**Palladium-Catalyzed Benzylation of Active Methine Compounds without Additional Base:
Remarkable Effect of 1,5-Cyclooctadiene**

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Supporting Information

General and Materials. NMR spectra were measured with Bruker AVANCE 400 (9.4 T magnet) spectrometer. IR spectra were measured with Nicolet Magna 560. Elemental analyses were performed by Service Centre of Elementary Analysis of Organic Compounds in Kyushu University. Short column chromatographies and medium-pressure liquid chromatographies (MPLC) were performed with silica gel 60 (230–400 mesh, Merck) and C. I. G. pre-packed column CPS-223L-1 (Kusano, Tokyo, Japan), respectively.

All reactions were conducted under nitrogen atmosphere. THF were distilled from sodium benzophenone ketyl. $\text{Cp}(\eta^3\text{-C}_3\text{H}_5)\text{Pd}$ was prepared according to literatures.^{1,2} DPPF was purchased from TCI.

General Procedure of Alkylation of Active Methine Compounds (2) with 1a (Table 1). A solution of **2** (1.0 mmol) and **1a** (216 mg, 1.0 mmol) in THF (0.5 ml) was added by a cannula to a solution of $\text{Cp}(\eta^3\text{-C}_3\text{H}_5)\text{Pd}$ (2.1 mg, 10 μmol) and DPPF (6.1 mg, 11 μmol) in THF (0.5 ml). The mixture was stirred at 80 °C until **1a** was consumed. The mixture was evaporated under reduced pressure, and the residue was purified by MPLC (EtOAc/hexane) after passing through a short column on silica gel (EtOAc/hexane = 1/3–3/1) to give the desired product.

General Procedure of Alkylation of 2 with 1b (Table 1). A solution of **2** (1.0 mmol) in THF (0.5 ml) was added by a cannula to a solution of $\text{Cp}(\eta^3\text{-C}_3\text{H}_5)\text{Pd}$ (2.1 mg, 10 μmol), DPPF (6.1 mg, 11 μmol), and **1b** (216 mg, 1.0 mmol) in THF (0.5 ml). The mixture was stirred at 80 °C until **1a** was consumed. The mixture was evaporated under reduced pressure, and the residue was purified by MPLC (EtOAc/hexane) after passing through a short column on silica gel (EtOAc/hexane = 1/3–3/1) to give the desired product.

Diethyl [(1-Naphthyl)methyl]phenylmalonate (3a) (Table 1, entry 1). The general procedure was followed with **2a** (259 mg, 1.09 mmol) and **1a** (216 mg, 1.00 mmol). The crude product was purified by MPLC (EtOAc/hexane = 1/3) to give **3a** (374 mg, 99%) as colorless oil: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 1.17 (t, J = 7.3 Hz, 6H), 4.10–4.26 (m, 6H), 7.10–7.42 (m, 9H), 7.61 (d, J = 8.6 Hz, 1H), 7.69 (d, J = 8.2 Hz, 1H), 7.76 (d, J = 8.1 Hz, 1H); ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 13.8, 37.8, 61.7, 63.8, 123.5, 125.0, 125.1, 125.4, 127.4, 127.72, 127.74, 128.4, 128.5, 132.5, 133.0, 133.5, 136.4, 170.4; IR (neat) 1732 cm^{-1} ; Anal. Calcd for $\text{C}_{24}\text{H}_{24}\text{O}_4$: C, 76.57; H, 6.43. Found: C, 76.38; H, 6.46.

Diethyl [(2-Naphthyl)methyl]phenylmalonate (3b) (Table 1, entry 2). The general procedure was followed with **2a** (261 mg, 1.10 mmol) and **1b** (217 mg, 1.00 mmol). The crude product was purified by MPLC (EtOAc/hexane = 1/3) to give **3b** (375 mg, >99%) as colorless oil: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 1.20 (t, J = 7.1 Hz, 6H), 3.77 (s, 2H), 4.21 (q, J = 7.1 Hz, 4H), 6.99 (dd, J = 1.5, 8.5 Hz, 1H), 7.23–7.29 (m, 5H), 7.35 (s, 1H), 7.38–7.43 (m, 2H), 7.59–7.65 (m, 2H), 7.74–7.77 (m, 1H); ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 13.9, 43.1, 61.7, 64.4, 125.5, 125.7, 127.1, 127.4, 127.6, 127.8, 128.3, 128.7, 129.3, 132.3, 133.1, 133.6, 137.0, 170.1; IR (neat) 1735 cm^{-1} ; Anal. Calcd for $\text{C}_{24}\text{H}_{24}\text{O}_4$: C, 76.57; H, 6.43. Found: C, 76.42; H, 6.46.

Diethyl Methyl[(1-naphthyl)methyl]malonate (3c) (Table 1, entry 3).³ The general procedure was followed with **2b** (192 mg, 1.10 mmol) and **1a** (214 mg, 0.99 mmol). The crude product was purified by MPLC (EtOAc/hexane = 1/2) to give **3c** (283 mg, 91%) as colorless oil: ¹H NMR (400 MHz, CDCl₃, TMS) δ 1.21 (t, *J* = 7.3 Hz, 6H), 1.33 (s, 3H), 3.77 (s, 2H), 4.13 (dq, *J* = 10.5, 7.3 Hz, 2H), 4.16 (dq, *J* = 10.5, 7.3 Hz, 2H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.42–7.50 (m, 2H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 7.5 Hz, 1H), 8.06 (d, *J* = 8.5 Hz, 1H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 13.9, 20.2, 36.1, 55.2, 61.3, 124.1, 125.1, 125.4, 125.7, 127.6, 128.2, 128.7, 132.8, 133.0, 133.8, 172.1.

Diethyl (N-Acetylamino)[(1-naphthyl)methyl]malonate (3d) (Table 1, entry 4).⁴ The general procedure was followed with **2c** (240 mg, 1.10 mmol) and **1a** (214 mg, 0.99 mmol). The crude product was purified by MPLC (EtOAc/hexane = 1/2) to give **3d** (346 mg, 98%) as colorless solid: ¹H NMR (400 MHz, CDCl₃, TMS) δ 1.31 (t, *J* = 7.1 Hz, 6H), 1.88 (s, 3H), 4.14 (s, 2H), 4.23 (dq, *J* = 7.1, 10.8 Hz, 2H), 4.28 (dq, *J* = 10.8, 7.1 Hz, 2H), 6.41 (br s, 1H), 7.17 (d, *J* = 6.8, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.43–7.48 (m, 2H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.80–7.85 (m, 1H), 7.97–8.02 (m, 1H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 13.9, 23.0, 33.9, 62.6, 67.5, 123.8, 125.0, 125.6, 125.8, 128.0, 128.1, 128.7, 131.8, 133.1, 133.8, 167.6, 169.4.

Dimethyl Methoxy[(1-naphthyl)methyl]malonate (3e) (Table 1, entry 5). The general procedure was followed with **2d** (178 mg, 1.10 mmol) and **1a** (215 mg, 1.00 mmol). The crude product was purified by MPLC (EtOAc/hexane = 1/1) to give **3e** (299 mg, 99%) as colorless oil: ¹H NMR (400 MHz, CDCl₃, TMS) δ 3.45 (s, 3H), 3.67 (s, 6H), 3.88 (s, 2H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.42–7.52 (m, 3H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 8.11 (d, *J* = 8.4 Hz, 1H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 35.0, 52.6, 54.2, 85.7, 124.1, 125.25, 125.35, 125.7, 127.7, 127.8, 128.6, 130.9, 132.7, 133.7, 168.8; IR (neat) 1740 cm⁻¹; Anal. Calcd for C₁₇H₁₈O₅: C, 67.54; H, 6.00. Found: C, 67.53; H, 6.00.

Ethyl 1-[(1-Naphthyl)methyl]-2-cyclohexanonecarboxylate (3f) (Table 1, entry 6). The general procedure was followed with **2e** (191 mg, 1.12 mmol) and **1a** (216 mg, 1.00 mmol). The crude product was purified by MPLC (EtOAc/hexane = 1/1) to give **3f** (309 mg, >99%) as colorless oil: ¹H NMR (400 MHz, CDCl₃, TMS) δ 1.01 (t, *J* = 7.2 Hz, 3H), 1.45–1.71 (m, 4H), 1.97–2.06 (m, 1H), 2.32–2.57 (m, 3H), 3.39 (d, *J* = 14.5 Hz, 1H), 3.87 (d, *J* = 14.5 Hz, 1H), 3.89 (q, *J* = 7.2 Hz, 2H), 7.30 (d, *J* = 6.9 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.40–7.48 (m, 2H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.80–7.84 (m, 1H), 7.96–8.00 (m, 1H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 13.6, 22.6, 27.6, 35.4, 36.3, 41.3, 61.3, 62.0, 124.1, 125.0, 125.3, 125.6, 127.4, 128.6, 128.7, 133.0, 133.1, 133.7, 171.1, 207.3; IR (neat) 1713 cm⁻¹; Anal. Calcd for C₂₀H₂₂O₃: C, 77.39; H, 7.14. Found: C, 77.10; H, 7.12.

Ethyl 1-[(2-Naphthyl)methyl]-2-cyclohexanonecarboxylate (3g) (Table 1, entry 7). The general procedure was followed with **2e** (186 mg, 1.09 mmol) and **1b** (216 mg, 1.00 mmol). The crude product was purified by MPLC (EtOAc/hexane = 1/1) to give **3g** (301 mg, 97%) as colorless oil: ¹H NMR (400 MHz, CDCl₃, TMS) δ 1.13 (t, *J* = 7.1 Hz, 3H), 1.46–1.78 (m, 4H), 1.96–2.05 (m, 1H), 2.38–2.53 (m, 3H), 3.07 (d, *J* = 13.7 Hz, 1H), 3.45 (d, *J* = 13.7 Hz, 1H), 4.08 (dq, *J* = 10.7, 7.1 Hz, 1H), 4.10 (dq, *J* = 10.7, 7.1 Hz, 1H), 7.27 (d, *J* = 8.3 Hz, 1H), 7.39–7.46 (m, 2H), 7.58 (s, 1H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.73–7.80 (m, 2H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 13.9, 22.5, 27.5, 36.0, 40.5, 41.3, 61.3, 62.3, 125.4, 125.8, 127.4, 127.50, 127.54, 128.6, 129.0, 132.3, 133.2, 134.2, 171.1, 207.3; IR (neat) 1713 cm⁻¹; Anal. Calcd for C₂₀H₂₂O₃: C, 77.39; H, 7.14. Found: C, 77.10; H, 7.15.

2-Acetyl-2-[(1-naphthyl)methyl]cyclohexanone (3h) (Table 1, entry 8). The general procedure was followed with **2f** (154 mg, 1.10 mmol) and **1a** (213 mg, 0.98 mmol). The crude product was purified by MPLC (EtOAc/hexane = 1/1) to give **3h** (268 mg, 97%) as colorless solid: mp 128.1 °C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 1.39–1.66 (m, 4H), 1.92–1.99 (m, 1H), 2.01 (s, 3H), 2.23–2.38 (m, 2H), 2.50–2.58 (m, 1H), 3.59 (d, *J* = 14.8 Hz, 1H), 3.70 (d, *J* = 14.8 Hz, 1H), 7.28 (d, *J* = 7.0 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.43–7.51 (m, 2H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 7.4 Hz,

1H), 7.96 (d, $J = 8.0$ Hz, 1H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 22.4, 26.9, 27.0, 34.1, 34.7, 42.0, 68.9, 124.0, 125.2, 125.5, 125.9, 127.5, 128.5, 128.8, 132.8, 133.0, 133.8, 206.7, 209.4; IR (nujol) 1688 cm^{-1} ; Anal. Calcd for $\text{C}_{19}\text{H}_{20}\text{O}_2$: C, 81.40; H, 7.19. Found: C, 81.13; H, 7.17.

4-[(1-Naphthyl)methyl]-2,4-diphenyl-4H-oxazol-5-one (3i) (Table 1, entry 9). The general procedure was followed with **2g** (261 mg, 1.10 mmol) and **1a** (210 mg, 0.97 mmol). The crude product was purified by MPLC (EtOAc/hexane = 1/3) to give **3i** (356 mg, 97%) as colorless solid: mp 103.9 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3 , TMS) δ 3.95 (d, $J = 13.9$ Hz, 1H), 4.05 (d, $J = 13.9$ Hz, 1H), 7.26–7.32 (m, 3H), 7.34–7.46 (m, 6H), 7.51–7.56 (m, 1H), 7.62–7.68 (m, 1H), 7.71 (d, $J = 8.4$ Hz, 1H), 7.88 (d, $J = 7.3$ Hz, 2H), 8.27 (d, $J = 8.6$ Hz, 1H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 43.5, 72.4, 125.0, 125.2, 125.4, 125.5, 125.9, 127.8, 128.25, 128.29, 128.37, 128.39, 128.76, 128.80, 130.7, 132.4, 132.7, 133.7, 138.3, 159.6, 178.3; IR (nujol) 1658, 1808 cm^{-1} ; Anal. Calcd for $\text{C}_{26}\text{H}_{19}\text{NO}_2$: C, 82.74; H, 5.07; N, 3.71. Found: C, 82.62; H, 5.14; N, 3.68.

4-[(1-Naphthyl)methyl]-2-phenyl-4-(2-propyl)-4H-oxazol-5-one (3h) (Table 1, entry 10). The general procedure was followed with **2h** (226 mg, 1.11 mmol) and **1a** (215 mg, 0.99 mmol). The crude product was purified by MPLC (EtOAc/hexane = 1/1) to give **3h** (340 mg, >99%) as colorless solid: mp 87.0 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3 , TMS) δ 1.09 (d, $J = 6.7$ Hz, 3H), 1.26 (d, $J = 6.7$ Hz, 3H), 2.46 (septet, $J = 6.7$ Hz, 1H), 3.53 (d, $J = 13.7$ Hz, 1H), 3.93 (d, $J = 13.7$ Hz, 1H), 7.20–7.29 (m, 3H), 7.32–7.40 (m, 3H), 7.48–7.54 (m, 3H), 7.61 (d, $J = 8.1$ Hz, 1H), 7.67 (d, $J = 8.1$ Hz, 1H), 8.22 (d, $J = 8.6$ Hz, 1H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 17.2, 17.4, 35.5, 37.5, 78.8, 125.0, 125.19, 125.27, 125.34, 125.5, 127.6, 128.0, 128.2, 128.3, 128.4, 131.3, 132.1, 132.6, 133.6, 159.5, 179.8; IR (nujol) 1656, 1816 cm^{-1} ; Anal. Calcd for $\text{C}_{23}\text{H}_{21}\text{NO}_2$: C, 80.44; H, 6.16; N, 4.08. Found: C, 80.32; H, 6.17; N, 4.04.

General Procedure of Benzylation of 2 (Table 3). A solution of 1,5-cyclooctadiene (10.9 mg, 0.10 mmol) in THF (1.0 ml) was added to a mixture of $\text{Cp}(\eta^3\text{-C}_3\text{H}_5)\text{Pd}$ (2.1 mg, 10 μmol), DPPF (6.1 mg, 11 μmol), and benzylic methyl carbonate **4** (1.0 mmol). Active methine compound **2** (1.0 mmol) was added to the solution. The solution was stirred at 80 $^{\circ}\text{C}$ until the benzylic methyl carbonate was consumed completely. The mixture was evaporated under reduced pressure, and the residue was purified by MPLC (EtOAc/hexane) after passing through a short column on silica gel (EtOAc/hexane = 1/3–3/1) to give the desired product.

Diethyl [(4-Methoxyphenyl)methyl]phenylmalonate (5a) (Table 2, entry 7).³ The general procedure was followed with **2a** (262 mg, 1.11 mmol) and **4b** (198 mg, 1.01 mmol). The crude product was purified by MPLC (EtOAc/hexane = 1/1) to give **5a** (353 mg, 98%) as colorless oil: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 1.21 (t, $J = 7.1$ Hz, 6H), 3.54 (s, 2H), 3.75 (s, 3H), 4.20 (q, $J = 7.1$ Hz, 4H), 6.68 (d, $J = 8.7$ Hz, 2H), 6.79 (d, $J = 8.7$ Hz, 2H), 7.24–7.29 (m, 5H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 13.9, 42.2, 55.1, 61.5, 64.4, 113.2, 127.3, 127.8, 128.0, 128.3, 131.4, 137.1, 158.4, 170.2.

Diethyl Benzylphenylmalonate (5b) (Table 3, entry 1).³ The general procedure was followed with **2a** (264 mg, 1.12 mmol) and **4a** (165 mg, 1.00 mmol) in the presence of 2 mol % of $\text{Cp}(\eta^3\text{-C}_3\text{H}_5)\text{Pd}$ –DPPF–5 COD catalyst (COD = 1,5-cyclooctadiene). The crude product was purified by MPLC (EtOAc/hexane = 1/3) to give **5b** (273 mg, 84%) as colorless oil: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 1.25 (t, $J = 7.4$ Hz, 6H), 1.33 (s, 3H), 3.23 (s, 2H), 4.19 (q, $J = 7.4$ Hz, 4H), 7.09–7.14 (m, 2H), 7.19–7.28 (m, 3H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 14.0, 19.7, 41.1, 54.8, 61.3, 126.9, 128.1, 130.2, 136.2, 172.0.

Diethyl [(4-Methylphenyl)methyl]phenylmalonate (5c) (Table 3, entry 2).³ The general procedure was followed with **2a** (262 mg, 1.11 mmol) and **4c** (181 mg, 1.01 mmol). The crude product was purified by MPLC (EtOAc/hexane = 1/3) to give **5c** (338 mg, 99%) as colorless oil: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 1.21 (t, $J = 7.2$ Hz, 6H), 2.27 (s, 3H), 3.56 (s, 2H), 4.20 (q, $J = 7.2$ Hz, 4H), 6.76 (d, $J = 8.0$ Hz, 2H), 6.94 (d, $J = 8.0$ Hz, 2H), 7.26 (s, 5H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 13.9, 21.0, 42.5, 61.5, 64.2, 127.3, 127.8, 128.3, 128.5, 130.3, 132.8, 136.3, 137.0, 170.2.

Diethyl [{4-(Methoxycarbonyl)phenyl}methyl]phenylmalonate (5d) (Table 3, entry 3).³ The general procedure was followed with **2a** (257 mg, 1.09 mmol) and **4d** (225 mg, 1.00 mmol). The crude product was purified by MPLC (EtOAc/hexane = 1/1) to give **5d** (384 mg, >99%) as colorless oil: ¹H NMR (400 MHz, CDCl₃, TMS) δ 1.21 (t, *J* = 7.2 Hz, 6H), 3.64 (s, 2H), 3.88 (s, 3H), 4.21 (q, *J* = 7.2 Hz, 4H), 6.95 (d, *J* = 8.6 Hz, 2H), 7.20–7.29 (m, 5H), 7.81 (d, *J* = 8.6 Hz, 2H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 13.9, 42.9, 52.0, 61.8, 64.1, 127.6, 128.0, 128.2, 128.6, 129.0, 130.5, 136.6, 141.6, 167.0, 169.9.

Diethyl [{4-(Trifluoromethyl)phenyl}methyl]phenylmalonate (5e) (Table 3, entry 4).³ The general procedure was followed with **2a** (262 mg, 1.11 mmol) and **4e** (233 mg, 1.00 mmol) in the presence of 2 mol % of Cp(η³-C₃H₅)Pd–DPPF–5 COD catalyst. The crude product was purified by MPLC (EtOAc/hexane = 1/1) to give **5e** (353 mg, 90%) as colorless oil: ¹H NMR (400 MHz, CDCl₃, TMS) δ 1.20 (t, *J* = 7.0 Hz, 6H), 3.65 (s, 2H), 4.20 (q, *J* = 7.0 Hz, 4H), 7.01 (d, *J* = 8.1 Hz, 2H), 7.22–7.31 (m, 5H), 7.39 (d, *J* = 8.1 Hz, 2H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 13.8, 42.6, 61.8, 64.1, 124.2 (q, *J* = 272 Hz), 124.6 (q, *J* = 4 Hz), 127.7, 128.0, 128.1, 129.0 (q, *J* = 33 Hz), 130.8, 136.6, 140.3, 169.9.

Diethyl [(2-Methylphenyl)methyl]phenylmalonate (5f) (Table 3, entry 5). The general procedure was followed with **2a** (262 mg, 1.11 mmol) and **4f** (181 mg, 1.00 mmol). The crude product was purified by MPLC (EtOAc/hexane = 1/3) to give **5f** (307 mg, 90%) as colorless oil: ¹H NMR (400 MHz, CDCl₃, TMS) δ 1.25 (t, *J* = 7.1 Hz, 6H), 1.61 (s, 3H), 3.64 (s, 2H), 4.26 (q, *J* = 7.1 Hz, 4H), 6.96 (d, *J* = 7.1 Hz, 1H), 6.99–7.10 (m, 5H), 7.16–7.25 (m, 3H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 13.9, 19.0, 38.7, 61.7, 64.2, 125.6, 126.7, 127.4, 127.6, 128.5, 129.6, 130.1, 134.6, 136.2, 138.3, 170.4; IR (neat) 1736 cm⁻¹; Anal. Calcd for C₂₁H₂₄O₄: C, 74.09; H, 7.11. Found: C, 73.98; H, 7.10.

Diethyl [(4-Methoxyphenyl)methyl]methylmalonate (5g) (Table 3, entry 6). The general procedure was followed with **2b** (189 mg, 1.08 mmol) and **4b** (198 mg, 1.01 mmol) in the presence of 2 mol % of Cp(η³-C₃H₅)Pd–DPPF–5 COD catalyst. The crude product was purified by MPLC (EtOAc/hexane = 1/1) to give **5g** (213 mg, 71%) as colorless oil: ¹H NMR (400 MHz, CDCl₃, TMS) δ 1.25 (t, *J* = 7.1 Hz, 6H), 1.32 (s, 3H), 3.16 (s, 2H), 3.77 (s, 3H), 4.19 (q, *J* = 7.1 Hz, 4H), 6.79 (d, *J* = 8.6 Hz, 2H), 7.03 (d, *J* = 8.6 Hz, 2H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 14.0, 19.7, 40.3, 54.9, 55.2, 61.2, 113.6, 128.2, 131.2, 158.5, 172.0; IR (neat) 1732 cm⁻¹; Anal. Calcd for C₁₆H₂₂O₅: C, 65.29; H, 7.53. Found: C, 65.26; H, 7.52.

Diethyl (N-Acetylamino)[(4-methoxyphenyl)methyl]malonate (5h) (Table 3, entry 7).³ The general procedure was followed with **2c** (239 mg, 1.10 mmol) and **4b** (198 mg, 1.01 mmol). The crude product was purified by a flash column chromatography on silica gel (EtOAc/hexane = 2/1) to give **5h** (310 mg, 92%) as colorless solid: ¹H NMR (400 MHz, CDCl₃, TMS) δ 1.30 (t, *J* = 7.4 Hz, 6H), 2.03 (s, 3H), 3.59 (s, 2H), 3.78 (s, 3H), 4.21–4.33 (m, 4H), 6.53 (br s, 1H), 6.79 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 14.0, 23.1, 37.0, 55.2, 62.6, 67.3, 113.7, 127.1, 130.8, 158.7, 167.6, 169.0.

Diethyl (N-Acetylamino)[(4-methylphenyl)methyl]malonate (5i) (Table 3, entry 8).³ The general procedure was followed with **2c** (241 mg, 1.11 mmol) and **4c** (179 mg, 0.99 mmol). The crude product was purified by a flash column chromatography on silica gel (EtOAc/hexane = 1/1) to give **5i** (272 mg, 85%) as colorless solid: ¹H NMR (400 MHz, CDCl₃, TMS) δ 1.30 (t, *J* = 7.2 Hz, 6H), 2.03 (s, 3H), 2.31 (s, 3H), 3.60 (s, 2H), 4.26 (dq, *J* = 10.5, 7.2 Hz, 2H), 4.28 (dq, *J* = 10.5, 7.2 Hz, 2H), 6.52 (br s, 1H), 6.89 (d, *J* = 7.8 Hz, 2H), 7.06 (d, *J* = 7.8 Hz, 2H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 14.0, 21.1, 23.0, 37.4, 62.6, 67.2, 129.0, 129.7, 132.0, 136.8, 167.6, 169.0.

Diethyl (N-Acetylamino)[{4-(methoxycarbonyl)phenyl}methyl]malonate (5j) (Table 3, entry 9). The general procedure was followed with **2c** (241 mg, 1.11 mmol) and **4d** (226 mg, 1.01 mmol). The crude product was purified by MPLC (EtOAc/hexane = 2/1) to give **5j** (334 mg, 90%) as colorless solid: ¹H NMR (400 MHz, CDCl₃, TMS) δ 1.30 (t, *J* = 7.1 Hz, 6H), 2.03 (s, 3H), 3.71 (s, 2H), 3.90 (s,

3H), 4.26 (dq, $J = 10.7, 7.1$ Hz, 2H), 4.28 (dq, $J = 10.7, 7.1$ Hz, 2H), 6.52 (br s, 1H), 7.08 (d, $J = 8.2$ Hz, 2H), 7.94 (d, $J = 8.2$ Hz, 2H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 14.0, 23.0, 37.8, 52.1, 62.8, 67.0, 129.2, 129.6, 129.9, 140.7, 166.8, 167.3, 169.2; IR (nujol) 1642, 1714, 1747, 3255 cm^{-1} ; Anal. Calcd for $\text{C}_{18}\text{H}_{23}\text{NO}_7$: C, 59.17; H, 6.34; N, 3.83. Found: C, 59.14; H, 6.28; N, 3.80.

Diethyl (N-Acetylamino)[(2-methylphenyl)methyl]malonate (5k) (Table 3, entry 10).³ The general procedure was followed with **2c** (238 mg, 1.10 mmol) and **4f** (182 mg, 1.01 mmol). The crude product was purified by a flash column chromatography on silica gel (EtOAc/hexane = 2/1) to **5k** (294 mg, 91%) as colorless solid: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 1.28 (t, $J = 7.1$ Hz, 6H), 2.01 (s, 3H), 2.23 (s, 3H), 3.70 (s, 2H), 4.23 (dt, $J = 10.8, 7.1$ Hz, 2H), 4.29 (dt, $J = 10.8, 7.1$ Hz, 2H), 6.57 (br s, 1H), 6.94 (d, $J = 7.6$ Hz, 1H), 7.03–7.16 (m, 3H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 13.9, 19.3, 23.1, 34.7, 62.6, 67.0, 125.6, 127.1, 130.4, 130.6, 133.5, 137.6, 167.9, 169.2.

Dimethyl Methoxy[(4-methoxyphenyl)methyl]malonate (5l) (Table 3, entry 11).³ The general procedure was followed with **2d** (196 mg, 1.00 mmol) and **4b** (178 mg, 1.09 mmol) in the presence of 2 mol % of $\text{Cp}(\eta^3\text{-C}_3\text{H}_5)\text{Pd-DPPF-5 COD}$ catalyst. The crude product was purified by a flash column chromatography on silica gel (EtOAc/hexane = 1/1) to give **5l** (253 mg, 90%) as yellow oil: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 3.30 (s, 2H), 3.46 (s, 3H), 3.75 (s, 6H), 3.77 (s, 3H), 6.80 (d, $J = 8.4$ Hz, 2H), 7.10 (d, $J = 8.4$ Hz, 2H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 38.4, 52.6, 54.0, 55.1, 85.9, 113.6, 126.5, 131.0, 158.7, 168.7.

Ethyl 1-[(4-methoxyphenyl)methyl]-2-cyclohexanonecarboxylate (5m) (Table 3, entry 12). The general procedure was followed with **2e** (185 mg, 1.09 mmol) and **4b** (198 mg, 1.01 mmol) in the presence of 2 mol % of $\text{Cp}(\eta^3\text{-C}_3\text{H}_5)\text{Pd-DPPF-5 COD}$ catalyst. The crude product was purified by a flash column chromatography on silica gel (EtOAc/hexane = 2/1) to give **5m** (217 mg, 74%) as colorless solid: mp 67.0 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3 , TMS) δ 1.19 (t, $J = 7.1$ Hz, 3H), 1.39–1.48 (m, 1H), 1.52–1.78 (m, 3H), 1.96–2.04 (m, 1H), 2.36–2.51 (m, 3H), 2.83 (d, $J = 13.9$ Hz, 1H), 3.23 (d, $J = 13.9$ Hz, 1H), 3.77 (s, 3H), 4.08 (dq, $J = 10.8, 7.1$ Hz, 1H), 4.12 (dq, $J = 10.8, 7.1$ Hz, 1H), 6.78 (d, $J = 8.6$ Hz, 2H), 7.03 (d, $J = 8.6$ Hz, 2H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 14.0, 22.5, 27.6, 35.9, 39.5, 41.3, 55.2, 61.2, 62.2, 113.4, 128.5, 131.3, 158.3, 171.1, 207.5; IR (neat) 1713 cm^{-1} ; Anal. Calcd for $\text{C}_{17}\text{H}_{22}\text{O}_4$: C, 70.32; H, 7.64. Found: C, 70.32; H, 7.59.

2-Acetyl-2-[(4-methoxyphenyl)methyl]cyclohexanone (5n) (Table 3, entry 13). The general procedure was followed with **2f** (153 mg, 1.09 mmol) and **4b** (197 mg, 1.00 mmol) in the presence of 2 mol % of $\text{Cp}(\eta^3\text{-C}_3\text{H}_5)\text{Pd-DPPF-5 COD}$ catalyst. The crude product was purified by MPLC (EtOAc/hexane = 1/2) to give **5n** (229 mg, 88%) as colorless oil: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 1.42 (ddd, $J = 4.3, 12.3, 13.7$ Hz, 1H), 1.54–1.77 (m, 3H), 1.92–2.00 (m, 1H), 2.09 (s, 3H), 2.24 (ddd, $J = 5.9, 12.6, 14.1$ Hz, 1H), 2.36 (dq, $J = 14.0, 2.9$ Hz, 1H), 2.47–2.54 (m, 1H), 3.03 (d, $J = 14.2$ Hz, 1H), 3.09 (d, $J = 14.2$ Hz, 1H), 3.77 (s, 3H), 6.78 (d, $J = 8.6$ Hz, 1H), 6.99 (d, $J = 8.6$ Hz, 1H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 22.2, 26.9, 27.0, 33.9, 39.1, 42.1, 55.2, 68.8, 113.6, 128.0, 131.2, 158.4, 205.9, 209.6; IR (neat) 1718, 1747 cm^{-1} ; Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{O}_3$: C, 73.82; H, 7.74. Found: C, 73.64; H, 7.71.

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