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Published in:
Chemsuschem

DOI:
[10.1002/cssc.201300276](https://doi.org/10.1002/cssc.201300276)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2013

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Gottumukkala, A. L., Suljagic, J., Matcha, K., de Vries, J. G., & Minnaard, A. J. (2013). Efficient Formation of Benzylic Quaternary Centers via Palladium Catalysis. *Chemsuschem*, 6(9), 1636-1639.
<https://doi.org/10.1002/cssc.201300276>

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Supporting Information

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Efficient Formation of Benzylic Quaternary Centers via Palladium Catalysis

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General Information:

Glassware and Handling:

All experiments were carried out in flame dried or oven dried (150 °C) glassware, in an atmosphere of dinitrogen, unless specified otherwise, by standard Schlenk techniques. Schlenk reaction tubes with screwcaps, and equipped with a teflon-coated magnetic stirbar were flame dried under vacuum and allowed to return to room temperature prior to being charged with reactants. A manifold permitting switching between dinitrogen atmosphere and vacuum was used to control the atmosphere in the reaction vessel.

Reaction temperature refers to the temperature of the oil bath.

Flash chromatography was performed using Merck silica gel type 9385 (230-400 mesh), using the indicated solvents, or using Grace Revelaris® automatic column machine, using silica gel column cartridges. Detection from the machine was performed using ELSD or UV.

Solvents and Reagents

All solvents used for filtration and chromatography were of commercial grade, and used without further purification. Anhydrous methanol, and acetonitrile were sourced from Sigma-Aldrich or Acros and stored under dinitrogen.

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Analysis

TLC was performed on Merck silica gel 60, 0.25 mm plates and visualization was done by UV and staining with Seebach's reagent (a mixture of phosphomolybdic acid (25 g), cerium (IV) sulfate (7.5 g), H₂O (500 mL) and H₂SO₄ (25 mL)) or Vanillin Stain (a mixture of vanillin (6 g), conc. Sulphuric acid (1.5 mL) and ethanol (95 mL)) or KMnO₄ stain.

¹H- and ¹³C-NMR were recorded on a Varian AMX400 (400, 100.59 MHz, respectively) using CDCl₃ as solvent, unless specified otherwise. Chemical shift values are reported in ppm with the solvent resonance as the internal standard (CHCl₃: δ 7.27 for ¹H, δ 77.1 for ¹³C). Data are reported as follows: chemical shifts (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants *J* (Hz), and integration.

GC-MS measurements were made using a HP 6890 Series Gas Chromatograph system equipped with a HP 5973 Mass Sensitive Detector. GC measurements were made using a Shimadzu GC 2014 gas

chromatograph system bearing a AT5 column (Grace Alltech) and FID detection. Whenever GC conversion are mentioned, it refers to the amount of the starting material consumed in the reaction, and was calculated in comparison with the initial concentration of substrate at the start of the reaction.

High Resolution Mass Spectrometry was performed using a ThermoScientific LTQ Orbitrap XL spectrometer.

General procedure for the conjugate addition of arylboronic acids to β,β -disubstituted enones

Method A: Conjugate addition to cyclic enones

To a Schlenk tube equipped with a magnetic stirring bar and a septum was added palladium trifluoroacetate (3.3 mg, 1 mol%, 0.01 mmol), and 2,2'-bipyridine (2.34 mg, 1.5 mol%, 0.015 mmol). The Schlenk tube was capped and alternated through 3 cycles of vacuum and dinitrogen. The mixture was dissolved in 2 ml of a solution of MeOH : H₂O (9 : 1) and the tube was placed in a pre-heated oil bath at 60 °C and allowed to stir for 15 min. The tube was removed from the oil bath, cooled to rt, followed by the addition of the enone (1 mmol, 1.0 equiv) via syringe or pipette and the boronic acid (2 mmol, 2 equiv), in one portion. The septum was replaced with a screw cap. Upon complete consumption of the enone (monitored by TLC / GC), the reaction mixture was allowed to cool to rt and filtered through a pad of silica. The filtrate was dried over MgSO₄, concentrated in vacuo and adsorbed onto silica before being loaded on a silica-gel column. Elution with a mixture of *n*-pentane: ether afforded the corresponding product.

Method B: Conjugate addition to acyclic (linear) enones

To a Schlenk tube equipped with a magnetic stirring bar and a septum was added palladium trifluoroacetate (8.3 mg, 5 mol%, 0.05 mmol), 2,2'-bipyridine (11 mg, 7 mol%,) and KSbF₆ (27.5 mg, 20 mol%, 0.2 equiv). The Schlenk tube was capped and alternated through 3 cycles of vacuum and dinitrogen. The mixture was dissolved in 2 ml of a solution of MeOH : H₂O (9 : 1). The tube was placed in a pre-heated oil bath at 80 °C and allowed to stir for 15 min. The tube was removed from the oil bath, cooled to rt, followed by the addition of the enone (0.5 mmol, 1.0 equiv) via syringe or pipette and the boronic acid (1 mmol, 2 equiv), in one portion. The septum was replaced with a screw cap. Upon complete consumption of the enone (monitored by TLC / GC), the reaction mixture was allowed to cool to rt and filtered through a pad of silica. The filtrate was dried over MgSO₄, concentrated in vacuo and adsorbed onto silica before being loaded on a silica-gel column. Elution with a mixture of *n*-pentane: ether afforded the corresponding product.

Characterization of synthesized compounds

3-Methyl-3-phenylcyclohexanone (3): Synthesized according to the general procedure (**Method A**) from 3-methyl-2-cyclohexen-1-one (110 μ l, 1.0 mmol) and phenylboronic acid (243 mg, 2.0 mmol), and purified by flash chromatography (*n*-pentane : Et₂O = 4:1) to afford **3** (174 mg, 92%) as a colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ 7.28 - 7.13 (m, 5H) 2.84 (d, *J* = 14.2 Hz, 1H), 2.39 (d, *J* = 14.2 Hz, 1H), 2.27 (t, *J* = 6.8 Hz, 2H), 2.21 – 2.08 (m, 1H), 1.96 – 1.74 (m, 2H), 1.69 – 1.53 (m, 1H), 1.28 (s, 3H). ¹³C-NMR (101 MHz, CDCl₃) δ 211.4, 147.4, 128.5, 126.2, 125.6, , 53.1, 42.8, 40.8, 37.9, 29.8, 22.0. HRMS (ESI+): Calculated for C₁₃H₁₇O [M+H]⁺: 189.1273, found [M+H]⁺: 189.1272. Characterization matches literature.^[1]

3-Methyl-3-(4-tolyl)cyclohexanone (3b): Synthesized according to the general procedure (**Method A**) from 3-methyl-2-cyclohexen-1-one (110 μ l, 1.0 mmol) and *p*-tolylboronic acid (272 mg, 2.0 mmol), and purified by flash chromatography (*n*-pentane : Et₂O = 4:1) to afford **3b** (190 mg, 94%) as a colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ 7.23 (d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 2.88 (d, *J* = 14.1 Hz, 1H), 2.43 (d, *J* = 14.1 Hz, 1H), 2.33 (s, 3H), 2.23 – 2.14 (m, 2H), 1.99 – 1.82 (m, 2H), 1.76 – 1.59 (m, 2H), 1.32 (s, 3H); ¹³C-NMR (101 MHz, CDCl₃) δ 211.5, 147.5, 128.6, 126.2, 125.6, 53.1, 42.9, 40.8, 38.0, 29.8, 22.0, 20.8., HRMS (ESI+): Calculated for C₁₄H₁₉O [M+H]⁺: 203.1430, found: 203.1429. Characterization matches literature.^[1]

3-Methyl-3-(3-tolyl)cyclohexanone (3c): Synthesized according to the general procedure (**Method A**) from 3-methyl-2-cyclohexen-1-one (110 μ l, 1.0 mmol) and *m*-tolylboronic acid (272 mg, 2.0 mmol), and purified by flash chromatography (*n*-pentane : Et₂O = 4:1) to afford **3c** (182 mg, 90%), as a colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ 7.22 (t, *J* = 7.7 Hz, 1H), 7.13 (d, *J* = 7.7 Hz, 2H), 7.03 (d, *J* = 7.2 Hz, 1H), 2.88 (d, *J* = 14.2 Hz, 1H), 2.43 (d, *J* = 14.2 Hz, 1H), 2.36 (s, 3H), 2.32 (t, *J* = 6.8 Hz, 2H), 2.24 – 2.12 (m, 1H), 1.98 – 1.82 (m, 2H), 1.78 – 1.62 (m, 1H), 1.32 (s, 3H). ¹³C-NMR (101 MHz, CDCl₃) δ 211.5, 147.5, 137.9, 128.4, 126.9, 126.3, 122.6, 53.1, 42.7, 40.8, 37.9, 29.7, 22.0, 21.7. HRMS (ESI+): Calculated for C₁₄H₁₉O [M+H]⁺: 203.1430, found: 203.1428. Characterization matches literature.^[1]

3-(4-Fluorophenyl)-3-methylcyclohexanone (3d): Synthesized according to the general procedure (**Method A**) from 3-methyl-2-cyclohexen-1-one (110 μ l, 1.0 mmol) and 4-fluorophenylboronic acid (280 mg, 2.0 mmol), and purified by flash chromatography (*n*-pentane : Et₂O = 4:1) to afford **3d** (145 mg, 70%) as a colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ 7.36 – 7.21 (m, 2H), 7.03 – 6.98 (m, 2H), 2.85 (d, *J* = 14.2, 1H), 2.44 (d, *J* = 14.2 Hz, 1H), 2.32 (t, *J* = 6.7 Hz, 2H) 2.23 – 2.09 (m, 1H), 1.98 – 1.81 (m, 2H), 1.69 – 1.61 (m, 1H), 1.32 (s, 3H). HRMS (ESI+): Calculated for C₁₃H₁₅FONa [M+Na]⁺: 229.1005, found: 229.0997. Characterization matches literature.^[1a]

3-(4-Methoxyphenyl)-3-methylcyclohexanone (3e): Synthesized according to the general procedure (**Method A**) from 3-methyl-2-cyclohexen-1-one (110 μ l, 1.0 mmol) and 4-methoxyphenylboronic acid (304 mg, 2.0 mmol), and purified by flash chromatography (*n*-pentane: Et₂O = 5:1) to afford **3e** (157 mg, 72%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.24 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 2.85 (d, *J* = 14.2 Hz, 1H), 2.42 (d, *J* = 14.2 Hz, 1H), 2.30 (t, *J* = 6.7 Hz, 2H), 2.21 – 2.10 (m, 1H), 1.94 – 1.82 (m, 2H), 1.71 – 1.60 (m, 1H), 1.30 (s, 3H). ¹³C-NMR (101 MHz, CDCl₃) δ 211.7, 157.7, 139.4, 126.7, 113.8, 55.2, 53.3, 42.3, 40.8, 38.1, 30.1, 22.0. HRMS (ESI⁺): calculated for C₁₄H₁₈O₂Na [M+Na]⁺: 241.1199, found: 241.1196. Characterization matches literature.^[1]

3-(3-Ethoxyphenyl)-3-methylcyclohexanone (3f): Synthesized according to the general procedure (**Method A**) from 3-methyl-2-cyclohexen-1-one (110 μ l, 1.0 mmol) and 3-ethoxyphenylboronic acid (332 mg, 2.0 mmol), and purified by flash chromatography (*n*-pentane : Et₂O = 6:1) to afford **3f** (198 mg, 85%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.21 (t, *J* = 8.1 Hz, 1H), 6.87 (d, *J* = 7.7 Hz, 2H), 7.03 (d, *J* = 8.1 Hz, 1H), 4.0 (q, *J* = 6.9 Hz, 2H), 2.85 (d, *J* = 14.2 Hz, 1H), 2.41 (d, *J* = 14.2 Hz, 1H), 2.30 (t, *J* = 10.6 Hz, 2H), 2.18 – 2.13 (m, 1H), 1.92 – 1.83 (m, 2H), 1.61 – 1.70 (m, 1H), 1.40 (t, *J* = 6.7 Hz, 3H) 1.38 (s, 3H). ¹³C-NMR (101 MHz, CDCl₃) δ 211.5, 159.1, 149.3, 129.5, 118.0, 112.8, 111.5, 63.4, 53.2, 42.9, 40.9, 38.0, 29.8. HRMS (ESI⁺): Calculated for C₁₅H₂₁O₂ [M+H]⁺: 233.1536, found: 233.1534. Characterization matches literature.^[1b]

3-(3-Chloro-4-methoxyphenyl)-3-methylcyclohexanone (3g): Synthesized according to the general procedure (**Method A**) from 3-methyl-2-cyclohexen-1-one (110 μ l, 1.0 mmol) and 3-chloro-4-methoxyphenylboronic acid (373 mg, 2.0 mmol) and purified by flash chromatography (*n*-pentane : Et₂O = 6:1) to afford **3g** (240 mg, 95%) as a colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ 7.35 (d, *J* = 2.5 Hz, 1H), 7.19 (dd, *J* = 2.5, 8.6 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 1H), 3.89 (s, 3H), 2.83 (d, *J* = 14.1 Hz, 1H), 2.43 (d, *J* = 14.1 Hz, 1H), 2.33 (t, *J* = 6.7 Hz, 2H), 2.18 – 2.12 (m, 1H), 1.96 – 1.83 (m, 2H), 1.76 – 1.62 (m, 1H), 1.31 (s, 3H). ¹³C-NMR (101 MHz, CDCl₃) δ 210.9, 153.1, 140.6, 127.6, 124.9, 122.3, 111.8, 56.1, 52.9, 42.2, 40.6, 37.8, 29.8, 21.9. HRMS (ESI⁺): Calculated for C₁₄H₁₈ClO₂⁺ [M+H]⁺: 253.0989, found: 253.0988. Characterization matches literature.^[1b]

3-(3-Chlorophenyl)-3-methylcyclohexanone (3h): Synthesized according to the general procedure (**Method A**) from 3-methyl-2-cyclohexen-1-one (110 μ l, 1.0 mmol) and 3-chlorophenylboronic acid (313 mg, 2.0 mmol), and purified by flash chromatography (*n*-pentane: Et₂O = 6:1) to afford **3h** (200 mg, 90%) as a colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ 8.61 (s, 1H), 8.59 – 8.54 (m, 1H), 8.52 – 8.48 (m, *J* = 7.4 Hz, 2H), 4.14 (d, *J* =

14.1 Hz, 1H), 3.75 (d, $J = 14.3$ Hz, 1H), 3.63 (t, $J = 6.6$ Hz, 2H), 3.52 – 3.39 (m, 1H), 3.27 – 3.18 (m, 2H), 3.07 – 2.92 (m, 1H), 2.62 (s, 3H). ^{13}C -NMR (101 MHz, CDCl_3) δ 210.7, 149.6, 129.8, 126.4, 125.9, 123.8, 52.9, 42.8, 40.7, 37.7, 29.5, 21.9, 15.3. HRMS (ESI⁺): Calculated for $\text{C}_{13}\text{H}_{16}\text{ClO}$ $[\text{M}+\text{H}]^+$: 223.0884, found: 223.0882.^[1a]

3-Methyl-3-phenylcyclopentanone (8a): Synthesized according to the general procedure (**Method A**) from 3-methyl-2-cyclopenten-1-one (107 μL , 1.0 mmol) and phenylboronic acid (243 mg, 2.0 mmol), and purified by flash chromatography (*n*-pentane: Et_2O = 6:1) to afford **8a** (165 mg, 95%) as a colorless oil. ^1H -NMR (400 MHz, CDCl_3) δ 7.36 – 7.13 (m, 5H), 2.61 (d, $J = 17.6$ Hz, 1H), 2.43 (d, $J = 17.6$ Hz, 1H), 2.39 – 2.16 (m, 2H), 2.33 – 2.26 (m, 2H), 1.34 (s, 3H). ^{13}C -NMR (101 MHz, CDCl_3) δ 218.5, 148.5, 128.5, 126.3, 125.4, 52.2, 43.8, 36.7, 35.8, 29.4. HRMS (ESI⁺): Calculated mass for $\text{C}_{12}\text{H}_{14}\text{ONa}$ $[\text{M}+\text{Na}]^+$: 197.0942, found: 197.0934. Characterization matches literature.^[1a]

3-Methyl-3-(4-tolyl)cyclopentanone (8b): Synthesized according to the general procedure (**Method A**) from 3-methyl-2-cyclopenten-1-one (107 μL , 1.0 mmol) and *p*-tolylboronic acid (272 mg, 2.0 mmol), and purified by flash chromatography (*n*-pentane : Et_2O = 6:1) to afford **8b** (180 mg, 96%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.19 (dd, apparent q, $J = 8.7$ Hz, 4H), 2.66 (d, $J = 17.8$ Hz, 1H), 2.47 (d, $J = 17.8$ Hz, 1H), 2.46 – 2.38 (m, 2H), 2.36 (s, 3H), 2.39-2.25 (m, 2H), 1.40 (s, 3H). ^{13}C -NMR (101 MHz, CDCl_3) δ 218.4, 145.4, 135.7, 129.1, 125.3, 52.3, 43.4, 36.7, 35.8, 29.3, 20.8. HRMS (ESI⁺): calculated mass $\text{C}_{13}\text{H}_{16}\text{ONa}$ $[\text{M}+\text{Na}]^+$: 211.1099, found: 211.1092.

3-Methyl-3-(4-tolyl)cyclopentanone (8c): Synthesized according to the general procedure (**Method A**) from 3-methyl-2-cyclopenten-1-one (107 μL , 1.0 mmol) and *m*-tolylboronic acid (272 mg, 2.0 mmol). The reaction mixture was purified by flash column chromatography (pentane : ether 6:1) to yield product **8c** (174 mg, 93%) as a colorless oil. ^1H -NMR (400 MHz, CDCl_3) δ 7.19 – 7.13 (m, 1H), 7.02 (d, $J = 6.5$ Hz, 2H), 6.98 (d, $J = 7.5$ Hz, 1H), 2.58 (d, $J = 17.6$ Hz, 1H), 2.38 (d, $J = 17.6$ Hz, 1H), 2.38 – 2.30 (m, 1H), 2.29 (s, 3H), 2.25 – 2.15 (m, 3H), 1.30 (s, 3H). ^{13}C -NMR (101 MHz, CDCl_3) δ 218.7, 148.4, 138.1, 128.4, 127.0, 126.2, 122.4, 52.3, 43.7, 36.7, 35.8, 29.4, 21.6. HRMS (ESI⁺): calculated mass $\text{C}_{13}\text{H}_{17}\text{O}$ $[\text{M}+\text{H}]^+$: 188.1279, found: 189.1273.

3-Methyl-3-(4-fluorophenyl)cyclopentanone (8d): Synthesized according to the general procedure (**Method A**) from 3-methyl-2-cyclopenten-1-one (107 μL , 1.0 mmol) and *p*-fluorophenylboronic acid (280 mg, 2.0 mmol). The reaction mixture was purified by flash column chromatography (*n*-pentane : ether 6:1) to yield product **8d** (170 mg, 88%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.18 (dd, $J = 7.8$ Hz, 2H), 6.95 (t, $J = 8.5$ Hz, 2H), 2.54 (d, $J = 17.6$

Hz, 1H), 2.40 (d, J = 17.6 Hz, 1H), 2.37 – 2.23 (m, 2H), 2.23 – 2.12 (m, 2H), 1.30 (s, 3H). HRMS (ESI⁺): calculated mass C₁₂H₁₄O₂ [M+H]⁺: 193.1029, found: 193.1023.

3-Methyl-3-(4-methoxyphenyl)cyclopentanone (8e): Synthesized according to the general procedure (**Method A**) from 3-methyl-2-cyclopenten-1-one (107 μ l, 1.0 mmol), and 4-methoxyphenylboronic acid (304 mg, 2.0 mmol). The reaction mixture was purified by flash column chromatography (*n*-pentane : ether 6:1) to yield product **8e** (170 mg, 88%) as a colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ 7.14 (d, J = 8.5 Hz, 2H), 6.81 (d, J = 8.5 Hz, 2H), 3.73 (s, 3H), 2.56 (d, J = 17.6 Hz, 1H), 2.37 (d, J = 17.6 Hz, 1H), 2.32 – 2.26 (m, 2H) 2.23 – 2.13 (m, 2H), 1.30 (s, 3H). ¹³C-NMR (101 MHz, CDCl₃) δ 218.8, 157.9, 140.5, 126.4, 113.8, 55.3, 52.5, 43.2, 36.8, 36.0, 29.5. HRMS (ESI⁺): calculated mass C₁₃H₁₇O₂ [M+H]⁺: 205.1229, found: 205.1222.

3-Methyl-3-(3-ethoxyphenyl)cyclopentanone (8f): Synthesized according to the general procedure (**Method A**) from 3-methyl-2-cyclopenten-1-one (107 μ l, 1.0 mmol), and 3-ethoxyphenylboronic acid (332 mg, 2.0 mmol). The reaction mixture was purified by flash chromatography (*n*-pentane : ether 6:1) to yield product **8f** (203 mg, 93%) as a colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ 7.18 (t, J = 9.8 Hz, 1H), 6.79 (d, J = 7.7 Hz, 1H), 6.76 (t, J = 2.1 Hz, 1H), 6.69 (dd, J = 8.1, 2.2 Hz, 1H), 3.97 (q, J = 7.0 Hz, 2H), 2.57 (d, J = 17.7 Hz, 1H), 2.39 (d, J = 17.7 Hz, 1H), 2.36 – 2.26 (m, 2H), 2.25-2.15 (m, 2H), 1.35 (t, J = 6.9 Hz, 3H), 1.30 (s, 3H). ¹³C-NMR (101 MHz, CDCl₃) δ 218.5, 159.0, 150.2, 129.5, 117.7, 112.8, 111.3, 63.4, 52.2, 43.8, 36.7, 35.7, 29.3, 14.8. HRMS (ESI⁺): calculated mass C₁₄H₁₉O₂ [M+H]⁺: 219.1385, found: 219.1379.

3-Methyl-3-(4-benzyloxyphenyl)cyclopentanone (8g): Synthesized according to the general procedure (**Method A**) from 3-methyl-2-cyclopenten-1-one (107 μ l, 1.0 mmol) and 4-(benzyloxy)phenylboronic acid (456 mg, 2.0 mmol), and purified by flash chromatography (*n*-pentane: Et₂O = 6:1) to afford **14g** (252 mg, 90%), as a colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ 7.41-7.33 (m, 5H), 7.22 (d, J = 8.8 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 5.07 (s, 2H), 2.64 (d, J = 18.0 Hz, 1H), 2.45 (d, J = 18.0 Hz, 1H), 2.41 – 2.33 (m, 1H), 2.32 – 2.21 (m, 2H), 2.19 (d, J = 1.0 Hz, 1H), 1.38 (s, 3H). ¹³C-NMR (101 MHz, CDCl₃) δ 218.7, 157.2, 140.8, 137.0, 128.6, 127.9, 127.4, 126.5, 114.8, 70.0, 52.5, 43.2, 36.8, 36.0, 29.5. HRMS (ESI⁺): Calculated mass C₁₉H₂₁O₂ [M+H]⁺: 281.1542, found: 281.1537.

3-Methyl-3-phenylcycloheptanone (9): Synthesized according to the general procedure (**Method A**) from 3-methyl-2-cycloheptenone-1-one (1.0 mmol, 1.0 eq) and phenylboronic acid (243 mg, 2.0 mmol, 2.0 eq) and purified by flash chromatography (*n*-pentane: Et₂O = 6:1) to afford **9** (162 mg, 80%). ¹H-NMR (400 MHz, CDCl₃) δ 7.32 (d, J = 4.3 Hz, 4H), 7.21 – 7.18 (m, 1H), 3.20 (d, J = 14.4 Hz, 1H), 2.71 (d, J = 14.4 Hz, 1H), 2.44 – 2.36 (m,

2H), 2.20 – 2.16 (m, 1H), 1.92 – 1.57 (m, 5H), 1.27 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 213.8, 147.9, 128.6, 126.0, 125.6, 55.7, 44.2, 43.5, 39.8, 31.9, 25.8, 23.9.; HRMS (ESI+): calculated mass $[\text{M}+\text{Na}]^+$ 225.1250, found: 225.1248 Characterization matches literature.^[1a, 2]

5-(*Tert*-butoxy)-4-methyl-4-phenylpentan-2-one (13): Synthesized according to the general procedure (**Method B**) from (*E*)-5-(*tert*-butoxy)-4-methylpent-3-en-2-one (0.5 mmol, 85 mg) and phenylboronic acid (1 mmol, 122 mg), and purified by flash chromatography (*n*-pentane: Et_2O = 20:1) to afford **13** (90 mg, 72%) as a colorless oil. ^1H -NMR (400 MHz, CDCl_3) δ 7.44 – 7.36 (m, 2H), 7.35 – 7.30 (m, 2H), 7.25 – 7.18 (m, 1H), 3.52 (d, J = 8.5 Hz, 1H), 3.36 (d, J = 8.5 Hz, 1H), 2.92 (d, J = 15.5 Hz, 1H), 2.87 (d, J = 15.5 Hz, 1H), 1.92 (s, 3H), 1.44 (s, 3H), 1.15 (s, 9H). ^{13}C -NMR (101 MHz, CDCl_3) δ 208.3, 146.0, 128.15, 128.14, 126.3, 126.1, 72.7, 69.6, 51.6, 41.3, 31.8, 27.4, 23.5. HRMS (ESI+): Calculated Mass for $\text{C}_{16}\text{H}_{25}\text{O}_2$ $[\text{M}+\text{H}]^+$: 249.1849, found: 249.1854.

5-(*Tert*-butoxy)-4-methyl-4-(*p*-tolyl)pentan-2-one (13b): Synthesized according to the general procedure (**Method B**) from (*E*)-5-(*tert*-butoxy)-4-methylpent-3-en-2-one (0.5 mmol, 85 mg) and *p*-tolylboronic acid (1 mmol, 136 mg), and purified by flash chromatography (*n*-pentane: Et_2O = 20:1) to afford **27b** (98 mg, 75%) as a colorless oil. ^1H -NMR (400 MHz, CDCl_3) δ 7.19– 7.12 (m, 3H), 6.96 – 6.94 (m, 1H), 3.43 (d, J = 8.5 Hz, 2H), 3.25 (d, J = 8.5 Hz, 2H), 2.28 (s, 3H), 1.84 (s, 3H), 1.35 (s, 3H), 1.07 (s, 9H). ^{13}C -NMR (101 MHz, CDCl_3) δ 208.4, 145.9, 137.4, 127.9, 127.0, 126.8, 123.2, 72.6, 69.6, 51.6, 41.2, 31.8, 27.4, 23.4, 21.7. HRMS (ESI+): Calculated Mass for $\text{C}_{13}\text{H}_{17}\text{O}$ $[\text{M}-\text{O}t\text{Bu}]^+$: 189.1279, found: 189.1274.

5-(*Tert*-butoxy)-4-(3-chloro-4-isopropoxyphenyl)-4-methylpentan-2-one (13d): Synthesized according to the general procedure (**Method B**) from (*E*)-5-(*tert*-butoxy)-4-methylpent-3-en-2-one (0.5 mmol, 85 mg) and 3-chloro-4-isopropoxyphenylboronic acid (1 mmol, 166 mg) and purified by flash chromatography (*n*-pentane: Et_2O = 20:1) to afford **27f** (133 mg, 78%) as a colorless oil. ^1H -NMR (400 MHz, CDCl_3) δ = 7.38 (s, 1H), 7.18 (d, J = 8.7 Hz, 1H), 6.87 (d, J = 8.7 Hz, 1H), 4.56 – 4.41 (m, 1H), 3.40 (d, J = 8.5 Hz, 1H), 3.31 (d, J = 8.5 Hz, 1H), 2.83 (q, J = 15.7 Hz, 2H), 1.95 (s, 3H), 1.38 (s, 3H), 1.36 (d, J = 6.1 Hz, 6H), 1.13 (s, 9H). ^{13}C -NMR (101 MHz, CDCl_3) δ 207.9, 151.7, 139.5, 128.5, 125.4, 123.7, 115.5, 72.7, 72.1, 69.5, 51.4, 40.6, 31.8, 27.4, 23.3, 22.1, 15.3. HRMS (ESI+): Calculated Mass for $\text{C}_{15}\text{H}_{20}\text{O}_2\text{Cl}$ $[\text{M}-\text{O}t\text{Bu}]^+$: 267.1152, found: 267.1145.

5-(*Tert*-butoxy)-4-(3-ethoxyphenyl)-4-methylpentan-2-one (13e): Synthesized according to the general procedure (**Method B**) from (*E*)-5-(*tert*-butoxy)-4-methylpent-3-en-2-one (0.5 mmol, 85 mg) and 3-

ethoxyphenylboronic acid (1 mmol, 166 mg) and purified by flash chromatography (*n*-pentane: Et₂O = 20:1) to afford **13e** (62 mg, 75%) as a colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ 7.23 (t, *J* = 9.3 Hz, 1H), 6.97 (d, *J* = 6.8 Hz, 1H), 6.95 (s, 1H), 6.74 (d, *J* = 7.7 Hz, 1H), 4.03 (q, *J* = 7.0 Hz, 2H), 3.49 (d, *J* = 8.6 Hz, 1H), 3.33 (d, *J* = 8.5 Hz, 1H), 2.86 (s, 2H), 1.92 (s, 3H), 1.51 – 1.31 (m, 6H), 1.14 (s, 9H). ¹³C-NMR (101 MHz, CDCl₃) δ 208.2 158.7, 147.7, 128.9, 118.6, 113.6, 111.3, 72.6, 69.6 63.3 51.6, 41.4 31.8 27.4, 23.4, 14.9. HRMS (ESI+) Calculated Mass for C₁₄H₁₉O₂ [M-O⁺tBu]⁺: 219.1385 found: 219.1379.

5-(Tert-butoxy)-4-(4-methoxy-3,5-dimethylphenyl)-4-methylpentan-2-one (13f): Synthesized according to the general procedure (**Method B**) from (*E*)-5-(*tert*-butoxy)-4-methylpent-3-en-2-one (0.5 mmol, 85 mg) and 3,5-dimethyl-4-methoxyphenylboronic acid (1 mmol, 180 mg) and purified by flash chromatography (*n*-pentane: Et₂O = 20:1) to afford **13f** (112 mg, 73%) as a colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ 6.99 (s, 2H), 3.70 (s, 3H), 3.46 (d, *J* = 8.6 Hz, 1H), 3.28 (d, *J* = 8.6 Hz, 1H), 2.83 (s, 2H), 2.27 (s, 6H), 1.92 (s, 3H), 1.38 (s, 3H), 1.14 (s, 9H). ¹³C-NMR (101 MHz, CDCl₃) δ 208.5, 155.1, 141.1, 130.0, 126.6, 72.6, 69.61, 59.6, 51.6, 40.8, 31.9, 27.4, 23.5, 16.4.

5-(Tert-butoxy)-4-(4-methoxyphenyl)-4-methylpentan-2-one (13g): Synthesized according to the general procedure (**Method B**) from (*E*)-5-(*tert*-butoxy)-4-methylpent-3-en-2-one (0.5 mmol, 85 mg) and 4-methoxyphenylboronic acid (1 mmol, 152 mg) and purified by flash chromatography (*n*-pentane: Et₂O = 20:1) to afford **13g** (101 mg, 72%) as a colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ 7.30 (d, *J* = 8.9 Hz, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 3.79 (s, 3H), 3.46 (d, *J* = 8.5 Hz, 1H), 3.30 (d, *J* = 8.5 Hz, 1H), 2.84 (q, *J* = 15.3 Hz, 2H), 1.90 (s, 3H), 1.40 (s, 3H), 1.13 (s, 9H). ¹³C-NMR (101 MHz, CDCl₃) δ 208.5, 157.7, 137.9, 127.3, 113.4, 72.6, 69.8, 55.1, 51.8, 40.7, 31.8, 27.4, 23.4. HRMS (ESI+): Calculated Mass for C₁₃H₁₇O₂ [M-O⁺tBu]⁺: 205.1229, found: 205.1222.

4-(Benzo[d][1,3]dioxol-5-yl)-5-(tert-butoxy)-4-methylpentan-2-one (13h): Synthesized according to the general procedure (**Method B**) from (*E*)-5-(*tert*-butoxy)-4-methylpent-3-en-2-one (0.5 mmol, 85 mg) and 3,4-(methylenedioxy)phenylboronic acid (1 mmol, 166 mg) and purified by flash chromatography (*n*-pentane: Et₂O = 20:1) to afford **13h** (101 mg, 70%) as a colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ 6.92 (s, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 6.74 (d, *J* = 8.2 Hz, 1H), 5.93 (s, 2H), 3.42 (d, *J* = 8.5 Hz, 1H), 3.29 (d, *J* = 8.5 Hz, 1H), 2.82 (q, *J* = 15.6 Hz, 2H), 1.93 (s, 3H), 1.38 (s, 3H), 1.13 (s, 9H). ¹³C-NMR (101 MHz, CDCl₃) δ 208.1, 147.4, 145.6, 140.0, 119.2, 107.7, 107.2, 100.8, 72.7, 69.8, 51.8, 41.1, 31.8, 27.4, 23.6. HRMS (ESI+): Calculated Mass for C₁₃H₁₅O₃ [M-O⁺tBu]⁺: 219.1021, found: 219.1014.

5-(Benzyloxy)-4-methyl-4-phenylpentan-2-one (15): Synthesized according to the general procedure (**Method B**) from (*E*) or (*Z*) 5-(benzyloxy)-4-methylpent-3-en-2-one (0.5 mmol, 102 mg) and phenylboronic acid (1 mmol, 122 mg) and purified by flash chromatography (*n*-pentane: ether = 20:1) to afford **15** (105 mg,

74%) as a colorless oil. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 7.51 – 7.15 (m, 10H), 4.53 (s, 2H), 3.69 (d, J = 8.9 Hz, 1H), 3.61 (d, J = 8.9 Hz, 1H), 2.94 (q, J = 15.5 Hz, 2H), 1.93 (s, 3H), 1.52 (s, 3H). $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ 207.7, 145.3, 138.4, 128.3, 128.2, 127.5, 127.4, 126.3, 126.1, 78.0, 73.2, 51.5, 41.7, 31.8, 23.5. HRMS (ESI⁺): calculated mass $[\text{M}+\text{Na}]^+$: 305.1512, found: 305.1511.

5-(Benzyloxy)-4-methyl-4-(*m*-tolyl)pentan-2-one (15b): Synthesized according to the general procedure (**Method B**) from (*E*)-5-(benzyloxy)-4-methylpent-3-en-2-one (0.5 mmol, 102 mg) and *m*-tolylboronic acid (1 mmol, 136 mg) and purified by flash chromatography (*n*-pentane: Et_2O = 20:1) to

afford **15b** (127 mg, 90%) as a colorless oil. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ = 7.27 – 6.92 (m, 9H), 4.42 (s, 2H), 3.57 (d, J = 8.9 Hz, 1H), 3.48 (d, J = 8.9 Hz, 1H), 2.82 (q, J = 15.4 Hz, 2H), 2.26 (s, 3H), 1.82 (s, 3H), 1.39 (s, 3H). $^{13}\text{C-NMR}$ (50 MHz, CDCl_3) δ : 208.0, 145.3, 138.5, 137.7, 128.4, 128.2, 127.6, 127.5, 127.1, 126.9, 123.2, 78.1, 73.3, 51.7, 41.7, 31.9, 23.6, 21.8. HRMS (ESI⁺): calculated mass $[\text{M}+\text{H}]^+$: 297.1849, found: 299.1851.

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