Synthesis of novel arylhydrazide molecular tweezer artificial receptors based on deoxycholic acid using microwave irradiation

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Eleven novel molecular tweezer anion receptors based on deoxycholic acid have been synthesised using microwave irradiation. Their structures were established 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 these molecular tweezers show good recognition properties for $H_2PO_4^-$, CH_3COO^- and NO_3^-.

Keywords: molecular tweezers, microwave irradiation, molecular recognition, deoxycholic acid

Anions play an important role in biology, pharmacy, catalysis and environmental science.[1] The study of artificial receptors for the detection of biologically relevant anions is an important challenge in modern bioorganic chemistry.[2–9] The basic strategies which have been exploited for the construction of anion-binding receptors involve electrostatic interactions, hydrogen bonding, hydrophobicity, coordination to a metal ion, or a combination of these. Among these noncovalent interactions, we have been interested in developing hydrogen bond-based neutral anion receptors. Owing to the relatively strong hydrogen bonding ability of the hydrazide and arylhydrazide groups, a number of molecules possessing hydrazides or arylhydrazides groups have been designed as neutral receptors for various anions.[10–12] For strong and selective binding, these groups should be preorganized to complement the target anion and minimize intramolecular hydrogen bonding. One way to achieve this goal is to make receptors with hydrazide or arylhydrazide groups connected to rigid spacers. The steroid nucleus is one of the largest rigid and chiral ubiquitous natural products. Based on these preorganized structural characteristics, the steroid cholic acid is an ideal building block for the construction of molecular tweezer artificial receptors. We have reported that alkoxycarbonyl thiosemicarbazide molecular tweezer receptors which contain three NH bonds have good recognition properties for anions.[13] On the basis of this, we have synthesised 11 novel arylhydrazide molecular tweezer artificial receptors **7a–k**, which contain four NH bonds. These receptors based on arylhydrazide arms, have the NH groups directed towards the centre of the cavity resulting in a high selectivity in combining with the substrates. The recognition properties of the receptors have been examined by UV-Vis spectra titration. The preliminary results indicate that this kind of molecular tweezers show good recognition properties for $H_2PO_4^-$, CH_3COO^-, NO_3^-. The synthetic route is shown in Scheme 1.

Results and discussion

In searching for the best reaction conditions of the synthesis of molecular tweezer artificial receptors, we used the synthesis of **7a** as an example and carried out several experiments under different conditions, such as microwave irradiation power, time and solvent to obtain the best results of this reaction. The results are shown in the following tables.

As shown in Table 1, we irradiated the reaction using different powers under the same reaction time (15 min). As a result, 150 W was the optimum power.

As shown in Table 2, we found that 15 min was the optimum reaction time when the yield was the highest using the same power (150 W). However, more byproducts were obtained when the reaction time was increased.

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As shown in Table 3, the effect of CH_2Cl_2, $CHCl_3$ and THF as a solvent on the reaction was investigated. The results showed that when CH_2Cl_2 was used, the yield was a little higher and considering CH_2Cl_2 is less toxic than $CHCl_3$, THF, hence CH_2Cl_2 was the best solvent for the reaction.

As shown in Table 4, we compared the synthesis of molecular tweezers **7a–k** by microwave irradiation and conventional heating. Compared to conventional thermal heating, microwave irradiation greatly decreased the reaction time from 480–600 min to 15–25 min. It was obvious that yields were increased from 35–50% to 87–94%. From these data, we conclude that microwave irradiation method is a rapid, efficient methodology.

The variations in the UV-Vis absorption of these complexing system has been used as an effective and simple method to measure the association constants of complexes in supramolecular systems.

Titration experiments for the anion recognition of receptors **7a**, **7e**, **7i**, **7j** were performed using UV-Vis spectroscopy in $CHCl_3$ at 25 °C. Using the linear fitting method, we obtained the association constants for complex formation. The preliminary results showed that these molecular tweezers possessed the ability to form complexes with the guest anions which were examined as shown in Fig. 1. The supramolecular complexes consisted of 1:1 host and guest molecules. The association constants of molecular tweezer **7i**, for example, are 465348, 124961, 32359 L mol^{-1} for $H_2PO_4^-$, CH_3COO^-, NO_3^- anions respectively. The main driving force are the multiple hydrogen bonds in molecular recognition. The UV-Vis plot of **7i** for $H_2PO_4^-$ is shown in Fig. 2.

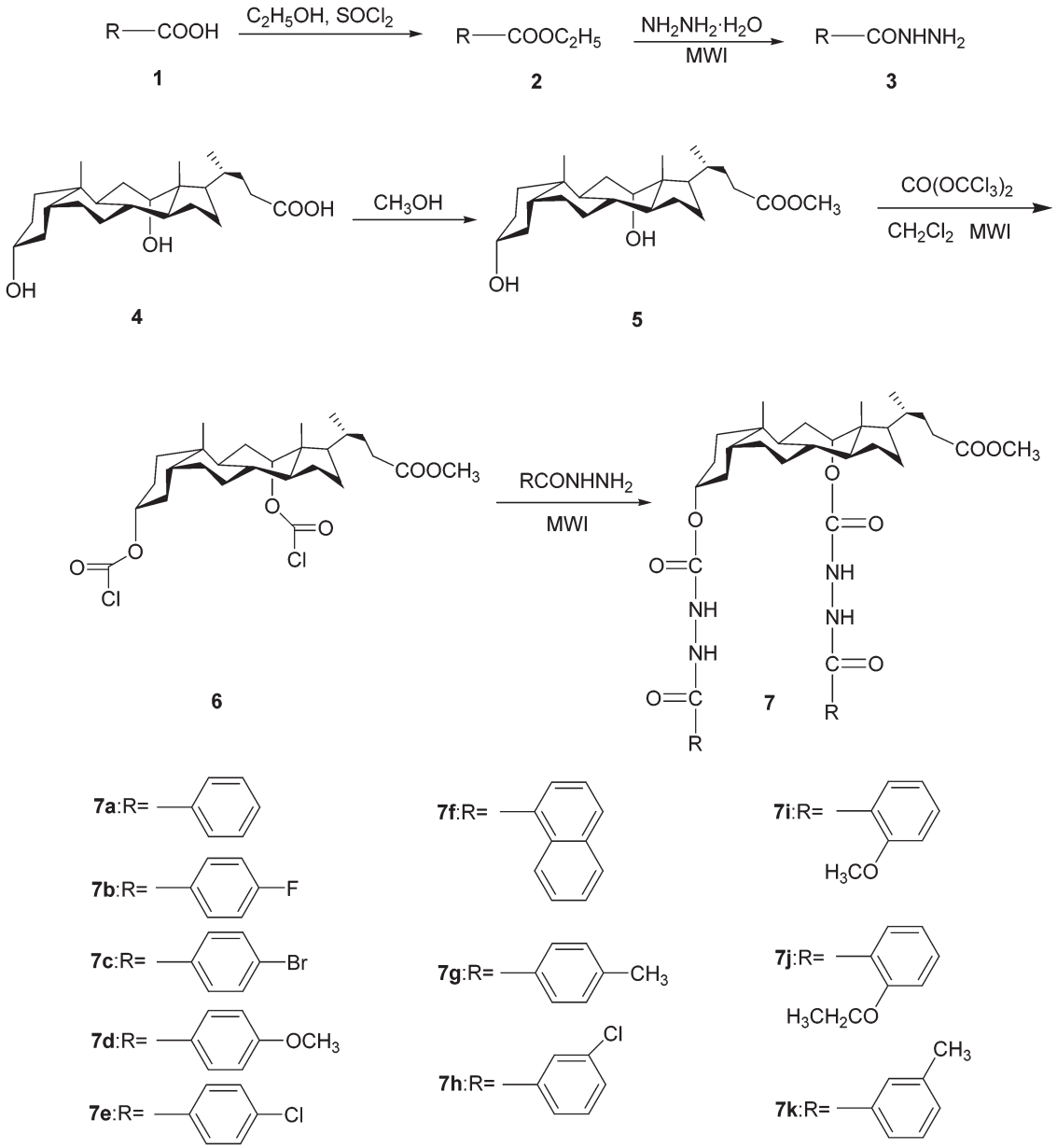
The main reason is that when the host **7i** is at the minimum energy, its conformation is similar to the X-ray crystal structure of desoxycholic acid *p*-bromoanilide, which has the ability to form complex with guest molecules.[14] The crystal structure of desoxycholic acid *p*-bromoanilide is shown in Fig. 3.

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 autoanalyzer. All reactions were performed in a commercial microwave reactor(XH-100A, 100–1000 W, Beijing Xianghu Science and Technology Development Co. Ltd, Beijing, P.R. China). All the solvents were purified before use. Optical rotations were measured on a Wzz-2B polarimeter. All the solvents were purified before use.

Preparation of **3a–k**; *general procedure*

The aromatic acid (5 mmol), thionyl chloride (0.2 mL) and ethanol (15 mL) were placed in a dried round-bottomed flask and the mixture was irradiated by microwaves (75 W) for 4 min. On completion of the reaction, the mixture was cooled to room temperature. The excess



Scheme 1 The synthetic route of molecular tweezers **7a–k**.

Table 1 The effect of microwave power on yield

Power/W	50	100	150	200	250
Yield/%	60	85	92	89	78

Table 2 The effect of microwave irradiation time on yield

Time/min	7	9	11	13	15	17
Yield/%	67	73	78	83	92	87

Table 3 The effect of solvent on yield

Entry	Solvent	Yield/%	Volume of solvent/mL
1	CH_2Cl_2	92	10
2	$CHCl_3$	86	10
3	THF	75	15

Table 4 Synthetic comparison of molecular tweezers **7a–7k** between microwave irradiation and conventional heating

Compd	Conventional method		Microwave method		t_C^a/t_{MW}^b
	t/min	Yield/%	t/min	Yield/%	
7a	480	50	15.0	92	32
7b	600	36	25.0	90	24
7c	480	50	15.0	89	32
7d	540	48	18.0	91	30
7e	480	45	15.0	92	32
7f	600	35	25.0	89	24
7g	480	48	16.0	88	30
7h	600	48	20.0	87	30
7i	540	37	19.0	94	28
7j	480	48	15.0	93	32
7k	540	45	20.0	90	27

T_C^a, time of conventional heating method; T_{MW}^b, time of microwave irradiation method.

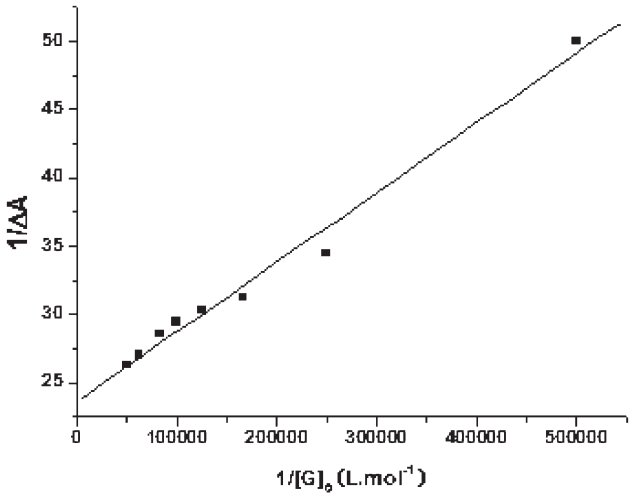


Fig. 1 Typical plot of $1/\Delta A$ versus $1/[G]_0$ for the inclusion complex of molecular tweezer **7i** with $H_2PO_4^-$ in $CHCl_3$ at 25 °C.

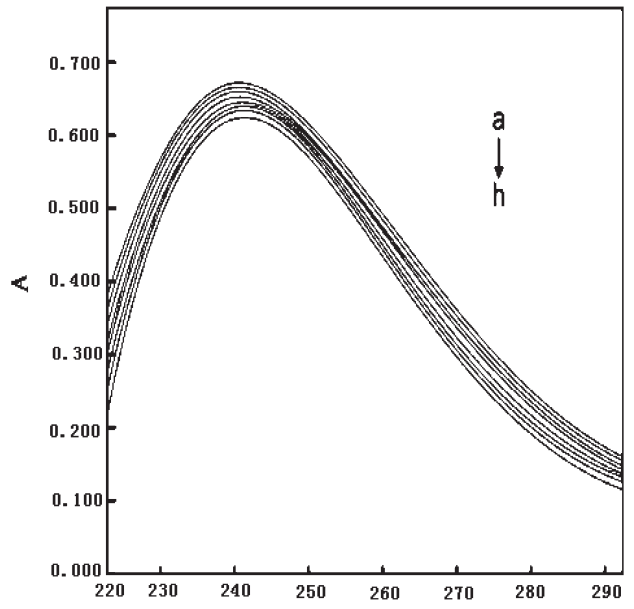


Fig. 2 UV-vis spectra of molecular tweezers **7i** (1.2×10^{-4}mol L^{-1}) in the presence of $H_2PO_4^-$ (a) 0 molL^{-1}; (b) 0.002×10^{-3}molL^{-1}; (c) 0.002×10^{-3}mol L^{-1}; (d) 0.002×10^{-3}molL^{-1}; (e) 0.002×10^{-3}molL^{-1}; (f) 0.002×10^{-3}molL^{-1}; (g) 0.004×10^{-3}mol L^{-1} with λ_{max} at 242.0 nm.

thionyl chloride was removed. Then the reaction mixture was added to 85% hydrazine hydrate (2 mL) and subjected to microwave irradiation (75 W) for 3 min. The mixture was evaporated to give the crude product. The crude product was recrystallised from ethanol to give a pure sample. The melting points of the hydrazides **3a–k** are shown in Table 5.

Preparation of compound **5**; *general procedure*

Deoxycholic acid **4** was converted to methyl 3α,12α-dihydroxy-7-deoxy-5β -cholan-24-oate **5** following the literature procedure.[16]

Microwave method for preparation of **7a–k**

Triphosgene (0.37 mol) was added to a solution of compound **5** (0.5 mmol) in 10 mL dry CH_2Cl_2 and 0.2 mL dry pyridine at room temperature. The reaction mixture was irradiated for 15 min at 150 W to give compound **6**. The arylhydrazide (1.5 mmol) and dry pyridine 0.2 mL were added directly to the mixture, Which was then irradiated continually for 15–25 min at 150 W. The solvent was removed and the residue was diluted with 20 mL ethyl acetate and washed with 10% HCl (10 mL×3), brine (10 mL×3), and finally dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography on silica gel H with dichloromethane/ethyl acetate as eluant. The whole progress was monitored by TLC. The physical and spectra data of the compounds **7a–k** are as follows.

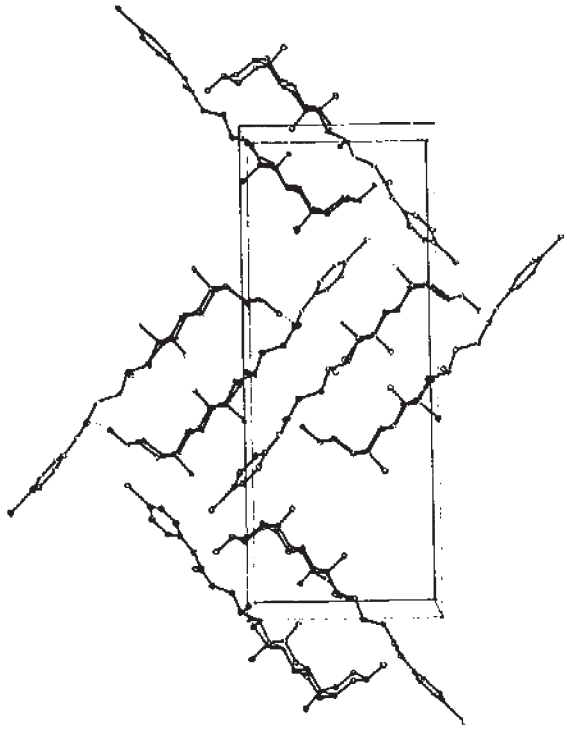


Fig. 3 A view of the contents of a unit cell in the crystal of desoxycholic acid *p*-bromoanilide(we thank John P. Schaefer and Larry L. Reed for the X-ray crystal structure of desoxycholic acid *p*-bromoanilide support).

Table 5 The melting points of hydrazides **3a–k**

Entry	Compound	Yield/%	M.p./°C	Lit. m.p./°C
1	**3a**	85	112–114	112.5[12]
2	**3b**	80	160–163	162–166[12]
3	**3c**	80	249–251	251–253[12]
4	**3d**	82	135–137	137–139[12]
5	**3e**	78	117–118	118–120[12]
6	**3f**	83	160–163	160–162.5[12]
7	**3g**	78	116–118	115[12]
8	**3h**	75	121–123	122–124[15]
9	**3i**	83	78–80	78–80[12]
10	**3j**	85	63–65	62–64[12]
11	**3k**	88	98–100	101–103[12]

7a: White crystals, yield 92%, m.p. 130–132 °C; $[\alpha]_D^{20}$ +83.6 (*c* 0.11, CH_2Cl_2); IR (KBr, cm^{-1}): 3287, 2950, 2869, 1736, 1673, 1525, 1486, 1245, 1024, 693; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 8.80 (s, 2H, CONH), 7.92 (d, *J* = 7.6 Hz, 2H, ArH), 7.84 (d, *J* = 7.2 Hz, 2H, ArH), 7.52 (t, *J* = 7.0 Hz, 3H, ArH and NHCOO), 7.43–7.37 (m, 5H, ArH), 5.02 (s, 1H, 12β-H), 4.63 (s, 1H, 3β-H), 3.66 (s, 3H, $COOCH_3$), 0.95 (s, 3H, 19-CH_3), 0.85 (d, *J* = 6.8 Hz, 3H, 21-CH_3), 0.68 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 1483.91 ([2M+Na]$^+$, 100). Anal. Calcd for $C_{41}H_{54}N_4O_8$: C, 67.38; H, 7.45; N, 7.67. Found: C, 67.25; H, 7.47; N, 7.66%.

7b: White crystals, yield 90%, m.p. 138–139 °C; $[\alpha]_D^{20}$ +150.8 (*c* 0.12, CH_2Cl_2); IR (KBr, cm^{-1}): 3299, 2949, 2870, 1736, 1671, 1604, 1501, 1238, 1160, 1039, 852, 762, 605; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 8.86 (s, 2H, CONH), 7.95 (s, 2H, ArH), 7.85 (s, 2H, ArH), 7.52 (s, 2H, NHCOO), 7.26–7.06 (m, 4H, ArH), 5.02 (s, 1H, 12β-H), 4.62 (s, 1H, 3β-H), 3.67 (s, 3H, $COOCH_3$), 0.96 (s, 3H, 19-CH_3), 0.86 (d, *J* = 6.8 Hz, 3H, 21-CH_3), 0.69 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 767.71 ([M+H]$^+$, 100). Anal. Calcd for $C_{41}H_{52}F_2N_4O_8$: C, 64.21; H, 6.83; N, 7.31. Found: C, 64.09; H, 6.85; N, 7.32%.

7c: White crystals, yield 89%, m.p. 145–146 °C; $[\alpha]_D^{20}$ +136.0 (*c* 0.15,CH_2Cl_2); IR (KBr, cm^{-1}): 3285, 2951, 2869, 1736, 1665, 1592,

1481, 1248, 1071, 1011, 845, 754, 617; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 8.92 (s, 2H, CONH), 7.78 (d, *J* = 7.2 Hz, 3H, ArH), 7.69 (d, *J* = 6.8 Hz, 2H, ArH), 7.55 (d, *J* = 8.0 Hz, 5H, ArH and NHCOO), 5.02 (s, 1H, 12*β*-H), 4.62 (s, 1H, 3*β*-H), 3.67 (s, 3H, $COOCH_3$), 0.94 (s, 3H, 19-CH_3), 0.87 (d, *J* = 6.4 Hz, 3H, 21-CH_3), 0.69 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 1799.33 ([2M+Na]$^+$, 100). Anal. Calcd for $C_{41}H_{52}Br_2N_4O_8$: C, 55.41; H, 5.90; N, 6.30. Found: C, 55.56; H, 5.89; N, 6.29%.

7d: White crystals, yield 91%, m.p. 137–138 °C; $[\alpha]_D^{20}$ +156.2 (*c* 0.13,CH_2Cl_2); IR (KBr, cm^{-1}): 3307, 2948, 2869, 1735, 1664, 1608, 1503, 1250, 1175, 1027, 846, 764, 609; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 8.65 (s, 2H, CONH), 7.89–7.80 (m, 4H, ArH), 7.26 (s, 2H, NHCOO), 6.91–6.85 (m, 4H, ArH), 5.02 (s, 1H, 12*β*-H), 4.63 (s, 1H, 3*β*-H), 3.83 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 3.67 (s, 3H, $COOCH_3$), 0.95 (s, 3H, 19-CH_3), 0.86 (d, *J* = 6.8 Hz, 3H, 21-CH_3), 0.68 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 1581.69 ([2M+H]$^+$, 100). Anal. Calcd for $C_{43}H_{58}N_4O_{10}$: C, 65.30; H, 7.39; N, 7.08. Found: C, 65.39; H, 7.37; N, 7.09%.

7e: White crystals, yield 92%, m.p. 148–149 °C; $[\alpha]_D^{20}$ +95.6 (*c* 0.11, CH_2Cl_2); IR (KBr, cm^{-1}): 3395, 2951, 2871, 1720, 1665, 1485, 1250, 1092, 1040, 848, 758; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 9.08 (s, 2H, CONH), 7.88 (d, *J* = 6.8 Hz, 2H, ArH), 7.77 (d, *J* = 6.8 Hz, 3H, ArH), 7.39 (t, *J* = 7.8 Hz, 3H, ArH and NHCOO), 7.27 (s, 2H, ArH), 5.01 (s, 1H, 12*β*-H), 4.61 (s, 1H, 3*β*-H), 3.67 (s, 3H, $COOCH_3$), 0.96 (s, 3H, 19-CH_3), 0.86 (d, *J* = 6.8 Hz, 3H, 21-CH_3), 0.68 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 799.50 ([M+H]$^+$, 100). Anal. Calcd for $C_{41}H_{52}Cl_2N_4O_8$: C, 61.57; H, 6.55; N, 7.01. Found: C, 61.49; H, 6.56; N, 7.00%.

7f: White crystals, yield 89%, m.p. 133–134 °C; $[\alpha]_D^{20}$ +128.6 (*c* 0.14,CH_2Cl_2); IR (KBr, cm^{-1}): 3299, 2947, 2868, 1735, 1677, 1511, 1470, 1244, 1218, 1040, 806, 782, 604; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 8.39 (s, 2H, CONH), 7.92–7.84 (m, 5H, ArH), 7.52 (s, 7H, ArH and NHCOO), 7.40 (s, 3H, ArH), 6.48 (s, 1H, ArH), 5.07 (s, 1H, 12*β*-H), 4.79 (s, 1H, 3*β*-H), 3.67 (d, *J* = 2.0 Hz, 3H, $COOCH_3$), 0.99 (s, 3H, 19-CH_3), 0.93 (d, *J* = 6.8 Hz, 3H, 21-CH_3), 0.75 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 831.74 ([M+H]$^+$, 100). Anal. Calcd for $C_{49}H_{58}N_4O_8$: C, 70.82; H, 7.03; N, 6.74. Found: C, 70.71; H, 7.05; N, 6.73%.

7g: White crystals, yield 88%, m.p. 134–135 °C; $[\alpha]_D^{20}$ +70.0 (*c* 0.12,CH_2Cl_2); IR (KBr, cm^{-1}): 3287, 2951, 2869, 1736, 1667, 1529, 1499, 1248, 1212, 1038, 1020, 837, 751; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 8.65 (s, 2H, CONH), 7.80–7.71 (m, 4H, ArH), 7.52 (s, 2H, NHCOO), 7.26–7.16 (m, 4H, ArH), 5.02 (s, 1H, 12*β*-H), 4.63 (s, 1H, 3*β*-H), 3.67 (s, 3H, $COOCH_3$), 2.37 (d, *J* = 3.6 Hz, 6H, CH_3), 0.96 (s, 3H, 19-CH_3), 0.86 (d, *J* = 6.8 Hz, 3H, 21-CH_3), 0.68 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 1518.74 ([2M+Na]$^+$, 100). Anal. Calcd for $C_{43}H_{58}N_4O_8$: C, 68.05; H, 7.70; N, 7.38. Found: C, 67.93; H, 7.72; N, 7.40%.

7h: White crystals, yield 87%, m.p. 126–127 °C; $[\alpha]_D^{20}$ +128.7 (*c* 0.15,CH_2Cl_2); IR (KBr, cm^{-1}): 3295, 2948, 2869, 1736, 1672, 1470, 1245, 1040, 747, 680; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 8.92 (s, 2H, CONH), 7.89 (s, 1H, ArH), 7.84–7.82 (m, 2H, ArH), 7.70 (d, *J* = 8.0 Hz, 2H, ArH), 7.52–7.46 (m, 3H, ArH and NHCOO), 7.42–7.34 (m, 2H, ArH), 5.03 (s, 1H, 12*β*-H), 4.66 (s, 1H, 3*β*-H), 3.67 (s, 3H, $COOCH_3$), 0.97 (s, 3H, 19-CH_3), 0.90 (d, *J* = 6.4 Hz, 3H, 21-CH_3), 0.69 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 799.42 ([M+H]$^+$, 100). Anal. Calcd for $C_{41}H_{52}Cl_2N_4O_8$: C, 61.57; H, 6.55; N, 7.01. Found: C, 61.47; H, 6.56; N, 7.00%.

7i: White crystals, yield 94%, m.p. 121–122 °C; $[\alpha]_D^{20}$ +122.3 (*c* 0.13,CH_2Cl_2); IR (KBr, cm^{-1}): 3385, 2949, 2869, 1736, 1673, 1602, 1482, 1279, 1238, 1018, 757, 616; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 9.60 (d, *J* = 3.6 Hz, 2H, CONH), 8.26–8.19 (m, 2H, NHCOO), 7.49 (t, *J* = 7.0 Hz, 4H, ArH), 7.10 (t, *J* = 7.4 Hz, 2H, ArH), 7.01 (t, *J* = 8.4 Hz, 2H, ArH), 5.06 (s, 1H, 12*β*-H), 4.71 (s, 1H, 3*β*-H), 4.03 (s, 3H, OCH_3), 3.99 (s, 3H, OCH_3), 3.67(s, 3H, $COOCH_3$), 0.99 (s, 3H, 19-CH_3), 0.90 (d, *J* = 6.8 Hz, 3H, 21-CH_3), 0.71 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 1581.60 ([2M+H]$^+$, 100). Anal. Calcd for $C_{43}H_{58}N_4O_8$: C, 65.30; H, 7.39; N, 7.08. Found: C, 65.19; H, 7.41; N, 7.07%.

7j: White crystals, yield 93%, m.p. 93–94 °C; $[\alpha]_D^{20}$ +125.0 (*c* 0.12, CH_2Cl_2); IR (KBr, cm^{-1}): 3387, 2948, 2870, 1736, 1674, 1474, 1236, 1035, 757, 613; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 9.90–9.82 (m, 2H, CONH), 8.23 (s, 1H, NHCOO), 8.2 (d, *J* = 7.6 Hz, 1H, NHCOO), 7.45 (s, 3H, ArH), 7.32 (s, 1H, ArH), 7.09–6.96 (m, 4H, ArH), 5.08 (s, 1H, 12*β*-H), 4.72 (s, 1H, 3*β*-H), 4.26–4.21 (m, 4H, OCH_2), 3.66 (s, 3H, $COOCH_3$), 1.64–1.56 (m, 6H, CH_3), 0.99 (s, 3H, 19-CH_3), 0.91 (d, *J* = 6.4 Hz, 3H, 21-CH_3), 0.72 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 819.70 ([M+H]$^+$, 100). Anal. Calcd for $C_{45}H_{62}N_4O_{10}$: C, 65.99; H, 7.63; N, 6.84. Found: C, 66.08; H, 7.61; N, 6.86%.

7k: White crystals, yield 90%, m.p. 123–124 °C; $[\alpha]_D^{20}$ +34.5 (*c* 0.11, CH_2Cl_2); IR (KBr, cm^{-1}): 3288, 2950, 2868, 1736, 1669, 1522, 1482, 1262, 1224, 1040, 744, 689; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 8.55 (s, 2H, CONH), 7.69 (s, 2H, ArH), 7.62 (s, 2H, NHCOO), 7.30 (d, *J* = 4.8 Hz, 6H, ArH), 5.03 (s, 1H, 12*β*-H), 4.65 (s, 1H, 3*β*-H), 3.66 (s, 3H, $COOCH_3$), 2.34 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 0.94 (s, 3H, 19-CH_3), 0.87 (d, *J* = 6.8 Hz, 3H, 21-CH_3), 0.69 (s, 3H, 18-CH_3); ESI-MS *m/z* (%): 1518.85 ([2M+H]$^+$, 100). Anal. Calcd for $C_{43}H_{58}N_4O_8$: C, 68.05; H, 7.70; N, 7.38. Found: C, 67.92; H, 7.72; N, 7.39%.

Conventional heating method for preparation of **7a–k**

Triphosgene (0.37 mol) was added to a solution of compound **5** (0.5 mmol) in 10 mL dry CH_2Cl_2 and 0.2 mL dry pyridine at room temperature. The solution was refluxed for 5 h, to give compound **6**. The arylhydrazide (1.5 mmol) and dry pyridine 0.2 mL were added directly to the mixture which was refluxed for a further 6–10 h. The solvent was removed and the residue was diluted with 20 mL ethyl acetate and washed with 10% HCl (10 mL×3), brine (10 mL×3), and finally dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography on silica gel H with dichloromethane/ethyl acetate as eluant to give the products in 35–50% yields.

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