Supporting Information
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Carbon-Carbon Double Bond Isomerization and Diels-Alder Reaction of Dimethyl 5-Methylene-4-isopropylidene-2-cycloheptene-1,1-dicarboxylate with Dienophiles

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Supporting Information

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1. Synthesis of compounds 4a-d:

(1a) Compound 4a

Typical procedure A: A solution of [RhCl(COD)]2 (1 mg, 0.002 mmol), dppe (2 mg, 0.005 mmol), and AgOTf (3 mg, 0.01 mmol) in 0.5 mL of toluene was stirred at rt for a couple of minutes. Then N-ethyl maleimide (26 mg, 0.2 mmol), 2a (26 mg, 0.1 mmol), and 0.5 mL of toluene were added successively. The resulting solution was stirred under reflux for 12 h until 2a was consumed completely (monitored by TLC). Then the solvent was removed by rotary evaporation and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1) to afford 37 mg (97%) of 4a: Solid; m.p.: 132-134 °C (ethyl acetate/petroleum ether); 1H NMR (300 MHz, CDCl3) δ 5.61 (t, J = 7.5 Hz, 1 H), 3.71 (s, 3 H), 3.70 (s, 3 H), 3.49-3.39 (m, 2 H), 3.10-2.98 (m, 2 H), 2.66-2.26 (m, 6 H), 2.17-2.07 (m, 1 H), 1.67 (s, 6 H), 1.07 (t, J = 7.2 Hz, 3 H); 13C NMR (75.4 MHz, CDCl3) δ 13.1, 21.2, 22.1, 30.5, 31.2, 32.7, 33.5, 34.7, 40.3, 45.5, 52.5, 52.6, 56.2, 123.0, 131.8, 136.0, 136.6, 171.8, 172.3, 177.9, 179.4; IR (KBr) 2957, 1736, 1687 cm⁻¹; MS(EI) m/z: 389 (M⁺, 14.25), 297 (100); Anal. calcd. for C21H27NO6: C 64.77, H 6.99, N 3.60; found: C 64.46, H 6.86, N 3.32.

(1b) Compound 4a
A solution of [RhCl(COD)]$_2$ (1 mg, 0.002 mmol), dppe (3 mg, 0.007 mmol), and AgOTf (3 mg, 0.01 mmol) in 0.5 mL of toluene was stirred at rt for a couple of minutes. Then N-ethyl maleimide (25 mg, 0.2 mmol), 2a (26 mg, 0.1 mmol), and 0.5 mL of toluene were added successively. The resulting solution was stirred under 80 °C for 42 h until 2a was consumed completely (monitored by TLC). Then the solvent was removed by rotary evaporation and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1) to afford 34 mg (89%) of 4a. $^1$H NMR (300 MHz, CDCl$_3$) δ 5.62 (t, $J = 7.5$ Hz, 1 H), 3.72 (s, 3 H), 3.70 (s, 3 H), 3.50-3.40 (m, 2 H), 3.11-2.98 (m, 2 H), 2.66-2.40 (m, 5 H), 2.39-2.28 (m, 1 H), 2.17-2.07 (m, 1 H), 1.68 (s, 6 H), 1.07 (t, $J = 7.1$ Hz, 3 H).

The following compounds 4b-4d were prepared according to the typical procedure A.

(2) Compound 4b:

\[
\begin{align*}
\text{MeO}_2\text{C} & \quad \text{MeO}_2\text{C} \\
\text{Ph} & \quad \text{NPh}
\end{align*}
\]

The reaction of [RhCl(COD)]$_2$ (1 mg, 0.002 mmol), dppe (2 mg, 0.005 mmol), AgOTf (3 mg, 0.01 mmol), N-phenyl maleimide (36 mg, 0.2 mmol), and 2a (26 mg, 0.1 mmol) in 1 mL of toluene afforded 37 mg (86%) of 4b: Solid; m.p.: 130-132 °C (diethyl ether/petroleum ether); $^1$H NMR (300 MHz, CDCl$_3$) δ 7.48-7.32 (m, 3 H), 7.17 (d, $J = 7.2$ Hz, 2 H), 5.65 (t, $J = 6.9$ Hz, 1 H), 3.72 (s, 3 H), 3.71 (s, 3 H), 3.33-3.20 (m, 2 H), 2.76-2.54 (m, 4 H), 2.48-2.34 (m, 2 H), 2.22-2.12 (m, 1 H), 1.78 (s, 3 H), 1.74 (s, 3 H); $^{13}$C NMR (75.4 MHz, CDCl$_3$) δ 21.4, 22.5, 30.6, 31.5, 32.6, 35.0, 40.7, 45.6, 52.6, 52.7, 56.2, 123.3, 126.2, 128.5, 129.1, 131.8, 132.5, 136.3, 136.6, 171.8, 172.4, 177.0, 178.7; IR (KBr) 2954, 1737, 1709, 1699, 1596, 1499, 1439, 1385, 1230, 1185, 1091, 1067 cm$^{-1}$; MS(ESI) $m/z$ 460.0 (M$^+$+Na); HRMS calcd. for C$_{25}$H$_{27}$NO$_6$Na (M$^+$+Na): 460.1731; found: 460.1742.
(3) Compound 4c:

The reaction of [RhCl(COD)]_2 (1 mg, 0.002 mmol), dppe (2 mg, 0.005 mmol), AgOTf (3 mg, 0.01 mmol), N-(p-iodophenyl) maleimide (60 mg, 0.2 mmol), and 2a (26 mg, 0.1 mmol) in 1 mL of toluene afforded 48 mg (86%) of 4c: Solid; m.p.: 134-135 °C (ethyl acetate/petroleum ether); ^1H NMR (300 MHz, CDCl_3) δ 7.75 (d, J = 8.7 Hz, 2 H), 6.94 (d, J = 8.7 Hz, 2 H), 5.64 (t, J = 7.2 Hz, 1 H), 3.72 (s, 6 H), 3.31-3.18 (m, 2 H), 2.75-2.51 (m, 4 H), 2.49-2.30 (m, 2 H), 2.21-2.10 (m, 1 H), 1.75 (s, 3 H), 1.70 (s, 3 H); ^13C NMR (75.4 MHz, CDCl_3) δ 21.4, 22.5, 30.6, 31.4, 32.6, 34.9, 40.7, 45.7, 52.6, 52.7, 56.1, 93.8, 123.4, 127.8, 131.5, 132.5, 136.3, 136.4, 138.2, 171.8, 172.3, 176.6, 178.3; IR (KBr) 2953, 2852, 1732, 1710, 1488, 1436, 1382, 1275, 1218, 1188, 1129, 1090, 1061, 1031, 1009 cm^{-1}; MS(ESI) m/z 586.3 (M^++Na), 618.3 (M^++MeOH+Na); Anal. calcd. for C_{25}H_{26}INO_6: C 53.30, H 4.65, N 2.49; found: C 53.23, H 4.99, N 2.17.

(4) Compound 4d:

...
The reaction of \([\text{RhCl(COD)}]_2\) (3 mg, 0.006 mmol), dppe (4 mg, 0.01 mmol), AgOTf (5 mg, 0.02 mmol), maleic anhydride (78 mg, 0.8 mmol), and 2a (53 mg, 0.2 mmol) in 2 mL of toluene afforded 48 mg (66%) of 4d: Solid; m.p.: 144-145 °C (diethyl ether/petroleum ether); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 5.67 (t, \(J = 6.9\) Hz, 1 H), 3.74 (s, 3 H), 3.71 (s, 3 H), 3.48-3.38 (m, 1 H), 3.33 (dd, \(J = 5.1\) and 9.6 Hz, 1 H), 2.74-2.58 (m, 2 H), 2.56-2.24 (m, 4 H), 2.17-2.07 (m, 1 H), 1.76 (s, 6 H); \(^1^3\)C NMR (75.4 MHz, CDCl\(_3\)) \(\delta\) 21.3, 22.2, 30.5, 31.2, 32.3, 34.3, 41.4, 46.4, 52.6, 52.8, 55.9, 123.4, 133.1, 136.4, 136.7, 171.5, 171.9, 172.1, 174.1; IR (KBr) 2960, 2851, 1843, 1772, 1772, 1722, 1460, 1434, 1382, 1292, 1263, 1242, 1214, 1172, 1137, 1096, 1078, 1060, 1031, 1015 cm\(^{-1}\); MS(EI) \(m/z\): 362 (M\(^+\), 8.83), 270 (100); Anal. calcd. for C\(_{19}\)H\(_{22}\)O\(_7\): C 62.97, H 6.12; found: C 62.96, H 6.38.

2. Synthesis of dimethyl 5-methyl-4-(propen-2’-yl) cyclohepta-3,5-diene-1,1-dicarboxylate (5a) and dimethyl 5-methyl-4-isopropylidene cyclohepta-2,5-diene-1,1-dicarboxylate (5a ‘):

A solution of \([\text{RhCl(COD)}]_2\) (3 mg, 0.006 mmol), dppe (4 mg, 0.01 mmol), and AgOTf (5 mg, 0.02 mmol) in 1 mL of toluene was stirred at rt for a couple of minutes. Then a solution of 2a (66 mg, 0.25 mmol) and 1,4-diacetoxy-2-butyn (68 mg, 0.4 mmol) in 5 mL of toluene was added. The resulting solution was stirred under reflux for 24 h. After cooling to rt, the solvent was removed by rotary evaporation, the residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 50:1) to afford 35 mg (53%) of 5a and 26 mg (40%) of 5a’, which was contaminated with other uncharacterized byproduct (See the following spectrum for further detail).
**5a**: Liquid, $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.08 (t, $J = 7.0$ Hz, 1 H), 6.01 (td, $J = 7.0$ and 1.6, 1 H), 4.94 (s, 1 H), 4.79 (d, $J = 1.6$ Hz, 1 H), 3.70 (s, 6 H), 2.41 (d, $J = 6.8$ Hz, 2 H), 2.34 (d, $J = 7.2$ Hz, 2 H), 1.85 (s, 3 H), 1.77 (s, 3 H).

**5a’**: Liquid, $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 6.49 (d, $J = 11.9$ Hz, 1 H), 5.57 (d, $J = 11.9$ Hz, 1 H), 5.46 (t, $J = 7.5$ Hz, 1 H), 3.72 (s, 6 H), 2.75 (d, $J = 7.5$ Hz, 2 H), 1.81 (s, 3 H), 1.76 (s, 3 H), 1.71 (s, 3 H).

(2)

A solution of $[\text{RhCl(COD)}]_2$ (3 mg, 0.006 mmol), dppe (4 mg, 0.01 mmol), and AgOTf (5 mg, 0.02 mmol) in 1 mL of toluene was stirred at rt for 2 min. Then a solution of 2a (53 mg, 0.2 mmol) in 5 mL of toluene was added. The resulting solution was stirred under reflux for 17 h. After cooling to rt, the solvent was removed by rotary evaporation, the residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 50:1) to afford 33 mg (62%) of 5a and 2 mg (4%) of 5a’, which was slightly contaminated with other uncharacterized byproduct (See the following spectrum for further detail).

**5a**: Liquid, $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 6.09 (t, $J = 6.9$ Hz, 1 H), 6.01 (td, $J = 7.2$ and 1.5, 1 H), 4.94 (s, 1 H), 4.79 (s, 1 H), 3.70 (s, 6 H), 2.41 (d, $J = 6.9$ Hz, 2 H), 2.34 (d, $J = 7.2$ Hz, 2 H), 1.85 (s, 3 H), 1.77 (s, 3 H); $^{13}$C NMR (75.4 MHz, CDCl$_3$) $\delta$ 20.7, 21.0, 31.6, 31.9, 52.5, 70.1, 114.2, 124.1, 126.5, 138.6, 141.9, 146.9, 171.9; IR (neat) 2953, 1735, 1437, 1328, 1273, 1235, 1213 cm$^{-1}$; MS(EI) m/z: 264 (M$^+$, 11.47), 145 (100); HRMS calcld. for C$_{15}$H$_{20}$O$_4$ (M$^+$): 264.1362; found: 264.1365.

**5a’**: Liquid, $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 6.49 (d, $J = 12.3$ Hz, 1 H), 5.57 (d, $J = 11.7$ Hz, 1 H), 5.51-5.43 (m, 1 H), 3.73 (s, 6 H), 2.75 (d, $J = 7.2$ Hz, 2 H), 1.82 (s, 3
H), 1.76 (s, 3 H), 1.71 (s, 3 H).

3. Synthesis of dimethyl 5-methyl-4-isopropylidene-cyclohepta-2,5-diene-1,1-
dicarboxylate (5a‘):

\[
\begin{align*}
\text{MeO}_2\text{C} & \quad \text{MeO}_2\text{C} \\
\text{2a} & \quad \text{5a‘} (54\%) \\
\text{CH}_2\text{Cl}_2 & \quad \text{rt, 18 h}
\end{align*}
\]

AlCl₃ (17 mg, 0.13 mmol), 2a (26 mg, 0.1 mmol), and 1 mL of CH₂Cl₂ were added successively to Shlenck tube, the resulting mixture was stirred at rt for 18 h. Then the solvent was removed by rotary evaporation, the residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate = 40:1) to afford 14 mg (54%) of 5a‘: Liquid, ¹H NMR (300 MHz, CDCl₃) δ 6.49 (d, J = 12.0 Hz, 1 H), 5.56 (d, J = 12.0 Hz, 1 H), 5.49-5.42 (m, 1 H), 3.72 (s, 6 H), 2.74 (d, J = 7.2 Hz, 2 H), 1.80 (d, J = 0.6 Hz, 3 H), 1.76 (s, 3 H), 1.70 (s, 3 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 20.7, 22.4, 22.7, 30.6, 52.8, 57.3, 120.5, 123.5, 130.7, 130.8, 134.3, 144.5, 170.8; IR (neat) 2953, 2855, 1753, 1437, 1376, 1261, 1230, 1163 cm⁻¹; MS(EI) m/z: 264 (M⁺, 19.26), 145 (100); HRMS calcd. for C₁₅H₂₀O₄ (M⁺): 264.1362; found: 264.1366.

4. Synthesis of compound 4e:

\[
\begin{align*}
\text{MeO}_2\text{C} & \quad \text{MeO}_2\text{C} \\
\text{5a} & \quad \text{4e} (95\%) \\
\text{toluene, rt} & \quad 18 \text{ h}
\end{align*}
\]

A solution of 5a (40 mg, 0.15 mmol) and 4-phenyl-4H-1,2,4-triazole-3,5-dione (53 mg, 0.3 mmol) in 2 mL of toluene was stirred at rt for 18 h. Then the solvent was removed by rotary evaporation, the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3:1) to afford 63 mg (95%) of 4e:
Solid; m.p.: 217-218 °C (ethyl acetate/petroleum ether); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.59-7.53 (m, 2 H), 7.50-7.42 (m, 2 H), 7.39-7.32 (m, 1 H), 5.62 (t, $J$ = 6.2 Hz, 1 H), 4.67-4.59 (m, 1 H), 4.24 (d, $J$ = 16.4 Hz, 1 H), 3.98 (d, $J$ = 16.4 Hz, 1 H), 3.77 (s, 3 H), 3.69 (s, 3 H), 2.91-2.83 (m, 1 H), 2.70-2.62 (m, 1 H), 2.54-2.46 (m, 1 H), 2.02 (dd, $J$ = 10.8 and 12.2 Hz, 1 H), 1.85 (s, 3 H), 1.76 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 16.9, 22.2, 31.5, 39.2, 47.2, 49.8, 52.6, 52.9, 56.0, 123.4, 123.7, 125.1, 127.9, 129.0, 130.8, 131.1, 140.1, 150.6, 152.7, 169.9, 171.5; IR (KBr) 1770, 1740, 1720, 1600, 1506, 1495, 1454, 1423, 1291, 1236, 1179, 1136, 1087, 1010 cm$^{-1}$; MS(EI) m/z: 439 (M$^+$, 100); Anal. calcd. for C$_{23}$H$_{25}$N$_3$O$_6$: C 62.86, H 5.73, N, 9.56; found: C 62.82, H 5.78, N 9.56.

5. Synthesis of compound 7:

\[
\begin{align*}
\text{MeO}_2\text{C} & \quad \text{MeO}_2\text{C} \\
\text{N} & \quad \text{N} \\
\text{NPh} & \quad \text{NPh} \\
\text{O} & \quad \text{O} \\
6 & \quad 2 \text{ equiv} \\
\begin{array}{c}
\text{N} \\
\text{N} \\
\text{PhN} \\
\text{O} \\
\text{MeO}_2\text{C}
\end{array} \\
+ & \\
\begin{array}{c}
\text{MeO}_2\text{C} \\
\text{O} \\
\text{N} \\
\text{N} \\
\text{PhN}
\end{array} \\
\rightarrow & \\
\begin{array}{c}
\text{MeO}_2\text{C} \\
\text{MeO}_2\text{C} \\
\text{O} \\
\text{N} \\
\text{N} \\
\text{PhN} \\
\text{O}
\end{array} \\
\text{7 (23%)} \\
\begin{array}{c}
\begin{array}{c}
\text{MeO}_2\text{C} \\
\text{O} \\
\text{N} \\
\text{N} \\
\text{PhN}
\end{array} \\
+ & \\
\begin{array}{c}
\text{MeO}_2\text{C} \\
\text{O} \\
\text{N} \\
\text{N} \\
\text{PhN}
\end{array} \\
\rightarrow & \\
\begin{array}{c}
\text{MeO}_2\text{C} \\
\text{MeO}_2\text{C} \\
\text{O} \\
\text{N} \\
\text{N} \\
\text{PhN} \\
\text{O}
\end{array} \\
\text{7 (23%)}
\end{align*}
\]

A solution of [RhCl(COD)$_2$] (3 mg, 0.006 mmol), dppe (4 mg, 0.01 mmol), and AgOTf (5 mg, 0.02 mmol) in 0.5 mL of toluene was stirred at rt for a couple of minutes. Then 4-phenyl-4$H$-1,2,4-triazole-3,5-dione 6 (70 mg, 0.4 mmol), 2a (53 mg, 0.2 mmol), and 1.5 mL of toluene was added. The resulting solution was stirred at rt for 22.5 h. Then the solvent was removed by rotary evaporation, the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3:1) to afford 28 mg (23%) of 7. $^1$H NMR (300 MHz, CDCl$_3$): δ 7.54-7.32 (m, 10 H), 6.49 (d, $J$ = 7.2 Hz, 1 H), 5.75 (d, $J$ = 7.2 Hz, 1 H), 4.74 (d, $J$ = 13.4 Hz, 1 H), 4.30 (d, $J$ = 13.4 Hz, 1 H), 3.78 (s, 3 H), 3.74 (s, 3 H), 2.75-2.61 (m, 1 H), 2.54 (d, $J$ = 14.7 Hz,
1 H), 2.38 (dd, $J = 15.0$ and 3.9 Hz, 1 H), 2.04 (s, 3 H), 1.59-1.41 (m, 4 H); $^{13}$C NMR (75.4 MHz, CDCl$_3$): $\delta$ 27.0, 27.2, 27.3, 31.9, 49.9, 51.5, 53.3, 58.1, 60.3, 62.2, 120.8, 125.5, 126.0, 128.35, 128.42, 129.1, 129.2, 130.7, 131.1, 143.9, 146.9, 147.9, 152.3, 153.5, 169.0, 170.0; IR (KBr) 2955, 1764, 1731, 1699, 1600, 1504, 1416, 1315, 1266, 1237, 1192, 1151, 1075, 1048 cm$^{-1}$; MS(ESI) $m/z$: 637 (M$^+$+Na), 615 (M$^+$+H), 1251 (2M$^+$+Na); HRMS calcd. for C$_{31}$H$_{31}$N$_6$O$_8$ (M$^+$+H): 615.2198; found: 615.2206.

A solution of 2a (26 mg, 0.1 mmol) and 4-phenyl-4$H$-1,2,4-triazole-3,5-dione 6 (70 mg, 0.4 mmol) in 2 mL of toluene was stirred at rt for 22 h. Then the solvent was removed by rotary evaporation, the residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3:1) to afford 57 mg (94%) of 7: Solid; m.p.: 215-216 °C (ethyl acetate/petroleum ether); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.54-7.32 (m, 10 H), 6.49 (d, $J = 7.5$ Hz, 1 H), 5.75 (d, $J = 7.5$ Hz, 1 H), 4.74 (d, $J = 12.9$ Hz, 1 H), 4.30 (d, $J = 12.9$ Hz, 1 H), 3.77 (s, 3 H), 3.73 (s, 3 H), 2.75-2.61 (m, 1 H), 2.54 (d, $J = 15.3$ Hz, 1 H), 2.37 (dd, $J = 15.0$ and 4.5 Hz, 1 H), 2.03 (s, 3 H), 1.59-1.41 (m, 4 H); $^{13}$C NMR (75.4 MHz, CDCl$_3$): $\delta$ 27.0, 27.2, 27.3, 31.9, 49.9, 51.5, 53.3, 58.1, 60.3, 62.2, 120.8, 125.5, 126.0, 128.37, 128.44, 129.1, 129.2, 130.7, 131.1, 143.9, 146.9, 147.9, 152.3, 153.5, 169.0, 170.0.
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