2SO_4. After removal of solvent under vacuum, the residue was purified by column chromatography on silica gel with CH_2Cl_2: hexane (1:3) as eluent to afford the product as a light yellowish oil (2.3 g, 86 % yield). ^{1}H NMR (400 MHz, $CDCl_3$, 300 K) δ 7.33 – 7.27 (m, 4H, Ph-H^a), 7.05 – 6.98 (m, 2H, Ph-H^c), 6.95 – 6.89 (m, 4H, Ph-H^b), 6.88 – 6.81 (m, 2H, Ph-H^d), 3.94 (t, J = 6.5 Hz, 2H), 1.78 (dq, J = 7.9, 6.5 Hz, 2H), 1.47 (p, J = 7.0 Hz, 2H), 1.41 – 1.30 (m, 4H), 1.00 – 0.83 (t, 3H), 0.24 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$, 300 K) δ 156.55, 147.60, 139.14, 132.93, 127.83, 122.12, 116.22, 115.51, 105.28, 93.22, 68.26, 31.59, 29.28, 25.74, 22.60, 14.02, 0.05. ESI-TOF (*m/z*): Calcd. $[C_{34}H_{43}NOSi_2 + H]^+$ for: 538.30, found: 538.27.



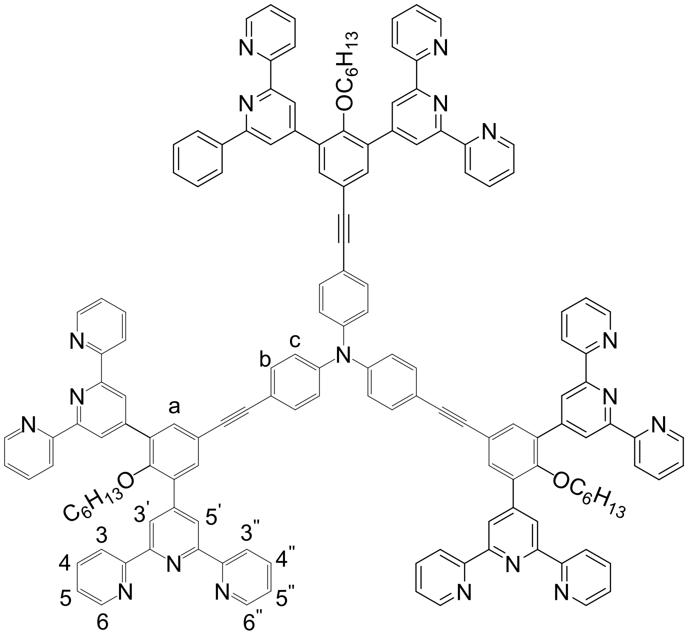
Compound **LA**. Compound **4** (1.07 g, 2.0 mmol), compound **1** (1.94 g, 5.0 mmol), $Pd(PPh_3)_4$ (254 mg, 0.22 mmol) and copper(I) iodide (28 mg, 0.15 mmol) was degassed under nitrogen for three times. After that, 40 mL anhydrous THF, 30 mL anhydrous Et_3N was added and then the mixture was stirred at 70 ºC for a while. TBAF (4 mmol, 1M in THF, 4 mL) was added and the reaction mixture was stirred at 70 ºC for another 2 days. The solvent was removed, and the residue was extracted with $CHCl_3$. The combined organic phase was washed with brine and dried with anhydrous Na_2SO_4. After removal of solvent under vacuum, the crude was purified by column chromatography on silica gel with chloroform: ethanol (100:2) as eluent to afford the product as a yellow solid (1.7 g, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 300 K) δ 8.74 (d, 8H, tpy-$H^{3',5'}$, tpy-$H^{6,6''}$), 8.67 (dt, *J* = 8.0, 1.1 Hz, 4H, tpy-$H^{3,3''}$), 8.07 (t, *J* = 1.7 Hz, 2H, Ph-H^{d}), 7.95 – 7.77 (m, 6H, tpy-$H^{4,4''}$, Ph-H^{a}), 7.59 (dt, *J* = 7.7, 1.3 Hz, 2H, Ph-H^{c}), 7.49 (d, *J* = 7.8 Hz, 2H, Ph-H^{b}), 7.45 (d, *J* = 8.7 Hz, 4H, Ph-H^{e}), 7.34 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 4H, tpy-$H^{5,5''}$), 7.10 (d, *J* = 8.9 Hz, 2H, Ph-H^{g}), 7.06 (d, *J* = 8.7 Hz, 4H, Ph-H^{f}), 6.89 (d, *J* = 8.9 Hz, 2H, Ph-H^{h}), 3.96 (t, *J* = 6.5 Hz, 2H), 1.89 – 1.71 (m, 2H), 1.59 – 1.44 (m, 2H), 1.40 – 1.26 (m, 4H), 0.93 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 300 K) δ 156.67, 156.15, 156.01, 149.58, 149.15, 147.60, 139.20, 138.73, 136.88, 132.70, 131.89, 130.32, 128.98, 128.08, 126.90, 124.44, 123.88, 122.33, 121.39, 118.86, 116.22, 115.62, 90.34, 88.49, 68.30, 31.62, 29.32, 25.78, 22.63, 14.07. ESI-TOF (*m/z*): Calcd. for $[C_{70}H_{53}N_7O + H]^+$: 1008.44, found: 1008.44. Calcd. for $[C_{70}H_{53}N_7O + 2H]^{2+}$: 504.72, found: 504.69.



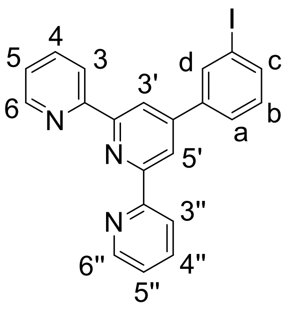
Compound **5**. Compound **5** was synthesized according to a literature method.[10] To a stirred solution of triphenylamine (10.0 g, 40 mmol) and KI (13.5 g, 80 mmol) in 340 mL acetic acid and 30 mL water at 80 ºC, KIO_3 (12.0 g, 56 mmol) was added slowly. After stirring at 50 ºC overnight, 200 mL water was added to induce precipitation of crude product. The precipitate was filtered under vacuum and washed with ethanol to give the product as a white powder (18 g, 83 % yield). ^1H NMR (500 MHz, $CDCl_3$, 300 K) δ 7.54 (d, J = 8.7 Hz, 6H), 6.81 (d, J = 8.7 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 300 K) δ 146.51, 138.41, 126.00, 86.56. ESI-TOF (*m/z*): Calcd. $[C_{18}H_{12}I_3N + H]^+$ for: 623.82, found: 623.82.



Compound **6**. Compound **6** was synthesized according to a literature method.[11] A mixture of compound **5** (1.245 g, 2 mmol), $Pd(PPh_3)_2Cl_2$ (92 mg, 0.12 mmol) and copper(I) iodide (15 mg, 0.08 mmol) was degassed under nitrogen for three times. After that, 30 mL anhydrous THF, 15 mL anhydrous Et_3N and ethynyltrimethylsilane (1.8 mL, 12 mmol) was added and then the mixture was stirred at 60 ºC overnight and then cooled to room temperature. The solvent was removed, and the residue was extracted with CH_2Cl_2. The combined organic phase was washed with brine and dried over Na_2SO_4. After removal of solvent under vacuum, the residue was purified by column chromatography on silica gel with CH_2Cl_2: hexane (4:1) as eluent to afford a yellow solid (960 mg, 90 % yield). ^1H NMR (400 MHz, $CDCl_3$, 300 K) δ 7.39 – 7.30 (m, 6H, Ph-H^a), 7.02 – 6.92 (m, 6H, Ph-*H*^{b}), 0.24 (s, 27H). ^{13}C NMR (100 MHz, CDCl$_3$, 300 K) δ 146.78, 133.15, 123.80, 117.82, 104.85, 93.95, 0.01. ESI-TOF (*m/z*): Calcd. [$C_{33}H_{39}NSi_3$ + H]$^+$ for: 534.25, found: 534.25.

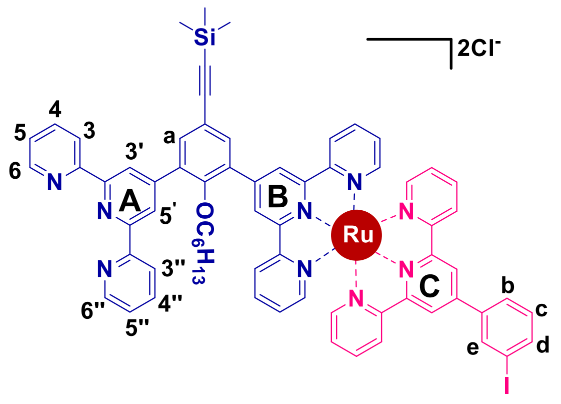


Compound **L.** Compound **6** (320 mg, 0.6 mmol), compound **2** (2.16 g, 3 mmol), Pd(PPh$_3$)$_4$ (152 mg, 0.11 mmol) and copper(I) iodide (14 mg, 0.08 mmol) was degassed under nitrogen for three times. After that, anhydrous THF (40 mL) and anhydrous Et$_3$N (40 mL) was added and the mixture was stirred at 80 ºC for a while. TBAF (3.6 mmol, 1M in THF, 3.6 mL) was added and the reaction mixture was stirred at 70 ºC for 2 days. The solvent was removed, and the residue was extracted with CHCl$_3$. The combined organic phase was washed with brine and dried with anhydrous Na$_2$SO$_4$. After removal of solvent under vacuum, the crude was purified by column chromatography on silica gel with chloroform: methanol (100:2) as eluent to afford the product as a yellow solid (1.1 g, 82% yield). ^{1}H NMR (400 MHz, CDCl$_3$, 300 K) δ 8.83 (s, 12H, tpy-*H*$^{3',5'}$), 8.78 – 8.73 (m, 12H, tpy-*H*$^{6,6''}$), 8.69 (d, *J* = 7.9 Hz, 12H, tpy-*H*$^{3,3''}$), 7.93 – 7.76 (m, 18H, tpy-*H*$^{4,4''}$, Ph-*H*^{a}), 7.49 (d, *J* = 8.3 Hz, 6H, Ph-*H*^{b}), 7.34 (dd, *J* = 7.4, 4.8 Hz, 12H, tpy-*H*$^{5,5''}$), 7.13 (d, *J* = 8.3 Hz, 6H, Ph-*H*^{c}), 3.40 (t, *J* = 6.0 Hz, 6H), 1.20 (dd, *J* = 9.0, 5.8 Hz, 6H), 0.93 (t, *J* = 7.6 Hz, 6H), 0.75 (dt, *J* = 7.9, 4.3 Hz, 12H), 0.49 (t, *J* = 6.5 Hz, 9H). ^{13}C NMR (100 MHz, CDCl$_3$, 300 K) δ 156.24, 155.51, 154.72, 149.21, 147.78, 146.78, 136.79, 134.27, 134.22, 132.86, 124.13, 123.76, 121.64, 121.26, 119.85, 117.84, 89.91, 88.37, 74.40, 31.34, 29.76, 25.44, 22.14, 13.80. ESI-TOF (*m/z*): Calcd. [$C_{151}H_{118}N_{18}O_3$ + 2H]$^{2+}$ for: 1116.49, found: 1116.49.

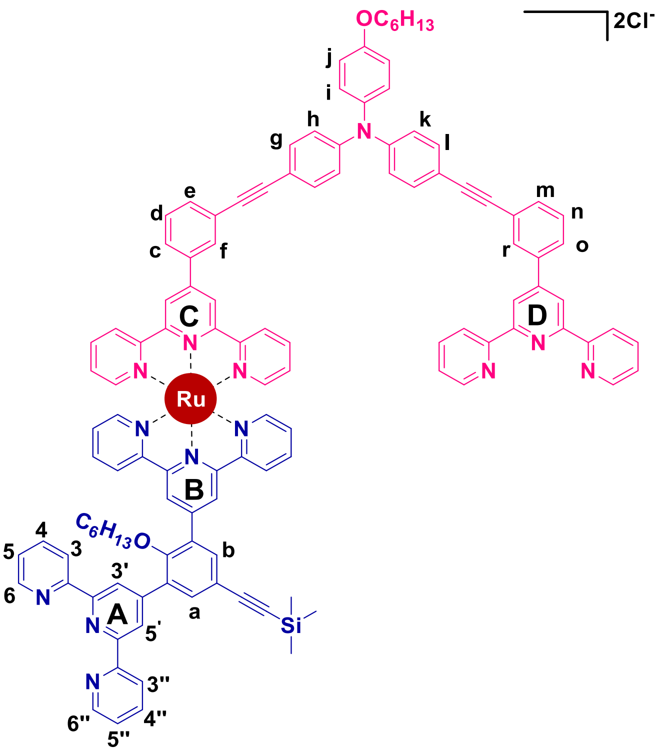


Compound **S-16**. Compound **S-16** was synthesized using the same method as compound **1**.[2] To a flask containing NaOH (4.8 g, 120 mmol) in EtOH (150 mL), 3-idobenzaldehyde (4.2 g, 20 mmol) and 2-acetylpyridine (5.3 g, 44 mmol) were subsequently added. After stirring at room temperature overnight, aqueous NH_3•H_2O (37 %, 150 mL) was added and the mixture was heated at 60 ºC overnight. After cooling down to room temperature, the precipitate was filtered under vacummn and washed with ethanol to give **S-16** as a white power (5.4 g, 62 % yield). ^{1}H NMR (400 MHz, $CDCl_3$, 300 K) δ 8.78 – 8.71 (m, 2H, tpy-$H^{6,6''}$), 8.69-8.62 (m, 4H, tpy- $H^{3',5'}$, tpy-$H^{3,3''}$), 8.23 (s, 1H, Ph-H^{d}), 7.92-7.85 (m, 3H, tpy-$H^{4,4''}$, Ph-H^{a}), 7.78 (dt, J = 7.9, 1.3 Hz, 1H, Ph-H^{c}), 7.36 (m, 2H, tpy-$H^{5,5''}$), 7.23 (m, 1H, Ph-H^{b}). ^{13}C NMR (100 MHz, $CDCl_3$, 300 K) δ 156.03, 155.97, 155.52, 149.11, 148.77, 140.72, 137.89, 136.88, 136.05, 130.53, 126.65, 123.93, 121.36, 118.75. ESI-TOF (*m/z*): Calcd. [$C_{21}H_{14}IN_3$ + H]$^+$ for: 436.03. Found: 436.03.

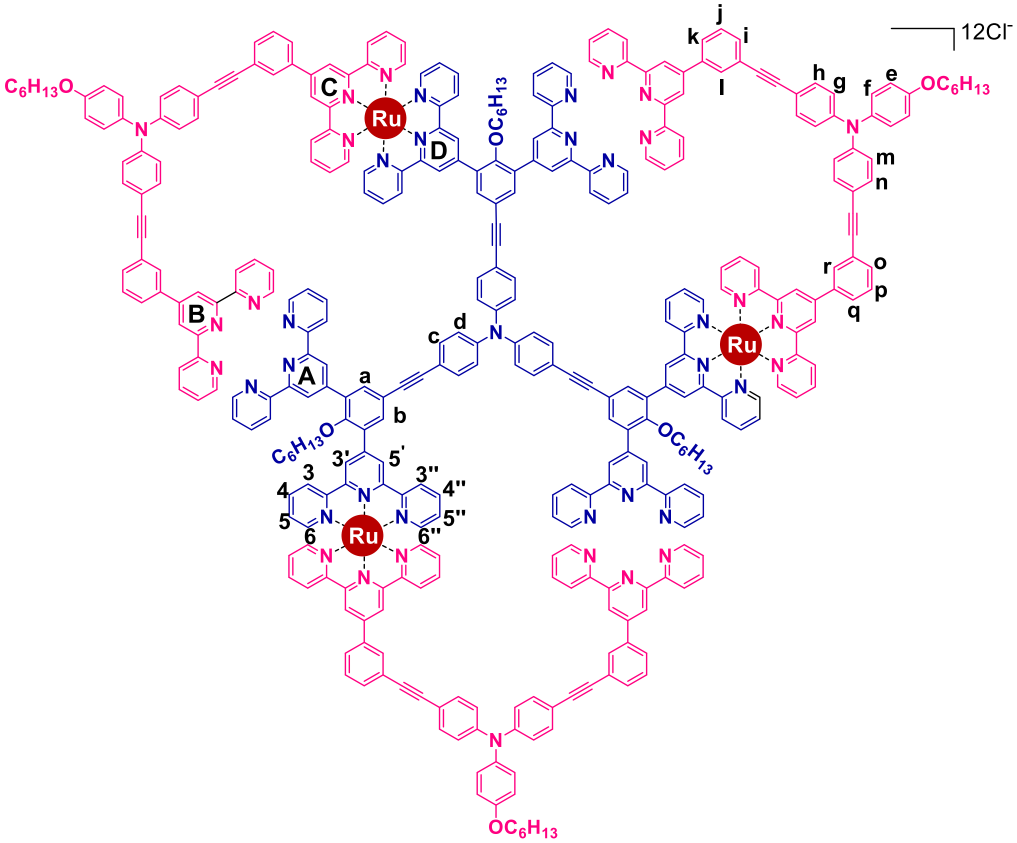
Compound **S-17.** Compound **S-17** was synthesized according to a literature method.[12] Compound **S-16** (218 mg, 0.5 mmol) was dissolved in 30 mL $CHCl_3$ and 30 mL MeOH. $RuCl_3\cdot xH_2O$ (315 mg, 1 mmol) was added and the suspension was refluxed for 48h. After cooling down, the resultant dark brown solid was filtered, washed with MeOH by centrifugation, and dried in vacuum to afford the product as a dark brown solid (250 mg, 78 % yield). This material was used without characterization.



Compound **S-18.** Compound **S-8** (176 mg, 0.24 mmol) was dissolved in 50 mL $CHCl_3$ and 50 mL MeOH, and compound **S-17** (76 mg, 0.12 mmol) was added. The suspension was stirred at room temperature for 1 h, then N-ethylmorpholine (500 µL) was added. The mixture was refluxed for 48 h. After cooling down to room temperature, the solvent was removed by evaporation. The crude was purified by column chromatography on neutral Al_2O_3 with chloroform: methanol (100: 1) as eluent to afford the product as a red solid (140 mg, 85 % yield). ^{1}H NMR (500 MHz, $CDCl_3$+3% CD_3OD, 300 K) δ 9.17 (s, 2H, tpy^{C}-$H^{3',5'}$), 9.05 (s, 2H, tpy^{B}-$H^{3',5'}$), 8.95 (d, J = 8.2 Hz, 2H, tpy^{C}-$H^{3,3''}$), 8.79 (s, 2H, tpy^{A}-$H^{3',5'}$), 8.75 – 8.68 (m, 4H, tpy^{A}-$H^{6,6''}$, tpy^{A}-$H^{3,3''}$), 8.65 (d, J = 8.1 Hz, 2H, tpy^{B}-$H^{3,3''}$), 8.50(s, 1H, Ph-H^{e}), 8.42 (d, J = 7.8 Hz, 2H, Ph-H^{d}), 8.16 (s, 1H, Ph-H^{f}), 8.07 – 7.95 (m, 5H, tpy^{C}-$H^{4,4''}$, tpy^{B}-$H^{4,4''}$, Ph-H^{a}), 7.95 – 7.88 (m, 3H, tpy^{A}-$H^{4,4''}$, Ph-H^{a}), 7.85 (d, J = 7.8 Hz, 2H, Ph-H^{b}), 7.52 – 7.36 (m, 5H, tpy^{A}-$H^{5,5''}$, tpy^{C}-$H^{6,6''}$, Ph-H^{c}), 7.36 – 7.27 (m, 4H, tpy^{C}-$H^{5,5''}$, tpy^{B}-$H^{6,6''}$,), 7.24 – 7.17 (m, 2H, tpy^{B}-$H^{5,5''}$), 3.56 (t, J = 6.1 Hz, 2H), 1.61 – 1.24 (m, 2H), 1.02 (m, 2H), 0.86 – 0.56 (m, 4H), 0.38 (q, J = 7.1, 5.5 Hz, 3H), 0.26 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$+3% CD_3OD, 300 K) δ 157.88, 157.49, 155.76, 155.64, 155.07, 154.78, 154.55, 152.23, 151.40, 149.05, 147.73, 146.91, 145.28, 139.20, 138.75, 138.42, 138.33, 137.12, 136.33, 136.20, 134.59, 134.47, 131.85, 131.43, 128.23, 128.13, 127.87, 125.90, 124.68, 124.11, 122.24, 121.47, 121.08, 120.79, 103.02, 96.19, 94.98, 75.04, 31.21, 29.98, 29.59, 25.81, 22.11, 13.60, -0.20. ESI-TOF (*m/z*): Calcd. $[C_{68}H_{58}Cl_2IN_9ORuSi - 2Cl]^{2+}$ for: 636.63, found: 636.59.



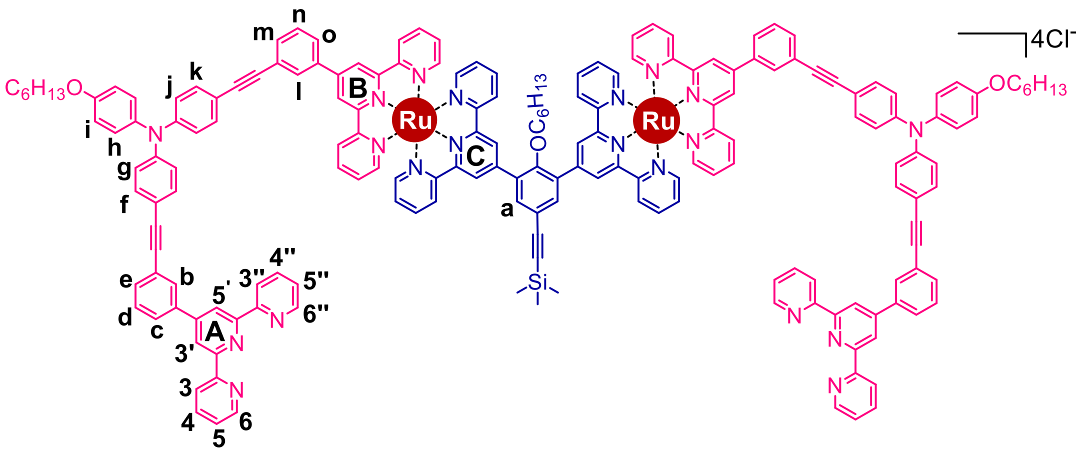
Compound **S-19.** Compound **S-18** (140 mg, 0.1 mmol), compound **S-15** (112 mg, 0.16 mmol), Pd(PPh$_3$)$_4$ (3 mg, 5 μmol) and copper(I) iodide (0.4 mg, 4 μmol) was degassed under nitrogen for three times. After that, 20 mL anhydrous DMF, 10 mL anhydrous DME, 10 mL anhydrous Et$_3$N was added and then the mixture was stirred at 80 °C overnight. After removal of solvent under vacuum, the crude was purified by column chromatography on neutral Al$_2$O$_3$ with chloroform: methanol (100:1) as eluent to afford the product as a dark red solid (154 mg, 80 % yield). ^{1}H NMR (500 MHz, CDCl$_3$+3% CD$_3$OD, 300 K) δ 9.06 (s, 2H, tpy^{C}-$H^{3',5'}$), 8.96 (s, 2H, tpy^{B}-$H^{3',5'}$), 8.90 – 8.81 (m, 4H, tpy^{C}-$H^{3,3"}$, tpy^{A}-$H^{3',5'}$), 8.78 – 8.68 (m, 8H , tpy^{A}-$H^{6,6"}$, tpy^{A}-$H^{3,3"}$, tpy^{D}-$H^{3',5'}$, tpy^{D}-$H^{6,6"}$), 8.66 (dd, J = 7.9, 1.1 Hz, 2H, tpy^{D}-$H^{3,3"}$), 8.58-8.51 (m, 3H, tpy^{B}-$H^{3,3"}$, Ph-H^{c}), 8.29 (d, J = 1.8 Hz, 1H, Ph-H^{f}), 8.17 (d, J = 2.1 Hz, 1H, Ph-H^{b}), 8.02 (d, J = 1.8 Hz, 1H, Ph-H^{a}), 7.98 – 7.84 (m, 9H, tpy^{C}-$H^{4,4"}$, tpy^{B}-$H^{4,4"}$, tpy^{D}-$H^{4,4"}$, tpy^{A}-$H^{4,4"}$, Ph-H^{r}), 7.81 (dt, J = 7.9, 1.4 Hz, 1H, Ph-H^{o}), 7.71 – 7.51 (m, 7H, tpy^{C}-$H^{6,6"}$, tpy^{B}-$H^{6,6"}$, Ph-H^{d}, Ph-H^{m}, Ph-H^{e}), 7.50 – 7.31 (m, 11H, tpy^{A}-$H^{5,5"}$, tpy^{B}-$H^{5,5"}$, tpy^{D}-$H^{5,5"}$, Ph-H^{g}, Ph-H^{l}, Ph-H^{n}), 7.31 – 7.26 (m, 2H, tpy^{C}-$H^{5,5"}$), 7.08 (d, J = 8.9 Hz, 2H, Ph-H^{i}), 7.05 – 6.97 (m, 4H, Ph-H^{k}, Ph-H^{h}), 6.87 (d, J = 9.0 Hz, 2H, Ph-H^{j}), 3.94 (t, J = 6.5 Hz, 2H), 3.64 (t, J = 5.8 Hz, 2H), 1.81 – 1.68 (m, 2H), 1.50 – 1.38 (m, 2H), 1.38-1.29 (m, 8H), 1.05 (tt, J = 9.7, 6.2 Hz, 2H), 0.89 (t, J = 6.8 Hz, 3H), 0.81-0.76 (m, 2H), 0.72-0.65 (m, 2H), 0.39 (t, J = 7.2 Hz, 3H), 0.29 (s, 9H). ^{13}C NMR (125 MHz, CDCl$_3$+3% CD$_3$OD, 300 K) δ 157.68, 157.46, 156.63, 156.00, 155.93, 155.86, 155.65, 154.80, 154.67, 154.61, 152.88, 152.32, 149.45, 149.11, 149.06, 148.14, 147.63, 147.41, 146.93, 144.91, 138.95, 138.61, 138.21, 138.02, 136.96, 136.86, 136.69, 136.31, 134.58, 134.49, 132.98, 132.71, 132.60, 131.88, 131.81, 130.41, 130.17, 129.90, 128.93, 128.69, 128.37, 128.02, 126.82, 125.57, 124.75, 124.60, 124.42, 124.27, 124.01, 123.87, 122.56, 122.30, 122.07, 121.36, 121.32, 121.12, 120.75, 118.73, 116.17, 115.74, 115.55, 103.13, 96.22, 91.08, 90.21, 88.41, 88.13, 75.37, 68.21, 31.85, 31.53, 31.28, 30.04, 29.62, 29.22, 25.89, 25.69, 22.55, 22.15, 13.99, 13.68, -0.06. ESI-TOF (*m/z*): Calcd. $[C_{117}H_{97}Cl_2N_{13}O_2RuSi - 2Cl]^{2+}$ for: 922.84, found: 922.84.



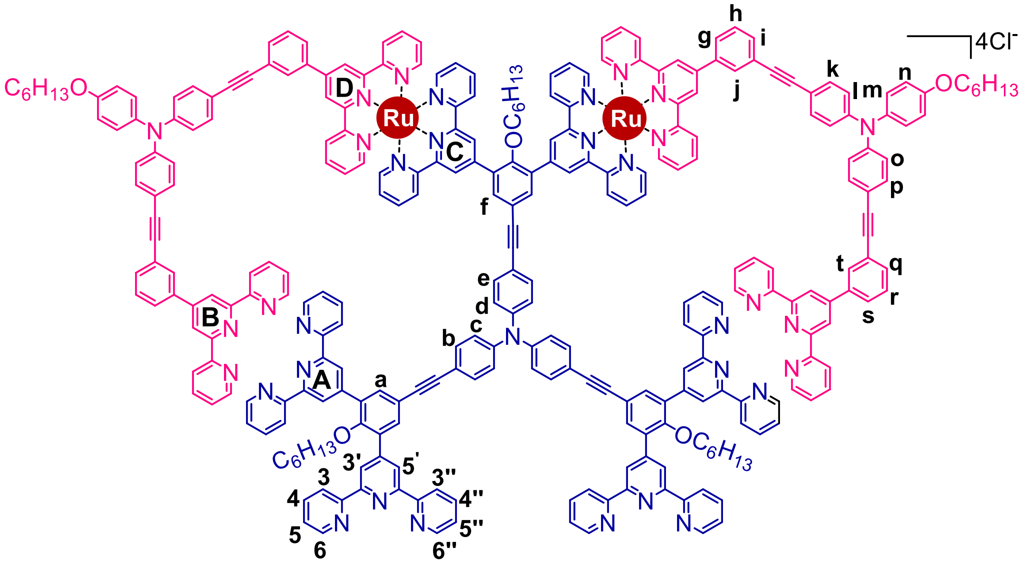
Compound **LB.** Compound **S-19** (300 mg, 0.16 mmol), compound **5** (28 mg, 0.048 mmol), $Pd(PPh_3)_4$ (7 mg, 15 μmol) and copper(I) iodide (1.0 mg, 8 μmol) was degassed under nitrogen for three times. After that, 25 mL anhydrous DMF, 10 mL anhydrous DME, 15mL anhydrous Et_3N was added at one time. After that, TBAF solution (0.2 mL, 1 M in THF) was added and the mixture was stirred at 80 ºC for two days. After removal of solvent under vacuum, the crude was directly purified by column chromatography on neutral Al_2O_3 with chloroform: methanol (100:3) as eluent to afford the product as a dark red solid (30 mg, 12 % yield). ^1H NMR (500 MHz, DMSO-d_6, 300

K) δ 9.56 (s, 6H, tpy^{C}-$H^{3',5'}$), 9.43 (s, 6H, tpy^{D}-$H^{3',5'}$), 9.18 (d, J = 8.3 Hz, 6H, tpy^{C}-$H^{3,3''}$), 9.05 (d, J = 8.3 Hz, 6H, tpy^{D}-$H^{3,3''}$), 8.87 (s, 6H, tpy^{A}-$H^{3',5'}$), 8.75-8.65 (m, 30H, tpy^{A}- $H^{3,3''}$, tpy^{A}- $H^{6,6''}$, tpy^{B}-$H^{3',5'}$, tpy^{B}-$H^{3,3''}$, tpy^{B}-$H^{6,6''}$), 8.60 (s, 3H, Ph-H^{r}), 8.45 (s, 3H, Ph-H^{q}), 8.25 (s, 3H, Ph-H^{b}), 8.16 – 7.99 (m, 33H, tpy^{C}-$H^{4,4''}$, tpy^{D}-$H^{4,4''}$, tpy^{A}-$H^{4,4''}$, tpy^{B}-$H^{4,4''}$, Ph-H^{a}, Ph-H^{l}, Ph-H^{o}), 7.95 (d, J = 7.6 Hz, 6H, Ph-H^{h}), 7.81 (m, 6H, Ph-H^{k}, Ph-H^{p}), 7.73 – 7.62 (m, 9H, Ph-H^{n}, Ph-H^{i}), 7.62 – 7.45 (m, 30H, tpy^{C}-$H^{6,6''}$, tpy^{D}-$H^{6,6''}$, tpy^{A}-$H^{5,5''}$, tpy^{B}-$H^{5,5''}$, Ph-H^{c}), 7.30 (m, 12H, tpy^{C}-$H^{5,5''}$, tpy^{D}-$H^{5,5''}$), 7.20 (m, 3H, Ph-H^{j}), 7.13 (m, 6H, Ph-H^{f}), 7.03 (m, 24H, Ph-H^{d}, Ph-H^{e}, Ph-H^{m}, Ph-H^{g}), 3.97 (m, 6H), 3.66 (m, 6H), 1.71 (q, J = 7.1 Hz, 6H), 1.49 – 1.18 (m, 24H), 1.06 (m, 6H), 0.93 – 0.70 (m, 12H), 0.57 (t, J = 7.5 Hz, 9H), 0.22 (t, J = 7.2 Hz, 9H). ^{13}C NMR (100 MHz, DMSO-d_6, 300 K) δ 158.57, 158.30, 157.09, 156.15, 155.74, 155.53, 155.32, 155.16, 155.05, 152.83, 149.80, 149.12, 147.85, 147.64, 147.12, 147.01, 146.59, 144.57, 138.57, 138.16, 137.13, 134.55, 133.90, 133.58, 133.40, 133.32, 133.21, 132.50, 130.77, 130.46, 129.89, 129.02, 128.30, 127.63, 125.19, 124.72, 124.32, 124.15, 122.53, 122.19, 121.95, 121.53, 121.33, 119.98, 118.61, 117.44, 117.03, 116.40, 115.80, 115.33, 91.09, 90.78, 88.90, 88.77, 79.65, 74.93, 68.15, 52.41, 31.48, 31.33, 29.95, 29.16, 25.97, 25.70, 22.57, 22.14, 14.42, 13.85. ESI-TOF (*m/z*): Calcd. $[C_{360}H_{276}Cl_6N_{40}O_6Ru_3 - 6Cl]^{6+}$ for: 927.00, found: 926.94.

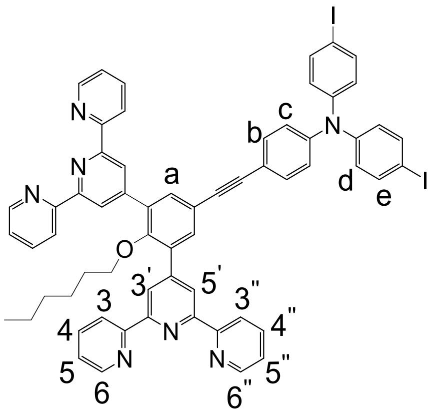
Compound **S-20.** Compound **S-20** was synthesized using the same method as **S-17**. Compound **S-8** (109 mg, 0.25 mmol) was dissolved in 30 mL $CHCl_3$ and 30 mL MeOH. $RuCl_3{\cdot}xH_2O$ (315 mg, 1 mmol) was added and the suspension was refluxed for 48h. After cooling down, the resultant dark red solid was filtered, washed with MeOH by centrifugation, and dried in vacum to afford the product as a dark red solid (156 mg, 69 % yield). This material was used without characterization due to its poor solubility.



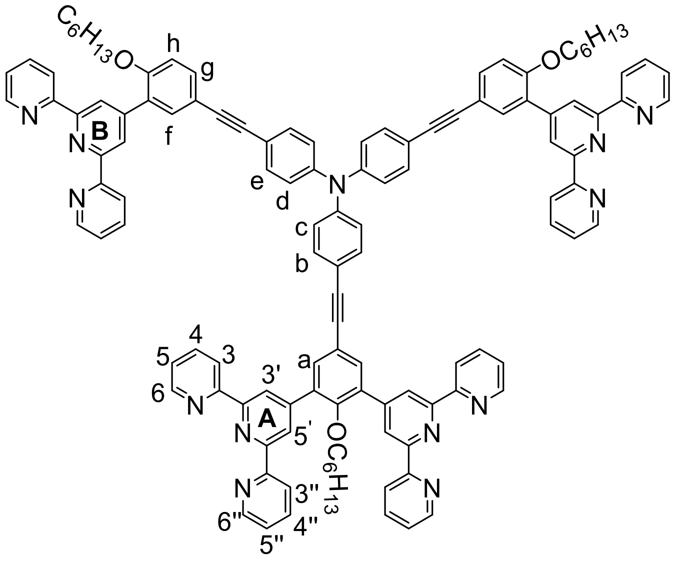
Compound **S-21.** Compound **S-20** (170 mg, 0.14 mmol) was dissolved in 50 mL $CHCl_3$ and 50 mL MeOH, and compound **LA** (330 mg, 0.32 mmol) was added. The suspension was stirred at room temperature for 1 h, then N-ethylmorpholine (500 μL) was added. The mixture was refluxed for 48 h. After cooling down to room temperature, the solvent was removed by evaporation. The crude was purified by column chromatography on neutral Al_2O_3 with chloroform: methanol (100: 2) as eluent to afford the product as a red solid (114 mg, 24 % yield). ^{1}H NMR (400 MHz, $CDCl_3$+3% CD_3OD, 300 K) δ 9.72 (s, 4H, tpy^{C}-$H^{3',5'}$), 9.29 (d, J = 8.2 Hz, 4H, tpy^{C}-$H^{3,3''}$), 9.17 (s, 4H, tpy^{B}-$H^{3',5'}$), 8.91 (d, J = 7.9 Hz, 4H, tpy^{B}-$H^{3,3''}$), 8.74 – 8.57 (m, 12H, tpy^{A}-$H^{3',5'}$, tpy^{A}-$H^{6,6''}$, tpy^{A}-$H^{3,3''}$), 8.42 (s, 2H, Ph-H^{a}), 8.22 (s, 2H, Ph-H^{b}), 8.18 (s, 2H, Ph-H^{l}), 7.98-8.06 (m, 12H, tpy^{C}-$H^{4,4''}$, tpy^{B}-$H^{4,4''}$, Ph-H^{c}, Ph-H^{o}), 7.92 – 7.79 (m, 6H, tpy^{A}-$H^{4,4''}$, Ph-H^{m}), 7.71 (d, J = 4.3 Hz, 2H, Ph-H^{k}), 7.56 (d, J = 7.6 Hz, 2H, Ph-H^{e}), 7.52 – 7.31 (m, 20H, tpy^{A}-$H^{5,5''}$, tpy^{C}-$H^{6,6''}$, tpy^{B}-$H^{6,6''}$, Ph-H^{d}, Ph-H^{n}, Ph-H^{f}), 7.25 (m, 8H, tpy^{C}-$H^{5,5''}$, tpy^{B}-$H^{5,5''}$), 7.08 (d, J = 8.9 Hz, 2H, Ph-H^{h}), 7.03 (d, J = 8.6 Hz, 8H, Ph-H^{g}, Ph-H^{j}), 6.87 (d, J = 8.9Hz, 2H, Ph-H^{i}), 3.94 (t, J = 6.5 Hz, 4H), 1.76 (m, 4H), 1.49 – 1.27 (m, 12H), 0.89 (m, 6H), -0.04 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6, 300 K) δ 158.63, 158.44, 157.09, 156.25, 155.59, 155.56, 155.28, 155.14, 155.07, 152.78, 152.33, 149.85, 149.09, 147.84, 147.65, 146.55, 145.12, 144.24, 138.67, 138.59, 138.03, 137.12, 133.50, 133.32, 133.22, 132.80, 132.48, 130.78, 130.46, 129.88, 129.02, 128.33, 128.27, 128.24, 127.61, 125.60, 125.49, 125.14, 124.32, 124.16, 122.53, 122.20, 121.96, 121.46, 118.54, 116.40, 115.79, 115.36, 91.08, 90.78, 88.92, 88.77, 68.15, 31.49, 29.16, 25.70, 22.58, 14.43, 0.43. ESI-TOF (m/z): Calcd. $[C_{187}H_{150}ClN_{20}O_3Ru_2Si - 3Cl]^{3+}$ for: 996.99, found: 996.94. Calcd. $[C_{187}H_{150}N_{20}O_3Ru_2Si - 4Cl]^{4+}$ for: 739.00, found: 738.96.



Compound **LC.** Compound **S-21** (55 mg, 0.018 mmol), compound **S-13** (43 mg, 0.027 mmol), $Pd(PPh_3)_4$ (3 mg, 7 μmol) and copper(I) iodide (0.5 mg, 4 μmol) was degassed under nitrogen for three times. After that, 20 mL anhydrous DMF, 10 mL anhydrous DME, 15mL anhydrous Et_3N was added at one time. After that, TBAF solution (0.1 mL, 1 M in THF) was added and the mixture was stirred at 80 ºC overnight. After removal of solvent under vacuum, the crude was directly purified by column chromatography on neutral Al_2O_3 with chloroform: methanol (100:2) as eluent to afford the product as a dark red solid (15 mg, 12 % yield). ^{1}H NMR (500 MHz, DMSO-d_6, 300 K) δ 9.78 (s, 4H, tpy^C-$H^{3',5'}$), 9.61 (s, 4H, tpy^D-$H^{3',5'}$), 9.28 (d, J = 8.0 Hz, 4H, tpy^C-$H^{3,3''}$), 9.23 (d, J = 8.1 Hz, 4H, tpy^D-$H^{3,3''}$), 8.88 – 8.64 (m, 36H, tpy^A-$H^{3',5'}$, tpy^A- $H^{3,3''}$, tpy^A- $H^{6,6''}$, tpy^B-$H^{3',5'}$, tpy^B-$H^{3,3''}$, tpy^B-$H^{6,6''}$), 8.64 (s, 2H, Ph-H^j), 8.51 (s, 2H, Ph-H^g), 8.43 (s, 2H, Ph-H^f), 8.18 – 8.02 (m, 20H, tpy^C-$H^{4,4''}$, tpy^D-$H^{4,4''}$, tpy^A-$H^{4,4''}$, tpy^B-$H^{4,4''}$), 7.97 (m, 4H, Ph-H^t, Ph-H^i), 7.90 (s, 4H, Ph-H^a), 7.82 (m, 6H, Ph-H^k, Ph-H^h), 7.75(m, 6H, Ph-H^e, Ph-H^p), 7.71 – 7.59 (m, 12H, tpy^C-$H^{6,6''}$, Ph-H^s, Ph-H^b, Ph-H^q), 7.55 (m, 18H, tpy^D-$H^{6,6''}$, tpy^A-$H^{5,5''}$, tpy^B-$H^{5,5''}$, Ph-H^r), 7.34 (m, 8H, tpy^C-$H^{5,5''}$, tpy^D-$H^{5,5''}$), 7.22 – 7.12 (m, 10H, Ph-H^d, Ph-H^l, Ph-H^m), 7.11 – 6.97 (m, 12H, Ph-H^c, Ph-H^n, Ph-H^o), 4.14 – 3.79 (m, 6H), 3.41 (m, 4H), 1.73 (m, 4H), 1.43 (m, 6H), 1.32 (m, 10H), 1.15 (m, 12H), 1.00 – 0.77 (m, 8H), 0.62 (m, 6H), 0.39 (t, J = 6.7 Hz, 6H), 0.12 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, 300 K) δ 158.61, 158.33, 157.09, 156.25, 155.60, 155.53, 155.32, 155.27, 155.14, 154.75, 149.85, 149.10, 147.86, 147.64, 147.15, 146.83, 146.63, 144.23, 138.61, 138.58, 138.03, 137.13, 134.63, 134.27, 133.62, 133.32, 133.21, 132.48, 130.77, 130.46, 129.88, 129.02, 128.21, 127.62, 125.14, 125.08, 124.81, 124.33, 124.15, 122.55, 122.18, 121.47, 121.33, 119.97, 118.54, 117.76, 116.40, 115.81, 115.31, 91.10, 90.77, 90.43, 88.88, 88.77, 88.63, 74.40, 68.15, 55.77, 31.48, 31.40, 31.10, 29.59, 29.49, 29.16, 26.16, 25.70, 25.43, 22.58, 22.21, 22.03, 14.42, 14.02, 13.74. ESI-TOF (*m/z*): Calcd. $[C_{290}H_{223}Cl_4N_{33}O_5Ru_2 - 4Cl+H]^{5+}$ for: 890.73, found: 890.72. Calcd. $[C_{290}H_{223}Cl_4N_{33}O_5Ru_2 - 4Cl+2H]^{6+}$ for: 742.44, found: 742.43.

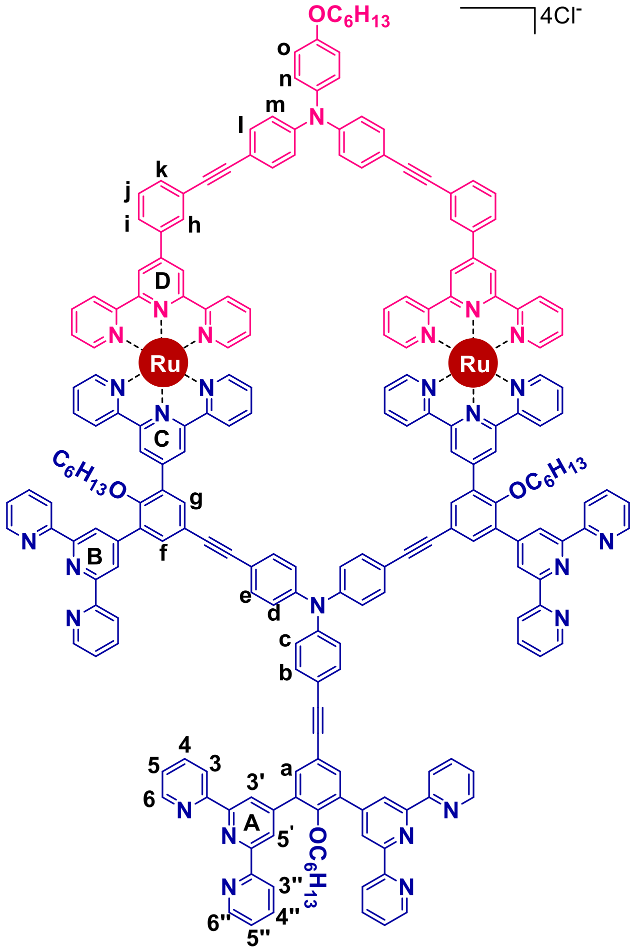


Compound **S-22.** Compound **5** (1.5 g, 2.5 mmol), compound **S-9** (400 mg, 0.6 mmol), Pd(PPh$_3$)$_4$ (70 mg, 0.06 mmol) and copper(I) iodide (10 mg, 0.05 mmol) was degassed under nitrogen for three times. After that, anhydrous THF (30 mL), anhydrous Et$_3$N (15 mL) was added and then the mixture was stirred at 70 °C overnight. The solvent was removed, and the residue was extracted with CHCl$_3$. The combined organic phase was washed with brine and dried with anhydrous Na$_2$SO$_4$. After removal of solvent under vacuum, the crude was purified by column chromatography on silica gel with chloroform: ethanol (100:2) as eluent to afford the product as a light-yellow solid (300 mg, 43% yield). ^{1}H NMR (400 MHz, , CDCl$_3$, 300 K) δ 8.82 (s, 4H, tpy-$H^{3',5'}$), 8.77 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 4H, tpy-$H^{6,6''}$), 8.71 (dt, *J* = 8.0, 1.1 Hz, 4H, tpy-$H^{3,3''}$), 7.90 (td, *J* = 7.7, 1.8 Hz, 4H, tpy-$H^{4,4''}$), 7.82 (s, 2H, Ph-H^{A}), 7.56 (m, 4H, Ph-H^{D}), 7.43(m, 2H, Ph-H^{C}), 7.37 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 4H, tpy-$H^{5,5''}$), 7.01(m, 2H, Ph-H^{B}), 6.85 (m, 4H, Ph-H^{E}), 3.39 (t, *J* = 6.0 Hz, 2H), 1.21 (td, *J* = 15.1, 13.6, 8.2 Hz, 2H), 0.98 – 0.87 (m, 2H), 0.75 (tt, *J* = 5.7, 3.3 Hz, 4H), 0.54 (t, *J* = 5.7 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$, 300 K) δ 156.06, 155.37, 154.71, 149.09, 147.77, 146.67, 146.59, 138.46, 136.97, 134.24, 134.17, 132.80, 126.42, 123.82, 123.32, 121.66, 121.36, 119.86, 117.68, 89.72, 88.30, 86.72, 77.19, 74.41, 31.67, 29.74, 25.41, 22.12, 13.77. ESI-TOF (*m/z*): Calcd. $[C_{62}H_{47}I_2N_7O + H]^+$ for: 1160.20, found: 1160.20.



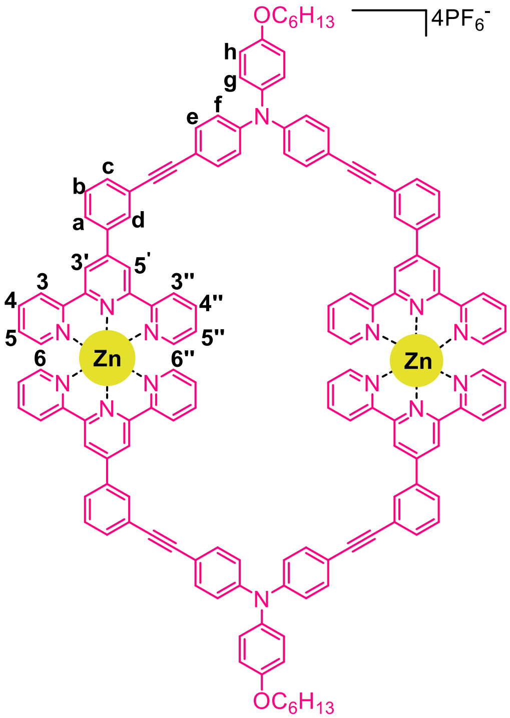
Compound **LD.** Compound **S-22** (300 mg, 0.26 mmol), compound **S-6** (433 mg, 1 mmol), $Pd(PPh_3)_4$ (70 mg, 0.06 mmol) and copper(I) iodide (10 mg, 0.05 mmol) was degassed under nitrogen for three times. After that, anhydrous THF (30 mL), anhydrous Et_3N (15 mL) was added and then the mixture was stirred at 70 ºC for two days. Then the solvent was removed, and the residue was extracted with $CHCl_3$. The combined organic phase was washed with brine and dried with anhydrous Na_2SO_4. After removal of solvent under vacuum, the crude was purified by column chromatography on silica gel with chloroform: ethanol (100:3) as eluent to afford the product as a brown solid (100 mg, 22 % yield). ^{1}H NMR (500 MHz, , $CDCl_3$, 300 K) δ 8.82 (s, 4H, tpy^{A}-$H^{3',5'}$), 8.75(m, 4H, tpy^{A}-$H^{6,6''}$), 8.73 – 8.63 (m, 16H, tpy^{B}-$H^{3',5'}$, tpy^{B}-$H^{6,6''}$, tpy^{A}-$H^{3,3''}$, tpy^{B}-$H^{3,3''}$), 7.95 – 7.81 (m, 10H, tpy^{A}-$H^{4,4''}$, tpy^{B}-$H^{4,4''}$, Ph-H^{a}), 7.77 (d, *J* = 2.1 Hz, 2H, Ph-H^{f}), 7.53 (dd, *J* = 8.6, 2.1 Hz, 2H, Ph-H^{g}), 7.46 (m, 6H, Ph-H^{c}, Ph-H^{d}), 7.34 (ddd, *J* = 15.2, 7.5, 4.9 Hz, 10H, tpy^{A}-$H^{5,5''}$, tpy^{B}-$H^{5,5''}$, Ph-H^{b}), 7.10 (d, *J* = 8.2 Hz, 4H, Ph-H^{e}), 6.97 (d, *J* = 8.6 Hz, 2H, Ph-H^{h}), 4.04 (t, *J* = 6.2 Hz, 4H), 3.39 (t, *J* = 6.0 Hz, 2H), 1.73 (dd, *J* = 9.0, 6.2 Hz, 4H), 1.40 (m, *J* = 7.6 Hz, 4H), 1.16 (m, 10H), 0.93 (m, *J* = 7.5 Hz, 2H), 0.73 (m, 10H), 0.50 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 300 K) δ 156.44, 156.31, 156.23, 155.48, 155.14, 154.68, 149.19, 149.08, 147.78, 147.64, 146.84, 146.50, 136.79, 136.72, 134.23, 134.18, 133.79, 133.21, 132.79, 132.65, 128.51, 124.13, 123.88, 123.74, 123.56, 121.81, 121.63, 121.26, 121.20, 119.81, 118.23, 117.60, 115.72, 112.18, 89.87, 88.96, 88.44, 88.23, 74.42, 68.66, 31.51, 31.32, 29.74, 29.08, 25.77, 25.42, 22.34, 22.12, 13.90, 13.77. ESI-TOF (*m/z*): Calcd. $[C_{120}H_{99}N_{13}O_3 + 2H]^{2+}$ for: 886.41, found: 886.40. Calcd. $[C_{120}H_{99}N_{13}O_3 + 3H]^{3+}$ for: 591.28, found: 591.26.

Compound **7.** Compound **7** was synthesized according to a literature method.[13]A nitrogen purged flask containing a solution of compound **LA** (151 mg, 0.15 mmol) and $Ru(DMSO)_4Cl_2$ (290 mg, 0.6 mmol) in 100 mL 1,2-dichloroethane was heated at reflux for two days. The solvent was removed, and the residue was washed with methanol by centrifugation for three times. About 200 mg dark red solid (88%) was obtained after dried in vacuum. The solid was used directly for further steps without characterization.

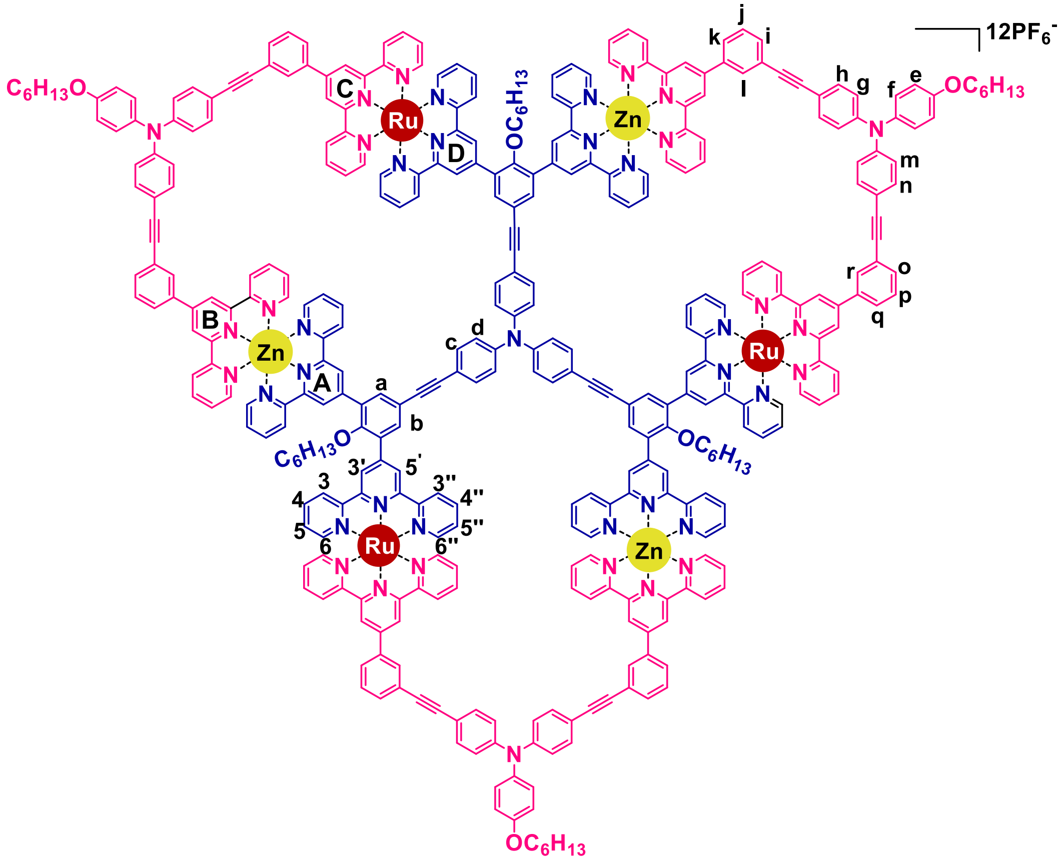


Compound **LE.** A flask containing a solution of compound **7** (48 mg, 0.032 mmol) and compound **L** (121 mg, 0.054 mmol) in 30 mL 1,2-dichloroethane and 30 mL ethanol was heated at reflux for two days. The solvent was removed, and the residue was purified by column chromatography on neutral aluminum oxide with chloroform: methanol (100:4) as eluent to afford the product as a dark red solid (18 mg, 13 % yield). ^{1}H NMR (500 MHz, DMSO-d_6, 300 K) δ 9.63 (s, 4H, tpy^{D}-$H^{3',5'}$), 9.45 (s, 4H, tpy^{C}-$H^{3',5'}$), 9.26 (d, J = 8.4 Hz, 4H, tpy^{D}-$H^{3,3''}$), 9.07 (d, J = 8.2 Hz, 4H, tpy^{C}-

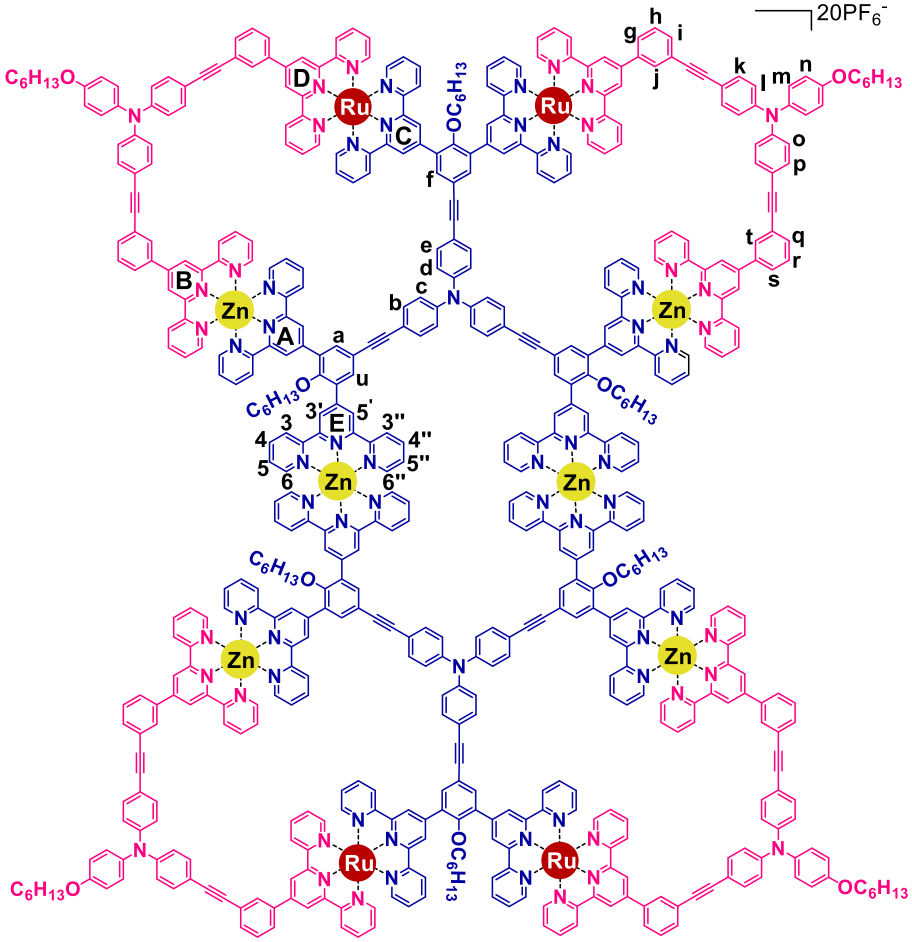
$H^{3,3''}$), 8.90 (s, 4H, tpy^{B}-$H^{3',5'}$), 8.84 – 8.65 (m, 22H, tpy^{A}-$H^{3',5'}$, tpy^{A}- $H^{3,3''}$, tpy^{A}- $H^{6,6''}$, tpy^{B}-$H^{3,3''}$, tpy^{B}-$H^{6,6''}$, Ph-H^{h}), 8.55 (d, J = 7.1 Hz, 2H, Ph-H^{i}), 8.25 (s, 2H, Ph-H^{g}), 8.09 (m, 16H, tpy^{C}-$H^{4,4''}$, tpy^{D}-$H^{4,4''}$, tpy^{A}-$H^{4,4''}$, tpy^{B}-$H^{4,4''}$), 7.92 (s, 2H, Ph-H^{f}), 7.83 (m, 4H, Ph-H^{a}, Ph-H^{j}), 7.68-7.48 (m, 26H, tpy^{C}-$H^{6,6''}$, tpyD-$H^{6,6''}$, tpy^{A}-$H^{5,5''}$, tpy^{B}-$H^{5,5''}$, Ph-H^{k}, Ph-H^{l}, Ph-H^{e}), 7.32 (m, 8H, tpy^{C}-$H^{5,5''}$, tpy^{D}-$H^{5,5''}$), 7.19 (m, 8H, Ph-H^{n}, Ph-H^{d}, Ph-H^{b}), 7.08 (m, 8H, Ph-H^{o}, Ph-H^{c}, Ph-H^{m}), 4.02 (m, 2H), 3.73 (m, 4H), 1.76 (m, 2H), 1.58 – 1.20 (m,10H), 1.12 (m, 6H), 0.98 – 0.77 (m, 12H), 0.64 (m, 8H), 0.41 (t, J = 7.4 Hz, 3H), 0.27 (t, J = 7.3 Hz, 6H).^{13}C NMR (100 MHz, DMSO-d_6, 300 K) δ 158.58, 158.30, 157.17, 155.76, 155.62, 155.56, 155.35, 155.03, 154.77, 152.78, 152.42, 149.86, 147.81, 147.17, 146.73, 146.41, 144.83, 138.63, 138.41, 138.08, 136.97, 135.77, 134.64, 134.48, 134.30, 133.95, 133.65, 133.49, 133.26, 131.28, 130.40, 128.99, 128.32, 128.12, 125.63, 125.18, 125.09, 124.84, 124.49, 124.30, 122.41, 121.84, 121.48, 121.34, 119.99, 117.83, 117.22, 116.45, 115.58, 90.95, 90.66, 90.45, 88.92, 88.66, 88.35, 75.00, 74.42, 68.19, 31.51, 31.35, 31.12, 29.94, 29.60, 29.18, 25.96, 25.72, 25.44, 22.60, 22.20, 22.04, 14.45, 14.03, 13.89. ESI-TOF (*m/z*): Calcd. $[C_{220}H_{170}Cl_4N_{26}O_4Ru_2 - 3Cl]^{3+}$ for: 1159.73, found: 1159.76. Calcd. $[C_{220}H_{170}Cl_4N_{26}O_4Ru_2 - 4Cl]^{4+}$ for: 861.05, found: 861.03.



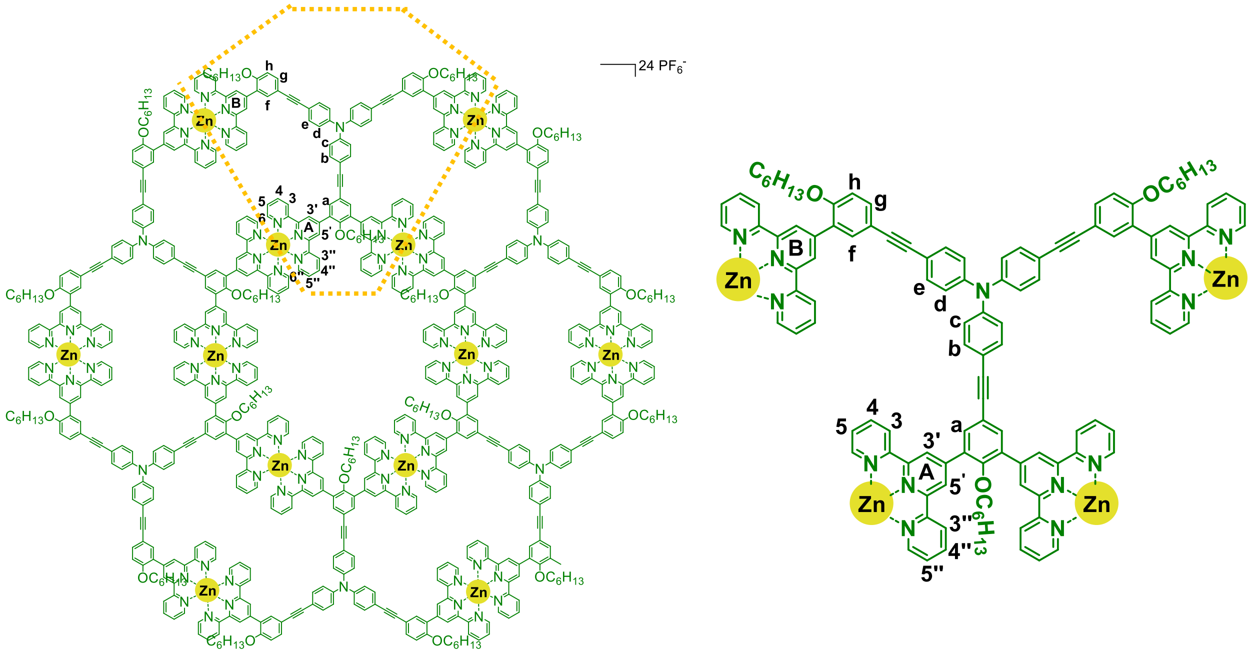
Complex **G1 [Zn$_2$LA$_2$]**: To a solution of ligand **LA** (4.7 mg, 4.7 μmol) in CHCl$_3$ (1.0 mL), a solution of Zn(NO$_3$)$_2$•6H$_2$O (1.4 mg, 4.7 μmol) in MeOH (3.0 mL) was added slowly. The mixture was heated at 50 °C for 10 h and then cooled down to room temperature. The mixture was then added to a solution of NH_4PF_6 (30 mg in 20 mL MeOH). After a while, a precipitate was formed, washed with MeOH for three times by centrifugation, dried in vacuum to give the product as a brown solid (5.9 mg, 93 % yield). ^1H NMR (500 MHz, CD_3CN, 300 K) δ 9.02 (d, J = 3.0 Hz, 8H, tpy-$H^{3',5'}$,), 8.75 (dd, J = 8.3, 3.7 Hz, , 8H, tpy-$H^{3,3''}$), 8.36 (d, J = 4.4 Hz, 4H, Ph-H^{d}), 8.19 (m, 12H, tpy-$H^{4,4''}$, Ph-H^{a}), 7.94 – 7.71 (m, 16H, tpy-$H^{6,6''}$, Ph-H^{c}, Ph-H^{b}), 7.53 (m, 8H, Ph-H^{e}), 7.44 (m, 8H, tpy-$H^{5,5''}$), 7.26 – 7.05 (m, 12H, Ph-H^{g}, Ph-H^{f}), 7.00 (d, J = 8.5 Hz, Ph-H^{h}), 4.02 (t, J = 6.3 Hz, 4H), 1.88 – 1.69 (m, 4H), 1.50 (m, 4H), 1.51 – 1.20 (m, 8H), 0.94 (t, J = 6.1 Hz, 6H). ^{13}C NMR (125 MHz, CD_3CN, 300 K) δ 158.17, 156.53, 150.93, 149.04, 148.83, 142.27, 139.77, 137.71, 134.60, 133.67, 131.69, 131.01, 129.56, 129.47, 128.82, 128.57, 125.80, 124.27, 123.25, 122.72, 116.80, 116.58, 91.67, 88.73, 69.20, 32.30, 29.94, 26.41, 23.32, 14.32. ESI-TOF (*m/z*): 1218.3 $[M\text{-}2PF_6^{-}]^{2+}$ (calcd *m/z*: 1218.3), 763.9 $[M\text{-}3PF_6^{-}]^{3+}$ (calcd *m/z*: 763.9), 536.7 $[M\text{-}4PF_6^{-}]^{4+}$ (calcd *m/z*: 536.7).



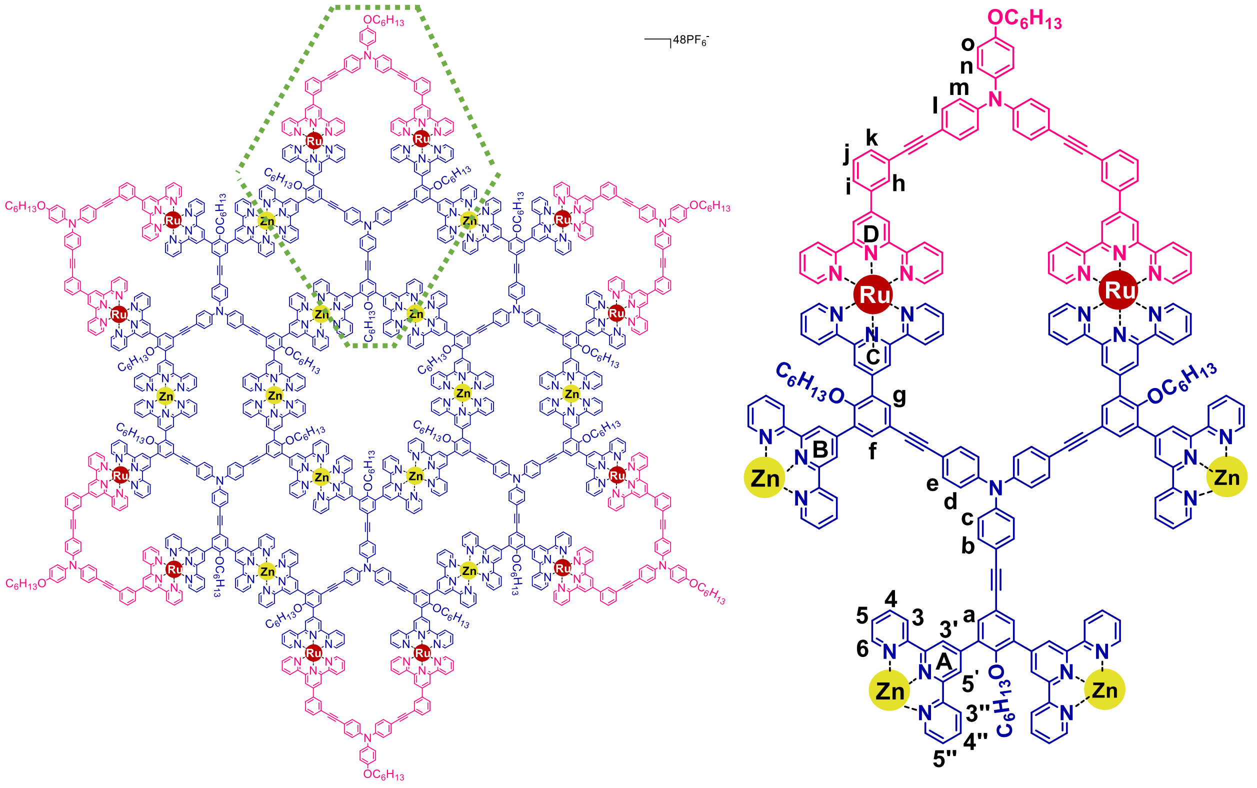
Complex **G2 [Zn$_3$LB]**: To a solution of ligand **LB** (4.0 mg, 0.69 μmol) in $CHCl_3$ (1.0 mL), a solution of $Zn(NO_3)_2$•$6H_2O$ (0.61 mg, 2.1 μmol) in MeOH (3.0 mL) was added slowly. The mixture was heated at 50 ºC for 10 h and then cooled down to room temperature. The mixture was then added to a solution of NH_4PF_6 (50 mg in 15 mL MeOH). After a while, a precipitate was formed, washed with MeOH for three times by centrifugation, dried in vacuum to give the product as a red solid (4.9 mg, 94 % yield). ^{1}H NMR (500 MHz, CD_3CN, 300 K) δ 9.23 (m, 12H, tpy^{D}-$H^{3',5'}$, tpy^{A}-$H^{3',5'}$), 9.07 (m, 12H, tpy^{B}-$H^{3',5'}$, tpy^{C}-$H^{3',5'}$), 8.79-8.68 (br, 24H, tpy^{D}-$H^{3,3''}$, tpy^{B}-$H^{3,3''}$, tpy^{A}-$H^{3,3''}$, tpy^{C}-$H^{3,3''}$), 8.47 – 8.14 (br, 30H, Ph-H^{l}, Ph-H^{r}, Ph-H^{a}, Ph-H^{b}, tpy^{D}-$H^{4,4''}$, tpy^{B}-$H^{4,4''}$, Ph-H^{k}, Ph-H^{q}), 8.04 – 7.76 (m, 36H, tpy^{A}-$H^{4,4''}$, tpy^{C}-$H^{4,4''}$, tpy^{D}-$H^{6,6''}$, tpy^{B}-$H^{6,6''}$, Ph-H^{p}, Ph-H^{j}, Ph-H^{o}, Ph-H^{i}), 7.66 (d, J = 8.2 Hz, 6H, Ph-H^{c}), 7.58 – 7.39 (m, 36H, tpy^{A}-$H^{6,6''}$, tpy^{C}-$H^{6,6''}$, tpy^{D}-$H^{5,5''}$, tpy^{B}-$H^{5,5''}$, Ph-H^{n}, Ph-H^{h}), 7.35 – 7.07 (m, 36H, tpy^{A}-$H^{5,5''}$, tpy^{C}-$H^{5,5''}$, Ph-H^{d}, Ph-H^{f}, Ph-H^{m}, Ph-H^{g}), 7.01 (d, J = 8.4 Hz, 6H, Ph-H^{e}), 4.04 (t, J = 6.6 Hz, 6H), 3.89 – 3.73 (m, 6H), 1.80 (q, J = 7.1 Hz, 6H), 1.60 – 1.15 (m, 34H), 1.02 – 0.79 (m, 17H), 0.73 (m, 3H), 0.33 (t, J = 7.4 Hz, 6H). ^{13}C NMR (125 MHz, CD_3CN, 300 K) δ 157.28, 157.15, 156.25, 154.56, 154.31, 152.27, 152.04, 151.15, 148.99, 148.61, 147.74, 147.46, 146.93, 146.62, 146.19, 140.88, 140.03, 137.69, 136.89, 136.39, 135.78, 132.51, 132.06, 131.40, 129.51, 128.78, 127.83, 127.03, 126.36, 124.26, 123.86, 123.14, 122.90, 121.96, 121.62, 121.36, 121.09, 120.43, 119.81, 89.69, 86.93, 86.74, 86.39, 67.29, 31.16, 30.38, 29.61, 29.24, 28.78, 28.44, 28.03, 27.27, 25.94, 25.19, 24.50, 23.74, 21.43, 21.22, 20.68, 20.38, 12.81, 12.41, 12.04, 11.27. ESI-TOF (*m/z*): 1104.6 $[M-6PF_6^{-}]^{6+}$ (calcd *m/z*: 1104.6), 926.1 $[M-7PF_6^{-}]^{7+}$ (calcd *m/z*: 926.1), 792.2 $[M-8PF_6^{-}]^{8+}$ (calcd *m/z*: 792.2)， 688.1 $[M-9PF_6^{-}]^{9+}$ (calcd *m/z*: 688.1), 604.8 $[M-10PF_6^{-}]^{10+}$ (calcd *m/z*: 604.8), 536.6 $[M-11PF_6^{-}]^{11+}$ (calcd *m/z*: 536.6).



Complex **G3 [Zn$_6$LC$_2$]**: To a solution of ligand **LC** (4.2 mg, 0.91 μmol) in CHCl$_3$ (1.0 mL), a solution of Zn(NO$_3$)$_2$•6H$_2$O (0.82 mg, 2.73 μmol) in MeOH (3.0 mL) was added slowly. The mixture was heated at 50 ºC for 10 h and then cooled down to room temperature. The mixture was then added to a solution of NH$_4$PF$_6$ (50 mg in 15 mL MeOH). After a while, precipitate was formed, washed with MeOH for three times by centrifugation, dried in vacuum to give the product as a red solid (4.4 mg, 94 % yield). ^{1}H NMR (500 MHz, CD$_3$CN, 300 K) δ 9.40 – 9.18 (m, 24H, tpy^C-$H^{3',5'}$, tpy^A-$H^{3',5'}$, tpy^E-$H^{3',5'}$), 9.06 (m, 16H, tpy^D-$H^{3',5'}$, tpy^B-$H^{3',5'}$), 8.84 – 8.59 (m, 40H, tpy^C-$H^{3,3''}$, tpy^E-$H^{3,3''}$, tpy^B-$H^{3,3''}$, tpy^A-$H^{3,3''}$, tpy^D-$H^{3,3''}$), 8.40 (m, 8H, Ph-H^j, Ph-H^t), 8.33 (m, 12H, Ph-H^a, Ph-H^f, Ph-H^u), 8.23 (br,36 H, tpy^C-$H^{4,4''}$, tpy^E-$H^{4,4''}$, tpy^B-$H^{4,4''}$, Ph-H^g, Ph-H^s, Ph-H^e), 7.98 (m,24H, tpy^A-$H^{4,4''}$, tpy^D-$H^{4,4''}$, Ph-H^q, Ph-H^i), 7.92– 7.77 (m, 36H, tpy^C-$H^{6,6''}$, tpy^E-$H^{6,6''}$, tpy^B-$H^{6,6''}$, Ph-H^h, Ph-H^r, Ph-H^d), 7.66 (d, J = 7.9 Hz, 8H, Ph-H^b), 7.58 – 7.38 (m, 56H, tpy^A-$H^{6,6''}$, tpy^D-$H^{6,6''}$, tpy^C-$H^{5,5''}$, tpy^E-$H^{5,5''}$, tpy^B-$H^{5,5''}$, Ph-H^k, Ph-H^p), 7.31 (m, d, J = 7.9 Hz, 8H, Ph-H^c), 7.23 (m, 16 H, tpy^A-$H^{5,5''}$, tpy^D-$H^{5,5''}$), 7.17 (d, J = 8.7 Hz, 8H, Ph-H^m), 7.11 (m, 16H, Ph-H^o, Ph-H^l), 6.94 (d, J = 8.7 Hz, 8H, Ph-*H*^{n}), 4.02 (m, 8H), 3.89 (m, 4H), 3.77 (m, 8H), 1.79 (t, *J* = 7.2 Hz, 8H), 1.57 – 1.14 (m, 66 H), 0.93 (t, *J* = 6.6 Hz, 16H), 0.71 (m, 8H), 0.32 (m, 12H). ^{13}C NMR (125 MHz, CD$_3$CN, 300 K) δ 159.14, 156.42, 156.15, 153.53, 150.86, 150.50, 139.14, 138.23, 137.66, 133.94, 133.59, 131.01, 129.41, 128.52, 125.37, 123.22, 122.69, 121.72, 118.26, 116.77, 100.91, 88.69, 69.18, 41.15, 32.25, 31.07, 30.82, 29.88, 26.90, 26.36, 23.28, 23.08, 23.01, 14.27, 13.89. ESI-TOF (*m/z*): 1379.6 [M-8PF$_6^-$]$^{8+}$ (calcd *m/z*: 1379.6), 1210.1 [M-9PF$_6^-$]$^{9+}$ (calcd *m/z*: 1210.1), 1074.6 [M-10PF$_6^-$]$^{10+}$ (calcd *m/z*: 1074.6)，963.8 [M-11PF$_6^-$]$^{11+}$ (calcd *m/z*: 963.8), 871.4 [M-12PF$_6^-$]$^{12+}$ (calcd *m/z*: 871.4), 793.2 [M-13PF$_6^-$]$^{13+}$ (calcd *m/z*: 793.2), 726.2 [M-14PF$_6^-$]$^{14+}$ (calcd *m/z*: 726.2), 668.1 [M-15PF$_6^-$]$^{15+}$ (calcd *m/z*: 668.1).



Complex **G4 [Zn$_6$LD$_6$]**: To a solution of ligand **LD** (5.2 mg, 2.9 μmol) in CHCl$_3$ (1.0 mL), a solution of Zn(NO$_3$)$_2$•6H$_2$O (1.73 mg, 5.8 μmol) in MeOH (3.0 mL) was added dropwise. The mixture was heated at 50 ºC for 8 h and then added to a solution of NH$_4$PF$_6$ (70 mg in 20 mL MeOH). After a while, a precipitate was formed, washed with MeOH for three times by centrifugation, dried in vacuum to give the product as a yellow solid (6.9 mg, 96 % yield). ^{1}H NMR (500 MHz, CD$_3$CN, 300 K) δ 9.27 (s, 24H, tpy^{A}-*H*$^{3',5'}$), 9.07 (s, 24H, tpy^{B}-*H*$^{3',5'}$), 8.81 (d, *J* = 8.1 Hz, 24H, tpy^{A}-*H*$^{3,3''}$), 8.66 (d, *J* = 8.5 Hz, 24H, tpy^{B}-*H*$^{3,3''}$), 8.36 (s, 12H, Ph-*H*^{a}), 8.23 (m, 48H, tpy^{A}-*H*$^{4,4''}$, tpy^{B}-*H*$^{4,4''}$), 8.08 (s, 12H, Ph-*H*^{f}), 7.99-7.81 (m, 60H, tpy^{A}-*H*$^{6,6''}$, tpy^{B}-*H*$^{6,6''}$, Ph-*H*^{b}), 7.71 – 7.56 (m, 36H, Ph-H^{g}, Ph-H^{e}), 7.46 (m, 48H, tpy^{A}-$H^{5,5''}$, tpy^{B}-$H^{5,5''}$), 7.38 (d, J = 8.8 Hz, 12H, Ph-H^{c}), 7.25 (m, 36H, Ph-H^{d}, Ph-H^{h}), 4.54 – 4.07 (m, 24H), 3.90 – 3.40 (m, 12H), 1.93 – 1.87 (m, 24H), 1.51 (m, 24H), 1.26 (m, 48H), 1.14 – 1.01 (m, 24H), 0.95 – 0.80 (m, 12H), 0.61 (m, 36H), 0.36 (m, 18H), 0.24 (t, J = 7.5 Hz, 12H). ^{13}C NMR (125 MHz, CD_3CN, 300 K) δ 155.82, 152.97, 148.71, 148.28, 147.14, 147.00, 140.52, 132.08, 131.88, 128.32, 126.65, 126.09, 125.04, 123.57, 123.41, 122.20, 115.07, 112.49, 87.74, 87.31, 68.23, 66.06, 30.48, 30.36, 29.37, 28.13, 25.20, 24.95, 21.36, 21.11, 12.30, 12.01. ESI-TOF (*m/z*): 1379.6 $[M\text{-}8PF_6^{-}]^{8+}$ (calcd *m/z*: 1379.6), 1210.1 $[M\text{-}9PF_6^{-}]^{9+}$ (calcd *m/z*: 1210.1), 1074.6 $[M\text{-}10PF_6^{-}]^{10+}$ (calcd *m/z*: 1074.6)， 963.8 $[M\text{-}11PF_6^{-}]^{11+}$ (calcd *m/z*: 963.8), 871.4 $[M\text{-}12PF_6^{-}]^{12+}$ (calcd *m/z*: 871.4), 793.2 $[M\text{-}13PF_6^{-}]^{13+}$ (calcd *m/z*: 793.2), 726.2 $[M\text{-}14PF_6^{-}]^{14+}$ (calcd *m/z*: 726.2), 668.1 $[M\text{-}15PF_6^{-}]^{15+}$ (calcd *m/z*: 668.1).



Complex **G5 [Zn6LE6]**: To a solution of ligand **LE** (7.1 mg, 2.0 μmol) in $CHCl_3$ (1.5 mL), a solution of $Zn(NO_3)_2$•$6H_2O$ (1.18 mg, 4.0 μmol) in MeOH (4.5 mL) was added dropwise. The mixture was heated at 50 ºC for 10 h and then added to a solution of NH_4PF_6 (80 mg in 20 mL MeOH). After a while, a precipitate was formed, washed with MeOH for three times by centrifugation, dried in vacuum to give the product as a red solid (9.0 mg, 96 % yield). ^{1}H NMR

(500 MHz, CD$_3$CN, 300 K) δ 9.32-9.27 (m, 72H, tpy$^{\mathrm{C}}$-$H^{3',5'}$, tpy$^{\mathrm{A}}$-$H^{3',5'}$, tpy$^{\mathrm{B}}$-$H^{3',5'}$), 9.13 (s, 24H, tpy$^{\mathrm{D}}$-$H^{3',5'}$), 8.92 – 8.65 (m, 108H, tpy$^{\mathrm{A}}$-$H^{3,3''}$, tpy$^{\mathrm{C}}$-$H^{3,3''}$, tpy$^{\mathrm{B}}$-$H^{3,3''}$, tpy$^{\mathrm{D}}$-$H^{3,3''}$, Ph-H^{h}), 8.41 (m, 48H, Ph-H^{a}, Ph-H^{f}, Ph-H^{g}, Ph-H^{i}), 8.35-8.27 (m, 72H, tpy$^{\mathrm{A}}$-$H^{4,4''}$, tpy$^{\mathrm{C}}$-$H^{4,4''}$, Ph-H^{j} , Ph-H^{b}), 8.07 – 7.95 (m, 108H, tpy$^{\mathrm{A}}$-$H^{6,6''}$, tpy$^{\mathrm{C}}$-$H^{6,6''}$, tpy$^{\mathrm{B}}$-$H^{4,4''}$, tpy$^{\mathrm{D}}$-$H^{4,4''}$, Ph-H^{k}), 7.83 (d, J = 8.9 Hz, 12H, Ph-H^{c}), 7.73 (d, J = 8.9 Hz, 24H, Ph-H^{e}), 7.53-7.48 (m, 120H, tpy$^{\mathrm{B}}$-$H^{6,6''}$, tpy$^{\mathrm{D}}$-$H^{6,6''}$, tpy$^{\mathrm{C}}$-$H^{5,5''}$, tpy$^{\mathrm{A}}$-$H^{5,5''}$, Ph-H^{l}), 7.36 (d, J = 8.9 Hz, 24H, Ph-H^{d}), 7.31 – 7.19 (m, 60H, tpy$^{\mathrm{B}}$-$H^{5,5''}$, tpy$^{\mathrm{D}}$-$H^{5,5''}$, Ph-H^{n}), 7.15 (d, J = 8.1 Hz, 24H, Ph-H^{m}), 7.04 (d, J = 8.3 Hz, 12H, Ph-H^{o}), 4.06 (t, J = 6.7 Hz, 12H), 3.80 (m, 36H), 1.64 – 1.18 (m, 84H), 1.06 – 0.83 (m, 48H), 0.68 (m, 60H), 0.30 (m, 72H). ^{13}C NMR (125MHz, CD$_3$CN, 300 K) δ 159.06, 156.45, 156.21, 153.60, 153.31, 150.52, 148.85, 142.50, 139.18, 138.37, 133.99, 133.61, 129.46, 128.60, 125.72, 125.39, 125.18, 123.21, 116.81, 100.94, 91.41, 69.21, 49.85, 32.29, 32.24, 31.18, 29.92, 27.05, 26.40, 23.31, 23.04, 22.94, 14.30, 13.90, 13.85. ESI-TOF (*m/z*): 1526.0 [M-17PF$_6^{-}$]$^{17+}$ (calcd *m/z*: 1526.0), 1433.2 [M-18PF$_6^{-}$]$^{18+}$ (calcd *m/z*: 1433.2), 1350.1 [M-19PF$_6^{-}$]$^{19+}$ (calcd *m/z*: 1350.1), 1275.4 [M-20PF$_6^{-}$]$^{20+}$ (calcd *m/z*: 1275.4), 1207.7 [M-21PF$_6^{-}$]$^{21+}$ (calcd *m/z*: 1207.7), 1146.2 [M-22PF$_6^{-}$]$^{22+}$ (calcd *m/z*: 1146.2).

5. ESI-MS spectra data of ligand LA-LE and complexes G1-G5.

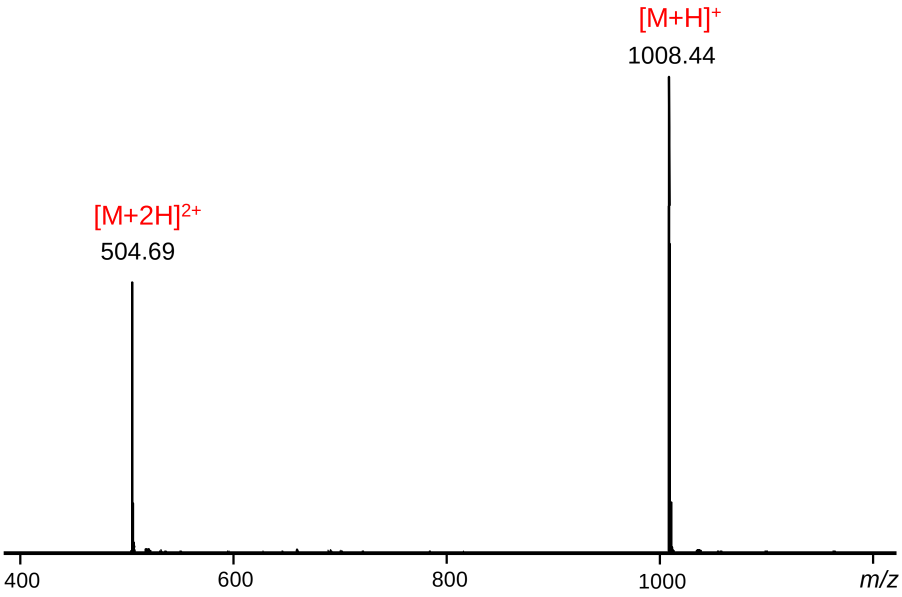


Figure S3. ESI-MS spectrum of **LA**.

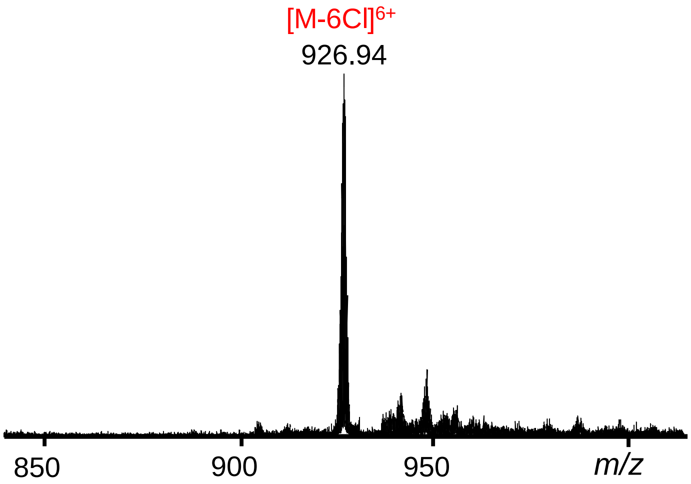


Figure S4. ESI-MS spectrum of **LB**.

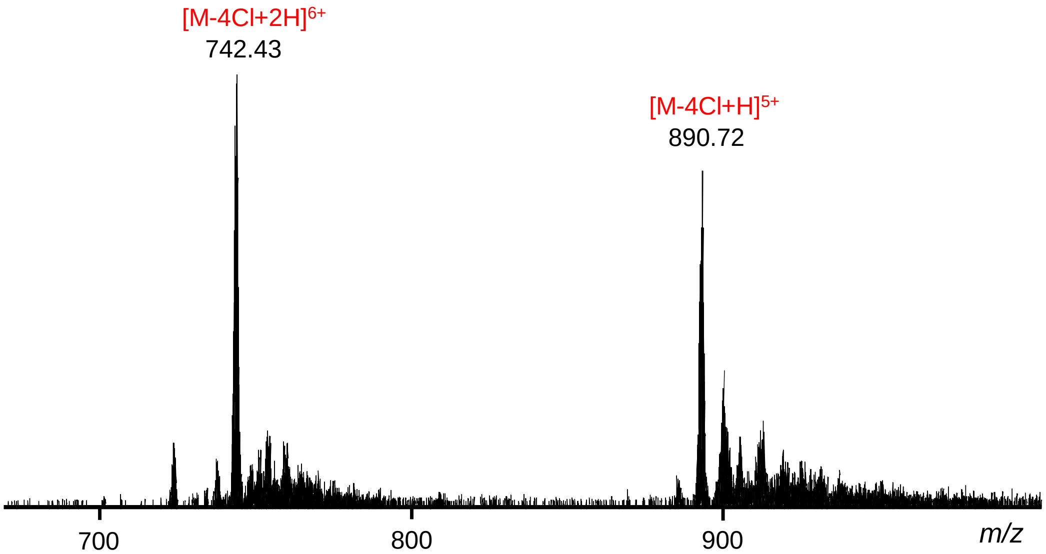


Figure S5. ESI-MS spectrum of **LC**.

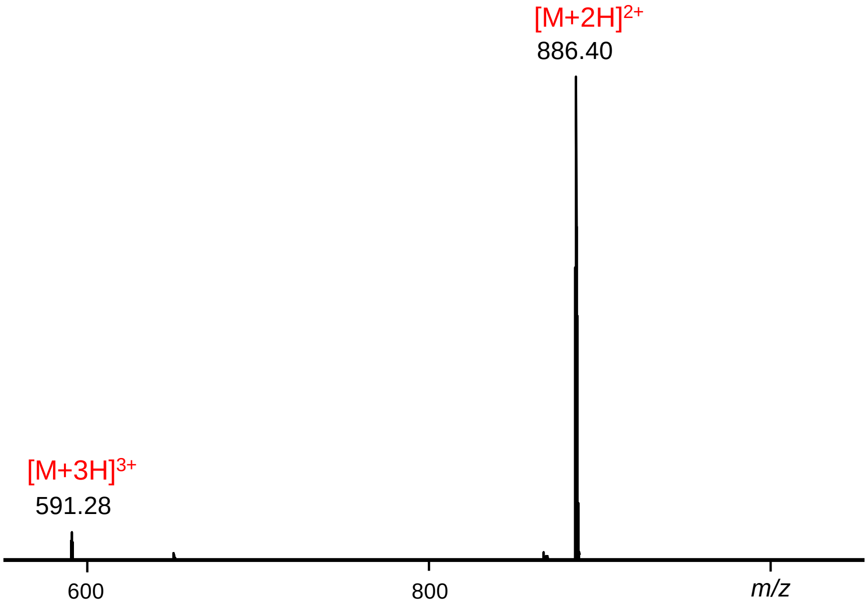


Figure S6. ESI-MS spectrum of **LD**.

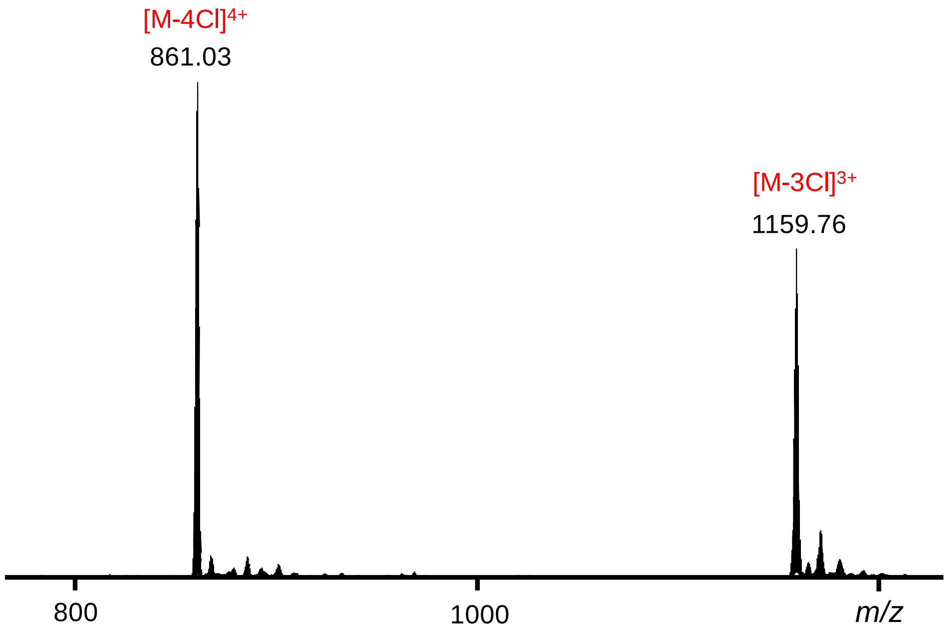


Figure S7. ESI-MS spectrum of **LE**.

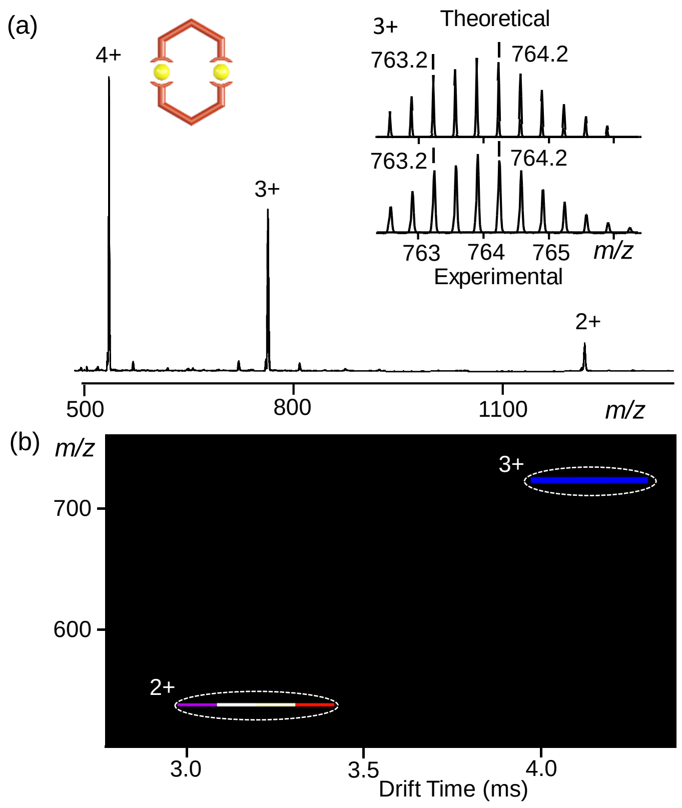


Figure S8. (a) ESI-MS and (b) TWIM-MS plot (*m/z* vs. drift time) of complex **G1 [LA_2Zn_2]**.

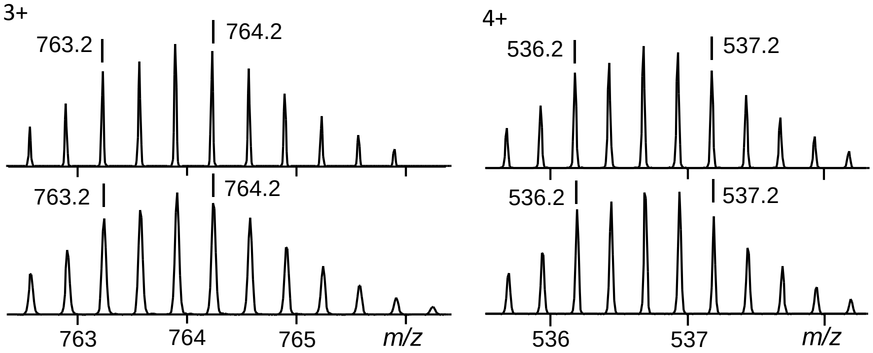


Figure S9. Calculated (top) and Measured (bottom) isotope patterns for different charge states observed from **G1** (PF_6^- as counterion).

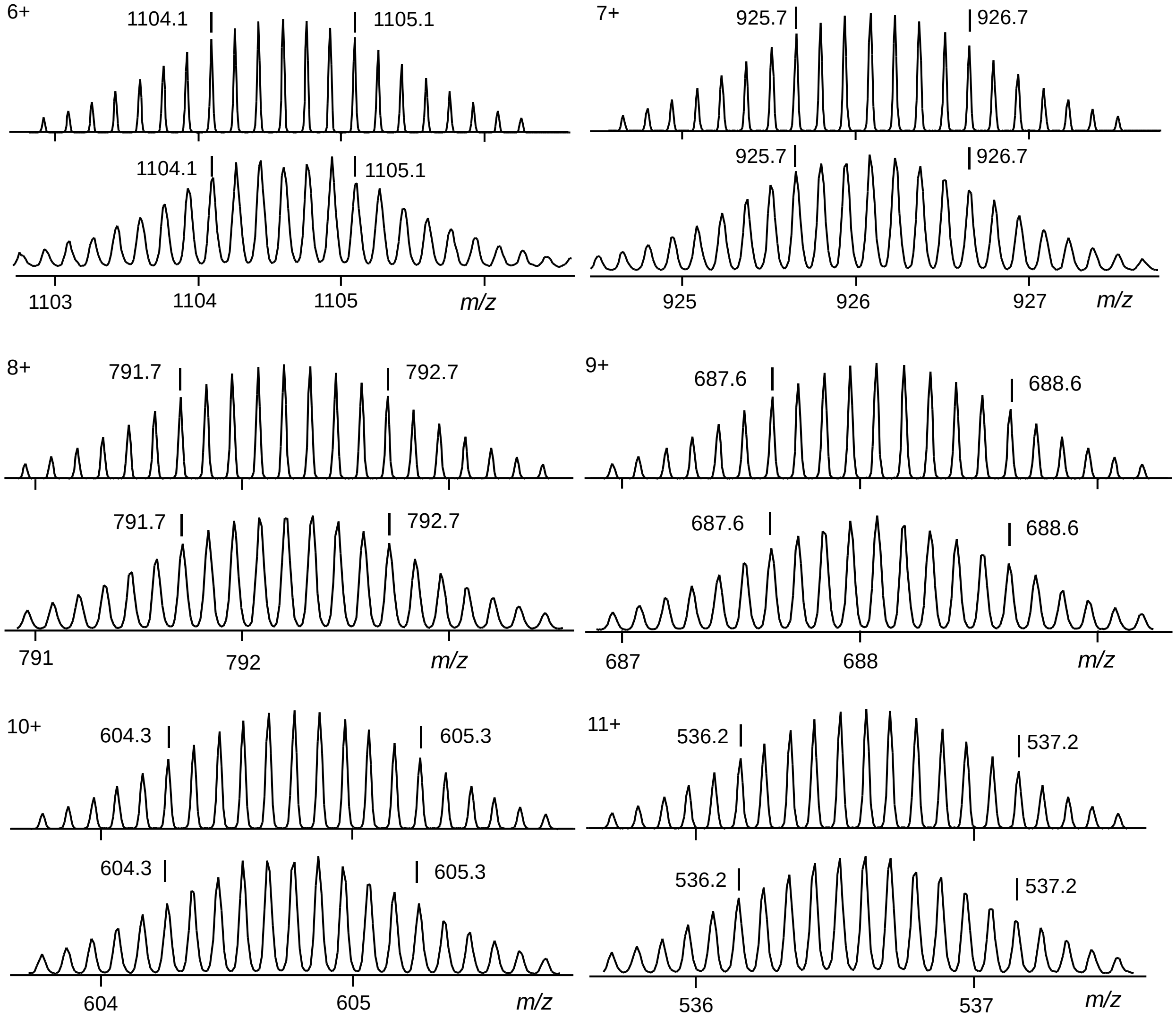


Figure S10. Calculated (top) and Measured (bottom) isotope patterns for different charge states observed from **G2[LBZn3]** (PF_6^- as counterion).

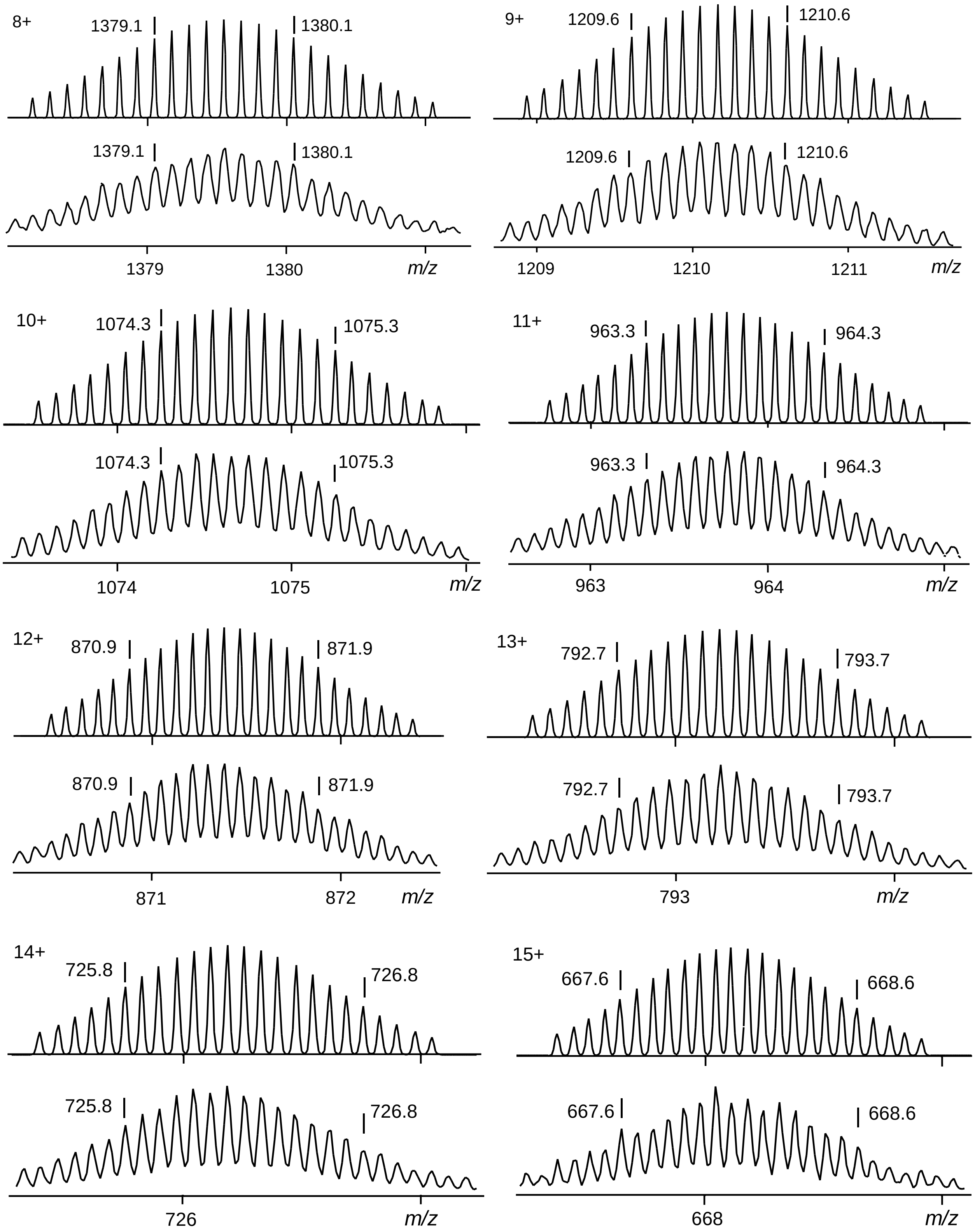
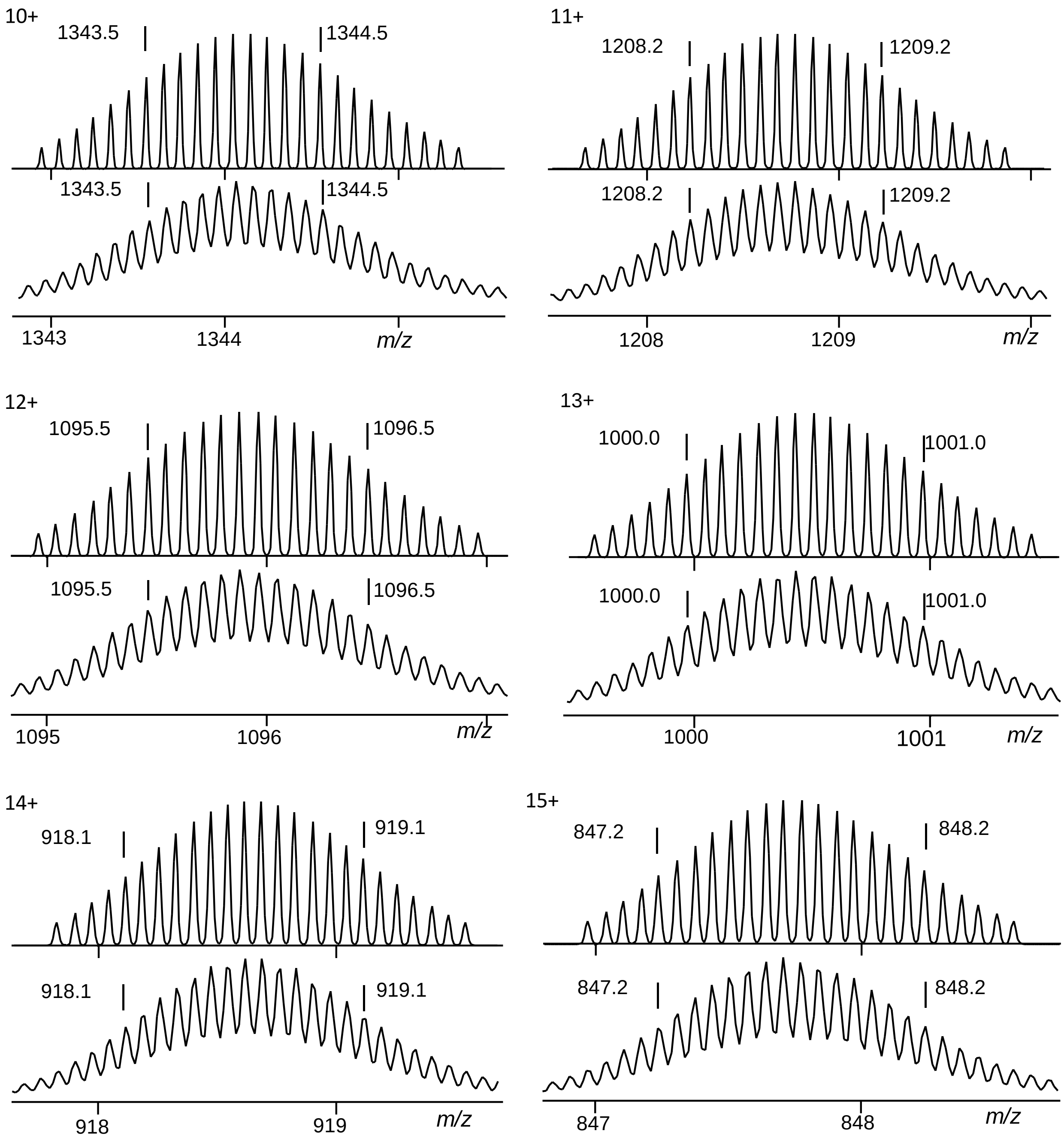


Figure S11. Calculated (top) and Measured (bottom) isotope patterns for different charge states observed from **G3 [LC$_2$Zn$_6$]**. (PF$_6^-$ as counterion).


10+
1343.5
1344.5
1343.5
1344.5
1343
1344
m/z
11+
1208.2
1209.2
1208.2
1209.2
1208
1209
m/z
12+
1095.5
1096.5
1095.5
1096.5
1095
1096
m/z
13+
1000.0
1001.0
1000.0
1001.0
1000
1001
m/z
14+
918.1
919.1
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848.2
847
848
m/z

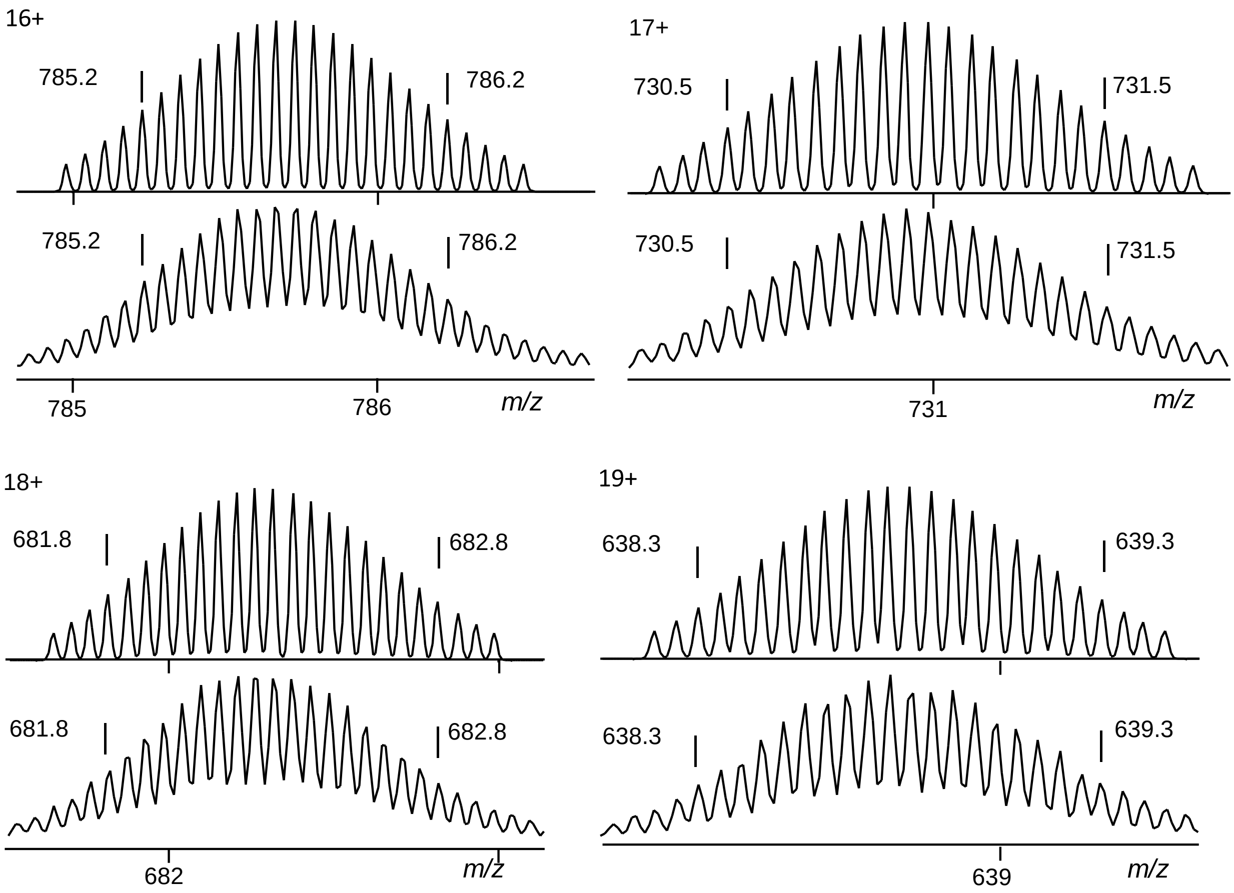

Figure S12. Calculated (top) and Measured (bottom) isotope patterns for different charge states observed from **G4 [LD$_6$Zn$_{12}$]**. (PF$_6^-$ as counterion).

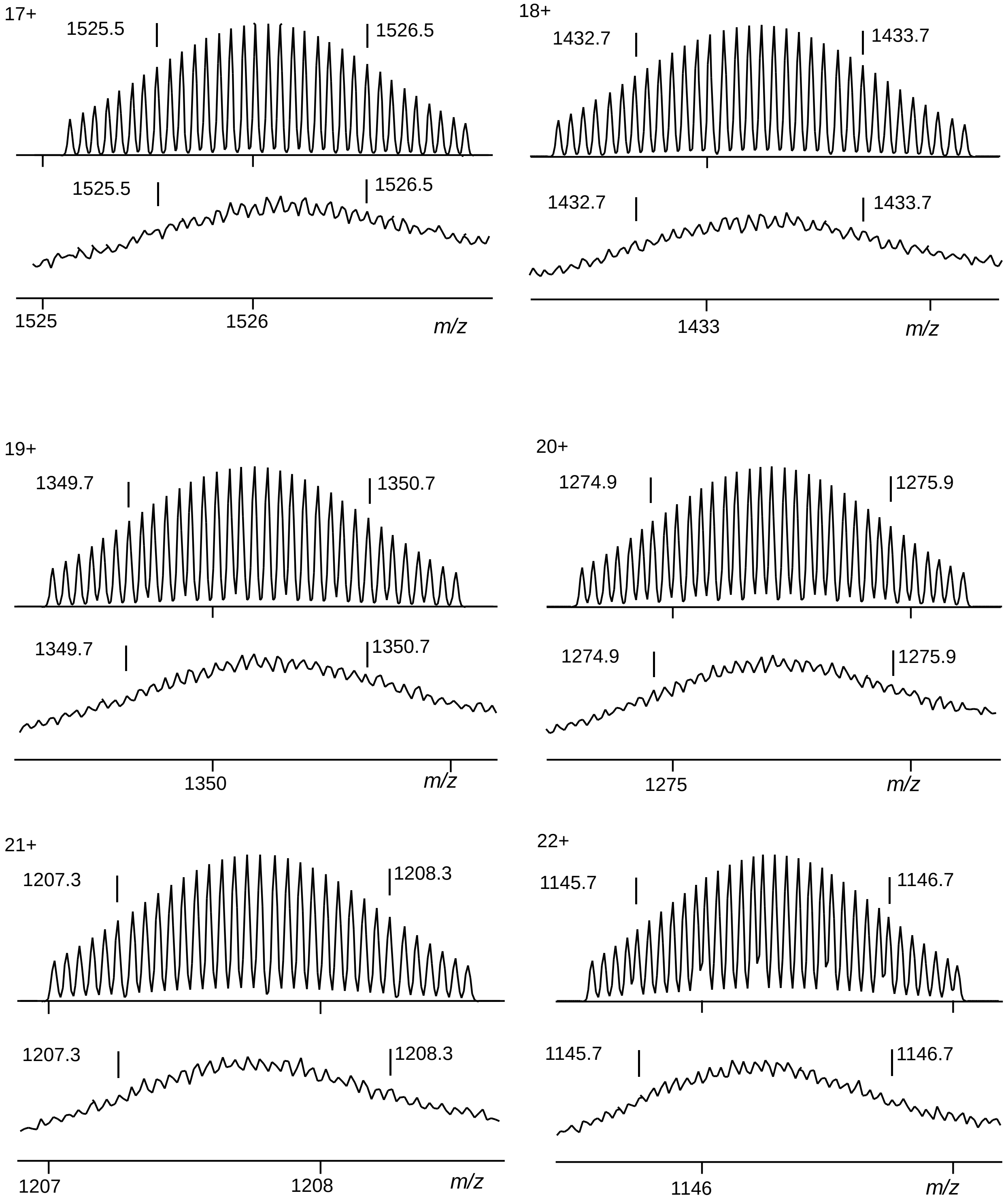

Figure S13. Calculated (top) and Measured (bottom) isotope patterns for different charge states observed from **G5 [LE$_6$Zn$_{12}$]**. (PF$_6^-$ as counterion).

6. ^{1}H NMR, ^{13}C NMR, 2D COSY NMR, 2D NOESY NMR spectra

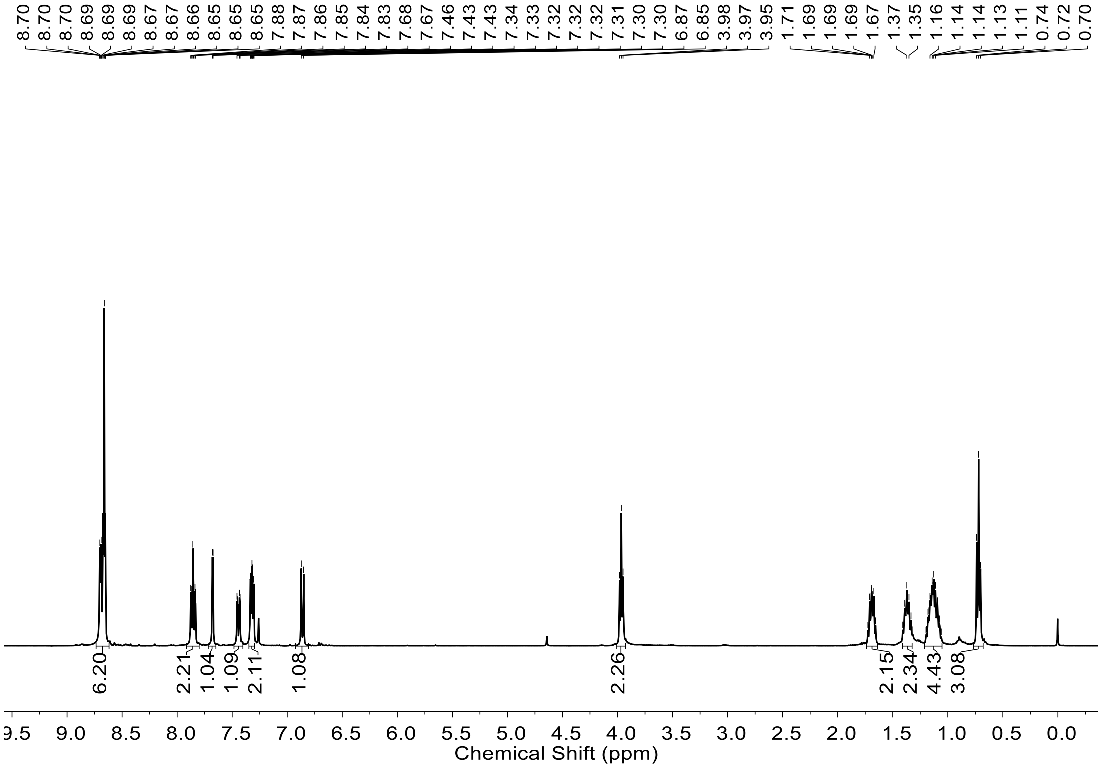

Figure S14. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S-4**.

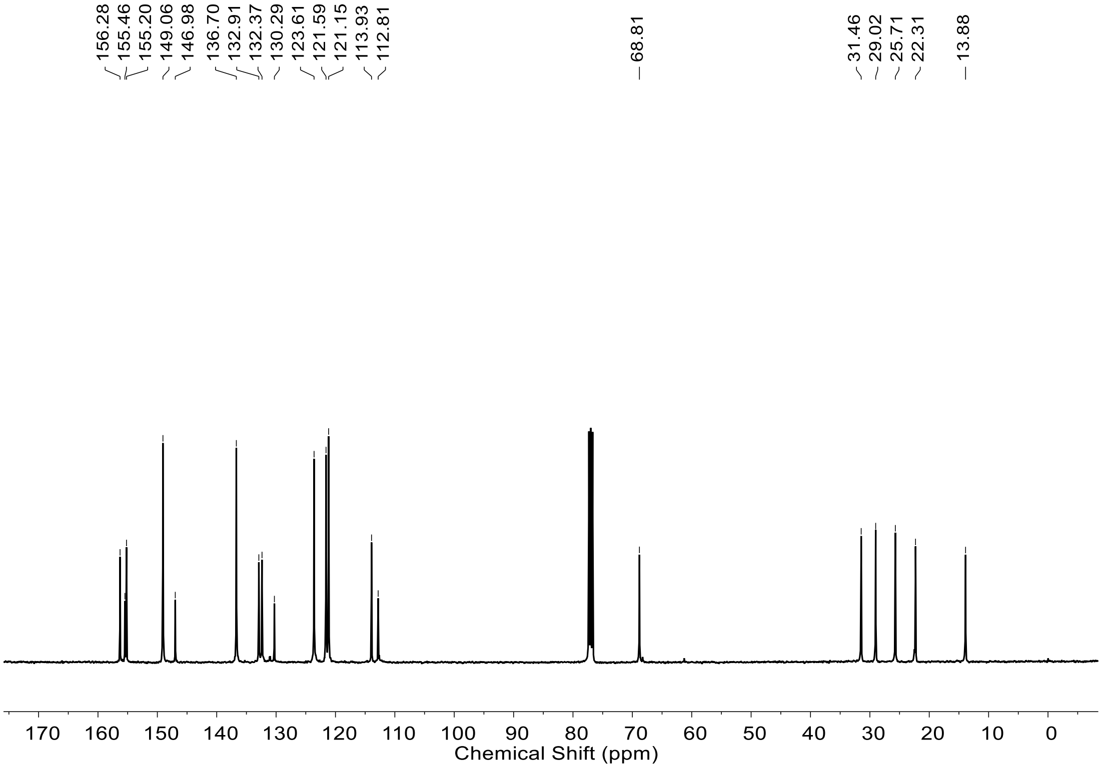

Figure S15. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ligand **S-4**.

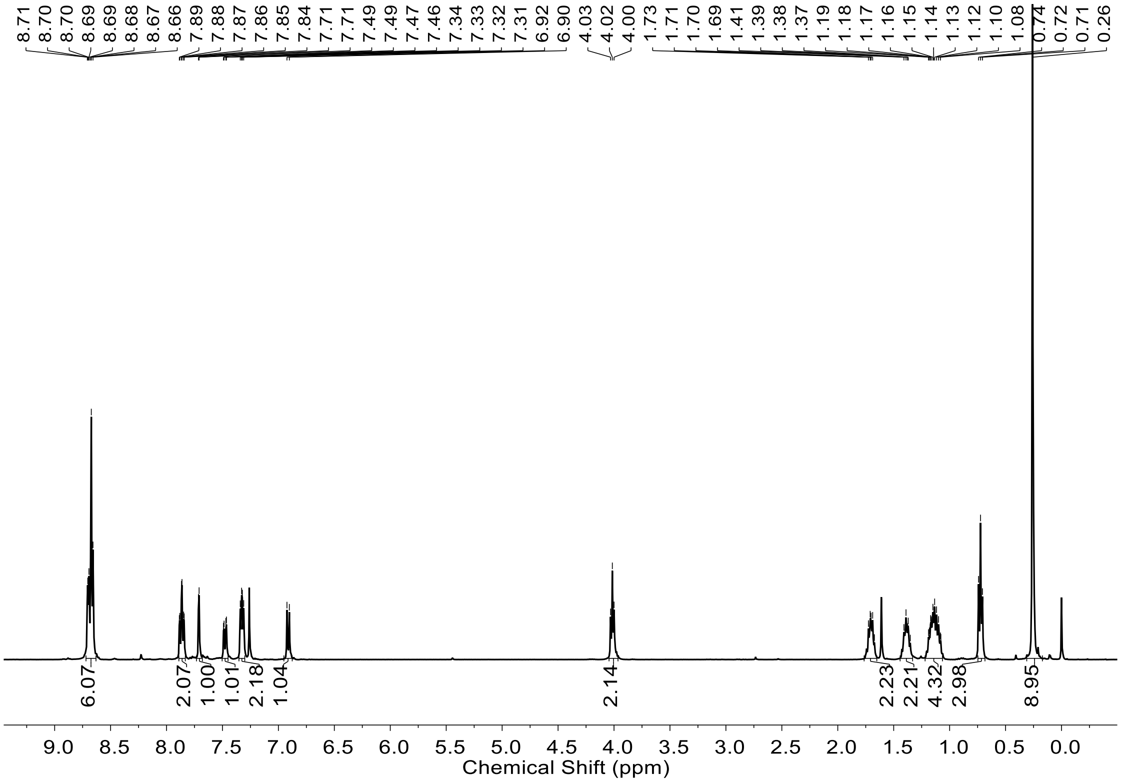

Figure S16. ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of **S-5**.

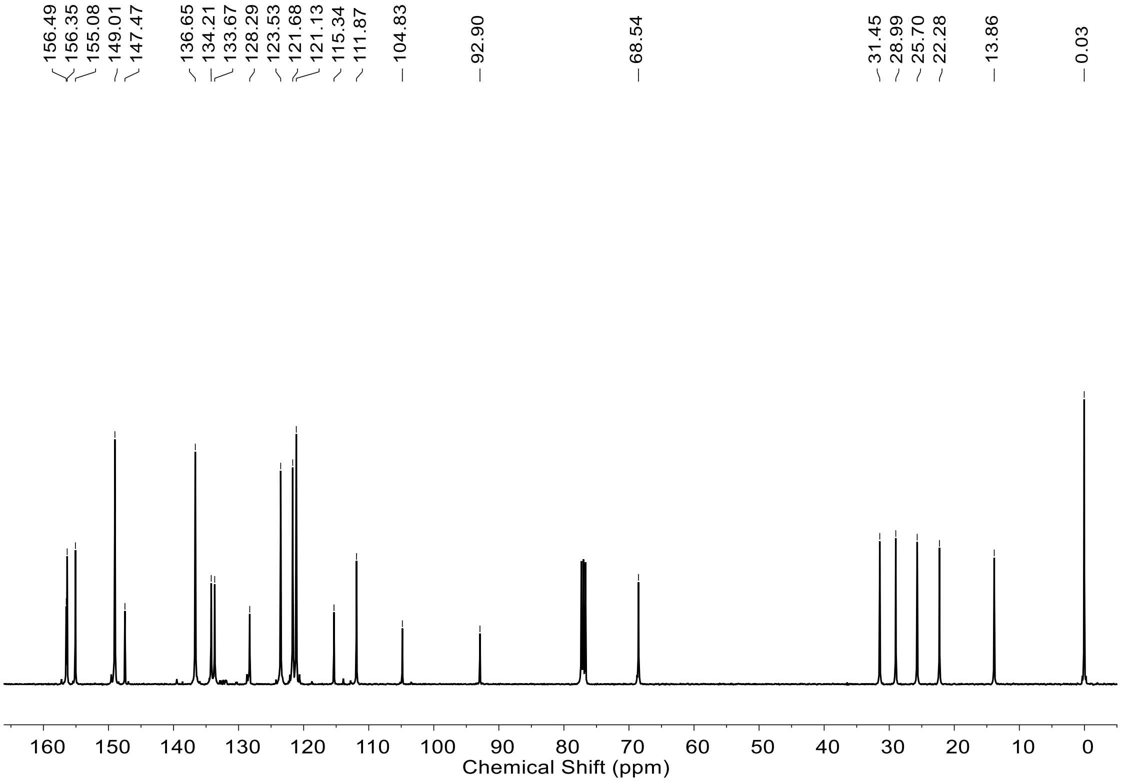

Figure S17. ^{13}C NMR (100 MHz, CDCl$_3$) spectrum of ligand **S-5**.

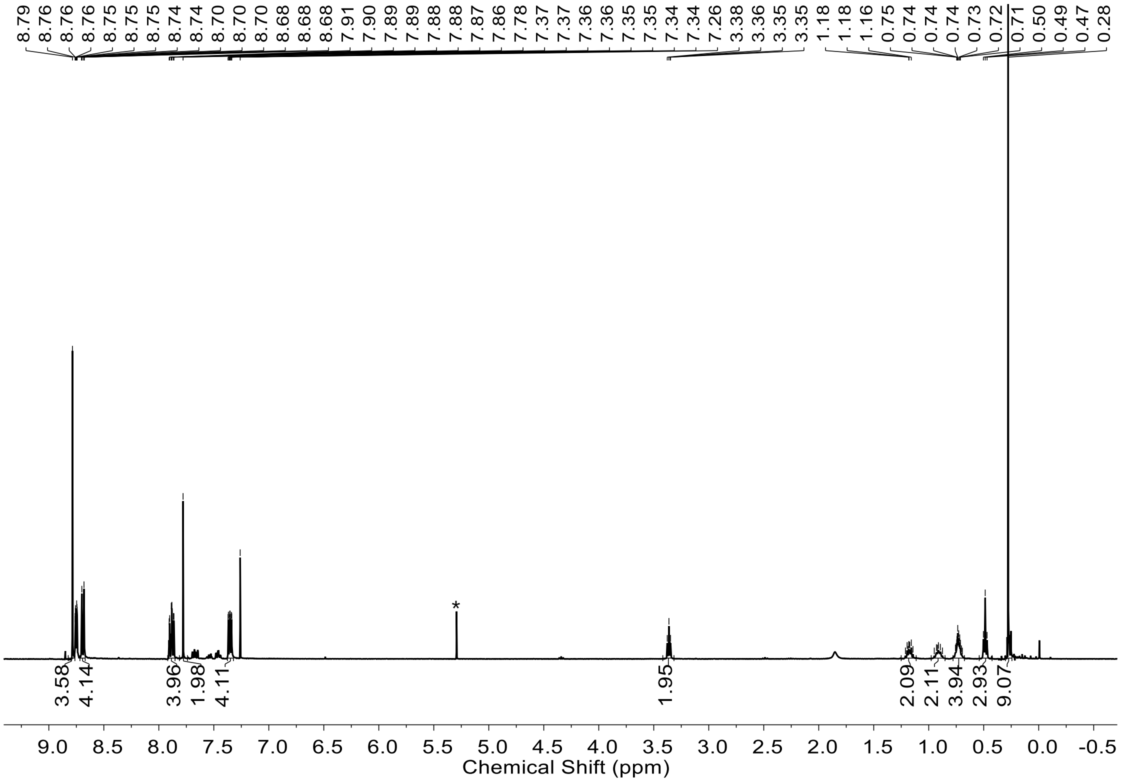

Figure S18. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S-8** (asterisk represent CH_2Cl_2).

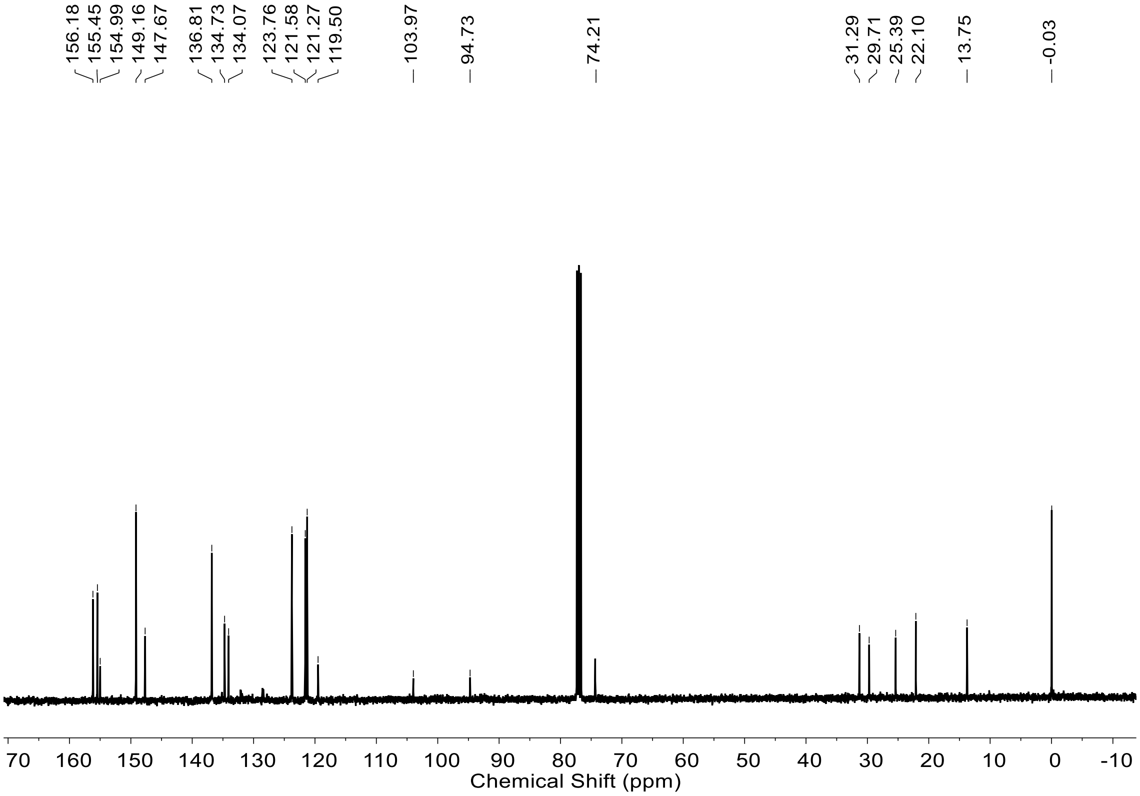

Figure S19. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ligand **S-8**.

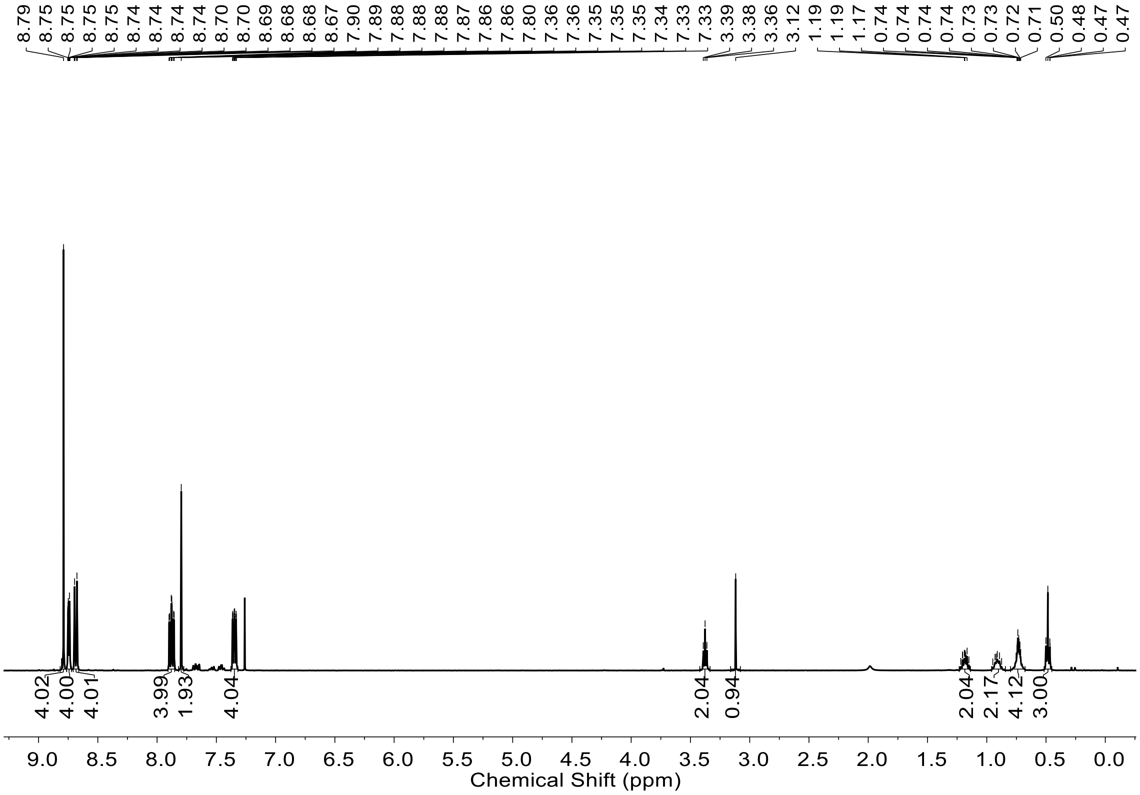

Figure S20. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S-9**.

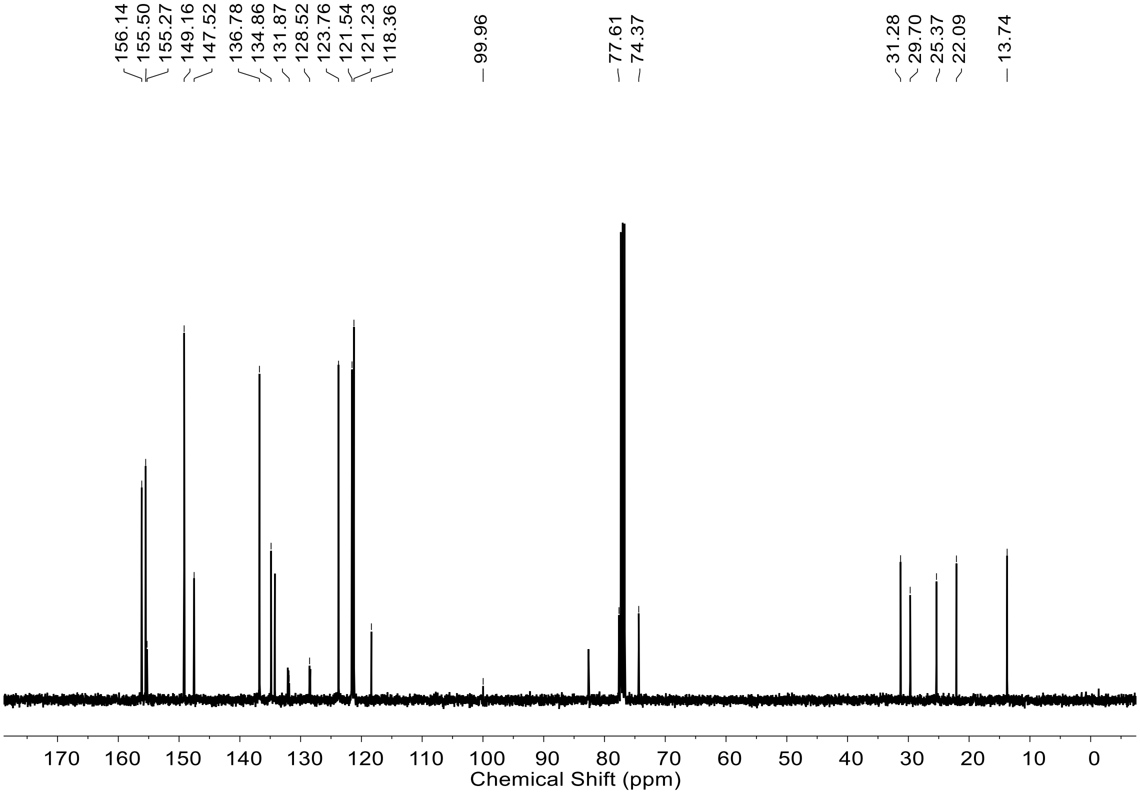

Figure S21. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ligand **S-9**.

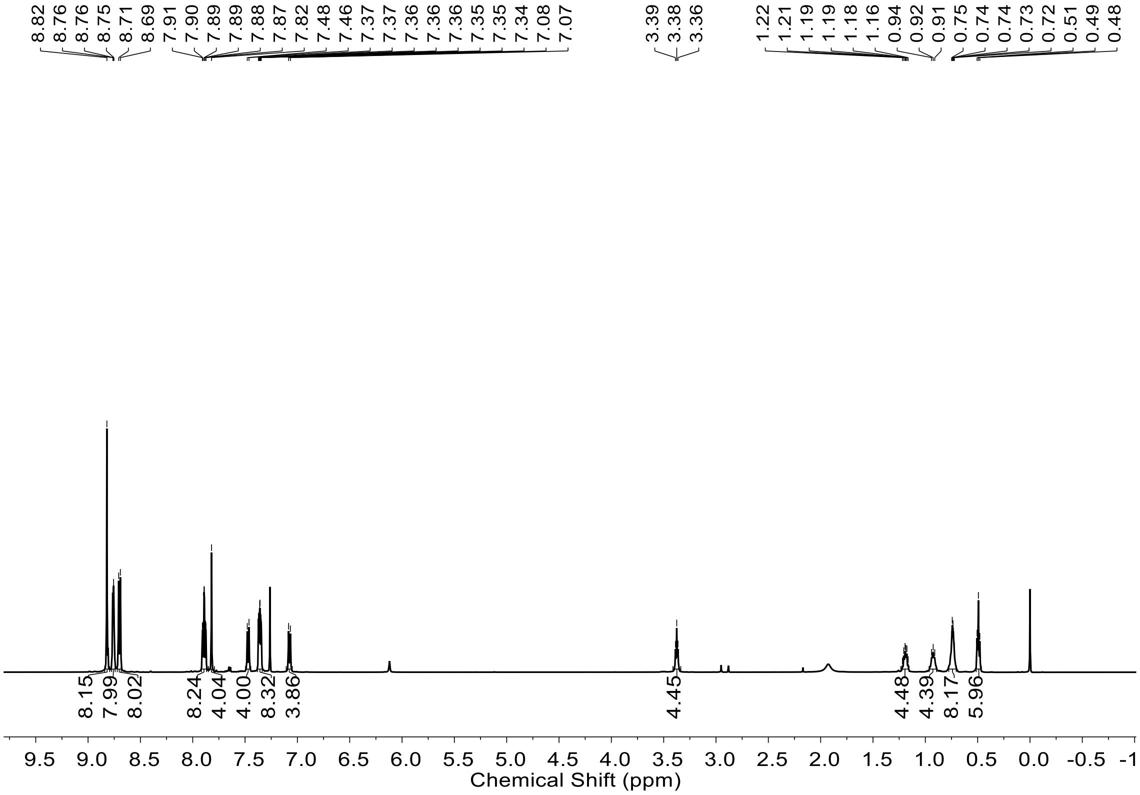

Figure S22. ^{1}H NMR (500 MHz, CDCl$_3$) spectrum of **S-12**.

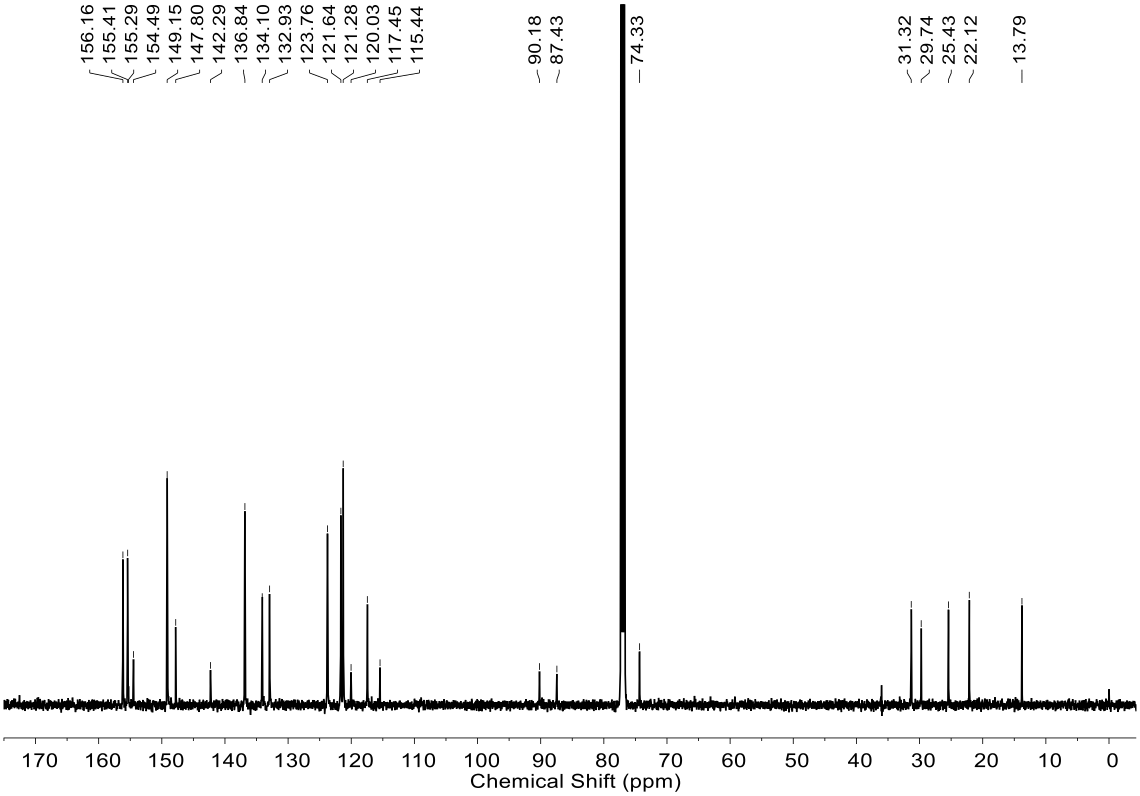

Figure S23. ^{13}C NMR (125 MHz, CDCl$_3$) spectrum of **S-12**.

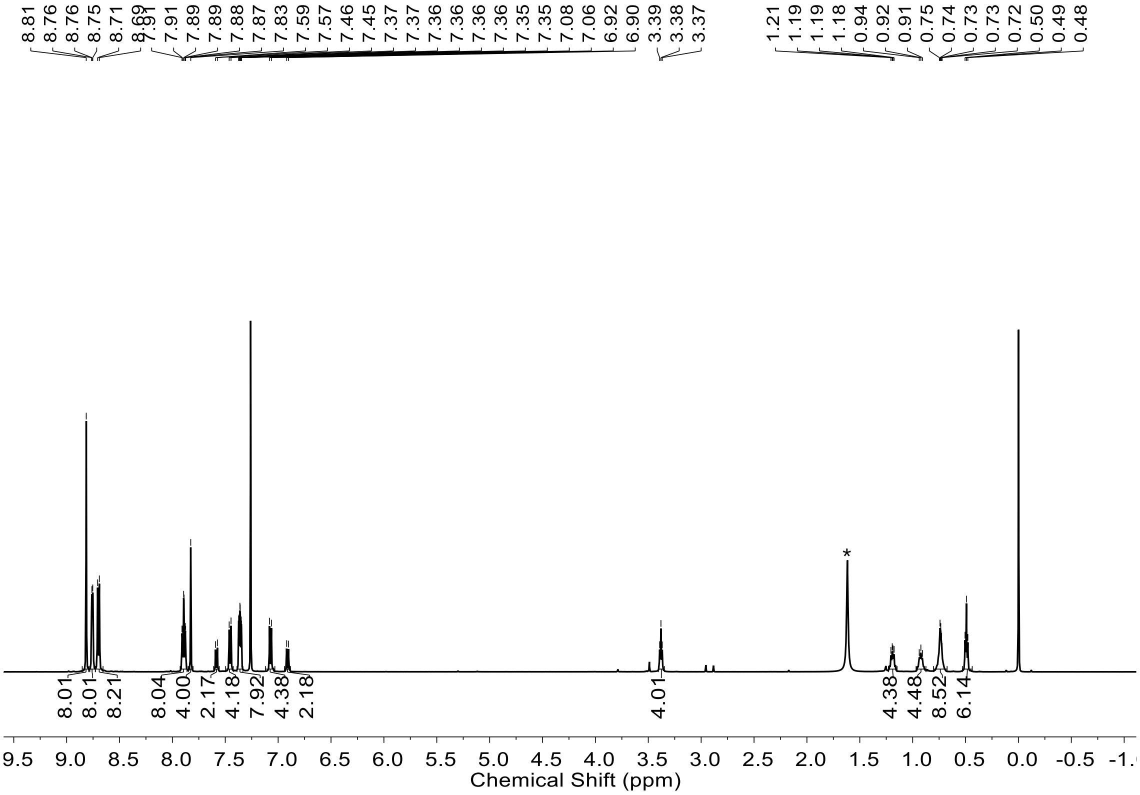

Figure S24. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **S-13** (asterisk represent H_2O).

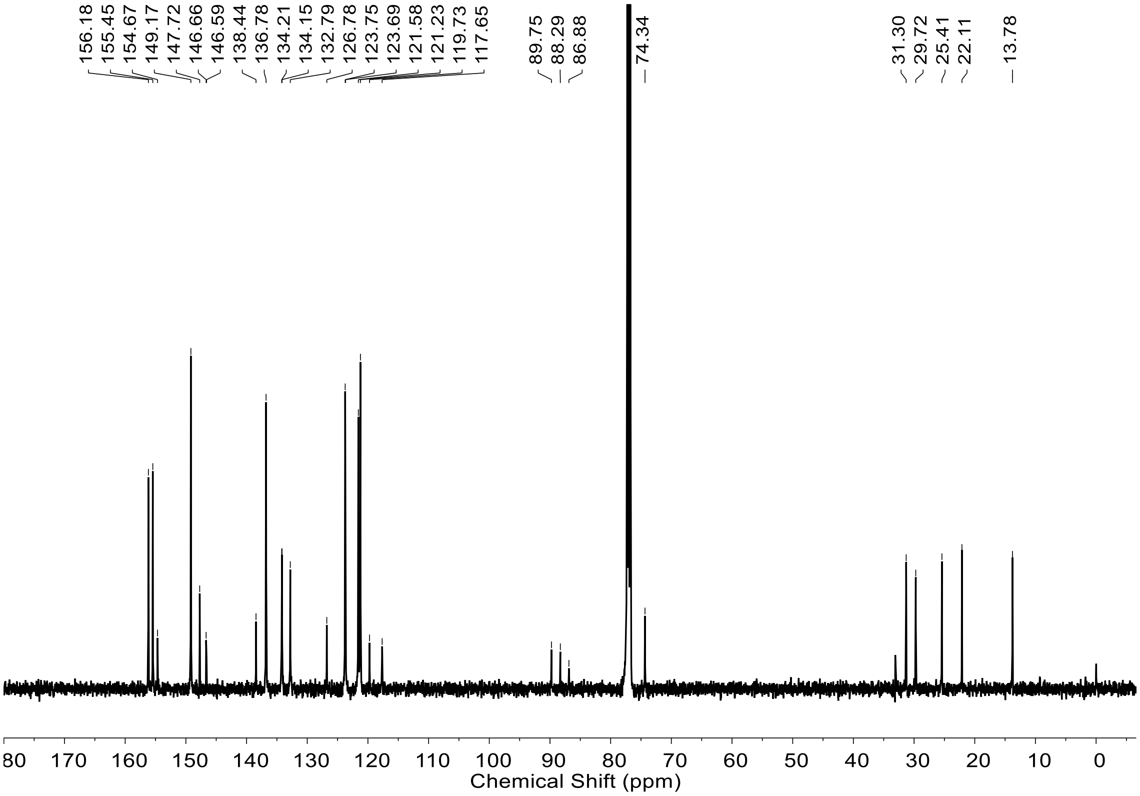

Figure S25. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **S-13**.

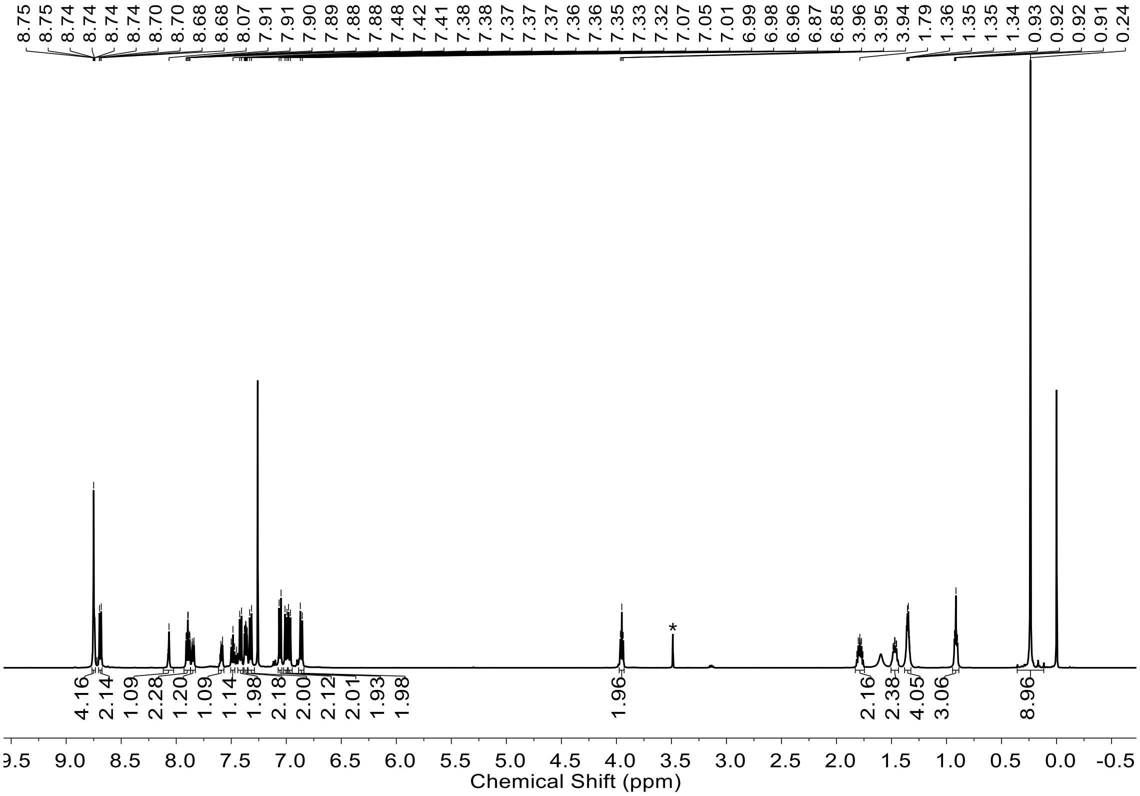

Figure S26. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **S-14** (asterisk represent CH_3OH).

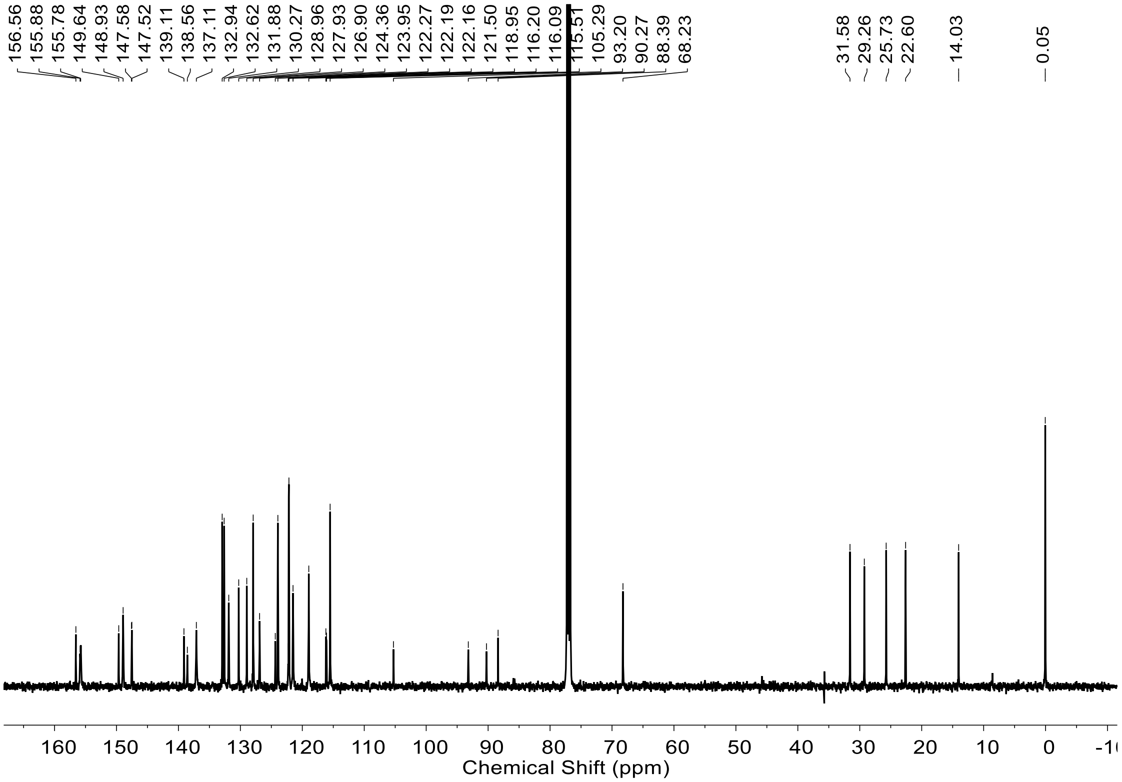

Figure S27. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **S-14**.

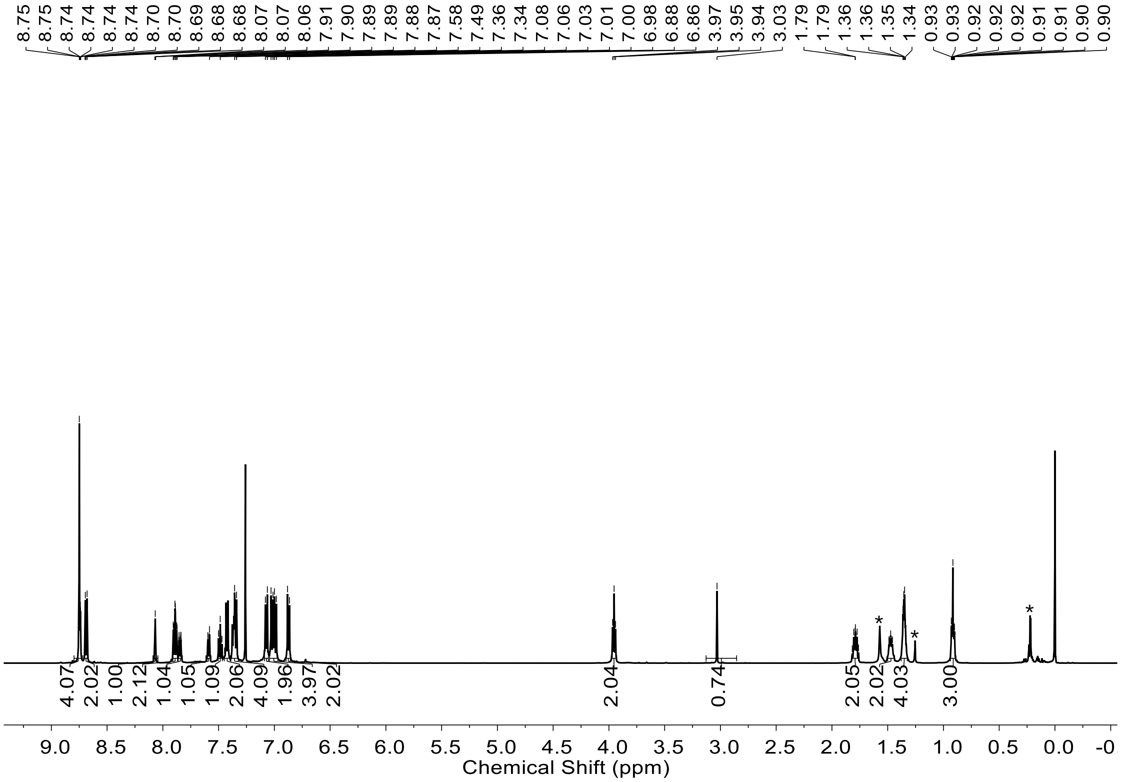

Figure S28. ^{1}H NMR (500 MHz, CDCl$_3$) spectrum of **S-15** (asterisk represent H$_2$O, grease, grease, from left to right).

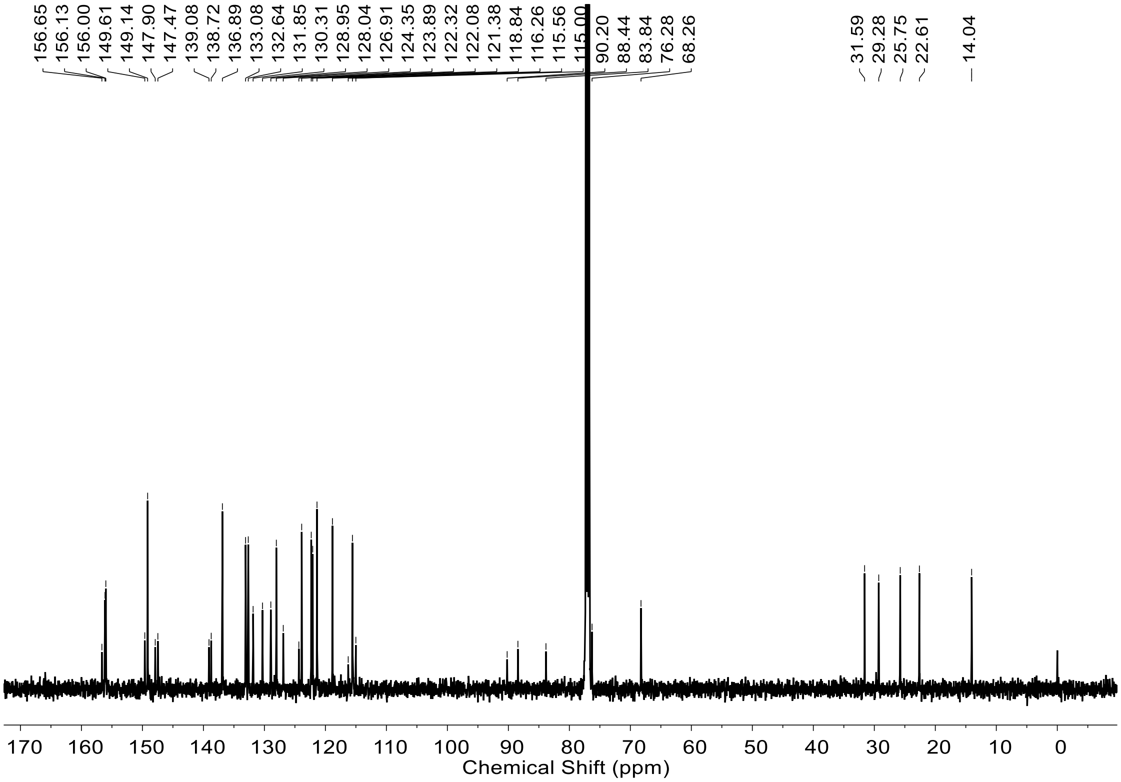

Figure S29. ^{13}C NMR (125 MHz, CDCl$_3$) spectrum of **S-15**.

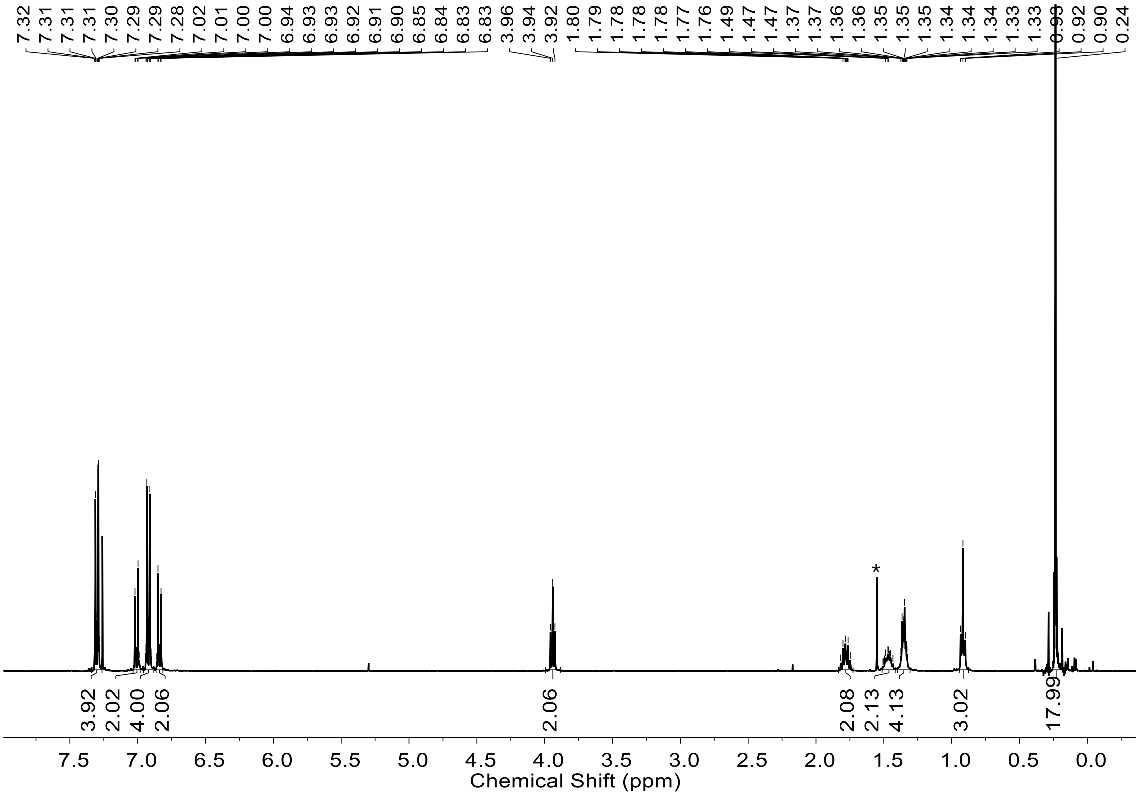

Figure S30. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4** (asterisk represent H_2O).

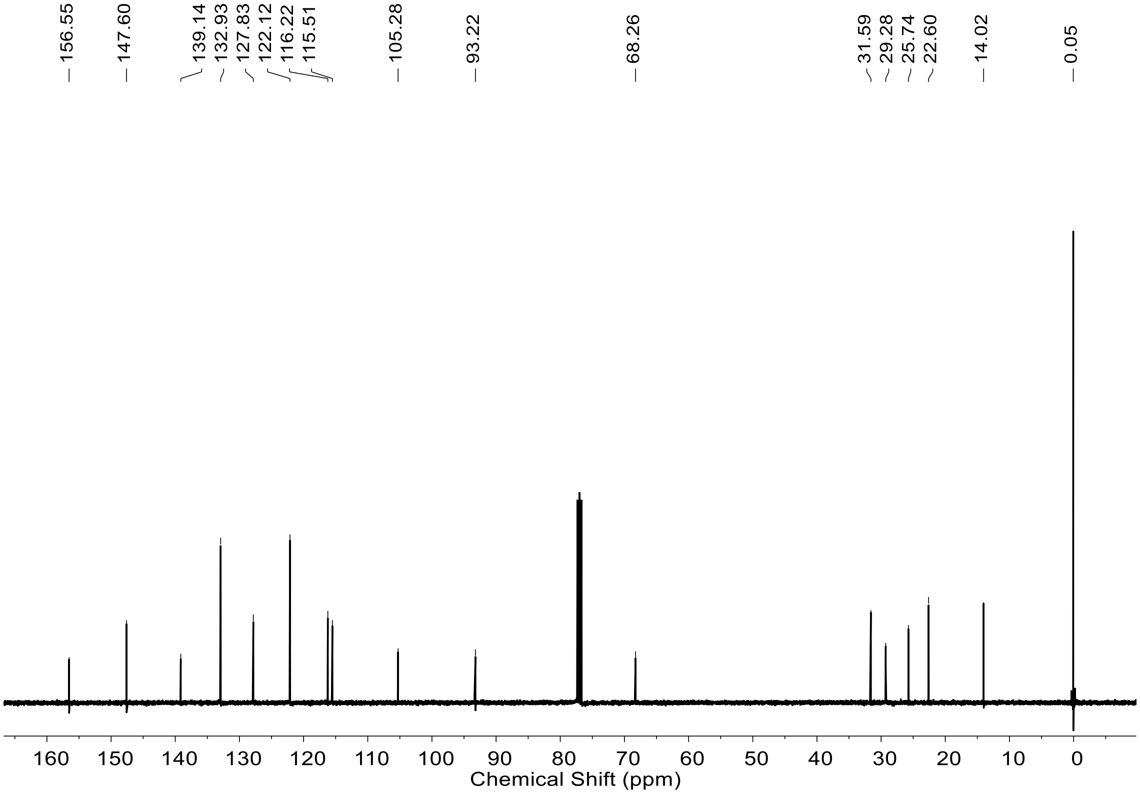

Figure S31. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4**.

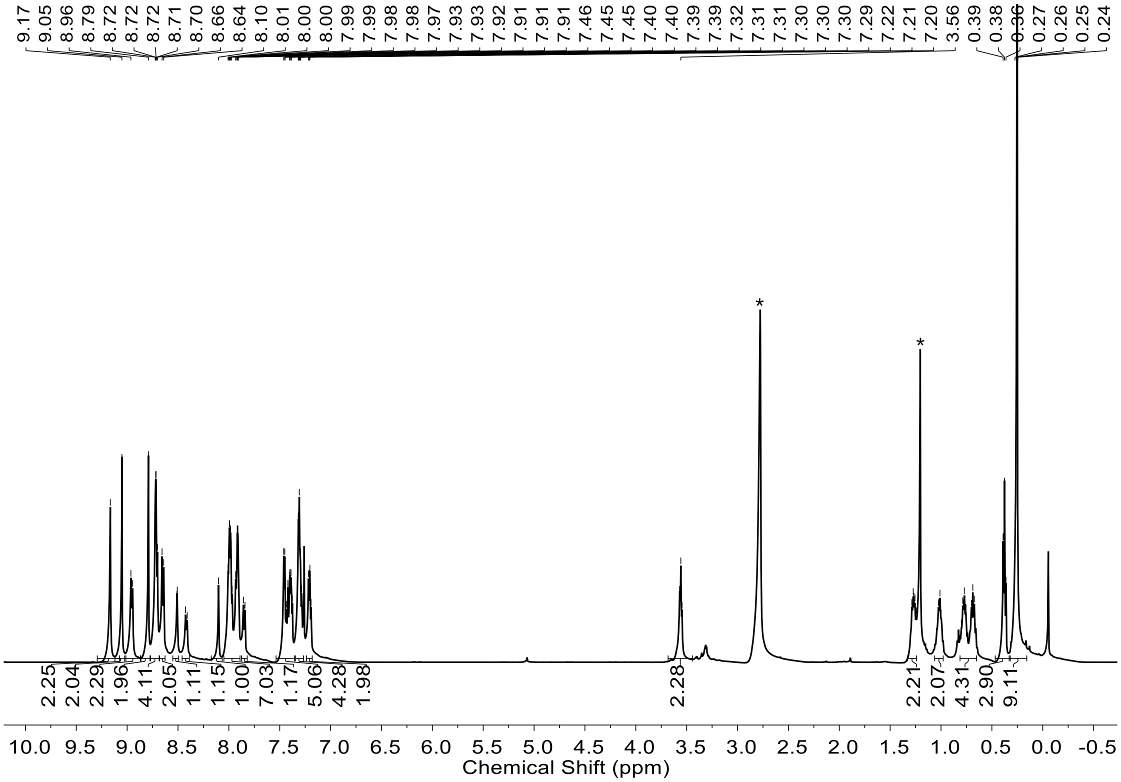

Figure S32. ^{1}H NMR (500 MHz, $CDCl_3$ + 3% CD_3OD) spectrum of **S-18** (asterisks represent residual solvent).

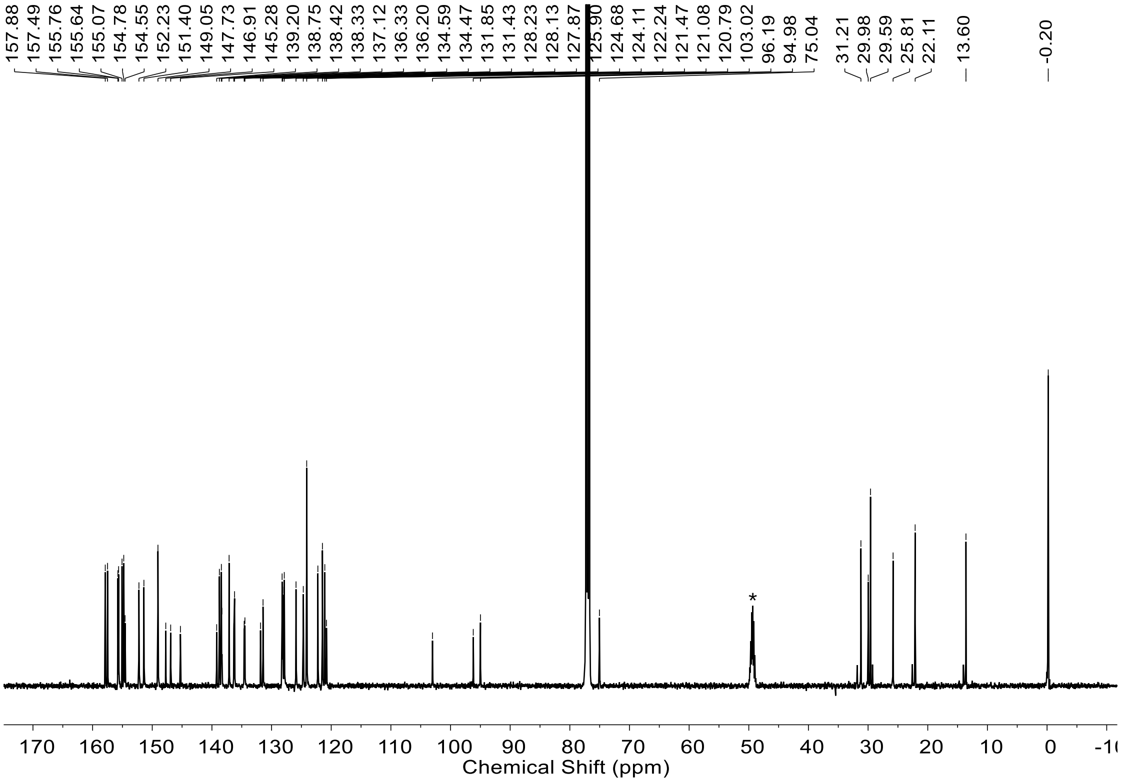

Figure S33. ^{13}C NMR (125 MHz, $CDCl_3$+ 3% CD_3OD) spectrum of **S-18** (asterisk represents residual solvent).

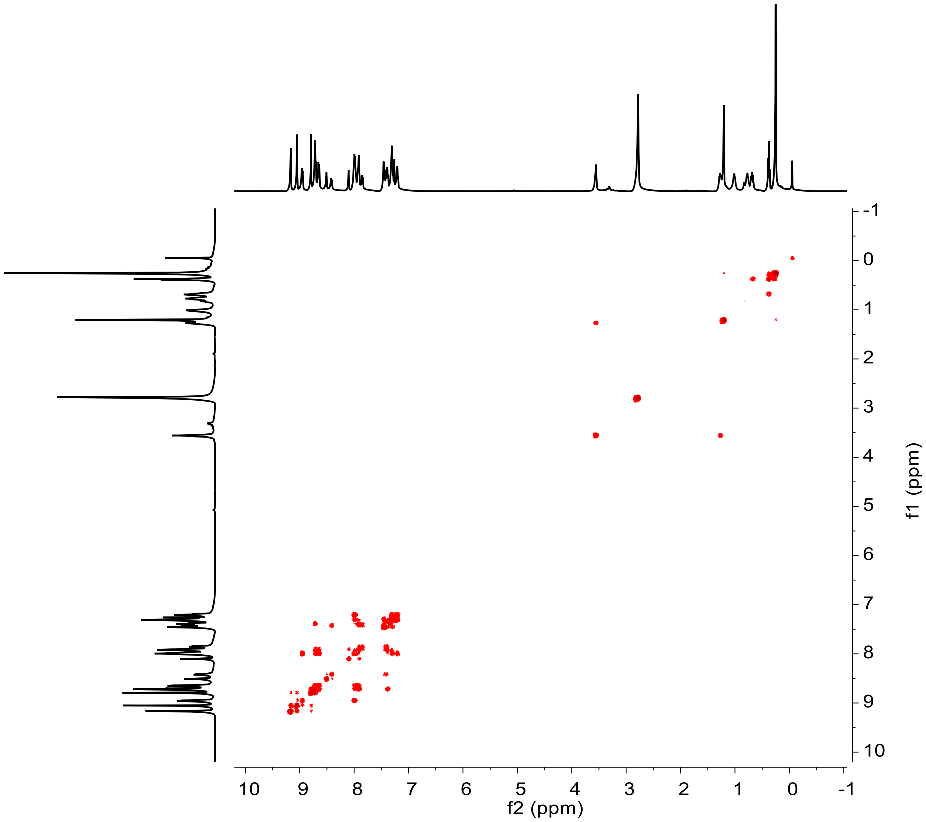

Figure S34. 2D COSY NMR (500 MHz, $CDCl_3$+3% CD_3OD) spectrum of **S-18**.

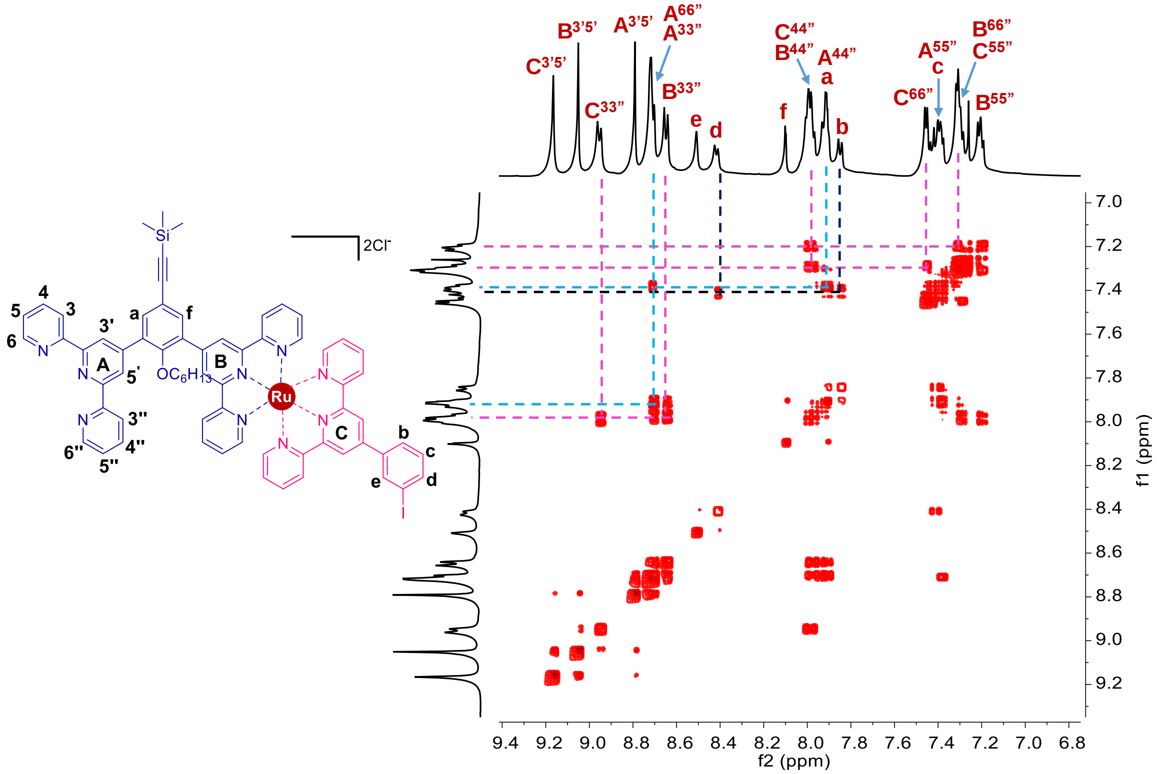

Figure S35. 2D COSY NMR (500 MHz, $CDCl_3$+3% CD_3OD) spectrum of **S-18** (aromatic region).

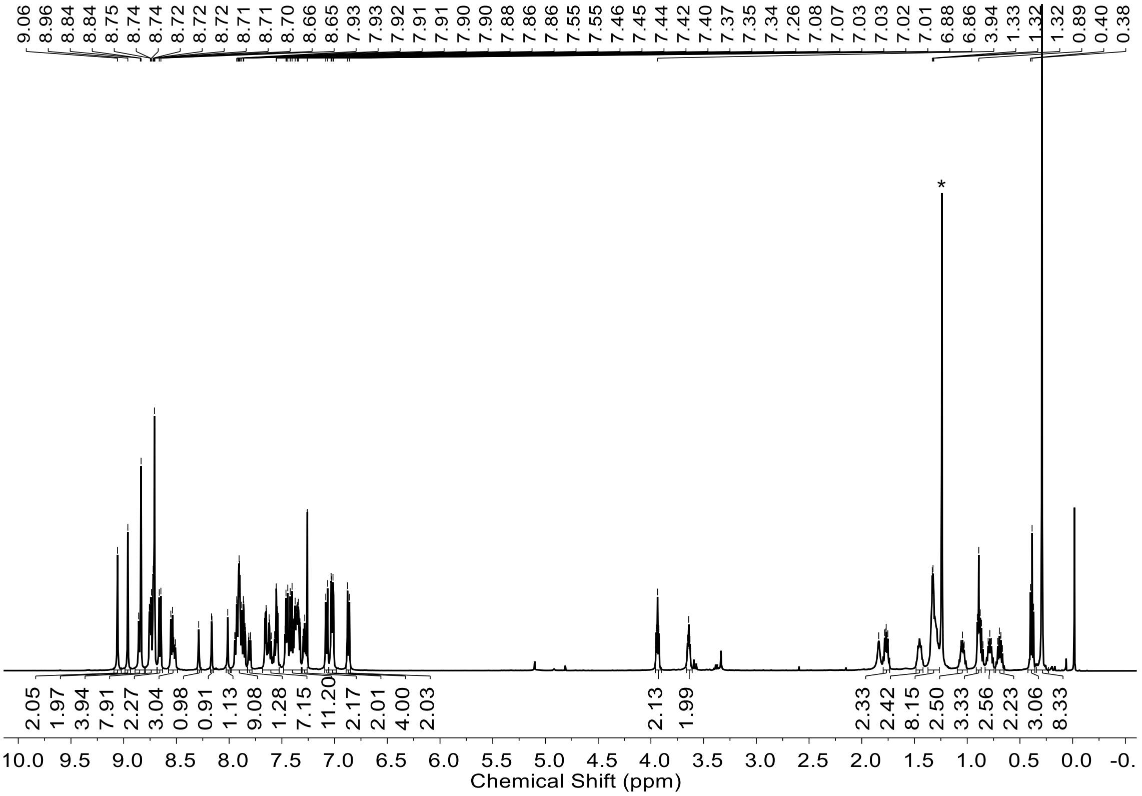

Figure S36. ^{1}H NMR (500 MHz, $CDCl_3$+3% CD_3OD) spectrum of **S-19** (asterisk represents residual solvent).

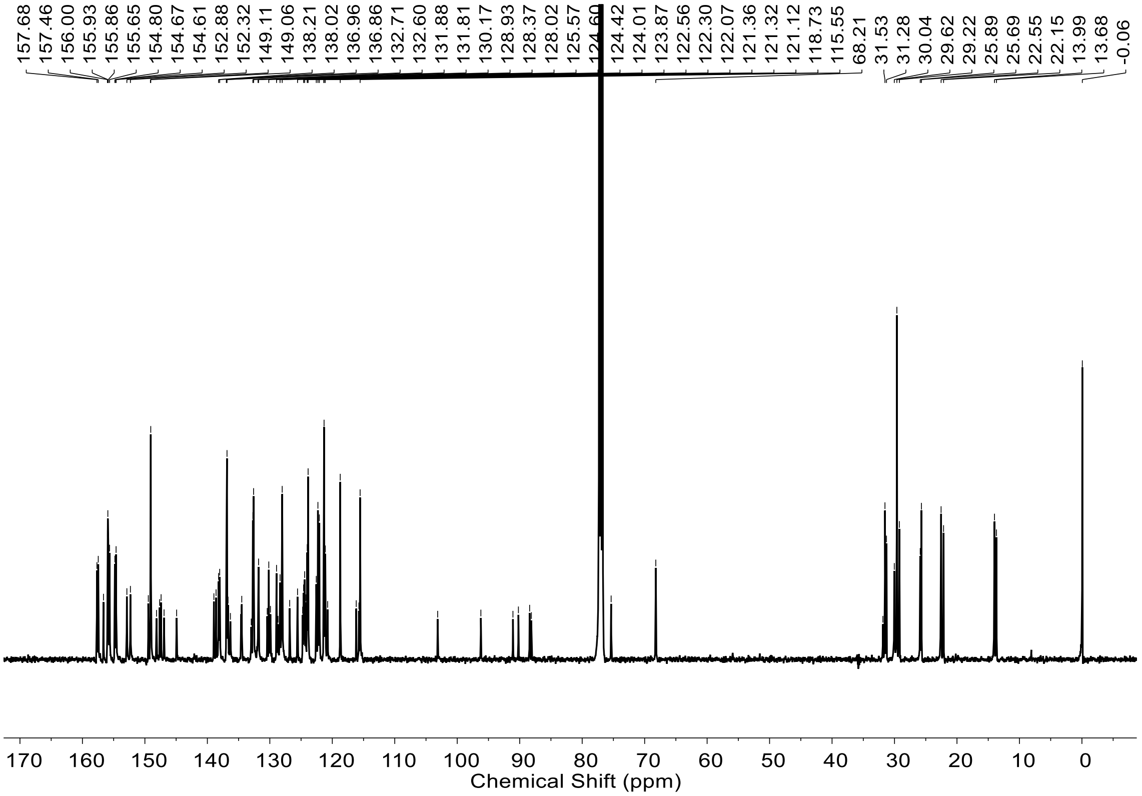

Figure S37. ^{13}C NMR (125 MHz, $CDCl_3$+3% CD_3OD) spectrum of **S-19**.

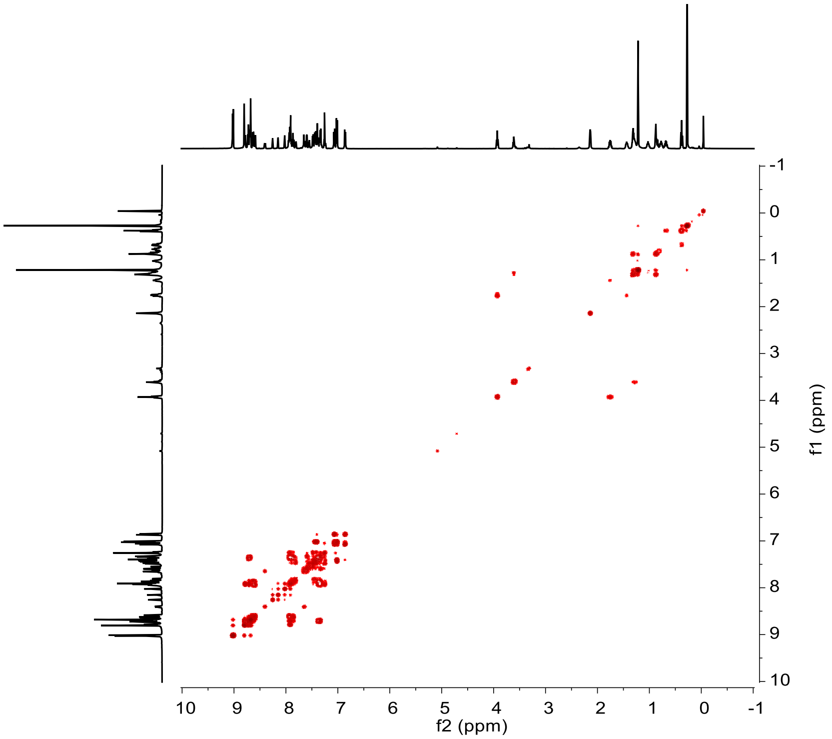

Figure S38. 2D COSY NMR (500 MHz, $CDCl_3$+3% CD_3OD) spectrum of **S-19**.

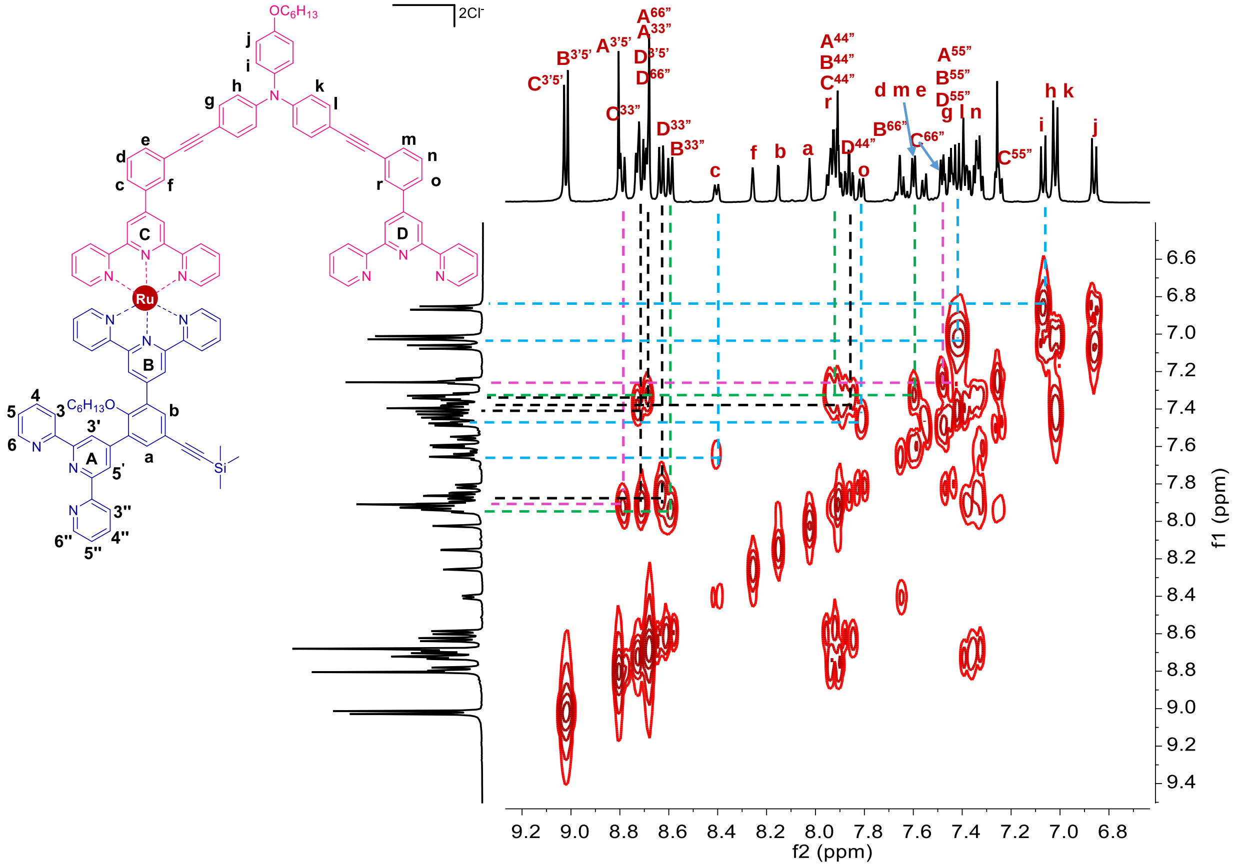

Figure S39. 2D COSY NMR (500 MHz, $CDCl_3$+3% CD_3OD) spectrum of **S-19** (aromatic region).

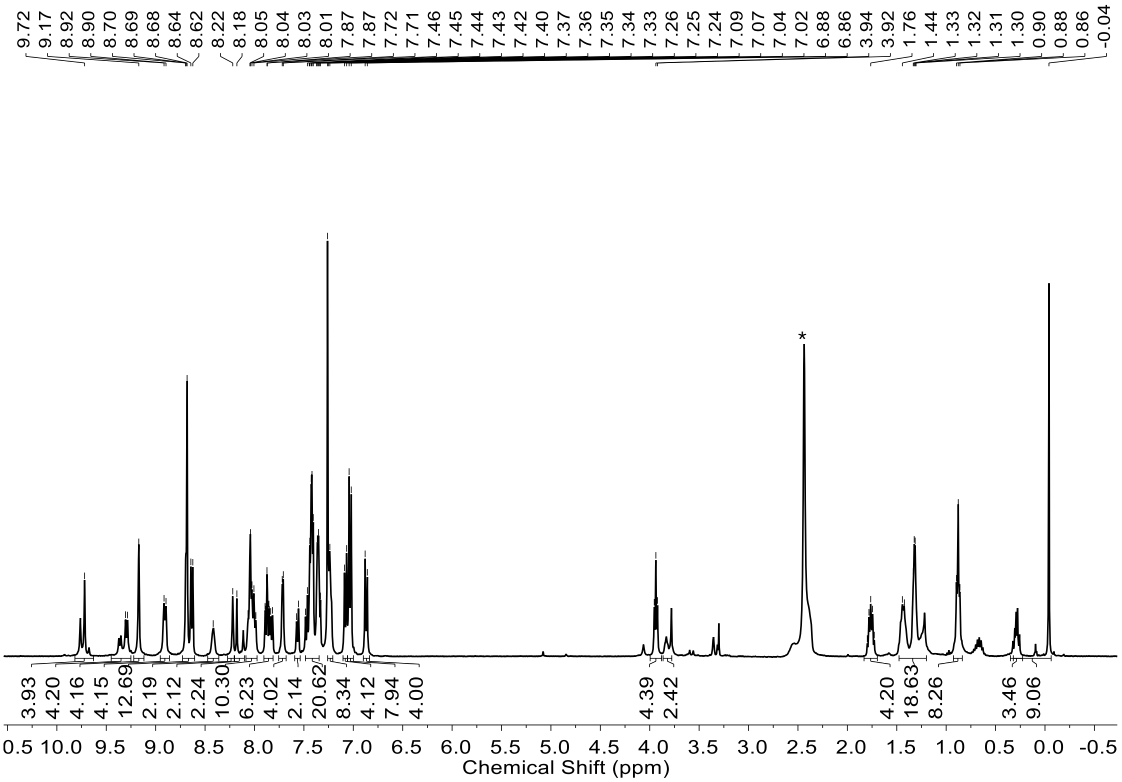

Figure S40. ^{1}H NMR (500 MHz, $CDCl_3$+3% CD_3OD) spectrum of **S-21** (asterisk represents residual solvent).

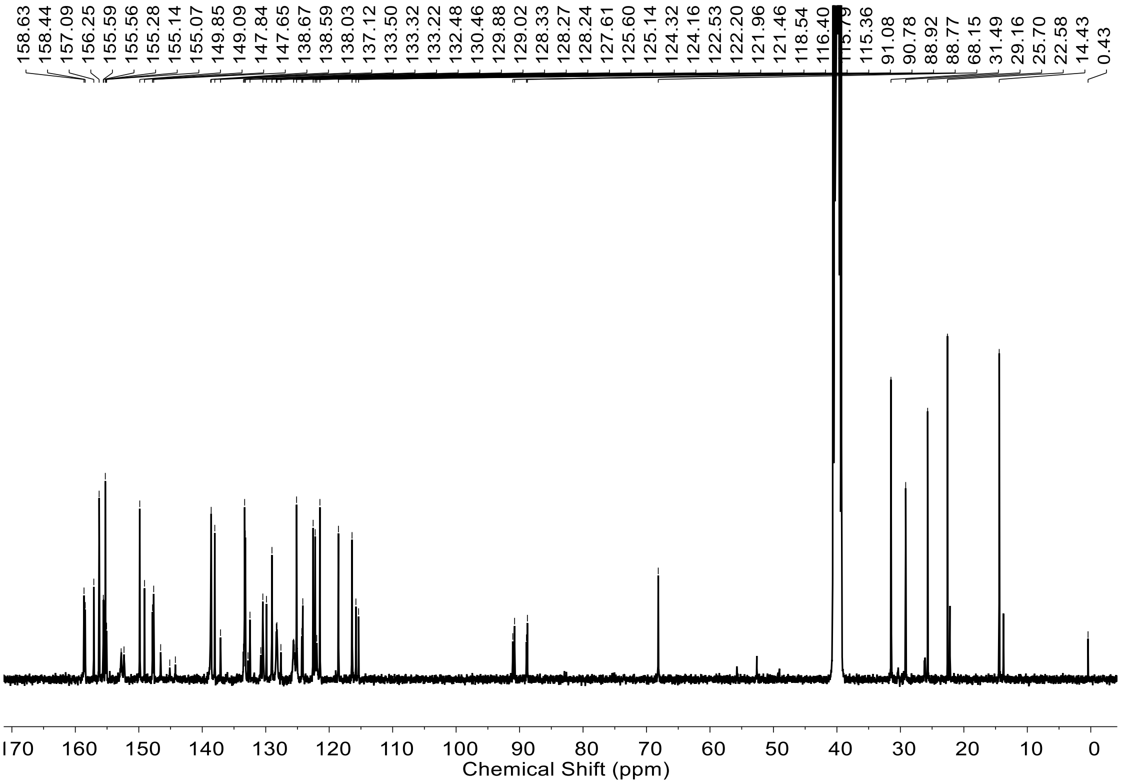

Figure S41. ^{13}C NMR (100 MHz, DMSO-*d6*) spectrum of **S-21**.

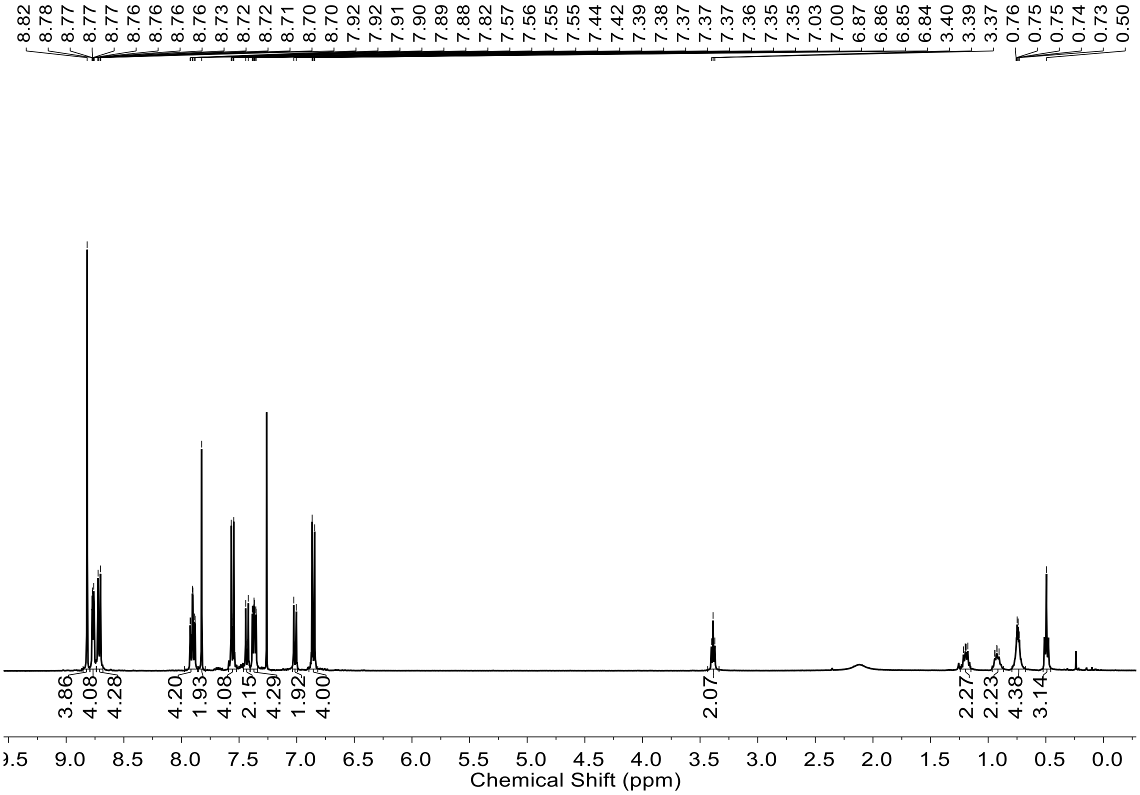

Figure S42. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S-22**.

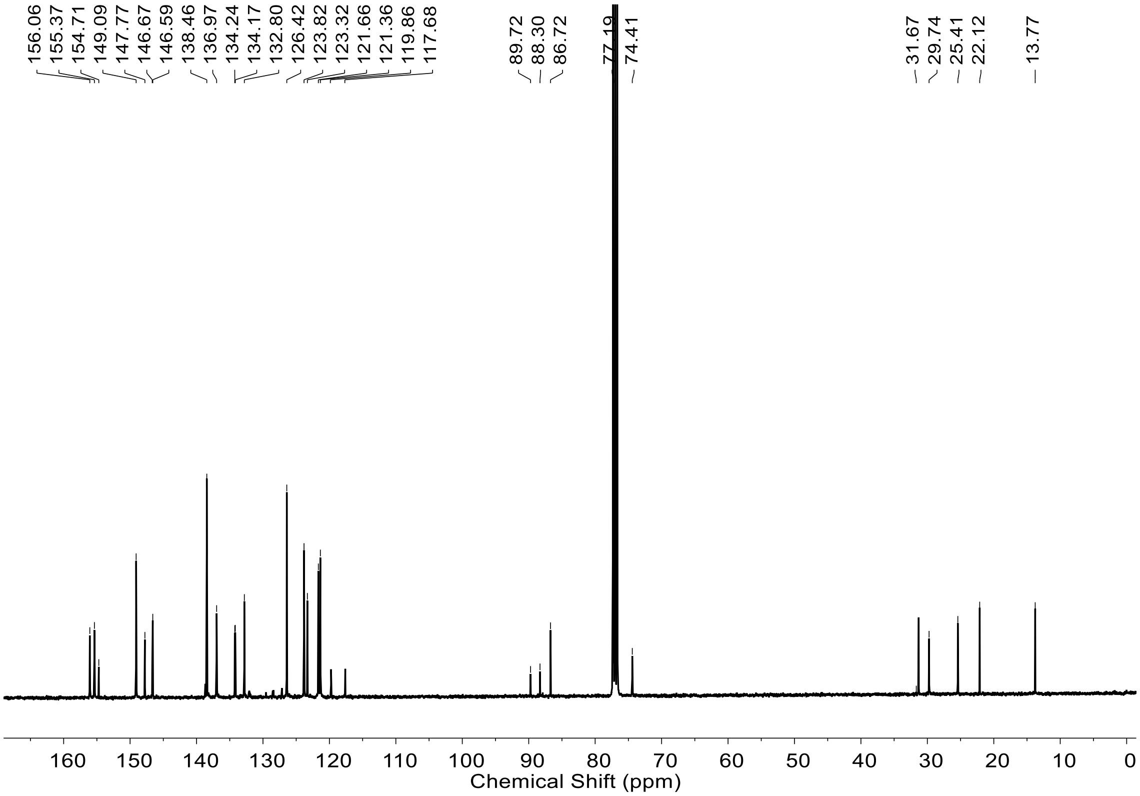

Figure S43. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **S-22**.

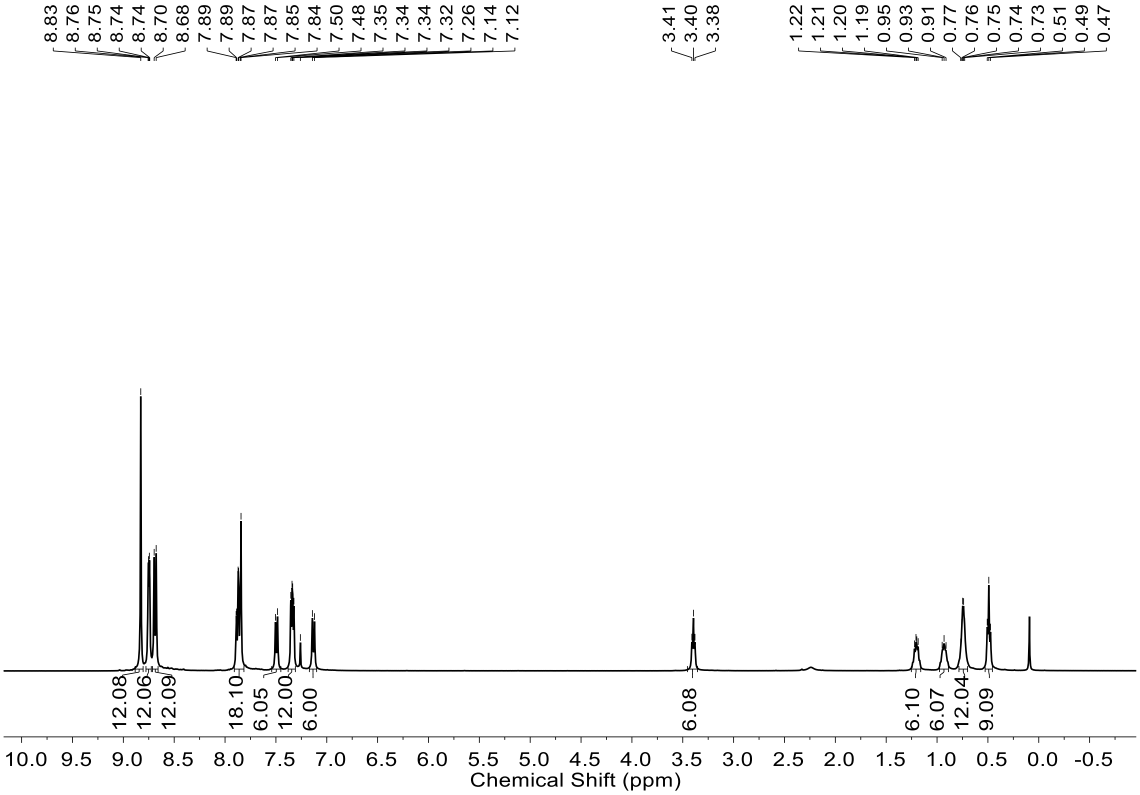

Figure S44. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **L**.

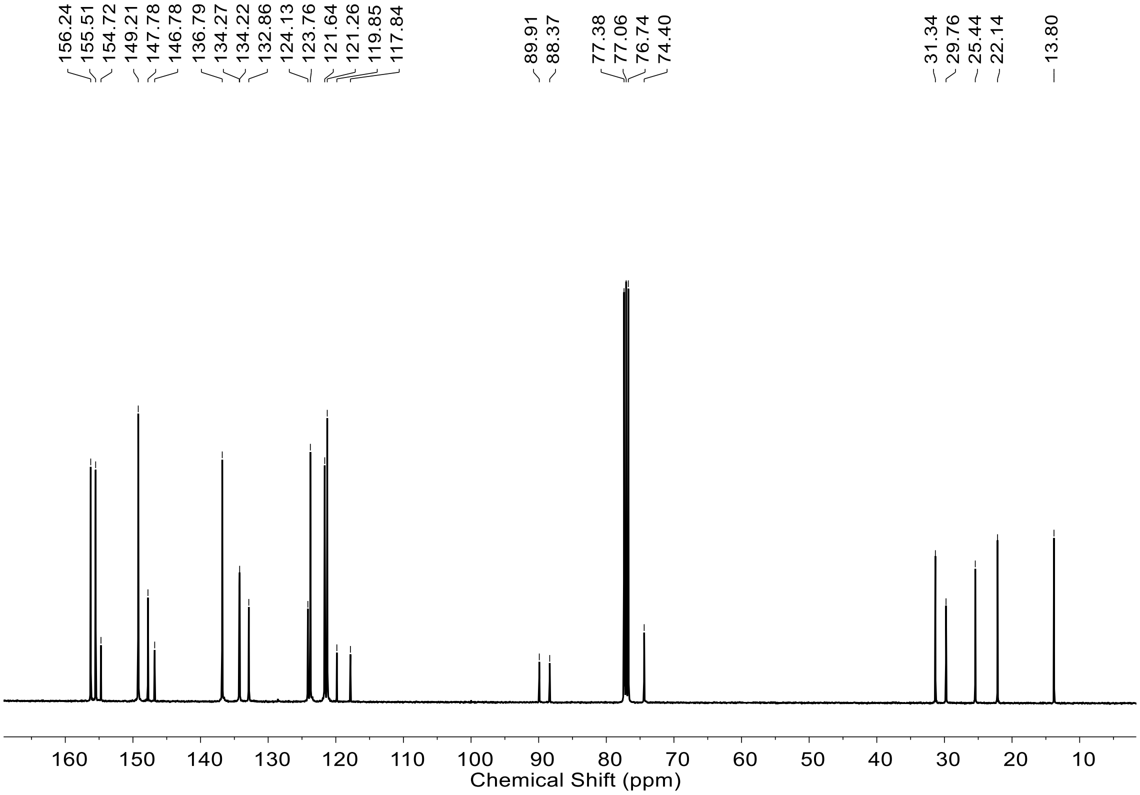

Figure S45. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **L**.

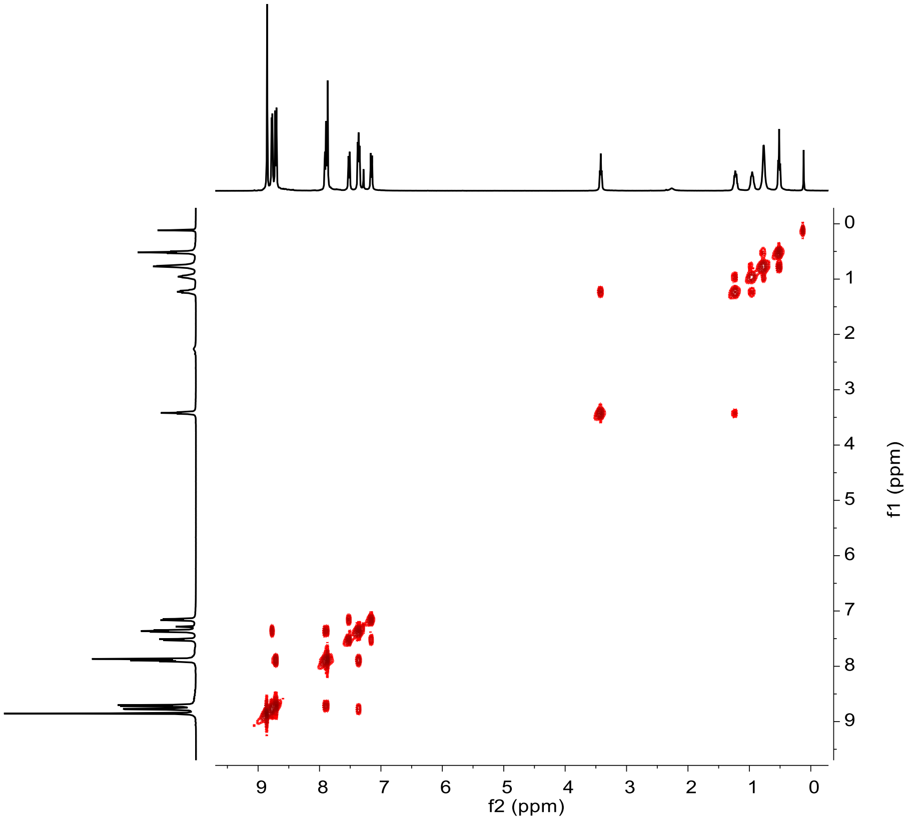

Figure S46. 2D COSY NMR (400 MHz, $CDCl_3$) spectrum of compound **L**.

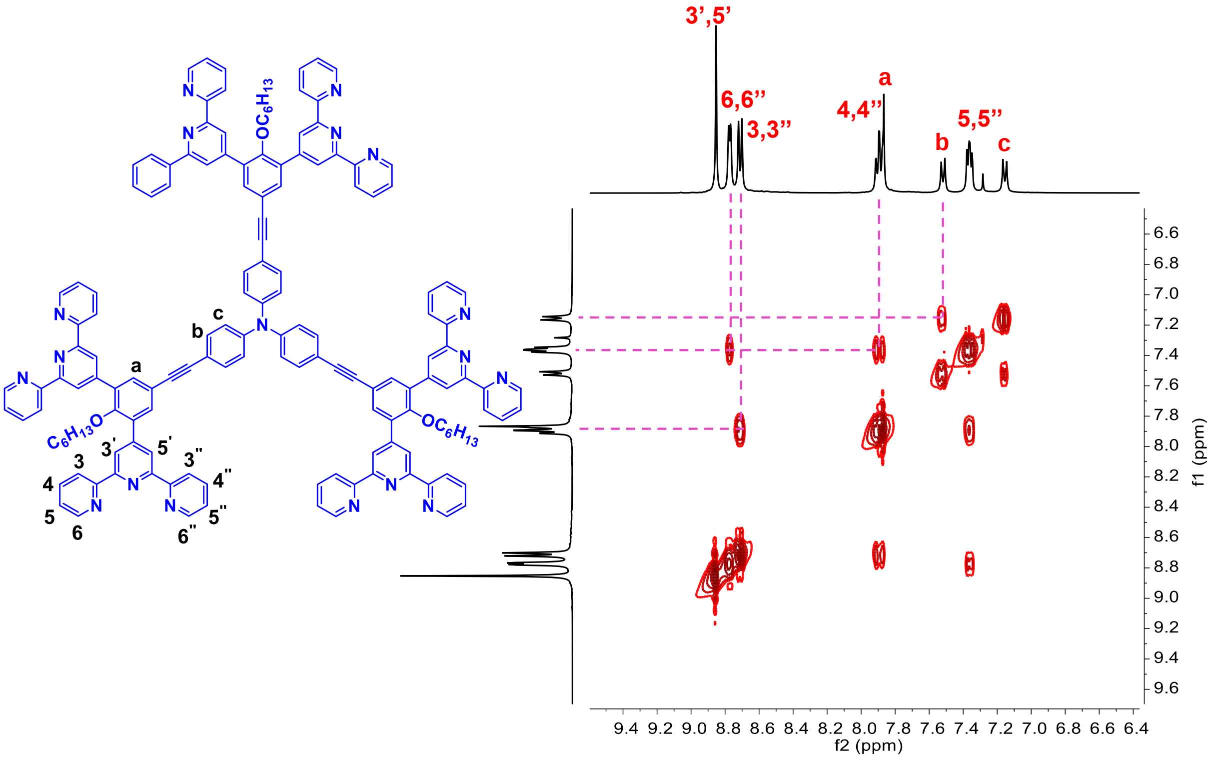

Figure S47. 2D COSY NMR (400 MHz, $CDCl_3$) spectrum of compound **L** (aromatic region).

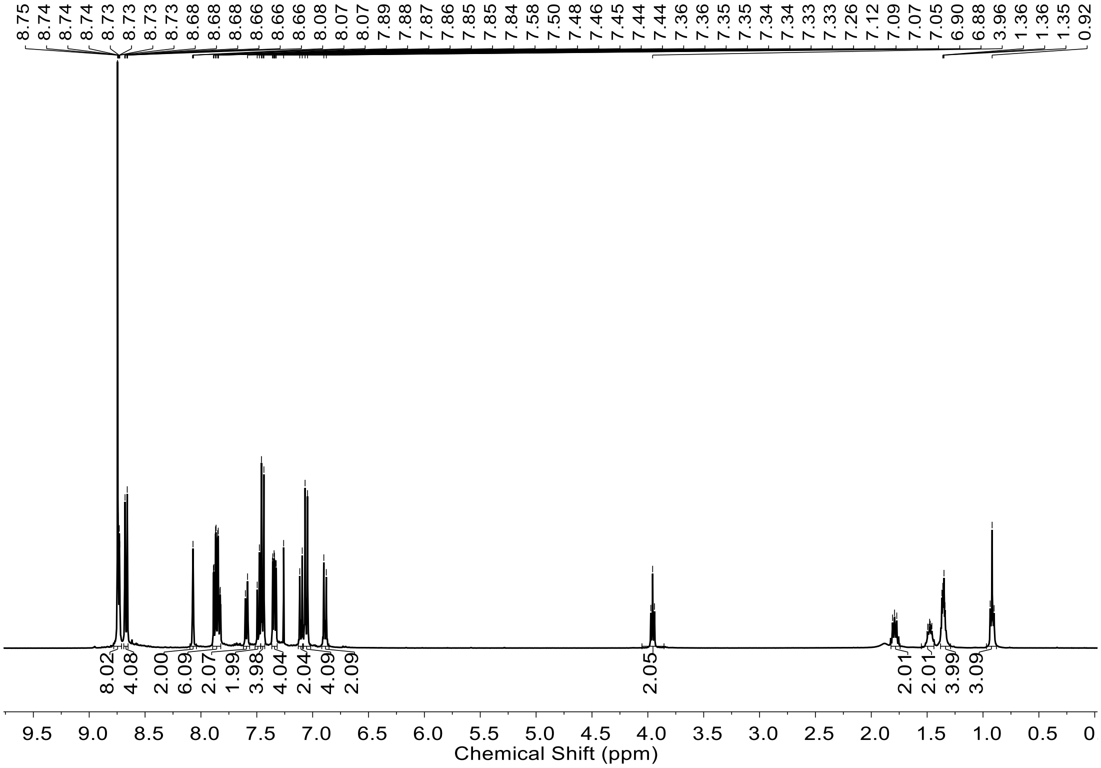

Figure S48. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ligand **LA**.

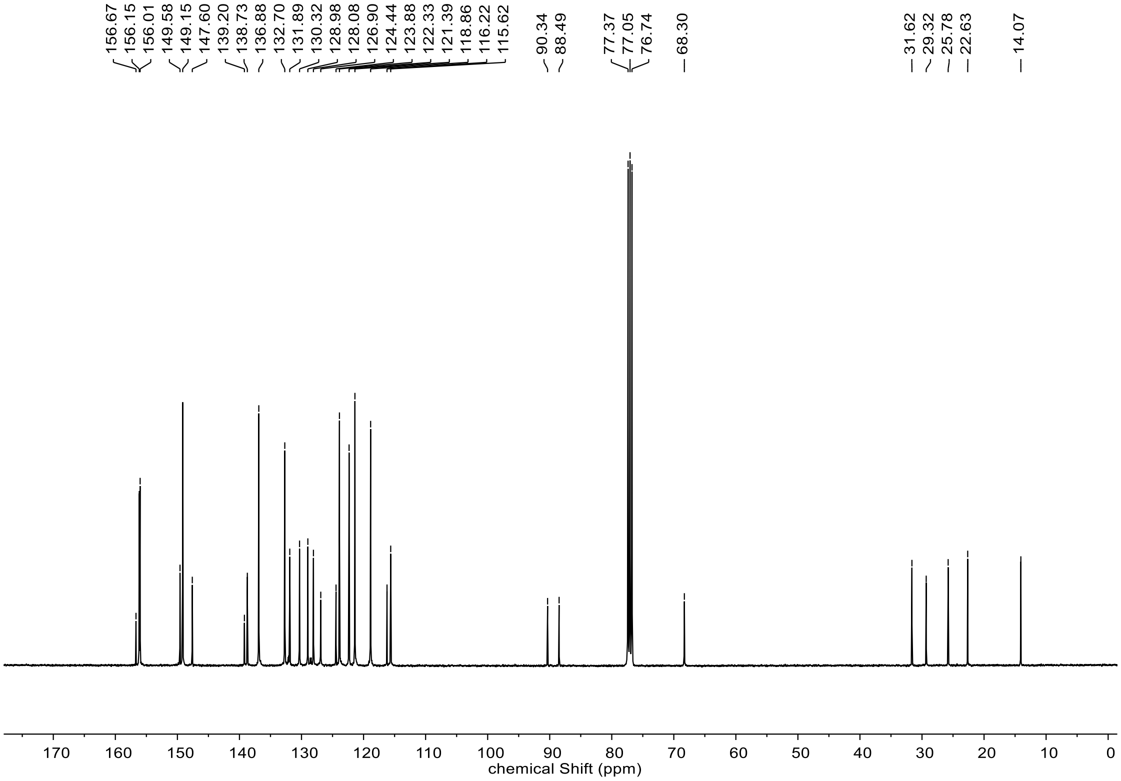

Figure S49. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ligand **LA**.

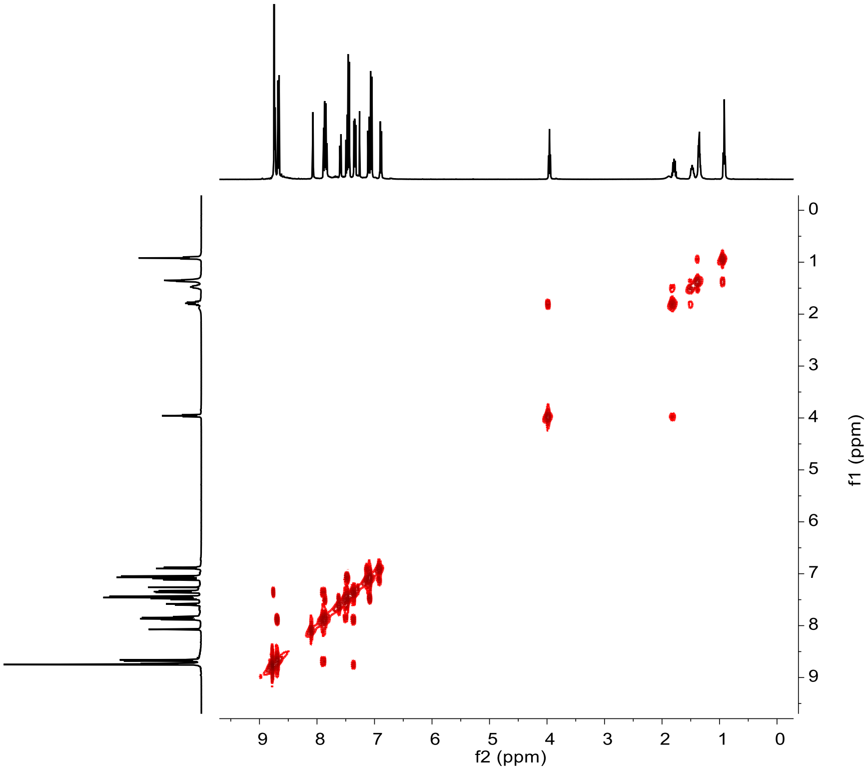

Figure S50. 2D COSY NMR (400 MHz, $CDCl_3$) spectrum of ligand **LA**.

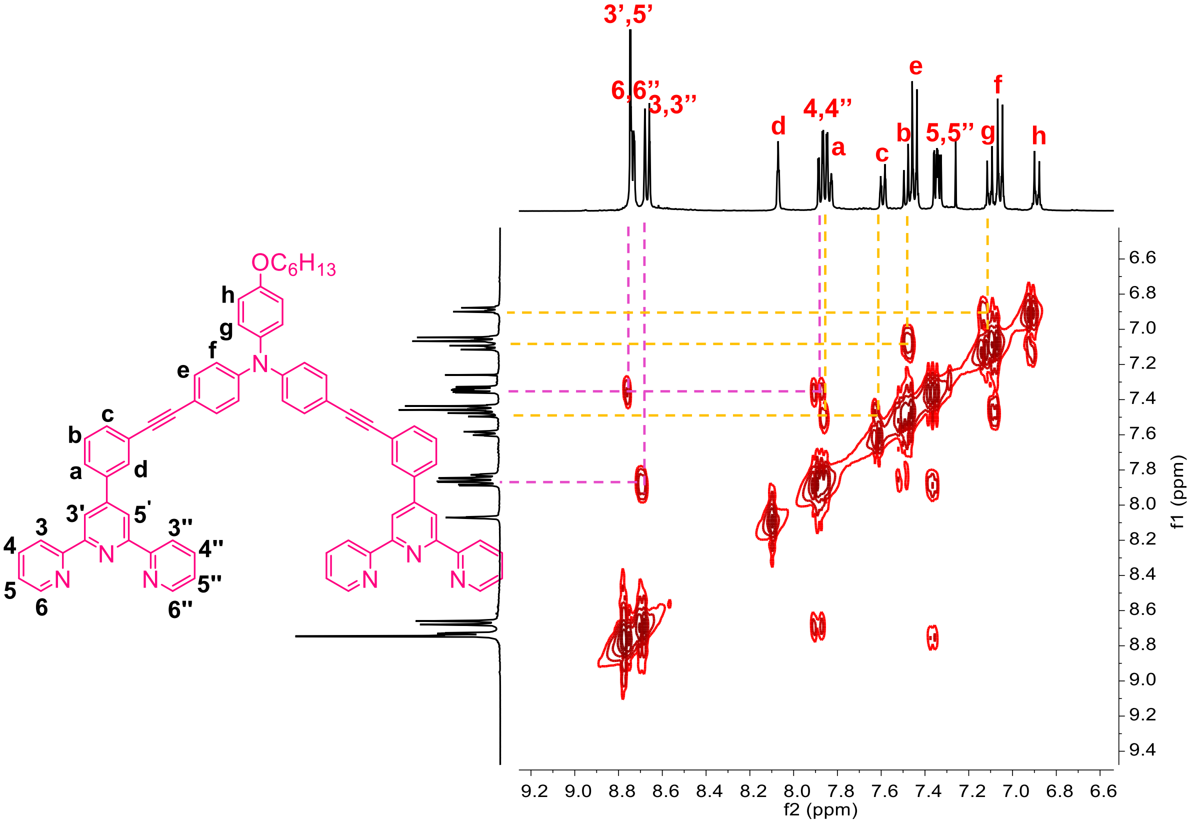

Figure S51. 2D COSY NMR (400 MHz, $CDCl_3$) spectrum of ligand **LA** (aromatic region).

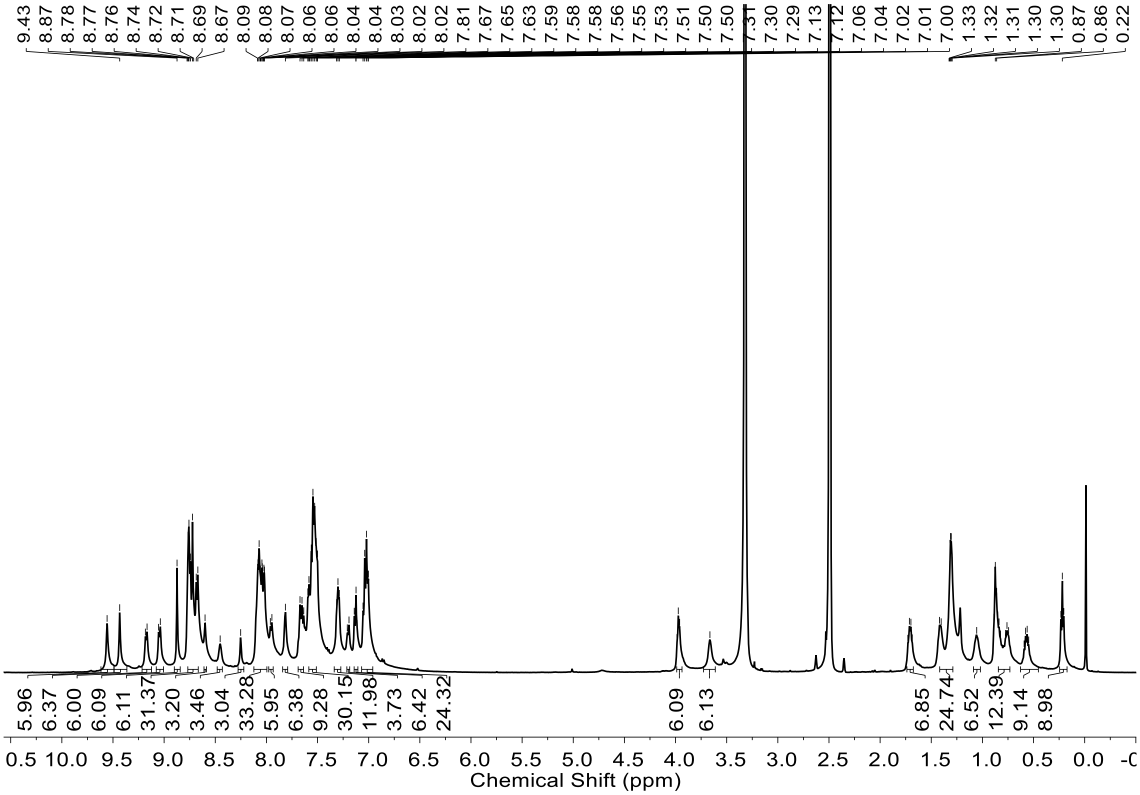

Figure S52. ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of ligand **LB**.

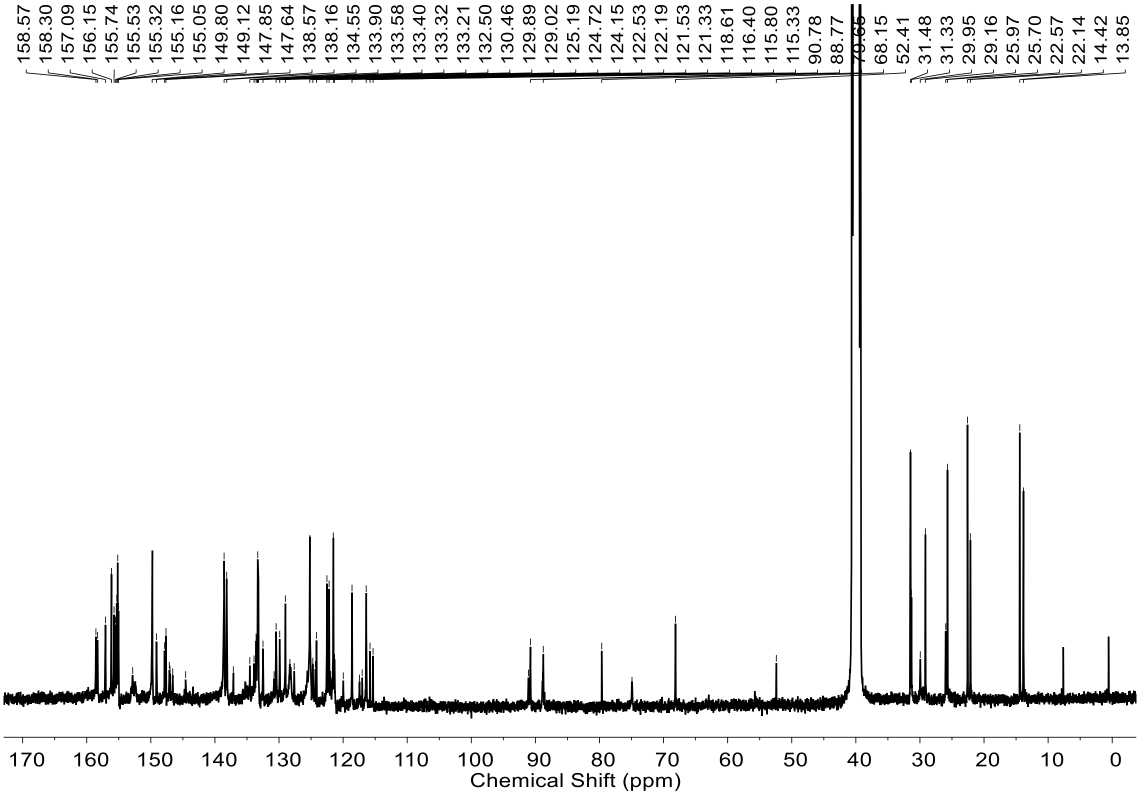

Figure S53. ^{13}C NMR (100 MHz, DMSO-d_6) spectrum of ligand **LB**.

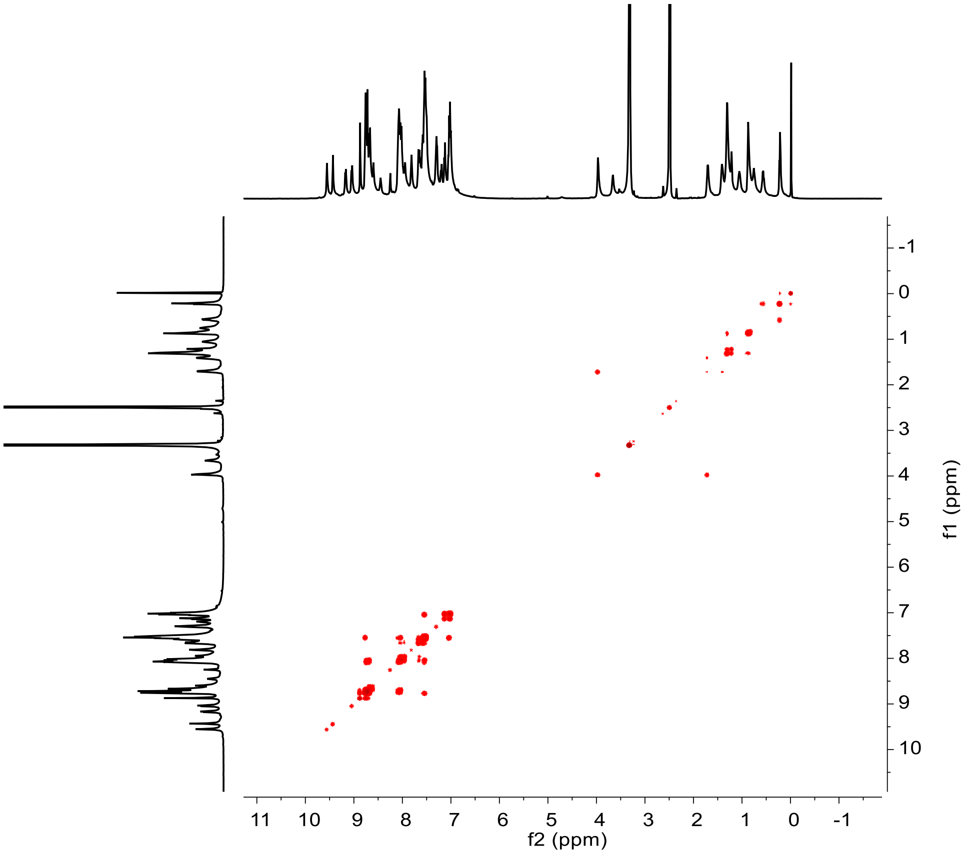

Figure S54. 2D COSY NMR (500 MHz, DMSO-d_6) spectrum of ligand **LB**.

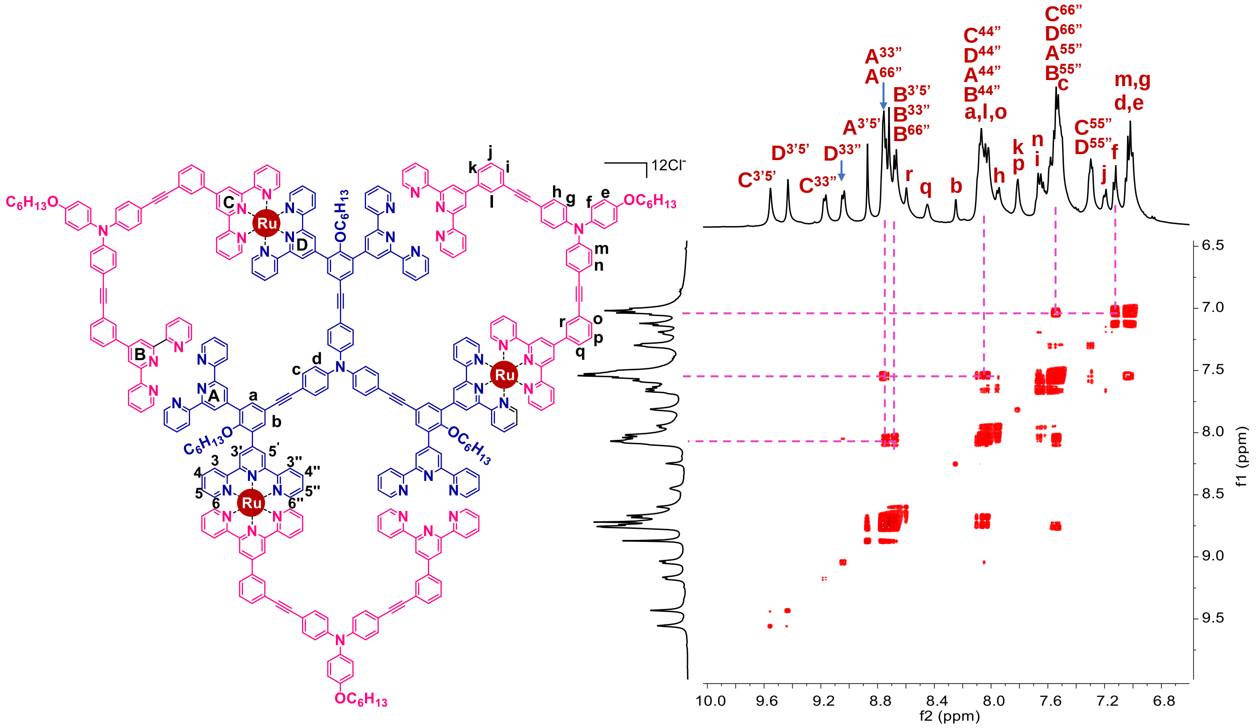

Figure S55. 2D COSY NMR (500 MHz, DMSO-d_6) spectrum of ligand **LB** (aromatic region).

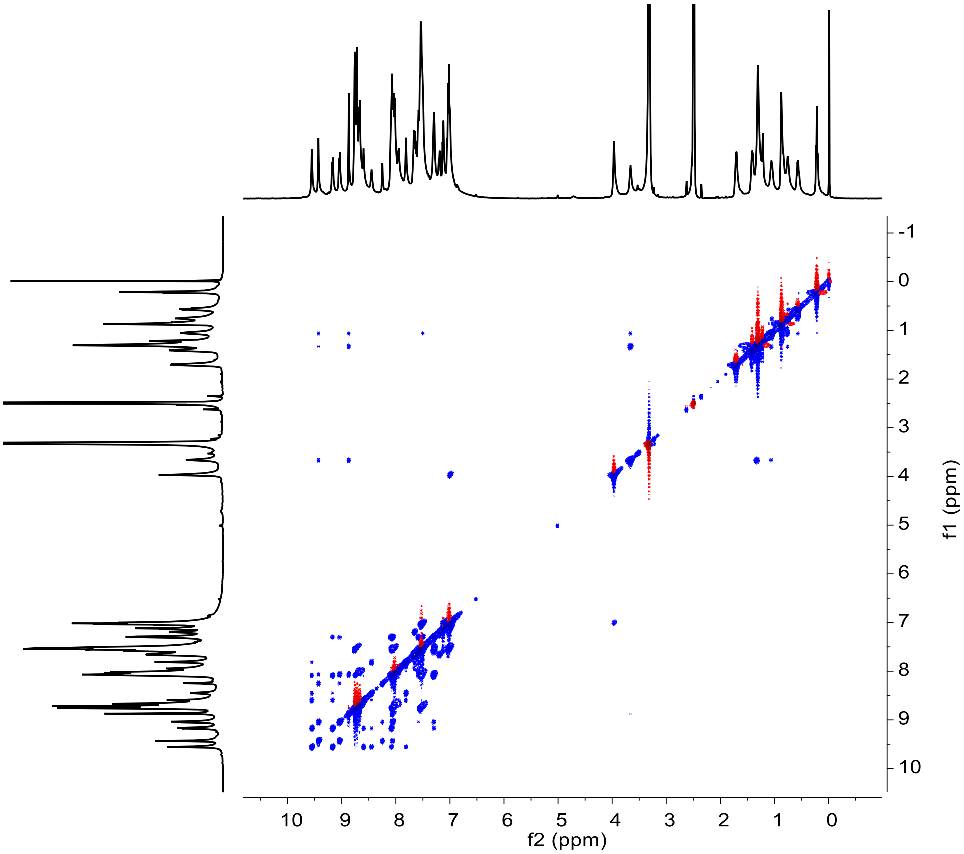

Figure S56. 2D NOESY NMR (500 MHz, DMSO-d_6) spectrum of ligand **LB**.

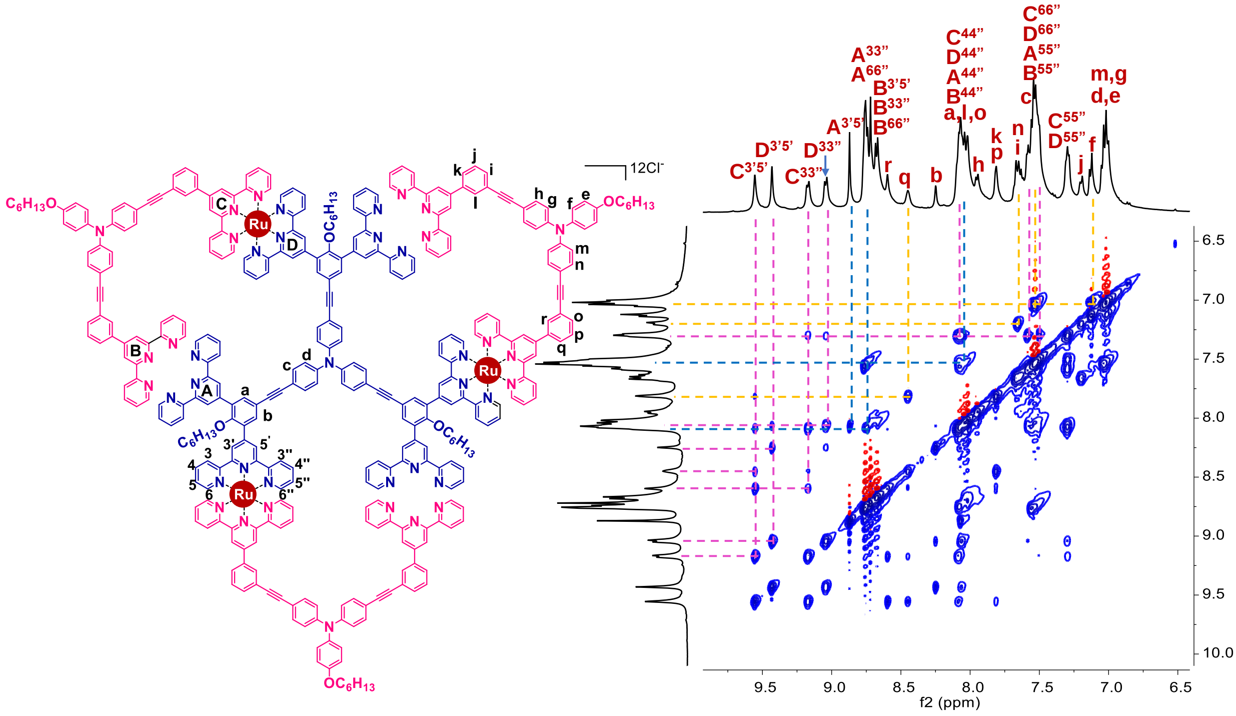

Figure S57. 2D NOESY NMR (500 MHz, DMSO-d_6) spectrum of ligand **LB** (aromatic region).

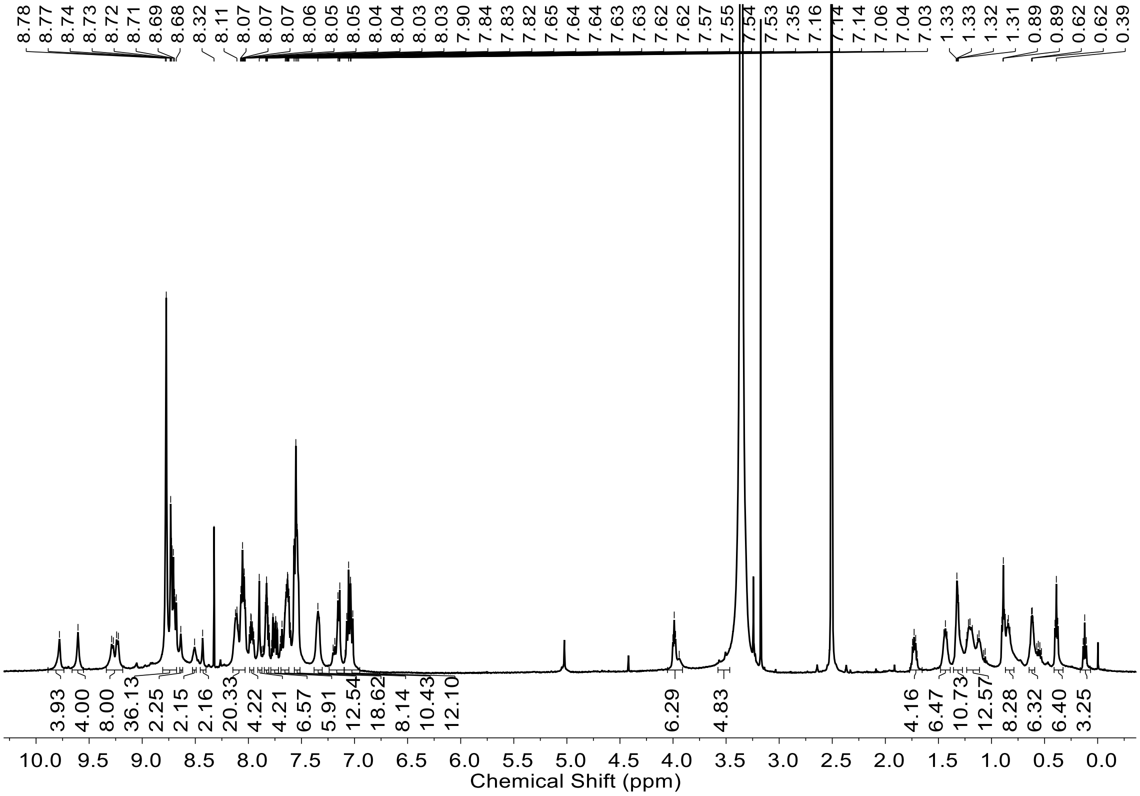

Figure S58. ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of ligand **LC**.

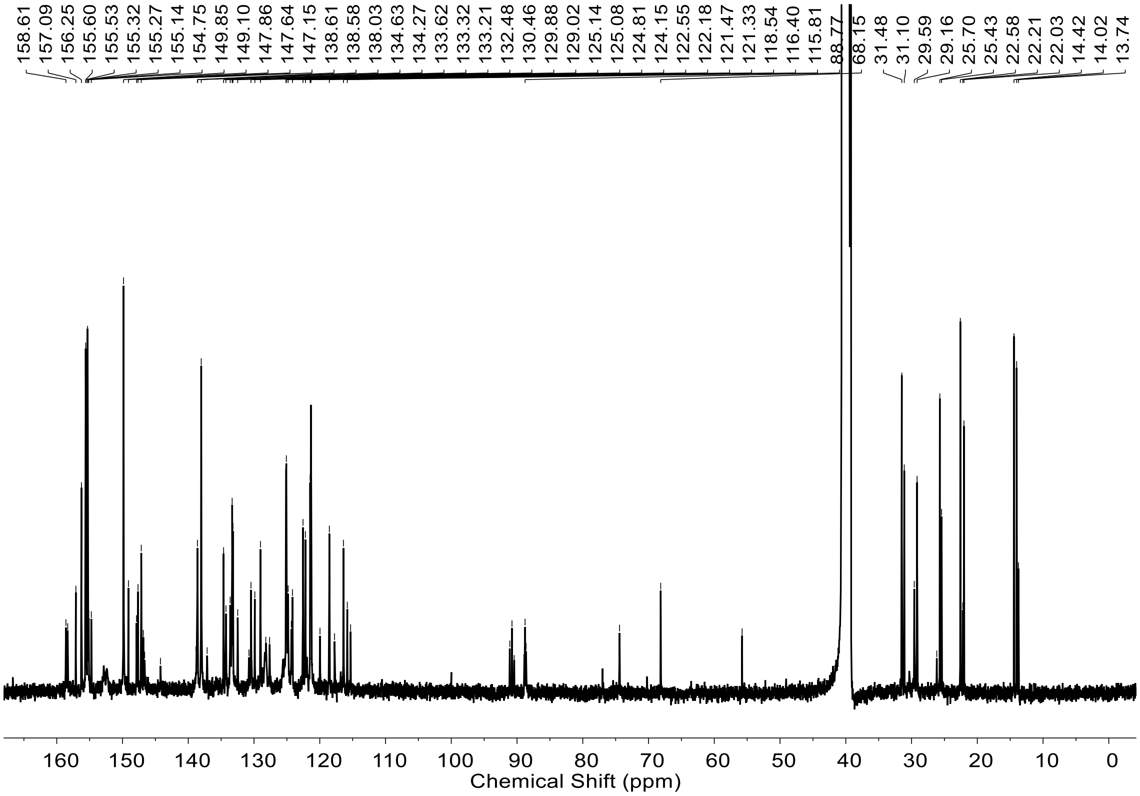

Figure S59. ^{13}C NMR (100 MHz, DMSO-d_6) spectrum of ligand **LC**.

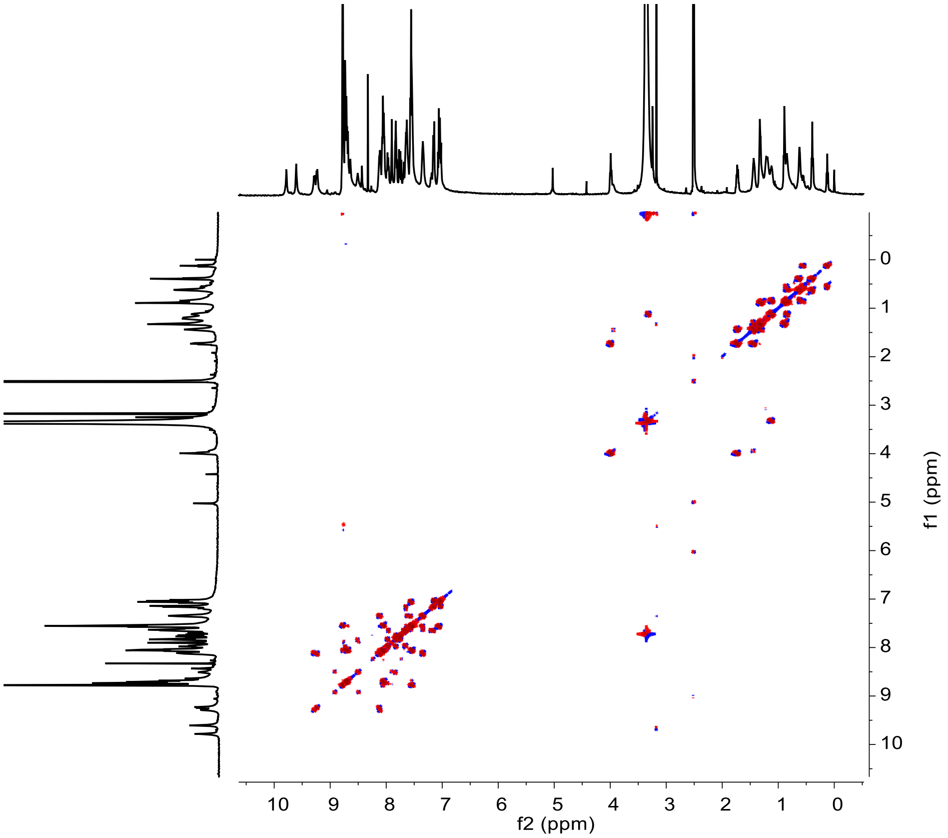

Figure S60. 2D COSY NMR (500 MHz, DMSO-d_6) spectrum of ligand **LC** (on a Bruker 500-MHz spectrometer).

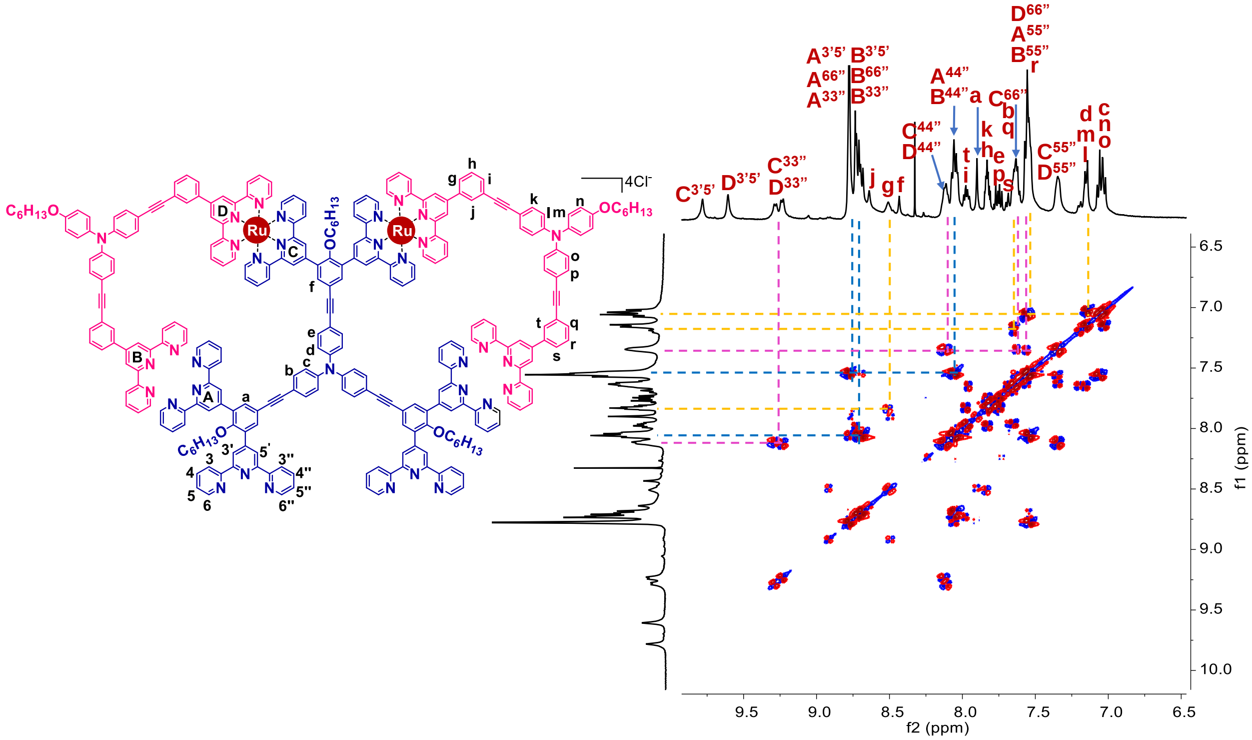

Figure S61. 2D COSY NMR (500 MHz, DMSO-d_6) spectrum of ligand **LC** (aromatic region, on a Bruker 500-MHz spectrometer).

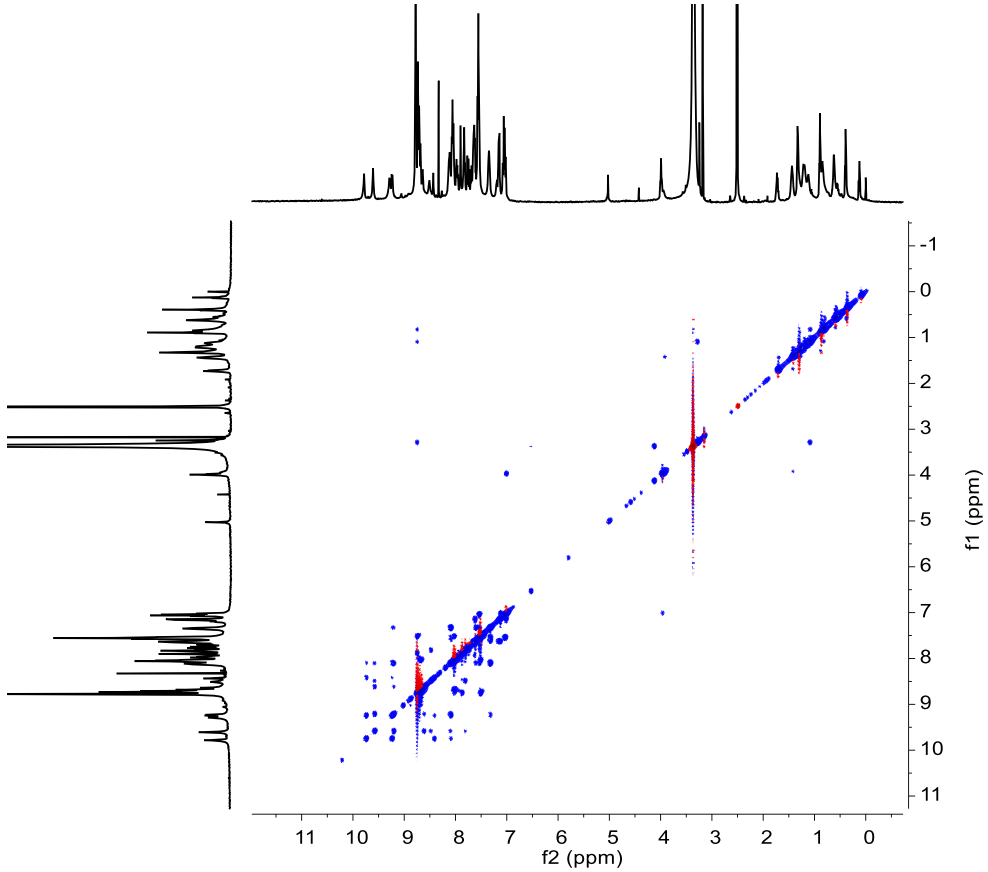

Figure S62. 2D NOESY NMR (500 MHz, DMSO-d_6) spectrum of ligand **LC**.

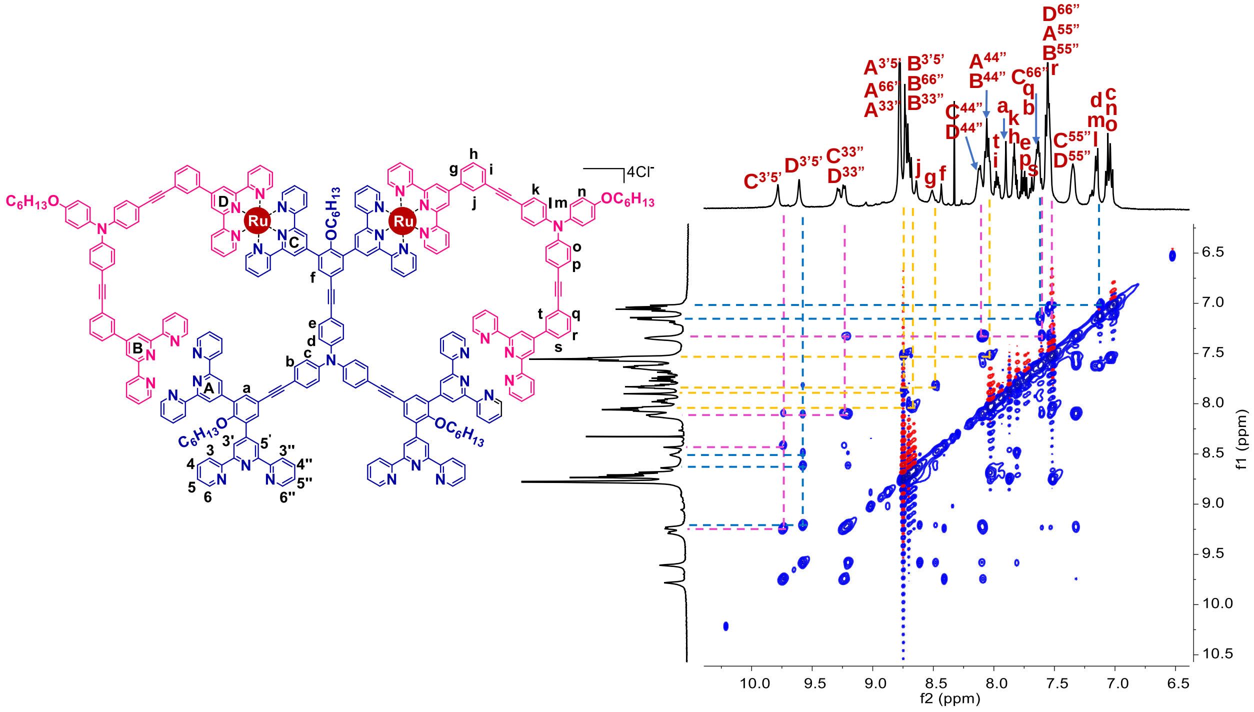

Figure S63. 2D NOESY NMR (500 MHz, DMSO-d_6) spectrum of ligand **LC** (aromatic region).

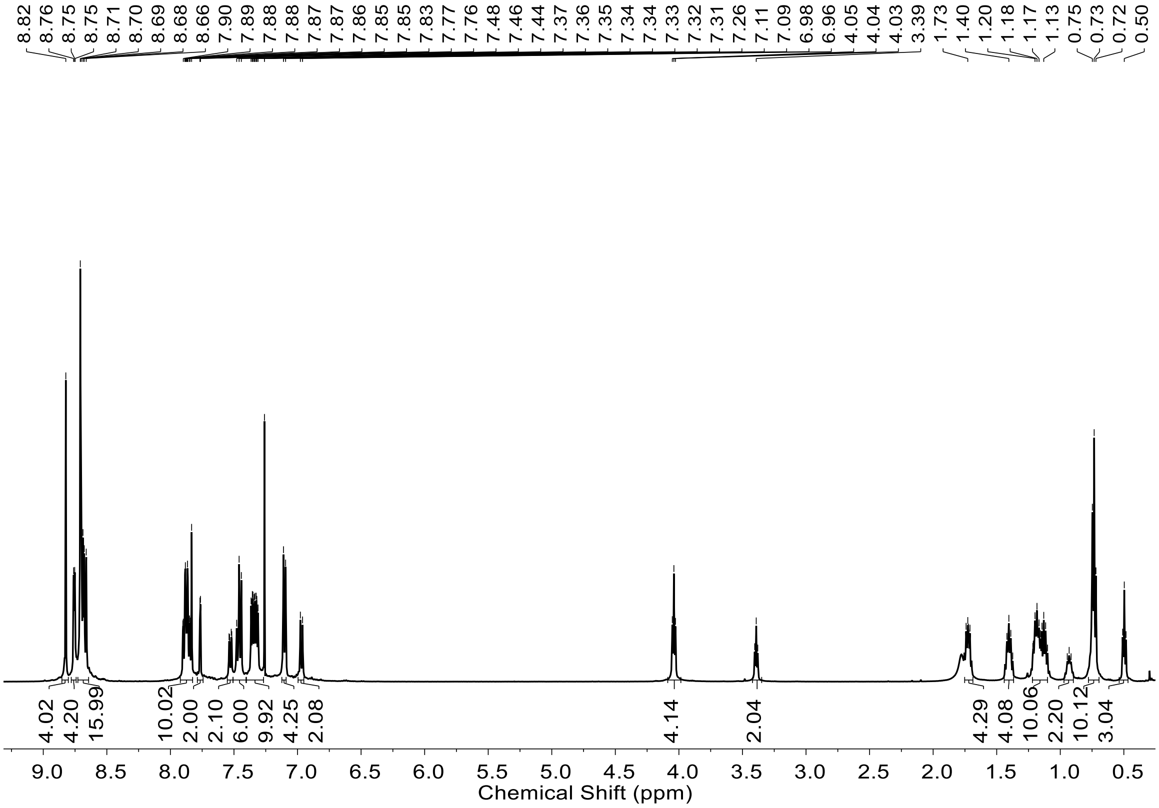

Figure S64. ^{1}H NMR (500 MHz, CDCl$_3$) spectrum of ligand **LD**.

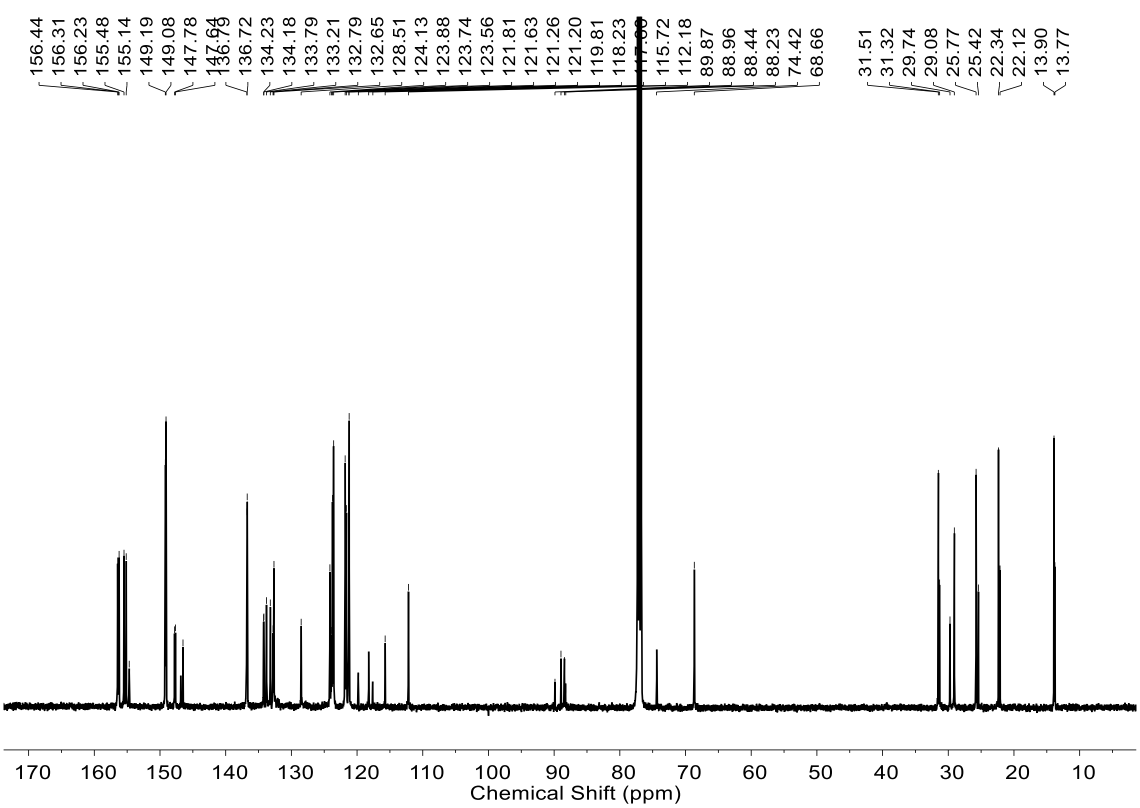

Figure S65. ^{13}C NMR (125 MHz, CDCl$_3$) spectrum of ligand **LD**.

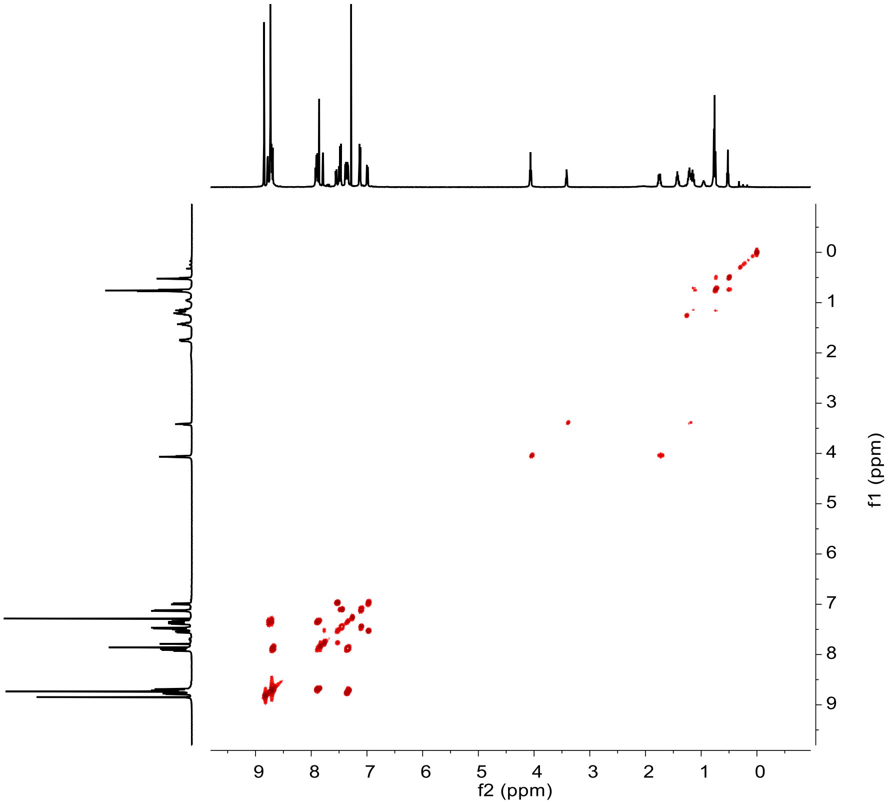

Figure S66. 2D COSY NMR (500 MHz, $CDCl_3$) spectrum of ligand **LD**.

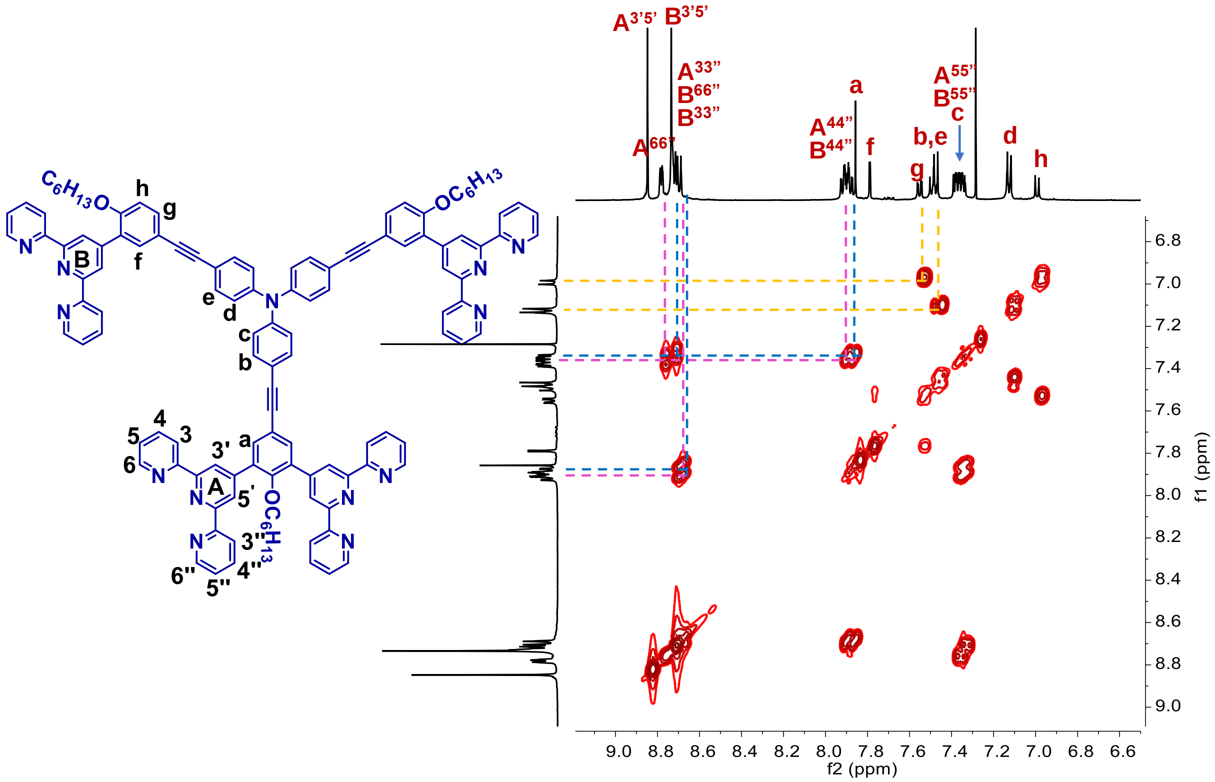

Figure S67. 2D COSY NMR (500 MHz, $CDCl_3$) spectrum of ligand **LD** (aromatic region).

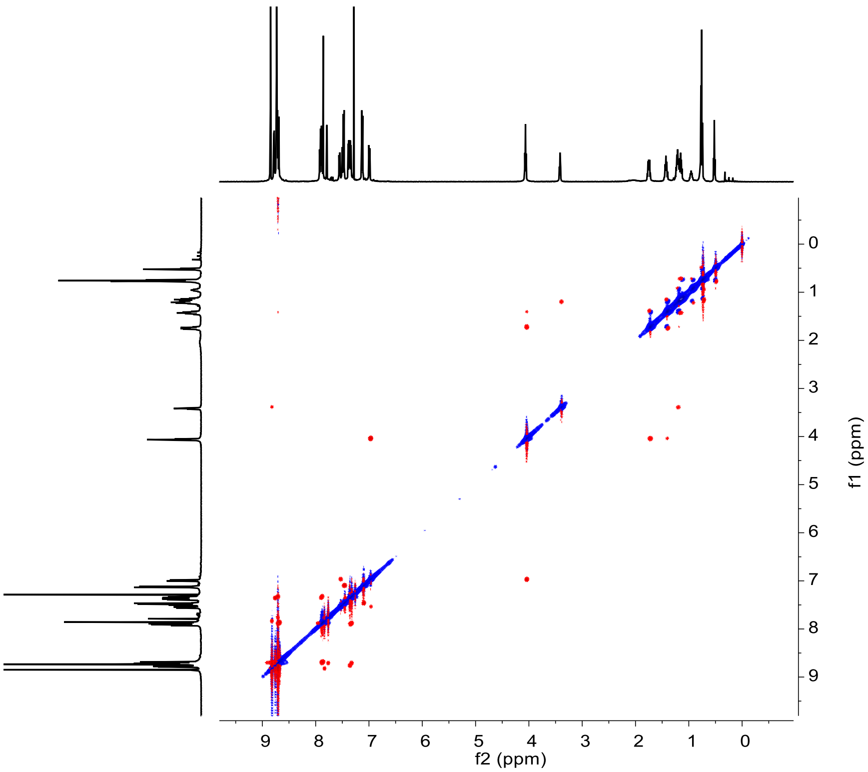

Figure S68. 2D NOESY NMR (500 MHz, $CDCl_3$) spectrum of ligand **LD**.

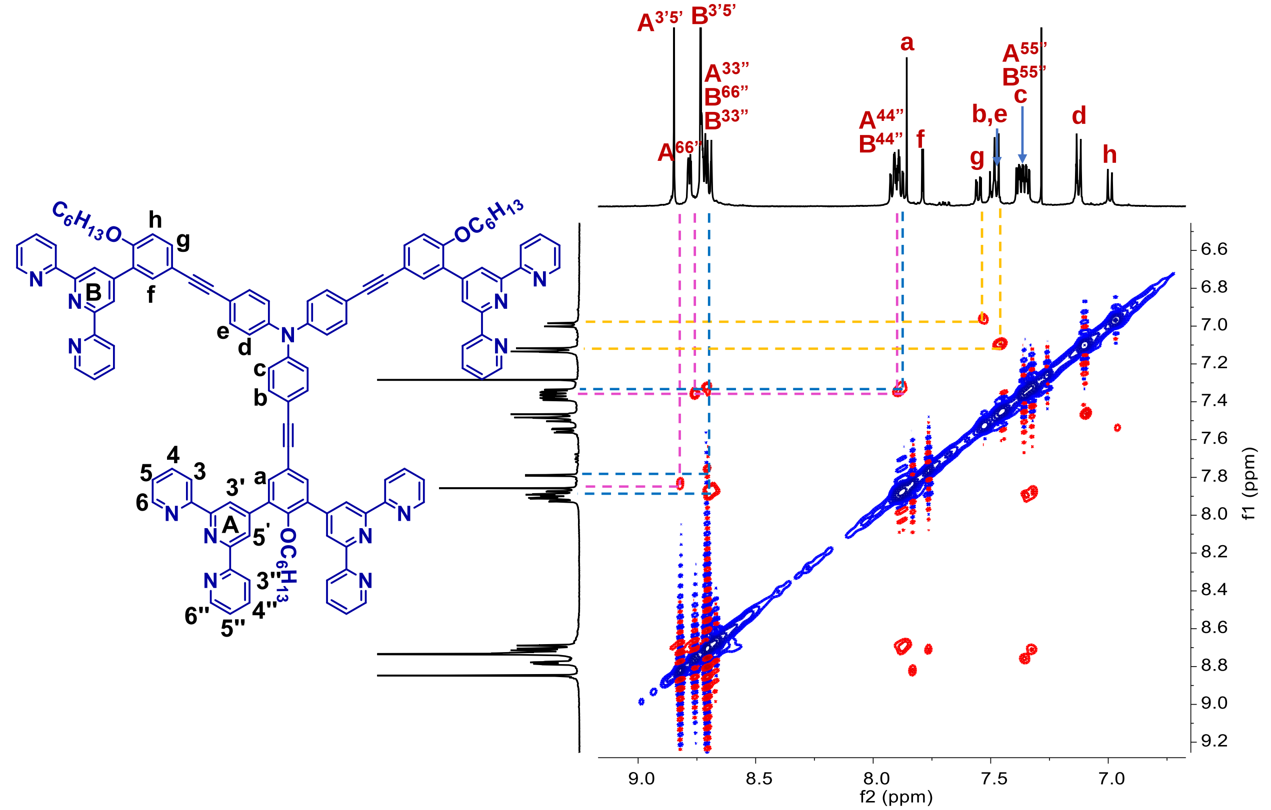

Figure S69. 2D NOESY NMR (500 MHz, $CDCl_3$) spectrum of ligand **LD** (aromatic region).

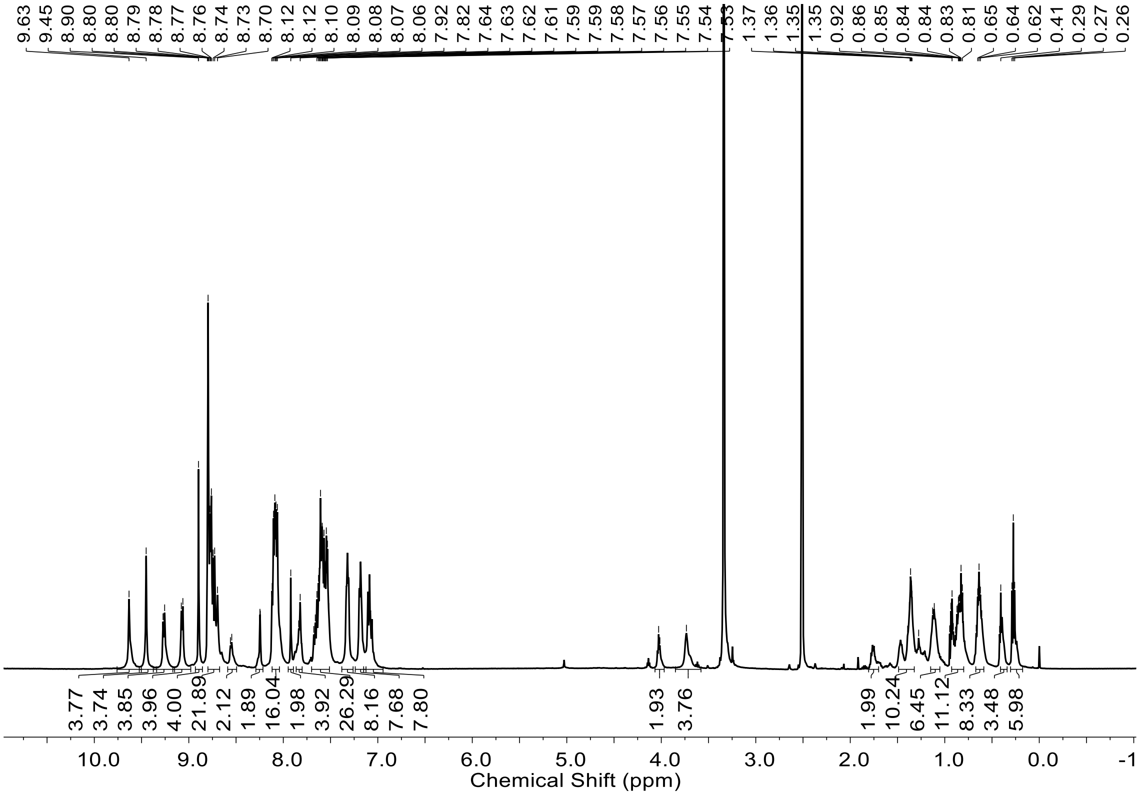

Figure S70. ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of ligand **LE**.

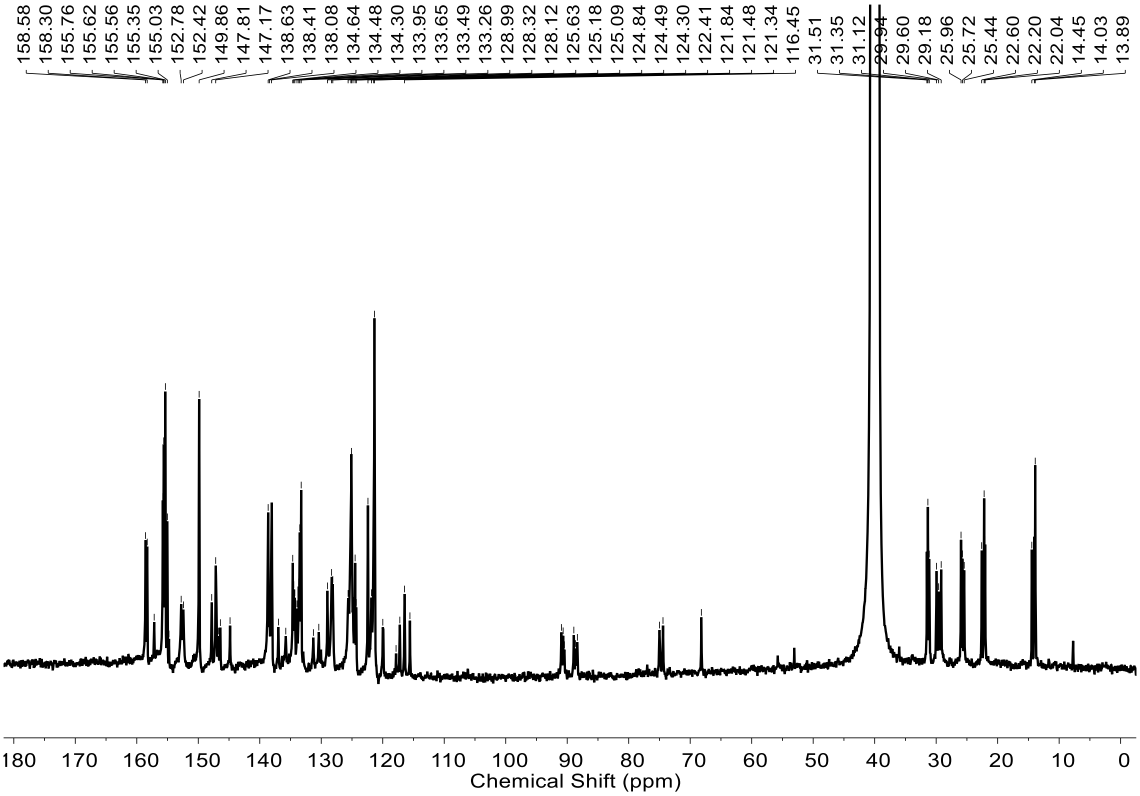

Figure S71. ^{13}C NMR (100 MHz, DMSO-d_6) spectrum of ligand **LE**.

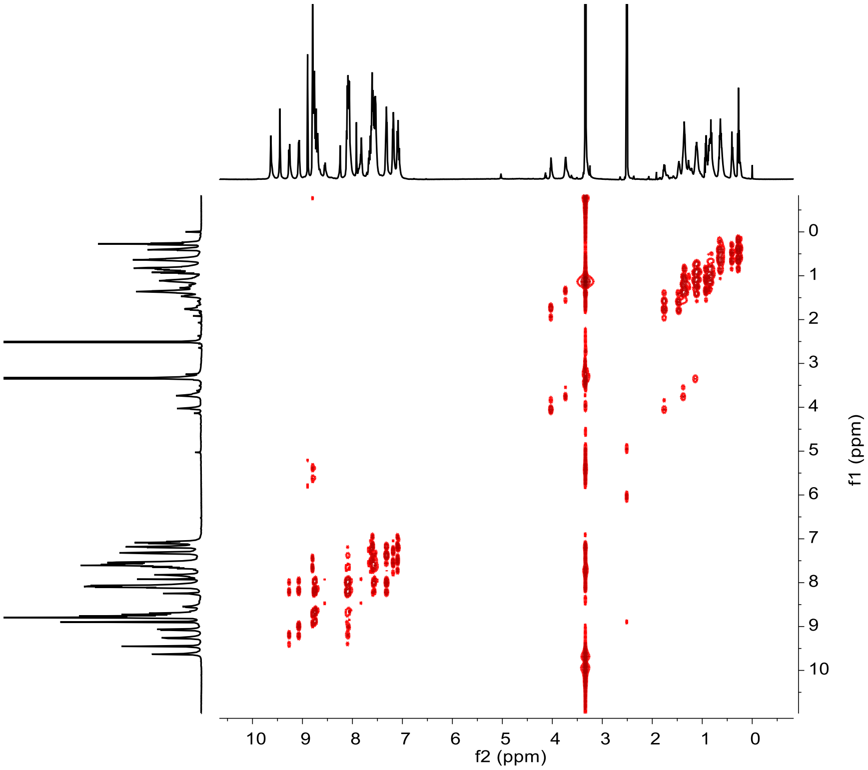

Figure S72. 2D COSY NMR (500 MHz, DMSO-d_6) spectrum of ligand **LE**.

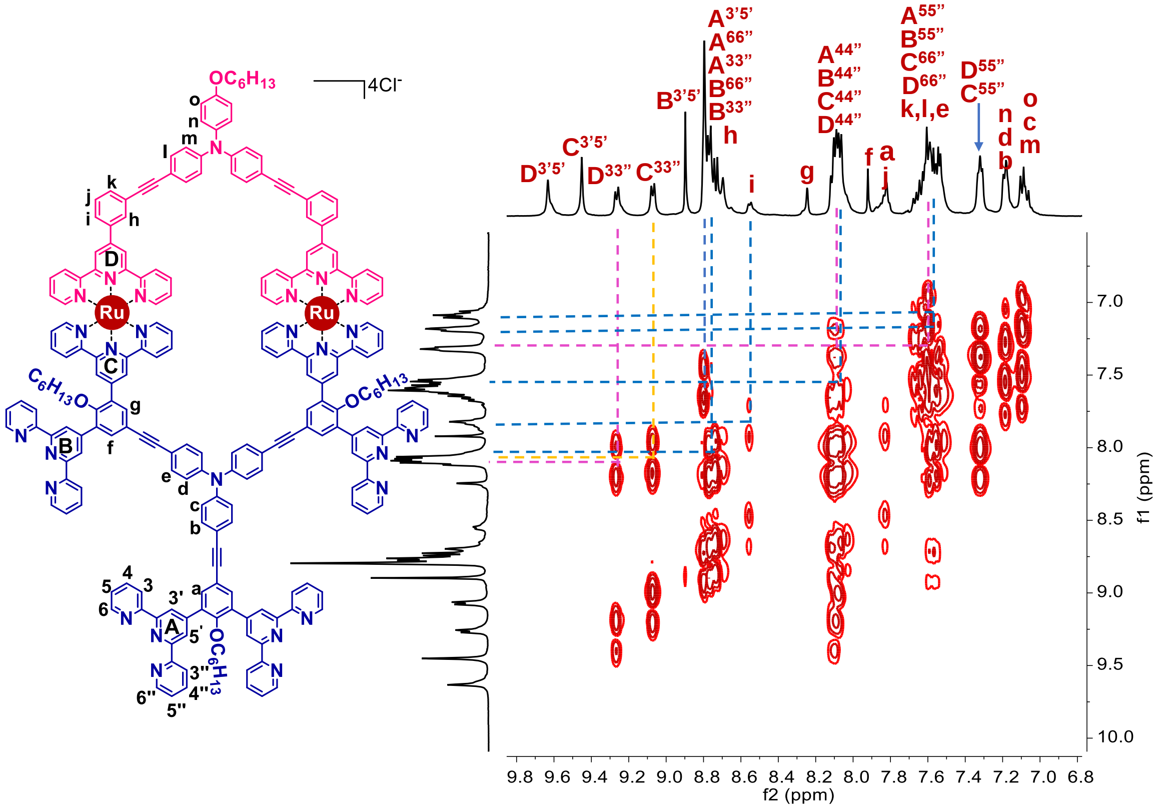

Figure S73. 2D COSY NMR (500 MHz, DMSO-d_6) spectrum of ligand **LE** (aromatic region).

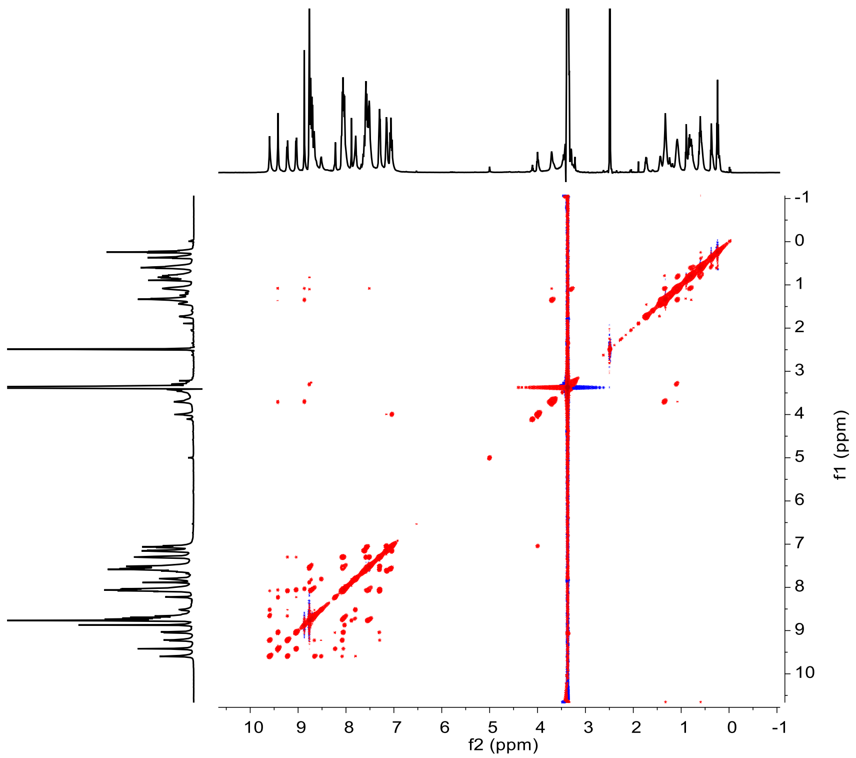

Figure S74. 2D NOESY NMR (500 MHz, DMSO-d_6) spectrum of ligand **LE**.

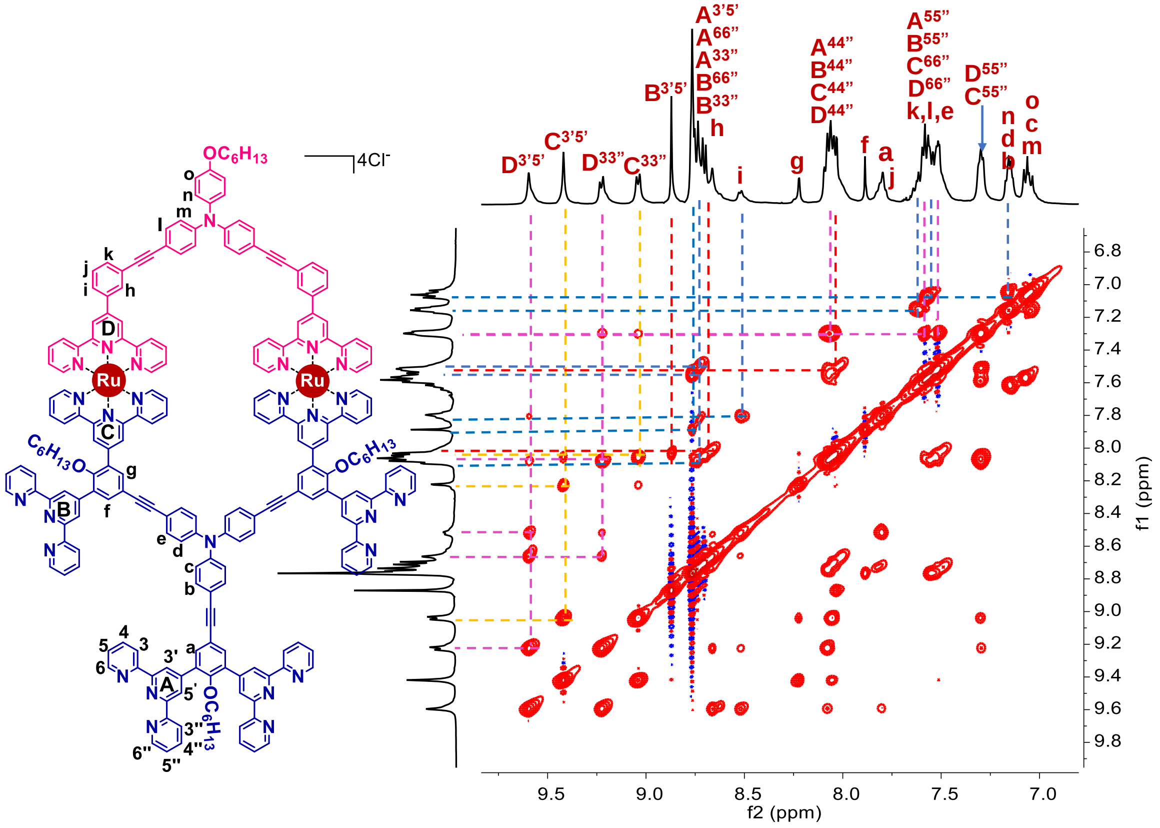

Figure S75. 2D NOESY NMR (500 MHz, DMSO-d_6) spectrum of ligand **LE** (aromatic region).

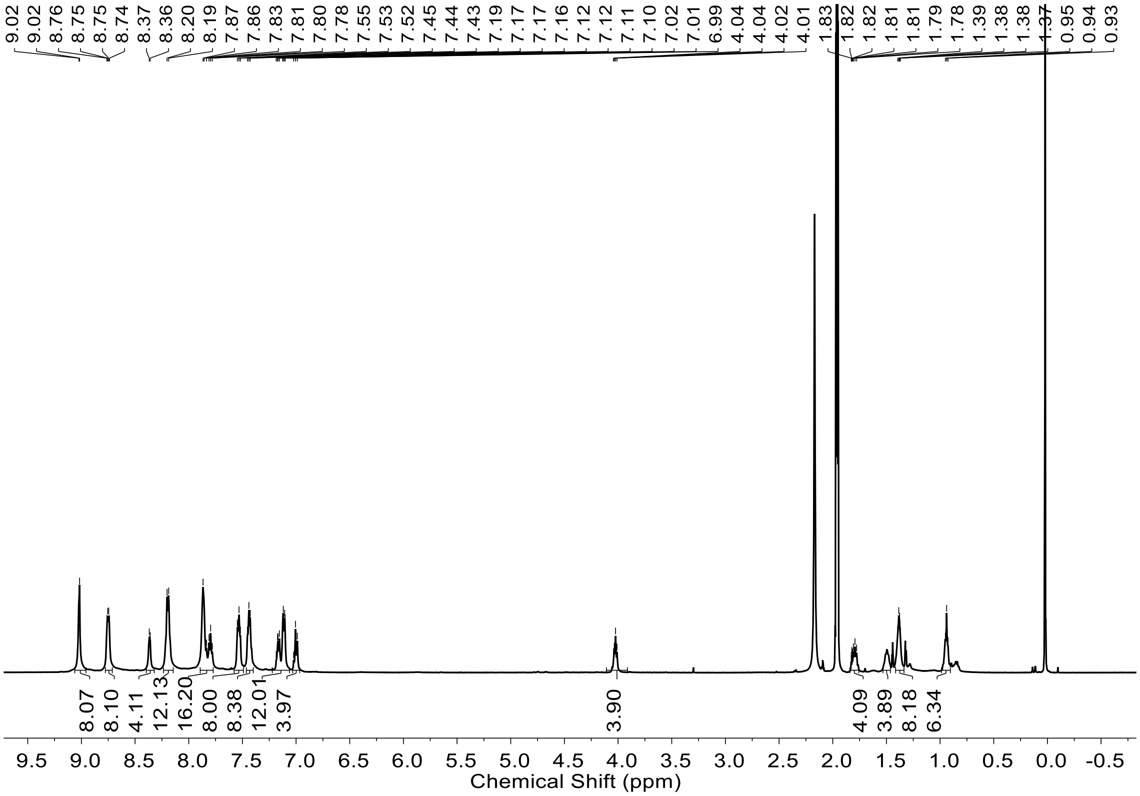

Figure S76. ^{1}H NMR (500 MHz, CD_3CN) spectrum of complex **G1**.

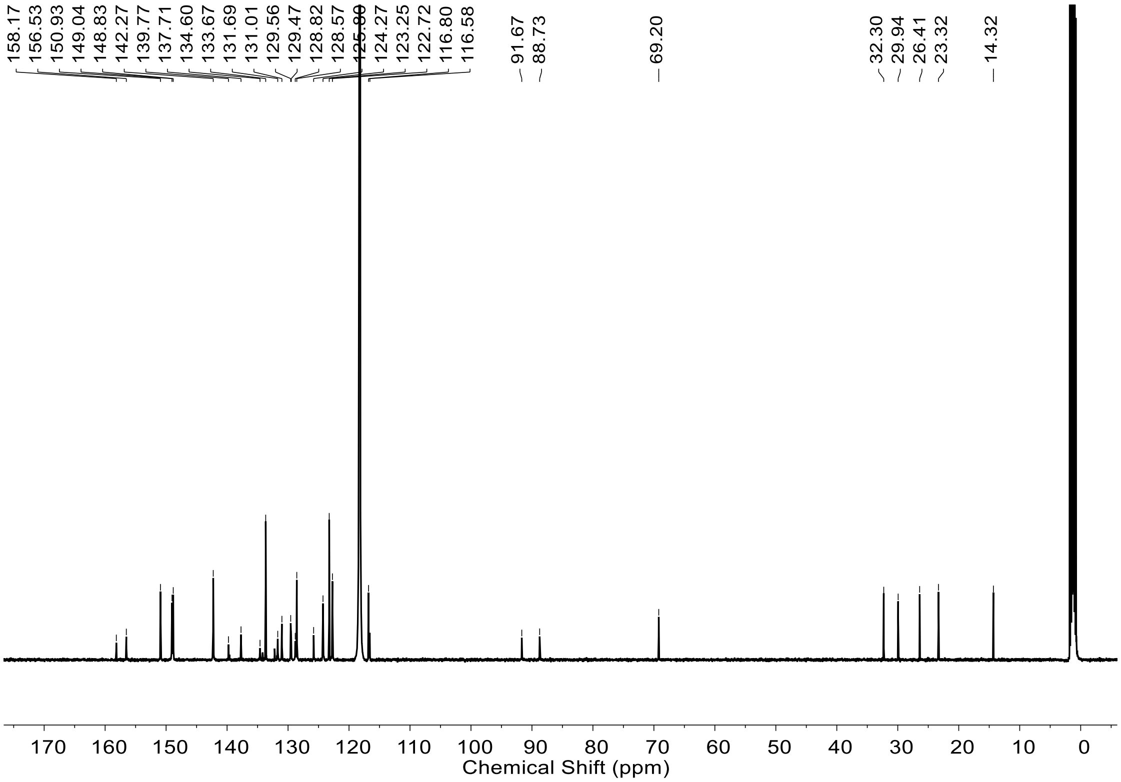

Figure S77. ^{13}C NMR (125 MHz, CD_3CN) spectrum of complex **G1**.

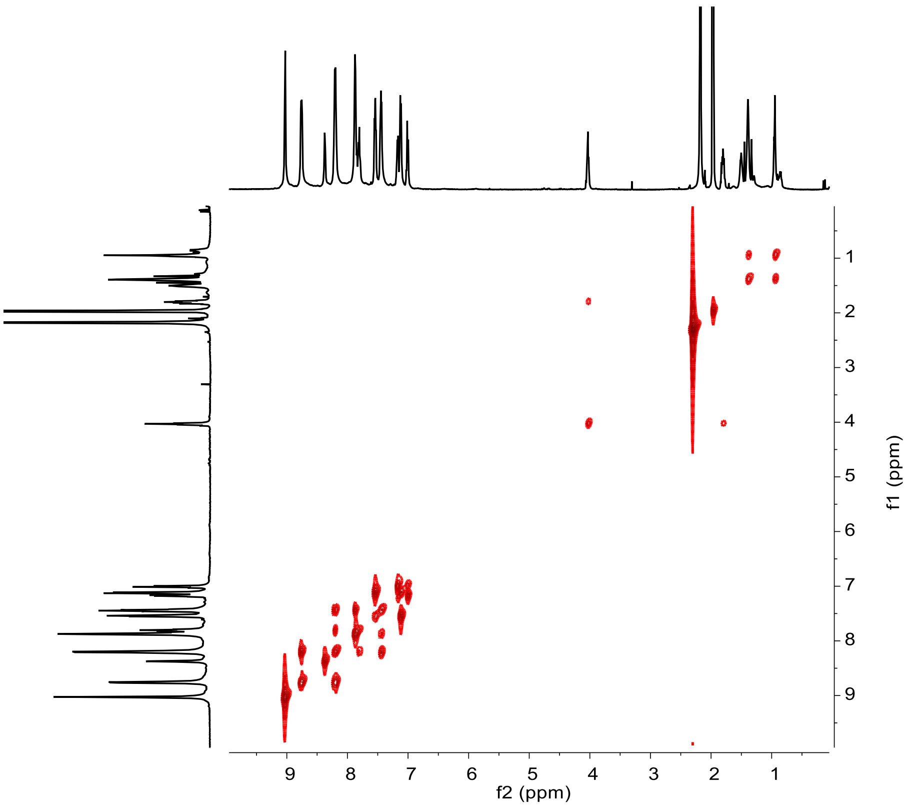

Figure S78. 2D COSY NMR (500 MHz, CD_3CN) spectrum of complex **G1**.

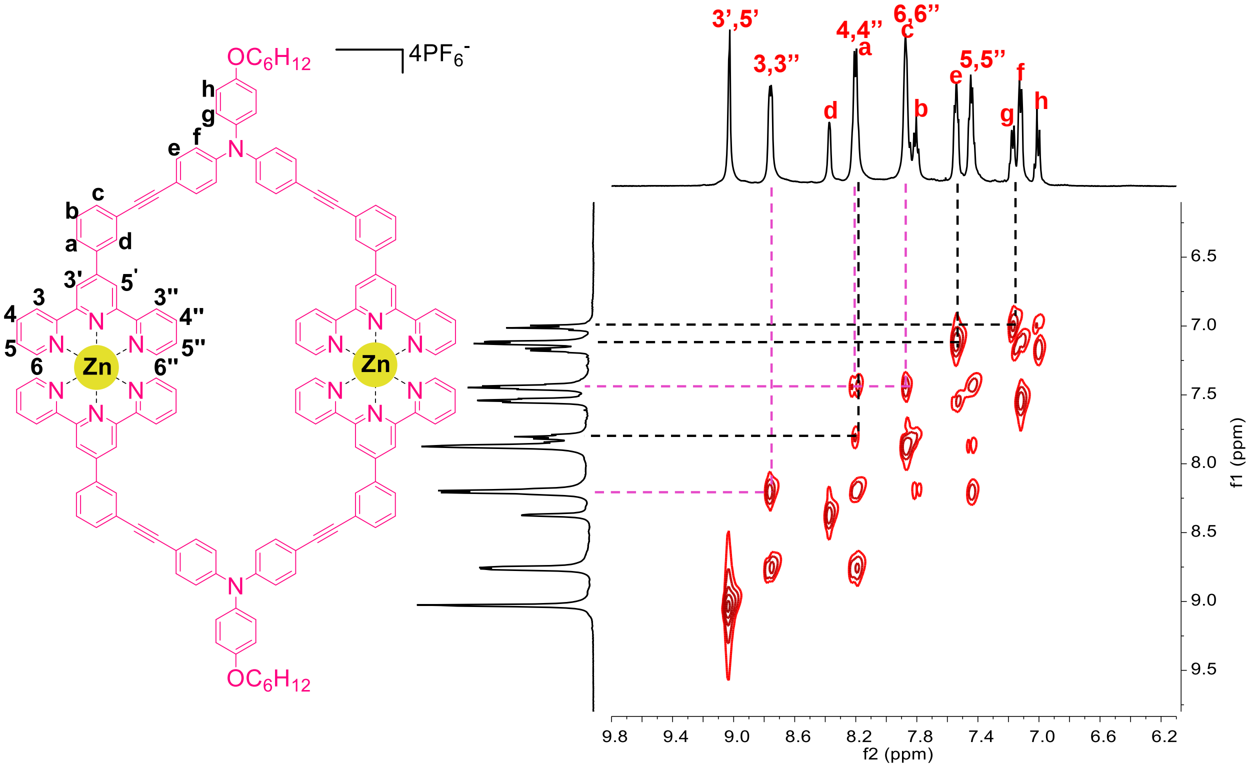

Figure S79. 2D COSY NMR (500 MHz, CD_3CN) spectrum of complex **G1**(aromatic region).

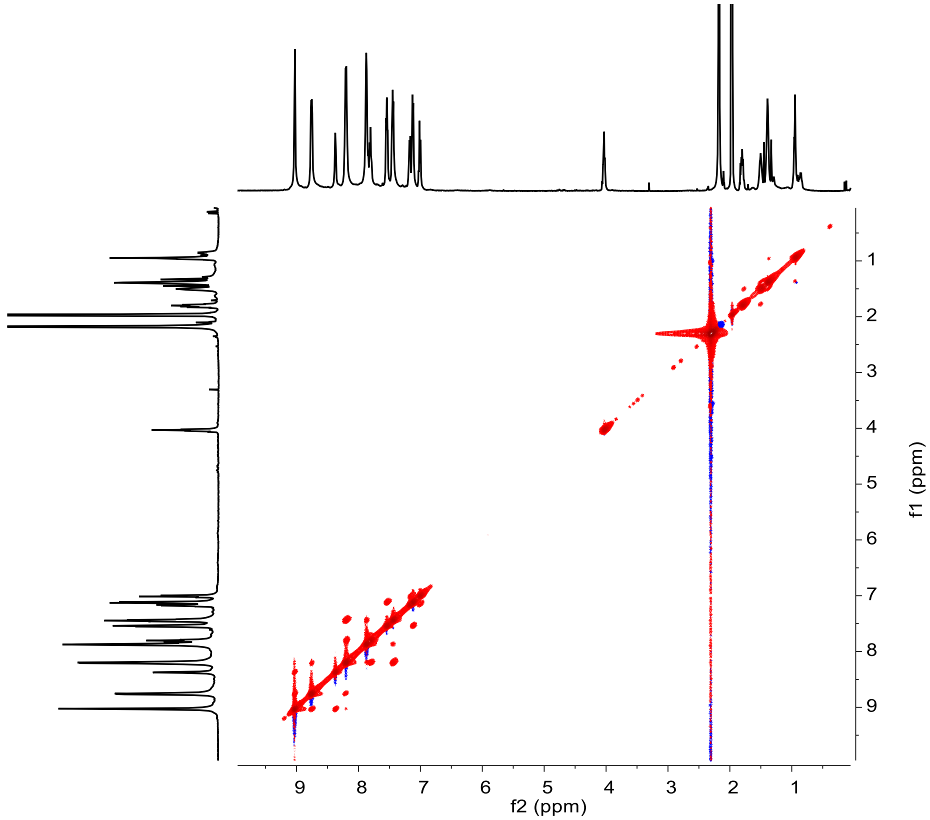

Figure S80. 2D NOESY NMR (500 MHz, CD_3CN) spectrum of complex **G1**.

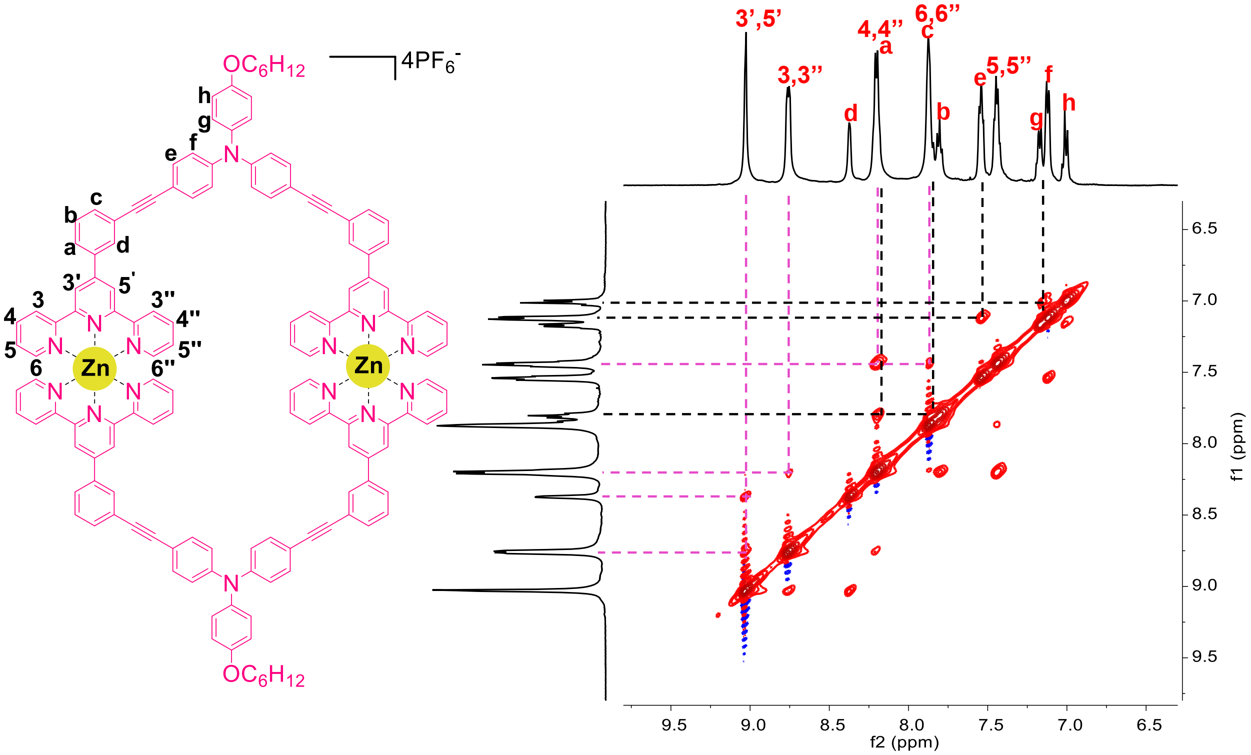

Figure S81. 2D NOESY NMR (500 MHz, CD_3CN) spectrum of complex **G1**(aromatic region).

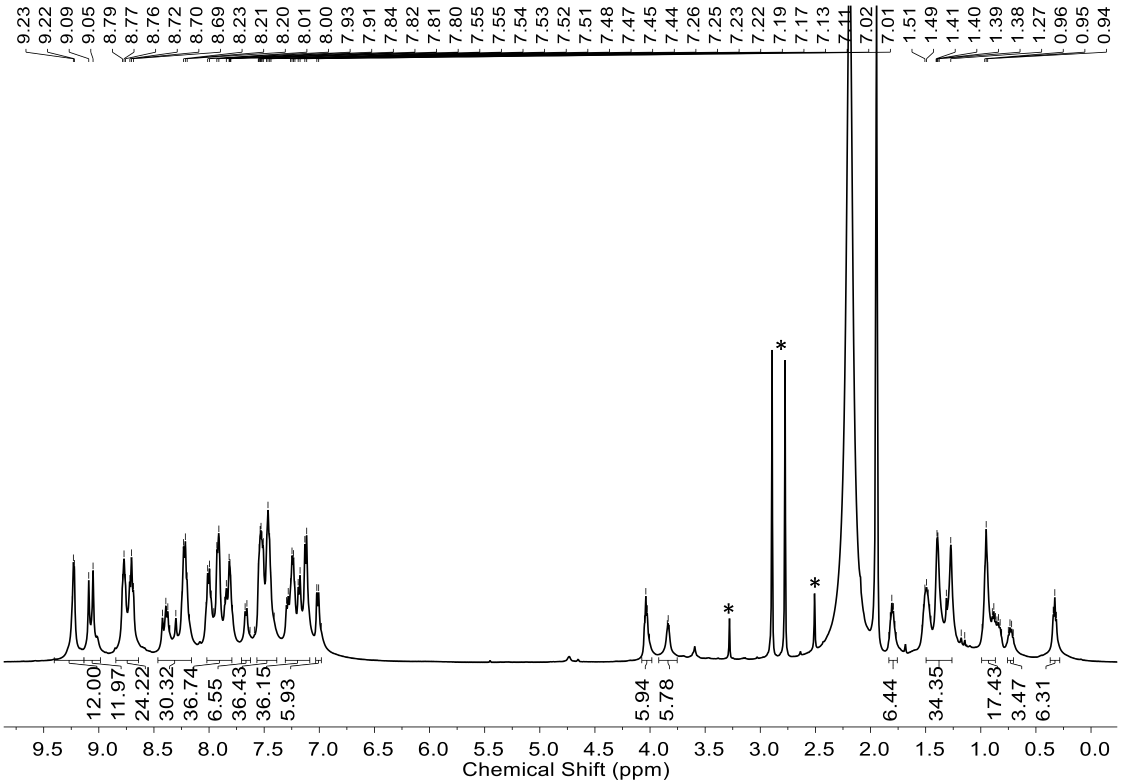

Figure S82. ^{1}H NMR (500 MHz, CD_3CN) spectrum of complex **G2** (asterisk represent CH_3OH, DMF, DMSO from left to right).

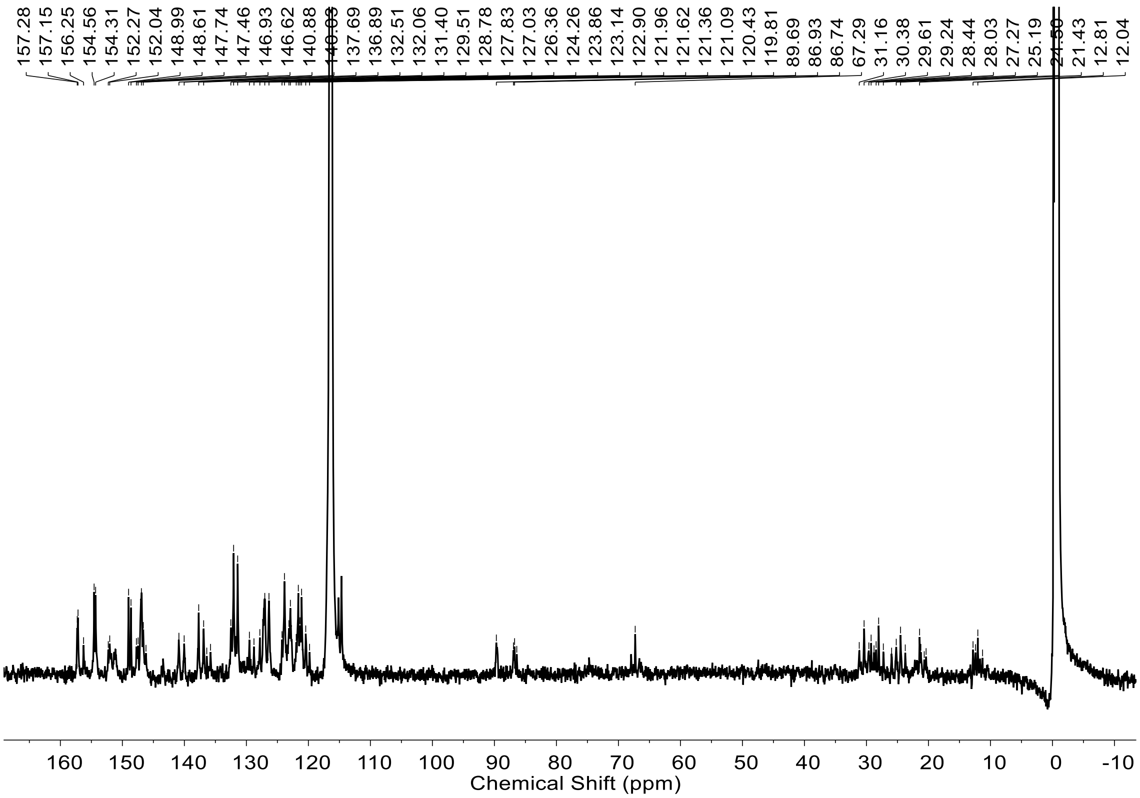

Figure S83. ^{13}C NMR (125 MHz, CD_3CN) spectrum of complex **G2**.

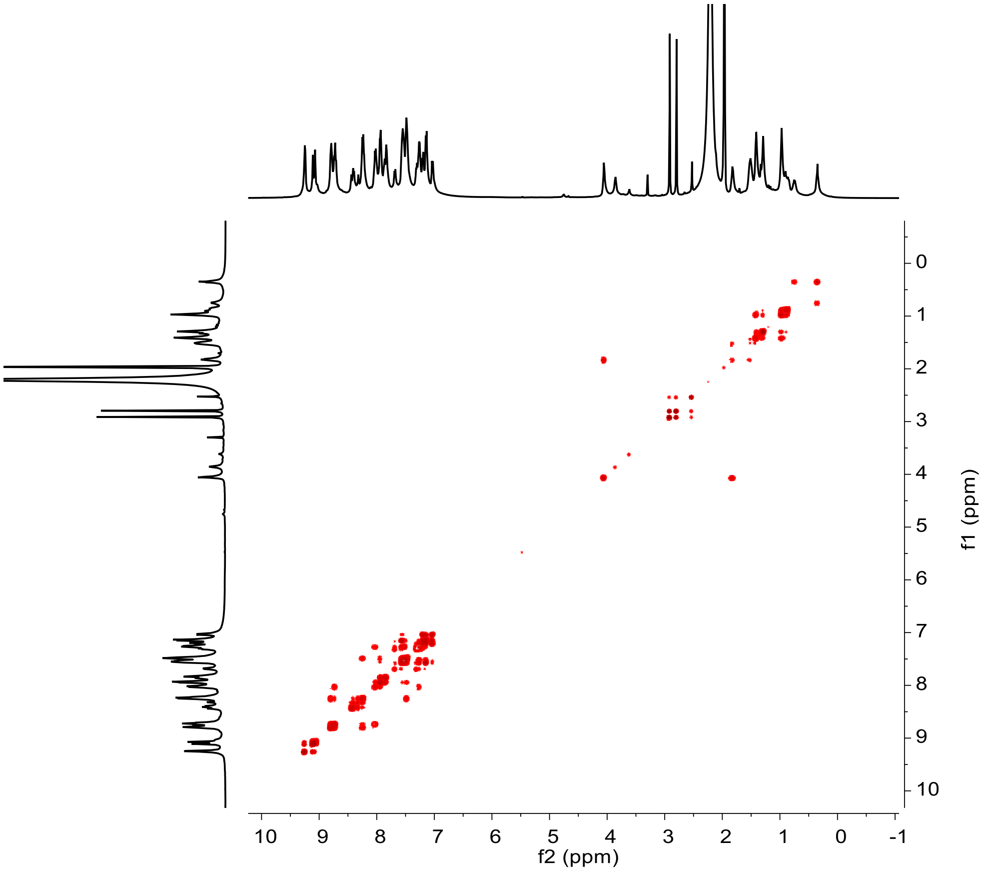

Figure S84. 2D COSY NMR (500 MHz, CD_3CN) spectrum of complex **G2**.

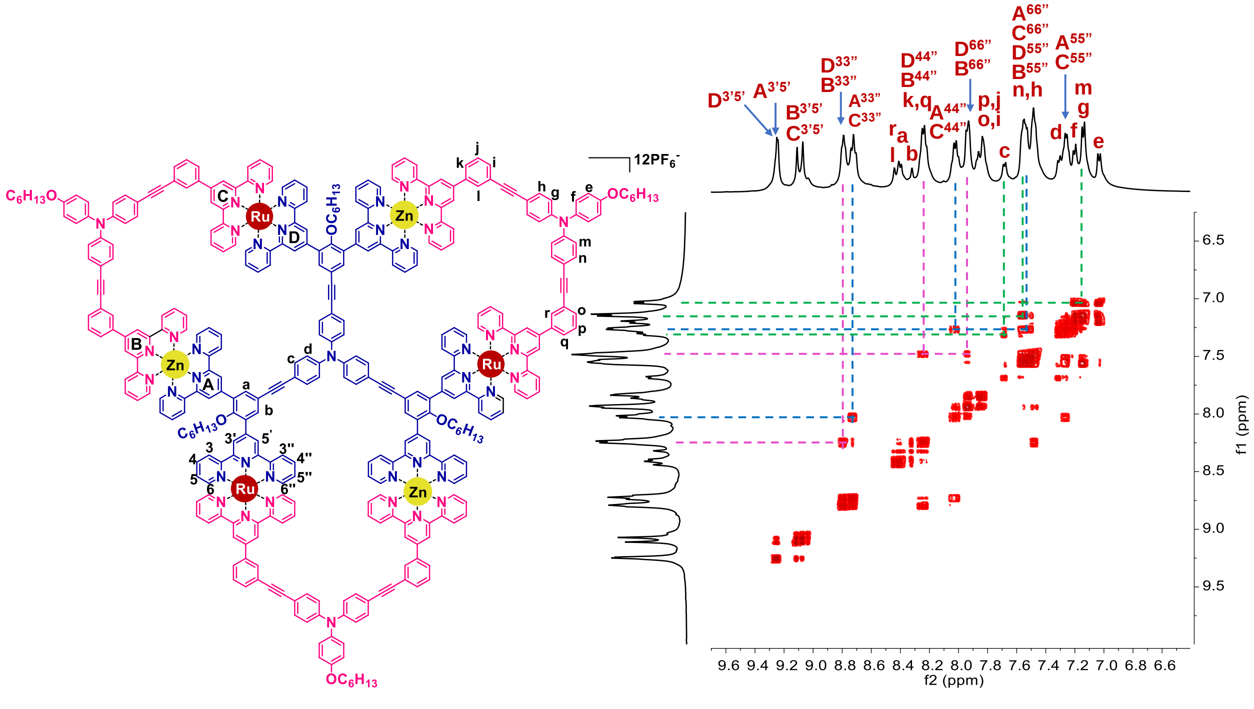

Figure S85. 2D COSY NMR (500 MHz, CD_3CN) spectrum of complex **G2** (aromatic region).

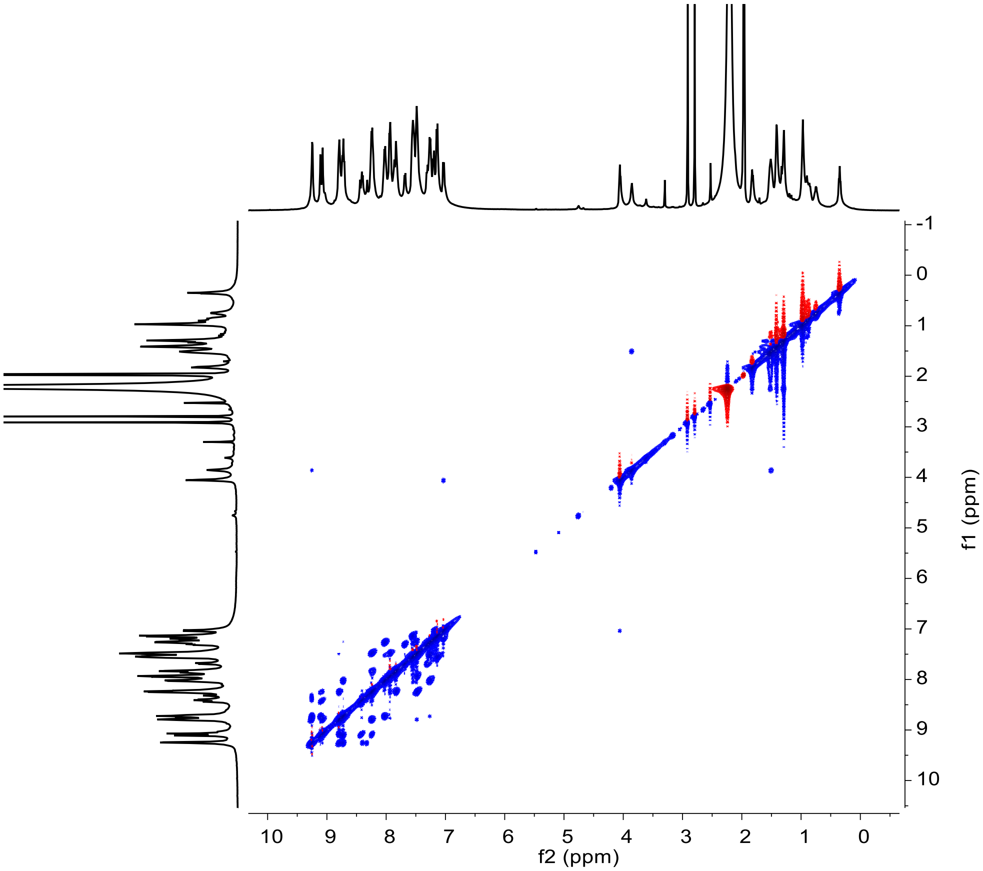

Figure S86. 2D NOESY NMR (500 MHz, CD_3CN) spectrum of complex **G2**.

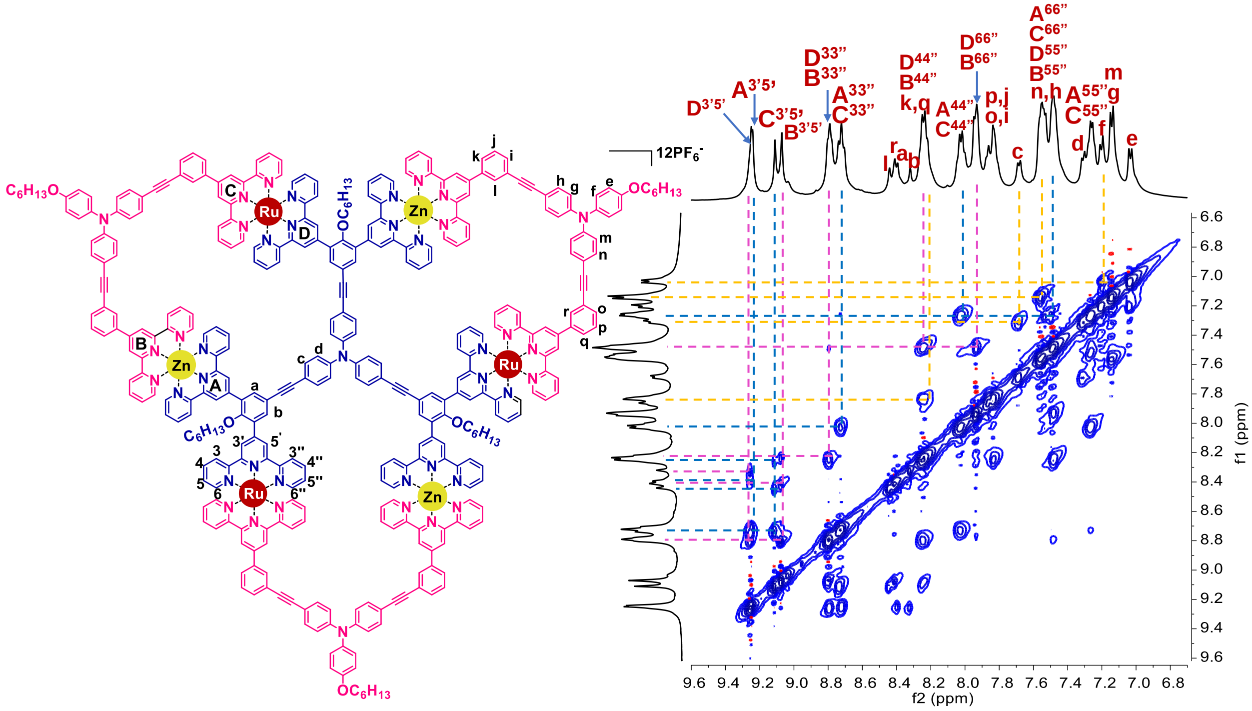

Figure S87. 2D NOESY NMR (500 MHz, CD_3CN) spectrum of complex **G2** (aromatic region).

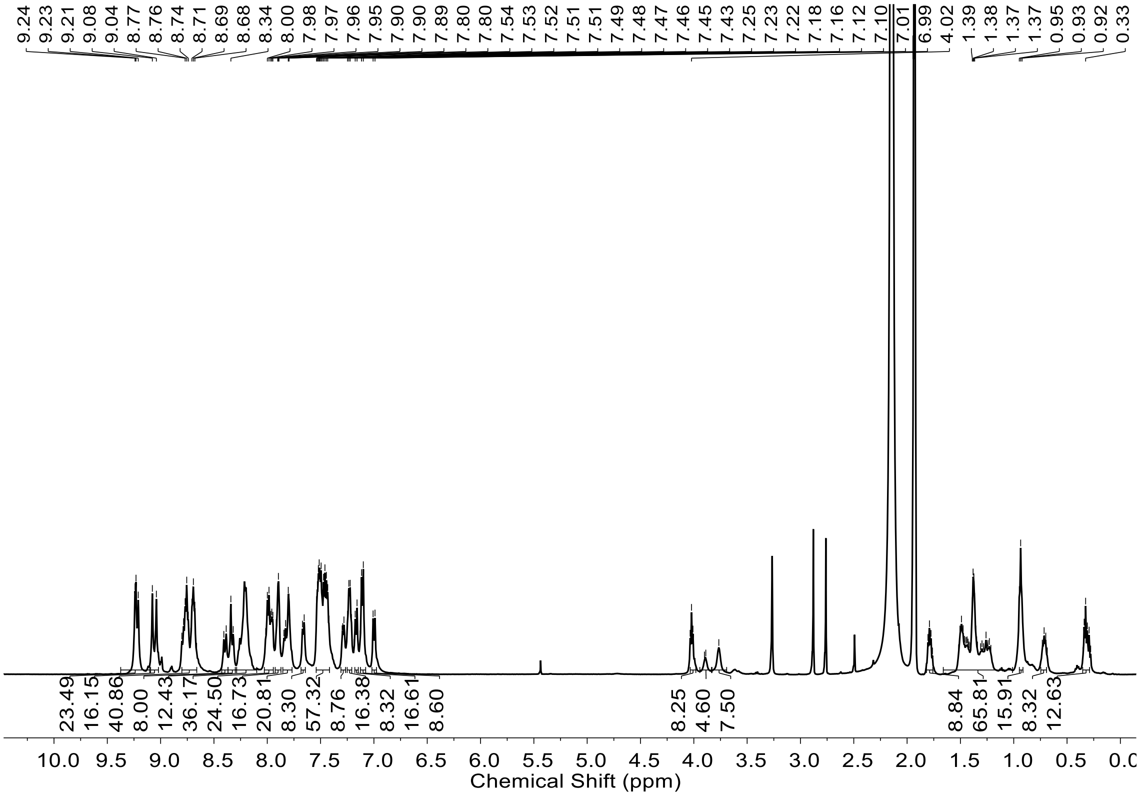

Figure S88. ^{1}H NMR (500 MHz, CD$_3$CN) spectrum of complex **G3**.

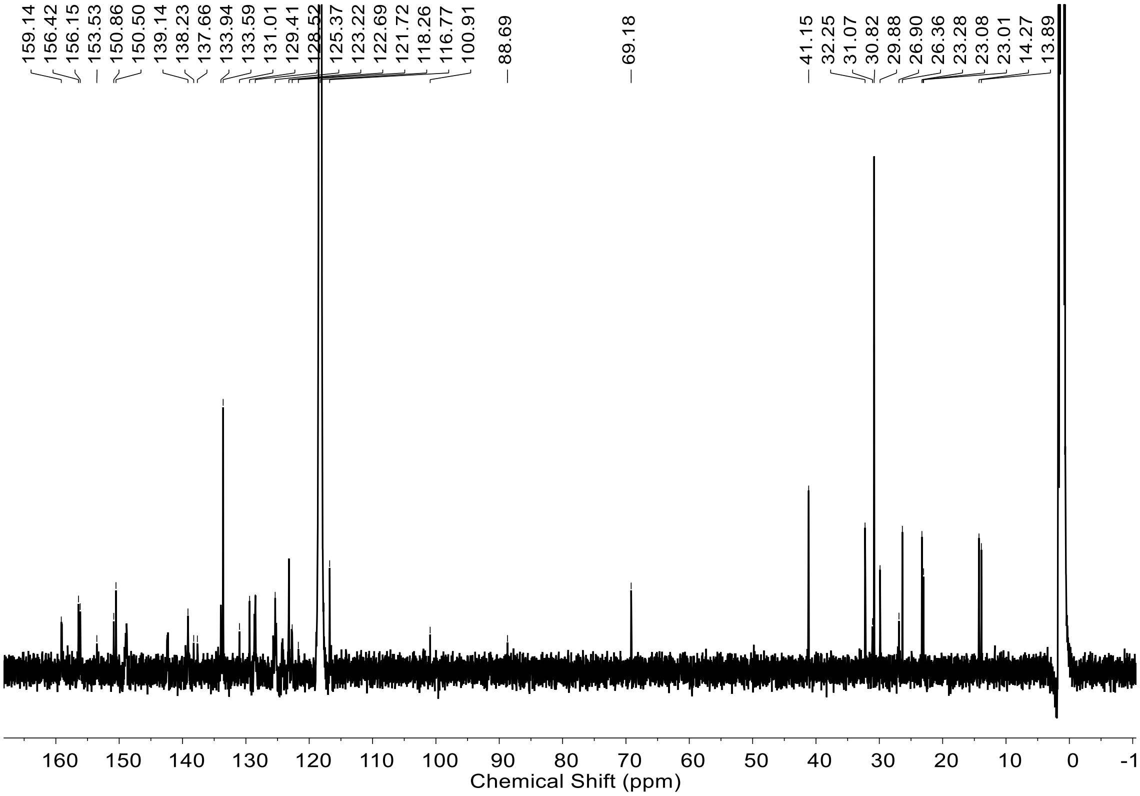

Figure S89. ^{13}C NMR (125 MHz, CD$_3$CN) spectrum of complex **G3**.

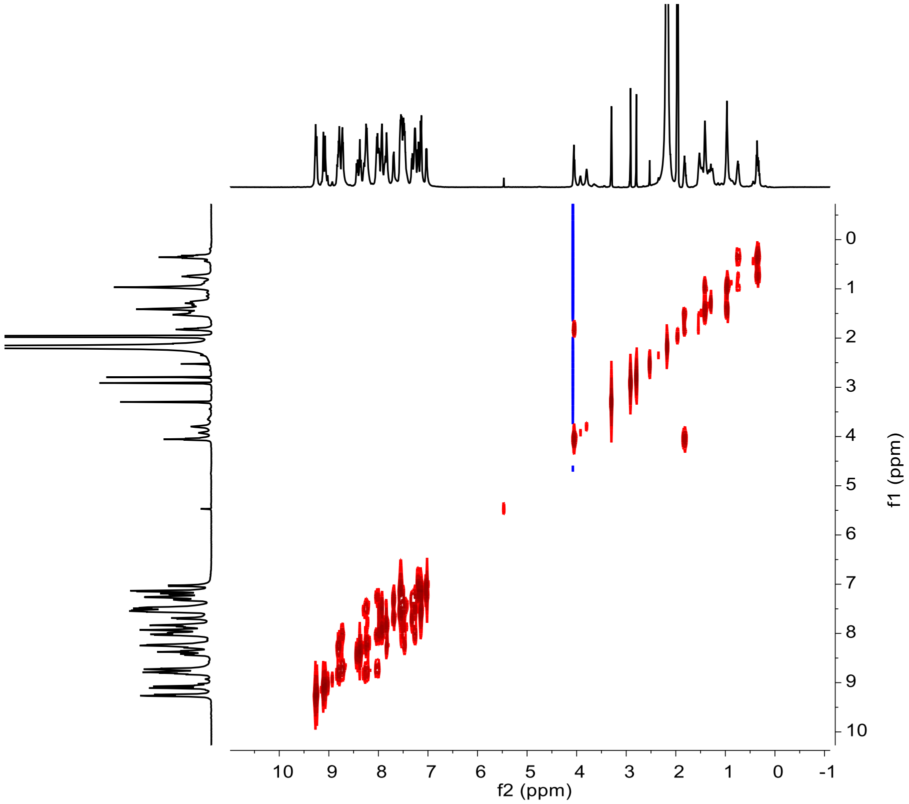

Figure S90. 2D COSY NMR (500 MHz, CD_3CN) spectrum of complex **G3**.

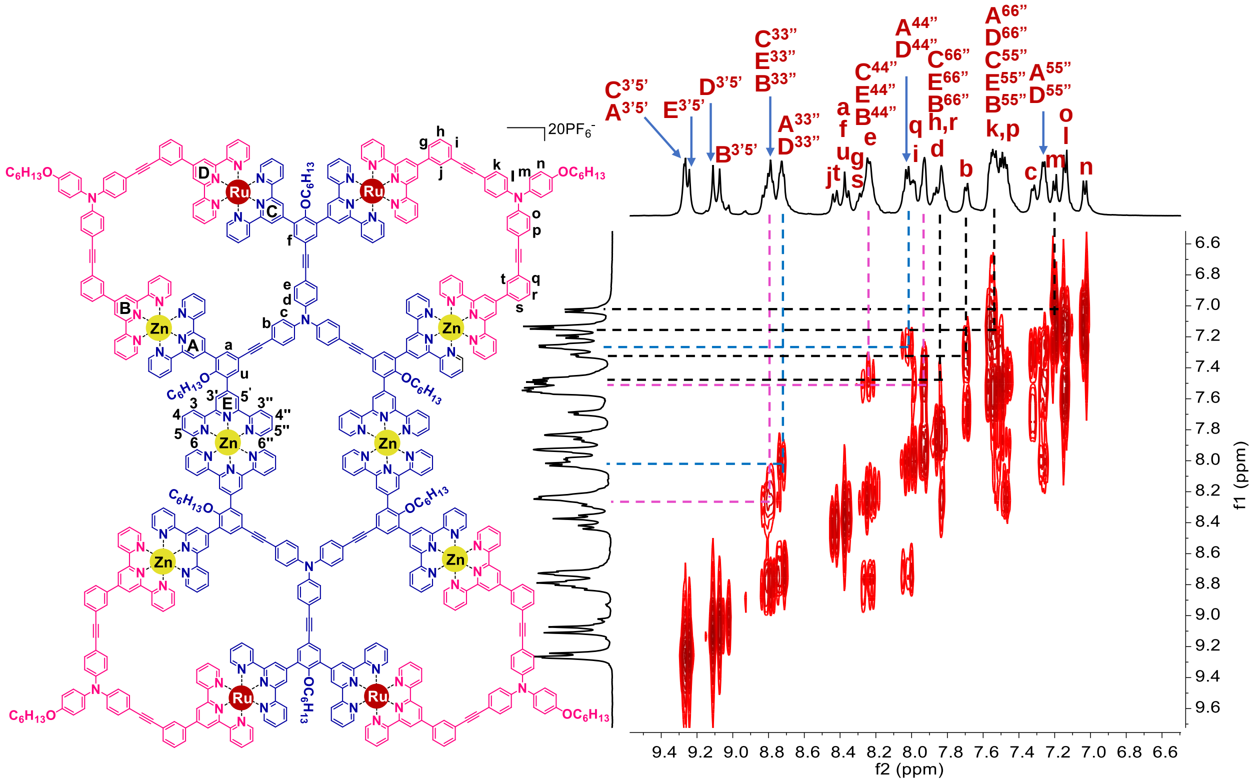

Figure S91. 2D COSY NMR (500 MHz, CD_3CN) spectrum of complex **G3** (aromatic region).

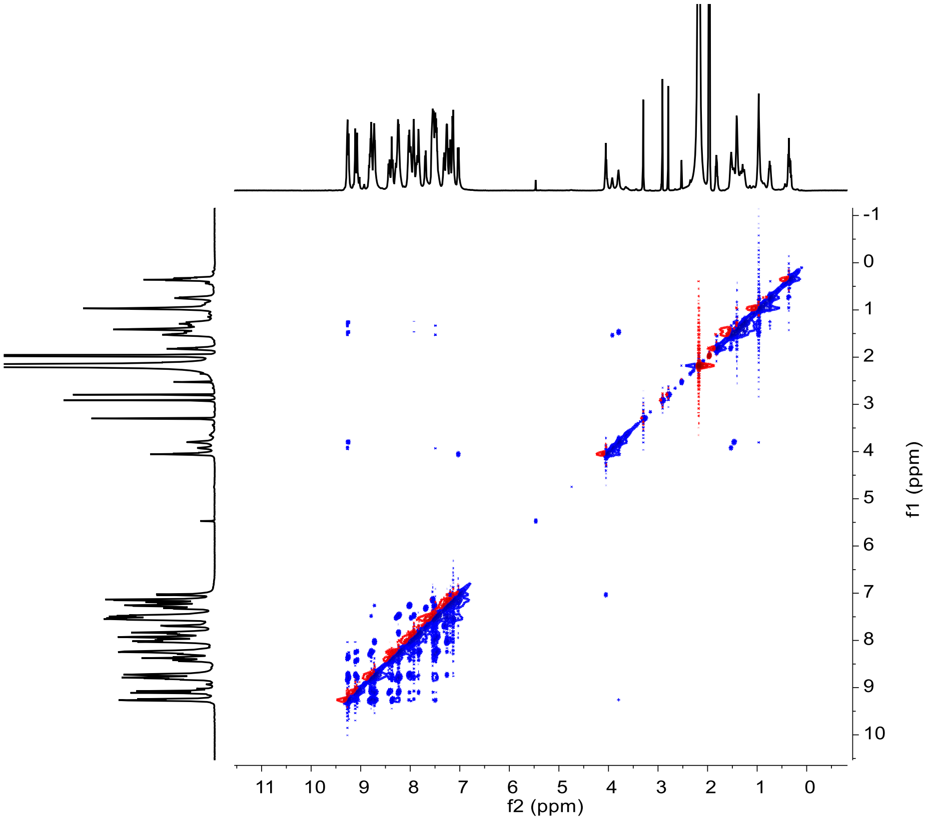

Figure S92. 2D NOSEY NMR (500 MHz, CD_3CN) spectrum of complex **G3** (aromatic region).

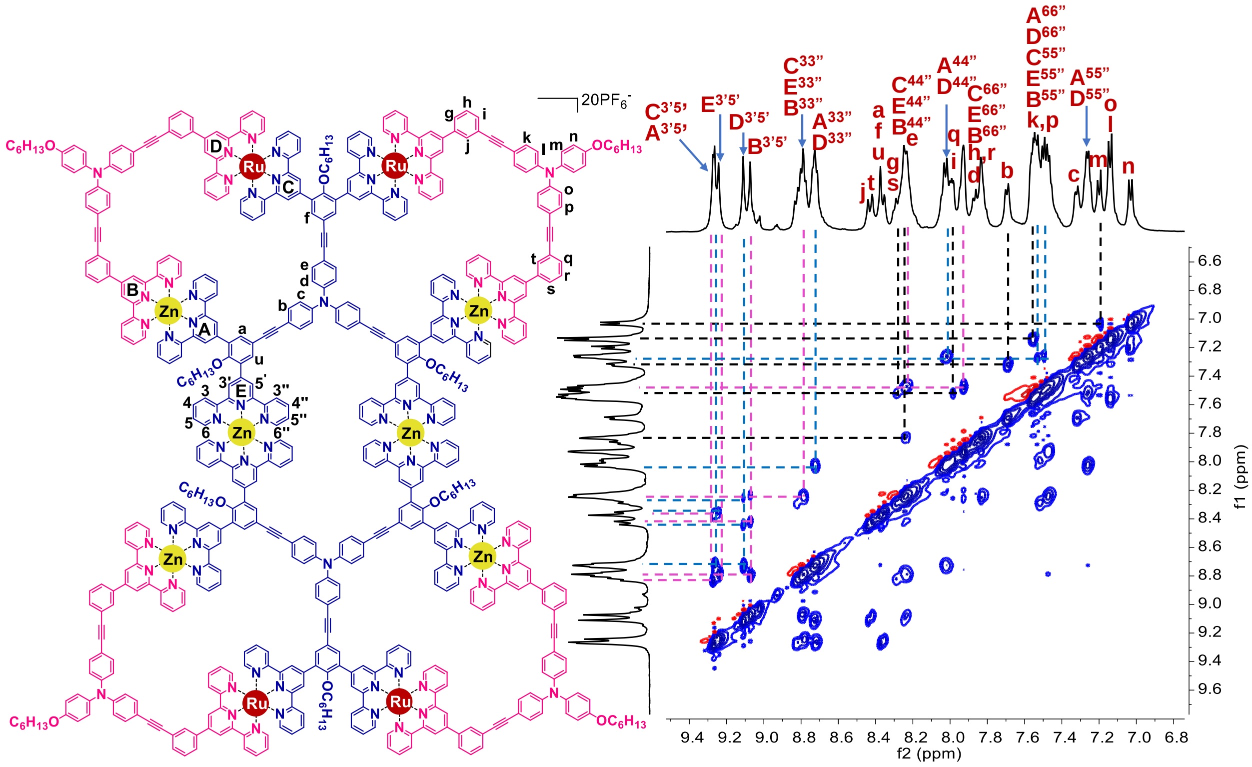

Figure S93. 2D NOESY NMR (500 MHz, CD_3CN) spectrum of complex **G3** (aromatic region).

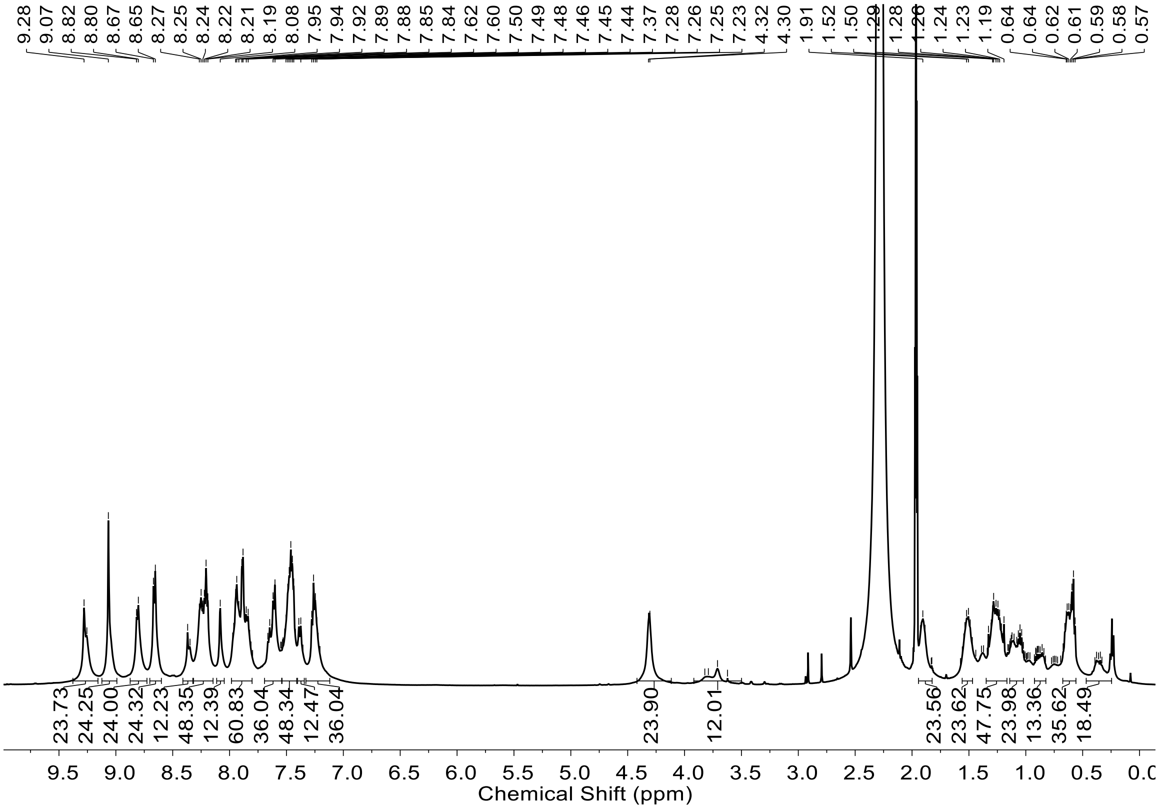

Figure S94. ^{1}H NMR (500 MHz, CD_3CN) spectrum of complex **G4**.

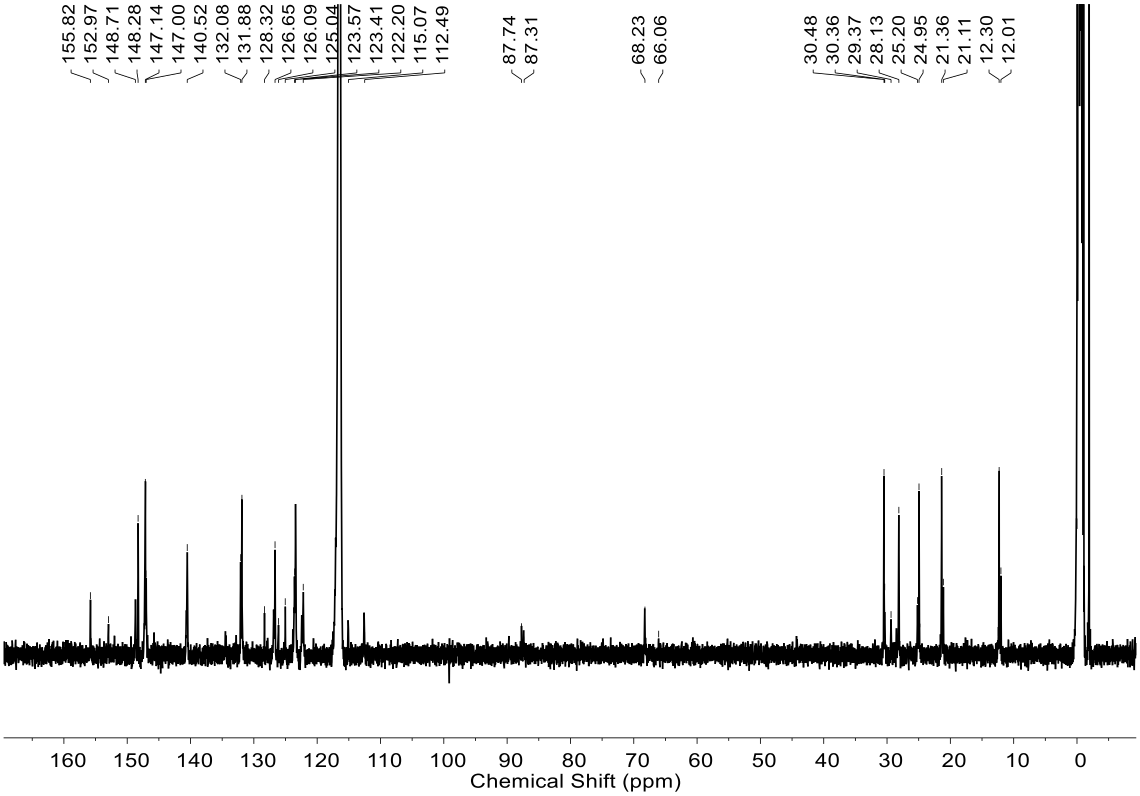

Figure S95. ^{13}C NMR (125 MHz, CD_3CN) spectrum of complex **G4**.

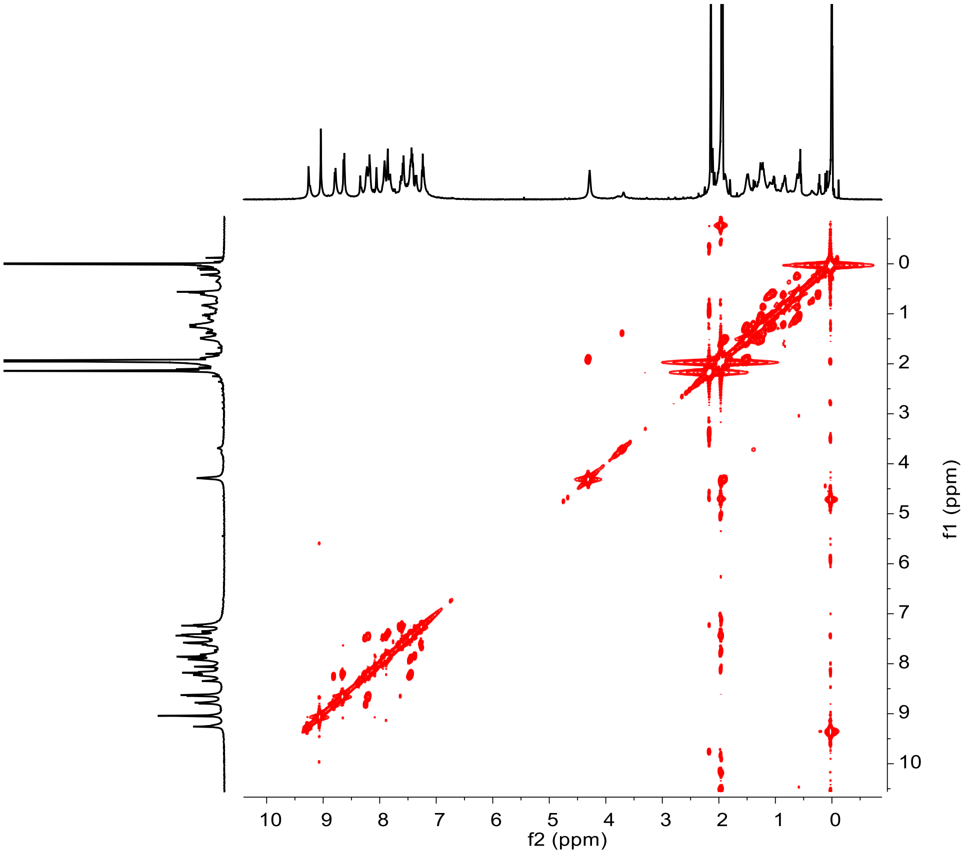

Figure S96. 2D COSY NMR (500 MHz, CD_3CN) spectrum of complex **G4**.

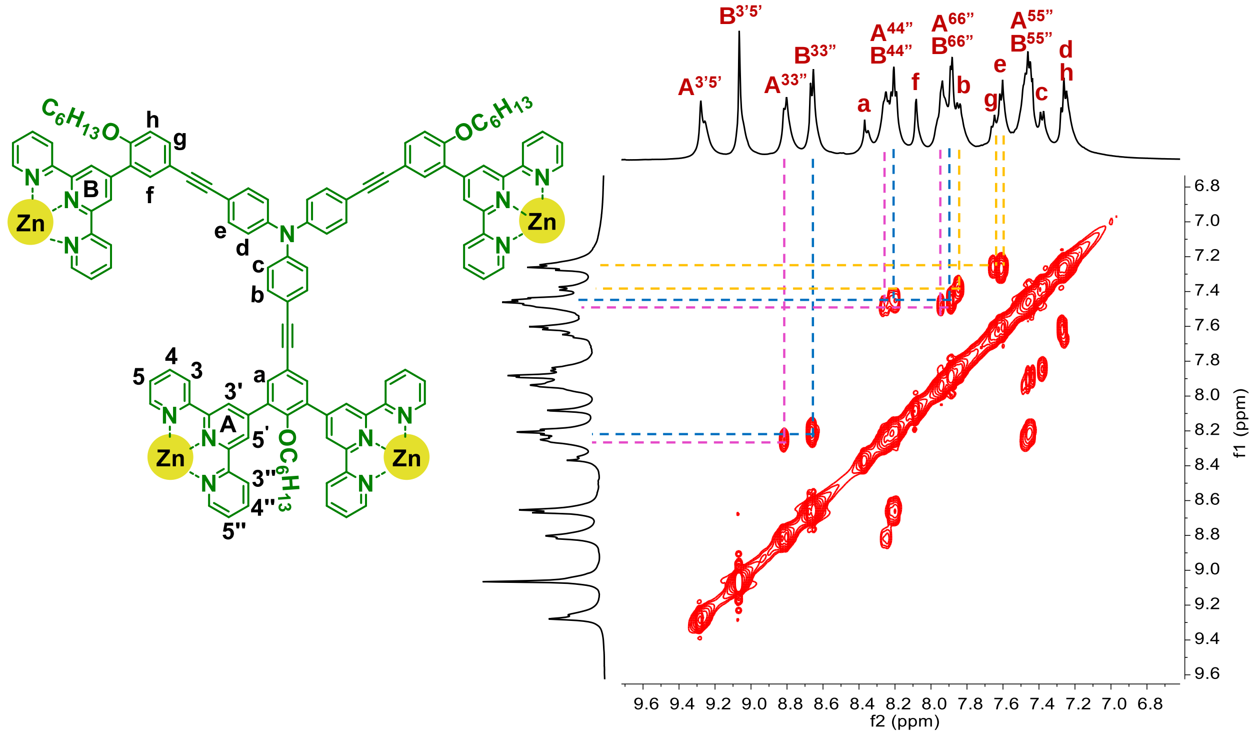

Figure S97. 2D COSY NMR (500 MHz, CD_3CN) spectrum of complex **G4** (aromatic region).

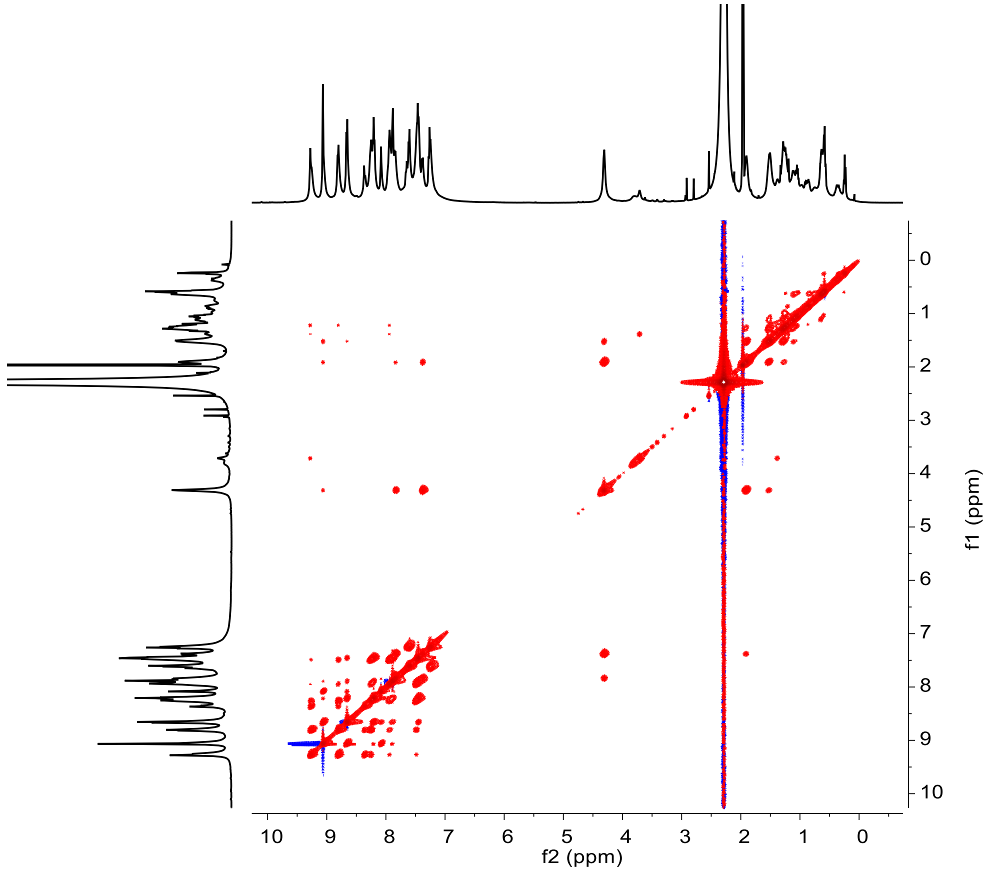

Figure S98. 2D NOESY NMR (500 MHz, CD_3CN) spectrum of complex **G4**.

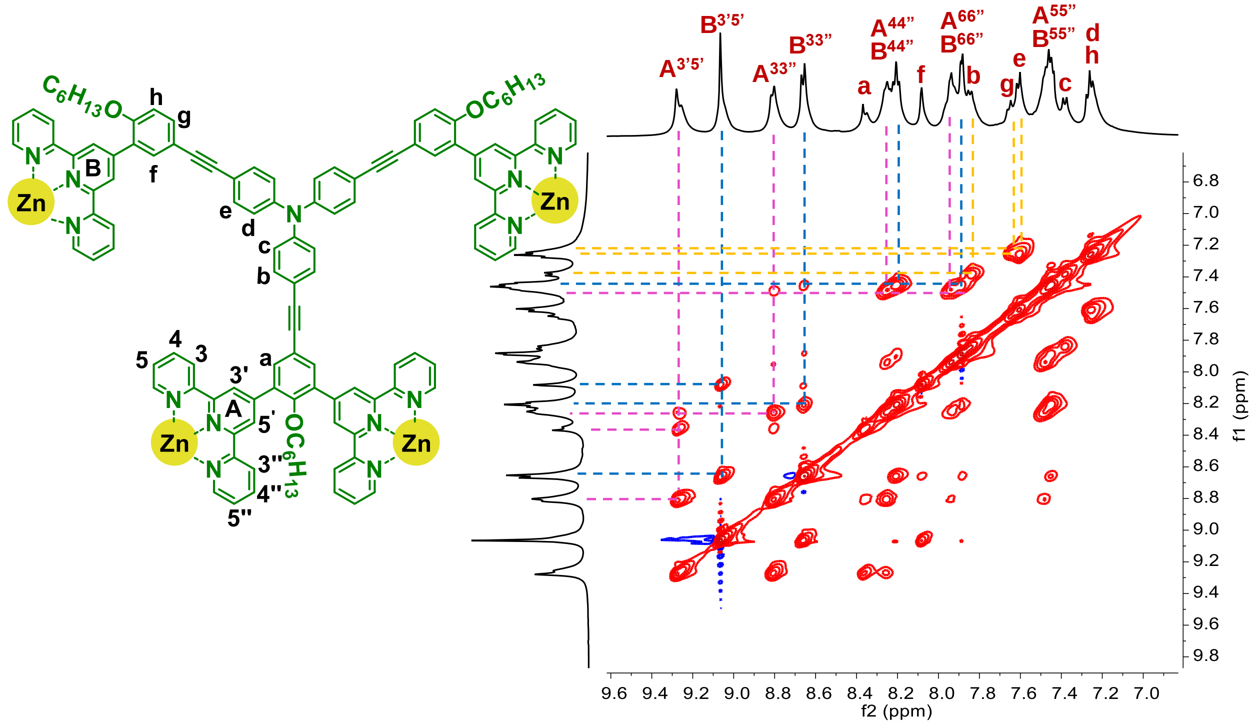

Figure S99. 2D NOESY NMR (500 MHz, CD_3CN) spectrum of complex **G4** (aromatic region).

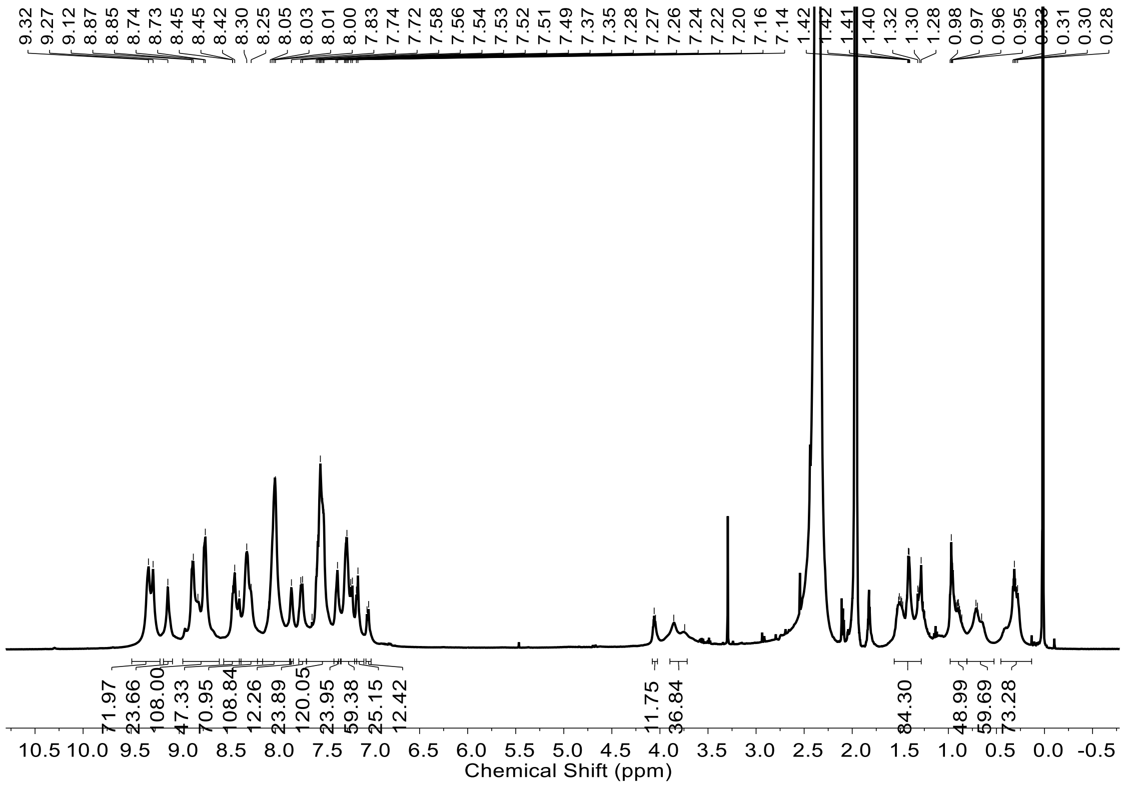

Figure S100. ^{1}H NMR (500 MHz, CD_3CN) spectrum of complex **G5**.

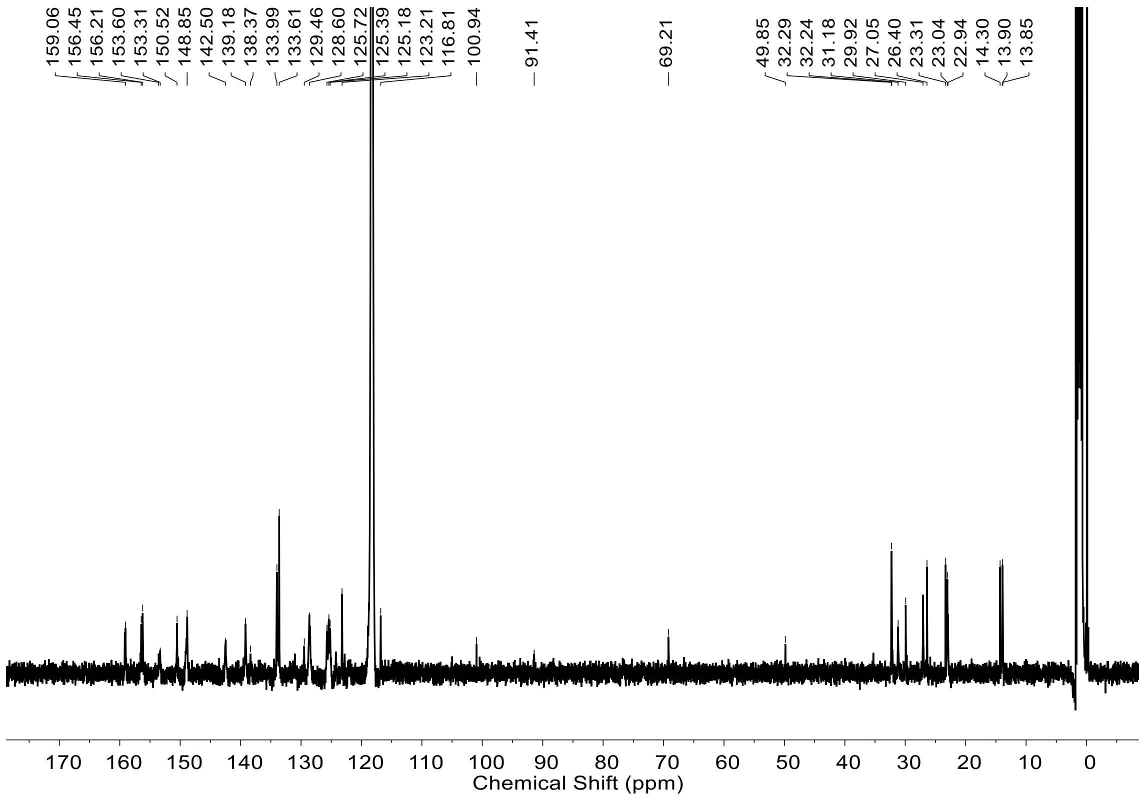

Figure S101. ^{13}C NMR (125 MHz, CD_3CN) spectrum of complex **G5**.

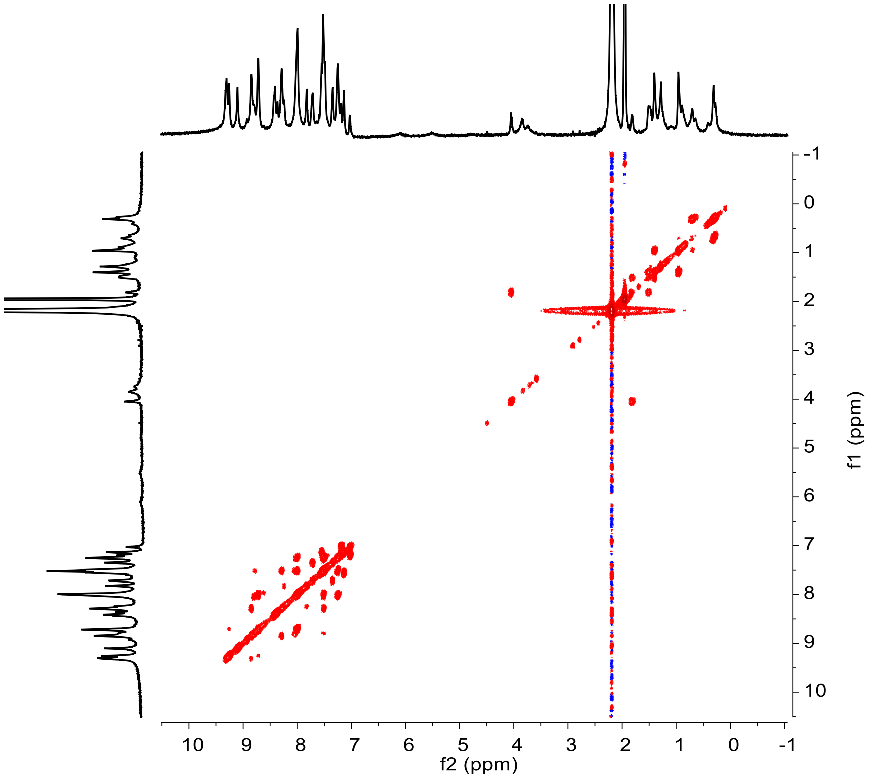

Figure S102. 2D COSY NMR (500 MHz, CD_3CN) spectrum of complex **G5**.

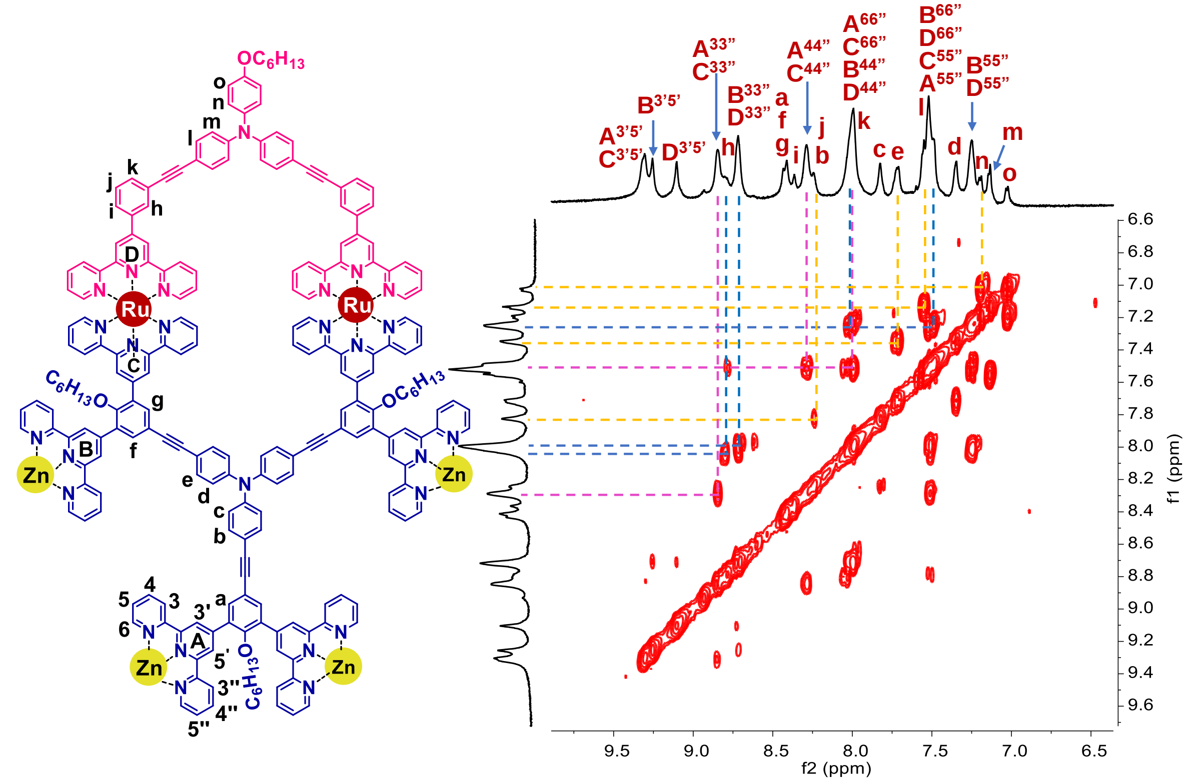

Figure S103. 2D COSY NMR (500 MHz, CD_3CN) spectrum of complex **G5** (aromatic region).

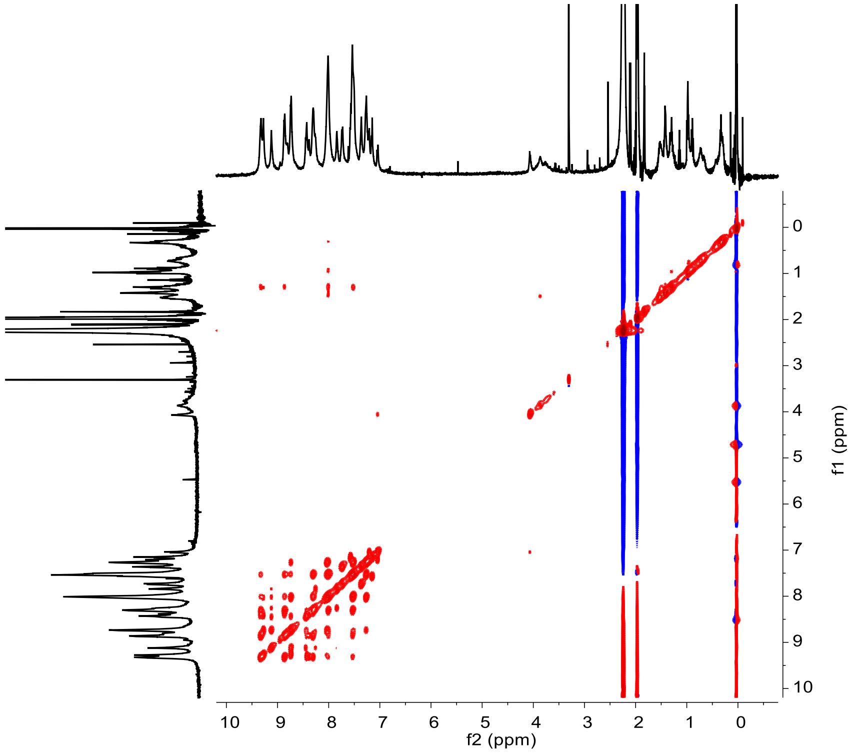

Figure S104. 2D NOESY NMR (500 MHz, CD_3CN) spectrum of complex **G5**.

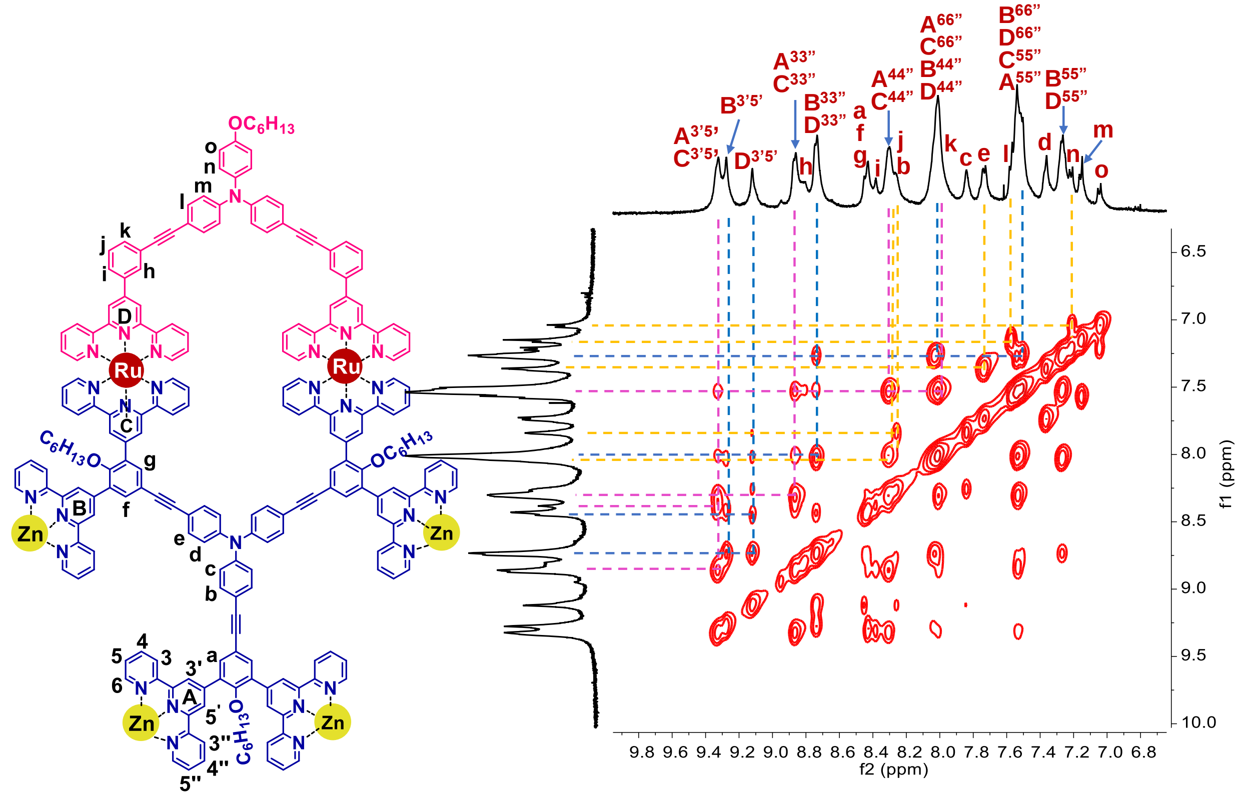

Figure S105. 2D NOESY NMR (500 MHz, CD_3CN) spectrum of complex **G5** (aromatic region).

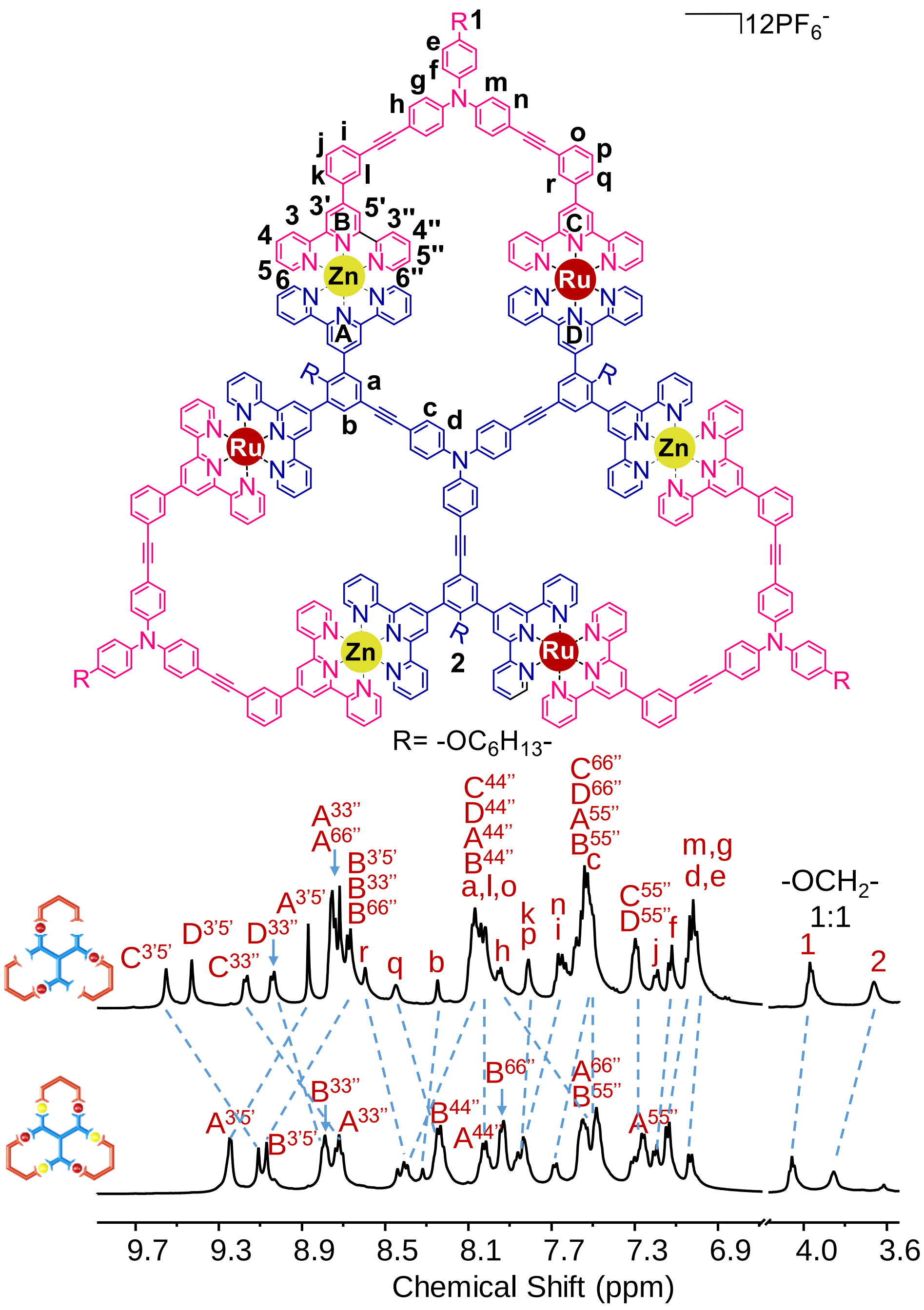

Figure S106. ^{1}H NMR spectra (500 MHz, 300 K) of **LB** in DMSO-d_6 and **G2** in CD$_3$CN.

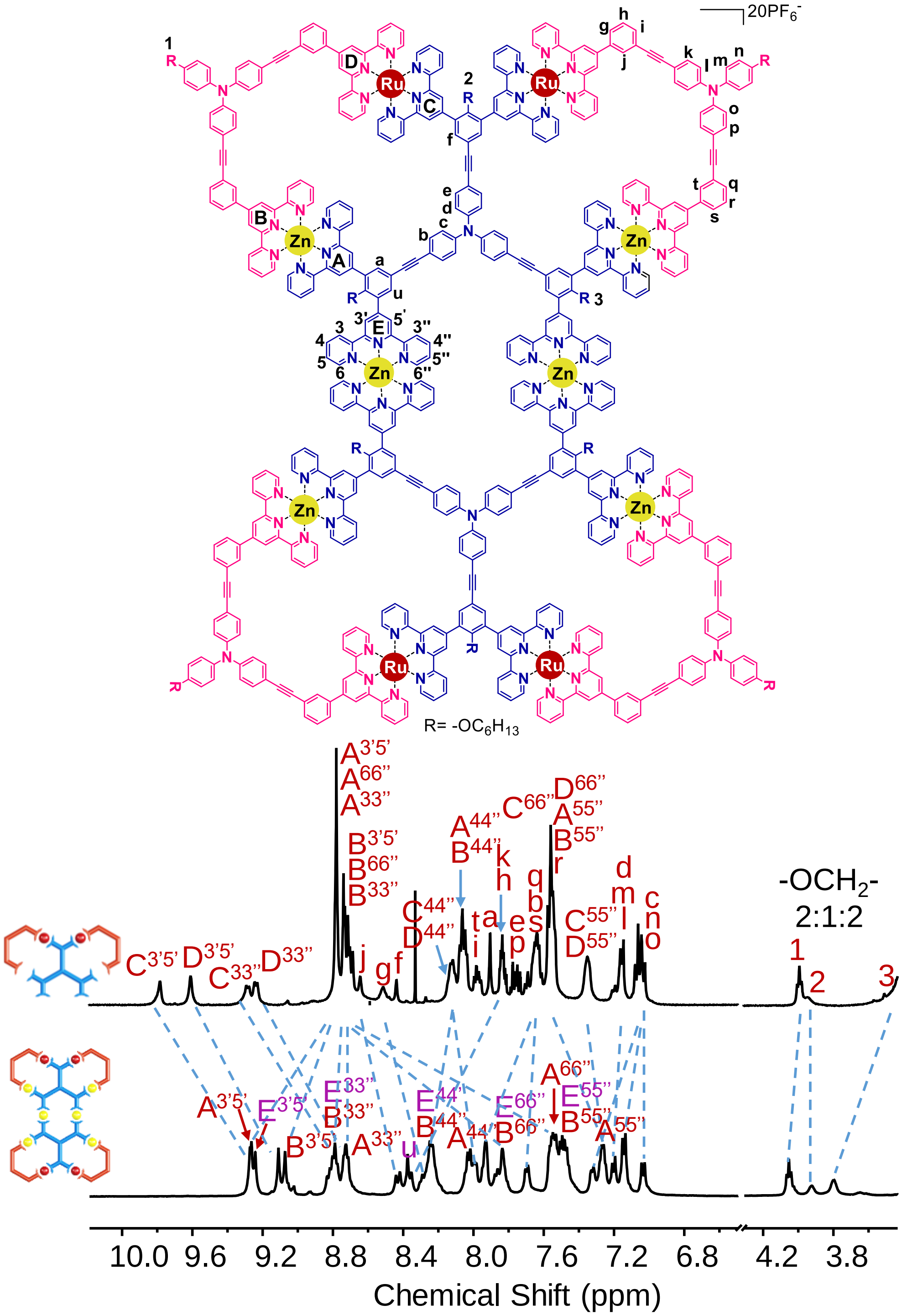

Figure S107. ^{1}H NMR spectra (500 MHz, 300 K) of **LC** in DMSO-d_6 and **G3** in CD$_3$CN.

7. Experimental diffusion coefficient and hydrodynamic radius

Table S1. Experimental diffusion coefficient (D) and hydrodynamic radius (r_{H})

fractal	D_{exp} (m^2/s)	Log D	r_H (from D, nm)	r (from modeling, nm)
G1	$4.99X10^{-10}$	-9.30	1.3	1.1
G2	$3.05X10^{-10}$	-9.52	2.4	2.5
G3	$2.63X10^{-10}$	-9.58	2.9	2.8
G4	$1.92X10^{-10}$	-9.62	4.2	3.5
G5	$1.46X10^{-10}$	-9.84	5.7	5.5

Note: the r_H obtained from D adopted the oblate spheroid model.[14-15] See the supporting information of reference for detailed calculation process.[16]

8. TEM and STM images

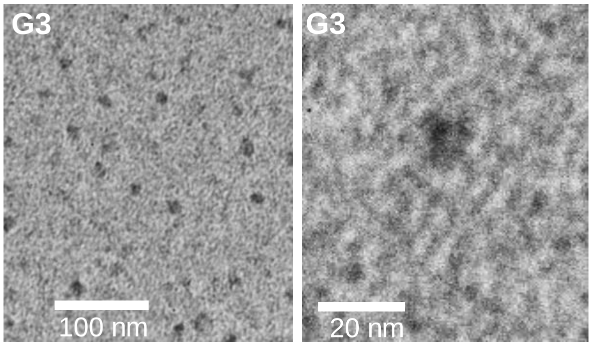

Figure S108. TEM images of **G3**.

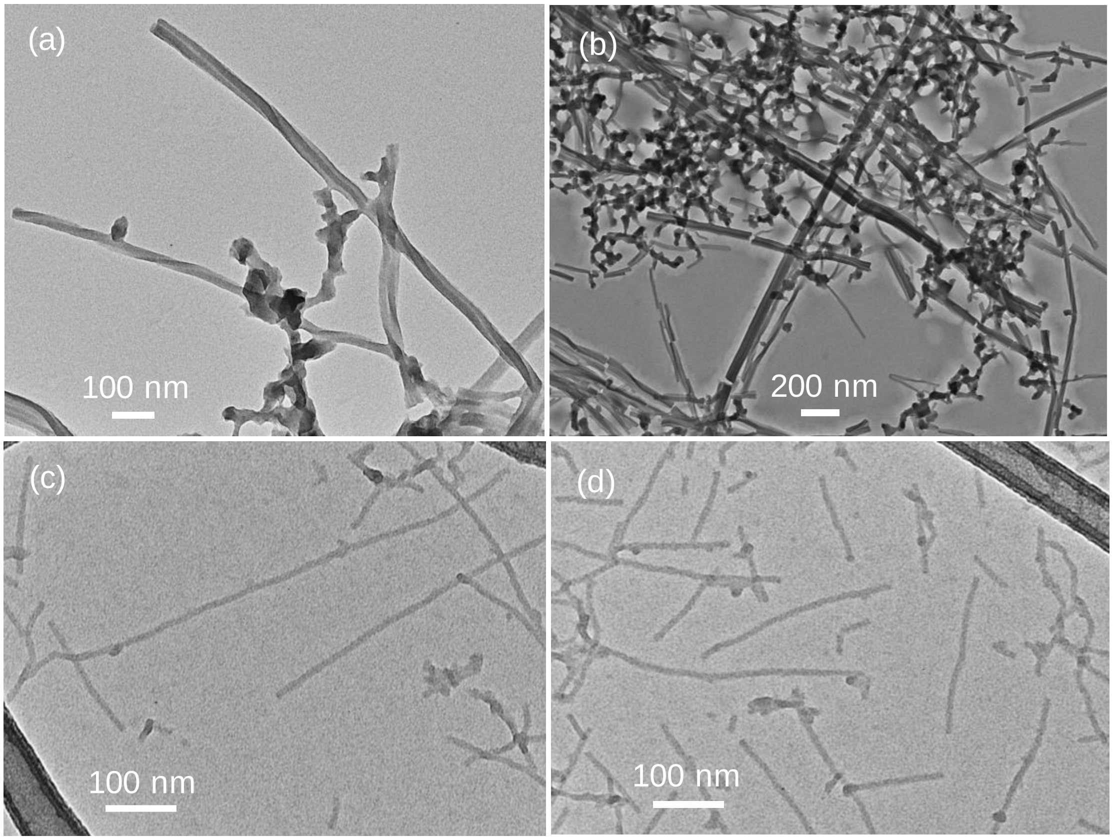

Figure S109. TEM images of tubular structure formed by **G4** (a, b) and **G5** (c, d).

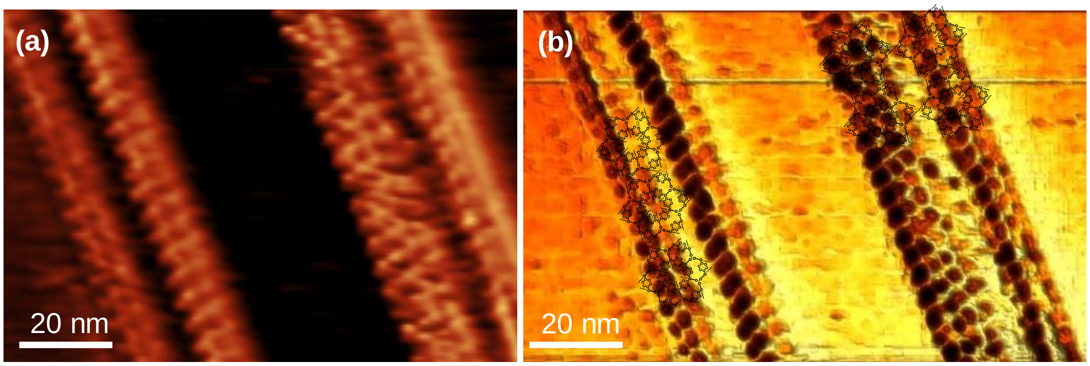

Figure S110. STM images of supramolecular metal-organic nanoribbons formed by **G4** on HOPG surface.

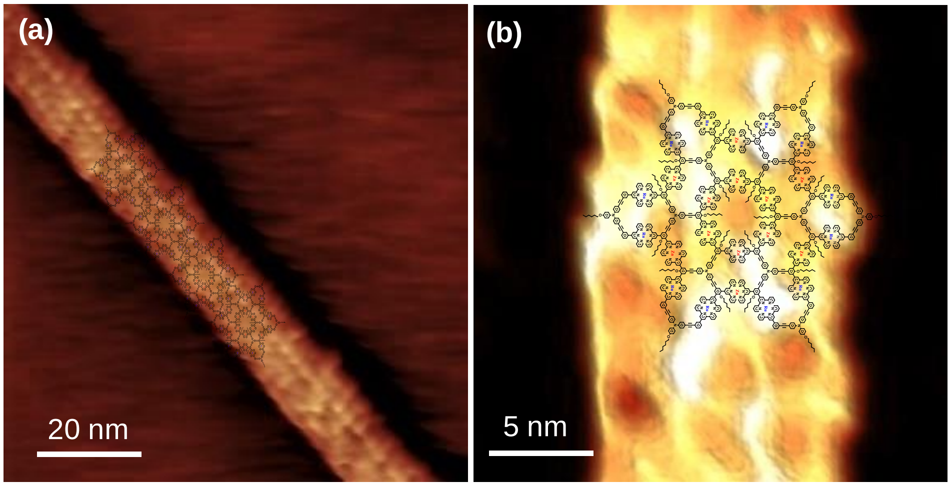

Figure S111. STM images of supramolecular metal-organic nanoribbons formed by formed by **G5** on HOPG surface.

9. UV-Vis and CV spectra

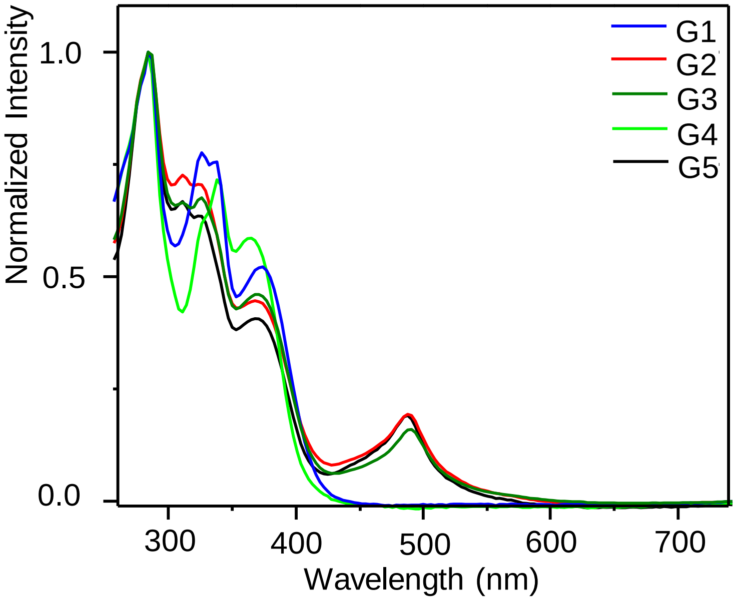

Figure S112. UV-vis (10^{-6} M in CH_3CN, 298 K) of fractals.

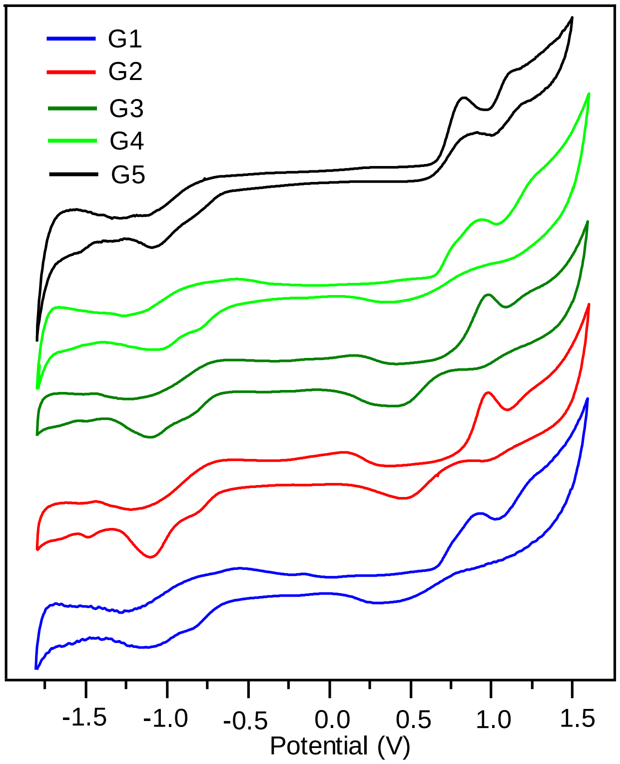

Figure S113. Cyclic voltammograms of five fractals (10^{-5} M in DMF with 0.1 M n-Bu_4PF_6, 298 K) at a scan rate of 100 mV/s.

10. Reference:

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