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Ring-Expansion Protocol: Preparation of Synthetically Versatile Dihydrotropones

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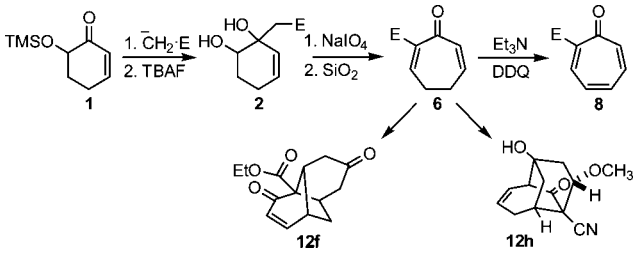
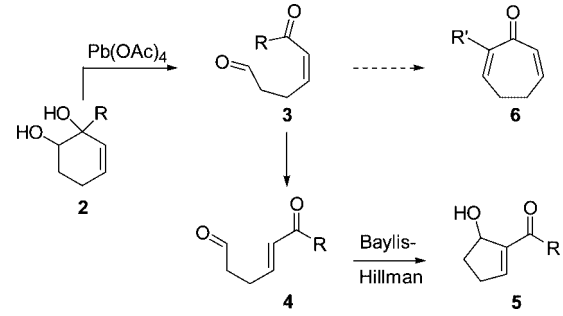


A ring-expansion protocol that consisted of the 1,2-addition of various enolate nucleophiles to 6-trimethylsiloxy-2-cyclohexene-1-one (**1**) and the $NaIO_4$-promoted oxidative ring opening of the resulting diols **2**, followed by an intramolecular Knoevenagel condensation, furnished versatile dihydrotropones **6**. Maintaining *Z*-configuration in the oxidative ring-opening products **3** is crucial for the success of the ring-expansion strategy. Dihydrotropones **6** are ripe for further elaborations such as oxidation to tropones **8** and Diels−Alder reaction with the Danishefsky's diene **10** to afford polycyclic compounds **12**.

Seven-membered unsaturated carbocyclic compounds are not only useful building blocks in organic synthesis[1] but also the key structural motifs of the biologically important natural products such as colchicine,[2] ingenol,[3] tropolone,[4] etc. The synthetic approaches to this unusual ring system have been mostly based on the ring-expansion strategies from the highly functionalized six-membered ring homologues.[5] We have demonstrated that the five-membered carbocyclic compounds **5** were efficiently assembled by the ring-contraction protocol from 3-cyclohexene-1,2-diols **2** utilizing the intramolecular Baylis−Hillman reaction of the $Pb(OAc)_4$-promoted oxidative ring-opening products **4** with *E*-configuration (Scheme 1).[6] It

SCHEME 1. Oxidative Ring Opening of 3-Cyclohexene-1,2-diols 2, Which May Lead to the Ring Contraction or the Ring-Expansion Products



was envisioned that the seven-membered conjugated carbonyl compounds **6** would be synthesized by the ring-expansion strategy from the same 3-cyclohexene-1,2-diols **2** utilizing the intramolecular aldol condensation of the immediate oxidative ring-opening products **3** with *Z*-configuration. The control of *E*/*Z*-configuration in the oxidative ring-opening reaction of 3-cyclcohexene-1,2-diols **2** therefore plays a decisive role in producing either the five-membered ring-contraction products **5** or the seven-membered ring-expansion products **6**. We have studied the conditions to exclusively provide *Z*-configuration in the oxidative ring-opening reaction of 3-cyclohexene-1,2-diols **2** and the subsequent cyclization of the resulting ω-formyl α,β-unsaturated carbonyl compounds **3** to produce the seven-membered unsaturated carbocyclic compounds, dihydrotropones **6**. Details of the studies and some representative reactions of the versatile dihydrotropones **6** are described in this paper.

We reported the exclusive preparation of the 1,6-dicarbonyl compounds **4** with *E*-configuration by the $Pb(OAc)_4$-promoted oxidative ring opening of 3-cyclohexene-1,2-diol **2** in MeCN, in which the initially formed ring-opening product **3** with *Z*-configuration was believed to undergo isomerization to the more stable **4**.[6] We reinvestigated this ring-opening reaction of **2c** (R = Me) to check the possibility of fishing **3c** out of the reaction mixture by shortening the reaction time.[6,7] An aliquot was taken from the reaction mixture every minute and quenched with 1 M HCl solution. The ^{1}H NMR analysis of each sample indicated that **4c** was predominantly obtained from the first sample and that it was not practical to isolate **3c** from the reaction mixture. We found, after many careful experiments, that the isomerization did not proceed under the reaction condition but mostly during the quenching/washing processes with an aqueous acidic solution (Table 1). When no acid was

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TABLE 1. Control of the Stereochemistry in the Oxidative Ring Opening of 3-Cyclohexene-1,2-diols 2

entry	compd	R	reagent	*t* (h)	**3** (%)[a]	**4** (%)[a]
1	**2a**	H	$Pb(OAc)_4$[b]	0.5	0	68
2	**2b**	Ph	$Pb(OAc)_4$[b]	0.5	0	70
3	**2c**	Me	$Pb(OAc)_4$[b]	0.5	0	89
4	**2c**	Me	$Pb(OAc)_4$[c]	0.5	63	0
5	**2d**	Et	$Pb(OAc)_4$[b]	0.5	0	62
6	**2e**	Bu	$Pb(OAc)_4$[b]	0.5	0	93
7	**2e**	Bu	$Pb(OAc)_4$[c]	0.5	53	2
8	**2a**	H	$NaIO_4$[d]	0.5	32	0
9	**2b**	Ph	$NaIO_4$[d]	5	53	0
10	**2c**	Me	$NaIO_4$[d]	2	70	0
11	**2d**	Et	$NaIO_4$[d]	1.25	66	0
12	**2e**	Bu	$NaIO_4$[d]	5	83	0

[a] Isolated yields after purification by SiO_2 flash column chromatography. ^1H NMR spectra are included in Supporting Information. [b] MeCN was used as a solvent at room temperature, and 1 M HCl was added for quench. [c] MeCN was used as a solvent at room temperature, and H_2O was added for quench and wash. [d] A 4:1 volumetric mixture of THF/H_2O was used as a solvent at room temperature, and no acid was used for wash.

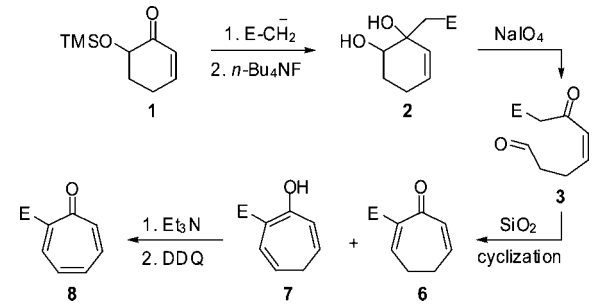
added to quench and wash the mixture of $Pb(OAc)_4$-mediated ring-opening reaction products, the *Z*-isomer **3** was obtained predominantly even after 30 min (entries 4 and 7). This was also confirmed by the complete and instantaneous isomerization of pure **3c** to **4c** in a 1:1 (v/v) mixture of MeCN and 1 M HCl.

Since it was unavoidable to form acetic acid under the condition using $Pb(OAc)_4$, thereby producing **4** even in a small amount (see entry 7), we selected an acid-free $NaIO_4$ condition to exclusively produce **3**. The $NaIO_4$-promoted oxidative ring opening of 3-cyclohexene-1,2-diols **2** was slower than that with $Pb(OAc)_4$. However, retention of *Z*-configuration was realized by using $NaIO_4$ without acid treatment to produce fair to good isolated yields of **3** (53−83%) except for unstable dialdehyde **3a** (32%), where the reaction was stopped in 30 min to minimize the decomposition of **3a** (entries 8−12).[8]

Attempted cyclization of **3c** (R = Me in Scheme 1) to dihydrotropone **6c** (R′ = H) by intramolecular aldol condensation failed under the conditions utilizing LDA or *t*-BuOK as a base and produced only complicated or polymerization products. It was necessary to activate the α-methylene unit of the carbonyl group in **3** by another electron-withdrawing group E for smooth intramolecular Knoevenagel condensation to produce dihydrotropones **6**. Preparation of the activated unsaturated carbonyl compounds **3f**−**3l** with *Z*-configuration and the subsequent cyclization process to dihydrotropones **6f**−**6l** are delineated and summarized in Scheme 2 and Table 2.

Various enolate nucleophiles prepared from ethyl acetate, acetone, acetonitrile, ethyl acetoacetate, acetophenone, *N*,*N*-dimethyl acetamide, and methyl phenyl sulfone were added to 6-trimethylsiloxy-2-cyclohexen-1-one (**1**)[9] in THF at −78 °C to produce 3-cyclohexene-1,2-diols **2f**−**2l** in 60−95% yields after desilylation with *n*-Bu_4NF. Two diastereomeric 1,2-diols were obtained in 1.3−10:1 ratios in the addition reactions depending on the enolate nucleophiles, but both isomers underwent a facile oxidative ring-opening reaction by silica-supported $NaIO_4$[10] to produce the same acyclic 1,6-dicarbonyl compounds **3** with *Z* configuration. The $NaIO_4$-promoted ring opening of **2k** (E = $CONMe_2$) was very sluggish, and $Pb(OAc)_4$

SCHEME 2. Reaction Sequence for Dihydrotropone Synthesis by the Ring-Expansion Strategy[a]



[a] See Table 2 for yields and conditions.

TABLE 2. Yields of Diols 2, Dihydrotropones 6/Cycloheptatrienols 7, and Tropones 8 in Scheme 2

entry	compd	E	**2** (%)[a,b]	**6/7** (%)[a]	**8** (%)[a]
1	**f**	CO_2Et	85 (6:1)	62/31	95
2	**g**	$C(O)CH_3$	63 (2.7:1)	70/ 9	96
3	**h**	CN	94 (1.3:1)	100/0	76
4	**i**	$C(O)CH_2CO_2Et$	65 (2.3:1)	73/0[c]	*d*
5	**j**	C(O)Ph	60 (10:1)	56/8	50[e]
6	**k**	$C(O)NMe_2$	85 (5:1)	63/0[f]	64[g]
7	**l**	SO_2Ph	95 (2:1)	58/19	86[h]

[a] Isolated yields after purification by SiO_2 flash column chromatography. [b] Diastereomeric ratios in parenthesis. [c] Crude yield. [d] Decomposition of **6i** presumably due to oligomerization. [e] Oxidation was carried out by DDQ in refluxing toluene without Et_3N. [f] $Pb(OAc)_4$ was used instead of $NaIO_4$ to induce oxidative ring-opening reaction. [g] DBU was used instead of Et_3N for tautomerization. [h] Cyclohepta-2,4,6-trienone (**8l**) was obtained by dehydrosulfonation.

had to be utilized to afford **3k**. The intramolecular Knoevenagel condensation of crude **3f**−**3l** under the mild condition using SiO_2 in CH_2Cl_2 at ambient temperature, which was serendipitously found during the purification process of the ring-opening product **3**, provided dihydrotropones **6f**−**6l** in decent yields together with varying amounts of their enol tautomers **7f**−**7l** (Table 2). The cyclization of **3k** (E = $CONMe_2$) again required the somewhat stronger condition of heating at 70 °C under SiO_2 in dichloroethane for 5 h to produce dihydrotropone **6k**. Dihydrotropones **6** are in equilibrium with easily separable enol tautomers **7** under the cyclization condition, but **6h** (E = CN), **6i** (E = $COCH_2CO_2Et$), and **6k** (E = $CONMe_2$) were exclusively obtained without their enol tautomers (entries 3, 4, and 6 in Table 2).

The structure of the tautomers **7** was unambiguously decided by analysis of ^1H NMR spectra, the formation of which was easily deduced from the acidity of the allylic proton conjugated with the two electron-withdrawing groups in dihydrotropones **6**. Symmetrical dispositions (coupling patterns) of the four vinylic protons (H_1−H_4) around the two central methylene protons (H_M) indicated the structure **7** [for example, H_1 6.16 ppm (d, J = 10.1 Hz, 1H), H_2 6.01 ppm (dt, J_d = 10.1, J_t = 7.0 Hz, 1H), H_M 2.40 ppm (dd, J = 7.0, 6.6 Hz, 2H), H_3 5.35 ppm (dt, J_d = 9.7, J_t = 6.6 Hz, 1H), H_4 6.45 ppm (d, J = 9.7 Hz, 1H) for **7f**].

Functionalized dihydrotropones **6** are versatile compounds that participate in many synthetically useful transformations.[11] Dihydrotropones **6** may undergo oxidation to tropones **8**. Several reaction conditions have been sought in a preliminary study. The mild bromination/dehydrobromination condition utilizing NBS together with catalytic TMS·OTf worked for the oxidation

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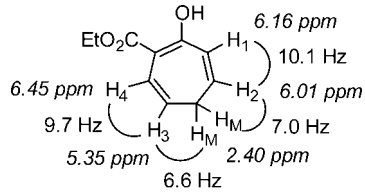


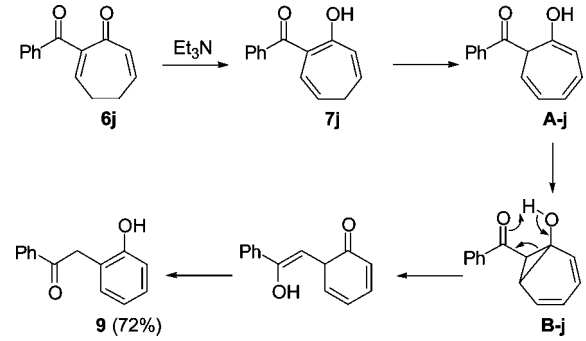
7f

of dihydrotropone **6f** to tropone **8f** (62% yield).[12] It was also found that the oxidation of **6f** to **8f** by DDQ required the condition of reflux in toluene for 2 h (70% yield),[13] whereas the enol tautomers **7f** underwent smooth oxidation to **8f** even at room temperature within 15 min (90% yield). We thus selected the condition of treating dihydrotropones **6** (or a mixture of **6** and **7**) first with a base (Et_3N or DBU) to induce tautomerization to **7** and then with DDQ for the facile oxidation to **8** (the last column in Table 2).[14]

Dihydrotropone **6i** containing both nucleophilic carbon and electrophilic carbon in one molecule was not stable, and attempted purification by silica gel chromatography as well as intended oxidation of the crude **6i** led to decomposition presumably by oligomerization. It was noted that dihydrotropone **6j** gave rise to phenolic compound **9**[15] (72% yield) upon treatment with Et_3N for tautomerization. This novel ring contraction/aromatization occurred only for dihydrotropone **6j**. The mechanism of this reaction is presumed to be the initial formation of tautomer **A-j**, 6π electrocyclization to bicyclo[4.1.0]-heptadiene **B-j**, and ring fragmentation followed by aromatization to give **9** (Scheme 3). Oxidation of dihydrotropone **6j** was thus carried out without the base treatment, only by DDQ at reflux in toluene to produce **8j** in 50% yield. It was also noted that the oxidation (Et_3N/DDQ) of **6l** with a benzene sulfonyl substituent produced the dehydrosulfonation product cyclohepta-2,4,6-trienone (**8l**) in 86% yield.

Dihydrotropones **6** are perfect substrates for the construction of the polycyclic compounds containing a seven-membered carbocycle (Scheme 4). The Diels−Alder reaction of dihydrotropone **6f** (E = CO_2Et) with Danishefsky's diene **10** in refluxing toluene produced bicyclic compound **11f** (92%) after acidic workup. Diene **10** reacted with the more electron-deficient alkene of **6** following the endo-rule (to the keto group) to produce **11f** with the designated regio- and stereochemistry. Treatment of **11f** with DBU induced further cyclization to tricyclic compound **12f** (75%) by the intramolecular conjugate addition of the γ-carbanion of the cycloheptenone to the conjugated cyclohexenone moiety. The Diels−Alder reaction of dihydrotropone **6h** (E = CN) with Danishefsky's diene **10** provided bicyclic compound **11h** (62%). The β-methoxy substituent to the carbonyl group in **11h** survived an acidic workup condition, and treatment of **11h** with DBU gave the tricyclic caged compound **12h** (66%) by the intramolecular aldol reaction of the α-carbanion of the cycloheptenone to the cyclohexanone moiety. The reactivity of the carbanions generated from the cycloheptenone moiety of bicyclic compounds **11** by DBU depends on the soft−hard nature of the electrophilic partners: conjugate addition for the soft γ-carbanion with the soft unsaturated carbonyl moiety in **11f** versus aldol reaction for the hard α-carbanion with the hard carbonyl moiety in **11h**.

SCHEME 3. Ring Contraction of Dihydrotropone 6j



In summary, a condition for exclusive *Z*-control in the oxidative ring-opening reaction of 3-cyclohexene-1,2-diols **2** has been established by utilizing $NaIO_4$ with no acid treatment. The resulting acyclic conjugated carbonyl compounds with *Z*-configuration undergo facile intramolecular Knoevenagel condensation to produce the ring-expanded dihydrotropones **6**, which are versatile compounds participating in various useful transformations. This process complements our ring-contraction protocol from 3-cyclohexene-1,2-diols **2** via the *E*-controlled oxidative ring-opening reaction followed by the intramolecular Baylis−Hillman reaction to produce cyclopentenols **5**.[6] Studies on the preparation of diversely substituted dihydrotropones, their reactions, and applications to the syntheses of the biologically important polycyclic natural products are currently underway.

Experimental Section

Ring-Opening Reaction of 3-Cyclohexen-1,2-diols 2 with $NaIO_4$ To Produce Unsaturated Carbonyl Compounds with Z-Configuration: 2-(*Z*)-Hexenedial (3a).[16] To a stirred solution of 3-cyclohexene-1,2-diol (**2a**) (0.47 g, 4.1 mmol) in THF/H_2O (32 mL/8 mL) was added $NaIO_4$ (1.07 g, 4.9 mmol). The mixture was stirred at room temperature for 30 min. The resulting mixture was then diluted with ethyl acetate, washed with water, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by SiO_2 flash chromatography to give **3a** (0.15 g, 1.3 mmol) in 32% yield. Data for **3a**: ^{1}H NMR δ 1.55−1.80 (m, 2H), 2.40−2.65 (m, 2H), 6.53 (ddd, J = 11.4, 7.8, 3.4 Hz, 1H), 7.31 (ddt, J_d = 11.4, 3.1, J_t = 7.9 Hz, 1H), 9.73 (d, J = 7.8 Hz, 1H), 9.79 (br s, 1H) ppm; ^{13}C NMR δ 21.4, 43.5, 137.9, 146.5, 192.5, 202.0 ppm.

Addition Reaction of the Enolates from Various Carbonyl Compounds to Cyclohexenone 1: (1,6-Dihydroxy-2-cyclohexen-1-yl)-acetic Acid, Ethyl Ester (2f). To a stirred solution of diisopropylamine (4.48 mL, 32 mmol) in THF (30 mL) at 0 °C was added a 1.6 M hexane solution of *n*-BuLi (18.75 mL, 30 mmol). The mixture was stirred for 30 min and then cooled to −78 °C. To this mixture was added ethyl acetate (2.78 mL, 28 mmol), and the mixture was stirred at −78 °C for 40 min. To this mixture was then added cyclohexenone **1** (3.70 g, 20 mmol). The reaction mixture was stirred at −78 °C for 1.5 h and quenched with H_2O.

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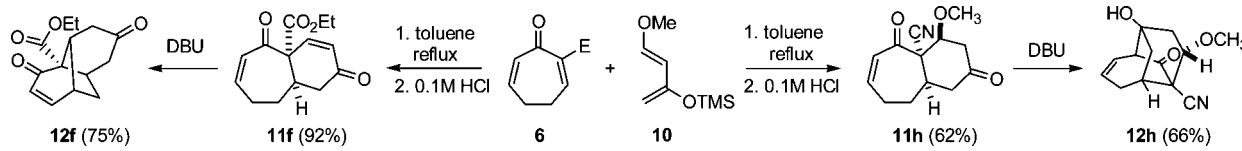
SCHEME 4. Diels−Alder Reaction of Dihydrotropones 6 To Produce Polycyclic Compounds



The mixture was diluted with EtOAc, washed with H_2O, dried over anhydrous K_2CO_3, filtered, and concentrated under reduced pressure. The crude product was dissolved in THF (30 mL), and treated with 1 M THF solution of *n*-Bu_4NF (22 mL, 22 mmol) at 0 °C. The mixture was stirred for 1 h, diluted with ethyl acetate, washed with H_2O, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by SiO_2 flash chromatography to give **2f** (3.41 g, 17 mmol, a 6:1 diastereomeric mixture) in 85% yield. Data for **2f** (major stereoisomer): ^{1}H NMR δ 1.29 (t, J = 7.1 Hz, 3H), 1.76−1.86 (m, 2H), 1.99−2.13 (m, 1H), 2.17−2.28 (m, 1H), 2.51 (A of ABq, J = 15.6 Hz, 1H), 2.68 (d, J = 7.7 Hz, 1H), 2.79 (B of ABq, J = 15.6 Hz, 1H), 3.60 (ddd, J = 8.1, 7.7, 5.7 Hz, 1H), 3.98 (s, 1H), 4.15 (q, J = 7.1 Hz, 2H), 5.67 (ddd, J = 10.0, 2.4, 1.5 HZ, 1H), 5.84 (ddd, J = 10.0, 4.5, 2.8 Hz, 1H) ppm; ^{13}C NMR δ 14.0, 23.9, 26.3, 42.7, 60.9, 69.7, 71.8, 129.1, 130.5, 172.7 ppm; IR (KBr) 3444, 1732, 1372, 1182 cm^{-1}; HRMS (FAB$^+$) calcd for $C_{10}H_{17}O_4$ 201.1127, found 201.1124.

Ring Opening of 3-Cyclohexen-1,2-diols 2 with SiO_2-Supported $NaIO_4$ and Subsequent Cyclization to Dihydrotropones: 7-Oxo-1,5-cycloheptadienecarboxylic Acid, Ethyl Ester (6f). To a stirred solution of diol **2f** (1.68 g, 8.42 mmol) in CH_2Cl_2 (30 mL) was added SiO_2-supported $NaIO_4$ (25.9 g, 8.63 mmol, 3 g/mmol). The mixture was stirred at room temperature for 4 h and filtered under reduced pressure. The filter cake was rinsed with $CHCl_3$, and the filtrate was concentrated under reduced pressure. The crude product was then dissolved in CH_2Cl_2 (30 mL), and 70−230 mesh silica gel (16.8 g, 2 g/mmol) was added. The mixture was stirred at room temperature for 2 h and filtered under reduced pressure. The filtered silica gel was rinsed with $CHCl_3$, and the filtrate was concentrated under reduced pressure. The crude product was purified by SiO_2 flash chromatography to give dihydrotropone **6f** (1.0 g, 5.2 mmol, 62% yield) and its tautomer **7f** (0.5 g, 2.6 mmol, 31% yield). Data for **6f**: ^{1}H NMR δ 1.31 (t, J = 7.1 Hz, 3H), 2.43−2.61 (m, 4H), 4.26 (q, J = 7.1 Hz, 2H), 6.17 (dt, J_d = 12.1, J_t = 1.7 Hz, 1H), 6.69 (dt, J_d = 12.1, J_t = 5.3 Hz, 1H), 7.35 (t, J = 6.6 Hz, 1H) ppm; ^{13}C NMR δ 14.1, 26.0, 26.6, 61.2, 132.4, 139.0, 145.5, 145.5, 165.6, 190.8 ppm; IR (KBr) 1732, 1651, 1275 cm^{-1}; HRMS (CI$^+$) calcd for $C_{10}H_{13}O_3$ 181.0865, found 181.0867. Data for **7f**: ^{1}H NMR δ 1.37 (t, J = 7.1 Hz, 3H), 2.40 (dd, J = 7.0, 6.6 Hz, 2H), 4.32 (q, J = 7.1 Hz, 2H), 5.35 (dt, J_d = 9.7, J_t = 6.6 Hz, 1H), 6.01 (dt, J_d = 10.1, J_t = 7.0 Hz, 1H), 6.16 (d, J = 10.1 Hz, 1H), 6.45 (d, J = 9.7 Hz, 1H), 12.72 (br s, 1H) ppm; ^{13}C NMR δ 14.2, 27.1, 61.1, 105.6, 118.2, 123.3, 124.7, 134.3, 170.1, 172.5 ppm; IR (KBr) 2971, 1739, 1652, 1557, 1372, 1227 cm^{-1}.

Oxidation of Dihydrotropones to Tropones: 7-Oxo-1,3,5-cycloheptatrienecarboxylic Acid, Ethyl Ester (8f). To a stirred solution of **6f** (0.2 g, 1.12 mmol) in CH_2Cl_2 (5 mL) was added Et_3N (0.18 mL, 1.23 mmol) at room temperature. The mixture was stirred for 15 min, and DDQ (0.26 g, 1.12 mmol) was added. The reaction mixture was stirred for 15 min, diluted with EtOAc, washed with 1 M $NaHCO_3$ solution, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by SiO_2 flash chromatography to give **8f** (0.19 g, 1.06 mmol) in 95% yield. Data for **8f**: ^{1}H NMR δ 1.36 (t, J = 7.1 Hz, 3H), 4.37 (q, J = 7.1 Hz, 2H), 6.97−7.20 (m, 4H), 7.53 (dd, J = 8.0, 1.1 Hz, 1H) ppm; ^{13}C NMR δ 14.1, 61.9, 132.8, 135.1, 135.8, 136.6, 142.8, 143.4, 167.3, 184.5 ppm; IR (KBr) 1728, 1634, 1590 1235 cm^{-1}; HRMS (CI$^+$) calcd for $C_{10}H_{11}O_3$ 179.0708, found 179.0709.

Ring Contraction/Aromatization of Dihydrotropone 6j: 2-(2-Hydroxyphenyl)-1-phenylethanone (9).[15] To a stirred solution of **6j** (0.25 g, 1.2 mmol) in CH_2Cl_2 (10 mL) was added Et_3N (0.5 mL, 3.6 mmol) at 0 °C. The mixture was stirred at 0 °C for 2 h and then diluted with CH_2Cl_2, washed with water, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude products was purified by SiO_2 flash chromatography to give **9** (0.18 g 0.86 mmol) in 72% yield. Data for **9**: ^{1}H NMR δ 4.29 (s, 2H), 6.84−6.92 (m, 1H), 6.93−6.99 (m, 1H), 7.13−7.22 (m, 2H), 7.47−7.55 (m, 2H), 7.58−7.66 (m, 1H), 8.06−8.14 (m, 2H) ppm; ^{13}C NMR δ 41.0, 117.6, 120.8, 121.0, 128.8, 129.0, 130.9, 134.0, 135.7, 155.5, 201.1 ppm; IR (KBr) 3412, 1677, 1596, 1456, 1343, 750 cm^{-1}.

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Supporting Information Available: General experimental, experimental procedures, analytical data, and ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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