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Regioselective synthesis of ω-bromo-3-ketosulfones, ω-bromo-3-ketonitriles and 2-(ω-bromoalkyl)benzofurans based on a 'ring-closing/ring-opening' strategy

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Abstract—ω-Bromo-3-ketosulfones, ω-bromo-3-ketonitriles and various functionalized 2-(ω-bromoalkyl)benzofurans were chemo- and regioselectively prepared by application of a 'ring-closing/ring-opening' strategy. The cyclization of 3-ketosulfone and 3-ketonitrile dianions with 1-bromo-2-chloroethane or 1,4-dibromobut-2-ene afforded functionalized 2-alkylidenetetrahydrofurans which were subsequently cleaved by reaction with boron tribromide or boron trichloride to give the final products.

1. Introduction

Boron tribromide (BBr_3) represents a widely used reagent for the cleavage of methoxyarenes.[1] Besides this well-known application of BBr_3, other reactions have only scarcely been reported in the literature. ω-Bromoalcohols[2] and ω-halocarboxylic acids[3] were prepared by BBr_3-mediated ring opening of cyclic ethers and lactones, respectively.[3] Recently, we reported the synthesis of 6-bromo-3-oxoalkanoates by reaction of BBr_3 with 2-alkylidenetetrahydrofurans.[4] The synthesis of benzofuran-3-carboxylic esters containing a remote bromide group—based on a BBr_3-mediated ring transformation—has also been reported.[5] Herein, we report the synthesis of ω-bromo-3-ketosulfones, ω-bromo-3-ketonitriles and 2-(ω-haloalkyl)-benzofurans based on the synthesis of 2-(sulfonylmethylidene)- and 2-(cyanomethylidene)-tetrahydrofurans and their subsequent BBr_3-mediated cleavage. The products are not readily available by other methods. Notably, functionalized benzofurans are of considerable pharmacological relevance and represent versatile synthetic building blocks in organic and medicinal chemistry.[6] For example, the benzofuran amiodarone is used in the clinic as a potent antiarrythmic and antianginal drug.[7] Various benzofurans occur in natural products. This includes, for example, longicaudatin,[8] the sessiliflorols A and B, flemistrictin E, tovophenone C, vismiaguianone C or piperaduncin B.[9]

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2. Results and discussion

2.1. Reactions of 3-ketosulfone dianions

2-(2-Oxoalkylidene)tetrahydrofurans are available by cyclization[10] of 1,3-dicarbonyl dianions or 1,3-bis(silyl enol ethers) ('masked dianions') with various electrophiles, such as 1-bromo-2-chloroethane,[11] 1,4-dibromobut-2-ene,[12] or epoxides.[13] 2-(Sulfonylmethylidene)tetrahydrofurans were prepared, for example, from β-iodovinyl sulfones,[14] ω-halo and ω-hydroxy-β-ketosulfones,[15] or ω-hydroxypropargylic sulfones.[16] Another approach relies on the cyclization of 3-ketosulfone dianions with cyclic sulfates.[17] Some years ago, we reported the synthesis of 7-sulfonyl-2,3,3a,4,5,6-hexahydrobenzofurans, which can be regarded as bicyclic 2-(sulfonylmethylidene)tetrahydrofurans, by cyclization of cyclic 3-ketosulfone dianions with 1,4-dibromobut-2-ene.[12]

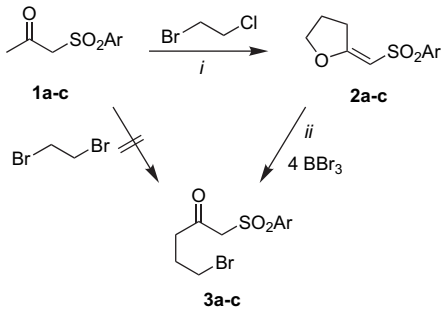
The cyclization of the dianions of 3-ketosulfones **1a–c**, generated by LDA (2.5 equiv), with 1-bromo-2-chloroethane afforded the 2-(sulfonylmethylidene)tetrahydrofurans **2a–c** (Scheme 1, Table 1). The reaction of a CH_2Cl_2 solution of **2a–c** with BBr_3 and subsequent addition of water afforded the ω-bromo-β-ketosulfones **3a–c**. The formation of **3a–c** can be explained as follows. The interaction of BBr_3 with the sulfonyl group effects a dramatic increase of the electrophilicity of carbon atom C-5 of the tetrahydrofuran moiety. Nucleophilic attack of a BBr_3-derived bromide ion onto carbon C-5 results in ring-opening and formation of an open-chain boron enolate. The latter is subsequently protonated

Table 1. Synthesis of **3a–c**

2,3	Ar	% (**2**)[a]	*E*/*Z* (**2**)[b]	% (**3**)[a]
a	Ph	45	7:3	95
b	4-MeC_6H_4	45	7:3	92
c	4-ClC_6H_4	40	6:4	65

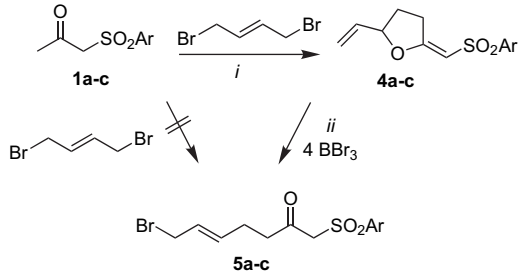
[a] Yields of isolated products.
[b] By ^{1}H NMR.

upon addition of water. Notably, products **3a–c** are *not* directly available by reaction of 3-ketosulfone dianions with 1,2-dibromoethane, due to a competing SET process (oxidative dimerization of the dianion and reduction of 1,2-dibromoethane to ethylene).[18]



Scheme 1. Synthesis of ω-bromo-3-ketosulfones **3a–c**. (i) (1) 2.5 equiv LDA, THF, 0 °C, 1 h; (2) $Br(CH_2)_2Cl$, −78→20 °C, 14 h, then reflux, 14 h; (ii) (1) 4.0 equiv BBr_3, CH_2Cl_2, 0→20 °C, 12 h, 20 °C, 8 h; (2) H_2O.

2-(Sulfonylmethylidene)-5-vinyltetrahydrofurans **4a–c** were prepared by cyclization of dilithiated 3-ketosulfones **1a–c** with 1,4-dibromobut-2-ene (Scheme 2, Table 2). The reaction of **4a–c** with BBr_3 afforded the ω-bromo-3-ketosulfones **5a–c**. The products were formed by cleavage of the 2-alkylidenetetrahydrofuran by an S_N' reaction. Notably, the products are *not* available by direct reaction of the dianions of **1a–c** with 1,4-dibromobut-2-ene, due to rapid cyclization.



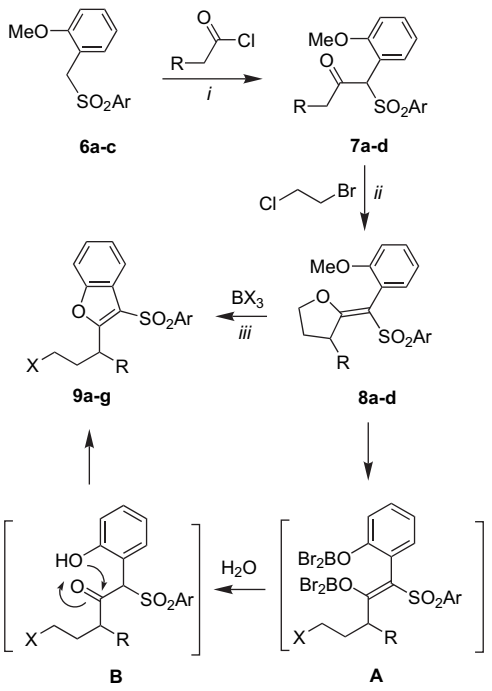
Scheme 2. (i) (1) 2.5 equiv LDA, THF, 0 °C, 1 h; (2) 1,4-dibromobut-2-ene, −78→20 °C, 20 h; (ii) (1) 5.0 equiv BBr_3, CH_2Cl_2, 0→20 °C, 12 h, 20 °C, 8 h; (2) H_2O.

3-Ketosulfones **7a–d** were prepared by acylation of aryl-[(2-methoxyphenyl)methyl]-sulfones **6a–c**. The cyclization of the dianions of **7a–c** with 1-bromo-2-chloroethane afforded the 2-alkylidenetetrahydrofurans **8a–d**. Treatment of **8a–d** with BBr_3 afforded the 2-(γ-bromoalkyl)-3-sulfonylbenzofurans **9a–d** (Scheme 3, Table 3). The reaction of **8a–c** with BCl_3 gave 2-(γ-hydroxypropyl)-3-sulfonylbenzofurans **9e–g**. The formation of benzofurans **9** can be explained by ring-opening of **8** and deprotection of the arylmethyl ether to give intermediate **A**, hydrolysis upon aqueous work-up (intermediate **B**) and subsequent acid mediated cyclization by attack of the hydroxy onto the carbonyl group. In case of **9e–g**, the chloride group was hydrolyzed.

Table 2. Synthesis of **5a–c**

4,5	Ar	% (**4**)[a]	*E*/*Z* (**4**)[b]	% (**5**)[a]
a	Ph	50	6:4	75
b	4-MeC_6H_4	38	6:4	75
c	4-ClC_6H_4	40	>98:2	70

[a] Yields of isolated products.
[b] By ^{1}H NMR.



Scheme 3. Synthesis of benzofurans **9a–e**. (i) (1) 2.5 equiv LDA, THF, 0 °C, 45 min; (2) acid chloride, −78→20 °C, 14 h; (ii) (1) 2.5 equiv LDA, THF, 0 °C, 1 h; (2) $Br(CH_2)_2Cl$, −78→20 °C, 14 h, then reflux, 14 h; (iii) (1) 5.0 equiv BBr_3, CH_2Cl_2, 0→20 °C, 12 h, 20 °C, 12 h; (2) H_2O.

The structure of all products was established by spectroscopic methods. The structures of **8a** and **9a** were independently confirmed by X-ray crystal structure analyses (Figs. 1 and 2).[19]

2.2. β-Ketonitriles

The known[11a] 2-alkylidenetetrahydrofuran **11** was prepared by cyclization of the dianion of cyanoacetone, generated by

Table 3. Synthesis of benzofurans **9a–g**

7,8	9	Ar	R	X	% (**7**)[a]	% (**8**)[a,c]	% (**9**)[a]
a	**a**	Ph	H	Br	56	45 (*E*)+22 (*Z*)	72
b	**b**	4-MeC_6H_4	H	Br	78	55 (*E*)	61
c	**c**	4-ClC_6H_4	H	Br	61	49 (*E*)+19 (*Z*)	68
d	**d**	Ph	Me	Br	40	46 (*E*/*Z*=8:1)	63
a	**e**	Ph	H	OH[b]	56	45 (*E*)+22 (*Z*)	40
b	**f**	4-MeC_6H_4	H	OH[b]	28	55 (*E*)	34
c	**g**	4-ClC_6H_4	H	OH[b]	61	49 (*E*)+19 (*Z*)	47

[a] Yields of isolated products.
[b] The product was formed when BCl_3 was used (by hydrolysis of the chloride group in the product).
[c] In brackets: configuration of the exocyclic double bond.

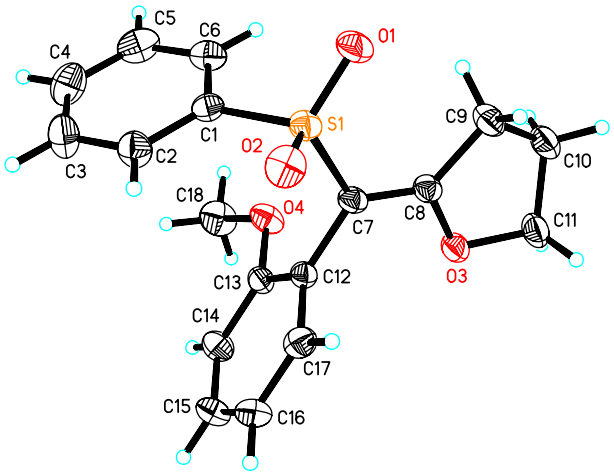


Figure 1. Ortep plot of **8a**.

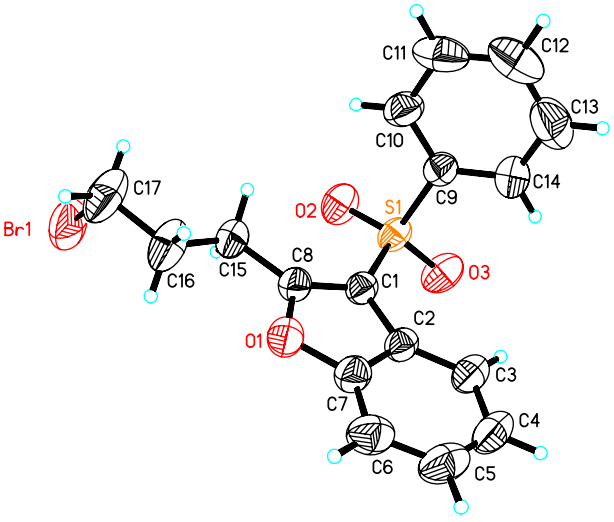
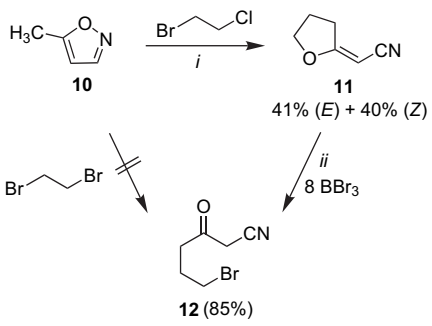


Figure 2. Ortep plot of **9a**.

treatment of 5-methyl-isoxazole with LDA, with 1-bromo-2-chloroethane. Treatment of **11** with BBr_3 afforded 1-cyano-5-bromo-pentan-2-one (**12**) (Scheme 4). It was possible to independently confirm the structure of **12** by an X-ray crystal structure analysis (Fig. 3).[19]



Scheme 4. Synthesis of 1-cyano-5-bromopentan-2-one (**12**). (i) (1) 2.5 equiv LDA, THF, 0 °C, 1 h; (2) $Br(CH_2)_2Cl$, −78→20 °C, 14 h, then reflux, 14 h; (ii) (1) 8.0 equiv BBr_3, CH_2Cl_2, 0→20 °C, 12 h, 20 °C, 8 h; (2) H_2O.

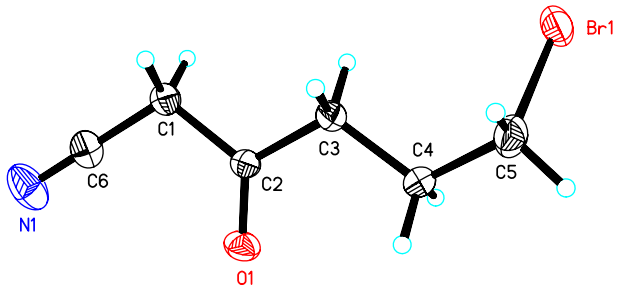
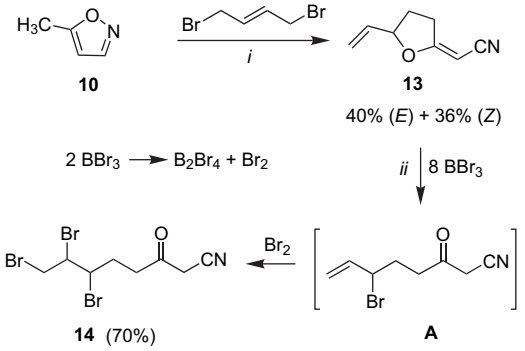


Figure 3. Ortep plot of **12**.

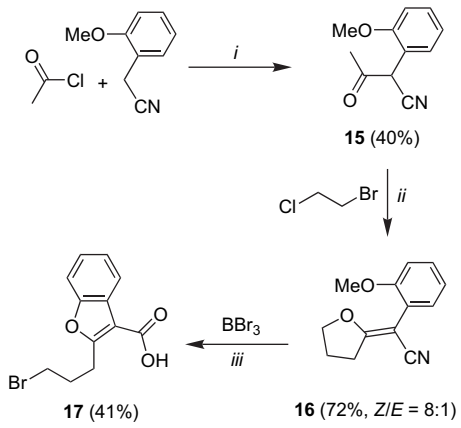
The cyclization of the dianion of cyanoacetone, generated by treatment of 5-methyl-isoxazole with LDA, with 1,4-dibromobut-2-ene afforded the known[11a] 2-alkylidenetetrahydrofuran **13**. Treatment of **13** with BBr_3 unexpectedly afforded tribromide **14** (Scheme 5). Product **14** is presumably formed by BBr_3-mediated ring opening and formation of intermediate **A**. Subsequently, the double bond is brominated (by the action of bromine formed under the reaction conditions from BBr_3).



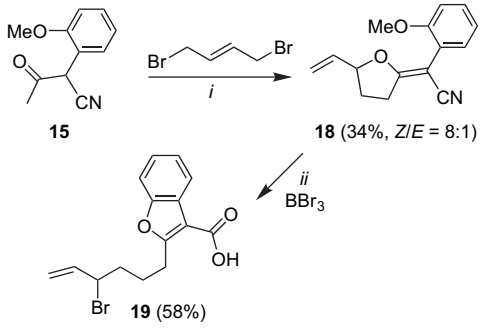
Scheme 5. i) (1) 2.5 equiv LDA, THF, 0 °C, 1 h; (2) 1,4-dibromobut-2-ene, −78→20 °C, 20 h; (ii) (1) 8.0 equiv BBr_3, CH_2Cl_2, 0→20 °C, 12 h, 20 °C, 6 h; (2) H_2O.

The acylation of (2-methoxyphenyl)acetonitrile with acetyl chloride afforded β-ketonitrile **15**. The cyclization of the dianion of **15** with 1-bromo-2-chloroethane gave 2-alkylidenetetrahydrofuran **16**. Treatment of the latter with BBr_3 and subsequently with HBr (62%) afforded the 2-(γ-bromoalkyl)-3-carboxybenzofuran **17** (Scheme 6). During the optimization of this reaction, the addition of concd hydrobromic acid proved to be important in order to induce a complete rearrangement. This was necessary, since nitrile **15** proved to be less reactive than sulfones **8** in the reaction with BBr_3. This can be explained by the lower electron-withdrawing effect of the nitrile compared to the sulfone. The nitrile was hydrolyzed to a carboxylic acid group upon addition of concd hydrobromic acid.

The cyclization of the dianion of **15** with 1,4-dibromobut-2-ene gave 2-alkylidene-5-vinyltetrahydrofuran **18**. Treatment of the latter with BBr_3 and subsequently with HBr (62%) afforded the 2-(ω-bromoalkyl)-3-carboxybenzofuran **19** (Scheme 7). The nitrile was again hydrolyzed to a carboxylic acid group upon addition of concd hydrobromic acid.



Scheme 6. Synthesis of benzofuran **17**. (i) (1) 2.5 equiv LDA, THF, 0 °C, 45 min; (2) acid chloride, −78→20 °C, 14 h; (ii) (1) 2.5 equiv LDA, THF, 0 °C, 1 h; (2) $Br(CH_2)_2Cl$, −78→20 °C, 14 h, then reflux, 14 h; (iii) (1) 7.0 equiv BBr_3, CH_2Cl_2, 0→20 °C, 12 h, 20 °C, 72 h; (2) HBr (62%) 6.0 equiv 20 °C, 20 h; (3) H_2O.



Scheme 7. Synthesis of benzofuran **19**. (i) (1) 2.5 equiv LDA, THF, 0 °C, 1 h; (2) 1,4-dibromobut-2-ene, −78→20 °C, 20 h; (ii) (1) 8.0 equiv BBr_3, CH_2Cl_2, 0→20 °C, 12 h, 20 °C, 72 h; (2) HBr (62%, 6.0 equiv), 20 °C, 20 h; (3) H_2O.

In conclusion, we reported an efficient approach to ω-bromo-3-ketosulfones, ω-bromo-3-ketonitriles and 2-(ω-bromoalkyl)-benzofurans based on one-pot cyclizations of 3-ketonitrile and 3-ketosulfone dianions and application of a 'ring-closing/ring-opening' strategy.

3. Experimental section

3.1. General procedure for the cyclization of 1-bromo-2-chloroethane with dianions

To a THF solution of LDA (prepared by addition of 5.0 mmol of *n*-BuLi, 2.5 M in hexane, to a solution of diisopropylamine (0.57 ml, 5.0 mmol) in 12 ml of THF, stirred for 30 min), was added 1-phenylsulfonyl-2-propanone (397 mg, 2.0 mmol) at 0 °C. The solution was stirred at 0 °C for 45 min. To this solution was added 1-bromo-2-chloroethane (0.17 ml, 2.1 mmol) at −78 °C. The temperature was allowed to rise to 20 °C during 14 h, and the solution was subsequently refluxed for 14 h. To the solution was added hydrochloric acid (1 M) and the mixture was subsequently extracted with EtOAc (3×200 ml). The organic layers were dried and filtered, the solvent of the filtrate was removed in vacuo and the residue was purified by chromatography (silica gel, EtOAc/*n*-heptane).

3.1.1. 2-[(Phenylsulfonyl)methylidene]tetrahydrofuran (2a). Starting with 1-phenylsulfonyl-2-propanone **1a** (3.90 g, 19.76 mmol) and 1-bromo-2-chloroethane (1.8 ml, 21.74 mmol), **2a** was isolated as a highly viscous colourless oil (1.99 g, 45%, *E*/*Z*=7:3); ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.92–2.09 (m, 2×2H, CH_2, both isomers), 2.60 (dt, 2H, *J*=7.7 Hz, *J*=1.2 Hz, CH_2), 3.05 (dt, 2H, *J*=7.9 Hz, *J*=1.8 Hz, CH_2), 4.15 (t, 2H, *J*=7.0 Hz, CH_2), 4.31 (t, 2H, *J*=6.8 Hz, CH_2), 5.39 (t, 1 H, *J*=1.2 Hz, C═C*H*, *Z*-isomer), 5.67 (t, 1H, *J*=1.8 Hz, C═C*H*, *E*-isomer), 7.41–7.48 (m, 2×3H, ArH, both isomers), 7.76–7.91 (m, 2×2H, ArH, both isomers); ^{13}C NMR (75 MHz, $CDCl_3$): δ=23.0, 24.1, 29.8, 32.2, 72.9, 75.4 (CH_2), 98.8, 100.1 (CH), 126.7 (2C, CH), 127.3 (2C, CH), 128.6, 129.0 (CH), 129.4 (2C, CH), 132.8 (2C, CH), 143.9, 144.2, 170.1, 174.3 (C); IR (neat): $\tilde{\nu}$ = 3086 (w), 3535 (w), 3061 (w), 2936 (m), 1720 (s), 1447 (s), 1402 (m), 1309 (s), 1153 (s), 688 (s), 528 (s) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%): 224.1 (M^+, 100), 160 (15), 147 (18), 131 (24), 118 (31), 89 (23), 77 (66), 51 (34); HRMS (ESI): calcd (%) for $C_{11}H_{12}O_3S$ ($[M+1]^+$) 224.05017, found 224.05017.

3.1.2. 2[((4-Methylphenyl)sulfonyl)methylidene]tetrahydrofuran (2b). Starting with 1-(4-methylphenyl)sulfonyl-2-propanone **1b** (3.00 g, 14.13 mmol), 1-bromo-2-chloroethane (1.4 ml, 16.96 mmol), **2b** was isolated as a colourless solid (1.51 g, 45%, *E*/*Z*=7:3), mp 87 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.98–2.09 (m, 2×2H, CH_2, both isomers), 2.34 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.59 (m, 2H, CH_2), 3.06 (dt, 2H, *J*=7.8 Hz, *J*=1.7 Hz, CH_2), 4.14 (t, 2H, *J*=7.0 Hz, CH_2), 4.31 (t, 2H, *J*=6.9 Hz, CH_2), 5.39 (t, 1H, *J*=1.3 Hz, C═C*H*, *Z*-isomer), 5.67 (t, 1H, *J*=1.7 Hz, C═C*H*, *E*-isomer), 7.19–7.29 (m, 2×2H, ArH, both isomers), 7.66–7.79 (m, 2×2H, ArH, both isomers); ^{13}C NMR (75 MHz, $CDCl_3$): δ=21.9, 22.0 (CH_3), 29.7, 32.2, 36.8, 41.3, 72.7, 75.3 (CH_2), 99.2, 100.6 (CH), 128.5 (2C, CH), 128.6 (2C, CH), 130.0 (2C, CH), 130.3 (2C, CH), 136.4, 138.0, 145.0, 145.7, 169.5, 173.7 (C); IR (KBr): $\tilde{\nu}$ = 2968 (w), 2925 (w), 2886 (w), 1719 (m), 1597 (w), 1314 (s), 1142 (s), 1079 (s), 995 (m), 777 (m), 561 (s) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%): 238 (M^+, 100), 174 (15), 172 (18), 132 (20), 131 (33), 118 (22), 105 (15), 91 (70), 65 (37); HRMS (ESI): calcd (%) for $C_{12}H_{14}O_3S$ ($[M+1]^+$) 238.06581, found 238.06582.

3.1.3. 2[((4-Chlorophenyl)sulfonyl)methylidene]tetrahydrofuran (2c). Starting with 1-(4-chlorophenyl)sulfonyl-2-propanone **1c** (1.50 g, 6.44 mmol) and 1-bromo-2-chloroethane (0.64 ml, 7.73 mmol), **2c** was isolated as a highly viscous colourless oil (668 mg, 40%, *E*/*Z*=6:4); ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.21–2.34 (m, 2×2H, CH_2, both isomers), 2.88 (dt, 2H, *J*=7.7 Hz, *J*=1.2 Hz, CH_2), 3.31 (dt, 2H, *J*=7.8 Hz, *J*=1.7 Hz, CH_2), 4.42 (t, 2H, *J*=7.0 Hz, CH_2), 4.58 (t, 2H, *J*=6.9 Hz, CH_2), 5.65 (t, 1H, *J*=1.1 Hz, C═C*H*, *Z*-isomer), 5.91 (t, 1H, *J*=1.7 Hz, C═C*H*, *E*-isomer), 7.64, 7.73 (2×d, 4H, *J*=8.7 Hz, *J*=8.5 Hz, ArH, both isomers), 7.98, 8.05 (2×d, 4H, *J*=8.7 Hz, *J*=9.1 Hz, ArH, both isomers); ^{13}C NMR (75 MHz, $CDCl_3$): δ=23.5, 24.1, 29.9, 32.2, 73.0, 75.5 (CH_2), 98.7, 99.8 (CH), 128.3 (2C, CH), 129.3 (2C, CH), 129.6 (2C, CH), 130.1 (2C, CH), 139.2, 139.4, 140.8, 142.2, 170.5, 174.7 (C); IR (neat): $\tilde{\nu}$ = 3090 (w), 2958 (m), 2933 (m), 1720 (m), 1627 (m), 1582 (m), 1394 (m),

1320 (s), 1155 (s), 1089 (s), 831 (m), 571 (m) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%): 258 (M^+, 100), 241 (5), 194 (25), 192 (19), 175 (11), 152 (31), 147 (29), 131 (35), 111 (56), 89 (36), 75 (44), 55 (37); HRMS (ESI): calcd (%) for $C_{11}H_{11}ClO_3S$ ($[M+1]^+$) 258.01082, found 258.01119.

3.2. General procedure for the reaction of 2-(alkylidene)tetrahydrofurans with boron tribromide or boron trichloride

To a CH_2Cl_2 solution (10 ml/mmol of substrate) of 2-(alkylidene)tetrahydrofuran (1.0 equiv) was added BBr_3 (4.0–8.0 equiv) at 0 °C. The reaction mixture was allowed to warm to 20 °C during 12 h and was stirred for 12 h at 20 °C. Water (15 ml/mmol of substrate) was slowly added to the reaction mixture and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (3×20 ml). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated in vacuo. The residue was purified by chromatography (silica gel, *n*-heptane/EtOAc).

3.2.1. 5-Bromo-1-(phenylsulfonyl)-2-pentanone (3a). Starting with **2a** (400 mg, 1.78 mmol) and BBr_3 (0.67 ml, 7.12 mmol), **3a** was isolated as a colourless solid (516 mg, 95%), mp 77 °C; ^1H NMR (300 MHz, $CDCl_3$): δ=2.30 (quint, 2H, *J*=6.6 Hz, CH_2), 3.09 (t, 2H, *J*=6.8 Hz, CH_2), 3.58 (t, 2H, *J*=6.4 Hz, CH_2), 4.37 (s, 1H, CH_2), 7.77 (m, 2H, ArH), 7.90 (m, 1H, ArH), 8.07 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=26.4, 32.9, 42.8, 67.4 (CH_2), 127.4 (2C, CH), 128.6 (2C, CH), 134.8 (CH), 139.0, 197.4 (C); IR (KBr): $\tilde{\nu}$ = 2973 (m), 2925 (m), 1716 (s), 1445 (m), 1321 (s), 1297 (s), 1153 (s), 1009 (w), 688 (m), 525 (m) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%): 306 (M^+, ^{81}Br, 0.30), 304 (M^+, ^{79}Br, 0.33), 242 (2), 240 (2), 198 (42), 151 (35), 149 (36), 141 (59), 77 (100), 51 (28), 41 (22); HRMS (ESI): calcd (%) for $C_{11}H_{13}BrO_3S$ ($[M+1]^+$, ^{81}Br) 303.97709, found 303.97763.

3.2.2. 5-Bromo-1-[(4-methylphenyl)sulfonyl]-2-pentanone (3b). Starting with **2b** (200 mg, 0.84 mmol) and BBr_3 (0.31 ml, 3.2 mmol), **3b** was isolated as a colourless solid (246 mg, 92%), mp 48 °C; ^1H NMR (300 MHz, $CDCl_3$): δ=2.04 (quint, 2H, *J*=6.4 Hz, CH_2), 2.38 (s, 3H, CH_3), 2.84 (t, 2H, *J*=6.8 Hz, CH_2), 3.33 (t, 2H, *J*=6.4 Hz, CH_2), 4.08 (s, 1H, CH_2), 7.29 (d, 2H, *J*=8.0 Hz, ArH), 7.69 (d, 2H, *J*=8.5 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=22.1 (CH_3), 26.4, 32.8, 42.8, 67.6 (CH_2), 128.6 (2C, CH), 130.4 (2C, CH), 136.1, 145.9, 197.5 (C); IR (KBr): $\tilde{\nu}$ = 3043 (w), 2920 (w), 1718 (s), 1405 (m), 1317 (s), 1149 (s), 1005 (w), 817 (m), 618 (w), 514 (m) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%): 320 (M^+, ^{81}Br, 0.40), 318 (M^+, ^{79}Br, 0.53), 256 (5), 254 (5), 238 (4), 212 (13), 155 (56), 151 (32), 149 (36), 148 (33), 91 (100), 65 (30), 41 (19); HRMS (ESI): calcd (%) for $C_{12}H_{15}BrO_3S$ ($[M+1]^+$, ^{81}Br) 317.99132, found 317.99198.

3.2.3. 5-Bromo-1-[(4-chlorophenyl)sulfonyl]-2-pentanone (3c). Starting with **2c** (274 mg, 1.05 mmol) and BBr_3 (0.39 ml, 4.2 mmol), **3c** was isolated as a colourless solid (234 mg, 65%), mp 68 °C; ^1H NMR (300 MHz, $CDCl_3$): δ=2.07 (quint, 2H, *J*=6.4 Hz, CH_2), 2.87 (t, 2H, *J*=6.8 Hz, CH_2), 3.35 (t, 2H, *J*=6.4 Hz, CH_2), 4.10 (s, 1H, CH_2), 7.48 (d, 2H, *J*=8.1 Hz, ArH), 7.77 (d, 2H, *J*=8.5 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=26.3, 32.7, 42.9, 67.2 (CH_2), 130.1 (2C, CH), 130.2 (2C, CH), 137.3, 141.7, 197.3 (C); IR (KBr): $\tilde{\nu}$ = 3090 (w), 2921 (w), 1717 (s), 1582 (m), 1322 (s), 1147 (s), 1088 (s), 827 (m), 530 (s), 460 (m) cm^{-1}; GC–MS (CI): *m/z* (%): 341 ($[M+1]^+$, ^{81}Br, 90), 339 ($[M+1]^+$, ^{79}Br, 86), 261 (40), 259 (100), 223 (5), 191 (13), 159 (5), 69 (8) (19); HRMS (CI): calcd (%) for $C_{11}H_{12}BrClO_3S$ ($[M+1]^+$, ^{81}Br) 338.94510, found 338.94518.

3.3. General procedure for the cyclization of 1,4-dibromo-2-butene with dianions

A THF solution of LDA (2.5 equiv) was prepared by addition of *n*-BuLi (1 ml, 2.5 mmol, 2.5 M solution in hexanes) to a THF solution (7 ml) of diisopropylamine (0.36 ml, 2.5 mmol) at 0 °C. After the solution was stirred for 30 min, 1-phenylsulfonyl-2-propanone (198 mg, 1.0 mmol) was added at 0 °C. After stirring for 45–60 min, to the solution was added a THF solution (4 ml) of 1,4-dibromo-2-butene (256 mg, 1.2 mmol) at −78 °C. The temperature was allowed to rise to 20 °C during 12–14 h, and the solution was stirred at 20 °C for 8–14 h. To the solution was added a diluted aqueous solution of HCl and the mixture was subsequently extracted with EtOAc (3×200 ml). The combined organic layers were dried and filtered, the solvent of the filtrate was removed in vacuo and the residue was purified by chromatography (silica gel, EtOAc/*n*-heptane).

3.3.1. 2-[(Phenylsulfonyl)methylidene]-5-vinyltetrahydrofuran (4a). Starting with 1-(4-methylphenyl)sulfonyl-2-propanone **1a** (2.00 g, 10.0 mmol) and 1,4-dibromo-2-butene (2.60 g, 12.1 mmol), **4a** was isolated as a highly viscous colourless oil (1.26 g, 50%, *E*/*Z*=6:4); ^1H NMR (300 MHz, $CDCl_3$): δ=1.85–2.05 (m, 2×1H, CH–CH_2, both isomers), 2.39–2.45 (m, 2×1H, CH–CH_2, both isomers), 2.83 (dt, 1H, *J*=6.9 Hz, *J*=1.1 Hz, CH_2–C), 3.43–3.46 (m, 1H, CH_2–C), 3.43–3.54, 3.71–3.77 (2×m, 2H, CH_2–C, *E*–*Z*), 4.95–5.02, 5.24–5.32 (2×m, 2H, C*H*–CH_2), 5.38–5.49 (m, 4H, CH_2=CH, both isomers), 5.66 (t, *J*=1.1 Hz, C=C*H*, *Z*-isomer), 5.93 (t, *J*=1.7 Hz, C=C*H*, *E*-isomer), 5.94–6.05 (m, 2H, CH_2=C*H*, both isomers), 7.64, 7.84 (m, 2×3H, ArH, both isomers), 8.01–8.17 (m, 2×2H, ArH, both isomers); ^{13}C NMR (75 MHz, $CDCl_3$): δ=26.1, 29.3, 29.8, 30.0 (CH_2), 85.1, 87.1, 99.5, 100.4 (CH), 116.5, 118.6 (CH_2), 126.8 (2C, CH), 127.7 (CH), 129.4 (2C, CH), 129.5 (2C, CH), 132.8, 135.3, 135.5 (CH), 143.8, 144.3, 169.1, 173.4 (C); IR (neat): $\tilde{\nu}$ = 3485 (w), 2985 (w), 2940 (w), 2210 (w), 1750 (m), 1627 (s), 1447 (m), 1308 (s), 1151 (s), 1083 (m), 589 (s) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%): 250 (M^+, 24), 183 (36), 141 (27), 125 (7), 109 (65), 91 (39), 77 (100), 67 (23), 51 (26); HRMS (ESI): calcd (%) for $C_{13}H_{14}O_3S$ ($[M+1]^+$) 250.06607, found 250.06582.

3.3.2. 2-[((4-Methylphenyl)sulfonyl)methylidene]-5-vinyltetrahydrofuran (4b). Starting with 1-(4-methylphenyl)sulfonyl-2-propanone **1b** (1.00 g, 4.71 mmol) and 1,4-dibromo-2-butene (1.30 g, 5.65 mmol), **4b** was isolated as a highly viscous colourless oil (475 mg, 38%, *E*/*Z*=6:4); ^1H NMR (300 MHz, $CDCl_3$): δ=1.66–1.78 (m, 2×1H, CH–CH_2, both isomers), 2.12–2.24 (m, 2×1H, CH–CH_2, both isomers), 2.33, 2.37 (2×s, 6H, CH_3), 2.59

(dt, 1H, J=7.9 Hz, J=1.8 Hz, CH_2–C), 2.87–2.99 (m, 1H, CH_2–C), 3.17–3.28, 3.46–3.50 (2×m, 2H, CH_2–C, *E*–*Z*), 4.69–4.77, 4.99–5.01 (2×m, 2H, C*H*–CH_2), 5.10–5.26 (m, 4H, CH_2=CH, both isomers), 5.40 (t, J=1.4 Hz, C=C*H*, *Z*-isomer), 5.68 (distorted t, J=1.9 Hz, C=C*H*, *E*-isomer), 5.71–5.78 (m, 2H, CH$_2$=C*H*, both isomers), 7.22, 7.28 (2×d, 4H, J=8.0 Hz, J=8.0 Hz, ArH, both isomers), 7.67, 7.78 (2×d, 4H, J=8.2 Hz, J=8.3 Hz, ArH, both isomers); ^{13}C NMR (75 MHz, $CDCl_3$): δ=21.9, 22.0 (CH_3), 29.3, 29.7, 30.0, 31.6 (CH_2), 85.0, 87.0, 99.7, 100.7 (CH), 117.7, 118.4 (CH_2), 126.8 (2C, CH), 127.7 (2C, CH), 129.5 (2C, CH), 129.9 (2C, CH), 135.3, 135.6 (CH), 141.0, 141.4, 143.5, 143.6, 169.0, 173.0 (C); IR (neat): $\tilde{\nu}$ = 3482 (w), 2983 (w), 2925 (w), 2211 (w), 1719 (m), 1628 (s), 1428 (m), 1317 (s), 1151 (s), 816 (m) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%): 264.1 (M$^+$, 27), 197 (28), 155 (23), 139.1 (8), 109.1 (50), 91.1 (100), 79.1 (20), 65.1 (23), 39.1 (11); HRMS (ESI): calcd (%) for $C_{14}H_{16}O_3S$ ([M+1]$^+$) 264.081655, found 264.08147.

3.3.3. 2-(*E*)-[((4-Chlorophenyl)sulfonyl)methylidene]-5-vinyltetrahydro-furan (4c). Starting with 1-(4-chlorophenyl)sulfonyl-2-propanone **1c** (1.00 g, 4.29 mmol) and 1,4-dibromo-2-butene (1.10 g, 5.15 mmol), **4c** was isolated as a highly viscous colourless oil (488 mg, 40%); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.73–1.85 (m, 1H, CH–CH_2), 2.16–2.27 (m, 1H, CH–CH_2), 2.89–2.95 (m, 1H, CH_2–C), 3.17–3.25 (m, 1H, CH_2–C), 4.73–4.80 (m, 1H, C*H*–CH_2), 5.16–5.27 (m, 2H, CH_2=CH), 5.67 (t, J=1.7 Hz, C=C*H*), 5.70–5.79 (m, 1H, CH$_2$=C*H*), 7.40 (d, 2H, J=8.7 Hz, ArH), 7.73 (d, 2H, J=8.7 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=29.9, 30.0 (CH_2), 85.3, 100.0 (CH), 118.7 (CH_2), 128.3 (2C, CH), 129.7 (2C, CH), 135.4 (CH), 139.3, 142.8, 173.9 (C); IR (neat): $\tilde{\nu}$ = 3088 (w), 3064 (w), 2946 (w), 1625 (s), 1582 (s), 1428 (m), 1319 (s), 1084 (s), 618 (s), 478 (s) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%): 284 (M, 38), 217 (45), 175 (51), 111 (88), 109 (100), 91 (59), 67 (34), 53 (19), 39 (17); elemental analysis: calcd (%) for $C_{13}H_{13}ClO_3S$ (208.0): C 54.83, H 4.60; found: C 54.82, H 4.77.

3.3.4. 7-Bromo-1-(phenylsulfonyl)-5-hepten-2-one (5a). Starting with **4a** (200 mg, 0.94 mmol) and BBr_3 (0.44 ml, 4.7 mmol), **5a** was isolated as a highly viscous colourless oil (234 mg, 75%); ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.26 (m, 2H, CH_2), 2.76 (t, 2H, J=7.0 Hz, CH_2), 3.83 (d, 2H, J=6.6 Hz, CH_2), 4.08 (s, 2H, CH_2), 5.63–5.66 (m, 2H, C*H*=C*H*), 7.49–7.55 (m, 2H, ArH), 7.60–7.63 (m, 1H, ArH), 7.80 (dd, 2H, J=7.0 Hz, 1.5 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=21.0, 25.8, 43.6, 67.3 (CH_2), 128.2 (CH), 128.6 (2C, CH), 129.8 (2C, CH), 133.8, 134.8 (CH), 139.0, 197.3 (C); IR (neat): $\tilde{\nu}$ = 3064 (m), 2991 (m), 2928 (s), 1731 (s), 1447 (s), 1309 (m), 1085 (s), 999 (m), 688 (m), 437 (w) cm^{-1}; GC–MS (CI): *m*/*z* (%): 333 ([M+H]$^+$, ^{81}Br, 7), 331 ([M+H]$^+$, ^{79}Br, 7), 253 (13), 252 (15), 251 (100), 143 (4), 127 (3), 111 (13), 109 (7), 79 (10), 71 (16), 69 (20); HRMS (CI): calcd (%) for $C_{13}H_{15}BrO_3S$ ([M+1]$^+$, ^{81}Br) 330.99857, found 330.99980.

3.3.5. 7-Bromo-1-[(4-methylphenyl)sulfonyl]-5-hepten-2-one (5b). Starting with **4b** (110 mg, 0.49 mmol) and BBr_3 (0.23 ml, 2.5 mmol), **5b** was isolated as a highly viscous colourless oil (109 mg, 75%); ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.27 (m, 2H, CH_2), 2.39 (s, 3H, CH_3), 2.76 (t, 2H, J=7.0 Hz, CH_2), 3.84 (distorted d, 2H, J=6.4 Hz, CH_2), 4.05 (s, 2H, CH_2), 5.63–5.66 (m, 2H, C*H*=C*H*), 7.30 (d, 2H, J=8.1 Hz, ArH), 7.66 (d, 2H, J=8.1 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=22.1 (CH_3), 25.8, 33.1, 43.6, 67.5 (CH_2), 128.2 (CH), 128.6 (2C, CH), 130.4 (2C, CH), 133.8 (CH), 136.0, 145.9, 197.5 (C); IR (neat): $\tilde{\nu}$ = 3031 (w), 2925 (m), 2210 (w), 1720 (s), 1320 (s), 1206 (m), 1152 (s), 815 (m), 733 (w), 515 (m) cm^{-1}; GC–MS (CI): *m*/*z* (%): 347 ([M+H]$^+$, ^{81}Br, 7), 345 ([M+H]$^+$, ^{79}Br, 7), 267 (6), 266 (13), 265 (100), 170 (2), 139 (3), 109 (4); elemental analysis: calcd (%) for $C_{14}H_{17}BrO_3S$ (345.25): C 48.70, H 4.96; found: C 48.19, H 4.98.

3.3.6. 7-Bromo-1-[(4-chlorophenyl)sulfonyl]-5-hepten-2-one (5c). Starting with **4c** (105 mg, 0.37 mmol) and BBr_3 (0.17 ml, 1.84 mmol), **5c** was isolated as a highly viscous colourless oil (95 mg, 70%); ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.56–2.56 (m, 2H, CH_2), 3.02 (t, 2H, J=7.0 Hz, CH_2), 4.10 (m, 2H, CH_2), 4.34 (s, 2H, CH_2), 5.90–5.93 (m, 2H, C*H*=C*H*), 7.75 (d, 2H, J=8.7 Hz, ArH), 8.01 (d, 2H, J=8.7 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=25.8, 33.0, 43.7, 67.1 (CH_2), 128.3 (CH), 130.1 (2C, CH), 130.2 (2C, CH), 133.6 (CH), 137.3, 141.6, 197.3 (C); IR (neat): $\tilde{\nu}$ = 3090 (w), 2927 (m), 2210 (w), 1721 (s), 1476 (s), 1154 (s), 969 (m), 815 (m), 763 (m), 469 (w) cm^{-1}; GC–MS (CI): *m*/*z* (%): 367 ([M+H]$^+$, ^{81}Br, 13), 465 ([M+H]$^+$, ^{79}Br, 10), 287 (39), 286 (14), 285 (100), 179 (2), 109 (6), 91 (3); HRMS (CI): calcd (%) for $C_{13}H_{14}BrClO_3S$ ([M+1]$^+$, ^{81}Br) 364.96221, found 364.96083.

3.4. 2-(*E*)(3-Phenyldihydro)-2(3*H*)-furanylidene-2-(2-methoxyphenyl)-4-phenylsulfone (8a)

Starting with 1-(2-methoxyphenyl)-1-(phenylsulfonyl)acetone **7a** (1.40 g, 4.6 mmol) and 1-bromo-2-chloroethane (0.45 ml, 5.5 mmol), **8a** (*E*-isomer) was isolated as a colourless solid (681 mg, 45%), mp 162 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.02–2.15 (m, 2H, CH_2), 3.28 (s, 3H, OCH_3), 3.31 (t, 2H, J=7.62 Hz, CH_2), 4.08 (t, 2H, J=7.05 Hz, CH_2), 6.61–6.90 (m, 2H, ArH), 7.13–7.31 (m, 4H, ArH), 7.36–7.242 (m, 1H, ArH), 7.54–7.57 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=24.8, 30.6 (CH_2), 55.5 (OCH_3), 72.5 (CH_2), 109.3 (C), 111.1, 120.7 (CH), 120.9 (C), 128.0 (2C, CH), 128.4 (2C, CH), 130.5, 132.4, 133.8 (CH), 142.8, 158.1, 169.8 (C); IR (KBr): $\tilde{\nu}$ = 3037 (w), 3031 (w), 2961 (w), 2842 (w), 1632 (s), 1595 (s), 1492 (s), 1376 (m), 1298 (s), 1239 (m), 1190 (s), 1054 (s), 896 (s), 750 (s), 544 (m) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%): 330 (M$^+$, 36), 189 (28), 131 (10), 91 (22), 77 (25), 71 (100), 43 (23); HRMS (ESI): calcd (%) for $C_{18}H_{18}SO_4$ ([M+1]$^+$) 330.09231, found 330.09180.

3.5. 2-(*Z*)(3-Phenyldihydro)-2(3*H*)-furanylidene-2-(2-methoxyphenyl)-4-phenylsulfone (8a)

^{1}H NMR (300 MHz, $CDCl_3$): δ=1.81–1.93 (m, 2H, CH_2), 2.27–2.432 (m, 2H, CH_2), 3.56 (s, 3H, OCH_3), 4.29–4.38 (m, 2H, CH_2), 6.71–6.91 (m, 2H, ArH), 7.12–7.24 (m, 2H, ArH), 7.31–7.28 (m, 3H, ArH), 7.85 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=23.3–31.8 (CH_2), 55.6 (OCH_3), 75.1 (CH_2), 108.0 (C), 111.3, 121.0 (CH), 122.5 (C), 128.2 (2C, CH), 128.5 (2C, CH), 130.6, 132.4, 133.9

(CH), 143.8, 158.1, 167.0 (C); IR (KBr): $\tilde{\nu}$ = 3064 (w), 2964 (w), 2904 (w), 2837 (w), 1723 (w), 1634 (s), 1595 (s), 1491 (m), 1446 (s), 1302 (s), 1141 (s), 1117 (m), 1084 (m), 1025 (m), 985 (m), 756 (s), 533 (m) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%): 330 (M^+, 28), 189 (27), 131 (10), 105 (9), 91 (24), 77 (26), 71 (100), 43 (25); HRMS (ESI): calcd (%) for $C_{18}H_{18}SO_4$ ([M+1]$^+$) 330.0923, found 330.09180.

3.6. 2-(*E*)(3-Phenyldihydro)-2(3*H*)-furanylidene-2-(2-methoxyphenyl)-(4-methylphenyl)sulfone (8b)

Starting with 1-(2-methoxyphenyl)-1-(4-methylphenylsulfonyl)acetone **7b** (1.20 g, 3.77 mmol) and 1-bromo-2-chloroethane (0.37 ml, 4.52 mmol), **8b** was isolated as a colourless solid (710 mg, 55%), mp 132 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.82–1.93 (m, 2H, CH_2), 2.30 (t, 2H, *J*=5 Hz, CH_2), 3.58 (s, 3H, OCH_3), 4.01–4.09 (m, 2H, CH_2), 6.76–7.88 (m, 2H, ArH), 7.13–7.19 (m, 3H, ArH), 7.20–7.26 (m, 1H, ArH), 7.71–7.74 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=21.9 (CH_3), 23.3, 31.8 (CH_2), 55.6 (OCH_3), 75.0 (CH_2), 108.0 (C), 111.3, 120.9 (CH), 122.9 (C), 128.2 (2C, CH), 129.1 (2C, CH), 130.5, 133.9 (CH), 141.0, 143.0, 158.5, 167.4 (C); IR (KBr): $\tilde{\nu}$ = 2970 (w), 2904 (w), 1634 (s), 1595 (m), 1491 (m), 1437 (s), 1306 (s), 1297 (s), 1139 (s), 1083 (m), 989 (m), 681 (m), 583 (s) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%): 344 (M^+, 52), 208 (6), 189 (31), 91 (26), 71 (100), 43 (24); HRMS (ESI): calcd (%) for $C_{19}H_{20}SO_4$ ([M+1]$^+$) 344.10768, found 344.107526.

3.7. 2-(3-Phenyldihydro)-2(3*H*)-furanylidene-2-(2-methoxyphenyl)-(4-chlorophenyl)sulfone (8c)

Starting with 1-(2-methoxyphenyl)-1-(4-chlorophenylsulfonyl)acetone (**7c**) (3.49 g, 10.32 mmol) and 1-bromo-2-chloroethane (1.0 ml, 12.38 mmol), **8c** (*E*-isomer) was isolated as a colourless oil (1.84 g, 49%) and **8c** (*Z*-isomer) was isolated as a colourless solid, mp 144 °C. *E-isomer*: ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.07 (m, 2H, CH_2), 3.28 (t, 2H, *J*=6.48 Hz, CH_2), 3.32 (s, 3H, OCH_3), 4.07 (t, 2H, *J*=7.44 Hz, CH_2), 6.62–6.88 (m, 2H, ArH), 7.14–7.26 (m, 4H, ArH), 7.44–7.49 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=23.02, 27.4 (CH_2), 55.5 (OCH_3), 72.6 (CH_2), 110.4 (C), 111.7, 120.8 (CH), 122.9 (C), 128.6 (2C, CH), 129.5 (2C, CH), 133.8, 138.9 (CH), 140.5, 142.9, 159.1, 171.8 (C); IR (KBr): $\tilde{\nu}$ = 3095 (w), 3081 (w), 2957 (w), 2902 (w), 1631 (s), 1594 (s), 1594 (m), 1490 (m), 1463 (m), 1306 (s), 1253 (s), 1239 (s), 1148 (s), 1052 (s), 899 (s), 761 (m), 616 (m), 599 (s) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%): 364 (M^+, 28), 189 (28), 161 (16), 131 (10), 91 (23), 71 (100), 43 (21); HRMS (ESI): calcd (%) for $C_{18}H_{17}ClSO_4$ ([M+1]$^+$) 364.05306, found 364.052826. *Z-isomer*: ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.84–1.97 (m, 2H, CH_2), 2.31–2.38 (m, 2H, CH_2), 3.60 (s, 3H, OCH_3), 4.31–4.40 (m, 2H, CH_2), 6.68–6.93 (m, 2H, ArH), 7.14–7.35 (m, 4H, ArH), 7.76–7.81 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=20.8, 23.3 (CH_2), 55.6 (OCH_3), 75.2 (CH_2), 108.4 (C), 111.3, 121.1 (CH), 122.2 (C), 128.6 (2C, CH), 129.9 (2C, CH), 131.3, 138.9 (CH), 138.5, 143.3, 158.3, 168.2 (C); IR (KBr): $\tilde{\nu}$ = 3080 (w), 3050 (w), 2951 (m), 2804 (m), 1631 (s), 1594 (m), 1585 (m), 1490 (s), 1463 (s), 1304 (s), 1253 (m), 1232 (s), 1144 (m), 1052 (s), 899 (m), 762 (s), 616 (s), 591 (s) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%): 364 (M^+, 24), 189 (28), 161 (7), 131 (10), 111 (10), 91 (23), 71 (100), 43 (22); HRMS (ESI): calcd (%) for $C_{18}H_{17}ClSO_4$ ([M+1]$^+$) 364.05306, found 364.05463.

3.8. (2-Methoxyphenyl)-[3-methyldihydo-2(3*H*)-furanylidene]methyl-phenylsulfone (8d)

Starting with 1-(2-methoxyphenyl)-1-(phenylsulfonyl)-2-butanone **7d** (500 mg, 1.5 mmol) and 1-bromo-2-chloroethane (0.15 ml, 1.8 mmol), **8d** was isolated as a colourless oil (248 mg, 46%, *E*/*Z*=8:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.70 (t, 3H, $J_{(Z)}$=5.25 Hz, CH_3), 0.79 (t, 3H, $J_{(E)}$=7.25 Hz, CH_3), 1.52–1.62 (m, 2×1H, CH_2, *Z*-isomer), 1.99–2.15 (m, 2×1H, CH_2, *E*-isomer), 2.25–2.67 (m, 2×1H, CH_2, *Z*-isomer), 2.70–2.81 (m, 2×1H, CH_2, *E*-isomer), 3.49 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 4.24–4.39 (m, 2×2H, CH, both isomers), 6.72–7.02 (m, 5H, ArH both isomers), 7.21–7.47 (m, 4×2H, ArH, both isomers), 7.77–7.83 (m, 2×1H, ArH, *Z*-isomer), 7.88–7.92 (m, 2×1H ArH, *E*-isomer); ^{13}C NMR (75 MHz, $CDCl_3$): δ=16.8, 18.2 (CH_3), 31.8, 31.9 (CH_2), 38.1, 38.9 (CH), 55.6 (OCH_3), 72.6 (CH_2), 110.0 (C), 111.2, 120.6, 121.0 (CH), 122.4 (C), 128.2 (2C, CH), 128.5 (2C, CH), 130.6, 130.9, 133.4, 133.5 (CH), 143.7, 144.0, 158.0, 159.7, 170.5, 171.8 (C); IR (KBr): $\tilde{\nu}$ = 3065 (w), 2968 (m), 2907 (m), 2934 (m), 1719 (m), 1633 (m), 1491 (s), 1447 (s), 1302 (s), 1290 (s), 1253 (s), 1145 (s), 1024 (s), 975 (w), 688 (s), 529 (m) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%): 340 (M^+, 27), 203 (100), 173 (15), 131 (14), 91 (42), 77 (33), 43 (27); HRMS (ESI): calcd (%) for $C_{19}H_{20}O_4S$ ([M+1]$^+$) 340.10768, found 340.10798.

3.9. 2-(3-Bromopropyl)-3-(phenylsulfonyl)-benzofuran (9a)

Starting with **8a** (148 mg, 0.44 mmol) and BBr_3 (0.21 ml, 2.24 mmol), **9a** was isolated as a colourless solid (122 mg, 72%), mp 92 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.62 (quint, 2H, *J*=6.6 Hz, CH_2), 3.65 (t, 2H, *J*=7.4 Hz, CH_2), 3.76 (t, 2H, *J*=6.4 Hz, C*H*$_2$–Br), 7.60 (m, 2H, ArH), 7.70 (m, 1H, ArH), 7.75–7.87 (m, 3H, ArH), 8.16 (m, 1H, ArH), 7.89 (dd, 2H, *J*=8.17 Hz, 1.5 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=26.6, 31.3, 32.6 (CH_2), 111.8 (CH), 118.7 (C), 120.8 (CH), 124.5 (C), 124.9 (CH), 125.9 (2C, CH), 127.1 (2C, CH), 129.7, 133.8 (CH), 142.7, 153.7, 162.7 (C); IR (KBr): $\tilde{\nu}$ = 3058 (w), 2927 (w), 1569 (s), 1451 (s), 1327 (s), 1111 (m), 1011 (w), 752 (s), 688 (s), 599 (s), 551 (s) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%): 380 (M^+, ^{81}Br, 100), 78 (M^+, ^{79}Br, 93), 330 (12), 299 (26), 237 (6), 272 (34), 181 (8), 158 (17), 131 (34), 69 (30), 43 (24); HRMS (ESI): calcd (%) for $C_{!7}H_{15}BrO_3S$ ([M+1]$^+$, ^{81}Br) 377.99143, found 377.99198.

3.10. 2-(3-Bromopropyl)-3-[(4-methylphenyl)sulfonyl]-benzofuran (9b)

Starting with **8b** (110 mg, 0.31 mmol) and BBr_3 (0.15 ml, 1.5 mmol), **9b** was isolated as a highly viscous colourless oil (77 mg, 61%); ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.26 (quint, 2H, *J*=6.5 Hz, CH_2), 2.31 (s, 3H, CH_3), 3.30 (t, 2H, *J*=7.2 Hz, CH_2), 3.42 (t, 2H, *J*=6.6 Hz, C*H*$_2$–Br), 7.22–7.27 (m, 4H, ArH), 7.34–7.37 (m, 1H, ArH), 7.80–7.86 (m, 3H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=20.5

(CH_3), 25.1, 29.9, 31.2 (CH_2), 110.3 (CH), 117.6 (C), 119.4 (CH), 123.1 (C), 123.4, 124.4, 125.7, 128.9 (CH), 138.4, 143.3, 152.3, 160 (C); IR (neat): $\tilde{\nu}=3433$ (m), 2984 (w), 2954 (m), 1595 (s), 1474 (s), 1326 (s), 1302 (s), 1255 (s), 1090 (m), 1050 (m), 815 (m), 749 (s), 719 (s), 673 (s), 643 (m), 585 (m), 535 (s) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%): 394 (M^+, ^{81}Br, 100), 392 (M^+, ^{79}Br, 95), 286 (35), 267 (9.07), 205 (14), 158 (19), 131 (41), 102 (28), 65 (16), 39 (7); HRMS (ESI): calcd (%) for $C_{18}H_{17}BrO_3S$ ($[M+1]^+$, ^{81}Br) 392.0.00763, found 392.0.00788.

3.11. 2-(3-Bromopropyl)-3-[(4-chlorophenyl)sulfonyl]-benzofuran (9c)

Starting with **8c** (663 mg, 1.8 mmol) and BBr_3 (0.86 ml, 9.1 mmol), **9c** was isolated as a colourless solid (515 mg, 68%), mp 116 °C; ^1H NMR (300 MHz, $CDCl_3$): δ=2.28 (quint, 2H, *J*=6.6 Hz, CH_2), 3.31 (t, 2H, *J*=7.4 Hz, CH_2), 3.43 (t, 2H, *J*=6.4 Hz, C*H*$_2$–Br), 7.26 (m, 2H, ArH), 7.36–7.42 (m, 3H, ArH), 7.79 (m, 1H, ArH), 7.89 (d, 2H, *J*=8.17 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=26.6, 31.2, 32.6 (CH_2), 111.9 (CH), 118.4 (C), 120.7 (CH), 124.3 (C), 125.0, 126.1 (CH), 128.6 (2C, CH), 130.0 (2C, CH), 140.4, 141.1, 153.7, 162.9 (C); IR (KBr): $\tilde{\nu}=3083$ (w), 3059 (w), 1575 (s), 1452 (s), 1157 (s), 1085 (s), 829 (m), 760 (s), 658 (s), 567 (s), 479 (w) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%): 414 (M^+, ^{81}Br, 100), 412 (M^+, ^{79}Br, 75), 306 (27), 305 (22), 237 (6), 205 (17), 159 (41), 131 (53), 102 (35), 75 (20); HRMS (ESI): calcd (%) for $C_{17}H_{14}BrClO_3S$ ($[M+1]^+$, ^{81}Br) 412.96127, found 412.96083.

3.12. 2-(3-Bromo-1-methylpropyl)-3-(phenylsulfonyl)-benzofuran (9d)

Starting with **8d** (90 mg, 0.26 mmol) and BBr_3 (0.12 ml, 1.3 mmol), **9d** was isolated as a highly viscous colourless oil (65 mg, 63%); ^1H NMR (300 MHz, $CDCl_3$): δ=1.30 (d, 3H, *J*=6.8 Hz, CH_3), 2.10–2.19 (m, 1H, CH–C*H*$_2$), 2.30–2.38 (m, 1H, CH–C*H*$_2$), 3.19–3.25 (m, 2H, C*H*$_2$–Br), 4.02–4.09 (m, 1H, CH_3–C*H*), 7.24–7.28 (m, 2H, ArH), 7.35–7.38 (m, 1H, ArH), 7.42–7.52 (m, 3H, ArH), 7.86–7.90 (m, 1H, ArH), 7.96–8.01 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=19.5 (CH_3), 30.6 (CH_2), 31.8 (CH), 38.0 (CH_2), 111.8 (CH), 118.4 (C), 121.1 (CH), 124.5 (C), 124.9 (CH), 125.9 (2C, CH), 127.1 (2C, CH), 129.7, 133.7 (CH), 142.8, 153.6, 165.8 (C); IR (KBr): $\tilde{\nu}=2974$ (w), 2921 (s), 2847 (w), 1567 (s), 1473 (s), 1251 (s), 1091 (s), 928 (w), 754 (s), 645 (m), 554 (s) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%): 394.1 (M^+, ^{81}Br, 47), 392.1 (M^+, ^{79}Br, 45), 285 (100), 233 (4), 156 (9), 144.1 (37), 128.1 (13), 115.1 (34), 89.1 (5), 77.1 (18), 51.1 (8); HRMS (ESI): calcd (%) for $C_{18}H_{17}BrO_3S$ ($[M+1]^+$, ^{81}Br) 392.00756, found 392.00763.

3.13. 2-(3-Hydroxypropyl)-3-(phenylsulfonyl)-benzofuran (9e)

Starting with **8a** (227 mg, 0.68 mmol) and BCl_3 (0.53 ml, 3.4 mmol), **9e** was isolated as a highly viscous colourless oil (87 mg, 40%); ^1H NMR (300 MHz, $CDCl_3$): δ=1.99 (quint, 2H, *J*=6.4 Hz, CH_2), 3.24 (t, 2H, *J*=7.2 Hz, CH_2), 3.63 (t, 2H, *J*=6.0 Hz, C*H*$_2$–OH), 7.23–7.27 (m, 2H, ArH), 7.36–7.38 (m, 1H, ArH), 7.40–7.53 (m, 3H, ArH), 7.81–7.84 (m, 1H, ArH), 7.94 (dd, 2H, *J*=8.0 Hz, 1.7 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=24.0, 31.2, 61.2 (CH_2), 111.7 (CH), 118.7 (C), 120.8 (CH), 124.5 (C), 124.8, 125.8 (CH), 127.0 (2C, CH), 129.7 (2C, CH), 133.8 (CH), 142.6, 153.7, 163.9 (C); IR (KBr): $\tilde{\nu}=2929$ (s), 2851 (w), 1711 (w), 1568 (s), 1448 (s), 1156 (s), 999 (m), 753 (s), 648 (s), 533 (s), 437 (w) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%): 316.1 (M^+, 35), 298.1 (40), 233.1 (12), 219.1 (24), 175.1 (100), 158.1 (15), 145.1 (21), 133 (48), 131.1 (64), 115.1 (50), 77.1 (48); HRMS (ESI): calcd (%) for $C_{17}H_{16}O_4S$ ($[M+1]^+$) 316.07716, found 316.07638.

3.14. 2-(3-Hydroxypropyl)-3-[(4-methylphenyl)sulfonyl]-benzofuran (9f)

Starting with **8b** (335 mg, 0.97 mmol) and BCl_3 (0.77 ml, 4.8 mmol), **9f** was isolated as a highly viscous colourless oil (108 mg, 34%); ^1H NMR (300 MHz, $CDCl_3$): δ=1.99 (quint, 2H, *J*=6.8 Hz, CH_2), 2.32 (s, 3H, CH_3), 3.24 (t, 2H, *J*=7.0 Hz, CH_2), 3.63 (t, 2H, *J*=5.9 Hz, C*H*$_2$–OH), 7.21–7.27 (m, 5H, ArH), 7.34–7.37 (m, 1H, ArH), 7.83 (d, 2H, *J*=8.1 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=21.9 (CH_3), 23.9, 31.2, 61.2 (CH_2), 111.7 (CH), 119.1 (C), 120.8 (CH), 124.6 (C), 124.8 (CH), 125.8 (2C, CH), 127.1 (2C, CH), 130.3 (CH), 139.7, 144.8, 153.7, 163.5 (C); IR (Nujol): $\tilde{\nu}=3420$ (w), 1717 (m), 1597 (s), 1331 (s), 1154 (s), 1036 (s), 813 (m), 750 (s), 674 (s), 585 (s), 537 (s) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%): 330.1 (M^+, 20), 281.1 (4), 207.1 (30), 175.1 (100), 131.1 (55), 115.1 (29), 91.1 (33), 65 (15), 39 (5); HRMS (ESI): calcd (%) for $C_{18}H_{18}O_4S$ ($[M+1]^+$) 330.09203, found 330.09203.

3.15. 2-(3-Hydroxypropyl)-3-[(4-chlorophenyl)sulfonyl]-benzofuran (9g)

Starting with **8c** (663 mg, 1.8 mmol) and BCl_3 (3.4 ml, 21.6 mmol), **9g** was isolated as a highly viscous colourless oil (300 mg, 47%); ^1H NMR (300 MHz, $CDCl_3$): δ=1.94–2.03 (m, 2H, *J*=6.8 Hz, CH_2), 3.23 (t, 2H, *J*=7.2 Hz, CH_2), 3.63 (t, 2H, *J*=5.9 Hz, C*H*$_2$–OH), 7.24–7.27 (m, 2H, ArH), 7.35–7.37 (m, 1H, ArH), 7.39 (d, 2H, *J*=8.7 Hz, ArH), 7.77–7.80 (m, 1H, ArH), 7.87 (d, 2H, *J*=8.7 Hz, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=42.0, 31.1, 61.3 (CH_2), 111.8 (CH), 118.4 (C), 120.6 (CH), 124.3 (C), 125.0, 126.0 (CH), 128.5 (2C, CH), 130.0 (2C, CH), 140.4, 141.1, 153.8, 164.2 (C); IR (neat): $\tilde{\nu}=3404$ (w), 2932 (w), 2876 (w), 1573 (s), 1452 (s), 1155 (s), 759 (s), 619 (s), 567 (m), 480 (m) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%): 350 (M^+, 13), 332 (16), 288 (5), 218 (21), 175 (100), 156 (11), 144 (26), 131 (61), 115 (42), 75 (15); HRMS (ESI): calcd (%) for $C_{17}H_{15}ClO_4S$ ($[M+1]^+$) 350.03687, found 350.03741.

3.16. 2-(Cyanomethylidene)tetrahydrofuran (11)

The synthesis of **11** has been previously reported.[11a] Starting with 5-methylisoxazole (3 ml, 36.82 mmol) and 1-bromo-2-chloroethane (3.7 ml, 44.18 mmol), **11** (*E*-isomer) was isolated as a colourless oil (1.61 g, 41%) and **11** (*Z*-isomer) was isolated as a colourless oil (1.56 g, 40%). *E-isomer*: ^1H NMR (300 MHz, $CDCl_3$): δ=2.08 (quint, 2H, *J*=7.0 Hz, CH_2), 2.81 (t, 2H, *J*=7.0 Hz, CH_2), 4.26 (t, 2H, *J*=7.0 Hz, CH_2), 4.50 (s, 1H, C*H*CN); ^{13}C NMR (75 MHz,

$CDCl_3$): δ=24.1, 30.6 (CH_2), 67.6 (*C*HCN), 74.6 (CH_2), 118.8 (CN), 178.0 (C); IR (neat): $\tilde{\nu}$ = 3086 (w), 2913 (s), 2211 (s), 1734 (w), 1429 (m), 1391 (s), 1186 (m), 1003 (s), 930 (m), 725 (m) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%): 109 (M^+, 82), 80 (7), 68 (100), 52 (14), 42 (68), 38 (6); HRMS (ESI): calcd (%) for C_6H_7NO ($[M+1]^+$) 109.05188, found 109.05222. *Z-isomer*: ^1H NMR (300 MHz, $CDCl_3$): δ=2.36 (quint, 2H, *J*=7.0 Hz, CH_2), 2.90 (t, 2H, *J*=6.6 Hz, CH_2), 4.47 (s, 1H, C*H*CN), 4.59 (t, 2H, *J*=6.8 Hz, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ=24.3, 31.2 (CH_2), 65.2 (*C*HCN), 74.4 (CH_2), 117.2 (CN), 177.6 (C); IR (neat): $\tilde{\nu}$ = 3086 (w), 2954 (m), 2854 (w), 1652 (s), 1458 (m), 1391 (s), 1186 (m), 1003 (s), 930 (m), 725 (m) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%): 109 (M^+, 75), 80 (5), 68 (100), 52 (13), 42 (71), 29 (3); HRMS (ESI): calcd (%) for C_6H_7NO ($[M+1]^+$) 109.05214, found 109.05222.

3.17. 5-Bromo-1-cyano-3-oxopentane (12)

Starting with **11** (363 mg, 3.33 mmol) and BBr_3 (2.51 ml, 26.64 mmol), **12** was isolated as a colourless solid (538 mg, 85%), mp 71 °C; ^1H NMR (300 MHz, $CDCl_3$): δ=2.40 (quint, 2H, *J*=6.4 Hz, CH_2), 3.05 (t, 2H, *J*=6.8 Hz, CH_2), 3.68 (t, 2H, *J*=6.2 Hz, CH_2), 3.74 (s, 1H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ=26.2, 32.6, 32.8, 40.5 (CH_2), 113.9 (CN), 196.8 (C); IR (KBr): $\tilde{\nu}$ = 2951 (m), 2920 (m), 2258 (w), 1719 (s), 1642 (m), 1405 (s), 1392 (s), 1328 (s), 977 (m), 581 (m) cm^{-1}; GC–MS (CI): *m*/*z* (%): 192 ($[M+H]^+$, ^{81}Br, 48), 190 ($[M+H]^+$, ^{79}Br, 59), 151 (9), 149 (9), 110 (100); elemental analysis: calcd (%) for C_6H_8BrNO (190): C 37.92, H 4.24; found: C 38.14, H 4.18.

3.18. 2-(Cyanomethylidene)-5-vinyltetrahydrofuran (13)

The synthesis of **13** has been previously reported.[11a] Starting with 5-methylisoxazole (3 ml, 36.82 mmol) and 1,4-dibromo-2-butene (9.45 g, 44.18 mmol), **13** (*E*-isomer) was isolated as a colourless oil (1.96 g, 40%) and **13** (*Z*-isomer) was isolated as a colourless oil (1.77 g, 36%). *E-isomer*: ^1H NMR (300 MHz, $CDCl_3$): δ=1.78–1.98 (m, 1H, CH–CH_2), 2.19–2.24 (m, 1H, CH–CH_2), 2.75–2.91 (m, 2H, CH_2), 4.57 (t, 1H, *J*=1.5 Hz, C*H*CN), 4.84–4.90 (m, 1H, C*H*–CH_2), 5.18–5.32 (m, 2H, CH_2=CH), 5.72–5.83 (m, 1H, CH_2=C*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ=30.0, 30.6 (CH_2), 68.2, 86.8 (CH), 118.5 (CH_2), 119.0 (CN), 135.4 (CH), 178.2 (C); IR (neat): $\tilde{\nu}$ = 3073 (w), 2988 (w), 2211 (s), 1641 (s), 1430 (m), 1217 (s), 1179 (s), 989 (m), 877 (m), 763 (m) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%): 135 (M^+, 90), 134 (91), 120 (49), 106 (49), 92 (21), 79 (37), 67 (100), 53 (50), 39 (53); HRMS (ESI): calcd (%) for C_8H_9NO ($[M+1]^+$) 135.06802, found 135.06787. *Z-isomer*: ^1H NMR (300 MHz, $CDCl_3$): δ=1.82–1.86 (m, 1H, CH–CH_2), 2.10–2.22 (m, 1H, CH–CH_2), 2.58–2.64 (m, 2H, CH_2), 4.19 (s, 1H, CHCN), 4.89–4.96 (m, 1H, CH–CH_2), 5.18–5.33 (m, 2H, CH_2=CH), 5.75–5.86 (m, 1H, CH_2=CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=30.2, 31.0 (CH_2), 65.8, 86.4 (CH), 116.9 (CN), 118.3 (CH_2), 135.4 (CH), 176.4 (C); IR (neat): $\tilde{\nu}$ = 3085 (w), 2942 (w), 2212 (s), 1652 (s), 1430 (m), 1364 (m), 1187 (m), 989 (m), 934 (m), 730 (w) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%): 135.1 (M^+, 83), 134.1 (92), 120.1 (51), 116.1 (10), 106.2 (42), 92.2 (21), 80.2 (34), 79.2 (39), 67.2 (100), 65.2 (19), 53.2 (52), 39.2 (51); HRMS (ESI): calcd (%) for C_8H_9NO ($[M+1]^+$) 135.06767, found 135.06787.

3.19. 6,7,8-Tribromo-1-cyano-3-oxoheptane (14)

Starting with **13** (153 mg, 1.13 mmol) and BBr_3 (0.85 ml, 9.04 mmol), **14** was isolated as a highly viscous colourless oil (296 mg, 70%); ^1H NMR (300 MHz, $CDCl_3$): δ=2.10–2.16 (m, 1H, Br–CH–XH_2), 2.43–2.48 (m, 1H, Br–CH–CH_2), 2.81–2.84 (m, 2H, CH_2CO), 3.45 (s, 2H, CH_2CN), 3.75–3.84 (m, 1H, Br–CH_2), 3.99–4.05 (m, 1H, Br–CH_2), 4.29–4.38 (m, 2H, Br–CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=29.7, 32.5, 37.0, 40.1 (CH_2), 54.5, 55.5 (CH), 113.7 (CN), 196.3 (C); IR (neat): $\tilde{\nu}$ = 2951 (m), 2914 (m), 2260 (w), 1731 (s), 1403 (m), 1307 (m), 1185 (w), 1082 (m), 617 (w), 557 (w) cm^{-1}; GC–MS (CI): *m*/*z* (%): 378 ($[M+H]^+$, ^{81}Br, 42), 376 ($[M+H]^+$, ^{79}Br, 43), 337 (9), 335 (9), 298 (95), 296 (72), 257 (20), 255 (11), 218 (85), 216 (100), 136 (86), 95 (10), 67 (15); HRMS (CI): calcd (%) for $C_8H_{10}Br_3NO$ ($[M+1]^+$, ^{81}Br) 373.83837, found 373.83853.

3.20. 2-Dihydro-2(3*H*)-furanylidene-2-(2-methoxyphenyl)acetonitrile (16)

Starting with 2-(2-methoxyphenyl)-3-oxobutanenitrile **15** (1.20 g, 6.38 mmol) and 1-bromo-2-chloroethane (0.58 ml, 7.1 mmol), **16** was isolated as a colourless solid (1.00 g, 72%, *Z*/*E*=8:1), mp 54 °C; ^1H NMR (300 MHz, $CDCl_3$): δ=2.15–2.21 (m, 2H, CH_2, *Z*-isomer), 2.27–2.36 (m, 2H, CH_2, *E*-isomer), 2.74, 3.20 (2×t, 4H, $J_{(Z)}$=7.8 Hz, $J_{(E)}$=7.8 Hz, CH_2), 3.97 (s, 3H, OCH_3), 3.99 (s, 3H, OCH_3), 4.45–4.57 (m, 2×2H, CH_2, both isomers), 7.06 (dd, 1H, *J*=8.9 Hz, 7.8 Hz, ArH), 7.29 (dd, 1H, *J*=5.91 Hz, 1.5 Hz, ArH), 7.37–7.49 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=24.1, 24.5, 30.2, 30.8 (CH_2), 55.9, 56.0 (CH_3), 73.9, 75.0 (CH_2), 77.1, 78.9, 109.0 (C), 111.0 (CH), 116.0 (CN), 120.7, 129.6, 131.4 (CH), 154.6, 155.0, 170.8, 172.5 (C); IR (KBr): $\tilde{\nu}$ = 3441 (w), 2963 (w), 2935 (w), 2205 (s), 1628 (s), 1578 (m), 1462 (m), 1265 (s), 1184 (s), 762 (s), 656 (w) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%): 215 (M^+, 100), 184 (15), 158 (22), 144 (29), 115 (18), 84 (52), 75 (10); HRMS (ESI): calcd (%) for $C_{13}H_{13}NO_2$ ($[M+1]^+$) 215.09408, found 215.09436.

3.21. 2-(3-Bromopropyl)-benzofuran-3-carboxylic acid (17)

Starting with **16** (600 mg, 2.7 mmol), BBr_3 (1.5 ml, 16.7 mmol) and HBr (0.7 ml, 16.7 mmol), **17** was isolated as a highly viscous colourless oil (322 mg, 41%); ^1H NMR (250 MHz, $CDCl_3$): δ=1.92–2.02 (m, 2H, CH_2), 2.91 (t, 2H, *J*=8.04 Hz, CH_2), 3.70 (t, 2H, *J*=6.98 Hz, CH_2), 6.98–7.19 (m, 3H, ArH), 7.36–7.42 (m, 4H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=25.6, 37.9, 61.7 (CH_2), 93.8 (C), 190.2, 117.7, 120.8, 123.2 (CH), 125.0, 148.2, 164.2, 194.6 (C); IR (KBr): $\tilde{\nu}$ = 3385 (s), 3273 (m), 3064 (w), 2924 (s), 2854 (m), 1653 (s), 1493 (s), 1459 (m), 1243 (w), 1173 (m), 1019 (m), 743 (m) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%): 281 (M^+, 25), 201 (100), 175 (20), 160 (80), 103 (10), 82 (12); HRMS (ESI): calcd (%) for $C_{12}H_{11}BrO_3$ ($[M+1]^+$) 281.52341, found 281.53216.

3.22. 2-(5-Vinyldihydro)-2(3*H*)-furanylidene-2-(2-methoxyphenyl)-acetonitrile (18)

Starting with 2-(2-methoxyphenyl)-3-oxobutanenitrile **15** (1.30 g, 6.8 mmol) and 1,4-dibromo-2-butene (1.60 g, 7.5 mmol), **18** was isolated as a colourless oil (622 mg, 37%, *Z*/*E*=8:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.51–2.69 (m, 2×2H, CH_2, both isomers), 2.99 (t, 2H, J=7.6 Hz, CH_2), 4.18 (s, 3H, OCH_3), 4.20 (s, 3H, OCH_3), 5.27–5.40 (m, 1H, CH), 5.60 (d, 2×1H, J=13.1 Hz, CH_2), 5.67 (d, 2×1H, J=17.1 Hz, CH_2), 6.18–6.33 (m, 2×1H, CH, both isomers), 7.18–7.35 (m, 2H, ArH), 7.51–7.81 (m, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=30.0, 31.6 (CH_2), 56.0 (OCH_3), 81.5 (C), 86.0, 87.2 (CH), 111.0 (CH), 116.0 (CN), 118.1 (CH_2), 119.4 (C), 120.8, 121.8, 128.9, 129.6, 131.5, 135.8 (CH), 156.9, 172.3, 173.9 (C); IR (KBr): $\tilde{\nu}$ = 2936 (m), 2839 (w), 2207 (m), 1731 (m), 1635 (s), 1595 (m), 1580 (w), 1464 (s), 1262 (s), 996 (s), 757 (m) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%): 241 (M^+, 100), 210 (39), 184 (15), 173 (49), 158 (21), 115 (28), 67 (23); HRMS (ESI): calcd (%) for $C_{15}H_{15}NO_2$ ([M+1]$^+$) 241.10983, found 241.10973.

3.23. 2-(3-Bromo-4-pentenyl)-benzofuran-3-carboxylic acid (19)

Starting with **18** (502 mg, 2.07 mmol), BBr_3 (1.17 ml, 12.44 mmol) and HBr (0.58 ml, 12.44 mmol), **19** was isolated as a colourless solid (375 mg, 58%), mp 112 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.84–2.09 (m, 2H, CH_2), 287 (t, 2H, J=8.4 Hz, CH_2), 4.20 (m, 1H, CH), 5.07 (d, 1H, J=13.4 Hz, CH_2), 5.25 (d, 1H, J=17.4 Hz, CH_2), 5.77–5.92 (m, 1H, CH), 7.11–7.49 (m, 4H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ=30.0, 37.8 (CH_2), 72.0 (CH), 94.1 (C), 110.7 (CH), 115.0 (CH_2), 119.1, 122.1, 124.6 (CH), 125.9 (C), 141.2 (CH), 149.1, 165.3, 195.4 (C); IR (KBr): $\tilde{\nu}$ = 3410 (m), 3252 (m), 3195 (m), 1653 (s), 1495 (s), 1479 (s), 1416 (m), 1371 (w), 1173 (m), 1017 (m), 959 (m), 729 (m) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%): 309 (M^+, 19), 227 (20), 175 (33), 160 (100), 133 (17), 104 (10), 77 (15); HRMS (ESI): calcd (%) for $C_{14}H_{13}BrO_3$ ([M+1]) 309.23461, found 309.23156.

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