One-pot synthesis of new carbamate-type molecular tweezers derived from deoxycholic acid under microwave irradiation

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A rapid, safe, and efficient method for the preparation of new carbamate type molecular tweezers based on deoxycholic acid was reported. Eleven new molecular tweezers have been synthesised in good yield(91–96%). The structures of these receptors were confirmed by ^{1}H NMR, IR, MS spectra and elemental analysis. These molecular tweezers not only recognised neutral molecules, but also showed good enantioselectivity for D-amino acid methyl esters.

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

Molecular recognition plays a pivotal role in life processes.[1] Ove the past two decades a number of artificial receptors for neutral organic molecules, chiral molecules, and anions have been successfully synthesised.[2–5] Among the various types of artificial receptors that have been synthesised, a special class of receptors called molecular tweezers are currently attracting great interest. The natural rigid concave structure and inherent asymmetry of cholic acid suggest it is an ideal building block for the construction of molecular tweezers. In recent years, some molecular tweezers based on steroidal cholic acid have been synthesised.[6–9]

The application of microwave techniques for organic synthesis has attracted considerable interest in recent years.[10–13] The reason is that this technology can enhance the selectivity and reactivity, increase the chemical yields and greatly shorten the reaction time. In our previous work,[14–15] it was found that by using microwave irradiation, the ester and carbamate molecular tweezers based on α-hyodeoxycholic acid can be successfully synthesised in less time, higher yields compared to the conventional method. Furthermore, these molecular tweezers have a good enantioselectivity for L-amino acid methyl esters. We have continued our programme to synthesise molecular tweezer artificial receptors using microwave methods[16–18] in order to investigate the effect of the microenvironment and cleft size on molecular recognition ability. We report here a facile and rapid synthetic method of carbamate type molecular tweezer derived from deoxycholic acid under microwave irradiation which, to the best of our knowledge, has not been attempted previously. We have made some preliminarily studies of the recognition properties of this kind of molecular tweezer for neutral molecules and chiral molecules. The synthetic route is depicted in Scheme 1.

Results and discussion

As illustrated in Table 1, microwave-enhanced method compared with the conventional solvent method has the following advantages: (1) the reaction avoids the use of very toxic phosgene and reduces the pollution of the environment; (2) the reaction rate increased 26–31 times, and greatly shortened the reaction time; and (3) the yields of molecular tweezers have increased from 65–73% to 91–96%. The microwave assisted procedure is a safe, fast, efficient and green synthetic method for carbamate type molecular tweezers based on deoxycholic acid.

The recognition of molecular tweezers **4a**, **4b** and **4e** for aromatic amines and D/L –amino acid methyl esters has been investigated by UV-visible spectra titration in $CHCl_3$ at 25 °C. We added aromatic amines and D/L-amino acid methyl esters solution of different concentrations to **4a, 4b** and **4e** of fixed concentration of 1×10^{-4}–10×10^{-4} mol L^{-1}, and measured the characteristic absorbance value of the host–guest complexes. As the guest molecules were being added, the absorbance rose in a regular pattern. It showed that these molecular tweezers possessed the ability to form complex with guests molecules examined. The titration data were analysed by using the Hildebrand-Benesi equation.[19] Based on the equation (1), when $[G]_0>>[H]_0$, the plots of $1/[G]_0$ versus $1/\Delta A$ were measured. The plot gave a straight line . From the intercept and the slope of the line, we calculated with the association constants (*Ka*). The free energy change ($-\Delta G^0$) was obtained according to equation (2). Association constants (*Ka*) and free energy changes ($-\Delta G^0$) for the inclusion complexes of aromatic amines and D/L –amino acid methyl esters with molecular tweezers **4a**, **4b** and **4e** are listed in Tables 2 and 3. As shown in Tables 2 and 3, these molecular tweezers possessed the ability to form complex as with the guest molecules that were examined. The supramolecular complexes consisted of 1:1 host and guest molecules. The association constants of molecular tweezer **4b**, for example, is 5191.20, 1756.30, 3832.40 L·mol^{-1} for *p*-nitroaniline, aniline, *p*-methoxyaniline, respectively. At the same time, these receptors showed good chiral recognition for D-amino acid methyl esters, the maximum K_D/K_L of molecular tweezer **4e** reaches 4.92 for D/L-Tyr-OMe. The details of the molecular recognition of these molecular tweezers are under further study.

$$\frac{1}{\Delta A}=\frac{1}{aKa[G]_0}+\frac{1}{a} \qquad (1)$$

$$\Delta G^0=-RTLnKa \qquad (2)$$

Experimental

Melting points were determined on a micro-melting point apparatus and the thermometer was uncorrected. IR spectra were obtained on 1700 Perkin-Elmer FTIR using KBr disks. ^{1}H NMR spectra were recorded on a Varian INORA 400MHz spectrometer in $CDCl_3$ as solvent and TMS as internal standard. Mass spectra were determined on Finnigan LCQ^{DECA} instrument. Elemental analyses were performed on a Car10-Erba-1106 auto analyser. Optical rotation was measured on a Wzz-2B polarimeter. Microwave irradiation was carried out with a MCL-3 microwave oven at full power (700 W). The oven was modified from a domestic microwave oven and tested to conform to the performance index before use. All the solvents were purified before use. Deoxycholic acid was converted to deoxycholic acid methyl ester following a reported procedure.[20]

Microwave method for the preparation of molecular tweezers **4a–k**

Triphosgene (0.11 g, 0.37 mmol)was added to a solution of methyl deoxycholate **2** (0.2 g, 0.5 mmol) in dry CH_2Cl_2 (10 mL) and dry pyridine (0.2 mL) at room temperature. The solution was placed in the microwave oven and irradiated for 10 min at 100 W. Intermediate **3** was formed and without separation, the aromatic amines (1.5 mmol) and dry pyridine (0.2 mL) were added directly to the mixture and the irradiation was continued for 10–15 min at the same power. The solvent was removed and the residue was diluted with ethyl acetate (30 mL) and washed with 10% $NaHCO_3$ (15 mL×3), brine (15 mL×3), and finally dried over anhydrous Na_2SO_4. The solvent was evaporated

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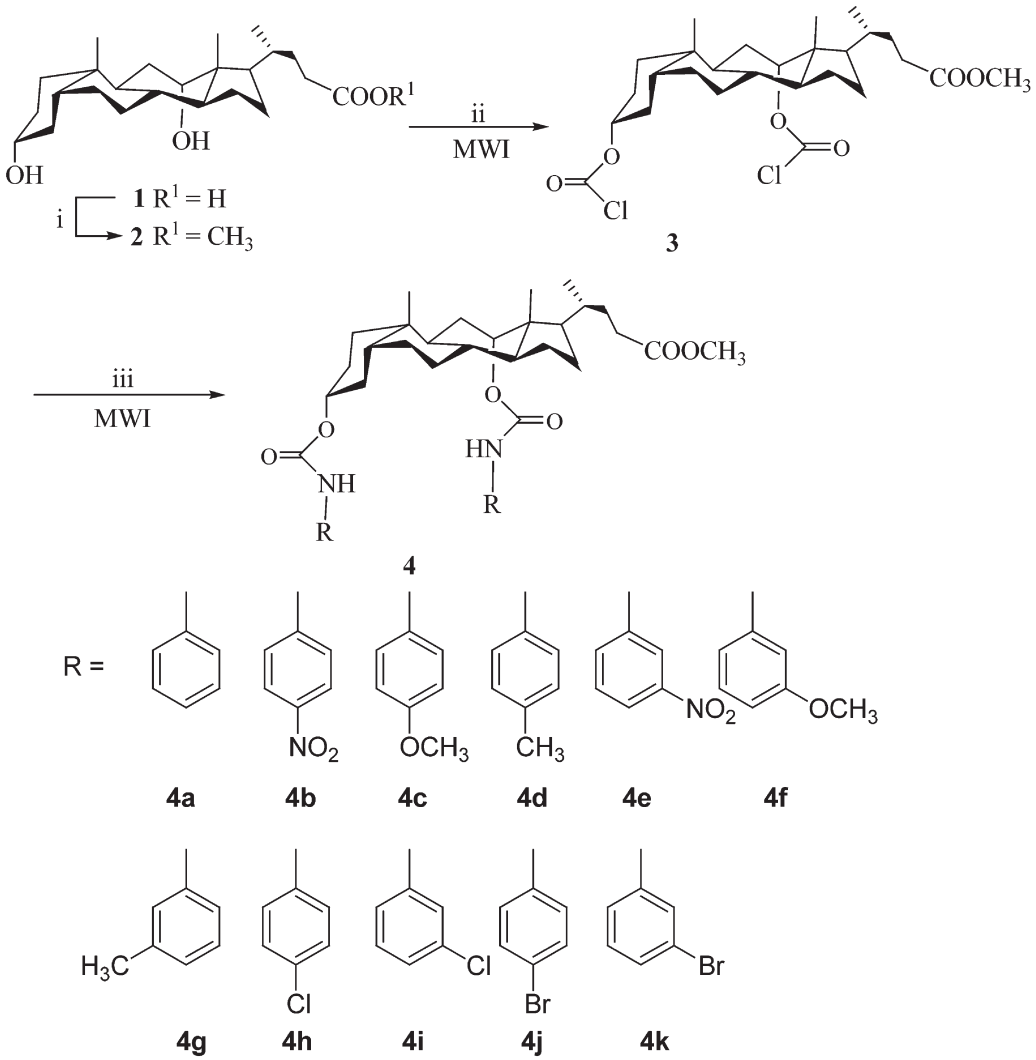

Scheme 1 Reagents and conditions: (i) CH_3COCl, CH_3OH; (ii) CH_2Cl_2, $CO(OCCl_3)_2$, pyridine; (iii) pyridine, $ArNH_2$.

to give the crude product. The crude product was purified by column chromatography on silica gel H with dichloromethane/ethyl acetate as eluant. The physical and spectra data of the compounds **4a–k** are as follows.

4a: White solid, yield 93%, m.p. 98–100 °C, $[\alpha]_D^{20}$+95.2 (*c* 0.13, CH_2Cl_2); IR (KBr)(cm^{-1}): 3346, 2946, 2882, 1726, 1534, 1442, 1220; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.46 (d, *J* = 8.0 Hz, 2H, ArH), 7.35–7.28 (m, 6H, ArH), 7.10–7.02 (m, 2H, ArH), 6.73 (s, 1H, CONH), 6.48 (s, 1H, CONH), 5.11 (s, 1H, 12β–H), 4.70–4.65 (m, 1H, 3β–H), 3.64 (s, 3H, $COOCH_3$), 0.93 (s, 3H, 19–CH_3), 0.89 (d, *J* = 6.4 Hz, 3H, 21–CH_3), 0.76 (s, 3H, 18–CH_3); ESI–MS *m/z* (%): 643.4 [$(M-H)^-$, 100]. Anal. Calcd for $C_{39}H_{52}N_2O_6$: C, 72.64; H, 8.13; N, 4.34. Found C, 72.41; H, 8.10; N 4.36%.

4b: Pale yellow solid, yield 95%, m.p. 127–128 °C, $[\alpha]_D^{20}$+128.2 (*c* 0.12, CH_2Cl_2); IR (KBr)(cm^{-1}): 3358, 2946, 2843, 1736, 1602, 1510, 1412, 1216, 1048; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.25 (d, *J* = 9.2 Hz, 2H, ArH), 8.20 (d, *J* = 9.2 Hz, 2H, ArH), 7.61 (d, *J* = 9.2 Hz, 2H, ArH), 7.54 (d, *J* = 9.2 Hz, 2H, ArH), 7.18 (s, 1H, CONH), 6.92 (s, 1H, CONH), 5.18 (s, 1H, 12β–H), 4.71–4.67 (m, 1H, 3β–H), 3.65 (s, 3H, $COOCH_3$), 0.95 (s, 3H, 19–CH_3), 0.90 (d, *J* = 6.4 Hz, 3H, 21–CH_3), 0.79 (s, 3H, 18–CH_3); ESI–MS *m/z* (%): 757.3 [$(M+Na)^+$, 100]. Anal. Calcd for $C_{39}H_{50}N_4O_{10}$: C, 63.75; H, 6.86; N, 7. 62. Found C, 63.50; H, 6.89; N, 7.64%.

4c: White solid, yield 94%, m.p. 88–90 °C, $[\alpha]_D^{20}$+79.9 (*c* 0.14, CH_2Cl_2); IR (KBr)(cm^{-1}): 3344, 2941, 2854, 1724, 1600, 1518, 1458, 1220, 1082; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.29–7.26 (m, 4H, ArH), 6.89–6.83 (m, 4H, ArH), 6.58 (br, 2H, CONH), 5.12 (s, 1H, 12β–H), 4.64 (br, s, 1H, 3β–H), 3.80 (s, 3H, $ArOCH_3$), 3.78 (s, 3H, $ArOCH_3$), 3.65 (s, 3H, $COOCH_3$), 0.96 (s, 3H, 19–CH_3), 0.91 (d, *J* = 6.4 Hz, 3H, 21–CH_3), 0.75 (s, 3H, 18–CH_3); ESI–MS *m/z* (%): 727.5 [$(M+Na)^+$, 100]. Anal. Calcd for $C_{41}H_{56}N_2O_8$: C, 69.86; H, 8.01; N, 3.97. Found C, 69.70; H, 8.03; N 3.99%.

4d: White solid, yield 92%, m.p. 101–103 °C, $[\alpha]_D^{20}$+105.3 (*c* 0.13, CH_2Cl_2); IR (KBr)(cm^{-1}): 3348, 2947, 2845, 1726, 1596, 1507, 1459, 1224, 1080; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.33 (d, *J* = 8.0 Hz, 2H, ArH), 7.23 (d, *J* = 8.0 Hz, 2H, ArH), 7.14 (d, *J* = 8.0 Hz, 2H, ArH), 7.09 (d, *J* = 8.0 Hz, 2H, ArH), 6.64 (s, 1H, CONH), 6.41 (s, 1H, CONH), 5.09 (s, 1H, 12β–H), 4.69–4.63 (m, 1H, 3β–H), 3.64 (s, 3H, $COOCH_3$), 2.31 (s, 3H, $ArCH_3$), 2.29 (s, 3H, $ArCH_3$), 0.93 (s, 3H, 19–CH_3), 0.89 (d, *J* = 6.4 Hz, 3H, 21–CH_3), 0.75 (s, 3H, 18–CH_3); ESI–MS *m/z* (%): 695.5 [$(M+Na)^+$, 100]. Anal. Calcd for $C_{41}H_{56}N_2O_6$: C, 73.18; H , 8.39; N, 4.16. Found C, 72.98; H, 8.41; N, 4.18%.

4e: Pale yellow solid, yield 95%, m.p. 105–106 °C, $[\alpha]_D^{20}$+95. 4 (*c* 0.17, CH_2Cl_2); IR (KBr)(cm^{-1}): 3360, 2946, 2844, 1734, 1598, 1432, 1222, 1062; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.36 (s, 1H, ArH), 8.31 (s, 1H, ArH), 7.94–7.88 (m, 3H, ArH), 7.67 (s, 1H, ArH), 7.52–7.43 (m,

Table 1 Synthetic comparison of molecular tweezers **4a–k** between microwave irradiation and conventional heating

Compd.	Conventional method		Microwave method		t_c/t_w[a]
	Time/min	Yield/%	Time/min	Yield/%	
4a	540	65	20	93	27
4b	600	73	23	95	26
4c	660	70	21	94	31
4d	660	67	24	92	28
4e	600	71	23	95	26
4f	660	69	21	91	31
4g	660	66	24	94	28
4h	720	72	25	95	29
4i	720	71	25	93	29
4j	720	68	25	96	29
4k	720	65	25	94	29

[a] t_c, Conventional method needs time; t_w, microwave method needs time.

Table 2 Association constants (*K*a) and Gibbs free energy changes ($-\Delta G°$) for the inclusion complexes of guests with molecular tweezers **4a, 4b** and **4e** in $CHCl_3$ at 25 °C

Host	Guest	*K*a/L mol^{-1}	$-\Delta G°$/kJ mol^{-1}
4a	*p*-Nitroaniline	1148.3	17.45
	Aniline	546.5	15.61
	p-Methoxyaniline	368.5	14.63
4b	*p*-Nitroaniline	5191.2	21.18
	Aniline	1756.3	18.50
	p-Methoxyaniline	3832.4	20.43
4e	*p*-Nitroaniline	776.1	16.48
	Aniline	629.3	15.96
	p-Methoxyaniline	536.5	15.56

Table 3 Association constants(*Ka*) and Gibbs free energy changes ($-\Delta G^0$) for the inclusion complexes of amino acid methyl esters with molecular tweezers **4a**, **4b**, **4e** in $CHCl_3$ at 25 °C

Host	Guest	*Ka*/L mol^{-1}	$-\Delta G°$/kJ mol^{-1}	K_D/K_L
4a	*D*-Phe-OMe	328.23	14.35	2.60
	L-Phe-OMe	126.41	11.98	
	D-Tyr-OMe	483.15	15.30	1.68
	L-Tyr-OMe	287.36	14.02	
4b	*D*-Phe-OMe	242.63	13.60	1.69
	L-Phe-OMe	143.39	12.30	
	D-Tyr-OMe	335.92	14.40	1.55
	L-Tyr-OMe	216.41	13.32	
4e	*D*-Phe-OMe	123.15	11.92	2.30
	L-Phe-OMe	53.54	9.86	
	D-Tyr-OMe	298.26	14.11	4.92
	L-Tyr-OMe	60.63	10.17	

2H, ArH), 7.23 (s, 1H, CONH), 6.93 (s, 1H, CONH), 5.16 (s, 1H, 12*β*–H), 4.70 (br, s, 1H, 3*β*–H), 3.65 (s, 3H, $COOCH_3$), 0.93 (s, 3H, 19–CH_3), 0.91 (d, *J* = 6.8 Hz, 3H, 21–CH_3), 0.77 (s, 3H, 18–CH_3); ESI–MS *m/z* (%): 757.3 [(M+Na)$^+$, 100]. Anal. Calcd for $C_{39}H_{50}N_4O_{10}$: C, 63.75; H, 6.86; N, 7. 62. Found C, 63.51; H, 6.88; N, 7.65%.

4f: White solid, yield 91%, m.p. 83–85 °C, $[\alpha]_D^{20}$+121.6 (*c* 0.15, CH_2Cl_2); IR (KBr)(cm^{-1}): 3346, 2949, 2843, 1732, 1606, 1547, 1468, 1222, 1044; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.24–7.15 (m, 5H, ArH), 6.99 (d, *J* = 8.0 Hz, 1H, ArH), 6.84 (d, *J* = 8.0 Hz, 2H, ArH), 6.82–6.58 (m, 2H, CONH), 5.11 (s, 1H, 12*β*–H), 4.65 (br, s, 1H, 3*β*–H), 3.81 (s, 3H, $ArOCH_3$), 3.78 (s, 3H, $ArOCH_3$), 3.65 (s, 3H, $COOCH_3$), 0.91 (s, 3H, 19–CH_3), 0.89 (d, *J* = 6.4 Hz, 3H, 21–CH_3), 0.75 (s, 3H, 18–CH_3); ESI–MS *m/z* (%): 727.6 [(M+Na)$^+$, 100]. Anal. Calcd for $C_{41}H_{56}N_2O_8$: C, 69.86; H, 8.01; N; 3. 97. Found C, 69.74; H, 7.98; N 3.94%.

4g: White solid, yield 94%, m.p. 90–92 °C, $[\alpha]_D^{20}$+123.1 (*c* 0.13, CH_2Cl_2); IR (KBr)(cm^{-1}): 3350, 2944, 2854, 1730, 1612, 1542, 1450, 1220, 1056; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.34 (s, 1H, ArH), 7.23–7.10 (m, 5H, ArH), 6.90–6.84 (m, 2H, ArH), 6.67 (s, 1H, CONH), 6.42 (s, 1H, CONH), 5.10 (s, 1H, 12*β*–H), 4.67–4.63 (m, 1H, 3*β*–H), 3.64 (s, 3H, $COOCH_3$), 2.35 (s, 3H, $ArCH_3$), 2.31 (s, 3H, $ArCH_3$), 0.93 (s, 3H, 19–CH_3), 0.89 (d, *J* = 6.4 Hz, 3H, 21–CH_3), 0.76 (s, 3H, 18–CH_3); ESI–MS *m/z* (%): 695.6 [(M+Na)$^+$, 100]. Anal. Calcd for $C_{41}H_{56}N_2O_6$: C, 73.18; H, 8.39; N 4.16. Found C, 72.96; H 8.37; N 4.14%.

4h: White solid, yield 95%, m.p. 101–102 °C, $[\alpha]_D^{20}$+100.0 (*c* 0.13, CH_2Cl_2); IR (KBr)(cm^{-1}): 3344, 2946, 2875, 1718, 1596, 1526, 1448, 1220, 1092; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.40 (d, *J* = 8.8 Hz, 2H, ArH), 7.30 (d, *J* = 8.8 Hz, 4H, ArH), 7.25 (d, *J* = 8.8 Hz, 2H, ArH), 6.76 (s, 1H, CONH), 6.53 (s, 1H, CONH), 5.11 (s, 1H, 12*β*–H), 4.68–4.62 (m, 1H, 3*β*–H), 3.64 (s, 3H, $COOCH_3$), 0.92 (s, 3H, 19–CH_3), 0.88 (d, *J* = 6.0 Hz, 3H, 21–CH_3), 0.76 (s, 3H, 18–CH_3); ESI–MS *m/z* (%): 735.4 [(M+Na)$^+$, 100]. Anal. Calcd for $C_{39}H_{50}Cl_2N_2O_6$: C, 65.63; H, 7.06; N 3.92. Found C, 65.50; H, 7.04; N 3.90%.

4i: White solid, yield 93%, m.p. 95–97 °C, $[\alpha]_D^{20}$+125.7 (*c* 0.12, CH_2Cl_2); IR (KBr)(cm^{-1}): 3343, 2942, 2883, 1716, 1586, 1530, 1484, 1218, 1062; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.57 (s, 1H, ArH), 7.48 (s, 1H, ArH), 7.31 (s, 1H, ArH), 7.24–7.18 (m, 3H, ArH), 7.06–7.00 (m, 2H, ArH), 6.87 (s, 1H, CONH), 6.57 (s, 1H, CONH), 5.11 (s, 1H, 12*β*–H), 4.69–4.63 (m, 1H, 3*β*–H), 3.65 (s, 3H, $COOCH_3$), 0.94 (s, 3H, 19–CH_3), 0.87 (d, *J* = 6.4 Hz, 3H, 21–CH_3), 0.75 (s, 3H, 18–CH_3); ESI–MS *m/z* (%): 735.4 [(M+Na)$^+$, 100]. Anal. Calcd for $C_{39}H_{50}Cl_2N_2O_6$: C, 65.63; H, 7.06; N 3.92. Found C, 65.72; H, 7.08; N 3.93%.

4j: White solid, yield 96%, m.p. 105–106 °C, $[\alpha]_D^{20}$+103.3 (*c* 0.15, CH_2Cl_2); IR (KBr)(cm^{-1}): 3350, 2944, 2875, 1720, 1584, 1522, 1477, 1218, 1048; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.44 (d, *J* = 8.8 Hz, 2H, ArH), 7.40 (d, *J* = 8.8 Hz, 2H, ArH), 7.36 (d, *J* = 8.8 Hz, 2H, ArH), 7.25 (d, *J* = 8.8 Hz, 2H, ArH), 6.79 (s, 1H, CONH), 6.56 (s, 1H, CONH), 5.10 (s, 1H, 12*β*–H), 4.68–4.64 (m, 1H, 3*β*–H), 3.64 (s, 3H, $COOCH_3$), 0.91 (s, 3H, 19–CH_3), 0.86 (d, *J* = 6.4 Hz, 3H, 21–CH_3), 0.75 (s, 3H, 18–CH_3); ESI–MS *m/z* (%): 825.5 [(M+Na)$^+$, 100]. Anal. Calcd for $C_{39}H_{50}Br_2N_2O_6$: C, 58.36; H, 6.28; N, 3.49. Found C, 58.20; H, 6.30; N 3.51%.

4k: White solid, yield 94%, m.p. 97–98 °C, $[\alpha]_D^{20}$+82.8 (*c* 0.17, CH_2Cl_2); IR (KBr)(cm^{-1}): 3342, 2946, 1718, 1582, 1526, 1480, 1217, 1050; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.72 (s, 1H, ArH), 7.62 (s, 1H, ArH), 7.39 (s, 1H, ArH), 7.28 (s, 1H, ArH), 7.19–7.11 (m, 4H, ArH), 6.94 (s, 1H, CONH), 6.63 (s, 1H, CONH), 5.10 (s, 1H, 12*β*–H), 4.66–4.64 (m, 1H, 3*β*–H), 3.65 (s, 3H, $COOCH_3$), 0.89 (s, 3H, 19–CH_3), 0.88 (d, *J* = 6.4 Hz, 3H, 21–CH_3), 0.77 (s, 3H, 18–CH_3); ESI–MS *m/z* (%): 825.3 [(M+Na)$^+$, 100]. Anal. Calcd for $C_{39}H_{50}Br_2N_2O_6$: C, 58.36; H, 6.28; N 3.49. Found C, 58.25; H, 6.26; N 3.47%.

Conventional method for the preparation of molecular tweezers **4a–k**
Triphosgene (0.11 g, 0.37 mmol)was added to a solution of methyl deoxycholate **2** (0.2 g, 0.5 mmol) in dry CH_2Cl_2 (20 mL) and dry pyridine (0.2 mL) at room temperature. It was then refluxed for 5 h. Intermediate **3** was formed and without separation, aromatic amines (1.5 mmol) and dry pyridine (0.2 mL) were added directly to the mixture and the reflux was continued for 4–7 h. The solvent was removed and the residue was diluted with ethyl acetate (30 mL) and washed with 10% $NaHCO_3$ (15 mL×3), brine (15 mL×3), and finally dried over anhydrous Na_2SO_4. The solvent was evaporated to give the crude product. The crude product was purified by column chromatography on silica gel H with dichloromethane/ethyl acetate as eluant.

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References

1 J. Rebek Jr., Science, 1987, **235**, 1478.
2 X.X. Zhang, J.S. Bradshaw and R.M. Izatt, *Chem. Rev.*, 1997, **97**, 3313.
3 F.P. Schmidtchen and M. Berger, *Chem. Rev.*, 1997, **97**. 1609.
4 X. Guo, F. Liu and G.Y. Lu, *Chin. J. Org. Chem.*, 2005, **25**, 1021 (in Chinese).
5 Z.C. Xu, S.K. Kim and Y. Yoon., *Chem. Soc. Rev.*, 2010, **39**, 1457.
6 K.S. Kim and H.S. Kim, *Tetrahedron*, 2005, **61**, 12366.
7 L. Siracusa, F.M. Hurley and S. Dresen, *Org. Lett.*, 2002, **4**, 4639.
8 Z.G. Zhao, P.Y. Zhang, Z.X. Yang and S.H. Chen, *Chin. J. Org. Chem.* 2005, **25**, 679 (in Chinese).
9 M. Chahar and P.S. Pandey, *Tetrahedron*, 2008, **64**, 6488.
10 P. Appukkuttan, V.P. Mehta and E.V. Van der Eycken, *Chem. Soc. Rev.*, 2010, **39**, 1467.
11 V. Polshettiwar and R.S. Varma, *Acc. Chem. Res.*, 2008, **41**, 629.
12 C.O. Kappe, *Angew. Chem. Int. Ed.*, 2004, **43**, 6250.
13 D. Dallinger and C.O. Kappe, *Chem.Rev.*, 2007, **107**, 2563.
14 X.M. Wu, Z.G. Zhao, X.L. Liu, Y. Chen and X.X. Zhao, *Chin. J. Org. Chem.*, 2009, **29**, 956 (in Chinese).
15 X.L. Xiu, Z.G. Zhao and S.H. Chen, *Chin. J. Org. Chem.*, 2007, **27**, 772 (in Chinese).
16 Z.G. Zhao, X.L. Liu and C.E. Zhou, *Chin. Chem. Lett.*, 2007, **18**, 1067.
17 B.T. Zeng, Z.G. Zhao, X.X. Zhao, Y. Ye, Y. Chen, Z.C. Shi and X.M. Wu, *Chin. J. Org. Chem.*, 2009, **29**, 1621 (in Chinese).
18 B.T. Zeng, Z.G. Zhao, X.L. Liu and Y. Shi, *Chin. Chem. Lett.*, 2008, **19**, 33.
19 C.H. Xue, R. Hu, Q.M. Mu, F. Li and S.H. Chen, *Acta Chim. Sinica.*, 2000, **58**, 717.
20 X.L. Liu, Z.G. Zhao and B.T. Zeng, *Chin. J. Org. Chem.*, 2007, **27**, 994 (in Chinese).