Supporting Information

Alkylation of Styrenes via Direct C(sp³)-Br/C(sp²)-H Functionalization Mediated by Photoredox and Copper Cooperative Catalysis

Xin Yong,† ¶ Ya-Fei Han, † Yang Li,*† Ren-Jie Song,*† and Jin-Heng Li*,†,‡

†Key Laboratory of Jiangxi Province for Persistent Pollutants Control and Resources Recycle, Nanchang Hangkong University, Nanchang 330063, China and ‡State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, China

liyang8825490@126.com, srj0731@hnu.edu.cn and jhli@hnu.edu.cn

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(A) Typical experimental procedure

To a Schlenk tube were added alkenes 1 (0.2 mmol), ω-carbonyl alkyl bromides 2 (0.4 mol), N,N-Disubstituted Anilines 3 (0.4 mmol), CuCl (10 mol%), [Ru(bpy)₃]Cl₂·6H₂O (2 mol%), K₂CO₃ (2 equiv) and MeCN (2 mL), the tube was then charged with argon. The mixture was stirred at room temperature until complete consumption of starting material as monitored by TLC and/or GC-MS analysis (about 2 h). After the reaction was finished, the reaction mixture was concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (Petroleum Ether/ethyl acetate) to afford the desired product 4.

(B) Analytical data

Methyl 4-(4-(dimethylamino)phenyl)-4-(4-methoxyphenyl)-2,2-dimethyl butanoate (4aaa):

62.7 mg, 85% yield; Colorless oil; Rᶠ = 0.50 (Petroleum Ether/EtOAc = 7:1); ¹H NMR (400 MHz, CDCl₃) δ: 7.14 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 6.77 (d, J = 8.4 Hz, 2H), 6.63 (d, J = 8.0 Hz, 2H), 3.87 (t, J = 7.2 Hz, 1H), 3.74 (s, 3H), 3.70-3.65 (m, 2H), 2.87 (s, 6H), 2.39-2.29 (m, 2H), 1.15 (s, 6H), 1.10 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 177.4, 157.6, 149.0, 138.1, 133.9, 128.7, 128.3, 113.6, 112.8, 60.1, 55.2, 46.7, 46.3, 42.0, 40.8, 26.2, 25.9, 14.0; LRMS (EI, 70eV) m/z (%): 369 (M⁺, 21), 240 (100), 225 (9); HRMS m/z (ESI) calcd for C₂₃H₃₂NO₃ ([M+H]+) 370.2377, found 370.2386.
Ethyl 4-(4-(dimethylamino)phenyl)-4-(4-methoxyphenyl)-2,2-dimethylbutanoate (4aab):

53.8 mg, 76% yield; Colorless oil; R<sub>f</sub> = 0.50 (Petroleum Ether/EtOAc = 7:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.14 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 6.77 (d, J = 8.4 Hz, 2H), 6.64 (d, J = 8.4 Hz, 2H), 3.87 (t, J = 6.8 Hz, 1H), 3.74 (s, 3H), 3.24 (s, 3H), 2.87 (s, 6H), 2.39-2.29 (m, 2H), 1.17 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 177.8, 157.6, 149.0, 138.0, 133.8, 128.7, 128.3, 113.6, 112.8, 55.2, 51.3, 46.8, 46.3, 42.0, 40.8, 26.2, 25.9; LRMS (EI, 70eV) m/z (%): 355 (M<sup>+</sup>, 21), 240 (100), 225 (9); HRMS m/z (ESI) calcd for C<sub>22</sub>H<sub>30</sub>NO<sub>3</sub> ([M+H]<sup>+</sup>) 356.2220, found 356.2230.

Ethyl 4-(4-(dimethylamino)phenyl)-2,2-difluoro-4-(4-methoxyphenyl)butanoate (4aac):

59.5 mg, 79% yield; Yellow oil; R<sub>f</sub> = 0.50 (Petroleum Ether/EtOAc = 8:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.13 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 8.4 Hz, 2H), 6.79 (d, J = 8.4 Hz, 2H), 6.66 (d, J = 8.4 Hz, 2H), 4.13 (t, J = 7.2 Hz, 1H), 3.88-3.83 (m, 2H), 3.75 (s, 3H), 2.88 (s, 6H), 2.86-2.78 (m, 2H), 1.17 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 164.0, 158.1, 149.2, 135.8, 131.6, 128.6, 128.2, 113.8, 113.0, 62.7, 55.2, 43.1, 43.1, 43.0, 40.8, 40.7, 40.5, 13.7; <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ: -104.48; LRMS (EI, 70eV) m/z (%): 377 (M<sup>+</sup>, 25), 240 (100), 225 (10); HRMS m/z (ESI) calcd for C<sub>21</sub>H<sub>26</sub>F<sub>2</sub>NO<sub>3</sub> ([M+H]<sup>+</sup>) 378.1875, found 378.1883.
Ethyl 1-(2-(4-(dimethylamino)phenyl)-2-(4-methoxyphenyl)ethyl)cyclobutane-1-carboxylate (4aad):

38.6 mg, 50% yield; Colorless oil; Rf = 0.50 (Petroleum Ether/EtOAc = 8:1); 1H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.13-7.01 (m, 4H), 6.77 (d, J = 8.4 Hz, 2H), 6.65 (d, J = 8.8 Hz, 2H), 3.80-3.75 (m, 2H), 3.74 (s, 3H), 3.72 (t, J = 3.6 Hz, 1H), 2.87 (s, 6H), 2.55 (d, J = 7.2 Hz, 2H), 2.34-2.26 (m, 2H), 1.89-1.76 (m, 4H), 1.12 (t, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl<sub>3</sub>) δ: 176.8, 157.8, 149.1, 137.8, 133.6, 128.8, 128.4, 113.6, 112.8, 60.1, 55.2, 47.8, 46.4, 44.4, 40.8, 22.7, 15.9, 14.0; LRMS (EI, 70eV) m/z (%): 381 (M<sup>+</sup>, 12), 240 (100), 121 (2); HRMS m/z (ESI) calcd for C<sub>24</sub>H<sub>32</sub>N<sub>2</sub>O<sub>3</sub> ([M+H]<sup>+</sup>) 382.2377, found 382.2384.

4-(1-(4-methoxyphenyl)-2-(5-nitro-1,3-dioxan-5-yl)ethyl)-N,N-dimethylaniline (4aae):

41.7 mg, 54% yield; Yellow oil; Rf = 0.50 (Petroleum Ether/EtOAc = 2:1); 1H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.10 (d, J = 9.0 Hz, 2H), 7.04 (d, J = 8.5 Hz, 2H), 6.80 (d, J = 9.0 Hz, 2H), 6.64 (d, J = 8.5 Hz, 2H), 4.89 (d, J = 6.0 Hz, 1H), 4.57 (d, J = 6.5 Hz, 1H), 4.42 (d, J = 12.5 Hz, 2H), 3.75 (s, 3H), 3.72 (t, J = 6.5 Hz, 1H), 3.57-3.53 (m, 2H), 2.89 (s, 6H), 2.45-2.43 (m, 2H); 13C NMR (125 MHz, CDCl<sub>3</sub>) δ: 158.22, 149.43, 135.80, 130.71, 128.20, 127.90, 114.03, 112.72, 93.64, 86.97, 71.06, 70.87, 55.17, 44.55, 40.47, 40.10; LRMS (EI, 70eV) m/z (%): 386 (M<sup>+</sup>, 13), 240 (100), 120 (21); HRMS m/z (ESI) calcd for C<sub>21</sub>H<sub>27</sub>N<sub>2</sub>O<sub>5</sub> ([M+H]<sup>+</sup>) 387.1914, found 387.1919.

S4
Methyl 4-(4-(dimethylamino)phenyl)-4-(4-methoxyphenyl)-2-methylbutanoate (4aaf):

60.8 mg, 89% yield; dr = 1:1.1; Yellow oil; R_f = 0.50
(Petroleum Ether/EtOAc = 7:1); 1H NMR (400 MHz, CDCl_3) δ: 7.05 (t, J = 8.0 Hz, 2H), 7.00 (t, J = 8.4 Hz, 2H), 6.72 (d, J = 8.0 Hz, 2H), 6.59 (d, J = 8.4 Hz, 2H), 3.75 (t, J = 8.0 Hz, 1H), 3.67 (s, 3H), 3.54 (s, 3H), 2.81 (s, 6H), 2.40-2.22 (m, 2H), 1.95-1.87 (m, 1H), 1.08 (d, J = 6.8 Hz, 3H); 13C NMR (100 MHz, CDCl_3) δ: 177.2 (2C), 157.8, 149.1 (2C), 137.4, 137.0, 132.8, 132.3, 128.6, 128.3, 113.7, 112.8 (2C), 55.2, 51.5, 47.0, 46.9, 40.7 (2C), 39.9, 39.8, 37.5, 37.5, 17.3, 17.2; LRMS (EI, 70eV) m/z (%): 341 (M^+, 10), 195 (98), 167 (100), 117 (49), 91(74); HRMS m/z (ESI) calcd for C_{21}H_{28}NO_3 ([M+H]^+) 342.2064 , found 342.2075.

Methyl 2-(2-(4-(dimethylamino)phenyl)-2-(4-methoxyphenyl)ethyl)hexanoate (4aag):

62.8 mg, 82% yield; dr =1:1.1; Colorless oil; R_f = 0.50
(Petroleum Ether/EtOAc = 8:1); 1H NMR (500 MHz, CDCl_3) δ: 7.13-7.11 (m, 2H), 7.07-7.05 (m, 2H), 6.82-6.78 (m, 2H), 6.68-6.65 (m, 2H), 3.76 (d, J = 6.0 Hz, 4H), 3.61 (d, J = 3.0 Hz, 3H), 2.90 (s, 3H), 2.89 (s, 3H), 2.36-2.26 (m, 2H), 2.10-2.04 (m, 1H), 1.62-1.57 (m, 4H), 1.52-1.45 (m, 2H), 0.84 (t, J = 7.0 Hz, 3H); 13C NMR (125 MHz, CDCl_3) δ: 176.8 (2C), 157.8, 157.7, 149.1 (2C), 137.6, 137.0, 132.5, 130.3 (2C), 128.8, 128.6, 128.4, 128.2, 113.8, 113.7, 112.8, 55.2, 55.2, 51.3 (2C), 47.4, 47.3, 43.7 (2C), 40.8, 40.7, 38.5 (2C), 32.5, 32.4, 29.3, 22.6, 22.6, 13.9; LRMS (EI, 70eV) m/z
(%): 383 (M+, 17), 240 (100), 225 (8); HRMS m/z (ESI) calcd for C_{24}H_{34}NO_{3} ([M+H]^+) 384.2533, found 384.2542.

**Diethyl 2-(2-(4-(dimethylamino)phenyl)-2-(4-methoxyphenyl)ethyl)malonate (4aah):**

41.3 mg, 50% yield; Colorless oil; R_f = 0.50 (Petroleum Ether/EtOAc = 5:1); ^1H NMR (400 MHz, CDCl_3) δ: 7.06 (d, J = 7.2 Hz, 2H), 7.01 (d, J = 7.2 Hz, 2H), 6.73 (d, J = 7.2 Hz, 2H), 6.59 (d, J = 7.2 Hz, 2H), 4.12-4.06 (m, 4H), 3.74 (t, J = 7.6 Hz, 1H), 3.68 (s, 3H), 3.17 (t, J = 6.0 Hz, 1H), 2.82 (s, 6H), 2.50 (t, J = 7.2 Hz, 2H), 1.17 (t, J = 6.4 Hz, 6H); ^13C NMR (100 MHz, CDCl_3) δ: 169.49, 157.88, 149.17, 136.35, 131.62, 128.68, 128.35, 113.76, 112.78, 61.26, 55.15, 50.35, 46.74, 40.64, 34.77, 14.02; LRMS (EI, 70eV) m/z (%): 413 (M+, 17), 253 (38), 240 (100); HRMS m/z (ESI) calcd for C_{24}H_{32}NO_{5} ([M+H]^+) 414.2275, found 414.2286.

**Dimethyl 2-(2-(4-(dimethylamino)phenyl)-2-(4-methoxyphenyl)ethyl)malonate (4aai):**

40.0 mg, 52% yield; Colorless oil; R_f = 0.50 (Petroleum Ether/EtOAc = 4:1); ^1H NMR (400 MHz, CDCl_3) δ: 7.13 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 8.4 Hz, 2H), 6.81 (d, J = 8.4 Hz, 2H), 6.67 (d, J = 8.4 Hz, 2H), 3.79 (t, J = 8.4 Hz, 1H), 3.76 (s, 3H), 3.69 (s, 6H), 3.29 (t, J = 7.2 Hz, 1H), 2.90 (s, 6H), 2.58 (t, J = 7.6 Hz, 2H); ^13C NMR (100 MHz, CDCl_3) δ: 169.9, 158.0, 149.2, 136.3, 131.6, 128.7, 128.4, 113.9, 112.9, 55.2, 52.4, 50.1, 46.9, 40.7, 34.9; LRMS (EI, 70eV) m/z (%): 385
(M⁺, 19), 253 (17), 240 (100); HRMS m/z (ESI) calcd for C_{22}H_{28}NO_5 ([M+H]^+) 386.1962, found 386.1975.

**Ethyl 4-(4-(dimethylamino)phenyl)-4-(4-methoxyphenyl)butanoate (4aaaj):**

![Chemical Structure]

34.8 mg, 51% yield; Yellow oil; Rf = 0.50 (Petroleum Ether/EtOAc = 8:1); ¹H NMR (400 MHz, CDCl₃) δ: 7.14 (d, J = 7.2 Hz, 2H), 7.08 (d, J = 7.6 Hz, 2H), 6.81 (d, J = 7.6 Hz, 2H), 6.67 (d, J = 7.2 Hz, 2H), 6.67 (d, J = 7.2 Hz, 2H), 4.11-4.06 (m, 2H), 3.80-3.76 (m, 4H), 2.89 (s, 6H), 2.35-2.26 (m, 4H), 1.22 (t, J = 6.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 173.67, 157.76, 149.07, 149.07, 137.15, 132.53, 128.62, 128.39, 113.72, 112.78, 60.19, 55.17, 48.66, 40.70, 32.94, 30.93, 14.20; LRMS (EI, 70eV) m/z (%): 341 (M⁺, 19), 240 (100), 225 (10); HRMS m/z (ESI) calcd for C_{21}H_{28}NO_3 ([M+H]^+) 342.2064, found 342.2057.

**Ethyl 4-(4-(diethylamino)phenyl)-4-(4-methoxyphenyl)-2,2-dimethylbutanoate (4aba):**

42.1 mg, 53% yield; Yellow oil; Rf = 0.50 (Petroleum Ether/EtOAc = 8:1); ¹H NMR (400 MHz, CDCl₃) δ: 7.08 (d, J = 8.8 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 6.70 (d, J = 8.4 Hz, 2H), 6.49 (d, J = 8.8 Hz, 2H), 3.78 (t, J = 7.2 Hz, 1H), 3.67 (s, 3H), 3.59-3.57 (m, 2H), 3.23-3.18 (m, 4H), 2.31-2.21 (m, 2H), 1.08 (s, 3H), 1.07 (s, 3H), 1.05-1.00 (m, 9H); ¹³C NMR (100 MHz, CDCl₃) δ: 177.4, 157.7, 146.2, 138.3, 132.7, 128.8, 128.5, 113.6, 112.0, 60.1, 55.2, 46.8, 46.3, 44.3, 42.0, 26.1,
25.9, 14.0, 12.6; LRMS (EI, 70eV) m/z (%): 397 (M⁺, 24), 268 (100), 134 (7); HRMS m/z (ESI) calcd for C₂₅H₃₆NO₃ ([M+H⁺]) 398.2690, found 398.2698.

Ethyl 4-(4-(diethylamino)phenyl)-4-(4-methoxyphenyl)-2,2-dimethylbutanoate (4aca):

62.8 mg, 74% yield; Yellow oil; Rₑ = 0.50 (Petroleum Ether/EtOAc = 9:1); ¹H NMR (400 MHz, CDCl₃) δ: 7.16 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 8.8 Hz, 2H), 6.77 (d, J = 8.4 Hz, 2H), 6.51 (d, J = 8.4 Hz, 2H), 6.34 (t, J = 6.8 Hz, 1H), 3.74 (s, 3H), 3.68-3.63 (m, 2H), 3.16 (t, J = 3.6 Hz, 4H), 2.38-2.28 (m, 2H), 1.60-1.50 (m, 6H), 1.16 (s, 2H), 1.14 (s, 2H), 1.09 (t, J = 5.2 Hz, 3H), 0.89 (t, J = 7.6 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ: 177.5, 157.6, 146.5, 138.2, 132.3, 128.8, 128.3, 113.6, 111.7, 60.1, 55.2, 53.0, 46.8, 46.3, 42.0, 26.1, 26.0, 20.4, 14.0, 11.4; LRMS (EI, 70eV) m/z (%): 425 (M⁺, 31), 396 (63), 296 (100); HRMS m/z (ESI) calcd for C₂₇H₄₀NO₃ ([M+H⁺]) 426.3003 , found 426.3013.

Ethyl 4-(4-methoxyphenyl)-2,2-dimethyl-4-(4-(methyl(phenyl)amino)phenyl)butanoate (4ada):

45.7 mg, 53% yield; Yellow oil; Rₑ = 0.50 (Petroleum Ether/EtOAc = 7:1); ¹H NMR (400 MHz, CDCl₃) δ: 7.15-7.06 (m, 6H), 6.87-6.79 (m, 5H), 6.72 (d, J = 7.2 Hz, 2H), 3.87-3.81 (m, 1H), 3.67 (s, 3H), 3.64-3.60 (m, 2H), 3.17 (s, 3H), 2.36-2.24 (m, 2H), 1.09 (s, 6H), 1.04 (t, J = 6.0 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ: 177.27, 157.75, 148.97, 146.85, 139.07, 137.48, 129.00, 128.75, 128.42,
121.26, 120.39, 119.18, 113.61, 60.12, 55.16, 46.67, 46.53, 41.91, 40.17, 26.09, 25.95, 13.95; HRMS m/z (ESI) calcd for C$_{28}$H$_{34}$NO$_3$ ([M+H]$^+$) 432.2533, found 432.2524.

**Ethyl 4-(4-methoxyphenyl)-2,2-dimethyl-4-(4-(piperidin-1-yl)phenyl)butanoate (4aea):**

48.4 mg, 59% yield; Yellow oil; $R_f = 0.50$ (Petroleum Ether/EtOAc = 8:1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.16-7.07 (m, 4H), 6.83-6.75 (m, 4H), 3.87 (t, $J = 7.2$ Hz, 1H), 3.74 (s, 3H), 3.70-3.65 (m, 2H), 3.06 (t, $J = 5.2$ Hz, 4H), 2.38-2.29 (m, 2H), 1.70-1.64 (m, 4H), 1.56-1.50 (m, 2H), 1.14 (s, 6H), 1.10 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 177.4, 157.8, 150.5, 138.0, 136.4, 128.8, 128.3, 116.5, 113.6, 60.1, 55.2, 50.9, 46.5, 42.1, 26.2, 25.9 (2C), 24.3, 14.0; LRMS (EI, 70eV) m/z (%): 409 (M$^+$, 12), 280 (100), 264 (7); HRMS m/z (ESI) calcd for C$_{26}$H$_{36}$NO$_3$ ([M+H]$^+$) 410.2690, found 410.2703.

**Ethyl 4-(4-methoxyphenyl)-2,2-dimethyl-4-(4-morpholinophenyl)butanoate (4afa):**

37.8 mg, 46% yield; Yellow oil; $R_f = 0.50$ (Petroleum Ether/EtOAc = 5:1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.15-7.12 (m, 4H), 6.80-6.76 (m, 4H), 3.89 (t, $J = 7.2$ Hz, 1H), 3.82 (t, $J = 4.8$ Hz, 4H), 3.74 (s, 3H), 3.71-3.65 (m, 2H), 3.08 (t, $J = 4.8$ Hz, 4H), 2.39-2.29 (m, 2H), 1.14 (s, 6H), 1.10 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 177.3, 157.8, 149.5, 137.8, 137.3, 128.7, 128.4, 115.7, 113.7, 66.9, 60.1, 55.2, 49.5, 46.6, 46.5, 42.0, 26.1, 25.9, 14.0; LRMS (EI, 70eV) m/z
Ethyl 4-(4-methoxyphenyl)-2,2-dimethyl-4-(4-(4-propionylpiperazin-1-y1)phenyl)butanoate (4aga):

33.3 mg, 36% yield; Yellow oil; R_f = 0.50 (Petroleum Ether/EtOAc = 2:1); ^1H NMR (400 MHz, CDCl_3) δ: 7.16-7.12 (m, 4H), 6.83-6.76 (m, 4H), 3.89 (t, J = 7.2 Hz, 1H), 3.77-3.73 (m, 5H), 3.70-3.65 (m, 2H), 3.58 (t, J = 5.2 Hz, 2H), 3.10-3.05 (m, 4H), 2.40-2.33 (m, 4H), 1.25-1.16 (m, 3H), 1.14 (s, 6H), 1.10 (t, J = 7.2 Hz, 3H); ^13C NMR (100 MHz, CDCl_3) δ: 177.3, 172.3, 157.8, 149.1, 137.9, 137.7, 128.7, 128.5, 116.7, 113.7, 60.1, 55.2, 49.9, 49.6, 46.5, 45.4, 42.0, 41.5, 26.5, 26.1, 26.0, 14.0, 9.5; LRMS (EI, 70eV) m/z (%): 466 (M^+, 23), 337 (100), 126 (9); HRMS m/z (ESI) calcd for C_{28}H_{39}N_{2}O_{4} ([M+H]^+) 467.2904, found 467.2918.

Ethyl 4-(4-(dimethylamino)-2,6-dimethylphenyl)-4-(4-methoxyphenyl)-2,2-dimethylbutanoate (4aha):

54.7 mg, 68% yield; Yellow oil; R_f = 0.50 (Petroleum Ether/EtOAc = 10:1); ^1H NMR (400 MHz, CDCl_3) δ: 7.07 (d, J = 8.8 Hz, 2H), 6.76 (d, J = 8.0 Hz, 2H), 6.40 (s, 2H), 4.36-4.33 (m, 1H), 3.88-3.80 (m, 1H), 3.75 (d, J = 1.2 Hz, 3H), 3.72-3.61 (m, 1H), 2.89 (d, J = 0.8 Hz, 6H), 2.56-2.17 (m, 6H), 2.10-2.07 (m, 2H), 1.26 (s, 3H), 1.13 (s, 3H), 1.11-1.07 (m, 3H); ^13C NMR (100 MHz, CDCl_3) δ: 177.6, 157.2,
148.6, 137.1, 130.7, 128.2, 113.2, 60.3, 55.2, 44.2, 42.6, 40.7, 39.1, 26.3, 26.0, 22.1, 13.9; LRMS (EI, 70eV) m/z (%): 397 (M+, 22), 268 (100), 134 (10); HRMS m/z (ESI) calcd for C_{25}H_{36}NO_{3} ([M+H]^+) 398.2690, found 398.2683.

**Ethyl 4-(4-methoxyphenyl)-2,2-dimethyl-4-(1-methyl-1,2,3,4-tetrahydroquinolin-6-yl)butanoate (4aia):**

49.0 mg, 62% Yellow oil; R_f = 0.50 (Petroleum Ether/EtOAc = 9:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ: 7.08 (d, J = 8.0 Hz, 2H), 6.84 (d, J = 8.0 Hz, 1H), 6.71-6.68 (m, 3H), 6.40 (d, J = 8.0 Hz, 1H), 3.75-3.71 (m, 1H), 3.66 (s, 3H), 3.62-3.56 (m, 2H), 3.06-3.03 (m, 2H), 2.73 (s, 3H), 2.63-2.59 (m, 2H), 2.32-2.17 (m, 2H), 1.85-1.79 (m, 2H), 1.08 (s, 3H), 1.06 (s, 3H), 1.02 (t, J = 9.0 Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ: 177.39, 157.53, 144.94, 137.94, 133.53, 128.72, 128.10, 125.89, 122.66, 113.47, 110.93, 60.04, 55.12, 51.23, 46.66, 46.33, 41.87, 39.18, 27.77, 26.33, 25.66, 22.45, 13.91; HRMS m/z (ESI) calcd for C_{25}H_{34}NO_{3} ([M+H]^+) 396.2533, found 396.2537.

**Ethyl 4-(4-(dimethylamino)phenyl)-4-(4-ethoxyphenyl)-2,2-dimethylbutanoate (4baa):**

70.6 mg, 92% yield; Yellow oil; R_f = 0.50 (Petroleum Ether/EtOAc = 8:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ: 7.13 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 12.0 Hz, 2H), 676 (d, J = 8.8 Hz, 2H), 6.64 (d, J = 8.8 Hz, 2H), 3.99-3.94 (m, 2H), 3.86 (t, J = 7.2 Hz, 1H), 3.71-3.66 (m, 2H), 2.87 (s, 6H), 2.35-2.30 (m, 2H), 1.36 (t, J
\[ \text{S12} \]

= 6.8 Hz, 3H), 1.14 (s, 6H), 1.10 (t, \( J = 7.2 \) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \):

177.4, 157.1, 149.0, 138.1, 134.0, 128.7, 128.3, 114.3, 112.9, 63.4, 60.1, 46.7, 46.4,
42.0, 40.8, 26.2, 25.9, 14.9, 14.0; LRMS (EI, 70eV) \( m/z \) (%): 383 (M\(^+\), 16), 254 (100),
226 (4); HRMS \( m/z \) (ESI) calcd for C\(_{24}\)H\(_{34}\)NO\(_3\) ([M+H\(^+\)]\(^+\)) 384.2533, found 384.2545.

**Ethyl 4-(4-(dimethylamino)phenyl)-2,2-dimethyl-4-(\( p \)-tolyl)butanoate (4caa):**

![Ethyl 4-(4-(dimethylamino)phenyl)-2,2-dimethyl-4-(\( p \)-tolyl)butanoate (4caa)](image)

43.9 mg, 62% yield; Yellow oil; \( R_f = 0.50 \) (Petroleum Ether/EtOAc = 9:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \): 7.

06-6.95 (m, 6H), 6.56 (d, \( J = 8.8 \) Hz, 2H), 3.80 (t, \( J = 6.8 \) Hz, 1H), 3.63-3.57 (m, 2H), 2.79 (s, 6H), 2.28 (t, \( J = 3.6 \) Hz, 2H), 2.18 (s, 3H), 1.07 (s, 6H), 1.02 (t, \( J = 7.2 \) Hz, 3H); \(^{13}\)C

NMR (100 MHz, CDCl\(_3\)) \( \delta \): 177.4, 149.1, 143.1, 135.1, 133.8, 128.9, 128.4, 127.6, 112.9, 60.1, 46.9, 46.5, 42.1, 40.8, 26.1, 26.0, 20.9, 13.9; LRMS (EI, 7

0eV) \( m/z \) (%): 353 (M\(^+\), 17), 237 (12), 224 (100); HRMS \( m/z \) (ESI) calcd for C\(_{23}\)H\(_{32}\)NO\(_2\) ([M+H\(^+\)]\(^+\)) 354.2428, found 354.2440.

**Ethyl 4-(4-chlorophenyl)-4-(4-(dimethylamino)phenyl)-2,2-dimethylbutanoate (4daa):**

![Ethyl 4-(4-chlorophenyl)-4-(4-(dimethylamino)phenyl)-2,2-dimethylbutanoate (4daa)](image)

19.4 mg, 26% Yellow oil; \( R_f = 0.50 \) (Petroleum Ether/EtOAc = 7:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \): 7.24

-7.14 (m, 4H), 7.07 (d, \( J = 7.2 \) Hz, 2H), 6.64 (d, \( J = 7.6 \) Hz, 2H), 3.93-3.84 (m, 1H), 3.72-3.62 (m, 2H),
2.88 (s, 6H), 2.34-2.33 (m, 2H), 1.15 (s, 6H), 1.10 (t, \( J = 5.2 \) Hz, 3H); \(^{13}\)C

NMR (100 MHz, CDCl\(_3\)) \( \delta \): 177.24, 149.11, 144.44, 132.75, 131.43, 129.15, 1
28.28, 128.26, 112.71, 60.18, 46.58, 46.29, 41.94, 40.69, 26.28, 25.78, 13.93; HRMS m/z (ESI) calcd for C_{22}H_{29}ClNO \_2 ([M+H]^+) 374.1881, found 374.1884.

**Ethyl 4-(4-(dimethylamino)phenyl)-2,2-dimethyl-4-(m-tolyl)butanoate (4eaa):**

23.3 mg, 33% yield; Yellow oil; R_f = 0.50 (Petroleum Ether/EtOAc = 9:1); ^1H NMR (400 MHz, CDCl\_3) δ: 7.13-7.04 (m, 5H), 6.91 (d, J = 7.2 Hz, 1H), 6.64 (d, J = 8.8 Hz, 2H), 3.87 (t, J = 7.2 Hz, 1H), 3.69-3.64 (m, 2H), 2.87 (s, 6H), 2.37-2.35 (m, 2H), 2.28 (s, 3H), 1.15 (s, 6H), 1.09 (t, J = 7.2 Hz, 3H); ^13C NMR (100 MHz, CDCl\_3) δ: 177.4, 149.1, 146.0, 137.7, 133.6, 128.6, 128.4, 128.1, 126.6, 124.8, 112.9, 60.1, 47.2, 46.5, 42.1, 40.8, 26.0, 21.5, 14.0; LRMS (EI, 70eV) m/z (%): 353 (M\^+, 20), 237 (13), 224 (100); HRMS m/z (ESI) calcd for C_{23}H_{32}NO\_2 ([M+H\^+]^+) 354.2428, found 354.2439.

**Ethyl 4-(4-(dimethylamino)phenyl)-2,2-dimethyl-4-(o-tolyl)butanoate (4faa):**

29.7 mg, 42% Yellow oil; R_f = 0.50 (Petroleum Ether/EtOAc = 9:1); ^1H NMR (500 MHz, CDCl\_3) δ: 7.40 (d, J = 8.0 Hz, 1H), 7.18-7.14 (m, 1H), 7.09-7.02 (m, 4H), 6.62 (d, J = 8.5 Hz, 2H), 4.16 (t, J = 6.5 Hz, 1H), 3.68-3.57 (m, 2H), 2.86 (s, 6H), 2.39-2.31 (m, 5H), 1.17 (s, 3H), 1.14 (s, 3H), 1.09 (t, J = 7.0 Hz, 3H); ^13C NMR (125 MHz, CDCl\_3) δ: 177.4, 149.0, 143.5, 135.6, 132.7, 130.4, 128.7, 126.7, 125.8, 125.7, 112.7, 60.1, 47.0, 42.1, 42.0, 40.7, 26.4, 25.8, 20.0, 14.0; LRMS (EI, 70eV) m/z (%): 353 (M\^+, 23), 224 (100), 178 (9); HRMS m/z (ESI) calcd for C_{23}H_{32}NO\_2 ([M+H\^+]^+) 354.2428, found 354.2434.
Ethyl 4-(4-(dimethylamino)phenyl)-4-(2-methoxyphenyl)-2,2-dimethylbutanoate (4gaa):

60.5 mg, 82% yield; Yellow oil; R$_f$ = 0.50 (Petroleum Ether/EtOAc = 7:1); $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.25-7.22 (m, 1H), 7.16-7.06 (m, 3H), 6.87-6.77 (m, 2H), 6.64 (d, $J$ = 8.8 Hz, 2H), 4.49 (t, $J$ = 7.2 Hz, 1H), 3.80 (s, 3H), 3.65-3.60 (m, 2H), 2.87 (s, 6H), 2.37-2.27 (m, 2H), 1.15 (s, 6H), 1.09 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 177.6, 156.5, 148.9, 134.5, 133.3, 128.8, 128.0, 126.7, 120.3, 112.7, 110.7, 60.0, 55.4, 45.7, 42.1, 40.8, 38.5, 25.9, 25.8, 13.9; LRMS (EI, 70eV) m/z (%): 369 (M$^+$, 24), 240 (100), 134 (69); HRMS m/z (ESI) calcd for C$_{23}$H$_{32}$NO$_3$ ([M+H]$^+$) 370.2377, found 370.2387.

Ethyl 4-(2,3-dimethoxyphenyl)-4-(4-(dimethylamino)phenyl)-2,2-dimethylbutanoate (4haa):

63.1 mg, 79% yield; Yellow oil; R$_f$ = 0.50 (Petroleum Ether/EtOAc = 5:1); $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.16 (d, $J$ = 8.8 Hz, 2H), 7.00-6.95 (m, 2H), 6.71-6.62 (m, 3H), 4.48 (t, $J$ = 7.2 Hz, 1H), 3.81 (s, 3H), 3.72 (s, 3H), 3.71-3.62 (m, 2H), 2.86 (s, 6H), 2.41-2.21 (m, 2H), 1.17-1.15 (m, 6H), 1.10 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 177.5, 152.7, 149.0, 146.3, 139.9, 133.3, 128.8, 123.5, 120.0, 112.8, 109.9, 60.5, 60.1, 55.6, 46.1, 42.1, 40.8, 39.1, 26.2, 25.5, 13.9; LRMS (EI, 70eV) m/z (%): 399 (M$^+$, 37), 270 (100), 134 (72); HRMS m/z (ESI) calcd for C$_{24}$H$_{34}$NO$_4$ ([M+H]$^+$) 400.2482, found 400.2492.
Ethyl 4-(4-(dimethylamino)phenyl)-4-(4-methoxy-3-methylphenyl)-2,2-dimethylbutanoate (4iaa):

49.8 mg, 65% Yellow oil; Rf = 0.50 (Petroleum Ether/EtOAc = 7:1); ¹H NMR (400 MHz, CDCl₃) δ: 7.02 (d, J = 9.0 Hz, 2H), 6.95-6.92 (m, 2H), 6.62-6.56 (m, 3H), 3.76 (t, J = 8.0 Hz, 1H), 3.67 (s, 3H), 3.61-3.56 (m, 2H), 2.79 (s, 6H), 2.27-2.25 (m, 2H), 2.08 (s, 3H), 1.07 (s, 6H), 1.02 (t, J = 8.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 177.42, 155.79, 148.93, 137.68, 133.94, 130.06, 128.25, 126.07, 125.68, 112.79, 109.56, 60.05, 55.22, 46.62, 46.34, 41.93, 40.77, 26.05, 25.95, 16.35, 13.90; HRMS m/z (ESI) calcd for C₂₄H₃₄NO₃ ([M+H]+) 384.2533, found 384.2535.

Ethyl 4-(6-bromobenzo[d][1,3]dioxol-5-yl)-4-(4-(dimethylamino)phenyl)-2,2-dimethylbutanoate (4jaa):

46.2 mg, 50% Yellow oil; Rf = 0.50 (Petroleum Ether/EtOAc = 5:1); ¹H NMR (400 MHz, CDCl₃) δ: 7.11 (d, J = 8.8 Hz, 2H), 6.86 (s, 1H), 6.80 (s, 1H), 6.57 (d, J = 7.2 Hz, 2H), 5.80 (d, J = 21.6 Hz, 2H), 4.42 (t, J = 6.0 Hz, 1H), 3.71-3.66 (m, 2H), 2.80 (s, 6H), 2.29-2.14 (m, 2H), 1.10-1.05 (m, 9H); ¹³C NMR (100 MHz, CDCl₃) δ: 177.27, 149.11, 147.33, 146.17, 138.09, 132.08, 128.27, 114.32, 112.61, 112.48, 108.43, 101.47, 60.25, 46.17, 44.59, 42.05, 40.64, 26.03, 25.84, 13.92; HRMS m/z (ESI) calcd for C₂₃H₂₉BrNO₄ ([M+H]+) 462.1274, found 462.1279.

Ethyl 4-(4-(dimethylamino)phenyl)-2,2-dimethyl-4-(naphthalen-2-yl)butanoate
(4kaa):

31.1 mg, 40% yield; Yellow oil; \( R_f = 0.50 \) (Petroleum Ether/EtOAc = 7:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta: \) 7.77-7.67 (m, 4H), 7.40-7.35 (m, 3H), 7.17-7.14 (m, 2H), 6.66-6.62 (m, 2H), 4.09 (t, \( J = 7.6 \) Hz, 1H), 3.60-3.54 (m, 2H), 2.87 (s, 6H), 2.54-2.42 (m, 2H), 1.20 (s, 3H), 1.18 (s, 3H), 1.02 (t, \( J = 7.2 \) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta: \) 177.4, 149.1, 143.5, 133.5, 133.3, 132.0, 128.6, 127.8, 127.7, 127.6, 126.9, 125.7, 125.6, 125.1, 112.8, 60.1, 47.3, 46.2, 42.1, 40.7, 26.2, 26.0, 13.9; LRMS (EI, 70eV) \( m/z \) (%): 389 (M\(^+\), 20), 260 (100), 215 (18); HRMS \( m/z \) (ESI) calcd for C\(_{26}\)H\(_{32}\)NO\(_2\) ([M+H]\(^+\)) 390.2428, found 390.2417.

**Ethyl 4-(4-(dimethylamino)phenyl)-2,2-dimethyl-3,3-diphenylbutanoate (4laa):**

45.6 mg, 55% yield; Yellow oil; \( R_f = 0.50 \) (Petroleum Ether/EtOAc = 8:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta: \) 7.29 (d, \( J \) =7.2 Hz, 4H), 7.14-7.10 (m, 6H), 7.03 (t, \( J = 7.2 \) Hz, 2H), 6.52 (d, \( J = 8.8 \) Hz, 2H), 3.41-3.35 (m, 2H), 3.08 (s, 2H), 2.83 (s, 6H), 1.01 (s, 6H), 0.91 (t, \( J = 7.2 \) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta: \) 177.4, 148.3, 147.7, 134.7, 130.2, 129.4, 127.4, 125.5, 111.6, 60.0, 55.0, 47.8, 42.0, 40.5, 28.1, 13.7; HRMS \( m/z \) (ESI) calcd for C\(_{28}\)H\(_{34}\)NO\(_2\) ([M+H]\(^+\)) 416.2584, found 416.2595.

**Ethyl (E)-4-(4-methoxyphenyl)-2,2-dimethylbut-3-enoate (5):**

15.9 mg, 32% Yellow oil; \( R_f = 0.50 \) (Petroleum Ether/EtOAc = 10:1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta: \) 7.31 (d, \( J = 8.8 \) Hz, 2H), 6.85 (d, \( J = 8.8 \) Hz, 2H), 6.38 (d, \( J = \)
16.0 Hz, 1H), 6.26 (d, \( J = 16.0 \) Hz, 1H), 4.17-4.11 (m, 2H), 3.80 (s, 3H), 1.39 (s, 6H), 1.25 (t, \( J = 6.4 \) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \): 176.40, 159.05, 132.38, 129.94, 127.41, 127.28, 113.92, 60.68, 55.24, 44.25, 25.11, 14.13, 14.05; HRMS \( m/z \) (ESI) calcd for C\(_{15}\)H\(_{21}\)O\(_3\) ([M+H\(^+\)]\(^+\)) 249.1485, found 249.1489.

**Methyl 2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propanoate (6):**

37.9 mg, 78% yield; Colorless oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \):

4.36-4.31 (m, 1H), 3.71 (s, 3H), 1.58-1.51 (m, 1H), 1.41-1.39 (m, 7H), 1.29 (t, \( J = 14 \) Hz, 1H), 1.81 (s, 3H), 1.12 (s, 6H), 1.02 (s, 3H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) 174.56, 81.56, 60.03, 59.42, 51.45, 40.23, 40.02, 33.56, 32.80, 20.15, 20.00, 18.09, 17.06; HRMS \( m/z \) (ESI) calcd for C\(_{13}\)H\(_{26}\)NO\(_3\) ([M+H\(^+\)]\(^+\)) 244.1907, found 244.1915.
(C) Spectra

4-(4-(dimethylamino)phenyl)-4-(4-methoxyphenyl)-2,2-dimethylbutanoate (4aaa)
4-(4-(dimethylamino)phenyl)-4-(4-methoxyphenyl)-2,2-dimethylbutanoate (4aab)
Ethyl 4-(4-(dimethylamino)phenyl)-2,2-difluoro-4-(4-methoxyphenyl)butanoate

(4aac):

\[
\text{Structure Image}
\]
Ethyl 1-(2-(4-(dimethylamino)phenyl)-2-(4-methoxyphenyl)ethyl)cyclobutanecarboxylate (4aad)
4-(1-(4-methoxyphenyl)-2-(5-nitro-1,3-dioxan-5-yl)ethyl)-N,N-dimethylaniline

(4aae)
Methyl 4-(4-(dimethylamino)phenyl)-4-(4-methoxyphenyl)-2-methylbutanoate

(4aaf)
Methyl 2-(2-(4-(dimethylamino)phenyl)-2-(4-methoxyphenyl)ethyl)hexanoate

(4aag)
Iethyl 2-((4-(dimethylamino)phenyl)-2-(4-methoxyphenyl)ethyl)malonate

(4aah)
2-(2-(4-(dimethylamino)phenyl)-2-(4-methoxyphenyl)ethyl)malonate (4aai)
Ethyl 4-(4-(dimethylamino)phenyl)-4-(4-methoxyphenyl)butanoate (4aaaj)
4-(4-(diethylamino)phenyl)-4-(4-methoxyphenyl)-2,2-dimethylbutanoate (4aba)
4-(4-(dipropylamino)phenyl)-4-(4-methoxyphenyl)-2,2-dimethylbutanoate (4aca)
4-(4-methoxyphenyl)-2,2-dimethyl-4-(4-(methyl(phenyl)amino)phenyl)butanoate

(4ada)
4-(4-methoxyphenyl)-2,2-dimethyl-4-(4-(piperidin-1-yl)phenyl)butanoate (4aea)
Ethyl 4-(4-methoxyphenyl)-2,2-dimethyl-4-(4-morpholinophenyl)butanoate

(4afa)
Ethyl 4-(4-methoxyphenyl)-2,2-dimethyl-4-(4-(4-propionylpiperazin-1-yl)phenyl)butanoate (4aga)
4-(4-(dimethylamino)-2,6-dimethylphenyl)-4-(4-methoxyphenyl)-2,2-dimethylbutanoate (4aha)
Ethyl 4-(4-methoxyphenyl)-2,2-dimethyl-4-(1-methyl-1,2,3,4-tetrahydroquinolin-6-yl)butanoate (4aia)
4-(4-(dimethylamino)phenyl)-4-(4-ethoxyphenyl)-2,2-dimethylbutanoate (4baa)
4-(4-(dimethylamino)phenyl)-2,2-dimethyl-4-(p-tolyl)butanoate (4caa)
4-(4-(dimethylamino)phenyl)-2,2-dimethyl-4-(m-tolyl)butanoate (4eaa)
4-(4-(dimethylamino)phenyl)-2,2-dimethyl-4-(o-tolyl)butanoate (4faa)
Ethyl 4-(4-(dimethylamino)phenyl)-4-(2-methoxyphenyl)-2,2-dimethylbutanoate

(4gaa)
Ethyl 4-(2,3-dimethoxyphenyl)-4-(4-(dimethylamino)phenyl)-2,2-dimethyl butanoate (4haa)
Ethyl 4-(4-(dimethylamino)phenyl)-4-(4-methoxy-3-methylphenyl)-2,2-dimethylbutanoate (4laa)
Ethyl 4-(6-bromobenzo[d][1,3]dioxol-5-yl)-4-(4-(dimethylamino)phenyl)-2,2-dimethylbutanoate (4jaa)
4-(4-(dimethylamino)phenyl)-2,2-dimethyl-4-(naphthalen-2-yl)butanoate (4kaa)
4-(4-(dimethylamino)phenyl)-2,2-dimethyl-4,4-diphenylbutanoate (4laa)
Ethyl (E)-4-(4-methoxyphenyl)-2,2-dimethylbut-3-enoate (5)
Methyl 2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propanoate (6)