Efficient synthesis of 19–31 membered macrocyclic tetralactones via ring closing metathesis in ionic liquids

Sengodagounder Muthusamy *, Datschnamoorthy Azhagan

School of Chemistry, Bharathidasan University, Tiruchirappalli 620 024, India

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ABSTRACT

The ring closing metathesis reaction in the presence of Grubbs catalyst was demonstrated using several ionic liquids to synthesize a range of macrocyclic tetralactones having ring size of 19 to 31 membered with different spacers. The ionic liquid [mmim][PF$_6$] was found to be an excellent solvent and the recovery of the catalyst was demonstrated. X-ray analysis of a representative macrocyclic tetralactone was also reported.

1. Introduction

During the past decade, ring closing metathesis (RCM) has found increasing application in the synthesis of carbo- and heterocyclic ring systems.[1] The application of RCM as the key macrocyclization step in the synthesis of crown compounds has opened their importance in supramolecular chemistry.[2–6] The success of this reaction has been mainly due to the availability of Grubbs[7] (**1–3**) and Hoveyda[8] (**4,5**) catalysts (Fig. 1). But these catalysts are not recyclable and can only be separated via repeated chromatography severely hampers their application. Several reports have recently demonstrated the solutions for this problem. The methods rely on the removal of ruthenium complexes by exchange of their hydrophobic with hydrophilic ligands followed by aqueous extraction,[9] catalyst immobilization[10] or on removal of the catalyst by treatment with Pb(OAc)$_4$,[11] Ph$_3$PO or DMSO.[12]

Environmental concern associated with chemical synthesis has posed demands for environmentally benign reaction has become one of the main themes of modern synthesis. Towards this, ionic liquids helped as an environmentally friendly alternative for conventional organic solvents and gained much attention. Ionic liquids are known to be nonvolatile, nontoxic, reusable and compatible with many organic reactions. Our specific interest in ionic liquid was drawn by the recent disclosures that ionic liquid (IL) stabilizes
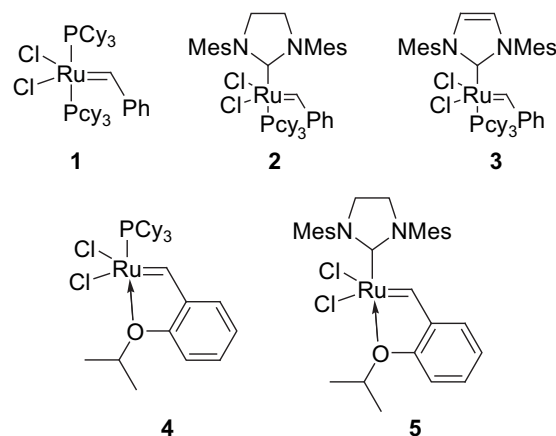

Figure 1.

many organometallic catalysts and helps for the catalyst recyclablity.[13]

Moreover, synthesis[14] and studies[15] of macrocyclic dilactones are impressive in organic chemistry due to their biological properties, complex formation, ion carriers and application in perfume industry. Even though literature methods provide a mixture of dilactones and tetralactones, the reactions give low yields and require drastic conditions. In continuation of our recent work[16] on the synthesis of macrocyclic tetralactones, we herein report a RCM reaction in the presence of Grubbs' catalyst to synthesize a variety

* Corresponding author. Tel.: +91 431 2407053; fax: +91 431 2407045; e-mail address: muthu@bdu.ac.in (S. Muthusamy).

macrocyclic tetralactones using ionic liquid in good yields with recyclability of the catalyst.

2. Results and discussion

Initially, we planned to study the RCM in various imidazole derivatives reported as ionic liquid medium. Towards this, we have synthesized[17] several ionic liquids for our present study (Fig. 2). Based on the desymmetrization[18] of anhydrides with alcohols, the desymmetrization reactions of 2 equiv of cyclic anhydride **6** with 1 equiv of dihydroxy compound **7** in the presence of triethylamine were performed to obtain the corresponding dicarboxylic acids **8a**–**l**. The dialkylation of **8a**–**l** with allyl bromide in the presence of triethylamine afforded the corresponding diolefins **9a**–**l** with different spacers in good yield. The reaction of diolefin **9a** in [mmim] PF_6 ionic liquid solution was carried out at 60 °C in the presence of Grubbs' first generation catalyst **1** under an argon atmosphere to furnish the crude reaction mixture. The purification by passing through silica gel column chromatography afforded the 21-membered macrocyclic tetralactone **10a** as a mixture of E/Z isomers in 95% yield (Scheme 1, Table 1, entry 1). The crude NMR spectrum indicated that the product **10a** obtained as a mixture of E/Z isomers in the ratio of 3:1. ^{1}H NMR spectrum showed the absence of terminal olefinic CH_2 hydrogens. Mass spectrum clearly indicated that the molecular ion with a reduction of 28 atomic mass unit from the starting material. To get a crystal for macrocycles is generally
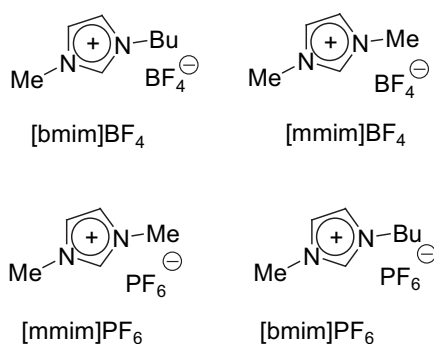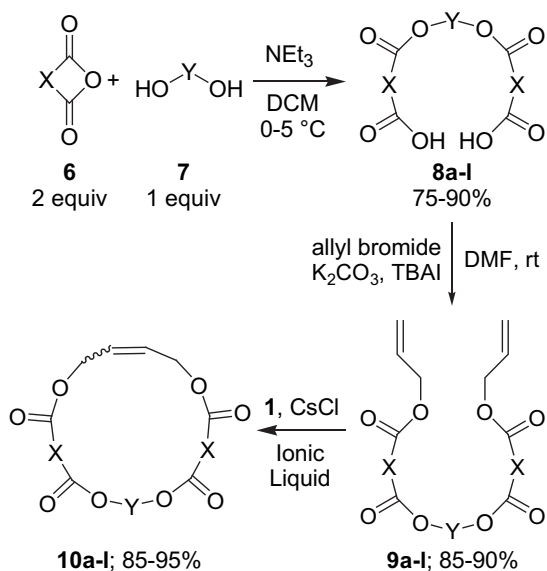

[bmim]BF$_4$

[mmim]BF$_4$

[mmim]PF$_6$

[bmim]PF$_6$

Figure 2.

Scheme 1. Synthesis of macrocyclic tetralactones **10**.

difficult task. The reaction mixture containing E/Z isomers was kept to obtain a good crystal using ethyl alcohol as solvent. The major isomer of **10a** was crystallized and characterized as an E-isomer by the X-ray crystallography (Fig. 3). To exploit this interesting result, the diolefinic compounds **9b**–**e**, prepared from phthalic anhydride system, was subjected to RCM reaction using 5 mol % of **1** to afford the corresponding tetralactones **10b**–**e** as a mixture of E/Z isomers in the ratio of 3:1. The RCM reaction of diolefin **9f** that was obtained from hexahydro-4-methylphthalic anhydride, furnished the respective tetralactone **10f** as a 2:1 mixture of E/Z isomers. The metathesis reaction of diolefins **9g**–**h** that was derived from cyclohexanedicarboxylic anhydride, yielded the respective tetralactones **10g**–**h** as a 2:1 mixture of E/Z isomers. The metathesis reaction of diolefins **10i**–**l** that was obtained from diphenic anhydride, afforded the respective macrocyclic tetralactones **10i**–**l** as a 3:1 mixture of E/Z isomers.

To study the RCM reaction of diolefinic compounds **9** in other ionic liquids, a representative reaction of compound **9l** was chosen. Initial investigation of **9l** was performed with ionic liquids having different counter anions. Thus, the ionic liquids containing bmim, bbim or mmim as counter cations and PF_6, BF_4, NO_2 or HSO_4^-—as counter anions were synthesized based on the literature.[17] Reaction of **9l** using bmim ionic liquid having different counter anions in the presence of 5 mol % of **1** at 60 °C was performed to furnish the corresponding macrocyclic compound **10l**. The similar reaction of **9l** with bbim ionic liquid having different counter anions furnished the corresponding macrocyclic compound **10l**. Reaction of **9l** with mmim ionic liquid having different counter anions also provided the corresponding macrocycle **10l**. The [mmim][PF$_6$] ionic liquid is found to be a good solvent and afforded the product **10l** in high yield. In turn, the ionic liquids having BF_4, NO_2-counter anions gave poor yield and the results are depicted in Table 2. The ionic liquid having HSO_4^- counter anion did not furnish any product.

There are no considerable differences in the reaction rates and yields by changing the substitution on the imidazole ring. The efficiency of the ionic liquid was strongly influenced by the nature of the anion. These results indicate that the anions play an important role in RCM reaction. In order to compare, the reaction of **9l** was carried out using organic solvents, such as dichloromethane, dichloroethane or toluene to afford the corresponding macrocyclic compound **10l** in moderate yield.

To study the template effect involved in the preparation of macrocycles, reaction of **9l** using ionic liquid or organic solvent was repeated in the presence of catalytic amount of **1** and CsCl under similar reaction conditions to furnish the macrocycle **10l** (Table 2). The minor effect in the presence of CsCl was observed.

To study the recovery and recycling of the expensive Grubbs' catalyst in line with the literature,[19] the reaction of **9a** was studied for the recovery of catalyst **1** with different temperatures for the duration of 10 h to optimize the reaction condition. The optimum temperature is found to be 60 °C for the RCM reactions using ionic liquids. The yield of the product **10a** was getting reduced when the reaction was performed above or below 60 °C during the recycling process (Table 3). The reason might be the thermal decomposition of **1** occurred at higher temperature.

Finally, the representative reaction of diolefin **9a** in the presence of catalyst **1** using mmim[PF$_6$] at 60 °C was performed. The pink coloured reaction mixture was extracted with dry ethyl acetate/ hexane (1:9) solution after the appropriate time duration to provide the product **10a** free from Grubbs' catalyst. The recovered pink coloured ionic liquid containing the catalyst **1** was dried under reduced pressure before performing the next reaction. The above reaction was repeated by adding the required starting material **9a** to provide the corresponding product **10a**. Notably, this process was repeated five times and the yields are provided in Table 4. The insolubility of ionic liquid in ethyl acetate/hexane (1:9) solution

Table 1
Synthesis of macrocyclic tetralactones **10** from diolefins **9** in the presence of Grubbs catalyst **1** using ionic liquid
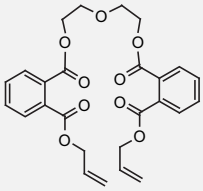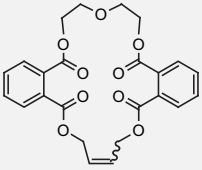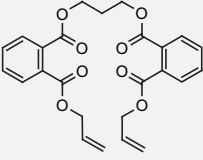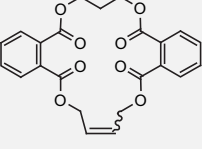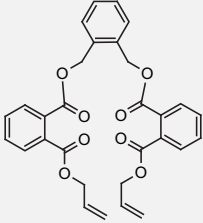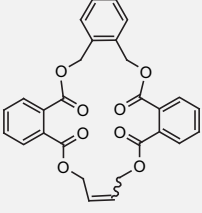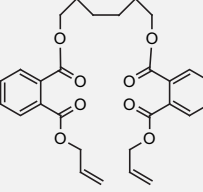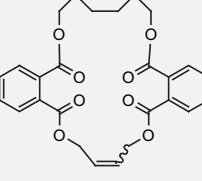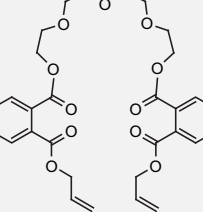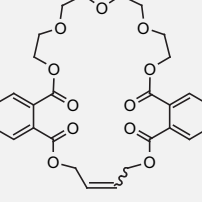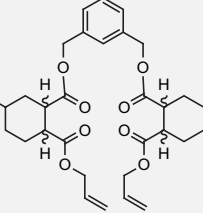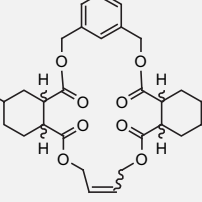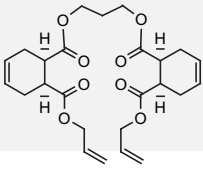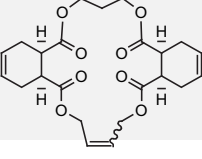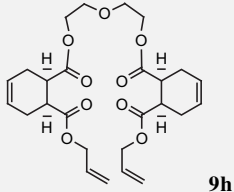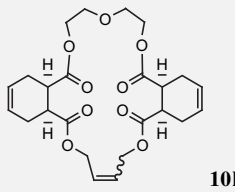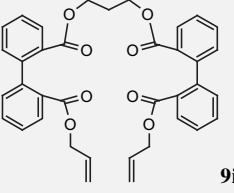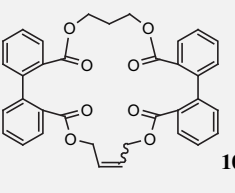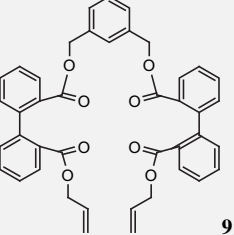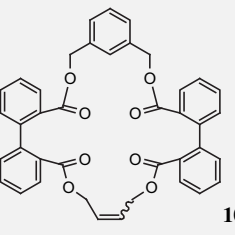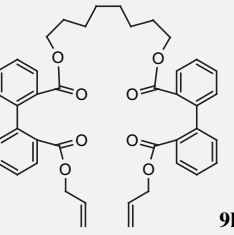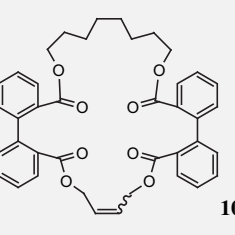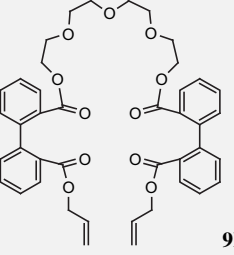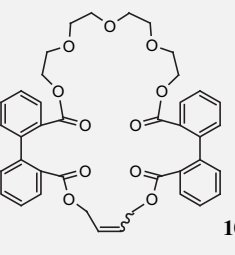
Entry	Diolefins **9**	Macrocyclic Tetralactones **10**	Time (hours)	Ring Size	Yield (%)[a]	E/Z [b]
1	**9a**	**10a**	11	21	95	3:1
2	**9b**	**10b**	11	19	94	3:1
3	**9c**	**10c**	9	20	92	3:1
4	**9d**	**10d**	9	22	90	3:1
5	**9e**	**10e**	9	24	94	3:1
6	**9f**	**10f**	8	21	86	2:1
7	**9g**	**10g**	8	19	85	2:1

Table 1 (*continued*)

Entry	Diolefins **9**	Macrocyclic Tetralactones **10**	Time (hours)	Ring Size	Yield (%)[a]	E/Z [b]
8	**9h**	**10h**	8	21	87	2:1
9	**9i**	**10i**	8	23	92	3:1
10	**9j**	**10j**	8	25	93	3:1
11	**9k**	**10k**	8	28	95	3:1
12	**9l**	**10l**	8	31	93	3:1

[a] Yields (unoptimized) refer to isolated pure compounds of macrocyclic tetralactones **10**.
[b] Ratio of isomers is determined by proton NMR spectroscopy.
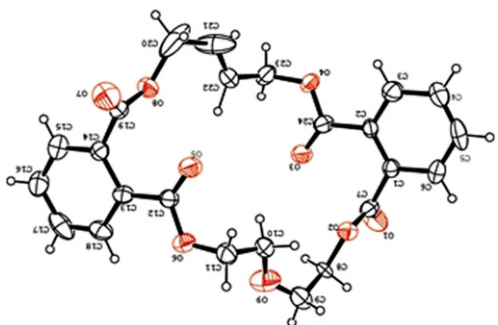
Figure 3. ORTEP view of compound **10a**.

and the very good solubility of Grubbs' catalyst in ionic liquid helped to productively recycle the catalyst. Based on this process, Grubbs' catalyst **1** could be immobilized in [mmim]PF$_6$ while performing the above RCM reaction. It is noteworthy to mention that the recovery of the catalyst **1** at 60 °C in ionic liquid was very good during recycling process rather it was observed as low.[19]

3. Conclusion

In conclusion, we have described the synthesis of various diolefins and their ring closing metathesis reaction was demonstrated to synthesize a range of macrocyclic tetralactones in several ionic liquids. The ionic liquid [mmim][PF$_6$] is an excellent solvent to synthesize macrocyclic tetralactones via RCM and the recovery of

Table 2
Reaction of **9l** at 60 °C with various ionic liquid or solvent

Entry	Ionic liquid or Solvent	Time (min)	Yield (%) of **10l**	
			Without CsCl[a]	With CsCl[a]
1	[bmim][PF$_6$]	8	85	87
2	[bmim][BF$_4$]	24	53	56
3	[bmim][NO$_3$]	24	20	22
4	[bmim][HSO$_4$]	24	—	—
5	[bbim][PF$_6$]	8	86	89
6	[bbim][BF$_4$]	24	56	60
7	[bbim][NO$_3$]	24	18	21
8	[mmim][BF$_4$]	24	59	61
9	[mmim][PF$_6$]	8	90	93
10	[mmim][NO$_3$]	24	21	26
11	DCM	24	68	90
12	DCE	24	65	89
13	Toluene	24	72	86

[a] Yields (unoptimized) refer to isolated pure compound **10l**.

Table 3
Studies on the reuse of catalyst **1** and temperature effect on **9a**

Entry	Temperature	Cycles, Yield of **10a** (%)[a]			
		I	II	III	IV
1	25	20	17	13	7
2	40	74	68	63	57
3	60	93	88	84	80
4	80	93	87	80	77
5	100	93	85	65	40

[a] Yields (unoptimized) refer to isolated pure compounds **10a**.

Table 4
Studies on the reuse of catalyst **1** and (mmim)(PF$_6$) on **9a**[a]

Entry	Yield of **10a** (%)[b]	Recovered ionic liquid
1	93	99
2	88	99
3	84	97
4	80	96
5	76	96

[a] All reactions were carried out at 60 °C.
[b] Yields (unoptimized) refer to isolated pure compounds **10a**.

the catalyst was also demonstrated. Most importantly, the process is friendly to the environment to synthesize various macrocyclic tetralactones having ring size of 19–31 membered with different spacers. These macrocyclic compounds are expected to be potentially important to the biologically significant materials and supramolecular chemistry.

4. Experimental section

4.1. General

All reactions were carried out in oven-dried glassware under an atmosphere of argon. All solvents were freshly purified by distillation. IR spectra were recorded neat on a Bruker Alpha FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded (400 and 100 MHz, respectively) on a Bruker Avance DPX 400 using CDCl$_3$. Chemical shifts for proton and carbon resonances are reported for the major isomer in parts per million (δ) relative to tetramethylsilane (δ 0.00) and chloroform (δ 77), respectively. Multiplicities are indicated by singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m). Coupling constants (J) were reported in hertz (Hz). Carbon types were determined from ^{13}C NMR and DEPT experiments. High resolution mass analyses were performed using electrospray ionization (ESI) technique on a Waters QTof-micro mass spectrometer. Analytical thin layer chromatography (TLC) was performed on silica and components were visualized by observation under iodine, UV-light or sulfuric acid charring. Column chromatography was performed on a silica gel (100–200 mesh) column.

4.2. General experimental procedure for the synthesis of macrocycle 10

The bis-olefin **9** (1.0 mmol) was taken in a well-dried ionic liquid (3.0 mL) under an argon atmosphere. The reaction mixture was stirred at room temperature for 5 min to obtain a clear oily solution. To this ionic liquid solution, 5 mol % of Grubbs' first generation catalyst and CsCl was added stirred at 60 °C for 8–12 h. The reaction was followed by TLC and ^{1}H NMR. After completion of the reaction, the crude reaction mixture was washed with 10% dry ethyl acetate in hexane (5×10 mL) till the absence of any organic compound in the solvent layer. The combined extracts were concentrated in vacuum and the resulting residue subjected on a 100–200 mesh silica gel column chromatography to afford the macrocycle **10**. The ionic liquid layer was dried on the vacuum line to use the next cycles during the recycling process.

*4.2.1. Compound **10a**.* A white solid; mp 144–146; ν_{max} (neat) 3022, 1725, 1435, 1281, 1116, 738, 668 cm^{-1}; δ_H (400 MHz, CDCl$_3$) 7.75–7.70 (4H, m, Ar–H), 7.57–7.53 (4H, m, Ar–H), 6.03–6.02 (2H, m, =CH), 4.85–4.84 (4H, m, OCH$_2$), 4.47–4.41 (4H, m, OCH$_2$), 3.79–3.77 (4H, m, OCH$_2$); δ_C (100 MHz, CDCl$_3$) 167.7 (C=O), 167.2 (C=O), 131.9 (CAr), 131.7 (CAr), 131.6 (CAr), 131.2 (=CH), 131.1 (=CH), 129.1 (=CH$_2$), 129.0 (=CH), 128.8 (=CH), 128.5 (=CH), 128.2 (=CH), 127.9 (=CH), 68.8 (OCH$_2$), 65.0 (OCH$_2$), 61.2 (OCH$_2$); HRMS (ESI$^+$) calcd for C$_{24}$H$_{22}$O$_9$ [M+Na]$^+$: 477.1162 found 477.1154.

Crystal data for the compound **10a** (CCDC 783915): C$_{24}$H$_{22}$O$_9$, M=454.42, 0.20×0.20×0.16 mm, Monoclinic, space group P-21 with a=7.182 (10) Å, b=8.495 (10) Å, c=17.763 (3) Å, α=90°, β=98.684 (10)°, γ=90°, V=1071.48 (3) Å^3, T=293(2) K, R_1=0.1016, wR_2=0.3972 on observed data, z=2, D_{calcd}=1.355 mg cm^{-3}, F(000)=532, Absorption coefficient=0.095 mm^{-1}, λ=0.71073 Å, 5906 reflections were collected on a smart apex CCD single crystal diffractometer 3669 observed reflections ($I \geq 2\sigma(I)$). The largest difference peak and hole=0.985 and −0.495 e Å^{-3}, respectively. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using SHELXL–97 software.

*4.2.2. Compound **10b**.* A white solid; mp 123–125; ν_{max} (neat) 2935, 1714, 1597, 1387, 1291, 1135, 1073, 744 cm^{-1}; δ_H (400 MHz, CDCl$_3$) 7.80–7.74 (4H, m, Ar–H), 7.73–7.74 (4H, m, Ar–H), 6.03–6.02 (2H, m, =CH), 4.97–4.96 (4H, m, =CH$_2$), 4.41 (4H, t, OCH$_2$, J 6 Hz), 2.20–2.14 (2H, m, CH$_2$); δ_C (100 MHz, CDCl$_3$) 167.7 (C=O), 167.1 (C=O), 132.3 (CAr), 131.4 (=CH), 131.2 (CAr), 129.4 (=CH), 128.9 (=CH), 127.9 (=CH), 127.8 (=CH), 64.9 (OCH$_2$), 62.7 (OCH$_2$), 62.5 (OCH$_2$), 61.4 (OCH$_2$), 28.0 (CH$_2$); HRMS (ESI$^+$) calcd for C$_{23}$H$_{20}$O$_8$ [M+Na]$^+$: 447.1056 found 447.1068.

*4.2.3. Compound **10c**.* A white solid; mp 149–151; ν_{max} (neat) 3037, 2930, 1720, 1599, 1448, 1283, 1138, 1034, 748 cm^{-1}; δ_H (400 MHz, CDCl$_3$) 7.73–7.64 (4H, m, Ar–H), 7.58–7.570 (4H, m, Ar–H), 7.49–7.65 (2H, m, Ar–H), 7.39–7.28 (2H, m, Ar–H), 5.84–5.83 (2H, m, =CH$_2$), 5.79–5.78 (4H, m, CH$_2$), 4.52 (4H, d, OCH$_2$ J 4 Hz); δ_C (100 MHz, CDCl$_3$) 167.7 (C=O), 167.3 (C=O), 167.2 (C=O), 166.9 (C=O), 134.3 (CAr), 133.8 (CAr), 132.5 (CAr), 131.6 (CAr), 131.5 (CAr), 131.5 (=CH), 131.3 (=CH), 131.0 (=CH), 130.8 (CAr), 129.8 (=CH), 129.3 (=CH), 129.2 (=CH), 129.0 (=CH), 129.0 (=CH), 128.9 (=CH), 128.6 (=CH), 128.1 (=CH), 127.5 (=CH), 65.0 (OCH$_2$), 64.9 (OCH$_2$), 64.7 (OCH$_2$), 61.1 (OCH$_2$); HRMS (ESI$^+$) calcd for C$_{28}$H$_{22}$O$_8$ [M+Na]$^+$: 509.1212 found 509.1221.

*4.2.4. Compound **10d**.* A white solid; mp 153–155; ν_{max} (neat), 3066, 2935, 1715, 1597, 1387, 1292, 1135, 1073, 742 cm^{-1}; δ_H

(400 MHz, CDCl$_3$) 7.68–7.63 (4H, m, Ar–H), 7.49–7.43 (4H, m, Ar–H), 5.94–5.94 (2H, m, =CH), 4.76 (4H, q, =CH_2, J 4 Hz), 4.24–4.20 (4H, m, OCH_2), 1.66–1.59 (4H, m, CH_2), 1.32–1.29 (4H, m, CH_2); δ_C (100 MHz, CDCl$_3$) 167.9 (C=O), 167.1 (C=O), 132.7 (CAr), 132.6 (CAr), 131.4 (=CH), 129.9 (CAr), 127.0 (=CH), 128.1 (=CH) 65.8 (OCH$_2$), 65.1 (OCH$_2$), 61.1 (CH$_2$), 32.6 (CH$_2$), 28.8 (CH$_2$), 28.6 (CH$_2$), 28.3 (CH$_2$), 25.6 (CH$_2$); HRMS (ESI$^+$) calcd for C$_{26}$H$_{26}$O$_8$ [M+Na]$^+$: 489.1525 found 489.1537.

*4.2.5. Compound **10e***. A white solid; mp 137–139; ν_{max} (neat) 2951, 2887, 1728, 1448, 1281, 1124, 1078, 738 cm^{-1}; δ_H (400 MHz, CDCl$_3$) 7.78–7.70 (4H, m, Ar–H), 7.59–7.52 (4H, m, Ar–H), 6.09–6.06 (2H, m, =CH), 4.89–4.84 (4H, m, OCH_2), 4.41–4.36 (4H, m, OCH_2), 3.76–3.64 (8H, m, OCH_2); δ_C (100 MHz, CDCl$_3$) 167.7 (C=O), 167.1 (C=O), 131.6 (CAr), 131.2 (=CH), 131.1 (=CH), 130.0 (=CH), 128.6 (=CH), 125.1 (CAr), 70.6 (OCH$_2$), 68.9 (OCH$_2$), 65.2 (OCH$_2$), 64.9 (OCH$_2$); HRMS (ESI$^+$) calcd for C$_{26}$H$_{26}$O$_{10}$Na [M+Na]$^+$: 521.1424, found 521.1411.

*4.2.6. Compound **10f***. Semisolid; ν_{max} (neat) 3030, 2925, 1729, 1440, 1372, 1295, 1185, 1033, 936 cm^{-1}; δ_H (400 MHz, CDCl$_3$) 7.26–7.19 (4H, m, Ar–H), 5.56–5.55 (2H, m, =CH), 5.17–4.85 (4H, m, =CH_2), 4.42 (4H, s, CH_2,) 3.22–3.20 (4H, m, OCH_2), 2.47–2.12 (2H, m, CH_2), 1.98–1.95 (2H, m, CH), 1.72–1.71 (4H, m, CH), 1.48–1.11 (8H, m, CH_2), 0.88 (6H, s, CH_3); δ_C (100 MHz, CDCl$_3$) 173.4 (C=O), 173.0 (C=O), 173.0 (C=O), 172.0 (C=O). 136.3 (CAr), 136.2 (CAr), 128.6 (=CH$_2$), 128.2 (=CH$_2$), 127.8 (=CH$_2$), 127.7 (=CH$_2$), 127.6 (=CH$_2$), 127.5 (=CH$_2$), 127.4 (=CH$_2$), 127.3 (=CH$_2$), 66.0 (OCH$_2$), 65.9 (OCH$_2$), 63.7 (OCH$_2$), 43.7 (CH), 43.5 (CH), 43.2 (CH), 43.2 (CH), 41.9 (CH), 41.8 (CH), 41.7 (CH), 41.2 (CH), 36.3 (CH$_2$), 33.8 (CH$_2$), 28.0 (CH$_2$), 24.1 (CH$_3$), 22.3 (CH$_3$); HRMS (ESI$^+$) calcd for C$_{30}$H$_{38}$O$_8$Na [M+Na]$^+$: 549.2464, found 549.2470.

*4.2.7. Compound **10g***. Semisolid; ν_{max} (neat) 3132, 3082, 2027, 1724, 1574, 1280, 754 cm^{-1}; δ_H (400 MHz, CDCl$_3$) 5.74–5.73 (2H, m, =CH), 5.61 (4H, s, =CH), 4.65–4.43 (2H, m, CH_2), 4.22–4.19 (2H, m, OCH_2), 4.07–4.00 (4H, m, OCH_2), 3.06–3.00 (4H, m, OCH), 2.46–2.27 (8H, m, CH_2), 1.87–1.84 (2H, m, CH_2); δ_C (100 MHz, CDCl$_3$) 172.7 (C=O), 172.7 (C=O), 172.6 (C=O), 172.6 (C=O), 128.0 (=CH), 127.9 (=CH), 127.6 (=CH), 127.6 (=CH), 127.6 (=CH), 63.9 (OCH$_2$), 61.4 (OCH$_2$), 61.3 (OCH$_2$), 39.9 (CH), 39.8 (CH), 28.2 (CH$_2$), 28.1 (OCH$_2$), 27.9 (CH$_2$), 25.7 (CH$_2$); HRMS (ESI$^+$) calcd for C$_{23}$H$_{28}$O$_8$ [M+Na]$^+$: 455.1682, found 455.1670.

*4.2.8. Compound **10h***. Colourless thick oil; ν_{max} (neat) 3031, 2894, 1732, 1440, 1351, 1297, 1192, 1250, 736 cm^{-1}; δ_H (400 MHz, CDCl$_3$) 5.86–5.79 (2H, m, =CH), 5.68 (4H, s, =CH), 4.79–4.50 (4H, m, OCH_2), 4.38–4.07 (4H, m, OCH_2), 3.65 (4H, t, OCH_2, J 5 Hz), 3.12–3.06 (4H, m, CH), 2.57–2.31 (8H, m, CH_2); δ_C (100 MHz, CDCl$_3$) 172.8 (C=O), 172.7 (C=O), 172.6 (C=O), 172.6 (C=O), 128.3 (=CH), 127.8 (=CH), 127.7 (=CH), 124.9 (=CH), 68.7 (OCH$_2$), 63.9 (OCH$_2$), 63.6 (OCH$_2$), 63.5 (OCH$_2$), 60.1 (OCH$_2$), 39.9 (CH), 39.7 (CH), 25.7 (CH$_2$), 25.6 (CH$_2$), 25.5 (CH$_2$), 25.3 (CH$_2$); HRMS (ESI$^+$) calcd for C$_{24}$H$_{30}$O$_9$ [M+Na]$^+$: 485.1788, found 485.1778.

*4.2.9. Compound **10i***. Semisolid; ν_{max} (neat) 3081, 2924, 2855, 1744, 1424, 1079, 755 cm^{-1}; δ_H (400 MHz, CDCl$_3$) 7.94–7.89 (4H, m, Ar–H), 7.47–7.39 (4H, m, Ar–H), 7.38–7.36 (4H, m, Ar–H), 7.13–7.11 (4H, m, Ar–H), 5.40–5.38 (2H, m, =CH), 4.56–4.29 (4H, m, OCH_2), 4.05–3.53 (4H, m, OCH_2), 1.18–1.13 (2H m, CH_2); δ_C (100 MHz, CDCl$_3$) 167.1 (C=O), 166.7 (C=O), 166.6 (C=O), 166.5 (C=O), 143.3 (CAr), 143.0 (CAr), 142.7 (CAr), 131.5 (=CH), 131.4 (=CH), 131.2 (=CH), 130.2 (=CH), 130.1 (=CH), 129.9 (=CH$_2$), 129.5 (=CH$_2$), 127.1 (=CH), 127.6 (=CH), 127.2 (=CH$_2$), 64.0 (OCH$_2$), 63.8 (OCH$_2$),

61.1 (OCH$_2$), 60.9 (OCH$_2$), 27.4 (CH_2); HRMS (ESI$^+$) calcd for C$_{35}$H$_{28}$O$_8$ [M+Na]$^+$: 599.1682, found 599.1699.

*4.2.10. Compound **10j***. Semisolid; ν_{max} (neat) 3132, 3082, 2027, 1724, 1577, 1280, 754 cm^{-1}; δ_H (400 MHz, CDCl$_3$) 7.96–7.93 (2H, m, Ar–H), 7.87–7.85 (2H, m, Ar–H), 7.45–7.40 (4H, m, Ar–H), 7.35–7.29 (4H, m, Ar–H), 7.17–6.96 (8H, m, Ar–H), 5.35–5.34 (2H, m, =CH), 4.97–4.87 (4H, m, CH_2), 4.32–4.14 (4H, m, OCH_2); δ_C (100 MHz, CDCl$_3$) 166.9 (C=O), 166.8 (C=O), 166.7 (C=O), 166.6 (C=O), 143.2 (CAr), 143.1 (CAr), 131.6 (CAr), 131.5 (=CH), 131.2 (=CH), 130.4 (=CH), 130.2 (=CH), 130.2 (=CH), 130.0 (=CH), 129.9 (=CH$_2$), 129.8 (=CH$_2$), 128.6 (=CH), 128.5 (=CH), 128.3 (=CH), 127.7 (=CH), 127.6 (=CH), 127.2 (=CH), 64.4 (OCH$_2$), 64.0 (OCH$_2$), 63.9 (OCH$_2$), 59.8 (OCH$_2$), 59.6 (OCH$_2$); HRMS (ESI$^+$) calcd for C$_{40}$H$_{30}$O$_8$ [M+Na]$^+$: 661.1838, found 661.1851.

*4.2.11. Compound **10k***. Semisolid; ν_{max} (neat) 3132, 3082, 2027, 1724, 1577, 1280, 754 cm^{-1}; δ_H (400 MHz, CDCl$_3$) 7.94–7.88 (4H, m, Ar–H), 7.45–7.30 (8H, m, Ar–H), 7.14–7.09 (4H, m, Ar–H), 5.24–5.22 (2H, m, =CH), 4.40–4.30 (4H, m, OCH_2), 3.89 (4H, t, OCH_2, J 6 Hz), 1.22–1.01 (12H, m, CH_2); δ_C (100 MHz, CDCl$_3$) 171.2 (C=O), 167.2 (C=O), 166.6 (C=O), 166.5 (C=O), 143.5 (CAr), 143.4 (CAr), 131.5 (=CH), 131.4 (=CH), 131.3 (=CH), 130.2 (=CH), 129.9 (=CH), 129.7 (=CH) 129.3 (=CH$_2$), 127.4 (=CH), 127.1 (=CH), 64.9 (OCH$_2$), 62.8 (OCH$_2$), 60.4 (OCH$_2$), 60.0 (OCH$_2$), 32.6 (CH$_2$), 29.2 (CH$_2$), 29.1 (CH$_2$), 28.9 (CH$_2$), 28.2 (CH$_2$), 28.1 (CH$_2$), 25.7 (CH$_2$), 25.6 (CH$_2$); HRMS (ESI$^+$) calcd for C$_{40}$H$_{38}$O$_8$ [M+Na]$^+$: 669.2464, found 669.2453.

*4.2.12. Compound **10l***. Semisolid; ν_{max} (neat) 3132, 3082, 2027, 1724, 1577, 1280, 754 cm^{-1}; δ_H (400 MHz, CDCl$_3$) 7.94–7.88 (4H, m, Ar–H), 7.45–7.30 (8H, m, Ar–H), 7.14–7.09 (4H, m, Ar–H), 5.25–5.23 (2H, m, =CH), 4.89–4.84 (4H, m, OCH_2), 4.41–4.36 (4H, m, OCH_2), 3.76–3.64 (12H, m, OCH_2); δ_C (100 MHz, CDCl$_3$) 171.3 (C=O), 167.1 (C=O), 166.6 (C=O), 166.5 (C=O), 143.4 (CAr), 143.5 (CAr), 131.5 (=CH), 131.4 (=CH), 131.3 (=CH), 130.2 (=CH), 129.9 (=CH), 129.7 (=CH) 129.3 (=CH$_2$), 127.4 (=CH), 127.1 (=CH), 70.6 (OCH$_2$), 68.9 (OCH$_2$), 65.2 (OCH$_2$), 64.9 (OCH$_2$), 64.1 (OCH$_2$), 62.8 (OCH$_2$), 60.4 (OCH$_2$), 60.0 (OCH$_2$); HRMS (ESI$^+$) calcd for C$_{40}$H$_{38}$O$_{11}$Na [M+Na]$^+$: 717.2312, found 717.2325.

Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.08.019.

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