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Supporting Information

Palladium-Catalyzed Borylative-Cyclization Cascade Reaction of

1,7 - Enynes: Access to Functionalized Cyclohexanes

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1. General information

All reactions were performed under an argon atmosphere with dry solvents under anhydrous conditions unless otherwise stated. DCM, toluene, THF, MeCN and DMF were distilled from 5% w/v calcium hydride under argon; all reagents used in the reactions were obtained from commercial sources without further purification. Reactions requiring anhydrous conditions were carried out under dry atmosphere filled with argon; glassware was dried using an industrial heating gun (550 °C air temperature) for at least 5 minutes prior to use (for small scale reactions), or by placing in an oven (120°C) for at least 6 hours and allowed to cool under an argon atmosphere (for large scale reactions); liquid reagents, solutions or solvents were added via syringe through rubber septum. Column chromatography was performed using silica gel (200-300 mesh). Thin layer chromatography (TLC) was used for monitoring reactions and visualized by a UV lamp (254 nm and 365 nm), I₂ and developing the plates with p-anisaldehyde. ¹H, ¹³C NMR spectra were recorded on Bruker DRX 400 MHz NMR spectrometer with TMS as internal standard and were calibrated using residual solvent as internal reference (CDCl₃: ¹H NMR = 7.260 ppm, ¹³C NMR = 77.160 ppm, Benzene-d⁶: ¹H NMR = 7.150 ppm, ¹³C NMR = 128.00 ppm). Abbreviations: in ¹H NMR data are illustrated as follows: s = singlet, d = doublet, t = triplet, dd = doublet of doublet, ddd = doublet of doublet of doublet, ddd= doublet of doublet of doublet of doublet, dt = doublet of triplet, td =triplet of doublet, tdd = triplet of doublet of doublet, m = multiplet. Coupling constants (J) are reported in Hertz (Hz). High resolution mass spectra (HRMS) were recorded on a Bruker-FT-MS spectrometer (ESI- FTMS). Infrared (IR) spectra were recorded as thin-films on a Perkin-Elmer Spectrum One FT-IR instrument and are reported in wavenumbers (cm⁻¹).

2. General Procedure for Synthesizing Substrates

2.1 Synthesis and characterization of 1,7-enynes

Diethyl 2-(but-3-en-1-yl)-2-(prop-2-yn-1-yl)malonate(1a),¹ Dimethyl 2-(but-3-en-1-yl)-2-(prop-2-yn-1-yl)malonate(1o),² Diethyl 2-allyl-2-(but-3-yn-1-yl)malonate(1p),³ Diethyl 2-(but-2-yn-1-yl)-2-(but-3-en-1-yl)malonate(1i),⁴ N-(but-3-en-1-yl)-4-methyl-N-(prop-2-yn-1yl)benzenesulfonamide(1t)³, 2-(prop-2-yn-1-yl)malononitrile (1uu)⁶ were prepared according to a previously described procedure.

Diethyl 2-(4-phenylbut-3-yn-1-yl) malonate(1qq)⁵ was prepared according to a previously described procedure.

2.2 General Method for the Sonogashira Reaction



To a flask with a stir bar was charged with Argon (three times), Pd (PPh₃)₄ (23.1 mg, 0.02 mmol, 0.1 equiv.) and CuI (6.2 mg, 10 mol%) in sequence. Then ArI (0.2 mmol, 1.0 equiv.) in degassed Et₃N (6 mL) was added. After vigorously stirred, and then enynes (300 mg, 1.19 mmol, 1 equiv.) was added. The flask was then immersed sideways into an oil bath at 60 °C overnight. After the enynes were consumed completely (monitored by TLC). Then, the reaction was diluted by 20 mL DCM. The solution was washed by 1N HCl (3×50 mL) and dried over anhydrous Na₂SO₄. The solvent was removed under vacuum and the product was purified by column chromatography to give the target products.

2.3 General Method for the Synthesis of Alcohol and Protected Alcohol Compounds.



To a flask with a stir bar was charged with Argon (three times), $Zn(OTf)_2$ (2.7 g, 7.55 mmol, 1.9 equiv.), and 20 mL toluene in sequence. Then TMEDA (923 mg, 7.95 mmol, 2.0 equiv.) was added followed by Et₃N (804 mg, 7.95 mmol, 2 equiv.), After vigorously stirred 2h, and enynes (150 mg, 0.53 mmol, 1.0 equiv.) in 5mL toluene was added. The resulting mixture was then stirred for 20 min before the paraformaldehyde was added in one potion. The flask was then immersed sideways into an oil bath at 60 °C for 4 h. After the enynes were consumed completely (monitored by TLC), the reaction was quenched by addition of saturated Na2HCO3 solution (10 mL) and diluted with EtOAc (20 mL). The solution was extracted with ethyl acetate (3 × 20 mL), and dried over anhydrous Na₂SO₄. The solvent was removed under vacuum and the product was purified by column chromatography (petroleum ether: EtOAc = 3:1) to give the propargylic alcohol **1j** (1.15 g, 5.4 mmol, 71%) as a colorless oil.



To a tube with a stir bar was charged with Argon (three times), enyne (150 mg, 0.53 mmol, 1 equiv.) and 2.5 mL DCM in sequence. Then Et_3N (0.64 mmol, 0.3 mL, 4.0 equiv.) was added. After cooled to 0°C, Ac₂O (0.64 mmol, 0.06 mL, 1.2 equiv.) was added. The resulting mixture was warmed to room temperature and stirred for 40 min. After the enyne were consumed completely (monitored by TLC), the crude mixture was directly purified by flash column chromatography (petroleum ether: EtOAc = 8:1) on silica gel to give **1k** (126 mg, 0.39 mmol, 73%) as a colorless



To a tube with a stir bar was charged with Argon (three times), enyne (150 mg, 0.53mmol, 1 equiv.) and 2.5 mL DCM in sequence. Then Et_3N (0.3 mL, 2.1 mmol, 4.0 equiv.). After cooled to 0 °C, PivCl (77.2 mg, 0.64 mmol, 1.2 equiv.) was added. The resulting mixture was warmed to room temperature and stirred for 40 min. After the enynes were consumed completely (monitored by TLC). The crude mixture was directly purified by flash column chromatography (petroleum ether: EtOAc = 10:1) on silica gel to give **11** (153 mg, 0.42 mmol, 79%) as a colorless oil.



To a tube with a stir bar was added DMAP (13 mg, 0.11 mmol, 0.2 equiv.) and imidazole (88.5 mg, 1.3 mmol, 2.5 equiv.). Then the mixture was recharged with Argon (three times) and enyne (150 mg, 0.53 mmol, 1 equiv.) in 2.5 mL DCM. After that TBSCl (0.17 mL, 1.3 mmol, 1.5 equiv.) was added dropwise. The resulting mixture was then stirred for 1h. After the enyne was consumed completely (monitored by TLC), the reaction was quenched by addition of saturated NaHCO₃ solution (2 mL) under 0 °C. The solution was extracted with ethyl acetate (3 × 10 mL), and dried over anhydrous Na₂SO₄. The solvent was removed under vacuum and the product was purified by column chromatography (petroleum ether: EtOAc = 10:1) to give **1m** (200 mg, 0.46 mmol, 86%) as a colorless oil.



To a tube with a stir bar was charged with Argon (three times), NaH (60% in mineral oil, 32 mg, 0.8 mmol, 1.5 equiv.), imidazole (3.6 mg, 0.8 mmol, 1.5 equiv.) and THF (1 mL) in sequence. Then the mixture was cooled to 0°C, and enyne (150 mg, 0.53 mmol, 1 equiv.) in 1 mL THF was added dropwise. After stirred for 30 min, TBAI (20 mg, 0.053 mmol, 0.1 equiv.) was added in one portion, and BnBr (0.1 mL, 0.8 mmol, 1.5 equiv.) in 0.5 mL THF was added dropwise. The mixture was warmed to room temperature and stirred for another 1h. After the starting material was consumed completely (monitored by TLC), the reaction was quenched by addition of saturated NH₄Cl solution (10 mL) under 0 °C. The solution was extracted with ethyl acetate (3 × 20 mL) and dried over anhydrous Na₂SO₄. The solvent was removed under vacuum and the crude product was purified by column chromatography (petroleum ether: EtOAc = 5:1) to give **1n** (122 mg, 0.32 mmol, 62%) as a colorless oil.

2.4 General procedure for the synthesis of 1,7 enynes via alkylation.



To a flask with a stir bar was charged with Argon (three times), NaH (60% in mineral oil, 0.64 mmol, 1.2 equiv.) and 2 mL THF in sequence. Then the mixture was cold to 0°C and diethyl 2-(but-3-ynyl) malonate (0.53 mmol, 1 equiv.) in 1 mL THF was added dropwise. After stirred for 30 min, bromide compound (0.64 mmol, 1.2 equiv.) was added dropwise. The mixture was warmed to room temperature and stirred for another 1h. After the starting material was consumed completely (monitored by TLC), the reaction was quenched by addition of saturated NH₄Cl solution (10 mL) under 0 °C. The solution was extracted with ethyl acetate (3×20 mL) and dried over anhydrous Na₂SO₄. The solvent was removed under vacuum and the crude product was purified by column chromatography to give the target product.

Characterization of compounds

Diethyl 2-(but-3-en-1-yl)-2-(3-phenylprop-2-yn-1-yl) malonate (1b)

Following the general procedure of the Sonogashira reaction for the synthesis of 1,7-enynes, **1b** was obtained after overnight at 50 °C in 96% yield as a colourless oil (petroleum ether: EtOAc = 20:1).

¹**H NMR (400 MHz, Chloroform-***d***):** δ 7.36 – 7.31 (m, 3H), 7.26 – 7.22 (m, 2H), 5.80 (m, 1H), 5.13 – 4.89 (m, 2H), 4.20 (m, 4H), 3.04 (s, 2H), 2.25 – 2.13 (m, 2H), 2.02 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 170.3, 137.5, 131.7, 128.2, 128.0, 123.3, 115.2, 84.4, 83.4, 77.2, 76.8, 76.5, 61.6, 56.9, 31.3, 28.4, 23.7, 14.1.

IR (neat): v 2980, 2352, 1731, 1642, 1367, 1273, 1187, 1030, 756, 692 cm⁻¹ HRMS (ESI-FTMS): m/z calcd for $C_{20}H_{23}O_4^+$ [M+H]⁺ 381.2448 found 381.2440

Diethyl 2-(but-3-en-1-yl)-2-(3-(4-(methoxycarbonyl) phenyl) prop-2-yn-1-yl) malonate (1c)



Following the general procedure of the Sonogashira reaction for the synthesis of 1,7-enynes, **1b** was obtained after overnight at 50 °C in 81% yield as a colourless oil (petroleum ether: EtOAc = 10:1).

¹**H NMR (400 MHz, Chloroform-***d***):** δ 7.99 – 7.91 (d, 2H), 7.45 – 7.38 (d, 2H), 5.82 (m, 1H), 5.07 (m, 1H), 5.03 – 4.95 (m, 1H), 4.23 m, 4H), 3.91 (s, 3H), 3.08 (s, 2H), 2.25 – 2.17 (m, 2H), 2.08 – 1.98 (m, 2H), 1.31 – 1.23 (m, 6H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 170.2, 166.6, 137.4, 131.6, 129.4, 129.3, 128.0, 115.3, 87.8, 82.8, 77.2, 76.8, 76.5, 61.7, 56.9, 52.2, 31.4, 28.4, 23.8, 14.1.

IR (neat): *v* 2981, 2349, 1726, 1437, 1274, 1189, 1109, 1020, 766, 750, 696 cm⁻¹ **HRMS (ESI-FTMS):** m/z calcd for C₂₂H₂₇O₆⁺ [M+H]⁺ 387.1808 found 387.1800

Diethyl 2-(but-3-en-1-yl)-2-(3-(naphthalen-2-yl) prop-2-yn-1-yl) malonate (1d)



Following the general procedure of the Sonogashira reaction for the synthesis of 1,7-enynes, **1d** was obtained after overnight at 50 °C in 77% yield as a colourless oil (petroleum ether: EtOAc = 20:1).

¹**H NMR (400 MHz, Chloroform-***d***):** δ 7.90 – 7.85 (m, 1H), 7.83 – 7.70 (m, 3H), 7.52 – 7.42 (m, 2H), 7.41 (dd, *J* = 8.4, 1.6 Hz, 1H), 5.85 (ddt, *J* = 16.7, 10.2, 6.4 Hz, 1H), 5.09 (dq, *J* = 17.1, 1.6 Hz, 1H), 5.00 (dq, *J* = 10.1, 1.3 Hz, 1H), 4.24 (m, 4H), 3.11 (s, 2H), 2.30 – 2.22 (m, 2H), 2.07 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 170.4, 137.5, 133.0, 132.7, 131.3, 128.6, 127.9, 127.7, 127.7, 126.5, 126.5, 120.6, 115.3, 84.7, 83.8, 77.2, 76.8, 76.5, 61.7, 57.0, 31.4, 28.5, 23.9, 14.1.
IR (neat): *v* 2980, 2349, 1730, 1447, 1270, 1187, 914, 859, 818, 749, 475 cm⁻¹
HRMS (ESI-FTMS): m/z calcd for C₂₄H₂₇O₄⁺ [M+H]⁺ 379.1909 found 379.1910

Diethyl 2-(but-3-en-1-yl)-2-(3-(4-cyanophenyl) prop-2-yn-1-yl) malonate (1e)



Following the general procedure of the Sonogashira reaction for the synthesis of 1,7-enynes, **1e** was obtained after overnight at 50 °C in 94% yield as a colourless oil (petroleum ether: EtOAc = 10:1).

¹**H NMR (400 MHz, Chloroform-***d***):** δ 7.61 – 7.53 (m, 2H), 7.47 – 7.40 (m, 2H), 5.81 (ddt, *J* = 16.7, 10.2, 6.4 Hz, 1H), 5.12 – 4.96 (m, 2H), 4.23 (m, 4H), 3.08 (s, 2H), 2.24 – 2.15 (m, 2H), 2.08 – 1.97 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 170.1, 137.3, 132.2, 132.0, 128.2, 118.5, 115.4, 111.4, 89.5, 82.1, 77.2, 76.8, 76.5, 61.7, 56.8, 31.4, 28.4, 23.8, 14.1.

IR (neat): *v* 2981, 2349, 2227, 1728, 1641, 1604, 1272, 1187, 1095, 1026, 915, 841, 750, 556 cm⁻¹ **HRMS (ESI-FTMS):** m/z calcd for C₂₁H₂₃NO₄⁺ [M+H]⁺ 376.1525 found 376.1530

Diethyl 2-(but-3-en-1-yl)-2-(3-(4-chlorophenyl) prop-2-yn-1-yl) malonate (1f)



Following the general procedure of the Sonogashira reaction for the synthesis of 1,7-enynes, **1f** was obtained after overnight at 50 °C in 95% yield as a colourless oil (petroleum ether: EtOAc = 20:1).

¹**H NMR (400 MHz, Chloroform-***d***):** δ 7.32 – 7.20 (m, 5H), 5.82 (ddt, *J* = 16.7, 10.1, 6.4 Hz, 1H), 5.07 (dq, *J* = 17.2, 1.6 Hz, 1H), 4.99 (dq, *J* = 10.2, 1.4 Hz, 1H), 4.22 (m, 4H), 3.04 (s, 2H), 2.24 – 2.15 (m, 2H), 2.08 – 1.94 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 6H), 1.23 (s, 1H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 170.3, 137.6, 137.4, 134.0, 132.9, 128.6, 121.7, 115.3, 115.1, 85.5, 82.4, 77.2, 76.8, 76.5, 61.6, 61.2, 56.9, 31.5, 31.3, 28.4, 23.7, 14.1.

IR (neat): *v* 2980, 2349, 1729, 1489, 1447, 1271, 1185, 1089, 1015, 914, 828, 751, 525 cm⁻¹ **HRMS (ESI-FTMS):** m/z calcd for C₂₀H₂₄ClO₄⁺ [M+H]⁺ 363.1363 found 363.1362

Diethyl 2-(but-3-en-1-yl)-2-(3-(4-fluorophenyl) prop-2-yn-1-yl) malonate (1g)



Following the general procedure of the Sonogashira reaction for the synthesis of 1,7-enynes, **1g** was obtained after overnight at 50 °C in 88% yield as a colourless oil (petroleum ether: EtOAc = 20:1).

¹**H NMR (400 MHz, Chloroform-***d***):** δ 7.38 – 7.28 (m, 2H), 7.02 – 6.91 (m, 2H), 5.82 (ddt, *J* = 16.8, 10.3, 6.4 Hz, 1H), 5.12 – 4.95 (m, 2H), 4.22 (m, 4H), 3.04 (s, 2H), 2.24 – 2.16 (m, 2H), 2.08 – 1.97 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 170.3, 137.5, 133.5, 133.5, 115.6, 115.4, 115.3, 84.1, 82.4, 77.2, 76.8, 76.5, 61.6, 56.9, 31.3, 28.4, 23.7, 14.1.

IR (neat): *v* 2981, 2352, 1732, 1507, 1247, 1187, 1156, 837, 750, 531 cm⁻¹ **HRMS (ESI-FTMS):** m/z calcd for C₂₀H₂₄FO₄⁺ [M+H]⁺ 347.1659 found 347.1652

Diethyl 2-(3-(4-bromophenyl) prop-2-yn-1-yl)-2-(but-3-en-1-yl) malonate (1h)



Following the general procedure of the Sonogashira reaction for the synthesis of 1,7-enynes, **1h** was obtained after overnight at 50 °C in 84% yield as a colourless oil (petroleum ether: EtOAc = 20:1).

¹H NMR (400 MHz, Chloroform-*d*): δ 7.44 – 7.37 (m, 2H), 7.25 – 7.18 (m, 2H), 5.82 (ddt, J = 16.7, 10.2, 6.4 Hz, 1H), 5.07 (dq, J = 17.1, 1.6 Hz, 1H), 4.99 (dq, J = 10.3, 1.4 Hz, 1H), 4.22 (m, 4H), 3.03 (s, 2H), 2.23 – 2.15 (m, 2H), 2.07 – 1.97 (m, 2H), 1.26 (t, J = 7.1 Hz, 5H), 1.25 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*): δ 170.4, 137.5, 133.2, 131.6, 122.0, 115.4, 85.8, 77.2, 76.8, 76.5, 61.8, 57.0, 31.5, 28.5, 23.9, 14.2.

IR (neat): v 2981, 2349, 1733, 1485, 1274, 1188, 1072, 1012, 825, 750, 522 cm⁻¹ **HRMS (ESI-FTMS):** m/z calcd for C₂₀H₂₄BrO₄⁺ [M+H]⁺ 407.0858 found 407.0856

Diethyl 2-(but-3-en-1-yl)-2-(4-hydroxybut-2-yn-1-yl) malonate (1j)

¹H NMR (400 MHz, Chloroform-*d*): δ 5.73 (m, 1H), 5.04 – 4.87 (m, 2H), 4.19 – 4.08 (m, 6H), 2.79 (q, J = 2.2 Hz, 2H), 2.12 – 2.01 (m, 2H), 1.95 – 1.84 (m, 2H), 1.19 (t, J = 7.2, 1.6 Hz, 6H).
¹³C NMR (101 MHz, Chloroform-*d*): δ 170.4, 137.3, 115.2, 81.6, 80.1, 80.1, 77.2, 76.8, 76.5, 61.6, 56.6, 50.9, 50.8, 31.1, 28.2, 23.1, 22.7, 14.0.

IR (neat): *v* 3468, 2981 2349, 1726, 1447, 1368, 1273, 1190, 1018, 915, 860, 750 cm⁻¹ **HRMS (ESI-FTMS):** m/z calcd for C₁₅H₂₂NaO₅⁺ [M+Na]⁺ 305.1365 found 305.1361

Diethyl 2-(4-acetoxybut-2-yn-1-yl)-2-(but-3-en-1-yl) malonate (1k)



¹H NMR (400 MHz, Chloroform-*d*): δ 5.80 (ddt, *J* = 16.7, 10.3, 6.4 Hz, 1H), 5.06 (dt, *J* = 17.0, 1.8 Hz, 1H), 4.98 (dt, *J* = 10.2, 1.5 Hz, 1H), 4.62 (t, *J* = 2.2 Hz, 2H), 4.20 (m, 4H), 2.88 (t, *J* = 2.3 Hz, 2H), 2.17 - 2.09 (m, 2H), 2.08 (s, 3H), 2.02 - 1.92 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 6H).
¹³C NMR (101 MHz, Chloroform-*d*): δ 170.3, 170.1, 137.4, 115.3, 81.9, 77.2, 76.8, 76.5, 61.6, 56.6, 52.5, 31.2, 28.3, 23.1, 20.8, 14.1.

IR (neat): v 2982, 2349, 1733, 1447, 1368, 1273, 1220, 1026, 916, 861, 750 cm⁻¹ **HRMS (ESI-FTMS):** m/z calcd for C₁₇H₂₅O₆⁺ [M+H]⁺ 325.1651 found 325.1650

Diethyl 2-(but-3-en-1-yl)-2-(4-(pivaloyloxy) but-2-yn-1-yl) malonate (11)



¹**H NMR (400 MHz, Chloroform-***d***):** δ 5.80 (ddt, *J* = 16.7, 10.1, 6.4 Hz, 1H), 5.10 – 4.94 (m, 2H), 4.61 (t, *J* = 2.2 Hz, 2H), 4.20 (m, 4H), 2.87 (t, *J* = 2.2 Hz, 2H), 2.17 – 2.08 (m, 2H), 2.02 – 1.92 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 6H), 1.20 (s, 9H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 177.7, 170.1, 137.4, 115.2, 81.4, 77.2, 76.8, 76.5, 61.6, 56.6, 52.4, 38.7, 31.2, 29.1, 28.3, 27.7, 27.1, 23.1, 22.6, 14.3, 14.1.

IR (neat): *v* 2978, 2349, 1732, 1449, 1367, 1275, 1188, 1137, 914, 859, 750 cm⁻¹ **HRMS (ESI-FTMS):** m/z calcd for C₂₀H₃₁O₆⁺ [M+H]⁺ 367.2121 found 367.2128 Diethyl 2-(but-3-en-1-yl)-2-(4-((triisopropylsilyl) oxy) but-2-yn-1-yl) malonate (1m)



¹**H NMR (400 MHz, Chloroform-***d***):** δ 5.72 (ddt, *J* = 16.7, 10.0, 6.4 Hz, 1H), 5.02 – 4.86 (m, 2H), 4.26 (t, *J* = 2.1 Hz, 2H), 4.12 (m, 4H), 2.80 (t, *J* = 2.1 Hz, 2H), 2.11 – 2.02 (m, 2H), 1.94 – 1.84 (m, 2H), 1.17 (t, *J* = 7.1 Hz, 6H), 1.10 – 0.95 (m, 21H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 170.1, 137.2, 114.9, 81.6, 79.0, 77.2, 76.8, 76.5, 61.3, 56.4, 51.8, 30.9, 28.1, 22.9, 17.7, 17.5, 13.9, 12.1, 11.8, -0.2.

IR (neat): *v* 2941, 2866, 2349, 1734, 1464, 1368, 1271, 1187, 1088, 314, 882, 750, 683, 658 cm⁻¹ **HRMS (ESI-FTMS):** m/z calcd for C₂₄H₄₃O₅Si⁺ [M+H]⁺ 439.2880 found 439.2880

Diethyl 2-(4-(benzyloxy) but-2-yn-1-yl)-2-(but-3-en-1-yl) malonate (1n)



¹**H NMR (400 MHz, Chloroform-***d***):** δ 7.38 – 7.25 (m, 5H), 5.80 (ddt, *J* = 16.7, 10.0, 6.4 Hz, 1H), 5.11 – 4.94 (m, 2H), 4.56 (s, 2H), 4.21 (m, 4H), 4.13 (t, *J* = 2.1 Hz, 2H), 2.91 (t, *J* = 2.1 Hz, 2H), 2.22 – 2.13 (m, 2H), 2.05 – 1.94 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 177.7, 170.1, 137.4, 115.2, 81.4, 77.2, 76.8, 76.5, 61.6, 56.6, 52.4, 38.7, 31.2, 28.3, 27.1, 23.1, 14.1.

IR (neat): v 2982, 2350, 1732, 1451, 1274, 1205, 1072, 915, 750, 699 cm⁻¹

HRMS (ESI-FTMS): m/z calcd for $C_{22}H_{29}O_5^+$ [M+H]⁺ 373.2015 found 373.2012

Diethyl 2-allyl-2-(4-phenylbut-3-yn-1-yl) malonate (1q)

Following the general procedure of alkylation for synthesis of 1,7-enynes, 1q was obtained after 3h at room temperature in 64% yield as a colourless oil (petroleum ether: EtOAc = 20:1).

¹**H NMR (400 MHz, Chloroform-***d***):** δ 7.38 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.33 – 7.23 (m, 3H), 5.69 (ddt, *J* = 17.3, 10.0, 7.3 Hz, 1H), 5.26 – 5.11 (m, 1H), 5.12 (m, 1H), 4.19 (m, 4H), 2.72 (d, *J* = 7.4 Hz, 2H), 2.41 (dd, *J* = 9.2, 6.7 Hz, 2H), 2.24 (dd, *J* = 7.8, 5.7, Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 6H). ¹³**C NMR (101 MHz, Chloroform-***d***):** δ 170.8, 132.2, 131.7, 131.5, 128.2, 127.7, 123.7, 119.8, 119.4, 88.9, 81.0, 77.2, 76.8, 76.5, 61.7, 61.4, 57.1, 56.9, 37.1, 36.6, 31.5, 23.5, 14.8, 14.1. **IR (neat):** *v* 2981, 2349, 1727, 1490, 1443, 1274, 1207, 1185, 1081, 1022, 922, 859, 756, 692, 529 cm⁻¹

HRMS (ESI-FTMS): m/z calcd for C₂₂H₂₅O₄⁺ [M+H]⁺ 329.1753 found 329.1755

Diethyl 2-(3-methylbut-3-en-1-yl)-2-(prop-2-yn-1-yl) malonate (1r)



Following the general procedure of alkylation for synthesis of 1,7-enynes, 1r was obtained after overnight at 50 °C in 61% yield as a colourless oil (petroleum ether: EtOAc = 20:1).

¹**H NMR (400 MHz, Chloroform-***d***):** δ 4.75 – 4.70 (s, 2H), 4.21 (q, *J* = 7.1 Hz, 4H), 2.84 (d, *J* = 2.7 Hz, 2H), 2.24 – 2.15 (m, 2H), 2.00 (t, *J* = 2.7 Hz, 1H), 1.94 – 1.85 (m, 2H), 1.74 (d, *J* = 1.4 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 170.0, 144.5, 110.3, 78.6, 77.2, 76.8, 76.5, 71.2, 61.4, 56.3, 31.9, 29.9, 22.5, 22.2, 13.9.

IR (neat): *v* 3286, 2982, 2341, 1733, 1449, 1368, 1275, 1235, 1184, 1093, 1029, 891, 750 cm⁻¹ **HRMS (ESI-FTMS):** m/z calcd for C₁₅H₂₂O₄⁺ [M+H]⁺ 267.1596 found 267.1595

Diethyl 2-(pent-3-en-1-yl)-2-(prop-2-yn-1-yl) malonate (1s)



Following the general procedure of alkylation for synthesis of 1,7-enynes, **1s** was obtained after 3h at room temperature in 74% yield as a colourless oil (petroleum ether: EtOAc = 20:1). This compound was isolated as E:Z isomers mixture (3.5:1). The ratio of E:Z isomers was determined with by integration of the¹H-NMR Allylic methylene signal: a doublet at 2.56 ppm for **(E)-1s** and a doublet at 2.67 ppm for **(Z)-1s**.

¹**H NMR (400 MHz, Chloroform-***d***):** δ 5.65 – 5.46 (m, 1H), 5.30 – 5.18 (m, 1H), 4.26 – 4.09 (m, 4H), 2.70 – 2.63 (d, *J* = 7.3 Hz, 2H-Z), 2.57 (d, *J* = 7.3 Hz, 2H-E), 2.22 – 2.07 (m, 4H), 1.95 (dt, *J* = 2.7, 1.3 Hz, 1H), 1.67 – 1.57 (m, 4H), 1.24 (t, *J* = 7.1 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 170.8, 170.7, 129.9, 127.9, 124.1, 123.1, 83.2, 77.2, 76.8, 76.5, 68.4, 68.4, 61.2, 61.1, 56.8, 56.6, 41.1, 35.7, 31.1, 31.1, 29.8, 22.4, 17.9, 13.9, 13.8, 13.7, 13.6, 12.8.

IR (neat): *v* 3291, 2982, 2349, 1729, 1447, 1368, 1273, 1185, 1025, 750 cm⁻¹ **HRMS (ESI-FTMS):** m/z calcd for C₁₅H₂₂O₄⁺ [M+H]⁺ 267.1596 found 267.1598

2-(but-3-en-1-yl)-2-(prop-2-yn-1-yl)malononitrile (1u)

Following the general procedure of alkylation for synthesis of 1,7-enynes, 1u was obtained after overnight at 60°C in DMF in 60% yield as a brown oil (petroleum ether: EtOAc = 10:1).

¹**H NMR (400 MHz, Chloroform-***d***):** δ 5.82 (m, 1H), 5.27 – 5.05 (m, 2H), 2.94 (d, *J* = 2.8 Hz, 2H), 2.53 – 2.34 (m, 3H), 2.23 – 2.08 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 134.02, 117.43, 114.16, 75.19, 74.18, 36.20, 35.48, 29.35, 28.27.

IR (neat): v 3007, 2350, 1276, 1261, 751, 657 cm⁻¹

3. General Procedure for Synthesizing Functionalized Cyclohexanes



To a tube with a stir bar was charged with Argon (three times), B_2Pin_2 (55.9 mg, 0.22 mmol, 1.1 equiv.), Pd (OPiv)₂ (6.2 mg, 10 mol%) and enynes (0.2 mmol, 1.0 equiv.) in 1.7 mL toluene in sequence. Then MCAA (Monochloroacetic acid) (32 mg, 0.34 mmol, 1.7 equiv.) in 0.35 mL toluene was added and the mixture was vigorously stirred, and evacuated and backfilled with oxygen for three times. The mixture was then immersed sideways into a water bath at 25 °C for several hours. After the enynes were consumed completely (monitored by TLC). Then, the reaction was treated with 1 mL saturated Na₂S₂O₃ solution. The solution was extracted with ethyl acetate (3 × 10 mL) and dried over anhydrous Na₂SO₄. The solvent was removed under vacuum and the product was purified by column chromatography to give the target products.

Diethyl 3-methylene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) methyl) cyclohexane-1,1-dicarboxylate (2a)



Following the general borylative cyclization procedure, 1a was obtained after 1.5 h at room temperature in 87% yield as a colourless oil (petroleum ether: EtOAc = 10:1).

¹**H NMR (400 MHz, Chloroform-***d***)**: δ 4.78 – 4.70 (m, 2H), 4.16 (m, 4H), 1.43 – 1.28 (m, 1H), 1.27 – 1.19 (m, 18H), 1.03 (dd, *J* = 15.6, 7.3 Hz, 1H), 0.81 (dd, *J* = 15.6, 7.5 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 171.6, 170.4, 148.3, 108.4, 82.8, 77.2, 76.8, 76.5, 61.1, 60.8, 56.7, 39.8, 38.0, 32.7, 30.4, 24.6, 24.5, 13.9, 13.8.

IR (neat): *v* 2978, 2929, 1730, 1446, 1367, 1315, 1240, 1144, 1066, 882, 848 cm⁻¹ **HRMS (ESI-FTMS):** m/z calcd for C₂₀H₃₄BO₆⁺ [M+H]⁺ 381.2448 found 381.2440 Diethyl (*E*)-3-benzylidene-4-((3,3,4,4-tetramethylborolan-1-yl) methyl) cyclohexane-1,1dicarboxylate (2b)



Following the general borylative cyclization procedure, **2b** was obtained after 6 h at room temperature in 79% yield as a colourless oil (petroleum ether: EtOAc = 10:1)

¹**H NMR (400 MHz, CDCl₃):** δ 7.31 – 7.22 (m, 3H), 7.16 – 7.08 (m, 2H), 6.26 (s, 1H), 4.09 – 3.97 (m, 3H), 3.91 – 3.76 (m, 1H), 3.19 (d, *J* = 13.8 Hz, 1H), 2.79 – 2.65 (d, *J* = 13.8 Hz, 1H), 2.56 – 2.42 (m, 1H), 2.25 (m, 1H), 2.01 – 1.83 (m, 2H), 1.65 – 1.52 (m, 1H), 1.24 – 1.17 (m, 12H), 1.17 – 1.12 (m, 1H), 1.10 (m, 3H), 1.05 – 0.98 (m, 3H), 0.94 (dd, *J* = 15.4, 7.1 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 171.9, 171.0, 144.7, 138.2, 128.7, 128.1, 128.0, 127.8, 125.8, 120.4, 83.0, 82.9, 77.2, 76.8, 76.5, 61.1, 61.0, 55.2, 41.1, 41.0, 36.4, 32.5, 26.0, 24.8, 24.6, 24.6, 22.4, 13.9, 13.8.

IR (neat): *v* 2978, 2926, 2855, 2350, 1732, 1490, 1449, 1365, 1314, 1244, 1145, 1092, 1017, 969, 865, 751 cm⁻¹

HRMS (ESI-FTMS): m/z calcd for C₂₆H₃₈BO₆⁺ [M+H]⁺457.2761 found 457.2760

Diethyl (*E*)-3-(4-(methoxycarbonyl) benzylidene)-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) methyl) cyclohexane-1,1- dicarboxylate (2c)



Following the general borylative cyclization procedure, 2c was obtained after 2.5 h at room temperature in 58% yield as a colourless oil (petroleum ether: EtOAc = 8:1).

¹**H NMR (400 MHz, Chloroform-***d***):** δ 8.00 – 7.94 (m, 2H), 7.28 (m, 2H), 6.36 (s, 1H), 4.12 – 3.93 (m, 3H), 3.90 (s, 3H), 3.79 (m, 1H), 3.24 (d, *J* = 13.8 Hz, 1H), 2.77 (d, *J* = 13.8 Hz, 1H), 2.52 (m, 1H), 2.26 (m, 1H), 2.01 – 1.87 (m, 2H), 1.20 (s, 12H), 1.19 – 1.11 (m, 1H), 1.07 (t, *J* = 7.1 Hz, 3H), 0.97 (t, *J* = 7.2 Hz, 4H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 171.2, 170.6, 166.9, 143.5, 142.8, 129.2, 128.7, 128.7, 127.4, 123.0, 83.6, 83.0, 77.2, 76.8, 76.5, 61.1, 60.9, 56.3, 51.8, 39.5, 32.2, 32.1, 29.5, 29.5, 24.7, 24.6, 24.6, 24.4, 13.7, 13.5, -0.2.

IR (neat): *v* 2978, 2927, 2350, 1723, 1607, 1365, 1313, 1276, 1144, 1106, 879, 848, 765, 707 cm⁻¹ **HRMS (ESI-FTMS):** m/z calcd for C₂₀H₃₄BO₆⁺ [M+H]⁺ 515.2816 found 515.2817

Diethyl (*E*)-3-(naphthalen-2-ylmethylene)-4-((3,3,4,4-tetramethylborolan-1-yl) methyl) cyclohexane-1,1-dicarboxylate (2d)



Following the general borylative cyclization procedure, 2d was obtained after 2.5 h at room temperature in 77% yield as a colourless oil (petroleum ether: EtOAc = 10:1).

¹H NMR (400 MHz, Chloroform-*d*): δ 7.82 – 7.73 (m, 3H), 7.63 (s, 1H), 7.43 (m, 2H), 7.34 (dd, J = 8.4, 1.7 Hz, 1H), 6.51 (s, 1H), 4.10 – 3.90 (m, 3H), 3.73 (m, 1H), 3.34 (d, J = 13.8 Hz, 1H), 2.85 (d, J = 13.8 Hz, 1H), 2.57 (m, 1H), 2.33 – 2.22 (m, 1H), 1.96 (m, 2H), 1.73 – 1.55 (m, 1H), 1.21 (s, 12H), 0.99 (m, 4H), 0.82 (t, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 171.3, 170.8, 141.7, 135.4, 133.2, 131.7, 127.6, 127.5, 127.3, 127.2, 127.1, 125.6, 125.2, 123.8, 82.9, 77.2, 76.8, 76.5, 60.9, 60.8, 56.3, 39.5, 32.3, 32.2, 29.6, 24.7, 24.6, 24.5, 13.6, 13.3.

IR (neat): *v* 2977, 2341, 1728, 1447, 1364, 1312, 1242, 1142, 1068, 968, 863, 847, 751, 477 cm⁻¹ **HRMS (ESI-FTMS):** m/z calcd for C₃₀H₄₀BO₆⁺ [M+H]⁺ 507.2918 found 507.2911

Diethyl (*E*)-3-(4-cyanobenzylidene)-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) methyl) cyclohexane-1,1-dicarboxylate (2e)



Following the general borylative cyclization procedure. **2e** was obtained after 2.5 h at room temperature in 73% yield as a colourless oil (petroleum ether: EtOAc = 8:1).

¹**H NMR (400 MHz, Chloroform-***d***):** δ 7.63 – 7.51 (m, 2H), 7.39 – 7.26 (m, 2H), 6.34 (s, 1H), 4.22 – 3.96 (m, 3H), 3.83 (m, 1H), 3.19 (d, *J* = 13.8 Hz, 1H), 2.74 (d, *J* = 13.8, 1H), 2.53 (m, 1H), 2.33 – 2.22 (m, 1H), 2.04 – 1.87 (m, 2H), 1.61 – 1.49 (m, 1H), 1.21 (s, 13H), 1.19 – 1.06 (m, 4H), 1.00 (m, 4H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 171.1, 170.5, 144.7, 142.8, 131.8, 131.7, 129.4, 129.4, 122.4, 119.0, 109.3, 83.7, 83.0, 77.2, 76.8, 76.5, 61.2, 61.0, 56.3, 39.5, 34.2, 32.2, 32.0, 29.4, 24.6, 24.6, 24.4, 13.8, 13.7, 13.6.

IR (neat): *v* 2978, 2930, 2349, 2226, 1728, 1648, 1604, 1142, 1364, 1315, 1243, 1143, 1069, 1024, 968, 870, 847, 749, 554 cm⁻¹

HRMS (ESI-FTMS): m/z calcd for C₂₇H₃₇BNO₆⁺ [M+H]⁺ 482.2714 found 482.2710

Diethyl (*E*)-3-(4-chlorobenzylidene)-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) methyl) cyclohexane-1,1-dicarboxylate (2f)



Following the general borylative cyclization procedure. **2f** was obtained after 7 h at room temperature in 76% yield as a colourless oil (petroleum ether : EtOAc = 10:1)

¹**H NMR (400 MHz, Chloroform-***d***):** δ 7.26 (d, J = 8.5 Hz, 2H), 7.23 – 7.10 (m, 2H), 6.29 (s, 1H), 4.15 – 3.94 (m, 3H), 3.83 (m, 1H), 3.20 (d, J = 13.8 Hz, 1H), 2.77 – 2.69 (m, 1H), 2.58 – 2.45 (m, 1H), 2.31 – 2.20 (m, 1H), 2.02 – 1.86 (m, 2H), 1.63 – 1.49 (m, 1H), 1.20 (s, 12H), 1.21 – 1.12 (m, 1H), 1.10 (t, J = 7.1 Hz, 3H), 1.01 (t, J = 7.1 Hz, 3H), 0.94 (dd, J = 15.4, 7.0 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 171.2, 170.7, 142.1, 136.3, 131.5, 130.2, 130.0, 128.0, 122.6, 82.9, 77.2, 76.8, 76.5, 61.0, 60.9, 56.2, 39.4, 32.0, 29.5, 24.7, 24.6, 13.7, 13.5.

IR (neat): v 2978, 2925, 2854, 2350, 1731, 1489, 1449, 1366, 1317, 1244, 1144, 1092, 849, 750 cm⁻¹

HRMS (ESI-FTMS): m/z calcd for C₂₆H₃₇BClO₆⁺ [M+H]⁺ 491.2372 found 491.2365

Diethyl (*E*)-3-(4-fluorobenzylidene)-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) methyl) cyclohexane-1,1-dicarboxylate (2g)



Following the general borylative cyclization procedure. 2g was obtained after 2.5 h at room temperature in 71% yield as a colourless oil (petroleum ether: EtOAc = 10:1).

¹**H NMR (400 MHz, Chloroform-***d***):** δ 7.22 – 7.12 (m, 2H), 7.04 – 6.93 (m, 2H), 6.30 (s, 1H), 4.04 (m, Hz, 3H), 3.93 – 3.77 (m, 1H), 3.20 (d, *J* = 13.8 Hz, 1H), 2.73 (d, *J* = 13.8 Hz, 1H), 2.55 – 2.44 (m, 1H), 2.25 (m, 1H), 2.00 – 1.86 (m, 2H), 1.63 – 1.50 (m, 1H), 1.21 (s, 12H), 1.16 (d, *J* = 7.3 Hz, 1H), 1.09 (t, *J* = 7.1 Hz, 3H), 1.01 (t, *J* = 7.1 Hz, 3H), 0.94 (dd, *J* = 15.4, 7.1 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 171.3, 170.8, 159.8, 141.3, 133.8, 133.7, 130.2, 130.2, 122.6, 114.8, 114.6, 82.9, 77.2, 76.8, 76.5, 61.0, 60.9, 56.2, 39.3, 32.0, 32.0, 29.5, 24.7, 24.6, 13.7, 13.5.

IR (neat): v 2978, 2927, 2351, 1729, 1507, 1364, 1313, 1241, 1220, 1143, 1093, 1068, 1024, 968, 865, 847, 750, 578, 518 cm⁻¹

HRMS (ESI-FTMS): m/z calcd for C₂₆H₃₇BFO₆⁺ [M+H]⁺ 475.2667 found 475.2674

Diethyl (*E*)-3-(4-bromobenzylidene)-4-((3,3,4,4-tetramethylborolan-1-yl) methyl) cyclohexane-1,1-dicarboxylate (2h)



Following the general borylative cyclization procedure. **2h** was obtained after 5 h at room temperature in 62% yield as a colourless oil (petroleum ether: EtOAc = 10:1).

¹**H NMR (400 MHz, Chloroform-***d***):** δ 7.45 – 7.38 (m, 2H), 7.16 – 7.04 (m, 2H), 6.27 (s, 1H), 4.16 – 3.94 (m, 3H), 3.83 (m, 1H), 3.20 (d, *J* = 13.8 Hz, 1H), 2.72 (d, *J* = 13.8, 1H), 2.50 (s, 1H), 2.26 (m, 1H), 1.93 (m, 2H), 1.61 – 1.49 (m, 1H), 1.22 – 1.18 (m, 12H), 1.21 – 1.06 (m, 4H), 1.01 (t, *J* = 7.1 Hz, 3H), 0.94 (dd, *J* = 15.5, 7.0 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 171.6, 171.0, 142.5, 137.1, 131.3, 130.7, 122.9, 119.9, 83.2, 77.2, 76.8, 76.5, 61.4, 61.2, 56.5, 39.7, 32.4, 32.4, 29.8, 25.0, 24.9, 14.0, 13.8.

IR (neat): *v* 2978, 2928, 2350, 1729, 1484, 1447, 1364, 1314, 1242, 1200, 1143, 1070, 1011, 968, 863, 750 cm⁻¹

HRMS (ESI-FTMS): m/z calcd for C₂₆H₃₇BBrO₆⁺ [M+H]⁺ 535.1867 found 535.1863

Diethyl (*E*)-3-ethylidene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) methyl) cyclohexane-1,1-dicarboxylate (2i)



Following the general borylative cyclization procedure. **2i** was obtained after 1.5 h at room temperature in 74% yield as a colourless oil (petroleum ether: EtOAc = 10:1).

¹**H NMR (400 MHz, Chloroform-***d***):** δ 5.33 – 5.22 (m, 1H), 4.24 – 4.05 (m, 4H), 3.04 (d, *J* = 13.6 Hz, 1H), 2.44 (d, *J* = 13.6 Hz, 1H), 2.34 – 2.22 (m, 2H), 1.92 (m, 1H), 1.85 – 1.73 (m, 1H), 1.61 (d, *J* = 6.7 Hz, 3H), 1.43 – 1.30 (m, 1H), 1.28 – 1.19 (m, 18H), 1.01 (dd, *J* = 15.4, 7.9 Hz, 1H), 0.80 (dd, *J* = 15.4, 7.3 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 172.0, 171.3, 138.5, 117.2, 83.1, 77.2, 76.8, 76.5, 61.3, 61.2, 56.7, 39.3, 32.8, 32.1, 30.3, 24.9, 24.9, 14.2, 13.0.

IR (neat): *v* 2979, 2928, 2350, 1731, 1448, 1365, 1313, 1242, 1212, 1145, 1067, 1025, 968, 884, 848, 750, 676, 641 cm⁻¹

HRMS (ESI-FTMS): m/z calcd for C₂₁H₃₆BO₆⁺ [M+H]⁺ 395.2605 found 395.2599

Diethyl (*E*)-3-(2-hydroxyethylidene)-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) methyl) cyclohexane-1,1-dicarboxylate (2j)



Following the general borylative cyclization procedure. 2j was obtained after 1 h at room temperature in 63% yield as a colourless oil (petroleum ether: EtOAc = 2:1).

¹**H NMR (400 MHz, Chloroform-***d***):** δ 5.59 (t, *J* = 7.6 Hz, 1H), 4.25 – 4.02 (m, 6H), 3.07 (dd, *J* = 13.7, 1.6 Hz, 1H), 2.58 (t, *J* = 5.9 Hz, 1H), 2.43 (d, *J* = 13.6 Hz, 1H), 2.39 – 2.27 (m, 2H), 2.05 (m, 1H), 1.79 (m, 1H), 1.28 – 1.19 (m, 18H), 1.07 – 0.99 (m, 1H), 0.85 (dd, *J* = 15.5, 7.6 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 171.4, 171.1, 142.5, 121.8, 82.9, 77.2, 76.8, 76.5, 61.4, 61.4, 57.8, 56.9, 39.0, 32.2, 29.7, 24.6, 24.5, 17.9, 13.8, 13.0.

IR (neat): *v* 3523, 2978, 2929, 2350, 1726, 1448, 1365, 1312, 1242, 1202, 1143, 1068, 1012, 967, 883, 847, 751, 679, 578 cm⁻¹

HRMS (ESI-FTMS): m/z calcd for C₂₁H₃₅BNaO₇⁺ [M+Na]⁺ 433.2374 found 433.2368

Diethyl (*E*)-3-(2-acetoxyethylidene)-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) methyl) cyclohexane-1,1-dicarboxylate (2k)



Following the general borylative cyclization procedure. $2\mathbf{k}$ was obtained after 1 h at room temperature in 79% yield as a colourless oil (petroleum ether: EtOAc = 10:1).

¹**H NMR (400 MHz, Chloroform-***d***):** δ 5.37 (t, J = 6.9 Hz, 1H), 4.75 (dd, J = 12.6, 7.4 Hz, 1H), 4.61 (dd, J = 12.7, 6.4 Hz, 1H), 4.25 – 4.03 (m, 4H), 3.07 (d, J = 13.9, 1H), 2.46 (d, J = 13.8 Hz, 1H), 2.38 – 2.31 (m, 1H), 2.30 (m, 1H), 1.94 (m, 1H), 1.83 (m, 1H), 1.44 – 1.30 (m, 1H), 1.29 – 1.20 (m, 18H), 1.03 (dd, J = 15.6, 7.7 Hz, 1H), 0.90 – 0.78 (m, 1H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 171.2, 170.8, 170.4, 143.7, 117.1, 82.9, 77.2, 76.8, 76.5, 61.3, 61.1, 60.9, 56.5, 39.0, 32.7, 32.5, 30.0, 24.6, 24.5, 20.8, 13.8, 13.8.

IR (neat): *v* 2979, 2930, 2349, 1731, 1448, 1366, 1313, 1232, 1144, 1023, 966, 884, 848, 751, 679 cm⁻¹

HRMS (ESI-FTMS): m/z calcd for C₂₃H₃₇BKO₇⁺ [M+K]⁺ 491.2219 found 491.2213

Diethyl (*E*)-3-(2-(pivaloyloxy) ethylidene)-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) methyl) cyclohexane-1,1-dicarboxylate (2l)



Following the general borylative cyclization procedure. **21** was obtained after 1 h at room temperature in 75% yield as a colourless oil (petroleum ether: EtOAc = 10:1).

¹**H NMR (400 MHz, Chloroform-***d***):** δ 5.35 (t, *J* = 6.7 Hz, 1H), 4.74 (dd, *J* = 12.9, 7.2 Hz, 1H), 4.59 (dd, *J* = 12.9, 6.1 Hz, 1H), 4.29 – 4.05 (m, 4H), 3.07 (d, *J* = 13.8, 1H), 2.46 (d, *J* = 13.8 Hz, 1H), 2.40 – 2.25 (m, 2H), 1.94 (m, 1H), 1.84 (m, 1H), 1.44 – 1.31 (m, 1H), 1.28 – 1.21 (m, 18H), 1.18 (s, 9H), 1.09 – 0.98 (m, 1H), 0.83 (dd, *J* = 15.6, 7.4 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 178.7, 171.6, 170.7, 143.5, 117.7, 83.2, 77.2, 76.8, 76.5, 61.6, 61.5, 61.5, 56.9, 39.2, 38.8, 33.1, 32.9, 30.4, 27.3, 24.9, 14.2.

IR (neat): v 2978, 2350, 1727, 1449, 1367, 1314, 1280, 1242, 1207, 1147, 1068, 1028, 968, 848, 751 cm⁻¹

HRMS (ESI-FTMS): m/z calcd for C₂₆H₄₃BNaO₈⁺ [M+Na]⁺ 517.2949 found 517.2945

Diethyl (*E*)-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) methyl)-3-(2-((triisopropylsilyl) oxy) ethylidene) cyclohexane-1,1-dicarboxylate (2m)



Following the general borylative cyclization procedure. **2m** was obtained after 1 h at room temperature in 79% yield as a colourless oil (petroleum ether: EtOAc = 10:1).

¹H NMR (400 MHz, Chloroform-*d*): δ 5.36 (t, J = 6.0 Hz, 1H), 4.39 (dd, J = 12.8, 6.6 Hz, 1H), 4.30 – 4.02 (m, 5H), 2.99 (d, J = 13.8 Hz, 1H), 2.41 (d, J = 13.7 Hz, 1H), 2.33 – 2.22 (m, 2H), 1.96 – 1.77 (m, 2H), δ 1.36 (m, 1H), 1.36 – 1.19 (m, 18H), 1.19 – 0.96 (m, 22H), 0.82 (dd, J = 15.6, 8.0 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 171.6, 170.6, 138.2, 123.7, 82.8, 77.2, 76.8, 76.5, 61.2, 61.0, 60.0, 56.4, 38.6, 32.9, 32.5, 30.2, 29.5, 24.6, 24.6, 17.9, 13.9, 11.8.

IR (neat): *v* 2939, 2865, 2349, 1732, 1464, 1463, 1367, 1313, 1239, 1204, 1145, 1093, 1065, 882, 848, 681, 657 cm⁻¹

HRMS (ESI-FTMS): m/z calcd for C₃₀H₅₅BNaO₇Si⁺ [M+Na]⁺ 589.3708 found 589.3712

Diethyl (*E*)-3-(2-(benzyloxy) ethylidene)-4-((3,3,4,4-tetramethylborolan-1-yl) methyl) cyclohexane-1,1-dicarboxylate (2n)



Following the general borylative cyclization procedure. **2n** was obtained after 1.5 h at room temperature in 69% yield as a colourless oil (petroleum ether: EtOAc = 10:1).

¹**H NMR (400 MHz, Chloroform-***d***):** δ 7.32 (d, *J* = 4.4 Hz, 4H), 7.27 (m, 1H), 5.44 (t, *J* = 6.6 Hz, 1H), 4.54 – 4.43 (m, 2H), 4.24 – 3.99 (m, 6H), 3.03 (d, *J* = 13.7, 1H), 2.44 (d, *J* = 13.7 Hz, 1H), 2.35 – 2.24 (m, 2H), 1.93 (m, 1H), 1.82 (m, 1H), 1.36 (m, 1H), 1.27 – 1.17 (m, 18H), 1.14 – 1.00 (m, 1H), 0.90 – 0.77 (m, 1H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 171.4, 170.6, 141.7, 138.4, 128.1, 127.5, 127.2, 119.9, 82.9, 77.2, 76.8, 76.5, 71.9, 66.3, 61.2, 61.0, 56.5, 38.9, 32.8, 32.4, 30.0, 24.7, 24.5, 13.8. IR (neat): *v* 2978, 2930, 2350, 1729, 1450, 1364, 1313, 1240, 1204, 1144, 1093, 1069, 1025, 967, 883, 848, 748, 698 cm⁻¹

HRMS (ESI-FTMS): m/z calcd for C₂₁H₃₅BNaO₇⁺ [M+Na]⁺ 539.2582 found539.2574

Dimethyl 3-methylene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) methyl) cyclohexane-1,1-dicarboxylate (20)



Following the general borylative cyclization procedure. **20** was obtained after 1h at room temperature in 74% yield as a colourless oil (petroleum ether: EtOAc = 10:1).

¹**H NMR (400 MHz, Chloroform-***d***):** δ 4.78 – 4.69 (m, 2H), 3.70 (d, *J* = 3.9 Hz, 6H), 2.91 (d, *J* = 13.4, 1H), 2.55 (d, *J* = 13.3 Hz, 1H), 2.37 – 2.23 (m, 2H), 1.94 – 1.78 (m, 2H), 1.41 – 1.20 (m, 13H), 1.03 (dd, *J* = 15.6, 7.3 Hz, 1H), 0.92 – 0.76 (dd, *J* = 15.6, 7.3 Hz, 2H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 172.3, 171.2, 148.5, 108.8, 83.2, 77.2, 76.8, 76.5, 57.2, 52.8, 52.5, 40.2, 38.3, 33.1, 30.9, 24.9, 24.9.

IR (neat): *v* 2977, 1734, 1435, 1373, 1316, 1247, 1203, 1144, 1069, 968, 899, 848 cm⁻¹ **HRMS (ESI-FTMS):** m/z calcd for C₁₈H₃₀BO₆⁺ [M+H]⁺ 353.2135 found 353.2138

Diethyl 4-methylene-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) methyl) cyclohexane-1,1-dicarboxylate (2p)



Following the general borylative cyclization procedure. **2p** was obtained after 2 h at room temperature in 77% yield as a colourless oil (petroleum ether: EtOAc = 10:1).

¹**H NMR (400 MHz, Chloroform-***d***):** δ 4.70 (s, 1H), 4.63 (s, 1H), 4.34 – 4.08 (m, 4H), 2.44 (m, 2H), 2.37 – 2.18 (m, 2H), 1.68 (td, *J* = 13.0, 4.9 Hz, 1H), 1.54 (m, 1H), 1.31 – 1.18 (m, 18H), 1.05 (dd, *J* = 15.5, 7.2 Hz, 1H), 0.83 (dd, *J* = 15.5, 6.8 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 171.9, 170.9, 151.6, 105.4, 82.8, 77.2, 76.8, 76.5, 61.1, 61.0, 55.4, 40.7, 35.1, 32.8, 32.6, 29.5, 24.6, 24.5, 13.9, 13.8, -0.2.

IR (neat): *v* 2979, 2927, 2855, 2356, 1731, 1448, 1373, 1322, 1239, 1147, 1094, 1024, 969, 891, 850, 751 cm⁻¹

HRMS (ESI-FTMS): m/z calcd for C₂₀H₃₄BO₆⁺ [M+H]⁺ 381.2448 found 381.2454

Diethyl (*E*)-4-benzylidene-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) methyl) cyclohexane-1,1-dicarboxylate (2q)



Following the general borylative cyclization procedure. 2q was obtained after 6 h at room temperature in 75% yield as a colourless oil (petroleum ether: EtOAc = 10:1)

¹**H NMR (400 MHz, Chloroform-***d***):** δ 7.37 – 7.25 (m, 3H), 7.19 – 7.11 (m, 2H), 6.26 (s, 1H), 4.35 – 4.09 (m, 4H), 2.84 (dt, *J* = 13.9, 3.9 Hz, 1H), 2.59 – 2.47 (m, 2H), 2.36 (m, 1H), 2.14 – 2.01 (m, 1H), 1.78 – 1.63 (m, 2H), 1.33 – 1.19 (m, 18H), 1.15 (dd, *J* = 15.5, 7.4 Hz, 1H), 0.96 – 0.83 (m, 1H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 172.2, 171.3, 145.0, 138.5, 129.1, 128.4, 128.3, 128.2, 126.1, 120.7, 83.3, 83.2, 77.2, 76.8, 76.5, 61.5, 61.3, 55.5, 41.5, 41.3, 36.7, 32.8, 26.4, 25.1, 25.0, 24.9, 22.8, 14.2, 14.1.

R (neat): *v* 2977, 2930, 1728, 1447, 1365, 1322, 1235, 1144, 1090, 1022, 967, 917, 848, 749, 700 cm⁻¹

HRMS (ESI-FTMS): m/z calcd for C₂₆H₃₇BO₆⁺ [M+H]⁺457.2761 found 457.2753

Diethyl 3-methyl-4-methylene-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) methyl) cyclohexane-1,1-dicarboxylate (2r)



Following the general borylative cyclization procedure. $2\mathbf{r}$ was obtained after 1.5 h at room temperature in 40% yield as a colourless oil (petroleum ether: EtOAc = 10:1)

¹**H NMR (400 MHz, Chloroform-***d***):** δ 4.79 – 4.71 (m, 2H), 4.16 (m, 4H), 2.78 (d, *J* = 3.1 Hz, 2H), 2.18 – 2.03 (m, 2H), 1.63 (m, 1H), 1.52 (m, 1H), 1.27 – 1.19 (m, 18H), 1.17 (s, 3H), 1.10 (d, *J* = 14.7 Hz, 1H), 0.95 (d, *J* = 14.6 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 171.5, 171.3, 151.6, 109.4, 83.0, 77.2, 76.8, 76.5, 61.3, 61.2, 56.9, 37.6, 37.3, 37.2, 27.6, 27.0, 25.0, 25.0, 14.2.

IR (neat): *v* 2978, 2931, 1732, 1447, 1358, 1326, 1248, 1146, 1064, 969, 849, 751 cm⁻¹ **HRMS (ESI-FTMS):** m/z calcd for C₂₁H₃₅BNaO₆⁺ [M+Na]⁺ 417.2424 found 417.2429

Diethyl 4-methylene-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) ethyl) cyclohexane-1,1-dicarboxylate (2s)



Following the general borylative cyclization procedure. **2s** was obtained after 3.5 h at room temperature in 41% yield (dr = 5:1) as a colourless oil (petroleum ether: EtOAc = 10:1)

¹**H NMR (400 MHz, Benzene-d6):** δ 5.06 – 4.68 (m, 2H), 4.10 – 3.80 (m, 4H), 2.97 (ddd, *J* = 13.0, 3.9, 2.4 Hz, 1H), 2.78 – 2.63 (m, 1H), 2.58 (m, 1H), 2.45 (td, *J* = 13.4, 4.4 Hz, 1H), 2.38 – 2.24 (m, 1H), 2.15 – 1.93 (m, 1H), 1.87 (t, *J* = 12.7 Hz, 1H), 1.49 – 1.36 (m, 1H), 1.23 (d, *J* = 7.4 Hz, 3H), 1.05 (d, *J* = 5.6 Hz, 12H), 0.94 (t, *J* = 7.1 Hz, 3H), 0.86 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, Benzene-*d*₆): δ 172.6, 171.5, 152.4, 150.9, 128.9, 128.6, 128.4, 107.9, 107.0, 83.5, 83.4, 61.7, 61.6, 56.5, 43.9, 42.6, 38.1, 37.9, 34.5, 34.5, 34.2, 33.5, 25.5, 25.3, 25.3, 14.7, 14.6, 14.5, 13.6, 0.6.

IR (neat): *v* 2978, 2350, 1729, 1449, 1370, 1317, 1235, 1144, 1020, 894, 864, 847, 751, 678, 647 cm⁻¹

HRMS (ESI-FTMS): m/z calcd for C₂₁H₃₆BO₆⁺ [M+H]⁺ 395.2605 found 395.2608

To determine the relative configuration of 2s, we carried out the derivative transformations. First, compound 2s was subjected to ozonolysis to afford compound 3s, which was then reduced and underwent oxidative deborylation to yield diol 4s. Subsequent protection of 4s gave 5s. The relative configuration of 5s was established through nuclear Overhauser effect (NOE) analysis, specifically by observing NOE correlations between the α -protons adjacent to the two oxygen atoms, as well as between these protons and the methyl group protons.



To a tube with a stir bar was added compound 2s (33 mg, 0.09 mmol, 1 equiv.) in 10 mL DCM. Then the mixture was cold to -78°C. The solvent was treated with ozone and stirred until completion ((monitored by TLC l). The reaction mixture was flushed with air and argon, Then triphenylphopshine (94.4 mg, 0.36 mmol, 0.36 equiv.) was added. The resulting solution was allowed to warm slowly to room temperature and stirred overnight. The solvent was removed under vacuum and the product was purified by column chromatography (petroleum ether: EtOAc = 10:1) to give 3s (27 mg, 0.073 mmol, 81%) as a colorless oil.

3-oxo-4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)cyclohexane-1,1-dicarboxylate (3s)



A colourless oil (petroleum ether: EtOAc = 10:1)

¹**H NMR (400 MHz, Chloroform-***d***):** δ 4.24 (dq, *J* = 39.9, 7.1 Hz, 4H), 2.85 (ddd, *J* = 13.5, 5.6, 3.2 Hz, 1H), 2.68 – 2.33 (m, 4H), 2.04 (td, *J* = 13.4, 4.8 Hz, 1H), 1.78 (t, *J* = 13.5 Hz, 1H), 1.33 – 1.20 (m, 21H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 211.39, 171.30, 170.51, 82.90, 61.97, 61.85, 54.47, 50.29, 37.59, 36.67, 31.43, 24.82, 24.73, 14.22, 14.14, 12.88.

IR (neat): v 2925, 2350, 1733, 1462, 1368, 1275, 1261, 751 cm⁻¹

HRMS (ESI-FTMS): m/z calcd for C₂₀H₃₃BO₇⁺ [M+NH₄]⁺414.2663 found 414.2666

To a tube with a stir bar was added compound **3s** (24 mg, 0.065 mmol, 1 equiv.) in 0.5 mL EtOH. Then the mixture was cold to -0°C and NaBH₄ (2.5 mg, 0.066 mmol, 1.1 equiv.) was added in one potion. The resulting mixture was then stirred for 1h. After the ketone was consumed completely (monitored by TLC), the reaction was added dropwise a solution of K_2CO_3 (22 mg, 0.1625 mmol, 2.5 equiv) and 30% (w/w) H_2O_2 (0.01 mL, 0.1625 mmol, 2.5 equiv) in 0.1 mL of H_2O under 0 °C. The reaction mixture was then allowed to stir at 0 °C for an additional 1 h. The solution was diluted by addition of 2 mL H_2O , extracted with ethyl acetate (5 × 10 mL), and dried over anhydrous Na₂SO₄. The solvent was removed under vacuum and the crude product was purified by column chromatography (petroleum ether: EtOAc = 1:2) to give **4s** (12 mg, 0.042 mmol, 64%) as a colorless oil.

Diethyl 3-hydroxy-4-(1-hydroxyethyl)cyclohexane-1,1-dicarboxylate (4s)

A colourless oil (petroleum ether: EtOAc = 1:2)

¹**H NMR (400 MHz, Chloroform-***d***):** δ 4.37 – 4.07 (m, 4H), 3.82 (dq, *J* = 8.0, 6.1 Hz, 1H), 3.61 (ddd, *J* = 11.1, 9.6, 4.6 Hz, 1H), 3.12 (s, 1H), 2.36 (ddt, *J* = 26.1, 13.4, 3.2 Hz, 2H), 1.94 (dq, *J* = 13.2, 3.8 Hz, 1H), 1.77 – 1.61 (m, 3H), 1.55 – 1.40 (m, 2H), 1.26 (m, 10H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 171.79, 170.28, 74.80, 73.64, 61.48, 61.25, 54.28, 46.68, 32.00, 31.35, 29.52, 29.22, 21.63, 13.89, 13.81.

IR (neat): v 2986, 2350, 1728, 1275, 1261, 750, 856 cm⁻¹

HRMS (ESI-FTMS): m/z calcd for C₁₄H₂₄O₆⁺ [M+Na]⁺311.1471 found 311.1467

To a tube with a stir bar was added compound **4s** (8.0 mg, 0.0277 mmol, 1 equiv.) in acetone 0.3 mL and Camphorsulfonic acid (2.5 mg, 0.011 mmol, 0.4 equiv.). Then the mixture was stirred for 30 min. After the diol compound was consumed completely (monitored by TLC), the reaction was quenched by addition of NEt₃ (1 mL) under 0 °C. The solvent was removed under vacuum and the crude product was purified by column chromatography (petroleum ether: EtOAc = 5:1) to give **5s** (7.5 mg, 0.0228 mmol, 82%) as a colorless oil.

Diethyl 2,2,4-trimethylhexahydro-7H-benzo[d][1,3]dioxine-7,7-dicarboxylate (5s)



A colourless oil (petroleum ether: EtOAc = 5:1)

¹**H** NMR (400 MHz, Chloroform-*d*): δ 4.33 – 4.09 (m, 4H), 3.68 (dq, J = 9.5, 6.0 Hz, 1H), 3.52 (td, J = 10.6, 4.1 Hz, 1H), 2.48 (dq, J = 13.8, 3.2 Hz, 1H), 2.33 (dt, J = 13.3, 2.9 Hz, 1H), 1.89 – 1.66 (m, 2H), 1.47 (s, 3H), 1.39 (s, 3H), 1.29 – 1.22 (m, 9H), 1.17 (d, J = 6.0 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*): δ 171.72, 170.21, 98.43, 71.84, 69.25, 61.46, 61.26, 54.60, 43.63, 31.25, 30.70, 29.98, 29.52, 29.40, 28.57, 19.72, 18.76, 13.90, 13.81. IR (neat): v 2985, 2931, 2350, 1731, 1454, 1365, 1276, 1260, 1137, 1112, 1026, 750 cm⁻¹ HRMS (ESI-FTMS): m/z calcd for C₁₇H₂₈O₆⁺ [M+Na]⁺351.1784 found 351.1781

3-methylene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1-tosylpiperidine (2t)



Following the general borylative cyclization procedure. **2t** was obtained after 1 h at room temperature in 41% yield as a colourless oil (petroleum ether: EtOAc = 10:1).

¹**H NMR (400 MHz, Chloroform-***d***):** δ 7.73 – 7.62 (s, 2H), 7.32 (s, 2H), 4.94 (s, 1H), 4.83 (s, 1H), 4.00 (d, *J* = 12.0 Hz, 1H), 3.60 (m, 1H), 3.02 (d, *J* = 12.0 Hz, 1H), 2.60 (td, *J* = 11.3, 3.1 Hz, 1H), 2.44 (s, 3H), 2.22 – 2.10 (m, 1H), 1.82 (m, 1H), 1.48 – 1.33 (m, 1H), 1.20 (d, *J* = 2.2 Hz, 12H), 1.01 (dd, *J* = 15.8, 7.2 Hz, 1H), 0.92 – 0.73 (m, 1H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 145.2, 143.3, 132.8, 129.4, 127.7, 127.4, 109.7, 83.0, 77.2, 76.8, 76.5, 52.6, 45.8, 36.5, 33.7, 24.6, 24.5, 22.4, 21.3.

IR (neat): *v* 2978, 2925, 2351, 1653, 1598, 1375, 1349, 1163, 1143, 1008, 964, 931, 901, 847, 816, 753, 710, 661, 615, 546 cm⁻¹

HRMS (ESI-FTMS): m/z calcd for C₂₀H₃₀BNO₄S⁺ [M+Na]⁺ 414.1886 found 414.1890

((3-methylene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)cyclohexane-1,1diyl)bis(ethyne-2,1-diyl))bis(¹λ-azane) (2u)



Following the general borylative cyclization procedure. 2u was obtained after 1.5h at room temperature in 28% yield as a white solid (petroleum ether: EtOAc = 10:1).

¹**H NMR (400 MHz, Chloroform-***d***):** δ 5.02 (d, J = 3.8 Hz, 2H), 2.91 (dd, J = 13.3, 2.1 Hz, 1H), 2.66 (d, J = 13.3 Hz, 1H), 2.52 – 2.26 (m, 2H), 2.14 (ddd, J = 13.5, 11.7, 3.8 Hz, 1H), 1.99 (dq, J = 13.5, 4.4 Hz, 1H), 1.50 (m, 1H), 1.23 (d, J = 2.0 Hz, 12H), 1.09 (dd, J = 15.8, 7.1 Hz, 1H), 0.89 (dd, J = 15.9, 7.4 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-d): δ 143.01, 115.74, 114.58, 113.21, 83.16, 42.85, 37.26, 34.16,

33.86, 31.03, 29.52, 24.64, 24.54. **IR (neat):** v 2986, 2350, 1377, 1275, 1262, 1145, 751, 657 cm⁻¹ **HRMS (ESI-FTMS):** m/z calcd for C₁₆H₂₃BN₂O₂⁺ [M+Na]⁺ 309.1750 found 309.1743

Diethyl 3,4-dimethylenecyclohexane-1,1-dicarboxylate (3a)

A colourless oil (petroleum ether: EtOAc = 20:1)

¹**H NMR (400 MHz, Chloroform-***d***):** δ 5.06 (dt, *J* = 2.2, 1.1 Hz, 1H), 4.99 (dt, *J* = 2.4, 1.2 Hz, 1H), 4.80 (q, *J* = 1.7 Hz, 1H), 4.70 (q, *J* = 1.6 Hz, 1H), 4.19 (m, 4H), 2.78 (s, 2H), 2.37 (dd, *J* = 6.7, 1.4 Hz, 2H), 2.15 (dd, *J* = 7.6, 5.4 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 6H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 171.1, 146.8, 144.4, 111.4, 109.1, 77.5, 77.2, 76.8, 61.5, 55.6, 39.5, 31.2, 31.0, 14.2, 0.1.

IR (neat): *v* 2982, 2350, 1731, 1445, 1367, 1297, 1245, 1187, 1080, 1056, 1022, 965, 897, 861, 750 cm⁻¹

HRMS (ESI-FTMS): m/z calcd for $C_{14}H_{20}O_4^+$ [M+H]⁺253.1440 found 253.1434

4. Procedure for Gram-scale Synthesizing

Functionalized Cyclohexanes



To a flask with a stir bar was charged with Argon (three times), B_2Pin_2 (1.88 g, 7.41 mmol, 1.1 equiv.), Pd (OPiv)₂ (208 mg, 10 mol%) and compound **1a** (1.7 g, 6.74 mmol, 1.0 equiv.). Then 60 mL toluene was added and the mixture was vigorously stirred. Then MCAA (Monochloroacetic acid) (1.08 g, 11.45 mmol, 1.7 equiv.) in 7 mL toluene was added dropwise, and evacuated and backfilled with oxygen for three times. The mixture was then immersed sideways into a water bath at 25 °C for 1.5 h. After the compound **1a** was consumed completely (monitored by TLC), the reaction was treated with 20 mL saturated Na₂S₂O₃ solution. The solution was extracted with ethyl acetate (3 ×50 mL) and dried over anhydrous Na₂SO₄. The solvent was removed under vacuum and the crude product was purified by column chromatography (petroleum ether : EtOAc = 10:1) to give the products **2a** (1.98 g, 5.19 mmol, 77%).

5.Procedure for Synthesizing Deuterated Functionalized Cyclohexanes



To a tube with a stir bar was charged with Argon (three times), B_2Pin_2 (118 mg, 0.46 mmol, 1.1 equiv.), Pd (OPiv)₂ (13mg, 10 mol%) and enynes (93 mg, 0.41 mmol, 1.0 equiv.) in 4 mL toluene in sequence. Then DOAc (43 mg, 0.7 mmol, 1.7 equiv.) was added and the mixture was vigorously stirred, and evacuated and backfilled with oxygen for three times. The mixture was then immersed sideways into an oil bath at 35 °C for 5 hours. After the enynes were consumed completely (monitored by TLC), the reaction was treated with 5 mL saturated Na₂S₂O₃ solution. The solution was extracted with ethyl acetate (3 × 10 mL) and dried over anhydrous Na₂SO₄. The solvent was removed under vacuum and the crude product was purified by column chromatography (petroleum ether: EtOAc = 10:1) to give the product **2od** (93 mg, 0.263 mmol, 64%).

Diethyl 3-(methylene-d2)-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) methyl)cyclohexane-1,1-dicarboxylate (2od)



Following the above procedure, **2ad** was obtained in 64% yield as a colourless oil (petroleum ether: EtOAc = 10:1).

¹**H NMR (400 MHz, Chloroform-***d***)**: δ 4.75 – 4.68 (m, 1.3H), 3.78 – 3.61 (m, 6H), 2.90 (dd, *J* = 13.3, 2.2 Hz, 1H), 2.54 (dd, *J* = 13.4, 1.5 Hz, 1H), 2.39 – 2.19 (m, 2H), 1.97 – 1.75 (m, 2H), 1.34 – 1.16 (m, 13H), 1.09 – 0.94 (m, 1H), 0.87 – 0.74 (m, 1H).

¹³C NMR (101 MHz, Chloroform-*d*): δ 172.01, 170.91, 148.20, 148.12, 108.51, 82.83, 56.87, 52.45, 52.18, 39.91, 39.86, 37.98, 37.95, 32.75, 30.54, 24.62, 24.53.

IR (neat): v 2926, 2350, 1734, 1368, 1317, 1276, 1261, 1146, 969, 751 cm⁻¹

HRMS (ESI-FTMS): m/z calcd for $C_{14}H_{19}D_2O_4^+$ [M]⁺255.1565 found 255.1572

6. Comparing Substrate Reactivity and Selectivity with Previous Work

entry	Cárdenas's work (<i>Chem. Comm.</i> , 2012 , <i>48</i> , 10517.) Pd(TFA) ₂ or Pd(OAc) ₂ , B ₂ Pin ₂ , MeOH toluene, 23°C - 80°C	our work Pd(OPiv) _{2 ,} MCAA, B ₂ Pin ₂ Toluene, O ₂ (g), rt
1	$\begin{array}{c} Ph \\ BPin \\ MeO_2C \\ MeO_2C \\ 25\% \end{array} + \begin{array}{c} Ph \\ MeO_2C \\ MeO_2C \\ MeO_2C \\ 13\% \end{array}$	Ph BPin EtO ₂ C EtO ₂ C 2b, 79%
2	MeO_2C	MeO ₂ C MeO ₂ C 2a, 74%
3	BPin + TsN 15% 5%	TsN 2s, 41%
4	$\begin{array}{c} Ph \\ BPin \\ MeO_2C \\ CO_2Me \end{array}$	$\begin{array}{c} Ph \\ BPin \\ EtO_2C \\ CO_2Et \\ 2n \\ 75\% \end{array}$
5		EtO_2CCO_2Et $2p, 77\%$

Considering that Ge's work (*Angew. Chem., Int. Ed.,* 2019, **58**, 8882–8886.) primarily focuses on quinolinone-type substrates, which differ significantly from ours, we focuses on comparing the work of Cárdenas et al (*Chem. Commun.,* 2012, **48**, 10517–10519). We listed the reactivity and selectivity differences for substrates that are identical or highly similar to ours in Cárdenas's work (with only methyl esters replaced by ethyl esters). For entries 1–3, in Cárdenas's work, besides unsatisfactory yields, regioisomeric byproducts were also observed, whereas our work showed no regioisomers and achieved good yields. For the substitution patterns in entries 4–5, although Cárdenas's work did not produce regioisomers, the yields were lower than those in our examples. Overall, our work exhibits better reactivity and regioselectivity than Cárdenas's work for these substrates.

7. Reference

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CDCI3		
7.289 7.284 7.273 7.267 7.267 7.263 7.260 7.253 7.253 7.248 7.253 7.248	5.820 5.820 5.777 5.085 5.081 5.081 5.081 4.998 4.243 4.248 4.248 4.248 4.233 4.233 4.225 4.233 4.225 4.233 4.207 4.207 4.207	3.038 2.212 2.212 2.198 2.198 2.198 2.198 2.198 2.189 2.189 2.037 2.007 2.037 2.007 2.007 2.0006 2.0007 2.0007 2.0006 2.0007 2.0007 2.0007 2.0007 2.0007 2.0007 2.0000000000



1f ¹H NMR (400 MHz, CDCl₃)






























S48

























CDCI3		Одн
7.260 7.260 4.199 4.199 4.197 4.197 4.197 4.185 4.185 4.185 4.182 4.182 4.182 4.172 4.172 4.172 4.172	4 162 4 154 4 154 4 154 4 154 4 155 7 155 7 2 256 7 2 256 7 2 256 7 2 256 7 2 256 7 2 2 256 7 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	1.255 1.948 1.948 1.948 1.651 1.654 1.647 1.647 1.633 1.633 1.633 1.633 1.633 1.633 1.633 1.633 1.654 1.598 1.598 1.598 1.265 1.2555 1.2555 1.2555 1.2555 1.2555 1.2555 1.2555 1.2555 1.2555 1.25555 1.25555 1.25555 1.255555 1.25555555555













1u ¹H NMR (400MHz, CDCl₃)



016	132	50 CDC13 50 CDC13 72 CDC13 75 CDC13 75 CDC13 76	23 8 0 23 8 0
134.(117.4	77.1(76.8, 76.5, 74.1,	36.20 35.4 29.3(
Ì			52.52

1u ¹³C NMR (101MHz, CDCl₃)























S68












S74



S75

















































S96



















2p ¹H NMR (400MHz, CDCl₃)









S106










S110













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