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# $SnCl_4$-Catalyzed Reaction of *o*-Benzoquinones and Aryl Acetylenes: An Unprecedented One-Pot Synthesis of Tropone Derivatives

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**Abstract:** Highly substituted tropone derivatives were obtained as a result of $SnCl_4$-catalyzed cycloaddition of 3-methoxy-substituted *o*-benzoquinones with aryl acetylenes and subsequent rearrangement of the adducts with concomitant decarbonylation.

The chemistry of *o*-quinones, especially their cycloadditions, has been the subject of considerable interest.[1] Our own studies have uncovered novel facets of the cycloadditions of *o*-quinones.[2] A reaction of particular interest has been the Diels—Alder cycloaddition of *o*-benzoquinones and aryl acetylenes leading to bicyclo[2.2.2]octenediones; the latter have been shown to undergo facile photolytic decarbonylation, thus constituting an efficient synthesis of polysubstituted aromatics.[3] During the course of some related investigations, we encountered a novel tropone synthesis, and it is described here.

Our investigations commenced with an attempt at the Diels—Alder cycloaddition of quinone **1** with phenylacetylene. In the event, bicycloadducts **2** and **3** (Figure 1) were obtained albeit in very low yields; the major product was a dimer of quinone **1**.

To enhance the efficiency of the reaction, an attempt was made to catalyze it with $SnCl_4$; the catalytic effect of Lewis acids in Diels—Alder reactions[4] is well-known since the original work of Yates and Eaton.[5] A facile reaction occurred, but to our surprise the major product formed was a tropone derivative **5** (Scheme 1). The [3.2.1] adduct **6** was obtained as a minor product; formation of **6** has precedence in our earlier work.[6]

The product **5** was characterized by spectroscopic methods. IR spectrum of **5** showed a very weak carbonyl

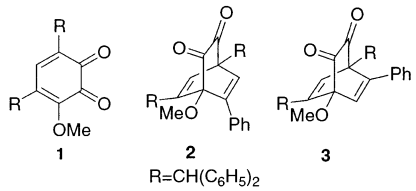
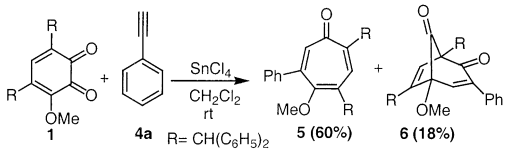



**FIGURE 1.**

**SCHEME 1**




absorption at 1686 $cm^{-1}$. In the $^1H$ NMR spectrum, the singlet due to the methoxy protons was present at $\delta$ 2.99. The benzylic protons were discernible at $\delta$ 5.93 and 6.10 as singlets. In the $^{13}C$ NMR spectrum, benzylic carbons resonated at $\delta$ 51.23 and 52.52. The methoxy carbon signal was visible at $\delta$ 59.94 and the carbonyl carbon at $\delta$ 184.52. Final proof for the structure of **5** was obtained by single-crystal X-ray analysis.

Although the reaction did not proceed along the expected lines, the facility of the reaction and the interest in tropones and tropolones[7] prompted us to explore the chemistry further. In this context, it is noteworthy that there are only two useful methods available for the conversion of *o*-benzoquinones to tropone derivatives, viz., the reaction of bismuthonium ylides with quinones[8a] and the Lewis acid-promoted rearrangement of homo-*o*-benzoquinones to α-tropolones;[8b] the homo-*o*-benzoquinones themselves are obtained by a multistep process from cyclohexadiene derivatives.

The $SnCl_4$-catalyzed cycloaddition of *o*-quinones was investigated with different aryl acetylenes. Results similar to that described above were obtained, and these are presented in Table 1.

Although the exact mechanism of the tropone formation is not known with certainty, a rationalization along the following lines can be invoked. Conceivably the first step will be a Lewis acid-catalyzed Diels—Alder reaction of *o*-bezoquinone **1** and phenylacetylene to form the bicyclo[2.2.2] adduct **2**. This adduct can undergo a Lewis

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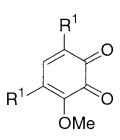
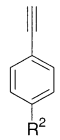
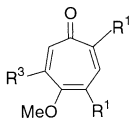
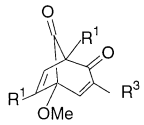
**TABLE 1: Reaction of O-benzoquinones 1, 7, and 8 with Aryl Acetylenes 4−f**


**1, 7& 8**

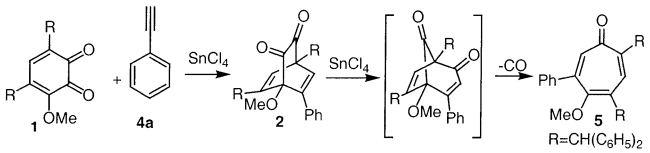

**4a,b,c,d,e & 4f**


**9-17**


**18-26**

| | | | |
|---|---|---|---|
| **7**: $R^1$ = CH(p-$CH_3$ $C_6H_4$)$_2$ | **4a**: $R^2$ = H | **9**: $R^1$ = CH(p-$CH_3$ $C_6H_4$)$_2$ $R^3$ = $C_6H_5$ (58%) | **18**: $R^1$=CH(p-$CH_3$ $C_6H_4$)$_2$ $R^3$ = $C_6H_5$ (12%) |
| **8**: $R^1$= CH(p-$^t$Bu $C_6H_4$)$_2$ | **4a** | **10**: $R^1$= CH(p-$^t$Bu $C_6H_4$)$_2$ $R^3$ = $C_6H_5$ (55%) | **19**: $R^1$=CH(p-$^t$Bu $C_6H_4$)$_2$ $R^3$ = $C_6H_5$ (17%) |
| **1** | **4b**: $R^2$ =$CH_3$ | **11**: $R^1$=CH($C_6H_5$)$_2$ $R^3$ = p-$CH_3$ $C_6H_4$ (61%) | **20**: $R^1$=CH($C_6H_5$)$_2$ $R^3$ = p-$CH_3$ $C_6H_4$ (14%) |
| **7** | **4b** | **12**: $R^1$ = CH(p-$CH_3$ $C_6H_4$)$_2$ $R^3$ = p-$CH_3$ $C_6H_4$ (57%) | **21**: $R^1$=CH(p-$CH_3$ $C_6H_4$)$_2$ $R^3$ = p-$CH_3$ $C_6H_4$(13%) |
| **8** | **4b** | **13**: $R^1$= CH(p-$^t$Bu $C_6H_4$)$_2$ $R^3$ = p-$CH_3$ $C_6H_4$ (56%) | **22**: $R^1$= CH(p-$^t$Bu $C_6H_4$)$_2$ $R^3$ = p-$CH_3$ $C_6H_4$(12%) |
| **1** | **4c**: $R^2$ = $nC_5H_{11}$ | **14**: $R^1$ = CH($C_6H_5$)$_2$ $R^3$ = p- $nC_5H_{11}$ $C_6H_4$(64%) | **23**: $R^1$ = CH($C_6H_5$)$_2$ $R^3$ = p- $nC_5H_{11}$ $C_6H_4$(11%) |
| **1** | **4d**: $R^2$ = Cl | **15**: $R^1$ = CH($C_6H_5$)$_2$ $R^3$ = p- Cl $C_6H_4$ (59%) | **24**: $R^1$ = CH($C_6H_5$)$_2$ $R^3$ = p- Cl $C_6H_4$ (15%) |
| **1** | **4e**: $R^2$ = $C_6H_5$ | **16**: $R^1$ = CH($C_6H_5$)$_2$ $R^3$ = p- $C_6H_5$ $C_6H_4$ (48%) | **25**: $R^1$ = CH($C_6H_5$)$_2$ $R^3$ = p- $C_6H_5$ $C_6H_4$(21%) |
| **1** | **4f**:  | **17**: $R^1$ = CH($C_6H_5$)$_2$ $R^3$ = $C_{10}H_7$ (66%) | **26**: $R^1$ = CH($C_6H_5$)$_2$ $R^3$ = $C_{10}H_7$ (10%) |

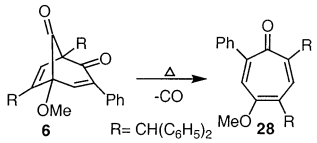
**SCHEME 2**




acid-catalyzed rearrangement[6] to form a [3.2.1] adduct **27**, which spontaneously eliminates a molecule of carbon monoxide to form the tropone derivative **5** (Scheme 2).

The above mechanistic pathway was supported by the following findings. We treated the adducts **2** and **3** independently with $SnCl_4$ under identical conditions. It was found that **2** was converted to **5** exclusively, whereas **3** produced only **6**. Also the [3.2.1] adduct **6**, when heated above its melting point, eliminated a molecule of CO to form another tropone derivative **28** which is isomeric with **5** (Scheme 3). The ease of decarbonylation of **27** vis a vis **6** may be attributed to the release of steric strain in the former.

**SCHEME 3**




In conclusion, we have uncovered a simple and efficient one-pot synthesis of highly substituted tropone derivatives.

## Experimental Section

3-Methoxycatechol, montmorillonite K-10, sodium periodate, and tin(IV) chloride were purchased. Aryl acetylenes used in the experiments were either purchased or synthesized.[9]

**Experimental Procedure for the Synthesis of Quinone 1.** 3-Methoxycatechol (2 g, 0.014 mol) and benzhydrol (5.78 g, 0.031 mol) were dissolved in dry dichloromethane (30 mL). To this mixture, 5.78 g of montmorillonite K-10 (pre heated to 80 °C and cooled under moisture free conditions) was added and stirred for 12 h. The reaction mixture was then filtered, and the filtrate was subjected to silica gel column chromatography using hexane−ethyl acetate mixture (85:15) to afford the substituted catechol (4.85 g, 72%). To this catechol (dissolved in 20 mL dichloromethane) was added a solution of sodium periodate (6.6 g, 0.030 mol in 20 mL water) and stirred for 10 h. The two layers were separated, and the water layer was extracted with dichloromethane (10 mL × 2). The combined extracts were dried over sodium sulfate and subjected to silica gel column chromatography using hexane−ethyl acetate mixture to afford the quinone **1** (3.86 g, 80%).

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**Spectral Data for the Quinone 1.** Dark brown solid; mp: 47−49 °C; IR (KBr) $\nu_{max}$: 700, 745, 979, 1064, 1309, 1449, 1493, 1600, 1666, 3026, 3059 cm$^{-1}$; $^1$H NMR: $\delta$ 3.81(s, 3H), 5.40 (s, 1H), 5.73 (s, 1H), 6.38 (d, 1H, $J$ = 1.2 Hz), 6.91−7.00 (m, 8H), 7.15−7.26 (m, 12H). $^{13}$C NMR: $\delta$ 48.19, 49.03, 60.41, 126.59, 127.10, 127.92, 128.34, 128.58, 128.64, 128.69, 137.77, 139.76, 140.41, 140.58, 140.85, 148.50, 176.95, 178.46. HRMS Calcd for $C_{33}H_{26}O_3$: 470.1882. Found: 470.1876.

**Experimental Procedure for the Synthesis of Tropone Derivatives and Bicycloadducts.** The general procedure for the synthesis of tropone derivatives and bicycloadducts is exemplified by the synthesis of **5** and **6**. To a stirred mixture of *o*-benzoquinone **1** (0.20 g, 4.25 × 10$^{-4}$ mol) and phenylacetylene (0.052 g, 5.10 × 10$^{-4}$ mol) in dry dichloromethane (2 mL) was added $SnCl_4$ (0.851 mL, 1 molar solution of $SnCl_4$ in heptane) and stirred for 2 h under an atmosphere of argon at room temperature. The reaction mixture was then quenched with water (5 mL) and extracted with dichloromethane (2 × 10 mL). The organic extract was concentrated and the crude product subjected to column chromatography on silica gel using hexane−ethyl acetate mixture (90:10) to afford the tropone derivative **5** (0.139 g, 60%) and the [3.2.1] adduct **6** (0.044 g, 18%). Tropone derivative **14** and bicycloadduct **23** were separated by column chromatography using hexane−dimethoxyethane (95:5) mixture.

**Spectral Data for Tropone Derivatives and Bicycloadducts.** 4-Methoxy-3-phenyl-5,7-bis(diphenyl methyl)-2,4,6-cycloheptatrien-1-one 5. Pale yellow crystals, recrystallized from hexane−dichloromethane; mp: 200−202 °C; IR (KBr) $\nu_{max}$: 689, 752, 989, 1151, 1201, 1439, 1489, 1551, 1686, 2930, 3030 cm$^{-1}$; $^1$H NMR: $\delta$ 2.99 (s, 3H), 5.93 (s, 1H), 6.10 (s, 1H), 6.84−6.85 (m, 5H), 6.95 (s, 1H), 7.07 (s, 1H), 7.13−7.45 (m, 20 H); $^{13}$C NMR: $\delta$ 51.23, 52.52, 59.94, 126.22, 126.49, 128.06, 128.18, 128.43, 129.00, 129.13, 129.20, 138.11, 140.09, 140.26, 140.66, 142.15, 142.24, 146.81, 150.99, 158.12, 184.52. Anal. Calcd for $C_{40}H_{32}O_2$: C, 88.20: H, 5.92. Found C, 88.28; H, 6.04.

**1,6-Bis(diphenylmethyl)-5-methoxy-3-phenylbicyclo-[3.2.1]oct-3,6-diene-2,8-dione 6.** Colorless crystals, recrystallized from hexane−dichloromethane; mp: 132−134 °C; IR (KBr) $\nu_{max}$: 1032, 1151, 1238, 1438, 1494, 1669, 1781, 2949 cm$^{-1}$. $^1$H NMR: $\delta$ 3.54 (s, 3H), 4.67 (s, 1H), 4.97 (s, 1H), 5.72 (s, 1H), 6.41 (s, 1H), 6.80−6.87 (m, 4H), 6.96−6.98 (m, 8H), 7.05−7.13 (m, 4H), 7.21−7.24 (m, 9H); $^{13}$C NMR: $\delta$ 49.29, 53.61, 55.53, 64.69, 99.29, 126.09, 126.45, 126.68, 126.99, 127.38, 127.73, 127.93, 128.27, 128.43, 128.77, 128.96, 129.32, 129.81, 130.86, 137.49, 137.58, 138.57, 139.31, 139.53, 140.42, 147.40, 165.25, 188.54, 198.00. Anal. Calcd for $C_{41}H_{32}O_3$: C, 85.99; H, 5.63. Found: C, 86.26; H, 5.85.

**4-Methoxy-3-phenyl-5,7-bis(bis(4-methylphenyl)methyl)-2,4,6-cycloheptatrien-1-one 9.** Pale yellow crystals, recrystallized from hexane−dichloromethane; mp: 189−191 °C; IR (KBr) $\nu_{max}$: 764, 805, 996, 1153, 1242, 1370, 1445, 1510, 1576, 1613, 1683, 2921, 3020 cm$^{-1}$; $^1$H NMR: $\delta$ 2.29 (s, 6H), 2.33 (s, 6H), 2.97 (s, 3H), 5.83 (s, 1H), 6.00 (s, 1H), 6.72−6.76 (m, 8H), 6.92−7.00 (m, 8H), 7.04 (s, 1H), 7.25 (s, 1H), 7.36−7.45 (m, 5H); $^{13}$C NMR: $\delta$ 21.02, 50.52, 51.89, 59.94, 128.00, 128.14, 128.79, 129.01, 129.07, 135.38, 135.76, 138.55, 139.42, 139.49, 140.13, 140.23, 140.49, 146.77, 151.31, 157.82, 184.68. Anal. Calcd for $C_{44}H_{40}O_2$: C; 87.96; H; 6.71. Found: C; 88.05, H, 6.69.

**1,6-Bis(bis(4-methylphenyl)methyl)-5-methoxy-3-phenylbicyclo[3.2.1]oct-3,6-diene-2,8-dione 18.** Colorless crystals, recrystallized from hexane−dichloromethane; mp: 177−179 °C; IR (KBr) $\nu_{max}$: 746, 1151, 1259, 1438, 1510, 1680, 1781, 2937 cm$^{-1}$; $^1$H NMR: $\delta$ 2.19 (s, 3H), 2.28 (s, 3H), 2.35 (s, 3H), 3.54 (s, 3H), 4.60 (s, 1H), 4.88 (s, 1H), 5.71 (s, 1H), 6.39 (s, 1H), 6.67−6.88 (m, 10H), 6.99−7.09 (m, 11H); $^{13}$C NMR: $\delta$ 21.06, 21.25, 48.58, 52.65, 55.60, 64.73, 99.42, 126.41, 126.51, 127.90, 128.46, 128.57, 128.90, 128.95, 129.20, 129.51, 129.68, 130.00, 135.36, 135.86, 136.02, 136.35, 136.60, 136.73, 136.97, 137.39, 137.77, 137.80, 147.48, 165.53, 188.83, 198.11. Anal. Calcd for $C_{45}H_{40}O_3$: C, 85.95; H, 6.41. Found: C, 86.13; H, 6.59.

**4-Methoxy-3-phenyl-5,7-bis(bis(4-*tert*-butylphenyl)methyl)-2,4,6-cycloheptatrien-1-one 10.** Pale yellow crystals, recrystallized from hexane−ethyl acetate; mp: 130−132 °C; IR (KBr) $\nu_{max}$: 575, 699, 821, 997, 1018, 1155, 1268, 1364, 1508, 1582, 1614, 1686, 2867, 2961 cm$^{-1}$; $^1$H NMR: $\delta$ 1.27 (m, 18H), 1.31 (m, 18H), 3.02 (s, 3H), 5.89 (s, 1H), 5.98 (s, 1H), 6.70−6.74 (m, 8H), 6.90 (s, 1H), 7.07 (s, 1H), 7.16−7.42 (m, 13H); $^{13}$C NMR: $\delta$ 26.92, 31.44, 34.32, 34.40, 50.50, 51.65, 60.07, 125.01, 125.25, 128.03, 128.14, 128.93, 129.03, 129.09, 139.28, 139.43, 140.44, 141.07, 146.75, 148.68, 149.17, 151.29, 157.85, 184.19. Anal. Calcd for $C_{56}H_{64}O_2$: C, 87.45; H, 8.39. Found: C, 87.19; H, 8.45.

**1,6-Bis(bis(4-*tert*-butylphenyl)methyl)-5-methoxy-3-phenylbicyclo[3.2.1]oct-3,6-diene-2,8-dione 19.** Colorless crystals, recrystallized from hexane−dichloromethane; mp: 194−196 °C; IR (KBr) $\nu_{max}$: 820, 1138, 1257, 1432, 1512, 1688, 1769, 2962 cm$^{-1}$; $^1$H NMR: $\delta$ 1.21 (s, 9H), 1.26 (s, 9H), 1.33 (s, 9H), 1.34 (s, 9H), 3.52 (s, 3H), 4.55 (s, 1H), 4.90, (s, 1H), 5.70, (s, 1H), 6.43, (s, 1H), 6.71−7.24 (m, 21H); $^{13}$C NMR: $\delta$ 31.27, 31.30, 31.38, 34.10, 34.35, 48.03, 52.88, 55.27, 64.93, 99.18, 124.30, 124.62, 124.84, 125.38, 126.20, 126.36, 127.57, 127.92, 128.42, 128.55, 129.38, 130.78, 136.05, 136.24, 136.39, 137.70, 137.77, 137.91, 147.08, 148.42, 149.01, 149.28, 149.63, 165.47, 188.47, 198.02. Anal. Calcd for $C_{57}H_{64}O_3$: C, 85.89; H, 8.09. Found: C, 86.06; H, 8.31.

**4-Methoxy-3-(4-methylphenyl)-5,7-bis(diphenylmethyl)-2,4,6-cycloheptatrien-1-one 11.** Pale yellow crystals, recrystallized from hexane−ethyl acetate; mp: 160−162 °C; IR (KBr) $\nu_{max}$: 699, 743, 994, 1153, 1368, 1447, 1492, 1572, 1601, 1689, 2931, 3024 cm$^{-1}$; $^1$H NMR: $\delta$ 2.38 (s, 3H), 2.99 (s, 3H), 5.93 (s, 1H), 6.09 (s, 1H), 6.84−6.87 (m, 8H), 6.93 (s, 1H), 7.06 (s, 1H), 7.12−7.36 (m, 16 H); $^{13}$C NMR: $\delta$ 21.32, 51.36, 52.63, 60.01, 126.32, 126.59, 128.29, 128.54, 128.90, 129.06, 129.27, 129.33, 137.36, 138.06, 138.25, 140.30, 140.59, 142.34, 142.42, 146.89, 151.00, 158.44, 184.71; HRMS Calcd for $C_{41}H_{34}O_2$: 558.2558. Found: 558. 2553.

**1,6-Bis(diphenylmethyl)-5-methoxy-3-(4-methylphenyl)-bicyclo[3.2.1]oct-3,6-diene-2,8-dione 20.** Pale yellow crystals, recrystallized from hexane−ethyl acetate; mp: 167−169 °C; IR (KBr) $\nu_{max}$: 689, 1022, 1146, 1177, 1448, 1493, 1686, 1775, 2947, 3025 cm$^{-1}$; $^1$H NMR: $\delta$ 2.24 (s, 3H), 3.53 (s, 3H), 4.71 (s, 1H), 4.96 (s, 1H) 5.71 (s, 1H), 6.39 (s, 1H), 6.80−6.97 (m, 13 H), 7.22−7.24 (m, 11 H); $^{13}$C NMR: $\delta$ 21.15, 49.18, 53.24, 55.32, 64.51, 99.22, 125.92, 126.02, 126.31, 126.55, 126.87, 127.26, 127.64, 128.15, 128.51, 128.64, 128.83, 129.21, 129.65, 130.77, 134.63, 137.30, 138.37, 138.44, 139.23, 139.62, 140.30, 147.11, 165.37, 188.51, 197.92. Anal. Calcd for $C_{42}H_{34}O_3$: C, 85.98; H, 5.84. Found: C, 85.92; H, 6.04.

**4-Methoxy-3-(4-methylphenyl)-5,7-bis(bis(4-methylphenyl)methyl)-2,4,6-cycloheptatrien-1-one 12.** Pale yellow crystals, recrystallized from hexane−ethyl acetate; mp: 83−85 °C; IR (KBr) $\nu_{max}$: 766, 996, 1153, 1204, 1368, 1510, 1572, 1594, 1611, 2921, 3020 cm$^{-1}$; $^1$H NMR: $\delta$ 2.31 (s, 6H), 2.35 (s, 6H), 2.40 (s, 3H), 3.00 (s, 3H), 5.85 (s, 1H), 6.03 (s, 1H), 6.74−6.76 (m, 4H), 6.94−7.38 (m, 14H), 7.06 (s, 1H), 7.20 (s, 1H); $^{13}$C NMR: $\delta$ 21.10, 21.29, 50.62, 51.98, 59.98, 128.87, 129.08, 129.13, 129.16, 135.44, 135.82, 137.46, 138.09, 138.49, 139.58, 139.64, 140.16, 140.40, 146.83, 151.29, 158.11, 184.82. Anal. Calcd for $C_{45}H_{42}O_2$: C; 87.91; H; 6.89. Found: C; 87.68, H; 7.15.

**1,6-Bis(bis(4-methylphenyl)methyl)-5-methoxy-3-(4-methylphenyl)bicyclo[3.2.1]oct-3,6-diene-2,8-dione 21.** Colorless crystals, recrystallized from hexane−dichloromethane; mp: 120−122 °C; IR (KBr) $\nu_{max}$: 807, 1020, 1145, 1245, 1439, 1676, 1776, 2987 cm$^{-1}$; $^1$H NMR: $\delta$ 2.20 (s, 3H), 2.25 (s, 3H), 2.27 (s, 3H), 2.35 (s, 3H), 2.36 (s, 3H), 3.52 (s, 3H), 4.64 (s, 1H), 4.87 (s, 1H), 5.70 (s, 1H), 6.36 (s, 1H), 6.66 (d, 2H, $J$ = 7.8 Hz), 6.75−7.10 (m, 18 H); $^{13}$C NMR: $\delta$ 20.97, 21.11, 21.16, 21.27, 48.45, 52.23, 55.41, 64.53, 99.36, 125.98, 126.42, 128.31, 128.41, 128.51, 128.78, 128.83, 129.08, 129.39, 129.49, 130.66, 134.86, 135.24, 135.75, 135.92, 136.27, 136.54, 136.63, 137.13, 137.25, 137.66, 138.43, 147.15, 165.72, 188.83, 198.05. Anal. Calcd for $C_{46}H_{42}O_3$: C, 85.95; H, 6.59. Found: C, 86.24; H, 6.70.

**4-Methoxy-3-(4-methylphenyl)-5,7-bis(bis(4-*tert*-butylphenyl)methyl)-2,4,6-cycloheptatrien-1-one 13.** Pale yellow crystals, recrystallized from hexane−ethyl acetate; mp: 115−117 °C; IR (KBr) $\nu_{max}$: 996, 1018, 1109, 1268, 1364, 1406, 1510, 1573, 1610, 1685, 2878, 2903 cm$^{-1}$; $^1$H NMR: $\delta$ 1.26 (s, 18H), 1.31 (s, 18H), 2.37 (s, 3H), 3.02 (s, 3H), 5.88 (s, 1H), 5.98 (s, 1H),

6.90−6.74 (m, 7H), 6.87 (s, 1H), 7.05 (s, 1H), 7.15−7.35 (m, 13H); $^{13}$C NMR: $\delta$ 21.30, 26.95, 31.46, 34.35, 34.43, 50.51, 51.64, 60.07, 125.02, 125.26, 128.78, 128.95, 129.05, 137.60, 137.99, 139.08, 139.33, 139.49, 140.94, 141.08, 147.04, 148.67, 149.16, 151.45, 158.06, 184.27; HRMS Calcd for $C_{57}H_{66}O_2$: 782.50628; Found: 782.50568.

**1,6-Bis(bis(4-*tert*-butylphenyl)methyl)-5-methoxy-3-(4-methylphenyl)bicyclo[3.2.1]oct-3,6-diene-2,8-dione 22.** Colorless crystals, recrystallized from hexane−dichloromethane; mp: 203−205 °C; IR (KBr) $\nu_{max}$: 578, 825, 1149, 1269, 1363, 1510, 1692, 1770, 2867, 2961 cm$^{-1}$; $^1$H NMR: $\delta$ 1.21 (s, 9H). 1.26 (s, 9H), 1.30 (s, 9H), 1.33 (s, 9H), 2.23 (s, 3H), 3.49 (s, 3H), 4.58 (s, 1H), 4.89 (s, 1H), 5.69 (s, 1H), 6.43 (s, 1H), 6.72−6.74 (m, 4H), 6.83−6.97 (m, 8H), 7.13−7.23 (m, 8H); $^{13}$C NMR: $\delta$ 21.10, 31.28, 31.38, 31.48, 34.09, 34.36, 48.16, 52.81, 55.09, 65.10, 99.44, 124.36, 124.52, 124.92, 125.44, 126.07, 126.28, 127.68, 128.31, 128.44, 128.59, 129.40, 130.27, 134.95, 135.87, 136.41, 136.46, 137.73, 138.09, 146.83, 148.44, 149.20, 149.43, 149.78, 165.73, 188.61, 198.26. Anal. Calcd for $C_{58}H_{66}O_3$: C, 85.88; H, 8.2O. Found: C, 86.02; H, 8.44.

**4-Methoxy-3-(4-*n*-pentylphenyl)-5,7-bis(diphenylmethyl)-2,4,6-cycloheptatrien-1-one 14.** Pale yellow crystals, recrystallized from pentane; mp: 103−105 °C; IR (KBr) $\nu_{max}$: 698,-742, 994, 1030, 1152, 1205, 1368, 1447, 1492, 1571, 1594, 1613, 2952, 3024 cm$^{-1}$.$^1$H NMR: $\delta$ 0.89 (t, 3H), 1.30−1.35 (m, 4H), 1.58−1.68 (m, 2H), 2.63 (t, 2H), 2.99 (s, 3H), 5.95 (s, 1H), 6.11 (s, 1H), 6.83−6.88 (m, 8H), 6.94 (s, 1H), 7.08 (s, 1H), 7.13−7.21 (m, 14H), 7.35−7.38 (m, 2H); $^{13}$C NMR: $\delta$ 14.01, 22.50, 30.96, 31.48, 35.63, 51.31, 52.65, 60.00, 126.30, 126.54, 128.20, 128.27, 128.49, 128.91, 129.26, 137.39, 138.01, 140.30, 140.45, 142.29, 142.36, 143.37, 146.99, 150.84, 158.51, 184.89. Anal. Calcd for $C_{45}H_{42}O_2$: C, 87.91; H, 6.89. Found: C, 87.66; H, 7.05.

**1,6-Bis(diphenylmethyl)-5-methoxy-3-(4-*n*-pentylphenyl)-bicyclo[3.2.1]oct-3,6-diene-2,8-dione 23.** Colorless crystals, recrystallized from pentane; mp: 136−138 °C; IR (KBr) $\nu_{max}$: 668, 698, 745, 1031, 1151, 1450, 1494, 1679, 1776, 2922, 2954 cm$^{-1}$; $^1$H NMR: $\delta$ 0.89 (s, 3H), 1.20−1.36 (m, 4H), 1.46−1.56 (m, 2H), 2.48 (t, 2H), 3.52 (s, 3H), 4.71 (s, 1H), 4.97 (s, 1H), 5.74 (s, 1H), 6.43 (s, 1H), 6.77−7.01 (m, 13H), 7.22−7.25 (m, 11H); $^{13}$C NMR: $\delta$ 14.02, 22.50, 30.93, 31.24, 35.52, 49.30, 53.47, 55.32, 64.74, 99.40, 125.92, 126.02, 126.36, 126.66, 126.91, 127.34, 127.65, 127.78, 127.94, 128.22, 128.73, 128.89, 129.27, 129.74, 130.78, 134.81, 137.55, 138.33, 139.29, 139.53, 140.34, 143.60, 147.15, 165.46, 188.65, 198.12. Anal. Calcd for $C_{46}H_{42}O_3$: C, 85.95; H, 6.59. Found: C, 85.71; H, 6.40.

**4-Methoxy-3-(4-chlorophenyl)-5,7-bis(diphenylmethyl)-2,4,6-cycloheptatrien-1-one 15.** Pale yellow crystals, recrystallized from hexane−ethyl acetate; mp: 189−191 °C; IR (KBr) $\nu_{max}$: 835, 993, 1014, 1090, 1154, 1204, 1448, 1496, 1571, 1594, 1614, 3011, 3024, 3060 cm$^{-1}$; $^1$H NMR: $\delta$ 3.00 (s, 3H), 5.94 (s, 1H), 6.09 (s, 1H), 6.82−6.87 (m, 8H), 6.98 (s, 1H), 7.04 (s, 1H), 7.14−7.24 (m, 12 H), 7.34−7.42 (m, 4H). $^{13}$C NMR: $\delta$ 51.32, 52.67, 60.20, 126.39, 126.66, 128.32, 128.43, 128.57, 129.19, 129.25, 130.45, 134.56, 138.53, 138.64, 140.52, 140.56, 142.10, 142.17, 145.89, 151.26, 157.84, 184.63. Anal. Calcd for $C_{40}H_{31}ClO_2$: C, 82.96; H, 5.40. Found: C, 83.17; H, 5.55.

**1,6-Bis(diphenylmethyl)-5-methoxy-3-(4-chlorophenyl)-bicyclo[3.2.1]oct-3,6-diene-2,8-dione 24.** Colorless crystals, recrystallized from hexane−ethyl acetate; mp: 155−157 °C; IR (KBr) $\nu_{max}$: 698, 749, 1090, 1151, 1448, 1492, 1593, 1678, 1776, 3052 cm$^{-1}$; $^1$H NMR: $\delta$ 3.52 (s, 3H). 4.60 (s, 1H), 4.97 (s, 1H), 5.71 (s, 1H), 6.43 (s, 1H), 6.78 (d, 2H, $J$ = 8.4 Hz), 6.81−6.85 (m, 2H), 6.97−7.05 (m, 7H), 7.06 (d, 2H, $J$ = 8.4 Hz), 7.20−7.27 (m, 11H); $^{13}$C NMR: $\delta$ 49.31, 53.56, 55.40, 64.64, 99.42, 126.31, 126.56, 126.76, 127.07, 127.44, 127.66, 127.71, 128.05, 128.16, 128.28, 128.78, 128.87, 129.26, 129.74, 130.71, 134.56, 135.82, 137.25, 138.20, 139.07, 140.16, 147.50, 163.98, 188.32, 197.74. Anal. Calcd for $C_{41}H_{31}ClO_3$: C, 81.11; H, 5.15. Found: C, 81.38; H, 5.44.

**4-Methoxy-3-(4-phenylphenyl)-5,7-bis(diphenylmethyl)-2,4,6-cycloheptatrien-1-one 16.** Pale yellow crystals, recrystallized from hexane−ethyl acetate; mp: 187−189 °C; IR (KBr) $\nu_{max}$: 844, 993, 1077, 1153, 1207, 1241, 1370, 1447, 1491, 1566, 1595, 1613, 3023, 3055 cm$^{-1}$; $^1$H NMR: $\delta$ 3.05(s, 3H), 5.96 (s, 1H), 6.13 (s, 1H), 6.85−6.89 (m, 8H), 6.98 (s, 1H), 7.13−7.22 (m, 13H), 7.36−7.65 (m, 9H); $^{13}$C NMR: $\delta$ 51.25, 52.60, 60.11, 126.26, 126.51, 126.72, 126.97, 127.56, 128.21, 128.45, 128.78, 129.14, 129.18, 129.44, 138.19, 139.00, 140.15, 140.32, 140.43, 141.07, 142.15, 142.22, 146.56, 150.95, 158.23, 184.74. Anal. Calcd for $C_{46}H_{36}O_2$: C, 89.00; H, 5.85. Found: C, 88.78; H, 5.68.

**1,6-Bis(diphenylmethyl)-5-methoxy-3-(4-phenylphenyl)-bicyclo[3.2.1]oct-3,6-diene-2,8-dione 25.** Colorless crystals, recrystallized from hexane−ethyl acetate; mp: 166−168 °C; IR (KBr) $\nu_{max}$: 837, 1031, 1150, 1449, 1493, 1599, 1679, 1775, 3029, 3057 cm$^{-1}$; $^1$H NMR: $\delta$ 3.54 (s, 3H), 4.72 (s, 1H), 4.99 (s, 1H), 5.79 (s, 1H), 6.48 (s, 1H), 6.84−6.87 (m, 2H), 6.92−7.03 (m, 8H), 7.23−7.48 (m, 19 H); $^{13}$C NMR: $\delta$ 49.31, 53.56, 55.33, 64.83, 99.41, 126.05, 126.16, 126.58, 126.69, 126.83, 126.95, 126.99, 127.37, 127.65, 127.73, 127.88, 128.23, 128.74, 128.86, 128.88, 129.26, 129.78, 130.71, 136.34, 137.46, 138.24, 139.23, 139.28, 140.20, 140.28, 141.32, 147.32, 164.97, 188.51, 197.99. Anal-.Calcd for $C_{47}H_{36}O_3$: C, 87.01; H, 5.59. Found: C, 87.18; H, 5.71.

**4-Methoxy-3-(2-naphthyl)-5,7-bis(diphenylmethyl)-2,4,6-cycloheptatrien-1-one 17.** Pale yellow crystals, recrystallized from hexane−ethyl acetate; mp: 192−194 °C; IR (KBr) $\nu_{max}$: 820, 993, 1153, 1205, 1237, 1375, 1448, 1490, 1565, 1594, 1612, 2999, 3023, 3059 cm$^{-1}$; $^1$H NMR: $\delta$ 2.98 (s, 3H), 5.98 (s, 1H), 6.14 (s, 1H), 6.87−6.89 (m, 8H), 7.00 (s, 1H), 7.14−7.24 (m, 13H), 7.50−7.59 (m, 3H), 7.83−7.89 (m, 3H), 7.96 (d, 1H, $J$ = 1.5 Hz); $^{13}$C NMR: $\delta$ 51.25, 52.58, 60.17, 126.29, 126.35, 126.54, 126.64, 126.98, 127.45, 127.56, 128.04, 128.24, 128.48, 129.16, 129.20, 132.87, 132.97, 137.84, 138.38, 140.50, 140.89, 142.16, 142.23, 146.97, 151.02, 158.34, 184.74. Anal. Calcd for $C_{44}H_{34}O_2$: C, 88.86; H, 5.76. Found: C, 88.57; H, 5.93.

**1,6-Bis(diphenylmethyl)-5-methoxy-3-(2-naphthyl)-bicyclo[3.2.1]oct-3,6-diene-2,8-dione 26.** Colorless crystals, recrystallized from hexane−ethyl acetate; mp: 157−159 °C; IR (KBr) $\nu_{max}$: 816, 892, 1033, 1150, 1219, 1448, 1494, 1680, 1773, 3007, 3028, 3068 cm$^{-1}$; $^1$H NMR: $\delta$ 3.55 (s, 3H), 4.76 (s, 1H), 5.00 (s, 1H), 5.82 (s, 1H), 6.53 (s, 1H), 6.83−7.04 (m, 10 H), 7.23−7.30 (m, 11H), 7.43−7.46 (m, 2H), 7.57−7.74 (m, 4H); $^{13}$C NMR: $\delta$ 49.33, 53.48, 55.35, 64.80, 99.45, 123.88,126.06, 126.10, 126.58, 126.61, 126.70, 126.84, 126.98, 127.39, 127.56, 127.67, 127.70, 127.73, 128.09, 128.26, 128.75, 128.91, 129.30, 129.6,130.71, 132.61, 134.83, 137.47, 138.23, 139.12, 139.44, 140.32, 147.30, 165.25, 188.49, 198.02. Anal. Calcd for $C_{45}H_{34}O_3$: C, 86.79; H, 5.50. Found: C, 86.87; H, 5.62.

**Experimental Procedure for the Synthesis of Tropone Derivative 28. 4-Methoxy-2-phenyl-5,7-bis(diphenylmethyl)-2,4,6-cycloheptatrien-1-one 28.** Bicycloadduct **6** (0.110 g, 2.01 × 10$^{-4}$ mol) was taken in a Schlenk tube under an atmosphere of argon. It was then heated at 150 °C for 30 min. The product obtained was subjected to column chromatography on silica gel using hexane−ethyl acetate mixture (90:10) to afford the product **28** (0.099 g, 94%).

Pale yellow crystals, recrystallized from hexane−ethyl acetate; mp: 152−154 °C; IR (KBr) $\nu_{max}$: 738, 1026, 1092, 1152, 1208, 1441, 1487, 1571, 1613, 1697, 3024, 3061 cm$^{-1}$; $^1$H NMR: $\delta$ 3.82 (s, 3H), 5.17 (s, 1H), 6.17 (s, 1H), 6.51−6.53 (m, 4H), 6.78 (s, 1H), 6.84−6.86 (m, 4H), 6.93−6.96 (d, 1H, $J$ = 6.76 Hz), 7.09−7.30 (m, 16 H); $^{13}$C NMR: $\delta$ 51.60, 56.66, 59.00, 126.42, 126.53, 127.67, 127.93, 128.17, 128.26, 128.44, 129.32, 138.86, 139.64, 140.35, 141.77, 141.98, 142.24, 144.95, 151.22, 161.86, 180.68. Anal. Calcd for $C_{40}H_{32}O_2$: C, 88.20; H, 5.92. Found: C, 88.48; H, 5.90.

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**Supporting Information Available:** ORTEP diagram and X-ray data for the tropone derivative **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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