Salen Promoted Enantioselective Nazarov Cyclizations of Activated and Unactivated Dienones

Supporting Information

Gerri E. Hutson, Yunus E. Türkmen, and Viresh H. Rawal*

Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637, United States

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General Experimental Procedures

All reactions were carried out in oven-dried glassware under an inert atmosphere of nitrogen or argon, unless otherwise noted. All cannula transfers were performed under argon pressure. Diethyl ether, tetrahydrofuran, dichloromethane, toluene, benzene, DMF, and acetonitrile were purged with nitrogen and dried over activated alumina using an Innovative Technology, Inc. Puresolv solvent purification system. Molecular sieves were activated by microwave. All other reagents were used as received unless indicated otherwise. $^1$H and $^{13}$C were recorded on Brüker DRX-400 and 500 MHz spectrometers at 298K. Proton chemical shifts were internally referenced to the residual solvent proton resonance (CHCl$_3$ δ 7.26) and splitting patterns were designated as: s = singlet, d = doublet, t = triplet, quartet = q, and m = multiplet. Carbon chemical shifts are internally referenced to the deuterated solvent signal (CDCl$_3$ δ 77.0). High pressure liquid chromatography was performed on an Agilent 1100 system using Daicel Chiracel columns and a 254 nm UV detector. Melting points were measured on a Thomas Hoover melting point apparatus and are uncorrected. Infrared spectra were obtained on a Nicolet 20 SXB FT-IR spectrometer and peak values are reported in reciprocal centimeters (cm$^{-1}$). Electrospray ionization high resolution mass spectra were recorded at Old Dominion University or at Hunter College. Optical rotations were recorded using a Jasco DIP-1000 instrument. Analytical thin layer chromatography was run on Whatman 0.25 mm K6F silica gel 60 Å plates. Flash chromatography was run using silica gel (60 Å, 230-400 mesh) obtained from Silicycle and used as received.

General Procedure: Synthesis of Biaryl Salicylaldehydes

A schlenk tube was charged with Cs$_2$CO$_3$ (5.91 mmol), boronic acid (2.96 mmol), aryl bromide (1.97 mmol), and PdCl$_2$dpff (0.0985 mmol). Solvent grade toluene (3 mL) and water (1 mL) were added to the schlenk tube. The reaction was heated at 100 °C for 12 hours, cooled to room temperature, diluted with a 1:1 diethyl ether/hexanes solution (30 mL), and then transferred to a separatory funnel. The mixture was washed with H$_2$O (10 mL x 2) and brine (10 mL). The aqueous layer was extracted with a 1:1 diethyl ether/hexanes solution (15 mL x 2). The combined organic extracts were dried over MgSO$_4$ and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (pure hexanes to 100:1 hexanes:EtOAc) to afford the corresponding product.

5-phenyl-3-tert-butyl-2-hydroxybenzaldehyde. The reaction was performed according to the General Procedure. The salicylaldehyde was isolated as a white solid in 72% yield. $^1$H NMR (500 MHz, CDCl$_3$, 298K) δ 11.79 (s, 1H), 9.96 (s, 1H), 7.76 (d, $J = 2.4$ Hz, 1H), 7.6 (d, $J = 2.2$ Hz, 1H), 7.55 (dd, $J = 7.7$ Hz, 3.3 Hz, 2H), 7.45 (d, $J = 7.5$ Hz, 2H), 7.35 (dd, $J = 7.7$ Hz, 1H),
1.47 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$, 298K) δ 197.24, 160.60, 140.11, 138.70, 133.18, 132.43, 130.04, 128.90, 127.16, 126.69, 120.70, 35.01, 29.21; IR (NaCl, thin film) 2959.2, 1649.7, 1441.5, 1407.8, 1268.3, 1164.3, 757.8, 696.6 cm$^{-1}$.

5-([trimethylbenzene]-3-tert-butyl-2-hydroxybenzaldehyde. The reaction was performed according to the General Procedure. The salicylaldehyde was isolated as a white solid in 69% yield. $^1$H NMR (500 MHz, CDCl$_3$, 298K) δ 11.79 (s, 1H), 9.87 (s, 1H), 7.32 (d, J = 2.1 Hz, 1H), 7.18 (d, J = 2.1 Hz, 1H), 6.97 (s, 2H), 2.34 (s, 3H), 2.03 (s, 6H), 1.43 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$, 298K) δ 197.18, 159.89, 138.37, 137.62, 136.97, 136.33, 135.68, 132.10, 131.69, 128.24, 120.56, 34.96, 29.34, 21.00, 20.84; IR (NaCl, thin film) 2958.7, 1649.1, 1612.4, 1442.9, 1265.7, 733.0 cm$^{-1}$.

5-([triisopropylbenzene]-3-tert-butyl-2-hydroxybenzaldehyde. The reaction was performed according to the General Procedure. The salicylaldehyde was isolated as a white solid in 74% yield. $^1$H NMR (500 MHz, CDCl$_3$, 298K) δ 11.79 (s, 1H), 9.87 (s, 1H), 7.36 (s, 1H), 7.21 (s, 1H), 7.08 (s, 2H), 3.01-2.90 (m, 1H), 2.67-2.55 (m, 2H), 1.44 (s, 9H), 1.32 (d, J = 8.1 Hz, 6H), 1.10 (dd, J = 8.1 Hz, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$, 298K) δ 197.25, 159.86, 148.29, 146.93, 137.79, 136.14, 135.74, 132.26, 131.45, 120.70, 120.22, 34.93, 34.30, 30.36, 29.38, 24.32, 24.06; IR (NaCl, thin film) 2959.1, 2868.2, 1652.1, 1458.2, 1436.2, 1409.9, 1362.0, 1311.1, 1265.8, 1164.2, 675.3 cm$^{-1}$.
Synthesis of 5-(tri-tert-butyl-benzene)-2-tert-butylanisole. A round-bottom flask was charged with magnesium turnings (14.9 mmol), dry THF (2 mL), and 1,2-dibromoethane (70 µL). The mixture was stirred at room temperature for 15 minutes, then a solution of 1-bromo-2,4,6-tri-tert-butylbenzene (0.894 mmol) in dry THF (4 mL) was added dropwise by cannula. The flask was suspended in a 60 °C oil bath, and then stirred overnight. The reaction mixture was cooled to room temperature and then transferred by cannula to a condenser-fitted round-bottom flask containing bromoanisole (1.49 mmol), Pd$_2$dba$_3$ (0.0745 mmol), 2,6-di-cyclohexylphosphino 2',6'-dimethoxybiphenyl (0.149 mmol), and dry toluene (3 mL). After 1 hour at 100 °C, the mixture was allowed to cool to room temperature, filtered through a pad of silica gel, and then concentrated in vacuo. Flash chromatography on silica gel using pure hexanes as eluent gave the title compound as a white solid in 93% yield. $^1$H NMR (500 MHz, CDCl$_3$, 298K) $\delta$ 7.52 (s, 2H), 7.22 (d, J = 2.2 Hz, 1H), 7.09 (dd, J = 8.3 Hz, 2.2 Hz, 1H), 6.77 (d, J = 8.2 Hz, 1H), 3.88 (s, 3H), 1.37 (s, 9H), 1.35 (s, 9H), 1.08 (s, 18H); $^{13}$C NMR (125 MHz, CDCl$_3$, 298K) $\delta$ 157.59, 148.49, 147.85, 138.73, 135.05, 133.50, 132.89, 132.00, 122.07, 108.91, 55.00, 37.58, 34.97, 34.69, 33.51, 31.51, 29.86.

Synthesis of 5-(tri-tert-butyl-benzene)-2-tert-butylphenol. A 50 mL round-bottom flask charged with anisole (1.22 mmol) and dry CH$_2$Cl$_2$ (15 mL) was cooled to 0°C, then charged with BBr$_3$ (2.44 mmol) dropwise over 5 minutes. The solution was warmed to room temperature, then stirred overnight. The reaction mixture was slowly quenched at 0°C with saturated aqueous NaHCO$_3$ (10 mL). The layers were separated, and then the aqueous layer was extracted with CH$_2$Cl$_2$ (40 mL). The organic layers were combined and washed with brine (25 mL x 2), then dried over MgSO$_4$. The solvent was removed in vacuo. Flash chromatography on silica gel (30:1 Hex:EtOAc) gave the title compound as a white solid in 70% yield. $^1$H NMR (500 MHz, CDCl$_3$, 298K) $\delta$ 7.51 (s, 2H), 7.21 (d, J = 2.2 Hz, 1H), 6.99 (dd, J = 8.2 Hz, 2.2 Hz, 1H), 6.57 (d, J = 8.2 Hz, 1H), 4.70 (s, 1H), 1.38 (s, 9H), 1.36 (s, 9H), 1.08 (s, 18H); $^{13}$C NMR (125 MHz, CDCl$_3$, 298K) $\delta$ 157.59, 148.49, 147.85, 138.73, 135.05, 133.50, 132.89, 132.00, 122.07, 108.91, 55.00, 37.58, 34.97, 34.69, 33.51, 31.51, 29.86.
Synthesis of 5-(tri-tert-butyl-benzene)-3-tert-butyl-2-hydroxybenzaldehyde. A 50 mL round-bottom flask was charged with dry paraformaldehyde (2.66 mmol), anhydrous MgCl₂ (1.52 mmol), dry THF (3 mL), and triethylamine (1.52 mmol). After the mixture was stirred 20 minutes, a solution of phenol (0.760 mmol) in dry THF (3 mL) was added dropwise by cannula. The reaction was stirred at 55 °C overnight. The mixture was cooled to room temperature, diluted with diethyl ether (30 mL), and then transferred to a separatory funnel. The mixture was washed with 2N HCl (5 mL x 2). After the layers were separated, the organic layer was washed with H₂O (10 mL x 2), and then dried over MgSO₄. The solvent was removed in vacuo. Flash chromatography on silica gel (30:1 Hex:EtOAc) gave the title compound as a pale yellow solid in 90% yield. ¹H NMR (500 MHz, CDCl₃, 298K) δ 11.82 (s, 1H), 9.83 (s, 1H), 7.54 (s, 1H), 7.54 (s, 2H), 7.33 (s, 1H), 1.41 (s, 9H), 1.37 (s, 9H), 1.09 (s, 18H); ¹³C NMR (125 MHz, CDCl₃, 298K) δ 197.17, 160.29, 148.71, 148.57, 140.55, 136.77, 136.41, 135.38, 132.86, 122.34, 118.79, 37.48, 35.01, 34.76, 33.58, 31.44, 29.29; IR (NaCl, thin film) 2961.6, 1649.2, 1409.8, 1264.6, 869.9 cm⁻¹.

General Procedure: Synthesis of Biaryl Salen Ligands A round-bottom flask containing a solution of (1R, 2R)-1,2-diaminocyclohexane L-tartrate (0.399 mmol) and K₂CO₃ (0.798 mmol) in H₂O (2 mL) was charged with salicylaldehyde (0.788 mmol) dissolved in benzene (3 mL) and ethanol (1 mL). The flask was fitted with a Dean-Stark apparatus, a condenser, and then refluxed overnight. The solvent was removed in vacuo. The crude mixture was passed through a pad of neutral alumina using CH₂Cl₂ as the eluent to afford the corresponding ligand. (R,R)-Bis(5-phenyl-3-tert-butylsalicylidene)-1,2-cyclohexanediamine. The reaction was performed according to the General Procedure. The salen ligand was isolated as a yellow solid in 88% yield. ¹H NMR (500 MHz, CDCl₃, 298K) δ 13.94 (s, 2H), 8.34 (s, 2H), 7.46 (d, J = 2.3 Hz, 2H), 7.45-7.34 (m, 8H), 7.29-7.25 (m, 2H), 7.19 (d, J = 2.3 Hz, 2H), 3.46-3.34 (m, 2H), 3.29-3.19 (m, 4H), 2.94-2.87 (m, 4H), 2.28-2.19 (m, 4H), 1.96-1.87 (m, 4H), 1.64-1.55 (m, 4H), 1.30-1.20 (m, 4H), 0.89-0.80 (m, 4H).
2.11-2.00 (d, J = 12.6 Hz, 2H), 1.98-1.87 (m, 1H), 1.86-1.74 (m, 1H), 1.44 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$, 298K) δ 165.74, 159.88, 141.05, 137.49, 130.86, 128.60, 128.43, 128.16, 126.64, 126.44, 118.65, 72.38, 34.91, 33.04, 29.34, 24.30; IR (NaCl, thin film) 2936.0, 1628.8, 1441.6, 1170.2, 763.4 cm$^{-1}$.

(R,R)-Bis(5-trimethylbenzene-3-tert-butylsalicylidene)-1,2-cyclohexanediamine. The reaction was performed according to the General Procedure. The salen ligand was isolated as a yellow solid in 90% yield. [$\alpha$]$^\text{D}_{23}$ 156.00$^\circ$ (c 1.00, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$, 298K) δ 13.87, (s, 2H), 8.29 (s, 2H), 7.01 (s, 2H), 6.91 (s, 2H), 6.89 (s, 2H), 6.79 (s, 2H), 3.40-3.33 (m, 2H), 2.39 (s, 6H), 2.04-2.00 (m, 2H), 1.98 (s, 6H), 1.92-1.87 (m, 7H), 1.85 (s, 6H), 1.80-1.71 (m, 2H), 1.51-1.45 (m, 2H), 1.36 (s, 18H); $^{13}$C NMR (125 MHz, CDCl$_3$, 298K) δ 165.59, 158.85, 138.66, 137.07, 136.53, 136.48, 136.40, 130.72, 130.05, 128.02, 118.53, 72.44, 34.82, 33.07, 29.45, 24.27, 20.98, 20.85; IR (NaCl, thin film) 2947.4, 1627.9, 1442.8, 1265.2, 1174.1, 908.9, 850.1, 729.8 cm$^{-1}$; HRMS (ESI, m/z) calcd for C$_{46}$H$_{58}$N$_2$O$_2$H$^+$ 671.4571, found 671.4572.

(R,R)-Bis(5-triisopropylbenzene-3-tert-butylsalicylidene)-1,2-cyclohexanediamine. The reaction was performed according to the General Procedure. The salen ligand was isolated as a yellow solid in 77% yield. $^1$H NMR (500 MHz, CDCl$_3$, 298K) δ 13.88 (s, 2H), 8.36 (s, 2H), 7.08 (s, 2H), 7.03 (s, 4H), 6.89 (s, 2H), 3.48-3.41 (m, 2H), 2.97-2.88 (m, 2H), 2.67-2.56 (m, 4H), 1.97 (s, J = 13.1 Hz, 2H), 1.91-1.85 (m, 2H), 1.77-1.67 (m, 2H), 1.52-1.45 (m, 2H), 1.36 (s, 18H), 1.30 (d, J = 7.0 Hz, 12H), 1.10-0.99 (m, 24H); $^{13}$C NMR (125 MHz, CDCl$_3$, 298K) δ 165.37, 158.85, 147.69, 147.09, 136.80, 135.31, 131.37, 130.32, 129.87, 120.55, 120.49, 118.27, 72.22, 34.83, 34.24, 33.55, 30.21, 29.51, 24.45, 24.20, 24.07; IR (NaCl, thin film) 2958.9, 1629.4, 1436.5, 1267.0, 1168.2, 731.2 cm$^{-1}$. 
Supporting Information, Hutson, Türkmen, and Rawal, J. Am. Chem. Soc. 2013

(R,R)-Bis(5-(tri-tert-butylbenzene)-3-tert-butylsalicylidene)-1,2-cyclohexanediamine. The reaction was performed according to the General Procedure. The salen ligand was isolated as a yellow solid in 88% yield. $^1$H NMR (500 MHz, CDCl$_3$, 298K) $\delta$ 13.87 (s, 2H), 8.29 (s, 2H), 7.50 (s, 2H), 7.48 (s, 2H), 7.22 (s, 2H), 6.97 (s, 2H), 3.41-3.33 (m, 2H), 2.01 (s, $J = 11.6$ Hz, 2H), 1.92-1.83 (m, 2H), 1.78-1.67 (s, 2H), 1.57-1.42 (m, 4H), 1.35 (s, 18H), 1.34 (s, 18H), 1.07 (s, 18H), 0.97 (s, 18H); $^{13}$C NMR (125 MHz, CDCl$_3$, 298K) $\delta$ 165.07, 159.32, 148.81, 148.59, 148.10, 138.05, 135.65, 134.76, 134.21, 130.96, 122.10, 122.06, 116.52, 72.64, 37.53, 37.44, 34.98, 34.65, 33.58, 33.54, 33.11, 31.48, 29.70, 29.52, 24.15; IR (NaCl, thin film) 2952.6, 1629.1, 1445.4, 1266.1, 1171.9, 733.1 cm$^{-1}$. General Procedure: Synthesis of Biaryl Chloro-Chromium-Salen Complexes. A round-bottom flask was charged with salen ligand (0.203 mmol), CrCl$_2$ (0.244 mmol), and dry THF (4 mL) and stirred at 55 °C. After 3 hours, the reaction was cooled to room temperature, exposed to air, and stirred overnight. The mixture was diluted with MTBE (20mL) and then washed with saturated aqueous NH$_4$Cl (10 mL x 7) and brine (10 mL x 2). The product was dried over Na$_2$SO$_4$. In vacuo solvent removal gave the desired product as a brown solid in 80% - 99% yield. General Procedure: Synthesis of Biaryl Hexafluoroantimonate-Chromium-Salen Complexes. To a solution of chromium (III) chloride complex (0.163 mmol) in dry CH$_2$Cl$_2$ (2.8 mL) was added AgSbF$_6$ (0.163 mmol) under light sensitive conditions. The reaction mixture was stirred at room temperature overnight while wrapped in aluminum foil. The dark brown mixture was passed through a pad of Celite® and concentrated in vacuo, affording a brown solid in >90% yield.
Synthesis of Divinyl Alcohols and Dienones:

(E)-1-(3,4-dihydro-2H-pyran-6-yl)-2-methyl-3-phenylprop-2-en-1-ol. The title compound was synthesized according to a published method and isolated as a yellow oil in 57% yield. Analytical data matched previously reported values.\(^1\)

(E)-1-(3,4-dihydro-2H-pyran-6-yl)-2-methyl-3-(naphthalen-2-yl)prop-2-en-1-ol. The title compound was synthesized according to a published method.\(^1\) Flash chromatography on silica gel (9:1 hexanes:EtOAc) afforded the title compound as a yellow oil in 80% yield. \(^1\)H NMR (500 MHz, CDCl\(_3\), 298K) \(\delta\) 7.88-7.74 (m, 4H), 7.49-7.42 (m, 3H), 6.78 (s, 1H), 4.91 (t, \(J = 3.8\) Hz, 1H), 4.56 (br s, 1H), 4.14-4.01 (m, 2H), 2.25 (d, \(J = 4.9\) Hz, 1H), 2.14-2.06 (m, 2H), 1.95 (s, 3H), 1.90-1.82 (m, 2H); \(^1\)C NMR (125 MHz, CDCl\(_3\), 298K) \(\delta\) 153.18, 137.92, 135.26, 133.31, 132.08, 127.88, 127.67, 127.56, 127.44, 126.28, 125.95, 125.60, 97.98, 77.58, 66.56, 22.39, 20.03, 14.66; IR (NaCl, thin film) 3421.8, 2938.0, 2847.9, 1675.0, 1273.0, 1231.5, 1086.5, 1062.5, 915.6, 818.5, 744.5 cm\(^{-1}\).

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\(^1\) Liang, G.; Gradl, N.; Trauner, D. *Org. Lett.* **2003**, 5, 4931-4934.
(E)-3-(4-bromophenyl)-1-(3,4-dihydro-2H-pyran-6-yl)-2-methylprop-2-en-1-ol. The title compound was synthesized according to a published method.\(^1\) Flash chromatography on silica gel (9:1 hexanes:EtOAc) afforded the title compound as a yellow oil in 87% yield.\(^1\) \(\text{H} \text{NMR} \quad (500 \text{ MHz, CDCl}_3, 298 \text{K}) \delta 7.44 \text{ (d, } J = 8.4 \text{ Hz, 2H), 4.17 \text{ (d, } J = 8.4 \text{ Hz, 2H), 6.56 \text{ (s, 1H), 4.86 \text{ (t, } J = 3.9 \text{ Hz, 1H), 4.48 \text{ (d, } J = 5.0 \text{ Hz, 1H), 4.09-3.97 \text{ (m, 2H), 2.23 \text{ (br s, 1H), 2.10-2.04 \text{ (m, 2H), 1.86-1.81 \text{ (m, 2H), 1.84 \text{ (s, 3H); 13C NMR (125 MHz, CDCl}_3, 298 \text{K}) } \delta 152.93, 138.25, 136.60, 131.12, 130.65, 124.99, 120.18, 98.14, 77.39, 66.54, 22.33, 19.98, 14.56; IR (NaCl, thin film) 3424.6, 2928.6, 2847.6, 1675.5, 1486.8, 1274.9, 1231.5, 1063.1, 1008.7, 916.8 \text{ cm}^{-1}.\)

(E)-3-(2-bromophenyl)-1-(3,4-dihydro-2H-pyran-6-yl)-2-methylprop-2-en-1-ol. The title compound was synthesized according to a published method.\(^1\) Flash chromatography on silica gel (9:1 hexanes:EtOAc) afforded the title compound as a yellow oil in 82% yield.\(^1\) \(\text{H} \text{NMR} \quad (500 \text{ MHz, CDCl}_3, 298 \text{K}) \delta 7.56 \text{ (d, } J = 7.8 \text{ Hz, 1H), 7.31-7.24 \text{ (m, 2H), 7.12-7.06 \text{ (m, 1H), 6.64 \text{ (s, 1H), 4.90 \text{ (t, } J = 3.6 \text{ Hz, 1H), 4.55 \text{ (d, } J = 5.6 \text{ Hz, 1H), 4.11-4.00 \text{ (m, 2H), 2.30 \text{ (d, } J = 5.6 \text{ Hz, 1H), 2.12-2.05 \text{ (m, 2H), 1.88-1.80 \text{ (m, 2H), 1.74 \text{ (d, } J = 1.1 \text{ Hz, 3H); 13C NMR (125 MHz, CDCl}_3, 298 \text{K}) } \delta 153.08, 139.07, 137.94, 132.53, 130.93, 128.15, 126.85, 125.89, 124.39, 98.13, 77.36, 66.63, 22.46, 20.11, 14.53; IR (NaCl, thin film) 3430.2, 2928.8, 2847.5, 1675.5, 1465.4, 1433.1, 1231.5, 1063.0, 1024.1, 917.2 \text{ cm}^{-1}.\)
The title compound was synthesized according to a published method. ¹ Flash chromatography on silica gel (9:1 hexanes:EtOAc) afforded the title compound as a yellow oil in 90% yield. ¹H NMR (500 MHz, CDCl₃, 298K) δ 7.37 (d, J = 2.1 Hz, 1H), 6.45 (s, 1H), 6.41-6.37 (m, 1H), 6.28 (d, J = 3.3 Hz, 1H), 4.84 (t, J = 3.8 Hz, 1H), 4.46 (d, J = 5.5 Hz, 1H), 4.07-3.95 (m, 2H), 2.21 (d, J = 5.5 Hz, 1H), 2.09-2.02 (m, 2H), 1.97 (s, 3H), 1.86-1.76 (m, 2H); ¹³C NMR (125 MHz, CDCl₃, 298K) δ 153.15, 152.87, 141.20, 135.89, 114.84, 111.10, 108.99, 98.18, 77.25, 66.52, 22.30, 19.97, 15.16; IR (NaCl, thin film) 3421.8, 2929.7, 1675.7, 1350.4, 1232.2, 1154.3, 1063.0, 917.4, 732.9 cm⁻¹.

The title compound was synthesized according to a published method. ¹ Flash chromatography on silica gel (9:1 hexanes:EtOAc) afforded the title compound as a yellow oil in 79% yield. ¹H NMR (500 MHz, CDCl₃, 298K) δ 7.53 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.27-7.18 (m, 2H), 6.63 (s, 1H), 6.59 (s, 1H), 4.88 (t, J = 3.4 Hz, 1H), 4.52 (br s, 1H), 4.09-3.98 (m, 2H), 2.30 (br s, 1H), 2.12 (s, 3H), 2.10-2.05 (m, 2H), 1.88-1.80 (m, 2H); ¹³C NMR (125 MHz, CDCl₃, 298K) δ 155.11, 154.30, 152.68, 140.10, 128.83, 123.96, 122.62, 120.60, 114.69, 110.88, 105.47, 98.60, 77.27, 66.58, 22.28, 19.99, 15.68; IR (NaCl, thin film) 3420.1, 2929.2, 1674.7, 1452.2, 1232.2, 1154.3, 1062.3, 750.4 cm⁻¹.
(E)-1-(3,4-dihydro-2H-pyran-6-yl)-2-methyl-3-(thiopen-2-yl)prop-2-en-1-ol. The title compound was synthesized according to a published method.\textsuperscript{1} Flash chromatography on silica gel (9:1 hexanes:EtOAc) afforded the title compound as a yellow oil in 71\% yield.\textsuperscript{1} \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, 298K) \( \delta \) 7.28-7.24 (m, 1H), 7.04-7.00 (m, 2H), 6.79 (s, 1H), 4.85 (t, \( J = 3.8 \) Hz, 1H), 4.51 (d, \( J = 5.4 \) Hz, 1H), 4.08-3.96 (m, 2H), 2.20 (d, \( J = 5.4 \) Hz, 1H), 2.10-2.03 (m, 2H), 1.97 (s, 3H), 1.85-1.78 (m, 2H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}, 298K) \( \delta \) 152.93, 140.78, 135.41, 127.23, 126.72, 124.89, 119.56, 98.05, 77.43, 66.50, 22.30, 19.96, 15.22; IR (NaCl, thin film) 3423.4, 2929.1, 1674.7, 1231.5, 1062.6, 9168, 695.9 cm\textsuperscript{-1}.

1-(5,6-Dihydro-4H-pyran-2-yl)-2-methyl-but-2-en-1-ol. The title compound was synthesized according to a published method. Analytical data matched previously reported values and obtained as a pale yellow oil in 86\% yield.\textsuperscript{1}

**General Procedure: Synthesis of Cyclohexenyl Divinyl Alcohols.** To a solution of 1-bromocyclohexene (2.50 mmol) in dry diethyl ether (0.5 mL) at -78°C was added \( t \)-BuLi (1.7M pentane solution, 5.50 mmol) over 15 minutes. After stirring at room temperature for 1 hour, the solution was cooled to -78 °C, charged with unsaturated aldehyde (3.00 mmol) in diethyl ether (1.5 mL), and then warmed to 0 °C. After 1 hour, the reaction mixture was quenched with H\textsubscript{2}O (10 mL), diluted with a 1:1 diethyl ether/hexanes solution (20 mL), then transferred to a separatory funnel. The two layers were separated and the organic layer was washed with brine (2 x 15 mL). The aqueous layer was extracted with a 1:1 diethyl ether/hexanes solution (2 x 20 mL) and then the organic layers were combined and then dried over MgSO\textsubscript{4}. Flash chromatography on silica gel (20:1 hexanes:EtOAc) afforded the corresponding alcohol.
(E)-1-cyclohexenyl-2-methyl-3-phenylprop-2-en-1-ol. The reaction was performed according to the General Procedure. Flash chromatography on silica gel afforded the title compound as a pale yellow oil in 50% yield. $^1$H NMR (500 MHz, CDCl$_3$, 298K) $\delta$ 7.36-7.19 (m, 5H), 6.61 (s, 1H), 5.84 (br s, 1H), 4.51 (s, 1H), 2.12-1.82 (m, 4H), 1.77 (s, 3H), 1.66-1.54 (m, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$, 298K) $\delta$ 138.35, 137.79, 137.70, 128.95, 128.06, 126.31, 125.62, 123.78, 81.06, 25.08, 24.25, 22.66, 22.54, 14.07; IR (NaCl, thin film) 3361.0, 2925.4, 1445.9, 1029.9, 749.4, 698.3 cm$^{-1}$.

(E)-1-cyclohexenyl-2-methylbut-2-en-1-ol. The reaction was performed according to the General Procedure. Flash chromatography on silica gel afforded the title compound as a yellow oil in 91% yield. $^1$H NMR (500 MHz, CDCl$_3$, 298K) $\delta$ 5.75 (br s, 1H), 5.54 (q, $J$ = 6.8 Hz, 1H), 4.31 (br s, 1H), 2.05 (br s, 2H), 1.87-1.72 (m, 2H), 1.62-1.52 (m, 4H), 1.52 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$, 298K) $\delta$ 137.95, 136.06, 122.36, 120.71, 80.79, 25.00, 24.56, 22.68, 22.62, 13.17, 11.68; IR (NaCl, thin film) 3361.3, 2924.7, 1437.7, 1025.0, 918.7 cm$^{-1}$.

(E)-1-cyclohexenyl-2-methylpent-2-en-1-ol. The reaction was performed according to the General Procedure. Flash chromatography on silica gel afforded the title compound as a yellow oil in 69% yield. $^1$H NMR (500 MHz, CDCl$_3$, 298K) $\delta$ 5.75 (br s, 1H), 5.46 (t, $J$ = 7.0 Hz, 1H), 4.30 (br s, 1H), 2.10-1.99 (m, 4H), 1.80 (g, $J$ = 17.5 Hz, 2H), 1.65-1.55 (m, 4H), 1.52 (br s, 1H), 1.49 (s, 3H), 0.98 (t, $J$ = 7.6 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$, 298K) $\delta$ 137.89, 134.53,
128.36, 122.45, 80.73, 25.01, 24.46, 22.68, 22.61, 20.96, 14.12, 11.81; IR (NaCl, thin film)
3367.4, 2929.1, 1437.9, 1023.9, 918.3 cm\(^{-1}\).

(\textit{E})-3-(4-bromophenyl)-1-cyclohexenyl-2-methylprop-2-en-1-ol. The reaction was performed according to the General Procedure. Flash chromatography on silica gel afforded the title compound as a yellow oil in 62\% yield. \(^1\)H NMR (500 MHz, CDCl\(_3\), 298K) \(\delta\) 7.44 (d, \(J = 8.2\) Hz, 2H), 7.15 (d, \(J = 8.2\) Hz, 2H), 6.54 (s, 1H), 5.85-5.81 (m, 1H), 4.48 (br s, 1H), 2.11-2.05 (m, 2H), 2.00-1.91 (m, 1H), 1.89-1.81 (m, 1H), 1.73 (d, \(J = 1.2\) Hz, 3H), 1.69 (d, \(J = 3.3\) Hz, 1H), 1.65-1.54 (m, 4H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\), 298K) \(\delta\) 139.20, 137.58, 136.70, 131.16, 130.56, 124.35, 124.23, 120.11, 80.93, 25.08, 24.13, 22.63, 22.50, 14.20; IR (NaCl, thin film) 3376.6, 2924.7, 1486.4, 1008.8, 794.5 cm\(^{-1}\).

(E)-1-cyclohexenyl-2-methyl-3-p-tolylprop-2-en-1-ol. The reaction was performed according to the General Procedure. Flash chromatography on silica gel (5\% to 7.5\% EtOAc in hexanes) afforded the title compound as a yellow oil in 88\% yield. \(^1\)H NMR (500 MHz, CDCl\(_3\), 298K) \(\delta\) 7.19 (d, \(J = 8.1\) Hz, 2H), 7.14 (d, \(J = 8.0\) Hz, 2H), 6.56 (s, 1H), 5.84-5.82 (m, 1H), 4.48 (s, 1H), 2.34 (s, 3H), 2.09-2.07 (m, 2H), 1.98-1.92 (m, 1H), 1.89-1.83 (m, 1H), 1.76 (d, \(J = 1.5\) Hz, 3H), 1.64-1.54 (m, 4H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\), 298K) \(\delta\) 137.7, 137.6, 136.0, 134.8, 128.83, 128.75, 125.6, 123.5, 81.1, 25.1, 24.3, 22.7, 22.5, 21.1, 14.0; IR (NaCl, thin film) 3371 (br), 2924, 2856, 1512, 1446, 1138, 1036 cm\(^{-1}\).
(E)-1-cyclohexenyl-3-(furan-2-yl)-2-methylprop-2-en-1-ol The reaction was performed according to the General Procedure. Flash chromatography on silica gel (19:1 to 9:1 hexanes:EtOAc) afforded the title compound as a yellow oil in 81% yield. $^1$H NMR (500 MHz, CDCl$_3$, 298K) $\delta$ 7.38 (dd, $J = 1.8, 0.6$ Hz, 1H), 6.43 (app s, 1H), 6.41 (ddd, $J = 3.3, 1.8, 0.4$ Hz, 1H), 6.28 (d, $J = 3.4$ Hz, 1H), 5.83-5.81 (m, 1H), 4.47 (s, 1H), 2.09-2.06 (m, 2H), 1.96-1.90 (m, 1H), 1.88 (d, $J = 1.0$ Hz, 3H), 1.85-1.79 (m, 1H), 1.63-1.53 (m, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$, 298K) $\delta$ 153.3, 141.1, 137.6, 137.1, 124.2, 114.2, 111.1, 108.6, 80.8, 25.1, 24.1, 22.6, 22.5, 14.8; IR (NaCl, thin film) 3363 (br), 2926, 1490, 1438, 1138, 1015 cm$^{-1}$; HRMS (ESI, m/z) calcd for C$_{18}$H$_{20}$O$_2$Na$^+$ 291.1356, found 291.1354.

(E)-3-(benzofuran-2-yl)-1-cyclohexenyl-2-methylprop-2-en-1-ol. The reaction was performed according to the General Procedure. Flash chromatography on silica gel (19:1 to 9:1 hexanes:EtOAc) afforded the title compound as a yellow oil in 80% yield. $^1$H NMR (500 MHz, CDCl$_3$, 298K) $\delta$ 7.52 (dt, $J = 7.6, 0.6$ Hz, 1H), 7.44 (d, $J = 7.9$ Hz, 1H), 7.24 (dt, $J = 8.3, 1.4$ Hz, 1H), 7.18 (dt, $J = 7.6, 1.0$ Hz, 1H), 6.62 (s, 1H), 6.57 (s, 1H), 5.85 (br s, 1H), 4.53 (s, 1H), 2.11-2.06 (m, 2H), 2.01 (d, $J = 0.5$ Hz, 3H), 1.99-1.95 (m, 1H), 1.87-1.82 (m, 1H), 1.76 (br s, 1H), 1.65-1.54 (m, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$, 298K) $\delta$ 155.2, 154.3, 141.3, 137.4, 128.9, 125.0, 123.9, 122.7, 120.6, 114.0, 110.9, 105.1, 80.9, 25.1, 23.9, 22.6, 22.5, 15.4; IR (NaCl, thin film) 3373 (br), 2926, 1492, 1438, 1138, 924 cm$^{-1}$; HRMS (ESI, m/z) calcd for C$_{18}$H$_{20}$O$_2$Na$^+$ 291.1356, found 291.1354.
(E)-1-cyclohexenyl-2-methyl-3-(thiophen-2-yl)prop-2-en-1-ol. The reaction was performed according to the General Procedure. Flash chromatography on silica gel (19:1 hexanes:EtOAc) afforded the title compound as a yellow oil in 92% yield. $^1$H NMR (500 MHz, CDCl$_3$, 298K) $\delta$ 7.26-7.24 (m, 1H), 7.03, 7.01 (m, 2H), 6.76-6.75 (m, 1H), 5.83-5.81 (m, 1H), 4.50 (s, 1H), 2.10-2.05 (m, 2H), 1.96-1.89 (m, 1H), 1.87 (d, $J$ = 1.0 Hz, 3H), 1.76 (br s, 1H), 1.64-1.52 (m, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$, 298K) $\delta$ 140.9, 137.6, 136.6, 127.0, 126.8, 124.7, 124.0, 118.9, 81.0, 25.1, 24.2, 22.6, 22.5, 14.8; IR (NaCl, thin film) 3359 (br), 2926, 2855, 2835, 1436, 1139, 1051, 1033 cm$^{-1}$.

General Synthesis of Divinyl Ketones. Divinyl ketones were synthesized according to a reported procedure by Trauner.$^1$ Flash chromatography on silica gel afforded the corresponding ketone.

(E)-1-(3,4-dihydro-2H-pyran-6-yl)-2-methyl-3-(naphthalen-2-yl)prop-2-en-1-one (2a) The title compound was synthesized according to a published method and isolated as a yellow oil in 68% yield. Analytical data matched previously reported values.$^1$

(E)-1-(3,4-dihydro-2H-pyran-6-yl)-2-methyl-3-(naphthalen-2-yl)prop-2-en-1-one (2b) The title compound was synthesized according to a published method.$^1$ Flash chromatography on silica gel (9:1 hexanes:EtOAc) afforded the title compound as a yellow solid in 65% yield. $^1$H NMR (500 MHz, CDCl$_3$, 298K) $\delta$ 7.91-7.80 (m, 4H), 7.56-7.47 (m, 3H), 7.41 (s, 1H), 5.87 (t, $J$ = 3.7 Hz, 1H), 4.19 (m, 2H), 2.31-2.25 (m, 2H), 2.23 (s, 3H), 1.97-1.91 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$, 298K) $\delta$ 193.67, 151.30, 138.89, 136.07, 133.34, 133.06, 132.83, 129.22, 128.22,
127.92, 127.62, 127.00, 126.65, 126.41, 113.10, 66.42, 21.56, 20.88, 14.87; IR (NaCl, thin film) 2930.5, 1644.4, 1623.5, 1259.1, 1220.0, 1062.1, 1018.9, 818.2, 744.2 cm\(^{-1}\).

**Figure 1.** (E)-1-(3,4-dihydro-2H-pyran-6-yl)-2-methyl-3-(naphthalen-2-yl)prop-2-en-1-one (2c) The title compound was synthesized according to a published method.\(^1\) Flash chromatography on silica gel (9:1 hexanes:EtOAc) afforded the title compound as a yellow solid in 65% yield. \(^1\)H NMR (500 MHz, CDCl\(_3\), 298K) \(\delta\) 7.91-7.80 (m, 4H), 7.56-7.47 (m, 3H), 7.41 (s, 1H), 5.87 (t, \(J = 3.8\) Hz, 1H), 4.19 (m, 2H), 2.31-2.25 (m, 2H), 2.23 (s, 3H), 1.97-1.91 (m, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\), 298K) \(\delta\) 193.67, 151.30, 138.89, 136.07, 133.34, 133.06, 132.83, 129.22, 128.22, 127.92, 127.62, 127.00, 126.65, 126.41, 113.10, 66.42, 21.56, 20.88, 14.87; IR (NaCl, thin film) 2930.5, 1644.4, 1623.5, 1259.1, 1220.0, 1062.1, 1018.9, 818.2, 744.2 cm\(^{-1}\).

**Figure 2.** (E)-3-(2-bromophenyl)-1-(3,4-dihydro-2H-pyran-6-yl)-2-methylprop-2-en-1-one (2d) The title compound was synthesized according to a published method.\(^1\) Flash chromatography on silica gel (9:1 hexanes:EtOAc) afforded the title compound as a yellow oil in 73% yield. \(^1\)H NMR (500 MHz, CDCl\(_3\), 298K) \(\delta\) 7.62 (d, \(J = 8.1\) Hz, 1H), 7.35-7.31 (m, 1H), 7.32 (s, 1H), 7.21-7.15 (m, 1H), 6.04 (t, \(J = 4.2\) Hz, 1H), 4.20-4.15 (m, 2H), 2.31-2.25 (m, 2H), 1.97 (s, 3H), 1.95-1.89 (m, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\), 298K) \(\delta\) 193.31, 150.85, 137.34, 137.01, 132.70, 130.41, 129.45, 127.08, 124.20, 114.67, 66.46, 21.50, 21.00, 14.44; IR (NaCl, thin film) 2930.1, 1653.1, 1624.4, 1464.4, 1287.2, 1221.2, 1062.8, 758.5 cm\(^{-1}\).

**Figure 3.** (E)-1-(3,4-dihydro-2H-pyran-6-yl)-3-(furan-2-yl)-2-methylprop-2-en-1-one (2e) The title compound was synthesized according to a published method.\(^1\) Flash chromatography on silica gel (9:1 hexanes:EtOAc) afforded the title compound as a yellow oil in 65% yield. \(^1\)H NMR (500 MHz, CDCl\(_3\), 298K) \(\delta\) 7.54 (d, \(J = 3.4\) Hz, 1H), 7.16 (s, 1H), 6.63 (d, \(J = 3.4\) Hz, 1H), 6.52-6.50 (m, 1H), 5.71 (t, \(J = 4.8\) Hz, 1H), 4.19-4.12 (m, 2H), 2.27-2.21 (m, 2H), 2.19 (s, 3H), 1.94-1.87 (m, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\), 298K) \(\delta\) 192.77, 151.82, 151.26, 144.01, 132.51, 127.04, 114.63, 112.21, 111.86, 66.40, 21.58, 20.76, 14.74; IR (NaCl, thin film) 2932.3, 1619.1, 1475.7, 1278.4, 1061.2, 921.2, 742.8 cm\(^{-1}\).
(E)-3-(benzofuran-2-yl)-1-(3,4-dihydro-2H-pyran-6-yl)-2-methylprop-2-en-1-one (2f) The title compound was synthesized according to a published method. Purification by column chromatography afforded the title compound as a yellow oil in 72% yield. $^1$H NMR (500 MHz, CDCl$_3$, 298K) $\delta$ 7.60 (d, $J = 8.1$ Hz, 1H), 7.49 (d, $J = 8.1$ Hz, 1H), 7.36-7.31 (m, 1H), 7.28-7.22 (m, 1H), 7.21 (s, 1H), 6.94 (s, 1H), 5.80 (t, $J = 4.3$ Hz, 1H), 4.22-4.14 (m, 2H), 2.34 (s, 3H), 2.30-2.22 (m, 2H), 1.97-1.89 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$, 298K) $\delta$ 192.63, 155.11, 153.32, 151.16, 136.08, 128.34, 126.54, 125.71, 123.21, 121.46, 112.74, 111.30, 110.57, 66.44, 21.55, 20.85, 15.32; IR (NaCl, thin film) 2913.7, 1621.9, 1448.9, 1271.13, 1061.8, 1020.2, 921.2, 751.9 cm$^{-1}$.

(E)-1-(3,4-dihydro-2H-pyran-6-yl)-2-methyl-3-(thiopen-2-yl)prop-2-en-1-one (2g) The title compound was synthesized according to a published method. Flash chromatography on silica gel (9:1 hexanes:EtOAc) afforded the title compound as a yellow oil in 58% yield. $^1$H NMR (500 MHz, CDCl$_3$, 298K) $\delta$ 7.52 (d, $J = 5.2$ Hz, 1H), 7.50 (s, 1H), 7.27 (d, $J = 3.7$ Hz, 1H), 7.12 (dd, $J = 5.2$ Hz, 3.7 Hz, 1H), 5.73 (t, $J = 4.1$ Hz, 1H), 4.20-4.13 (m, 2H), 2.27-2.22 (m, 2H), 2.21 (s, 3H), 1.95-1.89 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$, 298K) $\delta$ 192.93, 151.34, 139.37, 132.58, 131.55, 129.36, 127.37, 112.00, 66.42, 21.61, 20.80, 15.06; IR (NaCl, thin film) 2931.0, 1636.3, 1605.2, 1518.2, 1267.4, 1060.4, 1015.9, 713.8 cm$^{-1}$.

1-(5,6-Dihydro-4H-pyran-2-yl)-2-methylbut-2-en-1-one (2h) The title compound was synthesized according to a published method and isolated as a pale yellow oil in 57% yield. Analytical data matched previously reported values.

(E)-1-cyclohexenyl-2-methylbut-2-en-1-one (8a) The title compound was synthesized according to a published method. Flash chromatography on silica gel (30:1 hexanes:EtOAc)
afforded the title compound as a pale yellow oil in 59% yield. $^1$H NMR (500 MHz, CDCl$_3$, 298K) $\delta$ 6.39 (br s, 1H), 6.27 (q, $J = 7.0$ Hz, 1H), 2.29-2.23 (m, 2H), 2.23-2.16 (m, 2H), 1.84-1.78 (m, 6H), 1.69-1.58 (m, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$, 298K) 200.69, 138.86, 138.34, 137.02, 136.36, 25.68, 24.41, 22.09, 21.73, 14.27, 12.54; IR (NaCl, thin film) 2928.4, 1634.6, 1434.5, 1255.4 cm$^{-1}$.

(E)-1-cyclohexenyl-2-methylbut-2-en-1-one (8b) The title compound was synthesized according to a published method.$^1$ Flash chromatography on silica gel (30:1 hexanes:EtOAc) afforded the title compound as a pale yellow oil in 75% yield. $^1$H NMR (500 MHz, CDCl$_3$, 298K) $\delta$ 6.44-6.38 (m, 1H), 6.13 (t, $J = 7.2$ Hz, 1H), 2.28-2.22 (m, 2H), 2.22-2.15 (m, 4H), 1.81 (s, 3H), 1.70-1.58 (m, 4H), 1.04 (t, $J = 7.7$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$, 298K) 200.83, 143.17, 139.15, 138.35, 135.28, 25.72, 24.38, 22.08, 21.95, 21.73, 13.24, 12.71; IR (NaCl, thin film) 2933.0, 1635.1, 1435.1, 1277.1 cm$^{-1}$.

(E)-1-cyclohexenyl-2-methyl-3-phenylprop-2-en-1-one (8c) The title compound was synthesized according to a published method.$^1$ Flash chromatography on silica gel (20:1 hexanes:EtOAc) afforded the title compound as a white solid in 60% yield. $^1$H NMR (500 MHz, CDCl$_3$, 298K) $\delta$ 7.41-7.37 (m, 4H), 7.34-7.28 (m, 1H), 7.03 (s, 1H), 6.63 (br s, 1H), 2.37-2.32 (m, 2H), 2.28-2.22 (m, 2H), 2.11 (s, 3H), 1.75-1.64 (m, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$, 298K) $\delta$ 200.93, 140.60, 138.44, 137.60, 136.88, 136.15, 129.46, 128.36, 127.99, 25.91, 24.33, 22.08, 21.72, 14.88; IR (NaCl, thin film) 2930.5, 1630.1, 1446.8, 1235.2, 1007.5, 767.8, 697.6 cm$^{-1}$.

(E)-3-(4-bromophenyl)-1-cyclohexenyl-2-methylprop-2-en-1-one (8d) The title compound was synthesized according to a published method.$^1$ Flash chromatography on silica gel (20:1 hexanes:EtOAc) afforded the title compound as a yellow solid in 71% yield. $^1$H NMR (500 MHz, CDCl$_3$, 298K) $\delta$ 4.51 (d, $J = 8.6$ Hz, 2H), 7.25 (d, $J = 8.6$ Hz, 2H), 6.92 (s, 1H), 6.64-6.61 (m, 1H), 2.36-2.31 (m, 2H), 2.28-2.23(m, 2H), 2.08 (d, $J = 1.5$ Hz, 3H), 1.74-1.63 (m, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$, 298K) $\delta$ 200.55, 141.05, 138.37, 137.61, 135.88, 135.01, 131.55,
130.95, 122.03, 25.95, 24.23, 22.03, 21.68, 14.98; IR (NaCl, thin film) 2927.1, 1627.8, 1486.2, 1233.4, 1006.2 cm⁻¹.

\( \text{(E)-1-cyclohexenyl-2-methyl-3-p-tolylprop-2-en-1-one} \) (8e). The title compound was synthesized according to a published method.¹ Flash chromatography on silica gel (19:1 hexanes:EtOAc) afforded the title compound as a white solid in 92% yield. ¹H NMR (500 MHz, CDCl₃, 298K) \( \delta \) 7.31 (d, \( J = 8.1 \) Hz, 2H), 7.20 (d, \( J = 7.9 \) Hz, 2H), 7.03 (s, 1H), 6.60-6.57 (m, 1H), 2.38 (s, 3H), 2.36-2.33 (m, 2H), 2.27-2.22 (m, 2H), 2.12 (d, \( J = 1.0 \) Hz, 3H), 1.74-1.69 (m, 2H), 1.69-1.64 (m, 2H); \( ^{13} \)C NMR (125 MHz, CDCl₃, 298K) \( \delta \) 201.1, 140.1, 138.5, 138.10, 138.05, 136.0, 133.3, 129.5, 129.1, 25.9, 24.4, 22.1, 21.7, 21.3, 14.8; IR (NaCl, thin film) 2930, 2859, 1630, 1511, 1436, 1316, 1236 cm⁻¹.

\( \text{(E)-1-cyclohexenyl-3-(furan-2-yl)-2-methylprop-2-en-1-one} \) (8f). The title compound was synthesized according to a published method.¹ Flash chromatography on silica gel (19:1 hexanes:EtOAc) afforded the title compound as a brown solid in 88% yield. ¹H NMR (500 MHz, CDCl₃, 298K) \( \delta \) 7.53 (d, \( J = 1.7 \) Hz, 1H), 6.95 (d, \( J = 1.2 \) Hz, 1H), 6.60 (d, \( J = 3.5 \) Hz, 1H), 6.51 (ddd, \( J = 3.4, 1.8, 0.4 \) Hz, 1H), 6.47 (sep, \( J = 1.7 \) Hz, 1H), 2.34-2.31 (m, 2H), 2.26-2.22 (m, 2H), 2.19 (d, \( J = 1.0 \) Hz, 3H), 1.73-1.63 (m, 4H); \( ^{13} \)C NMR (125 MHz, CDCl₃, 298K) \( \delta \) 200.2, 151.9, 143.6, 138.9, 138.1, 133.6, 126.2, 113.8, 112.0, 25.7, 24.5, 22.0, 21.6, 14.8; IR (NaCl, thin film) 2933, 2859, 1621, 1479, 1276, 1257, 1209 cm⁻¹.

\( \text{(E)-3-(benzofuran-2-yl)-1-cyclohexenyl-2-methylprop-2-en-1-one} \) (8g). The title compound was synthesized according to a published method.¹ Flash chromatography on silica gel (19:1 hexanes:EtOAc) afforded the title compound as a white solid in 90% yield. ¹H NMR (500 MHz, CDCl₃, 298K) \( \delta \) 7.59 (ddd, \( J = 7.8, 1.3, 0.7 \) Hz, 1H), 7.49 (dq, \( J = 8.3, 0.9 \) Hz, 1H), 7.33 (ddd, \( J \)
Supporting Information, Hutson, Türkmen, and Rawal, J. Am. Chem. Soc. 2013

$\delta$ 199.9, 154.9, 153.5, 140.3, 138.1, 137.4, 128.4, 125.49, 125.45, 123.1, 121.3, 111.2, 109.7, 25.8, 24.4, 22.0, 21.7, 15.5; IR (NaCl, thin film) 2933, 2859, 1627, 1553, 1450, 1229, 1011 cm$^{-1}$; HRMS (ESI, m/z) calcd for C$_{18}$H$_{18}$O$_2$Na$^+$ 289.1199, found 289.1196.

(E)-1-cyclohexenyl-2-methyl-3-(thiophen-2-yl)prop-2-en-1-one (8h). The title compound was synthesized according to a published method.$^1$ Flash chromatography on silica gel (19:1 hexanes:EtOAc) afforded the title compound in 84% yield as a yellow oil which solidified upon standing in the refrigerator. $^1$H NMR (500 MHz, CDCl$_3$, 298K) $\delta$ 7.49 (d, $J = 5.1$ Hz, 1H), 7.31 (s, 1H), 7.25 (d, $J = 3.6$ Hz, 1H), 7.13-7.11 (m, 1H), 6.50-6.48 (m, 1H), 2.36-2.33 (m, 2H), 2.26-2.23 (m, 2H), 2.20 (s, 3H), 1.74-1.68 (m, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$, 298K) $\delta$ 200.3, 139.6, 139.2, 138.4, 133.8, 131.6, 130.9, 128.8, 127.3, 25.8, 24.6, 22.1, 21.7, 15.1; IR (NaCl, thin film) 2933, 2858, 1628, 1609, 1275, 1258, 1207, 1007 cm$^{-1}$.

General Procedure A: Catalyst, Counterion, and Solvent Screens for Salen-Catalyzed Nazarov Cyclizations A test tube was charged with chromium salen complex (0.00605 mmol), silver salt (0.0055 mmol), dry 4Å molecular sieves, and dry solvent (0.2 mL). The mixture was stirred under argon for 1.5 hours. A solution of divinyl ketone (0.110 mmol) in dry CH$_2$Cl$_2$ (0.5 mL) was added by cannula. The reaction was passed through a silica pipet column using 4:1 Hexanes/ EtOAc. In vacuo solvent removal gave the desired product.

General Procedure B: Salen-Catalyzed Nazarov Cyclization Reaction A 5 mL round-bottom flask was charged with chromium salen complex (0.0110 mmol), dry 4Å molecular sieves, and dry CH$_2$Cl$_2$ (0.5 mL). A solution of divinyl ketone (0.219 mmol) in dry CH$_2$Cl$_2$ (0.8 mL) was added by cannula. The reaction was monitored by TLC until complete, and then chromatographed directly on silica gel to give the corresponding cyclopentenone.

(5R, 6R) - 5-(4-bromophenyl)-6-methyl-3,4,5,6-tetrahydrocyclopenta[h]pyran-7(2H)-one (3a) The reaction was performed according to General Procedure B. Flash chromatography on
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Silica gel (4:1 hexanes:EtOAc) afforded the title compound as a pale yellow oil in 85% yield. Analytical data matched previously reported values.2 [α]D 23 +36.80° (c = 0.100, CHCl3); HPLC: AS-H, 95% Hexanes, 5% i-PrOH, 1.0 mL/min, 23.8 min (minor), 47.9 min (major).

(5R, 6R) - 5-(4-bromophenyl)-6-methyl-3,4,5,6-tetrahydrocyclopenta[b]pyran-7(2H)-one (3b) The reaction was performed according to General Procedure B. Flash chromatography on silica gel (4:1 hexanes:EtOAc) afforded the title compound as a yellow oil in 81% yield. Analytical data matched previously reported values.2 HPLC: AS-H, 93% Hexanes, 7% i-PrOH, 1.0 mL/min, 25.8 min (minor), 37.2 min (major).

(5R, 6R) - 5-(4-bromophenyl)-6-methyl-3,4,5,6-tetrahydrocyclopenta[b]pyran-7(2H)-one (3c) The reaction was performed according to General Procedure B. Flash chromatography on silica gel (4:1 hexanes:EtOAc) afforded the title compound as a yellow oil in 90% yield. [α]D 22 +18.29° (c 0.83, CHCl3); 1H NMR (500 MHz, CDCl3, 298K) δ 7.43 (d, J = 8.3 Hz, 2H), 6.90 (d, J = 8.3 Hz, 2H), 4.26-4.11 (m, 2H), 3.98 (d, J = 6.7 Hz, 1H), 2.79-2.71 (m, 1H), 2.21-2.10 (m, 2H), 2.03-1.88 (m, 2H), 0.68 (d, J = 7.6 Hz, 3H); 13C NMR (125 MHz, CDCl3, 298K) δ 202.50, 151.74, 144.09, 137.71, 131.64, 130.49, 121.00, 67.08, 48.30, 42.99, 22.39, 21.57, 12.33; IR (NaCl, thin film) 2932.9, 1710.4, 1406.7, 1139.7, 837.0 cm⁻¹; HRMS (ESI, m/z) calcd for C15H15BrO2Na⁺ 329.0148, found 329.0149; HPLC: AS-H, 93% Hexanes, 7% i-PrOH, 1.0 mL/min, 24.2 min (minor), 28.8 min (major).

(5R, 6R) - 5-(2-bromophenyl)-6-methyl-3,4,5,6-tetrahydrocyclopenta[b]pyran-7(2H)-one (3d) The reaction was performed according to General Procedure B. Flash chromatography on silica gel (4:1 hexanes:EtOAc) afforded the title compound as a pale yellow oil in 86% yield. 1H NMR (500 MHz, CDCl3, 298K) δ 7.59 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.26-7.21 (m, 1H), 7.13-

2 Reuping, M.; Ieawsuwan, W.; Antonchick, A. P.; Nachtsheim, B. J. Angew. Chem., Int. Ed. 2007, 46, 2097-2100.
7.09 (m, 1H), 6.84 (dd, J = 7.7 Hz, 1.7 Hz, 1H), 4.57 (d, J = 6.7 Hz, 1H), 4.26-4.13 (m, 2H), 2.88-2.80 (m, 1H), 2.30-2.18 (m, 2H), 2.01-1.91 (m, 2H), 0.66 (d, J = 7.8 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$, 298K) δ 202.66, 152.04, 143.70, 128.04, 133.03, 129.12, 128.54, 127.32, 126.30, 67.06, 42.09, 22.58, 21.52, 12.22; IR (NaCl, thin film) 2932.2, 1710.8, 1466.8, 1139.4, 751.1 cm$^{-1}$; HRMS (ESI, m/z) calcd for C$_{15}$H$_{15}$BrO$_2$Na$^+$ 329.0148, found 329.0146;

HPLC: AS-H, 93% Hexanes, 7% i-PrOH, 1.0 mL/min, 25.9 min (minor), 53.8 min (major).

$^{(5R, 6R)}$ - 5-(furan-2-yl)-6-methyl-3,4,5,6-tetrahydrocyclopenta[b]pyran-7(2H)-one (3e)

The reaction was performed according to General Procedure B. Flash chromatography on silica gel (4:1 hexanes:EtOAc) afforded the title compound as a pale yellow oil in 71% yield. [$\alpha$]$_D^{24}$ +23.65° (c 0.50, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$, 298K) δ 7.10 (dd, J = 1.8, 1.0 Hz, 1H), 6.31 (dd, J = 3.4 Hz, 1.8 Hz, 1H), 6.05 (d, J = 3.4 Hz, 1H), 4.23-4.12 (m, 2H), 4.10 (d, J = 6.5 Hz, 1H), 2.74-2.67 (m, 1H), 2.33-2.16 (m, 2H), 2.00-1.92 (m, 2H), 0.83 (d, J = 7.5 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$, 298K) δ 202.19, 152.59, 151.29, 142.02, 110.15, 108.06, 67.04, 43.22, 42.45, 22.46, 21.54, 11.71; IR (NaCl, thin film) 2933.0, 1711.9, 1654.6, 1402.0, 1160.2, 734.4 cm$^{-1}$; HRMS (ESI, m/z) calcd for C$_{13}$H$_{14}$O$_3$Na$^+$ 241.0835, found 241.0840; HPLC: AS-H, 93% Hexanes, 7% i-PrOH, 1.0 mL/min, 18.5 min (minor), 36.3 min (major).

$^{(5R, 6R)}$ - 5-(benzofuran-2-yl)-6-methyl-3,4,5,6-tetrahydrocyclopenta[b]pyran-7(2H)-one (3f)

The reaction was performed according to General Procedure B. Flash chromatography on silica gel (4:1 hexanes:EtOAc) afforded the title compound as a pale yellow oil in 86% yield. [$\alpha$]$_D^{24}$ -6.51° (c 0.55, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$, 298K) δ 7.51 (d, J = 7.7 Hz, 1H), 7.41 (d, J = 8.1 Hz, 1H), 7.28-7.12 (m, 2H), 6.48 (s, 1H), 4.26-4.14 (m, 3H), 2.84-2.76 (m, 1H), 2.38-2.20 (m, 2H), 2.03-1.95 (m, 2H), 0.92 (d, J = 7.7 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$, 298K) δ 201.80, 155.63, 154.80, 151.60, 141.39, 128.15, 123.82, 122.75, 120.54, 111.02, 105.21, 67.09, 42.94, 42.88, 22.45, 21.49, 11.71; IR (NaCl, thin film) 2976.6, 1711.2, 1453.8, 1141.7, 732.5 cm$^{-1}$; HRMS (ESI, m/z) calcd for C$_{17}$H$_{16}$O$_3$Na$^+$ 291.0992, found 291.0997; HPLC: AS-H, 95% Hexanes, 5% i-PrOH, 1.0 mL/min, 29.4 min (minor), 38.3 min (major).
(5R, 6R) - 6-methyl-5-(thiopheny-2-yI)-3,4,5,6-tetrahydrocyclopenta[b]pyran-7(2H)-one
(3g) The reaction was performed according to General Procedure B. Flash chromatography on silica gel (4:1 hexanes:EtOAc) afforded the title compound as a yellow solid in 70% yield. \([\alpha]_D^{23} +48.13^\circ\) (c 1.00, CHCl\(_3\)); \(^1\)H NMR (500 MHz, CDCl\(_3\), 298K) \(\delta\) 7.18 (d, \(J = 5.4\) Hz, 1H), 6.99-6.95 (m, 1H), 6.80-6.76 (m, 1H), 4.30 (d, \(J = 6.7\) Hz, 1H), 4.24-4.12 (m, 2H), 2.78-2.69 (m, 1H), 2.43-2.33 (m, 1H), 2.27-2.17 (m, 1H), 2.03-1.91 (m, 2H), 0.82 (d, \(J = 7.6\) Hz, 3H); \(^13\)C NMR (125 MHz, CDCl\(_3\), 298K) \(\delta\) 202.11, 151.14, 144.11, 142.48, 126.95, 126.19, 124.37, 67.11, 43.92, 43.69, 29.66, 22.47, 21.58, 11.72; IR (NaCl, thin film) 2931.5, 1711.2, 1649.7, 1401.1, 1155.2, 703.6 cm\(^{-1}\); HRMS (ESI, m/z) calcd for C\(_{13}\)H\(_{14}\)O\(_2\)SNa\(^+\) 257.0607, found 257.0611; HPLC: AS-H, 93% Hexanes, 7% i-PrOH, 1.0 mL/min, 21.2 min (minor), 43.1 min (major).

(5R, 6R) – 5,6-methyl-3,4,5,6-tetrahydrocyclopenta[b]pyran-7(2H)-one (3h) The reaction was performed according to General Procedure B. Flash chromatography on silica gel (4:1 hexanes:EtOAc) afforded the title compound as a pale yellow oil in 71% yield. Analytical data matched previously reported values.\(^{210}\) \([\alpha]_D^{26} -22.09^\circ\) (c 0.23, CHCl\(_3\)); HPLC: IA, 98.5% Hexanes, 1.5% i-PrOH, 1.0 mL/min, 30.9 min (major), 36.6 min (minor).

(5R, 6R) – 2-ethoxy-5-methyl-4-phenylcyclopent-2-enone (6) The reaction was performed according to General Procedure B. Flash chromatography on silica gel (4:1 hexanes:EtOAc) afforded the title compound as a yellow solid in 69% yield. \([\alpha]_D^{25} -0.58^\circ\) (c 0.55, CHCl\(_3\)); \(^1\)H NMR (500 MHz, CDCl\(_3\), 298K) \(\delta\) 7.33-7.23 (m, 3H), 7.09-7.05 (m, 2H), 4.17 (dd, \(J = 6.7\) Hz, 3.2 Hz, 1H), 4.02 (q, \(J = 7.0\) Hz, 2H), 2.83-2.76 (m, 1H), 1.45 (t, \(J = 7.0\) Hz, 3H), 0.69 (d, \(J = 7.7\) Hz, 3H); \(^13\)C NMR (125 MHz, CDCl\(_3\), 298K) \(\delta\) 205.16, 156.18, 139.81, 128.72, 128.31, 128.00, 127.04, 65.65, 45.00, 43.55, 14.33, 13.07; IR (NaCl, thin film) 2969.4, 1703.6, 1625.5, 1453.1, 1137.8 cm\(^{-1}\); HRMS (ESI, m/z) calcd for C\(_{14}\)H\(_{16}\)O\(_2\)Na\(^+\) 239.1043, found 239.1044; HPLC: IA, 99% Hexanes, 1% i-PrOH, 1.0 mL/min, 17.5 min (minor), 24.3 min (major).
(2S, 3R, 3aR) – 2,3-dimethyl-2, 3, 3a, 4, 5, 6-hexahydro-1H-inden-1-one (9a) The reaction was performed according to General Procedure B. Flash chromatography on silica gel (30:1 hexanes:EtOAc) afforded the title compound as a pale yellow oil in 60% yield. [α]D23 +175.83° (c 0.38, CHCl3); 1H NMR (500 MHz, CDCl3, 298K) δ 6.67 (br s, 1H), 2.35-2.23 (m, 1H), 2.21-2.00 (m, 3H), 1.94-1.74 (m, 2H), 1.59-1.45 (m, 1H), 1.21-1.13 (m, 4H), 1.07 (d, J = 7.0 Hz, 1H), 0.96 (q, J = 12.5 Hz, 1H); 13C NMR (125 MHz, CDCl3, 298K) δ 207.32, 140.84, 131.82, 51.25, 44.69, 43.93, 26.81, 25.52, 21.81, 16.76, 11.88; IR (NaCl, thin film) 2927.8, 1720.6, 1657.4, 1451.8, 1214.3 cm−1; HPLC: AS-H, 98% Hexanes, 2% i-PrOH, 1.0 mL/min, 7.5 min (major), 11.2 min (minor).

(2S, 3R, 3aR) – 2,3-dimethyl-2, 3, 3a, 4, 5, 6-hexahydro-1H-inden-1-one (9b) The reaction was performed according to General Procedure B. Flash chromatography on silica gel (30:1 hexanes:EtOAc) afforded the title compound as a pale yellow oil in 65% yield. 1H NMR (500 MHz, CDCl3, 298K) δ 6.70-6.67 (m, 1H), 2.29 (d, J = 19.5 Hz, 1H), 2.23-2.11 (m, 3H), 1.98-1.92 (m, 1H), 1.92-1.85 (m, 1H), 1.75-1.52 (m, 3H), 1.21-1.14 (m, 1H), 1.10 (d, J = 6.9 Hz, 3H), 1.04-1.01 (m, 1H), 1.00 (t, J = 7.8 Hz, 3H); 13C NMR (125 MHz, CDCl3, 298K) δ 207.67, 132.07, 90.54, 50.65, 48.53, 41.45, 27.93, 25.45, 24.52, 21.95, 12.95, 11.32; IR (NaCl, thin film) 2929.8, 1718.8, 1655.3, 1452.0, 1201.1, 924.4, 700.2 cm−1; HRMS (ESI, m/z) calcd for C16H18ONa+ 249.1250, found 249.1251; HPLC: AS-H, 99% Hexanes, 1% i-PrOH, 1.0 mL/min, 11.5 min (major), 14.6 min (minor).

(2S, 3R, 3aR) – 2-methyl-3-phenyl-2, 3, 3a, 4, 5, 6-hexahydro-1H-inden-1-one (9c) The reaction was performed according to General Procedure B. Flash chromatography on silica gel (20:1 hexanes:EtOAc) afforded the title compound as a pale yellow oil in 78% yield. [α]D26 +117.92° (c 0.20, CHCl3); 1H NMR (500 MHz, CDCl3, 298K) δ 7.40-7.34 (m, 2H), 7.31-7.25 (m, 3H), 6.81 (br s, 1H), 2.67-2.58 (m, 1H), 2.51-2.43 (m, 1H), 2.39-2.15 (m, 3H), 1.99-1.82 (m, 2H), 1.55-1.44 (m, 1H), 1.04 (d, J = 6.9 Hz, 3H); 13C NMR (125 MHz, CDCl3, 298K) δ 206.07, 140.96, 140.38, 132.95, 128.63, 127.44, 126.88, 56.42, 50.79, 44.05, 26.84, 25.61, 21.67, 12.03; IR (NaCl, thin film) 2929.8, 1718.8, 1655.3, 1452.0, 1201.1, 924.4, 700.2 cm−1; HRMS (ESI, m/z) calcd for C16H18ONa+ 249.1250, found 249.1251; HPLC: AS-H, 98% Hexanes, 2% i-PrOH, 1.0 mL/min, 10.4 min (major), 14.9 min (minor).
The reaction was performed according to General Procedure B. Flash chromatography on silica gel (20:1 hexanes:EtOAc) afforded the title compound as a pale yellow oil in 78% yield. 

$^1$H NMR (500 MHz, CDCl$_3$, 298K) $\delta$ 7.48 (d, $J = 8.6$ Hz, 2H), 7.14 (d, $J = 8.6$ Hz, 2H), 6.84-6.79 (m, 1H), 2.62-2.52 (m, 1H), 2.45-2.30 (m, 2H), 2.28-2.14 (m, 2H), 1.96-1.82 (m, 2H), 1.55-1.44 (m, 1H), 1.02 (d, $J = 6.8$ Hz, 3H), 1.07-1.02 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$, 298K) $\delta$ 205.41, 140.07, 140.03, 133.27, 131.78, 129.17, 120.62, 55.99, 50.78, 44.04, 26.79, 25.59, 21.64, 11.97; IR (NaCl, thin film) 2982.9, 1720.0, 1657.0, 1075.8 cm$^{-1}$; HPLC: OJ-H, 99.5\% Hexanes, 0.5\% i-PrOH, 1.0 mL/min, 21.8 min (major), 35.7 min (minor).

$\textbf{9e:}$ The reaction was performed according to General Procedure B. Flash chromatography on silica gel (19:1 hexanes:EtOAc) afforded the title compound as a yellow oil in 76\% yield. [$\alpha$]$^\text{D}_{26} +88.6^\circ$ (c 0.50, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$, 298K) $\delta$ 7.18-7.14 (m, 4H), 6.79 (q, $J = 3.3$ Hz, 1H), 2.62-2.55 (m, 1H), 2.47-2.40 (m, 1H), 2.36 (s, 3H), 2.36-2.30 (m, 1H), 2.26-2.14 (m, 2H), 1.97-1.92 (m, 1H), 1.88-1.82 (m, 1H), 1.53-1.44 (m, 1H), 1.09-1.01 (m, 1H), 1.03 (d, $J = 6.5$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$, 298K) $\delta$ 206.2, 140.5, 137.9, 136.5, 132.8, 129.3, 127.3, 56.1, 50.8, 44.1, 26.9, 25.6, 21.7, 21.0, 12.0; IR (NaCl, thin film) 2929, 2870, 1719, 1655, 1515, 1452, 1175 cm$^{-1}$; HRMS (ESI, m/z) calcd for C$_{17}$H$_{20}$ONa$^+$ 263.1406, found 263.1410; HPLC: AS-H, 98\% Hexanes, 2\% i-PrOH, 1.0 mL/min, 7.5 min (major), 10.9 min (minor).

$\textbf{9f:}$ The reaction was performed according to General Procedure B. Flash chromatography on silica gel (19:1 hexanes:EtOAc) afforded the title compound as a yellow oil in 55\% yield. [$\alpha$]$^\text{D}_{26} +145.6^\circ$ (c 0.50, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$, 298K) $\delta$ 7.38 (dd, $J = 1.8$, 0.8 Hz, 1H), 6.79 (q, $J = 3.4$ Hz, 1H), 6.35 (dd, $J = 3.2$, 1.9 Hz, 1H), 6.14 (d, $J = 0.6$ Hz, 1H), 2.71-2.66 (m,
1H), 2.53-2.48 (m, 1H), 2.42 (t, J = 12.2 Hz, 1H), 2.37-2.31 (m, 1H), 2.24-2.12 (m, 2H), 1.92-1.87 (m, 1H), 1.60-1.51 (m, 1H), 1.14 (d, J = 6.8 Hz, 3H), 1.13-1.06 (m, 1H); \(^{13}\text{C}\) NMR (125 MHz, CDCl\(_3\), 298K) \(\delta\) 205.5, 155.1, 141.6, 139.9, 133.3, 110.1, 105.6, 49.1, 48.7, 41.7, 27.3, 25.5, 21.6, 12.5; IR (NaCl, thin film) 2932, 2871, 1720, 1654, 1454, 1176, 1074 cm\(^{-1}\); HRMS (ESI, m/z) calcd for C\(_{14}\)H\(_{16}\)O\(_2\)Na\(^+\) 239.1043, found 239.1042; HPLC: OD-H, 99% Hexanes, 1% i-PrOH, 1.0 mL/min, 10.8 min (major), 12.5 min (minor).

9g: The reaction was performed according to General Procedure B. Flash chromatography on silica gel (19:1 hexanes:EtOAc) afforded the title compound as a yellow oil in 56% yield. \([\alpha]_D^{26}\) +146.4\(^\circ\) (c 0.50, CHCl\(_3\)); \(^1\text{H}\) NMR (500 MHz, CDCl\(_3\), 298K) \(\delta\) 7.53 (d, J = 7.6 Hz, 1H), 7.45 (d, J = 8.1 Hz, 1H), 7.27-7.21 (m, 2H), 6.83 (q, J = 3.2 Hz, 1H), 6.55 (s, 1H), 2.87-2.83 (m, 1H), 2.70-2.64 (m, 1H), 2.55 (t, J = 11.2 Hz, 1H), 2.39-2.34 (m, 1H), 2.27-2.13 (m, 2H), 1.92-1.88 (m, 1H), 1.61-1.52 (m, 1H), 1.18 (d, J = 6.8 Hz, 3H), 1.17-1.11 (m, 1H); \(^{13}\text{C}\) NMR (125 MHz, CDCl\(_3\), 298K) \(\delta\) 205.0, 158.0, 154.8, 139.6, 133.7, 128.5, 123.6, 122.7, 120.4, 111.0, 103.1, 49.6, 48.6, 41.5, 27.3, 25.5, 21.6, 12.6; IR (NaCl, thin film) 2931, 2870, 1721, 1655, 1455, 1252, 1176 cm\(^{-1}\); HRMS (ESI, m/z) calcd for C\(_{14}\)H\(_{16}\)O\(_2\)Na\(^+\) 255.0814, found 255.0815; HPLC: OD-H, 99% Hexanes, 2% i-PrOH, 1.0 mL/min, 10.7 min (major), 12.5 min (minor).

9h: The reaction was performed according to General Procedure B. Flash chromatography on silica gel (19:1 hexanes:EtOAc) afforded the title compound as a yellow oil in 62% yield. \([\alpha]_D^{26}\) +79.8\(^\circ\) (c 0.50, CHCl\(_3\)); \(^1\text{H}\) NMR (500 MHz, CDCl\(_3\), 298K) \(\delta\) 7.22 (dd, J = 5.2, 1.2 Hz, 1H), 7.00 (dd, J = 5.1, 3.5 Hz, 1H), 6.92 (dd, J = 3.4, 0.8 Hz, 1H), 6.80 (q, J = 3.1 Hz, 1H), 2.65-2.56 (m, 2H), 2.44-2.32 (m, 2H), 2.25-2.12 (m, 2H), 1.92-1.87 (m, 1H), 1.59-1.49 (m, 1H), 1.14 (d, J = 6.8 Hz, 3H), 1.12-1.05 (m, 1H); \(^{13}\text{C}\) NMR (125 MHz, CDCl\(_3\), 298K) \(\delta\) 205.1, 145.1, 139.9, 133.3, 126.9, 124.3, 123.4, 52.1, 51.4, 45.1, 27.0, 25.6, 21.6, 12.2; IR (NaCl, thin film) 2931, 2870, 1719, 1654 cm\(^{-1}\); HRMS (ESI, m/z) calcd for C\(_{14}\)H\(_{16}\)OSNa\(^+\) 255.0814, found 255.0815; HPLC: OD-H, 99% Hexanes, 1% i-PrOH, 1.0 mL/min, 13.8 min (major), 15.5 min (minor).
(5R, 6S) – Diisopropyl 1-(6-methyl-7-oxo-5-(4-bromophenyl)-2,3,4,5-hexahydrocyclopenta[b]pyran-6-yl)hydrazine-1,2-dicarboxylate (7) A round-bottom flask was charged with chromium salen complex (0.0110 mmol), dry 4Å molecular sieves, and dry CH₂Cl₂ (0.5 mL). A solution of divinyl ketone (0.219 mmol) and DIAD (0.219 mmol) in dry CH₂Cl₂ (0.8 mL) was added by cannula. The reaction was monitored by TLC, and then chromatographed directly on a silica gel (3:1 hexanes:EtOAc) affording the corresponding product (diastereomers are inseparable). The title compound was isolated as a white solid in 68% yield. ¹H NMR (500 MHz, CDCl₃, 318K, major isomer) δ 7.44 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 7.5 Hz, 2H), 6.40 (br s, 1H), 5.00-4.85 (m, 2H), 4.42 (s, 1H), 4.32-4.25 (m, 1H), 4.21-4.15 (s, 1H), 2.30-2.21 (m, 1H), 2.14-2.06 (m, 1H), 2.04-1.97 (m, 2H), 1.29 (d, J = 6.0 Hz, 3H), 1.27-1.19 (m, 12H), 0.83 (s, 3H); ¹³C NMR (125 MHz, CDCl₃, 318K, major isomer) δ 202.9, 159.39, 149.97, 140.71, 136.24, 132.17, 131.68, 131.32, 121.25, 70.82, 70.11, 67.01, 54.79, 22.14, 22.10, 22.01, 21.86, 21.77, 20.73; IR (NaCl, thin film) 3293.6, 2981.1, 1726.0, 1246.9, 1049.2, 910.0, 731.2 cm⁻¹.

10: To a solution of 9e (15.1 mg, 0.0628 mmol) in 1.0 mL of anhydrous CH₂Cl₂ was added 0.5 M solution Br₂ in CH₂Cl₂ (126 µL, 0.0628 mmol) dropwise, at room temperature. The resulting solution was stirred for 20 min, at which time the reaction was found to be complete by TLC analysis. All volatiles were removed by Rotavap, and diastereomeric ratio was determined to be 20:1 by ¹H-NMR analysis of the crude mixture. Purification by flash column chromatography (2% EtOAc in hexanes) afforded the title compound 10 (19.6 mg) as a colorless oil in 78% yield. ¹H NMR (500 MHz, CDCl₃, 298K) δ 7.18 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 7.5 Hz, 1H), 2.82 (dd, J = 11.0, 10.0 Hz, 1H), 2.65-2.58 (m, 1H), 2.39 (dt, J = 11.0, 4.0 Hz, 1H), 2.36 (s, 3H), 2.15-2.07 (m, 2H), 1.82-1.72 (m, 1H), 1.72-1.66 (m, 1H), 1.62-1.55 (m, 1H), 1.27 (d, J = 7.5 Hz, 3H), 1.29-1.26 (m, 1H); ¹³C NMR (125 MHz, CDCl₃, 298K) δ 206.3, 137.0, 136.1, 129.6, 127.7, 76.7, 52.2, 51.0, 49.4, 44.8, 30.1, 24.2, 21.0, 20.6, 15.4.
Crystallization of 10:

A solution of 10 (19 mg) in 2 mL of pentane was prepared in a 1 dram vial which was placed into a 20 mL scintillation vial containing toluene (5 mL). The outer scintillation vial was sealed with a screw cap, parafilmed and placed in a freezer (ca. -20 °C). Pentane was allowed to undergo slow vapor diffusion into the outer toluene phase. After one week, 10 was obtained as colorless crystals.
Crystallographic Experimental Section

Data Collection
An irregular broken fragment (0.48 x 0.36 x 0.20 mm) was selected under a stereo-microscope while immersed in Fluorolube oil to avoid possible reaction with air. The crystal was removed from the oil using a tapered glass fiber that also served to hold the crystal for data collection. The crystal was mounted and centered on a Bruker SMART APEX system at 100 K. The extinction under crossed polars was poor suggesting that the crystal was less than perfect. Still diffraction images showed the por and elongate diffractions. Because there was no obvious superior crystal, data were obtained on the best available. Frames separated in reciprocal space were obtained and provided an orientation matrix and initial cell parameters. Final cell parameters were obtained from the full data set.

A “full sphere” data set was obtained which samples approximately all of reciprocal space to a resolution of 0.84 Å using 0.3° steps in ω using 10 second integration times for each frame. Data collection was made at 100 K. Integration of intensities and refinement of cell parameters were done using SAINT [1]. Absorption corrections were applied using SADABS [1] based on redundant diffractions.

Structure solution and refinement
The space group was determined as P2₁ based on systematic absences and intensity statistics. Patterson methods were used to locate the Br atoms. Repeated difference Fourier maps allowed recognition of all expected C and O atoms. Following anisotropic refinement of all non-H atoms, ideal H atom position were calculated. Final refinement was anisotropic for non-H atoms and isotropic riding for H atoms. No anomalous bond lengths or thermal parameters were noted. The higher than normal R value (0.09) is most certainly due to the poor diffraction of the crystal. All ORTEP diagrams have been drawn with 50% probability ellipsoids.

The absolute structure was determined based on the Flack parameter. With heavy atoms present (Br), anomalous scattering will be present and this parameter will be 0.0 for the correct absolute structure and 1.0 for the inverted absolute structure. The structure described here gives a Flack parameter of 0.058 (0.041) which within error is near 0.0. The inverted structure gives a
Flack parameter of 0.941 (0.049) which indicates that the inverted absolute structure is incorrect and the structure described here is the correct absolute structure.

Equations of interest:

\[ R_{\text{int}} = \frac{\sum |F_o^2 - \langle F_o^2 \rangle|}{\sum F_o^2} \]

\[ R_1 = \frac{\sum |F_o - |F_c||}{\sum |F_o|} \]

\[ wR_2 = \left[ \frac{\sum [w \left( F_o^2 - F_c^2 \right)^2]}{\sum [w \left( F_o^2 \right)^2]} \right]^{1/2} \]

\[ \text{GooF} = S = \frac{\sum [w \left( F_o^2 - F_c^2 \right)^2]}{(n-p)^{1/2}} \]

where: \( w = q / \sigma^2 (F_o^2) + (aP)^2 + bP \);

\( q, a, b, P \) as defined in [1]

\( n = \) number of independent reflections;

\( p = \) number of parameters refined.

References

[1] All software and sources of scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI).
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| Property                                      | Value/Details |
|----------------------------------------------|---------------|
| Identification Code                         | Turk14        |
| Empirical formula                           | C\textsubscript{17}H\textsubscript{20}Br\textsubscript{2}O |
| Formula weight                               | 400.15        |
| Temperature                                  | 100 K         |
| Wavelength                                   | 0.71073 Å     |
| Crystal system                               | Monoclinic    |
| Space Group                                  | P\textsubscript{2}\textsubscript{1} |
| Unit cell dimensions                         | \(a = 10.254(11)\) Å, \(\alpha = 90.0^\circ\) \(b = 6.962(8)\) Å, \(\beta = 110.196(16)^\circ\) \(c = 11.580(13)\) Å, \(\gamma = 90.0^\circ\) |
| Volume                                        | 775.9(15) Å\(^3\) |
| \(Z\)                                        | 2             |
| Density (calculated)                         | 1.713 Mg/m\(^3\) |
| Absorption coefficient                       | 5.218 mm\(^{-1}\) |
| \(F(000)\)                                   | 400           |
| Crystal size, color, habit                   | 0.48 x 0.36 x 0.20 mm, clear, fragment |
| Theta range for data collection              | 1.87 – 25.20\(^\circ\) |
| Index ranges                                 | \(-12 \leq h \leq 12, -8 \leq k \leq 8, -13 \leq l \leq 13\) |
| Reflections collected                        | 6,969         |
| Independent reflections                      | 2,725 (\(R\_int = 0.0588\)) |
| Reflections with \(I > 4\sigma(F_o)\)        | 1,729         |
| Flack parameter                              | 0.06(4)       |
| Absorption correction                        | SADABS based on redundant diffractions |
| Max. and min. transmission                   | 1.0, 0.507    |
| Refinement method                            | Full-matrix least squares on F\(^2\) |
| Weighting scheme                             | \(w = q [\sigma^2 (F_o^2) + (aP)^2 + bP]^{-1}\) where: \(P = (F_o^2 + 2F_c^2)/3\), \(a = 0.1639\), \(b = 0.0\), \(q = 1\) |
| Data / restraints / parameters                | 2725 / 0 / 183 |
| Goodness-of-fit on F\(^2\)                   | 0.967         |
| Final R indices \([I > 2 \sigma(I)]\)        | \(R_I = 0.0891\), \(wR_2 = 0.2063\) |
| R indices (all data)                         | \(R_I = 0.1242\), \(wR_2 = 0.2237\) |
| Largest diff. peak and hole                  | 0.749, -0.805 eÅ\(^{-3}\) |
Table 2. Atomic coordinates \[x \times 10^4\] and equivalent isotropic displacement parameters \[\AA^2 \times 10^3\] for Turk14. \(U(\text{eq})\) is defined as one third of the trace of the orthogonalized \(U_{ij}\) tensor.

|    | x         | y         | z         | U(eq) | SOF |
|----|-----------|-----------|-----------|-------|-----|
| Br(1) | -372 (2)  | 6213 (3)  | 2878 (2)  | 39 (1)|     |
| Br(2) | 3283 (2)  | 3790 (3)  | 6058 (2)  | 41 (1)|     |
| C(1)  | 1439 (17) | 5000 (30) | 3785 (16) | 33 (4)|     |
| C(2)  | 1791 (17) | 5430 (30) | 5102 (16) | 33 (4)|     |
| C(3)  | 2200 (20) | 7560 (30) | 5369 (18) | 43 (5)|     |
| C(4)  | 3231 (17) | 8270 (20) | 4818 (16) | 39 (4)|     |
| C(5)  | 2827 (18) | 7760 (20) | 3465 (18) | 43 (5)|     |
| C(6)  | 2544 (17) | 5660 (20) | 3267 (15) | 29 (4)|     |
| C(7)  | 1148 (19) | 2940 (30) | 3300 (18) | 39 (5)|     |
| C(8)  | 1709 (19) | 2740 (20) | 2246 (16) | 35 (4)|     |
| C(9)  | 705 (17)  | 1690 (20) | 1169 (15) | 36 (4)|     |
| C(10) | 2116 (16) | 4780 (20) | 1996 (15) | 26 (4)|     |
| C(11) | 3169 (15) | 4740 (30) | 1375 (16) | 32 (4)|     |
| C(12) | 2784 (18) | 4670 (20) | 136 (17)  | 37 (4)|     |
| C(13) | 3747 (17) | 4670 (30) | -451 (16) | 36 (4)|     |
| C(14) | 5125 (18) | 4710 (20) | 189 (16)  | 35 (4)|     |
| C(15) | 5541 (17) | 4760 (30) | 1444 (17) | 38 (4)|     |
| C(16) | 4598 (16) | 4800 (20) | 2052 (16) | 30 (4)|     |
| C(17) | 6172 (19) | 4760 (20) | -451 (16) | 40 (5)|     |
| O(1)  | 620 (12)  | 1752 (15) | 3710 (11) | 39 (3)|     |
Table 3. Bond lengths [Å] and angles [°] for Turk14.

| Bond                  | Length/Angle       |
|-----------------------|--------------------|
| Br(1)-C(1)            | 1.977(18)          |
| Br(2)-C(2)            | 1.922(18)          |
| C(1)-C(2)             | 1.47(2)            |
| C(1)-C(6)             | 1.52(2)            |
| C(1)-C(7)             | 1.54(2)            |
| C(2)-C(3)             | 1.54(2)            |
| C(3)-C(4)             | 1.49(2)            |
| C(4)-C(5)             | 1.52(2)            |
| C(5)-C(6)             | 1.49(2)            |
| C(6)-C(10)            | 1.51(2)            |
| C(7)-O(1)             | 1.174(19)          |
| C(2)-C(1)-C(6)        | 113.5(14)          |
| C(2)-C(1)-C(7)        | 120.9(16)          |
| C(6)-C(1)-C(7)        | 102.2(13)          |
| C(2)-C(1)-Br(1)       | 108.4(11)          |
| C(6)-C(1)-Br(1)       | 110.8(12)          |
| C(7)-C(1)-Br(1)       | 100.1(12)          |
| C(1)-C(2)-C(3)        | 110.6(15)          |
| C(1)-C(2)-Br(2)       | 109.9(11)          |
| C(3)-C(2)-Br(2)       | 110.3(13)          |
| C(4)-C(3)-C(2)        | 114.7(15)          |
| C(3)-C(4)-C(5)        | 112.4(14)          |
| C(6)-C(5)-C(4)        | 111.0(16)          |
| C(5)-C(6)-C(10)       | 121.4(14)          |
| C(5)-C(6)-C(1)        | 111.3(14)          |
| C(10)-C(6)-C(1)       | 104.9(12)          |
| O(1)-C(7)-C(8)        | 127.9(16)          |
| O(1)-C(7)-C(1)        | 124.8(16)          |
| C(7)-C(7)-C(1)        | 107.3(13)          |
| C(8)-C(7)-C(1)        | 111.6(14)          |
| C(9)-C(8)-C(7)        | 116.5(15)          |
| C(9)-C(8)-C(10)       | 105.6(12)          |
| C(11)-C(10)-C(6)      | 117.5(14)          |
| C(11)-C(10)-C(8)      | 111.3(13)          |
| C(12)-C(11)-C(10)     | 117.4(15)          |
| C(12)-C(11)-C(16)     | 121.2(15)          |
| C(16)-C(11)-C(10)     | 121.4(15)          |
| C(11)-C(12)-C(13)     | 121.8(17)          |
| C(14)-C(13)-C(12)     | 121.4(17)          |
| C(13)-C(14)-C(15)     | 117.9(16)          |
| C(13)-C(14)-C(17)     | 121.4(16)          |
| C(15)-C(14)-C(17)     | 120.7(16)          |
| C(14)-C(15)-C(16)     | 121.8(17)          |
| C(15)-C(16)-C(11)     | 119.7(17)          |
Table 4. Anisotropic displacement parameters [Å² x 10³] for Turk14. The anisotropic displacement factor exponent takes the form:

\[-2\pi^2 [h^2 a^{*2} U_{11} + \ldots + 2hka'b'U_{12}]\]

|     |  U_{11} |  U_{22} |  U_{33} |  U_{23} |  U_{13} |  U_{12} |
|-----|--------|--------|--------|--------|--------|--------|
| Br(1) |  29(1) |  43(1) |  55(1) |  0(1)  |  27(1) |  4(1)  |
| Br(2) |  40(1) |  50(1) |  44(1) |  3(1)  |  28(1) |  6(1)  |
| C(1)  |  29(10)|  40(11)|  45(12)| -4(8)  |  29(9) |  6(8)  |
| C(2)  |  19(8) |  55(11)|  36(10)| -3(8)  |  24(8) |  7(8)  |
| C(3)  |  39(12)|  47(12)|  51(13)| -2(9)  |  27(10)|  3(9)  |
| C(4)  |  43(11)|  32(10)|  53(11)|  3(8)  |  33(9) |  7(8)  |
| C(5)  |  35(11)|  35(10)|  83(15)|-23(10)|  50(11)| -14(8) |
| C(6)  |  27(9) |  30(10)|  33(9) | -8(7)  |  15(7) | -12(7) |
| C(7)  |  39(11)|  37(10)|  56(12)| -2(9)  |  36(10)| -4(8)  |
| C(8)  |  51(11)|  23(9) |  46(11)| -7(8)  |  37(10)| -2(8)  |
| C(9)  |  38(10)|  30(11)|  47(11)| -13(8) |  24(9) | -12(7) |
| C(10) |  26(9) |  30(9) |  27(9) |  5(7)  |  16(7) |  8(7)  |
| C(11) |  17(9) |  43(10)|  43(11)|  9(8)  |  21(8) |  8(7)  |
| C(12) |  28(10)|  40(10)|  48(12)| -6(8)  |  18(9) |  13(8) |
| C(13) |  32(10)|  51(11)|  28(10)|  10(8) |  16(8) |  0(8)  |
| C(14) |  35(10)|  44(10)|  29(10)|  15(8) |  17(8) |  3(8)  |
| C(15) |  26(9) |  48(11)|  49(12)| -12(9) |  25(9) | -5(8)  |
| C(16) |  26(9) |  33(9) |  36(10)|  5(7)  |  15(8) |  3(7)  |
| C(17) |  61(13)|  25(9) |  45(11)| -2(8)  |  34(10)| -12(9) |
| O(1)  |  40(7) |  34(8) |  57(8) | -1(6)  |  35(7) | -1(5)  |
Table 5. Hydrogen coordinates \([ x \times 10^4]\) and isotropic displacement parameters \([\text{Å}^2 \times 10^3]\) for Turk14.

|     | x   | y   | z   | U(eq) |
|-----|-----|-----|-----|-------|
| H(2) | 958 | 5165| 5338| 40    |
| H(3A)| 1351| 8353| 5054| 51    |
| H(3B)| 2593| 7743| 6272| 51    |
| H(4A)| 4154| 7715| 5275| 47    |
| H(4B)| 3308| 9686| 4909| 47    |
| H(5A)| 1988| 8489| 2984| 52    |
| H(5B)| 3589| 8120| 3167| 52    |
| H(6) | 3421| 4989| 3767| 35    |
| H(8) | 2580| 1960| 2553| 41    |
| H(9A)| 454 | 459 | 1449| 54    |
| H(9B)| 1140| 1451| 550 | 54    |
| H(9C)| -133| 2467| 806 | 54    |
| H(10)| 1267| 5456| 1450| 31    |
| H(12)| 1824| 4613| -344| 45    |
| H(13)| 3435| 4646| -1325| 43   |
| H(15)| 6507| 4766| 1910| 45    |
| H(16)| 4914| 4875| 2925| 37    |
| H(17A)| 7109| 4638| 159 | 60    |
| H(17B)| 6094| 5974| -895| 60    |
| H(17C)| 5997| 3686| -1034| 60   |
Table 6. Torsion angles [°] for Turk14.

|        |        |        |
|--------|--------|--------|
|        |        |        |
| C(6) - C(1) - C(2) - C(3) | 51.4(19) | C(1) - C(7) - C(8) - C(9) | -136.2(16) |
| C(7) - C(1) - C(2) - C(3) | 173.4(15) | C(1) - C(7) - C(8) - C(10) | 173.2(2)   |
| Br(1) - C(1) - C(2) - C(3) | -72.1(15) | C(5) - C(6) - C(10) - C(11) | 68.2(2)    |
| C(6) - C(1) - C(2) - Br(2) | -70.7(16) | C(1) - C(6) - C(10) - C(11) | -164.9(14) |
| C(7) - C(1) - C(2) - Br(2) | 51.3(18)  | C(5) - C(6) - C(10) - C(8)  | -170.5(15) |
| Br(1) - C(1) - C(2) - Br(2) | 165.8(8)  | C(1) - C(6) - C(10) - C(8)  | -43.5(16)  |
| C(1) - C(2) - C(3) - C(4)  | -48(2)    | C(9) - C(8) - C(10) - C(11) | -78.3(19)  |
| Br(2) - C(2) - C(3) - C(4)  | 73.6(18)  | C(7) - C(8) - C(10) - C(11) | 157.1(15)  |
| C(2) - C(3) - C(4) - C(5)  | 49(2)     | C(9) - C(8) - C(10) - C(6)  | 155.9(14)  |
| C(3) - C(4) - C(5) - C(6)  | -52(2)    | C(7) - C(8) - C(10) - C(6)  | 31.4(17)   |
| C(4) - C(5) - C(6) - C(10) | 179.8(13) | C(6) - C(10) - C(11) - C(12) | -155.3(16) |
| C(4) - C(5) - C(6) - C(1)  | 55.6(19)  | C(8) - C(10) - C(11) - C(12) | 89(2)      |
| C(2) - C(1) - C(6) - C(5)  | -57(2)    | C(6) - C(10) - C(11) - C(16) | 24(2)      |
| C(7) - C(1) - C(6) - C(5)  | 171.1(16) | C(8) - C(10) - C(11) - C(16) | -92.5(19)  |
| Br(1) - C(1) - C(6) - C(5) | 65.1(18)  | C(16) - C(11) - C(12) - C(13) | 0(3)       |
| C(2) - C(1) - C(6) - C(10) | 169.9(13) | C(10) - C(11) - C(12) - C(13) | 178.5(16)  |
| C(7) - C(1) - C(6) - C(10) | 38.1(17)  | C(11) - C(12) - C(13) - C(14) | 3(3)       |
| Br(1) - C(1) - C(6) - C(10) | -67.9(14) | C(12) - C(13) - C(14) - C(15) | 0(3)       |
| C(2) - C(1) - C(7) - O(1)  | 33(3)     | C(12) - C(13) - C(14) - C(17) | -178.8(16) |
| C(6) - C(1) - C(7) - O(1)  | 160.6(19) | C(13) - C(14) - C(15) - C(16) | -1(3)      |
| Br(1) - C(1) - C(7) - O(1)  | -85(2)    | C(17) - C(14) - C(15) - C(16) | 177.3(16)  |
| C(2) - C(1) - C(7) - C(8)  | -144.8(15) | C(14) - C(15) - C(16) - C(11) | 2(3)      |
| C(6) - C(1) - C(7) - C(8)  | -17.6(19)  | C(12) - C(11) - C(16) - C(15) | -1(2)    |
| Br(1) - C(1) - C(7) - C(8)  | 96.5(14)  | C(10) - C(11) - C(16) - C(15) | 179.9(15)  |
| O(1) - C(7) - C(8) - C(9)  | 46(3)     |        |        |
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\[ \text{Structure Image} \]

\[ \text{Diagram Image} \]
$\text{OMe}$
$t$-Bu $t$-Bu $t$-Bu

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\[ \text{O} \]

\[ \text{Me} \]

\[ \text{Br} \]

\[ \text{O} \]

\[ \text{Me} \]

\[ \text{O} \]
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\[
\begin{align*}
&\text{Me} \\
&\text{Et} \\
&\text{O} \\
&\text{C} & \text{Me} & \text{Me} \\
&\text{C} & \text{C} & \text{C} \\
&\text{E} & \text{E} & \text{E} \\
&\text{E} & \text{E} & \text{E} \\
&\text{E} & \text{E} & \text{E} \\
\end{align*}
\]
### Spectral Information

| ppm  | Value  |
|------|--------|
| 12.02|        |
| 21.04|        |
| 21.70|        |
| 25.63|        |
| 26.87|        |
| 44.10|        |
| 50.79|        |
| 56.05|        |
| 76.75|        |
| 77.00|        |
| 77.26|        |
| 127.30|       |
| 129.33|       |
| 132.81|       |
| 136.45|       |
| 137.91|       |
| 140.50|       |
| 206.20|       |

### Parameters

| Parameter | Value |
|-----------|-------|
| Field     | 125.6924186 MHz |
|.si        | 65536 |
| SFO2      | 499.8734991 MHz |
| PL12      | 21.00 dB |
| PL2       | 1.00 dB |
| PCPD2     | 90.00 usec |
| CPDPRG2   | waltz16 |
| PL1       | 8.50 usec |
| PL2       | 0.00 dB |
| SFO1      | 125.7049802 MHz |
| P1        | 8.50 usec |
| P1        | 0.00 dB |
| NUC1      | 13C    |
| NUC2      | 1H     |
| DW        | 14.200 usec |
| DE        | 7.50 usec |
| D1        | 2.00000000 sec |
| d11       | 0.03000000 sec |
| TD0       | 1      |
| TD        | 142854 |
| d1        | 0.03000000 sec |
| d11       | 0.03000000 sec |

### Chemical Structure

![Chemical Structure Image]
| ppm  | 9.5  | 9.0  | 8.5  | 8.0  | 7.5  | 7.0  | 6.5  | 6.0  | 5.5  | 5.0  | 4.5  | 4.0  | 3.5  | 3.0  | 2.5  | 2.0  | 1.5  | 1.0  | 0.5  |
|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| 1.03 | 1.00 | 1.00 | 1.01 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |

**Chemical Shift Values:**

- **Me**
- **S**

**Additional Parameters:**

- **PC:** 1.00
- **GB:** 0.00 Hz
- **LB:** 0.00 Hz
- **PC:** 1.00

**Spectroscopic Details:**

- **Instrument:** spect
- **Solvent:** CDCl3
- **Spectral Parameters:**
  - **SF01:** 499.8740056 MHz
  - **SI:** 32768
  - **PL1:** 0.00 dB
  - **TD:** 59998
  - **NS:** 4
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Current Chromatogram(s)
DAD1 A, Sig=254.4 Ref=390,100 (GERIR/073020080000052.D)

DAD1 A, Sig=254.4 Ref=390,100 (GERIR/073020080000052.D)

mAU

15 20 25 30 35 40 min

15 20 25 30 35 40 min
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Current Chromatogram(s)

DAD1 A, Sig=254.4 Ref=360,100 (GERRI08262009000003.D)

mAU

0 10 20 30 40 50 60 70 80 90 100

15 20 25 30 35 40 min

DAD1 A, Sig=254.4 Ref=360,100 (GERRI08262009000002.D)

mAU

0 10 20 30 40 50 60 70 80 90 100

15 20 25 30 35 40 min

trans
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- **Signal 5: DAD1 E, Sig=240,16 Ref=360,100**

| peak | RetTime | Type | Width | Area  | Height | Area  |
|------|---------|------|-------|-------|--------|-------|
| #    | [min]   | [min] | [mAU*s] | [mAU] | %      |       |
| 1    | 7.963   | MM   | 0.2716 | 5456.64844 | 334.80984 | 49.9199 |
| 2    | 11.576  | MM   | 0.4184 | 5474.16748 | 218.05164 | 50.0801 |

**Totals:**

|       |       |
|-------|-------|
|       | 1.09308e4 | 552.86148 |

- **Signal 5: DAD1 E, Sig=240,16 Ref=360,100**

| peak | RetTime | Type | Width | Area  | Height | Area  |
|------|---------|------|-------|-------|--------|-------|
| #    | [min]   | [min] | [mAU*s] | [mAU] | %      |       |
| 1    | 7.515   | MM   | 0.2567 | 7055.30957 | 458.10699 | 90.4336 |
| 2    | 10.888  | MM   | 0.3585 | 746.33905 | 34.69613  | 9.5664  |

**Totals:**

|       |       |
|-------|-------|
|       | 7801.64862 | 492.80313 |
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Signal 5: DAD1 E, Sig=240,16 Ref=360,100

| Peak RetTime Type Width | Area [mAU*s] | Height [mAU] | Area % |
|------------------------|--------------|--------------|-------|
| #                      | [min]        | [min]        |       |
| 1                      | 9.871 MM     | 0.2877       | 7407.47803 | 429.18958 | 50.4043 |
| 2                      | 11.264 MM    | 0.3173       | 7288.64404 | 382.85593 | 49.5957 |
| Totals                 |              |              | 1.46961e4 | 812.04550 |

Signal 5: DAD1 E, Sig=240,16 Ref=360,100

| Peak RetTime Type Width | Area [mAU*s] | Height [mAU] | Area % |
|------------------------|--------------|--------------|-------|
| #                      | [min]        | [min]        |       |
| 1                      | 10.807 MM    | 0.4206       | 1.87526e4 | 743.03229 | 92.5555 |
| 2                      | 12.468 MM    | 0.3388       | 1508.32678 | 74.19528 | 7.4445 |
| Totals                 |              |              | 2.02609e4 | 817.22757 |

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Signal 4: DAD1 D, Sig=230,16 Ref=360,100

| Peak | RetTime | Type | Width | Area     | Height   | Area % |
|------|---------|------|-------|----------|----------|--------|
| #    | [min]   |      | [min] | [mAU*s]  | [mAU]    |        |
| 1    | 10.821  | MM   | 0.3268 | 1.04340e4| 532.05383| 49.9723|
| 2    | 12.635  | MM   | 0.3649 | 1.04455e4| 477.04846| 50.0277|

Totals: 2.08795e4 1009.10229

Signal 5: DAD1 E, Sig=240,16 Ref=360,100

| Peak | RetTime | Type | Width | Area     | Height   | Area % |
|------|---------|------|-------|----------|----------|--------|
| #    | [min]   |      | [min] | [mAU*s]  | [mAU]    |        |
| 1    | 10.827  | MM   | 0.3293 | 1.55225e4| 785.62903| 50.1661|
| 2    | 12.635  | MM   | 0.3671 | 1.54197e4| 700.01501| 49.8339|

Totals: 3.09422e4 1485.64404
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![Chemical Structure](image)

**Signal 4: DAD1 D, Sig=230,16 Ref=360,100**

| Peak | RetTime | Type | Width | Area | Height | Area % |
|------|---------|------|-------|------|--------|--------|
| 1    | 10.723  | MM   | 0.3203| 6763.22412 | 351.97324 | 92.1531 |
| 2    | 12.480  | MM   | 0.3365| 575.89368  | 28.52241  | 7.8469  |

**Totals:**

|          |        | 7339.11780 | 380.49565 |

**Signal 5: DAD1 E, Sig=240,16 Ref=360,100**

| Peak | RetTime | Type | Width | Area | Height | Area % |
|------|---------|------|-------|------|--------|--------|
| 1    | 10.722  | MM   | 0.3222| 1.00732e4 | 520.99799 | 92.2552 |
| 2    | 12.457  | MM   | 0.3399| 845.63806  | 41.46476  | 7.7448  |

**Totals:**

|          |        | 1.09188e4 | 562.46275 |
