Supporting Information
for DOI: 10.1055/s-0034-1380691
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Supporting Information for:

Rasta Resin-TBD-Catalyzed γ-Selective Morita-Baylis-Hillman Reactions of α,γ-Disubstituted Allenones

Shuang Ma, Yun-Chin Yang, Patrick H. Toy*

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, P. R. of China

Fax +852 28571586; E-mail: phtoy@hku.hk

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General experimental procedures

All reagents were obtained from Acros, Aldrich, or Lancaster chemical companies, and were used as received. $^1$H- and $^{13}$C-NMR spectra were recorded in CDCl$_3$ on a Bruker DRX-300 or DRX-400 spectrometer operating at 300/400 MHz for $^1$H and 75/101 MHz for $^{13}$C analysis. Chemical shift data is expressed in ppm with reference to TMS. Elemental analysis was performed at the Shanghai Institute of Organic Chemistry. Polymer 2 was prepared according to the literature procedure and analyzed by elemental analysis to determine its loading to be 1.418 mmol TBD/g. HR EI-MS data was recorded on a Finnigan MAT 96 mass spectrometer.

General Procedure for the Synthesis of Allenones 3A-D

$\alpha$-Bromoketone 4A or 4B (20.0 mmol), PPh$_3$ (6.29 g, 24.0 mmol), and benzene (100 mL) were added to a 250-mL round-bottomed flask equipped with a magnetic stirrer and a condenser. The reaction flask was immersed in an oil bath, and the reaction mixture was refluxed for 2 days. After cooling to room temperature, the solvent was removed under reduced pressure to afford crude phosphonium salt 5A or 5B as a viscous oil. The crude salt dissolved in chloroform (65 mL) was transferred to a 100-mL round-bottomed flask equipped with a magnetic stirrer. The reaction mixture was cooled to 0 °C with an ice-water bath and then NEt$_3$ (6.1 mL, 44 mmol) was added dropwise. The ice-water bath was removed, and the reaction mixture was then stirred at room temperature for 3 hours. The reaction mixture was cooled to 0 °C and the appropriate acid chloride (18.0 mmol) was added dropwise. After 1 hour, the reaction mixture was warm to room temperature and stirred for 10 hours more. The reaction mixture was transferred to a separation funnel and water (100 mL) was added. The organic layer was separated and washed with brine (50 mL) and then dried over MgSO$_4$. The solvent was removed under reduced pressure to afford a yellow oil which was then purified by silica gel column chromatography using a mixture of dichloromethane and hexane as the eluent.
4-Methylhepta-4,5-dien-3-one (3A): DCM/Hexane = 1/5, \( R_f = 0.30 \), light-yellow oil, 21% yield. \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \( \delta \) ppm 5.50-5.43 (m, 1H), 2.71-2.59 (m, 2H), 1.79 (d, \( J = 7.3 \) Hz, 3H), 1.76 (d, \( J = 2.7 \) Hz, 3H), 1.07 (t, \( J = 7.3 \) Hz, 3H); \(^{13}\)C-NMR (101 MHz, CDCl\(_3\)) \( \delta \) ppm 212.29, 202.88, 159.50, 138.13, 91.70, 88.92, 32.10, 13.49, 13.39, 8.99.

HRMS for C\(_8\)H\(_{12}\)O: calc 124.0883, found 124.0881.

4-Methyl-6-phenylhexa-4,5-dien-3-one (3B): DCM/Hexane = 1/5, \( R_f = 0.31 \), light-yellow oil, 68% yield. \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \( \delta \) ppm 7.36-7.25 (m, 5H), 6.52-6.51 (m, 1H), 2.76-2.60 (m, 2H), 1.92 (d, \( J = 2.8 \) Hz, 3H), 1.06 (t, \( J = 7.4 \) Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) ppm 214.21, 201.41, 132.33, 129.05, 127.88, 127.19, 107.13, 97.81, 77.60, 31.98, 13.50, 8.79.

HRMS for C\(_{13}\)H\(_{14}\)O: calc 186.1039, found 186.1036.

2-Methyl-1-phenylpenta-2,3-dien-1-one (3C): DCM/Hexane = 1/3, \( R_f = 0.44 \), light-yellow oil, 49% yield. \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \( \delta \) ppm 7.71 (d, \( J = 8.2 \) Hz, 2H), 7.47 (t, \( J = 7.5 \) Hz, 1H), 7.37 (t, \( J = 7.6 \) Hz, 2H), 5.34-5.28 (m, 1H), 1.98 (d, \( J = 2.7 \) Hz, 3H), 1.72 (d, \( J = 7.3 \) Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) ppm 214.47, 196.03, 138.70, 131.75, 128.84, 127.80, 101.95, 88.59, 15.00, 13.50.

HRMS for C\(_{12}\)H\(_{12}\)O: calc 172.0883, found 172.0878.

2-Methyl-1,4-diphenylbuta-2,3-dien-1-one (3D): DCM/Hexane = 1/5, \( R_f = 0.54 \), light-yellow solid, 65% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) ppm 7.75 (d, \( J = 7.5 \) Hz, 1H), 7.43 (t, \( J = 7.4 \) Hz, 1H), 7.37-7.26 (m, 5H), 6.43-6.39 (m, 1H), 2.14 (d, \( J = 2.14 \) Hz, 3H), 1.57 (s, 3H); \(^{13}\)C NMR (400 MHz, CDCl\(_3\)) \( \delta \) ppm 215.35, 194.36, 138.11, 132.40, 132.15, 128.94, 128.70, 127.91, 127.78, 127.32, 105.83, 97.29, 15.08.

HRMS for C\(_{17}\)H\(_{14}\)O: calc 234.1039, found 234.1041
General Procedure for the MBH Reactions

Allenone 3A-D (0.8 mmol), aldehyde 6a-e (0.4 mmol), NMP (1.0 mL), and 1, 2 or 8 (0.08 mmol) were added to a 10-mL round-bottomed flask equipped with a magnetic stirrer. The reaction mixture was stirred either at room temperature (when 1 was used as the catalyst) or at 50 °C (when 2 or 8 was used as the catalyst) for the reaction times indicated in Table 2. When 1 was used as the catalyst, solid NH₄Cl (0.006 g, 0.1 mmol) was added to the reaction mixture to quench the reaction. The reaction mixture was then transferred to a separation funnel, and then water (30 mL) and ethyl acetate (15 mL) were added. The organic layer was separated, washed with brine (30 mL), and dried over MgSO₄. The solvent was evaporated under reduced pressure to afford an oil, which was purified by silica gel column chromatography using a mixture of ethyl acetate and hexane as the eluent. When 2 was used as the catalyst, the reaction mixture was merely filtered, and the crude product was purified by silica gel column chromatography.

7-(4-Chlorophenyl)-7-hydroxy-4,6-dimethylhepta-4,5-dien-3-one (7Aa): ¹H NMR (400 MHz, CDCl₃) δ ppm 7.37-7.29 (m, 4H, CH₆Ar, both diastereomers), 5.26 (s, 1H, CHOCH, major diastereomer), 5.24 (s, 1H, CHOCH, minor diastereomer), 2.64-2.50 (m, 2H, COCH₂CH₃, both diastereomers), 2.43 (s br, 1H, OH, major diastereomer), 2.37 (s, 1H, OH, minor diastereomer), 1.78 (s, 3H, (CH₃)CCOEt, both diastereomers), 1.74 (s, 3H, (CH₃)CCHOH, both diastereomers), 1.05 (t, J = 7.4 Hz, 3H, CH₂CH₃, both diastereomers).

¹³C NMR (major diastereomer, 101 MHz, CDCl₃) δ ppm 208.73 (s, =C=), 202.80 (s, COEt), 140.12 (s, C₆ArCHOH), 133.73 (s, C₆ArCl), 128.62 (s, C₆ArH), 127.67 (s, C₆ArH), 106.43 (s, CCHOH), 105.04 (s, CCOEt), 74.48 (s, CCHOH), 32.43 (s, CH₂CH₃), 8.92 (s, CH₂CH₃). The signals for (CH₃)CCHOH and (CH₃)CCO (14.43, 14.20, 13.81) were not assigned due to overlapping signals.
13C NMR (minor diastereomer, 101 MHz, CDCl3) δ ppm 208.67 (s, =C=), 202.86 (s, COEt), 140.09 (s, C₆H₅CHOH), 133.80 (s, C₆H₅Cl), 128.67 (s, C₆H₅H), 127.74 (s, C₆H₅H), 106.42 (s, CCHOH), 105.32 (s, CCOEt), 74.39 (s, CHOH), 32.43 (s, CH₂CH₃), 8.88 (s, CH₂CH₃).

HRMS for C₁₃H₁₇ClO₂: calc 264.0912, found 264.0724.

7-(4-Cyanophenyl)-7-hydroxy-4,6-dimethylhepta-4,5-dien-3-one (7Ab): 1H NMR (300 MHz, CDCl₃) δ ppm 7.66-7.53 (m, 4H, CH₆Ar, both diastereomers), 5.40 (s, 1H, CHOH, major diastereomer), 5.37 (s, 1H, CHOH, minor diastereomer), 2.64-2.55 (m, 2H, COCH₂CH₃, both diastereomers), 2.88 (s br, 1H, OH, major diastereomer), 2.79 (s, 1H, OH, minor diastereomer), 1.02 (t, J = 7.5 Hz, 3H, CH₂CH₃, both diastereomers). The signals for (CH₃)CCHOH and (CH₃)CCO (1.79, 1.76, 1.72) were not assigned due to overlapping signals.

13C NMR (major diastereomer, 75 MHz, CDCl₃) δ ppm 208.51 (s, =C=), 202.14 (s, COEt), 146.68 (s, C₆H₅CHOH), 131.54 (s, C₆H₅CN), 126.37 (s, C₆H₅H), 126.30 (s, C₆H₅H), 118.08 (s, CN), 110.69 (s, C₆H₅CN), 106.25 (s, CCOEt), 104.43 (s, CCHOH), 73.56 (s, CHOH), 31.75 (s, CH₂CH₃), 8.19 (s, CH₂CH₃). The signals for (CH₃)CCHOH and (CH₃)CCO (13.70, 13.08, 12.96) were not assigned due to overlapping signals.

13C NMR (minor diastereomer, 75 MHz, CDCl₃) δ ppm 208.40 (s, =C=), 202.14 (s, COEt), 146.66 (s, C₆H₅CHOH), 133.80 (s, C₆H₅Cl), 128.67 (s, C₆H₅H), 127.74 (s, C₆H₅H), 118.08 (s, CN), 110.61 (s, C₆H₅CN), 106.40 (s, CCOEt), 103.97 (s, CCHOH), 73.56 (s, CHOH), 31.75 (s, CH₂CH₃), 8.16 (s, CH₂CH₃).

HRMS for C₁₆H₁₇NO₂: calc 255.1259, found 255.1250.

7-Hydroxy-4,6-dimethyl-7-(4-nitrophenyl)hepta-4,5-dien-3-one (7Ac): 1H NMR (400 MHz, CDCl₃) δ ppm 8.21 (d, J = 8.5 Hz, 2H, CH₆Ar, both diastereomers), 7.59 (d, J = 7.9 Hz, 2H, CH₆Ar, both diastereomers), 5.47 (s, 1H, CHOH, major diastereomer), 5.44 (s, 1H, CHOH, minor diastereomer), 3.71 (s, 1H, CHO₉H, minor diastereomer), 3.63 (s, 1H, CHOH, major diastereomer), 2.66-2.46 (m, 2H,
COCH₂CH₃, both diastereomers), 1.03 (t, J = 7.3 Hz, 3H, CH₂CH₃, both diastereomers). The signals for (CH₃)CCHOH and (CH₃)CCO (1.81, 1.78, 1.73) were not assigned due to overlapping signals.

¹³C NMR (major diastereomer, 101 MHz, CDCl₃) δ ppm 209.07 (s, C=), 202.71 (s, COEt), 149.07 (s, CArNO₂), 147.36 (s, CArCHOH), 127.00 (s, CArH), 123.56 (s, CArH), 105.93 (s, CCHOH), 104.74 (s, CCOEt), 74.11 (s, CHO), 32.40 (s, CH₂CH₃), 8.76 (s, CH₂CH₃). The signals for (CH₃)CCHOH and (CH₃)CCO (14.29, 13.71, 13.58) were not assigned due to overlapping signals.

¹³C NMR (minor diastereomer, 101 MHz, CDCl₃) δ ppm 208.92 (s, C=), 202.71 (s, COEt), 149.06 (s, CArNO₂), 147.38 (s, CArCHOH), 127.06 (s, CArH), 123.56 (s, CArH), 105.81 (s, CCHOH), 105.16 (s, CCOEt), 74.07 (s, CHO), 32.40 (s, CH₂CH₃), 8.75 (s, CH₂CH₃).

HRMS for C₁₃H₁₇NO₄: calc 275.1152, found 275.1155.

7-Hydroxy-4,6-dimethyl-7-phenylhepta-4,5-dien-3-one (7Ad): ¹H NMR (400 MHz, CDCl₃) δ ppm 7.37-7.26 (m, 5H, CHAr, both diastereomers), 5.23 (s, 1H, CHO, major diastereomer), 5.22 (s, 1H, CHO, minor diastereomer), 2.63-2.52 (m, 2H, COCH₂CH₃, both diastereomers), 1.73 (s, 6H, (CH₃)CCHOH and (CH₃)CCO, both diastereomers), 1.02-0.98 (m, 3H, CH₂CH₃, both diastereomers).

¹³C NMR (major diastereomer, 101 MHz, CDCl₃) δ ppm 208.96 (s, C=), 203.29 (s, COEt), 141.69 (s, CArCHOH), 128.31 (s, CArH), 127.87 (s, CArH), 126.20 (s, CArH), 106.74 (s, CCHOH), 104.88 (s, CCOEt), 74.98 (s, CHO), 32.26 (s, CH₂CH₃), 14.32 (s, (CH₃)CCO), 13.67 (s, (CH₃)CCHOH), 8.88 (s, CH₂CH₃).

¹³C NMR (minor diastereomer, 101 MHz, CDCl₃) δ ppm 208.95 (s, C=), 203.22 (s, COEt), 141.64 (s, CArCHOH), 128.36 (s, CArH), 127.93 (s, CArH), 126.25 (s, CArH), 106.69 (s, CCHOH), 104.67 (s, CCOEt), 74.84 (s, CHO), 32.26 (s, CH₂CH₃), 14.23 (s, (CH₃)CCO), 13.63 (s, (CH₃)CCHOH), 8.85 (s, CH₂CH₃).

HRMS for C₁₆H₂₀O₃: calc 260.1407, found 260.0910.
7-Hydroxy-4,6-dimethyl-7-(4-methoxyphenyl)hepta-4,5-dien-3-one (7An): $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.20 (d, $J = 7.2$ Hz, 2H, $CH_Ar$, both diastereomers), 7.78 (d, $J = 6.8$ Hz, 2H, $CH_Ar$, both diastereomers), 5.11 (s, 1H, $CHOH$, major diastereomer), 5.10 (s, 1H, $CHOH$, minor diastereomer), 3.69 (s, 3H, $OCH_3$, both diastereomers), 1.02-0.98 (m, 3H, $CH_2CH_3$, both diastereomers). The signals for ($CH_3$)CCHOH and ($CH_3$)CCHO ($1.67, 1.66, 1.65$) were not assigned due to overlapping signals.

$^{13}$C NMR (major diastereomer, 101 MHz, CDCl$_3$) δ ppm 208.87 (s, =C=), 203.17 (s, COEt), 159.11 (s, $C_Ar$OMe), 133.93 (s, $C_Ar$CHOH), 127.46 (s, $C_Ar$H), 113.61 (s, $C_Ar$H), 106.96 (s, CCHOH), 104.55 (s, CCOEt), 74.50 (s, CHOH), 55.15 (OCH$_3$), 32.19 (s, $CH_2CH_3$), 14.29 (s, (CH$_3$)CCHO), 13.58 (s, (CH$_3$)CCHOH), 8.87 (s, $CH_2CH_3$).

$^{13}$C NMR (minor diastereomer, 101 MHz, CDCl$_3$) δ ppm 208.88 (s, =C=), 203.26 (s, COEt), 159.16 (s, $C_Ar$OMe), 133.87 (s, $C_Ar$CHOH), 127.50 (s, $C_Ar$H), 113.66 (s, $C_Ar$H), 106.88 (s, CCHOH), 104.73 (s, CCOEt), 74.37 (s, CHOH), 55.15 (OCH$_3$), 32.18 (s, $CH_2CH_3$), 14.32 (s, (CH$_3$)CCHO), 13.67 (s, (CH$_3$)CCHOH), 8.83 (s, $CH_2CH_3$).

HRMS for C$_{18}$H$_{20}$O$_3$: calc 260.1407, found 260.1405.

7-(4-Chlorophenyl)-7-hydroxy-4-methyl-6-phenylhepta-4,5-dien-3-one (7An): $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.41-7.27 (m, 9H, $CH_Ar$, both diastereomers), 5.86 (s, 1H, $CHOH$, both diastereomers), 2.76-2.31 (m, 2H, $CH_2CH_3$), 1.85 (s, 3H, (CH$_3$)CCHOEt, minor diastereomer), 1.78 (s, 3H, (CH$_3$)CCHOEt, major diastereomer), 1.07-0.93 (m, 3H, $CH_2CH_3$, both diastereomers).

$^{13}$C NMR (major diastereomer, 101 MHz, CDCl$_3$) δ ppm 212.18 (s, =C=), 200.74 (s, COPh), 139.51 (s, $C_Ar$CHOH), 132.16 (s, $C_Ar$CCHOH), 128.35 (s, $C_Ar$H), 128.07 (s, $C_Ar$H), 127.49 (s, $C_Ar$H), 126.29 ((s, $C_Ar$H), 112.92 (s, CCOEt), 108.13 (s, CCHOH), 71.80 (s, CHOH), 32.14 (s, $CH_2CH_3$), 12.92 (s, $CH_2CCO$), 7.90 (s, $CH_2CH_3$).
$^{13}$C NMR (minor diastereomer, 101 MHz, CDCl$_3$) δ 212.25 (s, =C=), 200.36 (s, COPh), 139.57 (s, $C_A$CHOH), 133.30 (s, $C_A$CCHOH), 127.97 (s, $C_A$H), 127.52 (s, $C_A$H), 127.27 (s, $C_A$H), 126.49 (s, $C_A$H), 112.76 (s, CCOEt), 107.74s, CCHOH), 72.16 (s, CH$_2$CH$_3$), 12.69 (s, CH$_3$CCO), 7.83 (s, CH$_2$CH$_3$).

HRMS for C$_{28}$H$_{19}$ClO$_2$: calc 326.1068, found 326.1061.

7-(4-Cyanophenyl)-7-hydroxy-4-methyl-6-phenylepta-4,5-dien-3-one (7Bb): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.58-7.26 (m, 9H, CH$_A$, both diastereomers), 5.95 (s, 1H, CHOH, major diastereomer), 5.92 (s, 1H, CHOH, minor diastereomer), 3.79 (s, 1H, OH, major diastereomer), 3.72 (s, 1H, OH, minor diastereomer), 2.69-2.31 (m, 2H, CH$_2$CH$_3$), 1.82 (s, 3H, (CH$_3$)CCOEt, minor diastereomer), 1.68 (s, 3H, (CH$_3$)CCOEt, major diastereomer), 1.02-0.90 (m, 3H, CH$_2$CH$_3$, both diastereomers).

$^{13}$C NMR (major diastereomer, 101 MHz, CDCl$_3$) δ ppm 213.17 (s, =C=), 201.06 (s, COPh), 147.33 (s, $C_A$CHOH), 132.47 (s, $C_A$CCHOH), 132.16 (s, $C_A$H), 129.01 (s, $C_A$H), 127.14 (s, $C_A$H), 126.94 (s, $C_A$H), 118.66 (s, CCOEt), 113.34 (s, CN), 111.37 (s, CCHOH), 108.48 (s, $C_A$CN), 72.34 (s, CHOH), 32.78 (s, CH$_2$CH$_3$), 13.11 (s, CH$_3$CCO), 8.42 (s, CH$_2$CH$_3$).

HRMS for C$_{24}$H$_{19}$NO$_2$: calc 317.1410, found 317.1394.

5-(4-Chlorophenyl)-5-hydroxy-2,4-dimethyl-1-phenylpenta-2,3-dien-1-one (7Ca): $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.63-7.61 (m, 2H, CH$_A$, both diastereomers), 7.52-7.47 (m, 1H, CH$_A$, both diastereomers), 7.37-7.32 (m, 2H, CH$_A$, both diastereomers), 7.13-7.04 (m, 1H, CH$_A$, both diastereomers), 6.79-6.74 (m, 2H, CH$_A$, both diastereomers), 5.09 (s, 1H, CHOH, major diastereomer), 3.73 (s, 3H, OMe, both diastereomers), 2.65 (s, 3H, CHO, both diastereomers), 1.00-0.90 (m, 3H, CH$_2$CH$_3$, both diastereomers).
4.98 (s, 1H, CHOH, minor diastereomer), 2.92 (s, 1H, OH, major diastereomer), 2.61 (s, 1H, OH, minor diastereomer), 1.99 (s, 3H, (CH3)CCOPh, both diastereomers), 1.98 (s, 3H, (CH3)CCHOH), both diastereomers), 1.60 (s, 3H, (CH3)CCHOH, both diastereomers), 1.59 (s, 3H, (CH3)CCHOH, both diastereomers).

13C NMR (major diastereomer, 101 MHz, CDCl3) δ ppm 211.71 (s, =C=), 196.19 (s, CPh), 139.29 (s, Cα,CHOH), 138.93 (s, Cα,CO), 133.21 (s, Cα,H), 131.86 (s, Cα,Cl), 106.33 (s, CCOPh), 103.76 (s, CCHOH), 73.89 (s, CHOH). The signals for Cα (128.58, 128.35, 128.05, 128.02, 127.21), and the signals for (CH3)CCHOH and (CH3)CCO (14.95, 14.89, 13.34) were not assigned due to overlapping.

13C NMR (minor diastereomer, 101 MHz, CDCl3) δ ppm 210.88 (s, =C=), 196.29 (s, CPh), 139.29 (s, Cα,CHOH), 139.07 (s, Cα,CO), 133.74 (s, Cα,H), 131.80 (s, Cα,Cl), 106.77 (s, CCOPh), 104.78 (s, CCHOH), 74.44 (s, CHOH), 14.93 (s, CH3CCO), 13.27 (s, CH2CH3).

HRMS for C16H17ClO2: calc 312.0912, found 312.0917.

5-(4-Cyanophenyl)-5-hydroxy-2,4-dimethyl-1-phenylpenta-2,3-dien-1-one (7Cb): 1H NMR (300 MHz, CDCl3) δ ppm 7.62 (d, J = 7.3 Hz, 2H, CHAr, both diastereomers), 7.52 (t, J = 6.9 Hz, 1H, CHAr, both diastereomers), 7.41-7.32 (m, 4H, CHAr, both diastereomers), 7.03 (d, J = 8.2 Hz, 1H, CHAr, both diastereomers), 6.88 (d, J = 8.1 Hz, 1H, CHAr, both diastereomers), 5.22 (s, 1H, CHOH, major diastereomer), 5.10 (s, 1H, CHOH, minor diastereomer), 3.04 (s, 1H, OH, major diastereomer), 2.74 (s, 1H, OH, minor diastereomer), 2.00 (s, 3H, (CH3)CCOPh, minor diastereomer), 1.99 (s, 3H, (CH3)CCOPh, major diastereomer), 1.64 (s, 3H, (CH3)CCHOH), minor diastereomer), 1.61 (s, 3H, (CH3)CCHOH, major diastereomer).

13C NMR (major diastereomer, 75 MHz, CDCl3) δ ppm 211.58 (s, =C=), 195.65 (s, CPh), 145.84 (s, Cα,CHOH), 138.15 (s, Cα,CO), 127.34 (s, Cα,H), 125.73 (s, Cα,H), 118.17 (s, CCOPh), 110.60 (s, CCHOH), 104.77 (s, CN), 103.49 (s, Cα,CN), 73.62 (s, CHOH), 14.14 (s, CH3CCO), 12.11 (s, CH2CH3).

The signals for Cα,H (131.44, 131.30, 131.26, 131.21) were not assigned due to overlapping signals.
$^{13}$C NMR (minor diastereomer, 75 MHz, CDCl$_3$) δ ppm 210.59 (s, =C=), 196.53 (s, COPh), 145.87 (s, $C_{Ar}$CHOH), 138.19 (s, $C_{Ar}$CO), 127.45 (s, $C_{Ar}$H), 126.56 (s, $C_{Ar}$H), 118.06 (s, CCOPh), 110.03 (s, CCHOH), 104.37 (s, CN), 102.72 (s, $C_{Ar}$CN), 72.91 (s, CH$_2$CCO), 14.08 (s, CH$_3$CCO), 12.11 (s, CH$_2$CH$_3$).

HRMS for C$_{26}$H$_7$NO$_2$: calc 303.1254, found 303.1250.

5-Hydroxy-2,4-dimethyl-5-(4-nitrophenyl)-1-phenylpenta-2,3-dien-1-one (7Cc): $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 8.03-8.01 (d, $J = 8.0$ Hz, 2H, $CH_{Ar}$, minor diastereomer), 7.93-7.91 (d, $J = 7.9$ Hz, 2H, $CH_{Ar}$, major diastereomer), 7.67-7.63 (m, 2H, $CH_{Ar}$, both diastereomers), 7.55-7.52 (m, 1H, $CH_{Ar}$, both diastereomers), 7.42-7.37 (m, 2H, $CH_{Ar}$, both diastereomers), 5.29 (s, 1H, CHOH, major diastereomer), 5.18 (s, 1H, CHOH, minor diastereomer), 2.37 (s, 1H, OH, major diastereomer), 2.17 (s, 1H, OH, minor diastereomer), 2.04 (s, 3H, (CH$_3$)CCOPh, major diastereomer), 2.03 (s, 3H, (CH$_3$)CCOPh, major diastereomer), 1.65 (s, 3H, (CH$_3$)CCHOH, minor diastereomer), 1.64 (s, 3H, (CH$_3$)CCHOH, major diastereomer).

$^{13}$C NMR (major diastereomer, 101 MHz, CDCl$_3$) δ ppm 211.80 (s, =C=), 196.70 (s, COPh), 147.77 (s, $C_{Ar}$CHOH), 138.80 (s, $C_{Ar}$CO), 131.95 (s, $C_{Ar}$H), 105.09 (s, CCOPh), 103.96 (s, CCHOH), 73.62 (s, CH$_2$CCO), 14.73 (s, CH$_3$CCO), 12.81 (s, CH$_2$CH$_3$). The signals for $C_{Ar}$H (128.44, 128.11, 128.01, 127.19, 126.39, 123.56, 123.30) were not assigned due to overlapping signals.

$^{13}$C NMR (minor diastereomer, 101 MHz, CDCl$_3$) δ ppm 210.71 (s, =C=), 196.61 (s, COPh), 147.11 (s, $C_{Ar}$CHOH), 138.84 (s, $C_{Ar}$CO), 131.91 (s, $C_{Ar}$H), 105.36 (s, CCOPh), 103.76 (s, CCHOH), 74.16 (s, CH$_2$CCO), 14.78 (s, CH$_3$CCO), 14.48 (s, CH$_2$CH$_3$).

HRMS for C$_{19}$H$_7$NO$_4$: calc 323.1152, found 323.1153.

5-Hydroxy-2,4-dimethyl-1,5-diphenylpenta-2,3-dien-1-one (7Cd): $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.68-7.63 (m, 2H, $CH_{Ar}$, both diastereomers), 7.50-7.45 (m, 1H, $CH_{Ar}$, both diastereomers), 7.37-7.32 (m, 2H, $CH_{Ar}$, both diastereomers), 7.23-7.08 (m, 3H, $CH_{Ar}$, both diastereomers), 6.90 (t, $J = 7.7$ Hz, 2H,
$\text{CH}_2$, both diastereomers), 5.10 (s, 1H, CHO), major diastereomer), 5.02 (s, 1H, CHO, minor diastereomer), 2.57 (s, 1H, OH, major diastereomer), 2.32 (s, 1H, OH, minor diastereomer), 2.00 (s, 3H, (CH$_3$)CCOPh, both diastereomers), 1.62 (s, 3H, (CH$_3$)CCHOH), minor diastereomer), 1.60 (s, 3H, (CH$_3$)CCHOH, major diastereomer).

$^{13}\text{C}$ NMR (major diastereomer, 101 MHz, CDCl$_3$) δ ppm 211.51 (s, =C=), 196.18 (s, COPh), 140.81 (s, $C_A$CHOH), 138.92 (s, $C_A$CO), 131.71 (s, $C_A$H), 128.60 (s, $C_A$H), 128.38 (s, $C_A$H), 127.98 (s, $C_A$H), 127.90 (s, $C_A$H), 125.89 (s, $C_A$H), 105.16 (s, CCOPh), 103.75 (s, CCHOH), 7.52 (s, CHO), 15.00 (s, CH$_3$CCO), 14.86 (s, CH$_2$CH$_3$).

$^{13}\text{C}$ NMR (minor diastereomer, 101 MHz, CDCl$_3$) δ ppm 210.96 (s, =C=), 196.32 (s, COPh), 140.75 (s, $C_A$CHOH), 138.08 (s, $C_A$CO), 131.63 (s, $C_A$H), 128.57 (s, $C_A$H), 128.23 (s, $C_A$H), 127.90 (s, $C_A$H), 127.57 (s, $C_A$H), 126.59 (s, $C_A$H), 105.90 (s, CCOPh), 104.93 (s, CCHOH), 75.06 (s, CHO), 14.88 (s, CH$_2$CH$_3$), 13.76 (s, CH$_3$CCO).

HRMS for C$_{18}$H$_{18}$O$_2$: calc 278.1301, found 278.1302.

**5-Hydroxy-2,4-dimethyl-5-(4-methoxyphenyl)-1-phenylpenta-2,3-dien-1-one (7Ce):** $^1\text{H}$ NMR (400 MHz, CDCl$_3$) δ ppm 7.74-7.64 (m, 2H, $\text{CH}_2$, both diastereomers), 7.54-7.46 (m, 1H, $\text{CH}_2$, both diastereomers), 7.41-7.33 (m, 2H, $\text{CH}_2$, both diastereomers), 6.90 (d, $J = 8.7$ Hz, 1H, $\text{CH}_2$, both diastereomers), 6.69 (m, 2H, $\text{CH}_2$, both diastereomers), 5.06 (s, 1H, CHO, major diastereomer), 5.00 (s, 1H, CHO, minor diastereomer), 3.77 (d, $J = 3.4$ Hz, 3H, OCH$_3$, both diastereomers), 2.03 (3H, (CH$_3$)CCOPh, both diastereomers), 1.61 (s, 3H, (CH$_3$)CCHOH, both diastereomers).

$^{13}\text{C}$ NMR (major diastereomer, 101 MHz, CDCl$_3$) δ ppm 211.18 (s, =C=), 196.03 (s, COPh), 159.07 (s, $C_A$OCH$_3$), 138.94 (s, $C_A$CO), 132.93 (s, $C_A$H), 131.65 (s, $C_A$H), 128.61 (s, $C_A$H), 113.66 (s, $C_A$H), 105.35 (s, CCOPh), 103.67 (s, CCHOH), 74.08 (s, CHO), 56.21 (s, OCH$_3$), 15.09 (s, CH$_3$CCO), 14.02 (s, CH$_2$CH$_3$). The signals for $C_A$H (127.96, 127.92, 127.88, 127.24) were not assigned due to overlapping signals.
$^{13}$C NMR (minor diastereomer, 101 MHz, CDCl$_3$) δ ppm 210.74 (s, =C=), 196.33 (s, COPh), 159.31 (s, $C_A$OCH$_3$), 139.20 (s, $C_A$CO), 132.83 (s, $C_A$H), 131.56 (s, $C_A$H), 128.57 (s, $C_A$H), 113.76 (s, $C_A$H), 106.16 (s, CCOPh), 104.98 (s, CCHOH), 74.61 (s, CHOHOH), 56.24 (s, OCH$_3$), 14.87 (s, CH$_3$CCO), 14.02 (s, CH$_2$CH$_3$).

HRMS for C$_{29}$H$_{29}$O$_3$: calc 308.1407, found 308.1408.

5-(4-Chlorophenyl)-5-hydroxy-2-methyl-1,4-diphenylpenta-2,3-dien-1-one (7Da): $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.64-6.86 (m, 14H, $CH_A$, both diastereomers), 5.64 (s, 1H, CHOHOH, major diastereomer), 5.58 (s, 1H, CHOHOH, minor diastereomer), 2.05 (s, 3H, (CH$_3$)CCO, major diastereomer), 2.05 (s, 3H, (CH$_3$)CCO, minor diastereomer).

$^{13}$C NMR (major diastereomer, 101 MHz, CDCl$_3$) δ ppm 214.30 (s, =C=), 194.73 (s, COPh), 139.97 (s, $C_A$CHO), 138.42 (s, $C_A$CO), 133.56 (s, $C_A$CCHOH), 133.01 (s, $C_A$Cl), 112.72 (s, CCOPh), 107.17 (s, CCHOH), 72.71 (s, CHOHOH), 14.80 (s, CH$_3$CCO). The signals for $C_A$H (132.24, 132.06, 128.94, 128.92, 128.69, 128.62, 128.57, 128.54, 128.35, 128.14, 128.09, 128.05, 127.66, 127.54, 127.24) were not assigned due to overlapping signals.

$^{13}$C NMR (minor diastereomer, 101 MHz, CDCl$_3$) δ ppm 214.33 (s, =C=), 194.91 (s, COPh), 139.57 (s, $C_A$CHO), 138.62 (s, $C_A$CO), 133.84 (s, $C_A$CCHOH), 132.78 (s, $C_A$Cl), 112.23 (s, CCOPh), 108.03 (s, CCHOH), 72.66 (s, CHOHOH), 14.80 (s, CH$_3$CCO).

HRMS for C$_{29}$H$_{19}$ClO$_2$: calc 374.1068, found 374.1049.

5-(4-Cyanophenyl)-5-hydroxy-2-methyl-1,4-diphenylpenta-2,3-dien-1-one (7Db): $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.62-7.08 (m, 14H, $CH_A$, both diastereomers), 5.75 (s, 1H, CHOHOH, major diastereomer), 5.71 (s, 1H, CHOHOH, minor diastereomer), 2.09 (s, 3H, (CH$_3$)CCO, major diastereomer), 2.06 (s, 3H, (CH$_3$)CCO, minor diastereomer).
$^{13}$C NMR (major diastereomer, 101 MHz, CDCl$_3$) $\delta$ ppm 214.35 (s, =C=), 194.52 (s, COPh), 146.96 (s, $C_A$CHOH), 138.29 (s, $C_A$CO), 118.71 (s, CCOPh), 72.77 (s, CHOH), 14.65 (s, CH$_3$CCO). The signals for $C_A$H (132.72, 132.30, 132.15, 132.06, 129.00, 128.91, 128.57, 128.44, 128.25, 128.23, 128.13, 127.99, 127.57, 127.39, 127.16, 126.80, 112.40, 111.57, 111.38, 111.17, 107.73, 106.85) were not assigned due to overlapping signals.

$^{13}$C NMR (minor diastereomer, 101 MHz, CDCl$_3$) $\delta$ ppm 214.43 (s, =C=), 194.64 (s, COPh), 146.47 (s, $C_A$CHOH), 138.32 (s, $C_A$CO), 118.65 (s, CCOPh), 72.44 (s, CHOH), 14.65 (s, CH$_3$CCO).

HRMS for C$_{25}$H$_{19}$NO$_2$: calc 365.1410, found 365.1354.

**Recycling Experiments Using 2**

After the initial reaction (Table 2, entry 10), the resin was collected by filtration and the beads were then washed sequentially with methanol, THF, diethyl ether, and hexane, and dried *in vacuo*. Allenone 3C (0.8 mmol), aldehyde 6a (0.4 mmol), NMP (1.0 mL), and recycled 2 (0.08 mmol) were added to a 10-mL round-bottomed flask equipped with a magnetic stirrer. The reaction mixture was stirred at 50 °C (Table 2, entries 17 and 18). After 12 hours, the reaction mixture was filtered and the filtrate was transferred to a separation funnel, and then water (30 mL) and ethyl acetate (15 mL) were added. The organic layer was separated, washed with brine (30 mL), and dried over MgSO$_4$. The solvent was evaporated under reduced pressure to give an oil that was purified by silica gel column chromatography using a mixture of ethyl acetate and hexane as the eluent mixture.