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Novel synthesis of macrocycles with chalcone moieties through mixed aldol reaction

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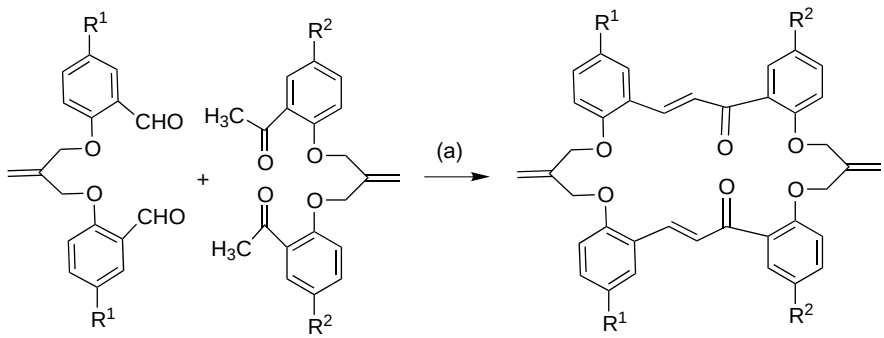
Abstract—24-Membered novel macrocycles with chalcone structural moieties and isobutenyl ether linkages in the core have been prepared through mixed aldol reaction.

Macrocyles with novel functionalities as part of the core are important for molecular recognition and photophysical properties.[1] In this respect, chalcone structural moiety has an excellent potential to be a part of macrocyclic structures, since the photophysical properties of chalcones have been well exploited for various optical applications.[2] So, we envisioned that the incorporation of chalcone moieties in macrocyclic core would be useful for molecular recognition studies and as photo-functional materials. The strategy to synthesize macrocycle with chalcone structural moiety was depicted in Scheme 1, where the mixed aldol reaction of bis-arylaldehyde **1** and bis-arylmethyl ketone **2** is expected to give a macrocyle **3** with two chalcone moieties incorporated into 24-membered ring along with two isobutenyl ether linkages. We report herein, our preliminary results on the synthesis of macrocylces of the type **3** with chalcone moieties.

The selection of **1** and **2** was important from the fact that either **1** or **2** easily undergo tandem Claisen rearrangement under thermal conditions, thus can generate phenolic hydroxy functionalities either in acyclic or cyclic structures.[3] Hence, the presence of ether linkages in the molecular core of **3** are useful for further modification of the macrocycles via tandem Claisen rear-



1 **2** **3**

1a. R^1 = H **2a**. R^2 = H
1b. R^1 = Cl **2b**. R^2 = OMe
1c. R^1 = CH_3 **2c**. R^2 = CH_3

(a) t-BuOK (10mol%), r.t., 16h, THF

1a + 2a = **3a** (41%)
1a + 2b = **3b** (28%)
1a + 2c = **3c** (33%)
1b + 2a = **3d** (26%)
1c + 2a = **3e** (39%)

Scheme 1. Macrocycles with chalcone moieties.

Keywords: mixed aldol reaction; potassium *tert*-butoxide; chalcones; macrcocyles.

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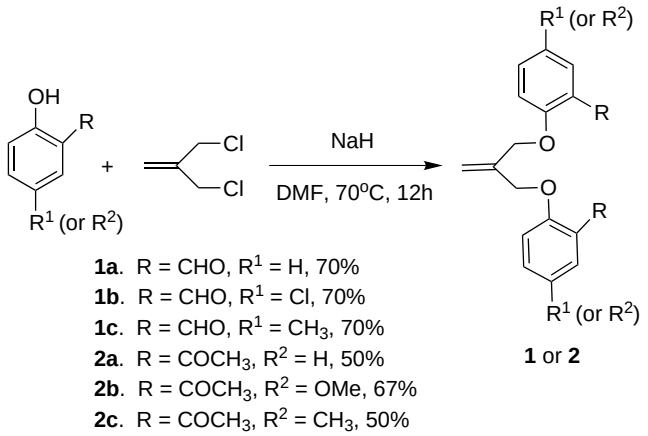
rangement. So, macrocycles thus formed will possess two chalcone moieties in addition to either two or four phenolic hydroxy groups (depending on tandem Claisen rearrangement) along with two isobutenyl groups. In fact, this strategy of generating phenolic hydroxy functionalities in crownophanes molecular structures has been earlier demonstrated at this laboratory.[3,4]

The bis-aldehyde **1** or bis-ketone **2** were prepared using the reported procedure from the coupling reaction of corresponding hydroxy aryl aldehydes or ketones with isobutenyl dichloride in the presence of NaH as given in Scheme 2.[3,5] The mixed aldol reaction of **1a** (1 equiv.) and **2a** (1 equiv.) was carried out using *t*-BuOK (1 equiv.) in THF (30 mL) for 16 h. Under these conditions, macrocycle **3a** (Scheme 1) was formed in 12% yield along with unwanted oligomer or polymer products. Whereas, the same reaction with *t*-BuOK in catalytic amount (10 mol% with respect to one aldehyde or ketone group) afforded the yield up to 41%.

The use of base as catalyst helped the reaction to undergo in controllable fashion to produce macrocycle **3a** in acceptable yield in the syntheses of such macrocycles. This is important from the point that we have not employed high dilution conditions or slow addition of the reaction components over a long period of time in our conditions.[6]



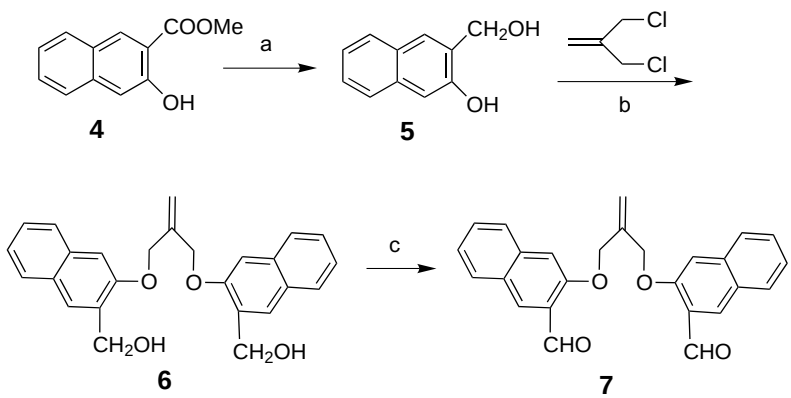
Scheme 2. Synthesis of **1** and **2**.[5]

The structure of the compound **3a** was fully characterized by NMR and other spectroscopic techniques.[7] The macrocycle **3a** has four phenyl groups, two chalcone moieties along with two isobutenyl ether linkages. The double bond of chalcone is *trans* configured judging from the coupling constants ($J=16.1$ Hz) obtained for the enone vinylic protons from ^{1}H NMR. With the same protocol, a variety of macrocycles **3a**–**3e**, with different substituents on aryl groups of **1** or **2**, have been synthesized. Thus, macrocycles **3a**–**3e** having chloro, methoxy and methyl substituents have been obtained in 26–41% yields after GPC isolation (Scheme 1). All the macrocycles were fully characterized by IR, NMR and ESI–MS.[7]

Here, we felt that the changing of phenyl groups to naphthyls in macrocycle **3** is useful for further modifications of the macrocycles using tandem Clasien rearrangement under thermal conditions at lower temperatures.[4c,8] Presence of the naphthyl rings will also allow macrocycles to exhibit enhanced photophysical properties. Hence, compound **7** which is a naphthyl derivative of **1** was synthesized (Scheme 3) starting from commercially available 2-hydroxy-3-naphthoic acid methyl ester **4**. Methyl ester **4** was reduced to alcohol **5** with lithium aluminum hydride. Coupling reaction of alcohol **5** with isobutenyl chloride afforded **6** which was further oxidized using PCC and obtained aldehyde **7** in good yield.

The mixed aldol reaction of aldehyde **7** and ketone **2a** with *t*-BuOK (10 mol% with respect to one aldehyde or ketone group) in dry THF gave macrocycle **8a** with naphthyl and phenyl groups in 31% yield (Fig. 1). And the reaction of aldehyde **7** with ketone **2b** afforded the macrocycle **8b** in 27% yield (Fig. 1)[10].

The molecular structure of **8a** obtained by single crystal X-ray analysis was given in Fig. 2.[11] From Fig. 2 it is clear that **8a** is a 24-membered macrocycle possessing naphthyl and phenyl groups along with two chalcone structural moieties and two isobutenyl ether linkages.



Scheme 3. Synthesis of compound **7**.[9] *Reagents and conditions*: (a) $LiAlH_4$, THF, rt, 70%; (b) NaH, DMF, 70°C, 83%; (c) pyridinium chlorochromate (PCC), dichloromethane, rt, 70%.

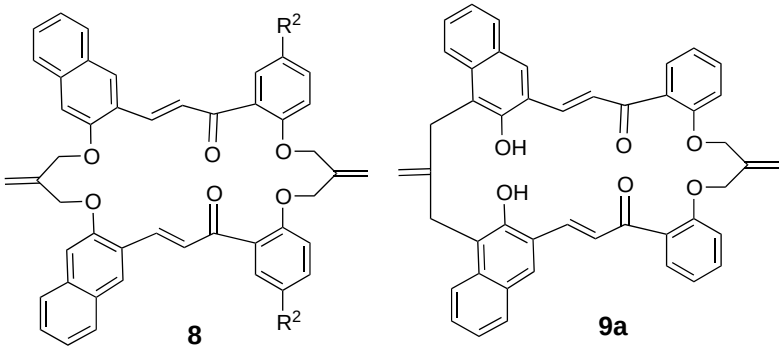


Figure 1. Macrocycles.

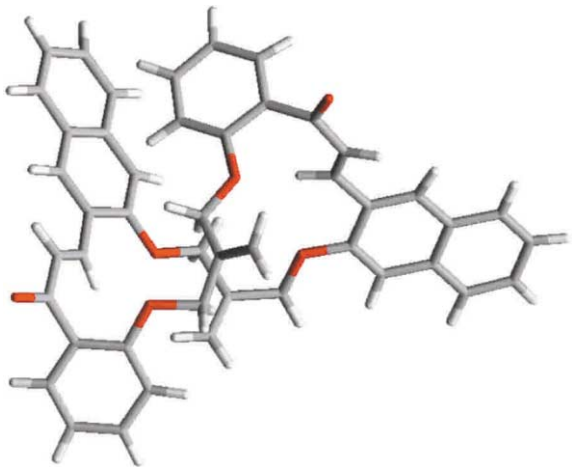


Figure 2. Molecular structure of **8a** determined by single crystal X-ray analysis.[11]

The double bond of enone moiety is *trans* configured. This is in agreement with ^{1}H NMR analysis showing high coupling constants ($J=16.1$ Hz) for enone vinylic protons. The twisted orientation of macrocycle **8a** was evidently due to the *trans* configuration of the two double bonds forcing the core to adopt such orientation. The tandem Claisen rearrangement of macrocycle **8a** also underwent cleanly at 155°C with the formation of a new 24-macrocycle **9a** (Fig. 1) having two phenolic hydroxy functionalities.[12] It is noteworthy to mention that the macrocycle **9a** has two phenolic hydroxy groups, two chalcone moieties along with two ether linkages.

In conclusion, we have demonstrated a novel approach to synthesize 24-membered macrocycles with two chalcone structural moieties and two isobutenyl ether linkages. The presence of two isobutenyl ether linkages are useful for modifications of the macrocycle core under thermal conditions as demonstrated in the conversion of macrocycle **8a** to **9a** (Fig. 1). The photophysical and molecular recognition properties of these macrocycles will be the focus of our further study.

References

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5. Characterization of **1a**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.79 (s, 4H, -OCH_2), 5.52 (s, 2H, =CH_2), 7.02 (d, 2H, $J=8.4$, Ar), 7.06 (t, 2H, $J=7.5$, Ar), 7.54 (m, 2H, Ar), 7.83 (dd, 2H, $J=1.8$, 7.6, Ar), 10.48 (s, 2H, -CHO); ^{13}C NMR (125.75 MHz, $CDCl_3$): δ 68.94, 112.71, 116.99, 121.28, 125.07, 128.90, 135.99, 138.92, 160.54, 189.28; ESI-MS: 319 (M+Na).
Characterization of **1b**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.77 (s, 4H, -OCH_2), 5.53 (s, 2H, =CH_2), 6.98 (d, 2H, $J=9.0$, Ar), 7.48 (dd, 2H, $J=2.7$, 8.9, Ar), 7.77 (d, 2H, $J=2.7$, Ar), 10.39 (s, 2H, -CHO); ^{13}C NMR (125.75 MHz, $CDCl_3$): δ 69.23, 114.32, 117.70, 125.89, 127.02, 128.46, 135.41, 138.17, 158.83, 187.81; ESI-MS: 387 (M+Na).
Characterization of **1c**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.31 (s, 6H, CH_3), 4.75 (s, 4H, -OCH_2), 5.49 (s, 2H, =CH_2), 6.91 (d, 2H, $J=8.5$, Ar), 7.34 (dd, 2H, $J=2.3$, 8.5, Ar), 7.62 (d, 2H, $J=2.3$, Ar), 10.45 (s, 2H, -CHO); ^{13}C NMR (125.75 MHz, $CDCl_3$): δ 20.20, 69.00, 112.71,

116.59, 124.68, 128.75, 130.65, 136.55, 139.20, 158.65, 189.40; ESI-MS: 347 (M+Na).

Characterization of **2a**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.60 (s, 6H, -COMe), 4.76 (s, 4H, -OCH_2), 5.50 (s, 2H, =CH_2), 6.98 (d, 2H, J=8.4, Ar), 7.02 (dt, 2H, J=0.8, 7.5, Ar), 7.44 (m, 2H, Ar), 7.71 (dd, 2H, J=1.9, 7.6, Ar); ^{13}C NMR (125.75 MHz, $CDCl_3$): δ 31.72, 69.18, 112.67, 117.29, 121.15, 128.74, 130.47, 133.57, 139.27, 157.46, 199.61; ESI-MS: 347 (M+Na).

Characterization of **2b**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.61 (s, 6H, -COMe), 3.79 (s, 6H, -OMe), 4.70 (s, 4H, -OCH_2), 5.46 (s, 2H, =CH_2), 6.91 (d, 2H, J=9.0, Ar), 7.00 (dd, 2H), J=3.4, 9.0, Ar), 7.26 (d, 2H, J=3.4, Ar); ^{13}C NMR (125.75 MHz, $CDCl_3$): δ 31.79, 55.81, 69.92, 113.99, 114.47, 116.95, 120.08, 129.01, 139.81, 151.98, 153.77, 199.21; ESI-MS: 407 (M+Na).

Characterization of **2c**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.28 (s, 6H, -Me), 2.58 (s, 6H, -COMe), 4.72 (s, 4H, -OCH_2), 5.47 (s, 2H, =CH_2), 6.87 (dd, 2H, J=1.4, 8.8, Ar), 7.23 (d, 2H, J=8.4, Ar), 7.50 (s, 2H, Ar); ^{13}C NMR (125.75 MHz, $CDCl_3$): δ 20.10, 31.60, 69.14, 112.61, 116.74, 128.17, 130.29, 130.50, 133.94, 139.46, 155.41, 199.60; ESI-MS: 375 (M+Na).

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7. Representative procedure for mixed aldol reaction for the synthesis of **3b**: Compound **1a**, 0.88 gm (3 mmol) and **2b**, 1.15 g (3 mmol) were taken in to a schlenk containing 30 ml of dry THF under nitrogen. Potassium *tert*-butoxide 0.067 gm (0.6 mmol) was added under nitrogen and the reaction mixture was stirred at rt for 16 h. Reaction mixture was quenched with dil. HCl and was extracted with dichloromethane (2×50 ml). The combined organic extract was washed with water, brine, dried over $MgSO_4$ and concentrated. The crude product obtained was subjected to GPC purification to obtain macrocycle **3b** in 28% (0.55 g) yield. Macrocycle **3b** was identified by IR, NMR and ESI-MS; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.75 (s, 6H, -OMe), 4.51 (s, 4H, -OCH_2), 4.60 (s, 4H, -OCH_2), 5.18 (s, 2H, =CH_2), 5.31 (s, 2H, =CH_2), 6.58 (d, 2H, J=9.0, Ar), 6.67 (dd, 2H, J=3.2, 9.0, Ar), 6.76 (d, 2H, J=8.1, Ar), 6.96 (t, 2H, J=7.8, Ar), 7.00 (d, 2H, J=3.2, Ar), 7.23 (m, 2H, Ar), 7.46 (dd, 2H, J=1.5, 6.1, Ar), 7.54 (d, 2H, J=16.0, -CH=CH), 7.70 (d, 2H, J=16.0, -CH=CH); ^{13}C NMR (125.75 MHz, $CDCl_3$): δ 55.62, 68.67, 69.88, 112.10, 113.64, 114.13, 115.23, 116.36, 118.39, 121.23, 123.78, 128.60, 130.07, 131.36, 132.07, 139.21, 139.35, 140.70, 150.40, 153.52, 157.34, 194.17; IR (KBr, cm^{-1}): 1651.7 (C=O), 1594 (C=C); ESI-MS: 667 (M+Na).

Characterization of **3a**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.56 (s, 8H, -OCH_2), 5.21 (s, 2H, =CH_2), 5.27 (s, 2H, =CH_2), 6.60 (d, 2H, J=8.4, Ar), 6.74 (d, 2H, J=8.4, Ar), 6.91 (t, 2H, J=7.3, Ar), 6.97 (t, 2H, J=7.4, Ar), 7.10 (m, 2H, Ar), 7.22 (m, 2H, Ar), 7.45 (m, 4H, Ar), 7.49 (d, 2H, J=16.1, -CH=CH), 7.69 (d, 2H, J=16.1, -CH=CH); ^{13}C NMR (125.75 MHz, $CDCl_3$): δ 68.77, 69.26, 112.03, 112.18, 115.68, 116.31, 120.95, 121.39, 123.87, 128.81, 129.69, 130.03, 131.50, 131.78, 132.34, 138.92, 139.29, 140.70, 156.10, 157.33, 194.91; IR (KBr, cm^{-1}): 1649.8 (C=O), 1598 (C=C); ESI-MS: 607 (M+Na).

Characterization of **3c**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.25 (s, 6H, Me), 4.56 (s, 4H, -OCH_2), 4.59 (s, 4H, -OCH_2), 5.19 (s, 2H, =CH_2), 5.30 (s, 2H, =CH_2), 6.55 (d, 2H, J=8.4, Ar), 6.75 (d, 2H, J=8.3, Ar), 6.88 (dd, 2H, J=2.2, 8.4, Ar), 6.98 (t, 2H, J=7.4, Ar), 7.20–7.25 (m, 4H, Ar), 7.48 (dd, 2H, J=1.5, 7.6, Ar), 7.54 (d, 2H, J=16.2, -CH=CH), 7.69 (d, 2H, J=16.2, -CH=CH); ^{13}C NMR (125.75 MHz, $CDCl_3$): δ 20.28, 68.78, 69.51, 112.21, 112.17, 115.29, 116.23, 121.25, 123.97, 128.94, 129.45, 130.24, 130.41, 131.30, 132.21, 132.93, 139.31, 139.36, 140.55, 154.22, 157.42, 194.94; IR (KBr, cm^{-1}): 1655.5 (C=O), 1593 (C=C); ESI-MS: 635 (M+Na).

Characterization of **3d**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.56 (s, 8H, -OCH_2), 5.24 (s, 2H, =CH_2), 5.27 (s, 2H, =CH_2), 6.67 (m, 4H, Ar), 6.99 (t, 2H, J=7.4, Ar), 7.12 (dd, 2H, J=2.4, 8.7, Ar), 7.26 (m, 2H, Ar), 7.38 (d, 2H, J=2.6, Ar), 7.47 (m, 2H, Ar), 7.49 (d, 2H, J=16.0, -CH=CH), 7.54 (d, 2H, J=16.0, -CH=CH); ^{13}C NMR (125.75 MHz, $CDCl_3$): δ 69.16, 69.24, 112.15, 113.60, 116.38, 117.31, 121.16, 125.53, 126.44, 129.33, 130.00, 130.38, 130.71, 131.28, 132.79, 138.44, 138.76, 138.83, 155.71, 156.36, 193.81; IR (KBr, cm^{-1}): 1648.8 (C=O), 1601 (C=C), ESI-MS: 675 (M+Na).

Characterization of **3e**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.29 (s, 6H, Me), 4.53 (s, 4H, -OCH_2), 4.56 (s, 4H, -OCH_2), 5.21 (s, 2H, =CH_2), 5.23 (s, 2H, =CH_2), 6.63 (m, 4H, Ar), 6.92 (t, 2H, J=7.4, Ar), 6.99 (d, 2H, J=7.3, Ar), 7.10 (d, 2H, J=7.0, Ar), 7.26 (d, 2H, J=6.0, Ar), 7.45 (d, 2H, J=7.4, Ar), 7.49 (d, 2H, J=16.0, -CH=CH), 7.65 (d, 2H, J=16.0, CH=CH); ^{13}C NMR (125.75 MHz, $CDCl_3$): δ 20.32, 68.85, 69.20, 112.03, 112.15, 115.60, 115.98, 120.77, 123.48, 128.61, 129.68, 130.02, 130.39, 131.97, 132.20, 132.28, 138.92, 139.58, 140.75, 155.36, 156.11, 194.71; IR (KBr, cm^{-1}); 1649.8 (C=O), 1600 (C=C), ESI-MS: 635 (M+Na).

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9. Synthesis of **5**: Lithium aluminum hydride 8.54 g (225 mmol) in 100 ml is slowly added to the R.B. flask containing 30 g (150 mmol) of 2-hydroxy-3-naphthoic acid methyl ester **4** in 300 ml of tetrahydrofuran under nitrogen. After addition is complete, the contents were stirred for 12 h at room temperature. Reaction mixture was poured carefully into a beaker containing crushed ice cubes. After all the excess lithium aluminum hydride destroyed, conc. hydrochloric acid is added with stirring till the white turbidity is dissolved. The organic product was extracted with excess chloroform repeatedly. Organic layer was washed with water, brine, dried over $MgSO_4$ and concentrated. White crystalline compound **5** was obtained in 70% (18.3 g) yield. Characterization of **5**: ^{1}H NMR (500 MHz, DMSO): δ 4.64 (s, 2H), 5.15 (s, 1H, -OH), 7.11 (s, 1H, Ar), 7.25 (t, 1H, J=7.6, Ar); 7.33 (t, 1H, J=7.6, Ar), 7.64 (d, 1H, J=8.1, Ar), 7.76 (d, 1H, J=8.1, Ar), 7.81 (s, 1H, Ar), 9.84 (s, 1H, Ar-OH); ^{13}C NMR (125.75 MHz, $CDCl_3$): δ 64.23, 113.55, 128.22, 130.99, 131.14, 132.95, 133.31, 137.47, 138.94, 158.70.

Synthesis of **6**: NaH 1.056 g (44 mmol) in dry DMF 20 ml is added slowly under nitrogen to the R.B. flask containing alcohol **5**, 7.66 g (44 mmol) in 150 ml dry DMF. The reaction mixture stirred further for 1 h at room temperature and isobutenyl chloride 2.48 g (19.84 mmol) in dry DMF 30 ml was added. The contents were stirred at 70°C overnight. After reaction mixture was brought to rt and 5 ml of water was added. DMF was

evaporated under reduced pressure and product was extracted with chloroform (2×100 ml). The combined extract was washed with water, brine, dried over $MgSO_4$ and concentrated. Compound **6** (yield = 6.64 g, 83%) was obtained in pure form after recrystallization from CH_2Cl_2/hexane mixture. Characterization of **6**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.50 (s, 2H, -CH_2OH), 4.82 (s, 4H, -$\underline{CH_2}$OH), 4.84 (s, 4H, -OCH_2), 5.52 (s, 2H, =CH_2), 7.15 (s, 2H, Ar), 7.34 (dt, 2H, J = 1.2, 7.4, Ar), 7.42 (dt, 2H, J = 1.3, 7.4, Ar), 7.67 (d, 2H, J = 8.1, Ar), 7.75 (s, 4H, Ar); ^{13}C NMR (125.75 MHz, $CDCl_3$): δ 62.04, 68.78, 106.42, 116.55, 124.15, 126.39, 126.50, 127.66, 127.78, 128.84, 130.53, 133.92, 139.75, 154.49; ESI-MS: 423 (M+Na).

Synthesis of **7**: To PCC 19.4 g (90 mmol) in dichloromethane (200 ml), 6 g of alcohol **6** (15 mmol) in 100 ml of dichloromethane was added slowly and contents were stirred at room temperature for 3 h. Diethyl ether 100 ml is added to the flask and the reaction mixture was filtered through a Celite bed. The filtrate again passed through small silica gel column to get pure pale yellow aldehyde **7** (yield = 4.0 g, 80%). Characterization of **7**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.94 (s, 4H, -OCH_2), 5.61 (s, 2H, =CH_2), 7.25 (s, 2H, Ar), 7.40 (t, 2H, J = 8.2, Ar), 7.54 (t, 2H, J = 8.2, Ar), 7.70 (d, 2H, J = 8.2, Ar), 7.88 (d, 2H, J = 8.2, Ar) 8.37 (s, 2H, Ar), 10.62 (s, 2H, -CHO); ^{13}C NMR (125.75 MHz, $CDCl_3$): δ 68.9, 107.59, 116.86, 124.94, 125.63, 126.71, 127.94, 129.38, 129.88, 131.47, 137.36, 139.01, 156.21, 189.75; ESI-MS: 419 (M+Na).

10. Characterization of **8a**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.56 (s, 4H, -OCH_2), 4.75 (s, 4H, -OCH_2), 5.22 (s, 2H, =CH_2), 5.37 (s, 2H, =CH_2), 6.48 (d, 2H, J = 8.2, Ar), 6.67 (t, 2H, J = 7.5, Ar), 6.79 (m, 2H, Ar), 6.99 (s, 2H, Ar), 7.40 (m, 4H, Ar), 7.47 (t, 2H, J = 7.0, Ar), 7.58 (d, 2H, J = 8.0, Ar), 7.73 (d, 2H, J = 16.0, -CH=CH), 7.80 (d, 2H, J = 8.0, Ar), 7.85 (d, 2H, J = 16.0, -CH=CH), 7.99 (s, 2H, Ar); ^{13}C NMR (125.75 MHz, $CDCl_3$): δ 68.96, 69.33, 107.26, 111.78, 115.87, 116.47, 120.88, 124.60, 125.37, 126.54, 127.80, 128.25, 128.70, 129.52, 129.71, 130.00, 132.28, 133.00, 135.04, 138.88, 139.30, 140.41, 154.82, 156.20, 194.45; IR (KBr, cm^{-1}): 1655.8 (C=O), 1599 (C=C); ESI-MS: 707 (M+Na).

Characterization of **8b**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.46 (s, 6H, -OMe), 4.44 (s, 4H, -OCH_2), 4.68 (s, 4H, -OCH_2), 5.11 (s, 2H, =CH_2), 5.34 (s, 2H, =CH_2), 6.33 (dd, 2H, J = 3.0, 9.0, Ar), 6.41 (d, 2H, J = 9.0, Ar), 6.95 (m, 4H, Ar), 7.32 (t, 2H, J = 7.1, Ar), 7.40 (t, 2H, J = 7.0, Ar), 7.54 (d, 2H, J = 8.2, Ar), 7.73 (d, 2H, J = 8.0, Ar), 7.77 (d, 2H, J = 16.0, -CH=CH), 7.83 (d, 2H, J = 16.0, -CH=CH), 7.89 (bs, 2H, Ar); ^{13}C NMR (125.75 MHz, $CDCl_3$): δ 55.80, 69.36, 70.30, 107.67, 113.83, 114.71, 115.44, 116.67, 118.61, 124.98, 125.71, 126.89, 128.26, 128.68, 129.03, 129.97, 130.33, 133.88, 135.41, 139.65, 139.76, 141.07, 151.01, 153.88, 155.34, 194.11; IR (KBr, cm^{-1}): 1651.3 (C=O), 1582 (C=C); ESI-MS: 767 (M+Na).

11. Crystal data for **8a**: $C_{53}H_{36}O_6$, M_w = 768.86, crystal system = triclinic, space group = $P\bar{1}$ (#2), Z = 4 in a cell of dimensions: a = 12.735(1), b = 16.112(1), c = 10.1921(6) Å, α = 91.044(2), β = 103.322(4), γ = 102.337(4)°, V = 1983.1(2) Å^3, D_{calcd} = 1.288 g cm^{-1}. The data were collected at −80°C on a Rigaku RAXIS-RAPID Imaging Plate diffractometer, λ (Mo Kα) = 0.7107 Å, μ = 0.83 cm^{-1}, 18830 measured and 8717 unique reflections ($2\theta_{max}$ = 55.00, R_{int} = 0.042). R = 0.127, R_w = 0.193. Note: The correct molecular formula for macrocycle **8a** is $C_{46}H_{36}O_6$. The obtained molecular formula $C_{53}H_{36}O_6$ was due to some solvent molecules in the crystal lattice, which are not identified.

12. Tandem Claisen rearrangement of **8a**: Compound **8a** was heated under neat conditions at 155°C for 1.5 h under vacuum to give **9a** (yield = 85%, by NMR). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.87 (s, 4H, CH_2-Ar), 4.65 (s, 4H, -OCH_2), 5.03 (s, 2H, =CH_2), 5.29 (s, 2H, =CH_2), 5.91 (s, 2H, Ar-OH), 6.90 (d, 2H, J = 8.2, Ar), 7.04 (t, 2H, J = 7.3, Ar), 7.28 (t, 2H, J = 7.7, Ar), 7.40–7.46 (m, 4H, Ar), 7.60–7.64 (m, 4H, Ar), 7.72–7.78 (m, 4H, Ar); ^{13}C NMR (125.75 MHz, $CDCl_3$): δ 32.10, 69.30, 112.71, 114.44, 114.81, 117.02, 121.50, 122.53, 123.91, 124.50, 127.81, 128.78, 129.15, 129.69, 129.87, 130.47, 130.78, 132.86, 134.03, 138.61, 139.88, 146.14, 150.87, 156.61, 193.78; ESI-MS: 707 (M+Na).