A rational approach to calix[*n*]furan precursors

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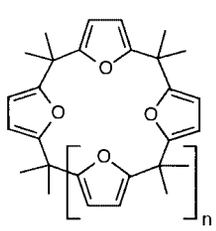
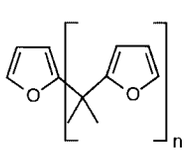
Several of the title compounds C_n are known to be available by cyclisation of the linear precursors with acetone and hydrochloric acid. A two-step synthesis of these linear precursors, L_n, with $n = 4$–9, and thus potentially of the title compounds, has been developed involving: (i) synthesis of the corresponding mono- or di-ketones from lithiofurans and tertiary amides; and (ii) *gem*-dimethylation at the keto group(s) using titanium tetrachloride and dimethylzinc.

In 1955, Ackman, Brown and Wright[1] demonstrated that furan and acetone with HCl catalysis interact to give the cyclic tetramer **1** in 18.5% yield. These systems are examples of hetero-calixarenes and can been termed calix[*n*]furans. Since the initial disclosure, numerous publications have appeared developing the chemistry by application of different ketones[1–3] and aldehydes[3,4] and 'improving' the methodology by, for example, utilisation of catalytic amounts of lithium perchlorate;[5] this was explained as a template effect, though this has been shown to be erroneous and other explanations have since been advanced.[3,6] Furthermore, the benefit of the lithium perchlorate has been questioned, though it does appear to increase the rate of the reaction and alter product ratios but not the yield[6] and the utilisation of acetals together with a Lewis acid[5] has also been described though yields appear to be lower with this variation! Given optimal conditions, calix[4]furan **1** can be obtained from furan and acetone in 35–37% yield. Other publications focus on the utilisation of the calix[4]furans for other syntheses such as opening of the furan rings and conversion thereby into pyrroles[6] and hydrogenation of the rings to give macrocyclic polyethers with crown-ether properties,[5,7] and extension of the reaction to other heterocycles.[8] The importance of these intriguing systems is exemplified by the publication of the above 'optimised' synthesis utilising the $LiClO_4$ catalysis in *Organic Syntheses*,[5] though the yield at best using this route is only about 25%.



1, n = 1
2, n = 2
3, n = 3



4, n = 1 **8**, n = 5
5, n = 2 **9**, n = 6
6, n = 3 **10**, n = 7
7, n = 4 **11**, n = 8

Recently, endeavours have focused upon generating the higher analogues of this system, *i.e.* calix[5]- **2** and calix[6]- **3** and calix[9]furan.[3,4,6] Not surprisingly, applying the existing methodology is fraught with problems owing to the formation of complex mixtures of products and polymers which results in low yields. In fact, under mild conditions, as the original authors showed,[1] furan and acetone give acceptable yields of a mixture of the linear dimer, 2,2-difuran-2-ylpropane **4** and the corresponding trimer **5** (and even small amounts of the tetramer **6**), easily separated by distillation. This reaction can be conducted on a scale utilising hundreds of grams of reactants. The two compounds **4** and **5** are the basic building blocks for all the methods currently in use for higher oligomers and for simplicity are referred to herein as L_2 and L_3 respectively, the calix[*n*]furans being referred to as C_n. It is well established that the optimal route to the C_n series is from the corresponding L_n precursor. Thus, for example, calix[4]furan **1** (C_4), calix[5]furan **2** (C_5), and calix[6]furan **3** (C_6), have been prepared in 45–52% yield from L_4 (**6**),[1] L_5 (**7**)[7] and L_6 (**8**)[3,7] respectively by treatment with acetone and hydrochloric acid. Even L_9 (**11**) gives C_9 in 45% yield in the same manner.[6b] By contrast, the one-step conversion of L_2 to C_4, and L_3 to C_6 gave at best 37 and 15% yield respectively as part of a complex mixture and long reaction times were required.[1,6] C_5 has been made in low yield and as part of a complex mixture from mixed L_2 and L_3 with acetone and acid, though we found this route to be capricious and at best the yields were very low.[6]

Given a ready source of the L_n series therefore, the C_n compounds should be readily accessible. This would be particularly valuable for the poorly accessible odd numbered C_n systems such as L_5 and L_7. We now wish to disclose our attempts to develop a rational synthesis of the key acyclic linear precursors, L_n. Our two-step approach is shown in Scheme 1:

Step 1: A linear mono- (**14**) or di-ketone (**17** or **18**) is derived from lithiation of L_2 or L_3 followed addition of a suitable amide electrophile. Both mono- (**13**) and di-lithio-compounds (**16**), and mono- (**12**) and di-amides (**15**) have been utilised in this reaction.

Step 2: The conversion of the keto group(s) into a CMe_2 moiety was achieved by application of Reetz's method[9,10] employing Me_2Zn–$TiCl_4$ in methylene chloride or toluene solution.

Four approaches to the ketones have been utilised as exemplified below and in Table 1. With monometalations a 10% excess of L_n was used and yields are based on the amide while with dimetalations a 10% excess of amide was used and yields are based upon the L_n utilised. Yields from reactions with carbamates are based upon 1 mole of the electrophile.

1. Monometalation of L_2 or L_3 followed by treatment with a carbamate derivative (we found *N*-ethoxycarbonylmorpholine

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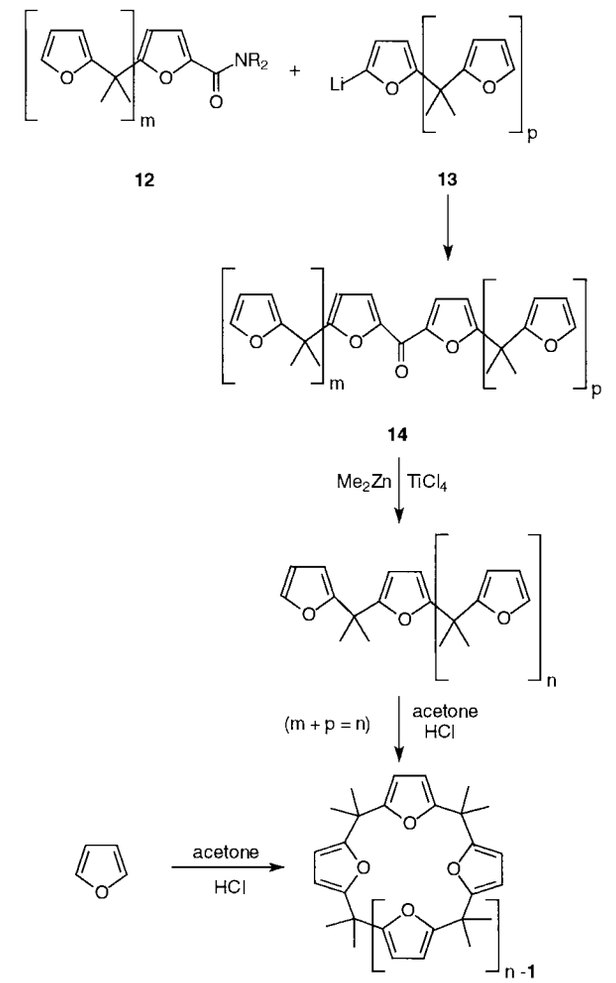
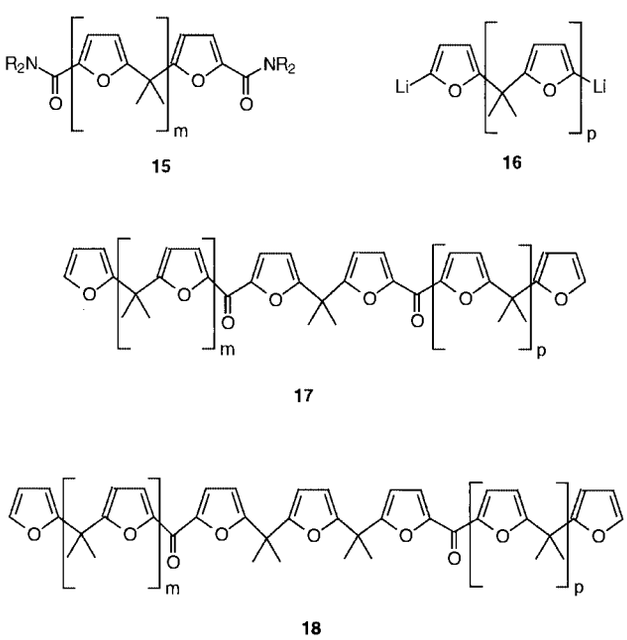


Scheme 1



to be best) yielded a symmetrical monoketone (**14**, $m = p = 1$, 42% or **14**, $m = p = 2$, 74%)[11] [expts. 1–4].

2. Monometalation of L_2 or L_3 followed by treatment with *N*-(2-furoyl)morpholine (**12**, $m = 0$) or with L_2-$CONC_4H_8O$ (**12**, $m = 1$) [itself easily prepared by treatment of monolithiated L_2 with commercially available chlorocarbonylmorpholine (50%)]. This method yields unsymmetrical monoketones (**14**, $m \neq p$) with 3–5 furan units in yields of 43–74% [expts. 5–11].

3. Dimetalation of L_2 or L_3, which proceeds much better for L_3 than for L_2, is followed by treatment with *N*-furoylmorpholine or with L_2-$CONC_4H_8O$. This approach yielded symmetrical diketones (**17** and **18**) with 4–7 furan units in yields of > 60% [expts. 12–19].

4. Monometalation of furans, L_2 and L_3, followed by treatment with an L_2- or L_3-based diamide (**15**, $m = 1$ or 2) yields a tetra-, penta-, hexa- hepta- or octacyclic diketone **17** ($m = p = 0$, 1 or 2) or **18** ($m = p = 0$, 1 or 2) in 21–60% yield [expts. 20–25].

A number of generalisations deserve mention:

(i) We found no advantage utilising lithiating reagents other than *n*-butyllithium (*e.g.* compare entries 7 and 8 and 15–17).

(ii) In all the reactions, yields tended to diminish with increasing length of the amide component.

(iii) L_3-Monolithio- and dilithio-derivatives proved more effective than those of L_2.

(iv) Method 3 above tended to give the highest yields of diketones. In these cases it was vital that the interaction of the lithio-derivative with the amide was given ~20 hours for good yields. L_3-amide (**12**, $m = 2$) proved to be a poor electrophile in this reaction. Thus, diketone (**18**, $m = p = 2$) with nine furan units can be made from dimetalation of L_3 followed by treatment with the L_3 (16%), or more effectively from L_3-diamide with the monolithio-derivative of L_3 (30%).

The *gem*-dimethylation reaction proved surprisingly different in operation compared to Reetz's recommendations for simpler ketones (see Table 2). Firstly, it was conducted at about −30 to 0 °C, though TLC indications suggested that no significant reaction occurred until about 0 °C (in contrast to benzophenone which is highly reactive and for which Reetz[10] recommends −50 °C giving 83% geminal dimethylation). Furthermore, we observed no significant advantage by working at lower temperatures (*cf.* entries 2 and 3; and 4–6). Again, the recommended solvent, dichloromethane, seems to confer limited benefit over toluene [in which solvent dimethylzinc is commercially available—compare entries 2 and 3]. We found that using the stoichiometry recommended by Reetz [$TiCl_4$–Me_2Zn, 1 : 1, giving Me_2TiCl_2, of which 2 moles per mole of ketone are required] was ineffective. After much experimentation we found that the optimum conditions for difuryl ketones required 2 : 4 : 1 molar ratios of the Lewis acid, zinc reagent and ketone respectively [*cf.* entries 3–10]. Difuryl ketones may be considered as vinylogous esters and thus weakly electrophilic [esters are *not* attacked by Reetz's reagent], thus requiring a more potent nucleophilic methylating agent. One possible explanation is that a more highly methylated and thus more nucleophilic reagent, Me_3TiCl or even Me_4Ti for example, is needed, though the last of these is known to react with other ketones only as far as the tertiary alcohol.[9] In order to activate the difuryl ketones we considered addition of a catalytic amount of a Lewis acid to the ketone prior to its addition to the Reetz reagent. This proved of small benefit; addition of a catalytic amount of $TiCl_4$ increased the yield of L_4 from 40% to 47%, while with $InCl_3$ the yield was 46%. Furthermore though Reetz also reported that the method is effective for the conversion of CMeOH groups into CMe_2 units and that these, as their lithium alcoholates, were intermediates in the process, we found that attempts to synthesise the tertiary difuryl alcohols were hampered by their instability and furthermore they gave complex mixtures with Reetz's reagent, which may explain our lower yields with difuryl ketones as substrates.

We have also briefly examined an alternative literature method used for the conversion of benzophenone to 2,2-diphenylpropane in 75% yield, by treatment with methyllithium under ultrasonic agitation and methyl iodide.[12] In fact, applied to the ketone **14**, ($m = p = 1$) this resulted only in decomposition.

In conclusion, despite the disappointing yields in the Reetz reaction stage, this two-step protocol has particular benefit for the synthesis of, for example L_5, which in our experience is not

Table 1 The synthesis of linear oligofuran monoketones **14**, and diketones **17** and **18**

	Reactants (mol/mol L_n)					Reaction conditions						
			Amide			Lithiation		Amide reaction		Products		
Entry	Furan deriv.	BuLi (equiv.)	Cpd	*m*	Equiv.	Temp./°C	Time/h	Temp./°C	Time/h	Cpd	*m*/*p*	Yield (%)
1	L_2	*n*-(1.1)	ECM[a]		0.45	−10 to 0	2.5	−40 to rt	12	**14**	1/1	21
2	L_2	*n*-(1.1)	ECM[a]		0.28	−30 to 10	3.5	−60 to 0	2.5	**14**	1/1	42
3	L_2	*n*-(1.1)	ECM[a]		0.28	0 to rt	3.5	−60 to 0	3	**14**	1/1	31
4	L_3	*n*-(1.1)	ECM[a]		0.28	−30 to 10	4	−60 to 0	3	**14**	2/2	74
5	L_2	*n*-(1.1)	**12**	0	0.56	−30 to 10	2.5	−60 to 0	2	**14**	0/1	74
6	L_3	*n*-(1.1)	**12**	0	0.56	−30 to 10	3.5	−60 to 0	2	**14**	0/2	50[b]
7	L_2	*n*-(1.1)	**12**	1	0.56	−30 to 10	2.5	−60 to 0	2	**14**	1/1	59[c]
8	L_2	*t*-(1.1)	**12**	1	0.91	−30 to rt	3.5	−60 to 0	3	**14**	1/1	45
9	L_3	*n*-(1.1)	**12**	1	0.56	−30 to 10	3.5	−60 to 0	2.5	**14**	1/2	43
10	L_2	*n*-(1.1)	**12**	2	0.56	−30 to 10	3	−60 to 0	3	**14**	1/2	45
11	L_3	*n*-(1.1)	**12**	2	0.56	−30 to 10	3	−60 to 0	3	**14**	2/2	34[d]
12	L_2	*n*-(2.2)	**12**	0	2.2	−30 to rt	4	−60 to rt	20	**17**	0/0	70[e]
13	L_2	*n*-(2.2)	**12**	1	3	−30 to rt	4	−60 to rt	20	**17**	1/1	30[f]
14	L_2	*n*-(2.2)	**12**	2	3	−30 to rt	4	−60 to rt	20	**17**	2/2	12[g]
15	L_3	*n*-(2.2)	**12**	0	2.2	−30 to rt	4	−60 to rt	20	**18**	0/0	89
16	L_3	*s*-(2.2)	**12**	0	2.2	−30 to rt	4	−60 to rt	20	**18**	0/0	54
17	L_3	*t*-(2.2)	**12**	0	2.2	−30 to rt	4	−60 to rt	20	**18**	0/0	57
18	L_3	*n*-(2.2)	**12**	1	3	−30 to rt	4	−60 to rt	20	**18**	1/1	14[h]
19	L_3	*n*-(2.2)	**12**	2	3	−30 to rt	4	−60 to rt	20	**18**	2/2	16[i]
20	Furan (1.8 M)	*n*-(2)	**12**	1	1	−30 to rt	4	−60 to rt	20	**14**	0/1	60
21	Furan (1.8 M)	*n*-(2)	**12**	2	1	−30 to rt	4	−60 to rt	20	**14**	0/2	77
22	Furan (3 M)	*n*-(3.3)	**15**	1	1	−40 to rt	2.5	−60 to 10	3	**17**	0/0	60
23	Furan (3 M)	*n*-(3.3)	**15**	2	1	−40 to rt	2.5	−60 to 10	3	**18**	0/0	54
24	L_2	*n*-(1.1)	**15**	1	0.33	−30 to 10	3.5	−60 to rt	3.5	**17**	1/1	21
25	L_2	*n*-(1.1)	**15**	2	0.33	−30 to 10	3.5	−60 to 10	3	**18**	1/1	34
26	L_3	*n*-(1.1)	**15**	1	0.33	−30 to 10	3	−60 to 10	3	**17**	2/2	48
27	L_3	*n*-(1.1)	**15**	2	0.33	−30 to 10	3	−60 to 10	3.5	**18**	2/2	30

[a] ECM = *N*-ethoxycarbonylmorpholine; [b] +**18**, *m* = *p* = 0, 16%. [c] +**17**, *m* = *p* = 1, 7%. [d] +**18**, *m* = *p* = 210%. [e] +**14**, *m* = 0, *p* = 1, 8%. [f] +**14**, *m* = *p* = 1, 31%. [g] +**14**, *m* = 1, *p* = 2, 11%. [h] +**14**, *m* = 1, *p* = 2, 23%. [i] +**14**, *m* = *p* = 2, 21%.

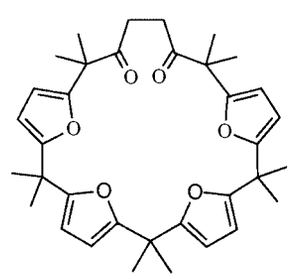
Table 2 The conversion of oligofuran ketones **14**, **17** and **18** into oligofurans L_{4-9} **6**–**11**

	Ketone						Product	
Entry	Cpd	*m*/*p*	Me_2Zn (equiv.)	$TiCl_4$ (equiv.)	Solvent	Temp/°C	Cpd	Yield (%)
1	**14**	1/1	2.2	2.2	DCM[a]	−50 to rt	L_4	0[b]
2	**14**	0/1	4.4	2.2	Toluene	−30 to rt	L_3	37
3	**14**	0/1	4.4	2.2	DCM	−50 to rt	L_3	40[c]
4	**14**	1/1	4.4	2.2	DCM	−50 to rt	L_4	48
5	**14**	1/1	4.4	2.2	DCM	−70 to rt	L_4	42
6	**14**	1/1	4.4	2.2	DCM	−30 to rt	L_4	46
7	**14**	1/1	3.3	2.2	DCM	−30 to rt	L_4	33
8	**14**	1/1	5.5	2.2	DCM	−30 to rt	L_4	52
9	**14**	1/1	6.6	3.3	DCM	−30 to rt	L_4	37
10	**14**	1/1	1	3	DCM	−30 to rt	L_4	0[d]
11	**14**	1/2	4.4	2.2	DCM	−30 to rt	L_5	20
12	**14**	2/2	4.4	2.2	DCM	−20 to rt	L_6	25
13	**18**	0/0	6.88	4.44	DCM	−20 to rt	L_5	22
14	**18**	1/1	6.88	4.44	DCM	−20 to rt	L_7	7
15	**17**	2/2	6.88	4.44	DCM	−20 to rt	L_8	13

[a] DCM = dichloromethane. [b] Decomposition occurred. [c] If a catalytic amount of a Lewis acid is added to the ketone before it is added to the other reagents, yields are increased; *e.g.* $TiCl_4$: 47%, $InCl_3$: 46%. [d] Starting material isolated.

easily accessible by other methods. It is also useful for the rapid assembly of specific long chain oligofurans. Thus L_7 and L_8 have been made for the first time.

Following the literature method[7] we have made C_5 from L_5 with acetone and hydrochloric acid. Though yields were similar to those quoted when the reaction was performed with only a few hours stirring of the reagents, it dropped sharply on using the longer times recommended by the authors, being replaced by a new compound which resulted from acid catalysed hydrolytic ring-opening of one of the furan rings to give the cyclic γ-diketone **19**. The requisite water in this rigorously dried medium probably derived from that generated during formation of C_5. As this is a useful intermediate for mixed hetero-



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cyclic macrocycle formation, this reaction deserves further investigation.

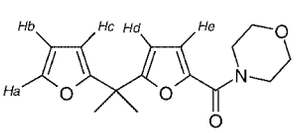
Experimental

Melting points were taken on a Reichert hot-stage apparatus and are uncorrected. Infrared spectra were recorded on a Unicam Research Series 1 FTIR instrument as liquid films (for oils) or KBr discs (for solids). NMR spectra were recorded on a JEOL 270 spectrometer. Chemical shifts are given in ppm and are referenced to the residual peak of the solvent or tetramethylsilane. Coupling constants are given in Hz. Accurate mass measurements were recorded on a Brüker APEX FTMS. TLC was performed using Merck silica 60F254 plates and flash chromatography with Fluka silica gel 60. Organic layers were dried over magnesium sulfate. Tetrahydrofuran (THF) was freshly distilled from sodium–benzophenone. Dichloromethane was distilled from calcium hydride. Reactions requiring anhydrous conditions were performed in oven-dried and flamed apparatus under argon. The following compounds were prepared according to the literature: L_2 (**4**) and L_3 (**5**),[1] *N*-ethoxycarbonylmorpholine[13] and *N*-furoylmorpholine.[14]

Preparation of amides 12 and 15

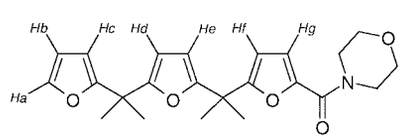
General procedure for monoamides. A solution of *n*-BuLi in hexane (1.6 M, 0.055 mol) was added dropwise at −30 °C to a solution of L_2 or L_3 (0.05 mol) in dry THF (50 mL). The mixture was stirred for 3 h allowing the temperature to rise slowly to 10 °C. This lithio-derivative was then added dropwise to a solution of morpholinocarbonyl chloride (14.97g, 11.68 mL, 0.1 mol) in dry THF (30 mL) cooled to −60 °C. Stirring was continued for 3 h, the temperature slowly rising to 10 °C. The reaction mixture was poured into cold aqueous ammonium chloride (2 M, 150 mL) and the aqueous layer extracted with ethyl acetate, the organic layer dried and the solvent evaporated under reduced pressure. Flash chromatography using hexane–ethyl acetate (1 : 1) gave the monoamide of L_2 and L_3 respectively (**12**, $m = 1$, 50% and **12**, $m = 2$, 66%). Further elution using pure ethyl acetate afforded the corresponding diamides (**15**, $m = 1$, 8% and **15**, $m = 2$, 21%).

***N*-[5-(α,α-Dimethylfurfuryl)-2-furoyl]morpholine (12, $m = 1$).**



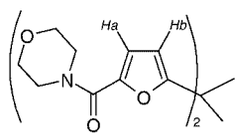
Yellow oil. HRMS (APCI, M + 1): Found, 290.1385. Calculated for $C_{16}H_{20}NO_4$, 290.1387; ν_{max} (neat) 2977, 2922, 2857, 1625, 1524, 1428, 1282, 1261, 1115, 1028 cm^{-1}; δ_H ($CDCl_3$) 1.66 (6H, s, 2 × CH_3), 3.72 (8H, m, 4 × CH_2), 6.07 (1H, dd, $J = 0.99$ and $J' = 3.3$ Hz, H_c), 6.13 (1H, d, $J = 3.3$ Hz, H_d), 6.29 (1H, dd, $J = 1.65$ and $J' = 3.3$ Hz, H_b), 6.96 (1H, d, $J = 3.3$ Hz, H_e), 7.31 (1H, dd, $J = 2$ and $J' = 0.99$ Hz, H_a); δ_C ($CDCl_3$) 26.00 (2C), 37.35, 66.84 (2C), 104.25, 105.89, 109.97, 117.66, 141.33, 146.18, 158.88, 159.02, 161.66.

***N*-{5-[5-(α,α-Dimethylfurfuryl)-α,α-dimethylfurfuryl]-2-furoyl}morpholine (12, $m = 2$).**



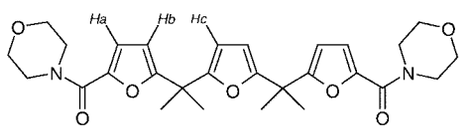
Yellow oil. HRMS (APCI, M + 1): Found, 398.1965. Calculated for $C_{23}H_{28}NO_5$, 398.1962; ν_{max} (neat) 2977, 2933, 2858, 1626, 1524, 1428, 1281, 1261, 1116, 1027 cm^{-1}; δ_H ($CDCl_3$) 1.59 (6H, s, 2 × CH_3), 1.62 (6H, s, 2 × CH_3), 3.72 (8H, m, 4 × CH_2), 5.90 (1H, d, $J = 3.3$ Hz, H_d), 5.91 (1H, dd, $J = 3.3$ and $J' = 0.99$ Hz, H_c), 5.96 (1H, d, $J = 3.3$ Hz, H_e), 6.05 (1H, d, $J = 3.3$ Hz, H_f), 6.25 (1H, dd, $J = 1.65$ and $J' = 3.3$ Hz, H_b), 6.96 (1H, d, $J = 3.3$ Hz, H_g), 7.28 (1H, dd, $J = 0.99$ and $J' = 1.65$ Hz, H_a); δ_C ($CDCl_3$) 25.97 (2C), 26.16 (2C), 37.34, 37.53, 66.78 (2C), 66.90 (2C), 103.89, 104.31, 104.56, 106.01, 109.86, 117.87, 140.98, 146.13, 157.36, 158.85, 159.11, 159.96, 162.00.

2,2-Bis[5-(morpholinocarbonyl)furan-2-yl]propane (15, $m = 1$).



Cream solid, mp 73 °C. HRMS (APCI, M + 1): Found, 403.1861. Calculated for $C_{21}H_{27}N_2O_6$, 403.1864. ν_{max} (KBr) 2975, 2920, 2856, 1630, 1523, 1429, 1364, 1300, 1281, 1261, 1174, 1114, 1028 cm^{-1}; δ_H ($CDCl_3$) 1.69 (6H, s, 2 × CH_3), 3.74 (16H, m, 8 × CH_2), 6.18 (2H, d, $J = 3.3$ Hz, 2 × H_b), 6.94 (2H, d, $J = 3.3$ Hz, 2 × H_a); δ_C ($CDCl_3$) 25.98 (2C), 37.67, 66.83 (8C), 106.25 (2C), 117.32 (2C), 146.49 (2C), 158.95 (2C), 160.64 (2C).

2,5-Bis[5-(morpholinocarbonyl)-α,α-dimethylfurfuryl]furan (15, $m = 2$).

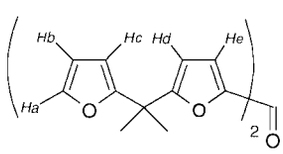


Yellow oil. HRMS (APCI, M + 1): Found, 511.2436. Calculated for $C_{28}H_{35}N_2O_7$, 511.2439. ν_{max} (neat) 2977, 2922, 2858, 1625, 1524, 1429, 1300, 1281, 1262, 1174, 1115 cm^{-1}; δ_H ($CDCl_3$) 1.62 (12H, s, 4 × CH_3), 3.72 (16H, m, 8 × CH_2), 5.97 (2H, s, 2 × H_c), 6.03 (2H, d, $J = 3.3$ Hz, 2 × H_b), 6.94 (2H, d, $J = 3.3$ Hz, 2 × H_a); δ_C ($CDCl_3$) 25.66 (4C), 37.17 (2C), 66.43 (8C), 104.43 (2C), 105.66 (2C), 117.31 (2C), 145.77 (2C), 157.36 (2C), 158.61 (2C), 161.41 (2C).

Reactions of lithiated furans (13) with *N*-ethoxycarbonylmorpholine to give ketones 14

General procedure. A solution of *n*-BuLi in hexane (1.6 M, 0.025 mol) was added dropwise to a solution of L_2 or L_3 (0.0226 mol) in dry THF (20 mL) at −30 °C. The mixture was stirred for 3.5 h allowing the temperature slowly to reach 10 °C. *N*-Ethoxycarbonylmorpholine (1.00g, 0.00629 mol) in dry THF (10 mL) was then added dropwise at −60 °C and the resulting solution stirred for 3 h, allowing the solution temperature to rise to 10 °C. The reaction mixture was poured into cold aqueous ammonium chloride (2 M) and the aqueous phase was extracted with ethyl acetate. After drying this extract, removal of the solvent under reduced pressure and flash chromatography of the crude product using hexane–ethyl acetate (9 : 1), the ketones **14** ($m = p = 1$, 42% and $m = p = 2$, 74% respectively) were obtained.

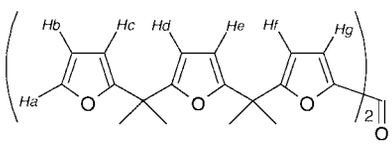
Bis[5-(α,α-dimethylfurfuryl)furan-2-yl] ketone (14, $m = p = 1$).



Beige solid, mp 63 °C. HRMS (APCI, M + 1): Found, 379.1540. Calculated for $C_{23}H_{23}O_5$, 379.1540. ν_{max} (KBr)

3174, 3149, 3114, 2977, 2934, 2872, 1640, 1504, 1461, 1359, 1317, 1253, 1239, 1163, 1028 cm^{-1}; δ_H ($CDCl_3$) 1.72 (12H, s, 4 × CH_3), 6.12 (2H, dd, J = 0.7 and J' = 3 Hz, 2 × H_c), 6.18 (2H, d, J = 3.3 Hz, 2 × H_d), 6.30 (2H, dd, J = 2 and J' = 3.3 Hz, 2 × H_b), 7.34 (2H, dd, J = 1 and J' = 2 Hz, 2 × H_a), 7.36 (2H, d, J = 3.6 Hz, 2 × H_e); δ_C ($CDCl_3$) 26.60 (4C), 38.27 (2C), 105.11 (2C), 107.81 (2C), 110.52 (2C), 120.74 (2C), 141.99 (2C), 150.94 (2C), 159.09 (2C), 165.31 (2C), 168.50.

Bis{5-[5-(α,α-dimethylfurfuryl)-α,α-dimethylfurfuryl]furan-2-yl} ketone (14, $m = p = 2$)

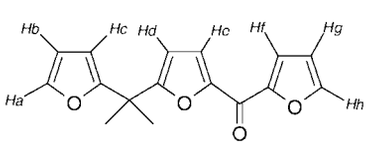


Yellow oil. HRMS (APCI, M + 1): Found, 595.2689. Calculated for $C_{37}H_{39}O_7$, 595.2690. ν_{max} (neat) 3124, 2979, 2935, 2873, 1631, 1579, 1511, 1504, 1364, 1314, 1269, 1235, 1160 cm^{-1}; δ_H ($CDCl_3$) 1.60 (12H, s, 4 × CH_3), 1.69 (12H, s, 4 × CH_3), 5.92 (2H, d, J = 3.3 Hz, 2 × H_c), 5.94 (2H, d, J = 3.6 Hz, 2 × H_d), 6.00 (2H, d, J = 3.3 Hz, 2 × H_e), 6.08 (2H, d, J = 3.6 Hz, 2 × H_f), 6.22 (2H, dd, J = 1.65 and J' = 3 Hz, 2 × H_b), 7.26 (2H, br s, 2 × H_a), 7.34 (2H, d, J = 3.3 Hz, 2 × H_g); δ_C ($CDCl_3$) 26.08 (4C), 26.18 (4C), 37.41 (2C), 37.97 (2C), 103.97 (2C), 104.41 (2C), 104.96 (2C), 107.42 (2C), 109.86 (2C), 120.58 (2C), 140.95 (2C), 150.30 (2C), 157.01 (2C), 159.05 (2C), 160.01 (2C), 165.34 (2C), 168.14.

Reaction between lithiated furans 13 and furan monoamides 12 to give ketones 14

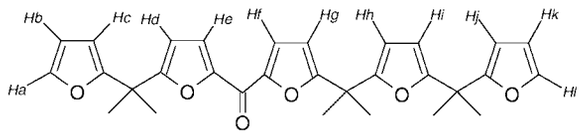
General procedure. A solution of L_2 or L_3 (0.0199 mol) in dry THF (20 mL) was treated dropwise with a solution of *n*-BuLi in hexane (1.6 M, 0.0218 mol) at −30 °C. Stirring was continued for 3 h, while the temperature slowly reached 10 °C. A solution of the amide (0.0110 mol) in dry THF (10 mL) was then added dropwise to the lithio-derivative at −60 °C and the mixture stirred for an additional 3 h, allowing the temperature to rise to 10 °C. The reaction was hydrolysed with cold aqueous ammonium chloride (2 M) and the aqueous layer extracted with ethyl acetate. The organic extract was dried and the solvent removed under reduced pressure. Flash chromatography of the crude product using hexane–ethyl acetate (for ratio see below) afforded the monoketone **14** in yields as recorded in Table 1.

2-(Furan-2-yl)-2-[5-(2-furoyl)furan-2-yl]propane (14, $m = 1$, $p = 0$).



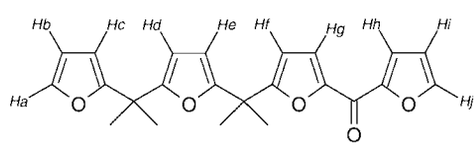
Chromatographic elution with 8 : 2 solvent ratio. Yellow oil. HRMS (APCI, M + Na): Found, 293.0783. Calculated for $C_{16}H_{14}O_4Na$, 293.0784. ν_{max} (neat) 3139, 3120, 2980, 2936, 1631, 1578, 1503, 1465, 1390, 1313 cm^{-1}; δ_H ($CDCl_3$) 1.74 (6H, s, 2 × CH_3), 6.14 (1H, dd, J = 0.7 and J' = 3.3 Hz, H_c), 6.24 (1H, d, J = 3.6 Hz, H_d), 6.32 (1H, dd, J = 1.65 and J' = 3.3 Hz, H_b), 6.58 (1H, dd, J = 1.65 and J' = 3.6 Hz, H_g), 7.36 (1H, dd, J = 0.7 and J' = 1.65 Hz, H_a), 7.42 (1H, d, J = 3.6 Hz, H_e), 7.48 (1H, dd, J = 0.7 and J' = 3.6 Hz, H_f), 7.66 (1H, dd, J = 1 and J' = 1.65 Hz, H_h); δ_C ($CDCl_3$) 26.07 (2C), 37.73, 104.61, 107.39, 110.04, 112.18, 119.41, 120.25, 141.54, 146.59, 150.36, 151.16, 158.43, 164.98, 168.22.

2-(5-{5-[5-(α,α-Dimethylfurfuryl)-2-furoyl]-α,α-dimethylfurfuryl}-α,α-dimethylfurfuryl)furan (14, $m = 1$, $p = 2$).



Chromatographic elution with 9 : 1 solvent ratio. Yellow oil. HRMS (APCI, M + 1): Found, 487.2112. Calculated for $C_{30}H_{31}O_6$, 487.2115. ν_{max} (neat) 3144, 3120, 2979, 2936, 2872, 1631, 1580, 1511, 1363, 1315, 1236, 1161, 1019 cm^{-1}; δ_H ($CDCl_3$) 1.60 (6H, s, 2 × CH_3), 1.68 (6H, s, 2 × CH_3), 1.72 (6H, s, 2 × CH_3), 5.92 (1H, d, J = 3.3 Hz, H_j), 5.94 (1H, d, J = 3.3 Hz, H_i), 6.00 (1H, d, J = 3 Hz, H_h), 6.09 (1H, d, J = 3.6 Hz, H_c), 6.12 (1H, d, J = 3Hz, H_g), 6.18 (1H, d, J = 3.3 Hz, H_d), 6.23 (1H, dd, J = 2 and J' = 3 Hz, H_k), 6.31 (1H, dd, J = 1.6 and J' = 3 Hz, H_b), 7.28 (1H, br s, H_l), 7.33 (1H, d, J = 3.6 Hz, H_f), 7.34 (1H, br s, H_a), 7.36 (1H, d, J = 3.6 Hz, H_e); δ_C ($CDCl_3$) 26.10 (2C), 26.16 (2C), 26.20 (2C), 37.41, 37.83, 37.96, 103.98, 104.41, 104.68, 104.96, 107.39, 107.42, 109.88, 110.10, 110.15, 120.38, 120.39, 140.98, 141.56, 150.39, 150.49, 157.04, 159.03, 160.03, 164.90, 165.24, 168.12.

2-(2-Furoyl)-5-[5-(α,α-dimethylfurfuryl)-α,α-dimethylfurfuryl]furan (14, $m = 2$, $p = 0$).

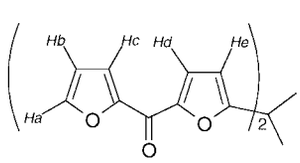


Chromatographic elution with 7 : 3 solvent ratio. Beige solid, mp 70 °C. HRMS (APCI, M + 1): Found, 379.1540. Calculated for $C_{23}H_{23}O_5$, 379.1540. ν_{max} (KBr) 3171, 3117, 2978, 2935, 2871, 1627, 1564, 1500, 1462, 1369, 1314, 1277, 1234, 1158 cm^{-1}; δ_H ($CDCl_3$) 1.60 (6H, s, 2 × CH_3), 1.71 (6H, s, 2 × CH_3), 5.94 (2H, d, J = 3.3 Hz, H_c and H_d), 6.02 (1H, d, J = 3Hz, H_e), 6.14 (1H, d, J = 3.6 Hz, H_f), 6.23 (1H, dd, J = 2 and J' = 3.3 Hz, H_b), 6.57 (1H, dd, J = 1.6 and J' = 3.6 Hz, H_j), 7.27 (1H, br s, H_a), 7.40 (1H, d, J = 3.6 Hz, H_g), 7.49 (1H, d, J = 3.3 Hz, H_h), 7.67 (1H, br s, H_j); δ_C ($CDCl_3$) 26.57 (2C), 26.63 (2C), 37.85, 38.39, 104.39, 104.85, 105.38, 107.93, 110.30, 112.68, 120.04, 120.87, 141.41, 147.06, 150.76, 151.63, 157.32, 159.55, 160.38, 165.80, 168.77.

Reaction between dilithiated furans 16 and furan monoamides 12 to give diketones 17 and 18

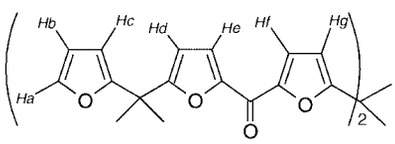
General procedure. A solution of L_2 or L_3 (0.00284 mol) in dry THF (20 mL) was treated dropwise with a solution of *n*-BuLi in hexane (1.6 M, 0.00625 mol) at −30 °C. The mixture was stirred and allowed to warm up to room temperature over 4 h. A solution of the amide (0.00852 mol) in dry THF (20 mL) was then slowly added at −60 °C and the resulting yellow solution stirred overnight allowing the temperature to reach ambient. The reaction was poured into cold aqueous ammonium chloride (2 M) and the aqueous phase was extracted with ethyl acetate. After drying, removal of the solvent under reduced pressure and flash chromatography using hexane–ethyl acetate afforded the diketones **17** or **18**, yields being recorded in Table 1.

2,2-Bis[5-(2-furoyl)furan-2-yl]propane (17, $m = p = 0$).



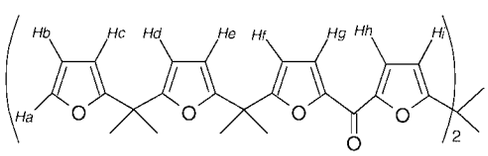
Chromatographic elution with 6 : 4 solvent ratio. Yellow solid, mp 90–91 °C. HRMS (APCI, M + 1): Found, 365.1018. Calculated for $C_{21}H_{17}O_6$, 365.1020. ν_{max} (KBr) 3138, 3123, 3057 (C_{sp2}-H), 2982, 2936, 2873, 1642, 1632, 1579, 1567, 1512, 1503, 1469, 1391, 1312, 1265, 1251 cm^{-1}; δ_H ($CDCl_3$) 1.85 (6H, s, 2 × CH_3), 6.36 (2H, d, J = 3.6 Hz, 2 × H_e), 6.58 (2H, dd, J = 1.3 and J' = 3.3 Hz, 2 × H_b), 7.47 (2H, d, J = 3.3 Hz, 2 × H_d), 7.52 (2H, d, J = 3.6 Hz, 2 × H_c), 7.67 (2H, br s, 2 × H_a); δ_C ($CDCl_3$) 26.10 (2C), 38.31, 107.86 (2C), 112.39 (2C), 119.62 (2C), 120.32 (2C), 146.73 (2C), 150.80 (2C), 151.28 (2C), 163.38 (2C), 168.29 (2C).

2,2-Bis{5-[5-(α,α-dimethylfurfuryl)-2-furoyl]furan-2-yl}-propane (17, $m = p = 1$).



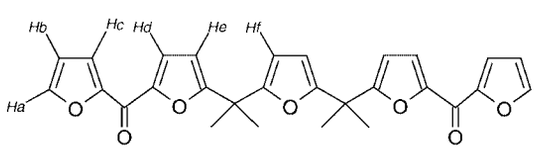
Chromatographic elution with 8 : 2 solvent ratio. Yellow oil. HRMS (APCI, M + 1): Found, 581.2166. Calculated for $C_{35}H_{33}O_8$, 581.2170. ν_{max} (neat) 3146, 3121, 2980, 2936, 2873, 1631, 1580, 1511, 1363, 1314, 1240, 1162 cm^{-1}; δ_H ($CDCl_3$) 1.71 (6H, s, 2 × CH_3), 1.80 (12H, s, 4 × CH_3), 6.12 (2H, dd, J = 0.7 and J' = 3.3 Hz, 2 × H_c), 6.20 (2H, d, J = 3.3 Hz, 2 × H_d), 6.30 (2H, dd, J = 1.65 and J' = 3.3 Hz, 2 × H_b), 6.32 (2H, d, J = 3.6 Hz, 2 × H_g), 7.33 (2H, dd, J = 1 and J' = 2 Hz, 2 × H_a), 7.38 (2H, d, J = 3.6 Hz, 2 × H_e), 7.40 (2H, d, J = 3.6 Hz, 2 × H_f); δ_C ($CDCl_3$) 25.93 (2C), 26.04 (4C), 37.70, 38.19 (2C), 104.59 (2C), 107.40 (2C), 107.75 (2C), 110.01 (2C), 120.19 (2C), 120.33 (2C), 141.48 (2C), 150.36 (2C), 150.67 (2C), 158.47 (2C), 163.21 (2C), 164.88 (2C), 167.90 (2C).

2,2-Bis(5-{5-[5-(α,α-dimethylfurfuryl)-α,α-dimethylfurfuryl]-2-furoyl}furan-2-yl)propane (17, $m = p = 2$).



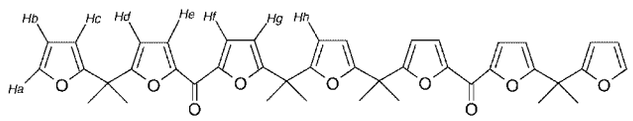
Chromatographic elution with 8 : 2 solvent ratio. Yellow oil. HRMS (APCI, M + 1): Found, 797.3320. Calculated for $C_{49}H_{49}O_{10}$ 797.3320. ν_{max} (neat) 2979, 2936, 2872, 1631, 1581, 1511, 1466, 1363, 1314, 1238, 1160 cm^{-1}; δ_H ($CDCl_3$) 1.59 (12H, s, 4 × CH_3), 1.68 (12H, s, 4 × CH_3), 1.81 (6H, s, 2 × CH_3), 5.91 (2H, d, J = 3.3 Hz, 2 × H_c), 5.93 (2H, d, J = 3 Hz, 2 × H_d), 6.00 (2H, d, J = 3 Hz, 2 × H_e), 6.11 (2H, d, J = 3.6 Hz, 2 × H_f), 6.22 (2H, dd, J = 2 and J' = 3 Hz, 2 × H_b), 6.28 (2H, d, J = 3.3 Hz, 2 × H_i), 7.26 (2H, br s, 2 × H_a), 7.36 (2H, d, J = 3.6 Hz, 2 × H_g), 7.38 (2H, d, J = 3.6 Hz, 2 × H_h); δ_C ($CDCl_3$) 26.04 (6C), 26.15 (4C), 37.34, 37.89 (2C), 38.26 (2C), 103.94 (2C), 104.37 (2C), 104.92 (2C), 107.47 (2C), 107.80 (2C), 109.83 (2C), 120.29 (2C), 120.41 (2C), 140.93 (2C), 150.30 (2C), 150.68 (2C), 156.89 (2C), 158.98 (2C), 159.91 (2C), 163.26 (2C), 165.22 (2C), 167.96 (2C).

2,5-Bis[5-(2-furoyl)-α,α-dimethylfurfuryl]furan (18, $m = p = 0$).



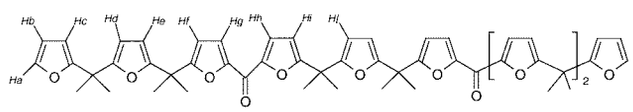
Chromatographic elution with 7 : 3 solvent ratio. Yellow oil. HRMS (APCI, M + 1): Found, 473.1597. Calculated for $C_{28}H_{25}O_7$, 473.1595. ν_{max} (neat) 3135, 3123, 2979, 2936, 2872, 1641, 1631, 1574, 1512, 1503, 1465, 1391, 1314, 1238, 1030 cm^{-1}; δ_H ($CDCl_3$) 1.71 (12H, s, 4 × CH_3), 6.08 (2H, s, 2 × H_f), 6.15 (2H, d, J = 3.6 Hz, 2 × H_e), 6.56 (2H, dd, J = 1.6 and J' = 3.6 Hz, 2 × H_b), 7.38 (2H, d, J = 3.6 Hz, 2 × H_d), 7.45 (2H, d, J = 3.6 Hz, 2 × H_c), 7.65 (2H, br s, 2 × H_a); δ_C ($CDCl_3$) 25.97 (4C), 37.85 (2C), 105.10 (2C), 107.39 (2C), 112.14 (2C), 119.26 (2C), 120.41 (2C), 146.56 (2C), 150.18 (2C), 151.17 (2C), 157.47 (2C), 165.07 (2C), 168.16 (2C).

2,5-Bis{5-[5-(α,α-dimethylfurfuryl)-2-furoyl]-α,α-dimethylfurfuryl}furan (18, $m = p = 1$).



Chromatographic elution with 8 : 2 solvent ratio. Yellow oil. HRMS (APCI, M + 1): Found, 689.2741. Calculated for $C_{42}H_{41}O_9$, 689.2745. ν_{max} (neat) 3121, 2979, 2935, 2872, 1630, 1580, 1511, 1465, 1363, 1315, 1269, 1236, 1161 cm^{-1}; δ_H ($CDCl_3$) 1.69 (12H, s, 4 × CH_3), 1.71 (12H, s, 4 × CH_3), 6.03 (2H, s, 2 × H_h), 6.12 (4H, d, J = 3.6 Hz, 2 × H_c and 2 × H_d), 6.18 (2H, d, J = 3.6 Hz, 2 × H_g), 6.30 (2H, dd, J = 2 and J' = 3.3 Hz, 2 × H_b), 7.32 (2H, d, J = 3.3 Hz, 2 × H_e), 7.33 (2H, dd, J = 1 and J' = 2 Hz, 2 × H_a), 7.35 (2H, d, J = 3.6 Hz, 2 × H_f); δ_C ($CDCl_3$) 26.10 (4C), 26.12 (4C), 37.78 (2C), 37.93 (2C), 104.66 (2C), 105.16 (2C), 107.33 (2C), 107.42 (2C), 110.08 (2C), 120.20 (2C), 120.39 (2C), 141.56 (2C), 150.35 (2C), 150.48 (2C), 157.56 (2C), 158.61 (2C), 164.87 (2C), 164.95 (2C), 168.01 (2C).

2,5-Bis(5-{5-[5-(α,α-dimethylfurfuryl)-α,α-dimethylfurfuryl]-2-furoyl}-α,α-dimethylfurfuryl)furan (18, $m = p = 2$).



Chromatographic elution with 8 : 2 solvent ratio. Yellow oil. HRMS (APCI, M + 1): Found, 905.3906. Calculated for $C_{56}H_{57}O_{11}$ 905.3895. ν_{max} (neat) 3124, 2979, 2936, 2872, 1631, 1579, 1511, 1466, 1363, 1314, 1267, 1235, 1160 cm^{-1}; δ_H ($CDCl_3$) 1.60 (12H, s, 4 × CH_3), 1.68 (12H, s, 4 × CH_3), 1.70 (12H, s, 4 × CH_3), 5.92 (2H, d, J = 3 Hz, 2 × H_c), 5.93 (2H, d, J = 3 Hz, 2 × H_d), 6.00 (2H, d, J = 3.3 Hz, 2 × H_e), 6.04 (2H, s, 2 × H_j), 6.10 (2H, d, J = 3.6 Hz, 2 × H_f), 6.12 (2H, d, J = 3.6 Hz, 2 × H_i), 6.22 (2H, dd, J = 2 and J' = 3.3 Hz, 2 × H_b), 7.26 (2H, dd, J = 0.99 and J' = 2 Hz, 2 × H_a), 7.33 (2H, d, J = 3.3 Hz, 2 × H_g), 7.35 (2H, d, J = 3.3 Hz, 2 × H_h); δ_C ($CDCl_3$) 26.05 (4C), 26.08 (4C), 26.13 (4C), 37.34 (2C), 37.89 (2C), 37.92 (2C), 103.93 (2C), 104.38 (2C), 104.92 (2C), 105.15 (2C), 107.30 (2C), 107.36 (2C), 109.83 (2C), 120.16 (2C), 120.38 (2C), 140.90 (2C), 150.30 (2C), 150.36 (2C), 156.94 (2C), 157.54 (2C), 158.95 (2C), 159.93 (2C), 164.90 (2C), 165.11 (2C), 167.96 (2C).

Reaction of 2-furyllithium and other lithiated furans 13 with diamides of furans 15

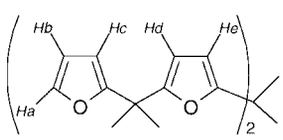
General procedure. A solution of *n*-BuLi in hexane (1.6 M, 0.0135 mol) was added dropwise to a solution of a furan (0.0123 mol) in dry THF (20 mL) [at −40 °C for furan and at −30 °C for L_2 and L_3]. Stirring was continued for 2–3 h allowing the temperature to rise to 10 °C). The lithio-derivative was then treated dropwise with a solution of the diamide (0.00411 mol) in dry THF (20 mL) at −60 °C. The mixture was stirred for 3 h while warming to 10 °C, then hydrolysed with cold aqueous ammonium chloride (2 M). The aqueous phase was extracted with ethyl acetate, the extract dried and the solvent removed under reduced pressure. Flash chromatography of the residue

as above afforded the same diketones **17** or **18** as prepared earlier in yields recorded in Table 1.

The Reetz reaction

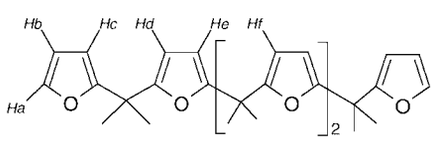
General procedure. A solution of titanium tetrachloride (2.22 equivalents per keto group) in dry dichloromethane (40 mL) was treated dropwise with a solution of dimethylzinc in dichloromethane (2–4 M, 4.44 equivalents per keto group) at −30 °C. The resulting brown solution was stirred at −30 °C for 1 h. A solution of the mono or diketone (1 equivalent) in dry dichloromethane (40 mL) was then added dropwise. The mixture was vigorously stirred at −30 °C for 1 h and then at room temperature for 2 h. The dark mixture was poured into cold saturated aqueous sodium bicarbonate and filtered through Celite. The aqueous phase was extracted with ethyl acetate and the dried solvent removed under reduced pressure. Flash chromatography of the residue using hexane–dichloromethane (4 : 1) afforded L_n (**5**–**10**) as colourless oils or solids as recorded in Table 2 and below.

2,2-Bis[5-(α,α-dimethylfurfuryl)furan-2-yl)]propane 6.



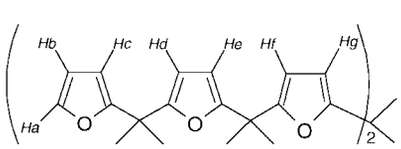
Colourless oil.[1] ν_{max} (neat) 3115, 2977, 2936, 2872, 1551, 1504, 1468, 1206, 1161, 1099, 1016 cm^{-1}; δ_H ($CDCl_3$) 1.56 (6H, s, 2 × CH_3), 1.60 (12H, s, 4 × CH_3), 5.83 (2H, d, J = 3 Hz, 2 × H_e), 5.88 (2H, d, J = 3 Hz, 2 × H_d), 5.95 (2H, d, J = 3Hz, 2 × H_c), 6.26 (2H, dd, J = 2 and J' = 3 Hz, 2 × H_b), 7.31 (2H, br s, 2 × H_a); δ_C ($CDCl_3$) 26.15 (2C), 26.21 (4C), 37.37, 37.43 (2C), 103.93 (2C), 104.11 (2C), 104.21 (2C), 109.85 (2C), 140.89 (2C), 158.21 (2C), 158.57 (2C), 160.21 (2C).

2,5-Bis[5-(α,α-dimethylfurfuryl)-α,α-dimethylfurfuryl]furan 7.



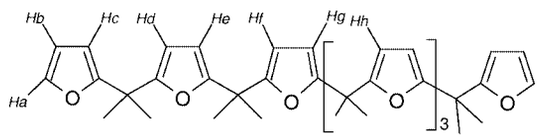
Colourless solid,[7] mp 41 °C (lit.[7] describes this compound as an oil). ν_{max} (KBr) 3144, 3123, 3105 (C_{sp2}-H), 2974, 2937, 2916, 2869 (C_{sp3}-H), 1601, 1578, 1553, 1504, 1447, 1381, 1360 cm^{-1}; δ_H ($CDCl_3$) 1.56 (6H, s, 2 × CH_3), 1.57 (6H, s, 2 × CH_3), 1.60 (6H, s, 2 × CH_3), 1.61 (6H, s, 2 × CH_3), 5.82 (2H, s, 2 × H_f), 5.84 (2H, d, J = 3 Hz, 2 × H_e), 5.88 (2, d, J = 3 Hz, 2 × H_d), 5.96 (2H, d, J = 3 Hz, 2 × H_c), 6.27 (2H, dd, J = 2 and J' = 3 Hz, 2 × H_b), 7.32 (2H, br s, 2 × H_a); δ_C ($CDCl_3$) 26.22 (4C), 26.25 (4C), 37.41 (2C), 37.47 (2C), 103.95 (2C), 104.10 (2C), 104.12 (2C), 104.21 (2C), 109.87 (2C), 140.91 (2C), 158.23 (2C), 158.43 (2C), 158.70 (2C), 160.28 (2C).

2,2-Bis{5-[5-(α,α-dimethylfurfuryl)-α,α-dimethylfurfuryl]-furan-2-yl}propane 8.



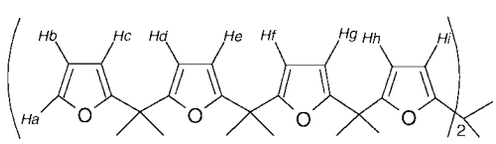
Colourless solid, mp 80 °C (lit.[7] 83–85 °C). ν_{max} (KBr) 3113, 2976, 2935, 2871, 1551, 1504, 1468, 1383, 1362, 1274, 1261 cm^{-1}; δ_H ($CDCl_3$) 1.56 (18H, s, 6 × CH_3), 1.60 (12H, s, 4 × CH_3), 5.78 (4H, s, 2 × H_f and 2 × H_g), 5.82 (2H, d, J = 3 Hz, 2 × H_e), 5.86 (2H, d, J = 3 Hz, 2 × H_d), 5.94 (2H, d, J = 3 Hz, 2 × H_c), 6.25 (2H, dd, J = 2 and J' = 3 Hz, 2 × H_b), 7.30 (2H, br s, 2 × H_a); δ_C ($CDCl_3$) 26.22 (4C), 26.24 (6C), 37.41, 37.47 (4C), 103.95 (2C), 104.08 (4C), 104.11 (2C), 104.19 (2C), 109.87 (2C), 140.93 (2C), 158.22 (2C), 158.41 (2C), 158.50 (2C), 158.72 (2C), 160.29 (2C).

2,5-Bis{5-[5-(α,α-dimethylfurfuryl)-α,α-dimethylfurfuryl]-α,α-dimethylfurfuryl}furan 9.



Colourless solid, mp 84 °C. HRMS (APCI, M + NH_4^+): Found, 734.4049. Calculated for $C_{46}H_{56}O_7N$, 734.4051. ν_{max} (KBr) 2974, 2934, 2871, 1602, 1553, 1504, 1457, 1447, 1381, 1360, 1276, 1097, 1019, 796 cm^{-1}; δ_H ($CDCl_3$) 1.56 (24H, s, 8 × CH_3), 1.60 (12H, s, 4 × CH_3), 5.79 (6H, s, 2 × H_h, 2 × H_g and 2 × H_f), 5.82 (2H, d, J = 3.3 Hz, 2 × H_e), 5.86 (2H, d, J = 3 Hz, 2 × H_d), 5.93 (2H, dd, J = 1 and J' = 3.3 Hz, 2 × H_c), 6.24 (2H, dd, J = 1.6 and J' = 3.3 Hz, 2 × H_b), 7.28 (2H, dd, J = 1 and J' = 2 Hz, 2 × H_a); δ_C ($CDCl_3$) 26.25 (4C), 26.27 (8C), 37.45 (2C), 37.51 (4C), 103.95 (2C), 104.11 (6C), 104.22 (2C), 109.88 (2C), 140.93 (2C), 158.27 (2C), 158.46 (2C), 158.53 (2C), 158.55 (2C), 158.76 (2C), 160.36 (2C).

2,2-Bis(5-{5-[5-(α,α-dimethylfurfuryl)-α,α-dimethylfurfuryl]-α,α-dimethylfurfuryl}furan-2-yl)propane 10.



Colourless solid, mp 101 °C. HRMS (EI): Found, 824.4280. Calculated for $C_{53}H_{60}O_8$ 824.4288. ν_{max} (KBr) 2996, 2974, 2934, 2870, 1553, 1504, 1457, 1447, 1380, 1359, 1276, 1239, 1204, 1161 cm^{-1}; δ_H ($CDCl_3$) 1.61 (24H, s, 8 × CH_3), 1.65 (18H, s, 6 × CH_3), 5.84 (8H, s, 2 × H_f, 2 × H_g, 2 × H_h and 2 × H_i), 5.86 (2H, d, J = 3.3 Hz, 2 × H_e), 5.90 (2H, d, J = 3.3 Hz, 2 × H_d), 5.98 (2H, dd, J = 1 and J' = 3.3 Hz, 2 × H_c), 6.28 (2H, dd, J = 1.65 and J' = 3 Hz, 2 × H_b), 7.32 (2H, dd, J = 1 and J' = 2 Hz, 2 × H_a); δ_C ($CDCl_3$) 26.28 (14C), 37.44, 37.51 (6C), 103.96 (2C), 104.12 (8C), 104.23 (2C), 109.88 (2C), 140.92 (2C), 158.25 (2C), 158.44 (2C), 158.52 (4C), 158.54 (2C), 158.74 (2C), 160.33 (2C).

Conversion of L_5 into C_5 and into compound 19

Dry hydrochloric acid gas was passed into a solution of L_5 (910 mg, 1.82 mmol) in a mixture of dry benzene (60 mL) and dry acetone (3 mL, 40.8 mmol) for 15 min. The deep red solution was stirred at room temperature for up to 2 days. An excess of saturated aqueous sodium hydrogen carbonate was added and the mixture extracted with ethyl acetate. The organic phase was dried ($MgSO_4$) and solvent removed and the residue separated by flash chromatography using firstly dichloromethane and hexane (95 : 5) which eluted C_5 (0.07 g, 7%) HRMS (EI): Found, 540.2892. Calculated for $C_{35}H_{40}O_5$, 5402876. ν_{max} (KBr) 2975, 2934, 2871, 1549, 1466, 1382, 1263, 1207, 1156, 1103, 1023 cm^{-1}; δ_H ($CDCl_3$) 1.57 (30H, s, 10 × CH_3), 5.82 (10H, s, 10 × CH); δ_C ($CDCl_3$) 26.22 (10C), 37.33 (5C), 103.78 (10C), 158.56 (10C) and then using pure dichloromethane which gave compound **19** (0.29 g, 29%) as a colourless solid, mp 115–117 °C. HRMS (EI): Found, 558.2995. Calculated for $C_{35}H_{42}O_6$, 558.2981. ν_{max} (KBr) 2977, 2936, 2872, 1711, 1598, 1549, 1465,

1383, 1365, 1265, 1205, 1106 cm^{-1}; δ_H ($CDCl_3$) 1.39 (6H, s, 2 × CH_3), 1.41 (12H, s, 4 × CH_3), 1.61 (12H, s, 4 × CH_3), 2.06 (4H, s, 2 × CH_2), 5.64 (2H, d, J = 3.0, H), 5.93 (2H, d, J = 3.3, H), 6.04 (2H, d, J = 3.3, H), 6.07 (2H, d, J = 3.3, H); δ_C ($CDCl_3$) 26.26 (4C), 25.39 (4C), 26.53 (2C), 31.51 (2C), 36.99 (2C), 37.67, 48.32 (2C), 103.4 (2C), 104.2 (2C), 104.6 (2C), 106.0 (2C), 156.3 (2C), 158.4 (2C), 158.8 (2C), 159.2 (2C), 211.1 (2C).

Acknowledgements

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