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A facile synthesis of chiral polyazamacrocycles and the UV spectroscopic and CD spectra studies on metal complexes

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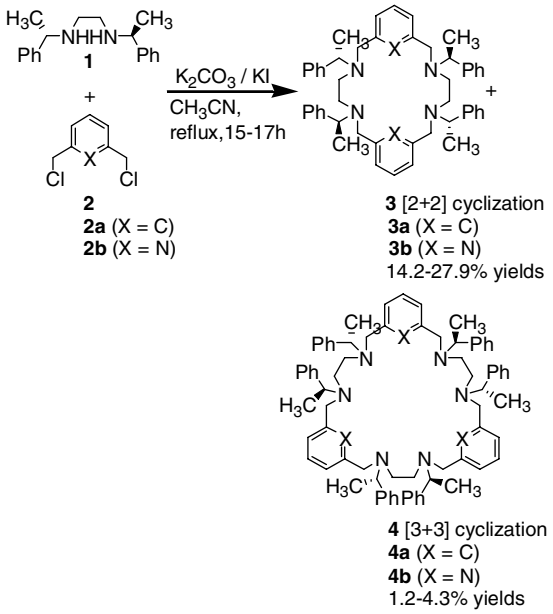
Abstract—A series of chiral polyazamacrocycles with 12, 18, 24, 27, 36-membered rings were designed and synthesized using (*S*)-α-phenylethylamine as initial chiral source. Herein 11 new chiral polyazamacrocycles were successfully prepared. The UV spectroscopic titration experiments of polyazamacrocycle **3b** with metal ions were carried out and the binding constants and free energy changes were calculated according to the modified Benesi–Hildebrand equation. Circular dichroism spectra were recorded for **3b** with metal ions.

The synthesis and applications of macrocyclic compounds have received considerable attention for the past few decades.[1] Among them polyazamacrocycles have been studied extensively because they exhibit a variety of special characteristics, especially the highly organized binding site for complex formation with both cations and host molecules.[2] In this area, the macrocycles that contain 2,6-disubstituted pyridine units have been reported[3] and the design and synthesis of such chiral macrocycles have drawn an increasing interest in recent years due to their potential applications in enantiomeric recognition,[4] asymmetric catalysis,[5] and in host–guest chemistry as receptors of organic and metal cations.[6]

To better explore the applications of chiral polyazamacrocycles, we visualized an efficient route to synthesize a series of optically active polyazamacrocycles. In our experiment, chiral diamine **1** was prepared.[7] The alkylation of diamine **1** with 1,3-bis-chloromethyl-benzene **2a** was carried out in the presence of KI and K_2CO_3 under reflux.[8] After usual work-up, the crude products were purified by repeated column chromatography on silica gel to provide products **3a** and **4a** in 14.2% and 4.3% yields, respectively. Under identical conditions, pyridine-containing macrocycles **3b** and **4b** were also synthesized from the reaction of **1** with 2,6-bis-chloromethyl-pyridine **2b** in 27.9% and 1.2% yields, respectively (Scheme 1).

Combining the ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) spectra and HRMS (FAB) analysis, the macrocyclic structures of products **3** and **4** were assigned to be the corresponding [2+2] and [3+3] cyclization



Scheme 1. Preparation of polyazamacrocycles **3** and **4**.

Keywords: Polyazamacrocycles; Synthesis; UV spectroscopic; CD spectra.
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products.[9] The X-ray crystal structure analysis of product **3b**[10] obtained by recrystallization from acetone confirms that **3b** furnished an 18-membered macrocycle from the formal [2+2] cyclization (Fig. 1).

As another route to synthesize chiral polyazamacrocycles, the reaction of diamine **5a** with **2a** was successfully accomplished in the presence of KI and K_2CO_3 under reflux. The crude products were purified by repeated column chromatography on silica gel to give compounds **6a**, **7a** and **8a** in 27.7%, 8.1% and 9.6% yields, respectively. The alkylation of **5a** with **2b** provides products **6b**, **7b** and **8b** in 23.0%, 7.9% and 4.2% yields, respectively. However, for the reaction of **5b** with **2b**, only the [2+2] cyclization product **7c** was obtained in 13.1% yield, with no detectable [1+1] and [3+3] cyclization products (Scheme 2).

Structures of these macrocycles[11] were identified by ^1H NMR, ^{13}C NMR, IR and HRMS (FAB).

The structure of **7c** was determined by X-ray crystallography as 24-membered ring of [2+2] cyclization product and is shown in Figure 2.[12]

In the UV spectroscopic titration experiments, addition of varying concentrations of guest cations resulted in a gradual increase of the characteristic absorptions of host **3b**. The typical UV spectra changes upon the addition of Ni^{2+} to **3b** are shown in Figure 3.

The association constants of the complexation system formed were calculated according to the modified Benesi–Hildebrand equation.[13] The binding constants and free energy changes of **3b** with cations obtained from usual curve fitting analyses ($R^2 > 0.99234$) of observed absorbance changes are summarized in Table 1.

Circular dichroism (CD) spectra of **3b** and the complex of **3b** and Mn^{2+} are shown in Figure 4.

The CD intensity observed indicates that the complex between **3b** and Mn^{2+} is formed and causes the conformational change of the macrocycle **3b**. CD spectra of

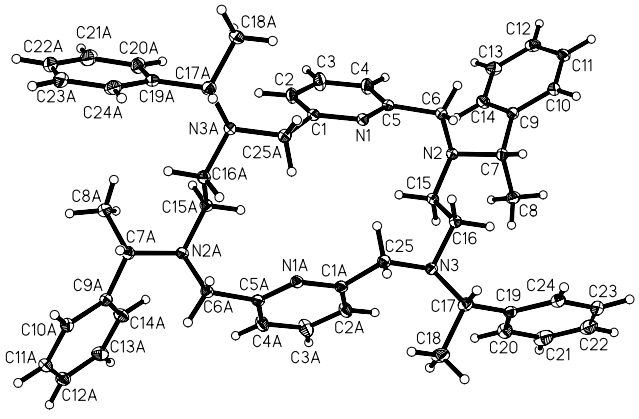
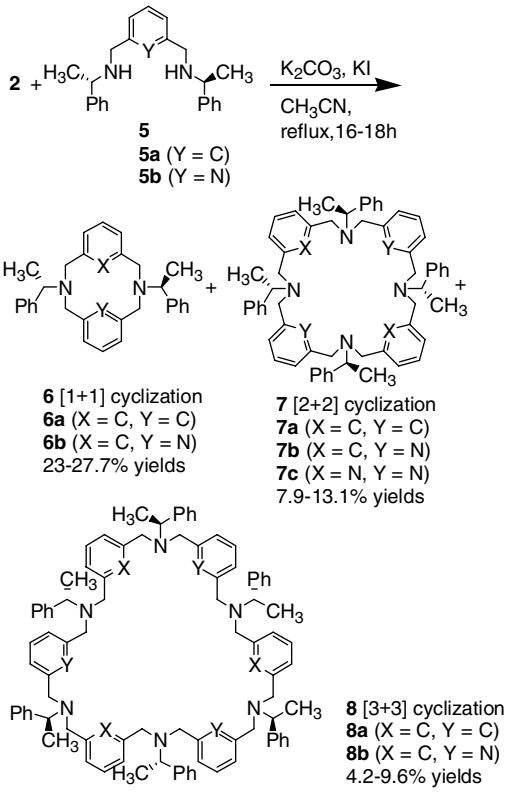


Figure 1. X-ray crystal structure of **3b**.



Scheme 2. Preparation of polyazamacrocycles **6**, **7** and **8**.

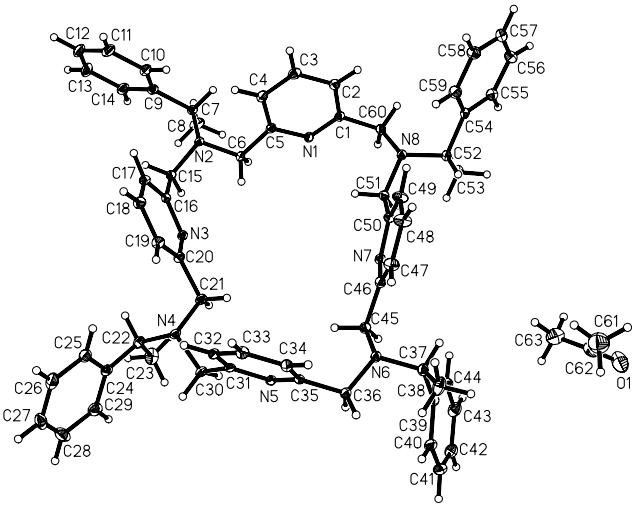


Figure 2. X-ray crystal structure of **7c**·**1/2CH$_3$COCH$_3$**.

complexes of **3b** with metal ions are summarized in Table 2.

In summary, a facile synthesis of chiral polyazamacrocycles has been developed to obtain [1+1], [2+2] and [3+3] cyclization products by the alkylation of the chiral diamines with 1,3-bis-chloromethyl-benzene and 2,6-bis-chloromethyl-pyridine. These polyazamacrocycles obtained contain 1,3- or 2,6-disubstituted aromatic groups as parts of the major ring and give from two to nine binding sites. The UV spectroscopic titration experi-

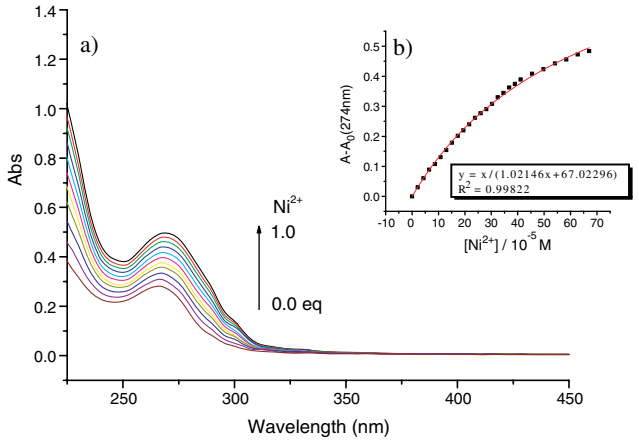


Figure 3. (a) Typical spectra UV–vis changes of **3b** (2.16×10^{-5} M) in acetonitrile with the addition of Ni^{2+} (0.0–2.16×10^{-5} M) at 298 ± 0.1 K. (b) Typical plot of ΔA versus $[Ni^{2+}]$ for complexation of **3b** and Ni^{2+}.

Table 1. Binding constants (K_a) and free energy of complexation ($-\Delta G°$) between **3b** and cations

Guest	K_a ($dm^3\ mol^{-1}$)	$-\Delta G°$ ($kJ\ mol^{-1}$)	R^2
Na^+	$(3.152 \pm 0.010) \times 10^4$	25.66	0.99729
K^+	$(3.408 \pm 0.023) \times 10^4$	25.85	0.99234
Mg^{2+}	$(2.483 \pm 0.012) \times 10^4$	25.07	0.99375
Ca^{2+}	$(2.050 \pm 0.018) \times 10^4$	24.59	0.99650
Mn^{2+}	$(2.202 \pm 0.010) \times 10^4$	24.77	0.99244
Fe^{2+}	$(1.730 \pm 0.011) \times 10^4$	24.17	0.99842
Co^{2+}	$(2.199 \pm 0.009) \times 10^4$	24.76	0.99487
Ni^{2+}	$(1.524 \pm 0.014) \times 10^4$	23.86	0.99822
Cu^{2+}	$(2.175 \pm 0.005) \times 10^4$	24.74	0.99871
Zn^{2+}	$(2.209 \pm 0.008) \times 10^4$	24.77	0.99595

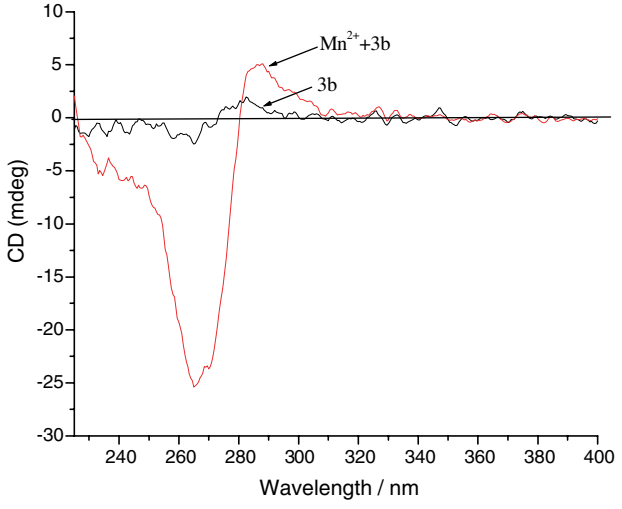


Figure 4. Circular dichroism spectra of the complex (1:1) between **3b** (1.0×10^{-3} M) and Mn^{2+} (1.0×10^{-3} M) in CH_3CN.

ments of macrocycle **3b** with metal ions were carried out and the binding constants and free energy changes were calculated according to the modified Benesi–Hildebrand equation. Circular dichroism spectra were recorded for **3b** with metal ions. Further research is in progress.

Table 2. CD spectra of complexes of macrocycle **3b** with metal ions in CH_3CN[a]

M^{n+}	$\Delta\varepsilon/M^{-1}cm^{-1}$ (wavelength/nm)	M^{n+}	$\Delta\varepsilon/M^{-1}cm^{-1}$ (wavelength/nm)
None[b]	−43.8 (265), 37.3 (282)		
Na^+	−38.6 (264), 34.0 (282)	Fe^{2+}	−1.39 (262), 97.6 (249)
K^+	−42.6 (265), 28.7 (286)	Co^{2+}	−569.9 (266), 202.2 (266)
Mg^{2+}	−127.8 (265), 42.7 (284)	Ni^{2+}	−431.6 (272)
Ca^{2+}	−121.1 (265), 40.8 (286)	Cu^{2+}	−283.9 (259), 228.7 (292)
Mn^{2+}	−439.9 (265), 85.1 (287)	Zn^{2+}	189.7 (264)

[a] $[\mathbf{3b}] = 1.0 \times 10^{-3}$ M, $[M^{n+}] = 1.0 \times 10^{-3}$ M; $\mathbf{3b}/M^{n+} = 1{:}1$.
[b] Only **3b**.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.02.002.

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9. General procedure for the synthesis of macrocycles **3**–**7**: To a solution of the different chiral diamine (2.0 mmol) in dry acetonitrile (60 mL) was added 1,3-bis-chloromethyl-benzene (2.0 mmol) or 2,6-bis-chloromethyl-pyridine (2.0 mmol) in the presence of K_2CO_3 (2.0 g) and KI (30.0 mg) under nitrogen atmosphere. The reaction mixture was stirred under reflux for 15–18 h, monitored by TLC and quenched by adding water (30 mL). After usual work-up, the crude residue was purified by repeated column chromatography on silica gel to give the corresponding chiral polyazamacrocycles. The crystals of the macrocycle **3b** and **7c** were obtained from acetone for the purpose of X-ray analysis. Compound **3a**: Yield 14.2%. $R_f = 0.33$ (petroleum/ethyl acetate = 20:1). mp 49–50 °C. $[\alpha]_D^{20}$ −34.2 (*c* 0.26, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 1.35 (d, $J = 6.7$ Hz, 12H), 2.46–2.52 (m, 4H), 2.60–2.62 (m, 4H), 3.33 (d, $J = 13.8$ Hz, 4H), 3.42 (d, $J = 13.8$ Hz, 4H), 3.81 (q, $J = 6.7$ Hz, 4H), 7.02–7.36 (m, 28H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.32, 48.06, 54.77, 58.58, 126.52, 126.72, 127.56, 127.80, 127.97, 128.84, 140.52, 144.18. IR (KBr): 2968, 1602, 1450, 699 cm^{-1}. HRMS (FAB, *m*/*z*): calcd for $C_{52}H_{61}N_4$ $(M+H)^+$ 741.4890, found: 741.4892. Compound **4a**: Yield 4.3%. $R_f = 0.18$ (petroleum/ethyl acetate = 20:1). Mp 52–53 °C. $[\alpha]_D^{20}$ −82.5 (*c* 0.12, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 1.26 (d, $J = 6.7$ Hz, 6H), 2.44 (q, $J = 10.6$ Hz, 2H), 2.55 (q, $J = 10.5$ Hz, 2H), 3.29 (d, $J = 13.9$ Hz, 2H), 3.45 (d, $J = 13.9$ Hz, 2H), 3.73 (q, $J = 6.8$ Hz, 2H), 7.07–7.30 (m, 14H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.95, 47.94, 55.02, 58.39, 126.55, 126.91, 127.84, 127.95, 128.95, 140.44, 143.86. IR (KBr): 3026, 2968, 1491, 1450, 699 cm^{-1}. HRMS (FAB, *m*/*z*): calcd for $C_{78}H_{91}N_6$ $(M+H)^+$ 1111.7299, found: 1111.7311. Compound **3b**: Yield 27.9%. $R_f = 0.30$ (petroleum/ethyl acetate = 5:1). mp 146–147 °C. $[\alpha]_D^{20}$ −32.0 (*c* 0.15, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 1.32 (d, $J = 6.7$ Hz, 12H), 2.35–2.40 (m, 4H), 2.45–2.49 (m, 4H), 3.42 (d, $J = 15.5$ Hz, 4H), 3.56 (d, $J = 15.5$ Hz, 4H), 3.77 (q, $J = 6.7$ Hz, 4H), 7.23–7.34 (m, 24H), 7.48–7.51 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.90, 50.67, 57.64, 60.98, 119.83, 126.72, 127.64, 128.11, 136.54, 144.05, 160.38. IR (KBr): 2973, 2950, 1592, 1452, 700 cm^{-1}. HRMS (FAB, *m*/*z*): calcd for $C_{50}H_{59}N_6$ $(M+H)^+$ 743.4795, found: 743.4803. Anal. Calcd for $C_{50}H_{88}N_6$: C, 80.82; H, 7.87; N, 11.31. Found: C, 80.66; H, 7.66; N, 11.36. Compound **4b**: Yield 1.2%. $R_f = 0.26$ (petroleum/ethyl acetate = 3:1). Mp 54–55 °C. $[\alpha]_D^{20}$ −36.9 (*c* 0.16, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 1.33 (d, $J = 6.7$ Hz, 6H), 2.51 (q, $J = 11.4$ Hz, 2H), 2.68 (q, $J = 11.4$ Hz, 2H), 3.52 (d, $J = 15.2$ Hz, 2H), 3.65 (d, $J = 15.2$ Hz, 2H), 3.82 (q, $J = 6.7$ Hz, 2H), 7.08–7.33 (m, 13H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.14, 49.29, 56.65, 58.82, 120.06, 126.68, 127.79, 128.04, 136.40, 143.70, 159.97. IR (KBr): 3026, 2969, 1714, 1452, 700 cm^{-1}. HRMS (FAB, *m*/*z*): calcd for $C_{75}H_{88}N_9$ $(M+H)^+$ 1114.7157, found: 1114.7188.

10. Crystal data for **3b**: $C_{50}H_{58}N_6$; $M = 743.02$; colorless, monoclinic; space group $C2$; $a = 33.889(5)$ Å, $b = 6.0661(10)$ Å, $c = 10.6701(18)$ Å; $V = 2181.6(6)$ Å^3; $\mu = 0.067$ mm^{-1}; $Z = 2$; $T = 293(2)$ K; $F_{000} = 800$; $R_1 = 0.0380$, $wR_2 = 0.0999$; The CCDC deposition number: 285277.

11. Compound **6a**: Yield 27.7%. $R_f = 0.25$ (petroleum/ethyl acetate = 100:1). Mp 111–112 °C. $[\alpha]_D^{20}$ −38.2 (*c* 0.23, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 1.67 (d, $J = 6.8$ Hz, 6H), 3.72 (s, 8H), 4.29 (q, $J = 6.7$ Hz, 2H), 6.52 (d, $J = 6.96$ Hz, 4H), 6.65 (t, $J = 7.41$ Hz, 2H), 7.36 (t, $J = 7.35$ Hz, 2H), 7.50 (t, $J = 7.56$ Hz, 4H), 7.65 (br, 2H), 7.73 (d, $J = 7.56$ Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.49, 58.91, 65.13, 126.33, 126.40, 126.95, 128.00, 128.21, 133.96, 139.11, 144.09. IR (KBr): 3029, 2965, 1491, 1450, 705 cm^{-1}. HRMS (FAB, *m*/*z*): calcd for $C_{32}H_{35}N_2$ $(M+H)^+$ 447.2795, found: 447.2789. Anal. Calcd for $C_{32}H_{34}N_2$: C, 86.05; H, 7.67; N, 6.27. Found: C, 85.95; H, 7.87; N, 6.02. Compound **7a**: Yield 8.1%. $R_f = 0.18$ (petroleum/ethyl acetate = 100:1). Mp 164–165 °C. $[\alpha]_D^{20}$ −147.8 (*c* 0.23, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 1.54 (d, $J = 6.8$ Hz, 12H), 3.44 (d, $J = 13.4$ Hz, 8H), 3.59 (d, $J = 13.4$ Hz, 8H), 3.97 (q, $J = 6.8$ Hz, 4H), 7.21 (s, 12H), 7.23–7.30 (m, 4H), 7.37–7.41 (m, 8H), 7.47–7.50 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.11, 53.70, 56.20, 126.72, 127.24, 127.99, 128.06, 129.52, 140.40, 142.88. IR (KBr): 3027, 2966, 1605, 1492, 1451, 700 cm^{-1}. HRMS (FAB, *m*/*z*): calcd for $C_{64}H_{69}N_4$ $(M+H)^+$ 893.5516, found: 893.5493. Compound **8a**: Yield 9.6%. $R_f = 0.11$ (petroleum/ethyl acetate = 100:1). Mp 74–75 °C. $[\alpha]_D^{20}$ −150.0. (*c* 0.12, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 1.42 (d, $J = 6.8$ Hz, 18H), 3.41 (d, $J = 13.8$ Hz, 12H), 3.56 (d, $J = 13.8$ Hz, 12H), 3.90 (q, $J = 6.7$ Hz, 6H), 7.15–7.41 (m, 54H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.79, 53.64, 56.12, 126.63, 127.10, 127.92, 128.03, 128.96, 140.25, 142.82. IR (KBr): 3026, 2967, 1605, 1450, 700 cm^{-1}. HRMS (FAB, *m*/*z*): calcd for $C_{96}H_{103}N_6$ $(M+H)^+$ 1339.8238, found: 1339.8245. Compound **6b**: Yield 23.0%. $R_f = 0.40$(petroleum/ethyl acetate = 10:1). $[\alpha]_D^{20}$ −11.1 (*c* 0.35, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 1.63 (d, $J = 6.7$ Hz, 6H), 3.66 (d, $J = 12.62$ Hz, 2H), 3.89 (d, $J = 12.14$ Hz, 2H), 3.75–3.83 (br, 4H), 6.63–6.75 (m, 5H), 7.05 (t, $J = 7.59$ Hz, 1H), 7.30–7.63 (m, 11H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.49, 58.76, 61.09, 65.24, 122.49, 126.66, 126.94, 127.34, 128.04, 128.15, 135.54, 135.88, 138.14, 143.72, 158.86. IR (KBr): 3026, 2968, 1591, 1451, 699 cm^{-1}. HRMS (FAB, *m*/*z*): calcd for $C_{31}H_{34}N_3$ $(M+H)^+$ 448.2747, found: 448.2731. Compound **7b**: Yield 7.9%. $R_f = 0.25$ (petroleum/ethyl acetate = 10:1). mp 73–74 °C. $[\alpha]_D^{20}$ −118.1 (*c* 0.12, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 1.46 (d, $J = 6.8$ Hz, 12H), 3.39 (d, $J = 13.6$ Hz, 4H), 3.55 (d, $J = 15.3$ Hz, 4H), 3.59 (d, $J = 13.6$ Hz, 4H), 3.71 (d, $J = 15.2$ Hz, 4H), 3.94 (q, $J = 6.8$ Hz, 4H), 7.08 (s, 6H), 7.21 (d, $J = 7.7$ Hz, 4H), 7.26–7.31 (m, 8H), 7.34–7.42 (s, 8H), 7.48 (d, $J = 7.5$ Hz, 8H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.54, 54.76, 56.27, 59.27, 120.17, 126.80, 127.30, 127.76, 127.96, 128.12, 129.39, 136.27, 140.02, 143.27, 159.83. IR (KBr): 3026, 2968, 1590, 1575, 1454, 700 cm^{-1}. HRMS (FAB, *m*/*z*): calcd for $C_{62}H_{67}N_6$ $(M+H)^+$ 895.5421, found: 895.5397. Compound **8b**: Yield 4.2%. $R_f = 0.18$ (petroleum/ethyl acetate = 10:1). Mp 60–61 °C. $[\alpha]_D^{20}$ −120.0 (*c* 0.17, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 1.44 (d, $J = 6.8$ Hz, 18H), 3.53 (d, $J = 13.8$ Hz, 6H), 3.62 (d, $J = 12.4$ Hz, 6H), 3.65 (d, $J = 14.3$ Hz, 6H), 3.81 (d, $J = 14.9$ Hz, 6H), 4.15 (q, $J = 7.1$ Hz, 6H), 7.14–7.73 (m, 51H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.54, 54.61, 55.55, 56.71, 120.16, 126.73, 127.58, 127.84, 127.92, 128.02, 128.54, 136.51, 140.19, 142.82, 160.33. IR (KBr): 3026, 2968, 1590, 1453, 700 cm^{-1}. HRMS (FAB, *m*/*z*): calcd for $C_{93}H_{100}N_9$ $(M+H)^+$ 1342.8096, found: 1342.8061. Compound **7c**: Yield 13.1%.$R_f = 0.28$ (petroleum/ethyl acetate = 1:10). Mp 173–174 °C. $[\alpha]_D^{20}$ −90.0 (*c* 0.28, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 1.43 (d, $J = 6.7$ Hz, 12H), 3.58 (d, $J = 14.6$ Hz, 8H), 3.75 (d, $J = 14.6$ Hz, 8H), 3.93 (q, $J = 6.7$ Hz, 4H), 7.12 (d, $J = 7.7$ Hz, 8H), 7.23–7.36 (m, 16H), 7.48 (d, $J = 7.5$ Hz, 8H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.81, 56.81, 60.39, 120.60, 126.80, 127.87, 128.13, 135.96, 143.63, 159.55. IR

(KBr): 3060, 2970, 2830, 1590, 1574, 1455, 699 cm^{-1}. MS (EI) (*m*/*z*): 899.09. HRMS (FAB, *m*/*z*): calcd for $C_{60}H_{65}N_8$ $(M+H)^+$ 897.5326, found: 897.5337.

12. Crystal data for **7c·1/2acetone**: $C_{61.50}H_{67}N_8O_{0.5}$; $M = 926.23$; colorless, triclinic; space group *P*-1; $a = 9.3905(15)$ Å, $b = 10.6258(17)$ Å, $c = 14.849(2)$Å; $V = 1399.0(4)$ $Å^3$; $\mu = 0.066$ mm^{-1}; $Z = 1$; $T = 294(2)$ K; $F_{000} = 496$; $R_1 = 0.0531$, $wR_2 = 0.1356$. The CCDC deposition number: 285278.
13. (a) Demirel, N.; Bulut, Y. *Tetrahedron: Asymmetry* **2003**, *14*, 2633; (b) Chow, C. F.; Lam, M. H. W.; Wong, W. Y. *Inorg. Chem.* **2004**, *43*, 8387.