Supporting Information

Rhodium(I)-Catalyzed Intramolecular Pauson-Khand-Type [2+2+1] Cycloaddition of Allenenes

Fuyuhiko Inagaki, Chisato Mukai*

Division of Pharmaceutical Sciences, Graduate School of Natural Science and Technology, Kanazawa University
Kakuma-machi, Kanazawa, 920-1192, Japan

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General Procedure for Preparation of Sulfonyllallenes 6d, 6f, and 10f.

To a solution of malonate (2.0 mmol) in THF (20 mL) was added NaH (2.0 mmol, 60% in oil) at 0 °C. After stirring for 30 min at the same temperature, a solution of 13 (2.2 mmol) in THF (20 mL) was slowly added to the mixture. The reaction mixture was further stirred for 30 min at 0 °C and quenched by addition of saturated aqueous NH₄Cl. The resulting mixture was extracted with CH₂Cl₂, which was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with hexane-AcOEt to afford the corresponding sulfonyllallenes.


General Procedure for Preparation of Sulfonyllallenes 6e, 6g, 6h, 10c, 10d, and 10e.

To a solution of alcohol (2.0 mmol) and Et₃N (6.0 mmol) in THF (20 mL) was gradually added PhSCI (3.0 mmol) at -78 °C. After stirring for 1.5 h at the same temperature, the
reaction was quenched by addition of saturated aqueous NaHCO₃, extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane-AcOEt to afford the crude sulfoxide. To a solution of the crude sulfoxide in CH₂Cl₂ (20 mL) was added mCPBA (2.2 mmol) at 0 °C. After stirring for 30 min, the reaction was quenched by addition of saturated aqueous Na₂S₂O₅ and NaHCO₃, and the mixture was extracted with CH₂Cl₂. The extract was washed with brine, dried, and concentrated to dryness. The residue was chromatographed with hexane-AcOEt to afford the corresponding sulfonyllallenes.


**Dimethyl 2-(4-methoxy-2-methylenebutyl)-2-[2-(phenylsulfonyl)buta-2,3-dienyl]malonate (6d).**

Compound 6d was a colorless oil; IR 1973, 1936, 1735, 1308, 1153 cm⁻¹; ¹H NMR δ 7.89-7.88 (m, 2H), 7.65-7.62 (m, 1H), 7.56-7.53 (m, 2H), 5.39 (t, 2H, J = 3.6 Hz), 4.80 (d, 1H, J = 1.2 Hz), 4.65 (d, 1H, J = 1.2 Hz), 3.63 (s, 6H), 3.38 (t, 2H, J = 6.8 Hz), 3.30 (s, 3H), 2.94 (t, 2H, J = 3.6 Hz), 2.76 (s, 2H), 2.07 (t, 2H, J = 6.8 Hz); ¹³C NMR δ 207.7, 170.2, 140.8, 139.9, 133.5, 129.1, 128.2, 116.4, 109.4, 86.0, 71.0, 58.5, 56.2, 52.6, 37.9, 36.2, 28.5; MS m/z 422 (M⁺, 0.2). HRMS calcd for C₁₁H₁₅O₃S 422.1399, found 422.1401.

**N-(2-Methyl-2-propenyl)-N-[2-(phenylsulfonyl)-2,3-butenadienyl]-4-methylbenzene)sulfonamide (6e).**

Compound 6e was a colorless oil; IR 1977, 1934, 1325, 1308, 1155 cm⁻¹; ¹H NMR δ 7.85 (d, 2H, J = 7.6 Hz), 7.66 (t, 1H, J = 7.6 Hz), 7.55 (t, 2H, J = 7.6 Hz), 7.50 (d, 2H, J
\[ \text{Dimethyl } 2\text{-}(2\text{-phenyl-2-propenyl})\text{-}2\text{-}[2\text{-}(phenylsulfonyl)buta-2,3-dienyl]malonate (6f).} \]

Compound 6f was a colorless plate, mp 100-101 °C (AcOEt); IR 1973, 1938, 1736, 1308, 1153 cm\(^{-1}\); \(^1\)H NMR \(\delta\) 7.89-7.86 (m, 2H), 7.68-7.52 (m, 3H), 7.28-7.17 (m, 5H), 5.43 (t, 2H, \(J = \) 3.8 Hz), 5.09 (d, 1H, \(J = \) 1.5 Hz), 4.91 (d, 1H, \(J = \) 1.5 Hz), 3.31 (s, 6H), 3.23 (s, 2H), 2.86 (t, 2H, \(J = \) 3.8 Hz); \(^{13}\)C NMR \(\delta\) 207.2, 169.6, 143.4, 140.6, 139.8, 133.5, 129.1, 128.2, 128.0, 127.5, 126.7, 118.9, 109.4, 86.2, 55.6, 52.3, 37.0, 27.5; MS \(m/z\) 440 (M\(^+\), 0.3). HRMS calcd for C\(_{23}\)H\(_{22}\)O\(_6\)S 440.1294, found 440.1295. Anal. Calcd for C\(_{23}\)H\(_{22}\)O\(_6\)S: C, 65.44; H, 5.49. Found: C, 65.32; H, 5.52.

\[ \text{Dimethyl } 2\text{-}[2\text{-}(phenylsulfonyl)penta-2,3-dienyl]-2\text{-}(2-propenyl)malonate (6g).} \]

Compound 6g was a colorless needle, mp 52-53.5 °C (AcOEt); IR 1961, 1734, 1306, 1151 cm\(^{-1}\); \(^1\)H NMR \(\delta\) 7.84 (d, 2H, \(J = \) 7.3 Hz), 7.59 (t, 1H, \(J = \) 7.3 Hz), 7.51 (t, 2H, \(J = \) 7.3 Hz), 5.70 (tq, 1H, \(J = \) 2.9, 7.3 Hz), 5.51 (ddt, 1H, \(J = \) 15.9, 8.8, 7.3 Hz), 4.94 (d, 1H, \(J = \) 8.8 Hz), 4.92 (d, 1H, \(J = \) 15.9 Hz), 3.61 (s, 6H), 2.88 (d, 2H, \(J = \) 2.9 Hz), 2.65-2.57 (m, 2H), 1.67 (d, 3H, \(J = \) 7.3 Hz); \(^{13}\)C NMR \(\delta\) 204.6, 170.0, 169.9, 139.9, 133.3, 131.6, 129.0, 128.0, 119.4, 108.4, 97.7, 56.8, 52.5, 52.4, 36.2, 28.6, 13.4; MS \(m/z\) 378 (M\(^+\), 1.6). HRMS calcd for C\(_{16}\)H\(_{22}\)O\(_6\)S 378.1137, found 378.1139. Anal. Calcd for C\(_{16}\)H\(_{22}\)O\(_6\)S: C, 60.30; H, 5.86. Found: C, 59.92; H, 5.87.

\[ \text{Dimethyl } 2\text{-}[4\text{-methyl-2-(phenylsulfonyl)penta-2,3-dienyl]-2-(2-propenyl)malonate (6h).} \]

Compound 6h was a colorless plate, mp 95-95.5 °C (AcOEt); IR 1963, 1733, 1306,
1150 cm⁻¹; ¹H NMR δ 7.85-7.84 (m, 2H), 7.61-7.58 (m, 1H), 7.53-7.50 (m, 2H), 5.52 (ddt, 1H, J = 17.0, 10.2, 7.3 Hz), 4.95 (d, 1H, J = 10.2 Hz), 4.92 (d, 1H, J = 17.0 Hz), 3.63 (s, 6H), 2.92 (s, 2H), 2.60 (d, 1H, J = 7.3 Hz), 1.68 (s, 6H); ¹³C NMR δ 201.8, 170.1, 140.2, 133.2, 131.8, 129.0, 128.0, 119.4, 108.9, 106.7, 56.8, 52.5, 36.2, 28.7, 19.7; MS m/z 392 (M⁺, 2.6). HRMS calcd for C₂₅H₂₄O₆S 392.1294, found 392.1290. Anal. Calcd for C₂₅H₂₄O₆S: C, 61.21; H, 6.16. Found: C, 61.25; H, 6.16.

3-(Phenylsulfonyl)nona-1,2,8-triene (10c).
Compound 10c was a colorless oil; IR 1971, 1944, 1309, 1147 cm⁻¹; ¹H NMR δ 7.85-7.83 (m, 2H), 7.59-7.55 (m, 1H), 7.50-7.47 (m, 2H), 5.71-5.62 (m, 1H), 5.32-5.30 (m, 2H), 4.91-4.83 (m, 2H), 2.21-2.16 (m, 2H), 1.95-1.90 (m, 2H), 1.42-1.27 (m, 4H); ¹³C NMR δ 207.5, 140.0, 138.1, 133.2, 128.8, 127.8, 114.4, 113.0, 84.1, 33.0, 27.7, 26.5, 26.2; MS m/z 262 (M⁺, 2.0). HRMS calcd for C₁₅H₁₆O₈S 262.1028, found 262.1021.

N-(2-Propenyl)-N-[3-(phenylsulfonyl)-3,4-pentadienyl]-(4-methylbenzene)sulfonamide (10d).
Compound 10d was a colorless needle, mp 67.5-68.5 °C (Et₂O); IR 1969, 1936, 1321, 1308, 1155 cm⁻¹; ¹H NMR δ 7.90-7.87 (m, 2H), 7.66-7.53 (m, 5H), 7.30-7.27 (m, 2H), 5.64-5.50 (m, 1H), 5.39-5.38 (m, 2H), 5.17-5.10 (m, 2H), 3.75 (d, 2H, J = 6.2 Hz), 3.28-3.22 (m, 2H), 2.52-2.45 (m, 2H), 2.42 (s, 3H); ¹³C NMR δ 207.8, 143.2, 139.4, 136.3, 133.5, 132.6, 129.5, 129.0, 127.9, 126.8, 119.1, 109.5, 84.5, 50.8, 45.5, 26.1, 21.2; MS m/z 417 (M⁺, 0.2). Anal. Calcd for C₂₁H₂₁NO₄S₂: C, 60.41; H, 5.55; N, 3.35. Found: C, 60.19; H, 5.60; N, 3.38.

3-(Phenylsulfonyl)-5-(2-propenloyloxy)-1,2-pentadiene (10e).
Compound 10e was a colorless oil; IR 1969, 1936, 1308, 1151 cm⁻¹; ¹H NMR δ 7.91-7.88 (m, 2H), 7.67-7.51 (m, 3H), 5.82 (ddt, 1H, J = 17.1, 10.4, 5.5 Hz), 5.39 (t, 2H, J = 3.1 Hz), 5.24-5.11 (m, 2H), 3.90-3.87 (m, 2H), 3.51 (t, 2H, J = 6.2 Hz), 2.53 (tt, 2H, J = 6.2, 3.1 Hz); ¹³C NMR δ 208.2, 140.0, 134.3, 133.4, 129.0, 128.0, 116.9, 110.0, 84.1,
71.7, 67.3, 27.3; MS m/z 264 (M⁺, 0.1). HRMS calcd for C₁₅H₁₆O₃S 264.0820, found 264.0821.

**Dimethyl 2-(3-methyl-3-butenyl)-2-[2-(phenylsulfonyl)buta-2,3-dienyl]malonate (10f).**

Compound 10f was a colorless oil; IR 1967, 1936, 1734, 1308, 1153 cm⁻¹; ¹H NMR δ 7.85-7.83 (m, 2H), 7.61-7.58 (m, 1H), 7.52-7.49 (m, 2H), 5.30 (t, 2H, J = 3.2 Hz), 4.64 (s, 1H), 4.58 (s, 1H), 3.62 (s, 6H), 2.90 (t, 2H, J = 3.2 Hz), 2.03-2.00 (m, 2H), 1.76-1.72 (m, 2H), 1.62 (s, 3H); ¹³C NMR δ 208.5, 170.6, 144.5, 140.1, 133.8, 129.3, 128.4, 110.7, 109.3, 85.6, 56.8, 52.7, 32.2, 30.3, 28.8, 22.6; MS m/z 392 (M⁺, 2.0). HRMS calcd for C₂₀H₂₅O₆S 392.1294, found 392.1293.

**General Procedure for Pauson-Khand-Type [2+2+1] Cycloaddition under an atmosphere of CO.**

To a solution of the allenene (0.10 mmol) in toluene (1.0 mL) was added 2.5 mol % Rh(I) catalyst. The reaction mixture was refluxed under a CO atmosphere until the complete disappearance of the starting material (monitored by TLC). Toluene was evaporated off, and the residual oil was chromatographed with hexane-AcOEt to afford the cyclized product. Chemical yields are summarized in Table 1.

**General Procedure for Pauson-Khand-Type [2+2+1] Cycloaddition under 5~10 atm of CO.**

To a solution of the allenene (0.10 mmol) in toluene (1.0 mL) was added 2.5~10 mol % Rh(I) catalyst. The reaction mixture was heated at 120 °C (oil bath temperature) under CO pressure as shown in Table until the complete disappearance of the starting material (monitored by TLC). Toluene was evaporated off, and the residual oil was chromatographed with hexane-AcOEt to afford the cyclized product. Chemical yields are summarized in Table 1~3.
(2R*,6S*)- and (2R*,6R*)-4,4-Bis(methoxycarbonyl)-2-(phenylsulfonyl)bicyclo[4.3.0]non-1(9)-en-8-one (cis-4a and trans-4a).

A mixture of cis-4a and trans-4a in the ratio of 21 to 79 was obtained as a colorless needle, mp 144.5-146.5 °C (AcOEt); IR 1732, 1718, 1620, 1310, 1151 cm⁻¹; ¹H NMR δ 7.97-7.95 (m, 71/100 x 2H), 7.81-7.26 (m, 79/100 x 3H, 21/100 x 5H), 6.64 (s, 79/100 x 1H), 5.50 (d, 21/100 x 1H, J = 1.7 Hz), 4.39 (dd, 79/100 x 1H, J = 12.9, 4.4 Hz), 4.34 (dd, 21/100 x 1H, J = 7.6, 2.4 Hz), 3.88 (s, 21/100 x 3H), 3.74 (s, 79/100 x 3H, 21/100 x 3H), 3.72 (s, 79/100 x 3H), 3.55-3.51 (m, 21/100 x 1H), 3.36-3.32 (m, 21/100 x 1H), 2.94 (ddd, 21/100 x 1H, J = 13.5, 5.7, 1.7 Hz), 2.76-2.59 (m, 79/100 x 4H, 21/100 x 2H), 2.09 (t, 79/100 x 1H, J = 12.9 Hz), 2.02 (dd, 21/100 x 1H, J = 19.1, 2.4 Hz), 1.70 (t, 79/100 x 1H, J = 14.4 Hz), 1.45 (t, 21/100 x 1H, J = 13.5 Hz), 1.26 (t, 79/100 x 1H, J = 7.3 Hz); ¹³C NMR δ 206.02, 205.98, 179.90, 169.80, 169.70, 169.20, 167.90, 137.10, 136.20, 134.40, 135.00, 129.50, 129.20, 128.80, 128.40, 62.00, 61.10, 54.30, 53.30, 53.20, 53.10, 53.00, 52.50, 42.10, 40.40, 38.70, 37.90, 37.10, 35.20, 32.00, 27.90; MS m/z 392 (M⁺, 0.1). Anal. Calcd for C₁₉H₂₀O₃S: C, 58.15; H, 5.14. Found: C, 58.00; H, 5.26.

(2R*,6S*)- and (2R*,6R*)-2-(Phenylsulfonyl)bicyclo[4.3.0]non-1(9)-en-8-one (cis-4b and trans-4b).

A mixture of cis-4b and trans-4b in the ratio of 62 to 38 was obtained as a colorless needle, mp 122-122.5 °C (AcOEt); IR 1709, 1317, 1150 cm⁻¹; ¹H NMR δ 7.94-7.90 (m, 38/100 x 2H), 7.82-7.79 (m, 62/100 x 2H), 7.71-7.51 (m, 62/100 x 3H, 38/100 x 3H), 6.54 (s, 38/100 x 1H), 5.54 (d, 62/100 x 1H, J = 2.0 Hz), 4.20 (d, 62/100 x 1H, J = 6.3 Hz), 3.91 (dd, 38/100 x 1H, J = 12.2, 4.3 Hz), 3.41-3.32 (m, 62/100 x 1H), 2.82-2.73 (m, 62/100 x 1H), 2.66 (dd, 62/100 x 1H, J = 19.2, 6.3 Hz), 2.65-2.50 (m, 38/100 x 2H), 2.26-2.13 (m, 62/100 x 2H, 38/100 x 2H), 2.02-1.95 (m, 38/100 x 1H), 2.00 (dd, 62/100 x 2H, J = 12.6, 2.0 Hz), 1.88-1.67 (m, 62/100 x 2H, 38/100 x 2H), 1.59-1.41 (m, 38/100 x 1H), 1.24-1.08 (m, 62/100 x 1H, 38/100 x 1H); ¹³C NMR δ 207.00, 206.70, 172.40, 170.70, 137.70, 137.30, 134.20, 134.10, 133.60, 129.40, 129.20, 128.70, 128.50, 65.40, 64.00, 42.70, 42.50, 40.90, 38.90, 34.20, 33.50, 27.90, 26.00, 24.20, 21.10; MS m/z 276 (M⁺, 0.1). HRMS calcd for
C$_{15}$H$_{16}$O$_3$S 276.0820, found 276.0818. Anal. Calcd for C$_{15}$H$_{16}$O$_3$S: C, 65.19; H, 5.84. Found: C, 65.16; H, 5.92.

(2R*,6R*)- and (2R*,6S*)-N-(4-Methylbenzenesulfonyl)-2-(phenylsulfonyl)-4-azabicyclo[4.3.0]nona-1(9)-en-8-one (cis-7a and trans-7a).

A mixture of cis-7a and trans-7a in the ratio of 71 to 29 was obtained as a colorless needle, mp 188-188.5 °C (AcOEt); IR 1718, 1327, 1167, 1155 cm$^{-1}$; $^1$H NMR δ 7.97-7.93 (m, 71/100 x 2H, 29/100 x 2H), 7.78-7.56 (m, 71/100 x 5H, 29/100 x 5H), 7.34-7.32 (m, 71/100 x 2H, 29/100 x 2H), 6.58 (s, 29/100 x 1H), 6.01 (d, 71/100 x 1H, $J$ = 1.2 Hz), 4.65 (d, 71/100 x 1H, $J$ = 14.0 Hz), 4.27-4.18 (m, 71/100 x 1H, 29/100 x 3H), 4.02 (dd, 71/100 x 1H, $J$ = 11.0, 6.7 Hz), 3.19-3.18 (m, 71/100 x 1H), 3.02-3.00 (m, 29/100 x 1H), 2.81-2.76 (m, 71/100 x 1H, 29/100 x 1H), 2.58-2.50 (m, 71/100 x 1H, 29/100 x 1H), 2.45 (s, 29/100 x 3H), 2.42 (s, 71/100 x 3H), 2.19 (t, 29/100 x 1H, $J$ = 11.6 Hz), 2.08 (t, 71/100 x 1H, $J$ = 11.0 Hz), 1.94-1.90 (m, 71/100 x 1H, 29/100 x 1H);

$^{13}$C NMR δ 205.0, 204.8, 166.5, 166.3, 144.6, 144.3, 137.3, 136.9, 135.4, 134.9, 134.8, 133.4, 133.0, 130.7, 130.2, 129.9, 129.8, 129.5, 129.4, 128.4, 127.6, 127.3, 63.2, 62.6, 51.9, 51.1, 46.2, 45.2, 40.9, 38.8, 38.2, 37.2, 21.5, 21.1; MS m/z 431 (M$^+$, 0.1). Anal. Calcd for C$_{21}$H$_{25}$NO$_5$S$_2$: C, 58.45; H, 4.91; N, 3.25. Found: C, 58.55; H, 5.00; N, 3.32.

(2R*,6R*)- and (2R*,6S*)-2-(Phenylsulfonyl)-4-oxabicyclo[4.3.0]nona-1(9)-en-8-one (cis-7b and trans-7b).

A mixture of cis-7b and trans-7b in the ratio of 82 to 18 was obtained as a colorless oil; IR 1713, 1325, 1153 cm$^{-1}$; $^1$H NMR δ 7.94 (d, 38/100 x 2H, $J$ = 7.6 Hz), 7.87 (d, 62/100 x 2H, $J$ = 7.3 Hz), 7.75-7.57 (m, 62/100 x 3H, 38/100 x 3H), 6.65 (s, 38/100 x 1H), 5.81 (d, 62/100 x 1H, $J$ = 1.7 Hz), 4.92 (d, 62/100 x 1H, $J$ = 12.7 Hz), 4.32 (dd, 62/100 x 1H, $J$ = 10.5, 6.8 Hz), 4.27-4.21 (m, 38/100 x 3H), 4.14-4.10 (m, 62/100 x 1H), 3.72 (dd, 62/100 x 1H, $J$ = 12.7, 3.9 Hz), 3.64 (t, 38/100 x 1H, $J$ = 9.5 Hz), 3.50-3.45 (m, 62/100 x 1H), 3.13-3.08 (m, 62/100 x 1H, 38/100 x 1H), 2.99-2.97 (m, 38/100 x 1H), 2.53 (dd, 62/100 x 1H, $J$ = 19.3, 6.8 Hz), 2.47 (dd, 38/100 x 1H, $J$ = 18.8, 6.8 Hz), 1.93-1.88 (m,
62/100 x 1H, 38/100 x 1H); 13C NMR δ 205.5, 205.4, 168.2, 167.2, 137.8, 137.4, 134.6, 134.5, 133.7, 129.7, 129.6, 129.4, 128.8, 128.5, 73.5, 73.3, 67.6, 66.2, 64.6, 63.9, 42.0, 38.6, 37.4, 35.8; MS m/z 278 (M+, 3.8). HRMS calcd for C_{14}H_{14}O_2S 278.0613, found 278.0615.

(2R*,6R*)-4,4-Bis(methoxycarbonyl)-6-methyl-2-(phenylsulfonyl)bicyclo[4.3.0]non-1(9)-en-8-one (trans-7c).

Compound 7c was a colorless plate, mp 191-193 °C (AcOEt); IR 1735, 1720, 1620, 1310, 1150 cm⁻¹; 1H NMR δ 8.00-7.96 (m, 2H), 7.77-7.62 (m, 3H), 6.61 (d, 1H, J = 1.5 Hz), 4.54 (ddd, 1H, J = 13.0, 3.4, 1.5 Hz), 3.72 (s, 3H), 3.69 (s, 3H), 2.73-2.63 (m, 2H), 2.31 (s, 2H), 2.12 (d, 1H, J = 14.3 Hz), 1.96 (t, 1H, J = 13.0 Hz), 1.10 (s, 3H); 13C NMR δ 205.0, 171.6, 171.2, 169.9, 137.5, 134.4, 129.5, 129.3, 128.5, 58.7, 53.4, 52.96, 52.93, 51.8, 44.0, 43.2, 33.0, 24.8; MS m/z 406 (M+, 1.1). Anal. Calcd for C_{20}H_{22}O_2S: C, 59.10; H, 5.46. Found: C, 58.89; H, 5.39.

(2R*,6S*)-4,4-Bis(methoxycarbonyl)-6-(2-methoxyethyl)-2-(phenylsulfonyl)bicyclo[4.3.0]non-1(9)-en-8-one (trans-7d)

Compound 7d was a colorless oil; IR 1732, 1695, 1310, 1151 cm⁻¹; 1H NMR δ 7.97 (d, 2H, J = 7.3 Hz), 7.71 (t, 1H, J = 7.3 Hz), 7.63 (d, 2H, J = 7.3 Hz), 6.63 (s, 1H), 4.58 (dd, 1H, J = 12.8, 3.7 Hz), 3.72 (s, 3H), 3.69 (s, 3H), 3.24-3.19 (m, 1H), 3.05 (s, 3H), 3.00-2.96 (m, 1H), 2.79 (ddd, 1H, J = 12.8, 3.7, 1.8 Hz), 2.72 (dd, 1H, J = 14.6, 1.8 Hz), 2.49 (d, 1H, J = 18.3 Hz), 2.18 (d, 1H, J = 18.3 Hz), 2.11 (d, 1H, J = 14.6 Hz), 1.97 (t, 1H, J = 12.8 Hz), 1.66-1.56 (m, 2H); 13C NMR δ 205.1, 171.5, 171.3, 170.0, 137.8, 134.3, 129.8, 129.4, 128.5, 68.4, 59.0, 58.7, 53.4, 53.1, 52.8, 49.1, 46.5, 42.9, 35.4, 32.9; MS m/z 450 (M+, 0.2). HRMS calcd for C_{22}H_{26}O_2S 450.1348, found 450.1352.

(2R*,6S*)-6-Methyl-N-(4-methylbenzenesulfonyl)-2-(phenylsulfonyl)-4-azabicyclo[4.3.0]non-1(9)-en-8-one (trans-7e)

Compound 7e was a colorless plate, mp 222-223.5 °C (Et₂O); IR 1720, 1323, 1312,
1167, 1155 cm\(^{-1}\); \(^1\)H NMR \(\delta\) 7.94 (d, 2H, \(J = 7.3\) Hz), 7.77 (t, 1H, \(J = 7.3\) Hz), 7.67 (t, 2H, \(J = 7.3\) Hz), 7.55 (d, 2H, \(J = 8.5\) Hz), 7.34 (d, 2H, \(J = 8.5\) Hz), 6.54 (s, 1H), 4.35-4.32 (m, 1H), 4.19-4.15 (m, 1H), 3.85 (dd, 1H, \(J = 11.6, 1.2\) Hz), 2.65 (t, 1H, \(J = 11.0\) Hz), 2.45 (s, 3H), 2.29 (d, 1H, \(J = 18.9\) Hz), 2.23 (d, 1H, \(J = 11.6\) Hz), 2.15 (d, 1H, \(J = 18.9\) Hz), 1.38 (s, 3H); \(^{13}\)C NMR \(\delta\) 204.2, 169.3, 144.6, 137.4, 134.9, 133.2, 130.1, 129.92, 129.87, 128.4, 127.3, 60.3, 57.1, 47.1, 46.5, 44.4, 23.5, 21.5; MS \(m/z\) 445 (M\(^+\), 0.1). HRMS calcd for C\(_{22}\)H\(_{23}\)NO\(_5\)S\(_2\) 445.1018, found 445.1016.

(2R*,6S*)- (2R*,6R*)-4,4-Bis(methoxycarbonyl)-9-methyl-2-(phenylsulfonfonyl)bicyclo[4.3.0]non-1(9)-en-8-one (cis-7g and trans-7g).

A mixture of cis-7g and trans-7g in the ratio of 33 to 67 was obtained as a colorless plate, mp 193-194 °C (Et\(_2\)O); IR 1734, 1709, 1310, 1150 cm\(^{-1}\); \(^1\)H NMR \(\delta\) 7.97-7.96 (m, 67/100 x 2H), 7.78-7.72 (m, 67/100 x 1H, 33/100 x 2H), 7.67-7.63 (m, 67/100 x 2H, 33/100 x 1H), 7.54 (t, 33/100 x 2H, \(J = 8.0\) Hz), 4.29 (d, 33/100 x 1H, \(J = 7.1\) Hz), 4.16 (dd, 67/100 x 1H, \(J = 12.6, 3.0\) Hz), 3.87 (s, 33/100 x 3H), 3.72 (s, 33/100 x 3H), 3.67 (s, 67/100 x 3H), 3.56 (s, 67/100 x 3H), 3.44 (dt, 33/100 x 1H, \(J = 15.6, 2.0\) Hz), 2.94 (ddd, 33/100 x 1H, \(J = 12.7, 5.5, 2.0\) Hz), 2.76-2.65 (m, 67/100 x 1H, 33/100 x 1H), 2.62-2.56 (m, 67/100 x 2H, 33/100 x 1H), 2.41 (ddd, 67/100 x 1H, \(J = 13.4, 4.4, 2.2\) Hz), 2.17 (t, 67/100 x 1H, \(J = 12.6\) Hz), 2.14 (s, 67/100 x 3H), 2.02 (dd, 67/100 x 1H, \(J = 20.9, 4.4\) Hz), 1.97 (dd, 33/100 x 1H, \(J = 19.3, 2.0\) Hz), 1.66-1.61 (m, 67/100 x 1H, 33/100 x 1H), 1.34 (t, 33/100 x 1H, \(J = 12.7\) Hz), 0.93 (d, 33/100 x 3H, \(J = 2.0\) Hz); \(^{13}\)C NMR \(\delta\) 207.1, 206.6, 171.2, 170.0, 169.9, 169.7, 160.4, 159.2, 141.5, 137.9, 137.1, 136.4, 134.3, 134.2, 129.5, 129.4, 128.8, 128.7, 62.6, 60.9, 54.8, 53.3, 53.2, 53.1, 53.00, 52.98, 41.2, 39.6, 39.1, 38.5, 37.9, 33.4, 32.9, 28.1, 10.4, 7.1; MS \(m/z\) 406 (M\(^+\), 0.3). HRMS calcd for C\(_{20}\)H\(_{22}\)O\(_5\)S 406.1086, found 406.1088.

(1R*,5S*)-3,3-Bis(methoxycarbonyl)-6-methylene-1-phenyl-5-(phenylsulfonfonyl)bicyclo[3.2.0]heptane (8).

Compound 8 was a colorless needle, mp 47-48 °C (Et\(_2\)O); \(^1\)H NMR \(\delta\) 7.90-7.20 (m,
10H), 5.17-5.15 (m, 2H), 3.75 (s, 3H), 3.68 (s, 3H), 3.67 (d, 1H, J = 13.4 Hz), 3.24 (d, 1H, J = 14.6 Hz), 3.15 (d, 1H, J = 13.4 Hz), 3.03 (d, 1H, J = 15.6 Hz), 2.73 (d, 1H, J = 15.6 Hz), 2.53 (d, 1H, J = 14.6 Hz); $^{13}$C NMR δ 171.2, 171.0, 142.0, 141.7, 136.8, 133.2, 130.2, 128.03, 128.01, 127.9, 127.0, 114.9, 82.7, 59.9, 56.2, 53.3, 53.0, 51.9, 40.8, 38.9; MS m/z 440 (M+, 0.9). HRMS calcd for C$_2$H$_2$O$_6$S 440.1294, found 440.1296. Anal. Calcd for C$_2$H$_2$O$_6$S: C, 65.44; H, 5.49. Found: C, 65.26; H, 5.49.

$(6R^*,9S^*)$-4,4-Bis(methoxycarbonyl)-9-methyl-2-(phenylsulfonyl)bicyclo[4.3.0]non-1-en-8-one (9).

Compound 9 was a colorless needle, mp 196-197.5 °C (AcOEt); IR 1736, 1308, 1150 cm$^{-1}$; $^1$H NMR δ 7.87 (d, 2H, J = 7.3 Hz), 7.63 (t, 1H, J = 7.3 Hz), 7.55 (t, 2H, J = 7.3 Hz), 4.01 (q, 1H, J = 7.6 Hz), 3.67 (s, 3H), 3.60 (s, 3H), 3.06 (d, 1H, J = 17.6 Hz), 2.94-2.91 (m, 1H), 2.71 (dd, 1H, J = 17.6, 8.5 Hz), 2.64 (dd, 1H, J = 13.1, 5.1 Hz), 2.58 (dd, 1H, J = 17.6s, 2.7 Hz), 2.09 (dd, 1H, J = 17.6, 12.7 Hz), 1.68 (dd, 1H, J = 13.1, 11.2 Hz), 1.30 (d, 3H, J = 7.6 Hz); $^{13}$C NMR δ 214.7, 170.6, 169.9, 153.8, 139.7, 133.7, 129.6, 129.3, 127.5, 53.2, 52.99, 52.95, 46.6, 44.5, 35.5, 32.5, 30.6, 17.6; MS m/z 406 (M+, 0.2). HRMS calcd for C$_{28}$H$_{22}$O$_8$S 406.1086, found 406.1088. Anal. Calcd for C$_{28}$H$_{22}$O$_8$S: C, 59.10; H, 5.46. Found: C, 58.73; H, 5.47.

$(2R^*,7S^*)$- and $(2R^*,7R^*)$-4,4-Bis(methoxycarbonyl)-2-(phenylsulfonyl)bicyclo[5.3.0]dec-1(10)-en-9-one (cis-11a and trans-11a).

A mixture of cis-11a and trans-11a in the ratio of 35 to 65 was obtained as a colorless plate, mp 137-138.5 °C (AcOEt); IR 1732, 1693, 1609, 1310, 1151 cm$^{-1}$; $^1$H NMR δ 7.95-7.93 (m, 65/100 x 2H), 7.81-7.79 (m, 35/100 x 2H), 7.71-7.68 (m, 35/100 x 3H), 7.61-7.56 (m, 65/100 x 3H), 6.79 (d, 65/100 x 1H, J = 1.7 Hz), 5.69 (s, 35/100 x 1H), 4.80 (dd, 35/100 x 1H, J = 12.5, 5.4 Hz), 4.20 (d, 65/100 x 1H, J = 11.2 Hz), 3.75 (s, 35/100 x 3H), 3.71 (s, 65/100 x 3H), 3.68 (s, 35/100 x 3H), 3.62 (s, 65/100 x 3H), 3.07 (d, 65/100 x 1H, J = 13.9 Hz), 2.98-2.90 (m, 65/100 x 1H, 35/100 x 2H), 2.64 (dd, 35/100 x 1H, J = 18.6, 6.8 Hz), 2.63 (dt, 65/100 x 1H, J = 18.6, 6.8 Hz), 2.46 (dd,
35/100 x 1H, J = 14.6, 12.5 Hz), 2.33-2.31 (m, 35/100 x 1H), 2.22 (dd, 65/100 x 1H, J = 15.1, 7.8 Hz), 2.10-1.93 (m, 65/100 x 2H, 35/100 x 3H), 1.84 (dt, 65/100 x 1H, J = 13.8, 5.9 Hz), 1.71-1.60 (m, 65/100 x 2H), 1.38-1.30 (m, 35/100 x 1H); $^{13}$C NMR δ 207.1, 206.7, 172.7, 171.8, 171.4, 170.80, 170.77, 169.9, 137.5, 136.4, 136.0, 134.6, 134.2, 132.6, 129.31, 129.29, 129.1, 128.9, 65.2, 61.6, 56.33, 56.25, 53.3, 53.1, 52.9, 52.8, 45.4, 43.0, 42.0, 41.6, 34.9, 34.3, 33.4, 30.2, 27.4, 25.2; MS m/z 406 (M+, 0.1). Anal. Calcd for C$_{20}$H$_{22}$O$_7$S: C, 59.10; H, 5.46. Found: C, 58.93; H, 5.37.

(2R*,7S*)- and (2R*,7R*)-2,4,4-Tris(phenylsulfonfonyl)bicyclo[5.3.0]dec-1(10)-en-9-one (cis-11b and trans-11b).

A mixture of cis-11b and trans-11b in the ratio of 60 to 40 was obtained as a colorless needle, mp 188-189.5 °C (AcOEt); IR 1717, 1325, 1310, 1161 cm$^{-1}$; $^1$H NMR δ 8.02-7.94 (m, 60/100 x 6H), 7.91-7.86 (m, 40/100 x 6H), 7.80-7.54 (m, 60/100 x 9H, 40/100 x 9H), 6.66 (s, 40/100 x 1H), 5.93 (s, 60/100 x 1H), 5.04 (dd, 60/100 x 1H, J = 11.7, 5.4 Hz), 4.86 (d, 40/100 x 1H, J = 11.2 Hz), 3.25 (d, 40/100 x 1H, J = 14.9 Hz), 3.20 (d, 60/100 x 1H, J = 6.4 Hz), 3.10-3.01 (m, 60/100 x 2H), 2.86 (d, 40/100 x 1H, J = 5.4 Hz), 2.71-2.63 (m, 60/100 x 1H, 40/100 x 1H), 2.59-2.51 (m, 40/100 x 2H), 2.42-2.14 (m, 60/100 x 3H, 40/100 x 3H), 2.04 (dd, 60/100 x 1H, J = 18.5, 1.5 Hz), 1.78 (dd, 40/100 x 1H, J = 19.0, 2.5 Hz), 1.61-1.54 (m, 60/100 x 1H); $^{13}$C NMR δ 207.6, 206.5, 171.4, 168.9, 137.6, 137.0, 135.93, 135.90, 135.80, 135.78, 135.4, 135.3, 135.2, 135.1, 134.9, 134.8, 134.4, 131.9, 131.8, 131.30, 131.29, 131.1, 129.5, 129.2, 129.13, 129.07, 128.9, 128.8, 89.1, 87.7, 64.6, 61.1, 45.4, 44.6, 41.4, 38.9, 30.7, 29.1, 27.1, 26.5, 25.8, 25.7; MS m/z 570 (M+, 0.1). Anal. Calcd for C$_{20}$H$_{22}$O$_7$S: C, 58.93; H, 4.59. Found: C, 58.67; H, 4.66.

(2R*,7S*)- and (2R*,7R*)-2-(Phenylsulfonfonyl)bicyclo[5.3.0]dec-1(10)-en-9-one (cis-11c and trans-11c).

A mixture of cis-11c and trans-11c in the ratio of 93 to 7 was obtained as a colorless plate, mp 163-164 °C (AcOEt); IR 1705, 1676, 1558, 1308, 1148 cm$^{-1}$; $^1$H NMR δ 7.87-
7.85 (m, 7/100 x 2H), 7.79-7.76 (m, 93/100 x 2H), 7.68-7.65 (m, 93/100 x 1H, 7/100 x 1H), 7.56-7.53 (m, 93/100 x 2H, 7/100 x 2H), 6.48 (d, 7/100 x 1H, J = 2.0 Hz), 5.88 (s, 93/100 x 1H), 4.33 (dd, 93/100 x 1H, J = 12.5, 5.4 Hz), 3.97 (dd, 7/100 x 1H, J = 10.2, 2.7 Hz), 2.85 (brs, 7/100 x 1H), 2.76-2.72 (m, 93/100 x 1H), 2.59 (dd, 93/100 x 1H, J = 18.3, 6.3 Hz), 2.58-2.54 (m, 7/100 x 1H), 2.46-2.40 (m, 93/100 x 1H, 7/100 x1H), 2.06-1.98 (m, 93/100 x 3H, 7/100 x 2H), 1.95-1.86 (m, 93/100 x 2H, 7/100 x 1H), 1.76-1.70 (m, 7/100 x 3H), 1.59-1.51 (m, 7/100 x 2H), 1.43-1.34 (m, 93/100 x 1H), 1.18-1.10 (m, 93/100 x 1H), 1.07 (ddd, 93/100 x 1H, J = 15.6, 12.5, 3.4 Hz); $^{13}$C NMR δ 207.6, 207.2, 174.0, 173.9, 138.0, 136.58, 138.56, 134.2, 134.0, 132.9, 129.3, 129.2, 129.1, 128.7, 68.5, 66.1, 45.6, 43.6, 43.0, 42.7, 38.8, 31.0, 30.1, 29.0, 27.6, 26.4, 25.7, 23.5; MS m/z 290 (M+, 0.7). HRMS calcd for C$_{16}$H$_{18}$O$_3$S 290.0977, found 290.0981. Anal. Calcd for C$_{16}$H$_{18}$O$_3$S: C, 66.18; H, 6.25. Found: C, 66.12; H, 6.34.

(2R*,7S*)- and (2R*,7R*)-N-(4-Methylbenzenesulfonyl)-2-(phenylsulfonyl)-5-azabicyclo[5.3.0]non-1(10)-en-9-one (cis-11d and trans-11d).

A mixture of cis-11d and trans-11d in the ratio of 80 to 20 was obtained as a colorless needle, mp 174-175 °C (AcOEt); IR 1717, 1325, 1310, 1161 cm$^{-1}$; $^1$H NMR δ 7.87-7.86 (m, 20/100 x 2H), 7.78-7.60 (m, 80/100 x 7H, 20/100 x 5H), 7.32-7.27 (m, 80/100 x 2H, 20/100 x 2H), 6.60 (s, 20/100 x 1H), 6.02 (s, 80/100 x 1H), 4.40 (dd, 80/100 x 1H, J = 12.0, 6.1 Hz), 4.19 (dd, 20/100 x 1H, J = 10.0, 4.6 Hz), 3.97-3.89 (m, 80/100 x 2H), 3.76 (dd, 20/100 x 1H, J = 14.0, 5.6 Hz), 3.60-3.55 (m, 20/100 x 1H), 3.25-3.19 (m, 20/100 x 1H), 3.07 (brs, 80/100 x 1H, 20/100 x 1H), 2.81 (dd, 20/100 x 1H, J = 14.0, 8.3 Hz), 2.70 (dd, 80/100 x 1H, J = 14.4, 9.6 Hz), 2.63 (dd, 80/100 x 1H, J = 18.6, 6.1 Hz), 2.54-2.32 (m, 80/100 x 3H, 20/100 x 3H), 2.42 (s, 20/100 x 3H), 2.41 (s, 80/100 x 3H), 2.16-2.10 (m, 80/100 x 1H, 20/100 x 1H); $^{13}$C NMR δ 205.9, 205.1, 170.1, 169.7, 143.93, 143.85, 138.3, 137.8, 136.3, 135.8, 135.5, 134.6, 134.3, 133.5, 130.0, 129.9, 129.5, 129.4, 129.1, 128.7, 126.93, 126.86, 67.1, 64.4, 53.7, 53.1, 47.8, 46.1, 45.5, 43.3, 41.9, 39.4, 28.3, 27.7, 21.4; MS m/z 445 (M+, 0.1). Anal. Calcd for C$_{22}$H$_{23}$NO$_3$S$_2$: C, 59.31; H, 5.20; N, 3.14. Found: C, 59.20; H, 5.15; N, 3.21.
(2R*,7S*)-2-(Phenylsulfonyl)-5-oxabicyclo[5.3.0]non-1(10)-en-9-one (cis-11e).

Compound 11e was a colorless oil; IR 1709, 1310, 1150 cm⁻¹; ¹H NMR δ 7.82-7.81 (m, 2H), 7.72-7.69 (m, 1H), 7.60-7.57 (m, 2H), 6.00 (s, 1H), 4.48-4.44 (m, 1H), 4.21-4.16 (m, 1H), 4.01 (dd, 1H, J = 11.7, 3.7 Hz), 3.28-3.23 (m, 1H), 3.08-3.04 (m, 1H), 2.96 (t, 1H, J = 11.7 Hz), 2.53 (dd, 1H, J = 18.7, 6.8 Hz), 2.43-2.38 (m, 2H), 1.88 (d, 1H, J = 18.7 Hz); ¹³C NMR δ 205.7, 171.5, 137.6, 136.2, 134.5, 129.4, 129.3, 76.1, 68.5, 67.0, 45.2, 39.3, 29.0; MS m/z 292 (M⁺, 0.1). HRMS calcd for C₁₅H₁₀O₂S 292.0769, found 292.0772.

4,4-Bis(methoxycarbonyl)-7,7-dimethyl-2-(phenylsulfonyl)bicyclo[4.2.0]oct-1-ene (12).

Compound 12 was a colorless oil. IR 1734, 1308, 1146 cm⁻¹; ¹H NMR δ 7.89-7.51 (m, 5H), 3.70 (s, 3H), 3.65 (s, 3H), 3.02 (d, 2H, J = 14.7 Hz), 2.85 (d, 1H, J = 14.7 Hz), 2.60-2.57 (m, 1H), 2.41 (d, 1H, J = 16.8 Hz), 2.22 (dd, 1H, J = 12.3, 6.4 Hz), 1.53 (t, 1H, J = 12.3 Hz), 1.27 (s, 3H), 0.95 (s, 3H); ¹³C NMR δ 171.2, 170.4, 152.4, 140.6, 133.2, 129.1, 127.4, 125.7, 53.8, 53.0, 52.9, 48.6, 46.0, 36.4, 29.7, 29.4, 26.6, 21.8. 12 was a known compound, see above reference (a).