

Synthesis of β,γ-Unsaturated Ketones from Acid Chlorides through Carbon–Pentamethylcyclopentadienyl Bond Formation and Cleavage

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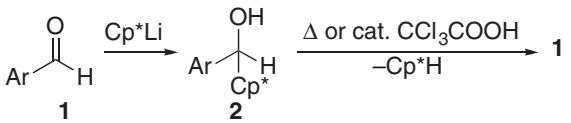
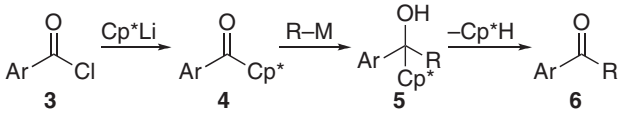
Reaction of acid chlorides with lithium pentamethylcyclopentadienide afforded the corresponding pentamethylcyclopentadienyl ketones in high yield. These ketones were treated with an allylaluminum reagent to form the corresponding 3-butenyl alcohols. Removal of pentamethylcyclopentadiene upon heating or treatment with a catalytic amount of trichloroacetic acid yielded the corresponding β,γ-unsaturated ketones in good yields.

We have been exploring applications of pentamethylcyclopentadiene (Me_5C_5H, Cp*H) as a reagent in organic synthesis and developing new reactions.[1] We have reported that Cp*Li reacted with aromatic aldehydes **1** to provide the corresponding secondary alcohols **2** in excellent yields. The secondary alcohols easily returned to the parent aldehydes and Cp*H under thermal or acidic conditions (Scheme 1).[1a,1c]

Thus, we expected that alcohol **5**, which is prepared from acid chloride **3** via **4**, would smoothly transform to ketone **6** by removal of Cp*H (Scheme 2). Using this approach, we planned to synthesize β,γ-unsaturated ketones.[2] Synthesis of β,γ-unsaturated ketones is often complicated, since β,γ-unsaturated ketones easily isomerize to α,β-unsaturated ketones under acidic or basic conditions. Here, we report[1e] a new method to synthesize β,γ-unsaturated ketones from acid chlorides in three steps as shown in Scheme 2, wherein R–M is an allylmetal reagent.



Scheme 1.

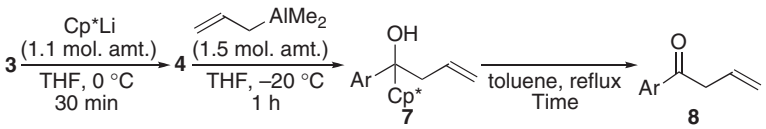


Scheme 2.

Results and Discussion

Treatment of Cp*Li (1.1 molar amount) with benzoyl chloride (**3a**) in THF at 0 °C for 30 min afforded pentamethylcyclopentadienyl phenyl ketone (**4a**) in excellent yield (Table 1, Entry 1). A variety of aromatic acid chlorides **3** were subjected to the nucleophilic addition reaction of Cp*Li to afford aryl pentamethylcyclopentadienyl ketones **4**. Acid chlorides **3** bearing an electron-withdrawing group (Entry 2) or an electron-donating group (Entry 3) afforded **4** in high yields. Bromine (Entry 4) and chlorine (Entry 5) on the aromatic ring did not

Table 1. Synthesis of Allyl Aryl Ketones



Entry	Ar	Yield (**4**)/%	Time/min	Yield (**8**)/%[a),b)]
1	Ph (**a**)	96	60	70
2	4-$CF_3C_6H_4$ (**b**)	92	75	68
3	4-$MeOC_6H_4$ (**c**)	85	60	90
4	4-BrC_6H_4 (**d**)	93	75	80
5	3-ClC_6H_4 (**e**)	98	90	66
6	2-MeC_6H_4 (**f**)	96	—	—
7	2-IC_6H_4 (**g**)	78	—	—
8	2-Thienyl (**h**)	91	30	65
9	2-Furyl (**i**)	91	45	8[c)]

a) Isolated yield based on **4**. b) Trace amounts (<0–7%) of α,β-unsaturated ketones were detected. c) NMR yield.

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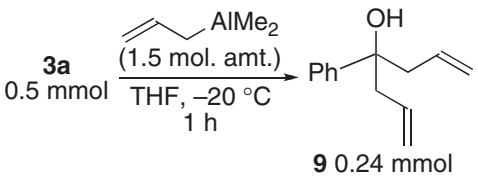
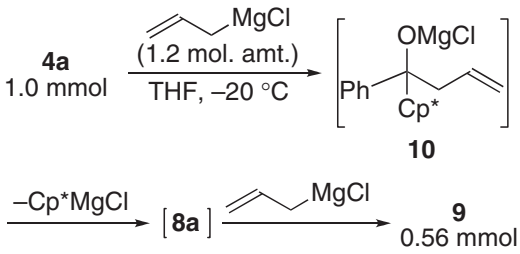
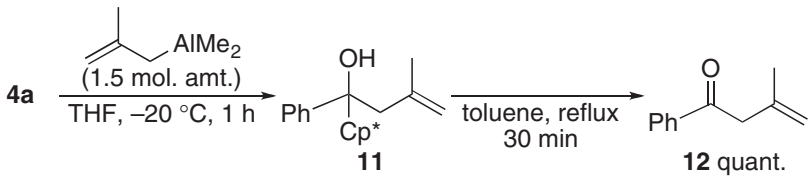


Scheme 3.



Scheme 4.



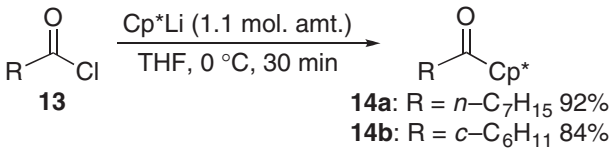
Scheme 5.

interfere with the reaction. Reaction of *ortho*-substituted **3** also proceeded smoothly (Entries 6 and 7). Heteroaromatic acid chlorides, such as thiophene- (Entry 8) and furancarbonyl chloride (Entry 9), could be used in this reaction.

Ketone **4a** was treated with 1.5 molar amount of an allylaluminum reagent, which was prepared from allylmagnesium bromide and dimethylaluminum chloride, at −20 °C for 1 h to afford the homoallyl alcohol **7a** in 98% yield.[3] In contrast, the reaction of benzoyl chloride (**3a**), instead of **4a**, with the allylaluminum reagent gave diallylated alcohol **9** (Scheme 3). In addition, when **4a** was treated with allylmagnesium chloride, instead of the allylaluminum reagent, **9** was obtained exclusively (Scheme 4). Nucleophilic addition of allylmagnesium chloride to ketone **8a**, which was generated by in situ elimination of Cp*MgCl from alkoxide **10**, should give **9**.

At room temperature, Cp*H was liberated from **7a** very slowly to give allyl phenyl ketone (**8a**). Then, we found that heating crude **7a** in toluene at reflux for 1 h provided **8a** in good yield (Table 1, Entry 1). The reaction of ketones **4** having trifluoromethyl (Entry 2), methoxy (Entry 3), bromo (Entry 4), or chloro moieties (Entry 5) also afforded **8** in moderate to good yields. Unfortunately, *ortho*-substituted **4f** and **4g** (Entries 6 and 7) did not undergo the nucleophilic addition reaction with the allylaluminum reagent even at 0 °C. Allylation of **4f** and **4g** took place at room temperature. However, similar diallylation as shown in Scheme 3 occurred. Although the reaction of 2-furyl pentamethylcyclopentadienyl ketone (**4i**) with the allylaluminum reagent afforded **7i** in high yield, heating **7i** provided a complex mixture (Entry 9).

2-Methyl-2-propenyl (here after named methallyl) phenyl ketone (**12**) was also synthesized in a similar manner from



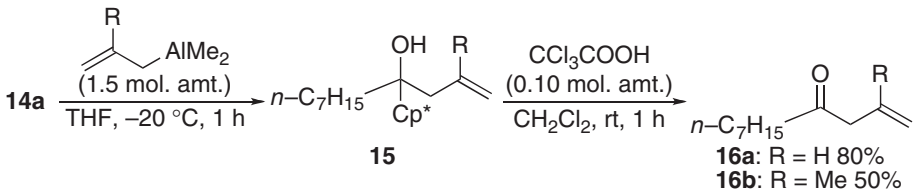
Scheme 6.

4a and a methallylaluminum reagent in quantitative yield (Scheme 5). Unfortunately, nucleophilic addition reactions of 2-butenyl- and 2-methyl-2-butenylaluminum reagents with **4a** resulted in recovery of **4a** even at 0 °C.

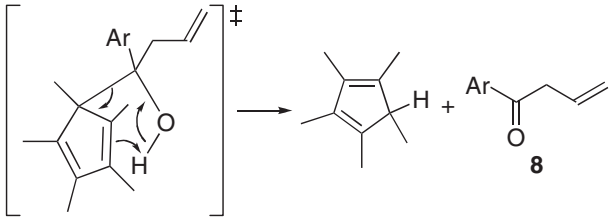
Preparation of aliphatic pentamethylcyclopentadienyl ketone **14** was performed in a similar fashion (Scheme 6). Although allylation and methallylation of heptyl ketone **14a** proceeded smoothly to provide alcohols **15** (Scheme 7), cyclohexyl ketone **14b** resisted the allylation. In contrast to aromatic alcohols **7**, alcohols **15** were stable at reflux in toluene (110 °C). However, **15** were unstable under acidic conditions and were transformed into the β,γ-unsaturated ketones effectively. Treatment of **15** with 0.10 molar amount of trichloroacetic acid in dichloromethane at room temperature for 1 h provided the corresponding ketones **16** in moderate to good yields (Scheme 7).

The proposed reaction mechanisms of the removal of Cp*H are shown in Schemes 8 and 9.[1a,1c] A retro-carbonyl-ene mechanism could be used to rationalize the fragmentation reaction under thermal conditions (Scheme 8). Protonation at the Cp* group could facilitate carbon–carbon bond cleavage under acidic conditions (Scheme 9).

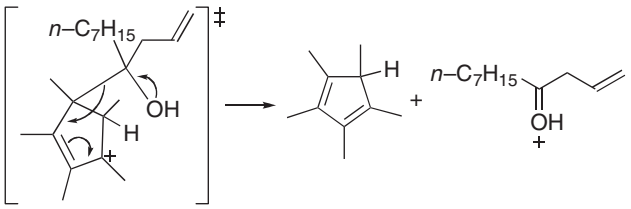
A typical Suzuki–Miyaura cross-coupling reaction needs a



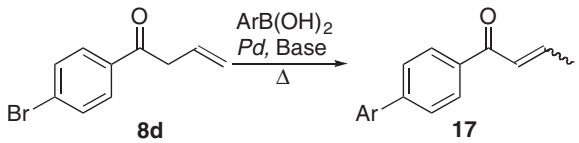
Scheme 7.



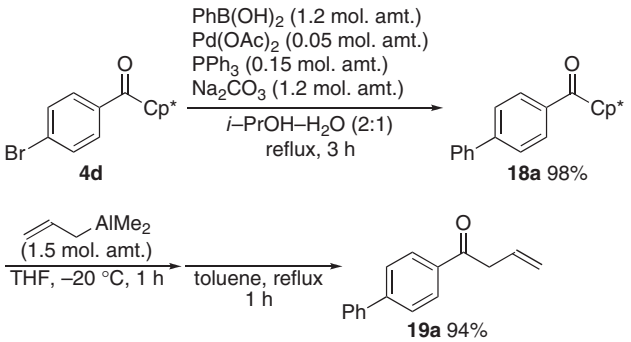
Scheme 8.



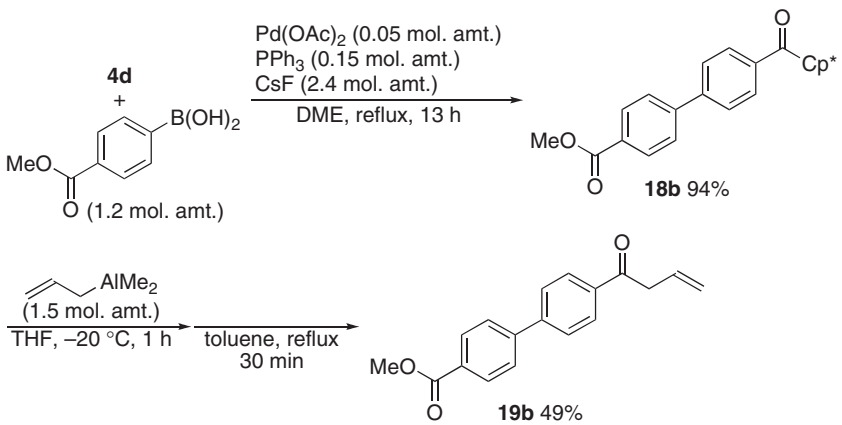
Scheme 9.



Scheme 10.



Scheme 11.

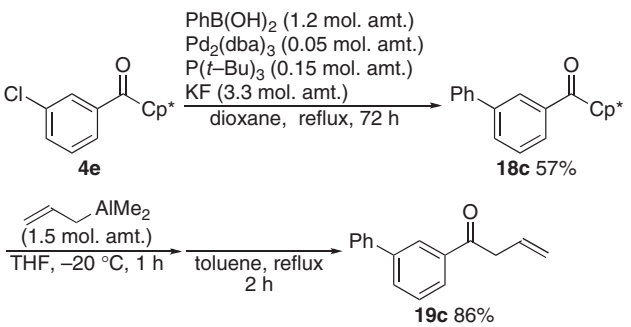


Scheme 12.

strong base and high temperature.[4] If **8d** was used as a substrate of Suzuki–Miyaura cross-coupling reaction, an α,β-unsaturated coupling product would be obtained (Scheme 10).

Thus, we examined an alternative method to prepare β,γ-unsaturated coupling product **19**. Aryl halides that have a pentamethylcyclopentadienylcarbonyl part were used in the cross-coupling reaction, and then the coupling products were transformed to β,γ-unsaturated ketones upon treatment with an allylaluminum reagent, followed by heating. Treatment of **4d** and **4e** with arylboronic acid under palladium catalysis yielded biaryls **18** in good yields (Schemes 11–13). Ketones **18** were converted into the corresponding β,γ-unsaturated ketones **19** under similar conditions shown in Table 1. Fortunately, an ester moiety survived during the nucleophilic addition reaction of the allylaluminum reagent (Scheme 12).

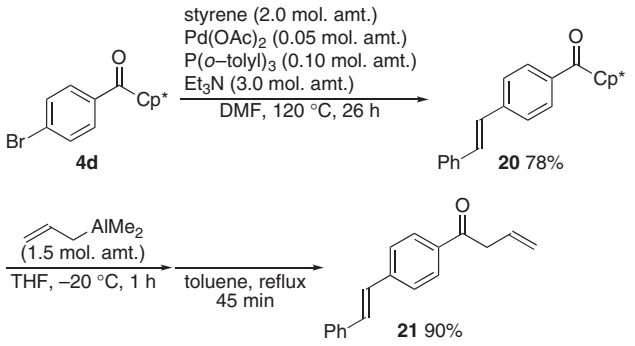
This approach could be also applicable to the Heck reaction, which requires basic conditions (Scheme 14).[5]



Scheme 13.

Experimental

General. ^{1}H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer unless otherwise noted. ^{1}H NMR and ^{13}C NMR spectra were obtained in $CDCl_3$ with tetramethylsilane as an internal standard or in C_6D_6. Chemical shifts (δ) are in parts per million relative to tetramethylsilane at 0.00 ppm for ^{1}H and relative to $CDCl_3$ at 77.0 ppm for ^{13}C in $CDCl_3$ and relative to benzene at 7.16 ppm for ^{1}H and at 128.0 ppm for ^{13}C in C_6D_6 unless otherwise noted. IR spectra were determined on a SHIMADZU FT-IR-8200PC spectrometer. Mass spectra were determined on a JEOL Mstation 700 spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel $60F_{254}$.



Scheme 14.

Silica gel (Wakogel 200 mesh and Silica Gel 60N 40–100 μm, spherical, neutral, Kanto Chemical Co., Ltd.) was used for column chromatography. Gel permeation chromatography (GPC) was performed by LC-908 (Japan Analytical Industry Ltd., two in-line JAIGEL-2H, toluene, 7.8 mL min^{-1}, UV and RI detectors). The analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. THF and ether were purchased from Kanto Chemical Co., stored under nitrogen, and used as provided. 1,2,3,4,5-Pentamethyl-1,3-cyclopentadiene was purchased from Kanto Chemical Co., and stored under argon.

General Procedure for Nucleophilic Addition Reaction of Cp*Li to Aromatic Acid Chlorides (Table 1). A solution of *n*-BuLi in hexane (1.60 mol dm^{-3}, 1.38 mL, 2.20 mmol) was added to a solution of 1,2,3,4,5-pentamethyl-1,3-cyclopentadiene (0.38 mL, 2.40 mmol) in THF (20 mL) at 0 °C. The mixture was stirred for 30 min at the same temperature to generate a white suspension of lithium pentamethylcyclopentadienide. After an addition of 3-chlorobenzoyl chloride (350 mg, 2.00 mmol) in THF (1 mL), the mixture was stirred for an additional 30 min at 0 °C. The reaction was quenched with water, and the mixture was extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo to give a crude oil. The oil was purified by chromatography on silica gel (hexane/ethyl acetate = 40:1) to afford 3-chlorophenyl 1,2,3,4,5-pentamethyl-2,4-cyclopentadienyl ketone (**4e**) (536 mg, 1.95 mmol, 98%).

General Procedure for Nucleophilic Addition Reaction of Allylaluminum Reagent to Aromatic Ketones and Thermal Cleavage Reaction (Table 1). A solution of dimethylaluminum chloride in hexane (1.04 mol dm^{-3}, 0.72 mL, 0.75 mmol) was added to a solution of allylmagnesium bromide in Et_2O (0.87 mol dm^{-3}, 0.86 mL, 0.75 mmol) at −20 °C. After the mixture was stirred for 10 min at the same temperature, **4e** (137 mg, 0.50 mmol) in THF (2.5 mL) was added to the reaction mixture. The mixture was stirred for 1 h at −20 °C. The reaction mixture was quenched with 1 mol dm^{-3} HCl. The mixture was extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo to give a crude oil. The oil was filtered through a short pad of silica gel (ethyl acetate), and the filtrate was concentrated in vacuo. The oil was used for the next step without further purification. The resulting oil was dissolved in toluene (5 mL) and heated at reflux for 1.5 h. The mixture was concentrated and purified by chromatography on silica gel (hexane/ethyl acetate = 20:1) and GPC (toluene) to afford allyl 3-chlorophenyl ketone (**8e**) (59.1 mg, 0.33 mmol, 66%).

The crude **7a** could be isolated by chromatography on silica gel (Silica Gel 60N, hexane/ethyl acetate = 10:1) in 98% yield (139 mg, 0.49 mmol).

General Procedure for Nucleophilic Addition Reaction of Allylic Aluminum Reagent to Aliphatic Ketones and Acid-Induced Cleavage Reaction (Scheme 7). A solution of dimethylaluminum chloride in hexane (1.04 mol dm^{-3}, 0.72 mL, 0.75 mmol) was added to a solution of 2-methyl-2-propenylmagnesium chloride in THF (0.89 mol dm^{-3}, 0.84 mL, 0.75 mmol) at −20 °C. After the suspension was stirred for 10 min at −20 °C, a solution of **14a** (131 mg, 0.50 mmol) in THF (2.5 mL) was added to the mixture. The whole mixture was stirred for 1 h at −20 °C. Hydrochloric acid (1 mol dm^{-3}) was added to quench the reaction. Extraction with ethyl acetate and evaporation under reduced pressure afforded the crude oil. The oil was passed through a pad of silica gel with ethyl acetate, and the filtrate was concentrated in vacuo. A solution of trichloroacetic acid in CH_2Cl_2 (0.1 mol dm^{-3}, 0.50 mL, 0.05 mmol) was added to a solution of the resulting oil in CH_2Cl_2 (3.3 mL) at room temperature. The mixture was stirred for 1 h at room temperature. After the reaction was quenched with saturated aqueous $NaHCO_3$, the mixture was extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Silica-gel column chromatography (hexane/ethyl acetate = 20:1) and GPC purification (toluene) provided heptyl 2-methyl-2-propenyl ketone (**16b**) (45.5 mg, 0.25 mmol, 50%).

Synthesis of 4-Biphenylyl 1,2,3,4,5-Pentamethyl-2,4-cyclopentadienyl Ketone (18a). A mixture of **4d** (638 mg, 2.00 mmol), phenylboronic acid (293 mg, 2.40 mmol), $Pd(OAc)_2$ (22.4 mg, 0.10 mmol), PPh_3 (78.7 mg, 0.30 mmol), and Na_2CO_3 (254 mg, 2.40 mmol) in *i*-PrOH (8 mL) and H_2O (4 mL) was heated at reflux for 3 h. The mixture was quenched with 1 mol dm^{-3} HCl, and the mixture was extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo to give a crude oil. The oil was purified by chromatography on silica gel (hexane/ethyl acetate = 20:1) to afford **18a** (621 mg, 1.96 mmol, 98%).

Synthesis of Methyl 4′-(1,2,3,4,5-Pentamethyl-2,4-cyclopentadienylcarbonyl)biphenyl-4-carboxylate (18b). A mixture of **4d** (479 mg, 1.50 mmol), 4-methoxycarbonylphenylboronic acid (324 mg, 1.80 mmol), $Pd(OAc)_2$ (17.0 mg, 0.075 mmol), PPh_3 (59.0 mg, 0.23 mmol), and CsF (547 mg, 3.60 mmol) in DME (10 mL) was heated at reflux for 13 h. After the reaction was quenched with water, the mixture was extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Silica-gel column chromatography (hexane/ethyl acetate = 20:1) provided **18b** (530 mg, 1.41 mmol, 94%).

Synthesis of 3-Biphenylyl 1,2,3,4,5-Pentamethyl-2,4-cyclopentadienyl Ketone (18c). A mixture of **4e** (1.78 g, 6.48 mmol), phenylboronic acid (949 mg, 7.78 mmol), $Pd_2(dba)_3$ (297 mg, 0.32 mmol), P(*t*-Bu)$_3$ in hexane (1.0 mol dm^{-3}, 0.96 mL, 0.96 mmol), and KF (1.24 g, 21.4 mmol) in dioxane (13 mL) was heated at reflux for 72 h. The reaction was quenched with 1 mol dm^{-3} HCl, and the mixture was extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo to give a crude oil. The oil was purified by chromatography on silica gel (hexane/ethyl acetate = 80:1) to afford **18c** (1.16 g, 3.67 mmol, 57%).

Synthesis of 1,2,3,4,5-Pentamethyl-2,4-cyclopentadienyl (*E*)-4-Stilbenyl Ketone (20). A solution of **4d** (319 mg, 1.00 mmol), styrene (0.23 mL, 2.00 mmol), $Pd(OAc)_2$ (11.2 mg, 0.050 mmol), P(*o*-tolyl)$_3$ (30.4 mg, 0.10 mmol), and Et_3N (0.42 mL, 3.00 mmol)

in DMF (1.2 mL) was heated at 120 °C for 26 h. After the reaction was quenched with saturated NH_4Cl, the mixture was extracted with hexane–ethyl acetate (5:1). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Silica-gel column chromatography (hexane/ethyl acetate = 40:1) provided **20** (268 mg, 0.78 mmol, 78%).

Characterization Data. The spectral data of the products **8a**,[6] **8b**,[7] **8c**,[8] **8d**,[9] **8i**,[2a] **12**,[10] and **16a**[11] can be found in the literature. Ketone **8h** is commercially available.

1,2,3,4,5-Pentamethyl-2,4-cyclopentadienyl Phenyl Ketone (4a): IR (nujol) 1669 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.24 (s, 3H), 1.68 (d, J = 1.0 Hz, 6H), 1.83 (d, J = 0.5 Hz, 6H), 7.20–7.25 (m, 2H), 7.36–7.41 (m, 1H), 7.50–7.54 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 10.60 (×2), 11.41 (×2), 19.19, 70.31, 127.32 (×2), 127.88 (×2), 131.86, 138.06 (×2), 138.23, 140.00 (×2), 202.37; Found: C, 84.85; H, 8.37%. Calcd for $C_{17}H_{20}O$: C, 84.96; H, 8.39%; Mp 45.0–45.5 °C.

1,2,3,4,5-Pentamethyl-2,4-cyclopentadienyl 4-Trifluoromethylphenyl Ketone (4b): IR (neat) 2921, 1674, 1325, 1169, 1130, 1068 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26 (s, 3H), 1.69 (s, 6H), 1.83 (s, 6H), 7.49 (d, J = 8.0 Hz, 2H), 7.59 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 10.57 (×2), 11.41 (×2), 18.64, 70.40, 123.71 (q, J = 272.5 Hz), 124.91 (q, J = 3.9 Hz, ×2), 127.47 (×2), 133.09 (q, J = 32.2 Hz), 138.99 (×2), 139.36 (×2), 141.10, 201.74; Found: C, 69.88; H, 6.33%. Calcd for $C_{18}H_{19}F_3O$: C, 70.12; H, 6.21%.

4-Methoxyphenyl 1,2,3,4,5-Pentamethyl-2,4-cyclopentadienyl Ketone (4c): IR (nujol) 1656, 1600, 1572, 1248, 1176 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 (s, 3H), 1.68 (d, J = 0.5 Hz, 6H), 1.85 (d, J = 0.5 Hz, 6H), 3.80 (s, 3H), 6.72 (d, J = 9.0 Hz, 2H), 7.60 (d, J = 9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 10.55 (×2), 11.37 (×2), 19.82, 55.14, 69.98, 113.01 (×2), 129.95 (×2), 130.64, 137.19 (×2), 140.94 (×2), 162.65, 199.93; Found: C, 79.78; H, 8.14%. Calcd for $C_{18}H_{22}O_2$: C, 79.97; H, 8.20%; Mp 135.0–136.0 °C.

4-Bromophenyl 1,2,3,4,5-Pentamethyl-2,4-cyclopentadienyl Ketone (4d): IR (nujol) 1652, 1582 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23 (s, 3H), 1.67 (d, J = 1.0 Hz, 6H), 1.83 (s, 6H), 7.35–7.38 (m, 2H), 7.40–7.43 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 10.54 (×2), 11.38 (×2), 19.09, 70.17, 126.75, 129.00 (×2), 131.10 (×2), 136.65, 138.27 (×2), 139.92 (×2), 201.08; Found: C, 63.88; H, 5.98%. Calcd for $C_{17}H_{19}OBr$: C, 63.96; H, 6.00%; Mp 58.0–59.0 °C.

3-Chlorophenyl 1,2,3,4,5-Pentamethyl-2,4-cyclopentadienyl Ketone (4e): IR (neat) 2972, 2916, 2855, 1674, 1668, 1569, 1443, 1230, 974 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23 (s, 3H), 1.68 (s, 6H), 1.84 (s, 6H), 7.16 (t, J = 8.0 Hz, 1H), 7.33–7.42 (m, 2H), 7.51 (t, J = 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 10.61 (×2), 11.42 (×2), 18.78, 70.35, 125.36, 127.56, 129.23, 131.77, 133.86, 138.75 (×2), 139.50, 139.67 (×2), 201.09; Found: C, 74.04; H, 7.25%. Calcd for $C_{17}H_{19}ClO$: C, 74.31; H, 6.97%.

1,2,3,4,5-Pentamethyl-2,4-cyclopentadienyl *o*-Tolyl Ketone (4f): IR (nujol) 1681 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.27 (s, 3H), 1.69 (d, J = 1.0 Hz, 6H), 1.77 (d, J = 0.5 Hz, 6H), 2.32 (s, 3H), 6.89–6.95 (m, 2H), 7.11–7.15 (m, 1H), 7.16–7.20 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 10.47 (×2), 11.36 (×2), 18.24, 20.47, 71.07, 124.69, 125.12, 129.66, 130.92, 135.44, 138.51 (×2), 138.57 (×2), 139.09, 206.12; Found: C, 84.71; H, 8.68%. Calcd for $C_{18}H_{22}O$: C, 84.99; H, 8.72%; Mp 36.0–37.0 °C.

2-Iodophenyl 1,2,3,4,5-Pentamethyl-2,4-cyclopentadienyl Ketone (4g): IR (nujol) 1684 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.32 (s, 3H), 1.76 (s, 12H), 6.86 (dd, J = 8.0, 1.5 Hz, 1H), 6.97 (dt, J = 8.0, 1.5 Hz, 1H), 7.08 (dt, J = 8.0, 1.0 Hz, 1H), 7.83 (dd, J = 8.0, 1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 10.79 (×2), 11.37 (×2), 17.75, 70.77, 91.66, 125.43, 126.91, 130.85, 137.96 (×2), 139.26 (×2), 140.26, 143.68, 204.93; Found: C, 55.70; H, 5.18%. Calcd for $C_{17}H_{19}IO$: C, 55.75; H, 5.23%; Mp 59.0–60.0 °C.

1,2,3,4,5-Pentamethyl-2,4-cyclopentadienyl 2-Thienyl Ketone (4h): IR (nujol) 1638 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.24 (s, 3H), 1.71 (d, J = 0.5 Hz, 6H), 1.86 (d, J = 0.5 Hz, 6H), 6.92 (dd, J = 5.0, 4.0 Hz, 1H), 7.37 (dd, J = 5.0, 1.0 Hz, 1H), 7.54 (dd, J = 4.0, 1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 10.53 (×2), 11.46 (×2), 17.63, 69.69, 127.07, 132.05, 132.13, 138.99 (×2), 139.50 (×2), 140.60, 193.31; Found: C, 72.96; H, 7.40%. Calcd for $C_{15}H_{18}OS$: C, 73.13; H, 7.36%; Mp 85.5–86.5 °C.

2-Furyl 1,2,3,4,5-Pentamethyl-2,4-cyclopentadienyl Ketone (4i): IR (nujol) 1653 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23 (s, 3H), 1.70 (s, 6H), 1.85 (s, 6H), 6.28–6.32 (m, 1H), 6.73–6.77 (m, 1H), 7.44–7.49 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 10.48 (×2), 11.42 (×2), 17.51, 68.83, 111.51, 116.73, 137.91 (×2), 139.68 (×2), 145.90, 150.13, 189.08; Found: C, 77.95; H, 7.86%. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88%; Mp 90.5–91.0 °C.

1-(1,2,3,4,5-Pentamethyl-2,4-cyclopentadienyl)-1-phenyl-3-buten-1-ol (7a): IR (neat) 2917, 1445, 1327, 1249, 992, 924, 761, 709 cm^{-1}; ^1H NMR (C_6D_6) δ 1.31 (s, 3H), 1.45 (d, J = 1.5 Hz, 3H), 1.60 (d, J = 1.0 Hz, 3H), 1.86 (s, 3H), 1.96 (s, 3H), 2.03 (s, 1H), 2.47 (dd, J = 13.5, 10.0 Hz, 1H), 2.94 (ddt, J = 13.5, 5.0, 1.5 Hz, 1H), 4.80 (ddt, J = 10.0, 1.5, 0.5 Hz, 1H), 4.90–4.95 (m, 1H), 5.31 (dddd, J = 17.5, 10.0, 10.0, 5.0 Hz, 1H), 6.99–7.13 (m, 3H), 7.27–7.33 (m, 2H); ^{13}C NMR (C_6D_6) δ 10.86, 11.14, 13.46, 13.72, 15.86, 41.86, 63.72, 78.51, 120.04, 126.56, 126.62 (×2), 126.65 (×2), 134.60, 135.65, 137.74, 138.66, 141.65, 143.85; Found: C, 84.88; H, 9.58%. Calcd for $C_{20}H_{26}O$: C, 85.05; H, 9.28%.

Allyl 3-Chlorophenyl Ketone (8e): IR (nujol) 1679 cm^{-1}; ^1H NMR (C_6D_6) δ 3.08 (dt, J = 6.5, 1.5 Hz, 2H), 4.93 (ddt, J = 17.0, 3.0, 1.5 Hz, 1H), 5.03 (ddt, J = 10.5, 3.0, 1.5 Hz, 1H), 5.97 (ddt, J = 17.0, 10.5, 6.5 Hz, 1H), 6.73 (t, J = 8.0 Hz, 1H), 7.06–7.09 (m, 1H), 7.43–7.48 (m, 1H), 7.74–7.78 (m, 1H); ^{13}C NMR (C_6D_6) δ 43.07, 118.30, 126.33, 128.54, 129.93, 131.23, 132.69, 134.87, 138.48, 195.29; Found: C, 66.70; H, 5.07%. Calcd for $C_{10}H_9ClO$: C, 66.49; H, 5.02%; Mp 32.0–33.0 °C.

Heptyl 1,2,3,4,5-Pentamethyl-2,4-cyclopentadienyl Ketone (14a): IR (neat) 2928, 1701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (t, J = 7.0 Hz, 3H), 1.09 (s, 3H), 1.67 (s, 6H), 1.84 (s, 6H), 1.13–1.42 (m, 10H), 1.84 (t, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 10.39 (×2), 11.41 (×2), 14.07, 14.70, 22.61, 24.03, 29.00, 29.20, 31.67, 34.63, 71.33, 136.98 (×2), 139.38 (×2), 210.42; Found: C, 82.14; H, 11.24%. Calcd for $C_{18}H_{30}O$: C, 82.38; H, 11.52%.

Cyclohexyl 1,2,3,4,5-Pentamethyl-2,4-cyclopentadienyl Ketone (14b): IR (neat) 2931, 2856, 1695, 1448, 989 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.99–1.67 (m, 10H), 1.08 (s, 3H), 1.69 (d, J = 1.0 Hz, 6H), 1.86 (d, J = 0.5 Hz, 6H), 2.05 (tt, J = 11.5, 3.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 10.94 (×2), 11.44 (×2), 14.62, 25.67 (×2), 25.71, 30.01 (×2), 43.22, 71.67, 136.55 (×2), 139.94 (×2), 213.51; Found: C, 82.58; H, 10.90%. Calcd for $C_{17}H_{26}O$: C, 82.87; H, 10.64%.

Heptyl 2-Methyl-2-propenyl Ketone (16b): IR (neat) 2929, 1717, 1649, 1458, 1376, 894 cm^{-1}; ^1H NMR (C_6D_6) δ 0.89 (t, J = 7.0 Hz, 3H), 1.10–1.30 (m, 8H), 1.46–1.55 (m, 2H), 1.66 (s, 3H), 2.07 (t, J = 7.0 Hz, 2H), 2.77 (d, J = 1.0 Hz, 2H), 4.70–4.74 (m, 1H), 4.82–4.86 (m, 1H); ^{13}C NMR (C_6D_6) δ 14.27, 22.59, 22.98, 23.96, 29.45, 29.48, 32.04, 41.67, 52.09, 114.48, 140.01, 206.43; Found: C, 79.32; H, 12.37%. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16%.

4-Biphenylyl 1,2,3,4,5-Pentamethyl-2,4-cyclopentadienyl Ketone (18a): IR (nujol) 1653 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.27 (s,

3H), 1.72 (s, 6H), 1.87 (s, 6H), 7.33–7.38 (m, 1H), 7.41–7.49 (m, 4H), 7.56–7.59 (m, 2H), 7.62–7.66 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 10.66 (×2), 11.46 (×2), 19.38, 70.30, 126.56 (×2), 127.06 (×2), 127.84, 128.06 (×2), 128.78 (×2), 136.78, 137.96 (×2), 140.08, 140.26 (×2), 144.50, 201.67; Found: C, 87.24; H, 7.68%. Calcd for $C_{23}H_{24}O$: C, 87.30; H, 7.64%; Mp 90.0–91.0 °C.

Methyl 4′-(1,2,3,4,5-Pentamethyl-2,4-cyclopentadienylcarbonyl)biphenyl-4-carboxylate (18b): IR (nujol) 1722, 1663, 1604, 1277, 1108 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.26 (s, 3H), 1.71 (s, 6H), 1.86 (s, 6H), 3.93 (s, 3H), 7.48–7.51 (m, 2H), 7.62–7.66 (m, 4H), 8.07–8.11 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 10.66 (×2), 11.47 (×2), 19.26, 52.17, 70.35, 126.79 (×2), 127.02 (×2), 128.12 (×2), 129.39, 130.10 (×2), 137.57, 138.18 (×2), 140.13 (×2), 143.18, 144.50, 166.85, 201.66; Found: C, 79.89; H, 7.02%. Calcd for $C_{25}H_{26}O_3$: C, 80.18; H, 7.00%; Mp 123.0–124.0 °C.

3-Biphenylyl 1,2,3,4,5-Pentamethyl-2,4-cyclopentadienyl Ketone (18c): IR (neat): 2918, 1668, 1451, 1218, 971, 760, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.29 (s, 3H), 1.73 (s, 6H), 1.88 (s, 6H), 7.31–7.38 (m, 2H), 7.42–7.46 (m, 2H), 7.48–7.53 (m, 2H), 7.56–7.60 (m, 1H), 7.64–7.67 (m, 1H), 7.86–7.89 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 10.67 (×2), 11.47 (×2), 19.28, 70.39, 126.20, 126.35, 126.77 (×2), 127.45, 128.44, 128.75 (×2), 130.37, 137.99 (×2), 138.43, 140.36, 140.53 (×3), 201.98; HRMS Found: 316.1826. Calcd for $C_{23}H_{24}O$: 316.1827.

Allyl 4-Biphenylyl Ketone (19a): IR (nujol) 1684 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.80 (dt, J = 7.0, 1.5 Hz, 2H), 5.25 (ddt, J = 17.0, 3.0, 1.5 Hz, 1H), 5.26 (ddt, J = 10.5, 3.0, 1.5 Hz, 1H), 6.12 (ddt, J = 17.0, 10.5, 7.0 Hz, 1H), 7.39–7.43 (m, 1H), 7.45–7.50 (m, 2H), 7.62–7.65 (m, 2H), 7.68–7.71 (m, 2H), 8.03–8.07 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 43.52, 118.76, 127.27 (×4), 128.25, 128.89 (×2), 128.95 (×2), 131.10, 135.25, 139.84, 145.86, 197.62; Found: C, 86.15; H, 6.55%. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35%; Mp 69.5–70.0 °C.

Methyl 4′-(3-Butenoyl)biphenyl-4-carboxylate (19b): IR (nujol) 1723, 1677, 1610 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.80 (dt, J = 6.5, 1.5 Hz, 2H), 3.95 (s, 3H), 5.24 (ddt, J = 17.0, 2.5, 1.0 Hz, 1H), 5.26 (ddt, J = 10.5, 2.5, 1.0 Hz, 1H), 6.11 (ddt, J = 17.0, 10.5, 6.5 Hz, 1H), 7.66–7.74 (m, 4H), 8.03–8.08 (m, 2H), 8.11–8.15 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 43.52, 52.21, 118.86, 127.20 (×2), 127.46 (×2), 128.94 (×2), 129.74, 130.20 (×2), 130.90, 135.86, 144.11, 144.49, 166.73, 197.50; Found: C, 76.87; H, 5.74%. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75%; Mp 139.0–140.0 °C.

Allyl 3-Biphenylyl Ketone (19c): IR (neat) 3032, 1687, 1598, 1478, 1452, 1418, 1296, 1188, 921 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.82 (dt, J = 7.0, 1.5 Hz, 2H), 5.25 (ddt, J = 17.0, 3.5, 1.5 Hz, 1H), 5.27 (ddt, J = 10.5, 3.5, 1.5 Hz, 1H), 6.13 (ddt, J = 17.0, 10.5, 7.0 Hz, 1H), 7.37–7.42 (m, 1H), 7.46–7.50 (m, 2H), 7.52–7.57 (m, 1H), 7.60–7.64 (m, 2H), 7.77–7.82 (m, 1H), 7.94–7.96 (m, 1H), 8.19–8.21 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 43.58, 118.80, 126.95, 127.08, 127.16 (×2), 127.80, 128.91 (×2), 129.06, 131.00, 131.78, 137.04, 140.12, 141.75, 197.95; Found: C, 86.57; H, 6.54%. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35%.

1,2,3,4,5-Pentamethyl-2,4-cyclopentadienyl (*E*)-4-Stilbenyl Ketone (20): IR (nujol) 1661, 1604 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 3H), 1.70 (d, J = 1.0 Hz, 6H), 1.86 (d, J = 0.5 Hz, 6H), 7.04 (d, J = 16.5 Hz, 1H), 7.14 (d, J = 16.5 Hz, 1H), 7.25–7.30 (m, 1H), 7.34–7.39 (m, 4H), 7.48–7.52 (m, 2H), 7.54–7.58 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 10.64 (×2), 11.45 (×2), 19.42, 70.29, 125.97 (×2), 126.68 (×2), 127.75, 128.05, 128.07 (×2), 128.73 (×2), 130.54, 136.91, 136.98, 137.90 (×2), 140.35 (×2), 140.84, 201.31; Found: C, 87.41; H, 7.76%. Calcd for $C_{25}H_{26}O$: C, 87.68; H, 7.65%; Mp 106.0–107.0 °C.

Allyl (*E*)-4-Stilbenyl Ketone (21): IR (nujol) 1685, 969, 818, 722 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.77 (d, J = 6.5 Hz, 2H), 5.20–5.28 (m, 2H), 6.10 (ddt, J = 17.0, 10.5, 6.5 Hz, 1H), 7.14 (d, J = 16.5 Hz, 1H), 7.24 (d, J = 16.5 Hz, 1H), 7.31 (t, J = 7.5 Hz, 1H), 7.39 (t, J = 7.5 Hz, 2H), 7.55 (d, J = 7.5 Hz, 2H), 7.60 (d, J = 8.5 Hz, 2H), 7.97 (d, J = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 43.40, 118.68, 126.50 (×2), 126.79 (×2), 127.35, 128.30, 128.76 (×2), 128.81 (×2), 131.12, 131.48, 135.27, 136.62, 142.03, 197.30; Found: C, 86.93; H, 6.62%. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.49%; Mp 105.0–106.0 °C.

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