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Efficient synthesis of 16–28 membered macrocyclic crown amides via ring closing metathesis

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Abstract—Ring closing metathesis of suitable diamides containing 1,ω-dienes led to efficient synthetic approaches towards macrocylic polyoxadiamides **1**–**18** with 16–28 membered ring sizes in good to excellent yields using Grubbs' catalyst.

1. Introduction

The development of neutral ionophores useful in measurements of intracellular as well as extracelluar cation concentrations is a subject of considerable current interest.[1] In general, crown compounds and azacrown compounds constitute important macrocyclic groups in supramolecular chemistry. They have been shown to exhibit important applications including selective ion separation and detection, molecular recognition, catalysis, biological applications as well as many other interesting applications in diverse fields of supramolecular chemistry.[2,3] Of particular interest are crown ethers incorporating amide groups, since such groups modify the binding properties of the crown compounds with respect to alkali metal ions.[1,3] Moreover, the number of ether oxygen, amide carbonyl groups, ring size, lipophilic groups as well as other structural features control the selectivity towards different ions.[1,3] Synthetic approaches towards such macrocycles usually suffer from low yields, the loss of considerable amounts of the starting precursors during the macrocyclization step due to polymer formation, in addition to the need for high dilution conditions and template effect.[2] We and others reported several moderate-to-good yielding synthetic approaches towards macrocyclic crown-amides some of which showed useful applications in ion selective electrodes.[3] However, previous synthetic approaches suffer from a considerable decrease in yields as the ring size increases, in favor of polymer formation.[3f] In the present investigation we report an efficient synthetic approach towards crown diamides with ring sizes extending from 16–28 membered rings, using ring closing metathesis as the key macrocyclization step.

Recently, ring closing metathesis (RCM) has been widely used as a versatile technique for the formation of cyclic olefins. It has been mainly applied for the formation of five- to seven-membered carbocycles and heterocycles.[4–8] Some examples of macrocycle synthesis via RCM have been reported.[8–17] Several reviews dealing with RCM and illustrating its wide range of applications have recently been published.[18] Molybdenum alkylidene (Schrock catalysts)[19] and ruthenium alkylidene (Grubbs' catalysts)[17,20] have shown the best catalytic activity in the area of RCM. The commercial availability and ease of handling of some of the Grubbs' catalysts (e.g. **I**) in addition to their tolerance of normal reaction conditions and to a wide range of functional groups attracted our attention for possible utility in the synthesis of crown and azacrown macrocycles. In a recent publication we demonstrated the versatile application of this technique for the efficient atom economic synthesis of a number of azacrowns, crowndiamides and crown-formazans with cyclic olefinic function with variable ring sizes.[21] Recently, isophthaloyl benzylic amide macrocycles possessing an internal olefin were prepared and shown to spontaneously self-assemble via interlocking to give [2]catenanes in >95% yield.[22] A special issue of advanced synthesis and catalysis was devoted to olefin metathesis.[23]

2. Results and discussion

In the present work we report our investigations (Scheme 1) on the application of RCM with catalyst **I** as the key macrocyclization step in the synthesis of macrocyclic polyethers containing amide groups in the macrocyclic ring. Results obtained in Table 1 provide reasonably good

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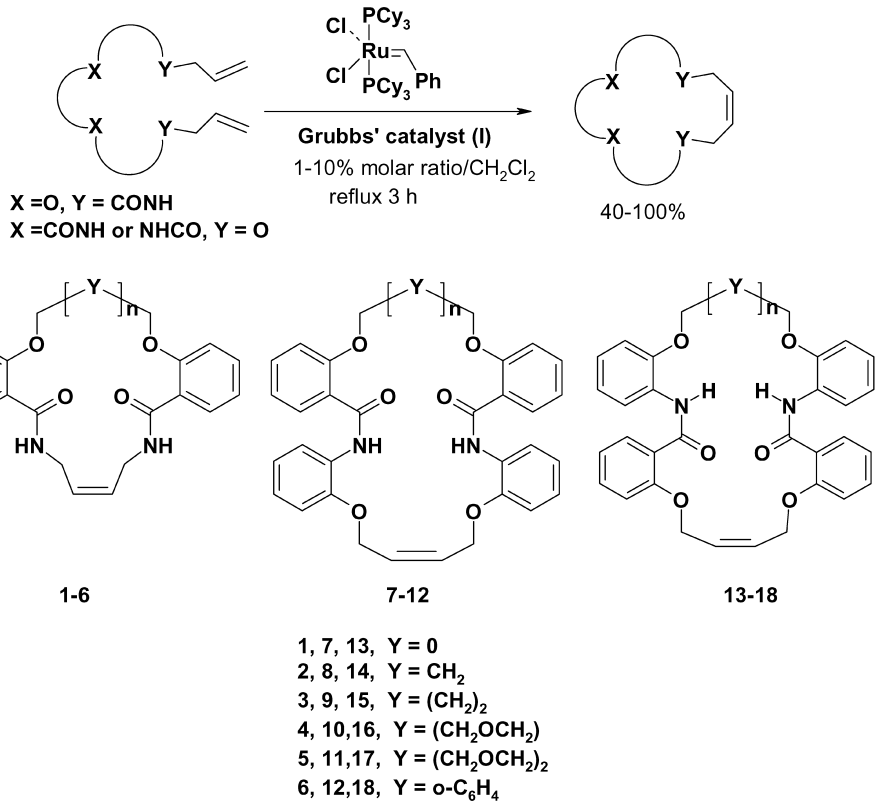


Scheme 1.

synthetic procedure towards macrocyclic crowndiamides with 16–22 membered rings. On the other hand, the results obtained in Tables 2 and 3 provide an efficient atom economic synthetic approach towards macrocylic polyoxadiamides with 22–28 membered rings.

Schemes 2 and 3 illustrate our synthetic routes towards the precursor 1,ω-dienes **21**–**26**, **29**–**34** needed for the RCM synthesis of **1**–**6**, **7**–**12**. The starting *N*-allylsalicylamide (**19**) and *N*-(*o*-allyloxyphenyl)salicylamide (**27**) were converted into the desired 1,ω-dienes via their potassium salt **20** and **28** upon treatment with the appropriate dihalo or ditosylate compounds.

On the other hand, the 1,ω-dienes **41**–**46** (Scheme 4) were readily obtained by reacting the appropriate bisamine dihydrochlorides **35**–**40** with *o*-allyloxybenzoyl chloride.

RCM of dienes **21**–**26** were investigated using different ratios of the catalyst **I** (2.5–10 mol%) and the best yields (40–60%) were obtained using 10 mol% of **I** in refluxing CH_2Cl_2 for 3 h (Table 1). On the other hand RCM of the dienes **29**–**34** and **41**–**46** (Tables 2 and 3) proceeded well with 1–5 mol% of **I** in refluxing CH_2Cl_2 for 3 h to give excellent yield of the corresponding macrocyclic products. In all RCM reactions the progress of the reaction was monitored by TLC and ^{1}H NMR analysis where no further increase in products was noticed after 3 h of reflux in CH_2Cl_2. The larger amount of catalyst required in the RCM of **21**–**26** might be due to the proximity effect of the C═O

Table 1. Synthesis of macrocytes **1**–**6**

Entry	Substrate[a]	Conditions/yield (%)[a]	Product[b] *E*:*Z* (%) ratio	^{1}H NMR of *E*/*Z* products			*J* (Hz)	^{13}C NMR
				NH	NCH_2	NCH_2CH═		CH_2CH═
1	**21**	a/5, b/10, c/40	**1**[c]	7.34	4.10 (s)	6.04 (s)		42.3
2	**22**	a/5, b/15, c/47	**2**[c]	7.86	4.16 (s)	6.00 (s)		39.9
3	**23**	a/5, b/25, c/50	**3**[c]	7.90	4.17 (s)	5.98 (s)		41.2
4	**24**	a/12, b/25, c/50	**4**[c]	8.16	4.15 (s)	5.91 (s)		41.5
5	**25**	a/10, b/25, c/50	**5**	8.22	4.12 (s)	5.86 (s)		41.3
			5:1	8.30	4.12 (m)	5.69 (t)	3.9	37.1
6	**26**	a/13, b/26, c/60	**6**	7.74	3.92 (s)	5.58 (s)		40.3
			3:1	7.74	3.92 (s)	5.41 (t)	4.2	36.0

(a) Substrate (0.2 mM), Grubbs' catalyst **I** (2.5 mol%); CH_2Cl_2 (5 mL), reflux 3 h. (b) Substrate (0.2 mM), **I** (5 mol%); CH_2Cl_2 (5 mL), reflux 3 h. (c) Substrate (0.2 mM), **I** (10 mol%); CH_2Cl_2 (5 mL), reflux 3 h.

[a] The yield was determined by 400 MHz ^{1}H NMR, unreacted starting substrates account for most of the remaining percent in each case.

[b] All substrates and products were analyzed by ^{1}H, ^{13}C NMR, GC-MS, and gave satisfactory elemental analysis.

[c] Only one isomer was detected most probably the *E*-isomer.

Table 2. Synthesis of macrocytes **7**–**12**

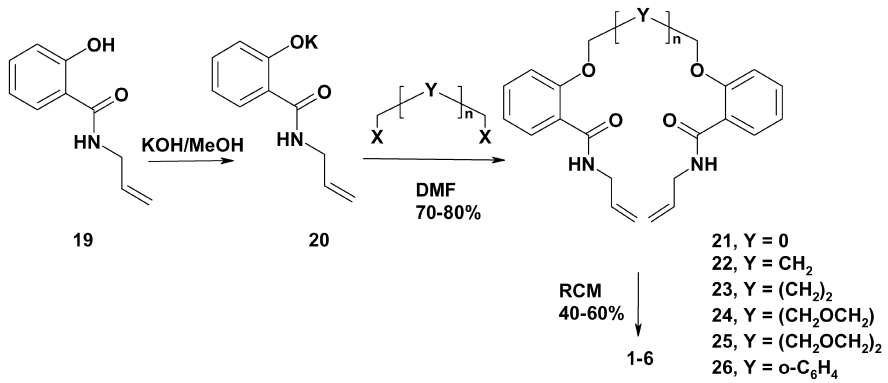
Entry	Substrate[a]	Conditions/yield (%)[a]	Product[b] *E*:*Z* (%) ratio	^{1}H NMR of *E*/*Z* products			*J* (Hz)	^{13}C NMR
				NH	OCH_2	OCH_2CH═		CH_2CH═
1	**29**	a/78, b/100	**7**	10.40	4.69 (s)	6.36 (s)		68.5
			5:1	10.35	4.84 (d)	6.18 (t)	5.0	65.1
2	**30**	a/81, b/100	**8**	10.19	4.60 (s)	6.22 (s)		69.0
			5:1	10.19	4.71 (d)	6.04 (t)	3.7	64.1
3	**31**	a/80, b/100	**9**	10.29	4.63 (s)	6.26 (s)		68.9
			5:1	10.37	4.81 (d)	6.08 (t)	3.7	63.4
4	**32**	b/90, c/100	**10**	10.20	4.75 (s)	6.28 (s)		68.9
			3:1	10.22	4.86 (d)	6.14 (t)	3.7	64.7
5	**33**	a/80, c/100	**11**	10.32	4.76 (s)	6.17 (s)		69.4
			3:1	10.26	4.83 (t)	6.03 (t)	2.9	65.5
6	**34**	a/100	**12**	10.56	4.15 (s)	5.84 (s)		69.5
			3:1	10.75	4.52 (d)	6.85 (t)	3.2	65.4

(a) Substrate (0.2 mM), Grubbs' catalyst **I** (1 mol%); CH_2Cl_2 (5 mL), reflux 3 h. (b) Substrate (0.2 mM), **I** (2 mol%); CH_2Cl_2 (5 mL), reflux 3 h. (c) Substrate (0.2 mM), **I** (5 mol%); CH_2Cl_2 (5 mL), reflux 3 h.
[a] The yield was determined by 400 MHz ^{1}H NMR, unreacted starting substrates account for most of the remaining percent in each case.
[b] All substrates and products were analyzed by ^{1}H, ^{13}C NMR, GC-MS, and gave satisfactory elemental analysis.

Table 3. Synthesis of macrocytes **13**–**18**

Entry	Substrate[a]	Conditions/yield (%)[a]	Product[b] *E*:*Z* (%) ratio	^{1}H NMR of *E*/*Z* products			*J* (Hz)	^{13}C NMR
				NH	OCH_2	OCH_2CH═		CH_2CH═
1	**41**	b/67, c/90	**13**	10.40	4.75 s	6.30 s		67.8
			4:1	10.45	4.98 d	6.18 t	3.2	
2	**42**	b/60, c/80	**14**	10.37	4.84 s	6.21 s		69.5
			3:1	10.30	4.96 s	6.21 s		65.9
3	**43**	b/82, c/82	**15**	10.20	4.83 s	6.23 s		
			4:1	10.29	5.01 s	6.05 s		
4	**44**	b/60, c/100	**16**	10.32	4.81 s	6.29 s		69.4
			5:1	10.47	5.09 d	6.29 t	3.1	65.6
5	**45**	b/65, c/100	**17**	10.44	4.83 s	6.26 s		70.6
			3:1	10.58	5.16 d	6.18 t	3.2	65.1
6	**46**	a, b/100	**18**	10.57	4.36 s	5.96 s		68.5
			2:1	10.43	4.49 d	5.63 t	2.8	65.5

(a) Substrate (0.2 mM), **I** (1 mol%); CH_2Cl_2 (5 mL), reflux 3 h. (b) Substrate (0.2 mM), **I** (2 mol%); CH_2Cl_2 (5 mL), reflux 3 h. (c) Substrate (0.2 mM), **I** (5 mol%); CH_2Cl_2 (5 mL), reflux 3 h.
[a] The yield was determined by 400 MHz ^{1}H NMR, unreacted starting substrates account for most of the remaining percent in each case.
[b] All substrates and products were analyzed by ^{1}H, ^{13}C NMR, GC-MS, and gave satisfactory elemental analysis.

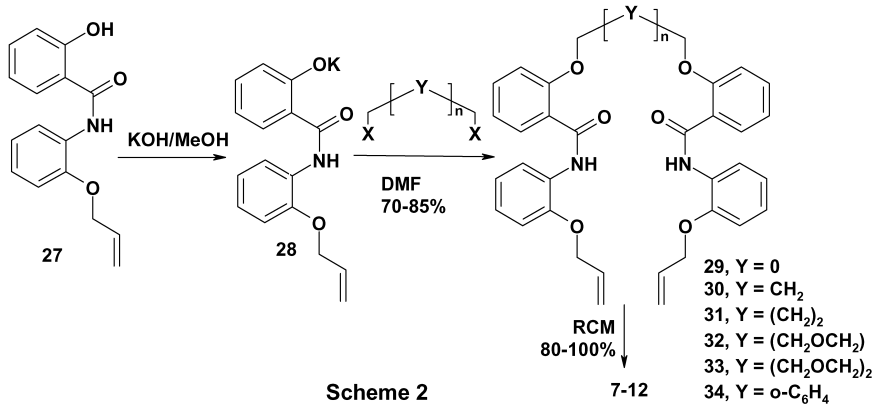


Scheme 2.

group which would chelate with ruthenium carbene, the catalyst thus being sequestered in the form of unproductive complex.[16]

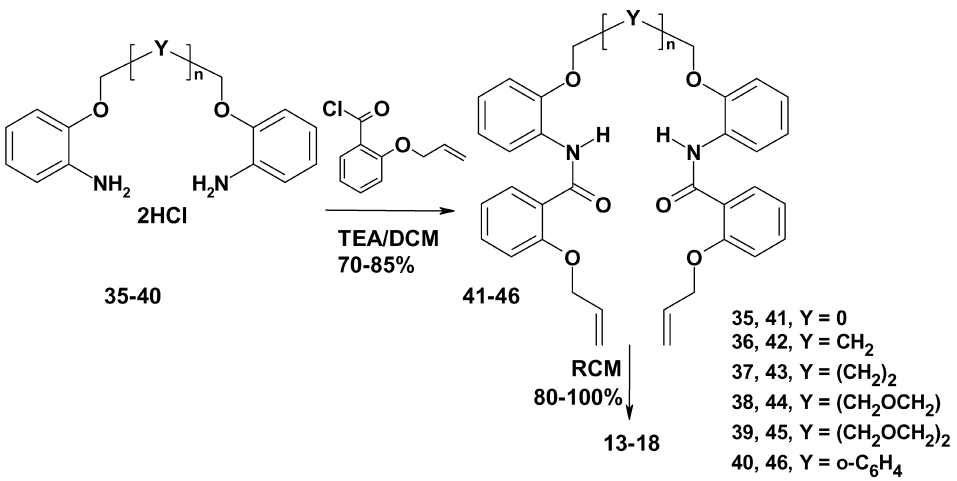
From Table 3 it is clear that larger amount of the catalyst **I** was needed in comparable entries to accomplish the systems of macrocycles of similar ring sizes to those in Table 2. Exception occurred in one case where olefin metathesis occurred with only 1% catalyst (entries 6 Tables 2 and 3) in which the two isomeric pentabenzo-24-crowndiamides **12** and **18** were obtained in almost quantitative yields.

The *E*:*Z* isomers of the olefinic crown diamides were readily assigned and their ratios were determined from the ^{1}H NMR and ^{13}C NMR spectra. The major products in all RCM reactions were shown to be the *E* isomers with the



Scheme 2

Scheme 3.



Scheme 4.

characteristic ^{13}C signal of the OCH_2 (of the $OCH_2-CH{=}CHCH_2O$) which appears more downfield than that for the corresponding *Z* isomer. On the contrary in ^1H NMR the OCH_2 of *E* isomers appears as almost singlet and more upfield than that of the *Z* isomer which splits into a doublet with $J=3-5$ Hz. Also, in ^1H NMR the CH= of the *E* isomers also appears as a singlet and further downfield than that of *Z* isomer which appears as a triplet (Tables 2 and 3). Similar observations were also, detected for the products **1**–**6** (Table 1) however, only the *E* isomers in the case of compounds **1**–**4** were detected.

3. Conclusions

The present work demonstrates the efficient application of RCM techniques for the synthesis of macrocyclic crowndiamide derivatives with potential diverse applications in supramolecular chemistry and as starting compounds for further synthetic transformations. The examples of RCM presented here represent one of the best macrocyclization reaction techniques for the synthesis of crown compounds. This paper also, expands the utility of RCM methodology and its application to the synthesis of cyclic olefins of large ring sizes with different functional groups.

4. Experimental

4.1. General

Melting points are uncorrected. IR: (KBr) Shimadzu IR-740 spectrometer. ^1H and ^{13}C NMR: Bruker Avance 400 spectrometer. MS: GC/MS INCOS XL Finnigan MAT. Microanalysis: LECO CHNS-932. Separation of reaction products was performed using preparative HPLC WATER PREP 4000 series with PDA detector WATER 2996 and ABZ+ column with a solvent mixture of acetonitrile and water (70:30).

4.1.1. *N*-Allylsalicylamide 19. To a solution of allylamine (5.7 g, 0.1 mol) in DCM (50 mL) at 0°C was added TEA (5 mL) followed by a dropwise addition of a solution of salicoyl chloride (15.65 g., 0.1 mol) in DCM (50 mL) over a period of 30 min. The reaction mixture was then kept stirring at room temperature overnight. The mixture was then diluted with DCM (50 mL) and washed with hydrochloric acid (2 M, 200 mL), then twice with a saturated solution of sodium carbonate and finally with water, the organic layer was then dried over anhydrous sodium sulfate and evaporated to dryness. The remaining product was crystallized from petroleum ether (40–60) to give **19** as colorless crystals, yield 74%; mp 50–52°C (literature[27] mp 51.5°C). ^1H NMR ($CDCl_3$) δ=4.06 (s, 2H,

NCH_2CH═), 5.19 (m, 2H, CH═CH_2), 5.91 (m, 1H, CH═CH_2), 6.83 (t, 1H, J=8 Hz), 6.96 (d, 1H, J=8 Hz), 7.08 (br, 1H, NH), 7.37 (dt, J=8, 1 Hz), 7.51 (dd, 1H, J=8, 1 Hz), 11.53 (br, 1H, OH).

4.1.2. *N*-(*o*-Allyloxyphenyl)salicylamide 27. To a solution of *o*-allyloxyaniline hydrochloride[24] (18.45 g, 0.1 mol) in DCM (50 mL) at 0°C was added TEA (5 mL) followed by a dropwise addition of a solution of salicoyl chloride (15.65 g., 0.1 mol) in DCM (50 mL) over a period of 30 min. The reaction mixture was then kept stirring at room temperature overnight. The mixture was then diluted with DCM (50 mL) and washed with hydrochloric acid (2 M, 200 mL), then twice with a saturated solution of sodium carbonate and finally with water, the organic layer was then dried over anhydrous sodium sulfate and evaporated to dryness. The remaining product was crystallized from ethanol/water to give **27** as colorless crystals, yield 74%; mp 84–86°C. IR: 3287, 3070 (br), 2697, 2554, 1692, 1605, 1548, 1487, 1455, 1225, 1343, 1284, 1241, 1212, 1159, 1089, 1017, 994, 943, 902, 761, 746, 694. ^{1}H NMR ($CDCl_3$) δ=4.69 (d, 2H, J=4.9 Hz, OCH_2CH═), 5.40, 5.48 (2d, 2H, J=10.4, 17.2 Hz, CH═CH_2), 6.12 (m, 1H, CH═CH_2), 6.95 (t, 2H, J=8 Hz), 7.07 (d, 2H, J=8 Hz), 7.12 (t, 1H, J=8 Hz), 7.45 (t, 1H, J=8 Hz), 7.52 (d, 1H, J=8 Hz), 8.43 (d, 1H, J=8 Hz), 8.80 (s, 1H, NH), 12.17 (s, 1H, OH). Anal. calcd for $C_{16}H_{15}NO_3$ (269.3): C, 71.38, H, 5.61, N, 5.20. Found C, 71.00, H, 5.62, N, 5.24.

4.2. Reaction of 19 and 27 with dihalo and ditosylates: synthesis of 21–26 and 29–34. General procedure

Each of compound **19** and **27** (10 mmol) was added to a solution of KOH (0.57 g, 10 mmol) in methanol (10 mL). The mixture was then stirred at room temperature for 15 min and the solvent was then removed in vacuo. The remaining solid was washed with dry ether, collected, dried to give the potassium salt **20** and **28**. To the latter was added DMF (10 mL) and the appropriate dihalo or ditosylates (5 mmol). The reaction mixture was then heated under reflux for 15 min. The mixture was cooled, diluted with water (20 mL) and the precipitate was collected, washed with cold water and finally crystallized from the proper solvent.

4.2.1. Compound 21. (From **20** and 1,2-dibromoethane), yield 70%; mp 150–152°C (colorless crystals from EteOH). IR: 3324, 3079, 2956, 2891, 1637, 1600, 1538, 1491, 1472, 1451, 1309, 1239, 1166, 1112, 1052, 1036, 993, 916, 752, 665. ^{1}H NMR ($CDCl_3$) δ=3.92 (t, 4H, J=6 Hz, NCH_2CH═), 4.54 (s, 4H, OCH_2CH_2O), 4.69, 4.92 (2d, 4H, J=10.1, 17.2 Hz, CH_2═CH), 5.65 (m, 2H, CH_2═$CH$$CH_2$), 6.99 (d, 2H, J=8 Hz), 7.16 (t, 2H, J=8 Hz), 7.48 (dt, 2H, J=8, 1.6 Hz), 8.24 (dd, 2H, J=8, 1.6 Hz), 7.78 (br, 2H, NH). MS: m/z (%)=380 (100) [M^+]. Anal. calcd for $C_{22}H_{24}N_2O_4$ (380.5): C, 69.46, H, 6.36, N, 7.36. Found C, 69.24, H, 6.38, N, 7.51.

4.2.2. Compound 22. (From **20** and 1,3-dibromopropane), yield 75%; mp 140–142°C (colorless crystals from EtOH). IR: 3331, 3076, 2946, 2924, 1635, 1600, 1537, 1489, 1465, 1450, 1411, 1310, 1241, 1161, 1110, 1062, 992, 976, 927, 760, 650. ^{1}H NMR ($CDCl_3$) δ=2.43 (quintet, 2H, J=6.1 Hz, OCH_2CH_2), 4.07 (m, 4H, NCH_2CH═), 4.35 (t, 4H, J=6.1 Hz, OCH_2CH_2), 5.11, 5.22 (2d, 4H, J=10.4, 17.2 Hz, CH_2═CH), 5.93 (m, 2H, CH_2═$CH$$CH_2$), 6.97 (d, 2H, J=8 Hz), 7.12 (t, 2H, J=8 Hz), 7.45 (dt, 2H, J=8, 1.6 Hz), 8.20 (dd, 2H, J=8, 1.6 Hz), 7.79 (br, 2H, NH). MS: m/z (%)=394 (20) [M^+]. Anal. calcd for $C_{23}H_{26}N_2O_4$ (394.5): C, 70.03, H, 6.64, N, 7.10. Found C, 69.96, H, 6.61, N, 7.27.

4.2.3. Compound 23. (From **20** and 1,4-dibromobutane), yield 78%; mp 138–140°C (colorless crystals from EtOH). IR: 3337, 3074, 2931, 2874, 1637, 1597, 1537, 1486, 1452, 1306, 1241, 1166, 1107, 1045, 980, 926, 846, 755, 655. ^{1}H NMR ($CDCl_3$) δ=2.09 (br, 4H, OCH_2CH_2), 4.12 (d, 4H, J=5.2 Hz, NCH_2CH═), 4.22 (br, 4H, OCH_2CH_2), 5.15, 5.27 (2d, 4H, J=10.4, 17.2 Hz, CH_2═CH), 5.96 (m, 2H, CH_2═$CH$$CH_2$), 6.98 (d, 2H, J=8.2 Hz), 7.12 (t, 2H, J=7.6 Hz), 7.46 (t, 2H, J=7.8 Hz), 8.23 (d, 2H, J=7.6 Hz), 7.91 (s, 2H, NH). MS: m/z (%)=408 (100) [M^+]. Anal. calcd for $C_{24}H_{28}N_2O_4$ (408.5): C, 70.57, H, 6.91, N, 6.86. Found C, 70.58, H, 6.86, N, 6.86.

4.2.4. Compound 24. (From **20** and diethyleneglycol ditosylate), yield 75%; mp 93–95°C (colorless crystals from EtOH). ^{1}H NMR ($CDCl_3$) δ=3.86, 4.22 (2t, 4H, 4H, J=4.3, 4.3 Hz, $(OCH_2CH_2O)_2$), 4.01 (t, 4H, J=5.1 Hz, NCH_2CH═), 4.99, 5.15 (2d, 4H, J=10.3, 17.2 Hz, CH_2═CH), 5.85 (m, 2H, CH_2═$CH$$CH_2$), 6.89 (d, 2H, J=8.2 Hz), 7.05 (t, 2H, J=7.6 Hz), 7.38 (t, 2H, J=7.6 Hz), 8.15 (d, 2H, J=8.2 Hz), 8.04 (br, 2H, NH). LC/MS; m/z (%)=425 [M+1]. Anal. calcd for $C_{24}H_{28}N_2O_5$ (424.5): C, 67.91, H, 6.65, N, 6.60. Found C, 67.99, H, 6.65, N, 6.75.

4.2.5. Compound 25. (From **20** and triethyleneglycol ditosylate), yield 70%; mp 80–82°C (colorless crystals from petroleum ether (60–80)). IR: 3266, 3075, 2978, 2902, 1651, 1633, 1599, 1559, 1484, 1451, 1388, 1347, 1310, 1291, 1270, 1239, 1228, 1164, 1106, 1007, 921, 757, 749, 685. ^{1}H NMR ($CDCl_3$): δ=3.62, 3.80, 4.17 (s, 2t, 4H, 4H, 4H, J=4.4, 4.4 Hz, $(OCH_2CH_2O)_3$), 4.04 (4H, t, J=4.7 Hz, NCH_2CH═), 5.07, 5.20 (2d, 4H, J=10.2, 17.4 Hz, CH_2═CH), 5.88 (m, 2H, CH_2═CH), 6.86 (d, 2H, J=8 Hz), 7.02 (t, 2H, J=8 Hz), 7.35 (t, 2H, J=8 Hz), 8.14 (d, 2H, J=8 Hz), 8.14 (br, 2H, NH). MS: m/z (%)=468 (20) [M^+]. Anal. calcd for $C_{26}H_{32}N_2O_6$ (468.6): C, 66.65, H, 6.88, N, 5.98. Found C, 66.61, H, 6.47, N, 6.50.

4.2.6. Compound 26. (From **20** and α,α-dibromo-*o*-xylene), yield 80%; mp 90–92°C (colorless crystals from EtOH). IR: 3404, 3054, 2985, 2921, 1654, 1600, 1530, 1481, 1452, 1421, 1379, 1297, 1265, 1226, 1162, 1105, 1048, 996, 927, 738, 703. ^{1}H NMR ($CDCl_3$) δ=3.95 (t, 4H, J=5.3 Hz, NCH_2CH═), 4.95, 4.97 (2d, 4H, J=9.6, 18.8 Hz, CH_2═CH), 5.29 (s, 4H, OCH_2Ar), 5.71 (m, 2H, CH_2═$CH$$CH_2$), 7.01 (d, 2H, J=8 Hz), 7.12 (t, 2H, J=7.6 Hz), 7.42–7.56 (m, 6H), 8.22 (d, 2H, J=7.8 Hz), 10.28 (br, 2H, NH). ^{13}C NMR ($CDCl_3$): δ=42.1, 68.9, 112.7, 116.0, 122.0, 122.1, 129.5, 130.0, 132.5, 132.9, 133.9, 134.1, 156.4, 164.9. MS: m/z=456 (M^+). Anal. calcd for $C_{28}H_{28}N_2O_4$ (456.6): C, 73.66, H, 6.18, N, 6.14. Found C, 73.70, H, 6.12, N, 6.10.

4.2.7. Compound 29. (From **28** and 1,2-dibromoethane), yield 78%; mp 113–115°C (colorless crystals from MeOH).

IR: 3358, 3069, 2937, 2868, 1664, 1599, 1535, 1479, 1452, 1421, 1331, 1290, 1235, 1161, 1133, 1090, 1045, 1013, 995, 917, 746, 674, 644. ^{1}H NMR ($CDCl_3$) δ=4.42 (d, 4H, J=5.1 Hz, OCH_2CH═), 4.66 (s, 4H, OCH_2CH_2O), 5.19, 5.30 (2d, J=10.8, 16.8 Hz, 4H, CH_2═CH), 5.93 (m, 2H, CH_2═$CH$$CH_2$), 6.76, 7.02, 7.12, 7.38, 8.18, 8.48 (m, 2H, 6H, 2H, 2H, 2H, 2H, ArH), 10.09 (s, 2H, NH). ^{13}C NMR ($CDCl_3$): δ=67.93, 69.46, 111.45, 113.55, 118.11, 120.09, 121.41, 122.36, 123.30, 123.69, 128.16, 132.53, 132.81, 132.98, 147.25, 156.10, 162.64. MS: m/z (%)=564 (100) [M^+]. Anal. calcd for $C_{34}H_{32}N_2O_6$ (564.6): C, 72.33, H, 5.71, N, 4.96. Found C, 72.12, H, 5.70, N, 5.18.

4.2.8. Compound 30. (From **28** and 1,3-dibromopropane), YIELD 85%; mp 146–148°C (colorless crystals from DMF). ^{1}H NMR ($CDCl_3$) δ=2.40 (quintet, 2H, J=6 Hz, OCH_2CH_2), 4.31 (t, 4H, J=6 Hz, OCH_2CH_2), 4.44 (d, 4H, J=5.3 Hz, OCH_2CH═), 5.14, 5.24 (2d, 4H, J=10.4, 17.2 Hz, CH_2═CH), 5.90 (m, 2H, CH_2═$CH$$CH_2$), 6.74, 6.83, 6.96, 7.03, 7.25, 8.16, 8.59 (m, 2H, 2H, 4H, 2H, 2H, 2H, 2H, ArH), 10.09 (s, 2H, NH). ^{13}C NMR ($CDCl_3$): δ=28.70, 67.88, 69.55, 111.73, 112.79, 118.01, 120.76, 121.49, 121.81, 122.98, 123.65, 128.42, 132.44, 132.92, 133.03, 147.22, 156.06, 163.27. MS: m/z (%)=578 (50) [M^+]. Anal. calcd for $C_{35}H_{34}N_2O_6$ (578.7): C, 72.65, H, 5.92, N, 4.84. Found C, 72.45, H, 5.52, N, 5.09.

4.2.9. Compound 31. (From **28** and 1,4-dibromobutane), yield 85%; mp 147–148°C (colorless crystals from DMF). IR: 3348, 3074, 2975, 2929, 1661, 1597, 1534, 1478, 1453, 1334, 1291, 1231, 1132, 1090, 1045, 998, 942, 918, 748, 675. ^{1}H NMR ($CDCl_3$) δ=2.07 (s, 4H, OCH_2CH_2), 4.20 (s, 4H, OCH_2CH_2), 4.57 (d, 4H, J=3.6 Hz, OCH_2CH═), 5.20, 5.29 (2d, 4H, J=10.5, 17.2 Hz, CH_2═CH), 5.97 (m, 2H, CH_2═$CH$$CH_2$), 6.86, 6.92, 7.03, 7.11, 7.41, 8.25, 8.64 (m, 2H, 2H, 4H, 2H, 2H, 2H, 2H, ArH), 10.19 (s, 2H, NH). Anal. calcd for $C_{36}H_{36}N_2O_6$ (592.7): C, 72.95, H, 6.12, N, 4.73. Found C, 72.75, H, 5.94, N, 4.73.

4.2.10. Compound 32. (From **28** and diethyleneglycol ditosylate), yield 70%; mp 86–88°C (colorless crystals from MeOH). IR: 3335, 3068, 2917, 2881, 1658, 1598, 1537, 1477, 1454, 1424, 1335, 1288, 1251, 1220, 1161, 1132, 1089, 1045, 1017, 1002, 936, 745, 678. ^{1}H NMR ($CDCl_3$) δ=3.84, 4.22 (2t, 4H, 4H, J=4, 4 Hz, $OCH_2CH_2OCH_2$-CH_2−O), 4.56 (d, 4H, J=4.5 Hz, OCH_2CH═), 5.23, 5.37 (2d, 4H, J=10.2, 17.2 Hz, CH_2═CH), 6.02 (m, 2H, CH_2═$CH$$CH_2$), 6.87 (m, 4H), 7.01 (m, 4H), 7.10 (t, 2H, J=7.6 Hz), 7.38 (t, 2H, J=7.6 Hz), 8.25 (dd, 2H, J=8, 1.6 Hz), 8.58 (d, 2H, J=8.4 Hz), 10.27 (s, 2H, NH). ^{13}C NMR ($CDCl_3$): δ=68.98, 69.29, 69.80, 111.94, 113.75, 118.11, 121.19, 121.53, 121.93, 123.13, 123.71, 128.63, 132.45, 132.93, 133.08, 147.63, 156.49, 164.00. MS; m/z (%)=608 (40) [M^+]. $C_{36}H_{36}$ N_2O_7 (608.7): C, 71.04, H, 5.96, N, 4.64. Found C, 70.82, H, 5.84, N, 4.71.

4.2.11. Compound 33. (From **28** and triethyleneglycol ditosylate), yield 70%; yellowish oil. IR: 3345, 3071, 2875, 1661, 1598, 1534, 1480, 1455, 1423, 1332, 1292, 1233, 1161, 1133, 1091, 1047, 1017, 930, 895, 753, 681. ^{1}H NMR ($CDCl_3$) δ=3.49, 3.72, 4.42 (s, 2t, 12H, J=5.2, 5.2 Hz, $OCH_2(CH_2OCH_2)_2CH_2O$), 4.62 (d, 4H, J=5.2 Hz, OCH_2-CH═), 5.27, 5.39 (2d, 4H, J=10.6, 17.6 Hz, CH_2═CH), 6.04 (m, 2H, CH_2═$CH$$CH_2$), 6.89, 7.03, 7.13, 7.44, 8.27, 8.59 (m, 2H, 6H, 2H, 2H, 2H, 2H, ArH), 10.29 (s, 2H, NH). Anal. calcd for $C_{38}H_{40}N_2O_8$ (652.7): C, 69.92, H, 6.12, N, 4.29. Found C, 69.65, H, 6.02, N, 4.45.

4.2.12. Compound 34. (From **28** and α,α-dibromo-*o*-xylene), yield 85%; mp 185–186°C (colorless crystals from DMF). IR: 3331, 3064, 2923, 2870, 1650, 1600, 1542, 1478, 1454, 1423, 1340, 1312, 1287, 1255, 1220, 1160, 1135, 1089, 1045, 1020, 936, 897, 748, 682. ^{1}H NMR ($CDCl_3$) δ=4.19 (d, 4H, J=4.6 Hz, OCH_2CH═), 5.04, 5.15 (2d, 4H, J=10.4, 17.2 Hz, CH_2═CH), 5.46 (s, 4H, OCH_2Ar), 5.72 (m, 2H, CH_2═$CH$$CH_2$), 6.80, 6.91, 7.01, 7.09, 7.21, 7.52, 8.23, 8.65 (m, 2H, 2H, 6H, 2H, 2H, 2H, 2H, 2H, ArH), 10.25 (s, 2H, NH). ^{13}C NMR ($CDCl_3$): δ=69.20, 69.25, 111.34, 113.12, 117.66, 120.62, 121.29, 121.93, 122.86, 123.61, 128.42, 128.75, 128.83, 132.51, 132.96, 133.02, 134.12, 147.16, 155.92, 163.12. MS: m/z=640 (M^+). Anal. calcd for $C_{40}H_{36}N_2O_6$ (640.6): C, 74.78, H, 5.66, N, 4.37. Found C, 74.88, H, 5.47, N, 4.52.

4.3. Reaction of *o*-allyloxybenzoyl chloride with bis-amines 35–40: synthesis of 41–46. General procedure

To a solution of each of the appropriate bis-amine hydrochlorides **35**–**40**[25] (10 mmol) in DCM (10 mL) at 0°C was added dropwise TEA (3 mL) followed by a dropwise addition of a solution of *o*-allyloxybenzoyl chloride[26] (4.1 g, 21 mmol) in DCM (10 mL) over a period of 30 min at 0°C. The reaction mixture was then kept stirring at room temperature overnight. The mixture was then diluted with DCM (50 mL) and washed with hydrochloric acid (2 M, 100 mL), then twice with saturated sodium carbonate solution and finally with water. The organic layer was then dried over anhydrous sodium sulfate and evaporated to dryness. The remaining bis-anilides **41**–**46** were recrystallized from the proper solvent.

4.3.1. Compound 41. Yield 75%; mp 175–177°C (pale yellow crystals from DMF/EtOH). ^{1}H NMR ($CDCl_3$) δ=4.46 (dd, 4H, J=3.2, 1.5 Hz, OCH_2CH═), 4.50 (s, 4H, OCH_2CH_2O), 5.06, 5.11 (2dd, 4H, J=10.4, 1.5, 17.6, 1.4 Hz, CH_2═CH), 5.72 (m, 2H, CH_2═$CH$$CH_2$), 6.77 (d, 2H, J=8.4 Hz), 6.98 (m, 4H), 7.08 (m, 4H), 7.35 (dt, 2H, J=8.4, 1.6 Hz), 8.05 (m, 2H), 8.69 (m, 2H), 10.37 (s, 2H, NH). ^{13}C NMR ($CDCl_3$): δ=67.09, 69.65, 111.02, 113.17, 117.50, 121.16, 121.44, 121.93, 122.05, 123.49, 128.80, 132.26, 132.41, 132.98, 147.16, 156.10, 163.28. Anal. calcd for $C_{34}H_{32}N_2O_6$ (564.6): C, 72.33, H, 5.71, N, 4.96. Found C, 72.05, H, 5.75, N, 5.28.

4.3.2. Compound 42. Yield 78%; mp 128–130°C (colorless crystals from EtOH). IR: 3354, 3068, 2968, 2946, 2881, 1659, 1598, 1533, 1480, 1451, 1331, 1288, 1252, 1219, 1133, 1090, 1048, 1015, 991, 926, 893, 750, 675. ^{1}H NMR ($CDCl_3$) δ=2.33 (quintet, 2H, J=6.2 Hz, OCH_2CH_2), 4.28 (t, 4H, J=4.6 Hz, OCH_2CH_2), 4.67 (d, 4H, J=5 Hz, OCH_2CH═), 5.22, 5.30 (2d, 4H, J=10.4, 17.2 Hz, CH_2═CH), 5.98 (m, 2H, CH_2═$CH$$CH_2$), 6.87, 6.92, 6.97, 7.00, 7.14, 7.45, 8.29, 8.62 (m, 2H, 2H, 2H, 2H, 2H, 2H, 2H, 2H, ArH), 10.30 (s, 2H, NH). ^{13}C NMR ($CDCl_3$): δ=28.99, 65.12, 70.32, 111.31, 113.61, 118.27, 121.25, 121.47, 121.82, 122.68, 123.80, 128.52, 132.33, 132.46, 133.01,

147.84, 156.34, 163.25. MS: *m/z* (%)=578 (50) [M^+]. Anal. calcd for $C_{35}H_{34}N_2O_6$ (578.7): C, 72.65, H, 5.92, N, 4.84. Found C, 72.55, H, 5.54, N, 4.86.

4.3.3. Compound 43. Yield 85%; mp 146–148°C (colorless crystals from DMF). ^{1}H NMR ($CDCl_3$) δ=2.01 (s, 4H, OCH_2CH_2), 4.15 (s, 4H, OCH_2CH_2), 4.69 (d, 4H, *J*=4.7 Hz, OCH_2CH=), 5.20, 5.30 (2d, 4H, *J*=10.6, 17.2 Hz, CH_2=CH), 5.98 (m, 2H, CH_2=$CHCH_2$), 6.91, 7.03, 7.10, 7.40, 8.27, 8.63 (m, 4H, 4H, 2H, 2H, 2H, 2H, ArH), 10.26 (s, 2H, NH). ^{13}C NMR ($CDCl_3$): δ=25.88, 68.08, 70.28, 111.10, 113.54, 118.20, 121.14, 121.31, 121.76, 122.73, 123.71, 128.49, 132.31, 132.41, 132.96, 147.61, 156.28, 163.22. Anal. calcd for $C_{36}H_{36}N_2O_6$ (592.7): C, 72.95, H, 6.12, N, 4.73. Found C, 72.80, H, 5.94, N, 4.73.

4.3.4. Compound 44. Yield 80%; mp 95–97°C (colorless crystals from MeOH). IR: 3332, 3067, 2916, 2874, 1656, 1597, 1535, 1478, 1454, 1333, 1287, 1252, 1221, 1161, 1133, 1092, 1046, 993, 946, 918, 751, 676. ^{1}H NMR ($CDCl_3$) δ=3.84, 4.20 (2t, 8H, *J*=4.6, 4.6 Hz, OCH_2CH_2–OCH_2CH_2O), 4.75 (d, 4H, *J*=5 Hz, OCH_2CH=), 5.23, 5.40 (2d, 4H, *J*=10.4, 17.2 Hz, CH_2=CH), 6.03 (m, 2H, CH_2=$CHCH_2$), 6.88, 7.04, 7.39, 8.24, 8.66 (m, 4H, 6H, 2H, 2H, 2H, ArH), 10.39 (s, 2H, NH). MS; *m/z* (%)=608 (80) [M^+]. Anal. calcd for $C_{36}H_{36}N_2O_7$ (608.7): C, 71.04, H, 5.96, N, 4.64. Found C, 70.82, H, 5.84, N, 4.71.

4.3.5. Compound 45. Yield 70%; yellowish oil. ^{1}H NMR ($CDCl_3$) δ=3.57, 3.78, 4.20 (s, 2t, 12H, *J*=4.6, 4.6 Hz, $OCH_2(CH_2OCH_2)_2CH_2O$), 4.83 (d, 4H, *J*=5.2 Hz, OCH_2-CH=), 5.29, 5.38 (2d, 4H, 10.8, 17.8, CH_2=CH), 6.09 (m, 2H, CH_2=$CHCH_2$), 6.94, 7.04, 7.12, 7.41, 8.27, 8.65 (m, 4H, 4H, 2H, 2H, 2H, 2H, ArH), 10.38 (s, 2H, NH). Anal. calcd for $C_{38}H_{40}N_2O_8$ (652.7): C, 69.92, H, 6.12, N, 4.29. Found C, 70.23, H, 5.85, N, 4.55.

4.3.6. Compound 46. Yield 80%; mp 134–136°C (colorless crystals from EtOH). IR: 3368, 3326, 2979, 2892, 1656, 1599, 1538, 1479, 1453, 1334, 1290, 1252, 1217, 1088, 1047, 1004, 928, 895, 755, 739, 681, 664. ^{1}H NMR ($CDCl_3$) δ=4.15 (d, 4H, *J*=4.8 Hz, OCH_2CH=), 5.06, 5.11 (2d, 4H, *J*=10.4, 17.2 Hz, CH_2=CH), 5.28 (s, 4H, OCH_2Ar), 5.68 (m, 2H, CH_2=$CHCH_2$), 6.88, 6.97, 7.12, 7.41, 7.51, 8.32, 8.66 (m, 6H, 2H, 2H, 4H, 2H, 2H, 2H, ArH), 10.49 (s, 2H, NH). MS: *m/z* (%)=640 (80) [M^+]. Anal. calcd for $C_{40}H_{36}N_2O_6$ (640.6): C, 74.78, H, 5.66, N, 4.37. Found C, 74.75, H, 5.73, N. Anal. calcd for 4.40.

4.3.7. Ring closing metathesis of 21–26, 29–34 and 41–46: synthesis of 1–18. General procedure. A solution of each of the substrates **21**–**26**, **29**–**34** and **41**–**46** (0.12 mmol) in DCM (10 mL) and Grubbs' Catalyst (**I**, 1–10 mg, ca. 1–10 mol% of the substrate) was heated under reflux for 3 h (Tables 1–3). The reaction mixture was then mixed well with silica gel (100–200 mm, 0.5 g) and filtered, and the silica was extracted twice with DCM (25 mL). The solvent was removed from the mixed DCM extract in vacuo and the remaining reaction products were analyzed by ^{1}H NMR. The product mixture was purified and separated either by column chromatography, preparative thin layer chromatography, or preparative HPLC (cf. Tables 1–3).

4.3.8. Compound 1. Mp 163–165°C, purified by ptlc (eluent: DCM/EtOAc/petroleum ether (40–60), 1:2:2, R_f=0.65). ^{1}H NMR ($CDCl_3$): δ=4.10 (s, 4H, CH_2N), 4.59 (s, 4H, CH_2O), 6.04 (s, 2H, CH=CH), 6.96 (d, 2H, *J*=8.2 Hz), 7.13 (t, 2H, *J*=7.6 Hz), 7.45 (t, 2H, *J*=8.1 Hz), 8.05 (d, 2H, *J*=7.6 Hz) 7.34 (br, 2H, NH). MS; *m/z* (%)=352 (40) [M^+]. Anal. calcd for $C_{20}H_{20}N_2O_4$ (352.39): C, 68.17, H, 5.72, N, 7.95. Found C, 67.95, H, 5.65, N, 8.20.

4.3.9. Compound 2. Mp 151–153°C, purified by ptlc (eluent: DCM/EtOAc/petroleum ether (40–60), 1:1:1, R_f=0.7). IR: 3054, 2919, 2850, 1651, 1601, 1534, 1467, 1382, 1295, 1265, 1105, 1051, 1018, 739, 705. ^{1}H NMR ($CDCl_3$): δ=2.45 (quintet, 2H, *J*=6.4 Hz, CH_2CH_2O), 4.16 (s, 4H, CH_2N), 4.34 (t, 4H, *J*=6.4 Hz, CH_2O), 6.00 (s, 2H, CH=CH), 7.02 (d, 2H, *J*=8.1 Hz), 7.15 (t, 2H, *J*=7.6 Hz), 7.46 (t, 2H, *J*=7.6 Hz), 8.18 (d, 2H, *J*=8.1 Hz), 7.86 (br, 2H, NH). ^{13}C NMR ($CDCl_3$): δ=29.9, 40.7, 66.6, 114.2, 122.5, 122.9, 129.1, 132.3, 132.7, 156.3, 164.9. MS; *m/z* (%)=366 (20) [M^+]. Anal. calcd for $C_{21}H_{22}N_2O_4$ (366.4): C, 68.84, H, 6.05, N, 7.65. Found C, 68.64, H, 5.85, N, 7.56.

4.3.10. Compound 3. Mp 128–130°C, purified by ptlc (eluent: DCM/EtOAc/petroleum ether (40–60), 1:1:1, R_f=0.8). IR: 3333, 3069, 2948, 1732, 1659, 1598, 1533, 1478, 1453, 1384, 1334, 1291, 1220, 1090, 1047, 1014, 994, 897, 751, 683. ^{1}H NMR ($CDCl_3$): δ=2.09 (s, 4H, CH_2CH_2O), 4.17 (s, 4H, CH_2N), 4.25 (s, 4H, CH_2O), 5.98 (s, 2H, CH=CH), 6.99 (d, 2H, *J*=8.4 Hz), 7.12 (t, 2H, *J*=7.6 Hz), 7.46 (t, 2H, *J*=8.1 Hz), 8.23 (d, 2H, *J*=8.0 Hz), 7.90 (br, 2H, NH). MS; *m/z* (%)=380 (20) [M^+]. Anal. calcd for $C_{21}H_{22}N_2O_4$ (380.5): C, 69.46, H, 6.36, N, 7.36. Found C, 69.36, H, 6.57, N, 6.94.

4.3.11. Compound 4. Mp 163–165°C, purified by ptlc (eluent: DCM/EtOAc/hexane 1:1:1, R_f=0.75). IR: 3394, 3070, 2929, 2875, 1649, 1600, 1533, 1483, 1448, 1298, 1234, 1161, 1125, 1106, 1048, 960, 940, 753. ^{1}H NMR ($CDCl_3$) δ=3.97, 4.29 (2t, 8H, *J*=3.6, 3.6 Hz, OCH_2 groups), 4.15 (s, 4H, NCH_2CH=), 5.91 (br, 2H, CH=CH), 6.95 (d, 2H, *J*=8.2 Hz), 7.12 (t, 2H, *J*=7.6 Hz), 7.44 (dt, *J*=8.1, 1.5 Hz), 8.24 (dd, 2H, 7.7, 1.5), 8.16 (s, 2H, NH). ^{13}C NMR ($CDCl_3$) (*E*-isomer): δ=41.5, 67.7, 68.2, 112.6, 122.1, 128.3, 132.6, 132.7, 132.9, 156.7, 165.0. MS; *m/z* (%): 396 (30) [M^+]. Anal. calcd for $C_{22}H_{24}N_2O_5$ (396.5): C, 66.65, H, 6.10, N, 7.07. Found C, 66.39, H, 6.31, N, 6.62.

4.3.12. Compound 5. (*E* and *Z*): mp 134–136°C, purified by ptlc (eluent: DCM/EtOAc/hexane 1:1:1, R_f=0.65). IR: 3387, 3053, 2926, 1727, 1657, 1601, 1531, 1485, 1449, 1302, 1265, 1252, 1133, 1106, 1086, 1051, 925, 737, 703. ^{1}H NMR ($CDCl_3$) δ=3.72, 3.90, 4.27 (s, 2t, 12H, *J*=4, 4 Hz, OCH_2 groups), 4.12 (m, 4H, NCH_2CH=), 5.69 (t, 2H, *J*=3.9 Hz, *Z*-CH=CH), 5.86 (s, 2H, *E*-CH=CH), 6.94 (d, 2H, *J*=8.2 Hz), 7.09 (t, 2H, *J*=7.6 Hz), 7.42 (dt, 2H, *J*=8.2, 1.5 Hz), 8.21 (dd, 2H, *J*=8.0, 1.5 Hz), 8.22 (br, 2H, NH, *E*), 8.30 (br, 2H, NH, *Z*). ^{13}C NMR ($CDCl_3$) (*E*-isomer): δ=41.3, 68.1, 69.5, 70.5, 112.7, 121.9, 128.7, 132.6, 132.7, 132.8, 156.7, 165.2; (*Z*-isomer): δ=37.1, 68.2, 69.6, 70.4, 112.6, 122.1, 129.3, 132.5, 132.7, 132.84, 156.7, 165.3. MS; *m/z* (%): 440 (40) [M^+]. Anal. calcd for $C_{24}H_{28}N_2O_6$

(440.5): C, 65.44, H, 6.41, N, 6.36. Found C, 65.19, H, 6.49, N, 6.12.

4.3.13. Compound 6. (*E* and *Z*): mp 240–242°C, purified by ptlc (eluent: DCM/EtOAc/petroleum ether (40–60), 1:1:1, R_f=0.71). ^{1}H NMR ($CDCl_3$) (*E*-isomer): δ=3.92 (s, 4H, CH_2N), 5.32 (s, 4H, CH_2O), 5.58 (s, 2H, CH=CH), 7.13 (m, 4H), 7.45–7.59 (m, 6H), 8.21 (d, 2H, *J*=7.6 Hz), 7.74 (br, 2H, NH), (*Z*-isomer): δ=5.23 (s, 4H, OCH_2), 5.41 (t, 2H, *J*=4.2 Hz, CH=CH). ^{13}C NMR ($CDCl_3$) (*E*-isomer): δ=40.3, 68.7, 113.4, 122.3, 122.5, 128.8, 129.5, 130.0, 132.4, 132.7, 133.9, 156.9, 164.4, (*Z*-isomer): δ=36.0, 68.6, 112.5, 121.6, 122.0, 129.6, 129.9, 131.4, 132.5, 133.9, 134.3, 157.0, 164.7 MS; *m*/*z* (%)=428 (50) [M^+]. Anal. calcd for $C_{26}H_{24}N_2O_4$ (428.5): C, 72.88, H, 5.65, N, 6.54. Found C, 72.62, H, 5.85, N, 6.33.

4.3.14. Compound 7. (*E* and *Z*): mp 200–202°C, purified by ptlc (eluent: MeOH/DCM/petroleum ether (40–60), 0.1:1:2, R_f=0.31). IR: 3343, 3066, 2962, 1662, 1599, 1537, 1478, 1454, 1383, 1335, 1290, 1251, 1216, 1162, 1134, 1092, 1044, 1019, 797, 750, 682. ^{1}H NMR ($CDCl_3$) (*E*-isomer): δ=4.69 (s, 8H, CH_2OAr, OCH_2CH=), 6.36 (s, 2H, CH=CH), 6.99–8.75 (m, 16H, ArH), 10.40 (s, 2H, NH). ^{13}C NMR ($CDCl_3$): δ=65.30, 68.53, 110.75, 113.05, 120.52, 121.80, 122.54, 123.14, 123.71, 128.39, 129.45, 132.71, 133.29, 147.34, 155.50, 162.83. ^{1}H NMR ($CDCl_3$) (*Z*-isomer): δ=4.69 (s, 4H, OCH_2 CH_2O), 4.84 (d, 4H, *J*=5 Hz, OCH_2CH=), 6.18 (t, 2H, *J*=5 Hz, CH=CH), 6.99–8.64 (m, 16H, ArH), 10.35 (s, 2H, NH). ^{13}C NMR ($CDCl_3$): δ=65.10, 65.37, 110.99, 113.31, 120.53, 121.97, 122.64, 123.14, 123.71, 128.83, 129.45, 132.85, 133.42, 147.34, 155.50, 162.83. MS; *m*/*z* (%)=536 (100) [M^+]. Anal. calcd for $C_{32}H_{28}N_2O_6$ (536.6): C, 71.63, H, 5.26, N, 5.22. Found C, 71.50, H, 5.34, N, 4.85.

4.3.15. Compound 8. (*E* and *Z*): mp 203–206°C, purified by ptlc (eluent: EtOAc/DCM/petroleum ether (40–60), 1:2:3, R_f=0.85). ^{1}H NMR ($CDCl_3$) (*E*-isomer): δ=2.52 (quintet, 2H, *J*=6.1 Hz, OCH_2CH_2), 4.36 (t, 4H, *J*=6.1 Hz, OCH_2CH_2), 4.60 (s, 4H, OCH_2CH=), 6.22 (s, 2H, CH=CH), 6.89–8.60 (m, 16H, ArH), 10.19 (s, 2H, NH). ^{13}C NMR ($CDCl_3$): δ=29.11, 67.42, 69.00, 111.63, 113.16, 121.43, 121.78, 121.94, 122.81, 123.85, 128.47, 128.96, 132.91, 133.21, 147.65, 156.33, 163.31. ^{1}H NMR ($CDCl_3$) (*Z*-isomer): δ=2.53 (quintet, 2H, *J*=6.1 Hz, OCH_2CH_2), 4.36 (t, 4H, *J*=6.1 Hz, OCH_2CH_2), 4.71 (d, 4H, *J*=3.7 Hz, OCH_2CH=), 6.04 (t, 2H, *J*=3.7 Hz, CH=CH), 6.84–8.58 (m, 16H, ArH), 10.19 (s, 2H, NH). ^{13}C NMR ($CDCl_3$): δ=29.11, 64.09, 66.90, 112.39, 112.61, 121.43, 121.78, 122.16, 122.50, 123.91, 128.53, 128.86, 132.47, 133.21, 147.40, 156.33, 163.25. MS; *m*/*z* (%)=550 (100) [M^+]. Anal. calcd for $C_{33}H_{30}N_2O_6$ (550.6): C, 71.99, H, 5.49, N, 5.09. Found C, 71.73, H, 5.65, N, 4.85.

4.3.16. Compound 9. (*E* and *Z*): mp 238–240°C, purified over short column of silca gel using DCM as an eluent. IR: 3347, 3069, 2965, 2886, 1656, 1597, 1532, 1478, 1455, 1331, 1293, 1252, 1217, 1135, 1089, 1041, 1015, 747, 678. ^{1}H NMR ($CDCl_3$) (*E*-isomer): δ=1.99 (br, 4H, CH_2CH_2O), 4.25 (br, 4H, OCH_2CH_2), 4.63 (d, 4H, *J*=3.7 Hz, OCH_2–CH=), 6.26 (t, 2H, *J*=3.7 Hz, CH=CH), 6.91–8.68 (m, 16H, ArH), 10.29 (s, 2H, NH). ^{13}C NMR ($CDCl_3$): δ=25.5, 67.9, 68.9, 110.6, 112.4, 121.2, 121.5, 121.6, 122.4, 123.7, 128.4, 130.2, 132.8, 133.2, 147.4, 156.0, 163.4. ^{1}H NMR ($CDCl_3$) (*Z*-isomer): δ=1.98 (br, 4H, CH_2CH_2O), 4.25 (br, 4H, OCH_2CH_2), 4.81 (d, 4H, *J*=3.7 Hz, OCH_2CH=), 6.08 (t, 2H, *J*=3.7 Hz, CH=CH), 6.90–8.66 (m, 16H, ArH), 10.37 (s, 2H, NH). MS; *m*/*z* (%): 564 (100) [M^+]. Anal. calcd for $C_{34}H_{32}N_2O_6$ (564.6): C, 72.33, H, 5.71, N, 4.96. Found C, 72.70, H, 5.70, N, 5.13.

4.3.17. Compound 10. (*E* and *Z*): mp 190–192°C, purified by pHPLC (eluent: CH_3CN/H_2O, 7:3). IR: 3364, 3332, 3065, 3035, 2938, 2875, 1657, 1598, 1533, 1478, 1453, 1385, 1330, 1290, 1217, 1162, 1132, 1088, 1044, 1000, 966, 894, 750, 661. ^{1}H NMR ($CDCl_3$) (*E*-isomer): δ=3.97, 4.27 (2t, 8H, *J*=5.8, 5.8 Hz, $(OCH_2CH_2O)_2$), 4.75 (s, 4H, OCH_2CH=), 6.28 (s, 2H, CH=CH), 6.90–8.62 (m, 16H, ArH), 10.20 (s, 2H, NH). ^{13}C NMR ($CDCl_3$) (*E*-isomer): δ=68.5, 68.8, 69.00, 111.5, 113.2, 121.7, 121.72, 121.9, 122.8, 123.9, 128.5, 128.6, 132.7, 133.1, 147.8, 156.3, 163.4. ^{1}H NMR ($CDCl_3$) (*Z*-isomer): δ 4.02, 4.31 (2t, 8H, *J*=5.6, 5.6 Hz, $(OCH_2CH_2O)_2$), 4.86 (d, 4H, *J*=3.7 Hz, OCH_2CH=), 6.14 (t, 2H, *J*=3.7 Hz, CH=CH), 6.98–8.65 (m, 16H, ArH), 10.22 (s, 2H, NH). ^{13}C NMR ($CDCl_3$) (*Z* isomer): δ=67.7, 68.8, 69.2, 111.4, 113.4, 121.7, 121.8, 122.1, 122.8, 123.1, 128.5, 132.7, 133.1, 147.5, 156.4, 163.3. MS; *m*/*z* (%): 580 (60) [M^+]; LCMS; *m*/*z*=581 [M+1]. Anal. calcd for $C_{34}H_{32}N_2O_7$ (580.6): C, 70.33, H, 5.56, N, 4.82. Found C, 69.78, H, 5.60, N, 4.91.

4.3.18. Compound 11. (*E* and *Z*): mp 196–198°C, purified by ptlc (eluent: EtOAc/DCM/hexane 1:1:2, R_f=0.42). IR: 3164, 3061, 2990, 2916, 2848, 1736, 1444, 1376, 1270, 1246, 1045, 918, 849, 738, 704. ^{1}H NMR ($CDCl_3$) (*E*-isomer): δ=3.51, 3.74, 4.22 (s, 2t, 12H, *J*=5.6, 5.6 Hz, OCH_2CH_2O), 4.76 (s, 4H, OCH_2CH=), 6.17 (s, 2H, CH=CH), 6.92–8.56 (m, 16H, ArH), 10.32 (s, 2H, NH). ^{1}H NMR ($CDCl_3$) (*Z*-isomer): δ 3.52, 3.85, 4.36 (s, 2t, 12H, *J*=5.6, 5.6 Hz, OCH_2CH_2O), 4.83 (d, 4H, *J*=2.9 Hz, OCH_2CH=), 6.03 (t, 2H, *J*=2.9 Hz, CH=CH), 6.94–8.54 (m, 16H, ArH), 10.26 (s, 2H, NH). LC/MS; *m*/*z*=625 [M+1]. Anal. calcd for $C_{36}H_{36}N_2O_8$ (624.7): C, 69.22, H, 5.81, N, 4.48. Found C, 69.50, H, 5.68, N, 4.50.

4.3.19. Compound 12. (*E* and *Z*): mp 240–242°C, purified by ptlc (eluent: EtOAc/DCM/hexane 5:2:5, R_f=0.95). IR: 3328, 3069, 3035, 2938, 2881, 1657, 1599, 1541, 1479, 1455, 1408, 1336, 1293, 1257, 1219, 1162, 1133, 1091, 1045, 1110, 965, 907, 753, 732, 675. ^{1}H NMR ($CDCl_3$) (*E*-isomer): δ=4.15 (s, 4H, OCH_2CH=), 5.35 (s, 4H, OCH_2Ar), 5.84 (s, 2H, CH=CH), 6.85–8.68 (m, 20H, ArH), 10.56 (s, 2H, NH). ^{1}H NMR ($CDCl_3$) (*Z*-isomer): δ=4.53 (d, 4H, *J*=3.2 Hz, OCH_2CH=), 5.44 (s, 4H, OCH_2Ar), 6.85 (t, 2H, *J*=3.2 Hz, CH=CH), 6.84–8.77 (m, 20H, ArH), 10.75 (s, 2H, NH). ^{13}C NMR ($CDCl_3$): (*E* and *Z* isomer) δ=65.36, 65.73, 65.90, 69.53. 111.18, 111.64, 113.39, 120.70, 121.09, 121.60, 121.66, 122.17, 122.33, 123.00, 123.75, 123.83, 126.77, 128.47, 128.50, 128.69, 132.45, 132.84, 133.19, 147.24, 156.14, 156.43, 163.07, 163.14. MS; *m*/*z* (%): 612 (60) [M^+]. Anal. calcd for $C_{38}H_{32}N_2O_6$ (612.7): C, 74.50, H, 5.26, N, 4.57. Found C, 74.65, H, 5.56, N, 4.62.

4.3.20. Compound 13. (*E* and *Z*): mp 224–226°C, purified

by ptlc (eluent: EtOAc/DCM/petroleum ether (40–60) 2:1:3 R_f=0.48). ^{1}H NMR ($CDCl_3$) (*E*-isomer): δ=4.40 (s, 4H, OCH_2CH_2O), 4.75 (s, 4H, OCH_2CH=), 6.30 (s, 2H, CH=CH), 6.94–8.66 (m, 16H, ArH), 10.40 (s, 2H, NH). ^{1}H NMR ($CDCl_3$) (*Z*-isomer): δ=4.51 (s, 4H, OCH_2CH_2O), 4.98 (d, 4H, *J*=3.2 Hz, OCH_2CH=), 6.18 (t, 2H, *J*=3.2 Hz, CH=CH), 6.94–8.64 (m, 16H, ArH), 10.45 (s, 2H, NH). ^{13}C NMR ($CDCl_3$) (*E*+*Z*): δ=67.1, 69.6 (2 OCH_2, OCH_2–CH=), 111.1, 113.2, 117.5, 121.2, 121.4, 121.9, 122.0, 123.5, 128.8, 132.3, 132.4, 132.9, 147.2, 156.1, 163.3 (all ^{13}C-signals of both *E* and *Z* isomers coincide except one in the sp^2 region most probably the CH=CH). MS; *m*/*z* (%)=536 (30) [M^+]. Anal. calcd for $C_{32}H_{28}N_2O_6$ (536.6): C, 71.63, H, 5.26, N, 5.22. Found C, 71.54, H, 5.16, N, 4.87.

4.3.21. Compound 14. (*E* and *Z*): mp 236–238°C, purified by ptlc (eluent: EtOAc/DCM/petroleum ether (40–60), 1:1:3, R_f=0.45). IR: 3342, 3069, 3035, 2930, 2881, 1656, 1598, 1535, 1478, 1453, 1378, 1333, 1291, 1250, 1214, 1133, 1090, 1048, 1003, 751, 674. ^{1}H NMR ($CDCl_3$) (*E*-isomer): δ=2.36 (quintet, 2H, *J*=6 Hz, CH_2CH_2O), 4.28 (t, 4H, *J*=6 Hz, OCH_2CH_2), 4.84 (s, 4H, OCH_2CH=), 6.21 (s, 2H, CH=CH), 6.92–8.70 (m, 16H, ArH), 10.37 (s, 2H, NH). ^{1}H NMR ($CDCl_3$) (*Z*-isomer): δ=2.42 (quintet, 2H, *J*=6 Hz, CH_2CH_2O), 4.29 (t, 4H, *J*=6 Hz, OCH_2CH_2), 4.96 (s, 4H, OCH_2CH=), 6.21 (s, 2H, CH=CH), 6.92–8.70 (m, 16H, ArH), 10.30 (s, 2H, NH). ^{13}C NMR ($CDCl_3$): δ=28.63 (*Z*), 29.26 (*E*), 65.36 (*E*), 65.73 (*Z*), 65.90 (*Z*), 69.53 (*E*), 111.18, 111.64, 113.39, 120.70, 121.09, 121.60, 121.66, 122.17, 122.33, 122.96, 123.75, 123.83, 126.77, 128.47, 128.60, 128.69, 132.55, 132.84, 133.19, 147.24, 156.14, 156.53, 163.07, 163.14 (sp^2 carbons of both *E* and *Z* isomers). MS; *m*/*z* (%): 550 (100) [M^+]. Anal. calcd for $C_{33}H_{30}N_2O_6$ (550.6): C, 71.99, H, 5.49, N, 5.09. Found C, 71.84, H, 5.47, N, 5.00.

4.3.22. Compound 15. (*E* and *Z*): mp 256–258°C, purified by ptlc (eluent: EtOAc/DCM/petroleum ether (40–60), 2:1:3, R_f=0.72). ^{1}H NMR ($CDCl_3$) (*E*-isomer): δ=2.03 (br, 4H, CH_2CH_2O), 4.16 (br, 4H, OCH_2CH_2), 4.83 (s, 4H, OCH_2CH=), 6.23 (s, 2H, CH=CH), 6.90–8.69 (m, 16H, ArH), 10.20 (s, 2H, NH). ^{1}H NMR ($CDCl_3$) (*Z*-isomer): δ=2.07 (br, 2H, CH_2CH_2O), 4.16 (br, 4H, OCH_2CH_2), 5.01 (s, 4H, OCH_2CH=), 6.05 (s, 2H, 1H, CH=CH), 6.90–8.69 (m, 16H, ArH), 10.29 (s, 2H, NH). ^{13}C NMR ($CDCl_3$) (*E* and *Z* isomer): δ=25.9, 68.1, 70.3, 110.6, 111.4, 118.2, 121.2, 121.22, 121.8, 123.7, 128.5, 129.1, 132.4, 133.0, 147.6, 156.3, 163.2. MS; *m*/*z* (%): 564 (50) [M^+]. Anal. calcd for $C_{34}H_{32}N_2O_6$ (564.6): C, 72.33, H, 5.71, N, 4.96. Found C, 72.50, H, 6.10, N, 4.62.

4.3.23. Compound 16. (*E* and *Z*): mp 198–200°C, purified by pHPLC (eluent: CH_3CN/H_2O, 7:3). IR: 3342, 3067, 3033, 2932, 2877, 1656, 1598, 1538, 1478, 1455, 1333, 1292, 1253, 1219, 1163, 1133, 1091, 1050, 985, 967, 747, 680. ^{1}H NMR ($CDCl_3$) (*E*-isomer): δ=3.88, 4.19 (2t, 8H, *J*=4.8, 4.8 Hz, $(OCH_2CH_2O)_2$), 4.90 (s, 4H, OCH_2CH=), 6.31 (s, 2H, CH=CH), 6.87–8.68 (m, 16H, ArH), 10.32 (s, 2H, NH). ^{1}H NMR ($CDCl_3$) (*Z*-isomer): δ 3.90, 4.28 (2t, 8H, *J*=4.9, 4.9 Hz, $(OCH_2CH_2O)_2$), 5.09 (d, 4H, *J*=3.1 Hz, OCH_2CH=), 6.19 (t, 2H, *J*=3.1 Hz, CH=CH), 6.87–8.74 (m, 16H, ArH), 10.47 (s, 2H, NH). ^{13}C NMR ($CDCl_3$): (*E* isomer) δ=68.3, 69.4, 69.5, 111.8, 112.2, 121.0, 121.8, 121.9, 122.9, 123.7, 128.1, 128.9, 132.7, 133.0, 147.4, 156.4, 163.2; ^{13}C NMR ($CDCl_3$): (*Z* isomer) δ=65.6, 68.2, 69.6, 111.4, 112.7, 121.0, 121.7, 121.9, 122.6, 123.6, 128.7, 129.0, 132.5, 132.9, 147.3, 156.0, 163.1. MS; *m*/*z* (%): 580 (60) [M^+]; LCMS; *m*/*z*=581 [M+1]. Anal. calcd for $C_{34}H_{32}N_2O_7$ (580.6): C, 70.33, H, 5.56, N, 4.82. Found C, 70.33, H, 5.58, N, 5.03.

4.3.24. Compound 17. (*E* and *Z*): mp 182–184°C, purified by ptlc (eluent: EtOAc/DCM/hexane 1:1:2, R_f=0.6). ^{1}H NMR ($CDCl_3$) (*E*-isomer): δ=3.64 (s, 4H, OCH_2CH_2O), 3.88, 4.21 (2t, 8H, *J*=4.3, 4.3 Hz, $(OCH_2CH_2O)_2$), 4.97 (s, 4H, OCH_2CH=), 6.26 (s, 2H, CH=CH), 6.87–8.68 (m, 16H, ArH), 10.44 (s, 2H, NH). ^{1}H NMR ($CDCl_3$) (*Z*-isomer): δ 3.61, (s, 4H, OCH_2CH_2O), 3.89, 4.26 (2t, 8H, *J*=4.6, 4.6 Hz, $(OCH_2CH_2O)_2$), 5.16 (d, 4H, *J*=3.2 Hz, OCH_2CH=), 6.18 (t, 2H, *J*=3.1 Hz, CH=CH), 6.84–8.76 (m, 16H, ArH), 10.58 (s, 2H, NH). ^{13}C NMR ($CDCl_3$): (*E* isomer) δ=68.18, 68.25, 69.26, 69.73, 111.43, 113.71, 121.01, 121.58, 121.88, 122.52, 123.59, 128.59, 128.79, 132.53, 132.87, 147.33, 156.24, 163.17. LCMS; *m*/*z*=625 [M+1]. Anal. calcd for $C_{36}H_{36}N_2O_8$ (624.7): C, 69.22, H, 5.81, N, 4.48. Found C, 69.50, H, 5.68, N, 4.50.

4.3.25. Compound 18. (*E* and *Z*): mp 277–279°C, purified by ptlc (eluent: EtOAc/DCM/hexane 1:1:1, R_f=0.93). IR: 3342, 3068, 3036, 2930, 2878, 1655, 1598, 1536, 1478, 1453, 1384, 1334, 1290, 1251, 1215, 1161, 1133, 1090, 1049, 1001, 896, 750, 675. ^{1}H NMR ($CDCl_3$) (*E*-isomer): δ=4.36 (s, 4H, OCH_2CH=), 5.39 (s, 4H, OCH_2Ar), 5.96 (s, 2H, CH=CH), 6.92–8.77 (m, 20H, ArH), 10.57 (s, 2H, NH). ^{1}H NMR ($CDCl_3$) (*Z*-isomer): δ=4.49 (d, 4H, *J*=2.8 Hz, OCH_2CH=), 5.35 (s, 4H, OCH_2Ar), 5.64 (t, 2H, *J*=2.8 Hz, CH=CH), 6.87–8.65 (m, 20H, ArH), 10.43 (s, 2H, NH). ^{13}C NMR ($CDCl_3$): (*E* and *Z* isomer) δ=65.46, 67.75, 67.93, 68.54. 110.80, 111.49, 112.67, 112.98, 120.88, 121.05, 121.45, 121.90, 121.97, 123.53, 123.41, 127.38, 127.65, 128.67, 128.77, 128.87, 132.78, 132.91, 133.03, 134.51, 146.89, 147.58, 155.87, 156.12, 162.94, 163.03. MS; *m*/*z* (%): 612 (60) [M^+]. Anal. calcd for $C_{38}H_{32}N_2O_6$ (612.7): C, 74.50, H, 5.26, N, 4.57. Found C, 74.33, H, 5.28, N, 4.49.

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