The synthesis of 1,2,3-triazole derivatives of deoxycholic acid for molecular tweezer metal ion recognition

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A series of molecular tweezer metal receptors based on [1,2,3-triazolo-acetyl]esters of methyl deoxycholate have been synthesised via the 3,12-azidoester using a click chemistry method. Their structures were characterized by ^{1}H NMR, IR, MS spectra and elemental analysis. Their binding properties were examined by UV-Vis spectra titration. The preliminary results indicate that this type of molecular tweezers have good recognition for metal ions.

Keywords: cation recognition, 1,2,3-triazole, click chemistry, deoxycholic acid

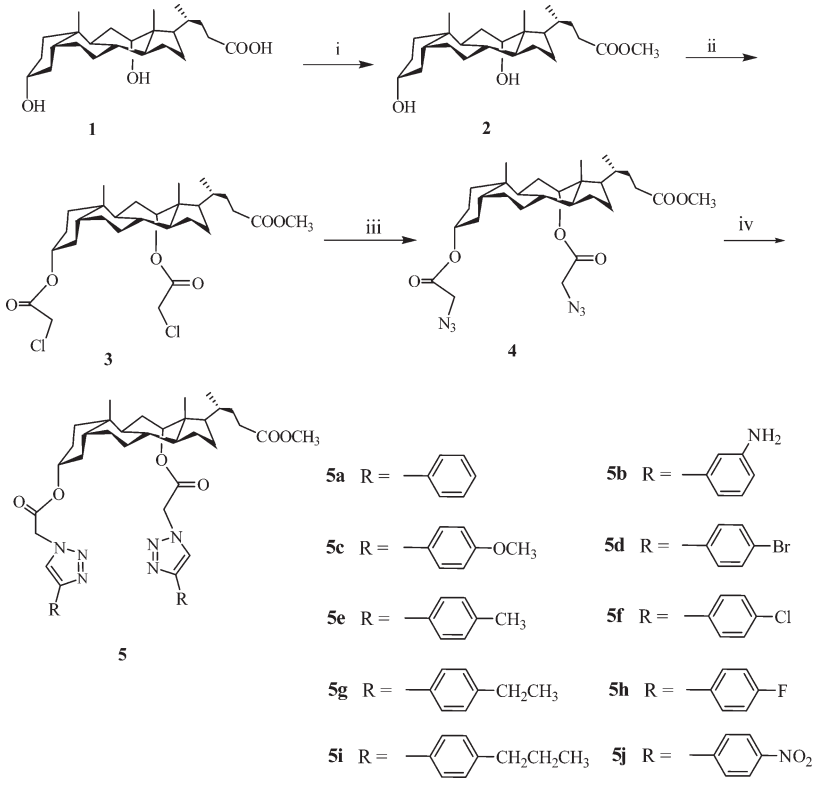
Cations have a variety of biochemical functions affecting enzymes, coenzymes, and cofactors.[1–5] The synthesis of new sensors for the efficient detection of trace metal ions is among the more important research topics in environmental chemistry and biology. Heavy metal ions are significant environmental pollutants that accumulate in plants, soil, and water.[7] A deficiency or an excess presence of these in biological fluids is harmful to health.[8–12] Accordingly, it is imperative to develop analytical methods for the sensitive and selective detection of trace amounts of cations.

Recently, the importance of the role of the 1,2,3-triazole ring as a potential ligand in the formation of stable metal complexes has been enhanced and some triazole-based receptors and dendrimers for the recognition of cation have been reported.[13,14] The application of click chemistry developed by Meldal and Sharpless involving a Cu(I)-catalysed 1,3-dipolar cycloaddition reaction between an azide and a terminal alkyne to yield the unique properties of the 1,4-disubstituted 1,2,3-triazole ring is rapidly growing. This is an easy way to synthesise 1,2,3-triazole ring under simple reaction conditions using a simple product isolation, and in high yield.[15–17] Moreover, the bile acids have attracted considerable interest for the design of receptors for molecular recognition due to their rigid framework, facial amphiphilicity, and suitably oriented hydroxyl groups.[18,19] However, steroid-based molecular tweezers with a 1,2,3-triazole ring for metal recognition through click chemistry have not been reported. We provide a route for the synthesis of a new series of molecular tweezers with this type of structure. The synthetic route is shown in Scheme 1.

Results and discussion

In searching for the best reaction conditions for the synthesis of molecular tweezer artificial receptors, we took the synthesis of **5a** as an example and carried out several experiments under different conditions, varying the solvent, temperature, and concentration of the catalyst to obtain the best results for this reaction. The results are shown in the following tables.

As shown in Table 1, the effect of DMSO, a mixture of DMSO and H_2O (10:1, V/V), CH_3OH and *t*-BuOH on the reaction was investigated. The results showed that although different



Scheme 1 The synthetic route of molecular tweezers **5a–j**. Reagents and conditions: (i) CH_3OH, CH_3COCl, ice bath; (ii) $ClCH_2COCl$, $CHCl_3$, pyridine, triethylamine, 60 °C; (iii) NaN_3, DMF, 60 °C; (iv) R-C≡H, *t*-BuOH, CuI, triethylamine, 50 °C.

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solvents were employed under similar reaction conditions, the results did not differ significantly. When *t*-BuOH was used, the yield was a little higher and hence *t*-BuOH was the best solvent for the reaction.

As shown in Table 2, different temperatures were employed under the similar reaction conditions. Although the results were different, 50 °C was the best temperature to obtain a good yield.

As shown in Table 3, different concentrations of catalysts were employed under similar reaction conditions. As a result, CuI (10 mol%) and Et_3N (40 mol%) was the optimum catalytic system.

From these data that we obtained from in this experiment, we concluded that this provided an easy and effective way for the preparation of 1,2,3-triazole-based type molecular cation receptors. There are obvious advantages in this method including high yield, simple reaction conditions and an easy separation of the products.

The molecular recognition properties of molecular tweezers **5a**, **5b**, **5g** for metal ions were investigated by UV-Vis spectra titration in $CHCl_3$/MeOH (7:3, V/V) at 25 °C. The UV-Vis plot of **5a** for Hg^{2+} is shown in Fig.1. The titration data were analysed by using the Hildebrand-Benesi equation. The plot of $1/\Delta A$ versus the $1/[G_0]$ gave a straight line (Fig. 2). It showed that these molecular tweezers possessed the ability to form complexes with the guest cations which were examined and that the complexes consisted of 1:1 host and guest molecules. Using the linear fitting method, we obtained the association constants for the complex. The results indicate that this kind of molecular tweezers exhibit a selectivity for metal ions. The association constants of the molecular tweezer **5a**, for example, are 3999, 62287, 13990 L mol^{-1} for Cu^{2+}, Hg^{2+}, Pb^{2+} metal ions respectively.

The main reason is that when the host **5a** is at the minimum energy, its conformation is a tweezer type, which has the ability to form complex with guest molecules. The main driving force for recognition comes from coordination bond between host and guest. The details of molecular recognition of **5a–j** are under further study.

Table 1 The effect of solvent on yields

Entry	Solvent	Yield/%
1	DMSO	23
2	DMSO and H_2O	39
3	CH_3OH	60
4	*t*-BuOH	84

Table 2 The effect of reaction temperatures on yields of compounds **5a**

Entry	Temperature/ °C	Yield/%
1	0	–
2	25	40
3	50	84
4	70	80

Table 3 The effect of concentration of catalysts on yields

Entry	Concentration/mol%		Yield/%
	CuI	Et_3N	
1	10	0	0
2	10	20	63
3	10	40	84
4	10	60	78

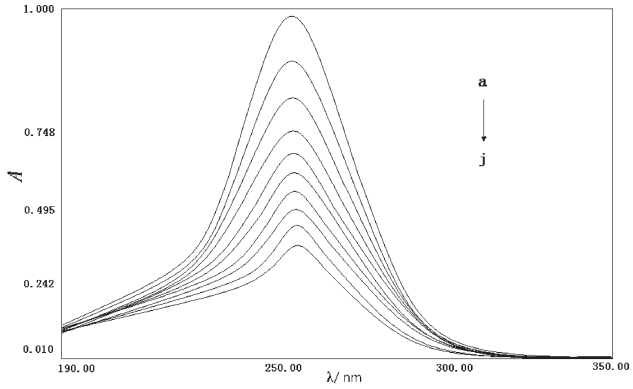

Fig. 1 UV-Vis spectra of molecular tweezers **5a** (3.2×10^{-5} mol L^{-1}) in the presence of Hg^{2+} (a) 0 mol L^{-1} (b) 0.32×10^{-4} mol L^{-1} (c) 0.64×10^{-4} mol L^{-1} (d) 0.96×10^{-4} mol L^{-1} (e) 1.28×10^{-4} mol L^{-1} (f) 1.60×10^{-4} mol L^{-1} (g) 1.92×10^{-4} mol L^{-1} (h) 2.24×10^{-4} mol L^{-1} (i) 2.56×10^{-4} mol L^{-1} (j) 2.88×10^{-4} mol L^{-1} with λ_{max} at 245.0 nm.

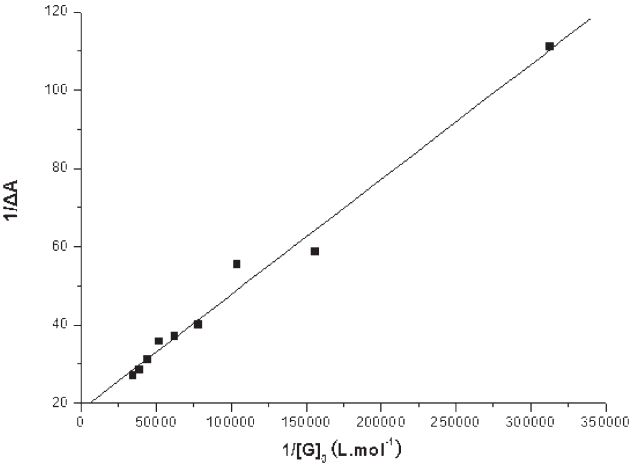

Fig. 2 Typical plot of $1/\Delta A$ *versus* $1/[G]_0$ for the inclusion complex of molecular tweezer **5a** with Hg^{2+} in $CHCl_3$/MeOH (7:3, V/V) at 25 °C.

Experimental

Melting points were determined on a micro-melting point apparatus and were uncorrected. IR spectra were obtained on 1700 Perkin-Elmer FTIR using KBr disks. ^{1}H NMR spectra were recorded on a Varian INOVA 400 MHz spectrometer using TMS as internal standard. Mass spectra were determined on FinniganLCQ^{DECA} instrument. Elemental analysis was performed on a Carlo-Erba-1106 autoanalyser. Optical rotations were measured on a Wzz-2B polarimeter. All the solvents were purified before use. Intermediate **2** was prepared following a reported procedure.[20] It was obtained as a white solid, yield 90%, m.p. 79–80 °C (lit.[20] 74–76 °C). Intermediate **3** was prepared following a reported procedure.[21] It was obtained as a white solid, yield 88%, m.p. 122–124 °C (lit.[21] 120 °C).

Synthesis of 3β, 12β-bis-(azidoacetyl)deoxycholate (**4**):[22] Sodium azide (9.24 mmol) was added to a solution of **3** (1.54 mmol) in 20 mL of DMF, and the solution was stirred at 60 °C for 12 h. The solution was diluted with water (40 mL) and extracted with ethyl acetate (30 mL) twice. The organic layer was washed with water and then with brine and dried over Na_2SO_4 and evaporated under a vacuum. The residue was purified by column chromatography on silica gel H with petroleum ether/ethyl acetate (5:1, V/V) as eluant and the product was obtained as a white solid, yield 95%, m.p. 91–93 °C; $[\alpha]_D^{20}$–104.5 (*c* 0.2, CH_2Cl_2); IR (KBr) (cm^{-1}): 2948, 2868, 2103, 1735, 1444, 1359, 1283, 1198, 1115, 968; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.26 (s, 1H, 12*β-H*), 4.78–4.85 (m, 1H, 3*β*-H), 3.90 (s, 2H, CH_2N_3), 3.84 (s, 2H, CH_2N_3), 3.66 (s, 3H, $COOCH_3$), 0.93 (s, 3H, 19-CH_3), 0.82 (d, J = 6.4 Hz, 3H, 21-CH_3), 0.76 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 595.42 ([M+Na]$^+$, 100). Anal. Calcd for $C_{29}H_{45}N_6O_6$: C, 60.82; H, 7.74; N, 14.67. Found: C, 60.65; H, 7.75; N, 14.64%.

Synthesis of acyclic compound **5a–j**

Phenyl acetylene or substituted phenylacetylene (1.14 mmol) were added to a solution of 3β, 12β-bis-(azidoacetyl)deoxycholate **4** (0.52 mmol) in *t*-BuOH (15 mL), CuI (10 mol%) and triethylamine (40 mol%) were added to this solution. The solution was stirred at 50 °C for 8–24 h. The solution was evaporated under vacuum. The residue was purified by column chromatography on silica gel H with petroleum ether/ethyl acetate/ethanol (4:1:1–15:1:1, V/V/V) as the eluant. The whole progress was monitored by TLC. The physical and spectra data of the compounds **5a–j** are as follows.

5a: White solid, yield 84%, m.p. 94–96 °C $[\alpha]_D^{20}$–120.5 (c 0.15, CH_2Cl_2); IR (KBr) (cm^{-1}): 2949, 2869, 1742, 1612, 1467, 1443, 1382, 1357, 1270, 1221, 1078, 1046, 976; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.08 (s, 1H, triazole-H), 7.90 (s, 1H, triazole-H), 7.84 (d, J = 8.2 Hz, 2H, ArH), 7.77 (d, J = 7.6 Hz, 2H, ArH), 7.28–7.46 (m, 6H, ArH), 5.31 (s, 2H, -$OCOCH_2$), 5.06–5.18 (m, 2H, -$OCOCH_2$), 5.16 (s, 1H, 12*β-H*), 4.79–4.84 (m, 1H, 3*β-H*), 3.68 (s, 3H, $COOCH_3$), 0.87 (s, 3H, 19–CH_3), 0.80 (d, J = 5.6 Hz, 3H, 21-CH_3), 0.69 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 777.57 ([M+H]$^+$, 100). Anal. Calcd for $C_{45}H_{56}N_6O_6$: C, 69.56; H, 7.26; N, 10.82. Found: C, 69.45; H, 7.25; N, 10.79%.

5b: Fine solid, yield 90%, m.p. 114–116 °C; $[\alpha]_D^{20}$–136.4 (c 0.2, CH_2Cl_2); IR (KBr) (cm^{-1}): 3449, 3369, 2949, 2870, 17380, 1621, 1593, 1451, 1358, 1270, 1222, 1079, 1048, 1001, 785; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.00 (s, 1H, triazole-H), 7.81 (s, 1H, triazole-H), 7.11–7.23 (m, 6H, ArH), 6.69 (d, J = 6.4 Hz, 1H, ArH), 6.63 (d, J = 6.8 Hz, 1H, ArH), 5.30 (s, 2H, -$OCOCH_2$), 5.02–5.15 (m, 2H, -$OCOCH_2$), 5.14 (s, 1H, 12*β-H*), 4.77–4.82 (m, 1H, 3*β-H*), 3.68 (s, 3H, $COOCH_3$), 3.09–3.11 (bs, 4H, Ar-NH_2), 0.86 (s, 3H, 19-CH_3), 0.80 (d, J = 5.2 Hz, 3H, 21-CH_3), 0.68 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 1635.94 ([2M+H]$^+$, 100). Anal. Calcd for $C_{45}H_{58}N_8O_6$: C, 66.97; H, 7.24; N, 13.89. Found: C, 66.86; H, 7.22; N, 13.91%.

5c: White solid, yield 94%, m.p. 88–90 °C; $[\alpha]_D^{20}$–34.1 (c 0.2, CH_2Cl_2); IR (KBr) (cm^{-1}): 2950, 2870, 1743, 1619, 1564, 1501, 1460, 1357, 1250, 1223, 1108, 1078, 1031, 976; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (s, 1H, triazole-H), 7.73 (s, 1H, triazole-H), 7.73–7.77 (m, 4H, ArH), 6.97 (s, 2H, ArH), 6.89 (s, 2H, ArH), 5.30 (s, 2H, -$OCOCH_2$), 5.11–5.15 (m, 2H, -$OCOCH_2$), 5.15 (s, 1H, 12*β-H*), 4.81 (bs, 1H, 3*β-H*), 3.86 (s, 3H, Ar-OCH_3), 3.81 (s, 3H, Ar-OCH_3), 3.67 (s, 3H, $COOCH_3$), 0.87 (s, 3H, 19-CH_3), 0.80 (d, J = 5.2 Hz, 3H, 21-CH_3), 0.69 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 837.24 ([M+H]$^+$,100). Anal. Calcd for $C_{47}H_{60}N_6O_8$: C, 67.44; H, 7.23; N, 10.04. Found: C, 67.37; H, 7.25; N, 10.05%.

5d: White solid, yield 89%, m.p. 99–101 °C; $[\alpha]_D^{20}$–68.2 (c 0.2, CH_2Cl_2); IR (KBr) (cm^{-1}): 2950, 2869, 1743, 1467, 1381, 1356, 1266, 1223, 1096, 1070, 1045, 1009, 975; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.08 (s, 1H, triazole-H), 7.93 (s, 1H, triazole-H), 7.69 (d, J = 8.4 Hz, 2H, ArH), 7.62 (d, J = 8.4 Hz, 2H, ArH), 7.56 (d, J = 8.4 Hz, 2H, ArH), 7.46 (d, J = 8.4 Hz, 2H, ArH), 5.30 (s, 2H, -$OCOCH_2$), 5.10–5.21 (m, 2H, -$OCOCH_2$), 5.16 (s, 1H, 12*β-H*), 4.78–4.84 (m, 1H, 3*β-H*), 3.68 (s, 3H, $COOCH_3$), 0.88 (s, 3H, 19-CH_3), 0.80 (d, J = 7.2 Hz, 3H, 21-CH_3), 0.69 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 935.40 ([M+H]$^+$, 100). Anal. Calcd for $C_{45}H_{54}Br_2N_6O_6$: C, 57.82; H, 5.82; N, 8.99. Found: C, 57.78; H, 5.80; N, 8.97%.

5e: White solid, yield 92%, m.p. 91–93 °C; $[\alpha]_D^{20}$–61.4 (c 0.2, CH_2Cl_2); IR (KBr) (cm^{-1}): 2950, 2869, 1743, 1500, 1459, 1381, 1356, 1268, 1218, 1077, 1045, 977; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (s, 1H, triazole-H), 7.84 (s, 1H, triazole-H), 7.71 (d, J = 8 Hz, 2H, ArH), 7.65 (d, J = 8 Hz, 2H, ArH), 7.24 (d, J = 8 Hz, 2H, ArH), 7.16 (d, J = 8 Hz, 2H, ArH), 5.29 (s, 2H, -$OCOCH_2$), 5.05–5.17 (m, 2H, -$OCOCH_2$), 5.15 (s, 1H, 12*β-H*), 4.78–4.83 (m, 1H, 3*β-H*), 3.67 (s, 3H, $COOCH_3$), 2.39 (s, 3H, Ar-CH_3), 2.35 (s, 3H, Ar-CH_3), 0.87 (s, 3H, 19-CH_3), 0.80 (d, J = 5.2 Hz, 3H, 21-CH_3), 0.69 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 805.27 ([M+H]$^+$, 100). Anal. Calcd for $C_{47}H_{60}N_6O_6$: C, 70.12; H, 7.51; N, 10.44. Found: C, 70.02; H, 7.53; N, 10.42%.

5f: White solid, yield 91%, m.p. 96–98 °C; $[\alpha]_D^{20}$–109.1 (c 0.2, CH_2Cl_2); IR (KBr) (cm^{-1}): 2960, 2870, 1743, 1458, 1412, 1382, 1356, 1266, 1221, 1093, 1045, 1012, 926; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.08 (s, 1H, triazole-H), 7.92 (s, 1H, triazole-H), 7.76 (d, J = 8.4 Hz, 2H, ArH), 7.69 (d, J = 8.4 Hz, 2H, ArH), 7.41 (d, J = 8 Hz, 2H, ArH), 7.31 (d, J = 8.4 Hz, 2H, ArH), 5.30 (s, 2H, -$OCOCH_2$), 5.10–5.22 (m, 2H, -$OCOCH_2$), 5.16 (s, 1H, 12*β-H*), 4.79–4.84 (m, 1H, 3*β-H*), 3.68 (s, 3H, $COOCH_3$), 0.88 (s, 3H, 19-CH_3), 0.81 (d, J = 4.8 Hz, 3H, 21-CH_3), 0.69 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 845.46 ([M+H]$^+$, 100). Anal. Calcd for $C_{45}H_{54}Cl_2N_6O_6$: C, 63.90; H, 6.43; N, 9.94. Found: C, 63.77; H, 6.45; N, 9.90%.

5g: White solid, yield 91%, m.p. 98–100 °C; $[\alpha]_D^{20}$–77.3 (c 0.2, CH_2Cl_2); IR (KBr) (cm^{-1}): 2956, 2870, 1743, 1500, 1459, 1381, 1356, 1267, 1218, 1076, 1046, 977; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.06 (s, 1H, triazole-H), 7.86 (s, 1H, triazole-H), 7.74 (d, J = 8.4 Hz, 2H, ArH), 7.69 (d, J = 8.4 Hz, 2H, ArH), 7.27 (d, J = 8 Hz, 2H, ArH), 7.19 (d, J = 8.4 Hz, 2H, ArH), 5.30 (s, 2H, -$OCOCH_2$), 5.06–5.18 (m, 2H, -$OCOCH_2$), 5.16 (s, 1H, 12*β-H*), 4.78–4.83 (m, 1H, 3*β-H*), 3.67 (s, 3H, $COOCH_3$), 2.62–2.72 (m, 4H, Ar-CH_2), 1.18–1.29 (m, 6H, ArCH_2-CH_3), 0.87 (s, 3H, 19-CH_3), 0.80 (d, J = 5.6 Hz, 3H, 21-CH_3), 0.69 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 833.60 ([M+H]$^+$, 100). Anal. Calcd for $C_{49}H_{64}N_6O_6$: C, 70.65; H, 7.74; N, 10.09. Found: C, 70.55; H, 7.76; N, 10.10%.

5h: White solid, yield 90%, m.p. 82–84 °C; $[\alpha]_D^{20}$–52.3 (c 0.2, CH_2Cl_2); IR (KBr) (cm^{-1}): 2950, 2871, 1743, 1614, 1563, 1499, 1461, 1416, 1382, 1356, 1267, 1223, 1159, 1095, 977; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.04 (s, 1H, triazole-H), 7.89 (s, 1H, triazole-H), 7.78–7.81 (m, 2H, ArH), 7.71–7.75 (m, 2H, ArH), 7.13 (t, J = 8.4 Hz, 2H, ArH), 7.04 (t, J = 8.4 Hz, 2H, ArH), 5.30 (s, 2H, -$OCOCH_2$), 5.11–5.22 (m, 2H, -$OCOCH_2$), 5.16 (s, 1H, 12*β-H*), 4.78–4.84 (m, 1H, 3*β-H*), 3.68 (s, 3H, $COOCH_3$), 0.88 (s, 3H, 19-CH_3), 0.81 (d, J = 5.6 Hz, 3H, 21-CH_3), 0.69 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 813.52 ([M+H]$^+$, 100). Anal. Calcd for $C_{45}H_{54}F_2N_6O_6$: C, 66.48; H, 6.70; N, 10.34. Found: C, 66.39; H, 6.71; N, 10.32%.

5i: White solid, yield 94%, m.p. 92–94 °C; $[\alpha]_D^{20}$–125 (c 0.2, CH_2Cl_2); IR (KBr) (cm^{-1}): 2955, 2869, 1743, 1499, 1459, 1381, 1357, 1265, 1217, 1077, 1045, 977; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.06 (s, 1H, triazole-H), 7.86 (s, 1H, triazole-H), 7.74 (d, J = 8 Hz, 2H, ArH), 7.68 (d, J = 8.4 Hz, 2H, ArH), 7.24 (d, J = 8 Hz, 2H, ArH), 7.17 (d, J = 7.6 Hz, 2H, ArH), 5.30 (s, 2H, -$OCOCH_2$), 5.06–5.19 (m, 2H, -$OCOCH_2$), 5.16 (s, 1H, 12*β-H*), 4.77–4.83 (m, 1H, 3*β-H*), 3.68 (s, 3H, $COOCH_3$), 2.57–2.64 (m, 4H, Ar-CH_2), 1.64–1.72 (m, 4H, Ar-CH_2-CH_2), 0.93–0.97 (m, 6H, Ar-C_2H_4-CH_3), 0.87 (s, 3H, 19-CH_3), 0.80 (d, J = 5.6 Hz, 3H, 21-CH_3), 0.69 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 861.68 ([M+H]$^+$, 100). Anal. Calcd for $C_{51}H_{68}N_6O_6$: C, 71.13; H, 7.96; N, 9.76. Found: C, 71.05; H, 7.98; N, 9.74%.

5j: Yellow solid, yield 94%, m.p. 115–117 °C, $[\alpha]_D^{20}$–36.4 (c 0.2, CH_2Cl_2); IR (KBr) (cm^{-1}): 2949, 2870, 1743, 1606, 1519, 1461, 1342, 1267, 1221, 1109, 1045, 976; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32 (s, 1H, triazole-H), 8.30 (s, 1H, triazole-H), 8.17–8.30 (m, 4H, ArH), 8.00 (d, J = 9.2 Hz, 2H, ArH), 7.95 (d, J = 9.2 Hz, 2H, ArH), 5.39 (s, 2H, -$OCOCH_2$), 5.21–5.35 (m, 2H, -$OCOCH_2$), 5.19 (s, 1H, 12*β-H*), 4.81–4.86 (m, 1H, 3*β-H*), 3.69 (s, 3H, $COOCH_3$), 0.89 (s, 3H, 19-CH_3), 0.82 (d, J = 5.2 Hz, 3H, 21-CH_3), 0.71 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 867.12 ([M+H]$^+$, 100). Anal. Calcd for $C_{45}H_{54}N_8O_{10}$: C, 62.34; H, 6.28; N, 12.92. Found: C, 62.30; H, 6.27; N, 12.89%.

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