Supporting Information

Rim-differentiated Co-pillar[4+1]arenes

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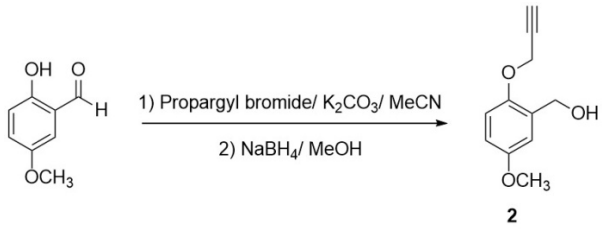
1. General Procedures

NMR spectroscopy was carried out by on Bruker Avance III 600 MHz at ambient temperature. Data are reported as chemical shifts (δ) in parts per million (ppm) relative to the solvent peak, and scalar coupling constants (*J*) are reported in units of hertz (Hz). High resolution mass spectra (HRMS) were measured on Thermo Scientific™ Q Exactive™ HF spectrometer in positive mode (ESI^+). HPLC analyses were performed on an Agilent 1260 liquid chromatography system with an Agilent ZORBAX SB-C18 column (150 mm × 4.6 mm, 5 μm). The LC-MS analyses were carried out in the positive ion mode on an Agilent 6230 TOF LC/MS. Flash column chromatography was performed over silica gel (200−300 mesh or 300−400 mesh). As detailed later, single crystal X-ray diffraction was carried out using an XtaLAB FRX (Rigaku, Japan), and the data were collected at 100 K (Oxford Cryosystems, UK). Prep-HPLC was performed using a semi-preparative HPLC system (Shimadzu Technologies, Japan) with a SHIMADZUShim-pack PRC-ODS PrepHT column (21.2 × 250 mm) (Shimadzu Technologies, Japan). RD-*Co*-P[4+1]s were separated using MeCN/H_2O (85/15 v/v) as the eluent, with a run time of 30 min and a flow rate of 10 mL/min. All reagents and solvents were of reagent grade purity and were used without further purification.

2.Synthetic Procedures



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Scheme S1. Synthesis of the Compound **2**.

Compound **2**: To a solution of 2-hydroxy-5-methoxybenzaldehyde (2.0 g, 13.1 mmol) in MeCN (60 mL) was added K_2CO_3 (3.6 g, 26.2 mmol) followed by 3-bromoprop-1-yne (1.47 mL, 19.7 mmol). The reaction mixture was sealed and refluxed for 4h. The reaction mixture was filtered to remove K_2CO_3 and then concentrated. The resulting residue was dissolved in MeOH (50 mL), to which $NaBH_4$ (250 mg, 6.5 mmol) was added. The solution was stirred at room temperature for 5 min and the solvent was then removed under reduced pressure. The residue was dissolved in H_2O (30 mL) and the aqueous solution was extracted with EtOAc (3 × 30 mL). The combined organic phase was dried (Na_2SO_4) and the solvent was removed under low pressure. The resulting crude product was purified by silica gel column chromatography using EtOAc/petroleum ether (PE) as eluents (from 1/9 to 1/6) to obtain product **1a** as a yellow oil (1.87 g, 75%).^{1}H NMR (600 MHz, $CDCl_3$) δ 6.94–6.91 (m, 2H, Ar-H), 6.79 (dd, J = 13.2, 4.8 Hz, 1H, Ar-H), 4.70 (d, J = 3.6 Hz, 2H, CH≡C-C$\underline{H}_2$), 4.68 (s, 2H, ArC$\underline{H}_2$OH), 3.78 (s, 3H, OCH_3), 2.51 (t, J = 7.2,3.6 Hz, 1H, C$\underline{H}$≡C-CH_2), 2.14 (s, 1H, OH). NMR data is in accordance with literature.[1]

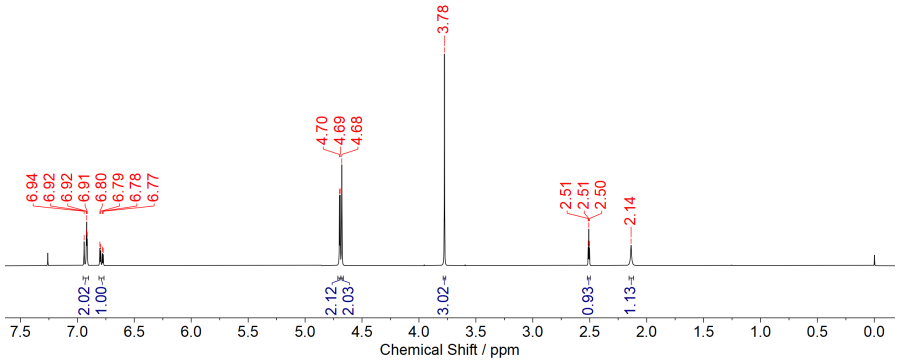
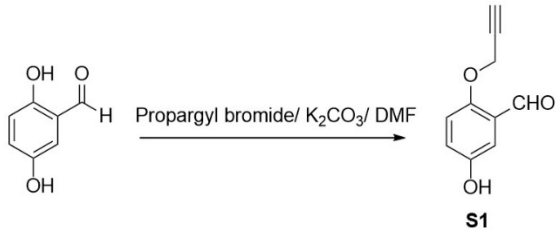


Figure S1. ^{1}H NMR (600 MHz) spectra of compound **2** ($CDCl_3$, 298 K).



Scheme S2. Synthesis of the Compound **S1**.

Compound **S1**: 2,5-dihydroxybenzaldehyde (1.0 g, 7.24 mmol) and K_2CO_3 (2.0 g, 14.5 mmol) were dissolved in DMF (50 mL) and stirred for 20 min at 0 °C. The propargyl bromide (0.9 g, 7.24 mmol) was added into the reaction mixture in dropwise. The mixture was further stirred for another 8 h at room temperature. After 2, 5-dihydroxybenzaldehyde was reacted completely, the reaction mixture was filtered to remove K_2CO_3 and the residue was dissolved in H_2O (30 mL) and the aqueous solution was extracted with EtOAc (3 × 30 mL). The combined organic phase was dried (Na_2SO_4) and the solvent was removed under low pressure. The resulting crude product was purified by silica gel column chromatography using EtOAc/PE = 1/12 as eluents to obtain product **1a** as a yellow oil (0.82 g, 64%).^{1}H NMR (600 MHz, $CDCl_3$) δ 10.42 (s, 1H, ArCHO), 7.31 (d, J = 3.0 Hz, 1H, Ar-H), 7.10 (dd, J = 9.0, 3.0 Hz, 1H, Ar-H), 7.05 (d, J = 9.0 Hz, 1H, Ar-H), 4.78 (d, J = 2.4 Hz, 2H, CH≡C-C$\underline{H}_2$), 2.55 (t, J = 4.8, 2.4 Hz, 1H,C$\underline{H}$≡C-CH$_2$). NMR data is in accordance with literature.[2]

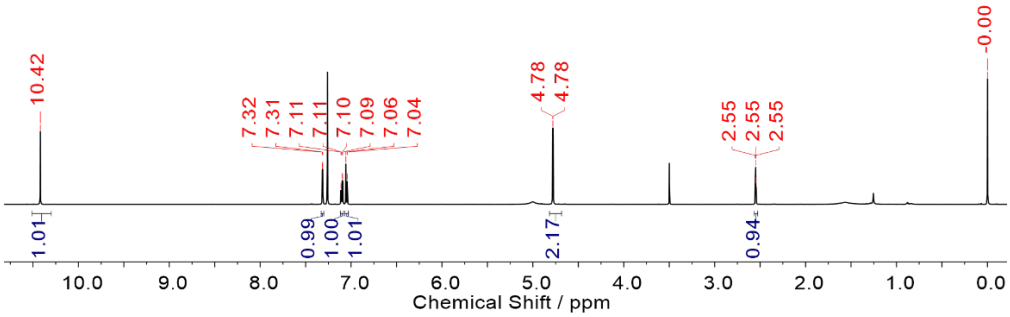
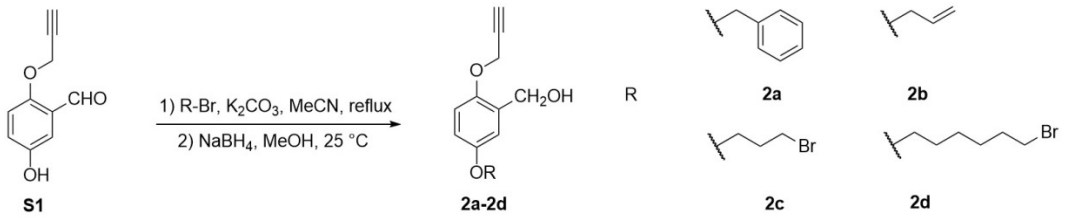


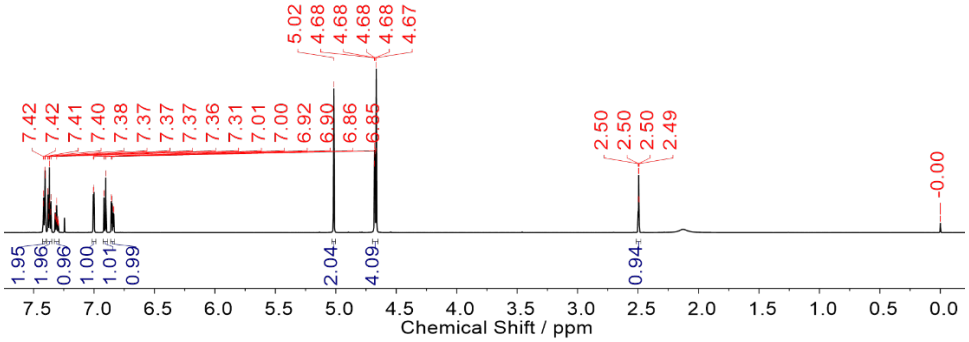
Figure S2. ^{1}H NMR (600 MHz) spectra of compound **S1** ($CDCl_3$, 298 K).



Scheme S3. Synthesis of the Compound **2a-2d**

Compound **2a:** To a slurry of **S1** (1.0 g, 5.68 mmol), K_2CO_3 (1.18 g, 8.51 mmol) in MeCN (10 mL) was added (bromomethyl)benzene (0.67 mL, 5.68 mmol). The mixture was sealed and refluxed overnight. The reaction progress was monitored by TLC until the starting material was consumed. And then, the rection mixture was filtered and concentrated. The resulting crude product was dissolved in MeOH (10 mL), to which $NaBH_4$ (106 mg, 2.84 mmol) was added. The solution was stirred at room temperature for 10 min until TLC indicated the complete conversion from aldehyde to alcohol, and the solvent was then removed under reduced pressure. The residue was dissolved in H_2O (10 mL) and the aqueous solution was extracted with EtOAc (3 × 10 mL). The combined organic phase was dried (Na_2SO_4) and the solvent was removed under low pressure. The crude product was purified by silica-gel column chromatography using EtOAc/PE = 1/6 as eluents to obtain product **2a** as a white solid (1.2 g, 76%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42–7.40 (m, 2H, Ar-H), 7.38–7.36 (m, 2H,Ar-H), 7.32–7.29 (m, 1H,Ar-H), 7.01 (d, J = 3.6 Hz, 1H, Ar-H), 6.91 (d, J = 9.0 Hz, 1H, Ar-H), 6.84 (dd, J = 9.0, 3.6 Hz, 1H, Ar-H), 5.02 (s, 2H, $ArCH_2O$), 4.69 (dd, J = 2.5, 1.1 Hz, 2H, CH≡C-C$\underline{H}_2$), 4.68 (s, 2H, ArC$\underline{H}_2$OH),2.51 (t, J = 4.8, 2.4 Hz, 1H, C$\underline{H}$≡C-CH_2). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.72, 149.61, 137.18, 131.37, 128.57, 127.92, 127.46, 115.83, 114.25, 113.58, 78.74, 75.61, 70.64, 61.56, 61.54, 56.89. HRMS (FD) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{16}O_3Na$, 291.0992; Found 291.0985.

(a)



(b)

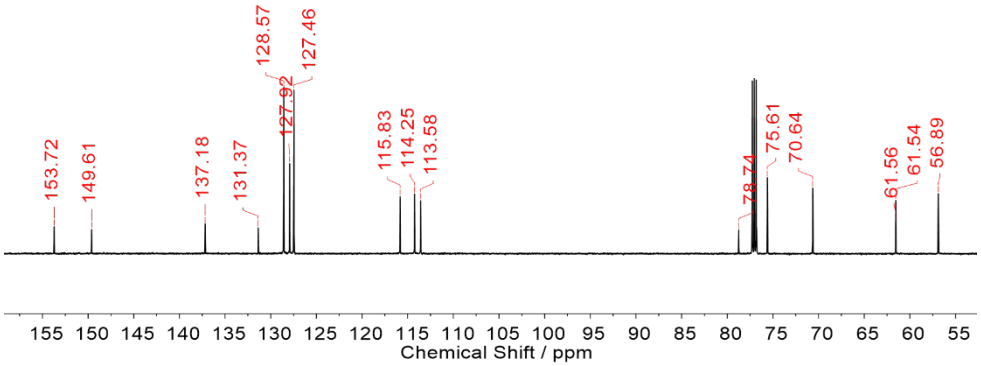
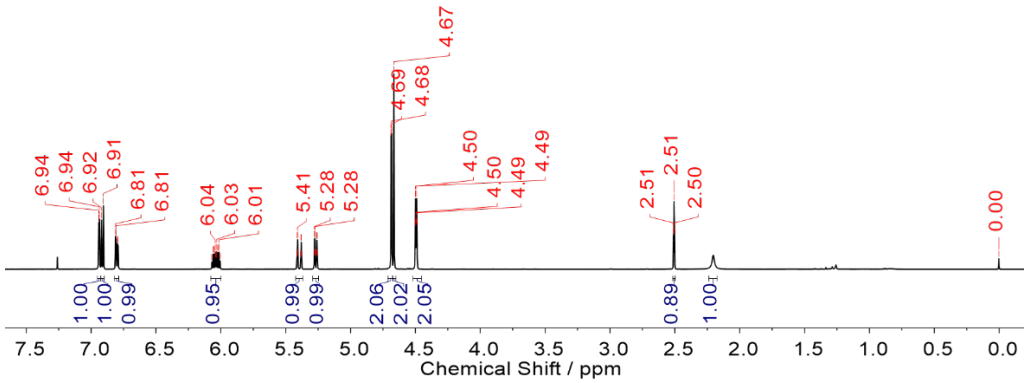


Figure S3. (a) ^{1}H NMR (600 MHz) and (b) ^{13}C NMR (151 MHz) spectra of compound **2a** ($CDCl_3$, 298 K).

Compound **2b**: To a slurry of **S1** (1.0 g, 5.68 mmol), K_2CO_3 (1.18 g, 8.51 mmol) and NaI (0.09 g, 0.6 mmol) in MeCN (10 mL) was added 4-bromobut-1-ene (0.5 mL, 5.68 mmol). The mixture was sealed and refluxed overnight. The reaction progress was monitored by TLC until the starting material was consumed. And then, the rection mixture was filtered and concentrated. The resulting crude productwas dissolved in MeOH (10 mL), to which $NaBH_4$ (106 mg, 2.84 mmol) was added. The solution was stirred at room temperature for 10 min until TLC indicated the complete conversion from aldehyde to alcohol, and the solvent was then removed under reduced pressure. The residue was dissolved in H_2O (10 mL) and the aqueous solution was extracted with EtOAc (1 × 10 mL). The combined organic phase was dried (Na_2SO_4) and the solvent was removed under low pressure. The crude product was purified by silica-gel column chromatography using EtOAc/PE = 1/8 as eluents to obtain product **2b** as a white solid (1.0 g, 82%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.94 (d, J = 3.0 Hz, 1H, Ar-H), 6.91 (d, J = 9.0 Hz, 1H, Ar-H), 6.81 (dd, J = 9.0, 3.0 Hz, 1H, Ar-H), 6.07–6.01 (m, 1H, CH_2=C<u>H</u>), 5.41–5.38 (m, 1H, C<u>H</u>$_2$=CH), 5.28–5.26 (m, 1H, C<u>H</u>$_2$=CH), 4.68 (d, J = 2.4 Hz, 2H, CH≡C-C<u>H</u>$_2$), 4.67 (s, 2H, ArC<u>H</u>$_2$OH), 4.50–4.49 (m, 2H, CH_2=CH-C<u>H</u>$_2$O), 2.51 (t, J = 4.8, 2.4Hz, 1H, C<u>H</u>≡C-CH_2), 2.20 (br, 1H, CH_2O<u>H</u>).^{13}C NMR (151 MHz, $CDCl_3$) δ 153.50, 153.49, 149.53, 133.48, 131.31, 131.30, 117.50, 115.67, 114.18, 113.56, 78.74, 75.59, 69.43, 61.51, 56.89. HRMS (FD) *m/z*: $[M + Na]^+$ Calcd for $C_{13}H_{14}O_3Na$, 241.0835; Found 241.0830.

(a)



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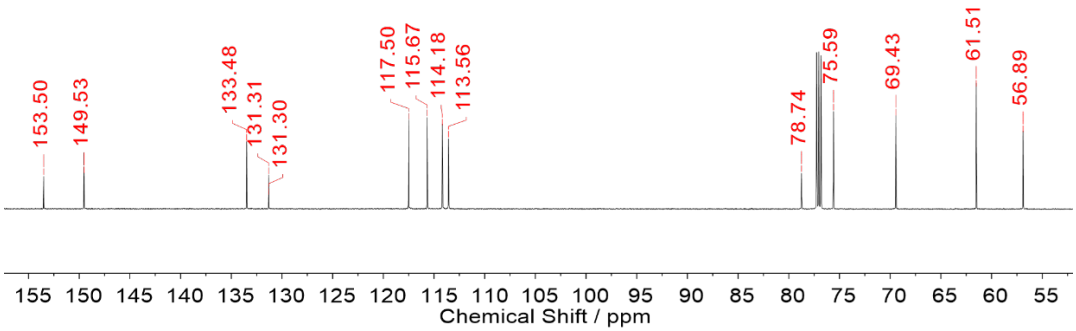
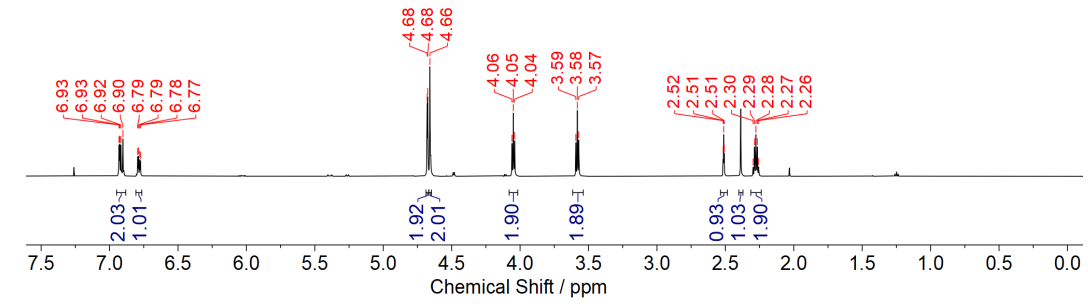


Figure S4. (a) ^{1}H NMR (600 MHz) and (b) ^{13}C NMR (151 MHz) spectra of compound **2b** ($CDCl_3$, 298 K).

Compound **2c**: To a slurry of **S1** (1.0 g, 5.68 mmol), K_2CO_3 (1.18 g, 8.51 mmol) in MeCN (10 mL) was added 1,3-dibromopropane (0.59 mL, 5.68 mmol). The mixture was sealed and refluxed overnight. The reaction progress was monitored by TLC until the starting material was consumed. And then, the rection mixture was filtered and concentrated. The resulting crude product was dissolved in MeOH (10 mL), to which $NaBH_4$ (106 mg, 2.84 mmol) was added. The solution was stirred at room temperature for 10 min until TLC indicated the complete conversion from aldehyde to alcohol, and the solvent was then removed under reduced pressure. The residue was dissolved in H_2O (10 mL) and the aqueous solution was extracted with EtOAc (3 × 10 mL). The combined organic phase was dried (Na_2SO_4) and the solvent was removed under low pressure. The crude product was purified by silica-gel column chromatography using EtOAc/PE = 1/4 as eluents to obtain **2c** as a white solid (1.2 g, 74%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.94–6.90 (m, 2H, Ar-H), 6.79 (dd, J = 8.4, 3.0 Hz,1H, Ar-H), 4.68 (d, J = 2.4 Hz, 2H, CH≡C-C$\underline{H}_2$), 4.66 (s, 2H, OC$\underline{H}_2$OH), 4.05 (t, J = 12.0, 6.0 Hz,2H, OC$\underline{H}_2$CH$_2$), 3.58 (t, J = 12.0, 6.0 Hz,2H, BrCH$_2$), 2.51 (t, J = 12.0, 6.0 Hz,1H, C$\underline{H}$≡C-CH$_2$), 2.39 (s, 1H, CH$_2$O$\underline{H}$), 2.30–2.26(m, 2H, CH$_2$C$\underline{H}_2$CH$_2$).^{13}C NMR (151 MHz, $CDCl_3$) δ 153.58, 149.57, 131.39, 115.51, 113.91, 113.62, 78.70, 75.61, 65.96, 61.50, 56.89, 32.45, 29.99. HRMS (ESI) *m/z*: Calcd for $C_{13}H_{15}BrO_3Na$ $[M + Na]^+$ 321.0097; Found 321.0091.

(a)



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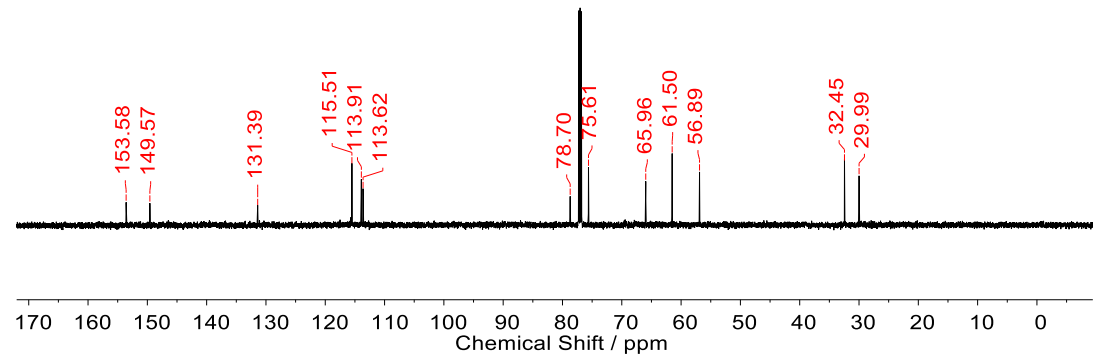


Figure S5. (a) ^{1}H NMR (600 MHz) and (b) ^{13}C NMR (151 MHz) spectra of compound **2c** ($CDCl_3$, 298 K).

Compound **2d**: To a slurry of **S1** (1.0 g, 5.68 mmol), K_2CO_3 (1.18 g, 8.51 mmol) in MeCN (10 mL) was added 1,6-dibromohexane (0.92 mL, 5.68 mmol). The mixture was sealed and refluxed overnight. The reaction progress was monitored by TLC until the starting material was consumed. And then, the rection mixture was filtered and concentrated. The resulting crude product was dissolved in MeOH (10 mL), to which $NaBH_4$ (106 mg, 2.84 mmol) was added. The solution was stirred at room temperature for 10 min until TLC indicated the complete conversion from aldehyde to alcohol, and the solvent was then removed under reduced pressure. The residue was dissolved in H_2O (10 mL) and the aqueous solution was extracted with EtOAc (3 × 10 mL). The combined organic phase was dried (Na_2SO_4) and the solvent was removed under low pressure. The crude product was purified by silica-gel column chromatography using EtOAc/PE as eluents (from 1/8 to 1/6) to obtain product **2d** as a yellow oil (1.35 g, 70%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.92–6.91 (m, 2H, Ar-H), 6.78 (dd, J = 9.0, 3.0 Hz, 1H, Ar-H), 4.69 (d, J = 2.4 Hz, 2H, CH≡C-C$\underline{H}_2$), 4.67 (s, 2H, OC$\underline{H}_2$OH), 3.92 (t, J = 12.0, 6.0 Hz, 2H, OC$\underline{H}_2$CH$_2$), 3.42 (t, J = 12.0, 6.0 Hz, 2H, BrCH$_2$), 2.51 (t, J = 4.8,2.4 Hz, 1H, C$\underline{H}$≡C-CH$_2$), 2.16 (s, 1H, CH$_2$O$\underline{H}$), 1.91–1.87 (m, 2H, OCH$_2$C$\underline{H}_2$), 1.78–1.76 (m, 2H, C$\underline{H}_2$CH$_2$Br), 1.53–1.48 (m, 4H, CH$_2$CH$_2$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.97, 149.35, 131.32, 115.41, 113.87, 113.67, 78.78, 75.56, 68.32, 61.55, 56.94, 33.73, 32.69, 29.16, 27.91, 25.29. HRMS (FD) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{21}BrO_3Na$, 363.0566; Found 363.0559.

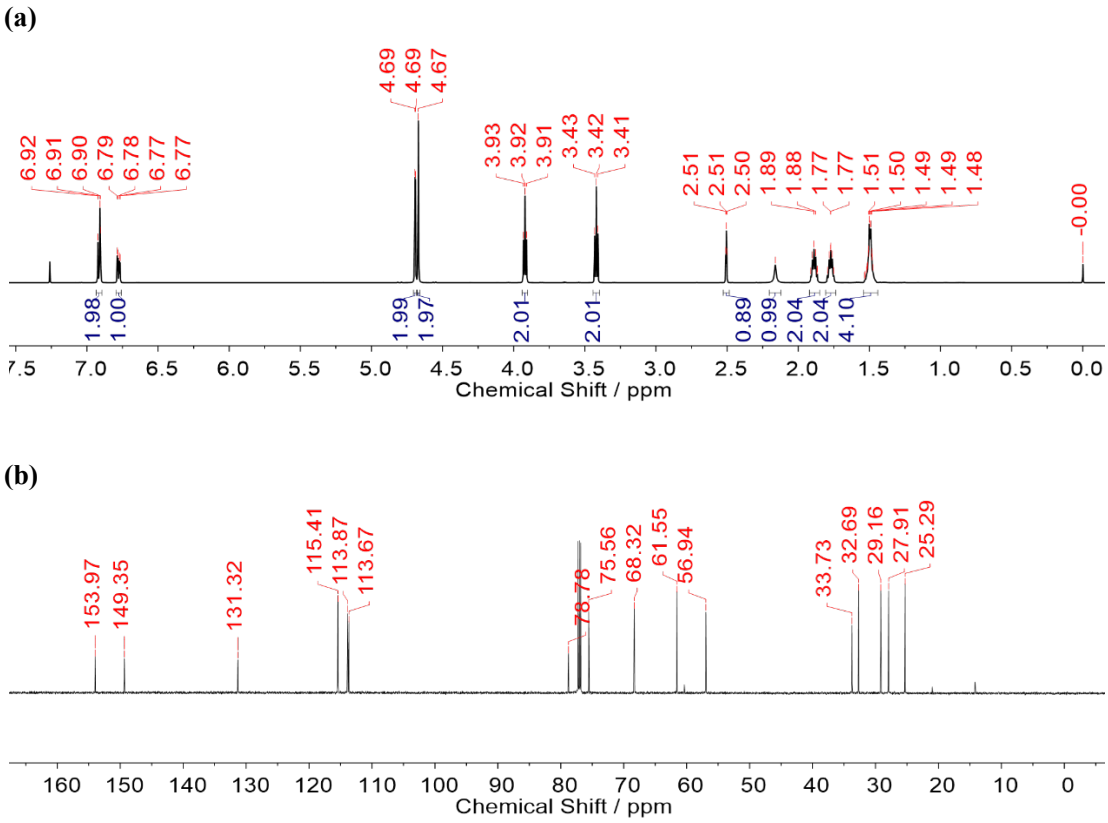
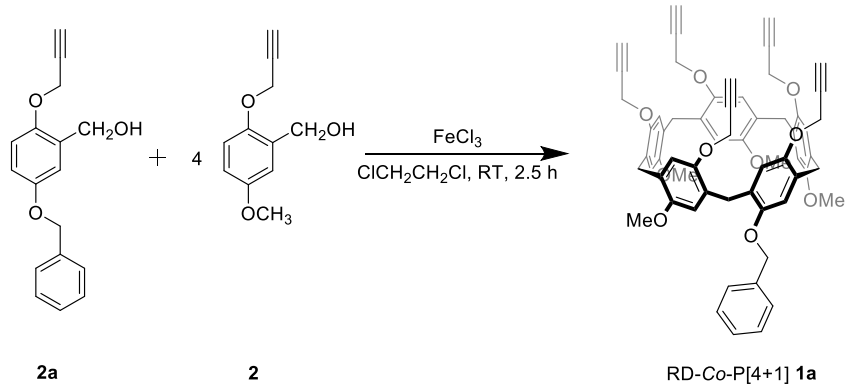


Figure S6. (a) ^{1}H NMR (600 MHz) and (b) ^{13}C NMR (151 MHz) spectra of compound **2d** ($CDCl_3$, 298 K).



Scheme S4. Synthesis of the RD-*Co*-P[4+1] **1a**.

RD-*Co*-P[4+1] **1a**:To a stirred suspension of **2** (968 mg, 5.04 mmol) and **2a** (150 mg, 0.56 mmol) in 1,2-dichloroethane (1000 mL) was added $FeCl_3$ (90 mg, 0.56 mmol) under a N_2 atmosphere. The reaction mixture was stirred at 25 °C for 3 h before MeOH (2 mL) was added to quench the reaction. The solvent was removed under reduced pressure to yield a crude product, which was purified by silica-gel column chromatography using CH_2Cl_2/PE = 1/3 as eluents to provide a mixture of the product together with RD-P[5]**1**[1] as a light yellow solid (107.2mg, 22.0%). Pure RD-*Co*-P[4+1]**1a** can be crystallised by methanol as a white solid (62mg, 12.0%). ^{1}H NMR (600 MHz, $CDCl_3$) δ7.43 (d, J = 6.0 Hz, 2H, OCH_2Ar-H), 7.36–7.33 (m, 2H, OCH_2Ar-H), 7.31–7.29 (m, 1H, OCH_2Ar-H), 6.89 (s, 1H, Ar-H), 6.84 (d, J = 6.0 Hz, 2H, Ar-H), 6.81 (d, J= 6.0 Hz, 3H, Ar-H), 6.75 (d, J = 9.6 Hz, 2H, Ar-H), 6.69 (s, 1H, Ar-H), 6.65 (s, 1H, Ar-H), 4.94 (s, 2H, OCH_2Ar), 4.50 (d, J = 2.4 Hz, 2H, CH≡C-CH_2), 4.46 (d, J = 2.4 Hz, 4H, CH≡C-CH_2), 4.44 (dd, J = 6.0, 2.4 Hz, 4H, CH≡C-CH_2), 3.84 (s, 2H, $ArCH_2Ar$), 3.80–3.79 (m, 6H, $ArCH_2Ar$), 3.77 (s, 2H, $ArCH_2Ar$), 3.73 (s, 3H, OCH_3), 3.71 (s, 3H, 3H, OCH_3), 3.69 (s, 3H, 3H, OCH_3), 3.39 (s, 3H, 3H, OCH_3), 2.20 (t, J = 4.8, 2.4 Hz, 1H, CH≡C-CH_2), 2.17–2.15 (m, 3H, CH≡C-CH_2), 2.08 (t, J = 4.8, 2.4 Hz, 1H, CH≡C-CH_2). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.16, 151.03, 151.01, 150.43, 148.90, 148.83, 148.81, 148.78, 148.77, 137.87, 129.09, 128.99, 128.88, 128.82, 128.51, 128.46, 128.33, 128.22, 128.11, 128.09, 128.05, 127.70, 127.45, 115.68, 115.51, 115.33, 115.31, 114.93, 114.07, 114.04, 113.93, 113.90, 79.35, 79.32, 79.30, 79.23, 74.81, 74.77, 70.44, 56.46, 56.44, 56.42, 56.29, 55.88, 55.85, 55.43, 30.30, 29.77, 29.69, 29.36, 29.29. HRMS (FD) *m/z*: $[M + NH_4]^+$ Calcd for $C_{61}H_{54}O_{10}NH_4$, 964.4055; Found 964.4033.

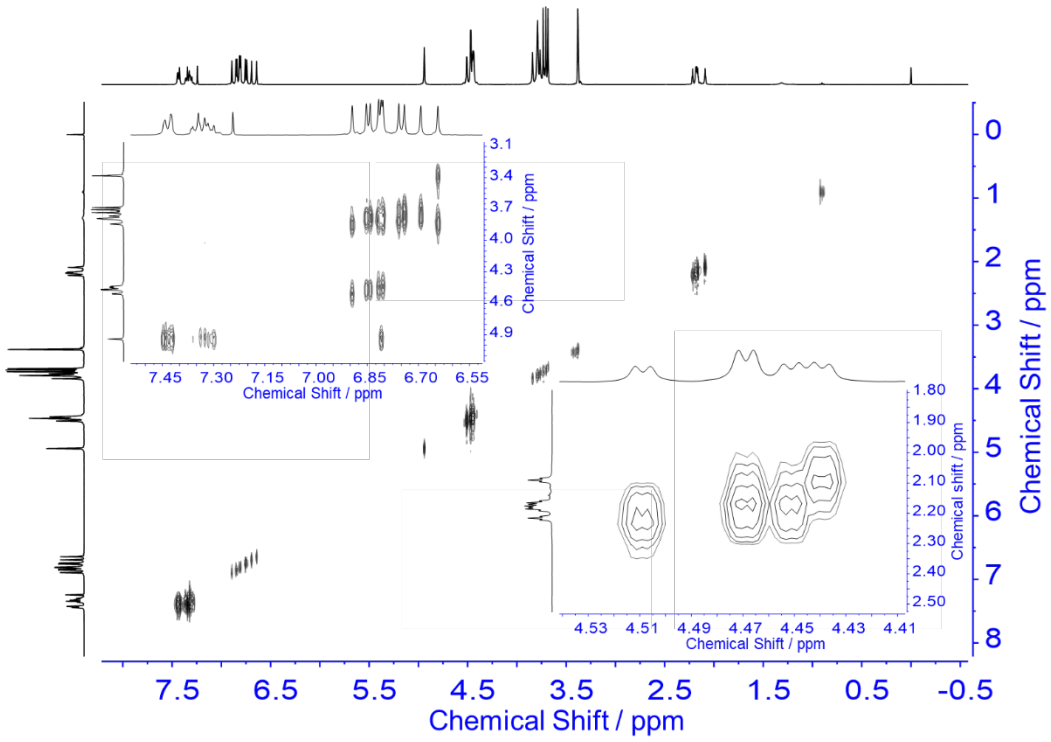


Figure S7. COSY spectrum (400 MHz, $CDCl_3$) recorded for RD-*Co*-P[4+1] **1a**.

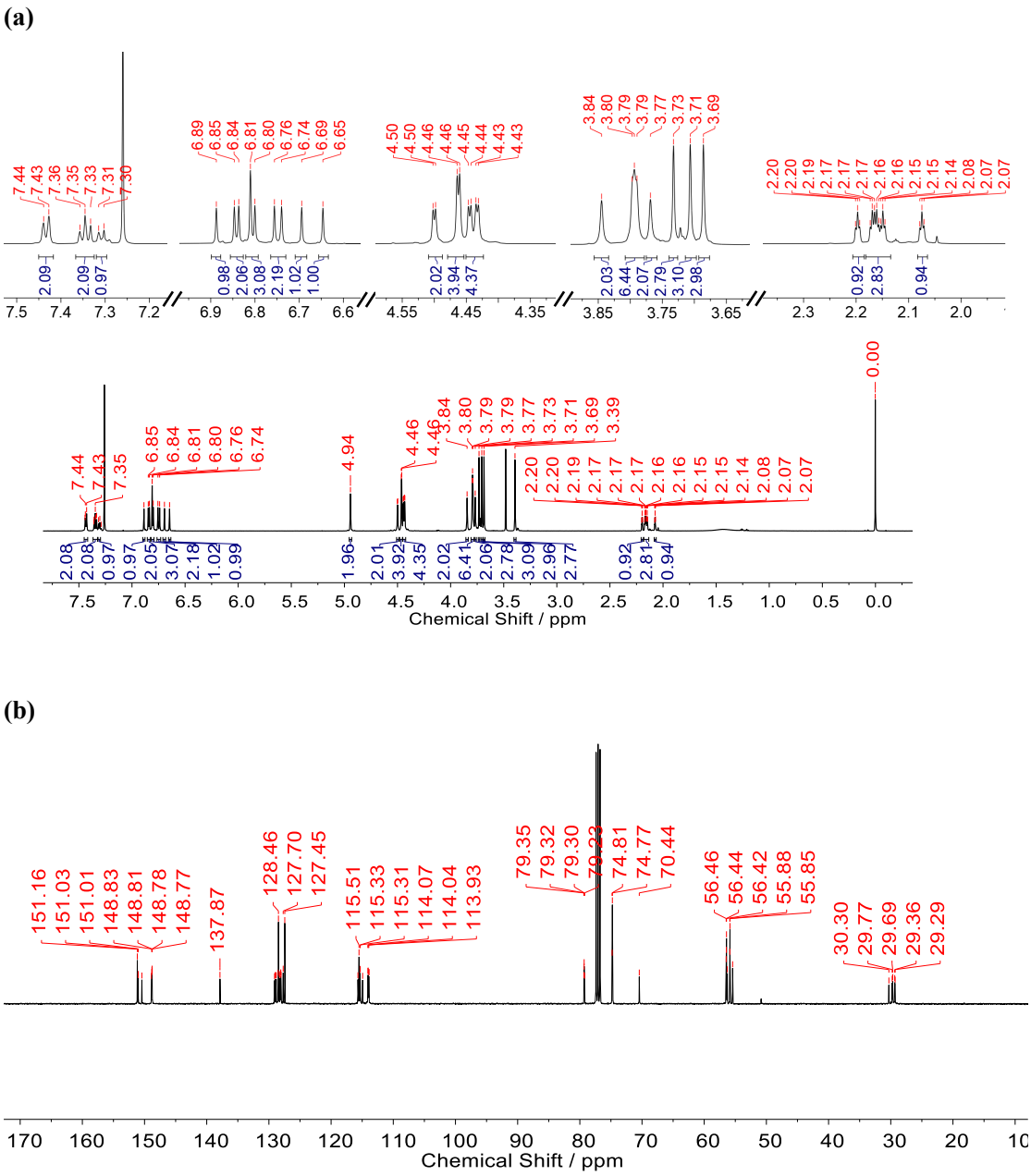
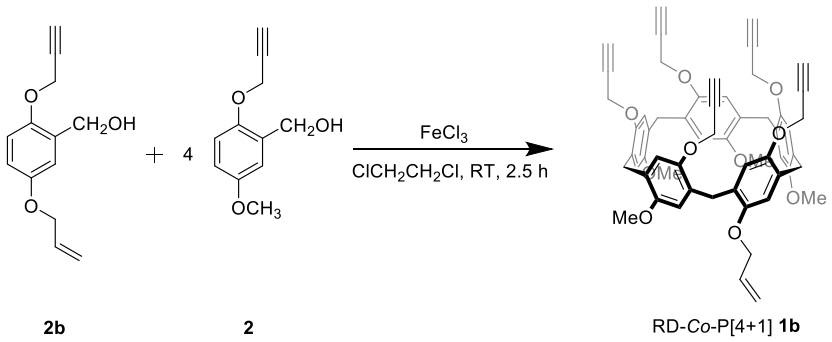


Figure S8. (a) ^{1}H NMR (600 MHz) and (b) ^{13}C NMR (151 MHz) spectra of RD-*Co*-P[4+1] **1a** ($CDCl_3$, 298 K).



Scheme S5. Synthesis of the RD-*Co*-P[4+1] **1b**.

RD-*Co*-P[4+1] **1b**: To a stirred suspension of **2** (968 mg, 5.04 mmol) and **2b** (122 mg, 0.56 mmol)in 1,2-dichloroethane (1000 mL) was added $FeCl_3$ (90 mg, 0.56 mmol) under a N_2 atmosphere. The reaction mixture was stirred at 25 °C for 3 h before MeOH (2 mL) was added to quench the reaction. The solvent was removed under reduced pressure to yield a residue, which was purified by semi-preparative HPLC using MeCN/H_2O = 85/15 as eluents to give RD-*Co*-P[4+1] **1b** as a white solid (49 mg, 10.0%) and RD-P[5] **1** as a light yellow solid (97.4 mg, 20.0%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.86 (d, J = 6.0 Hz, 2H, Ar-H), 6.84 (br, 2H, Ar-H), 6.79 (s, 1H, Ar-H), 6.77 (s, 2H, Ar-H), 6.75 (d, J = 6.0 Hz, 2H, Ar-H), 6.65 (s, 1H, Ar-H), 5.68–5.62 (m, 1H, CH_2=C<u>H</u>), 5.07 (d, J = 18.0 Hz, 1H, C<u>H</u>$_2$=CH), 4.82 (d, J = 12.0 Hz, 1H, C<u>H</u>$_2$=CH), 4.52 (d, J = 2.4 Hz, 2H, CH≡C-C<u>H</u>$_2$), 4.49 (dd, J = 12.0, 2.4 Hz, 4H, CH≡C-C<u>H</u>$_2$), 4.46 (d, J = 2.4 Hz, 2H, CH≡C-C<u>H</u>$_2$), 4.42 (d, J = 2.4 Hz, 2H, CH≡C-C<u>H</u>$_2$), 4.34 (d, J = 6.0 Hz,2H, CH_2=CH-C<u>H</u>$_2$O), 3.82–3.80 (m, 10H, $ArCH_2Ar$), 3.73 (s, 3H, OCH_3), 3.71 (d, J = 4.0 Hz, 6H, OCH_3), 3.70 (s, 3H, OCH_3), 2.46 (t, J = 4.8, 2.4 Hz, 1H, C<u>H</u>≡C-CH_2), 2.21 (t, J = 4.8, 2.4 Hz, 2H, C<u>H</u>≡C-CH_2), 2.18 (t, J = 4.8, 2.4 Hz, 1H, C<u>H</u>≡C-CH_2), 2.15 (t, J = 4.8, 2.4 Hz, 1H, C<u>H</u>≡C-CH_2).^{13}C NMR (151 MHz, $CDCl_3$) δ 171.11, 151.25, 151.22, 150.16, 149.56, 149.01, 148.91, 148.86, 148.82, 133.62, 133.46, 129.18, 129.12, 129.06, 129.01, 128.64, 128.46, 128.36, 128.21, 128.18, 117.49, 117.18, 115.98, 115.84, 115.73, 115.68, 115.60, 115.59, 115.50, 114.27, 114.18, 114.01, 113.91, 113.55, 79.39, 79.36, 79.32, 79.28, 75.60, 74.74, 74.70, 69.43, 69.28, 61.65, 60.38, 56.89, 56.70, 56.59, 56.55, 56.54, 56.50, 55.96, 55.86, 55.81, 30.53, 29.78, 29.71, 29.49, 29.16, 21.02, 14.19. HRMS (FD) *m/z*: [M + NH_4]$^+$ Calcd for $C_{57}H_{52}O_{10}NH_4$, 914.3899; Found 914.3899.

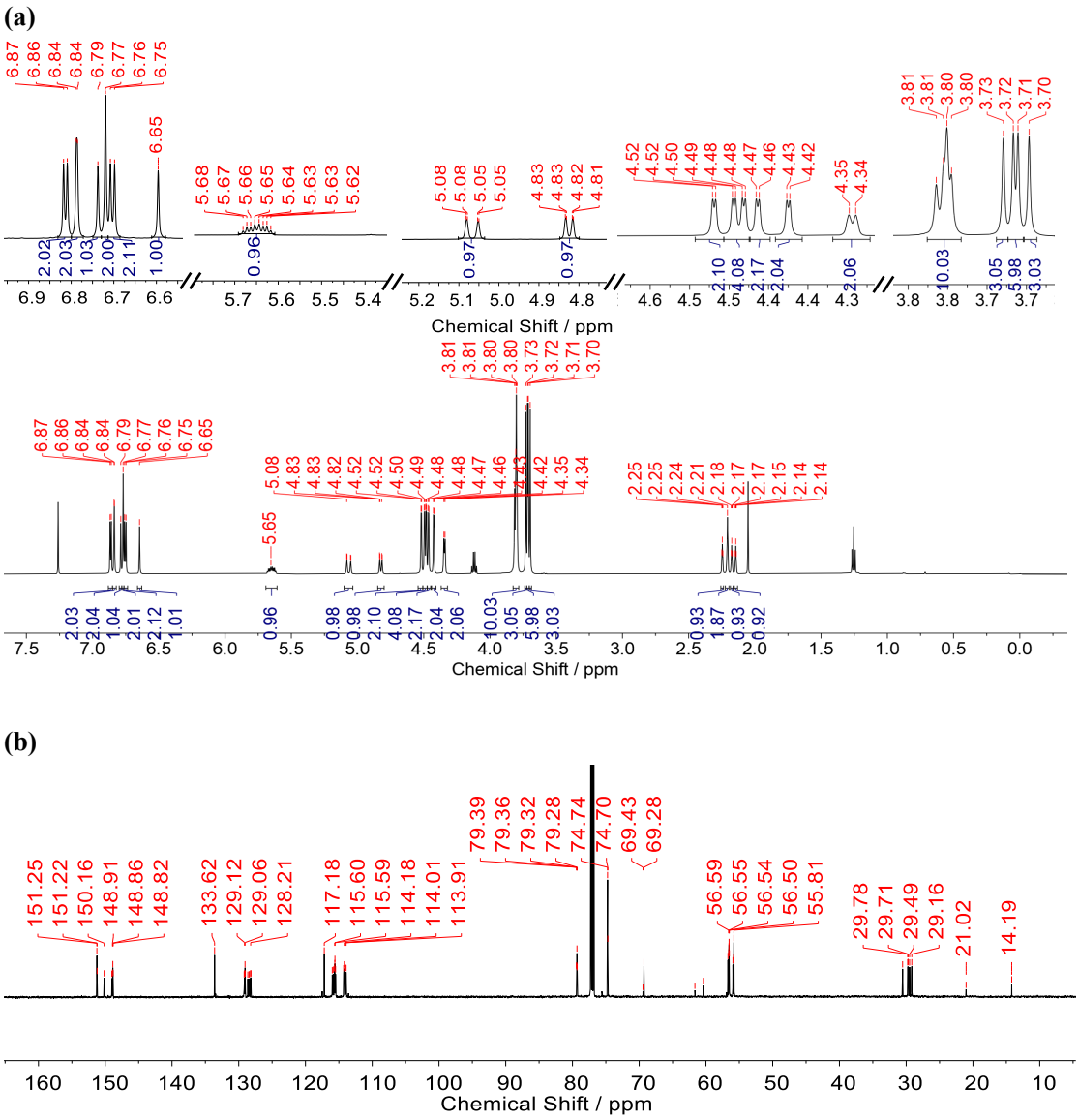
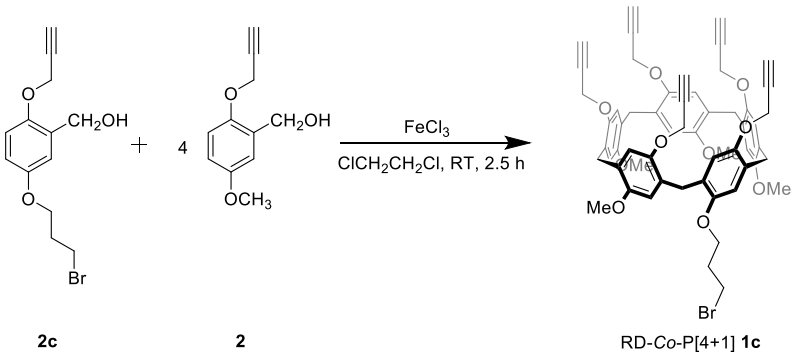


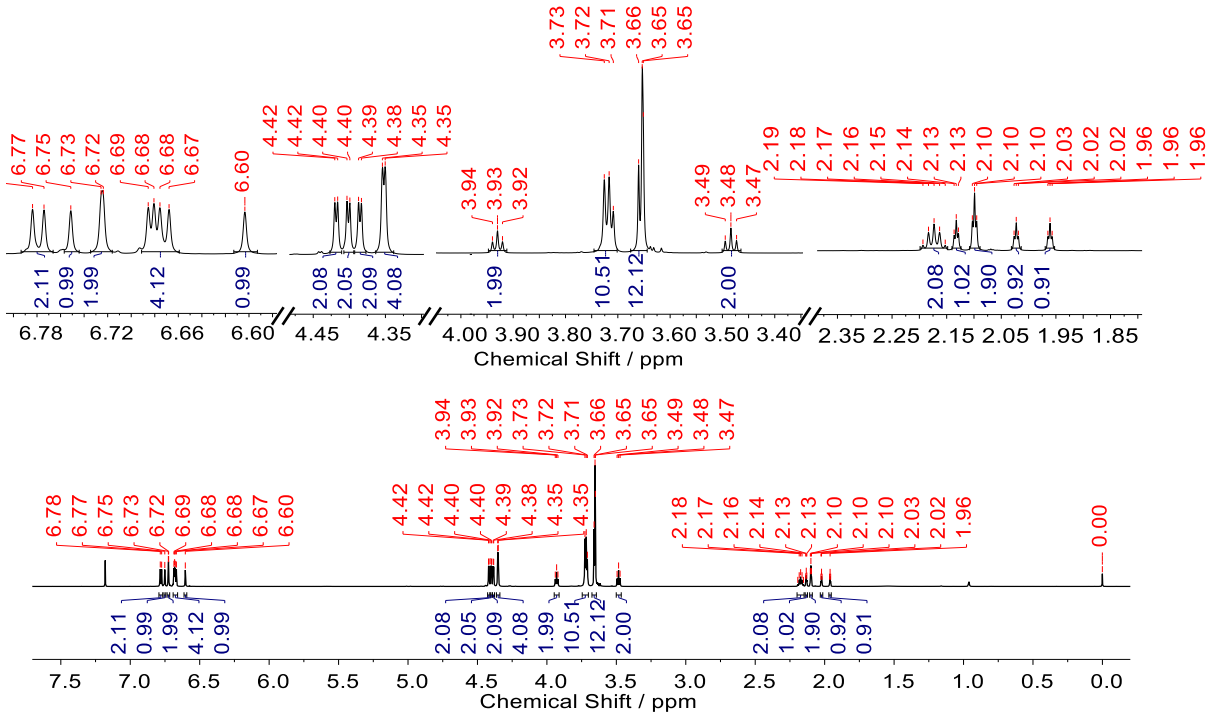
Figure S9. (a) ^{1}H NMR (600 MHz) and (b) ^{13}C NMR (151 MHz) spectra of RD-*Co*-P[4+1] **1b** ($CDCl_3$, 298 K).



Scheme S6. Synthesis of the RD-*Co*-P[4+1] **1c**.

RD-*Co*-P[4+1] **1c**: To a stirred suspension of **2** (968 mg, 5.04 mmol) and **2c** (167 mg, 0.56 mmol) in 1,2-dichloroethane (1000 mL) was added $FeCl_3$ (90 mg, 0.56 mmol) under N_2 atmosphere. The reaction mixture was stirred at 25 °C for 3 h before MeOH (2 mL) was added to quench the reaction. The solvent was removed under reduced pressure to yield a residue, which was purified by semi-preparative HPLC using MeCN/H_2O = 92/8 as eluents to give RD-*Co*-P[4+1] **1c** as a white solid (59 mg, 11.0%) and RD-P[5] **1** as a light yellow solid (110.9 mg, 23.0%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.87 (d, J = 6.0 Hz, 2H, Ar-H), 6.75 (s, 1H, Ar-H), 6.73 (br, 2H, Ar-H), 6.69–6.67 (m, 4H, Ar-H), 6.60 (s, 1H, Ar-H), 4.42 (d, J = 2.4 Hz, 2H, CH≡C-C$\underline{H}_2$), 4.40 (d, J =2.4 Hz, 2H, CH≡C-C$\underline{H}_2$), 4.39 (d, J = 2.4 Hz, 2H, CH≡C-C$\underline{H}_2$), 4.35 (d, J = 2.4 Hz, 4H, CH≡C-C$\underline{H}_2$), 3.93 (t, J = 12.0, 6.0 Hz, 2H, OC$\underline{H}_2$CH$_2$), 3.73 – 3.71 (m, 10H, ArCH$_2$Ar), 3.66–3.65 (m, 12H, OCH$_3$), 3.48 (t, J = 12.0, 6.0 Hz, 2H, Br-CH$_2$), 2.19–2.15 (m, 2H, CH$_2$C$\underline{H}_2$CH$_2$), 2.13 (t, J = 4.8, 2.4 Hz, 1H, C$\underline{H}$≡C-CH$_2$), 2.10 (t, J = 4.8, 2.4 Hz, 2H, C$\underline{H}$≡C-CH$_2$), 2.02 (t, J = 4.8, 2.4 Hz, 1H, C$\underline{H}$≡C-CH$_2$), 1.96 (t, J = 4.8, 2.4 Hz, 1H, C$\underline{H}$≡C-CH$_2$).^{13}C NMR (151 MHz, $CDCl_3$) δ 151.28, 151.26, 151.24, 150.09, 149.04, 148.88, 148.86, 148.83, 129.21, 129.08, 129.01, 128.97, 128.46, 128.43, 128.35, 128.23, 128.22, 115.85, 115.78, 115.65, 115.60, 115.13, 114.05, 113.99, 79.35, 79.32, 79.31, 79.18, 79.13, 74.74, 74.72, 74.71, 74.70, 66.13, 56.53, 56.51, 56.46, 56.40, 56.01, 55.91, 55.87, 32.75, 30.35, 29.81, 29.79, 29.77, 29.71, 29.65, 29.58. HRMS (FD) *m/z*: [M + Na]$^+$ Calcd for $C_{57}H_{53}BrO_{10}Na$, 999.2714; Found 999.2700.

(a)



(b)

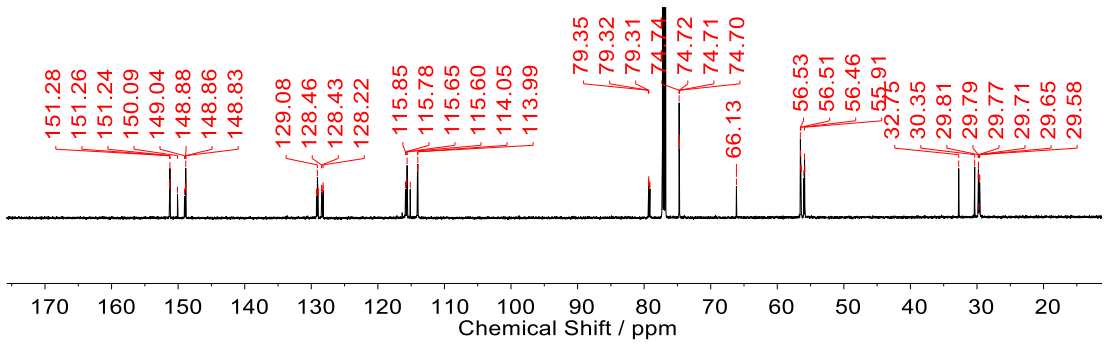
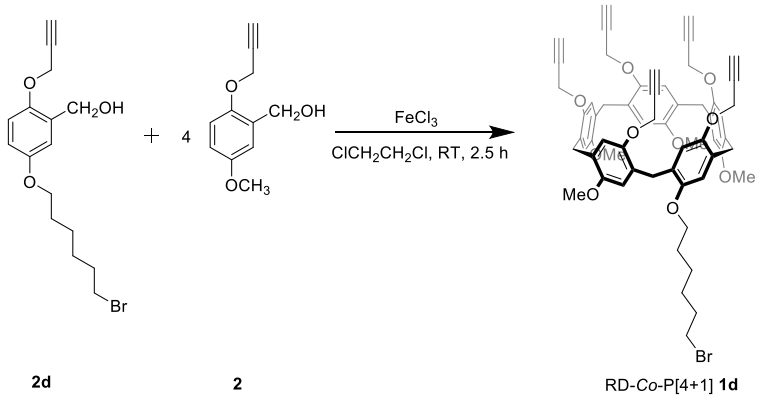


Figure S10. (a) ^{1}H NMR (600 MHz) and (b) ^{13}C NMR (151 MHz) spectra of RD-*Co*-P[4+1] **1c** ($CDCl_3$, 298 K).



Scheme S7. Synthesis of the RD-*Co*-P[4+1] **1d**.

RD-*Co*-P[4+1] **1d:** To a stirred suspension of **2** (968 mg, 5.04 mmol) and **2d** (190 mg, 0.56 mmol)in 1,2-dichloroethane (1000 mL) was added $FeCl_3$ (90 mg, 0.56 mmol) under a N_2 atmosphere. The reaction mixture was stirred at 25 °C for 3 h before MeOH (2 mL) was added to quench the reaction. The solvent was removed under reduced pressure to yield a residue, which was purified by semi-preparative HPLC using MeCN/H_2O = 92/8 as eluents to give RD-*Co*-P[4+1] **1d** as a white solid (58 mg, 10.0%) and RD-P[5] **1** as a light yellow solid (98.4 mg, 20.0%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.02–6.97 (m, 5H, Ar-H), 6.85–6.81 (m, 5H, Ar-H), 4.66 (br, 10H, CH≡C-C$\underline{H}_2$), 3.86–3.79 (m, 18H, $ArCH_2Ar$, OCH_3), 3.73 (d, J = 12 Hz, 6H, OCH_3, OCH_2), 2.47 (br, 5H, C$\underline{H}$≡C-CH_2), 1.59–1.52 (m, 4H, CH_2CH_2).^{13}C NMR (151 MHz, $CDCl_3$) δ 150.82, 150.73, 150.05, 149.21, 149.02, 148.76, 148.73, 128.96, 128.47, 128.36, 128.26, 128.21, 128.11, 127.92, 114.39, 114.25, 113.27, 79.53, 79.50, 79.45, 74.80, 74.77, 74.70, 68.53, 60.37, 56.49, 56.43, 56.35, 56.31, 55.46, 55.42, 33.25, 29.62, 29.47, 29.31, 29.22, 29.15, 27.98, 24.36, 21.01, 14.19. HRMS (FD) *m/z*: $[M + Na]^+$ Calcd for $C_{60}H_{59}BrO_{10}Na$, 1041.3184; Found 1041.3168.

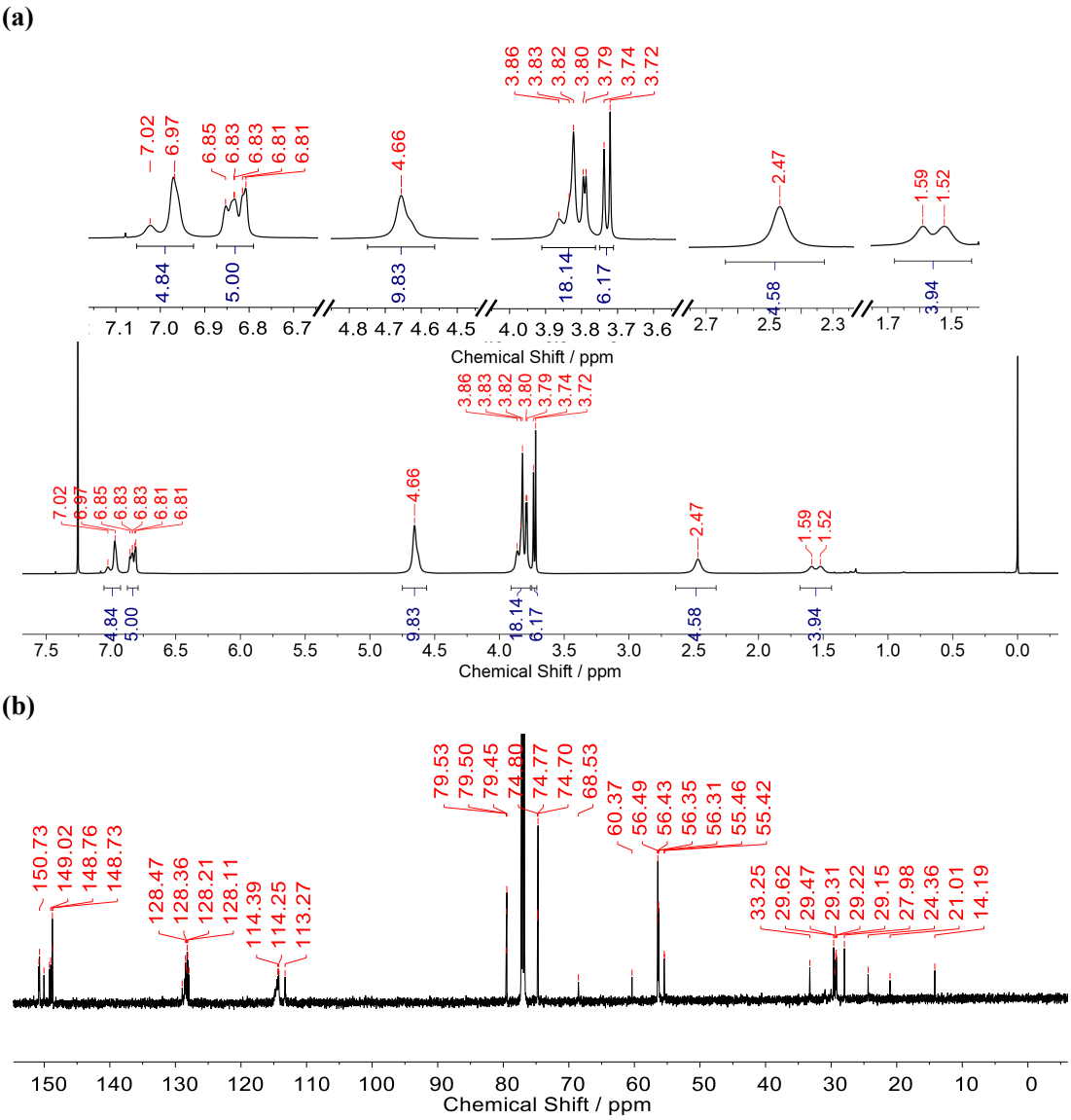
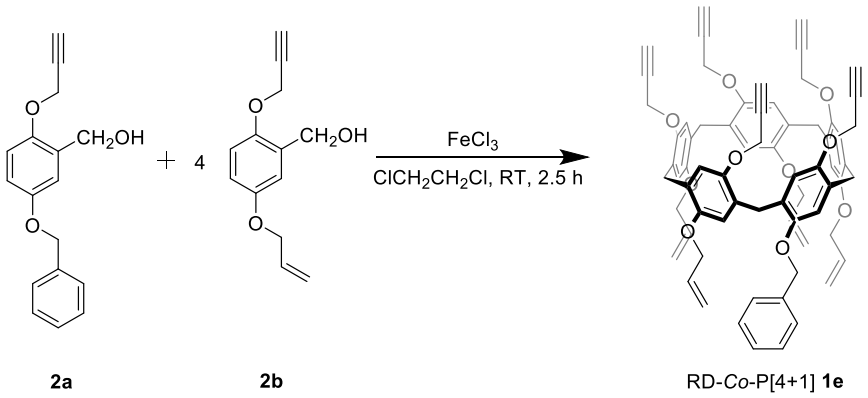


Figure S11. (a) ^{1}H NMR (600 MHz) and (b) ^{13}C NMR (151 MHz) spectra of RD-*Co*-P[4+1] **1d** ($CDCl_3$, 298 K).



Scheme S8. Synthesis of the RD-*Co*-P[4+1] **1e**.

RD-*Co*-P[4+1] **1e**: To a stirred suspension of **2b** (1.1 g, 5.04 mmol) and **2a** (194 mg, 0.56 mmol) in 1,2-dichloroethane (1000 mL) was added $FeCl_3$ (90 mg, 0.56 mmol) under a N_2 atmosphere. The reaction mixture was stirred at 25 °C for 3 h before MeOH (2 mL) was added to quench the reaction. The solvent was removed under reduced pressure to yield a residue, which was purified by semi-preparative HPLC using MeCN/H_2O = 95/5 as eluents to give RD-*Co*-P[4+1] **1e** as a white solid (54 mg, 8.0%) and RD-P[5]**1'**[1] as a light yellow solid (65.7 mg, 17.0%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, J = 7.2 Hz, 2H, OCH_2Ar-H), 7.36 (t, J = 9.0, 7.2 Hz, 2H, OCH_2Ar-H), 7.32 (t, J = 9.0, 7.2 Hz,1H, OCH_2Ar-H), 6.92 (s, 1H, Ar-H), 6.90 (s, 1H, Ar-H), 6.87 (s, 2H, Ar-H), 6.85 (s, 1H, Ar-H), 6.82 (s, 1H, Ar-H), 6.69 (d, J = 4.2 Hz, 2H, Ar-H), 6.65 (s, 1H, Ar-H), 6.61 (s, 1H, Ar-H), 5.84–5.78 (m, 1H, CH_2=CH), 5.73–5.62 (m, 3H, CH_2=CH), 5.27–5.19 (m, 1H, CH_2=CH), 5.12–5.07 (m, 3H, CH_2=CH), 4.99–4.96 (m, 1H, CH_2=CH), 4.94–4.92 (m, 1H, CH_2=CH), 4.90–4.86 (m, 4H, CH_2=CH, OCH_2Ar), 4.57 (d, J = 2.4 Hz, 2H, CH≡C-CH_2O), 4.55–4.53 (m, 8H, CH≡C-CH_2O), 4.31–4.29 (m, 4H, CH_2=CH-CH_2O), 4.27–4.26 (m, 2H, CH_2=CH-CH_2O), 3.90–3.89 (m, 2H, CH_2=CH-CH_2O), 3.84 (d, J = 4.0 Hz, 4H, $ArCH_2Ar$), 3.80 (d, J = 4.0 Hz, 4H, $ArCH_2Ar$), 3.78 (s, 2H, $ArCH_2Ar$), 2.34 (t, J = 5.0, 2.4 Hz, 1H, CH≡C-CH_2), 2.31 (t, J = 5.0, 2.4 Hz, 2H, CH≡C-CH_2), 2.29 (dt, J = 5.0, 2.4 Hz, 2H, CH≡C-CH_2). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.42, 150.09, 150.07, 150.02, 149.92, 148.96, 148.89, 148.88, 148.81, 148.79, 137.85, 133.87, 133.84, 133.81, 133.71, 129.10, 129.04, 129.01, 128.66, 128.57, 128.53, 128.50, 128.48, 128.36, 127.76, 127.39, 117.10, 117.06, 116.99, 116.62, 115.84, 115.76, 115.63, 115.61, 115.41, 115.36, 115.30, 115.19, 115.17, 114.89, 79.49, 79.47, 79.42, 74.80, 74.78, 74.76, 70.30, 69.15, 69.08, 68.63, 56.76, 56.73, 56.72, 56.64, 56.51, 29.87, 29.84, 29.80, 29.72, 29.47. HRMS (FD) *m/z*: [M + Na]$^+$Calcd for $C_{69}H_{62}O_{10}Na$, 1073.4235; Found 1073.4219.

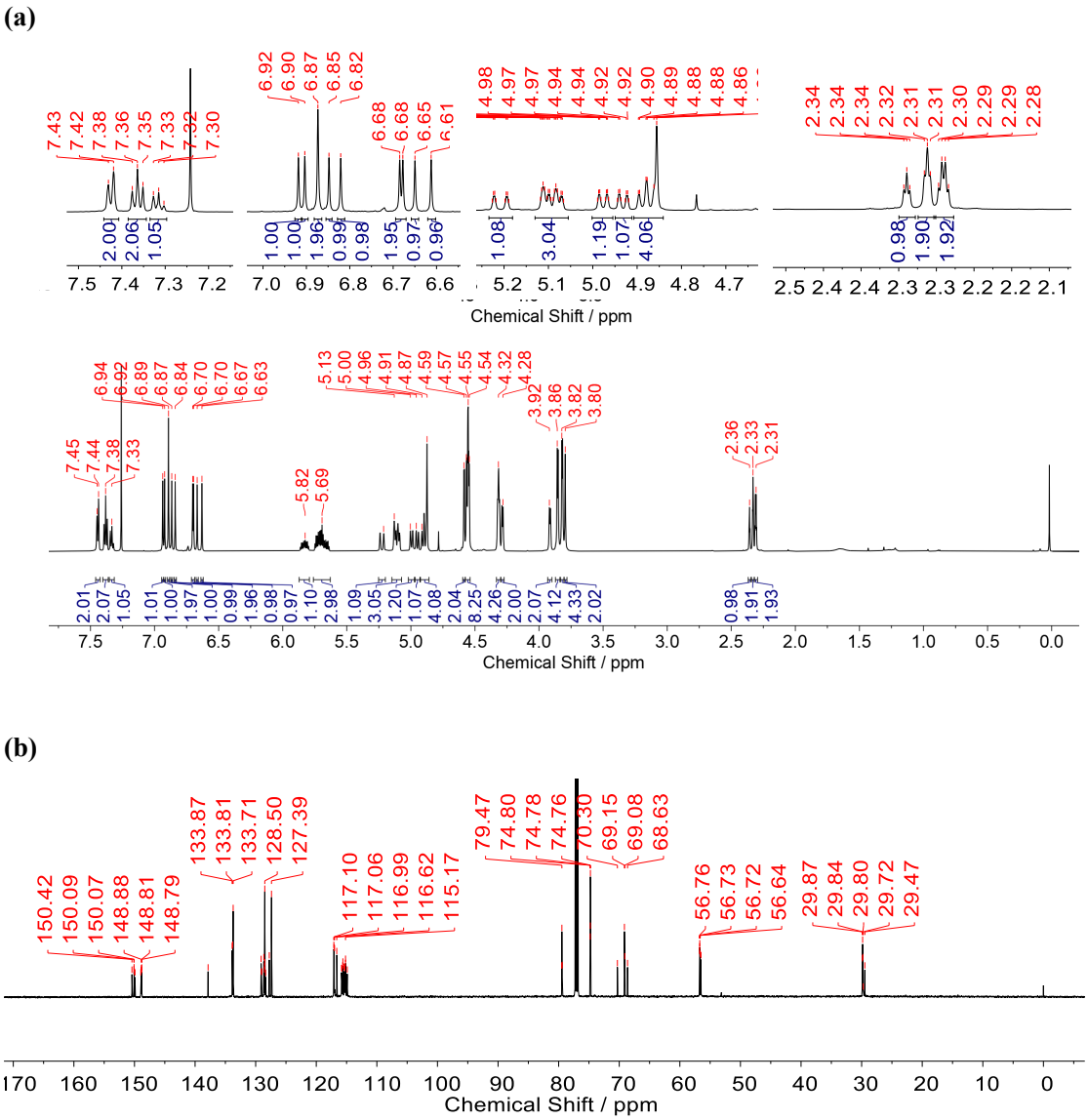
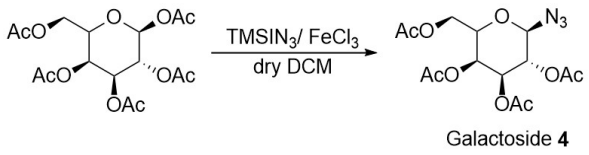


Figure S12. (a) ^{1}H NMR (600 MHz) and (b) ^{13}C NMR (151 MHz) spectra of RD-*Co*-P[4+1] **1e** ($CDCl_3$, 298 K).



Scheme S9. Synthesis of the Galactoside **4**.

Galactoside **4**: To a stirred suspension of $FeCl_3$ (100 mg, 0.62 mmol) in dry CH_2Cl_2 (25 mL) was added β-*D*-Galactose pentaacetate (5 g, 12.8 mmol) in dry CH_2Cl_2 (12.5 mL) under a N_2 atmosphere. The reaction mixture was stirred for 5 min, then add $TMSiN_3$ (2.51g, 21.8 mmol) and stirred for 16 h in room temperature. The reaction was quenched with saturated $NaHCO_3$ and extracted with CH_2Cl_2 and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give a crude product, which was purified by silica-gel column chromatography using PE/EtOAc = 4/1 as eluents to provide galactoside **4** as a white solid (3.91 g, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.42 (dd, J = 4.8, 1.8 Hz, 1H, CH-N_3), 5.16 (dd, J = 15.6, 13.2 Hz, 1H, CH-OAc), 5.03 (dd, J = 15.6, 4.8 Hz, 1H, CH-OAc), 4.60 (d, J = 13.2 Hz, 1H, CH-OAc), 4.21–4.13 (m, 2H, CH_2-OAc), 4.01 (td, J = 9.6, 1.8 Hz, 1H, CH-OAc), 2.18 (s, 3H, OAc), 2.10 (s, 3H, OAc), 2.07 (s, 3H, OAc), 1.99 (s, 3H, OAc). NMR data were in accordance with literature.[3]

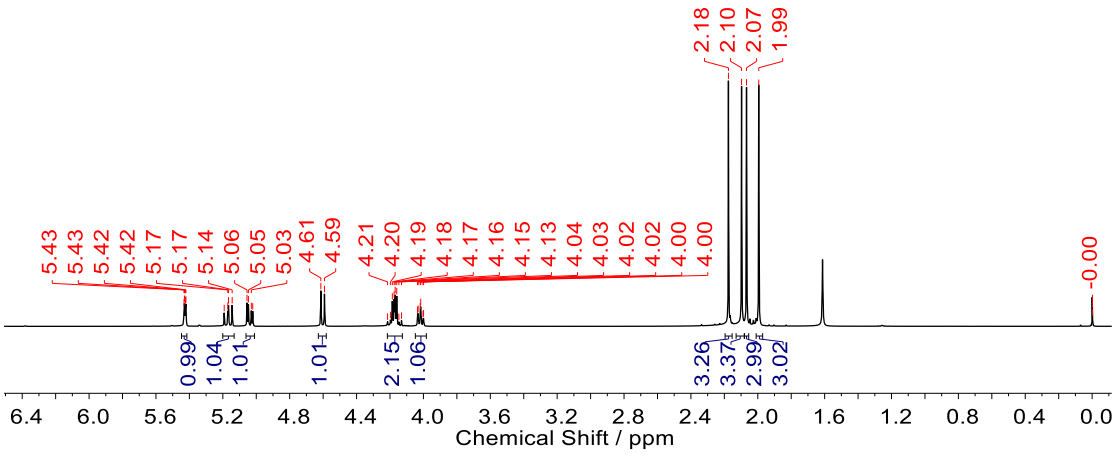
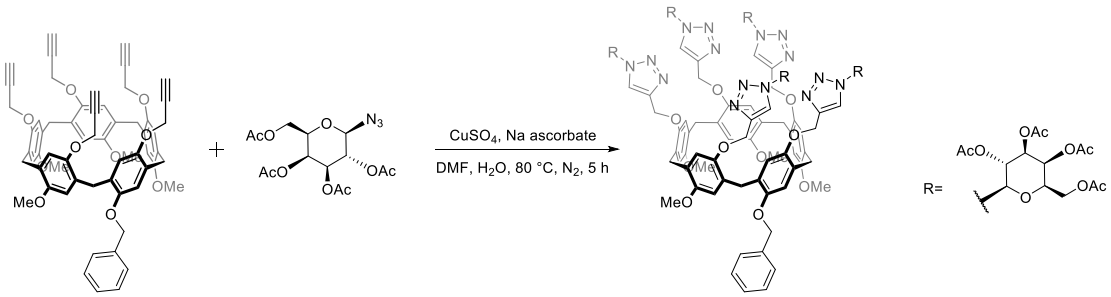


Figure S13. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) recorded for galactoside **4**.



RD-*Co*-P[4+1] **1a** Galactoside **4** **3**

Compound **3**: To a stirred suspension of compound RD-*Co*-P[4+1**] 1a** (100 mg, 0.10 mmol) and galactoside **4** (289 mg, 0.74 mmol) in DMF (60 mL) and H_2O (6 mL) was added $CuSO_4 \cdot 5H_2O$ (21 mg, 0.08 mmol) and Na ascorbate (33 mg, 0.17 mmol) under a N_2 atmosphere. The reaction mixture was stirred at 80 °C for 6 h. After cooled to room temperature, the reaction mixture was added to CH_2Cl_2 (50 mL) and washed with saturated NH_4Cl (50 mL). The organic layer was washed with saturated NH_4Cl (3 × 50 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give a crude product, which was purified by silica-gel column chromatography using PE/EA = 2/1 as eluents to provide **3** as a light yellow solid (220 mg, 73% yield).^{1}H NMR (600 MHz, DMSO-d_6) δ 8.52 – 8.40 (m, 5H, C=CH-N), 7.38 – 7.25 (m, 5H, OCH_2Ar-H), 6.97 – 6.74 (m, 10H, Ar-H), 6.28 (dd, J = 34.6, 9.3 Hz, 5H, CH-N), 5.74 (s, 2H, OCH_2Ar), 5.67 (t, J = 8.1 Hz, 5H, CH-OAc), 5.42 (d, J = 3.5 Hz, 10H, OCH_2C=CH), 5.27 – 5.09 (m, 5H, CH-OAc), 4.94–4.77 (m, 5H, CH-OAc), 4.53 (d, J = 24.7 Hz, 5H, CH-OAc), 4.12 (d, J = 6.8 Hz, 5H, CH-OAc), 4.00 (s, 5H, CH-OAc), 3.70 (d, J = 7.7 Hz, 4H, $ArCH_2Ar$), 3.66 (d, J = 8.7 Hz, 4H, $ArCH_2Ar$), 3.62 (d, J = 3.8 Hz, 2H, $ArCH_2Ar$), 3.60 (s, 3H, OCH_3), 3.59–3.52 (m, 3H, OCH_3), 3.50 (d, J = 8.3 Hz, 3H, OCH_3), 3.29 (s, 3H, OCH_3), 2.17 (s, 15H, OAc), 1.98–1.92 (m, 30H, OAc), 1.76 (s, 15H, OAc).^{13}C NMR (101 MHz, $CDCl_3$) δ 170.53, 170.24, 169.96, 169.12, 162.59, 151.06, 150.97, 150.16, 149.09, 148.95, 145.19, 145.12, 145.03, 138.00, 128.38, 128.19, 127.99, 127.41, 126.82, 122.32, 122.20, 114.76, 114.20, 114.07, 113.84, 85.82, 73.43, 70.81, 69.90, 68.41, 66.98, 66.94, 61.66, 60.98, 55.68, 55.60, 55.30, 55.09, 36.20, 31.88, 31.32, 29.71, 29.55, 29.35, 29.09, 26.39, 23.04, 22.67, 20.77, 20.63, 20.57, 20.27, 20.23, 14.13. HRMS (FD) *m/z*: $[M + 2Na]^{2+}$ Calcd for $C_{131}H_{149}N_{15}ONa_2$, 1429.4571; Found 1429.4552.

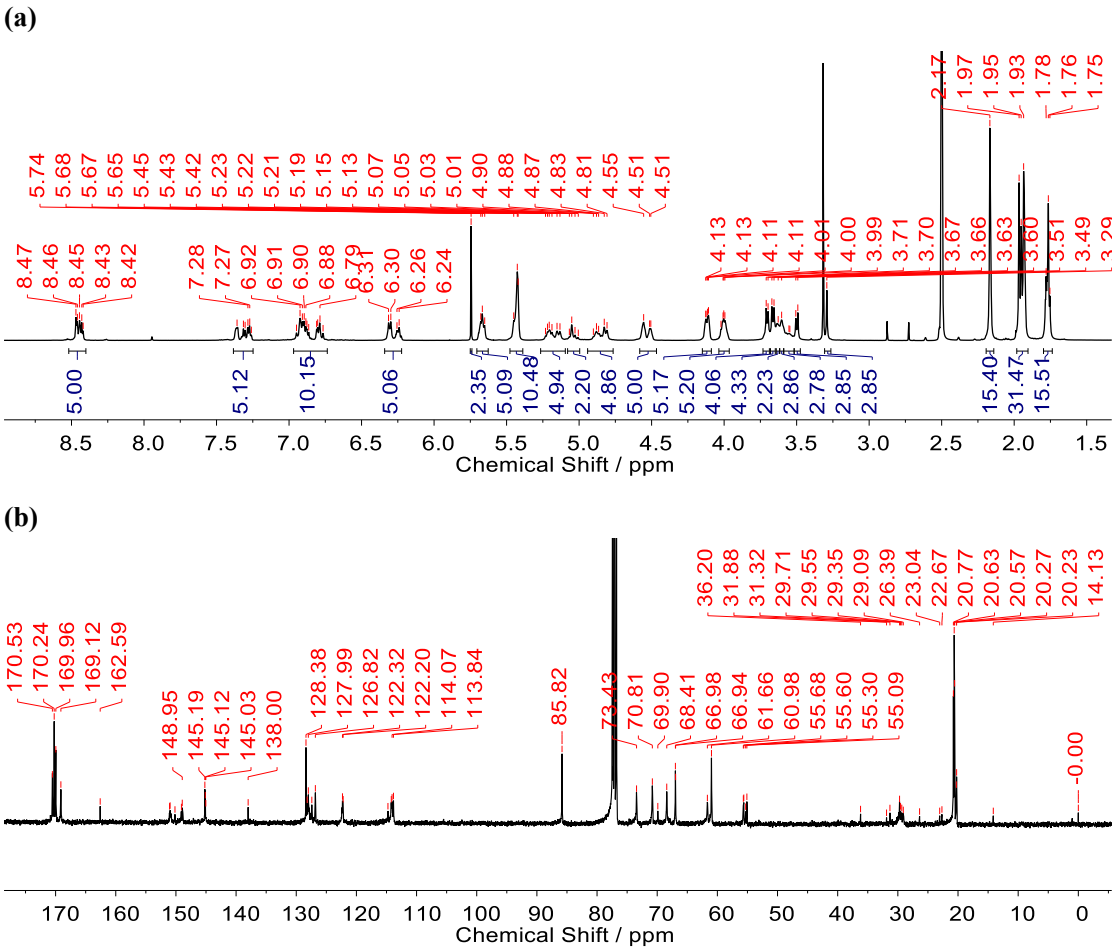


Figure S14. (a) ^{1}H NMR (400 MHz) and (b) ^{13}C NMR (101 MHz) spectra of compound **3**($CDCl_3$, 298 K).

3. HPLC and LC-MS Analyses

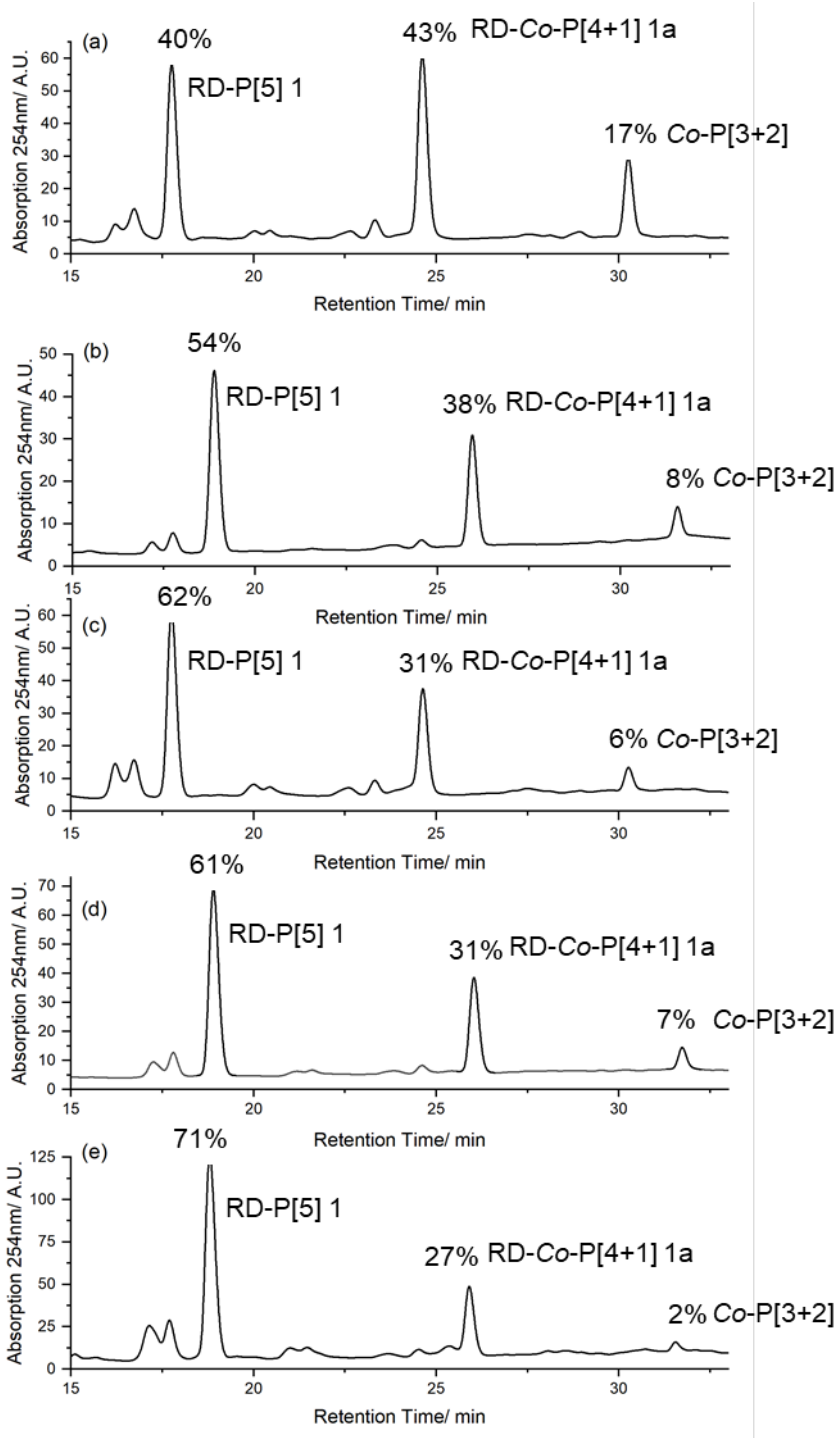


Figure S15. HPLC chromatograms of the crude reaction mixture of RD-*Co*-P[4+1] **1a** obtained from different ratio of monomer **2** and **2a** in (a) 4/1; (b) 8/1; (c) 9/1; (d) 10/1 and (e) 16/1 ratios.

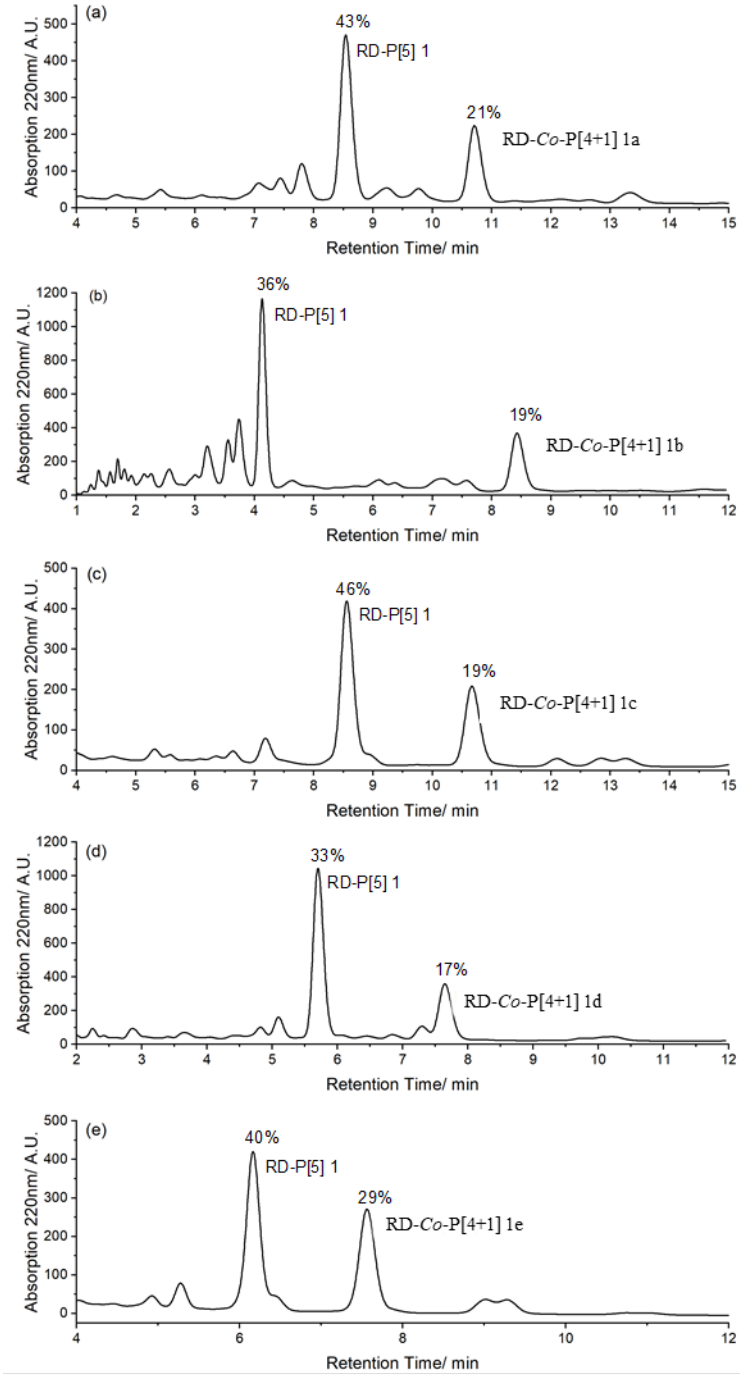


Figure S16. HPLC chromatograms of the crude reaction mixture of (a) RD-*Co*-P[4+1] **1a**, (b) RD-*Co*-P[4+1] **1b**, (c) RD-*Co*-P[4+1] **1c**, (d) RD-*Co*-P[4+1] **1d**, and (e) RD-*Co*-P[4+1] **1e**.

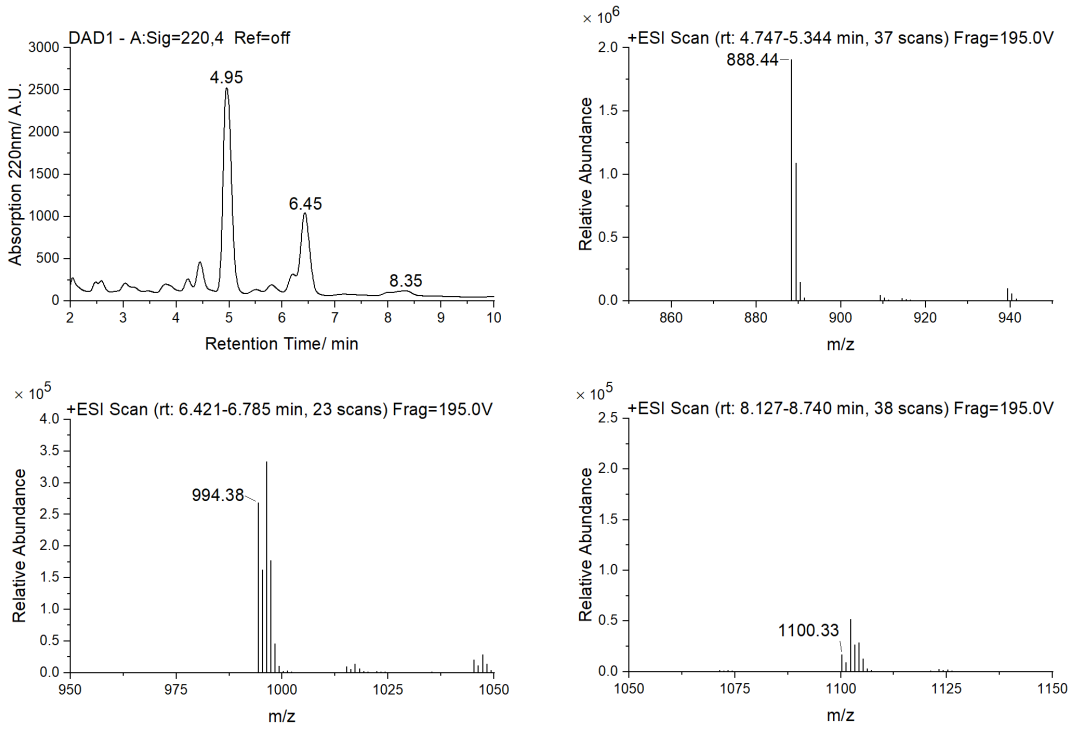


Figure S17. LC-MS of crude reaction mixture of RD-*Co*-P[4+1] **1a**.

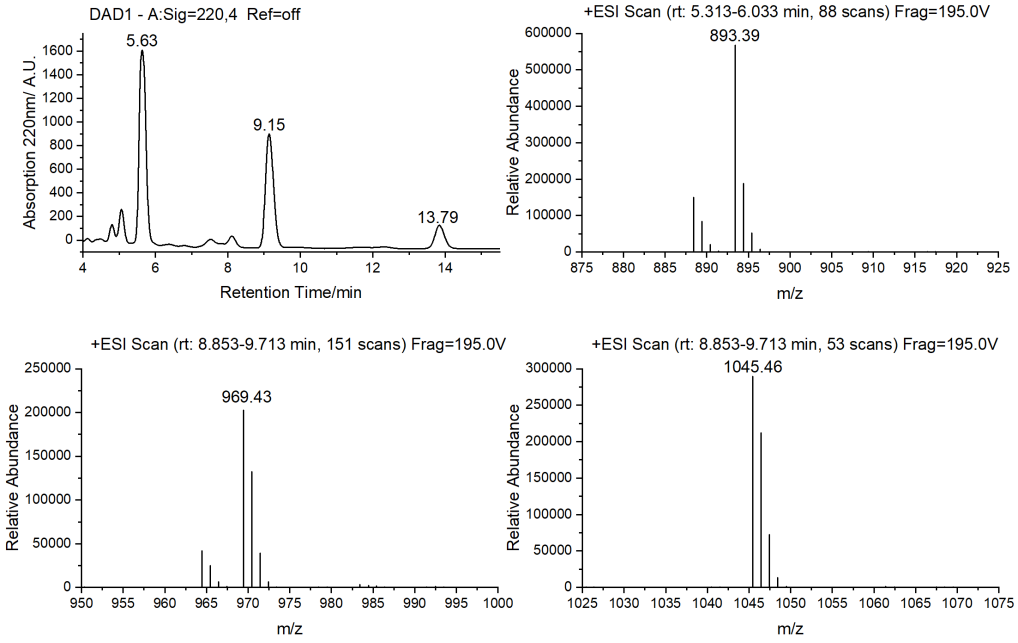


Figure S18. LC-MS of crude reaction mixture of RD-*Co*-P[4+1] **1b**.

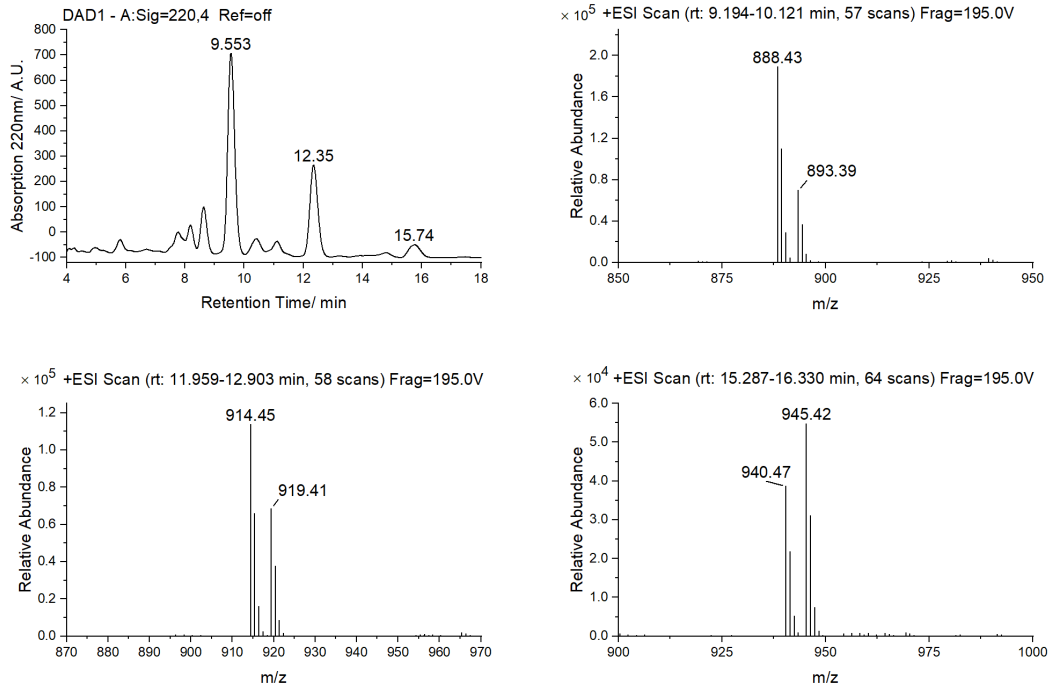


Figure S19. LC-MS of crude reaction mixture of RD-*Co*-P[4+1] **1c**.

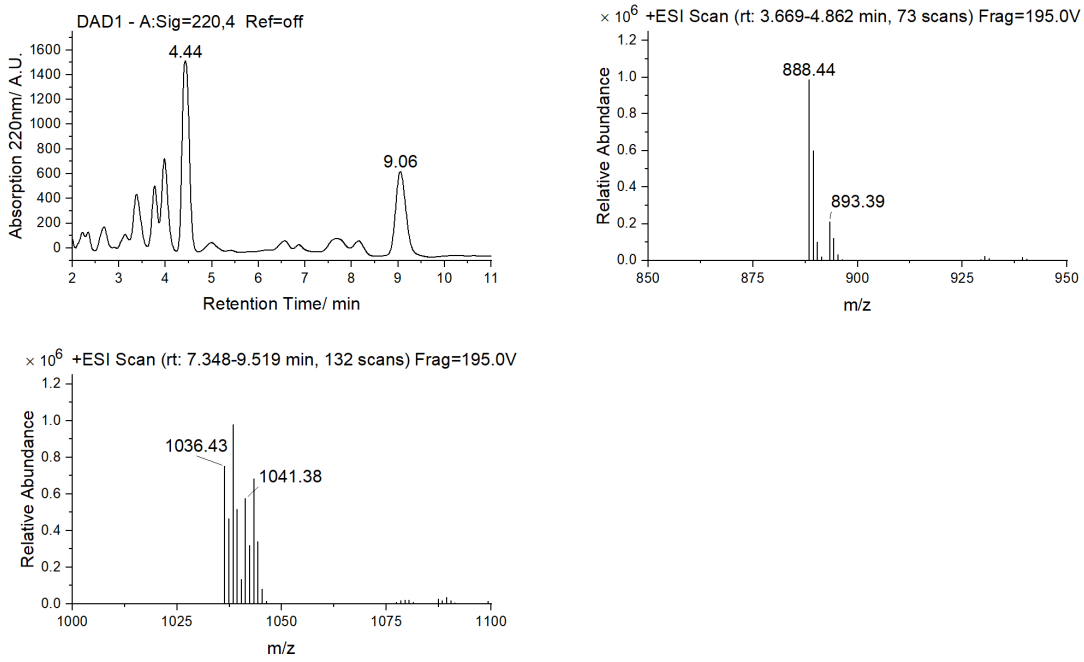


Figure S20. LC-MS of crude reaction mixture of RD-*Co*-P[4+1] **1d**.

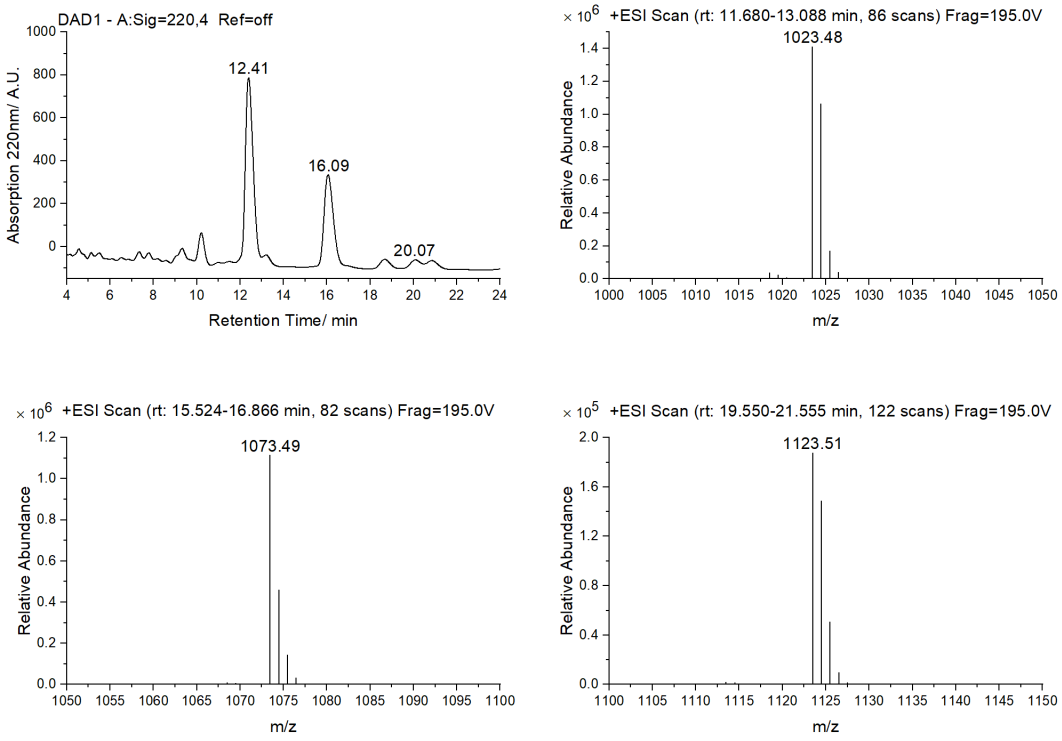


Figure S21. LC-MS of crude reaction mixture of RD-*Co*-P[4+1] **1e**.

4. NMR Analysis

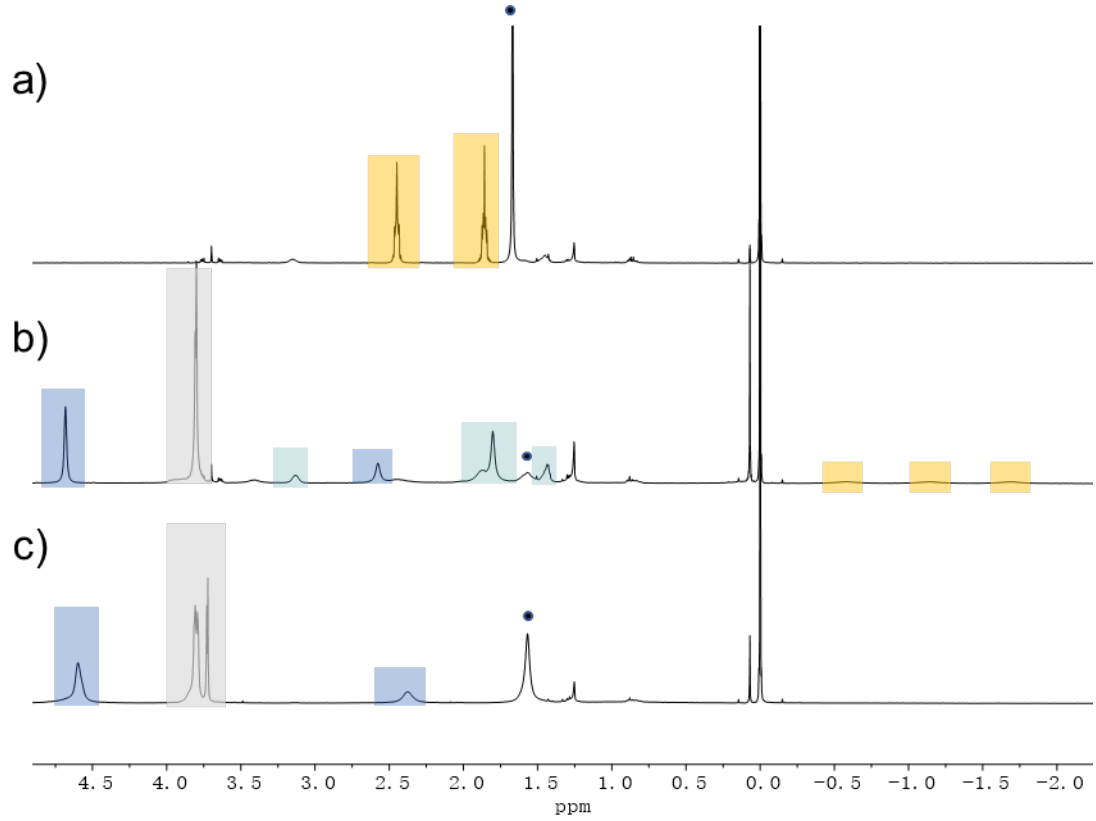


Figure S22. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of: a) 1,4-dicyanobutane(5 mM); b) RD-*Co*-P[4+1] **1d** and 1,4-dicyanobutane in a 1:1 ratio (5 mM/ 5 mM); c) RD-*Co*-P[4+1] **1d** (5 mM). Colourcode: orange, 1,4-dicyanobutane; blue, propargyl; green, 6-bromohexyl chain; grey, methoxy and methylene bridges. The • symbol denotes solvent residue peaks.

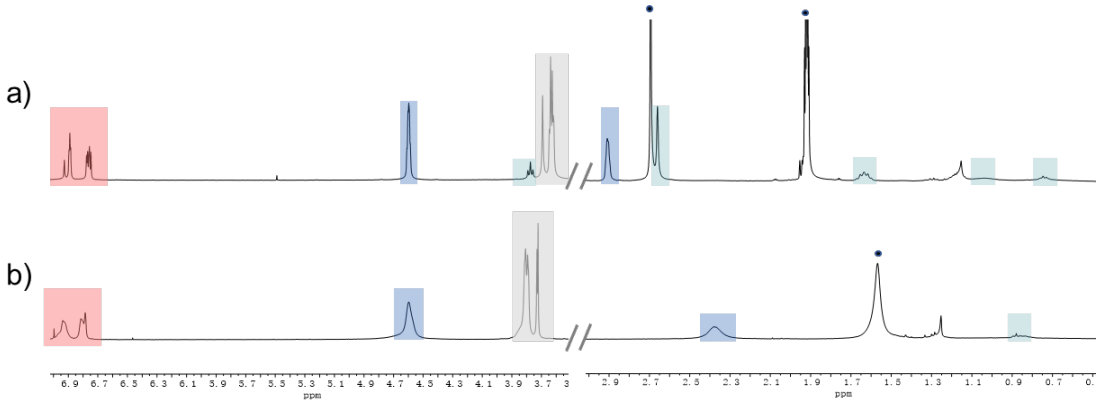


Figure S23. ^{1}H NMR spectra (400 MHz) of RD-*Co*-P[4+1] **1d** recorded in a) acetone-d_6; b) $CDCl_3$. Colour code: red, aromatic peaks; blue, propargyl group; green, 6-bromohexyl chain; grey, methoxy and methylene bridges. The • symbol denotes solvent residue peaks.

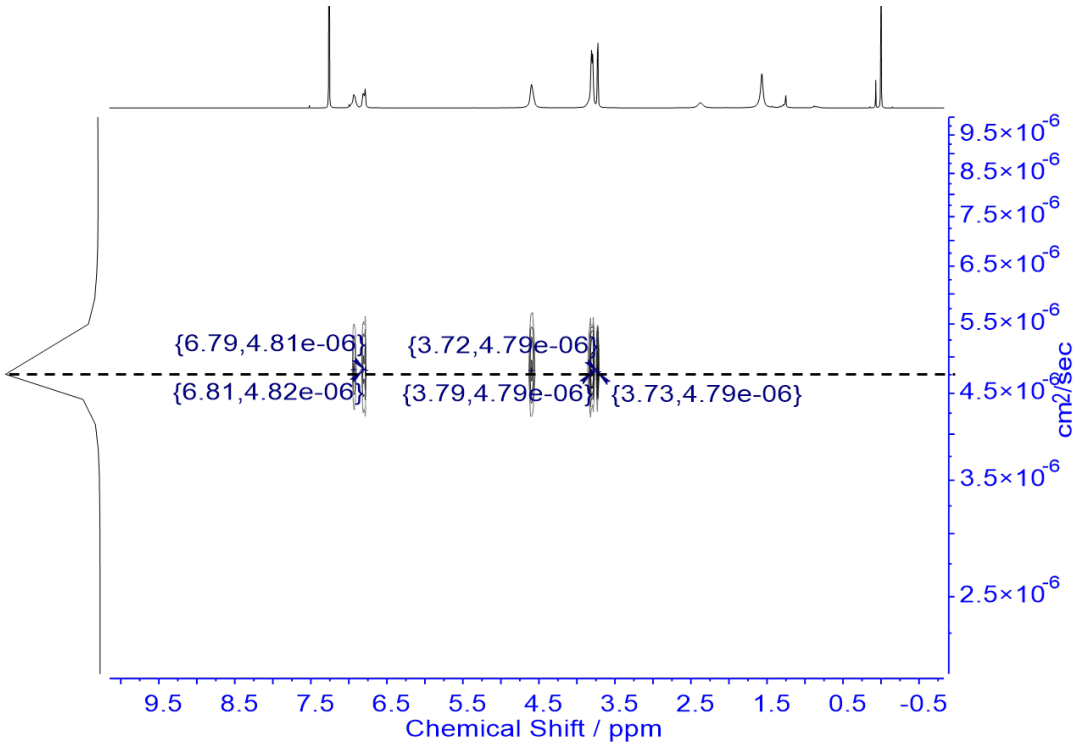


Figure S24. DOSY spectra (400 MHz, $CDCl_3$, 298 K) of RD-*Co*-P[4+1] **1d** recorded in 5 mM, the distinct weight average diffusion coefficients of 4.8×10^{-6} cm^2/s.

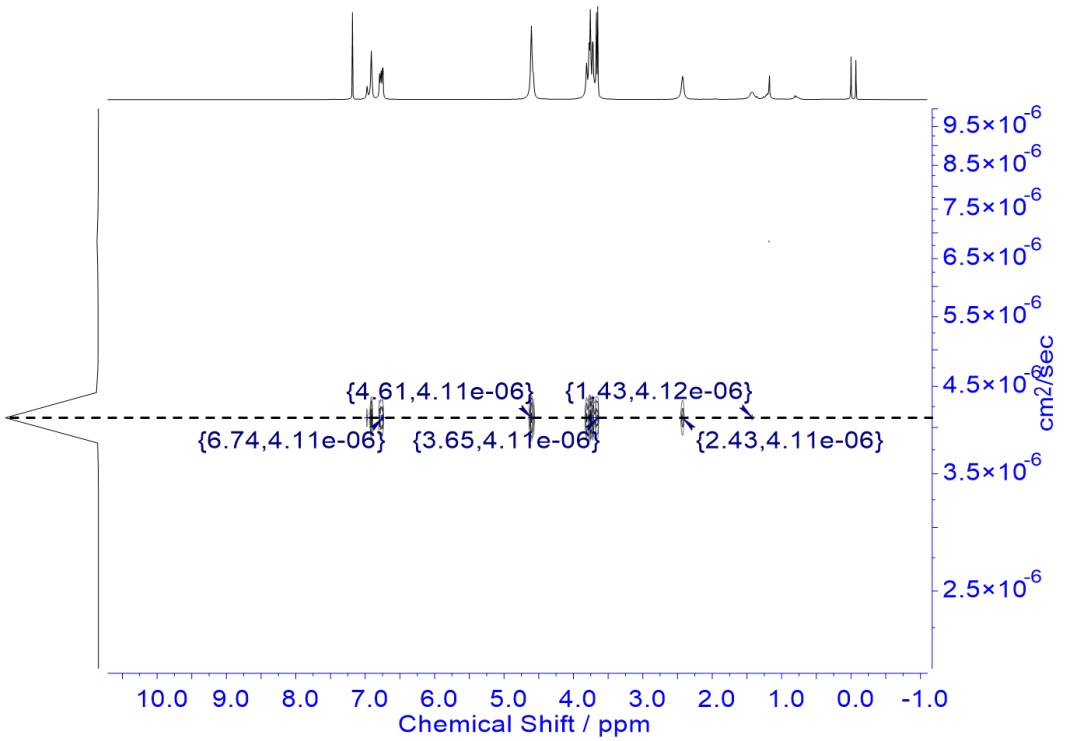


Figure S25. DOSY spectra (400 MHz, $CDCl_3$, 298 K) of RD-*Co*-P[4+1] **1d** recorded in 40 mM, the distinct weight average diffusion coefficients of 4.1×10^{-6} cm^2/s.

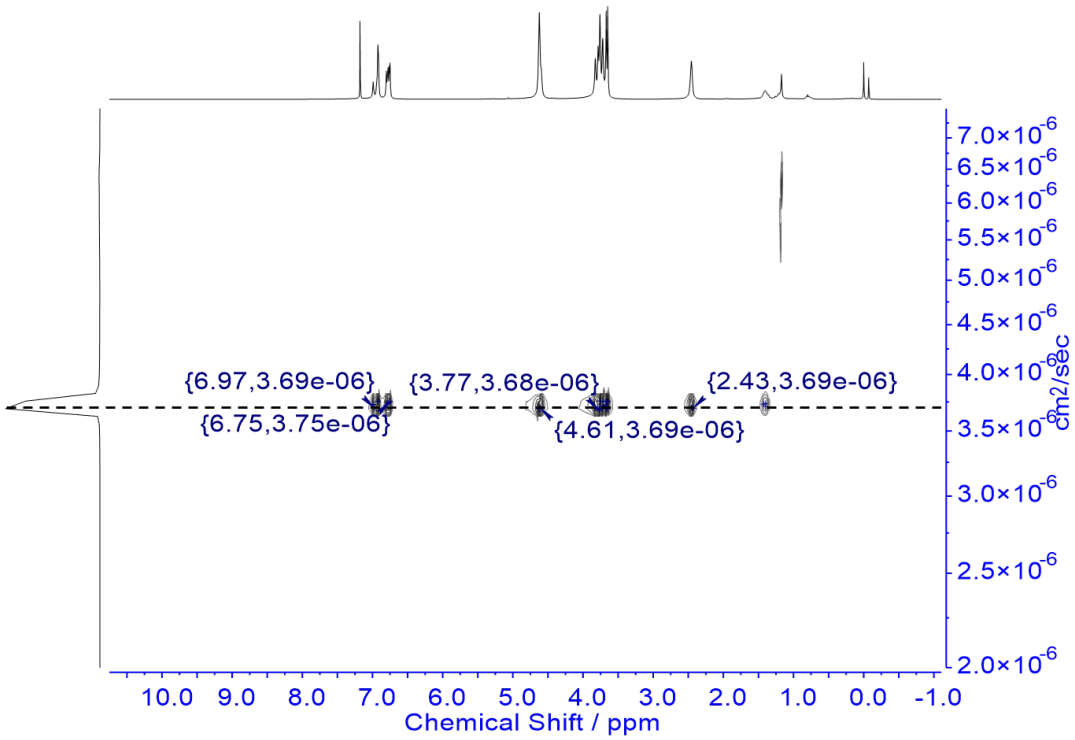


Figure S26. DOSY spectra (400 MHz, $CDCl_3$, 298 K) of RD-*Co*-P[4+1] **1d** recorded in 60 mM, the distinct weight average diffusion coefficients of 3.7×10^{-6} cm^2/s.

5. X-Ray Crystallography Data

Table S1. Crystal data and structure refinement for RD-*Co*-P[4+1] **1a**.

Identification code	CCDC 2106128
Empirical formula	$C_{61}H_{54}O_{10}$
Formula weight	947.04
Temperature/K	100.01(12)
Crystal system	triclinic
Space group	*P*-1
a/Å	12.0930(6)
b/Å	13.4589(8)
c/Å	17.0755(7)
α/°	88.492(4)
β/°	81.618(4)
γ/°	77.710(4)
Volume/Å^3	2686.5(2)
Z	2
ρ_{calc}g/cm^3	1.171
μ/mm^{-1}	0.079
F(000)	1000.0
Crystal size/mm^3	0.12 × 0.1 × 0.06
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.916 to 58.97
Index ranges	$-16 \le h \le 15$, $-18 \le k \le 18$, $-23 \le l \le 23$
Reflections collected	37326
Independent reflections	11810 [R_{int} = 0.0929, R_{sigma} = 0.1294]
Data/restraints/parameters	11810/0/645
Goodness-of-fit on F^2	0.963
Final *R* indexes [*I*>=2σ (I)]	R_1 = 0.0848, wR_2 = 0.2179
Final *R* indexes [all data]	R_1 = 0.1681, wR_2 = 0.2609
Largest diff. peak/hole /eÅ^{-3}	0.50/-0.41

Table S2. Crystal data and structure refinement for RD-*Co*-P[4+1] **1d**.

Identification code	CCDC 2106131
Empirical formula	$C_{121}H_{115}Br_2Cl_3O_{20}$
Formula weight	2155.29
Temperature/K	159.99(10)
Crystal system	triclinic
Space group	*P*-1
a/Å	12.9624(2)
b/Å	20.2304(2)
c/Å	23.4932(5)
α/°	88.7250(10)
β/°	77.306(2)
γ/°	79.7420(10)
Volume/Å^3	5913.17(17)
Z	2
ρ_{calc}g/cm^3	1.211
μ/mm^{-1}	2.007
F(000)	2244.0
Crystal size/mm^3	0.3 × 0.2 × 0.2
Radiation	Mo Kα (λ = 1.54184)
2Θ range for data collection/°	3.856 to 149.998
Index ranges	$-16 \le h \le 16$, $-23 \le k \le 25$, $-29 \le l \le 29$
Reflections collected	153530
Independent reflections	23156 [R_{int} = 0.0750, R_{sigma} = 0.0337]
Data/restraints/parameters	23156/0/1322
Goodness-of-fit on F^2	1.055
Final *R* indexes [*I*>=2σ (I)]	R_1 = 0.0955, wR_2 = 0.2614
Final *R* indexes [all data]	R_1 = 0.1049, wR_2 = 0.2699
Largest diff. peak/hole /eÅ^{-3}	1.43/-1.17

6.References

[1] M. Guo, X. Wang, C. Zhan, P. Demay-Drouhard, W. Li, K. Du, M. A. Olson, H. Zuilhof and A. C.-H. Sue, *J. Am. Chem. Soc.,* 2018, **140**, 74.

[2] J. Ding, J. Chen, W. Mao, J. Huang and D. Ma, *Org. Biomol. Chem.*, 2017, **15**, 7894.

[3] S. B. Salunke, N. S. Babu and C.-T. Chen, *Chem. Commun.*, 2011, **47**, 10440.