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Magnesium-Promoted Reductive Silylation and Acylation of Tropone and Tropone Acetal

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Magnesium-promoted reductive coupling of chlorotrialkylsilanes and tropone or tropone acetal in DMF, followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in benzene gives 2-trialkylsilyltropones as the main product, and the reductive coupling of tropone with acid anhydrides under similar reaction conditions yields benzene derivatives after ring contraction.

Tropone, tropolone, and azulene, a series of compounds that contain cycloheptatriene rings, are called non-benzenoid aromatic compounds and have attracted interest owing to their special reactivity, aromaticity, color, etc.[1] Tropone has a single seven-membered ring, and its structure is quite simple;[2–12] however, direct and selective introduction of a substituent, especially electrophilic substitution in the tropone ring remains difficult because of the electron-deficient nature of the cycloheptatriene ring.[4,13–18] On the other hand, it is well known that Grignard reagents attack the 2-position of tropone to give 2-alkyl- or 2-phenyltropones after subsequent oxidation.[19] Therefore, the general synthetic route to substituted tropones is ring expansion of six-membered rings bearing a functional group.[20–23]

In this study, the magnesium-promoted reduction of tropone in the presence of chlorotrialkylsilane, followed by oxidation of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) resulted in the selective formation of 2-trialkylsilyltropones in only two steps. Furthermore, the dimethyl acetal of tropone was also transformed into 2-trialkylsilyltropones under similar reaction conditions (Scheme 1).

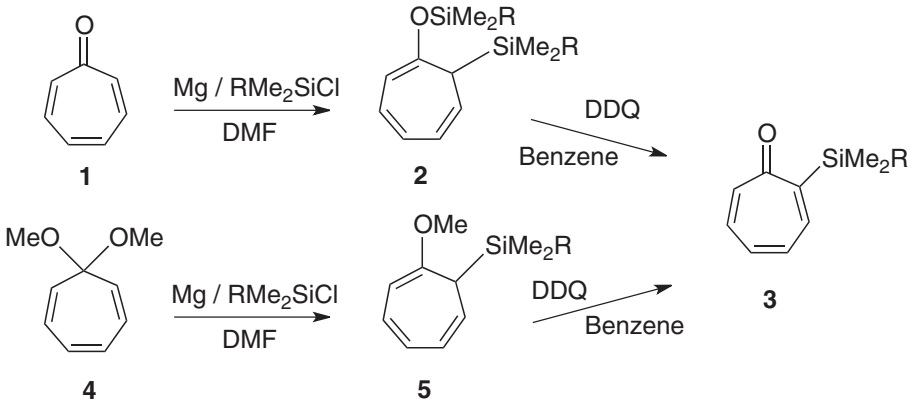
Results and Discussion

Reaction conditions for the reductive coupling between tropone and chlorotrimethylsilane were investigated, and under the optimized conditions, excess quantities of magnesium and chlorotrialkylsilane were required for effective disilylation. Furthermore, as shown in Table 1, compound **2** was the predominant product in most cases, although a small quantity of isomers was detected by gas chromatography and identified with mass spectrometry. Chlorotrialkylsilanes bearing bulky alkyl groups decreased the yield of the coupling product, and in particular, *tert*-butyl and phenyl groups completely prevented this coupling reaction.

Then, the transformation of **2a** into the corresponding substituted tropone **3a** using various oxidizing agents was investigated, and DDQ in benzene was found to be the best oxidant (Table 2). Compounds **2b** and **2c** were also oxidized by DDQ to give the corresponding tropones in good yields (Scheme 2).

The dimethyl acetal of tropone (7,7-dimethoxycyclohepta-1,3,5-triene, **4**) is known to be highly reactive with nucleophiles, such as Grignard and organolithium reagents.[5,24–27] Reductive coupling of the acetal with chlorotrialkylsilanes was also performed under reaction conditions that were similar to those used for tropone. The results are shown in Table 3.

The yield of the tropone precursors was improved for the trimethylsilyl and isopropyldimethylsilyl groups. In addition, surprisingly, dimethylphenylsilylation partially occurred despite the presence of the bulky moiety at the 2-position.



Scheme 1.

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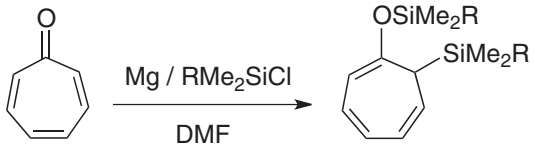
Table 1. Magnesium-Promoted Silylation of Tropone[a)]

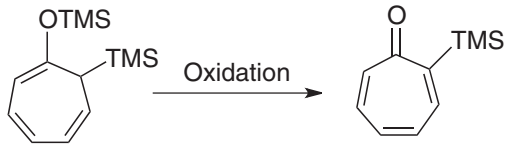


1 **2**

Entry	R	GC yield/%
1	Me	**2a**, 48
2	Et	**2b**, 46
3	*iso*-Pr	**2c**, 27
4	*tert*-Bu	0[b)]
5	Ph	0[b)]

a) Reaction conditions: Tropone (5 mmol), Mg (8 mol equiv), RMe_2SiCl (12 mol equiv), DMF (30 mL), r.t., 12 h, under N_2 atmosphere. b) Complex mixture.

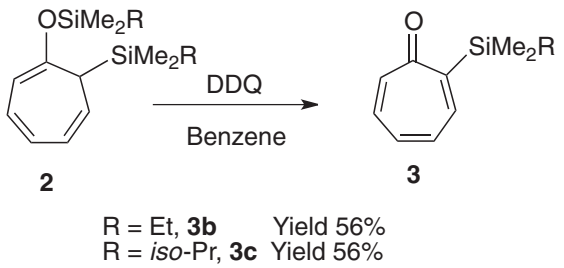
Table 2. Oxidation of **2a** under Various Reaction Conditions



2a **3a**

Entry	Oxidant	Solvent	Yield/%
1[a)]	DDQ	Benzene	70
2	DDQ	CH_2Cl_2	18
3	Ph_3CBF_4	CH_2Cl_2	0
4	$C_7H_7BF_4$	CH_2Cl_2	0

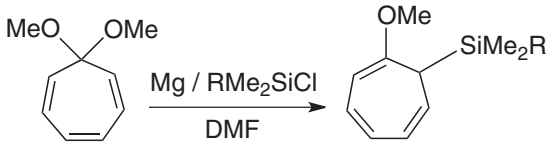
a) Silyl enol ether (3 mmol), DDQ (1.2 mol equiv), benzene (30 mL), r.t., 1 h, under N_2 atmosphere.



2 **3**

Scheme 2.

Table 3. Reductive Coupling of **4** with Silylating Agent[a)]

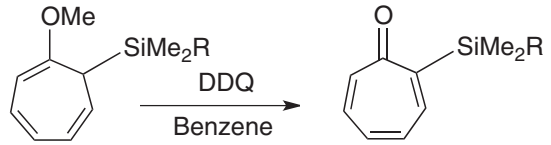


4 **5**

Entry	R	Yield/%
1	Me	**5a**, 59
2	Et	**5b**, 42
3	*iso*-Pr	**5c**, 43
4	*tert*-Bu	—[b)]
5	Ph	**5e**, 27

a) Reaction conditions: Tropone acetal (5 mmol), Mg (8 mol equiv), RMe_2SiCl (12 mol equiv), DMF (30 mL), 2–3 °C, 2 h, under N_2 atmosphere. b) Complex mixture.

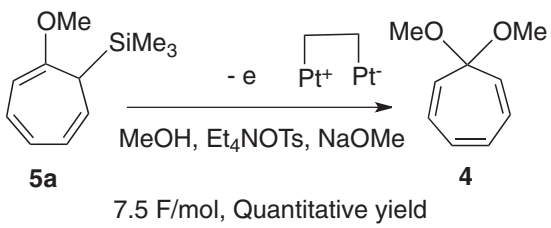
Table 4. Synthesis of 2-Silyltropones



5 **3**

Entry[a)]	R	Yield/%
1[b)]	Me	**3a**, 55
2	Et	**3b**, 59
3	*iso*-Pr	**3c**, 76
4	Ph	**3e**, 49

a) **5** (3 mmol), DDQ (1.2 mol equiv), benzene (30 mL), r.t., 1 h, under N_2 atmosphere. b) **5** (5 mmol), DDQ (1.2 mol equiv), benzene (50 mL), r.t., 1 h, under N_2 atmosphere.



5a **4**

Scheme 3.

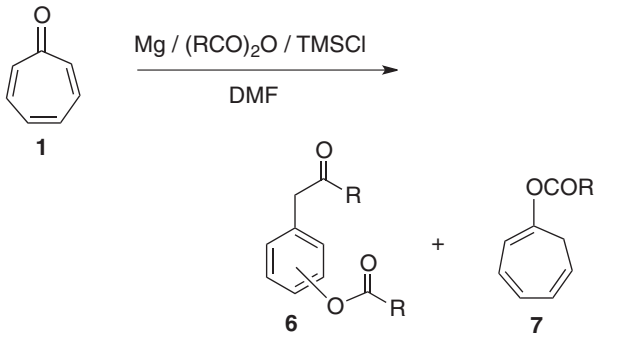
Compounds **5** were also oxidized with DDQ to give the corresponding tropones in moderate to good yields, as shown in Table 4. The oxidant is also important for this oxidation, because anodic oxidation of **5a** in methanol in an undivided cell gave tropone acetal **4** as a single product owing to elimination of the trimethylsilyl cation instead of a proton in the course of the oxidation, while the elimination of the silyl group at the allylic position was not the main reaction in the oxidation with DDQ (Schemes 2 and 3).

Next, reductive coupling of 2-methoxytropone and 2-phenyltropone with chlorotrimethylsilane was performed under the same reaction conditions, but no coupling products were formed. Meanwhile, the reaction of 2-methyltropone gave a mixture of regioisomeric silylated compounds in low yield.

From the perspective of new carbon–carbon formation, the acylation of tropone with an acid anhydride was investigated under similar reaction conditions to afford ring contraction compounds as the main products with a small amount of simply reduced compounds. The results are summarized in Table 5. For the coupling reactions of tropone with less reactive acid anhydride, three equivalent of chlorotrimethylsilane was used to avoid the formation of silylated compounds (Entries 2 and 3).

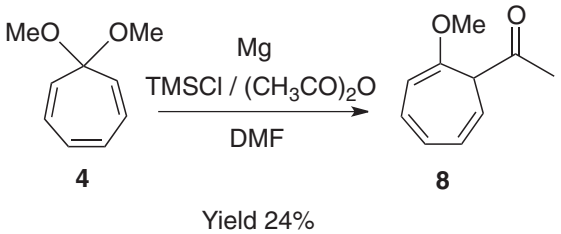
The use of acetyl chloride, or propionyl chloride in this acylation in place of the acid anhydride failed to give a complex mixture. On the other hand, acylation of tropone acetal **4** with acetic anhydride gave the corresponding acylated product **8** without ring contraction as the main product; however, the yield of **8** was not satisfactory, as shown in Scheme 4.

Table 5. Magnesium-Promoted Acylation of Tropone[a)]



Entry	R	TMSCl /equiv	Yield **6** /%	*ortho*:*para*	Yield **7** /%
1	Me	5	**6a**, 49	3:2	0
2	Et	3	**6b**, 45	3:1	**7b**, 20
3	*n*-Pr	3	**6c**, 48	3:1	**7c**, 11

a) Reaction conditions: Tropone (2.55 mmol), Mg (3 mol equiv), acid anhydride (15 mol equiv), DMF (30 mL), 16 h, under N_2 atmosphere.



Scheme 4.

To clarify the reaction mechanism, the redox potential of the starting materials was evaluated by cyclic voltammetry. Acetyl chloride, acetic anhydride, and chlorotrimethylsilane showed no significant reduction peaks, while tropone (**1**) and tropone acetal **4** showed reduction peaks at −1.59 and −1.64 V vs. Ag/AgCl, respectively. Therefore, silylation and acylation may be initiated by a single electron transfer from magnesium to **1** or **4**.

Considering our previous results which suggested that the more stable anion species would be formed finally after the second electron transfer,[28–30] no cycloheptatrienide derivative should be generated. A plausible reaction mechanism for the silylation and acylation of **1** is proposed in Scheme 5. The carbonyl group derived from the acylating agent stabilizes the anion **10** and **11** at the α-position of the carbonyl group, which would be the driving force for migration to the benzene ring, while the silyl group may not stabilize the anion. On the other hand, in the silylation and acylation of **4**, the methoxy group of **13** and **14** is a good eliminating group and thus, the reaction may proceed without ring contraction (Scheme 6). The reason for the regioselective coupling is not clear and a reactive electrophile such as chlorotrimethylsilane may coordinate the oxygen atom of tropone or the acetal of tropone and attack the seven-membered ring quickly to give the precursor of 2-trialkylsilyltropone, predominantly.

In summary, magnesium-promoted silylation of tropone and tropone acetal yields 2-silyltropones in only two steps, while acylation of tropone and tropone acetal under similar conditions is ineffective and results in undesirable ring contraction in the case of acylation of tropone.

Experimental

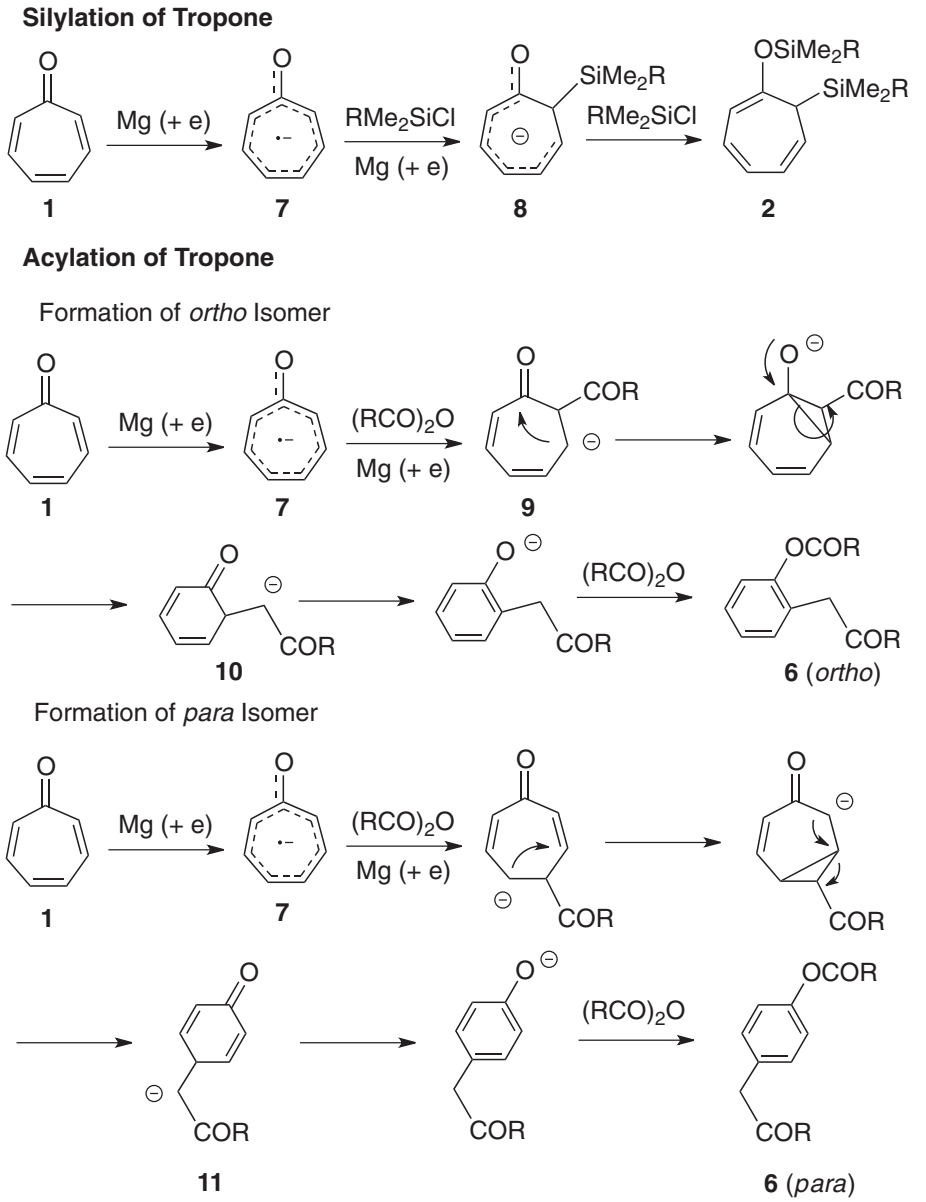
^{1}H NMR and ^{13}C NMR were measured on a JEOL JNM AL-400 (400 MHz), or a JEOL JNM EX-400 (400 MHz) spectrometer. Proton chemical shifts are expressed in parts per million (ppm) downfield from internal standard (tetramethylsilane, 0.00 ppm), and coupling constants are reported in hertz (Hz). Carbon chemical shifts are referenced to the carbon signal of the solvent at 77.00 ppm ($CDCl_3$). Infrared (IR) spectra were recorded on a JASCO 470Plus FTIR spectrometer. Mass spectra and high-resolution mass spectra were recorded on a JEOL JMS-600H spectrometer. Elemental analyses were measured on Yanaco CHN coder MT-6. Cyclic voltammograms were measured by ALS model 600. Cyclic voltammetry was carried out with a three-electrode system using a platinum working electrode, a platinum counter electrode, and Ag/AgCl as a reference electrode with sweeping rate of 200 mV s^{-1} in 1% tetrabutylammonium perchlorate/*N*,*N*-dimethylformamide (DMF).

DMF was distilled under reduced pressure after drying over calcium hydride. For thin-layer chromatography (TLC) analysis, Merck precoated plates (silica gel 60 F254, Art 5715, 0.25 mm) were used. Tropone (**1**)[5,9,10,27] and 7,7-dimethoxycyclohepta-1,3,5-triene (**4**)[27,31] were synthesized according to the reported procedures.

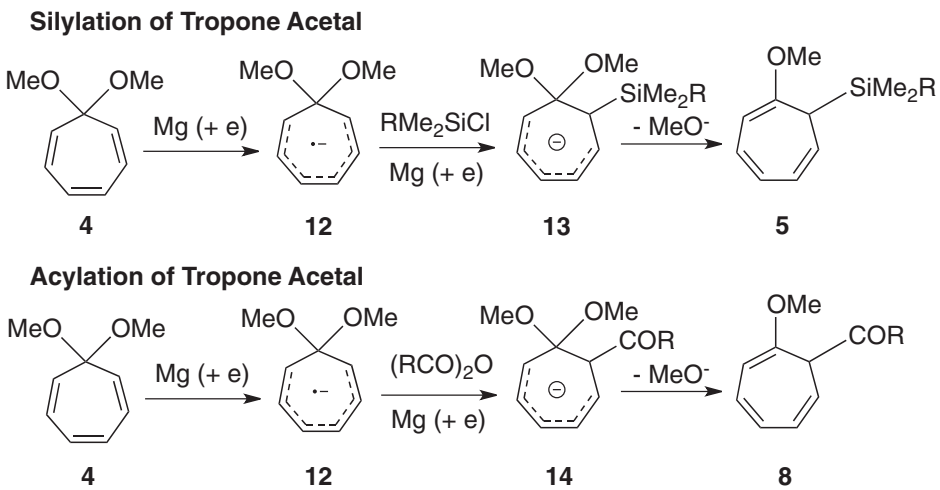
Typical Procedure for Coupling of Tropone with Chlorotrialkylsilane. Non-pretreated magnesium turnings (0.97 g, 40.0 mmol) for Grignard reagent in dry DMF (25 mL) were placed in a 100-mL four-necked flask at room temperature under nitrogen atmosphere and then chlorotrimethylsilane (7.67 mL, 60.0 mmol) was added in one portion. After activation of the magnesium for 1 h, the mixture was cooled in an ice bath and tropone (0.53 g, 5.0 mmol) in dry DMF (5 mL) was added dropwise. Stirring was continued at room temperature for 12 h. Then the reaction mixture was extracted with ether. The combined organic layers were washed with brine, dried over anhydrous magnesium sulfate, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography to give **2a**.

1-Trimethylsiloxy-7-trimethylsilylcyclohepta-1,3,5-triene (2a). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.09 (9H, s), 0.20 (9H, s), 1.65 (1H, d, $J = 8.2$ Hz), 5.09 (1H, t, $J = 8.2$ Hz), 5.38 (1H, d, $J = 7.2$ Hz), 6.02–6.08 (3H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ −1.88, 0.00, 37.99, 104.62, 120.74, 125.12, 127.10, 127.90, 148.21. IR (neat): 3012, 2956, 1610, 1593, 1254, 1186, 1139, 842, 755, 712 cm^{-1}. MS: *m*/*z* 252 (M^+). HRMS: Calcd for $C_{13}H_{24}OSi_2$: 252.1366. Found: 252.1346.

1-Ethyldimethylsiloxy-7-ethyldimethylsilylcyclohepta-1,3,5-triene (2b). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.06 (3H, s), 0.08 (3H, s), 0.19 (6H, s), 0.61 (2H, q, $J = 8.1$ Hz), 0.67 (2H, q, $J = 8.1$ Hz), 0.94 (3H, t, $J = 8.1$ Hz), 0.96 (3H, t, $J = 8.1$ Hz), 1.76 (1H, d, $J = 8.5$ Hz), 5.09 (1H, t, $J = 8.5$ Hz), 5.36 (1H, d, $J = 7.0$ Hz), 5.98–6.04 (3H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ −3.99, −3.90, 6.53, 6.61, 7.40, 8.25, 37.36, 104.60, 121.06, 125.23, 127.03, 128.01, 148.44. IR (neat): 3012, 2955, 2876, 1254, 1184, 1138, 837, 789, 699 cm^{-1}. MS: *m*/*z* 280 (M^+). HRMS: Calcd for $C_{15}H_{28}OSi_2$: 280.1679. Found: 280.1659.



Scheme 5.



Scheme 6.

1-Isopropyldimethylsiloxy-7-isopropyldimethylsilylcyclohepta-1,3,5-triene (2c). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.04 (3H, s), 0.07 (3H, s), 0.17 (3H, s), 0.18 (3H, s), 0.97–1.03 (14H, m), 1.90 (1H, d, $J = 8.6$ Hz), 5.11 (1H, t, $J = 8.6$ Hz), 5.36 (1H, d, $J = 7.2$ Hz), 5.96–6.00 (3H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ −5.24, −3.98, −3.71, 13.08, 14.41, 16.67 (×2), 17.72, 17.78, 36.51, 104.68, 121.41, 125.31, 126.78, 127.98, 148.31. IR (neat): 3012, 2955, 2865, 1254, 1183, 1140, 884, 832, 780 cm^{-1}. MS: m/z 308 (M^+). HRMS: Calcd for $C_{17}H_{32}OSi_2$: 308.1992. Found: 308.1953.

Typical Procedure for DDQ Oxidation of 2 and 5. To a solution of **2a** (3.0 mmol) in dry benzene (30 mL) was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (0.83 g, 3.6 mmol) at room temperature under nitrogen atmosphere, and the reaction mixture was stirred for 1 h. Then a 5% sodium hydroxide solution (100 mL) was added to the reaction mixture and the products were extracted with ether. The combined organic layers were washed with sodium hydrogen carbonate and brine, dried over anhydrous magnesium sulfate, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography to give **3a**.

2-Trimethylsilylcyclohepta-2,4,6-trien-1-one (3a).[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.15 (9H, s), 6.73–6.94 (4H, m), 7.24 (1H, d, $J = 7.8$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ −0.08, 135.09, 135.73, 135.94, 140.83, 142.81, 158.58, 193.00. IR (neat): 3026, 2953, 1627, 1577, 1246, 841 cm^{-1}. MS: m/z 178 (M^+).

2-Ethyldimethylsilylcyclohepta-2,4,6-trien-1-one (3b). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.22 (6H, s), 0.78 (2H, q, $J = 7.7$ Hz), 0.93 (3H, t, $J = 7.7$ Hz), 6.82 (1H, d, $J = 11.6$ Hz), 6.85–6.92 (1H, m), 6.93–6.99 (1H, m), 6.97–7.03 (1H, m), 7.30 (1H, dd, $J = 7.8$ Hz, 1.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ −3.35, 6.82, 7.52, 134.00, 134.62, 134.70, 139.80, 141.96, 156.81, 192.11. IR (neat): 3026, 2952, 2907, 2873, 1627, 1580, 1513, 1458, 1410, 1383, 1273, 1245, 1210, 1010, 981, 837, 813, 785, 697, 646, 617 cm^{-1}. MS: m/z 192 (M^+). HRMS: Calcd for $C_{11}H_{16}OSi$: 192.0971. Found: 192.0992.

2-Isopropyldimethylsilylcyclohepta-2,4,6-trien-1-one (3c). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.19 (6H, s), 0.94 (6H, d, $J = 7.5$ Hz), 1.28 (1H, sept, $J = 7.5$ Hz), 6.82 (1H, d, $J = 11.9$ Hz), 6.85–9.92 (1H, m), 6.93–6.99 (1H, m), 6.97–7.03 (1H, m), 7.29 (1H, dd, $J = 7.8$ Hz, 1.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ −5.11, 12.63, 17.72, 133.95, 134.54, 134.63, 139.64, 142.18, 156.40, 192.12. IR (neat): 3027, 2952, 2890, 2862, 1628, 1579, 1513, 1459, 1273, 1245, 1210, 1005, 976, 882, 834, 809, 784, 768, 686, 648 cm^{-1}. MS: m/z 206 (M^+). HRMS: Calcd for $C_{12}H_{18}OSi$: 206.1127. Found: 206.1121.

2-Dimethylphenylsilylcyclohepta-2,4,6-trien-1-one (3e). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.57 (6H, s), 6.82–6.91 (3H, m), 6.97–7.04 (1H, m), 7.15–7.20 (1H, m), 7.35–7.41 (3H, m), 7.59–7.63 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ −2.74, 127.79, 129.13, 134.32, 134.39, 134.66, 134.96, 137.71, 140.30, 143.18, 156.32, 191.86. IR (neat): 3068, 3047, 3024, 2955, 2899, 1626, 1574, 1514, 1459, 1427, 1275, 1246, 1212, 1113, 977, 814, 787, 739, 702, 658 cm^{-1}. MS: m/z 240 (M^+). HRMS: Calcd for $C_{15}H_{16}OSi$: 240.0971. Found: 240.0986.

Typical Procedure for Coupling of 7,7-Dimethoxycyclohepta-1,3,5-triene (4) with Chlorotrialkylsilane. Non-pretreated magnesium turnings (0.97 g, 40.0 mmol) for Grignard reagent in dry DMF (25 mL) were placed in a 100-mL four-necked flask at room temperature under nitrogen atmosphere and then chlorotrimethylsilane (7.67 mL, 60.0 mmol) was added in one portion. After activation of the magnesium for 1 h, the mixture was cooled in an ice bath and 7,7-dimethoxycyclohepta-1,3,5-triene (0.76 g, 5.0 mmol) in dry DMF (5 mL) was added dropwise. Stirring was continued at 2–3 °C for 2 h. Then the reaction mixture was poured into a saturated sodium hydrogen carbonate solution and was extracted with ether. The combined organic layers were washed with brine, dried over anhydrous magnesium sulfate, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography to give **5a**.

1-Methoxy-7-trimethylsilylcyclohepta-1,3,5-triene (5a). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.07 (9H, s), 1.95 (1H, dd, $J = 8.1$ Hz, 0.7 Hz), 3.57 (3H, s), 5.16 (1H, dt, $J = 8.1$ Hz, 2.1 Hz), 5.22 (1H, d, $J = 6.6$ Hz), 5.97–6.03 (2H, m), 6.08–6.14 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ −1.92, 37.06, 55.66, 95.81, 121.58, 124.57, 126.94, 128.04, 154.63. IR (neat): 3012, 2954, 2898, 2831, 1613, 1572, 1247, 1200, 1167, 1138, 1034, 1013, 841, 715 cm^{-1}. MS: m/z 194 (M^+). HRMS: Calcd for $C_{11}H_{18}OSi$: 194.1127. Found: 194.1117.

7-Ethyldimethylsilyl-1-methoxycyclohepta-1,3,5-triene (5b). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.05 (6H, s), 0.59 (2H, q, $J = 7.9$ Hz), 0.93 (3H, t, $J = 7.9$ Hz), 2.01 (1H, dd, $J = 8.9$ Hz, 1.0 Hz), 3.57 (3H, s), 5.16 (1H, t, $J = 8.9$ Hz), 5.21 (1H, d, $J = 6.9$ Hz), 5.96–6.02 (2H, m), 6.07–6.15 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ −4.02, −3.91, 6.56, 7.38, 36.08, 55.74, 95.93, 121.74, 124.71, 126.99, 128.20, 154.68. IR (neat): 3012, 2953, 2909, 2874, 2832, 1613, 1247, 1200, 1167, 1139, 1013, 836, 819, 714, 699 cm^{-1}. MS: m/z 208 (M^+). HRMS: Calcd for $C_{12}H_{20}OSi$: 208.1284. Found: 208.1267.

7-Isopropyldimethylsilyl-1-methoxycyclohepta-1,3,5-triene (5c). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.03 (3H, s), 0.04 (3H, s), 0.82–1.00 (7H, m), 2.06 (1H, d, $J = 9.0$ Hz), 3.57 (3H, s), 5.22 (1H, d, $J = 6.6$ Hz), 5.71 (1H, t, $J = 9.0$ Hz), 5.96–6.04 (2H, m), 6.10–6.17 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ −5.46, −5.23, 13.14, 17.69, 17.77, 34.79, 55.72, 96.01, 121.79, 124.75, 126.91, 128.26, 154.42. IR (neat): 3012, 2954, 2864, 2833, 1613, 1464, 1247, 1200, 1167, 1140, 1013, 1001, 883, 808, 715, 690 cm^{-1}. MS: m/z 222 (M^+). HRMS: Calcd for $C_{13}H_{22}OSi$: 222.1440. Found: 222.1483.

1-Methoxy-7-dimethylphenylsilylcyclohepta-1,3,5-triene (5e). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.38 (3H, s), 0.42 (3H, s), 2.21 (1H, d, $J = 8.9$ Hz), 3.53 (3H, s), 5.16 (1H, dt, $J = 8.9$ Hz, 1.6 Hz), 5.27 (1H, d, $J = 6.6$ Hz), 6.01–6.06 (2H, m), 6.13–6.19 (1H, m), 7.32–7.39 (3H, m), 7.54–7.59 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ −3.11, −3.07, 36.31, 55.70, 96.39, 121.02, 124.77, 127.39, 127.50, 128.24, 128.85, 133.93, 138.37, 153.97. IR (neat): 3068, 3048, 3011, 2956, 2903, 2832, 1613, 1427, 1248, 1200, 1168, 1140, 1113, 1034, 1013, 813, 701 cm^{-1}. MS: m/z 256 (M^+). HRMS: Calcd for $C_{16}H_{20}OSi$: 256.1284. Found: 256.1312.

Anodic Oxidation of 5a. Into a 50-mL beaker-type undivided cell equipped with platinum plates (4 cm^2) as the cathode and the anode, were introduced 30 mL of freshly distilled methanol as a solvent, tetraethylammonium *p*-toluenesulfonate (2 g, 6.6 mmol) and sodium methoxide (2 g, 37 mmol) as supporting electrolytes, and **5a** (0.58 g, 3 mmol) as the

starting substrate. The electrolysis was carried out under the constant current conditions (current density: 50 mA cm^{-2}) until 7.5 F mol^{-1} of electricity passed through the system at −5–5 °C. After the electrolysis, the reaction mixture was poured into a saturated sodium bicarbonate solution, and organic material was extracted with ether. The combined ethereal solution was washed with a saturated sodium chloride solution and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the product **4** was obtained in quantitative yield. The product was characterized by comparison of its spectroscopic and chromatographic behaviors with those of authentic samples.[26]

Typical Procedure for Coupling Reaction of Tropone with Acid Anhydride. A mixture of acetic anhydride (3.9 g, 38.25 mmol), chlorotrimethylsilane (1.38 g, 12.75 mmol), and non-pretreated magnesium turnings (0.18 g, 7.65 mmol) for Grignard reagent in dry DMF (25 mL) was placed in 50-mL four-necked flask at 5 °C under nitrogen atmosphere and tropone (0.27 g, 2.55 mmol) in dry DMF (5 mL) was added dropwise over 15 min. Stirring was continued at room temperature for 16 h. Then the reaction mixture was poured into a mixture of ether and saturated sodium hydrogen carbonate solution. Further stirring was continued for 30 min. The products were extracted with ether. The combined organic layers were washed with brine, dried over anhydrous magnesium sulfate, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography to give **6a**.

[2-(2-Oxopropyl)]phenyl Acetate (6a) *ortho*-Isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.11 (s, 3H), 2.29 (s, 3H), 3.60 (s, 2H), 7.10–7.34 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.77, 28.94, 46.21, 122.70, 126.40, 126.96, 128.58, 131.45, 149.17, 169.15, 205.53. IR (neat): 3065, 3032, 2934, 1764, 1713, 1490, 1370, 1210, 1173, 1102 cm^{-1}. MS: m/z 192 (M^+). Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29%. Found: C, 68.60; H, 6.41%.

[4-(2-Oxopropyl)]phenyl Acetate (6a) *para*-Isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.16 (s, 3H), 2.29 (s, 3H), 3.69 (s, 2H), 7.05–7.22 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.03, 29.29, 50.10, 121.77, 130.33, 131.67, 149.68, 169.39, 206.04. IR (neat): 3039, 3003, 2935, 1760, 1714, 1673, 1508, 1371, 1200, 1165, 1018, 912 cm^{-1}. MS: m/z 192 (M^+). Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29%. Found: C, 68.93; H, 6.52%.

[2-(2-Oxobutyl)]phenyl Propionate (6b) *ortho*-Isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.01 (t, 3H, $J = 7.3$ Hz), 1.26 (t, 3H, $J = 7.6$ Hz), 2.40 (q, 2H, $J = 7.3$ Hz), 2.58 (q, 2H, $J = 7.6$ Hz), 3.59 (s, 2H), 7.08–7.32 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 7.69, 9.02, 27.51, 34.81, 45.00, 122.65, 126.19, 127.14, 128.40, 131.45, 149.22, 172.55, 208.01. IR (neat): 3064, 3030, 2979, 2941, 1761, 1713, 1457, 1353, 1220, 1142, 755 cm^{-1}. MS: m/z 220 (M^+). Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32%. Found: C, 70.79; H, 7.13%.

[4-(2-Oxobutyl)]phenyl Propionate (6b) *para*-Isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (t, 3H, $J = 7.3$ Hz), 1.26 (t, 3H, $J = 7.6$ Hz), 2.48 (q, 2H, $J = 7.3$ Hz), 2.58 (q, 2H, $J = 7.6$ Hz), 3.67 (s, 2H), 7.04–7.22 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 7.66, 8.97, 27.67, 35.24, 48.92, 121.70, 130.27, 131.75, 149.68, 172.97, 208.91. IR (neat): 3067, 3038, 2980, 2940, 1760, 1713, 1508, 1459, 1355, 1206, 1167, 1146 cm^{-1}. MS: m/z 220 (M^+). Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32%. Found: C, 70.60; H, 7.51%.

[2-(2-Oxopentyl)]phenyl Butanoate (6c) *ortho*-Isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, 3H, $J = 7.3$ Hz), 1.04 (t, 3H, $J = 7.6$ Hz), 1.57 (sext, 2H, $J = 7.3$ Hz), 1.78 (sext, 2H, $J = 7.6$ Hz), 2.36 (t, 2H, $J = 7.3$ Hz), 2.53 (t, 2H, $J = 7.6$ Hz), 3.58 (s, 2H), 7.08–7.33 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.58, 13.65, 17.07, 18.33, 35.96, 43.50, 45.27, 122.62, 126.15, 127.00, 128.37, 131.44, 149.20, 171.75, 207.48. IR (neat): 3064, 3033, 2965, 2876, 1761, 1710, 1490, 1457, 1364, 1220, 1143, 1106, 753 cm^{-1}. MS: m/z 248 (M^+). Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12%. Found: C, 72.78; H, 8.00%.

[4-(2-Oxopentyl)]phenyl Butanoate (6c) *para*-Isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, 3H, $J = 7.3$ Hz), 1.04 (t, 3H, $J = 7.6$ Hz), 1.58 (sext, 2H, $J = 7.3$ Hz), 1.78 (sext, 2H, $J = 7.6$ Hz), 2.36 (t, 2H, $J = 7.3$ Hz), 2.53 (t, 2H, $J = 7.6$ Hz), 3.66 (s, 2H), 7.03–7.21 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.57, 13.62, 17.05, 18.30, 36.16, 43.93, 49.29, 121.73, 130.30, 131.42, 149.67, 172.09, 208.20. IR (neat): 3062, 3016, 2964, 2935, 2876, 1758, 1714, 1507, 1414, 1303, 1203, 1146, 752 cm^{-1}. MS: m/z 248 (M^+). Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12%. Found: C, 72.53; H, 7.85%.

1-Propionyloxycyclohepta-1,3,5-triene (7b). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20 (t, 3H, $J = 7.6$ Hz), 2.45 (q, 2H, $J = 7.6$ Hz), 2.56 (d, 2H, $J = 6.8$ Hz), 5.43 (dt, 1H, $J = 6.8$ Hz, $J = 9.4$ Hz), 5.93 (d, 1H, $J = 6.3$ Hz), 6.22 (dd, 1H, $J = 5.5$ Hz, $J = 9.4$ Hz), 6.38 (dd, 1H, $J = 6.3$ Hz, $J = 11.2$ Hz), 6.53 (dd, 1H, $J = 5.5$ Hz, $J = 11.2$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 8.89, 27.44, 31.91, 112.88, 120.59, 126.81, 127.29, 129.48, 139.55, 172.76. IR (neat): 3021, 2982, 2943, 2883, 1753, 1643, 1462, 1423, 1355, 1334, 1144, 1068, 711 cm^{-1}. MS: m/z 164 (M^+). Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37%. Found: C, 73.16; H, 7.32%.

1-Butyryloxycyclohepta-1,3,5-triene (7c). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.80 (t, 3H, $J = 7.4$ Hz), 1.51 (sext, 2H, $J = 7.4$ Hz), 2.19 (t, 2H, $J = 7.4$ Hz), 2.36 (d, 2H, $J = 6.8$ Hz), 5.23 (dt, 1H, $J = 6.8$ Hz, $J = 9.3$ Hz), 5.73 (d, 1H, $J = 6.3$ Hz), 6.02 (dd, 1H, $J = 5.6$ Hz, $J = 9.3$ Hz), 6.18 (dd, 1H, $J = 6.3$ Hz, $J = 11.2$ Hz), 6.33 (dd, 1H, $J = 5.6$ Hz, $J = 11.2$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.56, 18.29, 31.96, 35.93, 112.90, 120.57, 126.82, 127.29, 129.47, 139.57, 171.91. IR (neat): 3021, 2967, 2935, 2876, 1753, 1643, 1423, 1376, 1335, 1235, 1122, 1070, 846, 710 cm^{-1}. MS: m/z 178 (M^+). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92%. Found: C, 74.38; H, 7.89%.

Coupling Reaction of 7,7-Dimethoxycyclohepta-1,3,5-triene (4) with Acetic Anhydride. Non-pretreated magnesium turnings (0.36 g, 15.0 mmol) for Grignard reagent in dry DMF (55 mL) were placed in 100-mL four-necked flask at room temperature under nitrogen atmosphere and acetic anhydride (3.06 g, 30.0 mmol) and chlorotrimethylsilane (1.92 mL, 15.0 mmol) was added in one portion. After activation of the magnesium for 1 h, the mixture was cooled in an ice bath and 7,7-dimethoxycyclohepta-1,3,5-triene (0.76 g, 5.0 mmol) in dry DMF (5 mL) was added dropwise. Stirring was continued at room temperature for 2 h. Then the reaction mixture was poured into a 1 M sodium hydroxide solution (300 mL) and the products were extracted with ether. The combined organic

layers were washed with brine, dried over anhydrous magnesium sulfate, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography to give **8**.

7-Acetyl-1-methoxycyclohepta-1,3,5-triene (8).[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.11 (3H, s), 3.54 (1H, d, $J = 8.9$ Hz), 3.65 (3H, s), 5.22 (1H, t, $J = 8.9$ Hz), 5.57 (1H, d, $J = 6.8$ Hz), 6.27 (1H, dd, $J = 5.6$ Hz, 10.9 Hz), 6.33 (1H, dd, $J = 5.6$ Hz, 8.9 Hz), 6.39 (1H, dd, $J = 6.8$ Hz, 10.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.22, 56.52, 56.73, 97.93, 117.96, 124.23, 127.78, 128.56, 150.51, 203.42.

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