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A RADICAL CYCLISATION REACTION BASED STRATEGY TO 2,3,5-TRI- AND TETRASUBSTITUTED FURANS

A. Srikrishna* and G. Sundarababu
Department of Organic Chemistry, Indian Institute of Science
Bangalore - 560 012, INDIA

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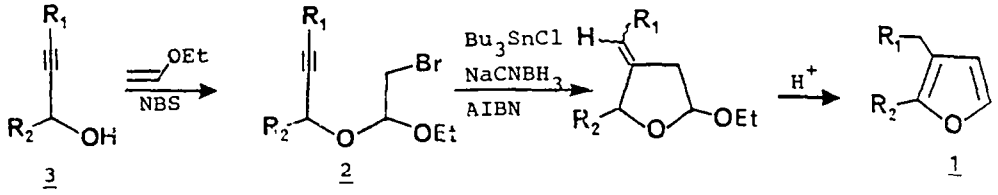
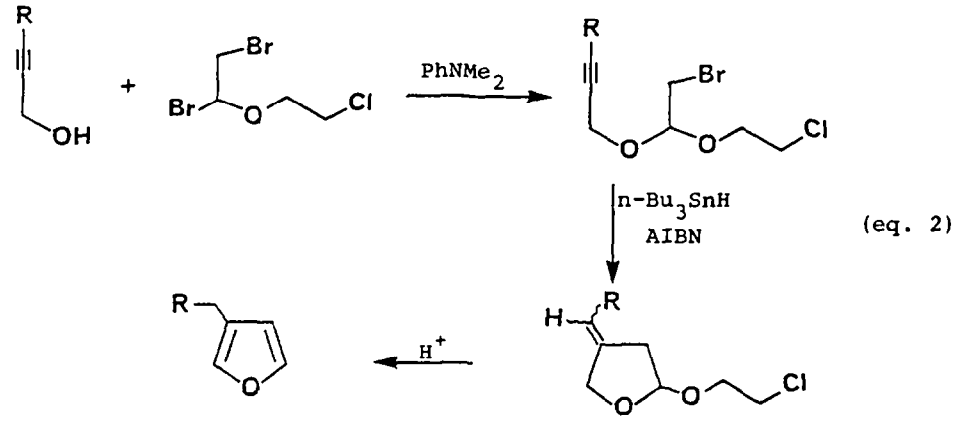
Abstract: Synthesis of 2,3,5-trisubstituted furans (5), starting from 2-methoxypropene and 1,3-disubstituted propargyl alcohols 3, via the radical cyclisation of the bromo acetal 4 followed by aromatisation, is reported. Analogously, 1-methoxycyclohexene and propargyl alcohols 3 furnished the tetrasubstituted furans 6.

The wide spread occurence of furans in nature and the role of furan derivatives as versatile synthetic intermediates[1] for the preparation of a wide range of cyclic and acyclic organic compounds makes the furans as the most prominent class of heteroaromatic compounds.[2] The presence of the furan nucleus in the structures of a variety of commercially important pharmaceuticals, and flavours and fragrances is also of importance.[3,4] During the last decade, intramolecular addition of carbon centered free radicals to olefins, i.e. radical cyclisations, of predictable regio- and stereoselectivity, provided a powerful technique for carbon - carbon bond formation in organic synthesis.[5] Five membered rings are readily prepared and the 5-exo cyclisation is generally favoured. The mildness of reaction conditions and the high levels of their chemoselectivity allow radical reactions to serve as powerful synthetic tools, whose applications often complement those of their ionic counter parts. Recently,[6] we have reported the synthesis of 3-mono and 2,3-disubstituted furans (1) based on a radical cyclisation reaction (eq. 1),



3 2 1

(eq. 1)



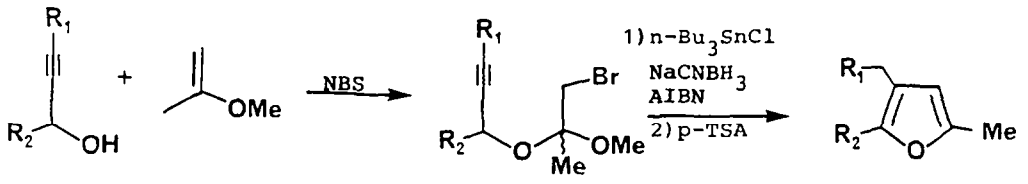
which, in principle, is the extension of the procedure originally developed by Stork and Mook[7] for β-alkylfurans using a chloro bromo acetal radical cyclisation (eq. 2). We have now extended our methodology, to establish the versatility of the sequence, to polysubstituted furans, and in this account we describe the syntheses of 2,3,5-tri- and 2,3,4,5-tetrasubstituted furans.

RESULTS AND DISCUSSION:

The methodology, as shown in the eq. 1, i.e., radical cyclisation of the bromo acetal 2, obtained from the N-bromosuccinimide (NBS) bromination of an enol ether in the presence of a substituted propargyl alcohol, and aromatisation of the resultant 3-alkylidene tetrahydrofuran to furans (1), clearly suggest the 1,3-disubstituted propargyl alcohols 3, and a di- or trisubstituted enol ether as necessary starting materials for the tri- and tetrasubstituted furans.[8]

2,3,5-TRISUBSTITUTED FURANS:

The requisite 1,3-disubstituted propargyl alcohols 3 were obtained by the reaction of the 1-lithio-1-octyne or 1-lithio-1-hexyne in dry THF with various aldehydes.[6a] 2-Methoxypropene, a gem disubstituted enol ether, was used, to generate a methyl substituent at C-5 position of the furan. Thus, the key radical precursors, bromo acetals 4, were obtained as a mixture of diastereomers, by a slow addition of 2-methoxypropene to a cold (-40 °C) solution of propargyl alcohols 3 and NBS in methylene chloride. The key radical cyclisations were achieved by using an *in situ* generated catalytic tri-n-butyltin hydride [n-Bu_3SnCl (0.15 equiv.), $NaCNBH_3$ (2 equiv.), t-BuOH][9] in the presence of a catalytic amount of azobisisobutyronitrile (AIBN). The cyclised



3 4 5

a. R_1 = n-hexyl; R_2 = phenyl
b. R_1 = n-hexyl; R_2 = p-tolyl
c. R_1 = n-hexyl; R_2 = i-propyl
d. R_1 = n-butyl; R_2 = phenyl
e. R_1 = n-butyl; R_2 = p-tolyl

products, obtained as a mixture of four isomers, were found to be too labile to purify and characterise,[6] and hence were directly aromatised to furans 5 using a catalytic amount of p-toluenesulfonic acid (p-TSA) in benzene at room temperature. The structures of the furans 5, were clearly delineated from their ^{1}H NMR spectra, in particular the presence of characteristic singlets at δ 5.5-6.0 for the β-proton (H-C-4) and at ≈2.3 ppm for the methyl group, typical for an α-methylfuran,[10] in addition to the other expected resonances for the substituents. The yields of the alcohols 3, the bromo acetals 4 and the furans 5 are listed in the table I.

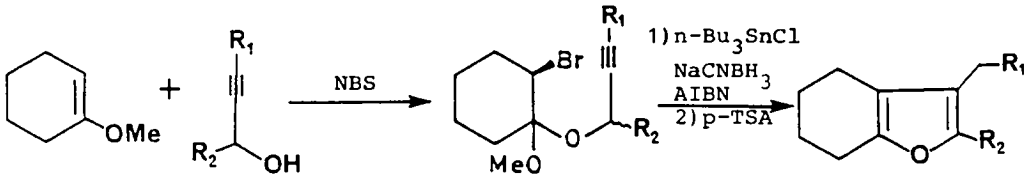
Table I: Synthesis of 2,3,5-trisubstituted furans[a]

Entry	R_1	R_2	alcohol	yield	bromide	yield[b]	furan	yield[c]
1	hexyl	phenyl	3a	85%	4a	65%	5a	50%
2	hexyl	p-tolyl	3b	90%	4b	60%	5b	60%
3	hexyl	i-propyl	3c	85%	4c	84%	5c	55%
4	butyl	phenyl	3d	90%	4d	65%	5d	52%
5	butyl	p-toyl	3e	97%	4e	70%	5e	53%

a) Yields (unoptimised) refer to isolated and chromatographically pure compounds. b) In addition, varying amounts (5-10%) of unreacted starting alcohols 3 were also obtained. c) Overall yield (two steps) from bromides 4.

TETRASUBSTITUTED FURANS:

Finally, the ultimate in the series, synthesis of tetrasubstituted furans 6, was achieved using 1-methoxycyclohexene,[11] a trisubstituted enol ether, in combination with 1,3-disubstituted propargyl alcohols 3. Thus, NBS



3a,d,e 7 6

a. R_1 = n-hexyl; R_2 = phenyl
b. R_1 = n-butyl; R_2 = phenyl
c. R_1 = n-butyl; R_2 = p-tolyl

bromination of 1-methoxycyclohexene in the presence of alcohols 3a,d,e in CH_2Cl_2 at -40 °C furnished the bromo acetals 7a-c. These bromo acetals 7a-c were found to be too labile and hence were directly used without any further purification. Radical cyclisation of the bromo acetals 7 using an *in situ* generated catalytic tri-n-butyltin hydride (n-Bu_3SnCl, $NaCNBH_3$, t-BuOH) in the presence of a catalytic amount of AIBN, and aromatisation of the crude cyclised products using p-TSA in benzene, as in the case of trisubstituted furans 5, furnished the tetrasubstituted furans 6. The overall yields starting from the alcohols 3 were in the range of 15-20%, mainly due to the instability of the intermediates, bromo acetals 7 and the cyclised products.

In conclusion, we expect that this radical cyclisation based strategy, for its mildness of reaction conditions, should constitute a valuable addition to the methodology for the synthesis of polysubstituted furans.[12]

EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer 781 spectrophotometer. ^1H NMR (60, 90, 270 MHz) spectra were recorded on a Varian T-60, Jeol FX-90Q and Brucker WH-270 spectrometers. Chemical shifts and coupling constants are reported in standard fashion (δ) with reference to internal tetramethylsilane. Low and high resolution mass measurements were carried out on a Jeol JMS-DX 303 GC-MS instrument using a direct inlet mode. Relative abundances of the fragments in LRMS are given in parentheses. Acme's silica gel (100-200 mesh) was used in the column chromatography. Acme's silica gel G (containing 13% calcium sulfate as binder) was used for TLC. All the moisture sensitive reactions were carried out using standard syringe-septum technique in nitrogen atmosphere. NBS was recrystallised from water. AIBN was recrystallised from methanol and stored in dark. All other commercial reagents were used as such with out further purification. THF was dried and distilled over sodium benzophenone ketyl prior to use. CH_2Cl_2 was distilled over P_2O_5. 1-Methoxy-cyclohexene was prepared according to the reported procedure.[13]

1-Phenylnon-2-yn-1-yl (1-bromo-2-methoxyprop-2-yl) ether (4a):

To a cold (-50 °C, EtOH-Liq. N_2 bath), magnetically stirred solution of the alcohol **3a** (650 mg, 3.0 mmol) and NBS (650 mg, 3.6 mmol) in 10 ml of dry CH_2Cl_2 was added, 2-methoxypropene (0.38 ml, 3.6 mmol) dropwise over a period of 1 hr. The reaction mixture was allowed to warm up to room temperature, and 3 ml of water was added. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 20 ml). The combined organic phase was washed with 2N aqueous NaOH (2 x 10 ml) and brine, and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on 10 g of silica gel with 1:4 ethyl acetate - hexane as eluent, furnished the diastereomeric mixture of the bromo acetal **4a** (490 mg, 60%). IR (neat): 2220, 1495, 1450, 1380, 1220, 1100, 1000, 710 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 7.48 (2 H, d, J = 7.5 Hz) and 7.2 - 7.4 (3 H, m) (aromatic), 5.45 and 5.42 (1 H, s, Ph-C<u>H</u>-O), 3.72 & 3.54 and 3.43 & 3.32 (2 H, AB q, J = 11 Hz), 3.27 and 3.18 (3 H, s, OMe), 2.21 (2 H, t, J = 7 Hz), 1.69 and 1.46 (3 H, s, O-C-Me), 1.15 - 1.6 (8 H, 4 x C<u>H</u>$_2$), 0.87 (3 H, t, J = 6.6 Hz, terminal Me); Mass: 256 (M^+-BrOMe, 20), 255 (75), 230 (22), 215 (30), 199 (65), 159 (100), 153 (90), 151 (95), 143 (35), 129 (40), 128 (45), 117 (40), 105 (35), 93 (25), 91 (90). Further elution of the column furnished 20 mg of unreacted alcohol **3a**.

3-n-Heptyl-5-methyl-2-phenylfuran (5a):

A suspension of the bromo acetal **4a** (185 mg, 0.5 mmol), n-Bu_3SnCl (0.02 ml, 0.075 mmol), $NaCNBH_3$ (65 mg, 1 mmol) and AIBN (catalytic) in 4 ml of t-butanol was refluxed for 3 hr. Solvent was evaporated under reduced pressure and the residue taken in 10 ml of water and extracted with CH_2Cl_2 (3 x 10 ml). The combined organic extract was washed with 1% aqueous NH_4OH (2 x 10 ml) and brine, and dried (Na_2SO_4). Evaporation of the solvent furnished the cyclised product, which was used as such with out further purification.

The cyclised product obtained above was taken in 5 ml of dry benzene and treated with small portions of p-TSA till the persistence of dark colour to the solution. The reaction mixture was stirred at room temperature for 2 hr and quenched with saturated aqueous $NaHCO_3$ (5 ml). The organic layer was separated and the aqueous phase was extracted with benzene (2 x 10 ml). The combined organic phase was washed with brine and dried (Na_2SO_4). Evaporation of the solvent and purification of the residue on 5 g of silica gel using 2% ethyl acetate in hexane as eluent furnished the furan **5a** (65 mg, 50%). IR (neat): 3030, 1605, 1570, 1490, 1460, 805, 760, 690 cm^{-1}; ^1H NMR (60 MHz, CCl_4): δ 7.05 - 7.6 (5 H, m, phenyl), 5.83 (1 H, br s, furan H-4), 2.57 (2 H, t, J = 7 Hz, furyl-C<u>H</u>$_2$), 2.3 (3 H, s, furyl-Me), 1.05 - 1.9 (10 H, 5 x C<u>H</u>$_2$), 0.9 (3 H, distorted t, terminal Me); Mass: 256 (M^+, 100), 257 (M^++1, 22), 172 (40), 171 (75), 143 (15), 128 (15), 105 (15); HRMS: Calcd. for $C_{18}H_{24}O$

256.1827; found, 256.1848.

1-(4-Methylphenyl)-non-2-yn-1-yl (1-bromo-2-methoxyprop-2-yl) ether (4b):

The reaction of the alcohol **3b** (500 mg, 2.15 mmol) with NBS (460 mg, 2.6 mmol) and 2-methoxypropene (0.18 ml, 2.6 mmol) and purification, as described for **4a**, furnished the diastereomeric mixture of the bromo acetal **4b** (490 mg, 60%). IR (neat): 2240, 1520, 1470, 1380, 1220, 1100, 1090, 990, 915, 700 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 7.36 (2 H, d, J = 8 Hz) and 7.16 (2 H, d, J = 8 Hz) (aromatic), 5.41 and 5.38 (1 H, s, Ar-C<u>H</u>-O), 3.71 & 3.52 and 3.42 & 3.31 (2 H, AB q, J = 11 Hz, C<u>H</u>$_2$-Br), 3.27 and 3.18 (3 H, s, -OMe), 2.34 (3 H, s, Ar-Me), 2.2 (2 H, t, J = 7 Hz, C≡C-C<u>H</u>$_2$), 1.67 and 1.45 (3 H, s, O-C-Me), 1.15 - 1.6 (8 H, m, 4 x C<u>H</u>$_2$), 0.87 (3 H, t, J = 7 Hz, terminal Me); Mass: 270 (M^+-BrOMe, 50), 269 (100), 186 (50), 185 (100), 170 (20), 143 (20), 119 (100), 91 (40). Further elution of the column furnished 30 mg of the unreacted alcohol **3b**.

3-n-Heptyl-5-methyl-2-(4-methylphenyl)furan (5b):

The radical cyclisation of the bromo acetal **4b**(190 mg, 0.5 mmol) with n-Bu_3SnCl (0.02 ml, 0.075 mmol), $NaCNBH_3$ (65 mg, 1 mmol) and AIBN (catalytic) in 4 ml of t-BuOH followed by aromatisation of the crude cyclised product with p-TSA in 5 ml of dry benzene and purification, as described for **5a**, furnished the furan **5b** (80 mg, 60%). IR (neat): 1670, 1610, 1510, 1470, 820 cm^{-1}; ^1H NMR (60 MHz, CCl_4): δ 7.35 (2 H, d, J = 8 Hz) and 7.03 (2 H, d, J = 8 Hz) (aromatic), 5.78 (1 H, s, furan H-4), 2.52 (2 H, t, J = 7 Hz, furan-C<u>H</u>$_2$), 2.33 (3 H, s, Ar-Me), 2.28 (3 H, s, furyl-Me), 1.0 - 1.5 (10 H, m, 5 x C<u>H</u>$_2$), 0.87 (3 H, t, J = 7 Hz, terminal Me); Mass: 269 (M^+-1), 229, 213 (100), 173, 151, 131, 119, 105, 91.

2-Methylundec-4-yn-3-yl (1-bromo-2-methoxyprop-2-yl) ether (4c):

The reaction of the alcohol **3c** (545 mg, 3 mmol) with NBS (650 mg, 3.6 mmol) and 2-methoxypropene (0.38 ml, 3.6 mmol) in 5 ml of dry CH_2Cl_2 and purification, as described for **4a**, furnished the diastereomeric mixture of the bromo acetal **4c** (840 mg, 84%). IR (neat): 2240, 1460, 1380, 1210, 1110, 1020, 680 cm^{-1}; ^1H NMR (60 MHz, CCl_4): δ 4.1 (1 H, m), 3.07 - 3.47 (2 H, m), 3.18 (3 H, s), 1.97 - 2.33 (2 H, m), 0.7 - 1.63 (21 H, m).

3-n-Heptyl-5-methyl-2-(1-methylethyl)-furan (5c):

The radical cyclisation of the bromo acetal **4c** (167 mg, 0.5 mmol) with n-Bu_3SnCl (0.02 ml, 0.075 mmol), $NaCNBH_3$ (65 mg, 1 mmol) and AIBN (catalytic) in 4 ml of t-BuOH for 3 hr followed by aromatisation with p-TSA in 5 ml of benzene and purification, as described for **5a**, furnished the furan **5c** (60 mg, 55%). IR (neat): 3020, 1590, 1460, 1380, 1250, 1050, 800 cm^{-1}; ^1H NMR (60 MHz, CCl_4): δ 5.57 (1 H, s), 2.85 (1 H, sep, J = 7 Hz), 2.0 - 2.45 (2 H, m),

2.2 (3 H, s), 1.1 - 1.57 (16 H, m), 0.91 (3 H, t, J = 7 Hz); Mass: 221 (M^+-1, 15), 197 (21), 196 (39), 195 (40), 111 (40), 110 (30), 95 (20), 83 (20), 81 (20), 71 (35); HRMS: Calcd. for $C_{15}H_{25}O$ (M^+-1) 221.1906; found 221.1897.

1-Phenylhept-2-yn-1-yl (1-bromo-2-methoxyprop-2-yl) ether (4d):

The reaction of the propargyl alcohol **3d** (565 mg, 3 mmol)[13] with NBS (650 mg, 3.6 mmol) and 2-methoxypropene (0.38 ml, 3.6 mmol) in 5 ml of CH_2Cl_2 and purification, as described for **4a**, furnished the diastereomeric mixture of the bromo acetal **4d** (663 mg, 65%). IR (neat): 2240, 1500, 1460, 1380, 1220, 1100, 1000, 700 cm^{-1}; ^1H NMR (60 MHz, CCl_4): δ 7.0 - 7.6 (5 H, m), 5.23 (1 H, m), 3.2 - 3.6 (2 H, m), 3.17 and 3.07 (3 H, s), 1.95 - 2.35 (2 H, m), 1.63 and 1.38 (3 H, s), 1.15 - 1.5 (4 H, m), 0.88 (3 H, t, J = 7 Hz).

5-Methyl-3-n-pentyl-2-phenylfuran (5d):

The radical cyclisation of the bromo acetal **4d** (170 mg, 0.5 mmol) with n-Bu_3SnCl (0.02 ml, 0.075 mmol), $NaCNBH_3$ (65 mg, 1 mmol) and AIBN (catalytic) in 4 ml of t-BuOH followed by aromatisation with p-TSA in 5 ml of dry benzene and purification, as described for **5a**, furnished the furan **5d** (60 mg, 52%). IR (neat): 1600, 1555, 1490, 800, 760, 695 cm^{-1}; ^1H NMR (60 MHz, CCl_4): δ 6.95 - 7.6 (5 H, m), 5.82 (1 H, s), 2.55 (2 H, t, J = 7 Hz), 2.3 (3 H, s), 1.05 - 1.85 (6 H, m), 0.88 (3 H, t, J = 7 Hz); Mass: 228 (M^+, 25), 227 (20), 200 (30), 187 (25), 172 (20), 145 (20), 139 (25), 106 (25), 105 (95), 77 (100); HRMS: Calcd. for $C_{16}H_{20}O$ 228.1514, found 228.1474.

1-(4-Methylphenyl)-hept-2-yn-1-yl (1-bromo-2-methoxyprop-2-yl) ether (4e):

The reaction of the alcohol **3e** (606 mg, 3 mmol) with NBS (650 mg, 3.6 mmol) and 2-methoxypropene (0.38 ml, 3.6 mmol) in 10 ml of dry CH_2Cl_2 and purification, as described for **4a** furnished the diastereomeric mixture of the bromo acetal **4e** (742 mg, 70%). IR (neat): 2240, 1460, 1380, 1220, 1100, 990, 840, 820 cm^{-1}; ^1H NMR (60 MHz, CCl_4): δ 7.23 (2 H, d, J = 8 Hz), 6.97 (2 H, d, J = 8 Hz), 5.22 (1 H, m), 3.23 - 3.6 (2 H, m), 3.16 and 3.05 (3 H, s), 2.3 (3 H, s), 1.9 - 2.3 (2 H, m), 1.57 and 1.35 (3 H, s), 1.0 - 1.7 (4 H, m), 0.93 (3 H, distorted t).

5-Methyl-2-(4-methylphenyl)-3-n-pentylfuran (5e):

The radical cyclisation of the bromo acetal **4e** (177 mg, 0.05 mmol) with n-Bu_3SnCl (0.02 ml, 0.075 mmol), $NaCNBH_3$ (65 mg, 1 mmol) and AIBN (catalytic) in 4 ml of t-BuOH for 3 hr followed by aromatisation of the cyclised product with p-TSA in 5 ml of dry benzene and purification, as described for **5a**, furnished the furan **5e** (95 mg, 53%). IR (neat): 3030, 1610, 1510, 1460, 1110, 820 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ 7.48 (2 H, d, J = 8 Hz), 7.2 (2 H, d, J = 8 Hz), 5.96 (1 H, s), 2.6 (2 H, t, J = 7 Hz), 2.4 (3 H, s), 2.34 (3 H, s), 1.1

- 1.9 (6 H, m), 0.92 (3 H, t, J = 7 Hz); Mass: 242 (M^+), 215 (30), 187 (30), 139 (25), 119 (98), 91 (100).

3-n-Heptyl-2-phenyl-4,5,6,7-tetrahydrobenzofuran (6a):

Reaction of the alcohol 3a (230 mg, 1 mmol) with NBS (213 mg, 1.2 mmol) and 1-methoxycyclohexene (135 mg, 1.2 mmol) in 5 ml of dry CH_2Cl_2 as described for 4a furnished the crude bromo acetal 7a (170 mg).

The radical cyclisation of the above crude bromo acetal 7a with n-Bu_3SnCl (0.02 ml, 0.075 mmol), $NaCNBH_3$ (65 mg, 1 mmol) and AIBN (catalytic) in 4 ml of t-BuOH followed by aromatisation with p-TSA in 4 ml of dry benzene as described for 5a and purification over 8 g of silica gel with 1:40 ethyl acetate - hexane, furnished the tetrahydrobenzofuran 6a (55 mg, 16% overall yield). IR (neat): 1520, 1460, 910, 820 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ 7.58 (2 H, d, J = 6.8 Hz), 7.38 (1 H, t, J = 6.8 Hz), 7.23 (2 H, d, J = 6.8 Hz), 2.64 (2 H, m), 2.56 (2 H, t, J = 7 Hz), 2.41 (2 H, m), 1.45 - 2.0 (4 H, m), 1.1 - 1.65 (10 H, m), 0.97 (3 H, t, J = 7 Hz).

3-n-Pentyl-2-phenyl-4,5,6,7-tetrahydrobenzofuran (6b):

Reaction of the alcohol 3d (230 mg, 1.2 mmol) with NBS (213 mg, 1.2 mmol) and 1-methoxycyclohexene (135 mg, 1.2 mmol) in 5 ml of dry CH_2Cl_2 as described for 4a furnished the crude bromo acetal 7b.

The radical cyclisation of the above crude bromo acetal 7b with n-Bu_3SnCl (0.02 ml, 0.075 mmol), $NaCNBH_3$ (65 mg, 1 mmol) and AIBN (catalytic) in 4 ml of t-BuOH followed by aromatisation with p-TSA in 3 ml of dry benzene and purification, as described for 5a, furnished the tetrasubstituted furan 6b (55 mg, 16% overall yield). IR (neat): 1600, 1500, 1450, 1070, 760, 690 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ 7.1 - 7.7 (5 H, m), 2.1 - 2.8 (6 H, m), 1.6 - 2.1 (4 H, m), 1.1 - 1.6 (6 H, m), 0.9 (3 H, t, J = 7 Hz); Mass: 266 (20), 105 (100), 77 (30); HRMS: Calcd. for $C_{19}H_{22}O$ 266.1671, found 266.1693.

3-n-Pentyl-2-(4-methylphenyl)-4,5,6,7-tetrahydrobenzofuran (6c):

Reaction of the alcohol 3e (202 mg, 1 mmol) with NBS (213 mg, 1.2 mmol) and 1-methoxycyclohexene (135 mg, 1.2 mmol) in 5 ml of dry CH_2Cl_2 as described for 4a, furnished the crude bromo acetal 7c.

The radical cyclisation of the above crude bromo acetal 7c with n-Bu_3SnCl (0.015 ml, 0.06 mmol), $NaCNBH_3$ (46 mg, 0.75 mmol) and AIBN (catalytic) in 4 ml of t-BuOH followed by aromatisation with p-TSA in benzene and purification, as described for 5a, furnished the tetrahydrobenzofuran 6c (50 mg, 20% overall yield). IR (neat): 1500, 1440, 1100, 815 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ 7.48 (2 H, d, J = 7.5 Hz), 7.2 (2 H, d, J = 7.5 Hz), 2.36 (3 H, s), 2.1 - 2.8 (6 H, m), 1.65 - 1.95 (4 H, m), 1.1 - 1.55 (6 H, m), 0.9 (3 H, t, J = 7 Hz); Mass: 282 (M^+, 100), 225 (40), 119 (25), 91 (20); HRMS: Calcd. for $C_{20}H_{26}O$

282.1984, found 282.1964.

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10) For example, In 2,5-dimethylfuran, the β-proton and the methyl protons resonate at δ 5.7 and 2.2 ppm respectively. Pouchert, C. J. The Aldrich Library of NMR spectra, 2nd ed.; Aldrich Chemical Co. Inc.: Milwaukee, WI 1983; Vol. 2, pp. 454.

11) Wohl, R. A. Synthesis 1974, 38.

12) For convenience, reactions were carried out on small scale (0.5-1 mmol). However, two of the sequences reported in this paper (6b, 6c) and three of the sequences reported in our earlier communication[6a] were repeated on increased scales (3-5 mmol) with only marginal reduction ($\ll$5%) in overall yield.

13) Takai, K.; Kuroda, T.; Nakatsukasa, S.; Oshima, K.; Nozaki, H. Tetrahedron Lett. 1985, 26, 5585.