Supplementary Information

Insulated π-Conjugated 2,2'-Bipyridine Transition-Metal Complexes: Enhanced Photoproperties in Luminescence and Catalysis

Tomohiro Iwai,* Shinsuke Abe, Shin-ya Takizawa, Hiroshi Masai and Jun Terao*

E-mail: ciwai@g.ecc.u-tokyo.ac.jp (T.I.),   cterao@mail.ecc.u-tokyo.ac.jp (J.T.)

Table of Contents

1. General remarks

1.1 Materials

Unless otherwise noted, manipulations were performed under nitrogen atmosphere using standard Schlenk-type glassware in a dual-manifold Schlenk line. Unless otherwise stated, commercially available chemicals were used as received. **1** was synthesized according to the literature.[1] Toluene, tetrahydrofuran, dichloromethane, and *N,N*-dimethylformamide (DMF) were purchased from KANTO CHEMICAL Co., Inc., and further purified by passage through activated alumina under positive nitrogen pressure as described by Grubbs *et al.*[2]

1.2 Experimental equipment

NMR spectroscopy: ^{1}H NMR (500 MHz), ^{13}C {^{1}H} NMR (126 MHz), and ^{1}H-^{1}H ROESY NMR (500 MHz) spectra were measured with a Bruker AVANCE III HD 500. The ^{1}H NMR chemical shifts were reported relative to residual protonated solvents (7.26 ppm) in $CDCl_3$. The ^{13}C NMR chemical shifts were reported relative to deuterated solvents (77.16 ppm) in $CDCl_3$.

High-Resolution Mass spectroscopy (HR-MS): Electrospray ionization time-of-flight (ESI-ToF) mass spectra were obtained using a Bruker micrOTOF II-KE02. The HR-MS spectra were internally calibrated using NaTFA clusters.

Flash column chromatography: Flash column chromatography was performed using Isolera One.

Preparative recycling gel permeation chromatography (GPC): Preparative recycling GPC was performed with a SHIMADZU LC-20AP System equipped with Shodex K-4002L and Shodex K-4002.5L columns, a SHIMADZU SPD-20A and a SHIMADZU RID-10A, or a JAI LC9130 System equipped with JAIGEL-2.5H column, a JAI UV DETECTOR UV 370 NEXT and a JAI RI DETECTOR RI-700-NEXT using chloroform as the eluent at a flow rate of 14 mL min^{-1}.

Light Source: LED irradiation experiments were conducted using a PhotoRedOx Box (HepatoChem, Inc.) equipped with Kessil PR 160L-427nm (40 W, maximum intensity).

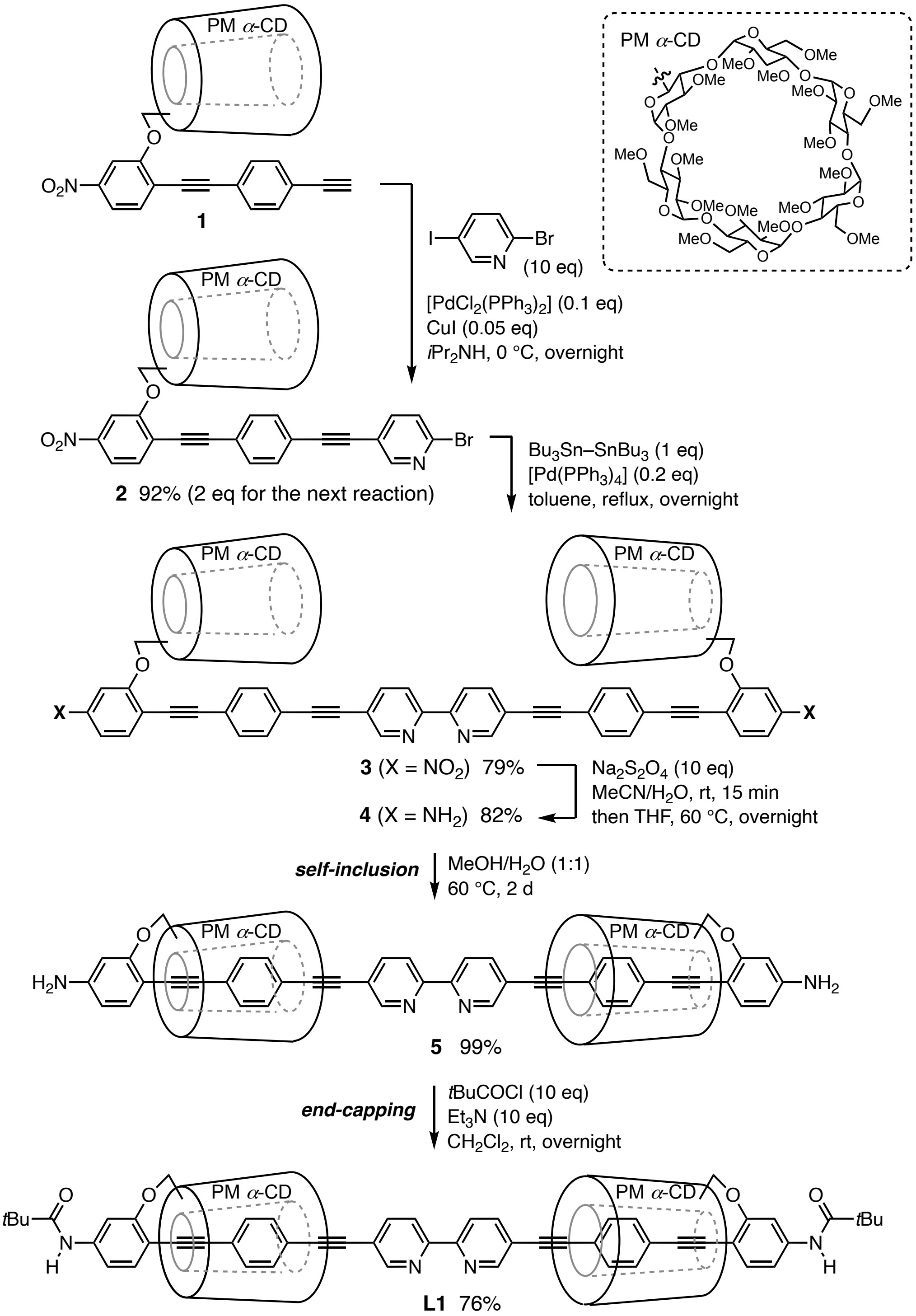
Absorption spectroscopy: Absorption spectra were measured with a SHIMADZU UV-2600 spectrophotometer using DMF or CH_2Cl_2 as the solvent under air atmosphere.

Emission spectroscopy: Emission spectra were measured with a Shimadzu RF-6000 fluorescence spectrophotometer using CH_2Cl_2 as the solvent under N_2 atmosphere.

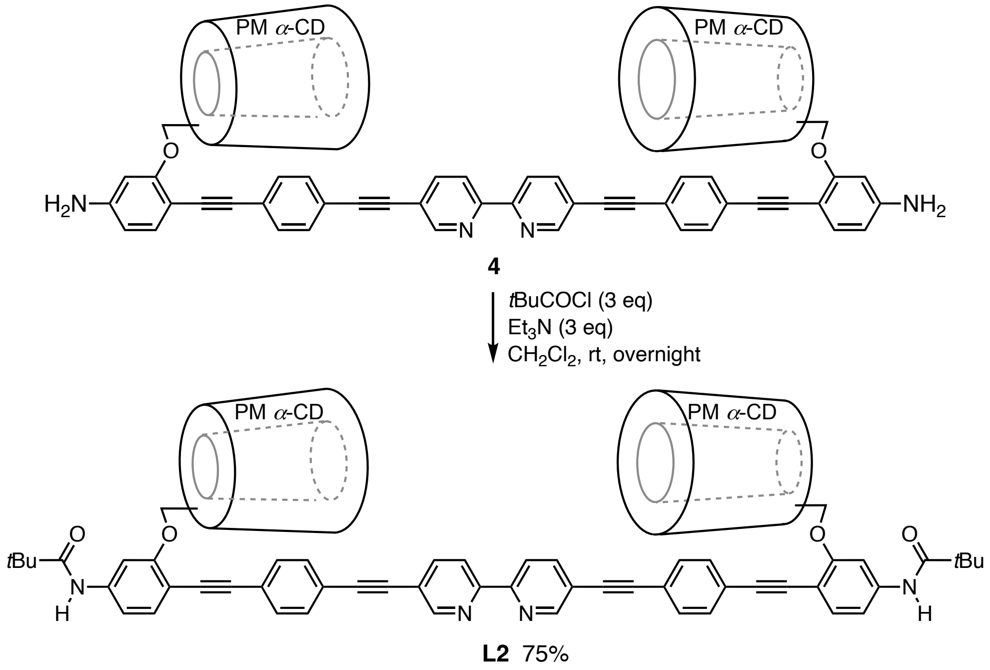
Photoluminescence quantum yield measurement: Absolute photoluminescence quantum yields were measured with the HAMAMATSU Photonics C11347 Absolute PL quantum yields measurement system under N_2 atmosphere, using an integrating sphere to collect all the emitted light. For solution measurements, concentrations of 1×10^{-6} or 1×10^{-5} M CH_2Cl_2 solutions were used. For the solid-state (film) measurements, films were prepared by drop-casting 100 μL of 1×10^{-4} M CH_2Cl_2 solutions of biscyclometalated iridium complexes onto quartz laboratory dishes and dried in vacuo at room temperature.

Electrochemical cyclic voltammetry: Electrochemical experiments were carried out with a CHI 620E electrochemical analyzer (CH Instruments Inc.) in a three-electrode system, with a Ag/Ag^+ (10 mM $AgNO_3$ in 0.1 M $n$$Bu_4NClO_4$–MeCN) reference electrode, a platinum wire as the counter electrode and a glassy carbon electrode as the working electrode.

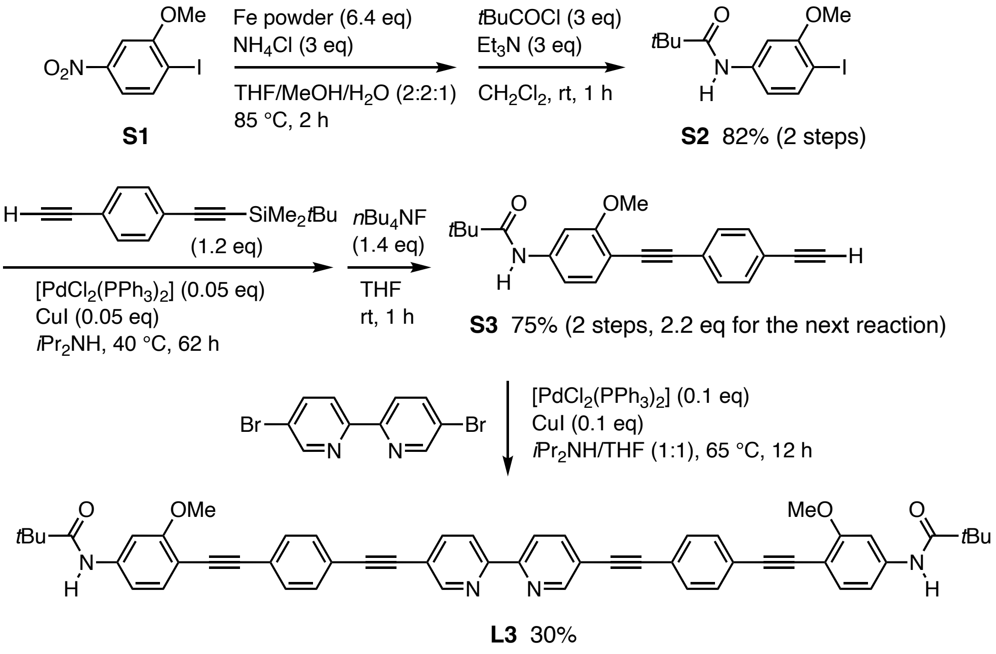
2. Synthetic procedures and NMR spectra of L1–L3



Scheme S1 Synthetic routes to **L1**

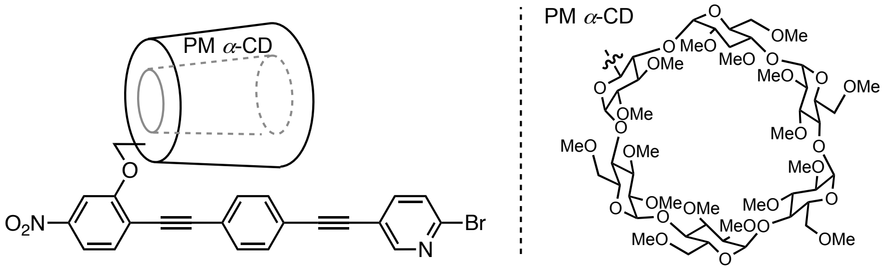


Scheme S2 Synthetic routes to **L2**



Scheme S3 Synthetic routes to **L3**

2.1 Synthesis and NMR spectra of compound 2



The mixture of **1** (1456.5 mg, 1 mmol), 2-bromo-5-iodopyridine (2838.9 mg, 10 mmol), $PdCl_2(PPh_3)_2$ (70.2 mg, 0.1 mmol) and CuI (9.5 mg, 50 μmol) in diisopropylamine (50 mL) was stirred overnight at 0 °C, and then the solvent was removed *in vacuo*. The residue was purified by flash column chromatography (hexane/50%→100% ethyl acetate, then ethyl acetate/0%→17% methanol) to give **2** as a pale yellow solid (1476.9 mg, 92%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.52 (d, J = 2.3 Hz, 1H), 7.83 (dd, J = 8.4, 2.0 Hz, 1H), 7.78 (d, J = 2.0 Hz, 1H), 7.66–7.59 (m, 4H), 7.52–7.48 (m, 3H), 5.11–4.96 (m, 6H), 4.83 (dd, J = 10.2, 2.1 Hz, 1H), 4.31 (d, J = 10.0 Hz, 1H), 4.22 (t, J = 9.3 Hz, 1H), 4.09 (d, J = 9.4 Hz, 1H), 3.83–3.12 (m, 82H), 3.01 (dd, J = 9.9, 3.2 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.54, 152.49, 148.15, 141.53, 140.63, 133.36, 132.10, 131.83, 127.87, 123.13, 122.95, 119.80, 119.48, 116.10, 106.86, 100.54, 100.42, 100.32, 100.29, 100.24, 100.12, 98.06, 93.48, 87.15, 86.81, 82.87, 82.72, 82.65, 82.64 (peaks overlapped), 82.57, 82.35, 82.33, 82.28 (peaks overlapped), 82.10 (peaks overlapped), 81.32 (peaks overlapped), 81.29 (peaks overlapped), 81.26, 81.11, 71.86, 71.83, 71.66 (peaks overlapped), 71.63, 71.58, 71.45, 71.42, 71.40, 71.33, 70.39, 68.46, 62.04, 61.95 (peaks overlapped), 61.91, 61.89 (peaks overlapped), 59.44, 59.22 (peaks overlapped), 59.21, 59.01, 58.37, 58.03, 58.00, 57.95, 57.92, 57.48.

HR-MS (ESI-ToF-MS) *m/z*: [**2**+Na]$^+$ calcd for $C_{74}H_{103}N_2O_{32}BrNa$ 1635.5556, found 1635.5549.

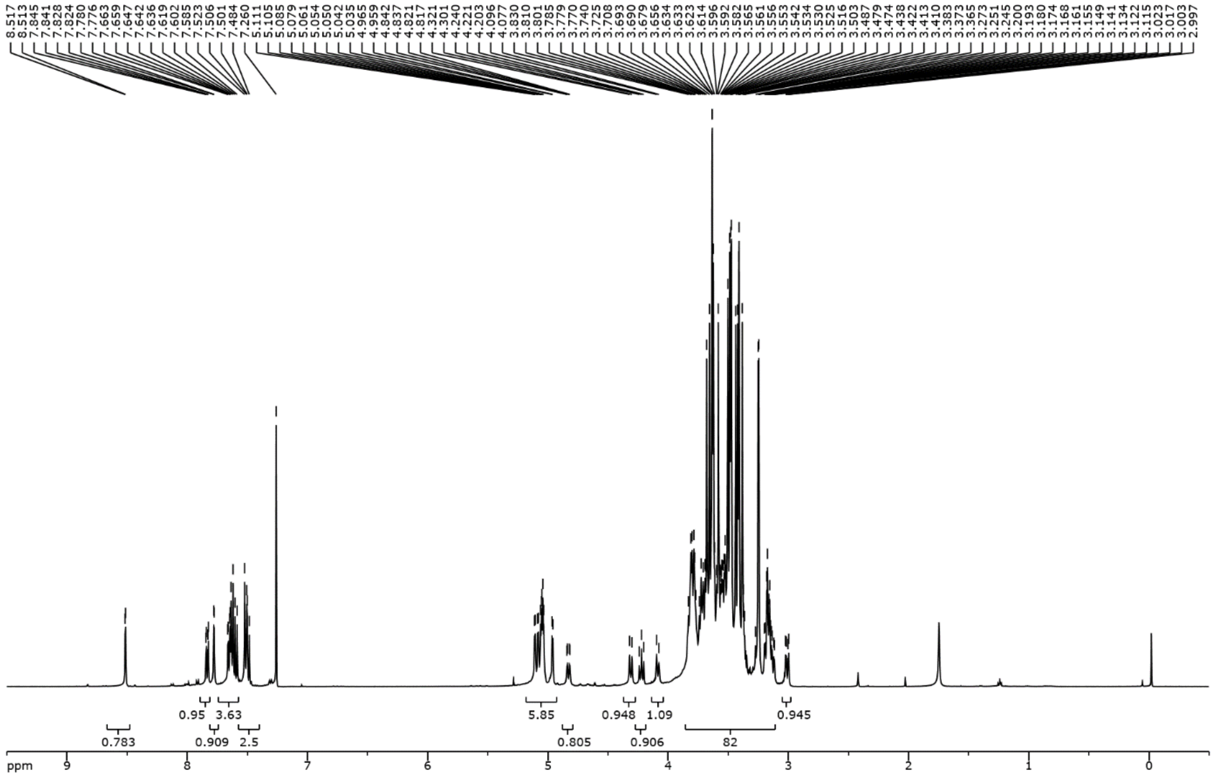


Fig. S1 ^{1}H NMR spectrum of compound **2** (500 MHz, CDCl$_3$).

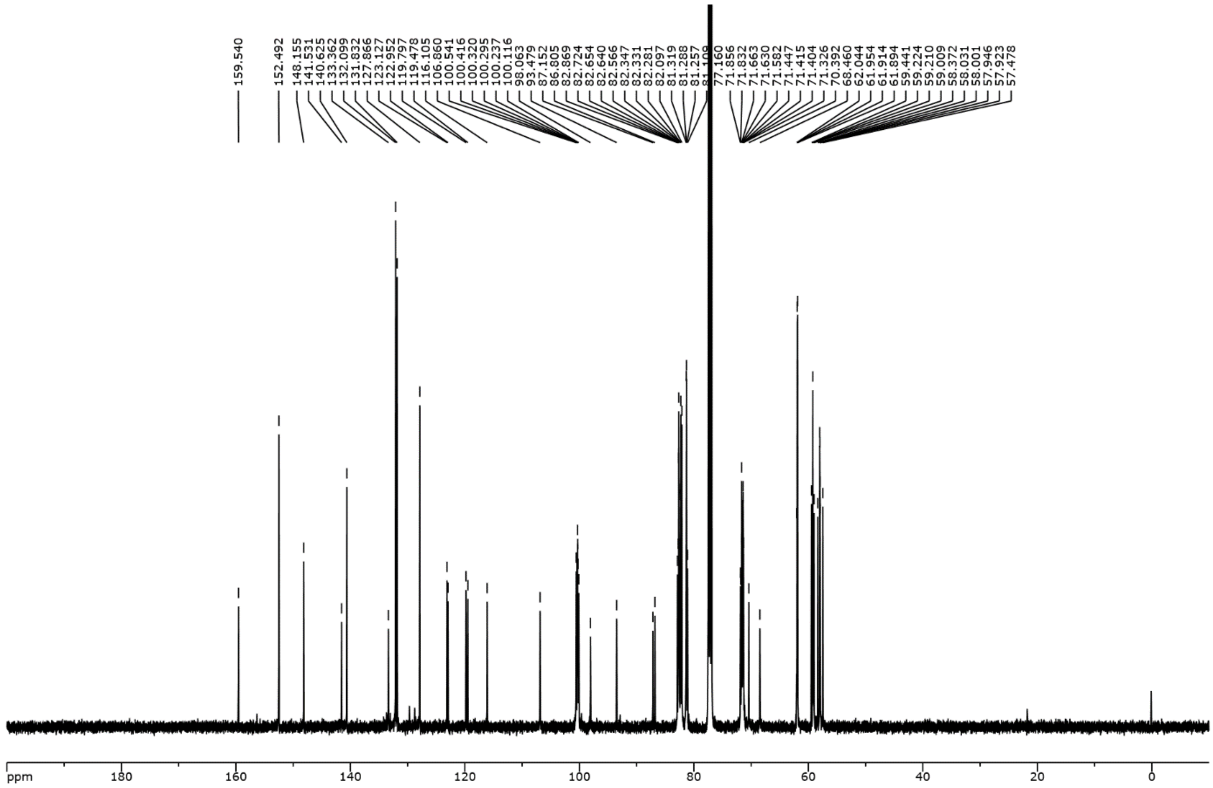
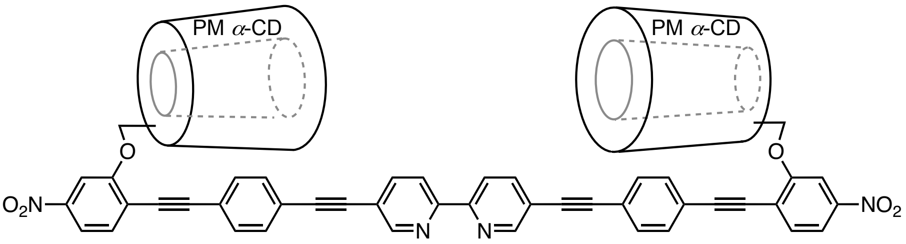


Fig. S2 ^{13}C NMR spectrum of compound **2** (126 MHz, CDCl$_3$).

2.2 Synthesis and NMR spectra of compound 3



To a solution of **2** (1290.0 mg, 0.8 mmol) and $Pd(PPh_3)_4$ (92.4 mg, 80 μmol) in toluene (40 mL), Sn_2*n*Bu_6 (200 μL, 0.4 mmol) was added at room temperature, and the mixture was refluxed (bath temp. 120 °C) overnight. After the reaction completed, the solvent was removed *in vacuo*. The residue was diluted with chloroform. The organic layer was washed with brine and NH_3 aq., dried over $MgSO_4$, filtered, and evaporated *in vacuo*. The residue was purified by GPC with chloroform as the eluent to yield **3** as a pale yellow solid (968.8 mg, 79%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.83 (s, 2H), 8.46 (d, *J* = 8.2 Hz, 2H), 7.96 (dd, *J* = 8.2, 1.8 Hz, 2H), 7.85 (dd, *J* = 8.4, 1.7 Hz, 2H), 7.79 (d, *J* = 1.5 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 4H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 4H), 5.13–4.97 (m, 12H), 4.84 (d, *J* = 8.7 Hz, 2H), 4.32 (d, *J* = 10.1 Hz, 2H), 4.24 (t, *J* = 9.2 Hz, 2H), 4.10 (d, *J* = 9.5 Hz, 2H), 3.84–3.13 (m, 164H), 3.03 (dd, *J* = 9.9, 3.0 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.55, 154.45, 151.89, 148.15, 139.55, 133.37, 132.12, 131.89, 123.38, 122.93, 120.84, 120.34, 119.89, 116.13, 106.87, 100.59, 100.44, 100.35, 100.32, 100.26, 100.15, 98.23, 93.46, 88.85, 86.75, 82.90, 82.75, 82.68, 82.66 (peaks overlapped), 82.60, 82.37, 82.35, 82.31 (peaks overlapped), 82.13 (peaks overlapped), 81.34 (peaks overlapped), 81.31 (peaks overlapped), 81.13, 71.88, 71.86, 71.68 (peaks overlapped), 71.65, 71.61, 71.47, 71.43 (peaks overlapped), 71.36, 70.42, 68.48, 62.07, 61.98 (peaks overlapped), 61.94, 61.92 (peaks overlapped), 59.46, 59.25 (peaks overlapped), 59.23, 59.03, 58.42, 58.05, 58.02, 57.96, 57.94, 57.51.

HR-MS (ESI-ToF-MS) *m*/*z*: [**3**+2Na]$^{2+}$ calcd for $C_{148}H_{206}N_4O_{64}Na_2$ 1555.1403, found 1555.1420.

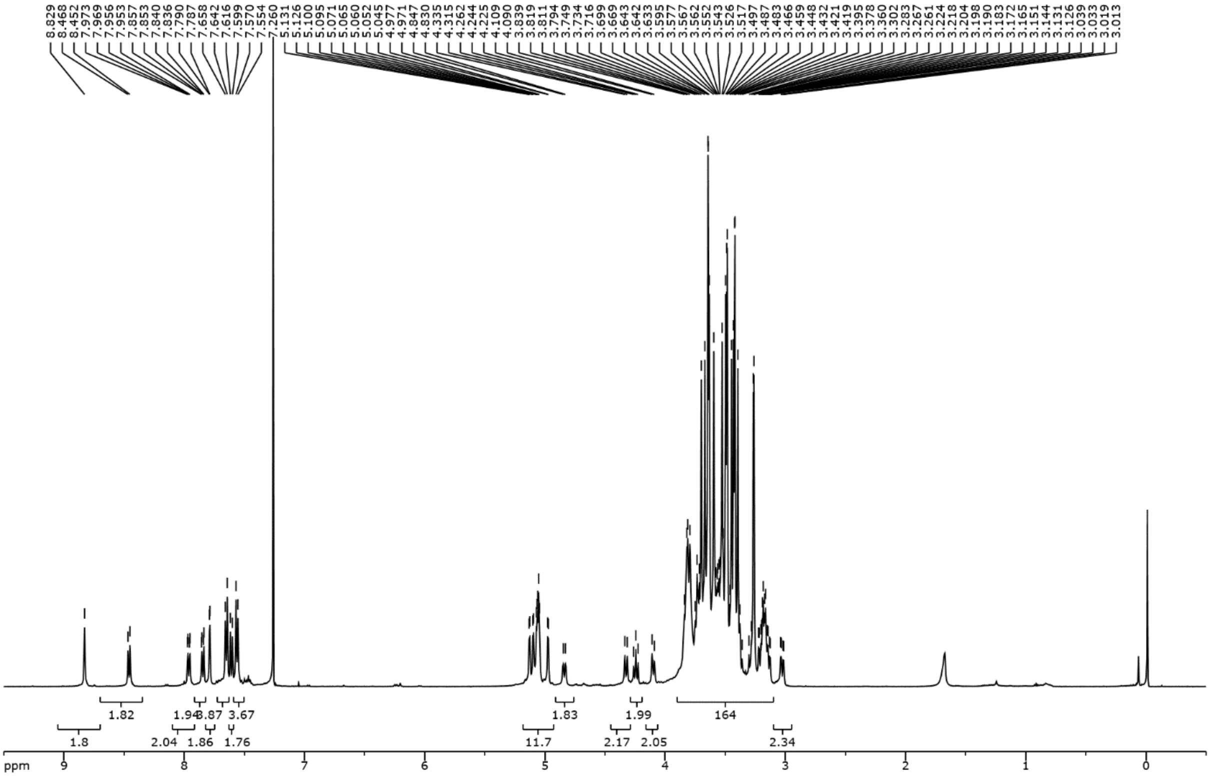


Fig. S3 ^{1}H NMR spectrum of compound **3** (500 MHz, $CDCl_3$).

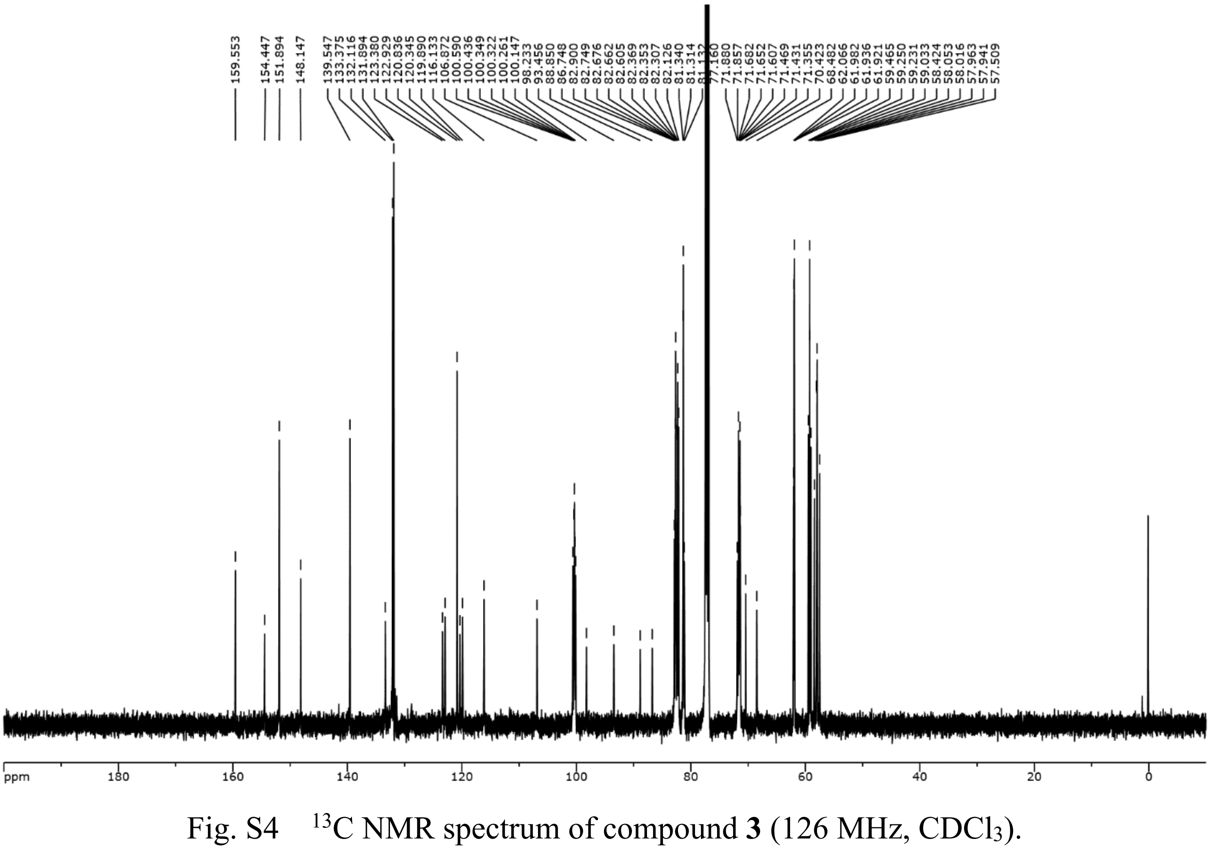
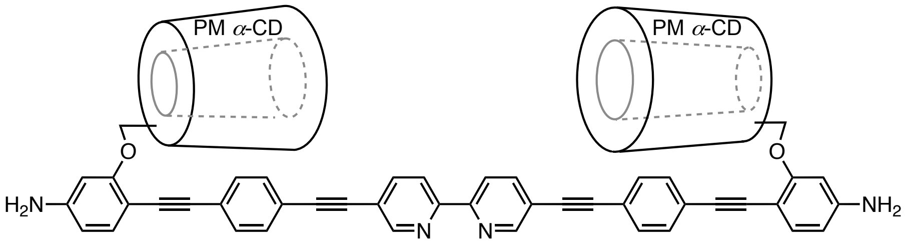


Fig. S4 ^{13}C NMR spectrum of compound **3** (126 MHz, $CDCl_3$).

2.3 Synthesis and NMR spectra of compound 4



The mixture of **3** (153.3 mg, 50 µmol) and $Na_2S_2O_4$ (87.1 mg, 0.5 mmol) in acetonitrile (5 mL) and H_2O (5 mL) was stirred at room temperature for 15 min. After the reaction completed, brine and ethyl acetate were added. The organic layer was dried over $MgSO_4$, filtered, and evaporated *in vacuo*. The residue was purified by GPC with chloroform as the eluent. The residue was dissolved in tetrahydrofuran (5 mL), and stirred overnight at 60 °C, and then the solvent was removed *in vacuo* to yield **4** as a pale yellow solid (123.3 mg, 82%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.81 (s, 2H), 8.43 (d, J = 8.2 Hz, 2H), 7.94 (dd, J = 8.3, 2.1 Hz, 2H), 7.55 (d, J = 8.4 Hz, 4H), 7.49 (d, J = 8.4 Hz, 4H), 7.25 (d, J = 8.3 Hz, 2H), 6.25–6.20 (m, 4H), 5.17–5.00 (m, 12H), 4.59 (dd, J = 10.6, 3.4 Hz, 2H), 4.28 (d, J = 10.4 Hz, 2H), 4.18 (t, J = 9.2 Hz, 2H), 4.04 (dd, J = 9.6, 2.3 Hz, 2H), 3.85–3.13 (m, 164H), 3.06 (dd, J = 9.9, 3.2 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 160.80, 154.26, 151.81, 148.61, 139.43, 134.44, 131.64, 131.37, 125.04, 121.29, 120.76, 120.58, 107.67, 102.77, 100.56, 100.41, 100.33, 100.24, 100.22, 99.76, 99.40, 93.99, 91.55, 89.78, 87.89, 82.90, 82.76, 82.67, 82.66, 82.51, 82.43, 82.35 (peaks overlapped), 82.26 (peaks overlapped), 82.17, 81.36 (peaks overlapped), 81.31 (peaks overlapped), 81.24, 71.90, 71.74, 71.66, 71.60, 71.52 (peaks overlapped), 71.43, 71.39 (peaks overlapped), 70.61, 67.88, 62.01, 61.97, 61.94 (peaks overlapped), 61.87, 59.31, 59.19 (peaks overlapped), 59.15, 59.07, 58.38, 58.05, 58.04, 57.97, 57.94, 57.56.

HR-MS (ESI-ToF-MS) *m*/*z*: [**4**+2Na]$^{2+}$ calcd for $C_{148}H_{210}N_4O_{60}Na_2$ 1525.1661, found 1525.1642.

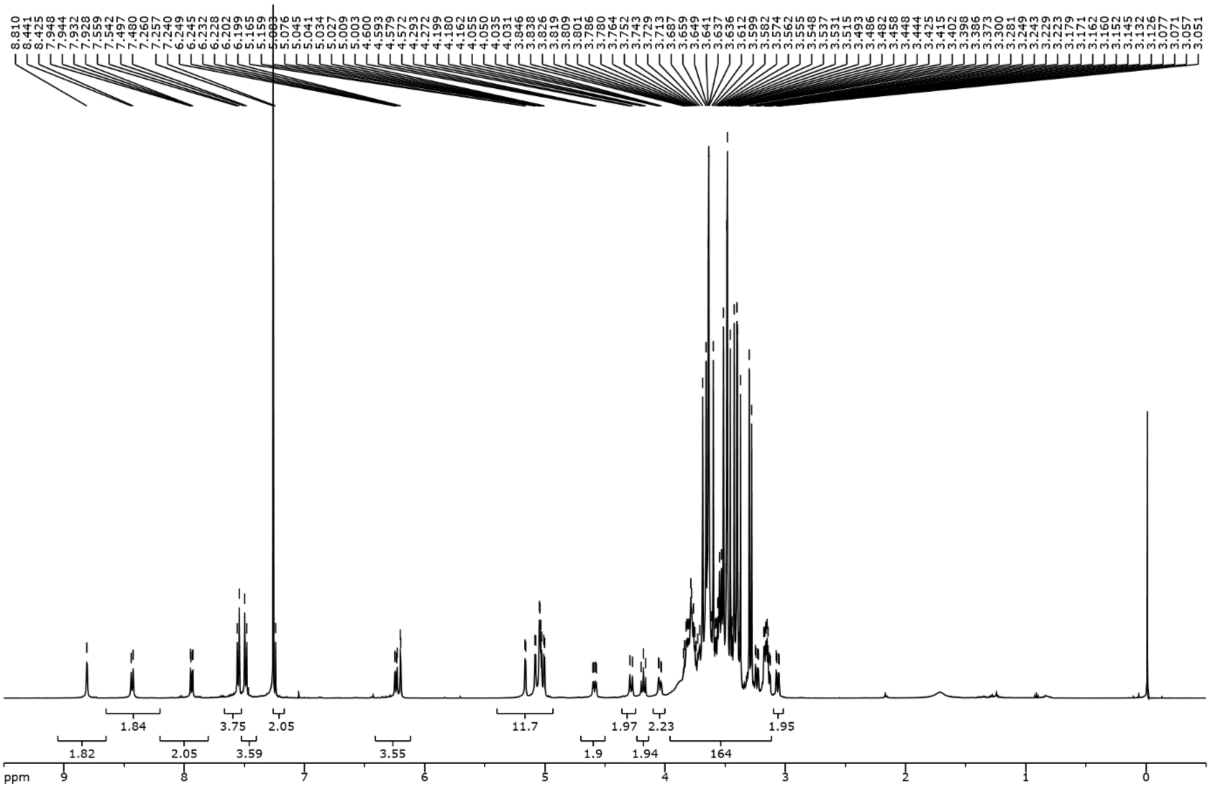


Fig. S5 ^{1}H NMR spectrum of compound **4** (500 MHz, $CDCl_3$).

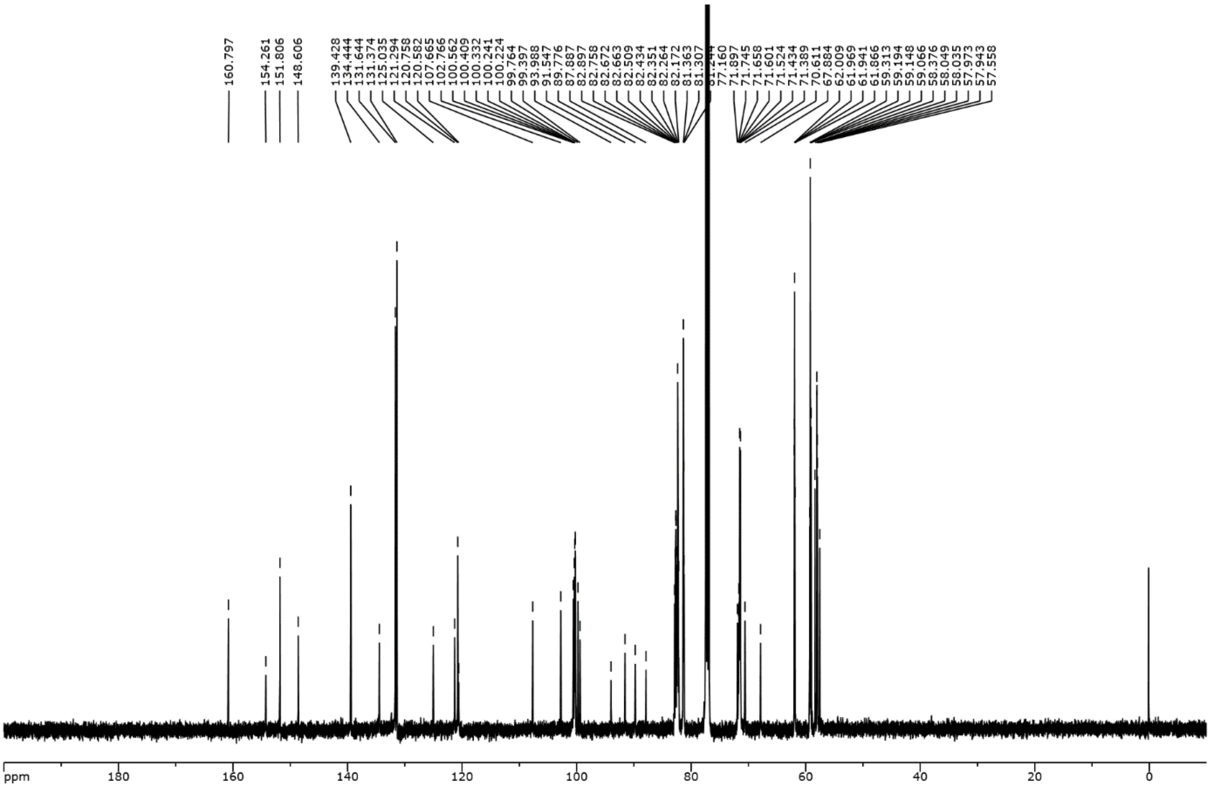
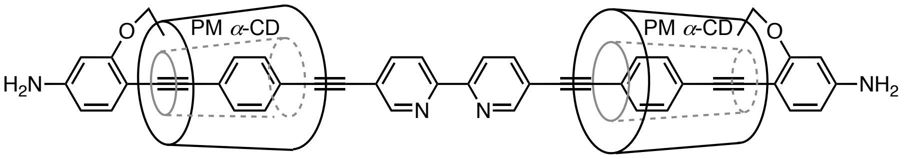


Fig. S6 ^{13}C NMR spectrum of compound **4** (126 MHz, $CDCl_3$).

2.4 Synthesis and NMR spectra of compound 5



4 (120.2 mg, 40 µmol) was dissolved in methanol (60 mL) and H_2O (60 mL). The mixture was stirred at 60 °C for 2 d, and then the solvent was removed *in vacuo* to yield **5** as a pale yellow solid (119.0 mg, 99%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.72 (s, 2H), 8.41 (d, *J* = 8.2 Hz, 2H), 8.02 (d, *J* = 8.1 Hz, 4H), 7.87 (dd, *J* = 8.3, 1.7 Hz, 2H), 7.61 (d, *J* = 8.1 Hz, 4H), 7.21 (d, *J* = 7.9 Hz, 2H), 6.44–6.42 (m, 4H), 5.09–4.95 (m, 12H), 4.83 (t, *J* = 8.6 Hz, 2H), 4.36–4.32 (m, 4H), 4.18–3.04 (m, 166H), 2.86 (d, *J* = 10.1 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 163.55, 154.26, 151.88, 149.02, 139.35, 134.38, 132.31, 131.44, 123.86, 122.34, 120.67, 120.41, 109.98, 108.11, 105.43, 100.88, 100.56, 100.30, 100.20, 100.07, 98.20, 93.37, 91.58, 90.22, 87.87, 83.96, 82.82, 82.70 (peaks overlapped), 82.61, 82.50, 82.31, 82.26 (peaks overlapped), 82.17, 82.13, 81.81, 81.59, 81.39 (peaks overlapped), 81.32, 81.28, 81.15, 76.26, 72.27, 71.96, 71.79, 71.63 (peaks overlapped), 71.31 (peaks overlapped), 71.20, 71.17, 70.83, 70.28, 62.09, 61.97 (peaks overlapped), 61.85 (peaks overlapped), 61.72, 59.17 (peaks overlapped), 59.04, 58.83, 58.82, 58.46, 58.11, 57.95, 57.83, 57.76, 57.61.

HR-MS (ESI-ToF-MS) *m*/*z*: [**5**+2Na]$^{2+}$ calcd for $C_{148}H_{210}N_4O_{60}Na_2$ 1525.1661, found 1525.1688.

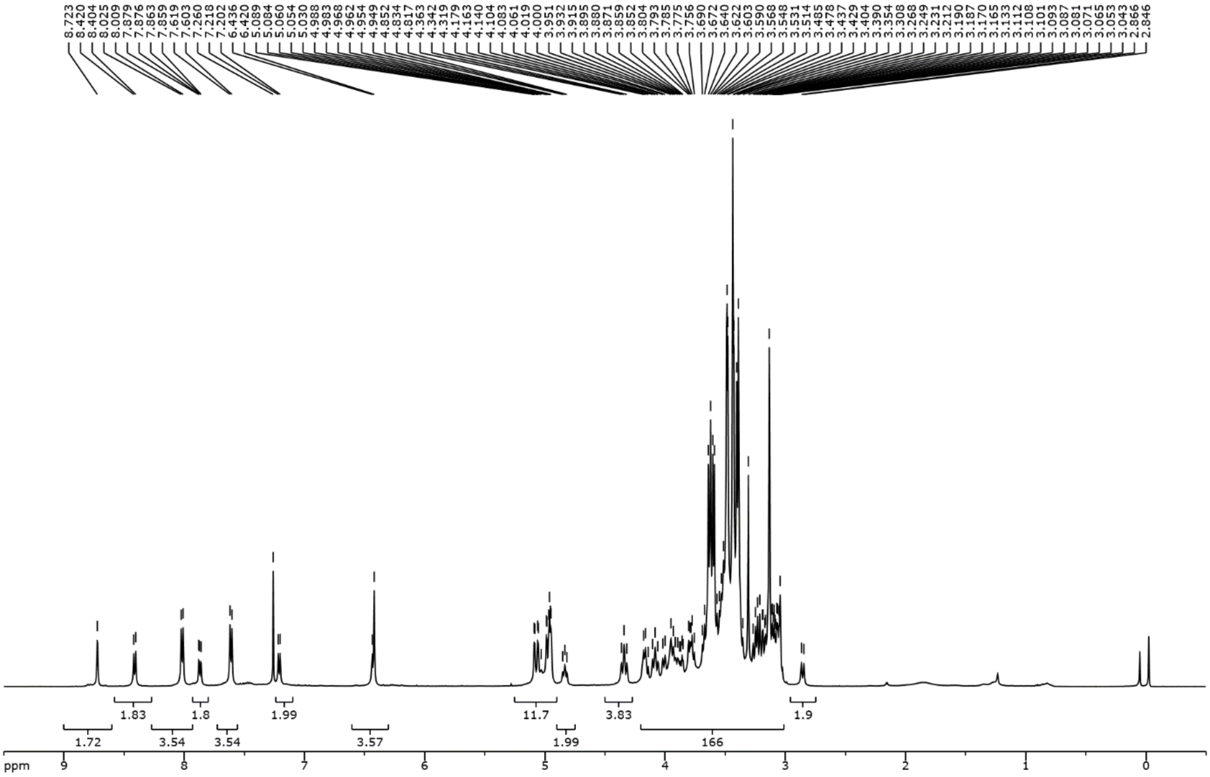


Fig. S7 ^{1}H NMR spectrum of compound **5** (500 MHz, $CDCl_3$).

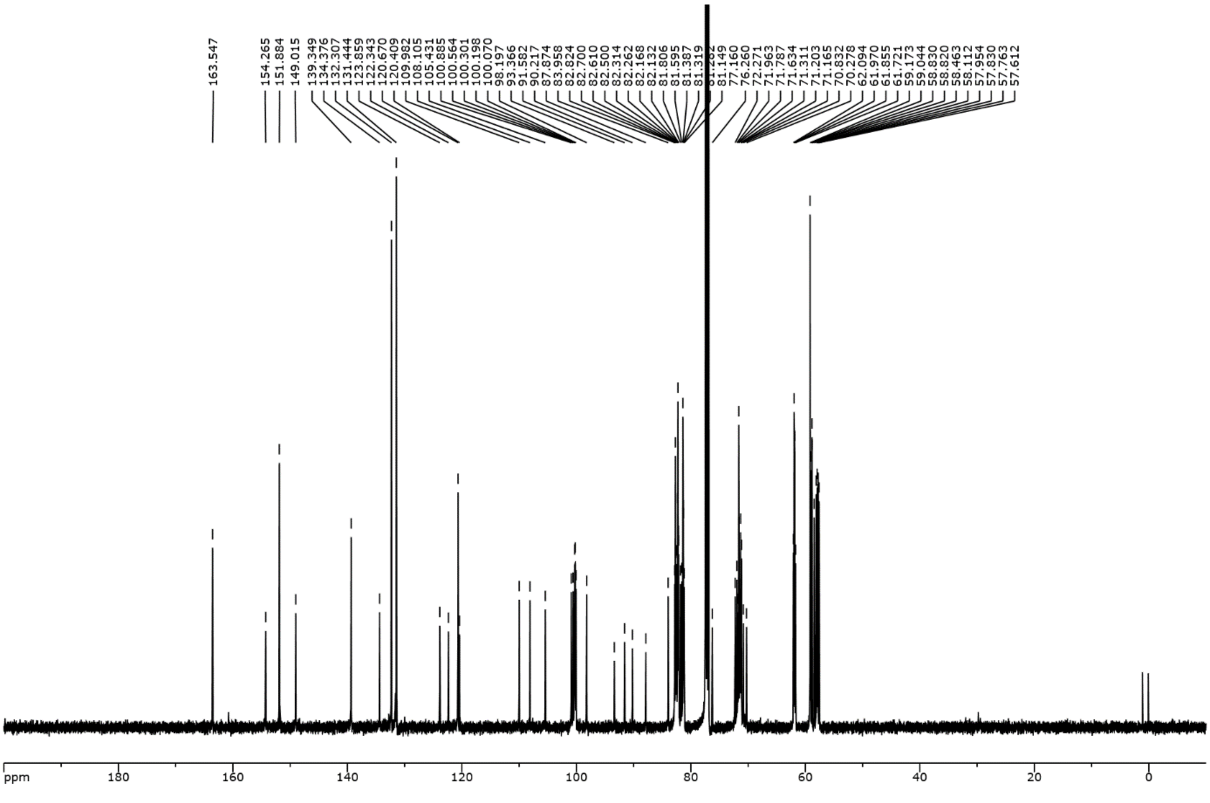
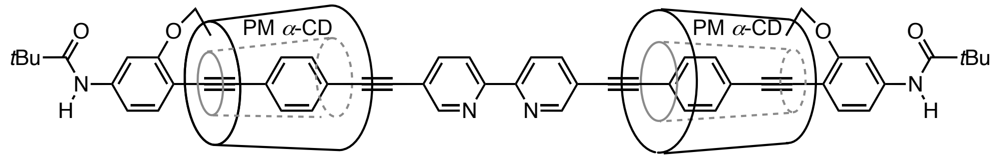


Fig. S8 ^{13}C NMR spectrum of compound **5** (126 MHz, $CDCl_3$).

2.5 Synthesis and NMR spectra of compound L1



To a solution of **5** (90.2 mg, 30 μmol) in dichloromethane (3 mL), pivaloyl chloride (36.5 μL, 0.3 mmol) and triethylamine (41.6 μL, 0.3 mmol) were added, and then the mixture was stirred overnight at room temperature. After the reaction completed, the solvent was removed *in vacuo*. The residue was purified by GPC with chloroform as the eluent to yield **L1** as a pale yellow solid (72.8 mg, 76%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.73 (s, 2H), 8.42 (d, J = 8.2 Hz, 2H), 8.07 (d, J = 6.7 Hz, 4H), 7.88 (d, J = 8.2 Hz, 2H), 7.64 (d, J = 6.7 Hz, 4H), 7.43–7.39 (m, 8H), 5.08–4.96 (m, 12H), 4.80 (t, J = 8.1 Hz, 2H), 4.40 (d, J = 11.5 Hz, 2H), 4.25–4.17 (m, 6H), 4.08–4.04 (m, 4H), 3.99 (d, J = 9.6 Hz, 2H), 3.91–3.74 (m, 12H), 3.67–3.07 (m, 144H), 2.81 (d, J = 10.7 Hz, 2H), 1.32 (s, 18H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 176.90, 162.74, 154.34, 151.93, 140.22, 139.42, 133.60, 132.63, 131.53, 123.17, 123.02, 120.72, 120.35, 114.47, 113.06, 111.84, 100.87, 100.60, 100.32, 100.23, 100.07, 98.23, 93.18, 93.06, 89.08, 88.20, 83.96, 82.89, 82.75, 82.64, 82.63, 82.52, 82.40, 82.27, 82.25, 82.13, 82.09, 81.69, 81.60, 81.40, 81.37, 81.34 (peaks overlapped), 81.19, 72.54, 72.04, 71.84, 71.71, 71.66, 71.45, 71.34, 71.28 (peaks overlapped), 70.75, 70.28, 62.06, 61.96 (peaks overlapped), 61.85 (peaks overlapped), 61.71, 59.26, 59.23, 59.05, 58.92, 58.89, 58.47, 58.18, 57.99, 57.84 (peaks overlapped), 57.68, 40.01, 27.69.

HR-MS (ESI-ToF-MS) *m/z*: [**L1**+2Na]$^{2+}$ calcd for $C_{158}H_{226}N_4O_{62}Na_2$ 1609.2236, found 1609.2218.

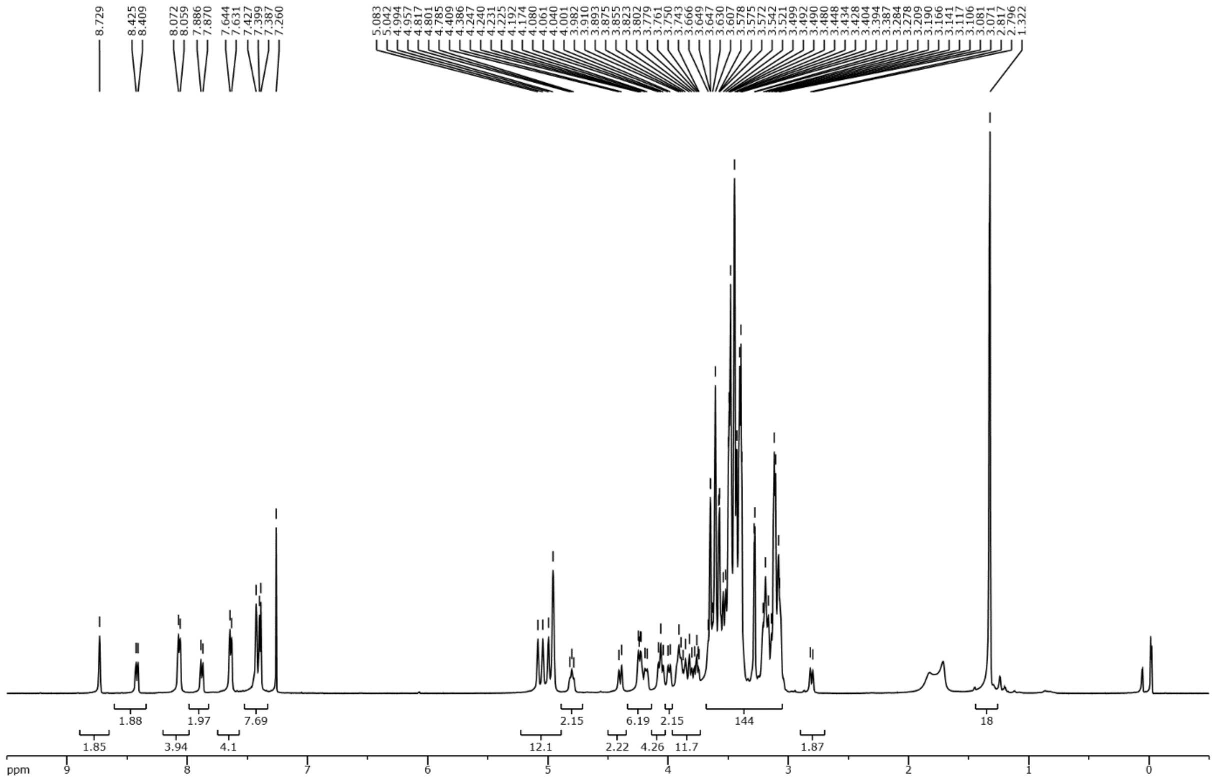


Fig. S9 ^{1}H NMR spectrum of compound **L1** (500 MHz, $CDCl_3$).

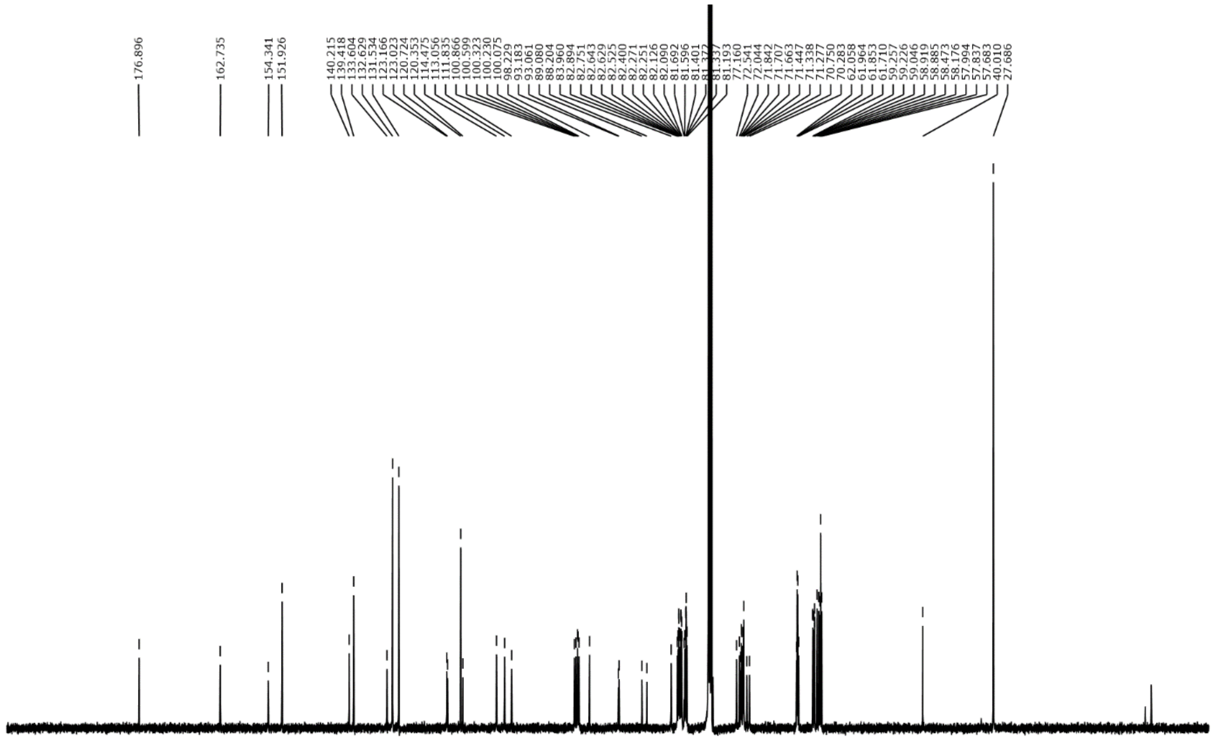


Fig. S10 ^{13}C NMR spectrum of compound **L1** (126 MHz, $CDCl_3$).

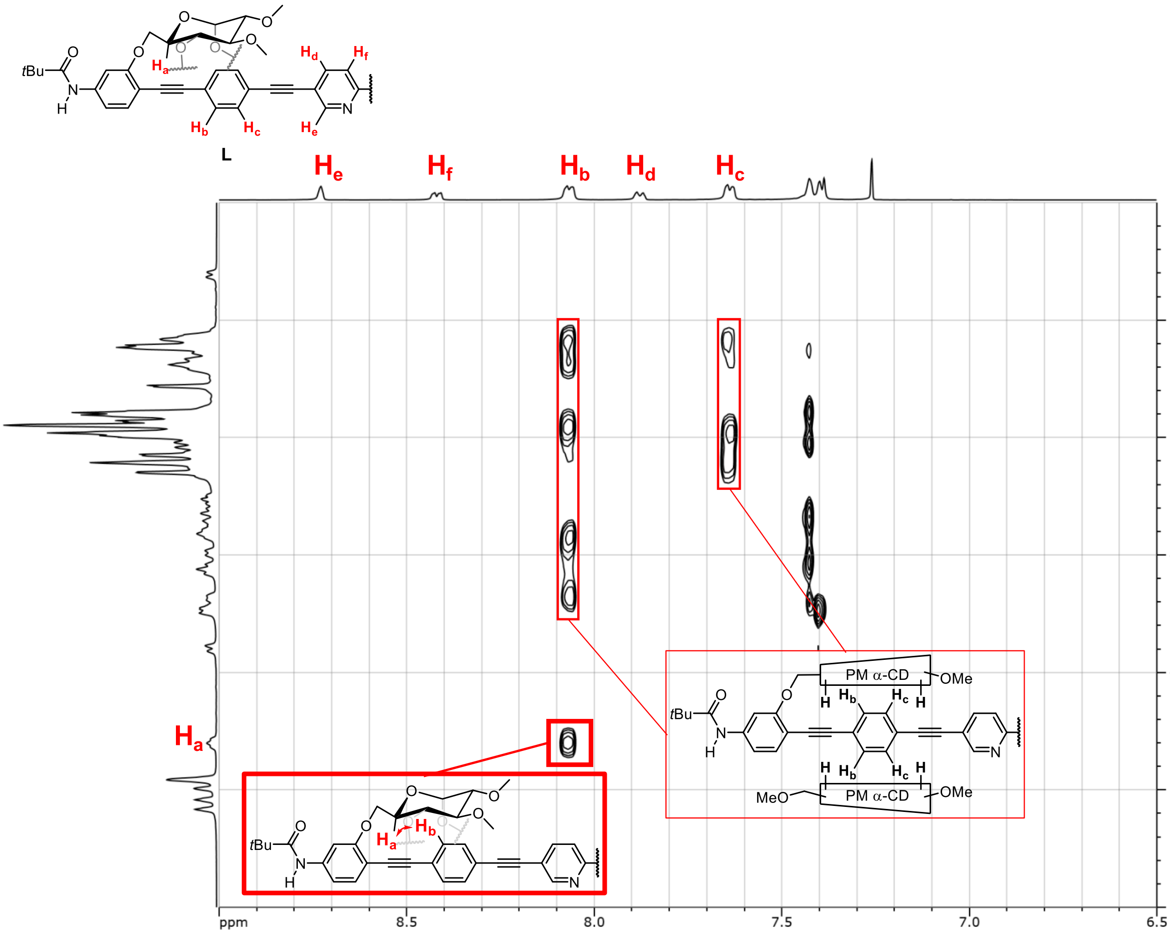
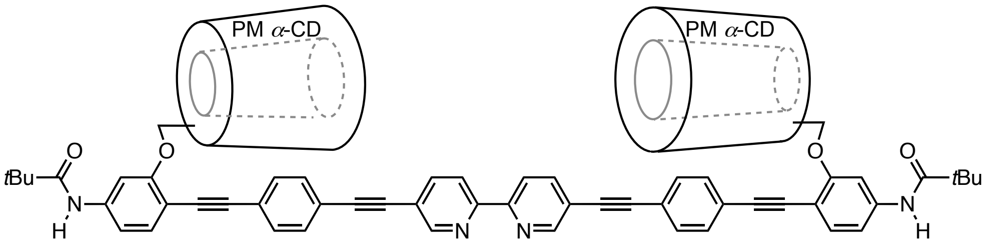


Fig. S11 Partial ^{1}H-^{1}H ROESY spectrum of compound **L1** (500 MHz, CDCl$_3$).

2.6 Synthesis and NMR spectra of compound L2



To a solution of **4** (90.2 mg, 30 μmol) in dichloromethane (3 mL), pivaloyl chloride (11.0 μL, 90 μmol) and triethylamine (12.5 μL, 90 μmol) were added, and then the mixture was stirred overnight at room temperature. After the reaction completed, the solvent was removed *in vacuo*. The residue was purified by GPC with chloroform as the eluent to yield **L2** as a pale yellow solid (71.2 mg, 75%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.81 (s, 2H), 8.44 (d, J = 8.2 Hz, 2H), 7.99 (s, 2H), 7.94 (d, J = 8.3 Hz, 2H), 7.59 (d, J = 7.8 Hz, 4H), 7.51 (d, J = 7.9 Hz, 4H), 7.40–7.37 (m, 4H), 6.55 (d, J = 8.3 Hz, 2H), 5.19–5.00 (m, 12H), 4.56 (d, J = 10.0 Hz, 2H), 4.35 (t, J = 9.2 Hz, 2H), 4.29 (d, J = 10.0 Hz, 2H), 4.02 (d, J = 9.7 Hz, 2H), 3.92 (d, J = 9.8 Hz, 2H), 3.86–3.12 (m, 162H), 3.03 (d, J = 6.4 Hz, 2H), 1.30 (s, 18H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 176.76, 160.19, 154.31, 151.83, 139.84, 139.47, 133.28, 131.73, 131.63, 124.34, 121.94, 120.78, 120.52, 110.99, 108.23, 103.75, 100.54, 100.47, 100.31 (peaks overlapped), 100.25, 100.01, 93.83, 92.99, 88.68, 88.13, 82.59, 82.56, 82.45, 82.38 (peaks overlapped), 82.32, 82.27 (peaks overlapped), 82.09, 81.82, 81.44, 81.40 (peaks overlapped), 81.35 (peaks overlapped), 81.19, 71.58, 71.49 (peaks overlapped), 71.47, 71.37 (peaks overlapped), 71.34, 71.08, 70.70 (peaks overlapped), 67.63, 62.01, 61.99, 61.95, 61.94, 61.89, 61.88, 59.43, 59.24, 59.18 (peaks overlapped), 58.77, 58.35, 58.04, 57.91 (peaks overlapped), 57.39, 39.97, 27.66.

HR-MS (ESI-ToF-MS) *m*/*z*: [**L2**+2Na]$^{2+}$ calcd for $C_{158}H_{226}N_4O_{62}Na_2$ 1609.2236, found 1609.2210.

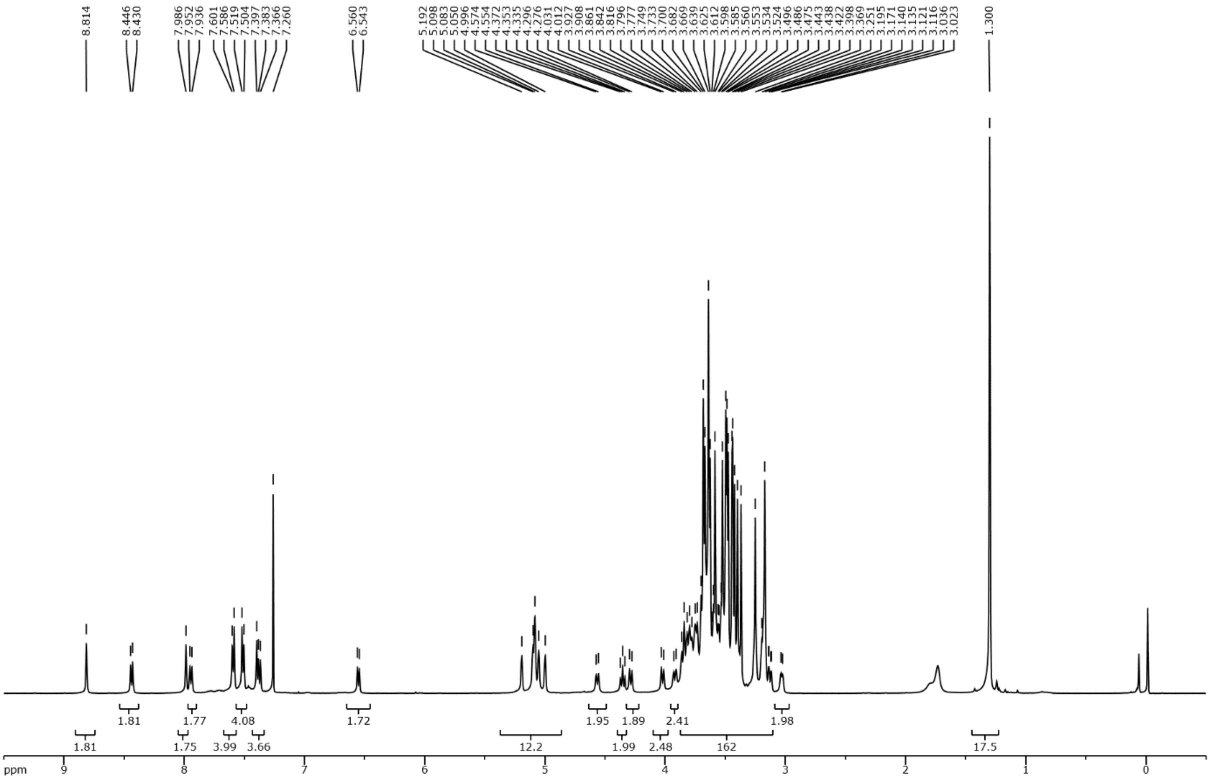


Fig. S12 ^{1}H NMR spectrum of compound **L2** (500 MHz, CDCl$_3$).

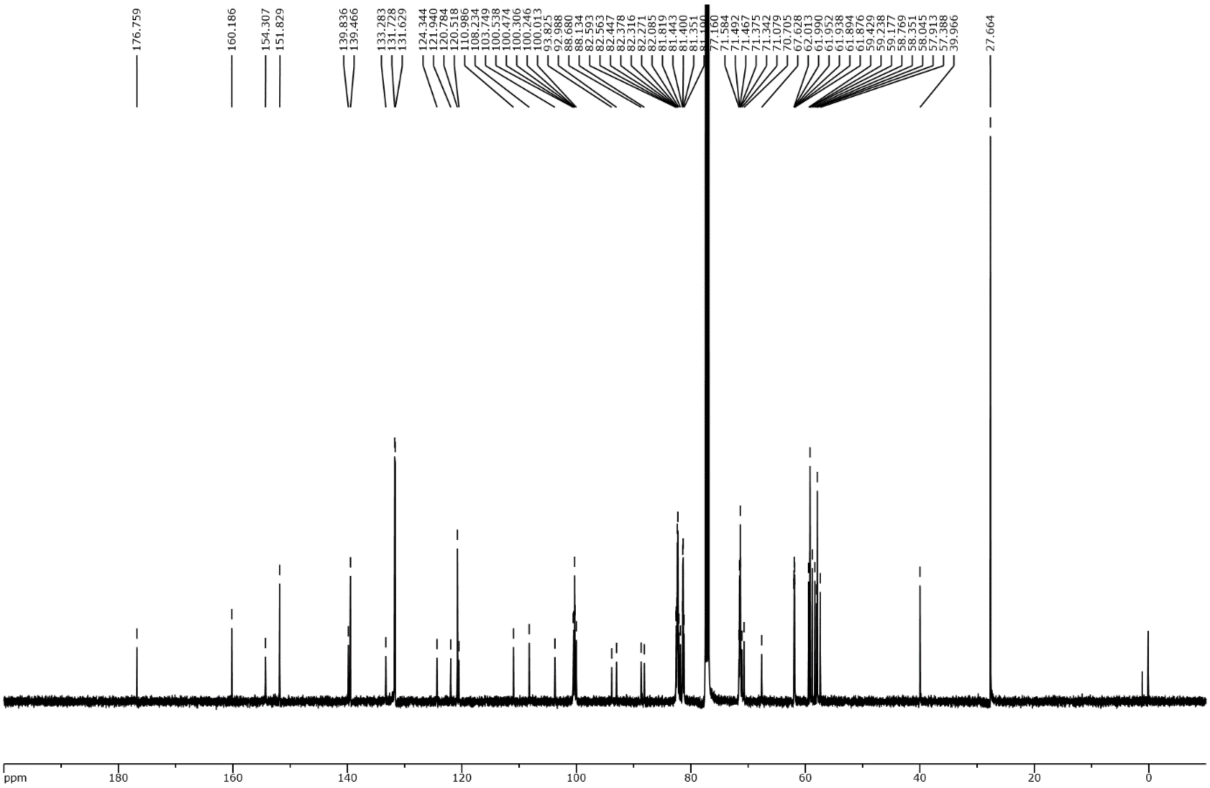
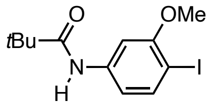


Fig. S13 ^{13}C NMR spectrum of compound **L2** (126 MHz, CDCl$_3$).

2.7 Synthesis and NMR spectra of compound S2



The mixture of 1-iodo-2-methoxy-4-nitrobenzene (**S1**, 697.6 mg, 2.5 mmol), NH_4Cl (401 mg, 7.5 mmol) and Fe powder (893 mg, 16 mmol) in THF (14 mL), MeOH (14 mL) and H_2O (7 mL) was stirred at 85 °C for 2 h. After cooling to room temperature, the mixture was diluted with EtOAc. The organic layer was washed with NH_4Cl aq., dried over $MgSO_4$, filtrated, and evaporated *in vacuo*. This crude product (4-iodo-3-methoxyaniline) was used for the next step without further purification.

To a solution of the crude product in dichloromethane (5 mL), pivaloyl chloride (924 μL, 7.5 mmol) and triethylamine (1.0 mL, 7.5 mmol) were added. The resulting mixture was stirred for 1 h at room temperature. After the reaction completed, the mixture was diluted with CH_2Cl_2. The organic layer was washed with 1N HCl and $NaHCO_3$ aq., dried over $MgSO_4$, filtrated, and evaporated *in vacuo* to yield **S2** as a pale brown solid (679.3 mg, 82% for 2 steps).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (d, J = 8.5 Hz, 1H), 7.54 (s, 1H), 7.47 (s, 1H), 6.63 (d, J = 8.5 Hz, 1H), 3.84 (s, 3H), 1.29 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 176.97, 158.01, 139.88, 138.87, 113.48, 103.51, 78.81, 56.39, 39.86, 27.62.

HR-MS (ESI-ToF-MS) *m*/*z*: [**S2**+Na]$^+$ calcd for $C_{12}H_{16}INO_2Na$ 356.01179, found 356.01169.

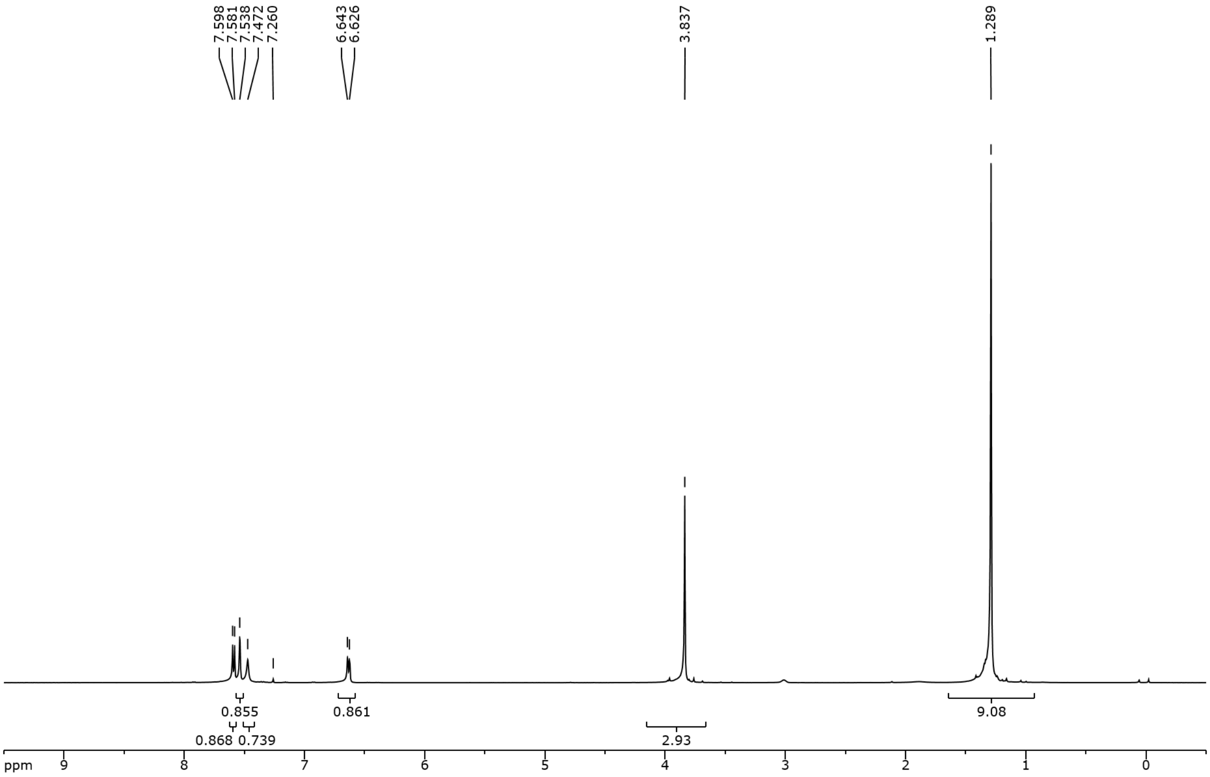


Fig. S14 ^{1}H NMR spectrum of compound **S2** (500 MHz, CDCl$_3$).

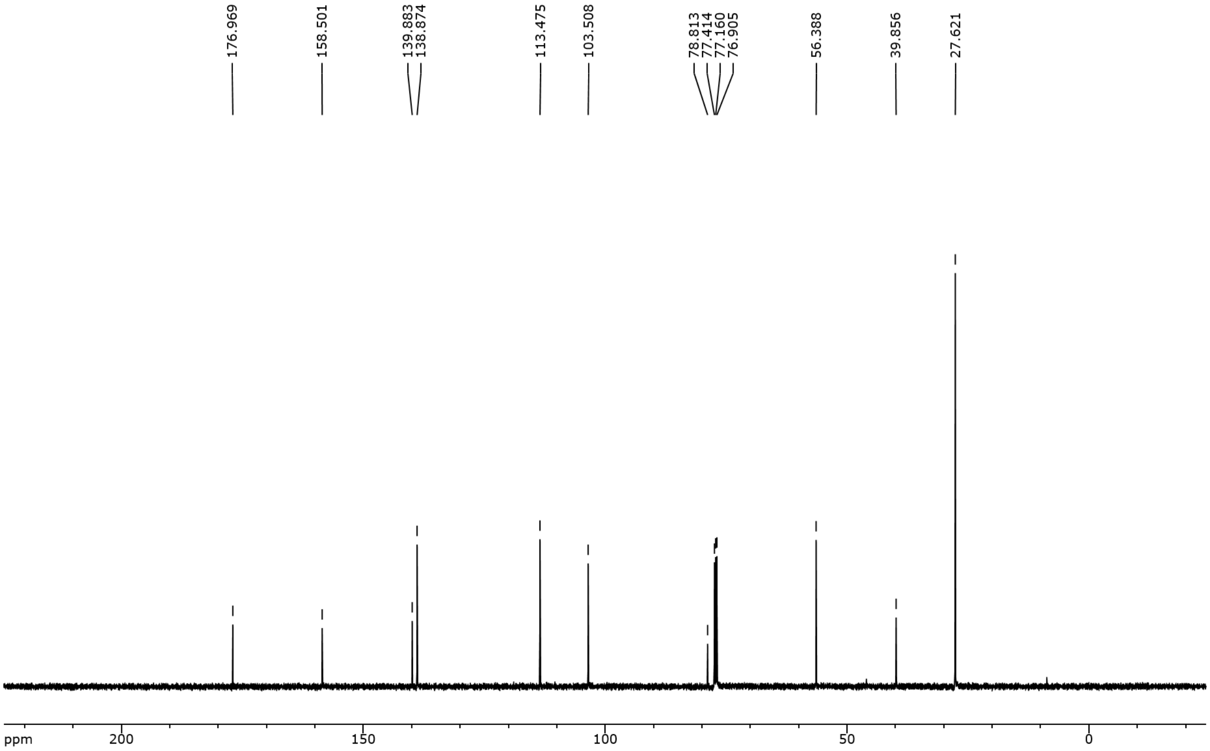
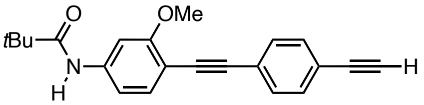


Fig. S15 ^{13}C NMR spectrum of compound **S2** (126 MHz, CDCl$_3$).

2.8 Synthesis and NMR spectra of compound S3



The mixture of **S2** (466 mg, 1.4 mmol), *tert*-butyl((4-ethynylphenyl)ethynyl)dimethylsilane[1] (395 mg, 1.64 mmol), $PdCl_2(PPh_3)_2$ (49.1 mg, 0.07 mmol) and CuI (13.3 mg, 0.07 mmol) in diisopropylamine (10 mL) was stirred at 40 °C for 62 h. After cooling to room temperature, the mixture was diluted with CH_2Cl_2. The organic layer was washed with 1N HCl aq. and brine, dried over $MgSO_4$, filtrated, and evaporated *in vacuo*. The residue was roughly purified by flash column chromatography (hexane/10%→33% ethyl acetate). The crude product was used for the next reaction without further purification.

To a solution of the crude product in THF (5 mL), nBu$_4$NF (1 M in THF, 2 mL, 2.0 mmol) was added. The resulting mixture was stirred for 1 h at room temperature. After the reaction completed, the mixture was diluted with Et_2O. The organic layer was washed with NH_4Cl aq., dried over $MgSO_4$, filtrated, and evaporated *in vacuo*. The residue was purified by flash column chromatography (hexane/ethyl acetate/$CHCl_3$ 5:1:1 to 2:1:1) to give **S3** as a pale yellow solid (348 mg, 75% for 2 steps).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (d, J = 2.0 Hz, 1H), 7.50–7.43 (m, 4H), 7.40 (d, J = 8.5 Hz, 1H), 7.37 (s, 1H), 6.77 (dd, J = 8.0, 2.0 Hz, 1H), 3.94 (s, 3H), 3.16 (s, 1H), 1.33 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 176.93, 160.77, 140.05, 133.68, 132.06, 131.50, 124.29, 121.58, 111.23, 107.59, 102.72, 92.48, 87.95, 83.52, 78.86, 56.03, 39.95, 27.67.

HR-MS (ESI-ToF-MS) m/z: [**S3**+Na]$^+$ calcd for $C_{22}H_{21}NO_2Na$ 354.14645, found 354.14535.

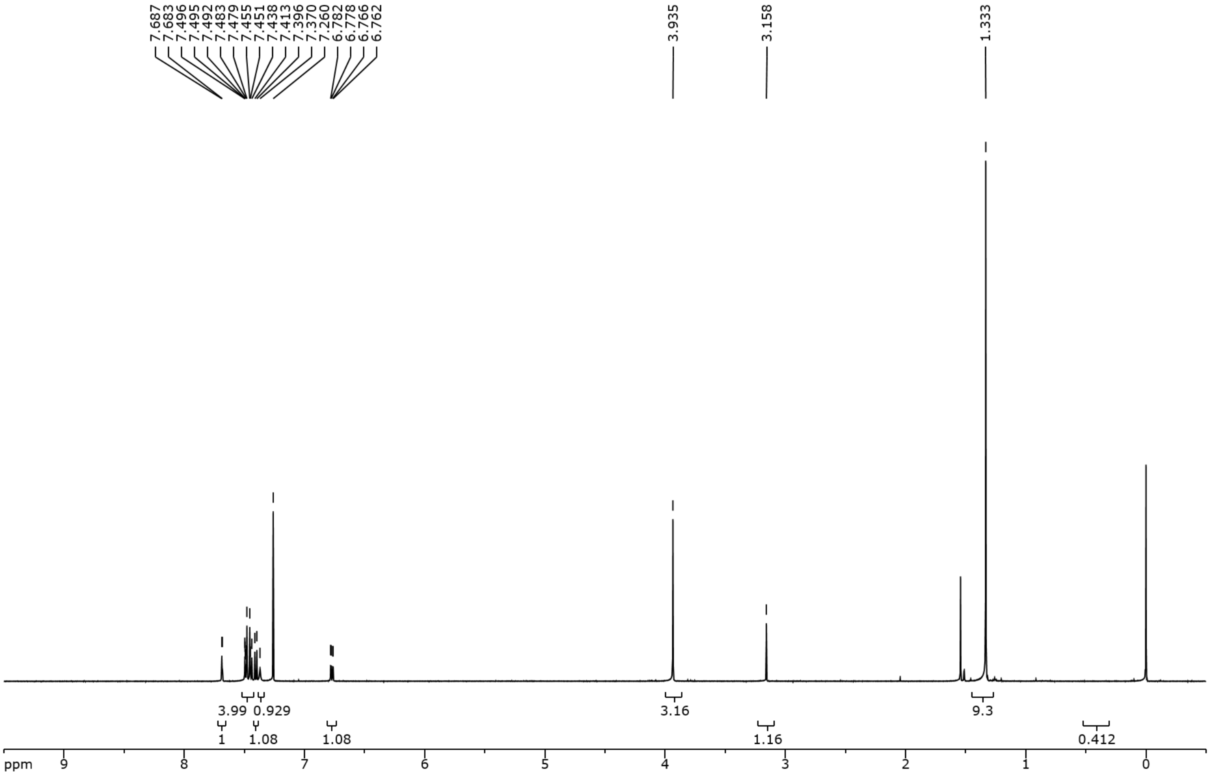


Fig. S16 ^{1}H NMR spectrum of compound **S3** (500 MHz, CDCl$_3$).

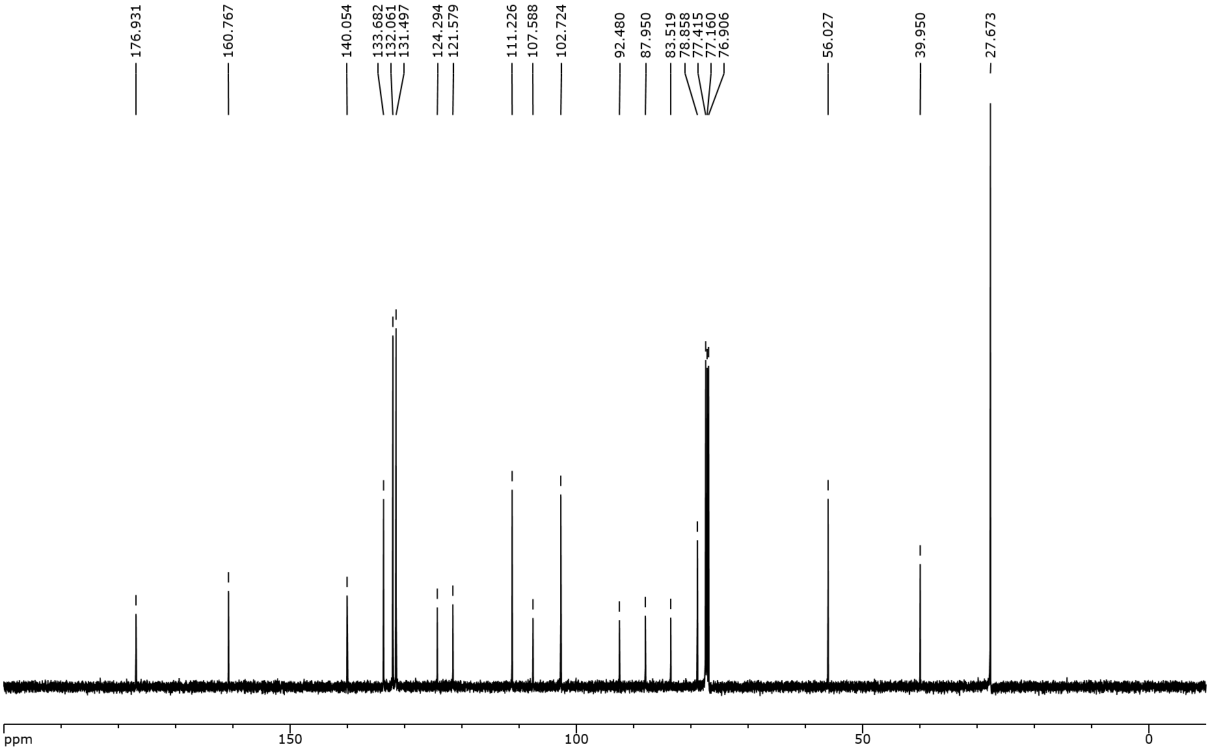
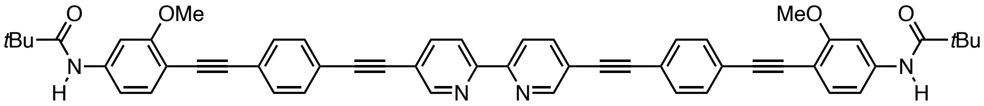


Fig. S17 ^{13}C NMR spectrum of compound **S3** (126 MHz, CDCl$_3$).

2.9 Synthesis and NMR spectra of compound L3



The mixture of **S3** (218.7 mg, 0.66 mmol), 5,5'-dibromo-2,2'-bipyridine (94.2 mg, 0.30 mmol), $PdCl_2(PPh_3)_2$ (21.0 mg, 0.030 mmol) and CuI (5.7 mg, 0.030 mmol) in diisopropylamine (5 mL) and THF (5 mL) was stirred at 65 °C for 12 h. After cooling to room temperature, the mixture was diluted with $CHCl_3$. The organic layer was washed with 1N HCl (adjusted to pH ~7) and brine, dried over $MgSO_4$, filtrated, and evaporated *in vacuo*. The residue was purified by flash column chromatography ($CHCl_3$/MeOH/Et_3N 100:1:1 to 100:5:1) and preparative TLC ($CHCl_3$/EtOAc 95:5). Further purification was carried out by acid-base extraction as follows: To the solution of the product in $CHCl_3$ was added 4 M HCl/EtOAc, and the resulting red solid was filtered and washed with small amount of $CHCl_3$. The red solid obtained was treated with Et_3N in $CHCl_3$, and the resulting organic layer was washed with H_2O, dried over $MgSO_4$, filtrated, and evaporated *in vacuo* to give **L3** as a yellow solid (74.5 mg, 30%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.82 (dd, J = 2.5, 0.5 Hz, 2H), 8.44 (d, J = 3.0, 0.5 Hz, 2H), 7.94 (dd, J = 8.5, 2.0 Hz, 2H), 7.70 (d, J = 8.5, 2.0 Hz, 2H), 7.62–7.50 (m, 8H), 7.42 (d, J = 8.5 Hz, 2H), 7.38 (s, 2H), 6.78 (dd, J = 8.0, 2.0 Hz, 2H), 3.95 (s, 6H), 1.34 (s, 18H).

^{13}C NMR (126 MHz, $CDCl_3$, 50 °C): δ 176.83, 161.12, 154.53, 151.93, 140.23, 139.43, 133.80, 131.77 (peaks overlapped), 124.63, 122.21, 120.84, 120.65, 111.36, 108.06, 103.15, 93.89, 92.74, 88.42, 88.25, 56.23, 40.06, 27.80.

HR-MS (ESI-ToF-MS) *m*/*z*: [**L3**+Na]$^+$ calcd for $C_{54}H_{46}N_4O_4Na$ 837.34113, found 837.34337.

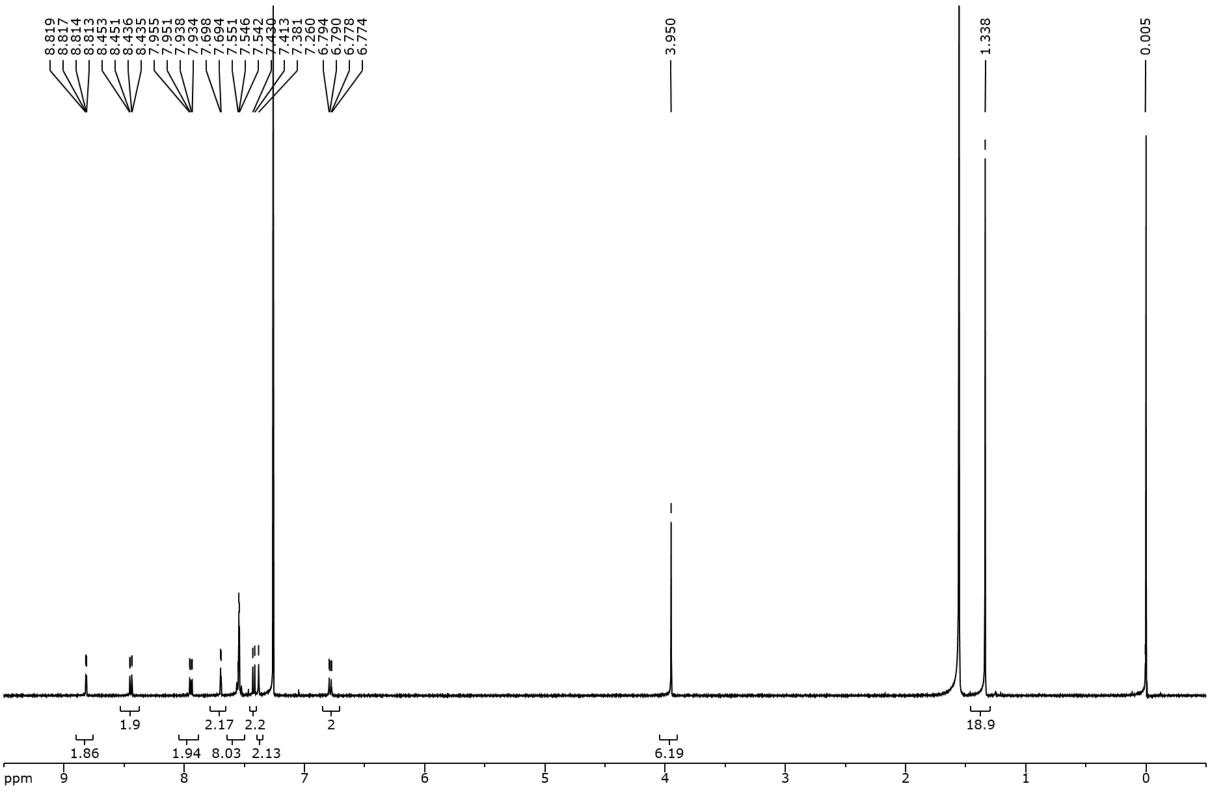


Fig. S18 ^{1}H NMR spectrum of compound **L3** (500 MHz, CDCl$_3$).

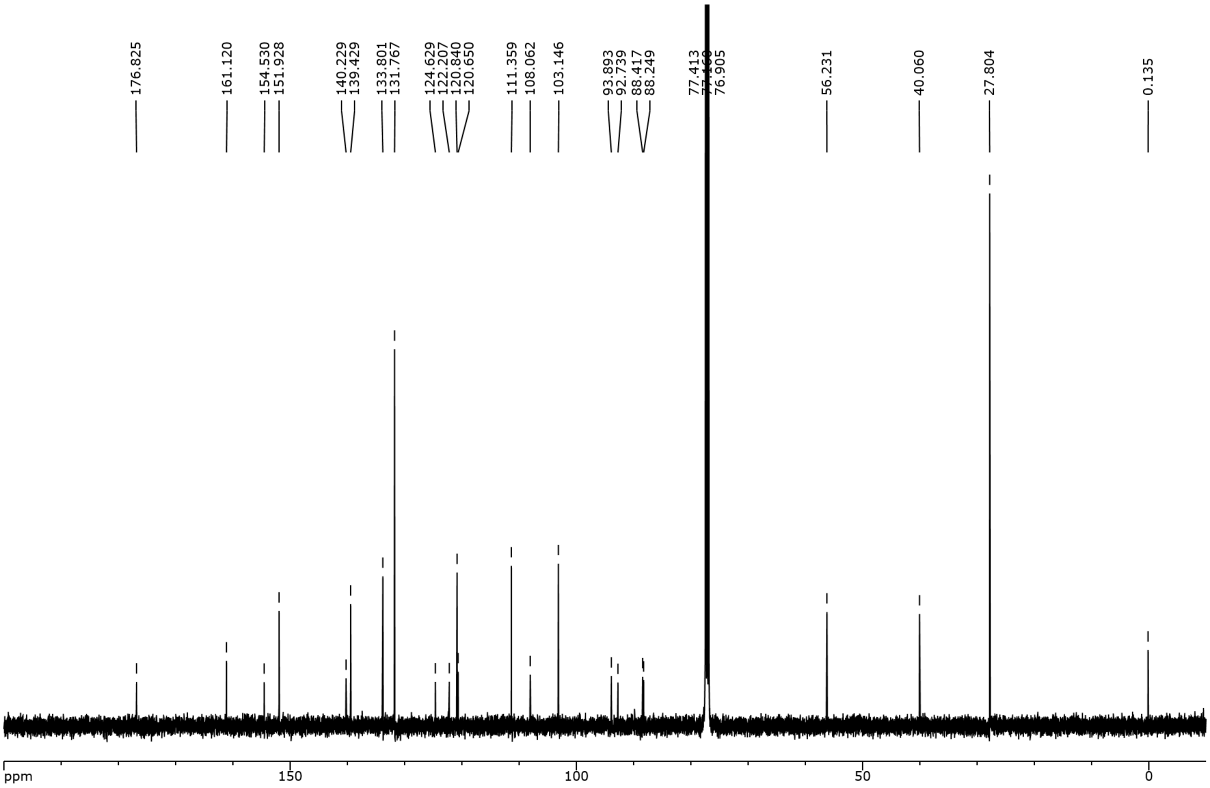
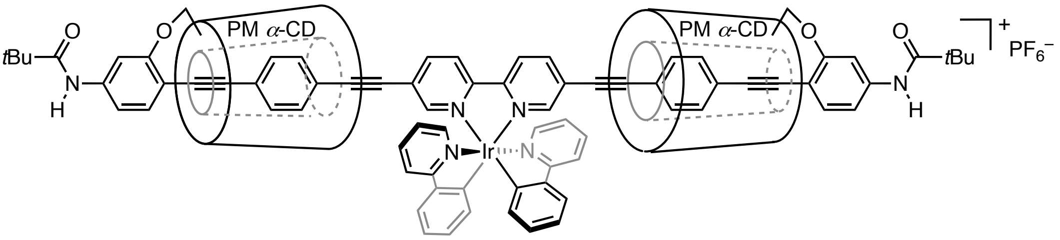


Fig. S19 ^{13}C NMR spectrum of compound **L3** (126 MHz, CDCl$_3$, 50 °C).

3. Synthetic procedures and NMR spectra of biscyclometalated iridium complexes

3.1 Synthesis and NMR spectra of complex [Ir(ppy)$_2$(L1)]PF$_6$



The mixture of **L1** (25.4 mg, 8 μmol) and [Ir(ppy)$_2$Cl]$_2$ (4.3 mg, 4 μmol) in dichloromethane (0.8 mL) and methanol (0.4 mL) was stirred overnight at 60 °C, and then the solvent was removed *in vacuo*. After the residue was redissolved in dichloromethane (3 mL), KPF$_6$ (14.7 mg, 80 μmol) was added. The mixture was stirred at room temperature for 10 min, and then the residue was filtered in order to eliminate the remaining inorganic salts. The resulting solution was evaporated *in vacuo*. The residue was purified by flash column chromatography (5%→10% methanol /dichloromethane) to give [Ir(ppy)$_2$(**L1**)]PF$_6$ as an orange solid (30.0 mg, 98%).

^{1}H NMR (500 MHz, CDCl$_3$): δ 8.74 (d, J = 8.6 Hz, 2H), 8.16 (d, J = 6.1 Hz, 2H), 8.05 (d, J = 8.1 Hz, 4H), 7.95 (d, J = 8.2 Hz, 2H), 7.83–7.80 (m, 4H), 7.67 (d, J = 7.8 Hz, 2H), 7.61–7.57 (m, 2H), 7.52 (d, J = 7.6 Hz, 4H), 7.43–7.40 (m, 8H), 7.13 (dt, J = 12.2, 6.3 Hz, 2H), 7.06 (t, J = 7.4 Hz, 2H), 6.92–6.88 (m, 2H), 6.29 (t, J = 6.7 Hz, 2H), 5.08–4.96 (m, 12H), 4.75 (t, J = 8.5 Hz, 2H), 4.40 (d, J = 11.3 Hz, 2H), 4.26–4.16 (m, 6H), 4.03 (t, J = 10.6 Hz, 4H), 3.96–3.01 (m, 158H), 2.82 (d, J = 10.3 Hz, 2H), 1.33 (s, 18H).

^{13}C NMR (126 MHz, CDCl$_3$): δ 176.93, 167.82, 167.80, 162.80, 154.12, 154.10, 152.08, 152.01, 149.33, 148.95, 148.85, 143.54, 143.50, 141.89, 141.85, 140.45, 138.48, 138.46, 133.59, 132.69, 131.88, 131.70, 131.01, 130.88, 125.79, 124.86, 124.76, 124.69, 124.32, 123.82, 123.77, 122.99, 121.55, 121.52, 119.94, 119.88, 114.43, 112.96, 111.58, 100.80, 100.54, 100.51, 100.24, 100.21, 100.19, 99.98, 98.19, 96.75, 96.69, 92.72, 89.76, 85.60, 83.96, 82.80, 82.66 (peaks overlapped), 82.62, 82.44, 82.34, 82.22 (peaks overlapped), 82.07, 82.05, 82.02, 81.66, 81.60, 81.52, 81.39, 81.33, 81.28, 81.17, 72.65, 72.63, 72.04, 71.82, 71.65 (peaks overlapped), 71.63, 71.47, 71.34, 71.23 (peaks overlapped), 70.71, 70.26, 62.09, 62.05, 61.96, 61.94, 61.92, 61.88, 61.87, 61.85, 61.82, 61.70, 61.67, 59.28, 59.23, 59.05, 58.96, 58.91, 58.49, 58.23, 58.21, 58.02, 57.99, 57.86, 57.84, 57.73, 40.03, 27.69.

HR-MS (ESI-ToF-MS) m/z: [{Ir(ppy)$_2$(**L1**)}+Na]$^{2+}$ calcd for $C_{180}H_{242}IrN_6O_{62}Na$ 1848.2765, found 1848.2748.

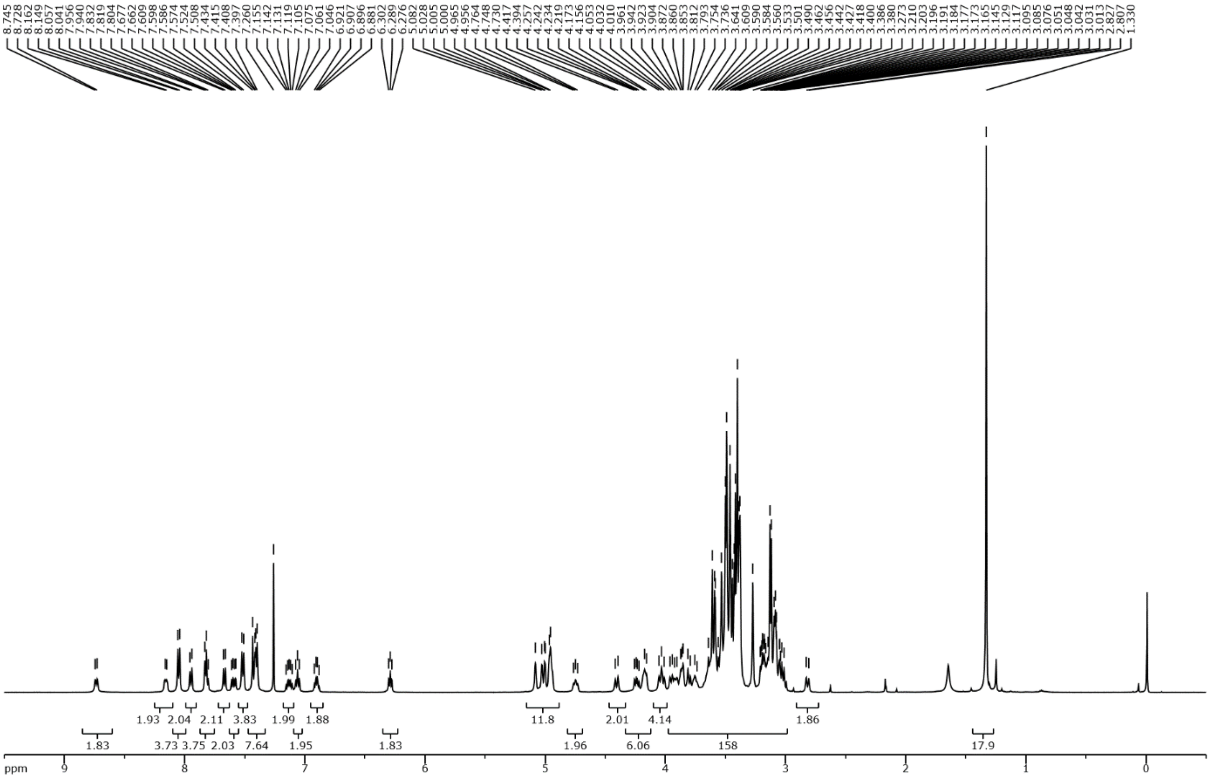


Fig. S20 ^{1}H NMR spectrum of complex [Ir(ppy)$_2$(**L1**)]PF$_6$ (500 MHz, CDCl$_3$).

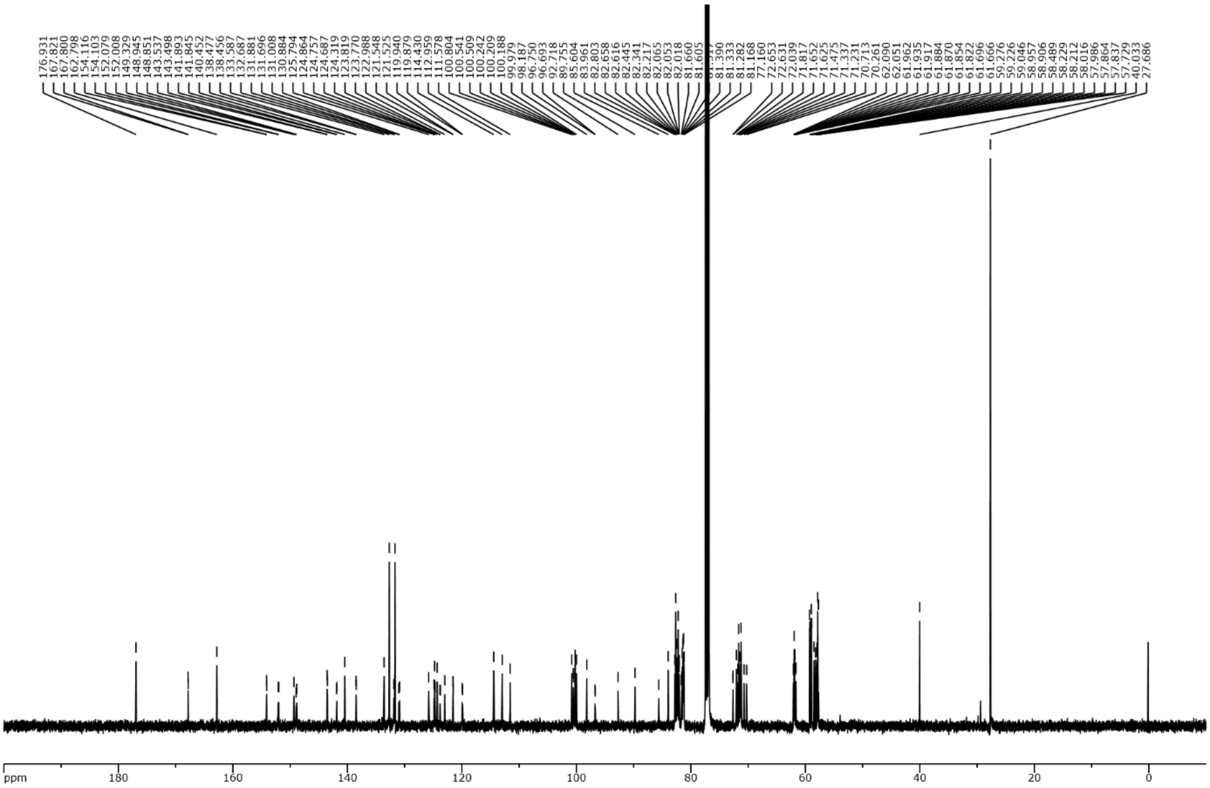
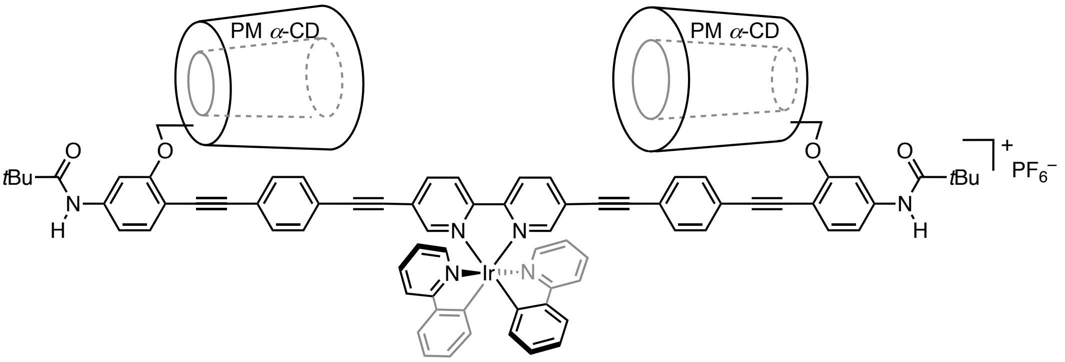


Fig. S21 ^{13}C NMR spectrum of complex [Ir(ppy)$_2$(**L1**)]PF$_6$ (126 MHz, CDCl$_3$).

3.2 Synthesis and NMR spectra of complex [Ir(ppy)$_2$(L2)]PF$_6$



The mixture of **L2** (25.4 mg, 8 µmol) and [Ir(ppy)$_2$Cl]$_2$ (4.3 mg, 4 µmol) in dichloromethane (0.8 mL) and methanol (0.4 mL) was stirred overnight at 60 °C, and then the solvent was removed *in vacuo*. After the residue was redissolved in dichloromethane (3 mL), KPF$_6$ (14.7 mg, 80 µmol) was added. The mixture was stirred at room temperature for 10 min, and then the residue was filtered in order to eliminate the remaining inorganic salts. The resulting solution was evaporated *in vacuo*. The residue was purified by flash column chromatography (5%→10% methanol /dichloromethane) to give [Ir(ppy)$_2$(**L2**)]PF$_6$ as an orange solid (28.5 mg, 93%).

^{1}H NMR (500 MHz, CDCl$_3$): δ 8.51 (t, J = 8.6 Hz, 2H), 8.17 (t, J = 8.6 Hz, 2H), 7.97–7.93 (m, 4H), 7.86–7.79 (m, 4H), 7.71 (d, J = 7.8 Hz, 2H), 7.55–7.52 (m, 8H), 7.35–7.33 (m, 4H), 7.28 (s, 2H), 7.10–7.05 (m, 4H), 6.95 (t, J = 7.4 Hz, 2H), 6.73 (d, J = 6.9 Hz, 2H), 6.28 (d, J = 6.9 Hz, 2H), 5.18–4.99 (m, 12H), 4.55 (d, J = 9.2 Hz, 2H), 4.36–4.31 (m, 4H), 4.05 (d, J = 9.6 Hz, 2H), 3.91–3.15 (m, 164H), 3.01 (dd, J = 9.1, 2.9 Hz, 2H), 1.30 (s, 18H).

^{13}C NMR (126 MHz, CDCl$_3$): δ 177.00, 167.93, 160.21, 153.68, 152.19, 149.31, 148.71, 143.42, 141.82, 140.26, 138.40, 133.33, 131.94, 131.74, 131.61, 131.17, 125.50, 125.24, 125.15, 125.03, 123.57, 123.05, 120.32, 120.01, 111.14, 107.76, 103.77, 100.45, 100.40, 100.30 (peaks overlapped), 100.26, 100.07, 97.91, 92.68, 89.65, 85.75, 82.68, 82.50, 82.44, 82.40, 82.37, 82.34, 82.28 (peaks overlapped), 82.11, 81.82, 81.51, 81.43 (peaks overlapped), 81.38, 81.23, 71.50 (peaks overlapped), 71.44 (peaks overlapped), 71.36 (peaks overlapped), 70.99, 70.60, 67.67, 62.04, 62.00, 61.99, 61.95, 61.90 (peaks overlapped), 59.40, 59.23, 59.17 (peaks overlapped), 58.76, 58.22, 58.01, 57.90 (peaks overlapped), 57.89, 57.41, 39.98, 27.61.

HR-MS (ESI-ToF-MS) *m*/*z*: [{Ir(ppy)$_2$(**L2**)}+Na]$^{2+}$ calcd for $C_{180}H_{242}IrN_6O_{62}Na$ 1848.7776, found 1848.7777.

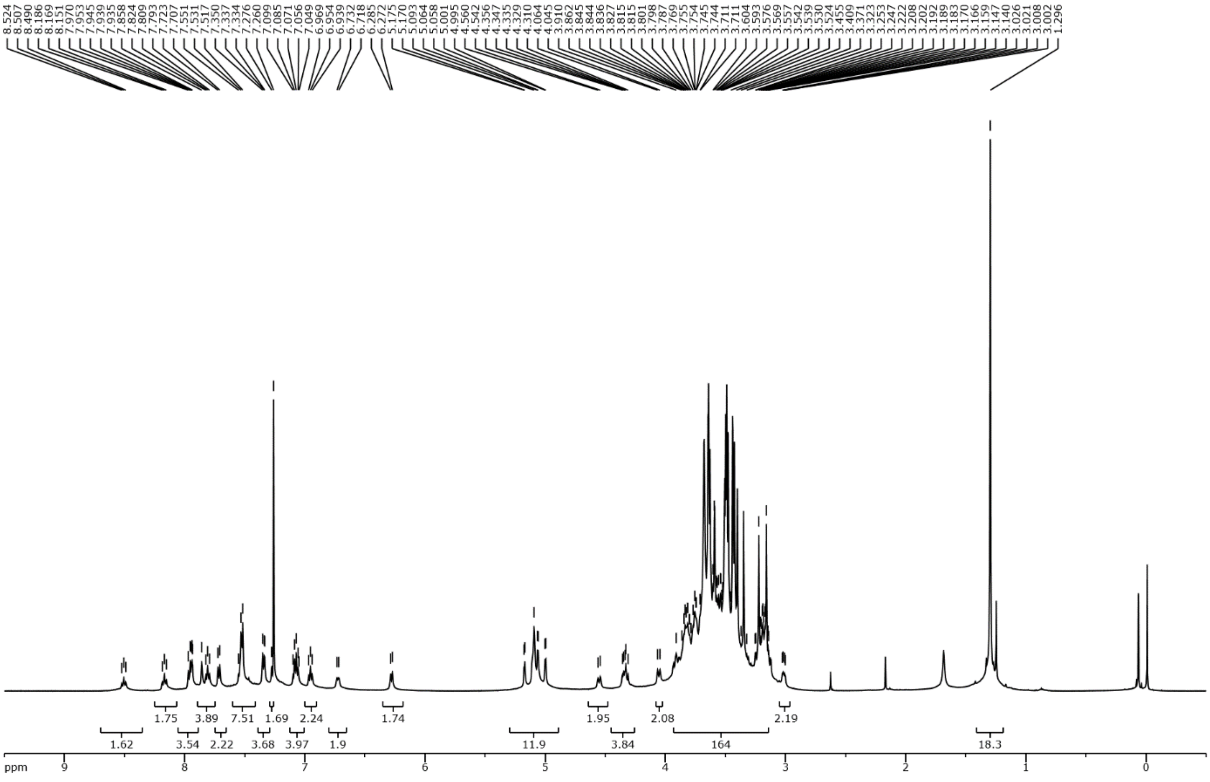


Fig. S22 ^{1}H NMR spectrum of complex [Ir(ppy)$_2$(**L2**)]PF$_6$ (500 MHz, CDCl$_3$).

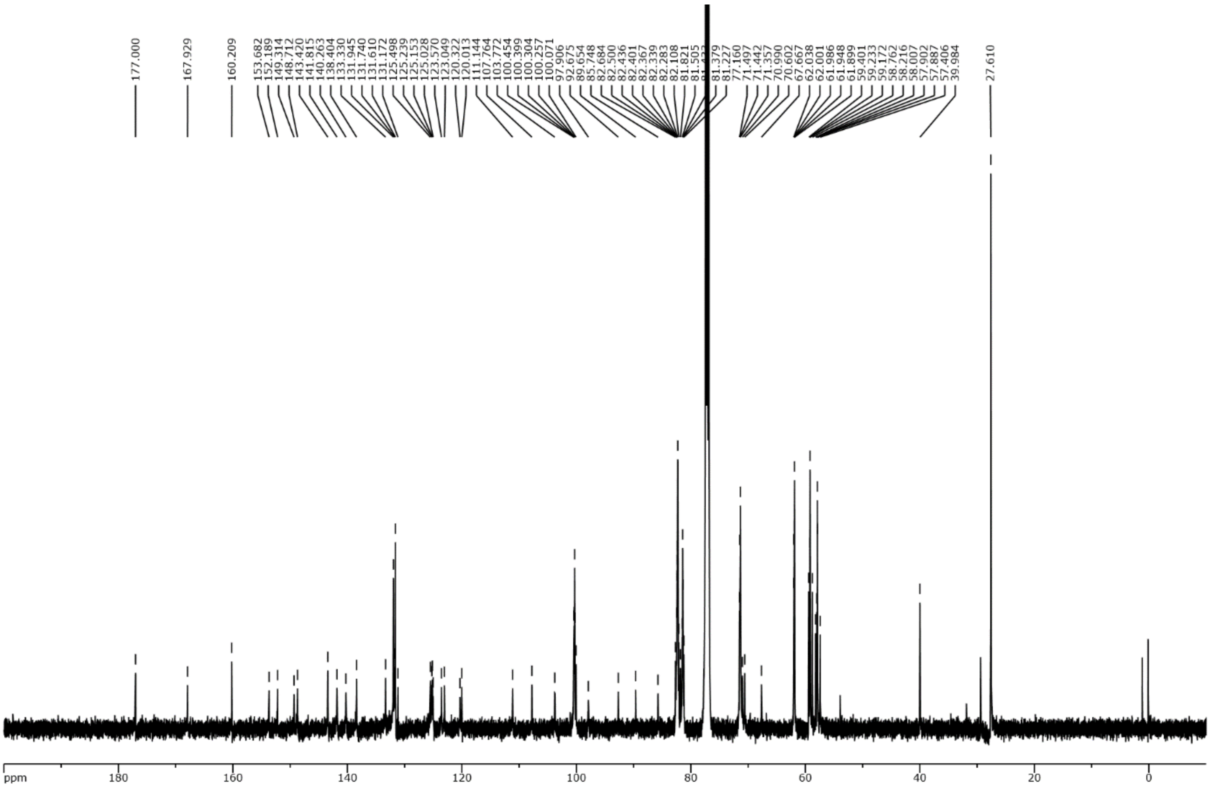
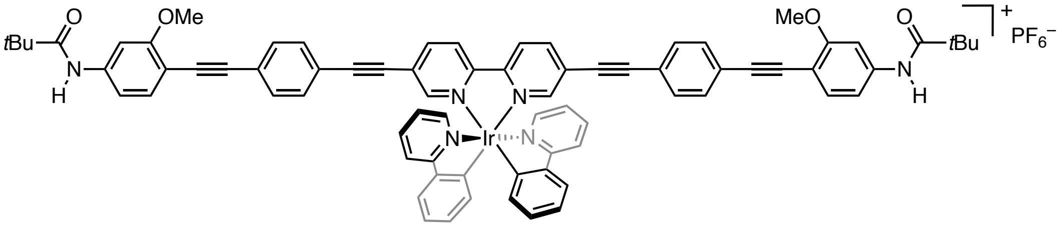


Fig. S23 ^{13}C NMR spectrum of complex [Ir(ppy)$_2$(**L2**)]PF$_6$ (126 MHz, CDCl$_3$).

3.3 Synthesis and NMR spectra of complex [Ir(ppy)$_2$(L3)]PF$_6$



The mixture of **L3** (16.3 mg, 20 μmol) and [Ir(ppy)$_2$Cl]$_2$ (10.7 mg, 10 μmol) in dichloromethane (3 mL) and methanol (1.5 mL) was stirred for 3 h at 60 °C, and then the solvent was removed *in vacuo*. After the residue was redissolved in dichloromethane (5 mL) and methanol (1 mL), KPF$_6$ (18.4 mg, 100 μmol) was added. The mixture was stirred at room temperature for 15 min, and then the volatiles were evaporated *in vacuo*. The residue was purified by flash column chromatography (1%→5% methanol /dichloromethane) and preparative TLC (10% methanol /dichloromethane) to give [Ir(ppy)$_2$(**L3**)]PF$_6$ as a red-orange solid (23.4 mg, 90%).

^{1}H NMR (500 MHz, CDCl$_3$): δ 8.53 (d, J = 8.5 Hz, 2H), 8.09 (dd, J = 8.5, 1.5 Hz, 2H), 7.99–7.87 (m, 4H), 7.78 (t, J = 8.0 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 1.5 Hz, 2H), 7.55 (s, 4H), 7.45 (d, J = 8.5 Hz, 4H), 7.42–7.31 (m, 6H), 7.22–7.00 (m, 4H), 6.99–6.88 (m, 4H), 6.27 (d, J = 7.5 Hz, 2H), 3.91 (s, 6H), 1.32 (s, 18H).

^{13}C NMR (126 MHz, CDCl$_3$): δ 177.21, 167.83, 160.82, 153.77, 152.10, 149.30, 148.75, 143.44, 141.77, 140.49, 138.43, 133.75, 131.91, 131.72, 131.68, 131.14, 125.45, 125.24, 125.13, 124.99, 123.62, 123.05, 120.47, 119.99, 111.45, 107.22, 102.81, 97.81, 92.38, 89.20, 85.76, 56.09, 40.01, 27.66.

HR-MS (ESI-ToF-MS) *m*/*z*: [Ir(ppy)$_2$(**L3**)]$^+$ calcd for $C_{76}H_{62}IrN_6O_4$ 1315.4464, found 1315.4449.

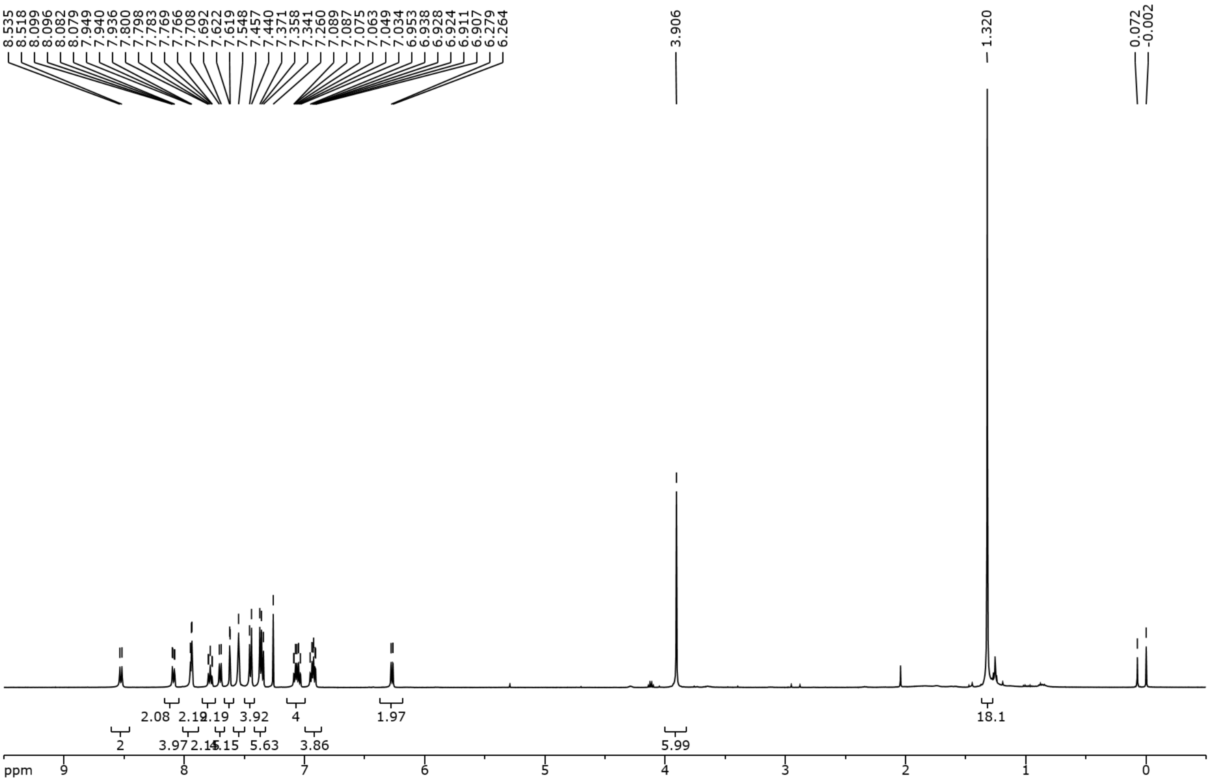


Fig. S24 ^{1}H NMR spectrum of complex [Ir(ppy)$_2$(**L3**)]PF$_6$ (500 MHz, CDCl$_3$).

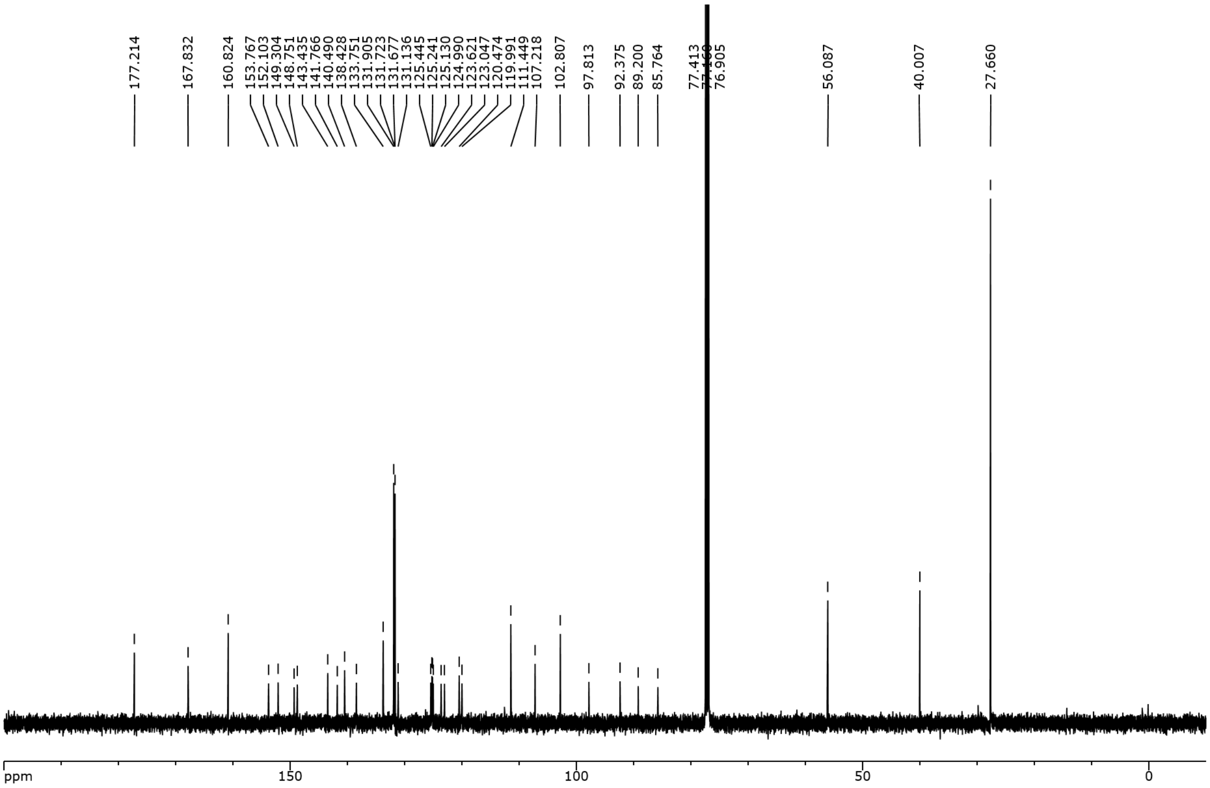


Fig. S25 ^{13}C NMR spectrum of complex [Ir(ppy)$_2$(**L3**)]PF$_6$ (126 MHz, CDCl$_3$).

4. General procedures for photochemical experiments

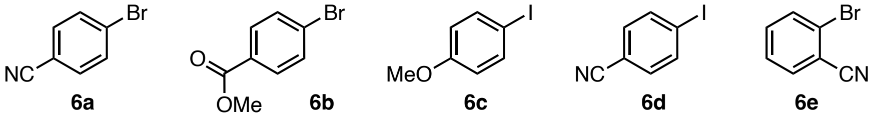


Fig. S26 Aryl halides used in this work.

4.1 Experimental procedure for C–O coupling reactions with alcohols

To a solution of $NiCl_2 \cdot DME$ in DMF (2 mM, 0.5 mL, 1 µmol) in a 5 mL vial with a stir bar, aryl halide (**6**, 0.1 mmol), alcohol (4 or 8 mmol), **L1** (3.2 mg, 1 µmol), iPr$_2$EtN (34 µL, 0.2 mmol) and 1,3,5-trimethoxybenzene (0.1 mmol) as an internal standard were added, and the mixture was stirred at 600 rpm under 427 nm LED irradiation with cooling fans for 20 or 48 h. After the respective reaction time, brine was added, and extracted with ethyl acetate. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The crude product was subjected to ^{1}H NMR analysis to determine the substrate conversion and product yield. Meanwhile, the same reaction without 1,3,5-trimethoxybenzene was carried out, and the resulting crude product was then purified by flash column chromatography (10 or 3% ethyl acetate/hexane in the reactions with primary or secondary alcohols, respectively) to isolate the desired product.

4.2 Experimental procedure for C–O coupling reactions with H_2O

To a solution of $NiCl_2 \cdot DME$ and **L1** in DMF (0.2 or 0.4 mM, 0.5 mL, 0.1 or 0.2 µmol) in a 5 mL vial with a stir bar, 4- or 2-bromobenzonitrile (**6a** or **6e**, 18.2 mg, 0.1 mmol), H_2O (72 µL, 4 mmol), iPr$_2$EtN (34 µL, 0.2 mmol) and 1,3,5-trimethoxybenzene (0.1 mmol) as an internal standard were added, and the mixture was stirred at 600 rpm under 427 nm LED irradiation with cooling fans for 3 or 6 h. After the respective reaction time, brine was added, and extracted with ethyl acetate. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The crude product was subjected to ^{1}H NMR analysis to determine the substrate conversion and product yield. Meanwhile, the same reaction without 1,3,5-trimethoxybenzene was carried out, and the resulting crude product was then purified by flash column chromatography (25% ethyl acetate/hexane) to isolate the desired product.

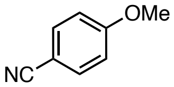
[For 10 mmol scale with 0.02 mol% Ni] To a solution of $NiCl_2 \cdot DME$ (0.44 mg in DMF 200 µL, 2 µmol) and **L1** (6.4 mg, 2 µmol) in DMF (7.3 mL, in total 7.5 mL) in a 20 mL Schlenk flask with a stir bar, 4-bromobenzonitrile (**6a**, 1.82 g, 10 mmol), H_2O (720 µL, 40 mmol), and iPr$_2$EtN (3.4 mL, 20 mmol) were added. The mixture was degassed by three freeze–pump–thaw cycles, and vigorously stirred at under 427 nm LED irradiation (4 cm away below the LEDs) with cooling fans for 17 h. After the respective reaction time, brine and 1N HCl aq. was added, and extracted with Et_2O/EtOAc. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by flash column chromatography (20%→50% ethyl acetate/hexane) to isolate the desired product **7f** as a colorless solids (781.2 mg, 66% yield).

4.3 Experimental procedure for C–N coupling reaction

To a solution of $NiCl_2$·DME in *N,N*-dimethylacetamide (DMA) (2 mM, 0.5 mL, 1 µmol) in a 5 mL vial with a stir bar, 4-bromobenzonitrile (**6a**, 18.2 mg, 0.1 mmol), *n*-octylamine (83 µL, 0.5 mmol), **L1** (3.2 mg, 1 µmol), 1,4-diazabicyclo[2.2.2]octane (DABCO) (22.4 mg, 0.2 mmol) and 1,3,5-trimethoxybenzene (0.1 mmol) as an internal standard were added, and the mixture was stirred at 600 rpm under 427 nm LED irradiation with cooling fans for 48 h. After the reaction time, brine was added, and extracted with ethyl acetate. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The crude product was subjected to ^1H NMR analysis to determine the substrate conversion and product yield. Meanwhile, the same reaction without 1,3,5-trimethoxybenzene was carried out, and the resulting crude product was then purified by flash column chromatography (10% ethyl acetate/hexane) to isolate the desired product.

5. Characterization of products

5.1 Characterization of 4-methoxybenzonitrile (7a)



The product **7a** was obtained from 4-bromobenzonitrile (**6a**, 18.2 mg, 0.1 mmol) and methanol (162 µL, 4 mmol) for 20 h as a white solid (94% NMR yield; 9.0 mg, 68% isolated yield).

^1H NMR (500 MHz, $CDCl_3$): δ 7.59 (d, J = 8.9 Hz, 2H), 6.95 (d, J = 8.9 Hz, 2H), 3.86 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 162.97, 134.12, 119.36, 114.88, 104.13, 55.68.

These spectral data match those reported in the literature.[3]

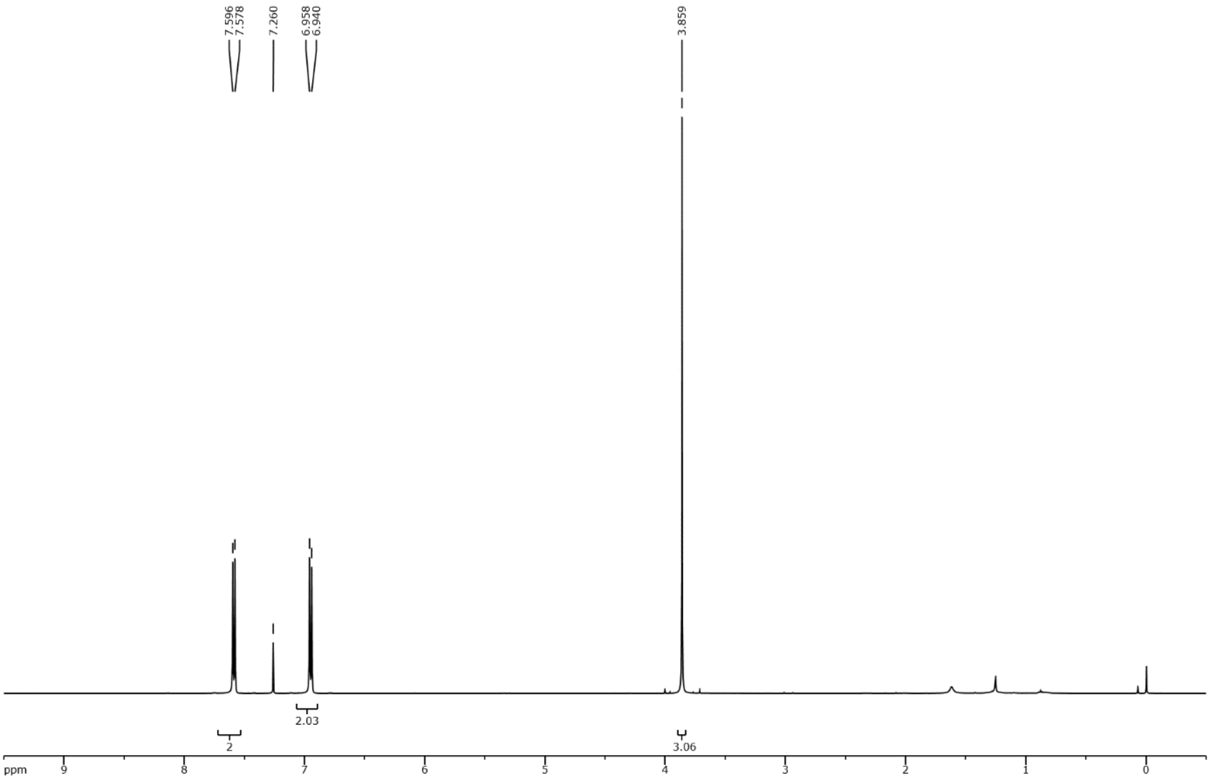


Fig. S27 ^{1}H NMR spectrum of compound **7a** (500 MHz, CDCl$_3$).

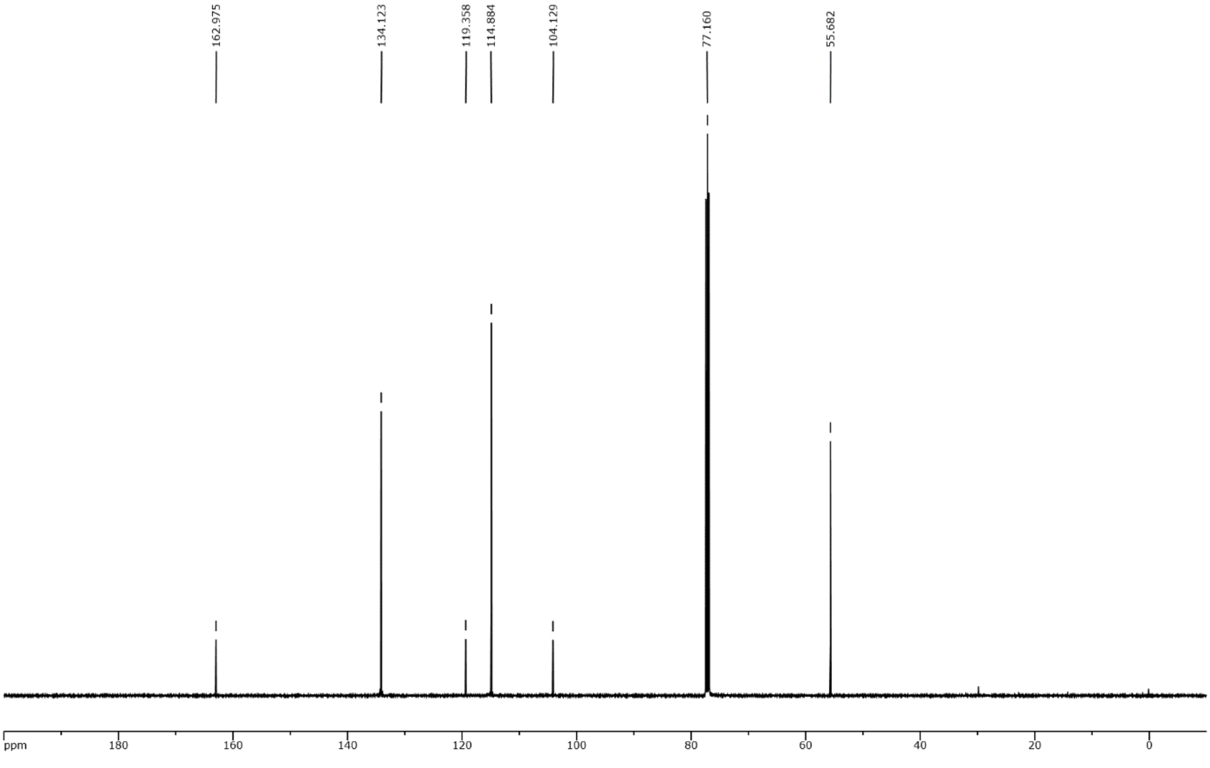
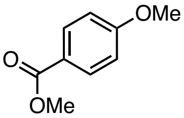


Fig. S28 ^{13}C NMR spectrum of compound **7a** (126 MHz, CDCl$_3$).

5.2 Characterization of methyl 4-methoxybenzoate (7b)



The product **7b** was obtained from methyl 4-bromobenzoate (**6b**, 21.5 mg, 0.1 mmol) and methanol (162 μL, 4 mmol) for 20 h as a white solid (97% NMR yield; 12.1 mg, 73% isolated yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (d, J = 9.0 Hz, 2H), 6.91 (d, J = 9.0 Hz, 2H), 3.88 (s, 3H), 3.86 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 167.00, 163.46, 131.72, 122.76, 113.74, 55.55, 52.00.

These spectral data match those reported in the literature.[3]

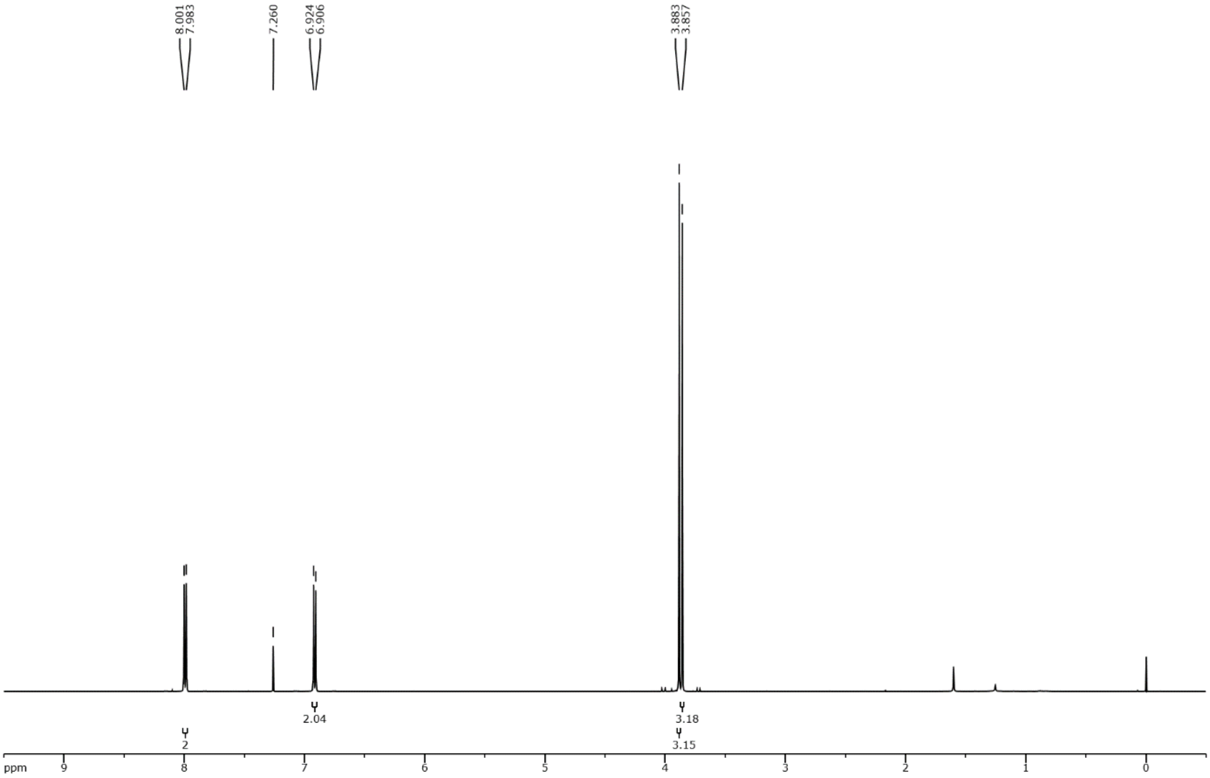


Fig. S29 ^{1}H NMR spectrum of compound **7b** (500 MHz, $CDCl_3$).

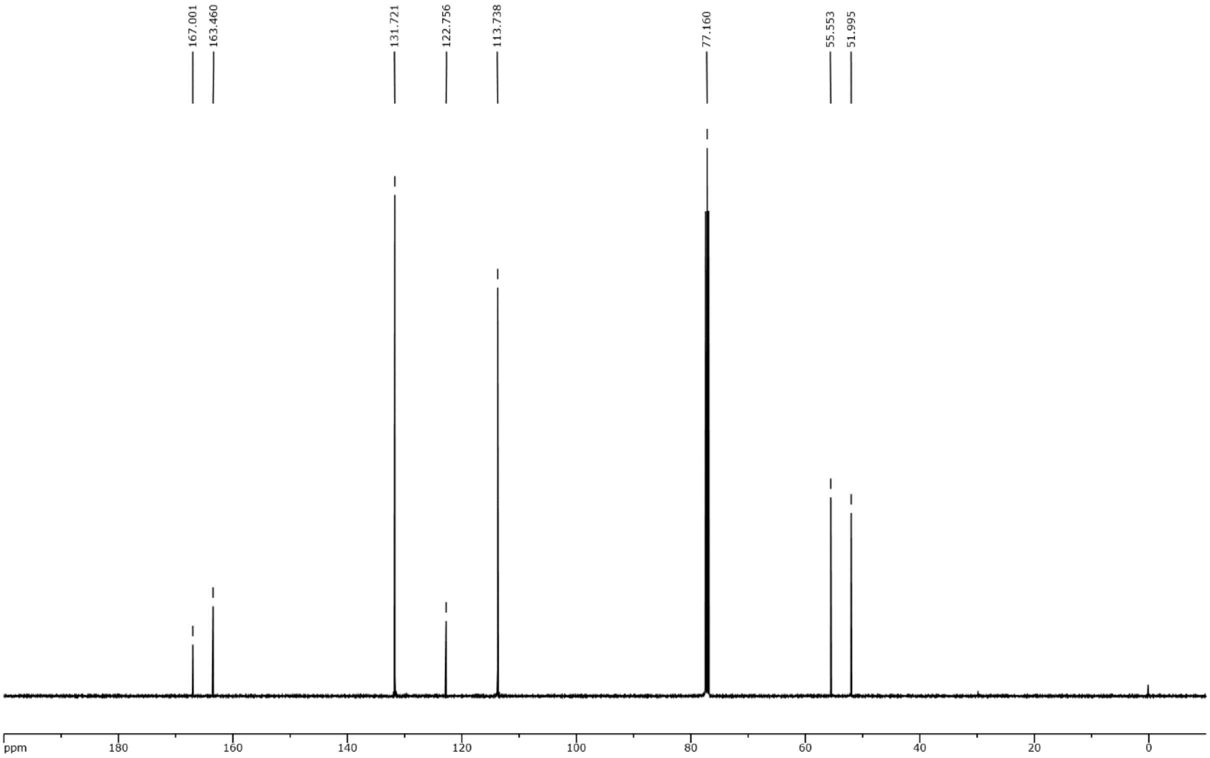
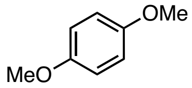


Fig. S30 ^{13}C NMR spectrum of compound **7b** (126 MHz, $CDCl_3$).

5.3 Characterization of 1,4-dimethoxybenzene (7c)



The product **7c** was obtained from 1-iodo-4-methoxybenzene (**6c**, 23.4 mg, 0.1 mmol) and methanol (324 μL, 8 mmol) for 48 h as a white solid (92% NMR yield; 8.3 mg, 60% isolated yield).

^{1}H NMR (500 MHz, CDCl$_3$): δ 6.84 (s, 4H), 3.77 (s, 6H).

^{13}C NMR (126 MHz, CDCl$_3$): δ 153.92, 114.81, 55.91.

These spectral data match those reported in the literature.[3]

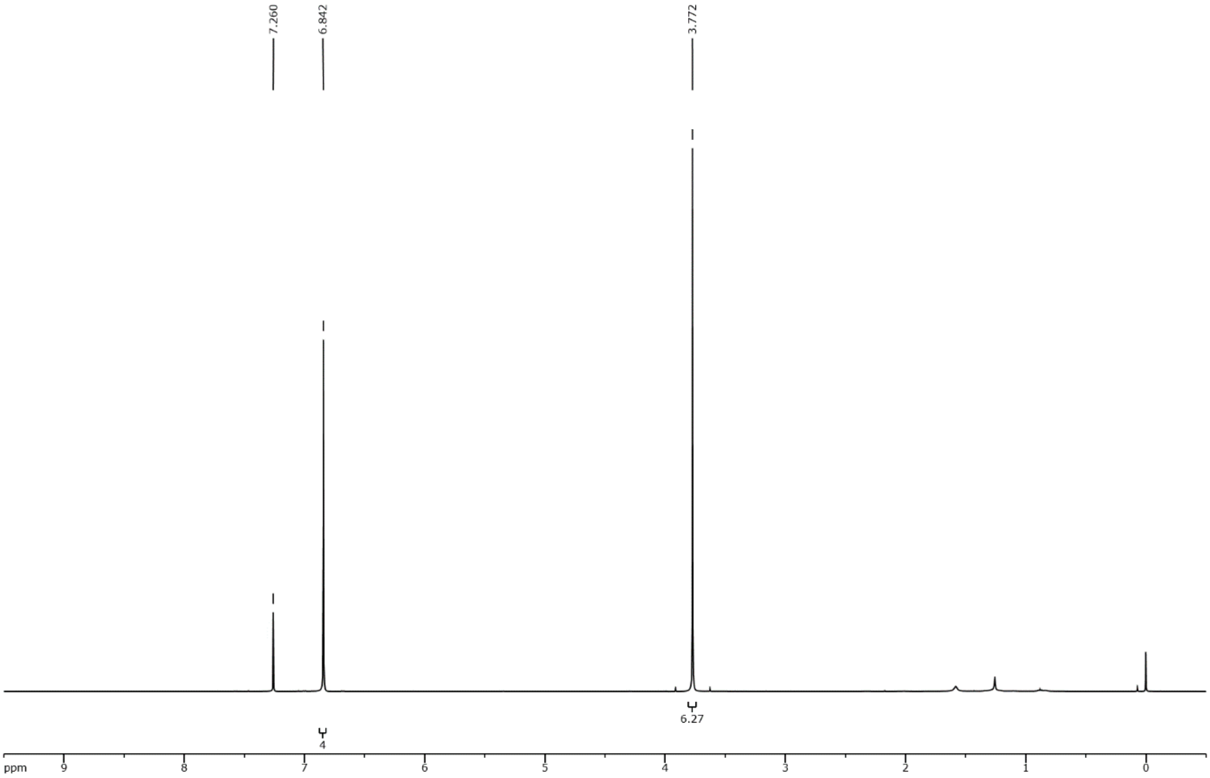


Fig. S31 ^{1}H NMR spectrum of compound **7c** (500 MHz, $CDCl_3$).

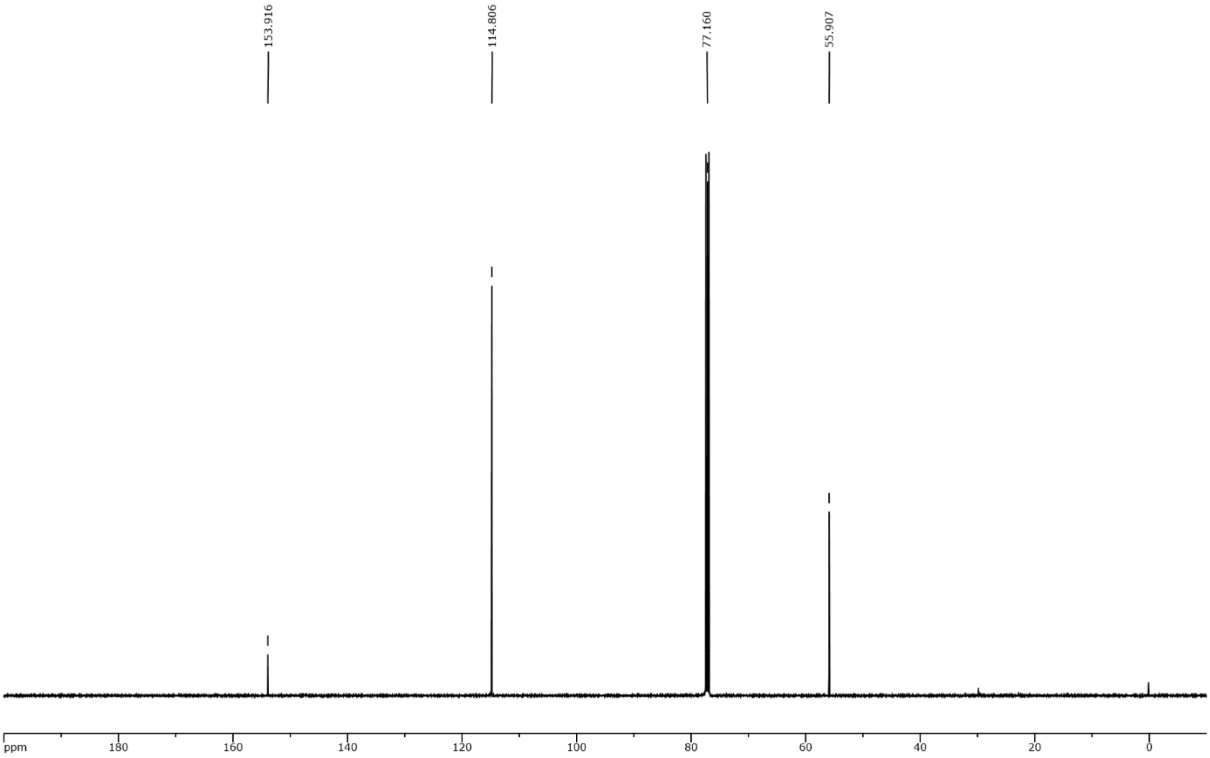
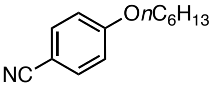


Fig. S32 ^{13}C NMR spectrum of compound **7c** (126 MHz, $CDCl_3$).

5.4 Characterization of 4-(hexyloxy)benzonitrile (7d)



The product **7d** was obtained from 4-bromobenzonitrile (**6a**, 18.2 mg, 0.1 mmol) and 1-hexanol (499 µL, 4 mmol) for 48 h as a colorless oil (71% NMR yield; 14.0 mg, 69% isolated yield). Hydration product, 4-hydroxybenzonitrile (**7f**, 28% NMR yield), was also observed in the crude product.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (d, J = 9.0 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 3.99 (t, J = 6.5 Hz, 2H), 1.79 (quintet, J = 7.1 Hz, 2H), 1.45 (quintet, J = 7.4 Hz, 2H), 1.35–1.32 (m, 4H), 0.91 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 162.59, 134.07, 119.46, 115.30, 103.76, 68.56, 31.62, 29.07, 25.74, 22.69, 14.13.

These spectral data match those reported in the literature.[4]

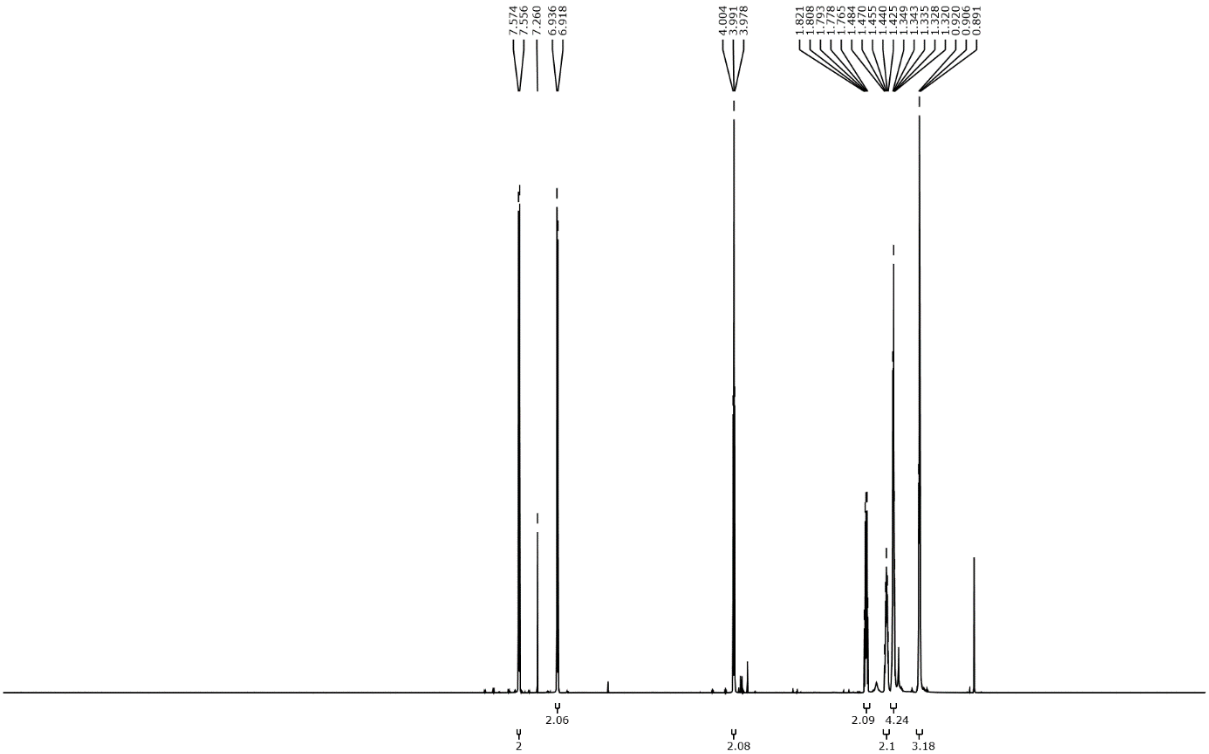


Fig. S33 ^{1}H NMR spectrum of compound **7d** (500 MHz, $CDCl_3$).

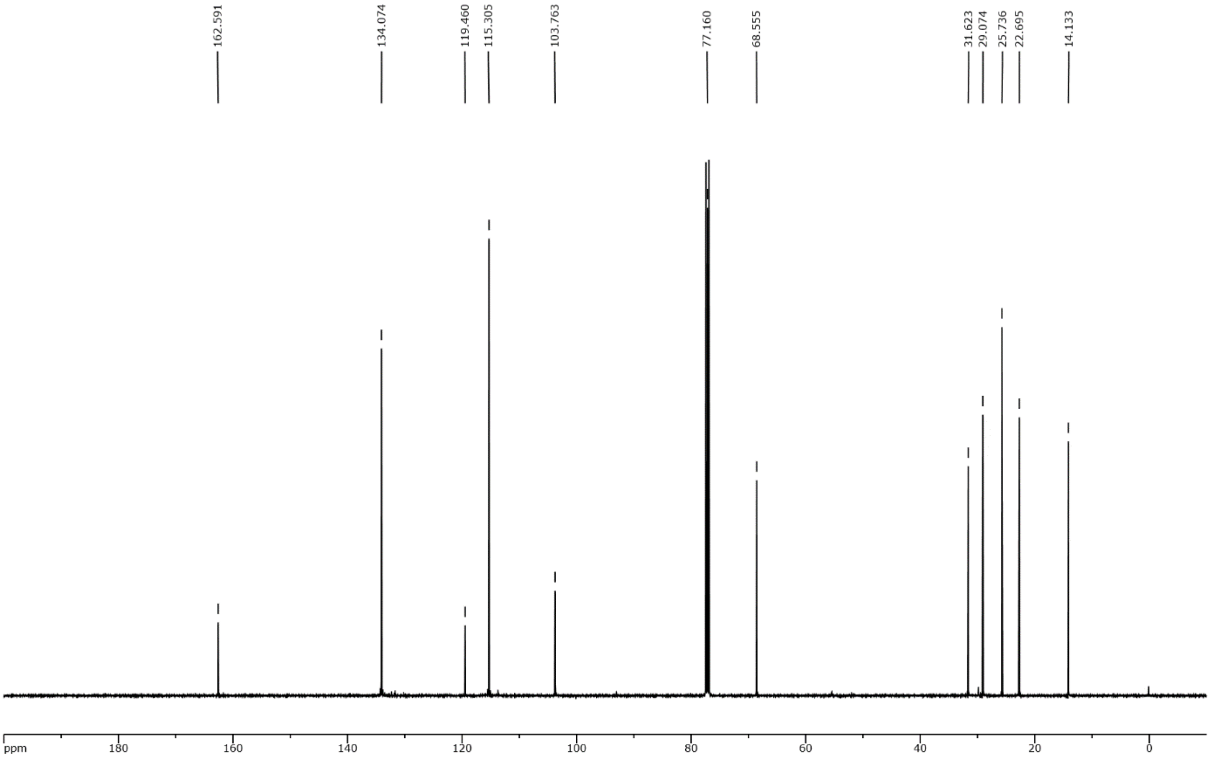
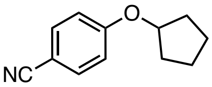


Fig. S34 ^{13}C NMR spectrum of compound **7d** (126 MHz, $CDCl_3$).

5.5 Characterization of 4-(cyclopentyloxy)benzonitrile (7e)



The product **7e** was obtained from 4-iodobenzonitrile (**6d**, 22.9 mg, 0.1 mmol) and cyclopentanol (725 µL, 8 mmol) for 48 h as a colorless oil (83% conversion, 60% NMR yield; 9.4 mg, 50% isolated yield). Dehaloprotonation product, benzonitrile (20% NMR yield), was also observed in the crude product.

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.55 (d, J = 8.9 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 4.80 (quintet, J = 3.0 Hz, 1H), 1.95–1.92 (m, 2H), 1.86–1.78 (m, 4H), 1.66–1.63 (m, 2H).

^{13}C NMR (126 MHz, CDCl$_3$): δ 161.69, 134.03, 119.56, 116.19, 103.39, 80.05, 32.92, 24.16.

These spectral data match those reported in the literature.[5]

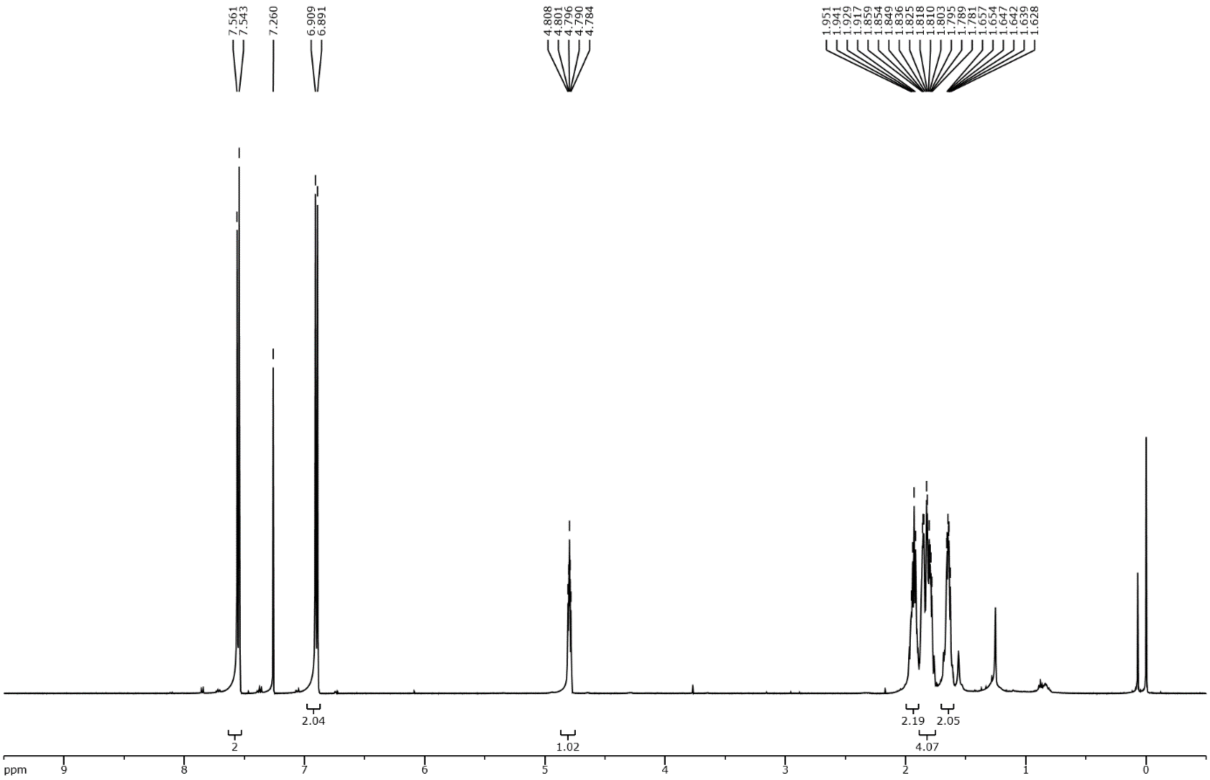


Fig. S35 ^{1}H NMR spectrum of compound **7e** (500 MHz, CDCl$_3$).

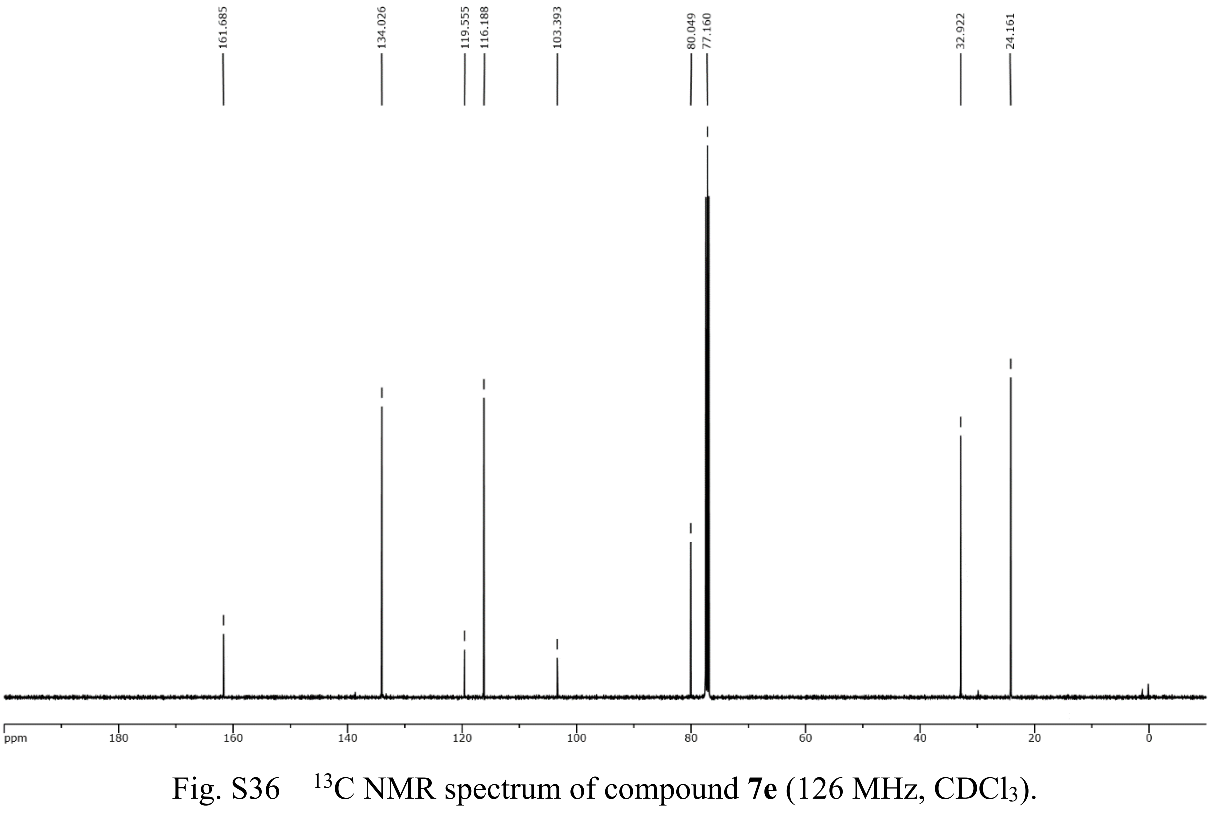
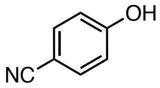


Fig. S36 ^{13}C NMR spectrum of compound **7e** (126 MHz, CDCl$_3$).

5.6 Characterization of 4-hydroxybenzonitrile (7f)



The product **7f** was obtained from 4-bromobenzonitrile (**6a**) with 0.1 mol% Ni/**L1** for 3 h as a white solid (94% NMR yield; 10.5 mg, 88% isolated yield). For 10 mmol scale with 0.02 mol% Ni/**L1** for 17 h; 781.2 mg, 66% isolated yield (TON 3300).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 6.34 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 160.05, 134.46, 119.33, 116.55, 103.58.

These spectral data match those reported in the literature.[6]

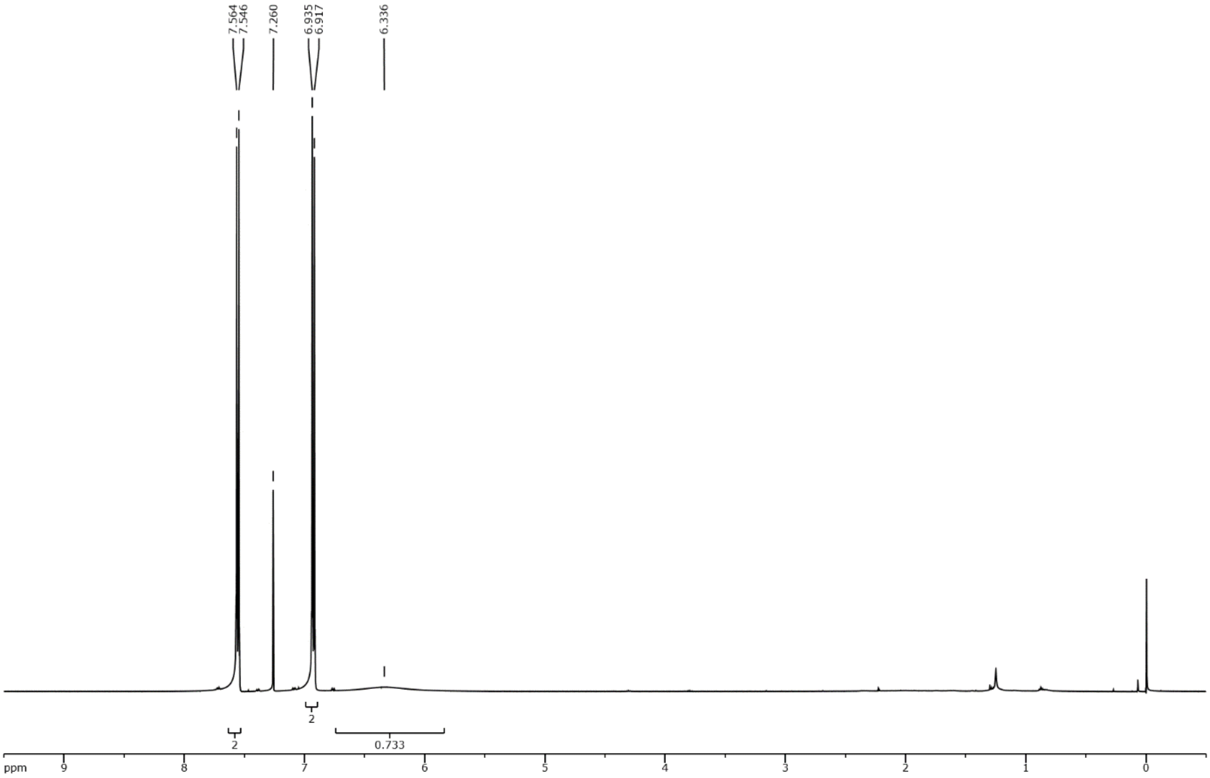


Fig. S37 ^{1}H NMR spectrum of compound **7f** (500 MHz, $CDCl_3$).

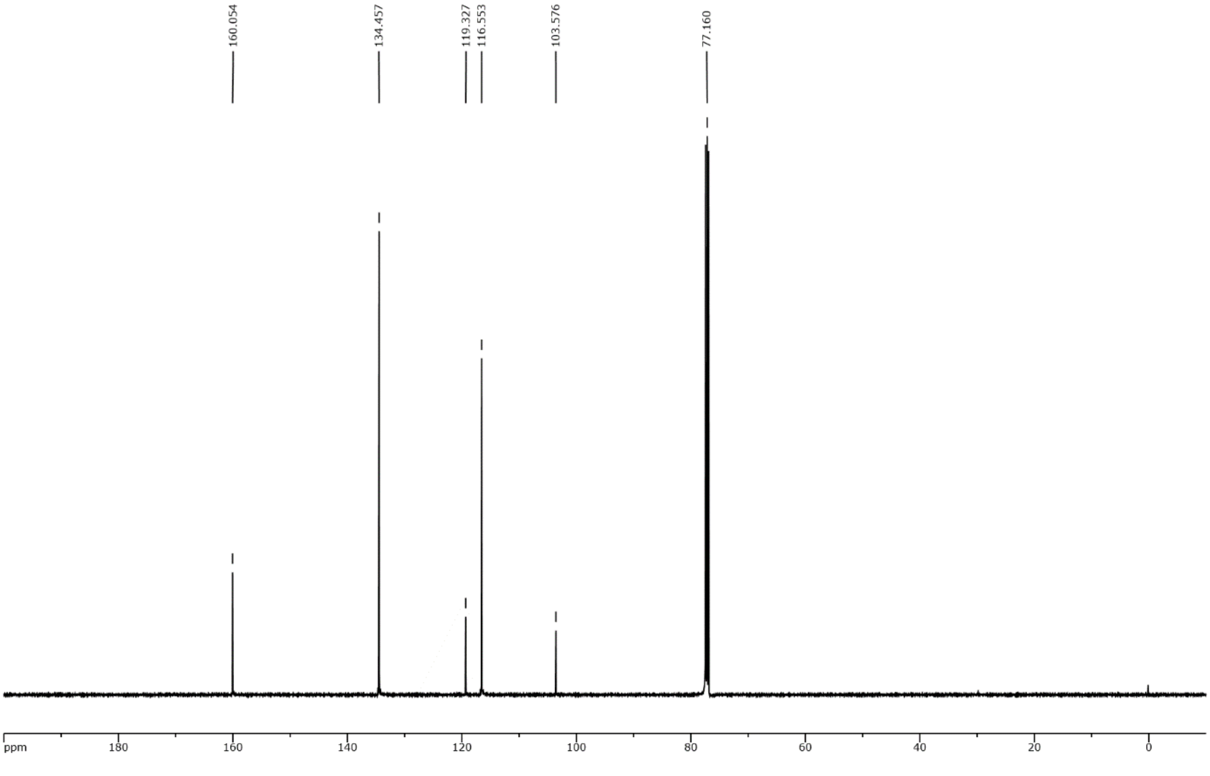
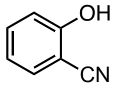


Fig. S38 ^{13}C NMR spectrum of compound **7f** (126 MHz, $CDCl_3$).

5.7 Characterization of 2-hydroxybenzonitrile (7g)



The product **7g** was obtained from 2-bromobenzonitrile (**6e**) with 0.2 mol% Ni/**L1** for 6 h as a white solid (76% NMR yield; 8.9 mg, 75% isolated yield). Homocoupling product, [1,1'-biphenyl]-2,2'-dicarbonitrile (24% NMR yield based on **6e**), was also observed in the crude product.

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.52–7.46 (m, 2H), 7.01–6.98 (m, 2H).

^{13}C NMR (126 MHz, CDCl$_3$): δ 158.60, 134.90, 133.00, 121.16, 116.76, 116.42, 99.65.

These spectral data match those reported in the literature.[6]

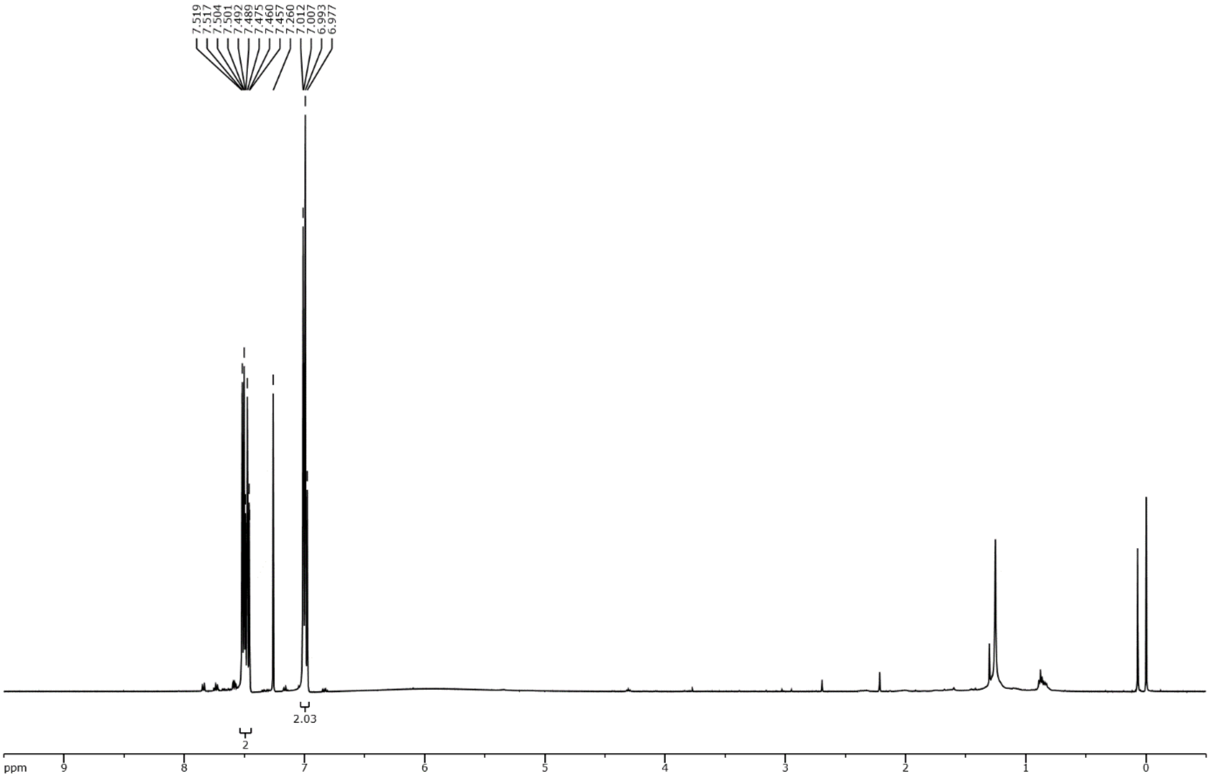


Fig. S39 ^{1}H NMR spectrum of compound **7g** (500 MHz, CDCl$_3$).

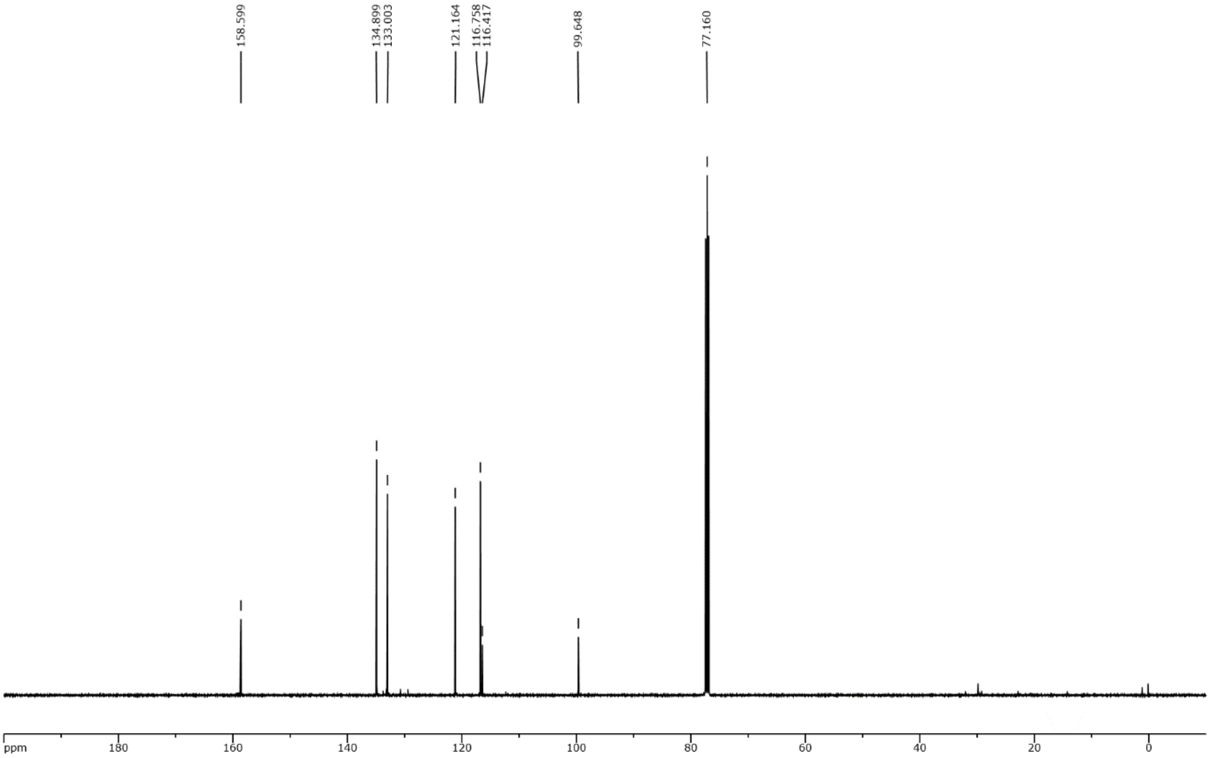
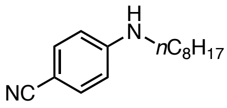


Fig. S40 ^{13}C NMR spectrum of compound **7g** (126 MHz, CDCl$_3$).

5.8 Characterization of 4-(octylamino)benzonitrile (8a)



The product **8a** was obtained as a white solid (86% NMR yield; 18.6 mg, 81% isolated yield). Hydration product, 4-hydroxybenzonitrile (**7f**, 13% NMR yield), was also observed in the crude product.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (d, J = 8.8 Hz, 2H), 6.53 (d, J = 8.8 Hz, 2H), 4.21 (s, 1H), 3.13 (q, J = 6.3 Hz, 2H), 1.62 (quintet, J = 7.3 Hz, 2H), 1.41-1.27 (m, 10H), 0.88 (t, J = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 151.59, 133.79, 120.71, 112.13, 98.36, 43.35, 31.90, 29.42, 29.32, 29.27, 27.14, 22.75, 14.20.

These spectral data match those reported in the literature.[7]

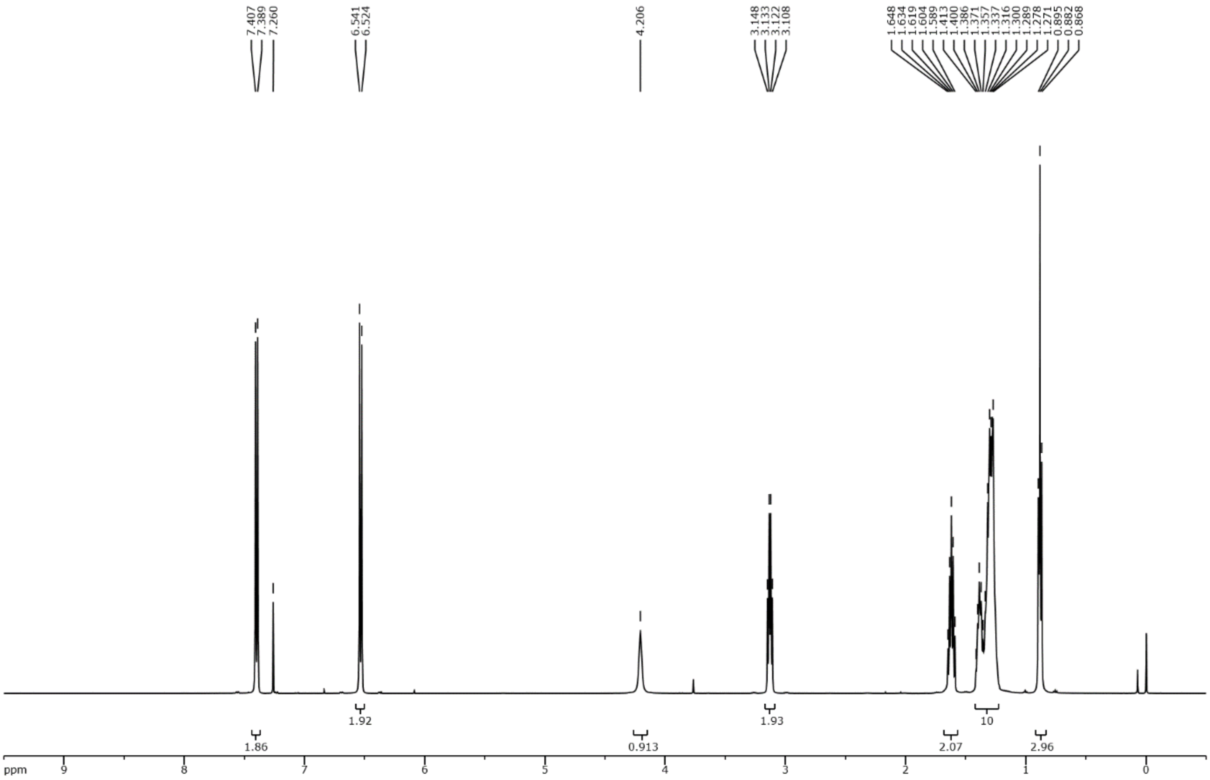


Fig. S41 ^{1}H NMR spectrum of compound **8a** (500 MHz, CDCl$_3$).

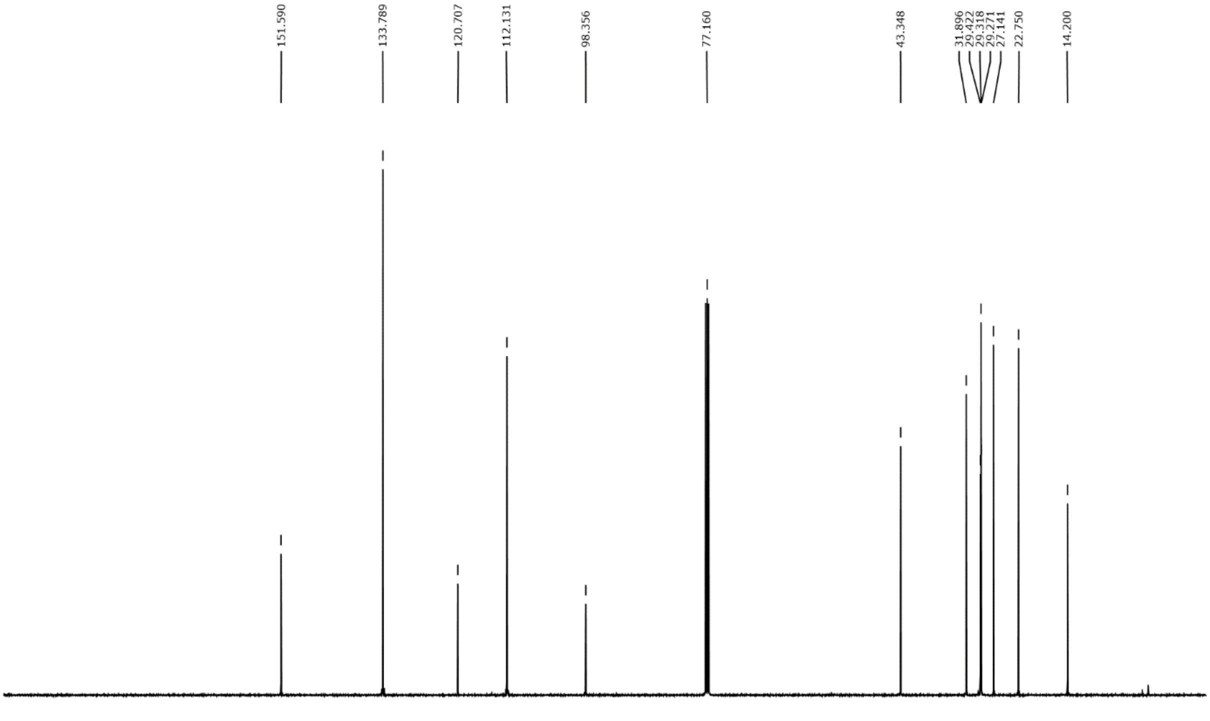


Fig. S42 ^{13}C NMR spectrum of compound **8a** (126 MHz, CDCl$_3$).

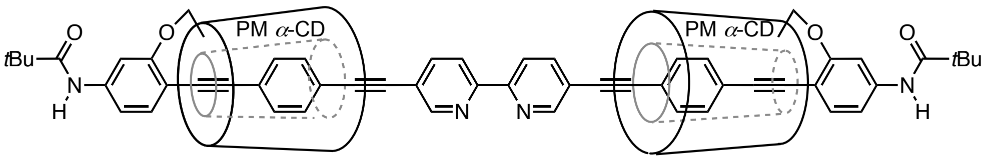
6. Theoretical calculations

Computation method calculations were performed using Gaussian 16 program. Structures were optimized to stationary points which were determined to be local minima by performing frequency calculations and verifying the absence of imaginary frequencies. Single point and time-dependent DFT calculations were performed at the same level of theory as the geometry optimizations.

Full Gaussian Citation:

Gaussian 16, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2019.

6.1 Theoretical calculation for L1



DFT calculation for **L1** was performed using the B3LYP hybrid density functional and 6-31G** basis set. Details of the optimized geometries are presented in Table S1.

Table S1 Optimized structural coordinates of **L1**.

Atom Number	Atomic Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	O	14.679252	2.256388	-0.822591
2	O	13.072154	4.433788	-1.443999
3	O	9.811380	6.050484	-1.922320
4	O	10.202181	4.527380	-4.312314
5	O	11.518941	2.025598	-3.761417
6	O	13.066368	0.701406	-4.932725
7	O	9.660698	1.638496	-5.935716
8	O	9.554332	-1.188783	-5.888450
9	O	15.135775	-0.595392	-3.545084
10	O	11.246399	-2.338379	-3.853257
11	O	12.633745	-4.166120	-3.368443
12	O	9.204651	-4.162243	-4.599008

13	O	8.964537	-5.494076	-2.076297
14	O	13.886252	-6.050650	-1.454590
15	O	10.873372	-4.427904	-0.118407
16	O	12.328913	-4.843371	1.685645
17	O	8.808301	-5.817866	1.278148
18	O	8.779712	-4.320094	3.684107
19	O	13.605289	-4.104620	4.182696
20	O	10.694104	-2.147707	3.620040
21	O	12.252842	-0.910927	4.874287
22	O	8.686712	-1.519612	5.540351
23	O	8.872250	1.312059	5.530033
24	O	13.797813	1.405738	5.453218
25	O	10.842949	2.280677	3.652036
26	O	12.438725	3.993668	3.445698
27	O	8.877171	4.262459	4.144207
28	O	9.124241	5.628405	1.645910
29	O	13.984653	5.832292	1.796625
30	O	11.189418	4.454095	-0.028222
31	C	11.931810	5.147964	-1.001241
32	C	11.049486	5.439169	-2.234871
33	C	10.736432	4.170795	-3.044632
34	C	11.978564	3.298030	-3.288578
35	C	12.783053	3.135181	-1.986961
36	C	14.122542	2.437910	-2.143050
37	C	9.907924	7.364684	-1.394518
38	C	8.781013	4.477658	-4.386060
39	C	11.961098	1.581416	-5.020165
40	C	10.825179	0.855284	-5.765511
41	C	10.428443	-0.443578	-5.057594
42	C	11.655388	-1.321253	-4.779745
43	C	12.839786	-0.516641	-4.201435
44	C	14.148967	-1.284009	-4.290716
45	C	9.728395	2.553248	-7.017573
46	C	8.190876	-1.164227	-5.495058
47	C	16.422241	-1.154854	-3.696514
48	C	11.536488	-3.682439	-4.133588
49	C	10.321621	-4.567266	-3.825295
50	C	9.976333	-4.524042	-2.334736
51	C	11.199666	-4.823204	-1.461537
52	C	12.467993	-4.078601	-1.938756
53	C	13.742109	-4.646258	-1.310680
54	C	8.588150	-5.207413	-5.333975
55	C	7.708626	-4.952222	-1.688302
56	C	14.503688	-6.479710	-2.658463
57	C	11.204052	-5.288056	0.955008
58	C	10.004052	-5.412092	1.916471
59	C	9.714991	-4.091921	2.638653
60	C	10.982486	-3.505415	3.264727
61	C	12.195008	-3.554972	2.312205
62	C	13.508652	-3.283113	3.033240
63	C	8.767819	-7.183968	0.899704
64	C	7.465248	-3.852466	3.415693
65	C	14.713839	-3.769485	4.993747
66	C	11.070567	-1.691420	4.898960
67	C	9.933078	-0.851133	5.514574
68	C	9.731777	0.475133	4.772662
69	C	11.059127	1.216851	4.592069
70	C	12.177589	0.287560	4.081046
71	C	13.551949	0.936004	4.140202
72	C	8.580484	-2.537573	6.521243
73	C	7.550648	1.422615	5.027430
74	C	14.958201	2.207379	5.535786
75	C	11.204791	3.590153	4.017535
76	C	10.127623	4.582659	3.558474
77	C	10.014392	4.581723	2.033287
78	C	11.375037	4.792951	1.362033
79	C	12.500480	3.947392	2.007588
80	C	13.900105	4.421410	1.635079
81	C	8.199311	5.365961	4.722322
82	C	8.017558	5.210066	0.859811
83	H	14.019353	1.483371	-2.657480
84	H	14.810353	3.070819	-2.717623
85	H	8.906621	7.799008	-1.444857
86	H	10.592333	7.987667	-1.989028

87	H	10.230376	7.362301	-0.346260	124	H	14.313174	0.196959	3.842382
88	H	8.508945	4.855936	-5.374771	125	H	13.582208	1.765102	3.423350
89	H	8.318898	5.110133	-3.622067	126	H	9.139299	-3.439450	6.242514
90	H	8.421771	3.445074	-4.291556	127	H	7.521901	-2.799578	6.591055
91	H	14.013583	-2.306223	-3.911636	128	H	8.920630	-2.183536	7.505870
92	H	14.442010	-1.345811	-5.352711	129	H	7.003370	2.055698	5.731469
93	H	8.720842	2.950393	-7.159280	130	H	7.058331	0.444631	4.969418
94	H	10.043333	2.052769	-7.944994	131	H	7.539294	1.907585	4.043367
95	H	10.405504	3.390947	-6.807555	132	H	15.069147	2.508331	6.580607
96	H	7.797872	-0.141271	-5.470439	133	H	14.870165	3.107680	4.910764
97	H	8.050967	-1.642669	-4.517817	134	H	15.861193	1.654032	5.231570
98	H	7.641831	-1.740072	-6.244978	135	H	14.128958	4.134696	0.604475
99	H	16.458713	-2.199995	-3.349526	136	H	7.255736	4.982473	5.118561
100	H	17.106432	-0.557815	-3.090911	137	H	7.992117	6.147528	3.981785
101	H	16.754837	-1.130034	-4.746374	138	H	8.772444	5.806096	5.552435
102	H	14.610298	-4.116851	-1.730209	139	H	7.373768	6.085485	0.734760
103	H	13.701141	-4.462666	-0.233998	140	H	7.442160	4.423350	1.366557
104	H	8.224092	-6.005100	-4.675006	141	H	8.337211	4.866196	-0.130318
105	H	9.273781	-5.644664	-6.075341	142	H	12.333377	6.072434	-0.573877
106	H	7.742701	-4.762768	-5.864321	143	H	11.641338	6.106551	-2.882579
107	H	7.003195	-5.787317	-1.659627	144	H	10.016300	3.561709	-2.482790
108	H	7.350051	-4.211735	-2.413951	145	H	12.604141	3.782024	-4.051249
109	H	7.763104	-4.508915	-0.687676	146	H	12.186500	2.560084	-1.274333
110	H	15.475998	-5.984715	-2.805364	147	H	12.327878	2.428717	-5.610139
111	H	13.881983	-6.286219	-3.538780	148	H	11.235018	0.580721	-6.750673
112	H	14.671458	-7.555327	-2.557648	149	H	9.954645	-0.198300	-4.098632
113	H	14.342747	-3.489344	2.343388	150	H	11.950777	-1.785789	-5.731200
114	H	13.544074	-2.224811	3.318212	151	H	12.614757	-0.288645	-3.152716
115	H	9.398094	-7.390932	0.025841	152	H	11.836491	-3.800996	-5.180652
116	H	7.731983	-7.407235	0.633692	153	H	10.612821	-5.594950	-4.082099
117	H	9.068225	-7.839059	1.730469	154	H	9.615277	-3.516119	-2.101612
118	H	7.445467	-2.759363	3.326699	155	H	11.394150	-5.901616	-1.494902
119	H	6.850801	-4.143939	4.271593	156	H	12.378461	-3.022842	-1.649332
120	H	7.053266	-4.313429	2.510431	157	H	11.498707	-6.267254	0.564112
121	H	15.666802	-3.902084	4.456945	158	H	10.292331	-6.153900	2.678222
122	H	14.701067	-4.444402	5.852993	159	H	9.317939	-3.368205	1.916750
123	H	14.652411	-2.730917	5.349584	160	H	11.220533	-4.088232	4.160606

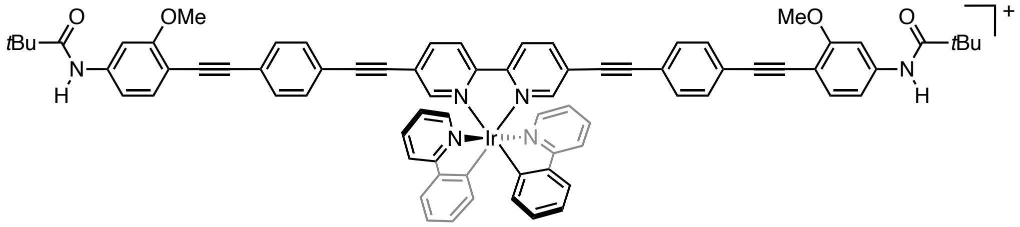
161	H	12.062280	-2.783654	1.541664
162	H	11.317760	-2.543165	5.541007
163	H	10.249065	-0.609137	6.542195
164	H	9.308987	0.267166	3.781146
165	H	11.361308	1.628509	5.560483
166	H	11.965968	0.025719	3.035614
167	H	11.349215	3.659233	5.100043
168	H	10.462793	5.576259	3.885960
169	H	9.614373	3.606608	1.733399
170	H	11.638157	5.852361	1.447833
171	H	12.386565	2.909301	1.669197
172	H	14.618428	3.917279	2.300331
173	C	2.762376	1.353441	-0.242731
174	C	3.499826	0.153161	-0.239926
175	C	2.759140	-1.049721	-0.243015
176	N	1.432850	-1.104726	-0.247163
177	C	0.739448	0.051419	-0.247959
178	C	1.377708	1.302309	-0.246570
179	C	7.556619	0.084836	-0.210123
180	C	8.303129	1.281114	-0.224879
181	C	9.690079	1.254915	-0.211255
182	C	10.386008	0.027223	-0.187123
183	C	9.640849	-1.170775	-0.166593
184	C	8.253844	-1.140703	-0.178414
185	H	3.284531	2.304758	-0.240506
186	H	3.288387	-2.000264	-0.241224
187	H	7.781343	2.231808	-0.243489
188	H	10.242478	2.187635	-0.210363
189	H	10.157383	-2.123547	-0.139830
190	H	7.692606	-2.068799	-0.163867
191	C	16.642386	1.002392	-0.427524
192	H	18.990222	-1.216381	0.394364
193	C	19.665039	0.627463	-0.158681
194	C	15.251899	1.052332	-0.510693
195	C	14.452988	-0.072149	-0.191221
196	C	15.121309	-1.255584	0.181908
197	C	16.502789	-1.315608	0.260776
198	C	17.281112	-0.181653	-0.033430
199	H	17.219162	1.884825	-0.660836
200	H	14.532488	-2.133075	0.422296
201	H	16.984109	-2.242503	0.562881
202	N	18.677166	-0.308587	0.083851
203	C	21.108737	0.123652	0.096373
204	O	19.424647	1.763208	-0.542066
205	C	11.811140	-0.004713	-0.187725
206	C	13.031179	-0.020318	-0.203050
207	C	6.135719	0.112623	-0.222983
208	C	4.918240	0.135676	-0.232470
209	H	0.772721	2.200488	-0.247311
210	C	21.416154	-1.090473	-0.809533
211	C	22.078312	1.268238	-0.238867
212	C	21.272133	-0.269147	1.582572
213	H	20.790582	-1.960628	-0.581689
214	H	22.458101	-1.398918	-0.674925
215	H	21.272898	-0.842120	-1.865817
216	H	21.979933	1.574992	-1.282817
217	H	23.109205	0.943483	-0.064857
218	H	21.878927	2.146584	0.379124
219	H	20.636734	-1.113981	1.870044
220	H	21.030450	0.570551	2.241527
221	H	22.309010	-0.562474	1.777102
222	C	15.269699	6.329019	1.487212
223	H	15.239408	7.414070	1.615840
224	H	16.038764	5.915110	2.158258
225	H	15.559871	6.097900	0.450976
226	C	-0.739370	-0.051151	-0.247977
227	N	-1.432774	1.104994	-0.247100
228	C	-1.377627	-1.302042	-0.246701
229	C	-2.759064	1.049987	-0.242978
230	C	-2.762295	-1.353176	-0.242889
231	H	-0.772639	-2.200220	-0.247504
232	C	-3.499748	-0.152897	-0.240001
233	H	-3.288313	2.000529	-0.241119
234	H	-3.284448	-2.304494	-0.240750

235	C	-4.918162	-0.135443	-0.232561
236	C	-6.135642	-0.112426	-0.223079
237	C	-7.556542	-0.084655	-0.210221
238	C	-8.303017	-1.280956	-0.225011
239	C	-8.253803	1.140861	-0.178469
240	C	-9.689968	-1.254800	-0.211365
241	H	-7.781205	-2.231634	-0.243658
242	C	-9.640809	1.170888	-0.166626
243	H	-7.692595	2.068975	-0.163900
244	C	-10.385933	-0.027129	-0.187179
245	H	-10.242334	-2.187540	-0.210500
246	H	-10.157377	2.123640	-0.139823
247	C	-11.811066	0.004752	-0.187737
248	C	-13.031106	0.020298	-0.203006
249	C	-14.452917	0.072055	-0.191106
250	C	-15.251776	-1.052454	-0.510613
251	C	-15.121288	1.255427	0.182128
252	O	-14.679066	-2.256452	-0.822610
253	C	-16.642263	-1.002599	-0.427383
254	C	-16.502769	1.315365	0.261061
255	H	-14.532508	2.132938	0.422545
256	C	-14.122434	-2.437864	-2.143116
257	C	-17.281040	0.181384	-0.033186
258	H	-17.218999	-1.885050	-0.660725
259	H	-16.984130	2.242213	0.563247
260	C	-12.782904	-3.135084	-1.987154
261	H	-14.019316	-1.483284	-2.657487
262	H	-14.810252	-3.070763	-2.717690
263	N	-18.677096	0.308235	0.084153
264	O	-13.071912	-4.433751	-1.444285
265	C	-11.978466	-3.297791	-3.288816
266	H	-12.186348	-2.560015	-1.274505
267	H	-18.990191	1.215996	0.394723
268	C	-19.664925	-0.627869	-0.158353
269	C	-11.931513	-5.147893	-1.001621
270	O	-11.518943	-2.025299	-3.761588
271	C	-10.736265	-4.170494	-3.044980
272	H	-12.604043	-3.781775	-4.051493
273	C	-21.108639	-0.124159	0.096816
274	O	-19.424483	-1.763592	-0.541767
275	O	-11.189136	-4.454055	-0.028564
276	C	-11.049210	-5.438947	-2.235302
277	H	-12.333010	-6.072422	-0.574319
278	C	-11.961168	-1.581072	-5.020298
279	O	-10.202046	-4.526951	-4.312712
280	H	-10.016150	-3.561399	-2.483126
281	C	-21.416215	1.089947	-0.809061
282	C	-22.078159	-1.268813	-0.238350
283	C	-21.271942	0.268622	1.583029
284	C	-11.374715	-4.793030	1.361668
285	O	-9.811060	-6.050215	-1.922831
286	H	-11.641043	-6.106317	-2.883039
287	O	-13.066512	-0.701164	-4.932777
288	C	-10.825327	-0.854792	-5.765621
289	H	-12.327887	-2.428368	-5.610318
290	C	-8.780885	-4.477111	-4.386523
291	H	-20.790690	1.960148	-0.581261
292	H	-22.458174	1.398314	-0.674374
293	H	-21.273018	0.841610	-1.865358
294	H	-21.979841	-1.575558	-1.282310
295	H	-23.109062	-0.944132	-0.064259
296	H	-21.878664	-2.147147	0.379622
297	H	-20.636577	1.113497	1.870453
298	H	-21.030151	-0.571062	2.241962
299	H	-22.308824	0.561879	1.777643
300	C	-10.014074	-4.581795	2.032929
301	C	-12.500202	-3.947581	2.007303
302	H	-11.637776	-5.852460	1.447387
303	C	-9.907515	-7.364474	-1.395158
304	C	-12.840022	0.516848	-4.201404
305	O	-9.660782	-1.637891	-5.935907
306	C	-10.428689	0.444052	-5.057616
307	H	-11.235212	-0.580195	-6.750755
308	H	-8.508834	-4.855309	-5.375269

309	H	-8.318682	-5.109592	-3.622587	346	O	-10.842723	-2.280895	3.651843
310	H	-8.421721	-3.444503	-4.291978	347	H	-11.348902	-3.659572	5.099762
311	O	-9.123872	-5.628404	1.645474	348	C	-15.269300	-6.329354	1.486955
312	C	-10.127301	-4.582852	3.558118	349	C	-11.536952	3.682756	-4.133358
313	H	-9.614093	-3.606638	1.733124	350	C	-16.422510	1.154734	-3.696315
314	O	-12.438425	-3.993938	3.445409	351	H	-7.798095	0.142001	-5.470553
315	C	-13.899804	-4.421672	1.634798	352	H	-8.051306	1.643279	-4.517776
316	H	-12.386360	-2.909465	1.668969	353	H	-7.642210	1.740894	-6.244935
317	H	-8.906195	-7.798747	-1.445590	354	H	-7.255351	-4.982709	5.118077
318	H	-10.591925	-7.987429	-1.989696	355	H	-7.991683	-6.147636	3.981137
319	H	-10.229923	-7.362209	-0.346885	356	H	-8.771988	-5.806509	5.551863
320	C	-11.655700	1.321604	-4.779681	357	C	-11.059006	-1.217137	4.591932
321	C	-14.149271	1.284108	-4.290603	358	H	-15.238934	-7.414411	1.615518
322	H	-12.614953	0.288799	-3.152705	359	H	-16.038319	-5.915527	2.158104
323	C	-9.728436	-2.552598	-7.017806	360	H	-15.559594	-6.098194	0.450763
324	O	-9.554656	1.189399	-5.888428	361	O	-12.634188	4.166329	-3.368119
325	H	-9.954853	0.198746	-4.098680	362	C	-10.322112	4.567628	-3.825082
326	C	-8.017270	-5.209971	0.859309	363	H	-11.837019	3.801358	-5.180399
327	O	-8.876867	-4.262655	4.143885	364	H	-16.459052	2.199849	-3.349254
328	C	-11.204499	-3.590413	4.017256	365	H	-17.106627	0.557598	-3.090725
329	H	-10.462445	-5.576484	3.885534	366	H	-16.755144	1.129960	-4.746163
330	O	-13.984251	-5.832571	1.796264	367	C	-9.731702	-0.475371	4.772671
331	H	-14.128706	-4.134913	0.604218	368	C	-12.177470	-0.287863	4.080888
332	H	-14.618143	-3.917631	2.300101	369	H	-11.361246	-1.628868	5.560297
333	O	-11.246771	2.338693	-3.853127	370	C	-12.468344	4.078718	-1.938448
334	H	-11.951146	1.786186	-5.731096	371	O	-9.205163	4.162721	-4.598888
335	O	-15.135993	0.595365	-3.544972	372	C	-9.976729	4.524318	-2.334548
336	H	-14.013966	2.306315	-3.911477	373	H	-10.613383	5.595313	-4.081797
337	H	-14.442356	1.345935	-5.352584	374	O	-8.872198	-1.312315	5.530051
338	H	-8.720843	-2.949611	-7.159598	375	C	-9.933113	0.850839	5.514655
339	H	-10.043494	-2.052111	-7.945183	376	H	-9.308847	-0.267322	3.781200
340	H	-10.405429	-3.390389	-6.807785	377	O	-12.252832	0.910565	4.874206
341	C	-8.191191	1.164924	-5.495064	378	C	-13.551804	-0.936376	4.139899
342	H	-7.373437	-6.085347	0.734184	379	H	-11.965785	-0.025940	3.035489
343	H	-7.441880	-4.423242	1.366048	380	C	-11.200025	4.823351	-1.461251
344	H	-8.337010	-4.866079	-0.130782	381	C	-13.742444	4.646268	-1.310247
345	C	-8.198910	-5.366203	4.721803	382	H	-12.378740	3.022944	-1.649105

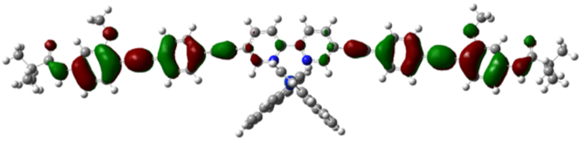
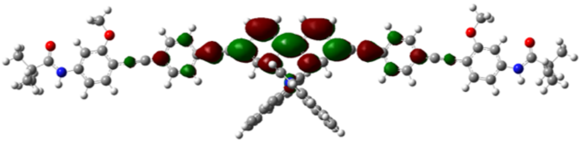
383	C	-8.588842	5.207954	-5.333916
384	O	-8.964978	5.494385	-2.076076
385	H	-9.615612	3.516397	-2.101511
386	C	-7.550530	-1.422720	5.027584
387	O	-8.686772	1.519358	5.540572
388	C	-11.070601	1.691115	4.899018
389	H	-10.249164	0.608762	6.542239
390	O	-13.797771	-1.406145	5.452884
391	H	-14.313041	-0.197368	3.842018
392	H	-13.581947	-1.765461	3.423028
393	O	-10.873648	4.427945	-0.118175
394	H	-11.394571	5.901755	-1.494515
395	O	-13.886680	6.050658	-1.454080
396	H	-14.610637	4.116828	-1.729724
397	H	-13.701373	4.462627	-0.233576
398	H	-8.224817	6.005687	-4.674982
399	H	-9.274583	5.645123	-6.075228
400	H	-7.743386	4.763402	-5.864329
401	C	-7.708951	4.952558	-1.688411
402	H	-7.003279	-2.055816	5.731632
403	H	-7.058288	-0.444692	4.969708
404	H	-7.539031	-1.907610	4.043483
405	C	-8.580712	2.537382	6.521419
406	O	-10.694054	2.147515	3.620160
407	H	-11.317887	2.542801	5.541106
408	C	-14.958050	-2.207959	5.535304
409	C	-11.204212	5.288029	0.955326
410	C	-14.504280	6.479738	-2.657861
411	H	-7.003554	5.787684	-1.659817
412	H	-7.350501	4.212157	-2.414206
413	H	-7.763194	4.509157	-0.687813
414	H	-9.139445	3.439254	6.242514
415	H	-7.522134	2.799359	6.591428
416	H	-8.921063	2.183418	7.506002
417	C	-10.982497	3.505229	3.264919
418	H	-15.069095	-2.508911	6.580115
419	H	-14.869793	-3.108255	4.910307
420	H	-15.861084	-1.654753	5.230957
421	O	-12.329016	4.843302	1.686033
422	C	-10.004136	5.411987	1.916704
423	H	-11.498890	6.267257	0.564524
424	H	-15.476583	5.984700	-2.804668
425	H	-13.882668	6.286318	-3.538259
426	H	-14.672094	7.555342	-2.556979
427	C	-9.715047	4.091773	2.638790
428	C	-12.195071	3.554840	2.312465
429	H	-11.220494	4.088005	4.160838
430	O	-8.808420	5.817764	1.278320
431	H	-10.292343	6.153760	2.678515
432	O	-8.779680	4.319901	3.684179
433	H	-9.318046	3.368103	1.916813
434	C	-13.508682	3.282908	3.033529
435	H	-12.062370	2.783598	1.541845
436	C	-8.767903	7.183905	0.900016
437	C	-7.465295	3.852076	3.415729
438	O	-13.605245	4.104264	4.183099
439	H	-14.342804	3.489252	2.343743
440	H	-13.544114	2.224571	3.318365
441	H	-9.398217	7.390984	0.026209
442	H	-7.732072	7.407159	0.633973
443	H	-9.068235	7.838920	1.730867
444	H	-7.445659	2.758965	3.326830
445	H	-6.850756	4.143550	4.271564
446	H	-7.053307	4.312912	2.510403
447	C	-14.713823	3.769113	4.994104
448	H	-15.666773	3.901864	4.457319
449	H	-14.700994	4.443910	5.853442
450	H	-14.652481	2.730491	5.349801

6.2 Theoretical calculation for [Ir(ppy)$_2$(L3)]$^+$



DFT and TD-DFT calculations for [Ir(ppy)$_2$(**L3**)]$^+$ were performed using the CAM-B3LYP hybrid density functional with LANL2DZ (Ir) and 6-31+G** (C, H, N, O) basis sets with PCM solvent model for CH_2Cl_2. Details of the optimized geometries are presented in Table S3.

Table S2 HOMO and LUMO distributions of [Ir(ppy)$_2$(**L3**)]$^+$.

Orbital	label	Energy	Diagram
Orbital 304	HOMO	-7.0284 eV	
Orbital 305	LUMO	-2.2528 eV	

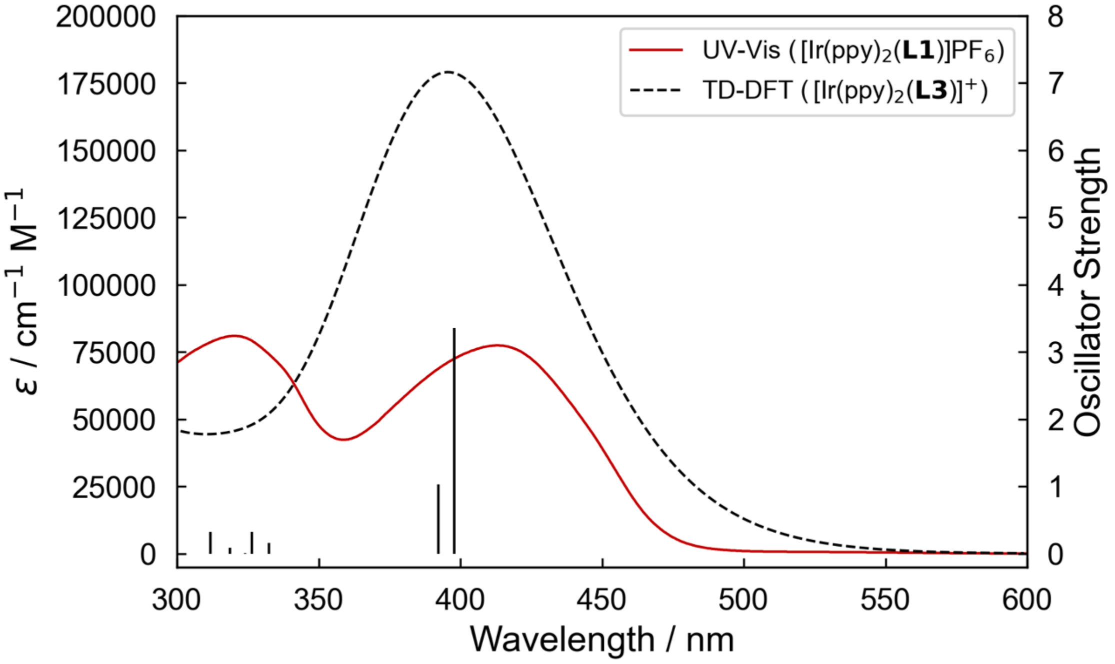


Fig. S43 Experimental and calculated UV/Visible spectra of [Ir(ppy)$_2$(**L1**)]PF$_6$ (in CH_2Cl_2, 1 × 10^{-5} M) and [Ir(ppy)$_2$(**L3**)]$^+$, respectively.

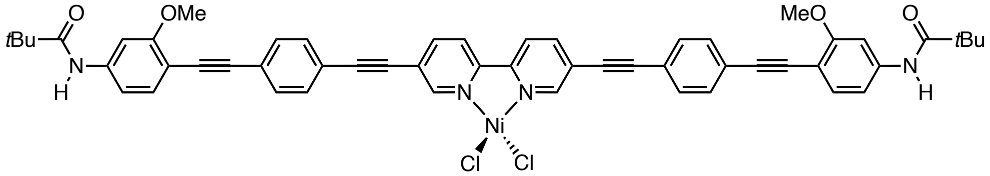
Table S3 Optimized structural coordinates of [Ir(ppy)$_2$(**L3**)]$^+$.

Atom Number	Atomic Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	2.879824	-2.967146	-0.010574
2	C	3.497202	-1.711732	0.025698
3	C	2.668566	-0.585361	0.060314
4	N	1.338175	-0.669015	0.063752
5	C	0.737490	-1.880034	0.031195
6	C	1.498471	-3.046854	-0.008926
7	C	7.536436	-1.285080	0.022201
8	C	8.372510	-2.412022	0.046888
9	C	9.749560	-2.263834	0.045010
10	C	10.329956	-0.985232	0.017315
11	C	9.491166	0.140876	-0.007166
12	C	8.113966	-0.006338	-0.004279
13	H	3.481427	-3.868137	-0.042045
14	H	3.089331	0.412938	0.086822
15	H	7.933830	-3.403692	0.067648
16	H	10.389387	-3.139077	0.064131
17	H	9.930035	1.132277	-0.028267
18	H	7.474508	0.869427	-0.023034
19	C	16.621662	-1.464175	0.073196
20	H	18.777252	1.054952	-0.135819
21	C	19.588089	-0.796685	0.032348
22	C	15.238990	-1.637664	0.084526
23	C	14.368192	-0.531187	-0.001069
24	C	14.933466	0.746686	-0.096949
25	C	16.303987	0.931844	-0.109715
26	C	17.156341	-0.176330	-0.025039
27	H	17.293614	-2.303623	0.138835
28	H	14.274129	1.605308	-0.162914
29	H	16.714935	1.933639	-0.185187
30	N	18.537177	0.078312	-0.047672
31	C	20.981904	-0.149848	-0.061971
32	O	19.430651	-2.007105	0.153876
33	C	11.749503	-0.833297	0.013053
34	C	12.954382	-0.707455	0.008349
35	O	14.649438	-2.851395	0.176111
36	C	6.116788	-1.436803	0.023572
37	C	4.913085	-1.563047	0.025110
38	H	1.023039	-4.017744	-0.045001
39	C	21.161174	0.452633	-1.468503
40	C	22.040575	-1.232120	0.164102
41	C	21.142932	0.945868	1.007396
42	H	20.454946	1.263240	-1.669900
43	H	22.170580	0.863656	-1.562152
44	H	21.033073	-0.309532	-2.242791
45	H	21.958098	-2.029742	-0.577070
46	H	23.036160	-0.786257	0.085110
47	H	21.942648	-1.683018	1.154720
48	H	20.474749	1.798002	0.851466
49	H	20.961464	0.550617	2.011159
50	H	22.165835	1.331860	0.976594
51	Ir	0.001112	1.059698	0.026071
52	N	0.309540	1.167142	-2.017535
53	C	-0.352028	0.434325	-2.928220
54	C	1.253780	2.057257	-2.418957
55	C	-0.111014	0.542644	-4.284525
56	H	-1.097483	-0.248927	-2.542259
57	C	1.538278	2.204948	-3.778300
58	C	0.856803	1.447490	-4.715409
59	H	-0.671826	-0.068064	-4.981393
60	H	2.290558	2.915816	-4.095250
61	H	1.074433	1.561471	-5.771920
62	N	-0.307297	1.178869	2.069053
63	C	0.351877	0.448910	2.983780
64	C	-1.249222	2.073660	2.465525
65	C	0.110819	0.565078	4.339429
66	H	1.095430	-0.238610	2.601714
67	C	-1.533616	2.229345	3.823998
68	C	-0.854495	1.474958	4.765282
69	H	0.669683	-0.043578	5.039646
70	H	-2.284036	2.943922	4.136985

71	H	-1.072055	1.595134	5.821117
72	C	1.413444	2.493469	-0.031388
73	C	1.990423	3.183557	1.041806
74	C	1.889698	2.800609	-1.325780
75	C	2.995225	4.127374	0.842303
76	H	1.654408	2.987695	2.055421
77	C	2.899143	3.748658	-1.528536
78	C	3.454163	4.414003	-0.444177
79	H	3.423381	4.646463	1.695181
80	H	3.257736	3.974027	-2.527771
81	H	4.236358	5.150066	-0.598290
82	C	-1.407702	2.497245	0.075609
83	C	-1.982800	3.183040	-1.001344
84	C	-1.883098	2.812767	1.368293
85	C	-2.984999	4.130694	-0.807014
86	H	-1.647319	2.980754	-2.013868
87	C	-2.889945	3.764672	1.565854
88	C	-3.443150	4.425600	0.477873
89	H	-3.411705	4.646312	-1.662724
90	H	-3.247925	3.996472	2.563838
91	H	-4.223317	5.164641	0.627951
92	C	-0.741311	-1.878488	0.038436
93	N	-1.339570	-0.666497	-0.001997
94	C	-1.504662	-3.043506	0.085406
95	C	-2.669809	-0.580204	-0.000474
96	C	-2.885845	-2.961081	0.085079
97	H	-1.031164	-4.015072	0.127973
98	C	-3.500705	-1.704714	0.039828
99	H	-3.088566	0.418744	-0.033630
100	H	-3.489271	-3.860676	0.121341
101	C	-4.916308	-1.553536	0.035660
102	C	-6.119855	-1.425884	0.030691
103	C	-7.539410	-1.273563	0.022426
104	C	-8.375655	-2.400656	0.018922
105	C	-8.116734	0.005527	0.016313
106	C	-9.752619	-2.252265	0.008642
107	H	-7.937148	-3.392606	0.023789
108	C	-9.493901	0.152974	0.006722
109	H	-7.477171	0.881411	0.018975
110	C	-10.332829	-0.973276	0.002240
111	H	-10.392567	-3.127621	0.005484
112	H	-9.932585	1.144669	0.001860
113	C	-11.752354	-0.821621	-0.009441
114	C	-12.957339	-0.697204	-0.020797
115	C	-14.371529	-0.524460	-0.034389
116	C	-15.238475	-1.636064	-0.086540
117	C	-14.941122	0.754567	0.002383
118	C	-16.621525	-1.466225	-0.101353
119	O	-14.644971	-2.850856	-0.120910
120	C	-16.312135	0.936185	-0.011596
121	H	-14.284787	1.617074	0.042541
122	C	-17.160579	-0.176981	-0.064075
123	H	-17.290500	-2.309618	-0.141636
124	H	-16.726351	1.939066	0.017326
125	N	-18.542148	0.073929	-0.076316
126	H	-18.786702	1.052898	-0.041668
127	C	-19.589729	-0.807161	-0.130722
128	C	-20.985095	-0.156894	-0.125774
129	O	-19.428234	-2.022146	-0.178044
130	C	-21.180135	0.641062	1.176954
131	C	-22.041558	-1.261699	-0.203375
132	C	-21.132645	0.772897	-1.344596
133	H	-20.488239	1.483762	1.264536
134	H	-22.195151	1.047895	1.204404
135	H	-21.048449	0.001654	2.054803
136	H	-21.965415	-1.944728	0.645636
137	H	-23.037721	-0.810304	-0.196210
138	H	-21.935479	-1.849979	-1.117747
139	H	-20.446078	1.624014	-1.314765
140	H	-20.959626	0.230303	-2.278670
141	H	-22.148956	1.176401	-1.371597
142	C	15.470024	-4.010506	0.266315
143	H	16.100051	-4.116923	-0.621979
144	H	16.097153	-3.980087	1.162484

145	H	14.783757	-4.853592	0.329841
146	C	-15.461391	-4.015040	-0.177885
147	H	-16.104200	-4.088877	0.704562
148	H	-16.075215	-4.021443	-1.083748
149	H	-14.772182	-4.857875	-0.198419

6.3 Theoretical calculation for $NiCl_2$(**L3**)



DFT and TD-DFT calculations for $NiCl_2$(**L3**) were performed using the CAM-UB3LYP hybrid density functional with LANL2DZ (Ni) and 6-31+G** (C, H, N, O, Cl) basis sets with PCM solvent model for DMF. Details of the optimized geometries are presented in Table S5.

Table S4 HOMO and LUMO distributions of $NiCl_2$(**L3**).

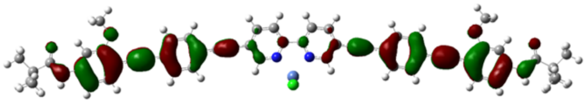
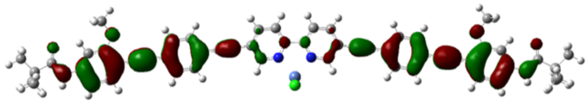
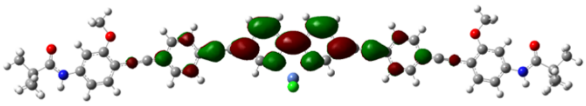
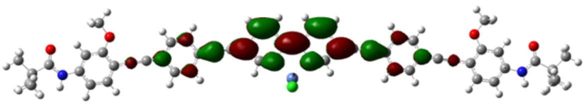
Orbital	label	Energy	Diagram
Orbital 242 (242A)	α-HOMO	-6.9340 eV	
Orbital 1630 (240B)	β-HOMO	-6.9343 eV	
Orbital 243 (243A)	α-LUMO	-2.0234 eV	
Orbital 1631 (241B)	β-LUMO	-2.006 eV	

Table S5 Optimized structural coordinates of $NiCl_2$(**L3**).

Atom Number	Atomic Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	Ni	0.000000	0.000000	1.473267
2	N	-0.027280	1.317917	-0.092879
3	C	-0.036865	2.641000	0.028257
4	C	-0.004741	0.739911	-1.308175
5	C	-0.023275	3.492926	-1.081832
6	H	-0.052943	3.040362	1.036338
7	C	0.012110	1.518716	-2.461988
8	C	0.003035	2.899090	-2.349359
9	C	-0.029212	4.906327	-0.907857
10	H	0.037210	1.061974	-3.442372
11	H	0.018201	3.520048	-3.237622
12	C	-0.031403	6.107710	-0.762606
13	C	-0.031130	7.524454	-0.583027
14	C	0.029831	8.382835	-1.691749

15	C	-0.089339	8.076333	0.705939
16	C	0.034115	9.756829	-1.515606
17	H	0.075279	7.964076	-2.691127
18	C	-0.085813	9.450385	0.881153
19	H	-0.136467	7.419785	1.567840
20	C	-0.023484	10.311310	-0.226568
21	H	0.082574	10.413178	-2.377477
22	H	-0.130231	9.868841	1.880605
23	C	-0.016553	11.727864	-0.044262
24	C	-0.008891	12.929183	0.113345
25	C	-0.002028	14.337958	0.328682
26	C	0.098133	15.238597	-0.752289
27	C	-0.093283	14.867822	1.622263
28	O	0.184616	14.682428	-1.982739
29	C	0.105849	16.616111	-0.539429
30	C	-0.086950	16.232428	1.846398
31	H	-0.170678	14.185437	2.461703
32	C	0.013391	17.114974	0.763367
33	H	0.181698	17.310090	-1.359791
34	H	-0.159355	16.616457	2.858849
35	N	0.016553	18.487645	1.059733
36	H	-0.051345	18.698519	2.045056
37	C	0.093285	19.563510	0.217319
38	C	0.067237	20.935853	0.913996
39	O	0.178034	19.442858	-1.001651
40	C	1.281722	21.062786	1.852838
41	C	0.137541	22.031344	-0.152721
42	C	-1.239590	21.091231	1.713786
43	H	1.255360	20.345006	2.677710
44	H	1.296212	22.064395	2.292186
45	H	2.219157	20.919100	1.307376
46	H	1.054118	21.955385	-0.742165
47	H	0.120570	23.010409	0.334283
48	H	-0.710554	21.973418	-0.839031
49	H	-1.321505	20.374405	2.535797
50	H	-2.114647	20.969439	1.068523
51	H	-1.278708	22.093086	2.150963
52	N	0.027280	-1.317917	-0.092879
53	C	0.036865	-2.641000	0.028257
54	C	0.004741	-0.739911	-1.308175
55	C	0.023275	-3.492926	-1.081832
56	H	0.052943	-3.040362	1.036338
57	C	-0.012110	-1.518716	-2.461988
58	C	-0.003035	-2.899090	-2.349359
59	C	0.029212	-4.906327	-0.907857
60	H	-0.037210	-1.061974	-3.442372
61	H	-0.018201	-3.520048	-3.237622
62	C	0.031403	-6.107710	-0.762606
63	C	0.031130	-7.524454	-0.583027
64	C	-0.029831	-8.382835	-1.691749
65	C	0.089339	-8.076333	0.705939
66	C	-0.034115	-9.756829	-1.515606
67	H	-0.075279	-7.964076	-2.691127
68	C	0.085813	-9.450385	0.881153
69	H	0.136467	-7.419785	1.567840
70	C	0.023484	-10.311310	-0.226568
71	H	-0.082574	-10.413178	-2.377477
72	H	0.130231	-9.868841	1.880605
73	C	0.016553	-11.727864	-0.044262
74	C	0.008891	-12.929183	0.113345
75	C	0.002028	-14.337958	0.328682
76	C	-0.098133	-15.238597	-0.752289
77	C	0.093283	-14.867822	1.622263
78	O	-0.184616	-14.682428	-1.982739
79	C	-0.105849	-16.616111	-0.539429
80	C	0.086950	-16.232428	1.846398
81	H	0.170678	-14.185437	2.461703
82	C	-0.013391	-17.114974	0.763367
83	H	-0.181698	-17.310090	-1.359791
84	H	0.159355	-16.616457	2.858849
85	N	-0.016553	-18.487645	1.059733
86	H	0.051345	-18.698519	2.045056
87	C	-0.093285	-19.563510	0.217319
88	C	-0.067237	-20.935853	0.913996

89	O	-0.178034	-19.442858	-1.001651
90	C	-1.281722	-21.062786	1.852838
91	C	-0.137541	-22.031344	-0.152721
92	C	1.239590	-21.091231	1.713786
93	H	-1.255360	-20.345006	2.677710
94	H	-1.296212	-22.064395	2.292186
95	H	-2.219157	-20.919100	1.307376
96	H	-1.054118	-21.955385	-0.742165
97	H	-0.120570	-23.010409	0.334283
98	H	0.710554	-21.973418	-0.839031
99	H	1.321505	-20.374405	2.535797
100	H	2.114647	-20.969439	1.068523
101	H	1.278708	-22.093086	2.150963
102	Cl	2.203192	0.117650	2.132884
103	Cl	-2.203192	-0.117650	2.132884
104	C	0.289387	15.534652	-3.118109
105	H	0.343022	14.872151	-3.980591
106	H	-0.589134	16.181047	-3.206370
107	H	1.195384	16.146070	-3.068923
108	C	-0.289387	-15.534652	-3.118109
109	H	-0.343022	-14.872151	-3.980591
110	H	0.589134	-16.181047	-3.206370
111	H	-1.195384	-16.146070	-3.068923

7. Absorption spectra

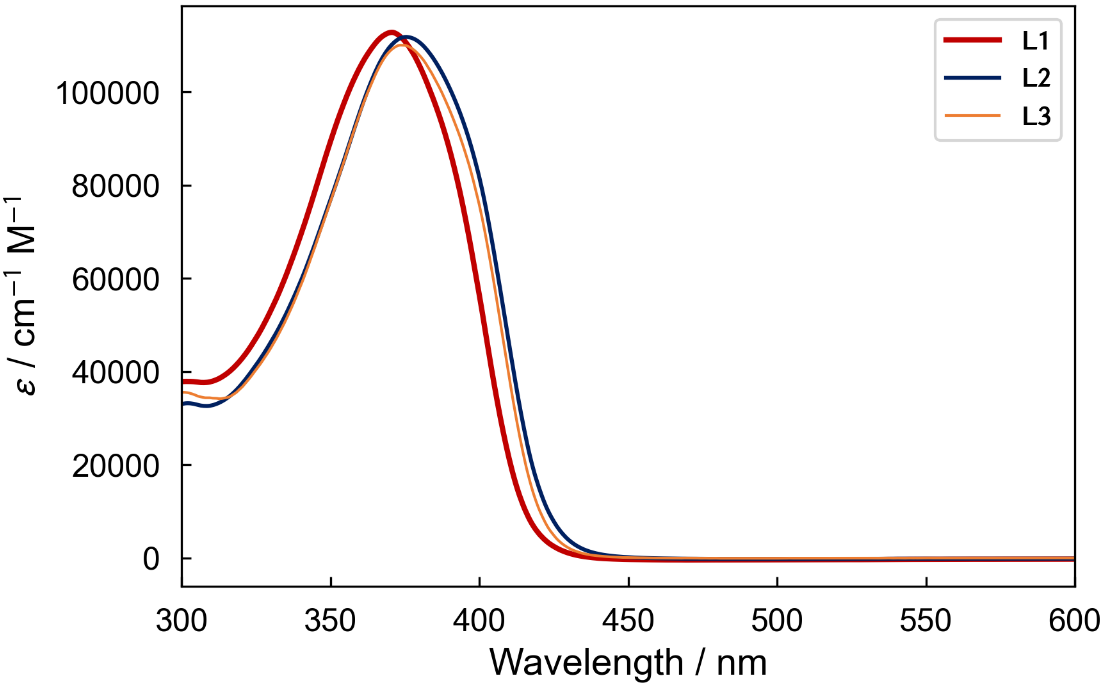


Fig. S44 Absorption spectra of **L1**–**L3** (in DMF, 1 × 10^{-5} M).

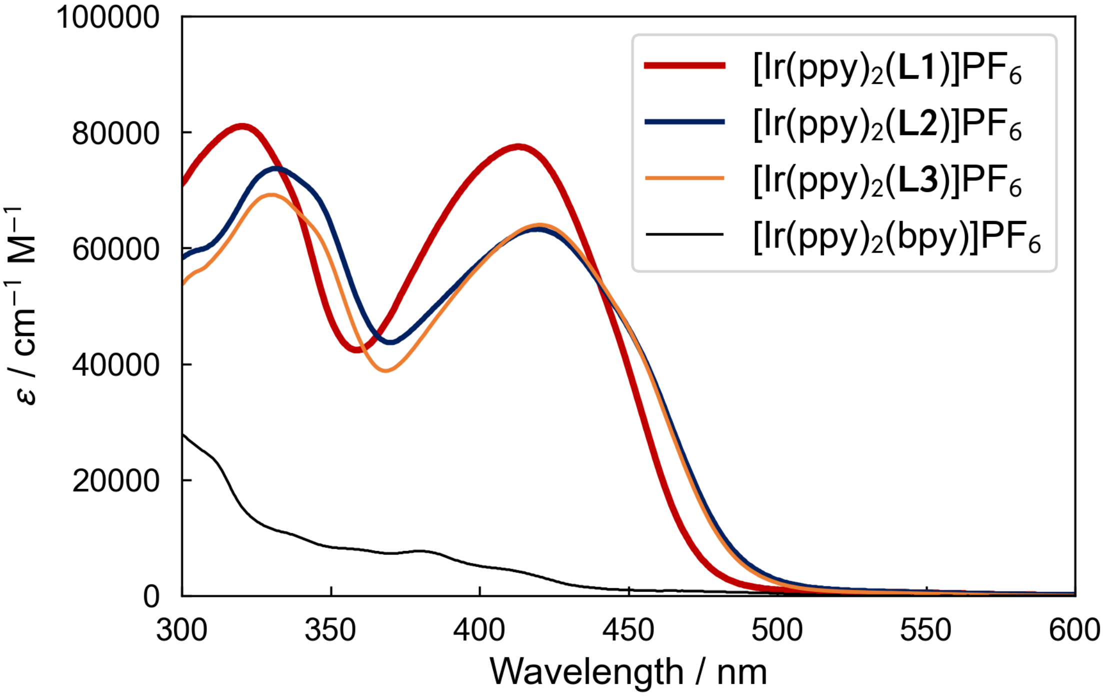


Fig. S45 Absorption spectra of [Ir(ppy)$_2$(**L1**)]PF$_6$, [Ir(ppy)$_2$(**L2**)]PF$_6$, [Ir(ppy)$_2$(**L3**)]PF$_6$, and [Ir(ppy)$_2$(bpy)]PF$_6$ (in CH_2Cl_2, 1 × 10^{-5} M).

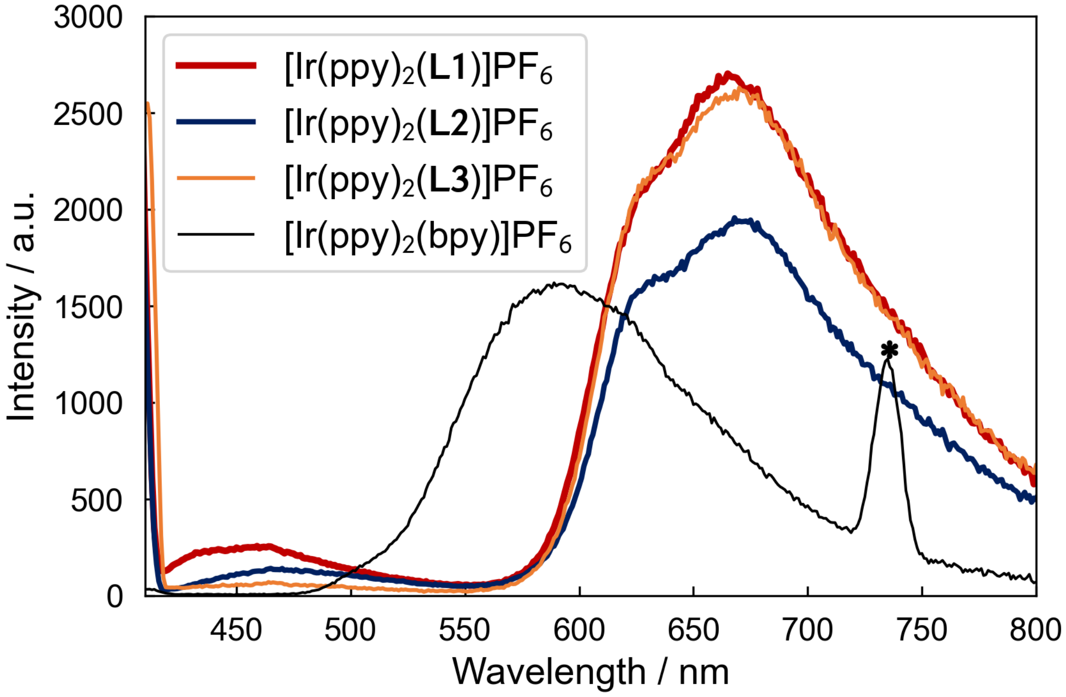


Fig. S46 Emission spectra of [Ir(ppy)$_2$(**L1**)]PF$_6$, [Ir(ppy)$_2$(**L2**)]PF$_6$, [Ir(ppy)$_2$(**L3**)]PF$_6$, and [Ir(ppy)$_2$(bpy)]PF$_6$ (in CH$_2$Cl$_2$, 1×10^{-6} M, under N$_2$ atmosphere, excited at 405, 405, 405, 365 nm, respectively). The asterisk indicates the second order of excitation wavelength.

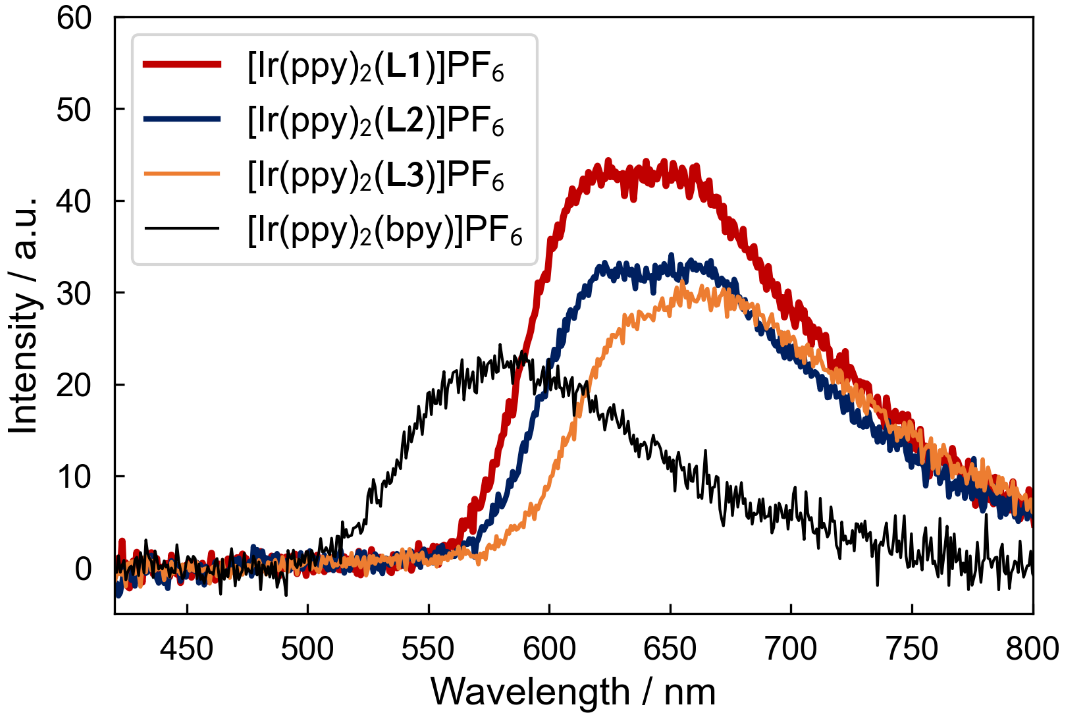


Fig. S47 Emission spectra of [Ir(ppy)$_2$(**L1**)]PF$_6$, [Ir(ppy)$_2$(**L2**)]PF$_6$, [Ir(ppy)$_2$(**L3**)]PF$_6$, and [Ir(ppy)$_2$(bpy)]PF$_6$ in solid states under N$_2$ atmosphere (excited at 405, 405, 405, 365 nm, respectively).

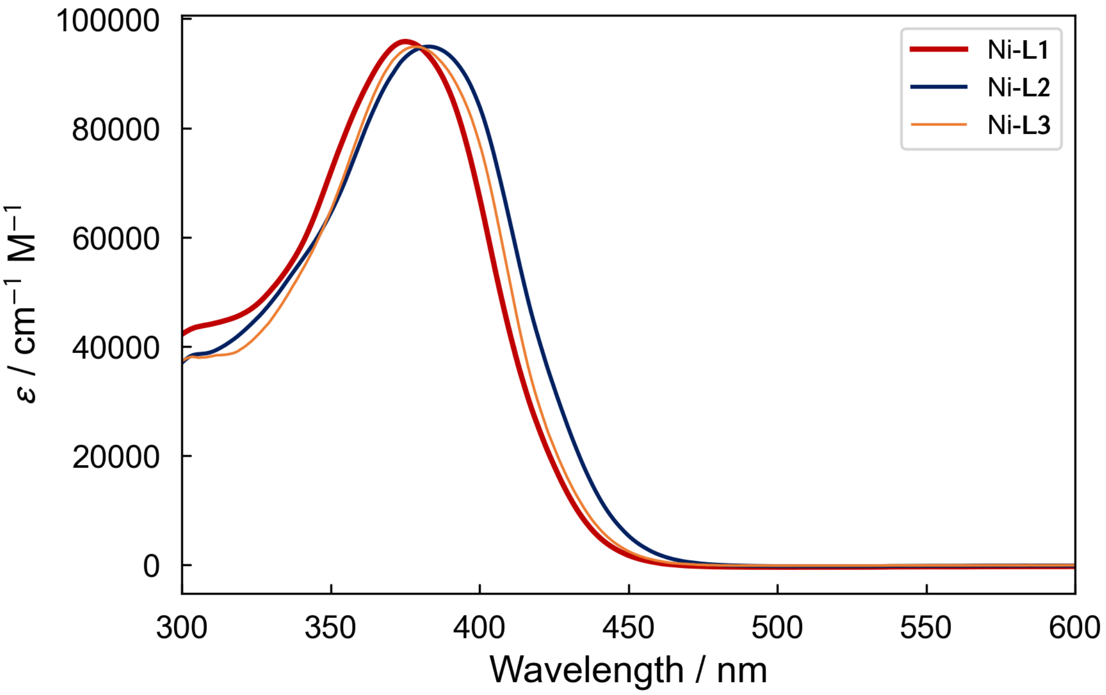


Fig. S48 Absorption spectra of Ni-**L1**, Ni-**L2**, and Ni-**L3** systems (in DMF, 1 × 10^{-5} M), which were prepared *in situ* from $NiCl_2 \cdot$DME with **L1**, **L2** and **L3**, respectively (1:1).

8. Cyclic voltammetry

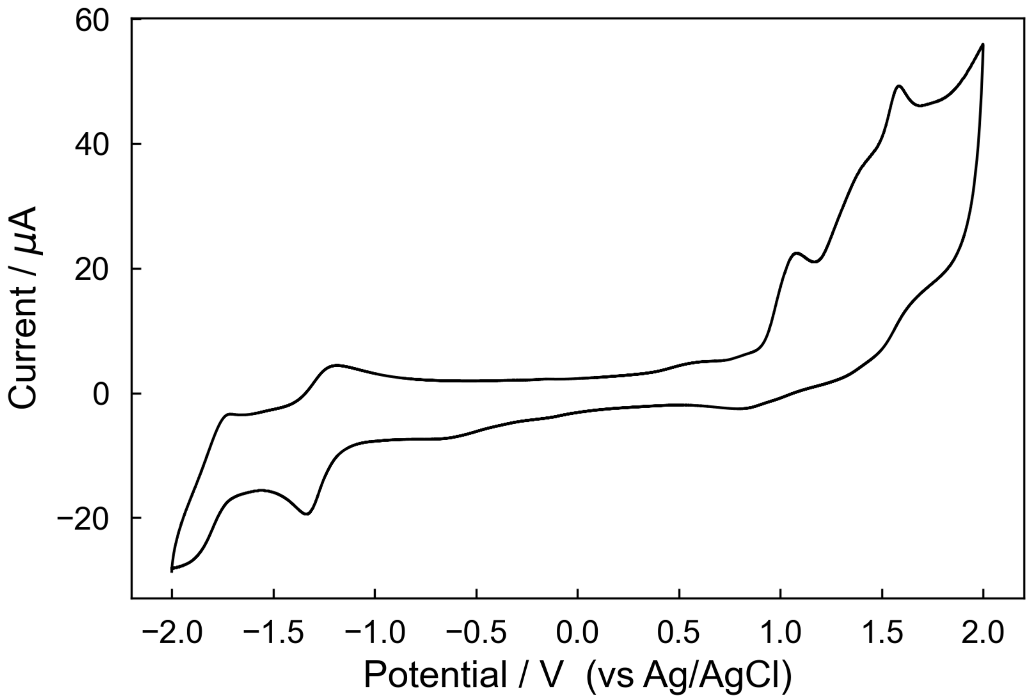


Fig. S49 Cyclic voltammogram of $[Ir(ppy)_2($**L1**$)]PF_6$ (in degassed MeCN, 1 mM with 0.1 M $n\text{Bu}_4\text{NPF}_6$ at a scan rate of 100 mV/s].

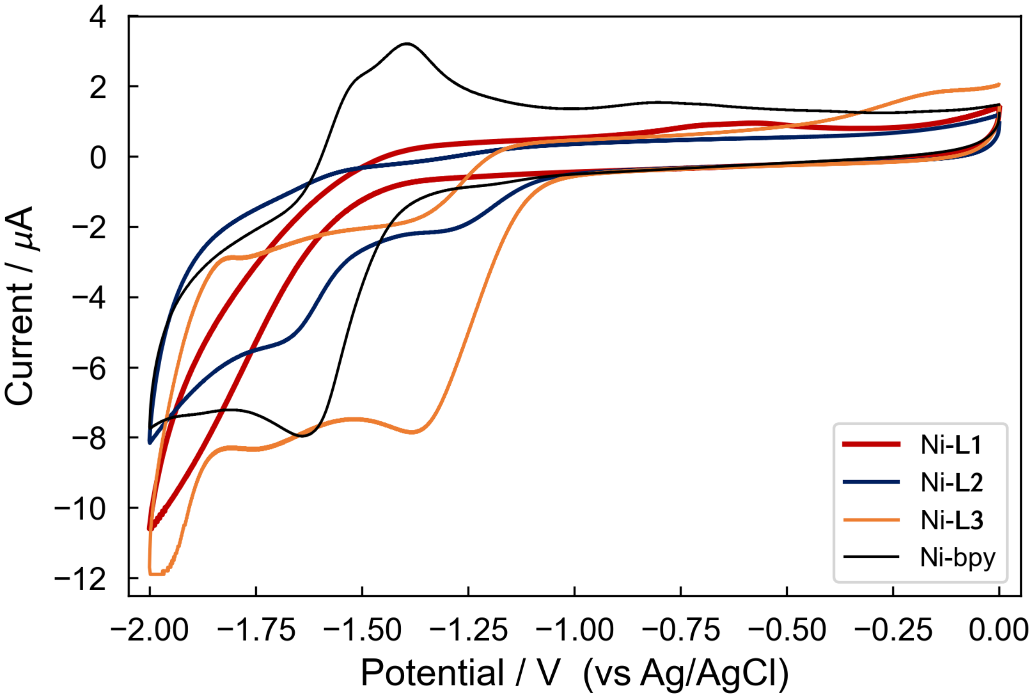
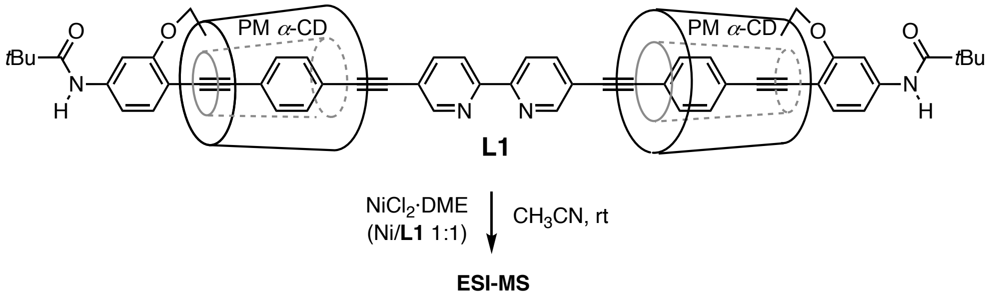


Fig. S50 Cyclic voltammogram of Ni-**L1**, Ni-**L2**, Ni-**L3** and Ni-bpy systems, which were prepared *in situ* from $NiCl_2{\cdot}DME$ with **L1**, **L2**, **L3**, and bpy, respectively (1:1) (in degassed DMF, 0.5 mM with 0.05 M $n Bu_4NPF_6$ at a scan rate of 100 mV/s). The cyclic voltammogram of Ni-**L1** system shows no distinct reduction peaks.

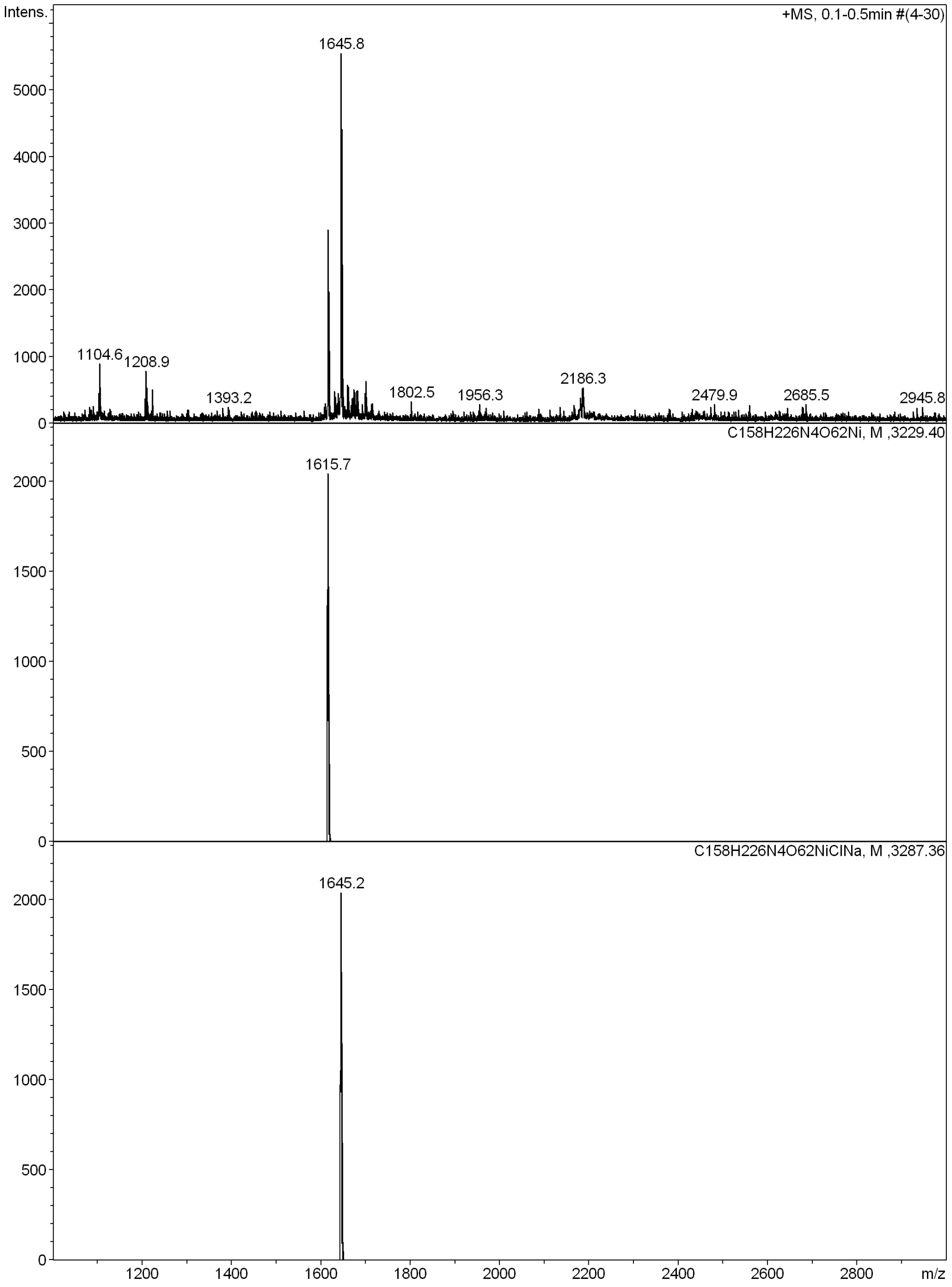
9. Mass and NMR spectroscopic studies on the coordination of L1 to Ni



The reaction mixture of $NiCl_2{\cdot}DME$ and **L1** (1:1) in CH_3CN was analyzed by ESI-MS (Figure S51). The ESI-mass peaks *m*/*z* 1645.8 and 1616.3 correspond to the mass of cationic Ni-**L1** monochloride complex sodium adduct $[\{NiCl(\mathbf{L1})\}{+}Na]^{2+}$ (*m*/*z* 1645.2, calculated) and dicationic Ni-**L1** complex $[Ni(\mathbf{L1})]^{2+}$ (*m*/*z* 1615.7, calculated), respectively. The minor peak *m*/*z* 1674.8 which corresponds to neutral Ni-**L1** dichloride complex disodium adduct $[\{NiCl_2(\mathbf{L1})\}{+}2Na]^{2+}$ (*m*/*z* 1674.2, calculated) is also detected. These results indicate that **L1** coordinate to the Ni center in which at least one chloride ion is bound.

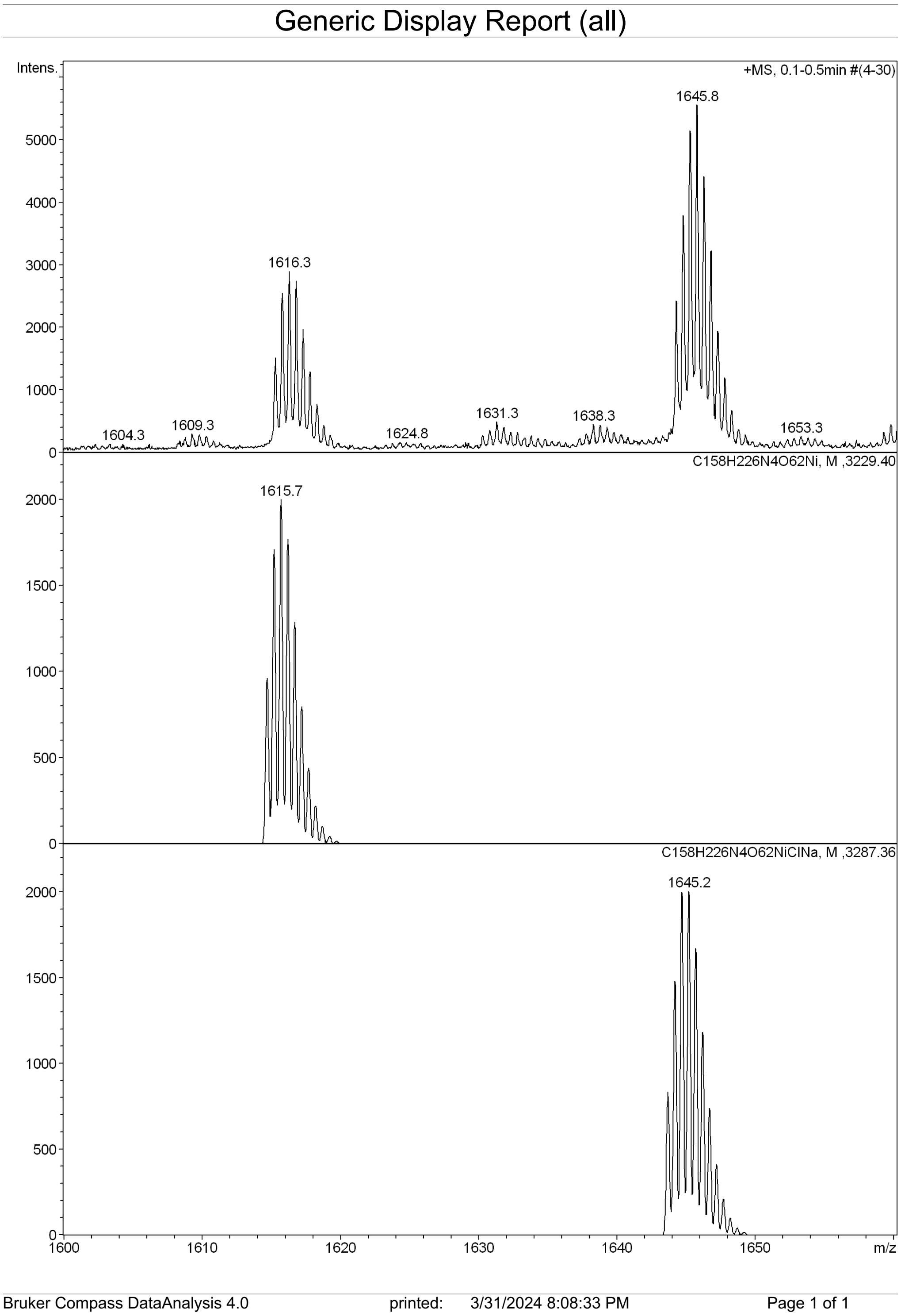
In the ^1H NMR measurement of the mixture of $NiCl_2{\cdot}DME$ and **L1** (1:1) in CD_3CN, the unique broad peaks appeared in the paramagnetic region of the Ni complex (~62, ~159 ppm in Figure S52).[8] Thus, the $NiCl_2$-**L1** complex is assigned as a paramagnetic species.

Generic Display Report (all)



Bruker Compass DataAnalysis 4.0 printed: 3/29/2024 2:29:34 AM Page 1 of 1

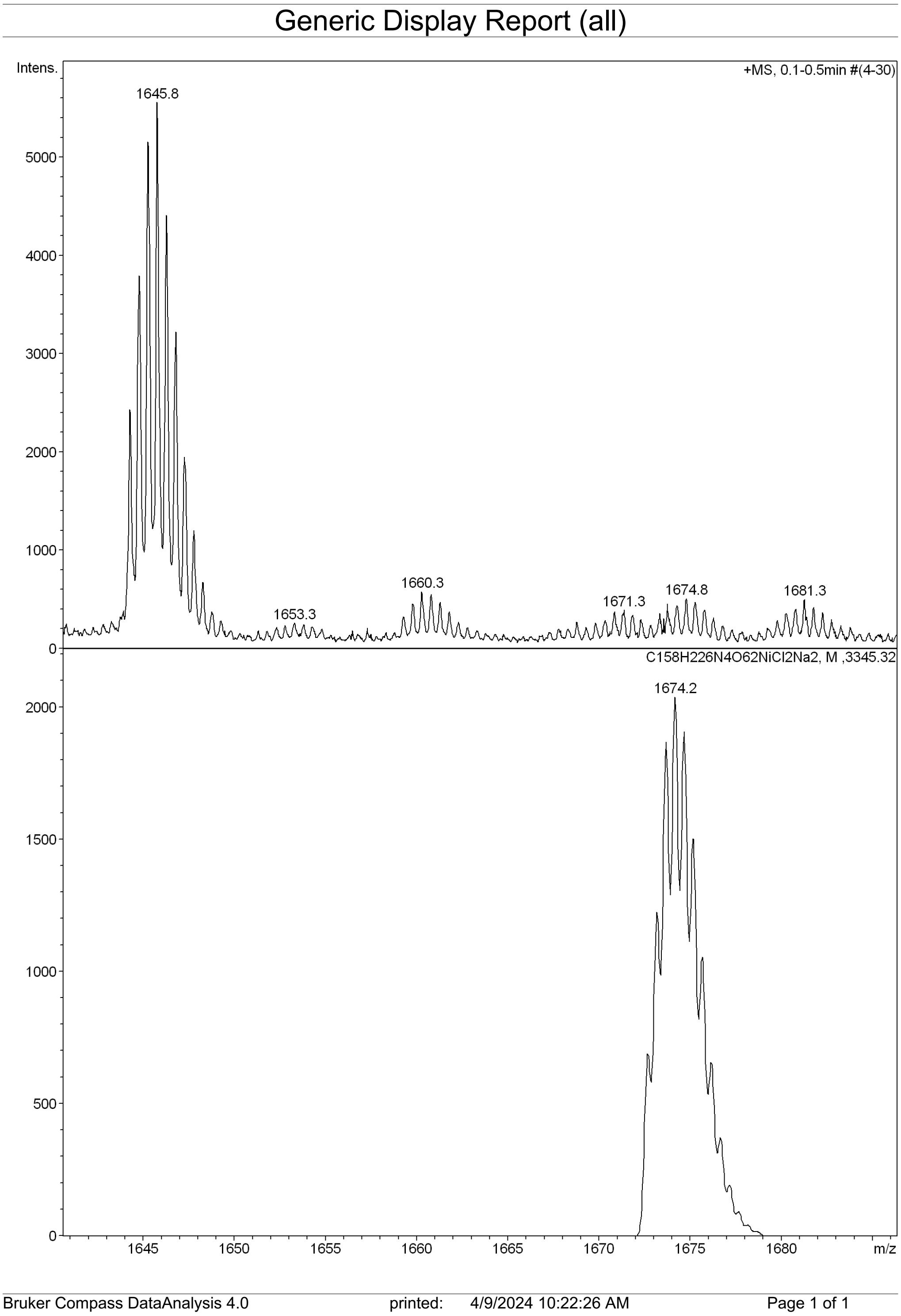
Figure S51 ESI mass spectrum of the mixture of $NiCl_2 \cdot DME$ and **L1** (in CH_3CN, 1:1), and simulate pattern



Generic Display Report (all)

Bruker Compass DataAnalysis 4.0 printed: 3/31/2024 8:08:33 PM Page 1 of 1

Figure S51 (continued) Local enlarged view from *m*/*z* 1600 to 1660



Generic Display Report (all)

Bruker Compass DataAnalysis 4.0 printed: 4/9/2024 10:22:26 AM Page 1 of 1

Figure S51 (continued) Local enlarged view from *m*/*z* 1640 to 1686

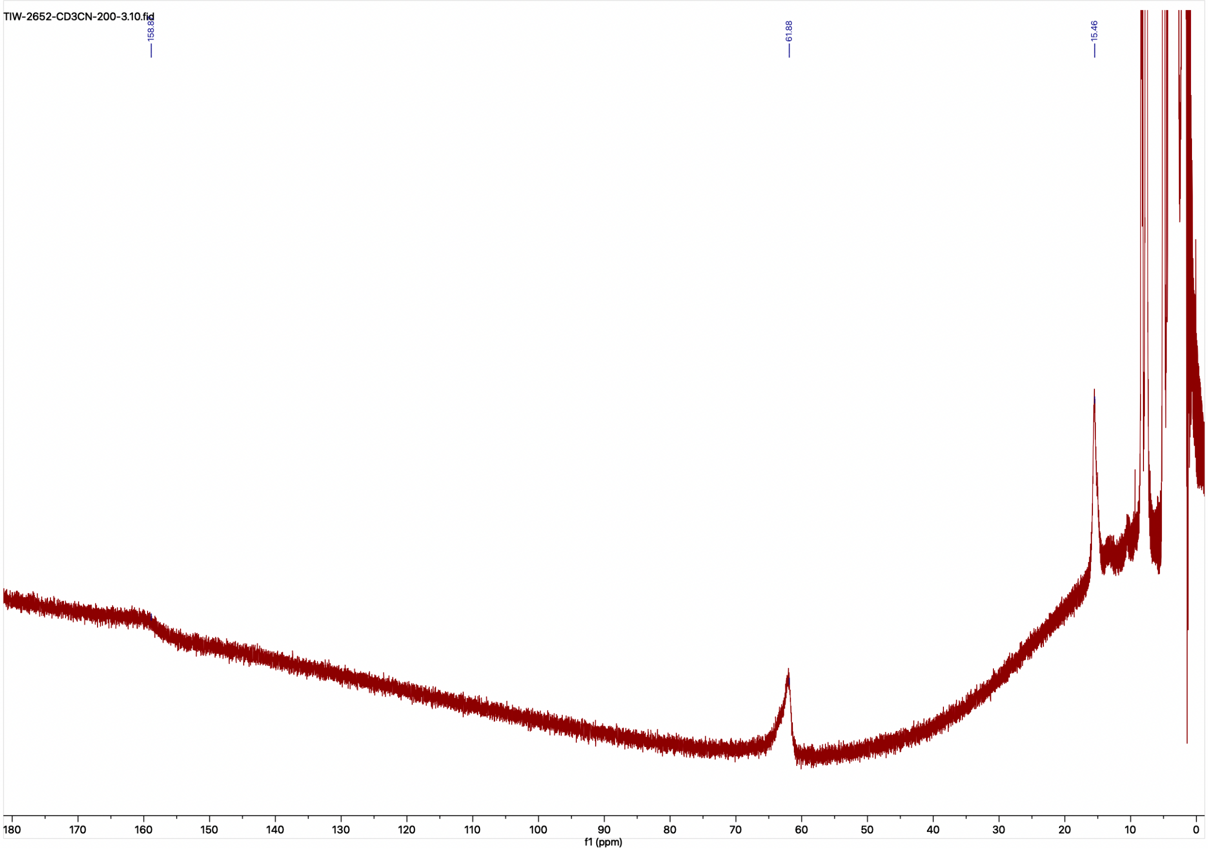


Figure S52 ^{1}H NMR spectrum (500 MHz, CD_3CN) of the unique paramagnetic peaks in the mixture of $NiCl_2$·DME and **L1** (1:1)

Abbreviation

bpy	2,2'-bipyridine	Me	methyl
Bu	butyl	min	minute(s)
d	day(s)	NMR	nuclear magnetic resonance
DABCO	1,4-diazabicyclo[2.2.2]octane	MS	mass spectrometer
DFT	density functional theory	NTO	natural transition orbital
DMA	*N,N*-dimethylacetamide	Ph	phenyl
DME	1,2-dimethoxyethane	PM α-CD	permethylated α-cyclodextrin
DMF	*N,N*-dimethylformamide	ppy	2-phenylpyridine
ESI	electronspray ionization	QY	quantum yield
Et	ethyl	ROESY	rotating frame nuclear overhauser effect spectroscopy
GPC	gel permeation chromatography		
h	hour(s)	rt	room temperature
HOMO	highest occupied molecular orbital	*t*Bu	*tert*-butyl
HR	high resolution	TD	time-dependent
*i*Pr	isopropyl	THF	tetrahydrofuran
LUMO	lowest unoccupied molecular orbital	ToF	time of flight

References

1. H. Masai, J. Terao, T. Fujihara and Y. Tsuji, *Chem. Eur. J.*, 2016, **22**, 6624–6630.
2. A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics,* 1996, **15**, 1518–1520.
3. T. Kawabata and H. Matsubara, *Tetrahedron Lett.*, 2023, **123**, 154554.
4. D.-L. Zhu, J. Li, Q. Wu, Y. Wang, D. J. Young and H.-X. Li, *Synthesis,* 2023, **55**, 637–646.
5. S. Wang, J. Liu, L. Niu, H. Yi, C.-W. Chiang and A. Lei, *J. Photochem. Photobiol. A,* 2018, **355**, 120–124.
6. N. Noto, A. Yada, T. Yanai and S. Saito, *Angew. Chem., Int. Ed.*, 2023, **62**, e202219107.
7. S. Sharif, R. P. Rucker, N. Chandrasoma, D. Mitchell, M. J. Rodriguez, R. D. J. Froese and M. G. Organ, *Angew. Chem., Int. Ed.*, 2015, **54**, 9507–9511.
8. M. M. Beromi, G. W. Brudvig, N. Hazari, H. M. C. Lant and B. Q. Mercado, *Angew. Chem., Int. Ed.*, 2019, **58**, 6094–6098.