Supporting Information (SI)

Transition-Metal-Free Base-Controlled Chemoselective Conjugate Addition and Reduction of α,β-Unsaturated Carbonyl Compounds via A Boration/Protodeboronation Strategy

Xi Huanga, Junjie Hua, Mengying Wua, Jiayi Wanga, Yanqing Penga, and Gonghua Songa,*

a Shanghai Key Laboratory of Chemical Biology, School of Pharmacy, East China University of Science and Technology, Shanghai, 200237, PR China. Fax: +86-21-64252603; E-mail: ghsong@ecust.edu.cn
1. Experimental Section

General Remarks

All reagents were of analytical grade and obtained from commercial suppliers; unless stated otherwise, all reagents were used without further purification. Chalcones were synthesized by standard method and were confirmed by GC-MS. The crude products were all recrystallized from 98% ethanol. The microwave synthesizer used in the experiments was a Biotage Initiator (max power 300 W, Biotage® from Uppsala, Sweden). The preparative thin-layer chromatography plates used were HSGF 254 plates (thickness of coating: 0.4-0.5 mm, 20 cm × 20 cm, Huanghai® from Yantai, Shandong province, China). The $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker AM-400 spectrometer (400 MHz and 100 MHz, respectively) using TMS as internal standard. CDCl$_3$ was used as the NMR solvent for α,β-unsaturated carbonyl compounds substrates in most cases. Chemical shifts were recorded in parts per million (d) relative to CDCl$_3$ at 7.26 for $^1$H NMR and 77.23 for $^{13}$C NMR. Gas chromatography-mass spectrometry (GC-MS) was performed on Agilent 7890A/5975C. Gas chromatograms were recorded on Agilent 7890A.

2. Experimental Procedure

General procedure

**General procedure A for optimization of reaction condition:** A mixture of the chalcone (104.1mg, 0.5 mmol), bis(pinacolato)diboron, base and solvent was placed in a 10-mL microwave tube with a magnetic stirring bar. After being sealed with a cap, the reaction tube was then placed into an oil bath and the reaction was conducted at 70 °C for the indicated period of time. After the reaction was finished, dodecane (50.0 mg) was added into the mixture as an internal standard. CDCl$_3$ was used as the NMR solvent for α,β-unsaturated carbonyl compounds substrates in most cases. Chemical shifts were recorded in parts per million (d) relative to CDCl$_3$ at 7.26 for $^1$H NMR and 77.23 for $^{13}$C NMR. Gas chromatography-mass spectrometry (GC-MS) was performed on Agilent 7890A/5975C. Gas chromatograms were recorded on Agilent 7890A.

**General procedure B (conventional heating) for β-boration of α,β-unsaturated carbonyl compounds with bis(pinacolato)diboron:** A mixture of the α,β-unsaturated enones/esters (0.5 mmol), bis(pinacolato)diboron (190.5mg, 0.75 mmol) and a mixed solvent (ethanol:water = 6:1, 1.5 mL) was placed in a 10-mL microwave tube with a magnetic stirring bar. After being sealed with a cap, the tube was heated at 70 °C for 2-12 hours. The resulting suspension was diluted with water (2.0 mL) and extracted with ethyl acetate (6.5 mL × 3). The combined organic layers were washed with brine and dried over MgSO$_4$, and the solvents were removed under vacuum. The resultant crude residue was purified by preparative thin-layer chromatography to give the product 3 (eluent: ethyl acetate: cyclohexane = from 1:10 to 1:100). The products were further characterized by GC/MS, $^1$H NMR and $^{13}$C NMR.

**General procedure C (conventional heating) for β-boration of α,β-unsaturated carbonyl compounds with bis(pinacolato)diboron in presence of base:** A mixture of the α,β-unsaturated enones/esters (0.5 mmol), bis(pinacolato)diboron (190.5mg, 0.75 mmol), Et$_3$N (5.1 mg, 0.05 mmol) and a mixed solvent (ethanol:water = 6:1, 1.5 mL) was placed in a 10-mL microwave tube with a magnetic stirring bar. After being sealed with a cap, the tube was heated at 70 °C for 0.5-2 hours. The resulting suspension was diluted with water (2.0 mL) and extracted with ethyl acetate (6.5 mL × 3). The combined organic layers were washed with brine and dried over MgSO$_4$, and the solvents were removed under vacuum. The resultant crude residue was purified by preparative thin-layer chromatography to give the product 3 (eluent: ethyl acetate: cyclohexane = from 1:10 to 1:100). The products were further characterized by GC/MS, $^1$H NMR and $^{13}$C NMR.

**General procedure D (microwave heating) for reduction of α,β-unsaturated carbonyl compounds with bis(pinacolato)diboron:** A mixture of the α,β-unsaturated carbonyl compounds (0.5 mmol), bis(pinacolato)diboron (190.5mg, 0.75 mmol), Cs$_2$CO$_3$ (16.3 mg, 0.05 mmol) and ethanol (1.5 mL) was placed in a 10-mL microwave tube with a magnetic stirring bar. After being sealed with a cap, the tube was then placed into the microwave synthesizer and the reaction was run at 110 °C for 20-60 minutes. The resulting suspension was diluted with water (2.0 mL) and extracted with ethyl acetate (6.5 mL × 3). The combined organic layers were washed with brine and dried over MgSO$_4$, and the solvents were removed under vacuum. The resultant crude residue was purified by preparative thin-layer chromatography to give the product 4 (eluent: ethyl acetate: cyclohexane = from 1:10 to 1:100). The products were further characterized by GC/MS, $^1$H NMR and $^{13}$C NMR.
3. Characterization and NMR spectra of the β-boration products:

3a 1,3-diphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one.¹

![Chemical structure of 3a](image)

¹¹H NMR (400 MHz, CDCl₃) δ 7.97 (s, 1H), 7.95 (d, J = 1.4 Hz, 1H), 7.57 – 7.50 (m, 1H), 7.43 (dd, J = 10.5, 4.7 Hz, 2H), 7.32 – 7.26 (m, J = 8.0 Hz, 4H), 7.19 – 7.14 (m, 1H), 3.56 (dd, J = 18.3, 10.9 Hz, 1H), 3.46 – 3.37 (dd, 1H), 2.80 (dd, J = 10.8, 5.0 Hz, 1H), 1.24 (s, 6H), 1.16 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 199.73, 141.96, 136.79, 132.95, 128.53 (2C), 128.51 (2C), 128.40 (2C), 125.61, 83.41 (2C), 43.28 (2C), 24.58 (2C), 24.54 (2C).

MS (GC-MS) m/z: 336 (M⁺), 321, 278, 253, 236, 209, 192, 103, 77, 55.

3b 1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(p-tolyl)propan-1-one.²

![Chemical structure of 3b](image)

¹¹H NMR (400 MHz, CDCl₃) δ 7.97 – 7.94 (m, 2H), 7.55 – 7.50 (m, 1H), 7.45 – 7.40 (m, 2H), 7.21 – 7.17 (m, 2H), 7.08 (d, J = 7.9 Hz, 2H), 3.53 (dd, J = 18.3, 10.8 Hz, 1H), 3.39 (dd, J = 15.1, 3.2 Hz, 1H), 2.76 (dd, J = 10.8, 5.0 Hz, 1H), 2.31 (s, 3H), 1.24 (s, 6H), 1.17 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 199.77, 138.82, 136.86, 134.99, 132.87, 129.24 (2C), 128.47 (2C), 128.28 (2C), 128.05 (2C), 83.34 (2C), 43.48 (2C), 24.59 (2C), 24.56 (2C), 20.99.

MS (GC-MS) m/z: 350 (M⁺), 325, 292, 267, 253, 236, 206, 105, 77, 51.

3c 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3-di-p-tolylpropan-1-one (new compound).

![Chemical structure of 3c](image)

¹¹H NMR (400 MHz, CDCl₃) δ 7.86 (s, 1H), 7.84 (s, 1H), 7.24 – 7.17 (m, 4H), 7.08 (d, J = 7.9 Hz, 2H), 3.50 (dd, J = 18.2, 10.9 Hz, 1H), 3.36 (dd, J = 18.3, 5.2 Hz, 1H), 2.74 (dd, J = 10.9, 5.1 Hz, 1H), 2.38 (s, 3H), 2.30 (s, 3H), 1.24 (s, 6H), 1.16 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 199.41, 143.60, 138.92, 134.94, 134.93, 129.23 (2C), 129.15 (2C), 128.29 (2C), 128.18 (2C), 83.30 (2C), 43.39 (2C), 24.60 (2C), 24.57 (2C), 21.63, 21.00.

MS (GC-MS) m/z: 364 (M⁺), 349, 306, 281, 264, 237, 220, 205, 145, 117, 91.

HRMS (EI) m/z calcd for C₂₃H₂₉BO₃ [M⁺] 364.2210, found 364.2211.

3d 3-(4-methoxyphenyl)-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one.²
\[\text{3e 1-(4-methoxyphenyl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one.}^3\]

\[\text{3f 3-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(p-tolyl)propan-1-one (new compound).}\]

\[\text{3g 1-(4-chlorophenyl)-3-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (new compound).}\]
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.90 – 7.84 (m, 2H), 7.41 – 7.34 (m, 2H), 7.24 – 7.17 (m, 2H), 6.86 – 6.79 (m, 2H), 3.75 (s, 3H), 3.46 (dd, $J = 18.3, 10.7$ Hz, 1H), 3.32 (dd, $J = 18.3, 5.2$ Hz, 1H), 2.74 (dd, $J = 10.7, 5.1$ Hz, 1H), 1.24 (s, 6H), 1.16 (s, 6H).  $^{13}$C NMR (101 MHz, CDCl$_3$) δ 198.56 (s), 157.71 (s), 139.25 (s), 135.14 (s), 133.62 (s), 129.48 (2C), 129.28 (2C), 128.77 (2C), 114.03 (2C), 83.39 (2C), 55.16, 43.44 (2C), 24.59 (2C), 24.55 (2C).

MS (GC-MS) m/z: C$_{22}$H$_{26}$B$_3$ClO$_4$ 400 (M+), 385, 342, 317, 300, 273, 162, 139, 111, 84.

MS (GC-MS) m/z: C$_{22}$H$_{26}$B$_3^{17}$ClO$_4$ 402 (M+), 387, 344, 319, 302, 275, 162, 141, 113, 84.

HRMS (EI) m/z calcd for C$_{22}$H$_{26}$B$_3$ClO$_4$ [M$^+$] 400.1613, found 400.1611.

HRMS (EI) m/z calcd for C$_{22}$H$_{26}$B$_3^{17}$ClO$_4$ [M$^+$] 402.1583, found 402.1588.

3h 4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-one.$^1$

3i 3-(4-fluorophenyl)-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one.$^4$

3j 1-(4-fluorophenyl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one.$^5$
1H NMR (400 MHz, CDCl3) δ 8.01–7.98 (m, 1H), 7.98–7.94 (m, 1H), 7.45–7.34 (m, 1H), 7.32–7.25 (m, 4H), 7.10 (dd, J = 14.3, 5.6 Hz, 2H), 3.52 (dd, J = 18.2, 10.9 Hz, 1H), 3.38 (dd, J = 18.4, 4.9 Hz, 1H), 2.79 (dd, J = 10.8, 5.0 Hz, 1H), 1.24 (s, 6H), 1.16 (s, 6H); 13C NMR (101 MHz, CDCl3) δ 198.14, 165.67 (d, JCF = 254.3 Hz, 1C), 141.79, 133.20 (d, JCF = 3.0 Hz, 1C), 130.66 (d, JCF = 9.3 Hz, 2C), 128.55 (2C), 128.36 (2C), 125.66, 115.56 (d, JCF = 21.8 Hz, 2C), 83.44 (2C), 43.13 (2C), 24.85 (2C), 24.55 (2C).

MS (GC-MS) m/z: 354 (M+), 339, 296, 271, 254, 227, 210, 123, 84.

3k 3-(4-fluorophenyl)-1-(3-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (new compound).

1H NMR (400 MHz, CDCl3) δ 7.54 (d, J = 7.7 Hz, 1H), 7.48 (s, 1H), 7.34 (t, J = 7.9 Hz, 1H), 7.27–7.23 (m, 2H), 7.09 (dd, J = 8.3, 2.3 Hz, 1H), 6.96 (t, J = 8.7 Hz, 2H), 3.84 (s, 3H), 3.49 (dd, J = 18.2, 10.3 Hz, 1H), 3.38 (dd, J = 18.3, 5.4 Hz, 1H), 2.77 (dd, J = 10.3, 5.3 Hz, 1H), 1.24 (s, 6H), 1.17 (s, 6H); 13C NMR (101 MHz, CDCl3) δ 199.35, 161.17 (d, JCF = 243.3 Hz, 1C), 159.78, 138.08, 137.52 (d, JCF = 3.1 Hz, 1C), 129.71 (d, JCF = 7.7 Hz, 2C), 129.51, 120.72, 119.48, 115.24 (d, JCF = 21.0 Hz, 2C), 112.30, 83.49 (2C), 55.45, 43.34 (2C), 24.57 (2C), 24.52 (2C).

MS (GC-MS) m/z: 384 (M+), 369, 301, 284, 257, 240, 225, 196, 133, 107, 84, 55.

HRMS (EI) m/z calcld for C22H26BF4O4 [M]+: 384.1908, found 384.1912.

3l 3-(4-chlorophenyl)-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one.

1H NMR (400 MHz, CDCl3) δ 7.87 (d, J = 7.3 Hz, 2H), 7.45 (t, J = 7.4 Hz, 1H), 7.35 (t, J = 7.6 Hz, 2H), 7.15 (s, 4H), 3.42 (dd, J = 18.3, 10.4 Hz, 1H), 3.31 (dd, J = 18.3, 5.3 Hz, 1H), 2.69 (dd, J = 10.3, 5.3 Hz, 1H), 1.15 (s, 6H), 1.08 (s, 6H); 13C NMR (101 MHz, CDCl3) δ 199.40, 140.54, 136.64, 133.07, 131.31 129.74 (2C), 128.59 (2C), 128.54 (2C), 128.06 (2C), 83.54 (2C), 42.95 (2C), 24.58 (2C), 24.53 (2C).

MS (GC-MS) m/z: C21H22B3ClO3 370 (M+), 355, 312, 287, 270, 243, 191, 103, 84.

MS (GC-MS) m/z: C21H22B3ClO3 372 (M+), 357, 314, 289, 272, 245, 193, 103, 84.

3m 1-(4-chlorophenyl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one.
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.91 (t, $J = 2.2$ Hz, 1H), 7.89 (t, $J = 2.1$ Hz, 1H), 7.41 (dt, $J = 4.1$, 2.6 Hz, 2H), 7.31 – 7.26 (m, 4H), 7.20 – 7.14 (m, 1H), 1.24 (s, 6H), 1.16 (s, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 199.39, 141.08, 136.61, 133.09, 131.54 (2C), 130.17 (2C), 128.56 (2C), 128.07 (2C), 119.37, 83.56 (2C), 42.91 (2C), 24.59 (2C), 24.55(2C).

MS (GC-MS) m/z: C$_{21}$H$_{24}$B$_7$ClO$_3$ 414 (M+), 399, 385, 333, 314, 287, 270, 243, 226, 191, 139, 111, 84.

3n 3-(4-bromophenyl)-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one.$^4$ 

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.95 (d, $J = 7.1$ Hz, 2H), 7.53 (t, $J = 7.4$ Hz, 1H), 7.43 (t, $J = 7.6$ Hz, 2H), 7.40 – 7.36 (m, 2H), 7.21 – 7.16 (m, 2H), 3.51 (dd, $J = 18.3$, 10.4 Hz, 1H), 3.40 (dd, $J = 18.3$, 5.4 Hz, 1H), 2.76 (dd, $J = 10.3$, 5.3 Hz, 1H), 1.24 (s, 6H), 1.17 (s, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 199.37, 141.09, 136.60, 133.08, 131.53 (2C), 130.17 (2C), 128.55 (2C), 128.05 (2C), 119.35, 83.55 (2C), 42.88 (2C), 24.58 (2C), 24.54 (2C).

MS (GC-MS) m/z: C$_{21}$H$_{24}$B$_7$ClO$_3$ 414 (M+), 399, 385, 333, 314, 287, 270, 243, 226, 191, 105, 84.

3o 1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(4-(trifluoromethyl)phenyl)propan-1-one.$^4$

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.96 (dd, $J = 5.2$, 3.3 Hz, 2H), 7.53 (ddd, $J = 7.4$, 3.9, 1.5 Hz, 3H), 7.43 (td, $J = 6.8$, 1.4 Hz, 4H), 3.56 (dd, $J = 18.3$, 10.3 Hz, 1H), 3.44 (dd, $J = 18.3$, 5.3 Hz, 1H), 2.89 (dd, $J = 10.2$, 5.3 Hz, 1H), 1.25 (s, 6H), 1.17 (s, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 199.14, 146.50 (d, $J = 1.1$ Hz, 1C), 136.57, 133.13, 128.68 (2C), 128.57 (2C), 128.06 (2C), 127.90 (q, $J = 33.3$ Hz, 1C), 125.38 (q, $J = 3.8$ Hz, 2C), 124.45 (dd, $J = 271.7$ Hz, 1C), 83.66 (2C), 42.68 (2C), 24.55 (2C), 24.52 (2C).

MS (GC-MS) m/z: 404 (M+), 389, 346, 304, 260, 191, 105, 84, 77, 51.

3p benzy1 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate. $^6$
1H NMR (400 MHz, CDCl₃) δ 7.30 – 7.18 (m, 5H), 5.02 (s, 2H), 2.41 (t, J = 7.5 Hz, 2H), 1.13 (s, 12H), 0.96 (t, J = 7.5 Hz, 2H); 13C NMR (101 MHz, CDCl₃) δ 174.42, 136.25, 128.46 (2C), 128.06 (2C), 128.04, 83.22 (2C), 66.04, 28.82 (2C), 24.74 (4C).

MS (GC-MS) m/z: 290 (M⁺), 275, 190, 161, 141, 91, 69, 55.

3q methyl 3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate.⁵

1H NMR (400 MHz, CDCl₃) δ 7.26 (t, J = 7.4 Hz, 2H), 7.21 (d, J = 6.8 Hz, 2H), 7.15 (t, J = 7.0 Hz, 1H), 3.65 (s, 3H), 2.90 (dd, J = 15.9, 9.8 Hz, 1H), 2.74 (dd, J = 9.7, 6.0 Hz, 1H), 2.66 (dd, J = 15.9, 5.9 Hz, 1H), 1.22 (s, 6H), 1.17 (s, 6H); 13C NMR (101 MHz, CDCl₃) δ 173.85, 141.29, 128.51 (2C), 128.18 (2C), 125.71, 83.59 (2C), 51.58, 37.12 (2C), 24.57 (2C), 24.48 (2C).

MS (GC-MS) m/z: 290 (M⁺), 275, 259, 232, 190, 146, 131, 117, 104, 83, 55.

3r ethyl 3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate.⁵

1H NMR (400 MHz, CDCl₃) δ 7.21 – 7.16 (m, 2H), 7.15 – 7.11 (m, 2H), 7.06 (ddd, J = 6.1, 3.6, 1.7 Hz, 1H), 4.09 – 3.97 (m, 2H), 2.80 (dd, J = 16.0, 9.9 Hz, 1H), 2.66 (dd, J = 9.9, 6.0 Hz, 1H), 2.57 (dd, J = 16.0, 6.0 Hz, 1H), 1.17 – 1.12 (m, 9H), 1.09 (s, 6H); 13C NMR (101 MHz, CDCl₃) δ 173.42, 141.37, 128.45 (2C), 128.20 (2C), 125.65, 83.54 (2C), 60.35, 37.32 (2C), 24.58 (2C), 24.49 (2C), 14.24.

MS (GC-MS) m/z: 304 (M⁺), 289, 259, 233, 176, 145, 131, 104, 83, 55.

3s benzyl 3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate.³

1H NMR (400 MHz, CDCl₃) δ 7.36 – 7.31 (m, 3H), 7.30 (d, J = 4.4 Hz, 2H), 7.24 (d, J = 7.0 Hz, 2H), 7.21 (d, J = 6.7 Hz, 2H), 7.15 (ddd, J = 8.2, 2.3, 1.4 Hz, 1H), 5.09 (ddd, J = 29.1, 12.4 Hz, 2H), 2.95 (dd, J = 15.2, 8.7 Hz, 1H), 2.78 (dd, J =
11.9, 5.6 Hz, 1H), 2.72 (dd, \( J = 15.2, 6.2 \) Hz, 1H), 1.19 (s, 6H), 1.14 (s, 6H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 173.28, 141.26, 136.05, 128.53 (2C), 128.50 (2C), 128.23 (2C), 128.13 (2C), 128.10, 125.74 , 83.63 (2C), 66.19, 37.29 (2C), 24.58 (2C), 24.49 (2C).
MS (GC-MS) m/z: 366 (M+), 351, 233, 217, 180, 131, 117, 91, 77, 55.
4. Characterization and NMR spectra of the reduction products:

4a 1,3-diphenylpropan-1-one.\(^7\)

\[
\begin{align*}
\text{(1,3-diphenylpropan-1-one)}
\end{align*}
\]

\(\text{\(^1\)H NMR (400 MHz, CDCl}_3\text{)} \delta 7.94 (d, J = 7.3 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.33 – 7.26 (m, 2H), 7.24 (d, J = 7.0 Hz, 2H), 7.19 (t, J = 7.0 Hz, 1H), 3.28 (t, J = 7.7 Hz, 2H), 3.06 (t, J = 7.7 Hz, 2H); \text{\(^{13}\)C NMR (101 MHz, CDCl}_3\text{)} \delta 199.23, 141.34, 136.90, 133.10, 128.65 (2C), 128.58 (2C), 128.48 (2C), 128.08 (2C), 126.18, 40.48, 30.17. \text{MS (GC-MS) m/z: 210 (M+), 192, 105, 91, 77, 65, 51.}\)

4b 3-(2,4-dichlorophenyl)-1-phenylpropan-1-one.\(^8\)

\[
\begin{align*}
\text{(3-(2,4-dichlorophenyl)-1-phenylpropan-1-one)}
\end{align*}
\]

\(\text{\(\text{\(^1\)H NMR (400 MHz, CDCl}_3\text{)} \delta 7.94 (d, J = 7.6 Hz, 2H), 7.54 (t, J = 7.3 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.34 (d, J = 1.4 Hz, 1H), 7.24 (d, J = 8.2 Hz, 1H), 7.15 (dd, J = 8.2, 1.5 Hz, 1H), 3.28 (t, J = 7.4 Hz, 2H), 3.13 (t, J = 7.4 Hz, 2H); \text{\(^{13}\)C NMR (101 MHz, CDCl}_3\text{)} \delta 198.60, 137.45, 136.65, 134.59, 133.24, 132.66, 131.69, 129.30, 128.67 (2C), 128.05 (2C), 127.21, 38.13, 27.69. \text{C}_{15}\text{H}_{13}\text{Cl}_3\text{O MS (GC-MS) m/z: S278 (M+), 243, 225, 159, 105, 91, 77, 51.}}\)

4c 3-(4-chlorophenyl)-1-phenylpropan-1-one.\(^7\)

\[
\begin{align*}
\text{(3-(4-chlorophenyl)-1-phenylpropan-1-one)}
\end{align*}
\]

\(\text{\(\text{\(^1\)H NMR (400 MHz, CDCl}_3\text{)} \delta 7.99 – 7.88 (m, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 3.27 (t, J = 7.5 Hz, 2H), 3.04 (t, J = 7.5 Hz, 2H); \text{\(^{13}\)C NMR (101 MHz, CDCl}_3\text{)} \delta 198.85, 139.76, 136.76, 133.19, 131.88, 129.85 (2C), 128.66 (2C), 128.61 (2C), 128.03 (2C), 40.15 (s), 29.39 (s).} \text{C}_{15}\text{H}_{13}\text{Cl}_3\text{O MS (GC-MS) m/z: 244 (M+), 226, 209, 139, 111, 105, 91, 77, 51.} \text{C}_{15}\text{H}_{13}\text{Cl}_3\text{O MS (GC-MS) m/z: 246 (M+), 228, 209, 141, 113, 105, 91, 77, 51.}\)

4d 1-(4-chlorophenyl)-3-phenylpropan-1-one.\(^7\)

\[
\begin{align*}
\text{(1-(4-chlorophenyl)-3-phenylpropan-1-one)}
\end{align*}
\]
1H NMR (400 MHz, CDCl₃) δ 7.83 – 7.73 (m, 2H), 7.35 – 7.26 (m, 2H), 7.23 – 7.17 (m, 2H), 7.17 – 7.08 (m, 3H), 3.21 – 3.10 (m, 2H), 2.96 (t, J = 7.6 Hz, 2H). 13C NMR (101 MHz, CDCl₃) δ 197.97, 141.09, 139.51, 135.18, 129.49 (2C), 128.94 (2C), 128.61 (2C), 128.45 (2C), 126.26, 40.45, 30.07.

C₁₅H₁₃ClO MS (GC-MS) m/z: 244 (M+), 226, 209, 139, 111, 91, 77, 51.

C₁₅H₁₃ClO MS (GC-MS) m/z: 246 (M+), 228, 209, 141, 113, 91, 77, 51.

4g 1-(4-fluorophenyl)-3-phenylpropan-1-one.⁷

![Structure of 4g](image)

1H NMR (400 MHz, CDCl₃) δ 7.96 (dd, J = 8.8, 5.4 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.20 (dd, J = 8.5, 5.5 Hz, 2H), 6.96 (t, J = 8.7 Hz, 2H), 3.27 (t, J = 7.5 Hz, 2H), 3.03 (t, J = 7.5 Hz, 2H).

13C NMR (101 MHz, CDCl₃) δ 199.03, 161.42 (d, JₐCF = 243.8 Hz, 1C), 136.99 (d, JₐCF = 3.2 Hz, 1C), 135.62, 134.14, 132.54, 129.92 (d, JₐCF = 7.8 Hz, 2C), 128.65 (2C), 128.04 (2C), 115.26 (d, JₐCF = 21.1 Hz, 2C), 40.43, 29.27.

MS (GC-MS) m/z: 228 (M+), 210, 123, 105, 95, 77, 63, 51.

4f 3-(4-fluorophenyl)-1-phenylpropan-1-one.⁷

![Structure of 4f](image)

1H NMR (400 MHz, CDCl₃) δ 7.94 (d, J = 7.2 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.20 (dd, J = 8.5, 5.5 Hz, 2H), 6.96 (t, J = 8.7 Hz, 2H), 3.27 (t, J = 7.5 Hz, 2H), 3.03 (t, J = 7.5 Hz, 2H).

13C NMR (101 MHz, CDCl₃) δ 199.03, 161.42 (d, JₐCF = 243.8 Hz, 1C), 136.99 (d, JₐCF = 3.2 Hz, 1C), 136.81, 133.16, 129.87 (d, JₐCF = 7.8 Hz, 2C), 128.65 (2C), 128.04 (2C), 115.26 (d, JₐCF = 21.1 Hz, 2C), 40.43, 29.27.

MS (GC-MS) m/z: 228 (M+), 210, 123, 105, 95, 77, 63, 51.

4h 3-(4-fluorophenyl)-1-(naphthalen-2-yl)propan-1-one (new compound).

![Structure of 4h](image)

1H NMR (400 MHz, CDCl₃) δ 8.33 (s, 1H), 7.91 (d, J = 8.2 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.78 – 7.71 (m, 2H), 7.45 (dt, J = 14.8, 7.1 Hz, 2H), 7.16 – 7.07 (m, 2H), 6.88 (t, J = 8.6 Hz, 2H), 3.28 (t, J = 7.6 Hz, 2H), 2.98 (t, J = 7.5 Hz, 2H).

13C NMR (101 MHz, CDCl₃) δ 198.96, 161.46 (d, JₐCF = 243.8 Hz, 1C), 136.99 (d, JₐCF = 3.2 Hz, 1C), 136.81, 133.16, 132.54, 129.92 (d, JₐCF = 7.8 Hz, 2C), 129.71, 129.57, 128.53 (2C), 127.82, 126.85, 123.82, 115.31 (d, JₐCF = 21.1 Hz, 2C), 40.52, 29.42.

MS (GC-MS) m/z: 278 (M+), 259, 155, 141, 127, 109, 96, 77, 51.

HRMS (EI) m/z calcld for C₁₉H₁₅F₂O [M⁺] 278.1107, found 278.1108.

4h 3-(4-bromophenyl)-1-phenylpropan-1-one.⁷

![Structure of 4h](image)

1H NMR (400 MHz, CDCl₃) δ 7.94 (d, J = 7.4 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.40 (d, J = 8.2 Hz, 2H), 7.12 (d, J = 8.1 Hz, 2H), 3.27 (t, J = 7.5 Hz, 2H), 3.02 (t, J = 7.5 Hz, 2H).
^1^C NMR (101 MHz, CDCl\textsubscript{3}) δ 198.80, 140.29, 136.75, 133.20, 131.57 (2C), 130.27 (2C), 128.67 (2C), 128.03 (2C), 119.90, 40.07, 29.44.

C\textsubscript{15}H\textsubscript{13}BrO MS (GC-MS) m/z: 288 (M+), 272, 209, 169, 105, 90, 77, 51.

C\textsubscript{15}H\textsubscript{13}BrO MS (GC-MS) m/z: 290 (M+), 274, 209, 171, 105, 90, 77, 51.

4i 1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one.\textsuperscript{7}

\[
\text{F}_3\text{C} \quad \text{O} \quad \text{C}_{\text{C}} \quad \text{O} \quad \text{C}_{\text{C}}
\]

^1^H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.86 (d, J = 7.5 Hz, 2H), 7.51 – 7.41 (m, 3H), 7.36 (t, J = 7.6 Hz, 2H), 7.28 (d, J = 7.9 Hz, 2H), 3.23 (t, J = 7.5 Hz, 2H), 3.04 (t, J = 7.4 Hz, 2H); \(^1^C NMR (101 MHz, CDCl\textsubscript{3}) δ 197.52, 144.43 (d, J\textsubscript{CF} = 1.0 Hz, 1c), 135.63, 132.22, 127.78 (2C), 127.64 (2C), 127.42 (m, J\textsubscript{CF} = 32.3 Hz, 1C), 126.97 (2C), 124.39 (q, J\textsubscript{CF} = 3.8 Hz, 2C), 123.42 (q, J\textsubscript{CF} = 271.1 Hz, 1C), 38.77, 28.72.

MS (GC-MS) m/z: 278 (M+), 259, 213, 145, 105, 91, 77, 51.

4j 3-phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-one.\textsuperscript{7}

\[
\text{OC}\quad \text{C}_{\text{C}}
\]

^1^H NMR (400 MHz, CDCl\textsubscript{3}) δ 8.05 (d, J = 8.2 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H), 7.34 – 7.28 (m, 2H), 7.23 (dd, J = 16.3, 7.7 Hz, 2H), 3.33 (t, J = 7.6 Hz, 2H), 3.09 (t, J = 7.6 Hz, 2H); \(^1^C NMR (101 MHz, CDCl\textsubscript{3}) δ 198.22, 140.85, 139.50 (d, J\textsubscript{CF} = 1.1 Hz, 1C), 134.40 (q, J\textsubscript{CF} = 32.9 Hz, 1C), 128.61 (2C), 128.40 (2C), 128.36 (2C), 126.31, 125.70 (d, J\textsubscript{CF} = 3.7 Hz, 2C), 123.59 (q, J\textsubscript{CF} = 272.7 Hz, 1C), 40.75, 29.94.

MS (GC-MS) m/z: 278 (M+), 259, 213, 145, 105, 91, 77, 51.

4k 1-phenyl-3-(p-tolyl)propan-1-one.\textsuperscript{7}

\[
\text{O} \quad \text{C}_{\text{C}}
\]

^1^H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.94 (d, J = 7.4 Hz, 2H), 7.53 (t, J = 7.3 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.12 (q, J = 7.9 Hz, 4H), 3.26 (t, J = 7.7 Hz, 2H), 3.02 (t, J = 7.7 Hz, 2H), 2.31 (s, 3H); \(^1^C NMR (101 MHz, CDCl\textsubscript{3}) δ 199.36, 138.25, 136.93, 135.65, 133.08, 129.26 (2C), 128.64 (2C), 128.36 (2C), 128.09 (2C), 40.65, 29.76, 21.07.

MS (GC-MS) m/z: 224 (M+), 209, 119, 105, 91, 77, 65, 51.

4l 1,3-di-p-tolylpropan-1-one.\textsuperscript{9}

\[
\text{O} \quad \text{C}_{\text{C}}
\]

^1^H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.84 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.11 (q, J = 7.9 Hz, 4H), 3.23 (t, J = 7.7 Hz, 2H), 3.00 (t, J = 7.7 Hz, 2H), 2.38 (s, 3H), 2.31 (s, 3H); \(^1^C NMR (101 MHz, CDCl\textsubscript{3}) δ 199.02, 143.82, 138.35, 135.60, 134.47, 129.32 (2C), 129.24 (2C), 128.35 (2C), 128.22 (2C), 40.55, 29.85, 21.67, 21.06.

MS (GC-MS) m/z: 238 (M+), 223, 119, 105, 95, 77, 65, 51.

4m 1-(4-methoxyphenyl)-3-phenylpropan-1-one.\textsuperscript{7}

\[
\text{O} \quad \text{C}_{\text{C}}
\]

^1^H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.84 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.11 (q, J = 7.9 Hz, 4H), 3.23 (t, J = 7.7 Hz, 2H), 3.00 (t, J = 7.7 Hz, 2H), 2.38 (s, 3H), 2.31 (s, 3H); \(^1^C NMR (101 MHz, CDCl\textsubscript{3}) δ 199.02, 143.82, 138.35, 135.60, 134.47, 129.32 (2C), 129.24 (2C), 128.35 (2C), 128.22 (2C), 40.55, 29.85, 21.67, 21.06.

MS (GC-MS) m/z: 238 (M+), 223, 119, 105, 95, 77, 65, 51.
1H NMR (400 MHz, CDCl₃) δ 7.93 (d, J = 8.8 Hz, 2H), 7.32 – 7.26 (m, 2H), 7.24 (d, J = 7.1 Hz, 2H), 7.19 (t, J = 7.0 Hz, 1H), 6.90 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H), 3.27 – 3.19 (m, 2H), 3.04 (t, J = 7.7 Hz, 2H); 13C NMR (101 MHz, CDCl₃) δ 197.83, 163.48, 141.51, 130.34 (2C), 129.99, 128.54 (2C), 128.47 (2C), 126.12, 113.76 (2C), 55.48, 40.13, 30.36.

MS (GC-MS) m/z: 240 (M+), 209, 223, 135, 121, 107, 92, 77, 64, 51.

4n 1-(4-fluorophenyl)-3-(3-methoxyphenyl)propan-1-one.¹⁰

1H NMR (400 MHz, CDCl₃) δ 8.03 – 7.94 (m, 2H), 7.23 – 7.15 (m, 2H), 7.12 – 7.05 (m, 2H), 6.87 (ddd, J = 10.9, 8.7, 4.4 Hz, 2H), 3.81 (s, 3H), 3.25 – 3.18 (m, 2H), 3.07 – 2.99 (m, 2H); 13C NMR (101 MHz, CDCl₃) δ 198.37, 165.65 (d, J_{CF} = 254.2 Hz, 1C), 157.52, 133.44 (d, J_{CF} = 3.0 Hz, 1C), 130.74 (d, J_{CF} = 9.3 Hz, 2C), 130.19, 129.37, 127.61, 120.59, 115.58 (d, J_{CF} = 21.8 Hz, 2C), 110.29, 55.20, 38.88, 25.80.

MS (GC-MS) m/z: 258 (M+), 240, 225, 149, 135, 123, 108, 95, 77, 65, 51.

4o 3-(4-fluorophenyl)-1-(m-tolyl)propan-1-one (new compound).

1H NMR (400 MHz, CDCl₃) δ 7.74 (dd, J = 6.9, 4.6 Hz, 2H), 7.33 (dt, J = 14.9, 7.5 Hz, 2H), 7.22 – 7.13 (m, 2H), 7.01 – 6.89 (m, 2H), 3.24 (t, J = 7.5 Hz, 2H), 3.02 (t, J = 7.5 Hz, 2H), 2.38 (s, 3H); 13C NMR (101 MHz, CDCl₃) δ 199.21, 161.42 (d, J_{CF} = 243.7 Hz, 1C), 138.44, 137.01 (d, J_{CF} = 3.2 Hz, 1C), 136.88, 133.90, 129.88 (d, J_{CF} = 7.8 Hz, 2C), 128.58, 128.52, 125.26, 115.24 (d, J_{CF} = 21.1 Hz, 2C), 40.46, 29.31, 21.36.

MS (GC-MS) m/z: 242 (M+), 227, 133, 119, 109, 91, 77, 65, 51.

HRMS (EI) m/z calc'd for C₁₆H₁₅FO [M⁺] 242.1107, found 242.1108.

4p 3-(4-fluorophenyl)-1-(3-methoxyphenyl)propan-1-one (new compound).

1H NMR (400 MHz, CDCl₃) δ 7.42 (dd, J = 7.6, 0.9 Hz, 1H), 7.40 – 7.35 (m, 1H), 7.25 (t, J = 7.9 Hz, 1H), 7.15 – 7.05 (m, 2H), 7.00 (ddd, J = 8.2, 2.6, 0.8 Hz, 1H), 6.92 – 6.81 (m, 2H), 3.74 (s, 3H), 3.16 (t, J = 7.5 Hz, 2H), 2.93 (t, J = 7.5 Hz, 2H); 13C NMR (101 MHz, CDCl₃) δ 198.80, 161.41 (d, J_{CF} = 243.8 Hz, 1C), 159.89, 138.20, 136.89, 129.88 (d, J_{CF} = 7.8 Hz, 2C), 128.58, 128.52, 125.26, 115.24 (d, J_{CF} = 21.1 Hz, 2C), 40.46, 29.31, 21.36.

MS (GC-MS) m/z: 258 (M+), 227, 135, 121, 107, 92, 77, 64, 51.

HRMS (EI) m/z calc'd for C₁₆H₁₅FO₂ [M⁺] 258.1056, found 258.1055.

4q 3-(3,5-dimethoxyphenyl)-1-phenylpropan-1-one.
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.95 (d, $J = 8.0$ Hz, 2H), 7.55 (t, $J = 7.3$ Hz, 1H), 7.45 (t, $J = 7.6$ Hz, 2H), 6.41 (s, 2H), 6.32 (s, 1H), 3.77 (s, 6H), 3.29 (t, $J = 7.7$ Hz, 2H), 3.01 (t, $J = 7.7$ Hz, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 199.23, 160.90 (2C), 143.73, 136.84 (s), 133.11, 128.63 (2C), 128.06 (2C), 106.50 (2C), 98.06, 55.28 (2C), 40.30, 30.45.

MS (GC-MS) m/z: 270 (M+), 252, 165, 150, 135, 105, 91, 77, 64, 51.

HRMS (EI) m/z calcd for C$_{17}$H$_{18}$O$_3$ [M]$^+$ 270.1256, found 270.1255.

$^3$r 1-phenyl-3-(3,4,5-trimethoxyphenyl)propan-1-one (new compound).

$^3$s 3-(4-(dimethylamino)phenyl)-1-(4-methoxyphenyl)propan-1-one (new compound).

$^3$t 3-(benzo[d][1,3]dioxol-5-yl)-1-phenylpropan-1-one.

$^3$u methyl 3-phenylpropanoate.$^5$
1H NMR (400 MHz, CDCl$_3$) δ 7.26 (dd, $J$ = 10.4, 4.4 Hz, 2H), 7.20 – 7.13 (m, 3H), 3.62 (s, 3H), 2.93 (t, $J$ = 7.8 Hz, 2H), 2.64 – 2.57 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 173.27 (s), 140.58 (s), 128.54 (s), 128.31 (s), 126.31 (s), 51.55 (s), 35.71 (s), 30.99 (s).

MS (GC-MS) m/z: 164 (M+), 133, 104, 91, 77, 65, 51.

4v ethyl 3-phenylpropanoate.$^5$

1H NMR (400 MHz, CDCl$_3$) δ 7.29 – 7.22 (m, 2H), 7.22 – 7.13 (m, 3H), 4.10 (q, $J$ = 7.1 Hz, 2H), 2.93 (t, $J$ = 7.8 Hz, 2H), 2.63 – 2.55 (m, 2H), 1.20 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 172.84 (s), 140.63 (s), 128.50 (s), 128.34 (s), 126.26 (s), 60.37 (s), 35.96 (s), 31.02 (s), 14.23 (s).

MS (GC-MS) m/z: 178 (M+), 133, 104, 91, 79, 65, 51.

4w benzyl 3-phenylpropanoate.

1H NMR (400 MHz, CDCl$_3$) δ 7.37 – 7.23 (m, 7H), 7.18 (dd, $J$ = 8.9, 7.3 Hz, 3H), 5.10 (s, 2H), 2.96 (t, $J$ = 7.8 Hz, 2H), 2.67 (t, $J$ = 7.8 Hz, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 172.73, 140.46, 136.01, 128.58 (2C), 128.55 (2C), 128.35 (2C), 128.24 (2C), 126.32 (2C), 66.31, 35.93, 31.00.

MS (GC-MS) m/z: 240 (M+), 180, 149, 107, 91, 79, 65, 51.

HRMS (EI) m/z calc for C$_{16}$H$_{16}$O$_2$ [M]$^+$ 240.1150, found 240.1152.

4x 1-(4-methoxyphenyl)-3-(pyridin-2-yl)propan-1-one.$^{11}$

1H NMR (400 MHz, CDCl$_3$) δ 8.53 (s, 1H), 8.45 (d, $J$ = 4.1 Hz, 1H), 7.93 (d, $J$ = 8.9 Hz, 2H), 7.59 (d, $J$ = 7.9 Hz, 1H), 7.22 (dd, $J$ = 7.7, 4.9 Hz, 1H), 6.93 (d, $J$ = 8.9 Hz, 2H), 3.86 (s, 3H), 3.27 (t, $J$ = 7.5 Hz, 2H), 3.07 (t, $J$ = 7.4 Hz, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 197.03, 163.59, 149.86, 147.51, 136.85, 136.17, 130.28 (2C), 129.71, 123.40, 113.80 (2C), 55.49, 39.37, 27.27.

MS (GC-MS) m/z: 241 (M+), 224, 212, 135, 121, 107, 92, 77, 64, 55.

4y 4-phenylbutan-2-one.$^{9}$
\[ ^1\text{H NMR} \ (400 \text{ MHz, CDCl}_3) \delta \ 7.27 \ (t, \ J = 7.5 \text{ Hz}, \ 2\text{H}), \ 7.18 \ (t, \ J = 6.8 \text{ Hz}, \ 3\text{H}), \ 2.89 \ (t, \ J = 7.6 \text{ Hz}, \ 2\text{H}), \ 2.75 \ (t, \ J = 7.6 \text{ Hz}, \ 2\text{H}), \ 2.13 \ (s, \ 3\text{H}); \ \ ^{13}\text{C NMR} \ (101 \text{ MHz, CDCl}_3) \delta \ 207.96 \ (s), \ 141.01 \ (s), \ 128.51 \ (2\text{C}), \ 128.31 \ (2\text{C}), \ 126.13 \ (s), \ 45.19 \ (2\text{C}), \ 30.08 \ (2\text{C}), \ 29.75 \ (2\text{C}). \]

MS (GC-MS) \( m/z \): 148 (M+), 133, 115, 105, 91, 77, 65, 51.

4z 1,5-diphenylpent-4-en-1-one.\(^\text{12}\)

\[ \begin{array}{c}
\text{苯} \\
\downarrow \\
\text{\(4z\)} \\
\text{\(\text{1,5-diphenylpent-4-en-1-one.}\)\(^\text{12}\)}
\end{array} \]

\[^1\text{H NMR} \ (400 \text{ MHz, CDCl}_3) \delta \ 7.91 – 7.84 \ (m, \ 2\text{H}), \ 7.55 \ (t, \ J = 7.4 \text{ Hz}, \ 1\text{H}), \ 7.45 \ (t, \ J = 7.5 \text{ Hz}, \ 2\text{H}), \ 7.34 – 7.27 \ (m, \ 2\text{H}), \ 7.22 \ (dd, \ J = 7.1, 4.9 \text{ Hz}, \ 3\text{H}), \ 7.07 \ (dq, \ J = 20.9, 7.0 \text{ Hz}, \ 1\text{H}), \ 6.86 \ (d, \ J = 15.4 \text{ Hz}, \ 1\text{H}), \ 2.84 \ (q, \ J = 7.4 \text{ Hz}, \ 2\text{H}), \ 2.69 – 2.59 \ (m, \ 2\text{H}); \ ^{13}\text{C NMR} \ (101 \text{ MHz, CDCl}_3) \delta \ 190.92, \ 148.48, \ 140.83, \ 137.88, \ 132.68, \ 128.57 \ (2\text{C}), \ 128.53 \ (2\text{C}), \ 128.52 \ (2\text{C}), \ 128.43 \ (2\text{C}), \ 126.57, \ 126.22, \ 34.55, \ 34.52. \]

MS (GC-MS) \( m/z \): 236 (M+), 217, 145, 129, 115, 105, 91, 77, 65, 51.
5. ICP-AES Detection Report of the β-boration and reduction reaction liquids:

<table>
<thead>
<tr>
<th>部门</th>
<th>东北大学</th>
</tr>
</thead>
<tbody>
<tr>
<td>试样名称</td>
<td>GREHX</td>
</tr>
<tr>
<td>编号</td>
<td>YP20170554</td>
</tr>
<tr>
<td>试验日期</td>
<td>2017.11.14</td>
</tr>
</tbody>
</table>

试样结果：

1. 和2号相同
2. Co: <2mg/kg  Cr: <2mg/kg  Cu: <2mg/kg
3. Fe: <5mg/kg  Mn: <2mg/kg  Ni: <2mg/kg
4. Pb: <2mg/kg  Pt: <2mg/kg  Rh: <2mg/kg
5. Zn: <5mg/kg
6. VX未检出
6. $^1$H NMR of Isotope-Labeled Experiments

Sheme 2a: D-deuterated 4a-D 1,3-diphenylpropan-1-one-2,2,3-d$_3$

\[
\begin{array}{c}
\text{O} \\
\text{D} \\
\text{D} \\
\text{D} \\
\text{D}
\end{array}
\]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87 (s, 1H), 7.85 (s, 1H), 7.45 (t, $J = 7.3$ Hz, 1H), 7.35 (t, $J = 7.6$ Hz, 2H), 7.24 – 7.18 (m, 2H), 7.16 (d, $J = 7.4$ Hz, 2H), 7.11 (t, $J = 7.1$ Hz, 1H), 3.17 (d, $J = 6.9$ Hz, 0.15H), 2.95 (d, $J = 6.0$ Hz, 1.06H).

HR-MS(ToF MS El$^+$, 1.91e4): 213.1223 (M$^+$).

Sheme 2b: 3a 1,3-diphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one-2-d

\[
\begin{array}{c}
\text{B} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O}
\end{array}
\]

(20%)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94 (d, $J = 7.2$ Hz, 2H), 7.50 (t, $J = 7.4$ Hz, 1H), 7.40 (t, $J = 7.6$ Hz, 2H), 7.28 (dt, $J = 15.2$, 7.4 Hz, 4H), 7.19 – 7.10 (m, 1H), 3.54 (dd, $J = 18.3$, 10.9 Hz, 1H), 3.39 (dd, $J = 18.3$, 5.0 Hz, 0.8H), 2.80 (dd, $J = 10.9$, 5.2 Hz, 1H), 1.24 (s, 6H), 1.16 (s, 6H).

Sheme 2c: 3a 1,3-diphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one

\[
\begin{array}{c}
\text{B} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O}
\end{array}
\]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85 (d, $J = 7.3$ Hz, 2H), 7.42 (t, $J = 7.4$ Hz, 1H), 7.32 (t, $J = 7.6$ Hz, 2H), 7.24 – 7.15 (m, 4H), 7.10 – 7.00 (m, 1H), 3.45 (dd, $J = 18.3$, 10.9 Hz, 1H), 3.31 (dd, $J = 18.3$, 5.0 Hz, 1H), 2.70 (dd, $J = 10.9$, 5.0 Hz, 1H), 1.15 (s, 6H), 1.07 (s, 6H).

Sheme 2d: 3a 1,3-diphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one

\[
\begin{array}{c}
\text{B} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{O}
\end{array}
\]

(15%)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.96 (d, $J = 7.2$ Hz, 2H), 7.53 (t, $J = 7.4$ Hz, 1H), 7.43 (t, $J = 7.6$ Hz, 2H), 7.33 – 7.25 (m, 4H), 7.19 – 7.13 (m, 1H), 3.55 (dd, $J = 18.3$, 10.9 Hz, 1H), 3.42 (dd, $J = 18.3$, 5.0 Hz, 0.85H), 2.80 (dd, $J = 10.9$, 5.1 Hz, 1H), 1.24 (s, 6H), 1.16 (s, 6H).

References
$^1$H NMR spectra of 3a

$^{13}$C NMR spectra of 3a
$^1H$ NMR spectra of 3b

$^{13}C$ NMR spectra of 3b
$^1H$ NMR spectra of $3c$

$^{13}C$ NMR spectra of $3c$
$^1H$ NMR spectra of 3d

$^{13}C$ NMR spectra of 3d
$^1$H NMR spectra of $3e$

$^{13}$C NMR spectra of $3e$
$^1$H NMR spectra of 3f

$^{13}$C NMR spectra of 3f
$^1H$ NMR spectra of 3g

$^{13}C$ NMR spectra of 3g
$^1H$ NMR spectra of 3h

$^{13}C$ NMR spectra of 3h
$^1$H NMR spectra of 3i

$^{13}$C NMR spectra of 3i
$^1$H NMR spectra of 3j

$^{13}$C NMR spectra of 3j
$^1$H NMR spectra of 3k

$^{13}$C NMR spectra of 3k
$^1$H NMR spectra of 3l

$^{13}$C NMR spectra of 3l
$^1$H NMR spectra of 3m

$^{13}$C NMR spectra of 3m
$^{1}H$ NMR spectra of 3n

$^{13}C$ NMR spectra of 3n
$^1\text{H}$ NMR spectra of 3o

$^{13}\text{C}$ NMR spectra of 3o
$^1$H NMR spectra of 3p

$^{13}$C NMR spectra of 3p
$^1$H NMR spectra of 3q

$^{13}$C NMR spectra of 3q
$^1$H NMR spectra of 3r

$^{13}$C NMR spectra of 3r
$^1H$ NMR spectra of $3s$

$^{13}C$ NMR spectra of $3s$
$^1$H NMR spectra of 4a

$^{13}$C NMR spectra of 4a
$^1$H NMR spectra of 4b

$^{13}$C NMR spectra of 4b
$^1$H NMR spectra of 4c

$^{13}$C NMR spectra of 4c
$^1H$ NMR spectra of 4d

$^{13}C$ NMR spectra of 4d
$^1$H NMR spectra of 4e

$^{13}$C NMR spectra of 4e
$^1H$ NMR spectra of 4f

$^{13}C$ NMR spectra of 4f
$^1$H NMR spectra of 4g

$^{13}$C NMR spectra of 4g
$^1$H NMR spectra of 4h

$^{13}$C NMR spectra of 4h
$^1$H NMR spectra of 4i

$^{13}$C NMR spectra of 4i
$^1$H NMR spectra of 4j

$^{13}$C NMR spectra of 4j
$^1$H NMR spectra of 4k

$^{13}$C NMR spectra of 4k
$^1H$ NMR spectra of 4l

$^{13}C$ NMR spectra of 4l
$^1$H NMR spectra of 4m

$^{13}$C NMR spectra of 4m
$^1\text{H}$ NMR spectra of 4n

$^{13}\text{C}$ NMR spectra of 4n
$^1\text{H}$ NMR spectra of 4o

$^{13}\text{C}$ NMR spectra of 4o
$^1$H NMR spectra of 4p

$^{13}$C NMR spectra of 4p
$^1$H NMR spectra of 4q

$^{13}$C NMR spectra of 4q
$^1H$ NMR spectra of 4r

$^{13}C$ NMR spectra of 4r
$^1$H NMR spectra of 4s

$^{13}$C NMR spectra of 4s
$^1$H NMR spectra of 4t

$^{13}$C NMR spectra of 4t
$^1$H NMR spectra of 4u

$^{13}$C NMR spectra of 4u
$^1$H NMR spectra of 4v

$^{13}$C NMR spectra of 4v
$^1$H NMR spectra of 4w

$^{13}$C NMR spectra of 4w
$^1H$ NMR spectra of 4x

$^{13}C$ NMR spectra of 4x
$^1H$ NMR spectra of 4y

$^{13}C$ NMR spectra of 4y
$^1H$ NMR spectra of $4z$

$^{13}C$ NMR spectra of $4z$
$^1$H NMR spectra of 4a of Scheme 2a

$^1$H NMR spectra of 3a of Scheme 2b
$^1H$ NMR spectra of 3a of Scheme 2c

$^1H$ NMR spectra of 3a of Scheme 2d