Supporting Information

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

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General Procedure for Preparation of Sulfonylallenes **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**¹ (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 NH_4Cl . The resulting mixture was extracted with CH_2Cl_2 , which was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with hexane-AcOEt to afford the corresponding sulfonylallenes.

(1) Jaganathan, S.; Okamura, W. H. *Tetrahedron Lett.* **1982**, 23, 4763-4764.

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

Reaction conditions: (b) PhSCl , Et_3N , THF, -78 °C; (c) mCPBA, CH_2Cl_2 , 0 °C, **6e** (43%), **6g** (61%), **6h** (89%), **10c** (30%), **10d** (58%), **10e** (30%).

To a solution of alcohol (2.0 mmol) and Et_3N (6.0 mmol) in THF (20 mL) was gradually added PhSCl (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 NaHCO_3 , 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 CH_2Cl_2 (20 mL) was added *m*CPBA (2.2 mmol) at 0 °C. After stirring for 30 min, the reaction was quenched by addition of saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ and NaHCO_3 , and the mixture was extracted with CH_2Cl_2 . The extract was washed with brine, dried, and concentrated to dryness. The residue was chromatographed with hexane-AcOEt to afford the corresponding sulfonylallenes.

Sulfonylallenes **3a,b,6a-c,10a,b** were known compounds, see: (a) Padwa, A.; Filipkowski, M. A.; Meske, M.; Watterson, S. H.; Ni, Z. *J. Am. Chem. Soc.* **1993**, *115*, 3776-3777. (b) Padwa, A.; Meske, M.; Murphree, S.; Watterson, S. H.; Ni, Z. *J. Am. Chem. Soc.* **1995**, *117*, 7071-7080. (c) Padwa, A.; Lipka, H.; Watterson, S. H.; Murphee, S. S. *J. Org. Chem.* **2003**, *68*, 6238-6250.

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); ^{13}C 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 $\text{C}_{21}\text{H}_{26}\text{O}_7\text{S}$ 422.1399, found 422.1401.

***N*-(2-Methyl-2-propenyl)-*N*-[2-(phenylsulfonyl)-2,3-butadienyl]-(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

= 8.1 Hz), 7.21 (d, 2H, J = 8.1 Hz), 5.13 (t, 2H, J = 3.4 Hz), 4.76 (s, 1H), 4.63 (s, 1H), 4.07 (t, 2H, J = 3.4 Hz), 3.69 (s, 2H), 2.39 (s, 3H), 1.57 (s, 3H); ^{13}C NMR δ 208.1, 143.3, 140.1, 139.2, 137.4, 133.7, 129.5, 129.2, 128.0, 127.2, 115.2, 109.6, 85.9, 53.8, 43.2, 21.4, 19.7; MS m/z 417 (M^+ , 0.1). HRMS calcd for $\text{C}_{21}\text{H}_{23}\text{NO}_4\text{S}_2$ 417.1068, found 417.1071.

Dimethyl 2-(2-phenyl-2-propenyl)-2-[2-(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} ; ^1H NMR δ 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 δ 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 $\text{C}_{24}\text{H}_{24}\text{O}_6\text{S}$ 440.1294, found 440.1295. Anal. Calcd for $\text{C}_{24}\text{H}_{24}\text{O}_6\text{S}$: C, 65.44; H, 5.49. Found: C, 65.32; H, 5.52.

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

Compound **6g** was a colorless needle, mp 52-53.5 °C (AcOEt); IR 1961, 1734, 1306, 1151 cm^{-1} ; ^1H NMR δ 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 δ 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 $\text{C}_{19}\text{H}_{22}\text{O}_6\text{S}$ 378.1137, found 378.1139. Anal. Calcd for $\text{C}_{19}\text{H}_{22}\text{O}_6\text{S}$: C, 60.30; H, 5.86. Found: C, 59.92; H, 5.87.

Dimethyl 2-[4-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); ^{13}C 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 $\text{C}_{20}\text{H}_{24}\text{O}_6\text{S}$ 392.1294, found 392.1290. Anal. Calcd for $\text{C}_{20}\text{H}_{24}\text{O}_6\text{S}$: 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); ^{13}C 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 $\text{C}_{15}\text{H}_{18}\text{O}_2\text{S}$ 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 $^{\circ}\text{C}$ (Et_2O); 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); ^{13}C 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 $\text{C}_{21}\text{H}_{23}\text{NO}_4\text{S}_2$: C, 60.41; H, 5.55; N, 3.35. Found: C, 60.19; H, 5.60; N, 3.38.

3-(Phenylsulfonyl)-5-(2-propenyloxy)-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); ^{13}C 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 $C_{14}H_{16}O_3S$ 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); ^{13}C 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 $C_{20}H_{24}O_6S$ 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 $^{\circ}C$ (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.

(2*R,6*S**)- and (2*R**,6*R**)-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, 170.9, 169.8, 169.7, 169.2, 167.9, 137.1, 136.2, 134.4, 130.0, 129.5, 129.2, 128.8, 128.4, 62.0, 61.1, 54.3, 53.3, 53.2, 53.1, 53.0, 52.5, 42.1, 40.4, 38.7, 37.9, 37.1, 35.2, 32.0, 27.9; MS *m/z* 392 (M⁺, 0.1). Anal. Calcd for C₁₉H₂₀O₇S: C, 58.15; H, 5.14. Found: C, 58.00; H, 5.26.

(2*R,6*S**)- and (2*R**,6*R**)-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 207.0, 206.7, 172.4, 170.7, 137.7, 137.3, 134.2, 134.1, 133.6, 129.4, 129.2, 128.7, 128.5, 65.4, 64.0, 42.7, 42.5, 40.9, 38.9, 34.2, 33.5, 27.9, 26.0, 24.2, 21.1; MS *m/z* 276 (M⁺, 0.1). HRMS calcd for

C₁₅H₁₆O₃S 276.0820, found 276.0818. Anal. Calcd for C₁₅H₁₆O₃S: C, 65.19; H, 5.84. Found: C, 65.16; H, 5.92.

(2*R,6*R**)- and (2*R**,6*S**)-N-(4-Methylbenzenesulfonyl)-2-(phenylsulfonyl)-4-azabicyclo[4.3.0]non-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; ¹H 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); ¹³C 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 C₂₁H₂₁NO₅S₂: C, 58.45; H, 4.91; N, 3.25. Found: C, 58.55; H, 5.00; N, 3.32.

(2*R,6*R**)- and (2*R**,6*S**)-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; ¹H 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); ^{13}C 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 $\text{C}_{14}\text{H}_{14}\text{O}_4\text{S}$ 278.0613, found 278.0615.

(2*R,6*R**)-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); ^{13}C 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 $\text{C}_{20}\text{H}_{22}\text{O}_7\text{S}$: C, 59.10; H, 5.46. Found: C, 58.89; H, 5.39.

(2*R,6*S**)-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); ^{13}C 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 $\text{C}_{22}\text{H}_{26}\text{O}_8\text{S}$ 450.1348, found 450.1352.

(2*R,6*S**)-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 (Et_2O); IR 1720, 1323, 1312,

1167, 1155 cm^{-1} ; ^1H NMR δ 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 δ 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 $\text{C}_{22}\text{H}_{23}\text{NO}_5\text{S}_2$ 445.1018, found 445.1016.

(2*R,6*S**)- and (2*R**,6*R**)-4,4-Bis(methoxycarbonyl)-9-methyl-2-(phenylsulfonyl)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 $^\circ\text{C}$ (Et_2O); IR 1734, 1709, 1310, 1150 cm^{-1} ; ^1H NMR δ 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 δ 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 $\text{C}_{20}\text{H}_{22}\text{O}_7\text{S}$ 406.1086, found 406.1088.

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

Compound **8** was a colorless needle, mp 47-48 $^\circ\text{C}$ (Et_2O); ^1H NMR δ 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 $\text{C}_{24}\text{H}_{24}\text{O}_6\text{S}$ 440.1294, found 440.1296. Anal. Calcd for $\text{C}_{24}\text{H}_{24}\text{O}_6\text{S}$: C, 65.44; H, 5.49. Found: C, 65.26; H, 5.49.

(6*R,9*S**)-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} ; ^1H 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, $J = 17.6, 2.7$ 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 $\text{C}_{20}\text{H}_{22}\text{O}_7\text{S}$ 406.1086, found 406.1088. Anal. Calcd for $\text{C}_{20}\text{H}_{22}\text{O}_7\text{S}$: C, 59.10; H, 5.46. Found: C, 58.73; H, 5.47.

(2*R,7*S**)- and (2*R**,7*R**)-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} ; ^1H 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 $\text{C}_{20}\text{H}_{22}\text{O}_7\text{S}$: C, 59.10; H, 5.46. Found: C, 58.93; H, 5.37.

(2*R,7*S**)- and (2*R**,7*R**)-2,4,4-Tris(phenylsulfonyl)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} ; ^1H 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 $\text{C}_{28}\text{H}_{26}\text{O}_7\text{S}_3$: C, 58.93; H, 4.59. Found: C, 58.67; H, 4.66.

(2*R,7*S**)- and (2*R**,7*R**)-2-(Phenylsulfonyl)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} ; ^1H 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 x 1H), 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 $\text{C}_{16}\text{H}_{18}\text{O}_3\text{S}$ 290.0977, found 290.0981. Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{O}_3\text{S}$: C, 66.18; H, 6.25. Found: C, 66.12; H, 6.34.

(2*R,7*S**)- and (2*R**,7*R**)-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} ; ^1H 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 $\text{C}_{22}\text{H}_{23}\text{NO}_5\text{S}_2$: C, 59.31; H, 5.20; N, 3.14. Found: C, 59.20; H, 5.15; N, 3.21.

(2*R,7*S**)-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); ^{13}C 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 $\text{C}_{15}\text{H}_{16}\text{O}_4\text{S}$ 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); ^{13}C 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).