82. Face Selectivity of the *Diels-Alder* Additions and Cheletropic Additions of Sulfur Dioxide to 2-Vinyl-7-oxabicyclo[2.2.1]hept-2-ene Derivatives

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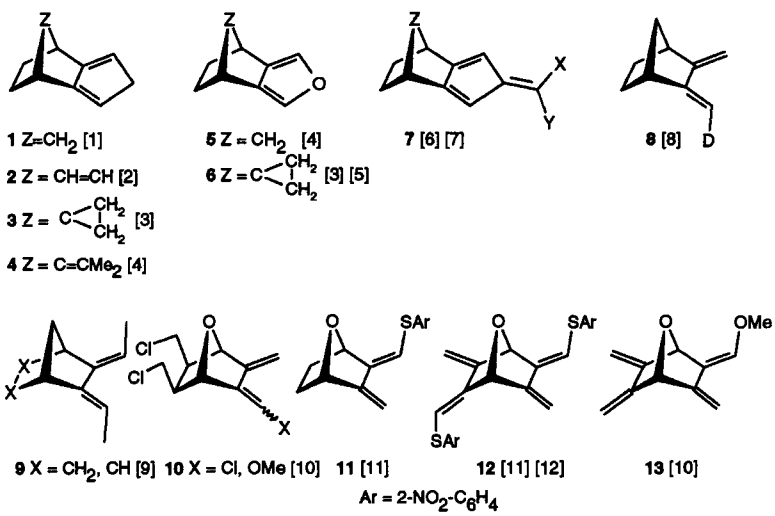
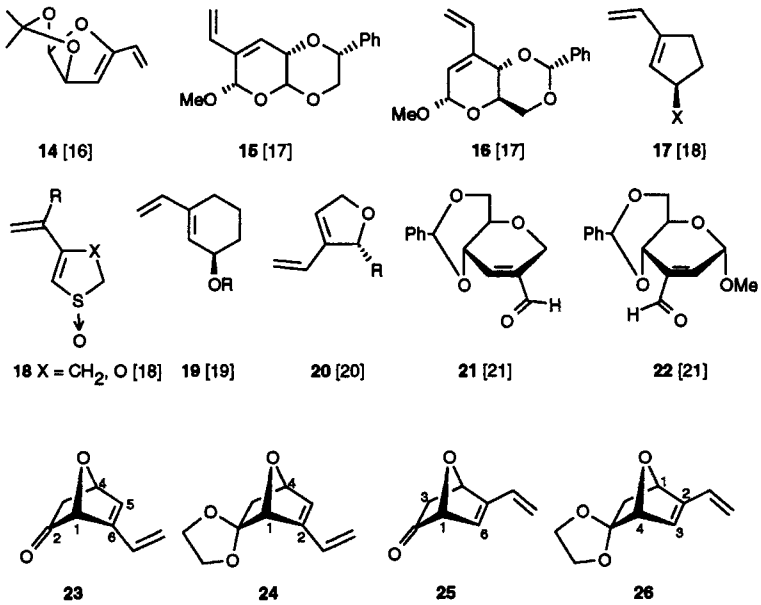
Racemic 6-ethenyl-7-oxabicyclo[2.2.1]hept-5-en-2-one (**23**), 5-ethenyl-7-oxabicyclo[2.2.1]hept-5-en-2-one (**25**) and their ethylene acetals **24** and **26**, respectively, were derived from the *Diels-Alder* adduct of furan to 1-cyanovinyl acetate (**27**). The *Diels-Alder* additions of **26** to dimethyl acetylenedicarboxylate, to methyl propynoate, to *N*-phenylmaleimide, and to methyl acrylate were highly *exo*-face selective, as were the cycloadditions of methyl propynoate to dienones **23** and **25** and of dimethyl acetylenedicarboxylate to ethylenedioxy-diene **24**. The cheletropic additions of SO_2 to **23–26** gave exclusively the corresponding sulfolenes **57–60** resulting from the *exo*-face attack of the semicyclic dienes under conditions of kinetic and thermodynamic control.

Introduction. – The face selectivity of the *Diels-Alder* additions of conformationally rigid s-*cis*-butadiene systems attached to bicyclic skeletons (*e.g.* **1–13**) were studied extensively [1–15]. The face selectivity depends on the nature of the bridges that constitute the bicyclic system, on the nature of the dienophile, and in some cases on the solvent [13]. The results were interpreted in terms of stereoelectronic factors [1e,f,g,h], of torsional effects [4] [14], and of steric hindrance [8] [11] [15]. In the case of semicyclic 1,3-dienes grafted onto monocyclic skeletons (*e.g.* **14–22**), the face *'anti'* to the substituent the closest to the diene moiety is generally preferred for the *Diels-Alder* addition, suggesting that repulsive steric factors govern the stereoselectivity of these cycloadditions [16–21].

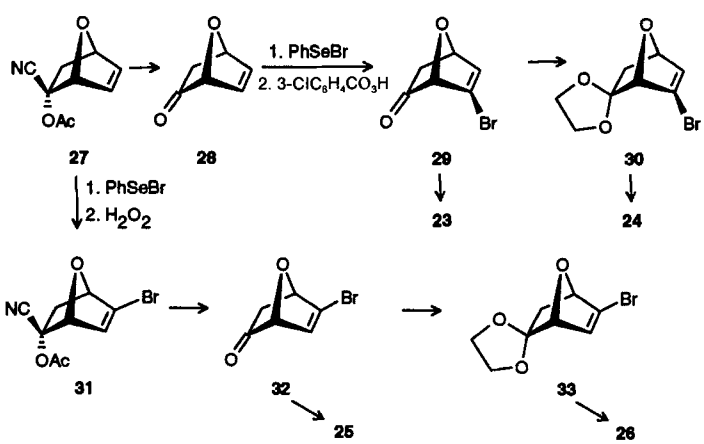




We report here on the synthesis of new semicyclic dienes **23–26** grafted onto 7-oxabicyclo[2.2.1]heptane skeletons. We shall show that their *Diels-Alder* additions strongly prefer the *exo*-face of the bicyclic systems. Under conditions of kinetic and thermodynamic control, the cheletropic additions of SO_2 to these 1,3-dienes also lead to adducts resulting from the addition onto their *exo*-face.

Results and Discussion. – The racemic dienes **23** and **24** were prepared from bromoenone **29** [22] derived from (±)-7-oxabicyclo[2.2.1]hept-5-en-2-one (**28**) [23] (*Scheme 1*). *Stille*'s coupling [24] of **29** with CH_2=$CHSnBu_3$ and a catalytic amount of $[Pd(Ph_3P)_4]$ in

Scheme 1

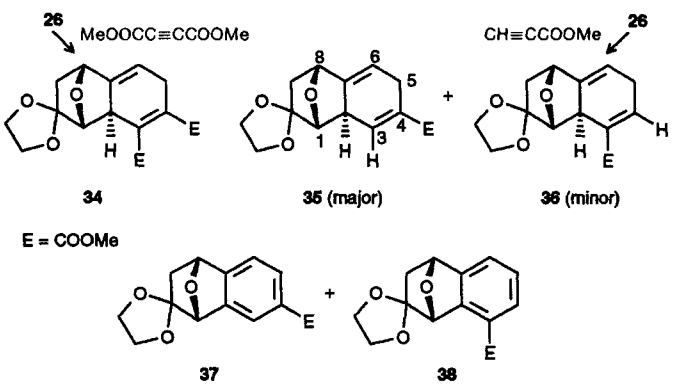


degassed DMF (55°, 3 h) afforded **23** in 63% yield. Acetalization of **29** with 1,2-bis[(trimethylsilyl)oxy]ethane and $CF_3SO_3SiMe_3$ in CH_2Cl_2 (0°) [25] gave **30** (74%) which was converted as above into diene **24** (58%). Addition of benzeneselenenyl bromide to the *Diels-Alder* adduct **27** of furan to 1-cyanovinyl acetate [22], followed by oxidative elimination of the selenium moiety with H_2O_2 afforded the bromoenyl acetate **31**. Saponification of **31**, followed by treatment with formaline (40% CH_2O in H_2O) gave the bromoenone **32** [26] which was converted into the corresponding ethylene acetal **33** (93%) with 1,2-bis[(trimethylsilyl)oxy]ethane and $CF_3SO_3SiMe_3$. *Stille*'s coupling as above of **32** and **33** with CH_2=CHSnBu$_3$ provided dienes **25** (60%) and **26** (94%), respectively.

The semicyclic dienes were unstable compounds that polymerized quickly in the presence of light or/and air. Concentrating degassed solutions of **23–26** led to their *Diels-Alder* cyclodimerization[1]). Dienone **23** was dimerized quickly already at 0°. The ethylenedioxy-diene **26** was the slowest to dimerize and thus chosen to study the facial selectivity of its *Diels-Alder* additions to various strong dienophiles such as dimethyl acetylenedicarboxylate (MeOOC≡CCOOMe), methyl propynoate (CH≡CCOOMe), *N*-phenylmaleimide, and methyl acrylate (CH_2=CHCOOMe).

When 0.5M **26** in neat MeOOCC≡CCOOMe was allowed to stand at 25° for 24 h, a 65% yield of the corresponding adduct **34** was obtained after chromatographic purification and recrystallization (*Scheme 2*). The 360-MHz ^{1}H-NMR spectrum of the crude

Scheme 2



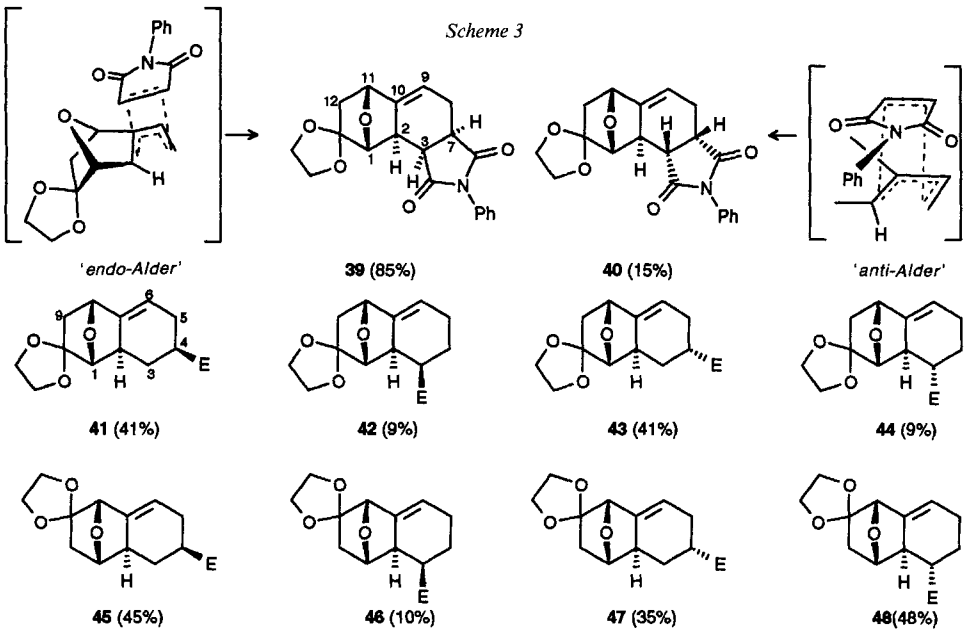
product showed *ca.* 5–15% of a dimer of **26**, but no trace of an isomer of adduct **34** could be detected, thus demonstrating the high facial selectivity of the *Diels-Alder* cycloaddition. The absence of a vicinal coupling constant between the bridgehead proton H–C(1) and H_{endo}–C(2) proved that the dienophile had attacked diene **26** on its *exo*-face [27]. In neat CH≡CCOOMe, **26** (0.5M) gave a 75% yield of the two regioisomeric adducts **35** and **36** after 8 days at 25°. The product ratio **35**/**36** was 78:22. It was 80:20 when the reaction was run at 55° for 24 h (yield 64%). No trace of any isomeric adducts could be detected in the 360-MHz ^{1}H-NMR spectra of the crude reaction mixture. In this case, the proportion

[1]) The structures of these dimers will be reported elsewhere.

of dimers of **26** varied between 10 and 25%. Again, the *exo*-face of diene **26** was preferred for the *Diels-Alder* addition to CH≡CCOOMe. The structures of adducts **35** and **36** were deduced from their spectral data, including NOE measurements in their ^{1}H-NMR spectra (see *Exper. Part*). Adducts **35** and **36** were rapidly oxidized into the methyl naphthoate **37** and **38**, respectively, in the presence of air.

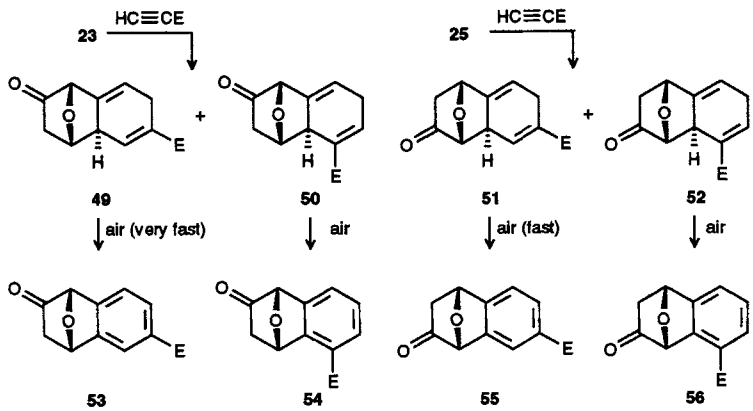
In benzene solution (0.25M), diene **26** added to *N*-phenylmaleimide at 25° yielding a 85:15 mixture of adducts **39** and **40** (90%; *Scheme 3*). These adducts could be separated by column chromatography and were characterized by their spectral data. In this case also, the *Diels-Alder* addition preferred the *exo*-face of diene **26** for both the *'endo-Alder'* [28] mode (giving **39**) and the *'anti-Alder'* mode (giving **40**) of reaction. The cycloaddition of CH_2=CHCOOMe to **26** was highly *exo*-face selective giving a 40.5:8.5:41:9 mixture **41**/**42**/**43**/**44** (67% yield) after 24 h at 55° in neat CH_2=CHCOOMe (89% yield after 6 days at 25°; *Scheme 3*). In this case, the *'endo-Alder'* rule was not followed since both modes of cycloadditions occurred with the same rate. Interestingly though, the facial selectivity and the regioselectivity was the same for both modes of addition.

Scheme 3



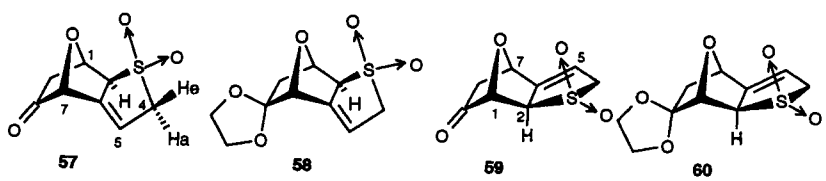
When the ethylenedioxy-diene **24** was allowed to react in neat CH_2=CHCOOMe (25°, 6 days), a 95% yield of a 34:13:43:10 mixture **45**/**46**/**47**/**48** was formed (*Scheme 3*). When run at 55° (24 h), the reaction led to a 45:10:35:10 mixture (90%) **45**/**46**/**47**/**48**. These results suggested that the position of the remote ethylene acetal moiety has a minor role to play on the regioselectivity of the cycloaddition. To test whether it could control the *exo*-facial selectivity of the *Diels-Alder* additions, dienones **23** and **25** were allowed to react with neat CH≡CCOOMe (55°, 17–24 h). They furnished a 69:31 mixture **49**/**50** and

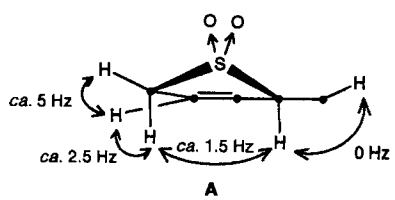
Scheme 4



a 72:28 mixture **51**/**50** (85%), respectively, together with the corresponding cyclodimers (*Scheme 4*). No trace of adducts resulting from the addition onto the *endo*-face of dienones **23** and **25** could be detected by 360-MHz ^{1}H-NMR, thus suggesting that the *exo*-facial selectivity of the *Diels-Alder* additions of dienes **23**–**26** is due the steric factors specific of the 7-oxabicyclo[2.2.1]heptane skeleton. Adducts **49**–**52** were rapidly transformed by air (faster than **35** and **36**) into the corresponding methyl naphthoates **53**–**56**. The structures of compounds **39**–**56** were all deduced from their spectral data, including double-irradiation experiments and NOE measurements in their ^{1}H-NMR spectra.

Like the *Diels-Alder* additions of most dienophiles, the cheletropic addition of SO_2 to the deuterated 2,3-dimethylidenebicyclo[2.2.1]heptane **8** [8] was *endo*-face-selective under conditions of kinetic control. Under equilibrium conditions, a 1:1 mixture of the two possible sulfolenes (= 2,5-dihydrothiophene 1,1-dioxides) was obtained. When 0.02–0.1M solutions of dienes **23**–**26** in CD_2Cl_2 were mixed with a large excess of SO_2, slow formation of the corresponding sulfolenes **57**–**60** was observed at −20°. Equilibria were reached after 2–3 days at 20°. Using CD_2Cl_2/SO_2 2:3 (5-mm NMR tubes sealed under





A

vacuum) and a 0.1M solution of the dienes, the following proportions of dienes *vs.* sulfolenes (1% toluene as internal reference) were obtained at 20°: **23** + SO_2/**57** 12:88, **24** + SO_2/**58** 5:95, **25** + SO_2/**59** 50:50, and **26** + SO_2/**60** < 5:95. When heated above 40° (opened tubes), the sulfolenes **57–60** were quickly decomposed into the corresponding dienes **23–26** and SO_2. The reactions were accompanied by partial dimerizations and/or decomposition of the dienes. The nature of the sulfolene was the same at the beginning of the cheletropic additions at −20° (kinetic control) than under equilibrium conditions at 20–40°. The same results were obtained with solutions containing 5% CF_3COOH. The structures of sulfolenes **57–60** were given by their spectral data (see *Exper. Part*).

The *endo* relative configuration of the proton at C(2) of **57–60** was established by the absence of a vicinal coupling constant between this proton and the neighbouring bridgehead proton [27]. It was confirmed by the observation of a NOE between H–C(2) and H_{endo}–C(9) in the ^{1}H-NMR spectra. Distinction between the pseudoaxial and pseudoequatorial protons H_a–C(4) and H_{eq}–C(4), respectively, was based on the observation of ^4J coupling constant between H_{ax}–C(4) and H–C(2) of 1.5 Hz in the four sulfolenes **57–60**, the corresponding coupling between H_{eq}–C(4) and H–C(2) being inexistant. These coupling constants are in fact of the homoallylic type. This, together with the vicinal coupling constants between H–C(5) and CH_2(4) suggested the conformation shown in **A** for these compounds [29].

As for other bicyclo[2.2.1]heptane derivatives, sulfolenes **57–60** were expected to be more stable than their *endo*-isomers for steric reasons [30]. It appears, therefore, that the *Diels-Alder* and the cheletropic additions of the semicyclic dienes **23–26** obey the *Dimroth* principle [31], *i.e.*, the more exothermic the reaction, the faster it is. It is not excluded yet that the factors that make these cycloadditions *exo*-face-selective under conditions of kinetic control are the same as those rendering the resulting *exo*-adducts more stable than their *endo*-isomers.

Conclusion. – As for the semicyclic dienes **14–20** and the oxadienes **21–22**, the new dienes **23–26** grafted onto 7-oxabicyclo[2.2.1]heptane skeletons add to strong dienophiles and to SO_2 onto their less hindered *exo*-face.

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Experimental Part

General. See [32]. None of the procedures was optimized. 400-MHz ^{1}H-NMR and 100.61-MHz ^{13}C-NMR Spectra: *Bruker-ARX-400* spectrometer, *Aspect-X32/3* computer, 1.5 MBYTE max. acquisition memory. 150.9-MHz ^{13}C-NMR Spectra: *Bruker-AMX2-600* spectrometer, *RISC-CPU-R-3000* computer, 3 MBYTE max. aquisition memory. FC = Flash chromatography, CC = column chromatography.

(±)-2-Bromo-6,6-(ethylenedioxy)-7-oxabicyclo[2.2.1]hept-2-ene (**30**). At 0°, 1,2-bis[(trimethylsilyl)oxy]-ethane (3.08 ml, 12.5 mmol) and then $CF_3SO_3SiMe_3$ (45 µl) were added under Ar to a stirred soln. of **29** [22b] (2 g, 10.5 mmol) in anh. CH_2Cl_2 (22.5 ml). After stirring at 0° for 48 h, sat. aq. $NaHCO_3$ soln. (15 ml) was added and the mixture extracted with CH_2Cl_2 (50 ml, 3 times). The combined org. extract was washed with H_2O (10 ml) and brine (10 ml), dried ($MgSO_4$), and evaporated and the residue recrystallized from Et_2O/light petroleum ether 1:1: 1.8 g (74%). Colourless crystals. M.p. 84–85°. UV (MeCN): 213 (2500). IR (KBr): 2990, 2955, 2880, 1575, 1010, 895, 860. ^{1}H-NMR (250 MHz, $CDCl_3$): 6.58 (*d*, ^3J = 2.0, H–C(3)); 5.02 (*ddd*, ^3J = 4.5, 2.0, $^4J \approx 1.0$, H–C(4)); 4.35 (*d*, $^4J \approx 1.0$, H–C(1)); 4.10–4.00 (*m*, OCH_2CH_2O); 2.20 (*dd*, ^2J = 12.0, ^3J = 4.5, H_{exo}–C(5)); 1.84 (*d*, ^2J = 12.0, H_{endo}–C(5)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 136.5 (*d*, ^1J(C,H) = 181, C(3)); 124.8 (br. *s*, C(2)); 114 (*s*, C(6)); 84.8 (*dt*, ^1J(C,H) = 168, C(1)); 80.5 (*d*, ^1J(C,H) = 163, C(4)); 64.4, 65.4 (2*t*, ^1J(C,H) = 150, OCH_2CH_2O); 37.8 (*t*,

^1J(C,H) = 137, C(5)). MS (70 eV): 232 (1), 204 (3), 154 (1), 153 (4), 131 (2), 117 (1.5), 107 (37), 86 (100). Anal. calc. for $C_8H_9BrO_3$ (233.1): C 41.23, H 3.89; found: C 41.25, H 3.90.

(±)-2-Bromo-5,5-(ethylenedioxy)-7-oxabicyclo[2.2.1]hept-2-ene (**33**). As described above, from bromoenone (±)-**32** [26]. Yield 93%. Colourless crystals. M.p. 112–113°. UV (MeCN): 205 (3700). IR (KBr): 3095, 3000, 2970, 2890, 1575, 1320, 1240, 1130, 1040, 1015, 830, 625. ^{1}H-NMR (250 MHz, $CDCl_3$): 6.44 (*d*, ^3J = 2.0, H–C(3)); 4.80 (*dd*, ^3J = 4.5, ^4J = 1.0, H–C(1)); 4.42 (br. *s*, H–C(4)); 3.94–4.10 (*m*, OCH_2CH_2O); 2.16 (*dd*, ^2J = 12.0, ^3J = 4.5, H_{exo}–C(6)); 1.75 (*d*, ^2J = 12.0, H_{endo}–C(6)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 131.6 (br. *d*, ^1J(C,H) = 183, C(3)); 129.3 (*s*, C(2)); 118.2 (*s*, C(5)); 83.6 (br. *d*, ^1J(C,H) = 169, C(1)); 83.0 (br. *d*, ^1J(C,H) = 166, C(4)); 64.7, 65.4 (2*t*, ^1J(C,H) = 149, OCH_2CH_2O); 38.0 (*t*, ^1J(C,H) = 137, C(6)). MS (70 eV): 232 (0.2), 153 (1.0), 172 (1.4), 159 (5), 146 (7), 131 (5), 117 (7), 86 (100). Anal. calc. for $C_8H_9BrO_3$ (233.1): C 41.23, H 3.89; found: C 41.16, H 3.94.

(±)-6-Ethenyl-7-oxabicyclo[2.2.1]hept-5-en-2-one (**23**). A mixture of **29** [22b] (189 mg, 1 mmol), $[Pd(Ph_3P)_4]$ (58 mg, 0.05 mmol), and CH_2=CHSnBu_3 (321 µl, 1.1 mmol) in anh. DMF (8 ml) in a *Pyrex* tube was thoroughly degassed by several freeze-thaw cycles on the vacuum line ($< 10^{-2}$ Torr). The tube (containing a magnetic stirring bar) was sealed under vacuum, the mixture stirred at 55° for 3 h, the tube cooled in liq. N_2 and opened, and the yellow soln. taken in AcOEt (20 ml). After the addition of KF (1 g), the mixture was stirred at 25° for 2 h, and then filtered through *Celite*. The solvent was evaporated and the yellow residue purified by FC (silica gel (50 g, 230–400 mesh), CH_2Cl_2): 86 mg (63%) of colourless oil that cyclodimerized and polymerized quickly at 0°. UV ($CHCl_3$): 243 (*ca.* 10000). IR (film): 3005, 2920, 1760, 1570, 1410, 1280, 1210. ^{1}H-NMR (250 MHz, $CDCl_3$): 6.50 (*m*, H–C(5)); 6.50 (*dd*, ^3J(*trans*) = 17.5, ^3J(*cis*) = 11.0); 5.42 (*d*, ^3J = 17.5); 5.38 (*m*, H–C(4)); 5.33 (*d*, ^3J = 11.0); 4.83 (*s*, H–C(1)); 2.38 (*dd*, ^2J = 16.0, ^3J = 4.0, H_{exo}–C(3)); 2.02 (*d*, ^2J = 16.0, H_{endo}–C(3)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 207.8 (C(2)); 139.4 (C(6)); 136.6 (C(5)); 127.6, 118.6 (CH_2=CH); 82.1 (C(4)); 79.8 (C(1)); 35.1 (C(3)). MS (70 eV): 136 (1.2, $M^{+\cdot}$), 107 (15), 94 (57), 77 (29), 67 (22), 65 (36), 57 (100).

(±)-2-Ethenyl-6,6-(ethylenedioxy)-7-oxabicyclo[2.2.1]hept-2-ene (**24**). As described above, from **30** (233 mg, 1 mmol; 55°, 48 h): 105 mg (58%). Colourless oil. UV (MeOH): 234 (8000), 205 (5500). UV (CH_2Cl_2): 243 (12000). IR (film): 2990, 2940, 2910, 2880, 1675, 1630, 1570. ^{1}H-NMR (250 MHz, $CDCl_3$): 6.59 (*dd*, ^3J = 18.0, 11.0); 6.36 (*d*, ^3J = 1.8, H–C(3)); 5.23 (*d*, ^3J = 11.0); 5.23 (*d*, ^3J = 18.0); 5.04 (*ddd*, ^3J = 5.0, 1.8, ^4J = 1.0, H–C(4)); 4.68 (br. *s*, H–C(1)); 4.12, 3.95 (2*m*, OCH_2CH_2O); 2.22 (*dd*, ^2J = 12.0, ^3J = 5.0, H_{exo}–C(5)); 1.72 (*d*, ^2J = 12.0, H_{endo}–C(5)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 146.0 (br. *s*, C(2)); 134.4, 130.1 (2*d*); 116.1 (*dd*); 114.2 (*s*, C(6)); 80.9 (*dt*, C(1)); 79.4 (*dm*, C(4)); 65.7, 64.5 (2*t*, OCH_2CH_2O); 39.2 (*t*, C(5)). MS (70 eV): 180 (0.1, $M^{+\cdot}$), 152 (2), 118 (2), 107 (4), 94 (9), 86 (100).

(±)-5-Ethenyl-7-oxabicyclo[2.2.1]hept-5-en-2-one (**25**). As described above, from **32** [26] (189 mg, 1 mmol; 55°, 15 h): 82 mg (60%). Colourless oil. UV (MeCN): 241 (5700), 196 (8600). IR (film): 2990, 2910, 2830, 1705, 1575, 1515, 1360, 1155, 1035, 940, 870, 790. ^{1}H-NMR (250 MHz, $CDCl_3$): 6.57 (*dd*, ^3J = 17.5, 11.0); 6.17 (*m*, H–C(6)); 5.40 (*d*, ^3J = 4.0, H–C(4)); 5.37 (*d*, ^3J = 11.0); 5.27 (*d*, ^3J = 17.5); 4.66 (*d*, ^3J = 2.0, H–C(1)); 2.35 (*dd*, ^2J = 16.0, ^3J = 4.0, H_{exo}–C(3)); 1.83 (*d*, ^2J = 16.0, H_{endo}–C(3)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 206.0 (*s*, C(2)); 153.4 (*s*, C(5)); 128.7, 124.6 (2*d*); 118.7 (*t*, CH_2=CH); 83.3 (*d*, C(1)); 78.3 (*d*, C(4)); 34.5 (*t*, C(3)). MS (70 eV): 136 (0.5, $M^{+\cdot}$), 107 (8), 94 (100).

(±)-2-Ethenyl-5,5-(ethylenedioxy)-7-oxabicyclo[2.2.1]hept-2-ene (**26**). As described above, from **33** (233 mg, 1 mmol; 55°, 20 h): 170 mg (94%). Colourless oil. UV (MeCN): 237 (15300). IR (film): 2980, 2940, 2880, 1665, 1640, 1625, 1570, 1315, 1240, 1130, 1040, 1020, 840. ^{1}H-NMR (250 MHz, $CDCl_3$): 6.50 (*dd*, ^3J = 17.0, 11.0); 6.17 (*d*, ^3J = 1.5, H–C(3)); 5.20 (br. *d*, ^3J = 11.0); 5.17 (br. *d*, ^3J = 17.0); 5.12 (br. *d*, ^3J = 5.0, H–C(1)); 4.46 (*dd*, ^3J = 1.5, ^4J = 1.0, H–C(4)); 4.06, 3.87 (2*m*, OCH_2CH_2O); 2.18 (*dd*, ^2J = 12.0, ^3J = 5.0, H_{exo}–C(6)); 1.55 (*d*, ^2J = 12.0, H_{endo}–C(6)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 150.4 (br. *s*, C(2)); 128.8 (*d*, ^1J(C,H) = 178); 128.7 (*d*, ^1J(C,H) = 158); 114.8 (*s*, C(5)); 82.2, 78.2 (2*d*, ^1J(C,H) = 165, C(1), C(4)); 65.2, 64.5 (2*t*, ^1J(C,H) = 153, OCH_2CH_2O); 38.8 (*t*, ^1J(C,H) = 137, C(6)). MS (70 eV): 180 (23, $M^{+\cdot}$), 152 (17), 118 (8.0), 107 (16), 94 (42), 86 (100).

Dimethyl (1RS,2SR,8RS)-10,10-(Ethylenedioxy)-11-oxatricyclo[6.2.1.0^{2,7}]undeca-3,6-diene-3,4-dicarboxylate (**34**). A mixture of MeOOCC≡CCOOMe (500 µl) and **26** (45 mg, 0.25 mmol) was stirred at 25° for 23 h. Evaporation of the excess of MeOOCC≡CCOOMe *in vacuo* and CC (silica gel, CH_2Cl_2, then CH_2Cl_2/AcOEt 9:1) of the residue gave an oil that crystallized from Et_2O/light petroleum ether 1:1: 52.4 mg (65%). Colourless crystals. M.p. 130.5–131.5°. IR (KBr): 3000, 2940, 2900, 2880, 1710, 1630, 1260, 945, 840, 750, 640. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.85 (br. *dd*, ^3J = 6.5, ^4J = 3.0, H–C(6)); 4.82 (*d*, ^3J = 6.0, H–C(8)); 4.28 (*s*, H–C(1)); 4.07, 3.97 (2*m*, OCH_2CH_2O); 3.83, 3.77 (2*s*, 2 MeO); 3.40 (*ddd*, ^3J(H–C(2), H–C(1)) = 0, ^4J(H–C(2),H–C(6)) = 3.0, ^5J(H_{ax}–C(2),H_{ax}–C(5)) = 12.0, ^2J(H_{ax}–C(2),H_{eq}–C(5)) = 4.0, H–C(2)); 3.22 (*ddd*, ^2J = 21.0, ^3J = 6.5, ^5J = 4.0, H_{eq}–C(5)); 2.79 (*ddd*, ^2J = 21.0, ^3J(H–C(5),H–C(6)) ≈ 1, ^5J = 12.0, H_{ax}–C(5)); 2.32 (*dd*, ^2J = 13.5, ^3J = 6.0 H_{exo}–C(9)); 2.00 (*d*, ^2J = 13.5, H_{endo}–C(9)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 167.5, 167.1 (2*s*, 2 CO); 141.9 (*s*,

C(7)); 137.5, 135.2 (2*s*, C(3), C(4)); 115.1 (*d*, C(6)); 114.5 (*s*, C(10)); 80.7, 78.6 (2*d*, C(1), C(8)); 65.2, 64.5 (2*t*, OCH_2CH_2O); 52.3, 52.2 (2*q*, 2 MeO); 40.9 (*t*, C(5)); 39.9 (*d*, C(2)); 28.4 (*t*, C(9)). MS (70 eV): 322 (0.5, M^+), 307 (0.8), 293 (23), 263 (8), 235 (2), 219 (10), 189 (12), 86 (73), 73 (100). Anal. calc. for $C_{16}H_{18}O_7$ (322.3): C 59.62, H 5.63; found: C 59.74, H 5.74.

Methyl (1RS,2RS,8RS)-10,10-(Ethylenedioxy)-11-oxatricyclo[6.2.1.0^{2,7}]undeca-3,6-diene-4-carboxylate (**35**) *and Methyl (1RS,2SR,8RS)-10,10-(Ethylenedioxy)-11-oxatricyclo[6.2.1.0^{2,7}]undeca-3,6-diene-3-carboxylate* (**36**). A mixture of methyl propynoate (0.5 ml) and **26** (45 mg, 0.25 mmol) was stirred at 25° for 8 days or at 55° for 24 h. The excess of dienophile was recovered by distillation *in vacuo* and the residue purified by CC (silica gel, CH_2Cl_2, CH_2Cl_2/AcOEt 9:1): 50 mg (75%; reaction at 25°) or 42 mg (64%; reaction at 55°) of **35**/**36** 78:22 to 80:20. Further CC (*Lobar* (type *A*), CH_2Cl_2/AcOEt 95:5) gave the aromatized **37** and **38** (10 mg; see below), **35** (30 mg, after recrystallization from Et_2O/light petroleum ether), and **36** (8 mg).

Data of **35**: Colourless crystals. M.p. 90°. IR (KBr): 2990, 2940, 2860, 1705, 1620, 1430, 1260, 1130, 1070, 1010. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.19 (*dd*, ^3J = 2.5, ^4J = 3.5, H–C(3)); 5.87 (*dm*, ^3J = 6.5, H–C(6)); 4.80 (*d*, ^3J = 6.0, H–C(8)); 4.19 (br. *s*, ^3J(H–C(1),H–C(2)) = 0, H–C(1)); 4.12, 3.95 (2*m*, OCH_2CH_2O); 3.79 (*s*, MeO); 3.22 (*ddd*, ^2J = 21.0, ^3J = 6.5, ^4J = 3.5, H_{eq}–C(5)); 3.17 (*m*, H–C(2)); 2.64 (*m*, H_{ax}–C(5)); 2.32 (*ddd*, ^2J = 13.5, ^3J = 6.0, ^4J = 1.0, H_{exo}–C(9)); 1.99 (*d*, ^2J = 13.5, H_{endo}–C(9)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 166.7 (*s*, CO); 142.1 (*s*, C(7)); 139.8 (*d*, C(3)); 132.4 (*s*, C(4)); 116.4 (*d*, C(6)); 114.7 (*s*, C(10)); 82.5, 78.5 (2*d*, C(1), C(8)). MS (70 eV): 264 (44, M^+), 249 (5), 235 (100), 233 (5), 205 (15), 191 (51), 168 (6), 103 (51). Anal. calc. for $C_{14}H_{16}O_5$ (264.2): C 63.63, H 6.10; found: C 63.70, H 6.07.

Data of **36**: Colourless crystals. M.p. 129–131°. IR ($CHCl_3$): 1705. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.10 (*m*, H–C(4)); 5.76 (*m*, H–C(6)); 4.77 (*d*, ^3J = 6.0, H–C(8)); 4.72 (br. *s*, ^3J(H–C(1),H–C(2)) = 0, H–C(1)); 4.06, 3.95 (2*m*, OCH_2CH_2O); 3.78 (*s*, MeO); 3.28 (*m*, H–C(2)); 2.92 (br. *ddd*, ^2J = 22.0, ^3J = 5.5, ^5J = 11.0, H_{eq}–C(5)); 2.75 (*dddd*, ^2J = 22.0, ^3J = 2.5, 2.0, ^5J = 11.0, H_{ax}–C(5)); 2.34 (*ddd*, ^2J = 13.5, ^3J = 6.0, ^4J = 1.0, H_{exo}–C(9)); 2.04 (*d*, ^2J = 13.5, H_{endo}–C(9)). MS (70 eV): 264 (2, M^+), 235 (73), 233 (5), 203 (5), 177 (5), 131 (8), 118 (16), 87 (24), 86 (32), 73 (100).

Mixture of Methyl (5RS,8RS)-7,7-(Ethylenedioxy)-5,6,7,8-tetrahydro-5,8-epoxynaphthalene-2-carboxylate (**37**) *and Methyl (5RS,8RS)-7,7-(Ethylenedioxy)-5,6,7,8-tetrahydro-5,8-epoxynaphthalene-1-carboxylate* (**38**): White crystals. IR (CH_2Cl_2): 1705. ^{1}H-NMR (250 MHz, $CDCl_3$) of **37**: 8.02 (br. *s*, H–C(1)); 7.97 (*dd*, ^3J = 7.5, ^4J = 1.5, H–C(3)); 7.32 (*d*, ^3J = 7.5, H–C(4)); 5.47 (*d*, ^3J = 5.5, H–C(5)); 4.92 (*s*, H–C(8)); 4.15, 3.99 (2*m*, OCH_2CH_2O); 3.90 (*s*, MeO); 2.49 (*dd*, ^2J = 12.5, ^3J = 5.5, H_{exo}–C(6)); 1.75 (*d*, ^2J = 12.5, H_{endo}–C(6)). ^{1}H-NMR (250 MHz, $CDCl_3$) of **38**: 7.85, 7.46 (2 br. *d*, ^3J = 7.5, H–C(2), H–C(4)); 7.31 (*t*, ^3J = 7.5, H–C(3)); 5.65 (*s*, H–C(8)); 5.45 (*d*, ^3J = 5.5, H–C(5)); 4.15, 3.99 (2*m*, OCH_2CH_2O); 3.94 (*s*, MeO); 2.52 (*dd*, ^2J = 12.5, ^3J = 5.5, H_{exo}–C(5)); 1.77 (*d*, ^2J = 12.5, H_{endo}–C(5)). MS (70 eV): 262 (5, M^+), 231 (7), 189 (3), 176 (100), 161 (5), 145 (14), 177 (10), 86 (35).

(1RS,2RS,3SR,7RS,11RS)-13,13-(Ethylenedioxy)-5-phenyl-14-oxa-5-azatetracyclo[9.2.1.0^{2,10}.0^{3,7}]tetradec-9-ene-4,6-dione (**39**) *and (1RS,2RS,3RS,7SR,11RS)-13,13-(Ethylenedioxy)-5-phenyl-14-oxa-5-azatetracyclo[9.2.1.0^{2,10}.0^{3,7}]tetradec-9-ene-4,6-dione* (**40**). A mixture of **26** (119 mg, 0.66 mmol) and *N*-phenylmaleimide (572 mg, 3.30 mmol) in dry benzene (2.5 ml) was stirred at 25° for 3 h. After evaporation, the residue was purified by CC (silica gel CH_2Cl_2/AcOEt 95:5): 209 mg (89.5%) of **39**/**40** 85:15. Separation by CC (*Lobar* (type *A*), CH_2Cl_2/AcOEt 95:5) yielded 170 mg of **39**, recrystallized from toluene, and 25 mg of **40**, crystallized from MeOH.

Data of **39**: Colourless crystals. M.p. 211–212°. IR (KBr): 3020, 2990, 2950, 2900, 2880, 1710, 1595, 1495, 1380, 1180, 1010. ^{1}H-NMR (360 MHz, $CDCl_3$): 7.40, 7.29 (2*m*, Ph); 5.85 (*dm*, ^3J = 7.5, H–C(9)); 4.80 (br. *s*, ^3J(H–C(1),H–C(2)) = 6, H–C(1)); 4.75 (*d*, ^3J = 6.0, H–C(11)); 4.12, 3.95 (2*m*, OCH_2CH_2O); 3.47 (*dd*, ^3J = 9.0, 8.5, H–C(3)); 3.32 (*ddd*, ^3J = 8.5, 5.0, 2.0, H–C(7)); 2.93 (*ddd*, ^2J = 15.0, ^3J = 7.5, 2.0, H_{eq}–C(8)); 2.90 (*dm*, ^3J = 9.0, H–C(2)); 2.32 (*dd*, ^2J = 13.0, ^3J = 6.0, ^4J = 1.0, H_{exo}–C(12)); 2.15 (*dm*, ^2J = 15.0, H_{ax}–C(8)); 1.90 (*d*, ^2J = 13.0, H_{endo}–C(12)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 178.1, 176.8 (2 CO); 144.5 (C(10)); 131.8 (arom. C); 128.9, 128.3, 126.3 (arom. C); 115.2 (C(9)); 114.1 (C(13)); 80.1, 77.9 (C(1), C(11)); 65.3, 64.5 (OCH_2CH_2O); 42.2 (C(2)); 40.5, 40.3 (C(3), C(7)); 37.1 (C(12)); 23.2 (C(8)). MS (70 eV): 353 (3, M^+), 335 (23), 325 (58), 267 (16), 119 (34), 86 (100), 77 (92). Anal. calc. for $C_{20}H_{19}NO_5$ (353.35): C 67.98, H 5.42, N 3.96; found: C 67.84, H 5.52, N 4.02.

Data of **40**: Colourless crystals. M.p. 173–175°. IR (KBr): 3060, 2955, 2890, 1770, 1705, 1595, 1490, 1380, 1180, 1155. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.55–7.30 (*m*, Ph); 5.92 (*m*, H–C(9)); 4.88 (*d*, ^3J = 6.0, H–C(11)); 4.59 (br. *s*, ^3J(H–C(1),H–C(2)) = 0, H–C(1)); 4.11, 3.95 (2*m*, OCH_2CH_2O); 3.04 (*dt*, ^3J = 10.0, 7.5, 7.5, H–C(7)); 2.86 (*dt*, ^2J = 15.0, ^3J = 7.5, 7.5, H_{eq}–C(8)); 2.82 (*t*, ^3J = 10.0, H–C(3)); 2.57 (*d*, ^3J(H–C(2),H–C(3)) = 10.0, H–C(2)); 2.36 (*dd*, ^2J = 13.5, ^3J = 6.0, H_{exo}–C(12)); 2.12 (*dm*, ^2J = 15.0, H_{ax}–C(8)); 1.93 (*d*, ^2J = 13.5, H_{endo}–C(12)). MS (70 eV): 353 (4, M^+), 335 (4), 325 (21), 267 (3), 119 (2), 86 (100), 77 (33).

Methyl (1RS,2RS,4RS,8RS)-10,10-(Ethylenedioxy)-11-oxatricyclo[6.2.1.0^{2,7}]undec-6-ene-4-carboxylate (**41**), *Methyl (1RS,2RS,3RS,8RS)-10,10-(Ethylenedioxy)-11-oxatricyclo[6.2.1.0^{2,7}]undec-6-ene-3-carboxylate* (**42**), *Methyl (1RS,2RS,4SR,8RS)-10,10-(Ethylenedioxy)-11-oxatricyclo[6.2.1.0^{2,7}]undec-6-ene-4-carboxylate* (**43**), *and Methyl (1RS,2RS,3SR,8RS)-10,10-(Ethylenedioxy)-11-oxatricyclo[6.2.1.0^{2,7}]undec-6-ene-3-carboxylate* (**44**). A soln. of **26** (45 mg, 0.25 mmol) in methyl acrylate (0.5 ml) was stirred at 25° for 6 days. The excess of dienophile was recovered by distillation under vacuum and the residue purified by CC (silica gel, CH_2Cl_2, then CH_2Cl_2/AcOEt 9:1): 60 mg (89%) of **41**/**42**/**43**/**44** 40:8:41:11. When run at 55° for 24 h, 44 mg (66%) of **41**/**42**/**43**/**44** 40.5:8.5:41:9 were obtained. These two mixtures were combined and separated by CC (*Lobar* (type *B*), AcOEt/light petroleum ether 7:3) giving 15 mg of **41**/**42**/**44**, 50 mg of **41**/**42**/**43**/**44**, and 18 mg of pure **43**. The mixture **41**/**42**/**44** was taken with Et_2O (0.5 ml) which gave pure **41**, and **43** was recrystallized from Et_2O/light petroleum ether 1:3.

Data of **41**: Colourless crystals. M.p. 90–91° (Et_2O). IR (KBr): 2990, 2950, 2920, 2860, 1725, 1165, 1015. ^{1}H-NMR (360 MHz, $CDCl_3$): 5.68 (*m*, ^4J = 4.0, H–C(6)); 4.74 (*d*, ^3J = 6.0, H–C(8)); 3.95 (*s*, ^3J(H–C(1),H–C(2)) = 0, H–C(1)); 4.06, 3.92 (2*m*, OCH_2CH_2O); 3.70 (*s*, MeO); 2.72 (*m*, H–C(4)); 2.61 (*dm*, ^2J = 12.5, H–C(3)); 2.43 (*ddt*, ^2J = 18.5, ^3J = 7.5, ^4J = 2.5, H_{eq}–C(5)); 2.29 (*dddd*, ^2J = 18.5, ^3J = 7.5, 2.5, ^4J = 2.5, H_{ax}–C(5)); 2.23 (*dd*, ^2J = 13.5, ^3J = 6.0, H_{exo}–C(9)); 2.18 (*dt*, ^3J = 12.5, ^3J = 4.0, ^4J = 4.0, H–C(2)); 1.91 (*d*, ^2J = 13.5, H_{endo}–C(9)); 1.35 (*m*, ^2J = 12.5, ^3J(H–C(2),H_{ax}–C(3)) = 12.5, H_{ax}–C(3)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 176.2 (*s*, CO); 142.6 (*s*, C(7)); 115.8 (*d*, C(6)); 115.8 (*s*, C(10)); 82.1, 79.8 (2*d*, C(1), C(8)); 65.3, 64.4 (2*t*, OCH_2CH_2O); 51.8 (*q*, MeO); 40.9 (*t*, C(5)); 39.4 (*d*, C(4)); 37.1 (*d*, C(2)); 28.2, 26.8 (2*t*, C(3), C(9)). MS (70 eV): 266 (3, M^+), 238 (59), 237 (48), 235 (22), 220 (5), 207 (1), 94 (17), 91 (100), 86 (74), 67 (24). Anal. calc. for $C_{14}H_{18}O_5$ (266.3): C 63.15, H 6.81; found: C 63.08, H 6.89.

Data of **42**: ^{1}H-NMR (250 MHz, $CDCl_3$): 5.51 (*m*, H–C(6)); 4.66 (*d*, ^3J = 6.0, H–C(8)); 4.14 (*s*, ^3J(H–C(1),H–C(2)) = 0, H–C(1)); 4.05, 3.92 (2*m*, OCH_2CH_2O); 3.72 (*s*, MeO); 2.85–2.07 (*m*, 6 H); 1.95 (*d*, ^2J = 13.0, H_{endo}–C(9)); 1.75 (*m*, H_{ax}–C(4)).

Data of **43**: Colourless crystals. M.p. 101–102° (Et_2O). IR (KBr): 2990, 2950, 2940, 2870, 1725, 1445, 1350, 1230, 1190, 1165, 1015. ^{1}H-NMR (400 MHz, C_6D_6): 5.36 (*dm*, ^3J = 5.4, H–C(6)); 4.48 (*d*, ^3J = 6.0, H–C(8)); 3.98 (*s*, ^3J(H–C(1),H–C(2)) = 0, H–C(1)); 3.35 (*s*, MeO); 3.53, 3.33 (2*m*, OCH_2CH_2O); 2.83 (*ddd*, ^3J = 12.6, 4.6, ^4J = 2.1, H–C(2)); 2.59 (*ddd*, ^2J = 17.2, ^3J = 5.8, 2.2, H_{ax}–C(5)); 2.54 (*m*, H_{ax}–C(4)); 2.34 (*ddd*, ^2J = 12.2, ^3J = 4.6, ^4J = 2.6, H_{eq}–C(3)); 2.23 (*ddd*, ^2J = 12.8, ^3J = 6.0, ^4J = 0.8, H_{exo}–C(9)); 2.07 (*ddm*, ^2J = 17.2, ^3J = 5.4, H_{eq}–C(5)); 1.86 (*d*, ^2J = 12.8, H_{endo}–C(9)); 1.46 (*ddd*, ^2J = 12.2, ^3J = 12.6, 6.3, H_{ax}–C(3)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 176.4 (*s*, CO); 144.4 (*s*, C(7)); 116.4 (*s*, C(10)); 115.4 (*d*, C(6)); 83.1, 80.3 (2*d*, C(1), C(8)); 65.8, 64.9 (2*t*, OCH_2CH_2O); 52.4 (*q*, MeO); 41.8 (*t*, C(5)); 37.1 (*d*, C(4)); 34.3 (*d*, C(2)); 27.8, 25.6 (2*t*, C(3), C(9)). MS (70 eV): 266 (0.05, M^+), 238 (47), 237 (26), 235 (4), 220 (2), 180 (9), 94 (18), 91 (100), 86 (93), 67 (17). Anal. calc. for $C_{14}H_{18}O_5$ (266.3): C 63.15, H 6.81; found: C 63.24, H 6.72.

Data of **44**: ^{1}H-NMR (250 MHz, $CDCl_3$): 5.70 (*m*, H–C(6)); 4.62 (*d*, ^3J = 6.0, H–C(8)); 4.32 (*s*, ^3J(H–C(1),H–C(2)) = 0, H–C(1)); 4.05, 3.92 (2*m*, OCH_2CH_2O); 3.62 (*s*, MeO); 2.95 (*m*, H–C(9)); 2.85–2.07 (*m*, 6 H); 1.87 (*d*, ^2J = 13.0, H_{endo}–C(9)); 1.75 (*m*, H_{ax}–C(4)).

Methyl (1RS,2SR,4SR,8RS)-9,9-(Ethylenedioxy)-11-oxatricyclo[6.2.1.0^{2,7}]undec-6-ene-4-carboxylate (**45**), *Methyl (1RS,2SR,3SR,8RS)-9,9-(Ethylenedioxy)-11-oxatricyclo[6.2.1.0^{2,7}]undec-6-ene-3-carboxylate* (**46**), *Methyl (1RS,2SR,4RS,8RS)-9,9-(Ethylenedioxy)-11-oxatricyclo[6.2.1.0^{2,7}]undec-6-ene-4-carboxylate* (**47**), *and Methyl (1RS,2SR,3RS,8RS)-9,9-(Ethylenedioxy)-11-oxatricyclo[6.2.1.0^{2,7}]undec-6-ene-4-carboxylate* (**48**). As described above from **24**. At 25° (6 days), **45**/**46**/**47**/**48** 34:13:43:10 (63 mg, 95%) was obtained. At 55° (24 h), **45**/**46**/**47**/**48** 45:10:35:10 (60 mg, 90%) was isolated. The combined mixtures were separated by CC (*Lobar* (type *B*), AcOEt/light petroleum ether 3:7): 9.5 mg of **46**, 20 mg of **45**, 75 mg of **46**/**47**/**48**, and 10 mg of pure **47**.

Data of **45**: Colourless crystals. M.p. 92–93° (Et_2O). IR (KBr): 2980, 2960, 2910, 2880, 1725, 1430, 1300, 1240, 1180, 1050, 1010, 805. ^{1}H-NMR (360 MHz, $CDCl_3$): 5.76 (*m*, H–C(6)); 4.39 (*d*, ^3J(H–C(1),H_{exo}–C(10)) = 5.5, ^3J(H–C(1),H–C(2)) = 0, H–C(1)); 4.29 (*s*, H–C(8)); 4.06, 3.99, 3.89 (3*m*, OCH_2CH_2O); 3.68 (*s*, MeO); 2.72 (*m*, H_{ax}–C(4)); 2.50 (*dddd*, ^2J = 18.5, ^3J = 7.5, ^3J = 3.0, ^4J = 2.5, H_{eq}–C(5)); 2.32 (*dddd*, ^2J = 18.5, ^3J = 10.0, 4.0, ^5J = 2.5, H_{ax}–C(5)); 2.25 (*dd*, ^2J = 13.0, ^3J = 5.5, H_{exo}–C(10)); 2.20 (*m*, H–C(3)); 2.16 (*m*, H_{ax}–C(2)); 1.82 (*d*, ^2J = 13.0, H_{endo}–C(10)); 1.31 (*m*, ^2J = 12.0, H_{ax}–C(3)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 176.1 (*s*, CO); 138.9 (*s*, C(7)); 119.6 (*d*, C(6)); 114.1 (*s*, C(9)); 83.7, 79.3 (2*d*, C(1), C(8)); 65.3, 64.5 (2*t*, OCH_2CH_2O); 51.8 (*q*, MeO); 45.5 (*t*, C(5)); 42.9 (*d*, C(4)); 39.1 (*d*, C(2)); 28.8, 27.1 (2*t*, C(3), C(10)). MS (70 eV): 266 (1, M^+), 235 (3), 179 (0.3), 121 (3), 120 (1), 99 (100), 86 (13). Anal. calc. for $C_{14}H_{18}O_5$ (266.3): C 63.15, H 6.81; found: C 63.26, H 6.75.

Data of **46**: Colourless crystals. M.p. 87–88° (Et_2O/light petroleum ether). IR (CH_2Cl_2): 2950, 2880, 1725, 1310, 1015. ^{1}H-NMR (360 MHz, $CDCl_3$): 5.76 (*m*, H–C(6)); 4.52 (*d*, ^3J = 5.5, H–C(1)); 4.31 (*s*, H–C(8)); 4.05, 3.84 (2*m*, OCH_2CH_2O); 3.73 (*s*, MeO); 2.35 (*m*, H_{eq}–C(5), H–C(3)); 2.26 (*dd*, ^2J = 12.5, ^3J = 5.5, H_{exo}–C(10));

2.18 (*m*, H–C(2),H_{ax}–C(5)); 2.06 (*dddd*, ^2J = 13.5, ^3J = 7.5, 3.0, 1.0, H_{eq}–C(4)); 1.90 (*d*, ^2J = 12.5, H_{endo}–C(10)); 1.72 (*m*, ^2J = 13.5, ^3J = 10.0, 7.5, H_{ax}–C(4)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 175.9 (*s*, CO); 137.3 (*s*, C(7)); 120.5 (*d*, C(6)); 114.1 (*s*, C(9)); 83.8, 78.5 (2*d*, C(1), C(8)); 65.5, 64.5 (2*t*, OCH_2CH_2O); 51.8 (*q*, MeO); 45.3 (*t*, C(5)); 42.1 (*d*, C(3)); 29.7 (*d*, C(2)); 25.3, 24.5 (2*t*, C(4), C(10)). MS (70 eV): 266 (4, $M^{+\cdot}$), 238 (4), 235 (1.5), 224 (12), 180 (1), 133 (5), 121 (4), 99 (100), 86 (34).

Data of **47**: Colourless crystals. M.p. 80–81° (Et_2O/light petroleum ether). IR (KBr): 2980, 2950, 2920, 2890, 1715, 1440, 1325, 1230, 1195, 1040, 1010, 810. ^{1}H-NMR (360 MHz, $CDCl_3$): 5.75 (*m*, ^3J = 5.5, H–C(6)); 4.37 (*d*, ^3J(H–C(1),H–C(2)) = 0, ^3J(H–C(1),H_{exo}–C(10)) = 6.0, H–C(1)); 4.30 (*s*, H–C(8)); 4.08, 3.85 (2*m*, OCH_2CH_2O); 3.71 (*s*, MeO); 2.76 (*dddd*, ^3J = 8.5, 7.0, 4.0, 3.0, H_{ax}–C(4)); 2.55 (*dm*, ^2J = 18.0, H_{eq}–C(5)); 2.38 (*dddd*, ^2J = 18.0, ^3J = 8.5, 5.5, ^4J = 1.5, H_{ax}–C(5)); 2.33 (*ddd*, ^2J = 12.5, ^3J = 5.0, 3.0, H–C(3)); 2.25 (*dd*, ^2J = 13.0, ^3J = 6.0, H_{exo}–C(10)); 2.04 (*dm*, H_{ax}–C(2)); 1.83 (*d*, ^2J = 13.0, H_{endo}–C(10)); 1.29 (*td*, ^2J = 12.5, ^3J = 12.5, 7.0, H_{ax}–C(3)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 176.3 (*s*, CO); 140.5 (*s*, C(7)); 118.5 (*d*, C(6)); 114.2 (*s*, C(9)); 83.5, 79.8 (2*d*, C(1), C(8)); 65.5, 64.5 (2*t*, OCH_2CH_2O); 51.9 (*q*, MeO); 44.7 (*t*, C(5)); 39.6 (*d*, C(4)); 36.1 (*d*, C(2)); 27.9, 25.4 (2*t*, C(3), C(10)). MS (70 eV): 266 (3, $M^{+\cdot}$), 235 (1), 207 (2), 149 (1), 121 (3), 99 (100), 86 (23). Anal. calc. for $C_{14}H_{18}O_5$ (266.3): C 63.15, H 6.81; found: C 63.08, H 6.97.

Data of **48**: IR (CH_2Cl_2): 2950, 2880, 1725, 1320, 1015, 810. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.80 (*m*, H–C(6)); 4.71 (*d*, ^3J(H–C(1),H–C(2)) = 0, ^3J(H–C(1),H_{exo}–C(10)) = 6.0, H–C(1)); 4.16 (*s*, H–C(8)); 4.00, 3.82 (2*m*, OCH_2CH_2O); 3.55 (*s*, MeO); 2.92 (*m*, H–C(3)); 2.58–2.08 (*m*, 5 H); 1.75 (*d*, ^2J = 13.0, H_{endo}–C(10)). MS (70 eV): 266 (2, $M^{+\cdot}$), 235 (2), 207 (2), 133 (2), 99 (100), 86 (22).

*Methyl (1*RS,*2*SR,*8*RS*)-9-Oxo-11-oxatricyclo[6.2.1.0^{2,7}]undeca-3,6-diene-4-carboxylate* (**49**), *Methyl (1*RS,*2*RS,*8*RS*)-9-Oxo-11-oxatricyclo[6.2.1.0^{2,7}]undeca-3,6-diene-3-carboxylate* (**50**). A mixture of **23** (35 mg, 0.25 mmol) in methyl propynoate (0.5 ml) was stirred at 55° for 24 h. After evaporation of the excess of dienophile *in vacuo*, the residue was purified by CC (silica gel, AcOEt/light petroleum ether 2:8) giving 37 mg (67%) of **49**/**50** 69:31 which were aromatized into **53**/**54** (see below) on standing in the air. Further purification by CC (*Lobar* (type *A*), AcOEt/light petroleum ether 3:7) gave **53**/**54** (10 mg), **49**/**50** (15 mg), and **49** (5 mg) which was aromatized into **53**.

Data of **49**: IR (CH_2Cl_2): 2955, 1725, 1715, 1395, 1205, 1095. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.23 (*m*, H–C(3)); 6.21 (*dm*, ^3J = 6.5, H–C(6)); 5.00 (*d*, ^3J = 6.0, H–C(1)); 4.61 (*s*, H–C(8)); 3.79 (*s*, MeO); 3.34 (*dd*, ^2J = 17.0, ^3J = 6.5, H_{eq}–C(5)); 2.62–2.76 (*m*, H_{exo}–C(10), H_{ax}–C(5), H_{ax}–C(2)); 2.17 (*d*, ^2J = 17.0, H_{endo}–C(10)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 207.5 (*s*, C(9)); 166.5 (*s*, COO); 138.7 (*d*, C(3)); 134.6 (*s*, C(7)); 133.1 (*s*, C(4)); 123.4 (*d*, C(6)); 82.0, 79.2 (2*d*, C(1), C(8)); 51.9 (*q*, MeO); 45.0 (*d*, C(2)); 44.8 (*t*, C(5)); 27.1 (*t*, C(10)). MS (70 eV): 220 (3, $M^{+\cdot}$), 205 (5), 190 (40), 189 (24), 178 (1), 163 (9), 159 (16), 145 (26), 119 (8), 105 (56), 91 (100), 59 (40).

Data of **50**: ^{1}H-NMR (250 MHz, $CDCl_3$): 7.15 (*dm*, ^3J = 6.5, H–C(4)); 6.07 (*dm*, ^3J = 6.5, H–C(6)); 4.46 (*d*, ^3J = 6.0, H–C(1)); 4.57 (*s*, H–C(8)); 3.81 (*s*, MeO); 3.00 (*dt*, ^2J = 17.5, ^3J = 6.5, H_{eq}–C(5)); 2.85 (*m*, H_{ax}–C(2)); 2.75 (*m*, H_{ax}–C(5)); 2.70 (*dd*, ^2J = 17.0, ^3J = 6.0, H_{exo}–C(10)); 2.22 (*d*, ^2J = 17.0, H_{endo}–C(10)). MS (70 eV): 220 (1, $M^{+\cdot}$), 190 (19), 189 (12), 178 (1), 163 (7), 159 (8), 145 (33), 119 (8), 105 (73), 91 (57), 77 (100), 59 (43).

Methyl 5,6,7,8-Tetrahydro-6-oxo-5,8-epoxynaphthalene-2-carboxylate (**53**). IR (CH_2Cl_2): 2950, 1760, 1720. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.01 (br. *s*, H–C(1)); 7.99 (*dd*, ^3J = 8.0, ^4J = 1.2, H–C(3)); 7.50 (*d*, ^3J = 8.0, H–C(4)); 5.82 (*d*, ^3J = 5.0, H–C(8)); 5.09 (*s*, H–C(5)); 3.92 (*s*, MeO); 2.67 (*dd*, ^2J = 15.0, ^3J = 5.0, H_{exo}–C(7)); 2.05 (*d*, ^2J = 15.0, H_{endo}–C(5)). MS (70 eV): 218 (0.1, $M^{+\cdot}$), 190 (25, $[M-18]^{+\cdot}$), 176 (100), 159 (20), 131 (54), 117 (25), 103 (52), 89 (63), 77 (98), 63 (74).

*Methyl (1*RS,*2*RS,*8*RS*)-10-Oxo-11-oxatricyclo[6.2.1.0^{2,7}]undeca-3,6-diene-4-carboxylate* (**51**), *Methyl (1*RS,*2*SR,*8*RS*)-10-Oxo-11-oxatricyclo[6.2.1.0^{2,7}]undeca-3,6-diene-3-carboxylate* (**52**). As described for **49**/**50** starting with 35 mg (0.25 mmol) of **25**; **51**/**52** 72:28 (47 mg, 85%). Purification by CC (*Lobar* (type *A*), AcOEt/CH_2Cl_2 2:98) gave the aromatized **55**/**56** (10 mg; see below), **51** (22 mg), and **52** (12 mg) which was recrystallized from Et_2O/light petroleum ether.

Data of **51**: ^{1}H-NMR (250 MHz, $CDCl_3$): 7.15 (*dd*, ^3J = 2.0, ^4J = 3.0, H–C(3)); 6.07 (*dm*, ^3J = 6.5, H–C(6)); 5.14 (*d*, ^3J = 5.5, H–C(8)); 4.47 (*s*, H–C(1)); 3.77 (*s*, MeO); 3.30 (*ddd*, ^2J = 19.5, ^3J = 6.5, ^4J = 3.0, H_{eq}–C(5)); 2.85–2.60 (*m*, 3 H, H_{exo}–C(9), H_{ax}–C(5), H_{ax}–C(2)); 2.62 (*ddd*, ^2J = 17.5, ^3J = 5.5, ^4J = 1.0, H_{exo}–C(9)); 2.31 (*d*, ^2J = 17.5, H_{endo}–C(9)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 208.8 (*s*, C(10)); 166.1 (*s*, COO); 139.5 (*s*, C(7)); 137.1 (*d*, C(3)); 133.3 (*s*, C(4)); 119.7 (*d*, C(6)); 82.2, 78.5 (2*d*, C(1), C(8)); 51.8 (*q*, MeO); 40.3 (*d*, C(2)); 40.1, 26.7 (2*t*, C(5), C(9)). MS (70 eV): 220 (< 0.01, $M^{+\cdot}$), 205 (1), 190 (38), 189 (10), 178 (1), 163 (6), 159 (11), 119 (5), 105 (16), 91 (38), 77 (57), 57 (100).

Data of **52**: Colourless crystals. M.p. 95–96°. IR (CH_2Cl_2). 1760, 1710. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.20 (*dd*, ^3J = 2.0, ^4J = 3.0, H–C(4)); 5.99 (*dm*, ^3J = 5.5, H–C(6)); 5.12 (*dt*, ^3J = 6.0, ^4J = 1.0, H–C(8)); 5.00 (*s*, H–C(1));

3.82 (*s*, MeO); 3.06–2.84 (*m*, CH_2(5), H_{ax}–C(2)); 2.62 (*ddd*, ^2J = 17.5, ^3J = 6.0, ^4J = 1.0, H_{exo}–C(9)); 2.31 (*d*, ^2J = 17.5, H_{endo}–C(9)). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 208.8 (*s*, C(10)); 165.7 (*s*, COO); 141.1 (*d*, C(4)); 140.1 (*s*, C(7)); 128.7 (*s*, C(3)); 117.7 (*d*, C(6)); 81.4, 78.7 (2*d*, C(1), C(8)); 51.8 (*q*, MeO); 39.9, 27.8 (2*t*, C(5), C(9)); 38.1 (*d*, C(2)). MS (70 eV): 220 (1, M^+), 205 (1), 190 (2), 189 (11), 178 (27), 163 (34), 159 (6), 119 (17), 105 (53), 91 (96), 77 (83), 59 (100).

Methyl 5,6,7,8-Tetrahydro-7-oxo-5,8-epoxynaphthalene-2-carboxylate (**55**). ^{1}H-NMR (250 MHz, $CDCl_3$): 8.10 (br. *s*, H–C(1)); 8.05 (*dd*, ^3J = 8.0, ^4J = 1.2, H–C(3)); 7.42 (*d*, ^3J = 8.0, H–C(4)); 5.80 (*d*, ^3J = 5.0, H–C(5)); 5.10 (*s*, H–C(8)); 3.92 (*s*, MeO); 2.62 (*dd*, ^2J = 15.0, ^3J = 5.0, H_{exo}–C(6)); 2.05 (*d*, ^2J = 15.0, H_{endo}–C(6)).

Sulfolenes **57–60**. A soln. of 0.05 mmol of each of dienes **23–26** in 0.2 ml of CD_2Cl_2 was degassed on the vacuum line in a 5-mm NMR tube (freeze/thaw cycles). Pure SO_2 (0.30–0.33 ml) was transferred to the tube which was then sealed under vacuum. The tube was allowed to stand at 20° for 3 days, then cooled in liq. N_2, opened, and allowed to warm up to 20° in a few h. The residue was taken with CH_2Cl_2 and the solvent evaporated *in vacuo* at low temp. (< 0°). The oily residues were analyzed quickly as such. Cheletropic elimination of SO_2 occurred already at 20° for solns. of these oils in $CDCl_3$.

*(1*RS*,2*SR*,7*RS*)-10-Oxa-3-thiatricyclo[5.2.1.0^{2,6}]dec-5-en-8-one 3,3-Dioxide* (**57**). IR ($CHCl_3$): 1760, 1670, 1335, 1135, 1090. ^{1}H-NMR (250 MHz, CD_2Cl_2/SO_2): 6.30 (*m*, $^3J(H_{eq}$–C(4),H–C(5)) = 5.0, $^3J(H_{ax}$–C(4),H–C(5)) = 2.5, ^4J(H–C(2),H–C(5)) = 3.0, ^4J(H–C(5),H–C(7)) = 0.5, ^5J(H–C(1),H–C(5)) = 0.5, H–C(5)); 5.30 (*dd*, ^3J(H–C(1),H_{exo}–C(9)) = 6.0, ^5J(H–C(1),H–C(5)) = 0.5, H–C(1)); 4.70 (br. *s*, ^4J(H–C(5),H–C(7)) = ^4J(H–C(7),H_{exo}–C(9)) = $^5J(H_{ax}$–C(4),H–C(7)) = 0.5, H–C(7)); 4.05 (*m*, ^2J = 16.0, ^3J = 2.5, ^4J(H–C(2),H_{ax}–C(4)) = 1.5, $^5J(H_{ax}$–C(4),H–C(7)) = 0.5, $^5J(H_{ax}$–C(4),H–C(7)) = 0.5, H_{ax}–C(4)); 3.80 (*dd*, ^2J = 16.0, ^3J = 5.0, H_{eq}–C(4)); 3.70 (*m*, ^3J(H–C(1),H–C(2)) = 0, ^4J(H–C(2),H–C(5)) = 3.0, ^4J(H–C(2),H_{exo}–C(9)) = 1.0, ^4J(H–C(2),H_{ax}–C(4)) = 1.5, H–C(2)); 2.70 (br. *ddd*, ^2J = 18.0, ^3J = 6.0, ^4J = 1.0, 0.5, H_{exo}–C(9)); 2.18 (*d*, ^2J = 18.0, H_{endo}–C(9)). ^{13}C-NMR (100.61 MHz, CD_2Cl_2/SO_2): 209.5 (*s*, C(8)); 137.9 (*s*, C(6)); 124.2 (*d*, ^1J(C,H) = 182, C(5)); 80.6, 74.7 (2*d*, ^1J(C,H) = 174, C(1), C(7)); 68.0 (*d*, ^1J(C,H) = 155, C(2)); 60.9 (*t*, ^1J(C,H) = 146, C(4)); 43.2 (*t*, ^1J(C,H) = 139, C(9)). CI-MS (NH_3): 201 (1.6, $[M + H]^+$), 200 (1, M^+), 183 (6), 152 (5), 137 (0.6), 136 (1.3), 108 (3.6), 94 (100), 79 (17), 77 (16).

*(1*RS*,2*SR*,7*RS*)-8,8-(Ethylenedioxy)-10-oxa-3-thiatricyclo[5.2.1.0^{2,6}]dec-5-ene 3,3-Dioxide* (**58**). ^{1}H-NMR (360 MHz, CD_2Cl_2/SO_2): 6.20 (*m*, $^3J(H_{eq}$–C(4),H–C(5)) = 5.0, $^3J(H_{ax}$–C(4),H–C(5)) = 2.5, ^4J(H–C(2),H–C(5)) = 3.0, ^4J(H–C(5),H–C(7)) = 0.5, ^5J(H–C(1),H–C(5)) = 0.5, H–C(5)); 5.05 (*dd*, ^3J(H–C(1),H_{exo}–C(9)) = 6.0, ^5J(H–C(1),H–C(5)) = 0.5, H–C(1)); 4.60 (br. *s*, $^5J(H_{ax}$–C(4),H–C(7)) < 0.5, ^4J(H–C(7),H_{exo}–C(9)) < 0.5, ^4J(H–C(5),H–C(7)) = 0.5, H–C(7)); 4.05 (*m*, ^2J = 16.0, ^3J = 2.5, ^4J(H–C(2),H_{ax}–C(4)) = 1.5, $^5J(H_{ax}$–C(4),H–C(7)) < 0.5, H_{ax}–C(4)); 4.1–3.85 (*m*, OCH_2CH_2O); 3.80 (*dd*, ^2J = 16.0, ^3J = 5.0, H_{eq}–C(4)); 3.70 (*m*, ^3J(H–C(1),H–C(2)) = 0, ^4J(H–C(2),H–C(5)) = 3.0, ^4J(H–C(2),H_{exo}–C(9)) = 1.0, ^5J = 1.5, H–C(2)); 2.35 (br. *ddd*, ^2J = 14.0, ^3J = 6.0, ^4J = 1.0, H_{exo}–C(9)); 1.90 (*d*, ^2J = 14.0, H_{endo}–C(9)). ^{13}C-NMR (150.9 MHz, CD_2Cl_2/SO_2): 142.7 (*s*, C(6)); 113.9 (*s*, C(8)); 119.9 (*d*, ^1J(C,H) = 179, H–C(5)); 81.1, 74.7 (2*d*, ^1J(C,H) = 165, 169, C(1), C(7)); 68.3 (*d*, ^1J(C,H) = 151, C(2)); 65.3 (*t*, ^1J(C,H) = 149, OCH_2CH_2O); 60.2 (*t*, ^1J(C,H) = 140, C(4)); 44.2 (*t*, ^1J(C,H) = 135, C(9)).

*(1*RS*,2*SR*,7*SR*)-10-Oxa-3-thiatricyclo[5.2.1.0^{2,6}]dec-5-en-9-one 3,3-Dioxide* (**59**). IR ($CHCl_3$): 2920, 2860, 1760, 1600, 1455, 1335, 1135. ^{1}H-NMR (360 MHz, CD_2Cl_2/SO_2): 6.12 (*m*, $^3J(H_{eq}$–C(4),H–C(5)) = 5.0, $^3J(H_{ax}$–C(4),H–C(5)) = 2.5, ^4J(H–C(2),H–C(5)) = 3.0, ^4J(H–C(5),H–C(7)) = 0.5, H–C(5)); 5.25 (br. *d*, ^3J(H–C(7),H_{exo}–C(8)) = 6.0, H–C(7)); 4.70 (br. *s*, ^4J(H–C(1),H_{exo}–C(8)) ≈ 1.0, H–C(1)); 3.95 (br. *ddd*, ^2J = 15.0, ^3J = 2.5, $^4J(H_{ax}$–C(4),H–C(2)) = 1.5, $^5J(H_{ax}$–C(4),H–C(7)) = 0.5, H_{ax}–C(4)); 3.75 (*dd*, ^2J = 16.0, ^3J = 5.0, H_{eq}–C(4)); 3.65 (*m*, ^4J(H–C(2),H–C(5)) = 3.0, ^4J(H–C(2),H_{ax}–C(4)) = 1.5, H–C(2)); 2.50 (br. *dd*, ^2J = 18.0, ^3J = 6.0, H_{exo}–C(8)); 2.18 (*d*, ^2J = 18.0, H_{endo}–C(8)). ^{13}C-NMR (100.61 MHz, CD_2Cl_2/SO_2): 209.5 (*s*, C(9)); 139.5 (*s*, C(6)); 120.1 (*d*, ^1J(C,H) = 195, C(5)); 77.2, 76.6 (2*d*, ^1J(C,H) = 170, 177, C(1), C(7)); 63.4 (*d*, ^1J(C,H) = 151, C(2)); 61.1 (*t*, ^1J(C,H) = 146, C(4)); 39.6 (*t*, ^1J(C,H) = 137, C(8)). CI-MS (NH_3): 201 (0.5), 200 (1, M^+), 169 (7), 155 (2), 154 (2), 153 (2), 138 (1.5), 137 (2), 136 (2), 107 (13), 106 (2), 97 (6), 96 (2), 94 (100), 79 (12), 77 (10).

*(1*RS*,2*SR*,7*SR*)-9,9-(Ethylenedioxy)-10-oxa-3-thiatricyclo[5.2.1.0^{2,6}]dec-5-ene 3,3-Dioxide* (**60**). IR (KBr): 2950, 1300, 1235, 1135, 1100, 1000. ^{1}H-NMR (360 MHz, CD_2Cl_2/SO_2): 5.95 (*ddd*, ^3J = 5.0, 2.5, ^4J = 3.0, H–C(5)); 4.85 (br. *d*, ^3J(H–C(7),H_{exo}–C(8)) = 6.0, ^5J(H–C(7),H_{ax}–C(4)) = 0.5, H–C(7)); 4.45 (*s*, ^3J(H–C(1),H–C(2)) = 0, H–C(1)); 3.7–4.0 (*m*, OCH_2CH_2O); 3.98 (*dd*, ^4J = 3.0, ^4J(H–C(2),H_{ax}–C(4)) = 1.5, H–C(2)); 3.80 (*m*, ^2J = 16.0, ^3J = 2.5, ^5J = 1.5, ^5J = 0.5, H_{ax}–C(4)); 3.65 (*dd*, ^2J = 16.0, ^3J = 5.0, H_{eq}–C(4)); 2.15 (*dd*, ^2J = 14.0, ^3J = 6.0, H_{exo}–C(8)); 1.85 (*d*, ^2J = 14.0, H_{endo}–C(8)). ^{13}C-NMR (100.61 MHz, CD_2Cl_2/SO_2): 145.4 (*s*, C(6)); 116.9 (*d*, ^1J(C,H) = 174, C(5)); 114.1 (*s*, C(9)); 76.5, 76.2 (2*d*, ^1J(C,H) = 168, C(1), C(7)); 65.4, 64.6 (2*t*,

^1J(C,H) = 152, OCH_2CH_2O); 63.8 (*d*, ^1J(C,H) = 141, C(2)); 59.9 (*t*, ^1J(C,H) = 145, C(4)); 39.1 (*t*, ^1J(C,H) = 136, C(8)). CI-MS (NH_3): 263 (4), 262 (25), 261 (2), 245 (1.6, $[M + H]^+$), 218 (1), 183 (1), 183 (10), 153 (1), 152 (2), 119 (8), 118 (0.5), 107 (6), 94 (7), 86 (100).

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