



SUPPLEMENTARY MATERIAL TO

**Preparation of 2-heteroatom substituted-4-oxo-4-arylbutanoates
via thio- and aza-Michael addition**

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SPECTRAL DATA FOR THE PRODUCTS

The structural elucidations of the products were based on their spectral (^1H -NMR, ^{13}C -NMR, elemental analysis, and mass) data as given below.

Ethyl 4-oxo-4-phenyl-2-(phenylthio)butanoate (3a).^{1,2} Yield: 90 %; white solid; m.p. 46–48 °C (oil)³¹; ^1H -NMR (400 MHz, CDCl_3 , δ / ppm): 7.93 (2H, *m*), 7.58–7.53 (3H, *m*), 7.46 (2H, *t*, $J = 8.0$ Hz), 7.36–7.33 (3H, *m*), 4.24 (1H, *dd*, $J_1 = 4.4$ Hz, $J_2 = 10.2$ Hz), 4.14 (2H, *q*, $J = 7.2$ Hz), 3.71 (1H, *dd*, $J_1 = 10.2$ Hz, $J_2 = 18.0$ Hz), 3.39 (1H, *dd*, $J_1 = 4.4$ Hz, $J_2 = 18.0$ Hz), 1.18 (3H, *t*, $J = 7.2$ Hz); ^{13}C -NMR (100 MHz, CDCl_3 , δ / ppm): 196.9, 171.7, 136.1, 133.8, 133.6, 132.4, 129.1, 128.7, 128.6, 128.1, 61.4, 45.2, 40.9, 14.0.

Ethyl 4-(3,4-dimethylphenyl)-4-oxo-2-(phenylthio)butanoate (3b). New compound. Yield: 95 %; white solid; m.p. 63–65 °C; Anal. Calcd. for $\text{C}_{20}\text{H}_{22}\text{O}_3\text{S}$: C, 70.15; H, 6.48 %. Found: C, 70.32; H, 6.45 %; ^1H -NMR (400 MHz, CDCl_3 , δ / ppm): 7.70 (1H, *s*), 7.67 (1H, *d*, $J = 7.6$ Hz), 7.55–7.52 (2H, *m*), 7.35–7.32 (3H, *m*), 7.20 (1H, *d*, $J = 7.6$ Hz), 4.25 (1H, *dd*, $J_1 = 4.4$ Hz, $J_2 = 10.2$ Hz), 4.13 (2H, *q*, $J = 6.8$ Hz), 3.66 (1H, *dd*, $J_1 = 10.2$ Hz, $J_2 = 18.0$ Hz), 3.36 (1H, *dd*, $J_1 = 4.4$ Hz, $J_2 = 18.0$ Hz), 2.37 (3H, *s*), 2.30 (3H, *s*), 1.17 (3H, *t*, $J = 6.8$ Hz); ^{13}C -NMR (100 MHz, CDCl_3 , δ / ppm): 196.7, 171.8, 143.2, 137.1, 134.1, 133.6, 132.6, 129.9, 129.2, 129.0, 128.4, 125.9, 61.4, 45.4, 40.7, 20.1, 19.8, 14.0; MS (ESI): m/z 365 $[\text{M} + \text{Na}]^+$.

Ethyl 4-(4-chlorophenyl)-4-oxo-2-(phenylthio)butanoate (3c). New compound. Yield: 89 %; white solid; m.p. 80–82 °C; Anal. Calcd. for $\text{C}_{18}\text{H}_{17}\text{ClO}_3\text{S}$: C, 61.97; H, 4.91 %. Found: C, 61.72; H, 4.94 %; ^1H -NMR (400 MHz, CDCl_3 , δ / ppm): 7.87 (2H, *d*, $J = 8.8$ Hz), 7.54–7.52 (2H, *m*), 7.43 (2H, *d*, $J = 8.8$ Hz), 7.35–7.33 (3H, *m*), 4.22 (1H, *dd*, $J_1 = 4.4$ Hz, $J_2 = 10.0$ Hz), 4.14 (2H, *q*, $J = 7.2$

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Hz), 3.66 (1H, *dd*, $J_1 = 10.0$ Hz, $J_2 = 18.0$ Hz), 3.34 (1H, *dd*, $J_1 = 4.4$ Hz, $J_2 = 18.0$ Hz), 1.18 (3H, *t*, $J = 7.2$ Hz); ^{13}C -NMR (100 MHz, CDCl_3 , δ / ppm): 195.7, 171.6, 140.0, 134.4, 133.8, 132.3, 129.5, 129.1, 129.0, 128.6, 61.5, 45.1, 40.8, 14.0; MS (ESI): m/z 371 (^{35}Cl), 373.0 (^{37}Cl) [$\text{M} + \text{Na}$] $^+$.

Benzyl 4-(4-chlorophenyl)-4-oxo-2-(phenylthio)butanoate (3d). New compound. Yield: 93 %; white solid; m.p. 87–89 °C; ^1H -NMR (400 MHz, CDCl_3 , δ / ppm): 7.86 (2H, *d*, $J = 8.4$ Hz), 7.43 (4H, *d*, $J = 8.4$ Hz), 7.33–7.26 (8H, *m*), 5.13 (2H, *dd*, $J_1 = 12.4$ Hz, $J_2 = 27.2$ Hz), 4.29 (1H, *dd*, $J_1 = 4.4$ Hz, $J_2 = 10.0$ Hz), 3.66 (1H, *dd*, $J_1 = 10.0$ Hz, $J_2 = 18.0$ Hz), 3.36 (1H, *dd*, $J_1 = 4.4$ Hz, $J_2 = 18.0$ Hz); ^{13}C -NMR (100 MHz, CDCl_3 , δ / ppm): 195.6, 171.4, 140.1, 135.4, 134.4, 133.9, 132.0, 129.5, 129.1, 129.0, 128.7, 128.5, 128.3, 128.2, 67.2, 45.1, 40.8; MS (ESI): m/z 433 (^{35}Cl), 435 (^{37}Cl) [$\text{M} + \text{Na}$] $^+$; HRMS (ESI): Calcd. for $\text{C}_{23}\text{H}_{19}\text{ClO}_3\text{S}$ [$\text{M} + \text{Na}$] $^+$: 433.0636. Found: 433.0656.

Ethyl 4-(naphthalen-2-yl)-4-oxo-2-(phenylthio)butanoate (3e). New compound. Yield: 92 %; white solid; m.p. 126–128 °C; ^1H -NMR (400 MHz, CDCl_3 , δ / ppm): 8.45 (1H, *s*), 8.00–7.98 (2H, *m*), 7.89–7.86 (2H, *m*), 7.62–7.54 (4H, *m*), 7.36–7.34 (3H, *m*), 4.33 (1H, *dd*, $J_1 = 4.8$, $J_2 = 9.6$ Hz), 4.16 (2H, *q*, $J = 7.2$ Hz), 3.85 (1H, *dd*, $J_1 = 9.6$ Hz, $J_2 = 18.0$ Hz), 3.53 (1H, *dd*, $J_1 = 4.8$ Hz, $J_2 = 18.0$ Hz), 1.20 (3H, *t*, $J = 7.2$ Hz); ^{13}C -NMR (100 MHz, CDCl_3 , δ / ppm): 196.8, 171.7, 135.8, 133.7, 133.5, 132.6, 132.5, 130.0, 129.7, 129.1, 128.7, 128.6, 128.5, 127.8, 126.9, 123.7, 61.4, 45.4, 40.9, 14.0; MS (ESI): m/z 387 [$\text{M} + \text{Na}$] $^+$; HRMS (ESI): Calcd. for $\text{C}_{22}\text{H}_{20}\text{O}_3\text{S}$ [$\text{M} + \text{Na}$] $^+$: 387.1025, Found: 387.1023.

Ethyl 4-(furan-2-yl)-4-oxo-2-(phenylthio)butanoate (3f). New compound. Yield: 52 %; yellow viscous oil; Anal. Calcd. for $\text{C}_{22}\text{H}_{20}\text{O}_3\text{S}$: C, 63.14; H, 5.30 %. Found: C, 62.99; H, 5.33 %; ^1H -NMR (400 MHz, CDCl_3 , δ / ppm): 7.58–7.57 (1H, *m*), 7.53–7.51 (2H, *m*), 7.34–7.32 (3H, *m*), 7.20 (1H, *d*, $J = 3.6$ Hz), 6.53 (1H, *dd*, $J_1 = 2.0$ Hz, $J_2 = 3.6$ Hz), 4.22 (1H, *dd*, $J_1 = 4.8$ Hz, $J_2 = 9.6$ Hz), 4.13 (2H, *q*, $J = 7.2$ Hz), 3.53 (1H, *dd*, $J_1 = 9.6$ Hz, $J_2 = 17.6$ Hz), 3.26 (1H, *dd*, $J_1 = 4.8$ Hz, $J_2 = 17.6$ Hz), 1.17 (3H, *t*, $J = 7.2$ Hz); ^{13}C -NMR (100 MHz, CDCl_3 , δ / ppm): 185.7, 171.5, 152.1, 146.7, 133.8, 132.3, 129.0, 128.6, 117.6, 112.4, 61.5, 44.9, 40.4, 14.0; MS (ESI): m/z 327 [$\text{M} + \text{Na}$] $^+$.

Ethyl 2-((4-methoxyphenyl)thio)-4-oxo-4-phenylbutanoate (3g). New compound. Yield: 88 %; yellow solid; m.p. 58–60 °C; Anal. Calcd. for $\text{C}_{19}\text{H}_{20}\text{O}_4\text{S}$: C, 66.26; H, 5.85 %. Found: C, 66.40; H, 5.82 %; ^1H -NMR (400 MHz, CDCl_3 , δ / ppm): 7.92–7.90 (2H, *m*), 7.58–7.54 (1H, *m*), 7.47–7.43 (4H, *m*), 6.86 (2H, *d*, $J = 8.8$ Hz), 4.14 (2H, *q*, $J = 7.2$ Hz), 4.09 (1H, *dd*, $J_1 = 4.4$ Hz, $J_2 = 10.0$ Hz), 3.80 (3H, *s*), 3.62 (1H, *dd*, $J_1 = 10.0$ Hz, $J_2 = 18.0$ Hz), 3.34 (1H, *dd*, $J_1 = 4.4$, $J_2 = 18.0$ Hz), 1.21 (3H, *t*, $J = 7.2$ Hz); ^{13}C -NMR (100 MHz, CDCl_3 , δ / ppm): 197.0, 171.7, 160.5, 136.9, 136.2, 133.5, 128.7, 128.1, 122.3, 114.6, 61.3, 55.4, 45.8, 40.8, 14.1; MS (ESI): m/z 367 [$\text{M} + \text{Na}$] $^+$.

Ethyl 2-(1H-benzotriazol-1-yl)-4-oxo-4-phenylbutanoate (5a). New compound. Yield: 92 %; white solid; m.p. 95–97 °C; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 8.07 (1H, *d*, *J* = 8.4 Hz), 7.99 (2H, *d*, *J* = 8.0 Hz), 7.73 (1H, *d*, *J* = 8.4 Hz), 7.62–7.54 (2H, *m*), 7.50–7.46 (2H, *m*), 7.42–7.39 (1H, *m*), 6.22 (1H, *t*, *J* = 7.2 Hz), 4.35 (1H, *dd*, *J*₁ = 6.0, *J*₂ = 18.0 Hz), 4.25–4.16 (3H, *m*), 1.17 (3H, *t*, *J* = 7.2 Hz); ¹³C-NMR (100 MHz, CDCl₃, δ / ppm): 195.4, 168.1, 145.9, 135.8, 133.9, 133.4, 128.8, 128.3, 127.9, 124.2, 120.1, 109.8, 62.6, 56.3, 39.9, 13.9; MS (ESI): *m/z* 324 [M + H]⁺; HRMS (ESI) Calcd. for C₁₈H₁₇N₃O₃ [M + H]⁺: 324.1343. Found: 324.1347.

Ethyl 2-(1H-benzotriazol-1-yl)-4-oxo-4-(p-tolyl)butanoate (5b). New compound. Yield: 90 %; white solid; m.p. 90–92 °C; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 8.06 (1H, *d*, *J* = 8.4 Hz), 7.88 (2H, *d*, *J* = 8.0 Hz), 7.73 (1H, *d*, *J* = 8.4 Hz), 7.53 (1H, *t*, *J* = 8.0 Hz), 7.39 (1H, *t*, *J* = 8.0 Hz), 7.25 (2H, *d*, *J* = 8.0 Hz), 6.21 (1H, *t*, *J* = 6.8 Hz), 4.31 (1H, *dd*, *J*₁ = 6.0 Hz, *J*₂ = 18.0 Hz), 4.23–4.13 (3H, *m*), 2.39 (3H, *s*), 1.15 (3H, *t*, *J* = 7.2 Hz); ¹³C-NMR (100 MHz, CDCl₃, δ / ppm): 195.0, 168.2, 145.9, 144.9, 133.5, 133.3, 129.5, 128.4, 127.9, 124.2, 120.1, 109.8, 62.6, 56.4, 39.8, 21.7, 13.9; MS (ESI): *m/z* 338 [M + H]⁺; HRMS (ESI) Calcd. for C₁₉H₁₉N₃O₃ [M + H]⁺: 338.1499. Found: 338.1505.

Benzyl 2-(1H-benzotriazol-1-yl)-4-oxo-4-(p-tolyl)butanoate (5c). New compound. Yield: 80 %; white solid; m.p. 99–101 °C; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 8.07 (1H, *d*, *J* = 8.4 Hz), 7.87 (2H, *d*, *J* = 8.0 Hz), 7.68 (1H, *d*, *J* = 8.4 Hz), 7.51 (1H, *t*, *J* = 7.2 Hz), 7.39 (1H, *t*, *J* = 7.6 Hz), 7.27–7.25 (5H, *m*), 7.13–7.11 (2H, *m*), 6.28 (1H, *t*, *J* = 6.4 Hz), 5.20–5.13 (2H, *m*), 4.31 (1H, *dd*, *J*₁ = 6.0 Hz, *J*₂ = 18.0 Hz), 4.20 (1H, *dd*, *J*₁ = 7.6 Hz, *J*₂ = 18.0 Hz), 2.41 (3H, *s*); ¹³C-NMR (100 MHz, CDCl₃, δ / ppm): 194.9, 168.1, 145.9, 144.9, 134.7, 133.5, 133.3, 129.5, 128.5, 128.4, 128.3, 128.0, 127.9, 124.2, 120.1, 109.8, 68.0, 56.4, 39.7, 21.7; MS (ESI): *m/z* 400 [M + H]⁺; HRMS (ESI) Calcd. for C₂₄H₂₁N₃O₃ [M + H]⁺: 400.1656. Found: 400.1651.

Benzyl 2-(1H-benzotriazol-1-yl)-4-(3,4-dimethylphenyl)-4-oxobutanoate (5d). New compound. Yield: 88 %; white solid; m.p. 135–137 °C; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 8.06 (1H, *d*, *J* = 8.4 Hz), 7.74–7.67 (3H, *m*), 7.50 (1H, *t*, *J* = 7.2 Hz), 7.37 (1H, *t*, *J* = 8.0 Hz), 7.26–7.12 (6H, *m*), 6.29 (1H, *t*, *J* = 6.0 Hz), 5.17 (2H, *s*), 4.34–4.15 (2H, *m*), 2.31 (3H, *s*), 2.29 (3H, *s*); ¹³C-NMR (100 MHz, CDCl₃, δ / ppm): 195.1, 168.1, 146.0, 143.5, 137.1, 134.8, 133.8, 133.5, 130.0, 129.4, 128.5, 128.4, 127.9, 127.8, 126.0, 124.1, 120.1, 109.8, 67.9, 56.5, 39.7, 20.0, 19.6; MS (ESI): *m/z* 414 [M + H]⁺; HRMS (ESI) Calcd. for C₂₅H₂₃N₃O₃ [M + H]⁺: 414.1812. Found: 414.1821.

Ethyl 2-(1H-benzotriazol-1-yl)-4-oxo-4-(4-phenoxyphenyl)butanoate (5e). New compound. Yield: 83 %; white solid; m.p. 128–130 °C; ¹H-NMR (400 MHz, CDCl₃, δ / ppm): 8.06 (1H, *d*, *J* = 8.4 Hz), 7.96 (2H, *d*, *J* = 8.8 Hz), 7.73 (1H, *d*, *J* = 8.4 Hz), 7.55 (1H, *t*, *J* = 8.0 Hz), 7.39 (3H, *t*, *J* = 7.6 Hz), 7.20 (1H, *t*,

7.6 Hz), 7.06 (2H, *d*, $J = 8.4$ Hz), 6.99 (2H, *d*, $J = 8.8$ Hz), 6.20 (1H, *t*, $J = 6.4$ Hz), 4.28 (1H, *dd*, $J_1 = 6.4$ Hz, $J_2 = 18.0$ Hz), 4.24–4.13 (3H, *m*), 1.15 (3H, *t*, $J = 7.2$ Hz); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , δ / ppm): 193.9, 168.2, 162.7, 155.2, 145.9, 133.5, 130.6, 130.4, 130.1, 127.9, 124.9, 124.2, 120.3, 120.1, 117.4, 109.8, 62.6, 56.4, 39.6, 13.9; MS (ESI): m/z 416 $[\text{M} + \text{H}]^+$; HRMS (ESI) Calcd. for $\text{C}_{24}\text{H}_{21}\text{N}_3\text{O}_3$ $[\text{M} + \text{H}]^+$: 416.1605. Found: 416.1597.

Ethyl 2-(1H-benzotriazol-1-yl)-4-(4-chlorophenyl)-4-oxobutanoate (5f). New compound. Yield: 90 %; white solid; m.p. 105–107 °C; $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ / ppm): 8.08 (1H, *d*, $J = 8.4$ Hz), 7.95–7.93 (2H, *m*), 7.72 (1H, *d*, $J = 8.4$ Hz), 7.59–7.55 (1H, *m*), 7.48–7.45 (2H, *m*), 7.44–7.40 (1H, *m*), 6.18 (1H, *t*, $J = 6.4$ Hz), 4.32 (1H, *dd*, $J_1 = 6.4$ Hz, $J_2 = 18.0$ Hz), 4.25–4.14 (3H, *m*), 1.16 (3H, *t*, $J = 7.2$ Hz); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , δ / ppm): 194.3, 168.0, 145.9, 140.5, 134.1, 133.4, 129.7, 129.2, 128.0, 124.3, 120.2, 109.7, 62.7, 56.2, 39.8, 13.9; MS (ESI): m/z 358 (^{35}Cl), 360 (^{37}Cl) $[\text{M} + \text{H}]^+$; HRMS (ESI) Calcd. for $\text{C}_{18}\text{H}_{16}\text{ClN}_3\text{O}_3$ $[\text{M} + \text{H}]^+$: 358.0953. Found: 358.0959.

Ethyl 2-(1H-benzotriazol-1-yl)-4-(furan-2-yl)-4-oxobutanoate (5g). New compound. Yield: 57 %; yellow solid; m.p. 91–93 °C; $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ / ppm): 8.04 (1H, *d*, $J = 8.4$ Hz), 7.68 (1H, *d*, $J = 8.0$ Hz), 7.59 (1H, *d*, $J = 0.8$ Hz), 7.53 (1H, *t*, $J = 7.2$ Hz), 7.38 (1H, *t*, $J = 7.2$ Hz), 7.26–7.25 (1H, *m*), 6.54–6.53 (1H, *m*), 6.17 (1H, *t*, $J = 7.2$ Hz), 4.22–4.02 (4H, *m*), 1.14 (3H, *t*, $J = 7.2$ Hz); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , δ / ppm): 184.1, 167.9, 151.7, 147.2, 145.8, 133.4, 128.0, 124.3, 120.0, 118.4, 112.6, 109.8, 62.7, 55.8, 39.5, 13.9; MS (ESI): m/z 314 $[\text{M} + \text{H}]^+$; HRMS (ESI) Calcd. for $\text{C}_{16}\text{H}_{15}\text{N}_3\text{O}_4$ $[\text{M} + \text{H}]^+$: 314.1135. Found: 314.1131.

Ethyl 2-(1H-benzotriazol-1-yl)-4-oxopentanoate (5h). New compound. Yield: 62 %; yellow solid; m.p. 70–72 °C; $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ / ppm): 7.87 (2H, *dd*, $J_1 = 3.2$ Hz, $J_2 = 6.8$ Hz), 7.40 (2H, *dd*, $J_1 = 3.2$ Hz, $J_2 = 6.8$ Hz), 6.13 (1H, *t*, $J = 7.2$ Hz), 4.26–4.16 (2H, *m*), 3.72–3.60 (2H, *m*), 2.27 (3H, *s*), 1.20 (3H, *t*, $J = 6.8$ Hz); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , δ / ppm): 203.4, 167.8, 144.4, 126.9, 118.3, 63.6, 62.7, 44.3, 30.1, 14.0; MS (ESI): m/z 262 $[\text{M} + \text{H}]^+$; HRMS (ESI) Calcd. for $\text{C}_{13}\text{H}_{15}\text{N}_3\text{O}_3$ $[\text{M} + \text{H}]^+$: 262.1186. Found: 262.1191.

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