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Synthesis and Trapping of Some Substituted 1-Bromocyclopropenes

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Summary. Treatment of a number of 2-substituted 1,1,2-tribromocyclopropanes with MeLi at −78°C gave the corresponding 1-bromocyclopropenes, which were reacted with three cyclic dienes to yield the [4 + 2]-cycloadducts. Cycloaddition with 1,3-diphenylisobenzofuran (*DPIBF*) gave the *exo* adducts, in most cases in excellent yield, whereas cyclopentadiene afforded *endo* adducts only, but in moderate yield. In most reactions with furan no adduct was formed, but two 1-bromocyclopropenes derivatives with an aromatic side chain were exceptions and furnished mixtures of *exo* and *endo* adducts in moderate yields.

Keywords. Cycloadditions; Small rings; Organolithium compounds; Alkynes; Allenes.

Introduction

During the last few decades the interest in the chemical properties of cyclopropenes has grown considerably. New synthesis methods have been developed and made a variety of such compounds more easily available [1–4]. As a result, cyclopropenes have gradually emerged as a valuable group of synthetic intermediates, particularly for the synthesis of polycyclic and strained hydrocarbons [2–4]. Most of the cyclopropenes prepared and investigated have been alkyl- and aryl-substituted compounds, but more recently 1-halocyclopropenes have attracted considerably more attention due to their ability to rearrange, to form versatile organolithium reagents which react with a range of electrophiles, and to undergo [4 + 2] cycloaddition reactions (*Diels-Alder* reactions).

The most predictable and versatile reaction involving any cyclopropene is the *Diels-Alder* reaction, usually with the cyclopropene as the dienophile [5–7]. Most of these reactions have involved cyclic dienes, *e.g.* cyclopentadiene, furan, 1,3-diphenylisobenzofuran (*DPIBF*), and thiophene dioxide [5, 8–11], but some acyclic dienes have also been employed. The simplest example involving an acyclic, conjugated diene is the reaction between cyclopropene itself [1] and

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buta-1,3-diene, which has been thoroughly studied and proved to proceed *via* an *endo* transition state due to decisive influence of favourable secondary orbital interactions (SOI) [12, 13]. An analogous transition state is probably involved when the same cyclopropene reacts with cyclopentadiene, but when reacted with *DPIBF*, a 3:1 mixture of the *exo* and the *endo* adducts is formed [5]. The predominant formation of the *exo* adduct in the latter reaction is explained as lack of stabilising SOI [5].

In addition to reactions with cyclopropene itself, some cyclopropene derivatives have been used in *Diels-Alder* reactions for synthetic purposes. Most of them have been either 1,2-dihalocyclopropenes or tetrahalocyclopropenes, which have been utilized to synthesize some highly strained cycloproparenes [14–16], but in recent years a growing number of 1-halocyclopropenes have proved to be excellent dienophiles as well. Thus, *Banwell et al.* used a 1-chlorocyclopropene in a crucial step in the synthesis of the colchicine framework [8], and *Ng* and *Wege* used a similar compound in their total synthesis of favelanone [17]. Furthermore, a few substituted 1-halocyclopropenes have been trapped with dienes to prove the (transcient) existence of the former [6, 18–20].

Based on the willingness of 1-halocyclopropenes to undergo *Diels-Alder* reactions and the fact that 1-halocyclopropenes appear to be easily available from readily accessible 1,1,2-trihalocyclopropanes, we decided to study the reactivity of selected 2-substituted 1-bromocyclopropenes as dienophiles toward some conjugated dienes, with special emphasis on stereochemical aspects. The results of our investigations are reported here.

Results and Discussion

The 2-substituted 1,1,2-tribromocyclopropanes **1** used as precursors for the cyclopropenes **2** in this study were synthesized from the corresponding 2-bromo-1-alkenes as described in literature [21–24]. Formation of **2** was achieved by dehalogenation of **1** with *Me*Li based on a procedure published by *Baird et al.* [6, 25]. As expected the conversion of **1** to **2** was accompanied by a spontaneous change of colour, from colourless to yellow/orange [26]. The compounds included in this study are summarized in Fig. 1.

In order to find the optimum conditions for the whole process from **1** to the [4 + 2] cycloadducts, exploratory experiments were performed with some of the

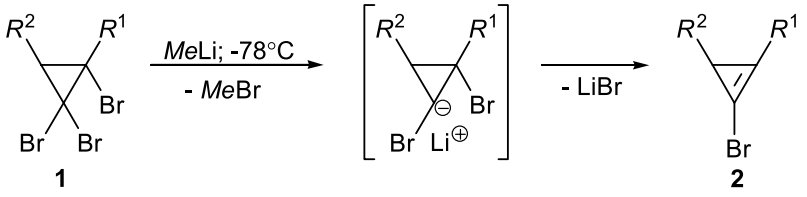
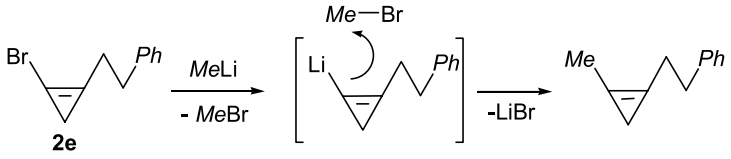


Fig. 1. Addition of *Me*Li to **1** leads to bromine-lithium exchange, followed by elimination of LiBr and formation of **2**; **a**: $R^1,R^2 = -CH_2CH_2CH_2CH_2CH_2CH_2-$; **b**: R^1 = phenoxymethyl, R^2 = H; **c**: R^1 = (4-methylphenoxy)methyl, R^2 = H; **d**: R^1 = phenyl, R^2 = H; **e**: R^1 = 2-phenylethyl, R^2 = H; **f**: R^1 = propyl, R^2 = H; **g**: R^1 = pentyl, R^2 = H; **h**: R^1 = octyl, R^2 = H; **i**: R^1 = cyclohexylmethyl, R^2 = H; **j**: R^1 = isobutyl, R^2 = H; **k**: R^1 = *tert*-butyl, R^2 = H

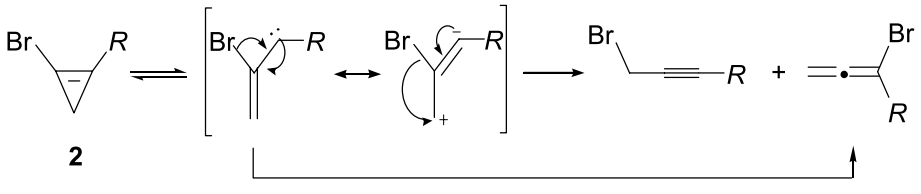


Scheme 1

cyclopropanes, varying the relative amount of *Me*Li and the reaction temperatures. When the former parameter was varied, it appeared that even a moderate excess of the reagent led to lithiation of the primary product and subsequent formation of by-products. Thus, when **1e** was treated with more than 1.2 equivalents of *Me*Li, 2-methyl-1-(2-phenylethyl)cyclopropene was obtained in addition to 1-bromo-2-(2-phenylethyl)cyclopropene (**2e**). The hydrocarbon is conceivably formed in a two-step process, *i.e.* lithiation of **2e** and formation of 1-lithio-2-(2-phenylethyl)cyclopropene, which reacts with MeBr (Scheme 1), and its formation is no surprise when results reported in literature are considered [3, 27]. We therefore decided to perform the conversion of **1** to **2** with a very small (1–3%) excess of *Me*Li.

Secondly, it appeared to be important to control the reaction temperatures properly due to the somewhat limited stability of the primary products, *i.e.* 1-bromocyclopropene derivatives **2**. Thus, treatment of **1a** with *Me*Li afforded 9-bromobicyclo[6.1.0]non-1(9)-ene (**2a**) (in quantitative yield), which turned out to be stable at least for one week in the refrigerator, but which decomposes rapidly at room temperature [28]. The product formed during such decomposition has been studied by *Lee et al.*, who reported that the chloro analogue to **2a**, 9-chlorobicyclo[6.1.0]non-1(9)-ene, decomposes to an aldehyde and an allylic alcohol when kept at room temperature [19]. It is therefore preferable to carry out the *Diels-Alder* reaction well below room temperature if the reaction rates so permit.

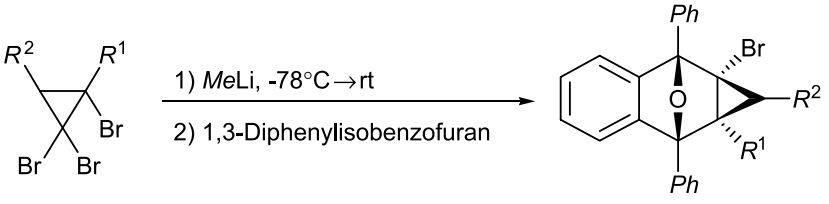
Finally, it also appeared that the stability of some 1-bromocyclopropenes could be increased by storing the compounds as solutions in *THF*. For instance, treatment of 1,1,2-tribromo-2-octylcyclopropane (**1h**) with 1.02 equivalents of *Me*Li gave 1-bromo-2-octylcyclopropene (**2h**), which was stable in *THF* at room temperature for an extended period of time, but which turned out to decompose when kept neat under otherwise identical conditions. Two rearrangement products, an acetylene and an allene, were formed in a 3:1 ratio and identified as 1-bromoundec-2-yne and 3-bromoundeca-1,2-diene on the basis of thorough spectroscopic analyses. Other 2-substituted 1-bromocyclopropenes (**2d**, **2g**, and **2i**) behaved in a similar fashion. On the basis of reports published by *Baird* and others formation of both compounds may be explained in terms of a 1,2-bromo



Scheme 2

shift in an intermediate vinylcarbene as outlined in Scheme 2 [29]. It is interesting to observe that 1-bromoundec-1-yne, which conceivably could result from a 1,2-alkyl shift in the alternative vinylcarbene, carrying a bromo substituent at the divalent carbon, is not observed.

In order to minimise the possibility for the by-product formation discussed above, the *Diels-Alder* reactions were carried out below room temperature. Three dienes were employed, *viz.* 1,3-diphenylisobenzofuran (*DPIBF*), cyclopentadiene, and furan, which have been reported to react with some cyclopropene derivatives, albeit with different rates. Thus, *DPIBF* and cyclopentadiene react smoothly with such dienophiles at room temperature [30–32], whereas furan reacts more reluctantly [18] and therefore can be used to uncover reactivity differences among the cyclopropene derivatives. A deficiency of the diene was used in the experiments with both *DPIBF* and cyclopentadiene, the former because unreacted *DPIBF* proved difficult to remove, and the latter because dicyclopentadiene formation hampered the product isolation. (Removal of *DPIBF* could be achieved by oxida-



1 **3**

Scheme 3

Table 1. 1,2-Dehalogenation of 2-substituted 1,1,2-tribromocyclopropanes (**1**) with *Me*Li and subsequent trapping of **2** with different dienes

Entry	Cyclopropane	Isolated yield of adducts/%		
		Exo-**3** (*DPIBF*)	*Endo*-**4** (cyclopentadiene)	*Exo*-**5** (furan)
1	**1a**	94	72	0[a]
2	**1b**	81	70	46[b]
3	**1c**	76	74	49
4	**1d**	88	54	0
5	**1e**	75	56[a]	0[a]
6	**1f**	84	22	0
7	**1g**	86	29	0
8	**1h**	80	35[a]	0[c]
9	**1i**	82	19[a,c]	0[a]
10	**1j**	63	26	0
11	**1k**	33	12[d]	0

[a] 1-Bromocyclopropene (**2**) was isolated; [b] pure *exo* (31%) and impure *endo*-**5b** (15%) were isolated; [c] by-products were isolated; [d] the yield is based on ^{1}H NMR data from a 3:6:1 mixture of **1k**, *endo*-**4k**, and *exo*-**4k**

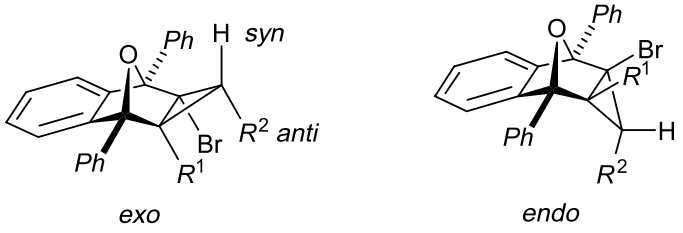
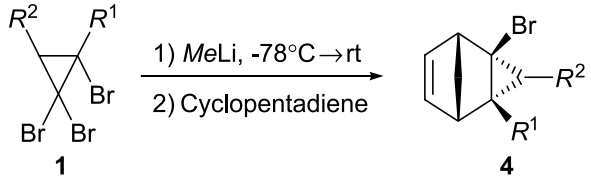


Fig. 2. The *syn* and *anti* positions of the *exo* and *endo* isomers of cycloadducts **3**

tion with air [33], but this oxidation was slow and a complete conversion of *DPIBF* to *o*-benzoylbenzophenone took several days.)

When cyclopropenes **2a**–**2k** were reacted with *DPIBF*, the corresponding cycloadduct **3** was isolated in good to excellent yield in all cases except one, *viz.* **3k** (R^1 = *tert*-butyl) which was isolated in 33% only (Scheme 3; Table 1, Entry 11). All adducts were formed and isolated as a single isomer, which in all cases was assigned the *exo* configuration on the basis of spectroscopic evidence. NMR spectroscopy appeared to be particularly informative in the case of compounds **3b**–**3k** because one of the cyclopropyl protons appeared consistently at a much lower field than the other: The signal associated with the proton *anti* to the oxygen atom was found at 1.69–2.17 ppm, while the *syn* proton appeared between 2.80 and 3.09 ppm. This difference may conceivably be attributed to the diamagnetic anisotropy of the oxygen atom, which causes a decrease in the shielding of the *syn* proton relative to the *anti* proton (Fig. 2) [34]. This interpretation is in agreement with that reported by *Binger et al.* [5], which showed that the formation of the *exo* isomer at the expense of *endo* was due to the lack of a favourable SOI in the transition state. Moreover, it is noteworthy that halogen-substituted dienophiles are believed to favour *endo* addition to dienes, and in some cases the halogen substituent may even compete with carboxyl groups for the *endo* orientation [35–37].

When *DPIBF* was replaced by cyclopentadiene, the addition to cyclopropenes **2a**–**2k** and the formation of the corresponding cycloadducts **4a**–**4k** proceeded much slower and were significantly less efficient than when *DPIBF* was used (Scheme 4). The yield ranged from poor to good, but in all cases adduct **4** was obtained in lower yield than the corresponding adduct **3**. The best yields were furnished when substituent R^1 contained an aromatic moiety (Table 1, Entries 2–5), and this trend clearly indicates the influence of some sort of π–π interaction, which overcomes the steric repulsion otherwise present (Table 1, Entries 9–11). Since monitoring of the reaction by TLC and GC showed a rapid and complete conversion of **1** to **2**, the low yields of adducts **4** must be due to poor reactivity towards cyclopentadiene. It is therefore not surprising that considerable amounts of unreacted **2** were isolated in some cases



Scheme 4

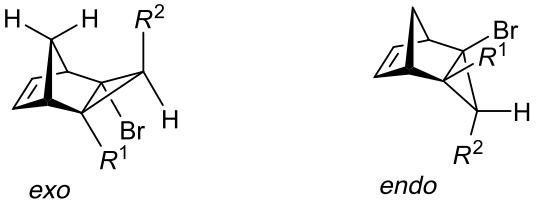
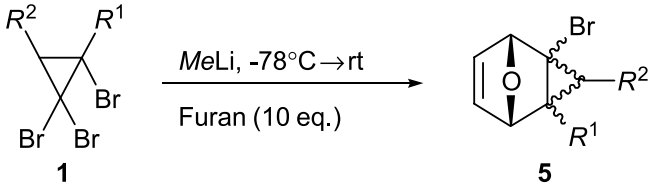


Fig. 3. Favourable SOI and steric hindrance favour the *endo* adduct over the *exo* analogue

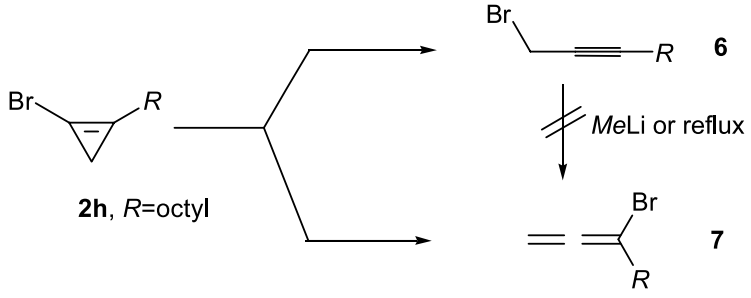
(Table 1, Entries 5, 8, and 9; 13, 39, and 35%), and in the reaction with **1i** 1-bromo-4-cyclohexylbut-2-yne (5%) was also isolated.

The reactions with cyclopentadiene proceed in accordance with *Alder's endo* rule [38] in all cases except one, *viz.* the reaction with **1k** (R^1 = *tert*-butyl) where the *endo* and *exo* isomers were formed in a 6:1 ratio. The small difference in the shift values of the cyclopropyl protons supported the assignment. In **4d** (R^1 = phenyl) the two protons even gave signals that overlapped so extensively that a broad singlet appeared at 1.78 ppm in the ^{1}H NMR spectrum. In addition to favourable secondary orbital interactions, steric hindrance caused by the methylene bridge is probably a decisive factor for the outcome of the reaction (Fig. 3). This reasoning is supported by observations reported by *Closs et al.*, who isolated only the *endo* adduct when 3-methylcyclopropene reacted with cyclopentadiene, whereas no adduct was observed at all when 3,3-dimethylcyclopropene was reacted under similar conditions [4, 39].

Furan, the least reactive of the dienes used in this study, did not react with the cyclopropenes under the conditions employed for cyclopentadiene and *DPIBF*; this is not surprising considering the fact that *Diels-Alder* reactions involving furan are usually performed around 80°C [30]. Since such a high temperature is incompatible with the relatively low thermal stability of the cyclopropenes generated in this study, we adopted a modified procedure, developed by *Baird et al.* [18], which makes use of a large excess of furan (10 eq.) that is present during the *Me*Li addition and the generation of **2** (Scheme 5). In spite of this modification, however, cycloadduct formation was observed in two reactions only, *viz.* those involving 1-bromo-2-(phenoxymethyl)cyclopropene (**2b**) and 1-bromo-2-[(4-methylphenoxy)-methyl]cyclopropene (**2c**). The corresponding cycloadducts **5b** and **5c** were formed as mixtures of the *exo* and *endo* isomers, but due to formation of at least four other products, complete analysis of the reaction mixtures and proper isolation of the cycloadducts were hampered. However, it was determined that *exo*-**5b** and *exo*-**5c** each was formed in 45–50% yield (Table 1, Entries 2 and 3) and that the corresponding *endo* isomers were obtained in significantly lower yield (see Experimen-



Scheme 5



Scheme 6

tal). Furthermore, pure samples of *exo*-**5b** and *exo*-**5c** were isolated in 31 and 49% yield.

The reactions with **1a**, **1e**, and **1i** afforded no cycloadduct, but were nevertheless very clean and gave one product only. In each case the product appeared to be the corresponding 1-bromocyclopropene, which was isolated in 100, 96, and 74% yield. The rest of the 1,1,2-tribromocyclopropanes, however, gave complex reaction mixtures, from which it was generally very difficult to isolate pure samples of the individual compounds. One exception is the reaction involving furan and 1,1,2-tribromo-2-octylcyclopropane (**1h**); from the product mixture 1-bromoundec-2-yne (**6**) and 3-bromoundeca-1,2-diene (**7**) were isolated in 22 and 17% yield (Scheme 6). These products are most likely formed as outlined in Scheme 3, although formation of **7** from **6** can be envisaged. However, when pure **6** in *THF* was refluxed in the presence and absence of *Me*Li, no allene was formed; hence, the allene does not originate from the acetylene by rearrangement.

On the basis of the results reported here, it can be concluded that the 1-bromocyclopropenes studied here exhibit the same reactivity toward cyclopentadiene, *DPIBF*, and furan as cyclopropene and alkyl-substituted cyclopropenes, *viz.* the reaction rate and the chemical yield vary in the order *DPIBF* > cyclopentadiene ≫ furan. Due to the reluctance of furan to react the thermal instability of the cyclopropenes becomes important; as a result most of the product mixtures from the furan reactions contain several compounds formed by decomposition of the 1-bromocyclopropenes. Furthermore, it appears that the lack of secondary orbital interactions are important in the reactions with *DPIBF*; thus, in these cycloadditions *exo* adducts are formed exclusively whereas *Alder's endo* rule is followed when cyclopentadiene is involved.

Experimental

General Remarks

The instrumentation and analyses methods have been described in Ref. [24]. Some of the HRMS analyses were obtained on an Autospec Ultima2000 Micromass spectrometer with EBE-geometry. The spectrometer was operated in the EI mode at 70 eV and the samples were injected at an ion source temperature of 170°C.

THF was distilled from Na-benzophenone ketyl under N_2 immediately prior to use. *Me*Li was obtained from commercial sources (Fluka) and standardized by titration against butan-2-ol in xylene with *N*-phenyl-1-naphthylamine as indicator [40].

The structure elucidation of the adducts (**3**, **4**, and **5**) was simplified with the use of 2D NMR experiments (COSY, HSQC, HMBC and N*O*ESY) [41], in addition to the standard analyses listed under Experimental. The connectivity between ^{1}H nuclei was revealed by COSY, whereas HSQC and HMBC gave an overview of the H,C correlation and in some cases useful information about close spatial relationship between ^{1}H nuclei were given by using the N*O*ESY experiment.

*Formation and Trapping of 1-Bromocyclopropenes **2** with DPIBF; General Procedure*

The cyclopropane **1** was dissolved in 40 cm^3 *THF* in a round-bottomed flask, equipped with a condenser connected to a N_2 inlet. The solution was cooled to −78°C (acetone/dry-ice or ethyl acetate/liquid N_2). *Me*Li (1.01–1.03 eq) was added dropwise with magnetic stirring. Stirring was continued at rt for 1 h, before *DPIBF* (0.8 eq) was added at a temperature well below 0°C [6]. The reactions were monitored by TLC and quenched with a portion of water. The product **3** was extracted with diethyl ether, the solution was dried ($MgSO_4$), filtrated, and evaporated *in vacuo*, and finally **3** was isolated by either flash chromatography or recrystallization.

10-Bromo-14-oxa-1,11-diphenyl-12,13-benzotetracyclo[9.2.1.0^{2,9}.0^{2,10}]tetradecane
(**3a**, $C_{29}H_{27}OBr$)

The synthesis was carried out with 0.90 g **1a** (2.49 mmol), 1.60 cm^3 *Me*Li (1.60 *M*, 2.56 mmol), and 0.54 g *DPIBF* (2.00 mmol). Flash chromatography (*n*-hexane:ethyl acetate = 98:2) afforded 0.89 g **3a** (94%) as a colourless oil. Subsequent recrystallization (*n*-hexane) gave white crystals, mp 187–188°C. IR (KBr): $\bar{\nu}$ = 3036 m, 2914 s, 2852 s, 1496 w, 1454 s, 1343 m, 1295 m, 1273 m, 1168 w, 989 br, 916 m, 753 br, 700 s cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ = 0.90–1.10 (2H, m), 1.28–1.56 (8H, m), 1.64–1.68 (1H, m), 1.95–2.00 (1H, m), 2.54–2.58 (1H, m), 7.24–7.51 (9H, m), 7.75–7.78 (2H, m), 7.84–7.90 (3H, m) ppm; ^{13}C NMR (100 MHz; $CDCl_3$; Me_4Si): δ = 25.5 (CH_2), 25.6 (CH_2), 25.9 (CH_2), 26.5 (CH_2), 26.8 (CH_2), 27.6 (CH_2), 32.4 (CH), 39.8 (C), 57.6 (CBr), 89.5 (CO), 89.8 (CO), 121.6 (CH_2), 122.7 (CH_2), 126.0 (CH), 126.2 (CH), 126.5 (CH), 127.9 (CH), 128.0 (CH), 128.3 (CH), 128.9 (CH), 129.7 (CH), 133.8 (C), 137.2 (C), 146.7 (C), 148.4 (C) ppm; MS (EI): m/z (%) = 391 (M^+ − Br, 100), 270 (25), 105 (80), 91 (16), 77 (24); HRMS (EI): m/z calcd. for M^+ − Br, $C_{29}H_{27}O^+$, 391.2062; found 391.2083.

2-Bromo-8-oxa-4-phenoxymethyl-1,5-diphenyl-6,7-benzotricyclo[3.2.1.0^{2,4}]octane
(**3b**, $C_{30}H_{23}O_2Br$)

The synthesis was carried out with 0.96 g **1b** (2.49 mmol), 1.70 cm^3 *Me*Li (1.50 *M*, 2.55 mmol), and 0.54 g *DPIBF* (2.00 mmol). Flash chromatography (*n*-hexane:ethyl acetate = 97.5:2.5) afforded 0.80 g **3b** (81%) as a colourless oil. Subsequent recrystallization (*n*-hexane) gave white crystals, mp 146–148°C. IR (KBr): $\bar{\nu}$ = 3041 m, 2907 m, 2857 m, 1595 m, 1495 m, 1452 m, 1395 w, 1337 w, 1295 m, 1242 s, 1176 w, 1124 w, 1077 w, 1033 m, 982 m, 945 w, 895 w, 755 s, 695 s cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ = 2.07 (1H, d, J = 6.5 Hz), 2.98 (1H, dd, J = 6.5 and 0.7 Hz), 3.91 (1H, d, J = 10.7 Hz, OCH), 4.14 (1H, dd, J = 10.7 and 0.7 Hz, OCH), 6.77–6.81 (2H, m), 6.91–6.95 (1H, m), 7.21–7.51 (12H, m), 7.79–7.87 (4H, m) ppm; ^{13}C NMR (50 MHz; $CDCl_3$; Me_4Si): δ = 28.2 (CH_2), 36.6 (C), 49.9 (CBr), 67.9 (OCH_2), 90.0 (CO), 90.3 (CO), 114.4 (CH), 120.9 (CH), 121.7 (CH), 122.9 (CH), 126.5 (CH), 126.6 (CH), 128.2 (CH), 128.4 (CH), 128.8 (CH), 128.9 (CH), 129.1 (CH), 129.2 (CH), 129.3 (CH), 133.2 (C), 133.9 (C), 147.6 (C), 148.0 (C), 158.4 (C) ppm; MS (EI): m/z (%) = 415 (M^+ − Br, 30), 321 (46), 270 (10), 105 (100), 77 (35); HRMS (EI): m/z calcd. for M^+ − Br, $C_{30}H_{23}O_2^+$, 415.1698; found 415.1699.

2-Bromo-4-(4-methylphenoxy)methyl-8-oxa-1,5-diphenyl-6,7-benzotricyclo[3.2.1.0^{2,4}]octane
(**3c**, $C_{31}H_{25}O_2Br$)

The synthesis was carried out with 1.00 g **1c** (2.51 mmol), 1.60 cm^3 *Me*Li (1.60 *M*, 2.56 mmol), and 0.54 g *DPIBF* (2.01 mmol). Flash chromatography (*n*-hexane:ethyl acetate = 97.5:2.5) afforded 0.78 g **3c** (76%) as a colourless oil. Subsequent recrystallization (*n*-hexane) gave white crystals, mp 140°C. IR

(KBr): $\bar{\nu} = 3030$ m, 2915 m, 2855 m, 1510 s, 1449 m, 1390 w, 1298 m, 1237 s, 1175 m, 1031 m, 983 m, 811 br, 755 s, 698 s cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$; Me_4Si): $\delta = 2.06$ (1H, d, $J = 6.3$ Hz, CH), 2.26 (3H, s, CH_3), 2.96 (1H, d, $J = 6.3$ Hz, CH), 3.88 (1H, d, $J = 10.4$ Hz, OCH), 4.11 (1H, d, $J = 10.4$ Hz, OCH), 6.67–6.70 (2H, m, 2 × CH), 7.03–7.04 (2H, m, 2 × CH), 7.27–7.50 (10H, m, 10 × CH), 7.79–7.81 (2H, m, 2 × CH), 7.85–7.86 (2H, m, 2 × CH) ppm; ^{13}C NMR (100 MHz; $CDCl_3$; Me_4Si): $\delta = 20.3$ (CH_3), 28.1 (CH_2), 36.7 (C), 49.9 (CBr), 68.0 (OCH_2), 90.0 (CO), 90.3 (CO), 114.2 (2 × CH), 121.7 (CH), 122.8 (CH), 126.4 (CH), 126.6 (CH), 128.2 (2 × CH), 128.4 (2 × CH), 128.8 (2 × CH), 128.9 (CH), 129.1 (CH), 129.2 (2 × CH), 129.7 (2 × CH), 130.1 (C), 133.2 (C), 133.9 (C), 147.7 (C), 148.0 (C), 156.3 (C) ppm; MS (EI): m/z (%) = 510/508 (M^+, 1/1), 429 (26), 403/401 (13/13), 321 (100), 270 (14), 105 (83), 91 (7), 77 (19); HRMS (EI): m/z calcd. for M^+, $C_{31}H_{25}O_2Br^+$, 508.1038; found 508.1002.

2-Bromo-8-oxa-1,4,5-triphenyl-6,7-benzotricyclo[3.2.1.0^{2,4}]octane (**3d**, $C_{29}H_{21}OBr$)
The synthesis was carried out with 0.89 g **1d** (2.51 mmol), 1.70 cm^3 *Me*Li (1.50 *M*, 2.55 mmol), and 0.54 g *DPIBF* (2.00 mmol). Flash chromatography (*n*-hexane:ethyl acetate = 95:5) afforded 0.82 g **3d** (88%) as a colourless oil. Subsequent recrystallization (*n*-hexane) gave white crystals, mp 134–136°C. IR (KBr): $\bar{\nu} = 3062$ m, 3028 m, 2999 m, 2954 m, 2867 m, 1495 m, 1448 m, 1345 m, 1297 m, 1177 w, 1013 w, 977 s, 912 w, 883 m, 760 br, 700 s cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$; Me_4Si): $\delta = 1.90$ (1H, d, $J = 5.8$ Hz), 3.09 (1H, d, $J = 5.8$ Hz), 6.59–6.62 (2H, m), 7.14–7.55 (15H, m), 7.91–7.94 (2H, m) ppm; ^{13}C NMR (100 MHz; $CDCl_3$; Me_4Si): $\delta = 29.4$ (CH_2), 44.4 (C), 49.1 (CBr), 90.1 (CO), 90.3 (CO), 122.1 (CH), 123.0 (CH), 126.2 (CH), 126.6 (CH), 126.7 (2 × CH), 127.48 (2 × CH), 127.50 (CH), 127.9 (3 × CH), 128.4 (2 × CH), 129.1 (CH), 129.3 (2 × CH), 131.7 (2 × CH), 133.7 (C), 134.8 (C), 135.2 (C), 147.7 (C), 147.9 (C) ppm; MS (EI): m/z (%) = 466/464 (M^+, 2/2), 385 ($M^+ - Br$, 100), 270 (27), 105 (48), 77 (36); HRMS (EI): m/z calcd. for $M^+ - Br$, $C_{29}H_{21}O^+$, 385.1592; found 385.1595.

2-Bromo-8-oxa-1,5-diphenyl-4-(2-phenylethyl)-6,7-benzotricyclo[3.2.1.0^{2,4}]octane
(**3e**, $C_{31}H_{25}OBr$)
The synthesis was carried out with 0.96 g **1e** (2.50 mmol), 1.60 cm^3 *Me*Li (1.60 *M*, 2.56 mmol), and 0.54 g *DPIBF* (2.00 mmol). Flash chromatography (*n*-hexane:ethyl acetate = 97.5:2.5) afforded 0.74 g **3e** (75%) as a colourless oil. Subsequent recrystallization (*n*-hexane) gave white crystals, mp 142–143°C. IR (KBr): $\bar{\nu} = 3065$ m, 3026 m, 2929 m, 2857 m, 1496 w, 1451 m, 1348 m, 1300 m, 1156 w, 978 br, 910 w, 754 br, 699s cm^{-1}; ^1H NMR (200 MHz; $CDCl_3$; Me_4Si): $\delta = 1.48$–1.64 (1H, m), 1.77 (1H, d, $J = 6.3$ Hz, CH), 1.91–2.07 (1H, m), 2.54–2.63 (2H, m, CH_2), 2.85 (1H, d, $J = 6.3$ Hz, CH), 7.01–7.32 (7H, m, 7 × CH), 7.41–7.52 (8H, m, 8 × CH), 7.72–7.77 (2H, m, 2 × CH), 7.81–7.87 (2H, m, 2 × CH) ppm; ^{13}C NMR (50 MHz; $CDCl_3$; Me_4Si): $\delta = 27.8$ (CH_2), 30.3 (CH_2), 34.4 (CH_2), 36.9 (C), 50.5 (CBr), 90.2 (CO), 90.3 (CO), 121.8 (CH), 122.8 (CH), 125.8 (CH), 126.2 (CH), 126.4 (CH), 128.1 (2 × CH), 128.2 (2 × CH), 128.3 (2 × CH), 128.4 (2 × CH), 128.5 (2 × CH), 128.9 (CH), 129.0 (CH), 129.2 (2 × CH), 133.5 (C), 134.4 (C), 141.5 (C), 147.1 (C), 148.0 (C) ppm; MS (EI): m/z (%) = 413 ($M^+ - Br$, 50), 270 (19), 105 (100), 91 (34), 77 (25); HRMS (EI): m/z calcd. for $M^+ - Br$, $C_{31}H_{25}O^+$, 413.1905; found 413.1902.

2-Bromo-8-oxa-1,5-diphenyl-4-propyl-6,7-benzotricyclo[3.2.1.0^{2,4}]octane (**3f**, $C_{26}H_{23}OBr$)
The synthesis was carried out with 0.80 g **1f** (2.50 mmol), 1.70 cm^3 *Me*Li (1.50 *M*, 2.55 mmol), and 0.55 g *DPIBF* (2.02 mmol). Flash chromatography (*n*-hexane:ethyl acetate = 98:2) afforded 0.72 g **3f** (84%) as a light yellow oil. IR (film): $\bar{\nu} = 3061$ s, 3041 s, 2959 s, 2931 s, 2870 s, 1604 w, 1497 m, 1453 s, 1422 m, 1348 s, 1301 s, 1181 m, 1160 w, 1093 m, 1058 w, 981 br, 938 m, 907 br, 754 br, 700 s cm^{-1}; ^1H NMR (200 MHz; $CDCl_3$; Me_4Si): $\delta = 0.81$ (3H, t, $J = 7.0$ Hz, CH_3), 1.10–1.37 (3H, m), 1.57–1.64 (1H, m), 1.69 (1H, d, $J = 6.3$ Hz), 2.80 (1H, d, $J = 6.3$ Hz), 7.22–7.48 (10H, m), 7.68–7.72 (2H, m), 7.82–7.86 (2H, m) ppm; ^{13}C NMR (50 MHz; $CDCl_3$; Me_4Si): $\delta = 14.2$ (CH_3), 21.4 (CH_2), 27.6 (CH_2), 30.3 (CH_2), 36.9 (C), 50.7 (CBr), 90.26 (CO), 90.33 (CO), 121.8 (CH), 122.7

(CH), 126.1 (CH), 126.2 (CH), 128.3 (CH), 128.4 (CH), 128.6 (CH), 128.8 (CH), 128.9 (CH), 129.2 (CH), 133.6 (C), 134.5 (C), 147.2 (C), 148.0 (C) ppm; MS (EI): m/z (%) = 351 ($M^+ - Br$, 75), 327 (15), 270 (6), 246 (30), 103 (100), 91 (63), 77 (73); HRMS (EI): m/z calcd. for M^+, $C_{26}H_{23}OBr^+$, 430.0932; found 430.0934.

2-Bromo-8-oxa-4-pentyl-1,5-diphenyl-6,7-benzotricyclo[3.2.1.0^{2,4}]octane (**3g**, $C_{28}H_{27}OBr$)
The synthesis was carried out with 0.88 g **1g** (2.52 mmol), 1.60 cm^3 *Me*Li (1.60 *M*, 2.56 mmol), 0.55 g *DPIBF* (2.02 mmol). Flash chromatography (*n*-hexane:ethyl acetate = 98:2) afforded 0.80 g **3g** (86%) as a colourless oil. Subsequent recrystallization (*n*-hexane) gave white crystals, mp 84–86°C. IR (KBr): $\bar{\nu}$ = 3064 m, 3037 m, 2932 s, 2854 s, 1600 w, 1497 w, 1451 s, 1423 w, 1347 m, 1297 s, 1180 w, 1100 w, 1004 m, 982 br, 934 w, 909 w, 875 br, 753 s, 699 s cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ = 0.80–0.84 (3H, m, CH_3), 1.14–1.34 (7H, m), 1.62–1.68 (1H, m), 1.71 (1H, d, J = 6.2 Hz), 2.80 (1H, d, J = 6.2 Hz), 7.25–7.32 (3H, m), 7.38–7.49 (7H, m), 7.69–7.71 (2H, m), 7.83–7.85 (2H, m) ppm; ^{13}C NMR (100 MHz; $CDCl_3$; Me_4Si): δ = 13.9 (CH_3), 22.3 (CH_2), 27.6 (CH_2), 27.8 (CH_2), 27.9 (CH_2), 31.9 (CH_2), 37.0 (C), 50.8 (CBr), 90.3 (CO), 90.4 (CO), 121.8 (CH), 122.7 (CH), 126.1 (CH), 126.3 (CH), 128.3 (CH), 128.4 (CH), 128.6 (CH), 128.8 (CH), 128.9 (CH), 129.2 (CH), 133.7 (C), 134.6 (C), 147.3 (C), 148.1 (C) ppm; MS (EI): m/z (%) = 379 ($M^+ - Br$, 100), 270 (25), 105 (96), 77 (36); HRMS (EI): m/z calcd. for $M^+ - Br$, $C_{28}H_{27}O^+$, 379.2062; found 379.2104.

2-Bromo-4-octyl-8-oxa-1,5-diphenyl-6,7-benzotricyclo[3.2.1.0^{2,4}]octane (**3h**, $C_{31}H_{33}OBr$)
The synthesis was carried out with 0.98 g **1h** (2.50 mmol), 1.70 cm^3 *Me*Li (1.50 *M*, 2.55 mmol), and 0.54 g *DPIBF* (2.00 mmol). Flash chromatography (*n*-hexane:ethyl acetate = 97.5:2.5) afforded 0.80 g **3h** (80%) as a light yellow oil. IR (film): $\bar{\nu}$ = 3061 m, 3041 m, 2926 s, 2856 s, 1497 m, 1454 s, 1349 m, 1300 s, 1178 w, 1110 w, 1058 w, 982 br, 935 w, 909 m, 879 m, 756 s, 700 s cm^{-1}; ^{1}H NMR (200 MHz; $CDCl_3$; Me_4Si): δ = 0.82–0.88 (3H, m, CH_3), 1.19–1.30 (13H, m), 1.62–1.68 (1H, m), 1.70 (1H, d, J = 6.2 Hz), 2.80 (1H, d, J = 6.2 Hz), 7.25–7.32 (3H, m), 7.38–7.48 (7H, m), 7.69–7.71 (2H, m), 7.83–7.85 (2H, m) ppm; ^{13}C NMR (50 MHz; $CDCl_3$; Me_4Si): δ = 14.0 (CH_3), 22.5 (CH_2), 27.6 (CH_2), 28.0 (CH_2), 28.1 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 29.7 (CH_2), 31.7 (CH_2), 37.0 (C), 50.8 (CBr), 90.3 (CO), 90.4 (CO), 121.8 (CH), 122.7 (CH), 126.1 (CH), 126.2 (CH), 128.3 (CH), 128.4 (CH), 128.6 (CH), 128.8 (CH), 128.9 (CH), 129.2 (CH), 133.7 (C), 134.6 (C), 147.3 (C), 148.1 (C) ppm; MS (EI): m/z (%) = 421 ($M^+ - Br$, 100), 316 (32), 270 (20), 105 (48), 77 (12); HRMS (EI): m/z calcd. for $M^+ - Br$, $C_{31}H_{33}O^+$, 421.2531; found 421.2530.

2-Bromo-4-cyclohexylmethyl-8-oxa-1,5-diphenyl-6,7-benzotricyclo[3.2.1.0^{2,4}]octane
(**3i**, $C_{30}H_{29}OBr$)
The synthesis was carried out with 0.94 g **1i** (2.50 mmol), 1.70 cm^3 *Me*Li (1.50 *M*, 2.55 mmol), and 0.54 g *DPIBF* (2.00 mmol). Flash chromatography (*n*-hexane:ethyl acetate = 98:2) afforded 0.80 g **3i** (82%) as a white powder, mp 54–56°C. IR (KBr): $\bar{\nu}$ = 3060 br, 2921 s, 2847 s, 1497 w, 1449 m, 1347 m, 1298 m, 1174 w, 1122 w, 1078 w, 981 br, 906 w, 874 w, 754 s, 697 s cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ = 0.76–0.84 (2H, m), 0.99–1.25 (5H, m), 1.49–1.70 (6H, m), 1.76 (1H, d, J = 6.3 Hz), 2.93 (1H, d, J = 6.3 Hz), 7.27–7.32 (3H, m), 7.39–7.48 (7H, m), 7.74–7.76 (2H, m), 7.82–7.85 (2H, m) ppm; ^{13}C NMR (100 MHz; $CDCl_3$; Me_4Si): δ = 26.1 (2 × CH_2), 26.3 (CH_2), 28.5 (CH_2), 33.5 (CH_2), 33.6 (CH_2), 35.1 (C), 35.4 (CH_2), 35.6 (CH), 50.3 (CBr), 90.2 (CO), 90.5 (CO), 122.1 (CH), 122.8 (CH), 126.1 (CH), 126.3 (CH), 128.3 (4 × CH), 128.8 (2 × CH), 128.9 (2 × CH), 129.3 (2 × CH), 133.6 (C), 134.6 (C), 147.1 (C), 148.0 (C) ppm; MS (EI): m/z (%) = 405 ($M^+ - Br$, 100), 300 (20), 270 (26), 105 (71), 77 (21); HRMS (EI): m/z calcd. for M^+, $C_{30}H_{29}OBr^+$, 484.1402; found 484.1442.

2-Bromo-4-isobutyl-8-oxa-1,5-diphenyl-6,7-benzotricyclo[3.2.1.0^{2,4}]octane (**3j**, $C_{27}H_{25}OBr$)
The synthesis was carried out with 0.84 g **1j** (2.50 mmol), 1.70 cm^3 *Me*Li (1.50 *M*, 2.55 mmol), and 0.54 g *DPIBF* (2.00 mmol). Flash chromatography (*n*-hexane:ethyl acetate = 95:5) afforded 0.56 g **3j**

(63%) as a colourless oil. IR (film): $\bar{\nu} = 3061$ m, 2956 s, 2926 m, 2870 m, 1497 w, 1454 m, 1348 m, 1300 m, 1271 w, 1179 w, 1105 w, 983 br, 908 m, 754 br, 701 s, 650 m cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): $\delta = 0.84$ (6H, t, $J = 6.7$ Hz, $2 \times CH_3$), 0.94–1.04 (1H, m), 1.50–1.63 (2H, m), 1.79 (1H, d, $J = 6.3$ Hz), 2.94 (1H, d, $J = 6.3$ Hz), 7.21–7.28 (3H, m), 7.33–7.44 (7H, m), 7.74–7.76 (2H, m), 7.83–7.86 (2H, m) ppm; ^{13}C NMR (100 MHz; $CDCl_3$; Me_4Si): $\delta = 22.7$ (CH_3), 22.8 (CH_3), 26.1 (CH), 28.2 (CH_2), 35.5 (C), 36.5 (CH_2), 50.3 (CBr), 90.1 (CO), 90.4 (CO), 121.9 (CH), 122.7 (CH), 126.1 (CH), 126.2 (CH), 128.22 ($2 \times$CH), 128.23 ($2 \times$CH), 128.6 ($2 \times$CH), 128.80 (CH), 128.82 (CH), 129.1 ($2 \times$CH), 133.6 (C), 134.6 (C), 147.0 (C), 147.9 (C) ppm; MS (EI): m/z (%) = 446/444 (M^+, 2/2), 403/401 (11/11), 365 ($M^+ - Br$, 100), 270 (30), 105 (83), 77 (32); HRMS (EI): m/z calcd. for $M^+ - Br$, $C_{27}H_{25}O^+$, 365.1905; found 365.1923.

2-Bromo-4-tert-butyl-8-oxa-1,5-diphenyl-6,7-benzotricyclo[3.2.1.0^{2,4}]octane (**3k**, $C_{27}H_{25}OBr$)
The synthesis was carried out with 0.84 g **1k** (2.50 mmol), 1.70 cm^3 *Me*Li (1.50 *M*, 2.55 mmol), and 0.54 g *DPIBF* (2.00 mmol). TLC indicated that at least three compounds were formed, but flash chromatography (*n*-hexane:ethyl acetate = 97.5:2.5) afforded only 0.29 = g **3k** (33%) as a colourless oil. This was recrystallized (*n*-hexane) to give white crystals, mp 145–146°C. IR (KBr): $\bar{\nu} = 3059$ m, 3036 m, 2958 s, 2909 m, 2872 m, 1452 m, 1396 w, 1364 w, 1342 w, 1292 m, 1203 w, 1151 w, 1004 w, 979 m, 905 br, 874 w, 756 s, 698 br cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): $\delta = 0.83$ (9H, s, $3 \times CH_3$), 2.17 (1H, d, $J = 6.2$ Hz), 3.04 (1H, d, $J = 6.2$ Hz), 7.31–7.46 (9H, m), 7.70–7.72 (1H, m), 7.78–7.80 (2H, m), 7.85–7.87 (2H, m) ppm; ^{13}C NMR (100 MHz; $CDCl_3$; Me_4Si): $\delta = 28.8$ (CH_2), 31.0 ($3 \times CH_3$), 32.0 (C), 43.8 (C), 49.2 (CBr), 89.6 (CO), 90.9 (CO), 123.2 (CH), 123.8 (CH), 125.8 (CH), 126.3 (CH), 128.2 ($2 \times$CH), 128.3 ($2 \times$CH), 128.5 ($2 \times$CH), 128.8 (CH), 128.9 (CH), 129.5 ($2 \times$CH), 133.4 (C), 136.5 (C), 147.4 (C), 148.6 (C) ppm; MS (EI): m/z (%) = 446/444 (M^+, 3/3), 390/388 (10/10), 365 ($M^+ - Br$, 66), 270 (37), 105 (100), 77 (24), 57 (81); HRMS (EI): m/z calcd. for $M^+ - Br$, $C_{27}H_{25}O^+$, 444.1089; found 444.1090.

*General Procedure for the Formation and Trapping of **2** with Cyclopentadiene*
The cyclopropane **1** was dissolved in 40 cm^3 *THF* in a round-bottomed flask, equipped with a condenser connected to a N_2 inlet. The solution was cooled to −78°C (acetone/dry-ice or ethyl acetate/liquid N_2). *Me*Li (1.00–1.20 eq) was added dropwise with magnetic stirring. Stirring was continued at rt for 1 h, before cyclopentadiene (0.88–0.97 eq) was added at a temperature well below 0°C [6]. The reactions were monitored by either TLC or GC and quenched with a portion of water. The product **4** was extracted with diethyl ether, the solution was dried ($MgSO_4$), filtrated, and evaporated *in vacuo*, and finally **4** was isolated by flash chromatography.

10-Bromotetracyclo[9.2.1.0^{2,9}.0^{2,10}]tetradec-12-ene (**4a**, $C_{14}H_{19}Br$)
The synthesis was carried out with 0.91 g **1a** (2.52 mmol), 1.60 cm^3 *Me*Li (1.50 *M*, 2.56 mmol), and 0.20 cm^3 cyclopentadiene ($d = 0.80$ g/cm^3, 2.42 mmol). TLC and GC indicated that at least four compounds were formed, but flash chromatography (*n*-hexane) afforded only 0.47 g **4a** (72%) as a colourless oil. IR (film): $\bar{\nu} = 3061$ w, 2973 s, 2921 s, 2856 s, 1451 m, 1356 w, 1323 w, 1250 m, 1164 w, 1096 w, 1060 br, 1034 w, 948 w, 887 w, 797 w, 736 m cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): $\delta = 1.01$–1.04 (1H, m), 1.28–1.44 (6H, m), 1.51–1.76 (7H, m), 2.08 (1H, td, $J = 7.3$ and 1.8 Hz), 2.74–2.76 (1H, m), 3.09–3.11 (1H, m), 5.88–5.90 (1H, m, =CH), 5.98–6.00 (1H, m, =CH) ppm; ^{13}C NMR (100 MHz; $CDCl_3$; Me_4Si): $\delta = 26.5$ (CH_2), 26.8 (CH_2), 27.2 (CH_2), 27.6 (CH_2), 27.9 (CH_2), 28.6 (CH_2), 28.8 (C), 37.9 (CH), 48.3 (CH), 52.8 (CBr), 56.4 (CH), 58.6 (CH_2), 132.5 (=CH), 134.1 (=CH) ppm; MS (EI): m/z (%) = 268/266 (M^+, 2/2), 187 ($M^+ - Br$, 41), 145 (14), 131 (22), 117 (44), 105 (49), 91 (100), 79 (57), 67 (69), 55 (41).

2-Bromo-4-phenoxymethyltricyclo[3.2.1.0^{2,4}]oct-6-ene (**4b**, $C_{15}H_{15}OBr$)
The synthesis was carried out with 1.02 g **1b** (2.65 mmol), 2.00 cm^3 *Me*Li (1.50 *M*, 3.00 mmol), and 0.20 cm^3 cyclopentadiene ($d = 0.80$ g/cm^3, 2.42 mmol). GC indicated that at least three compounds

were formed, but flash chromatography (*n*-hexane:ethyl acetate = 98:2) afforded only 0.49 g **4b** (70%) as a colourless liquid. IR (film): $\bar{\nu}$ = 3063 w, 2982 m, 2937 m, 2866 w, 1599 s, 1495 s, 1388 s, 1367 s, 1300 m, 1240 s, 1172 m, 1033 s, 856 w, 752 s, 691 s cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ = 1.35 (1H, dd, J = 6.6 and 2.5 Hz), 1.59 (1H, dd, J = 6.6 and 1.1 Hz), 1.81–1.84 (1H, m), 2.35–2.38 (1H, m), 3.05–3.07 (1H, m), 3.14–3.16 (1H, m), 4.20 (1H, d, J = 10.0 Hz, OCH), 4.30 (1H, d, J = 10.0 Hz, OCH), 6.01–6.07 (2H, m, HC=CH), 6.91–6.98 (3H, m, Ph), 7.25–7.32 (2H, m, Ph) ppm; ^{13}C NMR (100 MHz; $CDCl_3$; Me_4Si): δ = 28.5 (C), 33.6 (CH_2), 43.7 (CBr), 47.3 (CH), 54.5 (CH), 60.6 (CH_2), 72.4 (OCH_2), 114.7 (2 × CH), 120.8 (CH), 129.3 (2 × CH), 133.2 (=CH), 135.2 (=CH), 159.0 (C) ppm; MS (EI): m/z (%) = 292/290 (M^+, 2/2), 198/196 (21/21), 117 (100), 91 (44), 77 (37); HRMS (EI): m/z calcd. for M^+, $C_{15}H_{15}OBr^+$, 290.0306; found 290.0326. After a couple of months in the freezer, white crystals were formed and isolated by filtration, mp 38–39°C.

2-Bromo-4-(4-methylphenoxy)methyltricyclo[3.2.1.0^{2,4}]oct-6-ene (**4c**, $C_{16}H_{17}OBr$)
The synthesis was carried out with 1.00 g **1c** (2.51 mmol), 2.00 cm^3 *Me*Li (1.50 M, 3.00 mmol), and 0.20 cm^3 cyclopentadiene (d = 0.80 g/cm^3, 2.42 mmol). GC indicated that at least five compounds were formed, but flash chromatography (*n*-hexane:ethyl acetate = 95:5) afforded only 0.55 g **4c** (74%) as a light yellow oil. IR (film): $\bar{\nu}$ = 3063 w, 2982 m, 2935 m, 2865 m, 1613 w, 1585 w, 1512 s, 1458 w, 1388 w, 1290 m, 1237 s, 1175 w, 1099 w, 1026 s, 856 w, 814 s, 742 m, 717 w cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ = 1.33 (1H, dd, J = 6.6 and 2.6 Hz), 1.57 (1H, dd, J = 6.6 and 1.0 Hz), 1.79–1.82 (1H, m), 2.28 (3H, s, CH_3), 2.34–2.36 (1H, m), 3.03–3.06 (1H, m), 3.12–3.15 (1H, m), 4.16 (1H, d, J = 10.0 Hz, OCH), 4.26 (1H, dd, J = 10.0 and 1.1 Hz, OCH), 6.00–6.02 (1H, m, =CH), 6.03–6.05 (1H, m, =CH), 6.83–6.87 (2H, m, 2 × CH), 7.07–7.09 (2H, m, 2 × CH) ppm; ^{13}C NMR (100 MHz; $CDCl_3$; Me_4Si): δ = 20.4 (CH_3), 28.5 (C), 33.5 (CH_2), 43.6 (CBr), 47.3 (CH), 54.4 (CH), 60.5 (CH_2), 72.6 (OCH_2), 114.5 (2 × CH), 129.7 (2 × CH), 129.9 (C), 133.2 (=CH), 135.1 (=CH), 156.9 (C) ppm; MS (EI): m/z (%) = 306/304 (M^+, 4/4), 198/196 (25/25), 117 (100), 108 (83), 91 (64), 77 (28); HRMS (EI): m/z calcd. for M^+, $C_{16}H_{17}OBr^+$, 304.0463; found 304.0465.

2-Bromo-4-phenyltricyclo[3.2.1.0^{2,4}]oct-6-ene (**4d**, $C_{14}H_{13}Br$)
The synthesis was carried out with 0.96 g **1d** (2.71 mmol), 2.00 cm^3 *Me*Li (1.50 *M*, 3.00 mmol), and 0.20 cm^3 cyclopentadiene (d = 0.80 g/cm^3, 2.42 mmol). GC indicated that at least six compounds were formed, but flash chromatography (*n*-hexane) afforded only 0.34 g **4d** (54%) as a colourless oil. IR (film): $\bar{\nu}$ = 3061 m, 2979 s, 2870 w, 1600 w, 1498 m, 1448 m, 1321 m, 1255 m, 1101 m, 1058 m, 1014 m, 899 w, 856 m, 761 m, 741 s, 698 s cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ = 1.78 (2H, br s, CH_2), 1.91–1.93 (1H, m), 2.62–2.64 (1H, m), 3.05–3.07 (1H, m), 3.24 (1H, m), 6.08–6.10 (1H, m, =CH), 6.17–6.19 (1H, m, =CH), 7.23–7.40 (5H, m, Ph) ppm; ^{13}C NMR (100 MHz; $CDCl_3$; Me_4Si): δ = 32.6 (CH_2), 33.2 (C), 46.9 (CBr), 52.1 (CH), 54.7 (CH), 61.0 (CH_2), 126.4 (CH), 128.1 (2 × CH), 128.3 (2 × CH), 134.6 (=CH), 135.7 (=CH), 140.2 (C) ppm; MS (EI): m/z (%) = 262/260 (M^+, 6/6), 181 ($M^+ - Br$, 100), 77 (30); HRMS (EI): m/z calcd. for $M^+ - Br$, $C_{14}H_{13}^+$, 181.1017; found 181.1008.

2-Bromo-4-(2-phenylethyl)tricyclo[3.2.1.0^{2,4}]oct-6-ene (**4e**, $C_{16}H_{17}Br$)
The synthesis was carried out with 0.96 g **1e** (2.51 mmol), 1.70 cm^3 *Me*Li (1.50 *M*, 2.55 mmol), and 0.20 cm^3 cyclopentadiene (d = 0.80 g/cm^3, 2.42 mmol). TLC and GC indicated that at least seven compounds were formed. Purification by flash chromatography (*n*-hexane) afforded 0.39 g **4e** (56%) as a colourless liquid (R_f = 0.22). IR (film): $\bar{\nu}$ = 3063 m, 3025 m, 2967 s, 2931 s, 2861 m, 1603 w, 1495 m, 1449 m, 1357 w, 1321 m, 1256 m, 1121 w, 1091 m, 1048 m, 1027 m, 959 w, 900 br, 856 m, 795 w, 742 s, 701 s cm^{-1}; ^{1}H NMR (200 MHz; $CDCl_3$; Me_4Si): δ = 0.96 (1H, dd, J = 6.3 and 2.5 Hz), 1.35 (1H, dd, J = 6.3 and 1.4 Hz), 1.68–1.74 (1H, m), 1.81–2.14 (2H, m, CH_2), 2.17 (1H, td, J = 7.3 and 1.7 Hz), 2.61–2.66 (1H, m), 2.65–2.91 (2H, m, CH_2), 3.07–3.12 (1H, m), 5.85–5.89 (1H, m, =CH), 5.95–6.00 (1H, m, =CH), 7.13–7.32 (5H, m, Ph) ppm; ^{13}C NMR (50 MHz; $CDCl_3$; Me_4Si): δ = 28.7 (C), 33.6 (CH_2), 34.6 (CH_2), 35.9 (CH_2), 46.7 (CBr), 48.1 (CH), 54.7 (CH), 59.8 (CH_2), 125.7 (CH), 128.2 (2 × CH), 128.4 (2 × CH), 132.8 (=CH), 135.0 (=CH), 141.9 (C) ppm; MS (EI):

m/z (%) = 290/288 (M^+, 1/1), 209 ($M^+ - Br$, 10), 117 (31), 105 (21), 91 (100), 77 (12), 65 (19), 51 (10); HRMS (EI): m/z calcd. for M^+, $C_{16}H_{17}{}^{81}Br^+$, 290.0493; found 290.0500.

In addition 0.07 g 1-bromo-2-(2-phenylethyl)cyclopropene (**2e**, 13%) were isolated as a light yellow liquid (R_f = 0.34). IR (film): $\bar{\nu}$ = 3062 w, 3027 m, 2963 s, 2926 s, 2880 s, 1836 w, 1603 w, 1495 m, 1451 m, 1078 w, 1034 s, 746 m, 699 s cm^{-1}; ^1H NMR (200 MHz; $CDCl_3$; Me_4Si): δ = 1.55 (2H, t, J = 0.5 Hz, CH_2), 2.70–2.96 (4H, m, 2 × CH_2), 7.16–7.35 (5H, m, Ph) ppm; ^{13}C NMR (50 MHz; $CDCl_3$; Me_4Si): δ = 17.2 (CH_2), 27.3 (CH_2), 32.4 (CH_2), 92.9 (C), 117.1 (C), 126.1 (CH), 128.2 (2 × CH), 128.3 (2 × CH), 140.7 (C) ppm; MS (EI): m/z (%) = 224/222 ($M^+ - C_5H_6$, 1/1), 143 ($M^+ - C_5H_6$-Br, 40), 128 (25), 105 (5), 91 (100), 77 (6), 65 (20), 51 (42); HRMS (EI): m/z calcd. for M^+, $C_{11}H_{11}Br^+$, 222.0044; found 222.0028.

2-Bromo-4-propyltricyclo[3.2.1.0^{2,4}]oct-6-ene (**4f**, $C_{11}H_{15}Br$)

The synthesis was carried out with 0.80 g **1f** (2.49 mmol), 1.70 cm^3 *Me*Li (1.50 *M*, 2.55 mmol), and 0.20 cm^3 cyclopentadiene (d = 0.80 g/cm^3, 2.42 mmol). According to TLC at least eight products were formed, but flash chromatography (*n*-hexane) yielded only 0.12 g **4f** (22%) as a colourless liquid. IR (film): $\bar{\nu}$ = 3063 m, 2962 s, 2931 s, 2869 s, 1456 m, 1377 w, 1322 w, 1268 w, 1245 w, 1074 m, 995 w, 898 w, 857 w, 738 m cm^{-1}; ^1H NMR (200 MHz; $CDCl_3$; Me_4Si): δ = 0.88–1.01 (5H, m), 1.34–1.76 (5H, m), 2.17 (1H, td, J = 7.3 and 1.7 Hz), 2.71–2.76 (1H, m), 3.07–3.12 (1H, m), 5.89–5.94 (1H, m, =CH) and 5.97–6.02 (1H, m, =CH) ppm; ^{13}C NMR (50 MHz; $CDCl_3$; Me_4Si): δ = 14.2 (CH_3), 21.4 (CH_2), 28.7 (C), 33.6 (CH_2), 35.8 (CH_2), 46.7 (CBr), 48.1 (CH), 54.7 (CH), 59.7 (CH_2), 132.7 (=CH), 135.1 (=CH) ppm; MS (EI): m/z (%) = 228/226 (M^+, 3/3), 185/183 (16/16), 147 ($M^+ - Br$, 80), 117 (40), 105 (96), 91 (100), 77 (48), 51 (34); HRMS (EI): m/z calcd. for M^+, $C_{11}H_{15}Br^+$, 226.0357; found 226.0369.

2-Bromo-4-pentyltricyclo[3.2.1.0^{2,4}]oct-6-ene (**4g**, $C_{13}H_{19}Br$)

The synthesis was carried out with 0.87 g **1g** (2.50 mmol), 2.35 cm^3 *Me*Li (1.27 *M*, 2.98 mmol), 0.21 cm^3 cyclopentadiene (d = 0.80 g/cm^3, 2.42 mmol). TLC indicated that at least five compounds were formed, but flash chromatography (*n*-hexane) afforded only 0.18 g **4g** (29%) as a colourless liquid. IR (film): $\bar{\nu}$ = 3064 m, 2960 s, 2927 s, 2860 s, 1456 s, 1375 w, 1322 m, 1256 m, 1081 s, 1052 m, 1015 m, 898 m, 858 m, 800 w, 735 cm^{-1}; ^1H NMR (200 MHz; $CDCl_3$; Me_4Si): δ = 0.87 (4H, m), 1.30–1.62 (8H, m), 1.65–1.79 (2H, m), 2.14–2.19 (1H, m, CH), 2.70–2.75 (1H, m, CH), 3.07–3.12 (1H, m, CH), 5.89–5.93 (1H, m, =CH), 5.97–6.01 (1H, m, =CH) ppm; ^{13}C NMR (50 MHz; $CDCl_3$; Me_4Si): δ = 14.0 (CH_3), 22.6 (CH_2), 27.8 (CH_2), 28.8 (C), 31.9 (CH_2), 33.6 (CH_2), 33.7 (CH_2), 46.8 (CBr), 48.0 (CH), 54.7 (CH), 59.7 (CH_2), 132.7 (=CH), 135.1 (=CH) ppm; MS (EI): m/z (%) = 256/254 (M^+, 6/6), 185/183 (23/23), 175 ($M^+ - Br$, 65), 117 (44), 105 (100), 91 (96), 77 (40), 55 (48); HRMS (EI): m/z calcd. for $M^+ - Br$, $C_{13}H_{19}{}^+$, 175.1487; found 175.1486.

2-Bromo-4-octyltricyclo[3.2.1.0^{2,4}]oct-6-ene (**4h**, $C_{16}H_{25}Br$)

The synthesis was carried out with 0.99 g **1h** (2.53 mmol), 1.70 cm^3 *Me*Li (1.50 *M*, 2.55 mmol), and 0.20 cm^3 cyclopentadiene (d = 0.80 g/cm^3, 2.42 mmol). According to TLC and GC at least five compounds were formed. Purification by flash chromatography (*n*-hexane) afforded 0.25 g **4h** (35%) as a colourless liquid (R_f = 0.73). IR (film): $\bar{\nu}$ = 3064 w, 2973 s, 2926 s, 2856 s, 1458 m, 1374 w, 1321 w, 1255 w, 1085 w, 1051 w, 1034 w, 897 w, 857 w, 737 m cm^{-1}; ^1H NMR (200 MHz; $CDCl_3$; Me_4Si): δ = 0.85–1.00 (5H, m), 1.29–1.75 (6H, m), 2.14–2.19 (1H, m), 2.71–2.74 (1H, m), 3.08–3.11 (1H, m), 5.89–5.93 (1H, m, =CH), 5.97–6.01 (1H, m, =CH) ppm; ^{13}C NMR (50 MHz; $CDCl_3$; Me_4Si): δ = 14.0 (CH_3), 22.6 (CH_2), 28.2 (CH_2), 28.9 (C), 29.2 (CH_2), 29.5 (CH_2), 29.7 (CH_2), 31.8 (CH_2), 33.6 (CH_2), 33.7 (CH_2), 46.8 (CBr), 48.1 (CH), 54.8 (CH), 59.8 (CH_2), 132.7 (=CH), 135.1 (=CH) ppm; MS (EI): m/z (%) = 298/296 (M^+, 9/9), 217 ($M^+ - Br$, 64), 185/183 (29/29), 117 (43), 105 (100), 91 (84), 77 (28), 57 (42); HRMS (EI): m/z calcd. for M^+, $C_{16}H_{25}{}^{81}Br^+$, 298.1119; found 298.1119.

In addition 0.23 g 1-bromo-2-octylcyclopropene (**2h**, 39%) were isolated as a light yellow liquid (R_f = 0.90). IR (film): $\bar{\nu}$ = 2927 s, 2857 s, 1836 w, 1461 m, 1375 w, 1259 w, 1106 w, 1033 m, 804 w,

722 w cm^{-1}; ^{1}H NMR (200 MHz; $CDCl_3$; Me_4Si): $\delta = 0.85$–0.92 (3H, m, CH_3), 1.28–1.43 (10H, m, $5 \times CH_2$), 1.52 (2H, t, $J = 0.5$ Hz, CH_2), 1.53–1.62 (2H, m, CH_2), 2.42 (2H, t, $J = 7.0$ Hz, CH_2) ppm; ^{13}C NMR (50 MHz; $CDCl_3$; Me_4Si): $\delta = 14.0$ (CH_3), 17.1 (CH_2), 22.6 (CH_2), 25.3 (CH_2), 26.2 (CH_2), 29.1 (CH_2), 29.2 ($2 \times CH_2$), 31.7 (CH_2), 92.1 (C), 117.9 (C) ppm; MS (EI): m/z (%) = 151 ($M^+ - Br$, 11), 134/132 (18/18), 109 (21), 95 (59), 81 (49), 67 (46), 55 (78), 41 (100).

2-Bromo-4-cyclohexymethyltricyclo[3.2.1.0^{2,4}]oct-6-ene (**4i**, $C_{15}H_{21}Br$)

The synthesis was carried out with 0.96 g **1i** (2.56 mmol), 1.70 cm^3 *Me*Li (1.50 *M*, 2.55 mmol), and 0.21 cm^3 cyclopentadiene ($d = 0.80$ g/cm^3, 2.42 mmol). TLC indicated that at least three compounds were formed. Purification by flash chromatography (*n*-hexane) afforded 0.13 g **4i** (19%) as a colourless liquid ($R_f = 0.62$). IR (film): $\bar{\nu} = 3062$ w, 2923 br, 2850 s, 1448 m, 1321 w, 1257 w, 1078 br, 1006 w, 966 w, 902 w, 857 w, 738 m cm^{-1}; ^{1}H NMR (200 MHz; $CDCl_3$; Me_4Si): $\delta = 1.03$ (1H, dd, $J = 6.3$ and 2.4 Hz), 1.07–1.39 (5H, m), 1.42 (1H, dd, $J = 6.3$ and 1.7 Hz), 1.69–1.78 (9H, m), 2.13–2.18 (1H, m), 2.71–2.76 (1H, m), 3.07–3.12 (1H, m), 5.91–5.95 (1H, m, =CH), 5.97–6.02 (1H, m, =CH) ppm; ^{13}C NMR (50 MHz; $CDCl_3$; Me_4Si): $\delta = 26.2$ (CH_2), 26.3 (CH_2), 26.5 (CH_2), 27.1 (C), 32.9 (CH_2), 34.0 (CH_2), 34.1 (CH_2), 37.6 (CH), 40.9 (CH_2), 46.7 (CBr), 48.7 (CH), 54.8 (CH), 59.6 (CH_2), 132.8 (=CH), 134.9 (=CH) ppm; MS (EI): m/z (%) = 282/280 (M^+, 5/5), 201 ($M^+ - Br$, 12), 185/183 (8/8), 117 (29), 105 (70), 91 (37), 55 (100); HRMS (EI): m/z calcd. for $M^+ - Br$, $C_{15}H_{21}^+$, 201.1643; found 201.1650.

In addition two by-products, 1-bromo-2-(cyclohexylmethyl)cyclopropene (**2i**, 0.19 g, 35%) and 1-bromo-4-cyclohexylbut-2-yne (0.03 g, 5%) were also isolated ($R_f = 0.79$ and 0.42). **2i**: IR (film): $\bar{\nu} = 2924$ s, 2852 s, 1834 w, 1711 br, 1615 w, 1447 m, 1266 m, 1210 m, 1076 w, 1032 s, 956 w, 908 w, 736 br, 687 w cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): $\delta = 0.96$–1.32 (5H, m), 1.51 (2H, t, $J = 0.5$ Hz, CH_2), 1.57–1.75 (6H, m), 2.32 (2H, d, $J = 6.6$ Hz) ppm; ^{13}C NMR (50 MHz; $CDCl_3$; Me_4Si): $\delta = 17.3$ (CH_2), 26.07 ($2 \times CH_2$), 26.13 (CH_2), 32.99 ($2 \times CH_2$), 33.03 (CH_2), 36.0 (CH), 92.6 (C), 117.1 (C) ppm; MS (EI): m/z (%) = 135 ($M^+ - Br$, 16), 105 (14), 91 (23), 67 (94), 55 (100).

1-Bromo-4-cyclohexylbut-2-yne: IR (film): $\bar{\nu} = 2923$ s, 2851 s, 2249 w, 1448 m, 1211 m, 607 m cm^{-1}; ^{1}H NMR (200 MHz; $CDCl_3$; Me_4Si): $\delta = 0.86$–1.82 (11H, m), 2.13 (2H, td, $J = 2.4$ and 6.6 Hz, CH_2), 3.94 (2H, t, $J = 2.4$ Hz, $(CH_2)Br$) ppm; ^{13}C NMR (50 MHz; $CDCl_3$; Me_4Si): $\delta = 15.8$ (CH_2), 26.0 ($2 \times CH_2$), 26.1 (CH_2), 26.6 (CH_2), 32.5 ($2 \times CH_2$), 37.0 (CH), 76.0 (C), 87.2 (C) ppm; MS (EI): m/z (%) = 216/214 (M^+, 0.3/0.3), 135 ($M^+ - Br$, 26), 107 (6), 93 (17), 83 (98), 67 (24), 55 (100).

2-Bromo-4-isobutyltricyclo[3.2.1.0^{2,4}]oct-6-ene (**4j**, $C_{12}H_{17}Br$)

The synthesis was carried out with 0.83 g **1j** (2.49 mmol), 1.70 cm^3 *Me*Li (1.50 *M*, 2.55 mmol), and 0.20 cm^3 cyclopentadiene ($d = 0.80$ g/cm^3, 2.42 mmol). TLC and GC indicated that at least four compounds were formed, but purification by flash chromatography (*n*-hexane) afforded only 0.15 g **4j** (26%) as a colourless oil. IR (film): $\bar{\nu} = 3063$ m, 2958 br, 2871 s, 2841 m, 1462 m, 1366 w, 1324 m, 1249 w, 1081 br, 1004 w, 956 w, 901 w, 856 m, 738 m cm^{-1}; ^{1}H NMR (200 MHz; $CDCl_3$; Me_4Si): $\delta = 0.90$ (3H, d, $J = 6.5$ Hz, CH_3), 0.97 (3H, d, $J = 6.3$ Hz, CH_3), 1.04 (1H, dd, $J = 6.3$ and 2.5 Hz), 1.25–1.38 (1H, m), 1.44 (1H, dd, $J = 6.3$ and 1.6 Hz), 1.68–1.86 (3H, m), 2.16 (1H, td, $J = 7.3$ and 1.7 Hz), 2.73–2.78 (1H, m), 3.08–3.13 (1H, m), 5.90–5.95 (1H, m, =CH), 5.98–6.03 (1H, m, =CH) ppm; ^{13}C NMR (50 MHz; $CDCl_3$; Me_4Si): $\delta = 22.2$ (CH_3), 23.4 (CH_3), 27.6 (C), 28.1 (CH), 34.1 (CH_2), 42.2 (CH_2), 46.5 (CBr), 48.6 (CH), 54.8 (CH), 59.6 (CH_2), 132.8 (=CH), 134.9 (=CH) ppm; MS (EI): m/z (%) = 242/240 (M^+, 3/3), 185/183 (14/14), 161 ($M^+ - Br$, 20), 117 (53), 105 (100), 91 (67), 77 (40), 57 (39); HRMS (EI): m/z calcd. for M^+, $C_{12}H_{17}Br^+$, 240.0514; found 240.0500.

*Reaction with **1k***

The synthesis was carried out with 0.85 g **1k** (2.54 mmol), 1.70 cm^3 *Me*Li (1.50 *M*, 2.55 mmol), and 0.20 cm^3 cyclopentadiene ($d = 0.80$ g/cm^3, 2.42 mmol). TLC and GC indicated that at least nine compounds were formed. Purification by flash chromatography (*n*-hexane) yielded a colourless oil (0.10 g, $R_f = 0.63$). NMR analysis proved that this was a mixture of **1k**, and the *endo* and *exo* isomers

of 2-bromo-4-*tert*-butyltricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**4k**) in a 3:6:1 ratio. Thus, the combined yield of the *endo* and *exo* isomers of **4k** is 12%. The cyclopropane ring protons in **1k** give rise to two doublets at 1.90 and 2.21 ppm in the ^{1}H NMR spectrum, while the two multiplets at 5.75–5.98 and 5.88–6.04 ppm are due to the vinylic protons in the *endo* and *exo* isomers of **4k**, respectively.

General Procedure for the Formation and Trapping of 1-Bromocyclopropenes with Furan

Cyclopropane **1** and furan (~10 eq) were dissolved in 40 cm^3 *THF* in a round-bottomed flask, equipped with a condenser connected to a N_2 inlet. The solution was cooled to −78°C (acetone/dry-ice or ethyl acetate/liquid N_2). *Me*Li (1.01–1.13 eq) was added dropwise with a syringe with magnetic stirring. The reactions were monitored by either TLC or GC and quenched with a portion of water. The product **5** was extracted with diethyl ether, the solution was dried ($MgSO_4$), filtrated, and evaporated *in vacuo*, and finally **5** was isolated by flash chromatography.

*Reaction with **1a***

The synthesis was carried out with 0.95 g **1a** (2.63 mmol), 2.00 cm^3 *Me*Li (1.50 *M*, 3.00 mmol), and 2.00 cm^3 furan ($d = 0.94$ g/cm^3, 27.61 mmol). Evaporation *in vacuo* afforded 0.47 g 9-bromobicyclo-[6.1.0]non-1(9)-ene (**2a**, 100%) as a yellow oil [19, 42, 43]. IR (film): $\bar{\nu} = 2924$ s, 2855 s, 1702 m, 1452 s, 1348 w, 1319 w, 1237 w, 1059 m, 1019 m, 862 w, 754 w, 671 w cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): $\delta = 1.19$–1.67 (9H, m), 1.79–1.88 (1H, m), 2.12–2.23 (2H, m), 2.70 (1H, ddd, $J = 14.7$, 5.7 and 3.9 Hz) ppm; ^{13}C NMR (100 MHz; $CDCl_3$; Me_4Si): $\delta = 19.7$ (CH_2), 24.7 (CH_2), 24.97 (CH_2), 24.99 (CH_2), 29.0 (CH), 29.4 (CH_2), 30.5 (CH_2), 97.1 (C), 123.4 (C) ppm; MS (EI): m/z (%) = 202/200 (M^+, 25/25), 121 ($M^+ - Br$, 21), 105 (11), 93 (74), 91 (42), 79 (100), 67 (38).

2-Bromo-8-oxa-4-phenoxymethyltricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**5b**, $C_{14}H_{13}O_2Br$)

The synthesis was carried out with 0.96 g **1b** (2.50 mmol), 1.70 cm^3 *Me*Li (1.50 *M*, 2.55 mmol), and 2.00 cm^3 furan ($d = 0.94$ g/cm^3, 27.61 mmol). According to TLC and GC at least eight compounds were formed, but only 0.23 g **5b** (31%) were isolated by flash chromatography (*n*-hexane:ethyl acetate = 98:2) as a colourless oil. This was characterised as pure *exo* isomer, because of the large difference in the chemical shift of the doublet and double doublet at 1.44 and 2.41 ppm, which were assigned to the H atoms in the cyclopropane moiety. In addition impure *endo* isomer (0.11 g, 15%) was isolated. This was not pure enough to obtain satisfying spectra, but in the ^{1}H NMR spectrum a doublet at 1.76 ppm ($J = 6.9$ Hz) and a double doublet at 1.86 ppm ($J = 6.9$ and 1.4 Hz) were assigned to the H atoms in the cyclopropane moiety. *Exo*-**5b**: IR (film): $\bar{\nu} = 3062$ w, 3006 m, 2916 w, 2869 w, 1594 s, 1494 s, 1467 m, 1429 w, 1392 m, 1295 s, 1237 br, 1174 m, 1132 m, 1081 m, 1030 s, 919 s, 886 m, 873 s, 821 w, 782 w, 754 s, 692 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): $\delta = 1.44$ (1H, d, $J = 6.4$ Hz), 2.41 (1H, dd, $J = 6.4$ and 1.3 Hz), 3.95 (1H, d, $J = 10.5$ Hz, OCH), 4.05 (1H, dd, $J = 10.5$ and 1.3 Hz), 4.84 (1H, d, $J = 1.5$ Hz), 4.91 (1H, d, $J = 1.5$ Hz), 6.67 (1H, dd, $J = 5.7$ and 1.5 Hz, =CH), 6.72 (1H, dd, $J = 5.7$ and 1.5 Hz, =CH), 6.89–6.98 (3H, m, Ph), 7.25–7.30 (2H, m, Ph) ppm; ^{13}C NMR (50 MHz; $CDCl_3$; Me_4Si): $\delta = 29.4$ (CH_2), 34.4 (C), 44.8 (CBr), 69.6 (OCH_2), 79.0 (OCH), 81.4 (OCH), 114.4 (2 × CH), 121.0 (CH), 129.3 (2 × CH), 138.6 (=CH), 139.5 (=CH), 158.5 (C) ppm; MS (EI): m/z (%) = 294/292 (M^+, 4/4), 213 ($M^+ - Br$, 3), 91 (100), 77 (20), 65 (26).

2-Bromo-4-(4-methylphenoxy)methyl-8-oxatricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**5c**, $C_{15}H_{15}O_2Br$)

The synthesis was carried out with 1.04 g **1c** (2.61 mmol), 2.00 cm^3 *Me*Li (1.50 *M*, 3.00 mmol), and 2.00 cm^3 furan ($d = 0.94$ g/cm^3, 27.61 mmol). TLC and GC indicated that at least six compounds were formed. Purification by flash chromatography (*n*-hexane:ethyl acetate = 97.5:2.5) afforded 0.38 g **5c** (49%) as a colourless oil ($R_f = 0.16$). This was characterised as pure *exo* isomer on the same grounds as for **5b**. Traces of the *endo* isomer were observed in the ^{1}H NMR spectrum of the crude product as a doublet at 1.75 ppm ($J = 6.9$ Hz) and a double doublet at 1.85 ppm ($J = 6.9$ and 1.4 Hz), which were assigned to the H atoms in the cyclopropane moiety. Isolation efforts were unsuccessful. *Exo*-**5c**: IR (film): $\bar{\nu} = 3004$ m, 2919 m, 2866 w, 1612 m, 1587 w, 1512 s, 1464 m, 1433 w, 1391 m, 1293 s, 1235 br,

1179 m, 1127 m, 1028 s, 920 br, 871 s, 815 s, 753 w, 702 m, 614 w cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$; Me_4Si): $\delta = 1.44$ (1H, d, $J = 6.3$ Hz), 2.28 (3H, s, CH_3), 2.41 (1H, dd, $J = 6.3$ and 1.3 Hz), 3.94 (1H, d, $J = 10.5$ Hz, OCH), 4.04 (1H, dd, $J = 10.5$ and 1.3 Hz, OCH), 4.84 (1H, d, $J = 1.7$ Hz), 4.92 (1H, d, $J = 1.5$ Hz), 6.68 (1H, dd, $J = 5.8$ and 1.7 Hz, =CH), 6.74 (1H, dd, $J = 5.8$ and 1.5 Hz, =CH), 6.80–6.83 (2H, m, $2 \times$ CH), 7.07–7.09 (2H, m, $2 \times$ CH) ppm; ^{13}C NMR (100 MHz; $CDCl_3$; Me_4Si): $\delta = 20.4$ (CH_3), 29.5 (CH_2), 34.5 (C), 44.8 (CBr), 69.9 (OCH_2), 79.1 (CO), 81.4 (CO), 114.4 ($2 \times$ CH), 129.8 ($2 \times$ CH), 130.3 (C), 138.7 (=CH), 139.5 (=CH), 156.5 (C) ppm; MS (EI): m/z (%) = 308/306 (M^+, 8/8), 201/199 (4/4), 108 (26), 91 (100), 77 (15); HRMS (EI): m/z calcd. for M^+, $C_{15}H_{15}O_2Br^+$, 306.0255; found 306.0252.

In addition 0.08 g impure 1-bromo-2-[(4-methylphenoxy)methyl]cyclopropene (**2b**, 13%) were isolated as a yellow oil ($R_f = 0.34$). ^{13}C NMR (100 MHz; $CDCl_3$; Me_4Si): $\delta = 9.2$ (CH_2), 20.4 (CH_3), 63.9 (OCH_2), 105.9 (C), 110.8 (C), 114.5 ($2 \times$ CH), 129.7 ($2 \times$ CH), 129.8 (C), 156.1 (C) ppm.

*Reaction with **1d***

The synthesis was carried out with 0.89 g **1d** (2.51 mmol), 1.70 cm^3 *Me*Li (1.50 *M*, 2.55 mmol), and 2.00 cm^3 furan ($d = 0.94$ g/cm^3, 27.61 mmol). The brown crude product consisted of at least four compounds according to TLC. NMR analyses indicated that two compounds were 1-(3-bromoprop-1-ynyl)benzene and 1-(1-bromopropa-1,2-dienyl)benzene (in a 2:3 ratio). The acetylene gives rise to a singlet at 4.05 ppm, which is assigned to the methylene group. The same group in the allene gives rise to a singlet at 5.29 ppm. Efforts to isolate the products were unsuccessful.

*Reaction with **1e***

The synthesis was carried out with 0.96 g **1e** (2.51 mmol), 1.70 cm^3 *Me*Li (1.50 *M*, 2.55 mmol), and 2.00 cm^3 furan ($d = 0.94$ g/cm^3, 27.61 mmol). The yellow crude product was 0.54 g essentially pure **2e** (96%), but some was lost during purification by flash chromatography (*n*-hexane). The spectroscopic data were identical to those given above.

*Reaction with **1f***

The synthesis was carried out with 0.80 g **1f** (2.51 mmol), 1.70 cm^3 *Me*Li (1.50 *M*, 2.55 mmol), and 2.00 cm^3 furan ($d = 0.94$ g/cm^3, 27.61 mmol). Evaporation *in vacuo* afforded an orange liquid (0.42 g) which according to TLC consisted of at least five compounds. Isolation of the compounds by flash chromatography (*n*-hexane:ethyl acetate = 97.5:2.5) was not successful.

*Reaction with **1g***

The synthesis was carried out with 0.87 g **1g** (2.49 mmol), 1.70 cm^3 *Me*Li (1.50 *M*, 2.55 mmol), and 2.00 cm^3 furan ($d = 0.94$ g/cm^3, 27.61 mmol). Evaporation *in vacuo* afforded an orange liquid (0.65 g) which according to TLC consisted of at least four compounds. Purification by flash chromatography (*n*-hexane) yielded a colourless oil (0.42 g) which according to ^1H NMR consisted of some 1-bromooct-2-yne and 3-bromoocta-1,2-diene (in a 1:30 ratio). The acetylene gives rise to a singlet at 4.11 ppm, which are assigned to the methylene group at C1; the same group in the allene gives rise to a singlet at 5.00 ppm. However, isolation efforts were unsuccessful.

*Reaction with **1h***

The synthesis was carried out with 0.98 g **1h** (2.51 mmol), 1.70 cm^3 *Me*Li (1.50 *M*, 2.55 mmol), and 2.00 cm^3 furan ($d = 0.94$ g/cm^3, 27.61 mmol). Evaporation *in vacuo* afforded an orange liquid (0.60 g) which according to TLC consisted of at least five compounds. Purification by flash chromatography (*n*-hexane) afforded 0.13 g 1-bromoundec-2-yne (**6**) (22%) and 0.10 g 3-bromoundeca-1,2-diene (**7**) (17%) as colourless oils ($R_f = 0.44$ and 0.70).

6: IR (film): $\bar{\nu} = 2926$ s, 2857 s, 2249 w, 1461 m, 1374 w, 1330 w, 1212 m cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$; Me_4Si): $\delta = 0.87$–0.90 (3H, m, CH_3), 1.28–1.40 (10H, m, $5 \times CH_2$), 1.47–1.54 (2H, m, CH_2), 2.21–2.26 (2H, m, CH_2), 3.93 (2H, t, $J = 2.4$ Hz, (CH_2)Br) ppm; ^{13}C NMR (100 MHz;

$CDCl_3$; Me_4Si): $\delta = 14.0$ (CH_3), 15.7 (CH_2), 18.8 (CH_2), 22.5 (CH_2), 28.3 (CH_2), 28.7 (CH_2), 28.9 (CH_2), 29.0 (CH_2), 31.7 (CH_2), 75.1 (C), 88.2 (C) ppm; MS (EI): m/z (%) = 175/173 ($M^+ - Bu$, 4/4), 109 (26), 95 (100), 81 (54), 67 (43), 55 (43), 41 (44).

7: IR (film): $\bar{\nu} = 2927$ s, 2857 s, 1460 m, 1376 w, 1255 w, 1117 w, 1049 w, 962 w, 867 m cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$; Me_4Si): $\delta = 0.88$ (3H, t, $J = 6.9$ Hz, CH_3), 1.28–1.34 (10H, m, $5 \times CH_2$), 1.48–1.55 (2H, m, CH_2), 2.36–2.41 (2H, m, CH_2), 4.82 (2H, t, $J = 3.2$ Hz, $=CH_2$) ppm; ^{13}C NMR (100 MHz; $CDCl_3$; Me_4Si): $\delta = 14.0$ (CH_3), 22.5 (CH_2), 27.7 (CH_2), 28.4 (CH_2), 29.10 (CH_2), 29.14 (CH_2), 31.7 (CH_2), 37.1 (CH_2), 81.1 ($=CH_2$), 93.1 (=CBr), 203.9 (C) ppm; MS (EI): m/z (%) = 151 ($M^+ - Br$, 14), 134/132 (44/44), 109 (40), 95 (83), 81 (68), 67 (57), 55 (84), 41 (100).

*Reaction with **1i***

The synthesis was carried out with 0.93 g **1i** (2.48 mmol), 1.60 cm^3 *Me*Li (1.60 *M*, 2.56 mmol), and 2.00 cm^3 furan ($d = 0.94$ g/cm^3, 27.61 mmol). The orange crude product was 0.52 g essentially pure **2i** (74%), but some was lost during purification by flash chromatography (*n*-hexane:ethyl acetate = 98:2). The spectroscopic data were consistent with previous analyses.

*Reaction with **1j***

The synthesis was carried out with 0.83 g **1j** (2.48 mmol), 1.70 cm^3 *Me*Li (1.50 *M*, 2.55 mmol), and 2.00 cm^3 furan ($d = 0.94$ g/cm^3, 27.61 mmol). Evaporation *in vacuo* afforded a yellow liquid (0.52 g) which according to TLC consisted of at least four compounds. However, purification by flash chromatography (*n*-hexane:ethyl acetate = 98:2) was unsuccessful.

*Reaction with **1k***

The synthesis was carried out with 0.84 g **1k** (2.49 mmol), 1.60 cm^3 *Me*Li (1.60 *M*, 2.56 mmol), and 2.00 cm^3 furan ($d = 0.94$ g/cm^3, 27.61 mmol). Evaporation *in vacuo* afforded an orange liquid (0.64 g) which according to TLC consisted of at least four compounds. However, purification by flash chromatography (*n*-hexane:ethyl acetate = 98:2) was unsuccessful.

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