

# High-pressure cycloaddition reactions of 3-bromo-1,5-azulenequinone and 3-bromo-1,7-azulenequinone with dienophiles

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The high-pressure Diels–Alder reaction of 3-bromo-1,5-azulenequinone and 3-bromo-1,7-azulenequinone with several dienophiles under 300 MPa pressure gave 1 : 1 [4 + 2] cycloadducts in good yields. Bromoazulenequinones reacted with dienophiles on the seven-membered ring in such a way as not to produce a cyclopentadienone moiety.

Azulenequinones are regarded to be extended quinones and isomers of naphthoquinone. From theoretical calculations on the stabilities of azulenequinones, 1,2-, 1,5- and 1,7-azulenequinones were suggested to be stable.<sup>1</sup> In 1984, Scott *et al.* reported the synthesis of 1,5-azulenequinone and 1,7-azulenequinone and their Diels–Alder reaction with 1,3-diphenylbenzo[*c*]furan, which gave single [4 + 2]–[6 + 4] cycloadducts, respectively.<sup>2</sup> The stereochemistry and the mechanism of the adducts, however, have not been defined. Recently, a practical method to prepare 3-bromo-1,5-azulenequinone **B-5-AQ** and 3-bromo-1,7-azulenequinone **B-7-AQ** has been developed from the bromination of azulene in an aqueous medium.<sup>3</sup> The convenient preparation of bromoazulenequinones made it possible to investigate their chemical properties systematically.<sup>4</sup> It is known that tropone behaves as 2 $\pi$ , 4 $\pi$ , 6 $\pi$  and 8 $\pi$  components<sup>5</sup> in cycloadditions. Since both **B-5-AQ** and **B-7-AQ** contain a tropone and a cyclopentenone structure, it would be worth investigating cycloadditions of azulenequinones in respect to comparing them with those of tropones.<sup>6</sup>

## Results and discussion

### Cycloaddition of **B-5-AQ** with acyclic monoolefins

The Diels–Alder reaction of **B-5-AQ** with ethene **1** occurred by heating a chlorobenzene solution in an autoclave (4 MPa) at 150 °C for 5 h to afford a single product, compound **2**, in 55% yield. The mass spectrum and elemental analysis of product **2** showed that it is a 1 : 1-cycloadduct of substrates **B-5-AQ** and **1**. The <sup>1</sup>H NMR spectral data revealed four olefinic protons, a methine proton, and four methylene protons. This is characteristic of the dihydrohomobarrelenone system, which indicated that the reaction occurred on the tropone part to give a [4 + 2] adduct. The IR spectrum showed the presence of two kinds of  $\alpha,\beta$ -unsaturated carbonyl groups and the <sup>13</sup>C NMR spectrum of product **2** disclosed 12 lines. These data supported the proposed structure of compound **2** as tricyclo[6.2.2.0<sup>1,5</sup>]dodecane-3,5,9-triene-2,7-dione.

When a chlorobenzene solution of **B-5-AQ** and styrene **3** was heated at 130 °C under 300 MPa, two adducts **4** and **5** were obtained in 25 and 55% yield, respectively. Their mass spectra were consistent with a 1 : 1-adduct between substrates **B-5-AQ** and **3** and <sup>1</sup>H NMR spectra revealed four olefinic proton signals, two methine proton signals, and two methylene proton

signals. These data suggested that products **4** and **5** were derivatives of compound **2**. The splitting pattern of the bridgehead proton signal [ $\delta$  3.78 (ddm, *J* 8.4 and 6.2 Hz) for **4** and 3.78 (ddm, *J* 7.7 and 6.6 Hz) for **5**] indicated that the phenyl groups of compounds **4** and **5** were located at C-11. The stereochemistry of the phenyl group of compound **5** was determined to be  $\beta$  by the difference in chemical shift of the olefinic proton signals at C-3; the olefinic proton at C-3 of product **5** appeared at  $\delta$  6.32, which is to higher field than that for product **4** at  $\delta$  6.71. This should be an anisotropy effect of the phenyl group.

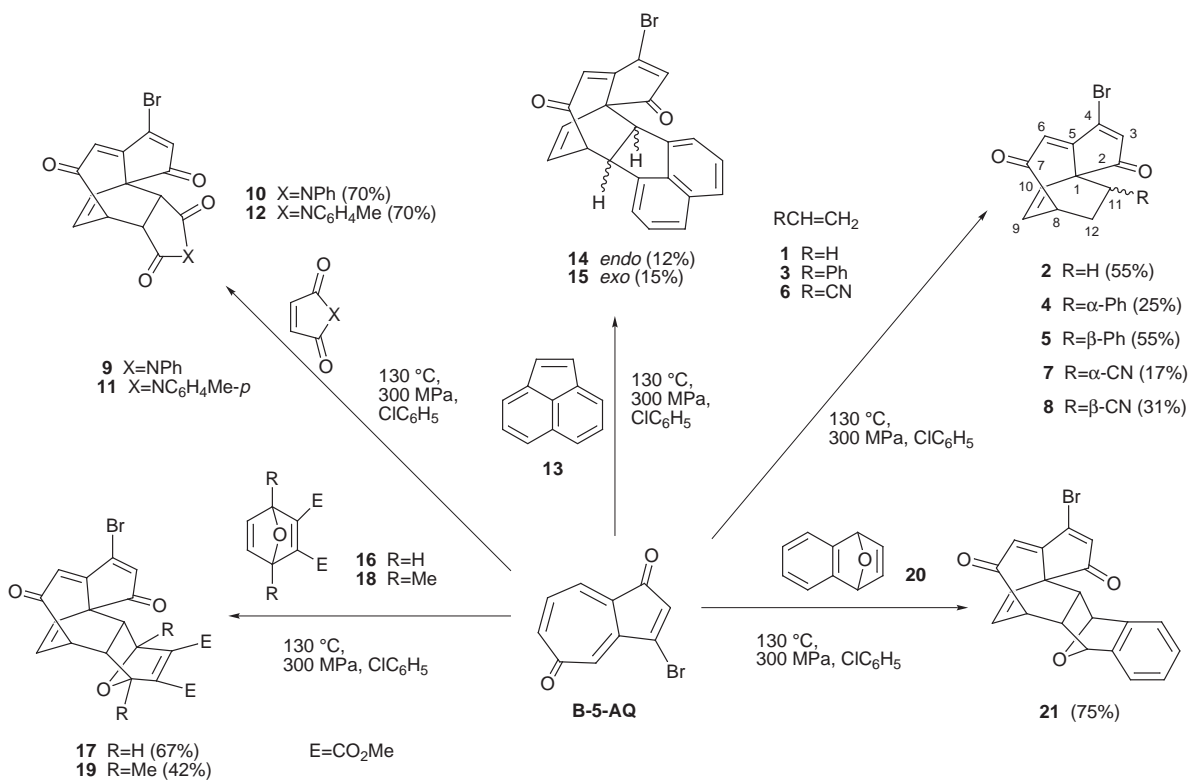
Thus, the reaction was not stereoselective, but regioselective. The preferential formation of the *exo* adduct suggests that the cycloaddition proceeded in a thermodynamically controlled manner under 300 MPa pressure.

In the reaction of **B-5-AQ** with acrylonitrile **6**, two adducts (**7** and **8**) were obtained in 17 and 31% yield, respectively. Their mass spectra were consistent with 1 : 1 adducts and the <sup>1</sup>H NMR spectrum revealed four olefinic proton signals and four methine proton signals. In the <sup>1</sup>H NMR spectrum of product **7**, a methine proton signal at C-8 appeared at  $\delta$  3.78 (ddm, *J* 8.1 and 7.0 Hz), which did not couple with a methine proton signal of C-11 at  $\delta$  3.21 and showed correlation to the signal at  $\delta$  2.39. Furthermore, the methine proton at C-11 behaved as a doublet with additional splittings; these spectral features indicated that the stereochemistry of the methine proton at C-11 was  $\beta$ . In the <sup>1</sup>H NMR spectrum of product **8**, the corresponding methine proton signal at C-11 appeared at  $\delta$  3.19, and its coupling constants, *J* 10.6 and 6.6 Hz, with the adjacent C-12 proton eliminated structures other than that depicted.

### Cycloaddition of **B-5-AQ** with cyclic olefins

When a chlorobenzene solution of **B-5-AQ** and *N*-phenylmaleimide **9** was heated at 120 °C under 300 MPa, a 1 : 1 [4 + 2] adduct **10** was isolated in 70% yield. The <sup>1</sup>H NMR spectral features were markedly different from those of compound **2** in respect of the chemical shifts. From the coupling constant of the bridgehead proton at  $\delta$  4.34 (dm, *J* 7.7 Hz), product **10** was an *endo* adduct as shown. Under the same conditions, **B-5-AQ** and *N-p*-tolylmaleimide **11** afforded a single product, compound **12**, in 70% yield, which was also an *endo* adduct.

Similarly, the reaction of **B-5-AQ** and acenaphthylene **13** gave two 1 : 1 adducts (**14** and **15**) in 12 and 15% yield,



Scheme 1

respectively. The main product **15** was an *exo* [4 + 2] adduct from the spectral data whereas the minor one **14** was an *endo* [4 + 2] adduct.

#### Cycloaddition of B-5-AQ with bicyclo[2.2.1]heptadienes

The reactions of **B-5-AQ** with 2,3-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]heptadiene **16** and its 1,4-dimethyl derivative **18** gave *endo* [4 + 2] adducts (**17** and **19**), implying reaction of the tropone moiety and substrates **16** and **18**.<sup>7</sup> Similarly, the reaction of **B-5-AQ** with 1,4-epoxy-1,4-dihydronaphthalene **20** gave the corresponding *endo* [4 + 2] adduct **21** as the sole product. All these reactions of **B-5-AQ** are shown in Scheme 1.

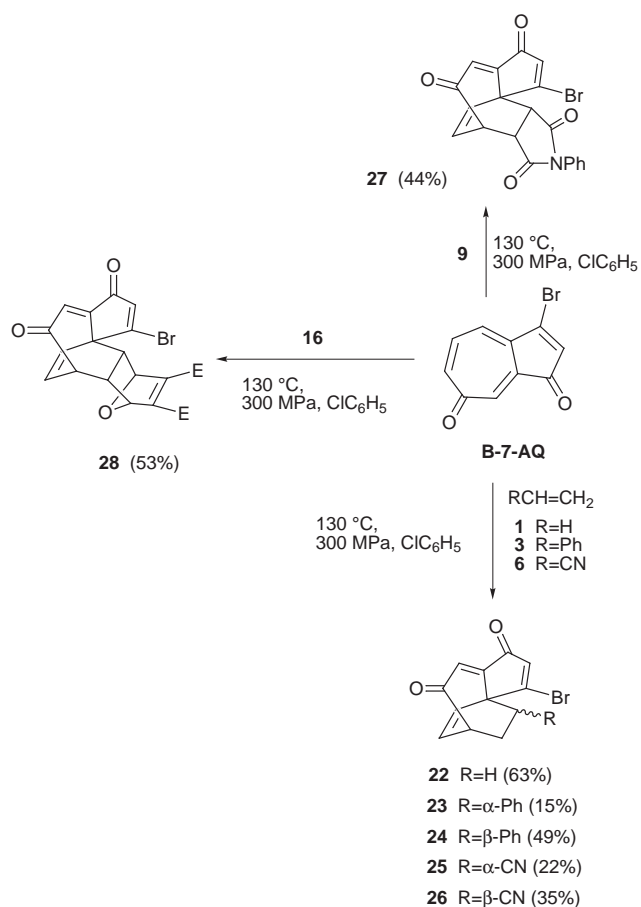
#### Cycloaddition of B-7-AQ with dienophiles

The reactivity of **B-7-AQ** with ethene **1** was similar to that of **B-5-AQ**, and gave a single 1 : 1 [4 + 2] adduct, compound **22**, by heating for 3 h in an autoclave. The reactivity of **B-7-AQ** with other dienophiles, however, was lower than that of **B-5-AQ**. From the reaction of styrene **3** and **B-7-AQ**, 1 : 1 [4 + 2] adducts **23** and **24** were obtained. With acrylonitrile **6** it was necessary to heat the reactants for prolonged period, 36 h, under similar conditions to obtain the stereoisomeric 1 : 1 [4 + 2] adducts **25** and **26**. A single 1 : 1 [4 + 2] cycloadduct **27** was formed from the reaction of **B-7-AQ** with *N*-phenylmaleimide **9** under the conditions used for the reaction of **B-5-AQ** with dienophile **9**. The reaction of **B-7-AQ** and bicycle **16** gave the corresponding *endo* [4 + 2] adduct **28** in 53% yield. These reactions of **B-7-AQ** are presented in Scheme 2.

#### <sup>13</sup>C NMR Chemical-shifts assignment of 11-cyano and 11-phenyl adducts

The <sup>13</sup>C NMR spectra provided a sound basis for structure identification of the 11-cyano- and 11-phenyl-homobarrelenone derivatives. Table 1 summarizes these data together with the chemical-shift differences of each carbon of the cyano and phenyl derivatives calculated therefrom.

Among the derivatives, the chemical shift differences ( $\Delta\delta$ ) were obtained from comparison with their parent compounds **2** and **22**. As can be seen in Table 1, compounds having the same



Scheme 2

stereochemistry show very similar chemical shifts. For example, in the 11 $\alpha$ -cyano compounds,  $\Delta\delta$  for C-8 were +2.7 and +2.1 ppm and those of C-12 were -5.5 and -7.3. In the 11 $\alpha$ -phenyl compounds,  $\Delta\delta$  for C-8 were -0.6 and -0.8 and those for C-12 were -11.6 and -12.0 ppm. Also, in the series with the 11 $\beta$ -cyano group,  $\Delta\delta$  for C-8 were +1.0 and +1.2 and

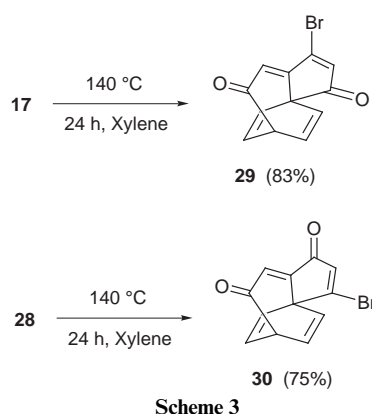
**Table 1**  $^{13}\text{C}$  NMR Spectral data of 1:1 adducts<sup>a</sup>

	<b>2</b>	<b>4</b> ( $\alpha$ -Ph)	<b>5</b> ( $\beta$ -Ph)	<b>7</b> ( $\alpha$ -CN)	<b>8</b> ( $\beta$ -CN)
C-1	54.4	58.2 (-3.8)	60.5 (-6.1)	52.4 (+2.0)	55.0 (-0.6)
C-2	201.8	199.0 (+2.8)	201.1 (+0.7)	196.0 (+5.8)	198.6 (+3.2)
C-3	133.1	131.4 (+1.7)	134.5 (-1.4)	130.1 (+3.0)	132.0 (+1.1)
C-4	159.0	159.8 (-0.8)	156.8 (+2.2)	154.0 (+5.0)	154.9 (+4.1)
C-5	151.6	150.5 (+1.1)	152.8 (-1.2)	150.6 (+1.0)	153.7 (-2.1)
C-6	129.9	131.3 (-1.4)	129.1 (+0.8)	129.9 (0)	131.1 (-1.2)
C-7	196.7	196.4 (+0.3)	196.7 (0)	193.0 (+3.7)	194.1 (+2.6)
C-8	51.8	52.4 (-0.6)	52.2 (-0.4)	49.1 (+2.7)	50.8 (+1.0)
C-9	138.9	141.6 (-2.7)	140.1 (-1.2)	138.0 (+0.9)	140.0 (-1.1)
C-10	123.3	123.1 (+0.2)	123.8 (-0.5)	123.3 (0)	124.3 (-1.0)
C-11	30.4	49.7 (-19.3)	48.6 (-18.2)	31.3 (-0.9)	32.0 (-1.6)
C-12	21.0	33.5 (-11.6)	29.3 (-7.4)	27.4 (-5.5)	26.6 (-4.7)
CN				117.6	117.8

	<b>22</b>	<b>23</b> ( $\alpha$ -Ph)	<b>24</b> ( $\beta$ -Ph)	<b>25</b> ( $\alpha$ -CN)	<b>26</b> ( $\beta$ -CN)
C-1	55.3	58.1 (-2.8)	60.6 (-5.3)	55.0 (+0.3)	56.8 (-1.5)
C-2	197.3	196.6 (+0.7)	197.1 (+0.2)	194.2 (+3.1)	194.6 (+2.7)
C-3	134.9	132.8 (+2.1)	136.8 (-1.9)	133.1 (+1.8)	133.7 (+1.2)
C-4	164.1	164.2 (-0.1)	162.1 (+2.0)	160.3 (+3.8)	158.0 (+6.1)
C-5	153.2	154.8 (-1.6)	151.4 (+1.8)	149.3 (+3.9)	149.0 (+4.2)
C-6	128.8	130.3 (-1.5)	129.7 (-0.9)	129.1 (-0.3)	129.7 (-0.9)
C-7	190.7	190.5 (+0.2)	190.7 (0)	188.6 (+2.1)	188.7 (+2.0)
C-8	52.0	52.8 (-0.8)	52.3 (-0.3)	49.9 (+2.1)	50.8 (+1.2)
C-9	136.8	141.2 (-4.4)	138.3 (-1.5)	139.6 (-2.8)	139.7 (-2.9)
C-10	122.5	121.9 (+0.6)	122.9 (-0.4)	123.6 (-1.1)	123.8 (-1.3)
C-11	32.3	52.5 (-20.2)	48.9 (-16.6)	35.0 (-2.7)	34.2 (-1.9)
C-12	22.1	34.1 (-12.0)	31.0 (-8.9)	29.4 (-7.3)	26.8 (-4.7)
CN				119.4	117.6

<sup>a</sup> + Means low-field shift, and - means high-field shift, compared with the chemical shift of the corresponding carbon in the unsubstituted parent adduct **2** or **22**.



those of C-12 were  $-4.7$  ppm. In the series with an  $11\beta$ -phenyl group,  $\Delta\delta$  for C-8 were  $-0.4$  and  $-0.3$  and those of C-12 were  $-7.4$  and  $-8.9$  ppm. These spectral data supported the assigned structures.

### Conclusions

High-pressure conditions were conveniently applied to the Diels–Alder reaction of **B-5-AQ** and **B-7-AQ** with dienophiles. Stable monoadducts were obtained in good yield. Consequently, compounds **B-5-AQ** and **B-7-AQ** always behaved as tropone derivatives to furnish 1:1 [4 + 2] cycloadducts. The sites of the reaction were determined not to yield a chemically reactive and electronically unstable cyclopentadienone chromophore.

### Experimental

Elemental analyses were performed at the elemental analysis laboratory of the Institute of Advanced Material Study, Kyushu University. Mps were obtained on a Yanagimoto Micro Melting Point Apparatus and are uncorrected. The NMR spec-

tra were measured on JEOL GSX 270H, LA 400, and LA 600 spectrometers for samples in  $\text{CDCl}_3$ ; chemical shifts are expressed in  $\delta$ -units and  $J$ -values are given in Hz. Mass spectra were measured with JEOL O1SG-2 and JMS-70 spectrometers. IR spectra were recorded on a JASCO IR-A102 spectrometer with KBr disks. The stationary phase for column chromatography was Wakogel C-300 and the eluent was a mixture of ethyl acetate and hexane. Crystalline compounds were recrystallized from a mixture of hexane and chloroform.

### Thermal reaction of B-5-AQ with ethene 1

A chlorobenzene solution ( $15 \text{ cm}^3$ ) of **B-5-AQ** (25 mg) was heated with ethene **1** in an autoclave (4 MPa) at  $150^\circ\text{C}$  for 5 h. After the volatile material had been removed *in vacuo*, the residue was chromatographed on a silica gel column to give adduct **2** (15.4 mg, 55%) as crystals, mp  $153$ – $155^\circ\text{C}$ ;  $\delta_{\text{H}}$  1.9–2.1 (4 H, m), 3.6–3.7 (1 H, m), 6.04 (1 H, dd,  $J$  1.8 and 0.7), 6.28 (1 H, dd,  $J$  8.4 and 1.5), 6.32 (1 H, dd,  $J$  8.4 and 6.6) and 6.79 (1 H, d,  $J$  0.7 Hz);  $\delta_{\text{C}}$  21.9, 30.4, 51.8, 54.4, 123.3, 129.9, 133.1, 138.9, 151.6, 159.0, 196.7 and 201.8;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  1713, 1663 and 1532;  $m/z$  (%) 266 ( $\text{M}^+$  for  $^{81}\text{Br}$ , 16), 264 ( $\text{M}^+$  for  $^{79}\text{Br}$ , 19), 238 (38), 236 (39), 157 (49), 128 (100) and 77 (30);  $\lambda_{\text{max}}(\text{MeOH})/\text{nm}$  230.9 ( $\epsilon$  6950) and 283.0 (15 800) (Found: C, 54.7; H, 3.6. Calc. for  $\text{C}_{12}\text{H}_9\text{BrO}_2$ : C, 54.37; H, 3.42%).

### High-pressure reactions of azulenequinones and dienophiles (general procedure)

A mixture of **B-5-AQ** (47.4 mg) and styrene **3** (41 mg) in chlorobenzene ( $5 \text{ cm}^3$ ) in a screw-capped Teflon cylinder was replaced in a pressure vessel filled with silicone oil as transmission medium. Reactions under a pressure of 300 MPa, which was applied *via* an oil-compressor and measured by a Heise-Bourdon gauge, were carried out using a Hikari-koatsu KP-5-B high-pressure reactor. The temperature was kept at  $130^\circ\text{C}$  for 15 h. After the mixture had been cooled and depressurized, the volatile material was removed *in vacuo*. The

residue was chromatographed on a silica gel column to give adducts **4** (16.6 mg, 25%), **5** (36 mg, 55%) and unchanged **B-5-AQ** (2 mg). Compound **4**: yellow crystals, mp 173–175 °C;  $\delta_{\text{H}}$  2.19 (1 H, ddd,  $J$  14.6, 6.2 and 4.4), 2.75 (1 H, ddd,  $J$  14.6, 9.9 and 0.7), 3.48 (1 H, dd,  $J$  9.9 and 4.4), 3.78 (1 H, ddm,  $J$  8.4 and 6.2), 6.11 (1 H, dd,  $J$  1.5 and 0.7), 6.25 (1 H, ddd,  $J$  8.4, 1.1 and 0.7), 6.62 (1 H, t,  $J$  8.4), 6.71 (1 H, s), 7.0–7.1 (2 H, m) and 7.2–7.3 (3 H, m);  $\delta_{\text{C}}$  33.5, 49.7, 52.4, 58.2, 123.1, 127.5, 128.1 (2 C), 128.7 (2 C), 131.3, 131.4, 139.2, 141.6, 150.5, 159.8, 196.4 and 199.0;  $\nu_{\text{max}}$ (KBr)/ $\text{cm}^{-1}$  1719, 1660, 1627, 1539, 1493 and 1268;  $m/z$  (%) 342 ( $\text{M}^+$  for  $^{81}\text{Br}$ , 43), 340 ( $\text{M}^+$  for  $^{79}\text{Br}$ , 35), 238 (5), 236 (10), 104 (100) and 77 (6);  $\lambda_{\text{max}}$ (MeOH)/nm 224.0sh ( $\epsilon$  11 940), 256.8sh (9350) and 282.6 (14 890) (Found: C, 63.6; H, 4.0. Calc. for  $\text{C}_{18}\text{H}_{13}\text{BrO}_2$ : C, 63.36; H, 3.84%). Isomer **5**: yellow crystals, mp 148.5–149.5 °C;  $\delta_{\text{H}}$  2.28 (1 H, dd,  $J$  14.6 and 7.3), 2.52 (1 H, ddd,  $J$  14.6, 9.9 and 6.6), 3.50 (1 H, dd,  $J$  9.9 and 7.3), 3.78 (1 H, ddm,  $J$  7.7 and 6.6), 6.25 (1 H, dd,  $J$  1.5 and 0.7), 6.32 (1 H, s), 6.35 (1 H, d,  $J$  8.4), 6.42 (1 H, dd,  $J$  8.4 and 7.7), 7.00–7.10 (2 H, m) and 7.20–7.25 (3 H, m);  $\delta_{\text{C}}$  29.3, 48.6, 52.2, 60.5, 123.8, 127.9, 128.5 (4 C), 129.1, 134.5, 137.8, 140.1, 152.8, 156.8, 196.7 and 201.1;  $\nu_{\text{max}}$ (KBr)/ $\text{cm}^{-1}$  1719, 1670, 1626, 1537, 1453 and 1266;  $m/z$  (%) 342 ( $\text{M}^+$  for  $^{81}\text{Br}$ , 65), 340 ( $\text{M}^+$  for  $^{79}\text{Br}$ , 55), 238 (17), 236 (13), 104 (100) and 91 (4);  $\lambda_{\text{max}}$ (MeOH)/nm 251.5 ( $\epsilon$  10 490) and 276.6sh (7500) (Found: C, 63.6; H, 3.9%).

#### Reaction of B-5-AQ with acrylonitrile **6**

Following the general procedure, a chlorobenzene solution of **B-5-AQ** (47 mg) and acrylonitrile **6** (10 mg) was heated to give adducts **7** (10 mg, 17%) and **8** (18 mg, 31%). Compound **7**: yellow powder, mp 105–106 °C;  $\delta_{\text{H}}$  2.39 (1 H, ddd,  $J$  14.7, 7.0 and 2.9), 2.60 (1 H, dd,  $J$  14.7 and 9.9), 3.21 (1 H, dd,  $J$  9.9 and 2.9), 3.78 (1 H, ddm,  $J$  8.1 and 7.0), 6.12 (1 H, d,  $J$  2.2), 6.40 (1 H, d,  $J$  8.4), 6.54 (1 H, dd,  $J$  8.4 and 8.1) and 6.89 (1 H, s);  $\delta_{\text{C}}$  27.4, 31.3, 49.1, 52.4, 117.6, 123.3, 129.9, 130.1, 138.0, 150.6, 154.0, 193.0 and 196.0;  $\nu_{\text{max}}$ (KBr)/ $\text{cm}^{-1}$  2242, 1715, 1670, 1539, 1453 and 1263;  $m/z$  (%) 291 ( $\text{M}^+$  for  $^{81}\text{Br}$ , 50), 289 ( $\text{M}^+$  for  $^{79}\text{Br}$ , 45), 263 (31), 238 (23), 236 (19), 155 (52), 127 (70) and 77 (70);  $\lambda_{\text{max}}$ (MeOH)/ $\text{cm}^{-1}$  231.5 ( $\epsilon$  8070) and 284.6 (13 950) (Found: C, 53.5; H, 3.0; N, 4.95. Calc. for  $\text{C}_{15}\text{H}_8\text{BrNO}_2$ : C, 53.82; H, 2.78; N, 4.83%). Isomer **8**: yellow powder, mp 215–216 °C;  $\delta_{\text{H}}$  2.34 (1 H, dddd,  $J$  14.3, 6.6, 1.1 and 0.7), 2.53 (1 H, ddd,  $J$  14.3, 10.6 and 6.2), 3.19 (1 H, dd,  $J$  10.6 and 6.6), 3.72 (1 H, ddm,  $J$  8.4 and 6.2), 6.22 (1 H, dd,  $J$  1.5 and 0.7), 6.27 (1 H, dd,  $J$  8.4 and 1.1), 6.42 (1 H, t,  $J$  8.4) and 6.97 (1 H, d,  $J$  0.7);  $\delta_{\text{C}}$  26.6, 32.0, 50.8, 55.0, 117.8, 124.3, 131.1, 132.0, 140.0, 153.7, 154.9, 194.1 and 198.6;  $\nu_{\text{max}}$ (KBr)/ $\text{cm}^{-1}$  2238, 1719, 1670, 1626, 1537, 1453 and 1266;  $m/z$  (%) 291 ( $\text{M}^+$  for  $^{81}\text{Br}$ , 34), 289 ( $\text{M}^+$  for  $^{79}\text{Br}$ , 31), 263 (30), 238 (16), 236 (23), 155 (45), 127 (77) and 77 (19);  $\lambda_{\text{max}}$ (MeOH)/nm 251.5 ( $\epsilon$  10 140) and 276.6sh (7250) (Found: C, 53.6; H, 2.9; N, 4.8%).

#### Reaction of B-5-AQ with *N*-phenylmaleimide **9**

Following the general procedure, a chlorobenzene solution of **B-5-AQ** (24 mg) and *N*-phenylmaleimide **9** (20 mg) was heated to give adduct **10** (28.7 mg, 70%) as a powder, mp 219–220 °C;  $\delta_{\text{H}}$  3.52 (1 H, d,  $J$  8.4), 3.66 (1 H, dd,  $J$  8.4 and 1.8), 4.34 (1 H, dm,  $J$  7.7), 6.14 (1 H, dd,  $J$  1.5 and 0.7), 6.38 (1 H, ddd,  $J$  8.4, 1.8 and 1.1), 6.49 (1 H, dd,  $J$  8.4 and 7.7), 6.98 (1 H, s), 7.22–7.28 (2 H, m) and 7.4–7.45 (3 H, m);  $\delta_{\text{C}}$  41.8, 47.4, 52.3, 52.4, 122.2, 125.2 (2 C), 128.0, 128.2 (2 C), 129.4, 129.8, 130.3, 139.2, 148.4, 157.4, 169.5, 173.1, 190.7 and 194.6;  $\nu_{\text{max}}$ (KBr)/ $\text{cm}^{-1}$  1727, 1670, 1628, 1539 and 1496;  $m/z$  (%) 411 ( $\text{M}^+$  for  $^{81}\text{Br}$ , 10), 409 ( $\text{M}^+$  for  $^{79}\text{Br}$ , 9), 302 (41), 236 (7), 155 (100), 127 (43) and 77 (16);  $\lambda_{\text{max}}$ (MeOH)/nm 226.0 ( $\epsilon$  14 350) and 292.6 (11 140) (Found: C, 58.6; H, 3.1; N, 3.5. Calc. for  $\text{C}_{20}\text{H}_{12}\text{BrNO}_4$ : C, 58.56; H, 2.95; N, 3.41%).

#### Reaction of B-5-AQ with *N*-*p*-tolylmaleimide **11**

Following the general procedure, a chlorobenzene solution of **B-5-AQ** (48 mg) and imide **11** (40 mg) was heated to give compound **12** (60 mg, 70%) as a powder, mp 250–251 °C;  $\delta_{\text{H}}$  2.37 (3 H, s), 3.50 (1 H, dd,  $J$  8.4 and 0.7), 3.65 (1 H, dd,  $J$  8.4 and 1.5), 4.32 (1 H, dm,  $J$  7.3), 6.14 (1 H, dd,  $J$  1.5 and 0.7), 6.37 (1 H, dt,  $J$  8.4 and 0.7), 6.48 (1 H, dd,  $J$  8.4 and 7.3), 6.97 (1 H, s), 7.12 (2 H, dm,  $J$  8.4) and 7.23 (2 H, dm,  $J$  8.4);  $\delta_{\text{C}}$  21.2, 42.8, 48.4, 53.3, 53.4, 123.2, 126.0 (2 C), 128.7, 129.8 (2 C), 130.4, 130.8, 139.2, 140.2, 149.4, 158.4, 170.7, 174.2, 191.8 and 195.6;  $\nu_{\text{max}}$ (KBr)/ $\text{cm}^{-1}$  1728, 1669, 1628, 1539 and 1256;  $m/z$  (%) 425 ( $\text{M}^+$  for  $^{81}\text{Br}$ , 29), 423 ( $\text{M}^+$  for  $^{79}\text{Br}$ , 27), 316 (86), 285 (14), 236 (6), 155 (89), 133 (100), 127 (21) and 77 (14);  $\lambda_{\text{max}}$ (MeOH)/nm 228.4 ( $\epsilon$  17 270) and 289.4 (11 410) (Found: C, 59.2; H, 3.0; N, 3.6. Calc. for  $\text{C}_{21}\text{H}_{14}\text{BrNO}_4$ : C, 59.45; H, 3.33; N, 3.30%).

#### Reaction of B-5-AQ with acenaphthylene **13**

Following the general procedure, a chlorobenzene solution of **B-5-AQ** (47 mg) and acenaphthylene **13** (32 mg) was heated to give adducts **14** (9 mg, 12%) and **15** (12 mg, 15%). Compound **14** was a powder, mp 190 °C (decomp.);  $\delta_{\text{H}}$  4.12 (1 H, m), 4.32 (1 H, d,  $J$  7.7), 4.41 (1 H, d,  $J$  7.7), 6.00 (2 H, dd,  $J$  8.1 and 1.8), 6.22 (1 H, d,  $J$  2.2), 7.00 (1 H, s), 7.17 (1 H, d,  $J$  7.0), 7.33 (1 H, d,  $J$  7.0), 7.47 (1 H, d,  $J$  8.0), 7.48 (1 H, d,  $J$  8.0) and 7.67 (2 H, dd,  $J$  8.0 and 7.0);  $\delta_{\text{C}}$  47.4, 53.5, 56.2, 59.0, 118.9, 122.9, 123.2, 123.8, 124.2, 127.7, 128.8, 130.5, 130.7, 131.2, 135.2, 139.7, 140.0, 144.0, 151.0, 159.3, 195.2 and 203.4;  $\nu_{\text{max}}$ (KBr)/ $\text{cm}^{-1}$  1715, 1663, 1544, 1497 and 1269;  $m/z$  (%) 390 ( $\text{M}^+$  for  $^{81}\text{Br}$ , 45), 388 ( $\text{M}^+$  for  $^{79}\text{Br}$ , 26), 253 (14), 251 (22), 202 (27), 200 (16), 165 (100), 154 (79), 125 (96), 113 (61) and 101 (40);  $\lambda_{\text{max}}$ (MeOH)/nm 280.6 ( $\epsilon$  17 230), 288.8 (18 150) and 299.8sh (12 920) (Found: C, 67.7; H, 3.1. Calc. for  $\text{C}_{22}\text{H}_{13}\text{BrO}_2$ : C, 67.89; H, 3.27%). Compound **15** was also a powder, mp 230 °C (decomp.);  $\delta_{\text{H}}$  4.34 (1 H, dm,  $J$  7.3), 4.44 (1 H, d,  $J$  8.1), 4.48 (1 H, d,  $J$  8.1), 5.49 (1 H, dd,  $J$  1.8 and 0.7), 6.45 (1 H, dd,  $J$  8.4 and 0.7), 6.55 (1 H, dd,  $J$  8.4 and 7.3), 6.88 (1 H, s), 6.90 (1 H, m), 7.31 (1 H, d,  $J$  7.0), 7.34 (1 H, d,  $J$  8.1), 7.44 (1 H, dd,  $J$  8.1 and 7.1) and 7.58 (2 H, dd,  $J$  8.1 and 2.6);  $\delta_{\text{C}}$  46.9, 53.0, 56.5, 58.7, 120.5 (2 C), 123.7, 124.3, 124.5, 127.3, 128.1, 130.9, 131.4, 134.4, 134.5, 139.8, 140.5, 142.0, 154.1, 156.2, 194.6 and 202.0;  $\nu_{\text{max}}$ (KBr)/ $\text{cm}^{-1}$  1712, 1663, 1538, 1495 and 1272;  $m/z$  (%) 390 ( $\text{M}^+$  for  $^{81}\text{Br}$ , 52), 388 ( $\text{M}^+$  for  $^{79}\text{Br}$ , 36), 281 (89), 253 (100), 251 (42), 238 (31), 236 (23), 202 (65), 200 (29), 165 (20), 75 (25) and 63 (15);  $\lambda_{\text{max}}$ (MeOH)/nm 278.9 ( $\epsilon$  16 640), 286.1 (16 580), and 298.7sh (11 460) (Found: C, 68.05; H, 3.5%).

#### Reaction of B-5-AQ with 2,3-bis(methoxycarbonyl)-7-oxa-bicyclo[2.2.1]heptadiene **16**

Following the general procedure, a chlorobenzene solution of **B-5-AQ** (47.4 mg) and diester **16** (63 mg) was heated to give adduct **17** (60 mg, 67%) as a powder, mp 182–183.5 °C;  $\delta_{\text{H}}$  2.60 (1 H, dd,  $J$  8.1 and 0.7), 2.70 (1 H, d,  $J$  8.1), 3.78 (6 H, s), 3.81 (1 H, dm,  $J$  7.7), 5.00 (1 H, d,  $J$  1.1), 5.66 (1 H, d,  $J$  1.1), 5.98 (1 H, d,  $J$  1.8), 6.18 (1 H, ddd,  $J$  8.4, 1.8 and 1.1), 6.35 (1 H, ddd,  $J$  8.4, 7.7 and 0.7) and 6.81 (1 H, d,  $J$  0.7);  $\delta_{\text{C}}$  42.6, 50.3, 52.5, 52.6, 54.1, 56.4, 81.7, 86.1, 122.8, 129.9, 130.4, 139.2, 145.0, 146.1, 151.1, 159.9, 162.1, 162.7, 194.2 and 200.4;  $\nu_{\text{max}}$ (KBr)/ $\text{cm}^{-1}$  1740, 1715, 1670, 1644, 1541, 1294 and 1222;  $m/z$  (%) 448 ( $\text{M}^+$  for  $^{81}\text{Br}$ , 0.06), 446 ( $\text{M}^+$  for  $^{79}\text{Br}$ , 0.05), 416 (7), 384 (6), 264 (50), 236 (99), 234 (100), 156 (52), 127 (68), 77 (36) and 63 (14);  $\lambda_{\text{max}}$ (MeOH)/nm 232.0 ( $\epsilon$  12 670), 252.5 (10 040), 257.4 (9350) and 290.6 (15 440) (Found: C, 53.7; H, 3.6. Calc. for  $\text{C}_{20}\text{H}_{15}\text{BrO}_7$ : C, 53.71; H, 3.38%).

#### Reaction of B-5-AQ with 2,3-bis(methoxycarbonyl)-1,4-dimethyl-7-oxabicyclo[2.2.1]heptadiene **18**

Following the general procedure, a chlorobenzene solution of

**B-5-AQ** (35 mg) and dienophile **18** (35 mg) was heated to give adduct **19** (27 mg, 42%) as a powder, mp 186–187 °C;  $\delta_{\text{H}}$  1.61 (3 H, s), 1.64 (3 H, s), 2.79 (1 H, d, *J* 7.7), 2.83 (1 H, d, *J* 7.7), 3.78 (7 H, m), 6.02 (1 H, d, *J* 1.8), 6.32 (2 H, ddm, *J* 8.4 and 1.8) and 6.83 (1 H, s);  $\delta_{\text{C}}$  15.6, 17.1, 49.1, 52.4 (3 C), 55.4, 57.0, 88.2, 90.3, 122.8, 129.2, 129.4, 139.6, 146.8, 149.1, 149.8, 159.3, 163.2, 163.8, 194.4 and 199.1;  $\nu_{\text{max}}$ (KBr)/cm<sup>-1</sup> 1740, 1717, 1665, 1547, 1264 and 1247; *m/z* (%) 476 (M<sup>+</sup> for <sup>81</sup>Br, 2.2), 474 (M<sup>+</sup> for <sup>79</sup>Br, 2), 395 (2), 236 (5), 212 (91), 181 (51), 155 (100), 127 (27) and 77 (24);  $\lambda_{\text{max}}$ (MeOH)/nm 227.7sh ( $\epsilon$  13 070) and 288.5 (13 820) (Found: C, 55.9; H, 4.1. Calc. for C<sub>22</sub>H<sub>19</sub>BrO<sub>7</sub>: C, 55.60; H, 4.03%) and unchanged **B-5-AQ** (3 mg).

#### Reaction of B-5-AQ with 1,4-epoxy-1,4-dihydronaphthalene 20

Following the general procedure, a chlorobenzene solution of **B-5-AQ** (15 mg) and 1,4-epoxide **20** (20 mg) was heated to give adduct **21** (18 mg, 75%) as a powder, mp 90–91 °C;  $\delta_{\text{H}}$  2.44 (1 H, d, *J* 8.1), 2.58 (1 H, d, *J* 8.1), 4.37 (1 H, dm, *J* 7.7), 5.14 (1 H, s), 5.82 (1 H, s), 5.93 (1 H, dd, *J* 2.2 and 0.7), 6.24 (1 H, ddd, *J* 8.4, 7.7 and 1.1), 6.42 (1 H, dd, *J* 8.4 and 0.7), 6.81 (1 H, s) and 7.10–7.24 (4 H, m);  $\delta_{\text{C}}$  44.9, 52.3, 54.9, 57.3, 79.6, 84.8, 119.0, 119.3, 122.8, 126.9, 127.2, 129.9, 130.0, 139.1, 145.8, 146.2, 151.5, 160.1, 194.0 and 201.2;  $\nu_{\text{max}}$ (KBr)/cm<sup>-1</sup> 1711, 1667, 1650, 1564, 1460 and 1217; *m/z* (%) 382 (M<sup>+</sup> for <sup>81</sup>Br, 26), 380 (M<sup>+</sup> for <sup>79</sup>Br, 23), 283 (3), 264 (12), 255 (34), 215 (18), 155 (100), 128 (10), 119 (73), 77 (25) and 63 (33);  $\lambda_{\text{max}}$ (MeOH)/nm 226.6 ( $\epsilon$  8290), 265.8sh (790), 273.8sh (10 100) and 287.9 (12 490) (Found: C, 62.7; H, 3.8. Calc. for C<sub>20</sub>H<sub>13</sub>BrO<sub>3</sub>: C, 63.01; H, 3.44%).

#### Thermal reaction of B-7-AQ with ethene 1

A chlorobenzene solution (15 cm<sup>3</sup>) of **B-7-AQ** (20 mg) was heated with ethene **1** in an autoclave (4 MPa) at 150 °C for 3 h. After the volatile material had been redistilled *in vacuo*, the residue was chromatographed on a silica gel column to give adduct **22** (13 mg, 63%) as crystals, mp 119–120 °C;  $\delta_{\text{H}}$  1.90 (1 H, br m), 2.1–2.25 (3 H, m), 3.70 (1 H, br m), 6.23 (1 H, d, *J* 2.2), 6.29 (1 H, dd, *J* 8.4 and 7.7), 6.39 (1 H, dm, *J* 8.4) and 6.74 (1 H, s);  $\delta_{\text{C}}$  22.1, 32.3, 52.0, 55.3, 122.5, 128.8, 134.9, 136.8, 153.2, 164.1, 190.7 and 197.3;  $\nu_{\text{max}}$ (KBr)/cm<sup>-1</sup> 1698, 1666 and 1561; *m/z* (%) 266 (M<sup>+</sup> for <sup>81</sup>Br, 4), 264 (M<sup>+</sup> for <sup>79</sup>Br, 2), 236 (4), 185 (100), 157 (16), 128 (92) and 102 (15);  $\lambda_{\text{max}}$ (MeOH)/nm 256.2 ( $\epsilon$  13 500), 262.2 (13 300) and 280.2sh (9140) (Found: C, 54.3; H, 3.6. Calc. for C<sub>12</sub>H<sub>9</sub>BrO<sub>2</sub>: C, 54.37; H, 3.42%) and unchanged **B-7-AQ** (1.5 mg).

#### Reaction of B-7-AQ with styrene 3

Following the general procedure, a chlorobenzene solution of **B-7-AQ** (47 mg) and styrene **3** (40 mg) was heated at 130 °C for 36 h to give adducts **23** (10 mg, 15%) and **24** (33 mg, 49%). Compound **23** was obtained as yellow crystals, mp 200–202 °C;  $\delta_{\text{H}}$  2.28 (1 H, ddd, *J* 14.7, 6.2 and 4.4), 2.77 (1 H, ddm, *J* 14.7 and 9.5), 3.48 (1 H, ddd, *J* 9.5, 4.4 and 0.7), 3.81 (1 H, ddm, *J* 8.1 and 6.2), 6.28 (1 H, d, *J* 2.2), 6.45 (1 H, dt, *J* 8.4 and 0.7), 6.62 (1 H, dd, *J* 8.4 and 8.1), 6.76 (1 H, s) and 7.2–7.35 (5 H, m);  $\delta_{\text{C}}$  34.1, 52.5, 52.8, 58.1, 121.9, 128.0 (2 C), 128.3, 128.5, 130.3 (2 C), 132.8, 138.7, 141.2, 154.8, 164.2, 190.5 and 196.6;  $\nu_{\text{max}}$ (KBr)/cm<sup>-1</sup> 1705, 1669, 1560, 1491 and 1254; *m/z* (%) 342 (M<sup>+</sup> for <sup>81</sup>Br, 18), 340 (M<sup>+</sup> for <sup>79</sup>Br, 17), 262 (2), 203 (4), 104 (100) and 78 (8);  $\lambda_{\text{max}}$ (MeOH)/nm 226.7sh ( $\epsilon$  15 300), 256.6sh (9080) and 274.4sh (6600) (Found: C, 63.6; H, 4.0. Calc. for C<sub>18</sub>H<sub>13</sub>BrO<sub>2</sub>: C, 63.36; H, 3.84%). Isomer **24** was obtained as yellow crystals, mp 170–172 °C;  $\delta_{\text{H}}$  2.27 (1 H, dd, *J* 14.7 and 7.7), 2.69 (1 H, ddd, *J* 14.7, 9.9 and 7.3), 3.49 (1 H, dd, *J* 9.9 and 7.7), 3.76 (1 H, ddm, *J* 8.4 and 7.3), 6.33 (1 H, t, *J* 8.4), 6.39 (1 H, s), 6.45 (1 H, d, *J* 2.2), 6.57 (1 H, dd, *J* 8.4 and 0.7) and 7.20–7.40 (5 H, m);  $\delta_{\text{C}}$  31.0, 48.9, 52.3, 60.6, 122.9, 127.7, 128.0, 128.5, 128.6, 128.7, 129.7, 136.8, 137.8, 138.3, 151.4,

162.1, 190.7 and 197.1;  $\nu_{\text{max}}$ (KBr)/cm<sup>-1</sup> 1704, 1681, 1644, 1569, 1492 and 1262; *m/z* (%) 342 (M<sup>+</sup> for <sup>81</sup>Br, 30), 340 (M<sup>+</sup> for <sup>79</sup>Br, 25), 261 (2), 236 (3), 104 (100), 91 (6) and 78 (4);  $\lambda_{\text{max}}$ (MeOH)/nm 257.8 ( $\epsilon$  11 620) and 283.7sh (8350) (Found: C, 63.4; H, 3.9%).

#### Reaction of B-7-AQ with acrylonitrile 6

Following the general procedure, a chlorobenzene solution of **B-7-AQ** (47 mg) and acrylonitrile **6** (20 mg) was heated at 130 °C for 36 h to give adducts **25** (13 mg, 22%) and **26** (20 mg, 35%). Compound **25** was obtained as a yellow powder, mp 228–229 °C;  $\delta_{\text{H}}$  2.47 (1 H, ddd, *J* 14.7, 7.0 and 2.6), 2.64 (1 H, ddm, *J* 14.7 and 9.5), 3.21 (1 H, ddd, *J* 9.5, 2.6 and 0.7), 3.80 (1 H, ddm, *J* 8.4 and 7.0), 6.29 (1 H, d, *J* 2.2), 6.52 (1 H, dd, *J* 8.4 and 7.7), 6.61 (1 H, dd, *J* 7.7 and 0.7) and 6.93 (1 H, s);  $\delta_{\text{C}}$  29.4, 35.0, 49.9, 55.0, 119.4, 123.6, 129.1, 133.1, 139.6, 149.3, 160.3, 188.6 and 194.2;  $\nu_{\text{max}}$ (KBr)/cm<sup>-1</sup> 2238, 1713, 1660, 1646, 1569, 1455 and 1260; *m/z* (%) 291 (M<sup>+</sup> for <sup>81</sup>Br, 0.7), 289 (M<sup>+</sup> for <sup>79</sup>Br, 0.5), 263 (2), 210 (100), 182 (28), 154 (22), 127 (32) and 75 (17);  $\lambda_{\text{max}}$ (MeOH)/nm 251.5 ( $\epsilon$  14 810) and 279.7sh (10 990) (Found: C, 53.6; H, 2.9; N, 4.8. Calc. for C<sub>13</sub>H<sub>8</sub>BrNO<sub>2</sub>: C, 53.82; H, 2.78; N, 4.83%). Isomer **26** was obtained as yellow needles, mp 197–199 °C;  $\delta_{\text{H}}$  2.40 (1 H, ddd, *J* 14.3, 6.6 and 0.7), 2.66 (1 H, ddd, *J* 14.3, 10.6 and 6.6), 3.32 (1 H, dd, *J* 10.6 and 6.6), 3.75 (1 H, br m), 6.35–6.45 (3 H, m) and 7.00 (1 H, s);  $\delta_{\text{C}}$  26.8, 34.2, 50.8, 56.8, 117.6, 123.8, 129.7, 133.7, 139.7, 149.0, 158.0, 188.7 and 194.6;  $\nu_{\text{max}}$ (KBr)/cm<sup>-1</sup> 2242, 1704, 1678, 1651, 1564, 1451 and 1260; *m/z* (%) 291 (M<sup>+</sup> for <sup>81</sup>Br, 0.2), 289 (M<sup>+</sup> for <sup>79</sup>Br, 0.2), 210 (100), 182 (30), 154 (70), 127 (54) and 75 (21);  $\lambda_{\text{max}}$ (MeOH)/nm 233.4sh ( $\epsilon$  5510), 251.7 (15 020) and 281.6sh (4930) (Found: C, 53.7; H, 3.0; N, 4.5%).

#### Reaction of B-7-AQ with N-phenylmaleimide 9

Following the general procedure, a chlorobenzene solution of **B-7-AQ** (23.7 mg) and imide **9** (18 mg) was heated to give adduct **27** (18.5 mg, 44%) as pale yellow needles, mp 253–254 °C;  $\delta_{\text{H}}$  3.58 (1 H, dd, *J* 8.4 and 0.7), 3.68 (1 H, dd, *J* 8.4 and 1.5), 4.37 (1 H, dm, *J* 7.3), 6.31 (1 H, d, *J* 2.2), 6.49 (1 H, dd, *J* 8.4 and 7.3), 6.58 (1 H, d, *J* 8.4), 7.04 (1 H, s), 7.25–7.30 (2 H, m) and 7.45–7.5 (3 H, m);  $\delta_{\text{C}}$  43.4, 52.4, 53.2, 54.8, 122.1, 126.2 (2 C), 129.2, 129.3 (2 C), 129.4, 130.9, 132.6, 140.6, 154.0, 160.9, 171.3, 173.8, 188.5 and 192.1;  $\nu_{\text{max}}$ (KBr)/cm<sup>-1</sup> 1716, 1697, 1650, 1561 and 1387; *m/z* (%) 411 (M<sup>+</sup> for <sup>81</sup>Br, 3), 409 (M<sup>+</sup> for <sup>79</sup>Br, 7), 331 (42), 264 (17), 208 (17), 156 (60), 128 (100) and 77 (93);  $\lambda_{\text{max}}$ (MeOH)/nm 255.0 ( $\epsilon$  8550) and 291.5sh (5410) (Found: C, 58.5; H, 3.1; N, 3.3. Calc. for C<sub>20</sub>H<sub>12</sub>BrNO<sub>4</sub>: C, 58.56; H, 2.95; N, 3.41%).

#### Reaction of B-7-AQ with 2,3-bis(methoxycarbonyl)-7-oxabicyclo[2.2.1]heptadiene 16

Following the general procedure, a chlorobenzene solution of **B-7-AQ** (24 mg) and diester **16** (25 mg) was heated to give adduct **28** (24 mg, 53%) as a powder, mp 209–210 °C;  $\delta_{\text{H}}$  2.63 (1 H, d, *J* 7.7), 2.76 (1 H, d, *J* 7.7), 3.81 (6 H, s), 3.83 (1 H, m), 5.01 (1 H, d, *J* 1.1), 6.05 (1 H, d, *J* 1.1), 6.16 (1 H, d, *J* 2.2), 6.34 (2 H, s) and 6.81 (1 H, s);  $\delta_{\text{C}}$  44.1, 53.0, 53.1, 54.4, 55.9, 57.1, 82.3, 86.8, 122.2, 129.2, 131.8, 139.6, 145.5, 146.1, 154.9, 161.7, 162.5, 162.8, 190.2 and 194.9;  $\nu_{\text{max}}$ (KBr)/cm<sup>-1</sup> 1754, 1720, 1670, 1648, 1566, 1434, 1263 and 1232; *m/z* (%) 448 (M<sup>+</sup> for <sup>81</sup>Br, 0.04), 446 (M<sup>+</sup> for <sup>79</sup>Br, 0.02), 264 (12), 262 (13), 236 (8), 234 (8), 183 (46), 155 (49), 153 (100), 127 (67), 77 (6) and 63 (8);  $\lambda_{\text{max}}$ (MeOH)/nm 230.5 ( $\epsilon$  15 830), 258.6 (10 615) and 271.2 (11 140) (Found: C, 53.5; H, 3.4. Calc. for C<sub>20</sub>H<sub>15</sub>BrO<sub>7</sub>: C, 53.71; H, 3.38%).

#### Thermal reaction of compound 17

A xylene solution (5 cm<sup>3</sup>) of compound **17** (22.4 mg) was heated at 140 °C in an ampoule for 24 h. The solvent was removed *in*

*vacuo* and the residue was chromatographed on silica gel to give retro-Diels–Alder product **29** (11 mg, 83%) as a powder, mp 163–165 °C;  $\delta_{\text{H}}$  4.30–4.36 (1 H, m), 5.44 (1 H, dd, *J* 2.2 and 0.7), 6.39 (2 H, dd, *J* 7.0 and 1.5), 6.59 (2 H, t, *J* 7.0) and 6.79 (1 H, d, *J* 0.7);  $\delta_{\text{C}}$  57.6, 58.6, 118.6, 131.5 (2 C), 133.4 (2 C), 139.7, 151.6, 159.5, 187.8 and 199.8;  $\nu_{\text{max}}$ (KBr)/ $\text{cm}^{-1}$  1719, 1675, 1537 and 1230; *m/z* (%) 264 ( $\text{M}^+$  for  $^{81}\text{Br}$ , 0.5), 262 ( $\text{M}^+$  for  $^{79}\text{Br}$ , 0.6), 236 (37), 234 (36), 156 (42), 127 (100), 77 (37) and 63 (39);  $\lambda_{\text{max}}$ (MeOH)/nm 226.8 ( $\epsilon$  6340), 245.2sh (6220), 273.3 (11 530), 284.4sh (9630) and 318.3 (4020) (Found: C, 54.8; H, 2.9. Calc. for  $\text{C}_{12}\text{H}_7\text{BrO}_2$ : C, 54.78; H, 2.68%).

#### Thermal reaction of compound 19

A xylene solution (3  $\text{cm}^3$ ) of compound **19** (12 mg) was heated at 140 °C in an ampoule for 2 h. The solvent was removed *in vacuo* and the residue was chromatographed on silica gel to give retro-Diels–Alder product **29** (5.5 mg, 83%).

#### Thermal reaction of compound 28

A xylene solution (5  $\text{cm}^3$ ) of compound **28** (20 mg) was heated at 140 °C in an ampoule for 24 h. The solvent was removed *in vacuo* and the residue was chromatographed on silica gel to give retro-Diels–Alder product **30** (8.8 mg, 75%) as a powder, mp 136–138 °C;  $\delta_{\text{H}}$  4.43 (1 H, m), 5.62 (1 H, d, *J* 2.2), 6.58 (2 H, dd, *J* 7.4 and 1.5), 6.67 (2 H, t, *J* 7.4) and 6.84 (1 H, s);  $\delta_{\text{C}}$  58.8, 59.1, 116.7, 131.5 (2 C), 135.8 (2 C), 138.0, 154.1, 159.5, 187.8 and 190.3;  $\nu_{\text{max}}$ (KBr)/ $\text{cm}^{-1}$  1704, 1678, 1647, 1566 and 1218; *m/z* (%) 264 ( $\text{M}^+$  for  $^{81}\text{Br}$ , 0.3), 262 ( $\text{M}^+$  for  $^{79}\text{Br}$ , 0.2), 236 (10), 234 (9), 183 (48), 155 (33), 127 (100), 102 (14), 77 (19) and 63 (14);

$\lambda_{\text{max}}$ (MeOH)/nm 226.6 ( $\epsilon$  8620), 254 (8855) and 285.0sh (5150) (Found: C, 55.0; H, 2.9%. Calc. for  $\text{C}_{12}\text{H}_{17}\text{BrO}_2$ : C, 54.78; H, 2.68%).

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