Supporting Information

For

Catalyst-Free and Oxidant-Free Synthesis of 1,3,5-Trisubstituted Pyrazoles by Michael-Type Addition of Hydrazone sp² Nitrogen Atoms to Enones

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General Information

All reactions were carried out in capped vials. Column chromatography was generally performed on silica gel (200-300 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions. The $^1$H (400MHz) and $^{13}$C NMR (100MHz) data were recorded on Bruker AVANCE II 400MHz spectrometer using CDCl$_3$ as solvent. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. $^1$H NMR spectra was recorded with tetramethylsilane (δ = 0.00 ppm) as internal reference; $^{13}$C NMR spectra was recorded with CDCl$_3$ (δ = 77.00 ppm) as internal reference.

General procedures for reactions

A solution of enone$^1$ (0.5 mmol) and hydrazone$^2$ (0.6 mmol) in DMSO (0.2 mL) was stirred at 100 °C. The reaction was monitored by thin layer chromatography (TLC). It was diluted with water and extracted with ethyl acetate 3 times. Removal of solvent followed by flash column chromatographic purification afforded products using petroleum ether and ethyl acetate.
Compound characterizations

Methyl 1-((1-ethoxy-1-oxopropan-2-yl)-5-phenyl-1H-pyrazole-3-carboxylate (3aa). Petroleum ether/ethyl acetate = 5:1, white solid, 76% yield (115 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37-7.41 (m, 3H), 7.29-7.32 (m, 2H), 6.78 (s, 1H), 4.99 (q, $J$ = 7.2 Hz, 1H), 4.01-4.15 (m, 2H), 3.87 (s, 3H), 1.77 (d, $J$ = 7.2 Hz, 3H), 1.13 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.3, 162.5, 145.6, 143.0, 129.2, 129.1, 128.9, 128.7, 108.8, 61.6, 56.9, 51.7, 16.8, 13.7. IR (film) $\nu$/cm$^{-1}$ 3326 (s), 2977 (s), 2358 (w), 2254 (w), 1730 (s), 1437 (m). MS (ESI, m/z) 303.2 (M + H$^+$), 325.2 (M + Na$^+$). Anal. calcd for C$_{16}$H$_{18}$N$_2$O$_4$: C, 63.56; H, 6.00; N, 9.27. Found: C, 63.29; H, 5.87; N, 9.11.

Methyl 1-((1-ethoxy-1-oxopropan-2-yl)-5-(4-methoxyphenyl)-1H-pyrazole-3-carboxylate (3ba). Petroleum ether/ethyl acetate = 5:1, white solid, 63% yield (105 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.22 (ABd, $J$ = 8.8 Hz, 2H), 6.91 (ABd, $J$ = 8.8 Hz, 2H), 6.73 (s, 1H), 4.97 (q, $J$ = 7.2 Hz, 1H), 4.05-4.13 (m, 2H), 3.86 (s, 3H), 3.79 (s, 3H), 1.76 (d, $J$ = 7.2 Hz, 3H), 1.13 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.6, 162.9, 160.3, 145.6, 143.1, 130.5, 121.5, 114.3,
108.9, 61.8, 57.0, 55.3, 52.0, 17.0, 14.0. IR (film) $\nu$ cm$^{-1}$ 3452 (w), 3149 (w),
2949 (vs), 2562 (w), 2058 (w), 1730 (vs), 1426 (s), 1190 (s). MS (ESI, $m/z$)
333.2 (M + H$^+$), 355.2 (M + Na$^+$). Anal. calcd for C$_{17}$H$_{20}$N$_2$O$_5$: C, 61.44; H, 6.07;
N, 8.43. Found: C, 61.21; H, 5.91; N, 8.17.

Methyl 1-(1-ethoxy-1-oxopropan-2-yl)-5-(p-tolyl)-1H-pyrazole-3-carboxylate
(3ca). Petroleum ether/ethyl acetate = 5:1, white solid, 67% yield (106 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$
7.19-7.20 (m, 4H), 6.75 (s, 1H), 4.98 (q, $J$ = 7.2 Hz, 1H), 4.03-4.13 (m, 2H), 3.87 (s, 3H), 2.35 (s, 3H), 1.76 (d, $J$ = 7.2 Hz, 3H), 1.13
(t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$
169.6, 162.9, 145.8, 143.2, 139.4, 129.5, 129.0, 126.5, 108.9, 61.8, 57.0, 52.0, 21.2, 16.9, 13.9. IR (film)
$\nu$ cm$^{-1}$ 3465 (w), 3124 (w), 2925 (vs), 1719 (vs), 1448 (s), 1202 (s). MS (ESI, $m/z$)
317.2 (M + H$^+$), 339.2 (M + Na$^+$). Anal. calcd for C$_{17}$H$_{20}$N$_2$O$_4$: C, 64.54; H, 6.37; N, 8.86. Found: C, 64.31; H, 6.18; N, 8.77.

Methyl 1-(1-ethoxy-1-oxopropan-2-yl)-5-(4-fluorophenyl)-1H-pyrazole-3-carboxylate
(3da). Petroleum ether/ethyl acetate = 5:1, white solid, 84% yield
(134 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$
7.27-7.31 (m, 2H), 7.07-7.11 (m, 2H),
6.76 (s, 1H), 4.92 (q, J = 7.2 Hz, 1H), 4.02-4.15 (m, 2H), 3.87 (s, 3H), 1.77 (d, J = 7.6 Hz, 3H), 1.13 (t, J = 7.2 Hz, 3H). $^1$H NMR (100 MHz, CDCl$_3$) δ 169.4, 163.3 (d, J = 250 Hz), 162.7, 144.6, 143.2, 131.1 (d, J = 8.8 Hz), 125.4 (d, J = 2.9 Hz), 116.0 (d, J = 21.9 Hz), 109.2, 61.9, 57.1, 52.0, 16.9, 13.9. IR (film) $\nu$/cm$^{-1}$ 3465 (m), 2984 (vs), 2340 (m), 2246 (w), 1719 (vs), 1448 (w), 1215 (w).

MS (ESI, $m/z$) 321.2 (M + H$^+$), 343.2 (M + Na$^+$). Anal. calcd for C$_{16}$H$_{17}$FN$_2$O$_4$: C, 59.99; H, 5.35; N, 8.75. Found: C, 59.43; H, 5.11; N, 8.70.

Methyl 5-(4-chlorophenyl)-1-(1-ethoxy-1-oxopropan-2-yl)-1H-pyrazole-3-carboxylate (3ea). Petroleum ether/ethyl acetate = 5:1, white solid, 81% yield (136 mg). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.38 (ABd, J = 8.4 Hz 2H), 7.25 (ABd, J = 8.4 Hz 2H), 6.77 (s, 1H), 4.92 (q, J = 7.2 Hz, 1H), 4.02-4.15 (m, 2H), 3.86 (s, 3H), 1.77 (d, J = 7.2 Hz, 3H), 1.13 (t, J = 7.2 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 169.3, 162.5, 144.5, 143.2, 135.6, 130.4, 129.1, 127.8, 109.2, 61.9, 57.1, 51.9, 16.8, 13.8. IR (film) $\nu$/cm$^{-1}$ 3452 (w), 3149 (w), 2936 (vs), 2221(w), 1742 (vs), 1437 (s), 1202 (s). MS (ESI, $m/z$) 337.2 (M + H$^+$), 339.2 (M + 2H$^+$), 359.2 (M + Na$^+$), 361.2 (M + 2Na$^+$). Anal. calcd for C$_{16}$H$_{17}$ClN$_2$O$_4$: C, 57.06; H, 5.09; N, 8.32. Found: C, 56.87; H, 5.11; N, 8.10.
Methyl (E)-1-(1-ethoxy-1-oxopropan-2-yl)-5-styryl-1\textit{H}-pyrazole-3-carboxylate (3fa). Petroleum ether/ethyl acetate = 5:1, white solid, 68% yield (111 mg). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.39-7.41 (m, 2H), 7.26-7.33 (m, 3H), 7.02 (ABd, \( J = 16 \) Hz 1H), 6.99 (s, 1H), 6.78 (ABd, \( J = 16 \) Hz 1H), 5.19 (q, \( J = 7.2 \) Hz, 1H), 4.13 (dq, \( J = 1.2, 7.2 \) Hz, 2H), 3.87 (s, 3H), 1.84 (d, \( J = 7.2 \) Hz, 3H), 1.14 (t, \( J = 7.2 \) Hz, 3H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \( \delta \) 169.5, 162.7, 143.0, 135.9, 134.4, 128.9, 128.8, 126.8, 113.4, 106.4, 62.2, 58.3, 52.1, 16.9, 14.1. IR (film) \( \nu/cm^{-1} \) 3469 (m), 2956 (m), 1743 (s), 1207 (vs). MS (ESI, m/z) 329.2 (M + H\textsuperscript{+}), 351.2 (M + Na\textsuperscript{+}). Anal. calcd for C\textsubscript{18}H\textsubscript{20}N\textsubscript{2}O\textsubscript{4}: C, 65.84; H, 6.14; N, 8.53. Found: C, 65.49; H, 5.89; N, 8.22.

Methyl 5-(2-bromophenyl)-1-(1-ethoxy-1-oxopropan-2-yl)-1\textit{H}-pyrazole-3-
carboxylate (3ga). Petroleum ether/ethyl acetate = 5:1, white solid, 67% yield (127 mg). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.62-7.64 (m, 1H), 7.25-7.35 (m, 3H), 6.78 (s, 1H), 4.66 (brs, 1H), 3.96-4.09 (m, 2H), 3.88 (s, 3H), 1.82 (d, \( J = 5.6 \) Hz, 3H), 1.09 (t, \( J = 7.2 \) Hz, 3H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \( \delta \) 169.0, 162.4, 143.7, 143.0, 132.8, 132.2, 131.1, 130.3, 127.4, 124.1, 109.7, 61.5, 57.1, 51.7, 16.2, 13.7. IR (film) \( \nu/cm^{-1} \) 3429 (w), 2949 (m), 1719 (vs), 1448 (s), 1215 (vs). MS (ESI, m/z) 381.2 (M + H\textsuperscript{+}), 383.2 (M +2+ H\textsuperscript{+}), 403.2 (M + Na\textsuperscript{+}), 405.2 (M +2+ Na\textsuperscript{+}). Anal. calcd for C\textsubscript{18}H\textsubscript{17}BrN\textsubscript{2}O\textsubscript{4}: C, 50.41; H, 4.49; N, 7.35. Found: C, 50.57;
Methyl 5-(3-bromophenyl)-1-(1-ethoxy-1-oxopropan-2-yl)-1H-pyrazole-3-carboxylate (3ha). Petroleum ether/ethyl acetate = 5:1, white solid, 69% yield (131 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.53 (dt, $J = 7.2$, 2.0 Hz 1H), 7.48 (t, $J = 1.6$ Hz 1H), 7.23-7.30 (m, 2H), 6.79 (s, 1H), 4.93 (q, $J = 7.2$ Hz, 1H), 4.04-4.15 (m, 2H), 3.87 (s, 3H), 1.77 (d, $J = 7.2$ Hz, 3H), 1.14 (t, $J = 6.8$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.2, 162.5, 144.0, 143.2, 132.3, 132.0, 131.2, 130.3, 127.6, 122.8, 109.3, 61.9, 57.2, 51.9, 16.8, 13.9. IR (film) $\nu$/cm$^{-1}$ 3440 (vs), 2961(w), 2293 (w), 1742 (vs), 1426 (m), 1202 (vs). MS (ESI, m/z) 381.2 (M + H$^+$), 383.2 (M + 2H$^+$), 403.2 (M + Na$^+$), 405.2 (M + 2Na$^+$). Anal. calcd for C$_{16}$H$_{17}$BrN$_2$O$_4$: C, 50.41; H, 4.49; N, 7.35 Found: C, 50.23; H, 4.21; N, 7.08.

Methyl 5-(4-bromophenyl)-1-(1-ethoxy-1-oxopropan-2-yl)-1H-pyrazole-3-carboxylate (3ia). Petroleum ether/ethyl acetate = 5:1, white solid, 76% yield (144 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.53 (ABd, $J = 8.4$ Hz 2H), 7.18 (ABd, $J = 8.8$ Hz 2H), 6.77 (s, 1H), 4.92 (q, $J = 7.2$ Hz, 1H), 4.03-4.13 (m, 2H), 3.87
(s, 3H), 1.76 (d, J = 7.2 Hz, 3H), 1.13 (t, J = 7.2 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.4, 162.6, 144.6, 143.3, 132.2, 130.7, 128.3, 123.8, 109.2, 62.0, 57.2, 52.1, 16.9, 13.9. IR (film) $\nu$/cm$^{-1}$ 3224 (w), 2972 (s), 1764 (vs), 1448 (s), 1215 (vs). MS (ESI, m/z) 381.2 (M + H$^+$), 383.2 (M + 2H$^+$), 403.2 (M + Na$^+$), 405.2 (M + 2Na$^+$). Anal. calcd for C$_{16}$H$_{17}$BrN$_2$O$_4$: C, 50.41; H, 4.49; N, 7.35. Found: C, 50.53; H, 4.61; N, 7.47.

Methyl 1-(1-ethoxy-1-oxopropan-2-yl)-5-(3-fluorophenyl)-1H-pyrazole-3-carboxylate (3ja). Petroleum ether/ethyl acetate = 5:1, white solid, 81% yield (130 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42-7.48 (m, 1H), 7.10-7.18 (m, 3H), 6.87 (s, 1H), 5.04 (q, J = 7.2 Hz, 1H), 4.12-4.22 (m, 2H), 3.95 (s, 3H), 1.86 (d, J = 7.2 Hz, 3H), 1.21 (t, J = 7.2 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.3, 162.53(4) (d, J = 247.3 Hz), 162.53(1),144.3 (d, J = 2.5 Hz), 143.2, 131.2 (d, J = 8.2 Hz), 130.6 (d, J = 8.9 Hz),124.8 (d, J = 2.8 Hz), 116.3 (d, J = 20.5 Hz), 116.2 (d, J = 22.3 Hz),109.2, 61.9, 57.2, 52.0, 16.9, 13.9. IR (film) $\nu$/cm$^{-1}$ 3540 (vs), 3161(w), 1742 (vs), 1426 (m), 1202 (vs). MS (ESI, m/z) 321.2 (M + H$^+$), 343.2 (M + Na$^+$). Anal. calcd for C$_{16}$H$_{17}$FN$_2$O$_4$: C, 59.99; H, 5.35; N, 8.75. Found: C, 60.23; H, 5.25; N, 8.82.
Methyl 1-(1-ethoxy-1-oxopropan-2-yl)-5-(2-fluorophenyl)-1H-pyrazole-3-carboxylate (3ka). Petroleum ether/ethyl acetate = 5:1, white solid, 72% yield (115 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33-7.49 (m, 2H), 7.18-7.26 (m, 2H), 6.90 (s, 1H), 4.89 (q, $J = 7.2$ Hz, 1H), 4.07-4.13 (m, 2H), 3.95 (s, 3H), 1.89 (d, $J = 7.2$ Hz, 3H), 1.16 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.3, 162.6, 160.0 (d, $J = 247.0$ Hz), 143.4, 139.4, 131.8 (d, $J = 2.7$ Hz), 131.7 (d, $J = 8.1$ Hz), 117.1 (d, $J = 15.4$ Hz), 116.2 (d, $J = 22.5$ Hz), 110.4, 61.8, 57.4(7), 57.4(6), 52.0, 16.7, 13.9. IR (film) $\nu$/cm$^{-1}$ 3529 (w), 3149 (m), 1719 (vs), 1448 (s), 1215 (vs) MS (ESI, m/z) 321.2 (M + H$^+$), 343.2 (M + Na$^+$). Anal. calcd for C$_{16}$H$_{17}$FN$_2$O$_4$: C, 59.99; H, 5.35; N, 8.75. Found: C, 60.18; H, 5.49; N, 9.02.

Methyl 1-(1-ethoxy-1-oxopropan-2-yl)-5-(3-methoxyphenyl)-1H-pyrazole-3-carboxylate (3la). Petroleum ether/ethyl acetate = 5:1, white solid, 71% yield (118 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38 (t, $J = 8.0$ Hz, 1H), 6.91-7.01 (m, 3H), 6.85 (s, 1H), 5.09 (q, $J = 7.2$ Hz, 1H), 4.11-4.21 (m, 2H), 3.94 (s, 3H), 3.79 (s, 3H), 1.84 (d, $J = 7.2$ Hz, 3H), 1.21 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.5, 162.7, 159.7, 145.5, 143.1, 130.5, 129.9, 121.2, 114.8,
114.7, 108.9, 61.8, 57.0, 55.2, 51.9, 17.0, 13.9. IR (film) ν/cm⁻¹ 3452 (w), 3134 (w), 2957 (vs), 2542 (w), 2056 (w), 1731 (vs), 1428 (s), 1188 (s). MS (ESI, m/z) 333.2 (M + H⁺), 355.2 (M + Na⁺). Anal. calcd for C₁₇H₂₀N₂O₅: C, 61.44; H, 6.07; N, 8.43. Found: C, 61.63; H, 5.91; N, 8.23.

Methyl 1-(2-oxo-1,2-diphenylethyl)-5-phenyl-1H-pyrazole-3-carboxylate (3ab).

Petroleum ether/ethyl acetate = 5:1, white solid, 64% yield (127 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.55-7.58 (m, 2H), 7.22-7.42 (m, 11H), 7.17-7.19 (m, 2H), 6.83 (s, 1H), 6.81 (s, 1H), 3.81 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 192.0, 162.6, 145.7, 143.3, 134.7, 134.2, 133.1, 129.2, 129.1, 128.6, 128.5(8), 128.4, 128.2, 109.7, 68.6, 51.7. IR (film) ν/cm⁻¹ 3066 (w), 2936 (s), 2351 (vs), 1719 (vs), 1589 (s), 1426 (vs), 1226 (vs). MS (ESI, m/z) 397.3 (M + H⁺), 419.3 (M + Na⁺). Anal. calcd for C₂₅H₂₀N₂O₃: C, 75.74; H, 5.09; N, 7.07. Found: C, 75.67; H, 5.01; N, 6.88.

Methyl 5-(4-methoxyphenyl)-1-(2-oxo-1,2-diphenylethyl)-1H-pyrazole-3-carboxylate (3bb). Petroleum ether/ethyl acetate = 5:1, white solid, 58% yield
(198 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.55-7.57 (m, 2H), 7.38-7.41 (m, 1H), 7.24-7.27 (m, 5H), 7.20-7.22 (m, 2H), 7.11 (ABd, J = 8.8 Hz 2H), 6.82 (ABd, J = 8.8 Hz 2H), 6.80 (s, 1H), 6.77 (s, 1H), 3.79 (s, 3H), 3.77 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 192.0, 162.8, 160.3, 145.6, 143.4, 134.9, 134.5, 133.2, 130.7, 129.1, 128.7, 128.6, 128.5, 128.3, 121.4, 114.2, 109.6, 68.5, 55.3, 51.8.

IR (film) ν/cm⁻¹ 3440 (s), 2914 (s), 1695 (m), 1600 (s), 1448 (s), 1248 (m). MS (ESI, m/z) 427.3 (M + H⁺), 449.4 (M + Na⁺). Anal. calcd for C₂₆H₂₂N₂O₄: C, 73.23; H, 5.20; N, 6.57. Found: C, 72.98; H, 5.08; N, 6.46.

Methyl 1-(2-oxo-1,2-diphenylethyl)-5-(p-tolyl)-1H-pyrazole-3-carboxylate (3cb).

Petroleum ether/ethyl acetate = 5:1, white solid, 57% yield (117 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.54-7.56 (m, 2H), 7.37-7.41 (m, 1H), 7.25-7.28 (m, 4H), 7.21-7.24 (m, 3H), 7.08-7.14 (m, 4H), 6.79 (s, 1H), 6.77 (s, 1H), 3.79 (s, 3H), 2.32 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 192.0, 162.8, 145.9, 143.5, 139.5, 135.0, 134.5, 133.1, 129.5, 129.2, 129.1, 128.7, 128.6, 128.5, 128.4, 126.4, 109.7, 68.5, 51.8, 21.3. IR (film) ν/cm⁻¹ 3452 (m), 3136 (m), 1730 (s), 1390 (m), 1215 (s). MS (ESI, m/z) 411.4 (M + H⁺), 433.4 (M + Na⁺). Anal. calcd for C₂₆H₂₂N₂O₃: C, 76.08; H, 5.40; N, 6.82; Found: C, 75.87; H, 5.31; N, 6.78.
Methyl 5-(4-fluorophenyl)-1-(2-oxo-1,2-diphenylethyl)-1H-pyrazole-3-carboxylate (3db). Petroleum ether/ethyl acetate = 5:1, white solid, 78% yield (161 mg). \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.59-7.61 (m, 2H), 7.40-7.44 (m, 1H), 7.17-7.28 (m, 5H), 7.08-7.11 (m, 4H), 6.90-6.94 (m, 2H), 6.92 (s, 1H), 6.78 (s, 1H), 3.82 (s, 3H). \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 192.2, 163.1 (d, \( J = 246 \) Hz), 162.7, 144.9, 143.2, 134.7, 134.0, 133.5, 131.1 (d, \( J = 8.8 \) Hz), 129.3, 128.8, 128.7, 128.6, 128.5, 125.6 (d, \( J = 3.6 \) Hz), 115.6 (d, \( J = 21.9 \) Hz), 110.4, 69.7, 52.0. IR (film) \( \nu/cm^{-1} \) 3382 (vs), 2972 (m), 2374 (s), 1706 (vs), 1600 (w), 1215 (m). MS (ESI, \( m/z \)) 415.3 (M + H\(^+\)), 437.3 (M + Na\(^+\)). Anal. calcd for C\(_{25}\)H\(_{19}\)FN\(_2\)O\(_3\): C, 72.45; H, 4.62; N, 6.76. Found: C, 72.63; H, 4.81; N, 6.85.

Methyl 5-(4-chlorophenyl)-1-(2-oxo-1,2-diphenylethyl)-1H-pyrazole-3-carboxylate (3eb). Petroleum ether/ethyl acetate = 5:1, white solid, 75% yield (161 mg). \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.59-7.61 (m, 2H), 7.40-7.44 (m, 1H), 7.18-7.28 (m, 7H), 7.08-7.10 (m, 2H), 7.04-7.06 (m, 2H), 6.92 (s, 1H), 6.78 (s, 1H), 3.82 (s, 3H). \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 192.2, 162.6, 144.8, 143.3, 135.4, 134.7, 134.0, 133.5, 130.9, 129.3, 128.8, 128.7(6), 128.7(1), 128.6,
128.5, 128.0, 110.4, 69.8, 52.0. IR (film) $\nu$/cm$^{-1}$ 3440 (m), 3149 (m), 2925 (m), 1706 (m), 1589 (w), 1448 (s), 1202 (m). MS (ESI, $m/z$) 431.3 (M + H$^+$), 433.3 (M +2+ H$^+$), 453.3 (M + Na$^+$), 455.3 (M +2+ Na$^+$). Anal. calcd for C$_{25}$H$_{19}$ClN$_2$O$_3$: C, 69.69; H, 4.44; N, 6.50. Found: C, 69.43; H, 4.11; N, 6.23.

Methyl (E)-1-(2-oxo-1,2-diphenylethyl)-5-styryl-1H-pyrazole-3-carboxylate (3fb). Petroleum ether/ethyl acetate = 5:1, white solid, 62% yield (131 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.84-7.87 (m, 2H), 7.48-7.52 (m, 1H), 7.41 (s, 1H), 7.34-7.38 (m, 2H), 7.27-7.31 (m, 3H), 7.18-7.23 (m, 5H), 7.12-7.17 (m, 2H), 7.01 (s, 1H), 6.83 (ABd, $J$ = 16.4 Hz 1H), 6.57 (ABd, $J$ = 16.4 Hz 1H), 3.86 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 192.9, 162.6, 144.2, 142.9, 136.0, 134.9, 134.3, 133.9, 133.2, 129.0, 128.8, 128.7(9), 128.6(8), 128.5(9), 128.4, 126.7, 114.8, 107.0, 70.7, 52.0. IR (film) $\nu$/cm$^{-1}$ 3429 (s), 3124 (w), 1730 (vs), 1600 (w), 1461 (m), 1202 (vs). MS (ESI, $m/z$) 423.4 (M + H$^+$), 445.4 (M + Na$^+$). Anal. calcd for C$_{27}$H$_{22}$N$_2$O$_3$: C, 76.76; H, 5.25; N, 6.63. Found: C, 76.65; H, 5.07; N, 6.58.

Methyl 5-(2-bromophenyl)-1-(2-oxo-1,2-diphenylethyl)-1H-pyrazole-3-carboxylate (3gb). Petroleum ether/ethyl acetate = 5:1, white solid, 56% yield
Methyl 5-(3-bromophenyl)-1-(2-oxo-1,2-diphenylethyl)-1H-pyrazole-3-carboxylate (3hb). Petroleum ether/ethyl acetate = 5:1, white solid, 64% yield (152 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.61-7.63 (m, 2H), 7.45-7.49 (m, 1H), 7.39 (t, $J = 7.6$ Hz 1H), 7.14-7.26 (m, 11H), 6.83 (s, 1H), 3.81 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 192.1, 162.5, 144.4, 143.2, 144.4, 134.6, 134.3, 133.7, 133.5, 132.5, 132.1, 131.4, 129.8, 129.3, 128.9, 128.7, 128.6, 128.4, 128.2, 122.3, 110.5, 70.0, 52.0. MS (ESI, m/z) 475.3 (M + H$^+$), 477.3 (M +2+ H$^+$), 497.3 (M + Na$^+$), 499.3 (M +2+ Na$^+$). IR (film) $\nu$/cm$^{-1}$ 3371 (vs), 2972 (s), 1706 (m), 1461 (m), 1202 (m), 1062 (vs). Anal. calcd for C$_{25}$H$_{19}$BrN$_2$O$_3$: C, 63.17; H, 4.03; N, 5.89. Found: C, 62.93; H, 3.85; N, 5.68.
Methyl 5-(4-bromophenyl)-1-(2-oxo-1,2-diphenylethyl)-1H-pyrazole-3-carboxylate (3ib). Petroleum ether/ethyl acetate = 5:1, white solid, 71% yield (168 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59-7.61 (m, 2H), 7.40-7.44 (m, 1H), 7.35-7.37 (m, 2H), 7.18-7.28 (m, 5H), 7.08-7.10 (m, 2H), 6.97-7.00 (m, 2H), 6.92 (s, 1H), 6.78 (s, 1H), 3.82 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 192.2, 162.6, 144.8, 143.3, 134.6, 134.0, 133.5, 131.7, 131.1, 129.3, 128.8, 128.7(6), 128.6, 128.5, 128.4, 123.7, 110.4, 69.7, 52.0. MS (ESI, $m/z$) 475.3 (M + H$^+$), 477.3 (M + 2+ H$^+$), 497.3 (M + Na$^+$), 499.3 (M +2+ Na$^+$). IR (film) $\nu$/cm$^{-1}$ 3429 (w) 2940 (w), 1706 (vs), 1461 (m), 1226 (vs). Anal. calcd for C$_{25}$H$_{19}$BrN$_2$O$_3$: C, 63.17; H, 4.03; N, 5.89. Found: C, 63.24; H, 4.15; N, 5.98.

Methyl 5-(3-fluorophenyl)-1-(2-oxo-1,2-diphenylethyl)-1H-pyrazole-3-carboxylate (3jb). Petroleum ether/ethyl acetate = 5:1, white solid, 74% yield (153 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.67-7.69 (m, 2H), 7.47 (t, $J$ = 7.2 Hz, 1H), 7.02-7.34 (m, 11H), 6.88 (s, 1H), 3.87 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 192.0, 162.5, 162.2 (d, $J$ = 246.5 Hz), 144.5 (d, $J$ = 2.5 Hz), 143.2, 134.6,
133.8, 133.4, 131.4 (d, J = 8.1 Hz), 130.1 (d, J = 3.7 Hz), 129.2, 128.8, 128.7,
128.5, 128.4, 125.2 (d, J = 3.7 Hz), 116.5 (d, J = 20.8 Hz), 110.3, 69.6, 51.9. IR
(film) ν/cm⁻¹ 3268 (vs), 2978 (s), 1706 (m), 1461 (m), 1214 (m). MS (ESI, m/z)
415.3 (M + H⁺), 437.3 (M + Na⁺). Anal. calcd for C_{25}H_{19}FN_{2}O_{3}: C, 72.45; H, 4.62;
N, 6.76. Found: C, 72.29; H, 4.77; N, 6.54.

Methyl 5-(2-fluorophenyl)-1-(2-oxo-1,2-diphenylethyl)-1H-pyrazole-3-
carboxylate (3jb). Petroleum ether/ethyl acetate = 5:1, white solid, 71% yield
(147 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.71-7.73 (m, 2H), 7.12-7.49 (m, 12H),
6.95 (s, 1H), 3.88 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 192.0, 162.5, 159.5 (d, J =
247.6 Hz), 143.3, 139.1, 134.6, 133.3 (d, J = 4.3 Hz), 132.2, 131.6 (d, J =
7.8 Hz), 129.2, 128.8, 128.7, 128.6, 128.5, 128.4, 124.1 (d, J = 2.8 Hz), 115.7
(d, J = 20.7 Hz), 111.4, 69.6, 51.8. IR (film) ν/cm⁻¹ 3328 (m), 2947 (w), 1695 (s),
1586 (s), 1237 (s). MS (ESI, m/z) 415.3 (M + H⁺), 437.3 (M + Na⁺). Anal. calcd
for C_{25}H_{19}FN_{2}O_{3}: C, 72.45; H, 4.62; N, 6.76. Found: C, 72.57; H, 4.86; N, 6.92.
Methyl 5-(3-methoxyphenyl)-1-(2-oxo-1,2-diphenylethyl)-1H-pyrazole-3-carboxylate (3kb). Petroleum ether/ethyl acetate = 5:1, white solid, 55% yield (117 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.64-7.66 (m, 2H), 7.28-7.47 (m, 12H), 6.92 (s, 1H), 6.89 (s, 1H), 3.88 (s, 3H), 3.66 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 192.0, 162.7, 159.5, 145.6, 143.4, 134.9, 134.4, 133.2, 130.5, 129.8, 129.1, 128.7, 128.6, 128.5, 128.4, 121.6, 115.6, 114.2, 109.8, 68.8, 55.1, 51.9. IR (film) $\nu$/cm$^{-1}$ 3345 (s), 2926 (s), 1695 (m), 1437 (s), 1248 (vs). MS (ESI, m/z) 427.3 (M + H$^+$), 449.4 (M + Na$^+$). Anal. calcd for C$_{26}$H$_{22}$N$_2$O$_4$: C, 73.23; H, 5.20; N, 6.57. Found: C, 72.98; H, 5.42; N, 6.71.

Reference:


Spectroscopic Data for Products