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Intramolecular acylation of α-sulfinyl carbanions with masked α,β-unsaturated esters: a general strategy to 5-alkylidene-2-cyclopentenones

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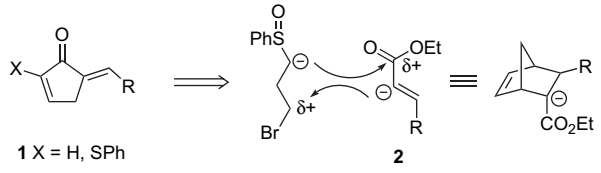
Abstract—A general method for the preparation of 5-alkylidene-2-cyclopentenones and their 2-phenylsulfanyl substituted derivatives, involving the intramolecular acylation of α-sulfinyl carbanions with cyclopentadiene-α,β-unsaturated esters as the key reaction followed by flash vacuum pyrolysis, is described. The reactions start from readily available Diels–Alder adducts, synthons of α-carbanions of α,β-unsaturated esters.

1. Introduction

Functionalized cyclopentenones are a commonly encountered structural unit in a number of prostaglandins and various bioactive natural products.[1] Furthermore, they are found to be versatile building block for the synthesis of some bioactive compounds possessing cyclopentane units. The development of strategies for the construction of these units and related structures has been of considerable interest in synthetic organic chemistry. These methods include the intramolecular aldol reaction,[2] the Pauson–Khand reaction,[3] the Nazarov cyclization,[4,5] and metal–carbene strategies.[6] As part of our study on the intramolecular acylation of α-sulfinyl carbanions for the preparation of cyclopentenone derivatives,[7] we have reported a general synthesis of 5-alkylidene-4-hydroxy-2-cyclopentenones.[8] In the present work, a general route to 5-alkylidene-2-cyclopentenones[9] and 5-alkylidene-2-phenylsulfanyl-2-cyclopentenones **1** is reported.

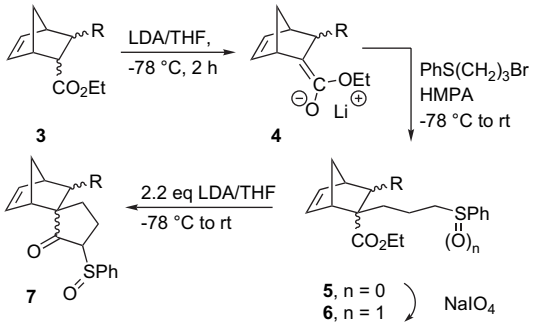
Our annulation strategy is based on the reaction of an α-carbanion synthon **2** of α,β-unsaturated esters with 3-bromo-1-phenylsulfinylpropane followed by a tandem intramolecular acylation and sulfoxide elimination as outlined in Scheme 1. Cyclopentadiene-α,β-unsaturated ester Diels–Alder adducts were used as masked α-carbanions of α,β-unsaturated esters **2**.[10]



Scheme 1.

2. Results and discussion

The synthetic route for the preparation of 5-alkylidene-2-cyclopentenones started from readily available bicyclic esters **3**. The key reaction involves intramolecular acylation of the α-sulfinyl carbanions derived from sulfoxides **6** leading to spirocyclopentanones **7** (Scheme 2), which are precursors for the preparation of cyclopentenones **8**, **9**, and **11** (Scheme 3).



Scheme 2.

The results of preparations are summarized in Table 1. The requisite starting sulfoxides **5** were obtained in two steps,

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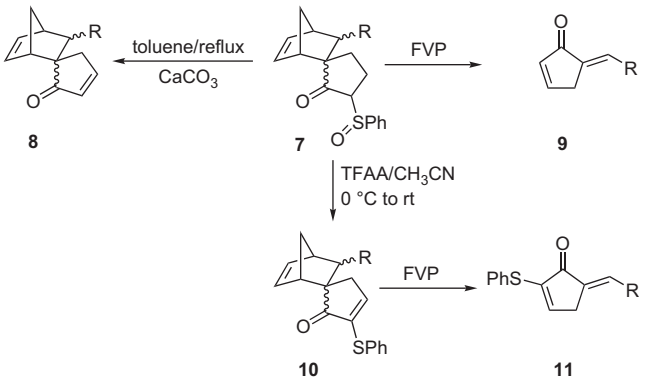
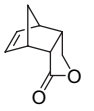
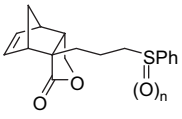
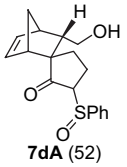
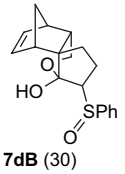


Scheme 3.

Table 1. Preparation of compounds **5**, **6**, and **7**

Entry	**3** (*endo*:*exo*)	Yields of **5** (%)[a,b]	Yields of **6** (%)[a,b]	Yields of **7** (%)[a,b]
1	**3a**, R=H (>99:1)	**5a** (90)	**6a** (98)	**7a** (90)
2	**3b**, R=CH_3 (50:50)	**5b** (67)	**6b** (84)	**7b** (80)
3	**3c**, R=Ph (65:35)	**5c** (60)	**6c** (85)	**7c** (70)
4	 **3d**, (>99:1)	 **5d**, n = 0 (47) **6d**, n = 1 (80)	 **7dA** (52)  **7dB** (30)	

[a] Yields of isolated products.
[b] Obtained as a mixture of diastereomers (see Section 4).

beginning with bicyclic esters **3**. Thus, treatment of a mixture (*endo*:*exo* >99:1 with respect to the ester group) of bicyclic ester **3a** with lithium diisopropylamide (LDA, 1.1 equiv) in THF at −78 °C (2 h), followed by trapping of the resulting enolate anion **4a** with 3-bromo-1-phenylsulfanylpropane in the presence of hexamethylphosphoramide (HMPA) at −78 °C to room temperature overnight afforded the corresponding alkylated product **5a** in 90% yield after chromatography, as a 86:14 mixture of *endo*:*exo* esters. The *endo* stereoselectivity for the formation of **5a** was presumably due to the fact that alkylation of the preformed enolate anion **4a** occurred preferentially from the less hindered *exo*-face leading to an *endo*-ester **5a** as the major isomer. Attempted separation of both isomers by preparative thin-layer chromatography was unsuccessful. Only a small amount of the *endo*-ester **5a** was obtained. Similarly, **5b** and **5c** were prepared as mixtures of diastereomers, employing the standard conditions as for **5a** starting from the mixtures of *endo*- and *exo*-isomers of bicyclic esters **3b** and **3c**. The 2-*endo*,3-*exo*- and 2-*endo*,3-*endo*-isomers of **5c** could be separated by preparative thin-layer chromatography in 44 and 16% yields, respectively. On the other hand, a 7:29:11:53 mixture of four diastereomers of **5b** was achieved under the standard conditions and the major 2-*endo*,3-*exo*-isomer of **5b** was obtained in a small amount after careful preparative thin-layer chromatography. The major 2-*endo*,3-*exo*-isomers of **5b** and **5c** could be explained from the fact that alkylation of the enolate anions **4b** and **4c** occurred from the less hindered *exo*-face. Alkylation of compound **3d** gave the alkylated product **5d** in 47% yield as the sole product. A comparable yield (45%) of **5d** was achieved when the alkylation was performed in the presence of 1 equiv of NaI instead of HMPA. The relative stereochemistry at 2- and 3-positions of 2-*endo*,3-*exo*-**5b** and the minor 2-*endo*,3-*endo*-isomer of **5c** was confirmed by NOE experiments as indicated in Figures 1 and 2.

Oxidation of the diastereomeric mixtures of **5a–c** and **5d** was accomplished by using $NaIO_4$ in aqueous methanol at 0 °C to room temperature to furnish the corresponding sulfoxides **6a–d** in good yields as diastereomeric mixtures. The 2-*endo*,3-*exo*-isomer of **6c** was isolated in pure form by preparative thin-layer chromatography, and its relative stereochemistry was established by the NOE experiment as illustrated in Figure 3.

Cyclization of the diastereomeric mixtures of the sulfoxides **6** to the required spiro-ketosulfoxides **7** was successfully effected by using LDA (2.2 equiv) in THF at −78 °C for 2 h, and at 0 °C for 2 h, followed by slowly warming up to room temperature overnight. The reaction proceeded via the intramolecular acylation of the initially formed α-sulfinyl carbanions of the sulfoxides **6**. As expected, spiro-ketosulfoxides **7a–c** were obtained in good yields as mixtures of diastereomers. Attempts to separate these diastereomers were not made, since it was expected that all of them could be converted into the required 5-alkylidene-2-cyclopentenones **9** and **11**. On the other hand, under the standard

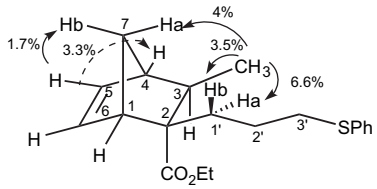


Figure 1. Observed NOE for 2-*endo*,3-*exo*-**5b**.

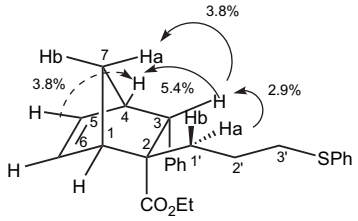


Figure 2. Observed NOE for the minor 2-*endo*,3-*endo*-isomer of **5c**.

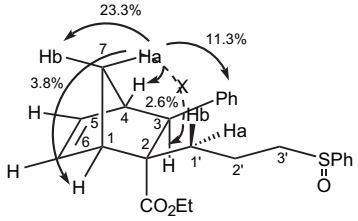


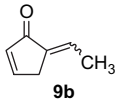
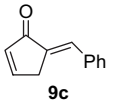
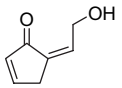
Figure 3. Observed NOE for the 2-*endo*,3-*exo*-isomer of **6c**.

conditions for the cyclization, the sulfoxide **6d** provided a mixture of compounds **7dA** and **7dB** in 52 and 30% yields, respectively. The formation of **7dB** resulted from lactol formation of the initially cyclized product **7dA**. The results are summarized in Table 1.

Having the spiro-ketosulfoxides **7** in hand, the sulfoxide elimination of **7a** and **7b** was investigated. Under reflux in toluene in the presence of $CaCO_3$ for 15 h, **7a** and **7b** provided the corresponding spirocyclopentenones **8a** and **8b** in 70 and 75% yields, respectively, as mixtures of diastereomers. No traces of α-alkylidene cyclopentenones **9a**,**b** arisen from the retro-Diels–Alder reactions of compounds **7a** and **7b** could be detected. However, flash vacuum pyrolysis of the diastereomeric mixtures of spiro-ketosulfoxides **7a–c** and **7dB** at 375–450 °C (0.03–0.05 mmHg) gave quantitative yields of the corresponding α-alkylidene cyclopentenones **9a–c**. Compounds **9b** and **9c** were obtained in good yields after preparative thin-layer chromatography, while compound **9a** is unstable due to rapid polymerization: purification was unsuccessful by preparative thin-layer chromatography. A low yield of compound **9d** (30% yield) was obtained presumably due to its decomposition under the pyrolytic conditions. The formation of **9** resulted from the tandem reaction involving the sulfoxide elimination followed by the retro-Diels–Alder reaction. The results are shown in Table 2.

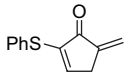
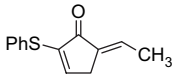
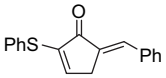
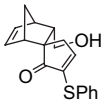
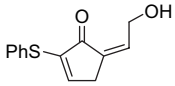
It was anticipated that the spiro-ketosulfoxides **7** could be used as precursors to functionalized cyclopentenones of types **10** and **11**, which might be useful for further synthetic applications. Thus, the spiro-ketosulfoxides **7a–c** were transformed into the corresponding phenylsulfanyl-substituted spirocyclopentenones **10a–c** in good yields by performing the second generation Pummerer rearrangement using trifluoroacetic anhydride in acetonitrile at 0 °C to room temperature overnight (Scheme 3). Flash vacuum pyrolyses of **10a–c** afforded good yields of the expected cyclopentenones **11a–c**. However, under the same conditions, **10d** provided **11d** in only 20% yield (Scheme 3 and Table 3).

Table 2. Preparation of 5-alkylidene-2-cyclopentenones **9**

Entry	Spiro-sulfoxide **7**	Product **9**	% Yield[a] (*E*:*Z* ratio)
1	**7a**	 **9a**	Quantitative
2	**7b**	 **9b**	82 (83:17)[b]
3	**7c**	 **9c**	85 (*E*-isomer)
4	**7d**	 **9d**	30 (*Z*-isomer)

[a] Isolated yields.
[b] The ratio was determined by integration of the ethylenic proton of the crude product.

Table 3. Preparation of spirocyclopentenones **10** by the Pummerer rearrangement of **7** and their pyrolyses to 2-phenylsulfanyl-5-alkylidene-2-cyclopentenones **11**

Entry	**7**	**10**[a] (% Yield)	**11**[a] (% Yield)
1	**7a**, R=H (87:13)	**10a** (80)	 **11a** (93)
2	**7b**, R=CH_3	**10b** (74)	 **11b** (96)
3	**7c**, R=Ph (78:22)	**10c** (78)	 **11c** (76)
4	**7dA** and **7dB**	 **10d** (78)	 **11d** (20)

[a] Yields of isolated products.

This result may be due to its rapid decomposition under the FVP conditions.

3. Conclusion

In summary, the synthetic utility of the intramolecular acylation of α-sulfinyl carbanion as a general method for the syntheses of 5-alkylidene-2-cyclopentenones and their 2-phenylsulfanyl substituted derivatives, starting from Diels–Alder adducts of cyclopentadiene-α,β-unsaturated esters, is demonstrated. The method could be applied to the preparation of a wide range of cyclopentanoid natural products.

4. Experimental

4.1. General

The ^1H and ^{13}C NMR spectra were recorded on Bruker DPX-300 (300 MHz), Bruker DPX-400 (400 MHz), and Bruker DPX-500 (500 MHz) spectrometer in $CDCl_3$ using tetramethylsilane as an internal standard. The chemical shifts (δ) reported are given in parts per million (ppm) and the coupling constants (J) are in hertz (Hz). Melting points were recorded on a Buchi 501 Melting Point Apparatus and are uncorrected. The IR spectra were recorded on a GX FTIR system Perkin–Elmer infrared spectrometer. The mass spectra were recorded by using a Thermo Finnigan Polaris Q mass spectrometer. The high-resolution mass spectra were recorded on HR-TOF-MS Micromass model, Chiangmai University. The elemental analyses were performed by a Perkin–Elmer Elemental Analyzer 2400 CHN. All glasswares and syringes were oven-dried and kept in a desiccator before use. The molarity of *n*-BuLi (in hexane) was determined by titration with diphenylacetic acid in THF at 0 °C. Tetrahydrofuran (THF) was distilled from sodium-benzophenone ketyl. Acetonitrile, dichloromethane, diisopropylamine, hexamethylphosphoramide (HMPA), triethylamine, and toluene were dried by

distilling over calcium hydride. Merck silica gel 60H and 60 PF_{245} were used for column chromatography and preparative thin-layer chromatography, respectively.

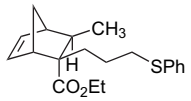
4.2. Preparation of sulfides 5

4.2.1. Ethyl 2-(3′-phenylsulfanylpropyl)bicyclo[2.2.1]-hept-5-ene-2-carboxylate (5a). *General procedure*: A THF solution (4 mL) of *endo*-**3a** (1.66 g, 10 mmol) was added slowly to a solution of LDA (12 mmol) at −78 °C under an argon atmosphere [prepared by reacting diisopropylamine (1.7 mL, 12 mmol) in THF (30 mL) with *n*-BuLi (1.41 M in hexane, 8.5 mL, 12 mmol) at −78 °C]. After stirring at −78 °C for 2 h, HMPA (2.0 mL) was added, followed by the addition of a THF (10 mL) solution of 3-bromo-1-phenylsulfanylpropane (2.52 g, 12 mmol). The resulting solution was stirred at −78 °C to room temperature overnight, quenched with a saturated aqueous NH_4Cl solution (40 mL), and extracted with hexanes (5×100 mL). The combined organic layers were washed with water and brine, and dried (anhyd Na_2SO_4). The organic phase was concentrated to give a 86:14 mixture of *endo*- and *exo*-isomers of the crude product as a viscous liquid. The ratio of the isomers was determined by ^{1}H NMR of the olefinic protons. The crude product was purified by column chromatography (silica gel, 0.5–2% ethyl acetate in hexanes) to give a pure colorless viscous liquid of a 86:14 ratio of *endo*:*exo*-**5a** (2.86 g, 90% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40–7.12 (m, 10H, Ar*H* of *endo*- and *exo*-isomers), 6.23 (m, 1H, C*H*═CH of *exo*-isomer), 6.15 (dd, *J*=5.6, 3.0 Hz, 1H, C*H*═CH of *endo*-isomer), 6.04 (m, 1H, CH═C*H* of *exo*-isomer), 5.96 (dd, *J*=5.6, 2.8 Hz, 1H, CH═C*H* of *endo*-isomer), 4.10–3.95 (m, 4H, $CO_2CH_2CH_3$ of *endo*- and *exo*-isomers), 2.98–2.77 [m, 8H, (CH_2SPh and CHCH═CHC*H*) of *endo*- and *exo*-isomers], 2.20–1.37 (m, 16H, $CH_2(CH_2)_2$SPh, CH_2CCO_2Et, CH_2CH_2SPh, and CH_2 of *endo*- and *exo*-isomers), 1.27–1.15 (m, 6H, $CO_2CH_2CH_3$ of *endo*- and *exo*-isomers).

A pure *endo*-**5a** was obtained in 68% yield after preparative thin-layer chromatography (PLC) (2% ethyl acetate in hexanes). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34–7.16 (m, 5H, Ar*H*), 6.16 (dd, *J*=5.6, 2.9 Hz, 1H, C*H*═CH), 5.99 (dd, *J*=5.6, 2.8 Hz, 1H, CH═C*H*), 4.04 (m, 2H, $CO_2CH_2CH_3$), 2.90 (t, *J*=6.9 Hz, 2H, CH_2SPh), 2.84 (br s, 2H, C*H*CH═CHC*H*), 2.05 (dt, *J*=12.5, 4.8 Hz, 1H, C*H*$(CH_2)_2$SPh), 1.88 (dd, *J*=12.0, 2.5 Hz, 1H, C*H*$HCCO_2Et$), 1.80–1.40 (m, 6H, $CHCH_2CH_2$SPh, $CHCCO_2Et$, and CH_2), 1.19 (t, *J*=7.1 Hz, 3H, $CO_2CH_2CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.0 (C═O), 138.2 (CH), 136.3 (C), 134.6 (CH), 129.1 (2×CH), 128.8 (2×CH), 125.8 (CH), 60.1 (CH_2), 54.3 (C), 50.7 (CH), 47.1 (CH_2), 42.6 (CH), 39.0 (CH_2), 35.7 (CH_2), 33.9 (SCH_2), 25.5 (CH_2), 14.2 (CH_3). IR (neat): ν_{max} 3060w, 2976s, 1728s, 1584w, 1481m, 1439m, 1334m, 1243s, 1184s, 1159s, 1114m, 1096m, 1060m, 1026m, 739s, 712s, 691m cm^{-1}. MS: *m*/*z* (%) relative intensity 318 (M^++2, 6), 317 (M^++1, 25), 316 (M^+, 50), 273 (7), 272 (19), 271 (100), 250 (13), 242 (15), 205 (8), 176 (12), 165 (15), 160 (21), 149 (77), 141 (49), 134 (13), 114 (19), 95 (12), 67 (24), 66 (8). Anal. Calcd for $C_{19}H_{24}O_2S$: C, 72.11; H, 7.64. Found: C, 72.19; H, 7.80.

4.2.2. Ethyl 2-(3′-phenylsulfanylpropyl)-3-methylbicyclo[2.2.1]hept-5-ene-2-carboxylate (5b). According to the general procedure described for compound **5a**, a solution of a 50:50 mixture of *endo*- and *exo*-**3b** (0.45 g, 2.5 mmol) in THF (1 mL) was added dropwise to a THF (8 mL) solution of LDA (3 mmol) at −78 °C under an argon atmosphere. After stirring at −78 °C for 2 h, HMPA (1.2 mL) was added followed by the addition of a THF (3 mL) solution of 3-bromo-1-phenylsulfanylpropane (0.578 g, 2.5 mmol). After usual work-up, the crude product was purified by column chromatography (silica gel, 0.5–2% ethyl acetate in hexanes) to give a pure colorless viscous liquid of **5b** (0.554 g, 67% yield) as a 7:29:11:53 mixture of *exo*,*endo*:*endo*,*endo*:*exo*,*exo*:*endo*,*exo*-isomers. The mixture was used for further oxidation.

Compound **5b** (a mixture of four isomers): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40–7.14 (m, Ar*H*), 6.37 (dd, *J*=5.4, 3.0 Hz, C*H*═CH), 6.20 (dd, *J*=5.6, 3.0 Hz, C*H*═CH), 6.14–6.04 (m, CH═C*H*), 4.16–3.90 (m, $CO_2CH_2CH_3$), 3.03 (br s, C*H*CH═CHCH), 3.00–2.77 (m, CH_2SPh and C*H*CH═CHCH), 2.66 and 2.61 (each br s, CHCH═CHC*H*), 2.38 (br s, CHCH═CHC*H*), 2.19–1.98 (m, C*H*CH_3 and C*H*HCH_2CH_2SPh), 1.93–1.45 (m, $CH_2CH_2CH_2$SPh and CH_2), 1.43 (d, *J*=8.7 Hz, CH*H*), 1.35 (dd, *J*=9.0, 1.6 Hz, CH*H*), 1.28–1.14 (m, $CO_2CH_2CH_3$ and $CHCH_3$), 1.10 (d, *J*=7.2 Hz, $CHCH_3$), 0.92 (d, *J*=7.2 Hz, $CHCH_3$), 0.86 (d, *J*=7.2 Hz, $CHCH_3$).

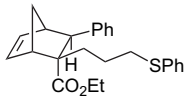


endo,*exo*-**5b**

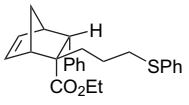
A pure colorless viscous liquid of *endo*,*exo*-isomer of **5b** was obtained in a small quantity by careful preparative thin-layer chromatography. *endo*,*exo*-**5b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29–7.03 (m, 5H, Ar*H*), 6.10 (dd, *J*=5.4, 3.0 Hz, 1H, C*H*═CH), 5.99 (dd, *J*=5.4, 2.7 Hz, 1H, CH═C*H*), 3.91 (m, 2H, $CO_2CH_2CH_3$), 2.83 (t, *J*=6.6 Hz, 2H, CH_2SPh), 2.72 (br s, 1H, C*H*CH═CHCH), 2.27 (br s, 1H, CHCH═CHC*H*), 1.95 (dq, *J*=7.0, 1.4 Hz, 1H, C*H*CH_3), 1.82–1.40 (m, 5H, $CH_2CH_2CH_2$SPh and C*H*H), 1.26 (dd, *J*=9.0, 1.5 Hz, 1H, CH*H*), 1.08 (t, *J*=7.1 Hz, 3H, $CO_2CH_2CH_3$), 1.00 (d, *J*=7.0 Hz, 3H, $CHCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.7 (C═O), 138.2 (CH), 136.2 (C), 136.2 (CH), 129.2 (2×CH), 128.8 (2×CH), 125.9 (CH), 59.9 (CH_2), 55.4 (C), 49.7 (CH), 49.4 (CH), 43.7 (CH_2), 40.6 (CH), 34.2 (CH_2), 34.1 (SCH_2), 25.8 (CH_2), 16.8 (CH_3), 14.2 (CH_3). IR (neat): ν_{max} 3059w, 2963s, 1725s, 1585w, 1481m, 1439m, 1240s, 1175m, 1148m, 1026m, 738s, 718m, 691m cm^{-1}. MS: *m*/*z* (%) relative intensity 331 (M^++1, 13), 330 (M^+, 26), 286 (19), 285 (100), 265 (14), 264 (54), 219 (18), 191 (12), 190 (27), 156 (17), 155 (98), 149 (38), 127 (33), 109 (20), 82 (48), 79 (20), 77 (9), 65 (7). Anal. Calcd for $C_{20}H_{26}O_2S$: C, 72.69; H, 7.93. Found: C, 72.83; H, 8.18.

4.2.3. Ethyl 2-(3′-phenylsulfanylpropyl)-3-phenylbicyclo[2.2.1]hept-5-ene-2-carboxylate (5c). According to the general procedure described for compound **5a**, a solution of a 65:35 mixture of *endo*- and *exo*-**3c** (0.60 g, 2.5 mmol)

in THF (1 mL) was added dropwise to a solution of LDA (3 mmol) in THF (8 mL) at −78 °C under an argon atmosphere. After stirring at −78 °C for 2 h, HMPA (1.2 mL) was added, followed by the addition of a THF (4 mL) solution of 3-bromo-1-phenylsulfanylpropane (0.695 g, 3 mmol). After usual work-up, the crude product was purified by column chromatography (silica gel, 0.2–2% ethyl acetate in hexanes) to give **5c** (0.631 g, 64% yield) as a 70:30 mixture of *endo*,*exo*- and *endo*,*endo*-isomers.



endo,exo-**5c**



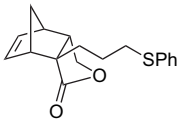
endo,endo-**5c**

A mixture of *endo*,*exo*- and *endo*,*endo*-**5c**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40–7.01 (m, 20H, Ar*H* of *endo*,*exo*- and *endo*,*endo*-isomers), 6.67 (m, 1H, C*H*=CH of *endo*,*endo*-isomer), 6.36 (dd, J=5.4, 3.2 Hz, 1H, C*H*=CH of *endo*,*exo*-isomer), 6.22 (m, 2H, CH=C*H* of *endo*,*exo*- and *endo*,*endo*-isomers), 4.09 (m, 2H, $CO_2CH_2CH_3$ of *endo*,*exo*-isomer), 3.65 (m, 1H, CO_2CHHCH_3 of *endo*,*endo*-isomer), 3.37 (m, 1H, CO_2CHHCH_3 of *endo*,*endo*-isomer), 3.25 (s, 1H, C*H*Ph of *endo*,*exo*-isomer), 3.11 (d, J=3.0 Hz, 1H, C*H*Ph of *endo*,*endo*-isomer), 3.02–2.83 [m, 6H, C*H*CH=CHC*H* of *endo*,*exo*-isomers and (C*H*CH=CHC*H* and CH_2SPh) of *endo*,*endo*-isomer], 2.54 (m, 2H, CH_2SPh of *endo*,*exo*-isomer), 2.35 (dt, J=12.8, 4.1 Hz, 1H, C*H*H$(CH_2)_2$SPh of *endo*,*endo*-isomer), 2.02 (d, J=9.0 Hz, 1H, C*H*H of *endo*,*exo*-isomer), 1.94–1.67 (m, 3H, CH*H*C*H*HCH$_2$SPh and C*H*H of *endo*,*endo*-isomer), 1.65–1.47 [m, 4H, (CH*H* and CH*H*CH$_2$SPh) of *endo*,*endo*-isomer and (CH*H* and C*H*H$(CH_2)_2$SPh) of *endo*,*exo*-isomer], 1.45–1.17 (m, 6H, C*H*HCH$_2$SPh, $CO_2CH_2CH_3$ and CH*H*$(CH_2)_2$SPh of *endo*,*exo*-isomer), 0.12 (t, J=7.2 Hz, 3H, $CO_2CH_2CH_3$ of *endo*,*endo*-isomer).

The *endo*,*exo*- and *endo*,*endo*-isomers were separated by PLC to give *endo*,*exo*-**5c** (0.433 g, 44% yield) and *endo*,*endo*-**5c** (0.158 g, 16% yield) as pale yellow viscous liquids. *endo*,*exo*-**5c** (less polar): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35–7.00 (m, 10H, Ar*H*), 6.29 (dd, J=5.5, 3.2 Hz, 1H, C*H*=CH), 6.12 (dd, J=5.5, 2.8 Hz, 1H, CH=C*H*), 4.00 (m, 2H, $CO_2CH_2CH_3$), 3.17 (br s, 1H, C*H*Ph), 2.90 (br s, 1H, C*H*CH=CHCH), 2.85 (br s, 1H, CHCH=CHC*H*), 2.45 (m, 2H, CH_2SPh), 1.92 (d, J=8.7 Hz, 1H, C*H*H), 1.54 (dd, J=8.7, 1.3 Hz, 1H, CH*H*), 1.39 (m, 1H, C*H*H$(CH_2)_2$SPh), 1.30–1.10 (m, 6H, CH*H*C*H*$_2$CH$_2$SPh and $CO_2CH_2CH_3$). IR (neat): ν_{max} 3060m, 2974s, 1721s, 1601m, 1584m, 1495m, 1481s, 1454s, 1320m, 1237s, 1169s, 1148s, 1092s, 1025s, 740s, 703s, 692s cm^{-1}. MS: *m*/*z* (%) relative intensity 393 (M^++1, 5), 392 (M^+, 3), 348 (11), 347 (46), 327 (21), 326 (85), 319 (8), 281 (9), 252 (16), 235 (11), 224 (7), 218 (15), 217 (78), 189 (25), 177 (34), 171 (47), 150 (30), 149 (43), 143 (100), 142 (37), 128 (19), 115 (18), 91 (14), 66 (7), 65 (8).

endo,*endo*-**5c** (more polar): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30–6.90 (m, 10H, Ar*H*), 6.58 (dd, J=5.2, 3.2 Hz, 1H, C*H*=CH), 6.13 (dd, J=5.2, 3.0 Hz, 1H, CH=C*H*), 3.56 (dq, J=10.7, 7.1, 7.1 Hz, 1H, CO_2CHHCH_3), 3.29 (dq, J=10.7, 7.2, 7.1 Hz, 1H, CO_2CHHCH_3), 3.05 (d, J=2.9 Hz, 1H, C*H*Ph), 2.91 (br s, 1H, C*H*CH=CHCH), 2.87–2.76 (m, 3H, CHCH=CHC*H* and CH_2SPh), 2.27 (dt, J=12.7, 4.1 Hz, 1H, C*H*H$(CH_2)_2$SPh), 1.87–1.61 (m, 3H, CH*H*C*H*HCH$_2$SPh and C*H*H), 1.49–1.27 (m, 2H, CH*H* and CH*H*CH$_2$SPh), 0.55 (t, J=7.1 Hz, 3H, $CO_2CH_2CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.5 (C=O), 142.5 (C), 139.9 (CH), 136.2 (C), 133.9 (CH), 129.2 (2×CH), 128.8 (2×CH), 128.6 (2×CH), 127.5 (2×CH), 126.1 (CH), 125.9 (CH), 63.1 (C), 60.0 (CH), 59.8 (CH_2), 49.4 (CH), 48.2 (CH), 47.8 (CH_2), 40.6 (CH_2), 33.9 (SCH_2), 25.4 (CH_2), 13.3 (CH_3). IR (neat): ν_{max} 3060w, 2975s, 1721s, 1602w, 1584m, 1495m, 1480m, 1454m, 1439m, 1319w, 1237s, 1169m, 1148m, 1093m, 1026m, 740s, 703m, 691m cm^{-1}. MS: *m*/*z* (%) relative intensity 392 (M^+, 1), 348 (5), 327 (4), 326 (21), 320 (22), 319 (84), 281 (7), 252 (13), 241 (22), 236 (12), 235 (13), 218 (15), 217 (56), 209 (59), 189 (31), 182 (22), 177 (30), 171 (47), 167 (17), 165 (14), 149 (45), 143 (100), 142 (38), 141 (24), 128 (39), 123 (16), 115 (38), 91 (29), 77 (16), 65 (12). HRMS (ESI-TOF) calcd for $C_{25}H_{28}O_2SNa$: 415.1708; found: 415.1708.

4.2.4. 2-(3′-Phenylsulfanylpropyl)-3-(hydroxymethyl)bicyclo[2.2.1]hept-5-ene-2-carboxylic acid lactone (5d). According to the general procedure described for compound **5a**, a solution of *endo*-**3d** (0.376 g, 2.5 mmol) in THF (1 mL) was added dropwise to a solution of LDA (3.75 mmol) in THF (8 mL) at −78 °C under an argon atmosphere. After stirring at −78 °C for 2 h, HMPA (1.2 mL) was added followed by the addition of a THF (5 mL) solution of 3-bromo-1-phenylsulfanylpropane (2.31 g, 10 mmol). After usual work-up, the crude product was purified by column chromatography (silica gel, 10–20% ethyl acetate in hexanes) to give a colorless solid of *endo*-**5d** (0.354 g, 47% yield, mp 70–72 °C) and the starting material **3d** (0.131 g, 35% yield). The reaction proceeded to give a comparable yield of **5d** (45% yield), when NaI (0.09 g, 0.6 mmol) was used instead of HMPA.



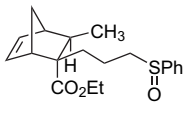
endo-**5d**

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28–7.05 (m, 5H, Ar*H*), 6.23 (dd, J=5.2, 2.8 Hz, 1H, C*H*=CH), 6.17 (dd, J=5.2, 2.8 Hz, 1H, CH=C*H*), 4.00 (app. t, J=9.6 Hz, 1H, CO_2CHH), 3.65 (dd, J=9.6, 2.8 Hz, 1H, CO_2CHH), 3.00–2.85 (m, 2H, C*H*HSPh and C*H*CH=CHCH), 2.85–2.71 (m, 2H, CH*H*SPh and CHCH=CHC*H*), 2.55 (td, J=8.7, 3.6 Hz, 1H, C*H*CH$_2$OCO), 2.05 (m, 1H, C*H*HCH$_2$CH$_2$SPh), 1.77–1.53 (m, 5H, CH_2 and CH*H*C*H*$_2$CH$_2$SPh). ^{13}C NMR (75 MHz, $CDCl_3$): δ 180.0 (C=O), 137.9 (CH), 136.0 (C), 134.5 (CH), 129.3 (2×CH), 128.9 (2×CH), 126.1 (CH), 69.3 (CH_2), 58.7 (C), 51.4 (CH), 49.8 (CH_2), 46.6 (CH), 45.2 (CH), 35.9 (CH_2), 33.8 (CH_2), 26.00 (CH_2). IR (neat): ν_{max} 3060w, 2972s, 2909m, 1757s, 1583m, 1481m, 1439m, 1381m, 1229m, 1181s, 1148m, 1057m, 1000m, 742s, 692m cm^{-1}. MS: *m*/*z* (%) relative intensity 301 (M^++1, 23), 300 (M^+, 30), 234 (12), 191 (16), 135 (3), 125 (100), 110 (9), 97 (5), 81 (10), 79 (22), 77 (13), 66 (8), 65 (7). Anal. Calcd for $C_{18}H_{20}O_2S$: C, 71.96; H, 6.71. Found: C, 71.69; H, 6.71.

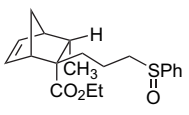
4.3. Preparation of sulfoxides 6

4.3.1. Ethyl 2-(3′-phenylsulfinylpropyl)bicyclo[2.2.1]-hept-5-ene-2-carboxylate (6a). *General procedure*: A solution of *endo*-**5a** (3.91 g, 12.37 mmol) in methanol (50 mL) was added dropwise to a suspension of powdered $NaIO_4$ (2.65 g, 12.37 mmol) in water (17 mL) at 0 °C. The mixture was stirred at 0 °C to room temperature overnight. The precipitates of $NaIO_3$ were filtered and washed several times with ethyl acetate. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with water, brine and dried over anhyd Na_2SO_4. Filtration followed by evaporation gave a yellow liquid, which was purified by column chromatography (silica gel, 30% ethyl acetate in hexanes) to furnish a pure colorless viscous liquid of *endo*-**6a** (4.03 g, 98% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60–7.37 (m, 5H, Ar*H*), 6.07 (dd, *J*=5.5, 2.9 Hz, 1H, C*H*=CH), 5.89 (dd, *J*=5.5, 2.7 Hz, 1H, CH=C*H*), 3.95 (m, 2H, $CO_2CH_2CH_3$), 2.70, (m, 4H, CH_2SOPh and C*H*CH=CHC*H*), 2.02–1.28 (m, 8H, $CH_2CH_2CH_2$SOPh, CH_2, and CH_2CCO_2Et), 1.10 (dt, *J*=7.1, 2.3 Hz, 3H, $CO_2CH_2CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.7 (2×C=O), 143.8 and 143.7 (C), 138.3 and 138.2 (CH), 134.5 and 134.5 (CH), 130.9 (2×CH), 129.1 (4×CH), 123.9 (4×CH), 60.2 (2×CH_2), 57.4 and 57.3 (CH_2), 54.4 (2×C), 50.7 and 50.6 (CH), 47.1 (2×CH_2), 42.6 (2×CH), 39.1 and 39.0 (CH_2), 35.8 and 35.6 (CH_2), 19.3 and 19.2 (CH_2), 14.2 (2×CH_3). IR (neat): ν_{max} 3060m, 2976s, 1728s, 1583w, 1478m, 1445s, 1336m, 1240s, 1185s, 1160s, 1087s, 1044s, 751s, 713s, 693m cm^{-1}. MS: *m*/*z* (%) relative intensity 334 (M^++1, 8), 333 (M^+, 36), 315 (26), 287 (13), 267 (16), 221 (39), 161 (16), 143 (52), 141 (100), 114 (54), 96 (29), 91 (16), 67 (26), 66 (10). Anal. Calcd for $C_{19}H_{24}O_3S$: C, 68.64; H, 7.28. Found: C, 69.09; H, 7.52.

4.3.2. Ethyl 2-(3′-phenylsulfinylpropyl)-3-methylbicyclo[2.2.1]hept-5-ene-2-carboxylate (6b). According to the general procedure described for compound **6a**, a mixture of powdered $NaIO_4$ (1.35 g, 6.32 mmol) in water (8 mL) and a solution of a 7:29:11:53 mixture of diastereomers of **5b** (2.00 g, 6.32 mmol) in methanol (23 mL) was stirred at 0 °C to room temperature overnight. The organic layer was separated and the aqueous layer was extracted with ethyl acetate and concentrated to give a 4:20:6:70 diastereomeric mixture of isomers of a crude product **6b** as a viscous liquid. The crude product was purified by column chromatography (silica gel, 30% ethyl acetate in hexanes) to give a pure colorless viscous liquid of **6b** (1.84 g, 84% yield) as a 93:7 mixture of *endo*,*exo*- and *endo*,*endo*-isomers.



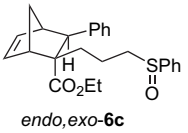
endo,exo-**6b**



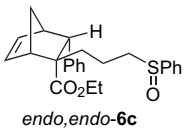
endo,endo-**6b**

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57–7.34 (m, 10H, Ar*H* of *endo*,*exo*- and *endo*,*endo*-isomers), 6.22 (m, 1H, C*H*=CH of *endo*,*endo*-isomer), 6.07 (dd, *J*=5.5, 3.0 Hz, 1H, C*H*=CH of *endo*,*exo*-isomer), 5.95 (dd, *J*=5.5, 2.7 Hz, 2H, CH=C*H* of *endo*,*exo*- and *endo*,*endo*-isomers), 4.07–3.77 (m, 4H, $CO_2CH_2CH_3$ of *endo*,*exo*- and *endo*,*endo*-isomers), 2.79–2.57 (m, 6H, CH_2SOPh and C*H*CH=CHCH of *endo*,*exo*- and *endo*,*endo*-isomers), 2.49 (br s, 1H, CHCH=CHC*H* of *endo*,*endo*-isomer), 2.25 (br s, 1H, CHCH=CHC*H* of *endo*,*exo*-isomer), 2.00–1.80 [m, 3H, (C*H*CH_3 and C*H*HCH_2CH_2SOPh) of *endo*,*endo*-isomer and C*H*CH_3 of *endo*,*exo*-isomer], 1.80–1.34 [m, 10H, (CH_2 and CH*H*C*H*$_2CH_2$SOPh) of *endo*,*endo*-isomer and (C*H*H and $CH_2CH_2CH_2$SOPh) of *endo*,*exo*-isomer], 1.26 (dd, *J*=9.1, 1.4 Hz, 1H, CH*H* of *endo*,*exo*-isomer), 1.15 (dt, *J*=7.6, 1.7 Hz, 3H, $CO_2CH_2CH_3$ of *endo*,*endo*-isomer), 1.10 (m, 3H, $CO_2CH_2CH_3$ of *endo*,*exo*-isomer), 0.95 (d, *J*=7.3 Hz, 3H, CHC*H*$_3$ of *endo*,*exo*-isomer), 0.78 (m, 3H, CHC*H*$_3$ of *endo*,*endo*-isomer). ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.4 (2×C=O), 143.9 and 143.7 (C), 138.2 (2×CH), 136.2 and 136.1 (CH), 131.0 and 130.9 (CH), 129.2 and 129.1 (2×CH), 124.0 (4×CH), 60.0 and 60.0 (CH_2), 57.7 and 57.3 (CH_2), 55.4 (2×C), 49.5 and 49.1 (CH), 48.9 and 48.3 (CH), 45.9 and 43.7 (CH_2), 40.7 and 40.6 (CH), 34.1 and 34.0 (CH_2), 19.5 and 18.9 (CH_2), 16.8 (2×CH_3), 14.2 (2×CH_3). IR (neat): ν_{max} 3059w, 2963s, 1722s, 1583w, 1463m, 1444m, 1369m, 1384m, 1340w, 1237s, 1176m, 1145m, 1088s, 1050s, 1023m, 749m, 693m cm^{-1}. MS: *m*/*z* (%) relative intensity 348 (M^++1, 12), 347 (M^+, 52), 329 (28), 301 (23), 283 (18), 281 (18), 236 (13), 235 (81), 175 (14), 156 (17), 155 (100), 147 (14), 128 (16), 127 (45), 110 (44), 105 (12), 91 (17), 82 (94), 79 (62), 77 (21), 66 (8). HRMS (ESI-TOF) calcd for $C_{20}H_{27}O_3S$: 347.1681; found: 347.1681.

4.3.3. Ethyl 2-(3′-phenylsulfinylpropyl)-3-phenylbicyclo[2.2.1]hept-5-ene-2-carboxylate (6c). According to the general procedure described for compound **6a**, a mixture of powdered $NaIO_4$ (0.565 g, 2.64 mmol) in water (4 mL) and a solution of a 70:30 diastereomeric mixture of *endo*,*exo*- and *endo*,*endo*-**5c** (0.864 g, 2.20 mmol) in methanol (8 mL) was stirred at 0 °C to room temperature overnight. The crude product was purified by column chromatography (silica gel, 25% ethyl acetate in hexanes) to give a pure pale yellow viscous liquid of **6c** (0.77 g, 85% yield) as a 67:33 diastereomeric mixture of *endo*,*exo*- and *endo*,*endo*-isomers.



endo,exo-**6c**



endo,endo-**6c**

A mixture of *endo*,*exo*- and *endo*,*endo*-**6c**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65–7.45 (m, 10H, SOAr*H* of *endo*,*exo*- and *endo*,*endo*-isomers), 7.38–6.95 (m, 10H, Ar*H* of *endo*,*exo*- and *endo*,*endo*-isomers), 6.65 (br s, 1H, C*H*=CH of *endo*,*endo*-isomer), 6.35 (m, 1H, C*H*=CH of *endo*,*exo*-isomer), 6.23 (br s, 2H, CH=C*H* of *endo*,*exo*- and *endo*,*endo*-isomers), 4.20–3.98 (m, 2H, CO_2CH_2 of *endo*,*exo*-isomer), 3.64 (m, 1H, CO_2CH*H* of *endo*,*endo*-isomer), 3.37 (m, 1H, CO_2CH*H* of *endo*,*endo*-isomer), 3.24 (s, 1H, C*H*Ph of *endo*,*exo*-isomer), 3.09 (d, *J*=3.0 Hz, 1H, C*H*Ph of *endo*,*endo*-isomer), 3.00 (br s, 2H, C*H*CH=CHCH of *endo*,*exo*- and *endo*,*endo*-isomers), 2.94 (br s, 1H, CHCH=CHC*H* of *endo*,*exo*-isomer), 2.89 (br s, 1H, CHCH=CHC*H* of *endo*,*endo*-isomer), 2.78 (m, 2H,

CH_2SOPh of *endo*,*endo*-isomer), 2.53–2.20 (m, 3H, CH_2SOPh of *endo*,*exo*-isomer and $CH(CH_2)_2$SOPh of *endo*,*endo*-isomer), 2.00–1.05 [m, 14H, (CH_2 and $CHHCH_2CH_2$SOPh) of *endo*,*endo*-isomer and (CH_2, $CH_2CH_2CH_2$SOPh and $CO_2CH_2CH_3$) of *endo*,*exo*-isomer], 0.64 (td, J=13.1, 6.8 Hz, 3H, $CO_2CH_2CH_3$ of *endo*,*endo*-isomer).

A pure *endo*,*exo*-**6c** was partially obtained by PLC as a pale yellow viscous liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59–7.34 (m, 5H, SOAr*H*), 7.30–7.05 (m, 5H, Ar*H*), 6.29 (m, 1H, C*H*=CH), 6.14 (m, 1H, CH=C*H*), 4.01 (m, 2H, $CO_2CH_2CH_3$), 3.17 (d, J=2.2 Hz, 1H, C*H*Ph), 2.95 (d, J=6.7 Hz, 1H, C*H*CH=CHCH), 2.85 (br s, 1H, CHCH=CHC*H*), 2.46–2.14 (m, 2H, CH_2SOPh), 1.95–1.00 (m, 9H, $CH_2CH_2CH_2$SOPh, $CO_2CH_2CH_3$, and CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.2 (2×C=O), 143.8 and 143.4 (C), 141.5 and 141.5 (C), 139.7 (2×CH), 137.4 (2×CH), 130.9 and 130.7 (CH), 129.1 and 129.0 (2×CH), 127.9 (8×CH), 126.1 (2×CH), 123.9 and 123.8 (2×CH), 60.44 and 60.36 (CH_2), 57.65 and 56.63 (OSCH), 57.1 (2×C), 51.68 and 51.65 (CH), 48.1 and 48.0 (CH), 47.2 (2×CH), 45.31 and 45.27 (CH_2), 36.0 and 35.8 (CH_2), 19.2 and 17.9 (CH_2), 14.3 and 14.2 (CH_3). IR (neat): ν_{max} 3060m, 3028m, 2977s, 1728s, 1716s, 1602m, 1583w, 1495m, 1478m, 1454s, 1445s, 1368m, 1323m, 1234s, 1165s, 1145s, 1089s, 1046s, 911m, 750s, 701s cm^{-1}. MS: *m*/*z* (%) relative intensity 409 (M^+, 10), 391 (3), 344 (11), 343 (41), 297 (31), 283 (7), 279 (6), 247 (13), 217 (39), 209 (9), 189 (27), 172 (18), 171 (100), 144 (21), 143 (67), 129 (19), 128 (20), 117 (15), 115 (19), 91 (15), 77 (6), 66 (5), 65 (6). HRMS (ESI-TOF) calcd for $C_{25}H_{28}O_3SNa$: 431.1657; found: 431.1656.

4.3.4. 2-(3′-Phenylsulfinylpropyl)-3-(hydroxymethyl)bicyclo[2.2.1]hept-5-ene-2-carboxylic acid lactone (6d). According to the general procedure described for compound **6a**, a mixture of powdered $NaIO_4$ (0.757 g, 3.54 mmol) in water (5 mL) and a solution of *endo*-**5d** (0.887 g, 2.95 mmol) in methanol (10 mL) was stirred at 0 °C to room temperature overnight. The crude product was purified by column chromatography (silica gel, 40–50% ethyl acetate in hexanes) to give a pure colorless solid of *endo*-**6d** (0.75 g, 80% yield, mp 86–88 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60–7.40 (m, 5H, Ar*H*), 6.24 (br s, 2H, C*H*=C*H*), 4.10 (td, J=23.4, 9.3 Hz, 1H, CO_2CHHCH_3), 3.70 (m, 1H, CO_2CHHCH_3), 3.00 (br s, 1H, C*H*CH=CHCH), 2.85–2.61 (m, 4H, CH_2SOPh, $CHCH_2OCO$, and CHCH=CHC*H*), 2.61–1.41 (m, 6H, $CH_2CH_2CH_2$SOPh and CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 179.7 (2×C=O), 143.6 and 143.1 (C), 137.5 (2×CH), 134.5 (2×CH), 130.9 (2×CH), 129.1 (4×CH), 123.7 and 123.6 (2×CH), 69.2 (2×CH_2O), 58.6 (2×C), 57.0 and 56.4 (CH_2), 51.3 and 51.2 (CH), 49.7 and 49.6 (CH_2), 46.50 and 46.48 (CH), 44.72 and 44.67 (CH), 35.9 and 35.3 (CH_2), 20.0 and 18.7 (CH_2). IR (neat): ν_{max} 3061w, 2973s, 1755s, 1643w, 1479m, 1444m, 1382m, 1342w, 1219m, 1183s, 1147m, 1088m, 1038s, 999s, 751s, 694m cm^{-1}. MS: *m*/*z* (%) relative intensity 317 (M^+, 10), 299 (2), 251 (3), 199 (11), 191 (6), 126 (9), 125 (100), 115 (4), 107 (3), 97 (16), 91 (9), 81 (17), 79 (50), 78 (10), 77 (28), 66 (7), 65 (8). HRMS (ESI-TOF) calcd for $C_{18}H_{20}O_3SNa$: 339.1031; found: 339.1031.

4.4. Preparation of spiro-sulfoxides 7 by cyclization of sulfoxides 6

4.4.1. 2′-Oxo-3′-phenylsulfinylcyclopentane-1′-spiro-2-bicyclo[2.2.1]hept-5-ene (7a). *General procedure*: A solution of a 86:14 mixture of *endo*- and *exo*-**6a** (0.50 g, 1.5 mmol) in THF (4.50 mL) was added dropwise at −78 °C to a solution of lithium diisopropylamide (LDA) under an argon atmosphere [prepared by reacting diisopropylamine (0.47 mL, 3.30 mmol) in THF (5 mL) with *n*-BuLi (1.41 M in hexane, 2.55 mL, 3.30 mmol) at −78 °C for 1 h]. The mixture was stirred at −78 °C for 2 h, 0 °C for 2 h and then quenched with a saturated NH_4Cl solution (6 mL). The mixture was extracted with EtOAc (3×25 mL). The combined organic layers were washed with water, brine and dried over anhyd Na_2SO_4. After removal of solvent under reduced pressure, a crude product **7a** was purified by preparative thin-layer chromatography (silica gel, 20% ethyl acetate in hexanes) to give three bands (PLC_1, PLC_2, and PLC_3) of **7a** (0.387 g, 90% combined yield) as a diastereomeric mixture.

PLC_1 (less polar): a pure isomer as a white solid (43 mg, 10% yield, mp 116–118 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60–7.36 (m, 5H, Ar*H*), 6.23 (dd, J=5.5, 3.0 Hz, 1H, C*H*=CH), 6.05 (dd, J=5.5, 3.1 Hz, 1H, CH=C*H*), 3.26 (dd, J=9.8, 8.6 Hz, 1H, C*H*SOPh), 3.15 (br s, 1H, C*H*CH=CHCH), 2.86 (br s, 1H, CHCH=CHC*H*), 2.37 (m, 1H, C*H*HCH$_2$CHSOPh), 2.10 (dd, J=11.5, 3.6 Hz, 1H, C*H*HCCO), 1.85–1.31 (m, 4H, C*H*H and CH*HCH*$_2$CHSOPh), 1.21 (d, J=8.9 Hz, 1H, CH*H*), 0.74 (dd, J=11.5, 2.9 Hz, 1H, CH*H*CCO). ^{13}C NMR (75 MHz, $CDCl_3$): δ 214.0 (C=O), 142.3 (C), 140.6 (CH), 133.4 (CH), 130.9 (CH), 129.2 (2×CH), 123.9 (2×CH), 71.4 (CH), 57.5 (C), 45.58 (CH), 45.56 (CH_2), 43.1 (CH), 37.6 (CH_2), 33.0 (CH_2), 14.8 (CH_2). IR (Nujol): ν_{max} 2955s, 1724m, 1334w, 1235w, 1163w, 1086w, 1046m, 1029w, 754w, 740w, 725m, 691w cm^{-1}. MS: *m*/*z* (%) relative intensity 287 (M^++1, 14), 269 (6), 162 (12), 161 (100), 143 (20), 133 (10), 128 (12), 126 (8), 117 (6), 105 (13), 97 (12), 95 (35), 91 (21), 79 (11), 78 (14), 77 (11), 67 (17), 66 (11), 65 (12).

PLC_2 (more polar): a pure isomer as a white solid (0.168 g, 39% yield, mp 119–121 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61–7.36 (m, 5H, Ar*H*), 6.22 (dd, J=5.6, 3.0 Hz, 1H, C*H*=CH), 5.80 (dd, J=5.6, 2.9 Hz, 1H, CH=C*H*), 3.24 (app. t, J=9.6 Hz, 1H, C*H*SOPh), 3.07 (br s, 1H, C*H*CH=CHCH), 2.83 (br s, 1H, CHCH=CHC*H*), 2.50 (m, 1H, C*H*HCH$_2$CHSOPh), 2.07 (dd, J=12.4, 7.2 Hz, 1H, C*H*HCHSOPh), 1.95 (dd, J=12.4, 6.8 Hz, 1H, CH*H*CHSOPh), 1.60–1.33 (m, 5H, CH_2, CH_2CCO and CH*H*CH$_2$CHSOPh). ^{13}C NMR (75 MHz, $CDCl_3$): δ 213.1 (C=O), 142.4 (C), 137.8 (CH), 132.6 (CH), 130.9 (CH), 129.2 (2×CH), 123.9 (2×CH), 71.1 (CH), 56.9 (C), 49.0 (CH), 48.6 (CH_2), 42.9 (CH), 38.4 (CH_2), 35.0 (CH_2), 15.0 (CH_2). IR (Nujol): ν_{max} 2955s, 1727m, 1334w, 1238w, 1085w, 1048m, 1020w, 760w, 743w, 728m, 692w cm^{-1}. MS: *m*/*z* (%) relative intensity 286 (M^+, 3), 267 (11), 243 (23), 231 (23), 205 (14), 203 (12), 201 (20), 193 (19), 181 (69), 178 (24), 149 (31), 143 (23), 131 (100), 125 (34), 121 (22), 109 (21), 99 (24), 97 (21), 95 (26), 93 (25), 83 (24), 81 (41), 79 (27), 77 (22), 69 (80), 67 (38), 65 (12), 51 (8).

PLC_3 (most polar): a 69:31 mixture of two isomers (A- and B-isomers) (0.176 g, 41% yield, mp 122–125 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70–7.45 (m, 10H, Ar*H* of A- and B-isomers), 6.31 (dd, *J*=5.5, 3.0 Hz, 1H, C*H*=CH of B-isomer), 6.20 (dd, *J*=5.5, 3.1 Hz, 1H, C*H*=CH of A-isomer), 5.94 (dd, *J*=5.5, 2.8 Hz, 1H, CH=C*H* of B-isomer), 5.68 (dd, *J*=5.5, 2.9 Hz, 1H, CH=C*H* of A-isomer), 3.82 (app. t, *J*=9.3 Hz, 1H, C*H*SOPh of A-isomer), 3.41 (dd, *J*=9.4, 5.2 Hz, 1H, C*H*SOPh of B-isomer), 2.94 (br s, 1H, C*H*CH=CHCH of B-isomer), 2.84 (br s, 1H, C*H*CH=CHCH of A-isomer), 2.75 (br s, 1H, CHCH=CHC*H* of B-isomer), 2.51 (m, 1H, C*H*HCH$_2$CHSOPh of B-isomer), 2.43–2.30 (m, 2H, C*H*HCH$_2$CHSOPh and CHCH=CHC*H* of A-isomer), 2.28–2.12 (m, 2H, CH*H*CH$_2$CHSOPh of A- and B-isomers), 2.10–1.84 (m, 4H, CH_2CHSOPh of A- and B-isomers), 1.66 (d, *J*=11.8 Hz, 1H, C*H*HCCO of B-isomer), 1.60–1.22 [m, 7H, (CH_2, CH*H*CCO, and CH_2CCO) of A-isomer and (CH_2 and CH*H*CCO) of B-isomer]. ^{13}C NMR (75 MHz, $CDCl_3$) of A-isomer: δ 212.1 (C=O), 140.6 (C), 137.6 (CH), 132.7 (CH), 131.5 (CH), 128.9 (2×CH), 125.3 (2×CH), 69.0 (CH), 56.7 (C), 49.5 (CH), 48.8 (CH_2), 42.7 (CH), 39.8 (CH_2), 35.7 (CH_2), 19.7 (CH_2); B-isomer: δ 213.0 (C=O), 142.7 (C), 138.3 (CH), 132.3 (CH), 131.0 (CH), 129.2 (2×CH), 124.2 (2×CH), 71.0 (CH), 56.9 (C), 51.2 (CH), 49.3 (CH_2), 43.0 (CH), 39.1 (CH_2), 36.5 (CH_2), 17.0 (CH_2). IR (Nujol): ν_{max} 2956s, 1735m, 1476m, 1444m, 1334m, 1238w, 1083m, 1042m, 1024m, 755m, 746m, 721m, 689m cm^{-1}. MS: *m*/*z* (%) relative intensity 286 (M^+, 8), 281 (18), 243 (16), 231 (22), 203 (27), 201 (46), 193 (26), 181 (60), 159 (25), 149 (57), 143 (27), 131 (94), 125 (100), 121 (32), 117 (34), 109 (31), 99 (82), 97 (35), 95 (54), 93 (46), 91 (40), 81 (80), 79 (41), 77 (35), 69 (86), 67 (53). Anal. Calcd for $C_{17}H_{18}O_2S$: C, 71.30; H, 6.64. Found: C, 71.15; H, 6.50.

4.4.2. 2′-Oxo-3′-phenylsulfinylcyclopentane-1′-spiro-2-(3-methylbicyclo[2.2.1]hept-5-ene) (7b). According to the general procedure described for compound **7a**, a diastereomeric mixture of **6b** (0.79 g, 2.28 mmol) was reacted with LDA (5.02 mmol) in THF (7 mL) to give a crude product, which was purified by preparative thin-layer chromatography (silica gel, 20% ethyl acetate in hexanes) to give three bands (PLC_1, PLC_2, and PLC_3) of **7b** (0.548 g, 80% combined yield) as a diastereomeric mixture.

PLC_1 (less polar): a pale yellow solid of a mixture of diastereomers (0.137 g, 20% yield): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60–7.38 (m, Ar*H*), 6.30–6.20 (m, olefinic protons), 6.18–5.98 (m, olefinic protons), 4.10 (m, C*H*SOPh of the minor isomer), 3.30–3.17 [m, (C*H*SOPh and C*H*CH=CHCH) of the major isomer and C*H*SOPh of the minor isomer], 2.86 (br s, C*H*CH=CHCH of the minor isomer), 2.75–2.55 (m, CHCH=CHC*H* of the major and minor isomers), 2.54–1.75 [m, CH_2CH$_2$CHSOPh of the major isomer and (CH_2CH$_2$CHSOPh, C*H*H, and CHCH=CHC*H*) of the minor isomer], 1.70 (d, *J*=8.7 Hz, C*H*H of the major isomer), 1.67–0.50 [m, CH_2, (CH_2CHSOPh and C*H*CH_3) of the major and minor isomers], 0.13 (d, *J*=7.3 Hz, CHCH_3 of the minor isomer). IR ($CHCl_3$): ν_{max} 3064w, 3010s, 2969s, 1726s, 1584w, 1478m, 1445m, 1345w, 1317m, 1158m, 1085s, 1048m, 691m, 665m cm^{-1}. MS: *m*/*z* (%) relative intensity 300 (M^+, 2), 251 (5), 235 (9), 217 (8), 175 (33), 157 (15), 149 (10), 147 (10), 133 (9), 129 (13), 125 (12), 110 (13), 109 (100), 105 (18), 97 (16), 93 (25), 91 (46), 81 (27), 79 (54), 77 (59), 66 (13), 65 (23).

PLC_2 (more polar): a pale yellow solid of a mixture of diastereomers (0.158 g, 23% yield): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60–7.35 (m, Ar*H*), 6.30–6.20 (m, olefinic protons), 6.29–6.00 (m, olefinic protons), 5.77 (dd, *J*=5.2, 2.8 Hz, olefinic proton of the major isomer), 5.60 (dd, *J*=5.6, 2.8 Hz, olefinic proton of the minor isomer), 4.01 (d, *J*=9.3 Hz, C*H*SOPh of the minor isomer), 3.90–3.69 (m, C*H*SOPh of the minor isomer), 3.20 (m, C*H*SOPh of the major isomer), 3.02 (br s, C*H*CH=CHCH of the major isomer), 2.90 (br s, C*H*CH=CHCH of the minor isomer), 2.85 (br s, C*H*CH=CHCH of minor isomer), 2.73–1.13 (m, CHCH=CHC*H*, CH_2CH_2CHSOPh, C*H*CH_3 and CH_2 of the major and minor isomers), 1.10–0.63 (m, CHCH_3 of the major and minor isomers), 0.55 (d, *J*=7.2 Hz, CHCH_3 of the minor isomer), 0.35 (d, *J*=7.3 Hz, CHCH_3 of the minor isomer). IR ($CHCl_3$): ν_{max} 3067w, 3010s, 2968s, 1728s, 1584w, 1478m, 1458m, 1445m, 1341w, 1315m, 1150m, 1086s, 1042m, 1023m, 690m cm^{-1}. MS: *m*/*z* (%) relative intensity 300 (M^+, 2), 251 (2), 235 (11), 176 (17), 175 (100), 157 (53), 147 (28), 142 (17), 133 (17), 129 (27), 125 (22), 119 (20), 115 (17), 110 (19), 109 (99), 105 (34), 97 (38), 93 (19), 91 (60), 81 (30), 79 (66), 77 (55), 66 (22), 65 (31).

PLC_3 (most polar): a pale yellow viscous liquid of a 66:34 mixture of two diastereomers (A- and B-isomers) (0.253 g, 37% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67–7.45 (m, 10H, Ar*H* of A- and B-isomers), 6.39 (dd, *J*=5.7, 3.1 Hz, 1H, C*H*=CH of A-isomer), 6.26 (dd, *J*=5.6, 3.1 Hz, 1H, C*H*=CH of B-isomer), 5.76 (dd, *J*=5.7, 2.9 Hz, 1H, CH=C*H* of A-isomer), 5.56 (dd, *J*=5.6, 2.9 Hz, 1H, CH=C*H* of B-isomer), 3.76 (dd, *J*=10.4, 8.9 Hz, 1H, C*H*SOPh of B-isomer), 3.39 (dd, *J*=9.8, 3.3 Hz, 1H, C*H*SOPh of A-isomer), 2.71 (br s, 1H, C*H*CH=CHCH of A-isomer), 2.55–2.47 (m, 3H, C*H*CH=CHCH of A-isomer and CH_2CH$_2$CHSOPh of B-isomer), 2.43–2.23 (m, 4H, CH_2CH$_2$CHSOPh of A-isomer and C*H*CH=CHC*H* of B-isomer), 2.08–1.68 [m, 6H, (CH_2CHSOPh and C*H*CH_3) of A-isomer and (CH_2CHSOPh and C*H*CH_3) of B-isomer], 1.66 (d, *J*=8.9 Hz, 1H, C*H*H of A-isomer), 1.52 (d, *J*=8.8 Hz, 1H, C*H*H of B-isomer), 1.45 (ddd, *J*=8.9, 3.5, 1.7 Hz, 1H, CH*H* of A-isomer), 1.33 (ddd, *J*=8.8, 3.3, 1.7 Hz, 1H, CH*H* of B-isomer), 1.01 (d, *J*=7.2 Hz, 3H, CHCH_3 of A-isomer), 0.93 (d, *J*=7.2 Hz, 3H, CHCH_3 of B-isomer). ^{13}C NMR (100 MHz, $CDCl_3$) of A-isomer: δ 213.6 (CO), 143.7 (C), 139.9 (CH), 131.8 (CH), 131.6 (CH), 129.8 (2×CH), 125.0 (2×CH), 71.3 (CH), 60.0 (C), 52.9 (CH), 51.3 (CH), 47.1 (CH_2), 41.2 (CH), 32.4 (CH_2), 18.8 (CH_2), 18.3 (CH_3); B-isomer: δ 212.4 (CO), 153.2 (C), 138.8 (CH), 132.8 (CH), 132.1 (CH), 129.5 (2×CH), 126.0 (2×CH), 69.7 (CH), 60.0 (C), 51.2 (CH), 51.2 (CH), 46.7 (CH_2), 41.8 (CH), 31.1 (CH_2), 20.9 (CH_2), 18.3 (CH_3). IR ($CHCl_3$): ν_{max} 3066w, 3010s, 2969s, 1726s, 1584w, 1478m, 1464m, 1445m, 1332w, 1154w, 1086m, 1048m, 1024m, 691m cm^{-1}. MS: *m*/*z* (%) relative intensity 300 (M^+, 10), 254 (6), 217 (10), 175 (74), 157 (43), 147 (21), 142 (18), 129 (25), 110 (31), 109 (100), 105 (28), 97 (17), 91 (56), 81 (33), 79 (62), 77 (44), 66 (18), 65 (22). Anal. Calcd for $C_{18}H_{20}O_2S$: C, 71.97; H, 6.71. Found: C, 71.83; H, 6.87.

4.4.3. 2′-Oxo-3′-phenylsulfinylcyclopentane-1′-spiro-2-(3-phenyl-bicyclo[2.2.1]hept-5-ene) (7c). According to the general procedure described for compound **7a**, a 70:30 mixture of *endo*,*exo*- and *endo*,*endo*-**6c** (1.27 g, 3.22 mmol) was reacted with LDA (7.09 mmol) in THF (10 mL) to give a crude product, which was purified by preparative thin-layer chromatography (silica gel, 20% ethyl acetate in hexanes) to give two bands (PLC_1 and PLC_2) of **7c** (0.817 g, 70% combined yield) as a diastereomeric mixture. ^{1}H NMR (300 MHz, $CDCl_3$) of a mixture of four diastereomers of **7c** (A-, B-, C-, and D-isomers): δ 7.59–7.36 (m, 20H, SOAr*H*), 7.29–6.88 (m, 20H, Ar*H*), 6.46 (m, 3H, C*H*=CH of A-, B-, and D-isomers), 6.35 (m, 2H, CH=C*H* of A-isomer and C*H*=CH of C-isomer), 5.94 (dd, J=5.5, 2.9 Hz, CH=C*H* of D-isomer), 5.88 (dd, J=5.6, 2.9 Hz, 1H, CH=C*H* of B-isomer), 5.73 (dd, J=5.5, 2.9 Hz, 1H, CH=C*H* of C-isomer), 3.58 (app. t, J=9.4 Hz, 1H, C*H*SOPh of C-isomer), 3.39 (dd, J=9.3, 4.6 Hz, 1H, C*H*SOPh of B-isomer), 3.33 (d, J=2.9 Hz, 1H, C*H*Ph of A-isomer), 3.24–2.82 [m, 10H, C*H*CH=CHC*H* of A-isomer, (C*H*CH=CHCH and C*H*Ph) of B- and C-isomers and (C*H*SOPh, C*H*CH=CHC*H*, and C*H*Ph) of D-isomer], 2.77 (br s, 1H, CHCH=CHC*H* of B-isomer), 2.60 (dd, J=9.5, 6.6 Hz, 1H, C*H*SOPh of A-isomer), 2.50 (br s, 1H, CHCH=CHC*H* of C-isomer), 2.43–2.02 (m, 7H, CH_2CO of A-, B-, and C-isomers and C*H*HCO of D-isomer), 1.95 (d, J=8.9 Hz, 2H, C*H*H of A- and D-isomers), 1.90–1.12 [m, 16H, (CH*H* and CH_2CHSOPh) of A-isomer, (CH_2 and CH_2CHSOPh) of B- and C-isomers and (CH_2 and CH*H*CH_2CHSOPh) of D-isomer].

PLC_1 (less polar): 0.630 g, 54% yield as a yellow solid of three isomers (A-, B-, and C-isomers). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59–7.32 (m, 15H, SOAr*H*), 7.30–6.88 (m, 15H, Ar*H*), 6.45 (m, 2H, C*H*=CH of A- and B-isomers), 6.35 (m, 2H, CH=C*H* of A-isomer and C*H*=CH of C-isomer), 5.87 (dd, J=5.6, 2.8 Hz, CH=C*H* of B-isomer), 5.72 (dd, J=5.6, 2.9 Hz, 1H, CH=C*H* of C-isomer), 3.59 (app. t, J=9.4 Hz, 1H, C*H*SOPh of C-isomer), 3.38 (dd, J=9.3, 4.6 Hz, 1H, C*H*SOPh of B-isomer), 3.33 (d, J=2.9 Hz, 1H, C*H*Ph of A-isomer), 3.13–2.86 [m, 6H, C*H*CH=CHC*H* of A-isomer and (C*H*CH=CHCH and C*H*Ph) of B- and C-isomers], 2.76 (br s, 1H, CHCH=CHC*H* of B-isomer), 2.60 (dd, J=9.6, 6.6 Hz, 1H, C*H*SOPh of A-isomer), 2.50 (br s, 1H, CHCH=CHC*H* of C-isomer), 2.44–2.02 (m, 6H, CH_2CO of A-, B-, and C-isomers), 1.95 (d, J=8.2 Hz, 1H, C*H*H of A-isomer), 1.90–1.10 [m, 11H, (CH*H* and CH_2CHSOPh) of A-isomer and (CH_2 and CH_2CHSOPh) of B- and C-isomers]. IR ($CHCl_3$): ν_{max} 3436w, 3066w, 3012s, 1729s, 1602w, 1498w, 1478w, 1445m, 1332w, 1241m, 1175w, 1153w, 1086m, 1050m, 706m cm^{-1}. MS: *m*/*z* (%) relative intensity 363 (M^+, 1), 298 (3), 297 (14), 237 (16), 236 (4), 219 (3), 173 (5), 172 (31), 171 (100), 170 (10), 169 (30), 153 (20), 141 (11), 129 (11), 128 (14), 115 (13), 91 (7), 78 (7), 66 (4), 65 (6).

PLC_2 (more polar): a pale yellow solid of a pure D-isomer (0.187 g, 16% yield, mp 142–144 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58–7.32 (m, 5H, SOAr*H*), 7.30–6.84 (m, 5H, Ar*H*), 6.44 (dd, J=5.4, 3.2 Hz, 1H, C*H*=CH), 5.94 (dd, J=5.4, 2.9 Hz, 1H, CH=C*H*), 3.26–3.12 (m, 2H, C*H*CH=CHCH and C*H*SOPh), 3.08 (br s, 1H, CHCH=CHC*H*), 3.00 (br s, 1H, C*H*Ph), 2.39 (m, 1H, C*H*HCH_2CHSOPh), 1.95 (d, J=8.8 Hz, 1H, C*H*H), 1.67 (d, J=8.8 Hz, 1H, CH*H*), 1.45 (m, 1H, CH*H*CH_2CHSOPh), 1.40–1.10 (m, 2H, CH_2CHSOPh). ^{13}C NMR (75 MHz, $CDCl_3$): δ 212.6 (C=O), 142.1 (C), 141.9 (C), 139.3 (CH), 133.7 (CH), 130.8 (CH), 129.1 (2×CH), 128.4 (2×CH), 128.1 (2×CH), 126.2 (CH), 123.8 (2×CH), 70.8 (CH), 61.2 (C), 52.3 (CH), 49.1 (CH), 48.4 (CH), 47.9 (CH_2), 31.5 (CH_2), 14.9 (CH_2). IR ($CHCl_3$): ν_{max} 3066w, 3010m, 1729s, 1602w, 1584w, 1498m, 1478w, 1446m, 1332w, 1242m, 1153m, 1086m, 1051m, 705m cm^{-1}. MS: *m*/*z* (%) relative intensity 363 (M^+, 2), 297 (13), 237 (42), 236 (12), 219 (10), 172 (31), 171 (100), 170 (14), 169 (38), 154 (9), 153 (21), 129 (16), 128 (20), 115 (18), 92 (15), 78 (7), 66 (5), 65 (6). Anal. Calcd for $C_{23}H_{22}O_2S$: C, 76.21; H, 6.12. Found: C, 76.06; H, 6.32.

4.4.4. 2′-Oxo-3′-phenylsulfinylcyclopentane-1′-spiro-2-(3-hydroxymethylbicyclo[2.2.1]hept-5-ene) (7dA) and compound 7dB. According to the general procedure described for compound **7a**, a 90:10 diastereomeric mixture of **6d** (0.442 g, 1.40 mmol) was reacted with LDA (3.08 mmol) in THF (4.5 mL) to give a crude product, which was purified by preparative thin-layer chromatography (silica gel, 70% ethyl acetate in hexanes) to afford two bands (PLC_1 and PLC_2) of products (0.365 g, 82% combined yield).

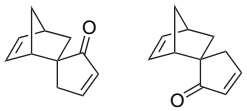
PLC_1 (less polar) was obtained as a colorless solid of a single diastereomer of **7dB** (0.135 g, 30% yield, mp 134–136 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75–7.47 (m, 5H, Ar*H*), 6.57 (dd, J=5.6, 3.0 Hz, 1H, C*H*=CH), 6.15 (dd, J=5.6, 2.9 Hz, 1H, CH=C*H*), 4.10 (app. t, J=8.5 Hz, 1H, C*H*HO), 3.49 (app. t, J=8.5 Hz, 1H, CH*H*O), 3.05 (dd, J=12.0, 6.1 Hz, 1H, C*H*SOPh), 2.87–2.74 (m, 2H, C*H*CH=CHCH and C*H*CH_2O), 2.65 (br s, 1H, O*H*), 2.58 (br s, 1H, CHCH=CHC*H*), 2.00–1.70 (m, 5H, CH_2C*H*HCHSOPh and CH_2), 1.27 (m, 1H, CH*H*CHSOPh). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.4 (C), 138.8 (CH), 132.5 (CH), 131.5 (CH), 129.2 (2×CH), 124.5 (2×CH), 112.2 (C–O), 74.6 (CH), 70.7 (CH_2), 68.2 (C), 60.3 (CH), 53.7 (CH_2), 51.6 (CH), 44.3 (CH), 39.4 (CH_2), 23.2 (CH_2). IR (Nujol): ν_{max} 3385m, 3053w, 2956s, 1441m, 1253w, 1242w, 1173w, 1027m, 1013m, 995m, 748m, 700w cm^{-1}. MS: *m*/*z* (%) relative intensity 316 (M^+, 1), 299 (12), 233 (48), 191 (75), 173 (50), 160 (36), 153 (38), 145 (64), 135 (28), 129 (30), 125 (100), 117 (49), 97 (32), 91 (68), 79 (61), 77 (60), 66 (39), 65 (37), 51 (26). HRMS (ESI-TOF) calcd for $C_{18}H_{20}O_3SNa$: 339.1031; found: 339.1031.

PLC_2 (more polar) was obtained as a pale yellow solid of **7dA** (0.231 g, 52% yield) as a mixture of diastereomers: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70–7.35 (m, Ar*H*), 6.52 (m, an olefinic proton of the minor isomer), 6.40 (dd, J=5.6, 3.0 Hz, olefinic proton of the major isomer), 6.27 (m, an olefinic proton of the major isomer), 6.20 (m, an olefinic proton of the minor isomer), 6.15–5.95 (m, olefinic protons of the minor isomer), 4.04 (app. t, J=8.6 Hz, C*H*HOH of the major isomer), 3.70 (app. t, J=8.8 Hz, C*H*HOH of the minor isomer), 3.50–3.28 (m, CH*H*OH of the major and minor isomers), 3.22 (app. t, J=10.7 Hz, C*H*SOPh of the minor isomer), 3.14–2.95 (m, C*H*SOPh of the major and minor isomers), 2.88–2.50 [m, (C*H*CH=CHC*H* and C*H*CH_2OH) of the major isomer and C*H*CH=CHC*H* of

the minor isomer], 2.50–2.08 (m, C*H*$_2$CH$_2$CHSOPh, O*H*, and C*H*CH$_2$OH) of the minor isomer and (C*H*HCH$_2$CHSOPh and O*H*) of the major isomer), 2.08–1.45 [m, (CH*H*CH$_2$CHSOPh and C*H*$_2$) of the major and minor isomers], 1.35 (d, *J*=9.4 Hz, CH*H* of the minor isomer). IR (neat): ν_{max} 3419s, 3060m, 2964s, 2874s, 1728s, 1651w, 1583w, 1479s, 1445s, 1341m, 1256s, 1085s, 1046s, 997s, 752s, 695s cm^{-1}. MS: *m*/*z* (%) relative intensity 317 (M$^+$, 4), 299 (13), 233 (38), 191 (86), 173 (53), 160 (32), 153 (33), 145 (59), 135 (23), 131 (23), 126 (29), 125 (100), 117 (44), 107 (28), 97 (26), 92 (68), 79 (62), 77 (39), 66 (28), 65 (28), 51 (19). HRMS (ESI-TOF) calcd for $C_{18}H_{20}O_3SNa$: 339.1031; found: 339.1029.

4.5. Preparation of spirocyclopentenones 8

4.5.1. 2′-Oxocyclopent-3′-ene-1′-spiro-2-bicyclo[2.2.1]-hept-5-ene (8a). A diastereomeric mixture of **7a** (1 g, 3.5 mmol) was dissolved in dry toluene (10 mL) and dry $CaCO_3$ (0.35 g, 3.5 mmol) was added. The mixture was refluxed under an argon atmosphere overnight. The precipitate of $CaCO_3$ was filtered and washed with ethyl acetate. The organic layer was concentrated to give an 88:12 mixture of *endo*- and *exo*-**8a**, which was purified by column chromatography (silica gel, 10% ethyl acetate in hexanes) to give two fractions of **8a** (0.395 g, 70% combined yield).

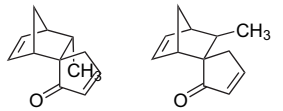


exo-**8a** *endo*-**8a**

The first fraction (less polar) of a 91:9 mixture of *endo*- and *exo*-**8a** was obtained as a pale yellow liquid (45 mg, 8% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62 (td, *J*=5.8, 2.8 Hz, 2H, C*H*=CHCO of *endo*- and *exo*-isomers), 6.38 (dd, *J*=5.6, 3.1 Hz, 1H, C*H*=CH of *exo*-isomer), 6.34 (m, 1H, C*H*=CH of *endo*-isomer), 6.17 [dd, *J*=5.4, 2.9 Hz, 2H, (CH=C*H* and CH=C*H*CO) of *exo*-isomer and CH=C*H*CO of *endo*-isomer], 5.97 (dd, *J*=5.7, 3.1 Hz, 1H, CH=C*H* of *endo*-isomer), 2.94 (br s, 1H, C*H*CH=CHCH of *endo*- and *exo*-isomers), 2.82 (dd, *J*=18.7, 2.8 Hz, 1H, C*H*HCCO of *endo*-isomer), 2.71–2.57 [m, 4H, (C*H*HCH=CHCO and CHCH=CHC*H*) of *exo*- and *endo*-isomers], 2.38 (dd, *J*=19.5, 2.3 Hz, 1H, CH*H*CH=CHCO of *exo*-isomer), 2.28 (d, *J*=8.5 Hz, 1H, C*H*H of *exo*-isomer), 2.12 (dd, *J*=11.4, 3.6 Hz, 1H, C*H*HCCO of *exo*-isomer), 1.69 (dd, *J*=11.5, 3.7 Hz, 1H, C*H*HCCO of *endo*-isomer), 1.59–1.44 (m, 3H, C*H*$_2$ and CH*H*CCO of *endo*-isomer), 1.32 (d, *J*=8.5 Hz, 1H, CH*H* of *exo*-isomer), 1.08 (dd, *J*=11.4, 2.9 Hz, 1H, CH*H*CCO of *exo*-isomer). IR (neat): ν_{max} 3063m, 2964s, 1695s, 1592m, 1475m, 1442m, 1344s, 1307m, 1147s, 1086m, 1016m, 798m, 755m, 723m, 690w, 596w cm^{-1}. MS: *m*/*z* (%) relative intensity 160 (M$^+$, 78), 149 (89), 131 (76), 130 (35), 129 (36), 125 (54), 115 (36), 105 (56), 99 (40), 91 (80), 81 (59), 78 (45), 77 (100), 67 (67), 55 (79).

The second fraction (more polar) of *endo*-**8a** was obtained as a pale yellow liquid (0.35 g, 62% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 (td, *J*=5.9, 2.7 Hz, 1H, C*H*=CHCO), 6.35 (dd, *J*=5.5, 3.0 Hz, 1H, C*H*=CH), 6.16 (td, *J*=5.9, 2.2 Hz, 1H, CH=C*H*CO), 5.99 (dd, *J*=5.5, 2.9 Hz, 1H, CH=C*H*), 2.98 (d, *J*=0.7 Hz, 1H, C*H*CH=CHCH), 2.90 (dd, *J*=19.0, 2.2 Hz, 1H, C*H*HCH=CHCO), 2.73 (dd, *J*=19.0, 2.4 Hz, 1H, CH*H*CH=CHCO), 2.51 (br s, 1H, CHCH=CHC*H*), 1.69 (dd, *J*=11.9, 3.6 Hz, 1H, C*H*HCCO), 1.50 (m, 3H, C*H*$_2$ and CH*H*CCO). ^{13}C NMR (75 MHz, $CDCl_3$): δ 211.8 (C=O), 161.0 (CH), 133.6 (CH), 132.6 (CH), 54.6 (CH), 52.4 (C), 50.1 (CH$_2$), 47.2 (CH$_2$), 43.5 (CH), 39.3 (CH$_2$). IR (neat): ν_{max} 3063m, 2964s, 1699s, 1593m, 1475m, 1443m, 1328s, 1309m, 1146s, 1078m, 797m, 753s, 717m, 687s, 595s cm^{-1}. MS: *m*/*z* (%) relative intensity 160 (M$^+$, 4), 159 (15), 141 (28), 131 (11), 125 (100), 115 (8), 109 (21), 97 (23), 95 (28), 91 (10), 77 (56), 65 (21), 51 (18). HRMS (ESI-TOF) calcd for $C_{11}H_{12}ONa$: 183.0786; found: 183.0786.

4.5.2. 2′-Oxocyclopent-3′-ene-1′-spiro-2-(3-methyl-bicyclo[2.2.1]hept-5-ene) (8b). A diastereomeric mixture of **7b** (0.40 g, 1.33 mmol) was dissolved in dry toluene (5 mL) and dry $CaCO_3$ (0.13 g, 1.33 mmol) was added. The mixture was refluxed under an argon atmosphere overnight. The crude product was purified by column chromatography (silica gel, 10% ethyl acetate in hexanes) to give two fractions of **8b** (0.174 g, 75% combined yield).



endo,endo-**8b** *endo,exo*-**8b**

The first fraction (less polar) was obtained as a pale yellow liquid of pure *endo*,*endo*-**8b** (21 mg, 19% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (td, *J*=5.9, 2.8 Hz, 1H, C*H*=CHCO), 6.31 (2dd, *J*=5.7, 2.9 Hz, 2H, C*H*=C*H*), 6.06 (td, *J*=5.9, 2.1 Hz, 1H, CH=C*H*CO), 2.90 (td, ABX system, *J*=19.2, 2.4 Hz, 1H, C*H*HCH=CHCO), 2.79 (td, ABX system, *J*=19.2, 2.5 Hz, 1H, CH*H*CH=CHCO), 2.74 (m, 1H, CHCH=CHC*H*), 2.57 (br s, 1H, C*H*CH=CHCH), 2.37 (dq, *J*=7.2, 3.3 Hz, 1H, C*H*CH$_3$), 1.57 (d, *J*=8.4 Hz, 1H, C*H*H), 1.51 (td, *J*=8.4, 1.7 Hz, 1H, CH*H*), 0.84 (d, *J*=7.2 Hz, 3H, CHC*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.5 (C=O), 161.7 (CH), 136.7 (CH), 135.6 (CH), 135.1 (CH), 55.6 (CH), 50.4 (CH), 50.0 (CH$_2$), 49.7 (CH$_2$), 49.6 (CH), 30.3 (C), 17.0 (CH$_3$). IR ($CHCl_3$): ν_{max} 3064w, 3020m, 2965m, 2876w, 1694s, 1596w, 1448m, 1346m, 1325m, 1261w, 1147s, 1085m, 1014m, 688m, 597s cm^{-1}. MS: *m*/*z* (%) relative intensity 175 (M$^+$+1, 7), 167 (11), 149 (34), 141 (12), 125 (100), 109 (28), 99 (36), 97 (31), 95 (11), 91 (13), 81 (27), 79 (13), 77 (59), 69 (18), 67 (12), 65 (18). HRMS (ESI-TOF) calcd for $C_{12}H_{14}ONa$: 197.0942; found: 197.0943.

The second fraction (more polar) was obtained as a 73:37 mixture of *endo*,*exo*- and *endo*,*endo*-isomers (0.13 g, 56% yield) as a pale yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59–7.50 (m, 2H, C*H*=CHCO of *endo*,*exo*- and *endo*,*endo*-isomers), 6.34 (dd, *J*=5.6, 3.2 Hz, 1H, C*H*=CH of *endo*,*exo*-isomer), 6.20 (m, 2H, C*H*=C*H* of *endo*,*endo*-isomer), 6.02 (td, *J*=3.6, 2.2 Hz, 1H, CH=C*H*CO of *endo*,*exo*-isomer), 5.96 (td, *J*=3.6, 2.2 Hz, 1H, CH=C*H*CO of *endo*,*endo*-isomer), 5.83 (dd, *J*=5.6,

2.9 Hz, 1H, CH=C*H* of *endo*,*exo*-isomer), 2.90 (dd, *J*=19.0, 2.1 Hz, 1H, C*H*HCH=CHCO of *endo*,*exo*-isomer), 2.80 (dd, *J*=19.2, 2.3 Hz, 1H, C*H*HCH=CHCO of *endo*,*endo*-isomer), 2.74–2.60 (m, 2H, CH*H*CH=CHCO and C*H*CH=CHCH of *endo*,*endo*-isomer), 2.47 (br s, 1H, CHCH=CHC*H* of *endo*,*endo*-isomer), 2.42 (br s, 1H, C*H*CH=CHCH of *endo*,*exo*-isomer), 2.37 (br s, 1H, CHCH=CHC*H* of *endo*,*exo*-isomer), 2.32–2.22 (m, 2H, CH*H*CH=CHCO of *endo*,*exo*-isomer and C*H*CH_3 of *endo*,*endo*-isomer), 1.74 (q, *J*=7.0 Hz, 1H, C*H*CH_3 of *endo*,*exo*-isomer), 1.55–1.33 (m, 4H, CH_2 of *endo*,*exo*- and *endo*,*endo*-isomers), 0.94 (d, *J*=7.0 Hz, 3H, CHCH_3 of *endo*,*exo*-isomer), 0.74 (d, *J*=7.2 Hz, 3H, CHCH_3 of *endo*,*endo*-isomer). IR (neat): ν_{max} 3063m, 2960s, 2873m, 1698s, 1594m, 1449m, 1376w, 1343m, 1200m, 1147s, 1078m, 1016w, 753m, 730m, 688m, 596s cm^{-1}. MS: *m*/*z* (%) relative intensity 175 (M^++1, 28), 174 (M^+, 41), 173 (26), 161 (17), 149 (20), 147 (30), 145 (30), 133 (35), 131 (34), 125 (23), 115 (20), 110 (25), 109 (100), 107 (26), 95 (22), 91 (62), 81 (30), 79 (48), 77 (46), 67 (14), 66 (20), 65 (23), 51 (13).

4.6. Flash vacuum pyrolysis of compounds 6 leading to 5-alkylidene-2-cyclopentenones

4.6.1. 5-Methylene-2-cyclopentenone (9a).[9b] Flash vacuum pyrolysis of a diastereomeric mixture of **7a** (100 mg, 0.35 mmol) (conditions: oven temperature 240 °C; column temperature 375 °C; pressure 0.03 mmHg) gave a crude colorless pyrolysate of **9a** in quantitative yield. Purification of **9a** was unsuccessful due to its rapid decomposition. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 (app. t, *J*=3.1 Hz, 1H, C*H*=CHCO), 6.30 (td, *J*=5.7, 3.0 Hz, 1H, CH=C*H*CO), 6.03 (s, 1H, C*H*H=CCO), 5.37 (s, 1H, CH*H*=CCO), 3.17 (s, 2H, CH_2). IR ($CHCl_3$): ν_{max} 3015s, 2970m, 1701s, 1650s, 1582m, 1430m, 1416m, 1344m, 1253m, 1138m, 933m, 909s, 836m, 747m, 697m cm^{-1}. MS: *m*/*z* (%) relative intensity 95 (M^++1, 100).

4.6.2. 5-Ethylidene-2-cyclopentenone (9b).[9c] Flash vacuum pyrolysis of a diastereomeric mixture of **7b** (100 mg, 0.33 mmol) gave a 85:15 mixture of *E*:*Z*-isomers of a crude pyrolysate of **9b**, which was purified by preparative thin-layer chromatography (silica gel, 15% ethyl acetate in hexanes) to give a yellow liquid of the *E*-isomer of **9b** (28 mg, 82% yield). The *Z*-isomer of **9b** was not obtained in pure form. ^{1}H NMR (300 MHz, $CDCl_3$) of the crude product of **9b** containing a mixture of *E*- and *Z*-isomers: δ 7.60–7.00 (m, 7H, C*H*=CHCO of *E*- and *Z*-isomers), 6.63 (q, *J*=6.9 Hz, 1H, C=C*H*CH_3 of *E*-isomer), 6.30 (app. d, *J*=6.0 Hz, 2H, CH=C*H*CO of *E*- and *Z*-isomers), 6.13 (m, 1H, C=C*H*CH_3 of *Z*-isomer), 3.13 (br s, 2H, CH_2 of *E*-isomer), 2.54 (s, 2H, CH_2 of *Z*-isomer), 2.18 (d, *J*=7.3 Hz, 3H, C=CHCH_3 of *Z*-isomer), 1.82 (d, *J*=6.9 Hz, 3H, C=CHCH_3 of *E*-isomer).

(*E*)-**9b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52 (m, 1H, C*H*=CHCO), 6.59 (q, *J*=7.0 Hz, 1H, C=C*H*CH_3), 6.28 (td, *J*=5.9, 2.1 Hz, 1H, CH=C*H*CO), 3.13 (br s, 2H, CH_2), 1.81 (d, *J*=7.0 Hz, 3H, C=CHCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.2 (C=O), 156.8 (CH), 135.9 (CH), 135.1 (C), 130.7 (CH), 31.8 (CH_2), 15.0 (CH_3). IR (neat): ν_{max} 3058m, 2961m, 2915m, 1699s, 1656s, 1582m, 1440m, 1415m, 1351m, 1272m, 1222s, 1092w, 977w, 940m, 782s, 765s, 737s cm^{-1}. MS: *m*/*z* (%) relative intensity 219 ($2M^+$+2, 9), 218 ($2M^+$+1, 46), 168 (M^++60, 11), 149 (M^++41, 15), 110 (M^++2, 100), 109 (M^++1, 90), 108 (M^+, 23), 95 (15), 91 (17), 81 (40), 79 (67), 77 (42), 66 (21), 65 (23), 51 (13).

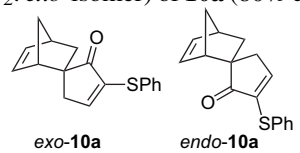
4.6.3. 5-Phenylidene-2-cyclopentenone (9c).[9c] Flash vacuum pyrolysis of PLC_2 of **7c** (100 mg, 0.28 mmol) gave a crude pyrolysate of the (*E*)-isomer of **9c**, which was purified by preparative thin-layer chromatography (silica gel, 15% ethyl acetate in hexanes) to give a pale yellow solid of (*E*)-**9c** (40.5 mg, 85% yield, mp 66–69 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68 (m, 1H, C*H*Ph), 7.63–7.32 (m, 6H, Ar*H* and C*H*=CHCO), 6.48 (td, *J*=6.0, 2.1 Hz, 1H, CH=C*H*CO), 3.59 (d, *J*=1.7 Hz, 2H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.5 (C=O), 157.1 (CH), 135.5 (CH), 135.1 (C), 132.3 (C), 132.1 (CH), 130.4 (2×CH), 129.5 (CH), 128.9 (2×CH), 34.3 (CH_2). IR (Nujol): ν_{max} 1688s, 1633s, 1590m, 1572m, 1493m, 1374w, 1292w, 1273m, 1228m, 1186s, 1099m, 950m, 789s, 690m cm^{-1}. MS: *m*/*z* (%) relative intensity 171 (M^++1, 8), 170 (34), 169 (100), 143 (16), 141 (36), 116 (8), 115 (29), 89 (6), 63 (6).

4.6.4. 5-(Hydroxymethyl)methylidene-2-cyclopentenone (9d). Flash vacuum pyrolysis of a mixture of diastereomeric mixture of **7dA** (70 mg, 0.22 mmol) (conditions: oven temperature 250 °C, column temperature 450 °C, pressure 0.05 mmHg) gave a crude pyrolysate of **9d**, which was purified by preparative thin-layer chromatography (silica gel, 40% ethyl acetate in hexanes) to give a pale yellow liquid of a labile (*Z*)-**9d** (8.3 mg, 30% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56 (m, 1H, C*H*=CHCO), 6.60 (app. t, *J*=5.4 Hz, 1H, C*H*CH_2OH), 6.34 (td, *J*=6.0, 2.2 Hz, 1H, CH=C*H*CO), 4.43 (d, *J*=5.4 Hz, 2H, CH_2OH), 3.23 (s, 2H, CH_2), 1.60 (br s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.6 (C=O), 157.6 (CH), 135.8 (CH), 132.6 (C), 129.3 and 129.1 (CH), 60.9 (CH_2OH), 32.2 (CH_2). IR (neat): ν_{max} 3420s, 2964s, 2926s, 1699s, 1447w, 1413w, 1261s, 1091s, 1022s, 800s, 736w cm^{-1}. MS: *m*/*z* (%) relative intensity 125 (M^++1, 21), 124 (M^+, 8), 123 (18), 121 (23), 120 (16), 115 (13), 111 (24), 105 (23), 97 (28), 95 (100), 92 (38), 91 (28), 83 (29), 81 (39), 78 (58), 77 (66), 71 (22), 69 (28), 67 (73), 65 (42), 63 (23), 57 (32), 55 (42), 51 (20). HRMS (ESI-TOF) calcd for $C_7H_8O_2SNa$: 147.0422; found: 147.0424.

4.7. The Pummerer rearrangement of spiro-sulfoxides 6: preparation of spirocyclopentenones 10

4.7.1. 2′-Oxo-3′-phenylsulfanylcyclopent-3′-ene-1′-spiro-2-bicyclo[2.2.1]hept-5-ene (10a). *General procedure*: Trifluoroacetic anhydride (0.08 mL, 0.60 mmol) was added slowly to an acetonitrile solution (3 mL) of an 88:12 diastereomeric mixture of **7a** (0.172 g, 0.6 mmol) under an argon atmosphere at 0 °C. The resulting solution was stirred at 0 °C to room temperature overnight. The mixture was quenched with water (3 mL) and extracted with EtOAc (3×25 mL). The combined organic layers were washed with water, brine and dried over anhyd Na_2SO_4. The organic phase was concentrated and purified by column chromatography to give an 88:12 mixture of *endo*- and *exo*-isomers of **10a**. The mixture of *endo*- and *exo*-**10a** were separated

by preparative thin-layer chromatography (silica gel, 5–10% ethyl acetate in hexanes) to give two fractions (PLC_1: *endo*-isomer and PLC_2: *exo*-isomer) of **10a** (80% combined yield).



exo-**10a** *endo*-**10a**

PLC_1 (less polar) was obtained as a pale yellow solid of *exo*-**10a** (16.7 mg, 10% yield, mp 118–119 °C): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47–7.21 (m, 5H, Ar*H*), 6.83 (t, *J*=2.9 Hz, 1H, C*H*=CSAr), 6.30 (dd, *J*=5.5, 3.0 Hz, 1H, C*H*=CH), 6.06 (dd, *J*=5.5, 2.9 Hz, 1H, CH=C*H*), 2.89 (br s, 1H, C*H*CH=CHCH), 2.68 (br s, 1H, CHCH=CHC*H*), 2.47 (dd, *J*=19.4, 3.1 Hz, 1H, C*H*HCH=CSAr), 2.30–2.15 (m, 2H, CH*H*CH=CSAr and C*H*H), 2.10 (dd, *J*=11.4, 3.6 Hz, 1H, C*H*HCCO), 1.26 (d, *J*=8.5 Hz, 1H, CH*H*), 1.03 (dd, *J*=11.4, 2.9 Hz, 1H, CH*H*CCO). ^{13}C NMR (75 MHz, $CDCl_3$): δ 208.5 (C=O), 153.1 (CH), 141.2 (C), 140.8 (CH), 135.2 (CH), 133.3 (2×CH), 131.3 (C), 129.4 (2×CH), 128.4 (CH), 53.7 (C), 51.3 (CH), 46.8 (CH_2), 43.2 (CH), 42.9 (CH_2), 41.6 (CH_2). IR ($CHCl_3$): ν_{max} 3064w, 3012m, 2967m, 1698s, 1630m, 1582m, 1477m, 1441m, 1373m, 1301m, 1276m, 1025m, 991w, 692m cm^{-1}. MS: *m*/*z* (%) relative intensity 268 (M^+, 42), 235 (5), 219 (13), 218 (15), 204 (20), 203 (100), 202 (16), 174 (11), 173 (13), 167 (14), 149 (20), 141 (11), 129 (13), 97 (24), 91 (9), 77 (9), 65 (18).

PLC_2 (more polar) was obtained as a pale yellow solid of *endo*-**10a** (0.112 g, 70% yield, mp 128–130 °C): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55–7.27 (m, 5H, Ar*H*), 6.92 (t, *J*=2.9 Hz, 1H, C*H*=CSAr), 6.34 (dd, *J*=5.4, 3.1 Hz, 1H, C*H*=CH), 5.97 (dd, *J*=5.4, 2.9 Hz, 1H, CH=C*H*), 2.98 (br s, 1H, C*H*CH=CHCH), 2.82 (dd, *J*=18.7, 2.7 Hz, 1H, C*H*HCH=CSAr), 2.64 (dd, *J*=18.7, 3.2 Hz, 1H, CH*H*CH=CSAr), 2.58 (br s, 1H, CHCH=CHC*H*), 1.71 (dd, *J*=11.5, 3.7 Hz, 1H, C*H*HCCO), 1.60–1.40 (m, 3H, CH_2 and CH*H*CCO). ^{13}C NMR (75 MHz, $CDCl_3$): δ 206.2 (C=O), 151.8 (CH), 141.8 (C), 138.2 (CH), 133.3 (CH), 132.5 (2×CH), 131.3 (C), 129.4 (2×CH), 128.3 (CH), 54.9 (CH), 53.6 (C), 49.9 (CH_2), 45.7 (CH_2), 43.6 (CH), 39.8 (CH_2). IR (Nujol): ν_{max} 3059w, 1699s, 1577m, 1468m, 1283m, 1273m, 1021m, 992m, 758m, 693m, 634w cm^{-1}. MS: *m*/*z* (%) relative intensity 270 (M^++2, 19), 269 (M^++1, 79), 268 (M^+, 100), 235 (7), 203 (53), 202 (15), 174 (21), 173 (24), 159 (14), 158 (17), 141 (10), 129 (11), 115 (5), 97 (15), 91 (9), 65 (7). Anal. Calcd for $C_{17}H_{16}OS$: C, 76.08; H, 6.01. Found: C, 75.75; H, 6.02.

4.7.2. 2′-Oxo-3′-phenylsulfanylcyclopent-3′-ene-1′-spiro-2-(3-methylbicyclo[2.2.1]hept-5-ene) (10b). According to the general procedure described for compound **10a**, the reaction of a diastereomeric mixture of **7b** (0.20 g, 0.66 mmol) with an acetonitrile solution (3 mL) of trifluoroacetic anhydride (0.08 mL, 0.60 mmol) gave a crude product of a 34:44:13:9 mixture of isomers of **10b**. It was purified by preparative thin-layer chromatography (silica gel, 5–10% ethyl acetate in hexanes) to give three fractions (PLC_1, PLC_2, and PLC_3) of **10b** (0.138 g, 74% combined yield). A mixture of *endo*,*endo*- and *endo*,*exo*-isomers (A- and B-isomers) and *exo*,*exo*- and *exo*,*endo*-isomers (C- and D-isomers) of **10b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60–7.20 (m, 20H, Ar*H*), 6.95 (t, *J*=3.0 Hz, 1H, C*H*=CSAr of B-isomer), 6.92–6.85 (m, 3H, C*H*=CSAr of A-, C-, and D-isomers), 6.42 (dd, *J*=5.6, 3.0 Hz, 2H, C*H*=CH of B- and D-isomers), 6.37–6.19 (m, 4H, C*H*=C*H* of A- and C-isomers), 6.12 (m, 1H, CH=C*H* of D-isomer), 5.90 (dd, *J*=5.6, 2.8 Hz, 1H, CH=C*H* of B-isomer), 2.81 (dd, *J*=18.8, 2.8 Hz, 1H, C*H*HCH=CSAr of B-isomer), 2.86–1.92 [m, 19H, (CH_2CH=CSAr, C*H*CH=CHC*H*, and C*H*CH_3) of A-isomer, (CH*H*CH=CSAr and C*H*CH=CHC*H*) of B-isomer, (CH_2CH=CSAr, C*H*CH=CHC*H*, C*H*CH_3, and C*H*H) of C-isomer and (CH_2CH=CSAr, C*H*CH=CHC*H*, and C*H*CH_3) of D-isomer], 1.87 (q, *J*=7.5 Hz, 1H, C*H*CH_3 of B-isomer), 1.70–1.20 (m, 7H, CH_2 of A-, B-, and D-isomers and CH*H* of C-isomer), 1.04 (d, *J*=7.5 Hz, 3H, CHC*H*$_3$ of B-isomer), 0.94 (d, *J*=7.8 Hz, 3H, CHC*H*$_3$ of D-isomer), 0.85 (d, *J*=7.2 Hz, 3H, CHC*H*$_3$ of A-isomer), 0.76 (d, *J*=7.2 Hz, 3H, CHC*H*$_3$ of C-isomer).

exo,exo-**10b**(C) *exo,endo*-**10b**(D)

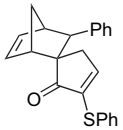
PLC_1 (less polar) was obtained as a yellow liquid of a 1.5:1 mixture of *exo*,*exo*- and *exo*,*endo*-diastereomers (C- and D-isomers) (37 mg, 20% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45–7.20 (m, 10H, Ar*H* of C- and D-isomers), 6.84 (t, *J*=3.0 Hz, 1H, C*H*=CSAr of C-isomer), 6.80 (t, *J*=3.0 Hz, 1H, C*H*=CSAr of D-isomer), 6.34 (dd, *J*=5.6, 3.1 Hz, 1H, C*H*=CH of D-isomer), 6.26 (dd, *J*=5.4, 3.0 Hz, 1H, C*H*=CH of C-isomer), 6.14 (dd, *J*=5.4, 3.1 Hz, 1H, CH=C*H* of C-isomer), 6.04 (dd, *J*=5.6, 2.9 Hz, 1H, CH=C*H* of D-isomer), 2.72–2.61 (m, 4H, C*H*CH=CHC*H* of C- and D-isomers), 2.49–2.28 (m, 4H, C*H*HCH=CSAr and C*H*CH_3 of C- and D-isomers), 2.28–2.17 (m, 2H, C*H*H of C-isomer and CH*H*CH=CSAr of D-isomer), 2.08 (dd, *J*=19.5, 3.1 Hz, 1H, CH*H*CH=CSAr of C-isomer), 1.56 (d, *J*=7.3 Hz, 1H, C*H*H of D-isomer), 1.31 (d, *J*=7.3 Hz, 1H, CH*H* of D-isomer), 1.24 (d, *J*=8.6 Hz, 1H, CH*H* of C-isomer), 0.96 (d, *J*=7.2 Hz, 3H, CHC*H*$_3$ of D-isomer), 0.66 (d, *J*=7.2 Hz, 3H, CHC*H*$_3$ of C-isomer). IR ($CHCl_3$): ν_{max} 3064w, 2966m, 1695s, 1630w, 1583w, 1477m, 1441m, 1374m, 1302w, 1261m, 1087w, 1024w, 691m cm^{-1}. MS: *m*/*z* (%) relative intensity 282 (M^+, 44), 218 (16), 217 (100), 216 (22), 188 (12), 173 (15), 111 (10), 110 (18), 91 (6), 79 (8), 77 (7), 66 (6), 65 (6).

PLC_2 (more polar) was obtained as a yellow solid of *endo*,*endo*-**10b** (A-isomer) (53 mg, 28% yield, mp 65–66 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46–7.20 (m, 5H, Ar*H*), 6.82 (t, *J*=2.9 Hz, 1H, C*H*=CSAr), 6.27–6.15 (m, 2H, C*H*=C*H*), 2.75 (dd, *J*=19.0, 2.9 Hz, 1H, C*H*HCH=CSAr), 2.68–2.56 (m, 2H, C*H*CH=CHCH and CH*H*CH=CSAr), 2.54 (br s, 1H, CHCH=CHC*H*), 2.30 (dq, *J*=7.1, 3.2 Hz, 1H, C*H*CH_3), 1.45 (m, 2H, CH_2), 0.77 (d, *J*=7.1 Hz, 3H, CHC*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 204.8 (C=O), 152.0 (CH), 142.3 (C), 135.7 (CH), 135.2 (CH), 133.5 (2×CH), 131.3 (C), 129.3 (2×CH), 128.3 (CH), 57.2 (C), 55.2 (CH), 50.0 (CH), 49.1 (CH_2), 49.0 (CH), 47.3 (CH_2), 16.3 (CH_3). IR (neat): ν_{max} 3061m, 2961s, 1699s, 1622s, 1583m, 1477m, 1440m, 1373m,

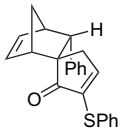
1299m, 1146m, 1024m, 990m, 743m, 692m cm^{-1}. MS: *m*/*z* (%) relative intensity 282 (M^+, 100), 249 (13), 232 (15), 218 (15), 217 (75), 216 (59), 188 (32), 183 (23), 173 (40), 111 (26), 110 (63), 91 (22), 79 (16), 77 (25), 66 (18), 65 (14).

PLC_3 (most polar) was obtained as a yellow solid of *endo*,*exo*-**10b** (B-isomer) (49 mg, 26% yield, mp 86–87 °C). ^1H NMR (300 MHz, $CDCl_3$): δ 7.50–7.28 (m, 5H, Ar*H*), 6.96 (t, *J*=3.0 Hz, 1H, C*H*=CSAr), 6.41 (dd, *J*=5.5, 3.0 Hz, 1H, C*H*=CH), 5.89 (dd, *J*=5.5, 2.8 Hz, 1H, CH=C*H*), 2.90 (dd, *J*=18.9, 2.7 Hz, 1H, C*H*HCH=CSAr), 2.52 (br s, 2H, C*H*CH=CHC*H*), 2.28 (dd, *J*=18.9, 3.2 Hz, 1H, C*H*HCH=CSAr), 1.87 (dq, *J*=7.3, 1.6 Hz, 1H, C*H*CH_3), 1.58 (d, *J*=8.7 Hz, 1H, C*H*H), 1.46 (dd, *J*=8.7, 1.6 Hz, 1H, CH*H*), 1.03 (d, *J*=7.3 Hz, 3H, CHCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 206.5 (C=O), 152.5 (CH), 141.2 (C), 139.1 (CH), 133.1 (2×CH), 131.8 (CH), 131.4 (C), 129.3 (2×CH), 128.3 (CH), 56.8 (C), 56.6 (CH), 51.0 (CH), 47.3 (CH_2), 41.6 (CH), 39.5 (CH_2), 18.7 (CH_3). IR (Nujol): ν_{max} 3056w, 1695s, 1577m, 1456s, 1279m, 1020w, 1000w, 833m, 758m, 733m, 697m cm^{-1}. MS: *m*/*z* (%) relative intensity 282 (M^+, 100), 249 (9), 218 (17), 217 (94), 216 (48), 188 (21), 173 (30), 112 (21), 110 (28), 91 (11), 80 (11), 77 (11), 66 (9), 65 (7). HRMS (ESI-TOF) calcd for $C_{18}H_{18}OSNa$: 305.0976; found: 305.0976.

4.7.3. 2′-Oxo-3′-phenylsulfanylcyclopent-3′-ene-1′-spiro-2-(3-phenylbicyclo[2.2.1]hept-5-ene) (10c). According to the general procedure described for compound **10a**, the reaction of a diastereomeric mixture of **7c** (0.281 g, 0.78 mmol) with an acetonitrile solution (4 mL) of trifluoroacetic anhydride (0.10 mL, 0.78 mmol) gave a 78:22 mixture of *endo*,*exo*- and *endo*,*endo*-isomers of **10c**. The mixture of isomers was separated by preparative thin-layer chromatography (silica gel, 5–10% ethyl acetate in hexanes) to give two fractions (PLC_1 and PLC_2) of **10c** (0.208 g, 78% combined yield). A mixture of *endo*,*exo*- and *endo*,*endo*-**10c**: ^1H NMR (300 MHz, $CDCl_3$): δ 7.44–6.90 [m, 21H, (Ar*H* and SAr*H*) of *endo*,*exo*-isomer and (Ar*H*, C*H*=CSAr, and SAr*H*) of *endo*,*endo*-isomer], 6.72 (t, *J*=3.0 Hz, 1H, C*H*=CSAr of *endo*,*exo*-isomer), 6.54–6.45 (m, 2H, C*H*=CH of *endo*,*exo*- and *endo*,*endo*-isomers), 6.21 (dd, *J*=5.6, 3.1 Hz, 1H, CH=C*H* of *endo*,*endo*-isomer), 6.04 (dd, *J*=5.5, 2.8 Hz, 1H, CH=C*H* of *endo*,*exo*-isomer), 3.68 (d, *J*=3.0 Hz, 1H, C*H*Ar of *endo*,*endo*-isomer), 3.18 (br s, 1H, C*H*CH=CHCH of *endo*,*endo*-isomer), 3.15–2.99 [m, 3H, (C*H*Ar and C*H*CH=CHCH) of *endo*,*exo*-isomer and C*H*HCH=CSAr of *endo*,*endo*-isomer), 2.85 (dd, *J*=19.1, 3.2 Hz, 1H, CH*H*CH=CSAr of *endo*,*endo*-isomer), 2.63 (br s, 2H, CHCH=CHC*H* of *endo*,*exo*- and *endo*,*endo*-isomers), 2.15–1.94 (2dd, *J*=20.3, 2.8 Hz, 2H, CH_2CH=CSAr of *endo*,*exo*-isomer), 1.85 (d, AB system, *J*=8.6 Hz, 1H, C*H*H of *endo*,*exo*-isomer), 1.68 (d, *J*=8.7 Hz, 2H, CH*H* of *endo*,*exo*- and *endo*,*endo*-isomers), 1.59 (d, *J*=8.6 Hz, 1H, CH*H* of *endo*,*endo*-isomer).



endo,*exo*-**10c**

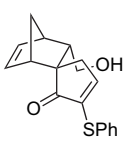


endo,*endo*-**10c**

PLC_1 (less polar) was obtained as a yellow solid of *endo*,*exo*-**10c** (0.154 g, 57% yield, mp 95–98 °C). ^1H NMR (300 MHz, $CDCl_3$): δ 7.42–6.90 (m, 10H, Ar*H* and SAr*H*), 6.73 (t, *J*=3.0 Hz, 1H, C*H*=CSAr), 6.49 (dd, *J*=5.5, 3.3 Hz, 1H, C*H*=CH), 6.05 (dd, *J*=5.5, 2.8 Hz, 1H, CH=C*H*), 3.08 (br s, 1H, C*H*CH=CHCH), 3.02 (s, 1H, C*H*Ar), 2.64 (br s, 1H, CHCH=CHC*H*), 2.15–1.98 (2dd, *J*=20.7, 2.7 Hz, 2H, CH_2CH=CSAr), 1.85 (d, *J*=8.6 Hz, 1H, C*H*H), 1.66 (dd, *J*=8.6, 1.6 Hz, 1H, CH*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 206.2 (C=O), 153.7 (CH), 142.3 (C), 141.0 (C), 139.7 (CH), 133.6 (CH), 133.1 (2×CH), 131.4 (C), 129.3 (2×CH), 128.6 (2×CH), 128.3 (CH), 127.7 (2×CH), 126.3 (CH), 58.2 (C), 55.4 (CH), 54.1 (CH), 49.4 (CH_2), 48.4 (CHAr), 40.9 (CH_2). IR (Nujol): ν_{max} 3055w, 1695s, 1580m, 1456s, 1274m, 1023m, 1005w, 839m, 751m, 734m, 702m cm^{-1}. MS: *m*/*z* (%) relative intensity 344 (M^+, 31), 279 (15), 278 (52), 277 (27), 173 (15), 170 (19), 169 (100), 142 (14), 141 (47), 129 (9), 116 (14), 115 (25), 91 (10), 65 (4).

PLC_2 (more polar) was obtained as a pale yellow solid of *endo*,*endo*-**10c** (54 mg, 20% yield, mp 118–120 °C). ^1H NMR (300 MHz, $CDCl_3$): δ 7.32–6.95 (m, 11H, Ar*H*, SAr*H* and C*H*=CSAr), 6.57 (dd, *J*=5.3, 2.9 Hz, 1H, C*H*=CH), 6.28 (dd, *J*=5.3, 3.2 Hz, 1H, CH=C*H*), 3.74 (d, *J*=2.5 Hz, 1H, C*H*Ar), 3.26 (br s, 1H, C*H*CH=CHCH), 3.16 (dd, *J*=19.1, 2.8 Hz, 1H, C*H*HCH=CSAr), 2.91 (dd, *J*=19.1, 3.1 Hz, 1H, CH*H*CH=CSAr), 2.64 (br s, 1H, CHCH=CHC*H*), 1.74 (d, *J*=8.5 Hz, 1H, C*H*H), 1.65 (d, *J*=8.5 Hz, 1H, CH*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 203.0 (C=O), 151.8 (CH), 142.5 (C), 140.4 (C), 135.8 (CH), 135.3 (CH), 132.7 (2×CH), 131.5 (C), 129.2 (2×CH), 128.6 (2×CH), 127.9 (CH), 127.8 (2×CH), 126.1 (CH), 61.3 (CH), 59.6 (C), 55.5 (CH), 49.9 (CH_2), 48.1 (CHAr), 47.7 (CH_2). IR (neat): ν_{max} 3060s, 3025s, 2959s, 2247w, 2053w, 1952w, 1885w, 1714s, 1695s, 1682s, 1582s, 1496s, 1479s, 1441s, 1339s, 1277s, 1190m, 1147m, 1024m, 911m, 741s, 701s cm^{-1}. MS: *m*/*z* (%) relative intensity 344 (M^+, 2), 280 (6), 279 (21), 278 (75), 173 (14), 170 (19), 169 (100), 142 (14), 141 (40), 129 (9), 116 (11), 115 (25), 91 (10), 65 (5). Anal. Calcd for $C_{23}H_{20}OS$: C, 80.20; H, 5.85. Found: C, 79.97; H, 5.71.

4.7.4. 2′-Oxo-3′-phenylsulfanylcyclopent-3′-ene-1′-spiro-2-(3-hydroxymethyl)bicyclo[2.2.1]hept-5-ene (10d). According to the general procedure described for compound **10a**, the reaction of a mixture of **7dA** and **7dB** (0.316 g, 1 mmol) with an acetonitrile solution (5 mL) of trifluoroacetic anhydride (0.13 mL, 1 mmol) gave a crude product, which was purified by preparative thin-layer chromatography (silica gel, 5–10% ethyl acetate in hexanes) to give a pure white solid of **10d** (0.232 g, 78% yield, mp 150–152 °C).



^1H NMR (400 MHz, $CDCl_3$): δ 7.58–7.33 (m, 5H, Ar*H*), 7.00 (t, *J*=3.0 Hz, 1H, C*H*=CSAr), 6.33 (dd, *J*=5.6, 3.2 Hz, 1H, C*H*=CH), 6.18 (dd, *J*=5.6, 2.8 Hz, 1H, CH=C*H*), 3.60 (m, 2H, CHCH_2OH), 2.96–2.92 (m, 2H,

C*H*CH=CHCH, and C*H*HCH=CSAr), 2.75 (dd, *J*=18.8, 3.2 Hz, 1H, CH*H*CH=CSAr), 2.64 (br s, 1H, CHCH=CHC*H*), 2.56 (ddd, *J*=9.2, 5.5, 3.1 Hz, 1H, C*H*CH_2OH), 2.05 (br s, 1H, O*H*), 1.63–1.56 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.6 (C=O), 153.5 (CH), 142.3 (C), 136.5 (CH), 135.2 (CH), 133.8 (2×CH), 132.0 (C), 130.0 (2×CH), 129.0 (CH), 63.4 (CH_2), 58.7 (CH), 56.9 (C), 56.0 (CH), 50.1 (CH_2), 47.9 (CH_2), 46.4 (CH). IR ($CHCl_3$): ν_{max} 3456m, 3026s, 3013s, 2971s, 1695s, 1583m, 1476m, 1441m, 1339m, 1305m, 1281m, 1025s, 833s, 692m cm^{-1}. MS: *m*/*z* (%) relative intensity 298 (M^+, 8), 268 (32), 267 (25), 203 (17), 190 (30), 186 (18), 171 (23), 158 (100), 157 (58), 147 (10), 144 (14), 130 (18), 129 (54), 128 (33), 115 (19), 110 (16), 105 (9), 91 (16), 77 (15), 66 (17), 65 (18). HRMS (ESI-TOF) calcd for $C_{18}H_{18}O_2SNa$: 321.0925; found: 321.0927.

4.8. Flash vacuum pyrolysis of compounds 10 leading to cyclopentenones 11

4.8.1. 5-Methylidene-2-phenylsulfanyl-2-cyclopentenone (11a). Flash vacuum pyrolysis of a 87:13 mixture of *endo*- and *exo*-**10a** (51 mg, 0.19 mmol) gave a crude pyrolysate, which was purified by preparative thin-layer chromatography (silica gel, 5–7% ethyl acetate in hexanes) to give a pale yellow solid of **11a** (39 mg, 93% yield, mp 76–78 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60–7.30 (m, 5H, Ar*H*), 6.85 (dt, *J*=2.9, 0.9 Hz, 1H, C*H*=CSAr), 6.18 (m, *J*=0.9 Hz, 1H, C*H*H=CCO), 5.49 (app. d, *J*=0.9 Hz, 1H, CH*H*=CCO), 3.20 (td, *J*=2.8, 1.5 Hz, 2H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.5 (C=O), 148.2 (CH), 145.0 (C), 140.6 (C), 133.9 (2×CH), 130.5 (C), 129.5 (2×CH), 128.7 (CH), 118.6 (CH_2), 32.9 (CH_2). IR (Nujol): ν_{max} 2727w, 1699s, 1646m, 1581m, 1307m, 1282m, 1024m, 838w, 742s, 691s cm^{-1}. MS: *m*/*z* (%) relative intensity 204 (M^++2, 8), 203 (M^++1, 28), 202 (M^+, 100), 201 (18), 174 (25), 173 (48), 141 (11), 129 (11), 97 (42), 65 (12). HRMS (ESI-TOF) calcd for $C_{12}H_{11}OS$: 203.0531; found: 203.0531.

4.8.2. 5-Ethylidene-2-phenylsulfanyl-2-cyclopentenone (11b). Flash vacuum pyrolysis of a pure diastereomer of **10b** obtained from PLC_3 (47.4 mg, 0.168 mmol) gave a crude pyrolysate, which was purified by preparative thin-layer chromatography (silica gel, 5–7% ethyl acetate in hexanes) to give a pale yellow solid of (*E*)-isomer of **11b** (45.4 mg, 96% yield, mp 66–68 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60–7.30 (m, 5H, Ar*H*), 6.80–6.65 (m, 2H, C*H*=CSAr and C=C*H*CH_3), 3.13 (br s, 2H, CH_2), 1.90 (d, *J*=7.1 Hz, 3H, C=CHC*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.3 (C=O), 146.8 (CH), 144.9 (C), 134.9 (C), 133.7 and 133.7 (2×CH), 132.4 and 132.3 (CH), 131.0 and 130.9 (C), 129.5 and 129.4 (2×CH), 128.53 and 128.49 (CH), 30.9 (CH_2), 15.1 and 15.0 (CH_3). IR (neat): ν_{max} 2925m, 1696s, 1658s, 1651s, 1475w, 1440m, 1378m, 1263m, 1087w, 1024m, 865m, 740m, 690m cm^{-1}. MS: *m*/*z* (%) relative intensity 218 (M^++2, 18), 217 (M^++1, 36), 216 (M^+, 100), 188 (34), 183 (23), 173 (47), 155 (16), 149 (15), 111 (31), 110 (74), 79 (18), 78 (17), 77 (43), 66 (14), 65 (15). HRMS (ESI-TOF) calcd for $C_{13}H_{13}OS$: 217.0687; found: 217.0687.

4.8.3. 5-Phenylidene-2-phenylsulfanyl-2-cyclopentenone (11c). Flash vacuum pyrolysis of a 78:22 mixture of *endo*,*exo*- and *endo*,*endo*-**10c** (100 mg, 0.29 mmol) gave a 86:14 mixture of (*E*)- and (*Z*)-**11c**. The crude product was purified by preparative thin-layer chromatography (silica gel, 5–7% ethyl acetate in hexanes) to give a pale yellow solid of (*E*)-**11c** (60 mg, 76% yield, mp 104–105 °C). A mixture of (*E*)- and (*Z*)-**11c** of the crude product: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55–7.00 (m, 22H, Ar*H*, SAr*H* and C=C*H*Ar of *E*- and *Z*-isomers), 6.78 (app. t, *J*=2.6 Hz, 1H, ArSC=C*H* of *E*-isomer), 6.69 (app. s, 1H, ArSC=C*H* of *Z*-isomer), 3.44 (m, 2H, CH_2 of *E*- and *Z*-isomers).

(*E*)-**11c**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50–7.17 (m, 11H, Ar*H*, SAr*H* and C=C*H*Ar), 6.75 (m, 1H, C*H*=CSAr), 3.39 (app. t, *J*=2.2 Hz, 2H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.5 (C=O), 146.9 (CH), 144.6 (C), 134.9 (C), 133.8 (2×CH), 133.1 (CH), 131.9 (CH), 130.6 (C), 130.5 (2×CH), 129.7 (CH), 129.5 (2×CH), 128.9 (2×CH), 128.6 (CH), 33.4 (CH_2). IR (Nujol): ν_{max} 1687m, 1637m, 1568w, 1449m, 1285m, 1181m, 916m, 771m, 758m, 747m, 690m cm^{-1}. MS: *m*/*z* (%) relative intensity 280 (M^++2, 35), 279 (M^++1, 23), 278 (M^+, 100), 277 (17), 250 (9), 234 (13), 218 (15), 178 (27), 173 (33), 171 (38), 169 (78), 167 (17), 149 (15), 110 (15). HRMS (ESI-TOF) calcd for $C_{18}H_{14}OSNa$: 301.0663; found: 301.0663.

4.8.4. 5-(Hydroxymethyl)methylidene-2-phenylsulfanyl-2-cyclopentenone (11d). Flash vacuum pyrolysis of **10d** (100 mg, 0.29 mmol) (conditions: oven temperature 240 °C, column temperature 425 °C, pressure 0.05 mmHg) gave a crude pyrolysate, which was purified by preparative thin-layer chromatography (silica gel, 15% ethyl acetate in hexanes) to give a pale yellow liquid of (*Z*)-**11d** (13.5 mg, 20% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52–7.25 (m, 5H, Ar*H*), 6.72 (s, 1H, C*H*=CSAr), 6.58 (t, *J*=6.1 Hz, 1H, C=C*H*CH_2OH), 4.71 (d, *J*=6.1 Hz, 2H, C=CHC*H*$_2$OH), 3.15 (s, 2H, CH_2), 1.60 (br s, 1H, O*H*). HRMS (ESI-TOF) calcd for $C_{13}H_{12}O_2SNa$: 255.0456; found: 255.0461.

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